Anhydrides as α,β-unsaturated acyl ammonium precursors: Isothiourea-promoted catalytic asymmetric annulation process

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Supporting Information

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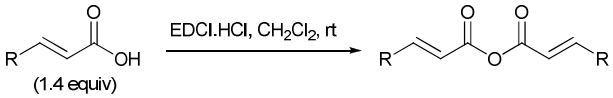
General Information

All reactions involving moisture sensitive reagents were performed under inert atmosphere (nitrogen or argon) *via* standard vacuum line techniques and with freshly dried solvents. All glassware was flame dried and allowed to cool under vacuum. Diethylether (Et_2O), tetrahydrofuran (THF), toluene (PhMe), hexane and dichloromethane (CH_2Cl_2) were obtained dry from a solvent purification system (MBraun, SPS-800). Petroleum ether is defined as 40–60 petrol. All solvents and commercial reagents were used as supplied without further purification unless stated otherwise. Room temperature refers to 20–25 °C. Temperatures of 0 °C and –78 °C were achieved using ice/water and CO_2(s)/acetone baths respectively. Reduced pressure refers to the use of a Büchi Rotavapor R-2000 rotary evaporator with a Vacubrand CVC_2 vacuum controller or a Heidolph Laborota 4001 rotary evaporator with a vacuum controller. Analytic thin layer chromatography was performed on aluminium sheets coated with 60 F_{254} silica. TLC visualisation was carried out with ultraviolet light (254 nm), followed by staining 1% aq. $KMnO_4$ solution. Flash column chromatography was performed on Kieselgel 60 silica in the solvent system stated. ^1H and ^{13}C NMR spectra were acquired on either a Bruker Avance 300 {δ_H (300 MHz), δ_C (75 MHz)}, a Bruker Avance II 400 {δ_H (400 MHz), δ_C (100 MHz)}, a Bruker Avance 500 {δ_H (500 MHz), δ_C (125 MHz)} or a Bruker Avance III 500 {δ_H (500 MHz), δ_C (125 MHz)} spectrometer at ambient temperature and in the deuterated solvent stated. Coupling constants (*J*) are reported in Hz. Data are expressed in chemical shifts in parts per million (ppm) relative to residual solvent as the internal standard. Multiplicities are indicated by: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sextet, sept (septet) and m (multiplet). Ar stands for aromatic, *app* for apparent and *br* for broad. Infrared spectra (ν_{max}) were recorded on a Shimadzu IRAffinity-1 fourier transform IR spectrophotometer using either thin film or solid using Pike MIRacle ATR accessory. Analysis was carried out using Shimadzu IRsolution v1.50, characteristic peaks are reported. Melting points were recorded on an electrothermal apparatus and are uncorrected. HPLC analyses were obtained on two different machines: a Gilson HPLC consisting of a Gilson 305 pump, Gilson 401C dilutor, Gilson 213XL sample injector and sample detection was performed with a Gilson 118UV/Vis detector; secondly a Shimadzu HPLC consisting of a DGU-20A5 degasser, LX-20AT liquid chromatograph, SIL-20AHT autosampler, CMB-20A column oven with variable temperature setting (25–40 °C). Separation was achieved using Chiralcel OD-H and OJ-H columns or Chiralpak AD-H, AS-H, IA, IC, IB and ID columns. Mass spectrometric (*m/z*) data was acquired either at the University of St Andrews Mass Spectrometry Facility or at the EPSRC National Mass Spectrometry Service Centre in Swansea.

HRMS carried out in St Andrews are quoted [M+H] and those carried out in Swansea are quoted $[M+H]^+$. Low and high resolution MS (ES) and MS (CI) were carried out on a Micromass LCT spectrometer and on a Micromass GCT spectrometer, respectively. Optical rotations were measured on a Perkin Elmer Precisely/Model-341 polarimeter operating at the sodium D line with a 100 mm path cell.

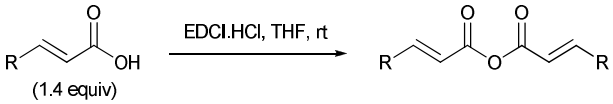
Preparation of α,β-unsaturated homoanhydrides

General Procedure A: in CH_2Cl_2



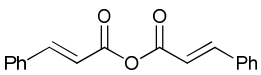
To a solution of carboxylic acid (1.4 equiv) in CH_2Cl_2 (0.8 M) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide.HCl (EDCI.HCl) (1.0 equiv) and the solution stirred for 1-2 h at room temperature. The solution was diluted with CH_2Cl_2 (50 mL) and then washed sequentially with water (2×50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to afford the *homoanhydride*.

General Procedure B: in THF



To a solution of carboxylic acid (1.4 equiv) in THF (0.8 M) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide.HCl (1.0 equiv) and the solution stirred for 1-2 h at room temperature. The solvent was removed *in vacuo* and the residue redissolved in CH_2Cl_2 (50 mL) and then washed sequentially with water (2×50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to afford the *homoanhydride*.

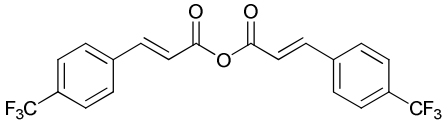
(*E*)-Cinnamic anhydride (3)



The title compound was prepared according to *General Procedure A* from (*E*)-cinnamic acid (741 mg, 5.00 mmol) and EDCI.HCl (959 mg, 5.00 mmol) in CH_2Cl_2 (6 mL) to give the *homoanhydride* **3** as a white solid (448 mg, 64%); mp 118-120 °C {Lit.[1] 130 °C}; δ_H (400 MHz, $CDCl_3$) 6.54 (2H, d, *J* 16.0,

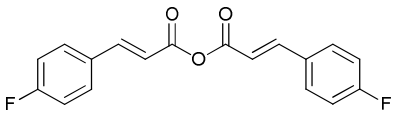
ArCH=C*H*), 7.40–7.47 (6H, m, Ar*H*), 7.54–7.63 (4H, m, Ar*H*), 7.86 (2H, d, *J* 16.0, ArC*H*=CH). Data in agreement with the literature.[1,2]

(*E*)-3-(4-(Trifluoromethyl)phenyl)acrylic anhydride (S1)



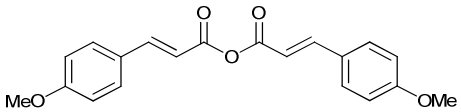
The title compound was prepared according to *General Procedure A* from 4-trifluoromethylcinnamic acid (1080 mg, 5.00 mmol) and EDCI.HCl (959 mg, 5.00 mmol) in CH_2Cl_2 (10 mL) to give the *homoanhydride* **S1** as a white solid (425 mg, 41%); mp 127-128 °C; ν_{max} (film)/cm^{-1} 1757, 1705 (C=O), 1631 (C=C), 1321 (CF_3); δ_H (300 MHz, $CDCl_3$) 6.61 (2H, d, *J* 16.0, CH=C*H*CO), 7.69 (8H, s, Ar*H*), 7.88 (2H, d, *J* 16.0, C*H*=CHCO); δ_C (75 MHz, DMSO) 119.7 (2×CH=*C*HCO), 123.9 (q, $^1J_{CF}$ 270.8, 2×*C*F_3), 125.9 (q, $^3J_{CF}$ 3.7, 4×Ar*C*(3)), 129.6 (4×Ar*C*(2)), 130.8 (q, $^2J_{CF}$ 32.0, 2×Ar*C*(4)), 137.5 (2×Ar*C*(1)), 146.7 (2×*C*H=CHCO), 162.2 (2×*C*O); δ_F (282 MHz, $CDCl_3$) –63.5; *m/z* (ES$^+$) 437 ([M+Na]$^+$, 20%), 301 ([M-6F]$^+$, 100%); HRMS (ES$^+$) $C_{20}H_{12}F_6O_3Na^+$ ([M+Na]$^+$) requires 437.0585, found 437.0588 (–0.8 ppm).

(*E*)-3-(4-Fluorophenyl)acrylic anhydride (S2)



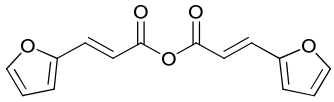
The title compound was prepared according to *General Procedure A* from (*E*)-3-(4-fluorophenyl)acrylic acid (166 mg, 1.00 mmol) and EDCI.HCl (96 mg, 0.50 mmol) in CH_2Cl_2 (4 mL) to give the *homoanhydride* **S2** as a white solid (207 mg, 66%); mp 86-90 °C; ν_{max} (film)/cm^{-1} 1755, 1699 (C=O), 1595, 1508; δ_H (300 MHz, $CDCl_3$) 6.44 (2H, d, *J* 16.2, ArCH=C*H*), 7.07-7.16 (4H, m, Ar*H*), 7.54-7.61 (4H, m, Ar*H*), 7.81 (2H, d, *J* 16.2, ArC*H*=CH); δ_C (75 MHz, $CDCl_3$) 116.3 (d, $^2J_{CF}$ 22.1, 4×Ar*C*(3)), 116.4 (d, $^6J_{CF}$ 2.2, 2×CH=*C*HCO), 129.9 (d, $^4J_{CF}$ 3.3, 2×Ar*C*(1)), 130.6 (d, $^3J_{CF}$ 8.7, 4×Ar*C*(2)), 147.3 (2×*C*H=CHCO), 162.3 (2×*C*O), 164.4 (d, $^1J_{CF}$ 253.2, 2×Ar*C*(4)); δ_F (300 MHz, $CDCl_3$) –108.1; *m/z* (FTMA$^+$) 149 ([M-$C_9H_6FO_2$]$^+$, 100%), 315 ([M+H]$^+$, 25%); HRMS (FTMS$^+$) $C_{18}H_{13}F_2O_3$ ([M+H]$^+$) requires 315.0827, found 315.0831 (+1.2 ppm).

(*E*)-3-(4-Methoxyphenyl)acrylic 3-(4-methoxyphenyl)propanoic anhydride (S3)



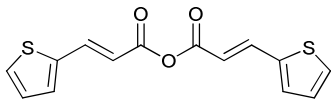
The title compound was prepared according to *General Procedure B* from 4-methoxycinnamic acid (891 mg, 5.00 mmol) and EDCI.HCl (959 mg, 5.00 mmol) in THF (20 mL) to give the *homoanydride* **S3** as a white solid (442 mg, 52%); mp 116-119 °C {Lit.[2] 104-105 °C}; δ_H (400 MHz, $CDCl_3$) 3.86 (6H, s, ArOC*H*$_3$), 6.39 (2H, d, *J* 15.8, ArCH=C*H*), 6.91-6.96 (4H, m, Ar*H*), 7.50-7.57 (4H, m, Ar*H*), 7.80 (2H, d, *J* 15.8, ArC*H*=CH). Data in agreement with the literature.[2]

(*E*)-3-(Furan-2-yl)acrylic anhydride (S4)



The title compound was prepared according to *General Procedure B* from furylacrylic acid (690 mg, 5.00 mmol) and EDCI.HCl (959 mg, 5.00 mmol) in THF (10 mL) to give the *homoanhydride* **S4** as a brown solid (485 mg, 75%); mp 68-71 °C; ν_{max} (film)/cm^{-1} 3142 (C-H), 3123 (C-H), 2965 (C-H), 2936 (C-H), 2909 (C-H), 2856 (C-H), 2818 (C-H), 1772 (C=O), 1695 (C=O), 1624 (furan), 1555 (furan), 1474 (furan), 1226 (C-O); δ_H (300 MHz, $CDCl_3$) 6.39 (2H, d, *J* 15.5, CH=C*H*CO), 6.53 (2H, dd, *J* 3.5, 1.8, furanylC(4)*H*), 6.75 (2H, d, *J* 3.5, furanylC(3)*H*), 7.55 (2H, d, *J* 1.7, furanylC(5)*H*), 7.58 (2H, d, *J* 15.5, C*H*=CHCO); δ_C (75 MHz, $CDCl_3$) 112.9 (2×furanyl*C*(4)), 114.3 (2×furanyl*C*(3)), 117.1 (2×CH=*C*HCO), 134.3 (2×*C*H=CHCO), 146.0 (2×furanyl*C*(5)), 150.6 (2×furanyl*C*(2)), 162.7 (2×*C*=O); *m/z* (NSI$^+$) 297 ([M+K]$^+$, 100%), 281 ([M+Na]$^+$, 20%); HRMS (NSI$^+$) $C_{14}H_{10}O_5Na^+$ ([M+Na]$^+$) requires 281.0420, found 281.0424 (+1.3 ppm).

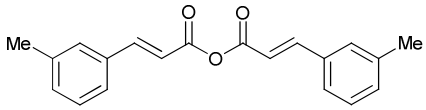
(*E*)-3-(Thiophen-2-yl)acrylic anhydride (S5)



The title compound was prepared according to *General Procedure B* from thienylacrylic acid (770 mg, 5.00 mmol) and EDCI.HCl (959 mg, 5.00 mmol) in THF (10 mL) to give the *homoanhydride* **S5** as a brown solid (522 mg, 72%); mp 86-88 °C; ν_{max} (film)/cm^{-1} 2972 (C-H), 1728 (C=O); 3069 (C-H), 3026 (C-H), 2966 (C-H), 1761 (C=O), 1694 (C=C), 1616 (C=C), 1413 (C-O), 1236 (C-S-C); δ_H (300 MHz, $CDCl_3$) 6.30 (2H, d, *J* 15.7, CH=C*H*CO), 7.10 (2H, dd, *J* 5.0, 3.7, thienylC(4)*H*), 7.31-7.38 (2H, d, *J* 3.7, thienylC(3)*H*), 7.48 (2H, d, *J* 5.0, 1.0, thienylC(5)*H*), 7.94 (2H, dt, *J* 15.7, 0.8, C*H*=CHCO); δ_C (75

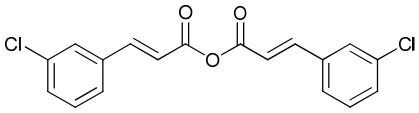
MHz, $CDCl_3$) 115.3 (2×CH=*C*HCO), 128.6 (2×thienyl*C*(4)), 130.3 (2×thienyl*C*(5)), 132.7 (2×thienyl*C*(3)), 139.1 (2×thienyl*C*(2)), 141.0 (2×*C*H=CHCO), 162.4 (2×*C*=O); *m/z* (ES^+) 313 ($[M+Na]^+$, 100%); HRMS (ES^+) $C_{14}H_{10}O_3NaS_2^+$ ($[M+Na]^+$) requires 312.9961, found 312.9969 (–2.6 ppm).

(*E*)-3-(3-Methylphenyl)acrylic anhydride (S6)



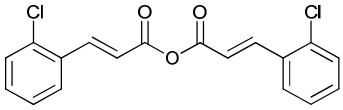
The title compound was prepared according to *General Procedure B* from 3-methylcinnamic acid (810 mg, 5.00 mmol) and EDCI.HCl (576 mg, 3.00 mmol) in CH_2Cl_2 (10 mL) to give the *homoanhydride* **S6** as a white solid (582 mg, 76%); mp 61-64 °C; ν_{max} (film)/cm^{-1} 2918 (C-H), 1755 (C=O), 1697 (C=O), 1697 (C=C); δ_H (400 MHz, $CDCl_3$) 2.39 (6H, s, CH_3), 6.52 (2H, d, *J* 15.9, C*H*=CHCO), 7.16-7.42 (8H, m, Ar*H*), 7.83 (2H, d, *J* 15.9, CH=C*H*CO); δ_C (75 MHz, $CDCl_3$) 21.5 (2×*C*H_3), 116.4 (2×CH=*C*HCO), 126.0 (2×Ar*C*(6)H), 129.1 (2×Ar*C*(2)H), 129.3 (2×Ar*C*(4)H), 132.3 (2×Ar*C*(5)H), 133.8 (2×Ar*C*(1)), 138.9 (2×Ar*C*(3)), 149.0 (2×*C*H=CHCO), 162.7 (2×*C*O); *m/z* (ES^+) 329 ($[M+Na]^+$, 100%); HRMS (ES^+) $C_{20}H_{18}O_3Na^+$ ($[M+Na]^+$) requires 329.1156, found 329.1154 (+0.7 ppm).

(*E*)-3-(3-Chlorophenyl)acrylic anhydride (S7)



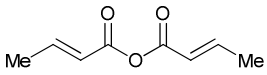
The title compound was prepared according to *General Procedure A* from 3-chlorocinnamic acid (732 mg, 4.00 mmol) and EDCI.HCl (461 mg, 2.40 mmol) in CH_2Cl_2 (20 mL) to give the *homoanydride* **S7** as a white solid (389 mg, 56%); mp 96-99 °C; ν_{max} (film)/cm^{-1} 3082 (C-H), 1759 (C=O), 1632 (C=C), 1095 (C-Cl); δ_H (400 MHz, $CDCl_3$) 6.52 (2H, d, *J* 15.9, CH=C*H*CO), 7.33-7.49 (6H, m, Ar*H*), 7.57 (2H, t, *J* 1.7, Ar*H*), 7.78 (2H, d, *J* 15.9, C*H*=CHCO); δ_C (100 MHz, $CDCl_3$) 118.2 (2×CH=*C*HCO), 126.9 (2×Ar*C*H), 128.4 (2×Ar*C*H), 130.5 (2×Ar*C*H), 131.3 (2×Ar*C*H), 135.3 (2×Ar*C*), 135.6 (2×Ar*C*), 147.2 (2×*C*H=CHCO), 162.0 (2×*C*=O); *m/z* (ES^+) 369 ($[M+Na]^+$, 10%); HRMS (ES^+) $C_{18}H_{12}Cl_2O_3Na^+$ ($[M+Na]^+$) requires 369.0065, found 369.0061 (+0.9 ppm).

(*E*)-3-(2-Chlorophenyl)acrylic anhydride (S8)



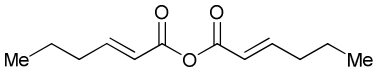
The title compound was prepared according to *General Procedure A* from 2-chlorocinnamic acid (913 mg, 5.00 mmol) and EDCI.HCl (576 mg, 3.0 mmol) in CH_2Cl_2 (20 mL) to give the *homoanhydride* **S8** as a white solid (417 mg, 48%); mp 139-139 °C; ν_{max} (film)/cm^{-1} 3082 (C-H), 1759 (C=O), 1632 (C=C), 1078 (C-Cl); δ_H (400 MHz, $CDCl_3$) 6.54 (2H, d, *J* 16.0, CH=C*H*CO), 7.30-7.40 (4H, m, Ar*H*), 7.44-7.47 (2H, m, ArC(5)*H*), 7.68 (2H, dd, *J* 7.6, 1.7, ArC(6)*H*), 8.29 (2H, d, *J* 16.0, C*H*=CHCO); δ_C (100 MHz, $CDCl_3$) 119.4 (2×CH=*C*HCO), 127.4 (2×Ar*C*H), 128.1 (2×Ar*C*H), 130.5 (2×Ar*C*H), 132.1 (2×Ar*C*H), 132.2 (2×Ar*C*Cl), 135.6 (2×Ar*C*), 144.4 (2×*C*H=CHCO), 161.9 (2×*C*O); *m/z* (ES$^+$) 369 ([M+Na]$^+$, 50%); HRMS (ES$^+$) $C_{18}H_{12}Cl_2O_3Na^+$ ([M+Na]$^+$) requires 369.0054, found 369.0061 (–1.9 ppm).

(*E*)-But-2-enoic anhydride (S9)



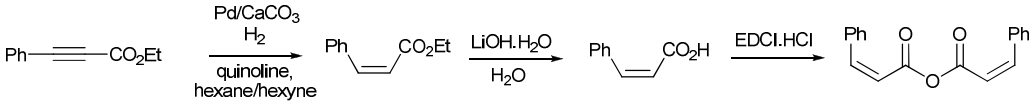
The title compound was prepared according to *General Procedure A* from crotonic acid (258 mg, 3.00 mmol) and EDCI.HCl (576 mg, 3.00 mmol) in CH_2Cl_2 (6 mL) to give the *homoanhydride* **S9** as a colourless oil (136 mg, 59%); δ_H (400 MHz, $CDCl_3$) 1.95 (6H, dd, *J* 7.0, 1.7, C*H*$_3$), 5.91 (2H, dq, *J* 15.5, 1.7, CH_3CH=C*H*), 7.14 (2H, dq, *J* 15.5, 7.0, CH_3C*H*=CH). Data in agreement with the literature.[3]

(*E*)-Hex-2-enoic anhydride (S10)



The title compound was prepared according to *General Procedure A* from *trans*-2-hexenoic acid (342 mg, 3.00 mmol) and EDCI.HCl (576 mg, 3.00 mmol) in CH_2Cl_2 (6 mL) to give the *homoanhydride* **S10** as a colourless oil (171 mg, 54%); ν_{max} (film)/cm^{-1} 2962 (C-H), 2934 (C-H), 2874 (C-H), 1780 (C=O), 1722 (C=O), 1645 (C=C); δ_H (300 MHz, $CDCl_3$) 0.88 (6H, t, *J* 7.4, C*H*$_3$), 1.45 (4H, h, *J* 7.4, C(5)*H*$_2$), 2.17 (4H, qd, *J* 7.2, 1.6, C(4)*H*$_2$), 5.81 (2H, dt, *J* 15.6, 1.6, CH=C*H*CO), 7.06 (2H, dt, *J* 15.6, 7.0, C*H*=CHCO); δ_C (75 MHz, $CDCl_3$) 13.6 (2×*C*H$_3$), 21.1 (2×*C*(5)H$_2$), 34.5 (2×*C*(4)H$_2$), 120.6 (2×*C*H=CHCO), 154.0 (2×CH=*C*HCO), 162.1 (2×*C*O); *m/z* (NSI$^+$) 228 ([M+NH$_4$]$^+$, 100%); HRMS (NSI$^+$) $C_{12}H_{22}NO_3^+$ ([M+NH$_4$]$^+$) requires 228.1594, found 228.1596 (+0.8 ppm).

(*Z*)-Cinnamic anhydride (22)



(*Z*)-Ethyl cinnamate (S11)

Ethyl phenylpropiolate (1.0 mL, 6.0 mmol) was dissolved in a mixture of hexane and 1-hexene (7:2 v/v, 12 mL), under N_2 atm at rt, followed by addition of quinoline (1.1 mL, 9 mmol) and palladium on calcium carbonate (Lindlar's catalyst, 360 mg). The resulting reaction mixture was connected to a hydrogen-filled balloon (1 atm) and stirred at rt. The progress of the reaction was monitored by TLC (CH_2Cl_2). The starting alkyne was consumed after 1 h and the reaction was stopped by displacement of the hydrogen atmosphere with nitrogen. The resulting mixture was filtered through a Celite pad, and the filtrate was washed with 10% acetic acid (4×50 mL), water (3×50 mL), and saturated $NaHCO_3$ (4×50 mL) and dried ($MgSO_4$). Solvent was removed under reduced pressure, and the residue was purified by column chromatography to give the *ester* **S11** as a clear oil (458 mg, 43%) in >99% purity (a mixture containing 76% *cis*-ethyl cinnamate, 18% over-reduced alkane and 6% *trans*-ethyl cinnamate was observed in the ^{1}H-NMR of the unpurifed reaction mixture); δ_H (300 MHz, $CDCl_3$) 1.25 (3H, t, *J* 7.2, C*H*$_3$), 4.17 (2H, q, *J* 7.2, OC*H*$_2$), 5.95 (1H, d, 12.6, PhCH=C*H*), 6.95 (1H, d, 12.6, PhC*H*=CH), 7.32-7.39 (3H, m, Ar*H*), 7.56-7.60 (2H, m, Ar*H*). Data in agreement with the literature.[4]

(*Z*)-Cinnamic acid (S12)

To a solution of *cis*-ethyl cinnamate (458 mg, 2.60 mmol) in THF (37 mL), was added a solution of $LiOH.H_2O$ (327 mg, 7.80 mmol) in H_2O (12 mL) at rt. The resulting reaction mixture was heated at 60 °C for 16 h. Then it was cooled to rt and acidified with 8 N HCl aq. The aqueous phase was extracted with Et_2O (3×50mL) and the combined organic layers were dried ($MgSO_4$). Solvent was removed under reduced pressure to give the *acid* **S12** as a pale yellow solid (327 mg, 85%); mp 64-68 °C {Lit.[11] 66-68 °C}; δ_H (400 MHz, $CDCl_3$) 5.97 (1H, d, *J* 12.8, PhCH=C*H*), 7.07 (1H, d, *J* 12.8, PhC*H*=CH), 7.34-7.39 (3H, m, Ar*H*), 7.58-7.62 (2H, m, Ar*H*). Data in agreement with the literature.[5]

(*Z*)-Cinnamic anhydride (22)

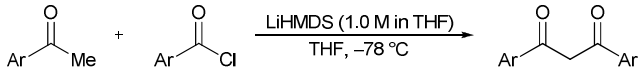
The title compound was prepared according to *General Procedure A* from (*Z*)-cinnamic acid (318 mg, 2.15 mmol) and EDCI.HCl (206 mg, 1.07 mmol) in CH_2Cl_2 (10 mL) to give the *homoanhydride* **22** as a white gum[i] (169 mg, 56%); ν_{max} (film)/cm^{-1} 2963 (C-H) , 1778 (C=O), 1717 (C=O), 1616 (C=C), 1020

[i] The product was approximately 90% pure and used without further purification.

(C-O); δ_H (400 MHz, $CDCl_3$) 5.85 (2H, d, *J* 12.5, ArCH=C*H*), 7.11 (2H, d, *J* 12.5, ArCH=C*H*), 7.32-7.42 (6H, m, Ar*H*), 7.56-7.71 (4H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 117.8 (2×ArCH=*C*H), 126.3 (4×Ar*C*H), 130.0 (2×Ar*C*H), 130.2 (4×Ar*C*H), 134.2 (2×Ar*C*), 147.9 (2×Ar*C*H=CH), 161.4 (2×*C*O); *m/z* (ES^+) 301 ($[M+Na]^+$, 100%); HRMS (ES^+) $C_{18}H_{14}O_3Na^+$ ($[M+Na]^+$) requires 301.0841, found 301.0840 (–0.3 ppm).

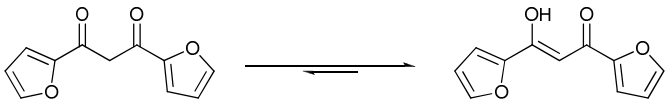
Preparation of Diketones

General Procedure C: using LiHMDS



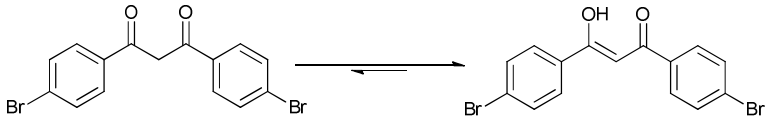
To a solution of arylketone (1.0 equiv) in THF (10 mL) at −78 °C was added LiHMDS (1.0 M in THF, 1.5 equiv) over 15 mins and the resulting mixture stirred at −78 °C for 1 h. Acid chloride (1.2 equiv) was added dropwise as a solution in THF (2 mL) at −78 °C over 5 mins and the solution warmed to room temperature over 1 h and stirred for a further 17 h. The reaction was quenched with 10% citric acid (20 mL) and extracted with EtOAc (2 × 100 mL). The combined organics were washed with H_2O (20 mL), dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by chromatography gave the *diketone*.

1,3-*bis*(Furan-2-yl)propane-1,3-dione (S13)



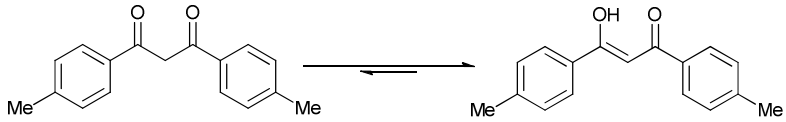
The title compound was prepared according to *General Procedure C* from 2-acetylfuran (550 mg, 5.00 mmol), furoyl chloride (590 µL, 6.00 mmol) and LiHMDS (1.0 M in THF, 7.50 mL, 7.50 mmol) and purified by chromatography (20% Et_2O/petrol) to afford the *diketone* **S13** as a pale-yellow solid (443 mg, 43% yield); mp 73-74 °C {Lit.[5] 74-75 °C}; δ_H (400 MHz, $CDCl_3$) 6.59 (2H, dd, *J* 3.5, 1.7, Ar(4)*H*), 6.62 (1H, s, =C*H*), 7.21 (2H, dd, *J* 3.5, 0.8, Ar(3)*H*), 7.62 (2H, dd, *J* 1.7, 0.8, Ar(5)*H*). Data in agreement with the literature.[6]

1,3-*bis*(4-Bromophenyl)propane-1,3-dione (S14)



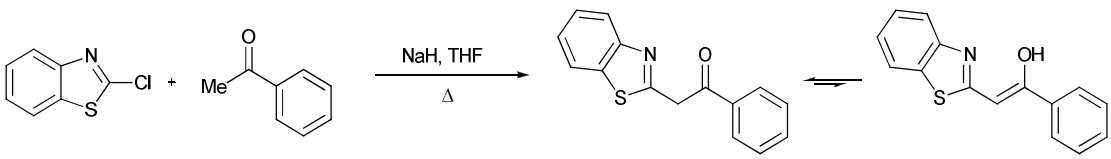
The title compound was prepared according to *General Procedure C* from 4-bromoacetophenone (995 mg, 5.00 mmol), 4-bromobenzoyl chloride (1.31 g, 6.00 mmol) and LiHMDS (1.0 M in THF, 7.50 mL, 7.50 mmol) and purified by chromatography (20% Et_2O/petrol) to afford the *diketone* **S14** as a pale-yellow powder (550 mg, 29% yield); mp 185-186 °C {Lit.[8] 185-186 °C}; δ_H (400 MHz, $CDCl_3$) 6.79 (1H, s, =C*H*), 7.64 (4H, d, *J* 8.7, Ar(3)*H*), 7.85 (4H, d, *J* 8.7, Ar(2)*H*). Data in agreement with the literature.[7]

1,3-*bis*(4-Methylphenyl)propane-1,3-dione (S15)



The title compound was prepared according to *General Procedure C* from 4-methylacetophenone (671 mg, 5.00 mmol), 4-toluoyl chloride (928 mg, 6.00 mmol) and LiHMDS (1.0 M in THF, 7.50 mL, 7.50 mmol) and purified by chromatography (20% Et_2O/petrol) to afford the *diketone* **S15** as a pale-yellow solid (499 mg, 40% yield); mp 125-126 °C {Lit.[7] 127-127.4 °C}; δ_H (400 MHz, $CDCl_3$) 2.44 (6H, s, 2×ArCH_3), 6.83 (1H, s, =C*H*), 7.30 (4H, d, *J* 8.1, Ar(3)*H*), 7.90 (4H, dd, *J* 8.1, Ar(2)*H*). Data in agreement with the literature.[8]

2-Phenacylbenzothiazole (35)



Acetophenone (9.32 mL, 80.0 mmol) was added slowly to a suspension of sodium hydride (60% in mineral oil, 4.80 g, 120 mmol) in dry THF (60 mL) under argon and the flask stirred for 10 minutes. 2-Chlorobenzothiazole (12.5 mL, 96.0 mmol) was added dropwise and the reaction heated at reflux for 15 hours. The reaction was quenched by dropwise addition of water at 0 °C, the acidified to pH 1-2 using a solution of 1M HCl. The mixture was diluted with ethyl acetate (150 mL) and then washed sequentially with water (100 mL × 2) and saturated $NaHCO_3$ solution (100 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude solid was recrystallised

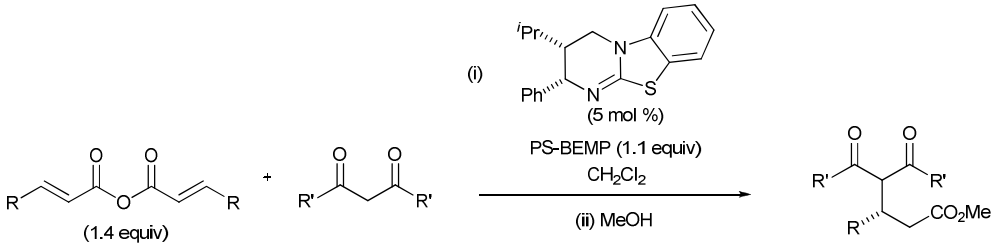
from toluene to give *azaaryl ketone* **35** as a yellow solid (10.22 g, 50%); mp 115-117 °C {Lit.[9] 113-114 °C}; δ_H (400 MHz, $CDCl_3$) 4.85 (2H, s, *keto*-CH_2COAr), 6.38 (1H, s, *enol*-C*H*COHAr), 7.31 (1H, t, *J* 7.6, *enol*-benzothiazoleC(6)*H*), 7.39 (1H, t, *J* 7.5, *enol*-benzothiazoleC(6)*H*), 7.42 – 7.52 (6H, m, Ar*H*), 7.51 (1H, t, *J* 7.7, *enol*-benzothiazoleC(4)*H*), 7.62 (1H, t, *J* 7.4, *keto*-benzothiazoleC(5)*H*), 7.79 (1H, d, *J* 9.9, *enol*-benzothiazoleC(4)*H*), 7.82 (1H, d, *J* 8.2, *enol*-benzothiazoleC(7)*H*)), 7.88 (3H, m, *keto*-benzothiazoleC(4)*H*, *enol*-phenacylC(2')*H*), 8.02 (1H, d, *J* 8.0, *keto*-benzothiazoleC(7)*H*), 8.10 (2H, d, *J* 7.5 *keto*-phenacylC(2')*H*). Data in agreement with the literature.[9]

Asymmetric Annulations with α,β-unsaturated anhydrides

(*R*)-B-benzoyl-4,6-diphenyl-3,4-dihydro-2H-pyran-2-one (2)

To a solution of (*E*)-cinnamic homoanhydride (100 mg, 0.36 mmol) in dry CH_2Cl_2 (0.25 ml) under argon, was added 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (11.1 mg, 0.036 mmol) and diisopropylethylamine (78 μL, 0.45 mmol) at 0 °C. The reaction mixture was stirred and gradually warmed to room temperature over 5 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (CH_2Cl_2) to afford *lactone* **2** as a white solid (30 mg, 49%); mp 120-125 °C; $[\alpha]_D^{22}$ –7.6 (*c* 0.5 in $CHCl_3$); {Lit.[9] $[\alpha]_D^{22}$ –6.5 (*c* 1.0 in $CHCl_3$) 95% ee}; chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 20 °C), t_R major: 14.7 min, t_R minor: 32.4 min, 95% ee; δ_H (300 MHz, $CDCl_3$) 3.04 (1H, dd, *J* 15.9, 2.5, C(3)H_2), 3.19 (1H, dd, *J* 15.9, 7.7, C(3)H_2), 4.55 (1H, dd, *J* 7.7, 2.5, C(4)*H*), 7.02-7.29 (11H, m, Ar*H*), 7.32-7.38 (2H, m, Ar*H*), 7.44-7.51 (2H, m, Ar*H*). Data in agreement with the literature.[10]

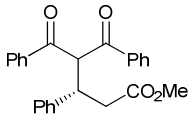
General Procedure D: Ring-opening with MeOH



To a solution of the corresponding *homoanhydride* (1.4 equiv) in dry CH_2Cl_2 (0.72 mM) under argon, was added isothiourea (HBTM 2.1, 0.05 equiv) and polymer-bound 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) (1.1 equiv) at 0 °C followed by addition of the

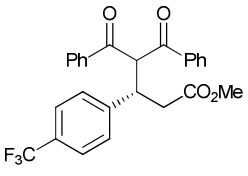
corresponding *diketone* (1.0 equiv). The reaction mixture was stirred at 0 °C and gradually warmed to room temperature over 5 h. The reaction was quenched with MeOH (2 mL) and stirred at room temperature for 16 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (CH_2Cl_2→2%EtOAc/ CH_2Cl_2) to afford the *ester* **6-22**.

(3*S*)-Methyl 4-benzoyl-5-oxo-3,5-diphenylpentanoate (6)



The title compound was prepared according to *General Procedure D* from (*E*)-cinnamic anhydride (70 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol), BEMP (2.0 mmol/g loading, 90 mg, 0.20 mmol) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **6** as a white solid (53 mg, 83%); mp 104-107 °C; $[\alpha]_D^{22}$ +9.6 (*c* 0.25 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 220 nm, 30 °C), t_R major: 11.8 min, t_R minor: 17.0 min, 96% ee; ν_{max} (film)/cm^{-1} 2367 (C-H), 1742 (C=O), 1690 (C=O), 1653 (C=O), 1489 (CH_3-O); δ_H (400 MHz, $CDCl_3$) 2.77-2.93 (2H, m, C(2)H_2), 3.50 (3H, s, OCH_3), 4.40 (1H, td, *J* 9.5, 4.9, C(3)*H*), 5.84 (1H, d, *J* 9.5, C(4)*H*), 7.04-7.19 (3H, m, Ar*H*), 7.21-7.33 (4H, m, Ar*H*), 7.37-7.48 (3H, m, Ar*H*), 7.54 (1H, t, *J* 7.4, Ar*H*), 7.75 (2H, dd, *J* 8.3, 1.3, Ar*H*), 7.98 (2H, dd, *J* 8.5, 1.1, Ar*H*); δ_C (100 MHz, $CDCl_3$) 38.2 (*C*(2)), 42.8 (*C*(3)), 51.7 (O*C*H_3), 62.4 (*C*(4)), 127.2 (Ar*C*(4)H), 128.5 (2×Ar*C*H), 128.6 (2×Ar*C*H), 128.7 (2×Ar*C*H), 128.7 (2×Ar*C*H), 129.0 (4×Ar*C*H), 133.4 (Ar*C*H), 133.8 (Ar*C*H), 136.7 (Ar*C*), 136.9 (Ar*C*), 140.4 (Ar*C*), 172.1 (*C*(1)), 194.5 (*C*O), 194.8 (*C*O); *m/z* (NSI^+) 387 ($[M+H]^+$, 100%), 404 ($[M+NH_4]^+$, 35%); HRMS (NSI^+) $C_{25}H_{23}O_4$ ($[M+H]^+$) requires 387.1591, found 387.1596 (+1.3 ppm).

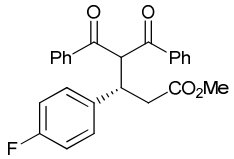
(3*S*)-Methyl 4-benzoyl-3-(4-trifluoromethylphenyl)-5-oxo-5-phenylpentanoate (7)



The title compound was prepared according to *General Procedure D* from (*E*)-4-trifluoromethyl cinnamic anhydride (103 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading, 90 mg, 0.20 mmol) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **7** as a white solid (64 mg, 79%); mp

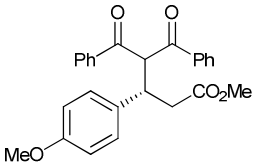
142-145 °C; $[\alpha]_D^{22}$ –2.5 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H, (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 20 °C), t_R major: 12.7 min, t_R minor: 22.1 min, 97% ee; ν_{max} (film)/cm^{-1} 2972 (C-H), 2853 (C-H), 2322 (C-H), 1734 (C=O), 1684 (C=O), 1325 (CF_3); δ_H (400 MHz, $CDCl_3$) 2.76-2.99 (2H, m, C(2)*H*), 3.51 (3H, s, OCH_3), 4.46 (1H, td, *J* 9.5, 4.7, C(3)*H*), 5.84 (1H, d, *J* 9.5, C(4)*H*), 7.27-7.51 (9H, m, ArH), 7.52-7.62 (1H, m, ArH), 7.66-7.80 (2H, m, ArH), 7.95-8.03 (2H, m, ArH); δ_C (75 MHz, $CDCl_3$) 37.9 (*C*(2)), 42.5 (*C*(3)), 51.8 (OCH_3), 61.8 (*C*(4)), 124.1 (q, $^1J_{CF}$ 270.2, *C*F_3), 125.5 (q, $^3J_{CF}$ 3.7, C(3)Ar*C*(3)), 128.6 (2×Ar*C*H), 128.8 (2×Ar*C*H), 129.0 (2×Ar*C*H), 129.0 (2×Ar*C*H), 129.1 (2×Ar*C*H), 129.4 (q, $^2J_{CF}$ 32.3, C(3)Ar*C*(4)), 133.7 (Ar*C*(4)H), 134.1 (Ar*C*(4)H), 136.5 (Ar*C*), 136.6 (Ar*C*), 144.7 (Ar*C*), 171.8 (*C*(1)), 194.2 (*C*O), 194.5 (*C*O); δ_F (282 MHz, $CDCl_3$) –63.14; m/z (NSI$^+$) 472 ($[M+NH_4]^+$, 100%), 455 ($[M+H]^+$, 90%); HRMS (NSI$^+$) $C_{26}H_{22}F_3O_4$ ($[M+H]^+$) requires 455.1465, found 455.1467 (+0.5 ppm).

(3*S*)-Methyl 4-benzoyl-3-(4-fluorophenyl)-5-oxo-5-phenylpentanoate (8)



The title compound was prepared according to *General Procedure D* from (*E*)-3-(4-fluorophenyl)acrylic anhydride (79 mg, 0.25 mmol), 1,3-diphenylpropane-1,3-dione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **8** as a white solid (60 mg, 82%); mp 92-96 °C; $[\alpha]_D^{22}$ +20.2 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak IA (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C), t_R major: 10.0 min, t_R minor: 14.3 min, 95% ee; ν_{max} (film)/cm^{-1} 2951 (C-H), 1734 (C=O), 1694 (C=O), 1260 (C-F); δ_H (400 MHz, $CDCl_3$) 2.78 (1H, dd, *J* 15.6, 9.6, C(2)*H*), 2.87 (1H, dd, *J* 15.6, 9.6, C(2)*H*), 3.51 (3H, s, O*C*H_3), 4.39 (1H, ddd, *J* 9.6, 9.6, 4.6, C(3)*H*), 5.79 (1H, d, *J* 9.6, C(4)*H*), 6.81-6.87 (2H, m, Ar*H*), 7.19-7.24 (2H, m, Ar*H*), 7.30-7.34 (2H, m, Ar*H*), 7.41-7.58 (4H, m, Ar*H*), 7.74-7.76 (2H, m, Ar*H*), 7.98-8.00 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 38.4 (*C*(2)), 42.1 (*C*(3)), 51.8 (OCH_3), 62.5 (*C*(4)), 115.4 (d, $^2J_{CF}$ 21.4, C(3)Ar*C*(3)H), 128.7 (2×Ar*C*H), 128.8 (2×Ar*C*H), 129.0 (2×Ar*C*H), 129.1 (2×Ar*C*H), 130.2 (d, $^3J_{CF}$ 8.1, C(3)Ar*C*(2)H), 133.5 (Ar*C*(4)H), 134.0 (Ar*C*(4)H), 136.1 (Ar*C*), 136.6 (Ar*C*), 136.8 (Ar*C*), 161.8 (d, $^1J_{CF}$ 240.3, *C*F), 172.0 (*C*(1)), 194.4 (*C*O), 194.6 (*C*O); δ_F (300MHz, $CDCl_3$) –115.9; *m/z* (NSI$^+$) 405 ($[M+H]^+$, 100%), 422 ($[M+NH_4]^+$, 45%); HRMS (NSI$^+$) $C_{25}H_{22}FO_4$ ($[M+H]^+$) requires 405.1497, found 405.1496 (–0.2 ppm).

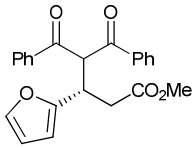
(3*S*)-Methyl 4-benzoyl-3-(4-methoxyphenyl)-5-oxo-5-phenylpentanoate (9)



The title compound was prepared according to *General Procedure D* from (*E*)-3-(4-methoxyphenyl)acrylic anhydride (85 mg, 0.25 mmol), 1,3-diphenylpropane-1,3-dione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **9** as a pale yellow solid (33 mg, 44%); mp 110-114 °C; $[\alpha]_D^{22}$ +18.1 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (15% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 20 °C), t_R major: 26.7 min, t_R minor: 44.7 min, 94% ee;

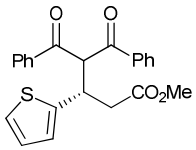
The reaction was repeated using a modified *General Procedure D* with increased catalyst loading from (*E*)-3-(4-methoxyphenyl)acrylic anhydride (85 mg, 0.25 mmol), 1,3-diphenylpropane-1,3-dione (40 mg, 0.18 mmol), HBTM 2.1 (5.6 mg, 0.018 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **9** as a pale yellow solid (42 mg, 56%); mp 110-114 °C; $[\alpha]_D^{22}$ +8.2 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (15% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 20 °C), t_R major: 26.7 min, t_R minor: 44.7 min, 88% ee; ν_{max} (film)/cm^{-1} 1732 (C=O), 1690 (C=O), 1252 (C-O), 1159 (C-O); δ_H (300 MHz, CDCl) 2.78 (1H, dd, *J* 15.6, 9.6, C(2)*H*), 2.86 (1H, dd, *J* 15.6, 5.1, C(2)*H*), 3.50 (3H, s, CO_2CH_3), 3.70 (3H, s, $ArOCH_3$), 4.36 (1H, ddd, *J* 9.6, 9.6, 4.8, C(3)*H*), 5.80 (1H, d, *J* 9.6, C(4)*H*), 6.66-6.71 (2H, m, Ar*H*), 7.13-7.18 (2H, m, Ar*H*), 7.28-7.57 (6H, m, Ar*H*), 7.74-7.78 (2H, m, Ar*H*), 7.98-8.00 (2H, m, Ar*H*); δ_C (75 MHz, $CDCl_3$) 38.5 (*C*(2)), 42.1 (*C*(3)), 51.7 (CO_2CH_3), 55.2 (OCH_3), 62.7 (*C*(4)), 113.9 (2×C(4)Ar*C*(3)H), 128.7 (2×C(4)Ar*C*(2)H), 128.7 (2×Ar*C*H), 129.0 (4×Ar*C*H), 129.5 (2×Ar*C*H), 132.3 (Ar*C*), 133.3 (Ar*C*H), 133.8 (Ar*C*H), 136.8 (Ar*C*), 136.9 (Ar*C*), 158.5 (Ar*C*), 172.2 (*C*(1)), 194.6 (*C*O), 194.9 (*C*O); *m/z* (NSI^+) 417 ($[M+H]^+$, 85%), 434 ($[M+NH_4]^+$,100%); HRMS (NSI^+) $C_{26}H_{25}O_5$ ($[M+H]^+$) requires 417.1697, found 417.1699 (+0.6 ppm).

(3*S*)-Methyl 4-benzoyl-3-(furan-2-yl)-5-oxo-5-phenylpentanoate (10)



The title compound was prepared according to *General Procedure D* from (*E*)-furylacrylic anhydride (65 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **10** as a dark yellow solid (46 mg, 69%); mp 74-77 °C; $[\alpha]_D^{22}$ +30.6 (*c* 0.5 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 20 °C), t_R major: 15.0 min, t_R minor: 17.1 min, 96% ee; ν_{max} (film)/cm^{-1} 1738 (C=O), 1697 (C=O), 1655(C=O), 1593 (furan), 1578 (furan), 1508 (furan), 1445 (C-O); δ_H (400 MHz, $CDCl_3$) 2.78-2.94 (2H, m, C(2)H_2), 3.60 (3H, s, OCH_3), 4.46 (1H, td, *J* 8.9, 4.5, C(3)*H*), 5.97-6.09 (3H, m, furanyl(*H*)), 7.13-7.19 (1H, m, C(4)H_2), 7.33-7.43 (4H, m, Ar*H*), 7.45-7.56 (2H, m, Ar*H*), 7.87 (4H, ddd, *J* 17.5, 8.4, 1.1, Ar*H*); δ_C (100 MHz, $CDCl_3$) 35.9 (*C*(2)H_2), 36.3 (*C*(3)H), 51.9 (O*C*H_3), 58.7 (*C*(4)H), 107.8 (furanyl*C*(4)H), 110.5 (furanyl*C*(3)H), 128.7 (2×Ar*C*H), 128.7 (2×Ar*C*H), 128.8 (2×Ar*C*H), 129.0 (2×Ar*C*H), 133.5 (Ar*C*(4)H), 133.8 (Ar*C*(4)H), 136.2 (Ar*C*(1)), 136.6 (Ar*C*(1)), 141.6 (furanyl*C*(5)H), 153.2 (furanyl*C*(2)), 172.1 (*C*(1)), 194.4 (*C*O), 194.7 (*C*O); *m/z* (NSI^+) 377 ($[M+H]^+$, 100%), 394 ($[M+NH_4]^+$, 45%); HRMS (NSI^+) $C_{23}H_{21}O_5$ ($[M+H]^+$) requires 377.1384, found 377.1387 (+0.9 ppm).

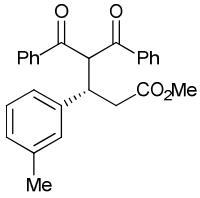
(3*S*)-Methyl 4-benzoyl-5-oxo-5-phenyl-3-(thiophen-2-yl)pentanoate (11)



The title compound was prepared according to *General Procedure D* from (*E*)-thienyl acrylic anhydride (73 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL). and purified by chromatography (CH_2Cl_2→ 2%EtOAc/CH_2Cl_2) to afford the *ester* **11** as a dark yellow solid (51 mg, 86%); mp 91-94 °C; $[\alpha]_D^{22}$ +29.5 (*c* 0.4 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 20 °C), t_R major: 16.1 min, t_R minor: 22.9 min, 94% ee; ν_{max} (film)/cm^{-1} 1736 (C=O), 1686 (C=O), 1655 (C=O), 1593 (C-C), 1578 (C-C), 1445 (C-O), 1263 (C-S); δ_H (400 MHz, $CDCl_3$) 2.80-2.99 (2H, m, C(2)H_2), 3.58 (3H, s, OCH_3), 4.70 (1H, td, *J* 8.9,

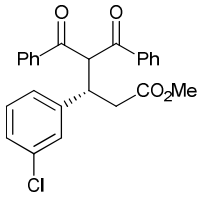
4.5, C(3)*H*), 5.99 (1H, d, *J* 9.0, C(4)*H*), 6.74 (1H, dd, *J* 5.1, 3.5, thienylC(4)*H*), 6.80-6.85 (1H, m, thienylC(3)*H*), 7.03 (1H, dd, *J* 5.1, 0.9, thienylC(5)*H*), 7.30-7.58 (6H, m, Ar*H*), 7.80-7.86 (2H, m, Ar*H*), 7.94-8.00 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 38.2 (*C*(3)H), 39.0 (*C*(2)H), 51.9 (O*C*H_3), 62.0 (*C*(4)H), 124.4 (thienyl*C*(5)H), 126.5 (thienyl*C*(3)H), 126.8 (thienyl*C*(4)H), 128.8 (4×Ar*C*H), 129.0 (2×Ar*C*H), 129.0 (2×Ar*C*H), 133.5 (Ar*C*(4)H), 133.9 (Ar*C*(4)H), 136.6 (Ar*C*), 136.7 (Ar*C*), 143.5 (thienyl*C*(2)), 172.1 (*C*(1)), 194.4 (*C*O), 194.5 (*C*O); *m/z* (NSI^+) 393 ($[M+H]^+$, 55%); HRMS (NSI^+) $C_{23}H_{21}O_4S$ ($[M+H]^+$) requires 393.1155, found 393.1157 (+0.5 ppm).

(3*S*)-Methyl 4-benzoyl-3-(3-methylphenyl)-5-oxo-5-phenylpentanoate (12)



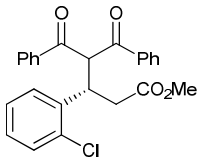
The title compound was prepared according to *General Procedure D* from (*E*)-3-(3-methylphenyl)acrylic anhydride (76 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **12** as an off-white solid (56 mg, 75%); mp 110-112 °C; $[\alpha]_D^{22}$ +19.8 (*c* 0.8 in $CHCl_3$); chiral HPLC analysis, Chiralcel AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C) t_R major (3*S*): 9.9 min, t_R minor (3*R*): 13.3 min, 91% ee; ν_{max} (film)/cm^{-1} 1728 (C=O, ester), 1688 (C=O), 1668 (C=O) 1257 (CH_3-O); δ_H (400 MHz, $CDCl_3$) 2.20 (3H, s, Ar*C*H_3), 2.81 (1H, dd, *J* 15.7, 9.3, C(2)H_2), 2.89 (1H, dd, *J* 15.7, 5.0, C(2)H_2), 3.51 (3H, s, $CO_2C$$H_3$), 4.36 (1H, td, *J* 9.3, 5.0, C(3)*H*), 5.83 (1H, d, *J* 9.4, C(4)*H*), 6.94-6.82 (1H, m, C(3)Ar(2)*H*), 7.03 (3H, dd, *J* 4.9, 3.8, C(3)Ar(4,5,6)*H*), 7.37-7.29 (2H, m, Ar*H*), 7.49-7.37 (3H, m, Ar*H*), 7.55 (1H, tt, *J* 7.4, 2.8, Ar*H*), 7.84-7.71 (2H, m, Ar*H*), 8.04-7.93 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 21.3 (C(3)Ar*C*H_3), 38.0 (*C*(2)), 42.5 (*C*(3)), 51.5 ($CO_2C$$H_3$), 62.1 (*C*(4)), 125.3 (C(3)Ar*C*(6)), 127.8 (C(3)Ar*C*(2)), 128.3 (C(3)Ar*C*H), 128.4 (2×C(5)Ar*C*H), 128.5 (2×C(5)Ar*CH*), 128.8 (4×C(5)Ar*C*H), 129.2 (C(3)Ar*C*H), 133.1 (C(5)Ar*C*H), 133.6 (C(5)Ar*C*(4)H), 136.6 (C(5)Ar*C*(1)), 136.8 (C(5)Ar*C*(1)), 137.9 (C(3)Ar*C*(3)), 140.1 (C(3)Ar*C*(1)), 172.04 (*C*(1)), 194.4 (Ar*C*), 194.8 (Ar*C*); *m/z* (ESI+) 401 ([M+H]+, 100%); HRMS (ESI+) $C_{26}H_{25}O_4$ ($[M+H]^+$), found 401.1750, requires 401.1747 (+0.7 ppm).

(3*S*)-Methyl 4-benzoyl-3-(3-chlorophenyl)-5-oxo-5-phenylpentanoate (13)



The title compound was prepared according to *General Procedure D* from (*E*)-3-(3-chlorophenyl)acrylic anhydride (87 mg, 0.25 mmol), 1,3-diphenylpropane-1,3-dione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) gave the *ester* **13** as a pale yellow solid (51 mg, 67%); mp 124-126 °C; $[\alpha]_D^{22}$ +18.1 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 220 nm, 30 °C), t_R major: 10.3 min, t_R minor: 13.2 min, 96% ee; ν_{max} (film)/cm^{-1} 2361 (C-H), 1738 (C=O), 1684 (C=O), 1261 (C-O); δ_H (400 MHz, $CDCl_3$) 2.74-2.95 (2H, m, C(2)H_2), 3.52 (3H, s, OCH_3), 4.36 (1H, td, *J* 9.5, 4.6, C(3)*H*), 5.82 (1H, d, *J* 9.5, C(4)*H*), 7.01-7.17 (3H, m, Ar*H*), 7.24 (1H, d, *J* 1.8, Ar*H*), 7.29-7.38 (2H, m, Ar*H*), 7.38-7.51 (3H, m, Ar*H*), 7.55 (1H, tt, *J* 6.9, 1.2, Ar*H*), 7.77 (2H, dd, *J* 8.4, 1.2, Ar*H*), 7.98 (2H, dd, *J* 8.4, 1.2, Ar*H*); δ_C (100 MHz, $CDCl_3$) 38.0 (*C*(2)), 42.4 (*C*(3)), 51.8 (O*C*H_3), 61.8 (*C*(4)), 127.0 (C(3)Ar*C*(6)H), 127.5 (C(3)Ar*C*(2)H), 128.6 (Ar*C*(1)H), 128.7 (2×Ar*C*H), 128.8 (2×Ar*C*H), 128.9 (2×Ar*C*H), 129.1 (2×Ar*C*H), 129.8 (C(3)Ar*C*(5)H), 133.6 (Ph*C*(4)H), 134.0 (Ph*C*(4)H), 134.3 (C(3)Ar*C*(3)Cl), 136.5 (Ph*C*(1)), 136.7 (Ph*C*(1)), 142.6 (C(3)Ar*C*(1)), 171.8 (*C*(1)), 194.2 (*C*O), 194.5 (*C*O); *m/z* (NSI^+) 421 ($[M+H]^+$, 100%); HRMS (NSI^+) $C_{25}H_{21}ClO_4$ ($[M+H]^+$) requires 421.1202, found 421.1201 (+0.2 ppm).

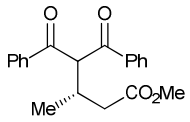
(3*S*)-Methyl 4-benzoyl-3-(2-chlorophenyl)-5-oxo-5-phenylpentanoate (14)



The title compound was prepared according to *General Procedure D* from (*E*)-3-(2-chlorophenyl)acrylic anhydride (87 mg, 0.25 mmol), 1,3-diphenylpropane-1,3-dione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2% EtOAc/CH_2Cl_2) gave the *ester* **14** as a yellow solid (53 mg, 69%); mp 93-96 °C; $[\alpha]_D^{22}$ –46.8 (*c* 1.3 in CH_2Cl_2); chiral HPLC analysis, ChiralPak AD-H (10% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C), t_R major: 10.8 min, t_R

minor: 14.1 min, 93% ee; ν_{max} (film)/cm^{-1} 2924 (C-H), 2361 (C-H), 1734 (C=O), 1686 (C=O), 1651 (C=O), 1258 (C-O); δ_H (400 MHz, $CDCl_3$) 2.90-3.09 (2H, m, C(2)H_2), 3.50 (3H, s, OCH_3), 4.79 (1H, q, *J* 7.8, C(3)*H*), 6.08 (1H, d, *J* 7.8, C(4)*H*), 7.04 (2H, pd, *J* 7.3, 1.8, Ar*H*), 7.22-7.31 (2H, m, Ar*H*), 7.36 (4H, dt, *J* 13.4, 7.7, Ph*H*), 7.43-7.58 (2H, m, Ph*H*), 7.79-7.93 (4H, m, Ph*H*); δ_C (100 MHz, $CDCl_3$) 35.8 (*C*(2)), 39.1 (*C*(3)), 51.7 (O*C*H$_3$), 59.1 (*C*(4)), 126.9 (C(3)Ar*C*(5)H), 128.4 (Ar*C*H), 128.7 (2×Ar*C*H), 128.8 (2×Ar*C*H), 128.9 (2×Ar*C*H), 128.9 (2×Ar*C*H), 130.2 (Ar*C*H), 133.4 (Ph*C*(4)H), 133.8 (Ph*C*(4)H), 134.0 (*C*Cl), 136.4 (Ph*C*(1)), 136.9 (Ph*C*(1)), 137.8 (C(3)Ar*C*(1)), 172.1 (*C*(1)), 194.4 (*C*O), 195.1 (*C*O); *m/z* (NSI$^+$) 421 ([M+H]$^+$, 100%); HRMS (NSI$^+$) $C_{25}H_{21}ClO_4$ ([M+H]$^+$) requires 421.1203, found 421.1201 (+0.4 ppm).

(3*S*)-Methyl 4-benzoyl-3-methyl-5-oxo-5-phenylpentanoate (15)

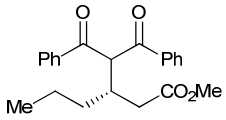


The title compound was prepared according to a *General Procedure D* from (*E*)-crotonic anhydride (39 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **15** as a colourless oil (39 mg, 67%); $[\alpha]_D^{22}$ +31.8 (*c* 1.25 in CH_2Cl_2); chiral HPLC analysis, ChiralPak AD-H (5% *i*-PrOH:hexane, flow rate 0.5 mL min^{-1}, 220 nm, 30 °C), t_R major: 35.0 min, t_R minor: 38.7 min, 70% ee; compound data as below.

The reaction was repeated using a modified *General Procedure D* at a lower temperature from (*E*)-crotonic anhydride (39 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL), the reaction was carried out at −78 °C and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **15** as a colourless oil (24 mg, 41%); $[\alpha]_D^{22}$ +32.7 (*c* 0.9 in CH_2Cl_2); chiral HPLC analysis, ChiralPak AD-H (5% *i*-PrOH:hexane, flow rate 0.5 mL min^{-1}, 220 nm, 30 °C), t_R major: 35.0 min, t_R minor: 38.7 min, 85% ee; ν_{max} (film)/cm^{-1} 2974 (C-H), 2953 (C-H), 2924 (C-H), 1724 (C=O), 1686 (C=O), 1670 (C=O), 1593 (O-CH$_3$); δ_H (300 MHz, $CDCl_3$) 1.09 (3H, d, *J* 7.0, CH(CH_3)), 2.38-2.68 (2H, m, C(2)H_2), 3.00-3.20 (1H, m, C(3)*H*), 3.65 (3H, s, OCH_3), 5.66 (1H, d, *J* 8.0, C(4)*H*), 7.37-7.62 (6H, m, Ar*H*), 7.95-8.06 (4H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 17.8 (CH(*C*H$_3$)), 31.5 (*C*(3)), 38.6 (*C*(2)), 51.7 (O*C*H$_3$), 60.0 (*C*(4)), 128.8 (2×Ar*C*H), 128.8 (2×Ar*C*H), 129.0 (2×Ar*C*H), 129.0 (2×Ar*C*H), 133.7 (2×Ar*C*), 136.6 (Ar*C*), 137.0 (Ar*C*), 173.2 (*C*(1)), 195.6 (*C*O), 195.8 (*C*O); *m/z*

(NSI$^+$) 325 ([M+H]$^+$, 100%), 342 ([M+NH$_4$]$^+$, 35%); HRMS (NSI$^+$) $C_{20}H_{21}O_4$ ([M+H]$^+$) requires 325.1434, found 325.1440 (+1.7 ppm).

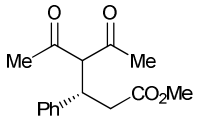
(3*S*)-Methyl 3-(1,3-dioxo-1,3-diphenylpropan-2-yl)hexanoate (16)



The title compound was prepared according to *General Procedure D* from (*E*)-hexenoic anhydride (53 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **16** as a colourless oil (36 mg, 57%); $[\alpha]_D^{22}$ 0.2 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (5% *i*-PrOH:hexane, flow rate 0.5 mL min^{-1}, 220 nm, 30 °C), t_R major: 29.5 min, t_R minor: 32.8 min, 80% ee; compound data as below.

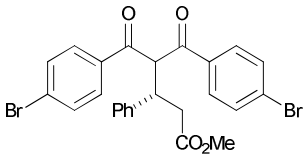
The reaction was repeated using a modified *General Procedure D* at a lower temperature from (*E*)-hexenoic anhydride (53 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) at –78 °C and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **16** as a colourless oil (22 mg, 35%); $[\alpha]_D^{22}$ +45.8 (*c* 0.5 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (5% *i*-PrOH:hexane, flow rate 0.5 mL min^{-1}, 220 nm, 30 °C), t_R major: 29.5 min, t_R minor: 32.8 min, 93% ee; ν_{max} (film)/cm^{-1} 2957 (C-H), 2932 (C-H), 2872 (C-H), 1730 (C=O), 1694 (C=O), 1668 (C=O), 1595 (O-CH$_3$); δ_H (400 MHz, $CDCl_3$) 0.81 (3H, t, *J* 7.1, C(6)H_3), 1.16-1.31 (1H, m, C(4)H_2), 1.33-1.45 (2H, m, C(5)H_2), 1.49-1.63 (1H, m, C(4)H_2), 2.47-2.72 (2H, m, C(2)H_2), 2.84-3.00 (1H, m, C(3)*H*), 3.62 (3H, s, OCH_3), 5.87 (1H, d, *J* 7.2, C*H*(COPh)$_2$), 7.35-7.63 (6H, m, Ar*H*), 8.00 (4H, dt, *J* 8.6, 1.4, Ar*H*); δ_C (100 MHz, $CDCl_3$) 14.1 (*C*(6)), 20.8 (*C*(5)), 33.5 (*C*(4)), 35.2 (*C*(2)$_3$), 36.3 (*C*(3))CH), 51.6 (O*C*H$_3$), 58.4 (*C*H(COPh)$_2$), 128.8 (2×Ar*C*H), 128.8 (2×Ar*C*H), 129.0 (2×Ar*C*H), 129.0 (2×Ar*C*H), 133.6 (Ar*C*H), 133.6 (Ar*C*H), 136.8 (Ar*C*), 137.0 (Ar*C*), 173.7 (*C*(1)), 195.9 (*C*O), 196.2 (*C*O); *m/z* (NSI$^+$) 353 ([M+H]$^+$, 100%); HRMS (NSI$^+$) $C_{22}H_{25}O_4$ ([M+H]$^+$) requires 353.1747, found 353.1753 (+1.6 ppm).

(3*S*)-Methyl 4-acetyl-5-oxo-3-phenylhexanoate (S16)



The title compound was prepared according to *General Procedure D* from (*E*)-cinnamic anhydride (70 mg, 0.25 mmol), pentane-2,4-dione (19 μL, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **S16** as a white solid (30 mg, 64%); mp 68-72 °C; $[\alpha]_D^{22}$ +57.3 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak OJ-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C), t_R major: 20.9 min, t_R minor: 34.2 min, 37% ee; ν_{max} (film)/cm^{-1} 1722, 1686, 1356, 1146; δ_H (400 MHz, $CDCl_3$) 1.85 (3H, d, *J* 0.4, CH_3), 2.27 (3H, d, *J* 0.4, CH_3), 2.58 (2H, dd, *J* 7.2, 6.6, C(2)H_2), 3.52 (3H, s, OCH_3), 3.97 (1H, ddd, *J* 11.6, 7.2, 6.6, C(3)*H*), 4.26 (1H, d, *J* 11.6, C(4)*H*), 7.18-7.24 (3H, m, Ar*H*), 7.26-7.31 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 29.7 (*C*H_3), 30.0 (*C*H_3), 39.3 (*C*(2)), 41.7 (*C*(3)), 51.8 (O*C*H_3), 74.2 (*C*(4)), 127.6 (C(3)Ar*C*(4)H), 128.1 (2×Ar*C*H), 129.0 (2×Ar*C*H), 139.9 (C(3)Ar*C*(1)), 171.6 (*C*(1)), 202.8 (*C*O), 203.0 (*C*O); *m/z* (NSI^+) 263 ($[M+H]^+$, 100%); HRMS (NSI^+) $C_{15}H_{19}O_4$ ($[M+H]^+$) requires 263.1278, found 263.1270 (–3.0 ppm).

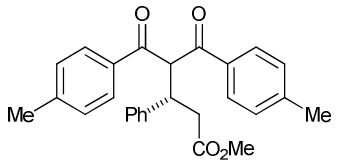
(3*S*)-Methyl-5-(4-bromophenyl)-4-[(4-bromophenyl)carbonyl]-5-oxo-3-phenylpentanoate (17)



The title compound was prepared according to *General Procedure D* from 1,3-*bis*(4-bromophenyl)propane-1,3-dione (55 mg, 0.18 mmol) and (*E*)-cinnamic anhydride (70 mg, 0.25 mmol) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **17** as a white solid (65 mg, 66%); mp 172-173 °C; $[\alpha]_D^{22}$ +9.2 (*c* 0.9 in $CHCl_3$); Chiral HPLC analysis; Chiralcel AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C) t_R major (3*S*): 13.8 min, t_R minor (3*R*): 18.3 min, 92% ee; ν_{max} (film) 1734 (C=O, ester), 1701 (C=O), 1664 (C=O), 1259 (CH_3-O); δ_H (400 MHz, $CDCl_3$) 2.80 (1H, dd, *J* 15.7, 9.0, (2)*H*), 2.87 (1H, dd, *J* 15.7, 4.8, (2)*H*), 3.52 (3H, s, CO_2CH_3), 4.37 (1H, td, *J* 9.3, 4.8, C(3)*H*Ph), 5.74 (1H, d, *J* 9.7, C(4)*H*), 7.28-6.82 (5H, m, 5×Ar(3)*H*,), 7.46 (2H, d, *J* 8.6, Ar(4,2)*H*), 7.58 (4H, dd, *J* 9.4, 8.6, Ar(4,2)*H*), 7.84 (2H, d, *J* 8.6 Hz, ArH); δ_C (100 MHz, $CDCl_3$) 38.0 (*C*(2)), 42.6 (*C*(3)), 51.7 (CO_2CH_3), 62.5 (*C*(4)), 127.3, 128.3, 128.6, 128.8 (C(5)Ar*C*), 129.3 (C(5)Ar*C*), 130.0 (C(5)Ar*C*H), 130.3 (C(5)Ar*C*H), 131.9 (C(5)Ar*C*H), 132.2 (C(5)Ar*C*H), 135.1

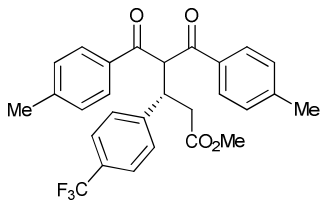
(C(5)Ar*C*), 135.2 (C(5)Ar*C*), 139.8 (C(3)Ar*C*(1)), 171.9 (*C*(1)), 193.3 (*C*(5)), 193.5 (*C*(5)); HRMS (ESI+) $C_{25}H_{21}{}^{79}Br_2O_4$ ($[M+H]^+$), found 542.9800, requires 542.9801 (–0.5 ppm).

(3*S*)-Methyl-5-(4-methylphenyl)-4-[(4-methylphenyl)carbonyl]-5-oxo-3-phenylpentanoate (18)



The title compound was prepared according to *General Procedure D* from 1,3-*bis*(4-methylphenyl)propane-1,3-dione (55 mg, 0.18 mmol) and (*E*)-cinnamic anhydride (70 mg, 0.25 mmol) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **18** as an off-white solid (30 mg, 40%); mp 142-143 °C; $[\alpha]_D^{22}$ –3.6 (*c* 0.65 in $CHCl_3$); chiral HPLC analysis; Chiralcel AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C) t_R major (3*S*): 16.9 min, t_R minor (3*R*): 23.6 min, 90% ee; ν_{max} (film) 2970 (C−H), 1736 (C=O, ester), 1693 (C=O), 1654 (C=O); δ_H (400 MHz, $CDCl_3$) 2.32 (3H, s, ArCH_3), 2.38 (3H, s, ArCH_3), 2.83 (1H, dd, *J* 15.7, 9.6, C(2)*H*), 2.88 (1H, dd, *J* 15.7, 4.7, C(2)*H*), 3.49 (3H, s, CO_2CH_3), 4.40 (1H, td, J 9.6, 4.7, C(3)*H*), 5.77 (1H, d, *J* 9.6, C(4)*H*), 7.35-7.03 (9H, m, 5×Ar(3)*H*, and 4×C(5)Ar(3)*H*), 7.68 (2H, d, *J* 8.3, C(5)Ar(2)*H*), 7.90 (2H, d, *J* 8.3, C(5)Ar(2)*H*); δ_C (100 MHz, $CDCl_3$) 21.6 (Ar*C*H_3), 21.6 (Ar*C*H_3), 38.2 (*C*(2)H_2), 42.6 (*C*(3)H), 51.5 (CO_2CH_3), 62.1 (*C*(4)H), 127.0 (C(3)Ar*C*(4)H), 128.3 (4×C(3)Ar*C*(2,3)H), 128.7 (2×C(5)Ar*C*(3)), 129.0 (2×C(5)Ar*C*(3')), 129.2 (2×C(5)Ar*C*(2)), 129.5 (2×C(5)Ar*C*(2')), 134.1 (C(5)Ar*C*(1)), 134.3 (C(5)Ar*C*(1')), 140.5 (C(3)Ar*C*(1)), 144.1 (C(5)Ar*C*(4)), 144.7 (C(5)Ar*C*(4')), 172.0 (*C*(1)), 193.8 (*C*O), 194.3 (*C*O); *m/z* (ESI+) 302 ([M+H]+, 100%); HRMS (ESI+) $C_{27}H_{27}O_4$ ($[M+H]^+$), found 415.1906, requires 415.1904 (+0.5 ppm).

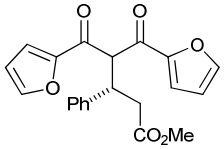
(3*S*)-Methyl-5-(4-methylphenyl)-4-[(4-methylphenyl)carbonyl]-5-oxo-3-[4-(trifluoromethyl) phenyl]pentanoate (19)



The title compound was prepared according to *General Procedure D* from (*E*)-3-(4-(Trifluoromethyl)phenyl)acrylic anhydride (104 mg, 0.25 mmol), 1,3-*bis*(4-Methylphenyl)propane-1,3-dione (45 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg,

0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **19** as an off-white solid (47 mg, 54%); mp 120-123 °C; $[\alpha]_D^{22}$ –23.2 (*c* 1.1 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 220 nm, 30 °C), t_R major: 14.1 min, t_R minor: 20.1 min, 97% ee; ν_{max} (film)/cm^{-1} 2954 (C-H), 1730 (C=O), 1686 (C=O), 1605 (C=C), 1110 (C-F); δ_H (500 MHz, $CDCl_3$) 2.32 (3H, s, PhCH_3), 2.38 (3H, s, PhCH_3), 2.74-2.96 (2H, m, C(2)H_2), 3.50 (3H, s, OCH_3), 4.45 (1H, td, *J* 9.6, 4.4, C(3)*H*), 5.77 (1H, d, *J* 9.6, C(4)*H*), 7.11 (2H, d, *J* 8.0, tolylC(2)*H*), 7.22 (2H, d, *J* 8.0, tolylC(2)*H*), 7.40 (4H, q, *J* 8.3, C(3)Ar*H*), 7.67 (2H, d, *J* 8.1, tolylC(3)*H*), 7.90 (2H, d, *J* 8.1, tolylC(3)*H*); δ_C (125 MHz, $CDCl_3$) 21.7 (Ar*C*H_3), 21.8 (Ar*C*H_3), 37.9 (*C*(2)H_2), 42.5 (*C*(3)H), 51.8 (O*C*H_3), 61.8 (*C*(4)H), 124.1 (q, $^1J_{CF}$ 272.0, *C*F_3), 125.4 (q, $^3J_{CF}$ 3.6, 2×C(3)Ar*C*(3)), 128.8 (2×Ar*C*H), 129.0 (2×Ar*C*H), 129.1 (2×Ar*C*H), 129.5 (2×Ar*C*H), 129.8 (2×Ar*C*H), 134.0 (C(5)Ar*C*(1)), 134.2 (C(5)Ar*C*(1)), 144.7 (C(3)Ar*C*(1)), 145.0 (C(5)Ar*C*(4)), 145.1 (C(5)Ar*C*(4)), 171.8 (O*C*H_3), 193.7 (*C*O), 194.1 (*C*O); δ_F (282 MHz, $CDCl_3$) –63.10; *m/z* (NSI^+) 483 ($[M+H]^+$, 100%), 500 ($[M+NH_4]^+$, 30%); HRMS (NSI^+) $C_{28}H_{26}F_3O_4$ ($[M+H^+]$) requires 483.1778, found 483.1775 (+0.8 ppm).

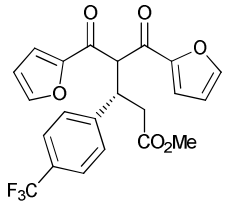
(3*S*)-Methyl-5-(furan-2-yl)-4-[(furan-2-yl)carbonyl]-5-oxo-3-phenylpentanoate (20)



The title compound was prepared according to *General Procedure D* from 1,3-*bis*(furan-2-yl)propane-1,3-dione (37 mg, 0.18 mmol) and (*E*)-cinnamic anhydride (70 mg, 0.25 mmol) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **20** as a pale yellow solid (61 mg, 93%); mp 131-133 °C; $[\alpha]_D^{22}$ +21.1 (*c* 1.65 in $CHCl_3$); chiral HPLC analysis; Chiralcel AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C) t_R major (3*S*): 14.1 min, t_R minor (3*R*): 21.1 min, 90% ee; ν_{max} (film) 1732 (C=O, ester), 1674 (C=O), 1645 (C=O); δ_H (400 MHz, $CDCl_3$) 2.86-2.82 (2H, m, C(2)*H*), 3.49 (3H, s, CO_2CH_3), 4.38 (1H, td, *J* 9.8, 4.7, C(3)*H*), 5.50 (1H, dd, *J* 10.4, 0.9, C(4)*H*), 6.42 (1H, ddd, *J* 3.7, 1.7, 0.9 Hz, furanyl(4)*H*), 6.54 (1H, ddd, 3.7, 1.7, 1.0, furanyl(4)*H*), 7.20-7.07 (4H, m, C(3)Ar(2,3)*H*), 7.27-7.25 (2H, m, C(3)Ar(4)*H* and furanyl(3)*H*), 7.37 (1H, dt, *J* 3.6, 0.9, furanyl(3)*H*), 7.50-7.49 (1H, m, furanyl(5)*H*), 7.60-7.59 (1H, m, furanyl(5)*H*); δ_C (100 MHz, $CDCl_3$) 38.4 (*C*(2)), 41.8 (*C*(3)), 51.5 (CO_2CH_3), 62.0 (*C*(4)), 112.7 (furanyl*C*(4)), 112.8 (furanyl*C*(4)), 118.7 (furanyl*C*(3)), 119.3 (furanyl*C*(3)), 127.1 (C(3)Ar(4)*H*), 128.2 (2×C(3)Ar(2)*C*H), 128.3 (2×C(3)Ar(3)*C*H), 139.8 (C(3)Ar*C*(1)), 146.8 (furanyl*C*(5)), 147.4 (furanyl*C*(5)), 151.9 (furanyl*C*(2)),

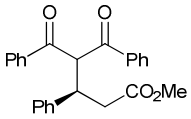
152.1 (furanyl*C*(2)), 171.6 (*C*(1)), 181.9 (*C*O), 182.0 (*C*O); *m/z* (ESI+) 367 ([M+H]+, 100%); HRMS (ESI+) $C_{21}H_{19}O_6$ ($[M+H]^+$), found 367.1175, requires 367.1176 (–0.3 ppm).

(3*S*)-Methyl-5-(furan-2-yl)-4-[(furan-2-yl)carbonyl]-5-oxo-3-[4-(trifluoromethyl)phenyl] pentanoate (21)



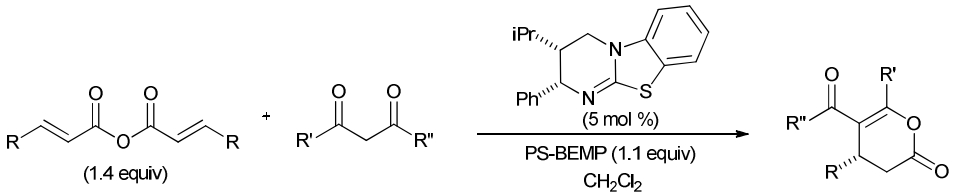
The title compound was prepared according to *General Procedure D* from (*E*)-3-(4-(Trifluoromethyl)phenyl)acrylic anhydride (104 mg, 0.25 mmol), 1,3-*bis*(furan-2-yl)propane-1,3-dione (37 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) gave **21** as a yellow solid (71 mg, 91%); mp 151-154 °C; $[\alpha]_D^{22}$ –10.8 (*c* 1.0 in CH_2Cl); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C), t_R major: 12.7 min, t_R minor: 21.4 min, 94% ee; ν_{max} (film)/cm^{-1} 2974 (C-H), 2926 (C-H), 1734 (C=O), 1670 (C=O), 1458 (furan), 1113 (C-F); δ_H (500 MHz, $CDCl_3$) 2.81 (2H, qd, *J* 15.9, 7.2, C(2)H_2), 3.49 (3H, s, OCH_3), 4.40 (1H, td, *J* 10.0, 4.5, C(3)*H*), 5.50 (1H, d, *J* 10.3, C(4)*H*), 6.43 (1H, dd, *J* 3.5, 1.5, furanyl(4)*H*), 6.55 (1H, dd, *J* 3.5, 1.5, furanyl(4)*H*), 7.12 (1H, d, *J* 3.5, furanyl(3)*H*), 7.34-7.46 (5H, m, 4×Ar*H* and furanyl(3)*H*), 7.50 (1H, s, furanyl(5)*H*), 7.59 (1H, s, furanyl(4)*H*); δ_C (125 MHz, $CDCl_3$) 38.1 (*C*(2)H_2), 41.6 (O*C*H_3), 51.8 (*C*(3)H), 61.6 (*C*(4)H), 113.0 (furanyl*C*(4)H), 113.1 (furanyl*C*(4)H), 119.1 (furanyl*C*(3)H), 119.6 (furanyl*C*(3)H), 124.1 (q, $^1J_{CF}$ 272.0, *C*F_3). 125.4 (d, $^3J_{CF}$ 3.6, 2×C(3)Ar*C*(3)H), 128.8 (2×C(3)Ar*C*(2)H), 129.4 (q, $^2J_{CF}$ 32.4, Ar*C*(4)CF_3), 144.3 (ArC(1)), 147.2 (furanyl*C*(5)H), 147.7 (furanyl*C*(5)H), 151.9 (furanyl*C*(2)), 152.2 (furanyl*C*(2)), 171.4 (*C*(1)), 181.8 (*C*O), 181.8 (*C*O); δ_F (282 MHz, $CDCl_3$) –63.12; *m/z* (NSI^+) 435 ($[M+H]^+$, 100%), 452 ($[M+NH_4]^+$, 70%); HRMS (NSI^+) $C_{22}H_{18}F_3O_6$ ($[M+H]^+$) requires 435.1050, found 435.1052 (+0.5 ppm).

(3*R*)-Methyl 4-benzoyl-5-oxo-3,5-diphenylpentanoate (6)



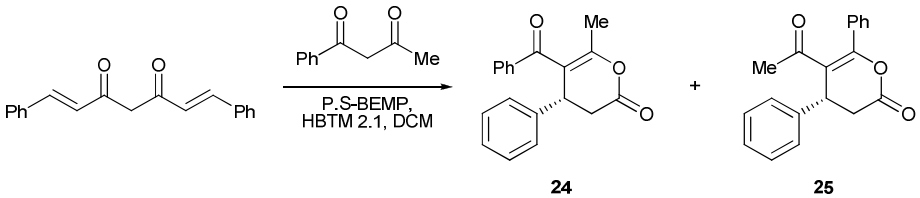
The title compound was prepared according to *General Procedure D* from (*Z*)-cinnamic anhydride (70 mg, 0.25 mmol), 1,3-diphenyl-1,3-propanedione (40 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) gave **21** as a yellow solid (28 mg, 41%); $[\alpha]_D^{22}$ −12.4 (*c* 0.5 in CH_2Cl_2); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C), t_R minor: 11.8 min, t_R major: 17.0 min, 30% ee. Data in agreement to that reported on page S12

General Procedure E: Lactone formation



To a solution of the corresponding homoanhydride (1.4 equiv) in dry CH_2Cl_2 (0.72 mM) under argon, was added dicarbonyl (1.0 equiv), isothiourea (HBTM 2.1, 0.05 equiv) and polymer-bound 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) (1.1 equiv) at 0 °C. The reaction mixture was stirred and gradually warmed to room temperature over 5 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (CH_2Cl_2) to afford the *lactones* **2, S16, S19-S20, 24-29**.

(*R*)-5-Benzoyl-6-methyl-4-phenyl-3,4-dihydro-2*H*-pyran-2-one, (*R*)-5-Acetyl-4,6-diphenyl-3,4-dihydro-2*H*-pyran-2-one (24, 25)

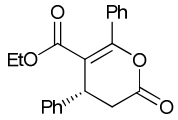


The title compound was prepared according to *General Procedure E* from (*E*)-cinnamic anhydride (70 mg, 0.25 mmol), 1-phenylbutane-1,3-dione (29 mg, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL). Chromatographic purification

of the residue (CH_2Cl_2) gave **24** as a white solid (15 mg, 29% in 96:4 rr), **25** as a white solid (2 mg, 4% in 3:96 rr) and a mixture of **24** and **25** (29 mg, 55% in 34:66 rr).

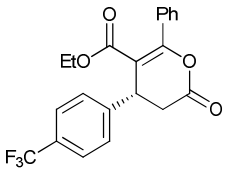
24: mp 80-84 °C; $[\alpha]_D^{22}$ –19.6 (*c* 1.0 in $CHCl_3$); {Lit.[10] $[\alpha]_D^{22}$ –26.7 (*c* 1.0 in $CHCl_3$) 96% ee}; chiral HPLC analysis, ChiralPak OD-H (15% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 20 °C), t_R major: 15.4 min, t_R minor: 18.9 min, 70% ee; δ_H (300 MHz, $CDCl_3$) 1.91 (3H, d, *J* 0.9, C*H*$_3$), 2.95 (1H, dd, *J* 15.9, 3.6, C*H*$_2$), 3.08 (1H, dd, *J* 15.9, 7.5, C*H*$_2$), 4.32-4.36 (1H, m, C*H*), 7.14-7.65 (10H, m, Ar*H*). Representative data for **25**: $[\alpha]_D^{22}$ –94.0 (*c* 0.15 in $CHCl_3$); chiral HPLC analysis, ChiralPak AS-H (15% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C), t_R major: 21.4 min, t_R minor: 30.7 min, 61% ee; δ_H (500 MHz, $CDCl_3$) 1.80 (3H, s, C*H*$_3$), 2.94 (1H, dd, *J* 16.0, 2.0, C*H*$_2$), 3.06 (1H, dd, *J* 16.0, 7.8, C*H*$_2$), 4.48-4.50 (1H, m, C*H*), 7.21-7.34 (6H, m, Ar*H*), 7.46-7.55 (4H, m, Ar*H*). Data in agreement with the literature.[10]

(*R*)-Ethyl 2-oxo-4,6-diphenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (27)



The title compound was prepared according to *General Procedure E* from (*E*)-cinnamic anhydride (70 mg, 0.25 mmol), ethyl 3-oxo-3-phenylpropanoate (31 μL, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2) to afford the *lactone* **27** as a yellow gum (35 mg, 60%); $[\alpha]_D^{22}$ –67.0 (*c* 1.0 in $CHCl_3$); {Lit.[9] $[\alpha]_D^{22}$ –70.0 (*c* 1.0 in $CHCl_3$) 92% ee}; chiral HPLC analysis, ChiralPak AD-H (3% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 20 °C), t_R major: 17.3 min, t_R minor: 26.1 min, 94% ee; δ_H (400 MHz, $CDCl_3$) 0.90 (3H, t, *J* 7.2, C*H*$_3$), 2.95 (1H, dd, *J* 15.8, 2.4, C(3)*H*$_2$), 2.98 (1H, dd, *J* 15.8, 7.6, C(3)*H*$_2$), 3.89-4.01 (2H, m, OC*H*$_2$), 4.43 (1H, dd, *J* 7.6, 2.4, C(4)*H*), 7.26-7.54 (10H, m, Ar*H*). Data in agreement with the literature.[10]

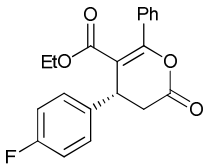
(*R*)-Ethyl 2-oxo-6-phenyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyran-5-carboxylate (28)



The title compound was prepared according to *General Procedure E* from (*E*)-3-(4-(trifluoromethyl)phenyl)acrylic anhydride (104 mg, 0.25 mmol), ethyl 3-oxo-3-phenylpropanoate (31

μL, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2) to afford the *lactone* **28** as a white gum (43 mg, 61%); $[\alpha]_D^{22}$ –56.6 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (15% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 20 °C), t_R major: 8.0 min, t_R minor: 11.0 min, 94% ee; ν_{max} (film)/cm^{-1} 1782 (C=O), 1694 (C=O), 1323 (C-F); δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.2, CH_3), 2.94 (1H, dd, *J* 16.0, 2.4, C(3)H_2), 3.15 (1H, dd, *J* 16.0, 7.6, C(3)H_2), 3.89-4.00 (2H, m, OCH_2), 4.47 (1H, dd, *J* 7.6, 2.4, C(4)*H*), 7.38-7.53 (7H, m, Ar*H*), 7.61 (2H, d, *J* 8.0, Ar*H*); δ_C (75 MHz, $CDCl_3$) 13.6 (*C*H_3), 36.1 (*C*(3)H_2), 38.8 (*C*(4)H), 61.3 (O*C*H_2), 111.0 (*C*(5)), 124.1 (q, $^1J_{CF}$ 270.1, *C*F_3), 126.4 (q, $^3J_{CF}$ 3.8, 2×C(4)Ar*C*(3)), 127.4 (2×Ar*C*H), 128.2 (2×Ar*C*H), 128.8 (2×Ar*C*H), 130.3 (q, $^2J_{CF}$ 32.3, C(4)Ar*C*(4)), 130.5 (Ar*C*H), 133.0 (Ph*C*(1)), 144.2 (CF_3Ph*C*(1)), 159.4 (*C*(6)), 165.5 (*C*O), 166.2 (*C*O); δ_F (300 MHz, $CDCl_3$) –63.1; *m/z* (NSI^+) 423 ($[M+CH_3OH+H]^+$, 100%), 391 ($[M+H]^+$, 30%); HRMS (NSI^+) $C_{21}H_{18}F_3O_4$ ($[M+H]^+$) requires 391.1152, found 391.1155 (+0.8 ppm).

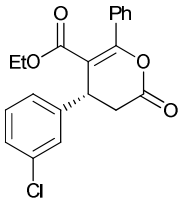
(*R*)-Ethyl 4-(4-fluorophenyl)-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-5-carboxylate (29)



The title compound was prepared according to *General Procedure E* from (*E*)-3-(4-fluorophenyl)acrylic anhydride (314 mg, 1.0 mmol), ethyl 3-oxo-3-phenylpropanoate (124 μL, 0.72 mmol), HBTM 2.1 (11.1 mg, 0.036 mmol) and BEMP (2.0 mmol/g loading) (360 mg, 0.80 mmol) in CH_2Cl_2 (1.0 mL) and purified by chromatography (CH_2Cl_2) to afford the *lactone* **29** as a pale yellow oil (171 mg, 70%); $[\alpha]_D^{22}$ –26.1 (*c* 1.0 in CH_2Cl_2); chiral HPLC analysis, ChiralPak AD-H (10% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 220 nm, 30 °C), t_R major: 9.4 min, t_R minor: 13.1 min, 89% ee; ν_{max} (film)/cm^{-1} 2926 (C-H), 1784 (C=O), 1705 (C=O), 1508 (C=C), 1224 (C-F); δ_H (300 MHz, $CDCl_3$) 0.91 (3H, t, *J* 7.1, CH_3), 2.94 (1H, dd, *J* 15.8, 2.4, C(3)H_2), 3.13 (1H, dd, *J* 15.8, 7.6, C(3)H_2), 3.97 (2H, qd, *J* 7.1, 2.2, OCH_2), 4.43 (1H, dd, *J* 7.6, 2.4, C(4)*H*), 6.99-7.12 (2H, m, FPhC(3,5)*H*), 7.22-7.28 (2H, m, FPhC(2,6)*H*), 7.38-7.58 (5H, m, Ph*H*); δ_C (75 MHz, $CDCl_3$) 13.6 (*C*H_3), 36.5 (*C*(3)H_2), 38.3 (*C*(4)H), 61.2 (O*C*H_2), 111.7 (*C*(5)), 116.2 (d, $^2J_{C\text{-}F}$ 21.6, 2×C(4)Ar*C*(3)H), 128.2 (2×Ar*C*H), 128.5 (d, $^3J_{C\text{-}F}$ 8.2, 2×C(4)Ar*C*(2)H), 128.8 (2×Ar*C*H), 130.4 (Ar*C*H), 133.1 (Ph*C*(1)), 135.8 (d, $^4J_{CF}$ 3.3, C(4)Ar*C*(1)), 158.8 (*C*(6)), 162.4 (d, $^1J_{C\text{-}F}$ 246.5, *C*F), 165.9 (*C*O), 166.4 (*C*O); δ_F (282 MHz,

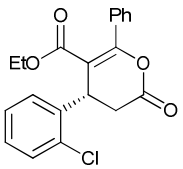
$CDCl_3$) –115.1; *m/z* (APCI$^+$) 341 ([M+H]$^+$, 100%); HRMS (APCI$^+$) $C_{20}H_{18}FO_4$ ([M+H]$^+$) requires 341.1184 found 341.1179 (–1.4 ppm).

(*R*)-Ethyl 4-(3-chlorophenyl)-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-5-carboxylate (30)



The title compound was prepared according to *General Procedure E* from (*E*)-3-chlorophenyl)acrylic anhydride (347 mg, 1.0 mmol), ethyl 3-oxo-3-phenylpropanoate (124 μL, 0.72 mmol), HBTM 2.1 (11.1 mg, 0.036 mmol) and BEMP (2.0 mmol/g loading) (360 mg, 0.80 mmol) in CH_2Cl_2 (1.0 mL) and purified by chromatography (CH_2Cl_2) to afford the *lactone* **30** as a pale yellow oil (121 mg, 47%); $[\alpha]_D^{22}$ –2.1 (*c* 0.38 in CH_2Cl_2); chiral HPLC analysis, ChiralPak AD-H (5% *i*-PrOH:hexane, flow rate 0.5 mL min^{-1}, 220 nm, 30 °C), t_R major: 25.5 min, t_R minor: 39.1 min, 92% ee; ν_{max} (film)/cm^{-1} 2980 (C-H), 1732 (C=O), 1708 (C=O), 1597 (C=C), 1066 (C-Cl); δ_H (400 MHz, $CDCl_3$) 0.92 (3H, t, *J* 7.1, C*H*$_3$), 2.96 (1H, dd, *J* 15.9, 2.4, C(3)*H*$_2$), 3.14 (1H, dd, *J* 15.9, 7.7, C(3)*H*$_2$), 3.98 (2H, qd, *J* 7.1, 2.0, OC*H*$_2$), 4.41 (1H, dd, *J* 7.7, 2.4, C(4)*H*), 7.17 (1H, dt, *J* 6.6, 1.9, Ar*H*), 7.25-7.30 (3H, m, Ar*H*), 7.42-7.55 (5H, m, Ar*H*); δ_C (75 MHz, $CDCl_3$) 13.6 (*C*H$_3$), 36.2 (*C*(4)H), 38.7 (*C*(3)H$_2$), 61.3 (O*C*H$_2$), 111.1 (*C*(5)H), 125.0 (Ar*C*H), 127.3 (Ar*C*H), 128.2 (2×Ar*C*H), 128.3 (Ar*C*H),128.8 (2×Ar*C*H), 130.4 (Ar*C*H), 130.7 (Ar*C*H), 133.0 (Ph*C*(1)), 135.1 (C(4)Ar*C*(3)), 142.1 (C(4)Ar*C*(1)), 159.3 (*C*(6)H), 165.7 (*C*O), 166.3 (*C*O); *m/z* (APCI$^+$) 357 ([M+H]$^+$, 90%); HRMS (NSI$^+$) $C_{20}H_{18}ClO_4$ ([M+H]$^+$) requires 357.0888, found 357.0888 (–0.0 ppm).

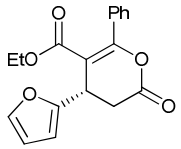
(*S*)-Ethyl 4-(2-chlorophenyl)-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-5-carboxylate (31)



The title compound was prepared according to *General Procedure D* from (*E*)-3-chlorophenyl)acrylic anhydride (89 mg, 0.25 mmol), ethyl 3-oxo-3-phenylpropanoate (31 μL, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2) to afford the *lactone* **31** as a pale yellow oil (29 mg, 46%) in

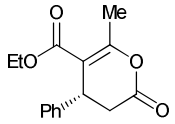
96% ee; $[\alpha]_D^{22}$ –25.0 (*c* 1.3 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (15% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 220 nm, 30 °C), t_R major: 6.3 min, t_R minor: 7.4 min, 96% ee; ν_{max} (film)/cm^{-1} 2980 (C-H), 1728 (C=O), 1687 (C=O), 1597 (C=C), 1037 (C-Cl); δ_H (400 MHz, $CDCl_3$) 0.90 (3H, t, *J* 7.1, CH_3), 2.99 (1H, dd, *J* 15.9, 2.4, C(3)H_2), 3.09 (1H, dd, *J* 16.0, 7.7, C(3)H_2), 3.94 (2H, qd, *J* 7.1, 2.7, OCH_2), 4.92 (1H, dd, *J* 7.7, 2.4, C(4)*H*), 7.21-7.29 (3H, m Ar*H*), 7.39-7.52 (4H, m, Ar*H*), 7.50-7.61 (2H, m, Ar*H*); δ_C (75 MHz, $CDCl_3$) 13.6 (*C*H_3), 34.7 (*C*(3)H_2), 35.9 (*C*(4)H), 61.2 (O*C*H_2), 110.6 (*C*(5)), 127.4 (Ar*C*H), 127.7 (Ar*C*H), 128.2 (2×Ar*C*H), 128.8 (2×Ar*C*H), 129.3 (Ar*C*H), 130.5 (Ar*C*H), 130.5 (Ar*C*H), 132.9 (Ph*C*(1)), 133.5 (C(4)Ar*C*(2)), 136.6 (C(4)Ar*C*(1)), 160.0 (*C*(6)), 165.7 (*C*O), 166.0 (*C*O); *m/z* (APCI$^+$) 357 ([M+H]$^+$, 65%), 375 ([M+NH_4]$^+$,50%); HRMS (APCI$^+$) $C_{20}H_{18}ClO_4$ ([M+H]$^+$) requires 357.0888, found 357.0885 (–0.9 ppm).

(*S*)-Ethyl 4-(furan-2-yl)-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-5-carboxylate (32)



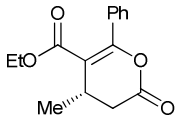
The title compound was prepared according to *General Procedure E* from (*E*)-3-(furan-2-yl)acrylic anhydride (258 mg, 1.0 mmol), ethyl 3-oxo-3-phenylpropanoate (124 μL, 0.72 mmol), HBTM 2.1 (11.1 mg, 0.036 mmol) and BEMP (2.0 mmol/g loading) (360 mg, 0.80 mmol) in CH_2Cl_2 (1.0 mL) and purified by chromatography (CH_2Cl_2) to afford the *lactone* **32** as a yellow oil (146 mg, 65%); $[\alpha]_D^{22}$ –6.19 (*c* 1.0 in CH_2Cl_2); chiral HPLC analysis, ChiralPak AD-H (5% *i*-PrOH:hexane, flow rate 0.5 mL min^{-1}, 220 nm, 30 °C), t_R major: 24.8 min, t_R minor: 29.2 min, 92% ee; ν_{max} (film)/cm^{-1} 2982 (C-H), 2928 (C-H), 1728 (C=O), 1684 (C=O), 1014 (C-OC); δ_H (500 MHz, $CDCl_3$) 0.96 (3H, t, *J* 7.1, CH_2CH_3), 2.99 (1H, dd, *J* 16.0, 7.2, C(3)H_2), 3.12 (1H, dd, *J* 16.0, 1.6, C(3)H_2), 3.98-4.05 (2H, m, OCH_2), 4.49 (1H, d, *J* 6.2, C(4)*H*), 6.18 (1H, d, *J* 3.0, furanylC(3)*H*), 6.29 (1H, s, furanylC(4)*H*), 7.35 (1H, s, furanylC(5)*H*), 7.37-7.48 (5H, m, Ph*H*); δ_C (75 MHz, $CDCl_3$) 13.6 (*C*H_3), 32.7 (*C*(4)H), 33.3 (*C*(3)H_2), 61.2 (O*C*H_2), 106.5 (furanyl*C*(3)H), 109.5 (*C*(5)H), 110.5 (furanyl*C*(4)H), 128.0 (2×Ar*C*H), 128.7 (2×Ar*C*H), 130.3 (Ar*C*H), 133.1 (Ph*C*(1)), 142.8 (furanyl*C*(5)H), 152.4 (furanyl*C*(2)H), 159.4 (*C*(6)H), 165.9 (*C*O), 166.1 (*C*O); *m/z* (APCI$^+$) 345 ([M+MeOH+H]$^+$, 100%), 313 ([M+H]$^+$, 25%); HRMS (APCI$^+$) $C_{18}H_{17}O_5$ ([M+H]$^+$) requires 313.1071, found 313.1068 (–0.8 ppm).

(*R*)-Ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (S17)



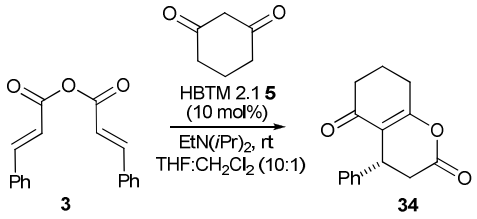
The title compound was prepared according to *General Procedure E* from (*E*)-cinnamic anhydride (280 mg, 1.00 mmol), ethyl acetoacetate (94 μL, 0.72 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (360 mg, 0.20 mmol) in CH_2Cl_2 (1.0 mL) and purified by chromatography (CH_2Cl_2) to afford the *lactone* **S17** as a white solid (135 mg, 72%); mp 79-80 °C {Lit[9] 83-84 °C} chiral HPLC analysis, ChiralPak OD-H (15% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 254 nm, 30 °C), t_R minor: 6.2 min, t_R minor: 10.5 min, 70% ee; $[\alpha]_D^{20}$ −101.5 (*c* 1.0 in CH_3Cl), {Lit[9] $[\alpha]_D^{20}$ −130.6 (*c* 1.0 in CH_3Cl); 91% ee}; δ_H (300 MHz, $CDCl_3$) 1.20 (3H, t, *J* 7.1, $CO_2CH_2CH_3$), 2.48 (3H, d, *J* 1.0, C(6)CH_3), 2.83 (1H, dd, *J* 15.9, 2.4, C(3)H_2), 2.96 (1H, dd, *J* 15.9, 7.5, C(3)H_2), 4.14 (2H, q, *J* 7.1, OCH_2), 4.26-4.28 (1H, m, C(4)*H*), 7.13-7.16 (2H, m, Ar*H*), 7.22-7.34 (3H, m, Ar*H*). Data in agreement with the literature.[9]

(*S*)-Ethyl 4-methyl-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-5-carboxylate (S18)



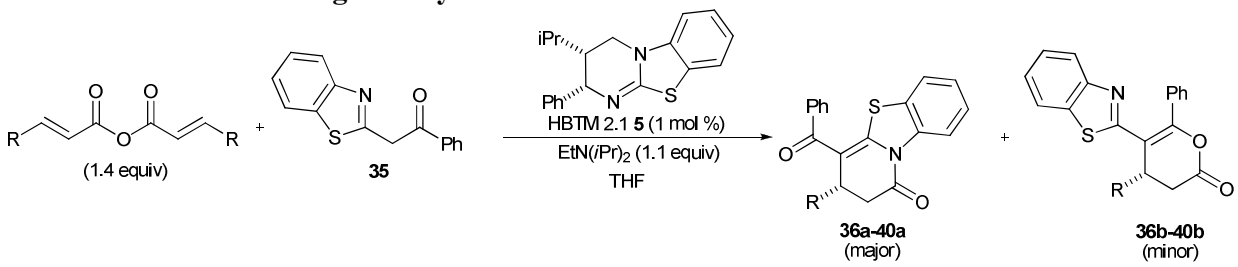
The title compound was prepared according to *General Procedure E* from (*E*)-but-2-enoic anhydride (39 mg, 0.25 mmol), ethyl 3-oxo-3-phenylpropanoate (31 μL, 0.18 mmol), HBTM 2.1 (2.8 mg, 0.009 mmol) and BEMP (2.0 mmol/g loading) (90 mg, 0.20 mmol) in CH_2Cl_2 (0.25 mL) and purified by chromatography (CH_2Cl_2) to afford the *lactone* **S18** as a colourless oil (21 mg, 45%); $[\alpha]_D^{22}$ +4.67 (*c* 0.5 in CH_2Cl_2); chiral HPLC analysis, ChiralPak OD-H (2.5% *i*-PrOH:hexane, flow rate 0.5 mL min^{-1}, 220 nm, 30 °C), t_R minor: 21.1 min, t_R major: 23.5 min, 65% ee; ν_{max} (film)/cm^{-1} 2978 (C-H), 2938 (C-H), 1728 (C=O), 1705 (C=O), 1690 (C=O); δ_H (500 MHz, $CDCl_3$) 0.98 (3H, t, *J* 7.1, CH_2CH_3), 1.24 (3H, d, *J* 7.1, C(4)CH_3), 2.65 (1H, dd, *J* 15.8, 2.1, C(3)H_2), 2.83 (1H, dd, *J* 15.8, 6.7, C(3)H_2), 3.20 (1H, tt, *J* 6.9, 3.6, C(4)*H*), 4.03 (2H, q, *J* 7.1, OCH_2), 7.38 (5H, dt, *J* 14.2, 7.4, Ph*H*); δ_C (100 MHz, $CDCl_3$) 13.7 (CH_2CH_3), 19.3 (C(4)(CH_3)), 28.4 (*C*(4)H), 35.7 (*C*(3)H_2), 61.0 (OCH_2), 114.1 (Ar*C*H), 128.0 (2×Ar*C*H), 128.6 (2×Ar*C*H), 130.0 (Ar*C*H), 133.3 (Ph*C*(1)), 157.5(*C*(6)), 166.8 (*C*O), 167.0 (*C*O); *m/z* (NSI^+) 261 ($[M+H]^+$, 60%); HRMS (NSI^+) $C_{15}H_{17}O_4$ ($[M+H]^+$) requires 261.1121, found 261.1125 (+1.4 ppm).

(*R*)-4-Phenyl-3,4,7,8-tetrahydro-2H-chromene-2,5(6H)-dione (34)



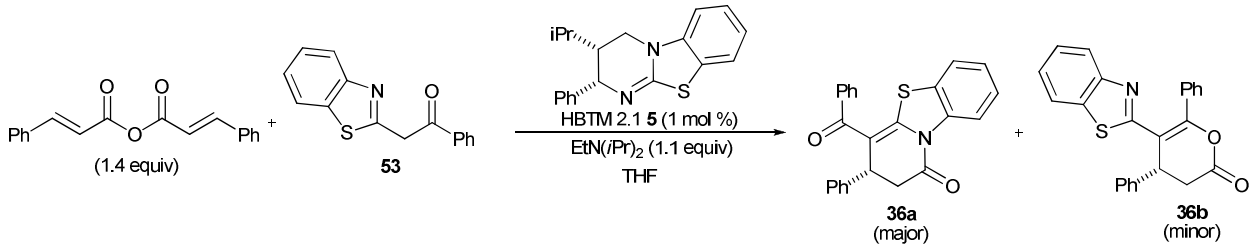
The title compounds were prepared according to *General Procedure E* using 1,3-cyclohexanedione (80 mg, 0.72 mmol), anhydride **3** (278 mg, 1.00 mmol), HBTM 2.1 (22 mg, 10 mol %) and EtN(*i*Pr)$_2$ (138 µL, 0.80 mmol) in THF:DCM (10:1, 2 mL) and purified by chromatography (CH_2Cl_2) to afford the title *lactone* **34** as a yellow solid (139 mg, 80%); mp 112-113 °C; $[\alpha]_D^{20}$ –118.2 (*c* 1.0, $CHCl_3$); HPLC analysis, ChiralPak AD-H (5% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 220 nm, 30 °C), t_R major: 14.9 min, t_R minor: 22.5, 82% ee; ν_{max} (film) 2953 (C-H), 1784 (C=O), 1705 (C=O); δ_H (400 MHz, $CDCl_3$) 2.06-2.18 (2H, m, C*H*$_2$), 2.45-2.48 (2H, m, C*H*$_2$), 2.61-2.75 (2H, m, C*H*$_2$), 2.90-2.99 (2H, m, C(3)*H*), 4.32 (1H, t, *J* 5.0, C(4)*H*), 7.14-7.17 (2H, m, 2×Ar*H*), 7.20-7.25 (1H, m, Ar*H*), 7.28-7.32 (2H, m, 2×Ar*H*); δ_C (100 MHz, $CDCl_3$) 20.5 (*C*(7)H$_2$), 27.2 (*C*(8)H$_2$), 33.7 (*C*(4)H), 36.2 (*C*(3)H$_2$), 36.6 (*C*(6)H$_2$), 117.1 (*C*=CO), 126.4 (2×C(4)Ar*C*(2)H), 127.4 (C(4)Ar*C*(4)H), 128.9 (2×C(4)Ar*C*(3)H), 140.4 (C(4)Ar*C*(1)), 165.8 (*C*(10)), 167.3 (*C*(2)O)), 196.2 (*C*(5)O); *m/z* (NSI$^+$) 243 ([M+H]$^+$, 60%); HRMS (NSI$^+$) $C_{15}H_{15}O_3$ ([M+H]$^+$) requires 243.1016, found 243.1018 (+0.9 ppm).

General Procedure F: Using Azaaryl Ketone 35



To a solution of the corresponding homoanhydride (1.05-1.4 equiv) in THF (0.72 mM), was added azaaryl ketone **35** (1.0 equiv), isothiourea (HBTM 2.1, 0.01 equiv) and EtN(*i*Pr)$_2$ (1.1 equiv) at 0 °C. The reaction mixture was stirred and gradually warmed to room temperature over 5 h. The solution was diluted with EtOAc and washed sequentially with 0.1 M HCl and saturated $NaHCO_3$ solution, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford dihydropyridones **36-40a** as the major product and dihydropyranones **36b-40b** as the minor product.

(11*R*)-10-Benzoyl-11-phenyl-8-thia-1-azatricyclo[7.4.0.0^{2,7}]trideca-2,4,6,9-tetraen-13-one (36a) and (4*R*)-5-(1,3-benzothiazol-2-yl)-4,6-diphenyl-3,4-dihydro-2H-pyran-2-one (36b)



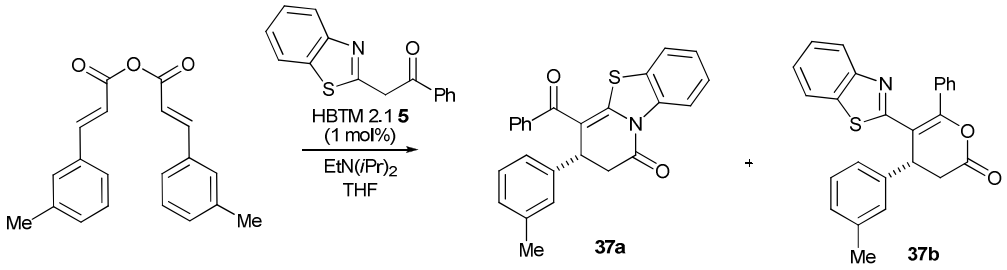
The title compounds were prepared according to *General Procedure F* using azaaryl ketone **35** (455 mg, 1.80 mmol), anhydride **3** (700 mg, 2.50 mmol), HBTM 2.1 (5.5 mg, 1 mol %) and EtN(*i*Pr)$_2$ (0.35 mL, 2.00 mmol) in THF (5 mL) and purified by chromatography on silica gel (10:2 CH_2Cl_2/hexane) to afford **36a** as a yellow solid (595 mg, 86%) and **36b** as a yellow solid (63 mg, 9%). The major isomer was suspended in Et_2O then recrystallised from EtOAc: crystals were obtained (68 mg, 10% overall yield, 4% ee) plus liquors which were concentrated *in vacuo* to give a yellow solid.

36a (major): (472 mg, 68% yield, 97% ee); mp 168-171 °C; $[\alpha]_D^{20}$ –148.5 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1 mL min^{-1}, 211 nm, 30 °C), t_R minor: 13.2 min, t_R major: 22.5 min, 97% ee; ν_{max} (film)/cm^{-1} 3024 (C-H), 2984 (C-H), 2913 (C-H), 1722 (C=O), 1597 (C=C), 1574 (C=C), 1477 (C-N), 1360 (C-S), 1269 (C-O); δ_H (500 MHz, $CDCl_3$) 3.05 (1H, dd, *J* 15.9, 2.2, C(12)H_2), 3.29 (1H, dd, *J* 15.9, 6.9, C(12)H_2), 4.38 (1H, dd, *J* 6.9, 2.2, C(11)*H*), 7.11 (2H, d, *J* 7.2, 2×C(11)PhC(2)*H*), 7.21-7.44 (10H, m, Ar*H*), 7.62 (1H, s, C(6)*H*), 8.47 (1H, d, *J* 7.8, C(3)*H*); δ_C (126 MHz, $CDCl_3$) 38.6 (*C*(11)H), 41.4 (*C*(12)H_2), 107.7 (*C*(10)), 117.5 (*C*(3)H), 122.0 (*C*(6)H), 125.9 (*C*(5)H), 126.8 (2×C(11)Ph*C*(2)H), 127.0 (2×C(10)COPh*C*(3)H, *C*(4)H), 127.6 (C(11)Ph*C*(4)H), 127.8 (*C*(7)), 128.1 (2×C(10)COPh*C*(2)H), 129.3 (2×C(11)Ph*C*(3)H), 130.3 (C(10)COPh*C*(4)H), 136.0 (*C*(2)), 139.4 (C(10)COPh*C*(1)), 140.8 (C(11)Ph*C*(1)), 156.2 (*C*(9)), 167.9 (*C*(13)O), 191.2 (C(10)*C*O); *m/z* (NSI$^+$) 384 ([M+H]$^+$, 60%); HRMS (NSI$^+$) $C_{24}H_{18}O_2NS$ ([M+H]$^+$) requires 384.1053, found 384.1052 (–0.2 ppm).

36b (minor): (63 mg, 9%); mp 192–194 °C; $[\alpha]_D^{20}$ –18.4 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1 mL min^{-1}, 211 nm, 30 °C), t_R major: 7.7 min, t_R minor: 10.8 min, 86% ee; ν_{max} (film)/cm^{-1} 2974 (C-H), 2372 (C-H), 1775 (C=O), 1647 (C=N), 1491 (C=C), 1435 (C=C), 1339 (C-S), 1271 (C-O); δ_H (300 MHz, $CDCl_3$) 3.08 (1H, dd, *J* 15.8, 1.6, C(3)H_2), 3.32 (1H, dd, *J* 15.8, 7.6, C(3)H_2), 5.03 (1H, dd, *J* 7.6, 1.6, C(4)*H*), 7.23-7.36 (6H, m, Ar*H*), 7.38-7.52 (3H, m, Ar*H*), 7.55-7.63 (4H, m, Ar*H*), 7.93 (1H, d, *J* 7.8, HetAr*H*); δ_C (75 MHz, $CDCl_3$) 36.9 (*C*(3)H_2), 41.3 (*C*(4)H), 115.1 (*C*(5)), 121.3 (C(5)HetAr*C*H), 123.1 (C(5)HetAr*C*H), 125.5

(C(5)HetAr*C*H), 126.1 (C(5)HetAr*C*H), 127.0 (2×C(4)Ph*C*(2)H), 127.8 (C(4)Ph*C*(4)H), 128.9 (2×C(6)Ph*C*(3)H), 129.3 (2×C(4)Ph*C*(3)H), 130.1 (2×C(6)Ph*C*(2)H), 130.8 (C(6)Ph*C*(4)H), 131.9 (C(6)Ph*C*(1)), 135.7 (C(5)HetAr*C*), 139.6 (C(4)Ph*C*(1)), 152.4 (C(5)HetAr*C*), 154.4 (*C*(6)), 164.2 (C(5)HetAr*C*=N), 166.6 (*C*(2)O); *m/z* (NSI$^+$) 384 ([M+H]$^+$, 60%); HRMS (NSI$^+$) $C_{24}H_{18}O_2NS$ ([M+H]$^+$) requires 384.1053, found 384.1052 (–0.2 ppm).

(11*R*)-10-Benzoyl-11-(3-methylphenyl)-8-thia-1-azatricyclo[7.4.0.0^{2,7}]trideca-2(7),3,5,9-tetraen-13-one (37a) and (*R*)-5-(benzo[d]thiazol-2-yl)-6-phenyl-4-*m*-tolyl-3,4-dihydro-2H-pyran-2-one (37b)



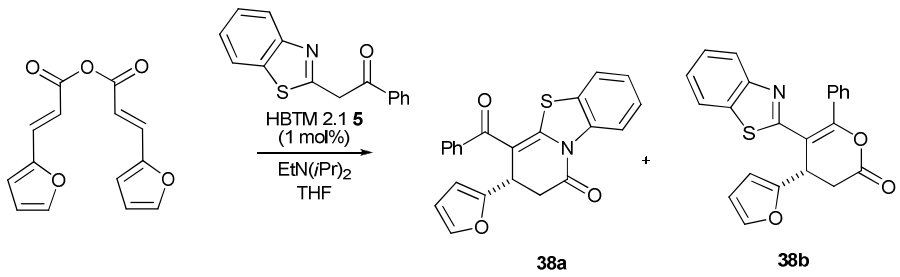
The title compounds were prepared according to *General Procedure F* using azaaryl ketone **35** (607 mg, 2.40 mmol), anhydride **S6** (771 mg, 2.52 mmol), HBTM 2.1 (7 mg, 1 mol %) and EtN(*i*Pr)$_2$ (0.46 mL, 2.64 mmol) in THF (4 mL) and purified by chromatography (20% hexane/CH_2Cl_2) to afford the title compounds **37a** and **37b** as yellow solids.

37a (major): (732 mg, 77%); mp 159-161 °C; $[\alpha]_D^{20}$ –101.0 (*c* 1.0, $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 211 nm, 30 °C), t_R minor: 10.8 min, t_R major: 16.4 min, 86% ee; ν_{max} (film) 1714(C=O), 1604 (C=O), 1481; δ_H (400 MHz, $CDCl_3$) 2.28 (3H, s, ArC*H*$_3$), 3.05 (1H, dd, *J* 15.9, 2.4, C(12)*H*$_2$), 3.27 (1H, dd, J 15.9, 6.9, C(12)*H*$_2$), 4.31 (1H, dd, *J* 6.9, 2.4, C(11)*H*), 6.89 (2H, d, *J* 9.3, Ar*H*), 7.06 (1H, d, *J* 7.5, Ar*H*), 7.17 (1H, t, *J* 7.5, Ar*H*), 7.28 (2H, s, Ar*H*), 7.29 (2H, s, Ar*H*), 7.32-7.42 (3H, m, ArH), 7.61-7.64 (1H, m, Ar*H*), 8.45-8.49 (1H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 21.5 (C(11)Ar*C*H$_3$), 38.4 (*C*(11)H), 41.3 (*C*(12)H$_2$), 107.7 (*C*10), 117.5 (C(6)Ar*C*H), 121.9 (C(5)Ar*C*H), 123.7 (C(11)Ar*C*(6)H), 125.8 (*C*(4)H), 126.9 (C(11)Ar*C*(4)H), 127.0 (2×C(10)Ar*C*(2)H), 127.4 (*C*(3)H), 127.8 (*C*(7)), 128.0 (2×C(10)Ar*C*(3)H), 128.3 (C(11)Ar*C*(5)H), 129.1 (C(11)Ar*C*(2)H), 130.2 (C(10)Ar*C*(4)H), 136.0 (C(11)Ar(3)*C*), 138.9 (C(10)Ar*C*(1)), 139.3 (C(2)Ar*C*), 140.7 (C(11)Ar*C*(1)), 156.1 (*C*(9)), 167.9 (*C*(13)=O), 191.2 (*C*(10)=O).

37b (minor): (39 mg, 4%); mp 146-147 °C; $[\alpha]_D^{20}$ –9.7 (*c* 0.75, $CHCl_3$); HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 211 nm, 30 °C), t_R minor: 6.9 min, t_R major: 9.7 min, 85% ee; ν_{max} (film) 2982 (C-H), 1772 (C=O), 1504; δ_H (400 MHz, $CDCl_3$) 2.31 (3H, s,

C(4)ArCH_3), 3.07 (1H, dd, *J* 15.7, 0.7, C(3)H_2), 3.31 (1H, dd, *J* 15.7, 7.6, C(3)H_2), 4.97 (1H, dd, *J* 7.7, 1.7, C(4)*H*), 7.04 (1H, d, *J* 7.8, C(4)ArC(4)*H*), 7.11-7.13 (1H, m, C(4)ArC(6)*H*), 7.16-7.22 (1H, m, C(4)ArC(2)*H*), 7.25-7.32 (2H, m, 2×C(5)HetArC*H*), 7.37-7.46 (3H, m, C(6)ArC(3,4)*H*), 7.48-7.53 (1H, m, C(4)ArC(5)*H*), 7.56-7.60 (2H, m, 2×C(6)ArC(2)*H*), 7.62 (1H, d, *J* 8.0, C(5)HetArC*H*), 7.93 (1H, d, *J* 8.2, C(5)HetArC*H*); δ_C (100 MHz, $CDCl_3$) 21.5 (Ar*C*H_3), 36.9 (*C*(3)H_2), 41.2 (*C*(4)H), 115.0 (*C*(6)), 121.2 (C(5)HetAr*C*H), 123.0 (C(5)HetAr*C*H), 123.8 (C(5)HetAr*C*H), 125.3 (C(4)Ar*C*(6)H), 125.9 (C(5)HetAr*C*H), 127.7 (C(4)Ar*C*(4)H), 128.5 (C(6)Ar*C*(4)H), 128.8 (2×C(6)Ar*C*(2)H), 129.0 (C(4)Ar*C*(5)H), 129.9 (2×C(6)Ar*C*(3)H), 130.7 (C(4)Ar*C*(2)H, 131.9 (C(6)Ar*C*(1)), 135.7 (C(5)HetAr*C*), 138.8 (C(4)Ar*C*(3)), 139.4 (C(4)Ar*C*(1)), 152.4 (*C*(5)), 154.1 (C(5)HetAr*C*), 164.1 (C(5)HetAr*C*=N), 166.6 (*C*(2)).

(11*S*)-10-Benzoyl-11-(furan-2-yl)-8-thia-1-azatricyclo[7.4.0.0^{2,7}]trideca-2,4,6,9-tetraen-13-one (38a) and (4*S*)-5-(1,3-benzothiazol-2-yl)-4-(furan-2-yl)-6-phenyl-3,4-dihydro-2H-pyran-2-one (38b)



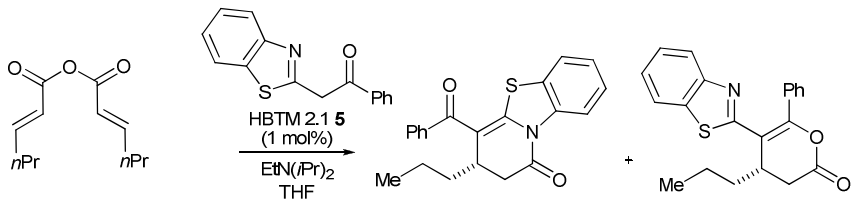
The title compounds were prepared according to *General Procedure F* using azaaryl ketone **35** (421 mg, 1.67 mmol), anhydride **S4** (430 mg, 1.67 mmol), HBTM 2.1 (5 mg, 1 mol %) and EtN(*i*Pr)$_2$ (319 µL, 1.8 mmol) in THF (3 mL) and purified by chromatography (20% hexanes/CH_2Cl_2) to afford the title compounds **38a** as a yellow solid and **38b** as a yellow solid.

38a (major): (446 mg, 72%); mp 127-128 °C; $[\alpha]_D^{20}$ −30.3 (*c* 1.0, $CHCl_3$); HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 211 nm, 30 °C), t_R minor: 15.0 min t_R major: 20.3 min, 80% ee; ν_{max} (film)/cm^{-1} 3142 (C-H), 3136 (C-H), 2363 (C-H), 1732 (C=O), 1626 (C=C), 1605 (C=C), 1474 (C-N), 1362 (C-S), 1275 (C-O); δ_H (400 MHz, $CDCl_3$) 3.16 (1H, dd, *J* 16.1, 6.0, CH_2), 3.24 (1H, dd, *J* 16.1 2.6, CH_2), 4.43 (1H, ddd, *J* 6.1, 2.6, 1.0, C(11)*H*), 5.95 (1H, m, furanylC(x)*H*), 6.24 (1H, dd, *J* 3.3, 1.9, furanylC(4)*H*), 7.29-7.51 (8H, m, Ar*H*), 7.54-7.61 (1H, m, Ar*H*), 8.46-8.53 (1H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 32.9 (*C*(11)H), 37.9 (*C*12)H_2), 105.6 (*C*(10)), 106.8 (furanyl*C*(3)H), 110.3 (furanyl*C*(4)H), 117.6 (Ar*C*H,), 121.9 (Ar*C*H), 125.8 (Ar*C*H), 126.9 (2×Ar*C*H),

127.0 (Ar*C*H), 127.5 (*C*(7)), 128.2 (2×Ar*C*H), 130.4 (Ar*C*H), 136.0 (C(10)Ar*C*(1)), 139.3 (*C*(2)), 142.7 (furanyl*C*(5)H), 153.5 (furanyl*C*(1)), 156.6 (*C*(9)), 167.7 (*C*(13)=O), 190.8 (C(10)*C*=O).

38b (minor): (60 mg, 10%) mp 122-125 °C; $[\alpha]_D^{22}$ –6.2 (*c* 1.0 in CH_2Cl_2); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1 mL min^{-1}, 211 nm, 30 °C), t_R minor: 7.6 min, t_R major: 15.0 min, 80% ee; ν_{max} (film)/cm^{-1} 3117 (C-H), 3063 (C-H), 2924 (C-H), 1782 (C=O), 1649 (C=N), 1597 (C=C), 1344 (C-S), 1277 (C-O); δ_H (300 MHz, $CDCl_3$) 3.20 (1H, dd, *J* 15.9, 6.7, C(3)H_2), 3.26 (1H, dd, *J* 15.9, 1.9, C(3)H_2), 5.14 (1H, dd, *J* 6.8, 2.0, C(4)*H*), 6.18 (1H, d, *J* 3.3, furanyl(3)*H*), 6.24 (1H, dd, J 3.3, 1.8, furanyl(4)*H*), 7.31 (1H, t, *J* 7.6, Ar*H*), 7.34 (1H, d, *J* 1.8, furanyl(5)*H*), 7.44 (3H, td, *J* 7.3, 1.5, Ar*H*), 7.49-7.57 (3H, m, Ar*H*), 7.61-7.68 (1H, m, Ar*H*), 7.98 (1H, d, *J* 8.2, Ar*H*); δ_C (75 MHz, $CDCl_3$) 33.9 (*C*(3)), 35.1 (*C*(4)), 106.9 (furanyl*C*(3)H), 110.4 (furanyl*C*(4)H), 113.3 (*C*(5)), 121.3 (C(5)HetAr*C*(7)H), 123.1 (C(5)HetAr*C*(4)H), 125.6 (C(5)HetAr*C*(6)H), 126.2 (C(5)HetAr*C*(5)H), 129.0 (2×C(6)Ph*C*(3)H), 130.1 (2×C(6)Ph*C*(2)H), 131.0 (C(6)Ph*C*(4)H), 131.8 (C(6)Ph*C*(1)), 135.7 (C(5)HetAr*C*(7a)), 142.8 (furanyl*C*(5)H), 152.2 (furanyl*C*(2)), 152.4 (C(5)HetAr*C*(3a)), 154.8 (*C*(6)), 164.0 (C(5)HetAr*C*=N), 166.4 (*C*(2)O).

(11*S*)-10-Benzoyl-11-propyl-8-thia-1-azatricyclo[7.4.0.0^{2,7}]trideca-2,4,6,9-tetraen-13-one (39a) and (4*S*)-5-(1,3-benzothiazol-2-yl)-6-phenyl-4-propyl-3,4-dihydro-2H-pyran-2-one (39b)



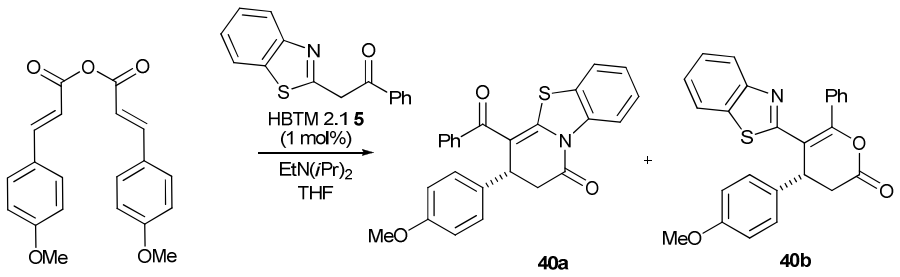
The title compounds were prepared according to *General Procedure F* using azaaryl ketone **35** (182 mg, 0.72 mmol), anhydride **S10** (314 mg, 1.00 mmol), HBTM 2.1 (2 mg, 1 mol %) and EtN(*i*Pr)$_2$ (138 µL, 0.79 mmol) in THF (2 mL) and purified by chromatography on silica gel (10:2 CH_2Cl_2/hexane) to afford **39a** as a yellow solid and **39b** as a yellow solid.

39a (major): (502 mg, 79%); mp 143-145 °C; $[\alpha]_D^{20}$ +148.1 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1 mL min^{-1}, 211 nm, 30 °C), t_R minor: 10.3 min, t_R major: 16.0 min, 88% ee; ν_{max} (film)/cm^{-1} 2957 (C-H), 2930 (C-H), 2870 (C-H), 1717 (C=O), 1599 (C=C), 1574 (C=C), 1474 (C-N), 1368 (C-S), 1275 (C-O); δ_H (400 MHz, $CDCl_3$) 0.55 (3H, t, *J* 7.3, CH_3), 1.04 (2H, dq, *J* 15.3, 7.9, 7.0, CH_2CH$_3$), 1.30 (2H, q, *J* 7.9, CH_2CH$_2$CH$_3$), 2.77 (1H, dd, *J* 16.2, 2.1, C(12)H_2), 2.96 (1H, dd, *J* 16.2, 6.3, C(12)H_2), 3.13 (1H, qd, *J* 7.0, 2.1, C(11)*H*), 7.17-7.23 (1H, m,

C(5)*H*), 7.23-7.29 (1H, m, C(4)*H*), 7.33-7.38 (3H, m, C(10)COPhC(3)*H*, C(10)COPhC(4)*H*), 7.39-7.42 (2H, m, C(10)COPhC(2)*H*), 7.44 (1H, dd, *J* 7.5, 1.1, C(6)*H*), 8.39- 8.47 (1H, m, C(3)*H*); δ_C (126 MHz, $CDCl_3$) 13.6 (*C*H_3), 19.6 (CH_2*C*H_2CH_3), 32.3 (*C*(11)H), 35.8(*C*$H_2CH_2CH_3$), 37.7, (*C*(12)H_2) 109.8 (*C*(10)), 117.6 (*C*(3)H), 121.9 (*C*(6)H), 125.8 (*C*(5)H), 127.0 (*C*(4)H), 127.2 (2×C(10)COPh*C*(3)H), 127.7 (*C*(7)), 128.4 (2×C(10)COPh*C*(2)H), 130.1 (C(10)COPh*C*(4)H), 136.2 (*C*(2)), 140.1 (C(10)COPh*C*(1)), 154.4 (*C*(9)), 169.1 (*C*(13)O), 191.8 (C(10)*C*O); *m/z* (NSI^+) 372 ($[M+Na]^+$, 100%), 350 ($[M+H]^+$, 30%); HRMS (NSI^+) $C_{21}H_{20}O_2NS$ ($[M+H]^+$) requires 350.1209, found 350.1204 (–1.5 ppm).

39b (minor): (47 mg, 7%); mp 192-194 °C; $[\alpha]_D^{20}$ –1.3 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1 mL min^{-1}, 211 nm, 30 °C), t_R minor: 4.9 min, t_R major: 7.0 min, 92% ee; ν_{max} (film)/cm^{-1} 2953 (C-H), 2926 (C-H), 2870 (C-H), 1770 (C=O), 1651 (C=N), 1491 (C=C), 1354 (C-S), 1273 (C-O); δ_H (500 MHz, $CDCl_3$) 0.90 (3H, t, *J* 7.2, C*H*$_3$), 1.32 (1H, dq, *J* 18.8, 6.1, C*H*$_2$CH$_2$CH$_3$), 1.40-1.58 (2H, m, CH$_2$C*H*$_2$CH$_3$), 1.61-1.71 (1H, m, C*H*$_2$CH$_2$CH$_3$), 2.85-3.00 (2H, m, C(3)*H*$_2$), 3.70-3.77 (1H, m, C(4)*H*), 7.32 (1H, t, *J* 7.5, C(5)HetArC*H*), 7.34-7.36 (2H, m, ArH), 7.37-7.49 (4H, m, Ar*H*), 7.66 (1H, d, *J* 8.0, C(5)HetAr*CH*), 7.98 (1H, d, *J* 8.2, (C(5)HetAr*CH)*; δ_C (126 MHz, $CDCl_3$) 14.1 (*C*H_3), 19.9 (CH_2*C*H_2CH_3), 33.5 (*C*$H_2CH_2CH_3$), 35.2 (*C*(4)H), 35.5 (*C*(3)H_2), 117.2 (*C*(5)), 121.4 (C(5)HetAr*C*(7)H), 123.0 (C(5)HetAr*C*(4)H), 125.5 (C(5)HetAr*C*(6)H), 126.2 (C(5)HetAr*C*(5)H), 128.9 (2×C(6)Ph*C*(3)H), 130.1 (2×C(6)Ph*C*(2)H), 130.6 (C(6)Ph*C*(4)H), 132.1 (C(6)Ph*C*(1)), 134.7 (C(5)HetAr*C*), 152.5 (C(5)HetAr*C*), 153.5 (*C*(6)), 164.7 (C(5)HetAr*C*=N), 167.8 (*C*(2)O); *m/z* (NSI^+) 372 ($[M+Na]^+$, 100%), 350 ($[M+H]^+$, 55%); HRMS (NSI^+) $C_{21}H_{20}O_2NS$ ($[M+H]^+$) requires 350.1209, found 350.1210 (+0.2 ppm).

(11*R*)-10-Benzoyl-11-(4-methoxyphenyl)-8-thia-1-azatricyclo[7.4.0.0^{2,7}]trideca-2,4,6,9-tetraen-13-one (40a) and (4*R*)-5-(1,3-benzothiazol-2-yl)-4-(4-methoxyphenyl)-6-phenyl-3,4-dihydro-2H-pyran-2-one (40b)



The title compounds were prepared according to *General Procedure F* using azaaryl ketone **35** (182 mg, 0.72 mmol), anhydride **S3** (314 mg, 1.00 mmol), HBTM 2.1 (2 mg, 1 mol %) and EtN(*i*Pr)$_2$ (138 µL, 0.79 mmol) in

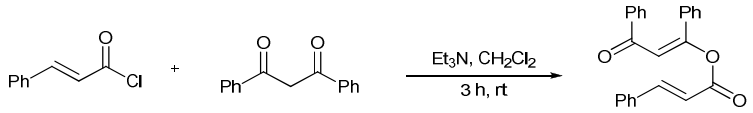
THF (2 mL) and purified by chromatography on silica gel (10:2 CH_2Cl_2/hexane) to afford **40a** as a yellow solid and **40b** as a yellow solid

40a (major): (436 mg, 59%); mp 190-191 °C; $[\alpha]_D^{20}$ –135.6 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1 mL min^{-1}, 211 nm, 30 °C), t_R minor: 18.4 min, t_R major: 31.1 min, 85% ee; ν_{max} (film)/cm^{-1} 2972 (C-H), 2843 (C-H), 1721 (C=O), 1603 (C=C), 1510 (C=C), 1474 (C-N), 1358 (C-S), 1298 (C-O); δ_H (300 MHz, $CDCl_3$) 3.00 (1H, dd, *J* 15.8, 2.3, C(12)H_2), 3.24 (1H, dd, *J* 15.8, 6.6 C(12)H_2), 3.77 (3H, s, OCH_3), 4.29 (1H, dd, *J* 6.6, 2.2, C(11)*H*), 6.78-6.84 (2H, m, C(11)ArC(3)*H*), 6.97-7.05 (2H, m, C(11)ArC(2)*H*), 7.23-7.31 (4H, m, Ar*H*), 7.32-7.43 (3H, m, Ar*H*), 7.56-7.65 (1H, m, C(6)*H*), 8.43-8.49 (1H, m, C(3)*H*); δ_C (75 MHz, $CDCl_3$) 38.0 (*C*(11)H), 41.8 (*C*(12)H_2), 55.4 (O*C*H_3), 108.2 (*C*(10)), 114.8 (2×C(11)Ar*C*(3)H), 117.7 (*C*(3)H), 122.1 (*C*(6)H), 126.0 (*C*(5)H), 127.2 (2×Ar*C*H and *C*(4)H), 127.9 (*C*(7)), 128.0 (2×Ar*C*H), 128.2 (2×Ar*C*H), 130.4 (C(10)COPh*C*(4)H), 132.7 (C(11)Ar*C*(1)), 136.2 (*C*(2)), 139.5 (C(10)COPh*C*(1)), 156.1 (*C*(9)), 159.0 (C(11)Ar*C*(4)), 168.2 (*C*(13)O), 191.4 (C(10)*C*O); *m/z* (NSI^+) 436 ($[M+Na]^+$, 100%), 414 ($[M+H]^+$, 60%); HRMS (NSI^+) $C_{25}H_{20}O_3NS$ ($[M+H]^+$) requires 414.1158, found 414.1160 (+0.4 ppm).

40b (minor): (41 mg, 6%); mp 148-151 °C; $[\alpha]_D^{20}$ +19.2 (*c* 1.0 in $CHCl_3$); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1 mL min^{-1}, 211 nm, 30 °C), t_R minor: 9.7 min, t_R major: 14.6 min, 89% ee; ν_{max} (film)/cm^{-1} 2944 (C-H), 1778 (C=O), 1645 (C=N), 1510 (C=C), 1435 (C=C), 1346 (C-S), 1240 (C-O); δ_H (500 MHz, $CDCl_3$) 3.06 (1H, dd, *J* 15.7, 1.4, C(3)H_2), 3.30 (1H, dd, *J* 15.7, 7.5, C(3)H_2), 3.75 (3H, s, OCH_3), 4.97 (1H, d, *J* 6.5, C(4)*H*), 6.84 (2H, d, *J* 8.7, C(4)ArC(3)*H*), 7.28 (3H, dd, *J* 16.1, 8.3, C(4)ArC(2)*H*, C(5)HetArC(5)*H*), 7.38-7.46 (3H, m, C(5)HetArC(6)*H*, C(6)PhC(3)*H*), 7.50 (1H, m, C(6)PhC(4)*H*), 7.55-7.59 (2H, m, C(6)PhC(2)*H*), 7.62 (1H, d, *J* 8.0, C(5)HetArC(4)*H*), 7.95 (1H, d, *J* 8.2, C(5)HetArC(7)*H*); δ_C (126 MHz, $CDCl_3$) 37.2 (*C*(3)H_2), 40.6 (*C*(4)H), 55.3 (O*C*H_3), 114.6 (2×C(4)Ar*C*(3)H), 115.4 (*C*(5)), 121.3 (C(5)HetAr*C*(7)), 123.1 (C(5)HetAr*C*(4)), 125.5 (C(5)HetAr*C*(6)), 126.2 (C(5)HetAr*C*(5)), 128.2 (2×Ar*C*H), 128.9 (2×Ar*C*H), 130.1 (2×Ar*C*H), 130.8 (C(6)Ph*C*(4)H), 131.6 (C(4)Ar*C*(1)), 131.9 (C(6)Ph*C*(1)), 138.2 (C(5)HetAr*C*), 152.2 (C(5)HetAr*C*), 154.2 (*C*(6)), 159.1 (C(4)Ar*C*(4)), 164.4 (C(5)HetAr*C*=N)), 166.8 (*C*(2)O); *m/z* (NSI^+) 436 ($[M+Na]^+$, 100%), 414 ($[M+H]^+$, 90%); HRMS (NSI^+) $C_{25}H_{20}O_3NS$ ($[M+H]^+$) requires 414.1158, found 414.1156 (–0.6 ppm).

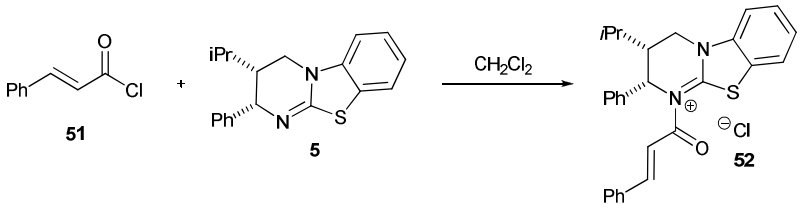
Mechanistic Investigations

(*E*)-3-Oxo-1,3-diphenylprop-1-enyl cinnamate (50)



Trans-cinnamoyl chloride (1.99 g, 12.0 mmol) was added to a solution of 1,3-diphenylpropane-1,3-dione (2.20 g, 10.0 mmol) in CH_2Cl_2 (15 mL) at room temperature. The solution was stirred for 3 h and then quenched with 0.1 M HCl (10 mL). The aqueous was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organics were washed with saturated $NaHCO_3$ (10 mL) solution and H_2O (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (20% Et_2O/petrol) to afford the *ester* **50** as a yellow solid (580 mg, 16%); mp 111-112 °C; ν_{max} (film) 1722 (C=O), 1664 (C=O), 1635, 1600, 1211; δ_H (400 MHz, $CDCl_3$) 6.73 (1H, d, *J* 16, PhCH=C*H*CO), 7.33 (1H, s, C(2)*H*), 7.42-7.58 (9H, m, Ar*H*), 7.60 (2H, dd, *J* 6.6, 3.0 Ar*H*), 7.74-7.80 (2H, m, Ar*H*), 7.90 (1H, d, *J* 16.0, PhC*H*=CHCO), 7.98-8.05 (2H, m, ArH); δ_C (100 MHz, $CDCl_3$) 109.8 (*C*(2)H), 116.6 (PhCH=*C*H), 126.1 (2×Ar*C*H), 128.2 (2×Ar*C*H), 128.4 (2×Ar*C*H), 128.5 (2×Ar*C*H)), 128.8 (3×Ar*C*H), 130.7 (2×Ar*C*H), 131.0 (Ar*C*H), 132.7 (Ar*C*H), 133.9 (Ar*C*), 134.0 (Ar*C*), 138.6 (Ar*C*), 147.2 (Ph*C*H=CH), 156.9 (*C*O_2), 163.8 (*C*(3)), 188.4 (*C*(1); HRMS (ESI^+) $C_{24}H_{18}O_3Na$ ($[M+Na]^+$), found 377.1138, requires 377.1138.

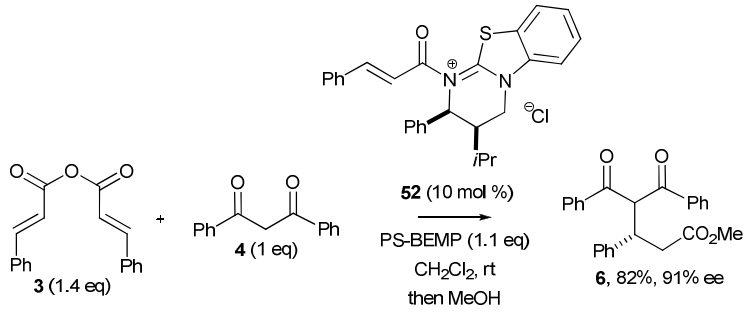
N-Cinnamoyl-(11*S*,12*R*)-11-phenyl-12-(propan-2-yl)-8-thia-1,10-diazatricyclo[7.4.0.0^{2,7}]trideca-2,4,6,9- tetraene (52)



Trans-cinnamoyl chloride (100 mg, 0.60 mmol) and HBTM 2.1 (185 mg, 0.60 mmol) were stirred in CH_2Cl_2 (2 mL) under N_2 at room temperature for 1 h. A white solid precipitate was formed and collected *via* vacuum filtration to afford the *acyl ammonium* **52** (205 mg, 72%); mp 248-250 °C (decomposition); $[\alpha]_D^{20}$ +53.0 (*c* 1.0, $CHCl_3$); ν_{max} (film) 2962 (C-H), 1678 (C=O), 1604, 1531, 1284; δ_H (400 MHz, $CDCl_3$) 0.90 (3H, d, *J* 6.8, CH_3), 1.42 (3H, d, *J* 6.8 CH_3), 1.89 (1H, h, *J* 6.8, CH_2), 3.03 (1H, ddt, *J* 12.3, 8.6, 4.6, C*H*CH_2), 3.98 (1H, t, *J* 13.0, CHPh), 5.01 (1H, dd, *J* 13.4, 4.5, CH_2), 6.68 (1H, d, *J* 4.5, C*H*^{i}Pr), 7.19-7.22 (2H, m, Ar*H*), 7.33-7.43 (6H, m, Ar*H*), 7.51 (1H, d, *J* 15.2 PhCH=C*H*), 7.62 (2H, dd, J 7.9, 1.7, ArH), 7.67 (1H, d, *J* 7.5, ArH), 7.81 (1H, ddd, *J* 8.5, 7.4, 1.2,

ArH), 7.90 (1H, d, 15.2, PhC*H*=CH), 8.00-8.08 (1H, m, ArH), 8.26 (1H, d, *J* 8.4, ArH); δ_C (100 MHz, $CDCl_3$) 19.3 (*C*H_3), 22.3 (*C*H_3), 26.7 (*C*H), 40.4 (*C*H), 44.9 (*C*H_2), 61.7 (*C*H), 113.9 (*C*H), 115.1 (*C*H) 122.9 (*C*H), 126.2 (*C*), 127.0 (2×*C*H), 127.8 (*C*H)), 129.1 (2×*C*H), 129.4 (2×*C*H), 129.6 (*C*H), 129.7 (*C*H), 129.8 (2×*C*H), 131.8 (*C*H), 133.7 (*C*), 135.1 (*C*), 136.5 (*C*), 151.5 (*C*H), 160.6 (*C*), 166.9 (*C*); HRMS (ESI^+) $C_{28}H_{27}ON_2S$ ([M+]), found 439.1832, requires 439.1832.

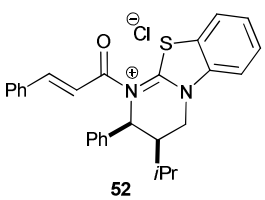
(3*S*)-Methyl 4-benzoyl-5-oxo-3,5-diphenylpentanoate (6)



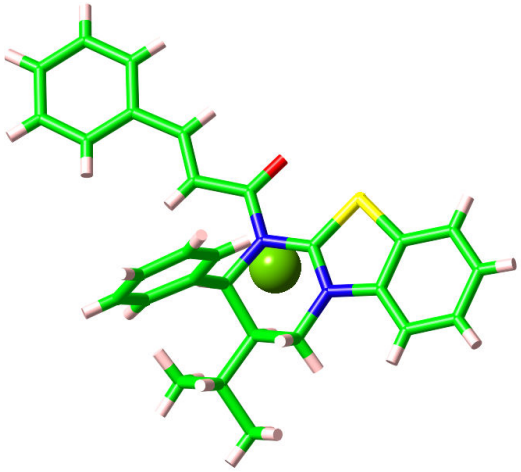
The title compound was prepared according to *General Procedure D* from (*E*)-cinnamic anhydride (278 mg, 1.40 mmol), **52** (34 mg, 0.072 mmol), BEMP (2.0 mmol/g loading, 360 mg, 1.10 mmol) and purified by chromatography (CH_2Cl_2→2%EtOAc/CH_2Cl_2) to afford the *ester* **6** as a white solid (223 mg, 81%); chiral HPLC analysis, ChiralPak AD-H (20% *i*-PrOH:hexane, flow rate 1.0 mL min^{-1}, 220 nm, 30 °C), t_R major: 11.9 min, t_R minor: 17.0 min, 91% ee; Data in agreement with compound **6** described on page S12.

X-ray Crystal Structure

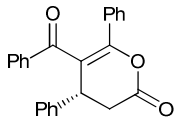
Asymmetric unit in the crystal structure of **52** (crystals grown *via* vapour diffusion [CH_2Cl_2/hexane]), from single crystal X-ray diffraction at T=93 K. Thermal ellipsoids are drawn at the 50% probability level.



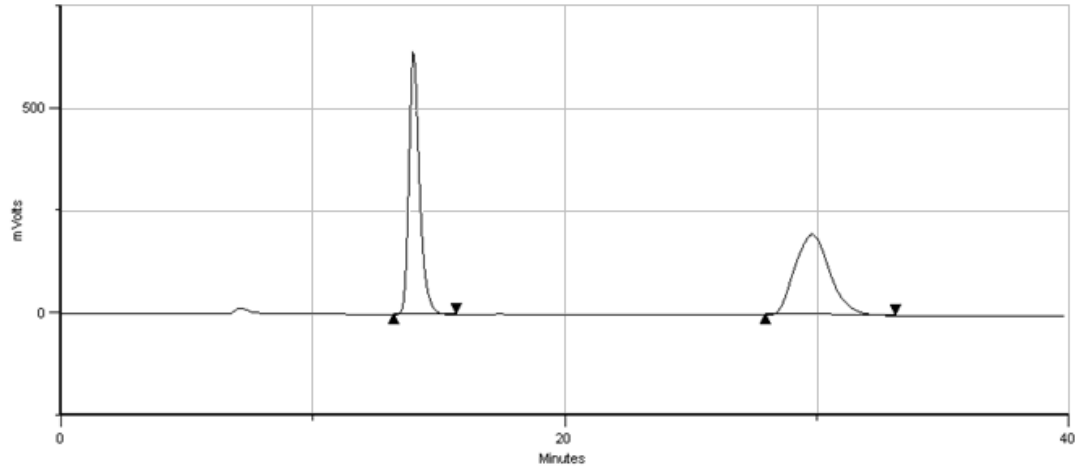
52



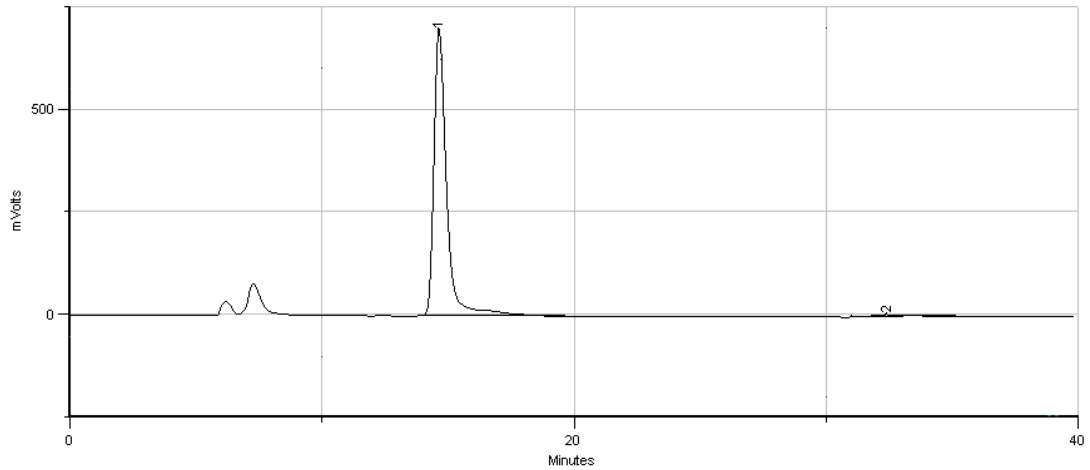
HPLC Spectra



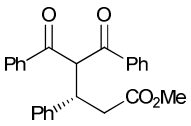
(2)



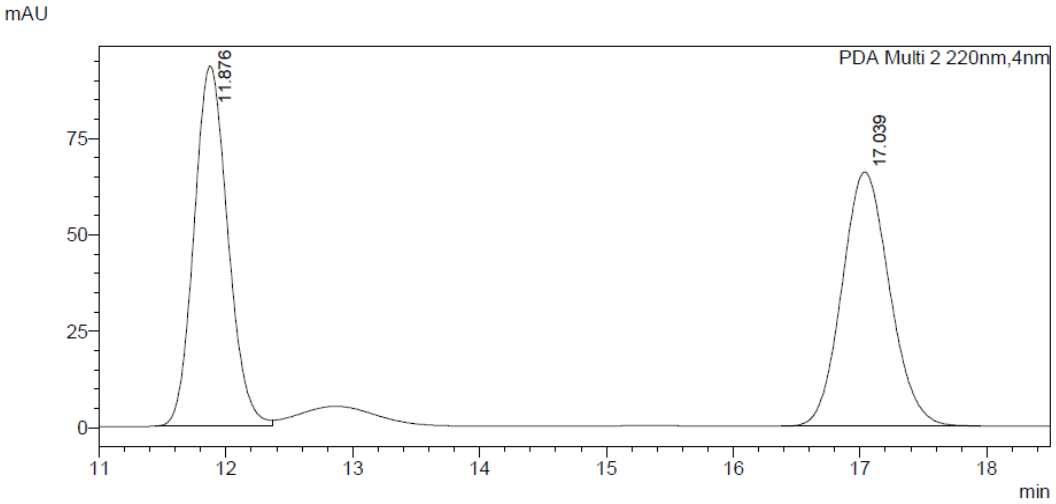
Peak Name	R. Time	Area	Area %
*1	14.00	31202176.00	49.36
*2	29.84	32012378.00	50.64



Peak Name	R. Time	Area	Area %
*1	14.65	1276768.00	97.46
*2	32.41	1074293.62	2.54



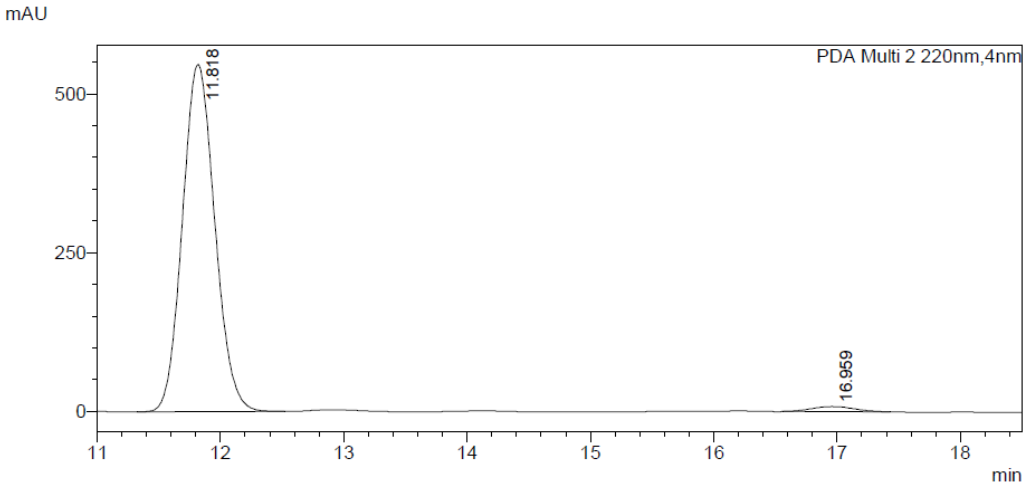
(6)



<Peak Table>

PDA Ch2 220nm

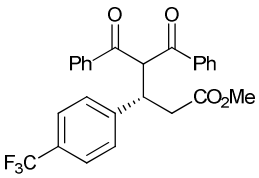
Peak#	Ret. Time	Area	Area%
1	11.876	1731954	50.165
2	17.039	1720589	49.835
Total		3452543	100.000



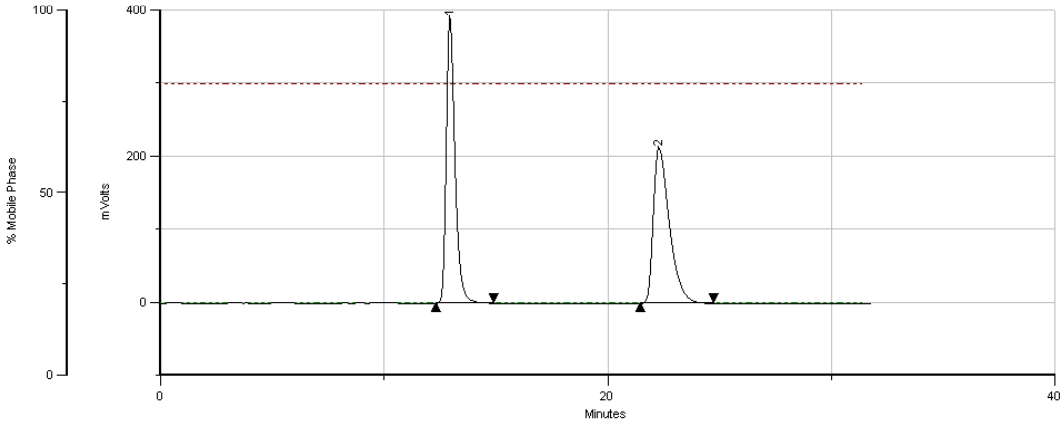
<Peak Table>

PDA Ch2 220nm

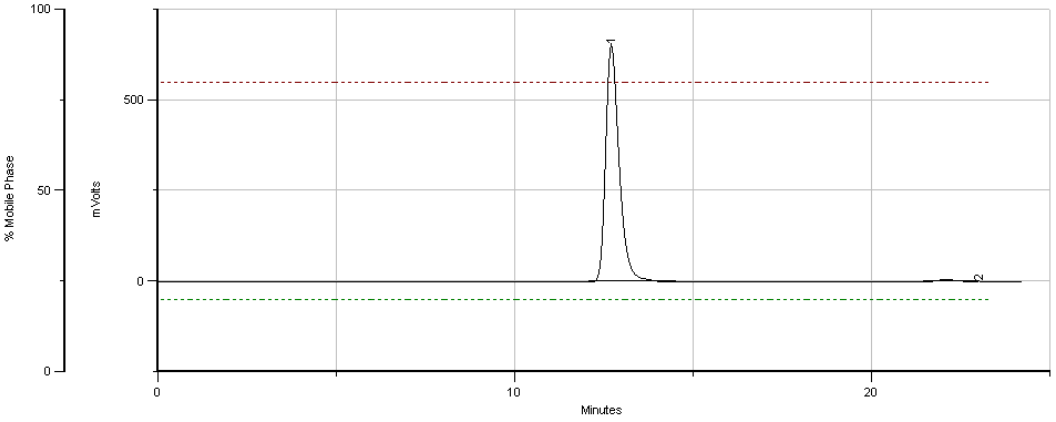
Peak#	Ret. Time	Area	Area%
1	11.818	10008385	98.074
2	16.959	196584	1.926
Total		10204970	100.000



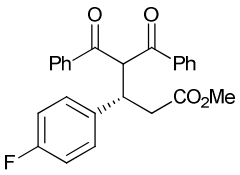
(7)



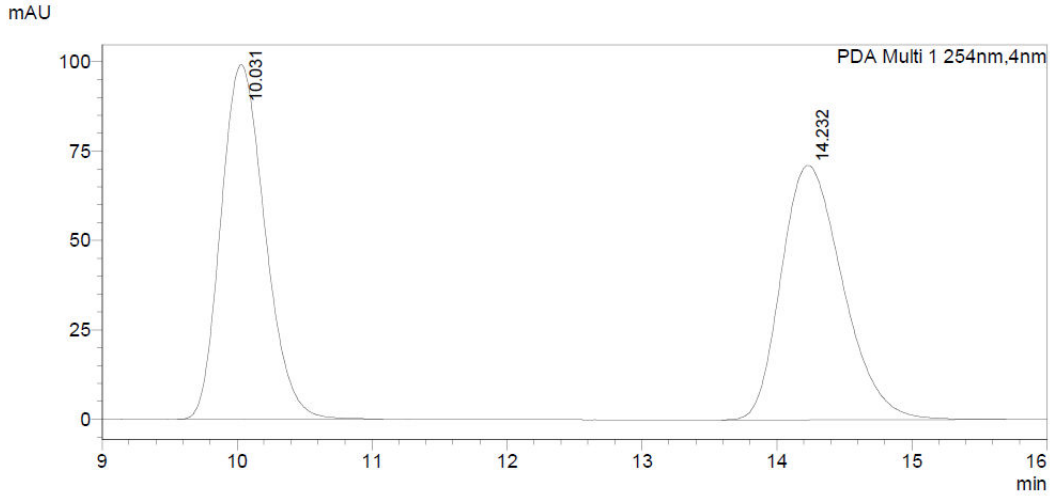
Peak Name	R. Time	Area	Area %
*1	12.94	17643908.00	49.91
2	22.30	17705074.00	50.09



Peak Name	R. Time	Area	Area %
*1	12.71	28851270.00	98.35
*2	22.09	483435.59	1.65



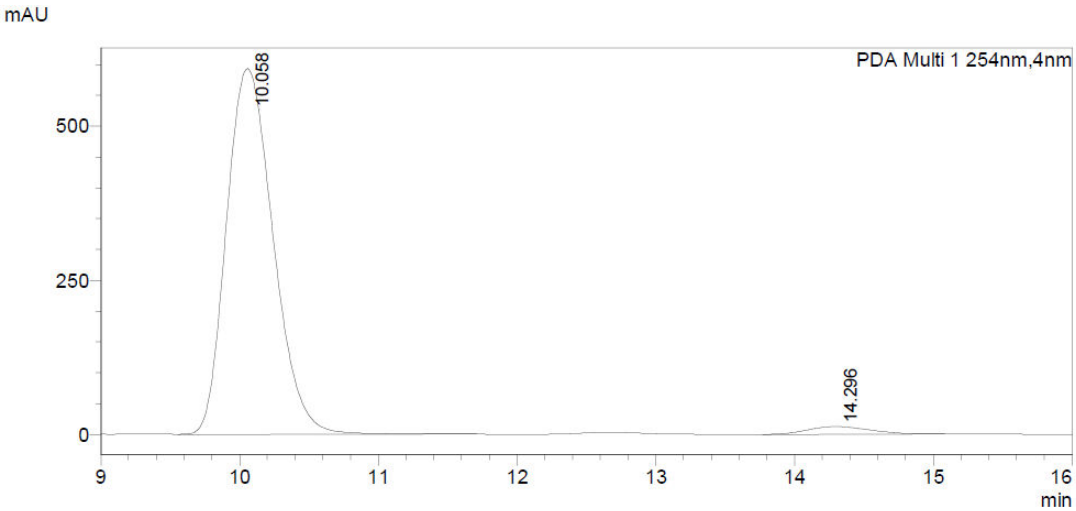
(8)



<Peak Table>

PDA Ch1 254nm

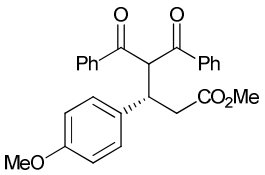
Peak#	Ret. Time	Area	Area%
1	10.031	2250282	49.983
2	14.232	2251852	50.017
Total		4502134	100.000



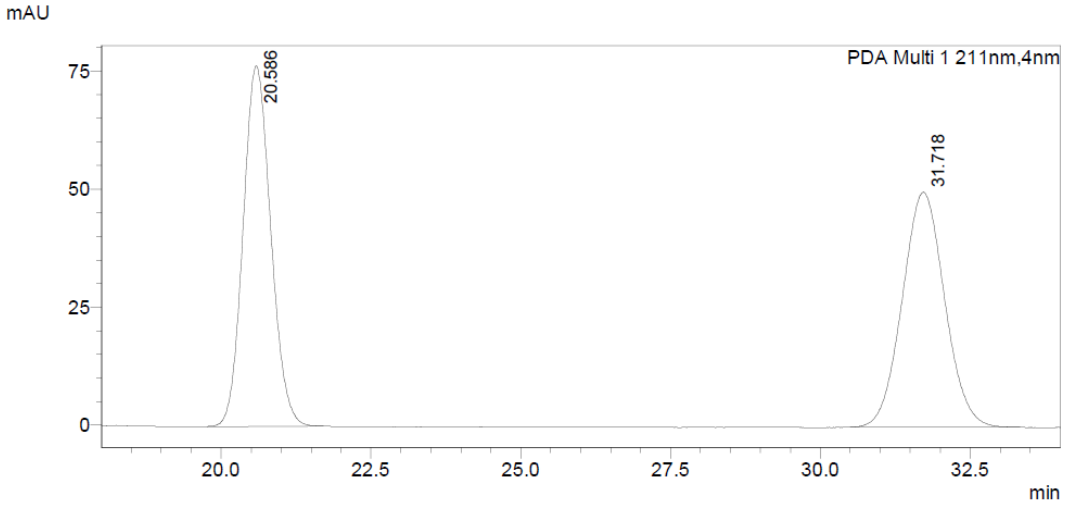
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.058	13876980	97.274
2	14.296	388920	2.726
Total		14265900	100.000



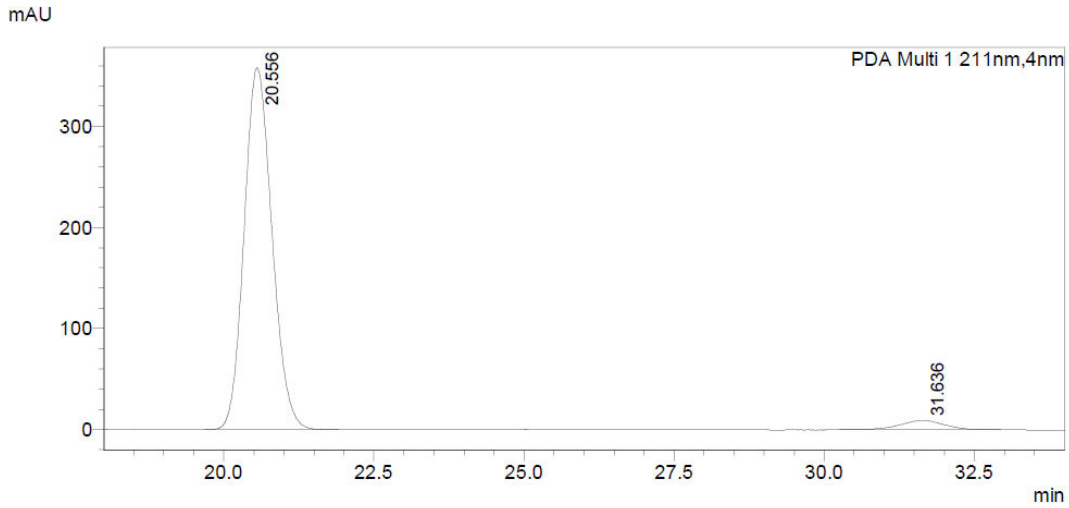
(9)



<Peak Table>

PDA Ch1 211nm

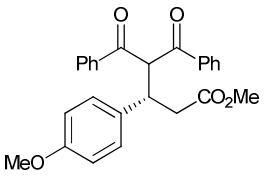
Peak#	Ret. Time	Area	Area%
1	20.586	2451994	50.002
2	31.718	2451803	49.998
Total		4903798	100.000



<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	20.556	11574590	95.939
2	31.636	489913	4.061
Total		12064504	100.000



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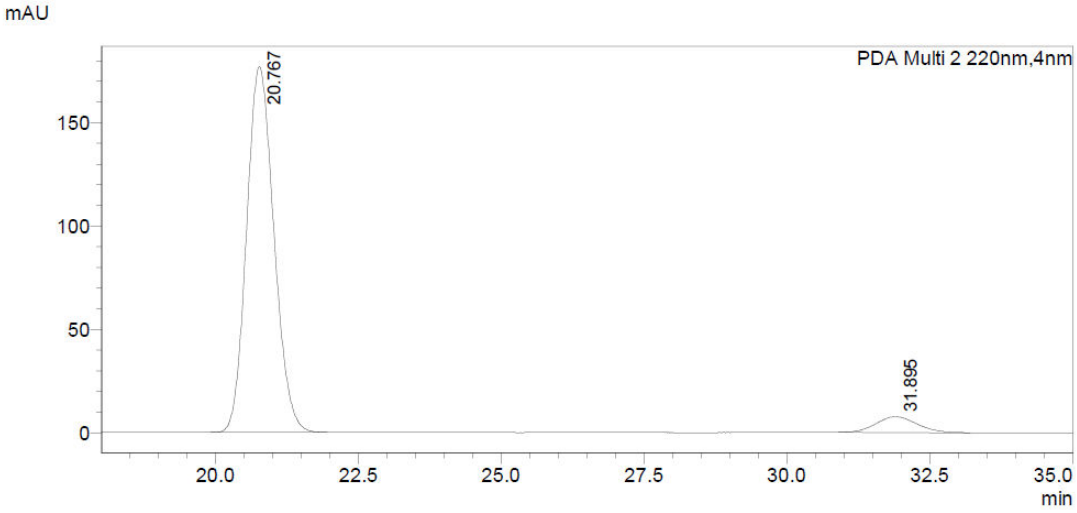
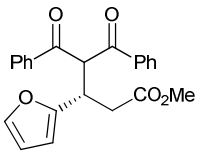


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	20.767	5895859	93.951
2	31.895	379606	6.049
Total		6275465	100.000



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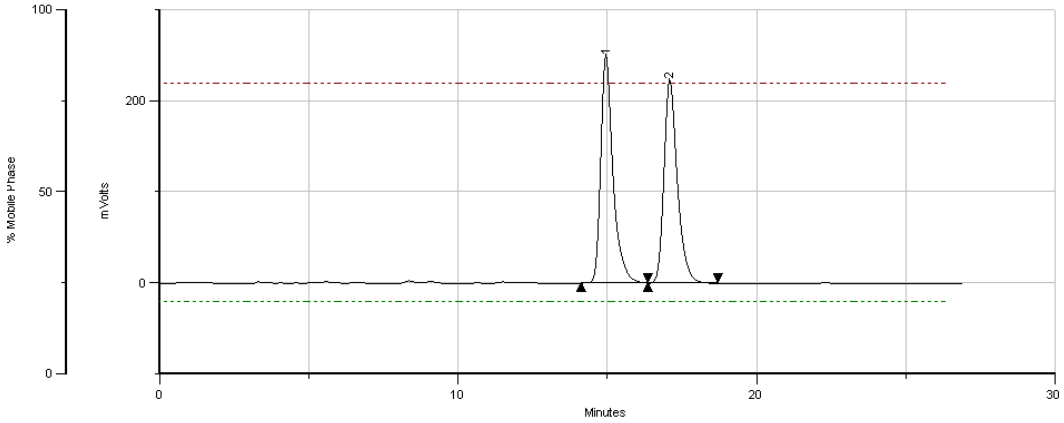
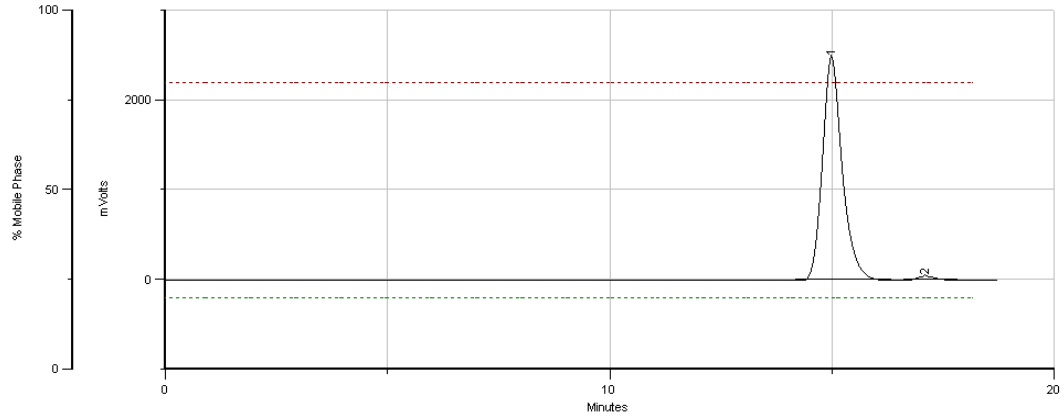
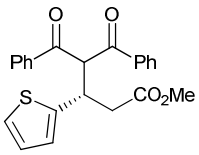


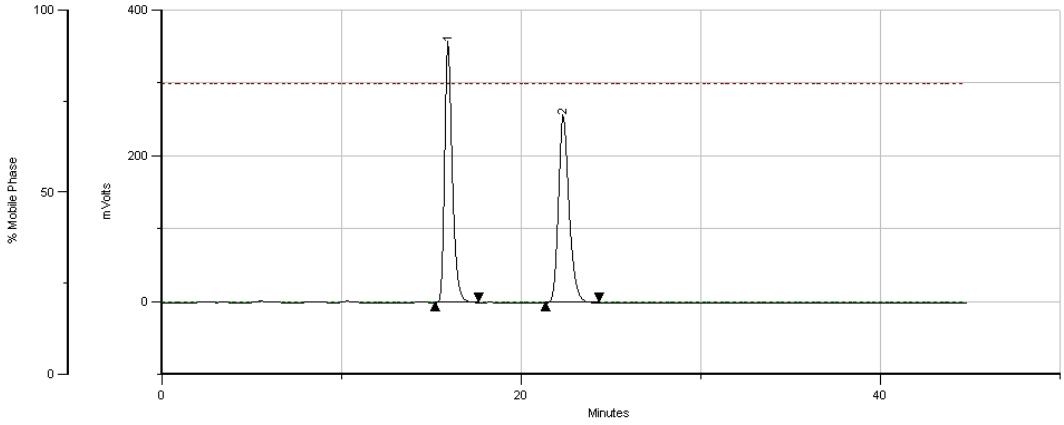
Peak Name	R. Time	Area	Area %
*1	14.95	1949417.00	50.83
2	17.09	1557860.00	49.17



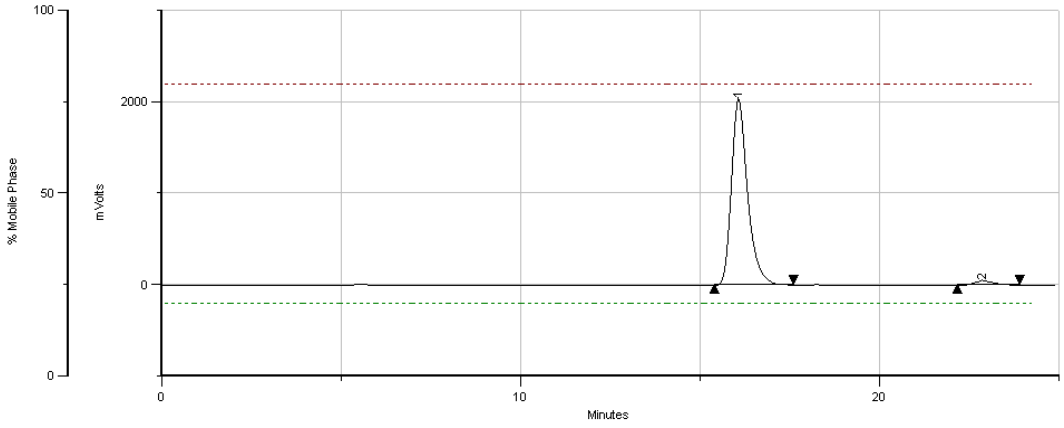
Peak Name	R. Time	Area	Area %
*1	14.99	29129056.00	98.11
*2	17.10	2483672.50	1.89



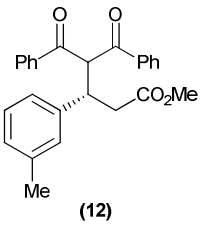
(11)



Peak Name	R. Time	Area	Area %
*1	15.92	17620036.00	50.05
2	22.34	17586184.00	49.95



Peak Name	R. Time	Area	Area %
*1	16.07	106536624.00	96.82
*2	22.88	3494136.00	3.18



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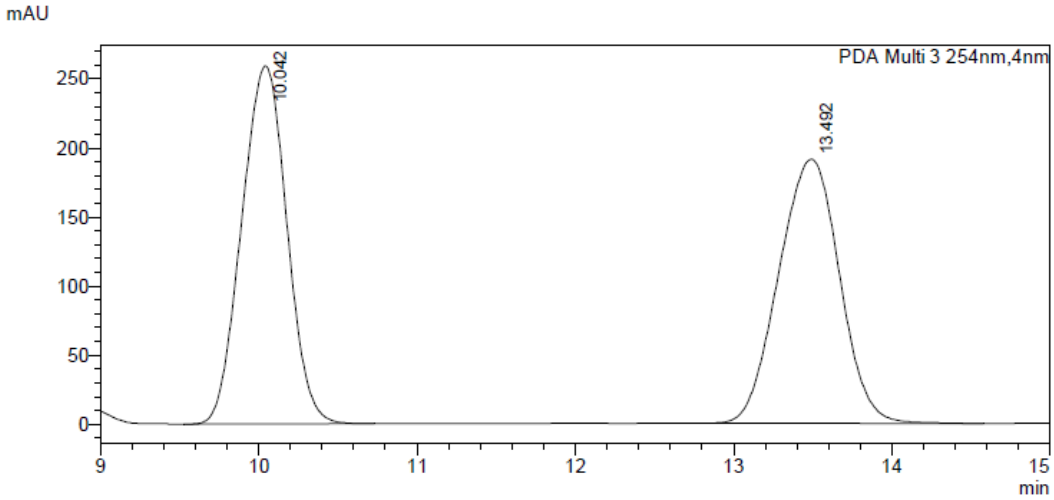
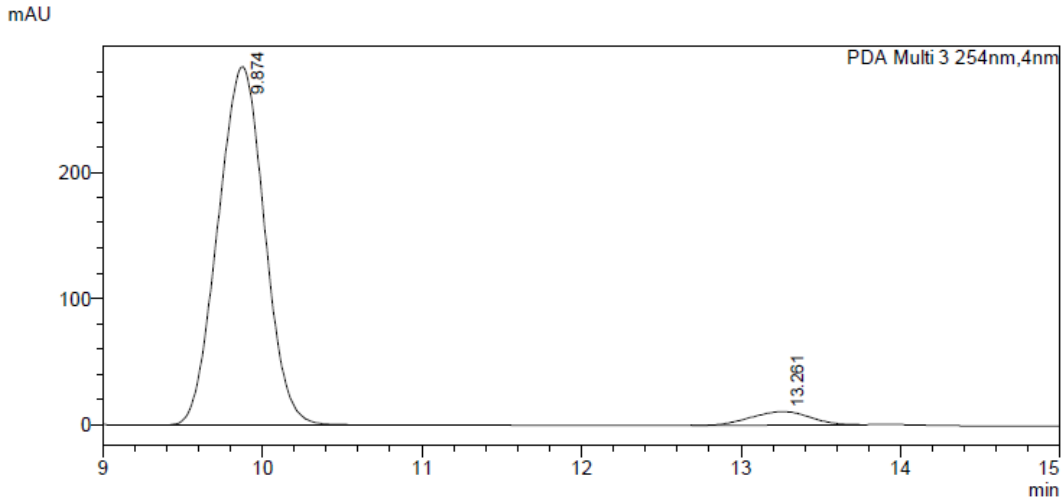


<Peak Table>

PDA Ch3 254nm

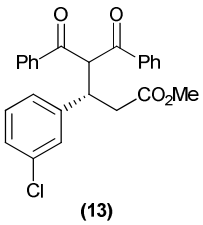
Peak#	Ret. Time	Area	Area%
1	10.042	5151322	50.227
2	13.492	5104838	49.773
Total		10256160	100.000



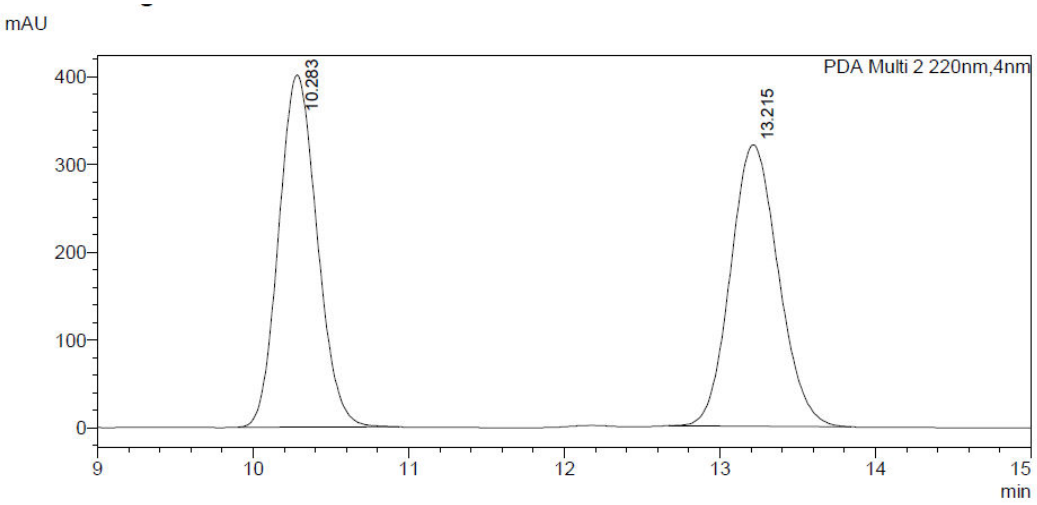
<Peak Table>

PDA Ch3 254nm

Peak#	Ret. Time	Area	Area%
1	9.874	5761508	95.469
2	13.261	273425	4.531
Total		6034932	100.000



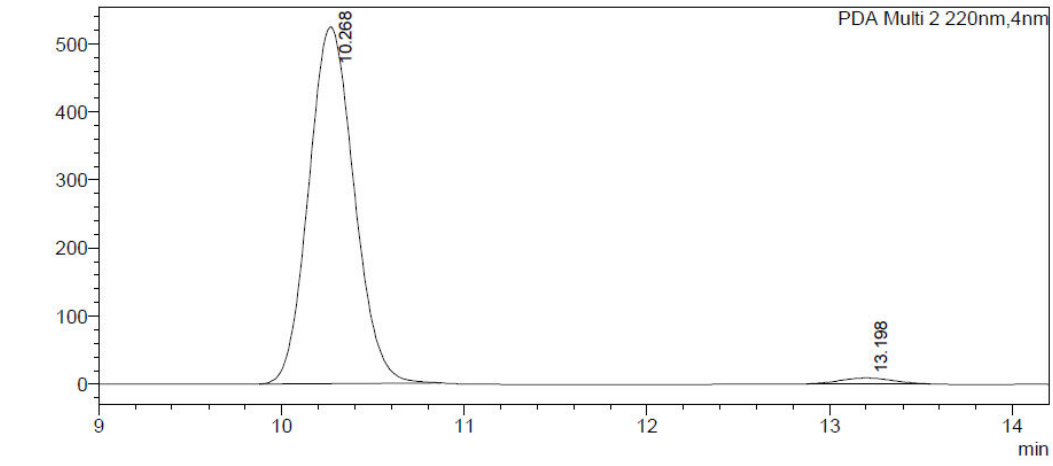
(13)



<Peak Table>

PDA Ch2 220nm

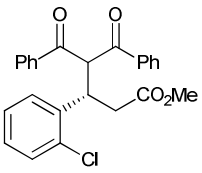
Peak#	Ret. Time	Area	Area%
1	10.283	6883624	50.054
2	13.215	6868682	49.946
Total		13752306	100.000



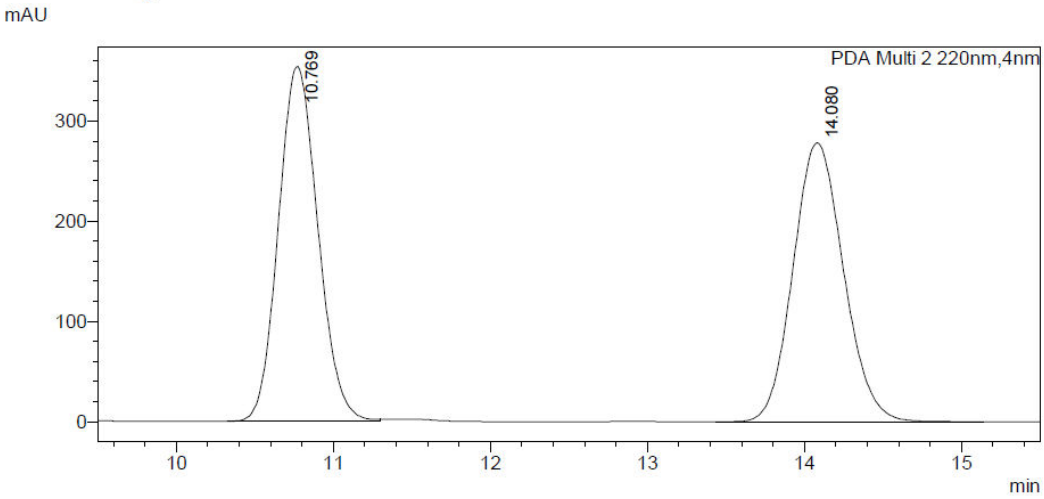
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	10.268	9048463	98.140
2	13.198	171455	1.860
Total		9219918	100.000



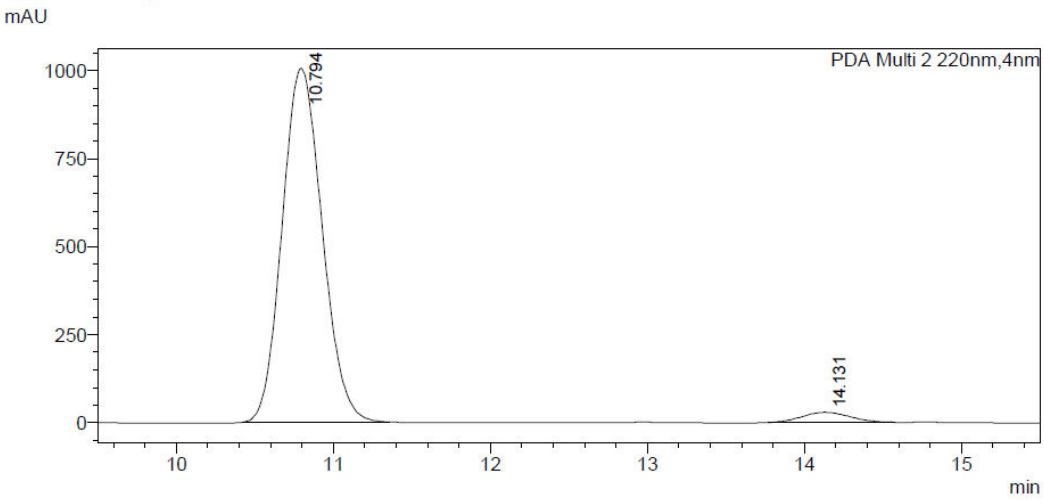
(14)



<Peak Table>

PDA Ch2 220nm

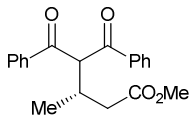
Peak#	Ret. Time	Area	Area%
1	10.769	6199114	49.945
2	14.080	6212775	50.055
Total		12411890	100.000



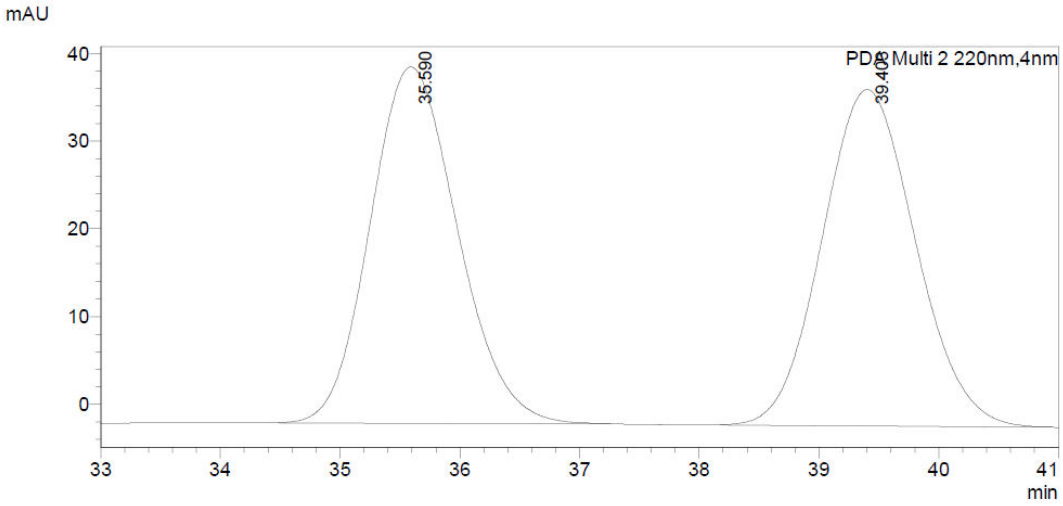
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	10.794	17850858	96.705
2	14.131	608289	3.295
Total		18459147	100.000



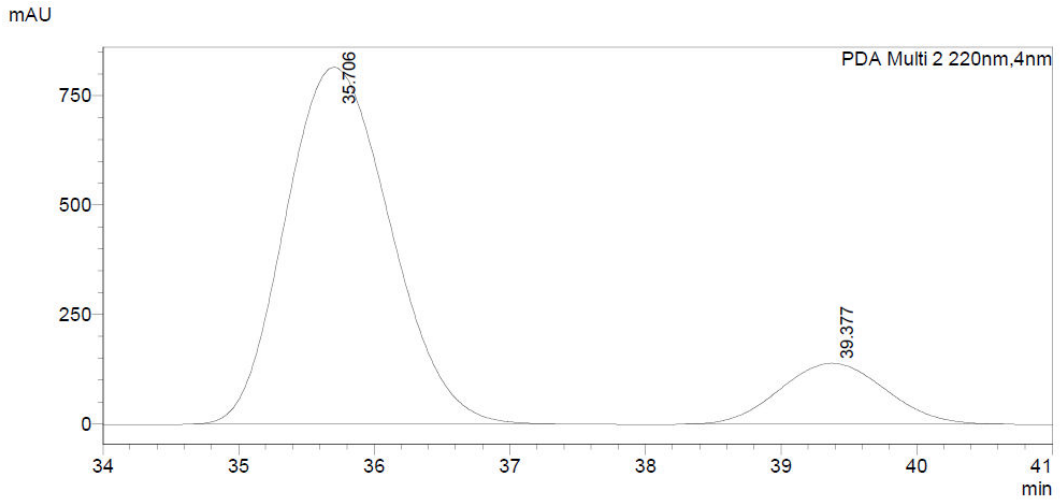
(15)



<Peak Table>

PDA Ch2 220nm

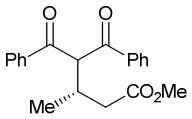
Peak#	Ret. Time	Area	Area%
1	35.590	2061526	49.852
2	39.403	2073751	50.148
Total		4135278	100.000



<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	35.706	43751068	85.235
2	39.377	7578584	14.765
Total		51329652	100.000



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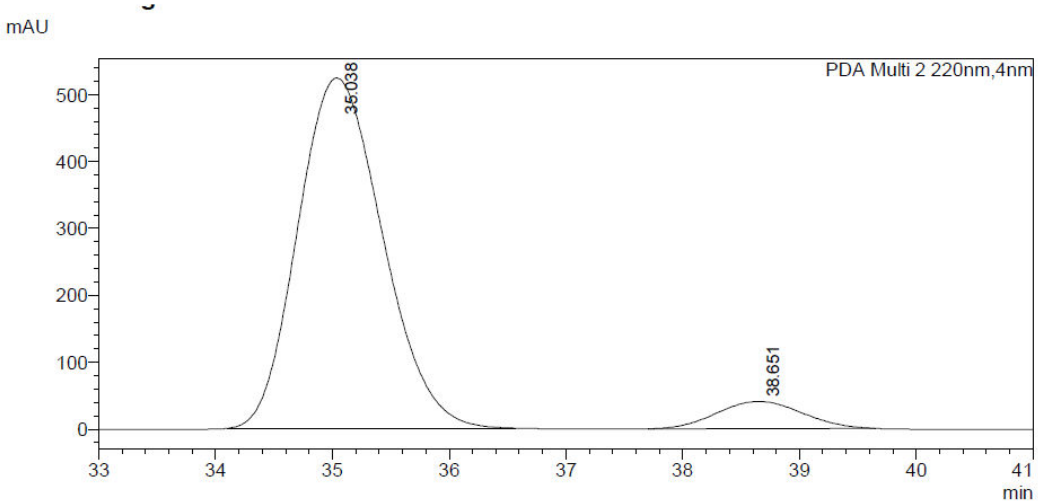
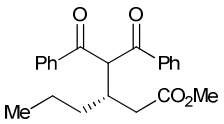


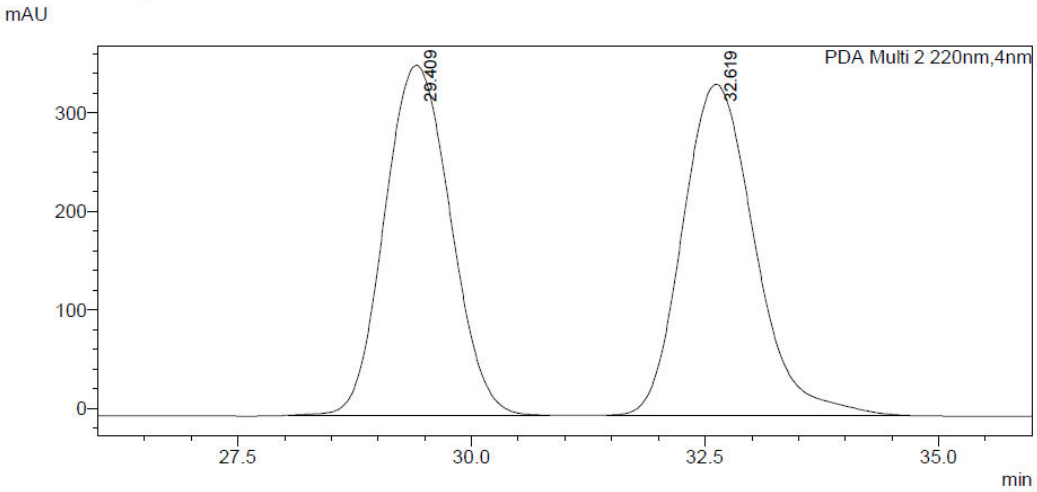
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	35.038	26427520	92.711
2	38.651	2077754	7.289
Total		28505275	100.000



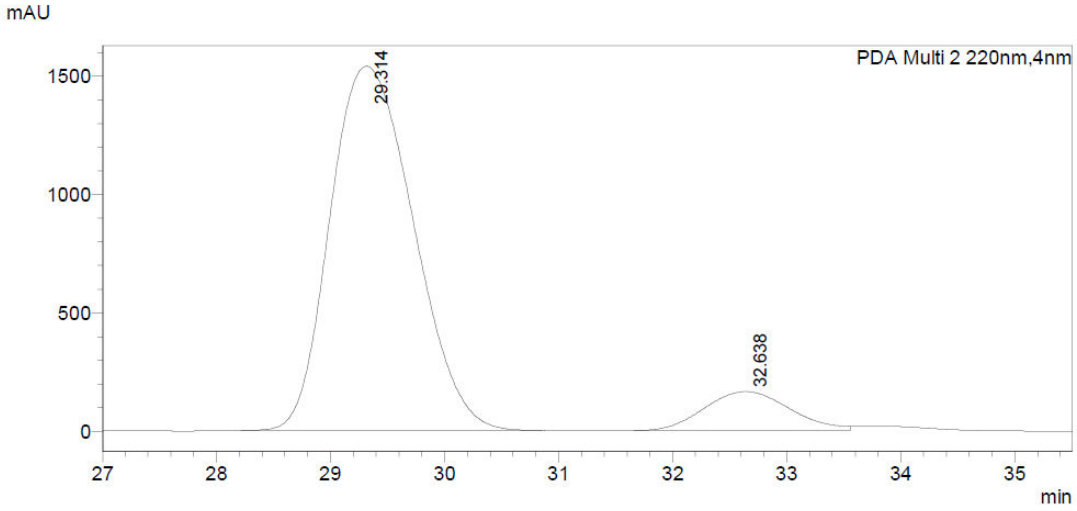
(16)



<Peak Table>

PDA Ch2 220nm

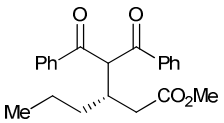
Peak#	Ret. Time	Area	Area%
1	29.409	17415240	49.112
2	32.619	18044974	50.888
Total		35460215	100.000



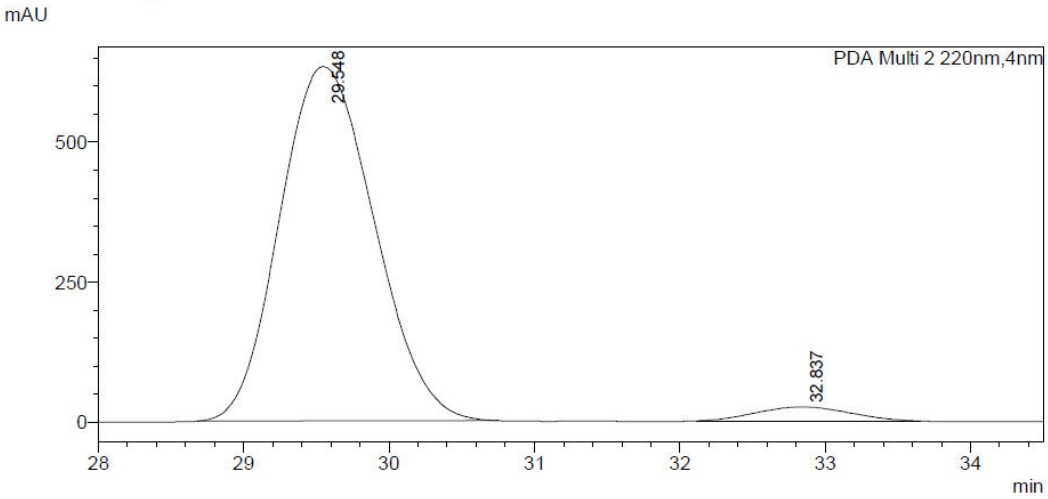
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	29.314	78205083	90.122
2	32.638	8571530	9.878
Total		86776613	100.000



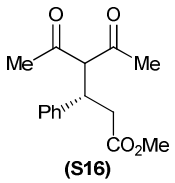
(16)



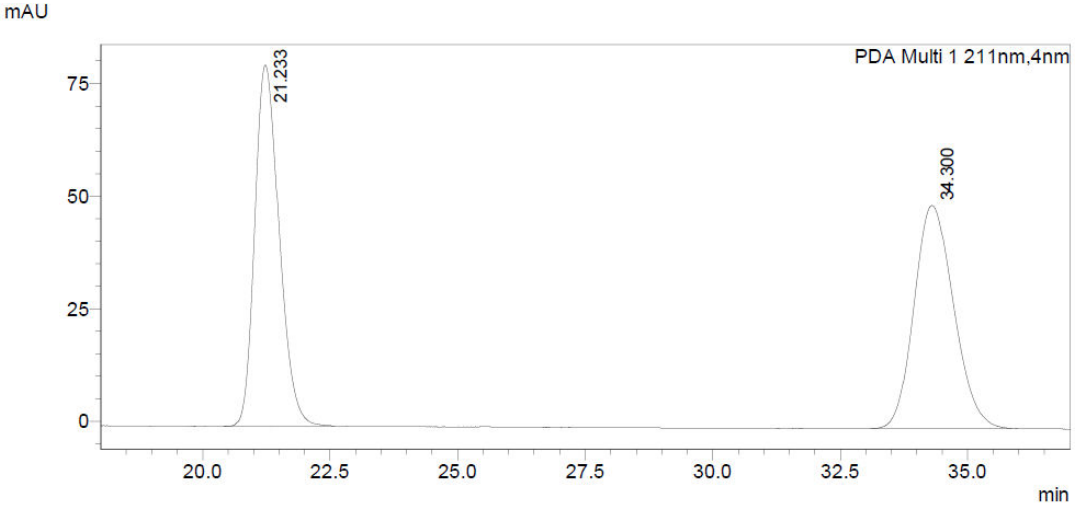
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	29.548	28642063	96.241
2	32.837	1118607	3.759
Total		29760669	100.000



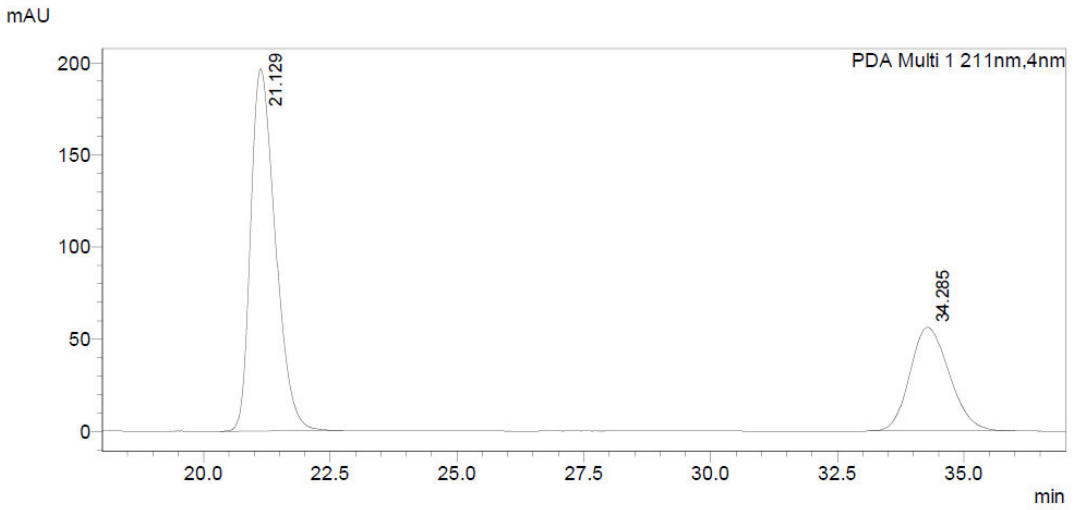
(S16)



<Peak Table>

PDA Ch1 211nm

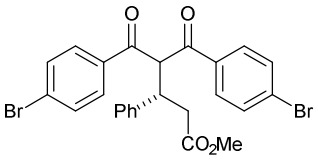
Peak#	Ret. Time	Area	Area%
1	21.233	2676179	50.009
2	34.300	2675262	49.991
Total		5351441	100.000



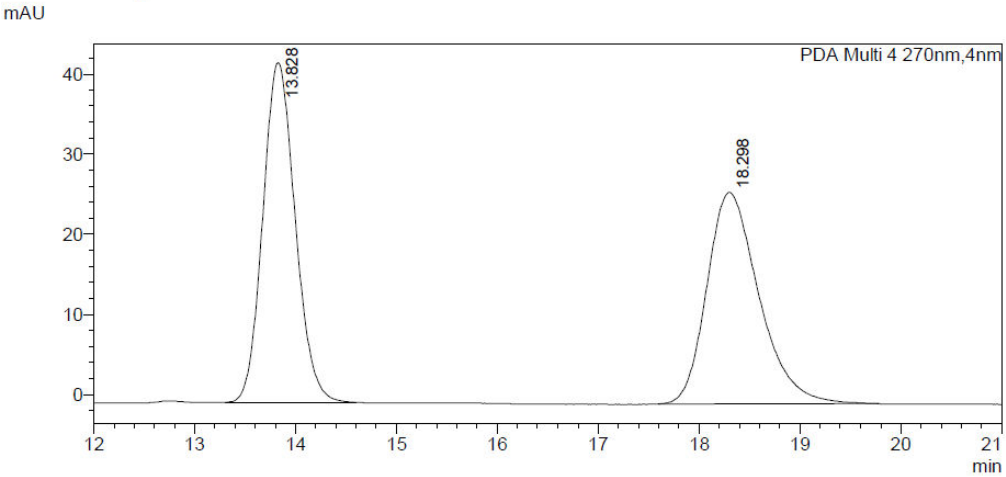
<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Height	Area%
1	21.129	6702730	196461	68.738
2	34.285	3048374	56291	31.262
Total		9751104	252753	100.000



(17)

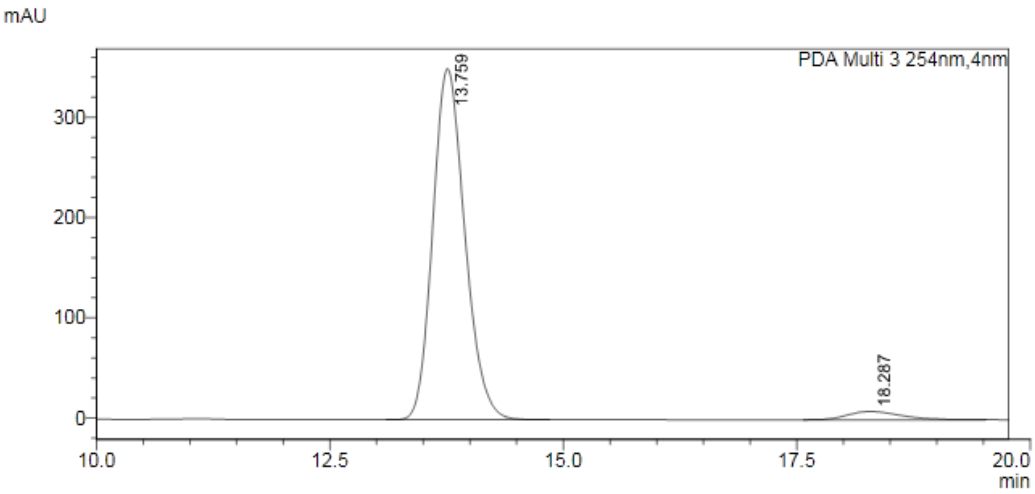


<Peak Table>

PDA Ch4 270nm

Peak#	Ret. Time	Area	Area%
1	13.828	947314	50.031
2	18.298	946147	49.969
Total		1893461	100.000

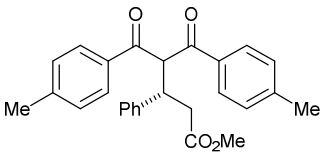
<Chromatogram>



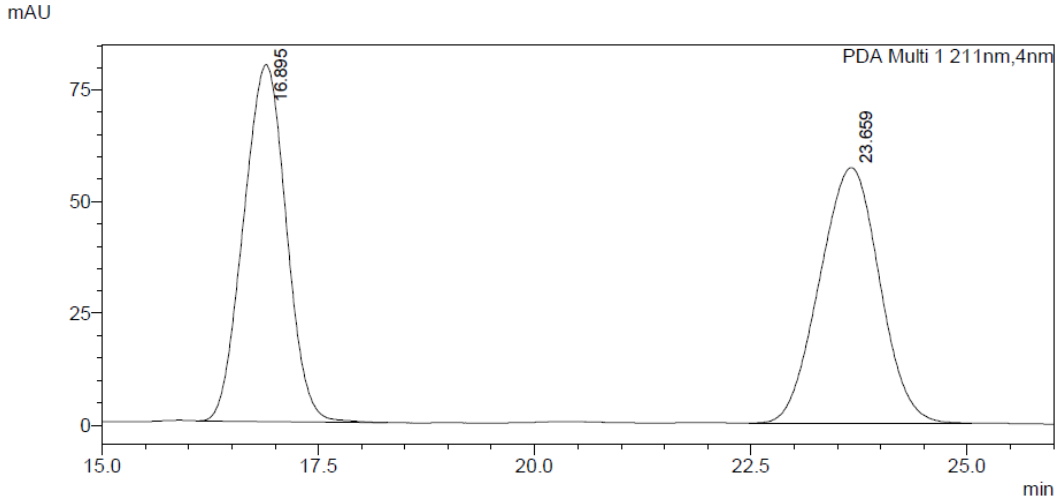
<Peak Table>

PDA Ch3 254nm

Peak#	Ret. Time	Area	Area%
1	13.759	8373032	96.144
2	18.287	335833	3.856
Total		8708865	100.000



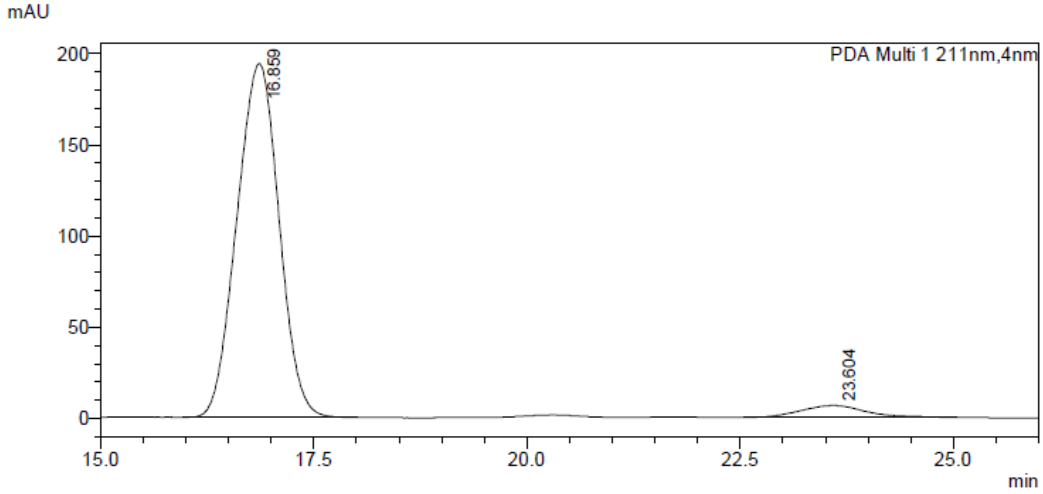
(18)



<Peak Table>

PDA Ch1 211nm

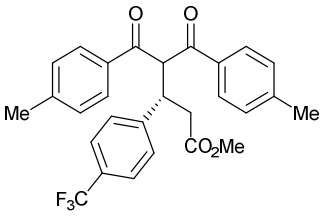
Peak#	Ret. Time	Area	Area%
1	16.895	2743841	49.858
2	23.659	2759484	50.142
Total		5503326	100.000



<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	16.859	6661835	95.067
2	23.604	345703	4.933
Total		7007537	100.000



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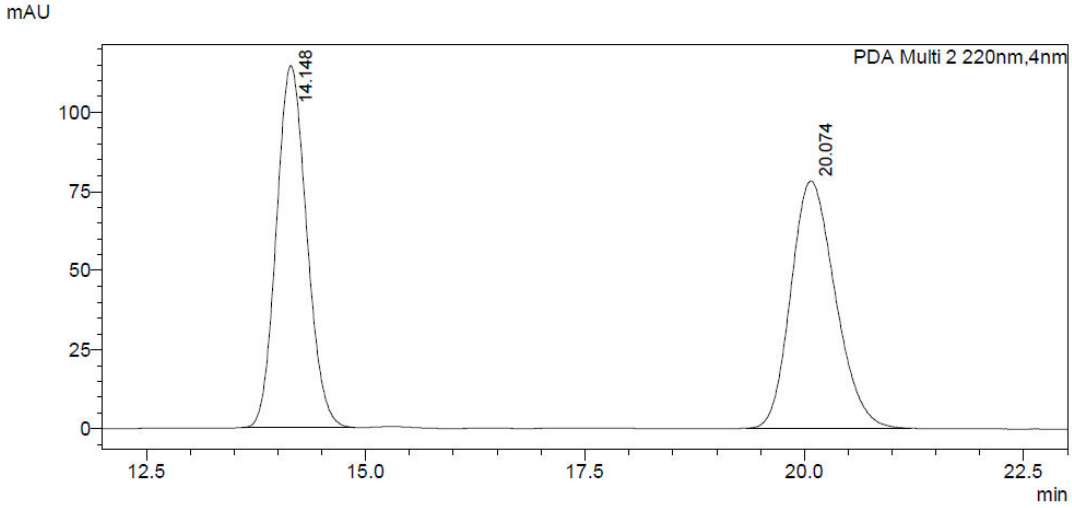
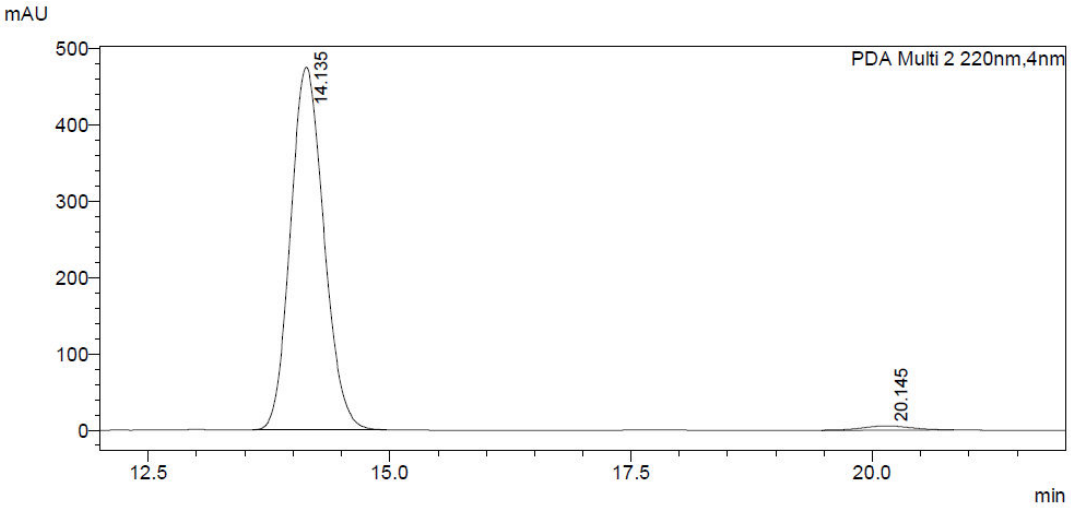


<Peak Table>

PDA Ch2 220nm

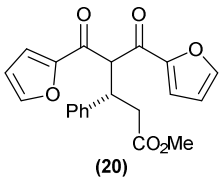
Peak#	Ret. Time	Area	Area%
1	14.148	2736637	49.955
2	20.074	2741531	50.045
Total		5478169	100.000



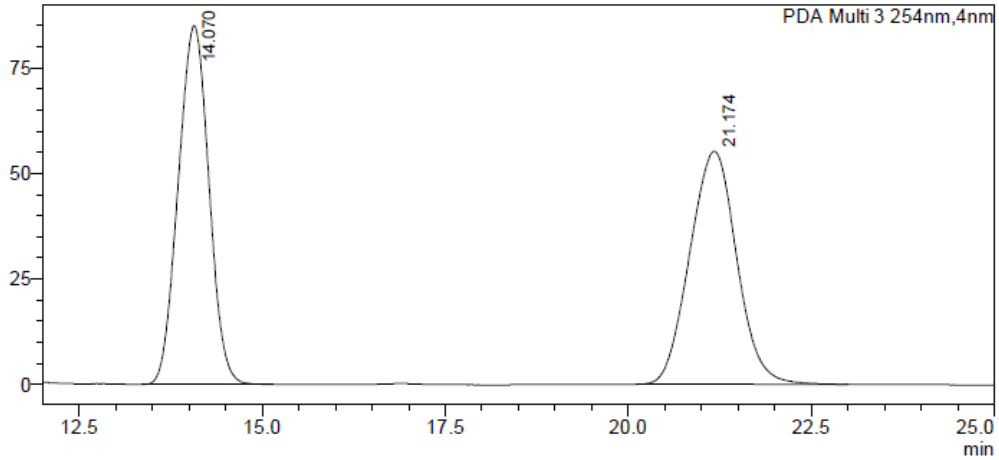
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	14.135	11442676	98.415
2	20.145	184244	1.585
Total		11626920	100.000



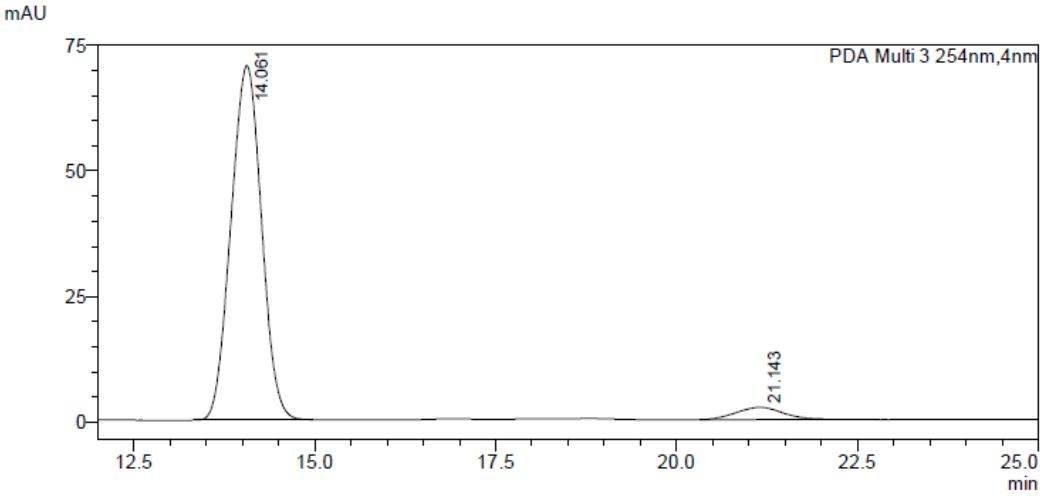
(20)



<Peak Table>

PDA Ch3 254nm

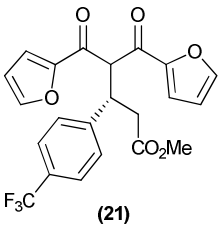
Peak#	Ret. Time	Area	Area%
1	14.070	2482303	50.110
2	21.174	2471371	49.890
Total		4953675	100.000



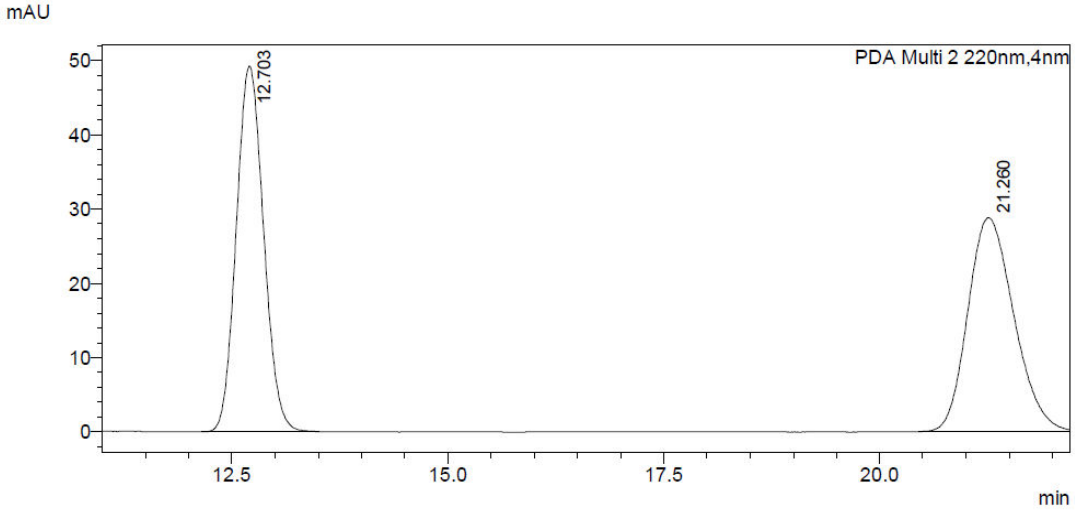
<Peak Table>

PDA Ch3 254nm

Peak#	Ret. Time	Area	Area%
1	14.061	2069942	95.124
2	21.143	106095	4.876
Total		2176037	100.000



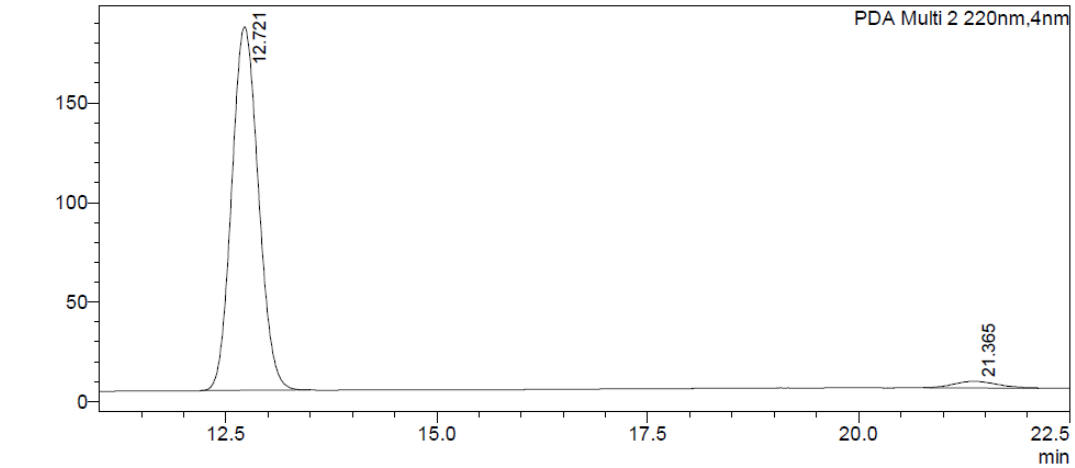
(21)



<Peak Table>

PDA Ch2 220nm

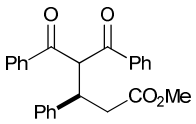
Peak#	Ret. Time	Area	Area%
1	12.703	1084220	50.355
2	21.260	1068925	49.645
Total		2153146	100.000



<Peak Table>

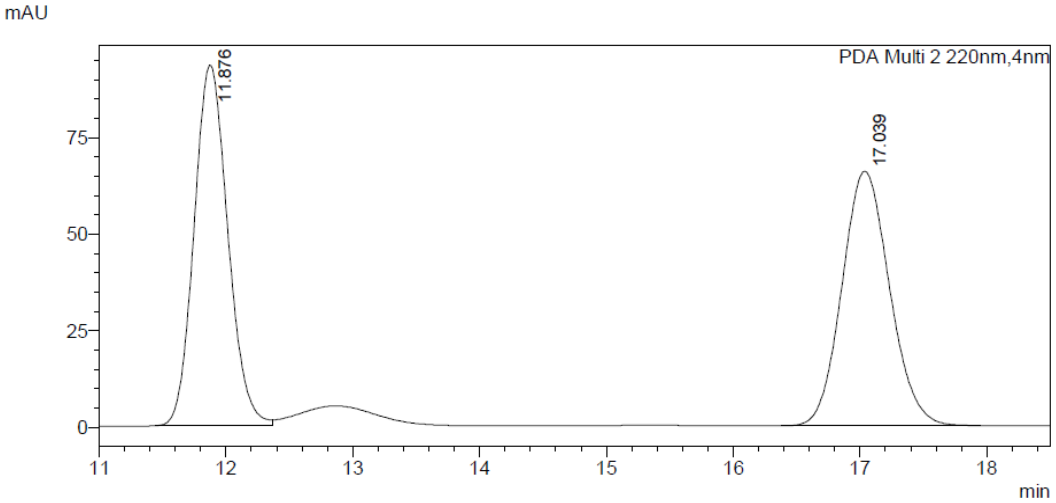
PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	12.721	4019567	97.144
2	21.365	118183	2.856
Total		4137749	100.000



(6)

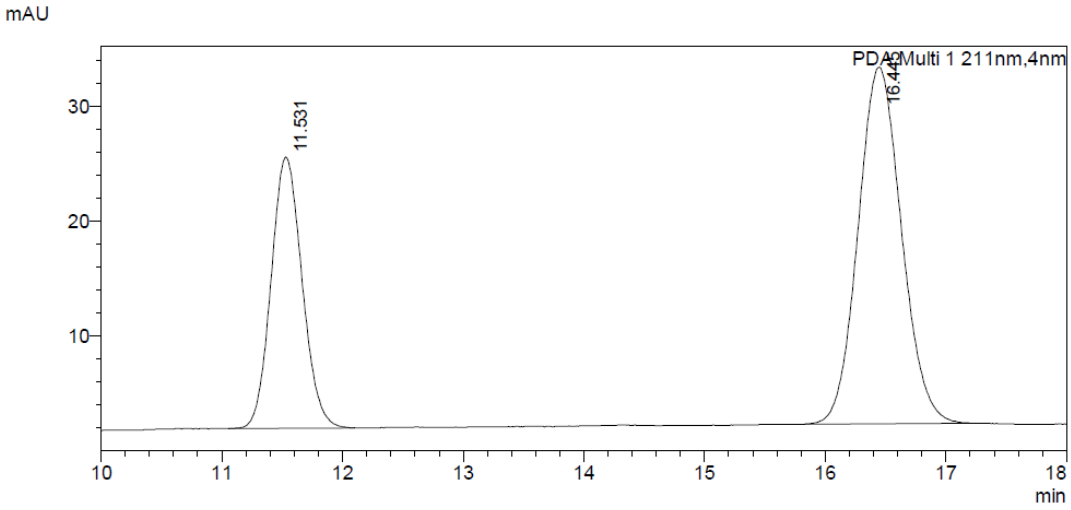
from cis-anhydride



<Peak Table>

PDA Ch2 220nm

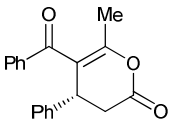
Peak#	Ret. Time	Area	Area%
1	11.876	1731954	50.165
2	17.039	1720589	49.835
Total		3452543	100.000



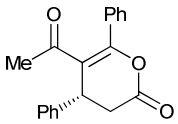
<Peak Table>

PDA Ch1 211nm

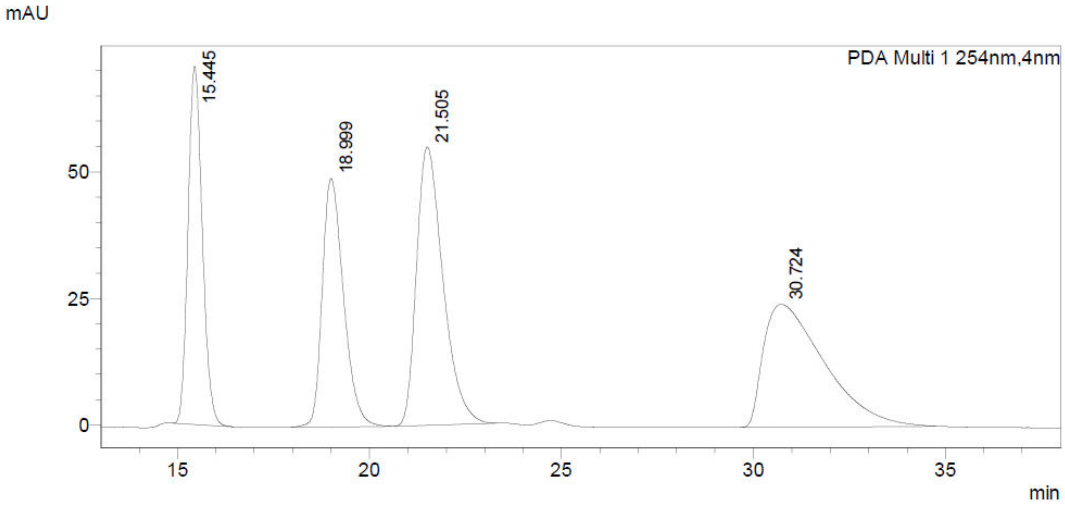
Peak#	Ret. Time	Area	Area%
1	11.531	422336	35.203
2	16.445	777366	64.797
Total		1199702	100.000



(24)



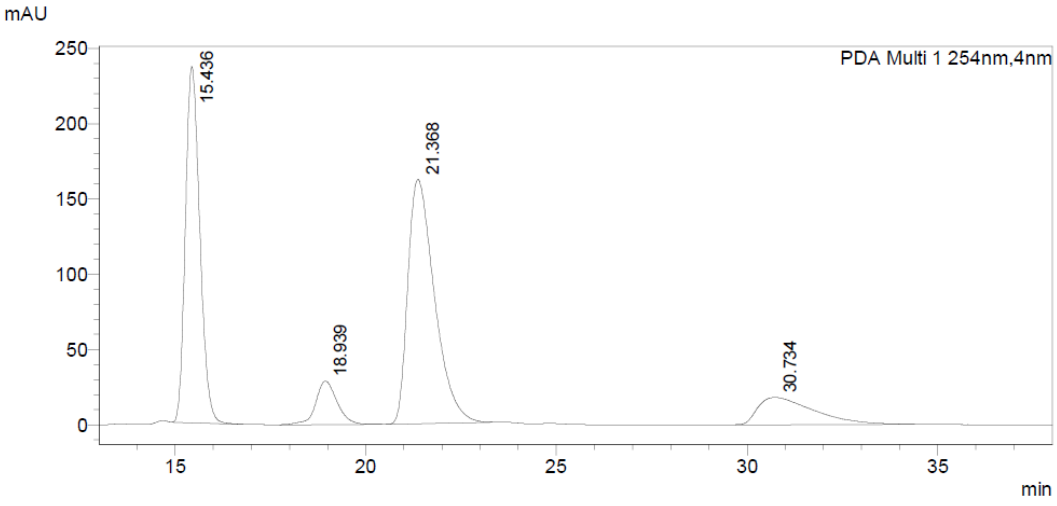
(23)



<Peak Table>

PDA Ch1 254nm

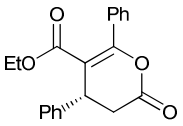
Peak#	Ret. Time	Area	Height	Area%
1	15.445	1834755	70769	20.289
2	18.999	1892528	49055	20.928
3	21.505	2642120	54974	29.217
4	30.724	2673557	24285	29.565
Total		9042960	199083	100.000



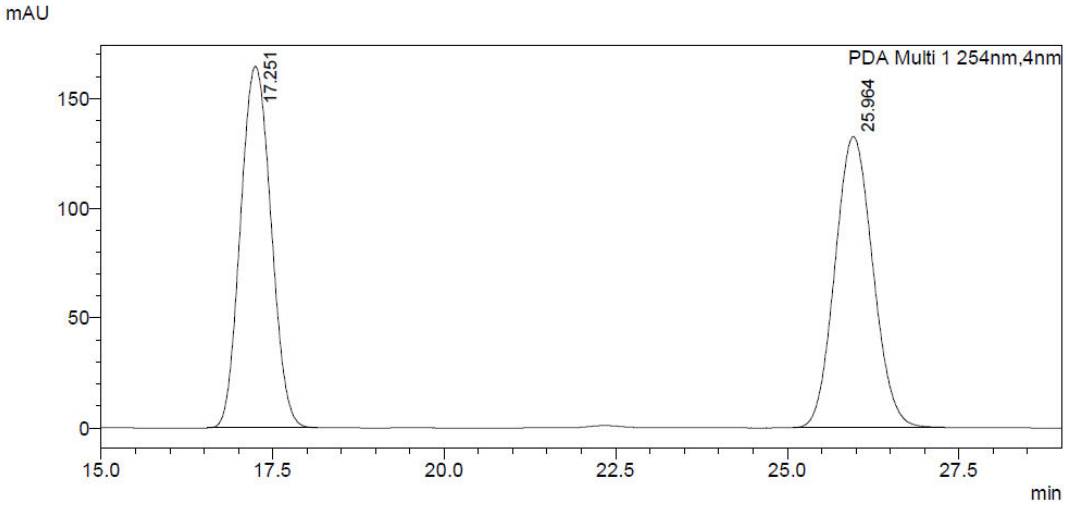
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.436	6223304	36.372
2	18.939	1128810	6.597
3	21.368	7927853	46.334
4	30.734	1830266	10.697
Total		17110233	100.000



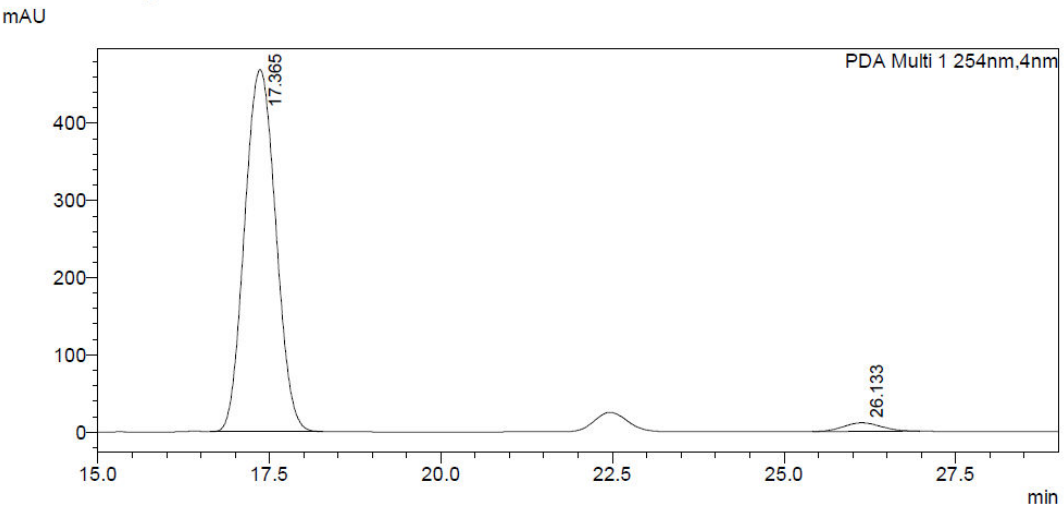
(27)



<Peak Table>

PDA Ch1 254nm

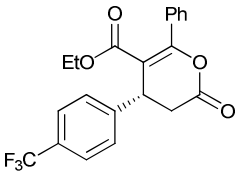
Peak#	Ret. Time	Area	Area%
1	17.251	5094176	49.971
2	25.964	5100187	50.029
Total		10194363	100.000



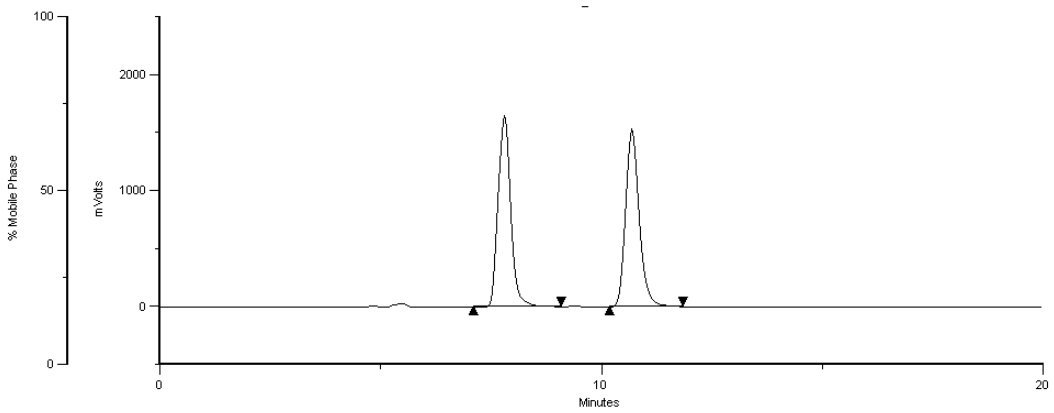
<Peak Table>

PDA Ch1 254nm

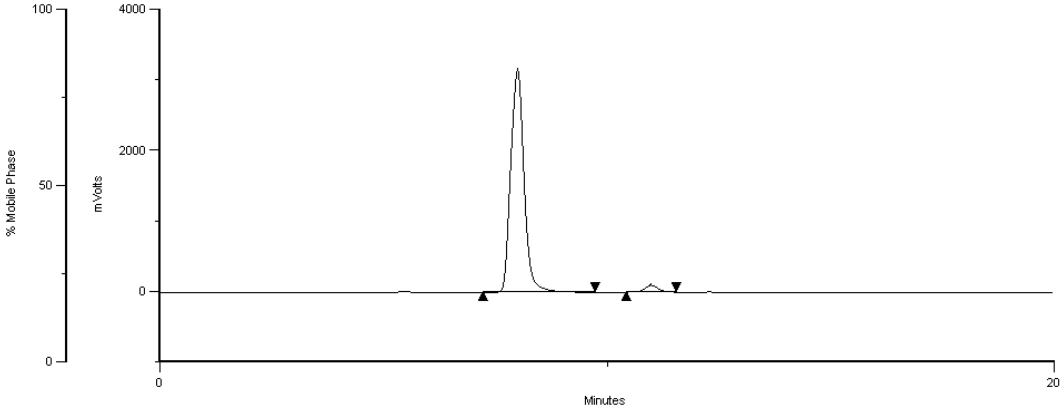
Peak#	Ret. Time	Area	Area%
1	17.365	14806114	97.211
2	26.133	424784	2.789
Total		15230898	100.000



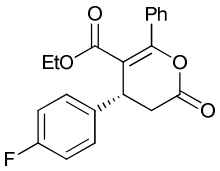
(28)



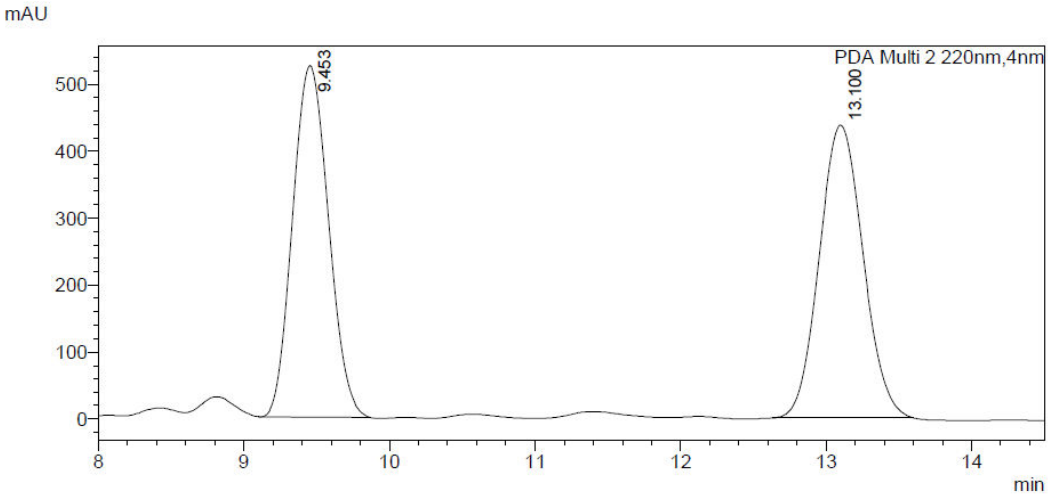
Peak Name	R. Time	Area	Area %
*1	7.81	55430956.00	49.94
*2	10.69	55560492.00	50.06



Peak Name	R. Time	Area	Area %
*1	8.00	109123360.00	96.86
*2	10.99	3539802.00	3.14



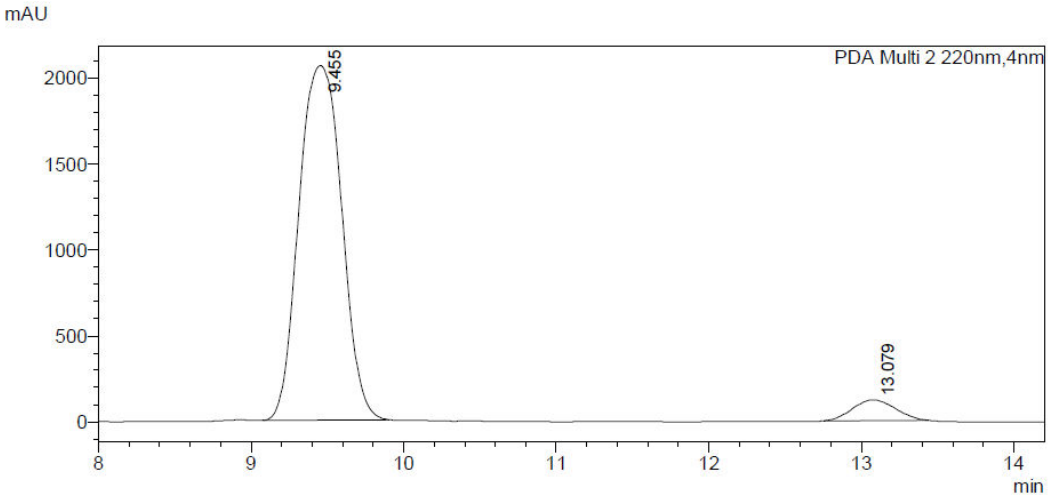
(29)



<Peak Table>

PDA Ch2 220nm

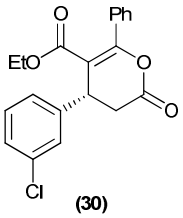
Peak#	Ret. Time	Area	Area%
1	9.453	9016849	49.634
2	13.100	9149649	50.366
Total		18166498	100.000



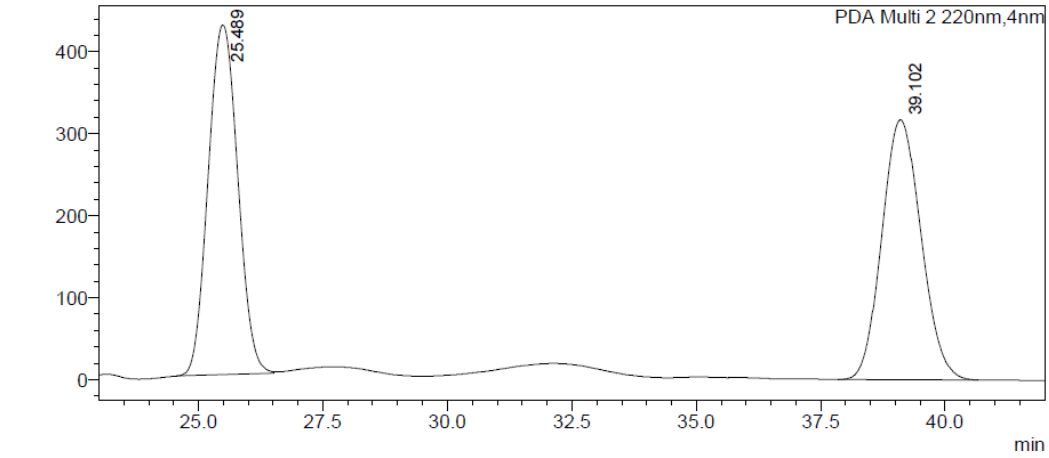
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	9.455	40283721	94.480
2	13.079	2353640	5.520
Total		42637360	100.000



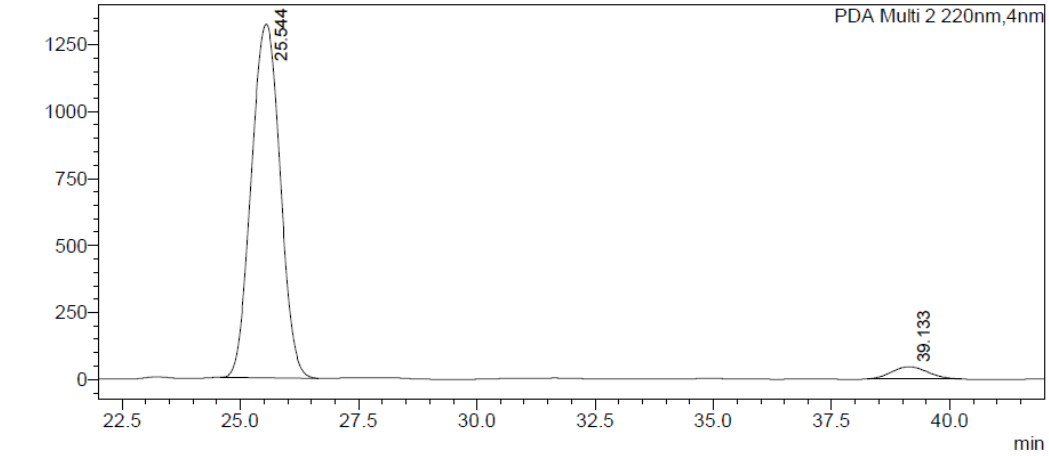
(30)



<Peak Table>

PDA Ch2 220nm

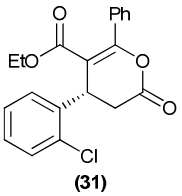
Peak#	Ret. Time	Area	Area%
1	25.489	17641048	50.370
2	39.102	17381910	49.630
Total		35022958	100.000



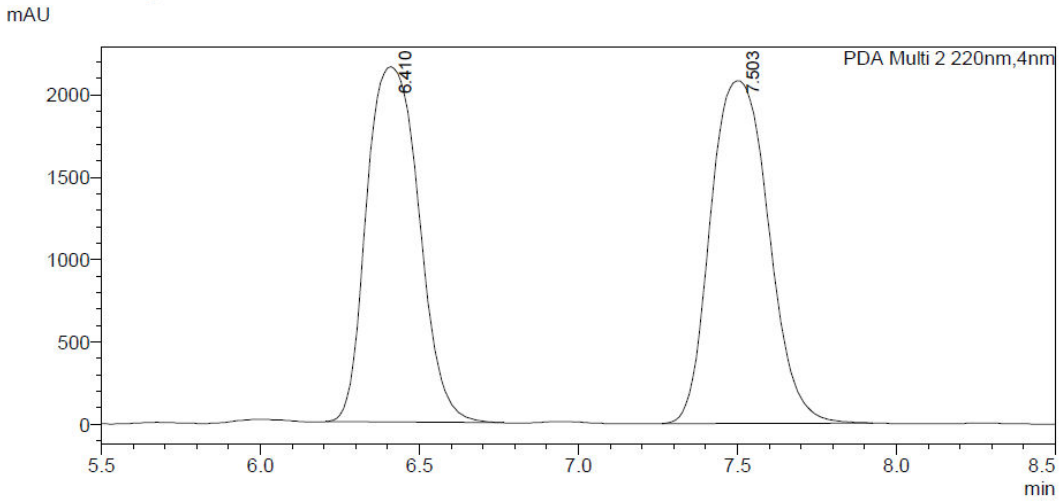
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	25.544	56012064	95.880
2	39.133	2406892	4.120
Total		58418956	100.000



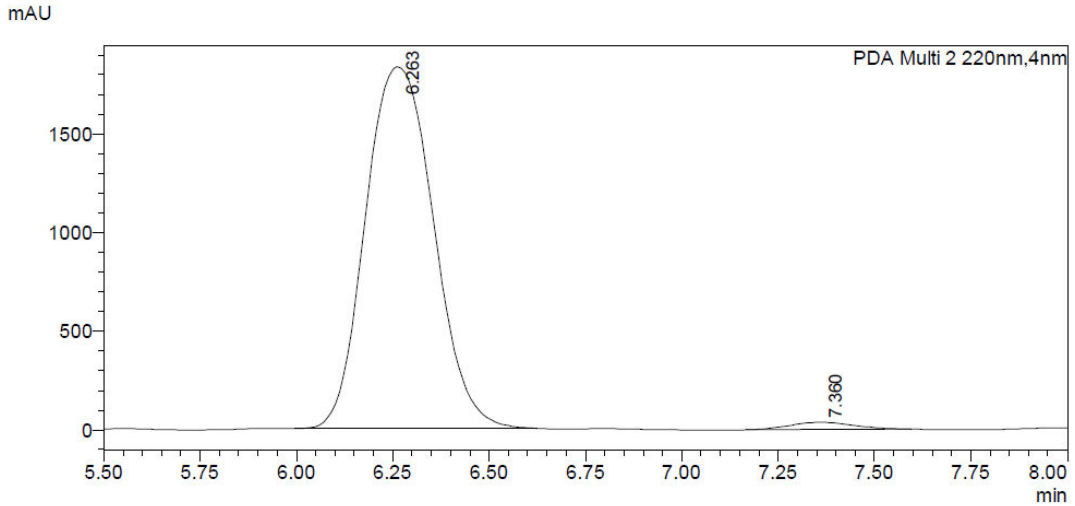
(31)



<Peak Table>

PDA Ch2 220nm

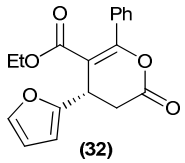
Peak#	Ret. Time	Area	Area%
1	6.410	24708204	48.324
2	7.503	26422298	51.676
Total		51130502	100.000



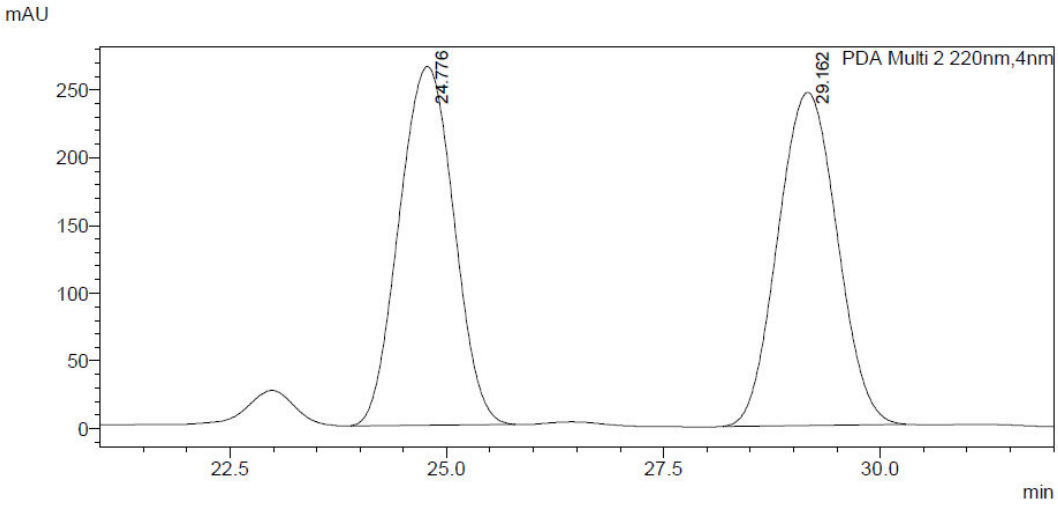
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	6.263	22579121	98.150
2	7.360	425549	1.850
Total		23004670	100.000



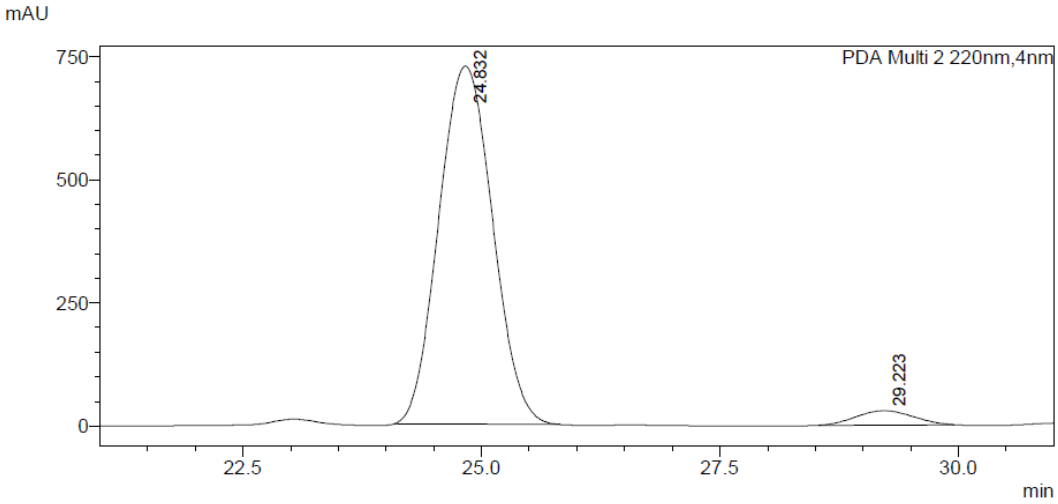
(32)



<Peak Table>

PDA Ch2 220nm

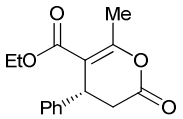
Peak#	Ret. Time	Area	Area%
1	24.776	11634036	49.863
2	29.162	11697951	50.137
Total		23331986	100.000



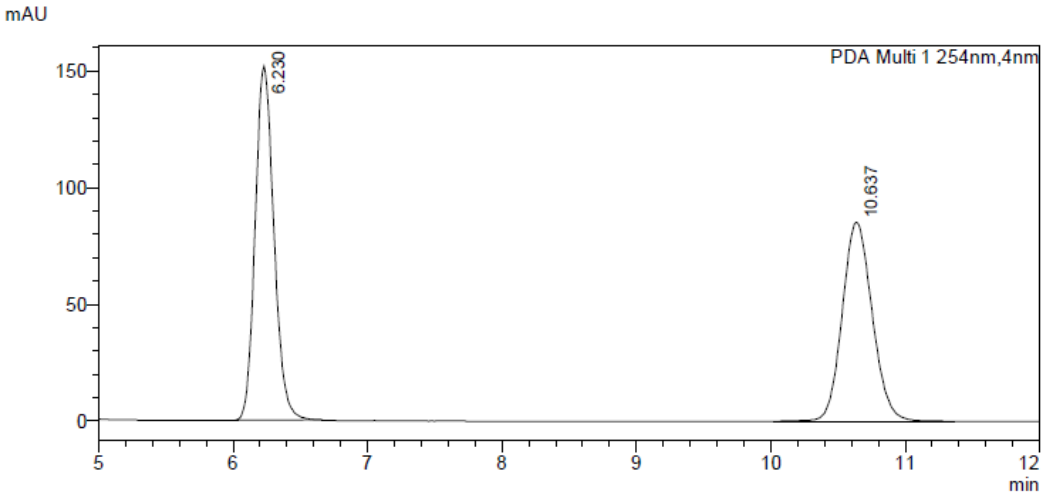
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	24.832	28622021	95.987
2	29.223	1196648	4.013
Total		29818669	100.000



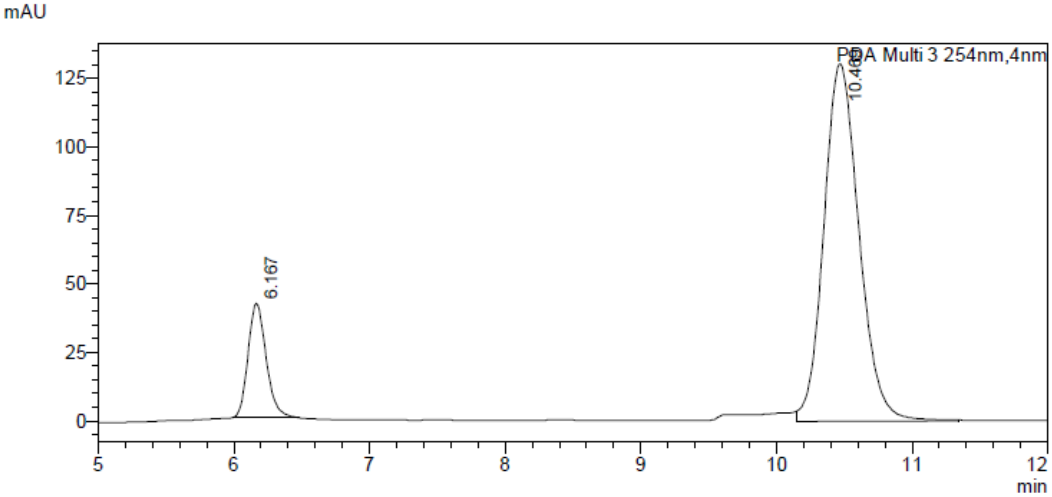
(S17)



<Peak Table>

PDA Ch1 254nm

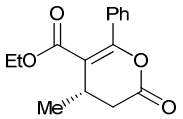
Peak#	Ret. Time	Area	Area%
1	6.230	1474174	52.824
2	10.637	1316536	47.176
Total		2790711	100.000



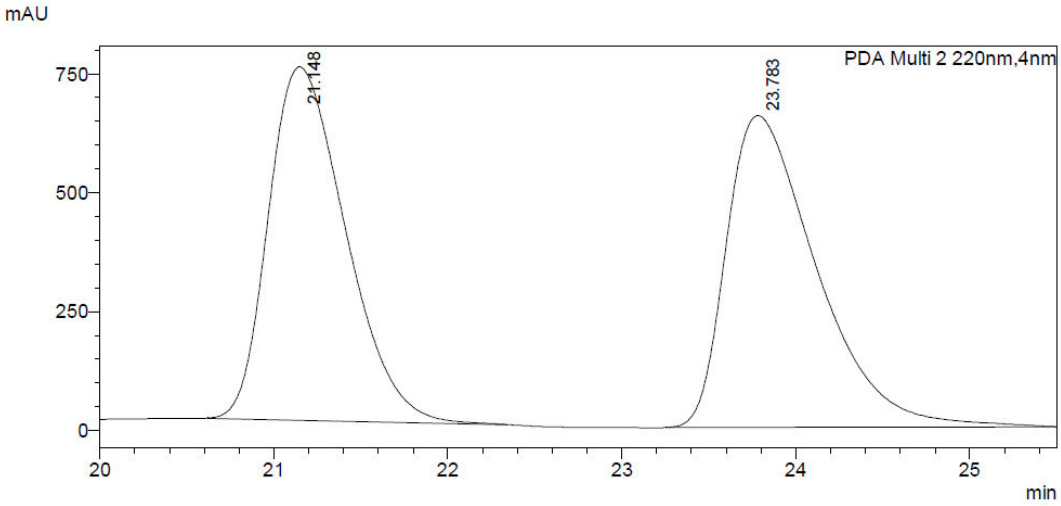
<Peak Table>

PDA Ch3 254nm

Peak#	Ret. Time	Area	Area%
1	6.167	388103	14.189
2	10.469	2347103	85.811
Total		2735205	100.000



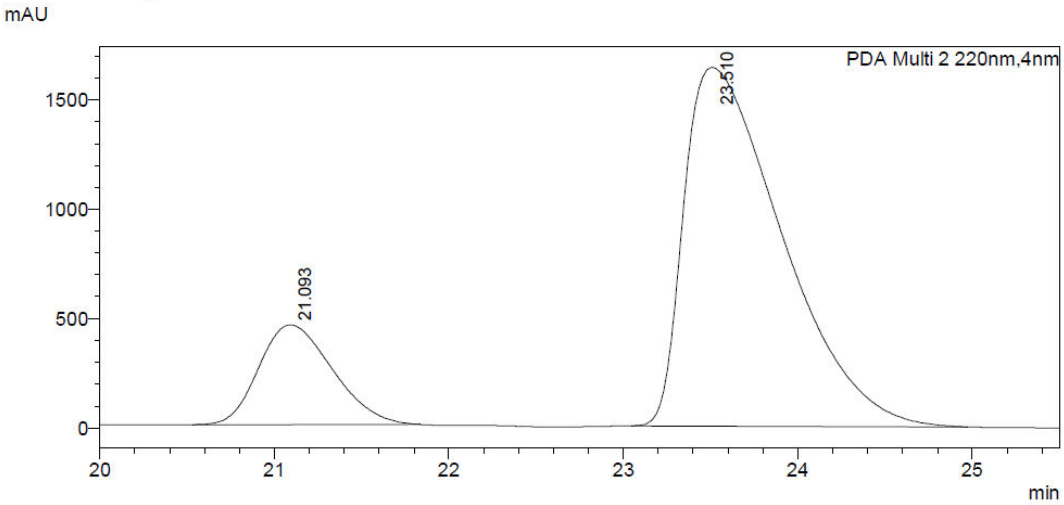
(S18)



<Peak Table>

PDA Ch2 220nm

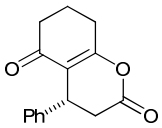
Peak#	Ret. Time	Area	Area%
1	21.148	22977826	49.181
2	23.783	23743505	50.819
Total		46721331	100.000



<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	21.093	13391681	17.301
2	23.510	64012169	82.699
Total		77403851	100.000



(34)

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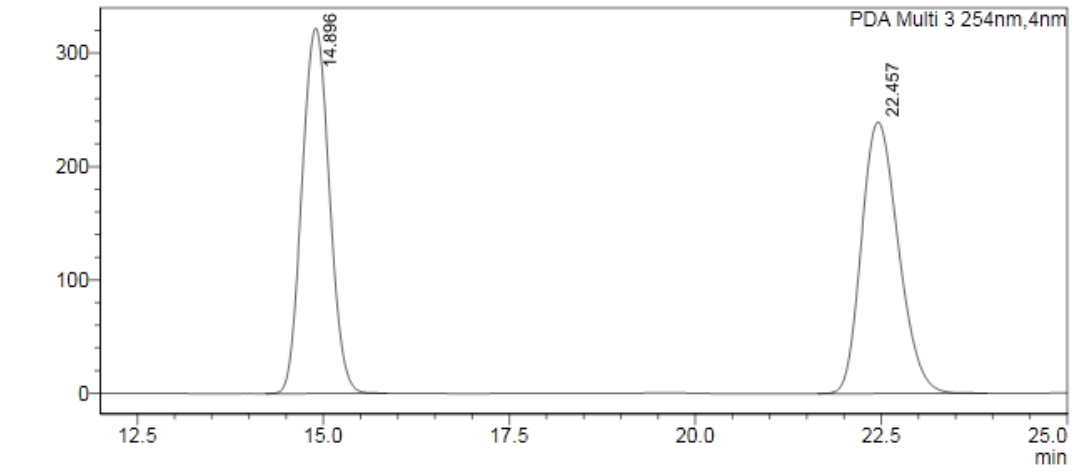
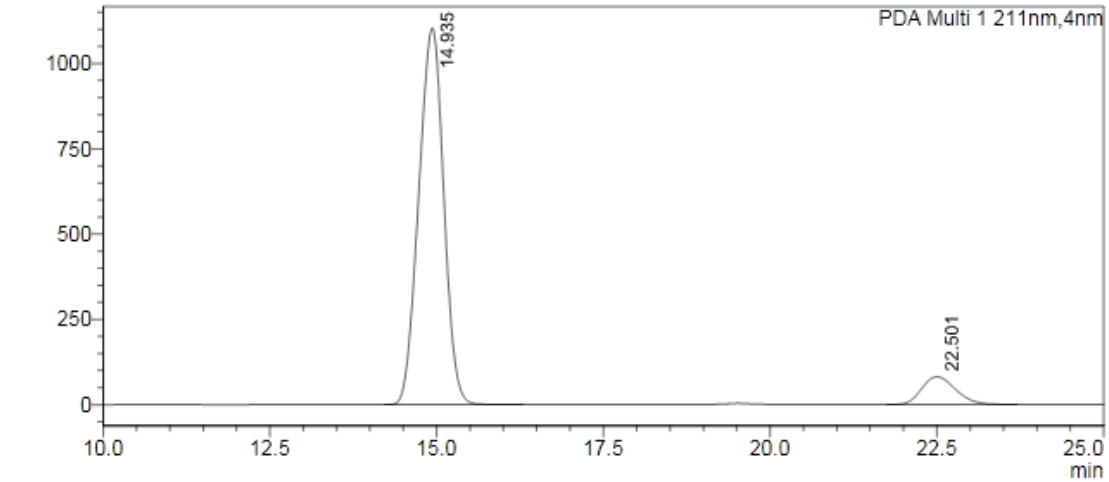


<Peak Table>

PDA Ch3 254nm

Peak#	Ret. Time	Area	Area%
1	14.896	8253586	50.001
2	22.457	8253183	49.999
Total		16506769	100.000

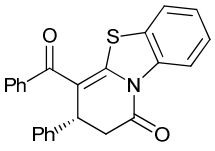
<Chromatogram>



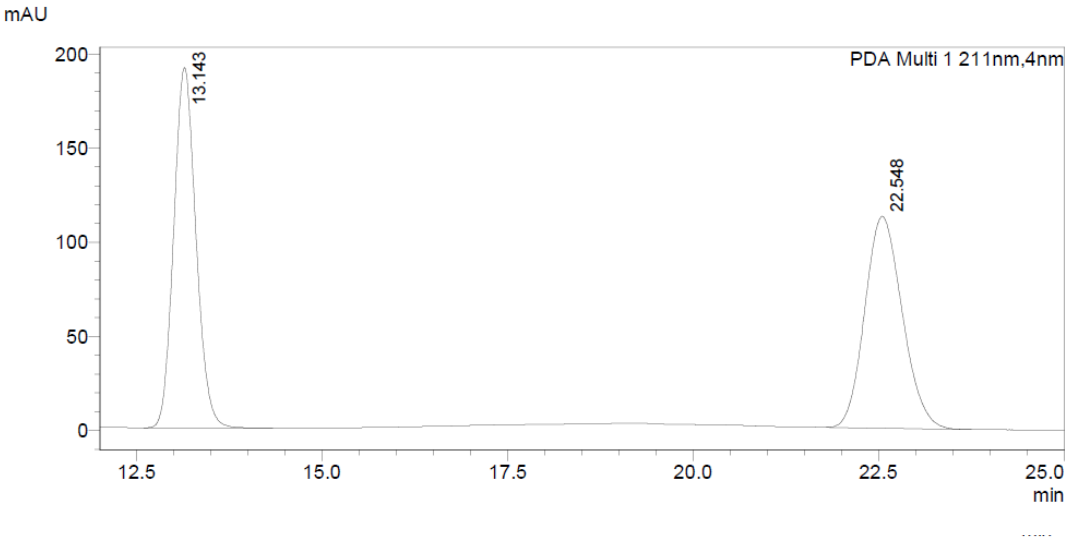
<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	14.935	28732660	90.909
2	22.501	2873139	9.091
Total		31605799	100.000



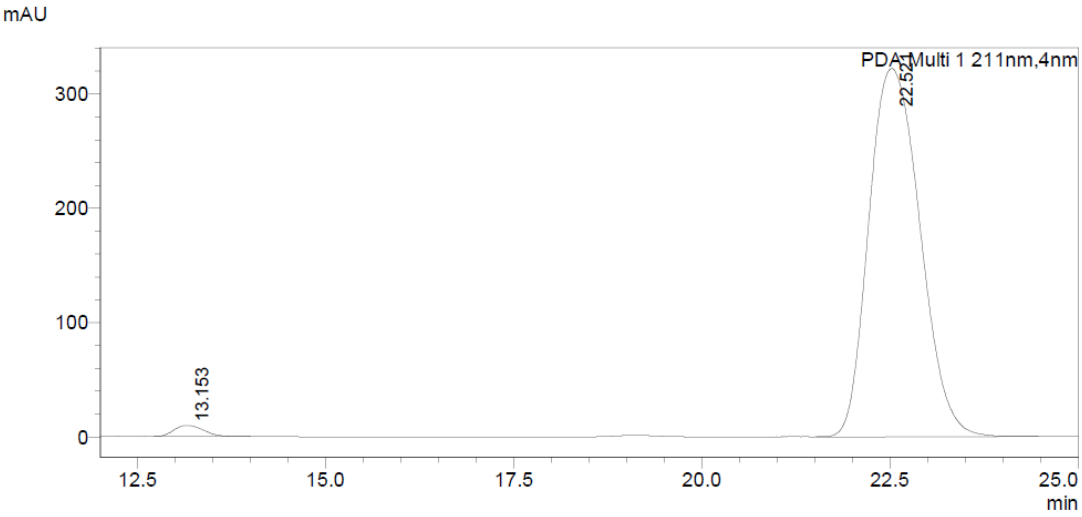
(36a)



<Peak Table>

PDA Ch1 211nm

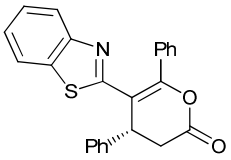
Peak#	Ret. Time	Area	Area%
1	13.143	3989307	50.198
2	22.548	3957761	49.802
Total		7947068	100.000



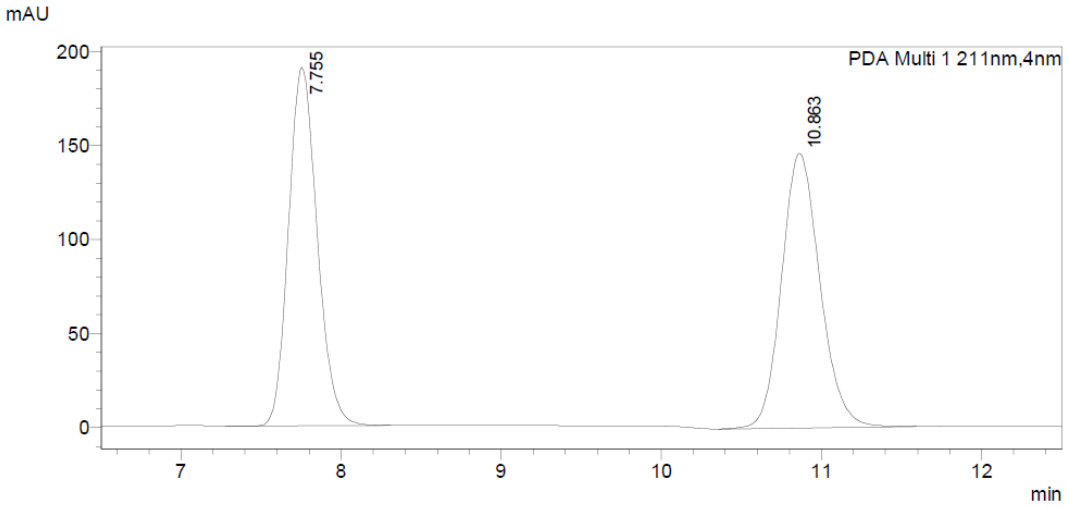
<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	13.153	267397	1.721
2	22.521	15266872	98.279
Total		15534269	100.000



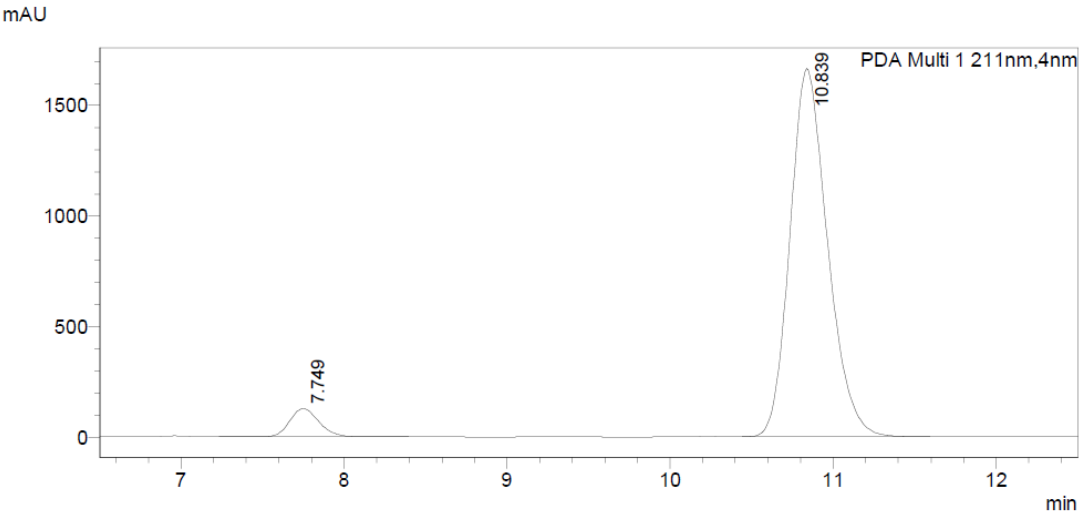
(36b)



<Peak Table>

PDA Ch1 211nm

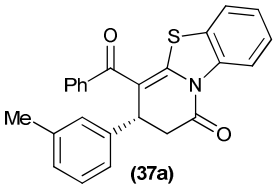
Peak#	Ret. Time	Area	Area%
1	7.755	2374617	49.400
2	10.863	2432318	50.600
Total		4806935	100.000



<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	7.749	1613932	5.704
2	10.839	26682109	94.296
Total		28296041	100.000



(37a)

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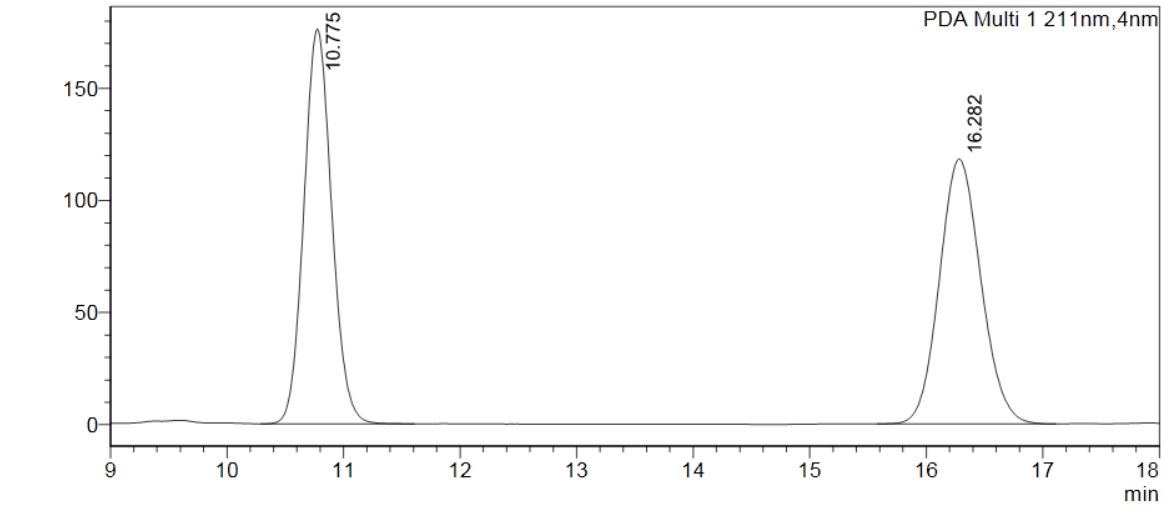
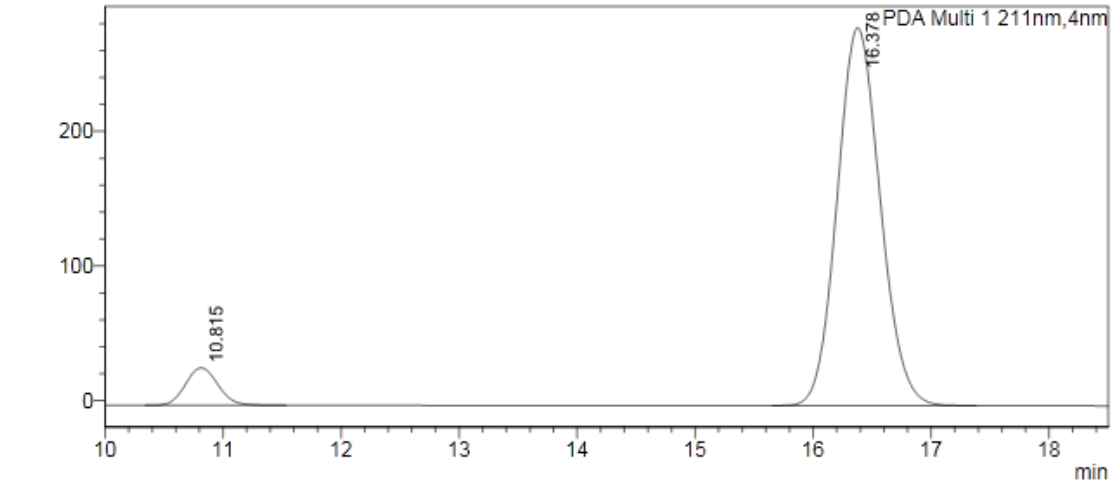


<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	10.775	2926645	50.049
2	16.282	2920933	49.951
Total		5847577	100.000

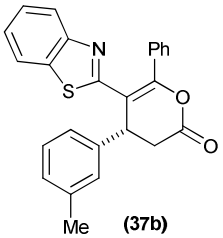
<Chromatogram>



<Peak Table>

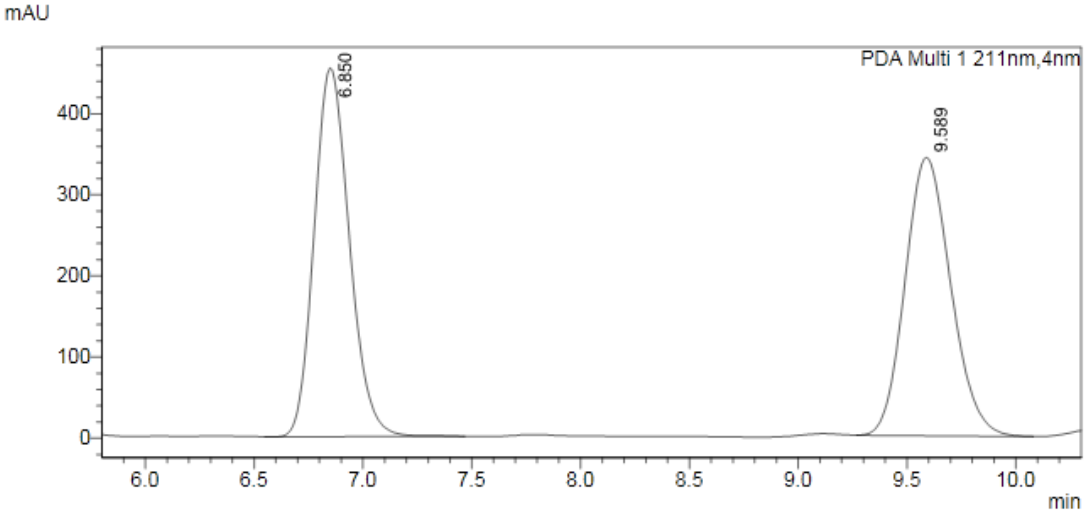
PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	10.815	534482	6.986
2	16.378	7116238	93.014
Total		7650720	100.000



(37b)

<Chromatogram>

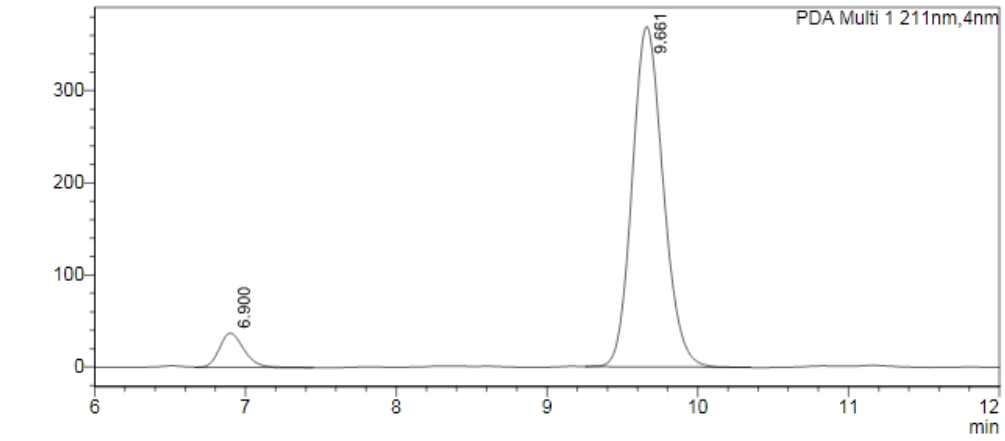


<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	6.850	5125088	50.540
2	9.589	5015508	49.460
Total		10140596	100.000

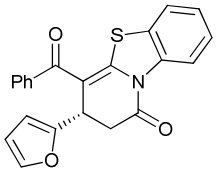
<Chromatogram>



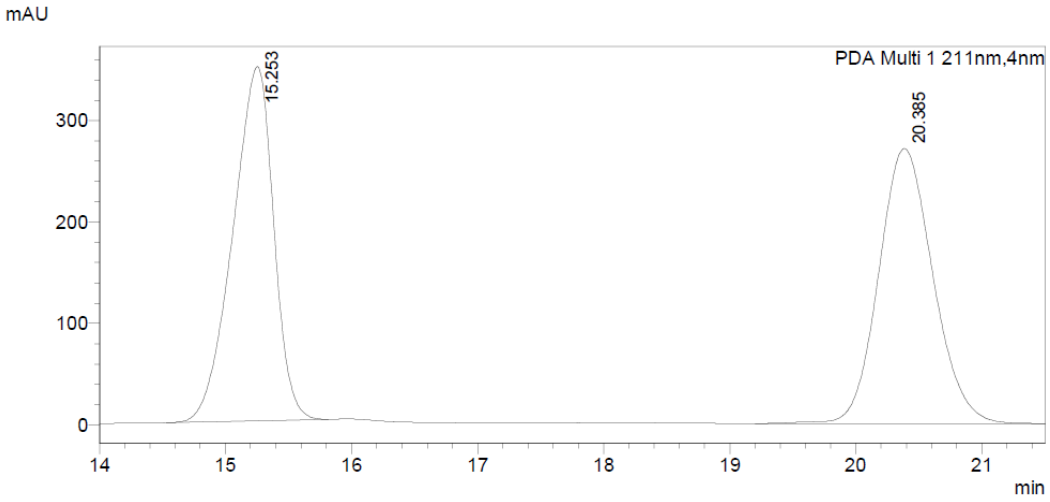
<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	6.900	415181	7.284
2	9.661	5284705	92.716
Total		5699885	100.000



(38a)

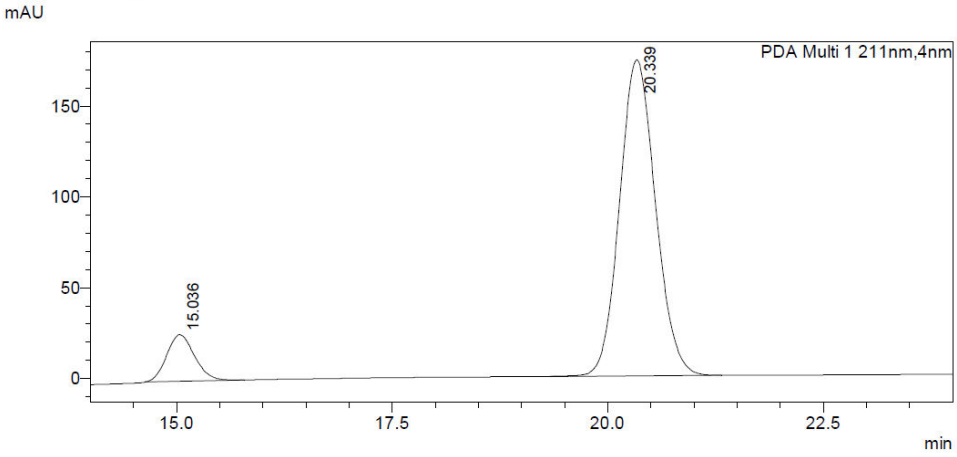


<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	15.253	7874774	49.261
2	20.385	8110945	50.739
Total		15985719	100.000

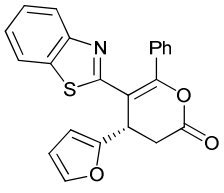
<Chromatogram>



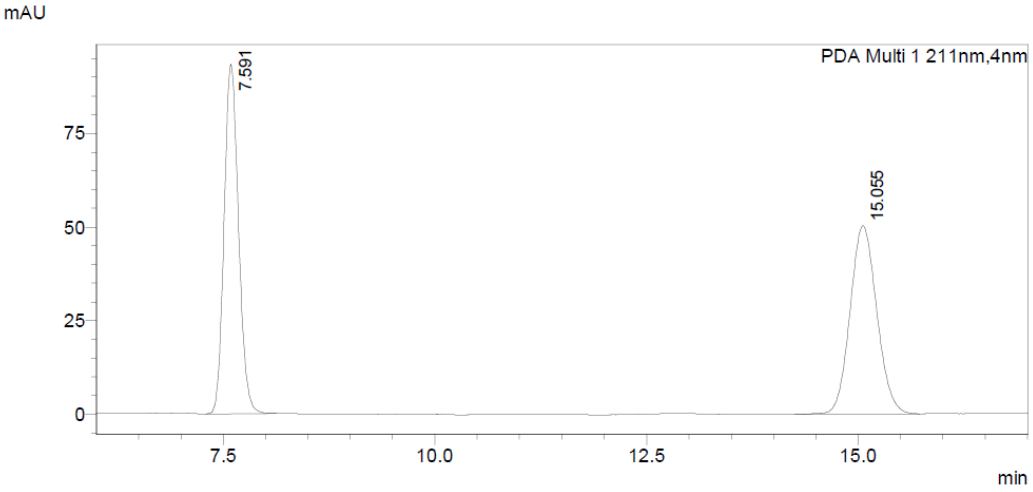
<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	15.036	580528	10.282
2	20.339	5065469	89.718
Total		5645997	100.000



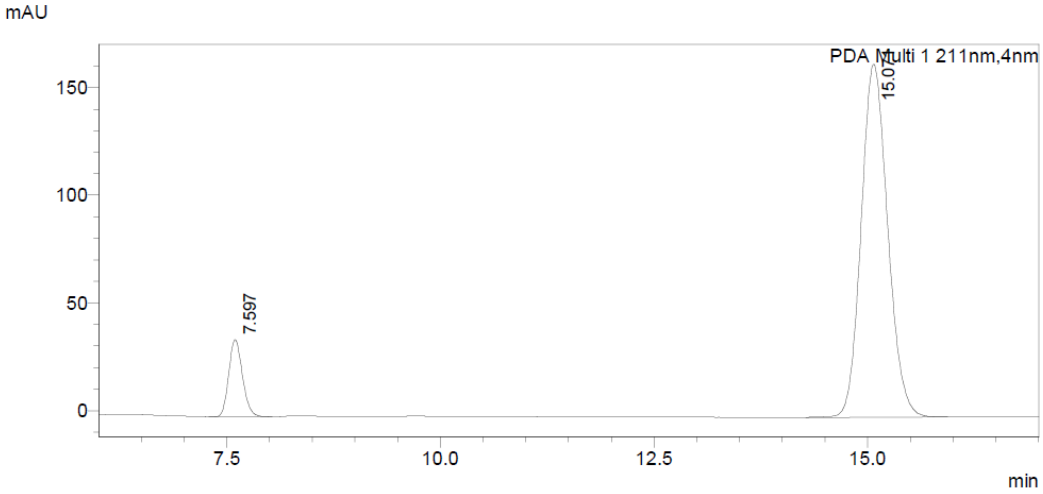
(38b)



<Peak Table>

PDA Ch1 211nm

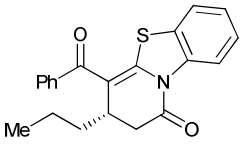
Peak#	Ret. Time	Area	Area%
1	7.591	1106875	49.955
2	15.055	1108864	50.045
Total		2215738	100.000



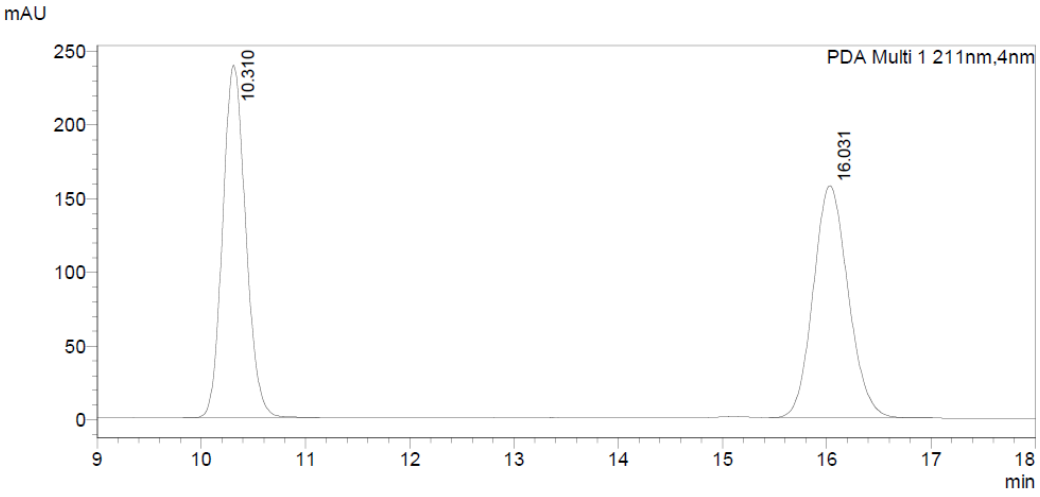
<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	7.597	401752	10.190
2	15.071	3540907	89.810
Total		3942659	100.000



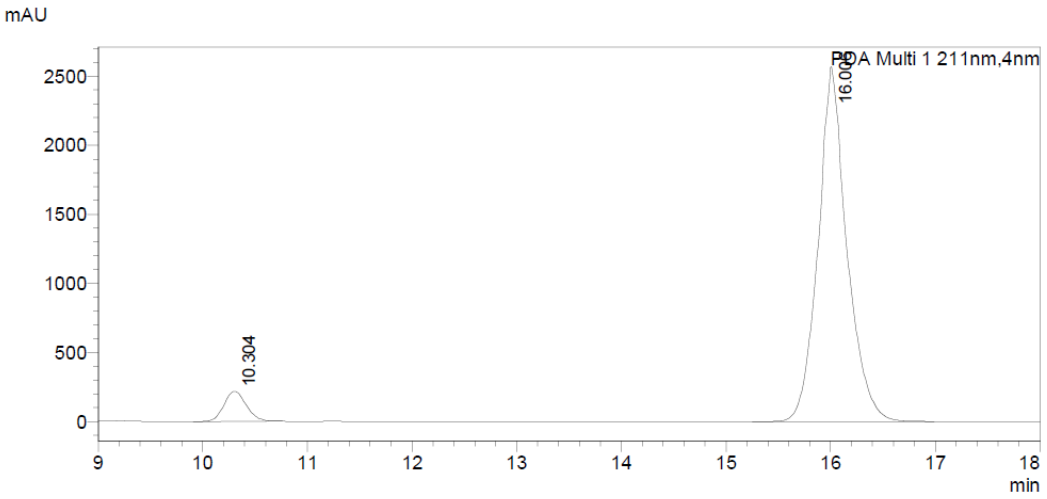
(39a)



<Peak Table>

PDA Ch1 211nm

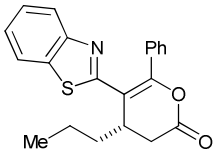
Peak#	Ret. Time	Area	Area%
1	10.310	3683426	50.046
2	16.031	3676616	49.954
Total		7360042	100.000



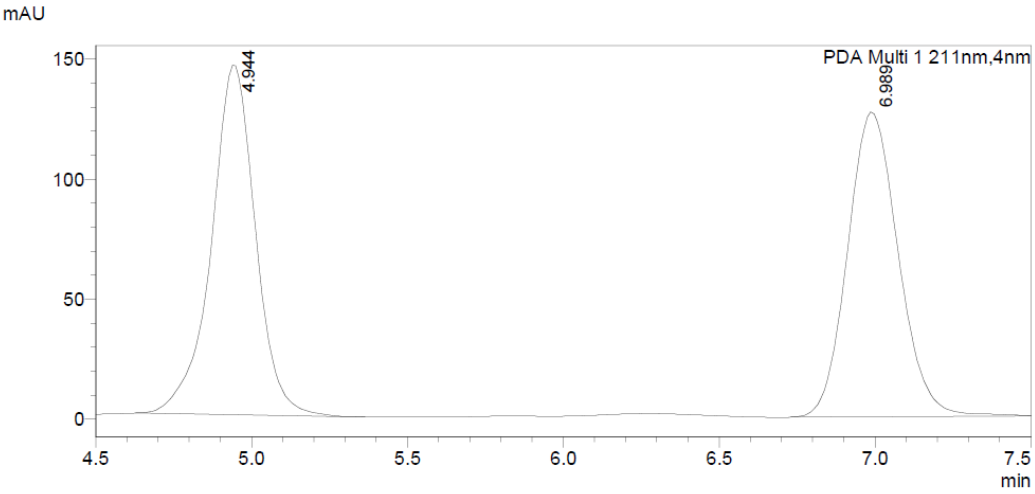
<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	10.304	3230901	6.210
2	16.006	48794070	93.790
Total		52024971	100.000



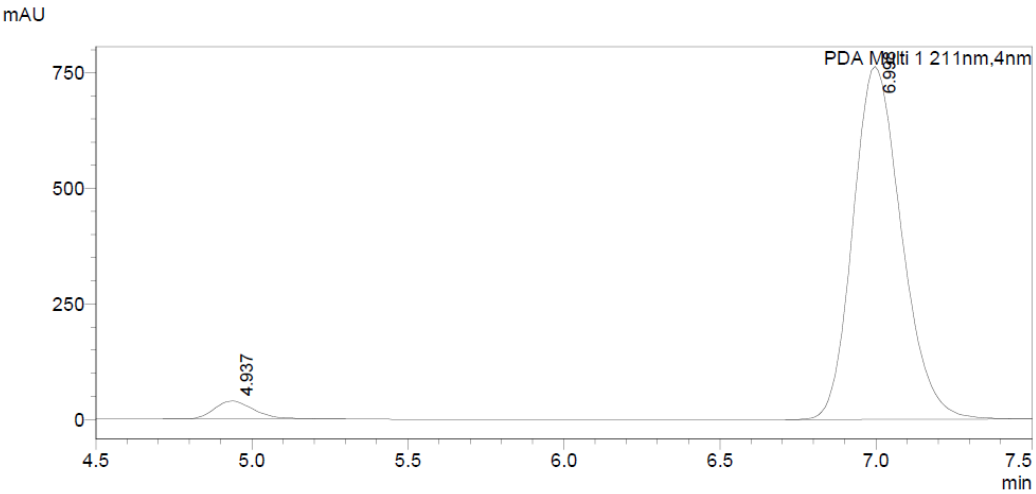
(39b)



<Peak Table>

PDA Ch1 211nm

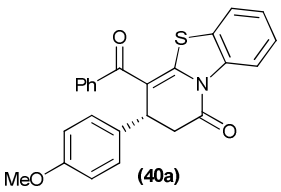
Peak#	Ret. Time	Area	Area%
1	4.944	1434346	49.942
2	6.989	1437690	50.058
Total		2872036	100.000



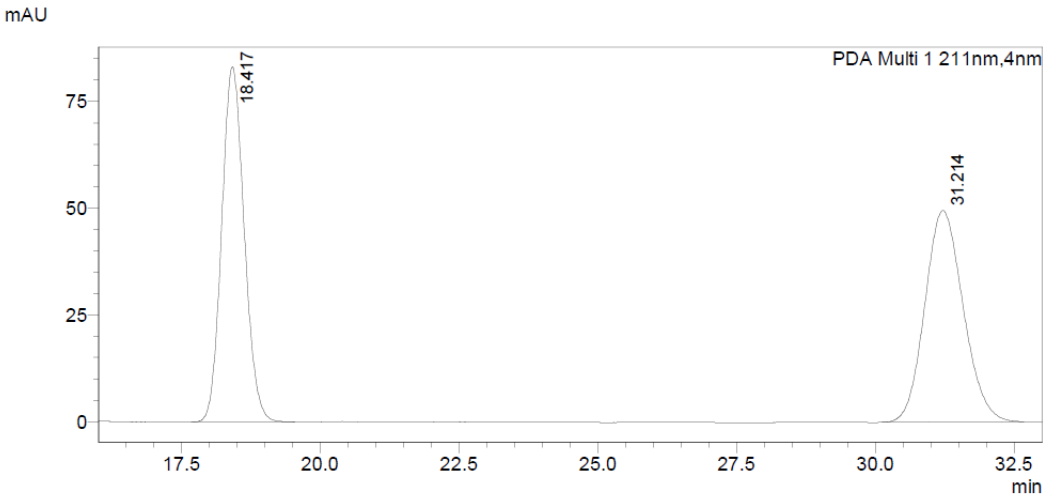
<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	4.937	355011	4.121
2	6.998	8260034	95.879
Total		8615045	100.000



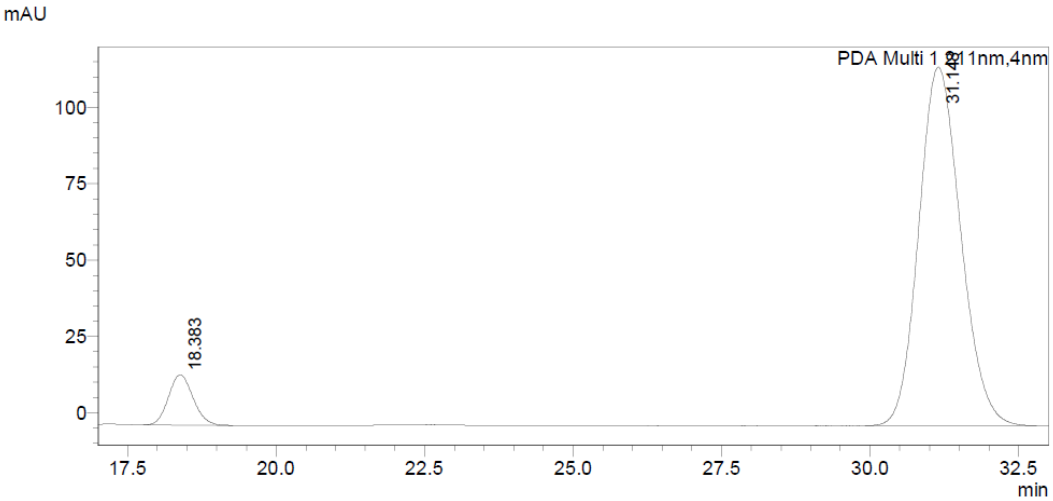
(40a)



<Peak Table>

PDA Ch1 211nm

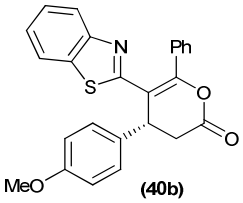
Peak#	Ret. Time	Area	Area%
1	18.417	2348456	49.550
2	31.214	2385992	50.342
3	33.808	5114	0.108
Total		4739562	100.000



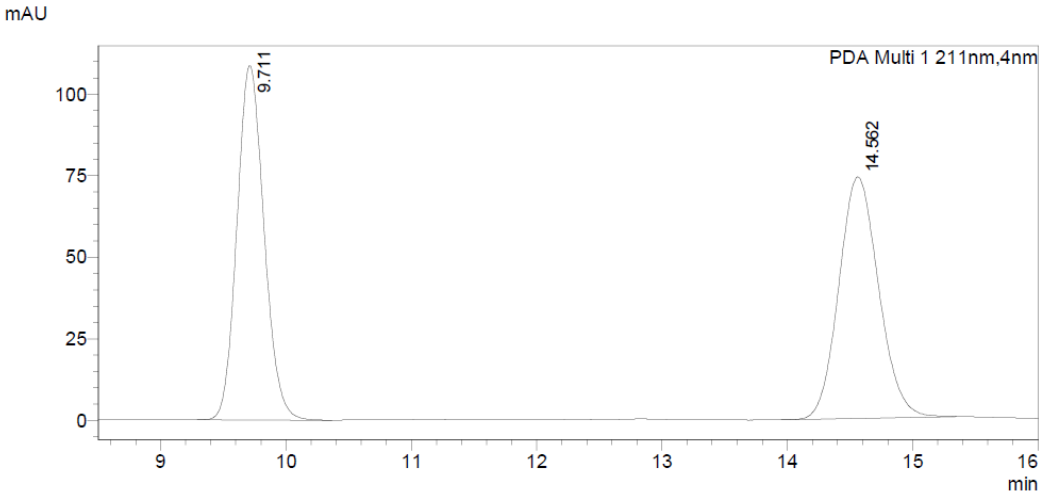
<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	18.383	473352	7.589
2	31.148	5763671	92.411
Total		6237023	100.000



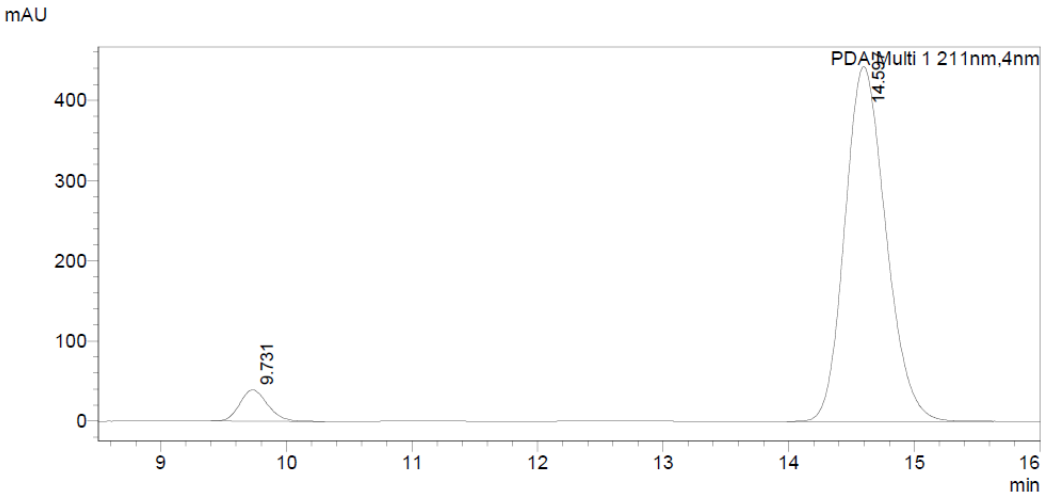
(40b)



<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area	Area%
1	9.711	1636034	49.971
2	14.562	1637944	50.029
Total		3273978	100.000

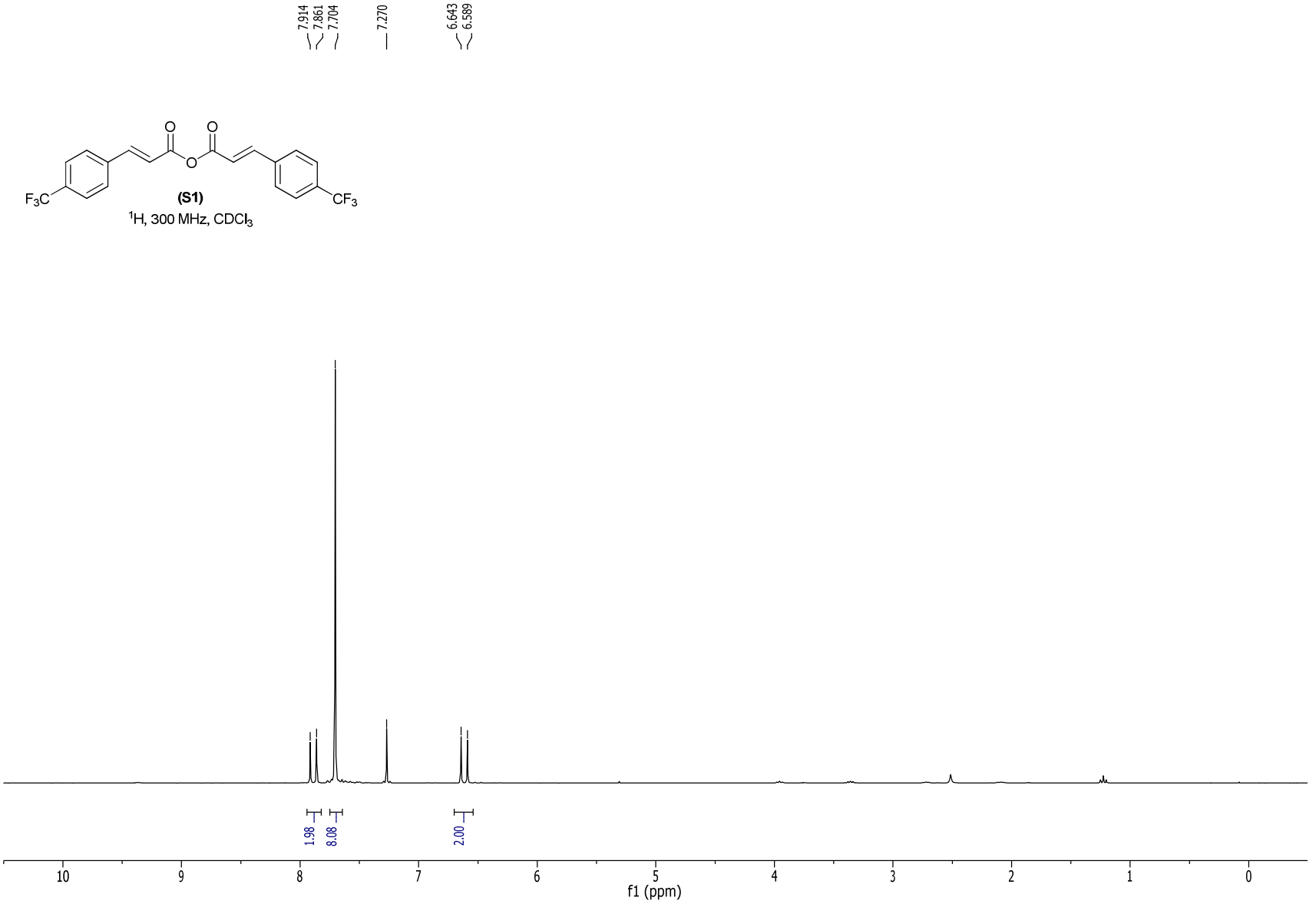


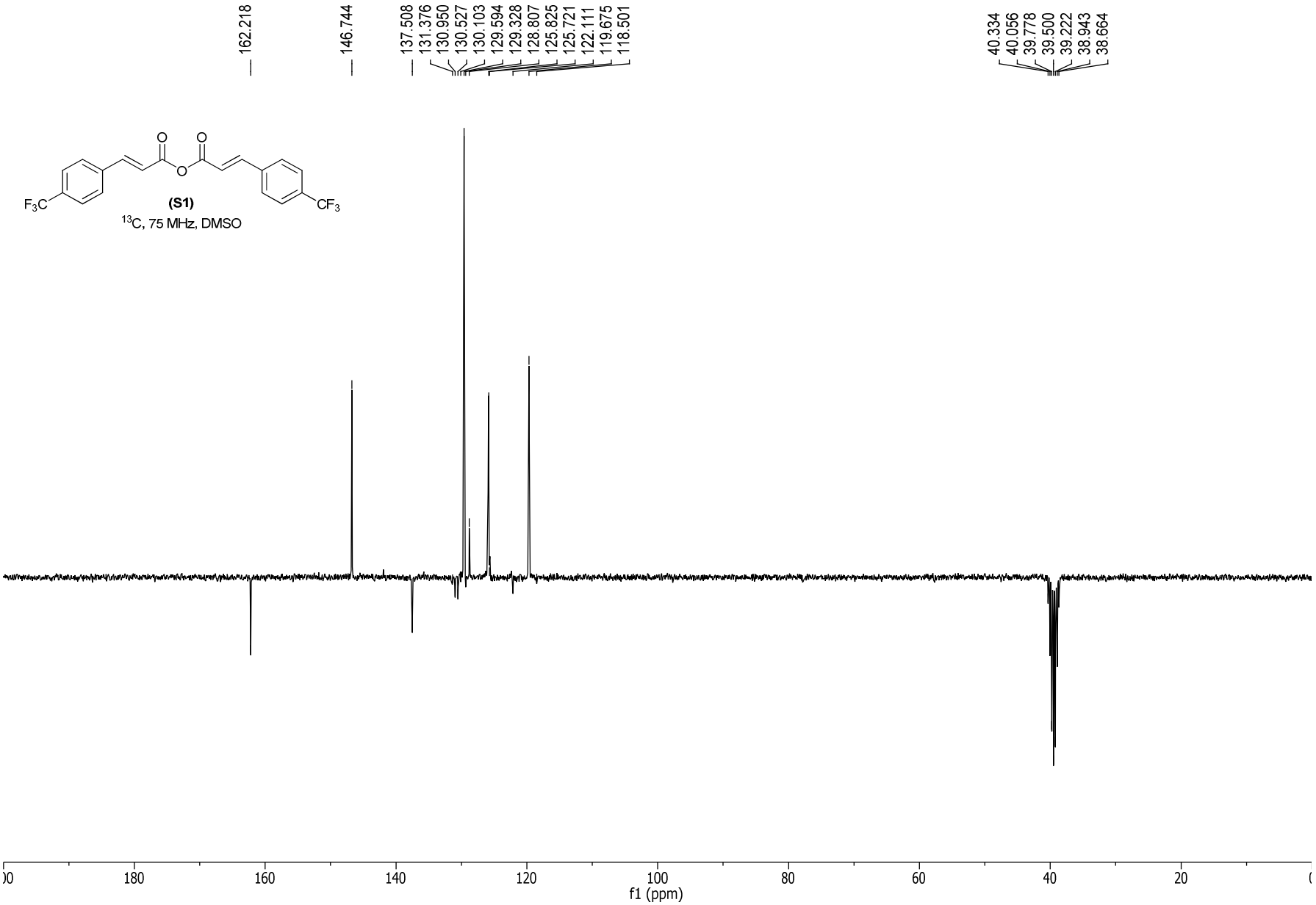
<Peak Table>

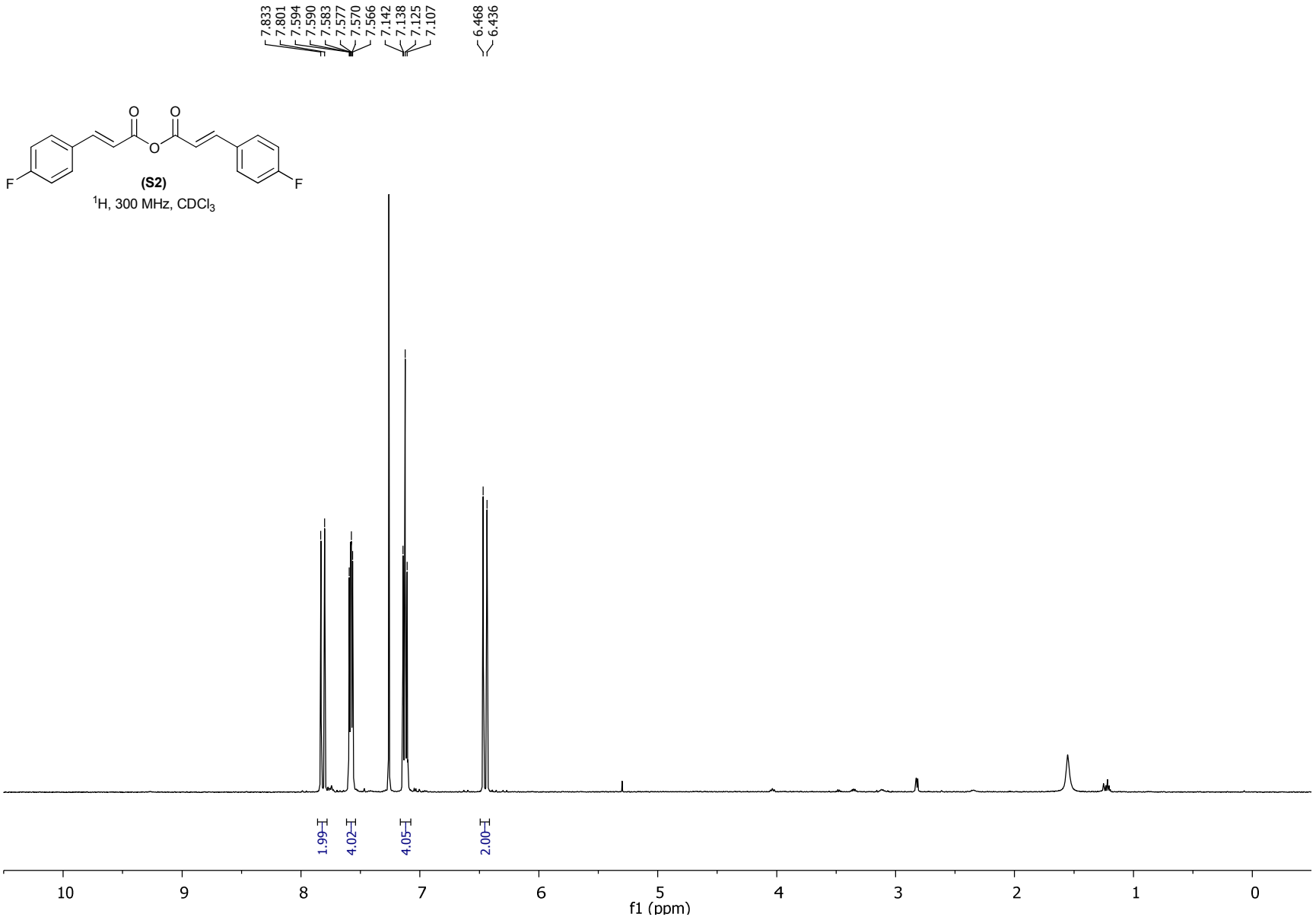
PDA Ch1 211nm

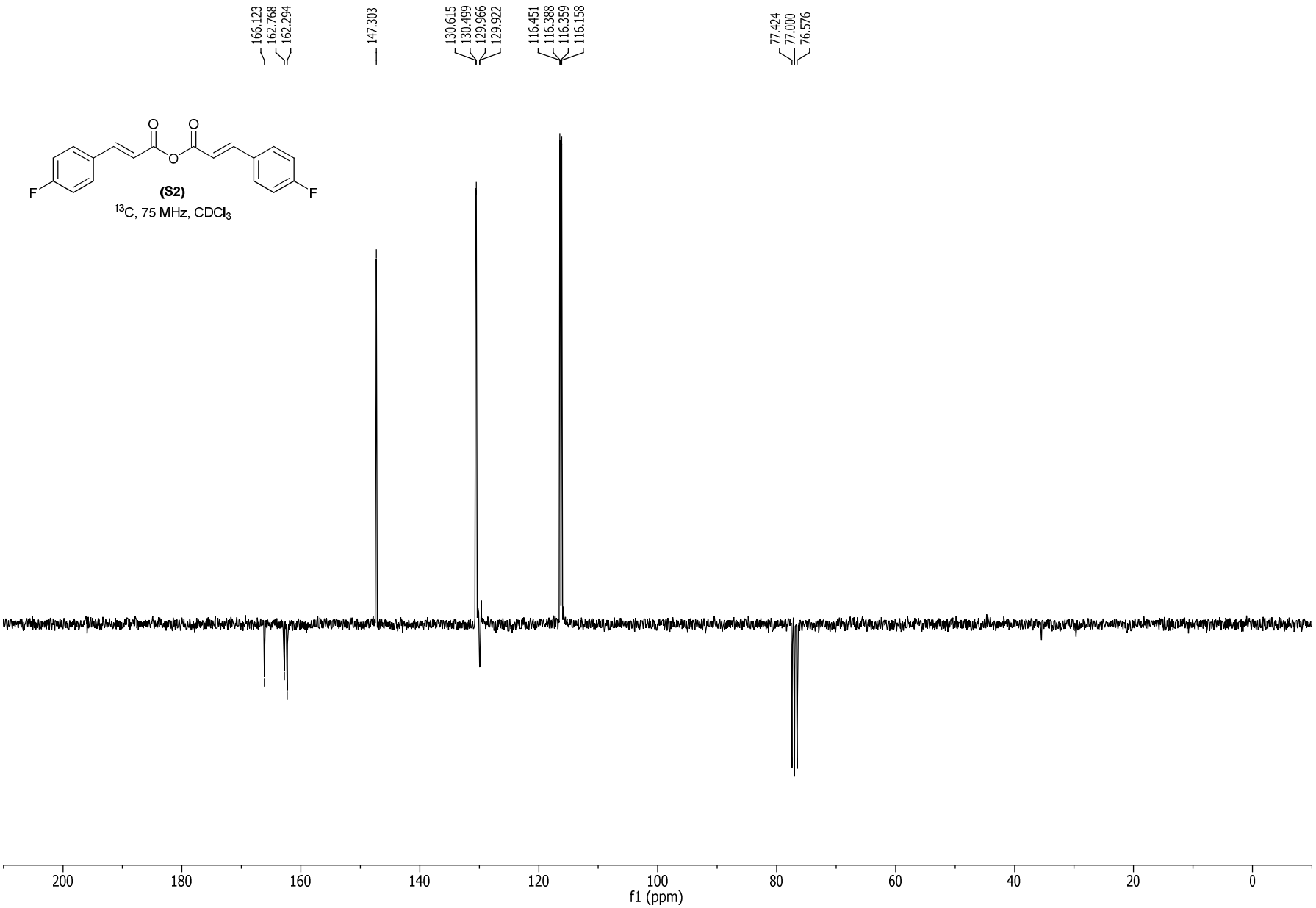
Peak#	Ret. Time	Area	Area%
1	9.731	604793	5.677
2	14.597	10047698	94.323
Total		10652491	100.000

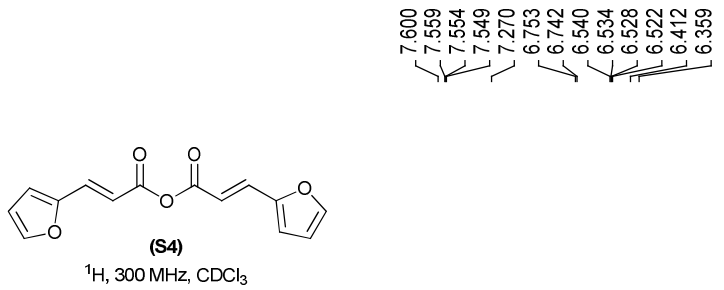
NMR Spectra

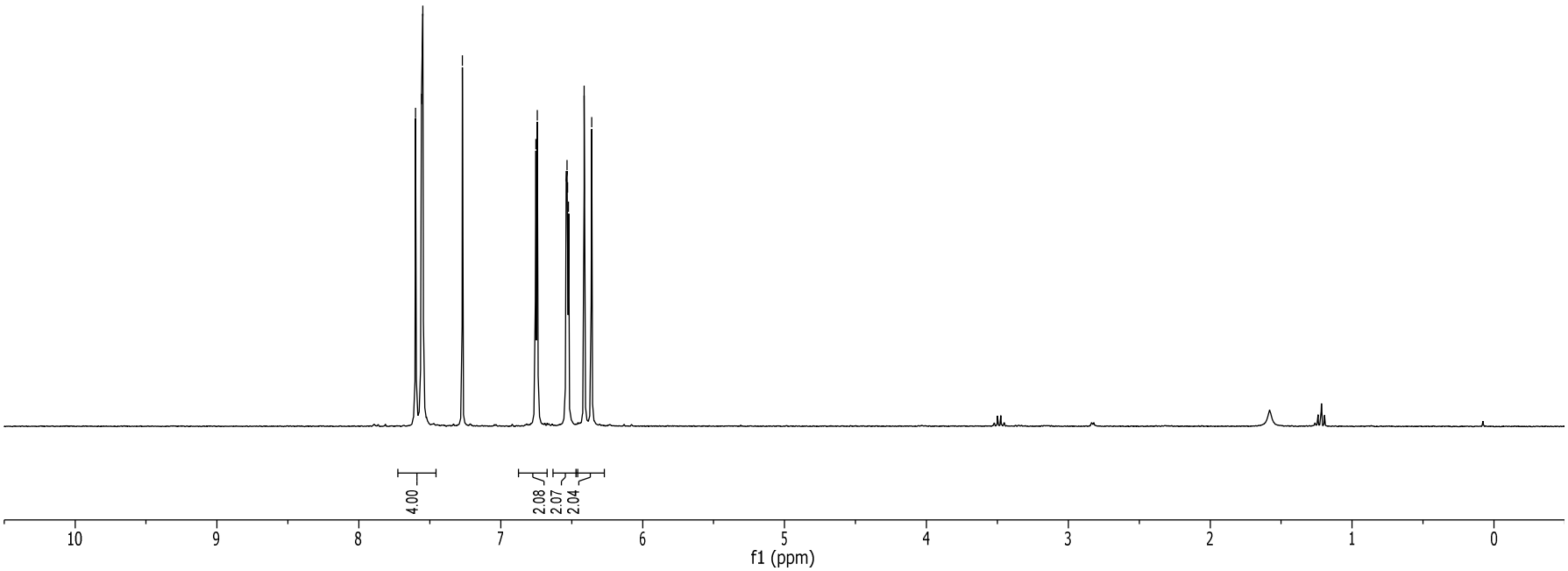


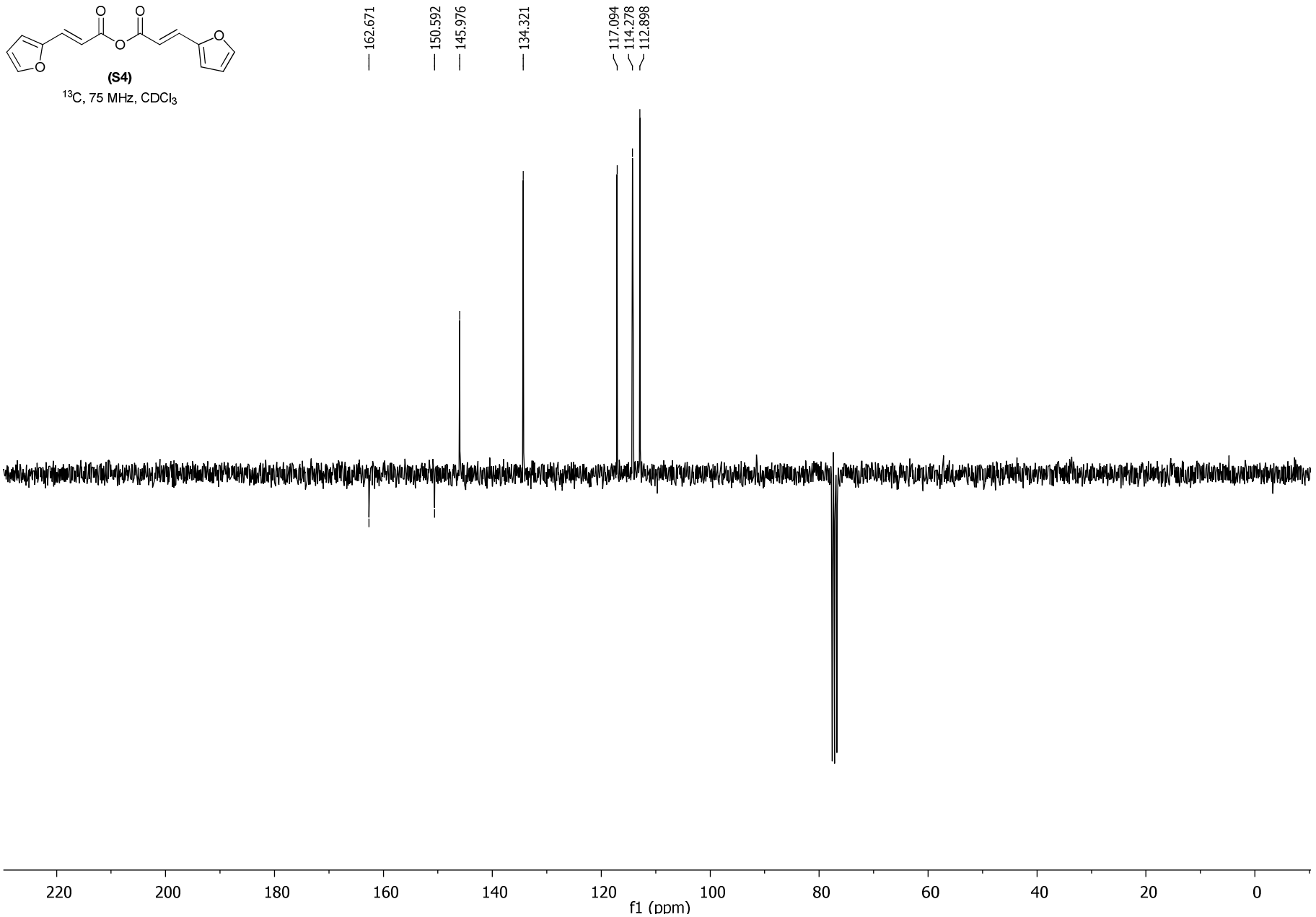


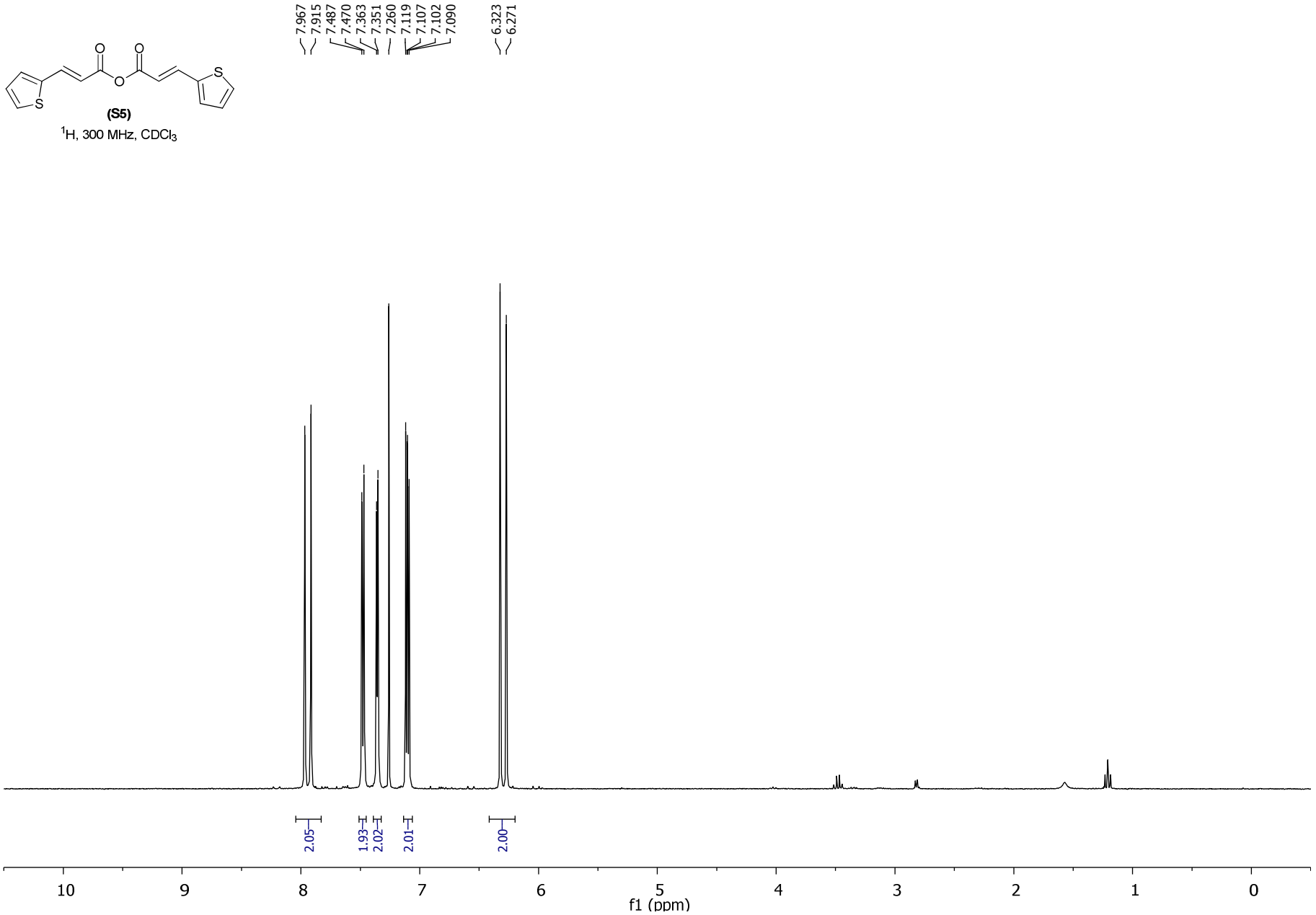


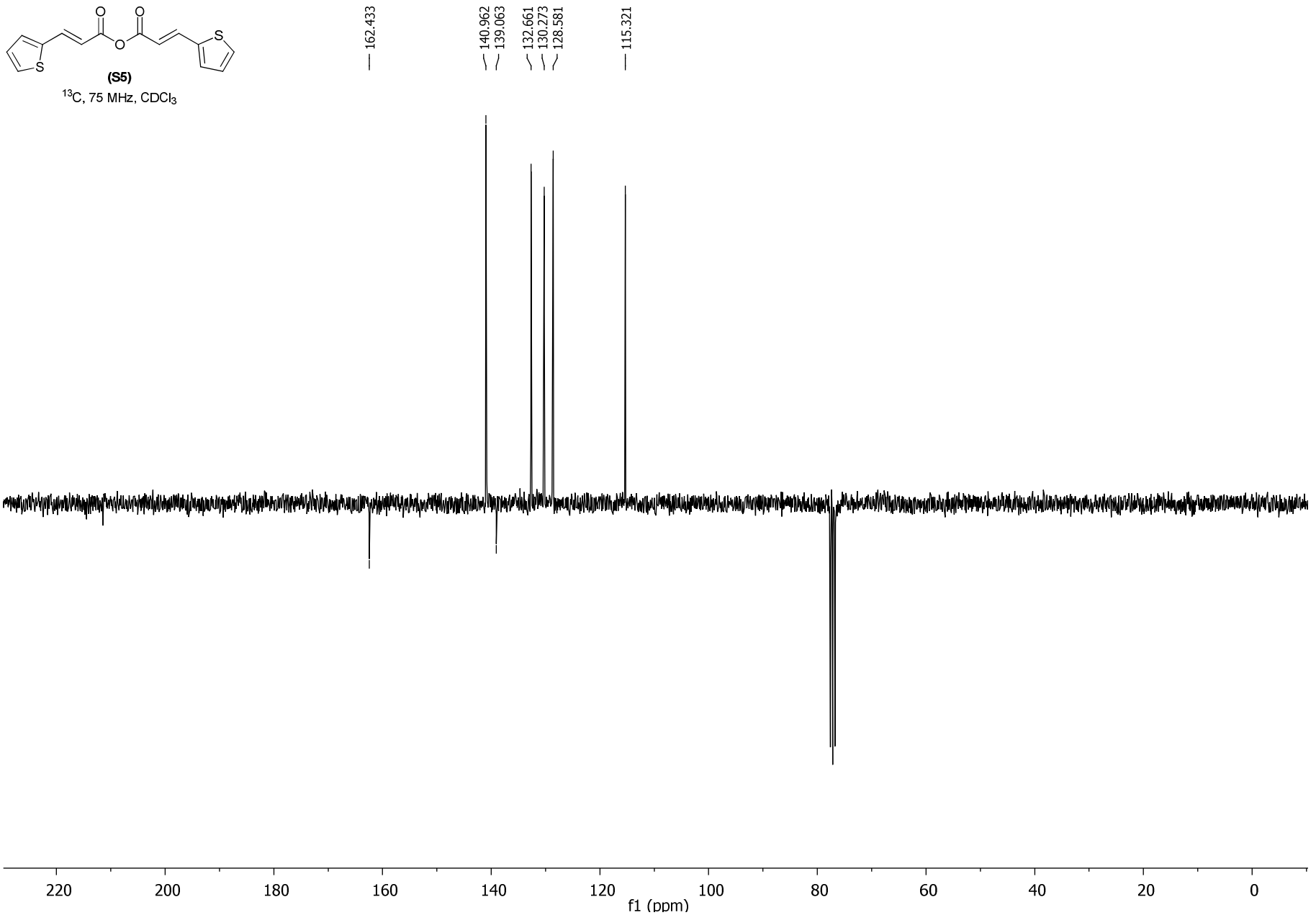


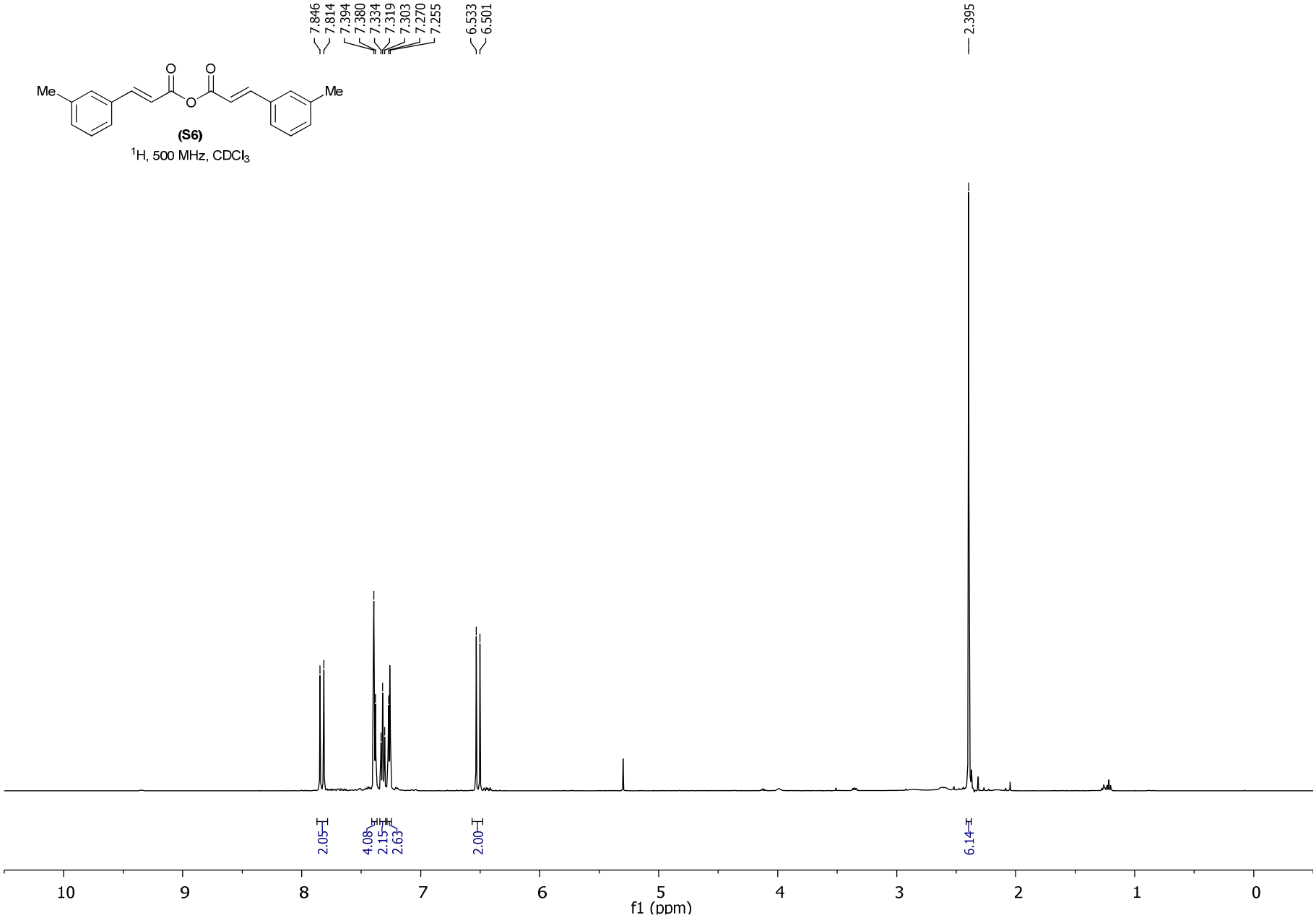


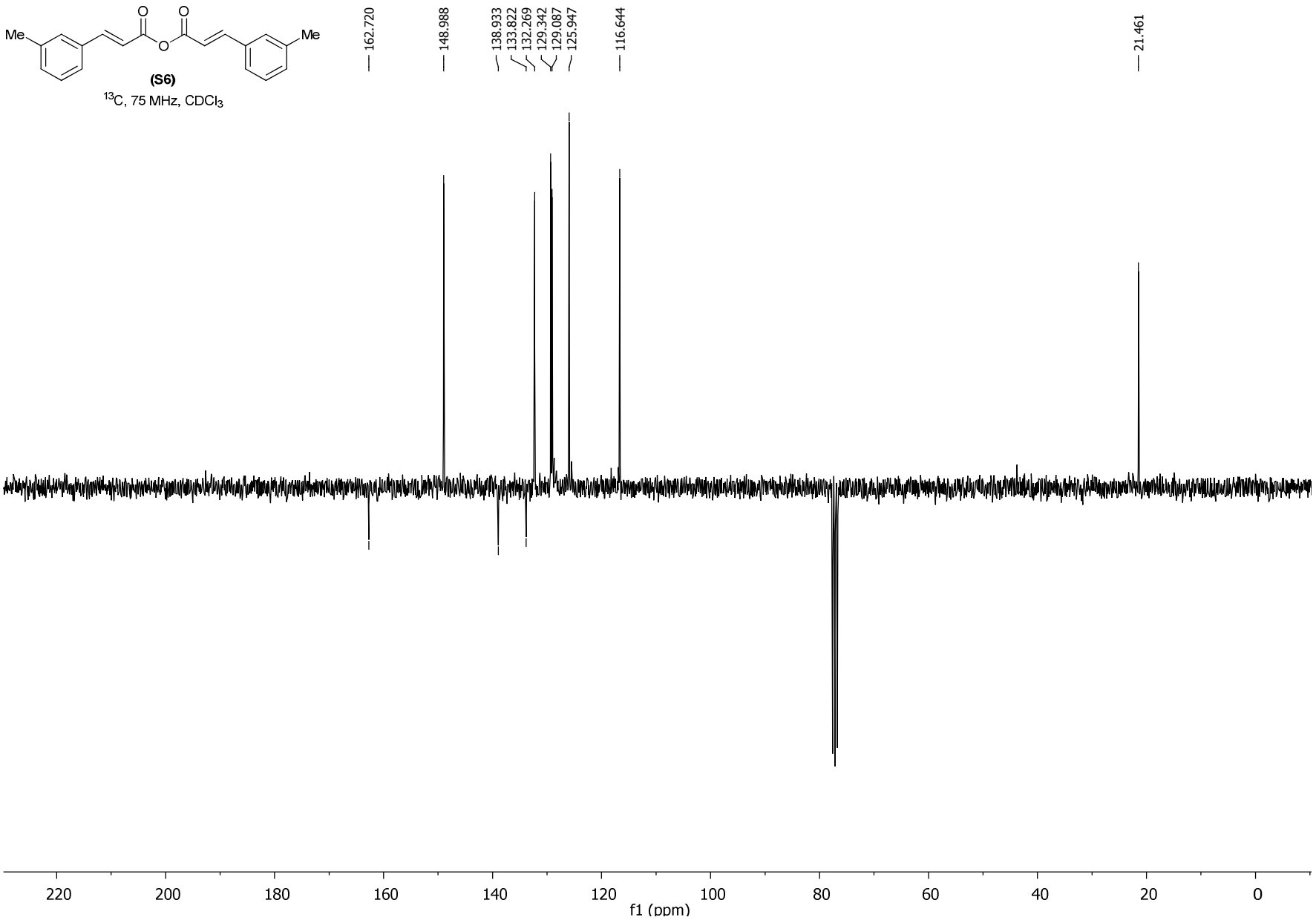


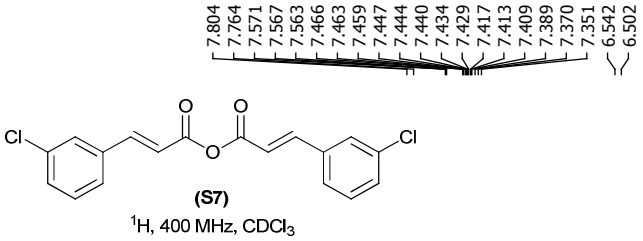






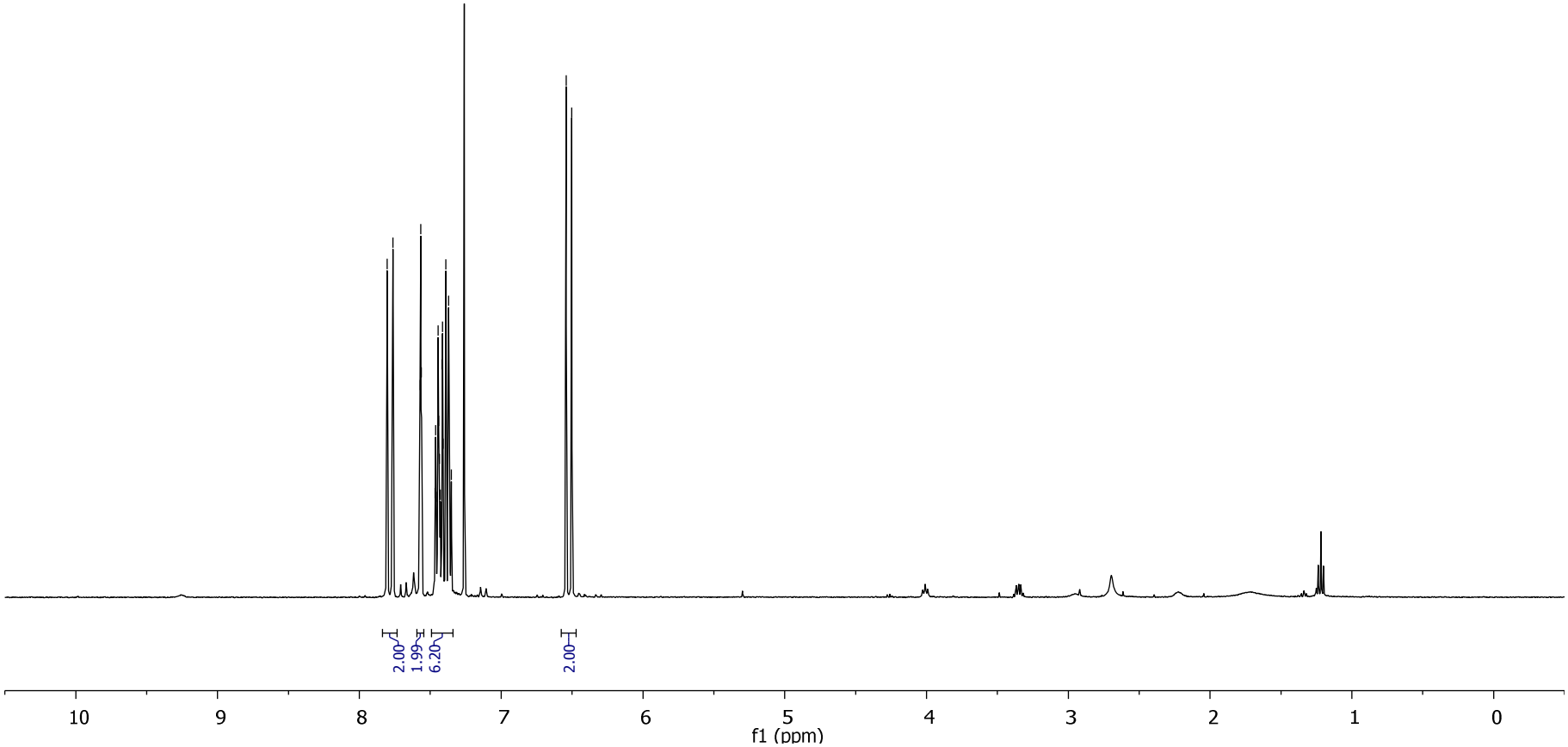


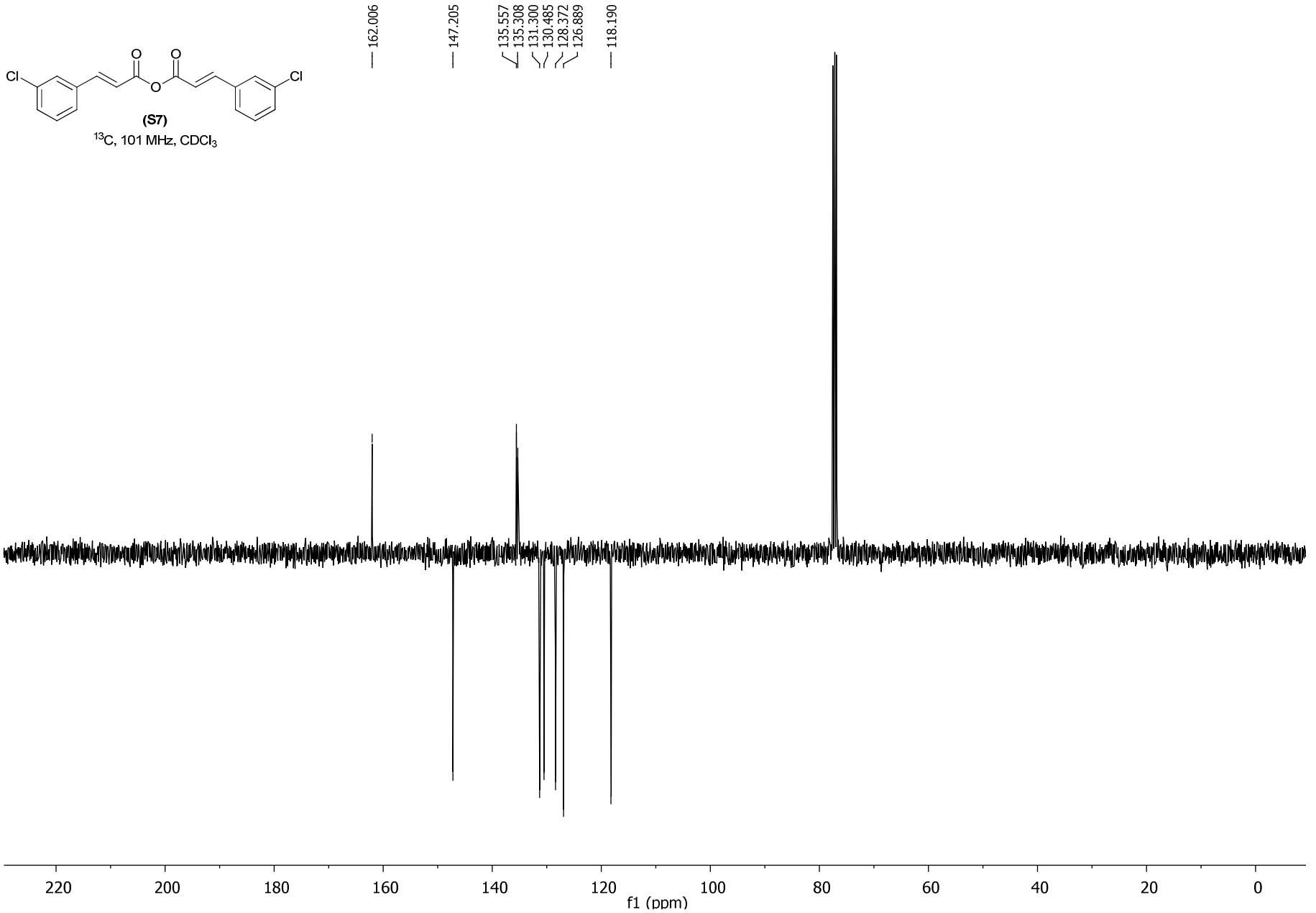


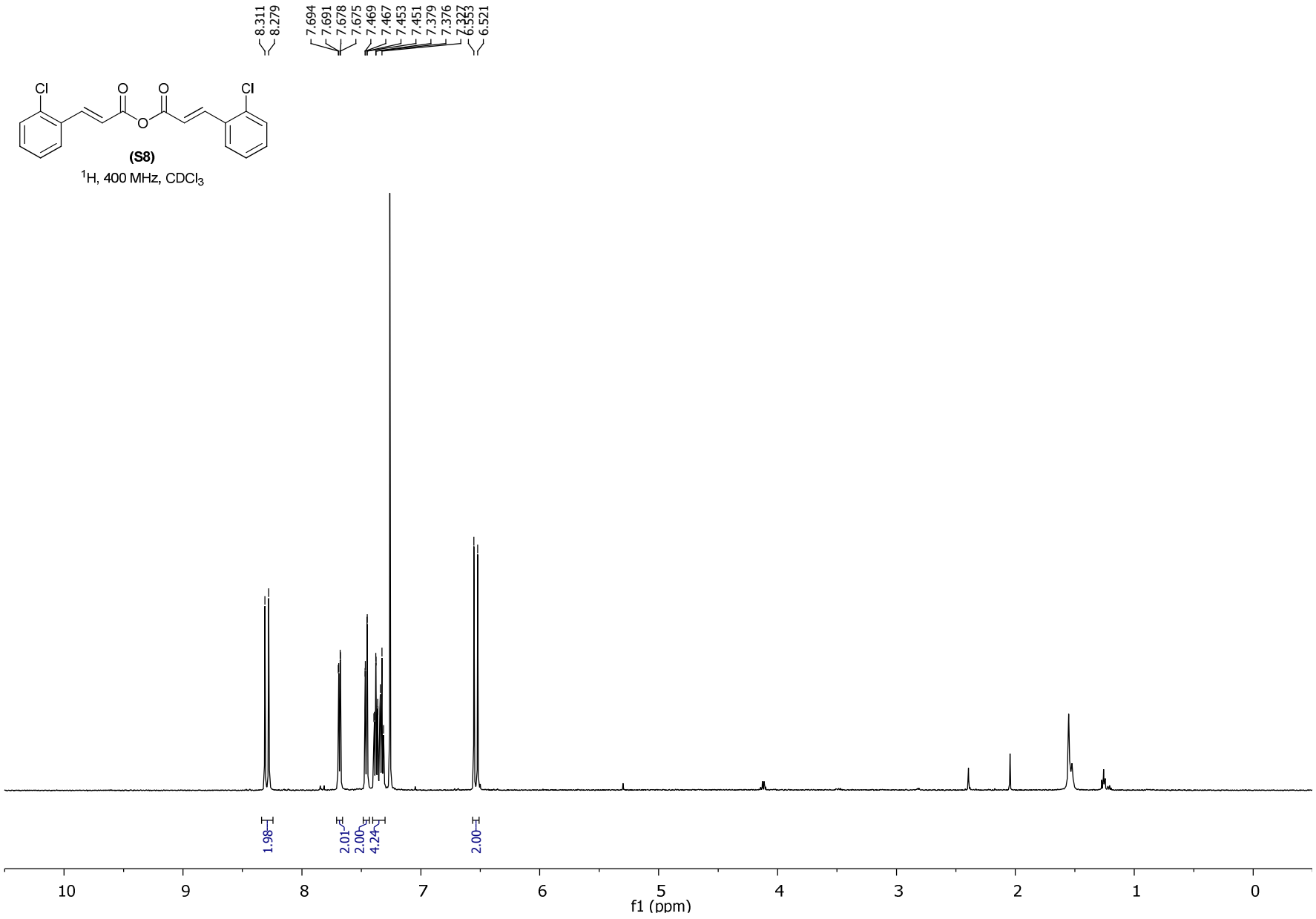


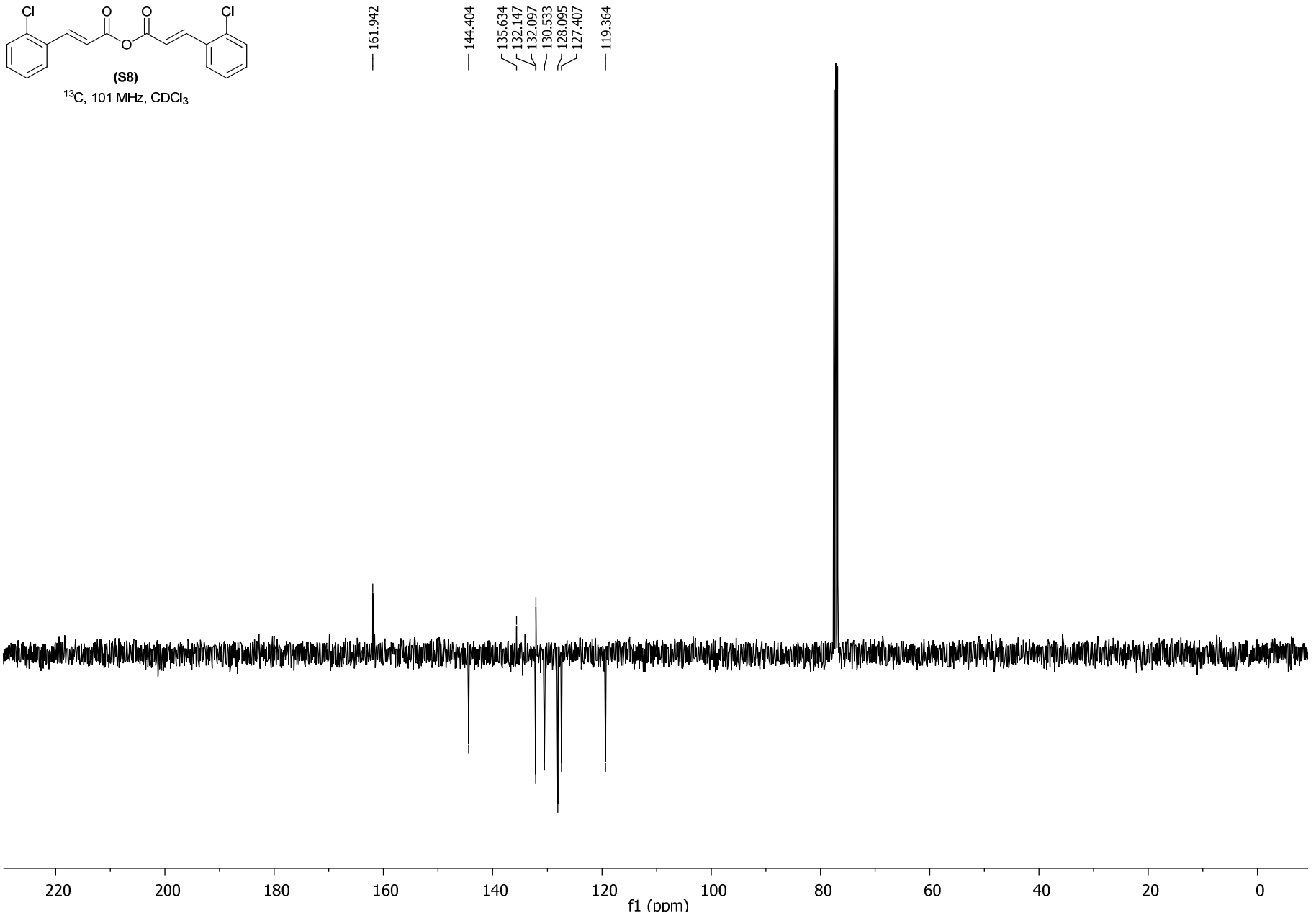
(S7)

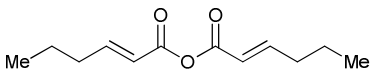
^{1}H, 400 MHz, $CDCl_3$





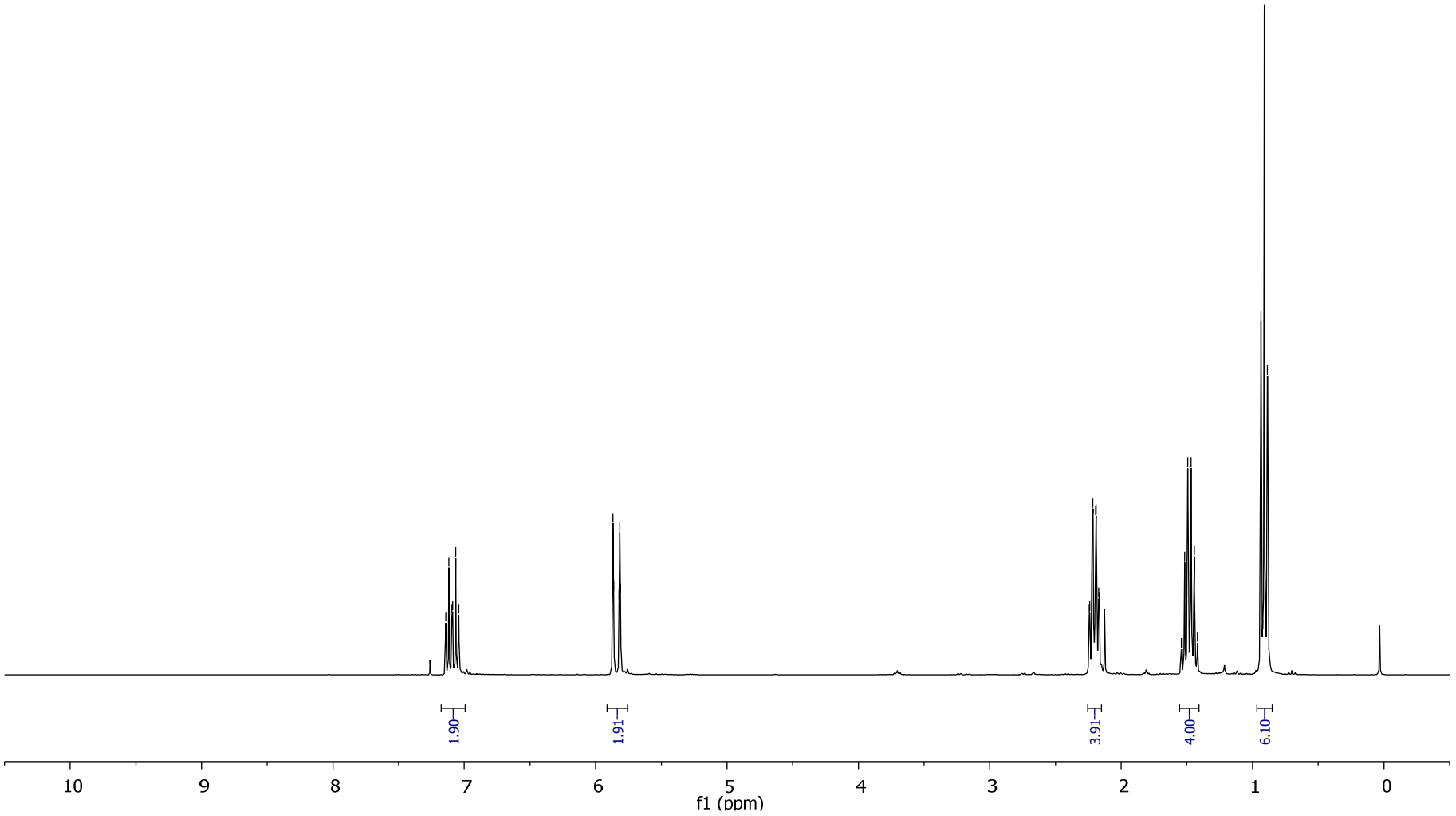


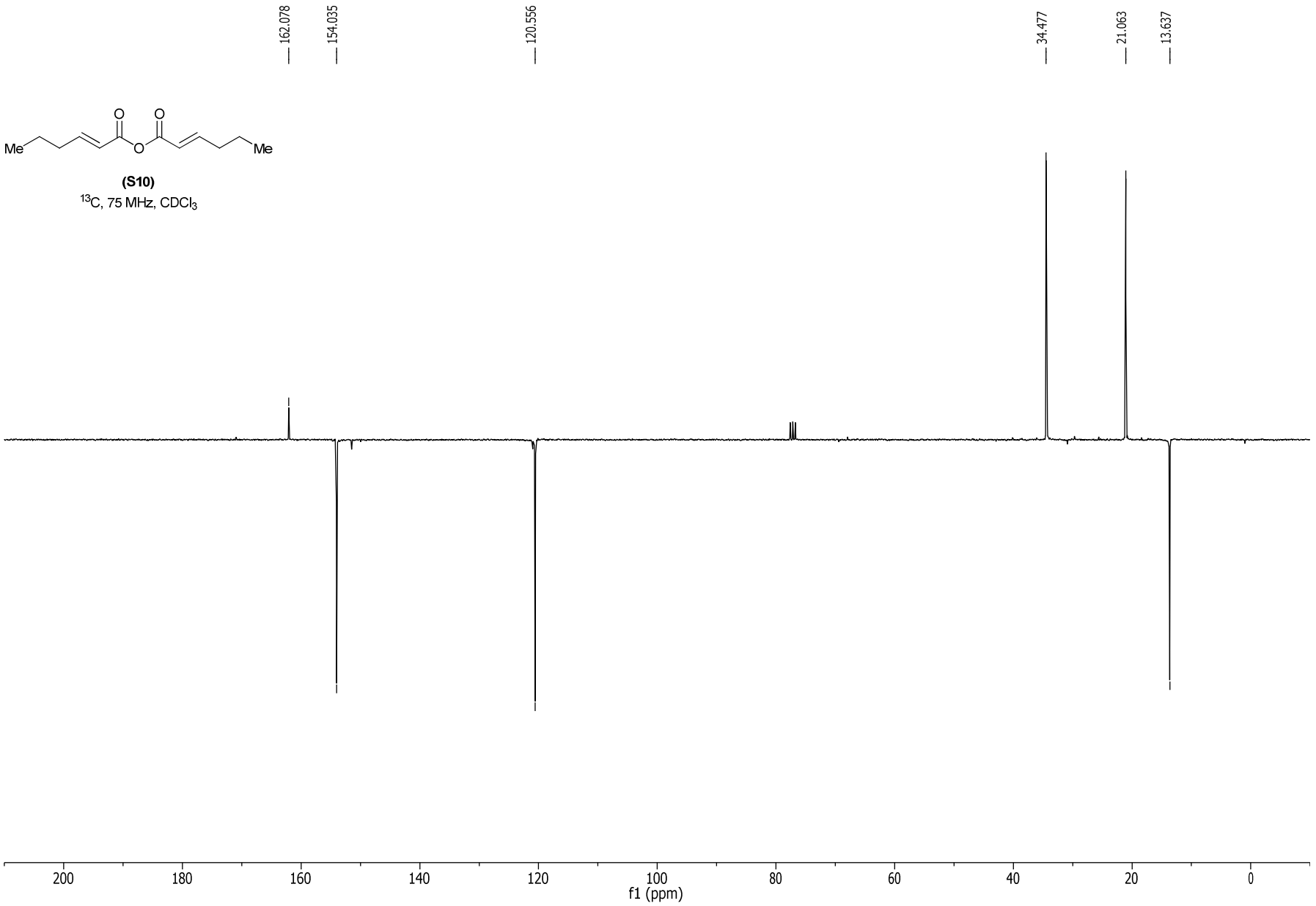




(S10)

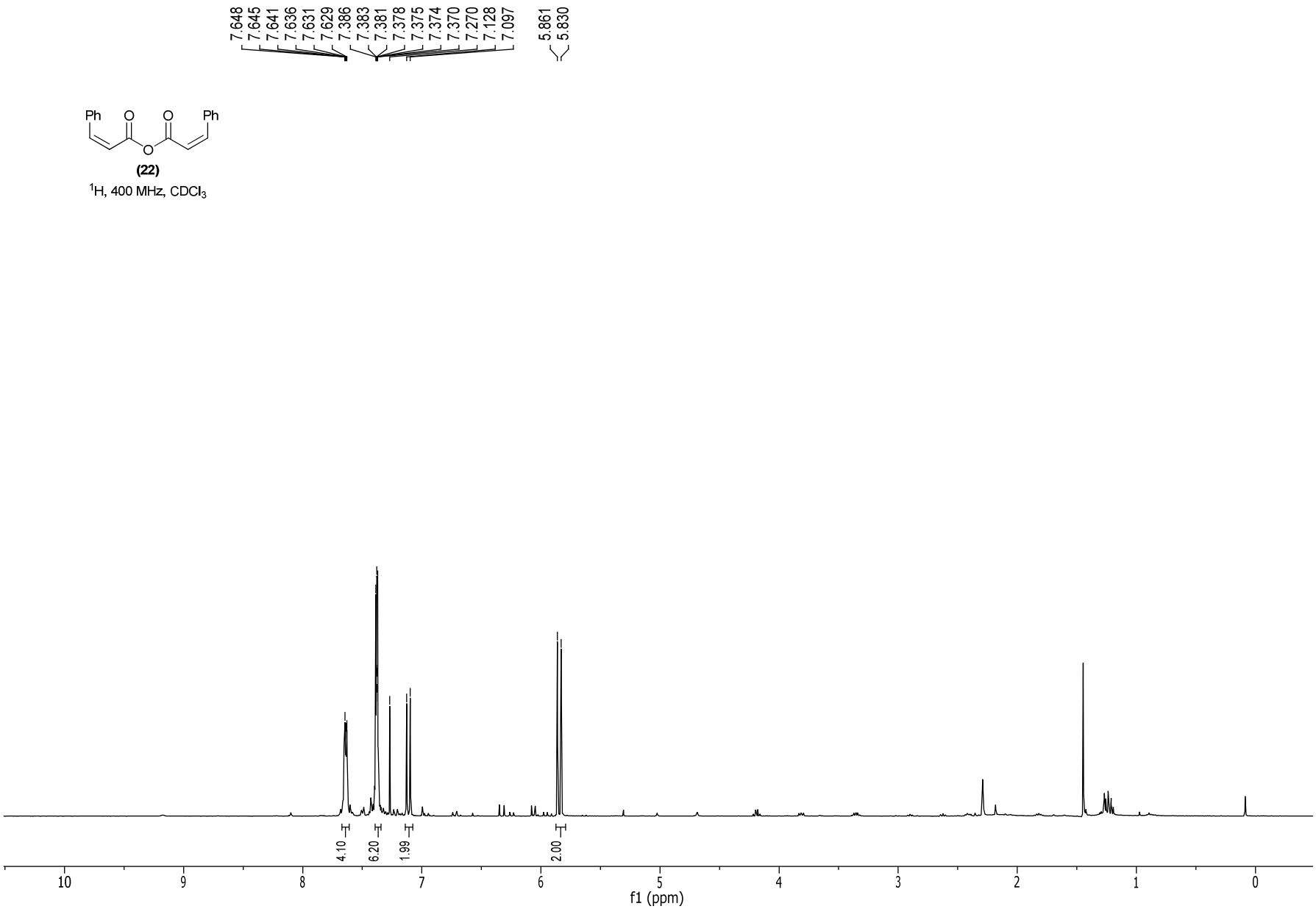
^{1}H, 300 MHz, $CDCl_3$

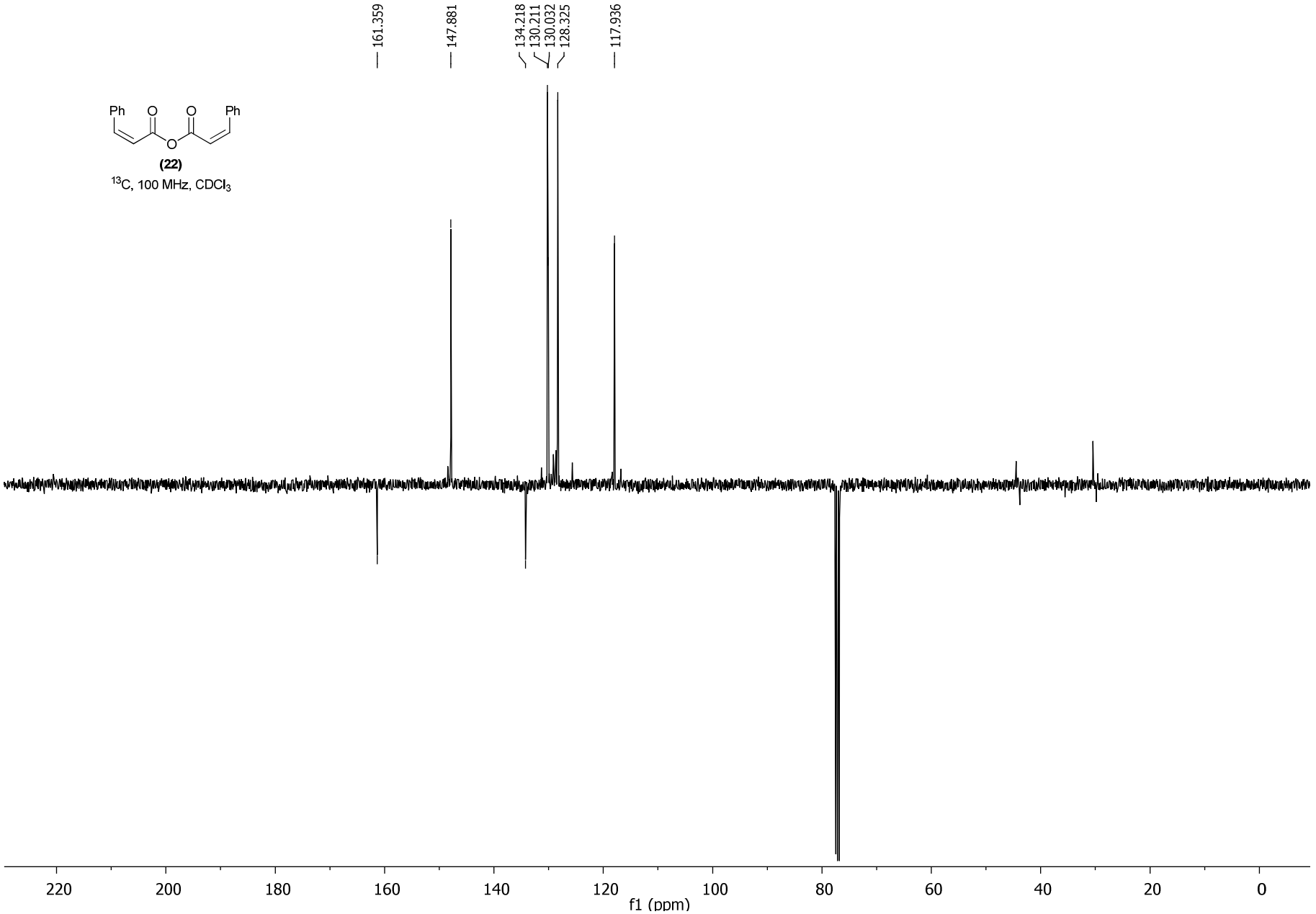


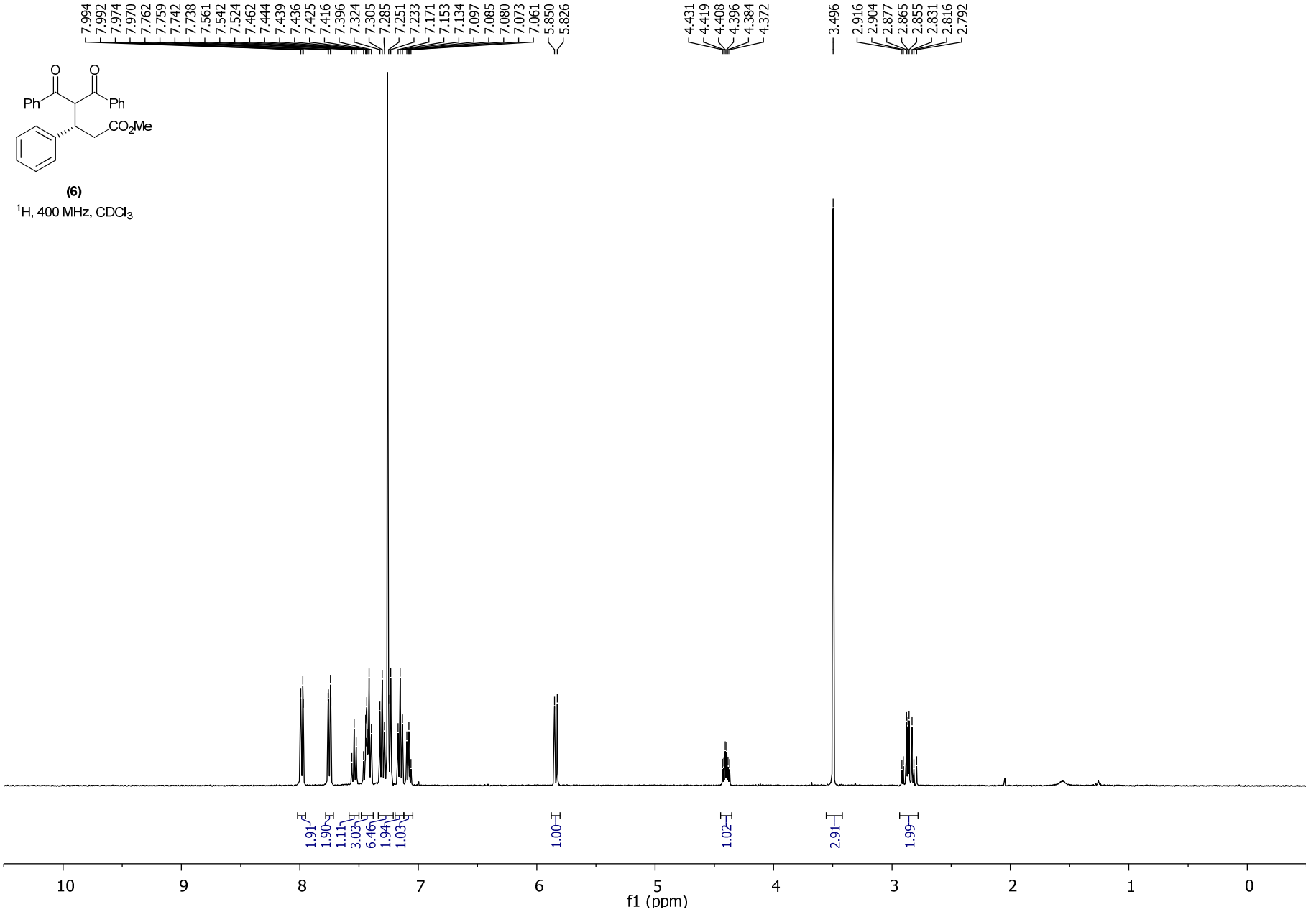


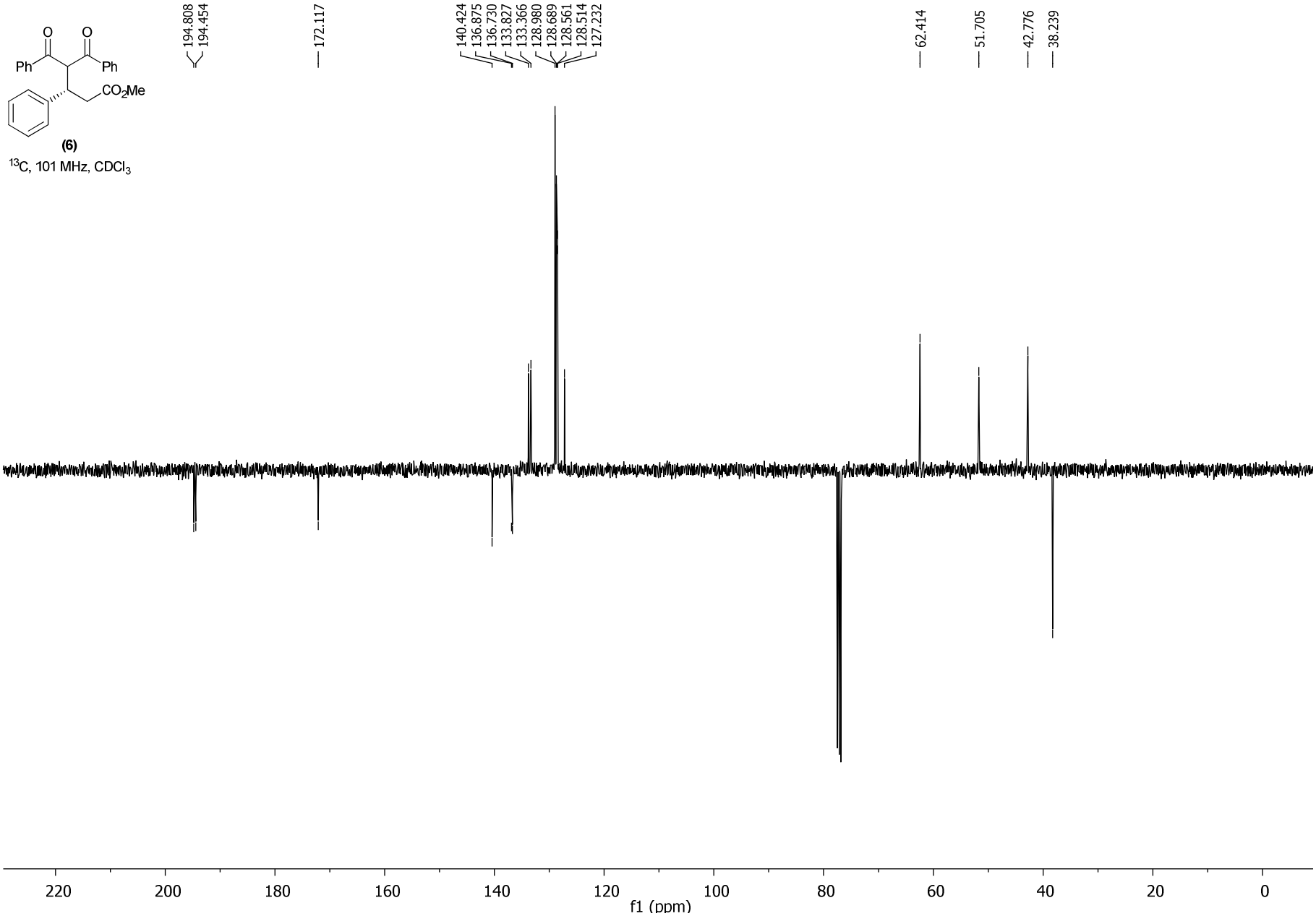
(S10)

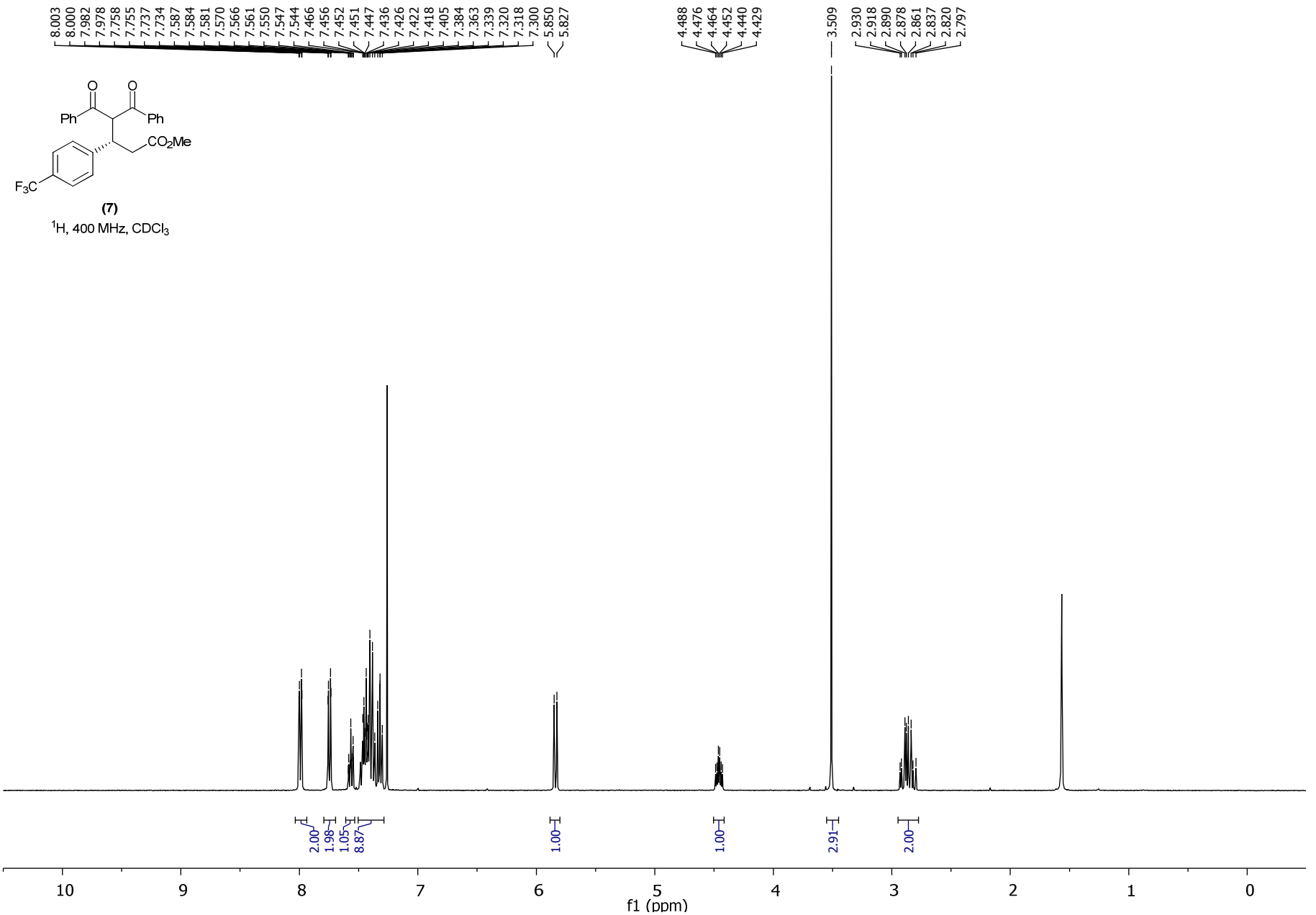
^{13}C, 75 MHz, $CDCl_3$

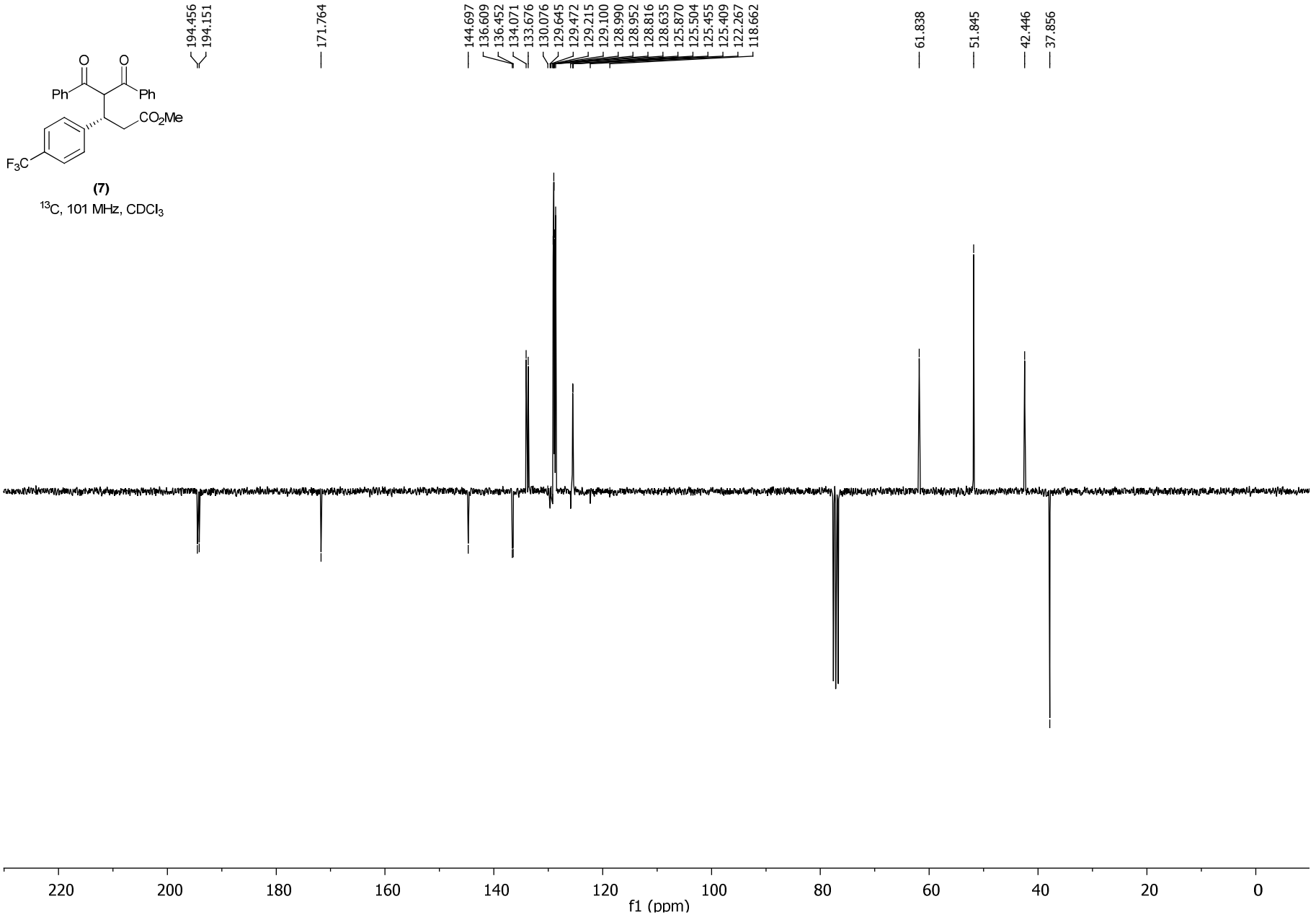


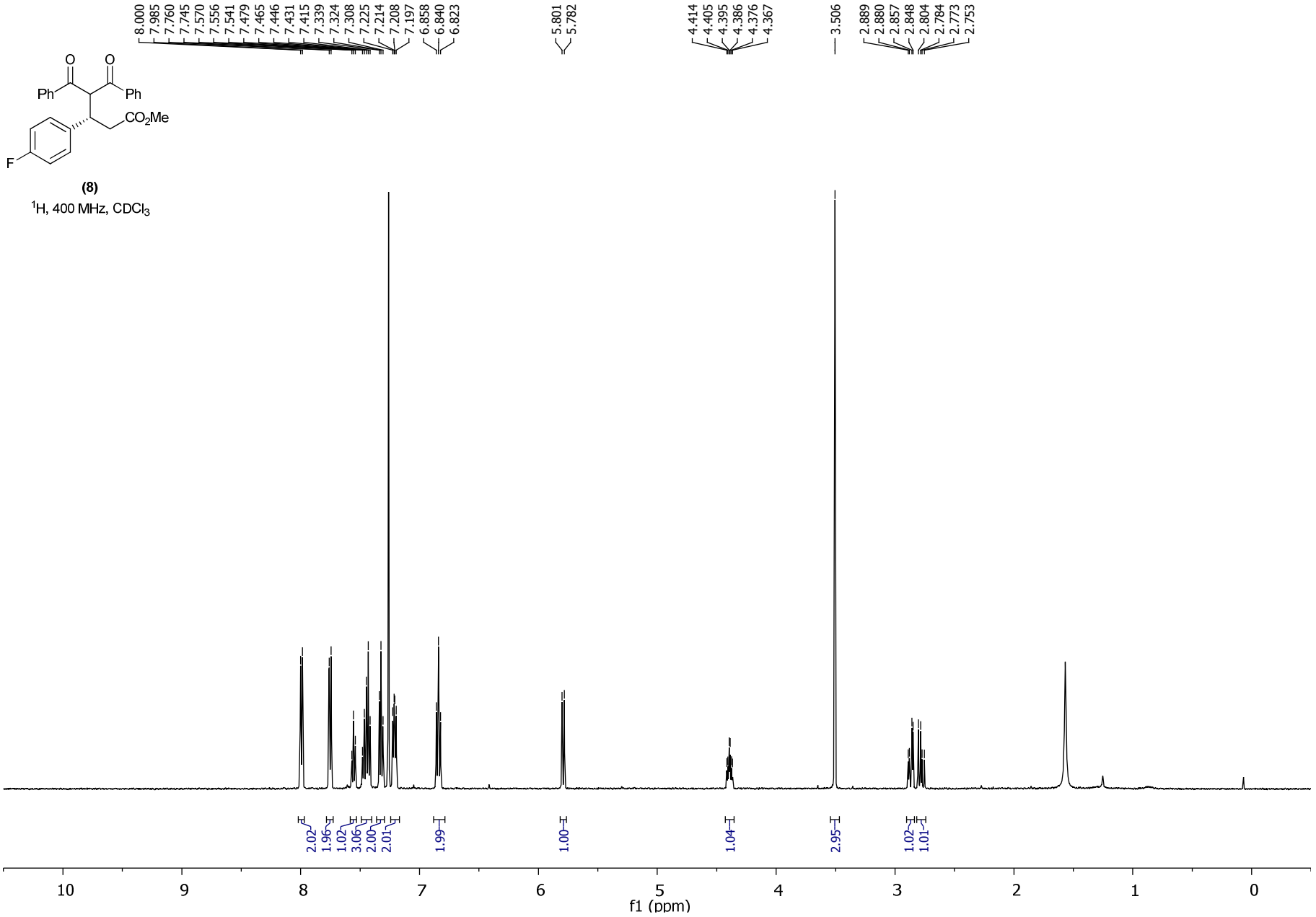


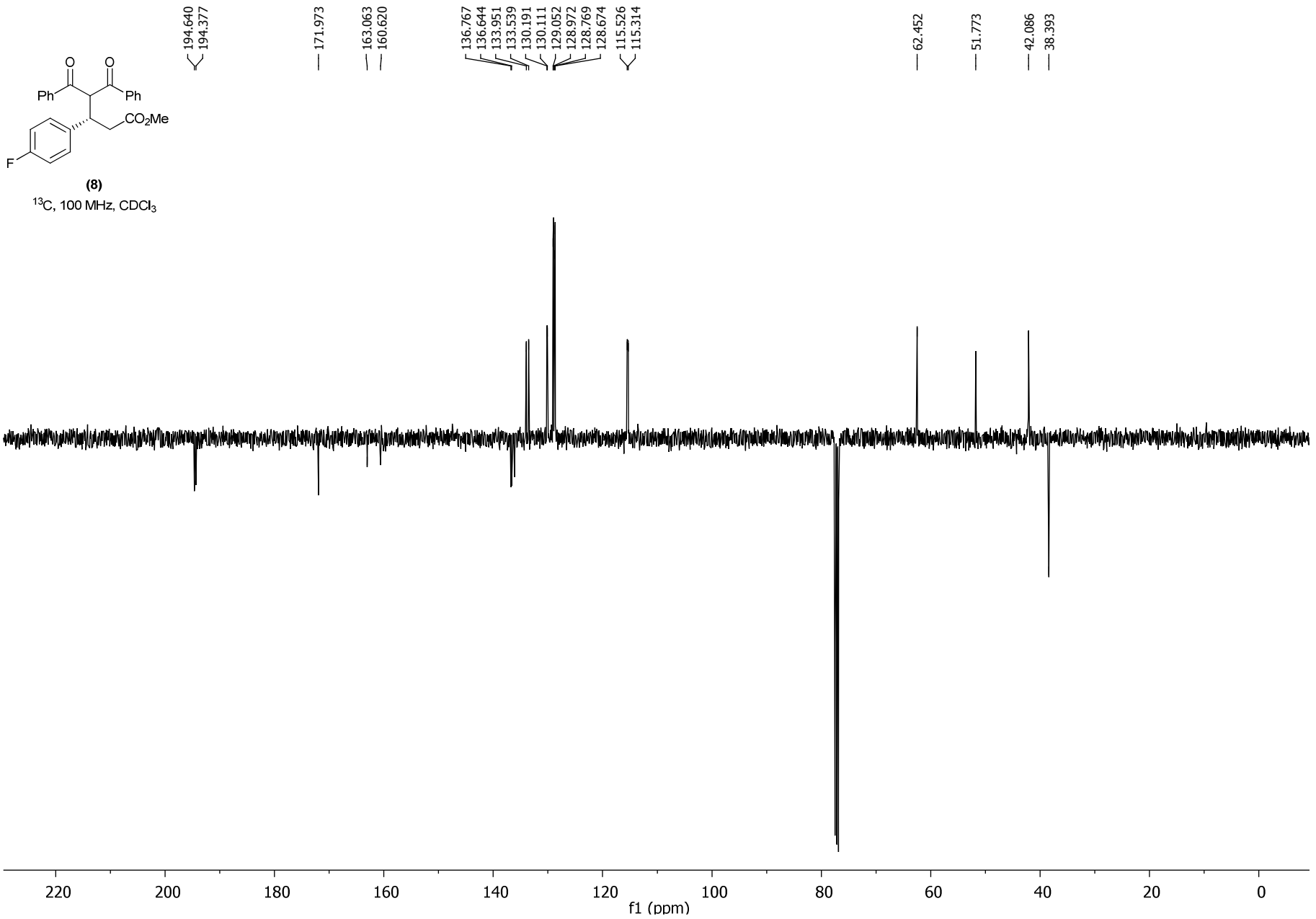






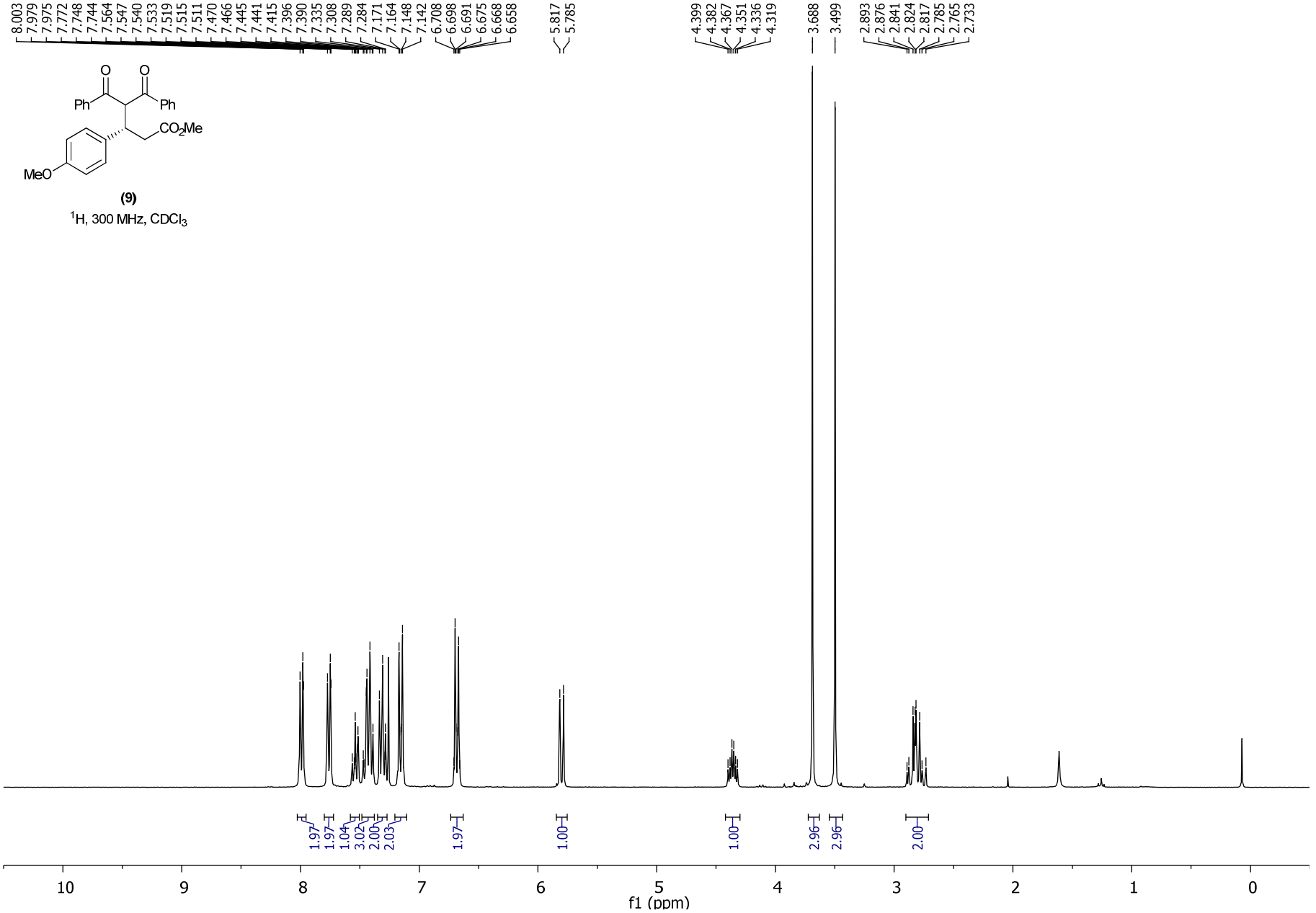


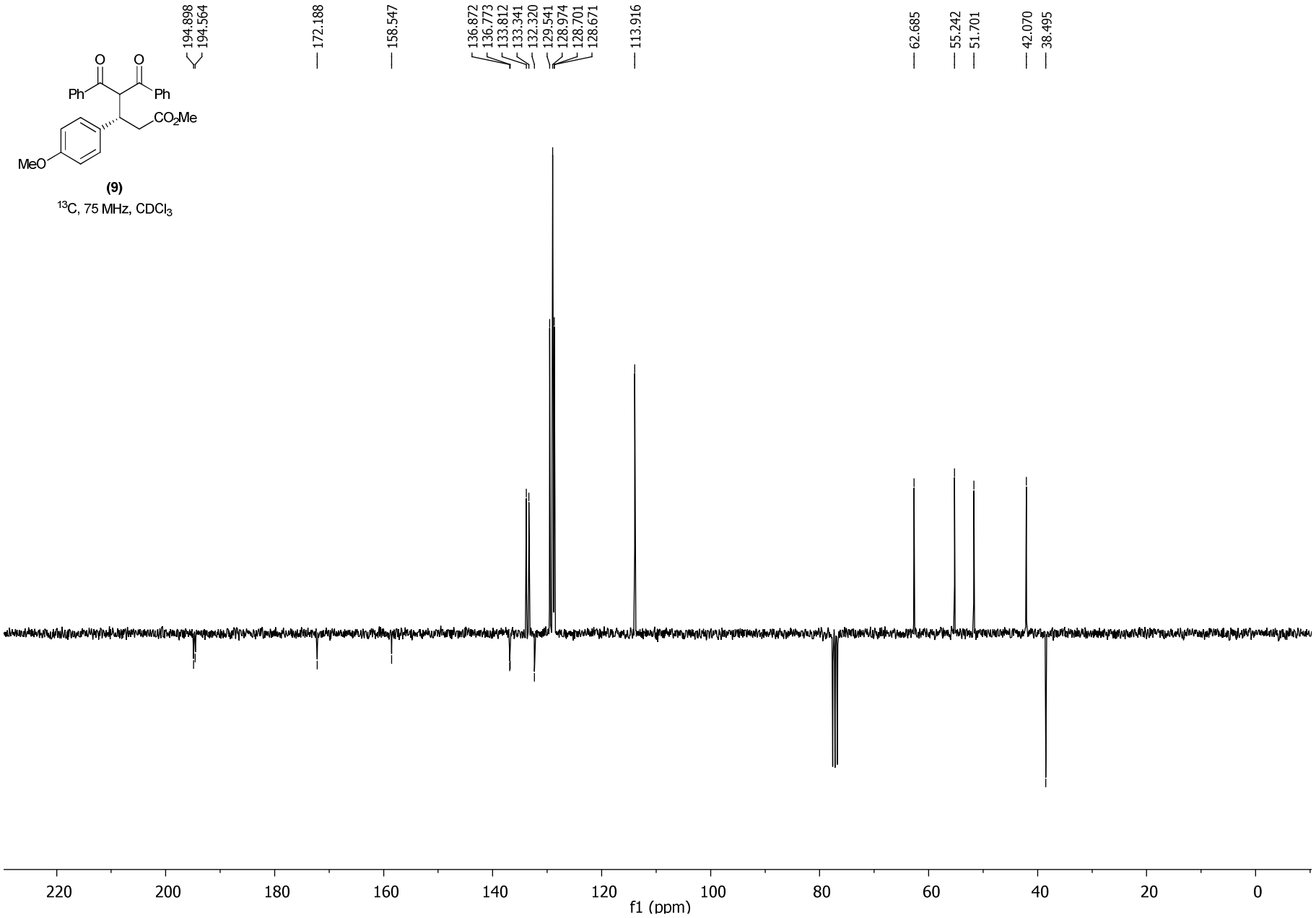


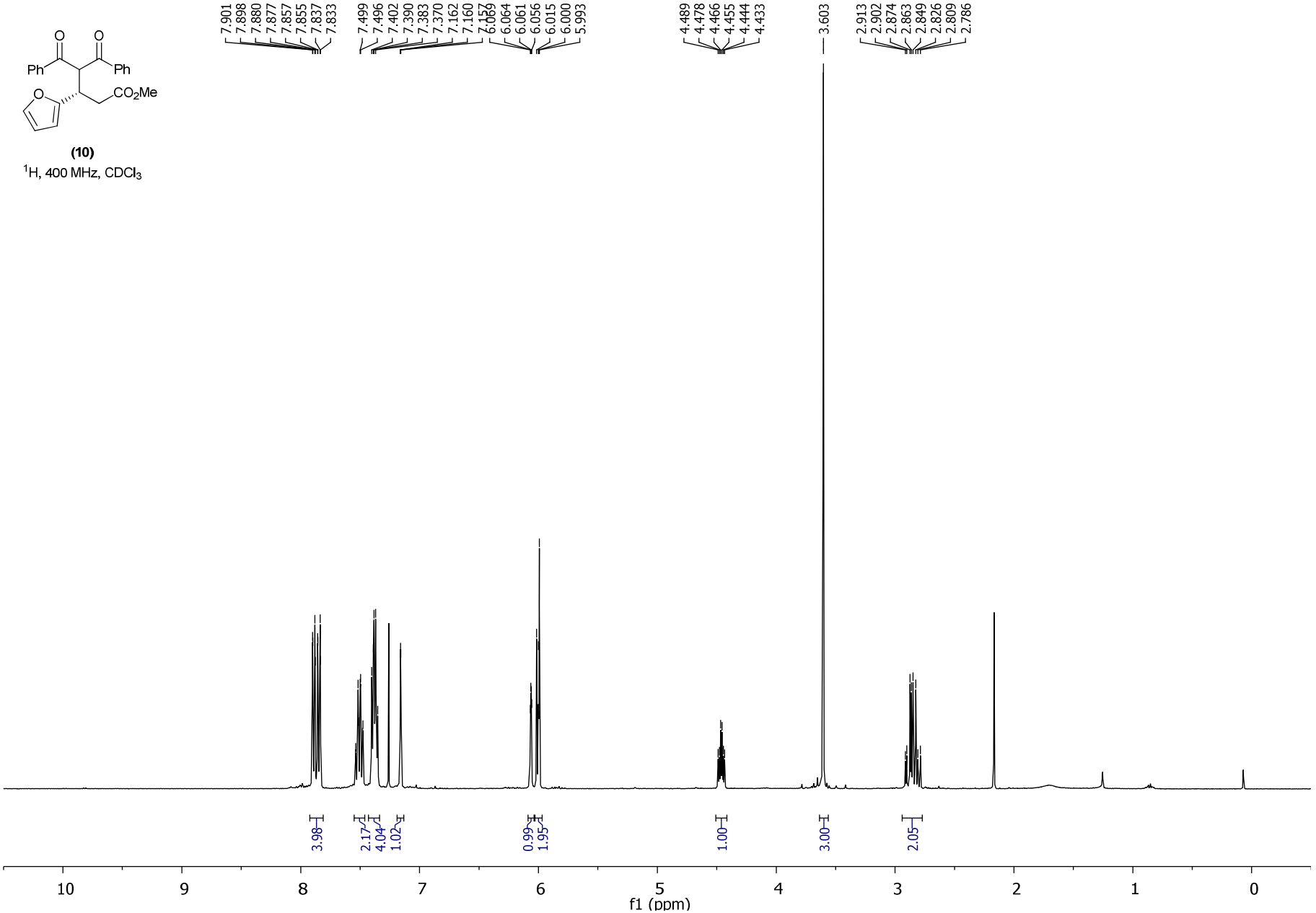


(8)

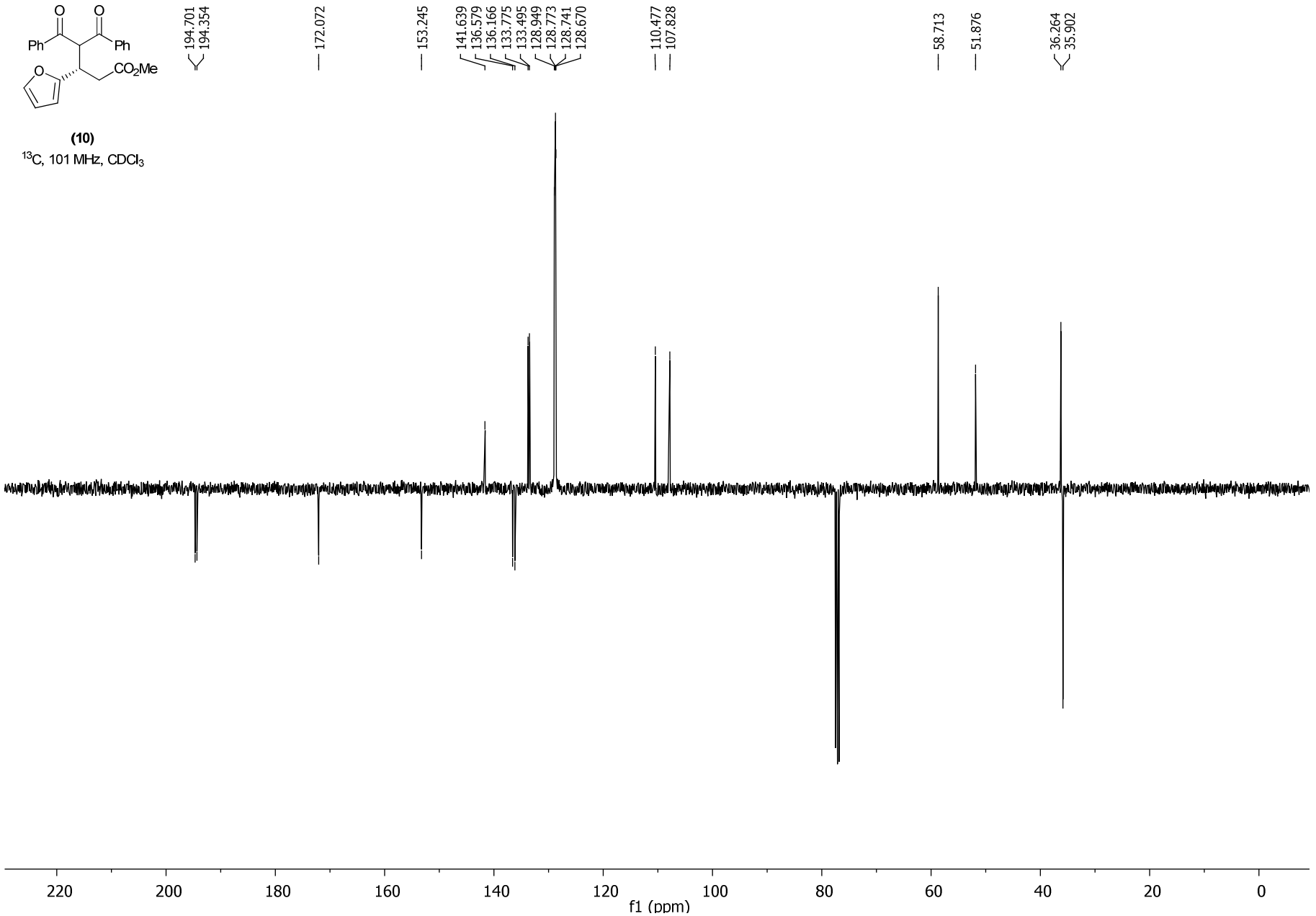
^{13}C, 100 MHz, $CDCl_3$





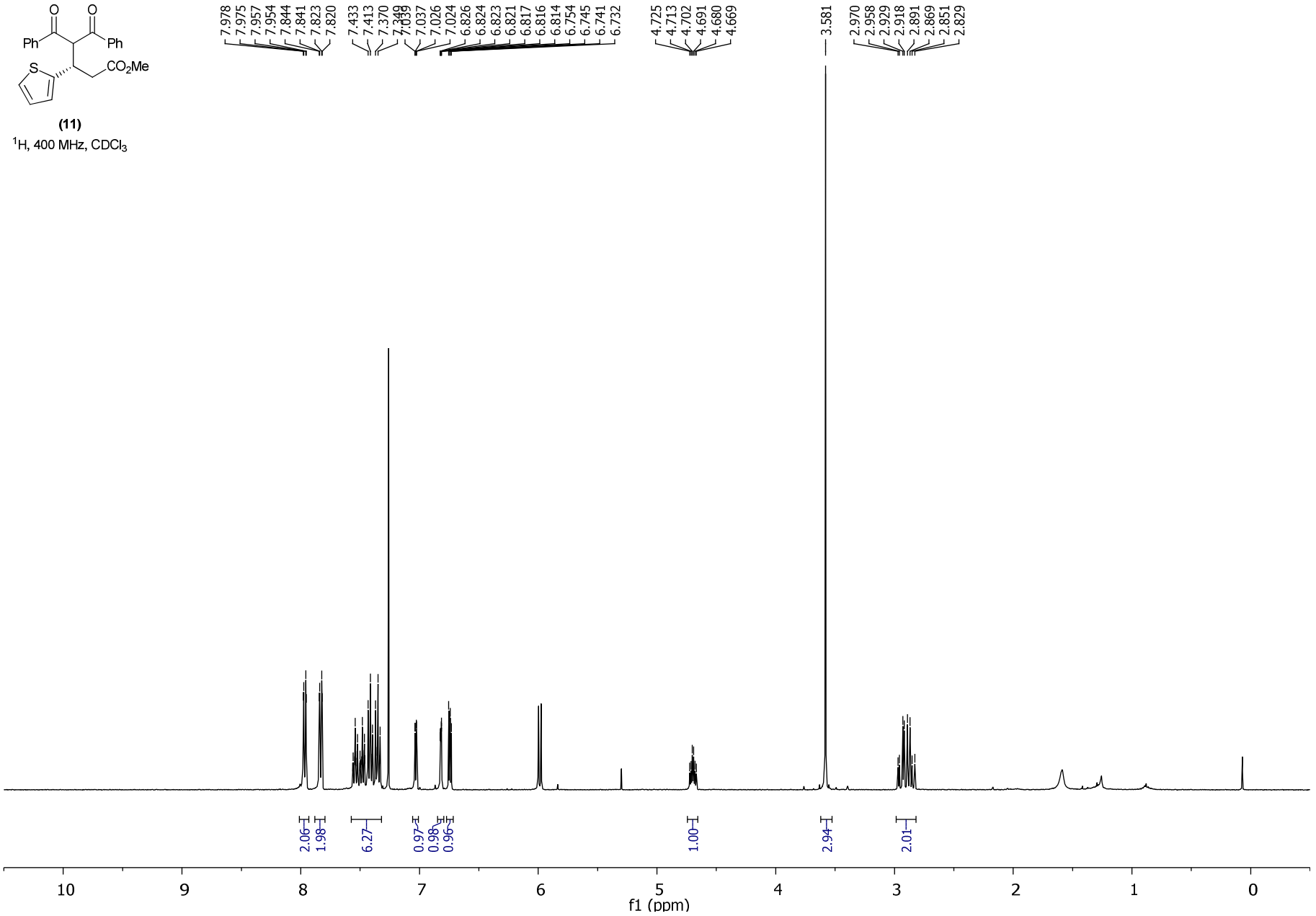


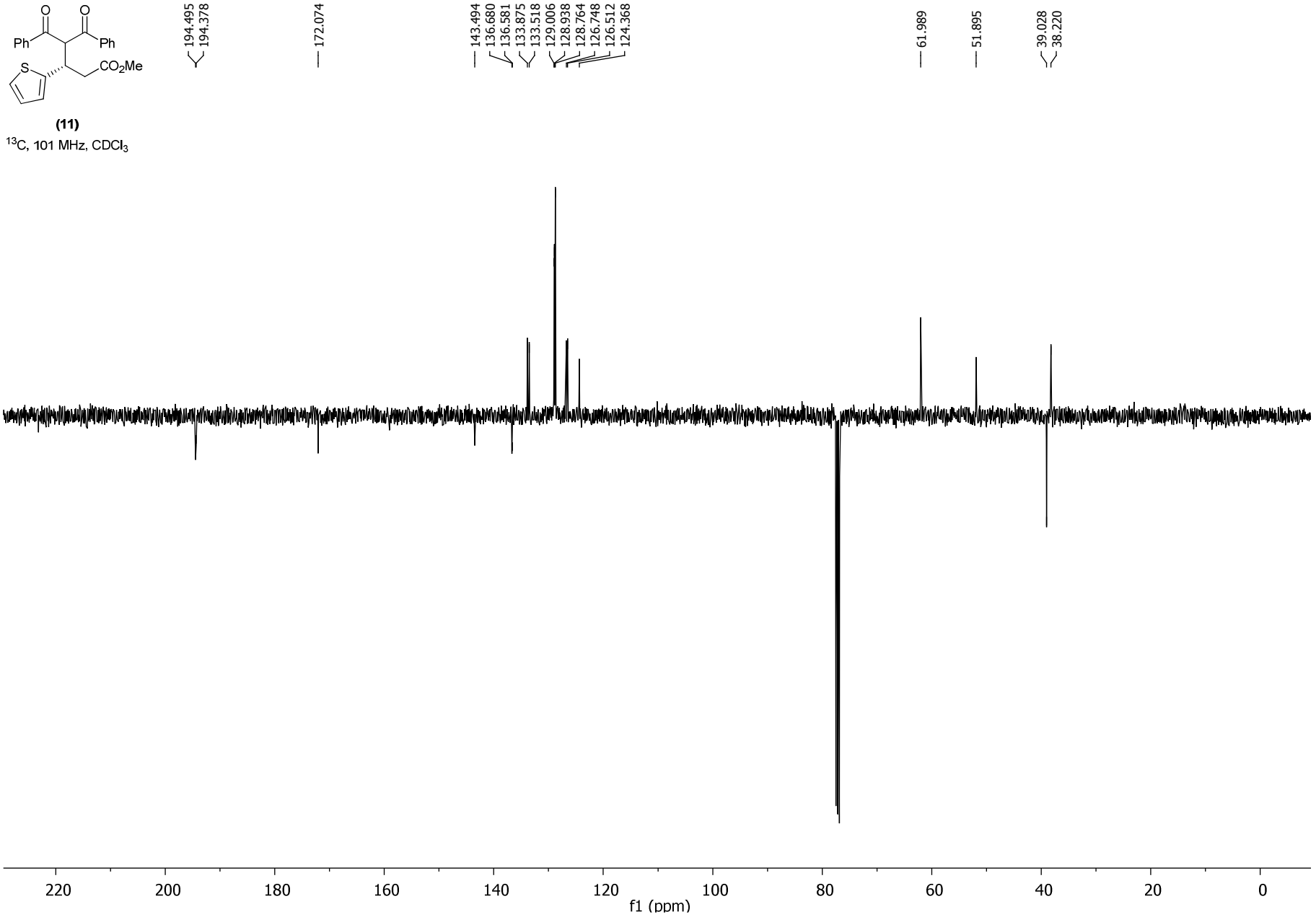
(10)
^{1}H, 400 MHz, $CDCl_3$



(10)

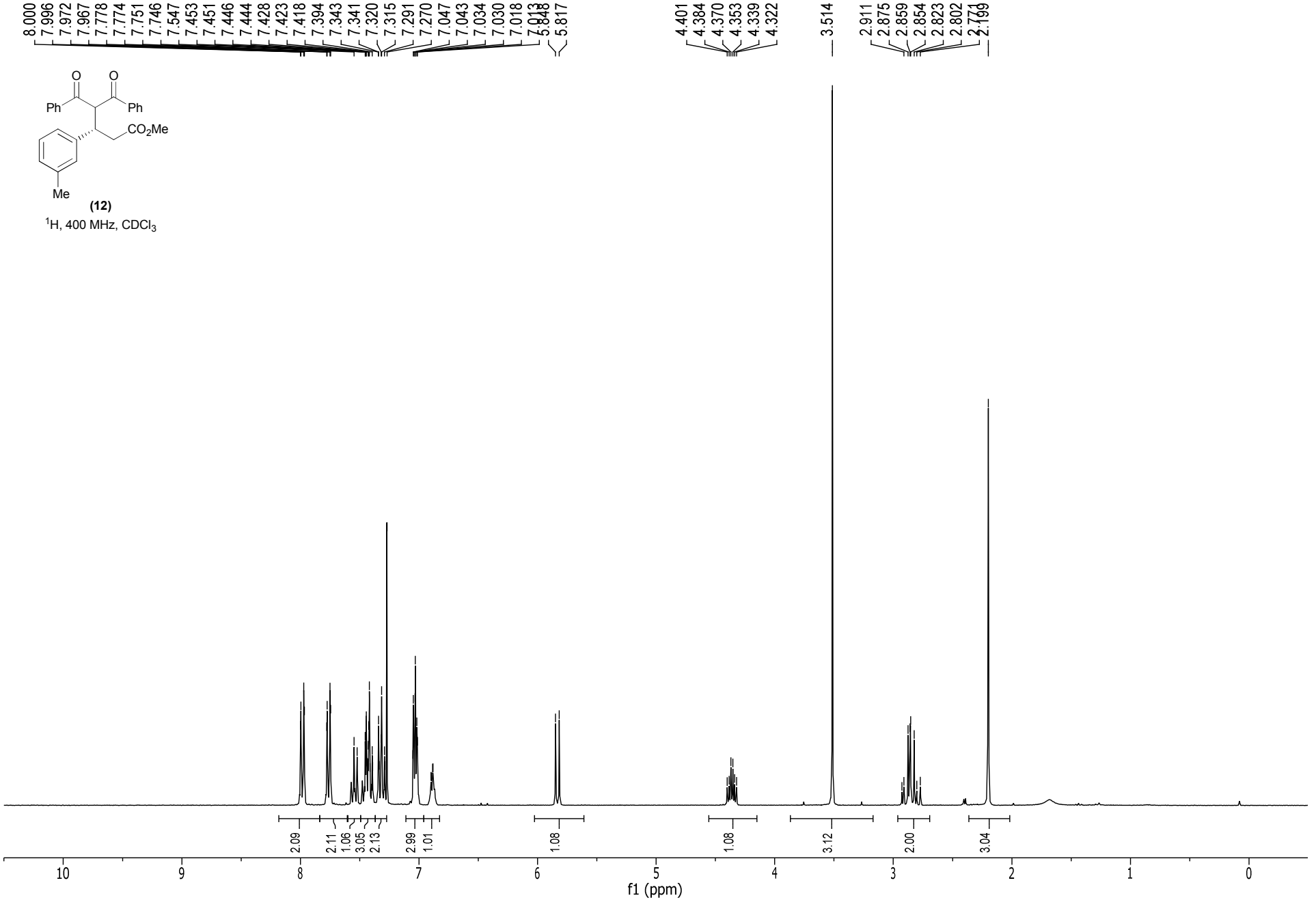
^{13}C, 101 MHz, $CDCl_3$

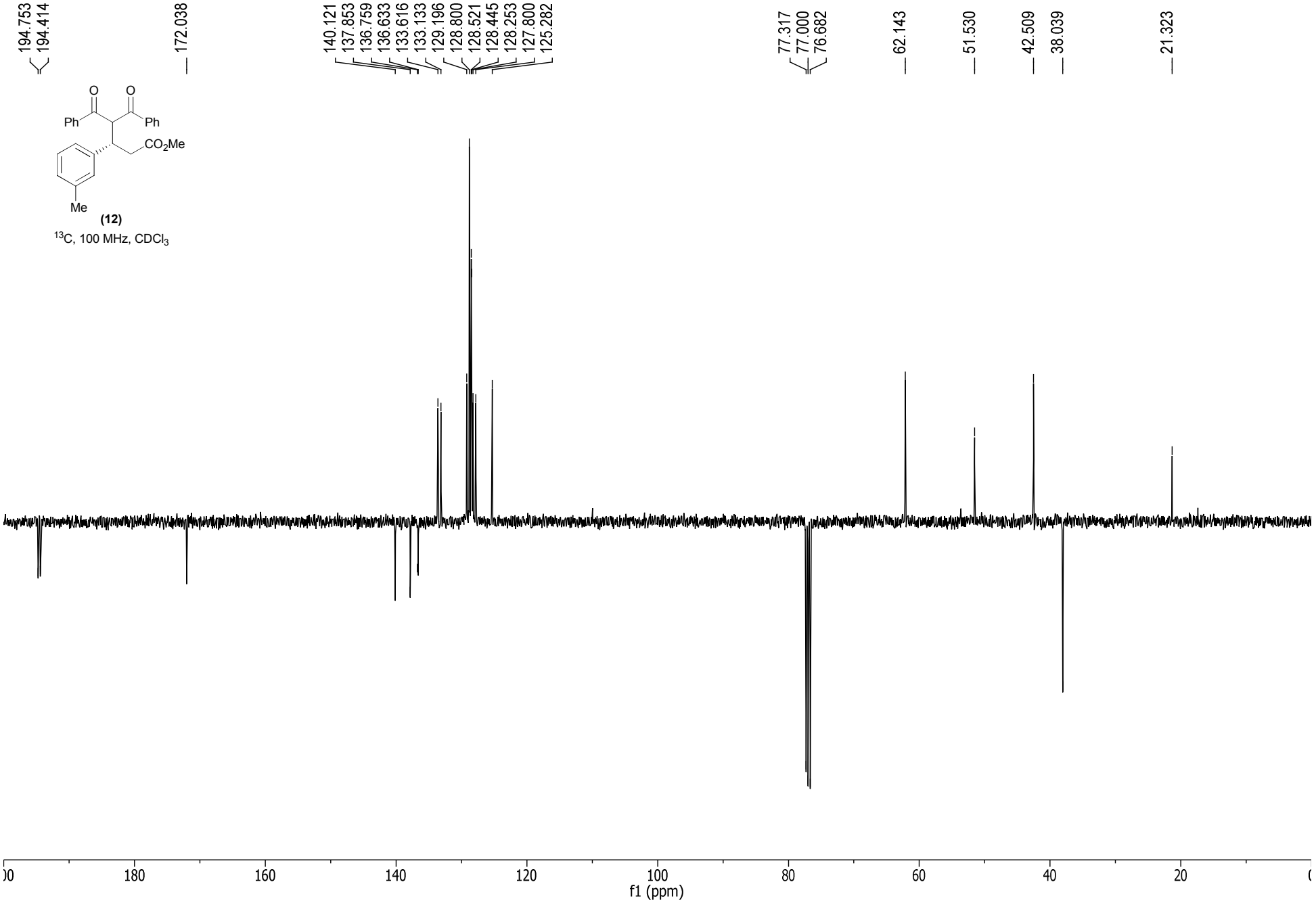


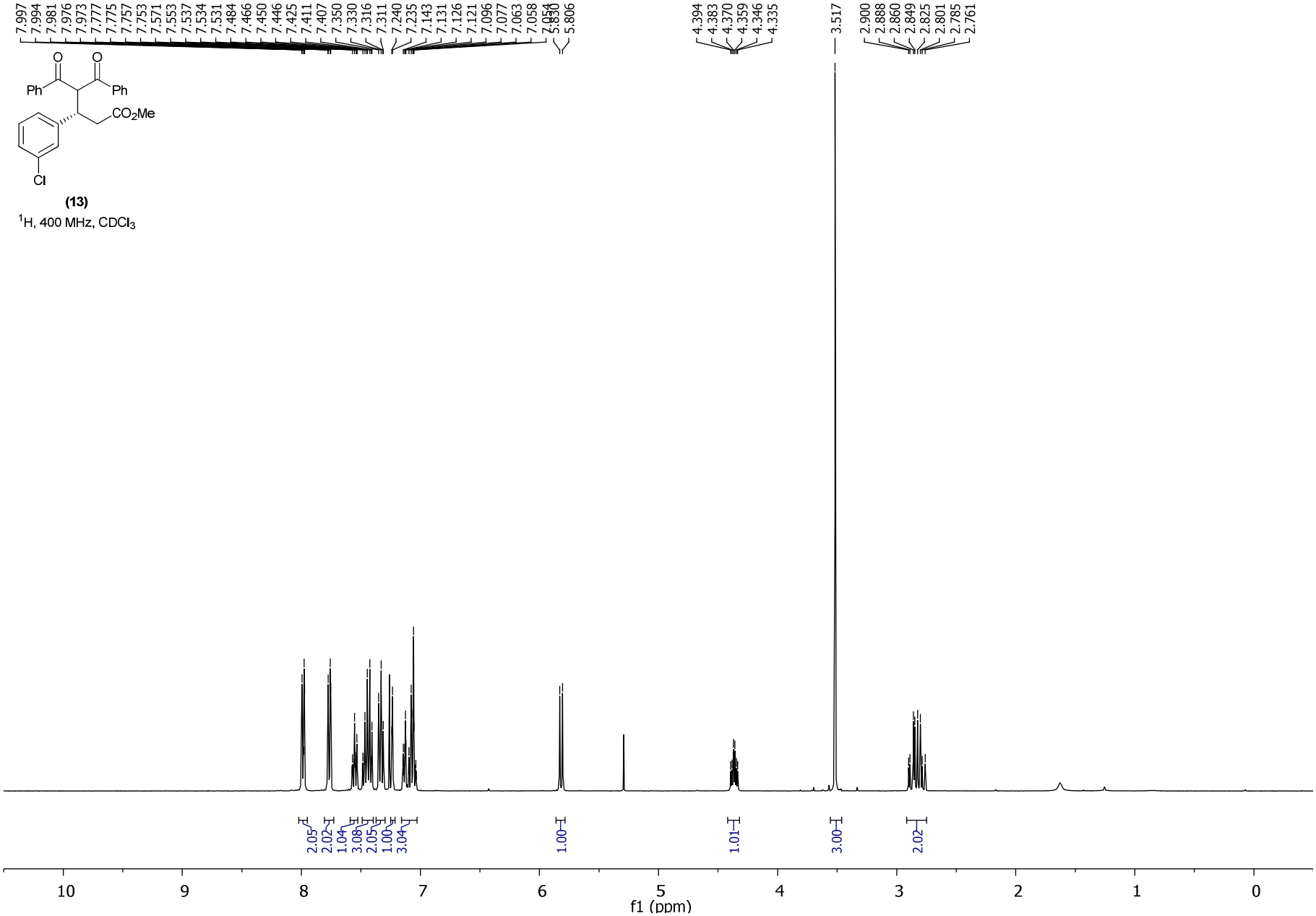


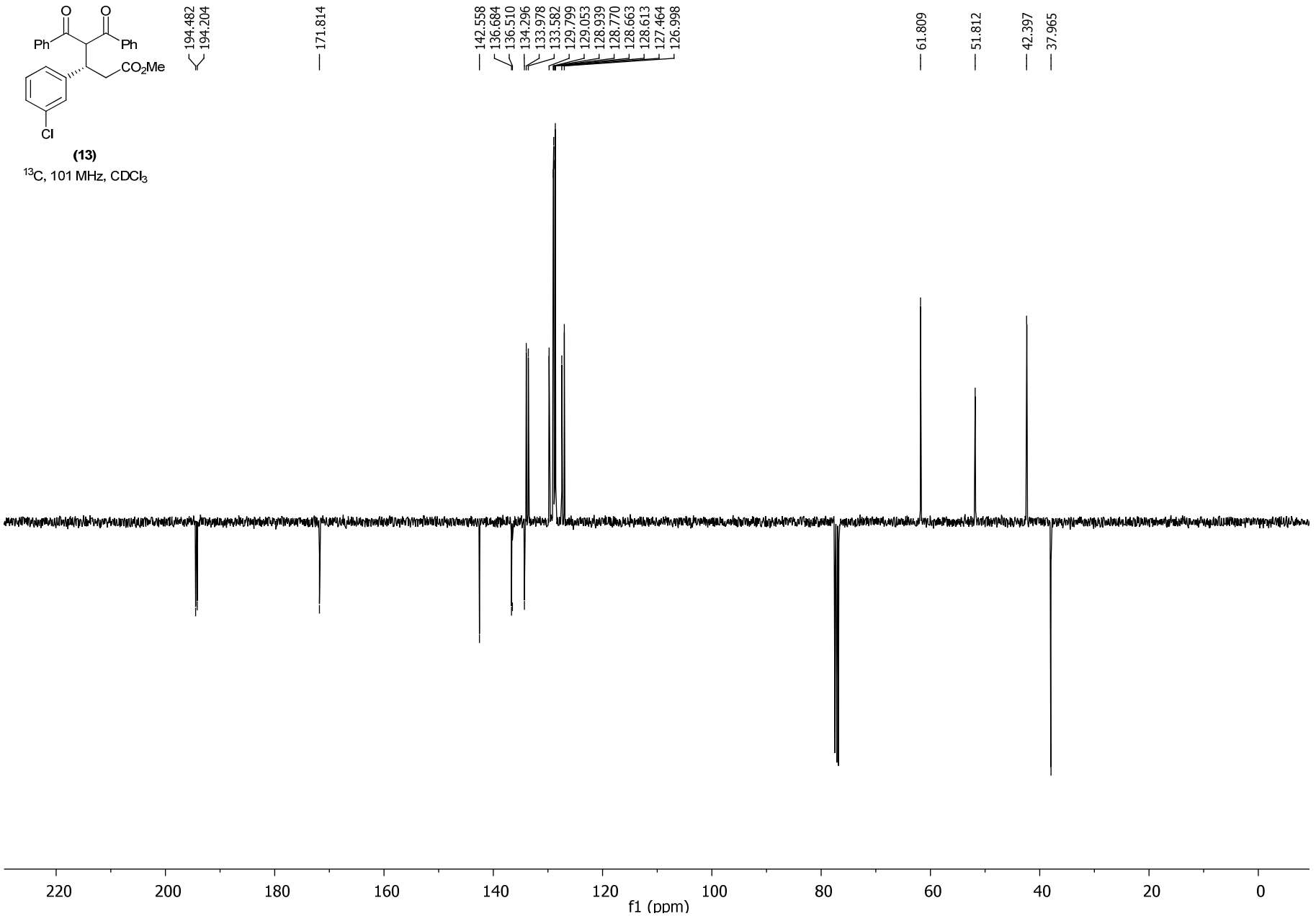
(11)

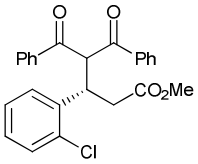
^{13}C, 101 MHz, $CDCl_3$





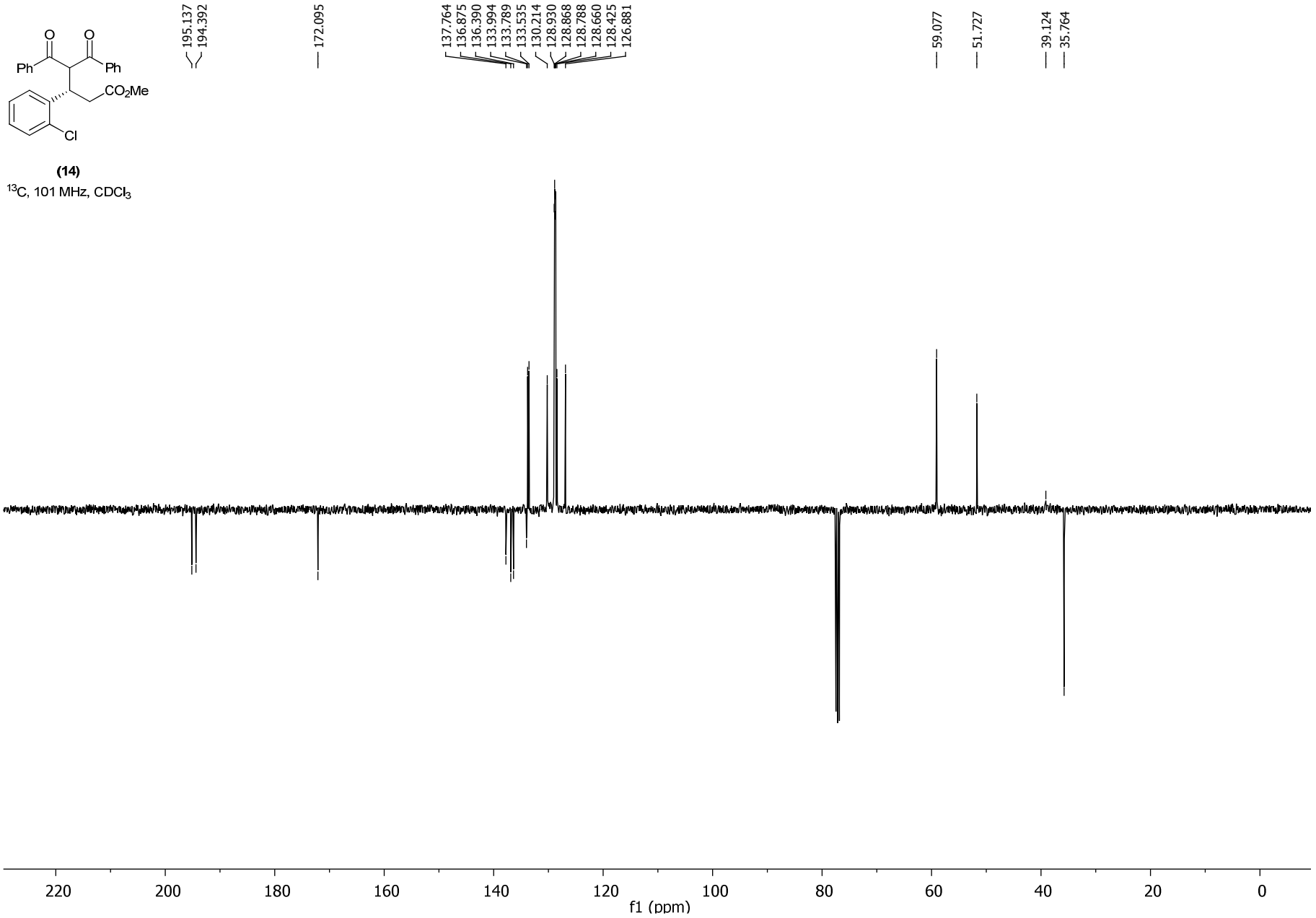


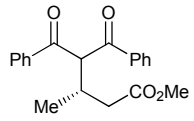




(14)

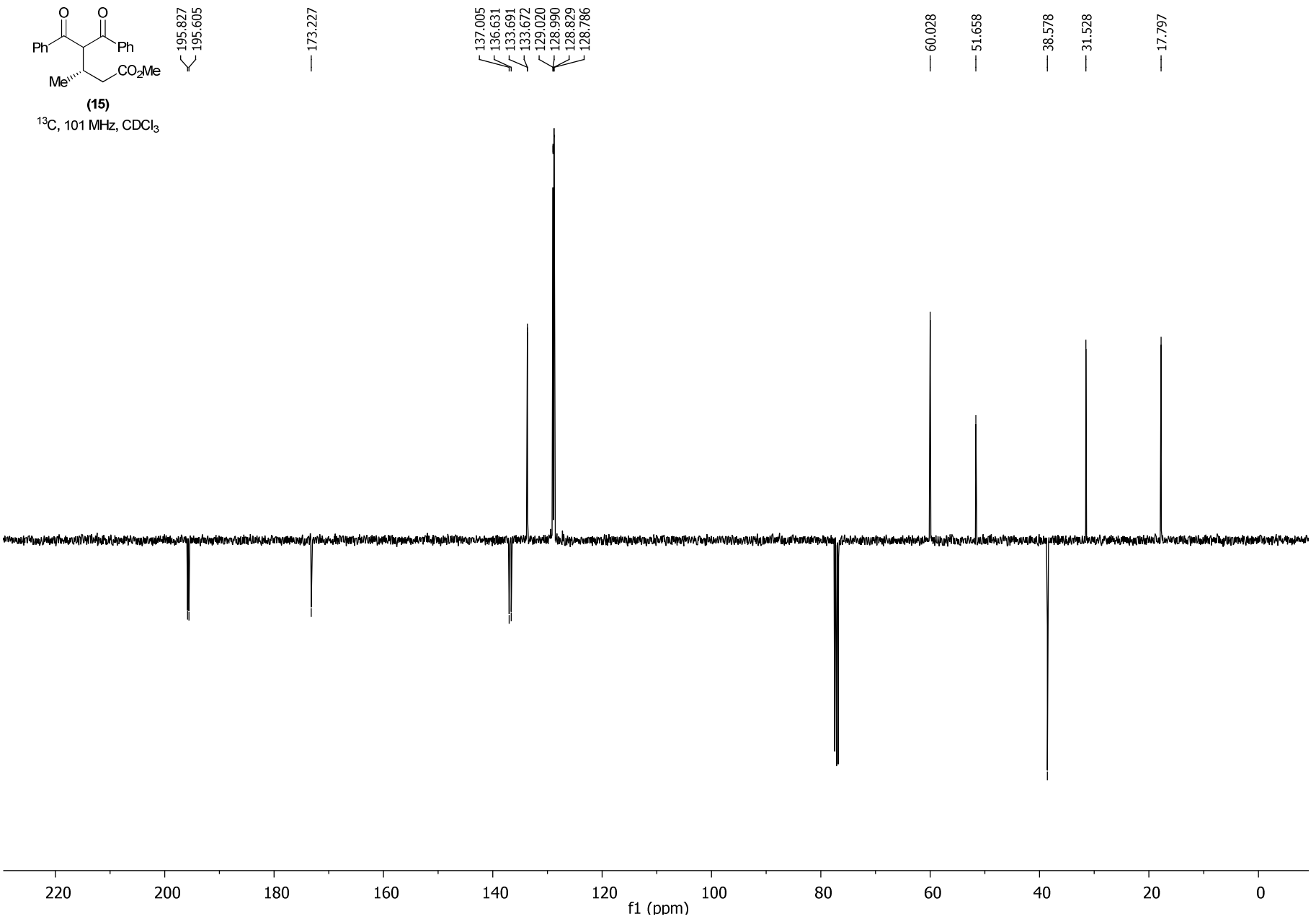
^{1}H, 400 MHz, $CDCl_3$

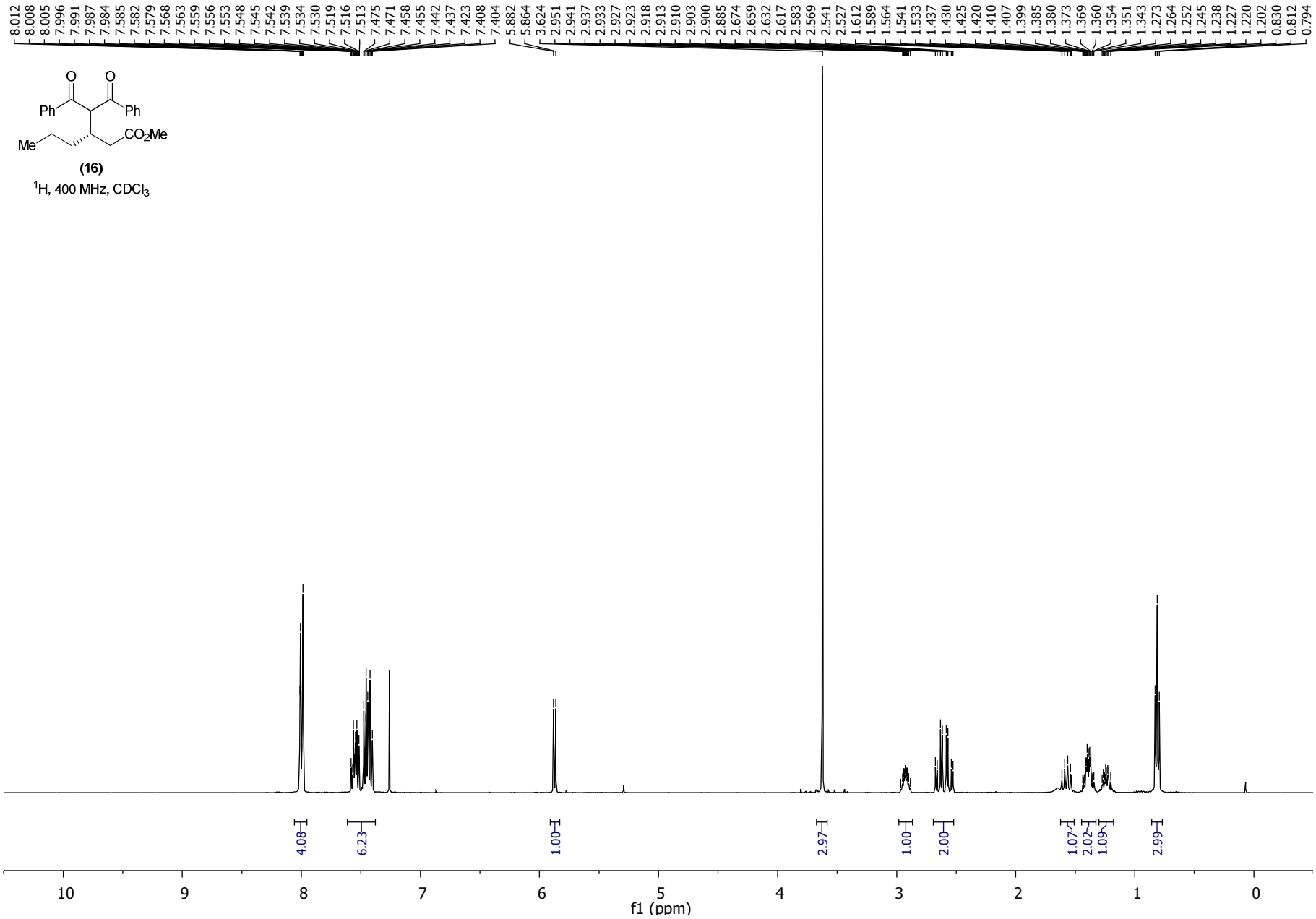


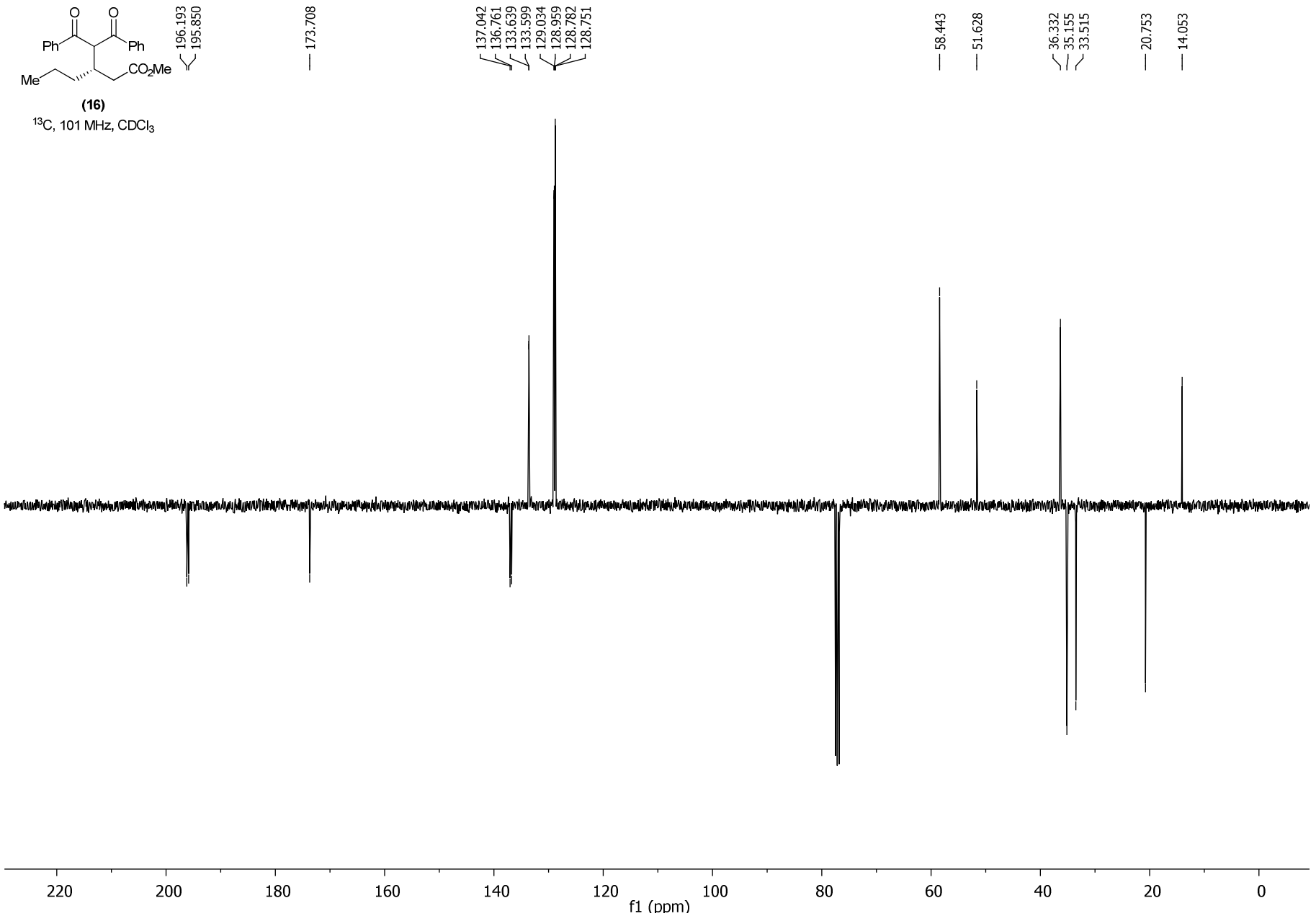


(15)

^{1}H, 400 MHz, $CDCl_3$

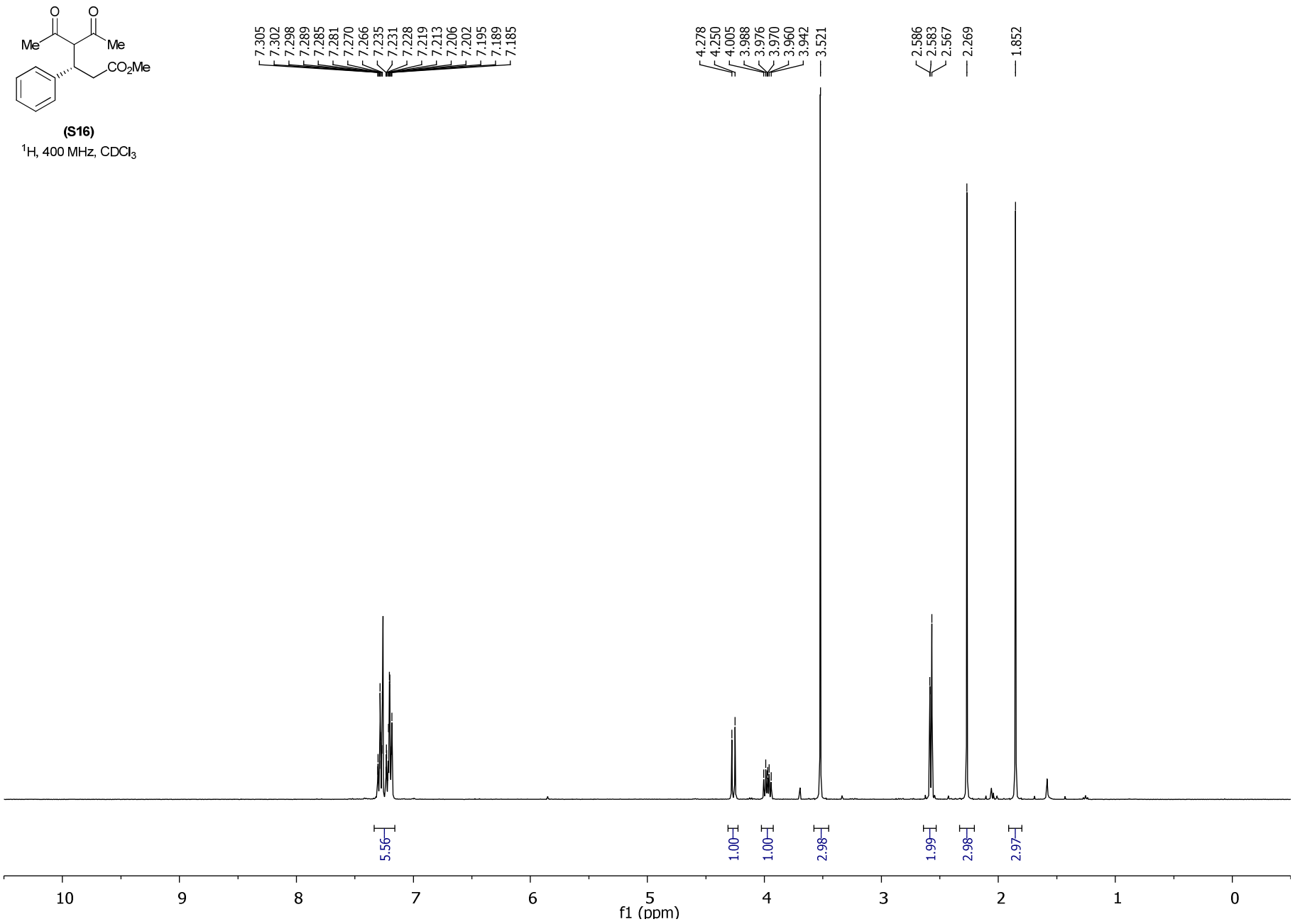


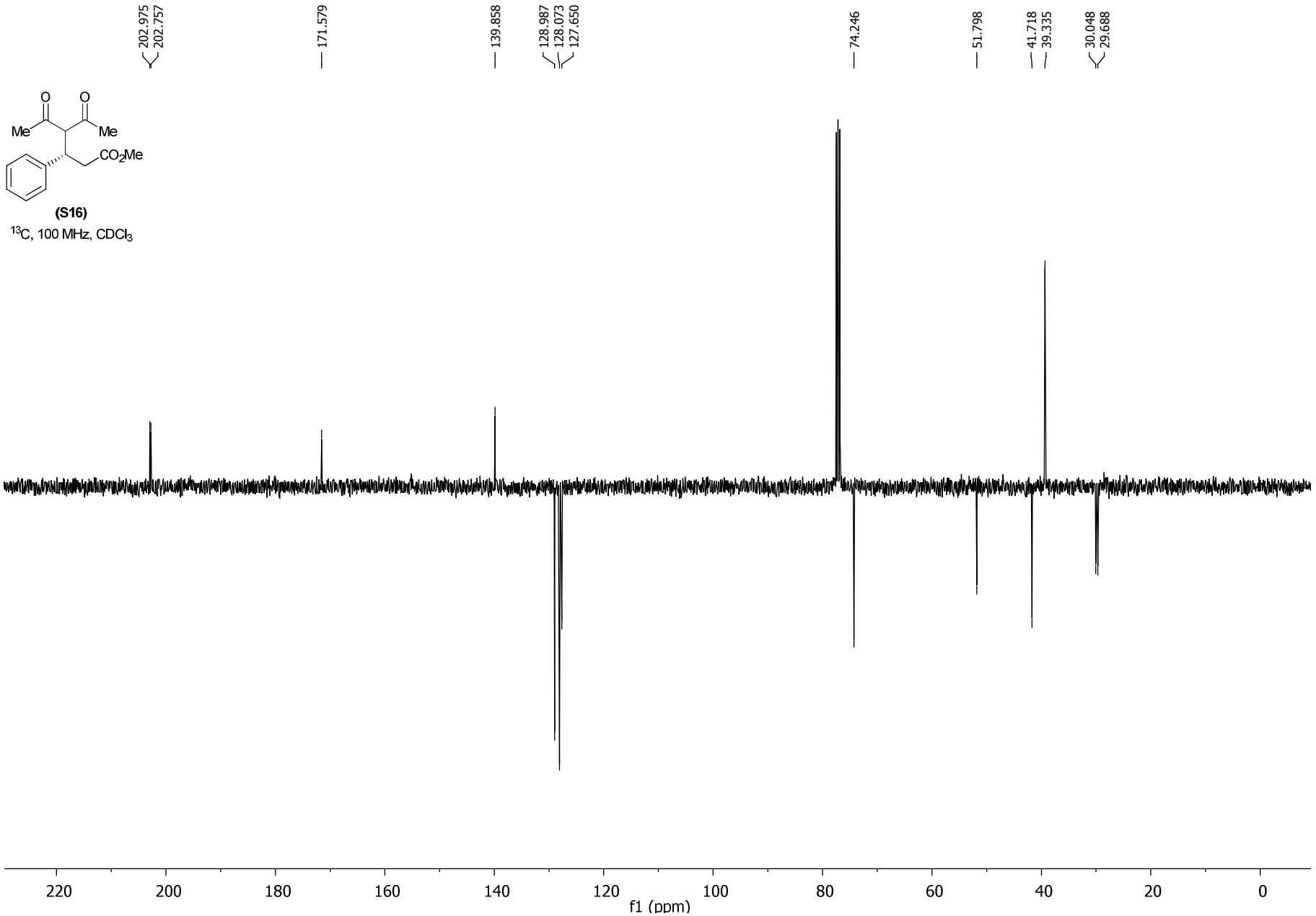


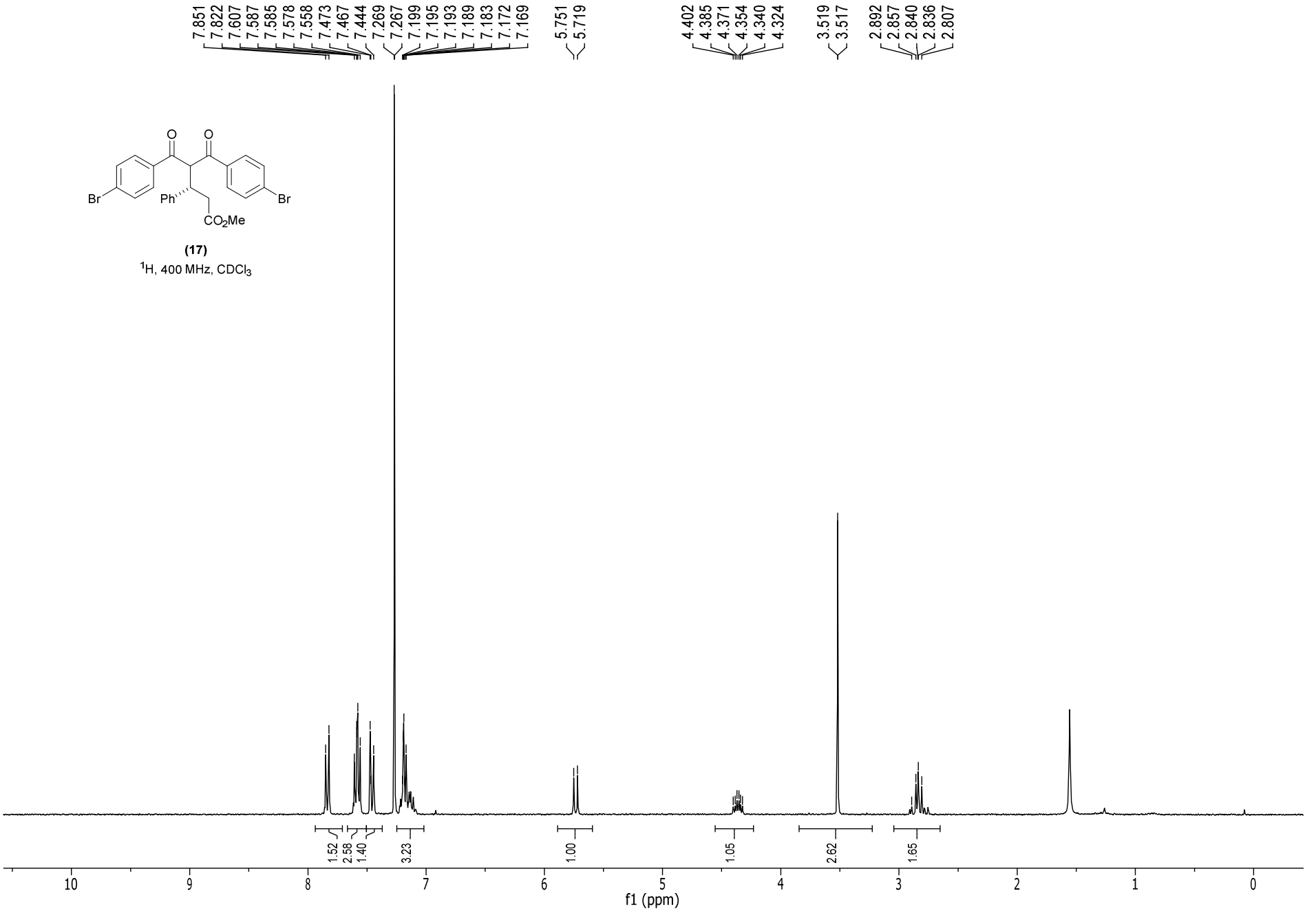


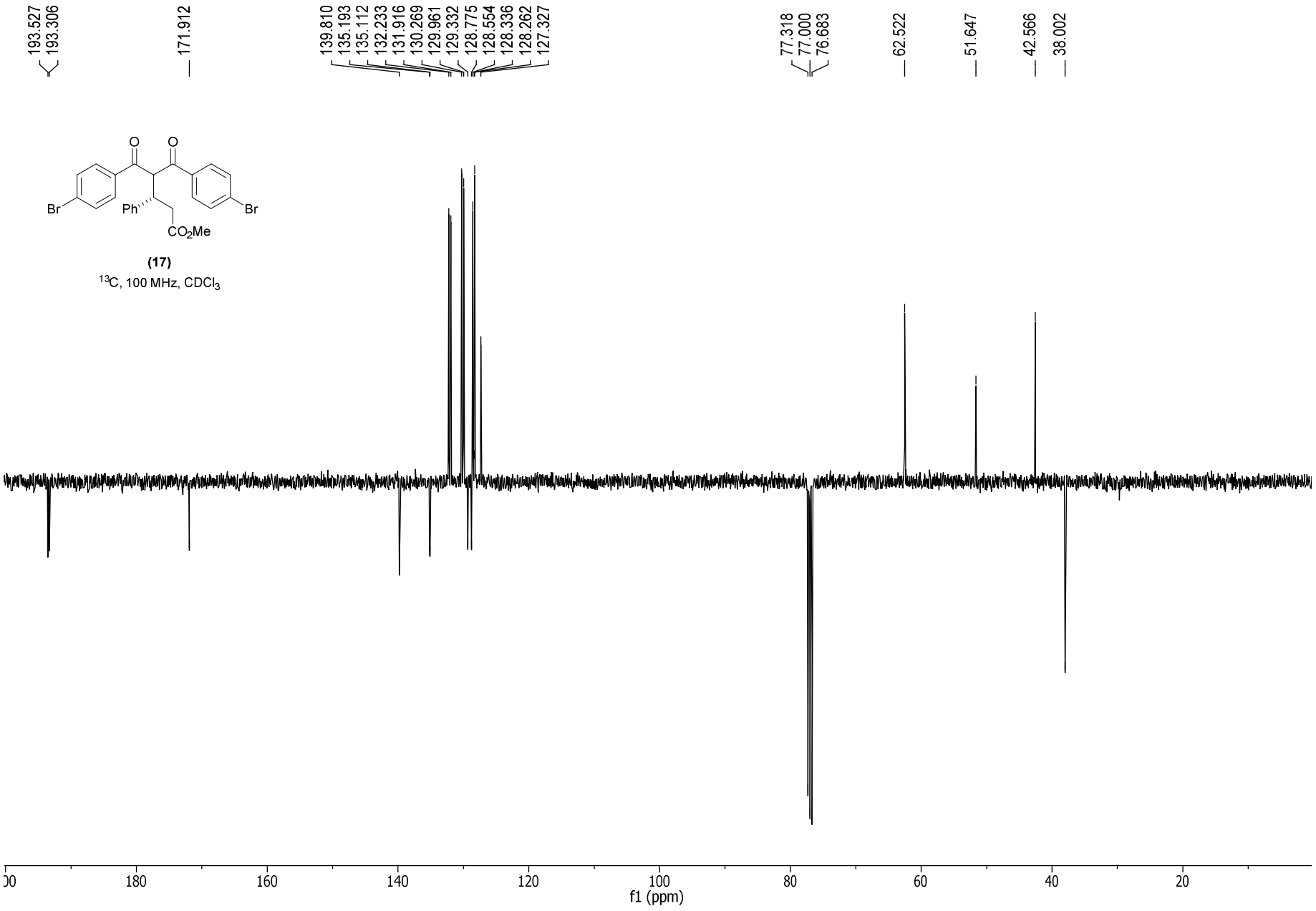
(16)

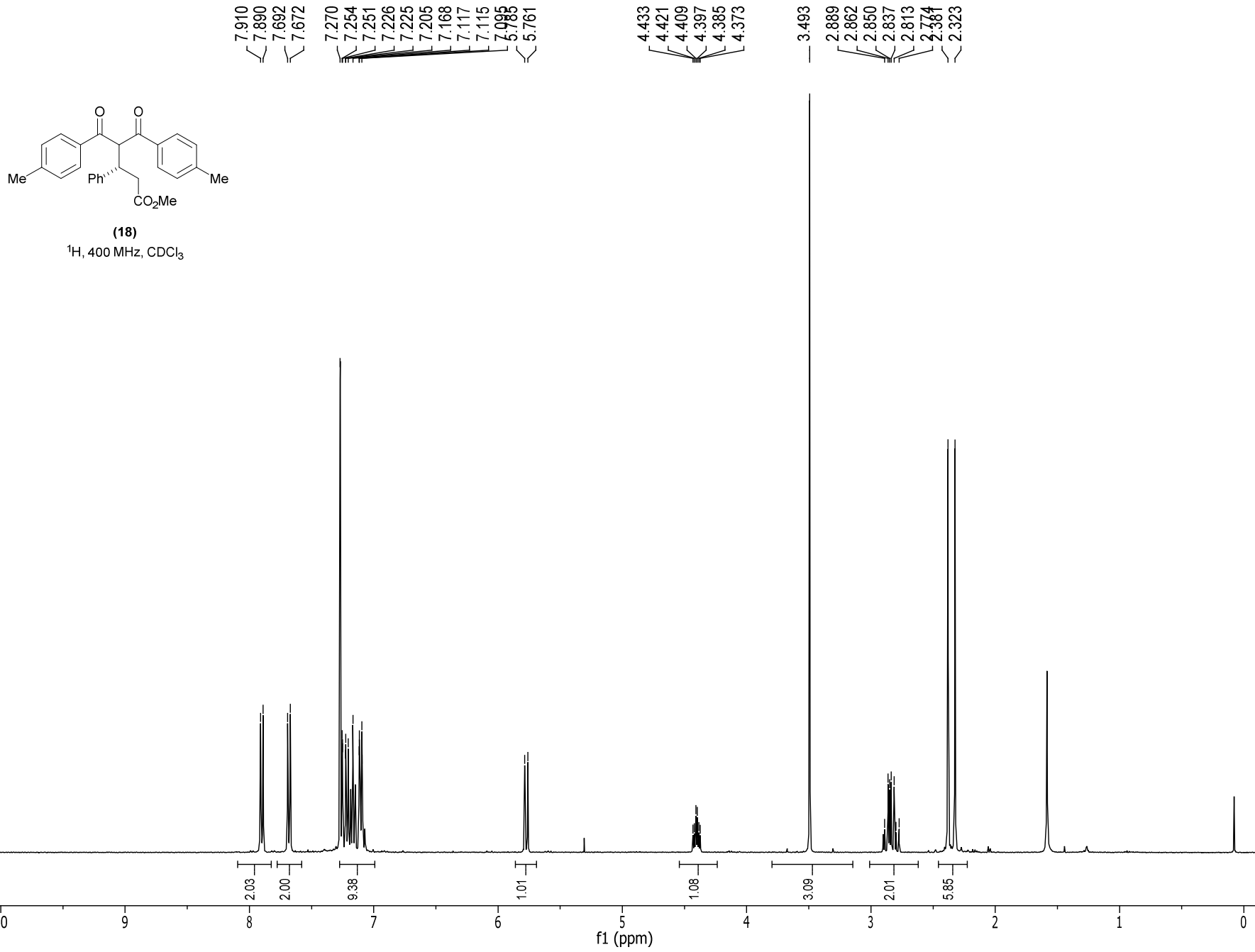
^{13}C, 101 MHz, $CDCl_3$

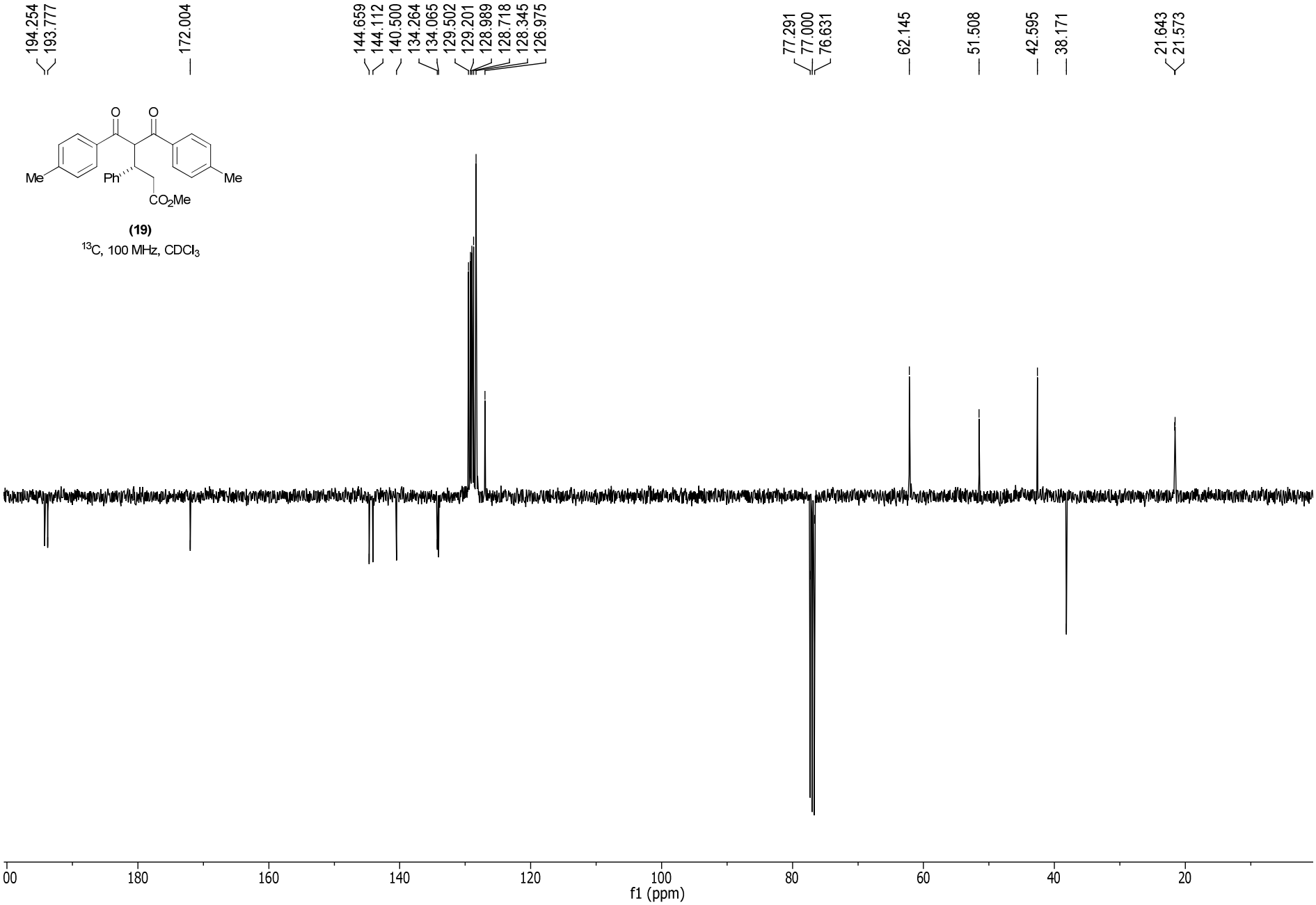


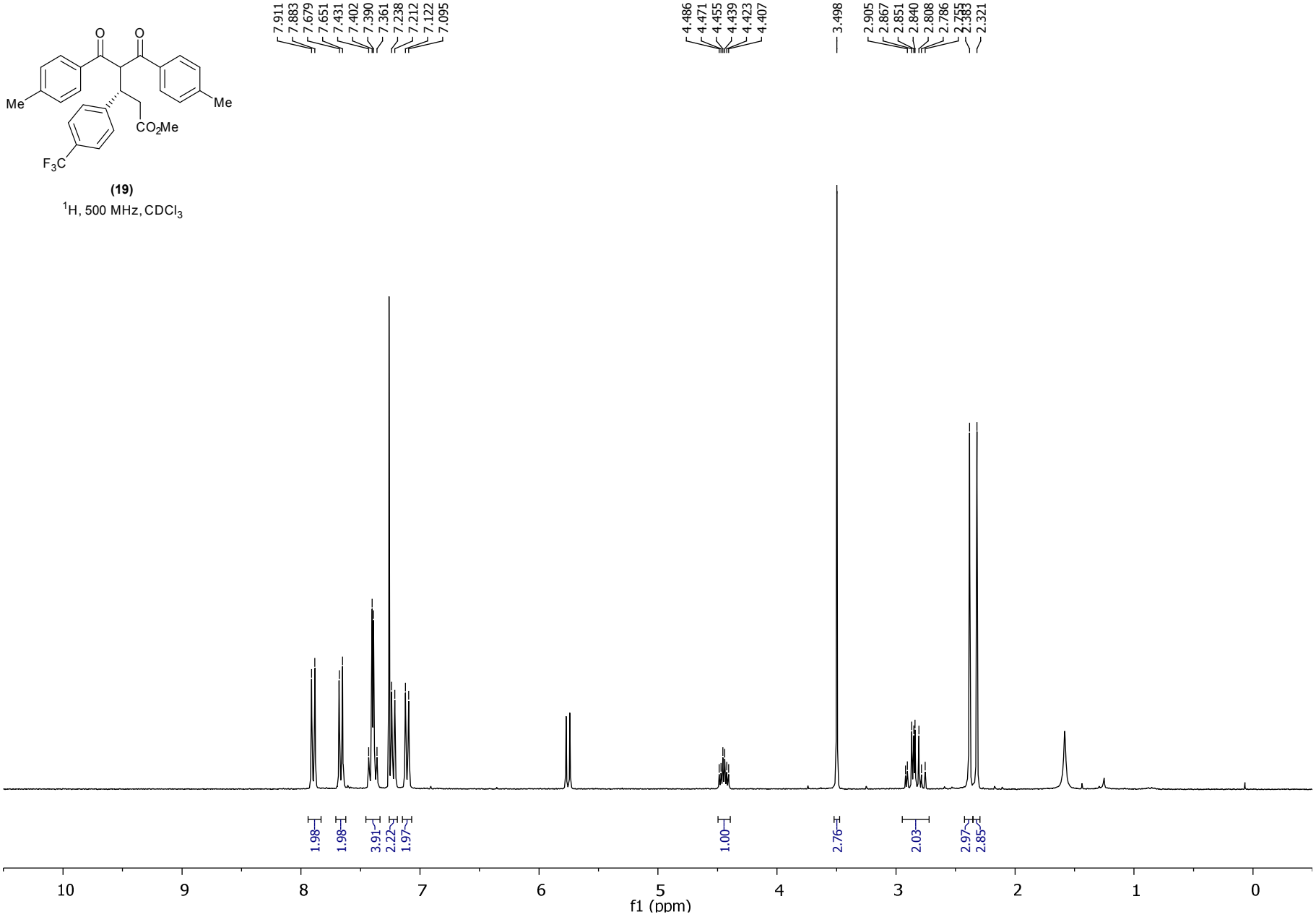


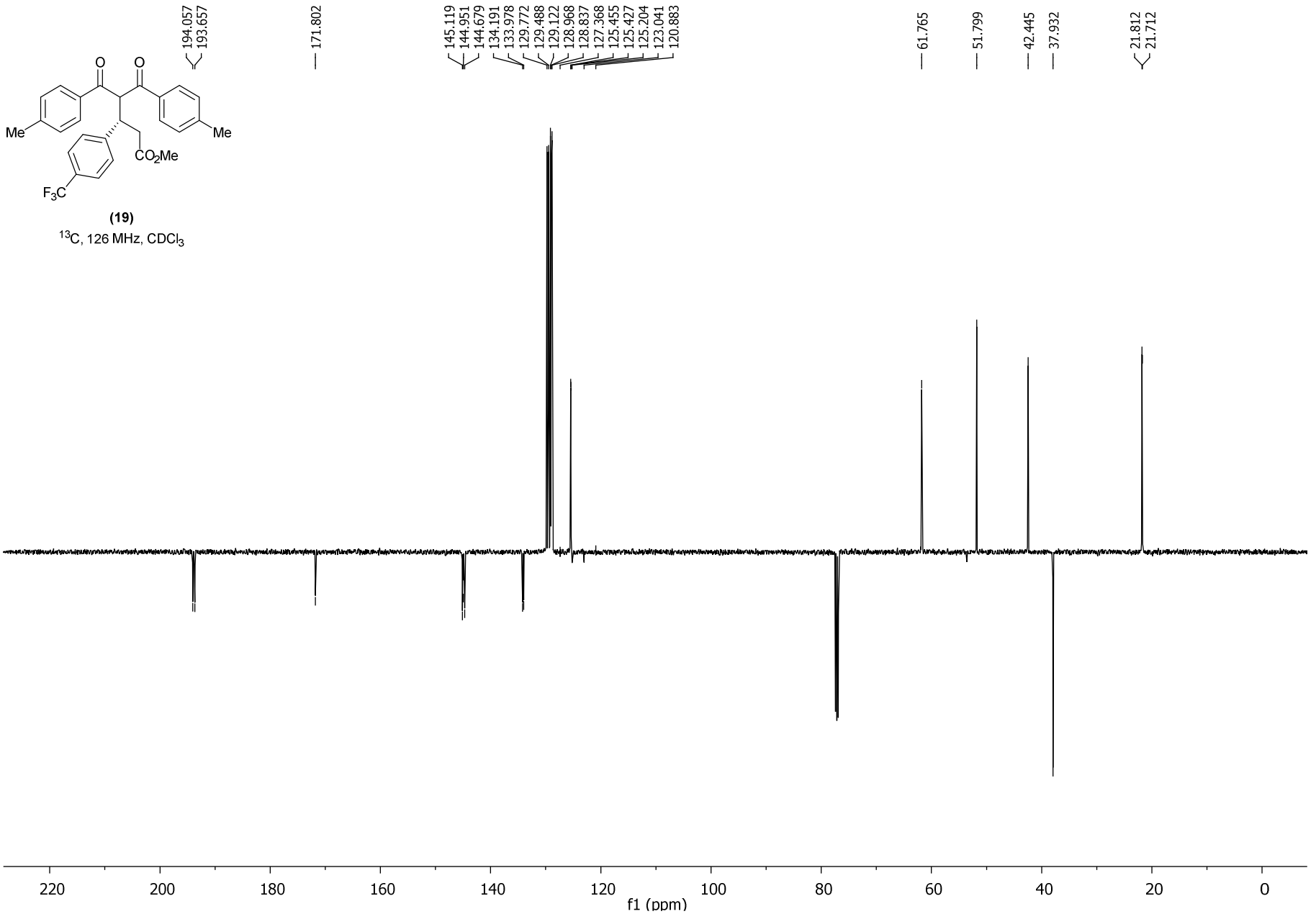






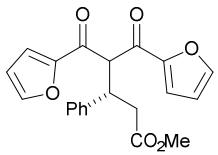






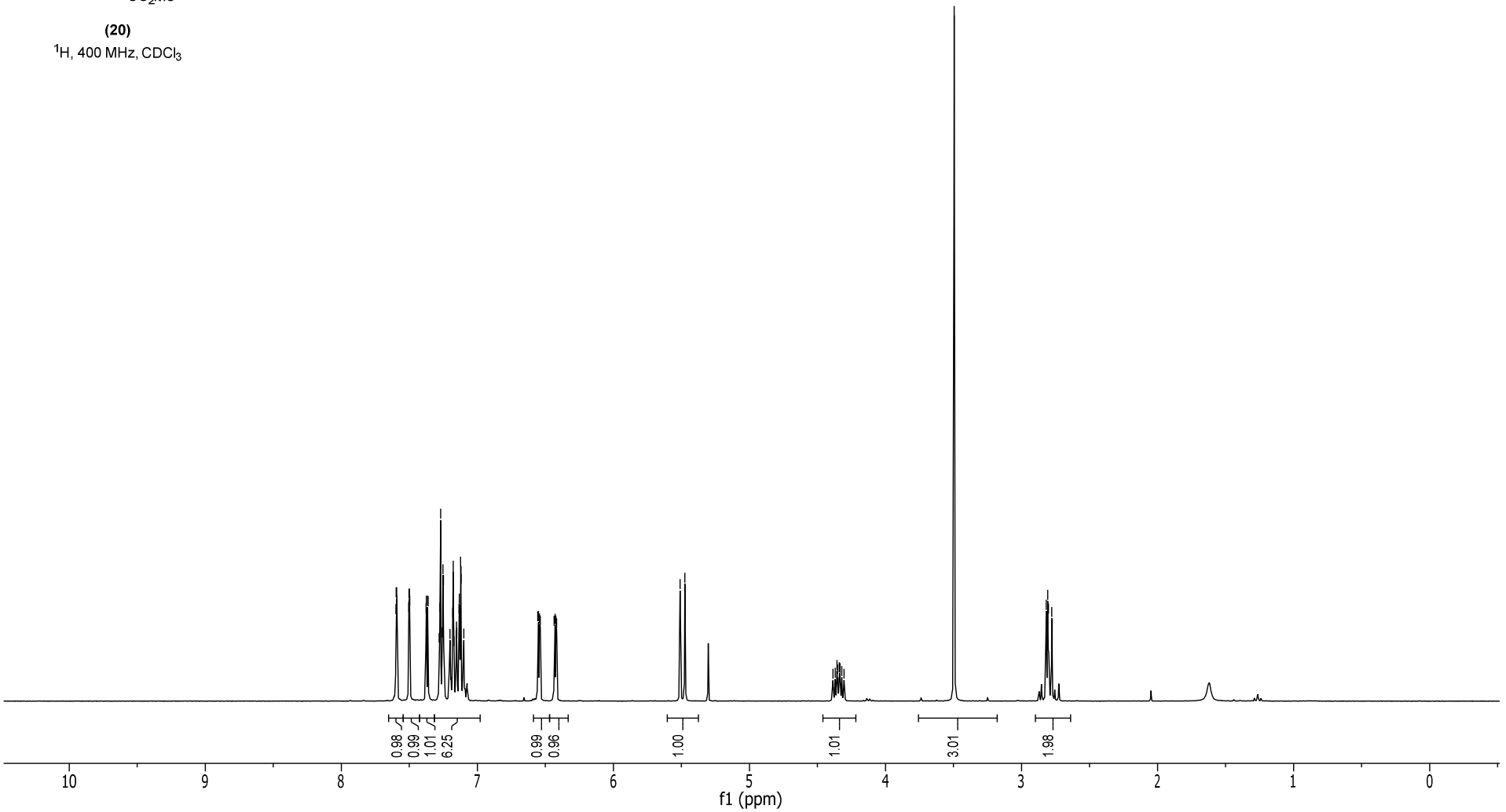
(19)

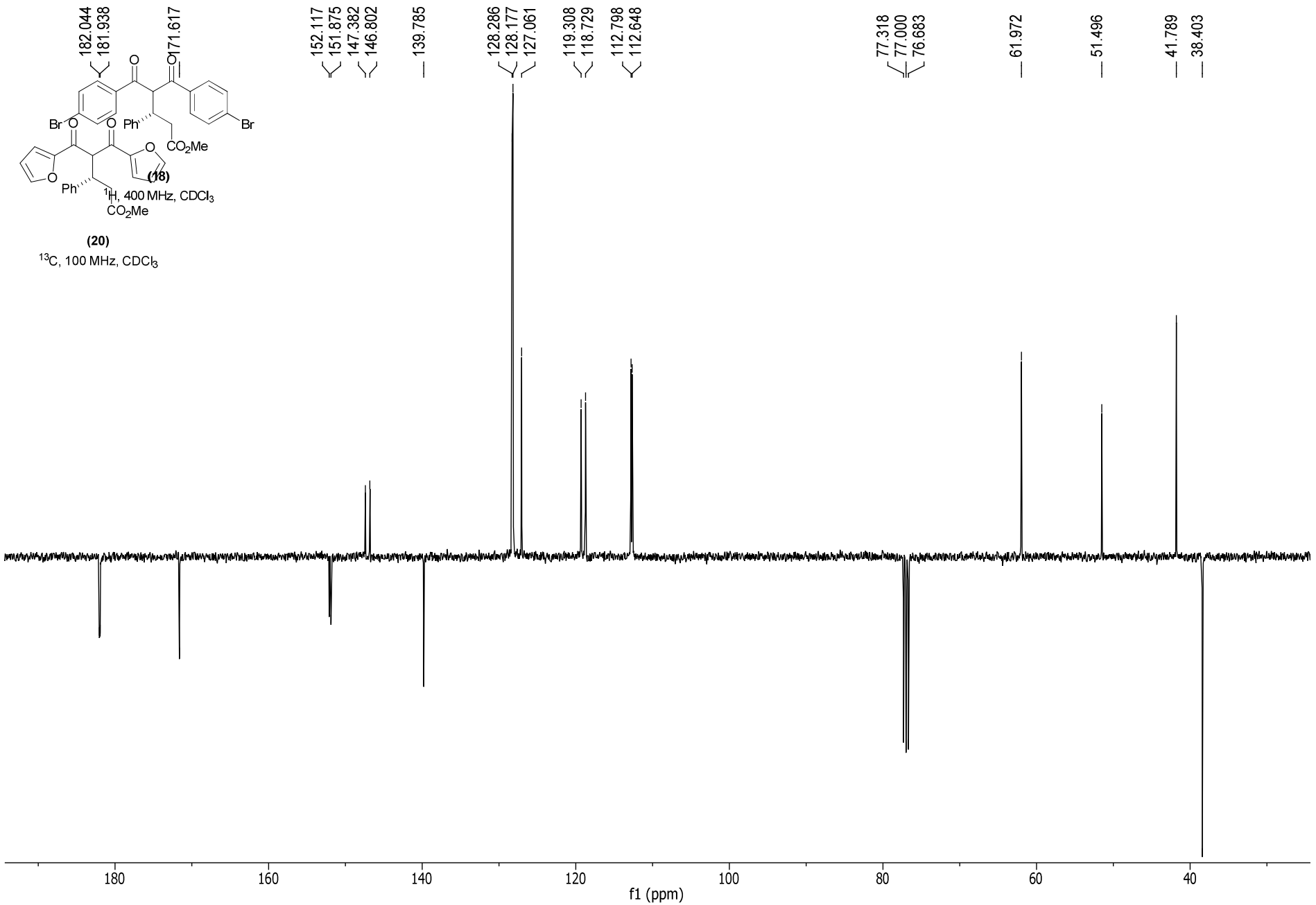
^{13}C, 126 MHz, $CDCl_3$

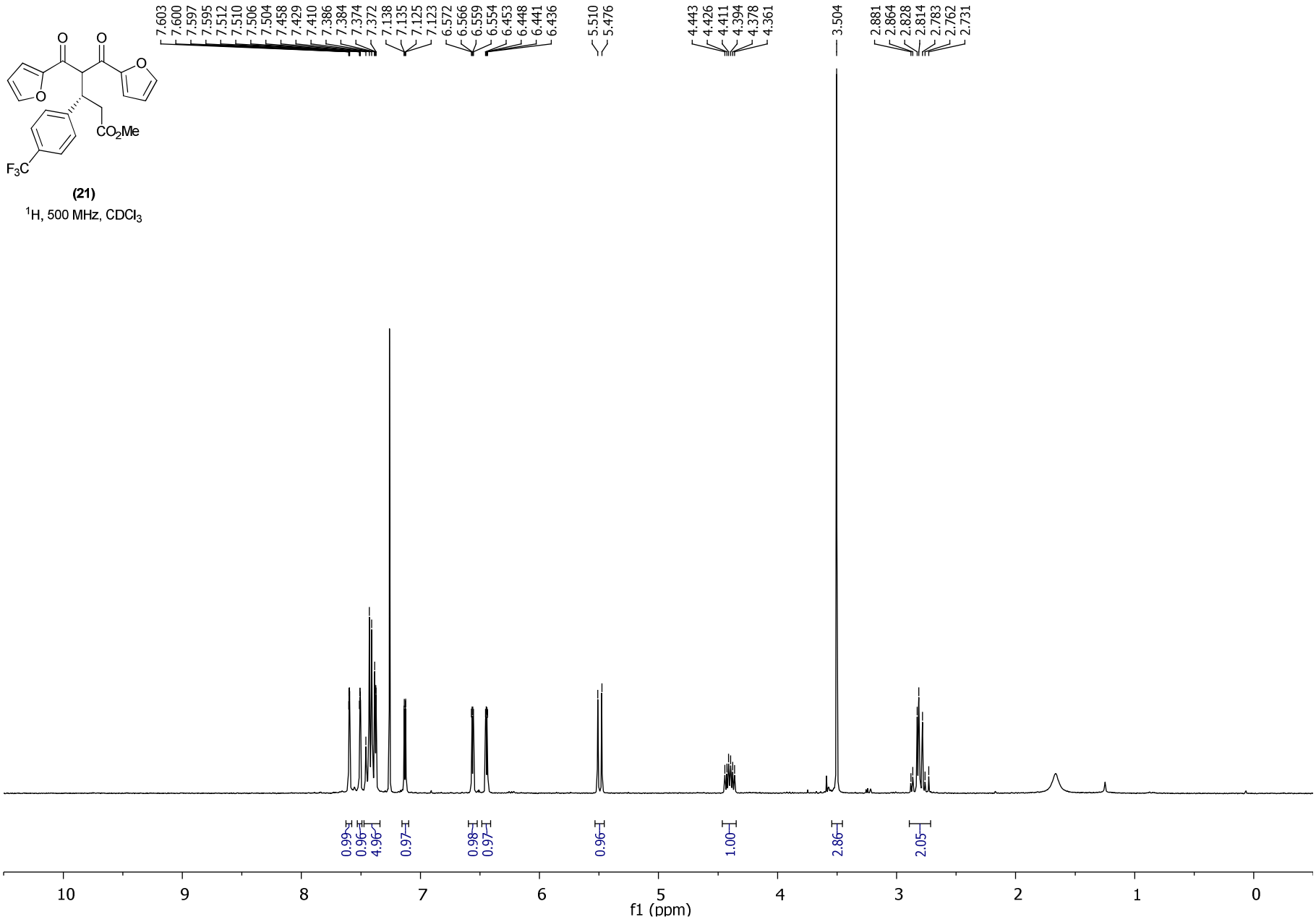


(20)

^{1}H, 400 MHz, $CDCl_3$

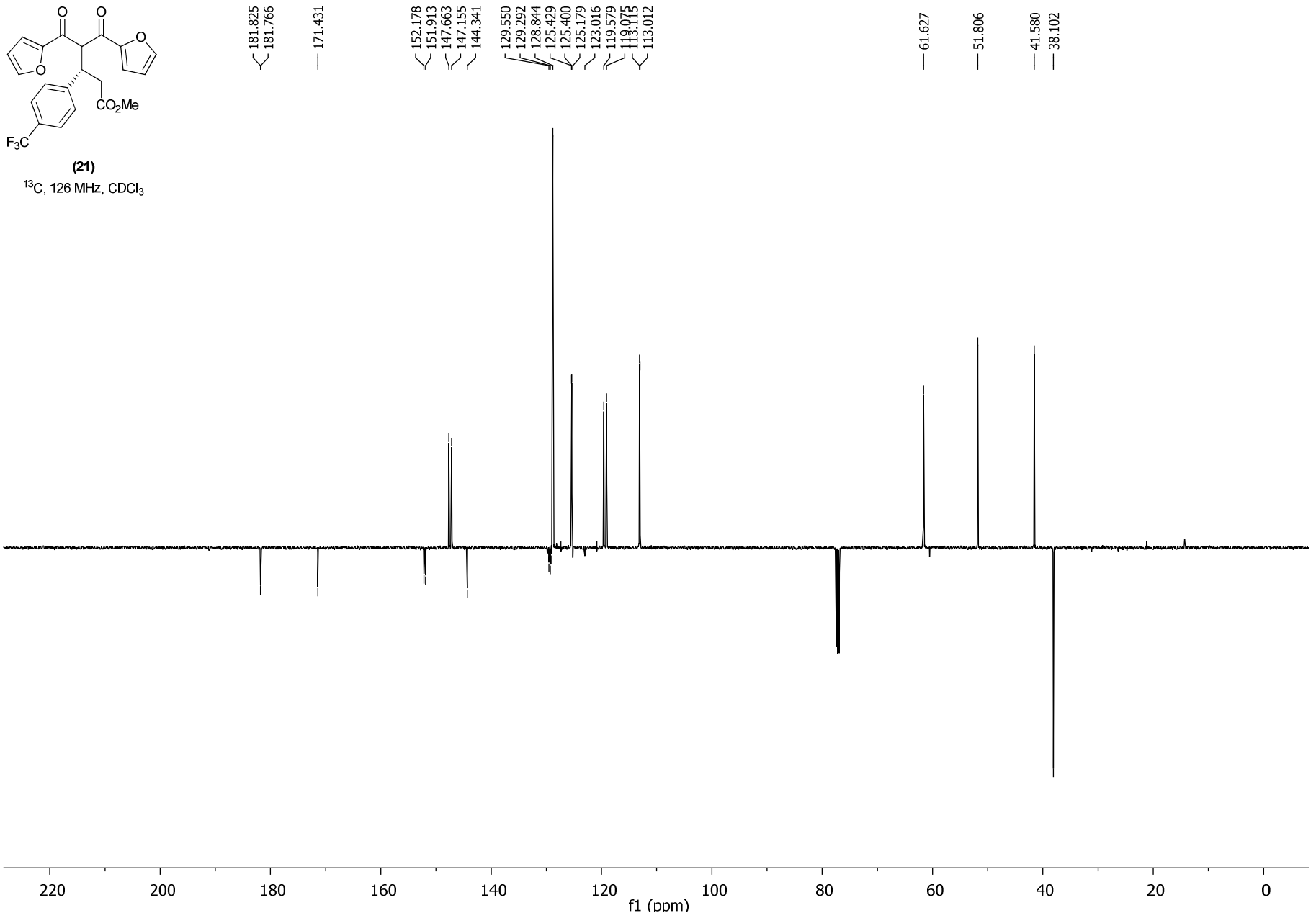






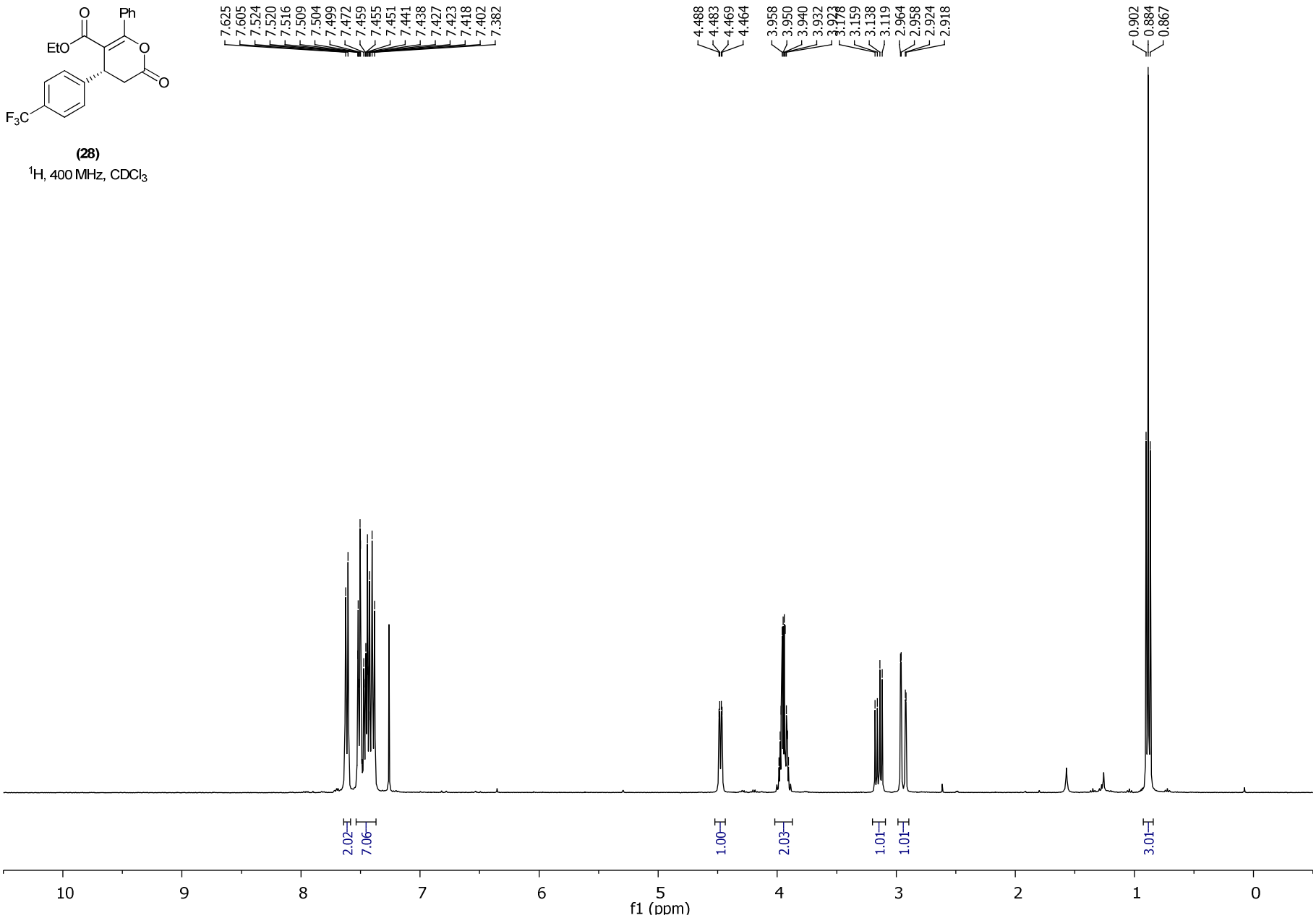
(21)

^{1}H, 500 MHz, $CDCl_3$



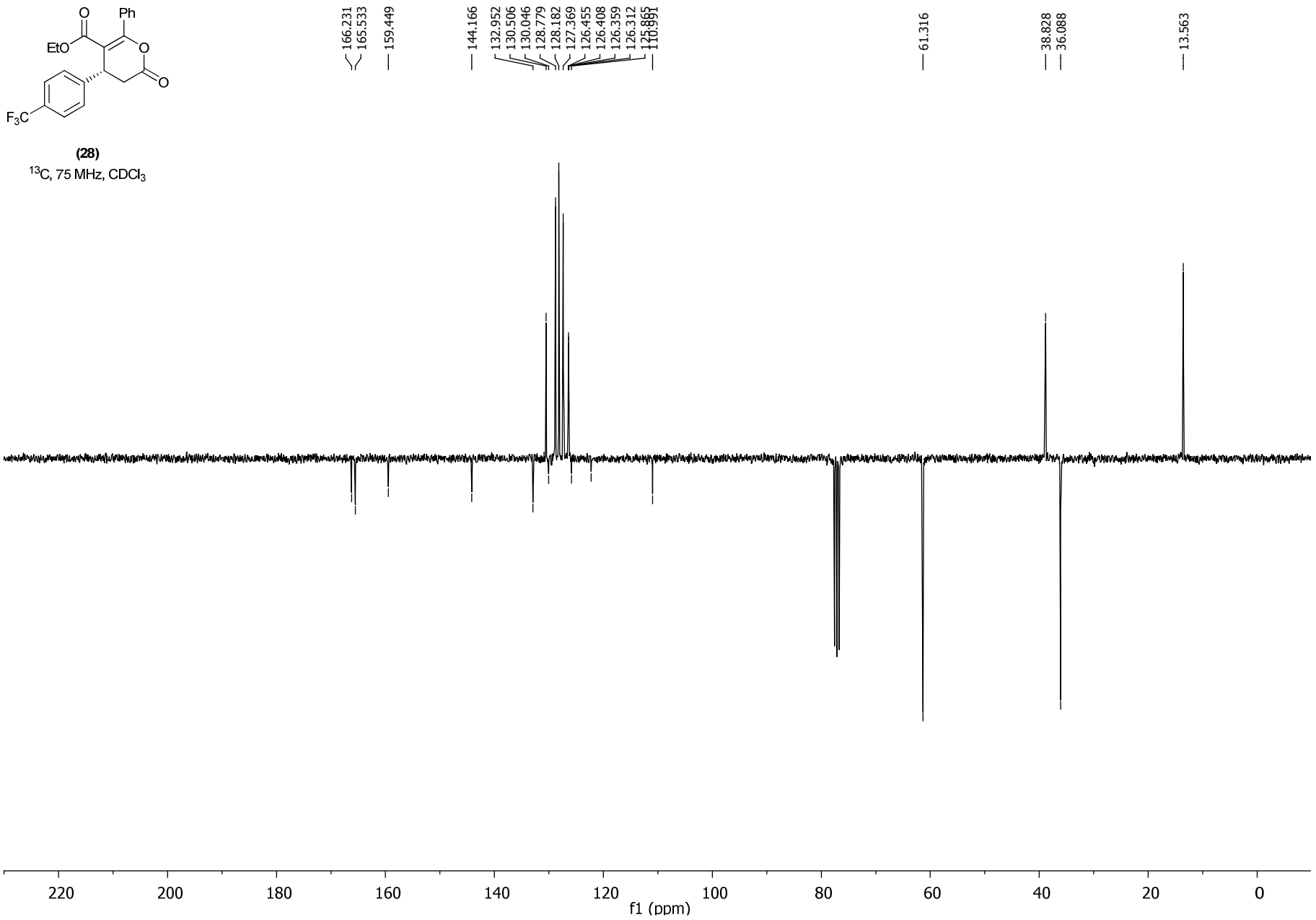
(21)

^{13}C, 126 MHz, $CDCl_3$



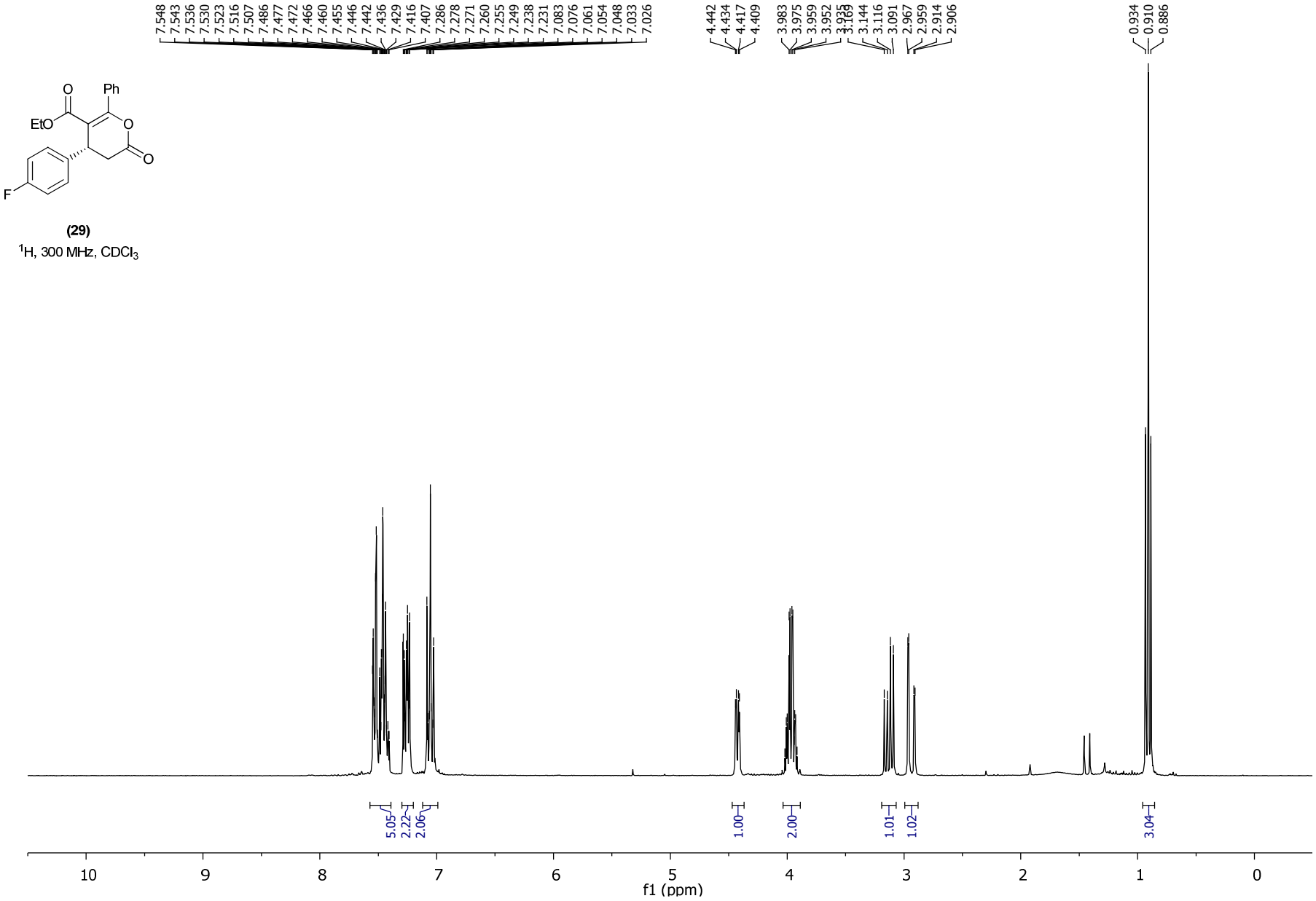
(28)

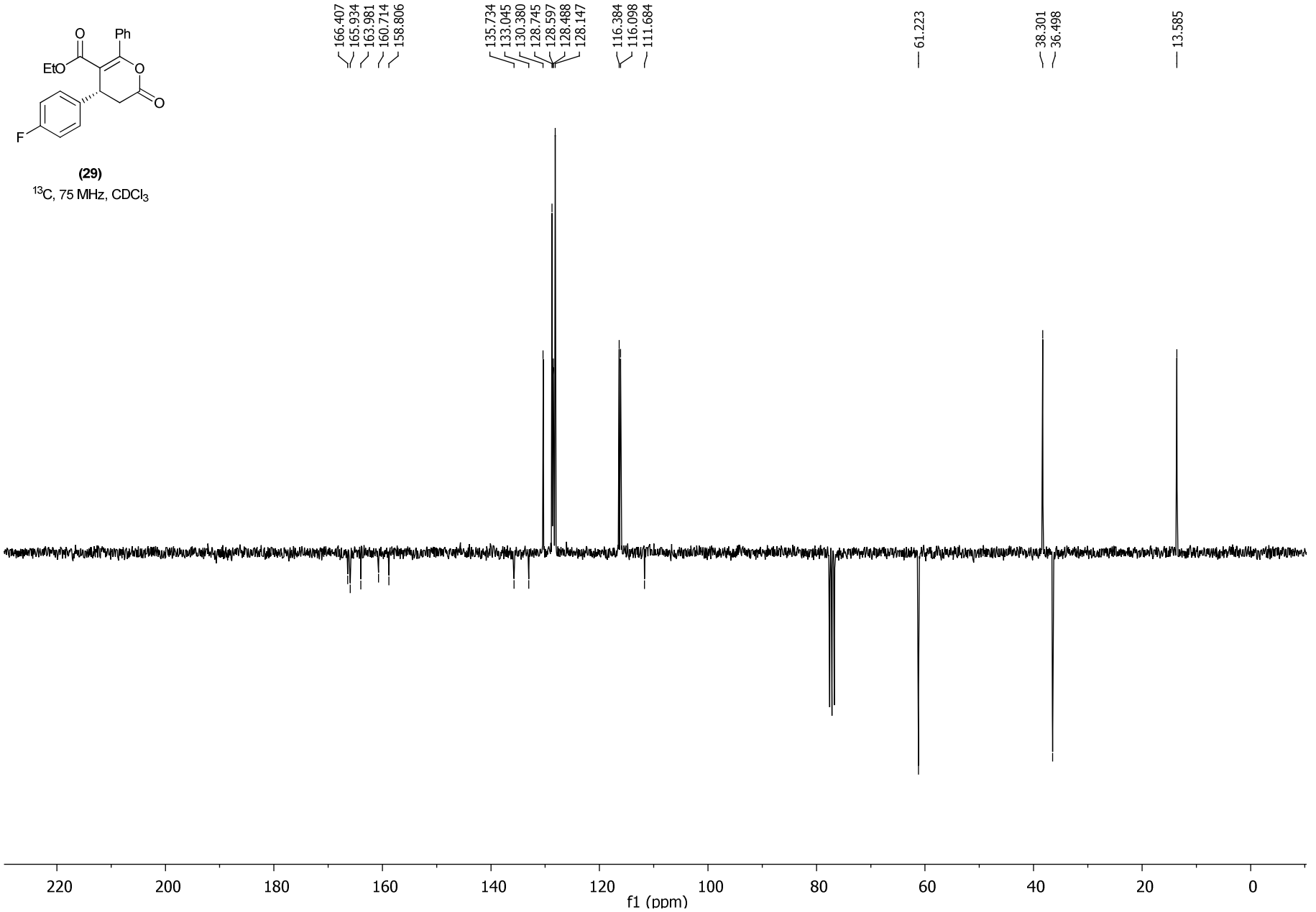
^{1}H, 400 MHz, $CDCl_3$



(28)

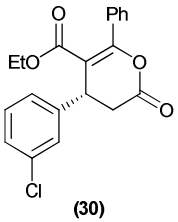
^{13}C, 75 MHz, $CDCl_3$





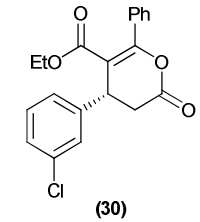
(29)

^{13}C, 75 MHz, $CDCl_3$



(30)

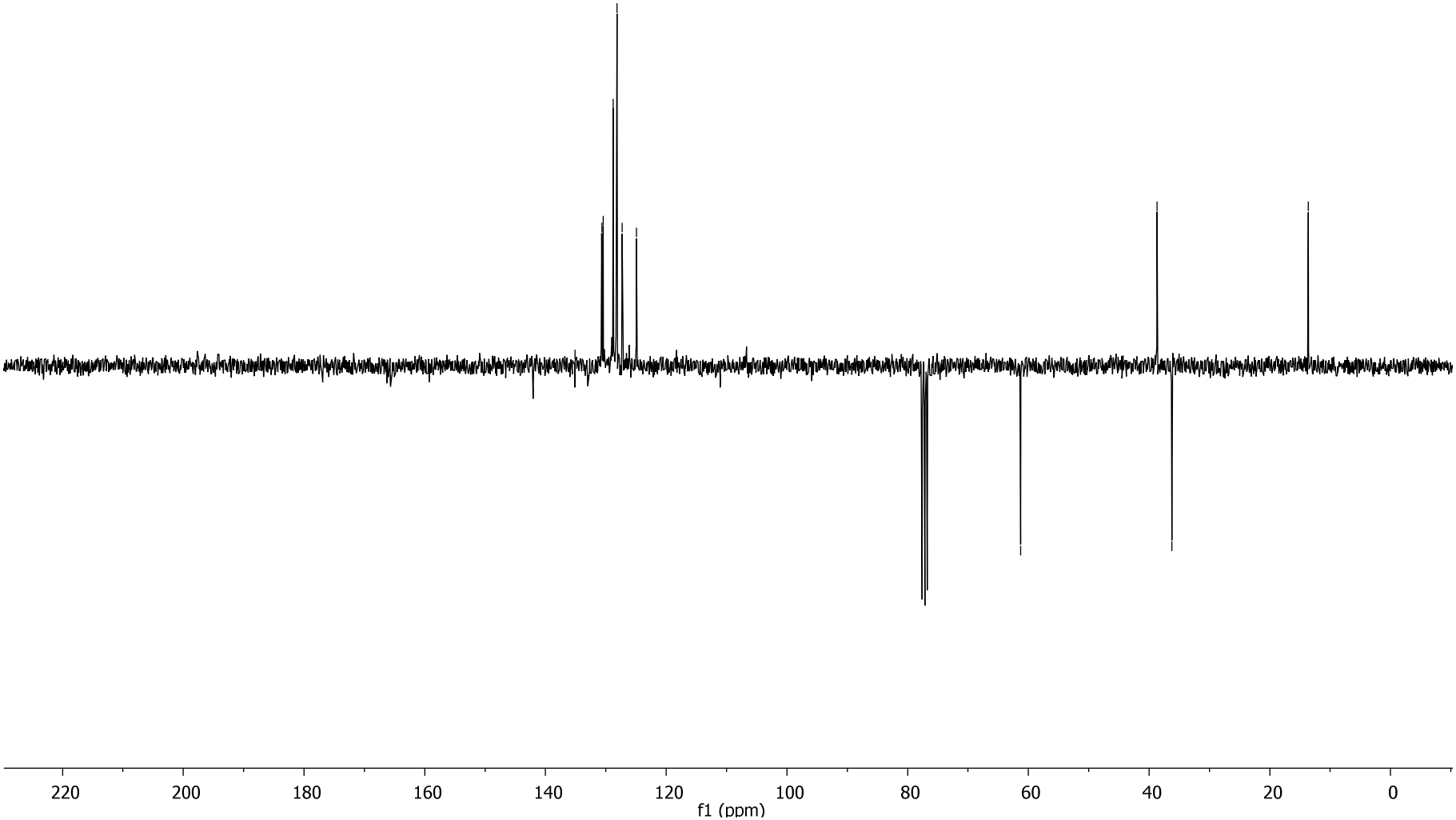
^{1}H, 400 MHz, $CDCl_3$

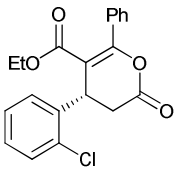


(30)

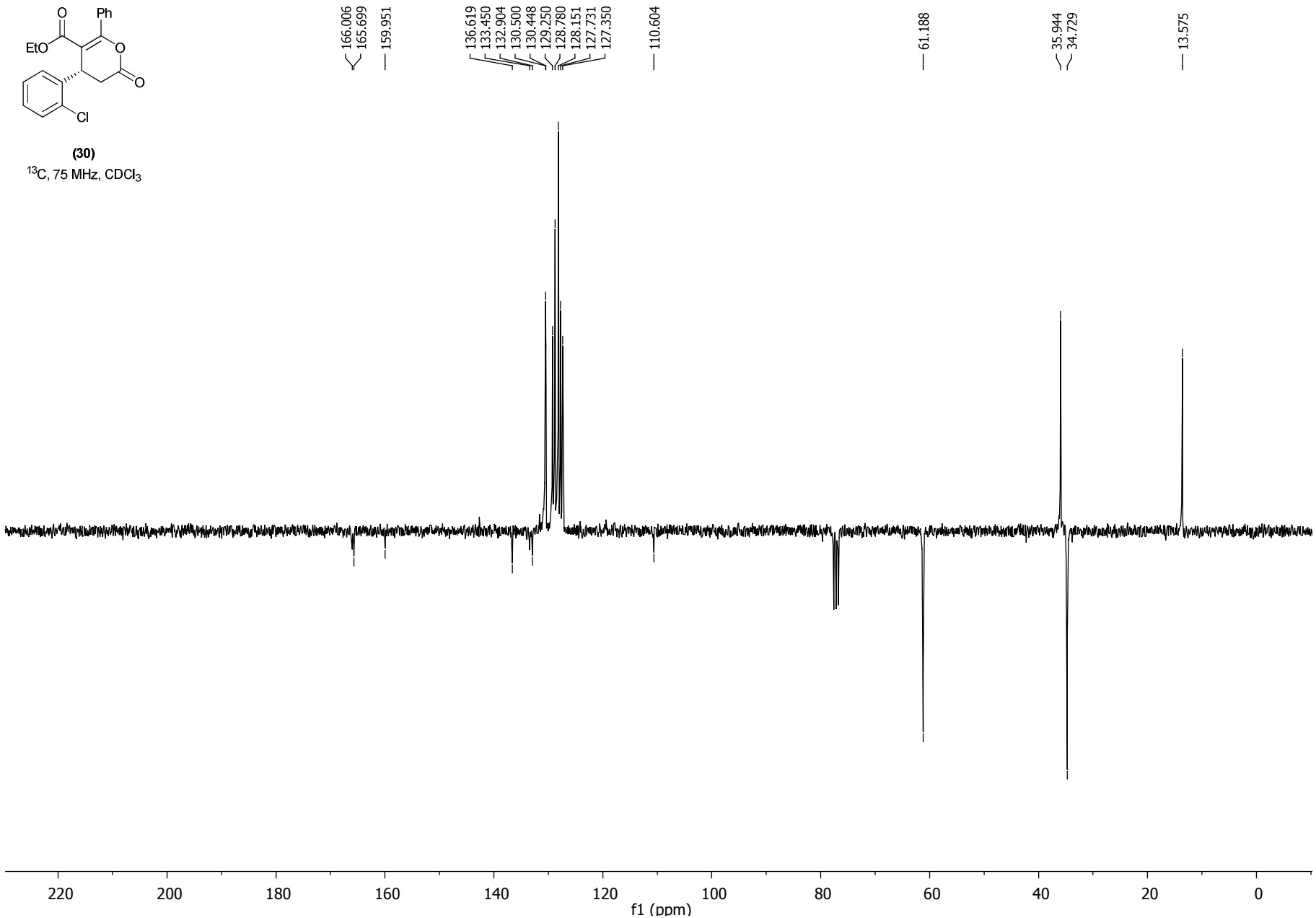
^{13}C, 75 MHz, $CDCl_3$

166.251
165.666
159.248
142.053
135.090
132.981
130.668
130.445
128.789
128.164
127.314
124.940
111.061
61.286
38.672
36.217
13.605



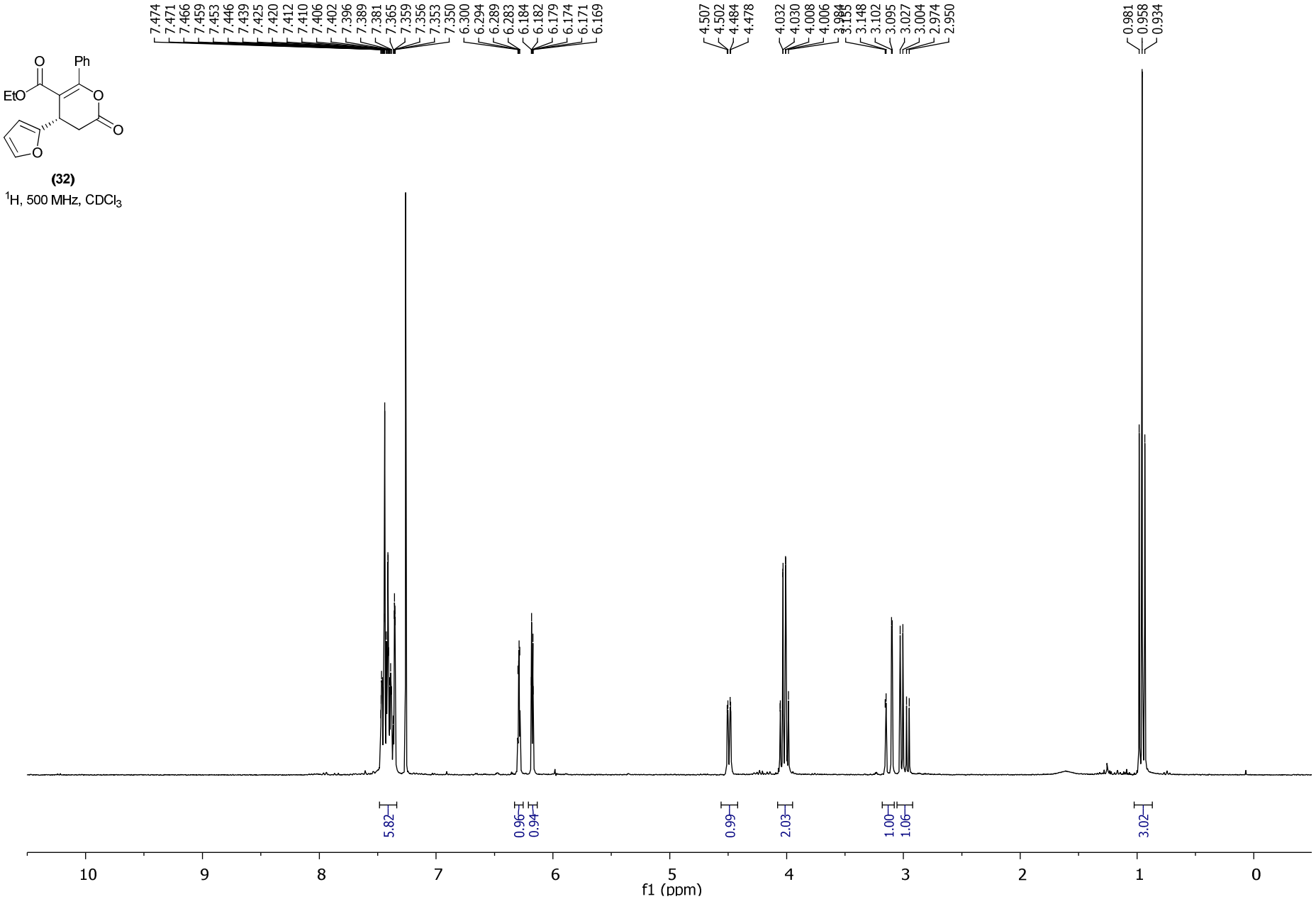


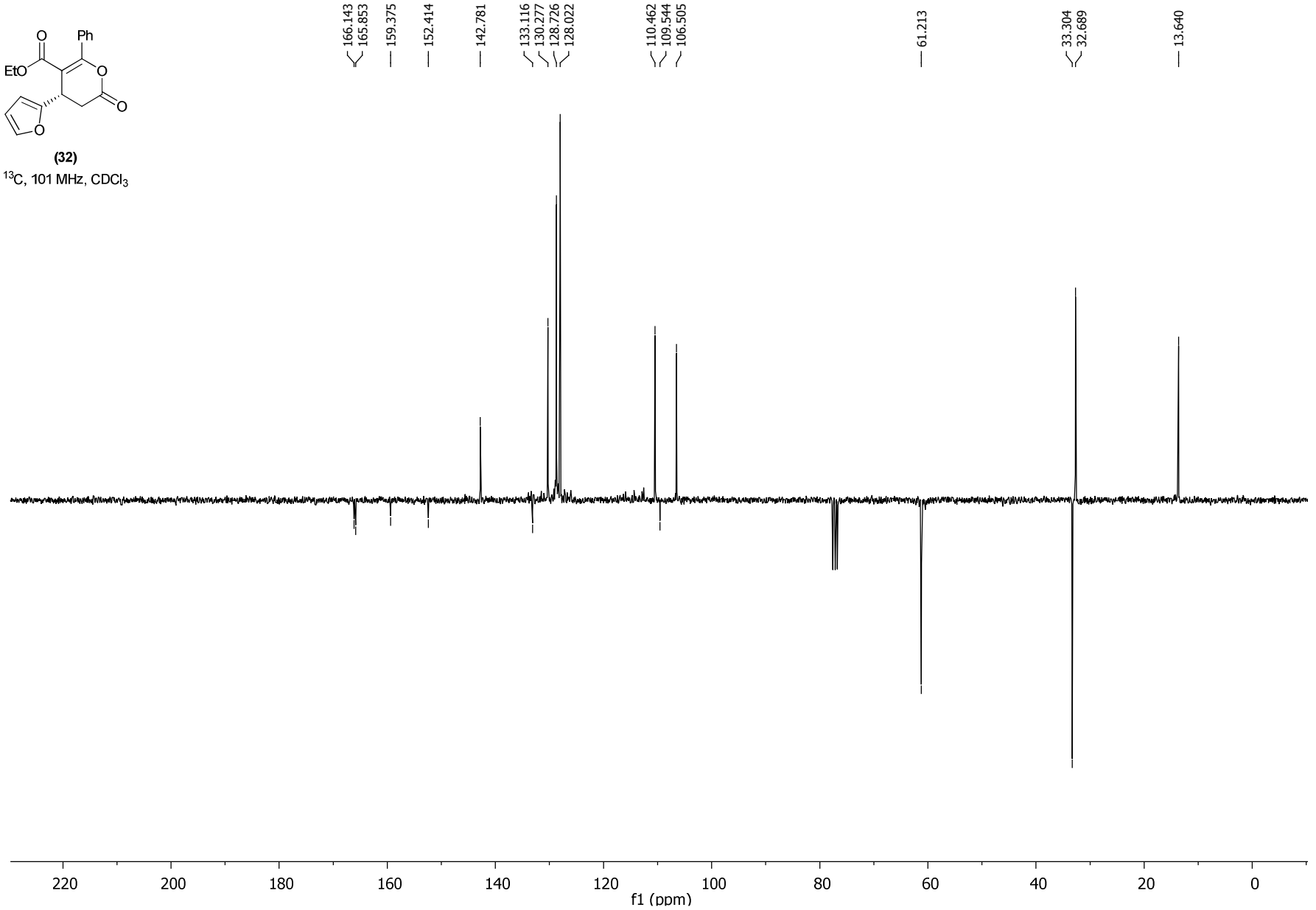
(31)
^{1}H, 300 MHz, $CDCl_3$

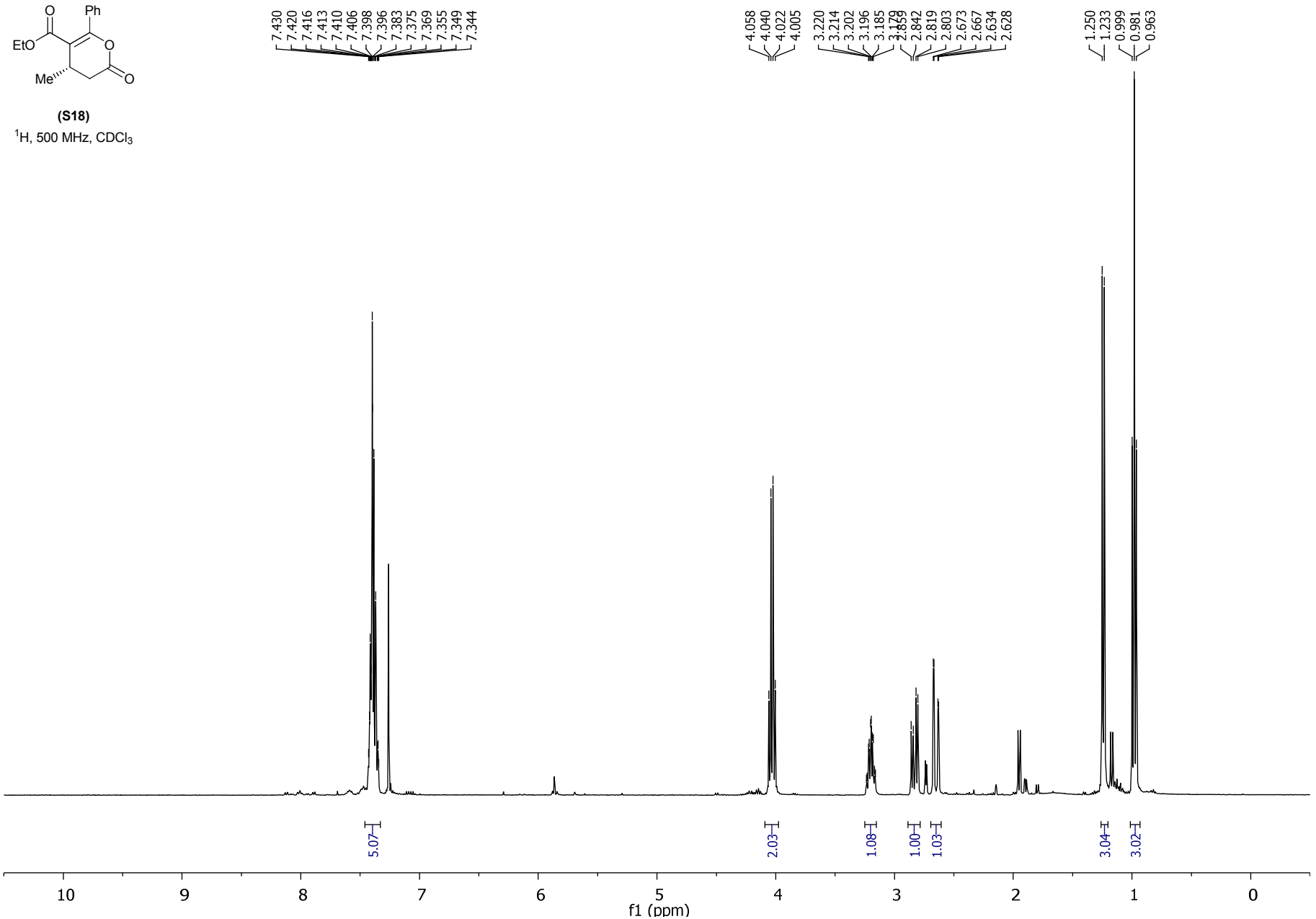


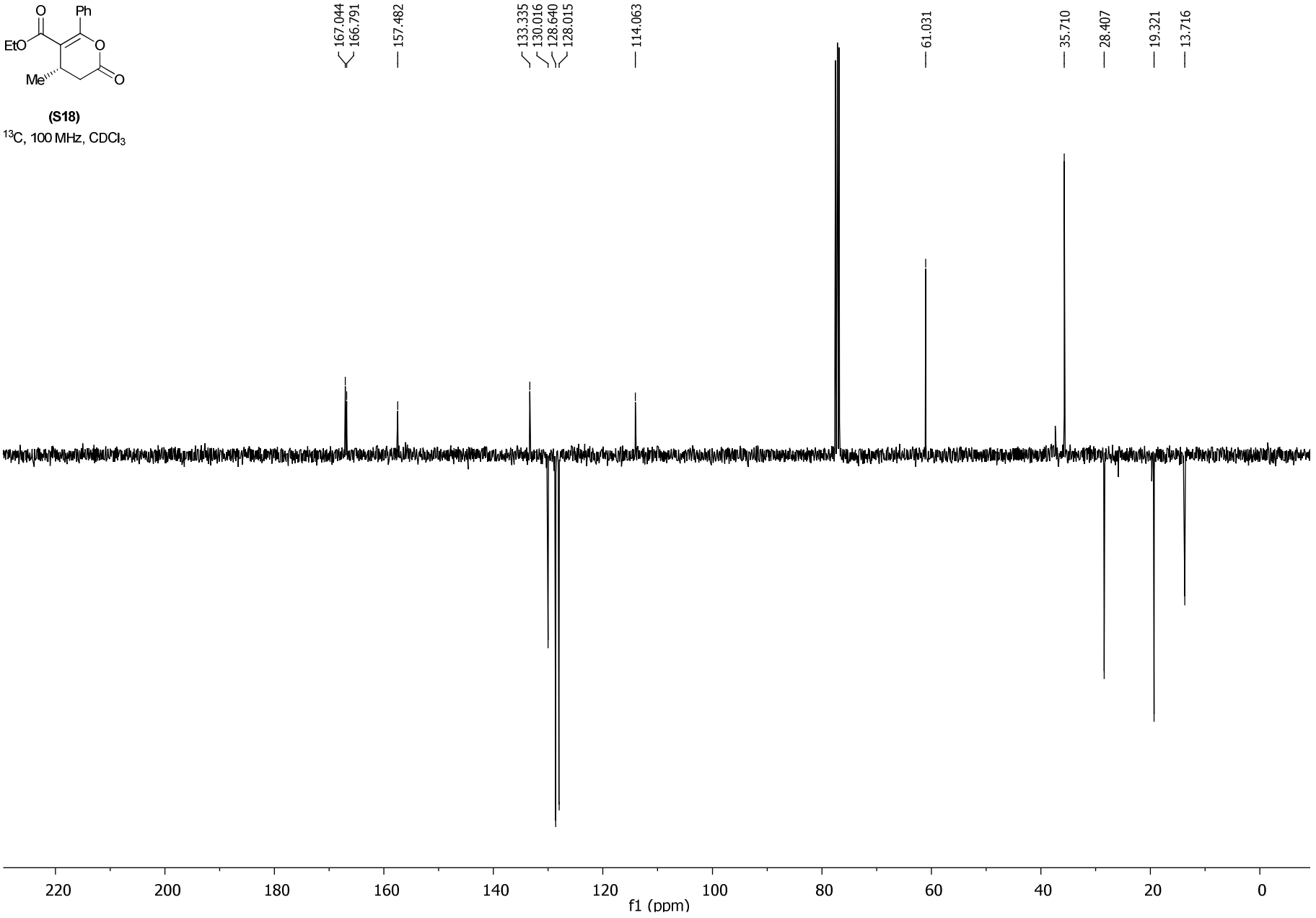
(30)

^{13}C, 75 MHz, $CDCl_3$



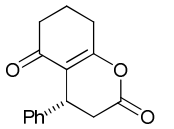






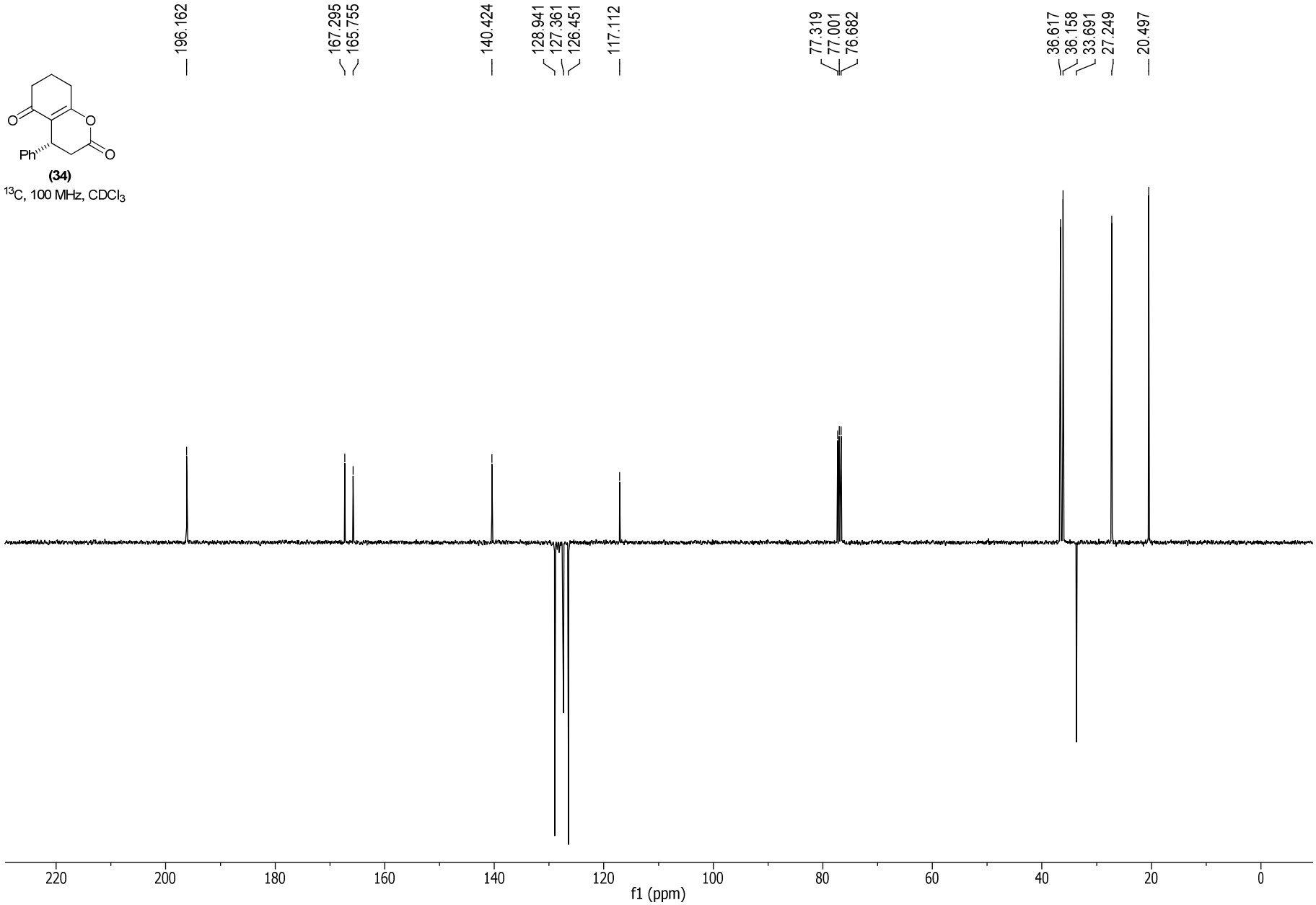
(S18)

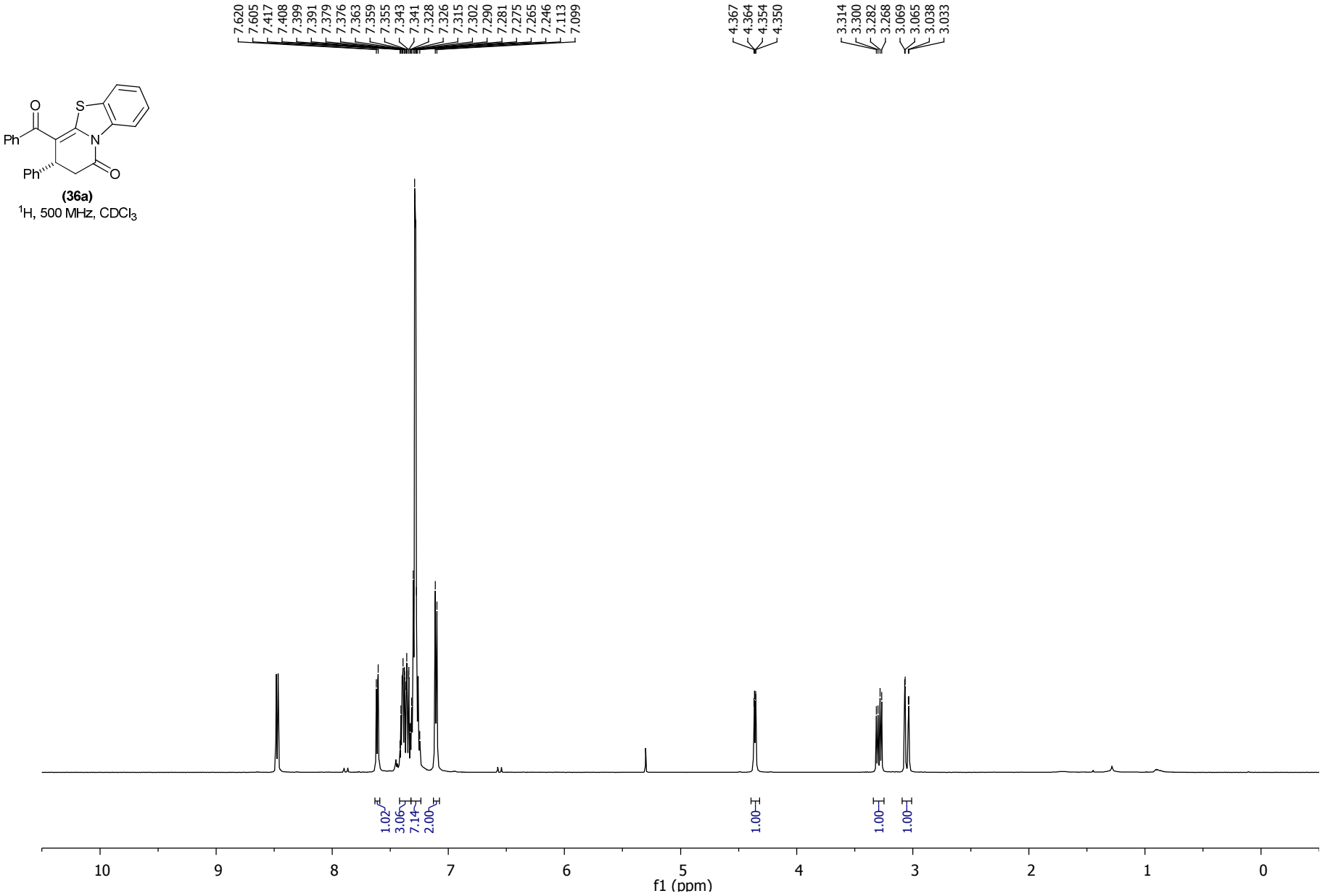
^{13}C, 100 MHz, $CDCl_3$



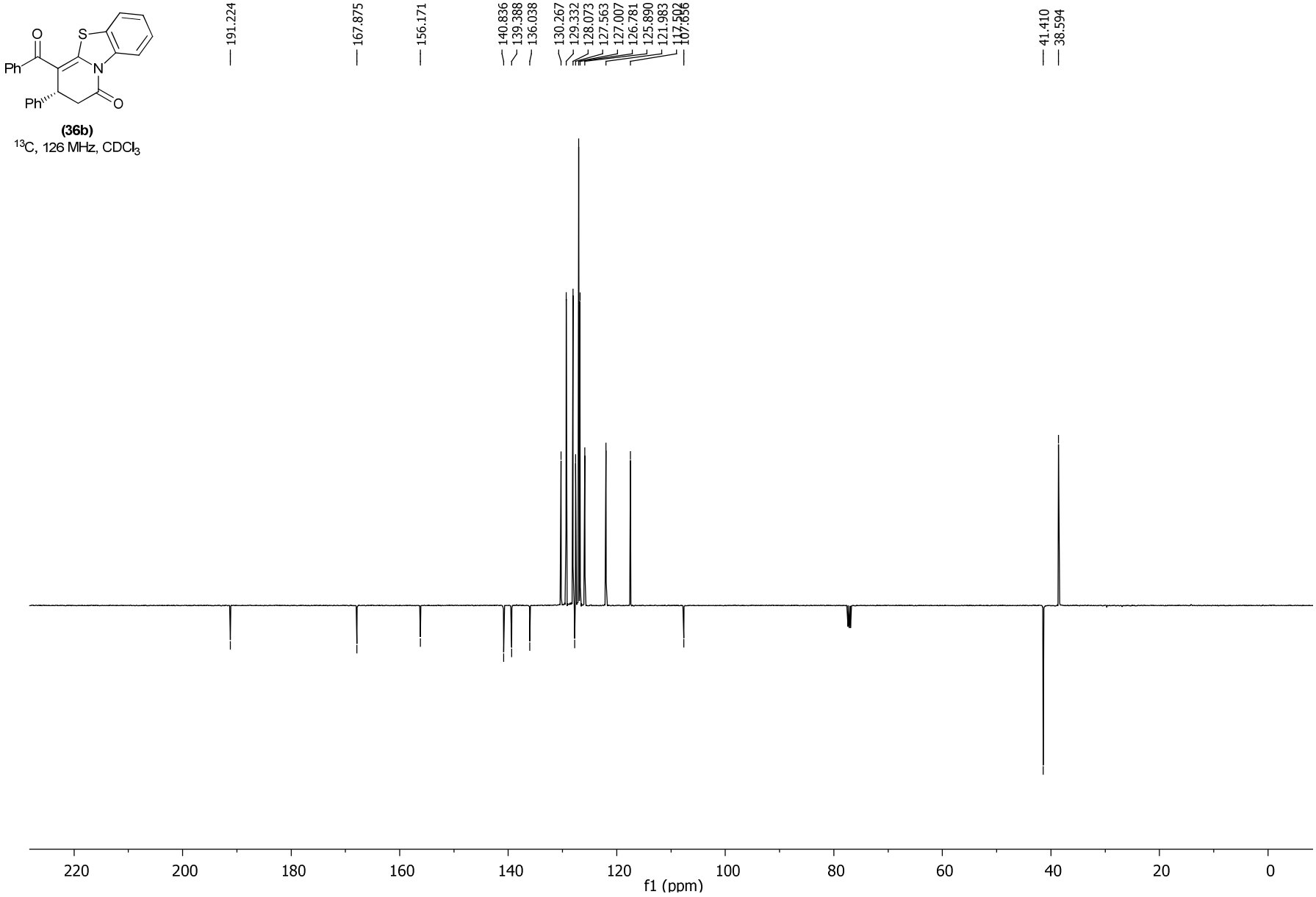
(34)

^{1}H, 400 MHz, $CDCl_3$

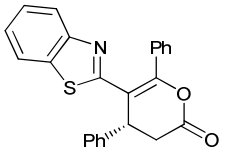




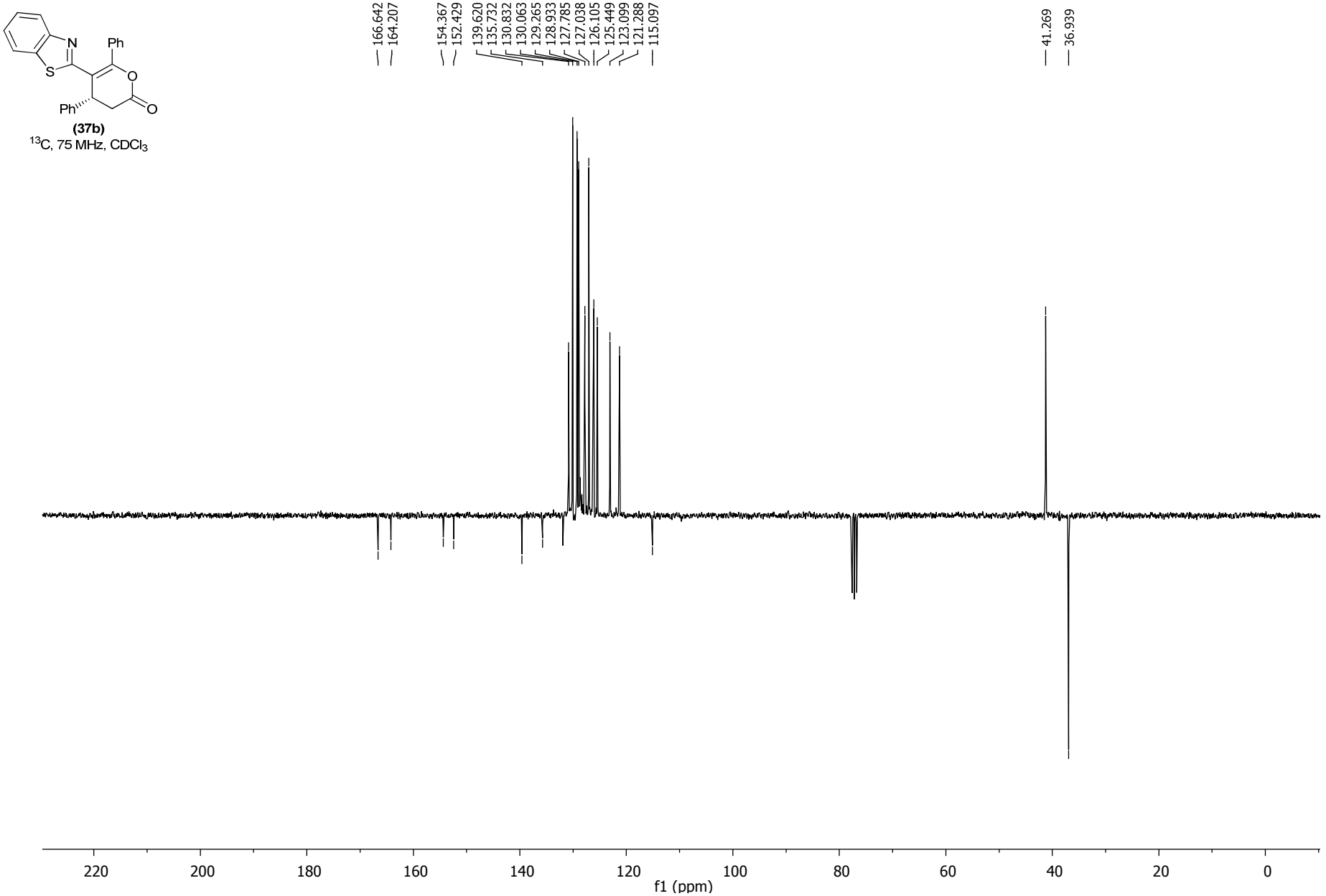
(36a)
^{1}H, 500 MHz, $CDCl_3$

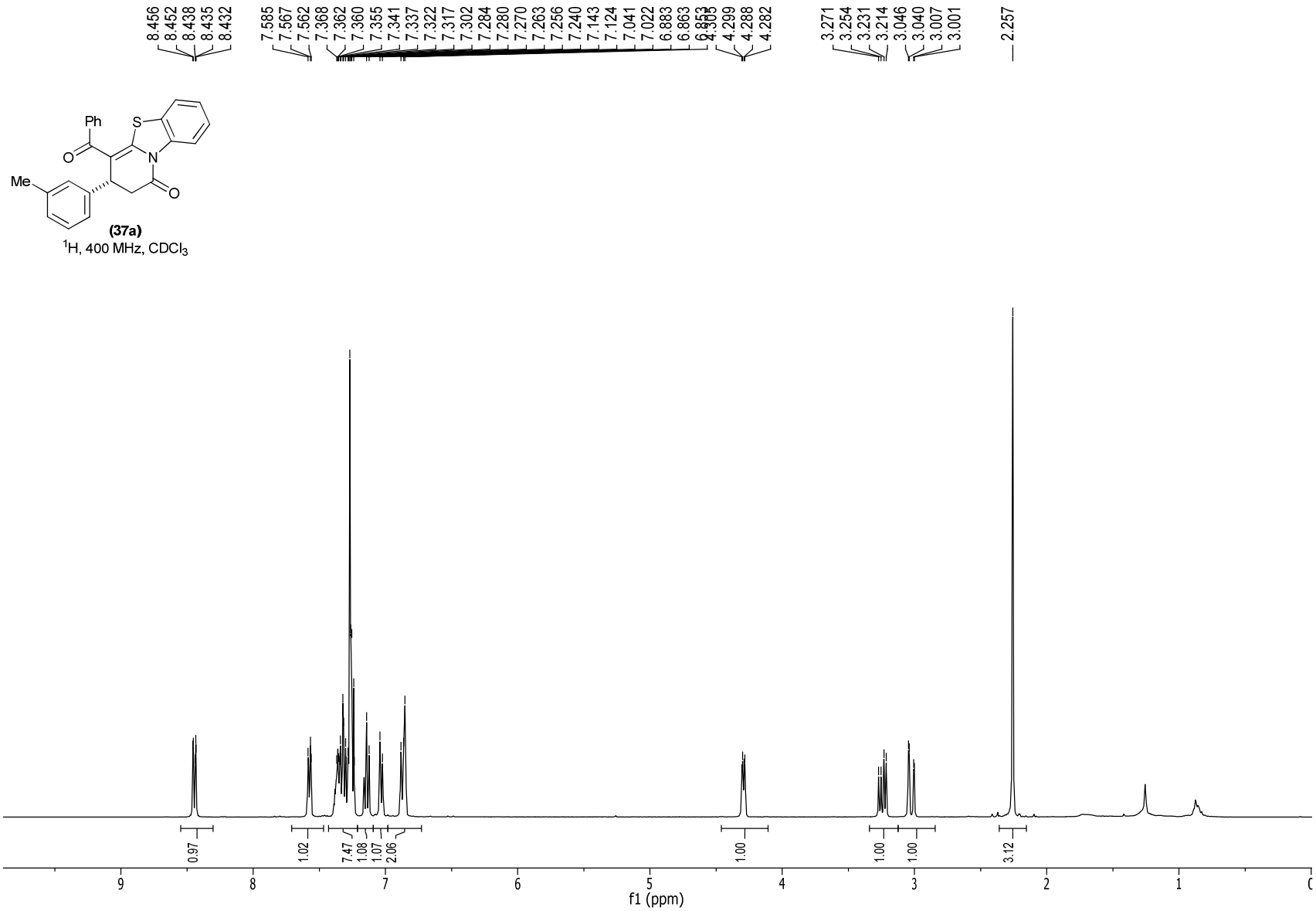


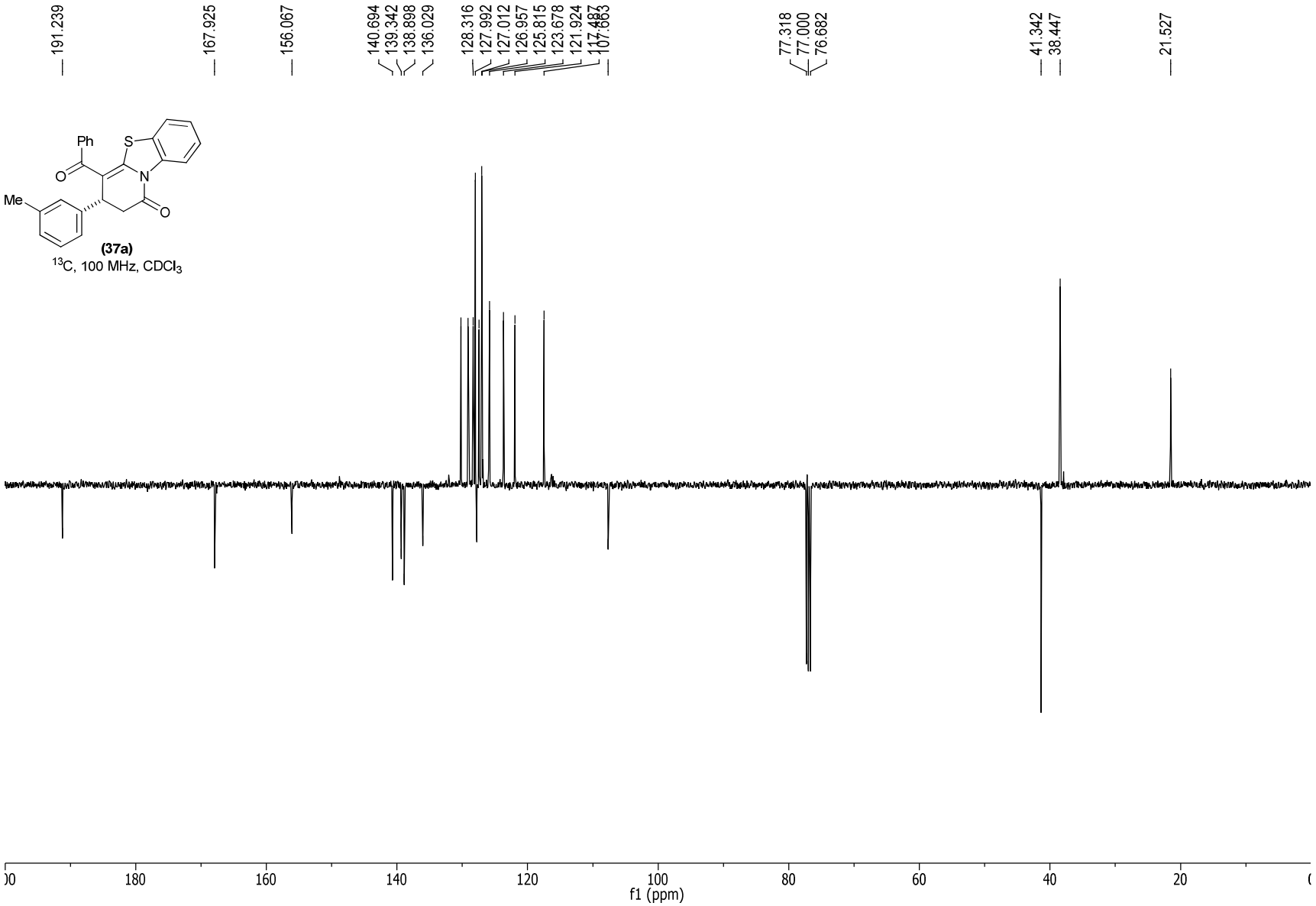
(36b)
^{13}C, 126 MHz, $CDCl_3$

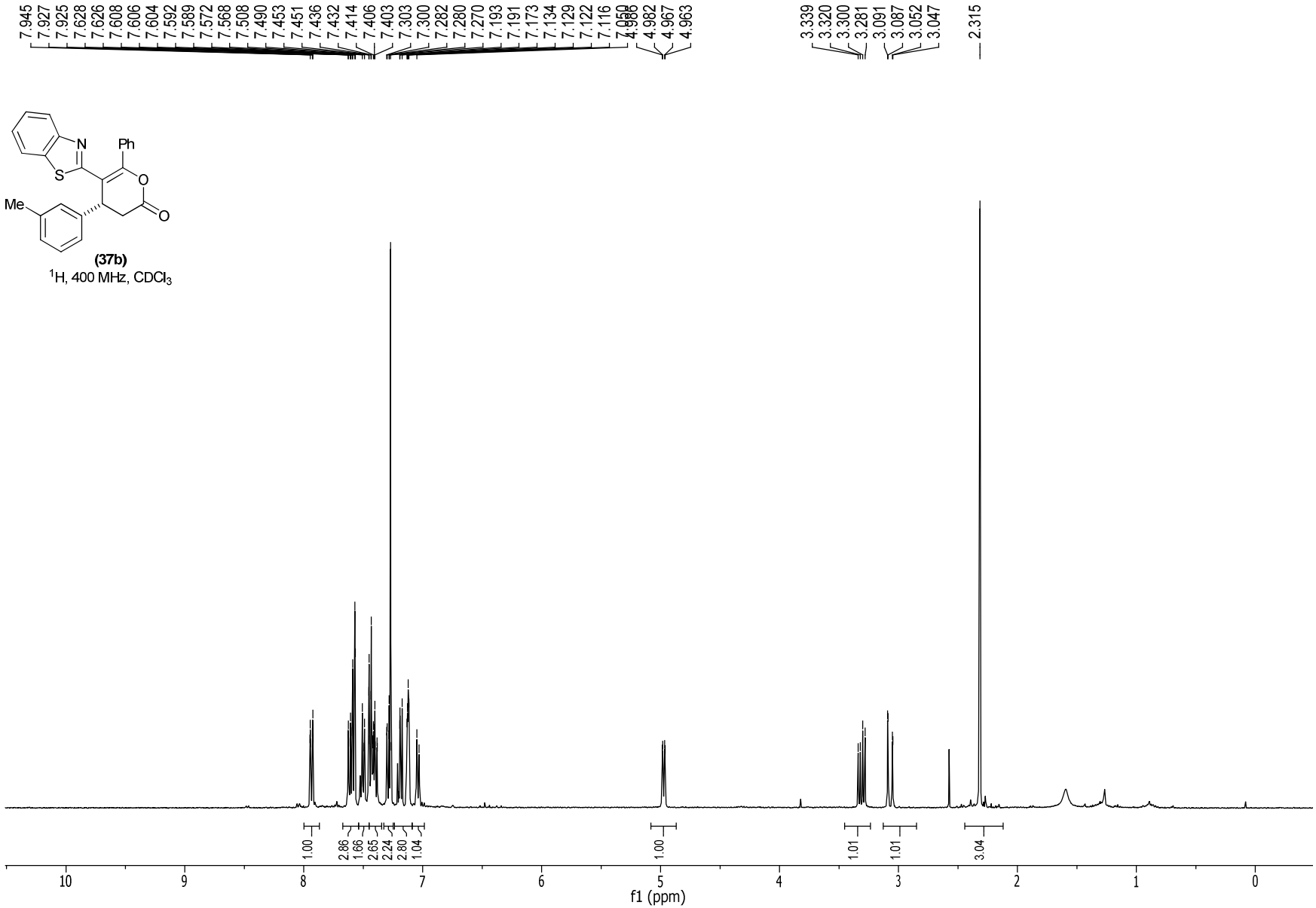


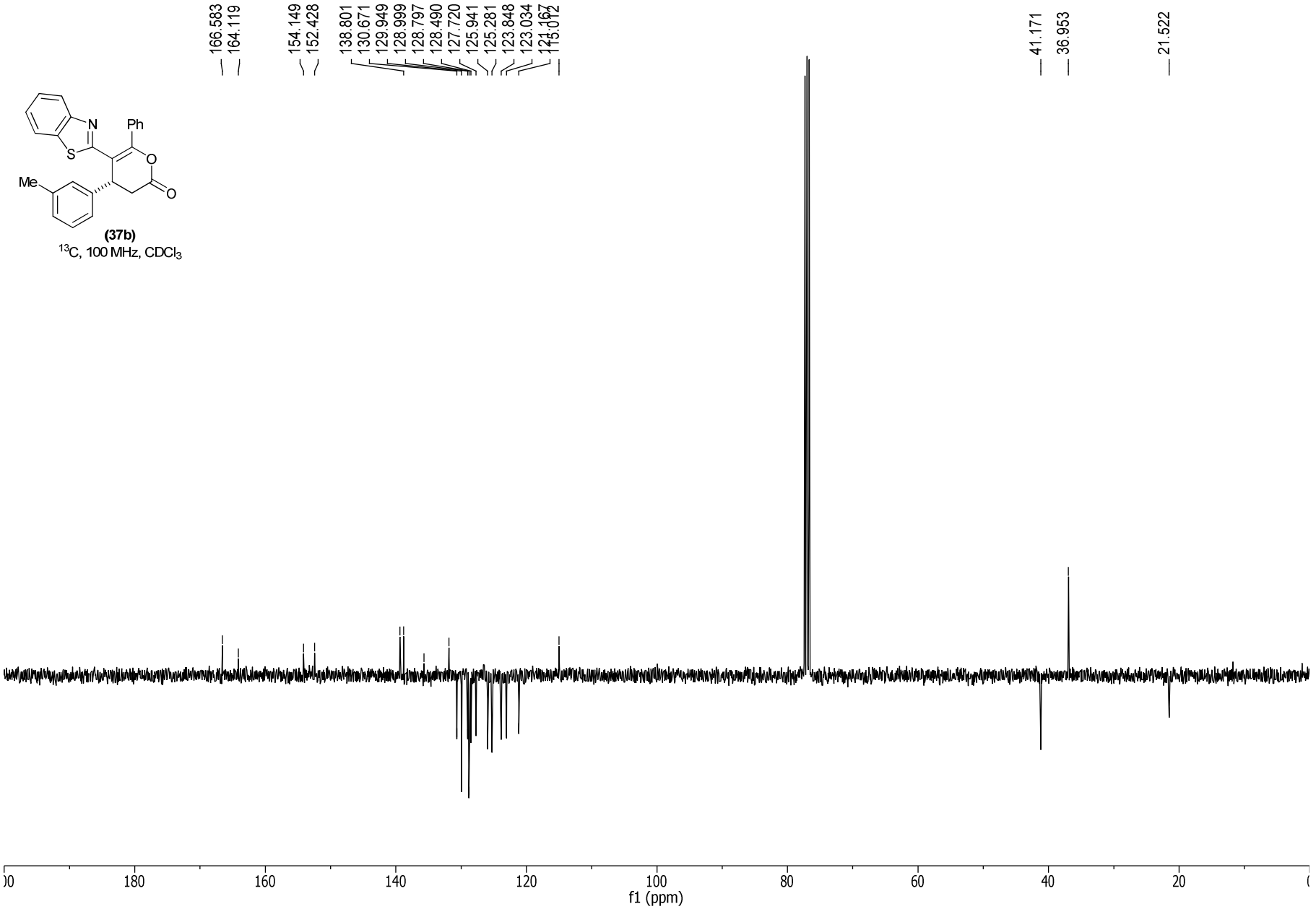
(37a)
^{1}H, 300 MHz, $CDCl_3$

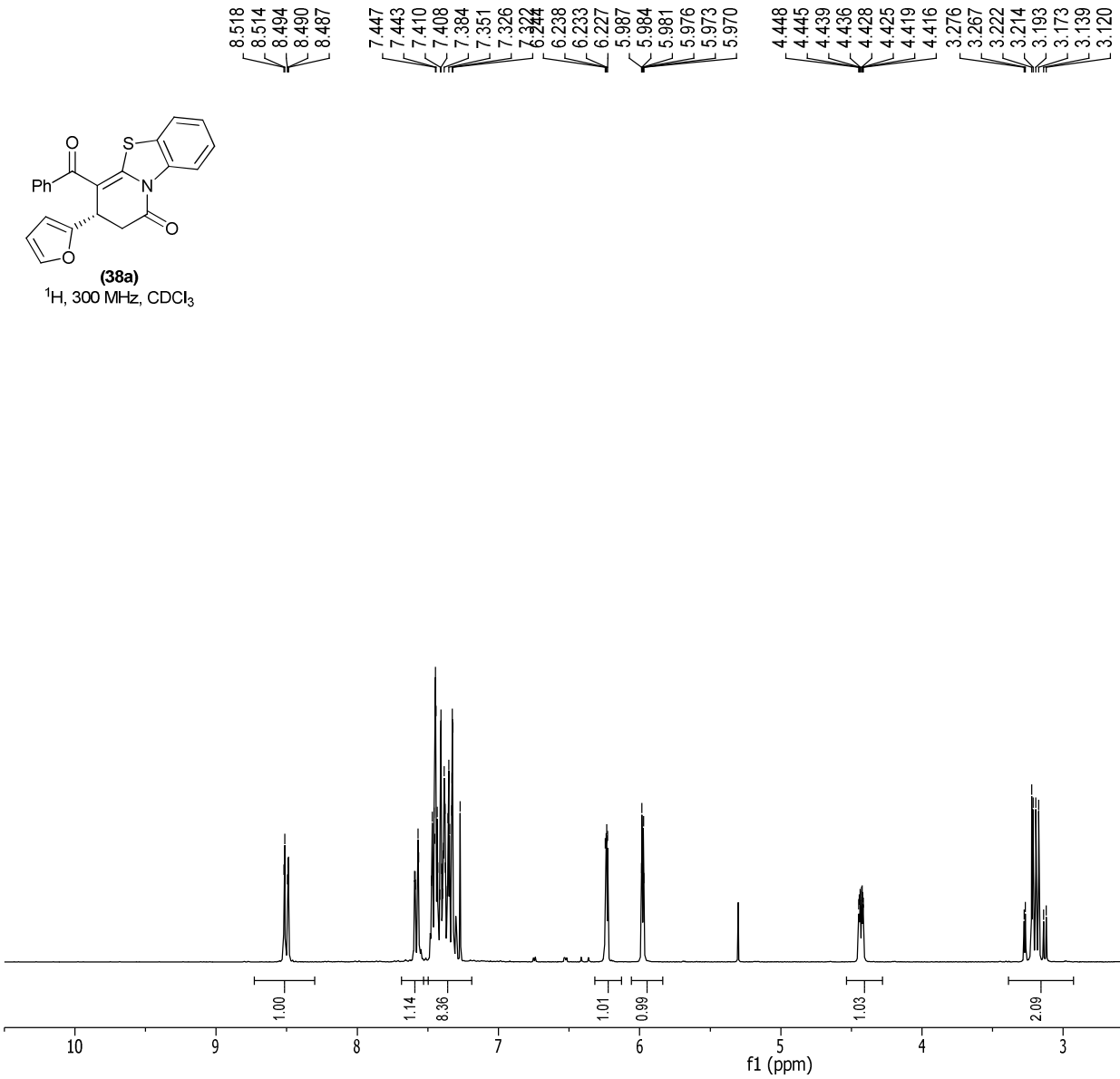




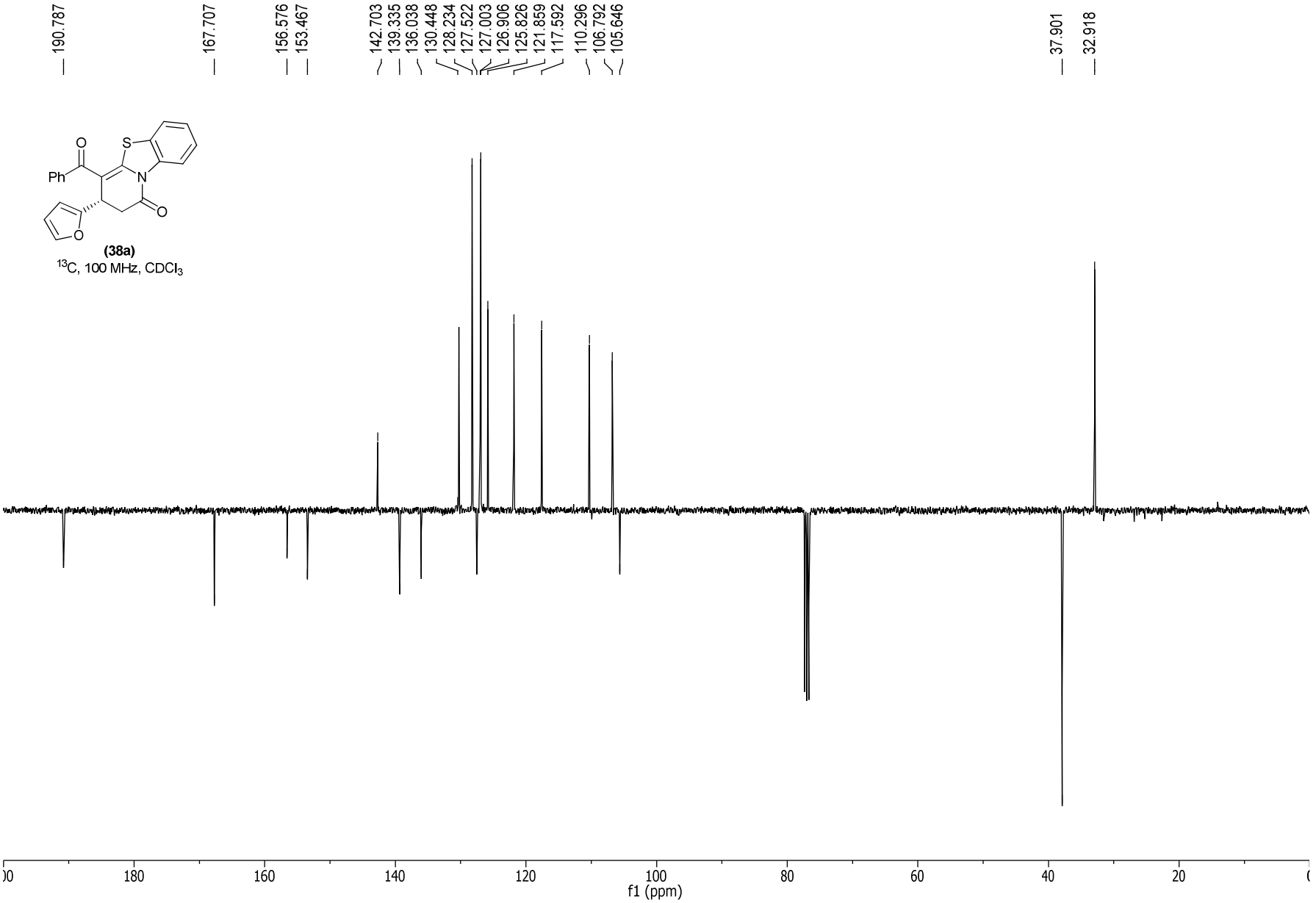


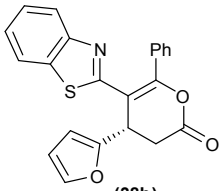






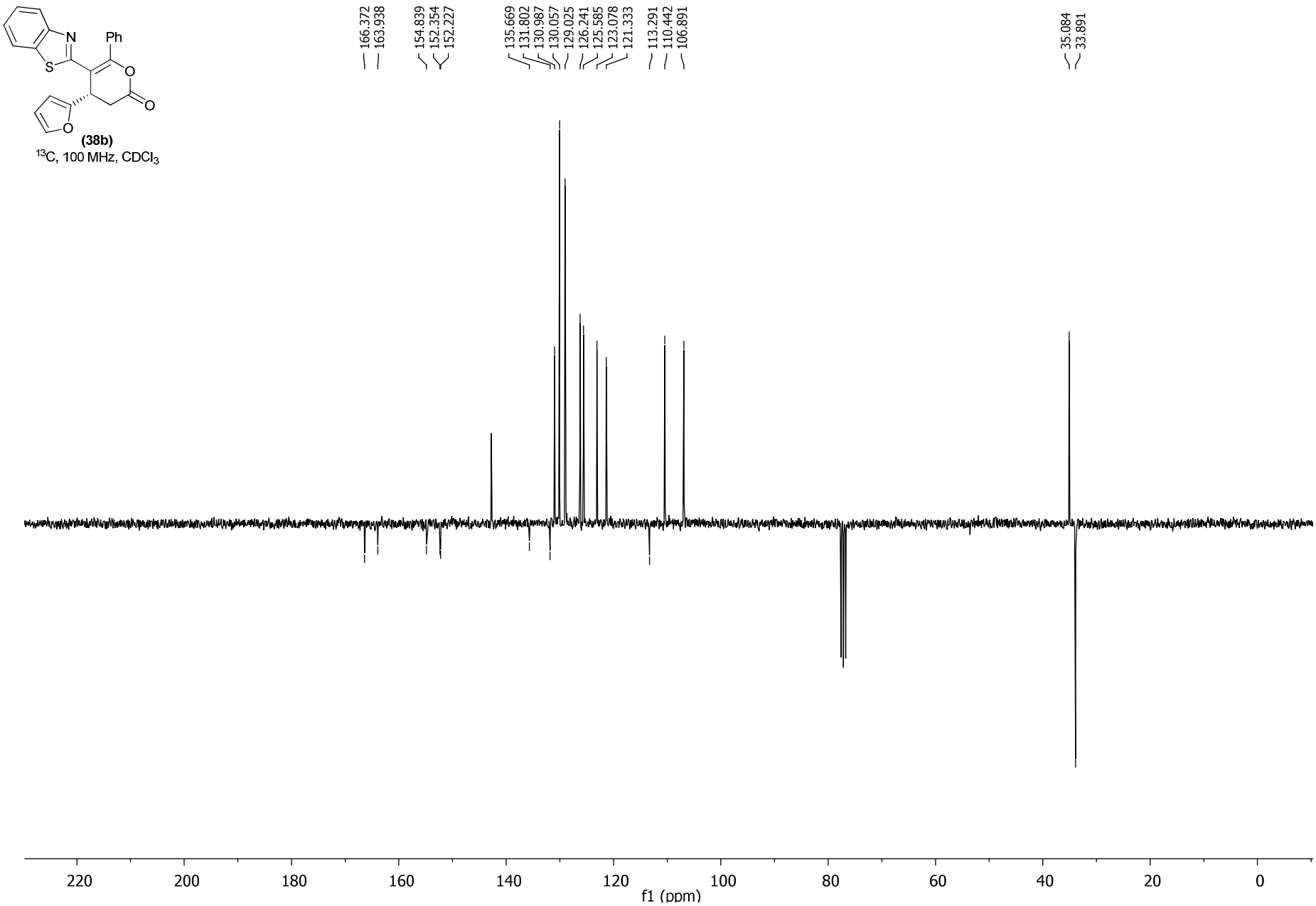
(38a)
^{1}H, 300 MHz, $CDCl_3$

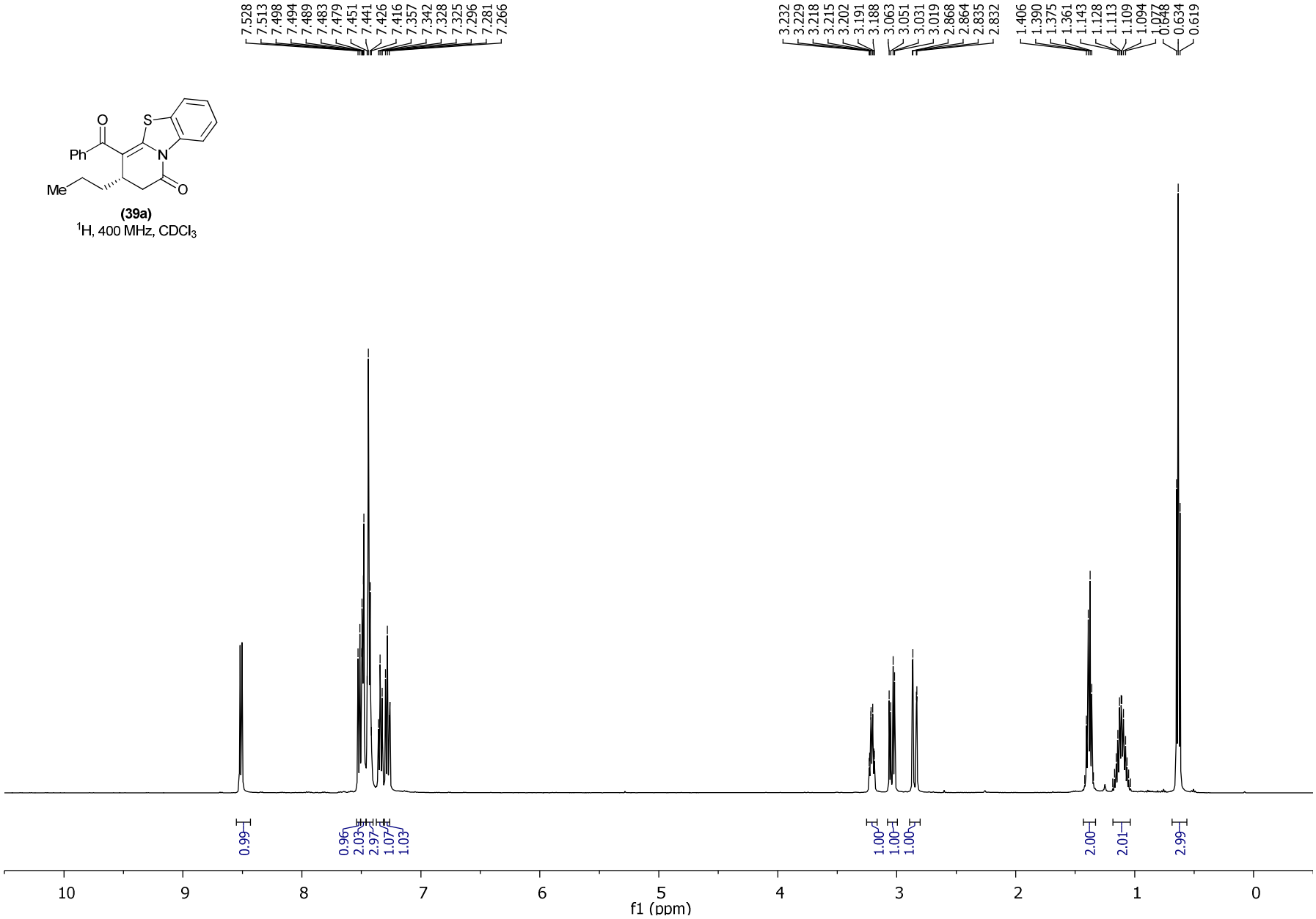


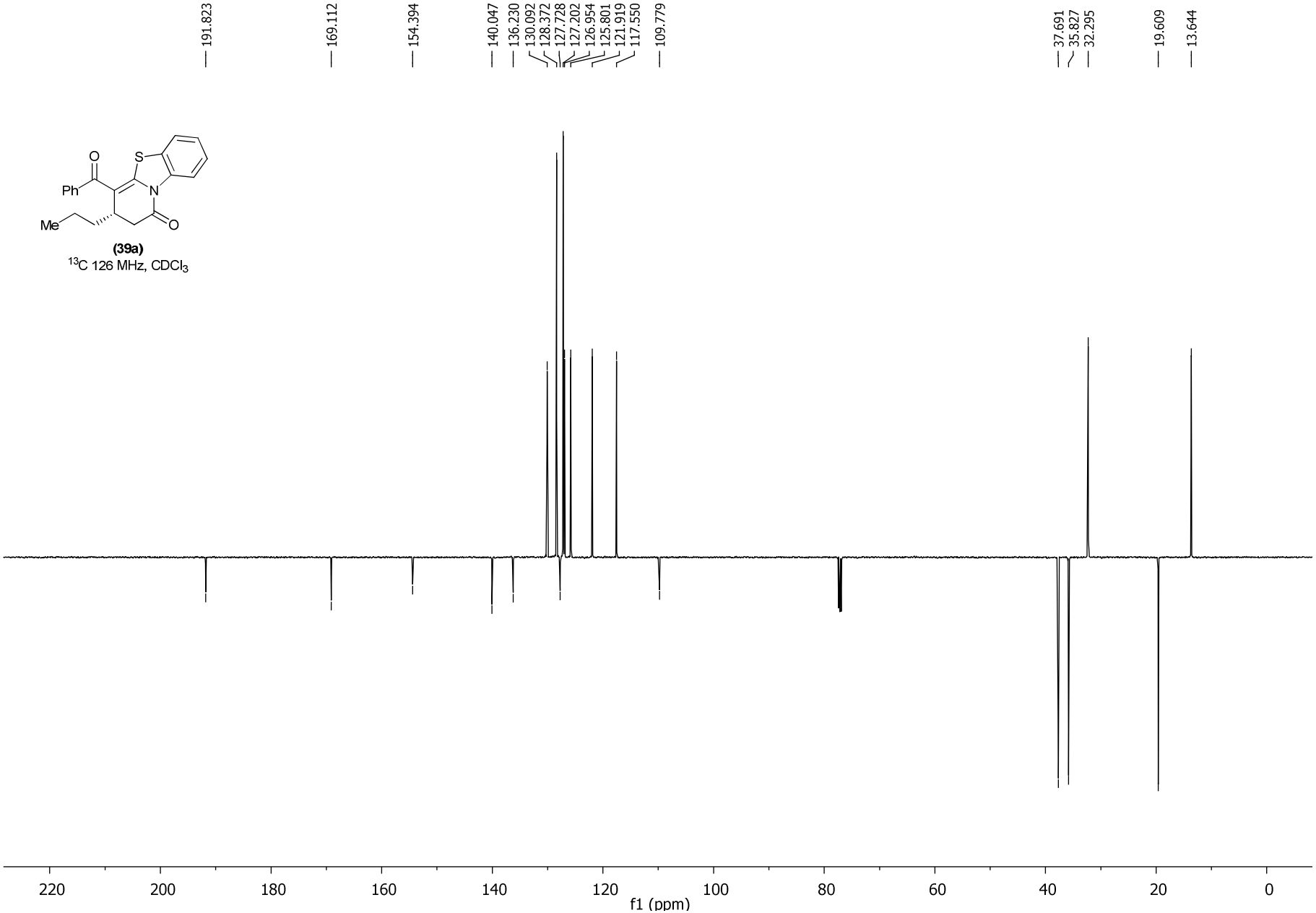


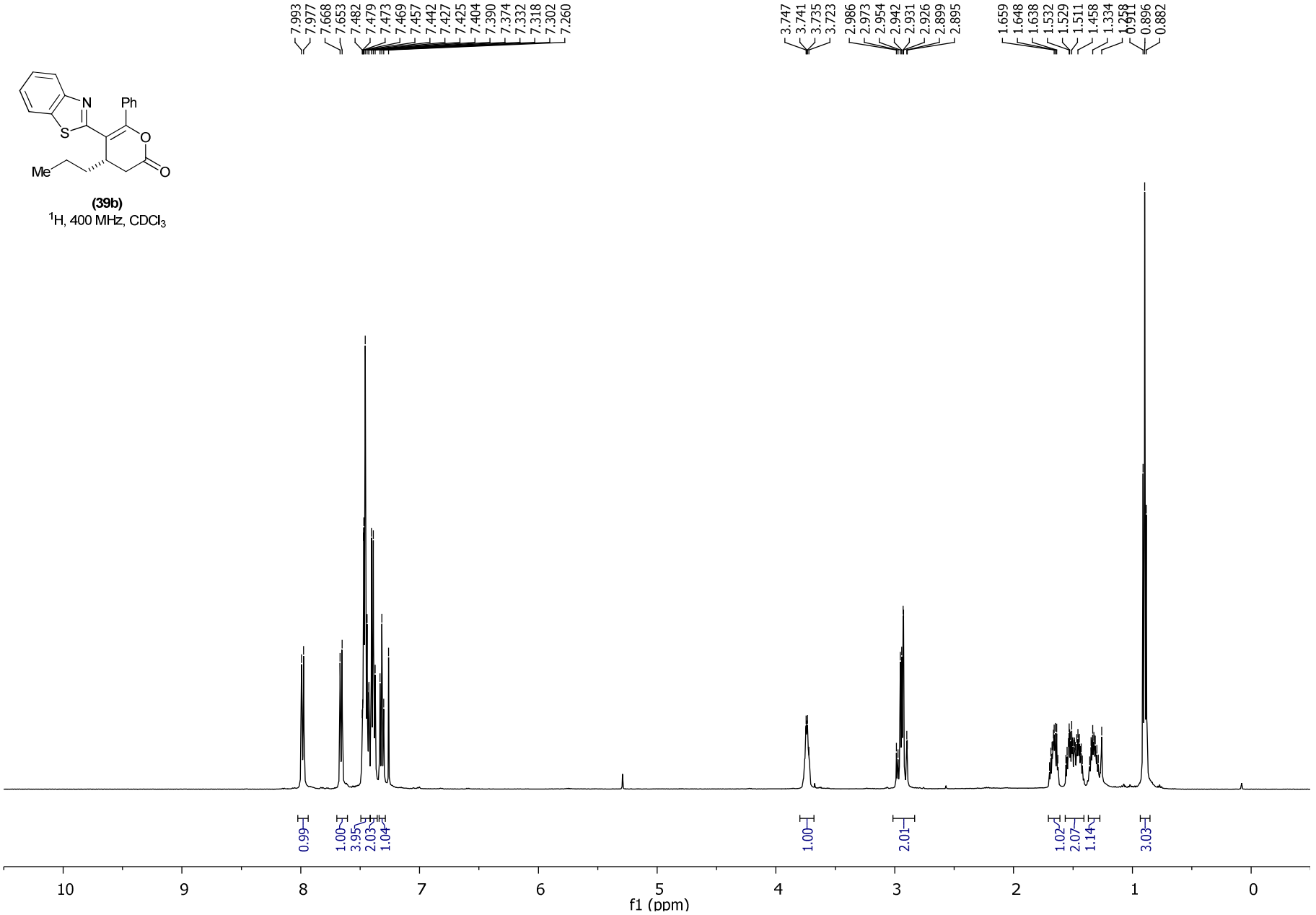
(38b)

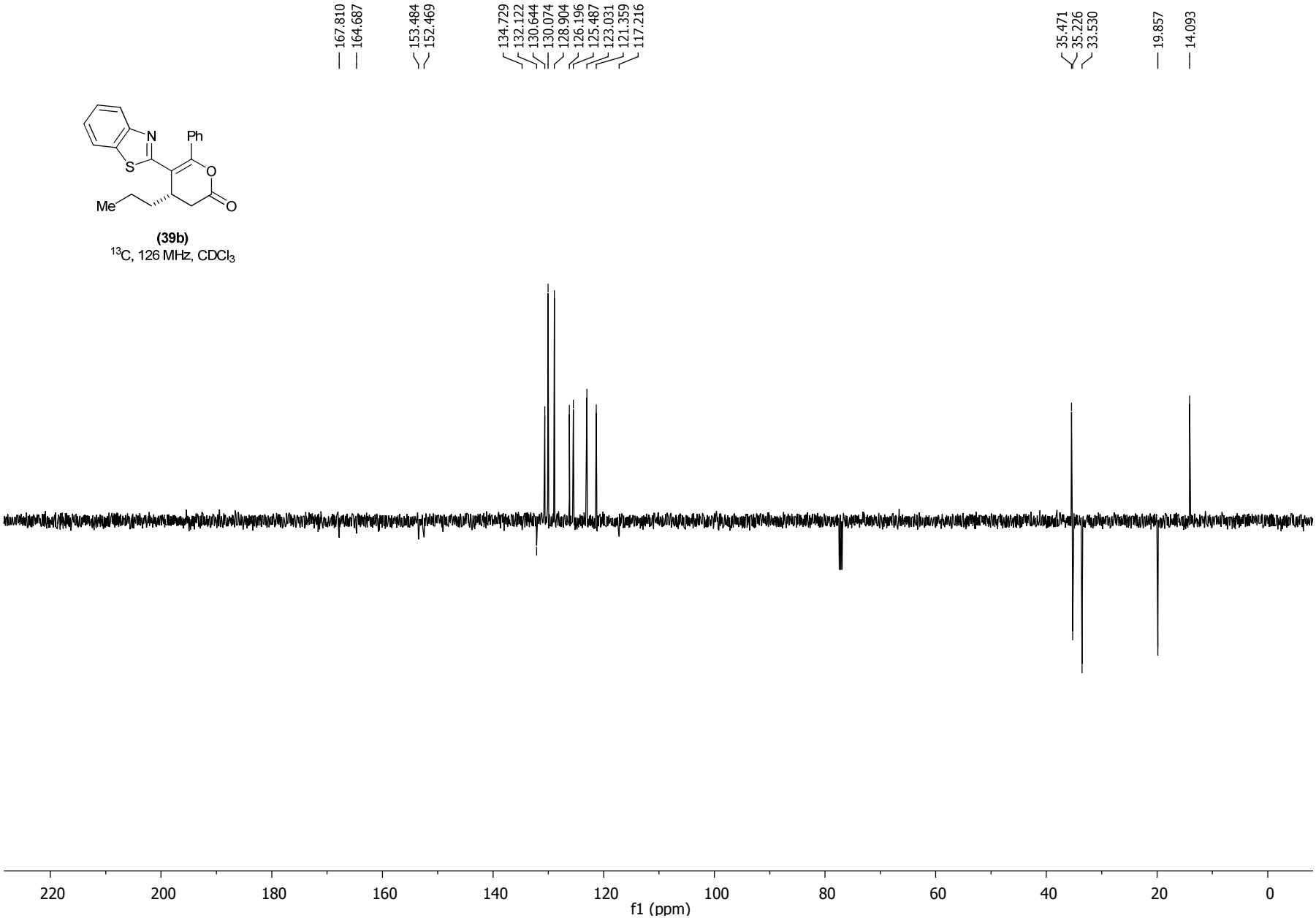
^{1}H, 400 MHz, $CDCl_3$



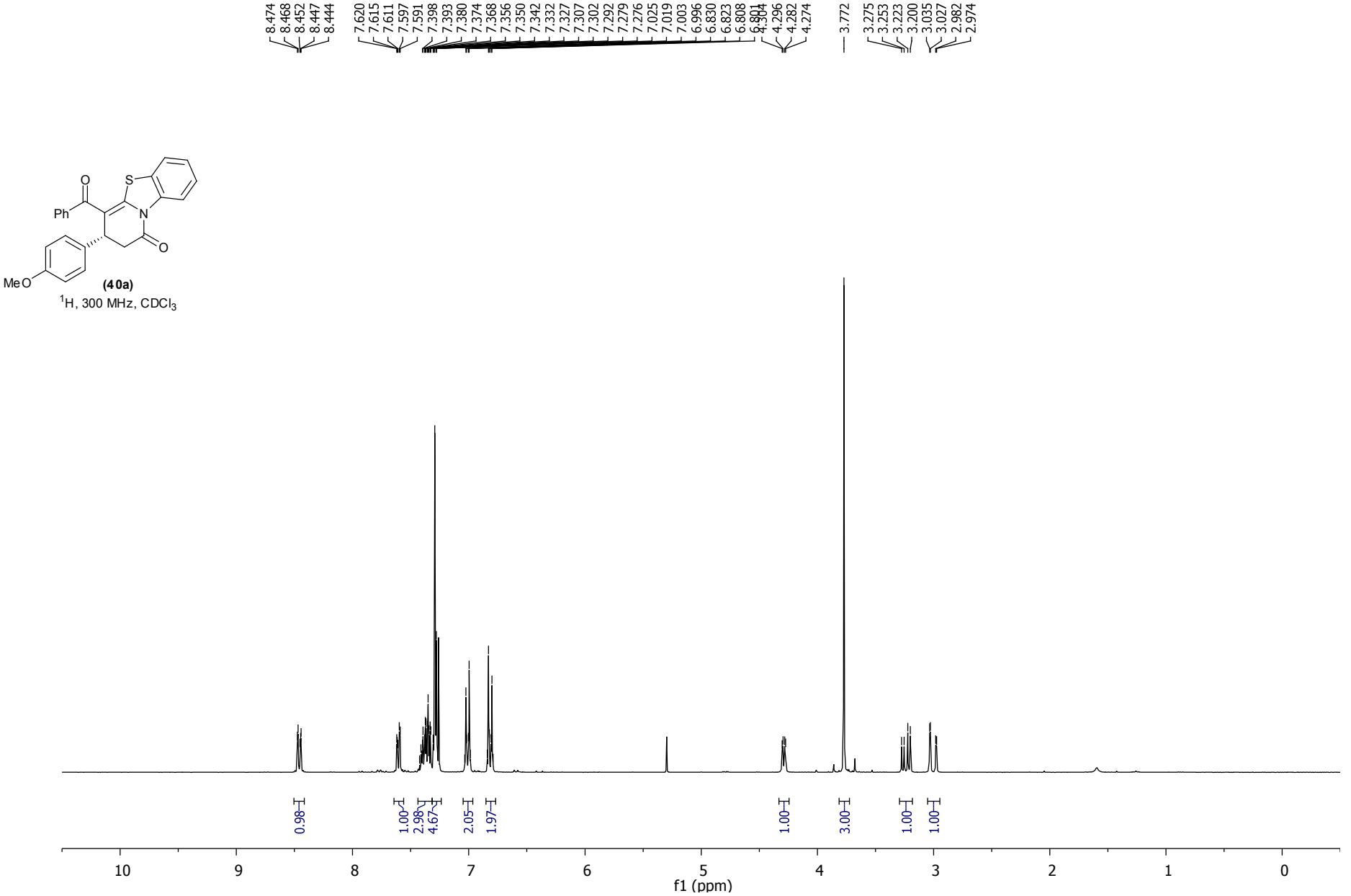


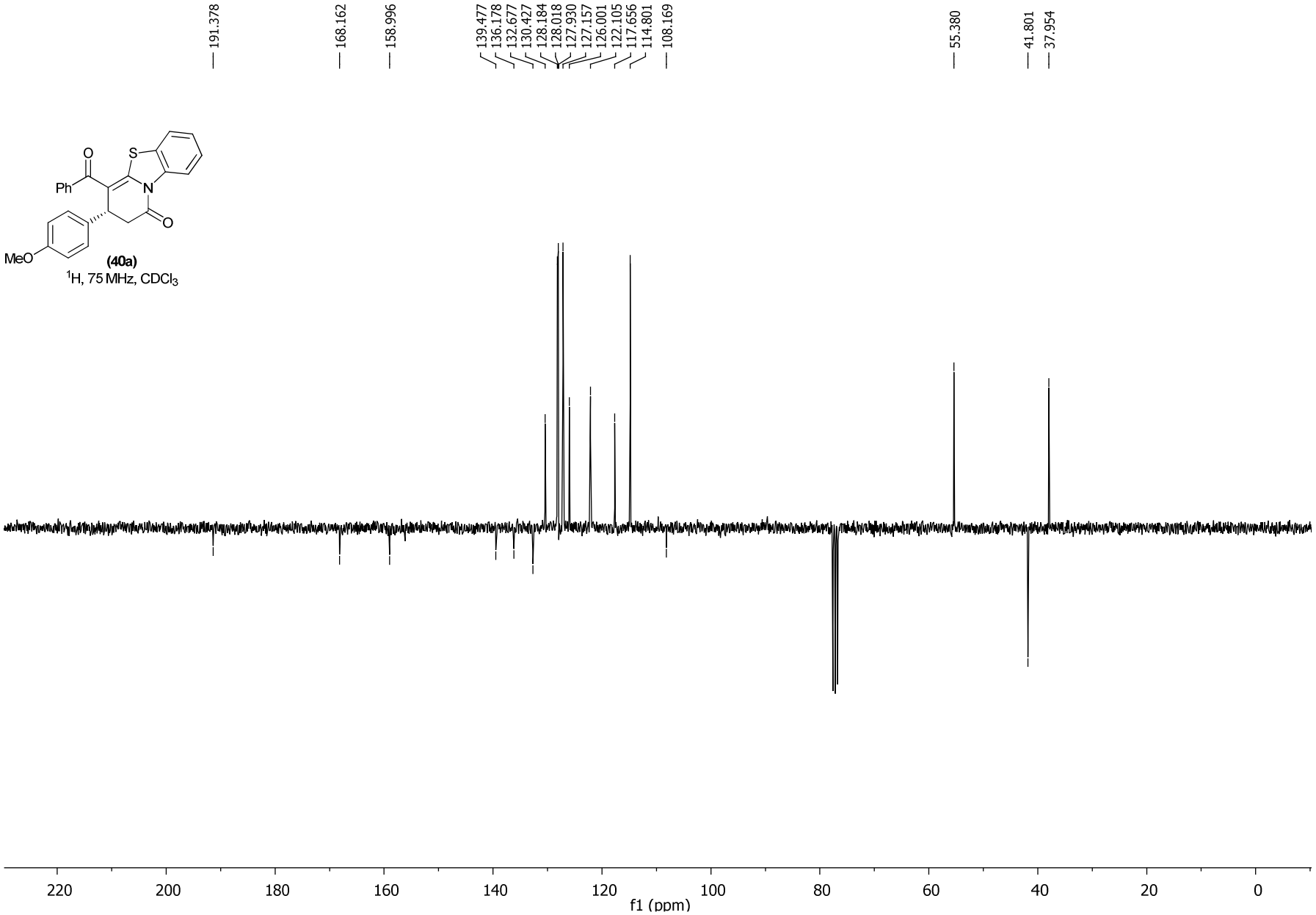


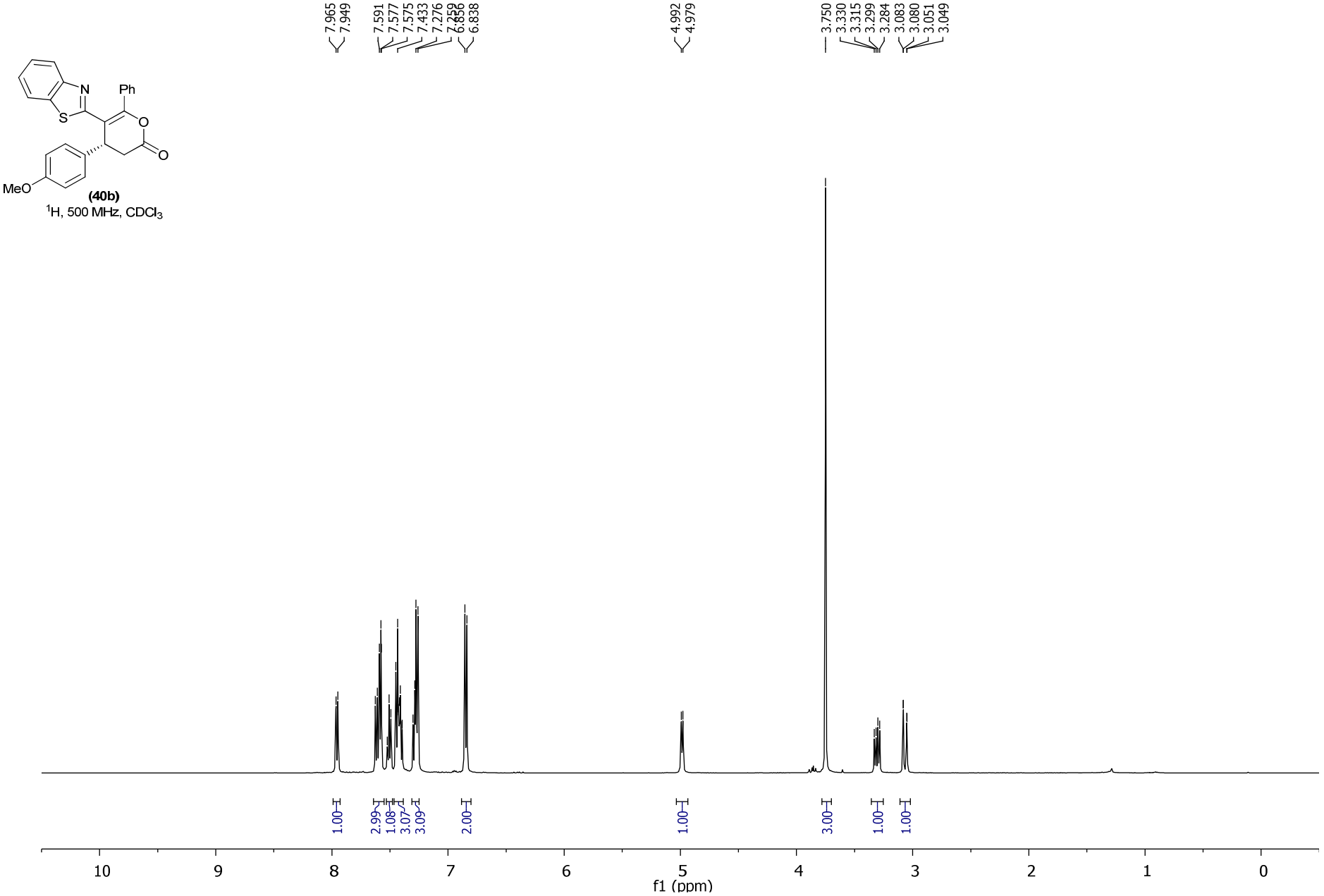


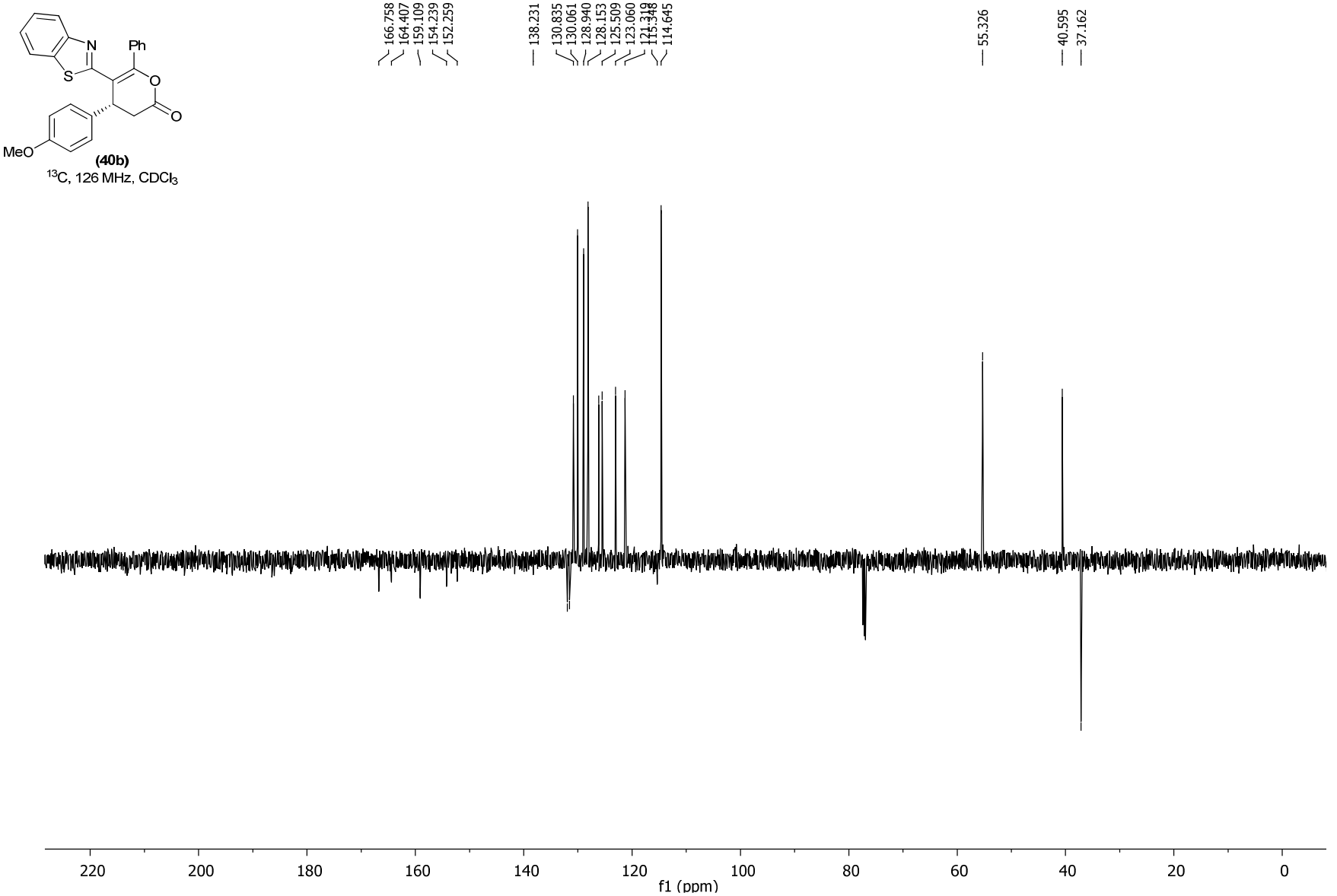


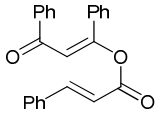
(39b)
^{13}C, 126 MHz, $CDCl_3$



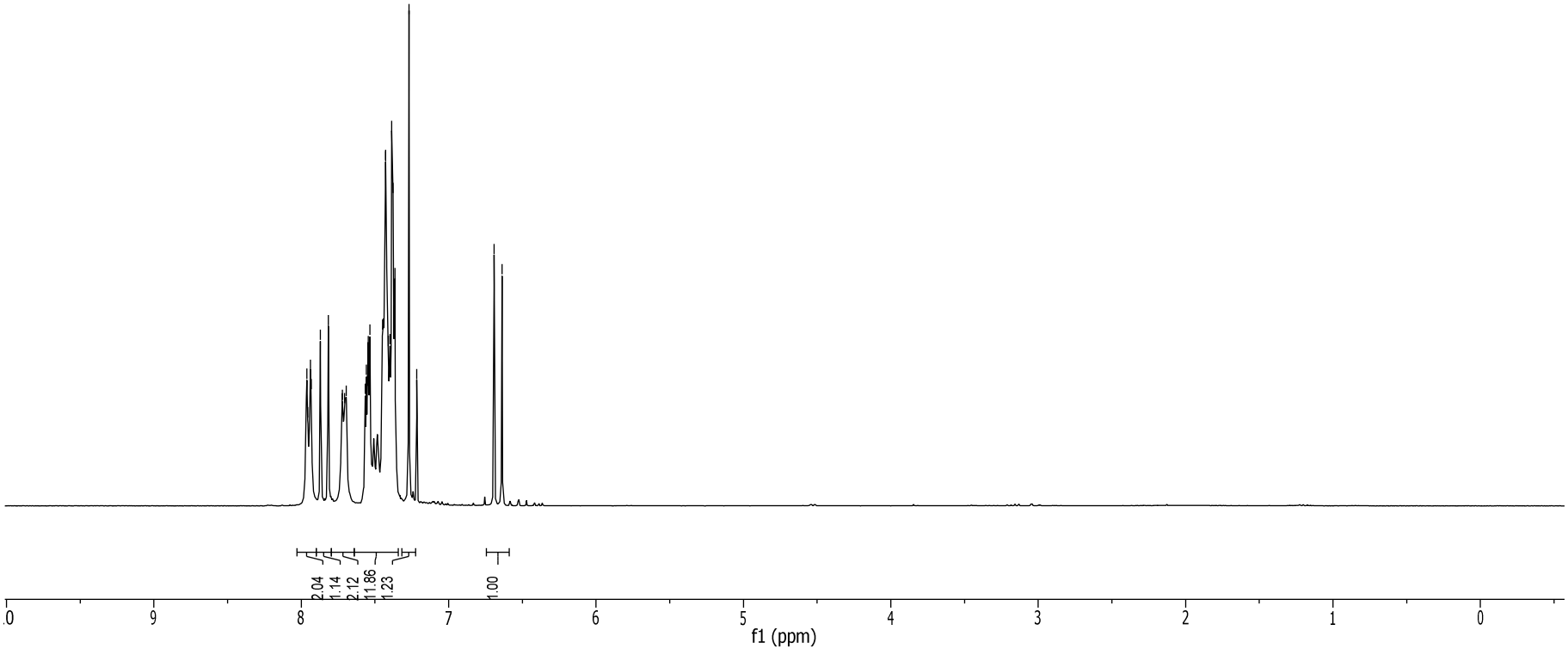


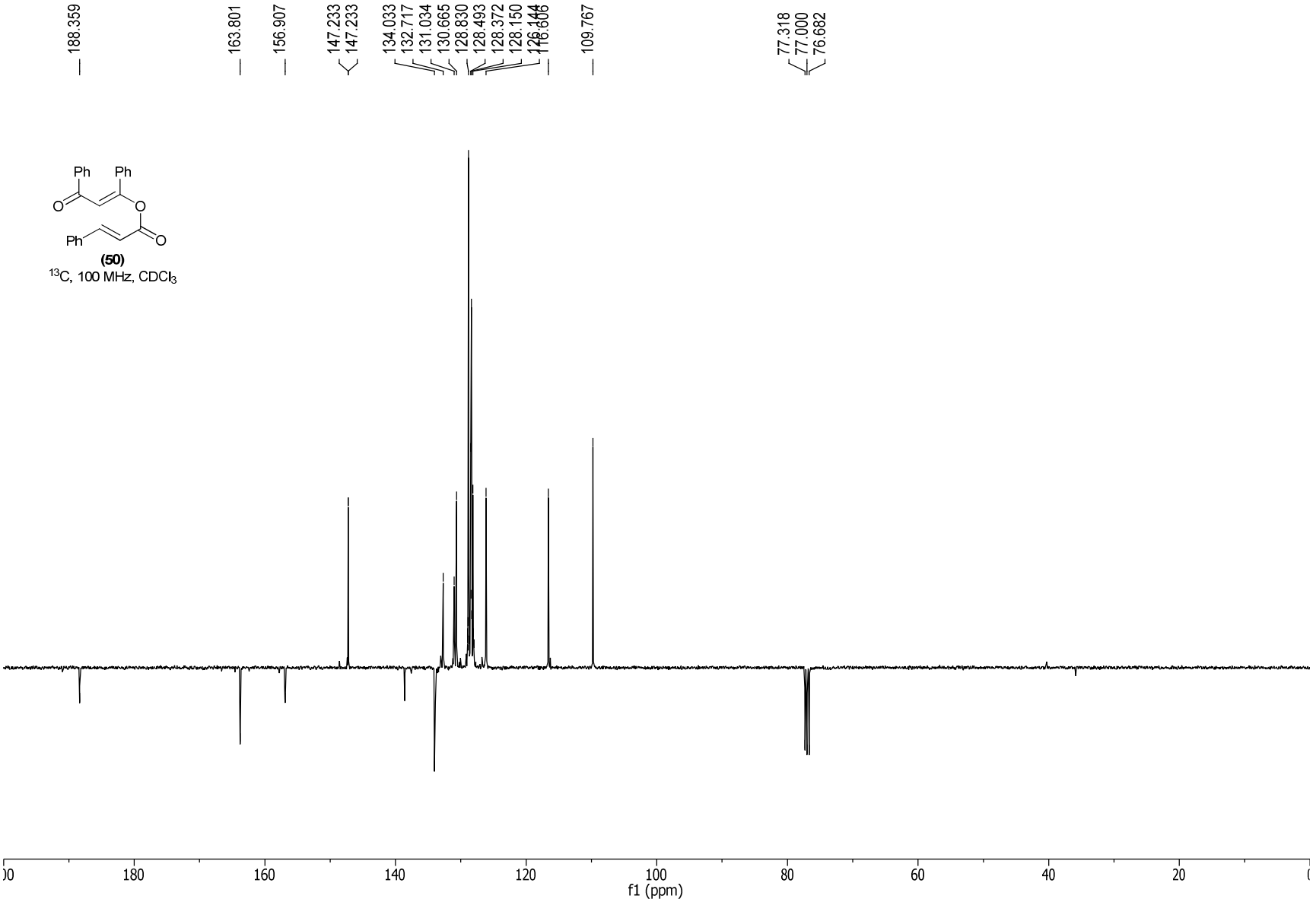


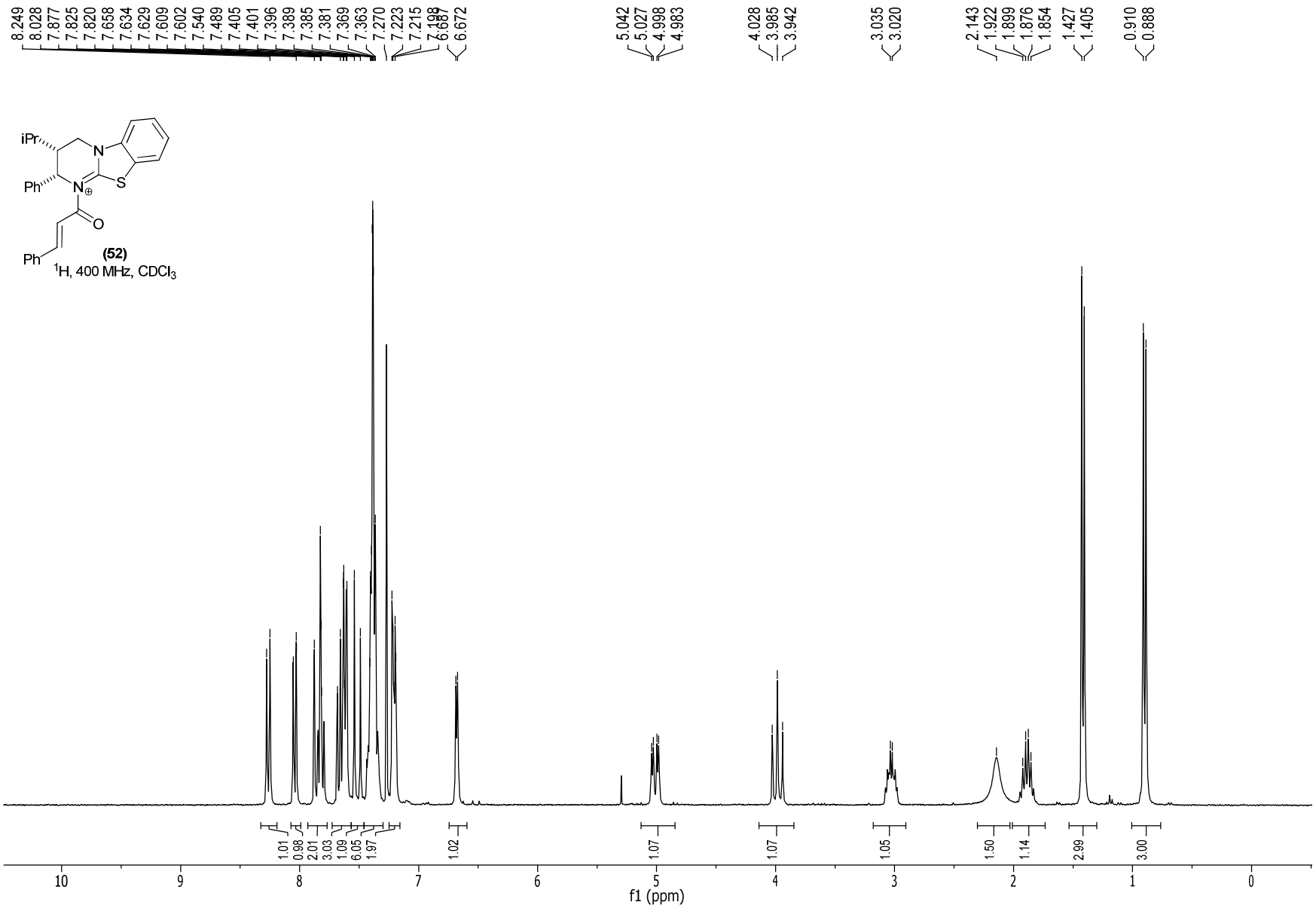


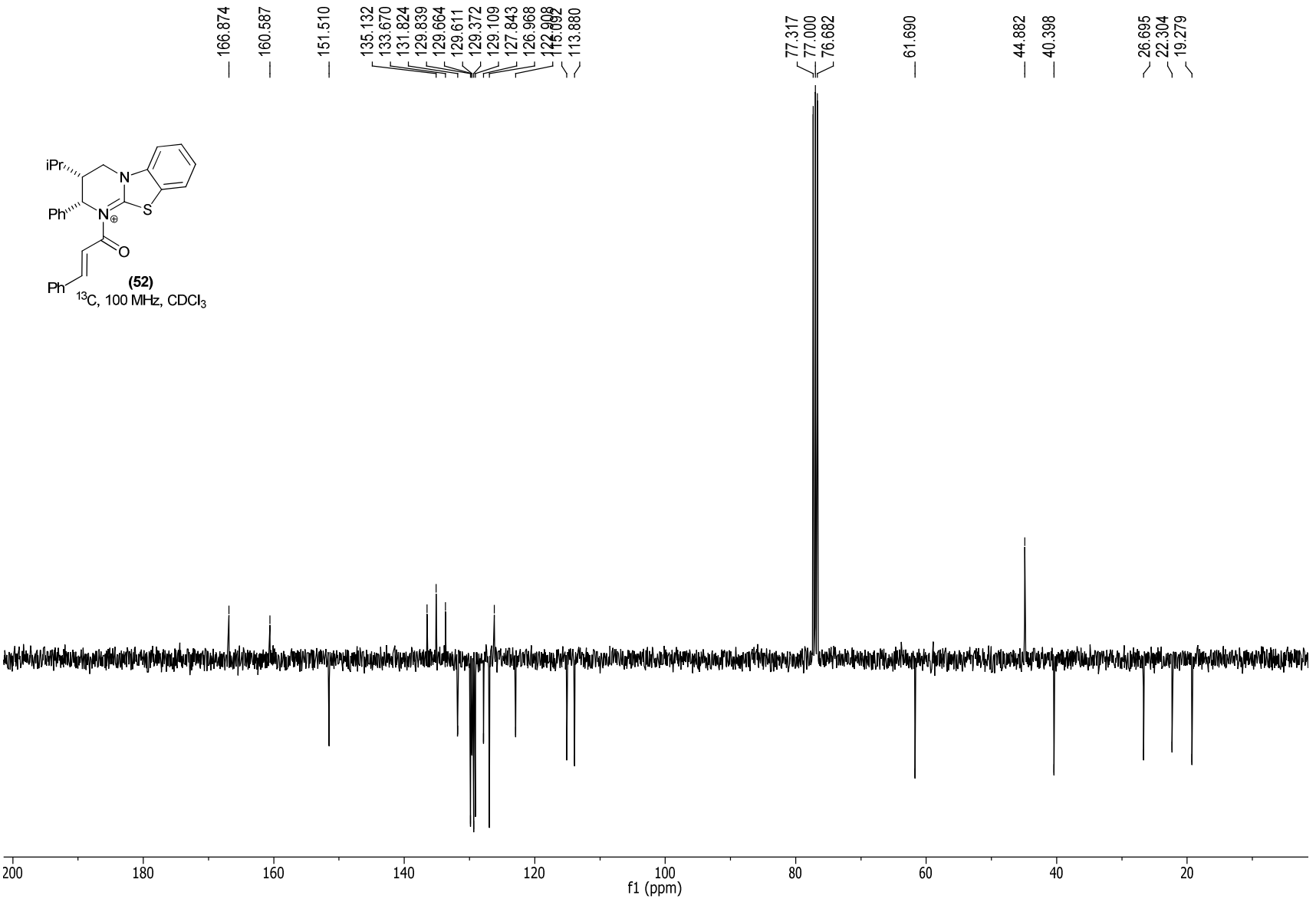


(50)
^{1}H, 400 MHz, $CDCl_3$









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