Regiodivergent Lewis-base promoted *O*- to *C*-carboxyl transfer of furanyl carbonates

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SUPPORTING INFORMATION

Contents

1.1 General information

Reactions involving moisture sensitive reagents were carried out under an argon atmosphere using standard vacuum line techniques in addition to freshly distilled solvents. All glassware used was flame dried and cooled under vacuum.

Solvents (THF, CH_2Cl_2, toluene, hexane and Et_2O) were obtained anhydrous and purified by an alumina column (Mbraun SPS-800). Anhydrous CH_3CN was obtained by distillation over calcium hydride. Petrol is defined as petroleum ether 40-60 °C. All other solvents and commercial reagents were used as supplied without further purification unless stated otherwise.

Methylmagnesium bromide and phenylmagnesium bromide were both used as a 3M solution in Et_2O as supplied (Aldrich). Potassium bis(trimethylsilyl)amide (KHMDS) was used as a 0.5M solution in toluene as supplied (Aldrich). Hydrogen chloride was used as a 4M solution in dioxane as supplied (Aldrich). Sodium hydride refers to a 60% wt. dispersion in mineral oil as supplied (Aldrich) and was used unwashed.

Room temperature (rt) refers to 20-25 °C. Temperatures of 0 °C and -78 °C were obtained using ice/water and CO_2(s)/acetone baths respectively. Temperatures of 0 °C to -50 °C for overnight reactions were obtained using an immersion cooler (HAAKE EK 90). Reflux conditions were obtained using an oil bath equipped with a contact thermometer. *In vacuo* 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.

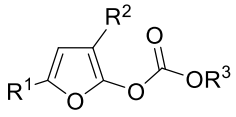
Analytical thin layer chromatography was performed on pre-coated aluminium plates (Kieselgel 60 F_{254} silica). TLC visualisation was carried out with ultraviolet light (254 nm), followed by staining with a 1% aqueous $KMnO_4$ solution. Flash column chromatography was performed on Kieselgel 60 silica in the solvent system stated.

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker Avance 300 (300 MHz, ^1H, 75 MHz ^{13}C) or a Bruker Avance II 400 (400 MHz, ^1H, 100 MHz ^{13}C) spectrometer at ambient temperature in the deuterated solvent stated. All chemical shifts are quoted in parts per million (ppm) relative to the residual solvent as the internal standard. All coupling constants, *J*, are quoted in Hz. Multiplicities are indicated by: s (singlet), d (doublet), t (triplet), q (quartet), ABq (AB quartet), sept (septet), oct (octet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets, dt (doublet of triplets) and td (triplet of doublets). The abbreviation Ar is used to denote aromatic, br to denote broad and app. to denote apparent.

Infrared spectra (ν_{max}) were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer using either thin films on NaCl plates or KBr discs. Only the characteristic peaks are quoted. Melting points were recorded on an Electrothermal apparatus and are uncorrected.

Mass spectrometry (*m/z*) data were acquired by electrospray ionisation (ESI), electron impact (EI) or nanospray ionisation (NSI) either at the University of St Andrews or the EPSRC National Mass Spectrometry Service Centre, Swansea. At the University of St Andrews, low and high resolution ESI MS were carried out on a Micromass LCT spectrometer. At the EPSRC National Mass Spectrometry Service Centre, low resolution NSI MS was carried out on a Micromass Quattro II spectrometer and high resolution NSI MS on a Thermofisher LTQ Orbitrap XL spectrometer.

The following furanyl carbonates were made according to the literature procedure:[1]



R^1 = Ph, R^2 = Me, R^3 = Ph, **5**
R^1 = Me, R^2 = Ph, R^3 = Ph, **11**
R^1 = Ph, R^2 = Bn, R^3 = Ph, **12**
R^1 = Ph, R^2 = Bn, R^3 = CH_2CCl_3, **13**
R^1 = Ph, R^2 = Et, R^3 = Ph, **14**
R^1 = Ph, R^2 = 4-BrC_6H_4, R^3 = Ph, **15**
R^1 = Ph, R^2 = Allyl, R^3 = Ph, **16**
R^1 = 4-FC_6H_4, R^2 = Me, R^3 = Ph, **17**
R^1 = 4-FC_6H_4, R^2 = Me, R^3 = CH_2CCl_3, **18**
R^1 = 4-FC_6H_4, R^2 = Bn, R^3 = Ph, **19**
R^1 = 4-FC_6H_4, R^2 = Et, R^3 = Ph, **20**
R^1 = 4-FC_6H_4, R^2 = 4-BrC_6H_4, R^3 = Ph, **21**
R^1 = 4-FC_6H_4, R^2 = Allyl, R^3 = Ph, **22**

1.2 General Experimental Procedures

General procedure A: *DMAP-promoted rearrangement.*

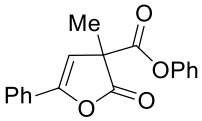
To a solution of carbonate (1 equiv.) in THF (~1 mL per 100 mg of carbonate) was added DMAP (10 mol%). The mixture was stirred for 5 min and then concentrated *in vacuo*.

General procedure B: *NHC-promoted rearrangement.*

To a solution of carbonate (1 equiv.) in THF (~1 mL per 100 mg of carbonate) was added the requisite triazolium salt (1 or 10 mol%) and finally KHMDS (0.9 or 9 mol%). The mixture was stirred for 1 min to 5 min and then concentrated *in vacuo*.

1.3 Experimental Procedures and Characterization Data

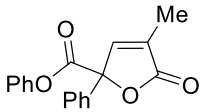
phenyl 3-methyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate



6

Following general procedure A, carbonate **5** (100 mg, 0.34 mmol) and DMAP (4.22 mg, 0.034 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 60:40). Chromatographic purification (eluent Et_2O:petrol 20:80) gave **6** (60.0 mg, 60%) as a colorless solid with spectroscopic data in accordance with the literature.[2] mp 61 °C {Lit.[1] mp 62-64 °C}; δ_H (400 MHz, $CDCl_3$) 1.82 (3H, s, C*H*$_3$), 6.03 (1H, s, C(4)*H*), 7.11-7.12 (2H, m, Ar*H*), 7.24-7.27 (1H, m, Ar*H*), 7.37-7.40 (2H, m, Ar*H*), 7.46-7.48 (3H, m, Ar*H*) and 7.69-7.71 (2H, m, Ar*H*).

phenyl 4-methyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

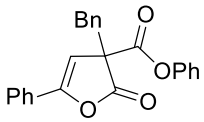


7

Following general procedure B, carbonate **5** (200 mg, 0.68 mmol), triazolium BF_4 salt precursor to **8** (14.1 mg, 0.068 mmol) and KHMDS (0.122 mL, 0.061 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 16:84). Chromatographic purification (eluent Et_2O:petrol 20:80) gave **7** (144 mg, 72%) as a colorless oil with spectroscopic data in accordance with the literature.[2] δ_H (400 MHz, $CDCl_3$) 1.99 (3H, s, C*H*$_3$), 6.98-7.00 (2H, m, Ar*H*), 7.18-7.20 (1H, m, Ar*H*), 7.30-7.34 (2H, m, Ar*H*) 7.39-7.44 (3H, m, Ar*H*) and 7.55-7.58 (3H, m, C(3)*H* and Ar*H*).

Following general procedure B, carbonate **5** (200 mg, 0.68 mmol), triazolium BF_4 salt precursor to **8** (1.41 mg, 6.80 μmol) and KHMDS (12.2 μL, 6.12 μmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ <2:98). Chromatographic purification (eluent Et_2O:petrol 20:80) gave **7** (170 mg, 85%) as a colorless oil. Data are in accordance with those given previously.

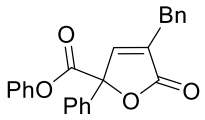
phenyl 3-benzyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate



23

Following general procedure A, carbonate **12** (100 mg, 0.34 mmol) and DMAP (4.22 mg, 0.034 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 64:36). Chromatographic purification (eluent Et_2O:petrol 10:90) gave **23** (45.2 mg, 45%) as a colorless solid with spectroscopic data in accordance with the literature.[1] mp 110-112 °C {Lit.[1] mp 110-112 °C}; δ_H (400 MHz; $CDCl_3$) 3.49 (1H, ABq, *J* 13.6, CH*H*), 3.64 (1H, ABq, *J* 13.6, C*H*H), 5.96 (1H, s, C(4)*H*), 7.04-7.08 (2H, m, Ar*H*), 7.22-7.27 (6H, m, Ar*H*), 7.35-7.40 (5H, m, Ar*H*) and 7.53-7.57 (2H, m, Ar*H*).

phenyl 4-benzyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

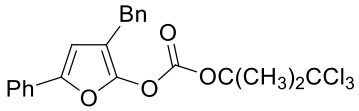


24

Following general procedure B, carbonate **12** (200 mg, 0.54 mmol), triazolium BF_4 salt precursor to **8** (14.7 mg, 0.054 mmol) and KHMDS (0.097 mL, 0.049 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 19:81). Chromatographic purification (eluent Et_2O:petrol 20:80) gave **24** (134 mg, 67%) as a colorless oil; IR (thin film) ν_{max}/cm^{-1}: 1773 (C=O), 1761 (C=O), 1647 (Ar C=C), 1493, 1451, 1189 (C-O), 1053, 1025, 734 and 676; δ_H (400 MHz, $CDCl_3$) 3.67 (1H, ABq, *J* 16.9, 1.6, CH*H*), 3.72 (1H, ABq, *J* 16.9, 1.6, C*H*H), 6.97–7.01 (2H, m, Ar*H*), 7.21–7.38 (9H, m, Ar*H* and C(3)*H*), 7.41–7.46 (3H, m, Ar*H*) and 7.53–7.56 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 32.0, 87.9, 121.0, 126.0, 126.7, 127.3, 129.1, 129.1, 129.2, 129.7, 129.7, 135.2, 135.4, 136.6, 147.1, 150.3, 166.1 and 171.3; *m/z* (ESI+) 388 (100, $[M+NH_4]^+$); HRMS (ESI+) $C_{24}H_{22}NO_4^+$ ($[M+NH_4]^+$) requires 388.1543, found 388.1543 (-0.1 ppm).

Following general procedure B, carbonate **12** (200 mg, 0.54 mmol), triazolium BF_4 salt precursor to **8** (1.47 mg, 5.40 μmol) and KHMDS (9.72 μL, 4.86 μmol) in THF (1 mL) for 1 min gave a ratio of products (α:γ 4:96). Chromatographic purification (eluent Et_2O:petrol 20:80) gave **24** (134 mg, 67%) as a colorless oil. Data are in accordance with those given previously.

3-benzyl-5-phenylfuran-2-yl (1,1,1-trichloro-2-methylpropan-2-yl) carbonate

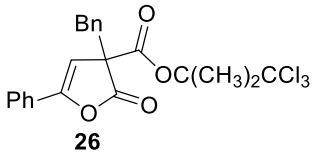


25

To a solution of 3-benzyl-5-phenylfuran-2(5*H*)-one[1] (0.80 g, 3.20 mmol) in THF (15 mL) at 0 °C was added triethylamine (0.89 mL, 6.40 mmol) and 1,1,1-trichloro-2-methylpropan-2-yl carbonochloridate (1.54 g, 6.40 mmol). After 30 min at rt the reaction mixture was poured into 0.5M HCl, and extracted with Et_2O (x 3). The organic fraction was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. Chromatographic purification (15:85, CH_2Cl_2/petrol) gave carbonate **25** (0.81 g, 55%) as a colorless solid; mp 78-80 °C; IR (KBr) ν_{max}/cm^{-1}: 2954, 1786 (C=O), 1234, 1153 (C-O), 801 and 694; δ_H (300 MHz; $CDCl_3$) 2.00 (6H, s, $(CH_3)_2$), 3.74 (2H, s, CH_2), 6.46 (1H, s, C(4)*H*), 7.22-7.38 (8H, m, Ar*H*) and 7.56-7.59 (2H, m, Ar*H*); δ_C (75 MHz, $CDCl_3$): 21.1, 30.0, 92.0, 104.8, 107.7, 108.6, 123.4, 126.5, 127.5, 128.7, 128.7, 128.8, 130.2, 129.2, 146.4, 147.4 and 149.1; *m/z* (ES+) 470.1 (39,

$[M+NH_4]^+$) and 453.0 (100, $[M+H]^+$); HRMS (ES+) $C_{22}H_{19}O_4Cl_3^+$ required 453.0422, found 453.0422 (+0.1 ppm).

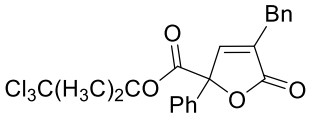
1,1,1-trichloro-2-methylpropan-2-yl 3-benzyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate



26

Following general procedure A, carbonate **25** (91.0 mg, 0.20 mmol) and DMAP (2.40 mg, 0.02 mmol) in THF (0.9 mL) for 15 min gave a ratio of products (α:γ 62:38). Chromatographic purification (eluent CH_2Cl_2:petrol 50:50 to 100% CH_2Cl_2) gave the alpha product **26** (51.0 mg, 56%) as a colorless solid and the gamma product (26.0 mg, 26%) as a pale yellow oil. Data for alpha product **26**; mp 132-134 ºC; IR (KBr) ν_{max}/cm^{-1}: 2938, 1792 (C=O), 1742 (C=O), 1233, 1152 (C-O), 993, 795 and 765; δ_H (300 MHz, $CDCl_3$) 1.88 (3H, s, C*H*$_3$), 1.92 (3H, s, C*H*$_3$), 3.38 (1H, ABq, *J* 13.6, CH*H*), 3.50 (1H, ABq, *J* 13.6, C*H*H), 5.80 (1H, s, C(4)*H*), 7.18-7.25 (5H, m, Ar*H*), 7.34-7.36 (3H, m, Ar*H*) and 7.46-7.49 (2H, m, Ar*H*); δ_C (75 MHz, $CDCl_3$): 21.3, 21.4, 40.2, 62.7, 90.8, 101.8, 105.5, 125.3, 127.6, 127.7, 128.6, 128.8, 130.1, 130.3, 134.4, 154.5, 165.3 and 172.9; *m/z* (ES+) 470.1 (100, $[M+NH_4]^+$) and 453.0 (5, $[M+H]^+$); HRMS (ES+) $C_{22}H_{23}O_4NCl_3^+$ required 470.0687, found 470.0687 (+0 ppm).

1,1,1-trichloro-2-methylpropan-2-yl 4-benzyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate



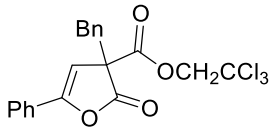
27

Following general procedure B, carbonate **25** (91.0 mg, 0.20 mmol), triazolium BF_4 salt precursor to **8** (5.50 mg, 0.02 mmol) and KHMDS (0.036 mL, 0.018 mmol) in THF (0.9 mL) for 5 min gave a ratio of products (α:γ 4:96). Chromatographic purification (eluent 100% CH_2Cl_2) gave **27** (72.8 mg, 80%) as a pale yellow oil; IR (thin film) ν_{max}/cm^{-1}: 2923, 1776 (broad, 2×C=O), 1452, 1152 (C-O), 1032, 791 and 697; δ_H (300 MHz, $CDCl_3$): 1.80 (3H, s, C*H*$_3$), 1.88 (3H, s, C*H*$_3$), 3.60 (1H, ABq, *J* 16.9, 1.7, CH*H*), 3.70 (1H, ABq, *J* 16.9, 1.6, C*H*H), 7.21-7.24 (3H, m, Ar*H*), 7.27-7.32 (2H, m, Ar*H*), 7.35 (1H, app. t, *J* 2.0, C(3)*H*), 7.37-7.41 (3H, m, Ar*H*) and 7.47-7.51 (2H, m, Ar*H*); δ_C (75 MHz, $CDCl_3$): 21.1, 21.4, 31.9, 88.1, 91.1, 105.3, 126.1, 127.2, 128.9, 129.0, 129.0, 129.5, 134.9, 135.2, 136.6, 146.9, 164.8 and

171.2; *m/z* (ES+) 470.1 (100, $[M+NH_4]^+$) and 453.0 (8, $[M+H]^+$); HRMS (ES+) $C_{12}H_{23}O_4NCl_3^+$ required 470.0687, found 470.0679 (-1.7 ppm).

Following general procedure B, carbonate **25** (91.0 mg, 0.20 mmol), triazolium BF_4 salt precursor to **8** (0.55 mg, 2.00 μmol) and KHMDS (3.6 μL, 1.80 μmol) in THF (1 mL) for 1 min gave a ratio of products (α:γ 1:99). Chromatographic purification (eluent 100% CH_2Cl_2) gave **27** (82.8 mg, 91%) as a pale yellow oil. Data are in accordance with those given previously.

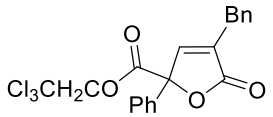
2,2,2-trichloroethyl 3-benzyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate



28

Following general procedure A, carbonate **13** (85.0 mg, 0.20 mmol) and DMAP (2.40 mg, 0.02 mmol) in THF (0.9 mL) for 15 min gave a ratio of products (α:γ 54:46). Chromatographic purification (eluent CH_2Cl_2:petrol 50:50 to 100% CH_2Cl_2) gave the alpha product **28** (37.6 mg, 44%) as a colorless solid and the gamma product (31.3 mg, 37%) as a colorless solid. Data for the alpha product **28**; Spectroscopic data in accordance with the literature.[1] mp 110-112 °C {Lit.[1] mp 110-112 °C}; δ_H (300 MHz; $CDCl_3$) 3.45 (1H, ABq, *J* 13.6, CH*H*), 3.56 (1H, ABq, *J* 13.6, C*H*H), 4.75 (1H, ABq, *J* 11.9, OCH*H*), 4.88 (1H, ABq, *J* 11.9, OC*H*H), 5.84 (1H, s, C(4)*H*), 7.18-7.26 (5H, m, Ar*H*), 7.35-7.39 (3H, m, Ar*H*) and 7.48-7.51 (2H, m, Ar*H*).

2,2,2-trichloroethyl 4-benzyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

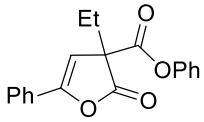


29

Following general procedure B, carbonate **13** (85.0 mg, 0.20 mmol), triazolium BF_4 salt precursor to **8** (5.50 mg, 0.02 mmol) and KHMDS (0.036 mL, 0.018 mmol) in THF (0.9 mL) for 5 min gave a ratio of products (α:γ 5:95). Chromatographic purification (eluent 100% CH_2Cl_2) gave **29** (60.4 mg, 71%) as a colorless solid with spectroscopic data in accordance with the literature.[1] mp 94-96 °C {Lit.[1] mp 94-96 °C}; δ_H (400 MHz; $CDCl_3$) 3.62 (1H, ABq, *J* 16.9, 1.7, CH*H*), 3.69 (1H, ABq, *J* 16.9, 1.6, C*H*H), 4.71 (1H, ABq, *J* 11.9, OCH*H*), 4.82 (1H, ABq, *J* 11.8, OC*H*H), 7.22-7.24 (2H, m, Ar*H*), 7.27-7.30 (2H, m, C(3)*H* and Ar*H*), 7.32-7.36 (2H, m, Ar*H*), 7.39-7.41 (3H, m, Ar*H*) and 7.48-7.51 (2H, m, Ar*H*).

Following general procedure B, carbonate **13** (85.0 mg, 0.20 mmol), triazolium BF_4 salt precursor to **8** (0.55 mg, 2.0 μmol) and KHMDS (4.00 μL, 1.80 μmol) in THF (0.9 mL) for 1 min gave a ratio of products (α:γ 1:99). Chromatographic purification (eluent 100% CH_2Cl_2) gave **29** (72.8 mg, 86%) as a colorless solid. Data are in accordance with those given previously.

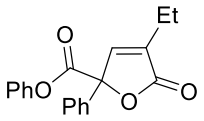
phenyl 3-ethyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate



30

Following general procedure A, carbonate **14** (61.7 mg, 0.20 mmol) and DMAP (2.40 mg, 0.02 mmol) in THF (0.7 mL) for 5 min gave a ratio of products (α:γ 47:53). Chromatographic purification (eluent CH_2Cl_2:petrol 50:50) gave **30** (20.0 mg, 32%) as a sticky colorless solid with spectroscopic data in accordance with the literature.[1] δ_H (300 MHz; $CDCl_3$) 1.05 (3H, t, *J* 7.5, C*H*$_3$), 2.30 (2H, q, *J* 7.5, C*H*$_2$), 5.96 (1H, s, C(4)*H*), 7.09 (2H, dd, *J* 8.6, 1.1, Ar*H*), 7.22-7.26 (1H, m, Ar*H*), 7.37 (2H, t, *J* 7.9, Ar*H*), 7.44-7.47 (3H, m, Ar*H*) and 7.68-7.71 (2H, m, Ar*H*).

phenyl 4-ethyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

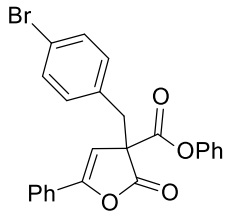


31

Following general procedure B, carbonate **14** (61.7 mg, 0.20 mmol), triazolium BF_4 salt precursor to **8** (5.50 mg, 0.02 mmol) and KHMDS (0.036 mL, 0.018 mmol) in THF (0.9 mL) for 5 min gave a ratio of products (α:γ 21:79). Chromatographic purification (eluent 100% CH_2Cl_2) gave **31** (33.3 mg, 54%) as a colorless oil; IR (KBr) ν_{max}/cm^{-1}: 2974, 1777 (broad, 2×C=O), 1493, 1191 (C-O), 1027, 965, 736 and 689; δ_H (400 MHz, $CDCl_3$) 1.24 (3H, t, *J* 7.4, C*H*$_3$), 2.34-2.49 (2H, m, C*H*$_2$), 7.02-7.04 (2H, m, Ar*H*), 7.22-7.26 (1H, m, Ar*H*), 7.34-7.38 (2H, m, Ar*H*), 7.42-7.48 (3H, m, Ar*H*), 7.54 (1H, t, *J* 1.8, C(3)*H*) and 7.60-7.63 (2H, m, Ar*H*). δ_C (100 MHz, $CDCl_3$): 11.7, 19.0, 87.7, 121.0, 125.9, 126.6, 129.2, 129.6, 129.7, 135.4, 136.9, 145.2, 150.3, 166.2 and 171.6; *m/z* (ES+) 326.1 (100, $[M+NH_4]^+$) and 309.1 (12, $[M+H]^+$); HRMS (ES+) $C_{19}H_{20}O_4N^+$ required 326.1387, found 326.1389 (+0.7 ppm).

Following general procedure B, carbonate **14** (61.7 mg, 0.20 mmol), triazolium BF_4 salt precursor to **8** (0.55 mg, 2.0 μmol) and KHMDS (4.00 μL, 1.80 μmol) in THF (0.9 mL) for 1 min gave a ratio of products (α:γ 1:99). Chromatographic purification (eluent 100% CH_2Cl_2) gave **31** (44.0 mg, 71%) as a colorless oil. Data are in accordance with those given previously.

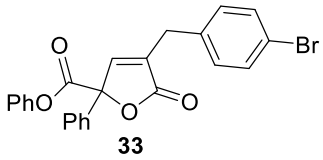
phenyl 3-(4-bromobenzyl)-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate



32

Following general procedure A, carbonate **15** (60.2 mg, 0.134 mmol) and DMAP (1.61 mg, 0.0134 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 53:47). Chromatographic purification (eluent CH_2Cl_2:petrol 50:50) gave **32** (25.9 mg, 43%) as a colorless solid with spectroscopic data in accordance with the literature.[1] mp 150-152 °C {Lit.[1] mp 150-152 °C}; δ_H (400 MHz; $CDCl_3$) 3.46 (1H, ABq, *J* 13.7, CH*H*), 3.58 (1H, ABq, *J* 13.7, C*H*H), 5.94 (1H, s, C(4)*H*), 7.06–7.09 (2H, m, Ar*H*), 7.12–7.16 (2H, m, Ar*H*), 7.26–7.29 (1H, m, Ar*H*), 7.37-7.43 (7H, m, Ar*H*) and 7.56–7.59 (2H, m, Ar*H*).

phenyl 4-(4-bromobenzyl)-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

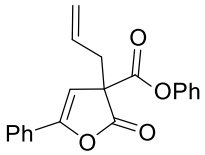


33

Following general procedure A, carbonate **15** (60.2 mg, 0.134 mmol), triazolium BF_4 salt precursor to **8** (3.65 mg, 0.0134 mmol) and KHMDS (0.024 mL, 0.012 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 10:90). Chromatographic purification (eluent 100% CH_2Cl_2) gave **33** (48.0 mg, 80%) as a colorless oil; IR ν_{max} (thin film) /cm^{-1} 3107, 3057, 1804 (C=O), 1760 (C=O), 1652, 1591 (C=C), 1490, 1406, 1281, 1188 (C-O), 1126, 1072, 1013, 94, 833, 755 and 688 (C-Br); δ_H (400 MHz, $CDCl_3$) 3.62 (1H, ABq, *J* 16.9, 1.5, CH*H*), 3.67 (1H, ABq, *J* 16.9, 1.5, C*H*H), 7.00–6.98 (2H, m, Ar*H*), 7.14 (2H, app d, *J* 8.4, Ar*H*), 7.24–7.20 (1H, m, Ar*H*), 7.38–7.35 (3H, m, Ar*H* and C(3)*H*), 7.49–7.43 (2H, m, Ar*H*), 7.56–7.54 (5H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 31.4, 88.0, 121.0, 121.3, 125.9, 126.7, 129.3, 129.7, 129.8, 130.8, 132.2, 134.7, 135.0, 135.5, 147.4, 150.3, 165.9 and 171.1; *m/z* MS (ESI+) 449 (100,

[{^{79}Br}M+H]$^+$) and 451 (98, [{^{81}Br}M+H]$^+$); HRMS (ESI+) $C_{24}H_{18}{}^{79}BrO_4^+$ ([{^{79}Br}M+H]$^+$) requires 449.0383, found 449.0378, (-1.1 ppm).

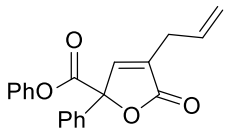
phenyl 3-allyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate



34

Following general procedure A, carbonate **16** (64.0 mg, 0.20 mmol) and DMAP (2.40 mg, 0.03 mmol) in THF (0.6 mL) for 5 min gave a ratio of products (α:γ 61:39). Chromatographic purification (eluent CH_2Cl_2:petrol 50:50 then 100% CH_2Cl_2) gave the alpha product **34** (34.5 mg, 54%) as a colorless oil and the gamma product (20.5 mg, 32%) as a colorless oil. Data for the alpha product **34**; Spectroscopic data in accordance with the literature.[1] δ_H (400 MHz; $CDCl_3$) 2.92 (1H, ABq, *J* 13.9, *J* 7.9, CH*H*), 3.05 (1H, ABq, *J* 13.9, *J* 6.8, C*H*H), 5.20-5.22 (1H, m, =CH*H*), 5.28 (1H, app. dd, *J* 17.0, 1.4, =C*H*H), 5.75-5.85 (1H, m, C*H*=CH_2), 5.98 (1H, s, C(4)*H*), 7.08-7.10 (2H, m, Ar*H*), 7.22-7.26 (1H, m, Ar*H*), 7.35-7.39 (2H, m, Ar*H*), 7.43-7.46 (3H, m, Ar*H*) and 7.67-7.69 (2H, m, Ar*H*).

phenyl 4-allyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate



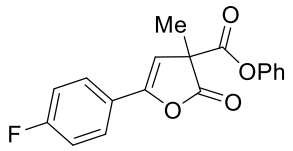
35

Following general procedure B, carbonate **16** (64.0 mg, 0.20 mmol), triazolium BF_4 salt precursor to **8** (5.50 mg, 0.02 mmol) and KHMDS (0.036 mL, 0.018 mmol) in THF (0.7 mL) for 5 min gave a ratio of products (α:γ 31:69). Chromatographic purification (eluent 100% CH_2Cl_2) gave the alpha product (15.3 mg, 24%) as a colorless oil and the gamma product **35** (32.1 mg, 50%) as a colorless oil. Data for the gamma product **35**; Spectroscopic data in accordance with the literature.[1] δ_H (400 MHz; $CDCl_3$) 3.08-3.19 (2H, m, CH_2), 5.21 (1H, t, *J* 1.3, =CH*H*), 5.23-5.25 (1H, m, =C*H*H), 5.85-5.98 (1H, m, C*H*=CH_2), 7.02-7.04 (2H, m, Ar*H*), 7.22-7.26 (1H, m, Ar*H*), 7.34-7.38 (2H, m, Ar*H*), 7.43-7.48 (3H, m, Ar*H*), 7.58 (1H, t, *J* 1.7, C(3)*H*) and 7.59-7.62 (2H, m, Ar*H*).

Following general procedure B, carbonate **16** (64.0 mg, 0.20 mmol), triazolium BF_4 salt precursor to **8** (0.55 mg, 2.00 μmol) and KHMDS (3.6 μL, 1.80 μmol) in THF (0.7 mL) for 1 min gave a ratio of products (α:γ 6:94). Chromatographic purification (eluent 100% CH_2Cl_2)

gave **35** (52.0 mg, 81%) as a colorless oil. Data are in accordance with those given previously.

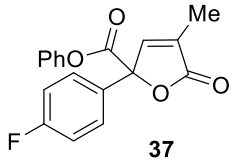
Phenyl 5-(4-fluorophenyl)-3-methyl-2-oxo-2,3-dihydrofuran-3-carboxylate



36

Following general procedure A, carbonate **17** (100 mg, 0.32 mmol) and DMAP (3.92 mg, 0.032 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 71:29). Chromatographic purification (eluent CH_2Cl_2:petrol 70:30) gave alpha product **36** (52.0 mg, 52%) as a colorless solid with spectroscopic data in accordance with the literature.[1] mp 42-44 °C {Lit.[1] mp 42-44 °C}; δ_H (400 MHz, $CDCl_3$) 1.71 (3H, s, C*H*$_3$), 5.86 (1H, s, C(4)*H*), 7.00-7.09 (4H, m, Ar*H*), 7.14-7.18 (1H, m, Ar*H*), 7.27-7.31 (2H, m, Ar*H*), 7.57-7.61 (2H, m, Ar*H*).

Phenyl 2-(4-fluorophenyl)-4-methyl-5-oxo-2,5-dihydrofuran-2-carboxylate

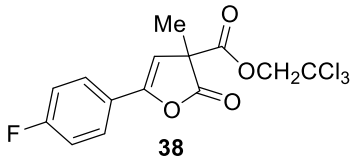


37

Following general procedure B, carbonate **17** (100 mg, 0.32 mmol), triazolium BF_4 salt precursor to **8** (8.75 mg, 0.032 mmol) and KHMDS (0.058 mL, 0.029 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 12:88). Chromatographic purification (eluent 100% CH_2Cl_2) gave gamma product **37** (67.0 mg, 67%) as a colorless oil; ν_{max} (thin film) 3532, 3084, 2960 (C-H), 1770 (C=O), 1660, 1603, 1509; δ_H (400 MHz, $CDCl_3$) 1.95 (3H, d, *J* 1.6, C*H*$_3$), 6.93-6.95 (2H, m, Ar*H*), 7.03-7.08 (2H, m, Ar*H*), 7.14-7.18 (1H, m, Ar*H*), 7.26-7.30 (2H, m, Ar*H*), 7.48-7.53 (3H, m, C(3)*H* and Ar*H*); δ_C (100 MHz, $CDCl_3$) 10.9, 87.0, 116.2 (d, *J* 22.2), 121.0, 126.7, 128.0 (d, *J* 8.3), 129.7, 131.3, 131.3, 146.3, 150.2, 163.2 (d, *J* 248.2), 166.0, 171.9; *m/z* (NSI^+) 330 ($[M+NH_4]^+$, 100%); HRMS (NSI^+) $C_{18}H_{17}O_4NF^+$ ($[M+NH_4]^+$) requires 330.1136; found 330.1137 (+0.3 ppm).

Following general procedure B, carbonate **17** (100 mg, 0.32 mmol), triazolium BF_4 salt precursor to **8** (0.875 mg, 3.2 μmol) and KHMDS (5.77 μL, 2.9 μmol) in THF (1 mL) for 1 min gave a ratio of products (α:γ 10:90). Chromatographic purification (eluent 100% CH_2Cl_2) gave **37** (71.0 mg, 71%) as a colorless oil. Data are in accordance with those given previously.

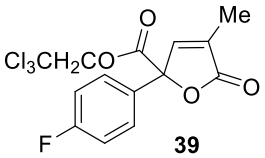
2,2,2-trichloroethyl 5-(4-fluorophenyl)-3-methyl-2-oxo-2,3-dihydrofuran-3-carboxylate



38

Following general procedure A, carbonate **18** (36.8 mg, 0.10 mmol) and DMAP (1.22 mg, 0.01 mmol) in THF (0.4 mL) for 5 min gave a ratio of products (α:γ 67:33). Chromatographic purification (eluent CH_2Cl_2:petrol 40:60) gave **38** (22.0 mg, 60%) as a colorless oil with spectroscopic data in accordance with the literature.[1] δ_H (500 MHz, $CDCl_3$) 1.69 (3H, s, CH_3), 4.67 (1H, ABq, *J* 11.9, C*H*H), 4.80 (1H, ABq, *J* 11.9, CH*H*), 5.77 (1H, s, C(4)*H*), 7.04-7.08 (2H, m, Ar*H*), 7.54-7.57 (2H, m, Ar*H*).

2,2,2-trichloroethyl 2-(4-fluorophenyl)-4-methyl-5-oxo-2,5-dihydrofuran-2-carboxylate

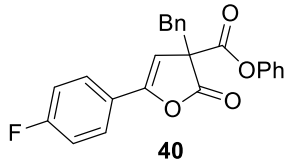


39

Following general procedure B, carbonate **18** (36.8 mg, 0.10 mmol), triazolium BF_4 salt precursor to **8** (2.73 mg, 0.01 mmol) and KHMDS (0.018 mL, 0.009 mmol) in THF (0.4 mL) for 5 min gave a ratio of products (α:γ 15:85). Chromatographic purification (eluent CH_2Cl_2:petrol 70:30) gave **39** (28.0 mg, 76%) as a colorless solid with spectroscopic data in accordance with the literature.[1] mp 84-86 °C {Lit.[1] mp 84-86 °C}; δ_H (500 MHz, $CDCl_3$) 1.94 (3H, d, *J* 1.5, CH_3), 4.69-4.74 (2H, m, CH_2), 7.02-7.05 (2H, m, Ar*H*), 7.43-7.44 (1H, m, C(3)*H*), 7.46-7.49 (2H, m, Ar*H*).

Following general procedure B, carbonate **18** (36.8 mg, 0.10 mmol), triazolium BF_4 salt precursor to **8** (0.27 mg, 1 μmol) and KHMDS (1.8 μL, 0.9 μmol) in THF (0.4 mL) for 10 min gave a ratio of products (α:γ 4:96). Chromatographic purification (eluent CH_2Cl_2:petrol 70:30) gave **39** (32.0 mg, 87%) as a colorless solid. Data are in accordance with those given previously.

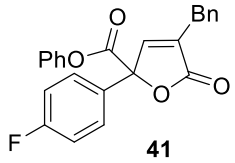
Phenyl 3-benzyl-5-(4-fluorophenyl)-2-oxo-2,3-dihydrofuran-3-carboxylate



40

Following general procedure A, carbonate **19** (50.0 mg, 0.13 mmol) and DMAP (1.58 mg, 0.013 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 71:29). Chromatographic purification (eluent CH_2Cl_2:petrol 50:50) gave **40** (28.0 mg, 56%) as a colorless solid with spectroscopic data in accordance with the literature.[1] mp 108-110 °C {Lit.[1] mp 108-110 °C}; δ_H (400 MHz, $CDCl_3$) 3.41 (1H, ABq, *J* 13.6, PhC*H*H), 3.55 (1H, ABq, *J* 13.6, PhCH*H*), 5.82 (1H, s, C(4)*H*), 6.98-7.02 (4H, m, Ar*H*), 7.16-7.20 (6H, m, Ar*H*), 7.28-7.32 (2H, m, Ar*H*), 7.44-7.47 (2H, m, Ar*H*).

Phenyl 4-benzyl-2-(4-fluorophenyl)-5-oxo-2,5-dihydrofuran-2-carboxylate

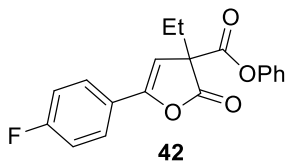


41

Following general procedure B, carbonate **19** (50 mg, 0.13 mmol), triazolium BF_4 salt precursor to **8** (3.52 mg, 0.013 mmol) and KHMDS (0.023 mL, 0.012 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 20:80). Chromatographic purification (eluent CH_2Cl_2:petrol 70:30) gave **41** (28.0 mg, 56%) as a colorless solid; mp 78-80 °C; ν_{max} (KBr) 3087, 2924 (C-H), 1776 (C=O), 1655, 1602, 1509; δ_H (400 MHz, $CDCl_3$) 3.57-3.67 (2H, m, CH_2Ph), 6.90-6.92 (2H, m, Ar*H*), 7.03-7.07 (2H, m, Ar*H*), 7.15-7.31 (9H, m, Ar*H* and C(3)*H*), 7.44-7.48 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 32.0, 87.4, 116.2 (d, *J* 21.9), 121.0, 126.7, 127.3, 128.0 (d, *J* 8.6), 128.9, 129.1, 129.7, 131.0 (d, *J* 3.0), 135.7, 136.4, 146.8, 150.2, 163.3 (d, *J* 248.3), 165.9 and 171.1; *m*/*z* (NSI^+) 406 ($[M+NH_4]^+$, 75%); HRMS (NSI^+) $C_{24}H_{21}O_4NF^+$ ($[M+NH_4]^+$) requires 406.1449; found 406.1449 (-0.0 ppm).

Following general procedure B, carbonate **19** (50.0 mg, 0.13 mmol), triazolium BF_4 salt precursor to **8** (0.352 mg, 1.29 μmol) and KHMDS (2.32 μL, 1.16 μmol) in THF (1 mL) for 1 min gave a ratio of products (α:γ 7:93). Chromatographic purification (eluent CH_2Cl_2:petrol 70:30) gave **41** (39.0 mg, 78%) as a colorless solid. Data are in accordance with those given previously.

phenyl 3-ethyl-5-(4-fluorophenyl)-2-oxo-2,3-dihydrofuran-3-carboxylate

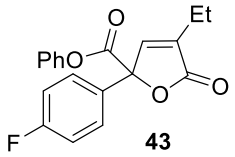


42

Following general procedure A, carbonate **20** (32.6 mg, 0.100 mmol) and DMAP (1.22 mg, 0.01 mmol) in THF (0.3 mL) for 5 min gave a ratio of products (α:γ 48:52). Chromatographic

purification (eluent CH_2Cl_2:petrol 50:50) gave **42** (15.0 mg, 46%) as a colorless solid with spectroscopic data in accordance with the literature.[1] mp 62-64 °C {Lit.[1] mp 62-64 °C}; δ_H (400 MHz, $CDCl_3$) 0.98 (3H, t, *J* 7.5, C*H*$_3$), 2.22 (2H, q, *J* 7.5, C*H*$_2$CH$_3$), 5.82 (1H, s, C(4)*H*), 7.01-7.10 (4H, m, Ar*H*), 7.15-7.19 (1H, m, Ar*H*), 7.28-7.33 (2H, m, Ar*H*), 7.59-7.63 (2H, m, Ar*H*).

phenyl 4-ethyl-2-(4-fluorophenyl)-5-oxo-2,5-dihydrofuran-2-carboxylate

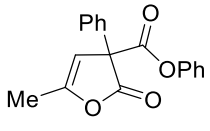


43

Following general procedure B, carbonate **20** (32.6 mg, 0.100 mmol), triazolium BF_4 salt precursor to **8** (2.73 mg, 0.01 mmol) and KHMDS (0.018 mL, 0.009 mmol) in THF (0.3 mL) for 5 min gave a ratio of products (α:γ 20:80). Chromatographic purification (eluent CH_2Cl_2:petrol 70:30) gave **43** (20.0 mg, 61%) as a colorless solid; mp 44-46 °C; ν_{max} (KBr) 3074, 2985 (C-H), 2944, 1769 (C=O), 1601, 1592, 1509; δ_H (400 MHz, $CDCl_3$) 1.18 (3H, t, *J* 7.5, C*H*$_3$), 2.30-2.38 (2H, m, C*H*$_2$CH$_3$), 6.94-6.97 (2H, m, Ar*H*), 7.05-7.09 (2H, m, Ar*H*), 7.16-7.20 (1H, m, Ar*H*), 7.27-7.31 (2H, m, Ar*H*), 7.44 (1H, t, *J* 1.8, C(3)*H*), 7.51-7.55 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$) 11.7, 19.0, 87.2, 116.2 (d, *J* 21.8), 121.0, 126.7, 128.0 (d, *J* 8.5), 129.7, 131.3 (d, *J* 3.3), 137.3, 144.9, 150.3, 163.2 (d, *J* 248.2), 166.2 and 171.4; *m*/*z* (NSI$^+$) 344 ([M+NH$_4$]$^+$, 100%); HRMS (NSI$^+$) $C_{19}H_{19}O_4NF^+$ ([M+NH$_4$]$^+$) requires 344.1293; found 344.1294 (+0.4 ppm).

Following general procedure B, carbonate **20** (32.6 mg, 0.1 mmol), triazolium BF_4 salt precursor to **8** (0.27 mg, 1 μmol) and KHMDS (1.8 μL, 0.9 μmol) in THF (0.3 mL) for 1 min gave a ratio of products (α:γ 4:96). Chromatographic purification (eluent CH_2Cl_2:petrol 70:30) gave **43** (27.0 mg, 83%) as a colorless solid. Data are in accordance with those given previously.

phenyl 5-methyl-2-oxo-3-phenyl-2,3-dihydrofuran-3-carboxylate

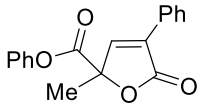


44

Following general procedure A, carbonate **11** (29.4 mg, 0.1 mmol) and DMAP (1.22 mg, 0.01 mmol) in THF (0.3 mL) for 5 min gave a ratio of products (α:γ 57:43). Chromatographic purification (eluent CH_2Cl_2:petrol 50:50) gave **44** (14.0 mg, 48%) as a colorless solid with

spectroscopic data in accordance with the literature.[1] mp 56-58 °C {Lit.[1] mp 56-58 °C}; δ_H (400 MHz, $CDCl_3$) 2.11 (3H, d, *J* 1.5, C*H*$_3$), 5.72 (1H, q, *J* 1.5, C(4)*H*), 6.97-7.00 (2H, m, Ar*H*), 7.14-7.18 (1H, m, Ar*H*), 7.26-7.38 (5H, m, Ar*H*), 7.49-7.52 (2H, m, Ar*H*).

phenyl 2-methyl-5-oxo-4-phenyl-2,5-dihydrofuran-2-carboxylate



45

Following general procedure B, carbonate **11** (29.4 mg, 0.1 mmol), triazolium BF_4 salt precursor to **8** (2.73 mg, 0.01 mmol) and KHMDS (0.018 mL, 0.009 mmol) in THF (0.3 mL) for 5 min gave a ratio of products (α:γ 1:99). Chromatographic purification (eluent CH_2Cl_2:petrol 70:30) gave **45** (25.0 mg, 85%) as a colorless oil with spectroscopic data in accordance with the literature.[1] δ_H (400 MHz, $CDCl_3$) 1.87 (3H, s, C*H*$_3$), 7.01-7.05 (2H, m, Ar*H*), 7.17-7.21 (1H, m, Ar*H*), 7.29-7.39 (5H, m, Ar*H*), 7.59 (1H, s, C(3)*H*), 7.83-7.86 (2H, m, Ar*H*).

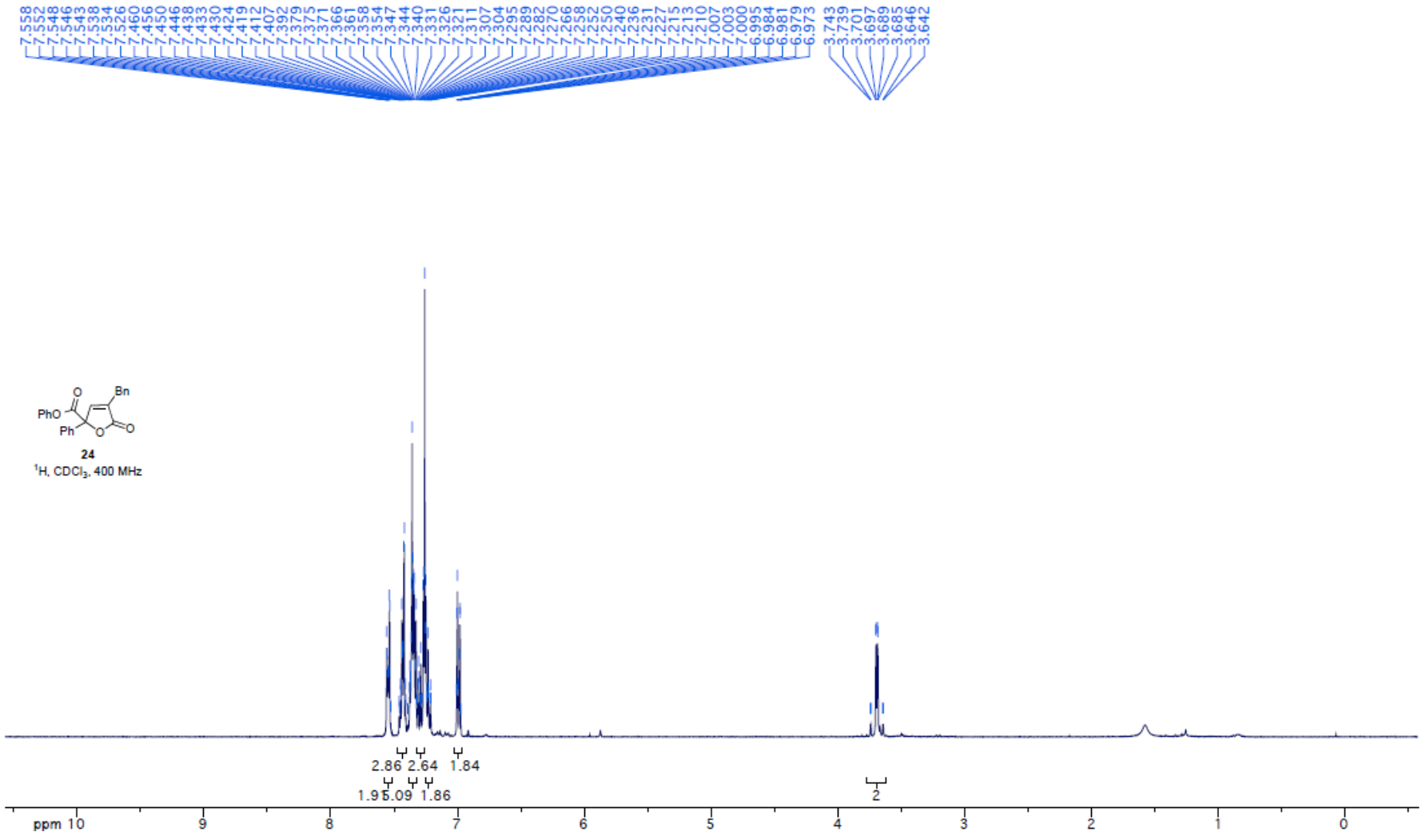
Following general procedure B, carbonate **11** (29.4 mg, 0.1 mmol), triazolium BF_4 salt precursor to **8** (0.27 mg, 1 μmol) and KHMDS (1.8 μL, 0.9 μmol) in THF (0.3 mL) for 1 h gave a exclusively the γ product. Chromatographic purification (eluent CH_2Cl_2:petrol 70:30) gave **45** (26.0 mg, 88%) as a colorless oil. Data are in accordance with those given previously.

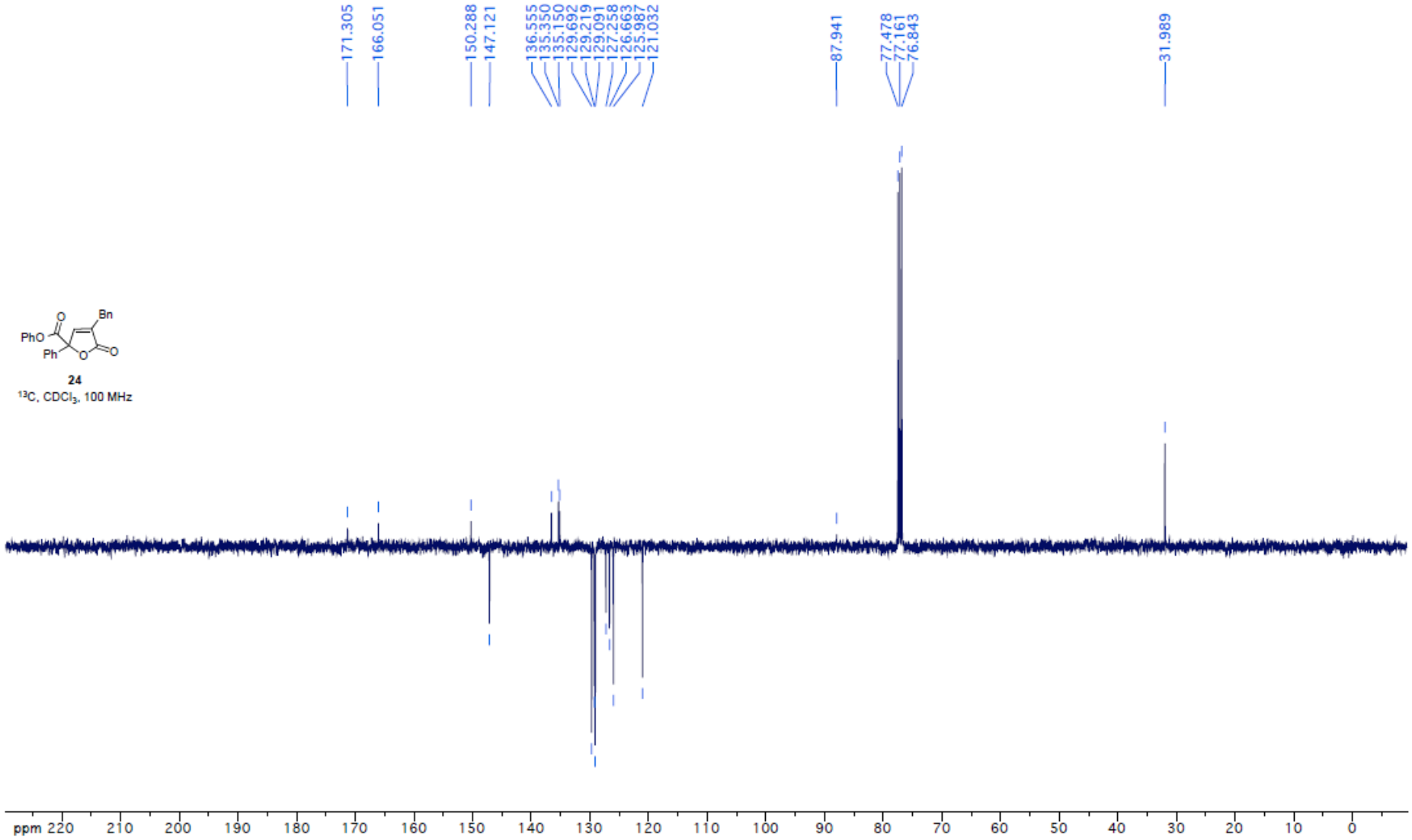
1.4 References and Notes:

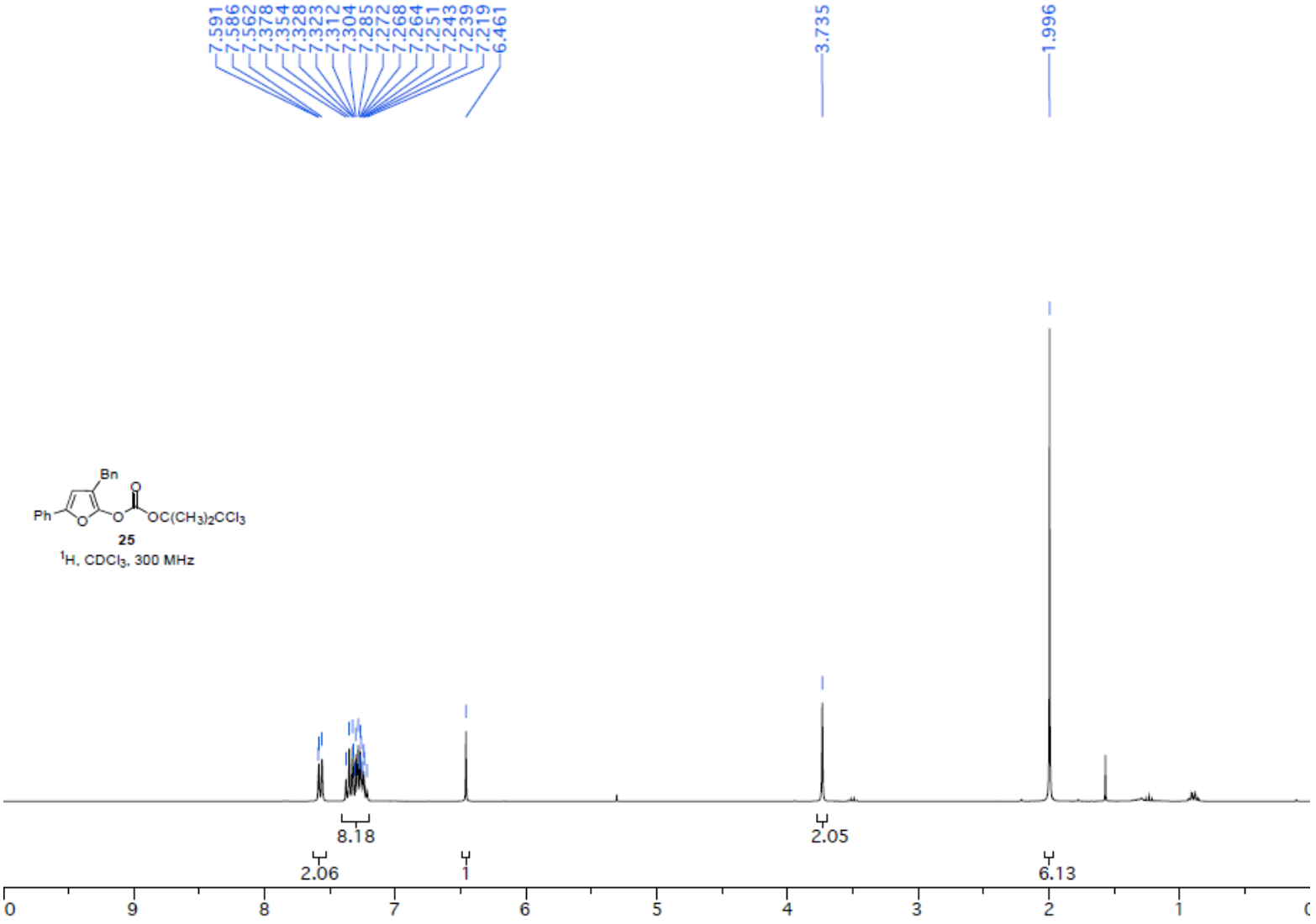
[1] C. Joannesse, L. C. Morrill, C. D. Campbell, A. M. Z. Slawin and A. D. Smith, *Synthesis*, 2011, 1865-1879.

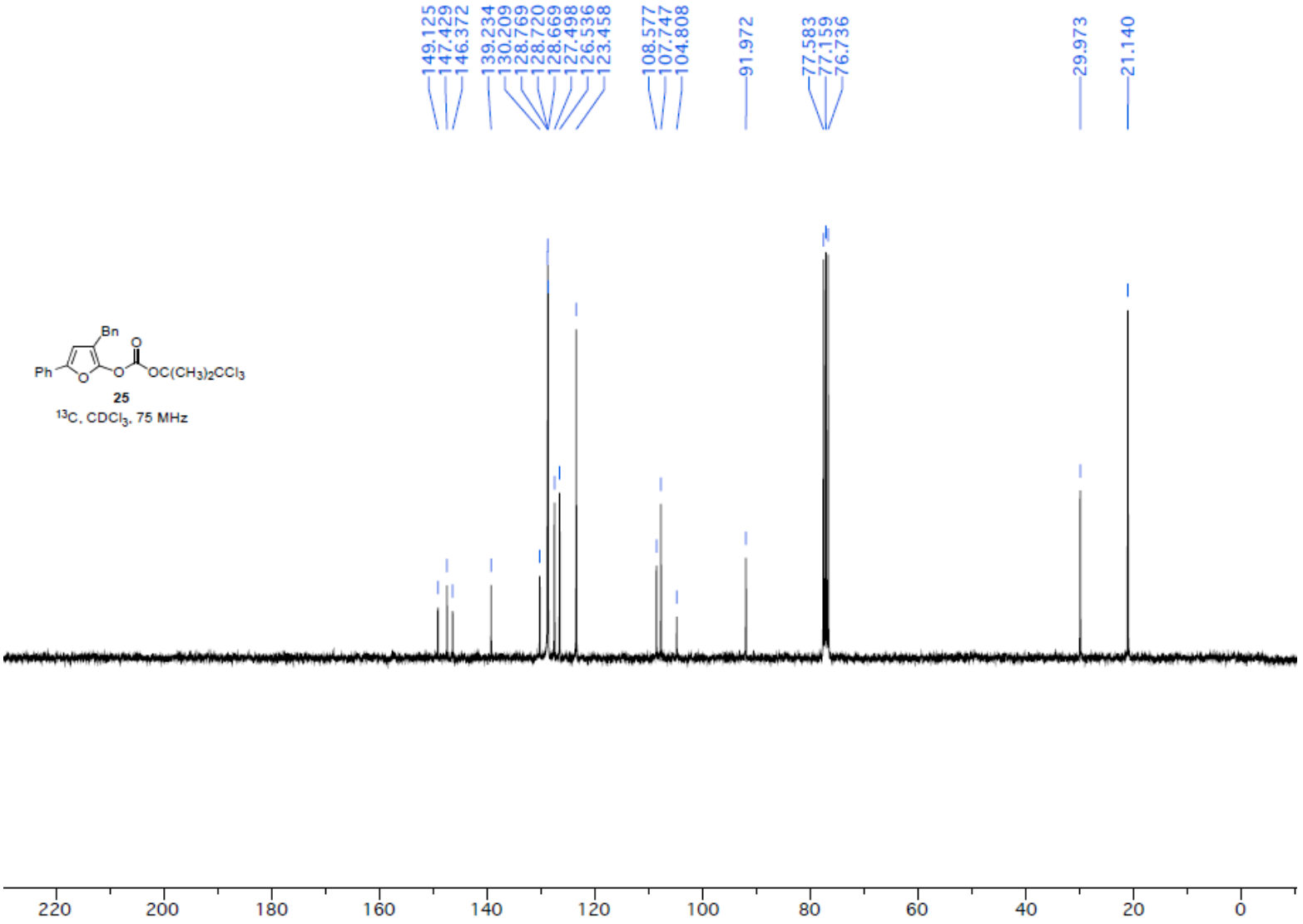
[2] P. Aleman, J. Christy, J. W. Kampf, S. A. Shaw, P. Va and E. Vedejs, *J. Am. Chem. Soc.*, 2006, **128**, 925-934.

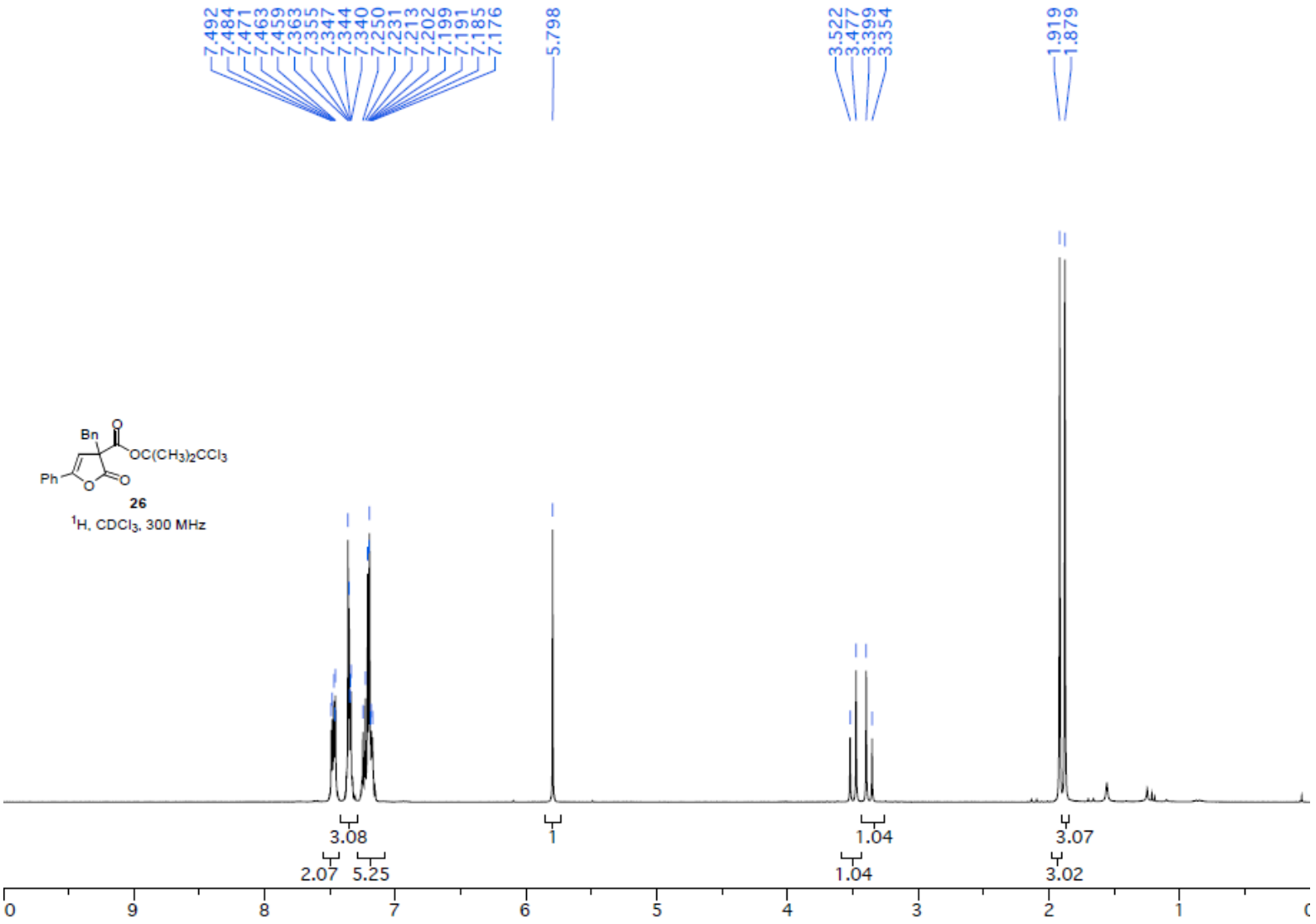
1.5 ^{1}H and ^{13}C NMR Spectra for Novel Compounds

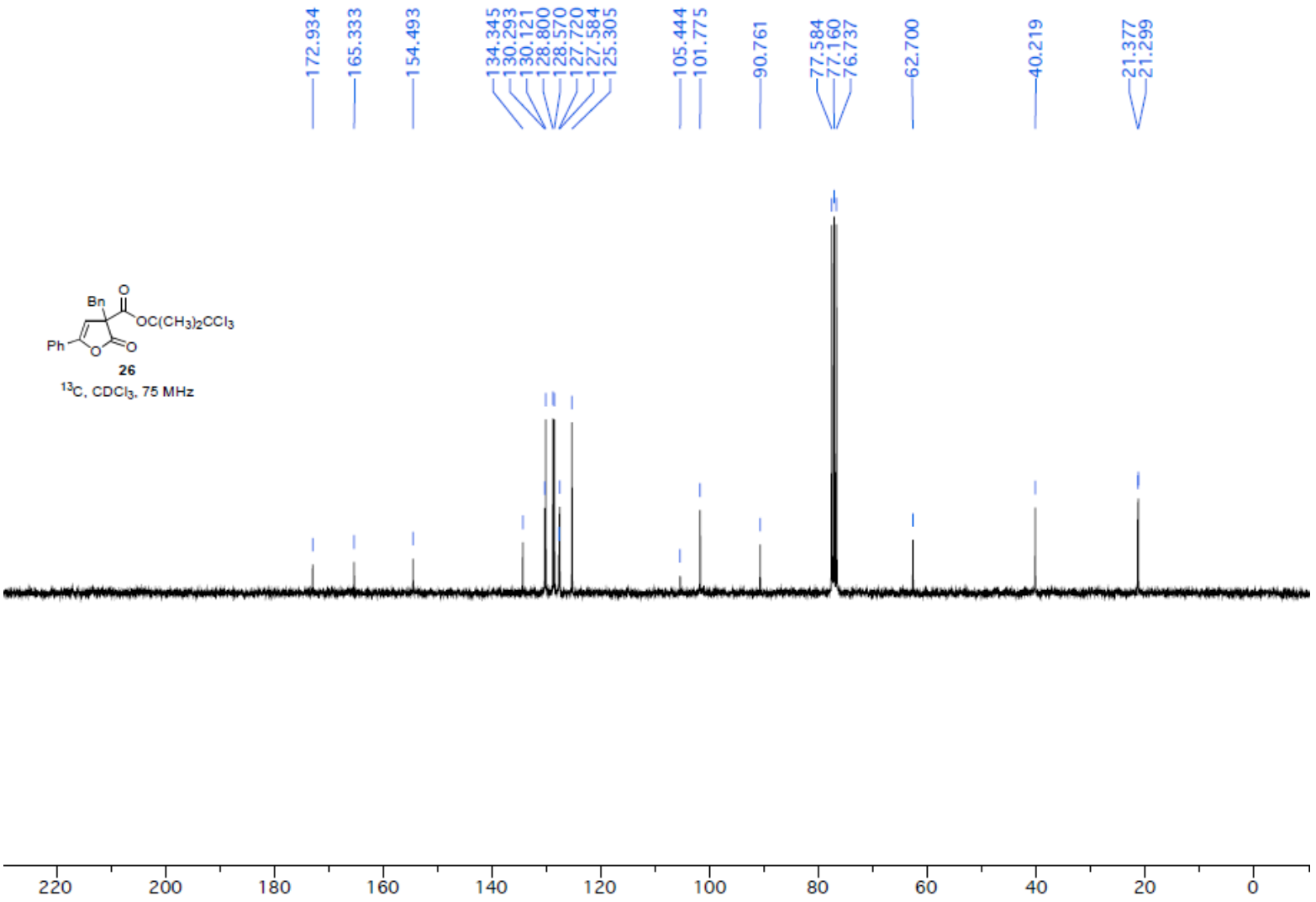


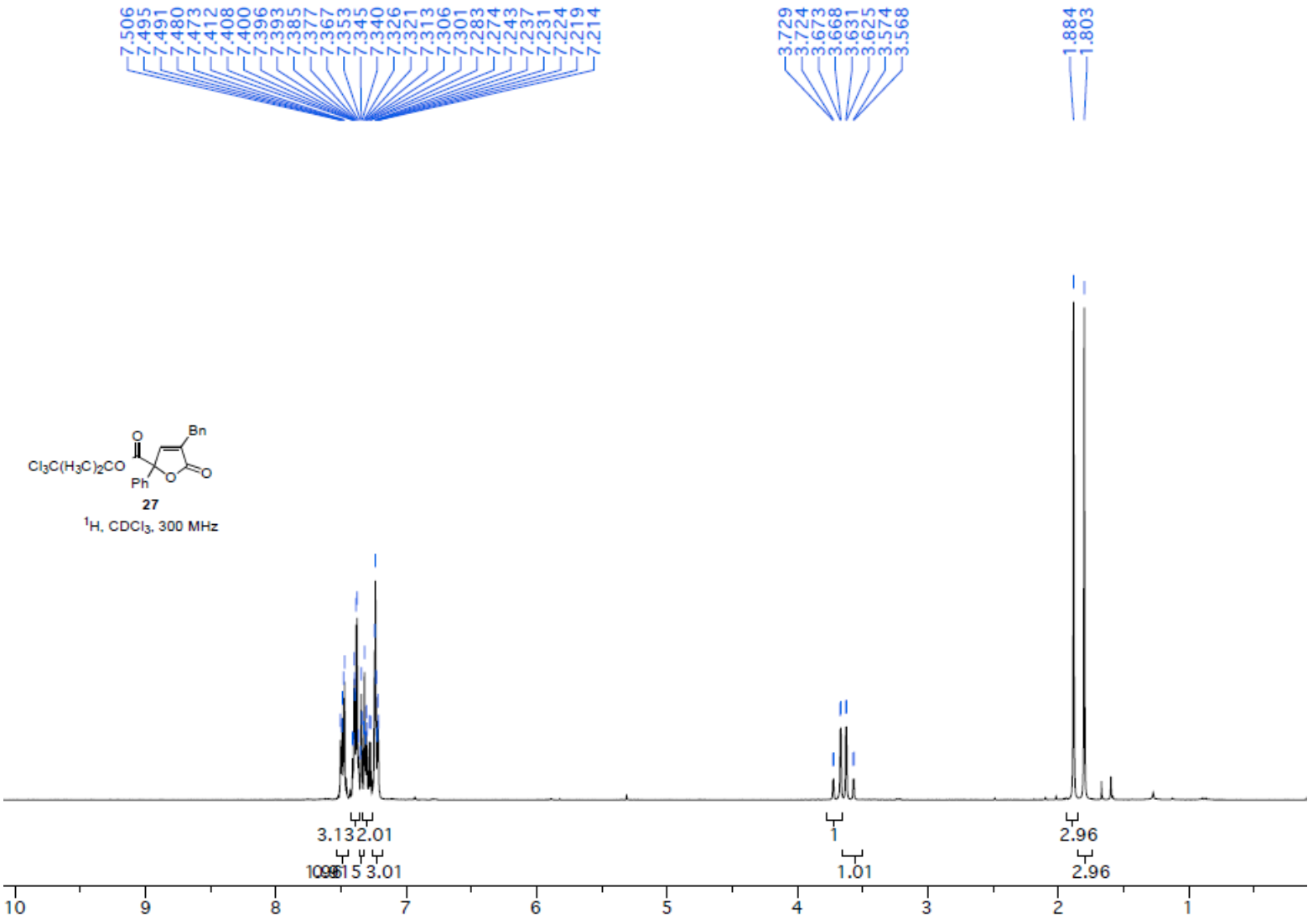

171.305
166.051
150.288
147.121
136.555
135.350
135.150
129.692
129.219
129.091
127.258
126.663
125.987
121.032
87.941
77.478
77.161
76.843
31.989
Bn
PhO
Ph
O
O
O
24
13C, CDCl3, 100 MHz
ppm 220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

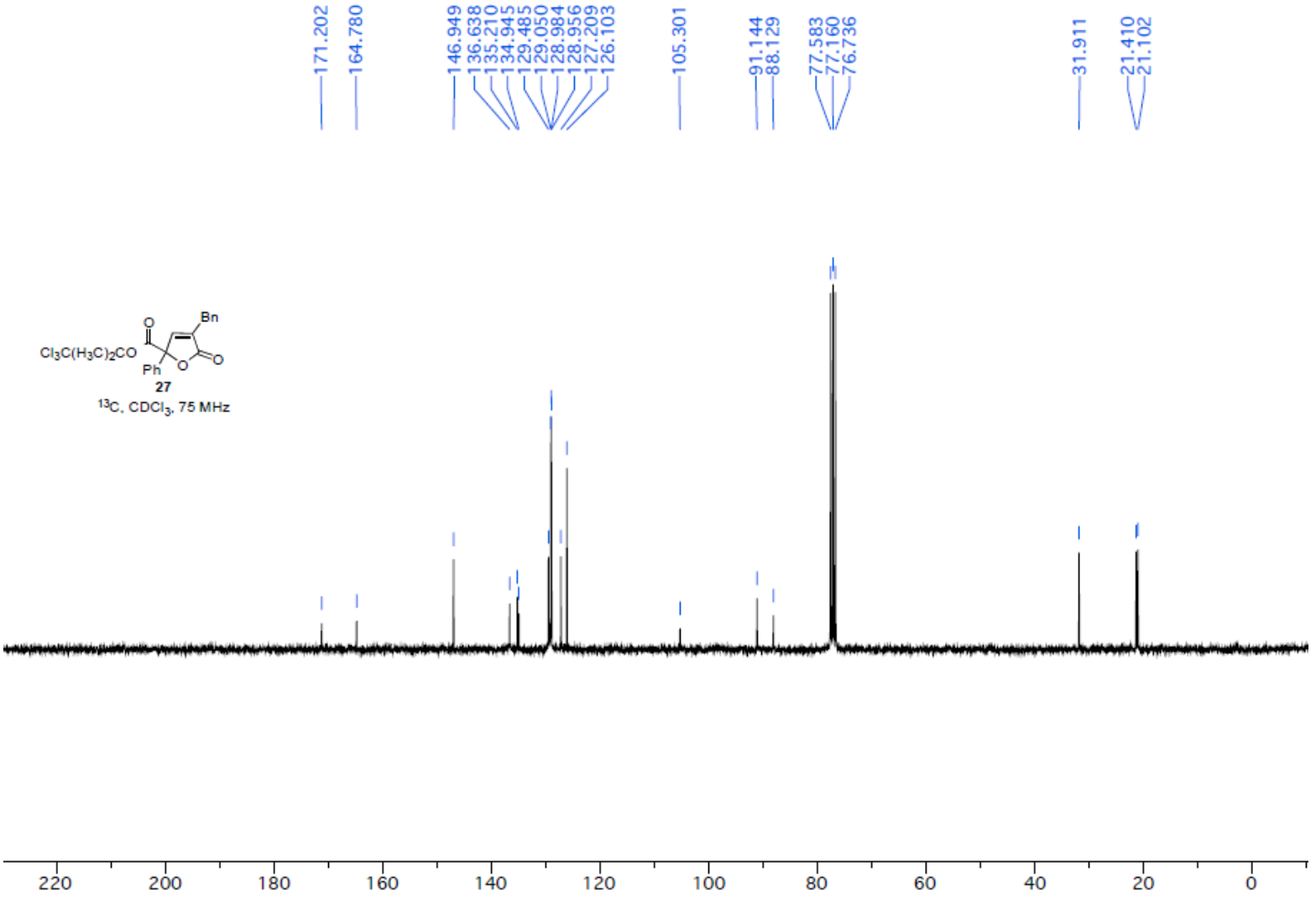

7.591
7.586
7.562
7.378
7.354
7.328
7.323
7.312
7.304
7.285
7.272
7.268
7.264
7.251
7.243
7.239
7.219
6.461
3.735
1.996
Bn
Ph
O
O
OC(CH3)2CCl3
25
1H, CDCl3, 300 MHz
8.18
2.05
2.06
1
6.13
0
9
8
7
6
5
4
3
2
1


149.125
147.429
146.372
139.234
130.209
128.769
128.720
128.669
127.498
126.536
123.458
108.577
107.747
104.808
91.972
77.583
77.159
76.736
29.973
21.140
Bn
Ph
O
OC(CH3)2CCl3
25
13C, CDCl3, 75 MHz
220
200
180
160
140
120
100
80
60
40
20
0


7.492
7.484
7.471
7.463
7.459
7.363
7.355
7.347
7.344
7.340
7.250
7.231
7.213
7.202
7.199
7.191
7.185
7.176
5.798
3.522
3.477
3.399
3.354
1.919
1.879
Bn
OC(CH3)2CCl3
Ph
O
O
O
26
1H, CDCl3, 300 MHz
3.08
1
1.04
3.07
2.07
5.25
1.04
3.02
0
9
8
7
6
5
4
3
2
1
0


172.934
165.333
154.493
134.345
130.293
130.121
128.800
128.570
127.720
127.584
125.305
105.444
101.775
90.761
77.584
77.160
76.737
62.700
40.219
21.377
21.299
Bn
O
OC(CH3)2CCl3
Ph
O
O
26
13C, CDCl3, 75 MHz
220
200
180
160
140
120
100
80
60
40
20
0


7.506
7.495
7.491
7.480
7.473
7.412
7.408
7.400
7.396
7.393
7.385
7.377
7.367
7.353
7.345
7.340
7.326
7.321
7.313
7.306
7.301
7.283
7.274
7.243
7.237
7.231
7.224
7.219
7.214
3.729
3.724
3.673
3.668
3.631
3.625
3.574
3.568
1.884
1.803
Bn
O
Cl3C(H3C)2CO
Ph
O
O
27
1H, CDCl3, 300 MHz
3.13
2.01
3.01
1
1.01
2.96
2.96
10
9
8
7
6
5
4
3
2
1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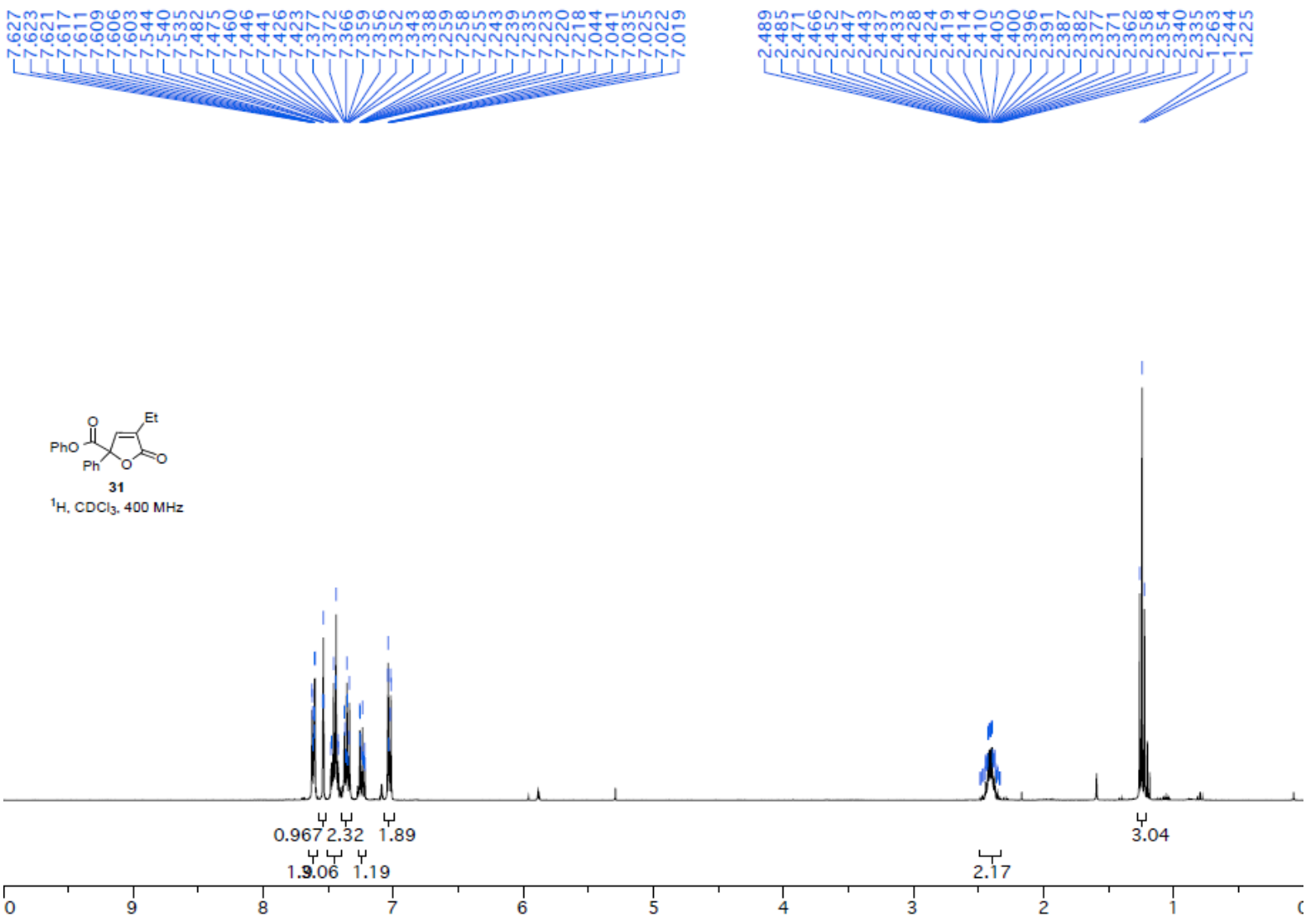
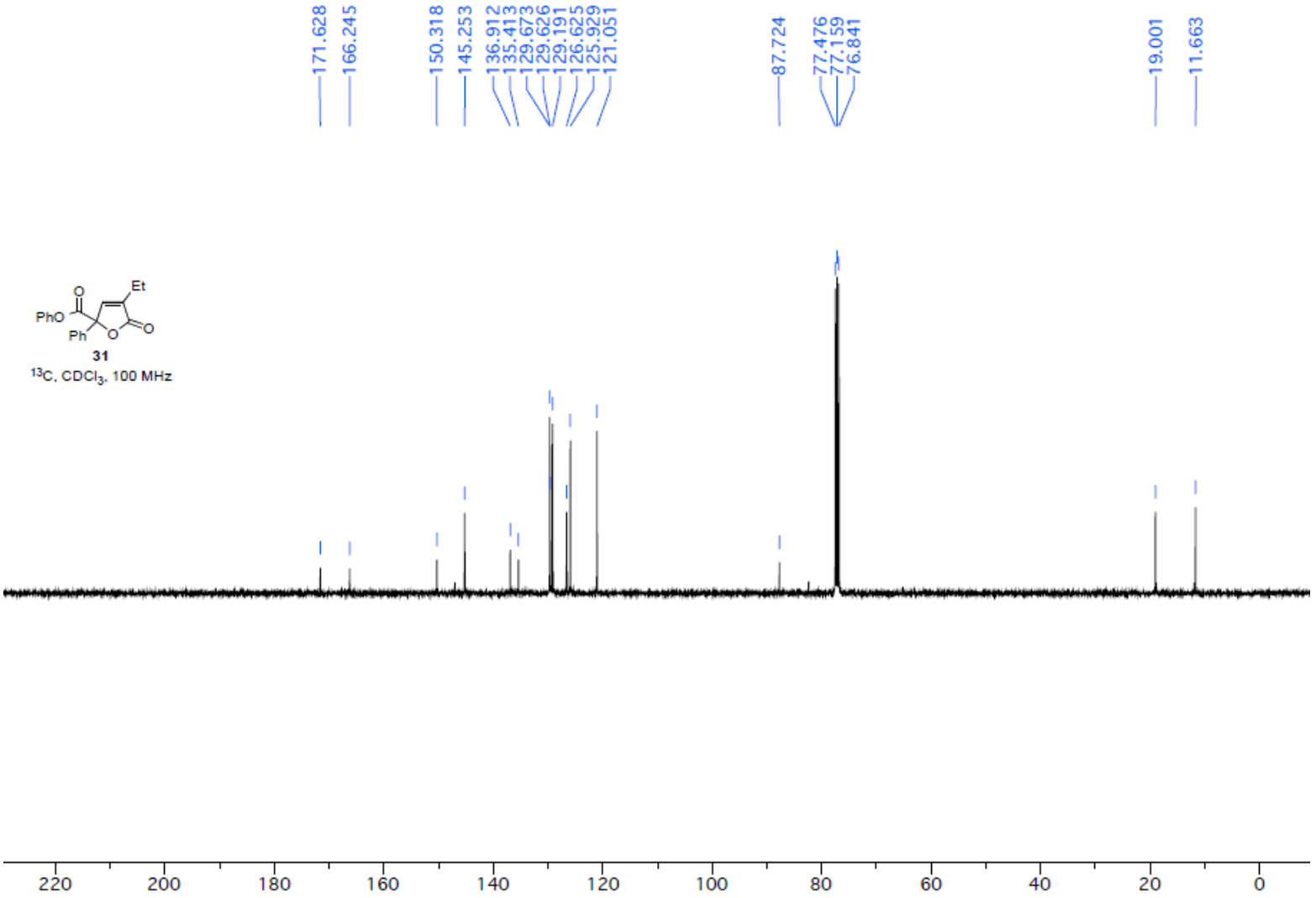
164.780
146.949
136.638
135.210
134.945
129.485
129.050
128.984
128.956
127.209
126.103
105.301
91.144
88.129
77.583
77.160
76.736
31.911
21.410
21.102
Bn
O
O
O
Ph
Cl3C(H3C)2CO
27
13C, CDCl3, 75 MHz
220
200
180
160
140
120
100
80
60
40
20
0


7.627
7.623
7.621
7.617
7.611
7.609
7.606
7.603
7.544
7.540
7.535
7.482
7.475
7.460
7.446
7.441
7.426
7.423
7.377
7.372
7.366
7.359
7.356
7.352
7.343
7.338
7.259
7.258
7.255
7.243
7.239
7.235
7.223
7.220
7.218
7.044
7.041
7.035
7.025
7.022
7.019
2.489
2.485
2.471
2.466
2.452
2.447
2.443
2.437
2.433
2.428
2.424
2.419
2.414
2.410
2.405
2.400
2.396
2.391
2.387
2.382
2.377
2.371
2.362
2.358
2.354
2.340
2.335
1.263
1.244
1.225
PhO
O
Et
Ph
O
O
31
1H, CDCl3, 400 MHz
0.967
2.32
1.89
3.04
1.19
2.17
0
9
8
7
6
5
4
3
2
1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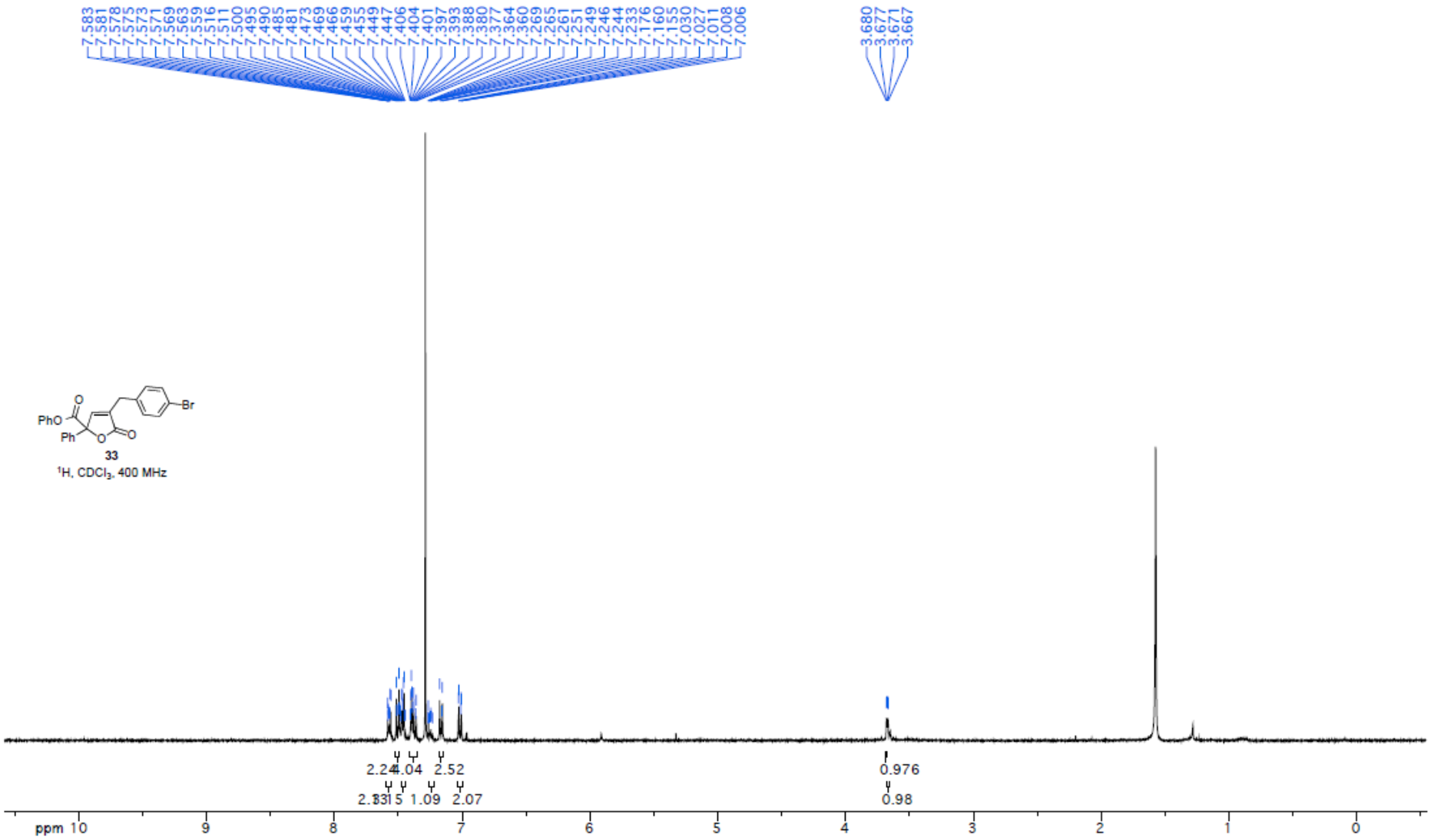
150.318
145.253
136.912
135.413
129.673
129.626
129.191
126.625
125.929
121.051
87.724
77.476
77.159
76.841
19.001
11.663
PhO
Et
Ph
31
13C, CDCl3, 100 MHz
220
200
180
160
140
120
100
80
60
40
20
0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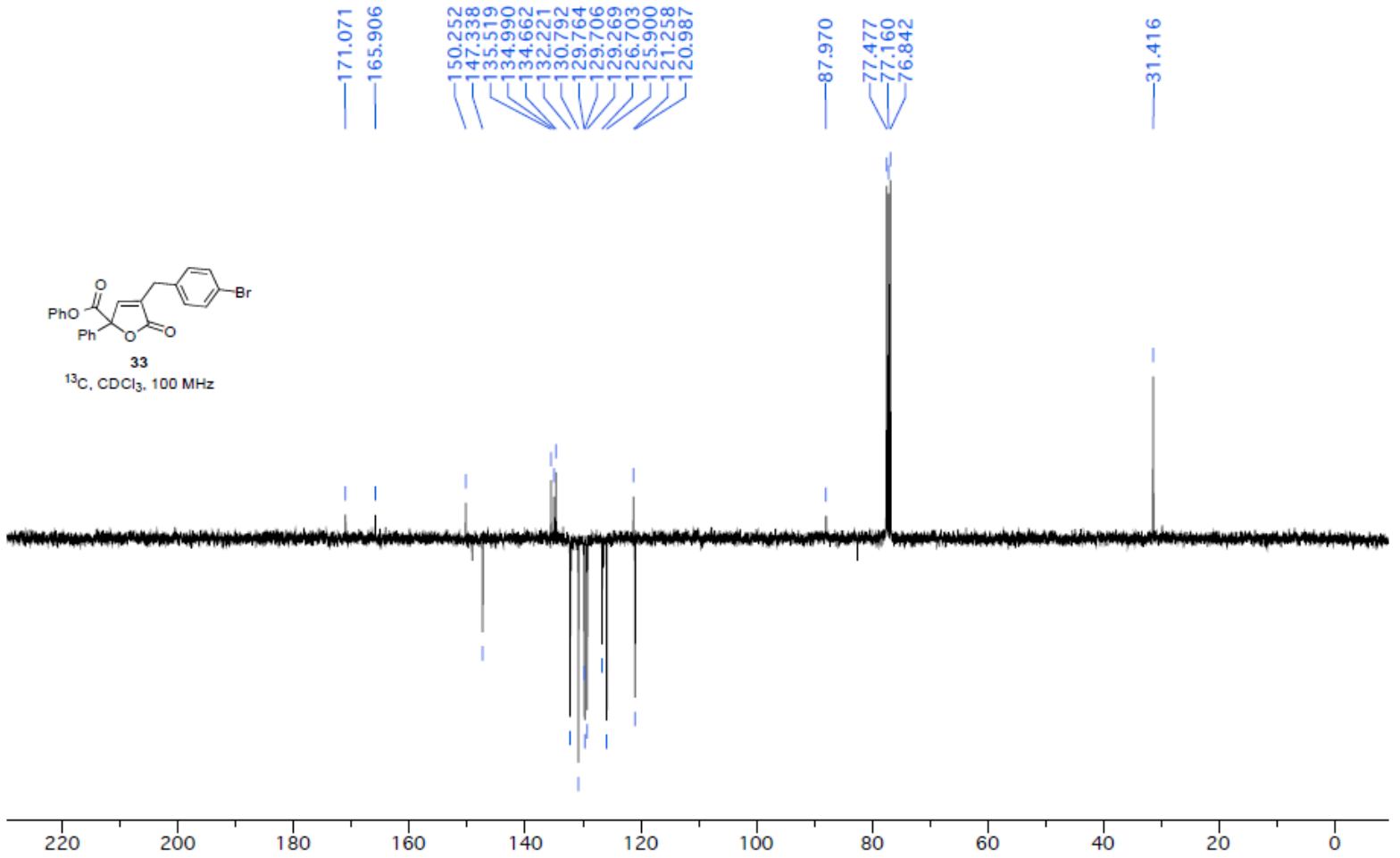
7.578
7.575
7.573
7.571
7.569
7.563
7.559
7.516
7.511
7.500
7.495
7.490
7.485
7.481
7.473
7.469
7.466
7.459
7.455
7.449
7.447
7.406
7.404
7.401
7.397
7.393
7.388
7.380
7.377
7.364
7.360
7.269
7.265
7.261
7.251
7.249
7.246
7.244
7.233
7.176
7.160
7.155
7.030
7.027
7.011
7.008
7.006
3.680
3.677
3.671
3.667
PhO
Ph
O
O
O
Br
33
1H, CDCl3, 400 MHz
2.24
4.04
2.52
2.33
1.15
1.09
2.07
0.976
0.98
ppm 10
9
8
7
6
5
4
3
2
1
0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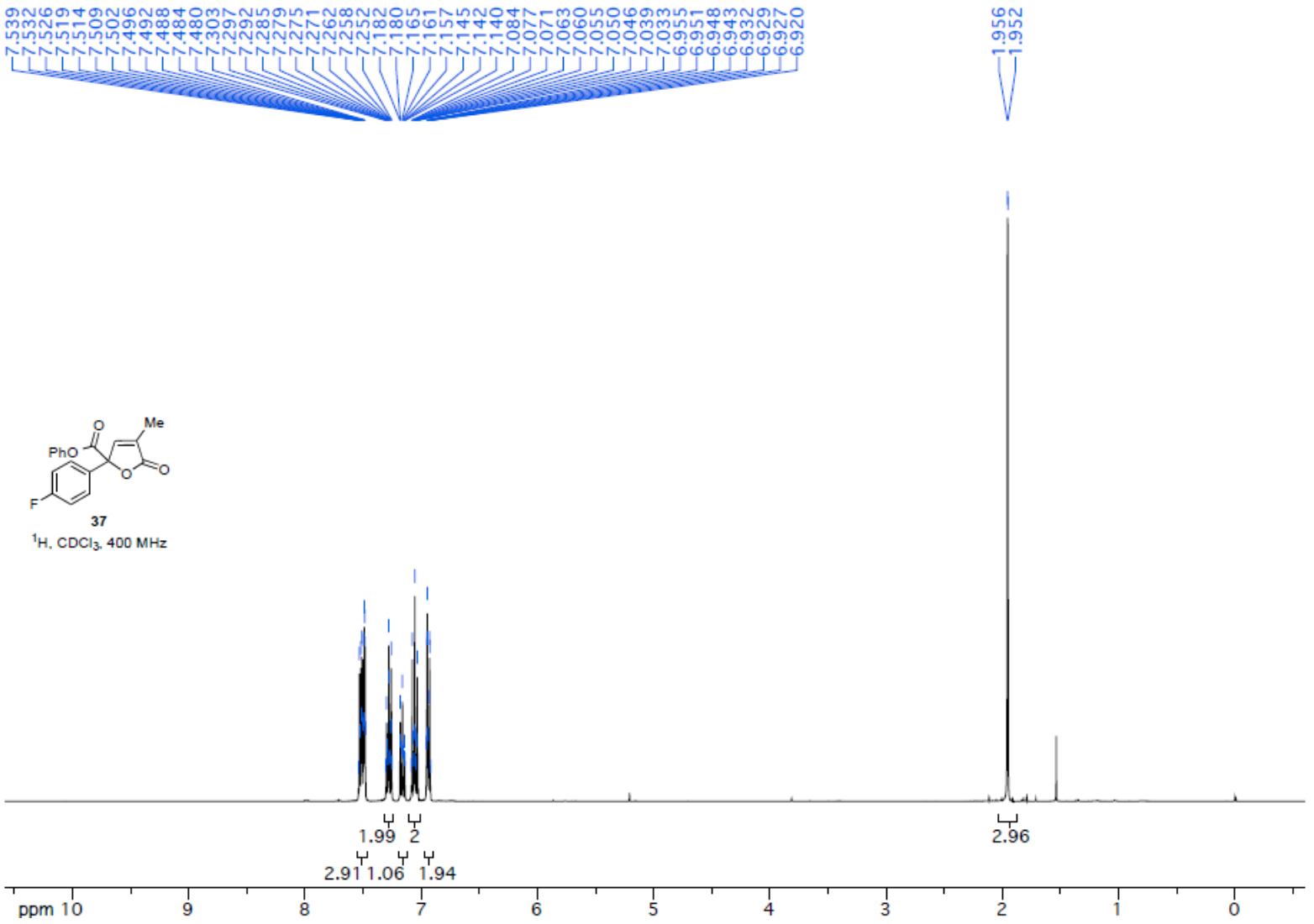
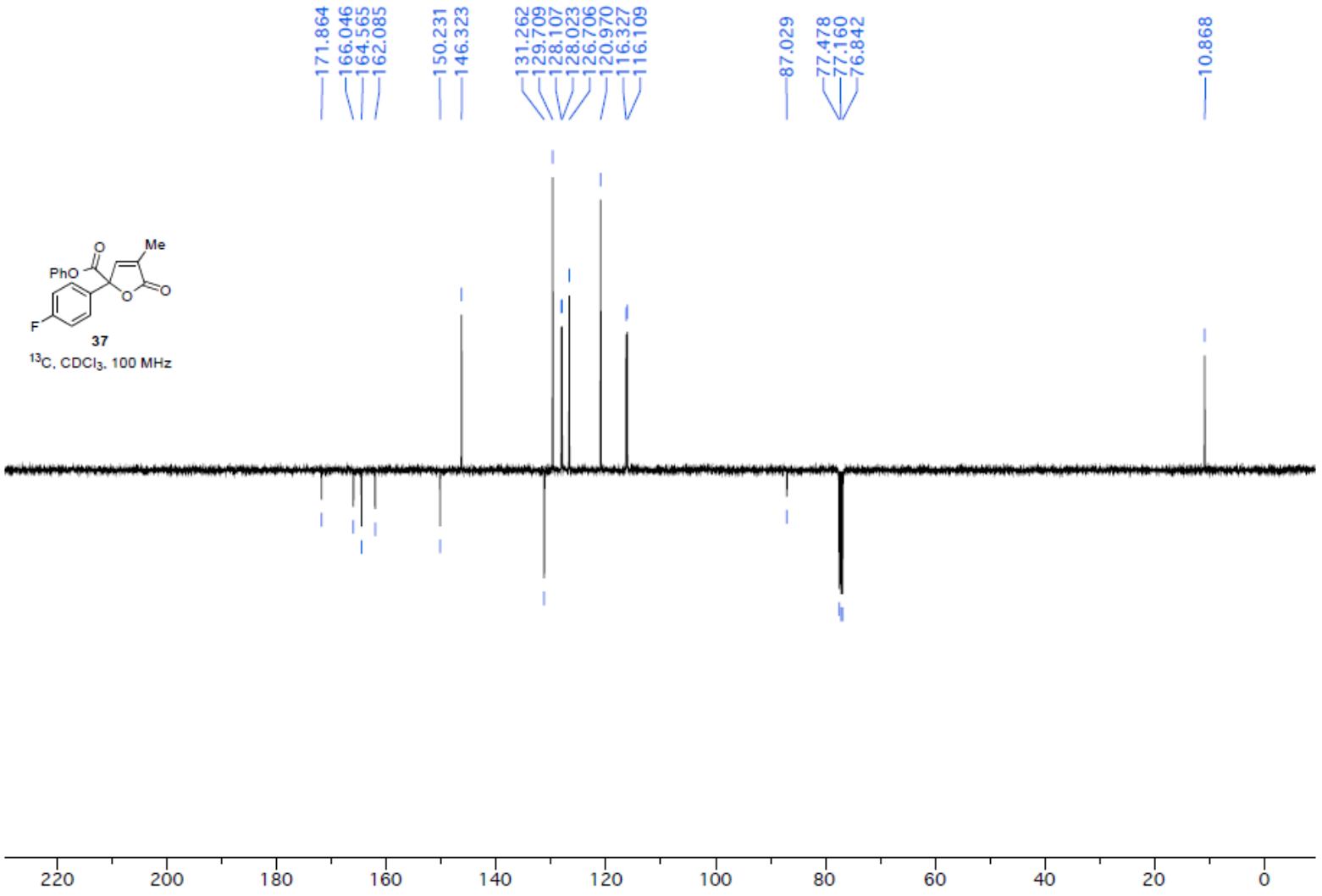
147.338
135.519
134.990
134.662
132.221
130.792
129.764
129.706
129.269
126.703
125.900
121.258
120.987
87.970
77.477
77.160
76.842
31.416
PhO
Ph
O
O
O
Br
33
13C, CDCl3, 100 MHz
220
200
180
160
140
120
100
80
60
40
20
0


7.539
7.532
7.526
7.519
7.514
7.509
7.502
7.496
7.492
7.488
7.484
7.480
7.303
7.297
7.292
7.285
7.279
7.275
7.271
7.262
7.258
7.252
7.182
7.180
7.165
7.161
7.157
7.145
7.142
7.140
7.084
7.077
7.071
7.063
7.060
7.055
7.050
7.046
7.039
7.033
6.955
6.951
6.948
6.943
6.932
6.929
6.927
6.920
1.956
1.952
Me
PhO
O
O
O
F
37
1H, CDCl3, 400 MHz
1.99
2
2.96
2.91
1.06
1.94
ppm 10
9
8
7
6
5
4
3
2
1
0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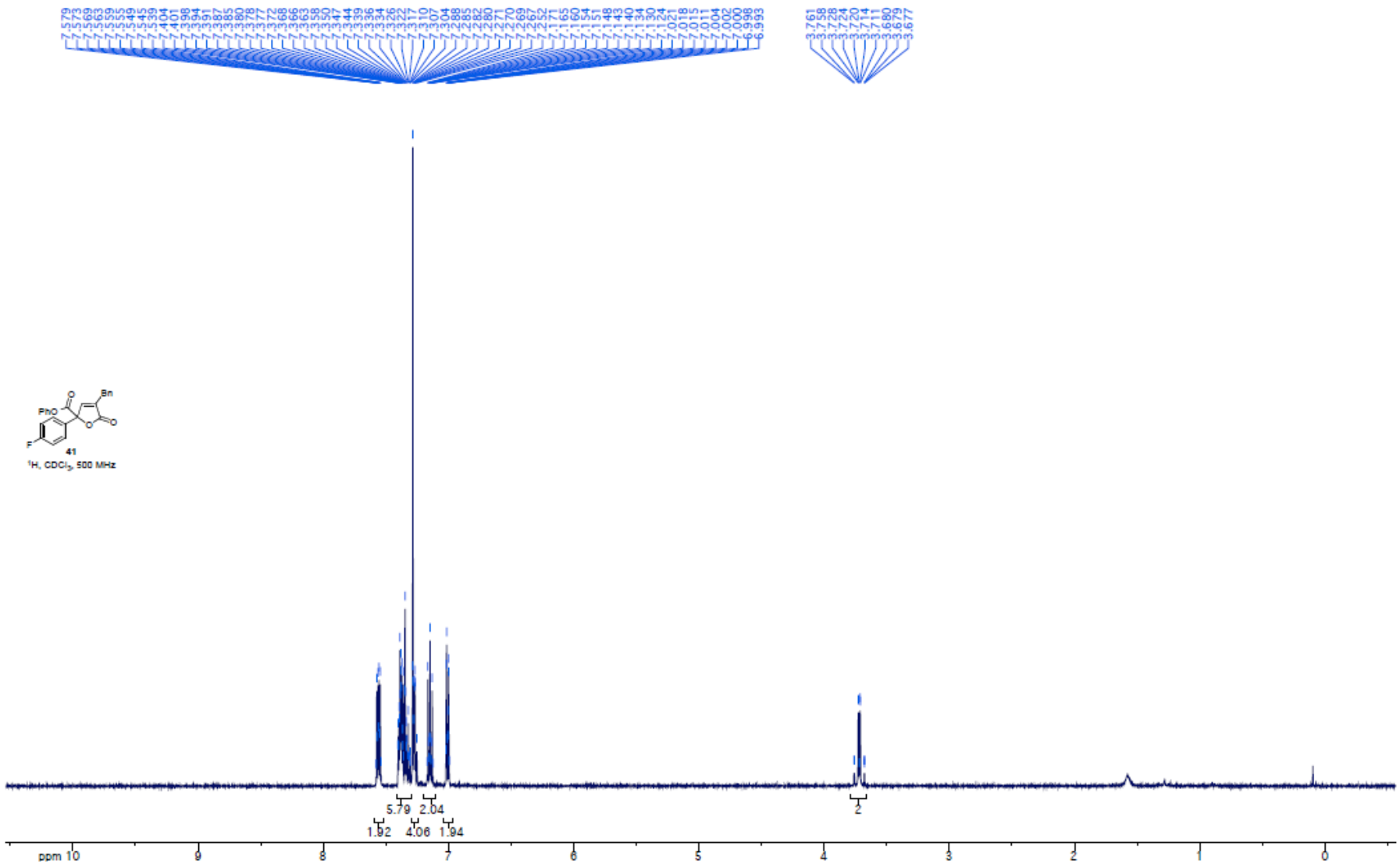
164.565
162.085
150.231
146.323
131.262
129.709
128.107
128.023
126.706
120.970
116.327
116.109
87.029
77.478
77.160
76.842
10.868
PhO
O
Me
O
O
F
37
13C, CDCl3, 100 MHz
220
200
180
160
140
120
100
80
60
40
20
0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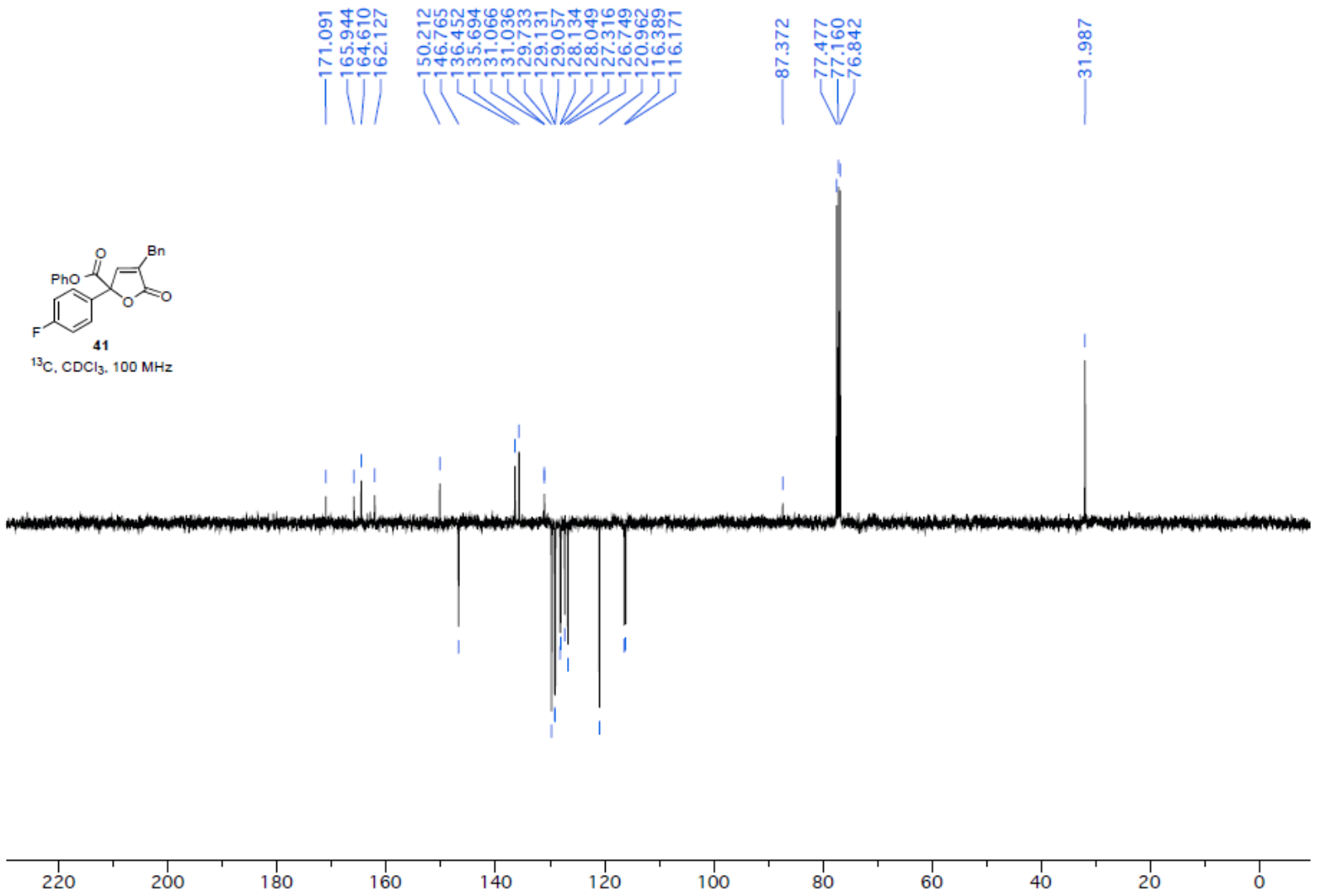
7.573
7.569
7.563
7.559
7.555
7.549
7.545
7.539
7.404
7.401
7.398
7.394
7.391
7.387
7.385
7.380
7.378
7.377
7.372
7.368
7.366
7.363
7.358
7.357
7.347
7.344
7.339
7.336
7.334
7.326
7.322
7.317
7.310
7.307
7.304
7.288
7.285
7.282
7.280
7.271
7.270
7.269
7.267
7.252
7.171
7.165
7.160
7.154
7.151
7.148
7.143
7.140
7.134
7.130
7.124
7.021
7.018
7.015
7.011
7.004
7.002
7.000
6.998
6.993
3.761
3.758
3.728
3.724
3.720
3.714
3.711
3.680
3.679
3.677
PhO
Bn
F
41
^{1}H, CDCl$_3$, 500 MHz
1.92
5.79
4.06
2.04
1.94
2
ppm 10
9
8
7
6
5
4
3
2
1
0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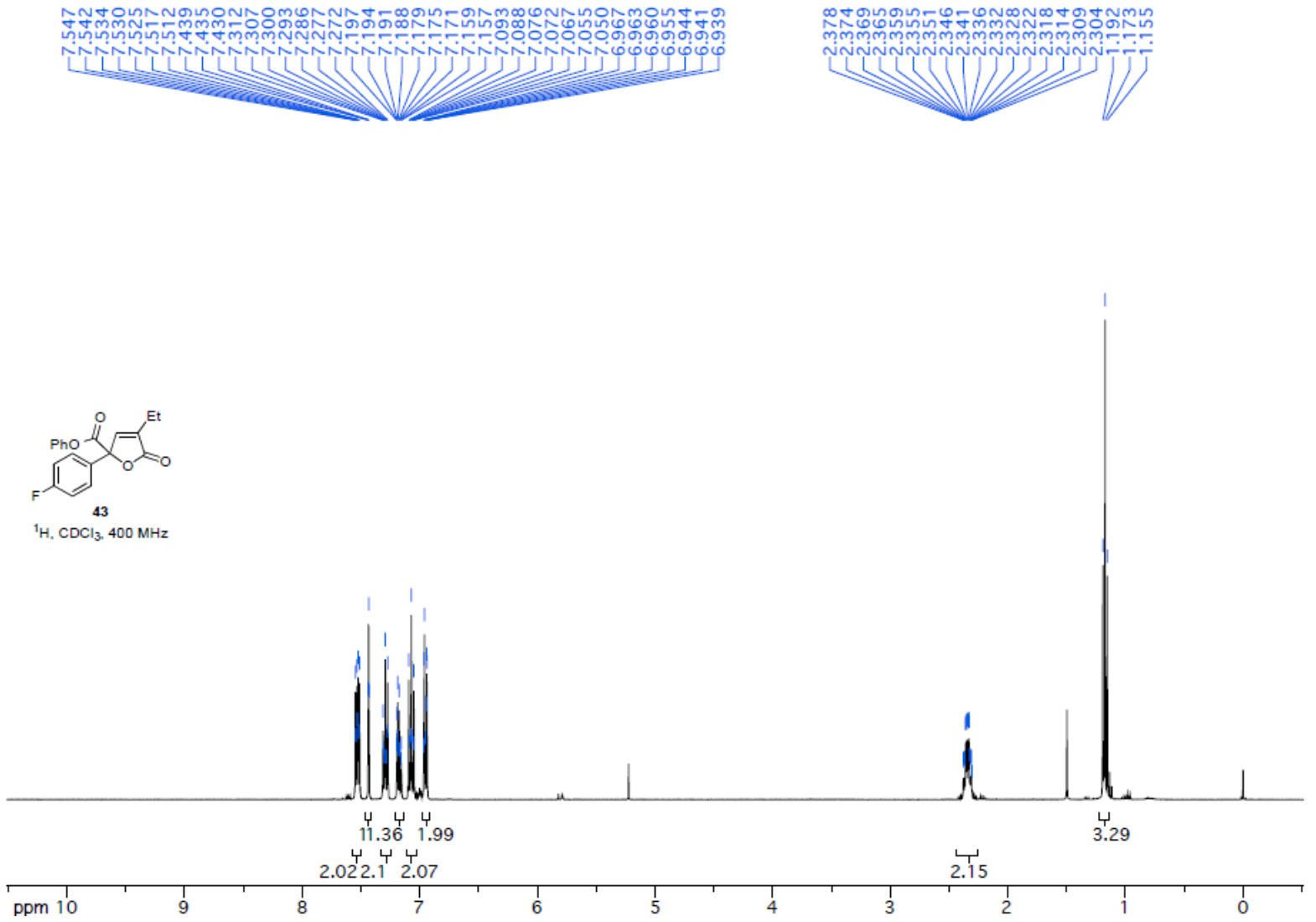
164.610
162.127
150.212
146.765
136.452
135.694
131.066
131.036
129.733
129.131
129.057
128.134
128.049
127.316
126.749
120.962
116.389
116.171
87.372
77.477
77.160
76.842
31.987
PhO
O
Bn
O
O
F
41
13C, CDCl3, 100 MHz
220
200
180
160
140
120
100
80
60
40
20
0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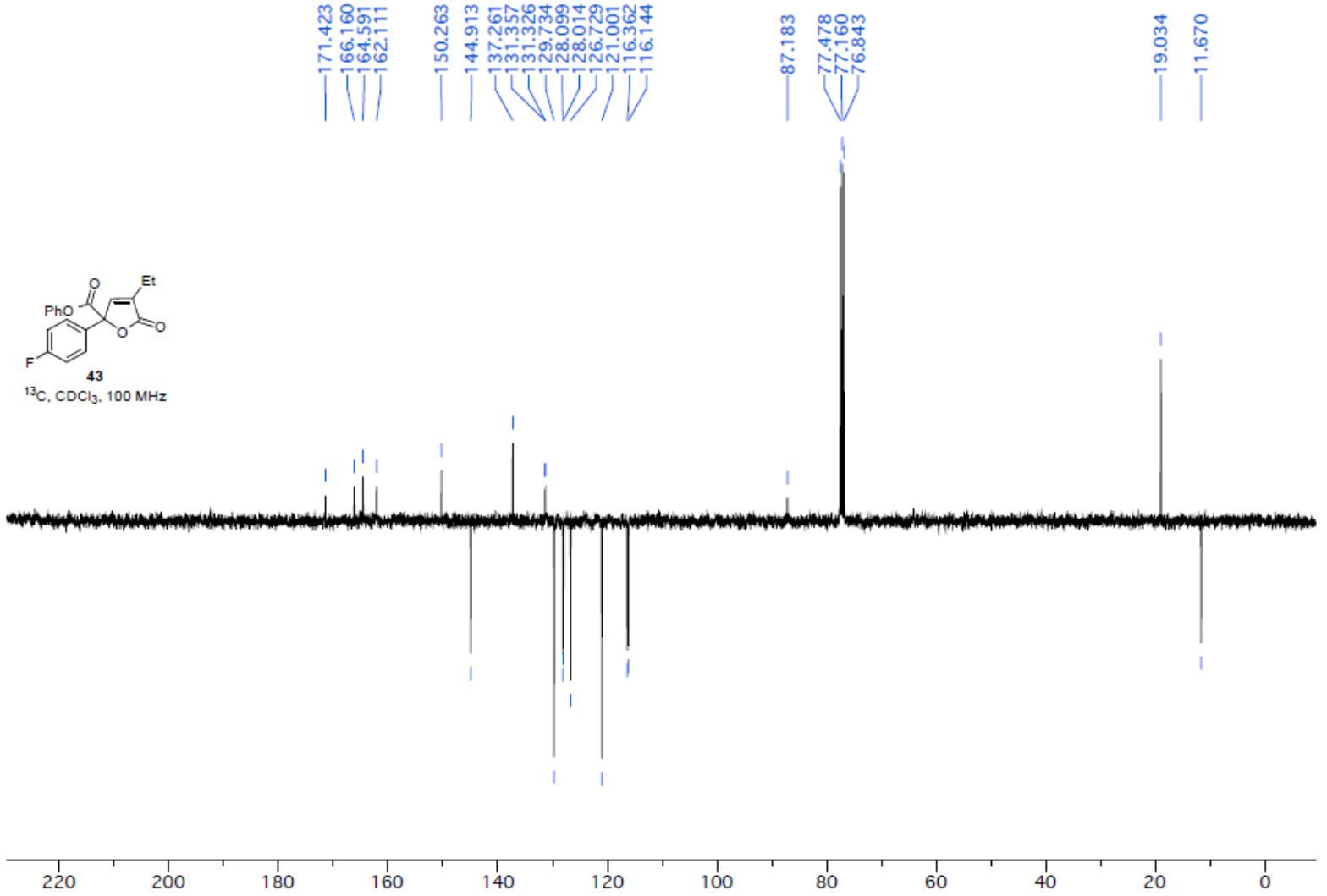
7.542
7.534
7.530
7.525
7.517
7.512
7.439
7.435
7.430
7.312
7.307
7.300
7.293
7.286
7.277
7.272
7.197
7.194
7.191
7.188
7.179
7.175
7.171
7.159
7.157
7.093
7.088
7.076
7.072
7.067
7.055
7.050
6.967
6.963
6.960
6.955
6.944
6.941
6.939
2.378
2.374
2.369
2.365
2.359
2.355
2.351
2.346
2.341
2.336
2.332
2.328
2.322
2.318
2.314
2.309
2.304
1.192
1.173
1.155
PhO
O
Et
O
O
F
43
1H, CDCl3, 400 MHz
11.36
1.99
2.02
2.1
2.07
2.15
3.29
ppm 10
9
8
7
6
5
4
3
2
1
0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164.591
162.111
150.263
144.913
137.261
131.357
131.326
129.734
128.099
128.014
126.729
121.001
116.362
116.144
87.183
77.478
77.160
76.843
19.034
11.670
PhO
O
Et
O
O
F
43
13C, CDCl3, 100 MHz
220
200
180
160
140
120
100
80
60
40
20
0