Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Chiral *N*-Heterocyclic Carbene Catalyzed Enantioselective Annulation of *α*,*β*-Unsaturated Aldehydes with 1,3-Dicarbonyls

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General Methods. All reactions were carried out under nitrogen atmosphere. All the reagents used were purchased from commercial sources and used without further purification. THF and toluene were freshly distilled from sodium wire. ^{1}H, ^{13}C NMR spectra were recorded in $CDCl_3$ on a spectrometer operating at 300 and 100 MHz, respectively. Chemical shifts are reported in parts per million relative to the appropriate standard: TMS for ^{1}H and ^{13}C NMR spectra. High Resoultion Mass spectra were recorded on a Waters Micromass GCT instrument. The IR spectra were recorded on a Shimadzu IR-440 spectrometer. Column chromatography was carried out on silica gel (300-400 mm).

General Procedure for Chiral *N*-Heterocyclic Carbene Catalyzed Enantioselective Annulation of Ynals with 1,3-Dicarbonyls (G1)

Into an oven dried 10 mL vial was weighed catalyst **C3** (7.4 mg, 0.02 mmol) and 4 Å MS (200 mg). Followed by the addition of a solution of ynal (0.3 mmol), 1,3-dicarbonyl (0.2 mmol) in toluene (2 mL). After stirring at 40 ^{o}C for 8 h, the reaction mixture was filtrated, and the solvent was evaporated under reduced pressure at room temperature to afford a residue. Further purification by flash column chromatography on silica gel gave the final product (Hexane : EtOAc = 10 : 1 to 8:1).

General Procedure for Chiral *N*-Heterocyclic Carbene Catalyzed Enantioselective Annulation of Enals with 1,3-Dicarbonyls (G2)

Into an oven dried 10 mL vial was weighed catalyst **C3** (11 mg, 0.03 mmol), oxidant (122.6 mg, 0.3 mmol) and 4 Å MS (300 mg). Followed by the addition of a solution of enal (0.45 mmol), 1,3-dicarbonyl (0.3 mmol) in toluene (3 mL). After stirring at 40 ^{o}C for indicated time, the reaction mixture was filtrated, and the solvent was evaporated under reduced pressure at room temperature to afford a residue. Further purification by flash column chromatography on silica gel to give the product (Hexane : EtOAc = 10 : 1 to 8:1).

Table 1. Optimization of Reaction Conditions for Chiral NHC-Catalyzed Enantioselective Annulation of Enals with 1,3-Dicarbonyls[a]

Entry	*Conditions*	Yield[b] (%)	Ee[c] (%)
1	**A**, DBU, THF, rt, 2 h	79	-4
2	**B**, DBU, THF, rt, 5 h	—	—
3	**C1**, DBU, THF, rt, 5 h	80	14
4	**C2**, DBU, THF, rt, 5 h	—	—
5	**C3**, DBU, THF, rt, 5 min	83	67
6	**C3**, DBU, THF, 0 °C, 5 min	85	71
7	**C3**, NaH, THF, 0 °C, 5min	78	83
8	**C3**, *t*-BuOK, THF, 0 °C, 5min	78	71
9	**C3**, NaH, THF, -20 °C, 30min,	81	80
10	**C3**, NaH, Et_2O, 0 °C, 5min	79	83
11	**C3**, NaH, toluene, 0 °C, 48 h	44	89
12[d,e]	**C3**, 4Å MS, toluene, 40 °C, 10 h	83	98
13[d,f]	**C3**, toluene, 40 °C, 10 h	33	85

[a] Performed on a 0.3 mmol scale in 3 ml solvent with 10 mol% of catalyst, 10 mol % of base, 1 equiv of **4a**, 1.5 equiv of **2a**, 1 equiv of **[O]**. [b] Isolated yield after chromatography. [c] Determined by HPLC analysis on a chiral column. [d] 1.5 equiv of **4a** and 1 equiv of **2a** were used. [e] 300 mg 4 Å MS was added instead of 10 mol% of base. [f] No base was used.

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

According to **G1**: 81% yield, 98% ee (PA-2 column, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 20.6 min, t_{minor} = 24.6 min), $[\alpha]_D^{20}$ = -167.2° (c = 1, $CHCl_3$). According to **G2** for 10 h: 83% yield, 98% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.09 (m, 5H), 4.26 (d, *J* = 7.3 Hz, 1 H), 4.12 (q, *J* = 7.3 Hz, 2 H), 2.95 (dd, *J* = 16.0, 7.3 Hz, 1 H), 2.81 (d, *J* = 16.0 Hz, 1 H), 2.47 (s, 3 H), 1.18 (t, *J* = 7.3 Hz, 3 H).

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

According to **G1**: 67% yield, 92% ee (Sino-OD column, *n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 12.2 min, t_{major} = 16.2 min), $[\alpha]_D^{20}$ = -124.0° (c = 1, $CHCl_3$). According to **G2**, except that 1 equiv of ynal and 1.5 equiv of 3-oxobutanoate were used and the reaction was performed at room temperature for 66 h: 73% yield, 91% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.7 Hz, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 4.21 (d, *J* = 7.3 Hz, 1 H), 4.13 (q, *J* = 7.0 Hz, 2 H), 3.76 (s, 3H), 2.92 (dd, *J* = 16.0, 7.3 Hz, 1 H), 2.78 (d, *J* = 16.0 Hz, 1 H), 2.46 (s, 3 H), 1.20 (t, *J* = 7.0 Hz, 3 H).

(*R*)-Ethyl 6-methyl-2-oxo-4-(p-tolyl)-3,4-dihydro-2H-pyran-5-carboxylate (**3c**)

According to **G1**: 82% yield, 97% ee (PA-2 column, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 20.5 min, t_{minor} = 26.4 min), $[\alpha]_D^{20}$ = -145.4° (c = 1, $CHCl_3$), According to **G2** for 24 h: 77% yield, 92% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.7 Hz, 2 H), 7.02 (d, *J* = 7.7 Hz, 2 H), 4.22 (d, *J* = 7.5 Hz, 1 H), 4.12 (q, *J* = 7.1 Hz, 2 H), 2.92 (dd, *J* = 16.0, 7.5 Hz, 1 H), 2.79 (d, *J* = 16.0 Hz, 1 H), 2.46 (s, 3

H), 2.29 (s, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H).

(*R*)-Ethyl 6-methyl-2-oxo-4-(m-tolyl)-3,4-dihydro-2H-pyran-5-carboxylate (**3d**)

According to **G1**: 87% yield, 95% ee. According to **G2** for 16 h: 87% yield, 97% ee (PA-2 column, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 18.3 min, t_{minor} = 22.0 min), $[\alpha]_D^{20}$ = -160.7º (c = 1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-6.87 (m, 4 H), 4.22 (d, *J* = 7.3 Hz, 1 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 2.94 (dd, *J* = 16.0, 7.5 Hz, 1 H), 2.80 (dd, *J* = 16.0, 2.1 Hz, 1 H), 2.48 (s, 3 H), 2.31 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 166.0, 161.2, 140.7, 138.7, 128.9, 128.3, 127.3, 123.7, 110.1, 60.8, 37.8, 36.4, 21.5, 18.9, 14.1; IR (film): ν = 2985, 2923, 2853, 1797, 1713, 1642, 1514, 1446, 1417, 1380, 1344, 1291, 1242, 1173, 1067, 1030, 965, 865, 816, 785, 733, 665, 593, 552, 507 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 274.1205; found, 274.1202.

(*R*)-Ethyl 6-methyl-2-oxo-4-(o-tolyl)-3,4-dihydro-2H-pyran-5-carboxylate (**3e**)

According to **G1**: 77% yield, 96% ee. According to **G2** for 18 h: 81% yield, 97% ee (PA-2 column, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 25.6 min, t_{minor} = 31.2 min), $[\alpha]_D^{20}$ = -175.8º (c = 1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-6.90 (m, 4 H), 4.50 (d, *J* = 7.9 Hz, 1 H), 4.18-3.98 (m, 2 H), 2.92 (dd, *J* = 15.6, 7.9 Hz, 1 H), 2.66 (dd, *J* = 15.6, 2.0 Hz, 1 H), 2.51 (s, 3 H), 2.38 (s, 3 H), 1.14 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 165.9, 161.7, 138.4, 134.9, 131.0, 127.5, 126.8, 125.3, 110.1, 60.8, 35.3, 34.0, 19.2, 18.8, 14.0; IR (KBr): ν = 3000, 2955, 1787, 1715, 1644, 1594, 1509, 1459, 1415, 1370, 1288, 1275, 1242, 1222, 1175, 1128, 1068, 835, 789, 734 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 274.1205; found, 274.1207.

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

According to **G1**: 66% yield, 96% ee (PA-2 column, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 22.3 min, t_{minor} = 27.8 min), $[\alpha]_D^{20}$ = -99.0º (c = 1, $CHCl_3$). According to **G2**, except that the reaction was performed at room temperature for 48 h: 74% yield, 92% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-6.91 (m, 4 H), 4.25 (d, *J* = 7.3 Hz, 1 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 2.95 (dd, *J* = 16.0, 7.3 Hz, 1 H), 2.79 (d, *J* = 16.0 Hz, 1 H), 2.47 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H).

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

According to **G1**, except that 1 equiv of ynal and 1.5 equiv of 3-oxobutanoate were used: 74% yield, 92% ee. According to **G2** for 12 h: 85% yield, 97% ee (OD-H column, *n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 10.0 min, t_{major} = 12.4 min), $[\alpha]_D^{20}$ = -151.7º (c = 1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-6.95 (m, 4 H), 4.59 (d, *J* = 7.5 Hz, 1 H), 4.22-4.03 (m, 2 H), 2.95 (dd, *J* = 16.0, 7.5 Hz, 1 H), 2.84 (dd, *J* = 16.0, 2.3 Hz, 1 H), 2.51 (s, 3 H), 1.17 (t, *J* = 7.1 Hz, 3 H); ^{19}F NMR (282 MHz, CDCl3) δ -118.09-118.23 (m, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 1 65.7, 165.6, 162.3, 161.6, 159.1, 129.3, 129.2, 127.80, 127.76, 127.4, 127.2, 124.55, 124.52, 115.9, 115.7, 108.4, 60.8, 35.0, 31.48, 31.45, 29.7, 18.8, 14.0; IR (KBr): v = 3000, 2955, 1787, 1715, 1644, 1594, 1509, 1459, 1415, 1370, 1288, 1275, 1242, 1222, 1175, 1128, 1068, 835, 789, 734 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 278.0954; found, 278.0956.

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

According to **G1**, except that the reaction was performed at room temperature for 48 h: 49% yield, 94% ee. According to **G2** for 12 h: 73% yield, 95% ee (OD-H column, *n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 8.6 min, t_{major} = 15.6 min), $[\alpha]_D^{20}$ = -164.0º (c = 1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 4.24 (d, *J* = 7.6 Hz, 1 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 2.95 (dd, *J* = 15.8, 7.6 Hz, 1 H), 2.79 (dd, *J* = 15.8, 2.1 Hz, 1 H), 2.48 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 161.7, 139.2, 133.4, 129.2, 128.1, 109.7, 61.0, 37.4, 36.2, 18.9, 14.1; IR (KBr): ν = 2982, 2927, 1789, 1714, 1649, 1492, 1412, 1370, 1287, 1243, 1174, 1117, 1075, 1031, 1015, 967, 825, 793, 672, 534 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 294.0659; found, 294.0664.

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

According to **G1**: 34% yield, 96% ee. According to **G2** for 12 h: 77% yield, 97% ee (OD-H column, *n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 8.3 min, t_{major} = 15.7 min), $[\alpha]_D^{20}$ = -146.8º (c = 1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 2 H), 7.02 (d, *J* = 8.7 Hz, 2 H), 4.22 (d, *J* = 7.5 Hz, 1 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 2.95 (dd, *J* = 15.9, 7.5 Hz, 1 H), 2.78 (d, *J* = 15.9 Hz, 1 H), 2.48 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H).

(*R*)-Ethyl 6-methyl-4-(naphthalen-1-yl)-2-oxo-3,4-dihydro-2H-pyran-5-carboxylate (**3j**)

According to **G1**: 81% yield, 92% ee (PA-2 column, *n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 10.4 min, t_{minor} = 12.0 min), $[\alpha]_D^{20}$ = -83.8º (c = 1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1 H), 7.89 (d, *J* = 7.8 Hz, 1 H), 7.76 (d, *J* = 8.2 Hz, 1 H), 7.63-7.46 (m, 2 H), 7.37 (t, *J* = 7.8 Hz, 1 H), 7.18 (d, *J* = 7.3 Hz, 1 H), 5.15 (d, *J* = 7.3 Hz, 1 H), 4.17-3.95 (m, 2 H), 3.07 (dd, *J* = 15.5, 7.3 Hz, 1 H), 2.95 (d, *J* = 15.5 Hz, 1 H), 2.58 (s, 3 H), 1.05 (t, *J* = 7.1 Hz, 3 H).

(*S*)-Ethyl 6-methyl-2-oxo-4-(thiophen-2-yl)-3,4-dihydro-2H-pyran-5-carboxylate (**3k**)

According to **G1**: 71% yield, 94% ee. According to **G2** for 16 h: 84% yield, 97% ee (OJ-H column, *n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 35.4 min, t_{minor} = 64.2 min), $[\alpha]_D^{20}$ = -118.8º (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 5.0 Hz, 1 H), 6.94-6.87 (m, 1 H), 6.85-6.80 (m, 1 H), 4.53 (d, *J* = 7.2 Hz, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 3.06-2.87 (m, 2 H), 2.43 (s, 3 H), 1.28 (t, *J* = 7.1 Hz, 3 H).

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

According to **G1**, except that the reaction was performed at room temperature for 48 h: 68% yield, 85% ee (PA-2 column, *n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 7.8 min, t_{major} = 11.0 min), $[\alpha]_D^{20}$ = -8.0º (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 4.32-4.15 (m, 2 H), 3.01-2.91 (m, 1 H), 2.70 (dd, *J* = 16.0, 1.8 Hz, 2 H), 2.58 (dd, *J* = 16.0, 6.6 Hz, 1 H), 2.34 (s, 3 H), 1.56-1.16 (m, 9 H), 0.88 (t, *J* = 6.7 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 166.4, 160.2, 111.8, 60.7, 33.10, 33.07, 31.6, 28.5, 22.4, 18.8, 14.2, 13.8; IR (film): ν = 3000, 2955, 1787, 1715, 1644, 1594, 1509, 1459, 1415, 1370, 1288, 1275, 1242, 1222, 1175, 1128, 1068, 835, 789, 734 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 240.1362; found, 240.1366.

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

According to **G1**, except that the reaction was performed at room temperature for 48 h: 52% yield, 85% ee (PC-2 column, *n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 6.2 min, t_{major} = 6.6 min), $[\alpha]_D^{20}$ = -11.1º (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 4.36-4.12 (m, 2 H), 2.91-2.83 (m, 1 H), 2.78 (d, *J* = 16.5 Hz, 1 H), 2.51 (dd, J = 16.5, 7.4 Hz, 1 H), 2.34 (s, 3 H), 1.79-0.79 (m, 14 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.7, 160.0, 110.6, 60.7, 41.4, 37.1, 30.8, 30.4, 29.0, 26.3, 26.2, 26.1, 18.8, 14.2; IR (KBr): ν = 3000, 2955, 1787, 1715, 1644, 1594, 1509, 1459, 1415, 1370, 1288, 1275, 1242, 1222, 1175, 1128, 1068, 835, 789, 734 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 266.1518; found, 266.1521.

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

According to **G1**: 71% yield, 95% ee (Sino-AD column, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 214 nm, t_{major} = 15.9 min, t_{minor} = 17.2 min), $[\alpha]_D^{20}$ = -135.0° (c = 1, $CHCl_3$). According to **G2** for 12 h: 67% yield, 94% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.09 (m, 5 H), 4.26 (d, J = 7.3 Hz, 1 H), 3.67 (s, 3 H), 2.94 (dd, J = 15.9, 7.3 Hz, 1 H), 2.82 (d, J = 15.9 Hz, 1 H), 2.48 (s, 3 H).

(*R*)-5-Acetyl-6-methyl-4-phenyl-3,4-dihydro-2H-pyran-2-one (**3o**)

According to **G1**: 46% yield, 95% ee (Sino-OD column, *n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 18.4 min, t_{major} = 22.8 min), $[\alpha]_D^{20}$ = -138.0° (c = 1, $CHCl_3$). According to **G2** for 22 h: 58% yield, 95% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.03 (m, 5 H), 4.08 (d, J = 7.1 Hz, 1 H), 2.90 (dd, J = 15.7, 7.1 Hz, 1 H), 2.76 (dd, J = 15.7, 2.6 Hz, 1 H), 2.36 (s, 3 H), 2.05 (s, 3 H).

(*R*)-5-Benzoyl-6-methyl-4-phenyl-3,4-dihydro-2H-pyran-2-one (**3p**)

According to **G1**, except that the reaction was performed at room temperature for 48 h. 60% yield, 96% ee (PA-2 column, *n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 17.9 min, t_{minor} = 31.5 min), $[\alpha]_D^{20}$ = -26.7° (c = 1, $CHCl_3$). According to **G2** for 24 h: 62% yield, 90% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.07 (m, 10 H), 4.32 (brs, 1 H), 3.07 (dd, J = 15.8, 7.0 Hz, 1 H), 2.92 (dd, J = 15.8, 3.4 Hz, 1 H), 1.89 (s, 3 H).

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

According to **G2** for 12 h: 37% yield, 96% ee (OD-H column, *n*-hexane/*i*-PrOH = 5/5, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 9.9 min, t_{major} = 20.4 min), $[\alpha]_D^{20}$ = -189.0° (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 4.32 (d, *J* = 7.7 Hz, 1 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 3.01 (dd, *J* = 15.9, 7.7 Hz, 1 H), 2.81 (dd, *J* = 15.9, 2.0 Hz, 1 H), 2.50 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.2, 162.3, 146.1, 133.0, 127.6, 118.4, 111.7, 109.0, 61.1, 38.1, 35.8, 19.0, 14.1; IR (KBr): ν = 2983, 2926, 2229, 1790, 1716, 1650, 1608, 1504, 1415, 1372, 1292, 1271, 1243, 1170, 1120, 1075, 1032, 966, 867, 848, 785, 560 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 285.1001; found, 285.1005.

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

According to **G2** for 12 h: 42% yield, 93% ee (OD-H column, *n*-hexane/*i*-PrOH = 5/5, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 7.2 min, t_{major} = 13.5 min), $[\alpha]_D^{20}$ = -133.3° (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 2 H), 7.27 (d, *J* = 7.9 Hz, 2 H), 4.33 (d, *J* = 7.8 Hz, 1 H), 4.14 (q, *J* = 7.0 Hz, 2 H), 3.00 (dd, *J* = 16.0, 7.8 Hz, 1 H), 2.82 (dd, *J* = 16.0, 1.9 Hz, 1 H), 2.50 (s, 3 H), 1.20 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 165.5, 162.0, 144. 8, 130.0 (q, *J* = 32.3 Hz), 127.1, 126.1 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 276.4 Hz), 109.4, 61.0, 37.8, 36.0, 19.0, 14.0; IR (KBr): ν = 2984, 2930, 1789, 1716, 1649, 1620, 1419, 1327, 1171, 1112, 1069, 1031, 847, 784 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 328.0922; found, 328.0923.

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

According to **G2** for 12 h: 67% yield, 98% ee (OD-H column, *n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 10.9 min, t_{major} = 27.2 min), $[\alpha]_D^{20}$ = -173.3^o (c = 1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2 H), 7.22 (d, *J* = 8.3 Hz, 2 H), 4.32 (d, *J* = 7.7 Hz, 1 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 3.90 (s, 3 H), 2.99 (dd, *J* = 15.9, 7.7 Hz, 1 H), 2.82 (dd, *J* = 15.9, 2.1 Hz, 1 H), 2.50 (s, 3 H), 1.18 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 165.7, 165.6, 161.9, 145.9, 130.4, 129.6, 126.8, 109.4, 61.0, 52.1, 37.9, 36.0, 18.9, 14.1; IR (KBr): ν = 2981, 2954, 2923, 1790, 1721, 1649, 1611, 1436, 1282, 1178, 1115, 1074, 1031, 963, 856, 772, 708 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 318.1103; found, 318.1109.

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

According to **G2** for 12 h: 72% yield, 96% ee (AD-H column, *n*-hexane/*i*-PrOH = 5/5, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 10.1 min, t_{major} = 17.7 min), $[\alpha]_D^{20}$ = -180.7^o (c = 1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 4.33 (d, *J* = 7.7 Hz, 1 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 3.00 (dd, *J* = 15.8, 7.7 Hz, 1 H), 2.82 (dd, *J* = 15.8, 2.3 Hz, 1 H), 2.58 (s, 3 H), 2.50 (s, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 165.7, 165.6, 161.9, 146.1, 136.5, 129.2, 127.0, 109.4, 61.0, 37.9, 36.0, 26.6, 19.0, 14.1; IR (KBr): ν = 2983, 2926, 1788, 1716, 1685, 1650, 1607, 1414, 1361, 1296, 1270, 1173, 1117, 1074, 1031, 959, 866, 847, 830, 782, 598 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 302.1154; found, 302.1151.

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

According to **G2** for 24 h: 56% yield, 97% ee (OD-H column, *n*-hexane/*i*-PrOH = 5/5, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 10.0 min, t_{major} = 19.9 min), $[\alpha]_D^{20}$ = -168.7° (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 8.15-8.00 (m, 2 H), 7.54-7.43 (m, 2 H), 4.38 (d, *J* = 7.9 Hz, 1 H), 4.14 (q, *J* = 7.5 Hz, 2 H), 3.02 (dd, *J* = 16.0, 7.5 Hz, 1 H), 2.84 (dd, *J* = 16.0, 2.1 Hz, 1 H), 2.50 (s, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.2, 162.6, 148.7, 142.9, 132.6, 130.2, 122.7, 122.1, 109.0, 61.2, 37.7, 36.0, 19.0, 14.1; IR (KBr): v = 2982, 2926, 1789, 1716, 1650, 1532, 1351, 1292, 1243, 1119, 1075, 1032, 862, 693 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 305.0899; found, 305.0901.

(*S*)-Ethyl 4,6-dimethyl-2-oxo-3,4-dihydro-2H-pyran-5-carboxylate (**3v**)

According to **G2**, except that the reaction was performed at room temperature for 66 h. 81% yield, 83% ee (PA-2 column, *n*-hexane/*i*-PrOH = 8/2, flow rate 0.7 mL/min, λ = 214 nm, t_{minor} = 13.5 min, t_{major} = 26.2 min), $[\alpha]_D^{20}$ = -18.3° (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 4.30-4.14 (m, 2 H), 3.12-2.99 (m, 1 H), 2.65 (dd, *J* = 15.7, 6.4 Hz, 1 H), 2.53 (dd, *J* = 15.6, 2.2 Hz, 1 H), 2.32 (s, 3 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 1.09 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 166.2, 160.2, 112.3, 60.7, 35.7, 27.1, 19.3, 18.8, 14.2; IR (film): v = 2980, 2930, 1790, 1714, 1650, 1462, 1382, 1349, 1297, 1250, 1133, 1082, 1009, 983, 925, 844, 779 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 198.0892; found, 198.0890.

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

According to **G2** for 22 h: 72% yield, 95% ee (Sino-AD column, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 214 nm, t_{major} = 16.9 min, t_{minor} = 18.8 min), $[\alpha]_D^{20}$ = -151.1° (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.08 (m, 5 H), 4.25 (dd, *J* = 7.3, 2.0 Hz, 1 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 3.00-2.73 (m, 4 H), 1.28 (t, *J* = 7.3 Hz, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H).

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

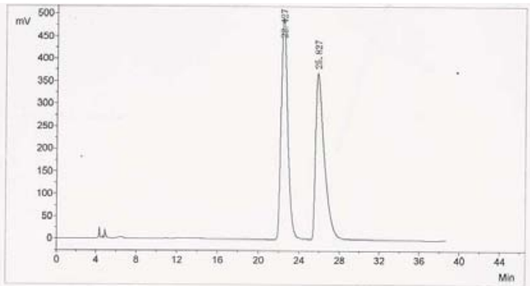
According to **G2** for 24 h: 66% yield, 92% ee (PA-2 column, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 28.3 min, t_{minor} = 31.9 min), $[\alpha]_D^{20}$ = -70.0º (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 7.56-7.20 (m, 10 H), 4.41 (dd, *J* = 7.6, 2.3 Hz, 1 H), 4.02-3.84 (m, 2 H), 3.11 (dd, *J* = 15.8, 7.6 Hz, 1 H), 2.94 (dd, *J* = 15.8, 2.3 Hz, 1 H), 0.87 (t, *J* = 7.2 Hz, 3 H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 166.0, 158.6, 140.0, 133.2, 130.2, 129.2, 128.7, 128.0, 127.8, 126.8, 111.8, 61.0, 38.9, 36.4, 13.5.

(*R*)-5-Benzoyl-4,6-diphenyl-3,4-dihydro-2H-pyran-2-one (**3y**)

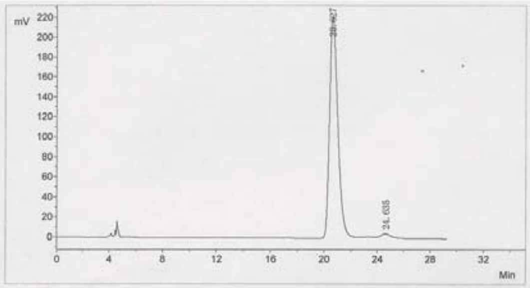
According to **G2** for 24 h: 90% yield, 90% ee (PA-2 column, *n*-hexane/*i*-PrOH = 8/2, flow rate 0.7 mL/min, λ = 214 nm, t_{major} = 25.9 min, t_{minor} = 39.9 min), $[\alpha]_D^{20}$ = -9.3º (c = 1, $CHCl_3$), ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.04 (m, 15 H), 4.57 (dd, *J* = 7.7, 2.3 Hz, 1 H), 3.22 (dd, *J* = 16.0, 7.7 Hz, 1 H), 3.06 (dd, *J* = 16.0, 2.3 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 166.7, 154.8, 139.8, 137.2, 132.6, 132.0, 130.3, 129.3, 129.0, 128.1, 128.0, 127.8, 126.9, 118.4, 40.4, 36.0.

HPLC spectra

PA-2 column (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm)

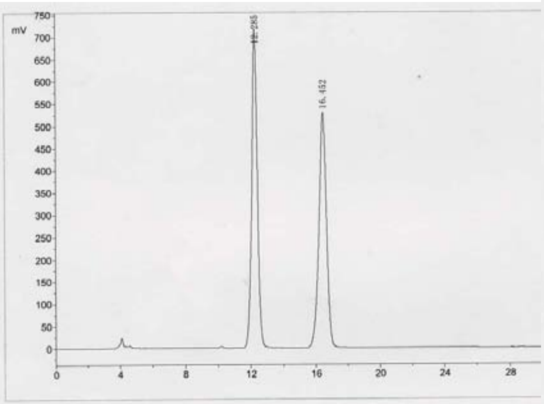


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		22.427	491728.0	22425647.1	50.1230
2	2		25.827	368955.3	22315540.8	49.8770
Total				860683.3	44741187.8	100.0000

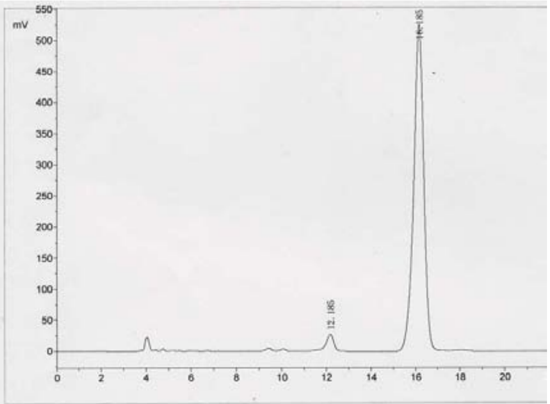


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		20.627	222009.0	9950859.6	99.1476
2	2		24.635	2636.0	85555.2	0.8524
Total				224645.0	10036414.8	100.0000

Sino-OD column (*n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm)

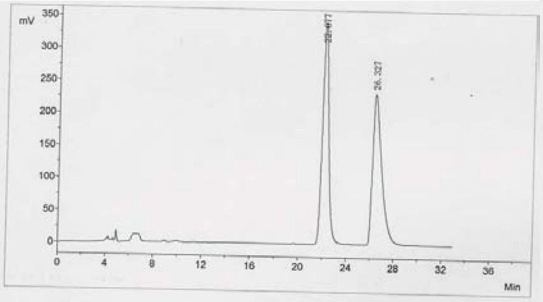


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		12.285	716362.6	17254011.3	49.9757
2	2		16.452	527620.1	17270762.8	50.0243
Total				1243982.7	34524774.1	100.0000

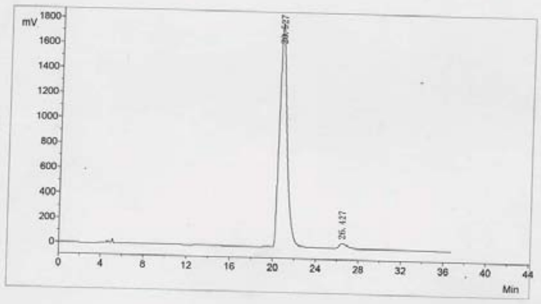


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		12.185	27170.8	658482.8	3.8142
2	2		16.185	525663.6	16605494.8	96.1858
Total				552834.5	17263977.7	100.0000

PA-2 column (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm)

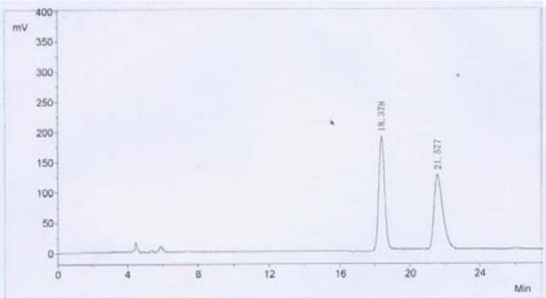


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		22.077	342108.6	12335202.3	50.1162
2	2		26.327	232354.4	12277995.0	49.8838
Total				574463.0	24613197.3	100.0000

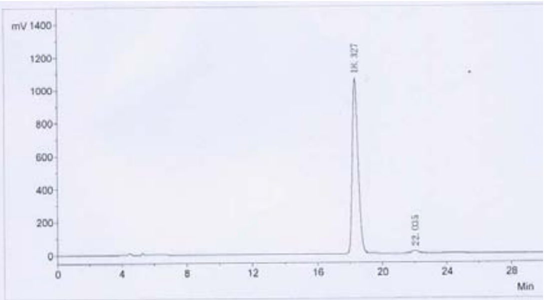


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		20.527	1784985.4	89816786.8	98.2638
2	2		26.427	34778.5	1586927.6	1.7362
Total				1819763.8	91403714.4	100.0000

PA-2 column (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm)



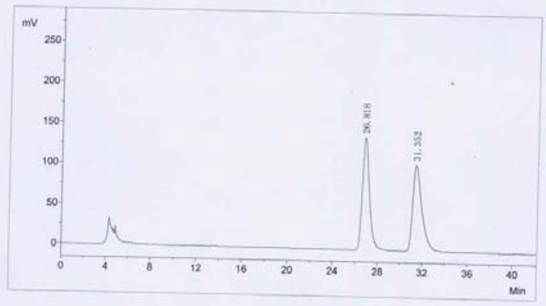
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	18.378	188494.2	4412697.3	50.7128
2	2	21.577	123489.6	4288657.0	49.2872
Total			311983.7	8701354.3	100.0000



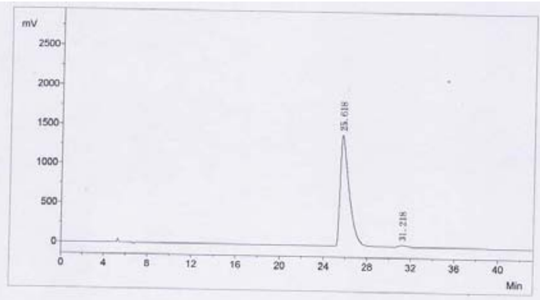
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	18.327	1062613.4	26393954.1	98.2571
2	2	22.035	15550.4	468168.7	1.7429
Total			1078163.8	26862122.8	100.0000

Electronic Supplementary Material (ESI) for Chemical Communications

PA-2 column (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm)

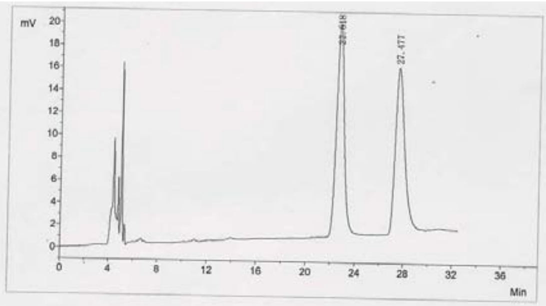


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		26.818	138804.2	6149057.3	50.4163
2	2		31.352	106115.0	6047499.0	49.5837
Total				244919.2	12196556.3	100.0000

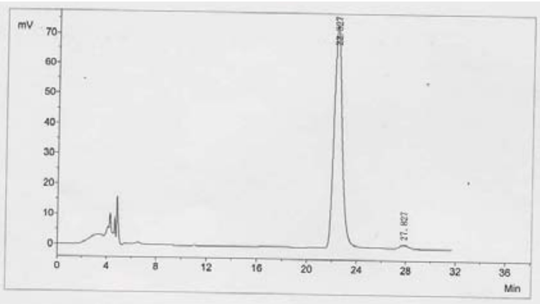


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		25.618	1404740.9	79785949.2	98.3845
2	2		31.218	24336.0	1310117.9	1.6155
Total				1429076.9	81096067.1	100.0000

PA-2 column (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 214 nm)

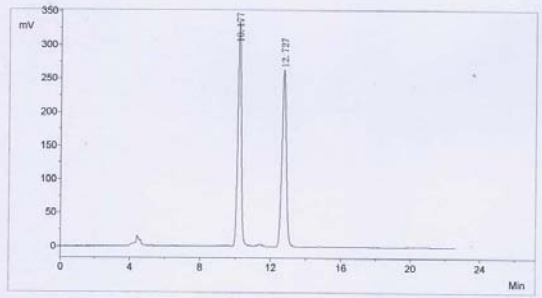


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		22.618	18332.2	768081.8	49.3644
2	2		27.477	14634.5	787862.2	50.6356
Total				32966.7	1555944.0	100.0000

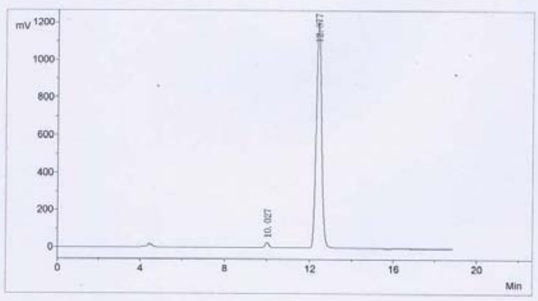


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		22.327	73514.7	3360331.2	98.1449
2	2		27.827	1271.0	63515.3	1.8551
Total				74785.7	3423846.5	100.0000

OD-H column (*n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm)

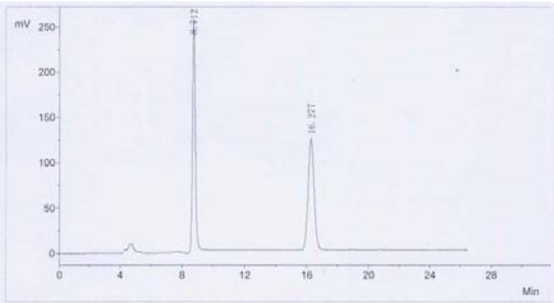


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		10.177	334494.8	4655115.1	50.1078
2	2		12.727	261038.5	4635093.9	49.8922
Total				595533.3	9290209.0	100.0000



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		10.027	27559.4	378032.3	1.7258
2	2		12.377	1205899.7	21526521.5	98.2742
Total				1233459.1	21904553.9	100.0000

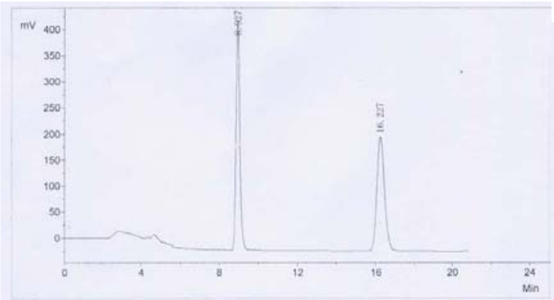
OD-H column (*n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm)



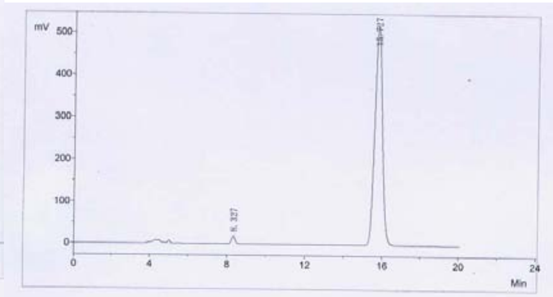
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	8.712	255512.8	3228791.5	49.3294
2	2	16.277	122500.2	3316571.7	50.6706
Total			378013.0	6545363.3	100.0000

No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	8.627	75716.7	1170666.0	2.6282
2	2	15.627	1592494.6	43371247.4	97.3718
Total			1668211.2	44541913.3	100.0000

OD-H column (*n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm)

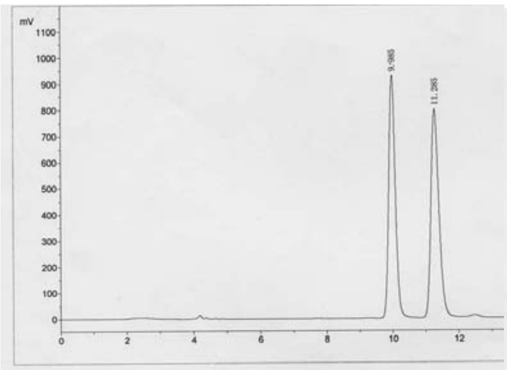


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.927	440538.7	5835788.5	49.1404
2	2	16.227	217802.4	6039951.3	50.8596
Total			658341.1	11875739.8	100.0000

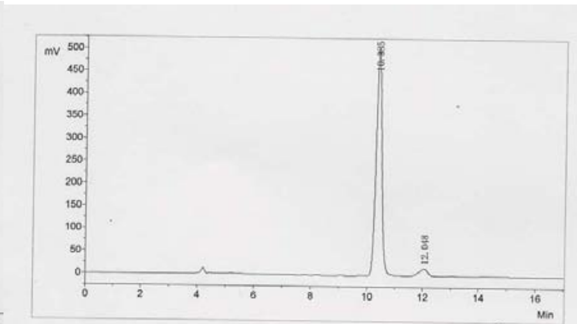


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		8.327	18931.7	235539.0	1.6155
2	2		15.727	521898.1	14344463.4	98.3845
Total				540829.7	14580002.3	100.0000

PA-2 column (*n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm)

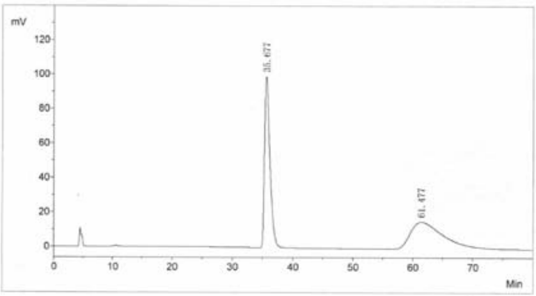


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		9.985	929269.1	12964510.5	49.0944
2	2		11.285	797833.4	13442785.5	50.9056
Total				1727102.5	26407296.0	100.0000

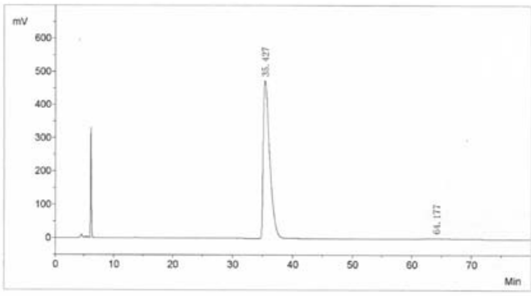


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		10.385	500317.8	7244857.5	96.0894
2	2		12.048	14789.1	294846.4	3.9106
Total				515107.0	7539703.9	100.0000

OJ-H column (*n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm)

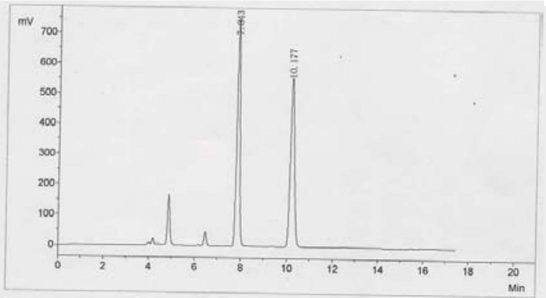


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		35.677	99187.8	6150412.5	50.7797
2	2		61.477	15596.3	5961547.0	49.2203
Total				114784.2	12111959.5	100.0000

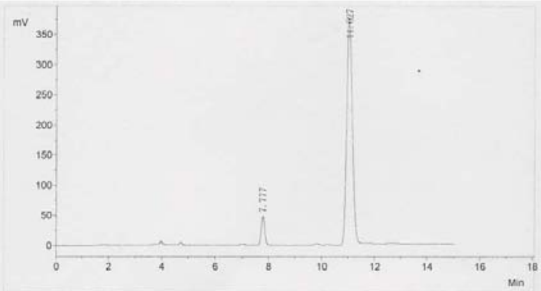


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		35.427	473983.1	35524545.6	98.3987
2	2		64.177	1600.7	578106.8	1.6013
Total				475583.8	36102652.4	100.0000

PA-2 column (*n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm)

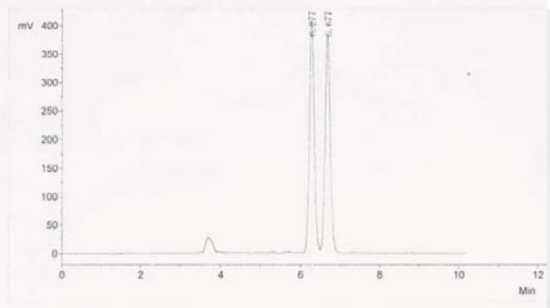


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		7.843	743125.9	6698840.0	49.2208
2	2		10.177	540599.5	6910948.3	50.7792
Total				1283725.4	13609788.3	100.0000

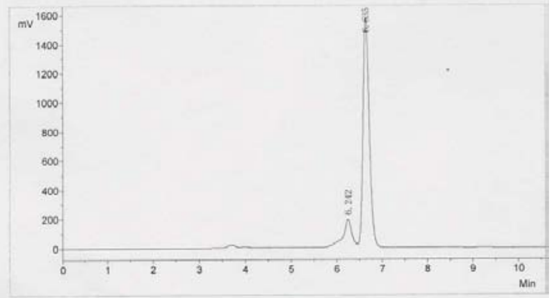


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	7.777	47541.4	461628.7	7.5856
2	2	11.027	376636.3	5623939.8	92.4144
Total			424177.7	6085568.6	100.0000

PC-2 column (*n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm)

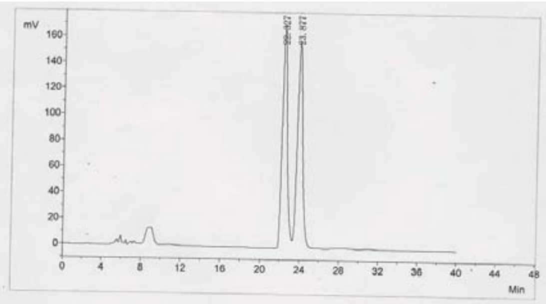


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	6.277	404276.4	3459662.1	49.7797
2	2	6.677	377834.4	3490283.1	50.2203
Total			782110.9	6949945.2	100.0000

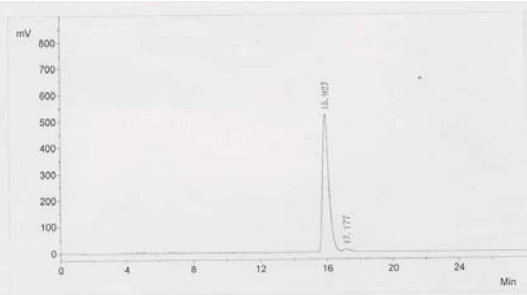


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	6.242	142156.7	1186880.9	7.4698
2	2	6.635	1551210.7	14702194.6	92.5302
Total			1693367.4	15889075.5	100.0000

Sino-AD column (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 214 nm)

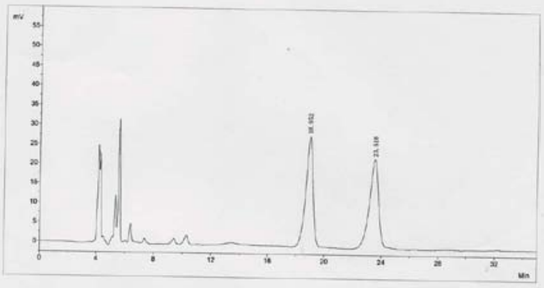


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		22.327	170902.7	6010025.1	49.9517
2	2		23.877	158287.9	6021652.2	50.0483
Total				329190.6	12031677.4	100.0000

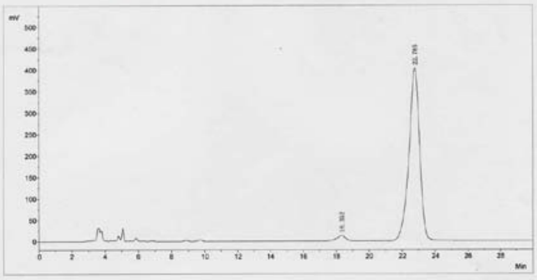


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	15.927	519912.5	13726195.6	97.3538
2	2	17.177	12625.4	373088.4	2.6462
Total			532537.9	14099284.0	100.0000

Sino-OD column (*n*-hexane/*i*-PrOH = 9/1, flow rate 0.7 mL/min, λ = 214 nm)

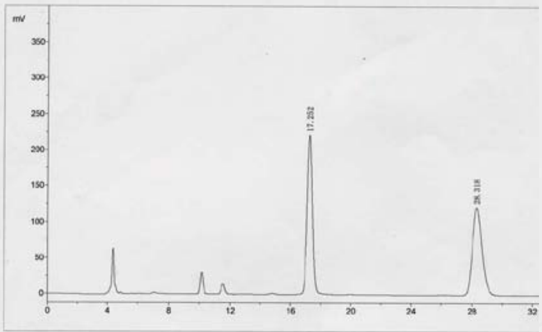


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		18.952	28330.0	1020458.1	49.3100
2	2		23.518	22951.0	1049018.1	50.6900
Total				51281.1	2069476.1	100.0000

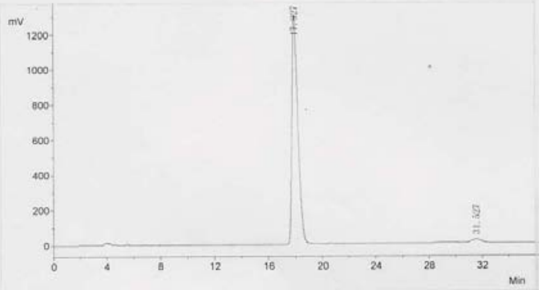


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		18.352	13212.8	476904.8	2.5468
2	2		22.785	403288.2	18248613.7	97.4532
Total				416501.0	18725518.5	100.0000

PA-2 column (*n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm)

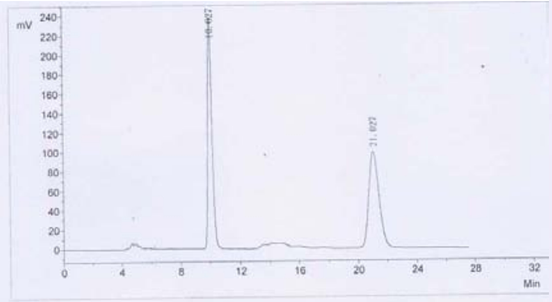


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		17.252	222037.1	5458694.2	50.4419
2	2		28.318	122387.8	5363043.1	49.5581
Total				344424.9	10821737.3	100.0000

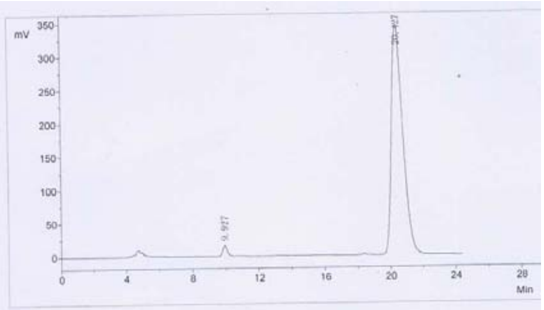


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	17.927	1307294.8	41004963.5	97.7639
2	2	31.527	19880.7	937879.2	2.2361
Total			1327175.5	41942842.6	100.0000

OD-H column (*n*-hexane/*i*-PrOH = 5/5, flow rate 0.7 mL/min, λ = 214 nm)

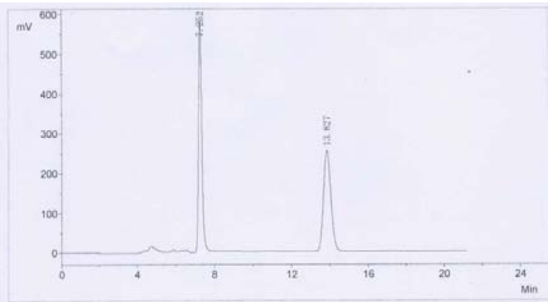


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	10.027	236976.8	4703222.8	49.5251
2	2	21.027	99019.5	4793417.8	50.4749
Total			335996.3	9496640.6	100.0000

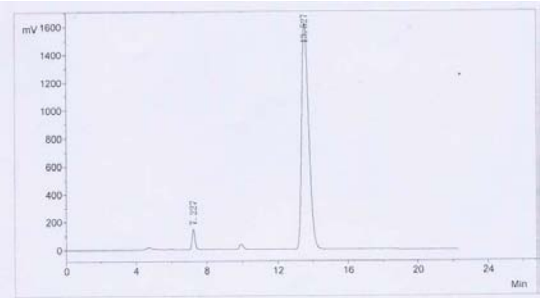


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	9.927	15947.7	314767.4	1.8459
2	2	20.427	345294.9	16737016.5	98.1541
Total			361242.6	17051783.9	100.0000

OD-H column (*n*-hexane/*i*-PrOH = 5/5, flow rate 0.7 mL/min, λ = 214 nm)

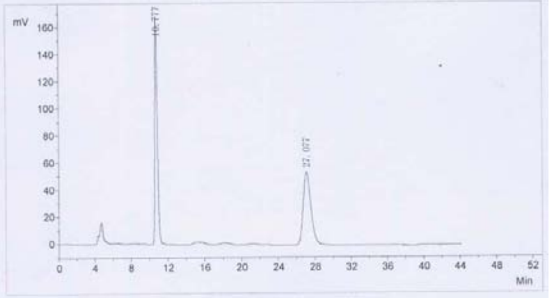


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	7.252	578056.7	6796803.7	49.6472
2	2	13.827	253890.0	6893390.9	50.3528
Total			831946.7	13690194.7	100.0000

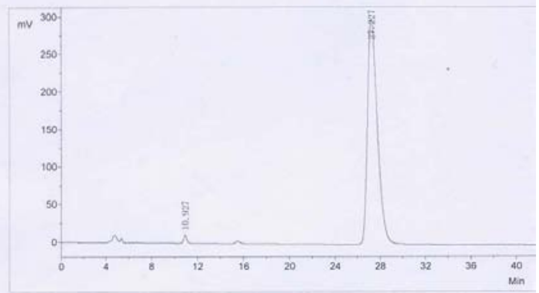


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	7.227	144983.0	1741595.1	3.6869
2	2	13.527	1614211.0	45496044.6	96.3131
Total			1759194.0	47237639.8	100.0000

OD-H column (*n*-hexane/*i*-PrOH = 7/3, flow rate 0.7 mL/min, λ = 214 nm)

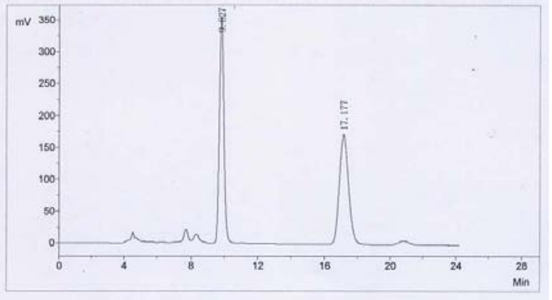


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	10.777	168780.1	3189461.5	50.0281
2	2	27.077	53885.5	3185874.5	49.9719
Total			222665.6	6375335.9	100.0000

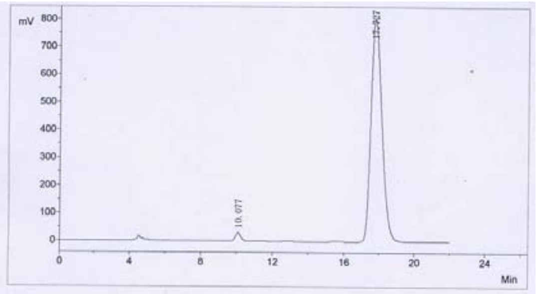


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	10.927	11613.9	222339.1	1.1967
2	2	27.227	301245.5	18356908.9	98.8033
Total			312859.4	18579248.0	100.0000

AD-H column (*n*-hexane/*i*-PrOH = 5/5, flow rate 0.7 mL/min, λ = 214 nm)

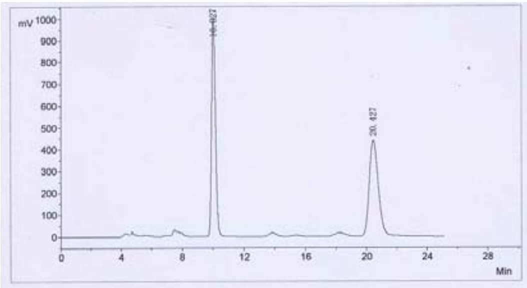


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		9.827	353218.9	6740135.2	50.1815
2	2		17.177	172548.9	6691365.9	49.8185
Total				525767.8	13431501.1	100.0000

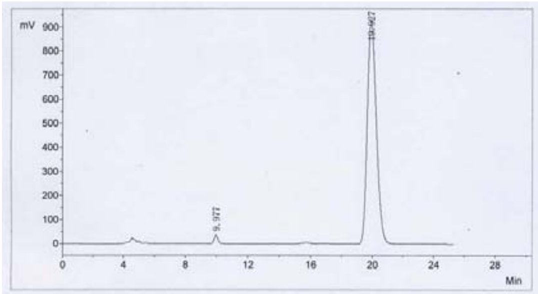


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		10.077	30264.6	621744.2	1.7539
2	2		17.727	806135.2	34826904.4	98.2461
Total				836399.8	35448648.6	100.0000

OD-H column (*n*-hexane/*i*-PrOH = 5/5, flow rate 0.7 mL/min, λ = 214 nm)

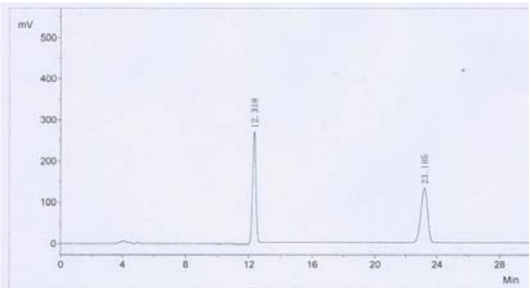


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		10. 027	1005602. 0	18241787. 1	49. 7058
2	2		20. 427	439156. 0	18457732. 7	50. 2942
Total				1444757. 9	36699519. 8	100. 0000

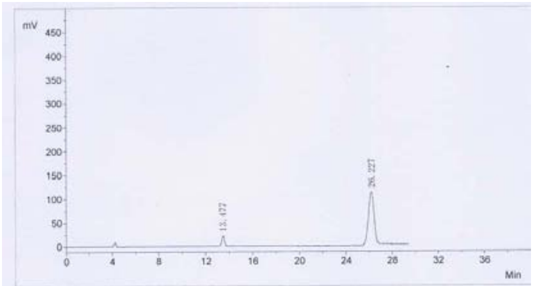


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		9. 977	33959. 5	585012. 8	1. 5102
2	2		19. 927	930339. 5	38152546. 9	98. 4898
Total				964299. 0	38737559. 7	100. 0000

PA-2 column (*n*-hexane/*i*-PrOH = 8/2, flow rate 0.7 mL/min, λ = 214 nm)

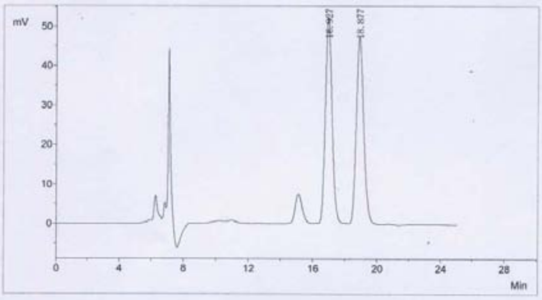


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	12. 318	269093. 5	4077073. 4	50. 7295
2	2	23. 185	131888. 9	3959819. 5	49. 2705
Total			400982. 3	8036892. 9	100. 0000

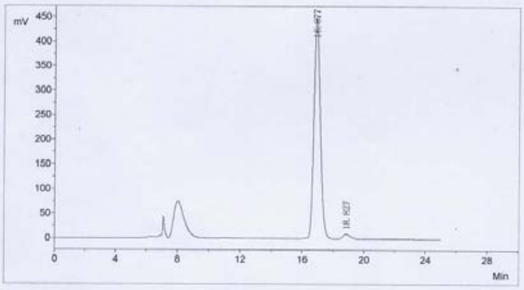


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	13. 477	21952. 6	364791. 9	8. 4235
2	2	26. 227	111943. 7	3965875. 5	91. 5765
Total			133896. 3	4330667. 3	100. 0000

Sino-AD column (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 214 nm)

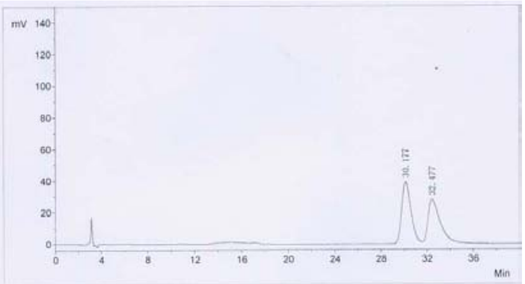


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		16.927	51960.3	1520751.8	49.9799
2	2		18.877	47347.5	1521973.1	50.0201
Total				99307.9	3042724.9	100.0000

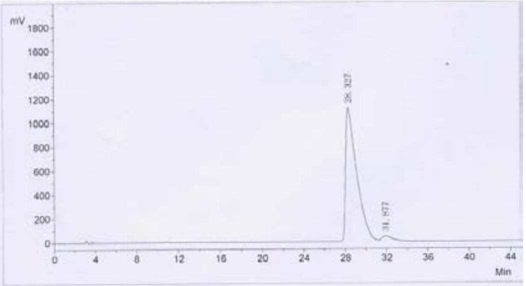


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		16.877	449044.0	12943376.6	97.6955
2	2		18.827	9704.2	305321.7	2.3045
Total				458748.2	13248698.3	100.0000

PA-2 column (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 214 nm)

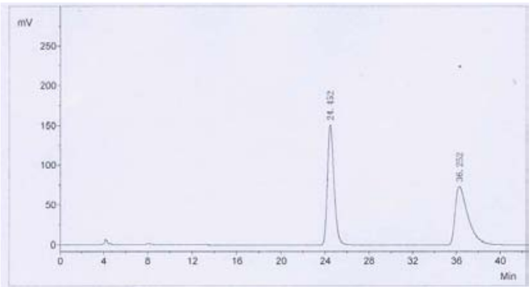


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	30.177	39241.1	2211322.1	51.2510
2	2	32.477	28089.2	2103368.3	48.7490
Total			67330.3	4314690.4	100.0000



No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	28.327	1119318.6	83535531.3	95.7784
2	2	31.877	46837.5	3681993.4	4.2216
Total			1166156.1	87217524.7	100.0000

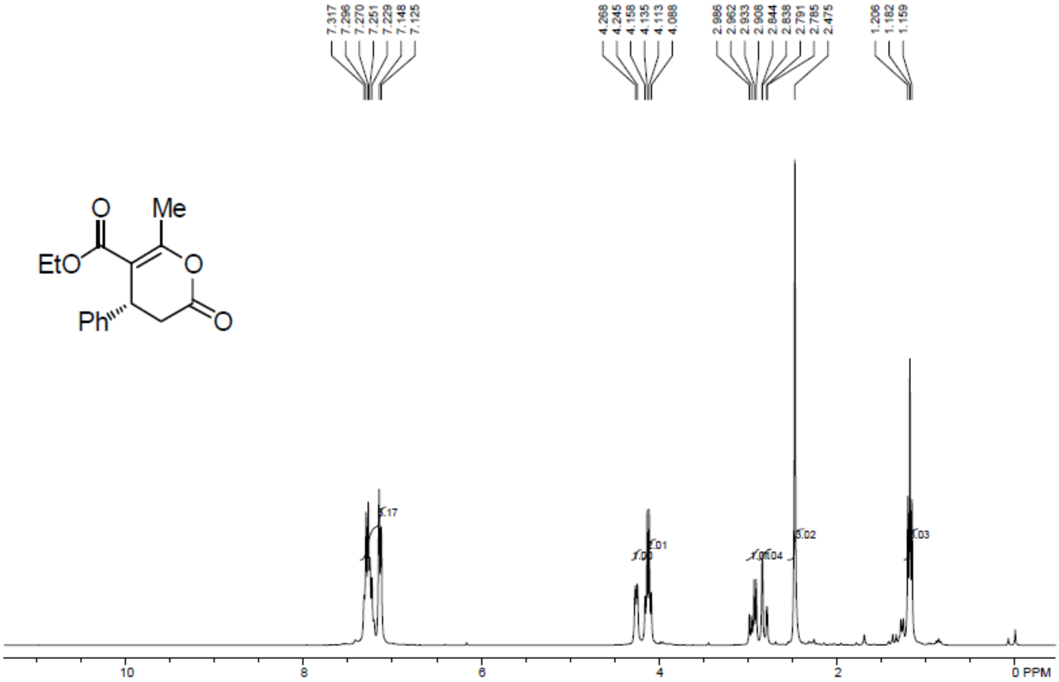
PA-2 column (*n*-hexane/*i*-PrOH = 8/2, flow rate 0.7 mL/min, λ = 214 nm)



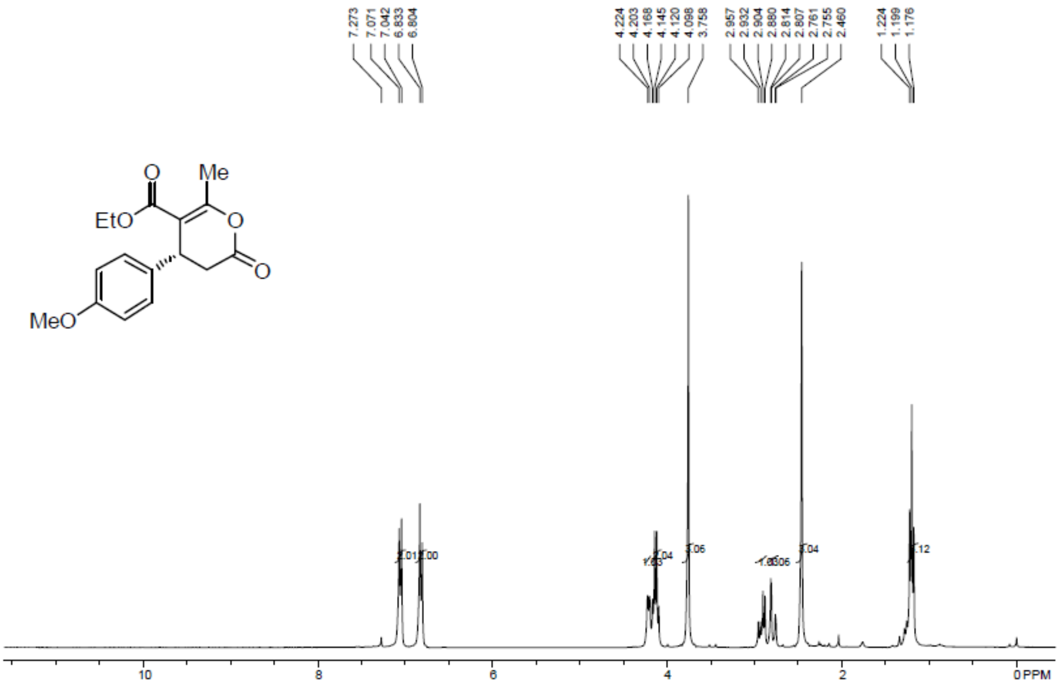
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	24.452	151831.4	6352467.9	51.0649
2	2	36.252	74471.2	6087532.3	48.9351
Total			226302.6	12440000.3	100.0000

No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	25.918	105413.0	4965162.1	95.1733
2	2	39.885	2810.0	251808.1	4.8267
Total			108223.0	5216970.3	100.0000

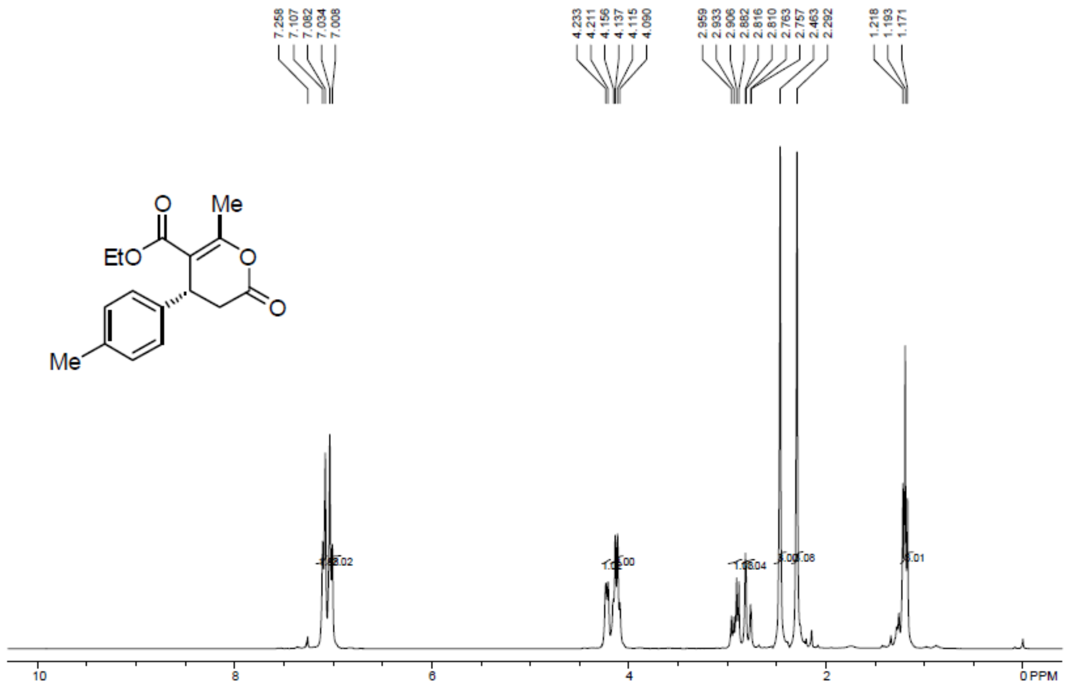
^{1}H NMR of **3a**



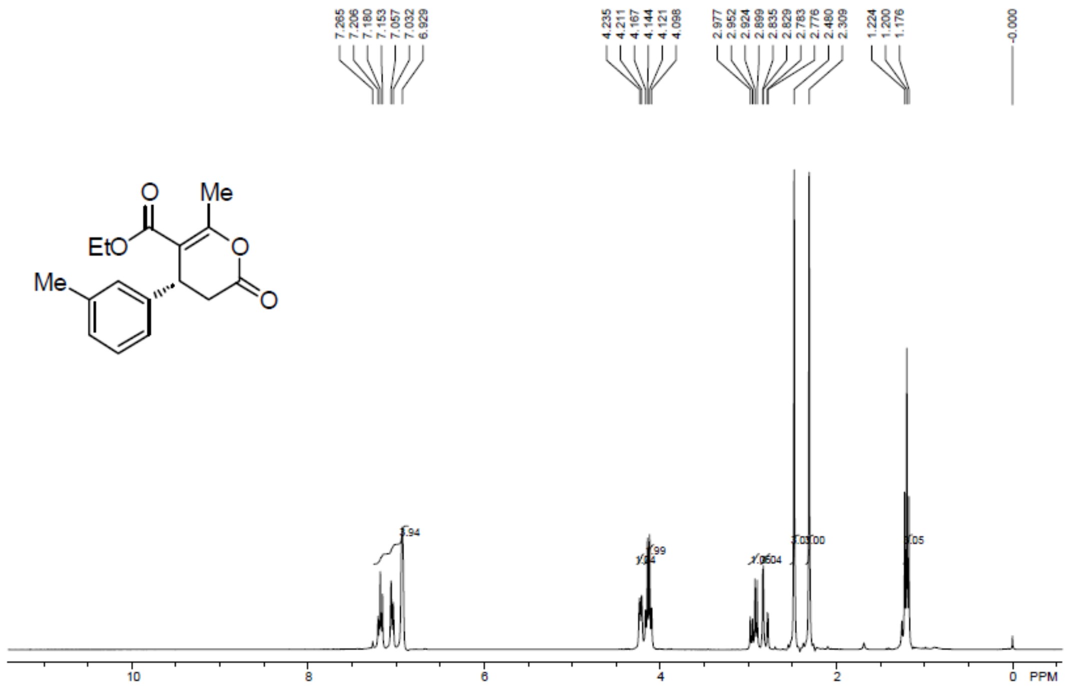
^{1}H NMR of **3b**



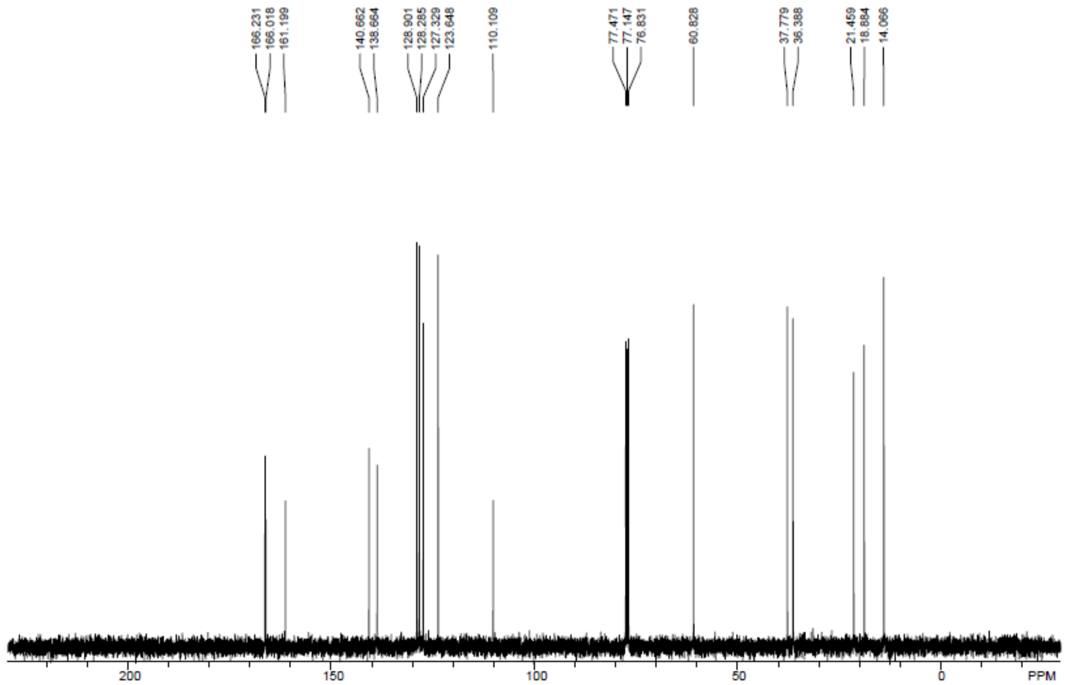
^{1}H NMR of **3c**



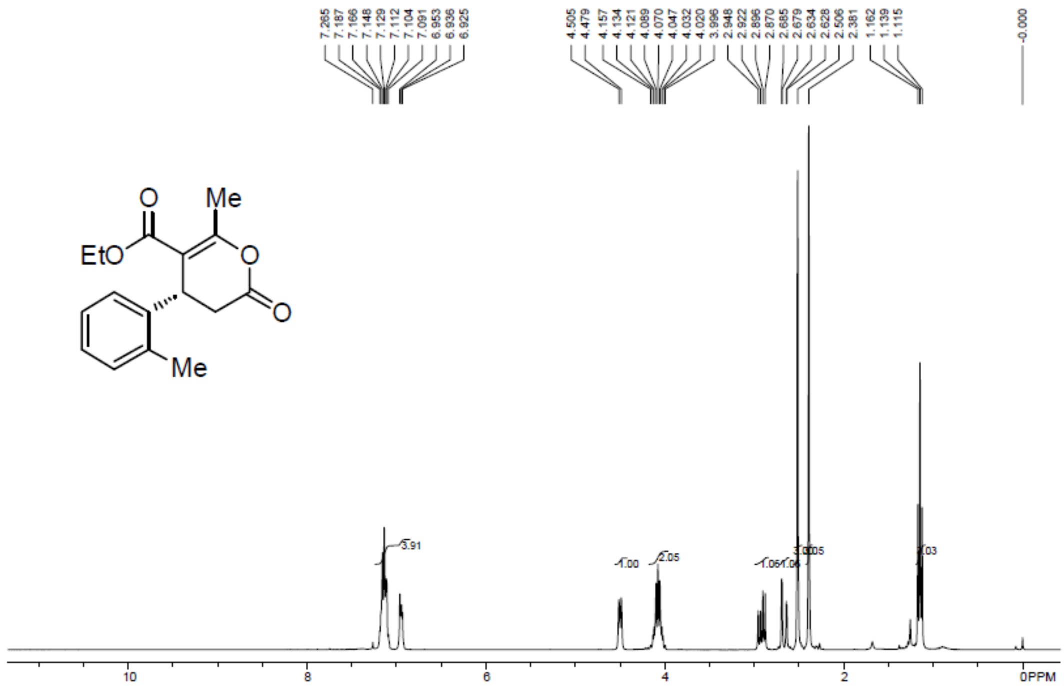
^{1}H NMR of **3d**



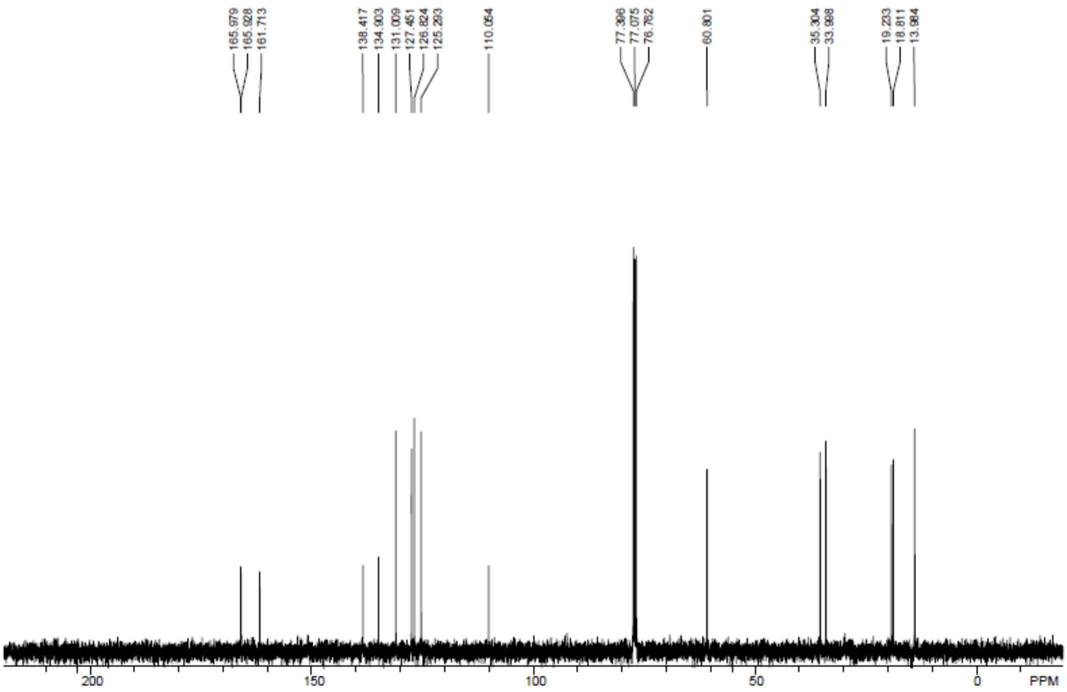
^{13}C NMR of **3d**



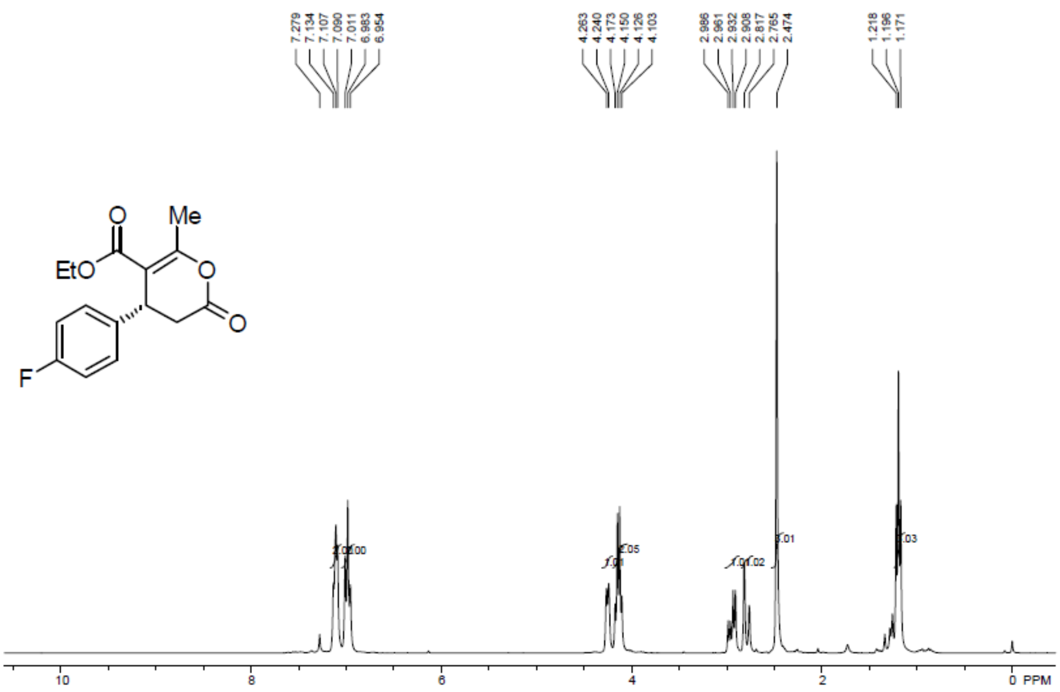
^{1}H NMR of **3e**



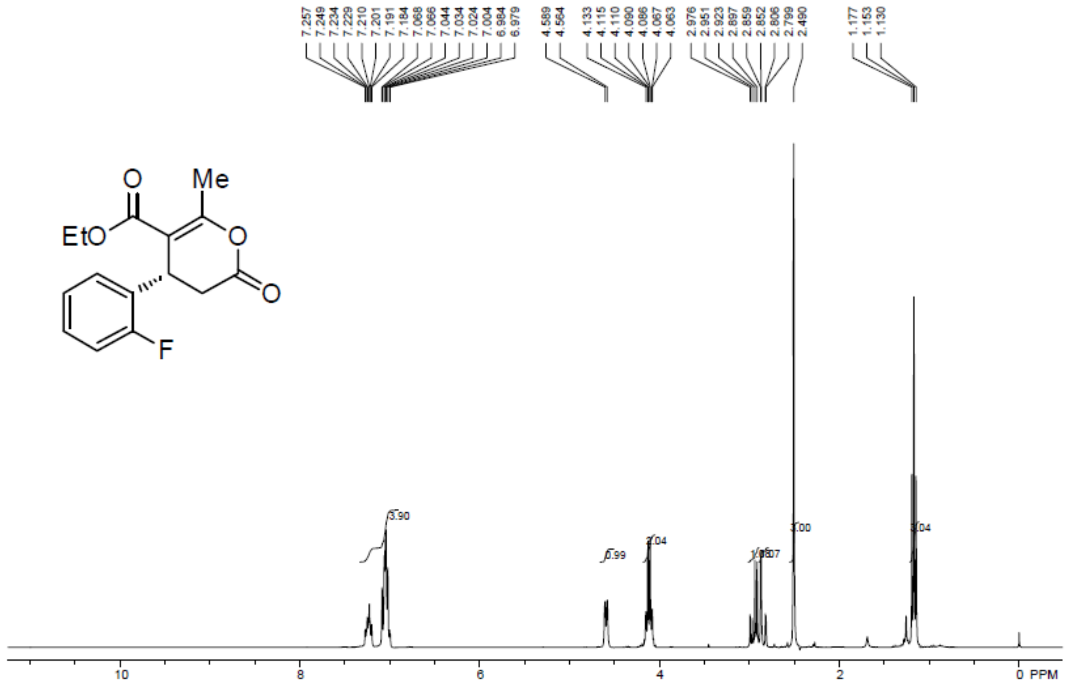
^{13}C NMR of **3e**



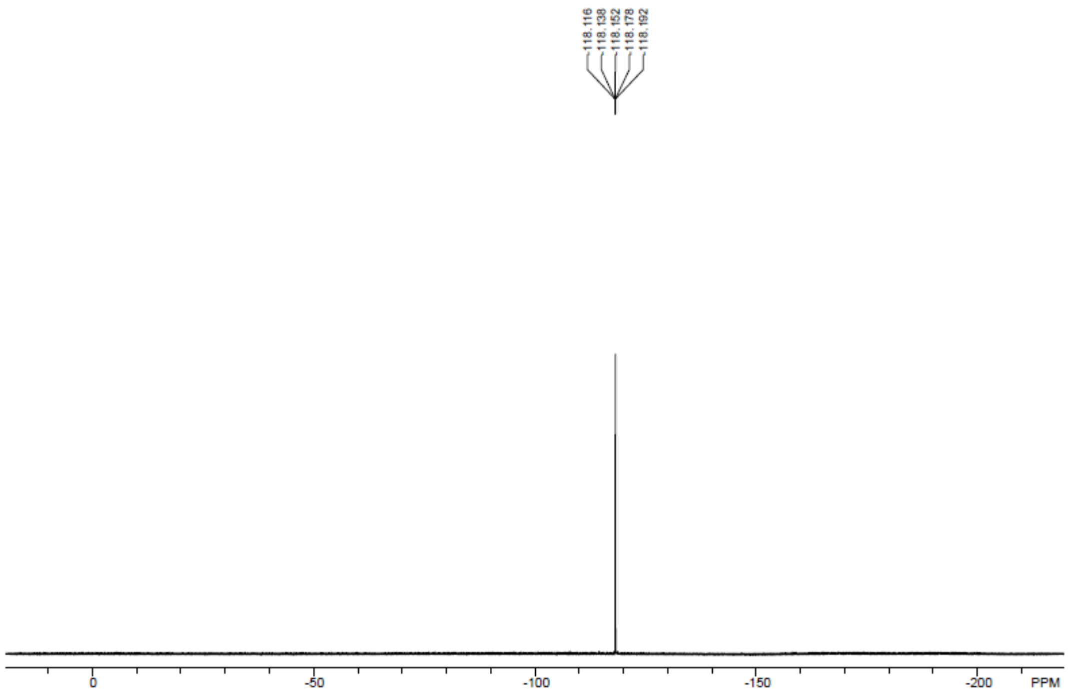
^{1}H NMR of **3f**



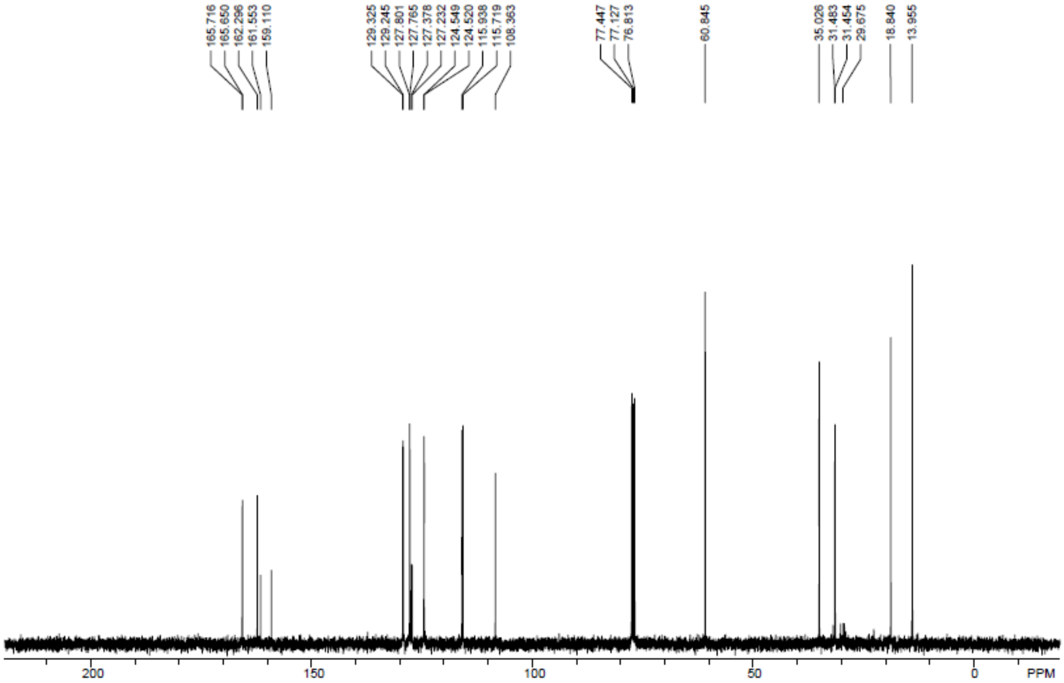
^{1}H NMR of **3g**



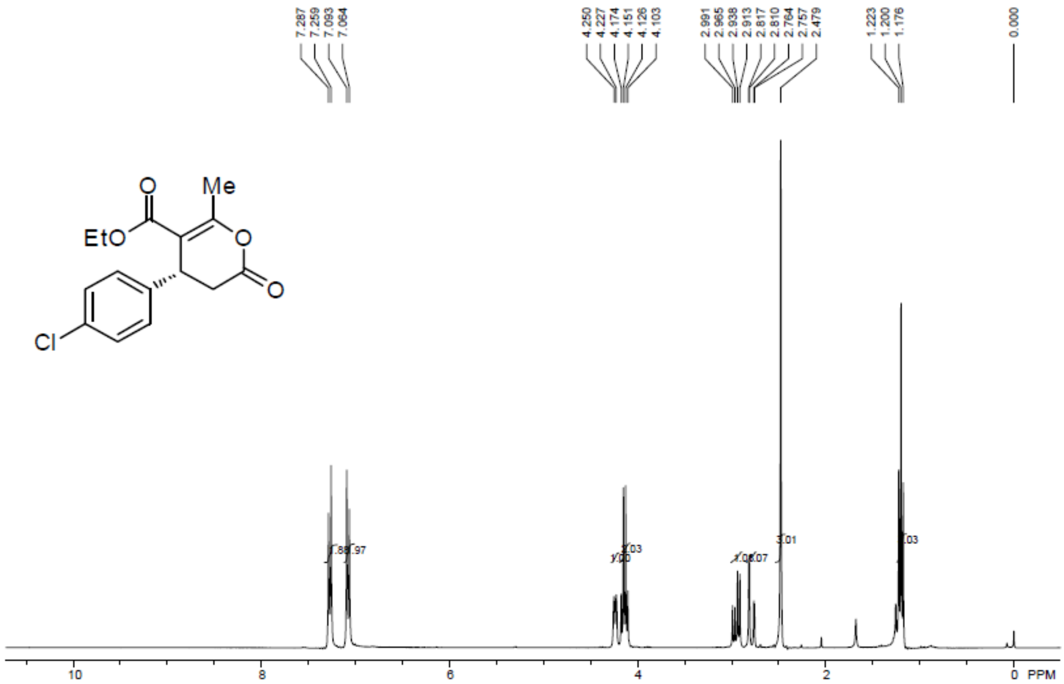
^{19}F NMR of **3g**



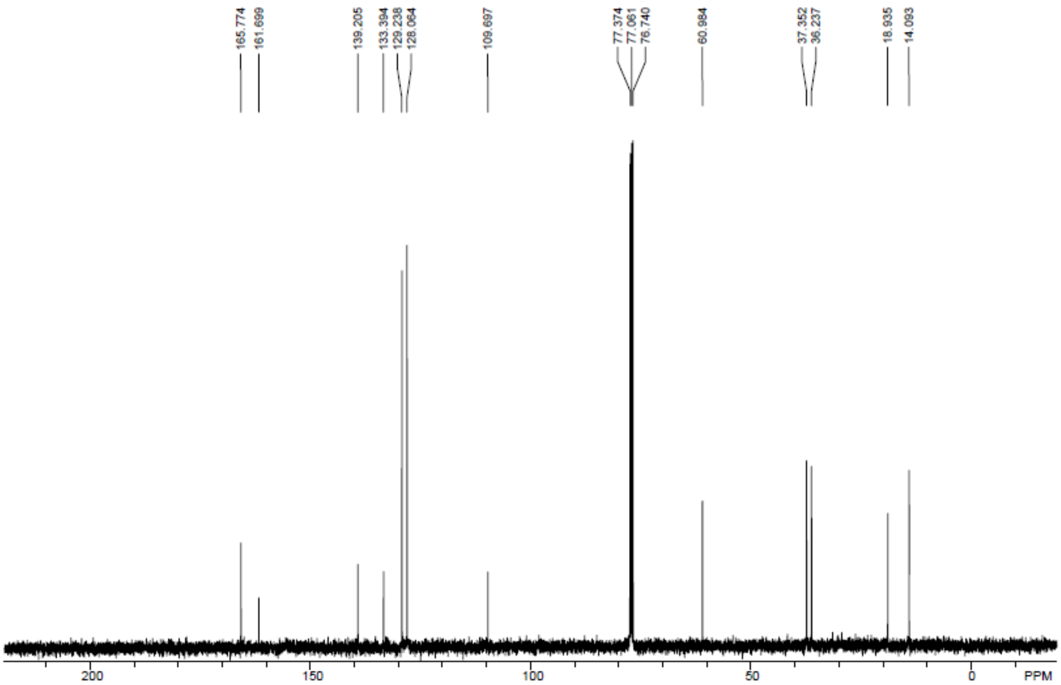
^{13}C NMR of **3g**



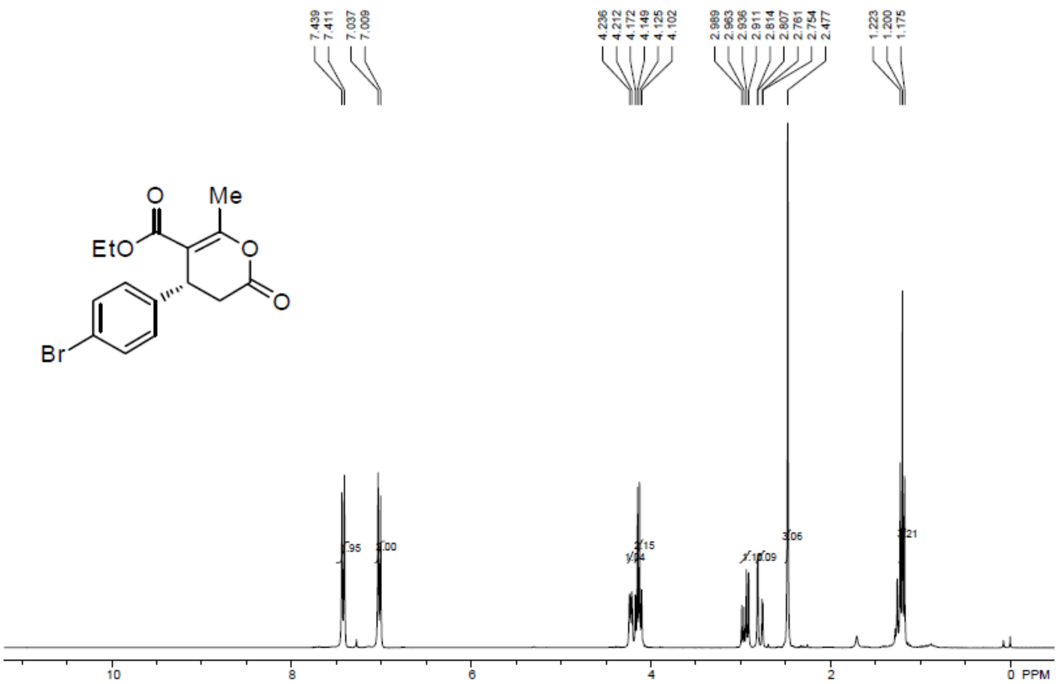
^{1}H NMR of **3h**



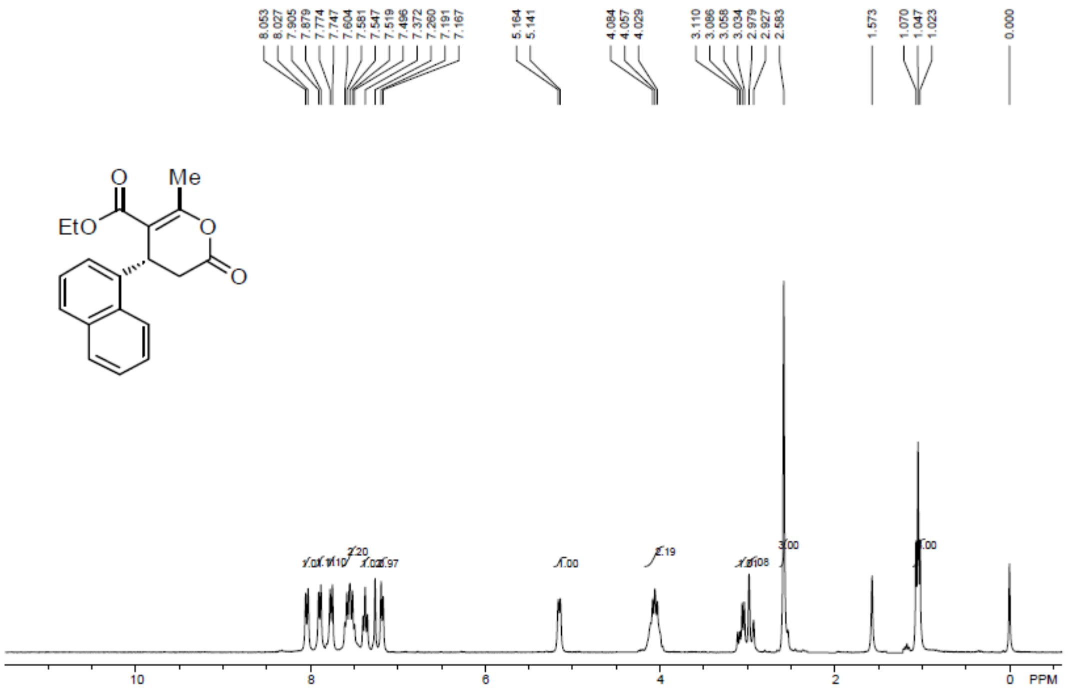
^{13}C NMR of **3h**



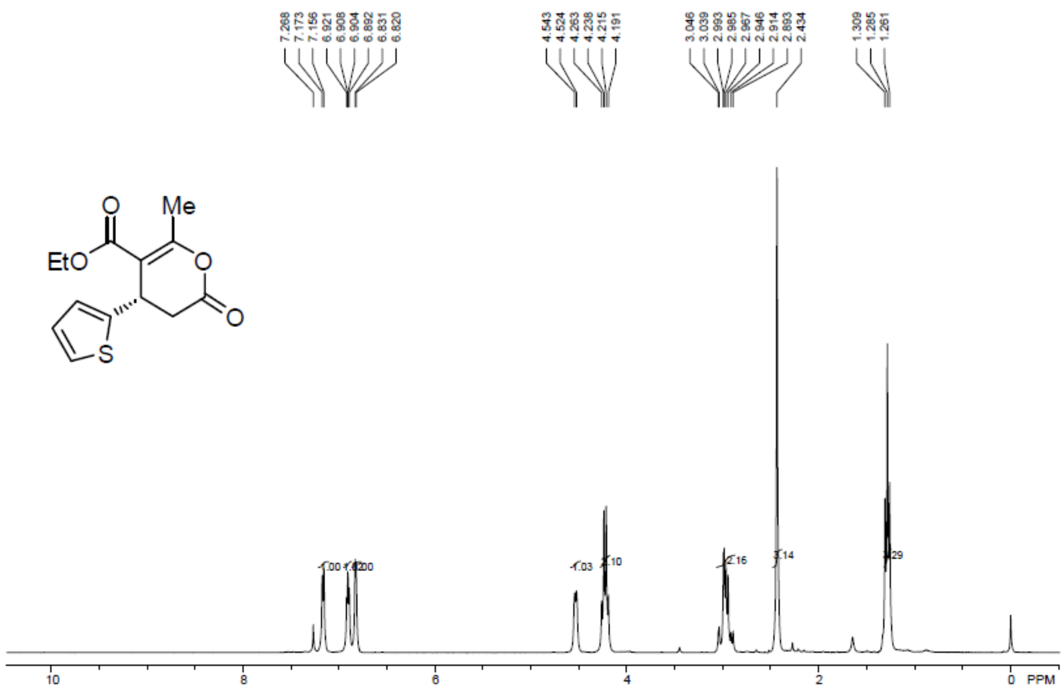
^{1}H NMR of **3i**



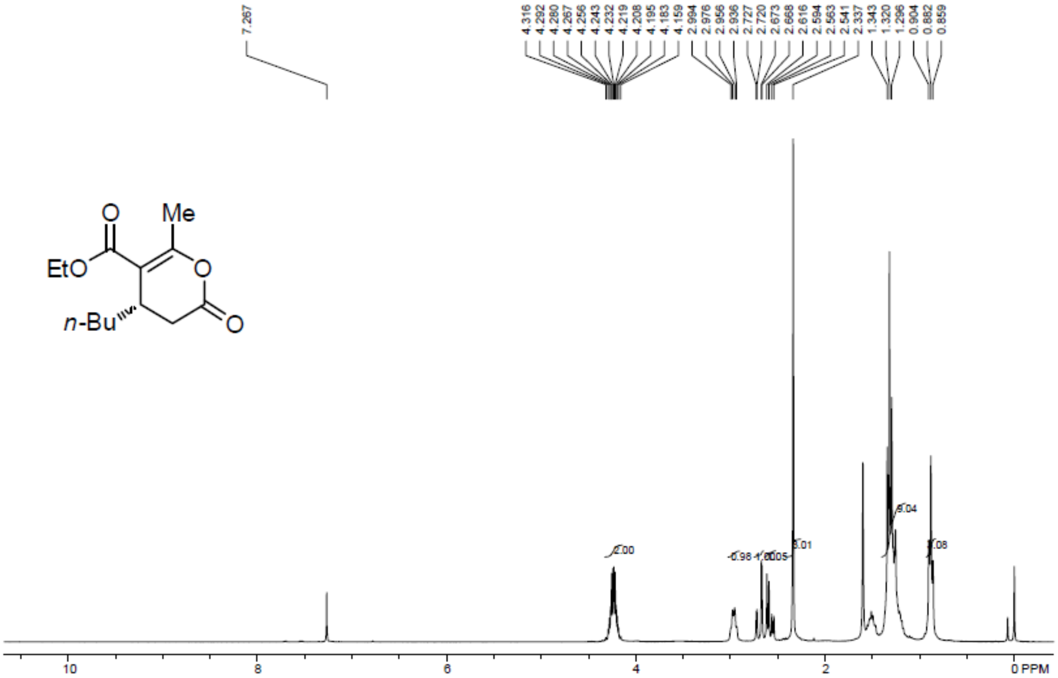
^{1}H NMR of **3j**



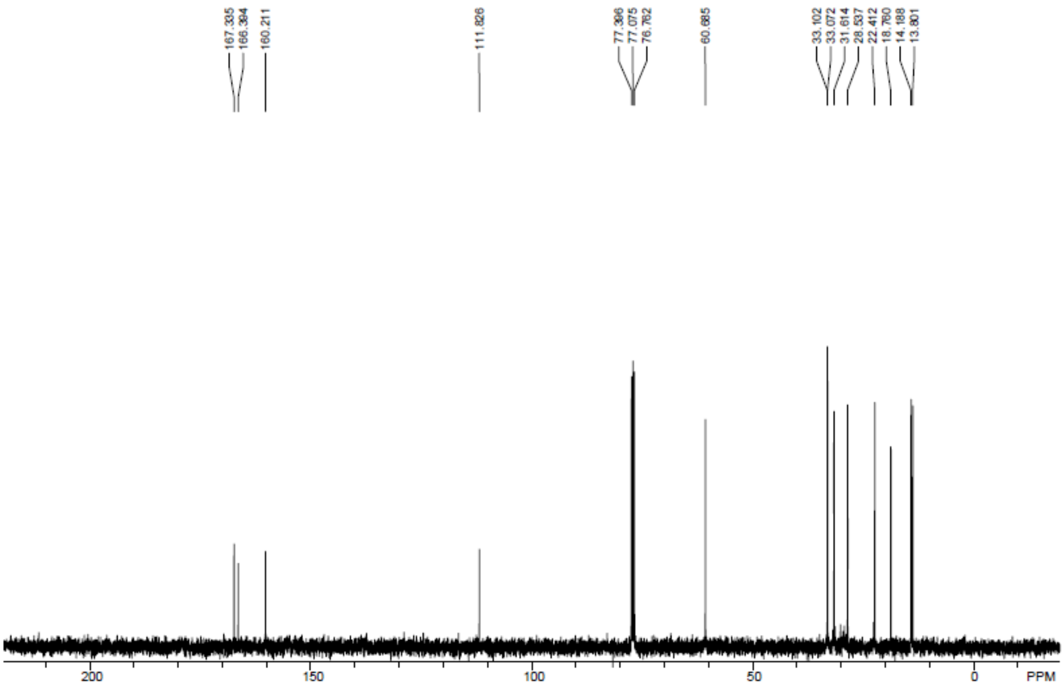
^{1}H NMR of **3k**



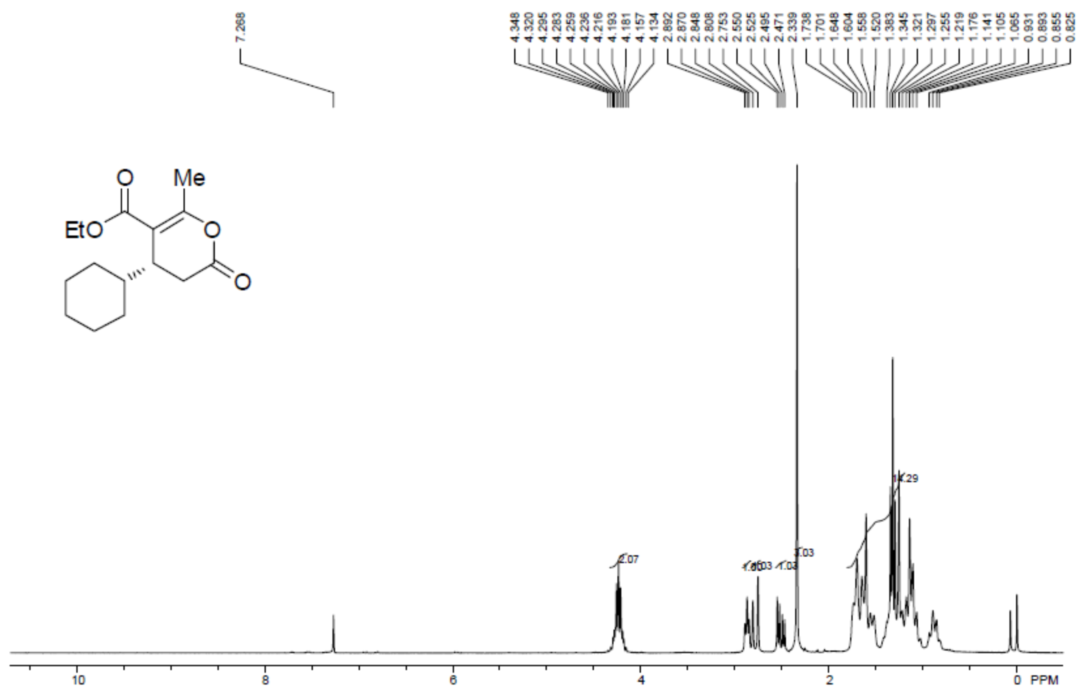
[1]H NMR of **3l**



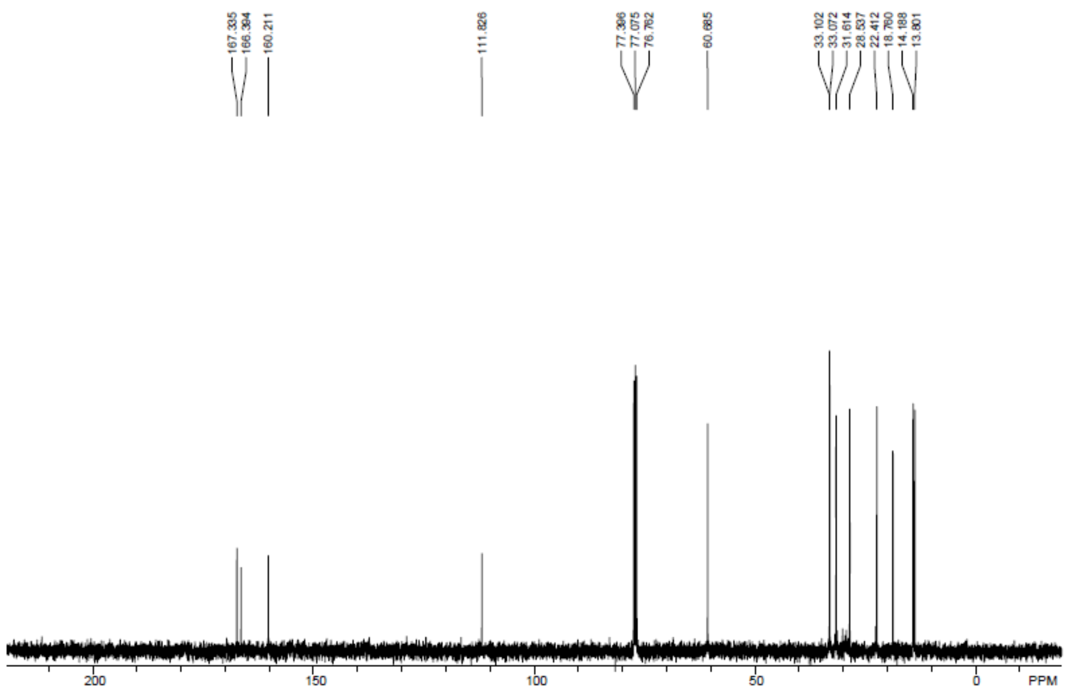
[13]C NMR of **3l**



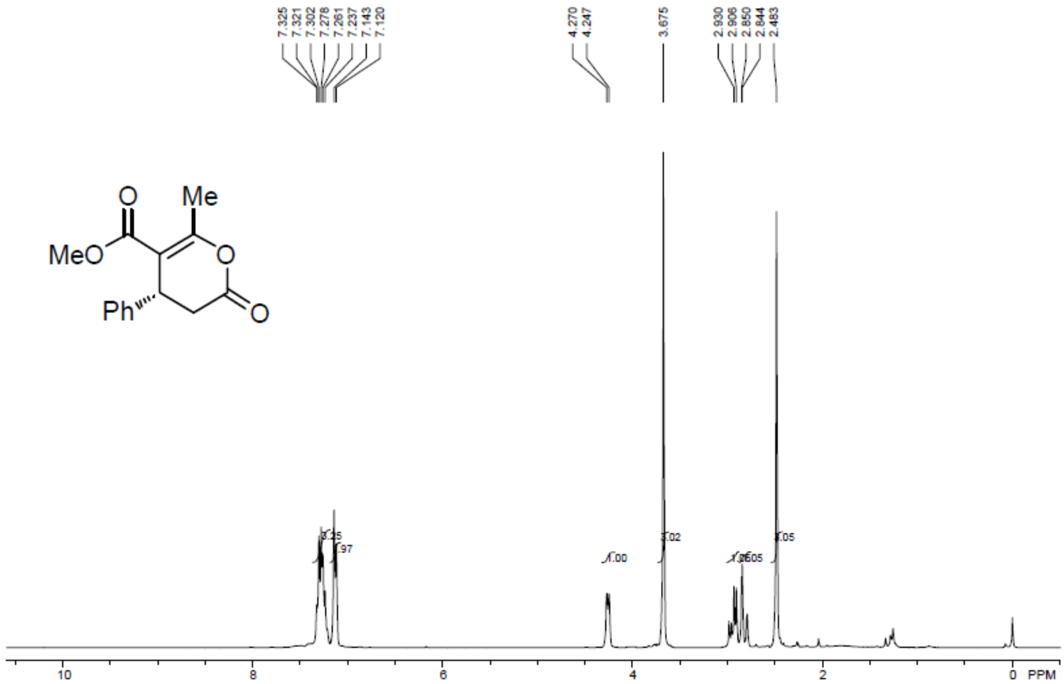
[1]H NMR of **3m**



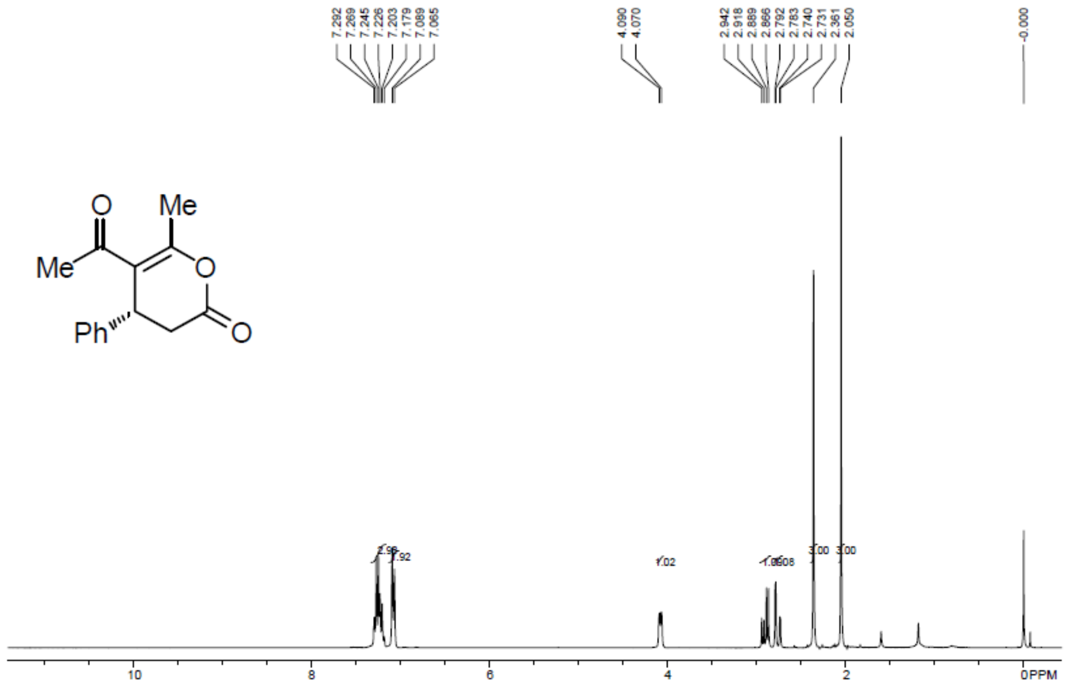
[13]C NMR of **3m**



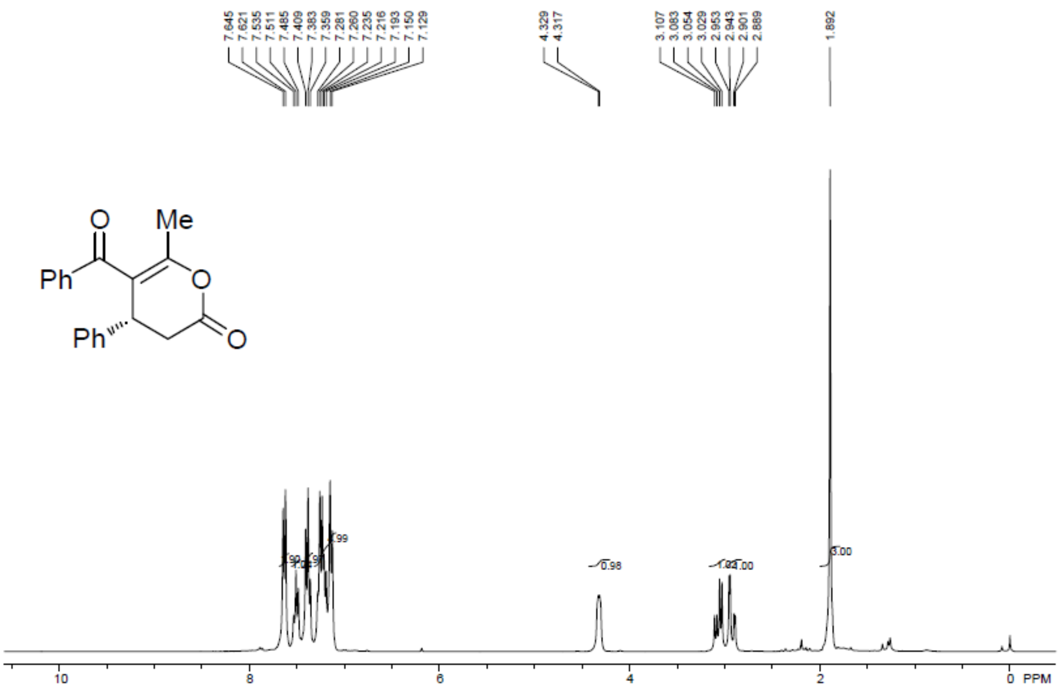
^{1}H NMR of **3n**



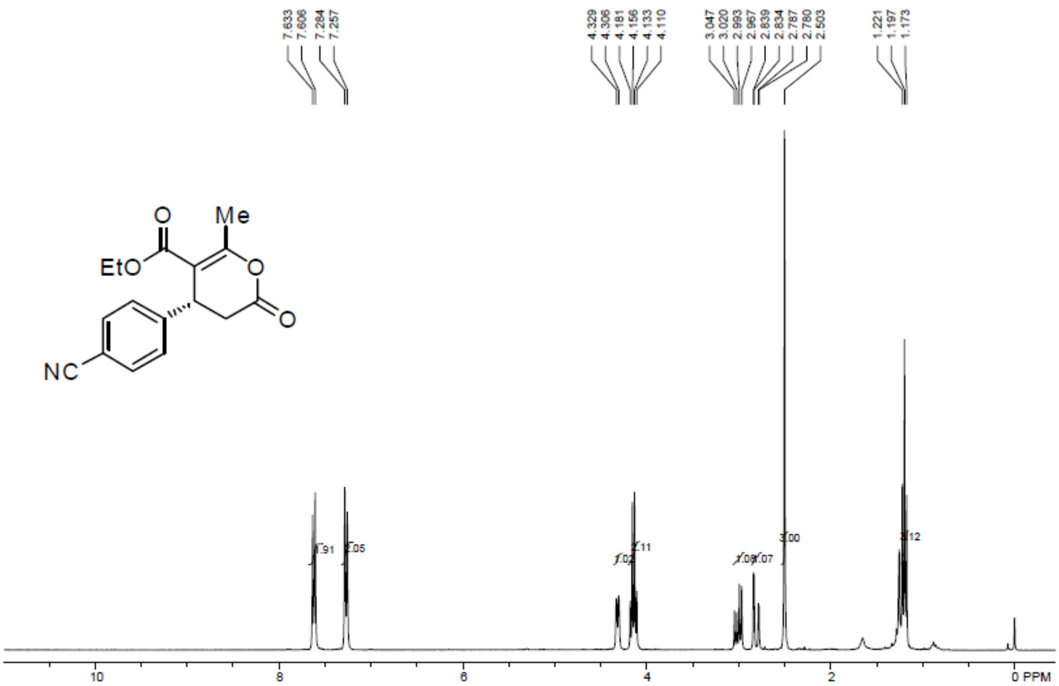
^{1}H NMR of **3o**



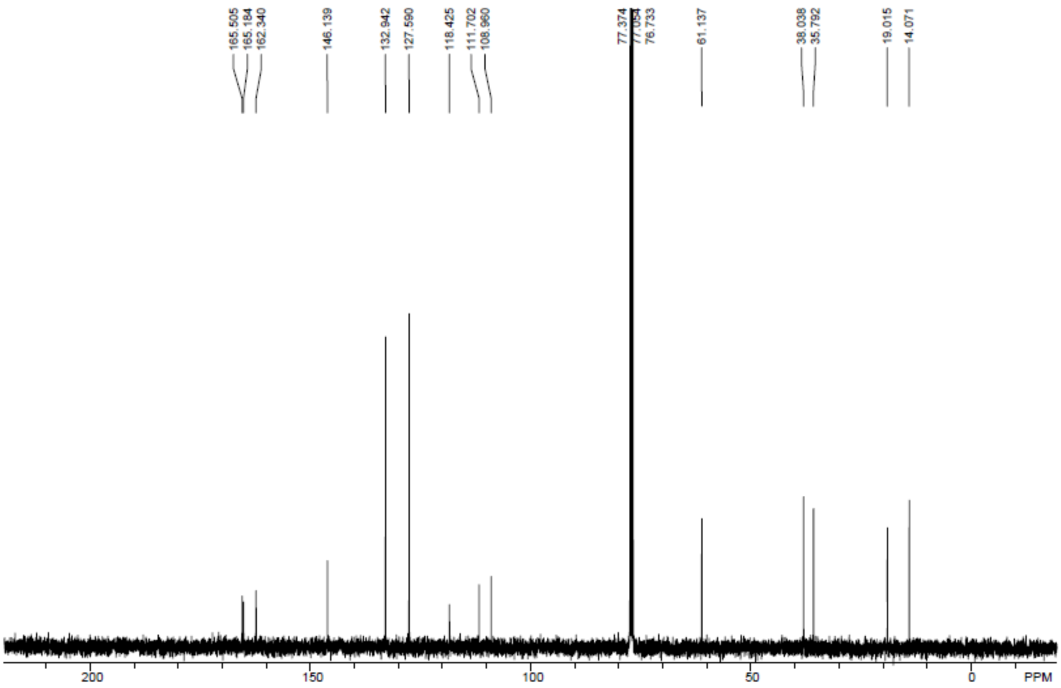
^{1}H NMR of **3p**



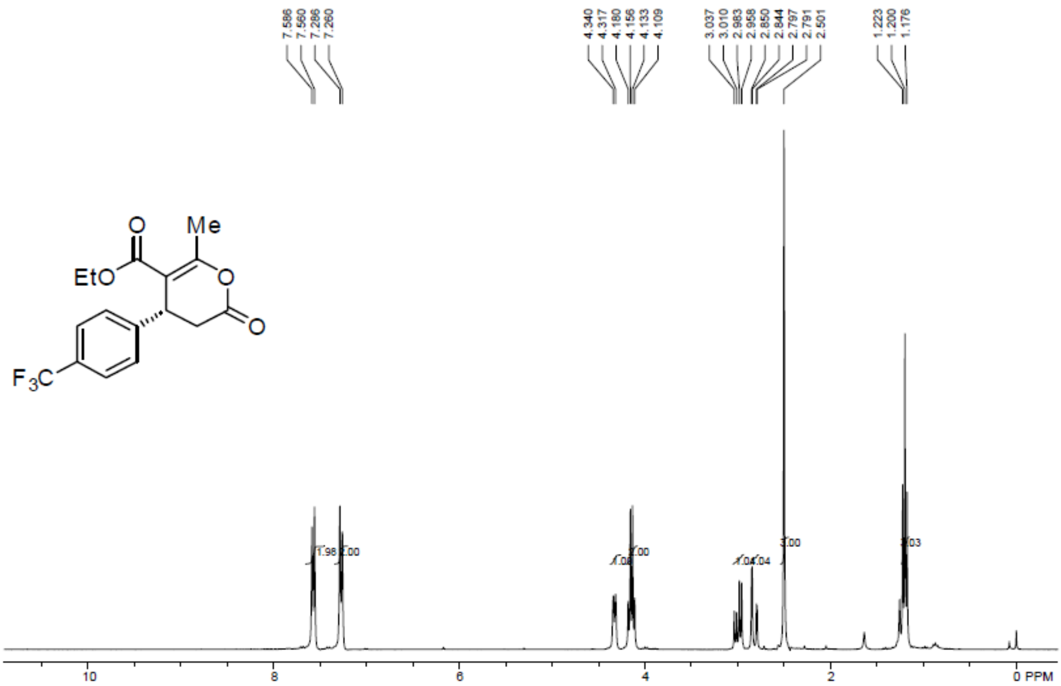
^{1}H NMR of **3q**



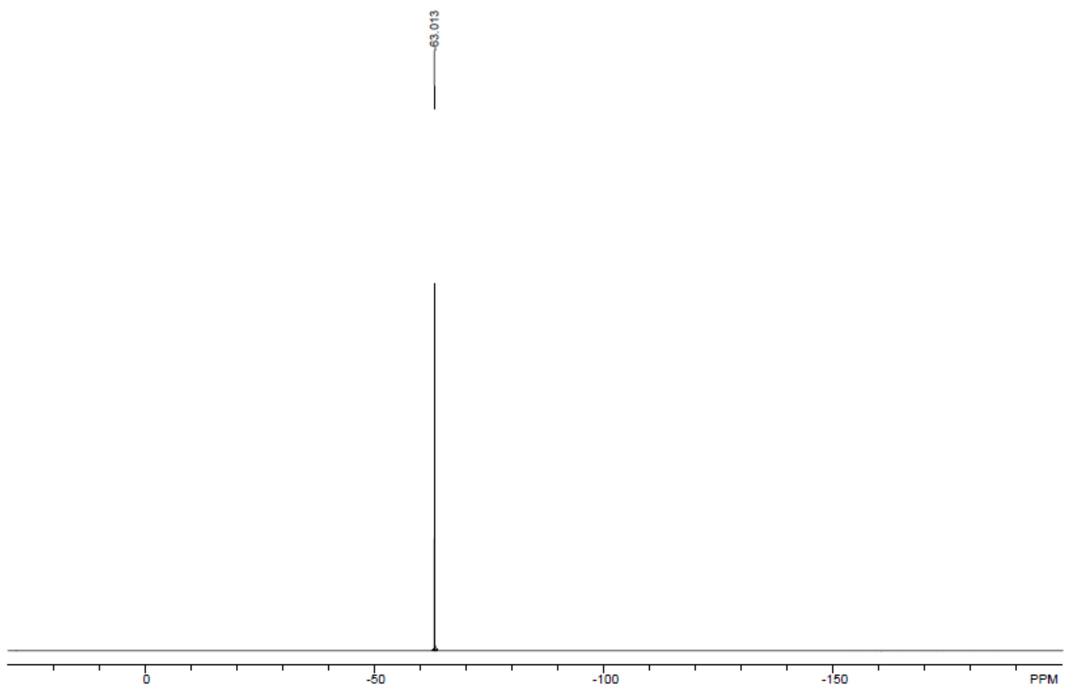
^{13}C NMR of **3q**



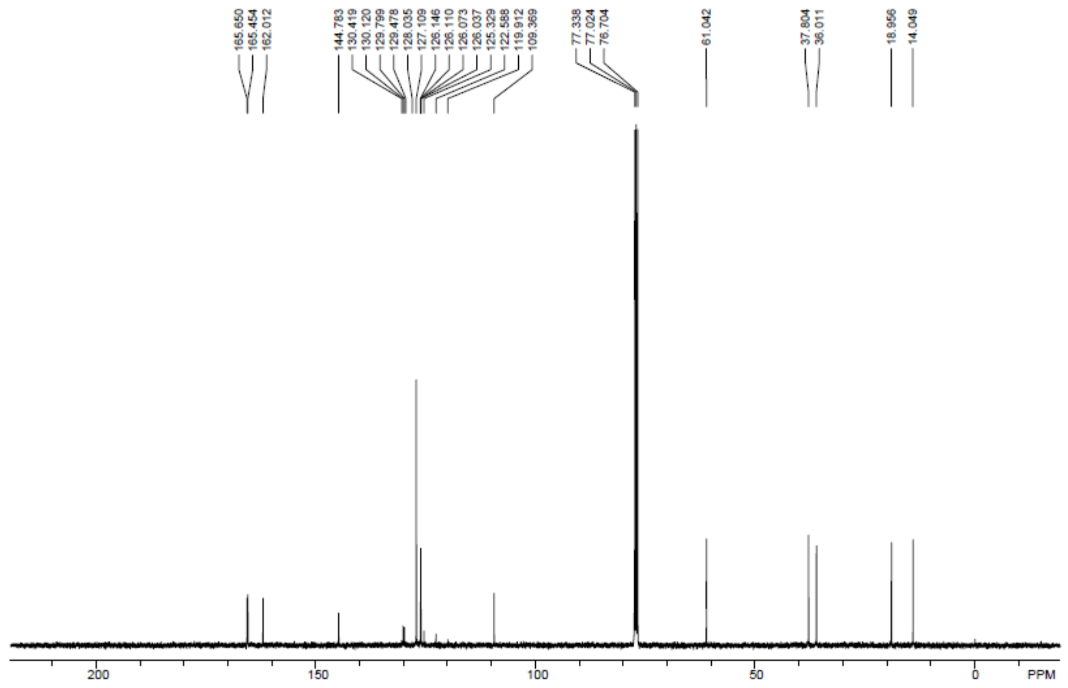
^{1}H NMR of **3r**



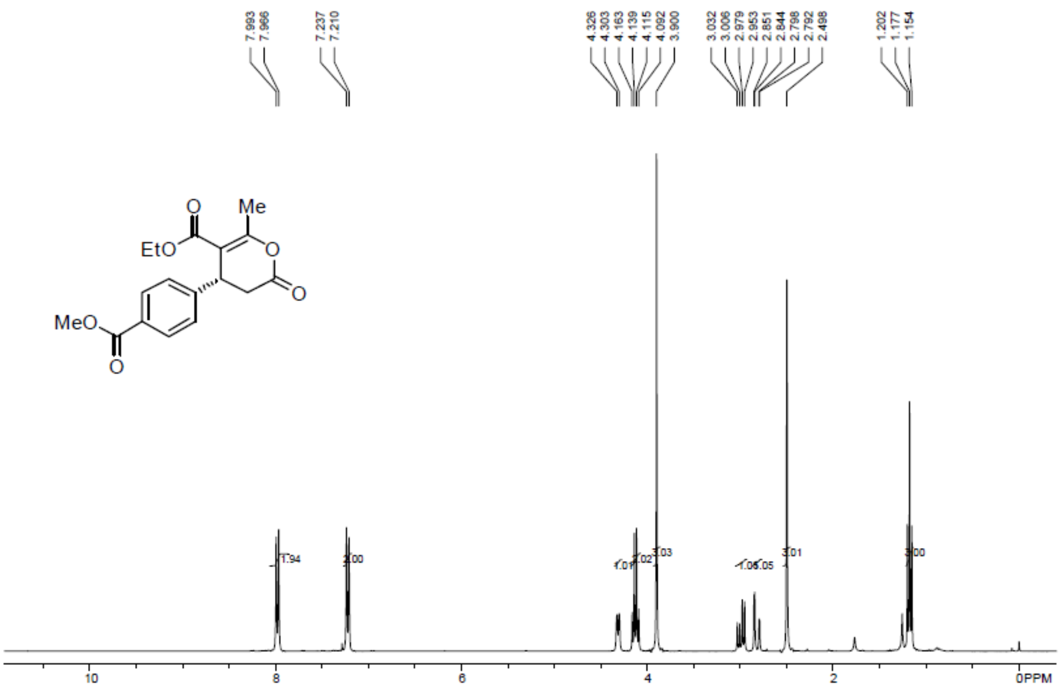
^{19}F NMR of **3r**



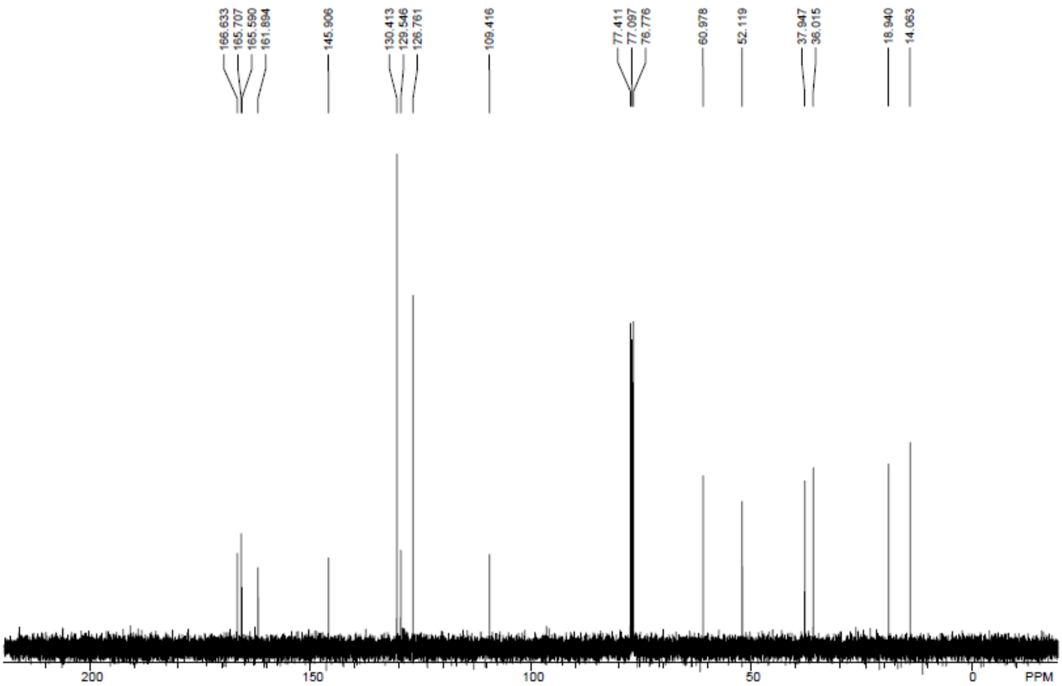
^{13}C NMR of **3r**



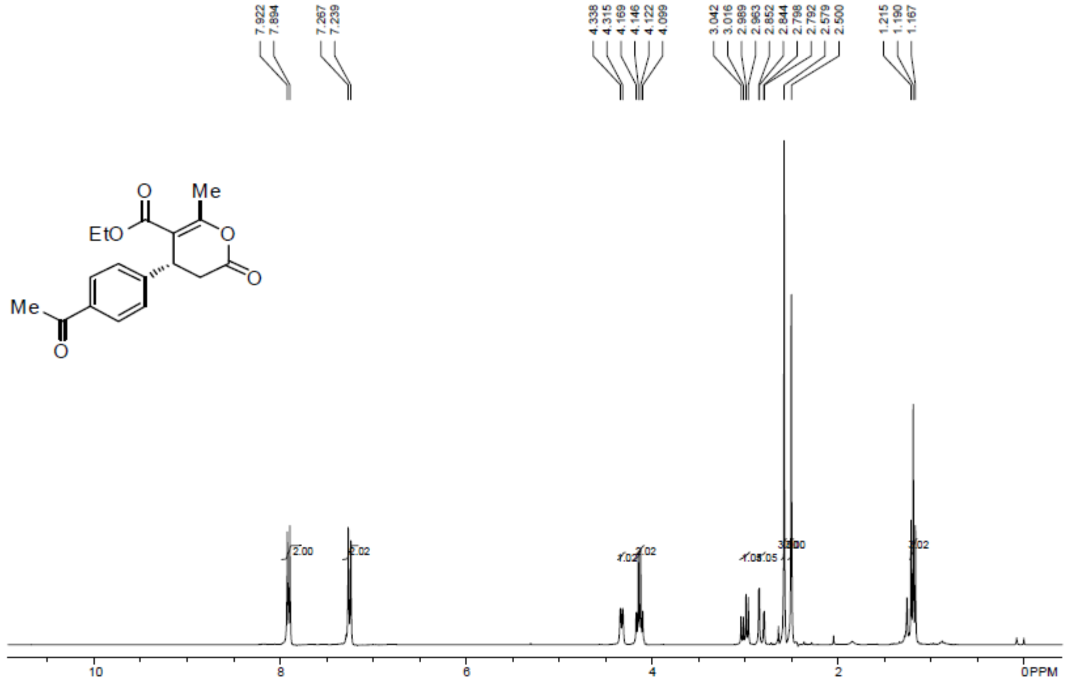
^{1}H NMR of **3s**



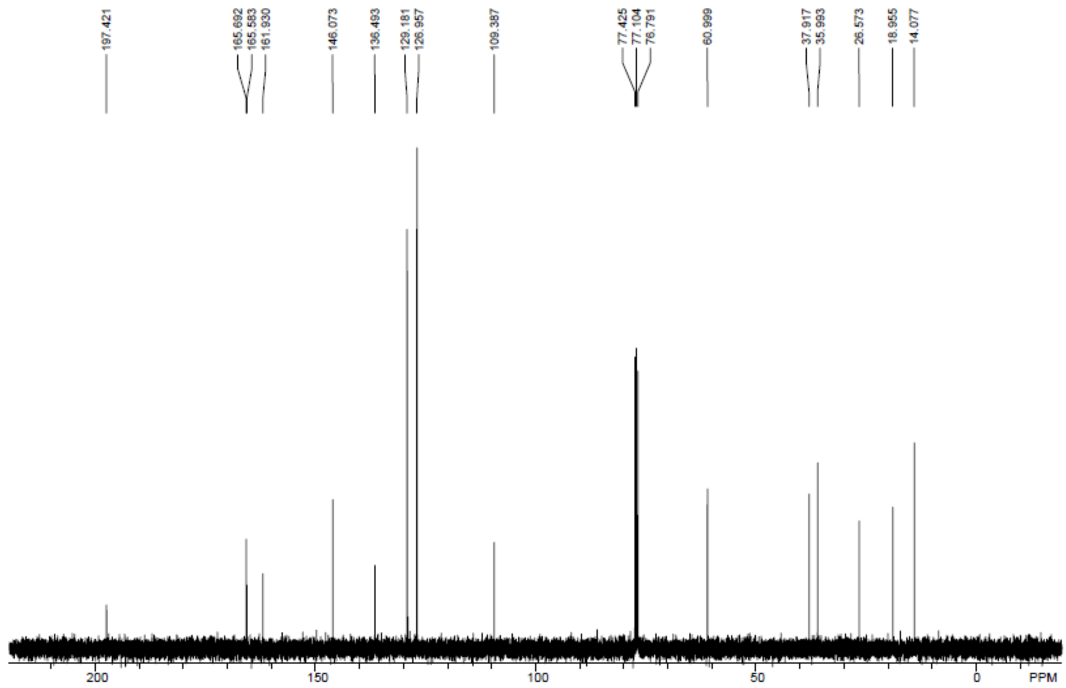
^{13}C NMR of **3s**



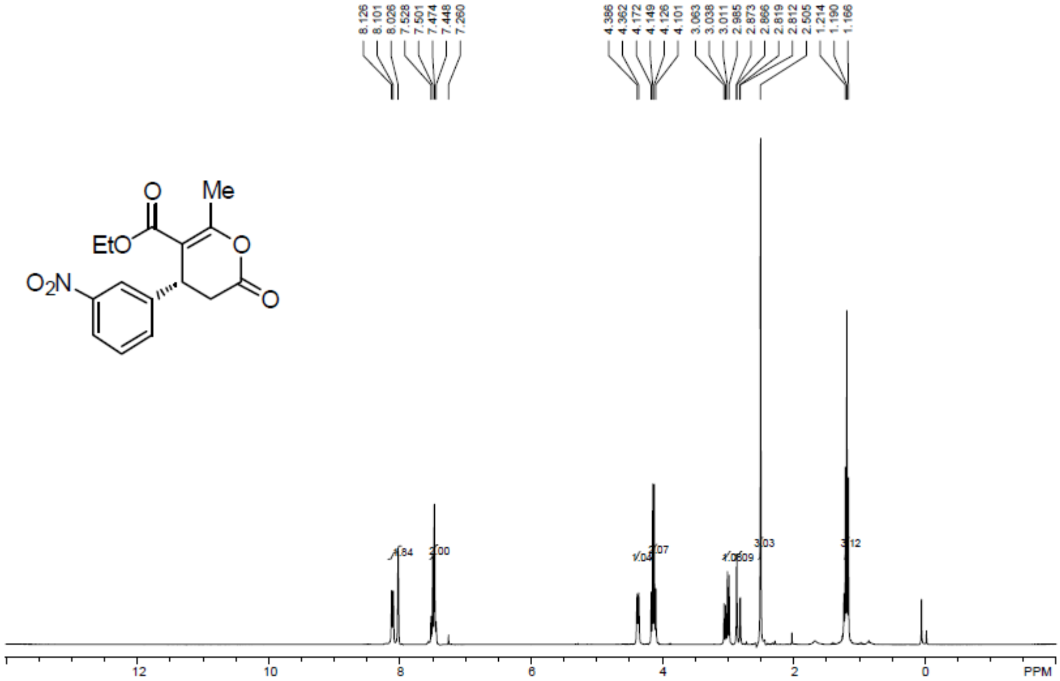
^{1}H NMR of **3t**



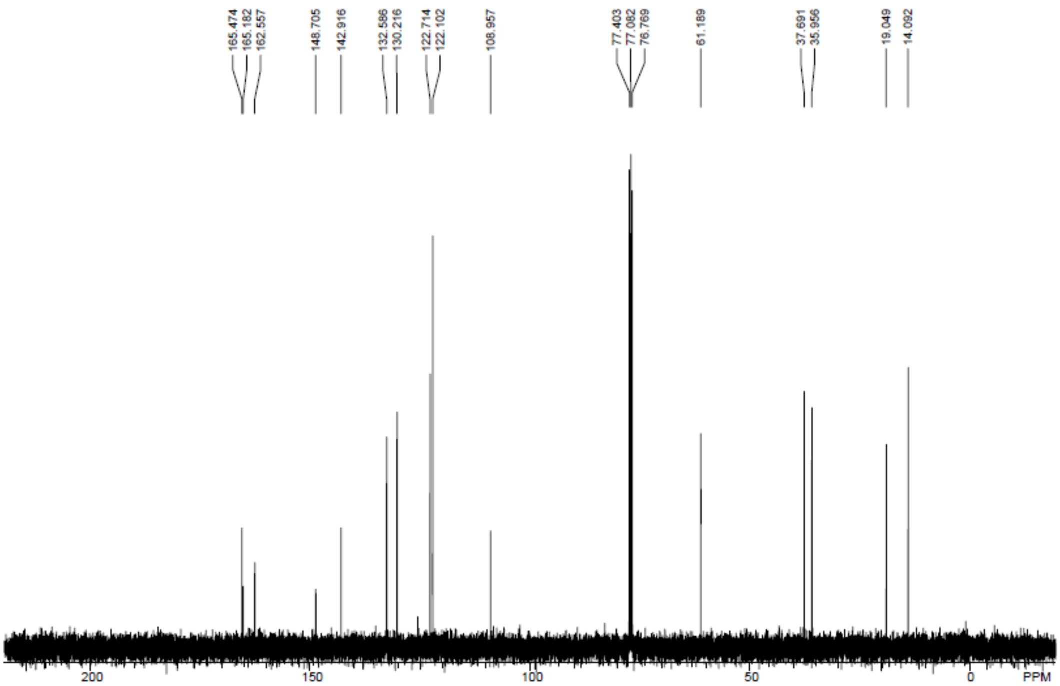
^{13}C NMR of **3t**



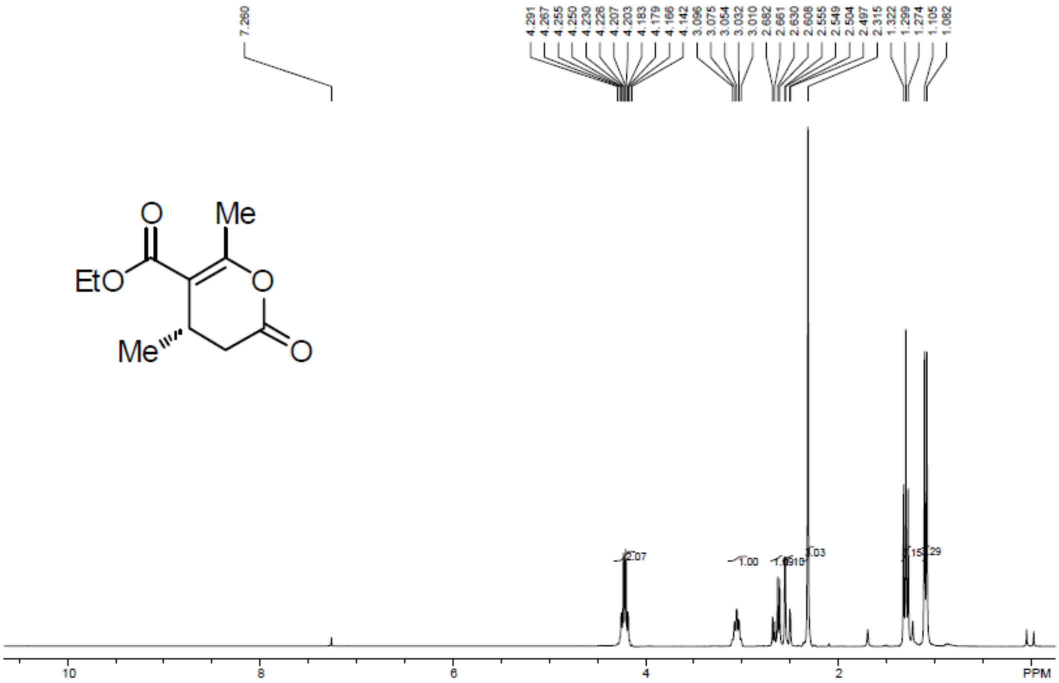
^{1}H NMR of **3u**



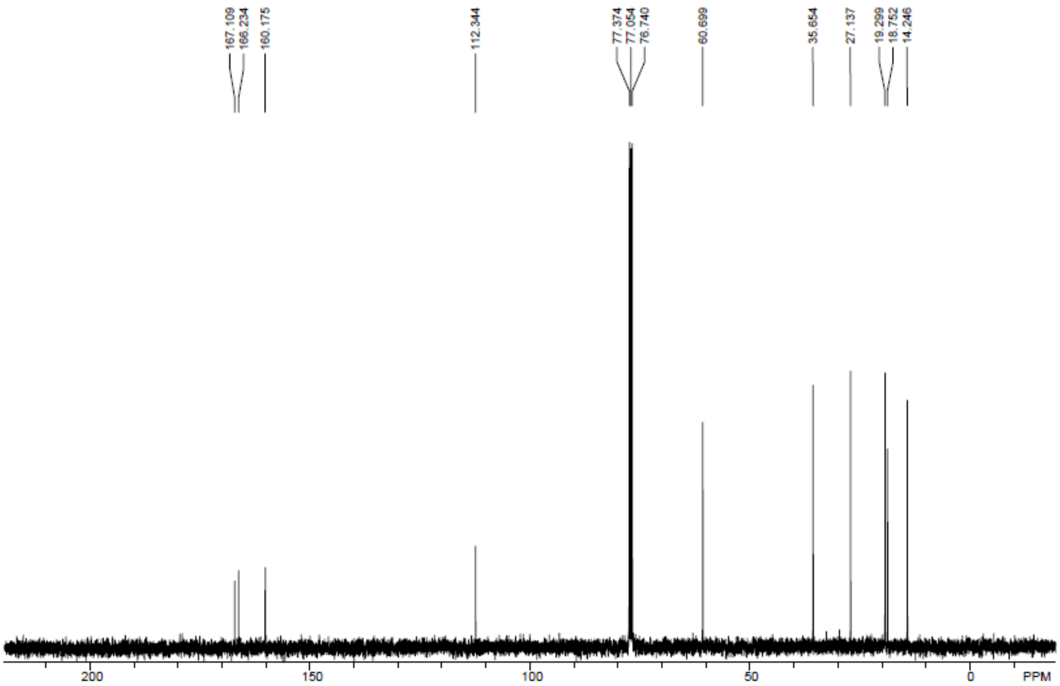
^{13}C NMR of **3u**



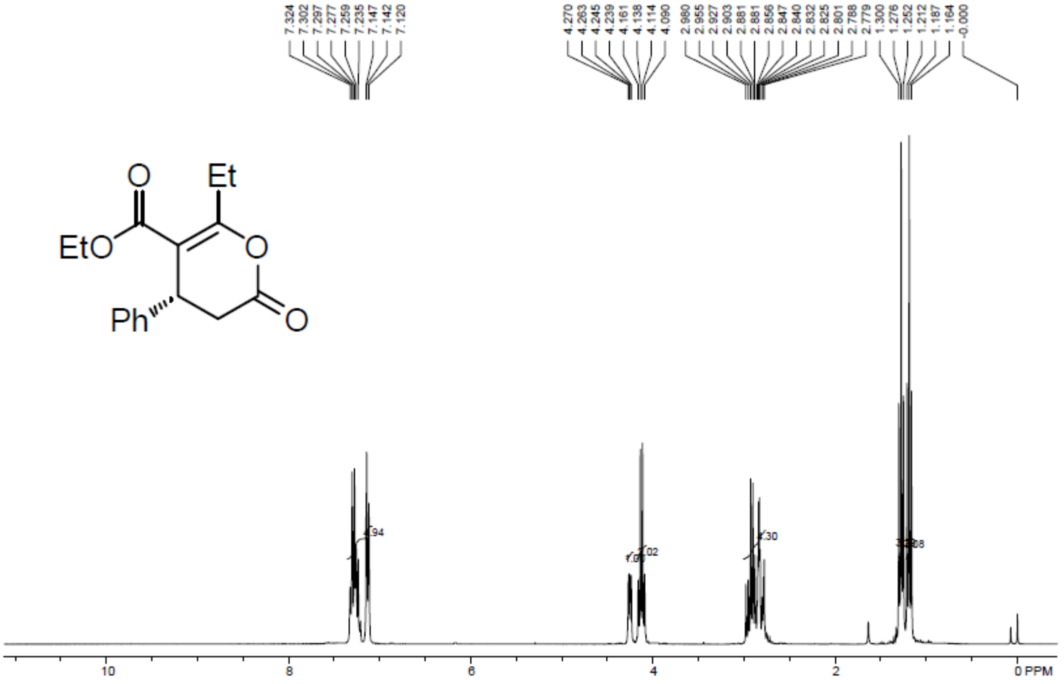
^{1}H NMR of **3v**



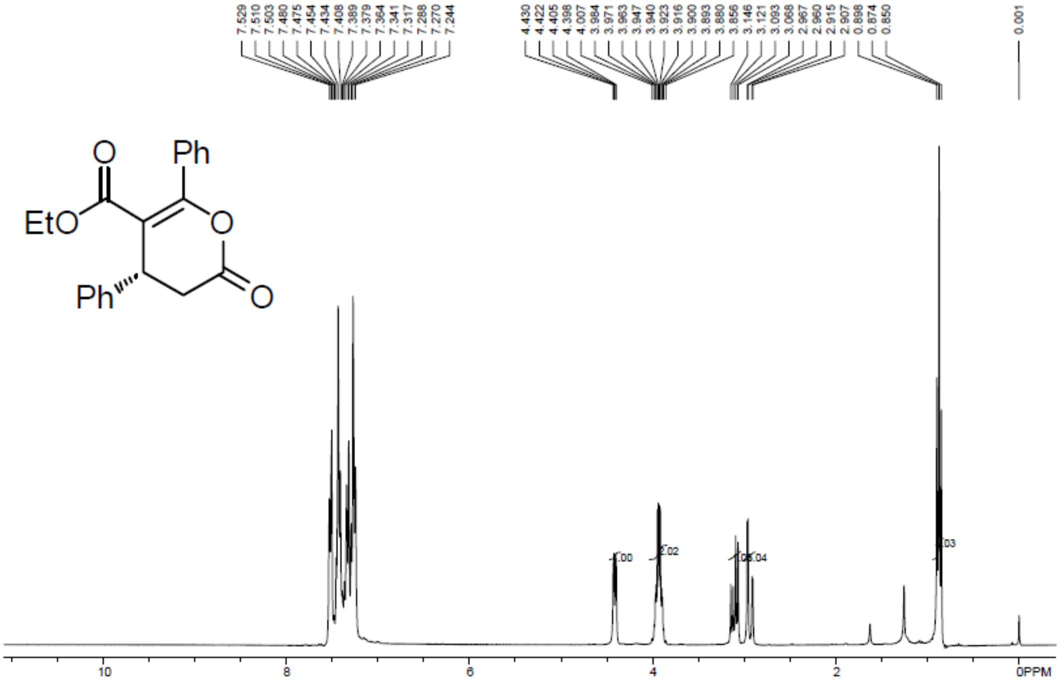
^{13}C NMR of **3v**



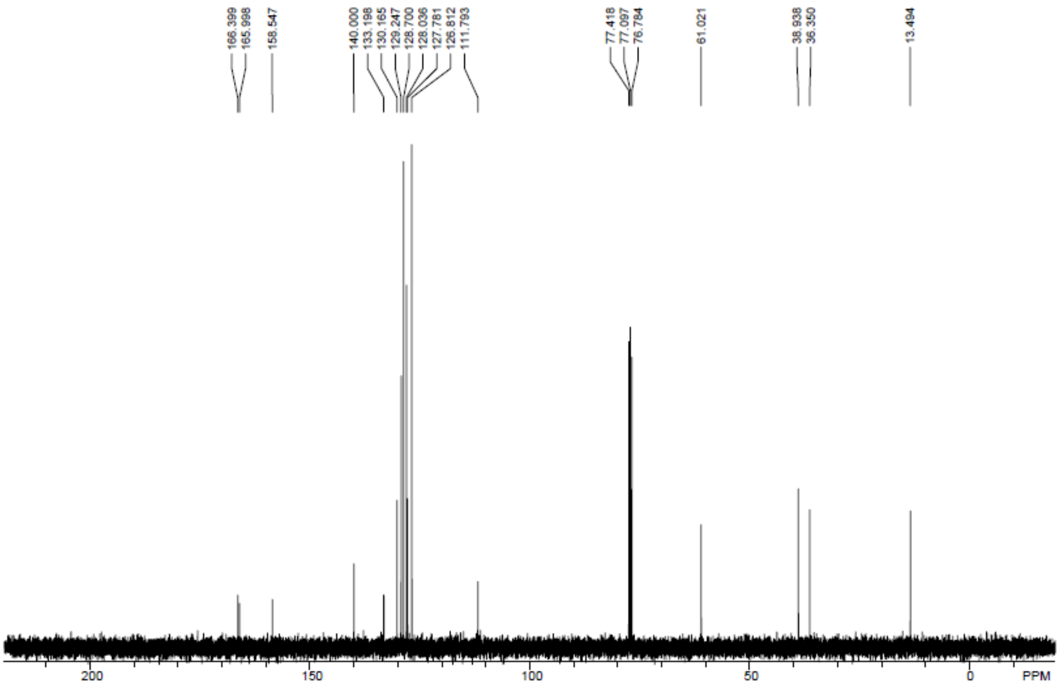
^{1}H NMR of **3w**



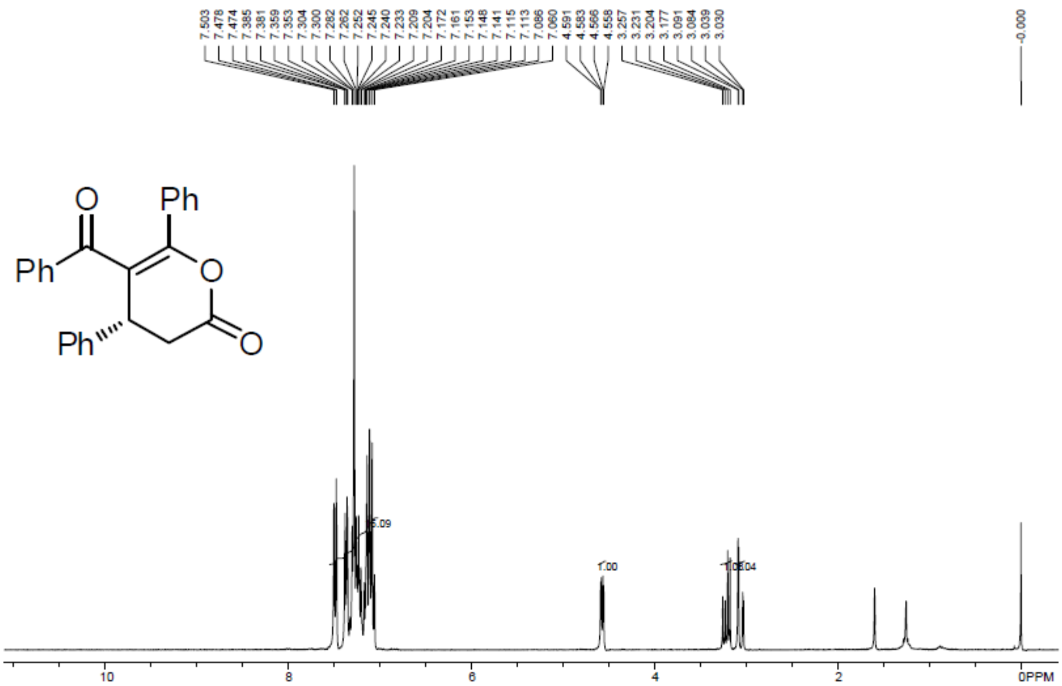
^{1}H NMR of **3x**



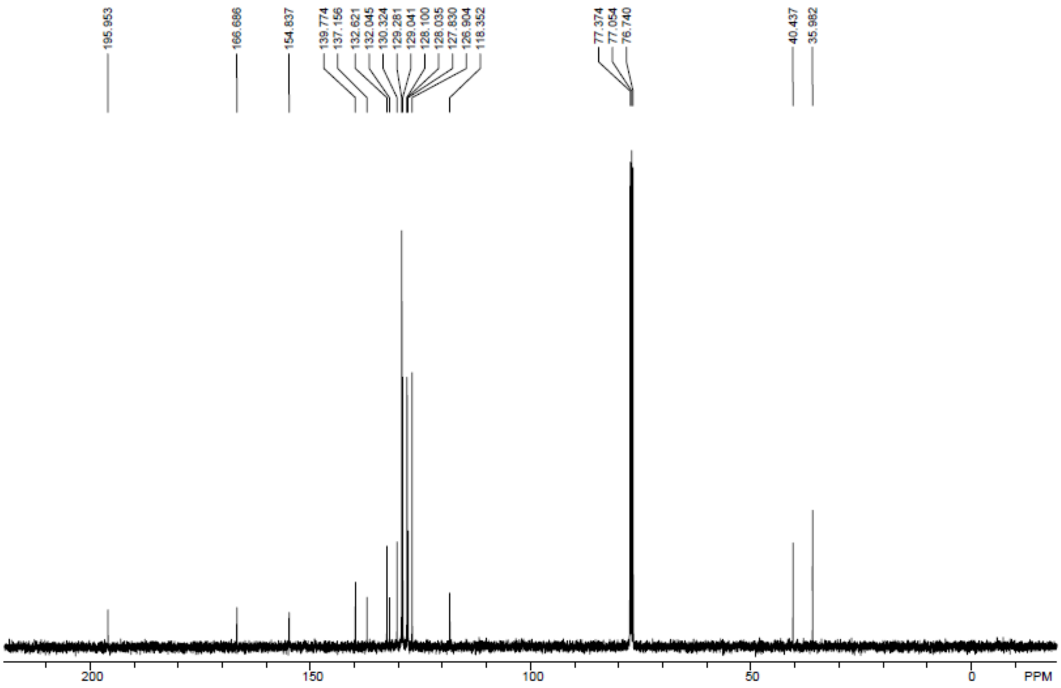
[13]C NMR of **3x**



[1]H NMR of **3y**



^{13}C NMR of **3y**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129.041
128.100
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126.904
118.352
77.374
77.054
76.740
40.437
35.982
200
150
100
50
0
PPM