

## Supporting Information

# Base- and Sulfur- Promoted Oxidative Lactonization of Chalcone-Acetate Michael Adducts: Access to Pyran-2-ones

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## General Information

Reagents ( $S_8$ , DMSO, DBU, DABCO as well as ethyl 2-phenylacetate **1a** and chalcone **2a**) were obtained from commercial supplier and used without further purification. Other chalcones were prepared from the corresponding benzaldehydes and acetophenones according to known procedures.<sup>1</sup> Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or KMnO<sub>4</sub> or vanillin stains. Flash column chromatography was carried out using kieselgel 35-70  $\mu\text{m}$  particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in ( $\delta$ ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference (CDCl<sub>3</sub>,  $\delta$  7.26 ppm for <sup>1</sup>H and  $\delta$  77.0 ppm for <sup>13</sup>C; (DMSO-d<sub>6</sub>,  $\delta$  2.50 ppm for <sup>1</sup>H and  $\delta$  39.5 ppm for <sup>13</sup>C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

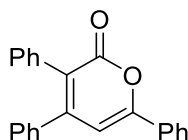
### Representative procedure for the synthesis of pyran-2-ones **3** and **5**

A mixture of chalcone **2a** (1 mmol, 1.0 equiv), ethyl 2-phenylacetate **1a** (1.05 mmol), DBU (30 mg, 0.2 mmol, 0.1 equiv) and DMSO (0.2 mL) was stirred and heated at 120 °C (aluminum or copper block heater) for 1.5 h in a 7-mL test tube closed with a plastic cap. Next, **S** (96 mg, 3 mmol) and DABCO (112 mg, 1 mmol, 1 equiv) were added to the reaction mixture and the tube was stirred and heated at 120 °C for 16 h. After cooling to room temperature, the reaction mixture was dissolved in ethyl acetate (10 mL). The resulting solution was washed successively with water (4 mL) and an aqueous solution of NH<sub>4</sub>Cl (2 mL, 10%). The separated organic layer was dried (MgSO<sub>4</sub>), filtered and evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane/ethyl acetate 19:1) to give the desired pyrone **3a** as a pale yellow solid.

A 10-mmol scale synthesis of **3a** from **2a** and **1a** was performed in the same manner using a 20-mL test tube as a reactor to provide **3a** as a pale yellow solid (2.69 g, 83%).

### Characterization of products **3** and **5**

#### 3,4,6-Triphenyl-2H-pyran-2-one (**3a**)



Yellow solid (275 mg, 85%).

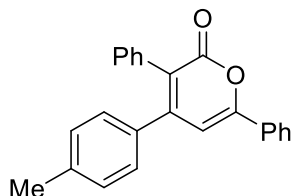
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (dd,  $J$  = 6.7, 3.0 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.29 – 7.14 (m, 10H), 6.83 (s, 1H).

<sup>1</sup> Nguyen, T. B.; Retailleau, P. *Org. Lett.* **2018**, *20*, 186. (b) Nguyen, T. B.; Retailleau, P. *Org. Lett.* **2017**, *19*, 4858. (c) Nguyen, T. B.; Retailleau, P. *Org. Lett.* **2017**, *19*, 3879.

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7, 158.3, 152.8, 137.8, 133.8, 131.4, 130.9 (2C), 130.8, 129.0 (2C), 128.8, 128.7 (2C), 128.4 (2C), 128.0 (2C), 127.7, 125.6 (2C), 123.2, 105.0.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{23}\text{H}_{17}\text{O}_2$  325.1229. Found 325.1232.

### 3,6-Diphenyl-4-(p-tolyl)-2H-pyran-2-one (3b)



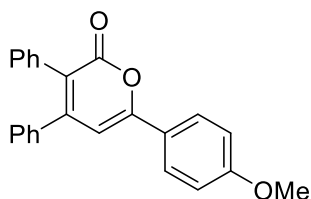
Yellow solid (270mg, 80%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (dd,  $J = 7.2, 3.9$  Hz, 2H), 7.51 – 7.44 (m, 3H), 7.25 – 7.19 (m, 5H), 7.06 (s, 4H), 6.84 (s, 1H), 2.31 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 158.2, 152.7, 138.9, 134.8, 134.1, 131.5, 130.9 (2C), 130.7, 129.1 (2C), 129.0 (2C), 128.7 (2C), 128.0 (2C), 127.6, 125.6 (2C), 122.8, 105.1, 21.3.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{24}\text{H}_{19}\text{O}_2$  339.1385. Found 339.1392.

### 6-(4-Methoxyphenyl)-3,4-diphenyl-2H-pyran-2-one (3c)



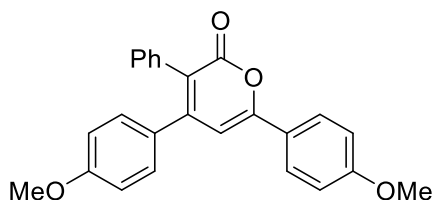
Yellow solid (265 mg, 75%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.9$  Hz, 2H), 7.26 – 7.13 (m, 10H), 6.98 (d,  $J = 8.9$  Hz, 2H), 6.73 (s, 1H), 3.87 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 161.8, 158.5, 153.2, 138.1, 134.0, 131.0 (2C), 128.8 (2C), 128.7, 128.4 (2C), 128.0 (2C), 127.6, 127.4 (2C), 124.0, 122.0, 114.4 (2C), 103.6, 55.5.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{24}\text{H}_{19}\text{O}_3$  355.1334. Found 355.1340.

### 4,6-bis(4-methoxyphenyl)-3-phenyl-2H-pyran-2-one (3d)



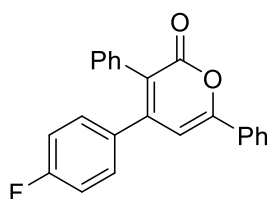
Yellow solid (276mg, 72%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.9$  Hz, 2H), 7.26 – 7.19 (m, 5H), 7.10 (d,  $J = 8.7$  Hz, 2H), 6.98 (d,  $J = 8.9$  Hz, 2H), 6.76 (d,  $J = 8.7$  Hz, 2H), 6.72 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.0, 161.7, 159.9, 158.3, 152.6, 134.4, 130.9 (2C), 130.3 (2C), 130.1, 128.1 (2C), 127.5, 127.3 (2C), 124.1, 121.2, 114.4 (2C), 113.8 (2C), 103.6, 55.5, 55.3.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[M + H]^+ C_{25}H_{21}O_4$  385.1440. Found 385.1446.

#### 4-(4-Fluorophenyl)-3,6-diphenyl-2H-pyran-2-one (3e)



Orange solid (267 mg, 78%).

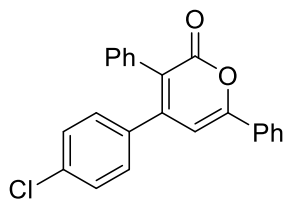
$^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.91 (dd,  $J = 6.7, 2.9$  Hz, 2H), 7.51 – 7.46 (m, 3H), 7.27 – 7.23 (m, 3H), 7.19 – 7.14 (m, 4H), 6.95 (t,  $J = 8.6$  Hz, 2H), 6.81 (s, 1H).

$^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  162.7 (d,  $J = 249.4$  Hz), 162.6, 158.5, 151.7, 133.8, 133.7, 131.3, 130.9, 130.8 (2C), 130.7 (d,  $J = 8.2$  Hz) (2C), 129.0 (2C), 128.1 (2C), 127.9, 125.6 (2C), 123.2, 115.6 (d,  $J = 21.6$  Hz) (2C), 104.7.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[M + H]^+ C_{23}H_{16}FO_2$  343.1134. Found 343.1139.

$^{19}F$  NMR (471 MHz, Chloroform- $d$ )  $\delta$  -111.72.

#### 4-(4-Chlorophenyl)-3,6-diphenyl-2H-pyran-2-one (3f)



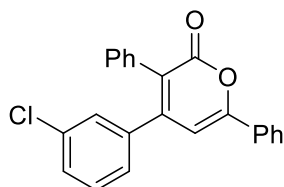
Yellow solid (261 mg, 73%).

$^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.90 (dd,  $J = 6.6, 3.0$  Hz, 2H), 7.52 – 7.45 (m, 3H), 7.27 – 7.21 (m, 5H), 7.19 (dd,  $J = 7.3, 2.4$  Hz, 2H), 7.11 (d,  $J = 8.5$  Hz, 2H), 6.79 (s, 1H).

$^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  162.4, 158.6, 151.4, 136.2, 134.9, 133.5, 131.3, 130.9, 130.8 (2C), 130.1 (2C), 129.0 (2C), 128.7 (2C), 128.2 (2C), 127.9, 125.6 (2C), 123.3, 104.5.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[M + H]^+ C_{23}H_{16}ClO_2$  359.0839. Found 359.0845.

#### 4-(3-Chlorophenyl)-3,6-diphenyl-2H-pyran-2-one (3g)



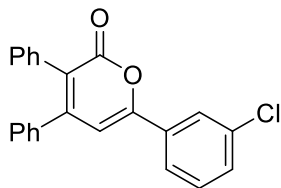
Yellow solid (250 mg, 70%).

$^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.91 (dd,  $J = 6.6, 3.0$  Hz, 2H), 7.51 – 7.45 (m, 3H), 7.27 – 7.17 (m, 7H), 7.15 (t,  $J = 7.9$  Hz, 1H), 6.98 (dt,  $J = 7.9, 1.2$  Hz, 1H), 6.79 (s, 1H).

$^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  162.4, 158.7, 151.2, 139.6, 134.5, 133.3, 131.2, 131.0, 130.8 (2C), 129.7, 129.0 (2C), 128.9, 128.6, 128.1 (2C), 128.0, 127.1, 125.7 (2C), 123.6, 104.4.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[M + H]^+ C_{23}H_{16}ClO_2$  359.0839. Found 359.0845.

**6-(3-Chlorophenyl)-3,4-diphenyl-2H-pyran-2-one (3h)**



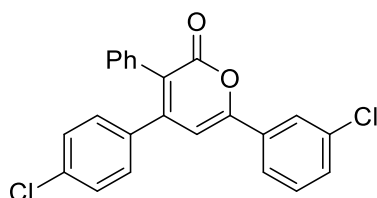
Orange solid (240 mg, 67%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (s, 1H), 7.79 (d,  $J = 7.3$  Hz, 1H), 7.47 – 7.38 (m, 2H), 7.31 – 7.13 (m, 10H), 6.84 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4, 156.6, 152.5, 137.6, 135.2, 133.6, 133.1, 130.8 (2C), 130.7, 130.3, 128.9, 128.7 (2C), 128.5 (2C), 128.0 (2C), 127.9, 125.6, 123.9, 123.6, 105.7.

HRMS (QTOF,  $\text{ESI}^+$ )  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{23}\text{H}_{16}\text{ClO}_2$  359.0839. Found 359.0845.

**6-(3-Chlorophenyl)-4-(4-chlorophenyl)-3-phenyl-2H-pyran-2-one (3i)**



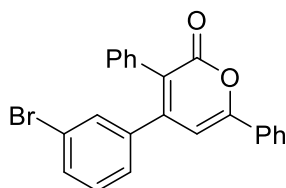
Orange solid (255 mg, 65%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (t,  $J = 1.9$  Hz, 1H), 7.81 (dt,  $J = 7.4, 1.7$  Hz, 1H), 7.50 – 7.41 (m, 2H), 7.32 – 7.26 (m, 5H), 7.21 (dd,  $J = 6.5, 3.2$  Hz, 2H), 7.13 (d,  $J = 8.5$  Hz, 2H), 6.81 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 156.9, 151.1, 135.9, 135.3, 135.1, 133.3, 133.0, 130.8 (2C), 130.7, 130.3, 130.1 (2C), 128.8 (2C), 128.2 (2C), 128.1, 125.7, 124.1, 123.7, 105.2.

HRMS (QTOF,  $\text{ESI}^+$ )  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{23}\text{H}_{15}\text{Cl}_2\text{O}_2$  393.0449. Found 393.0456.

**4-(3-Bromophenyl)-3,6-diphenyl-2H-pyran-2-one (3j)**



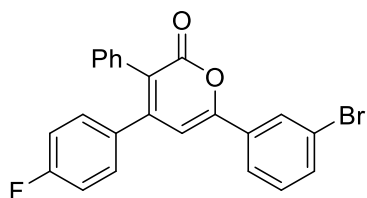
Yellow solid (261 mg, 65%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (dd,  $J = 6.9, 3.7$  Hz, 2H), 7.49 – 7.44 (m, 3H), 7.42 – 7.35 (m, 2H), 7.28 – 7.21 (m, 3H), 7.17 (dd,  $J = 7.3, 2.4$  Hz, 2H), 7.07 (t,  $J = 7.8$  Hz, 1H), 7.01 (dt,  $J = 7.9, 1.4$  Hz, 1H), 6.77 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4, 158.7, 151.1, 139.8, 133.3, 131.8, 131.5, 131.2, 131.0, 130.8 (2C), 129.9, 129.0 (2C), 128.2 (2C), 128.1, 127.6, 125.7 (2C), 123.6, 122.5, 104.4.

HRMS (QTOF,  $\text{ESI}^+$ )  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{23}\text{H}_{16}\text{BrO}_2$  403.0334. Found 403.0340.

**6-(3-Bromophenyl)-4-(4-fluorophenyl)-3-phenyl-2H-pyran-2-one (3k)**



Red brown solid (281 mg, 67%).

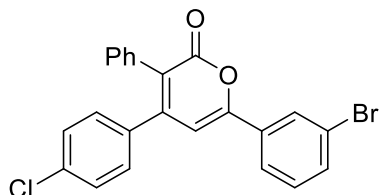
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (t,  $J = 1.8$  Hz, 1H), 7.86 (dt,  $J = 7.9, 1.4$  Hz, 1H), 7.62 (dt,  $J = 7.5, 1.7$  Hz, 1H), 7.38 (t,  $J = 8.0$  Hz, 1H), 7.32 – 7.25 (m, 3H), 7.23 – 7.15 (m, 4H), 6.98 (t,  $J = 8.6$  Hz, 2H), 6.82 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 (d,  $J = 249.9$  Hz), 162.2, 156.7, 151.3, 133.7, 133.5 (d,  $J = 3.3$  Hz), 133.4, 133.2, 130.8 (2C), 130.7 (d,  $J = 8.2$  Hz) (2C), 130.5, 128.5, 128.2 (2C), 128.0, 124.1, 124.0, 123.2, 115.7 (d,  $J = 21.6$  Hz) (2C), 105.4.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{23}\text{H}_{15}\text{BrFO}_2$  421.0239. Found 421.0245.

$^{19}\text{F}$  NMR (471 MHz, Chloroform- $d$ )  $\delta$  -111.41.

#### 6-(3-Bromophenyl)-4-(4-chlorophenyl)-3-phenyl-2H-pyran-2-one (3l)



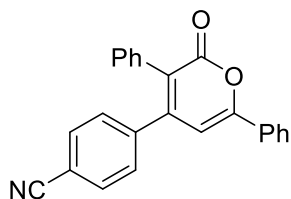
Orange solid (274 mg, 63%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (t,  $J = 1.8$  Hz, 1H), 7.85 (dt,  $J = 7.9, 1.3$  Hz, 1H), 7.63 (dt,  $J = 8.0, 1.8$  Hz, 1H), 7.38 (t,  $J = 8.0$  Hz, 1H), 7.33 – 7.25 (m, 5H), 7.21 (dd,  $J = 6.6, 2.9$  Hz, 2H), 7.13 (d,  $J = 8.5$  Hz, 2H), 6.81 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 156.8, 151.1, 135.9, 135.1, 133.7, 133.3, 133.2, 130.7 (2C), 130.5, 130.1 (2C), 128.8 (2C), 128.5, 128.2 (2C), 128.1, 124.12, 124.08, 123.3, 105.2.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{23}\text{H}_{15}\text{BrClO}_2$  436.9944. Found 436.9952.

#### 4-(2-Oxo-3,6-diphenyl-2H-pyran-4-yl)benzonitrile (3m)



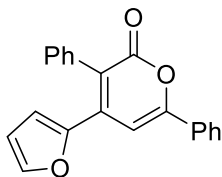
Yellow solid (251 mg, 72%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J = 6.8, 3.0$  Hz, 2H), 7.56 (d,  $J = 8.3$  Hz, 2H), 7.50 – 7.48 (m, 3H), 7.29 (d,  $J = 8.3$  Hz, 2H), 7.27 – 7.24 (m, 3H), 7.15 (dd,  $J = 7.5, 2.8$  Hz, 2H), 6.77 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 159.1, 150.6, 142.5, 132.9, 132.2 (2C), 131.2, 131.0, 130.8 (2C), 129.5 (2C), 129.1 (2C), 128.32, 128.30 (2C), 125.7 (2C), 124.0, 118.2, 112.5, 103.8.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{24}\text{H}_{15}\text{NO}_2$  350.1181. Found 350.1187.

#### 4-(Furan-2-yl)-3,6-diphenyl-2H-pyran-2-one (3n)



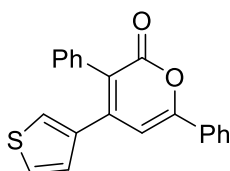
Yellow solid (182 mg, 58%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (dd,  $J = 7.2, 1.6$  Hz, 2H), 7.54 – 7.43 (m, 7H), 7.37 (s, 1H), 7.32 (dd,  $J = 6.7, 1.6$  Hz, 2H), 6.30 (dd,  $J = 3.4, 1.6$  Hz, 1H), 5.63 (d,  $J = 3.6$  Hz, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 158.5, 148.8, 144.3, 140.2, 135.0, 131.7, 130.7, 129.5 (2C), 129.3 (2C), 128.9 (2C), 128.6, 125.7 (2C), 119.3, 116.2, 112.8, 99.5.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{21}\text{H}_{15}\text{O}_3$  315.1021. Found 315.1026.

#### 3,6-Diphenyl-4-(thiophen-3-yl)-2H-pyran-2-one (3o)



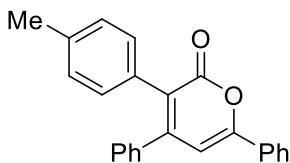
Yellow solid (254 mg, 77%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (dd,  $J = 6.6, 3.0$  Hz, 2H), 7.51 – 7.46 (m, 3H), 7.37 – 7.30 (m, 3H), 7.28 – 7.23 (m, 3H), 7.17 (dd,  $J = 5.1, 3.0$  Hz, 1H), 6.91 (s, 1H), 6.72 (dd,  $J = 5.1, 1.3$  Hz, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 158.3, 146.8, 138.1, 134.4, 131.4, 130.8, 130.5 (2C), 129.0 (2C), 128.4 (2C), 128.1, 127.9, 126.9, 125.7, 125.6 (2C), 122.3, 104.2.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{21}\text{H}_{14}\text{O}_2\text{S}$  331.0793. Found 331.0797.

#### 4,6-Diphenyl-3-(p-tolyl)-2H-pyran-2-one (3p)



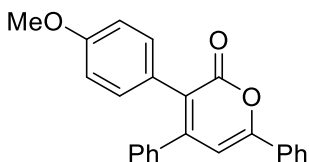
Yellow solid (270 mg, 80%) (1mmol scale).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J = 6.6, 2.9$  Hz, 2H), 7.50 – 7.44 (m, 3H), 7.31 – 7.25 (m, 3H), 7.18 (dd,  $J = 7.0, 2.7$  Hz, 2H), 7.09 (d,  $J = 7.9$  Hz, 2H), 7.04 (d,  $J = 8.1$  Hz, 2H), 6.83 (s, 1H), 2.30 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 158.1, 152.4, 138.1, 137.5, 131.5, 130.9, 130.8 (2C), 130.7, 129.0 (2C), 128.8 (2C), 128.7 (2C), 128.6, 128.4 (2C), 125.6 (2C), 123.3, 105.1, 21.3.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{24}\text{H}_{19}\text{O}_2$  339.1385. Found 339.1392.

#### 3-(4-Methoxyphenyl)-4,6-diphenyl-2H-pyran-2-one (3q)



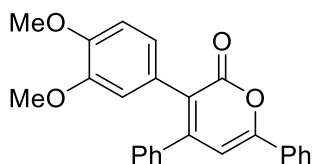
Yellow solid (209 mg, 59%) (1mmol scale)

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (dd,  $J = 6.6, 3.2$  Hz, 2H), 7.42 – 7.37 (m, 3H), 7.24 – 7.16 (m, 3H), 7.11 (dd,  $J = 6.6, 3.0$  Hz, 2H), 7.06 (d,  $J = 8.7$  Hz, 2H), 6.75 (s, 1H), 6.69 (d,  $J = 8.7$  Hz, 2H), 3.69 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.0, 159.0, 157.9, 152.1, 138.1, 132.2 (2C), 131.5, 130.6, 128.9 (2C), 128.7 (2C), 128.6, 128.4 (2C), 126.0, 125.5 (2C), 122.8, 113.5 (2C), 105.1, 55.2.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{24}\text{H}_{19}\text{O}_3$  355.1334. Found 355.1337.

### 3-(3,4-Dimethoxyphenyl)-4,6-diphenyl-2H-pyran-2-one (3r)



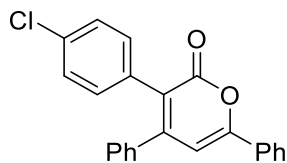
Yellow solid (211 mg, 55%) (1mmol scale)

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J = 6.5, 3.2$  Hz, 2H), 7.51 – 7.43 (m, 3H), 7.32 – 7.27 (m, 3H), 7.19 (dd,  $J = 6.7, 3.0$  Hz, 2H), 6.88 (dd,  $J = 8.3, 2.0$  Hz, 1H), 6.84 (s, 1H), 6.77 (d,  $J = 8.4$  Hz, 1H), 6.63 (d,  $J = 2.0$  Hz, 1H), 3.85 (s, 3H), 3.61 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8, 158.0, 152.3, 148.6, 148.2, 138.2, 131.4, 130.7, 129.0 (2C), 128.7, 128.6 (2C), 128.5 (2C), 126.1, 125.6 (2C), 123.8, 122.8, 114.3, 110.7, 105.0, 55.8, 55.7.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{25}\text{H}_{21}\text{O}_4$  385.1440. Found 385.1448.

### 3-(4-Chlorophenyl)-4,6-diphenyl-2H-pyran-2-one (3s)



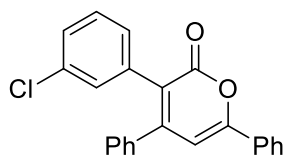
Yellow solid (240 mg, 67%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (dd,  $J = 6.7, 3.1$  Hz, 2H), 7.50 – 7.46 (m, 3H), 7.34 – 7.27 (m, 3H), 7.21 (d,  $J = 8.5$  Hz, 2H), 7.17 (dd,  $J = 7.8, 2.0$  Hz, 2H), 7.14 (d,  $J = 8.5$  Hz, 2H), 6.84 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5, 158.6, 153.2, 137.5, 133.7, 132.3 (2C), 132.2, 131.2, 130.9, 129.1 (2C), 129.0, 128.6 (4C), 128.3 (2C), 125.7 (2C), 121.8, 105.0.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{23}\text{H}_{16}\text{ClO}_2$  359.0839. Found 359.0845.

### 3-(3-Chlorophenyl)-4,6-diphenyl-2H-pyran-2-one (3t)



Yellow solid (229 mg, 64%).

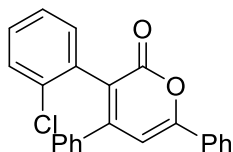
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (dd,  $J = 6.7, 3.1$  Hz, 2H), 7.49 – 7.47 (m, 3H), 7.34 – 7.27 (m, 3H), 7.24 (t,  $J = 1.9$  Hz, 1H), 7.21 – 7.13 (m, 4H), 7.05 (dt,  $J = 7.7, 1.5$  Hz, 1H), 6.84 (s, 1H).



$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 158.8, 153.5, 137.4, 135.7, 133.8, 131.2, 131.1, 131.0, 129.2 (2C), 129.1, 129.0 (2C), 128.7 (2C), 128.6 (2C), 127.9, 125.7 (2C), 121.7, 104.9.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{23}\text{H}_{16}\text{ClO}_2$  359.0839. Found 359.0845.

### 3-(2-Chlorophenyl)-4,6-diphenyl-2H-pyran-2-one (3u)



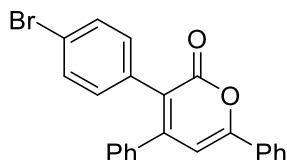
Yellow solid (204 mg, 57%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (dd,  $J = 6.8, 3.0$  Hz, 2H), 7.50 – 7.46 (m, 3H), 7.38 (d,  $J = 8.1$  Hz, 1H), 7.29 – 7.18 (m, 6H), 7.14 (t,  $J = 7.5$  Hz, 1H), 7.07 (dd,  $J = 7.6, 1.7$  Hz, 1H), 6.87 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 159.2, 154.3, 137.2, 134.8, 133.5, 132.3, 131.3, 131.0, 129.6, 129.5, 129.1, 129.0 (2C), 128.4 (2C), 128.0 (2C), 126.7, 125.8 (2C), 121.4, 104.3.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{23}\text{H}_{16}\text{ClO}_2$  359.0839. Found 359.0845.

### 3-(4-Bromophenyl)-4,6-diphenyl-2H-pyran-2-one (3v)



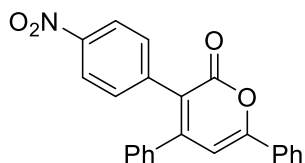
Yellow solid (277 mg, 69%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J = 6.8, 3.0$  Hz, 2H), 7.50 – 7.45 (m, 3H), 7.36 (d,  $J = 8.5$  Hz, 2H), 7.34 – 7.26 (m, 3H), 7.17 (dd,  $J = 7.8, 1.8$  Hz, 2H), 7.08 (d,  $J = 8.5$  Hz, 2H), 6.84 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4, 158.6, 153.2, 137.5, 132.8 (2C), 132.6 (2C), 131.2 (2C), 131.0, 129.1 (2C), 129.0, 128.7 (2C), 128.6 (2C), 125.7 (2C), 122.0, 121.9, 105.0.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{23}\text{H}_{16}\text{BrO}_2$  403.0334. Found 403.0338.

### 3-(4-Nitrophenyl)-4,6-diphenyl-2H-pyran-2-one (3w)



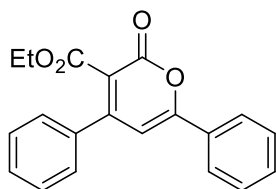
Red brown (229 mg, 62%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J = 8.7$  Hz, 2H), 7.92 (dd,  $J = 6.6, 3.2$  Hz, 2H), 7.55 – 7.46 (m, 3H), 7.39 (d,  $J = 8.8$  Hz, 2H), 7.37 – 7.27 (m, 3H), 7.16 (d,  $J = 7.0$  Hz, 2H), 6.88 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9, 159.6, 154.5, 147.0, 141.1, 137.0, 132.1 (2C), 131.4, 131.0, 129.5, 129.1 (2C), 128.9 (2C), 128.6 (2C), 125.8 (2C), 123.2 (2C), 120.7, 104.9.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+ \text{C}_{23}\text{H}_{16}\text{NO}_4$  370.1079. Found 370.1085.

### Ethyl 2-oxo-4,6-diphenyl-2H-pyran-3-carboxylate (5a)



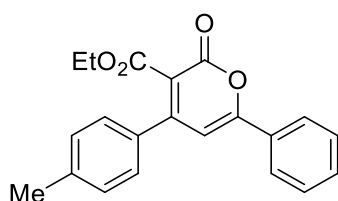
Yellow solid (224 mg, 70%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J = 6.4, 1.3$  Hz, 2H), 7.51 – 7.44 (m, 8H), 6.78 (s, 1H), 4.16 (q,  $J = 7.1$  Hz, 2H), 1.05 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8, 160.7, 159.4, 155.5, 136.4, 131.6, 130.8, 130.2, 129.1 (2C), 128.9 (2C), 127.2 (2C), 126.0 (2C), 116.7, 103.5, 61.8, 13.7.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{20}\text{H}_{17}\text{O}_4$  321.1127. Found 321.1132.

**Ethyl 2-oxo-6-phenyl-4-(p-tolyl)-2H-pyran-3-carboxylate (5b)**



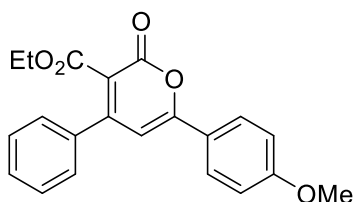
Yellow solid (227 mg, 68%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J = 6.6, 1.8$  Hz, 2H), 7.54 – 7.45 (m, 3H), 7.39 (d,  $J = 7.6$  Hz, 2H), 7.29 (d,  $J = 7.6$  Hz, 2H), 6.79 (s, 1H), 4.21 (q,  $J = 7.2$  Hz, 2H), 2.43 (s, 3H), 1.13 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 160.4, 159.5, 155.3, 140.7, 133.4, 131.5, 130.8, 129.6 (2C), 129.1 (2C), 127.3 (2C), 126.0 (2C), 116.3, 103.6, 61.8, 21.4, 13.8.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{21}\text{H}_{19}\text{O}_4$  335.1283. Found 335.1286.

**Ethyl 6-(4-methoxyphenyl)-2-oxo-4-phenyl-2H-pyran-3-carboxylate (5c)**



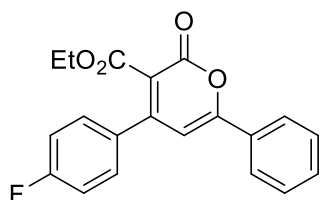
Yellow solid (227 mg, 65%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.9$  Hz, 2H), 7.49 – 7.42 (m, 5H), 6.97 (d,  $J = 8.9$  Hz, 2H), 6.66 (s, 1H), 4.14 (q,  $J = 7.2$  Hz, 2H), 3.87 (s, 3H), 1.03 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0, 162.4, 160.9, 159.5, 156.1, 136.8, 130.0, 128.8 (2C), 127.9 (2C), 127.2 (2C), 123.3, 115.3, 114.5 (2C), 102.1, 61.6, 55.5, 13.7.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{21}\text{H}_{19}\text{O}_5$  351.1232. Found 351.1238.

**Ethyl 4-(4-fluorophenyl)-2-oxo-6-phenyl-2H-pyran-3-carboxylate (5d)**



Yellow solid (220 mg, 65%).

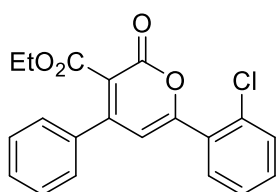
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J = 6.5, 1.8$  Hz, 2H), 7.53 – 7.45 (m, 5H), 7.16 (t,  $J = 8.6$  Hz, 2H), 6.73 (s, 1H), 4.19 (q,  $J = 7.2$  Hz, 2H), 1.11 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 163.8 (d,  $J = 251.3$  Hz), 160.8, 159.2, 154.3, 132.4, 131.7, 130.7, 129.4 (d,  $J = 8.6$  Hz) (2C), 129.1 (2C), 126.1 (2C), 116.7, 116.1 (d,  $J = 21.9$  Hz) (2C), 103.3, 61.9, 13.8.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{20}\text{H}_{16}\text{FO}_4$  339.1033. Found 339.1038.

$^{19}\text{F}$  NMR (471 MHz, Chloroform- $d$ )  $\delta$  -109.77.

**Ethyl 6-(2-chlorophenyl)-2-oxo-4-phenyl-2H-pyran-3-carboxylate (5e)**



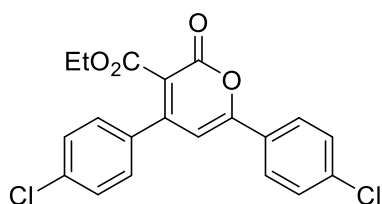
Yellow solid (212 mg, 60%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (dd,  $J = 7.3, 2.2$  Hz, 1H), 7.51 – 7.46 (m, 6H), 7.43 – 7.39 (m, 2H), 6.89 (s, 1H), 4.19 (q,  $J = 7.1$  Hz, 2H), 1.09 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 159.4, 158.2, 154.5, 136.0, 132.3, 131.7, 131.0, 130.8, 130.5, 130.3, 128.9 (2C), 127.4 (2C), 127.3, 117.6, 109.2, 61.9, 13.7.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{20}\text{H}_{16}\text{ClO}_4$  355.0737. Found 355.0731.

**Ethyl 4,6-bis(4-chlorophenyl)-2-oxo-2H-pyran-3-carboxylate (5f)**



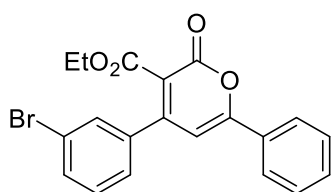
Yellow solid (260 mg, 67%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.7$  Hz, 2H), 7.50 – 7.46 (m, 4H), 7.43 (d,  $J = 8.6$  Hz, 2H), 6.72 (s, 1H), 4.22 (q,  $J = 7.1$  Hz, 2H), 1.14 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 159.7, 158.8, 154.0, 138.0, 136.6, 134.6, 129.5 (2C), 129.2 (2C), 129.1, 128.6 (2C), 127.3 (2C), 117.1, 103.3, 62.0, 13.8.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{20}\text{H}_{15}\text{Cl}_2\text{O}_4$  389.0347. Found 389.0354.

**Ethyl 4-(3-bromophenyl)-2-oxo-6-phenyl-2H-pyran-3-carboxylate (5g)**



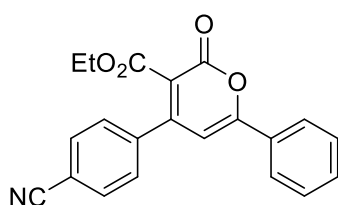
Yellow solid (251 mg, 63%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (dd,  $J = 7.6, 1.7$  Hz, 2H), 7.63 – 7.58 (m, 2H), 7.54 – 7.44 (m, 3H), 7.39 (dt,  $J = 7.8, 1.4$  Hz, 1H), 7.34 (t,  $J = 8.1$  Hz, 1H), 6.72 (s, 1H), 4.20 (q,  $J = 7.1$  Hz, 2H), 1.11 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 161.1, 159.0, 153.8, 138.3, 133.1, 131.8, 130.6, 130.4, 130.2, 129.2 (2C), 126.1 (2C), 125.9, 122.9, 117.0, 103.0, 62.0, 13.8.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{20}\text{H}_{16}\text{BrO}_4$  399.0232. Found 399.0238.

#### Ethyl 4-(4-cyanophenyl)-2-oxo-6-phenyl-2H-pyran-3-carboxylate (5h)



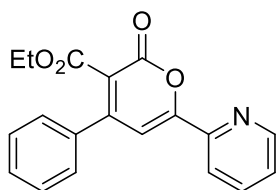
Yellow solid (231mg, 67%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (dd,  $J = 6.9, 1.5$  Hz, 2H), 7.77 (d,  $J = 8.4$  Hz, 2H), 7.57 (d,  $J = 8.3$  Hz, 2H), 7.54 – 7.47 (m, 3H), 6.69 (s, 1H), 4.17 (q,  $J = 7.2$  Hz, 2H), 1.09 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 161.6, 158.6, 153.7, 141.0, 132.6 (2C), 132.0, 130.4, 129.2 (2C), 128.1 (2C), 126.1 (2C), 117.9, 117.1, 113.9, 102.6, 62.1, 13.8.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{21}\text{H}_{16}\text{NO}_4$  346.1079. Found 346.1086.

#### Ethyl 2-oxo-4-phenyl-6-(pyridin-2-yl)-2H-pyran-3-carboxylate (5i)



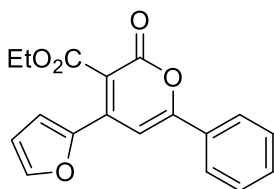
Yellow solid (173 mg, 54%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62 (dd,  $J = 4.9, 1.4$  Hz, 1H), 7.77 – 7.67 (m, 2H), 7.54 (s, 1H), 7.52 – 7.49 (m, 2H), 7.46 – 7.36 (m, 3H), 7.25 – 7.21 (m, 1H), 4.25 (q,  $J = 7.1$  Hz, 2H), 1.26 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 151.5, 149.9, 149.1, 148.1, 136.9, 135.8 (2C), 129.2 (2C), 128.4, 128.2, 128.0, 127.8 (2C), 123.1, 119.2, 61.0, 14.1.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{19}\text{H}_{16}\text{NO}_4$  322.1079. Found 322.1085.

#### Ethyl 4-(furan-2-yl)-2-oxo-6-phenyl-2H-pyran-3-carboxylate (5j)



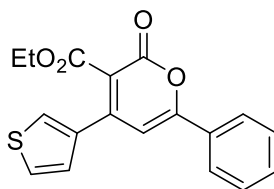
Yellow solid (161 mg, 52%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J = 7.6, 2.3$  Hz, 2H), 7.64 (d,  $J = 1.8$  Hz, 1H), 7.51 – 7.45 (m, 3H), 7.04 (d,  $J = 3.6$  Hz, 1H), 7.00 (s, 1H), 6.61 (dd,  $J = 3.6, 1.8$  Hz, 1H), 4.45 (q,  $J = 7.2$  Hz, 2H), 1.39 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 160.3, 160.0, 147.8, 146.3, 139.4, 131.4, 131.0, 129.1 (2C), 125.9 (2C), 115.6, 113.1, 111.8, 98.5, 62.3, 14.1.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{18}\text{H}_{15}\text{O}_5$  311.0919. Found 311.0924.

**Ethyl 2-oxo-6-phenyl-4-(thiophen-3-yl)-2H-pyran-3-carboxylate (5k)**



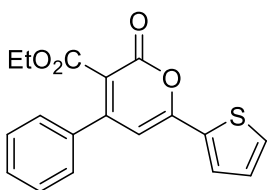
Red brown solid (196 mg, 60%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (dd,  $J = 7.9, 1.8$  Hz, 2H), 7.68 (dd,  $J = 3.0, 1.3$  Hz, 1H), 7.53 – 7.38 (m, 4H), 7.27 (dd,  $J = 5.1, 1.3$  Hz, 1H), 6.82 (s, 1H), 4.29 (q,  $J = 7.1$  Hz, 2H), 1.22 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 160.4, 159.7, 148.5, 136.5, 131.5, 130.8, 129.1 (2C), 127.2, 127.0, 126.7, 126.0 (2C), 115.8, 102.9, 62.1, 13.9.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{18}\text{H}_{15}\text{O}_4\text{S}$  327.0691. Found 327.0674.

**Ethyl 2-oxo-4-phenyl-6-(thiophen-2-yl)-2H-pyran-3-carboxylate (5l)**



Yellow solid (202 mg, 62%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (dd,  $J = 3.8, 1.2$  Hz, 1H), 7.52 (dd,  $J = 5.0, 1.2$  Hz, 1H), 7.50 – 7.41 (m, 5H), 7.14 (dd,  $J = 5.0, 3.8$  Hz, 1H), 6.59 (s, 1H), 4.14 (q,  $J = 7.1$  Hz, 2H), 1.03 (t,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8, 158.8, 156.3, 155.8, 136.4, 134.5, 130.2 (2C), 128.9 (2C), 128.7, 128.6, 127.2 (2C), 115.8, 102.5, 61.7, 13.7.

HRMS (QTOF, ESI+)  $m/z$  calculated for  $[\text{M} + \text{H}]^+$   $\text{C}_{18}\text{H}_{15}\text{O}_4\text{S}$  327.0691. Found 327.0674.

## Crystallographic data collection, structure determination and refinement

Thin platelet crystals of 4,6-diphenyl-3-(*p*-tolyl)-2*H*-pyran-2-one **3p** grew in an NMR tube filled with CDCl<sub>3</sub>. X-ray diffraction data were recorded from a single platelet at room temperature using a RIGAKU diffractometer comprising of a MM007 HF rotating-anode generator, which delivered copper radiation through Osmic CMF confocal optics, and a Rapid II curved Image Plate detector. The data was then integrated and scaled using *Fs\_process*<sup>[1]</sup> software under the *CrystalClear 2.0*<sup>[2]</sup> suite and absorption correction was applied through multi-scan *Abacor*.<sup>[2]</sup> Since the diffracted intensities fell beyond the atomic resolution limit, the reduced data set was truncated at  $\sin\theta/\lambda = 0.538$  (0.93Å). The structure was readily solved by intrinsic phasing methods (*SHELXT* program),<sup>[3]</sup> despite the Rint value being relatively high (around 12%). The structure was then refined using full-matrix least-squares methods on  $F^2$  with *SHELXL*,<sup>[5]</sup> achieving convergence with  $R1 > 7\%$ , and no evidence of twinning. Displacement parameters for all non-hydrogen (26) atoms, present inside the asymmetric unit (asu) of the monoclinic cell were refined anisotropically. Aromatic H atoms were positioned geometrically and refined with  $U_{iso}$  set to  $1.2U_{eq}(C)$  of the parent carbon atom. The methyl group was refined as an idealized rigid group that was allowed to rotate but not tip (AFIX 137), and  $U(H)$  values were fixed at  $1.5U_{eq}(C)$ . The structure of is shown in figure S1. The dihedral angles of the three aromatic rings substituted at the pyrone moiety are as follows 43.2° with the tolyl group at C1, and 54.4° and 19.4° for the phenyl groups at C2 and C4, respectively. The molecules are arranged pairwise in a head-to-tail fashion\* around an inversion centre to promote edge-to-face intermolecular interactions between the tolyl group at C1 and the opposite phenyl group at C4, the pyrone group being shifted face-to-face with a 5Å separation between centroids. \*Their arrangement is likely to reduce the electrostatic energy due to the dipole moment lying along the long molecular axis.<sup>[10]</sup> They are stacked in a herringbone fashion along the *a*-axis (Figure S2).

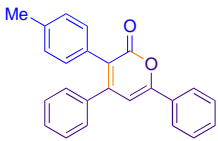
The overlays on the pyrone moiety of our structure and the nine hits which are substituted by three phenyl groups resulting from a search in the CSD<sup>[6]</sup> are displayed in figure S3.

Crystal data, data collection and structure refinement details are summarized in Table 1. CCDC 2311393 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

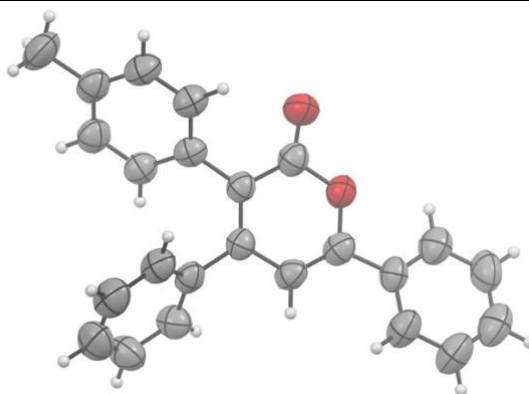
## References

- 1 Rigaku - Higashi T. (1998) *FS Process*, Rigaku Corporation, Tokyo, Japan.
- 2 Rigaku. (2009) *CrystalClear-SM Expert 2.0 r4* Rigaku Corporation, Tokyo, Japan.
- 3 Rigaku - Higashi T. (1998) *Abacor*, Rigaku Corporation, Tokyo, Japan.
- 4 Sheldrick, G. M. (2015). *Acta Crystallogr.*, **C71**, 3-8.
- 5 Sheldrick, G. M. (2015). *Acta Crystallogr.*, **A71**, 3-8.
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- 7 Chen, L., Li, F., Yang, Q., Ye, Y-F., Yang, W-W., Wang, Y-B. (2023) *J. Org. Chem.*, **88**, 5, 3079–3088.
- 8 Yata, T., Kita, Y., Nishimoto, Y., Yasuda M. (2019) *J. Org. Chem.*, **84**, 21, 14330–14341.
- 9 Keisuke, H., Satoshi, M., Mitsuo, K. (2001) *Chemistry Letters*, 30:1, 8-9.
- 10 Hirano, K., Minakata, S., Komatsu, M., Mizuguchi, J. (2002) *J. Phys. Chem. A*, **106**, 19, 4868–4871.
- 11 Zhou, P., Yang, W-T, Rahman, A. Ur, Li, G., Jiang, B. (2020) *J. Org. Chem.*, **85**, 2, 360–366

**Table 1** Crystal data, data collection and structure refinement details for the pyrone **3p**

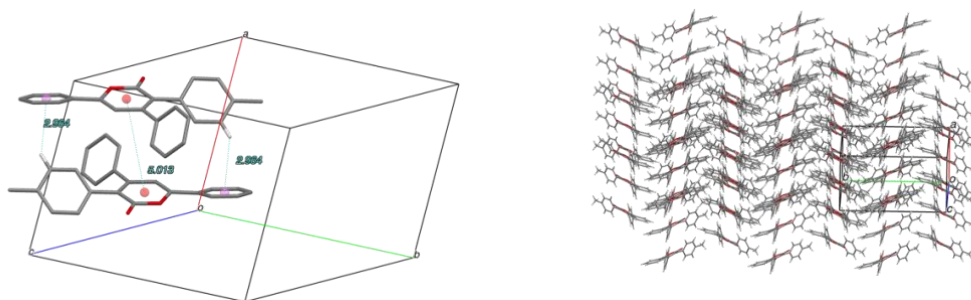
Compound <b>3p</b>	4,6-diphenyl-3-( <i>p</i> -tolyl)-2 <i>H</i> -pyran-2-one
	
Empirical formula	C <sub>24</sub> H <sub>18</sub> O <sub>2</sub>
Formula weight	338.38
Temperature (K)	293(2)
Wavelength (Å)	1.54187
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> /n
Unit cell dimensions   (Å)    (°)	9.459(4) 18.500(7) 11.372(4) 114.575(12)
Volume (Å <sup>3</sup> )	1809.7(12)
Z,	48,
Calculated density (Mg/m <sup>3</sup> )	1.242
Absorption coefficient (mm <sup>-1</sup> )	0.614
F(000)	712
Crystal size (mm)	0.25 x 0.16 x 0.03
θ range for data collection (°)	7.030 to 55.984
Limiting indices	-10 ≤ h ≤ 10, -18 ≤ k ≤ 19, -12 ≤ l ≤ 12
Reflections collected / unique	14152 / 2319
[R(int)]	0.127
Completeness to θ <sub>full</sub> (%)	98.5
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission		1.000 and 0.608
Refinement method		Full-matrix least-squares on $F^2$
Data / restraints / parameters		2317 / 0 / 236
Goodness-of-fit on $F^2$		1.023
Final R indices	R1	0.0640
$[I > 2\sigma(I)]$	wR2	0.1492
R indices	R1	0.0944,
(all data)	wR2	0.1895
Largest $\Delta$ peak and hole ( $e.\text{\AA}^{-3}$ )		0.213 and -0.237
CCDC deposit number		2311393



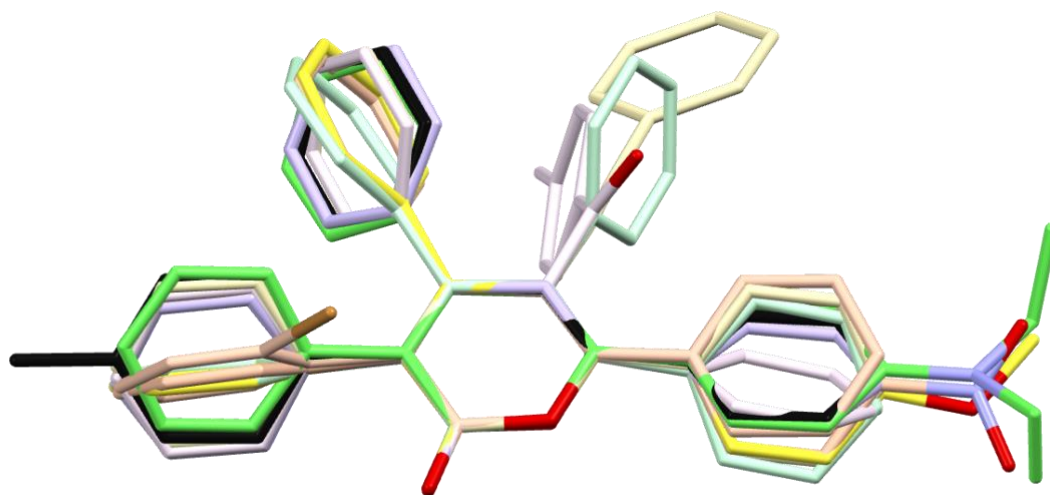
**Figure S1**

Ortep view of the structure of the 4,6-diphenyl-3-(*p*-tolyl)-2H-pyran-2-one **3p** with the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.



**Figure S2** Partial views of the crystal packing (a) showing the pairwise molecular interactions and (b) down the *ac* direction showing the herring-bone molecular assembly.

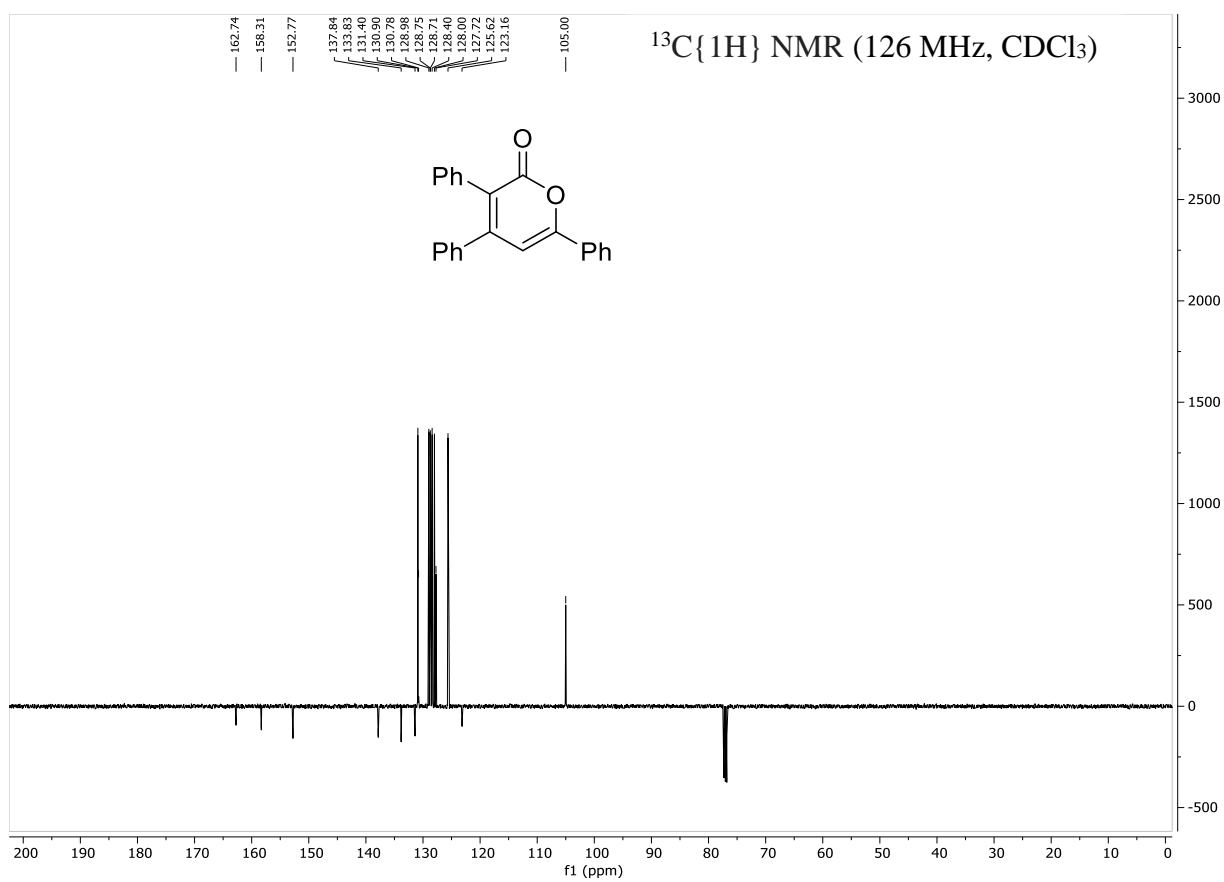
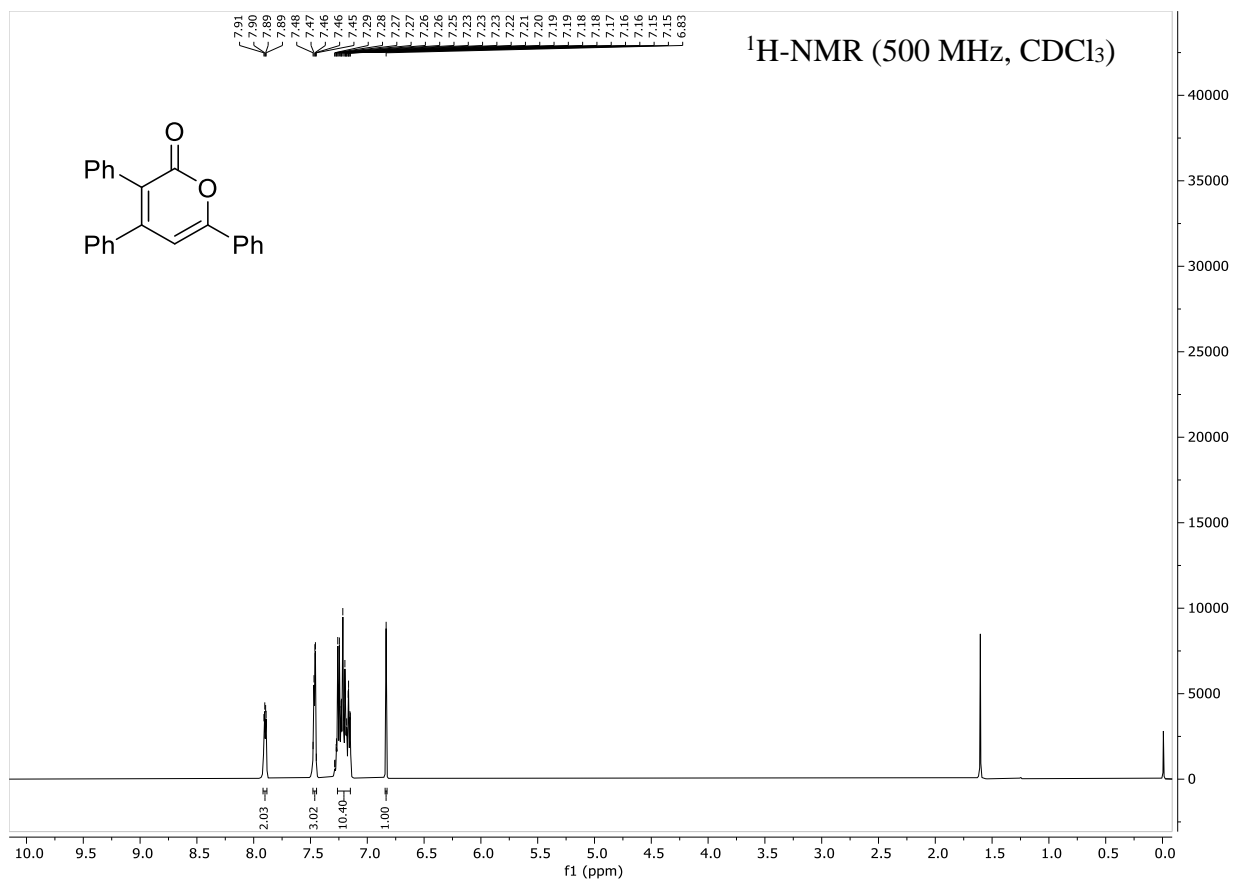




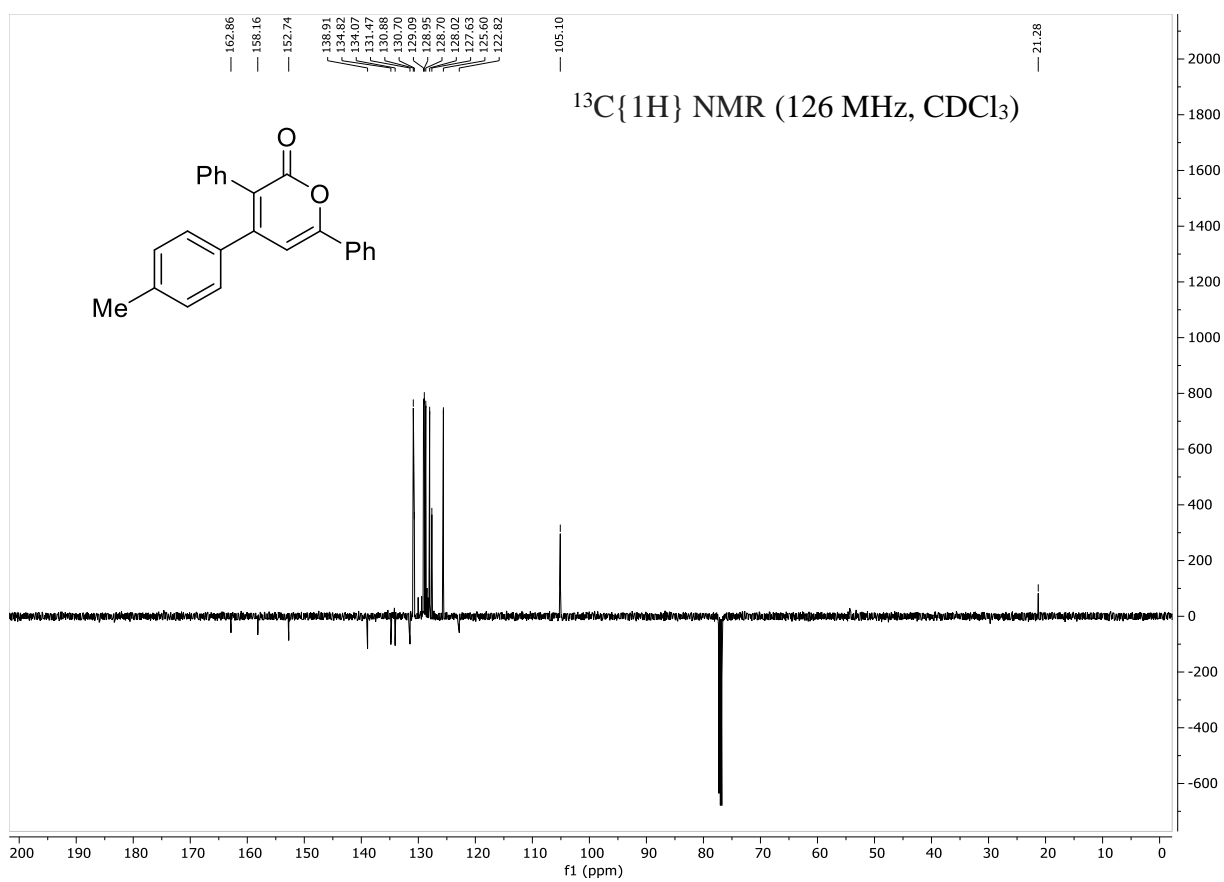
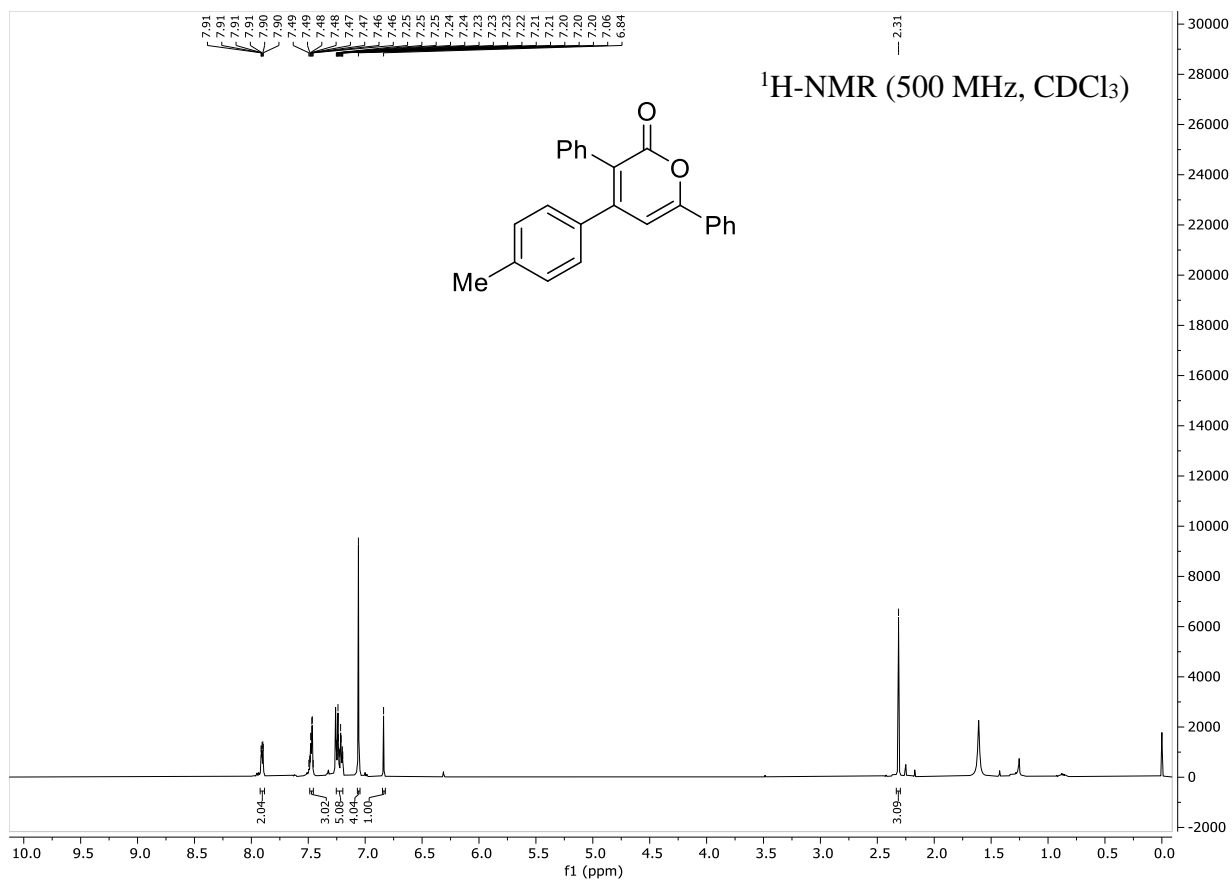
**Figure S3**

Overlay between the structure (carbons in black) and CSD Refcode WEWGOY<sup>[7]</sup> (in cyan) GOVVEV (in green water) / GOVVIZ (in white) / GOVVOF (in pale yellow),<sup>[8]</sup> MOKCAQ (in violin),<sup>[9]</sup> QADWOI (in salmon) / QADWUO (in green),<sup>[10]</sup> and XOQKUJ (in yellow).<sup>[11]</sup>

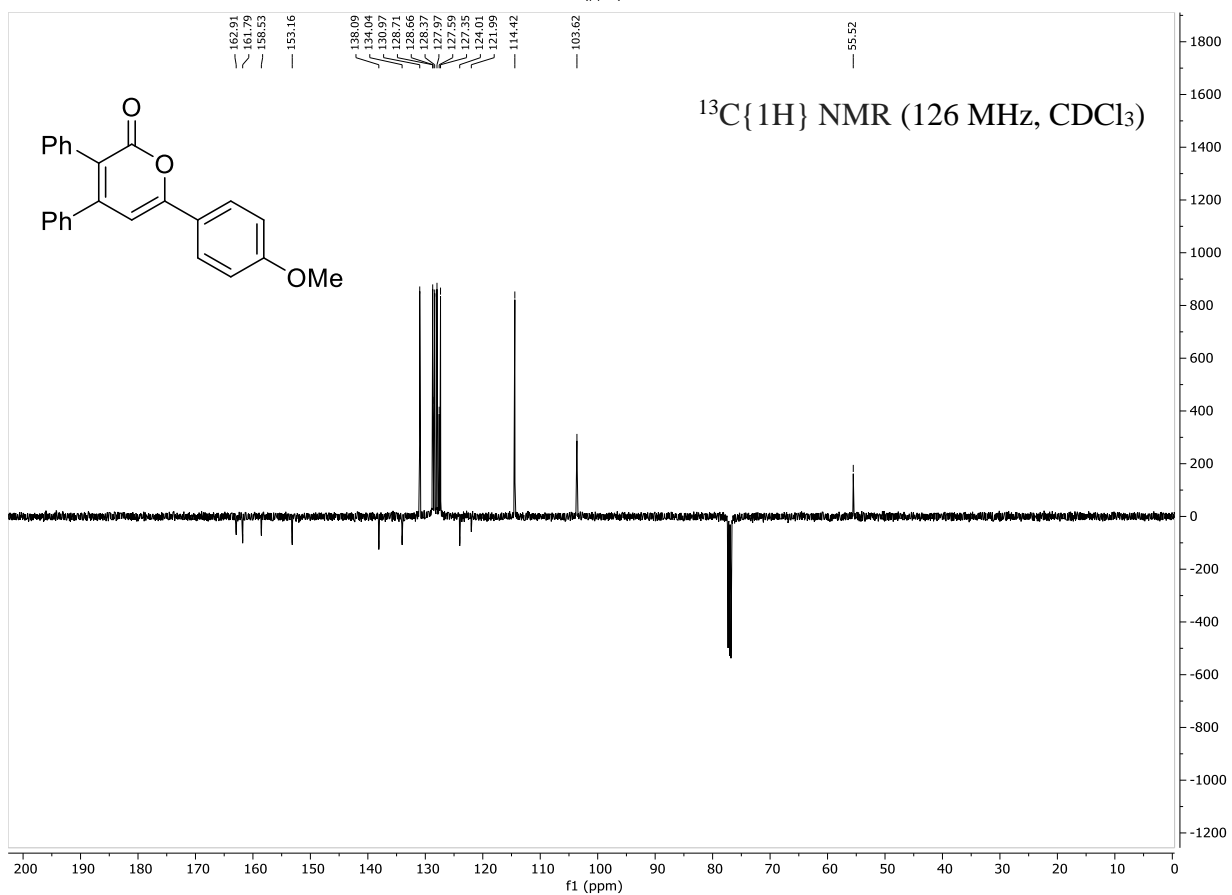
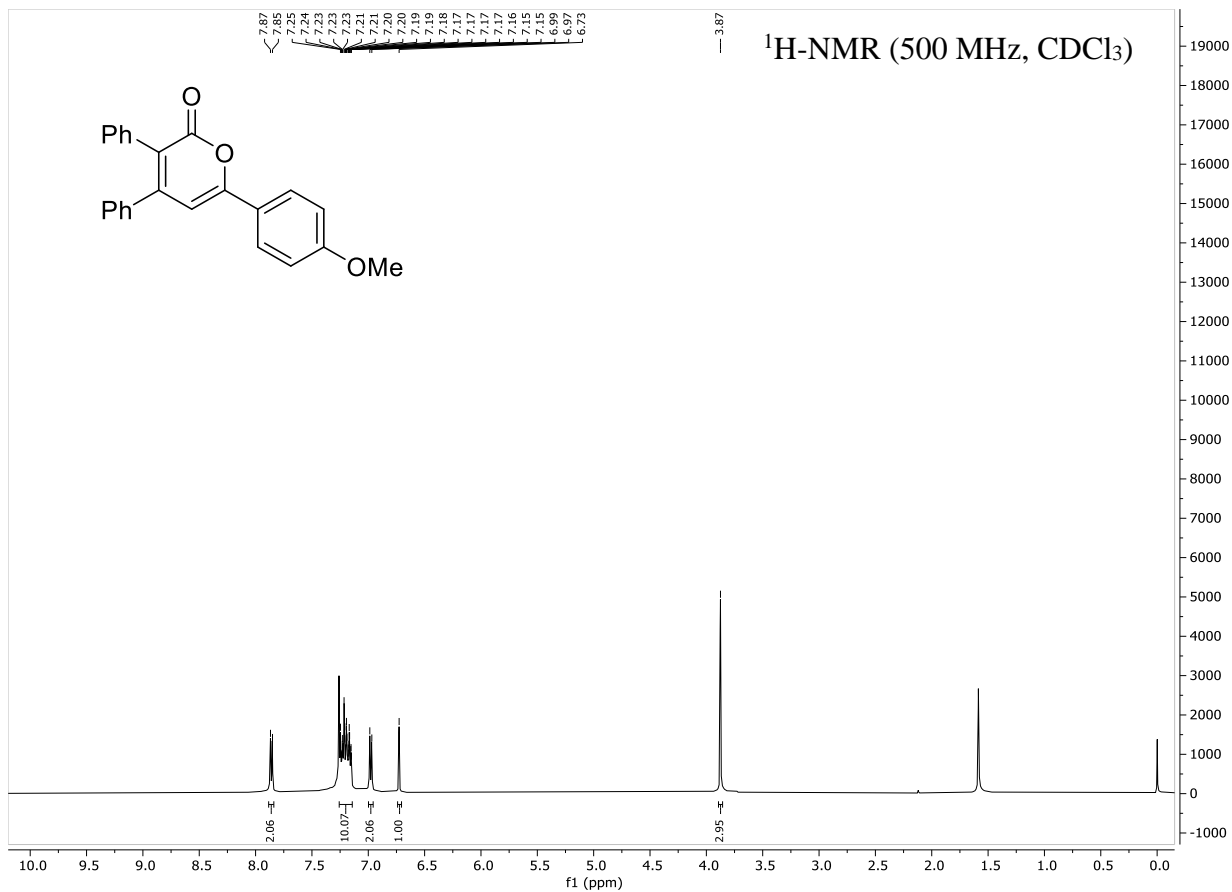
### 3,4,6-Triphenyl-2H-pyran-2-one (3a)



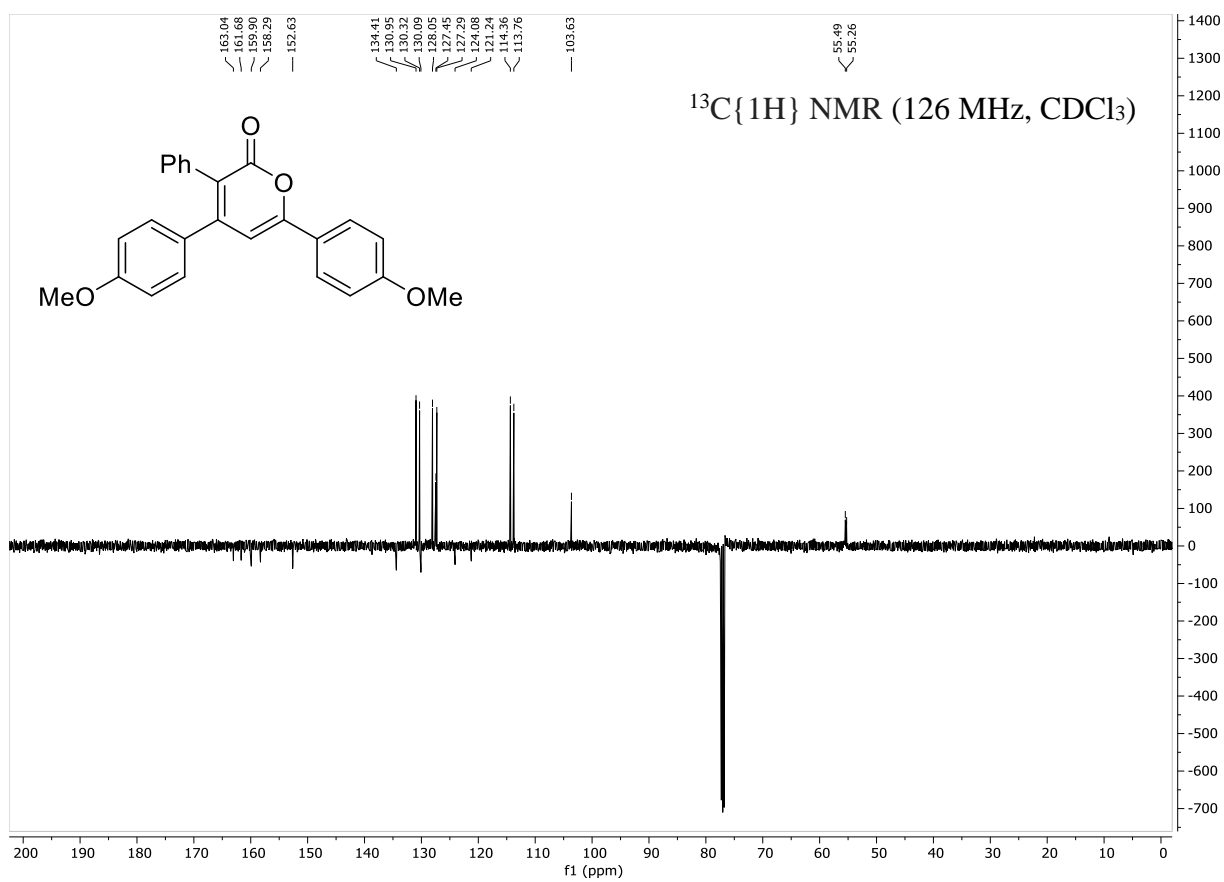
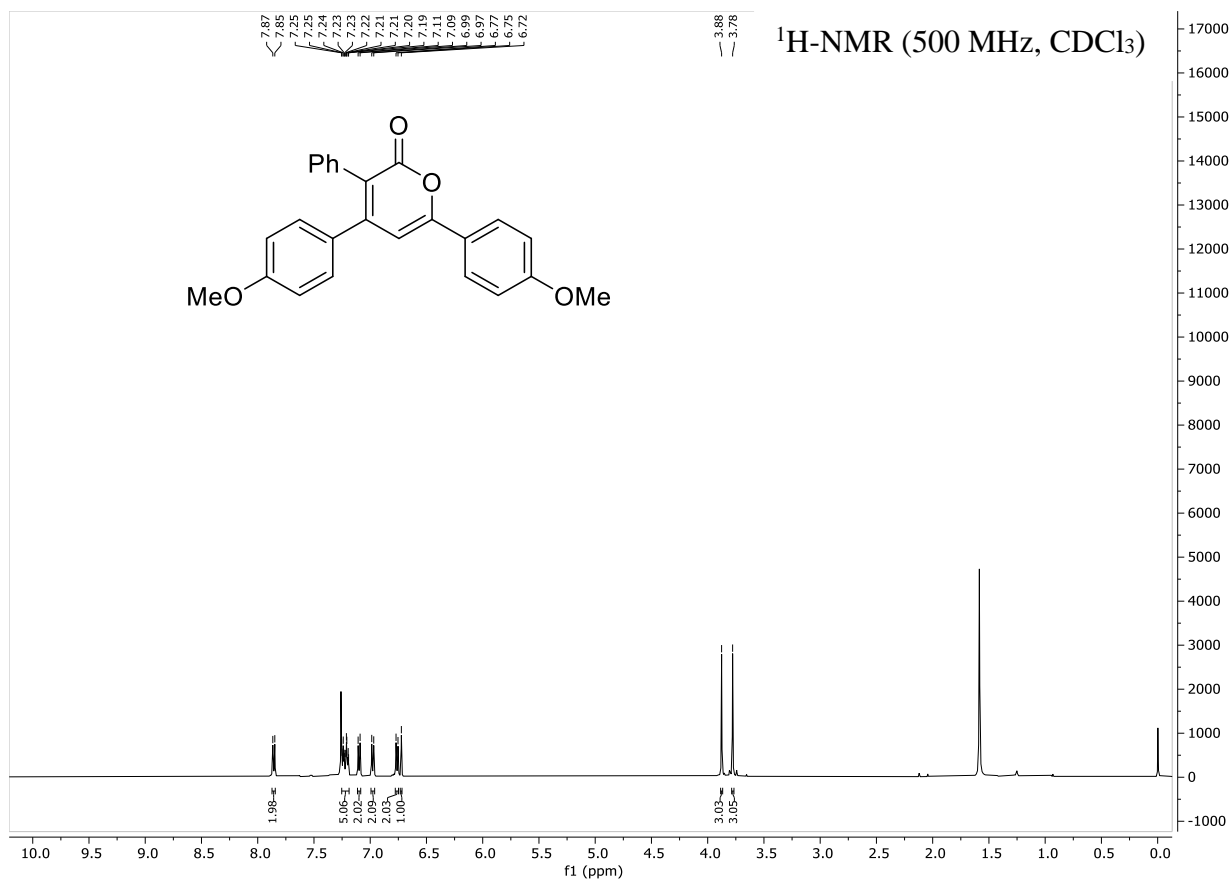
### 3,6-Diphenyl-4-(p-tolyl)-2H-pyran-2-one (3b)



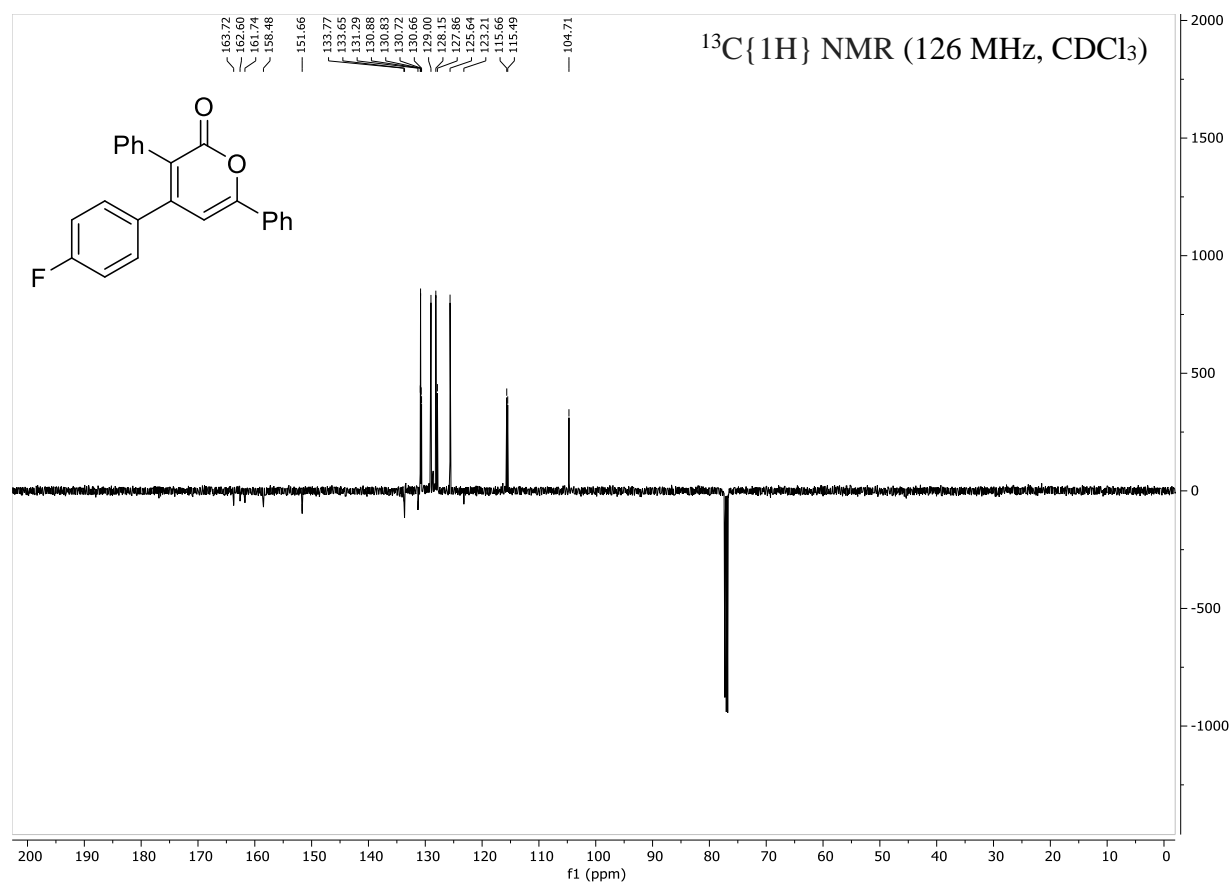
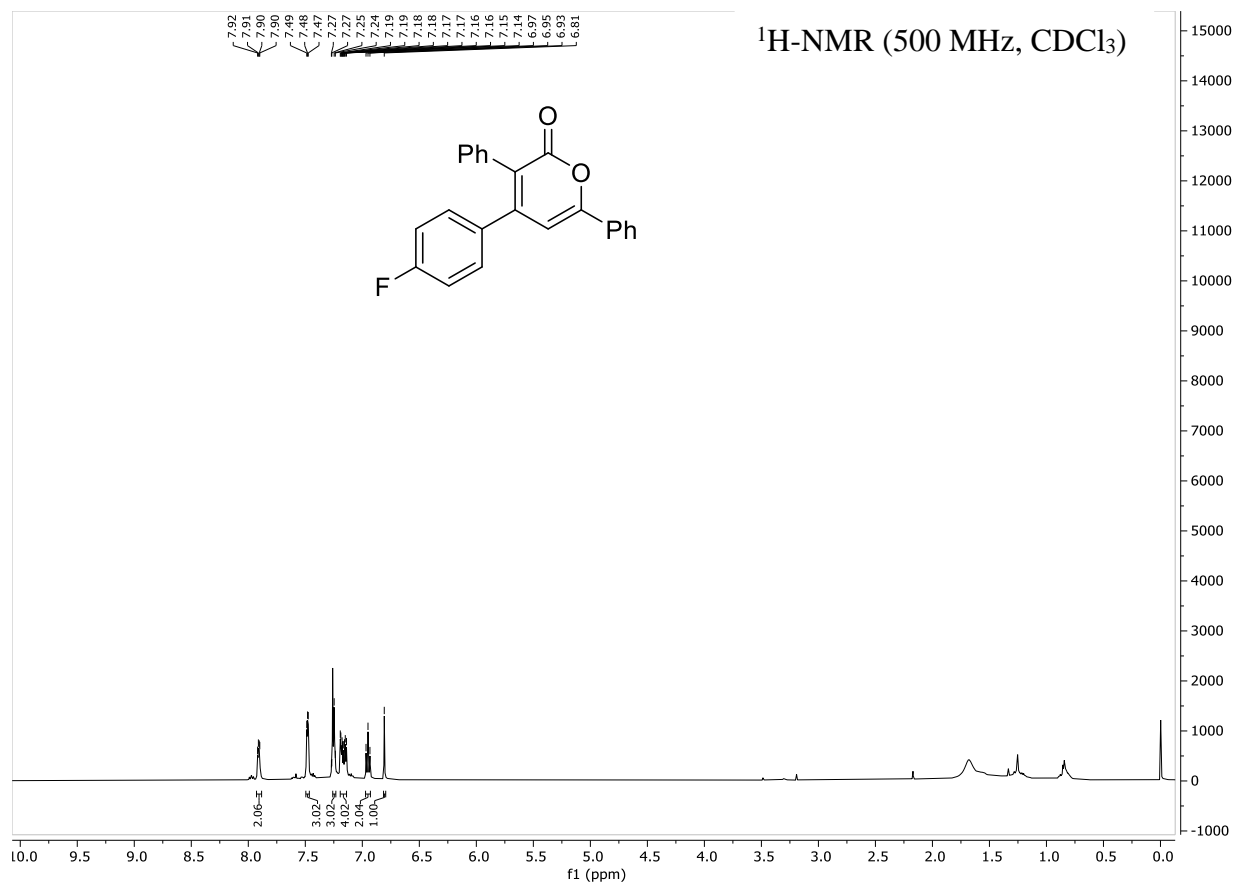
6-(4-Methoxyphenyl)-3,4-diphenyl-2H-pyran-2-one (3c)



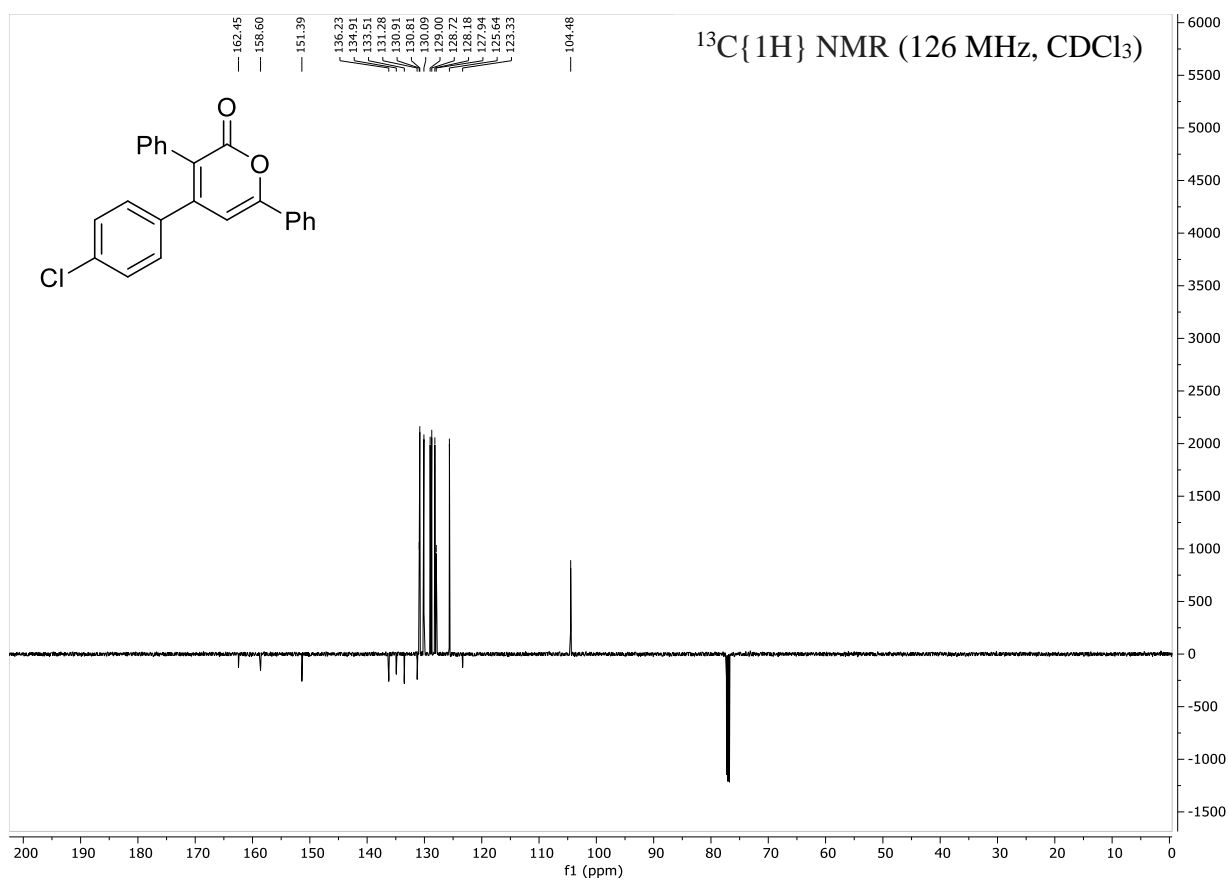
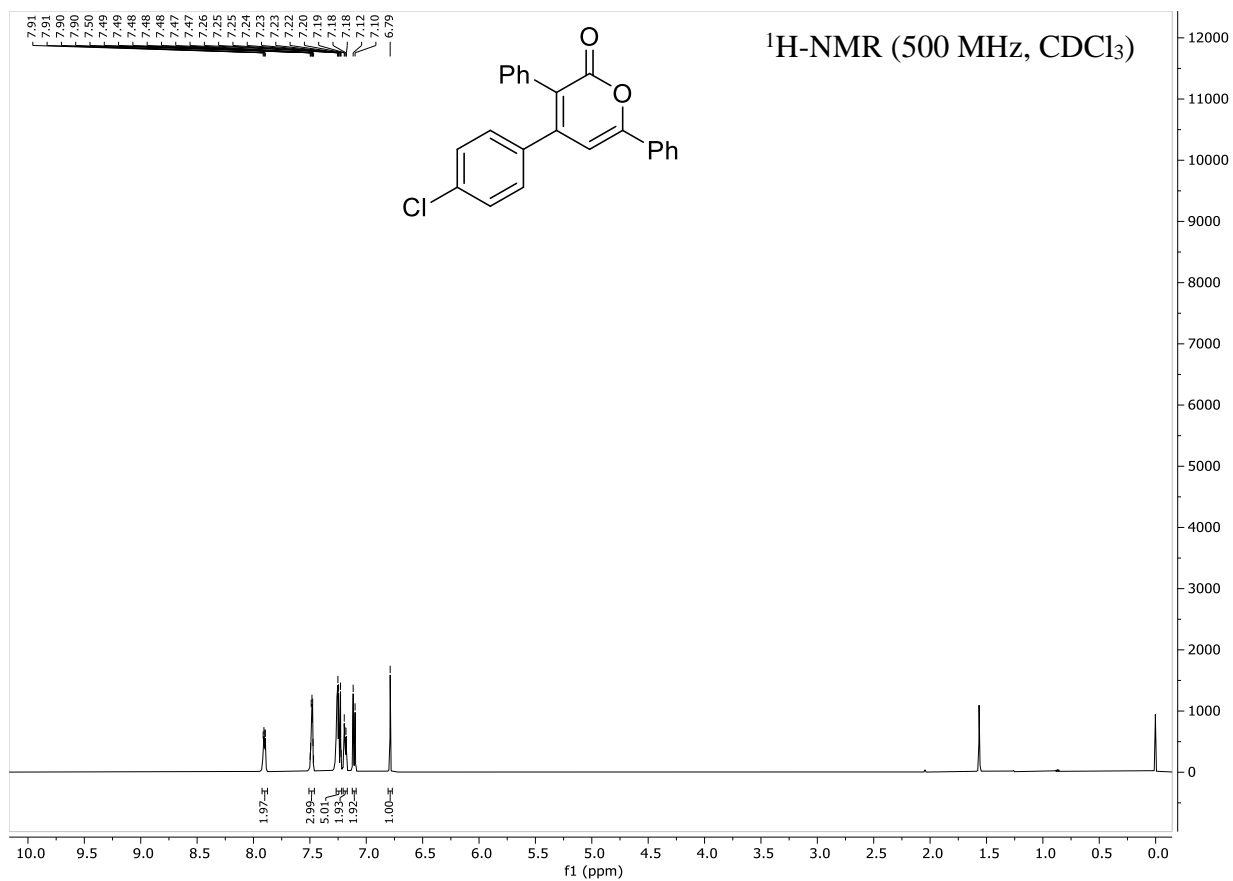
### 4,6-Bis(4-methoxyphenyl)-3-phenyl-2H-pyran-2-one (3d)



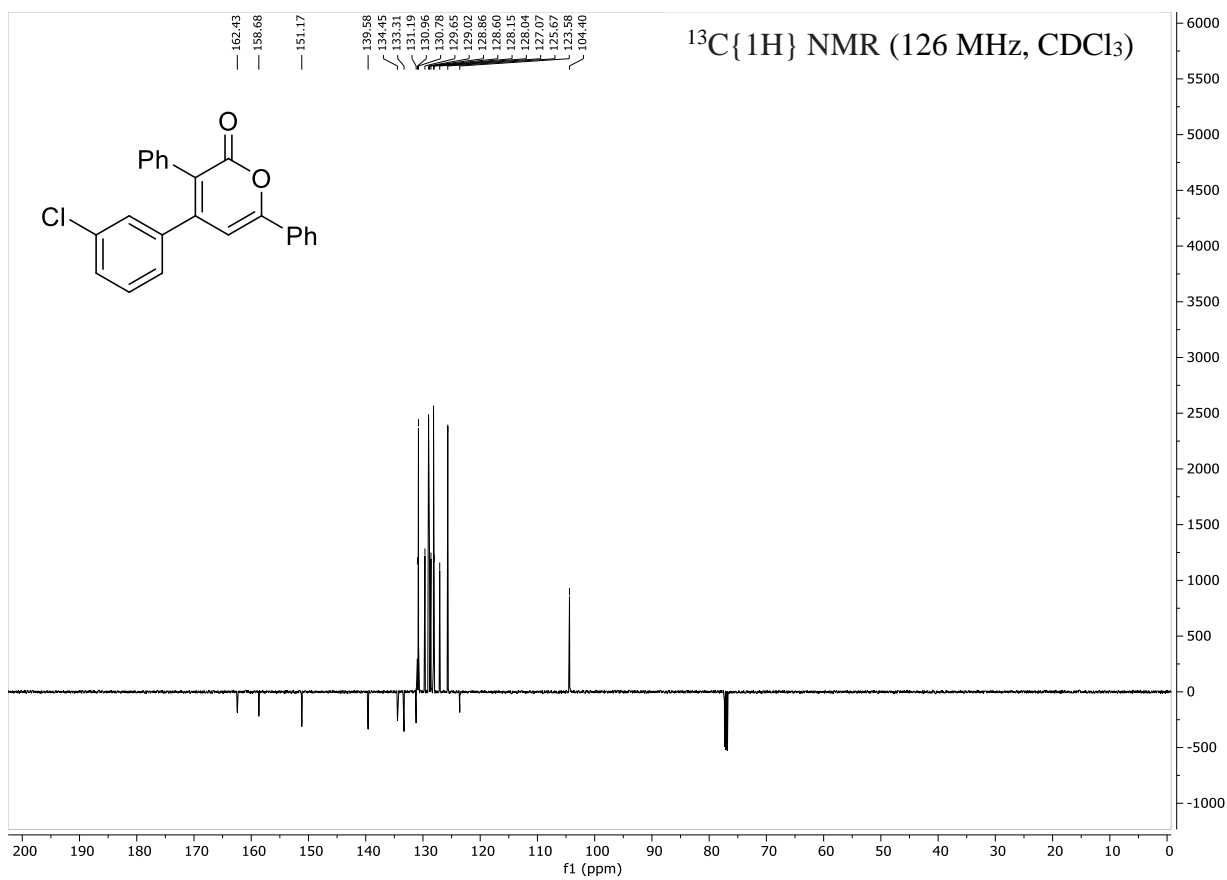
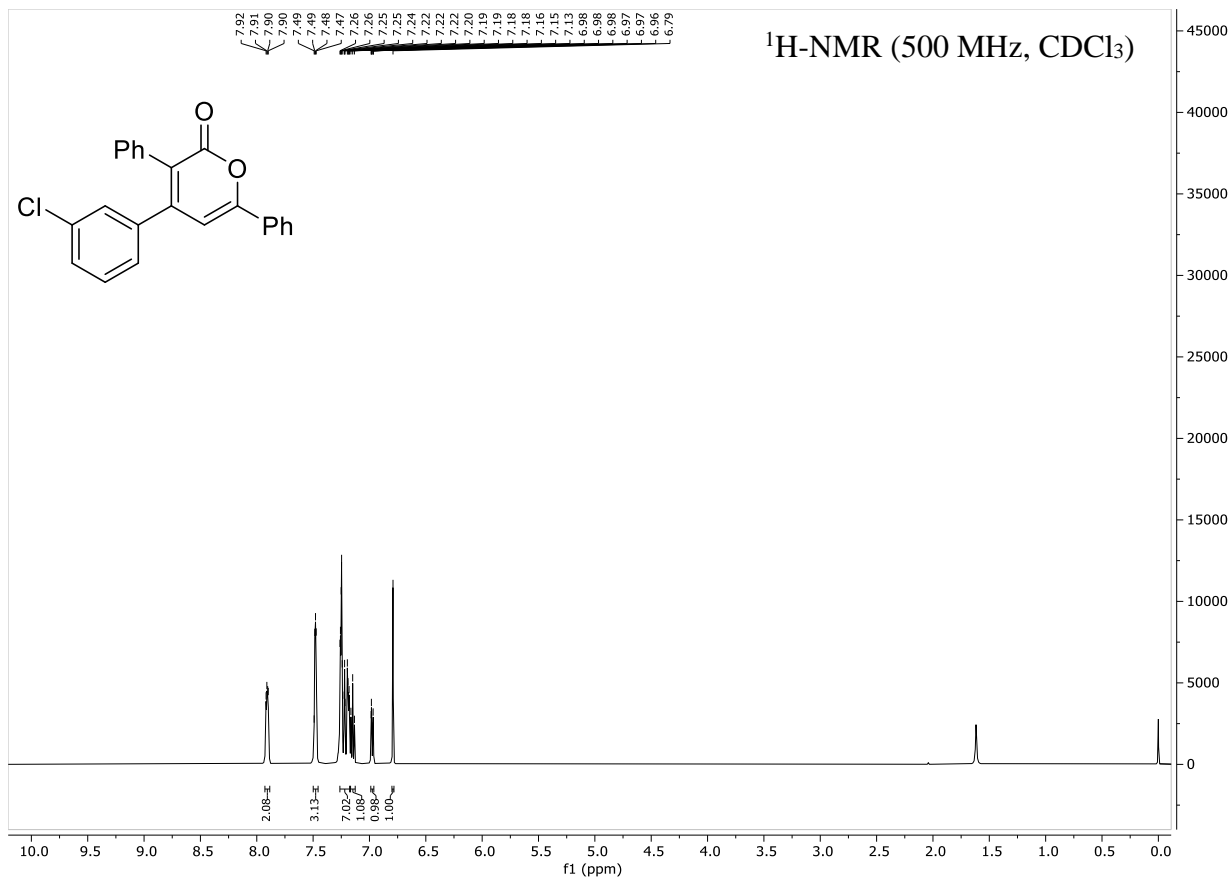
### 4-(4-Fluorophenyl)-3,6-diphenyl-2H-pyran-2-one (3e)



**4-(4-chlorophenyl)-3,6-diphenyl-2H-pyran-2-one (3f)**

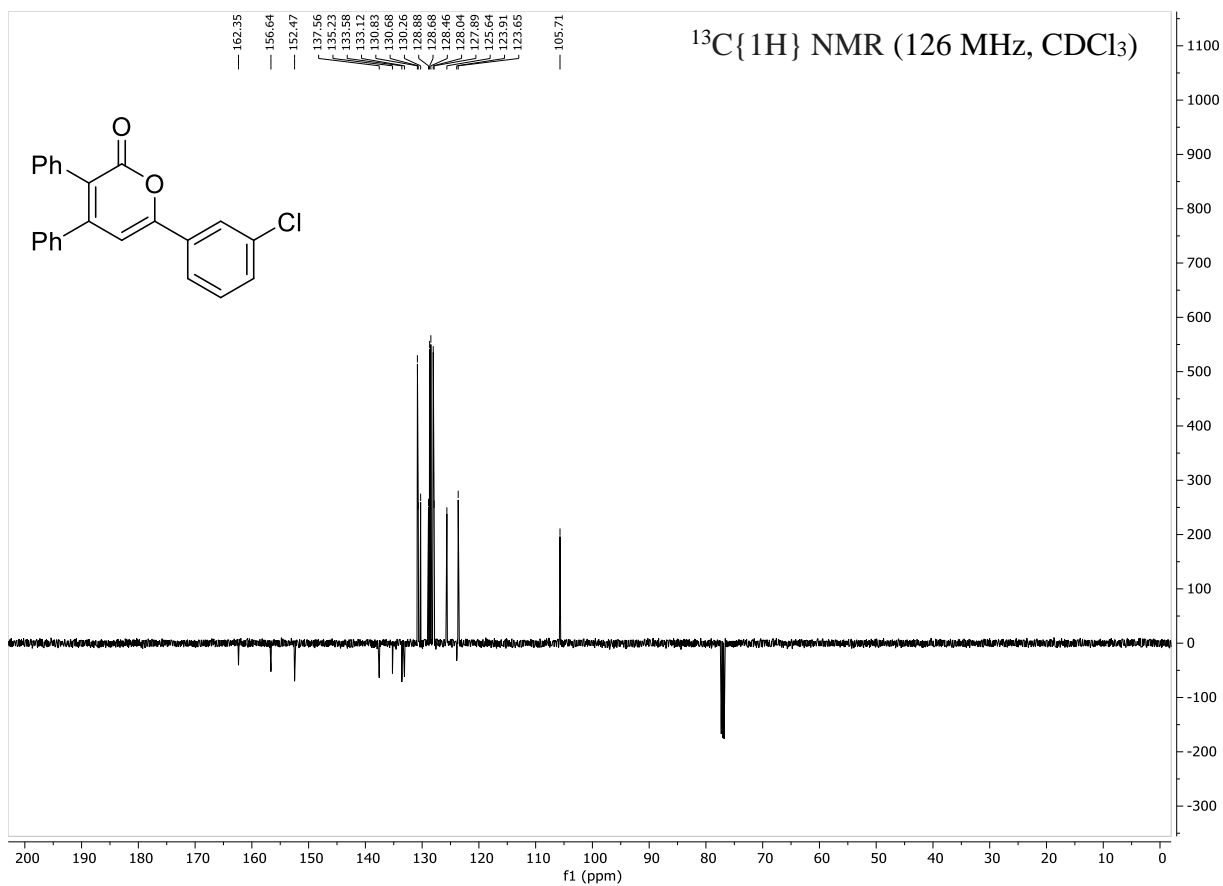
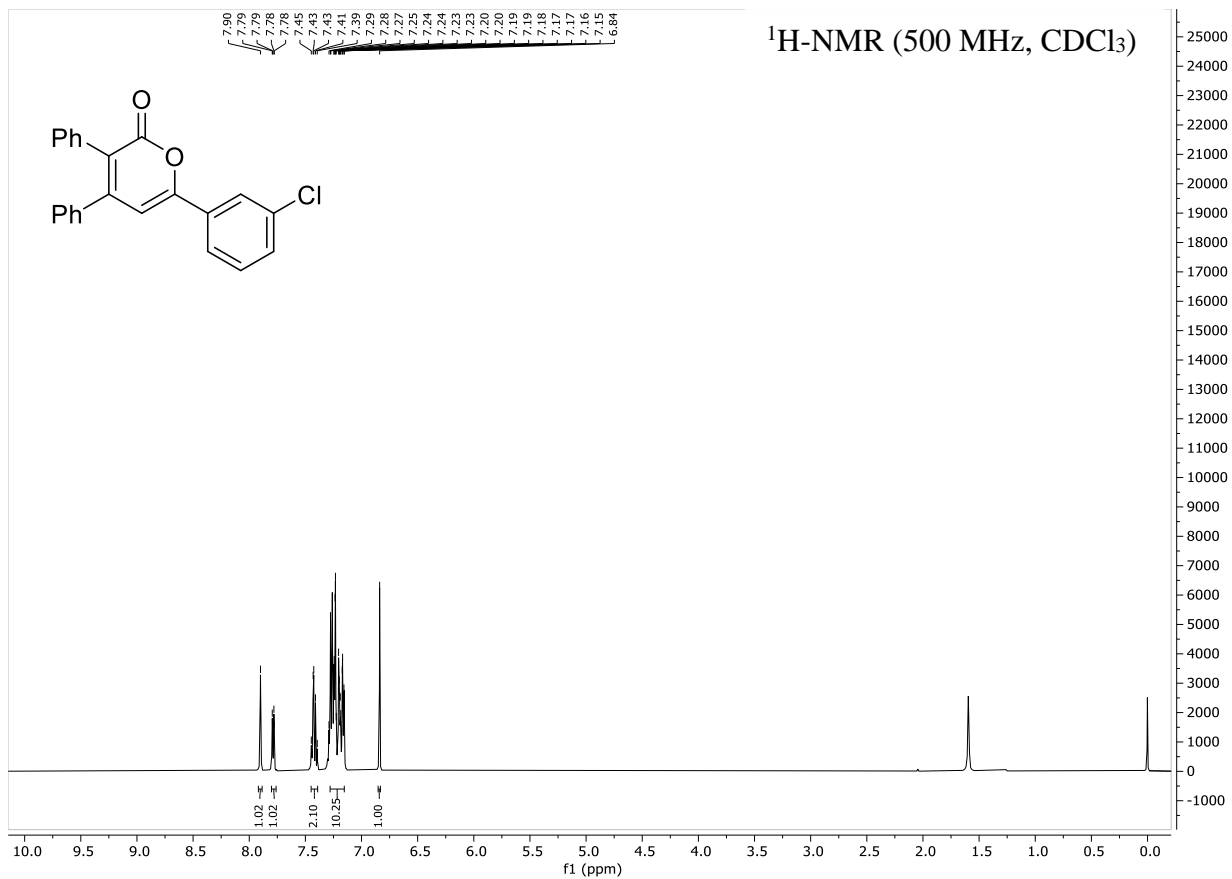


### 4-(3-Chlorophenyl)-3,6-diphenyl-2H-pyran-2-one (3g)

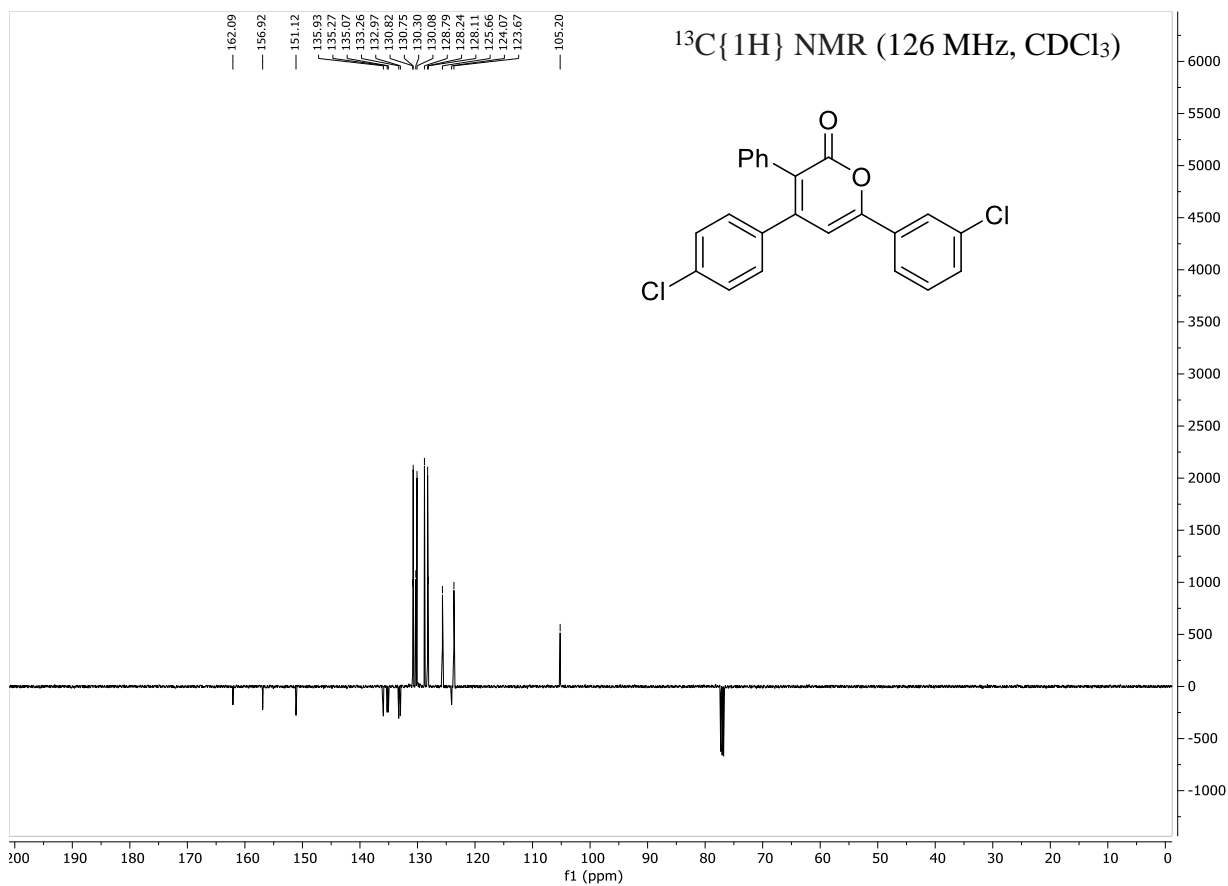
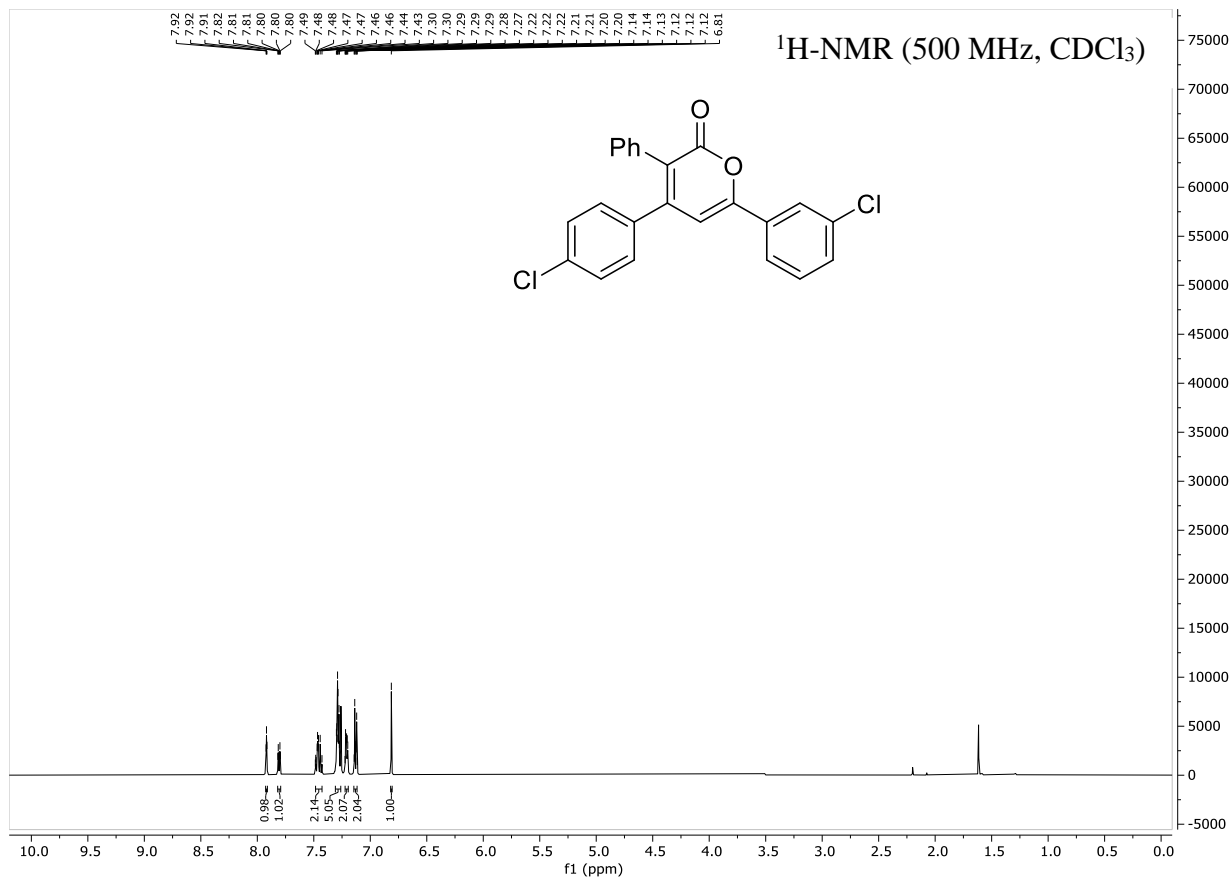




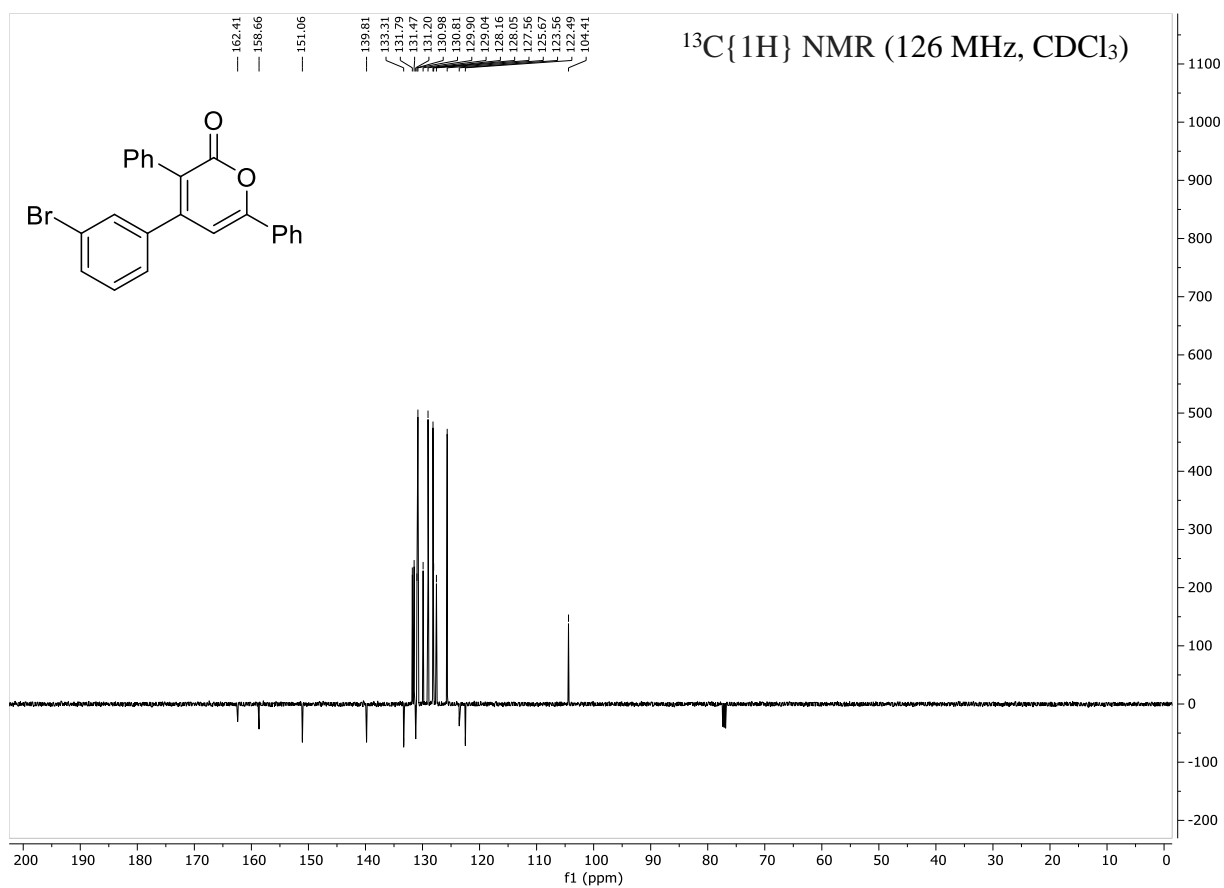
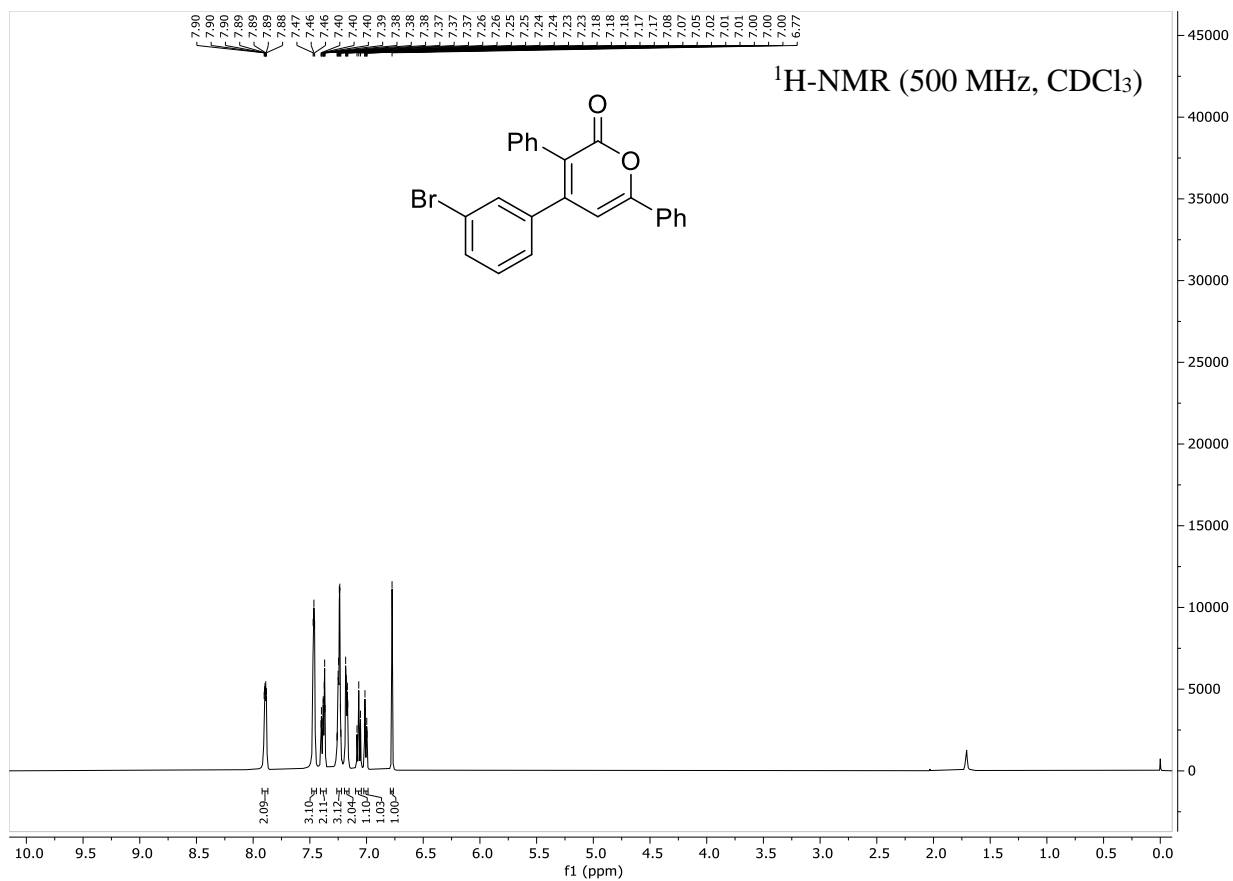
6-(3-Chlorophenyl)-3,4-diphenyl-2H-pyran-2-one (3h)



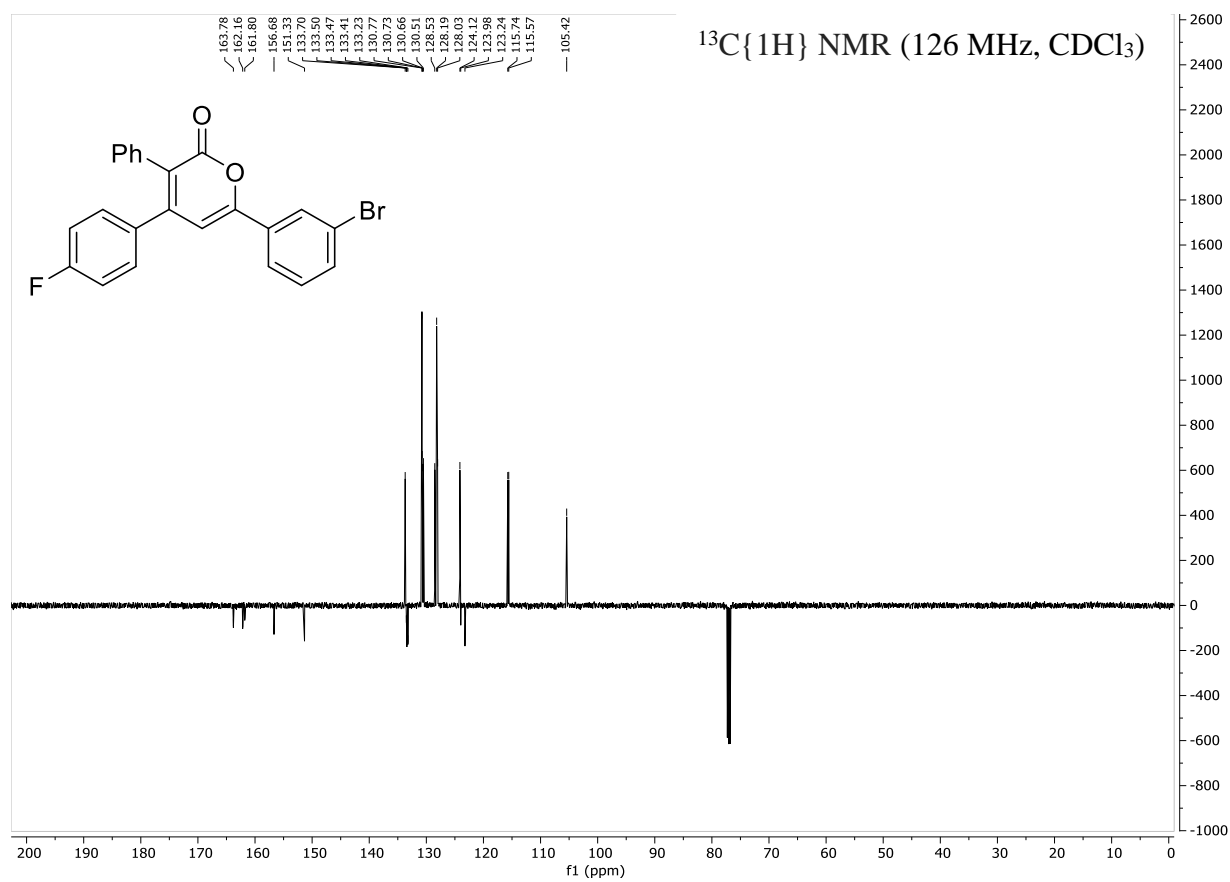
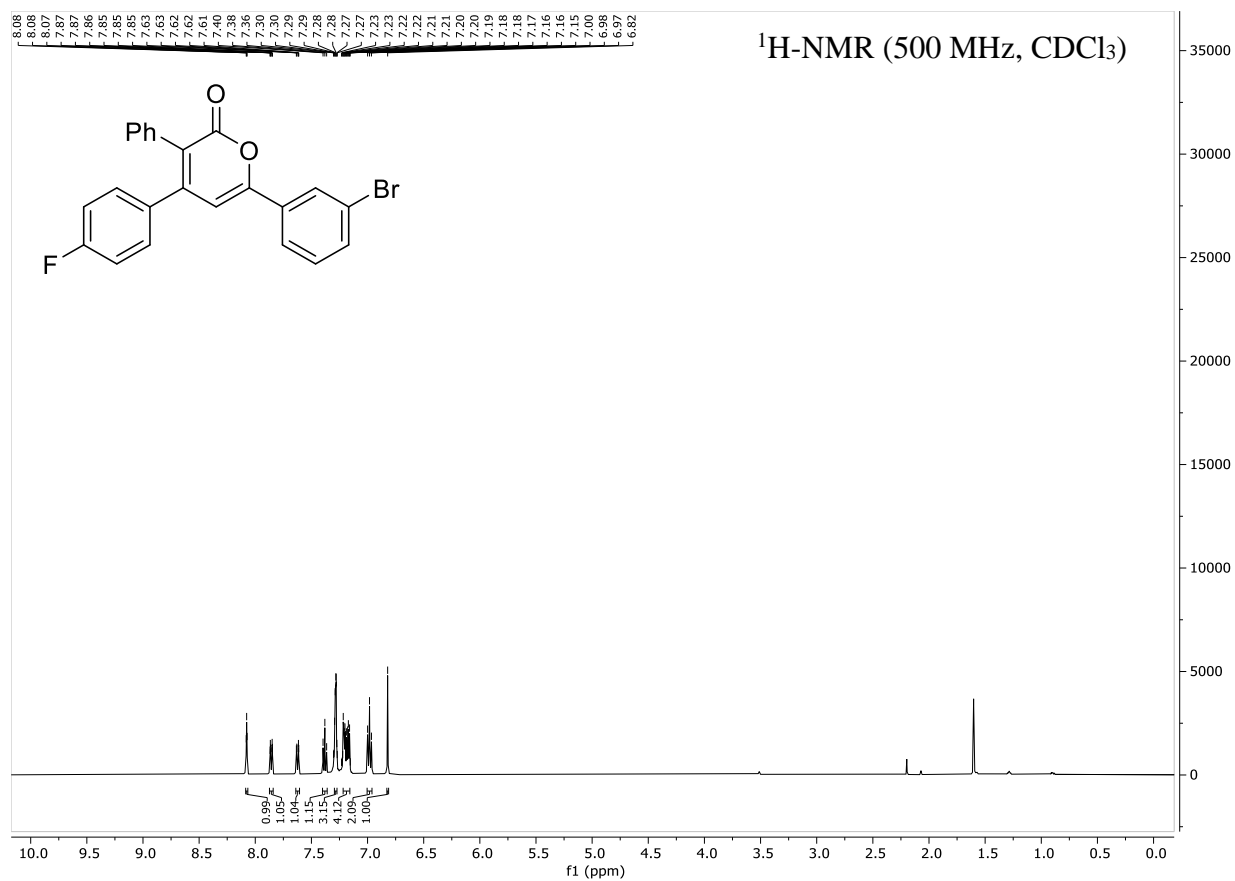
6-(3-Chlorophenyl)-4-(4-chlorophenyl)-3-phenyl-2H-pyran-2-one (3i)



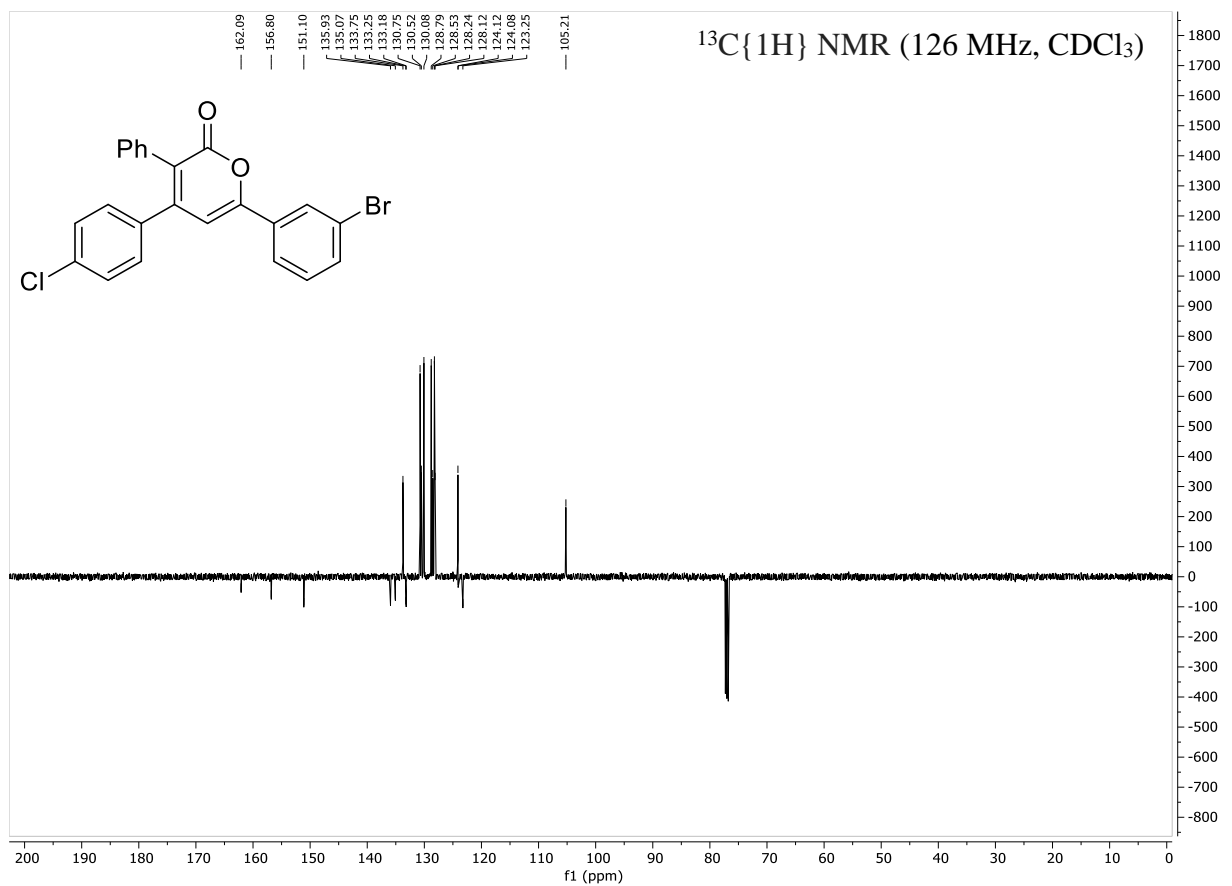
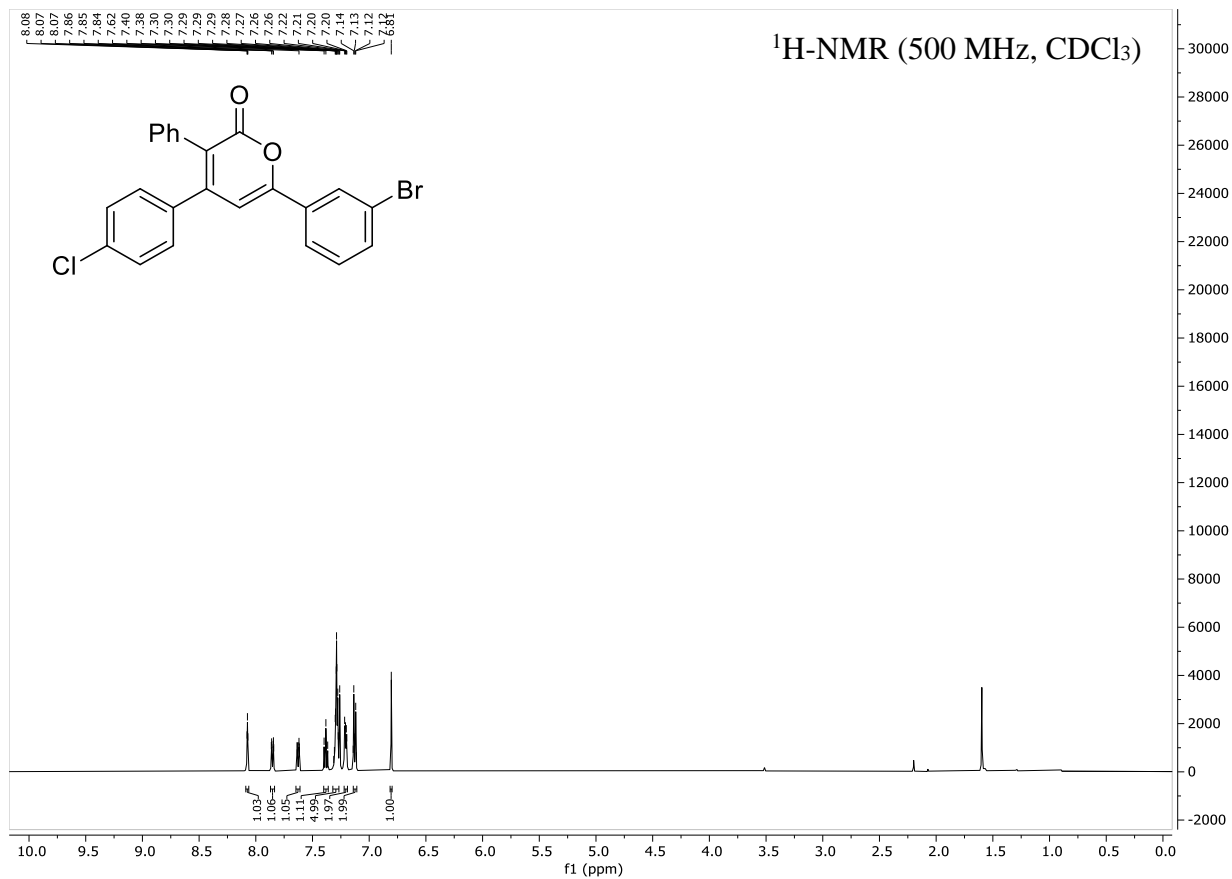
### 4-(3-Bromophenyl)-3,6-diphenyl-2H-pyran-2-one (3j)



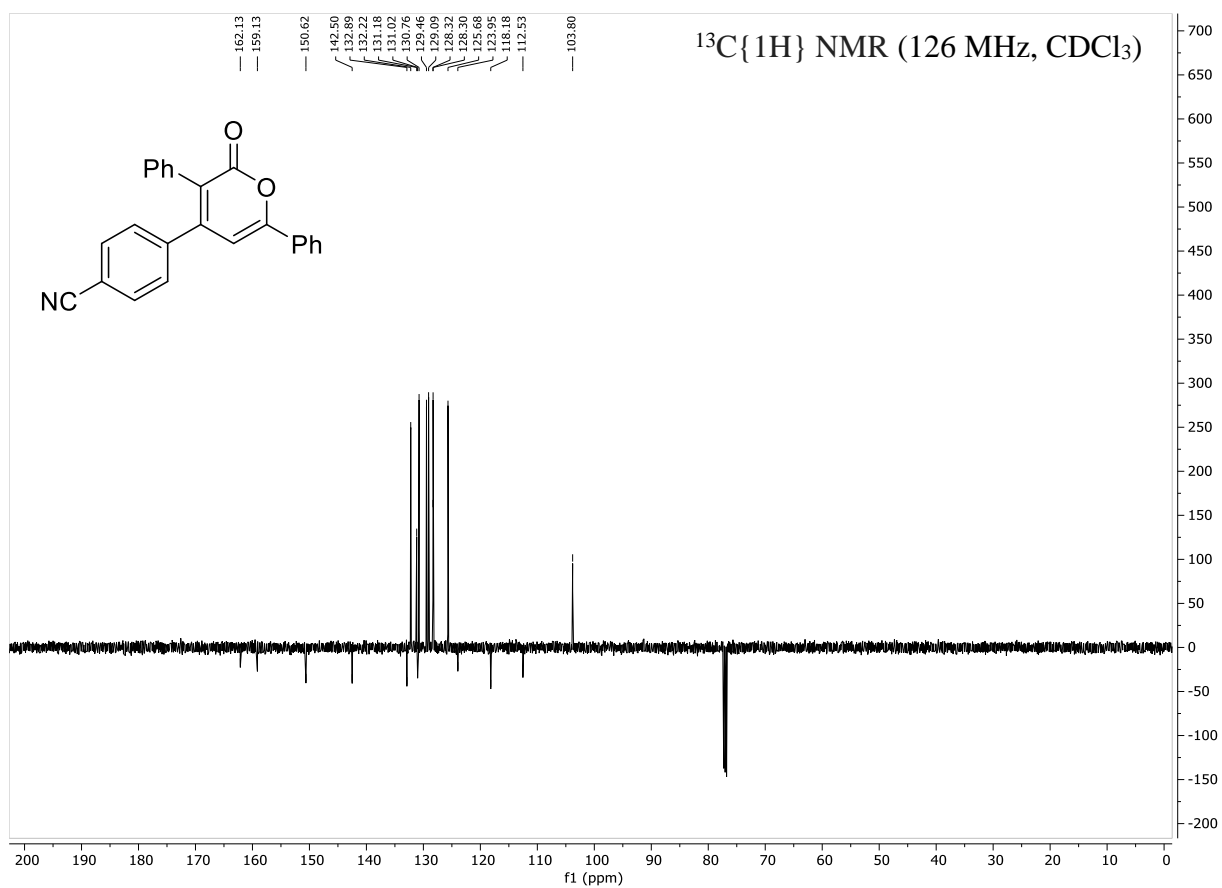
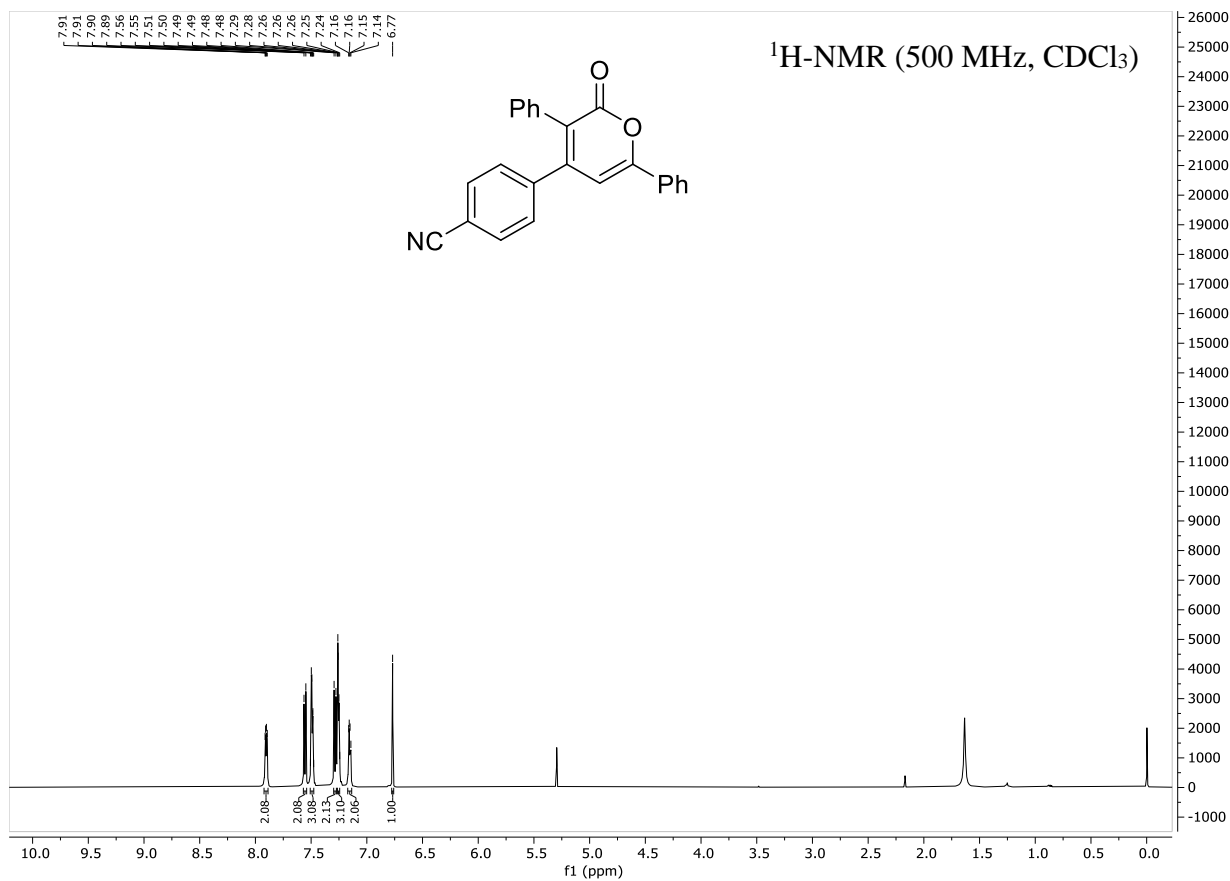
**6-(3-Bromophenyl)-4-(4-fluorophenyl)-3-phenyl-2H-pyran-2-one (3k)**



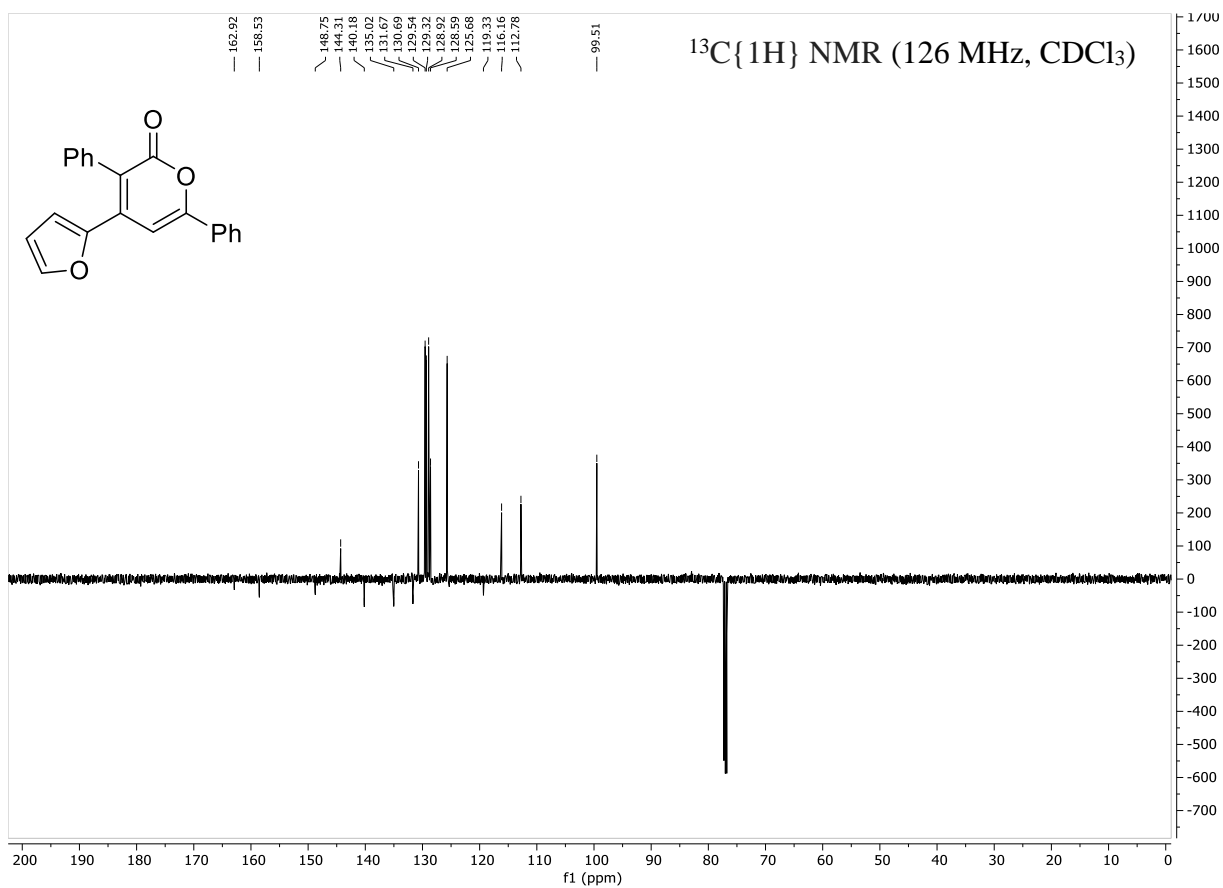
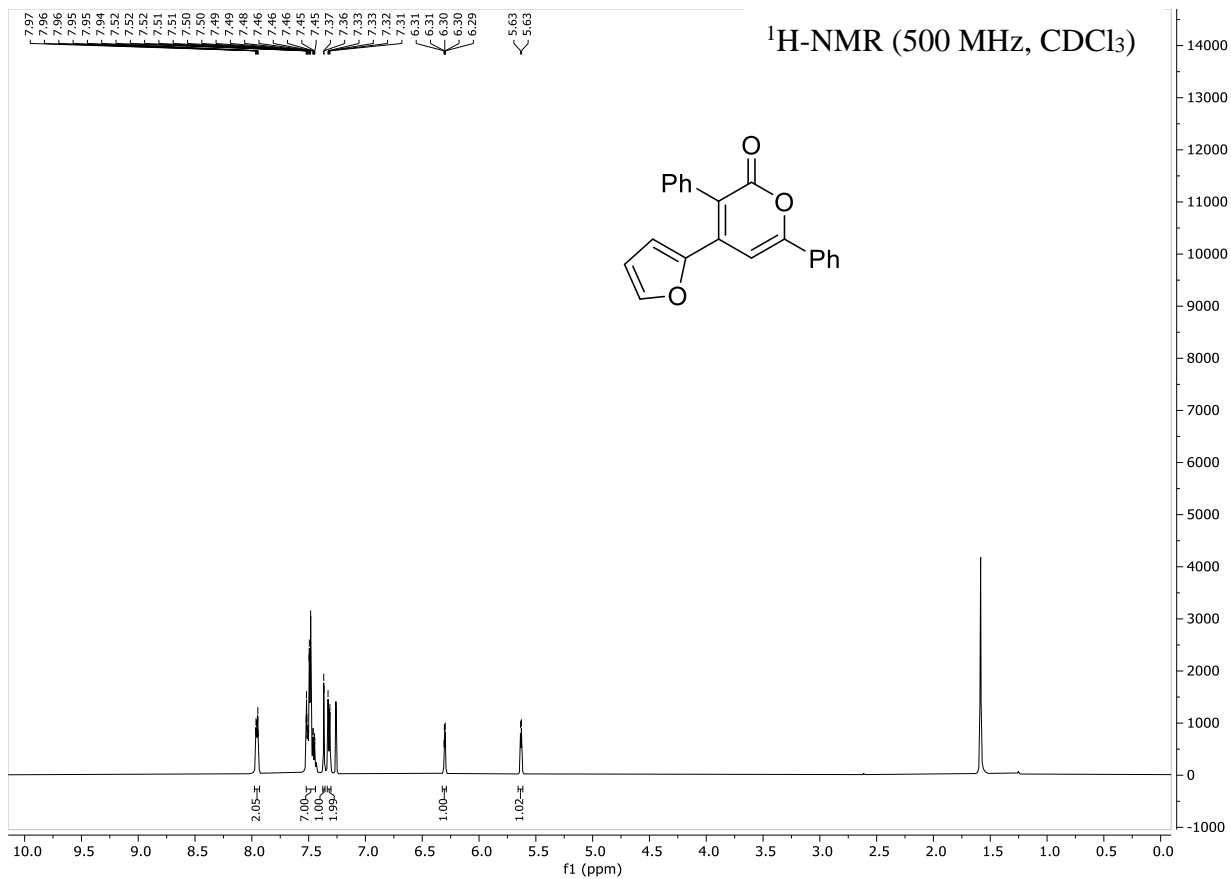
**6-(3-Bromophenyl)-4-(4-chlorophenyl)-3-phenyl-2H-pyran-2-one (3l)**



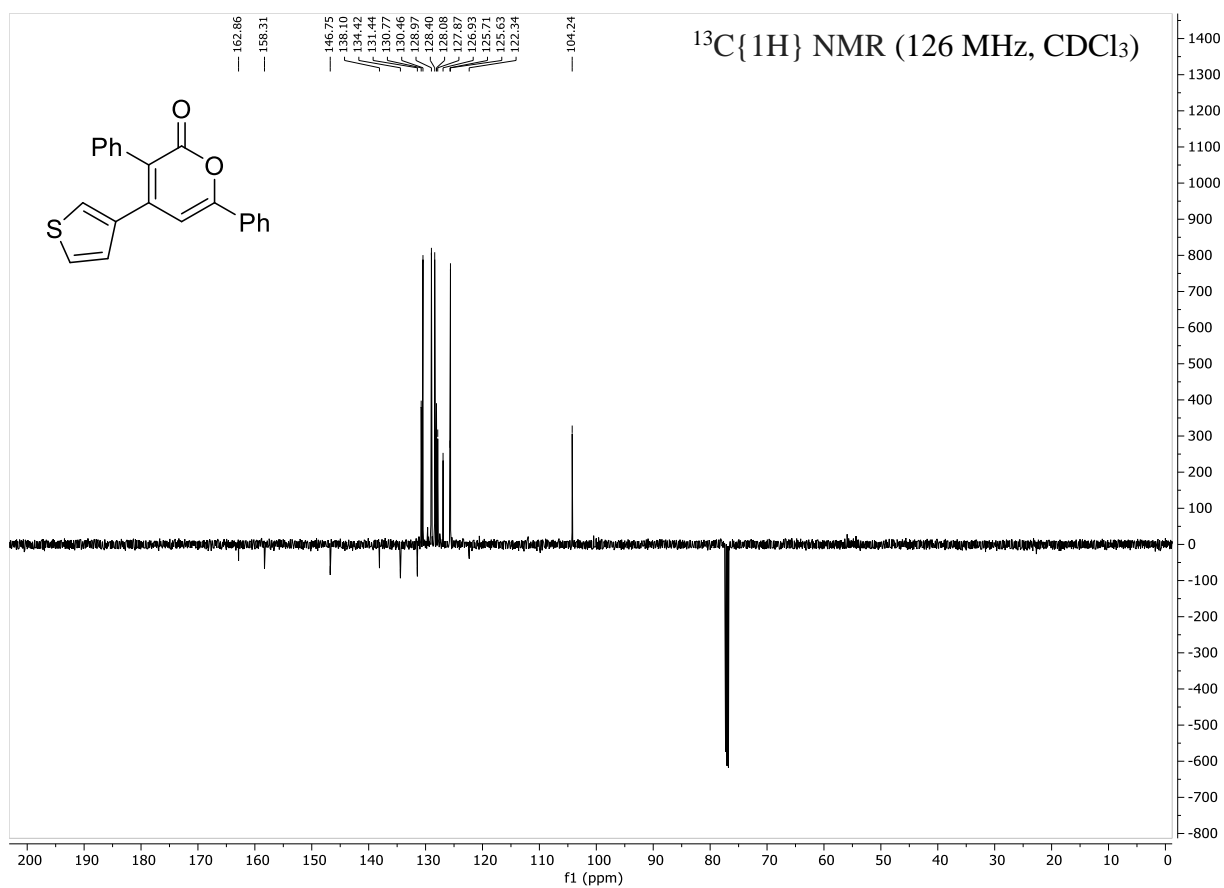
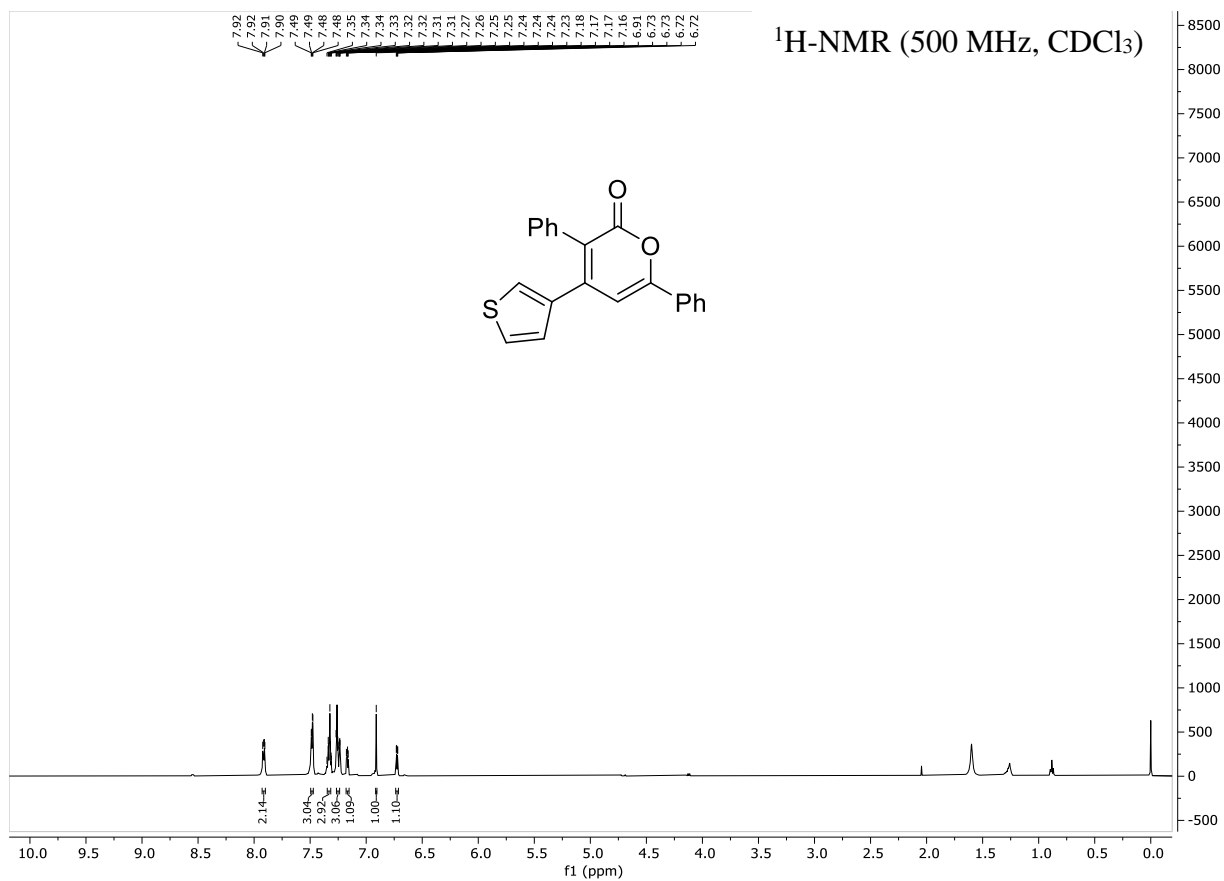
### 4-(2-Oxo-3,6-diphenyl-2H-pyran-4-yl)benzotrile (3m)



### 4-(Furan-2-yl)-3,6-diphenyl-2H-pyran-2-one (3n)

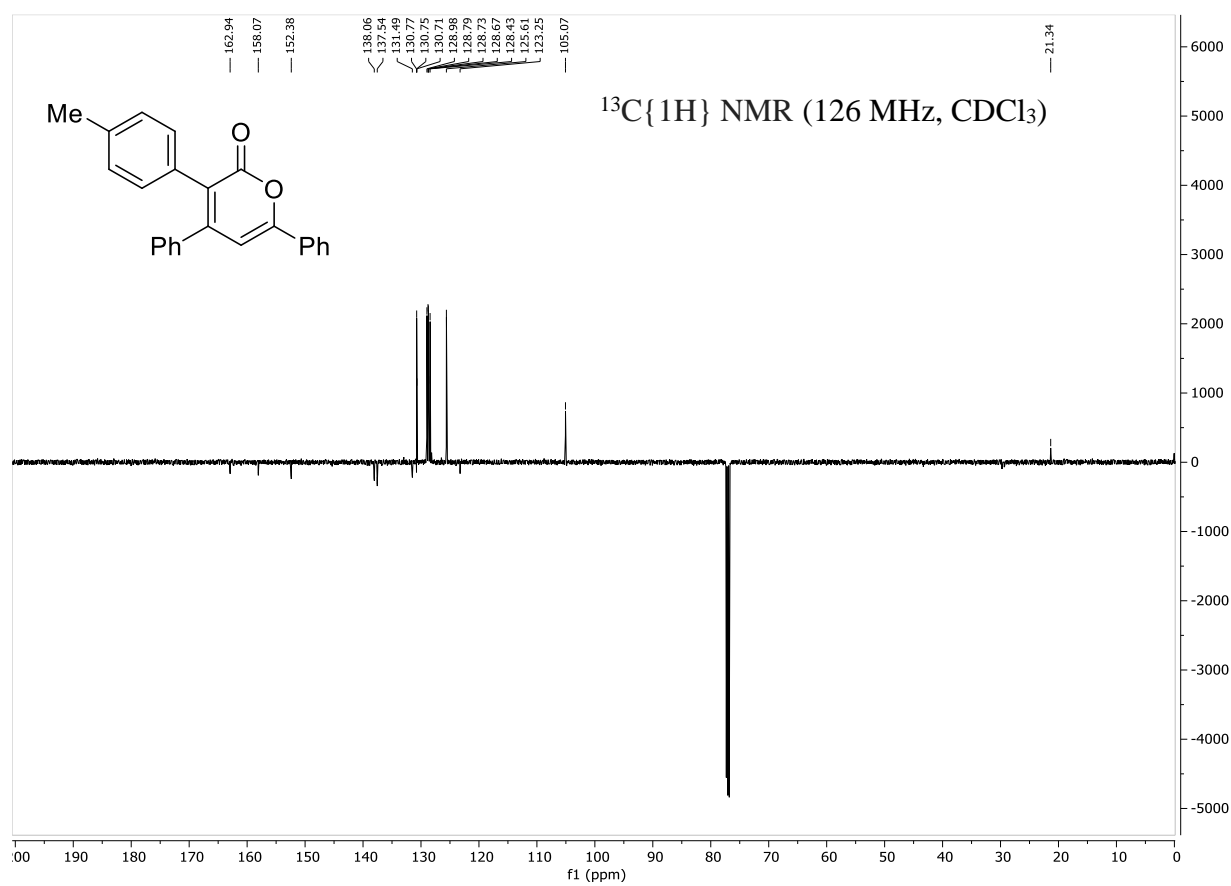
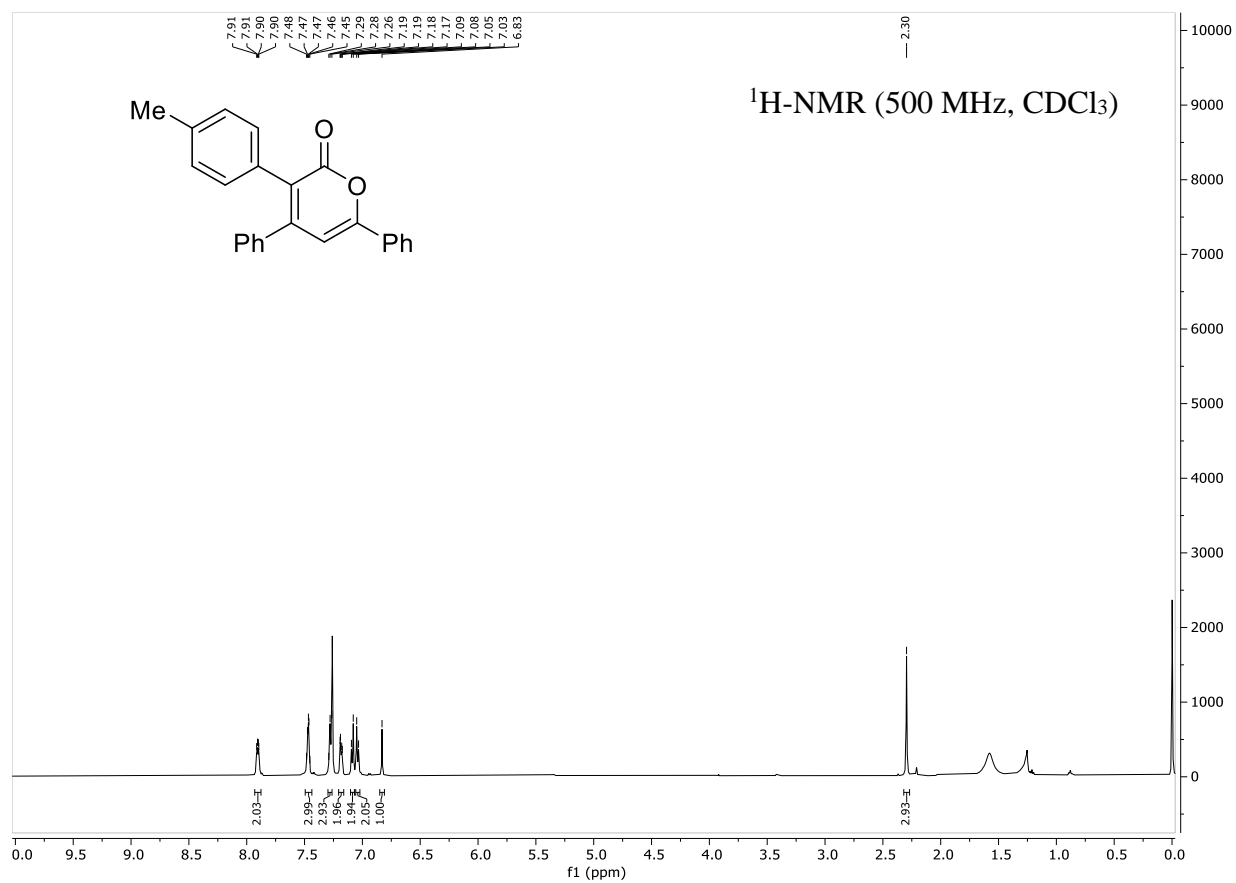


### 3,6-Diphenyl-4-(thiophen-3-yl)-2H-pyran-2-one (3o)

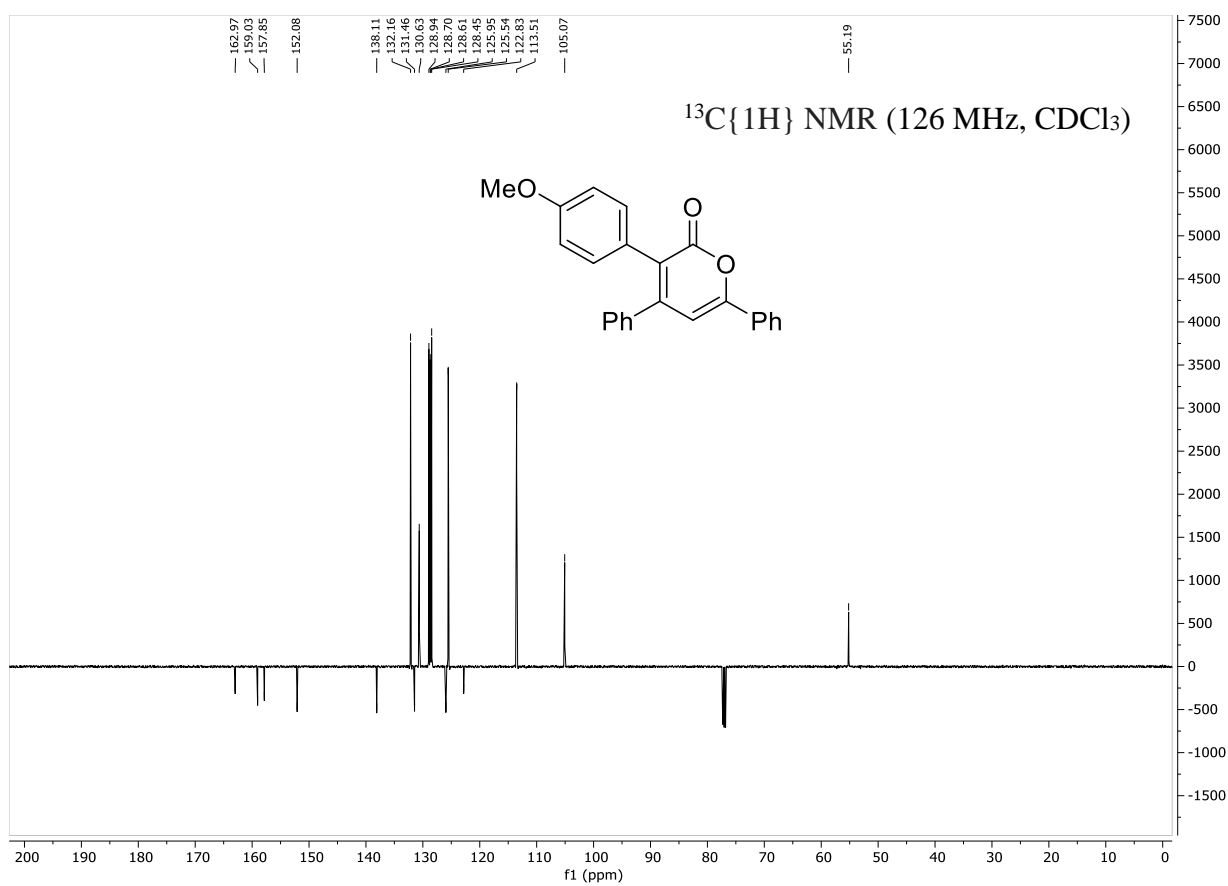
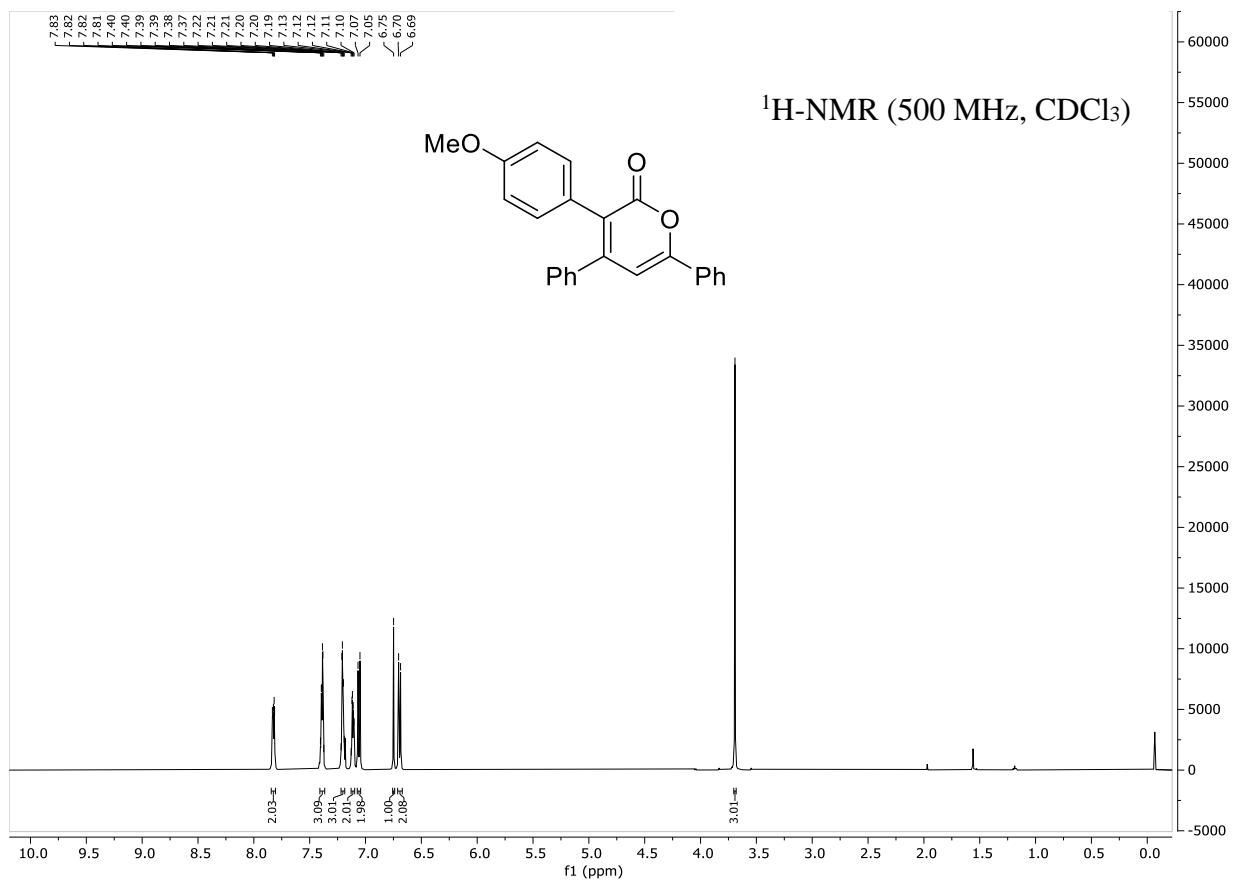




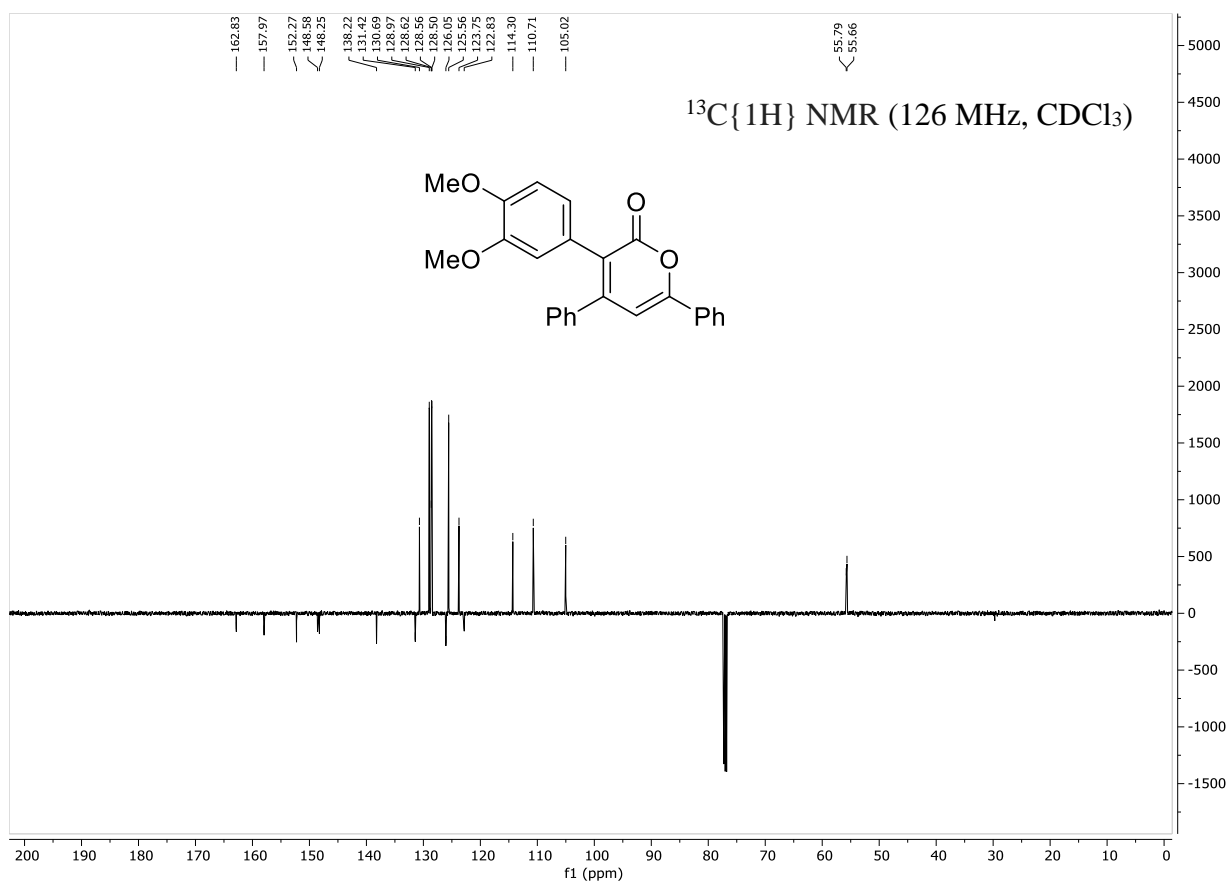
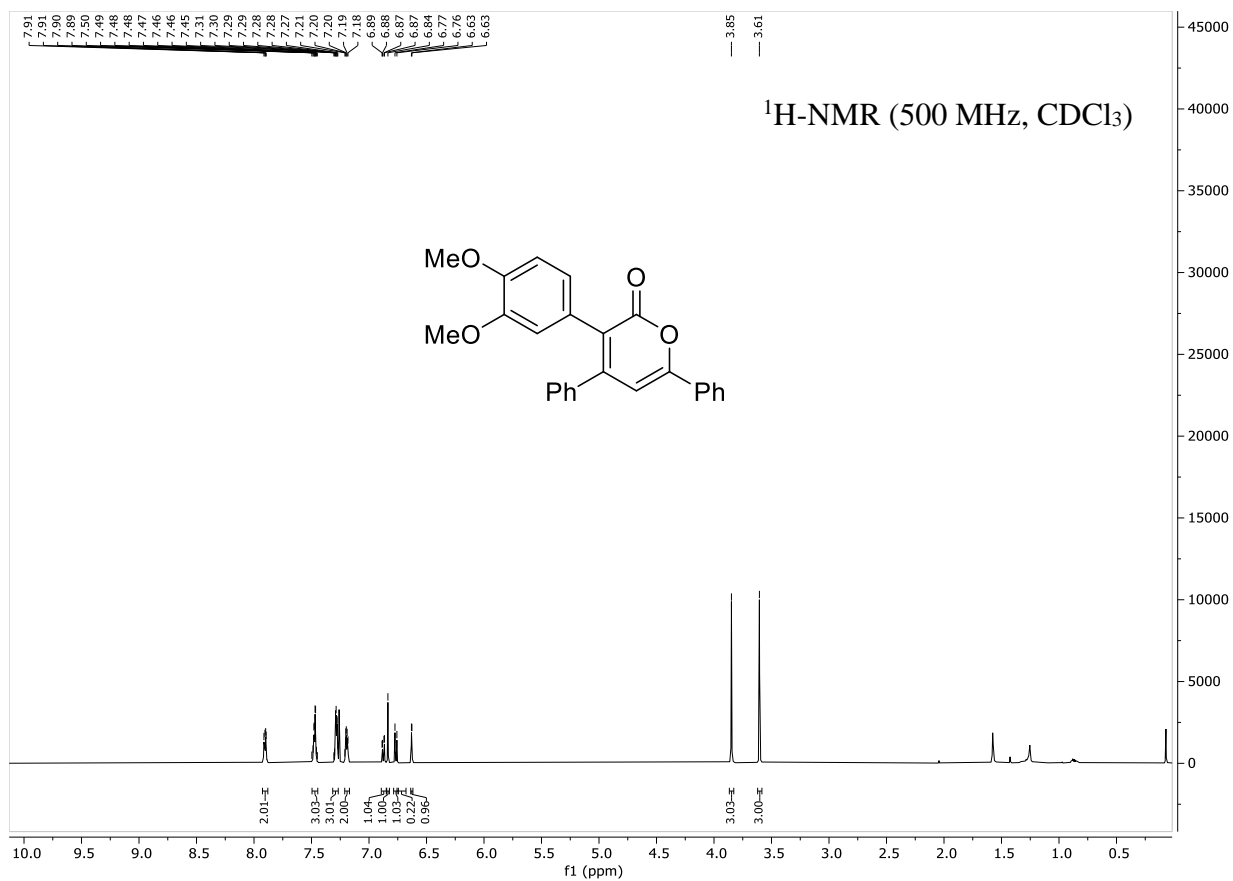
### 4,6-Diphenyl-3-(p-tolyl)-2H-pyran-2-one (3p)



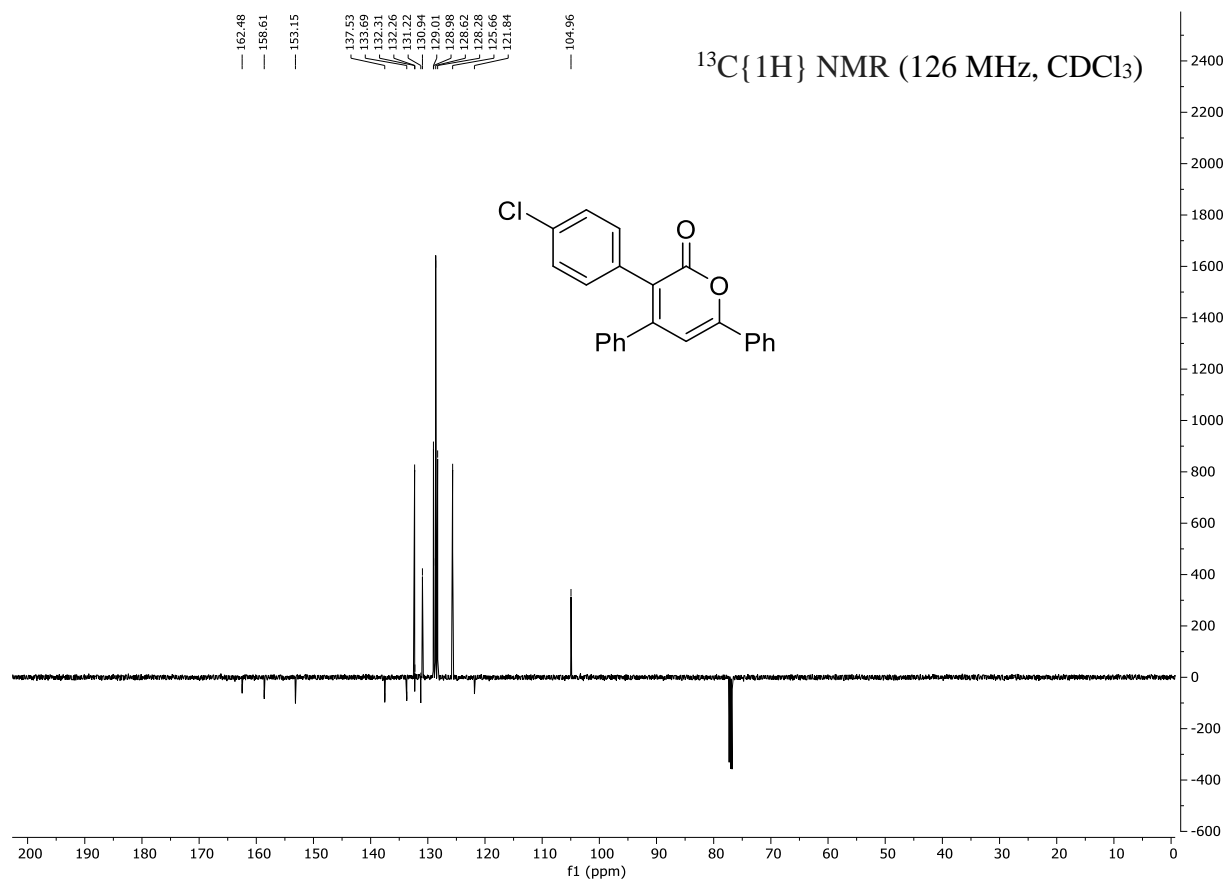
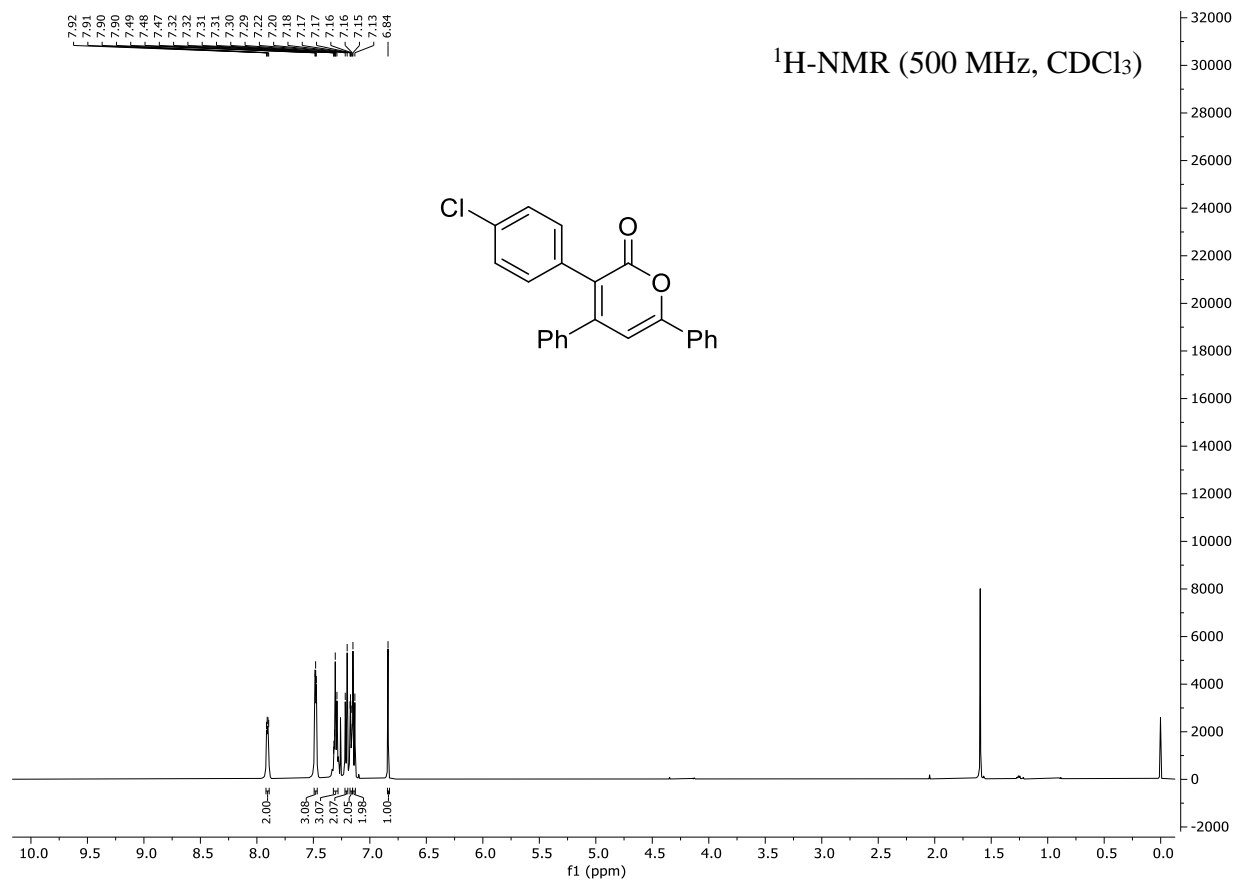
### 3-(4-Methoxyphenyl)-4,6-diphenyl-2H-pyran-2-one (3q)



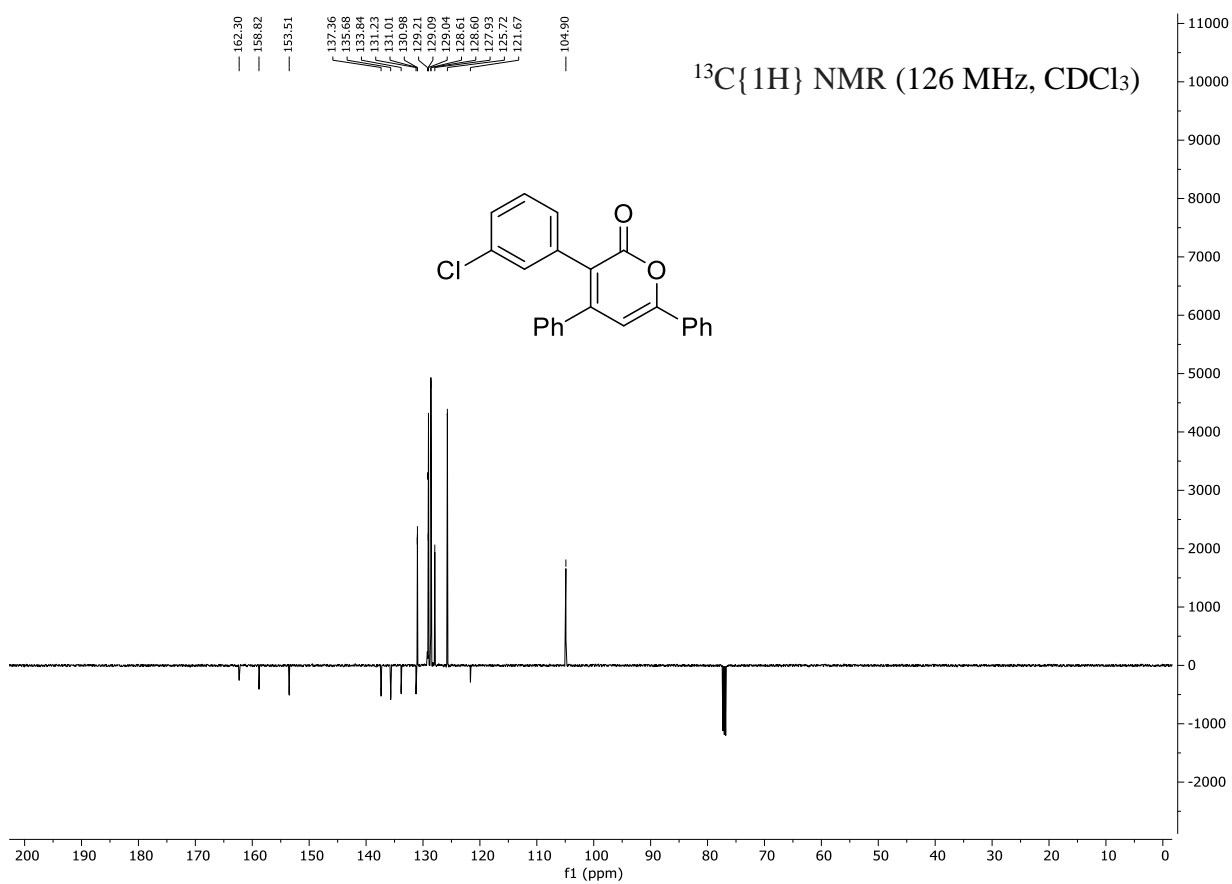
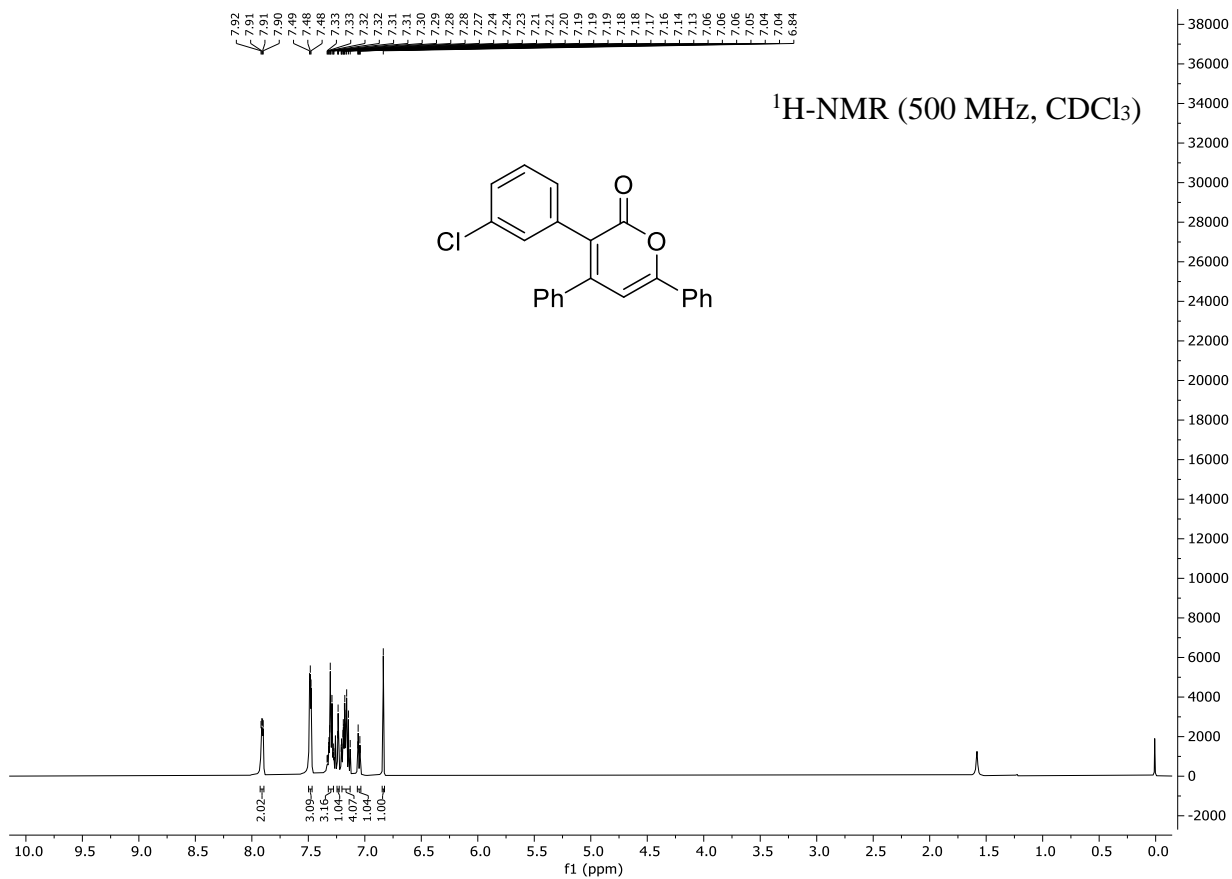
### 3-(3,4-Dimethoxyphenyl)-4,6-diphenyl-2H-pyran-2-one (3r)



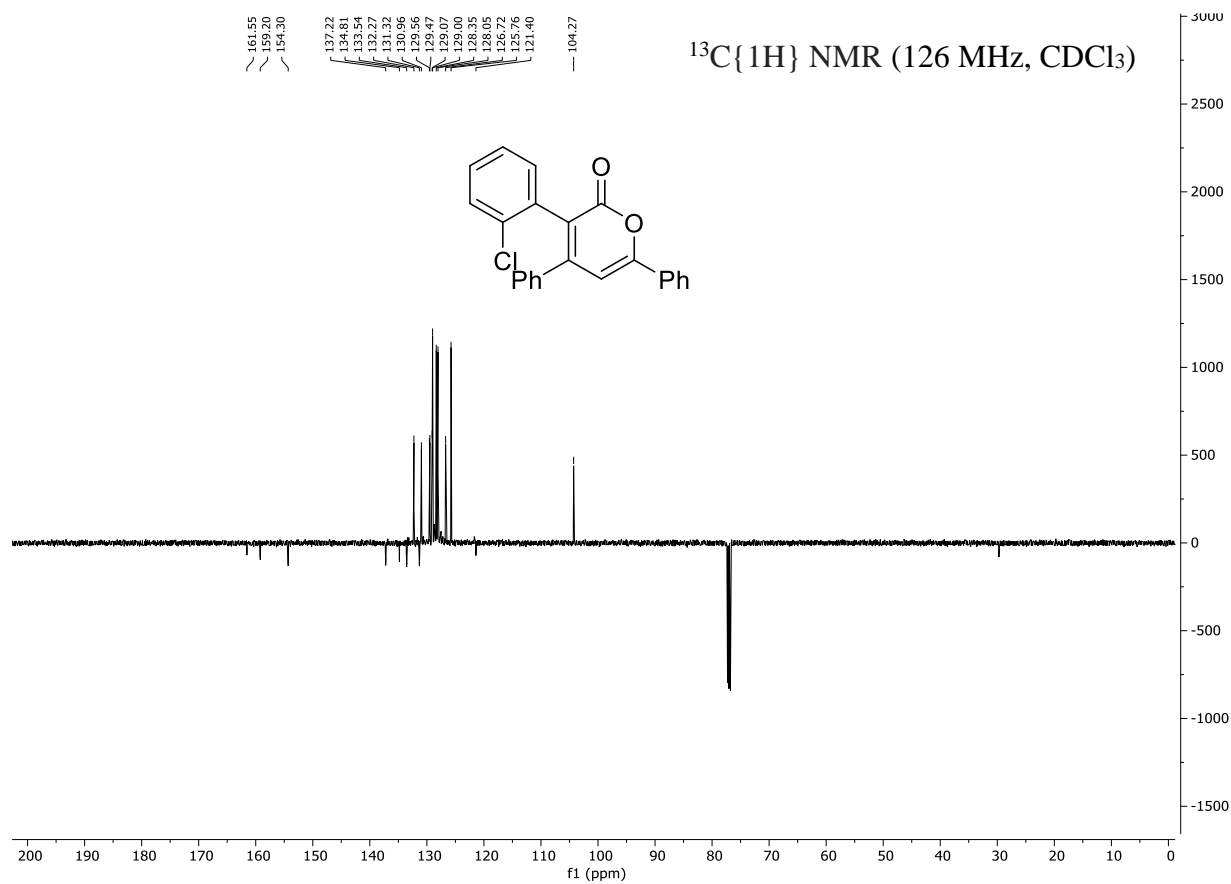
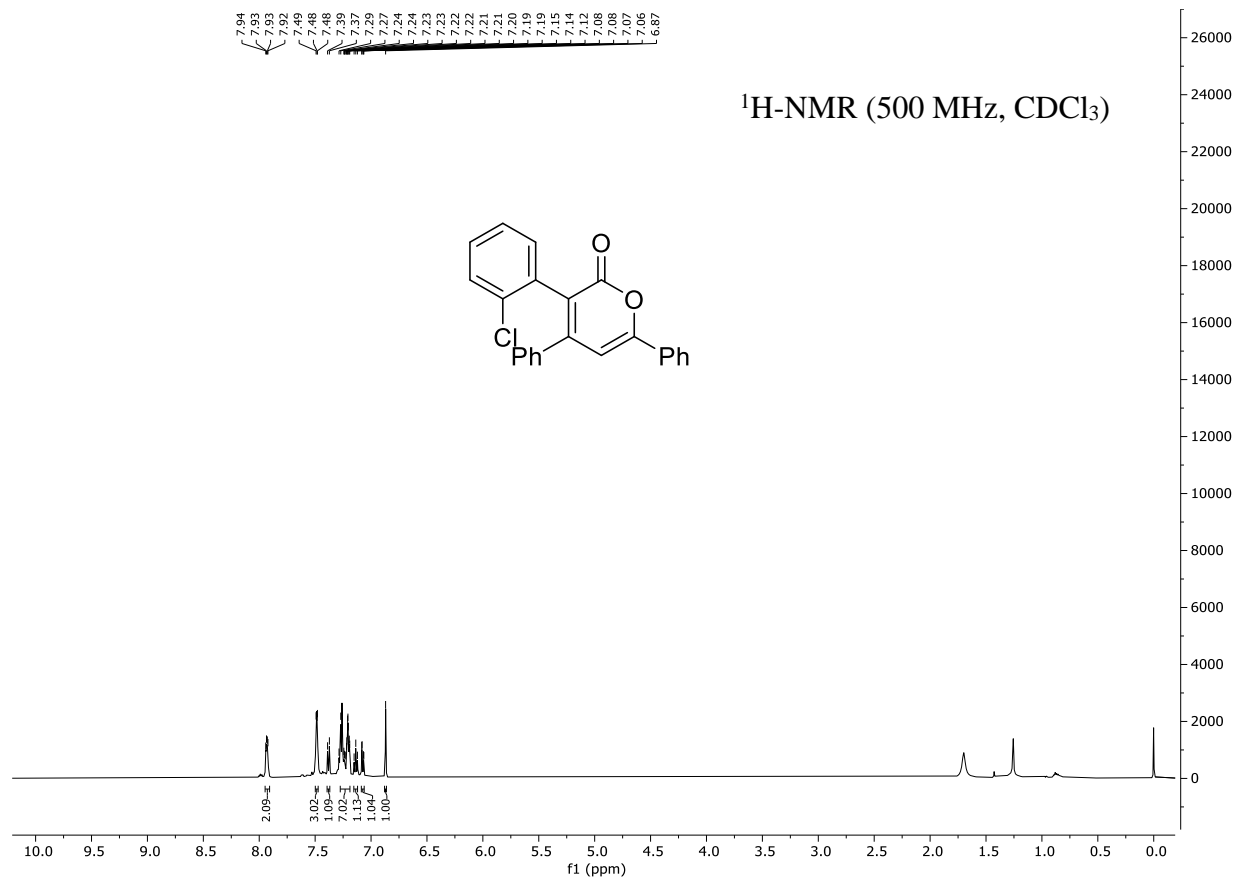
### 3-(4-Chlorophenyl)-4,6-diphenyl-2H-pyran-2-one (3s)



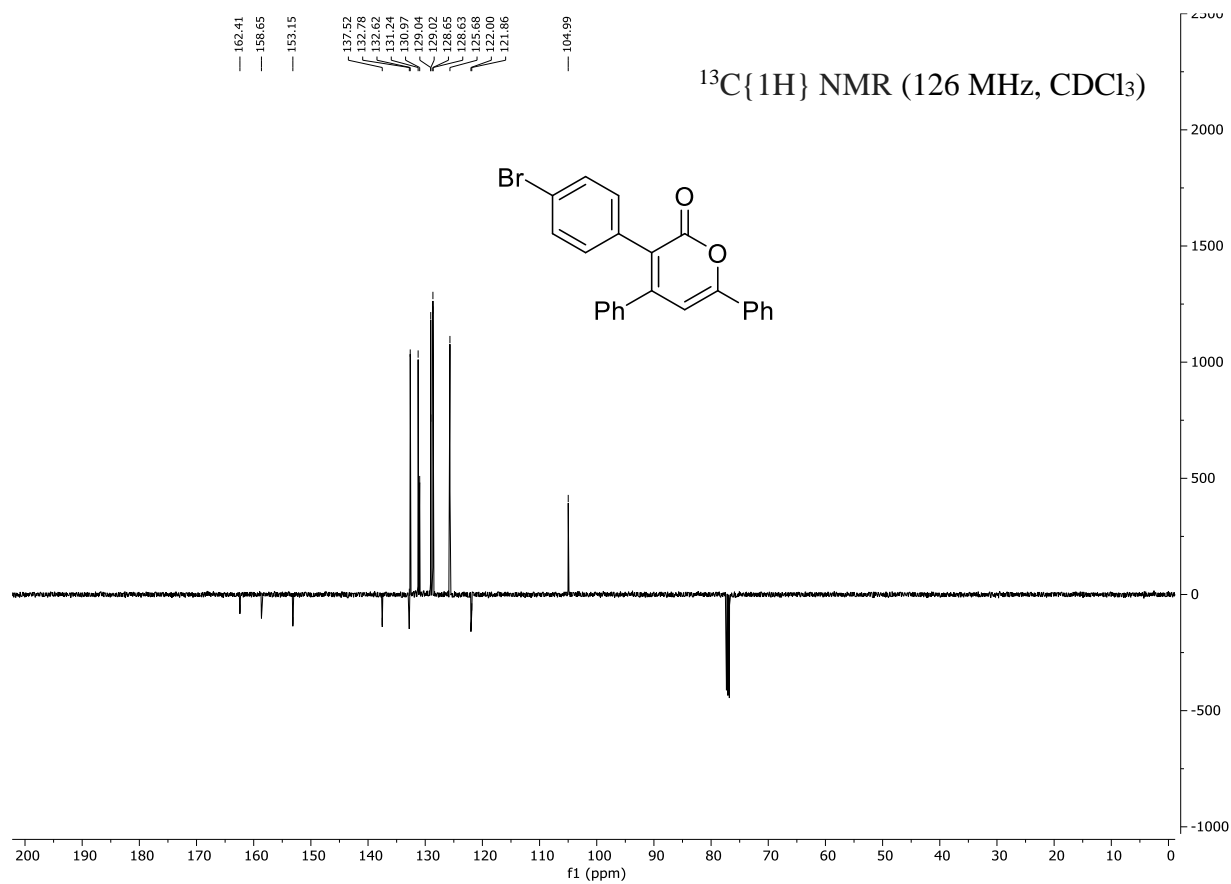
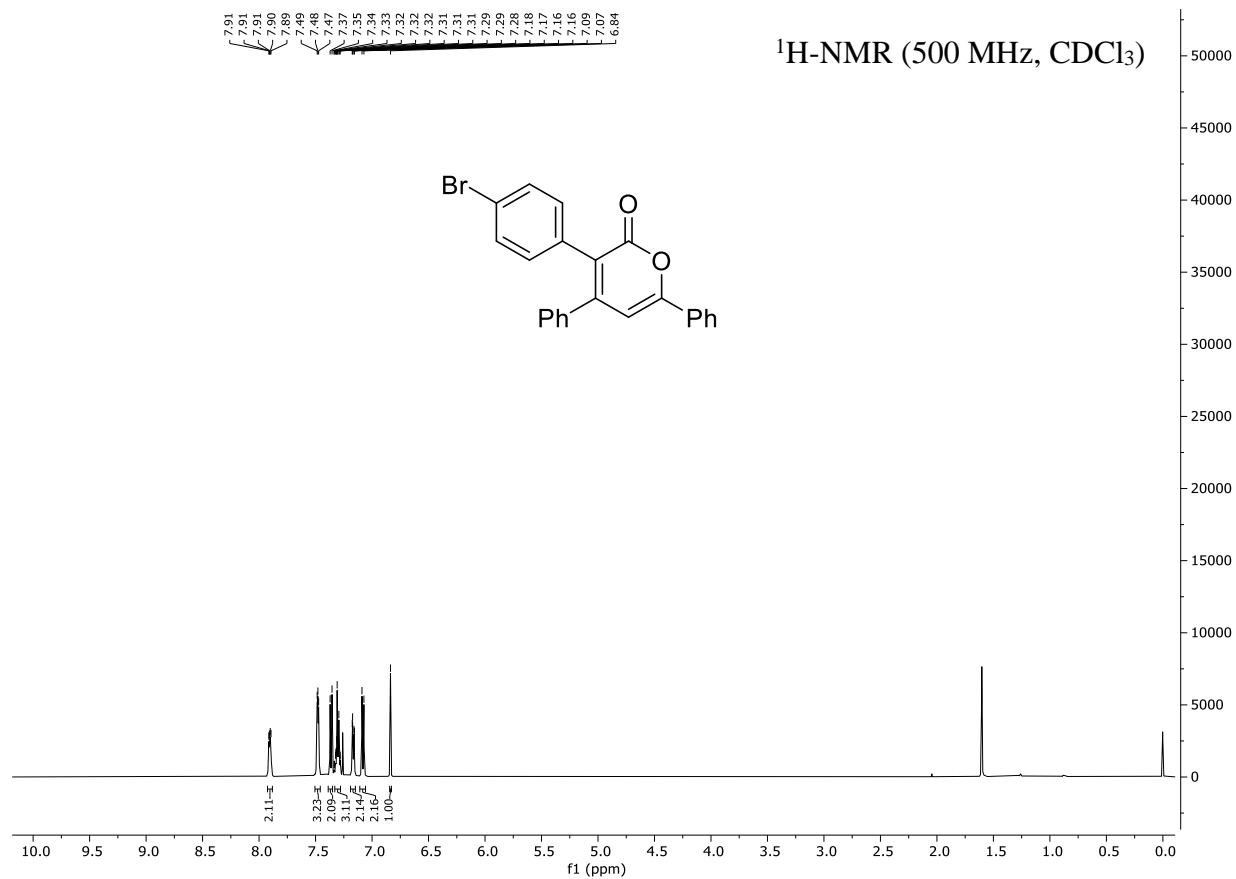
### 3-(3-Chlorophenyl)-4,6-diphenyl-2H-pyran-2-one (3t)



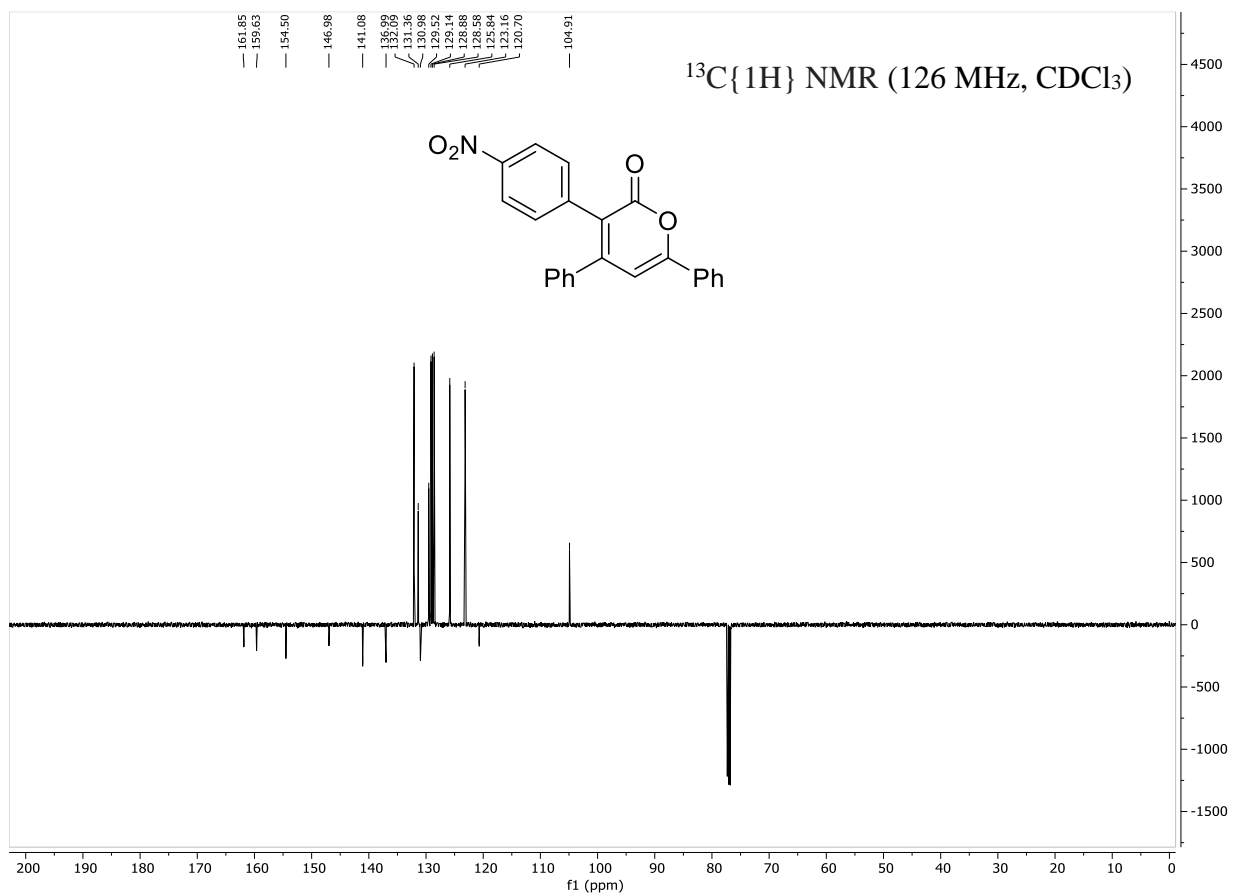
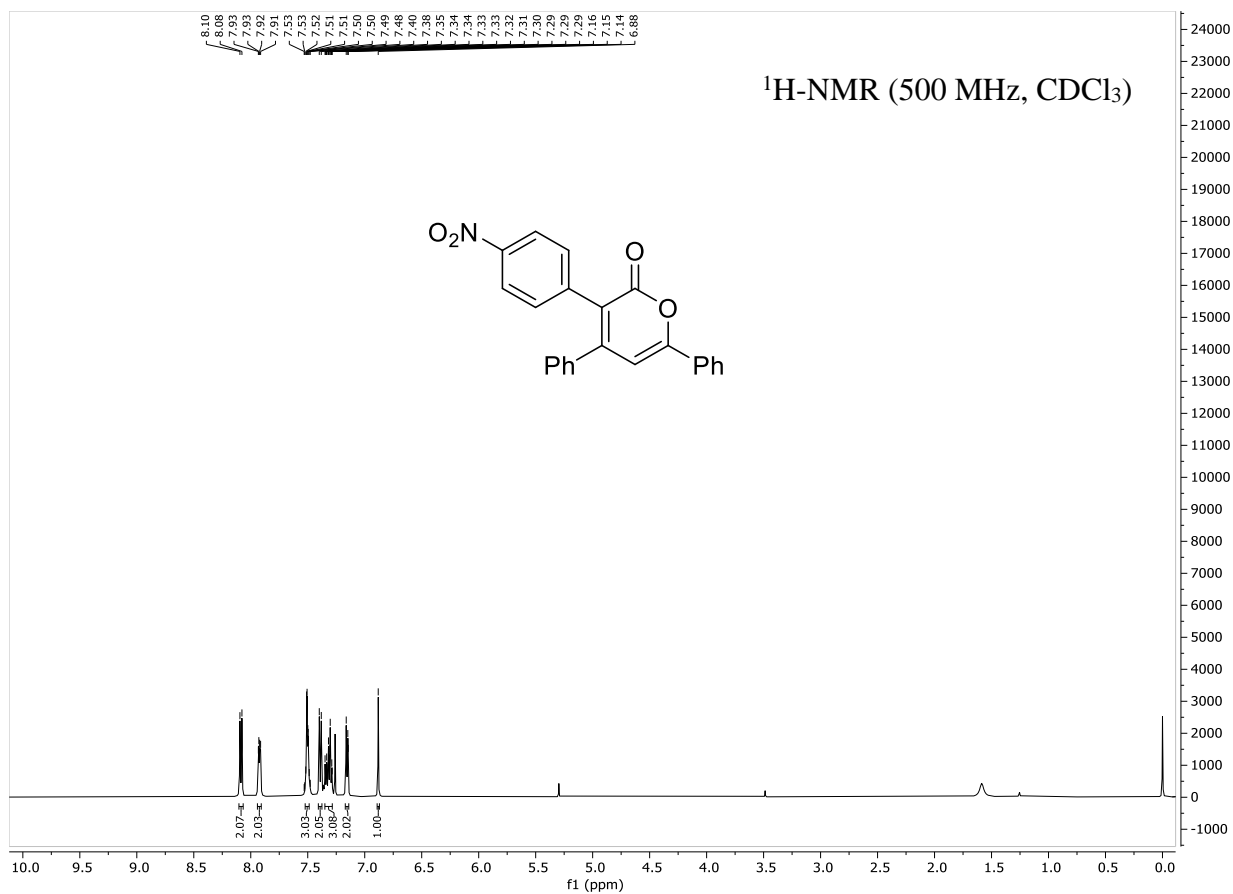
### 3-(2-Chlorophenyl)-4,6-diphenyl-2H-pyran-2-one (3u)



### 3-(4-Bromophenyl)-4,6-diphenyl-2H-pyran-2-one (3v)

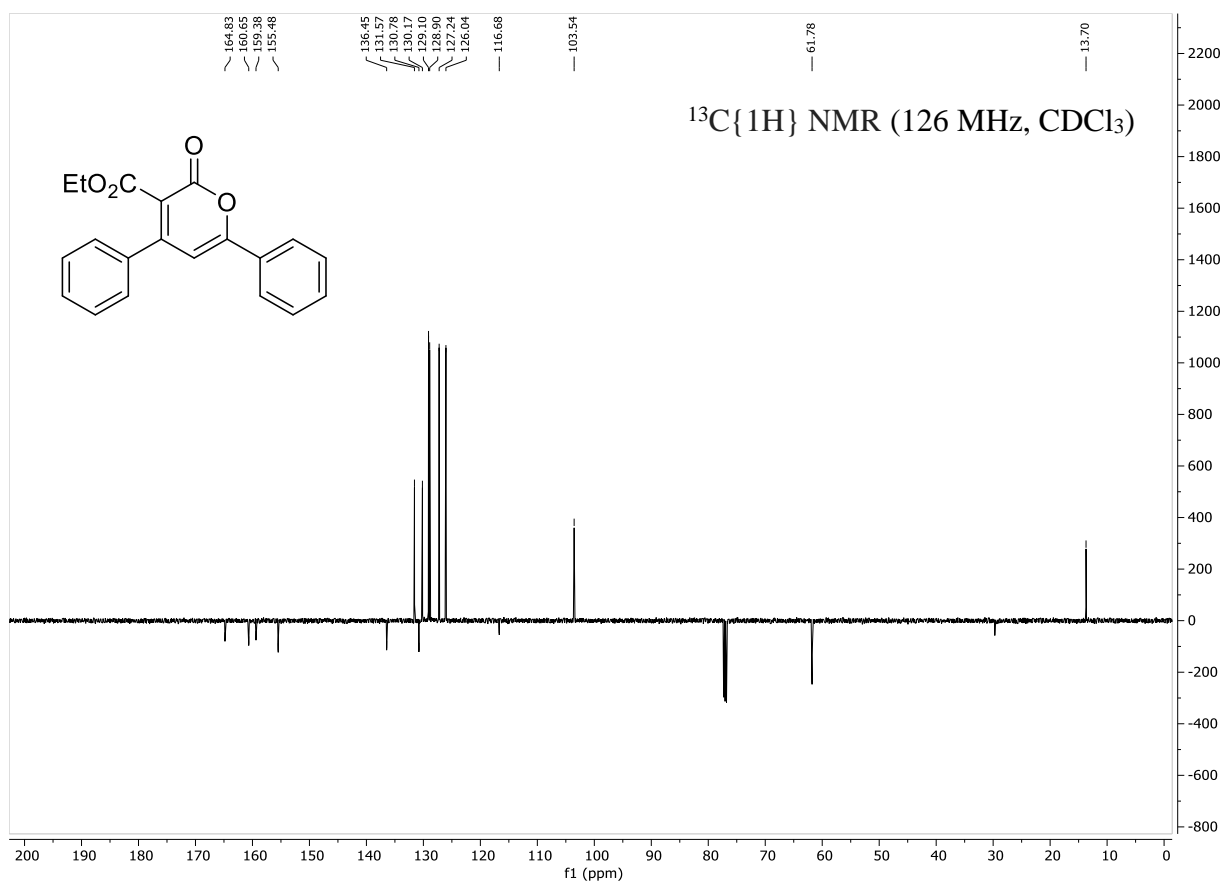
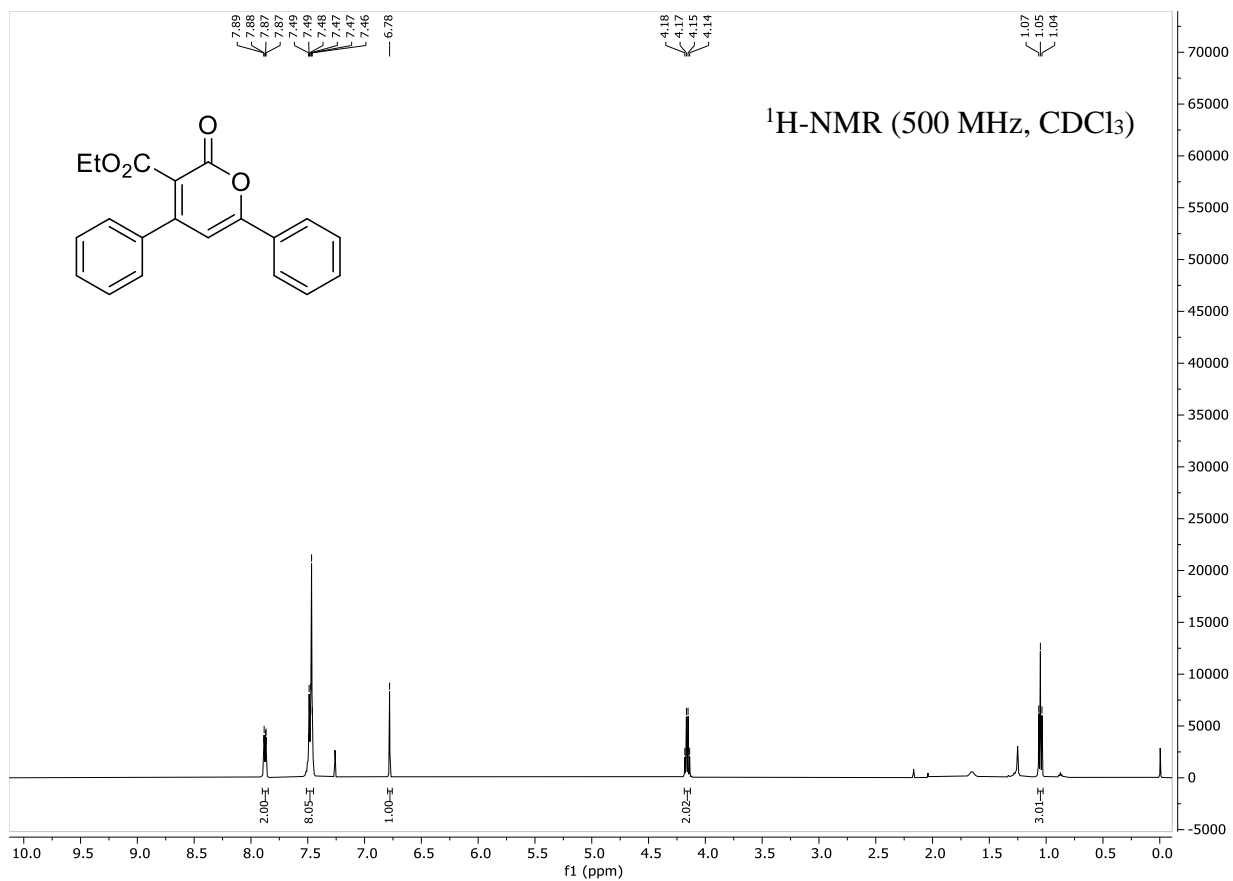


### 3-(4-Nitrophenyl)-4,6-diphenyl-2H-pyran-2-one (3w)

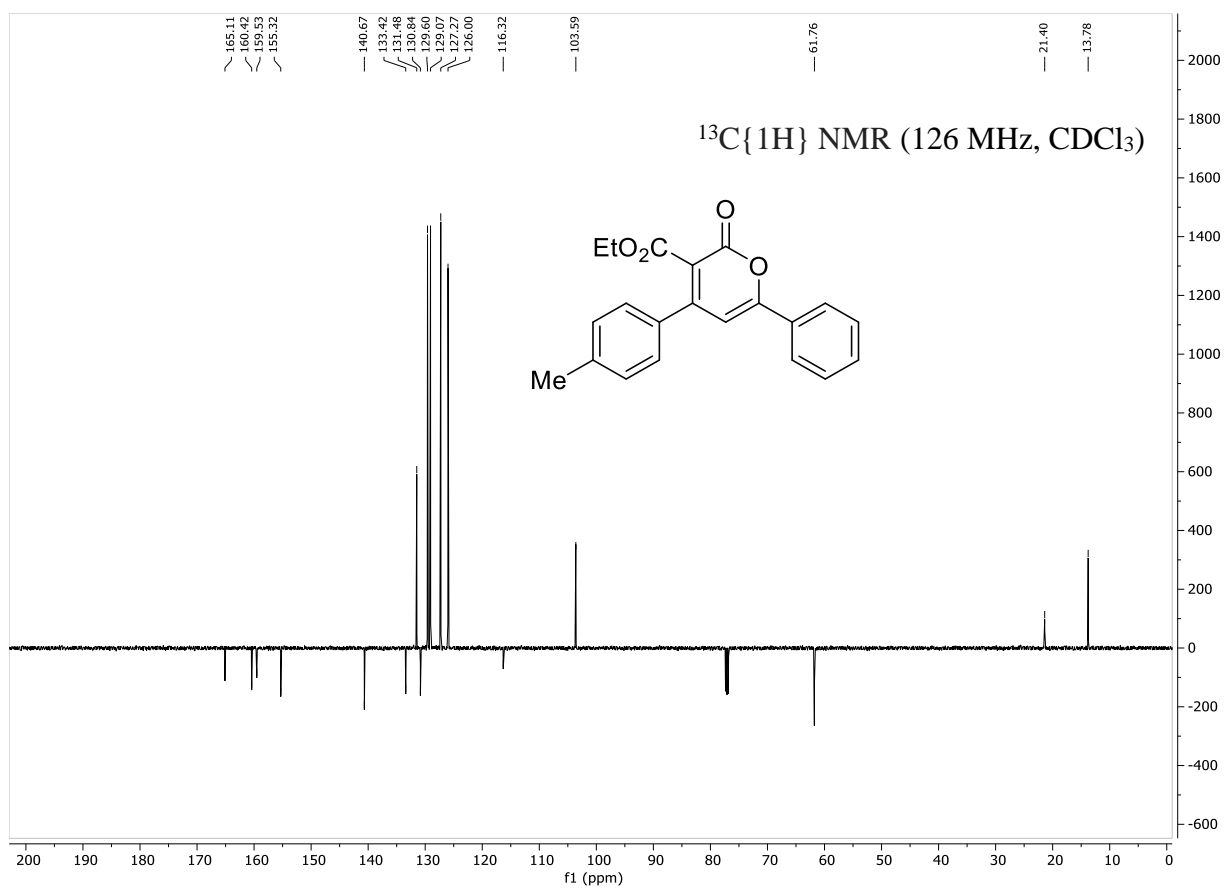
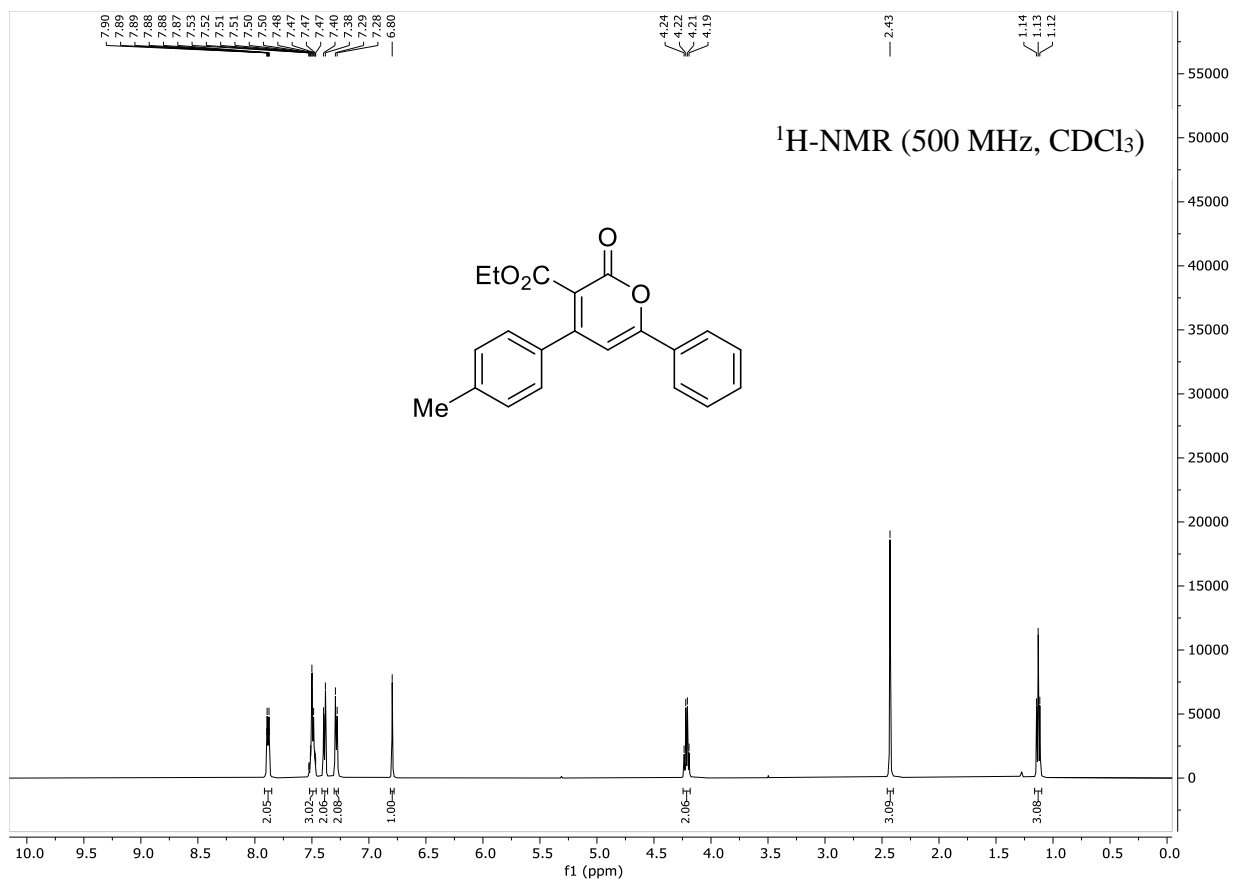




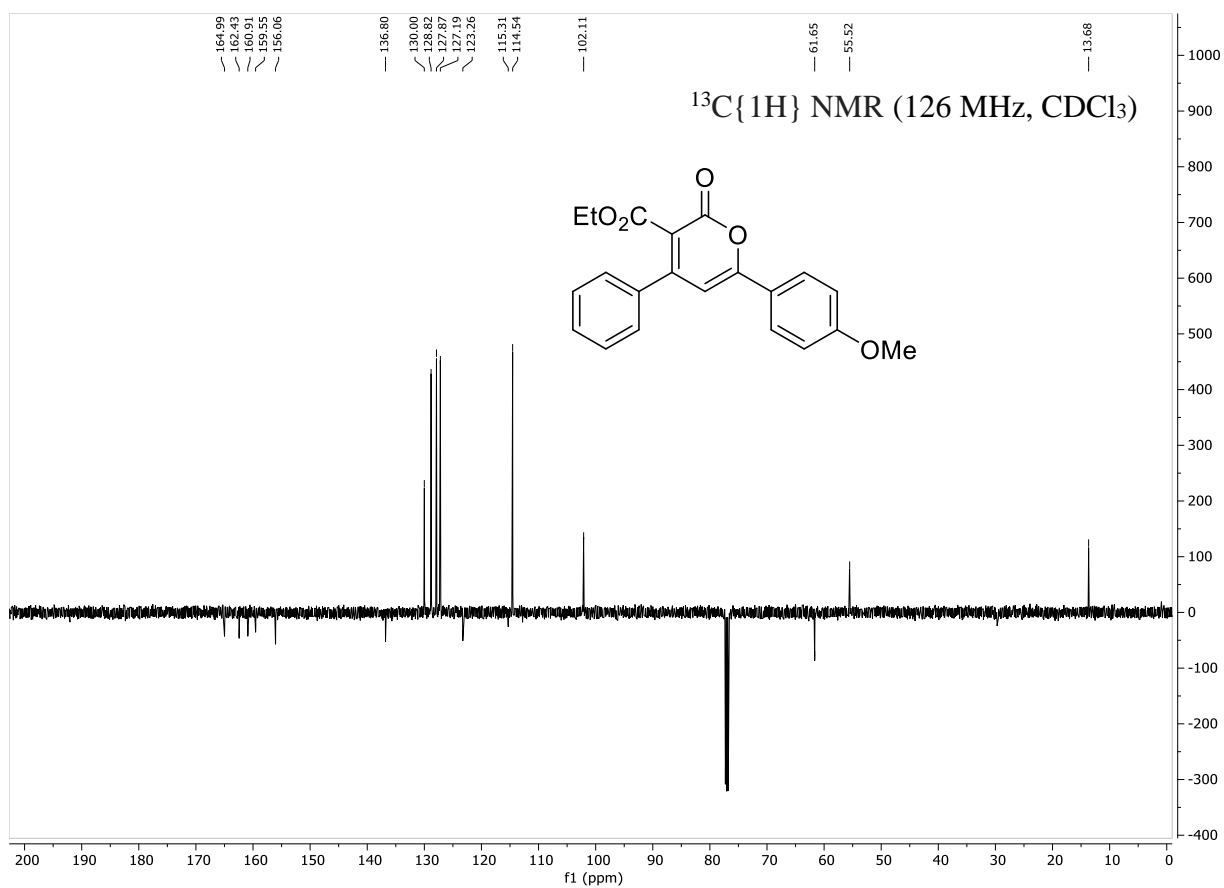
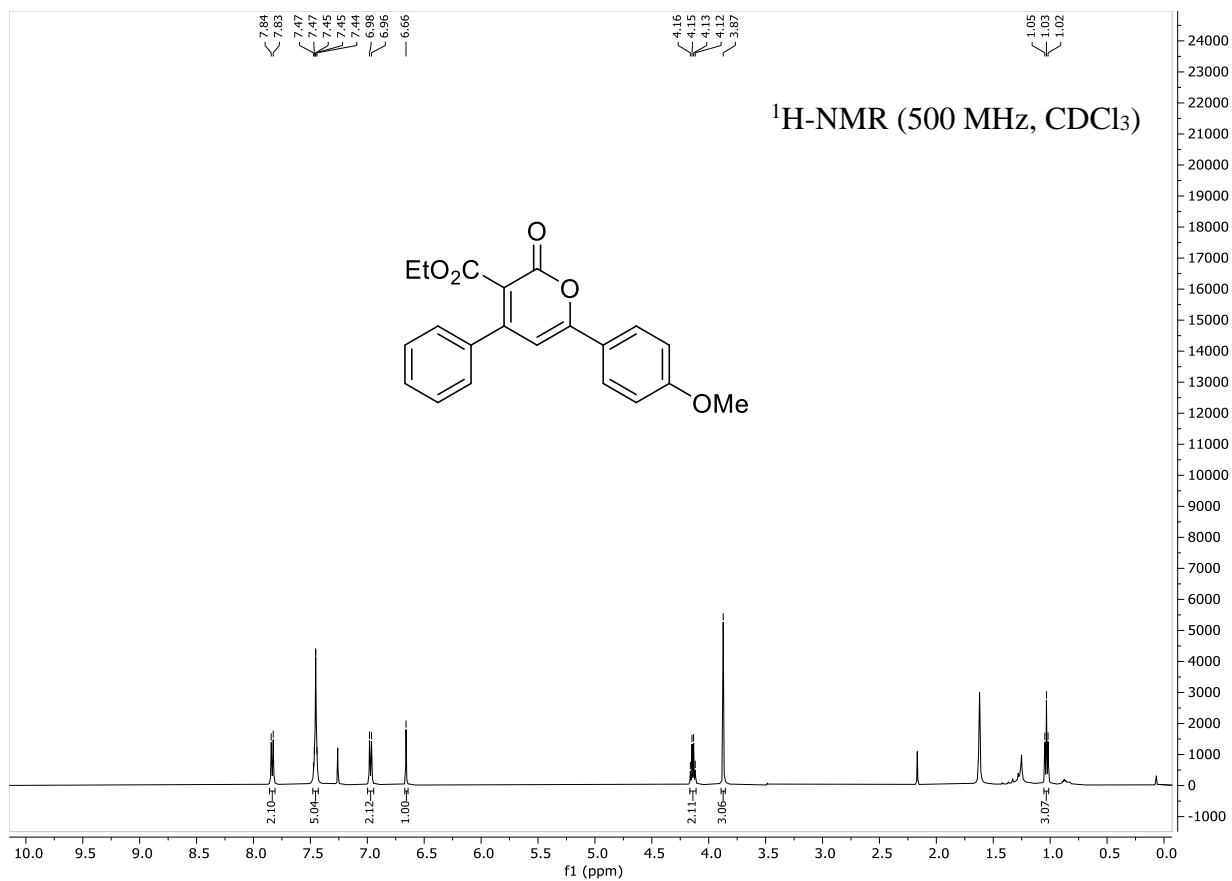
# Ethyl 2-oxo-4,6-diphenyl-2H-pyran-3-carboxylate (5a)



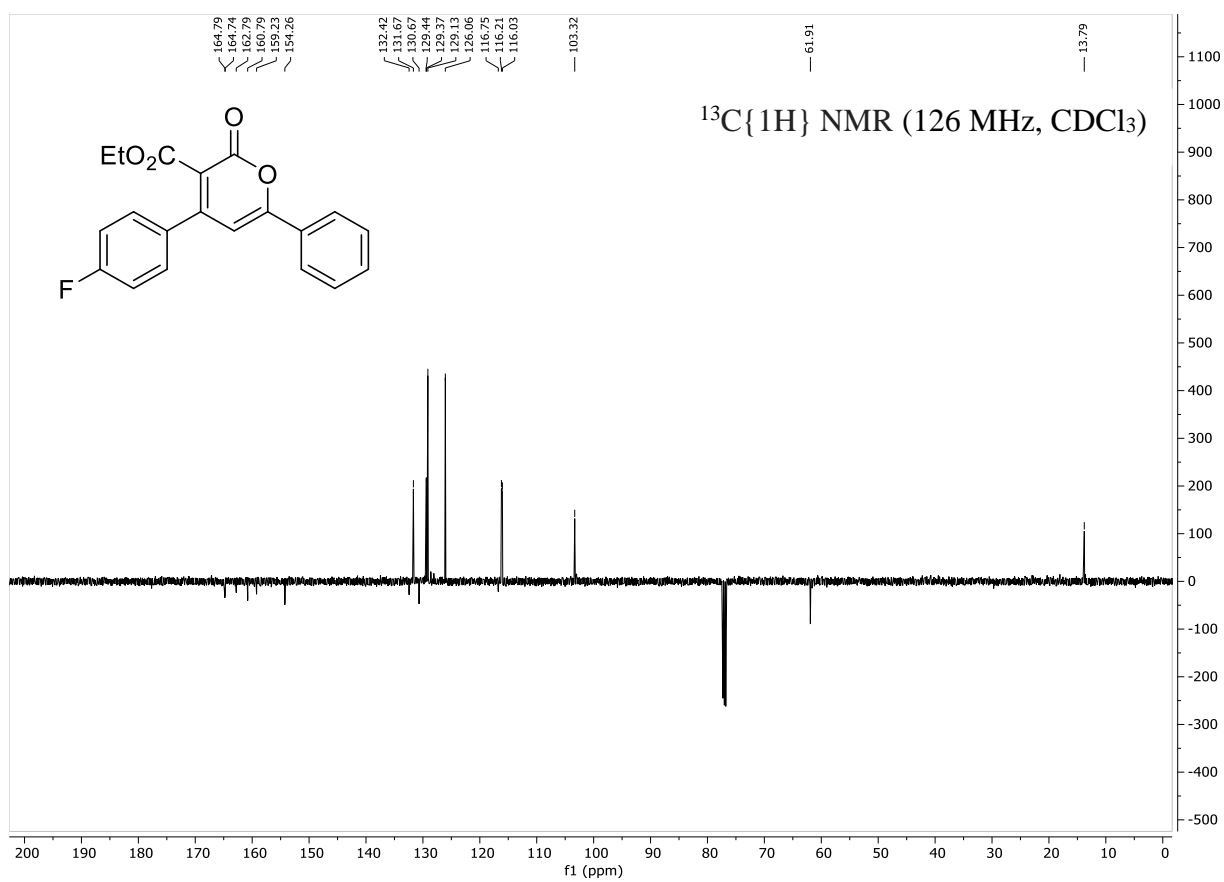
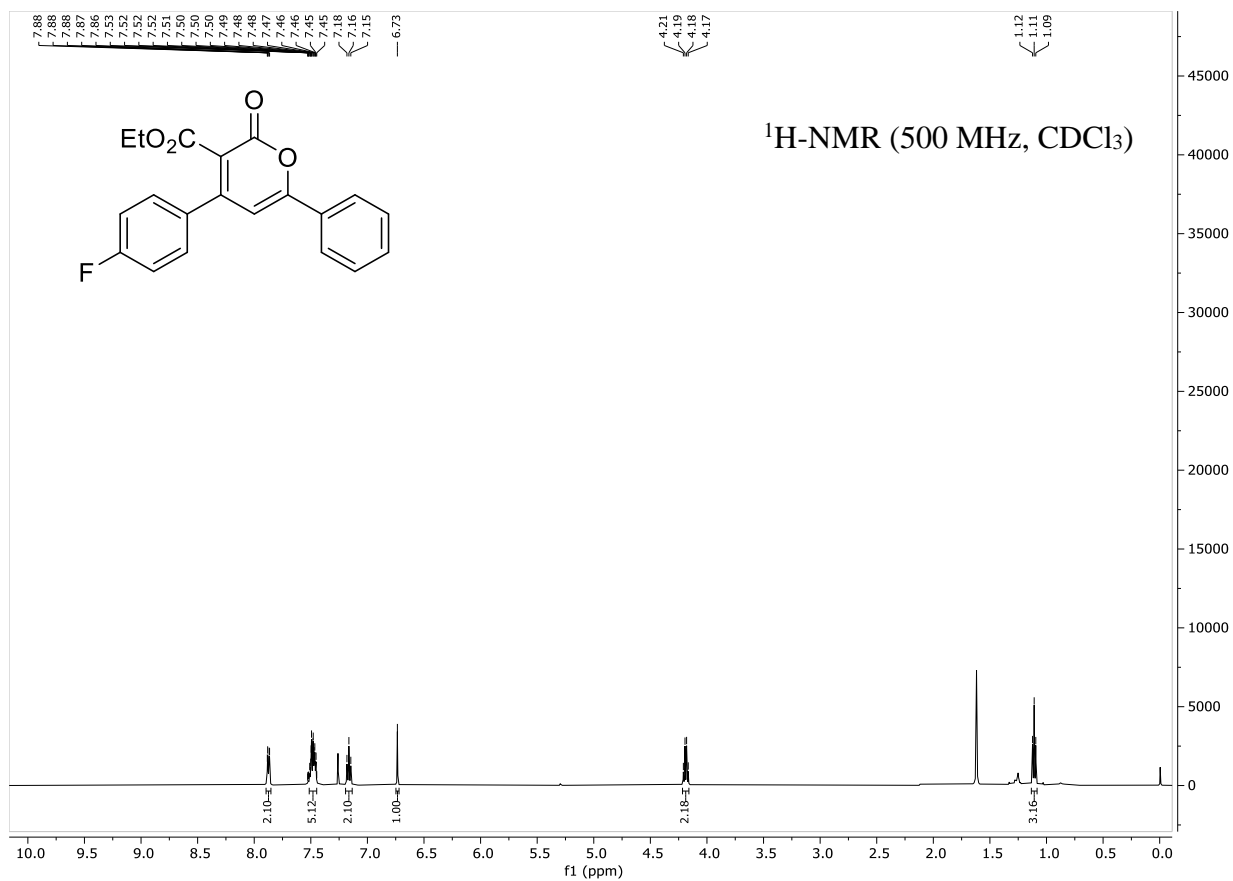
**Ethyl 2-oxo-6-phenyl-4-(p-tolyl)-2H-pyran-3-carboxylate (5b)**



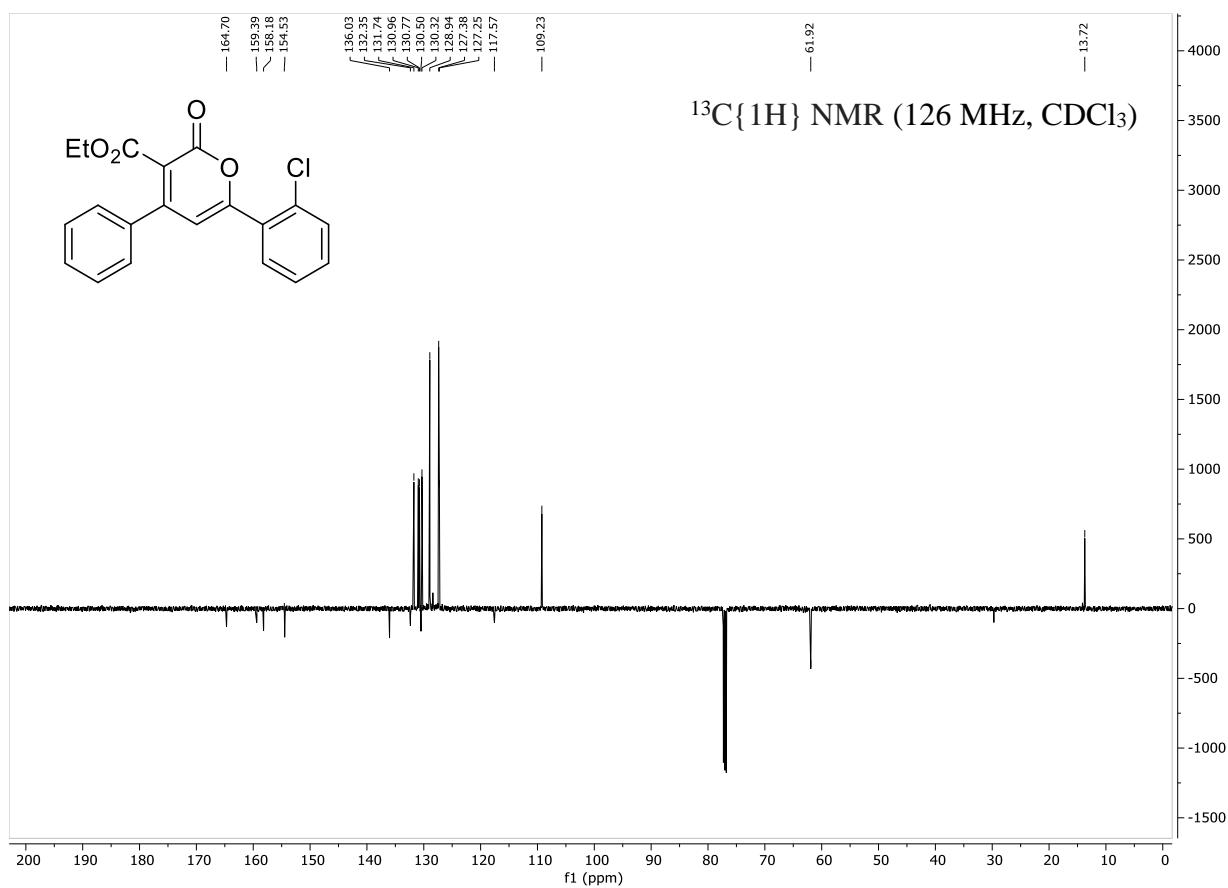
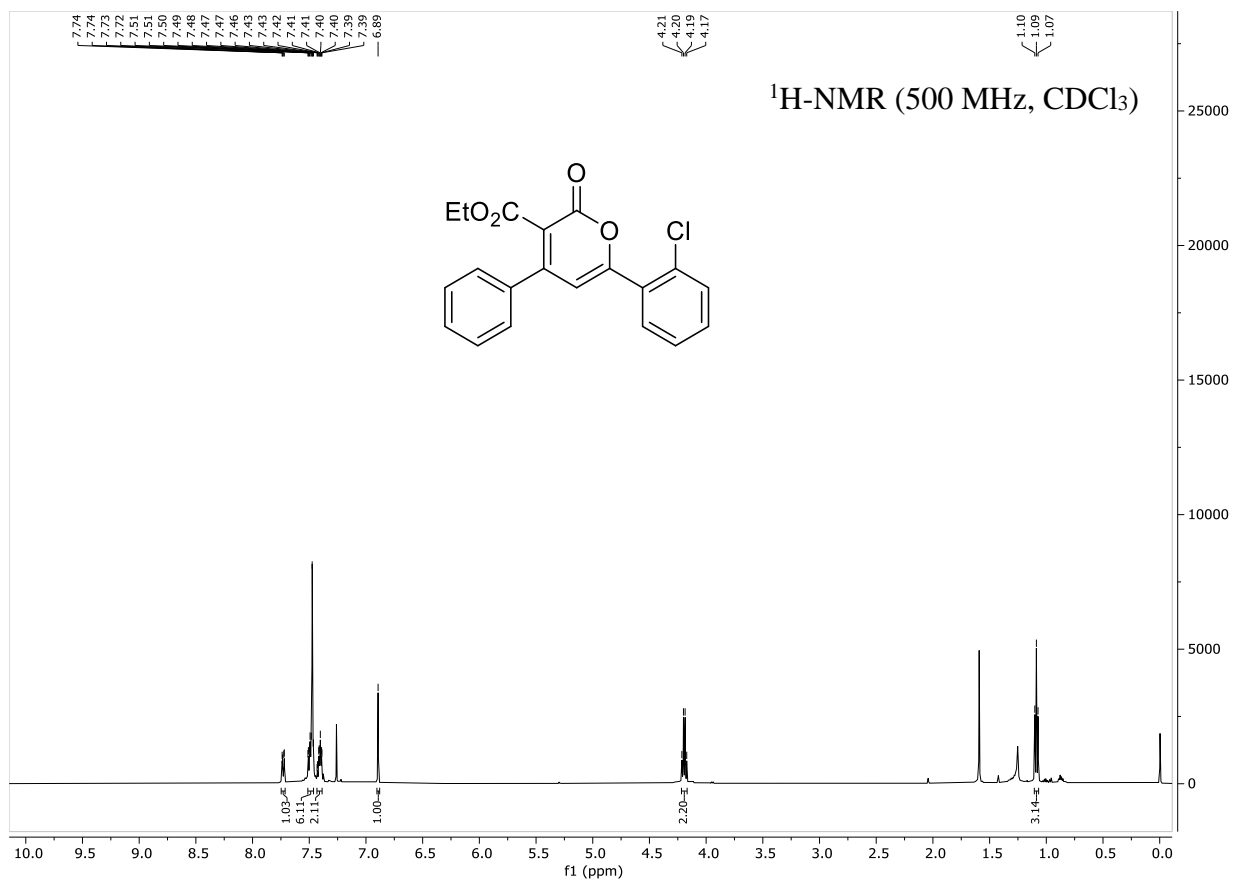
Ethyl 6-(4-methoxyphenyl)-2-oxo-4-phenyl-2H-pyran-3-carboxylate (5c)



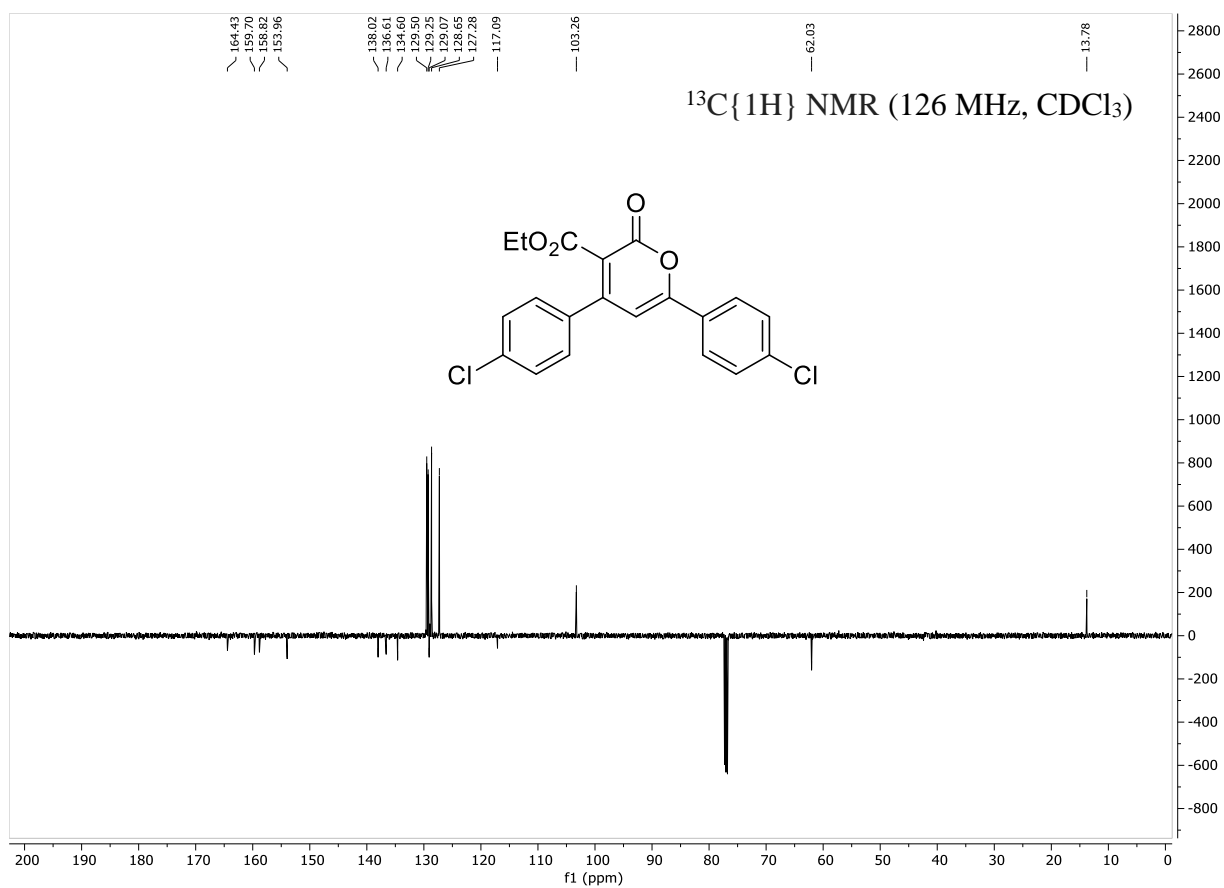
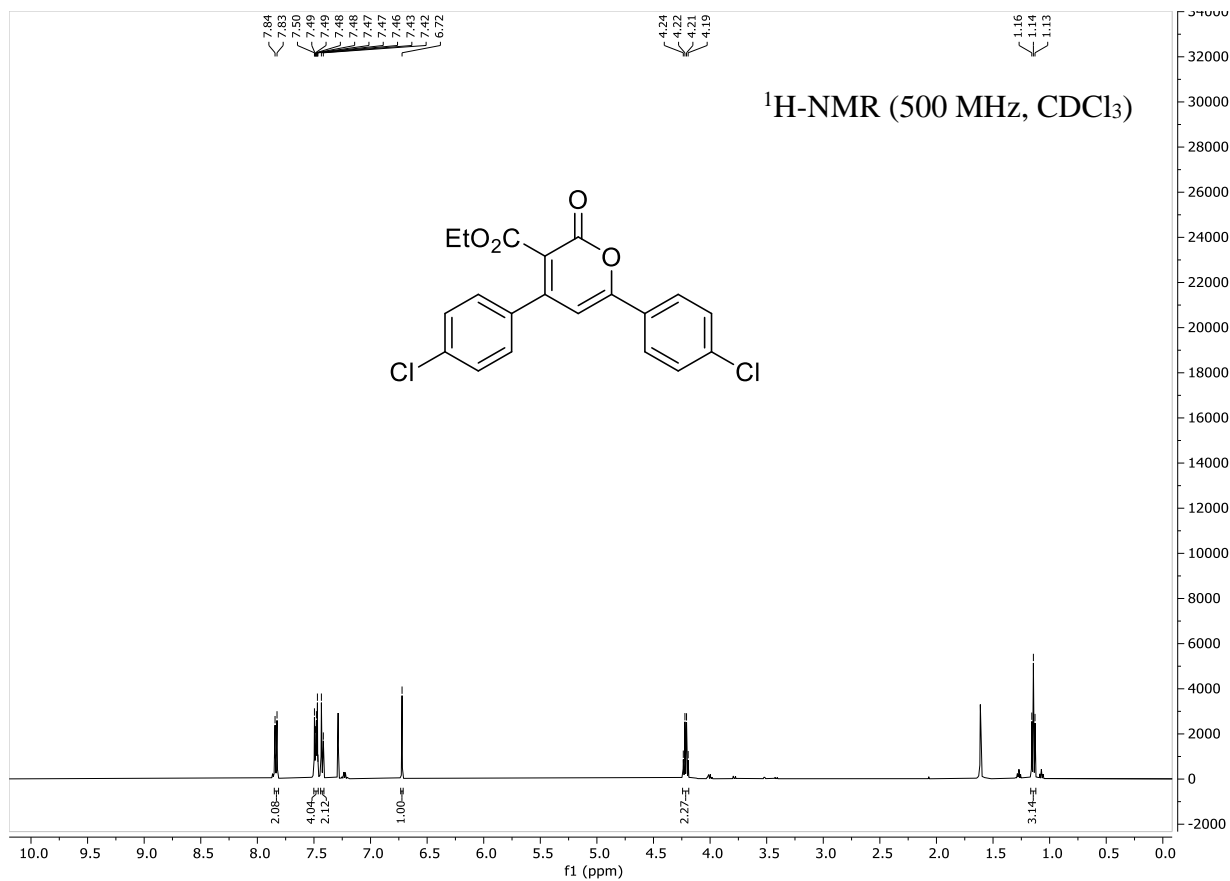
**Ethyl 4-(4-fluorophenyl)-2-oxo-6-phenyl-2H-pyran-3-carboxylate (5d)**



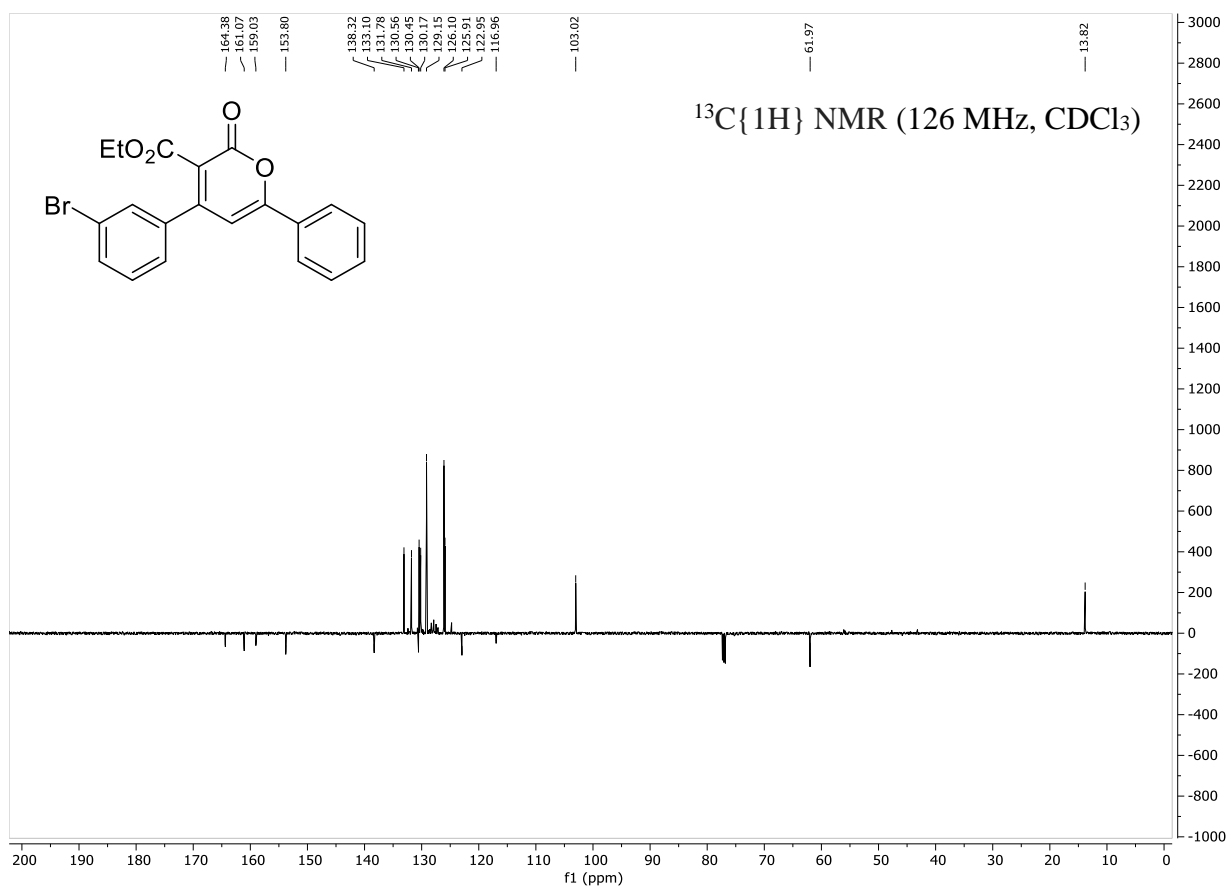
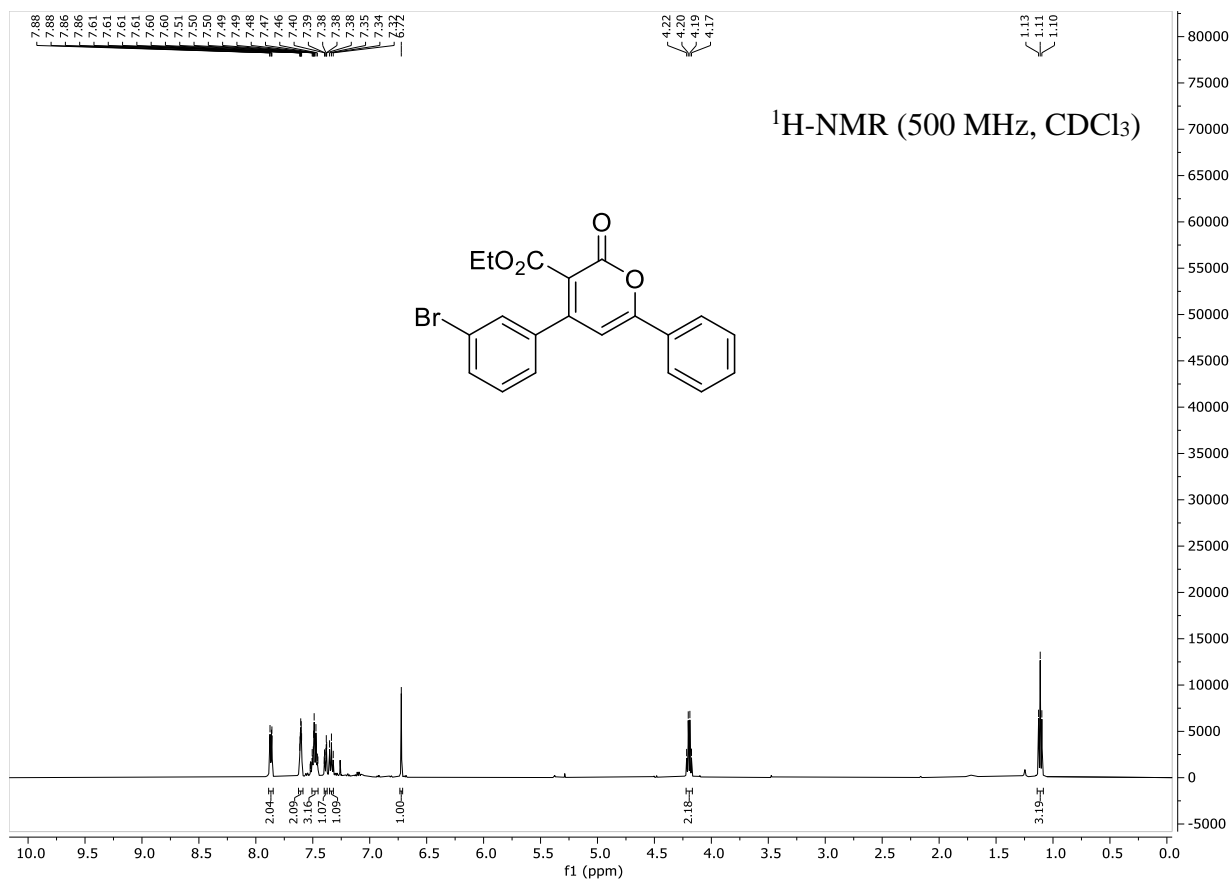
**Ethyl 6-(2-chlorophenyl)-2-oxo-4-phenyl-2H-pyran-3-carboxylate (5e)**



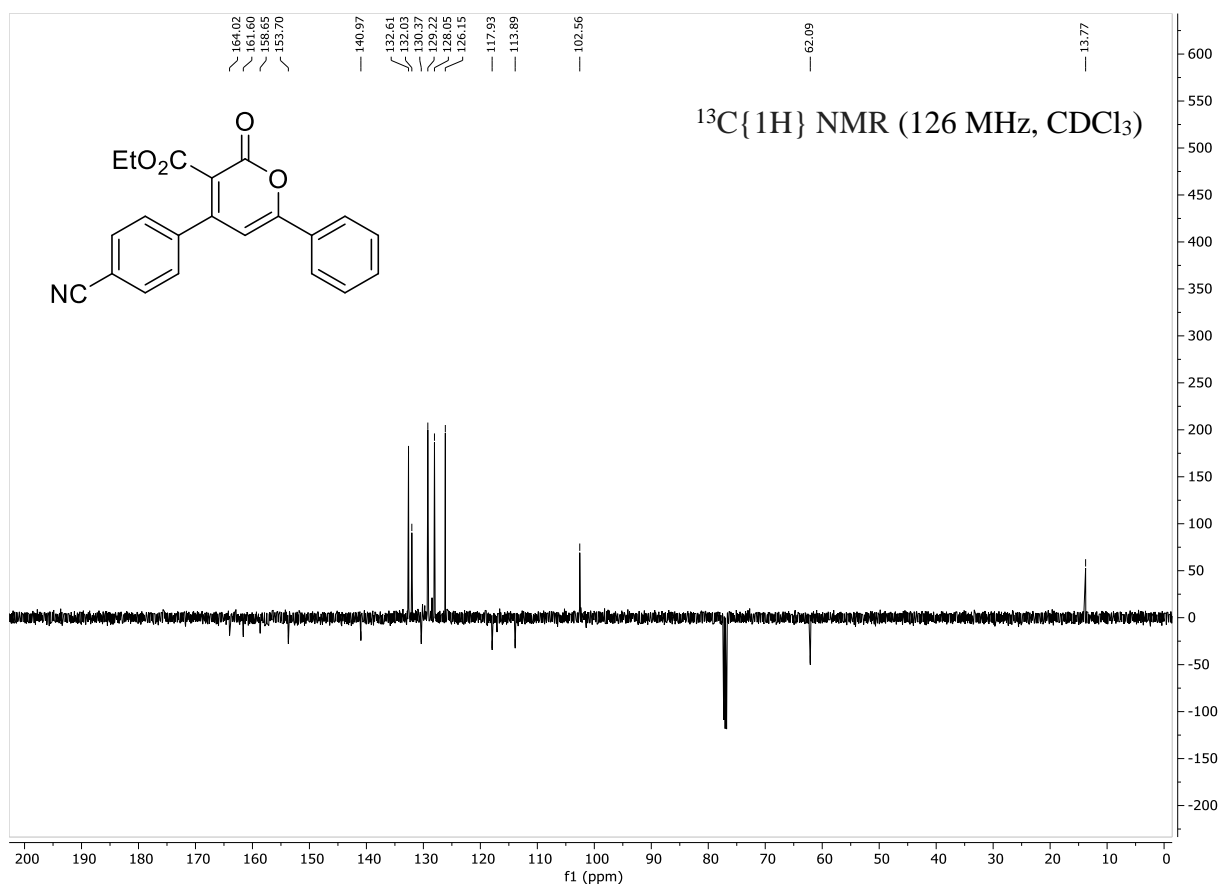
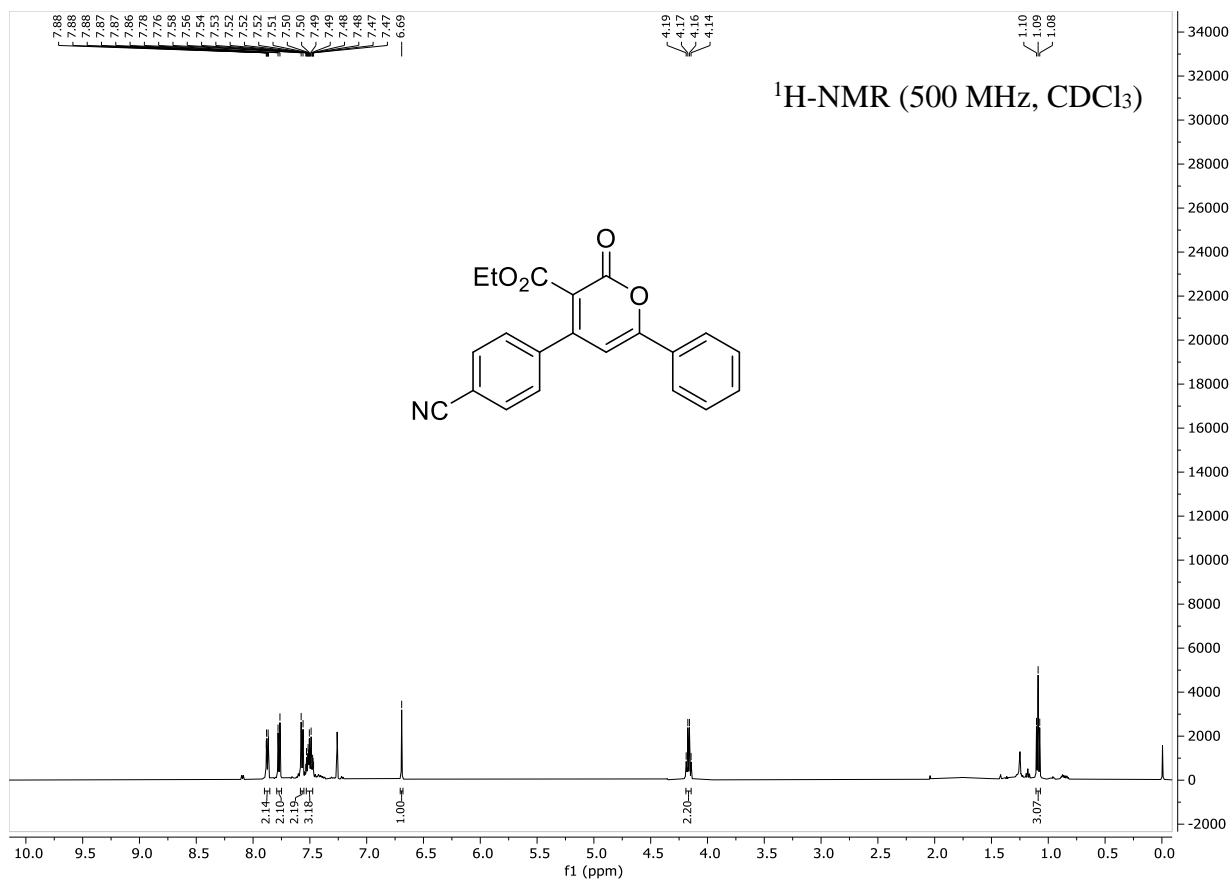
**Ethyl 4,6-bis(4-chlorophenyl)-2-oxo-2H-pyran-3-carboxylate (5f)**



Ethyl 4-(3-bromophenyl)-2-oxo-6-phenyl-2H-pyran-3-carboxylate (5g)

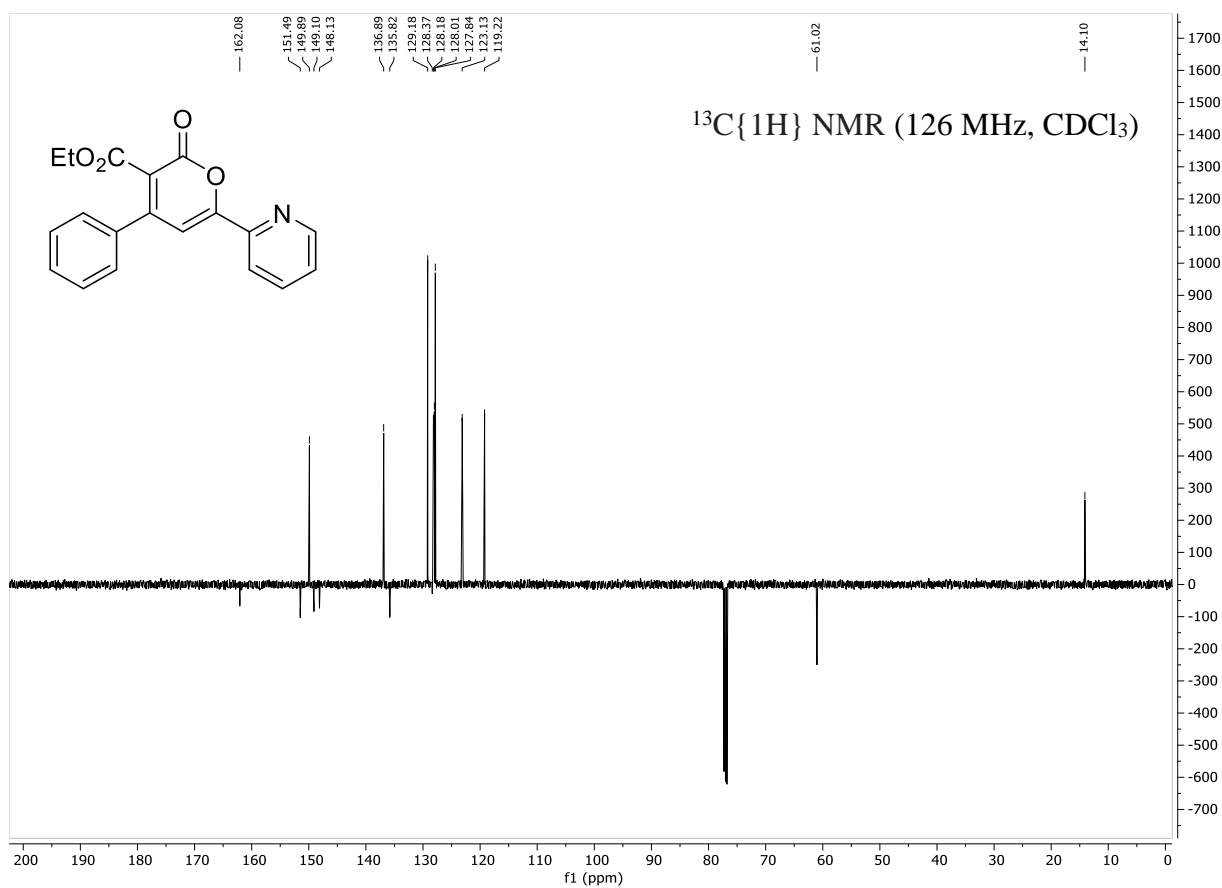
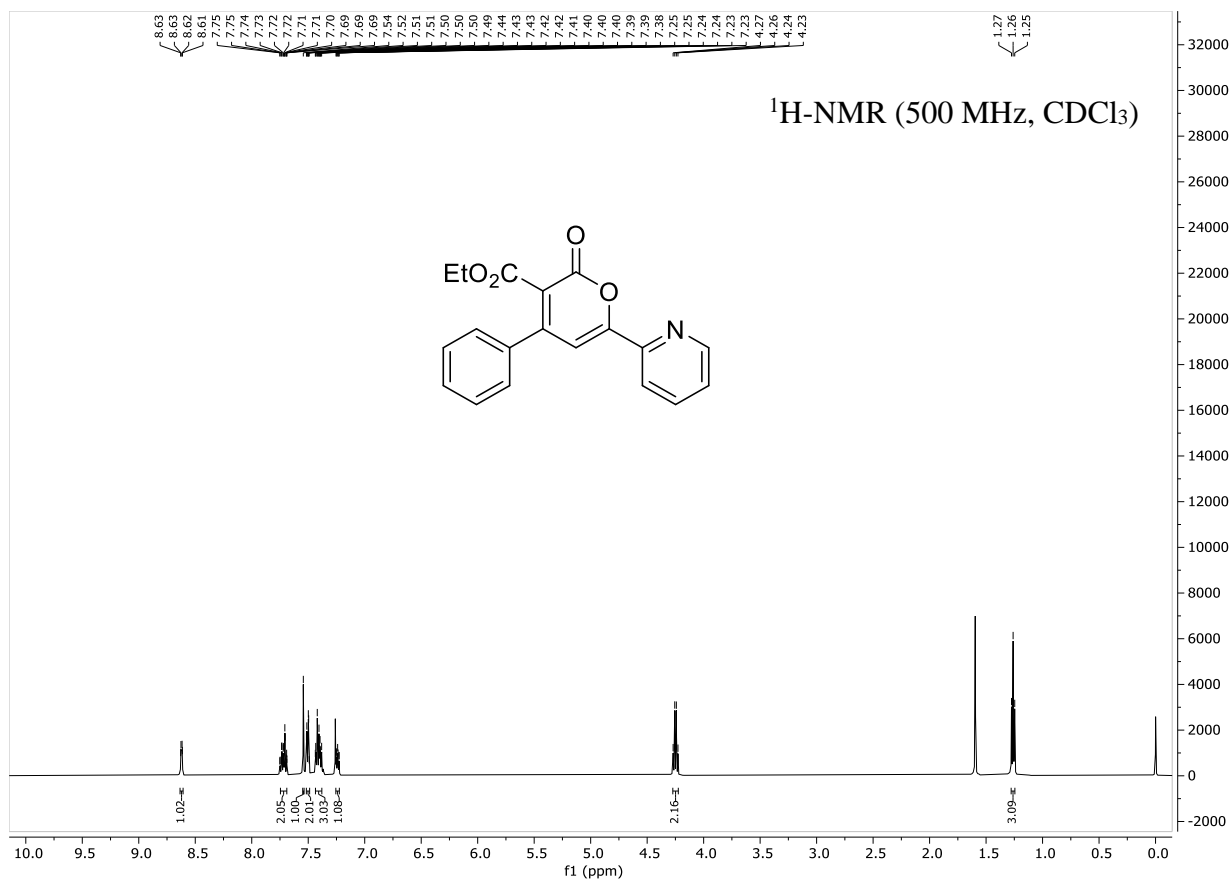


# Ethyl 4-(4-cyanophenyl)-2-oxo-6-phenyl-2H-pyran-3-carboxylate (5h)

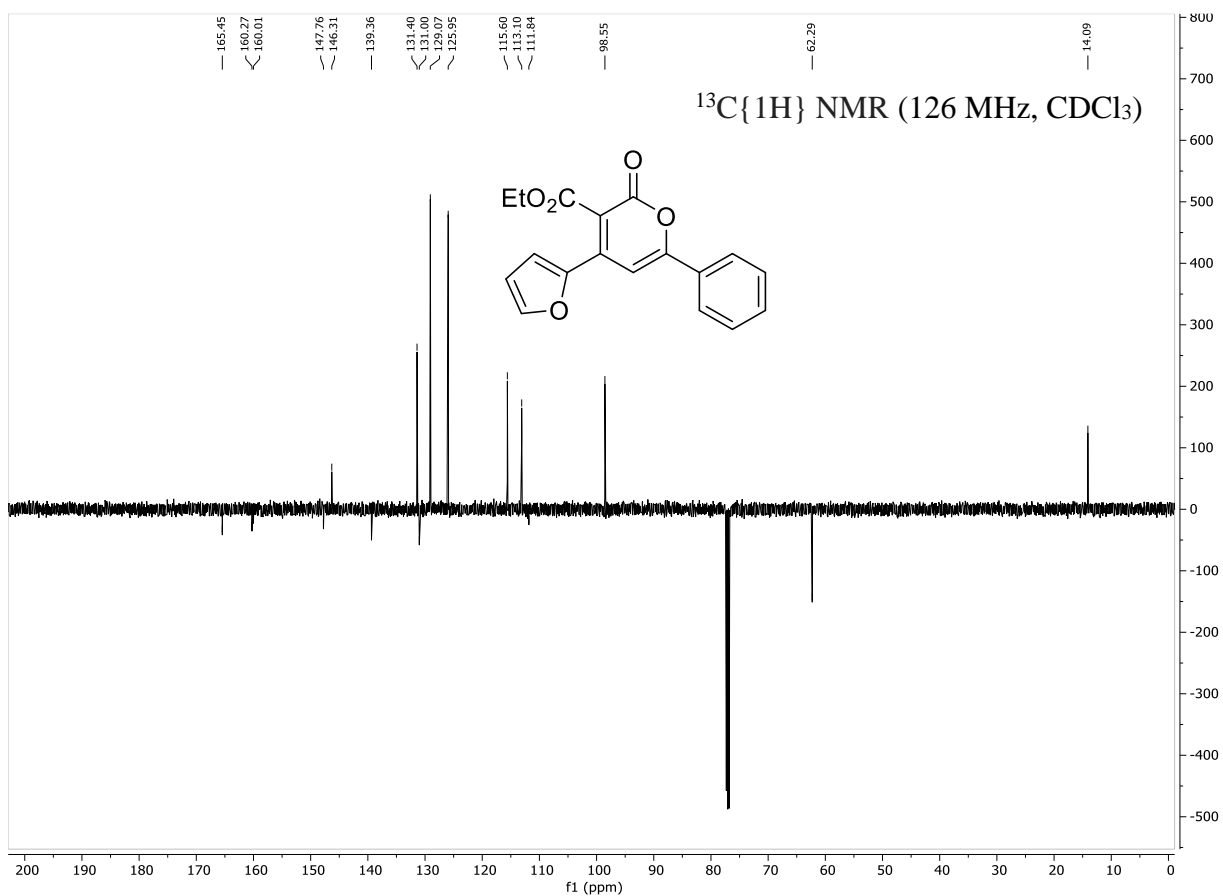
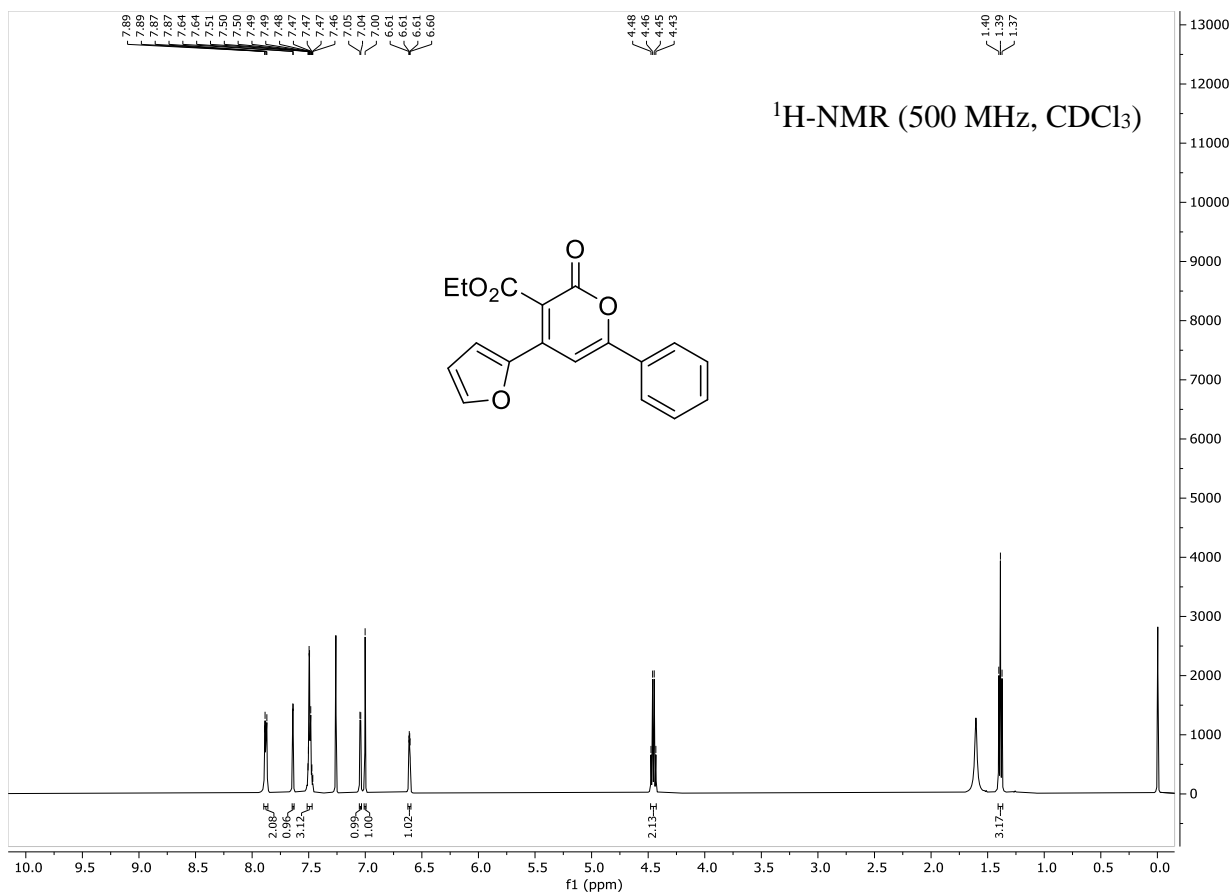




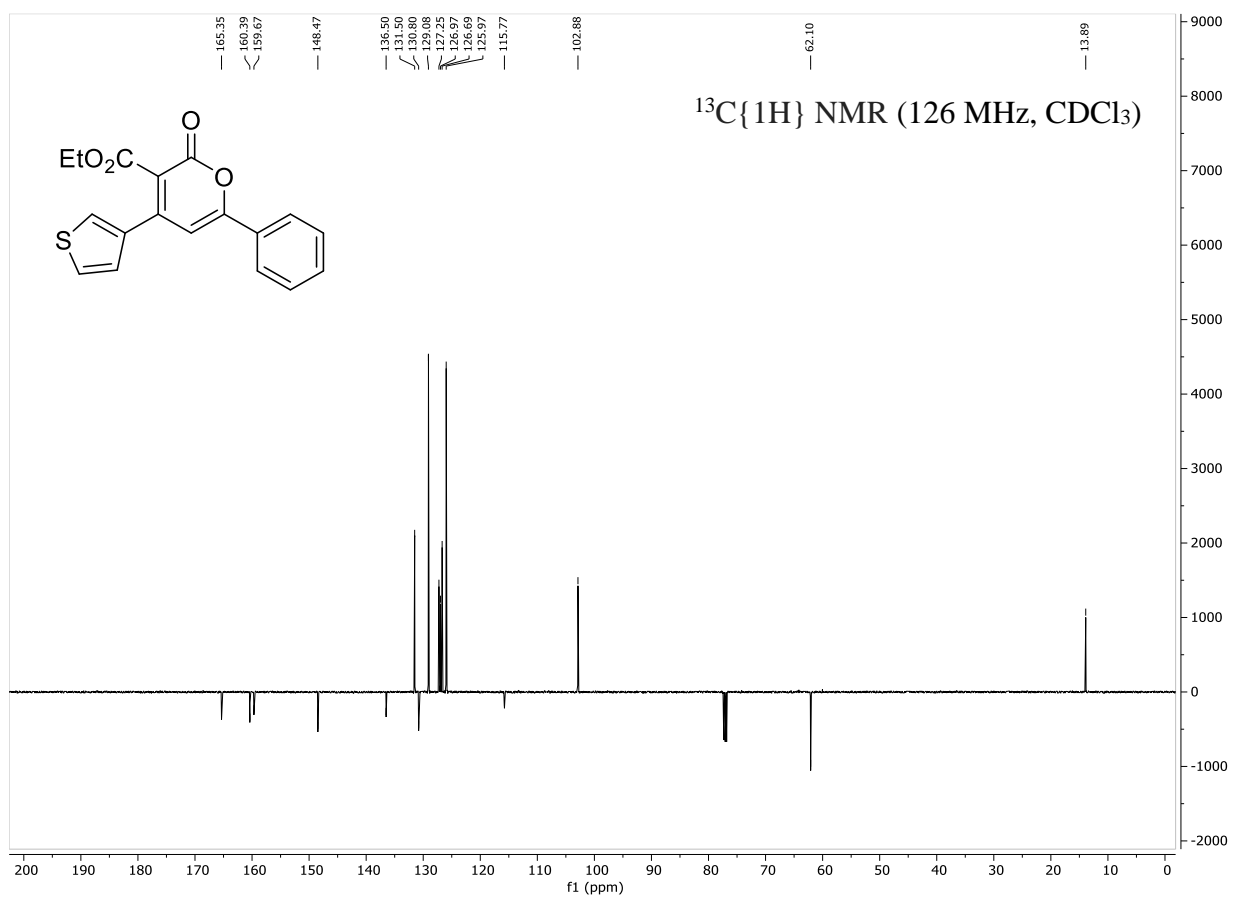
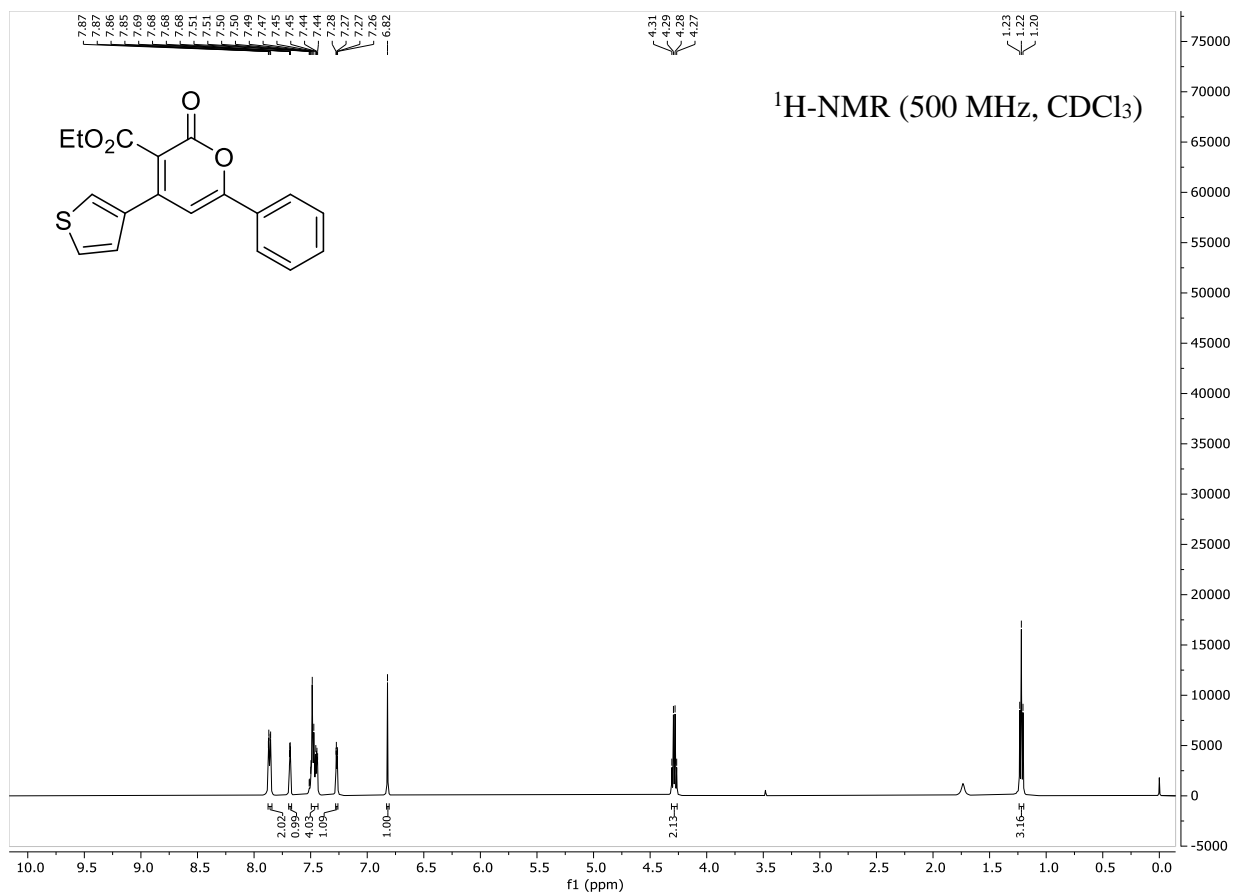
# Ethyl 2-oxo-4-phenyl-6-(pyridin-2-yl)-2H-pyran-3-carboxylate (5i)



**Ethyl 4-(furan-2-yl)-2-oxo-6-phenyl-2H-pyran-3-carboxylate (5j)**



**Ethyl 2-oxo-6-phenyl-4-(thiophen-3-yl)-2H-pyran-3-carboxylate (5k)**



Ethyl 2-oxo-4-phenyl-6-(thiophen-2-yl)-2H-pyran-3-carboxylate (5I)

