

## **Supporting Information**

### **Asymmetric Inverse-Electron-Demand Diels–Alder Reaction of $\beta,\gamma$ -unsaturated amides through Dienolate Catalysis**

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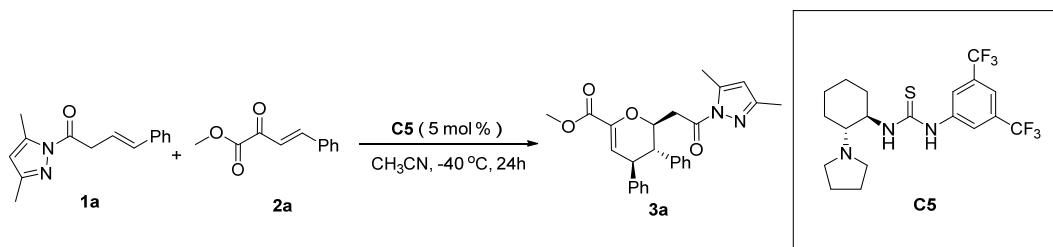
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## I. General Information.

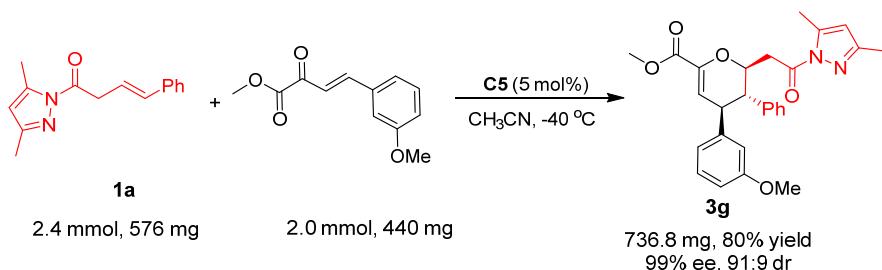
Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra and carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz and 100 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl<sub>3</sub>: 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl<sub>3</sub>: 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). High resolution mass spectra (EI) were measured on a Waters Micromass GCT spectrometer. High resolution mass spectrometry (ESI) were carried out using a Waters Quatro Macro triple quadrupole mass spectrometer. Optical rotations were measured on an Autopol III automatic polarimeter (Rudolph Research analytical). High performance liquid chromatography (HPLC) was performed on an Agilent 1260 Series chromatographs using chiral columns (DAICEL CHIRALPAK AD-H and DAICEL CHIRALPAK IB) as noted. All solvents and reagents were from commercial sources (Adamas-beta®) and used without purification unless otherwise noted. Allylic amides **1** were synthesized according to the following procedure.<sup>1,2</sup> β,γ-Unsaturated-α-ketoesters **2** were prepared according to the literature reports.<sup>3,4</sup>

## II. General procedure of Diels-Alder reaction.



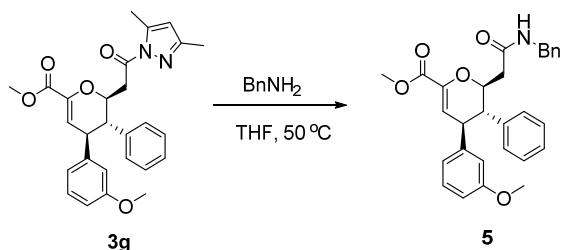
The mixture of β,γ-unsaturated amide **1a** (57.6 mg, 0.24 mmol, 1.2 equiv), β,γ-unsaturated-α-ketoester **2a** (38.0 mg, 0.2 mmol, 1.0 equiv) and catalyst **C5** (4.4 mg, 0.01 mmol) were added in 2 mL CH<sub>3</sub>CN at -40 °C and the reaction system was stirred for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography (hexanes/ethyl acetate, v:v = 10:1) to give the product **3a** (84.6 mg, 98% yield).

## Preparative-scale experiment



The mixture of  $\beta,\gamma$ -unsaturated amide **1a** (576 mg, 2.4 mmol, 1.2 equiv),  $\beta,\gamma$ -unsaturated- $\alpha$ -ketoester **2** (440 mg, 2.0 mmol, 1.0 equiv) and catalyst **C5** (44 mg, 0.1 mmol) were added in 20 mL CH<sub>3</sub>CN at -40 °C and the reaction was stirred for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography (hexanes/ethyl acetate, v:v = 10:1) to give the product **3g** (736.8 mg, 80% yield).

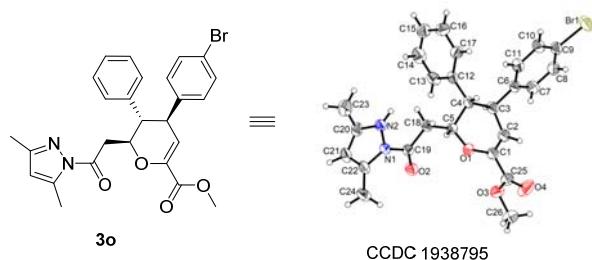
### III. Derivatization of product.



A dried 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with **3g** (92.1 mg, 0.2 mmol, 1.0 equiv) and BnNH<sub>2</sub> (42.9 mg, 0.4 mmol, 2.0 equiv). Anhydrous THF (2.0 mL) was added via syringe. The resulting mixture was stirred at 50 °C for 6 hours and then purified by silica gel column chromatography (hexanes/ethyl acetate, v:v = 10:1) to give **5** (84.9 mg, white solid, 90% yield).

### IV. X-ray crystallographic analysis.

CCDC 1938795 (**3o**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Table S1** Crystal data and structure refinement for **3an**.

Identification code	qjl01-20190307-2
Empirical formula	C <sub>26</sub> H <sub>26</sub> BrN <sub>2</sub> O <sub>4</sub>
Formula weight	510.40
Temperature/K	213.99(11)
Crystal system	orthorhombic
Space group	P <sub>2</sub> 12 <sub>1</sub> 2 <sub>1</sub>
a/Å	7.01180(10)
b/Å	11.39930(10)
c/Å	29.9026(3)

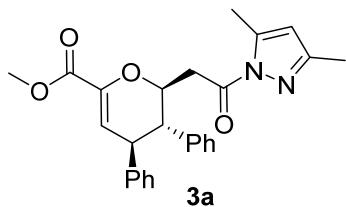
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	2390.10(5)
Z	4
$\rho_{\text{calcd}}/\text{cm}^3$	1.418
$\mu/\text{mm}^{-1}$	2.630
F(000)	1052.0
Crystal size/mm <sup>3</sup>	0.15 × 0.1 × 0.1
Radiation	CuK $\alpha$ ( $\lambda = 1.54184$ )
2 $\Theta$ range for data collection/°	5.912 to 153.618
Index ranges	-7 ≤ h ≤ 8, -10 ≤ k ≤ 14, -36 ≤ l ≤ 37
Reflections collected	13198
Independent reflections	4812 [ $R_{\text{int}} = 0.0252$ , $R_{\text{sigma}} = 0.0258$ ]
Data/restraints/parameters	4812/0/301
Goodness-of-fit on F <sup>2</sup>	1.035
Final R indexes [I>=2σ (I)]	$R_1 = 0.0265$ , $wR_2 = 0.0698$
Final R indexes [all data]	$R_1 = 0.0273$ , $wR_2 = 0.0704$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.22/-0.39
Flack parameter	-0.006(5)

## V. References

1. (a) Liu, X.; An, R.; Zhang, X.; Luo, J.; Zhao, X. *Angew. Chem., Int. Ed.* **2016**, 55, 5846-5850. (b) Zhang, H.-J.; Shi, C.-Y.; Zhong, F.; Yin, L. *J. Am. Chem. Soc.* **2017**, 139, 2196-2199.
2. (a) Dujardin, G.; Leconte, S.; Benard, A.; Brown, E. *Synlett.* **2001**, 1, 147-149. (b) Chang, J.-B.; Song, X.-X.; Hua, Y.-Z.; Liu, M.-M.; Wang, M.-C. *Chem. Eur. J.* **2015**, 21, 11994-11998.

## VI. Characterization Data

**3a: Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**



White solid, 85.2 mg, 99% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 81.3 (*c* 0.697, CH<sub>2</sub>Cl<sub>2</sub>), 90:10 d.r., 99% ee.

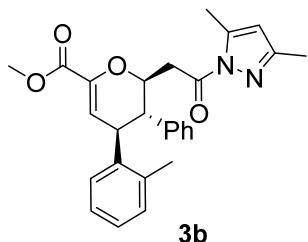
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.11 (m, 6H), 7.00 – 6.94 (m, 2H), 6.89 – 6.84 (m, 2H), 6.25 (d, *J* = 2.5 Hz, 1H), 5.89 (d, *J* = 1.1 Hz, 1H), 4.96 (ddd, *J* = 10.5, 8.6, 3.1 Hz, 1H), 3.82 – 3.78 (m, 3H), 3.77 (d, *J* = 2.6 Hz, 1H), 3.50 (m, 1H), 3.07 (m, 1H), 2.89 (t, *J* = 10.5 Hz, 1H), 2.47 (d, *J* = 1.0 Hz, 3H), 2.17 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.60, 163.06, 151.84, 144.23, 141.41, 139.21, 128.63, 128.41, 128.28, 127.91, 127.24, 126.85, 115.35, 111.12, 77.04, 52.19, 51.77, 47.52, 39.13, 14.44, 13.76.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 431.1926, found: 431.1975.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254nm): Rt (major) = 10.890 min, Rt (minor) = 12.153 min.

**3b: Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(o-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 80.2 mg, 90% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 85.3 (*c* 0.747, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r., 99% ee.

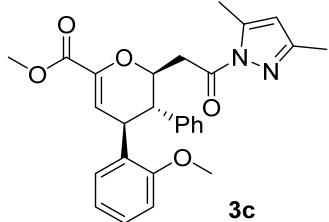
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.14 (m, 5H), 7.06 (td, *J* = 7.3, 1.8 Hz, 1H), 7.00 – 6.92 (m, 3H), 6.17 (d, *J* = 2.5 Hz, 1H), 5.92 (d, *J* = 1.1 Hz, 1H), 5.08 (ddd, *J* = 10.6, 8.9, 2.9 Hz, 1H), 4.06 (dd, *J* = 10.3, 2.6 Hz, 1H), 3.79 (s, 3H), 3.55 (m, 1H), 3.13 (m, 1H), 3.03 (t, *J* = 10.4 Hz, 1H), 2.52 (d, *J* = 1.0 Hz, 3H), 2.20 (s, 3H), 1.75 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.68, 163.10, 151.87, 144.10, 143.95, 139.70, 139.34, 136.19, 130.18, 128.58, 128.30, 127.75, 127.24, 126.63, 126.31, 116.24, 111.12, 77.07, 52.15, 51.36, 43.19, 39.22, 19.17, 14.46, 13.77.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 445.2083, found: 445.2023.

HPLC analysis: (IB column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt(major) = 11.956 min, Rt (minor) = 28.872 min.

**3c: Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(2-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 57.1 mg, 62% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 63.0 (*c* 0.482,  $\text{CH}_2\text{Cl}_2$ ), >95:5 d.r., 99% ee.

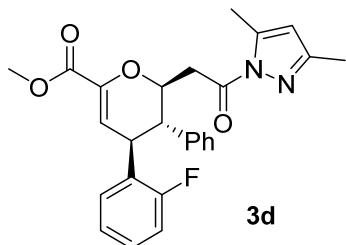
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.19 – 7.10 (m, 5H), 7.05 – 7.00 (m, 2H), 6.88 (td, *J* = 7.5, 1.1 Hz, 1H), 6.66 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.19 (d, *J* = 2.5 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 5.01 (ddd, *J* = 10.4, 8.8, 3.0 Hz, 1H), 4.38 (dd, *J* = 10.5, 2.6 Hz, 1H), 3.79 (s, 3H), 3.52 (m, 1H), 3.39 (s, 3H), 3.12 – 2.99 (m, 2H), 2.50 (d, *J* = 1.0 Hz, 3H), 2.20 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.71, 163.19, 157.05, 151.77, 144.10, 143.81, 139.43, 129.73, 128.48, 128.15, 127.84, 126.89, 120.70, 116.34, 111.07, 110.71, 77.35, 55.16, 52.10, 50.37, 39.79, 39.31, 14.48, 13.79.

HRMS (ESI) *m/z* calculated for  $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_4[\text{M}+\text{H}]^+$ : 461.2032, found: 461.2080.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 14.268 min, Rt (minor) = 12.786 min.

**3d: Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(2-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 82.7 mg, 92% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 79.2 (*c* 0.722,  $\text{CH}_2\text{Cl}_2$ ), >95:5 d.r., >99% ee.

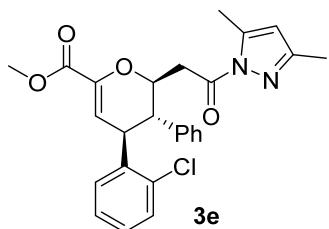
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.22 – 7.11 (m, 5H), 7.07 – 7.01 (m, 3H), 6.83 (ddd, *J* = 9.9, 8.6, 1.3 Hz, 1H), 6.18 (d, *J* = 2.4 Hz, 1H), 5.92 (d, *J* = 1.1 Hz, 1H), 5.01 (ddd, *J* = 10.4, 8.6, 3.0 Hz, 1H), 4.21 (dd, *J* = 10.5, 2.4 Hz, 1H), 3.80 (s, 3H), 3.53 (m, 1H), 3.14 – 3.01 (m, 2H), 2.50 (d, *J* = 0.9 Hz, 3H), 2.20 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.49, 162.94, 159.37, 151.84, 144.26, 144.06, 138.67, 129.32, 128.58, 128.53, 128.45, 128.26, 127.35, 124.26, 115.47, 114.52, 111.12, 76.78, 52.19, 50.19, 40.25, 39.14, 14.42, 13.76.

HRMS (ESI) *m/z* calculated for  $\text{C}_{26}\text{H}_{25}\text{FN}_2\text{O}_4[\text{M}+\text{H}]^+$ : 449.1832, found: 449.1829.

HPLC analysis: (IB column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 15.490 min, Rt (minor) = 23.258 min.

**3e: Methyl(2S,3S,4R)-4-(2-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 71.7 mg, 77% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 61.1 (*c* 0.593, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r., 99% ee.

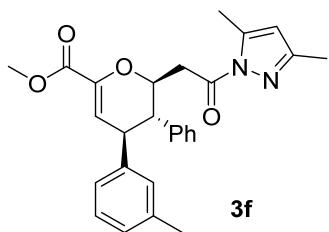
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.15 (m, 5H), 7.10 (ddd, *J* = 8.1, 7.0, 1.8 Hz, 2H), 7.05 – 7.02 (m, 2H), 6.14 (d, *J* = 2.5 Hz, 1H), 5.92 (d, *J* = 1.1 Hz, 1H), 5.04 (ddd, *J* = 10.5, 8.6, 3.1 Hz, 1H), 4.48 (d, *J* = 10.4 Hz, 1H), 3.79 (s, 3H), 3.53 (m, 1H), 3.13 (m, 2H), 2.50 (d, *J* = 1.0 Hz, 3H), 2.20 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.45, 161.90, 150.80, 143.03, 137.67, 137.25, 133.03, 128.50, 127.48, 127.42, 127.06, 126.31, 126.04, 113.80, 110.08, 75.73, 51.15, 49.25, 46.54, 38.06, 13.39, 12.72.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>4</sub>H[M+H]<sup>+</sup>: 465.1536, found: 465.1579.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 13.369 min, Rt (minor) = 12.994 min.

**3f: Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(m-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 88.0 mg, 99% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 93.2 (*c* 0.803, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r., 99% ee.

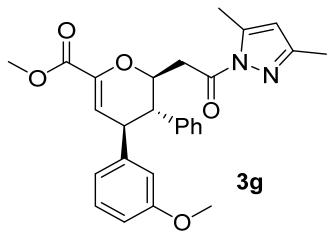
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.16 (m, 3H), 7.05 – 6.95 (m, 4H), 6.72 (d, *J* = 1.7 Hz, 1H), 6.65 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.27 (d, *J* = 2.5 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 4.97 (ddd, *J* = 10.6, 8.6, 3.1 Hz, 1H), 3.81 (s, 3H), 3.77 (dd, *J* = 10.4, 2.6 Hz, 1H), 3.52 (m, 1H), 3.09 (m, 1H), 2.92 (t, *J* = 10.5 Hz, 1H), 2.50 (d, *J* = 1.0 Hz, 3H), 2.23 (s, 3H), 2.19 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.62, 163.11, 151.82, 144.12, 141.29, 139.32, 137.87, 128.60, 128.51, 128.43, 128.05, 127.59, 127.20, 125.09, 115.60, 111.11, 76.74, 52.18, 47.40, 39.14, 21.35, 14.46, 13.77.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 445.2083, found: 445.2130.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 9.953 min, Rt (minor) = 11.103 min.

**3g: Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 91.2 mg, 99% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 89.5 (*c* 0.797, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r., >99% ee.

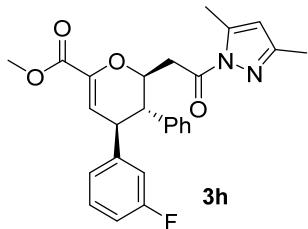
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.16 (m, 3H), 7.08 (t, *J* = 7.9 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.70 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.49 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.40 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.27 (d, *J* = 2.5 Hz, 1H), 5.91 (d, *J* = 1.2 Hz, 1H), 4.97 (ddd, *J* = 10.6, 8.7, 3.1 Hz, 1H), 3.80 (s, 3H), 3.77 (d, *J* = 2.5 Hz, 1H), 3.66 (s, 3H), 3.53 (m, 1H), 3.08 (m, 1H), 2.91 (t, *J* = 10.5 Hz, 1H), 2.49 (d, *J* = 1.0 Hz, 3H), 2.19 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.59, 163.02, 159.37, 151.84, 144.22, 142.97, 139.24, 129.23, 128.66, 128.43, 127.26, 120.26, 115.18, 113.43, 112.44, 111.12, 76.75, 55.08, 52.20, 51.56, 47.48, 39.13, 14.45, 13.77.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 461.2032, found: 461.2031.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 13.596 min, Rt (minor) = 16.440 min.

**3h: Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 88.8 mg, 99% yield (hexanes/ethyl acetate, v:v = 3:1),  $[\alpha]_D^{25}$ : 81.2 (*c* 0.769, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r., >99% ee.

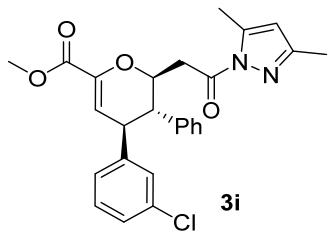
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 3H), 7.12 (td, *J* = 7.9, 6.0 Hz, 1H), 7.02 – 6.97 (m, 2H), 6.85 (tdd, *J* = 8.5, 2.6, 0.9 Hz, 1H), 6.67 – 6.60 (m, 2H), 6.23 (d, *J* = 2.5 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 4.97 (ddd, *J* = 10.6, 8.5, 3.1 Hz, 1H), 3.82 (s, 3H), 3.80 (d, *J* = 3.0 Hz, 1H), 3.52 (m, 1H), 3.09 (m, 1H), 2.89 (t, *J* = 10.5 Hz, 1H), 2.49 (d, *J* = 1.0 Hz, 3H), 2.19 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.46, 163.87, 162.90, 161.42, 151.87, 144.52, 144.06, 143.99, 138.81, 129.75, 128.86, 128.76, 128.56, 128.33, 127.46, 123.63, 114.35, 113.74, 111.15, 76.77, 52.24, 51.55, 47.21, 39.03, 14.42, 13.75.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>25</sub>FN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 449.1832, found: 449.1882.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 11.408 min, Rt (minor) = 13.559 min.

**3i: Methyl(2S,3S,4R)-4-(3-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 92.1 mg, 99% yield (hexanes/ethyl acetate, v:v = 3:1),  $[\alpha]_D^{25}$ : 87.2 (*c* 0.798, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r., 99% ee.

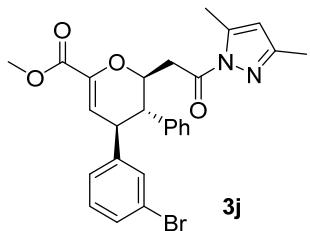
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.26 – 7.18 (m, 3H), 7.14 (ddd, *J* = 8.0, 2.1, 1.2 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.02 – 6.97 (m, 2H), 6.91 (t, *J* = 1.9 Hz, 1H), 6.72 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.22 (d, *J* = 2.5 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 4.97 (ddd, *J* = 10.6, 8.5, 3.2 Hz, 1H), 3.82 (s, 3H), 3.79 (dd, *J* = 10.4, 2.6 Hz, 1H), 3.52 (m, 1H), 3.10 (m, 1H), 2.88 (t, *J* = 10.5 Hz, 1H), 2.49 (d, *J* = 0.9 Hz, 3H), 2.19 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.47, 162.90, 151.91, 144.59, 144.08, 143.51, 138.71, 134.09, 129.49, 128.79, 128.35, 127.86, 127.49, 127.15, 126.28, 114.24, 111.17, 76.76, 52.29, 51.53, 47.19, 39.00, 14.46, 13.77.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 465.1536, found: 465.1529.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 11.293 min, Rt (minor) = 15.572 min.

**3j: Methyl (2S,3S,4R)-4-(3-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 90.5 mg, 89% yield (hexanes/ethyl acetate, v:v = 3:1),  $[\alpha]_D^{25}$ : 79.2 (*c* 0.783, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r., 99% ee.

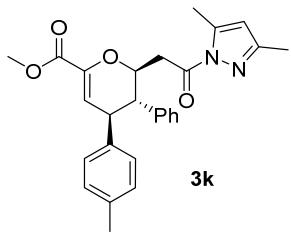
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.30 – 7.17 (m, 4H), 7.07 (t, *J* = 1.8 Hz, 1H), 7.03 – 6.97 (m, 3H), 6.76 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.22 (d, *J* = 2.4 Hz, 1H), 5.91 (d, *J* = 1.2 Hz, 1H), 4.97 (ddd, *J* = 10.6, 8.5, 3.1 Hz, 1H), 3.81 (s, 3H), 3.77 (dd, *J* = 10.4, 2.5 Hz, 1H), 3.52 (m, 1H), 3.10 (m, 1H), 2.88 (t, *J* = 10.5 Hz, 1H), 2.49 (d, *J* = 0.9 Hz, 3H), 2.19 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.45, 162.88, 151.90, 144.62, 144.07, 143.79, 138.69, 130.75, 130.07, 129.78, 128.78, 128.35, 127.50, 126.75, 122.36, 114.18, 111.17, 76.75, 52.28, 51.56, 47.17, 39.01, 14.44, 13.77.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>25</sub>BrN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 509.1031, found: 509.1039.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 11.463 min, Rt (minor) = 16.068 min.

**3k: Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(p-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 79.8 mg, 90% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 80.3 (*c* 0.691, CH<sub>2</sub>Cl<sub>2</sub>), 93:7 d.r., 99% ee.

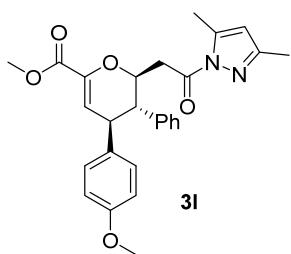
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.15 (m, 3H), 7.03 – 6.94 (m, 4H), 6.80 – 6.76 (m, 2H), 6.26 (d, *J* = 2.5 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 4.96 (ddd, *J* = 10.5, 8.7, 3.1 Hz, 1H), 3.80 (s, 3H), 3.79 – 3.76 (m, 1H), 3.52 (m, 1H), 3.08 (m, 1H), 2.90 (t, *J* = 10.5 Hz, 1H), 2.49 (d, *J* = 0.9 Hz, 3H), 2.27 (s, 3H), 2.19 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.63, 163.09, 151.81, 144.09, 144.06, 139.35, 138.33, 136.36, 128.97, 128.61, 128.45, 127.75, 127.19, 115.70, 111.10, 76.73, 52.16, 51.73, 47.06, 39.14, 21.03, 14.44, 13.77.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 445.2083, found: 445.2050.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 10.176 min, Rt (minor) = 11.353 min.

**3l: Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(4-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 56.0 mg, 61% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 63.1 (*c* 0.473, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r. 99% ee.

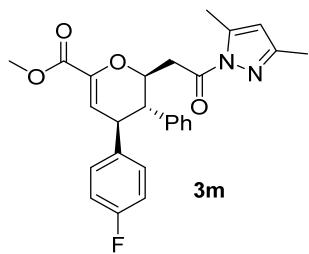
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.16 (m, 3H), 7.01 – 6.97 (m, 2H), 6.82 – 6.78 (m, 2H), 6.72 – 6.67 (m, 2H), 6.25 (d, *J* = 2.5 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 4.96 (ddd, *J* = 10.6, 8.7, 3.1 Hz, 1H), 3.81 (s, 3H), 3.77 (d, *J* = 2.5 Hz, 1H), 3.75 (s, 3H), 3.51 (m, 1H), 3.08 (m, 1H), 2.87 (t, *J* = 10.5 Hz, 1H), 2.49 (d, *J* = 1.0 Hz, 3H), 2.19 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.62, 163.10, 158.36, 151.83, 144.06, 139.37, 133.45, 129.15, 128.85, 128.77, 128.62, 128.45, 127.19, 115.74, 114.10, 113.65, 111.11, 76.77, 55.14, 52.18, 51.94, 46.70, 39.15, 14.44, 13.76.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 461.2032, found: 461.2066.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 13.669 min, Rt (minor) = 18.443 min.

**3m: Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(4-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 70.7 mg, 79% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 60.1 (*c* 0.593, CH<sub>2</sub>Cl<sub>2</sub>), 91:9 d.r., 99% ee.

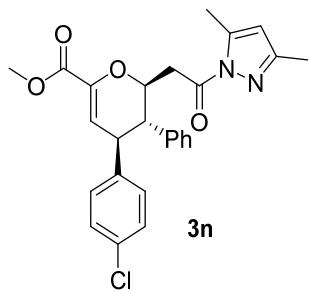
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.06 (m, 3H), 6.90 – 6.86 (m, 2H), 6.74 (d, *J* = 7.0 Hz, 4H), 6.14 (d, *J* = 2.4 Hz, 1H), 5.81 (d, *J* = 1.2 Hz, 1H), 4.88 (ddd, *J* = 11.2, 8.6, 3.0 Hz, 1H), 3.71 (s, 3H), 3.68 (d, *J* = 2.5 Hz, 1H), 3.42 (m, 1H), 2.99 (m, 1H), 2.76 (t, *J* = 10.5 Hz, 1H), 2.39 (d, *J* = 1.0 Hz, 3H), 2.09 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.66, 162.56, 159.36, 151.83, 144.38, 144.05, 143.06, 139.25, 129.22, 128.64, 128.43, 127.24, 120.29, 114.84, 113.44, 112.43, 111.10, 77.04, 61.17, 55.10, 51.62, 47.50, 39.17, 14.16.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>25</sub>FN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 449.1832, found: 449.1835.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 11.281 min, Rt (minor) = 13.312 min.

**3n: Methyl (2S,3S,4R)-4-(4-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 77.6 mg, 83% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 81.2 (*c* 0.623, CH<sub>2</sub>Cl<sub>2</sub>), 84:16 d.r., 99% ee.

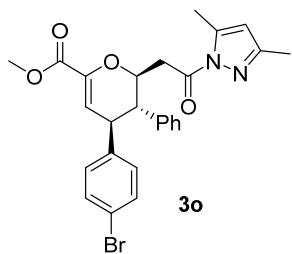
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.07 (m, 3H), 7.05 – 7.01 (m, 2H), 6.91 – 6.86 (m, 2H), 6.74 – 6.70 (m, 2H), 6.12 (d, *J* = 2.4 Hz, 1H), 5.82 (d, *J* = 1.2 Hz, 1H), 4.87 (ddd, *J* = 10.6, 8.6, 3.1 Hz, 1H), 3.71 (s, 3H), 3.68 (d, *J* = 2.5 Hz, 1H), 3.40 (d, *J* = 8.6 Hz, 1H), 2.99 (m, 1H), 2.76 (t, *J* = 10.5 Hz, 1H), 2.39 (d, *J* = 1.0 Hz, 3H), 2.09 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.48, 162.93, 151.91, 144.53, 144.09, 139.96, 138.83, 132.59, 129.50, 129.22, 129.01, 128.87, 128.77, 128.57, 128.50, 128.44, 128.37, 127.43, 114.53, 111.16, 76.74, 52.27, 51.73, 46.89, 39.02, 14.44, 13.76.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 465.1536, found: 465.1547.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 11.140 min, Rt (minor) = 13.732 min.

**3o: Methyl (2S,3S,4R)-4-(4-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 81.7 mg, 80% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 80.6 (*c* 0.679, CH<sub>2</sub>Cl<sub>2</sub>), 93:7 d.r., 99% ee.

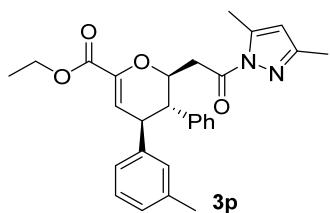
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.30 – 7.27 (m, 3H), 7.25 – 7.18 (m, 3H), 7.01 – 6.95 (m, 2H), 6.76 (dd, *J* = 8.3, 1.3 Hz, 2H), 6.21 (dd, *J* = 2.5, 1.2 Hz, 1H), 5.91 (s, 1H), 4.97 (dddd, *J* = 10.0, 8.6, 3.2, 1.2 Hz, 1H), 3.81 (d, *J* = 1.2 Hz, 3H), 3.80 – 3.76 (m, 1H), 3.51 (m, 1H), 3.09 (m, 1H), 2.85 (t, *J* = 10.5 Hz, 1H), 2.49 (d, *J* = 1.1 Hz, 3H), 2.19 (d, *J* = 1.2 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.46, 162.90, 151.88, 144.58, 144.07, 140.50, 138.80, 131.39, 129.60, 128.78, 128.37, 127.44, 120.71, 114.39, 111.15, 76.72, 52.25, 51.67, 46.96, 39.02, 14.43, 13.76.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>25</sub>BrN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 509.1031, found: 509.1077.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 11.076 min, Rt (minor) = 14.432 min.

**3p: Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(m-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 90.8 mg, 99% yield (hexanes/ethyl acetate, v:v = 3:1),  $[\alpha]_D^{25}$ : 94.7 (*c* 0.832, CH<sub>2</sub>Cl<sub>2</sub>), 91:9 d.r., 99% ee.

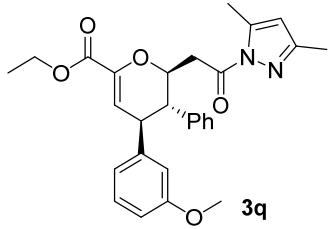
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.17 (dt, *J* = 12.3, 6.6 Hz, 3H), 7.04 – 6.92 (m, 4H), 6.71 (s, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.24 (d, *J* = 2.4 Hz, 1H), 5.88 (s, 1H), 4.94 (ddd, *J* = 10.3, 8.7, 3.2 Hz, 1H), 4.24 (qd, *J* = 7.1, 3.6 Hz, 2H), 3.75 (dd, *J* = 10.4, 2.6 Hz, 1H), 3.51 (m, 1H), 3.06 (m, 1H), 2.90 (t, *J* = 10.5 Hz, 1H), 2.47 – 2.46 (m, 3H), 2.21 (s, 3H), 2.17 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.68, 162.64, 151.80, 144.27, 144.03, 141.40, 139.34, 137.87, 128.60, 128.55, 128.43, 128.09, 127.60, 127.20, 125.11, 115.29, 111.11, 76.79, 61.15, 51.70, 47.42, 39.17, 21.37, 14.47, 14.18, 13.79.

HRMS (ESI) *m/z* calculated for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 459.2239, found: 459.2284.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 9.560 min, Rt (minor) = 10.177 min.

**3q: Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate :**



White solid, 91.0 mg, 96% yield (hexanes/ethyl acetate, v:v = 3:1),  $[\alpha]_D^{25}$ : 77.9 (*c* 0.741, CH<sub>2</sub>Cl<sub>2</sub>), 91:9 d.r., 99% ee.

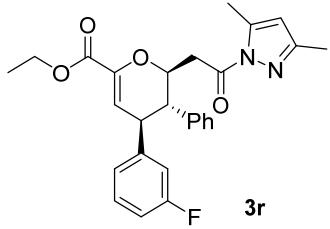
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.28 (s, 1H), 7.23 – 7.18 (m, 2H), 7.08 (t, *J* = 7.9 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.70 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.50 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.41 (dd, *J* = 2.5, 1.6 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 4.96 (ddd, *J* = 10.7, 8.7, 3.2 Hz, 1H), 4.31 – 4.23 (m, 2H), 3.81 – 3.76 (m, 1H), 3.66 (s, 3H), 3.53 (m, 1H), 3.08 (m, 1H), 2.91 (t, *J* = 10.5 Hz, 1H), 2.49 (d, *J* = 1.0 Hz, 3H), 2.20 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.66, 162.56, 159.36, 151.83, 144.38, 144.05, 143.06, 139.25, 129.22, 128.64, 128.43, 127.24, 120.29, 114.84, 113.44, 112.43, 111.10, 77.04, 61.17, 55.10, 51.62, 47.50, 39.17, 31.61, 22.68, 14.16.

HRMS (ESI) *m/z* calculated for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub>[M+H]<sup>+</sup>: 475.2188, found: 475.2233.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 12.835 min, Rt (minor) = 13.523 min.

**3r: Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 91.6 mg, 99% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 90.1(*c* 0.891, CH<sub>2</sub>Cl<sub>2</sub>), 91:9 d.r., 99% ee.

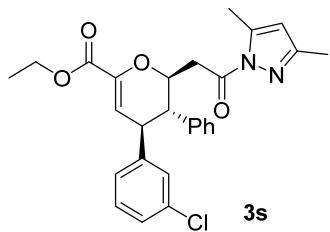
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.06 (m, 3H), 7.02 – 6.96 (m, 1H), 6.91 – 6.87 (m, 2H), 6.77 – 6.70 (m, 1H), 6.58 – 6.50 (m, 2H), 6.11 (d, *J* = 2.4 Hz, 1H), 5.80 (d, *J* = 1.2 Hz, 1H), 4.86 (ddd, *J* = 10.5, 8.6, 3.3 Hz, 1H), 4.16 (qq, *J* = 7.3, 3.7 Hz, 2H), 3.71 (dd, *J* = 10.4, 2.5 Hz, 1H), 3.41 (m, 1H), 2.98 (m, 1H), 2.79 (t, *J* = 10.5 Hz, 1H), 2.37 (d, *J* = 1.0 Hz, 3H), 2.08 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.50, 163.86, 162.41, 161.42, 151.84, 144.68, 144.02, 138.83, 129.75, 129.67, 128.74, 128.32, 127.44, 123.65, 114.02, 113.93, 112.07, 111.13, 76.74, 61.24, 51.62, 47.21, 39.06, 14.42, 14.15, 13.75.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>27</sub>FN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 463.1988, found: 463.2031.

HPLC analysis: (AD-H column, Hexane: 2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 10.908 min, Rt (minor) = 12.102 min.

**3s: Ethyl (2S,3S,4R)-4-(3-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 92.1 mg, 96% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 80.1 (*c* 0.792, CH<sub>2</sub>Cl<sub>2</sub>), 89:11 d.r., 99% ee.

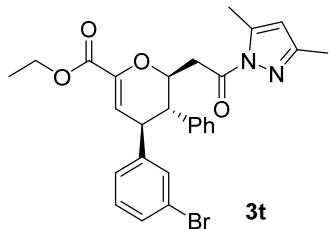
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23 – 7.15 (m, 3H), 7.11 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 7.00 – 6.95 (m, 2H), 6.90 (d, *J* = 1.9 Hz, 1H), 6.71 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 5.90 – 5.88 (m, 1H), 4.98 – 4.91 (m, 1H), 4.25 (qd, *J* = 7.1, 5.5 Hz, 2H), 3.77 (dd, *J* = 10.4, 2.5 Hz, 1H), 3.50 (m, 1H), 3.07 (m, 1H), 2.87 (t, *J* = 10.5 Hz, 1H), 2.46 (d, *J* = 1.1 Hz, 3H), 2.17 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.50, 162.42, 151.87, 144.75, 144.02, 143.60, 138.72, 134.07, 129.50, 128.34, 127.88, 127.47, 127.12, 126.30, 113.91, 111.15, 77.14, 61.28, 51.58, 47.19, 39.03, 14.45, 14.17, 13.78.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>27</sub>ClN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 479.1693, found: 479.1739.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 10.693 min, Rt (minor) = 12.677 min.

**3t: Ethyl (2S,3S,4R)-4-(3-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 103.6 mg, 99% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 92.2 (*c* 0.901, CH<sub>2</sub>Cl<sub>2</sub>), 90:10 d.r., 99% ee.

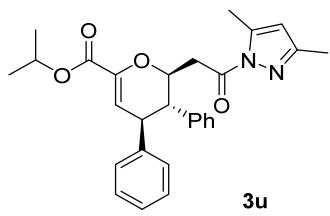
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.27 – 7.16 (m, 4H), 7.06 (t, *J* = 1.8 Hz, 1H), 7.01 – 6.95 (m, 3H), 6.75 (dt, *J* = 7.8, 1.3 Hz, 1H), 6.18 (d, *J* = 2.4 Hz, 1H), 5.89 (d, *J* = 1.1 Hz, 1H), 4.94 (ddd, *J* = 10.5, 8.6, 3.3 Hz, 1H), 4.30 – 4.20 (m, 2H), 3.75 (dd, *J* = 10.5, 2.5 Hz, 1H), 3.50 (m 1H), 3.07 (m, 1H), 2.86 (t, *J* = 10.5 Hz, 1H), 2.46 (d, *J* = 1.0 Hz, 3H), 2.17 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.50, 162.41, 151.87, 144.76, 138.69, 130.76, 130.05, 129.80, 128.77, 128.34, 127.48, 126.77, 122.36, 113.88, 111.15, 77.16, 61.29, 51.60, 47.17, 39.03, 14.46, 14.17, 13.79.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>27</sub>BrN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 523.1188, found: 523.1238.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 10.951 min, Rt (minor) = 12.673 min.

**3u: Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 90.8 mg, 99% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 77.4 (*c* 0.826, CH<sub>2</sub>Cl<sub>2</sub>), 84:16 d.r., 99% ee.

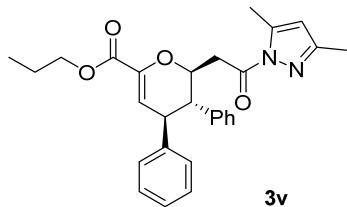
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.21 – 7.10 (m, 6H), 6.99 – 6.93 (m, 2H), 6.90 – 6.85 (m, 2H), 6.21 (d, *J* = 2.4 Hz, 1H), 5.89 (d, *J* = 1.1 Hz, 1H), 5.09 (p, *J* = 6.2 Hz, 1H), 4.95 (ddd, *J* = 10.5, 8.7, 3.3 Hz, 1H), 3.78 (dd, *J* = 10.4, 2.5 Hz, 1H), 3.51 (m, 1H), 3.05 (m, 1H), 2.90 (t, *J* = 10.5 Hz, 1H), 2.46 (dd, *J* = 3.6, 1.0 Hz, 3H), 2.17 (s, 3H), 1.26 (d, *J* = 6.2 Hz, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.71, 162.09, 151.80, 144.61, 144.04, 141.59, 139.24, 128.62, 128.40, 128.28, 127.97, 127.22, 126.83, 114.68, 111.10, 77.07, 68.74, 51.85, 47.54, 39.16, 21.80, 14.49, 13.80.

HRMS (ESI) *m/z* calculated for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 459.2239, found: 459.2285.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 11.014 min, Rt (minor) = 23.435 min.

**3v: Propyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 76.8 mg, 81% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 60.2 (*c* 0.522, CH<sub>2</sub>Cl<sub>2</sub>), 85:15 d.r., 99% ee.

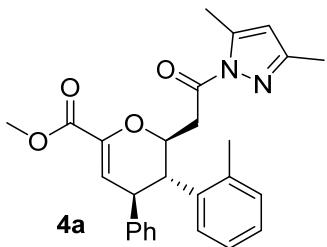
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.14 – 7.04 (m, 6H), 6.92 – 6.86 (m, 2H), 6.80 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.16 (d, *J* = 2.5 Hz, 1H), 5.84 – 5.79 (m, 1H), 4.88 (ddd, *J* = 10.6, 8.9, 3.2 Hz, 1H), 4.11 (td, *J* = 6.6, 1.2 Hz, 2H), 3.71 (dd, *J* = 10.4, 2.6 Hz, 1H), 3.48 – 3.40 (m, 1H), 2.95 (m, 1H), 2.81 (t, *J* = 10.5 Hz, 1H), 2.41 – 2.38 (m, 3H), 2.10 (s, 3H), 1.56 (dd, *J* = 8.6, 6.3 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.63, 161.60, 150.75, 143.41, 142.98, 140.48, 138.19, 127.58, 127.35, 127.23, 126.89, 126.18, 125.78, 113.86, 110.06, 75.69, 63.95, 50.85, 46.48, 38.08, 29.51, 18.11, 13.40, 12.73, 12.69.

HRMS (ESI) *m/z* calculated for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 459.2239, found: 459.2231.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 11.195 min, Rt (minor) = 10.821 min.

**4a: Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3-(o-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 87.1 mg, 98% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 84.3 (*c* 0.801, CH<sub>2</sub>Cl<sub>2</sub>), 91:9 d.r., 99% ee.

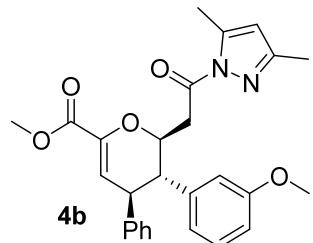
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23 (d, *J* = 4.3 Hz, 2H), 7.18 – 7.12 (m, 4H), 7.05 (dt, *J* = 7.7, 4.3 Hz, 1H), 6.92 – 6.85 (m, 2H), 6.33 (d, *J* = 2.4 Hz, 1H), 5.90 (d, *J* = 1.1 Hz, 1H), 4.99 (ddd, *J* = 11.5, 8.6, 3.2 Hz, 1H), 3.83 (s, 3H), 3.77 (dd, *J* = 10.4, 2.5 Hz, 1H), 3.50 (m, 1H), 3.22 (t, *J* = 10.4 Hz, 1H), 3.06 (m, 1H), 2.48 (d, *J* = 0.9 Hz, 3H), 2.19 (s, 3H), 1.67 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.63, 163.10, 151.77, 144.63, 144.02, 141.25, 137.92, 137.64, 130.08, 128.19, 127.86, 126.89, 126.75, 126.60, 126.29, 115.40, 111.10, 76.73, 52.22, 48.07, 46.17, 38.72, 19.45, 14.43, 13.75.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 445.2083, found: 445.2027.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 9.133 min, Rt (minor) = 10.851 min.

**4b: Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(3-methoxyphenyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 79.2 mg, 86% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 72.1 (*c* 0.611, CH<sub>2</sub>Cl<sub>2</sub>), 92:8 d.r., 99% ee.

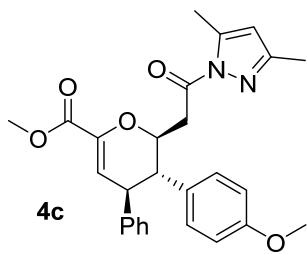
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.22 – 7.08 (m, 4H), 6.93 – 6.86 (m, 2H), 6.71 – 6.66 (m, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 2.5 Hz, 1H), 6.27 – 6.23 (m, 1H), 5.90 (s, 1H), 4.98 – 4.89 (m, 1H), 3.78 (d, *J* = 1.1 Hz, 3H), 3.76 – 3.75 (m, 1H), 3.68 (d, *J* = 1.1 Hz, 3H), 3.53 – 3.45 (m, 1H), 3.14 – 3.08 (m, 1H), 2.86 (t, *J* = 10.5 Hz, 1H), 2.48 (s, 3H), 2.17 (d, *J* = 1.1 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.58, 163.04, 159.61, 151.83, 144.21, 144.07, 141.41, 140.76, 129.62, 128.30, 127.91, 126.87, 120.94, 120.65, 114.32, 112.44, 111.09, 77.07, 55.09, 52.19, 51.80, 47.38, 39.11, 14.44, 13.76.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>[M+H]<sup>+</sup>: 461.2032, found: 461.2076.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 13.619 min, Rt (minor) = 15.048 min.

**4c: Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(4-methoxyphenyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 91.2 mg, 99% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 80.1 (*c* 0.892, CH<sub>2</sub>Cl<sub>2</sub>), 91:9 d.r., 99% ee.

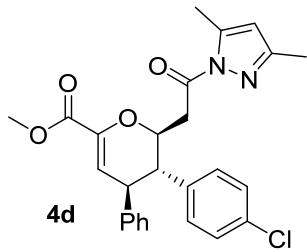
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.17 (dd, *J* = 5.3, 1.8 Hz, 3H), 6.93 – 6.87 (m, 4H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.26 (d, *J* = 2.4 Hz, 1H), 5.91 (s, 1H), 4.92 (ddd, *J* = 11.2, 8.4, 3.4 Hz, 1H), 3.80 (d, *J* = 0.8 Hz, 3H), 3.78 (d, *J* = 2.6 Hz, 1H), 3.75 (s, 3H), 3.49 (m, 1H), 3.13 (m, 1H), 2.85 (t, *J* = 10.5 Hz, 1H), 2.49 (s, 3H), 2.20 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.64, 163.10, 158.58, 151.79, 144.05, 141.56, 131.07, 129.37, 128.72, 128.26, 128.17, 127.94, 126.79, 115.38, 114.15, 113.99, 111.09, 76.73, 55.12, 52.18, 50.99, 47.49, 39.17, 14.42, 13.77.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>[M+H]<sup>+</sup>: 461.2032, found: 461.2036.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 13.927 min, Rt (minor) = 16.933 min.

**4d: Methyl (2S,3S,4R)-3-(4-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 92.1 mg, 99% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 81.1 (*c* 0.897, CH<sub>2</sub>Cl<sub>2</sub>), 91:9 d.r., 99% ee.

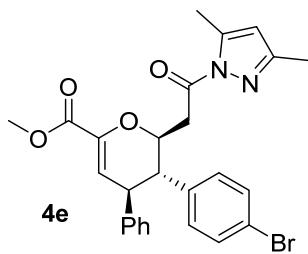
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.09 – 7.04 (m, 5H), 6.85 – 6.77 (m, 4H), 6.16 (d, *J* = 2.3 Hz, 1H), 5.82 (s, 1H), 4.84 (ddd, *J* = 11.1, 8.1, 3.5 Hz, 1H), 3.71 (s, 3H), 3.65 (dd, *J* = 10.4, 2.5 Hz, 1H), 3.37 (m, 1H), 3.05 (m, 1H), 2.81 (t, *J* = 10.5 Hz, 1H), 2.38 (s, 3H), 2.09 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.29, 162.95, 151.96, 144.21, 144.08, 141.01, 137.66, 133.05, 129.75, 128.98, 128.79, 128.44, 127.86, 127.80, 127.05, 115.13, 111.24, 77.14, 52.26, 51.32, 47.47, 39.10, 14.41, 13.78.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 465.1536, found: 465.1578.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 12.364 min, Rt (minor) = 14.850 min.

**4e: Methyl (2s,3s,4r)-3-(4-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 98.8 mg, 97% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 88.2 (*c* 0.881, CH<sub>2</sub>Cl<sub>2</sub>), 92:8 d.r., 99% ee.

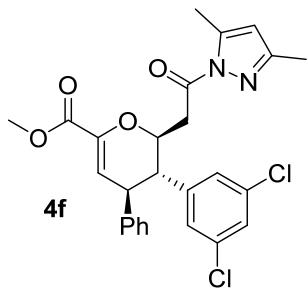
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.16 (dd, *J* = 5.1, 1.8 Hz, 3H), 6.90 – 6.82 (m, 4H), 6.24 (d, *J* = 2.5 Hz, 1H), 5.92 – 5.89 (m, 1H), 4.91 (ddd, *J* = 11.1, 8.0, 3.6 Hz, 1H), 3.78 (d, *J* = 1.4 Hz, 3H), 3.73 (dd, *J* = 10.4, 2.6 Hz, 1H), 3.44 (m, 1H), 3.14 (m, 1H), 2.88 (t, *J* = 10.5 Hz, 1H), 2.45 (s, 3H), 2.17 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.26, 162.93, 151.96, 144.20, 144.08, 140.98, 138.16, 131.93, 131.72, 130.32, 130.12, 128.85, 128.46, 128.13, 127.86, 127.07, 121.24, 115.13, 111.25, 77.15, 52.27, 51.41, 47.40, 39.11, 14.43, 13.79.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>25</sub>BrN<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 510.0977, found: 510.0958.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 13.498 min, Rt (minor) = 15.740 min.

**4f: Methyl (2S,3S,4R)-3-(3,5-dichlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 98.9 mg, 99% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 89.4 (*c* 0.884, CH<sub>2</sub>Cl<sub>2</sub>), 90:10 d.r., 99% ee.

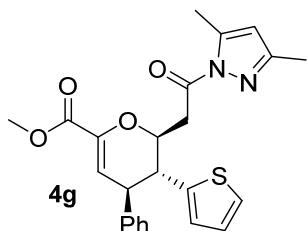
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.11 (m, 6H), 6.92 (dt, *J* = 7.0, 3.6 Hz, 2H), 6.30 – 6.22 (m, 1H), 5.90 (s, 1H), 4.94 – 4.84 (m, 1H), 3.80 (s, 3H), 3.76 – 3.66 (m, 2H), 3.51 (m, 1H), 3.09 (m, 1H), 2.45 (s, 3H), 2.18 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.25, 162.86, 152.01, 143.98, 140.08, 136.27, 135.65, 133.30, 129.25, 128.95, 128.48, 128.43, 127.83, 127.74, 127.65, 127.21, 115.05, 111.26, 77.14, 52.29, 47.47, 45.73, 38.75, 14.37, 13.78.

HRMS (ESI) *m/z* calculated for C<sub>26</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 499.1147, found: 499.1192.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 11.369 min, Rt (minor) = 15.193 min.

**4g: Methyl (2S,3R,4S)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3-(thiophen-2-yl)-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 86.4 mg, 99% yield (hexanes/ethyl acetate, v:v = 3:1),  $[\alpha]_D^{25}$ : 97.3 (*c* 0.998,  $\text{CH}_2\text{Cl}_2$ ), 84:16 d.r., 99% ee.

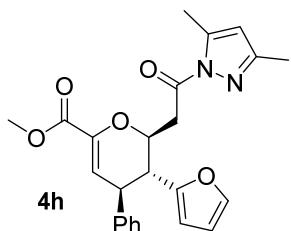
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.24 – 7.19 (m, 4H), 7.02 – 6.98 (m, 2H), 6.83 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.67 (dd, *J* = 3.5, 1.1 Hz, 1H), 6.23 (d, *J* = 2.5 Hz, 1H), 5.94 (d, *J* = 1.1 Hz, 1H), 4.89 (ddd, *J* = 10.4, 8.4, 3.1 Hz, 1H), 3.83 (s, 1H), 3.80 (s, 3H), 3.56 (m, 1H), 3.34 (t, *J* = 10.4 Hz, 1H), 3.25 (m, 1H), 2.52 (d, *J* = 1.0 Hz, 3H), 2.21 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.38, 162.93, 151.93, 144.12, 141.92, 141.26, 128.41, 127.82, 127.08, 126.83, 126.19, 124.70, 114.82, 111.14, 76.75, 52.23, 48.77, 47.22, 38.97, 14.47, 13.79.

HRMS (ESI) *m/z* calculated for  $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_4\text{S}[\text{M}+\text{H}]^+$ : 437.1490, found: 437.1535.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 13.298 min, Rt (minor) = 12.638 min.

**4h: Methyl (2S,3R,4S)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(furan-2-yl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 83.3 mg, 99% yield (hexanes/ethyl acetate, v:v = 3:1),  $[\alpha]_D^{25}$ : 79.9 (*c* 0.702,  $\text{CH}_2\text{Cl}_2$ ), 74:26 d.r., 99% ee.

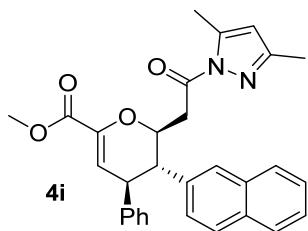
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.35 – 7.17 (m, 4H), 7.01 – 6.97 (m, 2H), 6.25 (d, *J* = 2.6 Hz, 1H), 6.16 (dd, *J* = 3.3, 1.9 Hz, 1H), 5.93 (d, *J* = 1.1 Hz, 1H), 5.91 (dd, *J* = 3.3, 0.8 Hz, 1H), 4.91 (ddd, *J* = 10.3, 7.6, 4.1 Hz, 1H), 4.04 (dd, *J* = 10.6, 2.6 Hz, 1H), 3.80 (s, 3H), 3.55 (m, 1H), 3.29 (m, 1H), 3.11 (t, *J* = 10.5 Hz, 1H), 2.50 (d, *J* = 1.1 Hz, 3H), 2.21 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.99, 162.94, 151.88, 151.54, 144.30, 144.10, 142.23, 141.40, 128.40, 127.69, 127.03, 114.71, 111.13, 110.19, 108.96, 77.06, 52.22, 45.63, 44.17, 38.96, 14.45, 13.79.

HRMS (ESI) *m/z* calculated for  $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_5[\text{M}+\text{H}]^+$ : 421.1719, found: 421.1783.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 13.441 min, Rt (minor) = 12.119 min.

**4i: Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(naphthalen-2-yl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 95.2 mg, 99% yield (hexanes/ethyl acetate, v:v = 4:1),  $[\alpha]_D^{25}$ : 79.4 (*c* 0.732, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r., >99% ee.

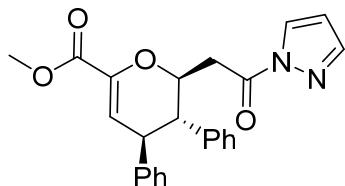
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.75 – 7.62 (m, 3H), 7.40 (h, *J* = 3.2, 2.3 Hz, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 4.1 Hz, 3H), 6.91 – 6.84 (m, 2H), 6.30 (d, *J* = 2.1 Hz, 1H), 5.76 (s, 1H), 5.06 (t, *J* = 9.0 Hz, 1H), 3.93 (d, *J* = 10.0 Hz, 1H), 3.79 (d, *J* = 1.8 Hz, 3H), 3.49 (m, 1H), 3.17 – 3.03 (m, 2H), 2.34 (d, *J* = 1.8 Hz, 3H), 2.11 (d, *J* = 1.8 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.45, 163.08, 151.79, 144.33, 143.95, 141.35, 136.54, 133.27, 132.64, 128.46, 128.36, 127.91, 127.77, 127.55, 126.90, 126.06, 125.85, 115.47, 111.08, 77.13, 52.24, 52.03, 47.31, 39.25, 14.30, 13.74.

HRMS (ESI) *m/z* calculated for C<sub>30</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 481.2083, found: 481.2130.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 13.537 min, Rt (minor) = 16.257 min.

**4j: Methyl (2S,3S,4R)-2-(2-oxo-2-(1H-pyrazol-1-yl)ethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**



White solid, 54.6 mg, 68% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 47.3 (*c* 0.437, CH<sub>2</sub>Cl<sub>2</sub>), 81:19 d.r., 95% ee.

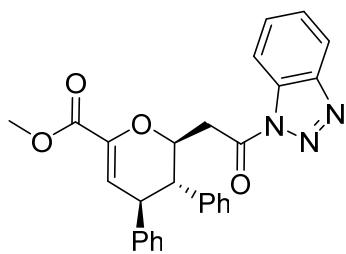
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.18 (q, *J* = 3.6, 2.8 Hz, 1H), 7.65–7.60 (m, 1H), 7.33 (t, *J* = 4.4 Hz, 1H), 7.25–7.23(m, 1H), 7.16–7.13 (m, 6H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.93 – 6.84 (m, 1H), 6.37 (s, 1H), 6.32 – 6.22 (m, 1H), 4.97 (t, *J* = 9.7 Hz, 1H), 3.84 – 3.78 (m, 1H), 3.78 – 3.75 (m, 3H), 3.63 – 3.48 (m, 1H), 3.15 – 3.01 (m, 1H), 2.91 (td, *J* = 10.5, 2.6 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.96, 162.93, 143.91, 143.24, 141.25, 138.95, 128.91, 128.81, 128.56, 128.33, 128.14, 127.89, 127.41, 127.38, 127.09, 126.93, 115.49, 109.66, 72.59, 52.22, 51.85, 49.33, 47.32, 37.90.

HRMS (ESI) *m/z* calculated for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 402.1580, found: 402.1591.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 18.014 min, Rt (minor) = 19.692 min.

**4k: Methyl (2S,3S,4R)-2-(2-(1H-benzo[d][1,2,3]triazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**



White solid, 51.5 mg, 67% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 40.2 (*c* 0.421, CH<sub>2</sub>Cl<sub>2</sub>), 61:17:18:4 d.r., 93 % ee.

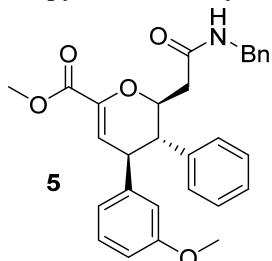
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.33 – 7.24 (m, 4H), 7.15 (d, *J* = 6.8 Hz, 4H), 6.93 – 6.87 (m, 2H), 6.30 (d, *J* = 2.1 Hz, 1H), 5.05 (q, *J* = 9.7, 8.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 1H), 3.73 (s, 3H), 3.38–3.30 (m, 2H), 2.98 (t, *J* = 10.5 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.16, 162.80, 146.10, 144.07, 141.06, 138.61, 130.35, 128.86, 128.55, 128.52, 128.37, 128.29, 128.16, 127.88, 127.56, 127.50, 127.18, 127.00, 126.17, 120.06, 115.62, 114.47, 72.38, 60.42, 52.20, 47.18, 39.54.

HRMS (ESI) *m/z* calculated for C<sub>27</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 453.1689, found: 453.1671.

HPLC analysis: (AD-H column, Hexane:2-propanol = 90:10, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 24.654 min, Rt (minor) = 23.827 min.

**5: Methyl (2S,3S,4R)-2-(2-(benzylamino)-2-oxoethyl)-4-(3-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



White solid, 84.9 mg, 90% yield (hexanes/ethyl acetate, v:v = 10:1),  $[\alpha]_D^{25}$ : 99.4 (*c* 0.812, CH<sub>2</sub>Cl<sub>2</sub>), >95:5 d.r., >99 % ee.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.08 (m, 8H), 6.95 (t, *J* = 7.9 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.57 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.34 (d, *J* = 7.6 Hz, 1H), 6.25 (t, *J* = 1.9 Hz, 1H), 6.17 (d, *J* = 2.4 Hz, 1H), 4.54 (td, *J* = 9.6, 8.9, 2.7 Hz, 1H), 4.37 – 4.25 (m, 2H), 3.70 – 3.64 (m, 1H), 3.64 – 3.60 (m, 1H), 3.58 (s, 3H), 3.50 (s, 3H), 2.63 (t, *J* = 10.3 Hz, 1H), 2.32 – 2.19 (m, 2H).

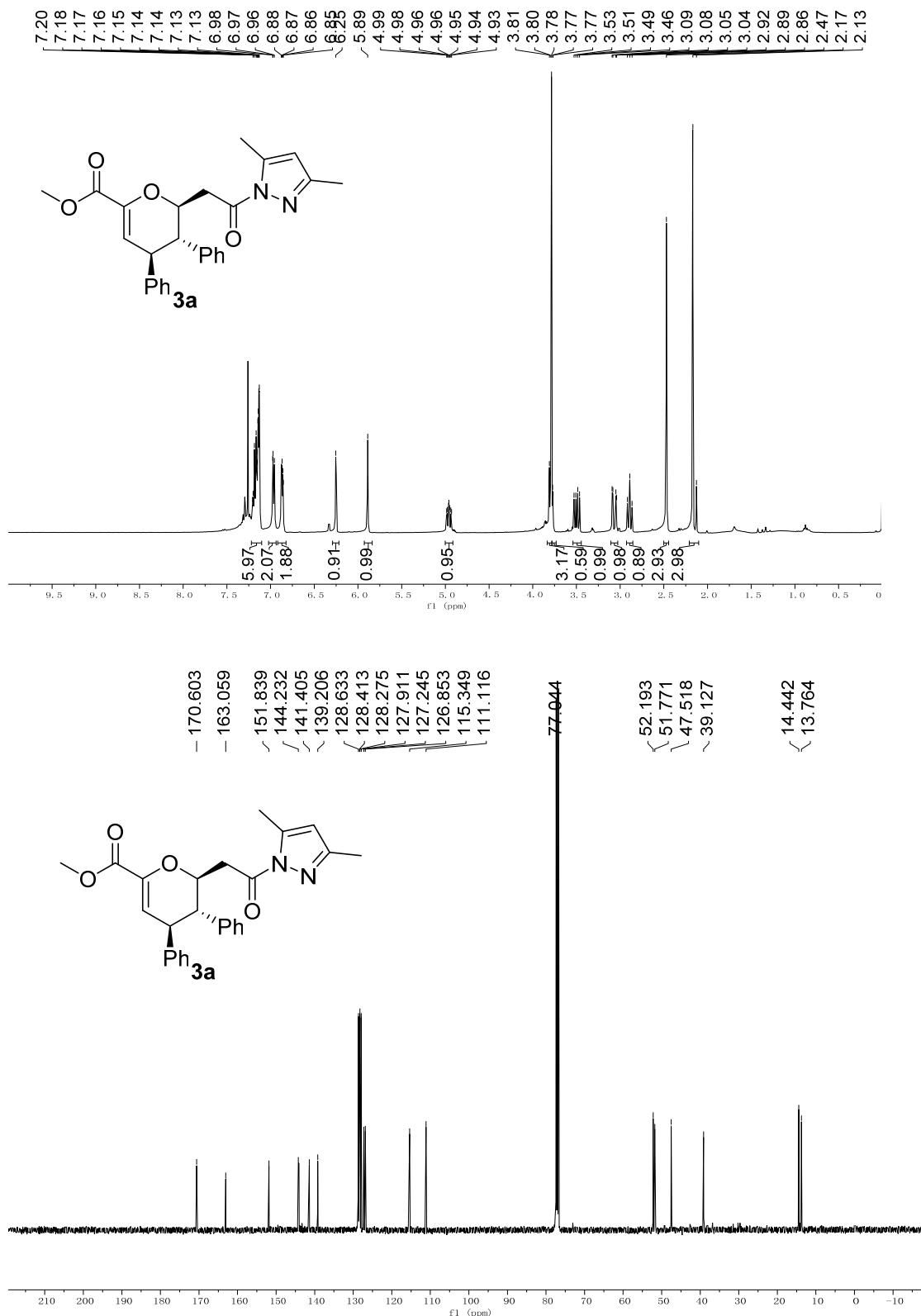
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.83, 162.72, 159.39, 143.51, 142.56, 138.88, 138.30, 129.29, 128.91, 128.62, 128.27, 127.77, 127.45, 127.33, 120.15, 115.92, 113.58, 112.39, 77.05, 55.07, 52.20, 52.12, 47.15, 43.65, 40.28.

HRMS (ESI) *m/z* calculated for C<sub>29</sub>H<sub>29</sub>NO<sub>5</sub>[M+H]<sup>+</sup>: 472.2079, found: 472.2124.

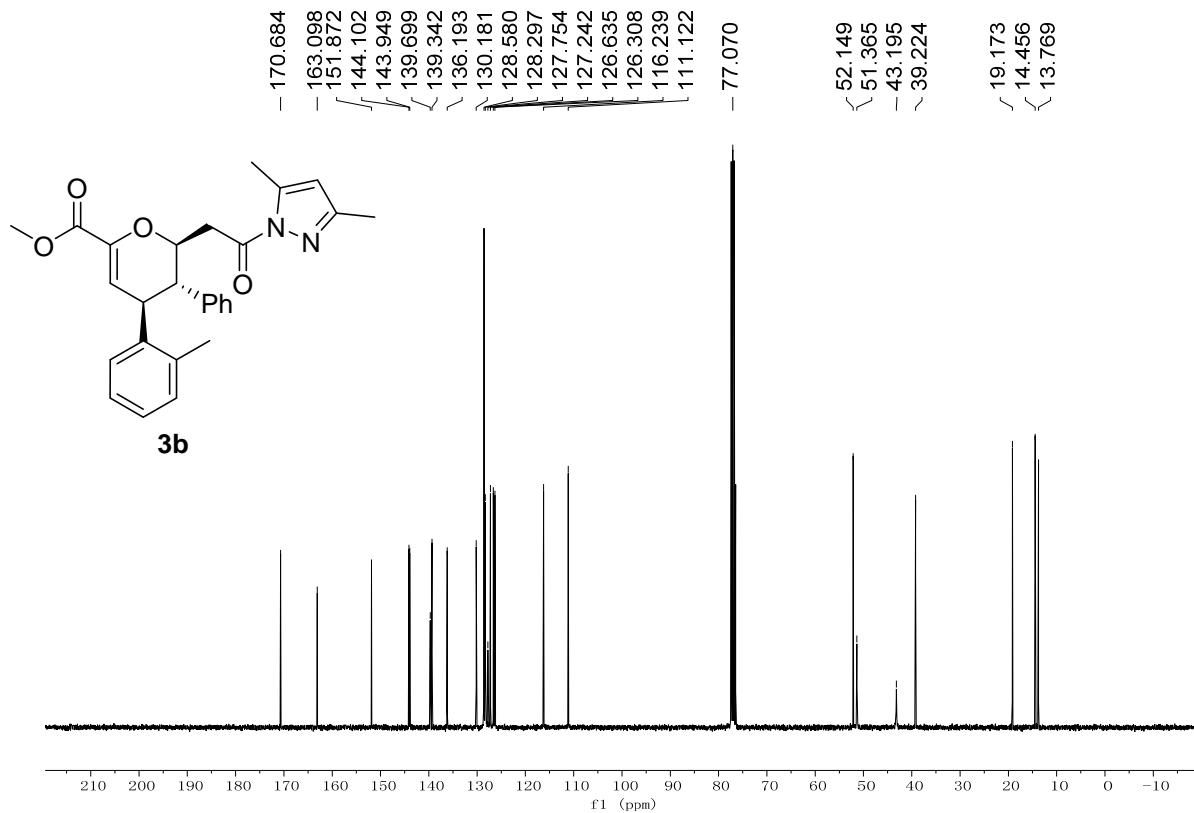
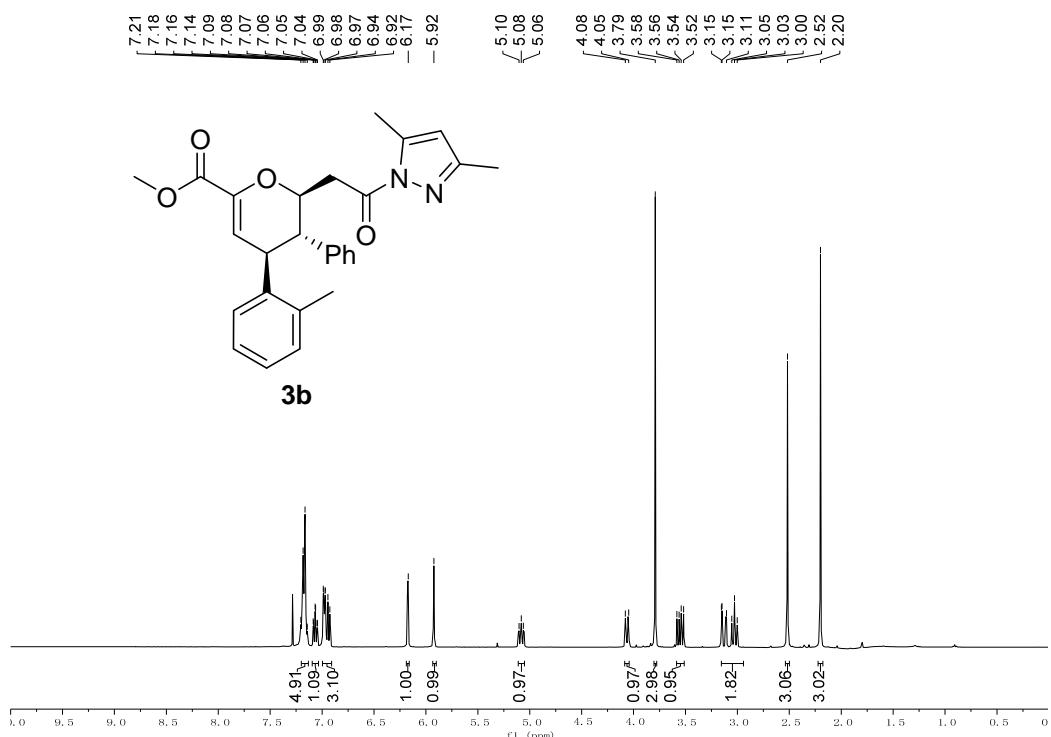
HPLC analysis: (IB column, Hexane:2-propanol = 80:20, flow rate = 0.5 mL/min, wavelength = 254 nm): Rt (major) = 19.403 min, Rt (minor) = 27.466 min.

## VII. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

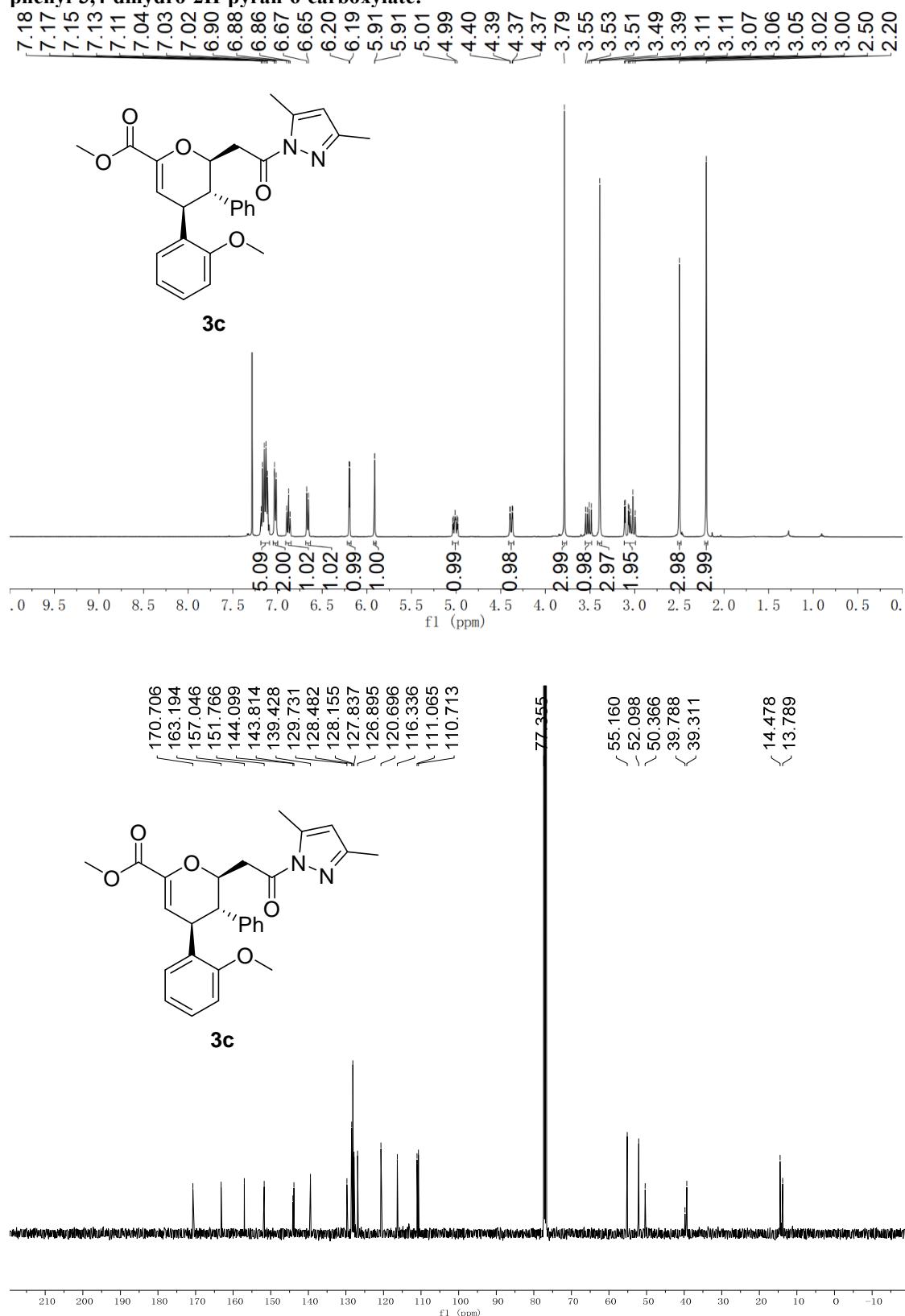
**3a:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**



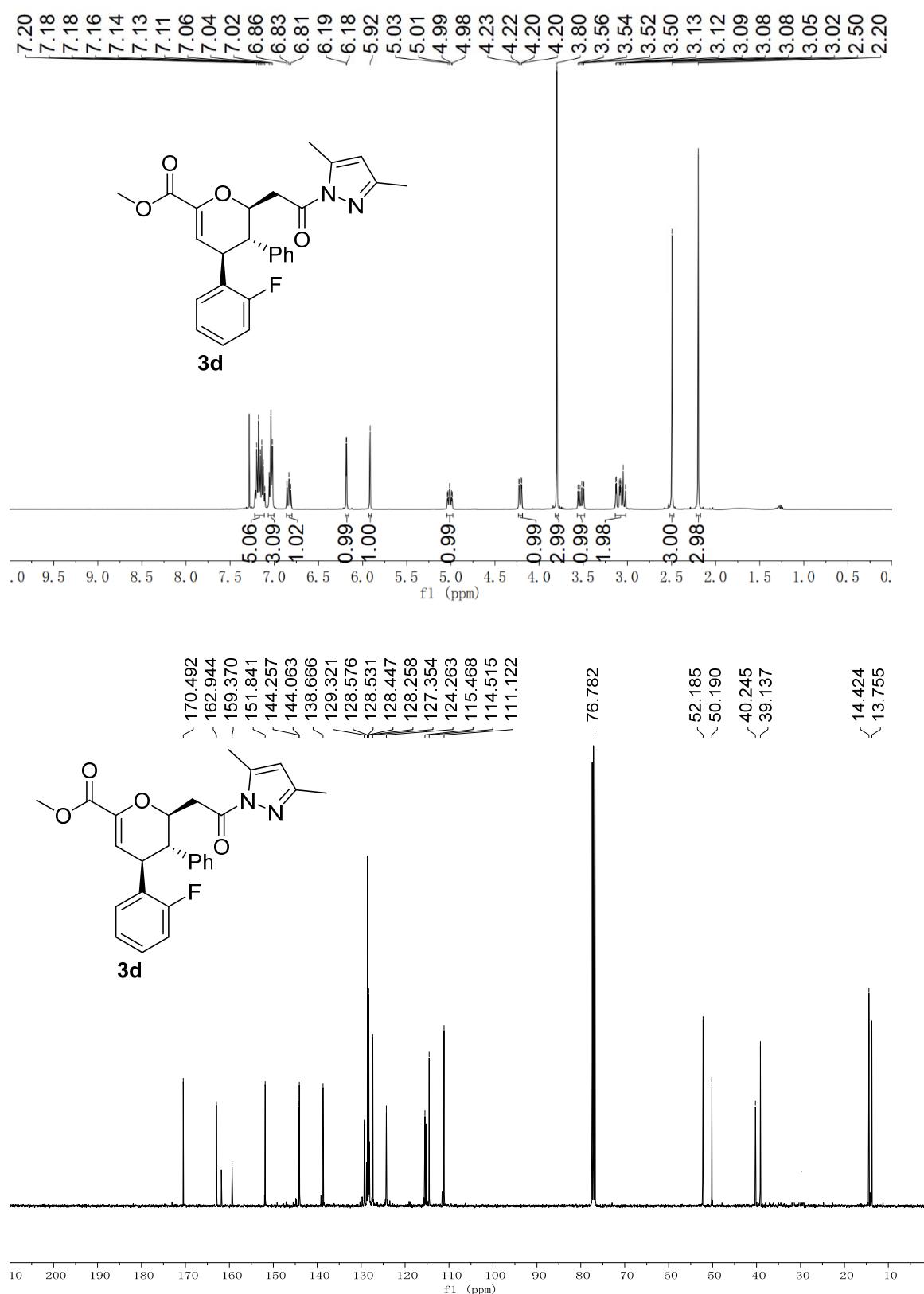
**3b:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(o-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



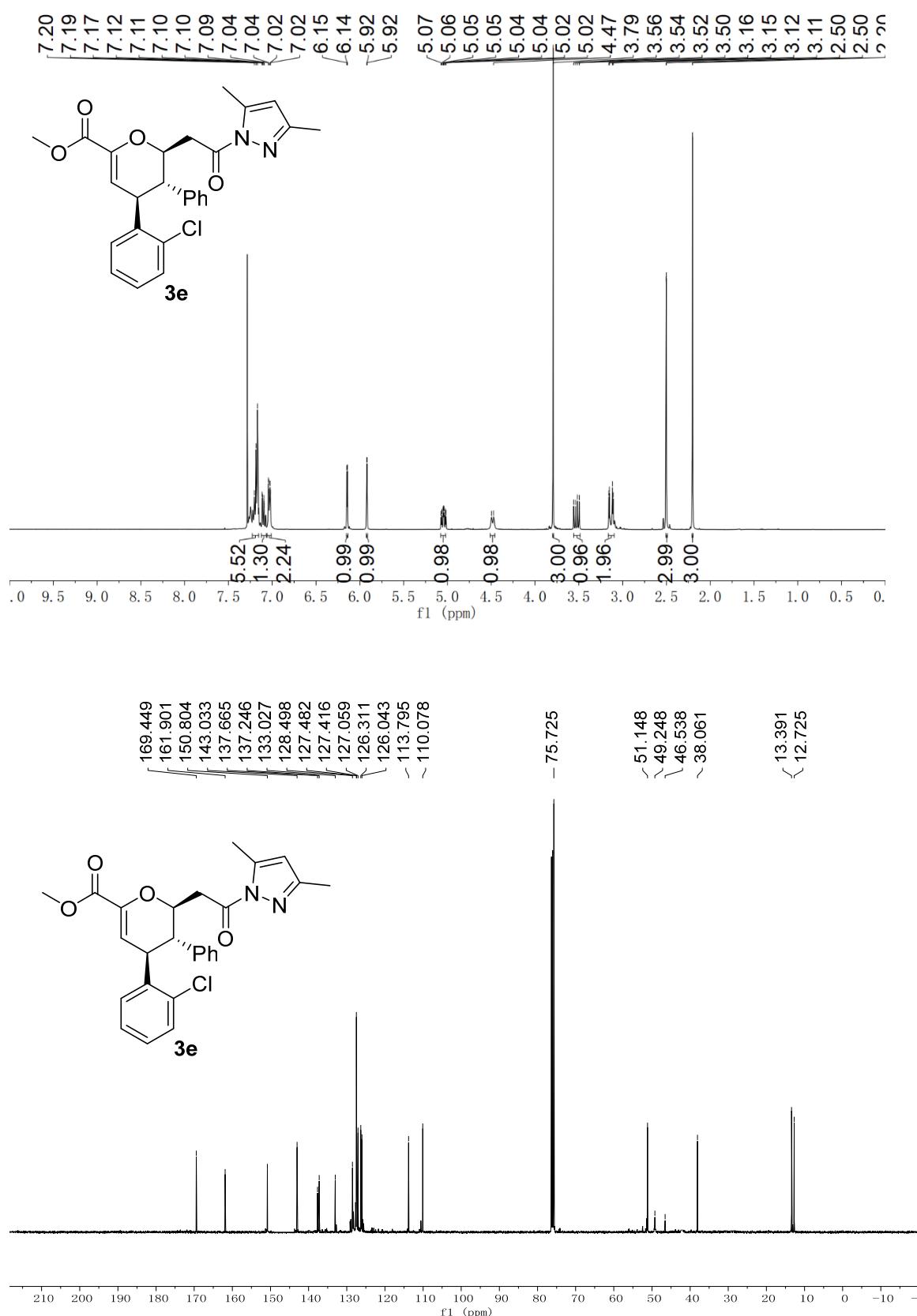
**3c:**Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(2-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:



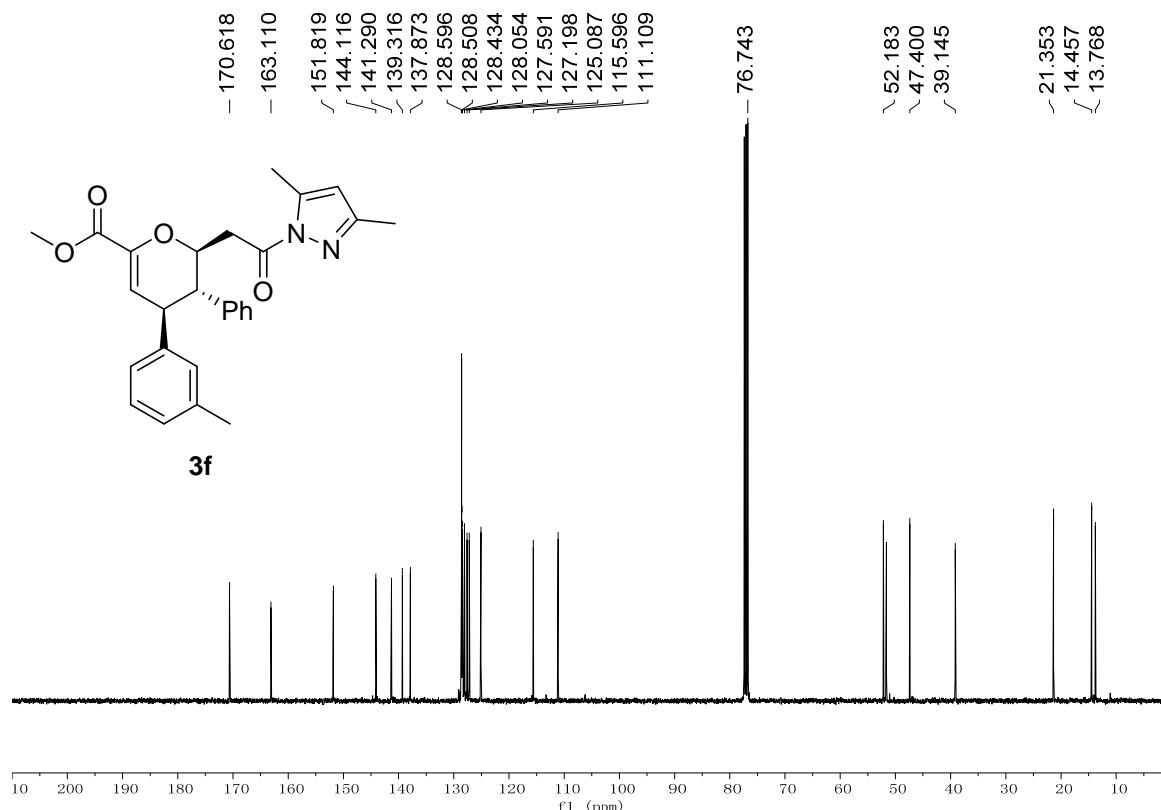
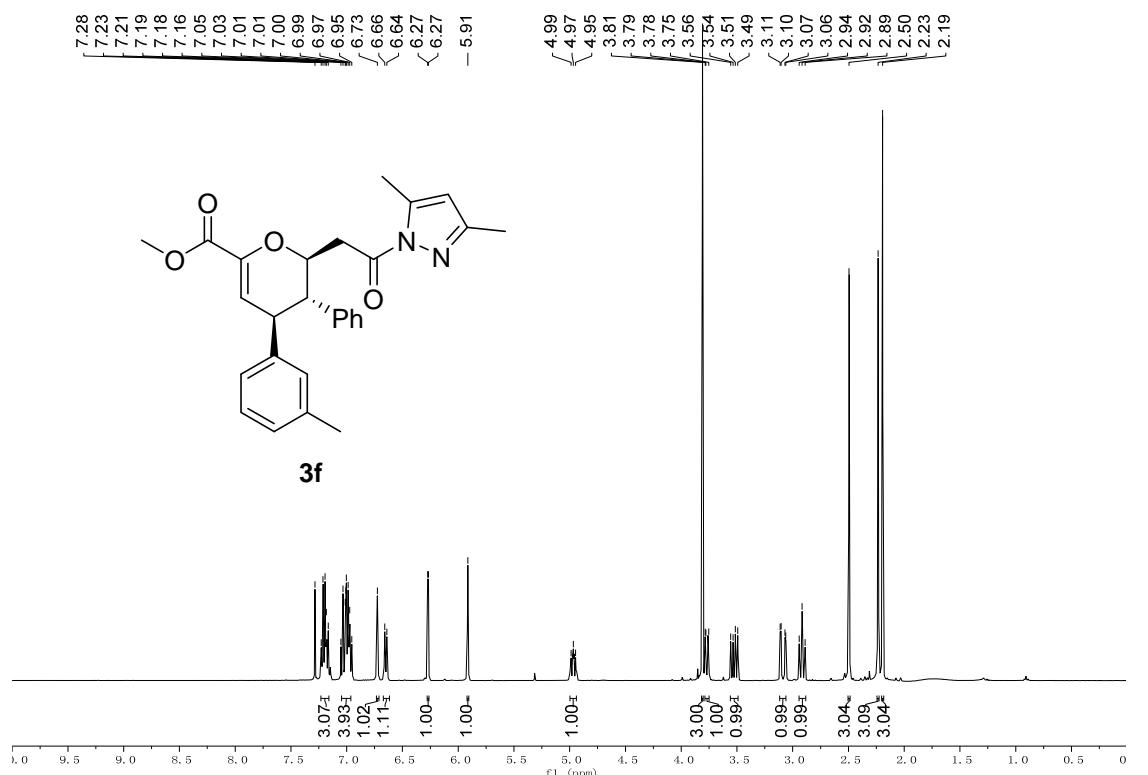
**3d:Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(2-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



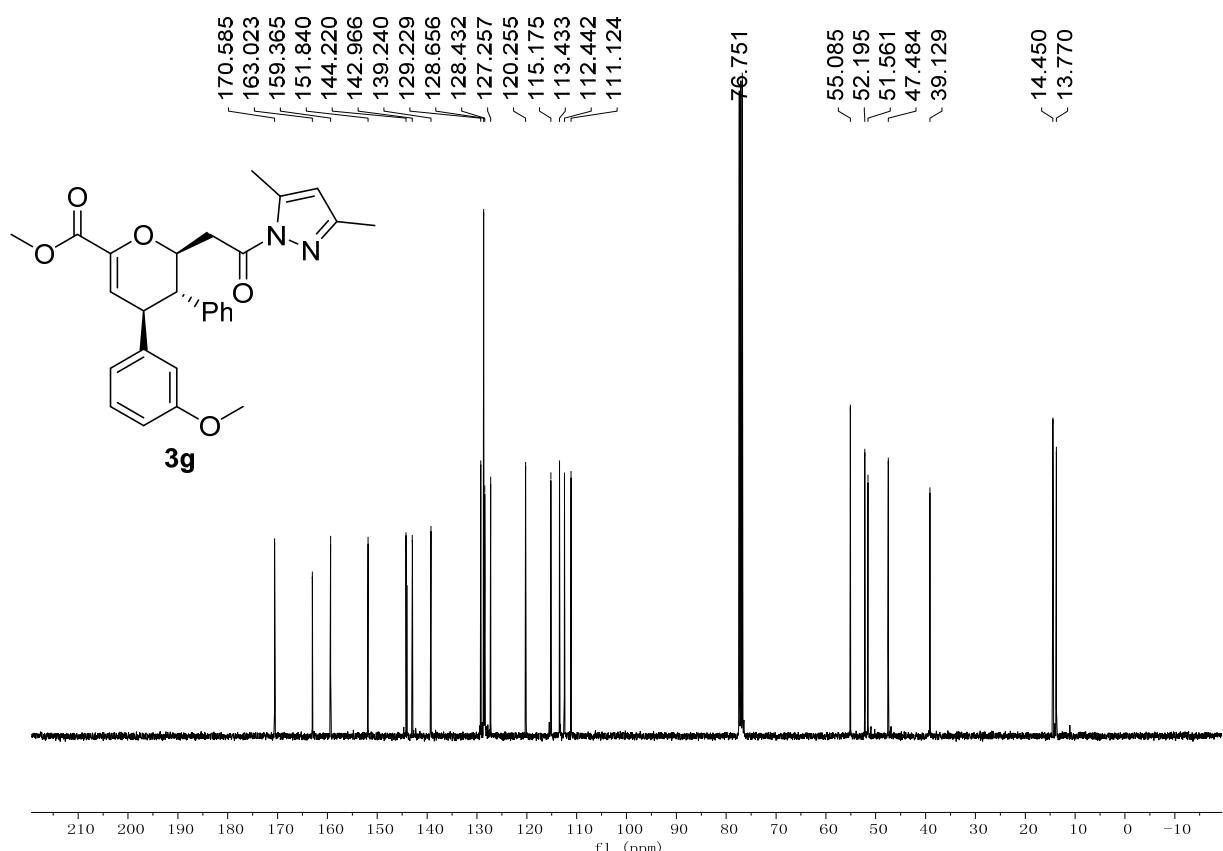
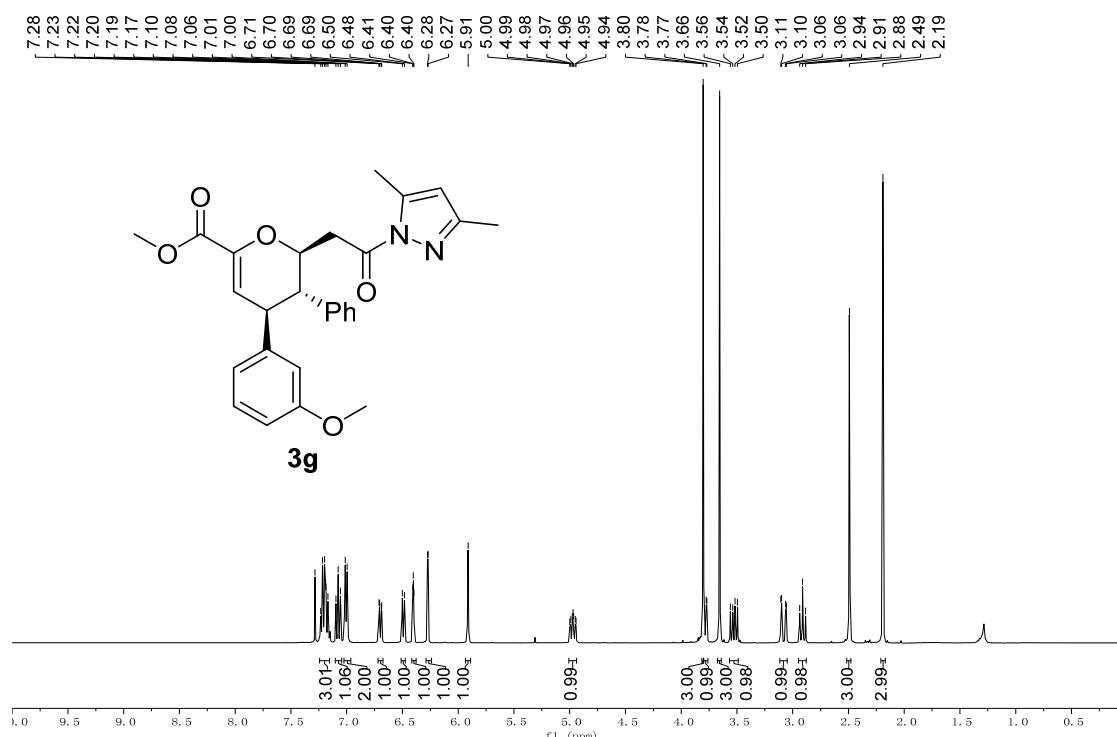
**3e:Methyl(2S,3S,4R)-4-(2-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



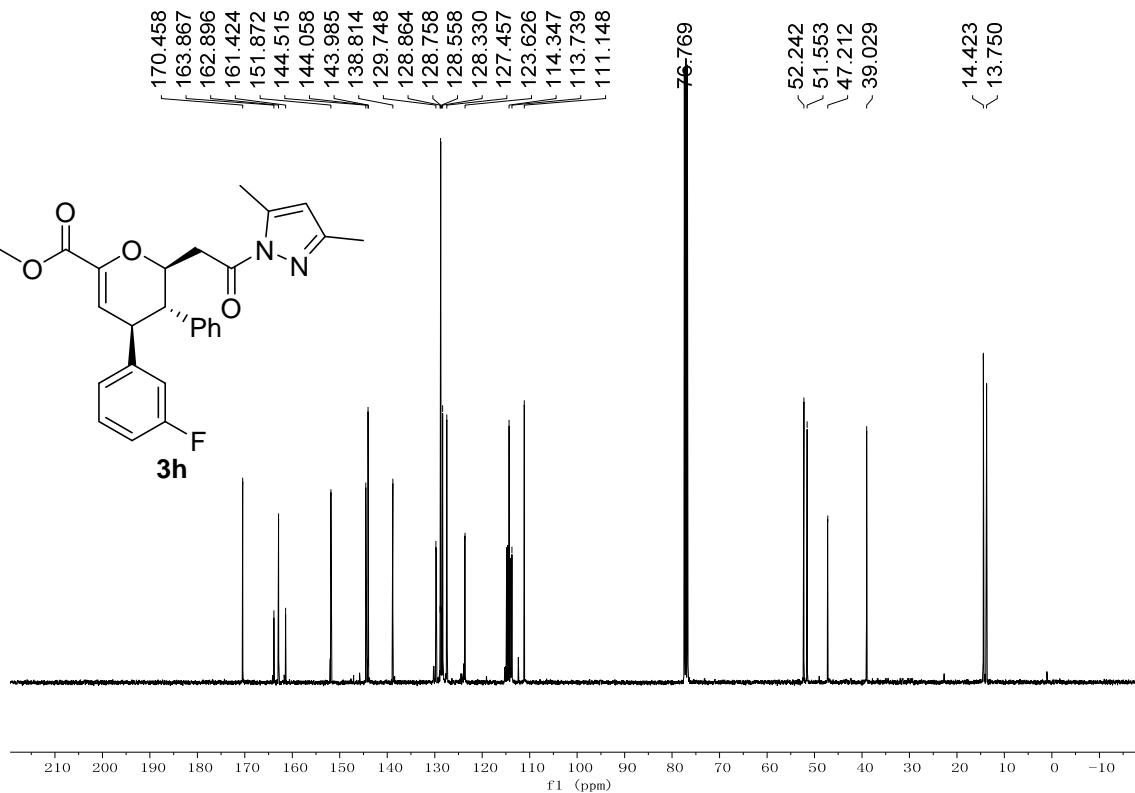
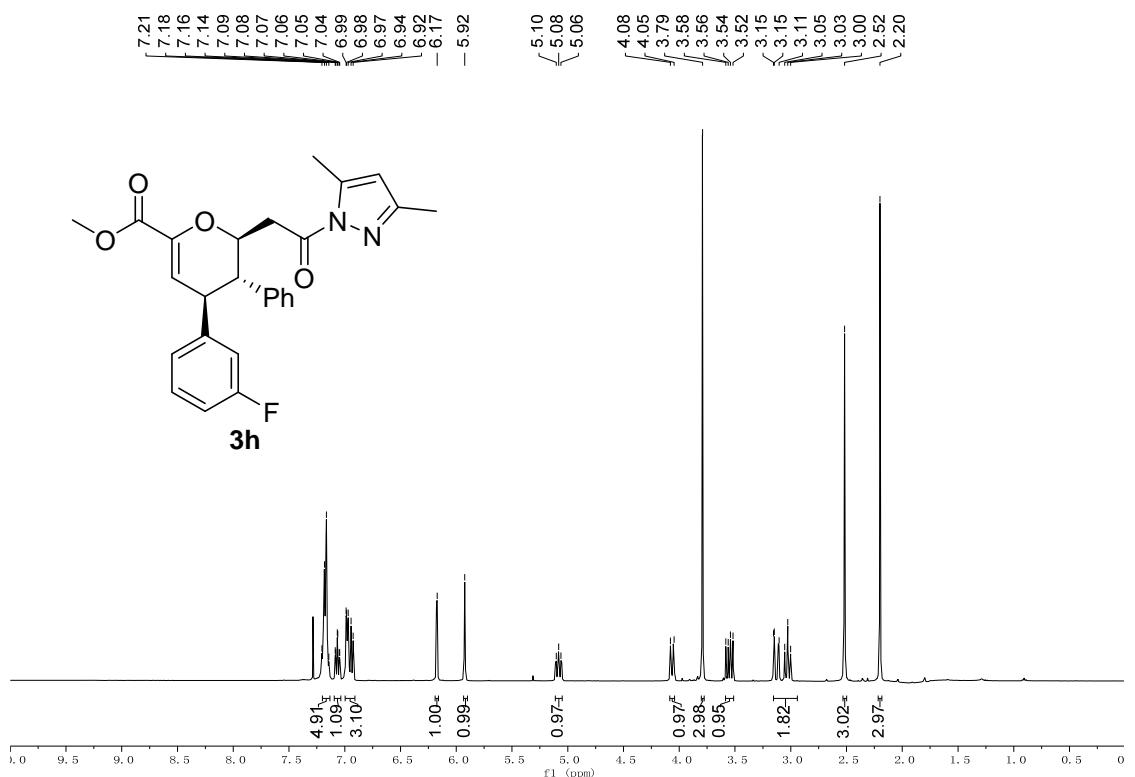
**3f:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(m-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



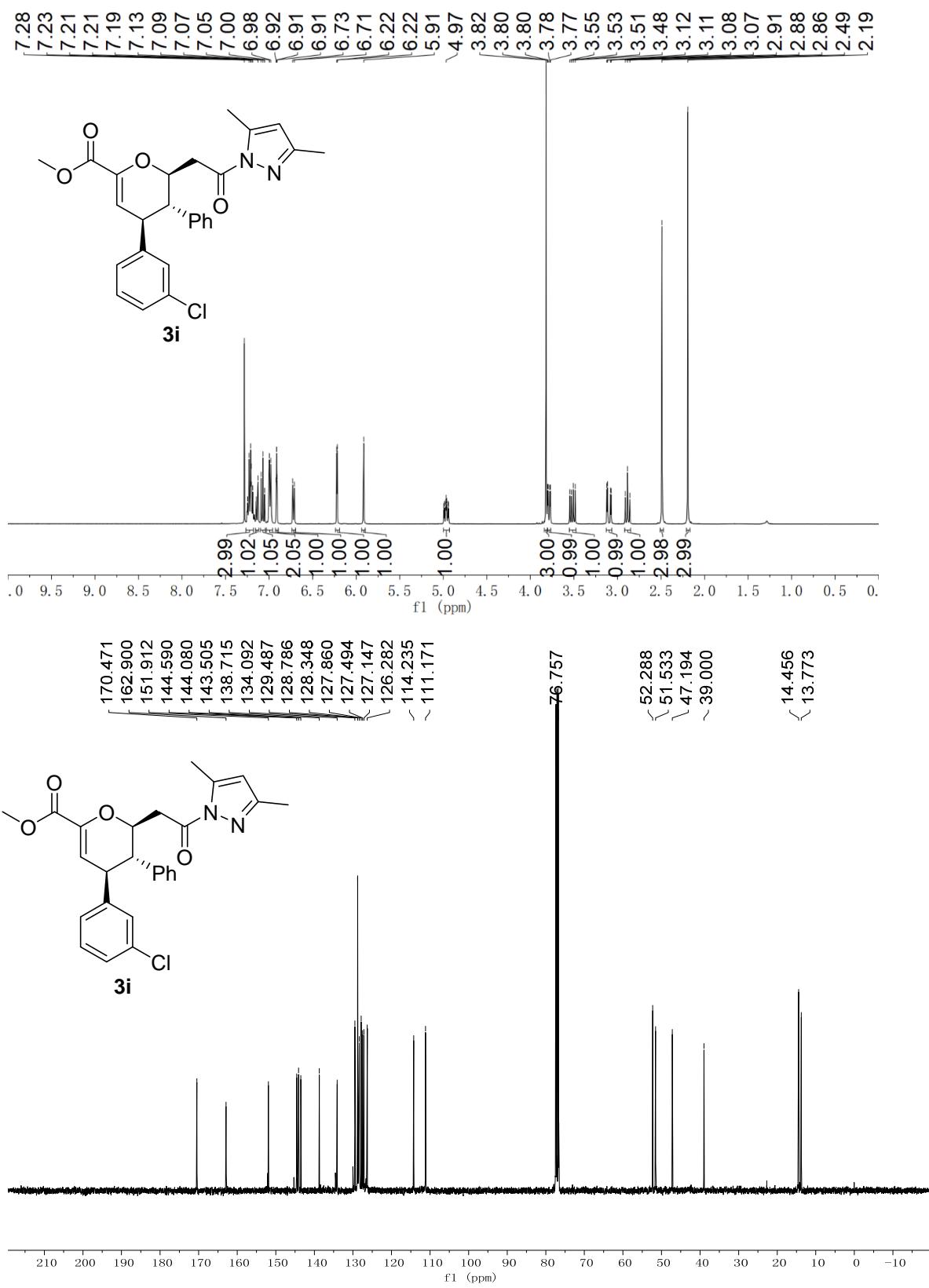
**3g:Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



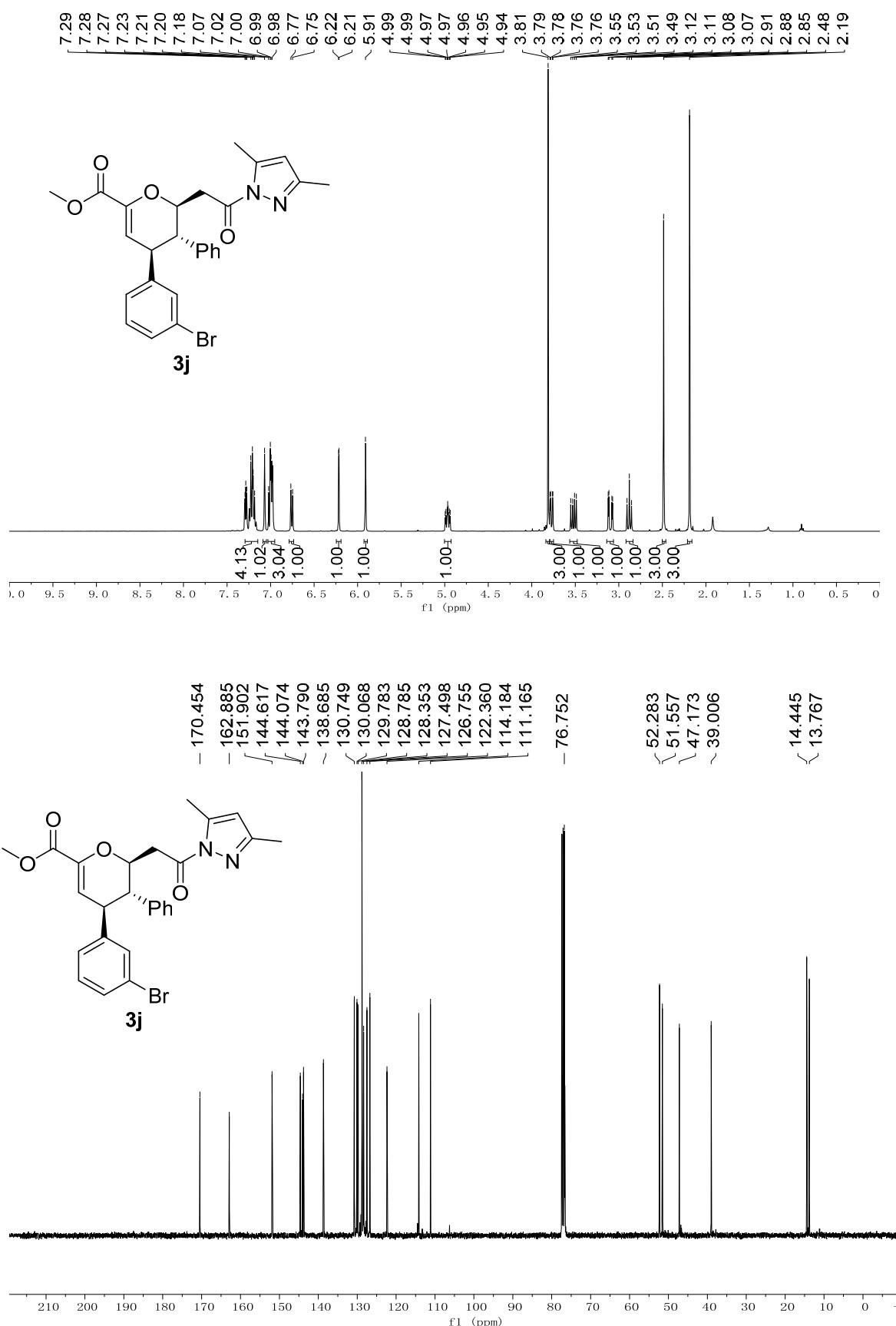
**3h: Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



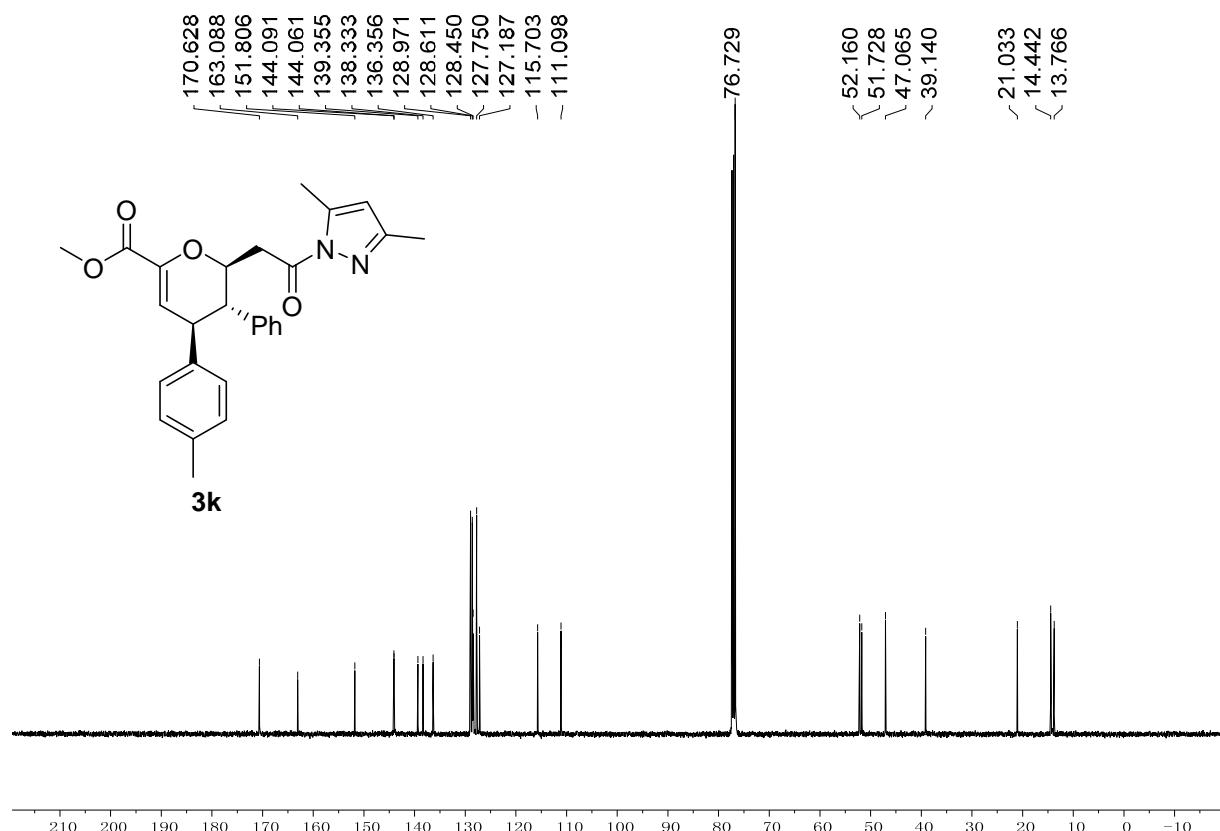
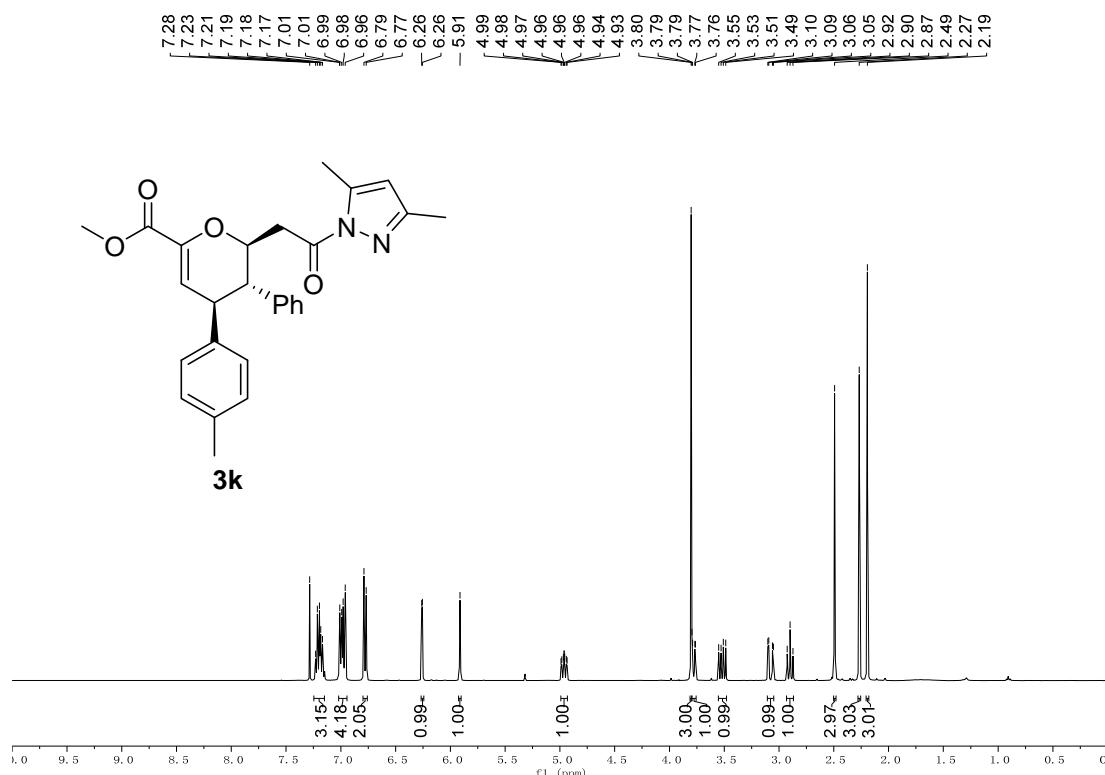
**3i: Methyl(2S,3S,4R)-4-(3-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



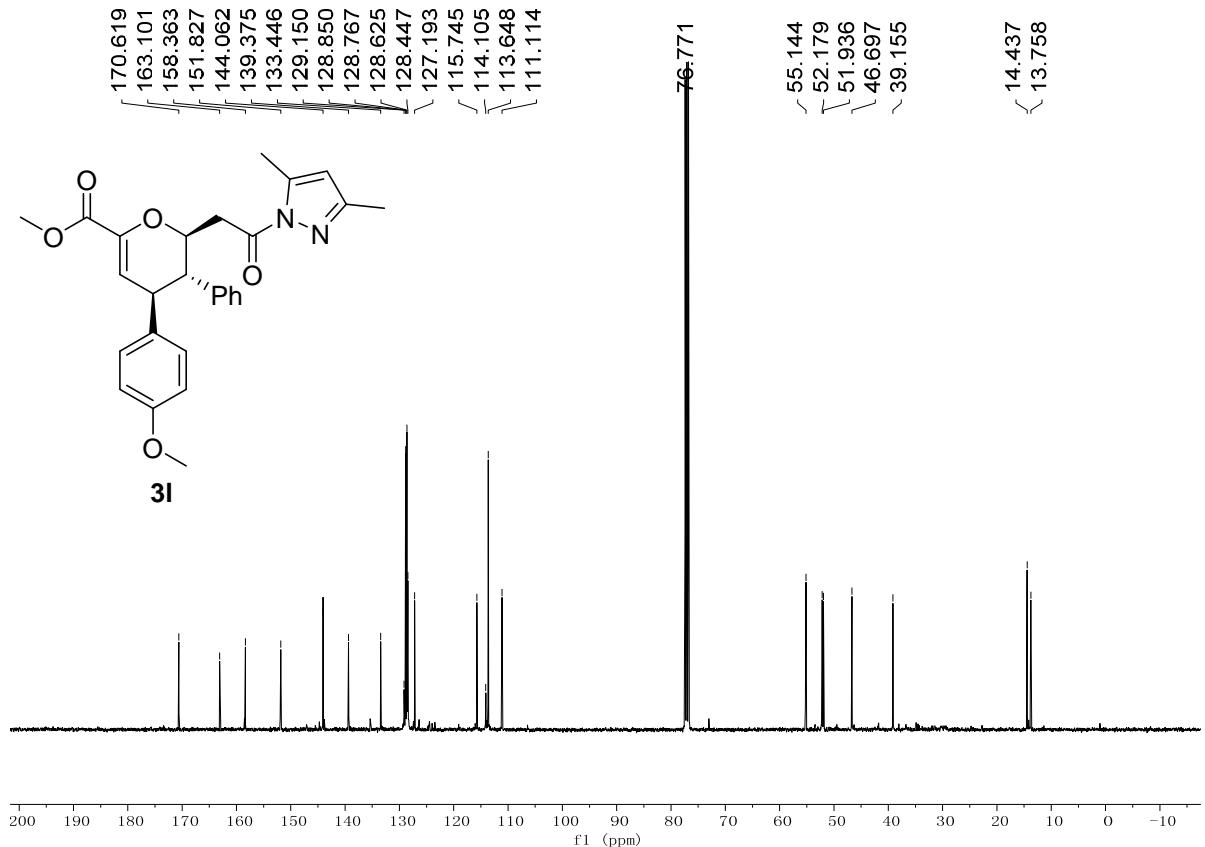
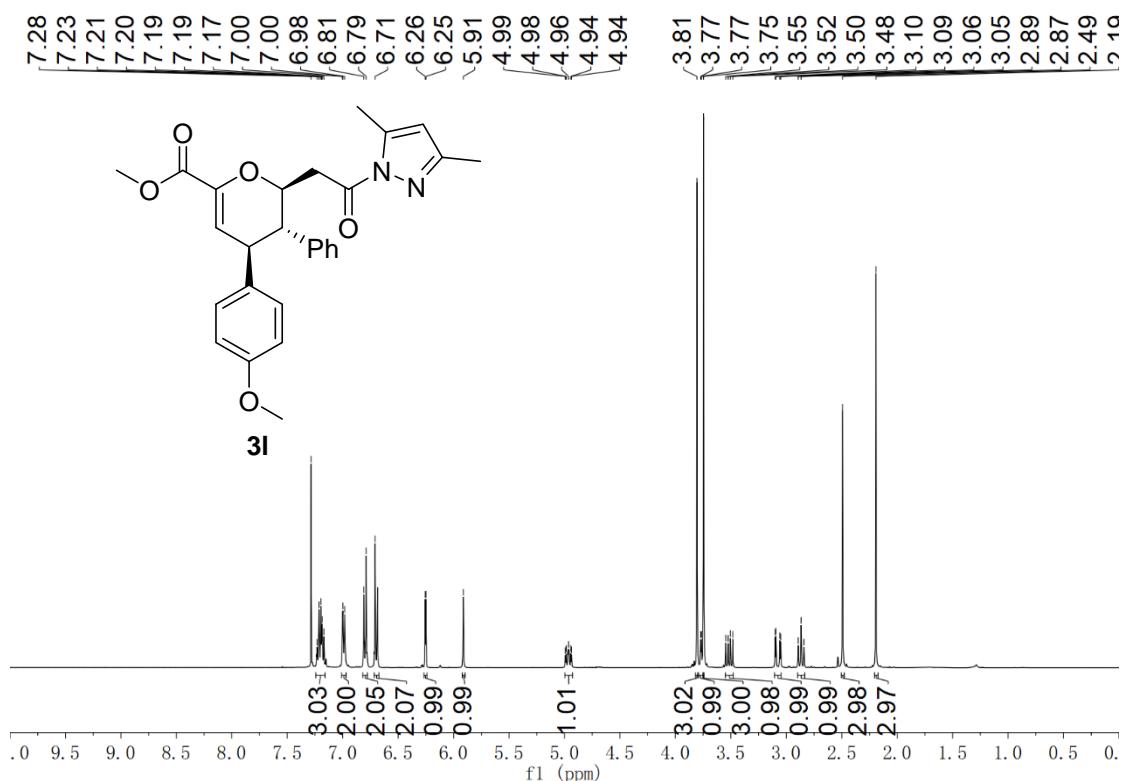
**3j:Methyl (2S,3S,4R)-4-(3-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



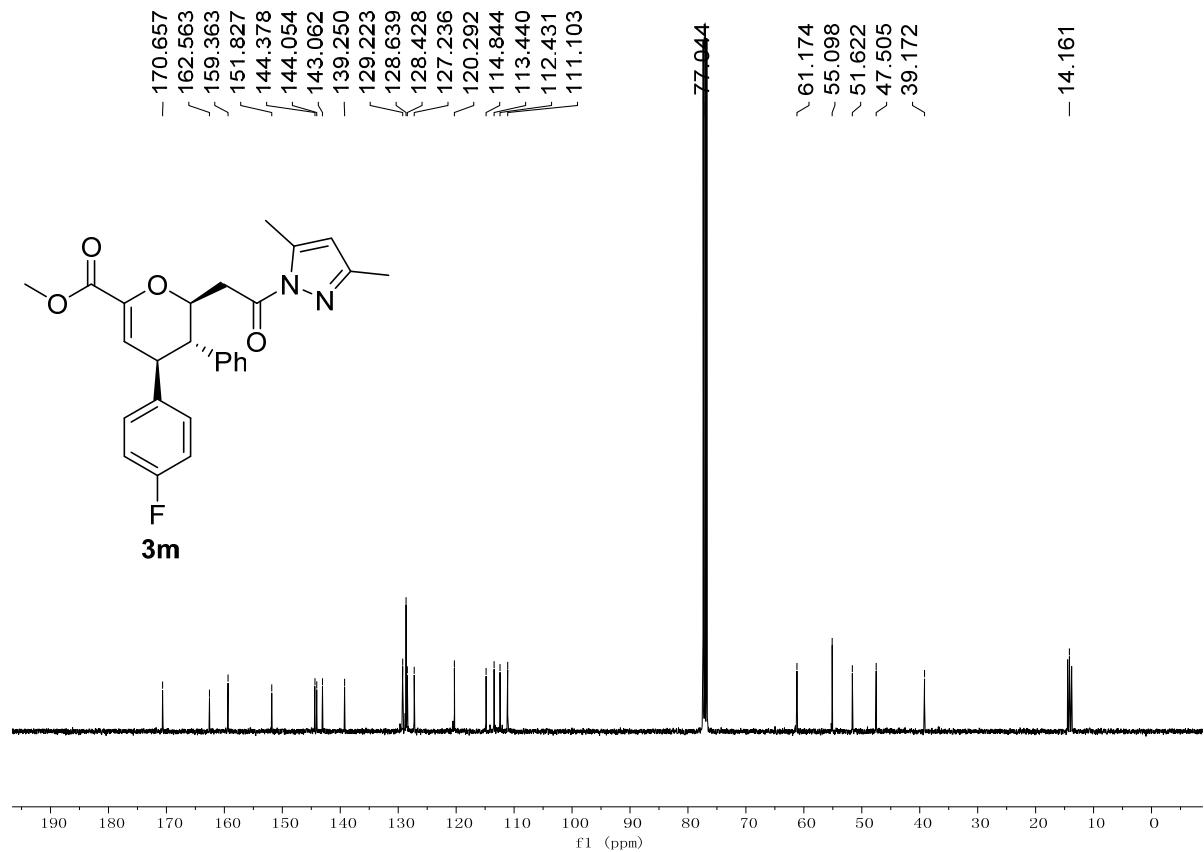
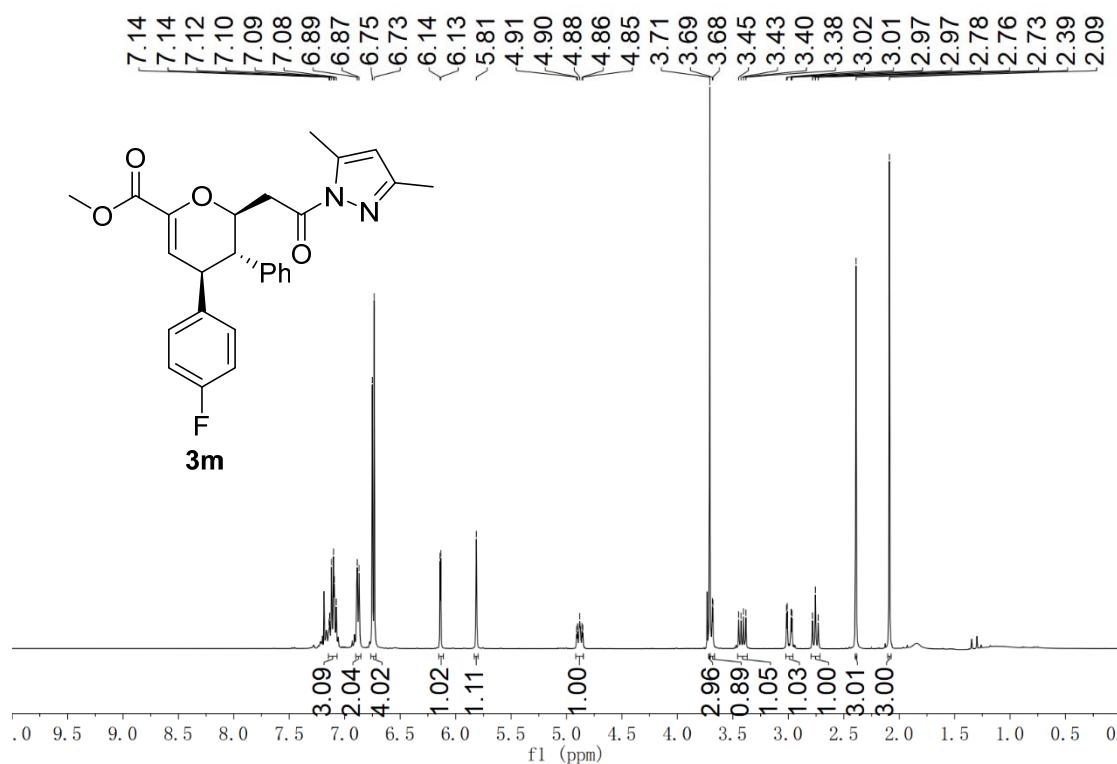
**3k:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(p-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



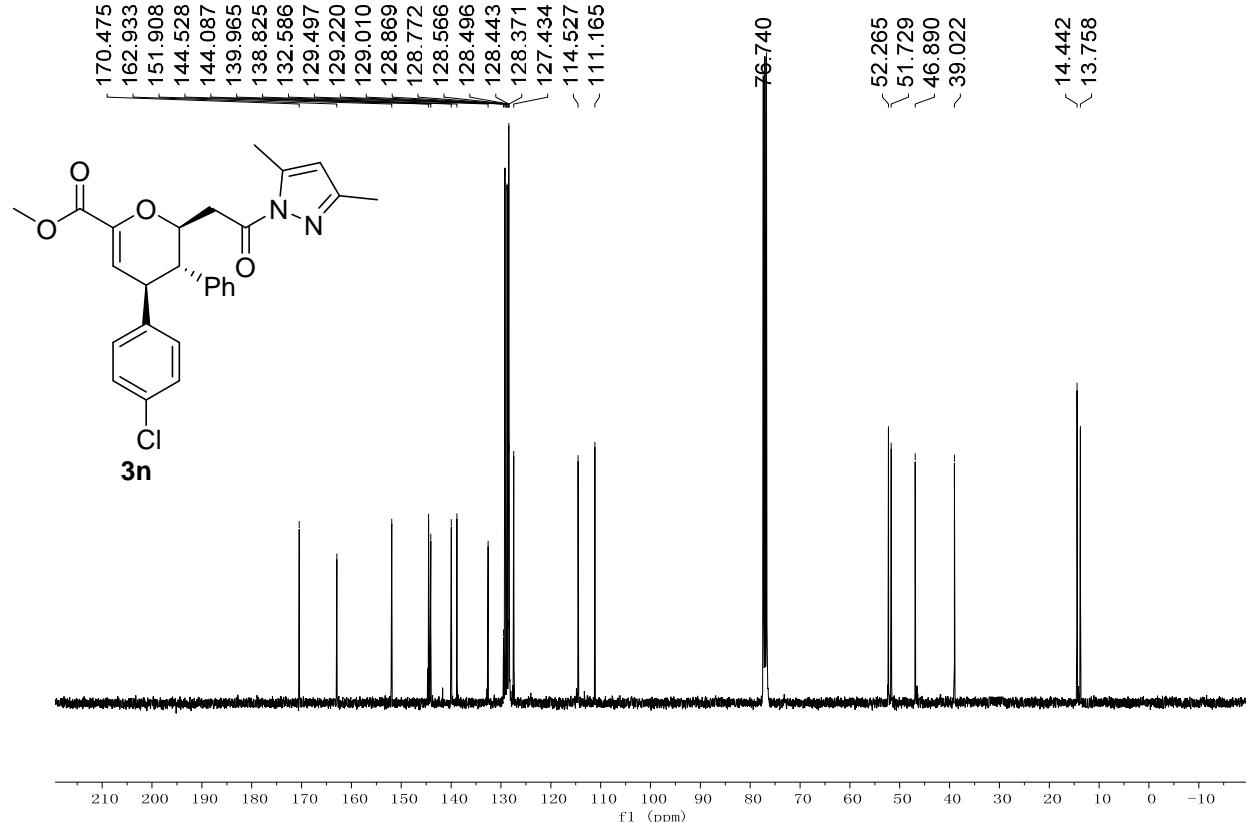
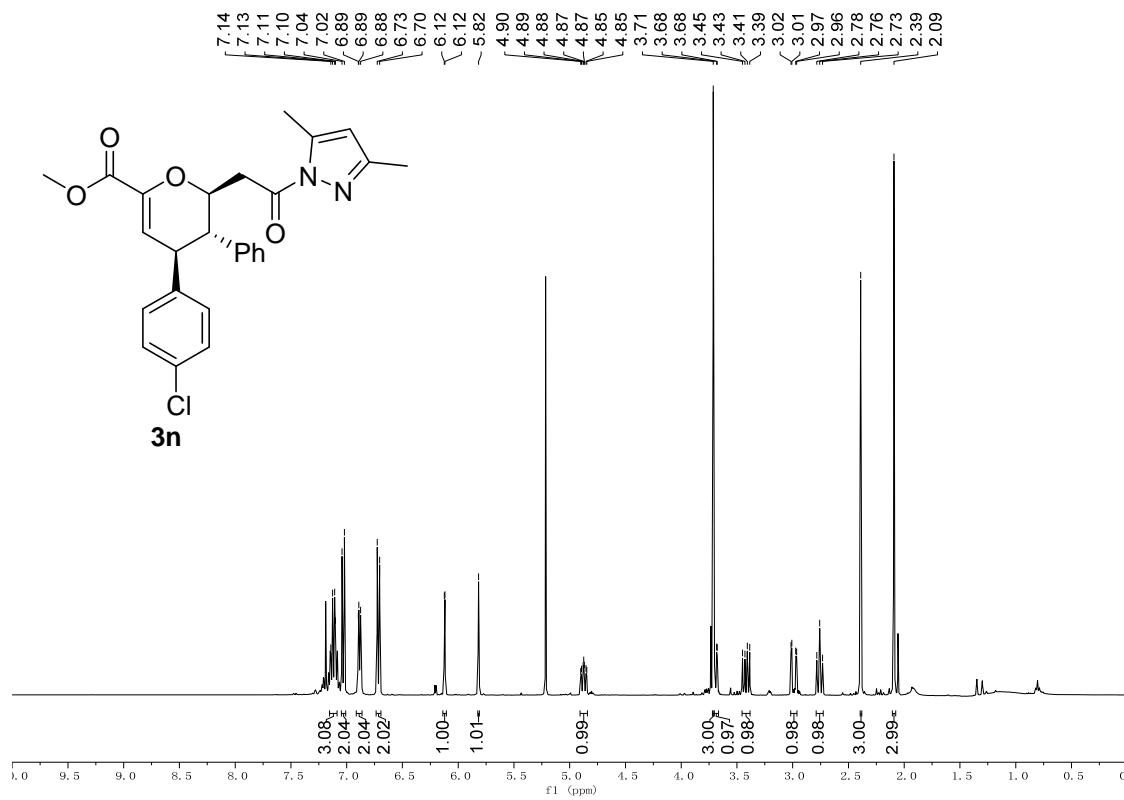
**3l: Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(4-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



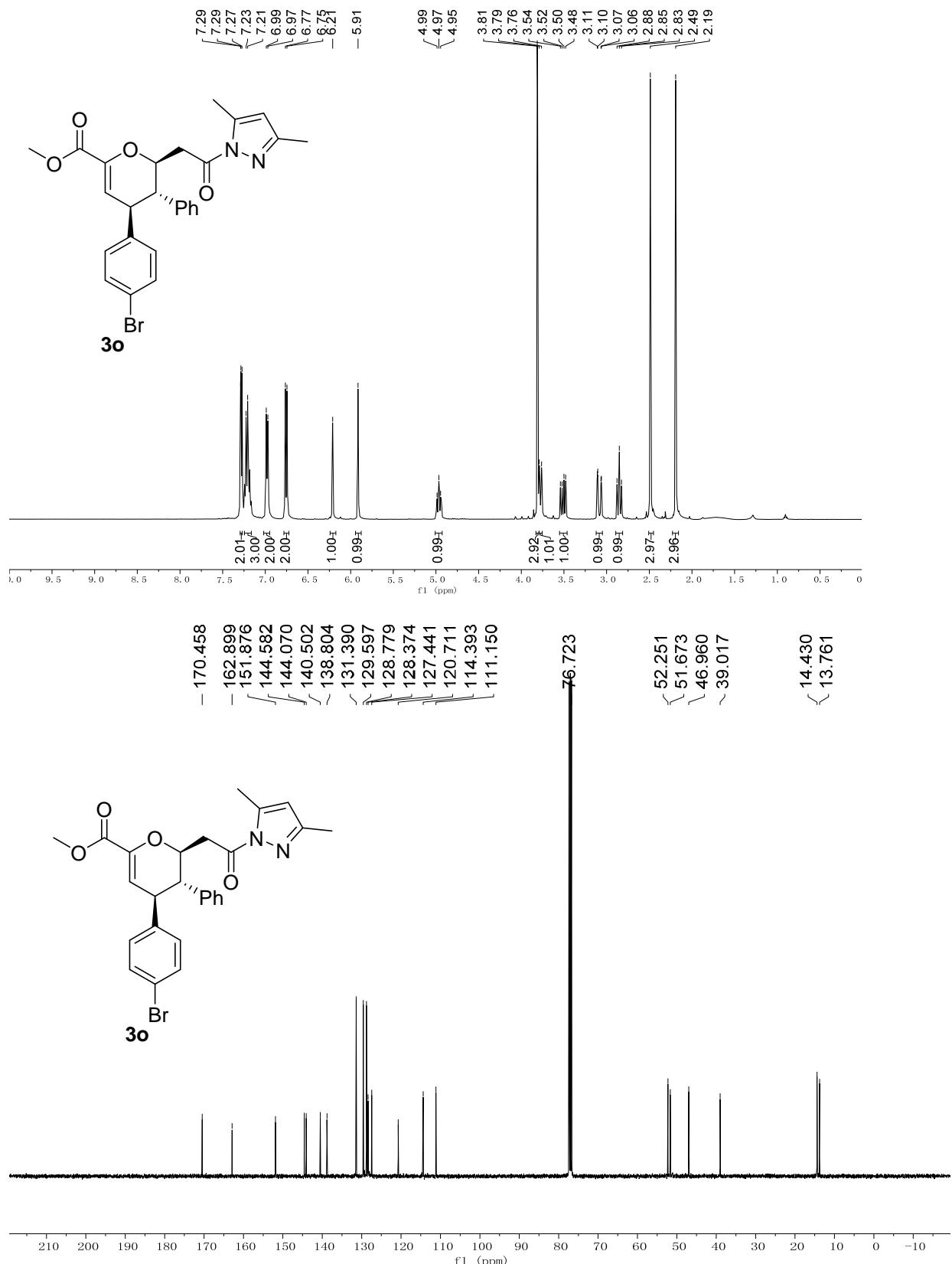
**3m:**Methyl(2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(4-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:



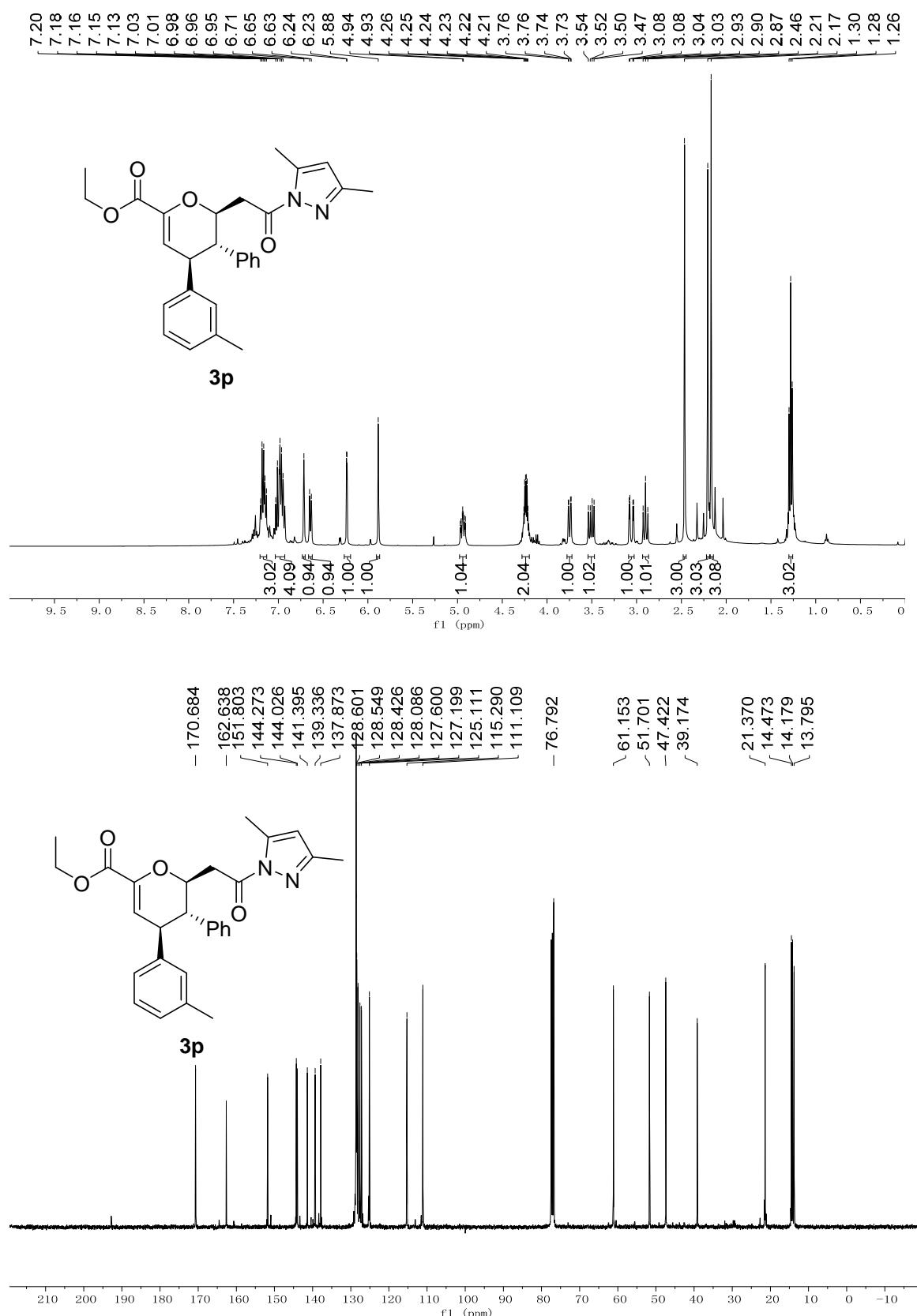
**3n: Methyl (2S,3S,4R)-4-(4-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



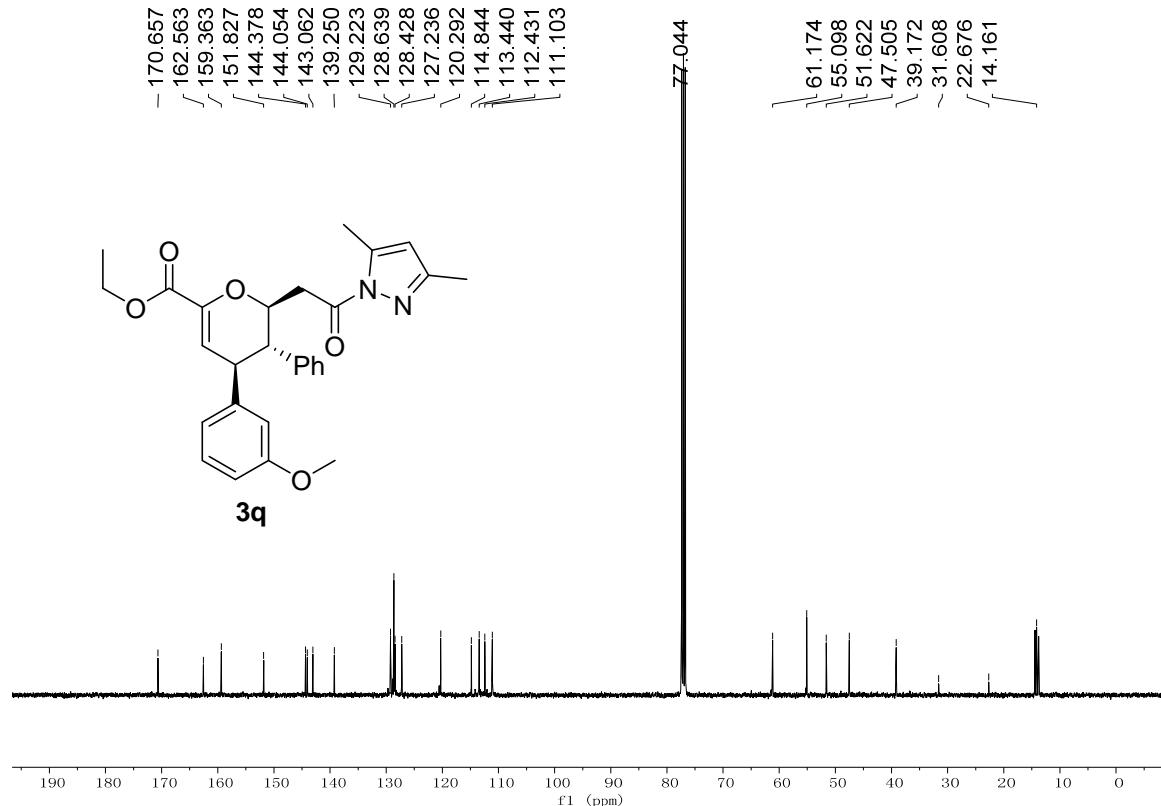
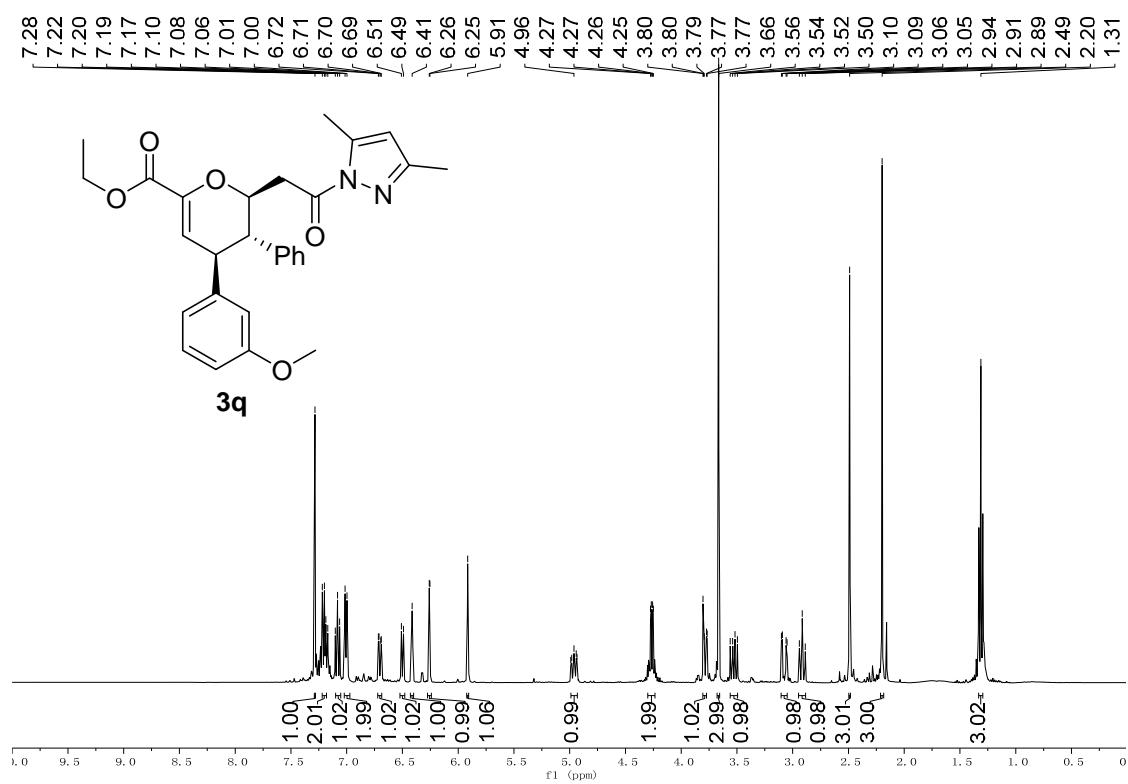
**3o:Methyl (2S,3S,4R)-4-(4-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



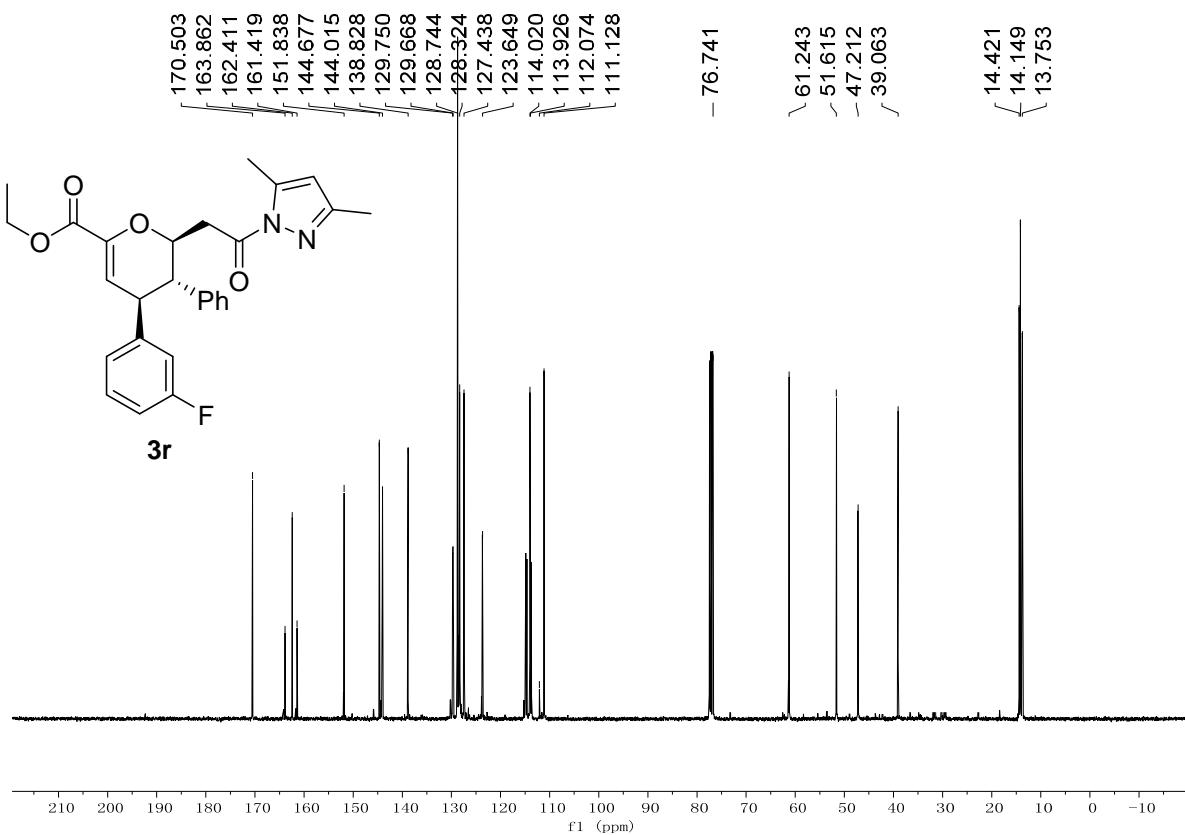
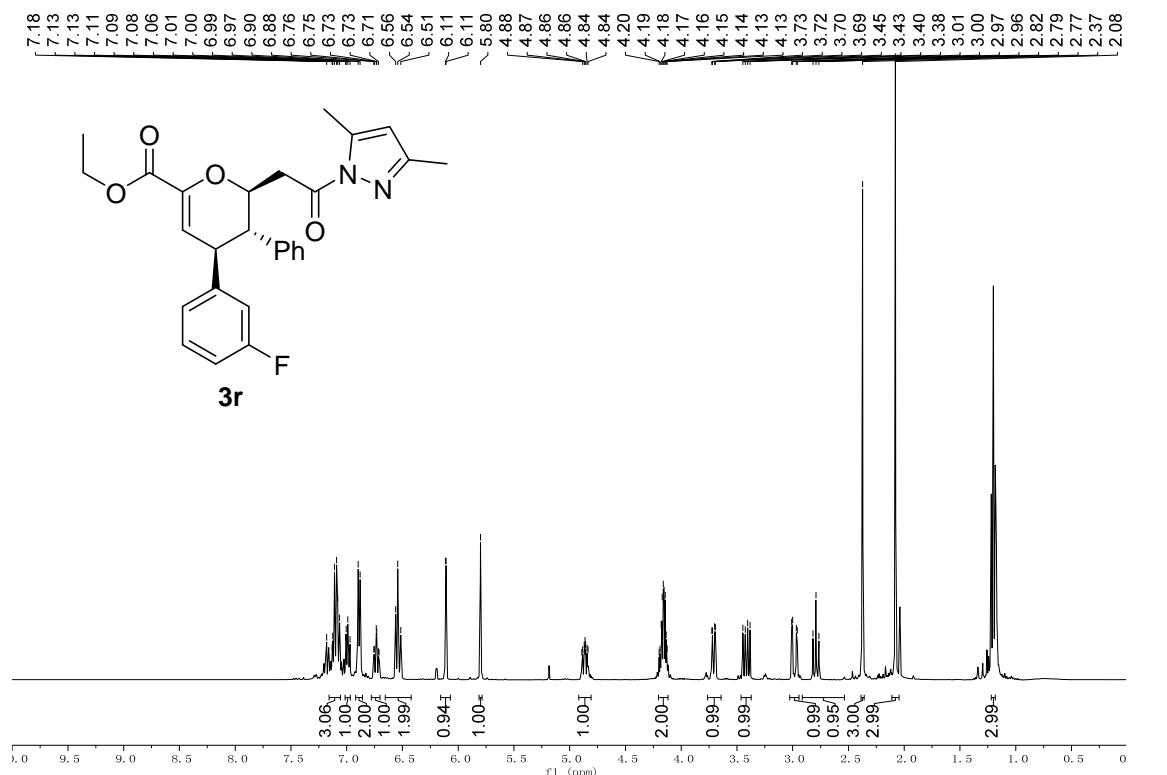
**3p:Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(m-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



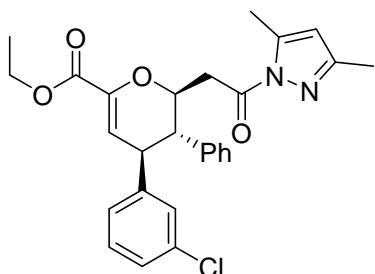
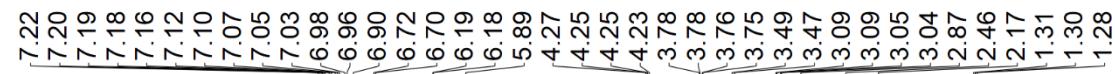
**3q:Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate :**



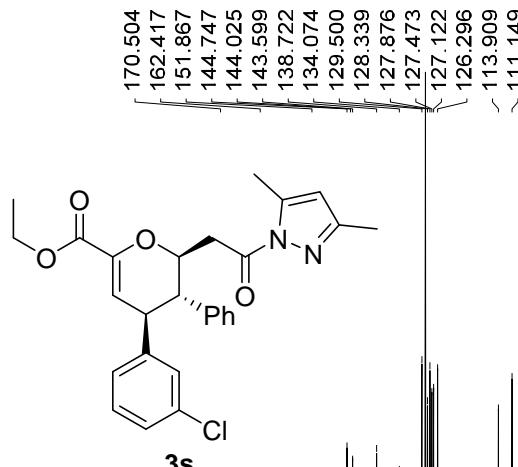
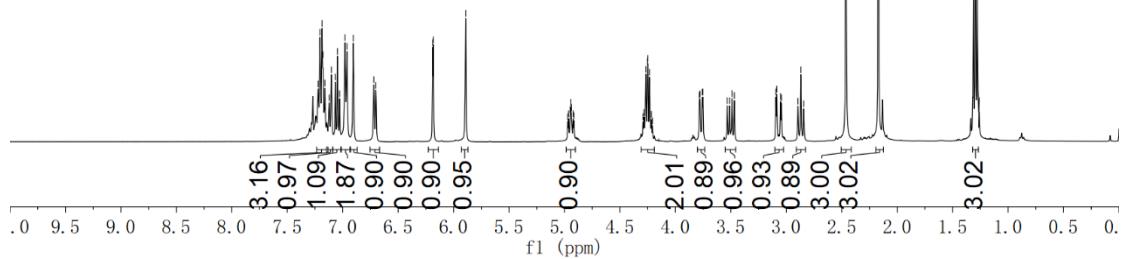
**3r:Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



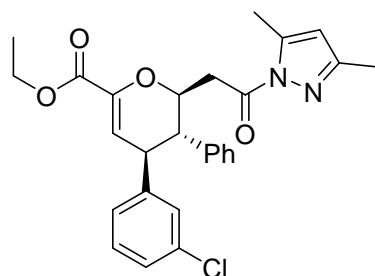
**3s: Ethyl (2S,3S,4R)-4-(3-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate :**



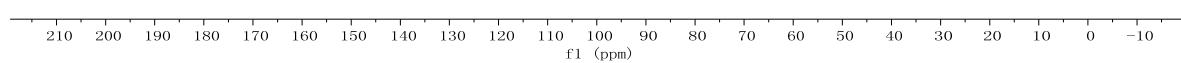
3s



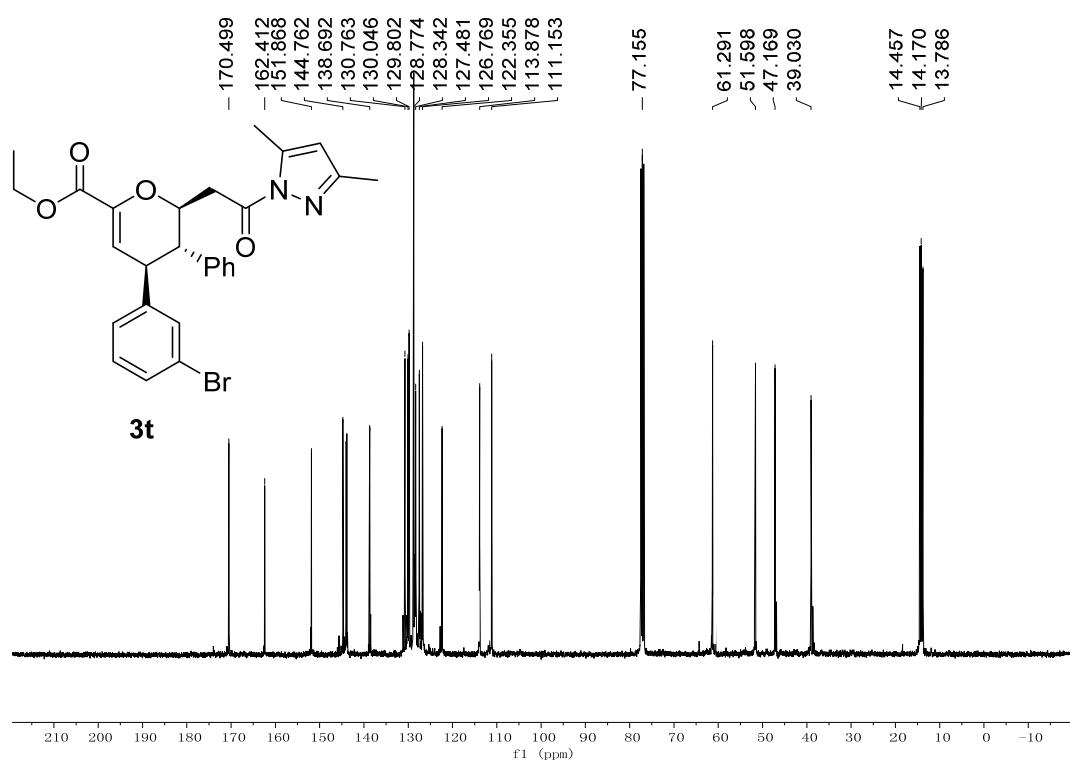
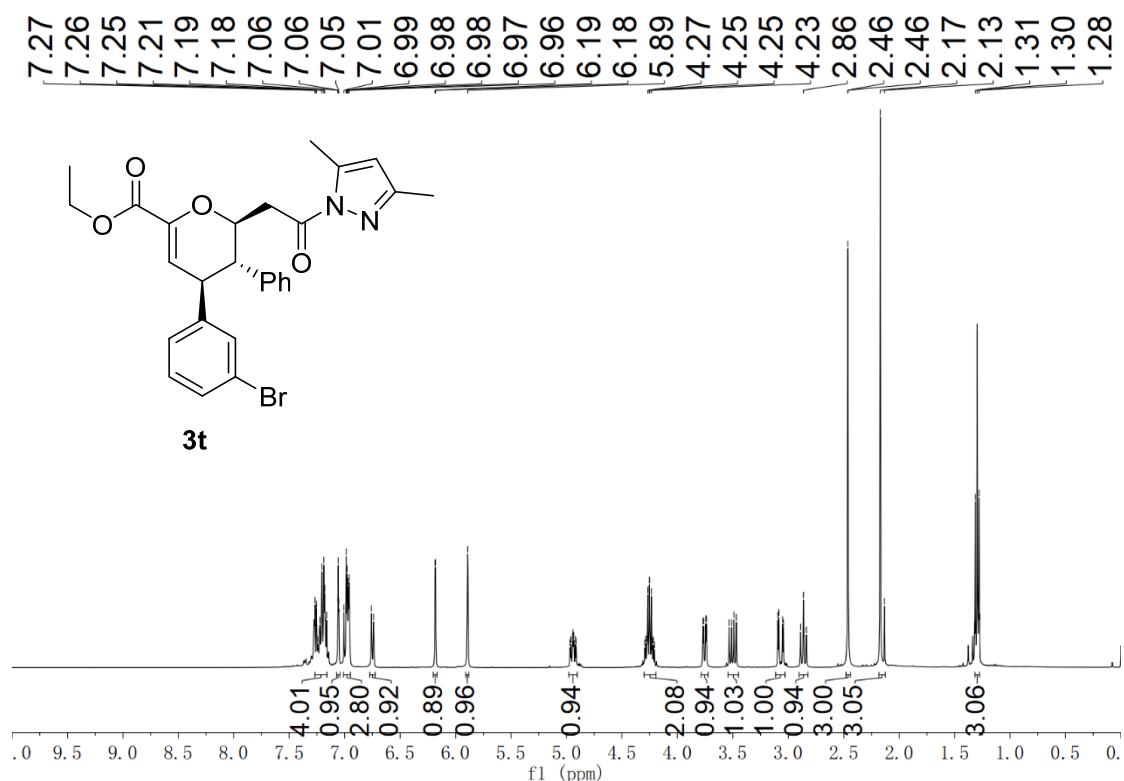
3s



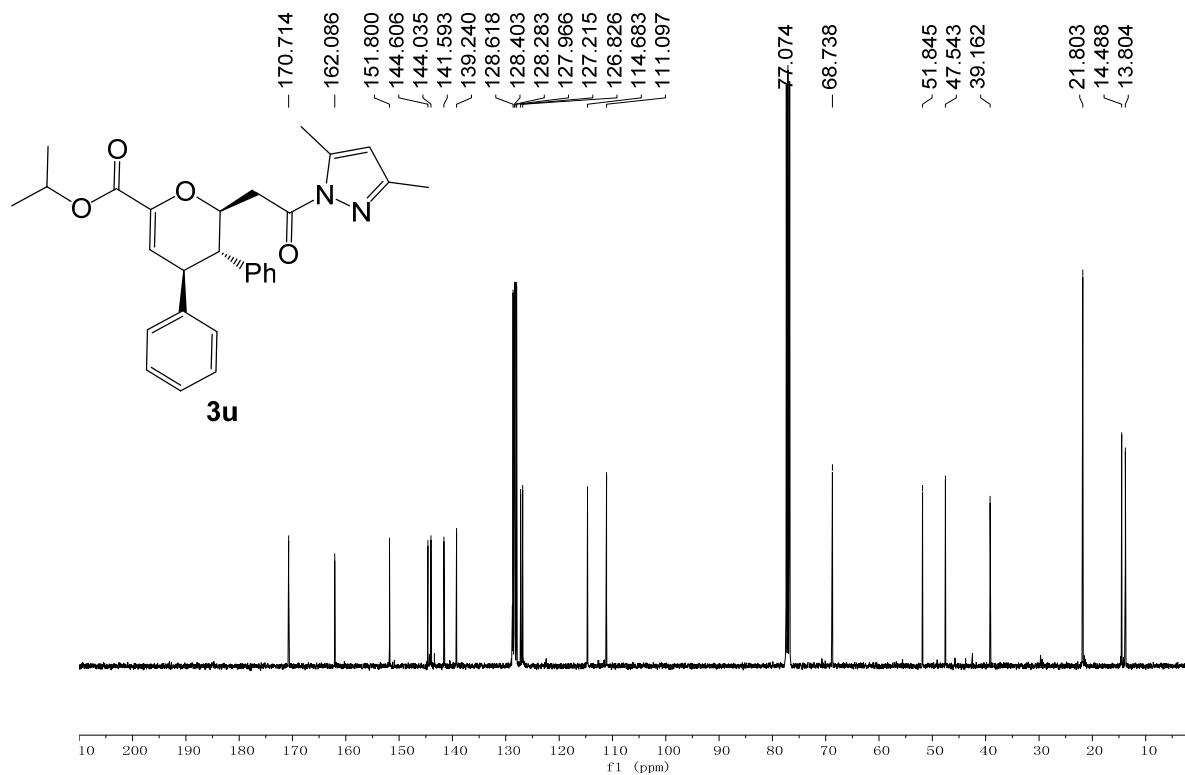
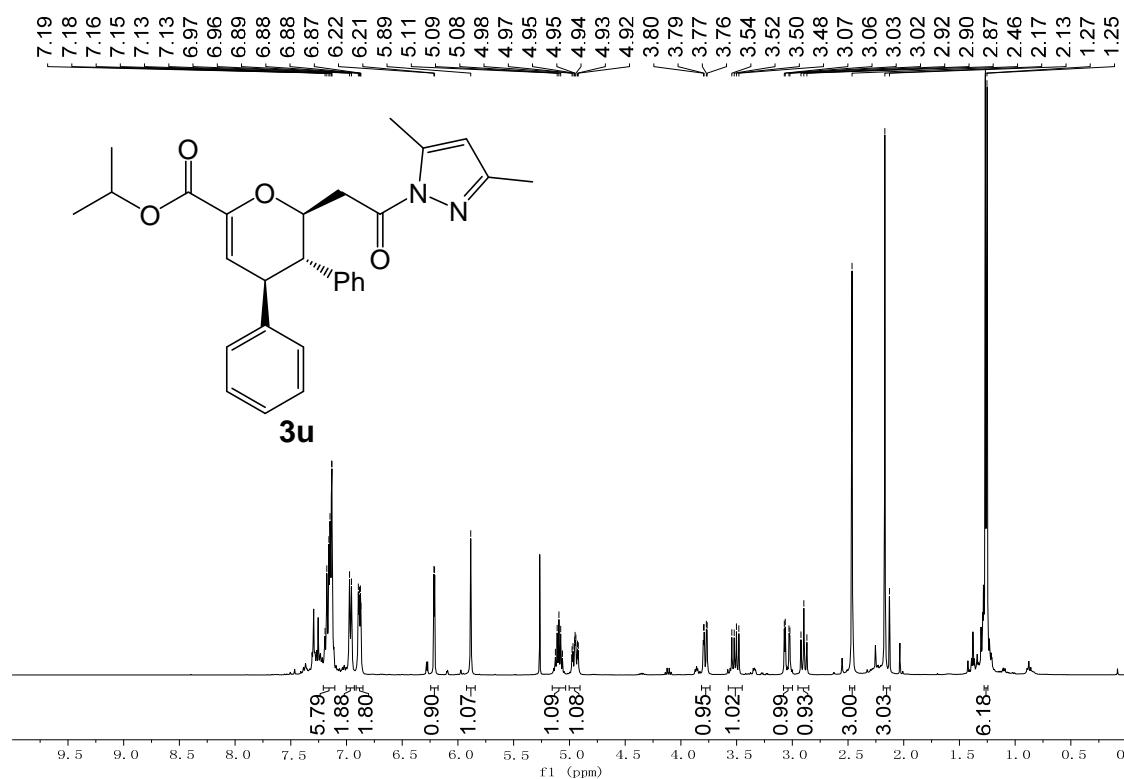
3s



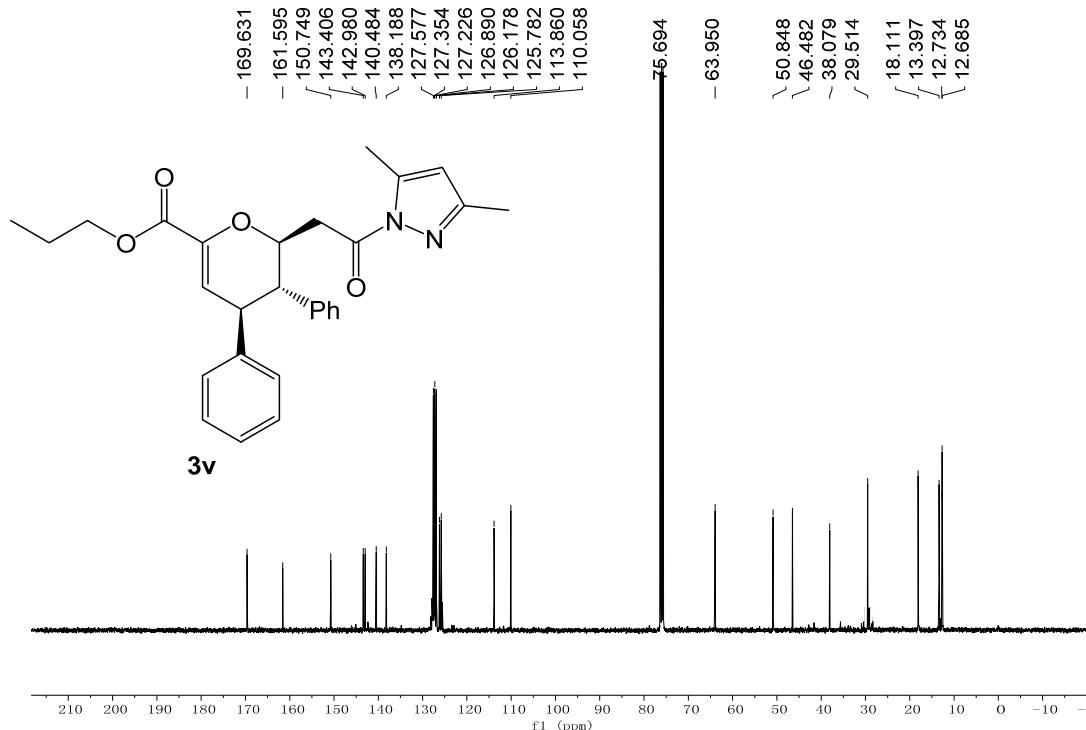
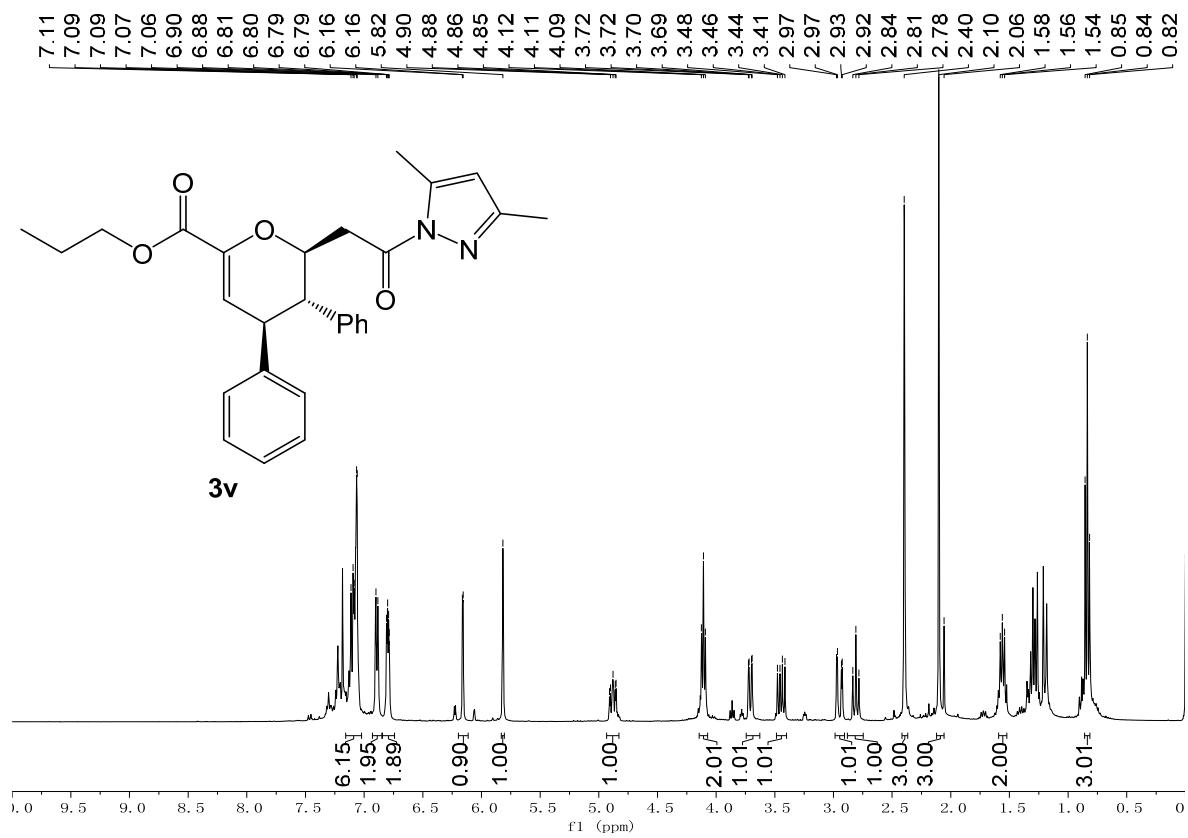
**3t:Ethyl (2S,3S,4R)-4-(3-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



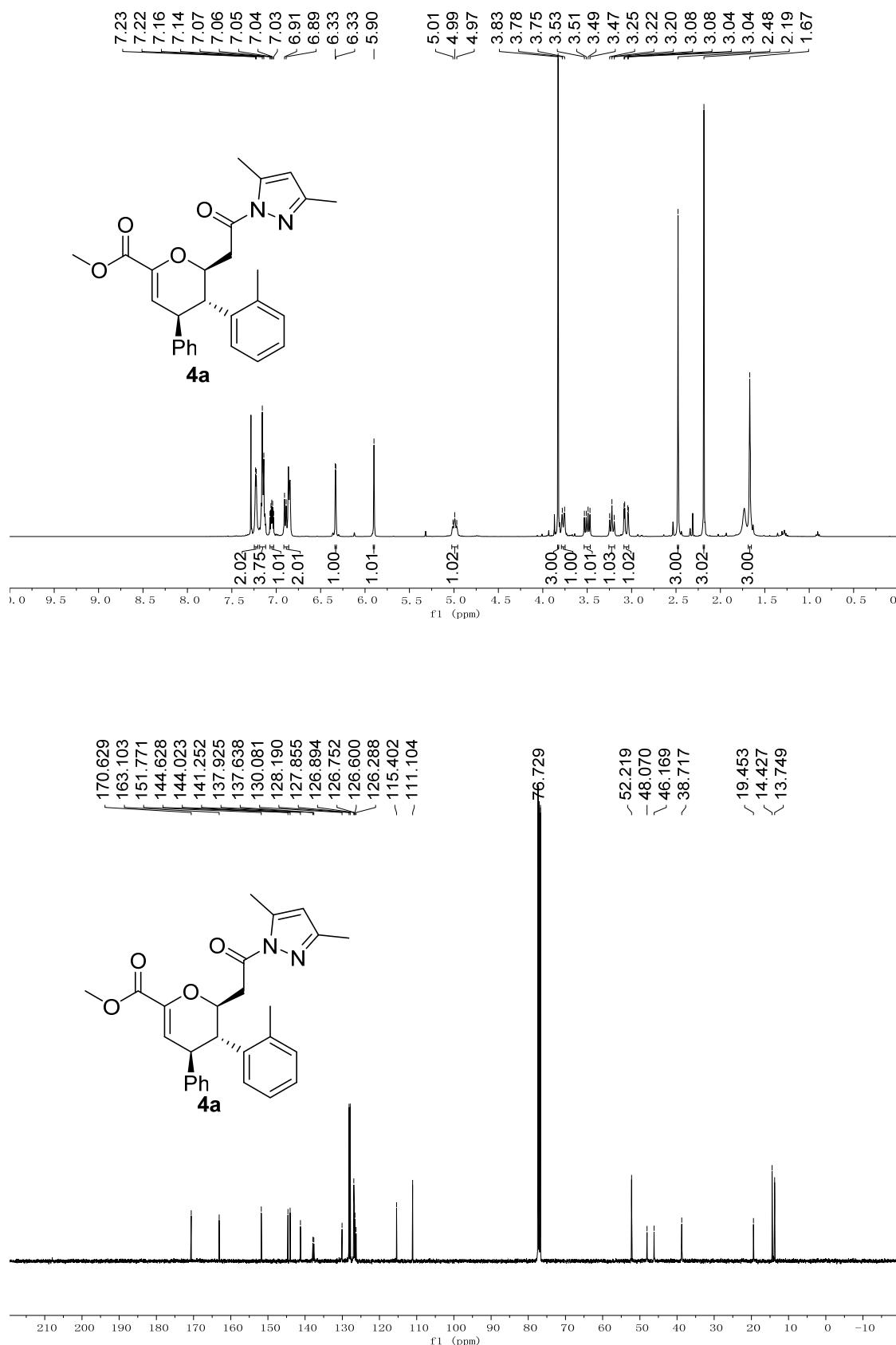
**3u: Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



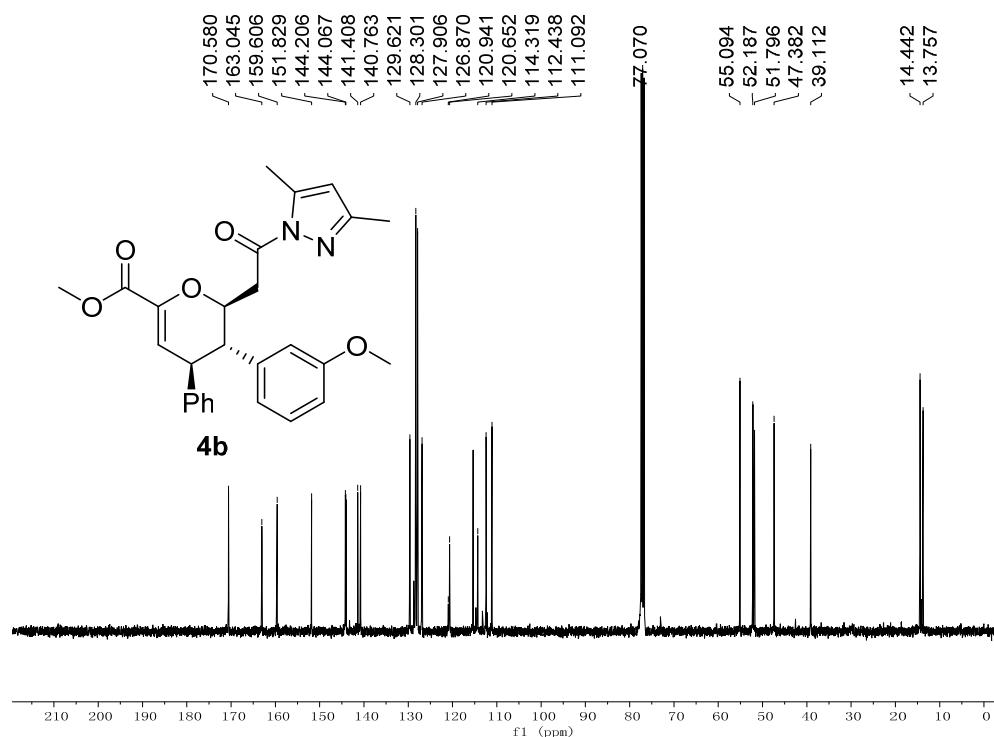
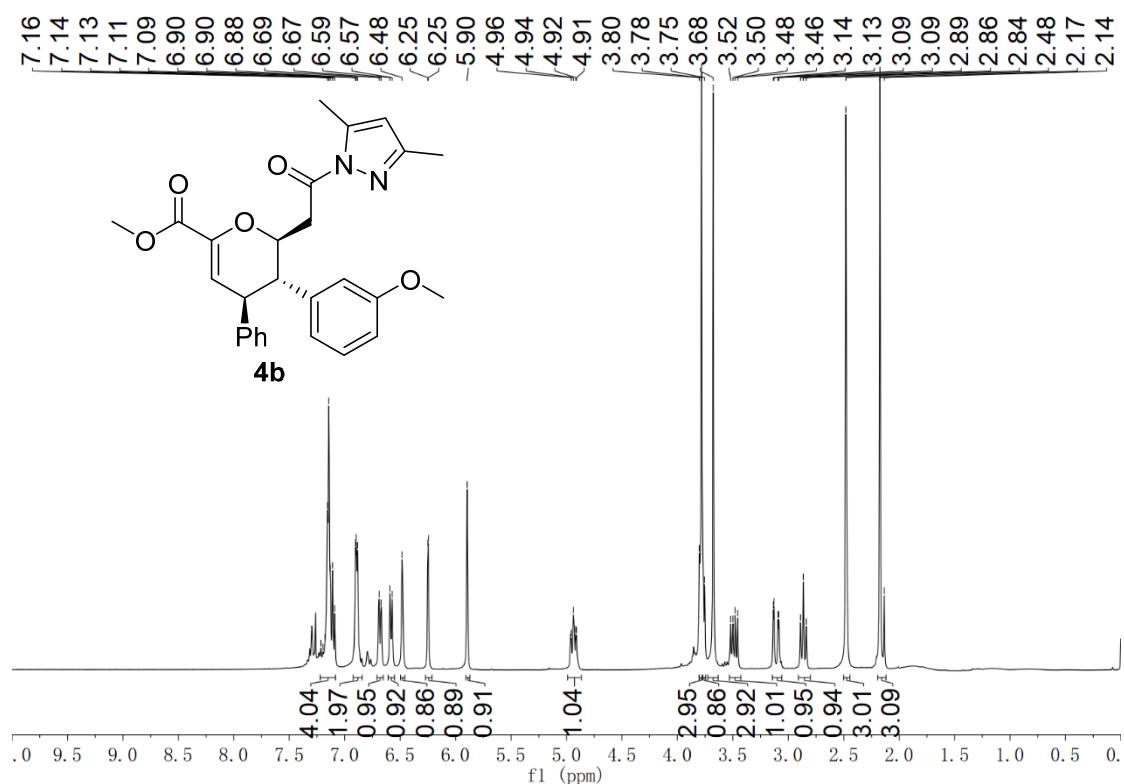
**3v: Propyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



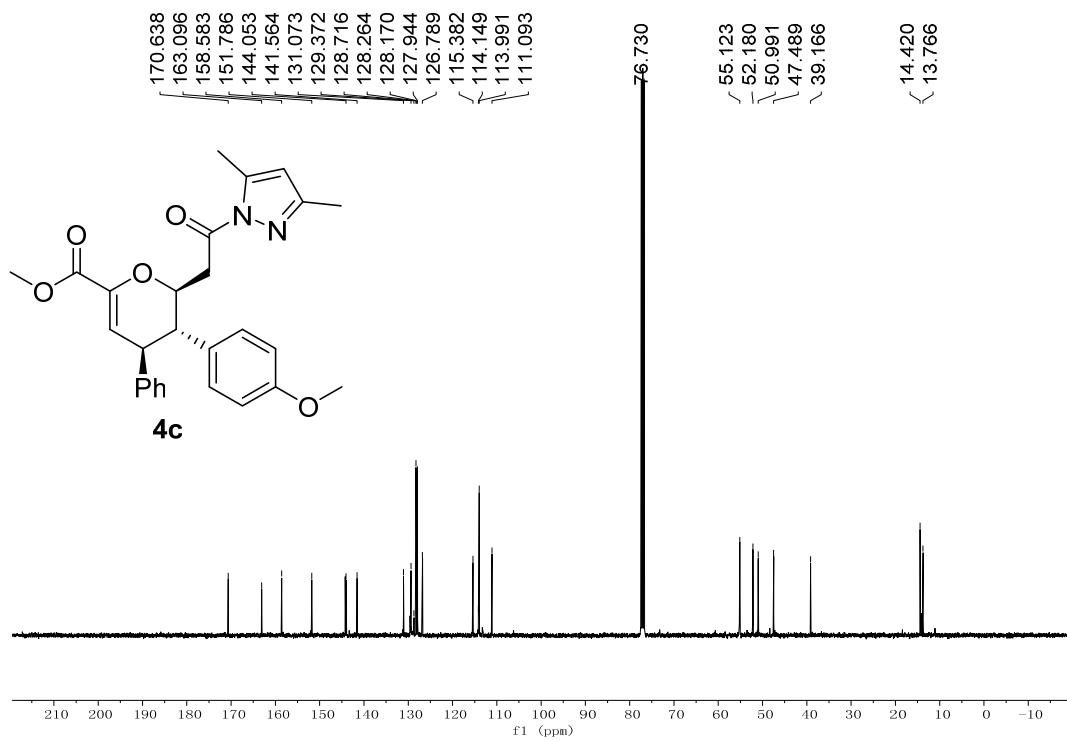
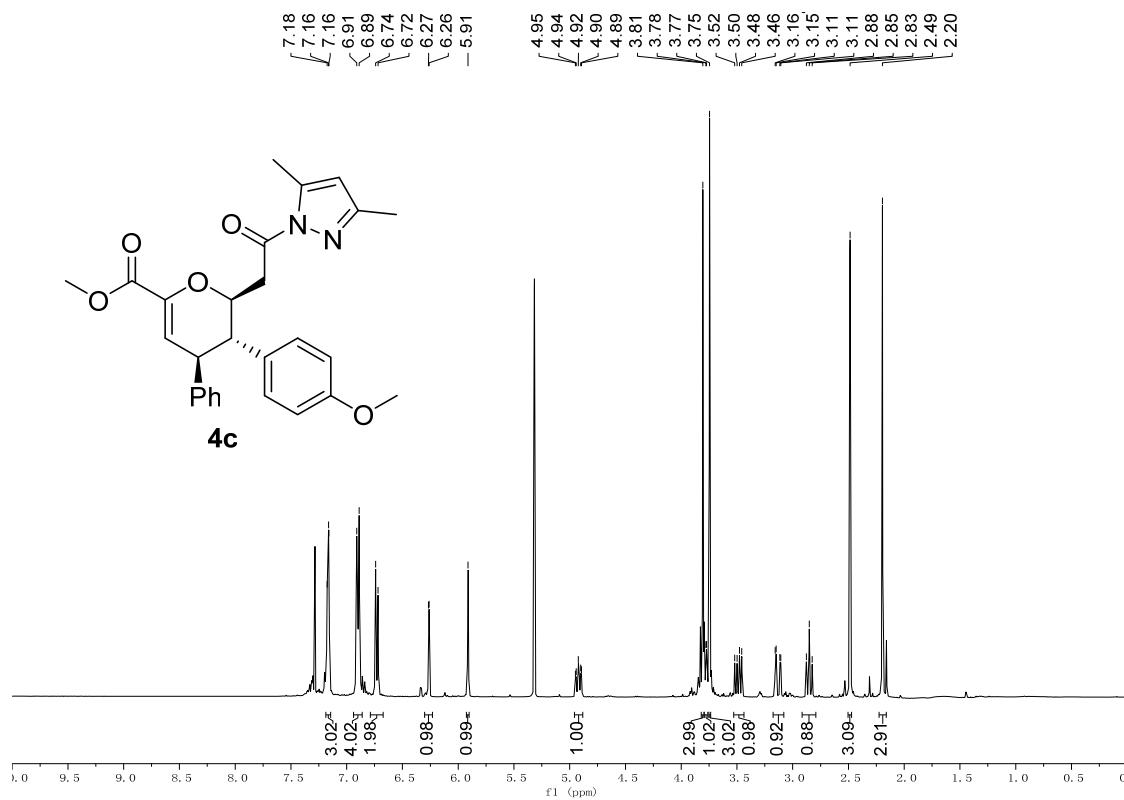
**4a:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3-(o-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate:**



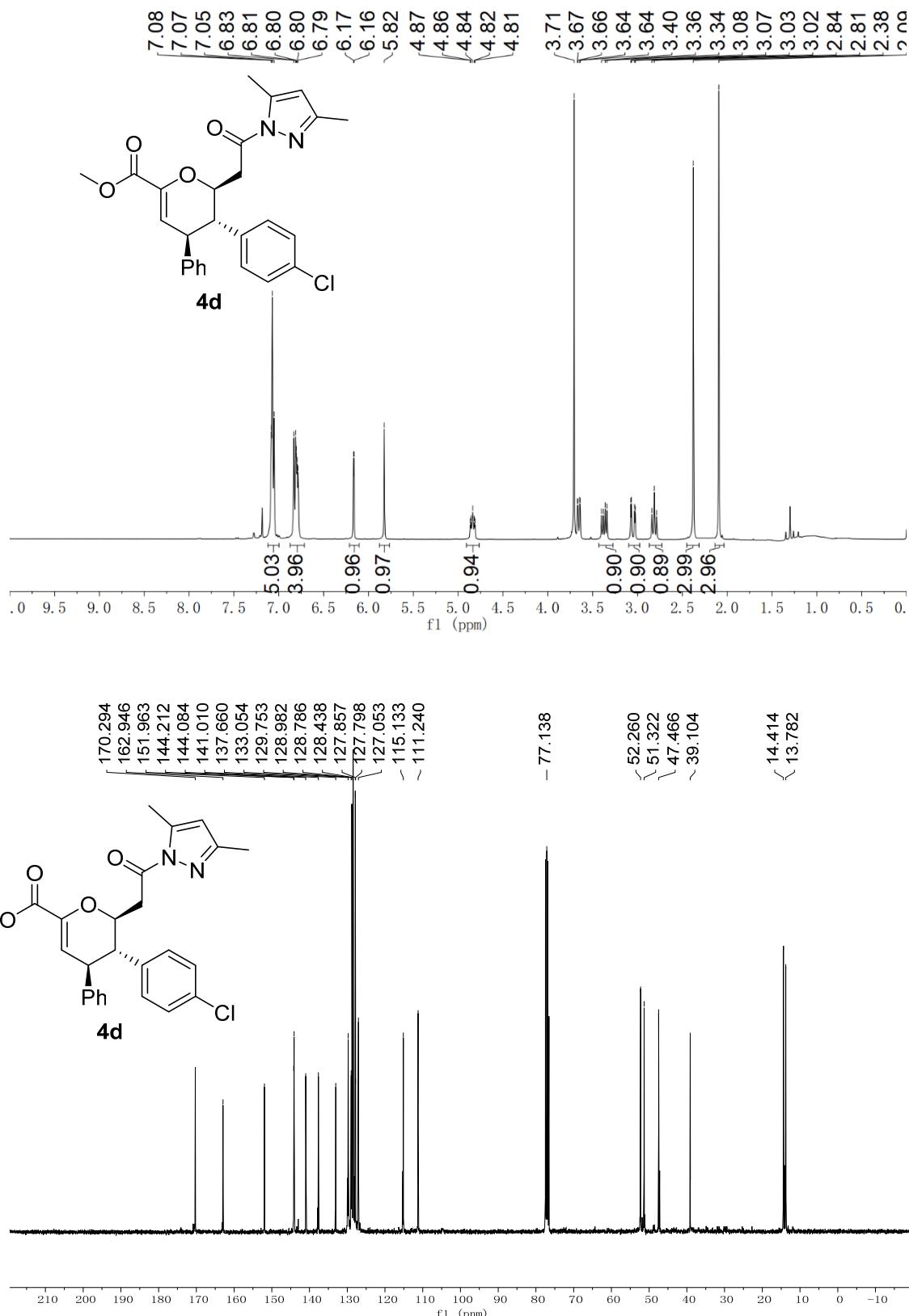
**4b:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(3-methoxyphenyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



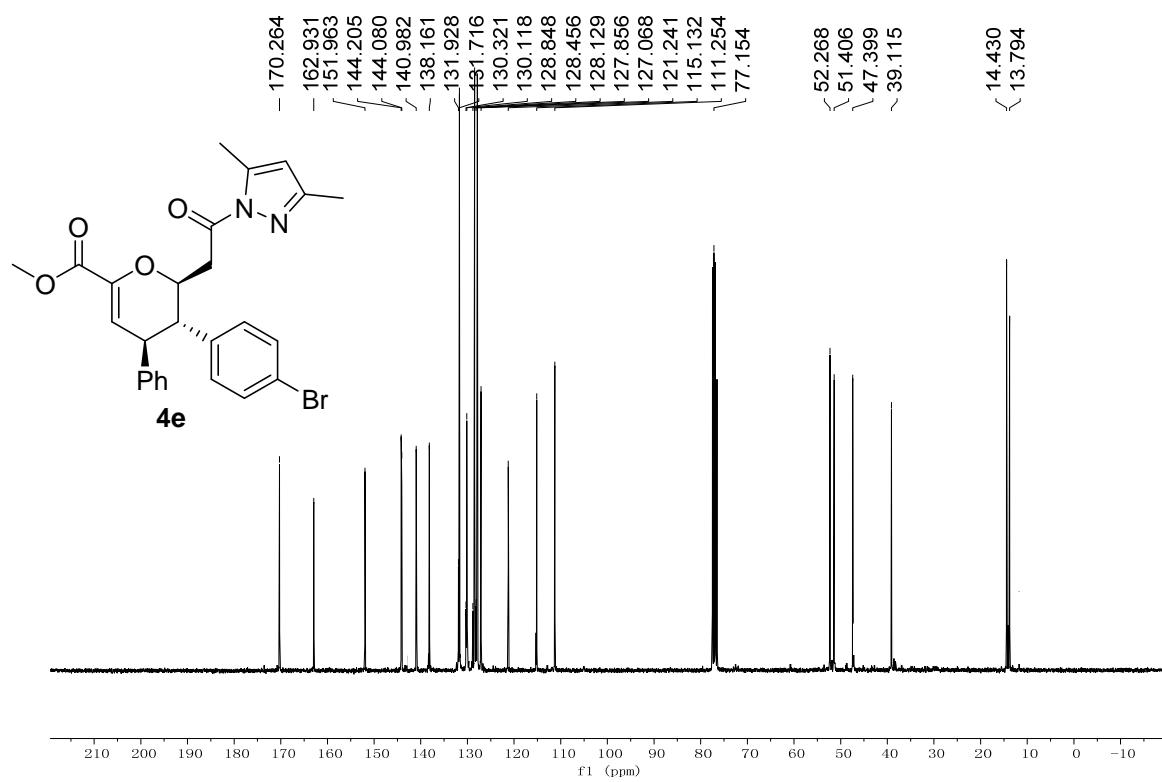
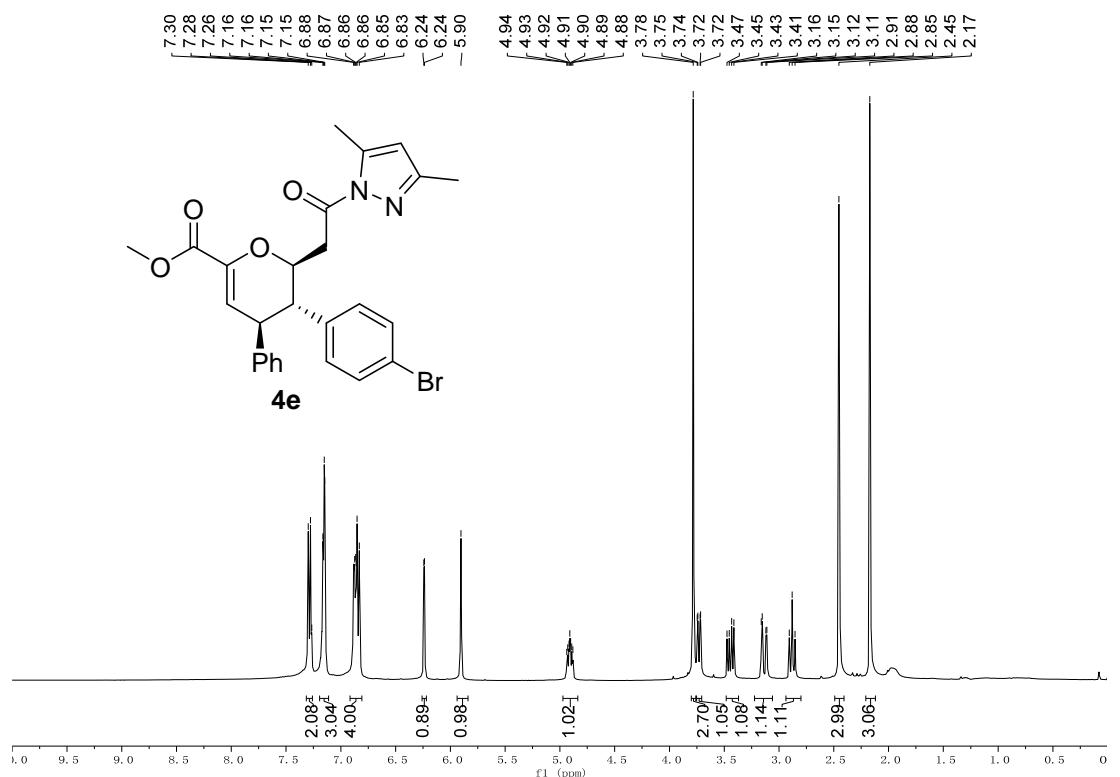
**4c:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(4-methoxyphenyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



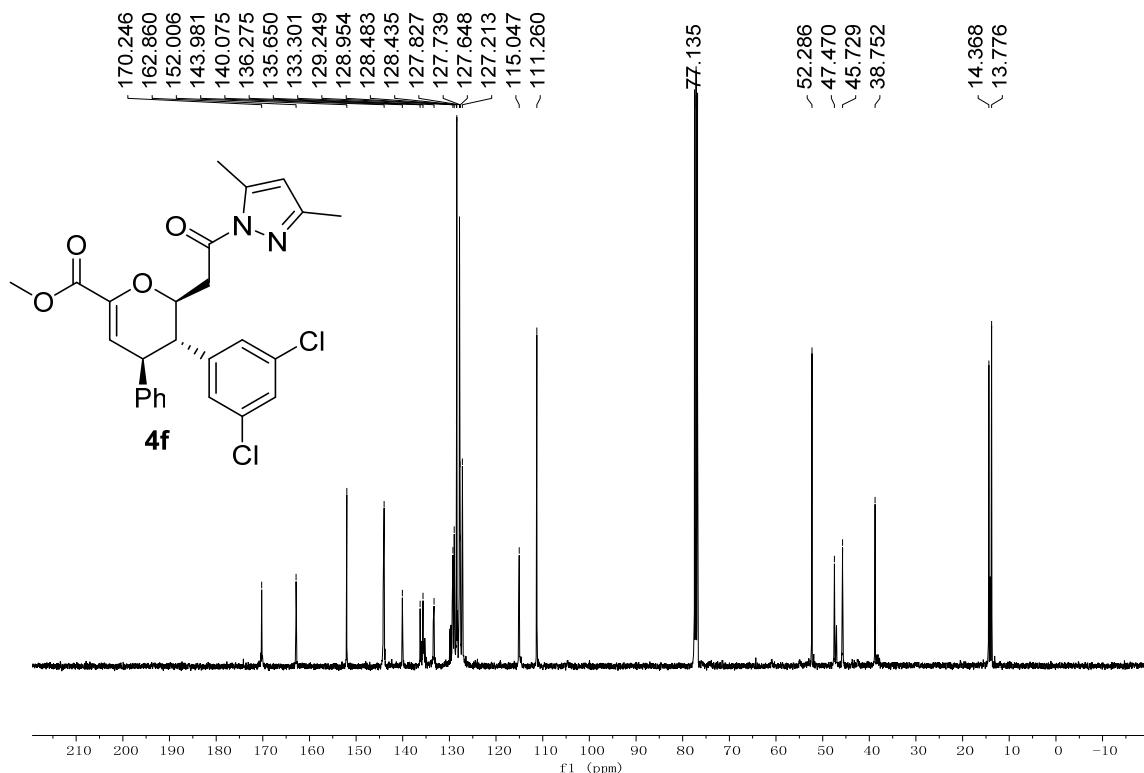
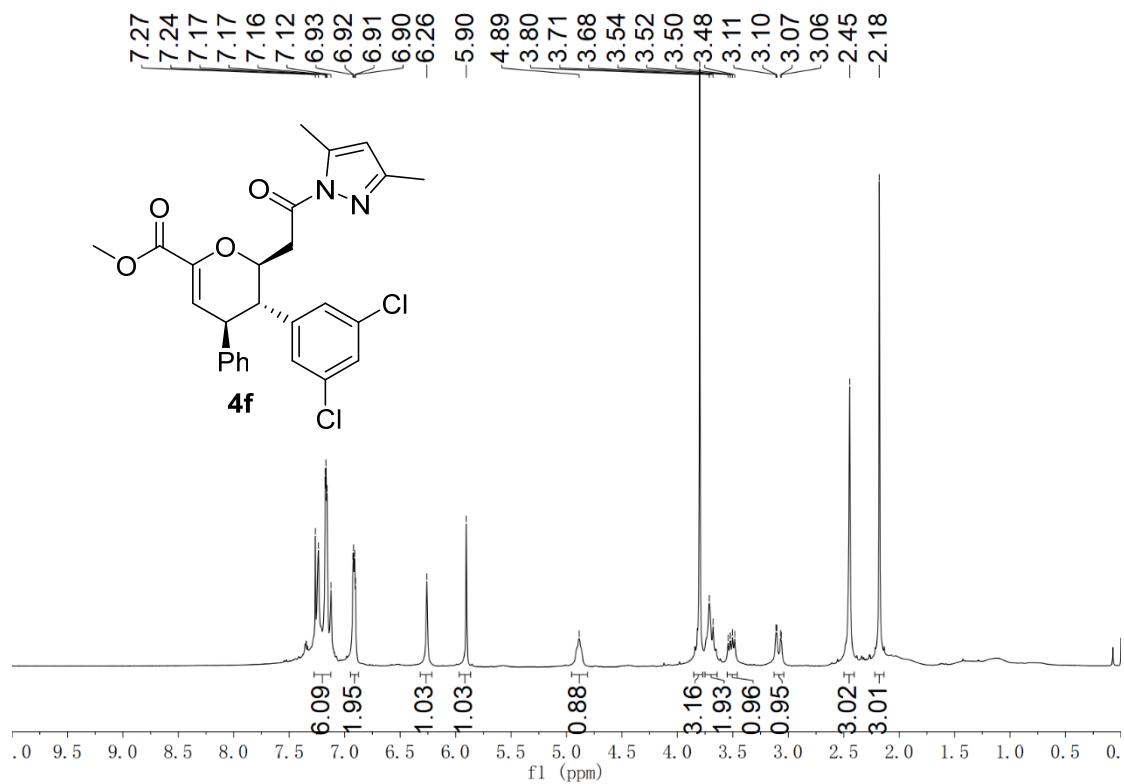
**4d:Methyl (2S,3S,4R)-3-(4-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



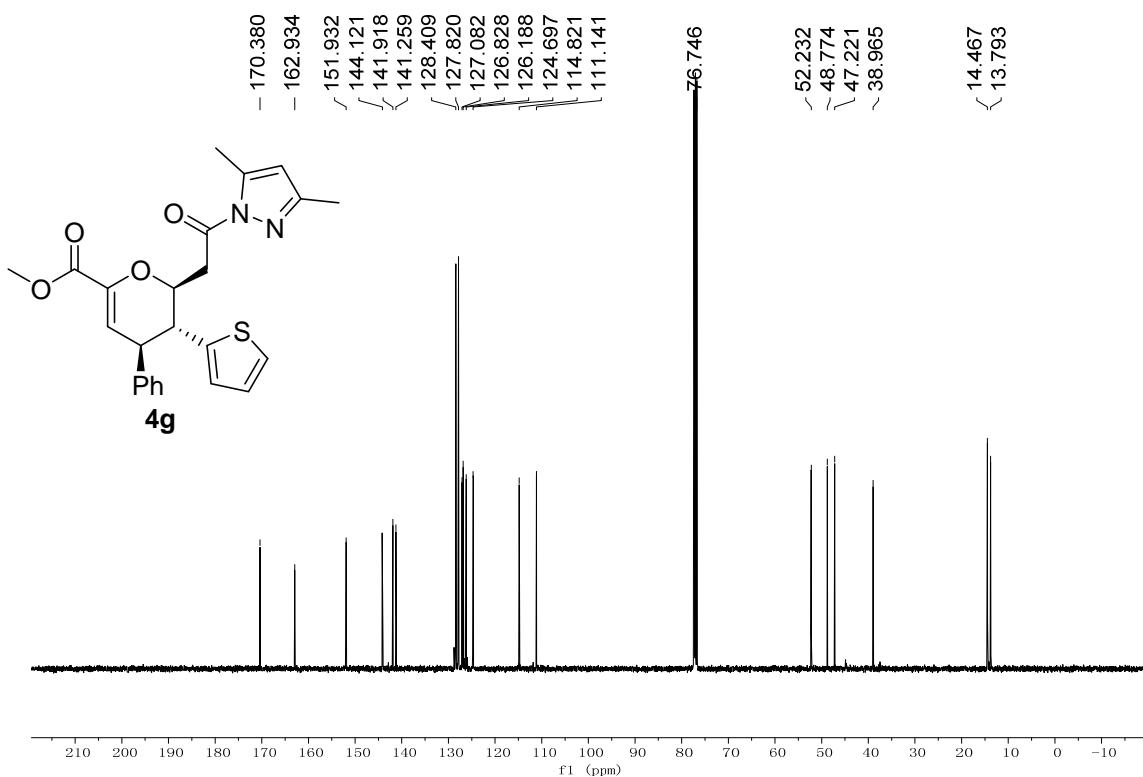
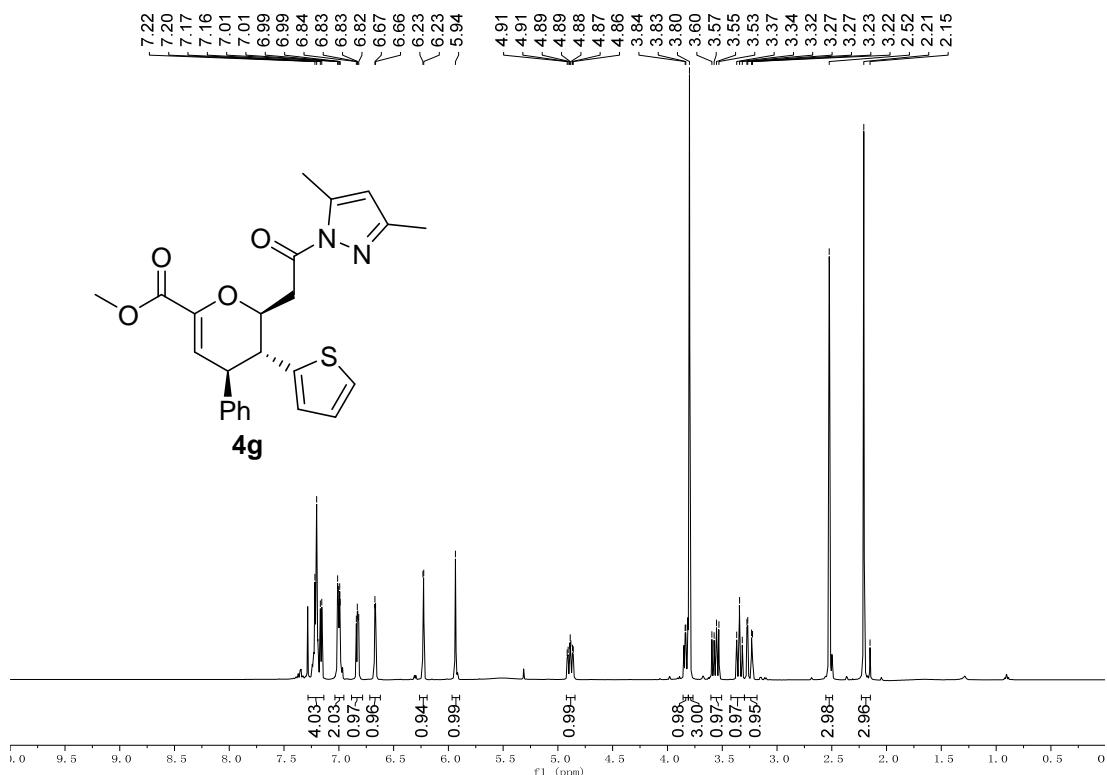
**4e:Methyl (2s,3s,4r)-3-(4-bromophenyl)-2-(2-(3,5-dimethyl-1h-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2h-pyran-6-carboxylate:**



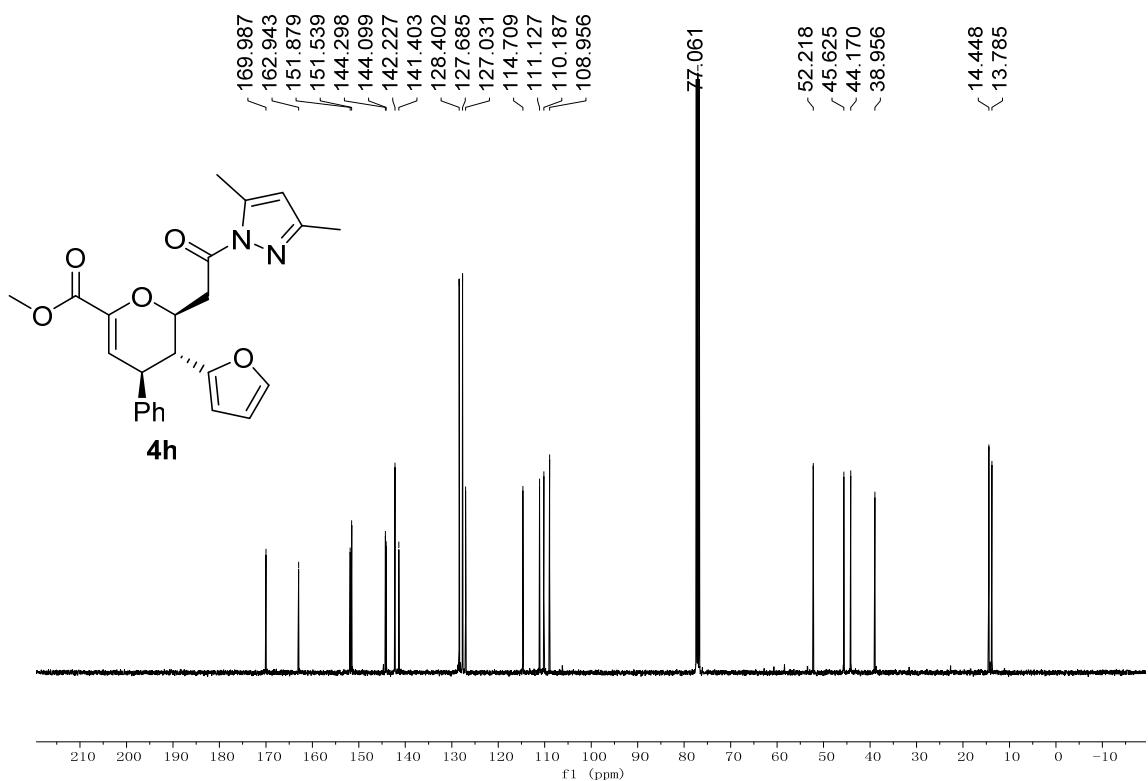
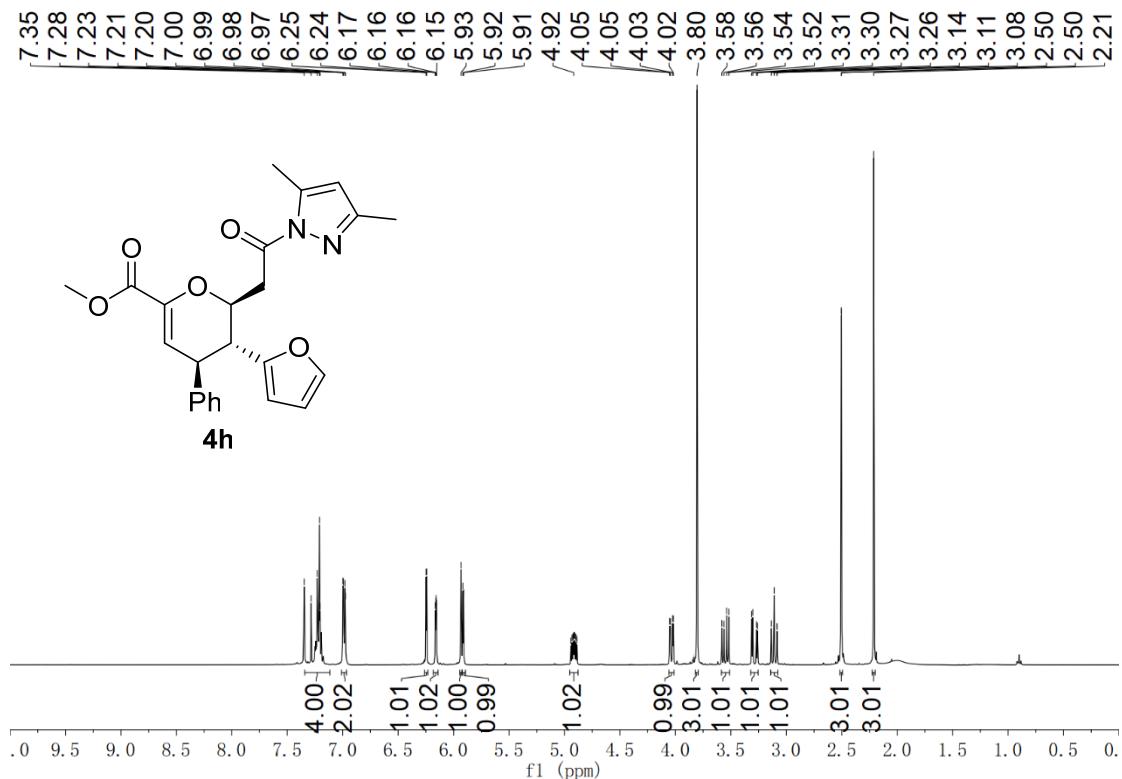
**4f:Methyl (2S,3S,4R)-3-(3,5-dichlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



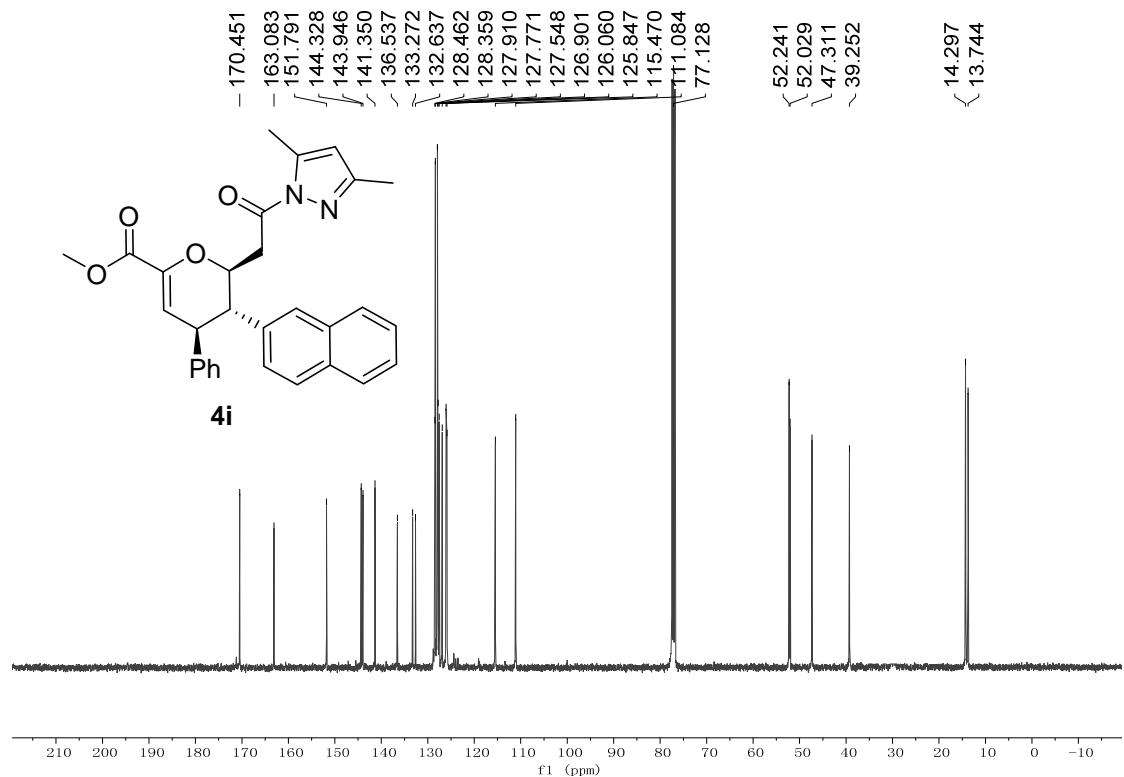
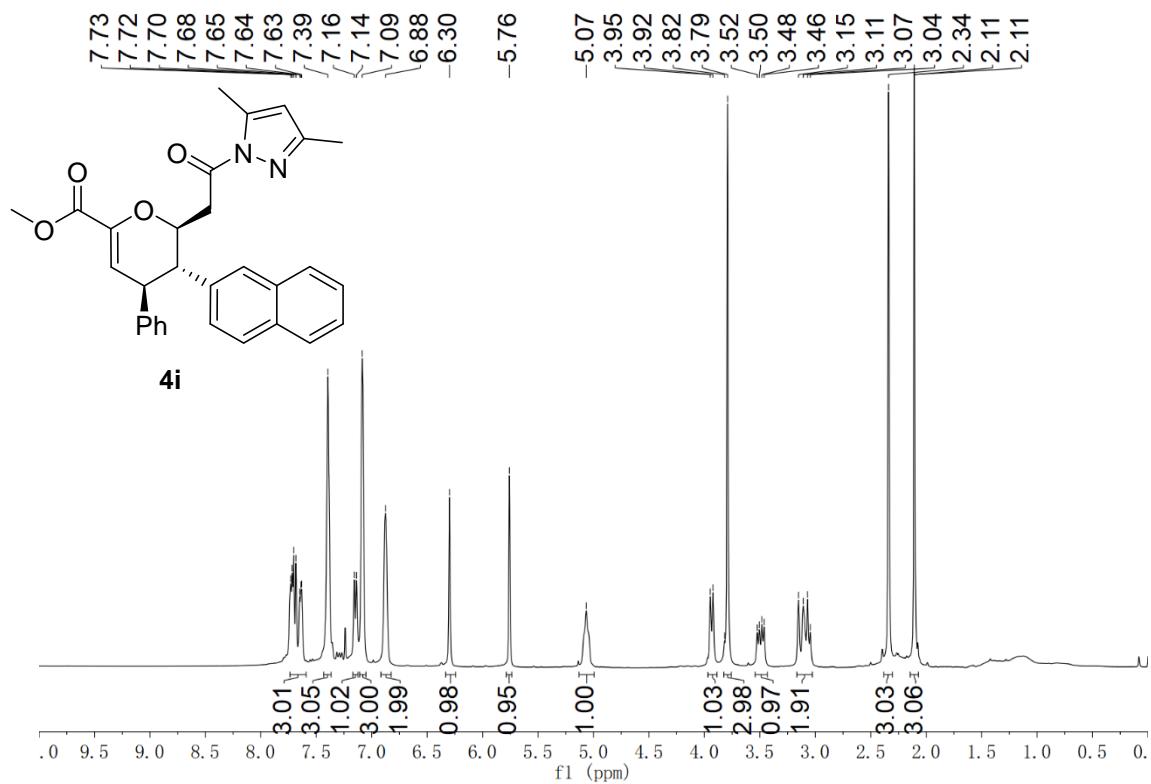
**4g: Methyl (2S,3R,4S)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3-(thiophen-2-yl)-3,4-dihydro-2H-pyran-6-carboxylate:**



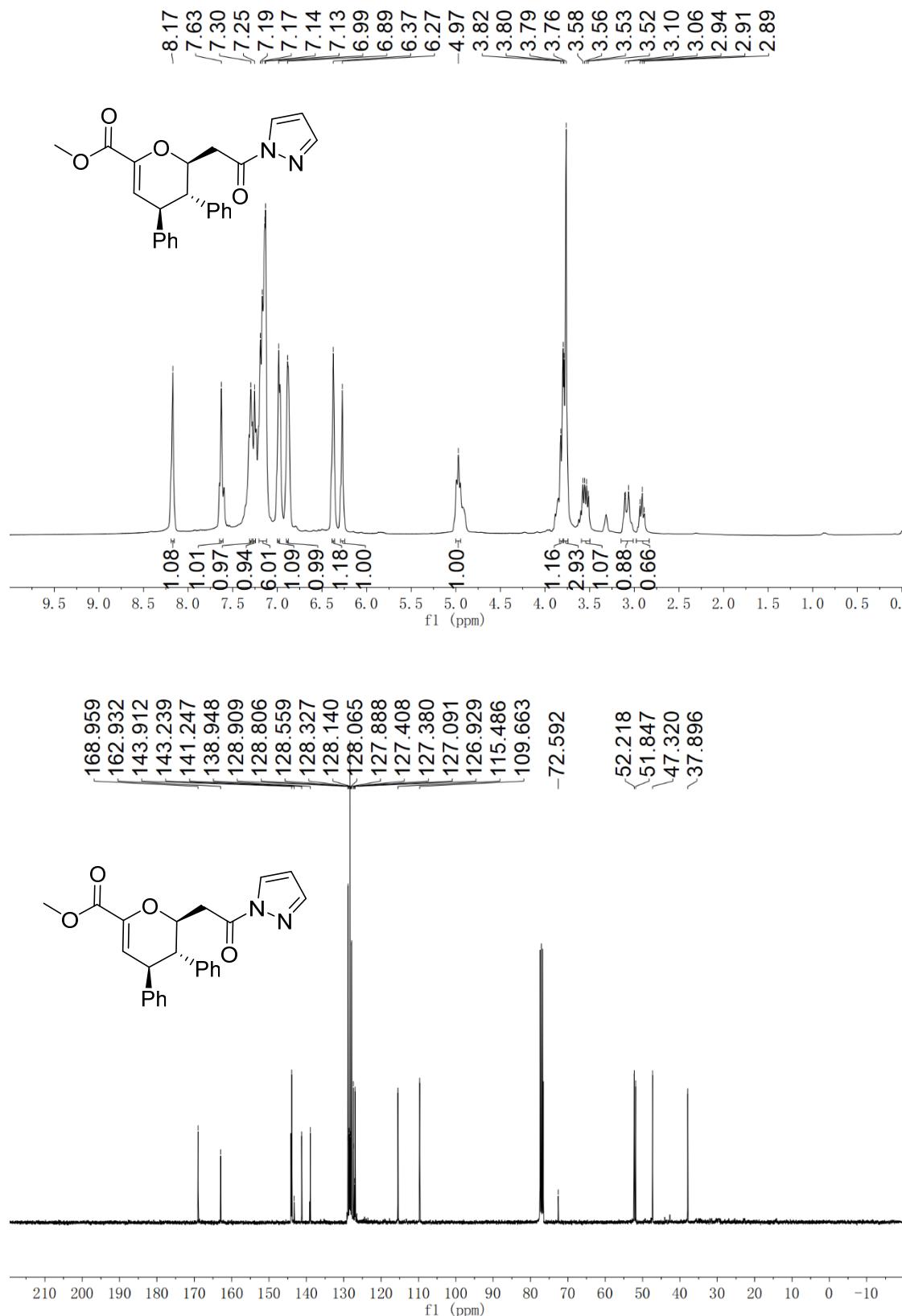
**4h: Methyl (2S,3R,4S)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(furan-2-yl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



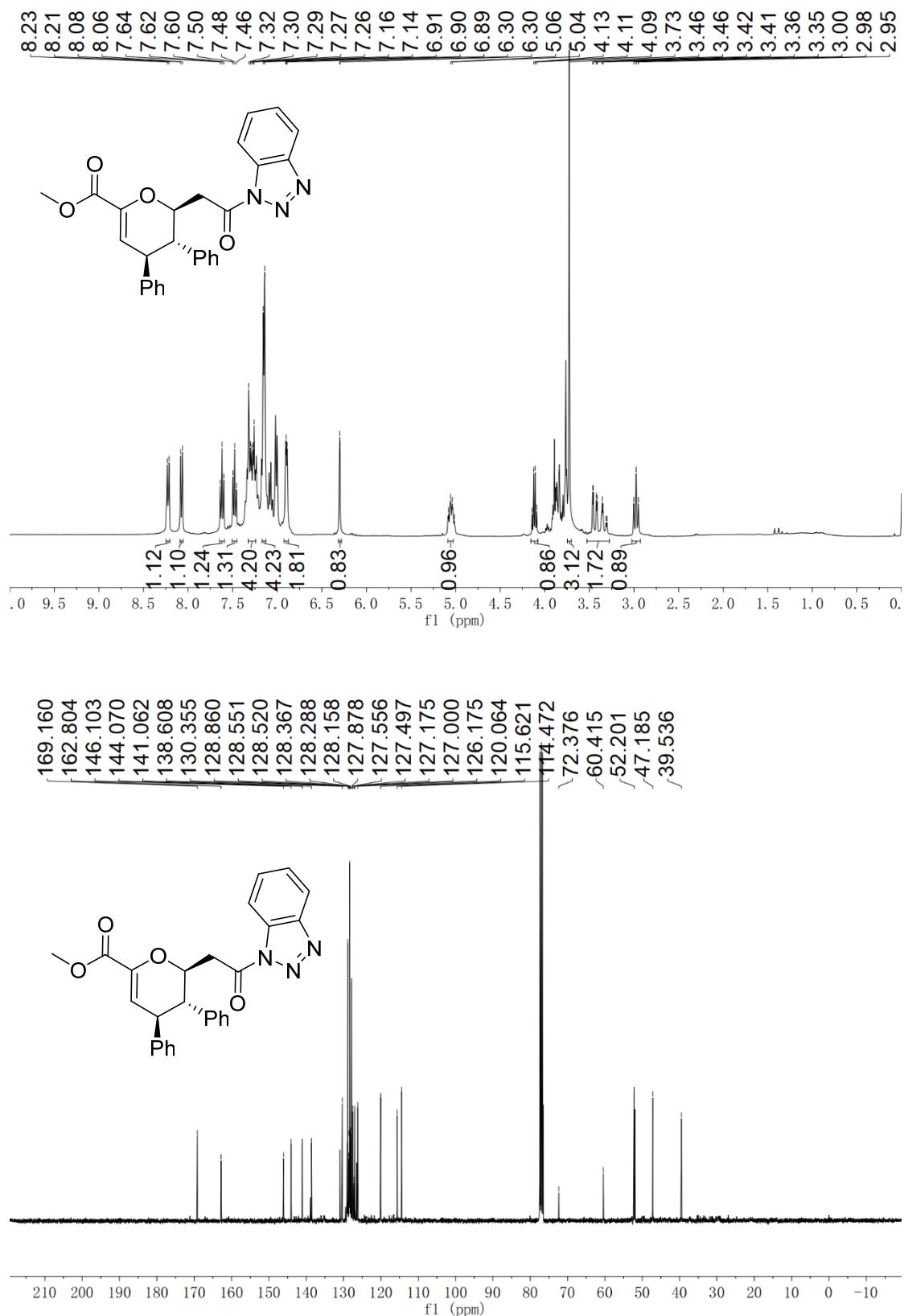
**4i:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(naphthalen-2-yl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**



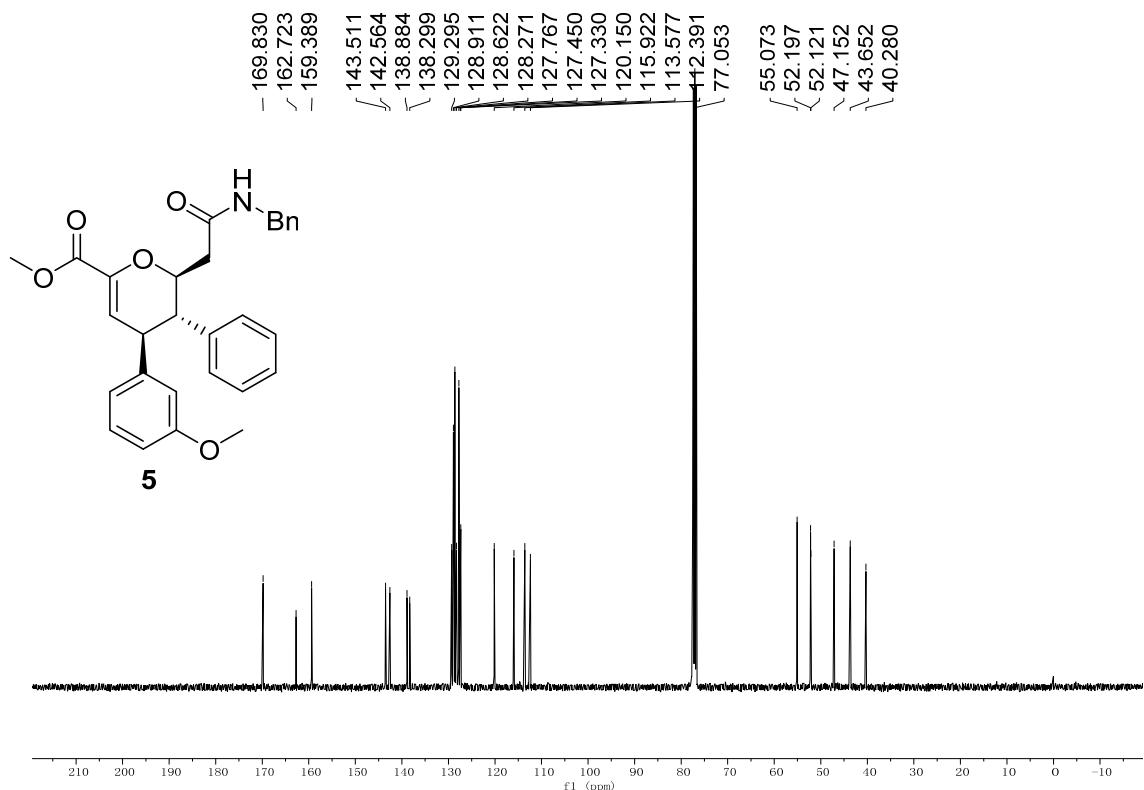
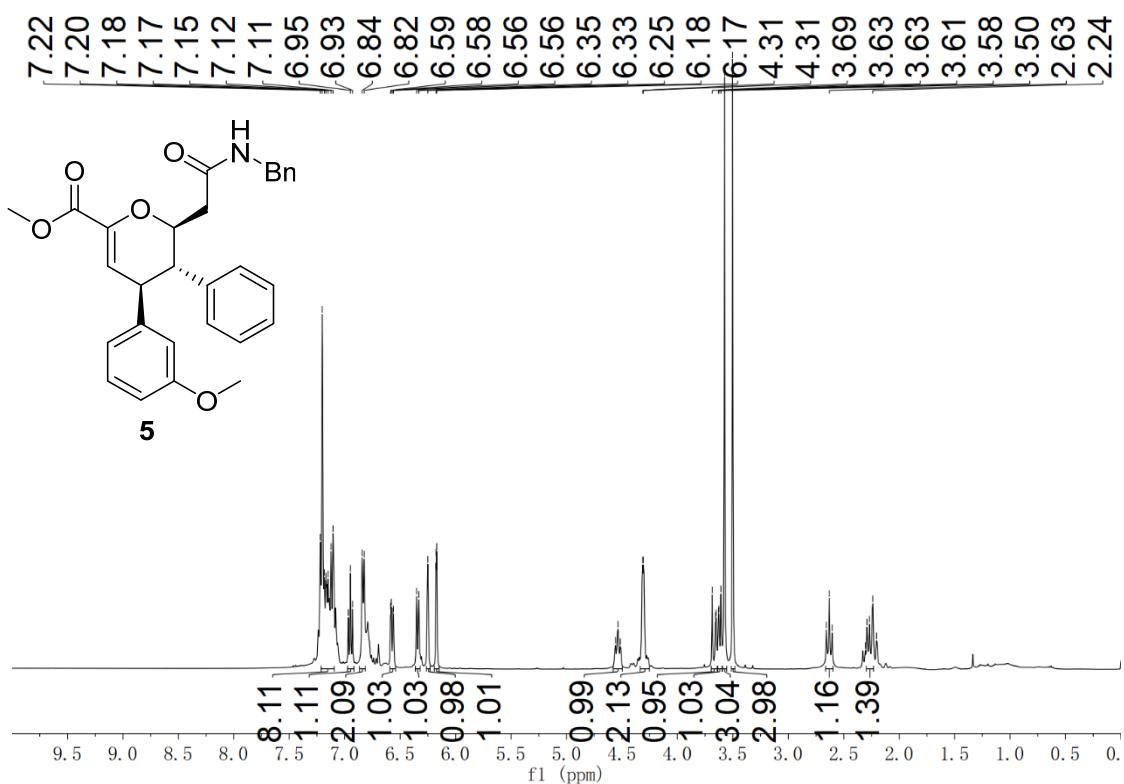
**4j: Methyl (2S,3S,4R)-2-(2-oxo-2-(1H-pyrazol-1-yl)ethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**



**4k: Methyl (2S,3S,4R)-2-(2-(1H-benzo[d][1,2,3]triazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**

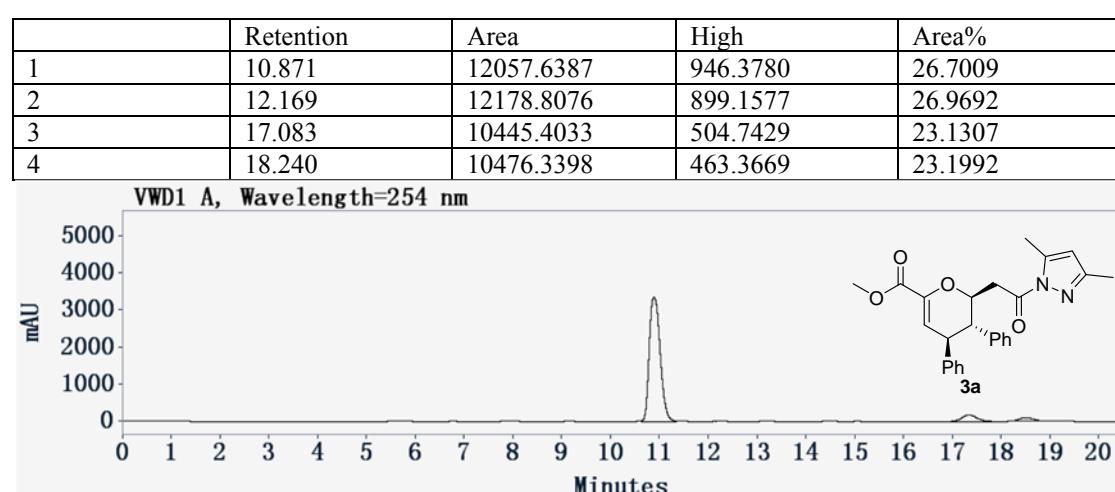
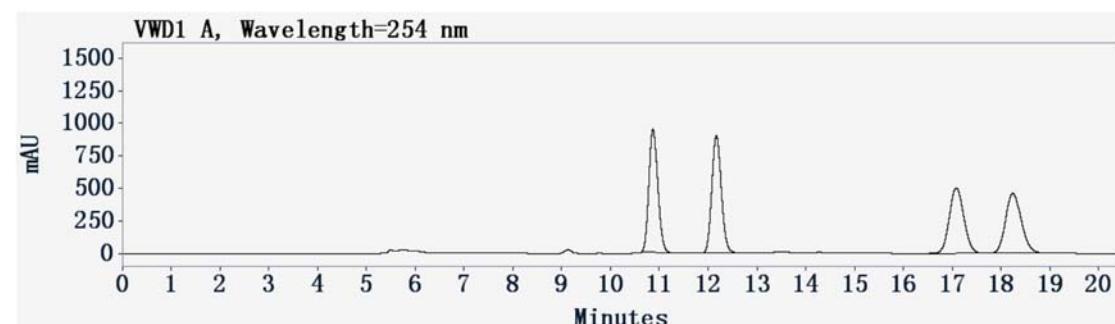


**5: Methyl (2S,3S,4R)-2-(2-(benzylamino)-2-oxoethyl)-4-(3-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate:**

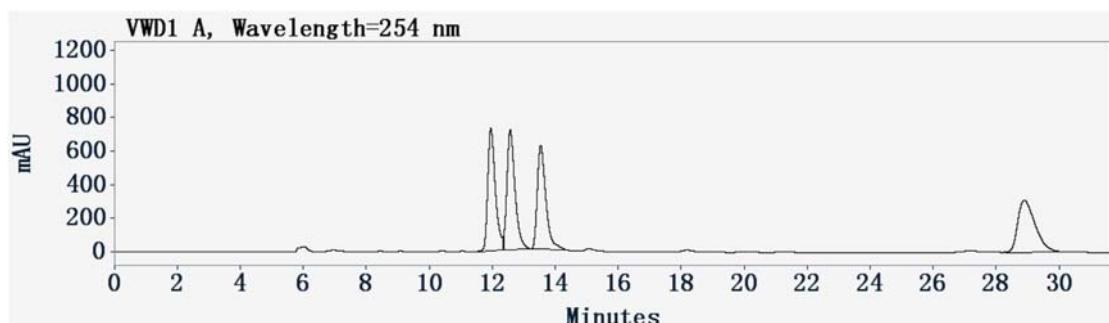


### VIII. HPLC spectra.

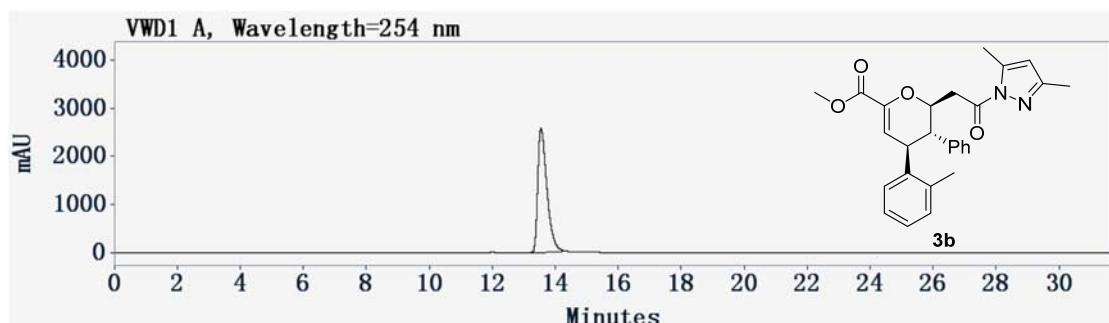
**3a:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**



**3b:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(o-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate**

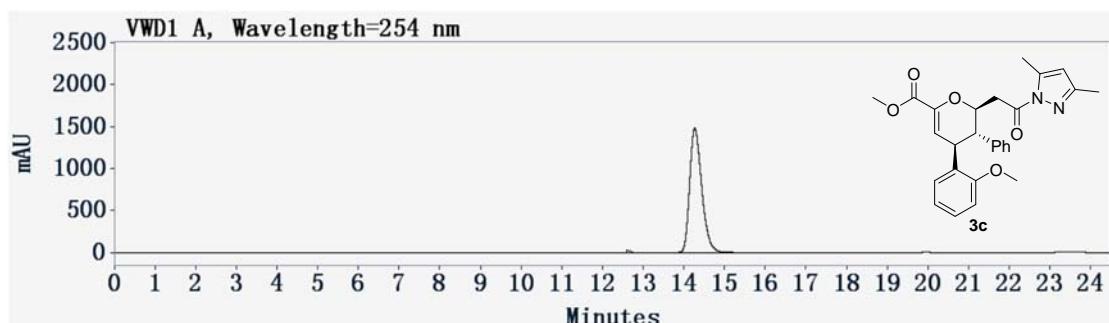
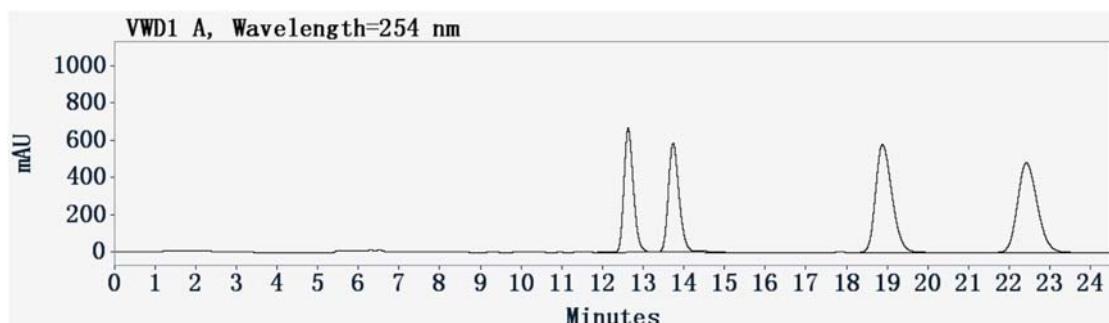


	Retention	Area	High	Area%
1	11.956	12260.3984	731.4773	25.1597
2	12.571	12799.9141	717.5598	26.2669
3	13.539	11731.8457	619.7164	24.0751
4	28.891	11938.1279	311.3366	24.4984



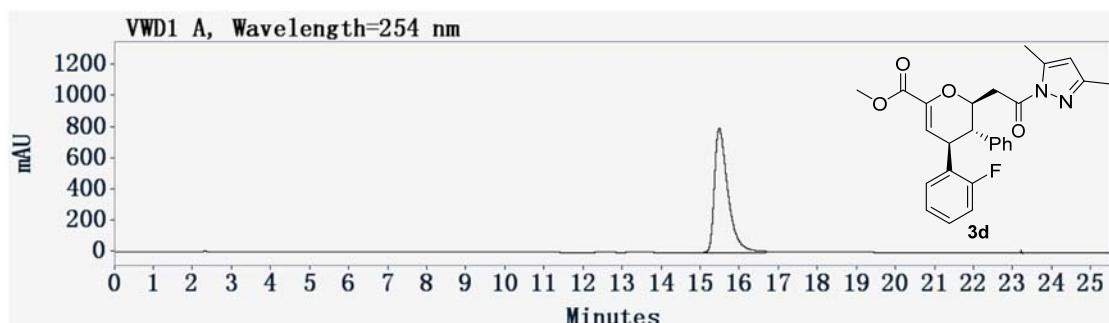
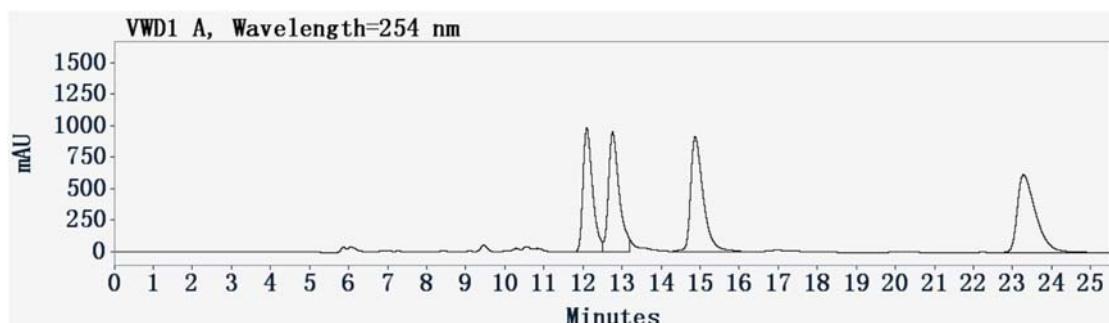
	Retention	Area	High	Area%
1	13.549	52534.5547	2586.6890	99.9857
2	28.872	7.5244	2.7739	0.0143

**3c:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(2-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**



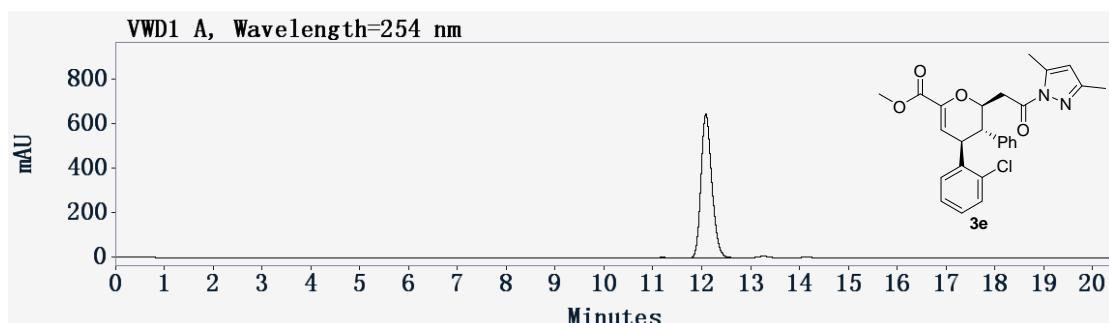
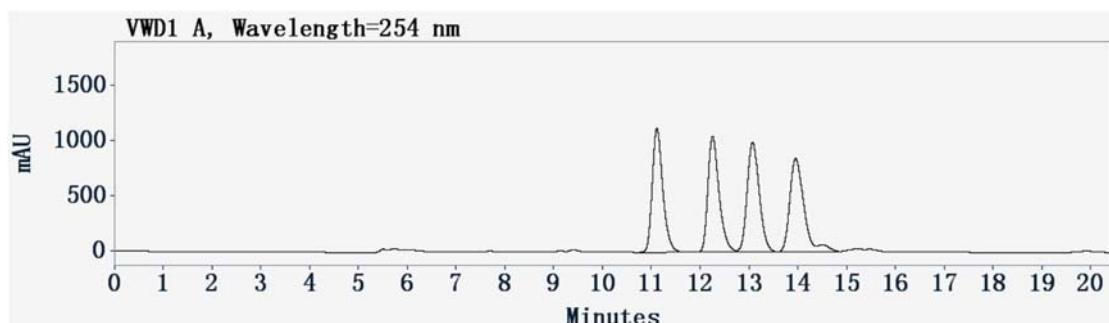
	Retention	Area	High	Area%
1	12.786	3.2717	3.5342	0.0107
2	14.268	30586.9180	1482.3131	99.9893

**3d:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(2-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**



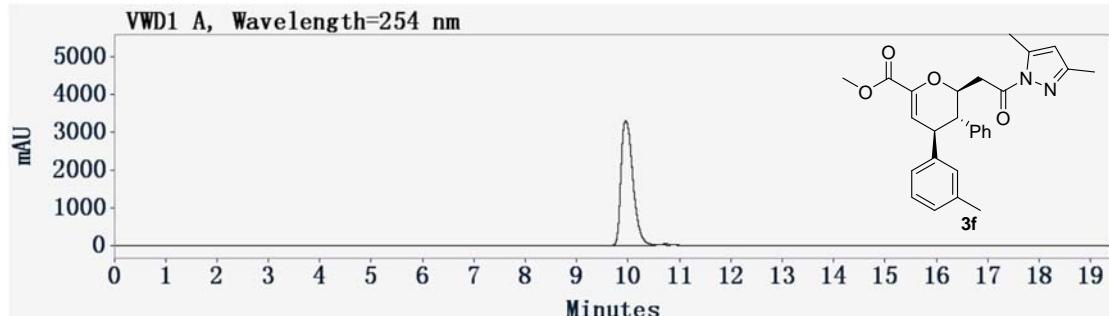
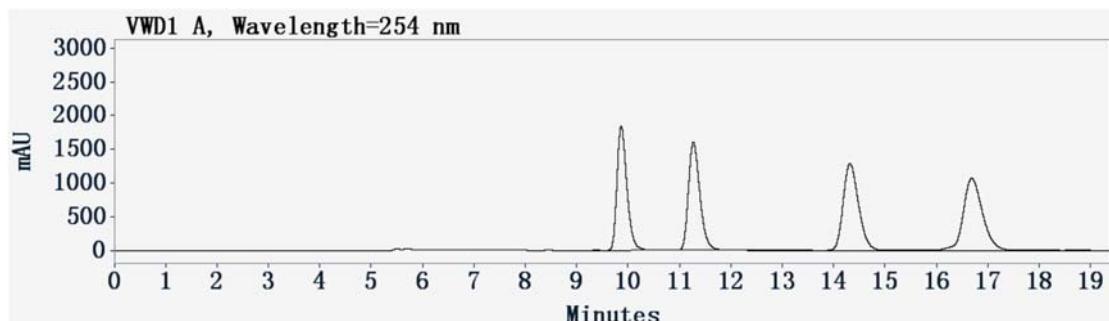
	Retention	Area	High	Area%
1	15.490	19221.7246	796.2267	99.9809
2	23.258	3.6767	6.9635	0.0191

**3e:Methyl (2S,3S,4R)-4-(2-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

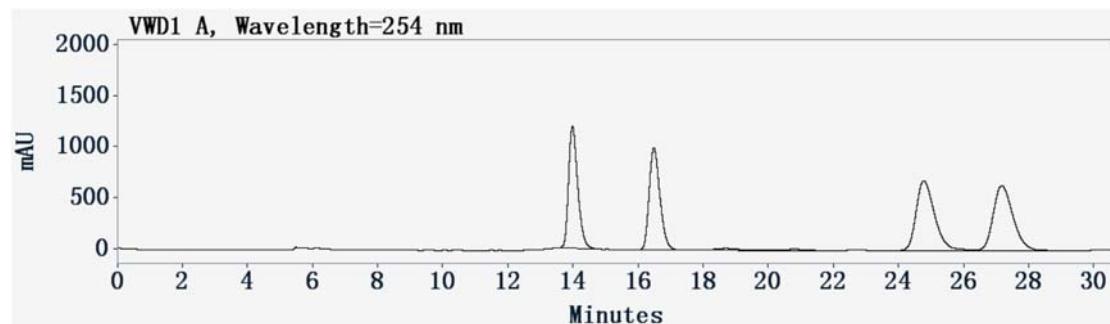


	Retention	Area	High	Area%
1	11.198	36.0473	2.1738	0.3601
2	12.085	9973.7744	645.2289	99.6399

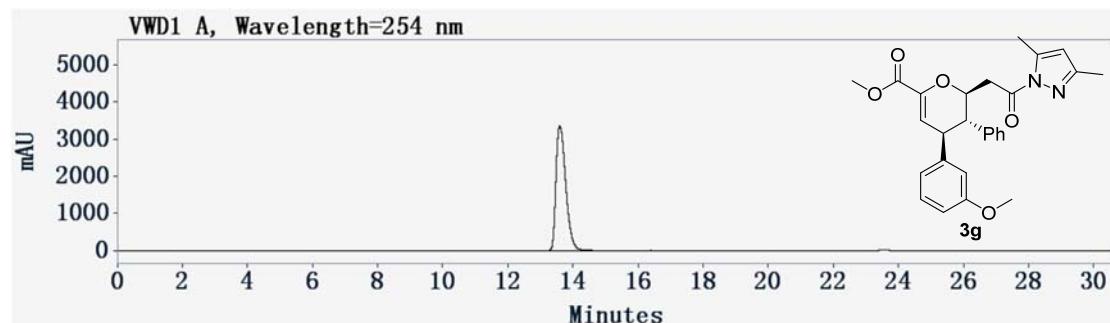
**3f:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(m-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate**



**3g:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

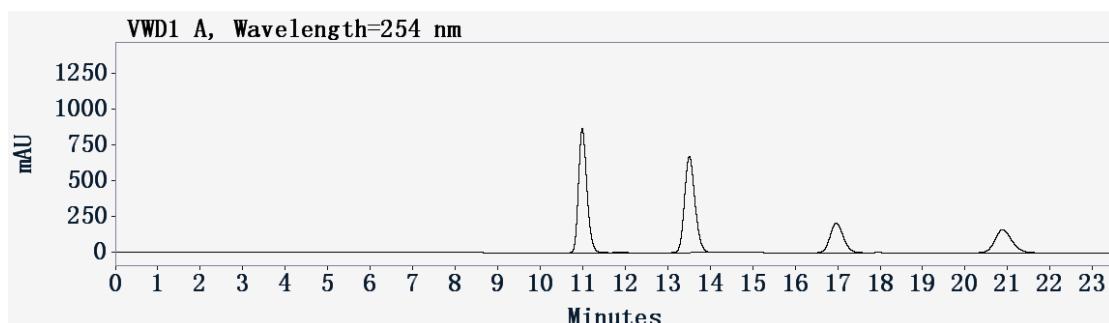


	Retention	Area	High	Area%
1	13.985	23396.0469	1195.3303	23.0498
2	16.488	24955.1504	1002.3771	24.5859
3	24.781	26630.1465	680.6673	26.2361
4	27.175	26520.6621	634.8660	26.1282

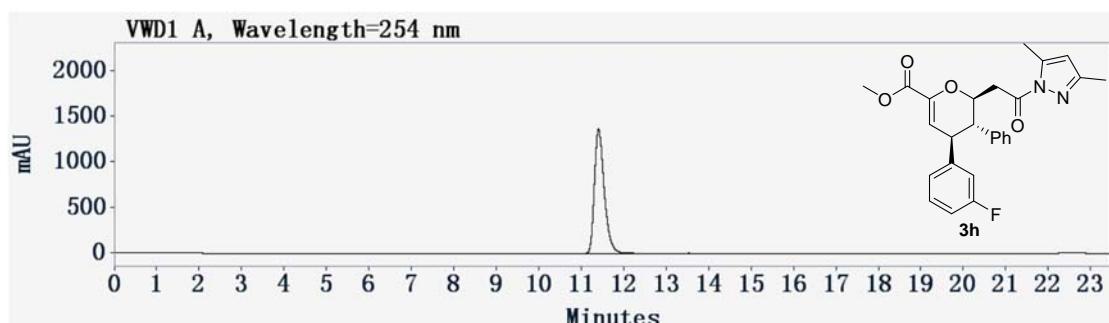


	Retention	Area	High	Area%
1	13.596	70205.4063	3346.6697	99.9971
2	16.440	2.0189	2.9839	0.0029

**3h:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

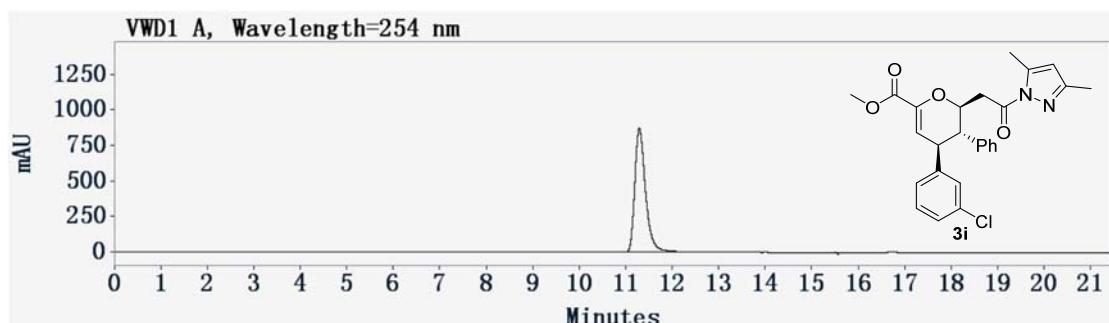
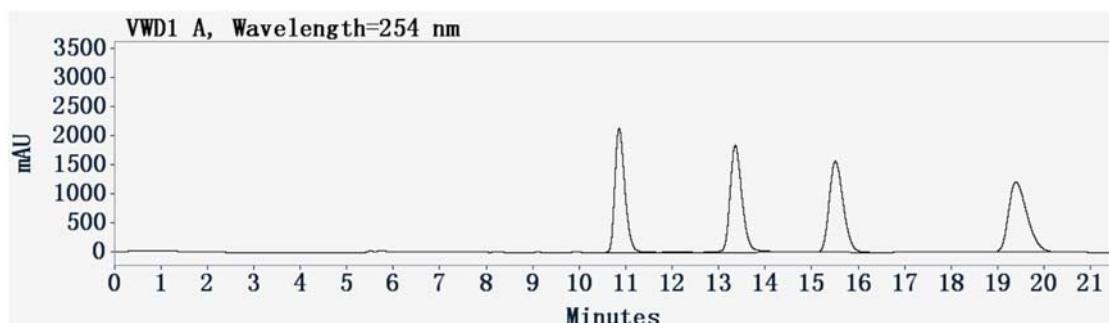


	Retention	Area	High	Area%
1	10.989	11904.1230	864.1928	36.8962
2	13.509	11447.6016	672.1904	35.4812
3	16.968	4448.8296	205.0921	13.7889
4	20.883	4463.2563	160.8520	13.8336



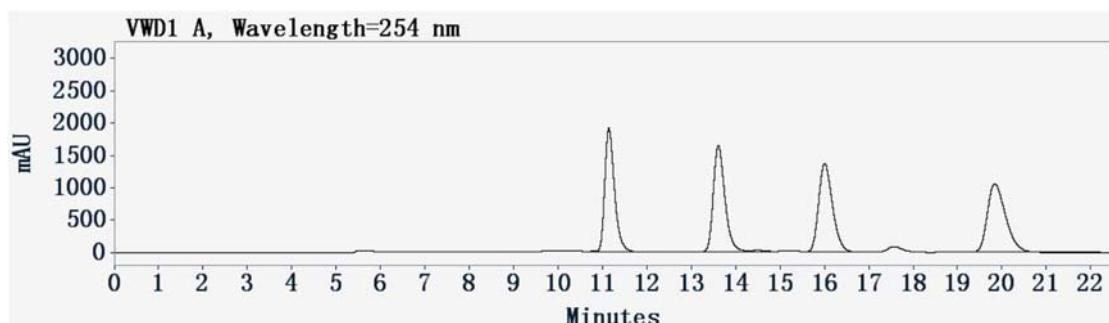
	Retention	Area	High	Area%
1	11.408	21921.5430	1359.7826	99.9919
2	13.559	1.7811	3.0091	0.0081

**3i:Methyl (2S,3S,4R)-4-(3-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

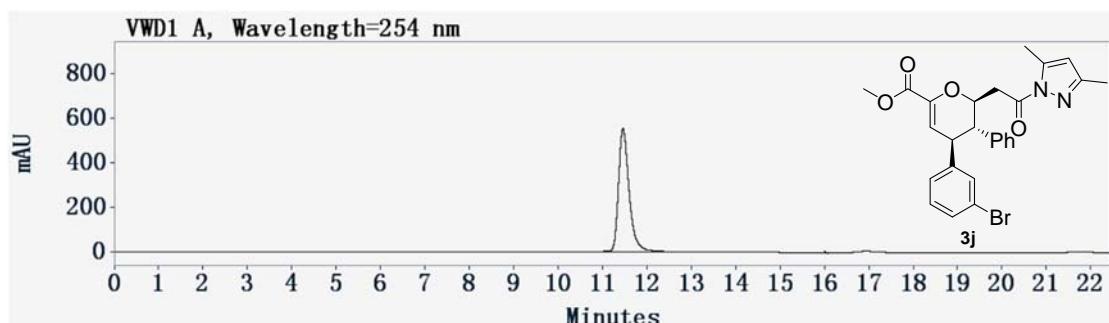


	Retention	Area	High	Area%
1	11.293	14146.7627	873.1612	99.8135
2	15.572	26.4276	18.0453	0.1865

**3j:Methyl (2S,3S,4R)-4-(3-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

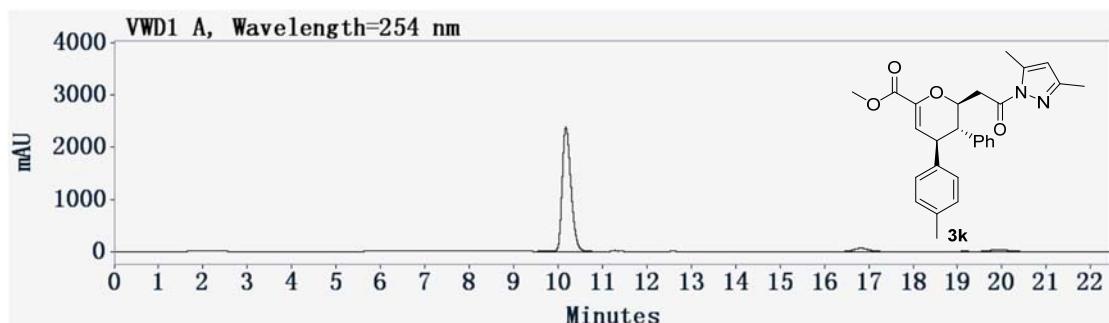
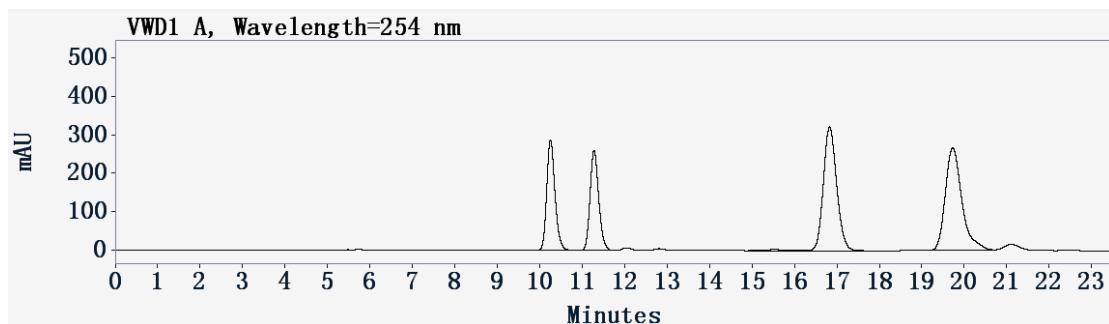


	Retention	Area	High	Area%
1	11.144	29039.6152	1910.8723	24.2224
2	13.610	30368.4668	1644.0940	25.3308
3	16.007	29588.5039	1362.7726	24.6802
4	19.839	30890.8359	1063.2804	25.7665



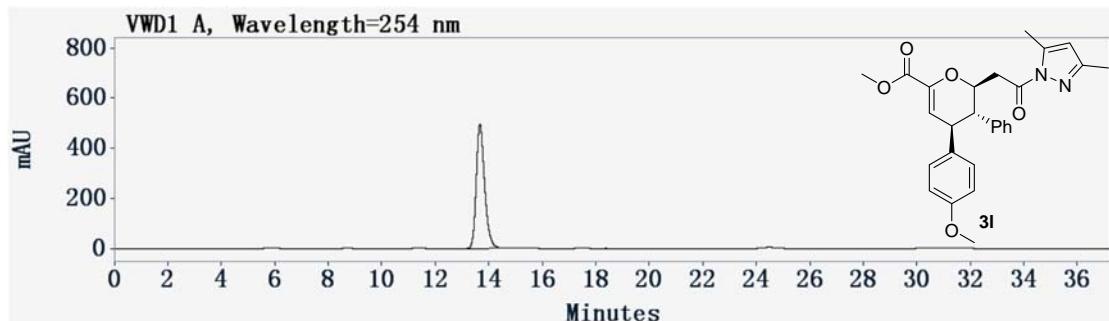
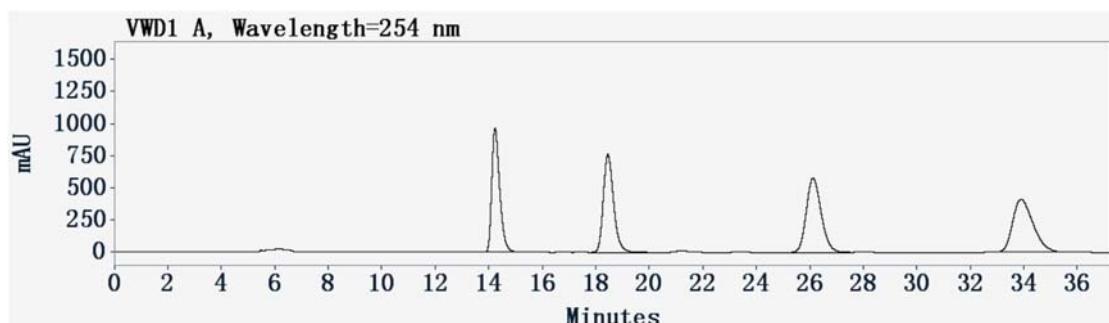
	Retention	Area	High	Area%
1	11.463	9340.3193	556.4163	99.9498
2	16.068	4.6905	5.5357	0.0502

**3k:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(p-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate**



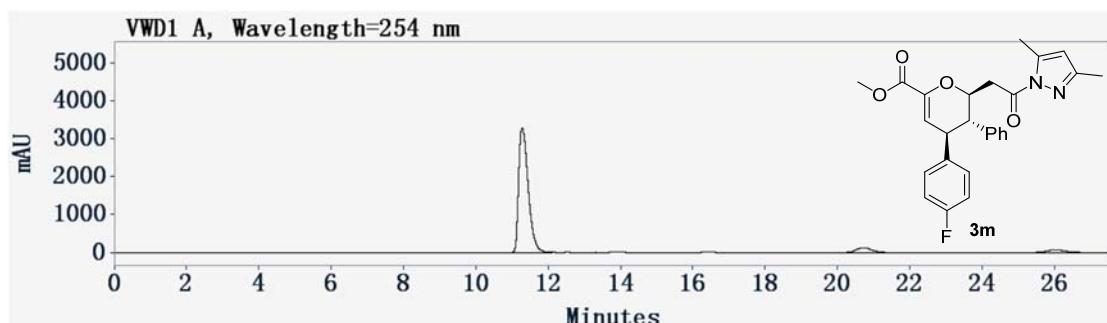
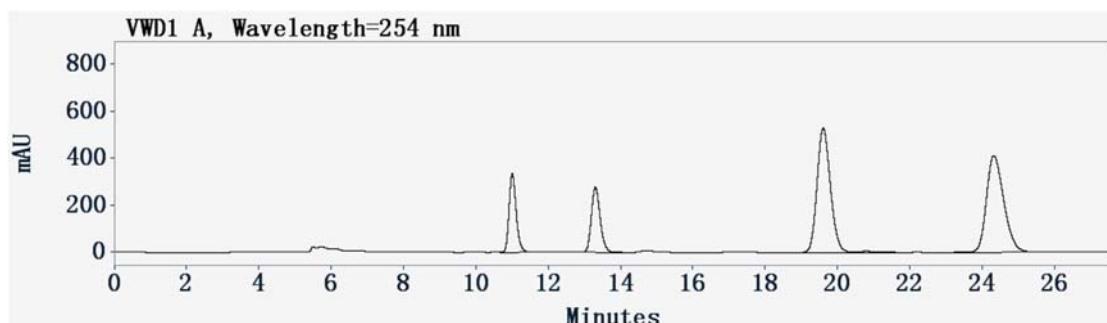
	Retention	Area	High	Area%
1	10.176	32677.9063	2375.0835	99.9465
2	11.353	18.6831	17.8046	0.0535

**3l: Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(4-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**



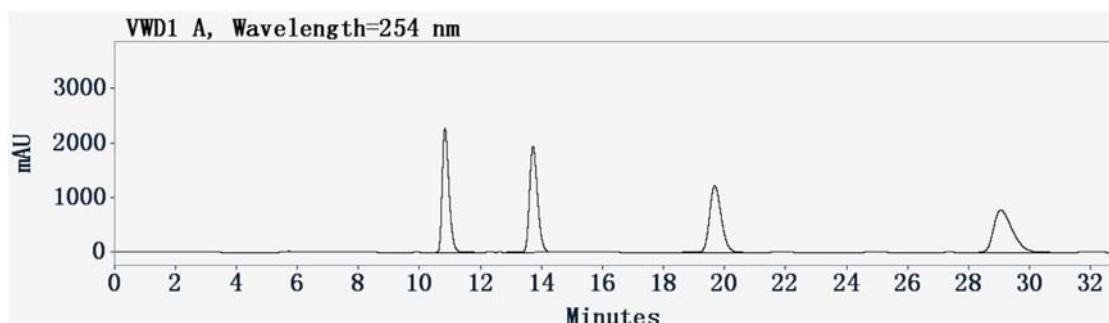
	Retention	Area	High	Area%
1	13.669	10805.4619	495.6756	99.9693
2	18.443	3.3205	2.5185	0.0307

**3m:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(4-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

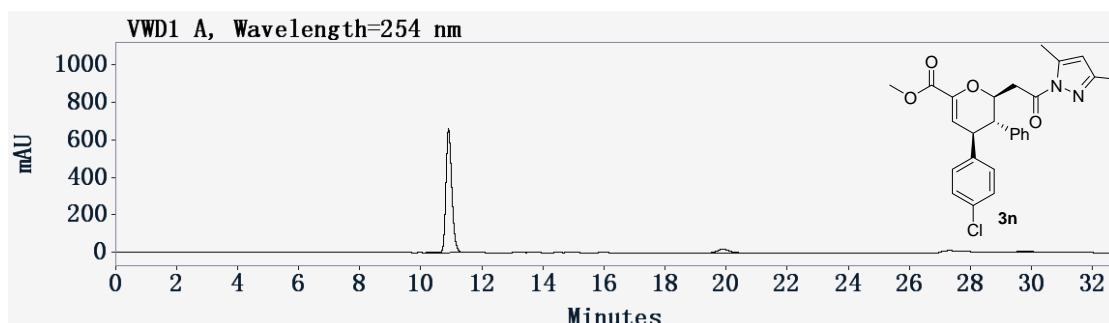


	Retention	Area	High	Area%
1	11.281	61405.8477	3286.6951	99.9997
2	13.312	1.8282	3.0588	0.0003

**3n:Methyl (2S,3S,4R)-4-(4-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

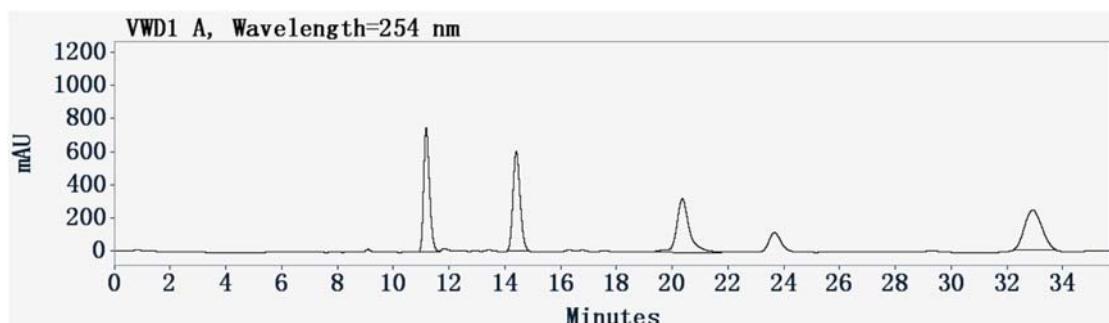


	Retention	Area	High	Area%
1	10.840	34731.9063	2274.5884	25.5219
2	13.724	35551.4727	1948.9069	26.1241
3	19.682	32672.7617	1221.5670	24.0088
4	29.054	33130.6445	775.0289	24.3452

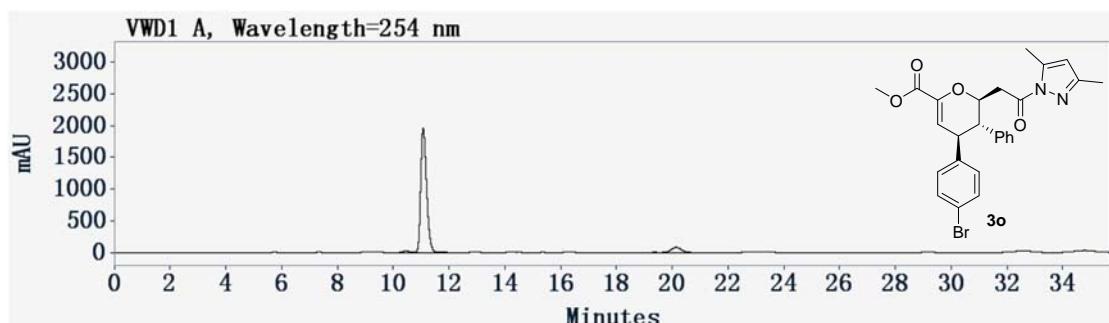


	Retention	Area	High	Area%
1	10.911	8828.2334	660.8326	99.9848
2	13.702	1.3379	19.9353	0.0152

**3o:Methyl (2S,3S,4R)-4-(4-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

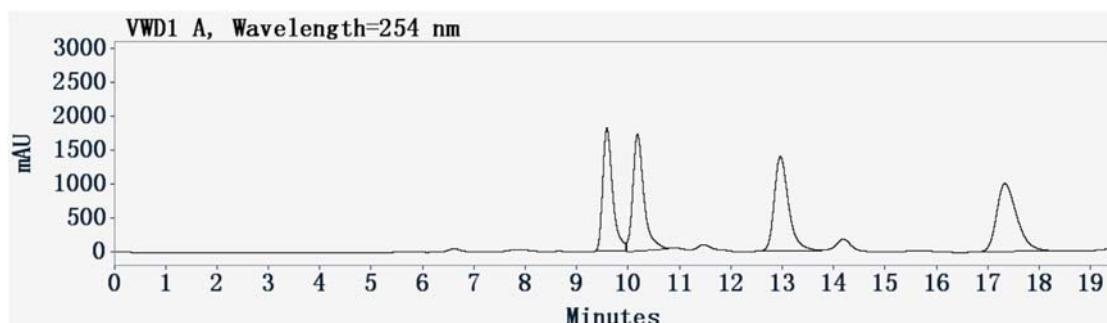


	Retention	Area	High	Area%
1	11.182	10759.7275	744.8848	25.3715
2	14.410	10778.0371	602.0595	25.4147
3	20.362	10409.1914	321.3209	24.5449
4	32.917	10461.7725	241.0632	24.6689

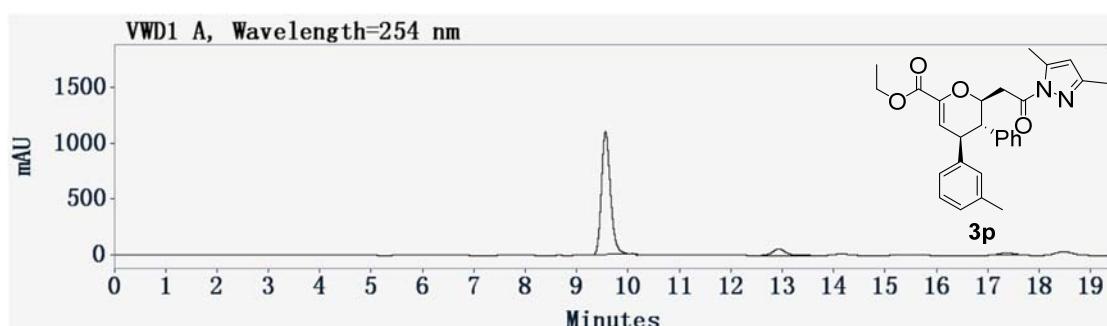


	Retention	Area	High	Area%
1	11.076	28795.8613	1959.1892	99.9999
2	14.432	2.3565	3.3721	0.0001

**3p:Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-4-(m-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate**

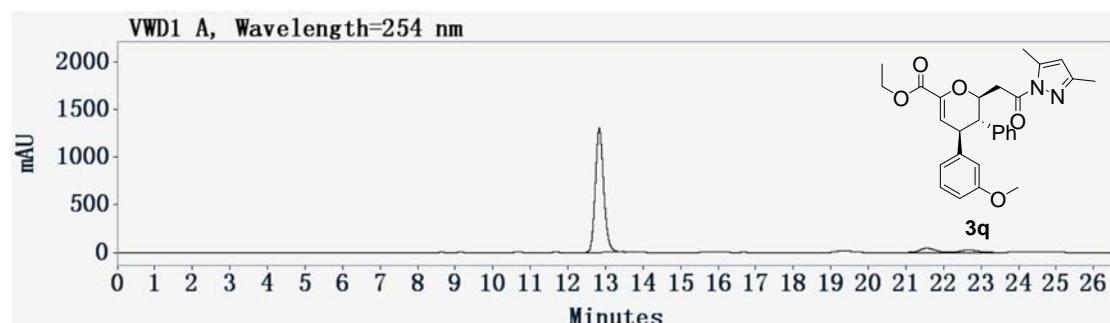
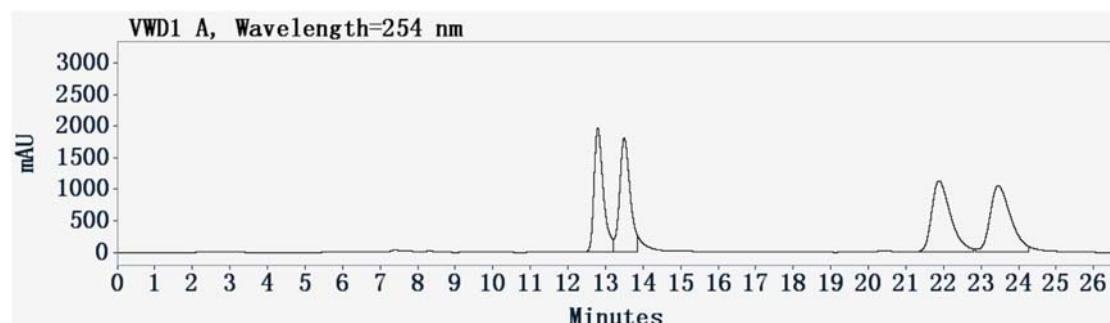


	Retention	Area	High	Area%
1	9.586	24297.0313	1814.0634	23.2792
2	10.183	25721.7969	1722.8361	24.6443
3	12.961	26875.9531	1393.6732	25.7501
4	17.334	27477.2773	1005.0031	26.3263



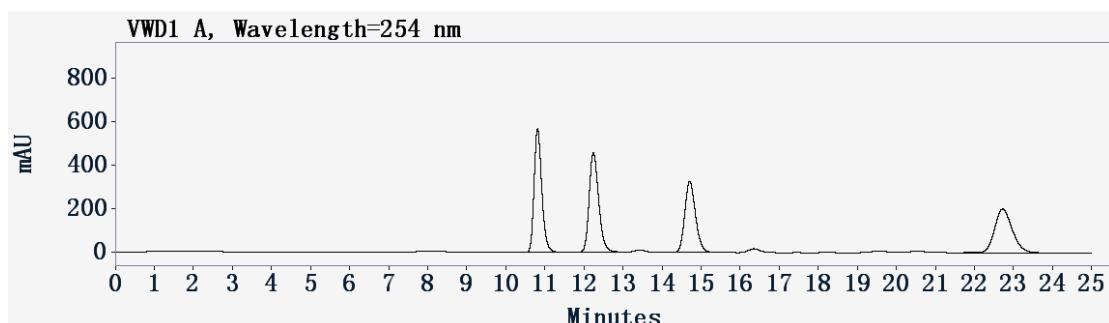
	Retention	Area	High	Area%
1	9.560	13455.8828	1102.4821	99.8363
2	10.177	22.0576	11.1066	0.1637

**3q:Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

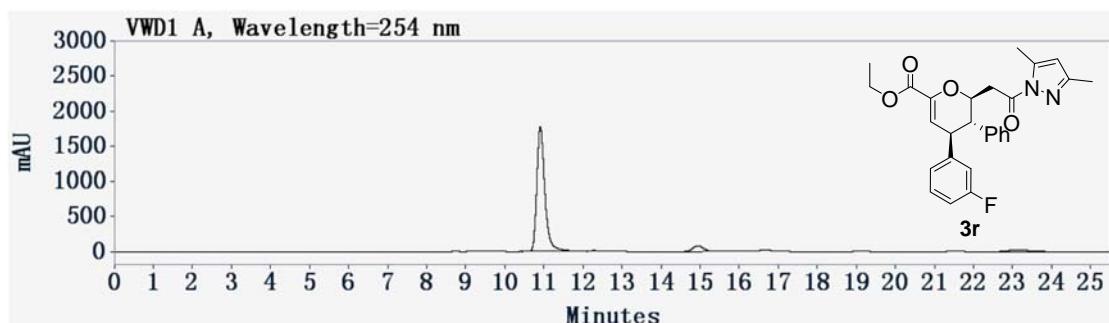


	Retention	Area	High	Area%
1	12.835	20284.7422	1305.8224	99.9729
2	13.523	5.4933	6.1157	0.0271

**3r:Ethyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-(3-fluorophenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

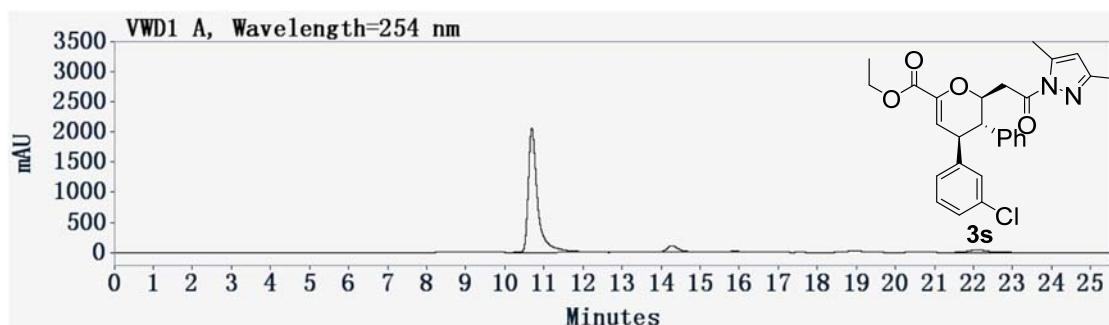
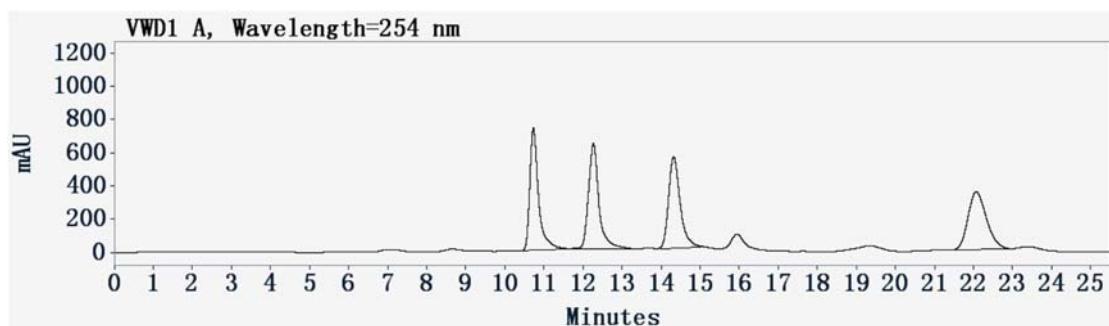


	Retention	Area	High	Area%
1	10.813	7834.3589	569.1346	27.7242
2	12.243	7832.9668	459.6831	27.7193
3	14.709	6253.8120	327.7409	22.1310
4	22.722	6337.0229	200.8695	22.4255



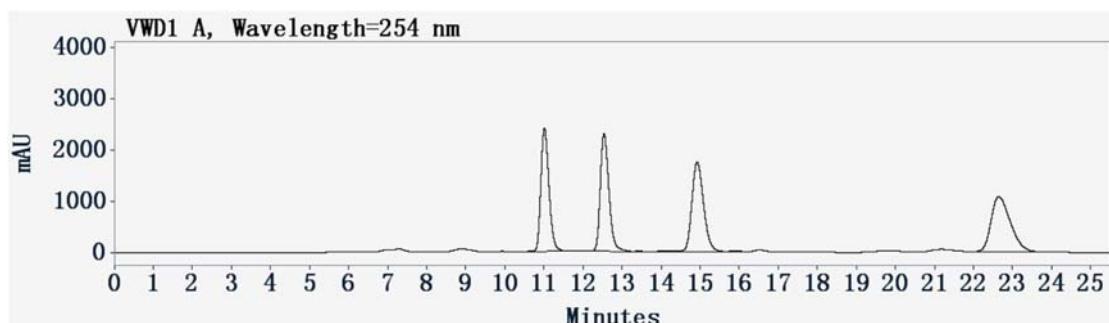
	Retention	Area	High	Area%
1	10.908	25252.2695	1764.6244	99.9816
2	12.102	4.6323	5.3996	0.0184

**3s:Ethyl (2S,3S,4R)-4-(3-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

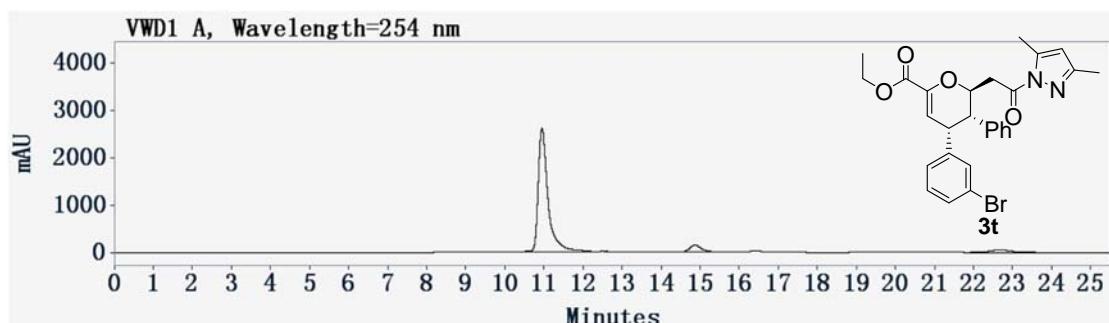


	Retention	Area	High	Area%
1	10.693	34380.8477	2059.7534	99.9618
2	12.677	13.1156	8.1879	0.0382

**3t:Ethyl (2S,3S,4R)-4-(3-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

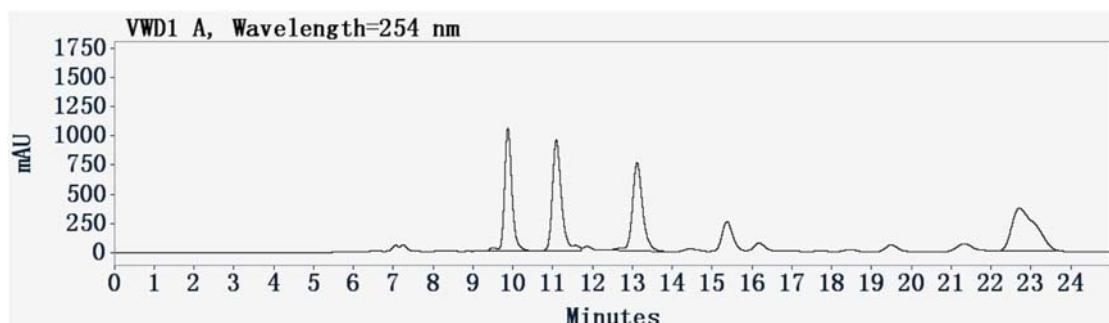


	Retention	Area	High	Area%
1	11.014	34971.5898	2409.4312	24.0453
2	12.540	35949.4648	2304.9907	24.7177
3	14.924	37407.5977	1751.2411	25.7203
4	22.648	37111.4844	1078.0035	25.5167

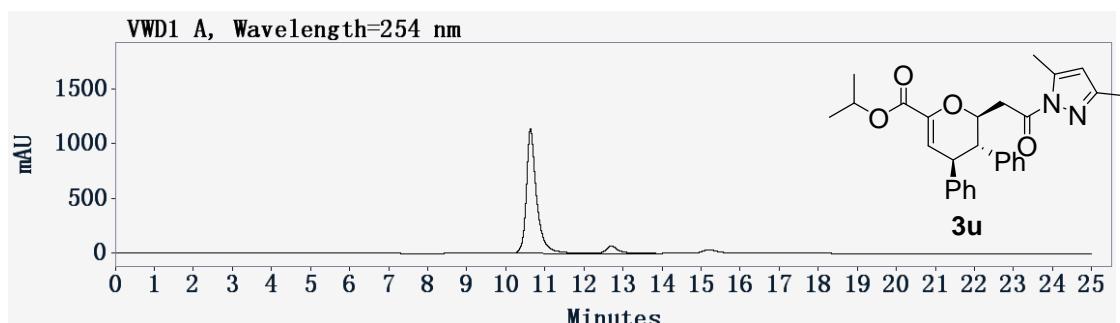


	Retention	Area	High	Area%
1	10.951	46076.3398	2616.5913	99.9950
2	12.673	2.2755	2.1799	0.0050

**3u: Isopropyl 2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**

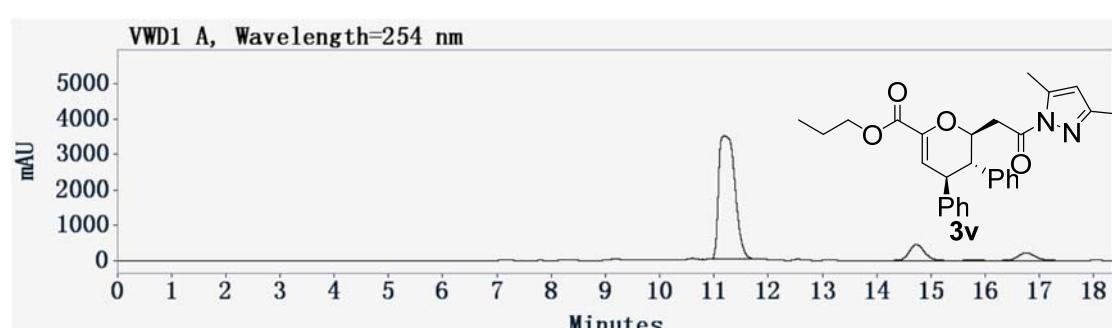
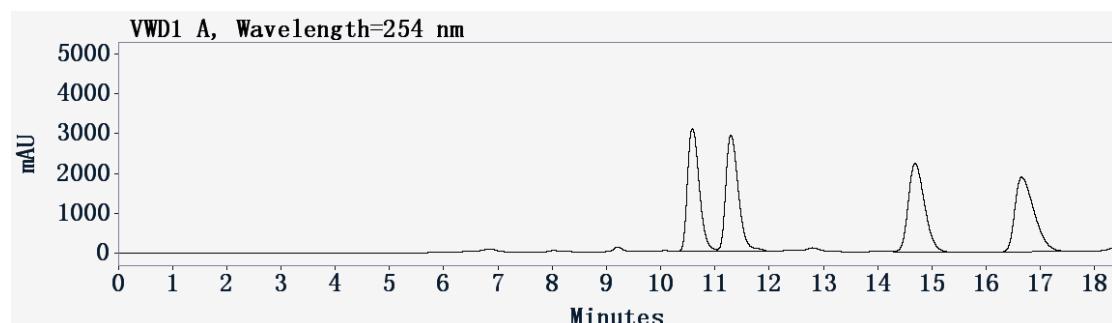


	Retention	Area	High	Area%
1	9.878	13636.7158	1053.1456	23.7531
2	11.092	13582.7207	951.9915	23.6591
3	13.117	15059.6309	758.5508	26.2316
4	22.716	15131.0947	367.2374	26.3561

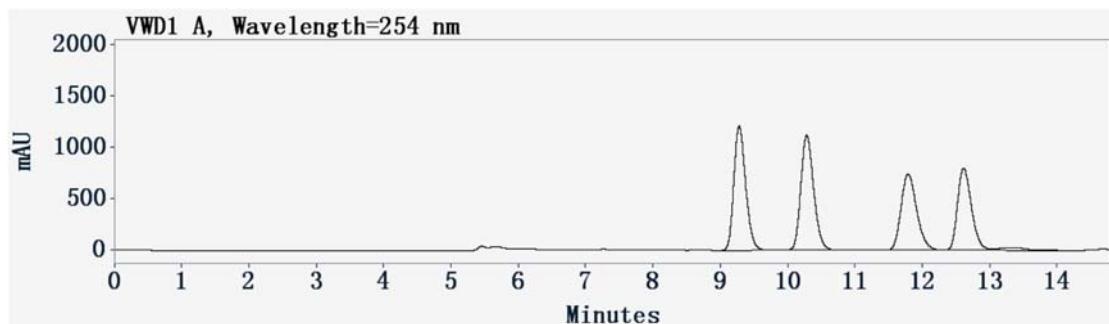


	Retention	Area	High	Area%
1	9.808	12.1156	7.1879	0.0588
2	10.632	20622.3262	1133.5975	99.9412

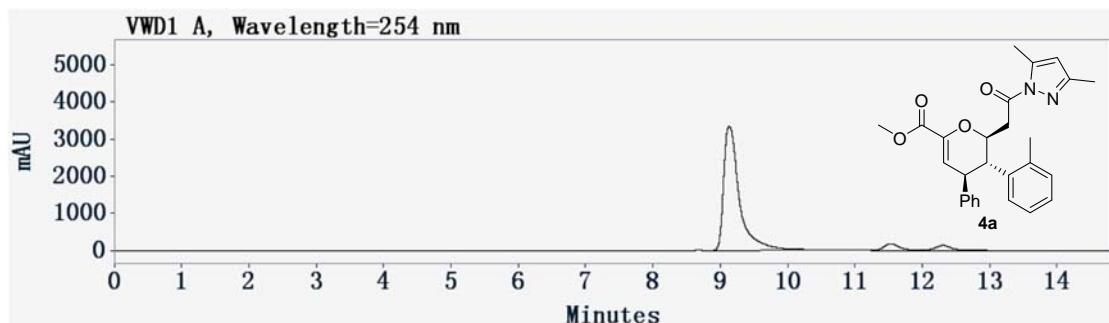
**3v:Propyl 2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**



**4a:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3-(o-tolyl)-3,4-dihydro-2H-pyran-6-carboxylate**

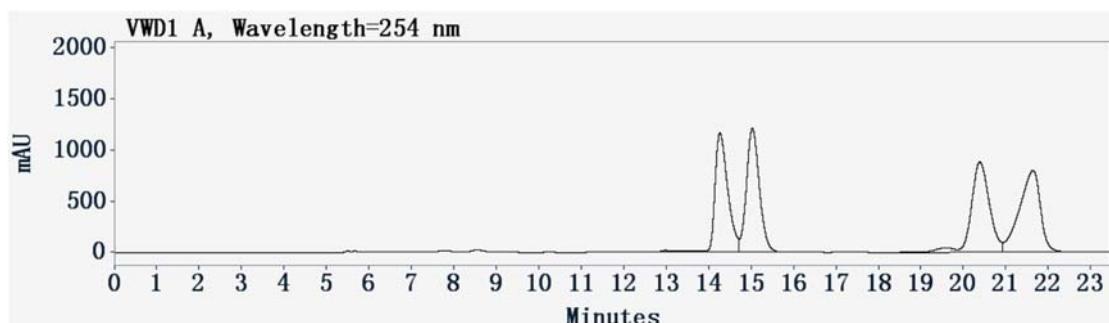


	Retention	Area	High	Area%
1	9.279	14697.3994	1206.7201	27.4030
2	10.282	14883.8799	1119.5297	27.7506
3	11.788	11953.1689	741.3408	22.2864
4	12.613	12099.9170	796.8195	22.5600

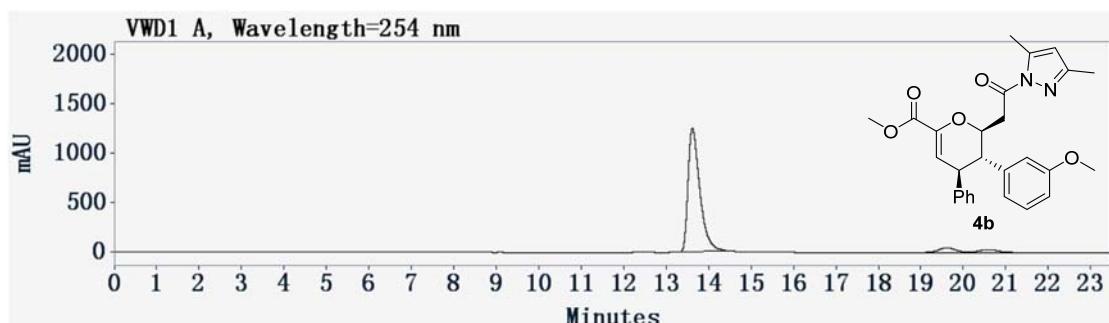


	Retention	Area	High	Area%
1	9.133	53934.0000	3346.7864	99.9978
2	10.851	1.1654	1.0980	0.0022

**4b:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(3-methoxyphenyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

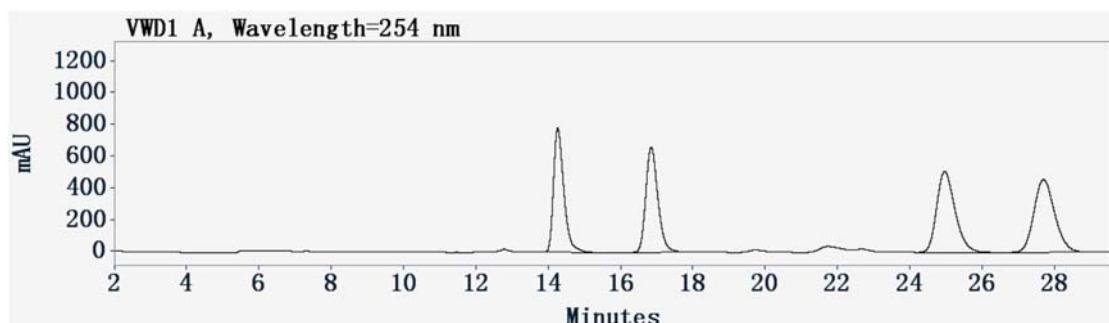


	Retention	Area	High	Area%
1	14.268	24769.6719	1164.0123	23.8297
2	15.031	25580.4609	1209.8247	24.6097
3	20.391	26439.3203	878.0933	25.4360
4	21.640	27155.0605	794.7610	26.1246

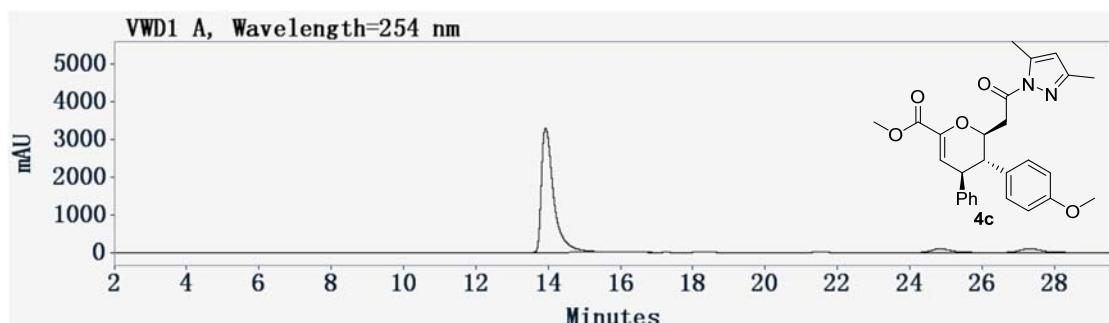


	Retention	Area	High	Area%
1	13.619	23987.6016	1247.5422	99.9949
2	15.048	1.1997	1.9039	0.0051

**4c:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(4-methoxyphenyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

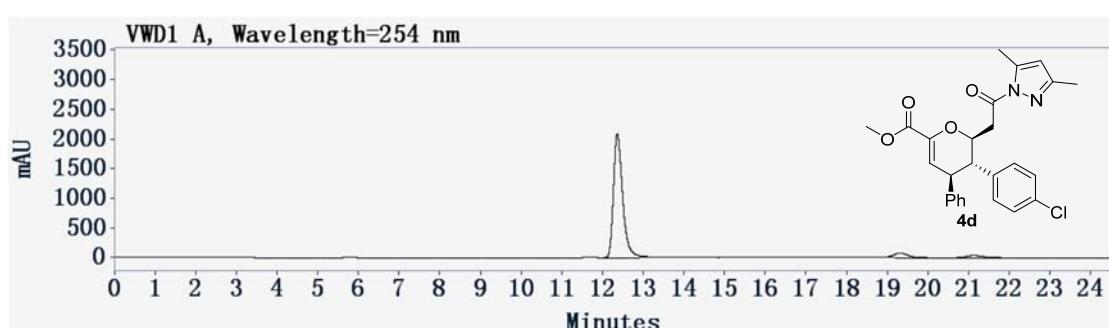
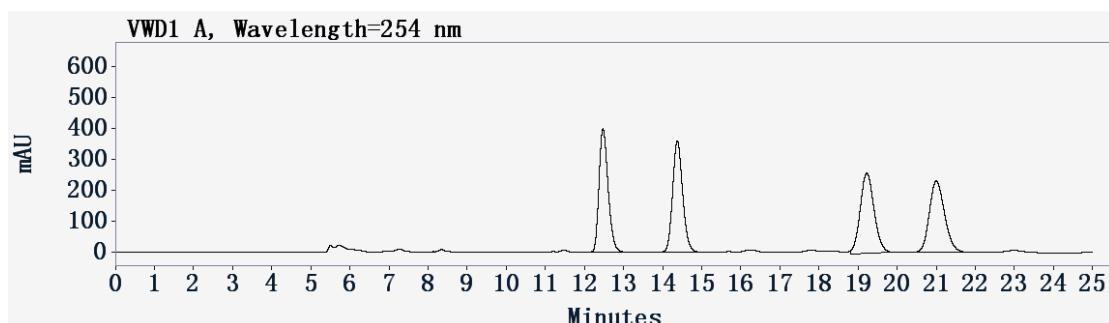


	Retention	Area	High	Area%
1	14.263	15371.2490	780.9291	22.8901
2	16.846	15399.9199	664.5552	22.9328
3	24.961	18030.0742	509.4660	26.8495
4	27.694	18351.1016	458.7929	27.3276



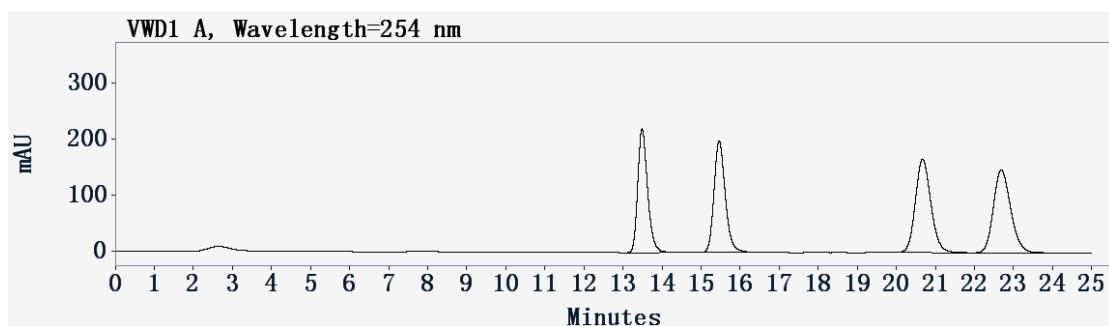
	Retention	Area	High	Area%
1	13.927	77928.5625	3298.6619	99.9875
2	16.933	9.7261	3.8674	0.0125

**4d:Methyl (2S,3S,4R)-3-(4-chlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

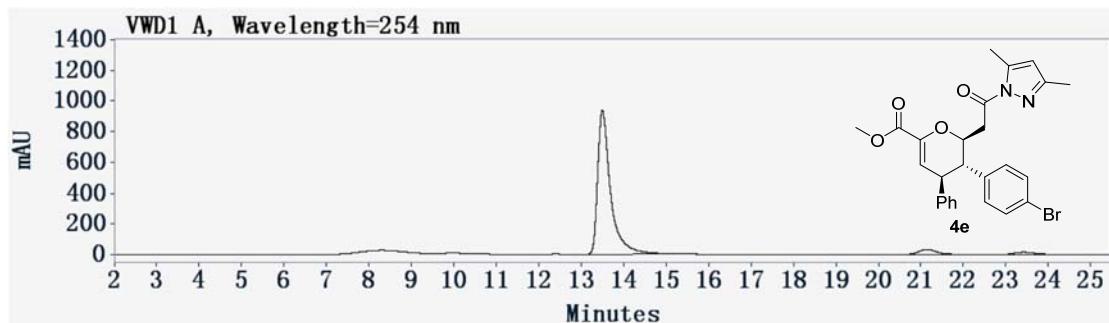


	Retention	Area	High	Area%
1	12.364	33012.3008	2086.0776	99.9955
2	14.850	1.4818	2.8866	0.0045

**4e:Methyl (2S,3S,4R)-3-(4-bromophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

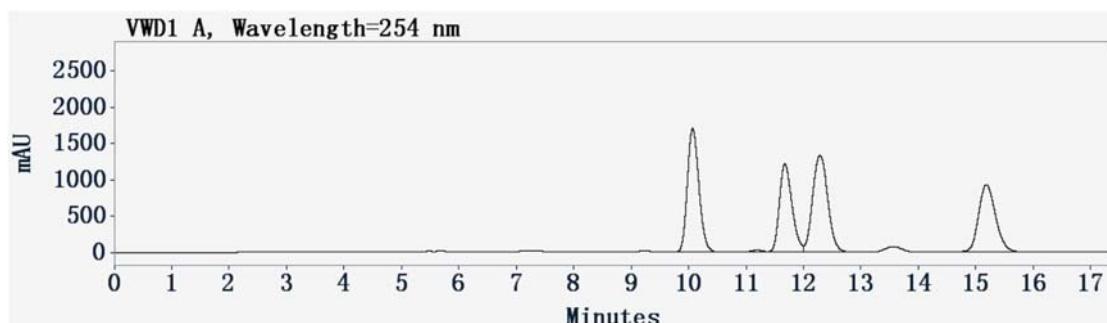


	Retention	Area	High	Area%
1	13.489	3882.1831	220.7111	22.8816
2	15.463	3981.5017	198.9233	23.4669
3	20.673	4569.9136	166.1879	26.9350
4	22.686	4532.8291	147.6083	26.7165

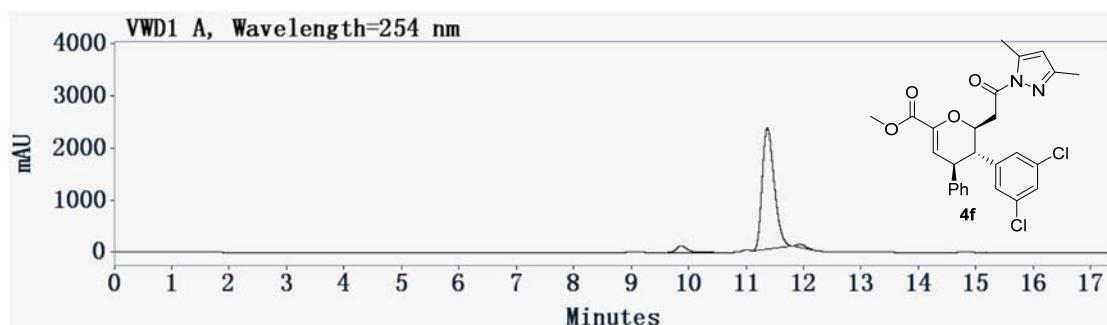


	Retention	Area	High	Area%
1	13.498	19846.6367	938.0360	99.9904
2	15.740	1.8876	1.8836	0.0096

**4f:Methyl (2S,3S,4R)-3-(3,5-dichlorophenyl)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

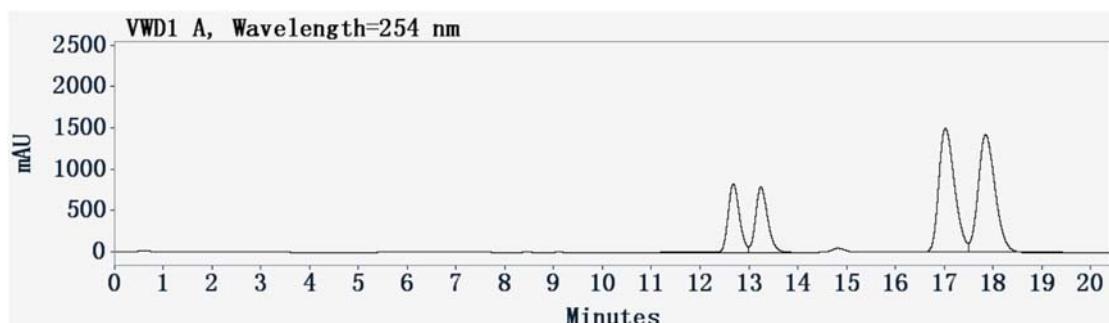


	Retention	Area	High	Area%
1	10.069	23848.4063	1707.6549	27.4867
2	11.676	19118.1953	1215.9420	22.0348
3	12.287	24493.4336	1334.2804	28.2301
4	15.184	19303.4141	930.9579	22.2483

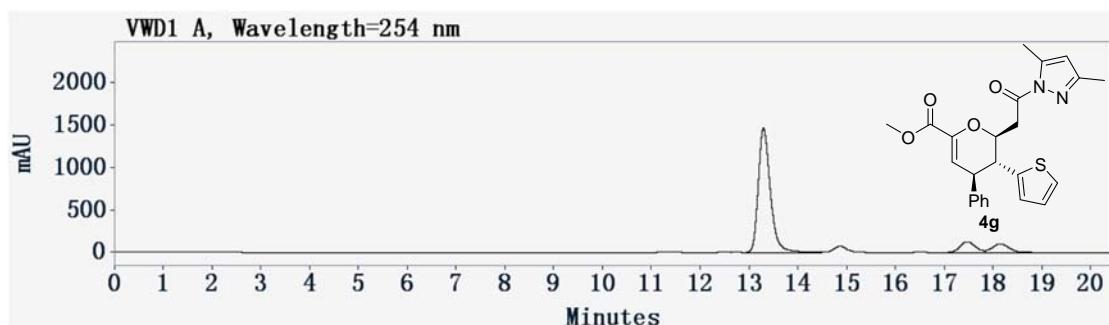


	Retention	Area	High	Area%
1	11.369	34216.2383	2324.1797	99.9940
2	15.193	2.0522	4.0837	0.0060

**4g:Methyl (2S,3R,4S)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-4-phenyl-3-(thiophen-2-yl)-3,4-dihydro-2H-pyran-6-carboxylate**

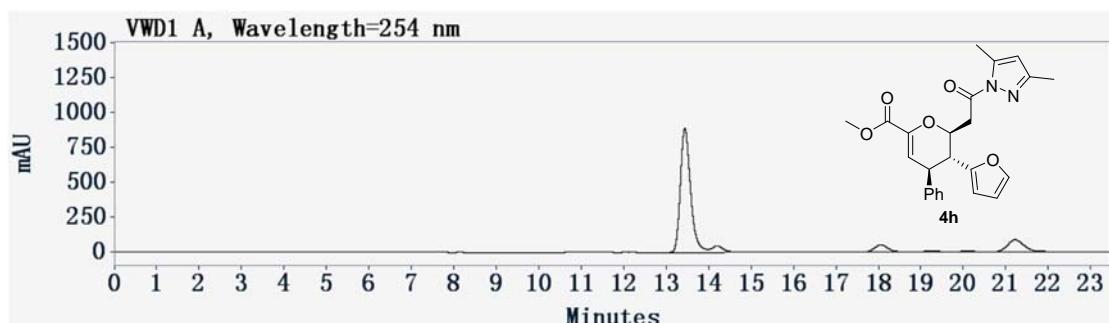
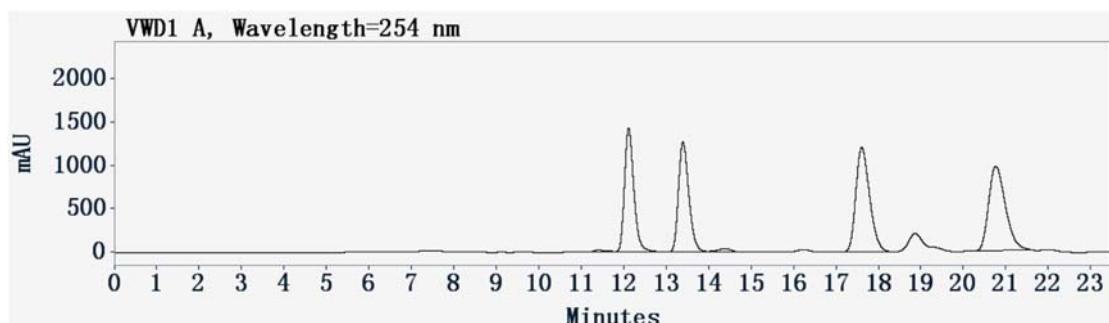


	Retention	Area	High	Area%
1	12.680	13474.5820	829.6476	14.1265
2	13.247	13587.9287	793.5939	14.2453
3	17.025	33662.6484	1502.7175	35.2913
4	17.849	34660.0391	1426.9667	36.3369



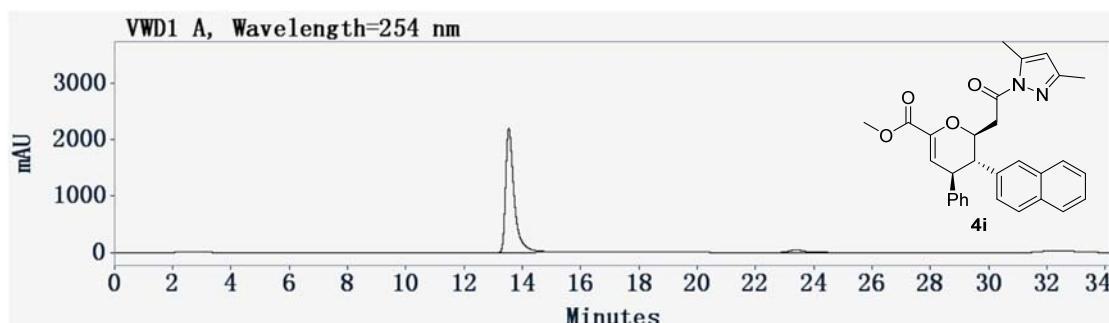
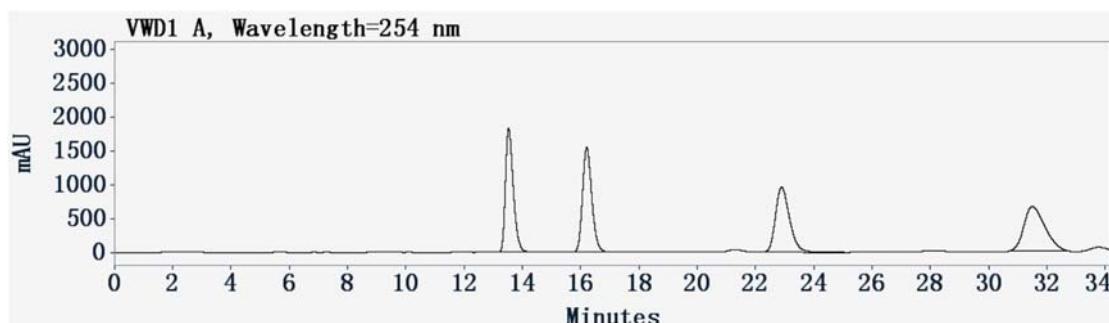
	Retention	Area	High	Area%
1	12.638	1.3379	3.2602	0.0054
2	13.298	25151.1504	1461.4344	99.9946

**4h:Methyl (2S,3R,4S)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(furan-2-yl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**



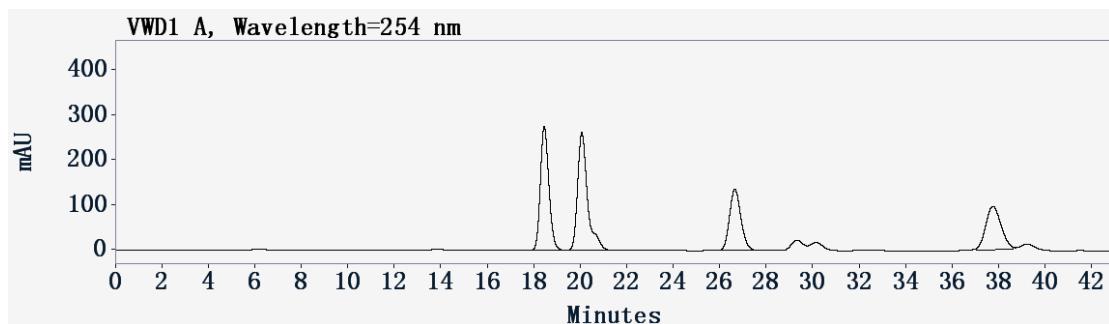
	Retention	Area	High	Area%
1	12.119	1.1617	1.9933	0.0074
2	13.441	15875.0547	890.0403	99.9926

**4i:Methyl (2S,3S,4R)-2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-3-(naphthalen-2-yl)-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**

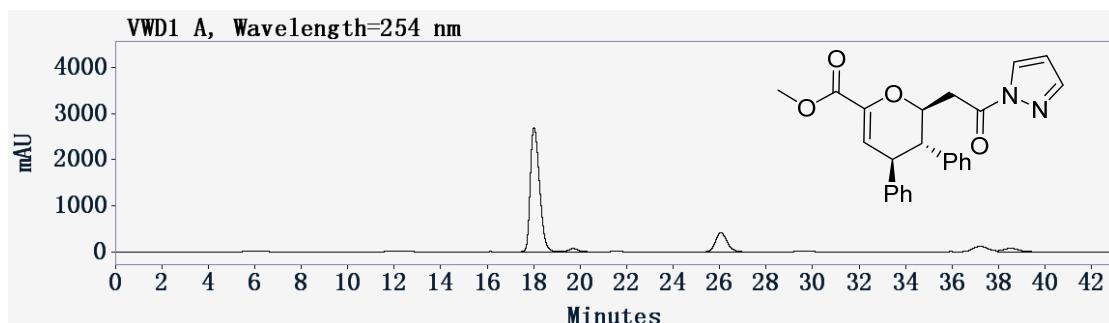


	Retention	Area	High	Area%
1	13.537	45451.6797	2198.0730	99.9968
2	16.257	1.4100	2.1999	0.0032

**4j: Methyl (2S,3S,4R)-2-(2-oxo-2-(1H-pyrazol-1-yl)ethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**

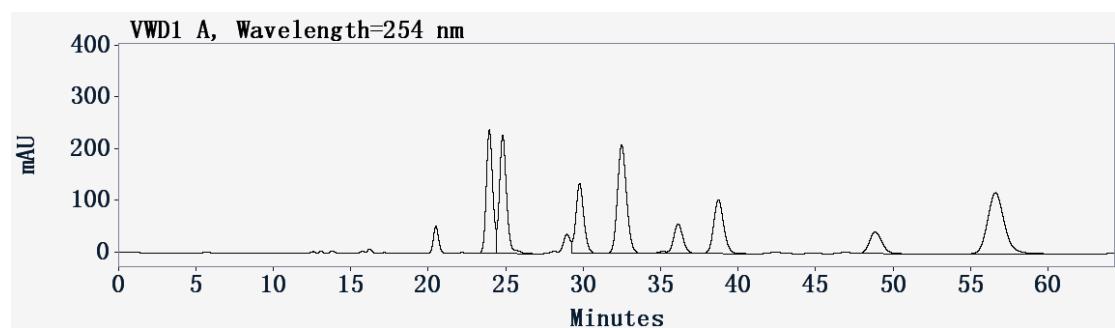


	Retention	Area	High	Area%
1	18.454	7034.6367	275.1493	29.4018
2	20.071	7830.2070	262.1314	32.7270
3	26.653	4640.0181	136.1010	19.3933
4	37.753	4420.9795	96.4090	18.4778

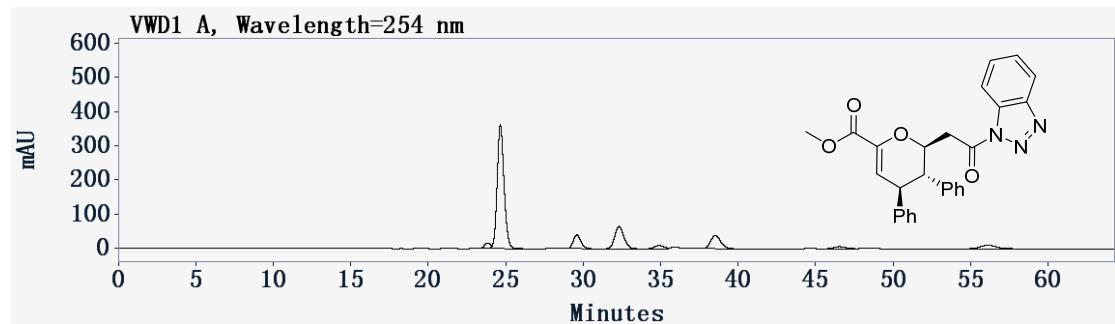


76327.208	Retention	Area	High	Area%
1	18.014	74379.9375	2697.5574	97.4487
2	19.692	1947.2705	70.0917	2.5513

**4k: Methyl (2S,3S,4R)-2-(2-(1H-benzo[d][1,2,3]triazol-1-yl)-2-oxoethyl)-3,4-diphenyl-3,4-dihydro-2H-pyran-6-carboxylate**

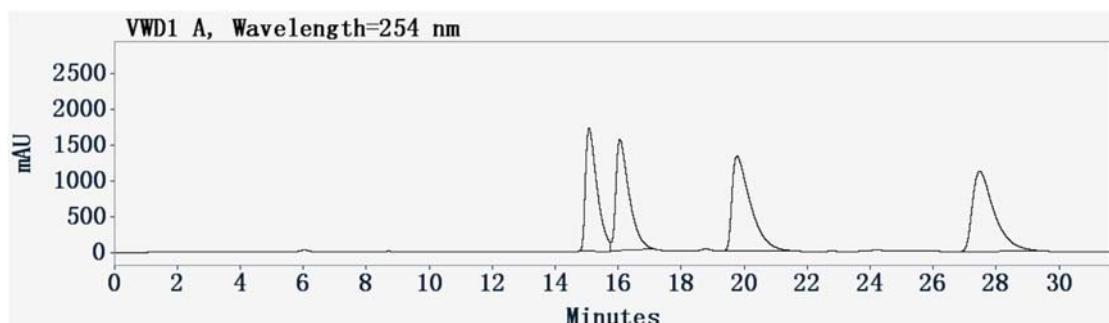


	Retention	Area	High	Area%
1	23.945	6864.5054	239.1635	14.9727
2	24.806	7292.0156	228.9921	15.9052
3	29.769	4819.1851	135.0444	10.5115
4	32.486	8610.4834	210.2052	18.7810
5	36.123	2498.4971	57.0417	5.4497
6	38.727	4642.0762	104.1384	10.1252
7	48.842	2324.9495	41.8752	5.0711
8	56.605	8794.9902	117.9467	19.1835

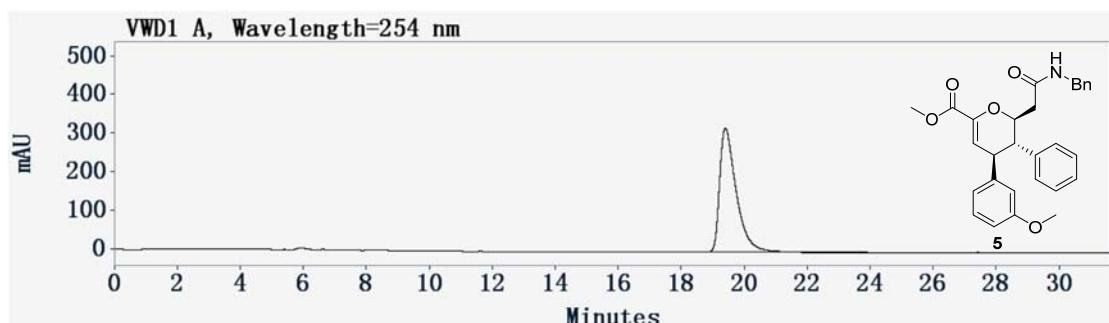


	Retention	Area	High	Area%
1	23.827	416.4915	16.4429	3.6050
2	24.654	11136.9199	362.7651	96.3950

**5:Methyl (2S,3S,4R)-2-(2-(benzylamino)-2-oxoethyl)-4-(3-methoxyphenyl)-3-phenyl-3,4-dihydro-2H-pyran-6-carboxylate**



	Retention	Area	High	Area%
1	15.074	44348.7461	1724.5308	22.3911
2	16.055	45626.6680	1559.0250	23.0363
3	19.774	54064.2344	1332.8655	27.2963
4	27.478	54024.3359	1122.5621	27.2762



	Retention	Area	High	Area%
1	19.403	11878.3730	321.0328	99.9863
2	27.466	1.6220	1.0232	0.0137