Supporting Information

NHC-Catalyzed Formal [3+3] Annulations of *δ*-Acetoxy Allenoates for the Synthesis of 4*H*-Pyran Derivatives

Bai Shi,[a] Fang-Yi Jin,[a] Qi Lv,[a] Xin-Rong Zhou,[a] Zhi-Xiao Liao,[a] Kai Zhang*,[a] and Chang-Sheng Yao*,[a]

[a]*Jiangsu Key Lab of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou Jiangsu 221116, P. R. China*

zhangkai@jsnu.edu.cn; csyao@jsnu.edu.cn

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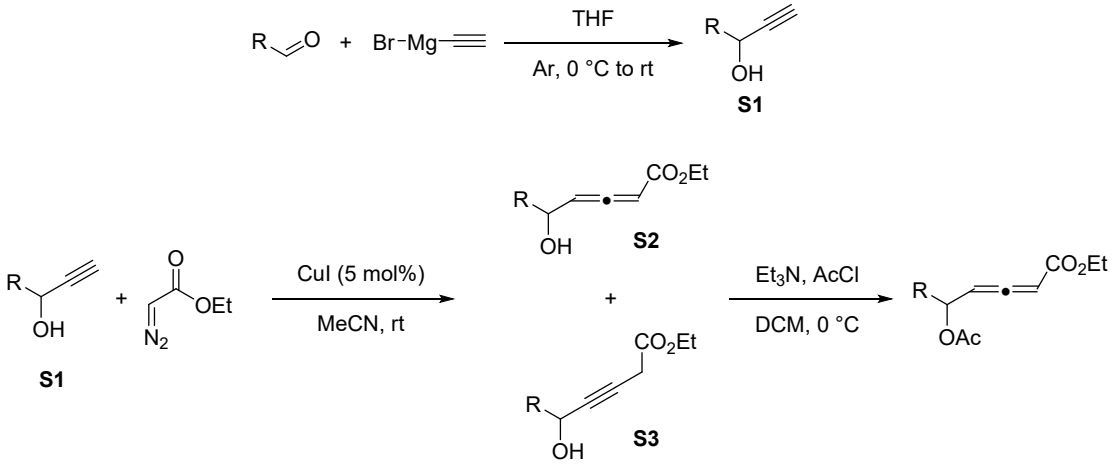
I. General Information

Unless otherwise mentioned, all reactions were carried out under an atmosphere of nitrogen in dry glassware and were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of the products was accomplished by flash chromatography using silica gel (200-300 mesh). Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR spectrometer in KBr pellets and reported in cm^{-1}. ^{1}H NMR spectra were measured on a 400 MHz spectrometer in $CDCl_3$ (100 MHz, ^{13}C NMR and 376 MHz, ^{19}F NMR) with chemical shift (δ) given in ppm relative to TMS as internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiple), coupling constants (Hz), integration. High-resolution mass spectra (HRMS) were measured with ESI in a positive mode.

II. General Procedure for the Synthesis of Allenoates

These allenoates were prepared according to the known reports[1-2].



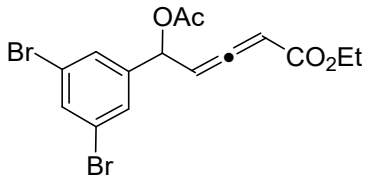
A solution of benzaldehyde (10 mmol) in distilled THF (5 mL) was treated at 0 °C with ethynylmagnesium bromide (30 mL, 15 mmol). The resulting mixture was stirred at 0 °C for 1 h

and for 19 h at room temperature. After treatment with a saturated aqueous solution of NH_4Cl and extractions with EA, the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by silica gel chromatography afforded the expected propargyl alcohol **S1** as a pale yellow oil (10 mmol, quantitative yield).

To the mixture of the corresponding propargylic alcohol **S1** (10 mmol) and CuI (0.5 mmol) in acetonitrile (10 mL) was added ethyl diazoacetate (10 mmol). The reaction mixture was stirred at room temperature for 12 h. The mixture was filtered, washed with diethyl ether and the solvent was evaporated under reduced pressure. Then, the residue was purified by column chromatography on silica gel to give the mixture of **S2** and **S3**.

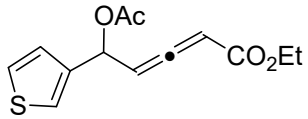
Under argon atmosphere, to a solution of the mixture (8 mmol) in DCM (8 mL) was added Et_3N (16 mmol) at 0 °C. After 30 min, a solution of AcCl (9.6 mmol) in DCM (8 mL) was added slowly, and the resulting mixture was stirred at 0 ℃ for 1 h, then the reaction mixture was washed with water and extracted with DCM. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The residue was directly subjected to a silica gel column chromatography to give the allenoate substrates.

Ethyl 5-acetoxy-5-(3,5-dibromophenyl)penta-2,3-dienoate (1m)



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.50 (s, 2H), 6.33–6.23 (m, 1H), 5.92–5.67 (m, 2H), 4.30–4.17 (m, 2H), 2.18–2.10 (m, 3H), 1.32 (q, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 212.0, 169.5, 169.4, 164.6, 164.6, 141.7, 141.5, 134.3, 134.2, 129.1, 128.8, 123.0, 123.0, 96.0, 95.8, 91.9, 91.5, 71.0, 70.4, 61.4, 61.3, 21.0, 20.9, 14.3; HRMS (ESI, *m/z*): calcd for $[M + H]^+$ $C_{15}H_{15}Br_2O_4$: 267.0686, found: 267.0684.

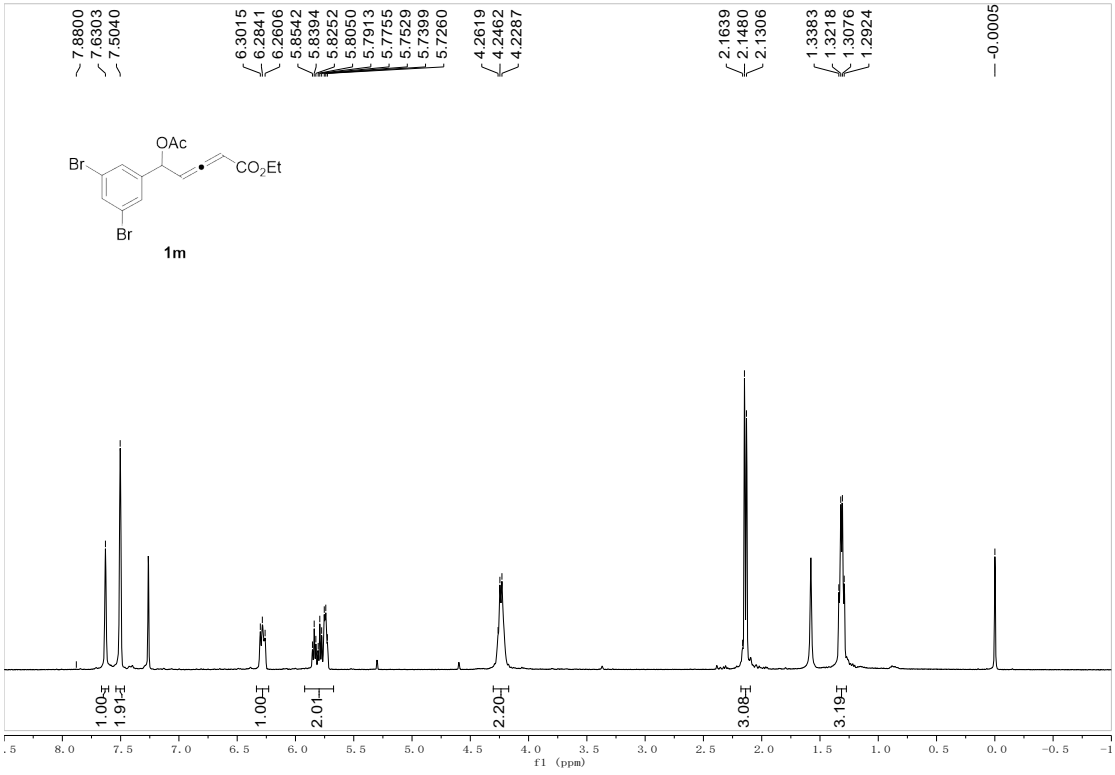
Ethyl 5-acetoxy-5-(thiophen-3-yl)penta-2,3-dienoate (1o)



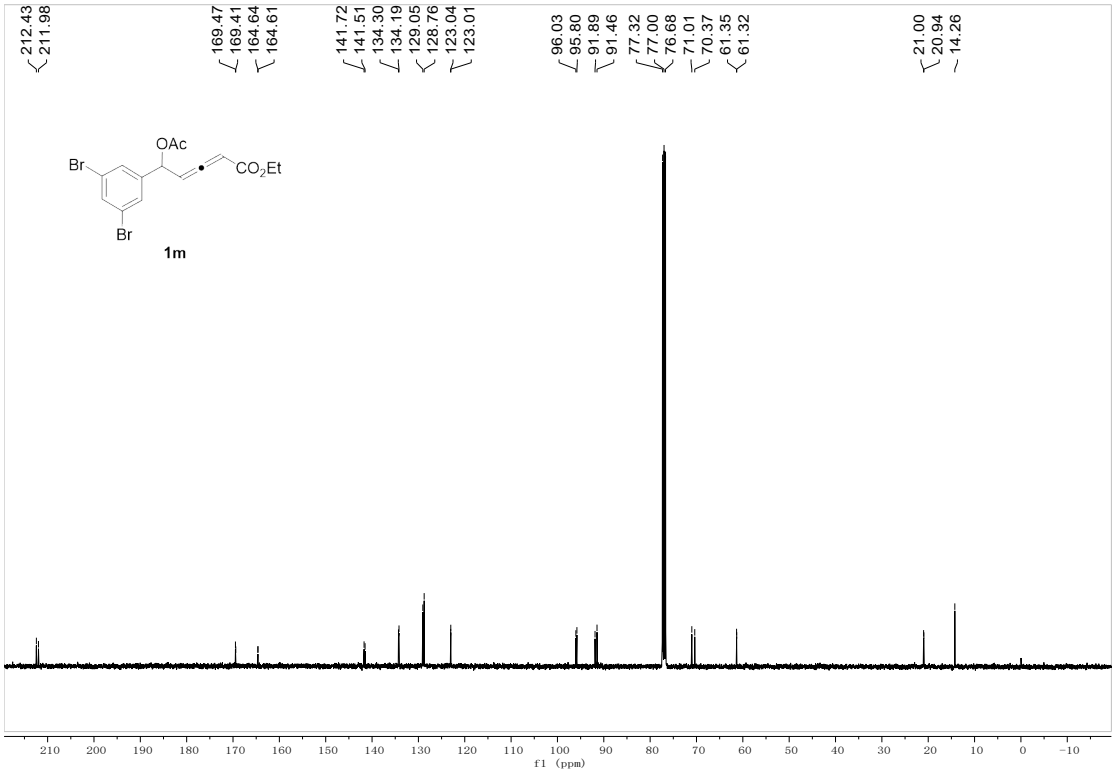
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 17.4 Hz, 1H), 7.33–7.29 (m, 1H), 7.19–7.12 (m, 1H), 6.47 (dd, J = 16.1, 6.1 Hz, 1H), 5.96–5.85 (m, 1H), 5.79–5.72 (m, 1H), 4.29–4.15 (m, 2H), 2.13–2.03 (m, 3H), 1.30 (q, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 212.0, 169.8, 169.7, 165.1, 165.0, 138.9, 138.6, 126.7, 126.4, 126.3, 126.3, 124.0, 123.3, 96.4, 96.2, 91.4, 91.1, 68.4, 67.6, 61.1, 21.1,

21.0, 14.2; HRMS (ESI, *m/z*): calcd for [M + H] $^{+}$ $C_{13}H_{15}O_4S$: 416.9332, found: 416.9330.

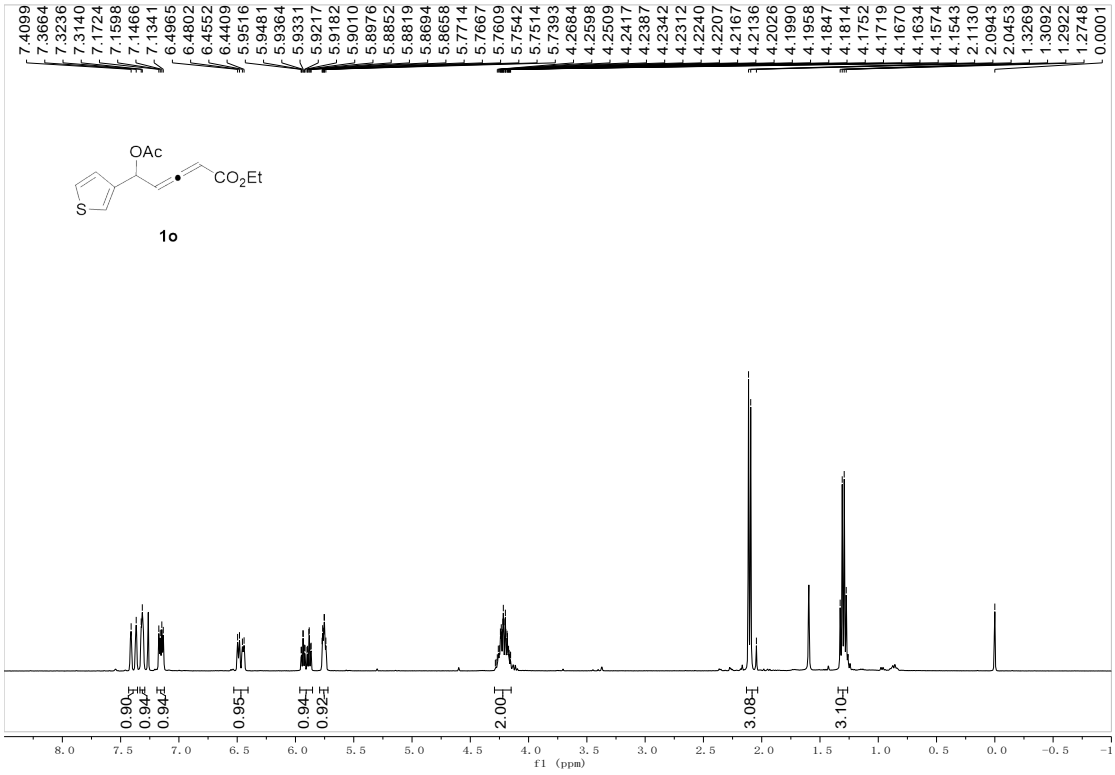
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**1m**)



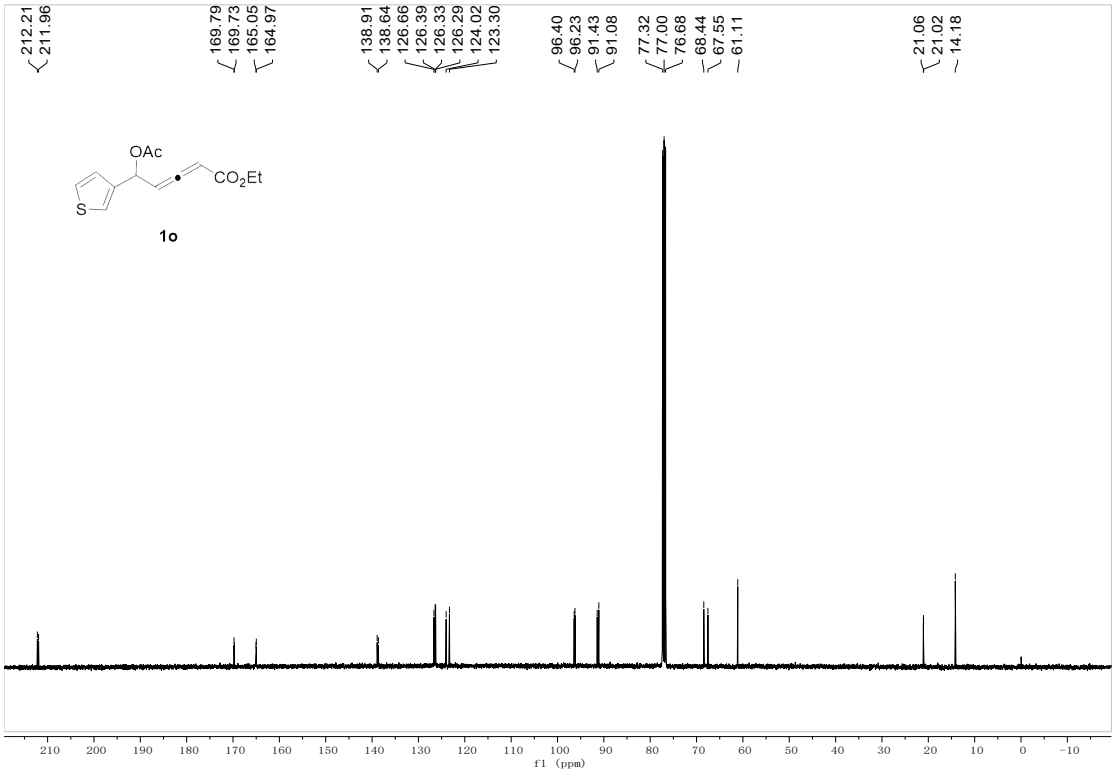
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**1m**)



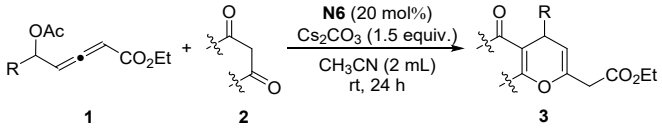
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**1o**)



^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**1o**)



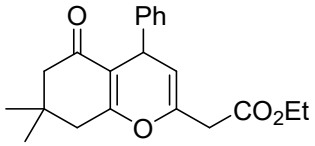
III. General Procedure



An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with *δ*–acetoxy allenoates **1** (0.2 mmol), 1C,3O–bisnucleophiles **2** (0.24 mmol), **N6** (20 mol%) and CS_2CO_3 (0.3 mmol). The tube was closed with a septum, evacuated, and refilled with argon. Freshly distilled CH_3CN (2 mL) was added into the mixture with a syringe. The mixture was stirred at room temperature until completion (monitored by TLC). After removal of the solvent under reduced pressure, the resulting crude residue was purified by column silica gel chromatography to afford the desired product **3**.

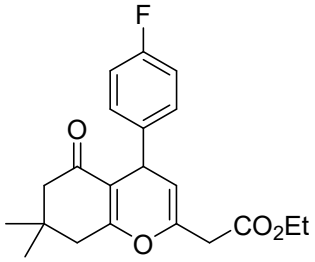
IV. Characterization of Products

Ethyl 2-(7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3aa)[3]



50 mg, 74% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.35–7.24 (m, 4H), 7.21–7.12 (m, 1H), 5.11 (d, *J* = 4.6 Hz, 1H), 4.35 (d, *J* = 4.4 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.18 (d, *J* = 2.9 Hz, 2H), 2.39 (s, 2H), 2.27–2.12 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.08 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 197.1, 169.2, 164.4, 145.1, 142.9, 128.3, 128.1, 126.5, 112.3, 107.9, 61.1, 50.8, 41.2, 38.7, 35.1, 32.0, 29.1, 27.5, 14.1.

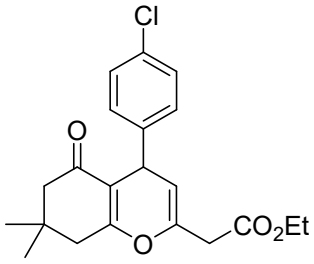
Ethyl 2-(4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ab)



37 mg, 51% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.35–7.22 (m, 2H), 7.02–6.88 (m, 2H), 5.08 (d, *J* = 4.6 Hz, 1H), 4.34 (d, *J* = 4.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.20 (s, 2H), 2.39 (s, 2H), 2.29–2.09 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.08 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 197.2, 169.2, 164.4, 161.5 (d, J_{CF} = 243.1 Hz), 143.2, 140.8 (d, J_{CF} = 2.9 Hz), 129.7 (d, J_{CF} = 8.0 Hz), 115.0 (d, J_{CF}

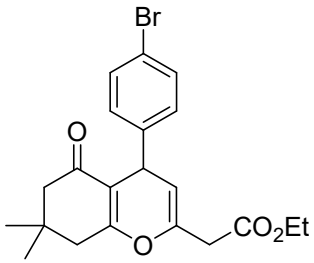
= 21.2 Hz), 112.3, 107.7, 61.2, 50.8, 41.2, 38.7, 34.4, 32.0, 29.0, 27.5, 14.1; ^{19}F NMR (376 MHz , $CDCl_3$): δ -116.7; IR (potassium bromide) (v, cm^{-1}): 3447, 2960, 1740, 1632, 1507, 1379, 1221, 1157, 1029, 837; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{21}H_{24}FO_4$: 359.1653, found: 359.1645.

Ethyl 2-(4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ac)



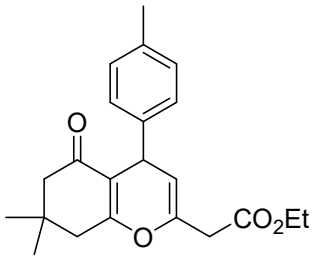
53 mg, 71% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.19 (m, 4H), 5.07 (d, J = 4.6 Hz, 1H), 4.33 (d, J = 4.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.19 (s, 2H), 2.39 (s, 2H), 2.29–2.07 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.08 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 169.1, 164.5, 143.6, 143.3, 132.2, 129.6, 128.4, 112.1, 107.4, 61.2, 50.8, 41.2, 38.7, 34.6, 32.0, 29.1, 27.5, 14.2; IR (potassium bromide) (v, cm^{-1}): 3447, 2960, 1740, 1632, 1489, 1379, 1220, 1158, 1143, 1029, 1014, 971; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{21}H_{24}ClO_4$: 375.1358, found 375.1350.

Ethyl 2-(4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromen-2-yl)acetate (3ad)



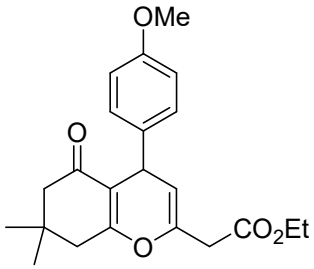
58 mg, 69% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 5.07 (d, J = 4.6 Hz, 1H), 4.31 (d, J = 4.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.19 (s, 2H), 2.39 (s, 2H), 2.28–2.10 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.08 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 169.1, 164.5, 144.1, 143.4, 131.4, 130.0, 120.4, 112.0, 107.3, 61.2, 50.8, 41.2, 38.7, 34.7, 32.0, 29.1, 27.5, 14.2; IR (potassium bromide) (v, cm^{-1}): 3447, 2960, 2872, 1740, 1633, 1487, 1378, 1220, 1159, 1143, 1030, 1010, 971, 827; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{21}H_{24}BrO_4$: 419.0852, found 419.0855.

Ethyl 2-(7,7-dimethyl-5-oxo-4-(p-tolyl)-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ae)



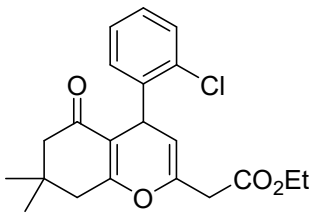
45 mg, 64% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 5.09 (d, J = 4.6 Hz, 1H), 4.31 (d, J = 4.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.17 (s, 2H), 2.39 (s, 2H), 2.28 (s, 3H), 2.25–2.12 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.08 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 169.3, 164.3, 142.7, 142.3, 136.0, 129.1, 128.0, 112.4, 108.1, 61.1, 50.8, 41.2, 38.8, 34.7, 32.0, 29.1, 27.6, 21.0, 14.1; IR (potassium bromide) (v, cm^{-1}): 3448, 2995, 1770, 1632, 1376, 1246, 1143, 1051; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{22}H_{27}O_4$: 355.1904, found 355.1899.

Ethyl 2-(4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3af)



44 mg, 60% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 8.3 Hz, 2H), 6.81 (d, J = 8.3 Hz, 2H), 5.09 (d, J = 4.6 Hz, 1H), 4.30 (d, J = 4.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 3.18 (s, 2H), 2.38 (s, 2H), 2.27–2.09 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.08 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 169.3, 164.2, 158.1, 142.8, 137.4, 129.1, 113.6, 112.6, 108.1, 61.1, 55.2, 50.8, 41.2, 38.8, 34.2, 32.0, 29.1, 27.5, 14.1; IR (potassium bromide) (v, cm^{-1}): 3447, 2959, 2836, 1740, 1633, 1510, 1378, 1252, 1159, 1143, 1031, 971, 831; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{22}H_{27}O_5$: 371.1853, found 371.1857.

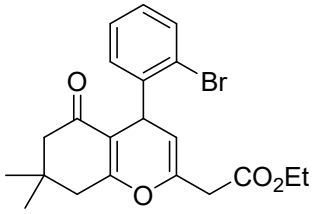
Ethyl 2-(4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ag)



54 mg, 71% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.49 (m, 1H), 7.27–7.21 (m, 1H), 7.16–7.11 (m, 1H), 7.05–6.99 (m, 1H), 5.14 (d, J = 4.3 Hz, 1H),

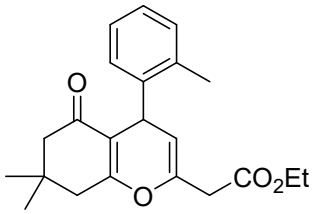
4.83 (d, J = 3.9 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.13 (s, 2H), 2.45 (d, J = 3.1 Hz, 2H), 2.31–2.16 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 169.1, 165.7, 142.9, 142.0, 132.7, 129.6, 129.4, 127.6, 127.0, 111.0, 106.3, 61.1, 50.7, 41.2, 38.7, 32.4, 32.0, 29.0, 27.9, 14.1; IR (potassium bromide) (v, cm^{-1}): 3447, 2959, 2836, 1740, 1633, 1510, 1378, 1252, 1159, 1142, 1031, 971, 832; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{21}H_{24}ClO_4$: 375.1358, found 375.1365.

Ethyl 2-(4-(2-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ah)



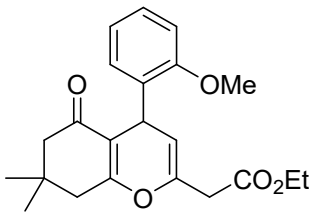
49 mg, 58% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 7.9 Hz, 1H), 7.21–7.06 (m, 3H), 5.13 (d, J = 4.3 Hz, 1H), 4.84 (d, J = 4.0 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.13 (s, 2H), 2.45 (s, 2H), 2.29–2.17 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 169.0, 164.7, 147.4, 143.4, 131.2, 129.8, 129.6, 126.9, 122.5, 111.8, 107.2, 61.2, 50.8, 41.2, 38.8, 34.9, 32.0, 29.0, 27.6, 14.2; IR (potassium bromide) (v, cm^{-1}): 3447, 2960, 1740, 1633, 1469, 1378, 1247, 1159, 1143, 1028, 972, 785; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{21}H_{24}BrO_4$: 419.0852, found 419.0855.

Ethyl 2-(7,7-dimethyl-5-oxo-4-(o-tolyl)-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ai)



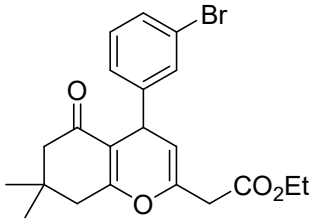
55 mg, 77% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15–7.01 (m, 4H), 5.04 (d, J = 4.4 Hz, 1H), 4.55 (d, J = 4.1 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.14 (s, 2H), 2.52 (s, 3H), 2.43 (s, 2H), 2.27–2.13 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.10 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 169.2, 164.8, 143.7, 142.5, 135.1, 130.1, 128.3, 126.2, 112.5, 107.6, 61.1, 50.8, 41.2, 38.8, 32.0, 31.0, 29.1, 27.7, 19.4, 14.1; IR (potassium bromide) (v, cm^{-1}): 3462, 2960, 1743, 1634, 1466, 1378, 1247, 1143, 1031, 971, 850; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{22}H_{27}O_4$: 355.1904, found 355.1916.

Ethyl 2-(4-(2-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3aj)



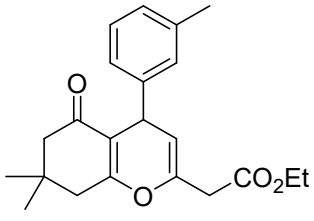
47 mg, 64% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.11 (m, 1H), 7.06–7.00 (m, 1H), 6.90–6.82 (m, 2H), 5.13 (d, J = 4.5 Hz, 1H), 4.76 (d, J = 4.1 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.10 (s, 2H), 2.43 (s, 2H), 2.32–2.16 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 169.3, 165.7, 156.3, 142.3, 133.2, 128.4, 127.4, 120.7, 111.2, 110.7, 107.4, 61.0, 55.6, 50.8, 41.3, 38.7, 31.9, 29.1, 28.7, 27.8, 14.1; IR (potassium bromide) (v, cm^{-1}): 3461, 2960, 2837, 1740, 1634, 1490, 1465, 1380, 1240, 1144, 1030, 972, 862; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{22}H_{27}O_5$: 371.1853, found 371.1866.

Ethyl 2-(4-(3-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ak)



46 mg, 55% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.32–7.22 (m, 2H), 7.14 (t, J = 7.8 Hz, 1H), 5.07 (d, J = 4.6 Hz, 1H), 4.32 (d, J = 4.4 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.27–3.12 (m, 2H), 2.40 (s, 2H), 2.29–2.13 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.09 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 169.0, 164.7, 147.4, 143.4, 131.2, 129.8, 129.6, 126.9, 122.5, 111.8, 107.2, 61.2, 50.8, 41.2, 38.8, 34.9, 32.0, 29.0, 27.6, 14.2; IR (potassium bromide) (v, cm^{-1}): 3447, 2960, 1739, 1632, 1470, 1378, 1339, 1247, 1142, 1029, 785; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{21}H_{24}BrO_4$: 419.0852, found 419.0875.

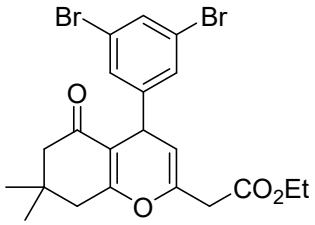
Ethyl 2-(7,7-dimethyl-5-oxo-4-(m-tolyl)-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3al)



37 mg, 52% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, J = 7.4 Hz, 1H), 7.12–7.06 (m, 2H), 6.98 (d, J = 7.3 Hz, 1H), 5.09 (d, J = 4.4 Hz, 1H), 4.30 (d, J = 4.1 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 3.24–3.12 (m, 2H), 2.40 (s, 2H), 2.31 (s, 3H), 2.25–2.13 (m, 2H), 1.28 (t, J = 7.3 Hz, 3H), 1.09 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 169.2, 164.5, 145.1, 142.7, 137.8, 128.8, 128.2, 127.3, 125.1, 112.3,

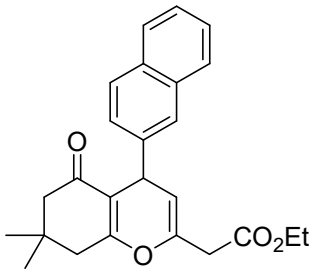
108.1, 61.1, 50.8, 41.2, 38.8, 35.1, 32.0, 29.1, 27.6, 21.4, 14.2; IR (potassium bromide) (ν, cm^{-1}): 3447, 2959, 1741, 1633, 1488, 1465, 1378, 1252, 1158, 1142, 1030, 971, 848; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{22}H_{27}O_4$: 355.1904, found 355.1898.

Ethyl 2-(4-(3,5-dibromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetat-e (3am)



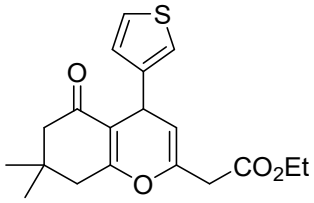
51 mg, 51% yield; yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 1H), 7.37 (s, 2H), 5.04 (d, J = 4.5 Hz, 1H), 4.30 (d, J = 4.2 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.31–3.11 (m, 2H), 2.41 (d, J = 7.3 Hz, 2H), 2.32–2.16 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.09 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 168.8, 165.0, 148.9, 143.9, 132.2, 130.1, 122.8, 111.3, 106.5, 61.3, 50.7, 41.1, 38.8, 34.8, 32.1, 28.9, 27.7, 14.2; IR (potassium bromide) (ν, cm^{-1}): 3447, 3070, 2959, 1740, 1633, 1466, 1379, 1220, 1159, 1143, 1030, 972, 854; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{21}H_{23}Br_2O_4$: 496.9958, found 496.9953.

Ethyl 2-(7,7-dimethyl-4-(naphthalen-1-yl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3an)



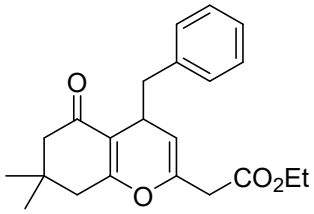
60 mg, 77% yield; yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83–7.70 (m, 4H), 7.50–7.35 (m, 3H), 5.16 (d, J = 4.6 Hz, 1H), 4.53 (d, J = 4.4 Hz, 1H), 4.30–4.14 (m, 2H), 3.31–3.13 (m, 2H), 2.43 (s, 2H), 2.30–2.11 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.09 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 169.2, 164.5, 143.1, 142.4, 133.4, 132.4, 128.0, 127.9, 127.5, 126.7, 126.5, 125.8, 125.4, 112.3, 107.8, 61.2, 50.8, 41.3, 38.8, 35.3, 32.0, 29.1, 27.5, 14.2; IR (potassium bromide) (ν, cm^{-1}): 3447, 3055, 2959, 1741, 1633, 1467, 1378, 1247, 1159, 1143, 1047, 972, 857; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{25}H_{27}O_4$: 391.1904, found 391.1903.

Ethyl 2-(7,7-dimethyl-5-oxo-4-(thiophen-3-yl)-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ao)



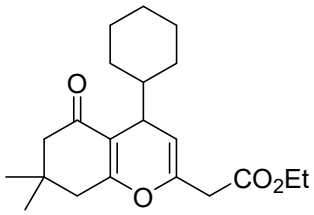
52 mg, 75% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20–7.16 (m, 1H), 7.11 (s, 1H), 7.06 (d, J = 4.9 Hz, 1H), 5.17 (d, J = 4.8 Hz, 1H), 4.50 (d, J = 4.6 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.21 (d, J = 2.9 Hz, 2H), 2.35 (s, 2H), 2.22 (d, J = 4.3 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H), 1.08 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 169.3, 164.3, 145.7, 143.4, 127.8, 125.1, 121.6, 112.4, 107.2, 61.2, 50.8, 41.2, 38.7, 32.0, 29.7, 29.0, 27.5, 14.2; IR (potassium bromide) (v, cm^{-1}): 3459, 2960, 1740, 1633, 1468, 1370, 1219, 1158, 1029, 972, 842; HRMS (TOF, ESI, *m/z*): calcd for [M + H]$^+$ $C_{19}H_{23}O_4S$: 347.1312, found 347.1315.

Ethyl 2-(4-benzyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ap)



26 mg, 36% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.28 (m, 2H), 7.25–7.18 (m, 3H), 5.10 (d, J = 2.8 Hz, 1H), 5.01 (q, J = 6.5 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.55 (d, J = 16.9 Hz, 1H), 3.41 (d, J = 16.8 Hz, 1H), 3.10–3.03 (m, 1H), 2.98–2.90 (m, 1H), 2.36–2.23 (m, 2H), 2.20 (s, 2H), 1.25 (t, J = 7.0 Hz, 3H), 1.06 (d, J = 2.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 171.6, 136.2, 129.5, 128.4, 127.2, 126.7, 117.7, 111.4, 77.4, 60.4, 51.5, 42.6, 41.2, 39.5, 31.5, 28.4, 27.9, 14.2; IR (potassium bromide) (v, cm^{-1}): 3448, 2960, 1741, 1635, 1469, 1380, 1219, 1159, 1145, 1035, 972, 848; HRMS (TOF, ESI, *m/z*): calcd for [M + H]$^+$ $C_{22}H_{27}O_4$: 355.1904, found 355.1907.

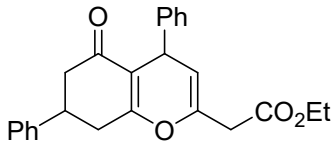
Ethyl 2-(4-cyclohexyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3aq)



24 mg, 35% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.98 (d, J = 5.0 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.26–3.05 (m, 3H), 2.31 (s, 2H), 2.26 (s, 2H), 1.80–1.51 (m, 6H), 1.45 (d, J = 9.4 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.18–0.98 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 169.4, 166.2, 144.3, 111.4, 105.1, 61.0, 51.1, 41.7, 41.3, 38.9, 34.2, 31.8, 29.9, 29.4, 27.9, 27.5, 26.5(7), 26.5(6), 26.2, 14.1; IR (potassium

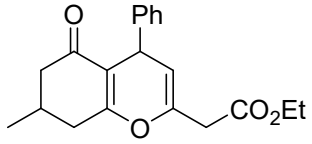
bromide) (v, cm^{-1}): 3447, 2925, 2852, 1743,1632, 1450, 1384, 1217, 1144, 1032, 974, 830; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{21}H_{31}O_4$: 347.2217, found 347.2213.

Ethyl 2-(5-oxo-4,7-diphenyl-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ba)[3]



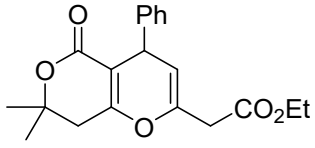
48 mg, 62% yield, 2:1 d.r.; colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.18 (m, 10H, major+minor), 5.16 (d, J = 4.6 Hz, 0.68H, major), 5.11 (d, J = 4.3 Hz, 0.32H, minor), 4.46–4.39 (m, 1H, major+minor), 4.24–4.16 (m, 2H, major+minor), 3.51–3.41 (m, 0.32H, minor), 3.34–3.16 (m, 2.68H, major+minor), 2.89–2.73 (m, 2H, major+minor), 2.68–2.51 (m, 2H, major+minor), 1.31–1.26 (m, 3H, major+minor); ^{13}C NMR (100 MHz, $CDCl_3$): δ (major+minor) 196.5, 196.3, 169.2, 165.4, 164.6, 145.0, 144.7, 143.2, 142.8, 142.5, 142.4, 128.8, 128.7, 128.4, 128.3, 127.0(4), 126.9(7), 126.7, 126.6, 126.5, 113.6, 113.3, 108.0, 107.8, 61.1(9), 61.1(6), 44.0, 38.8, 38.7(2), 38.6(5), 38.1, 35.3, 35.0, 34.9, 14.1.

Ethyl 2-(7-methyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3ca)



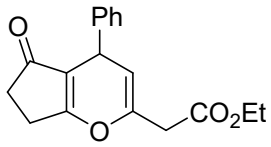
33 mg, 50 % yield, 2:1 d.r.; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.24 (m, 4H, major+minor), 7.21–7.12 (m, 1H, major+minor), 5.11 (d, J = 4.7 Hz, 0.64H, major), 5.08 (d, J = 4.5 Hz, 0.32H, minor), 4.36 (t, J = 5.0 Hz, 1H, major+minor), 4.20 (q, J = 7.1 Hz, 2H, major+minor), 3.19 (s, 2H, major+minor), 2.61–2.47 (m, 1H, major+minor), 2.45–2.13 (m, 3H, major+minor), 2.11–1.98 (m, 1H, major+minor), 1.29 (t, J = 7.1 Hz, 3H, major+minor), 1.05 (t, J = 4.6 Hz, 3H, major+minor); ^{13}C NMR (100 MHz, $CDCl_3$): δ (major+minor) 197.3(4), 197.2(6), 169.2, 165.8, 165.0, 145.1(1), 145.0(8), 143.0, 142.8, 128.3, 128.1, 126.5, 113.3, 112.9, 108.0, 107.8, 61.2, 45.4, 45.3, 38.8, 38.7, 35.7, 35.4, 35.3, 35.0, 28.5, 27.7, 20.8, 14.1; IR (potassium bromide) (v, cm^{-1}): 3447, 3061, 3027, 2959, 2930, 1739, 1630,1454, 1385, 1156, 1029, 915, 850, 699; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{20}H_{23}O_4$: 327.1591, found 327.1588.

Ethyl 2-(7,7-dimethyl-5-oxo-4-phenyl-7,8-dihydro-4*H*,5*H*-pyrano[4,3-*b*]pyran-2-yl)acetate (3da)[3]



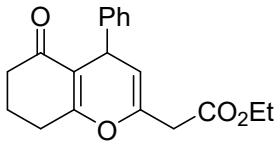
36 mg, 53% yield; white solid; M.p: 136-138 °C[3]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.26 (m, 4H), 7.23–7.17 (m, 1H), 5.12 (d, J = 4.5 Hz, 1H), 4.38 (d, J = 4.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.20 (s, 2H), 2.72 (d, J = 17.4 Hz, 1H), 2.43 (d, J = 17.3 Hz, 1H), 1.46 (s, 3H), 1.34 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 165.3, 158.6, 144.2, 143.0, 128.4, 128.2, 126.8, 107.5, 103.4, 77.6, 61.2, 38.6, 37.5, 35.9, 28.9, 26.4, 14.1.

Ethyl 2-(5-oxo-4-phenyl-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-2-yl)acetate (3ea)



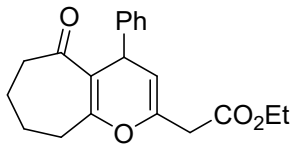
29 mg, 48 % yield; colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.16 (m, 5H), 5.08 (d, J = 3.6 Hz, 1H), 4.32 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.27 (s, 2H), 2.66 (d, J = 5.6 Hz, 2H), 2.41 (d, J = 5.2 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.7, 178.3, 169.0, 144.5, 142.9, 128.4, 128.1, 126.9, 117.0, 107.2, 61.3, 38.7, 35.4, 33.3, 25.4, 14.1; IR (potassium bromide) (v, cm^{-1}): 3447, 3061, 2982, 2929, 1739, 1693, 1637, 1454, 1388, 1241, 1155, 1028, 914, 854, 699; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{18}H_{19}O_4$: 299.1278, found 299.1276.

Ethyl 2-(5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromen-2-yl)acetate (3fa)[3]



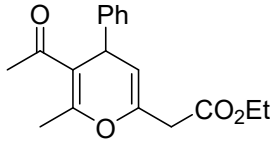
41 mg, 65% yield; white solid; M.p: 71-75 °C[3]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.23 (m, 4H), 7.20–7.15 (m, 1H), 5.11 (d, J = 4.6 Hz, 1H), 4.37 (d, J = 4.3 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.19 (s, 2H), 2.62–2.44 (m, 2H), 2.41–2.25 (m, 2H), 2.10–1.86 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 169.2, 166.1, 145.1, 142.9, 128.3, 128.2, 126.5, 113.6, 107.9, 61.2, 38.7, 37.0, 35.0, 27.5, 20.3, 14.1.

Ethyl 2-(5-oxo-4-phenyl-4,5,6,7,8,9-hexahydrocyclohepta[*b*]pyran-2-yl)acetate (3ga)



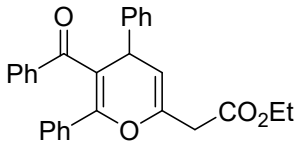
21 mg, 32% yield; colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.24 (m, 4H), 7.19–7.12 (m, 1H), 5.07 (d, J = 4.8 Hz, 1H), 4.43 (d, J = 4.7 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.17 (d, J = 2.6 Hz, 2H), 2.80–2.36 (m, 4H), 1.95–1.66 (m, 4H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 169.3, 165.2, 145.9, 142.8, 128.3, 128.0, 126.4, 116.0, 107.3, 61.1, 41.8, 38.7, 37.5, 31.2, 23.3, 20.7, 14.1.

Ethyl 2-(5-acetyl-6-methyl-4-phenyl-4*H*-pyran-2-yl)acetate (3ha)[3]



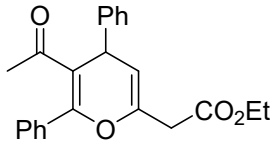
32 mg, 53% yield; colourless oil; ^{1}H NMR (400 MHz, CD_3OD): δ 7.33–7.27 (m, 2H), 7.25–7.15 (m, 3H), 5.11 (d, J = 4.6 Hz, 1H), 4.46 (d, J = 4.5 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.16 (s, 2H), 2.24 (s, 3H), 2.03 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 202.4, 171.1, 159.9, 147.1, 143.7, 129.8, 128.9, 127.9, 114.2, 108.1, 62.1, 40.5, 39.2, 29.8, 19.7, 14.5.

Ethyl 2-(5-benzoyl-4,6-diphenyl-4*H*-pyran-2-yl)acetate (3ia)[3]



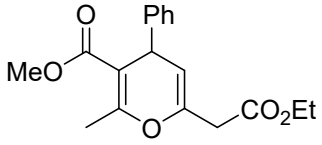
63 mg, 75% yield; yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.39 (d, J = 7.7 Hz, 2H), 7.32–7.24 (m, 5H), 7.21 (d, J = 7.1 Hz, 2H), 7.18–7.09 (m, 6H), 5.23 (d, J = 3.7 Hz, 1H), 4.57 (d, J = 3.3 Hz, 1H), 4.16 (q, J = 6.9 Hz, 2H), 3.44 (s, 2H), 1.23 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.6, 169.3, 153.1, 144.4, 144.3, 137.5, 133.5, 132.3, 129.7, 128.6(3), 128.5(5), 128.4, 128.2, 128.0(3), 127.9(6), 126.8, 112.9, 105.1, 60.6, 40.4, 38.1, 14.1.

Ethyl 2-(5-acetyl-4,6-diphenyl-4*H*-pyran-2-yl)acetate (3ja)[3]



23 mg, 32% yield; yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.55–7.46 (m, 3H), 7.43 (d, J = 7.5 Hz, 2H), 7.35–7.27 (m, 4H), 7.23–7.17 (m, 1H), 5.24 (d, J = 4.9 Hz, 1H), 4.44 (d, J = 4.8 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.34 (s, 2H), 1.59 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 199.2, 169.1, 157.4, 145.4, 143.6, 134.3, 130.5, 128.9, 128.7, 128.5, 127.7, 126.5, 115.6, 106.6, 60.5, 38.5, 37.7, 30.5, 14.1.

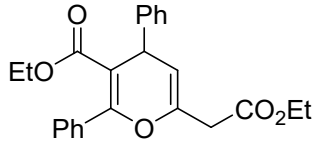
Methyl 6-(2-ethoxy-2-oxoethyl)-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate (3ka)



42 mg, 67% yield; colourless oil; ^{1}H NMR (400 MHz, CD_3OD): δ 7.29–7.19 (m, 4H), 7.18–7.12 (m, 1H), 5.05 (d, J = 4.5 Hz, 1H), 4.34 (d, J = 4.6 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.53 (s, 3H), 3.26–3.13 (m, 2H), 2.27 (s, 3H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 171.2, 169.5, 160.8, 147.4, 144.2, 129.4, 129.0, 127.6,

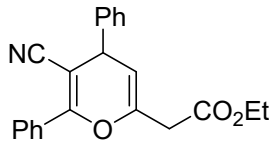
107.6, 106.3, 62.2, 51.6, 39.8, 39.3, 19.2, 14.5; IR (potassium bromide) (ν, cm^{-1}): 3421, 3062, 2983, 2951, 1741, 1719, 1632, 1454, 1339, 1270, 1156, 1030, 850, 700; HRMS (TOF, ESI, *m/z*): calcd for $[M + H]^+$ $C_{18}H_{21}O_5$: 317.1384, found 317.1386.

Ethyl 6-(2-ethoxy-2-oxoethyl)-2,4-diphenyl-4*H*-pyran-3-carboxylate (3la)[3]



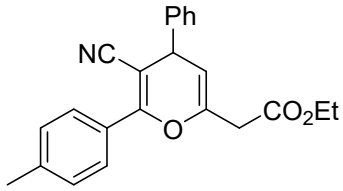
40 mg, 50% yield; yellow oil; ^{1}H NMR (400 MHz, CD_3OD): δ 7.48–7.27 (m, 9H), 7.20 (t, J = 6.7 Hz, 1H), 5.13 (d, J = 4.4 Hz, 1H), 4.48 (d, J = 4.3 Hz, 1H), 4.17 (q, J = 7.0 Hz, 2H), 3.76 (q, J = 7.1 Hz, 2H), 3.26 (d, J = 4.2 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H), 0.78 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 171.2, 169.3, 158.7, 146.7, 145.1, 136.5, 130.5, 129.6, 129.5, 129.3, 128.9, 127.9, 108.1, 107.0, 62.2, 61.3, 40.8, 39.3, 14.5, 13.8.

Ethyl 2-(5-cyano-4,6-diphenyl-4*H*-pyran-2-yl)acetate (3ma)[3]



39 mg, 57% yield; yellow solid; M.p: 127-129 °C[3]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.73–7.68 (m, 2H), 7.57–7.51 (m, 3H), 7.46–7.38 (m, 4H), 7.36–7.31 (m, 1H), 5.28 (d, J = 4.0 Hz, 1H), 4.42 (d, J = 3.8 Hz, 1H), 4.14 (q, J = 7.3 Hz, 2H), 3.47 (d, J = 4.0 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.9, 159.9, 143.9, 143.2, 131.3(4), 131.3(1), 128.9, 128.7, 128.0, 127.7, 118.6, 104.1, 87.6, 60.7, 39.0, 37.7, 14.1.

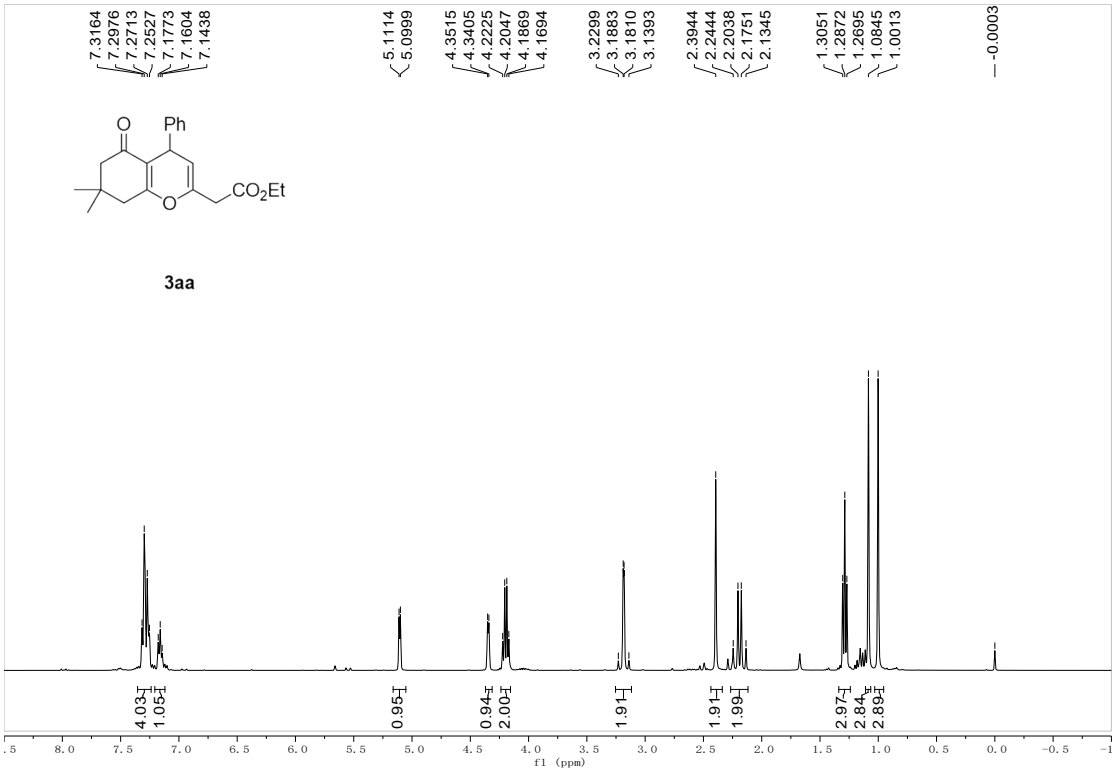
Ethyl 2-(5-cyano-4-phenyl-6-(*p*-tolyl)-4*H*-pyran-2-yl)acetate (3na)[3]



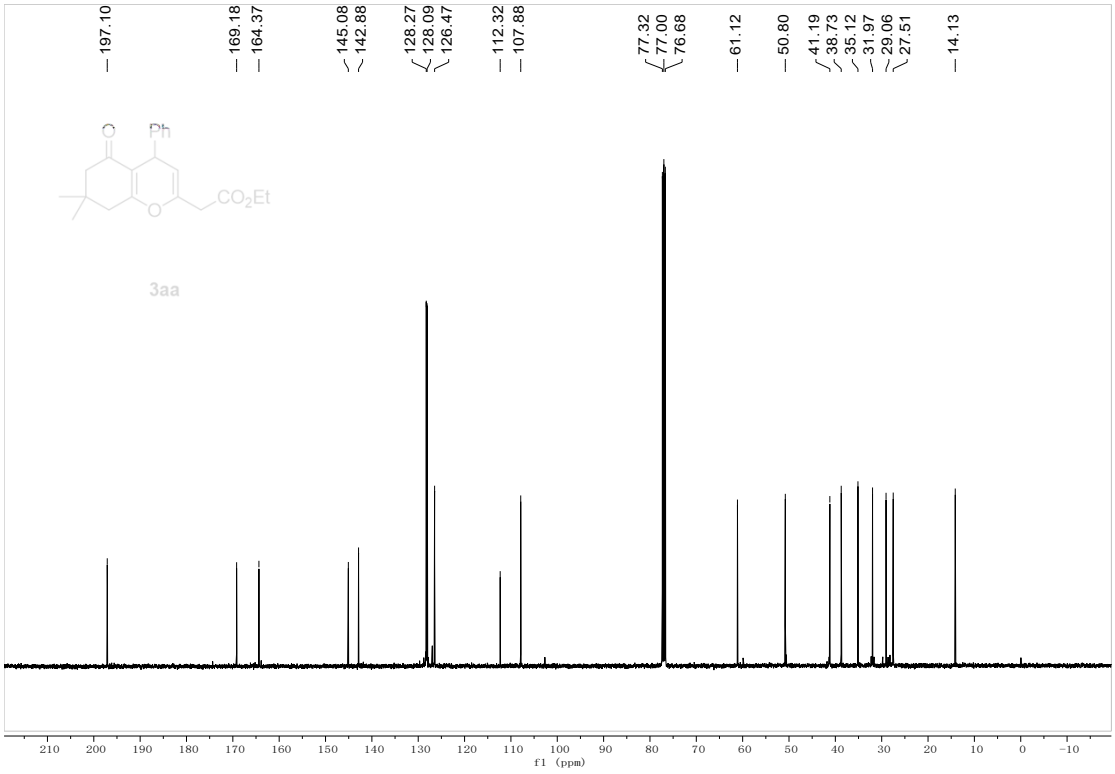
30 mg, 41% yield; white solid; M.p: 130-133 °C[3]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.66–7.56 (m, 2H), 7.45–7.30 (m, 7H), 5.26 (d, J = 4.1 Hz, 1H), 4.40 (d, J = 4.0 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.45 (d, J = 3.7 Hz, 2H), 2.37 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.9, 159.9, 143.9, 143.2, 141.4, 129.2, 128.9, 128.5, 127.9, 127.6, 127.5, 118.7, 104.1, 86.9, 60.7, 39.0, 37.7, 21.0, 14.1.

V. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

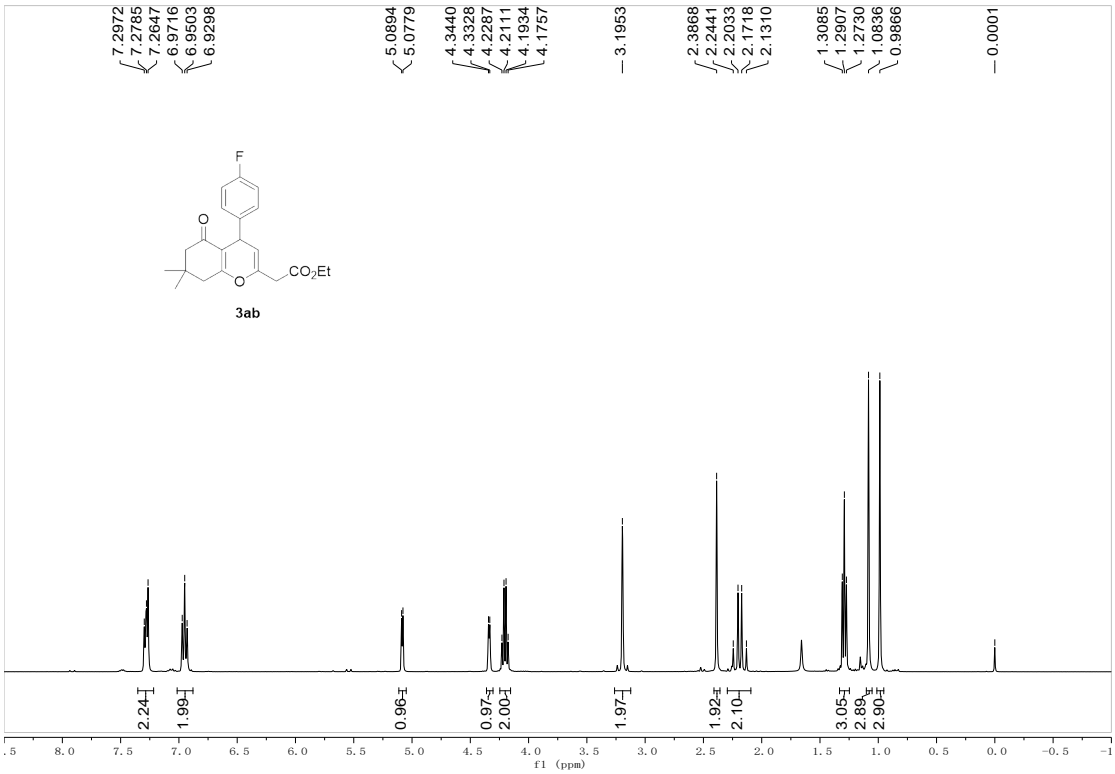
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3aa**)



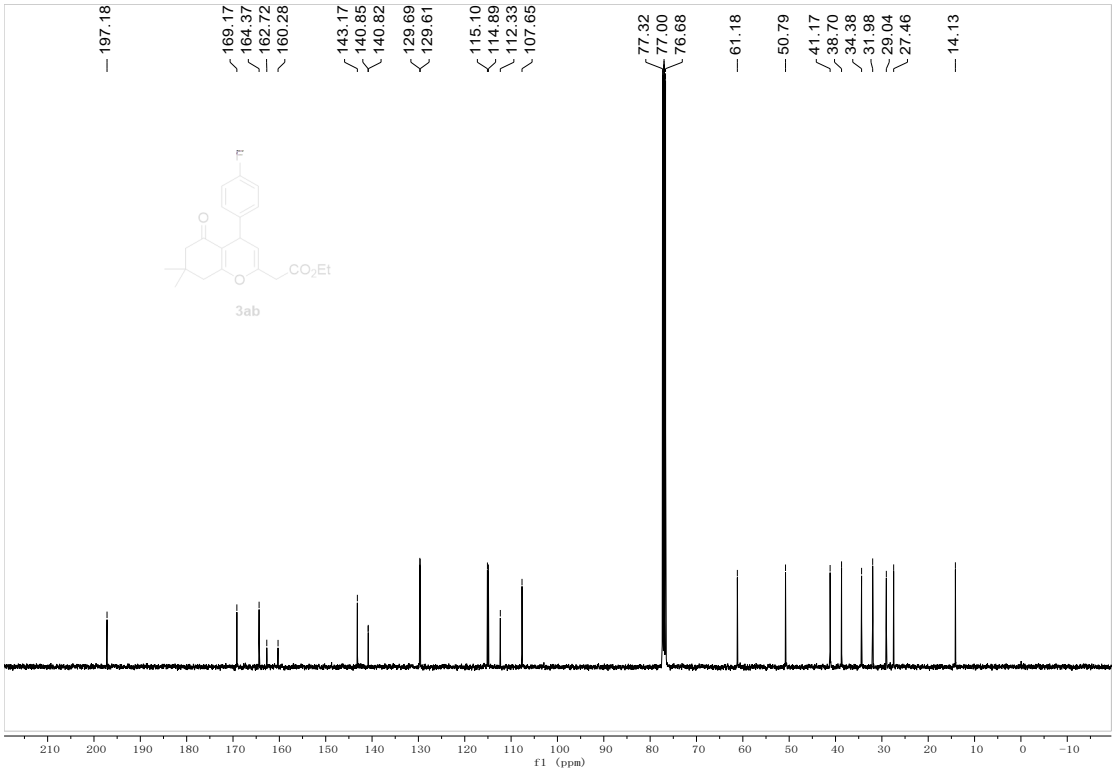
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3aa**)



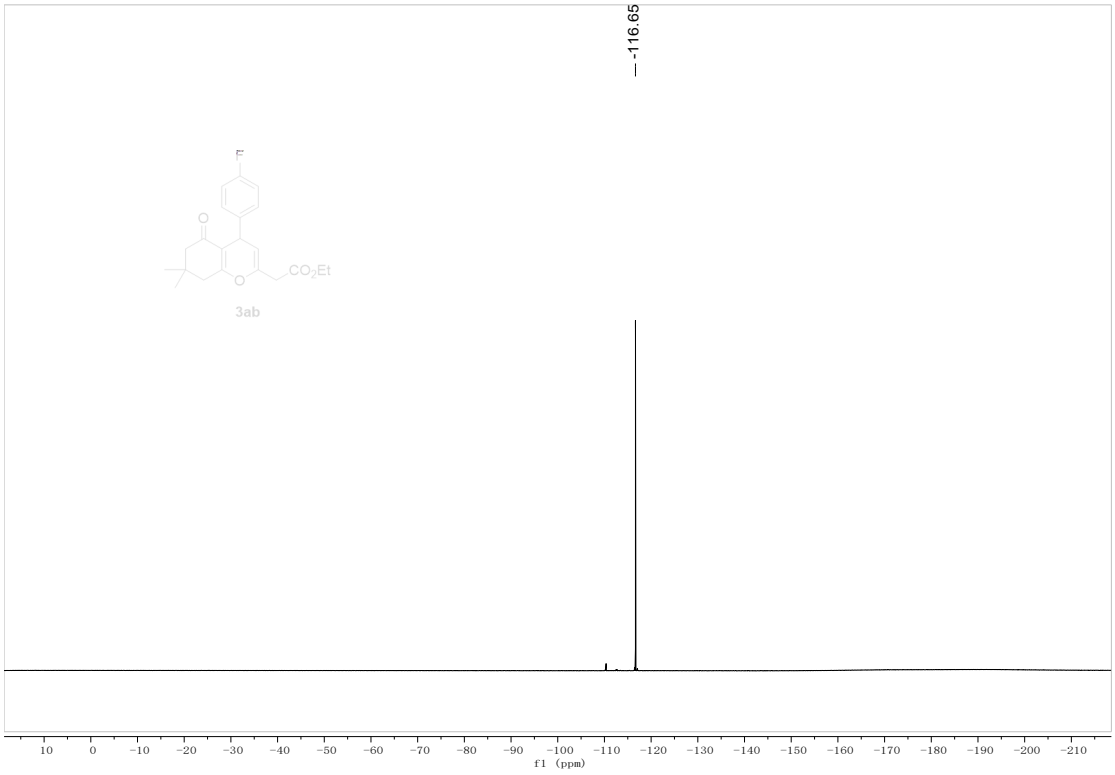
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ab**)



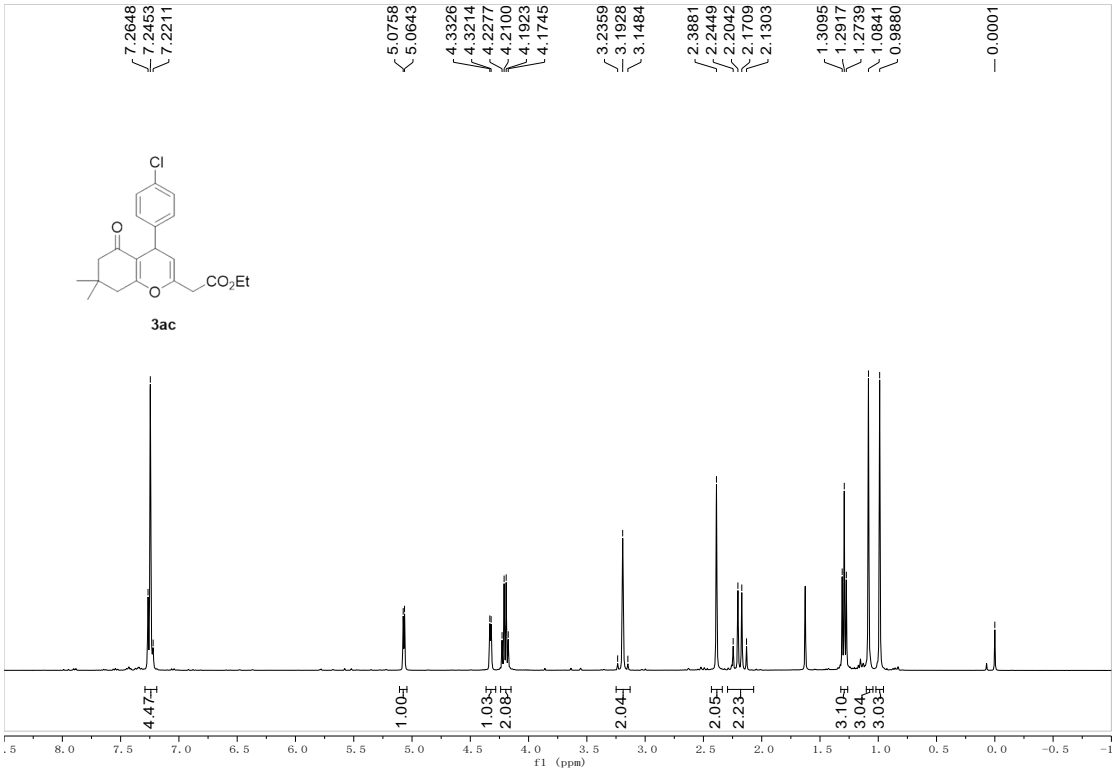
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ab**)



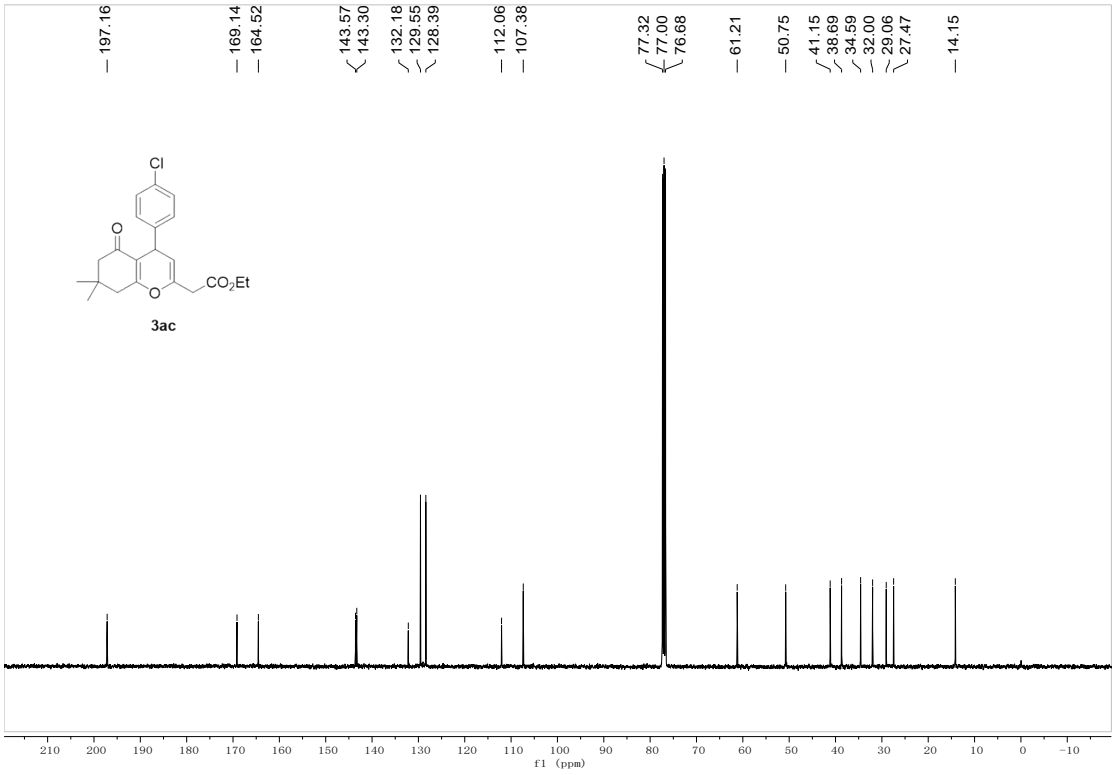
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound (**3ab**)



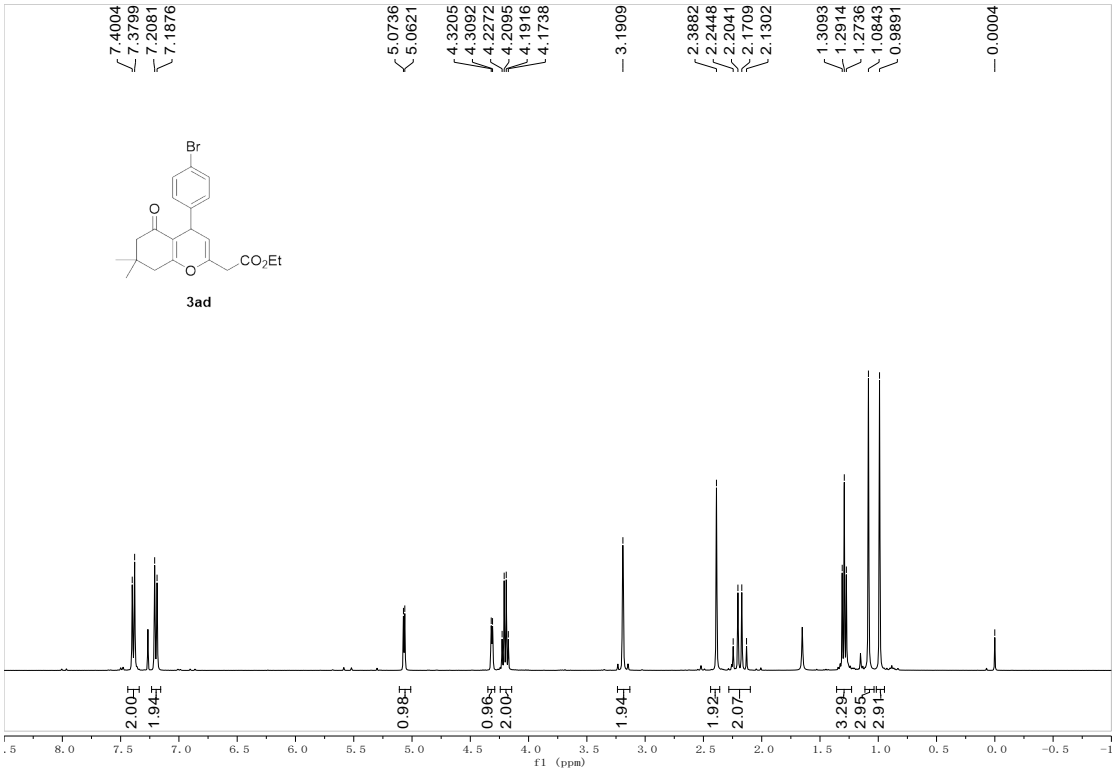
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ac**)



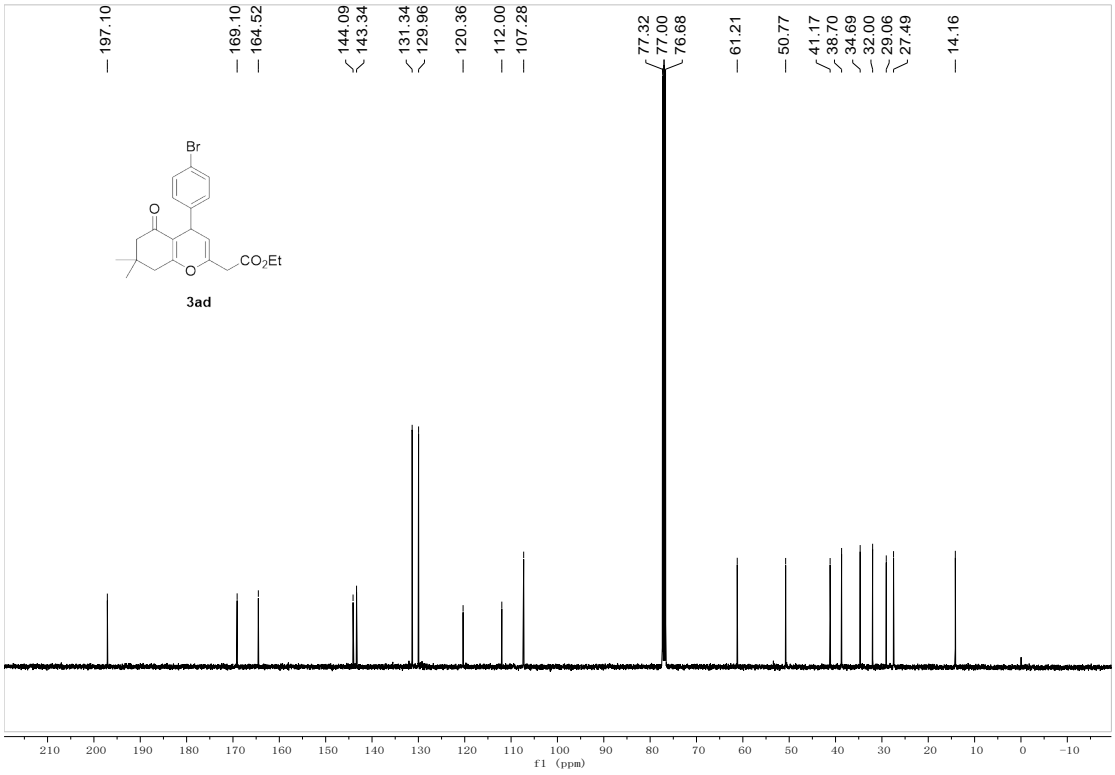
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ac**)



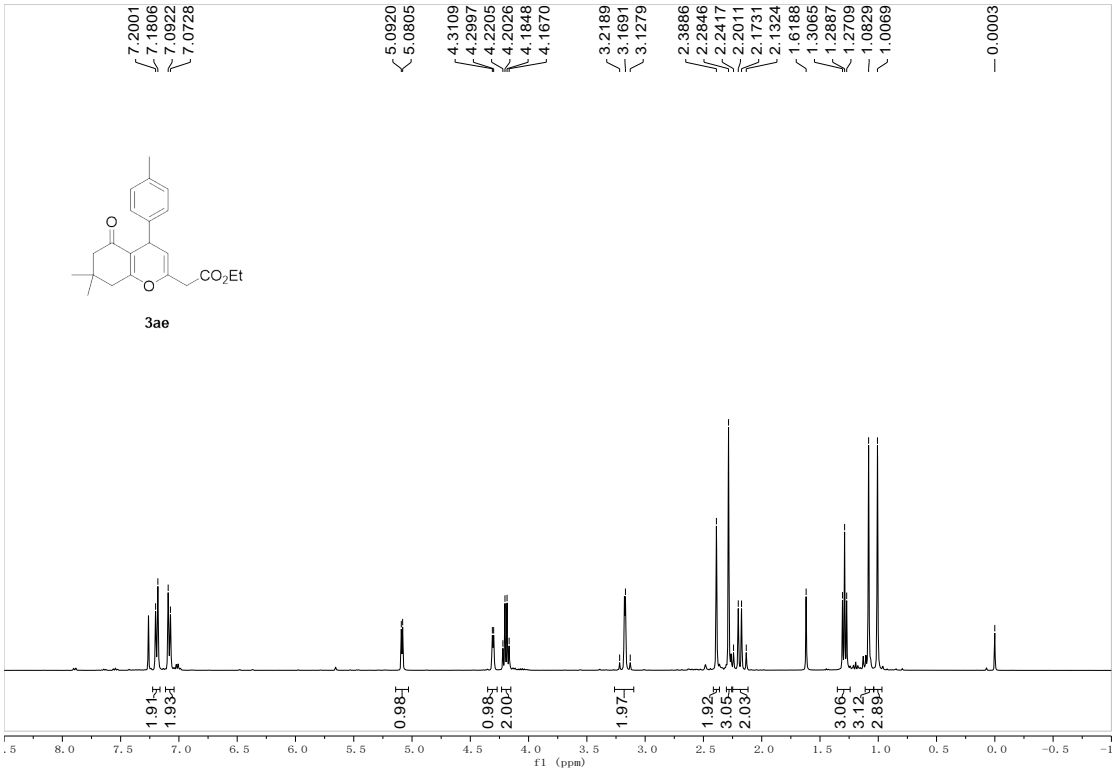
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ad**)



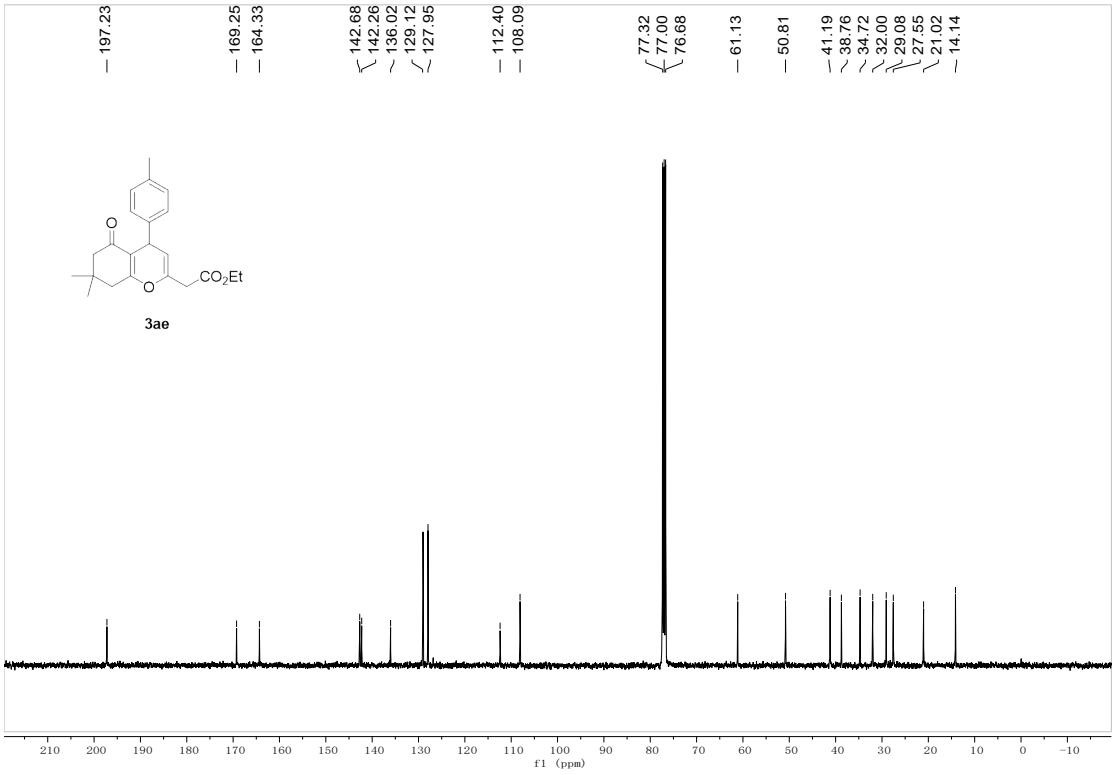
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ad**)



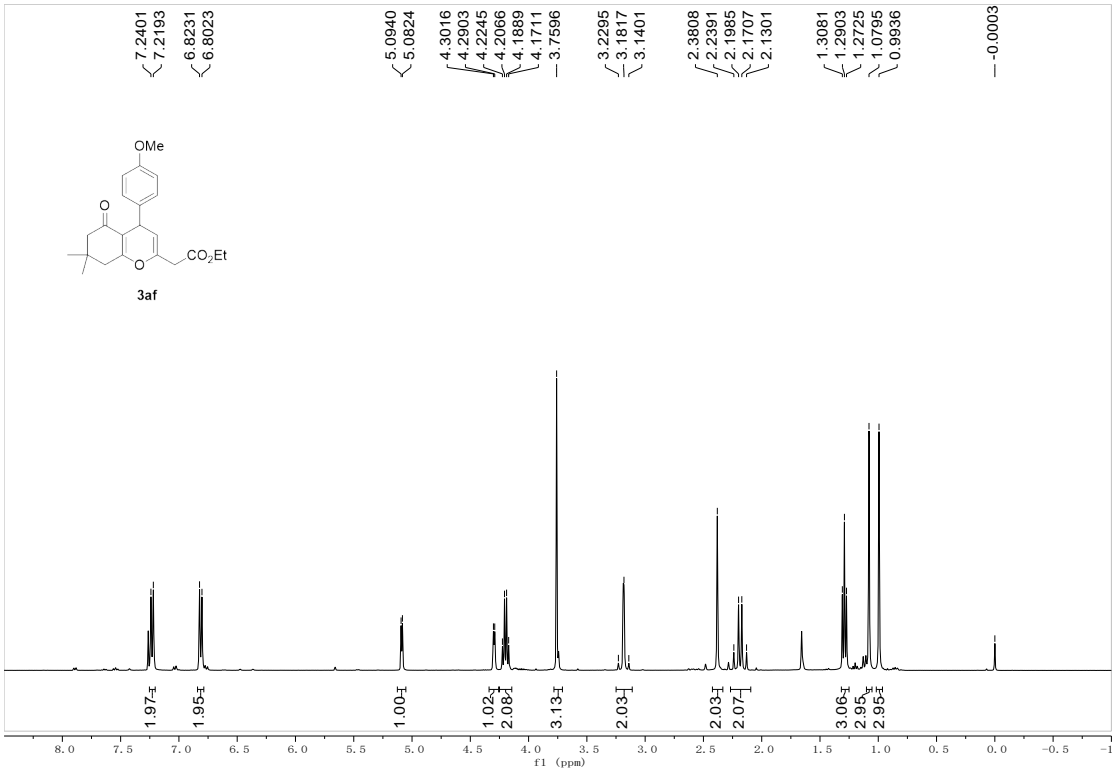
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ae**)



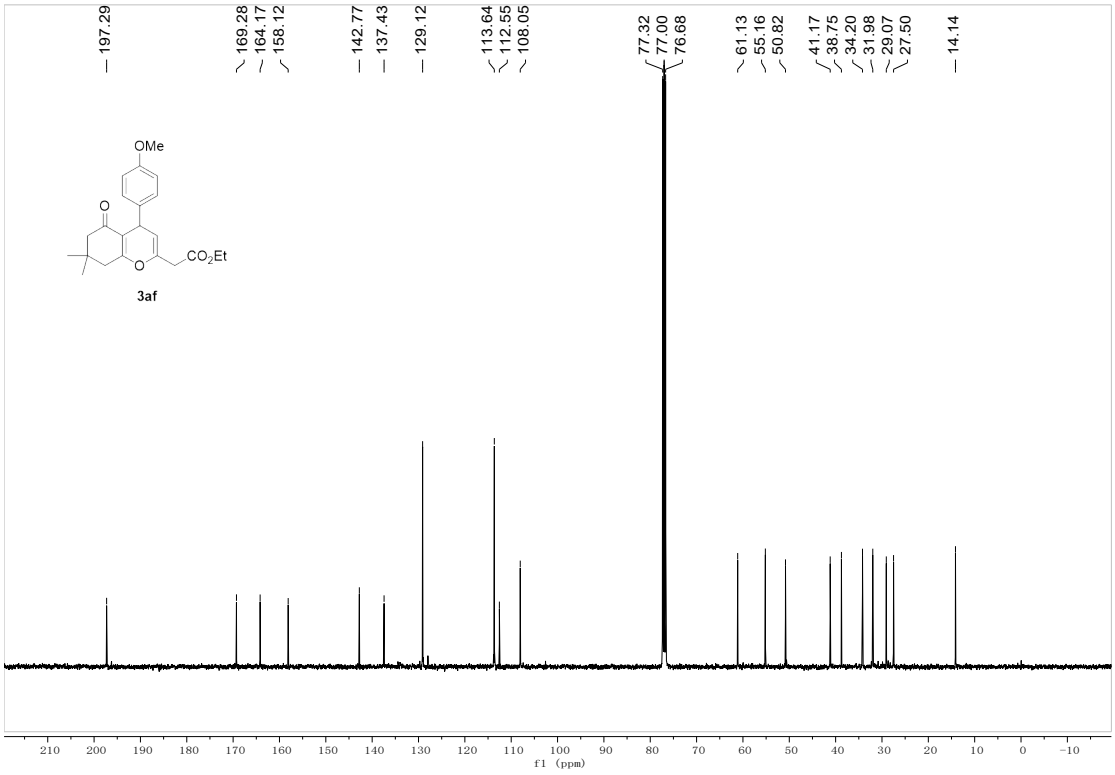
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ae**)



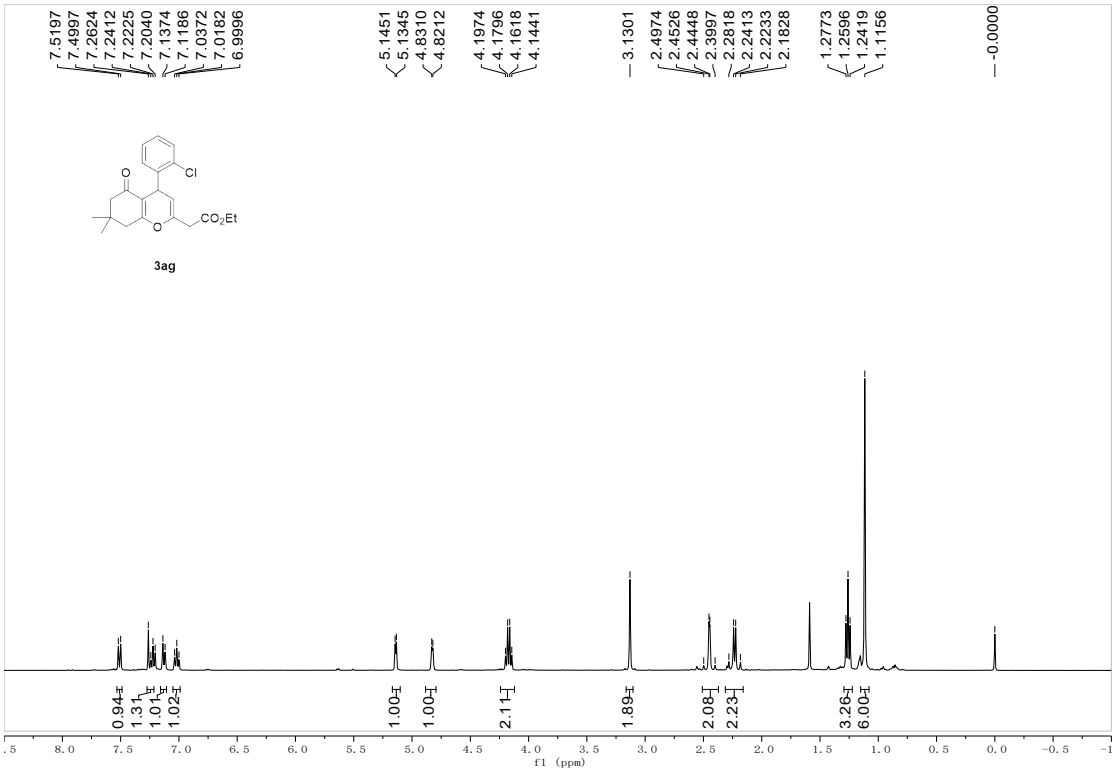
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3af**)



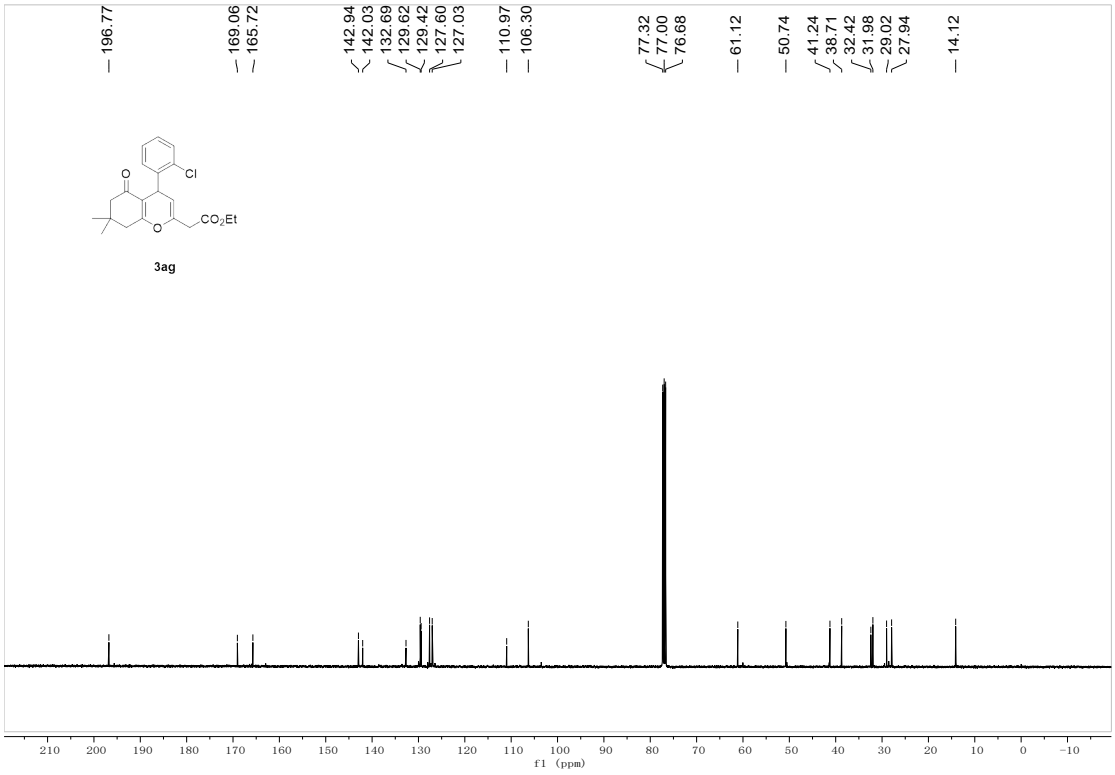
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3af**)



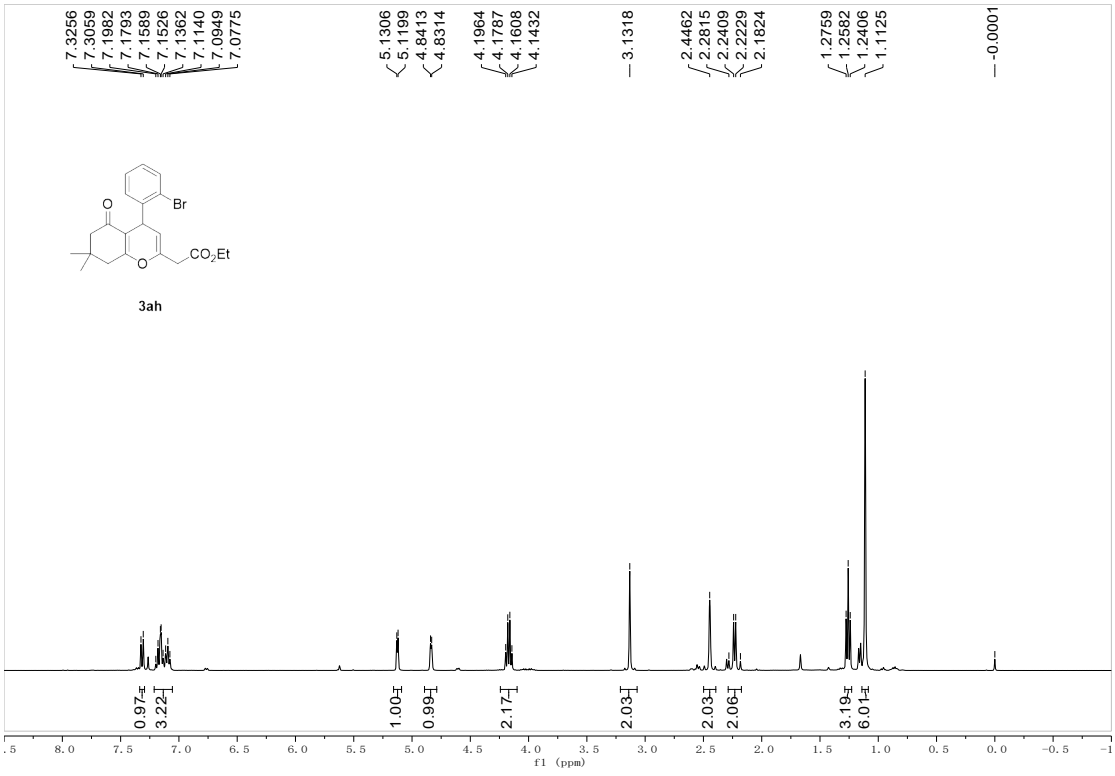
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ag**)



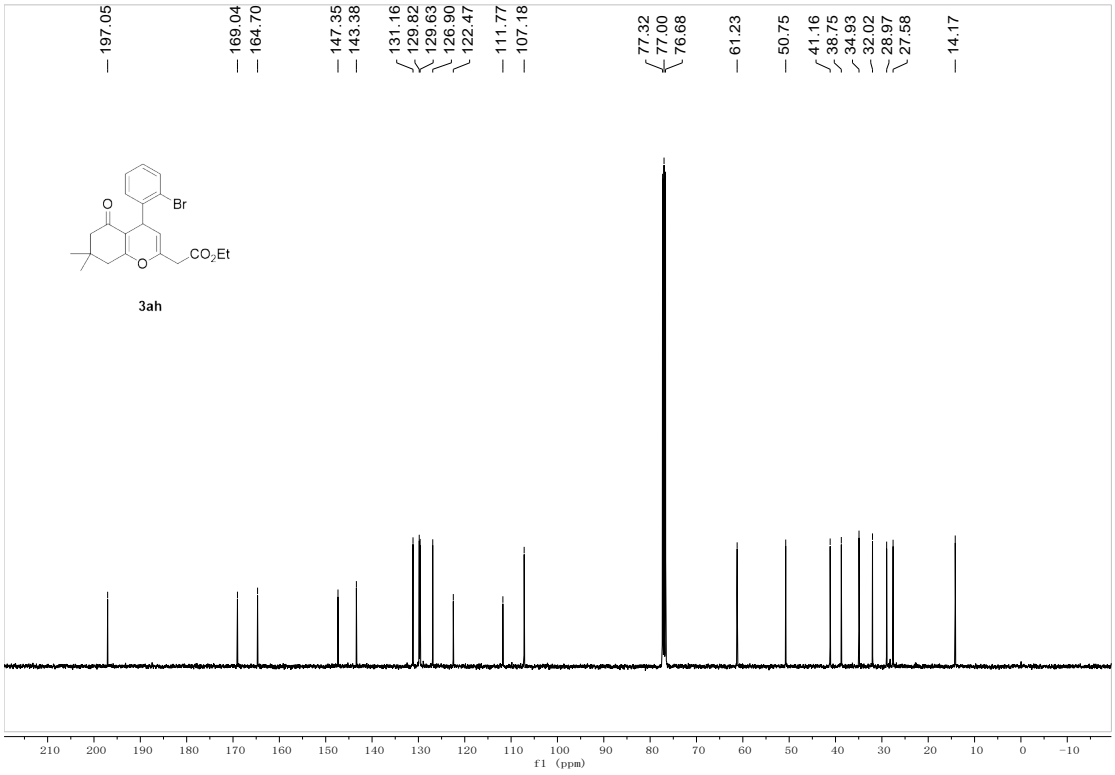
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ag**)



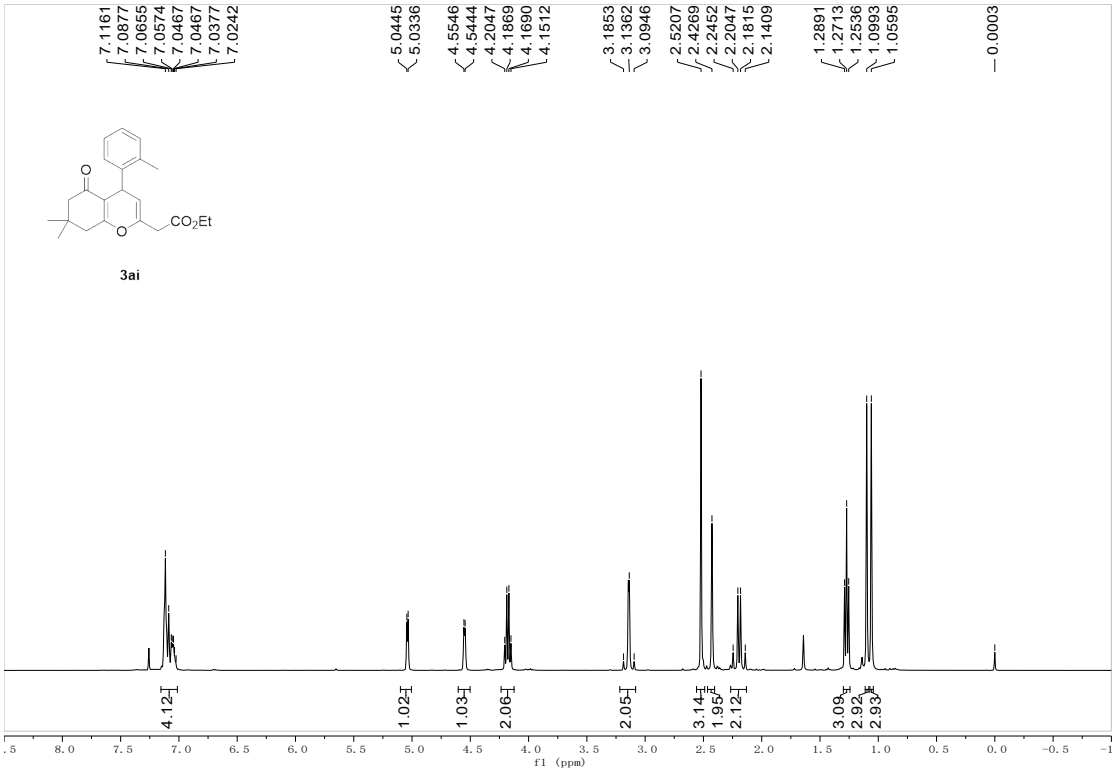
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ah**)



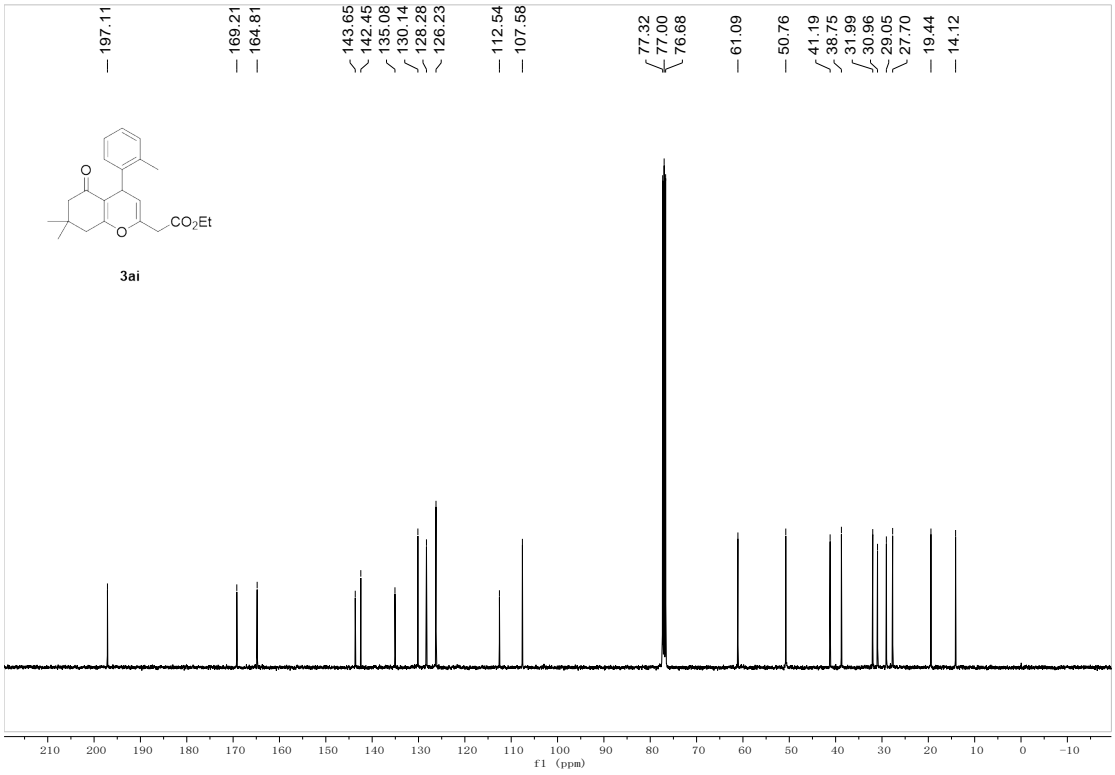
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ah**)



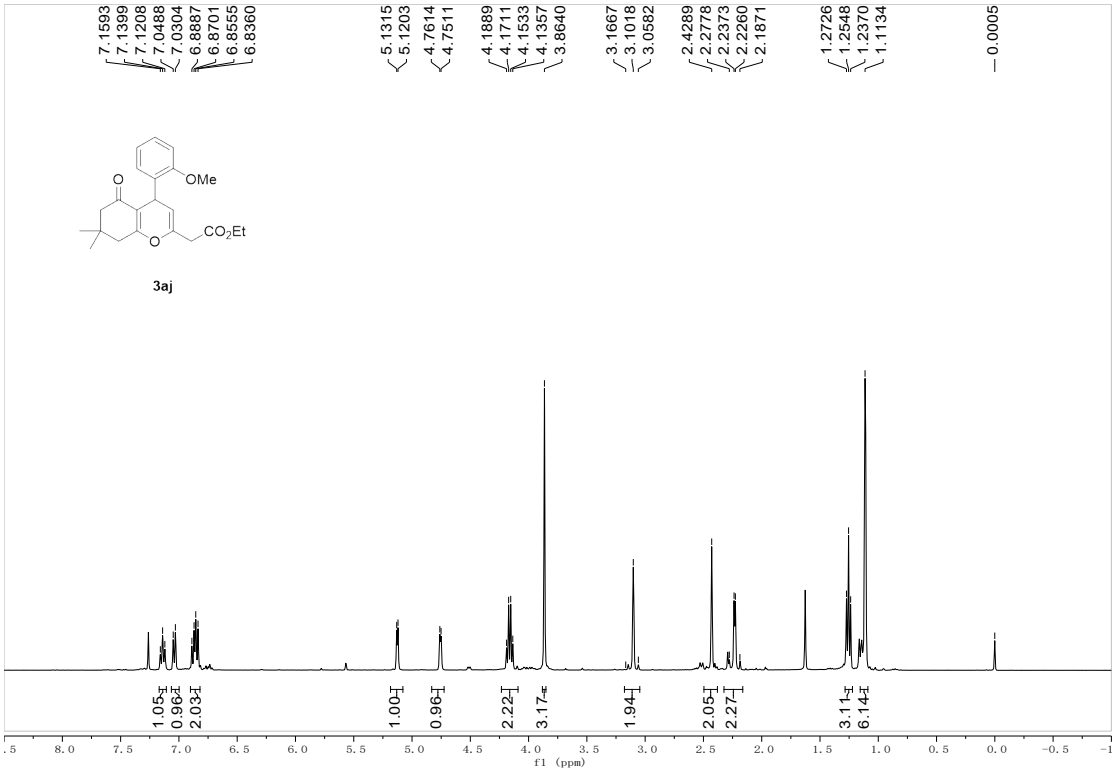
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ai**)



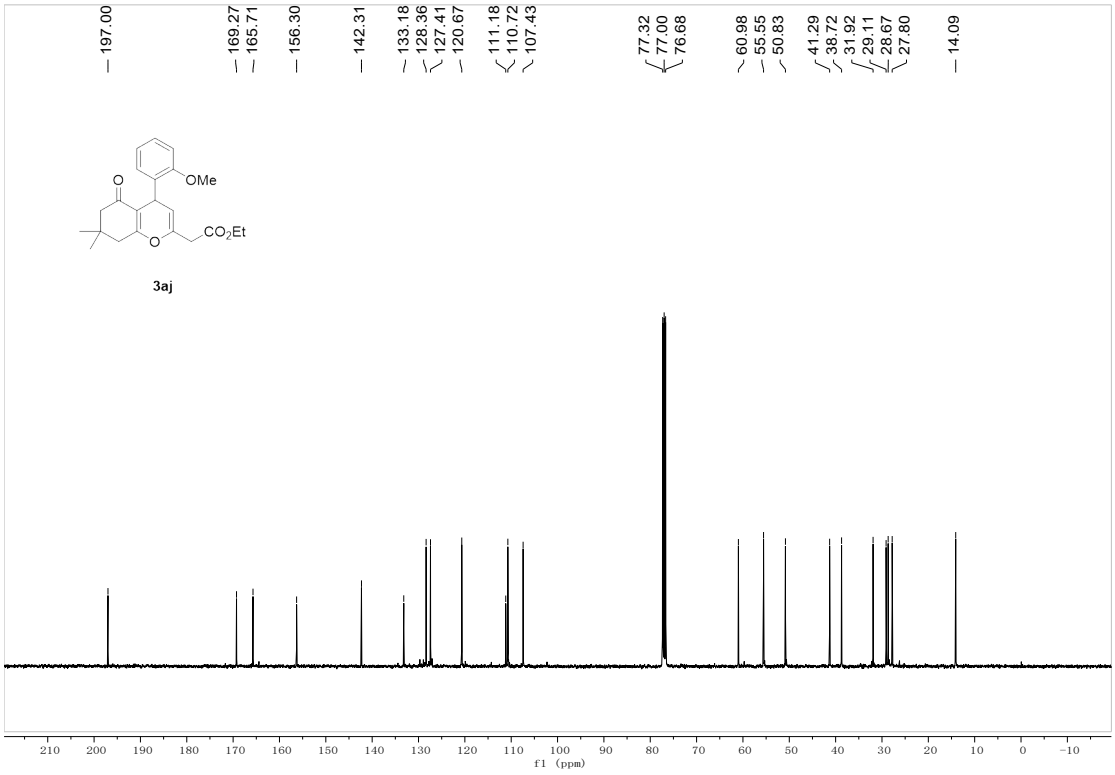
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ai**)



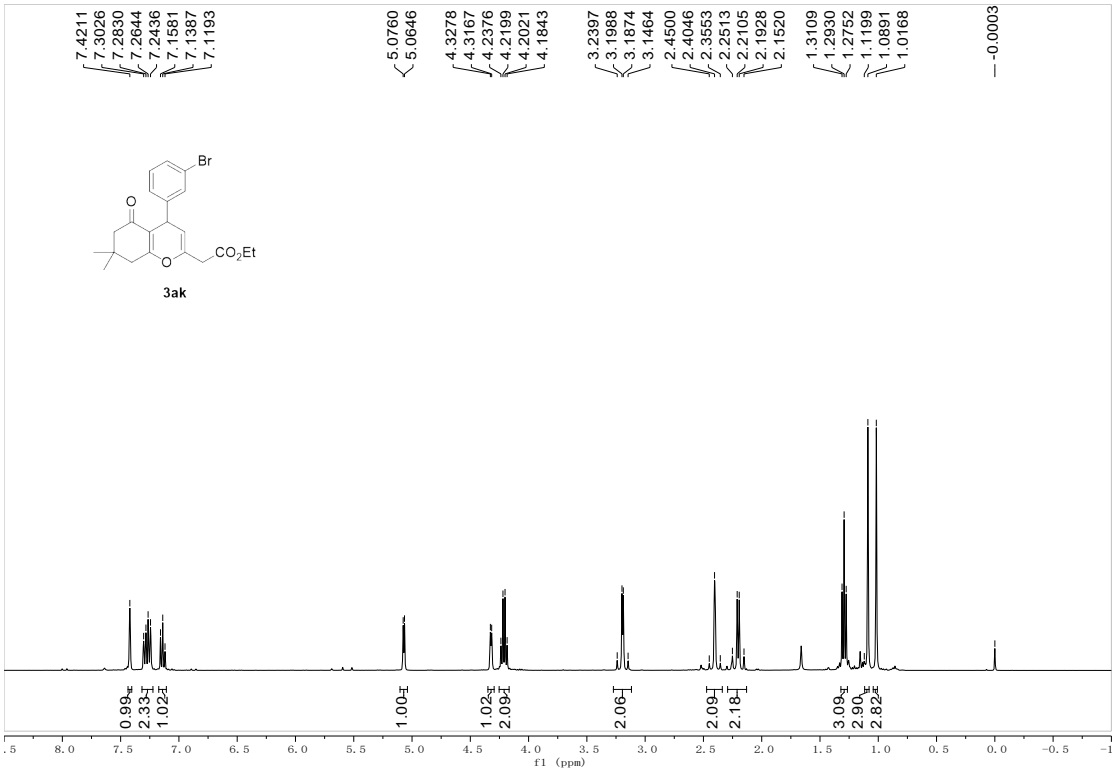
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3aj**)



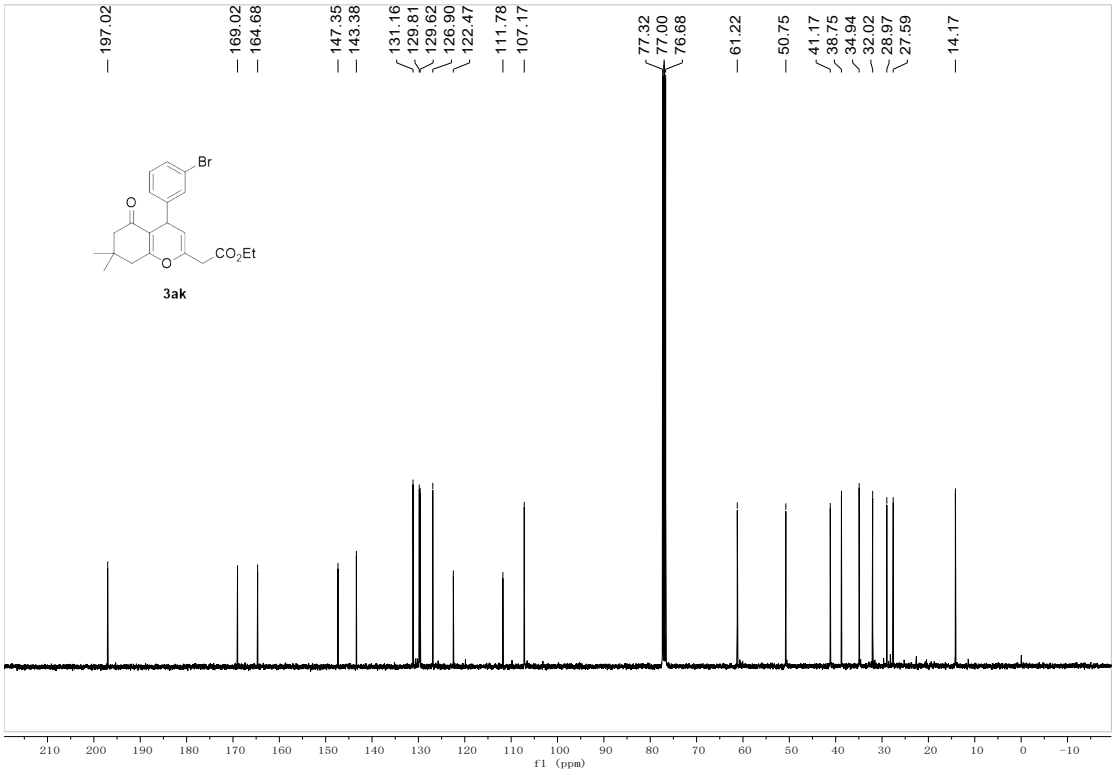
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3aj**)



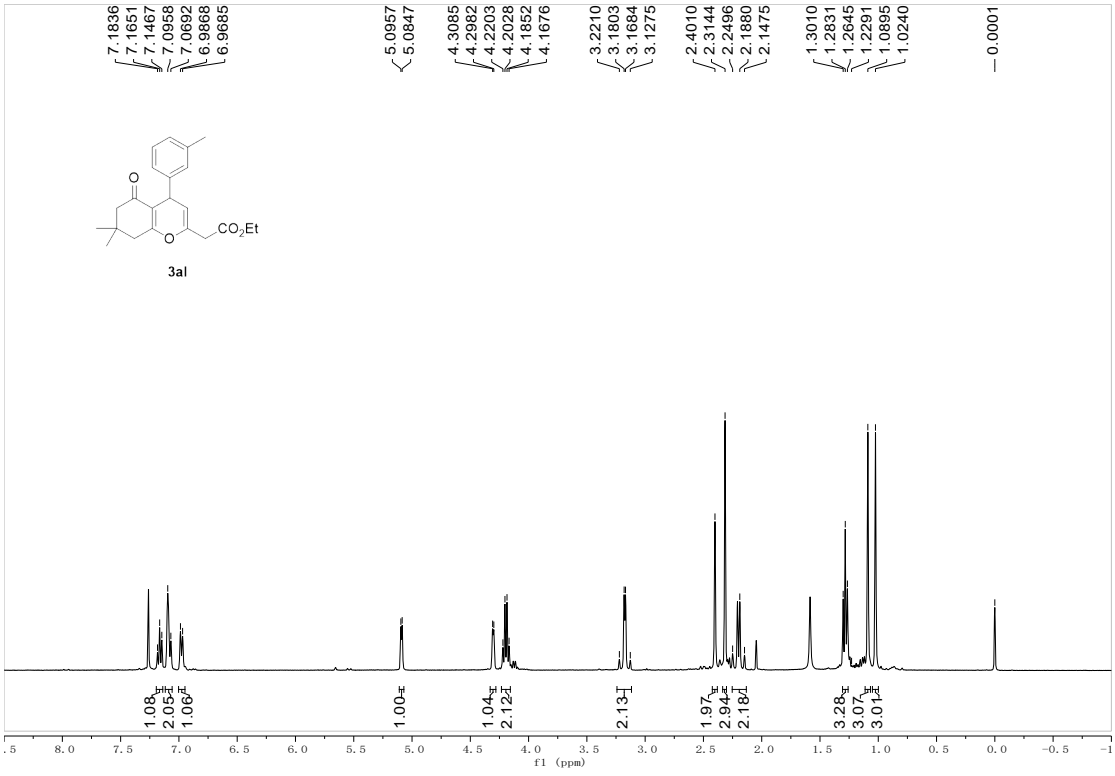
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ak**)



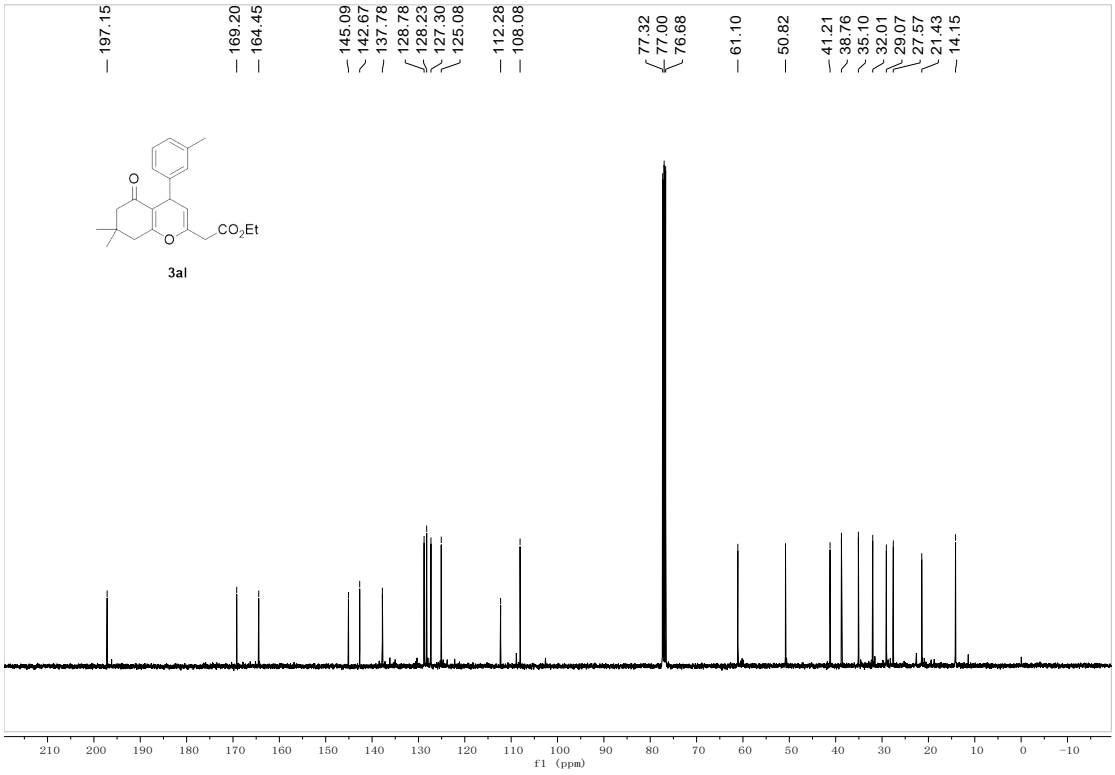
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ak**)



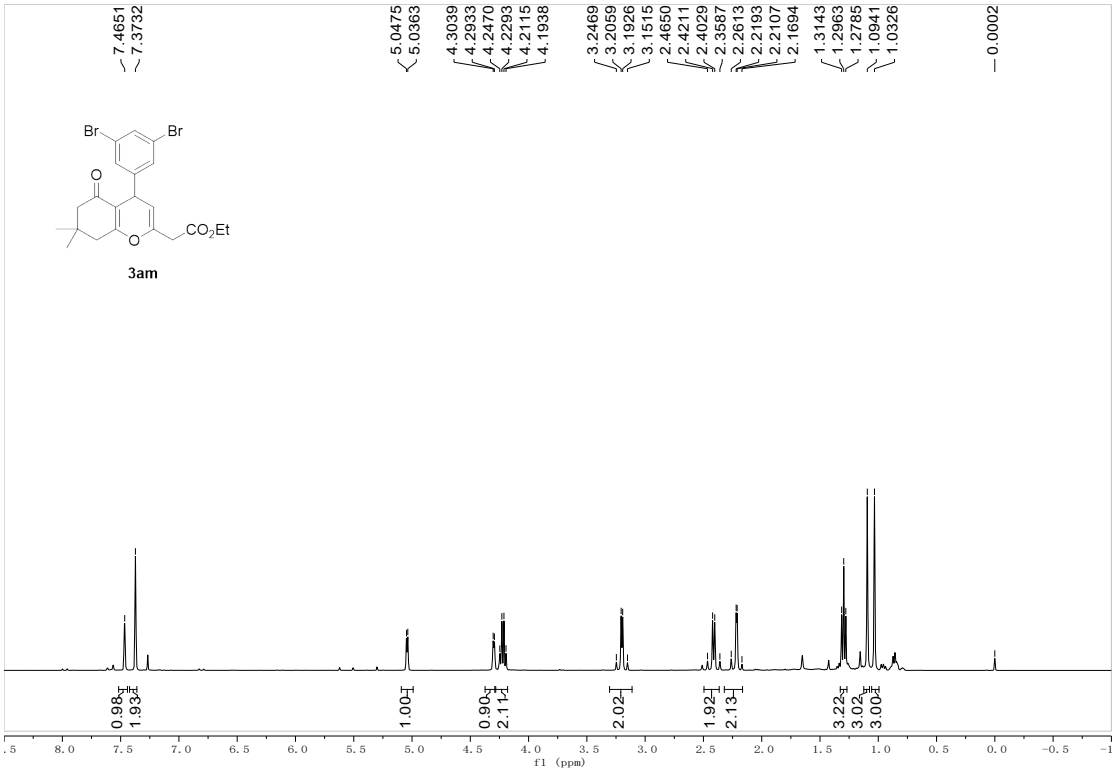
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3al**)



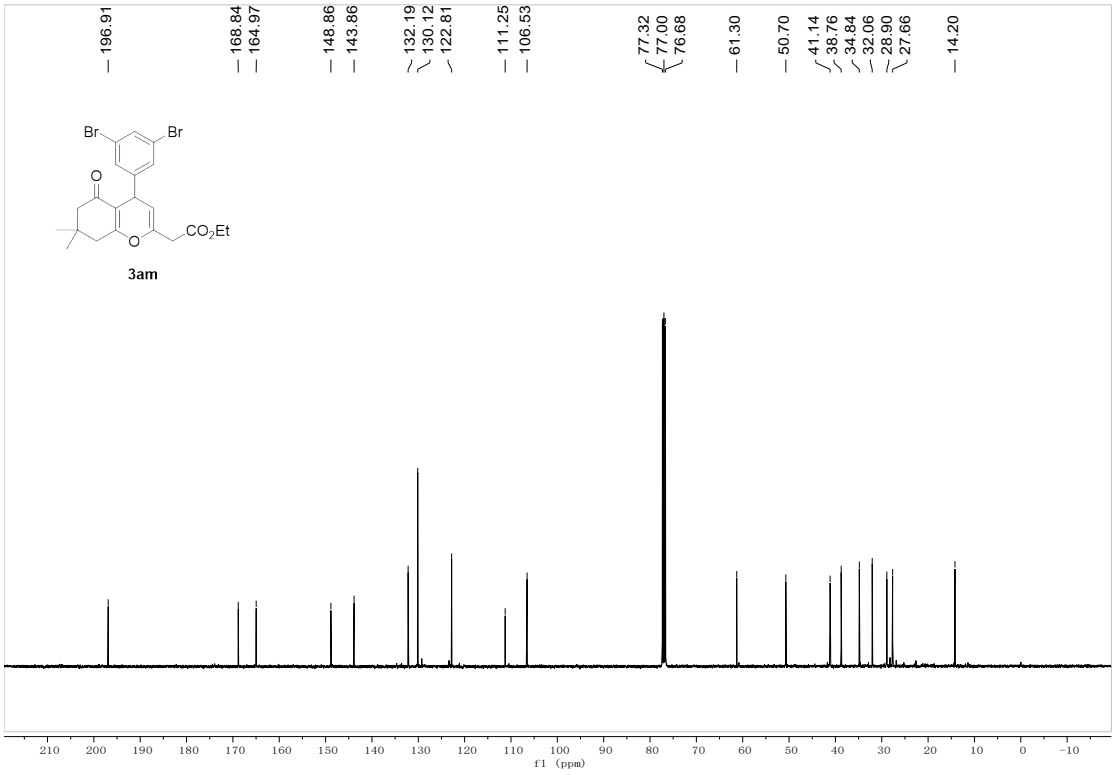
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3al**)



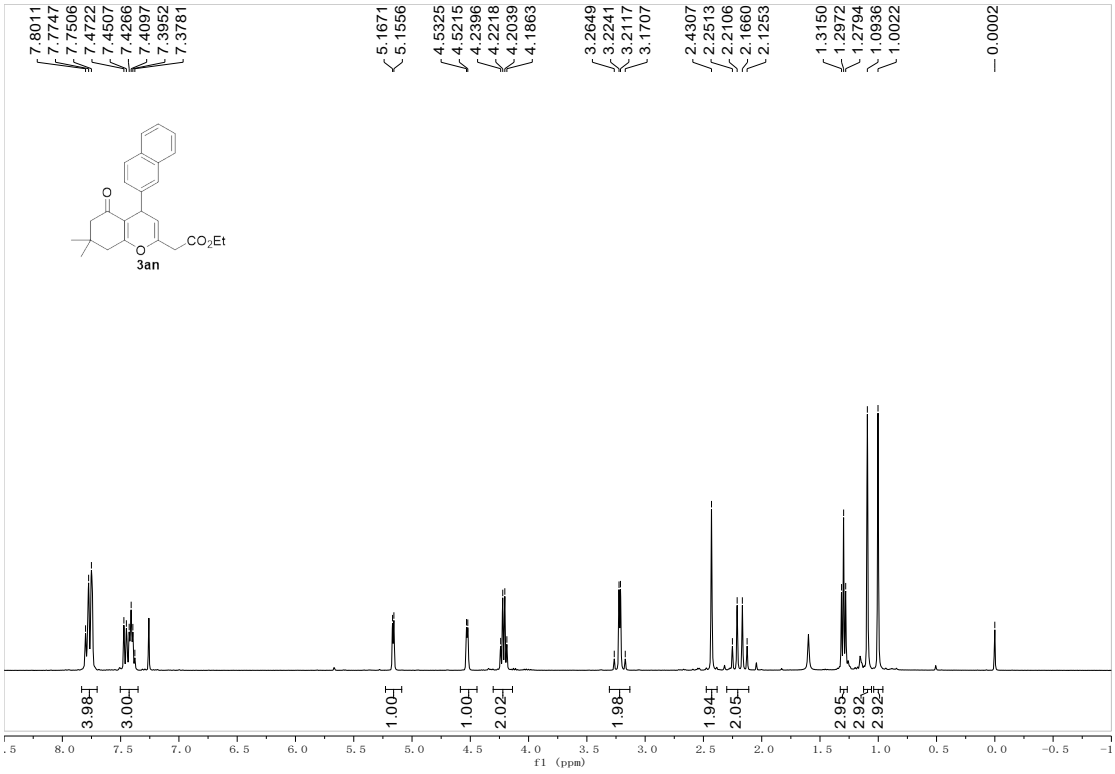
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3am**)



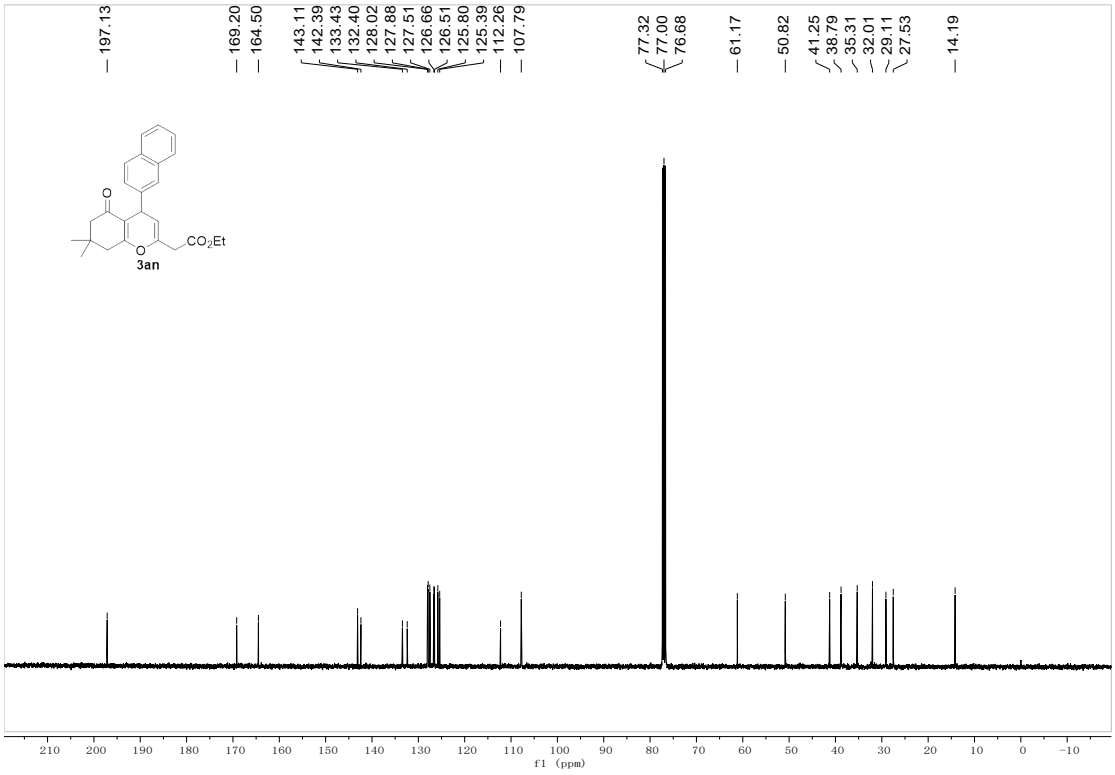
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3am**)



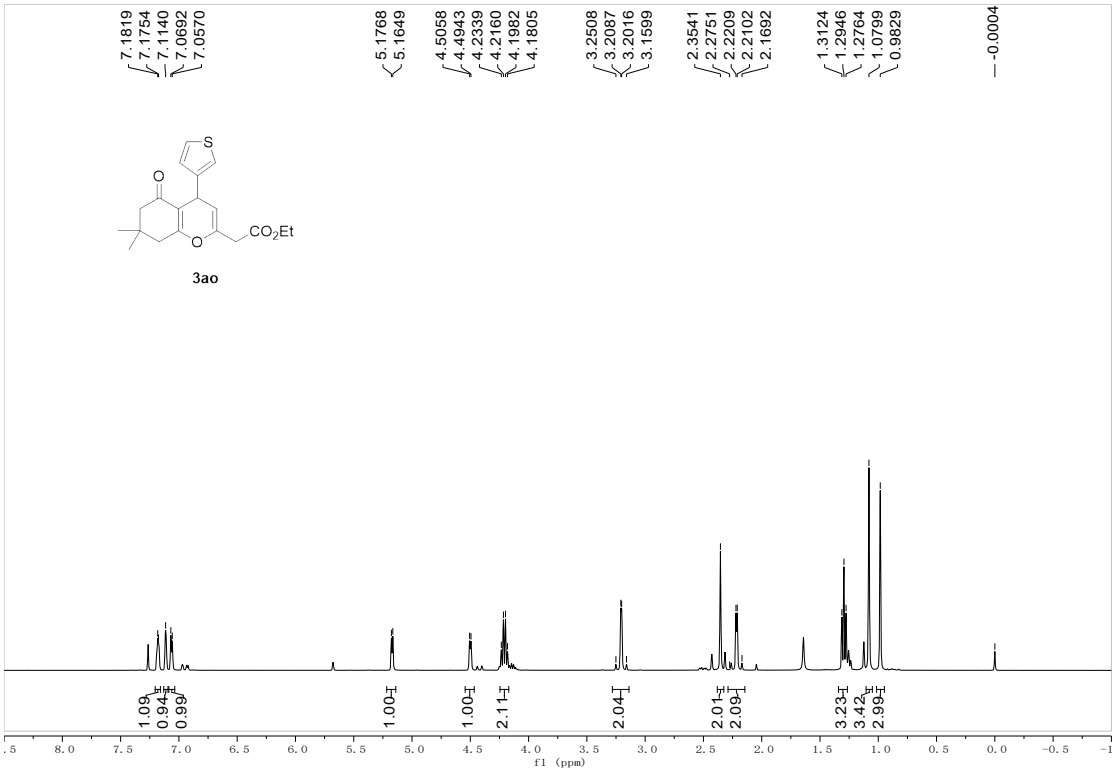
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3an**)



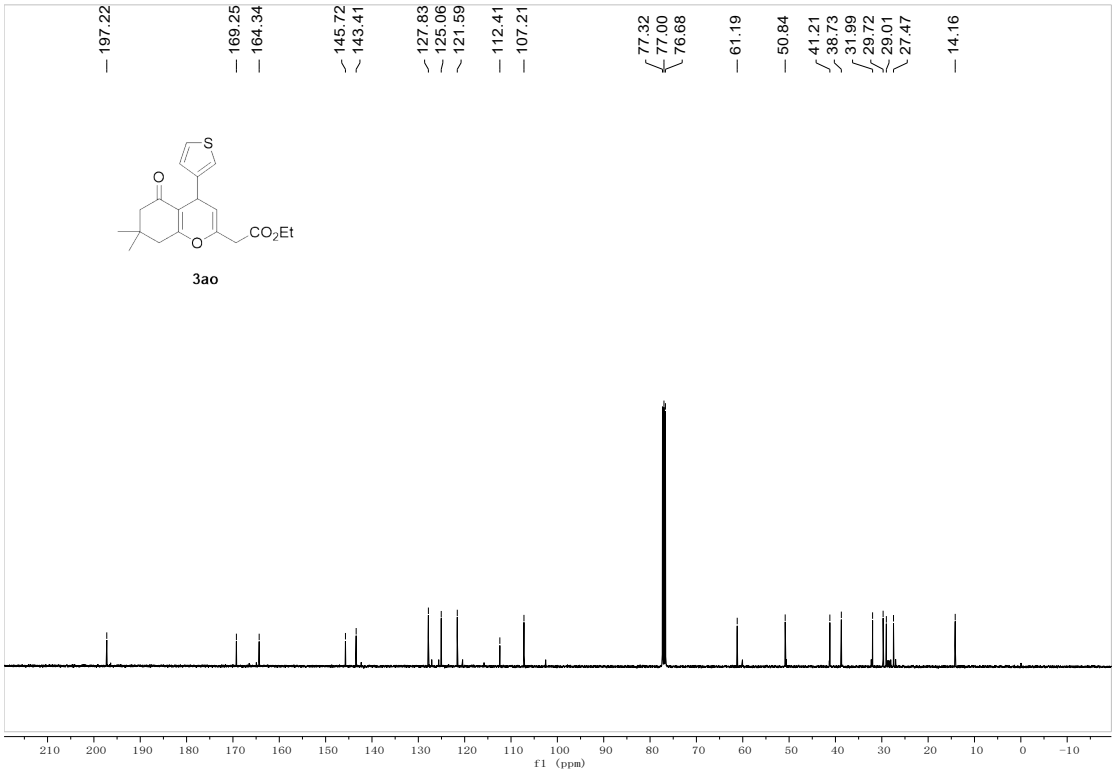
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3an**)



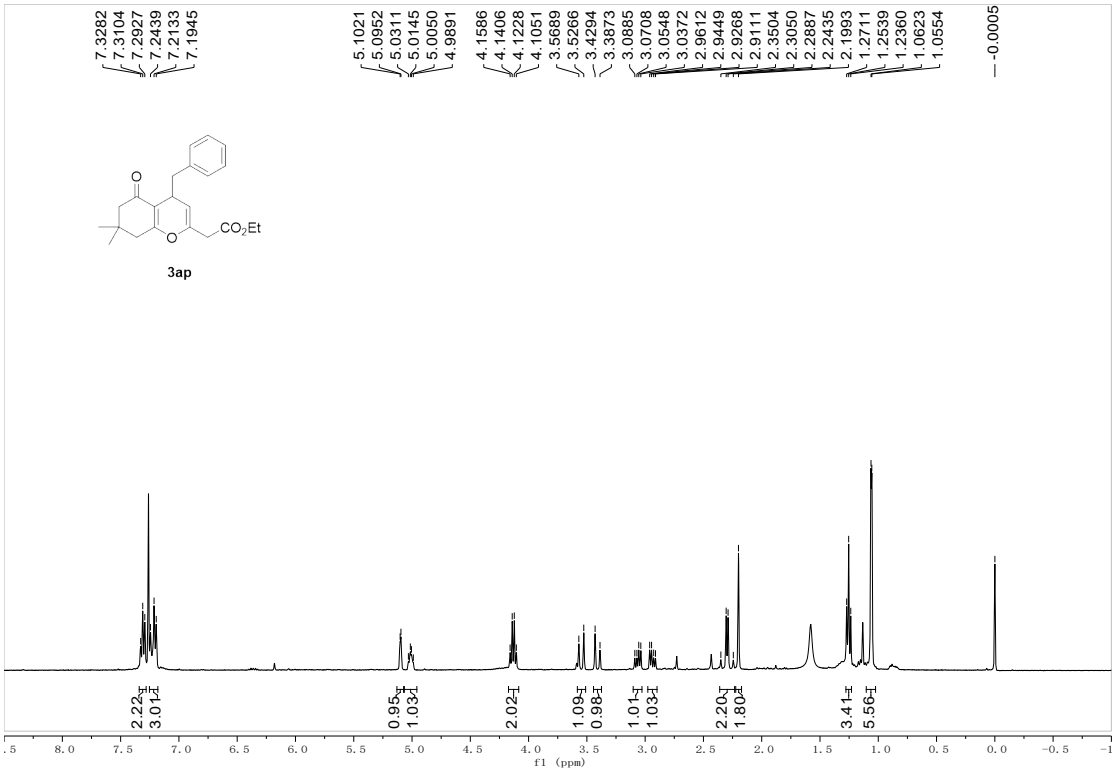
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ao**)



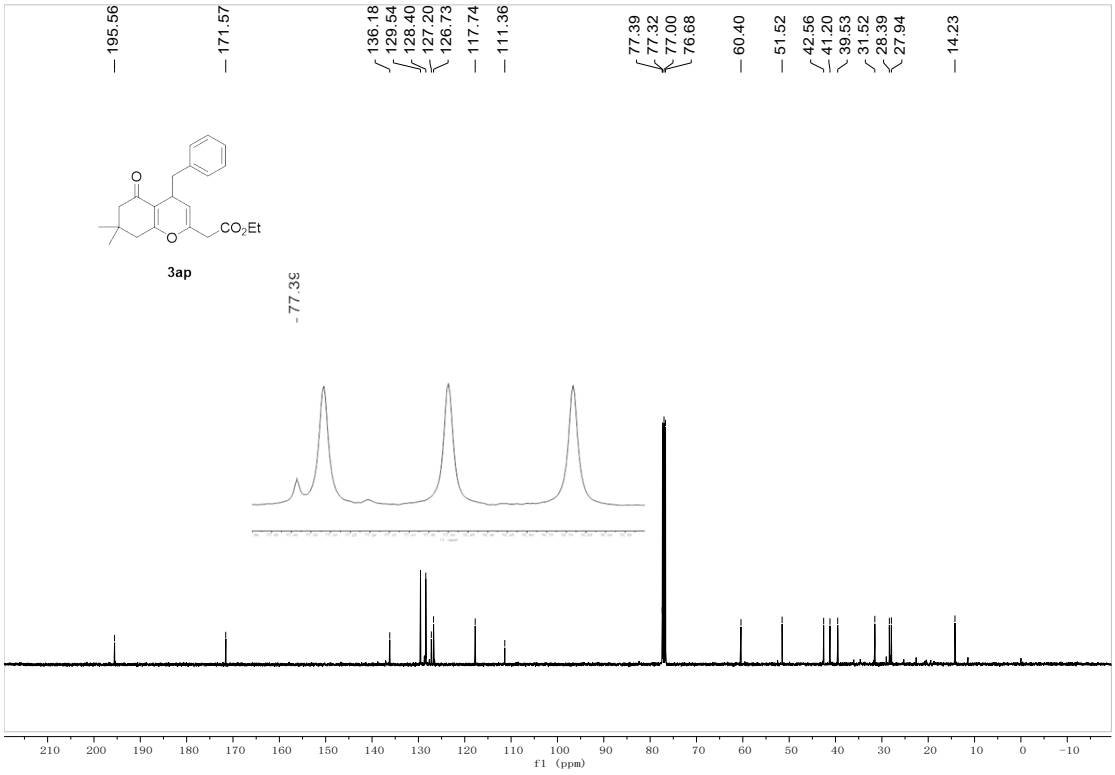
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ao**)



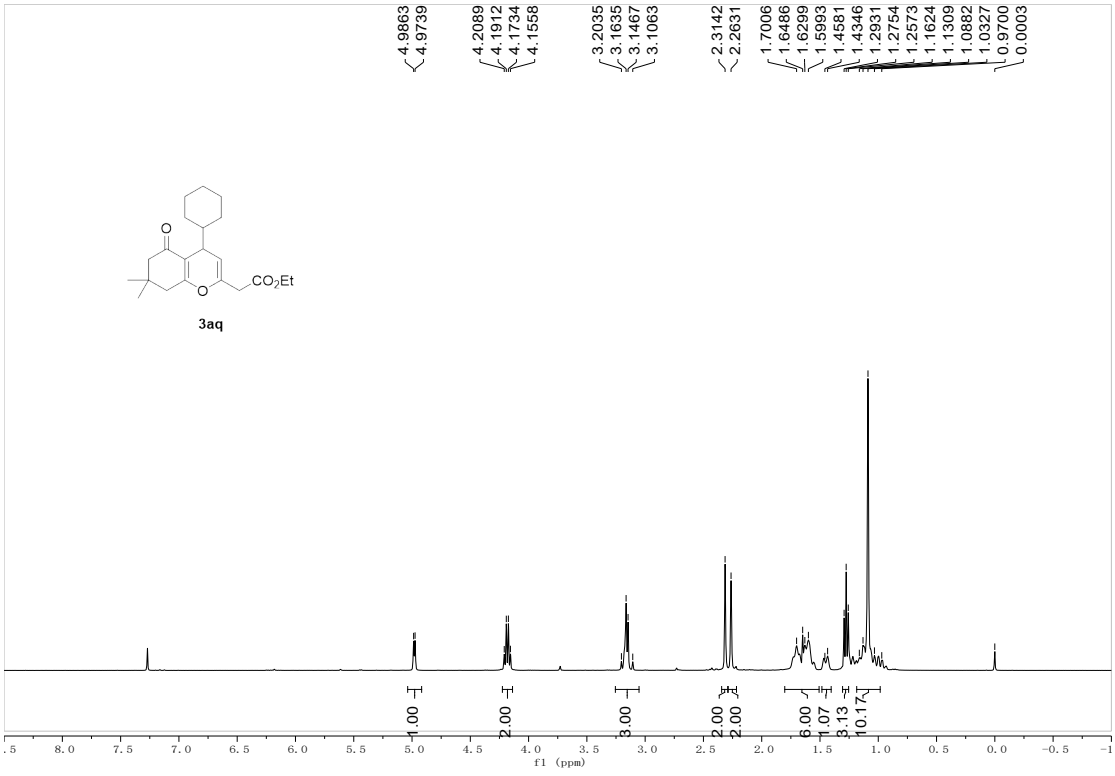
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ap**)



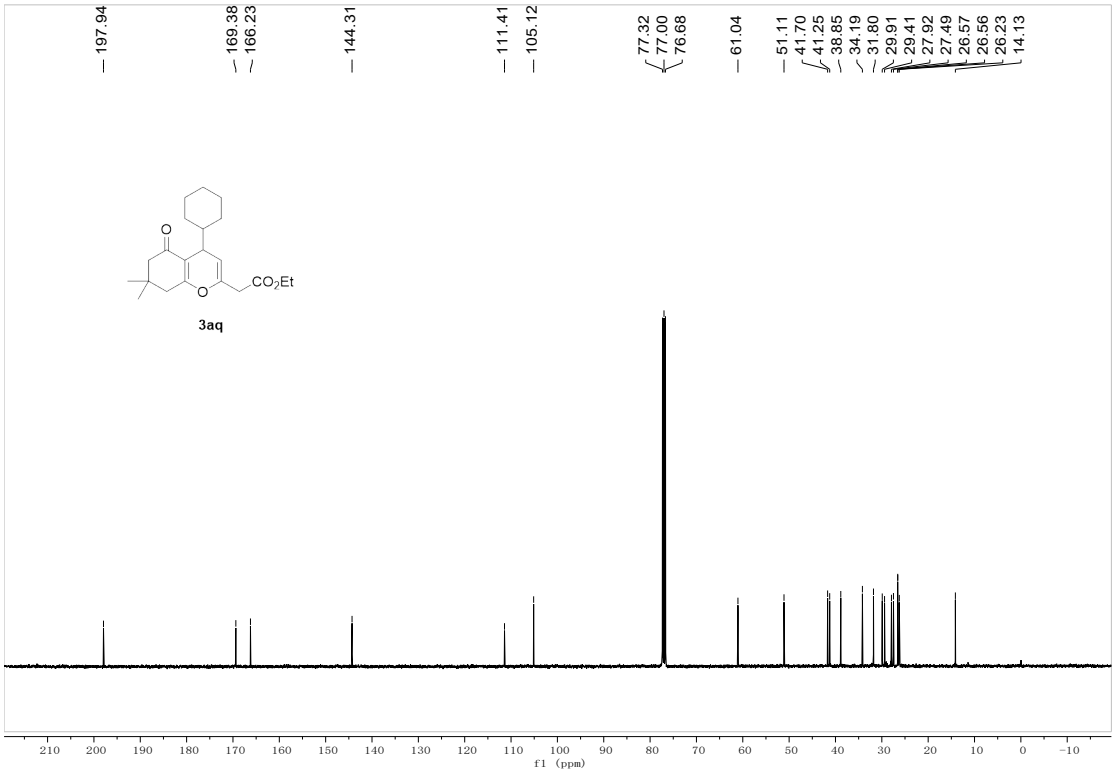
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ap**)



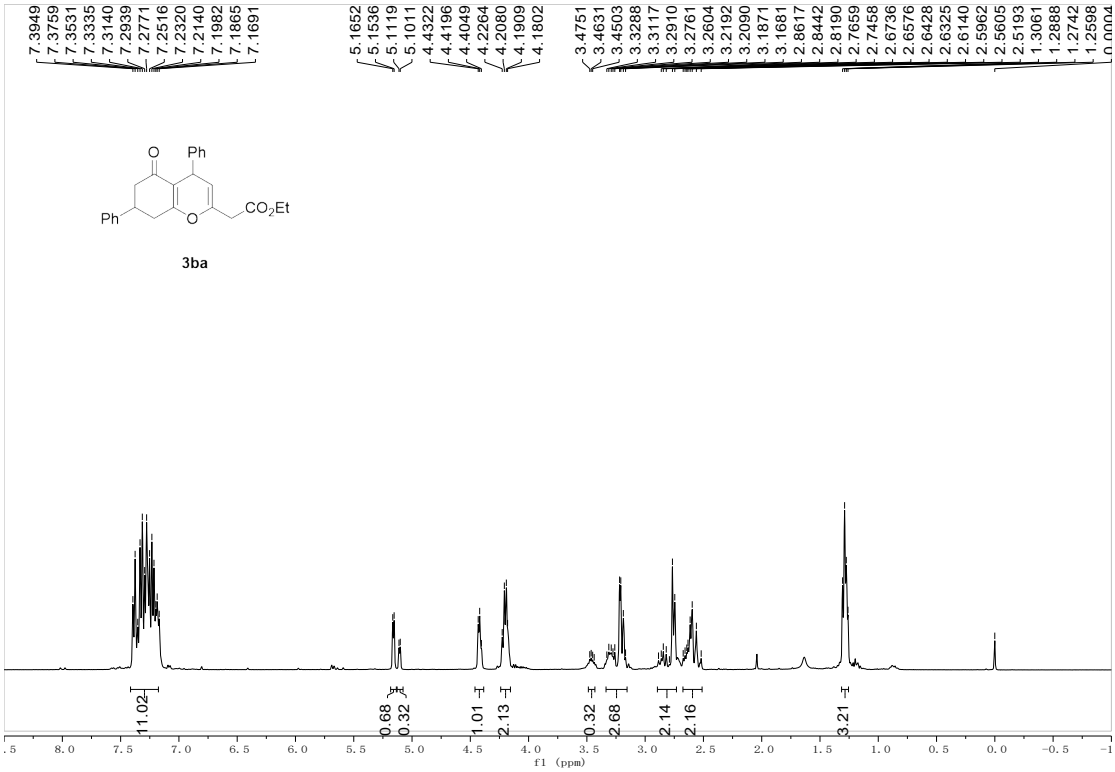
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3aq**)



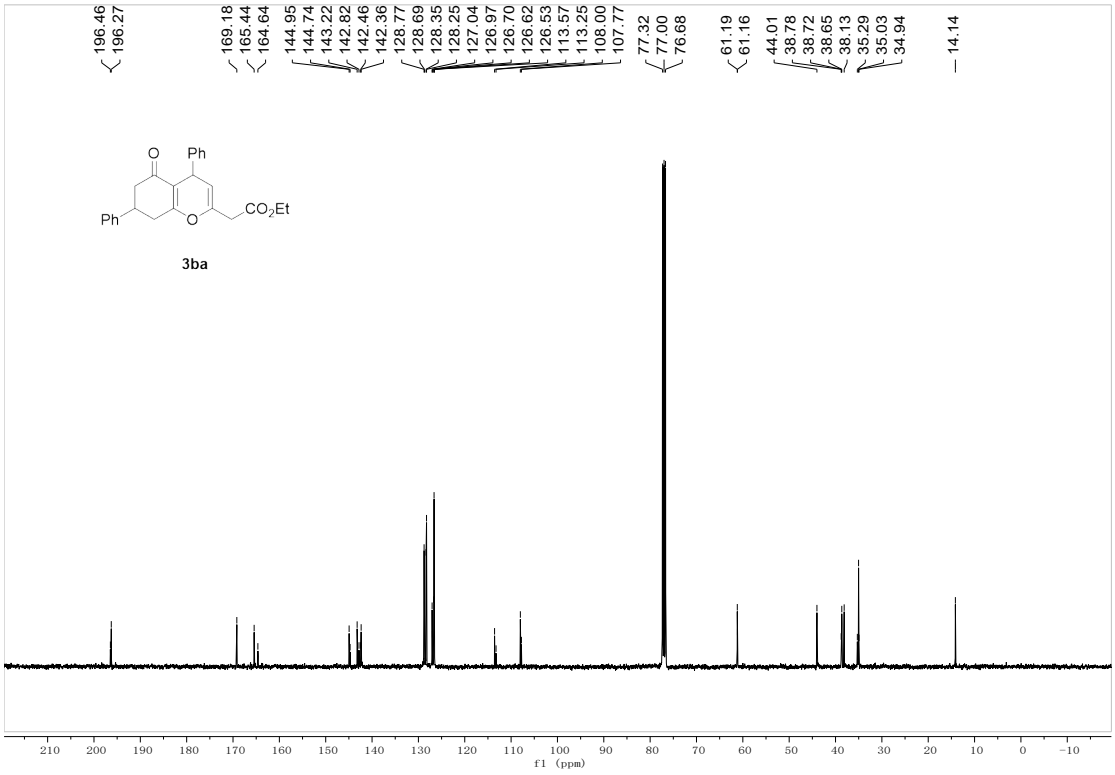
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3aq**)



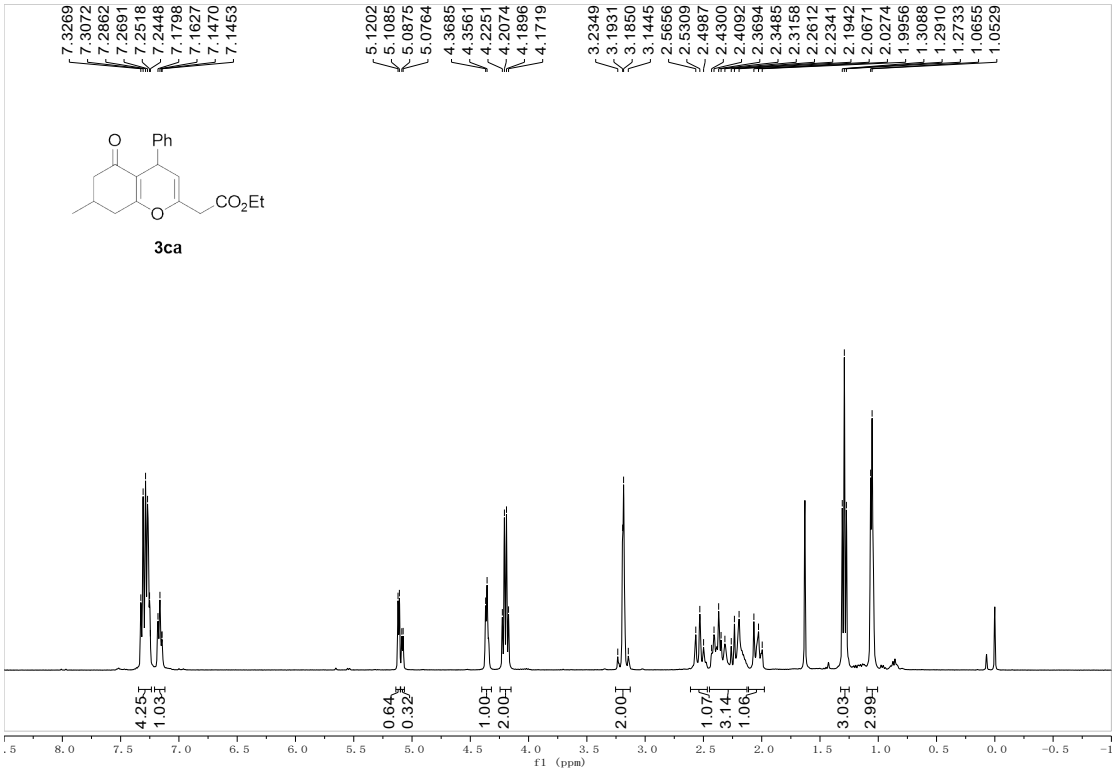
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ba**)



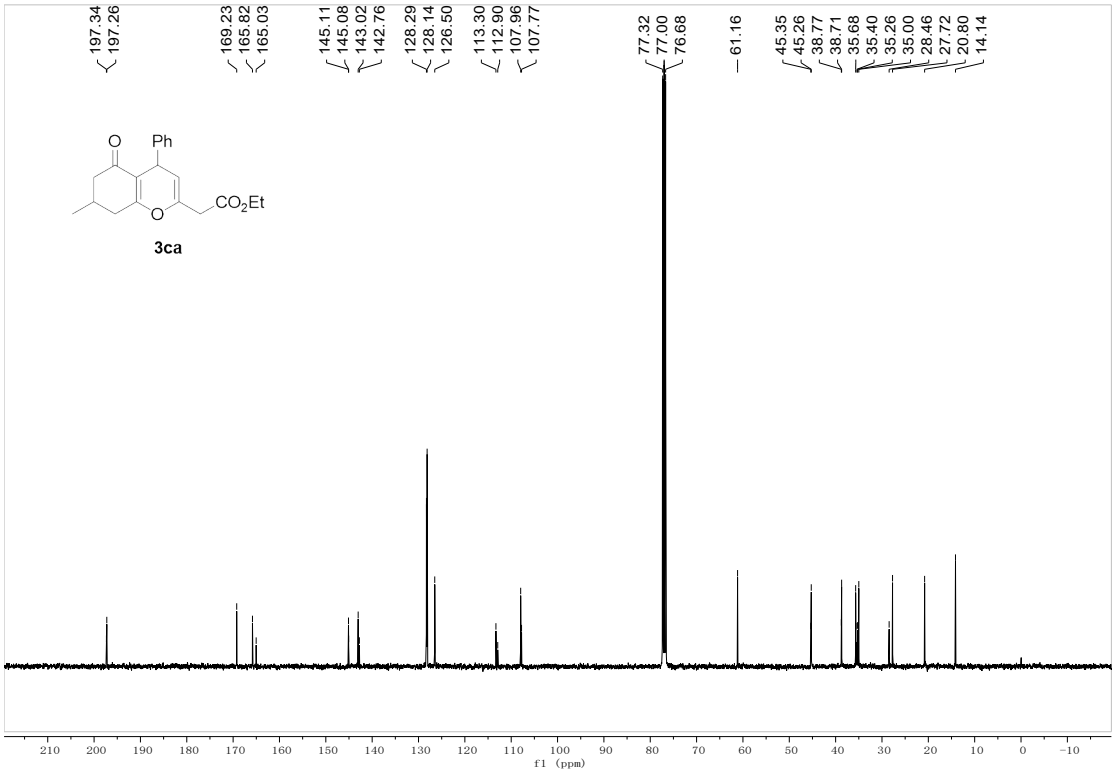
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ba**)



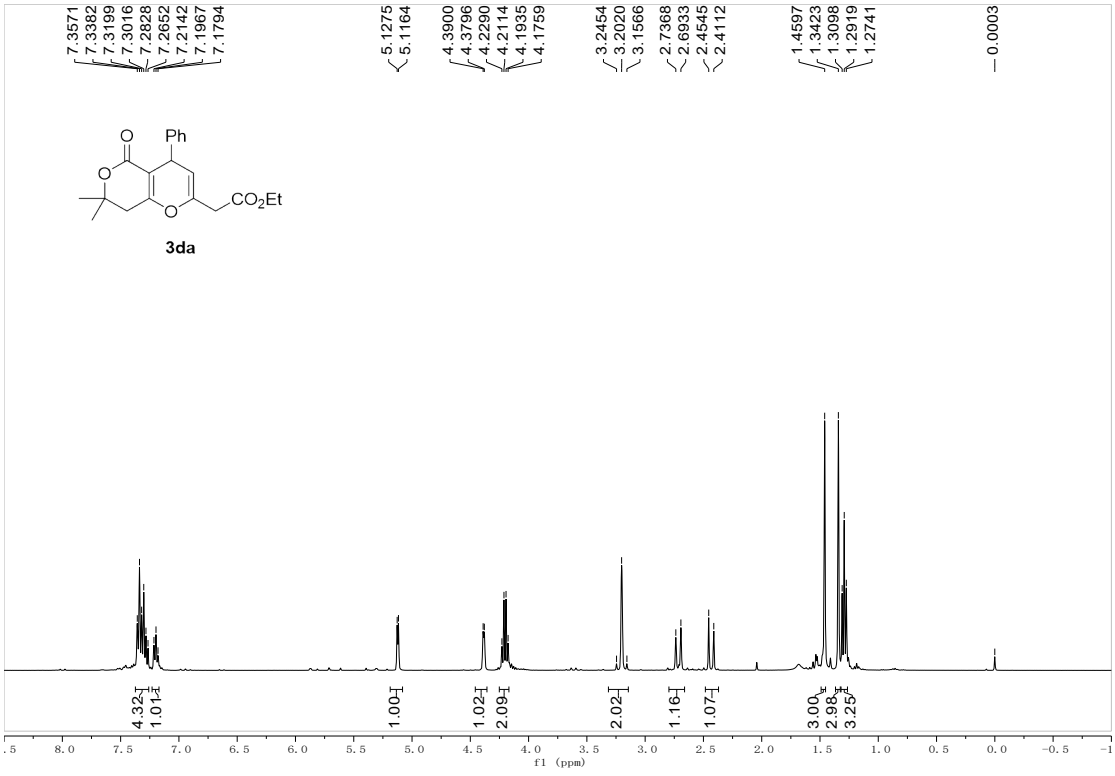
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ca**)



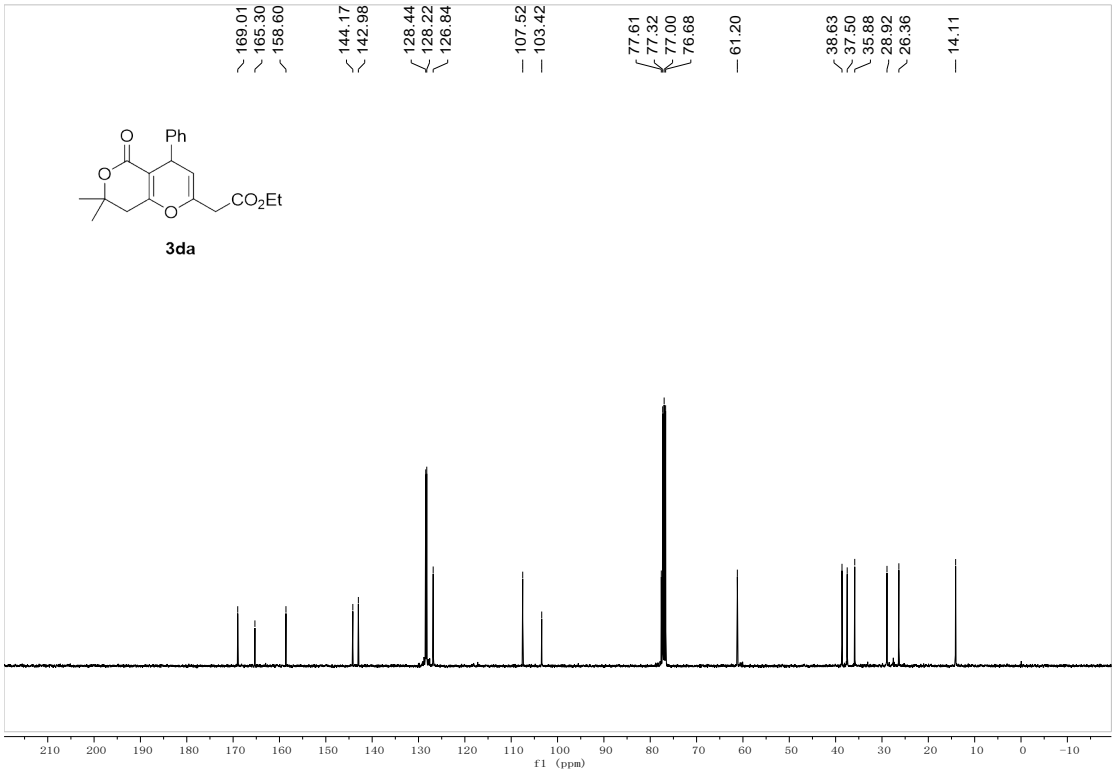
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ca**)



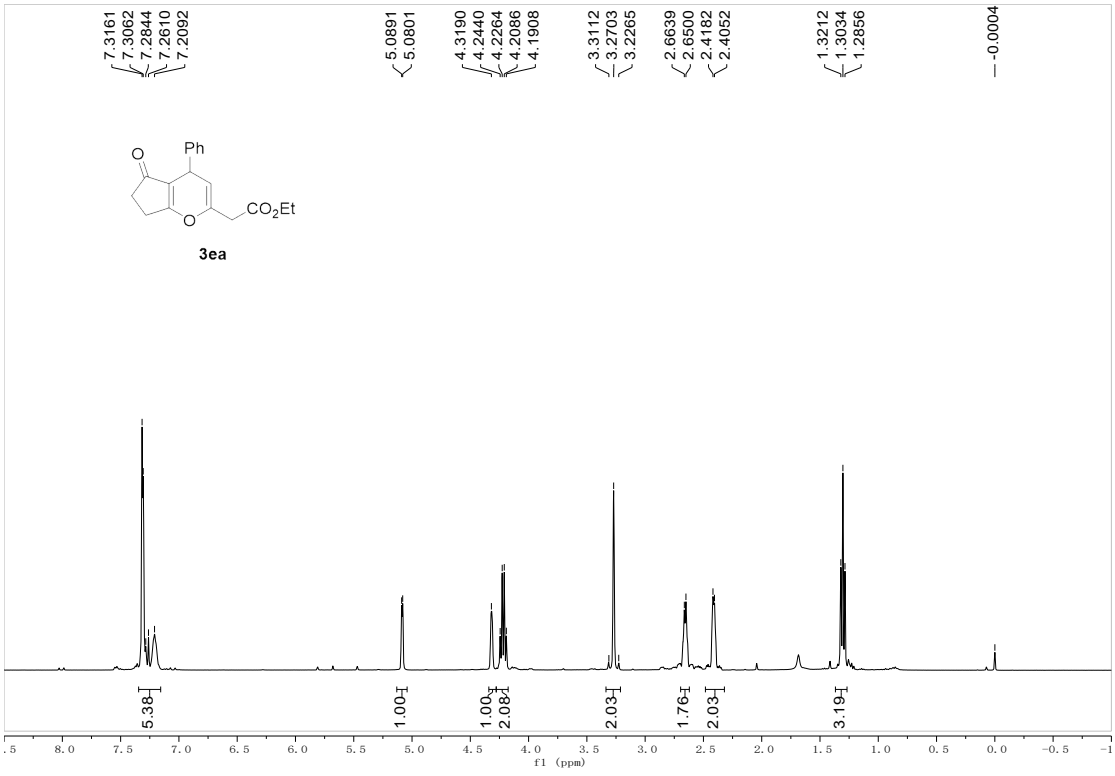
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3da**)



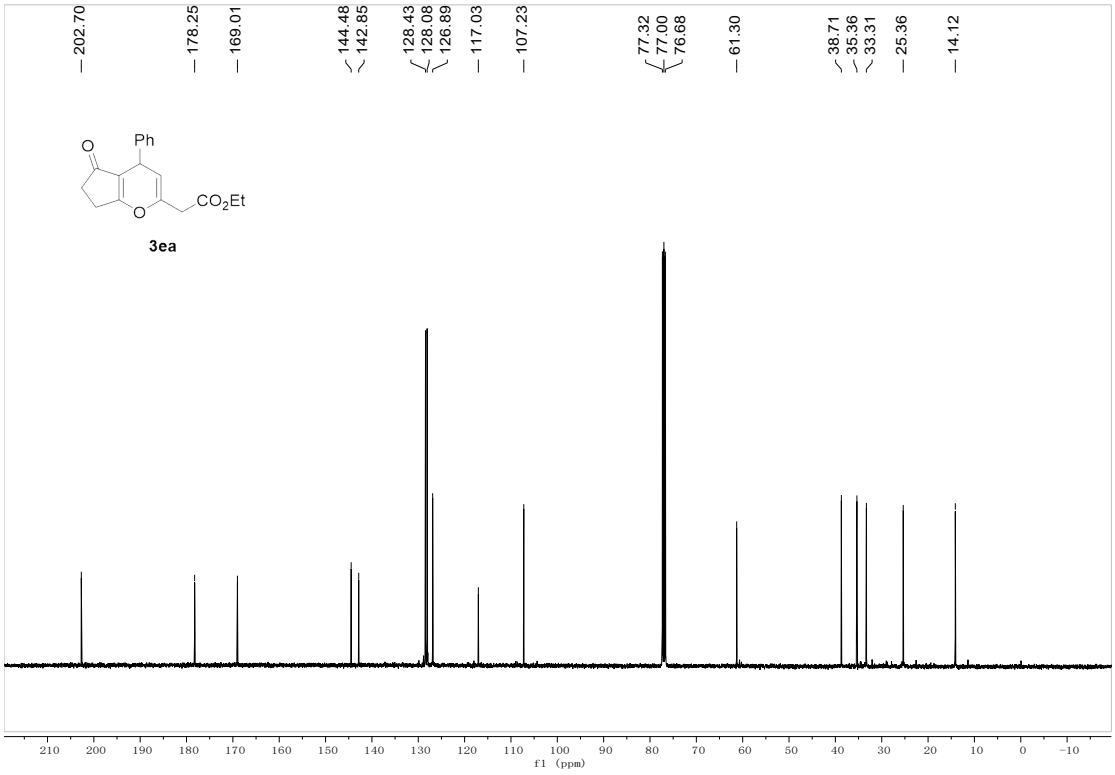
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3da**)



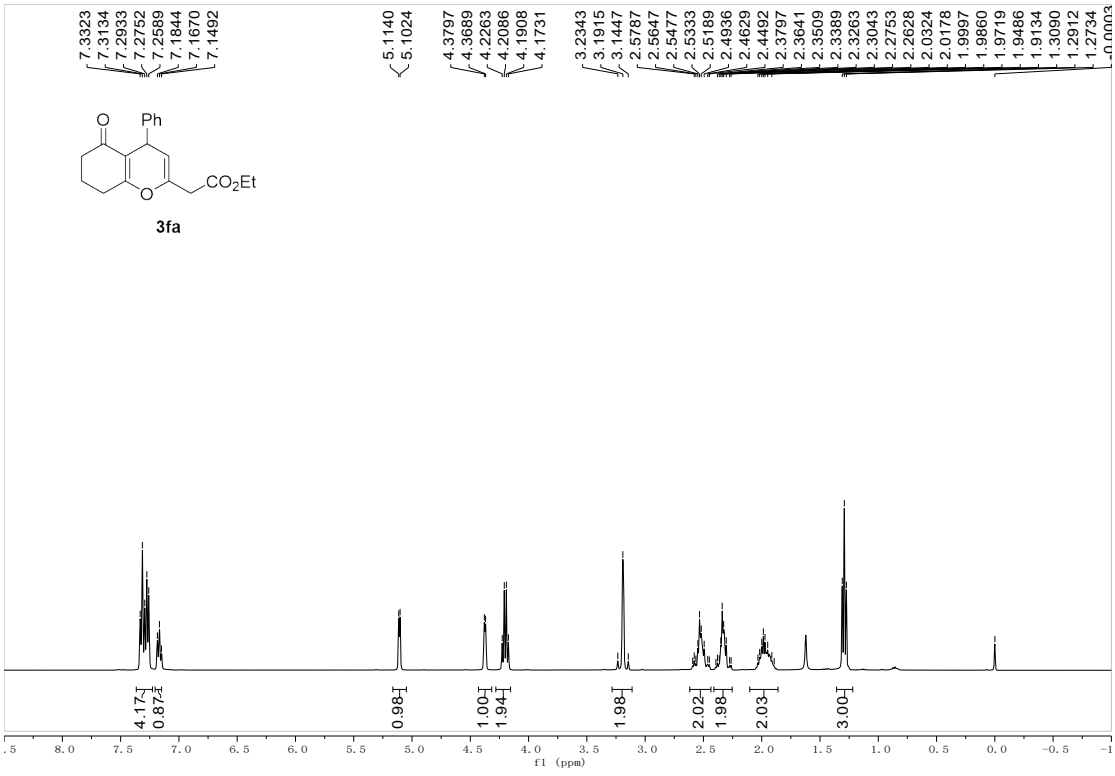
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ea**)



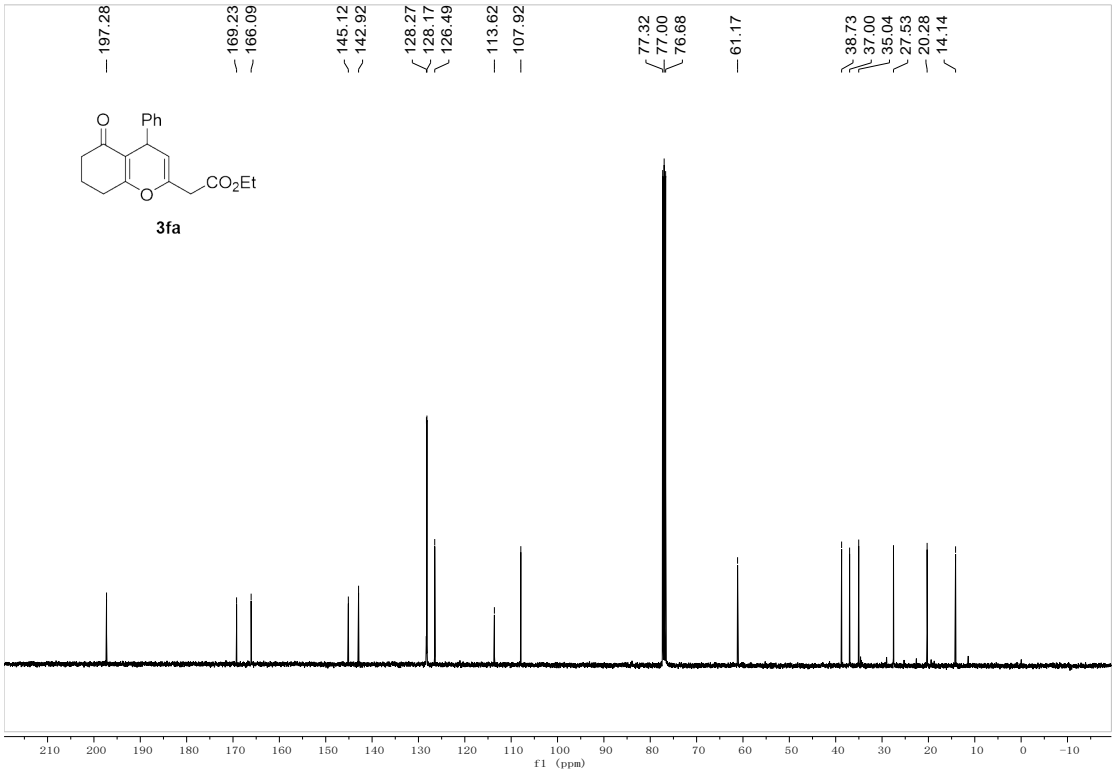
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ea**)



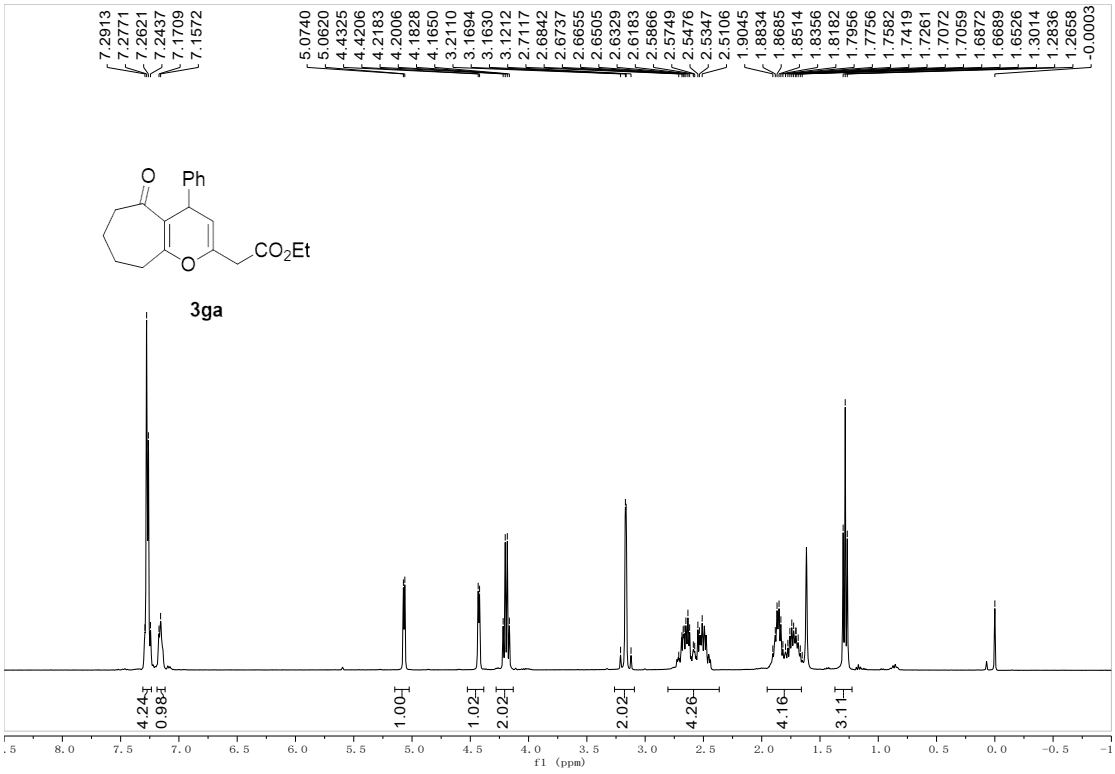
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3fa**)



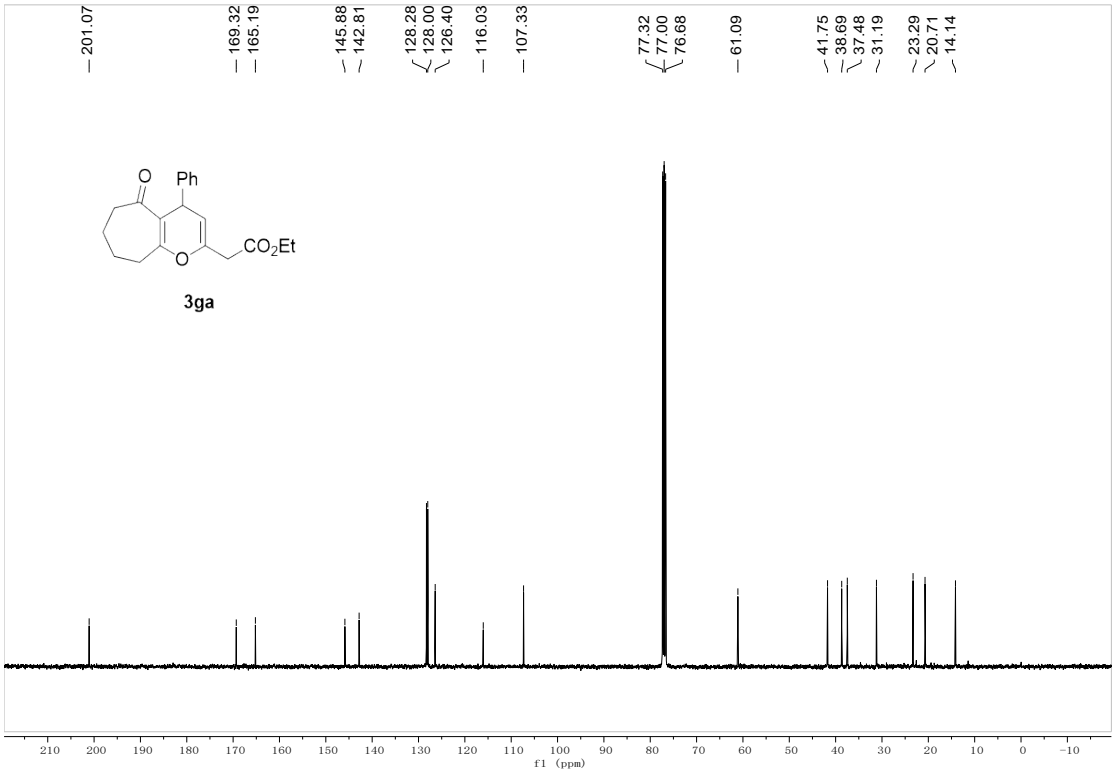
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3fa**)



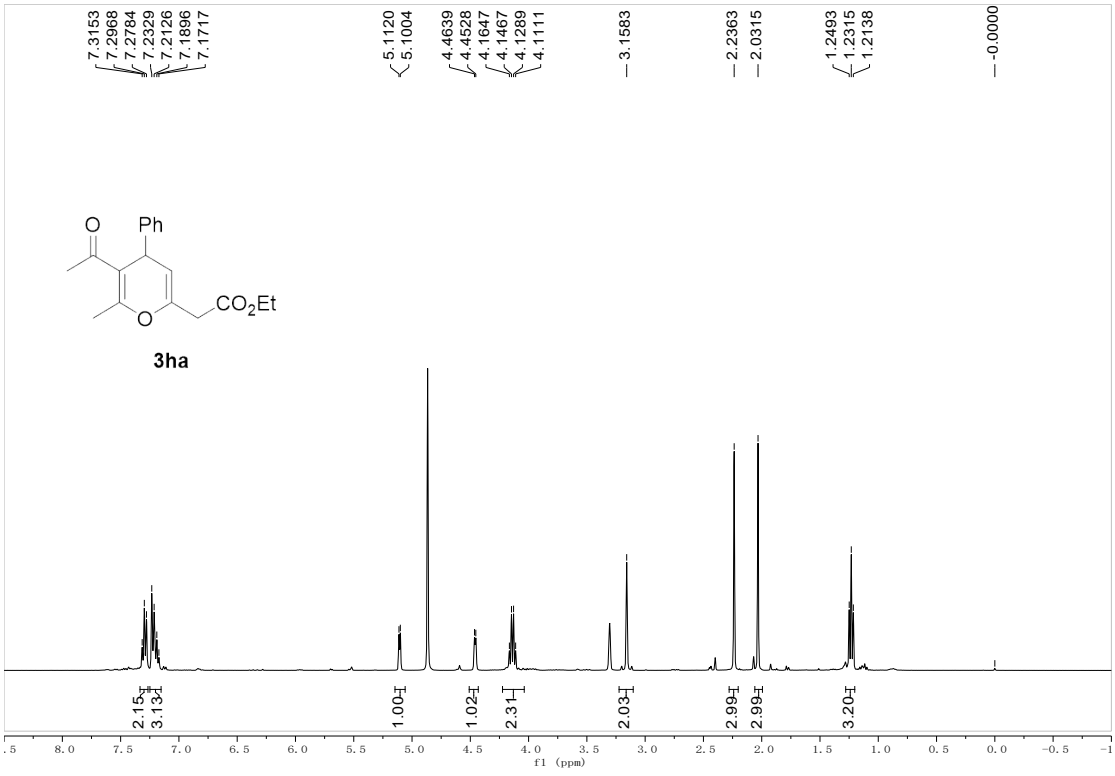
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (**3ga**)



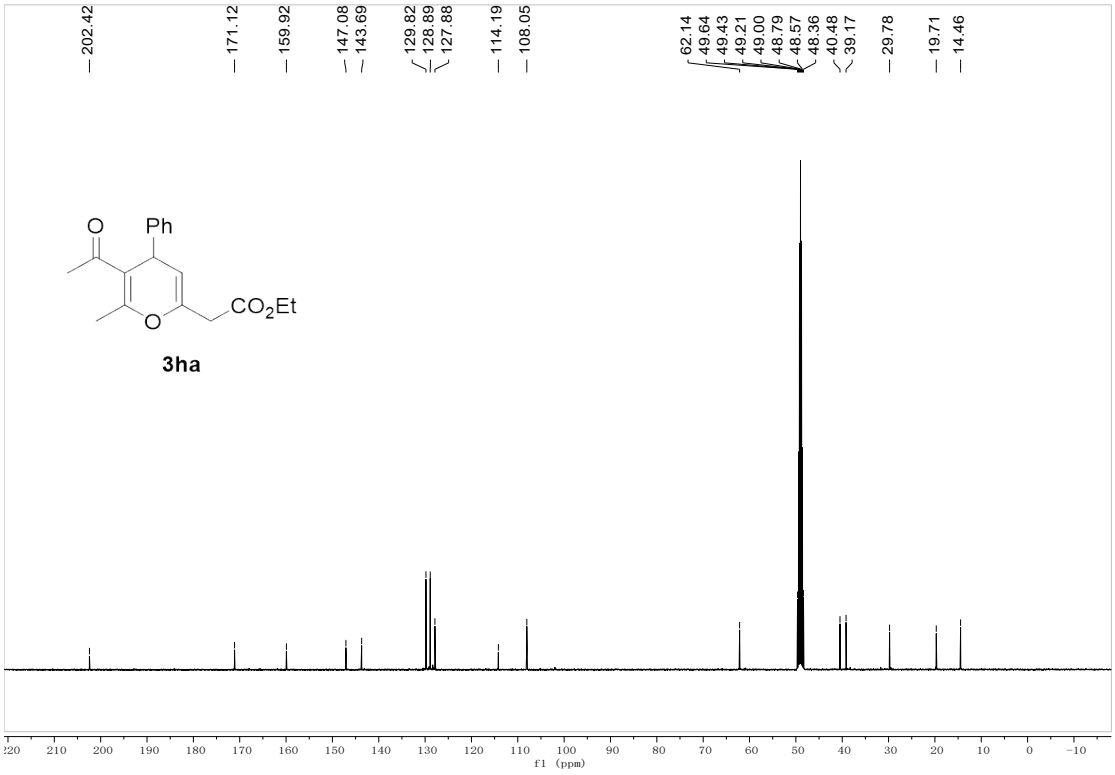
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound (**3ga**)



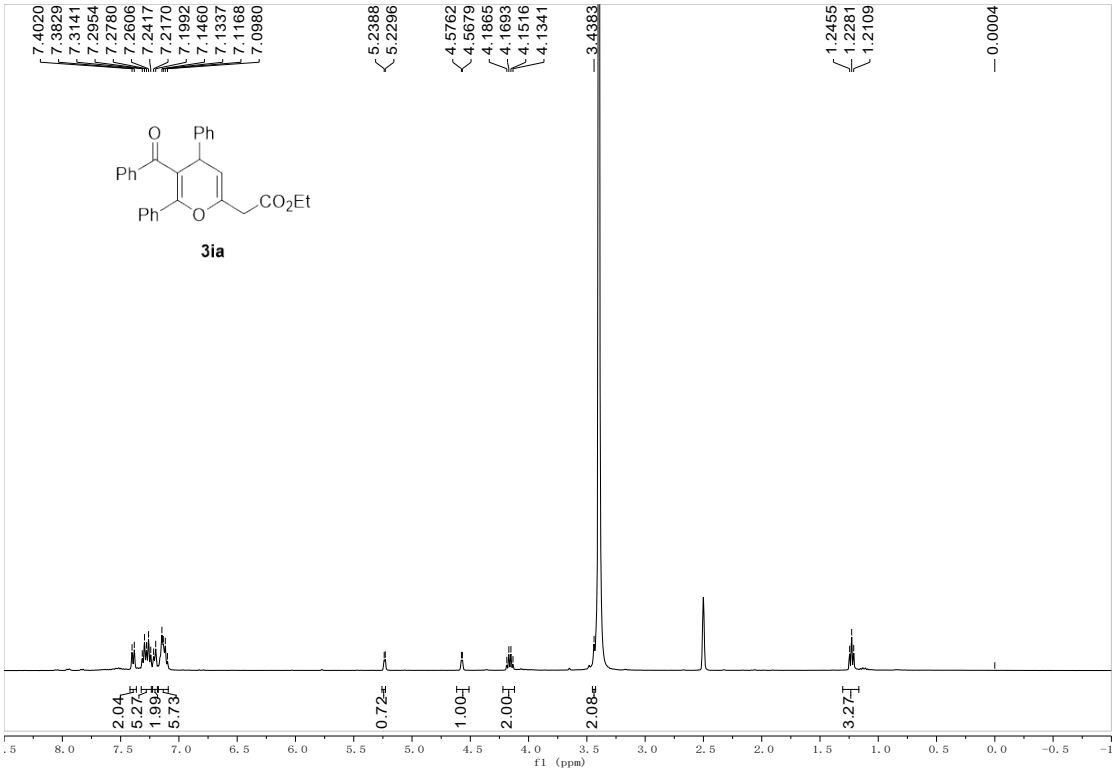
^{1}H NMR (400 MHz, CD_3OD) Spectrum of Compound (**3ha**)



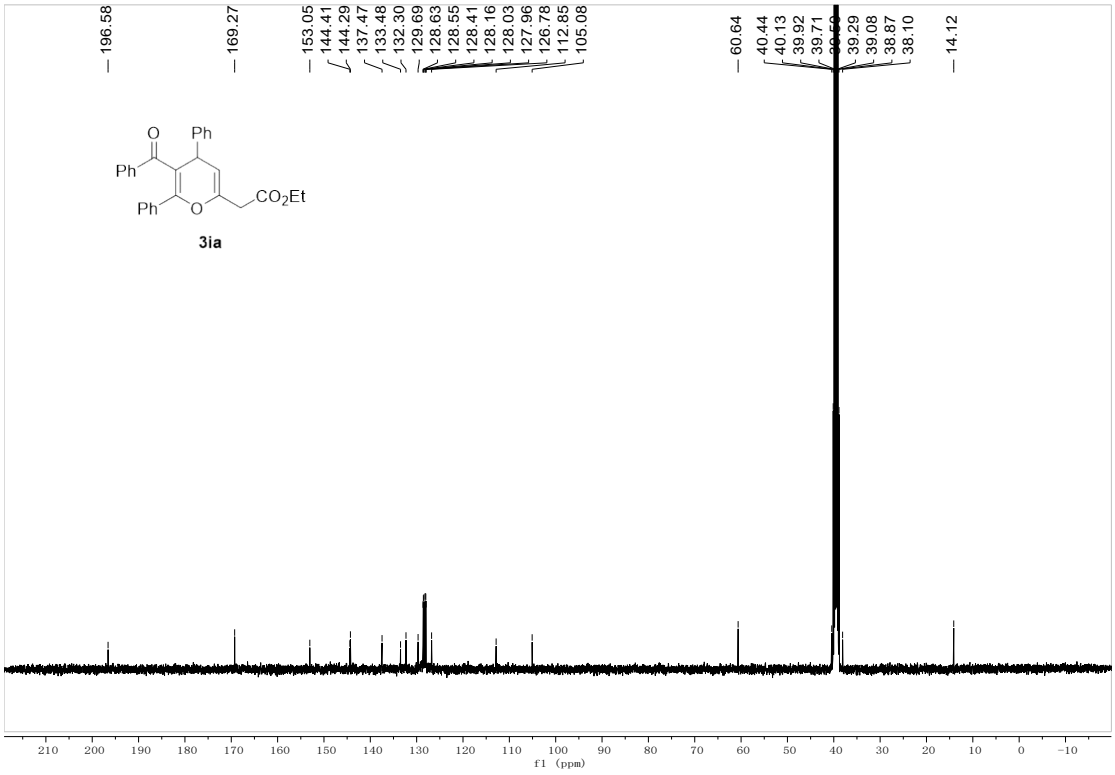
^{13}C NMR (100 MHz, CD_3OD) Spectrum of Compound (**3ha**)



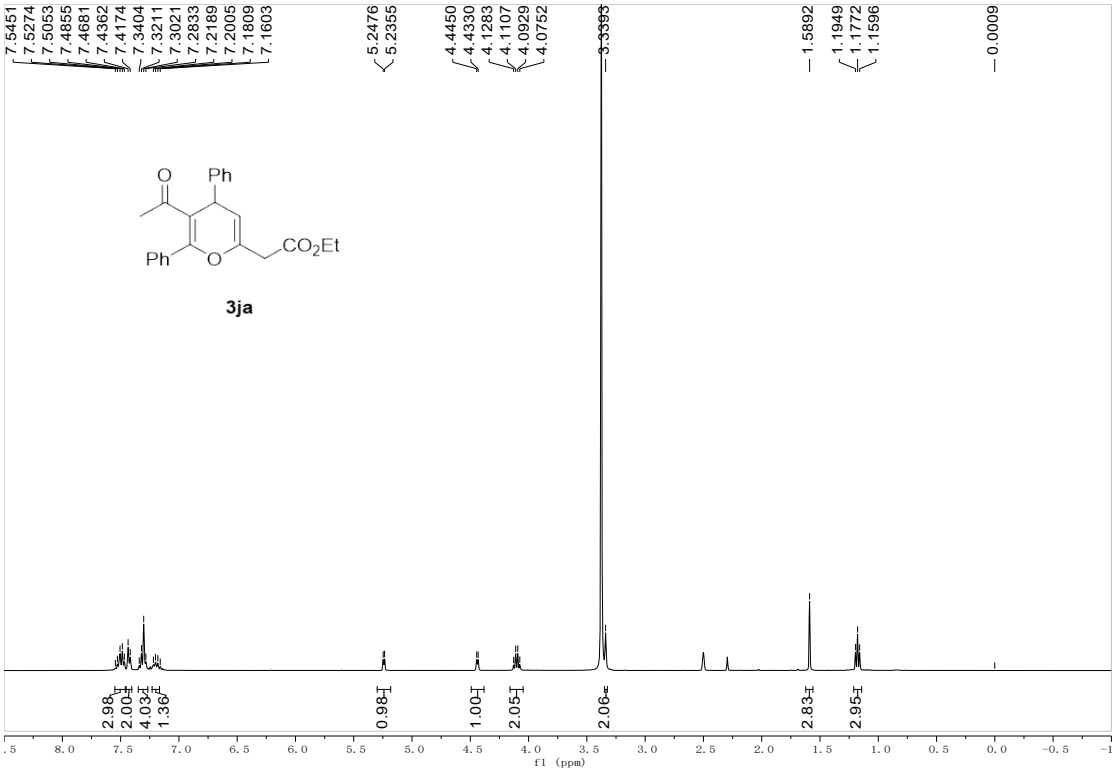
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of Compound (**3ia**)



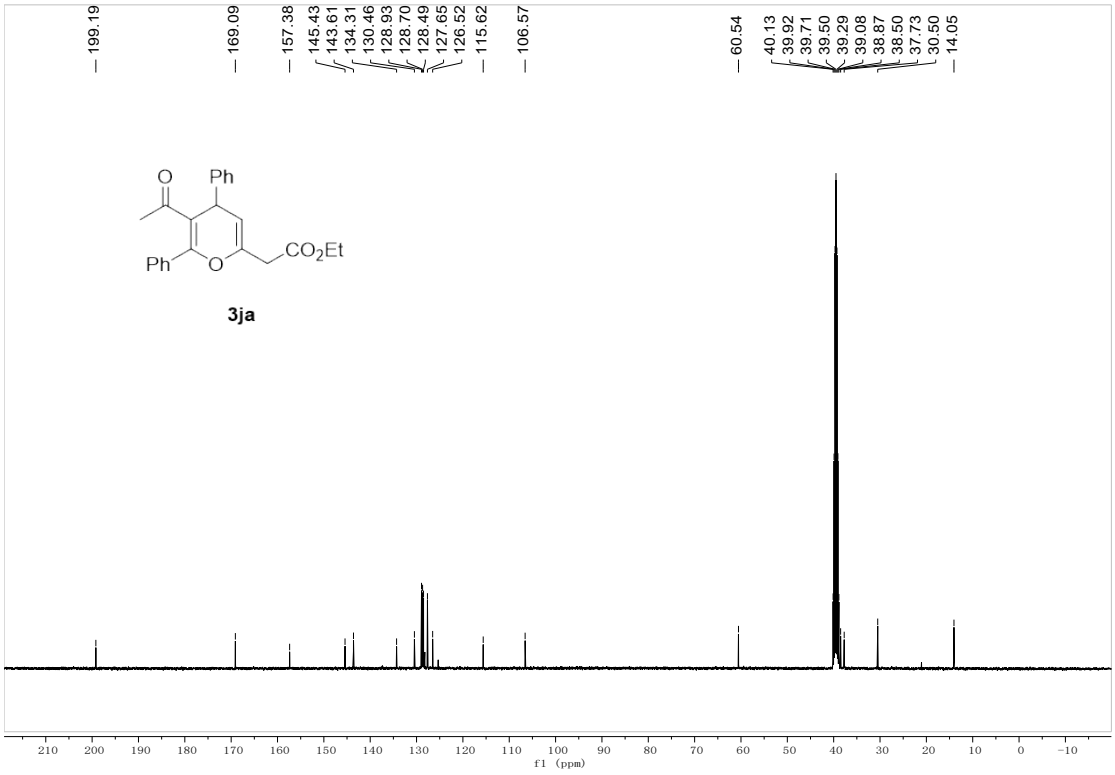
^{13}C NMR (100 MHz, DMSO-d_6) Spectrum of Compound (**3ia**)



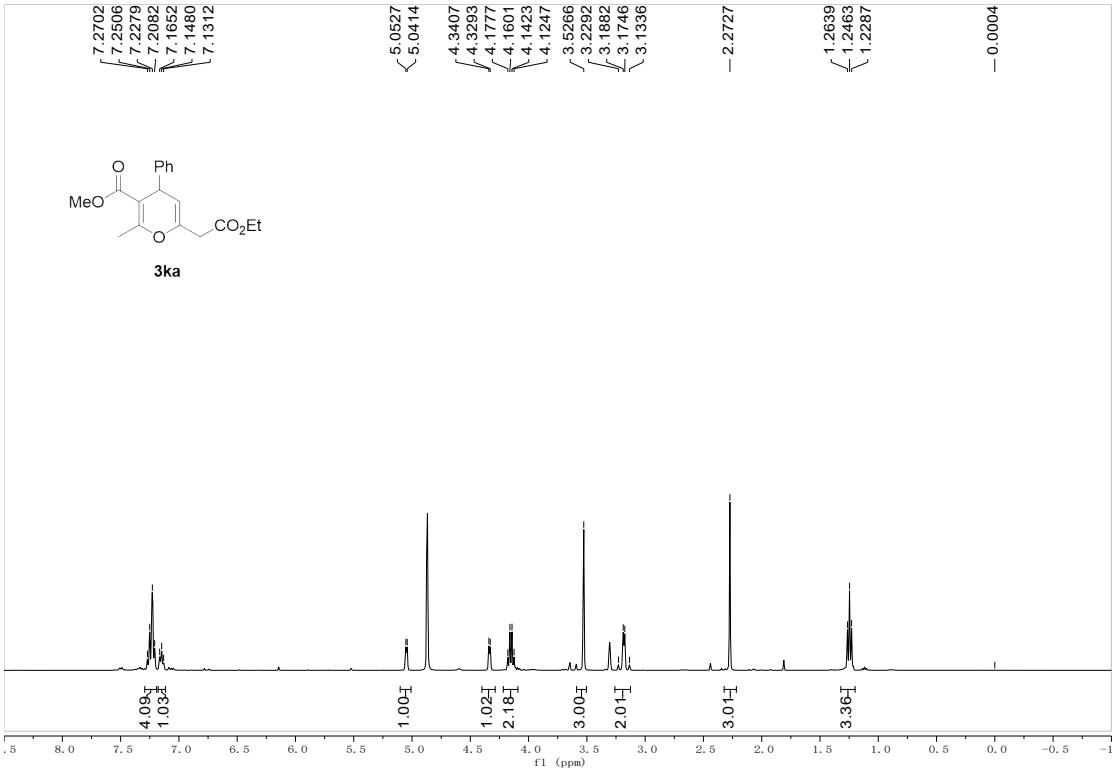
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of Compound (**3ja**)



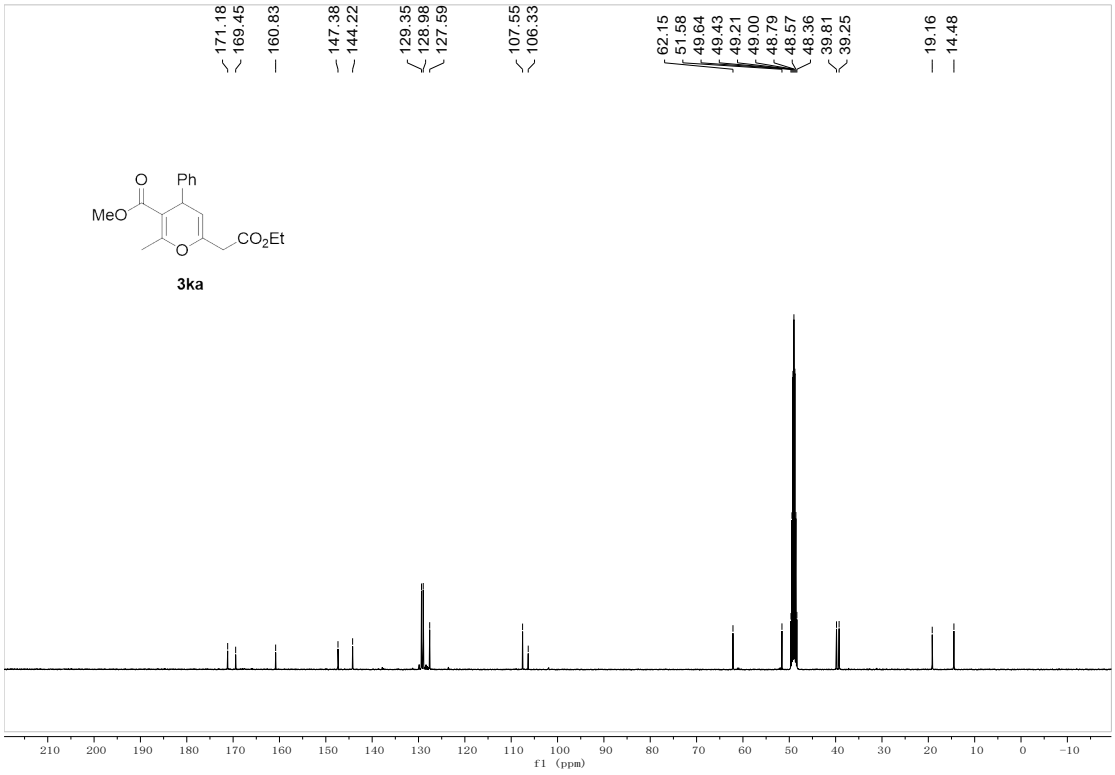
^{13}C NMR (100 MHz, DMSO-d_6) Spectrum of Compound (**3ja**)



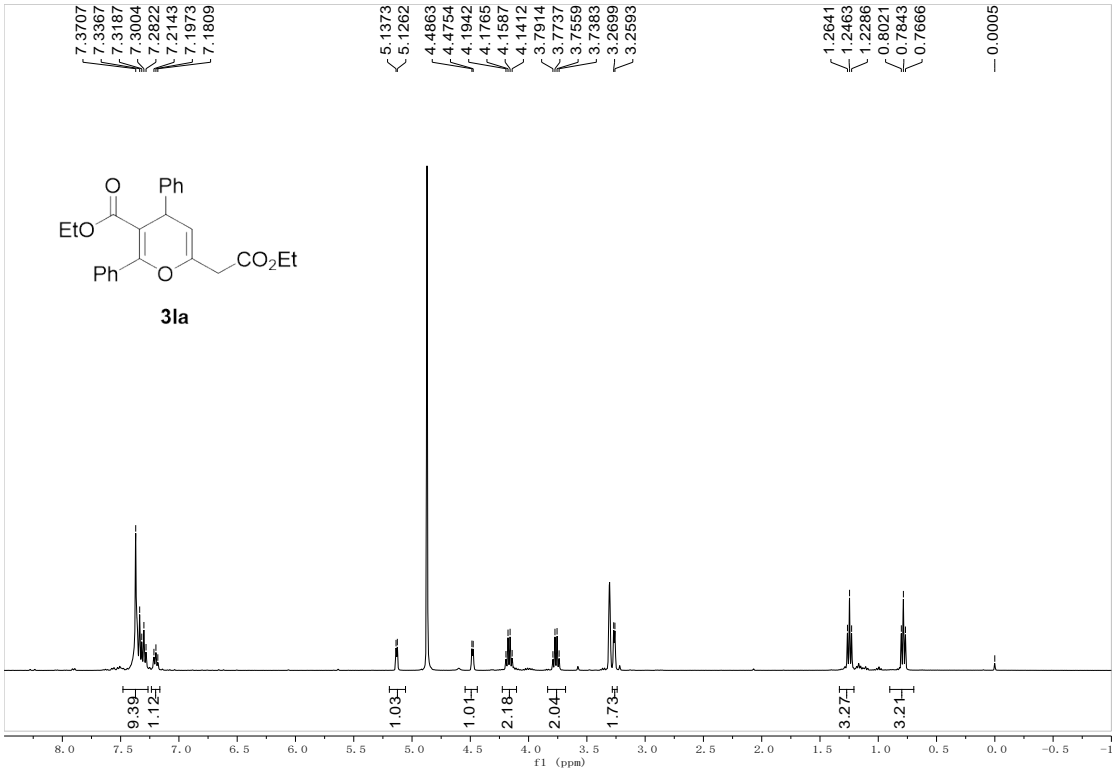
^{1}H NMR (400 MHz, CD_3OD) Spectrum of Compound (**3ka**)



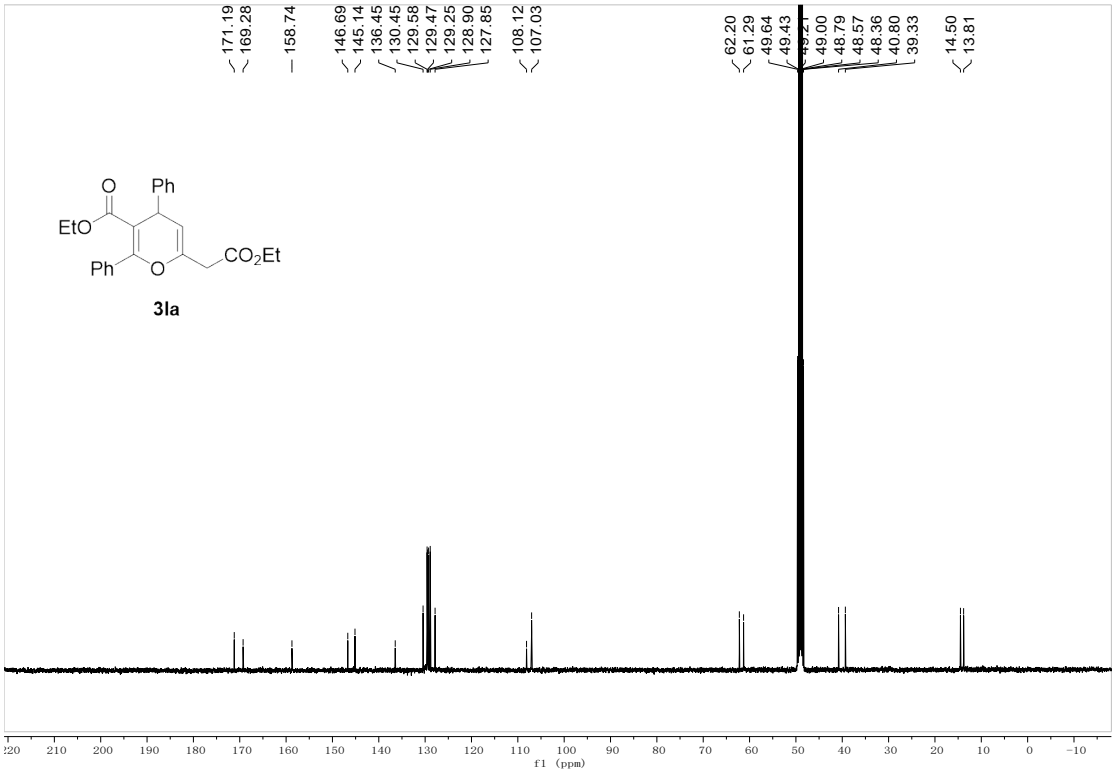
^{13}C NMR (100 MHz, CD_3OD) Spectrum of Compound (**3ka**)



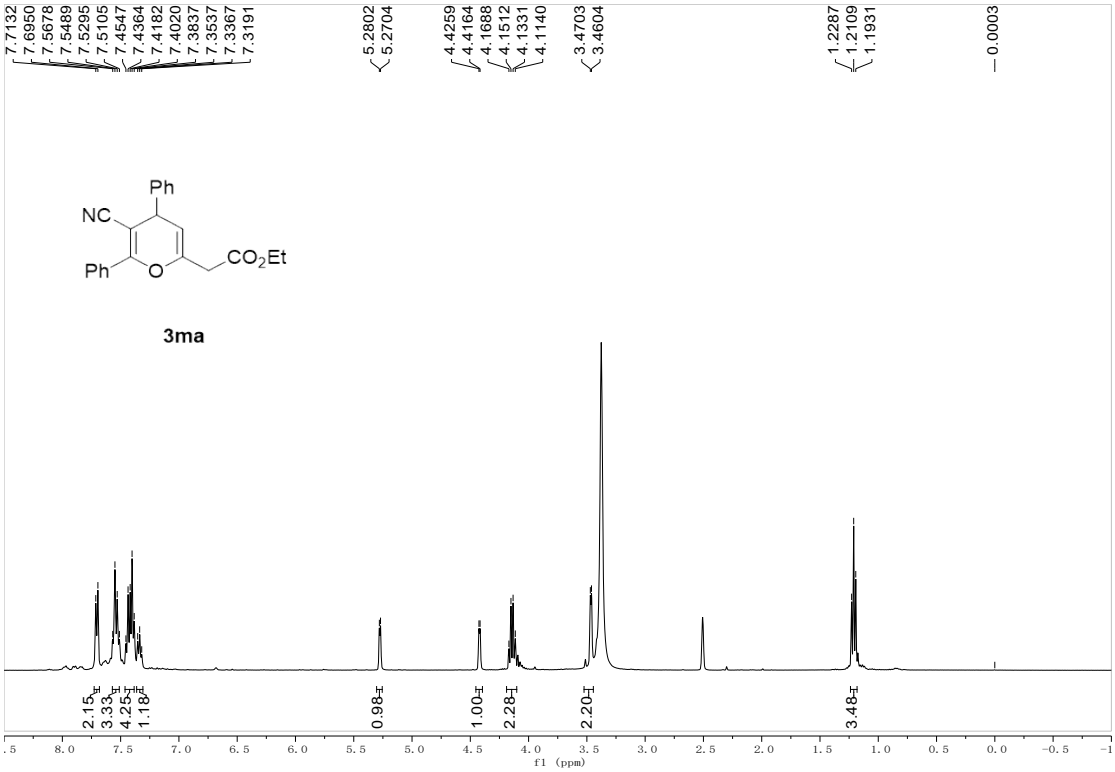
^{1}H NMR (400 MHz, CD_3OD) Spectrum of Compound (**3la**)



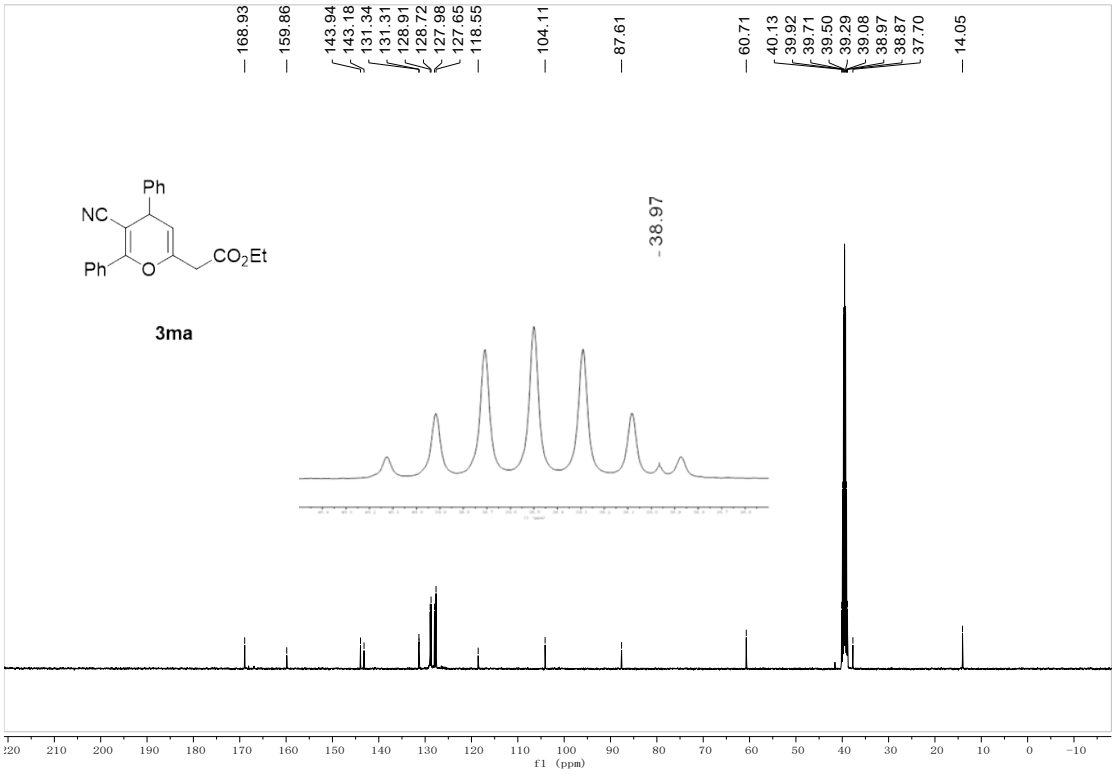
^{13}C NMR (100 MHz, CD_3OD) Spectrum of Compound (**3la**)



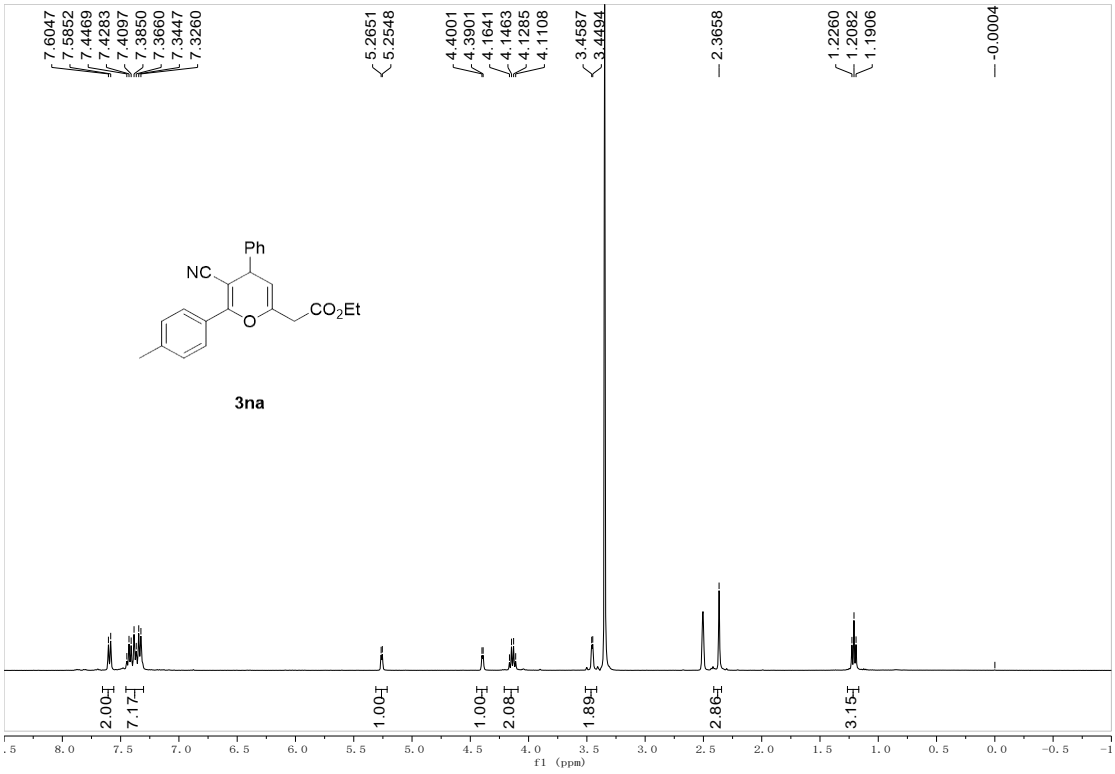
^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of Compound (**3ma**)



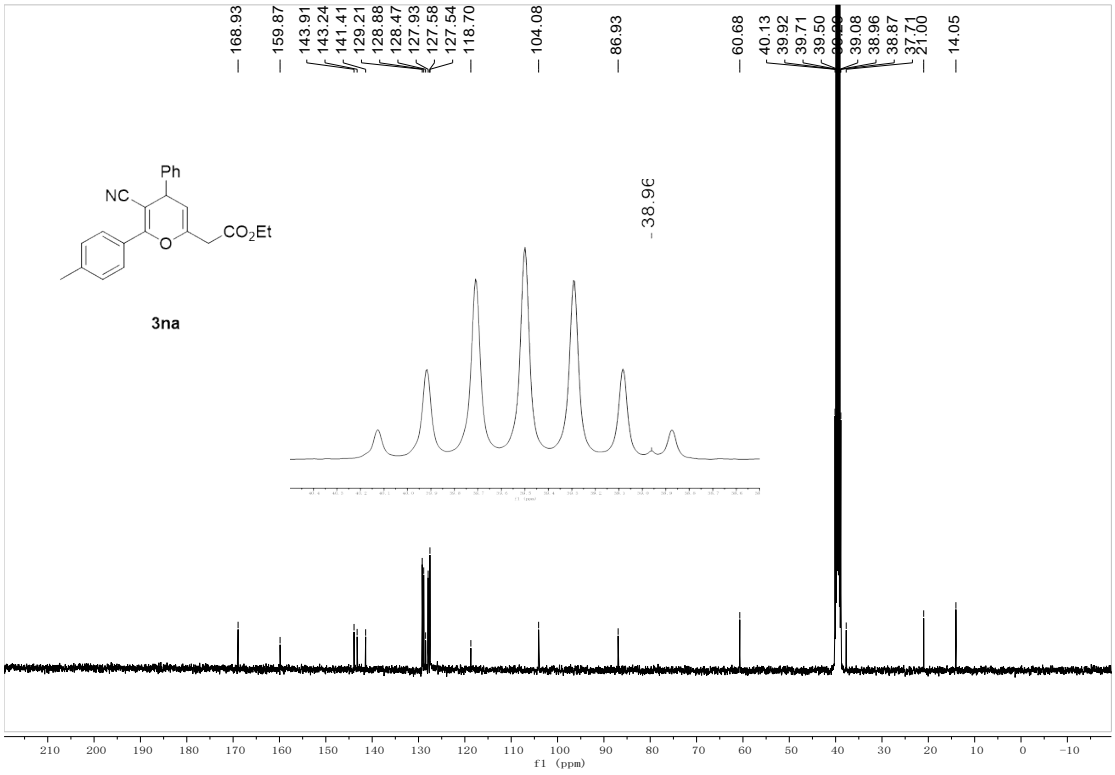
^{13}C NMR (100 MHz, DMSO-d_6) Spectrum of Compound (**3ma**)



^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of Compound (**3na**)

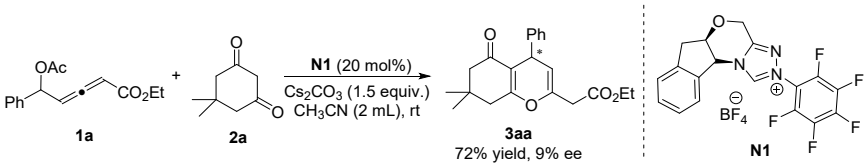


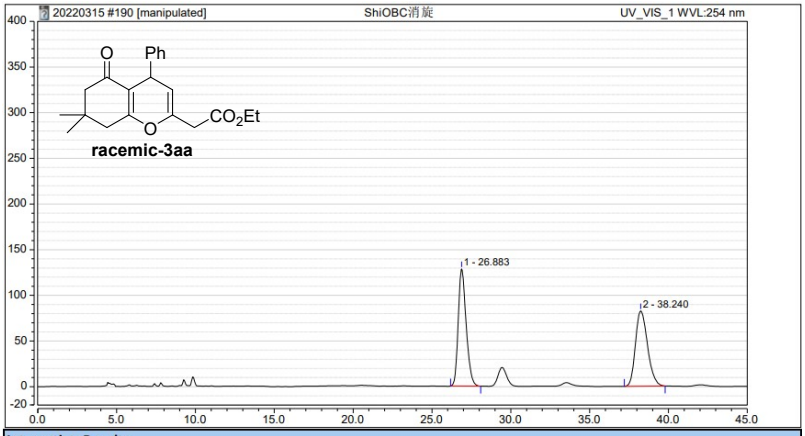
^{13}C NMR (100 MHz, DMSO-d_6) Spectrum of Compound (**3na**)



Ⅶ. HPLC data of 3aa

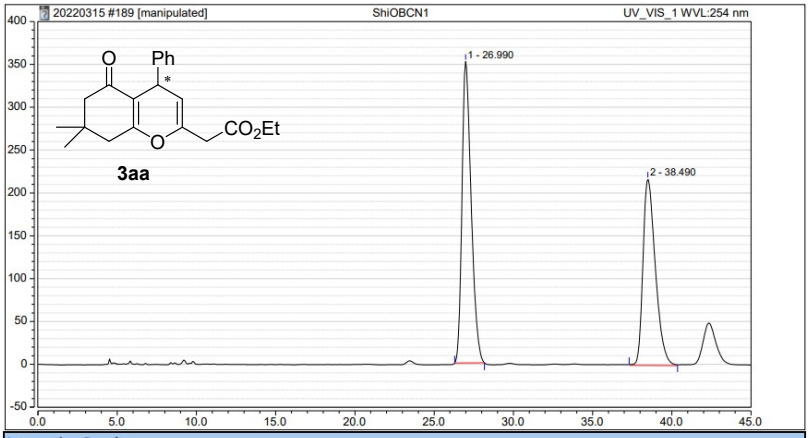
The enantiomeric excesses (ee) were determined by HPLC with a chiral IC column (hexane/i-PrOH = 90:10, 0.8 mL/min, λ = 254 nm,). These results are described as follows:





Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.883	74.667	128.353	50.55	60.87	n.a.
2		38.240	73.053	82.508	49.45	39.13	n.a.
Total:			**147.720**	**210.861**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.990	236.528	351.668	54.49	61.81	n.a.
2		38.490	197.587	217.273	45.51	38.19	n.a.
Total:			**434.116**	**568.941**	**100.00**	**100.00**	

VIII. References

1. K. Cocq, N. Saffon-Merceron, A. Poater, V. Maraval and R. Chauvin, Aromatic Rings and Aromatic Rods: Nonplanar Character of an Indeno-dehydro, *Synlett*, 2016, **27**, 2105-2112.

2. Y. Lei, J. Xing, Q. Xu, and M. Shi, Synthesis of 5,6-Dihydropyrazolo[5,1-*a*]isoquinoline and Ethyl (*Z*)-3-Acetoxy-3-tosylpent-4-enoate through Tertiary-Amine-Catalyzed [3+2] Annulation, *Eur. J. Org. Chem.*, 2016, **2016**, 3486-3490.

3. (a) W. Zhou, C. Ni, J. Chen, D. Wang and X. Tong, Enantioselective Synthesis of 4*H*-Pyran via Amine-Catalyzed Formal [3+3] Annulation of *δ*-Acetoxy Allenoate, *Org. Lett.*, 2017, **19**, 1890-1893; (b) C. Ni, W. Zhou and X. Tong, Tertiary Amine-catalyzed [3+3] Annulations of *δ*-Acetoxy Allenoates: Substrate Scope, Synthetic Application and Mechanistic insight, *Tetrahedron*, 2017, **73**, 3347-3354.