

Supporting Information

Phosphine-Catalyzed [2 + 4] Annulation of Allenates with Thiazolone-Derived Alkenes: Synthesis of Functionalized 6,7-Dihydro-5*H*-pyrano[2,3-*d*]thiazoles

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Table of Contents

General Information	S1
General Procedure for Synthesis of Substrates 1 and 2	S1
General Procedure of PMe ₂ Ph-catalyzed [2 + 4] Annulation	S1
General Procedure of Asymmetric [2 + 4] Annulation	S2
Screening of Reaction Conditions for Asymmetric Annulation	S2
Characterization Data of Products 3 and (+)- 3	S3 – S20
Transformations of the Product 3aa and Preparation on the Gram Scale	S20 – S21
Copies of ¹ H and ¹³ C NMR Spectra	S22 – S53
HPLC Chromatograms of the Products (+)- 3	S54 – S57
X-Ray Crystallographic Data of 3ma	S58 – S67

General Information

All reactions were performed under N₂ atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ¹H and ¹³C NMR spectra were recorded in CDCl₃ using a 300 MHz NMR instrument (referenced internally to Me₄Si). ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ¹³C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on a Perkin-Elmer 343 polarimeter. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. HPLC analysis was performed on Agilent 1100 series, UV detection monitored at 254 nm, using an R&C RC-OD column with hexane and *i*-PrOH as the eluent. X-ray crystallographic data were collected using a MM007HF Saturn724+.

Synthesis of Substrates 1 and 2

Allenoates **1** were synthesized by previous literature procedure.¹ Thiazolone-derived alkenes **2** used were prepared by the literature procedure.²

General Procedure for Preparation of Racemic Products 3 by [2 + 4] Annulation of Thiazolone-Derived Alkenes 2 with Allenoates 1.

Under nitrogen atmosphere, to a mixture of thiazolone-derived alkenes **2** (0.1 mmol) and additive 4 Å MS (100 mg) in 1 mL of toluene in a Schlenk tube, α -substituted allenoates **1** (1.5 eq., 0.15 mmol) followed with catalyst PMe₂Ph (10 mol %, 0.01 mmol) were added at 40 °C. The resulting mixture was stirred until the starting material was completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc/PE) to afford the corresponding cycloaddition product **3**.

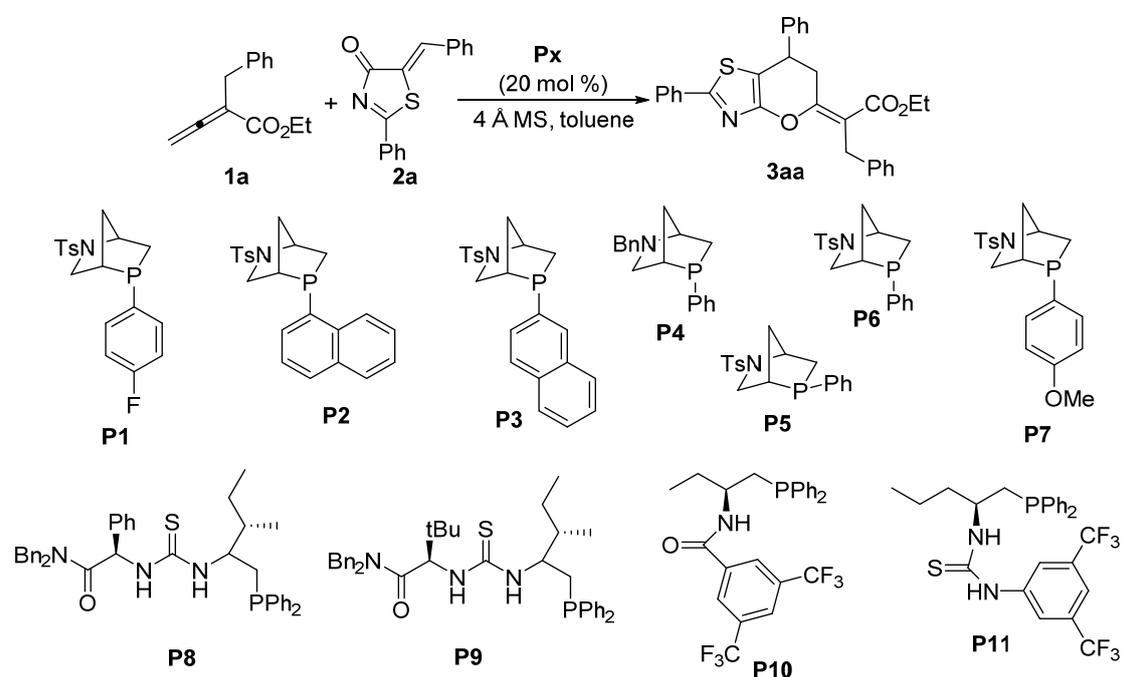
¹ Liu, H.; Liu, Y.; Yuan, C.; Wang, G.-P.; Zhu, S.-F.; Wu, Y.; Wang, B.; Sun, Z.; Xiao, Y.; Zhou, Q. L.; Guo, H. *Org. Lett.* **2016**, *18*, 1302.

² Lin, L.; Yang, Y.-H.; Wang, M.; Lai, L.-H.; Guo, Y.-R.; Wang, R. *Chem. Commun.* **2015**, *51*, 8134.

General Procedure for Asymmetric [2 + 4] Annulation

Under nitrogen atmosphere, to a mixture of thiazolone-derived alkenes **2** (0.05 mmol) and additive 4 Å MS (50 mg) in 1 mL of toluene in a Schlenk tube, α -substituted allenotes **1** (1.5 eq., 0.075 mmol) followed with catalyst **P1** (20 mol %, 0.01 mmol) were added at 80 °C. The resulting mixture was stirred until the starting material was completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc/PE) to afford the corresponding cycloaddition product (+)-**3**.

Table 1. Optimization of Reaction Conditions for Asymmetric Annulation^a

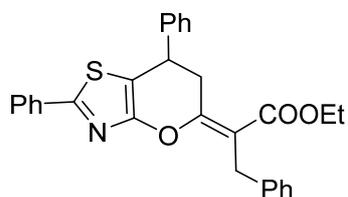


entry	Px	<i>t</i> (°C)	<i>t</i>	yield (%) ^b	ee (%) ^c
1	P1	25	3 d	62	>99
2	P2	25	3 d	trace	-
3	P3	25	3 d	52	>99
4	P4	25	3 d	38	>99
5	P5	25	3 d	68	-88
6	P6	25	3 d	25	>99
7	P7	25	3 d	40	>99
8	P8	25	3 d	40	86
9	P9	25	3 d	57	70
10	P10	25	3 d	90	23
11	P11	25	3 d	trace	-
12	P1	40	20 h	74	99
13	P1	60	6 h	77	98
14	P1	80	2.5 h	80	98

^aUnless otherwise stated, all reactions were carried out with **1a** (0.075 mmol), **2a** (0.05 mmol), catalyst (0.01 mmol) additive 4 Å MS (50 mg) in solvent (1 mL). ^bIsolated yield. ^cDetermined by chiral HPLC analysis.

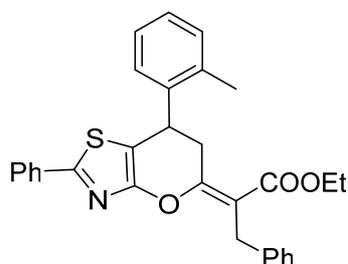
Characterization Data for the Racemic Products 3

Ethyl (*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate (3aa)



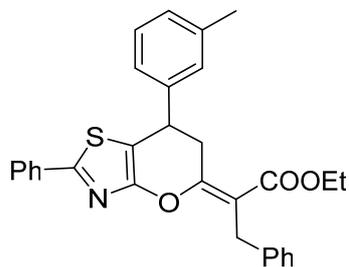
Prepared according to the general procedure as described above in 80% yield (37.4 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 82 – 90 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.86 (m, 2H), 7.48 – 7.40 (m, 3H), 7.35 – 7.29 (m, 5H), 7.28 – 7.15 (m, 5H), 4.38 – 4.28 (q, *J* = 7.1 Hz, 1H), 4.14 – 4.04 (m, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.86 – 3.76 (m, 1H), 3.61 – 3.51 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.6, 164.0, 157.6, 156.7, 141.9, 140.1, 133.1, 130.1, 128.8, 128.6, 128.5, 128.0, 127.4, 127.2, 125.7, 125.5, 114.6, 109.0, 60.3, 37.2, 32.7, 31.7, 13.9; IR (film) ν_{\max} 3029, 2981, 2378, 2345, 1704, 1632, 1601, 1556, 1495, 1454, 1361, 1275, 1186, 1155, 1104, 1032, 763, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₆NO₃S⁺ [M+H]⁺ 468.1628, found 468.1638.

Ethyl(*E*)-3-phenyl-2-(2-phenyl-7-(*o*-tolyl)-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)propanoate (3ab)



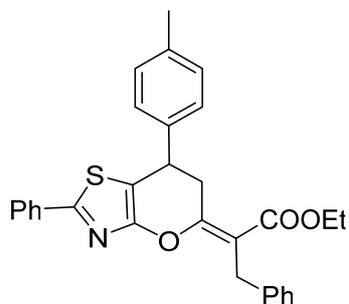
Prepared according to the general procedure as described above in 78% yield (37.5 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 92 – 98 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.90 (m, 2H), 7.49 – 7.42 (m, 3H), 7.37 – 7.28 (m, 4H), 7.25 – 7.12 (m, 4H), 7.08 – 7.02 (m, 1H), 4.64 – 4.56 (m, 1H), 4.17 – 3.95 (m, 4H), 3.81 (dd, *J* = 14.8, 5.6 Hz, 1H), 3.49 (dd, *J* = 14.7, 7.5 Hz, 1H), 2.52 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 163.8, 157.5, 157.1, 140.0, 139.7, 134.9, 133.0, 130.3, 129.9, 128.6, 128.4, 127.8, 127.0, 126.6, 126.2, 125.5, 114.6, 108.7, 60.1, 33.2, 31.6, 31.4, 19.1, 13.7; IR (film) ν_{\max} 3027, 2979, 1704, 1639, 1556, 1494, 1461, 1361, 1274, 1183, 1104, 1081, 1032, 951, 761, 700, 680 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₈NO₃S⁺ [M+H]⁺ 482.1784, found 482.1794.

Ethyl(*E*)-3-phenyl-2-(2-phenyl-7-(*m*-tolyl)-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)propanoate (3ac)



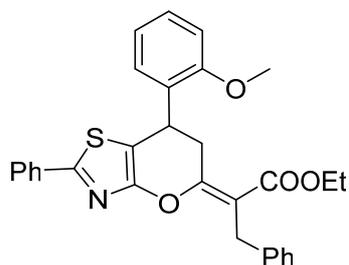
Prepared according to the general procedure as described above in 83% yield (40.0 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 52 – 60 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.87 (m, 2H), 7.48 – 7.38 (m, 3H), 7.35 – 7.23 (m, 4H), 7.22 – 7.10 (m, 5H), 4.33 – 4.25 (m, 1H), 4.15 – 3.94 (m, 4H), 3.87 – 3.77 (m, 1H), 3.55 – 3.44 (m, 1H), 2.36 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 163.7, 157.6, 156.4, 140.0, 138.8, 136.9, 133.0, 129.9, 129.1, 128.6, 128.4, 127.8, 126.9, 125.5, 114.4, 109.2, 60.1, 36.7, 32.6, 31.6, 20.7, 13.7; IR (film) ν_{max} 2964, 1705, 1639, 1556, 1513, 1495, 1454, 1361, 1261, 1183, 1103, 1029, 864, 800, 763, 700 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₈NO₃S⁺ [M+H]⁺ 482.1784, found 482.1797.

Ethyl (*E*)-3-phenyl-2-(2-phenyl-7-(*p*-tolyl)-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)propanoate (3ad)



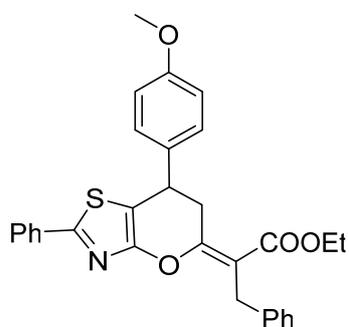
Prepared according to the general procedure as described above in 85% yield (40.9 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 102 – 110 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.94 – 7.86 (m, 2H), 7.46 – 7.39 (m, 3H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 7.20 – 7.11 (m, 5H), 4.34 – 4.25 (m, 1H), 4.15 – 3.93 (m, 4H), 3.86 – 3.76 (m, 1H), 3.54 – 3.43 (m, 1H), 2.36 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 163.7, 157.6, 156.4, 140.0, 138.8, 136.9, 133.0, 129.9, 129.1, 128.6, 128.3, 127.8, 126.9, 125.4, 114.3, 109.2, 60.1, 36.7, 32.6, 31.6, 20.7, 13.7; IR (film) ν_{max} 3029, 2981, 1705, 1641, 1604, 1557, 1494, 1454, 1361, 1260, 1181, 1105, 1031, 913, 879, 763, 701 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₈NO₃S⁺ [M+H]⁺ 482.1784, found 482.1784.

Ethyl (*E*)-2-(7-(2-methoxyphenyl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate (3ae)



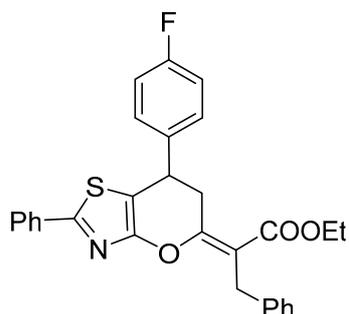
Prepared according to the general procedure as described above in 78% yield (38.8 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 62 – 70 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.88 (m, 2H), 7.46 – 7.39 (m, 3H), 7.34 – 7.22 (m, 5H), 7.21 – 7.13 (m, 1H), 7.04 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.95 – 6.84 (m, 2H), 4.79 (t, *J* = 5.9 Hz, 1H), 4.12 – 3.93 (m, 4H), 3.92 (s, 3H), 3.90 – 3.83 (m, 1H), 3.50 (dd, *J* = 15.0, 6.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 163.5, 158.0, 156.7, 156.2, 140.1, 133.1, 129.8, 129.7, 128.6, 128.4, 128.1, 127.7, 127.4, 125.4, 125.4, 120.4, 114.1, 110.1, 108.4, 60.0, 55.0, 31.6, 30.2, 30.2, 13.7; IR (film) ν_{max} 2964, 1704, 1636, 1601, 1557, 1493, 1462, 1439, 1361, 1261, 1178, 1104, 1029, 865, 800, 755, 700 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₈NO₄S⁺ [M+H]⁺ 498.1734, found 498.1736.

Ethyl (*E*)-2-(7-(4-methoxyphenyl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate (3af)



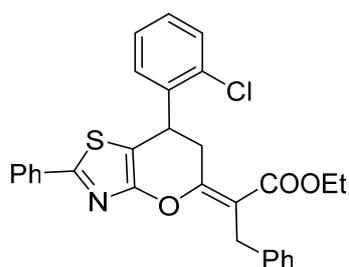
Prepared according to the general procedure as described above in 81% yield (40.3 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 51 – 57 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.87 (m, 2H), 7.49 – 7.39 (m, 3H), 7.34 – 7.24 (m, 4H), 7.22 – 7.11 (m, 3H), 6.91 – 6.83 (m, 2H), 4.34 – 4.24 (m, 1H), 4.17 – 3.94 (m, 4H), 3.81 (s, 3H), 3.80 – 3.74 (m, 1H), 3.56 – 3.44 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 163.7, 158.6, 157.6, 156.4, 140.0, 133.9, 133.0, 129.9, 128.6, 128.4, 128.0, 127.8, 125.45, 114.4, 113.8, 109.4, 60.1, 54.9, 36.3, 32.8, 31.6, 13.7; IR (film) ν_{max} 3029, 2981, 1704, 1641, 1603, 1556, 1508, 1454, 1361, 1256, 1228, 1186, 1159, 1104, 1031, 835, 763, 700, 678, 540 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₈NO₄S⁺ [M+H]⁺ 498.1734, found 498.1734.

Ethyl (*E*)-2-(7-(4-fluorophenyl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate (3ag)



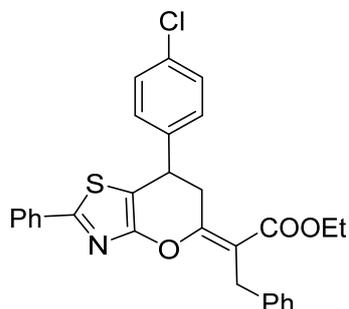
Prepared according to the general procedure as described above in 85% yield (41.3 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 88 – 97 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.88 (m, 2H), 7.48 – 7.39 (m, 3H), 7.32 – 7.23 (m, 4H), 7.21 – 7.13 (m, 3H), 7.05 – 6.96 (m, 2H), 4.38 – 4.28 (m, 1H), 4.15 – 3.90 (m, 4H), 3.77 – 3.65 (m, 1H), 3.64 – 3.52 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 164.0, 161.8 (d, *J* = 246.1 Hz), 157.08, 156.6, 139.9, 137.5 (d, *J* = 3.2 Hz), 132.9, 130.0, 128.6, 128.5, 128.3, 127.8, 125.5 (d, *J* = 2.9 Hz), 115.4, 115.1, 114.8, 108.4, 60.1, 36.3, 32.6, 31.5, 13.7; IR (film) ν_{max} 2980, 2837, 1704, 1636, 1611, 1557, 1512, 1455, 1360, 1251, 1179, 1104, 1033, 953, 830, 763, 737, 701, 678, 547 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅FNO₃S⁺ [M+H]⁺ 486.1534, found 486.1537.

Ethyl(*E*)-2-(7-(2-chlorophenyl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate (3ah)



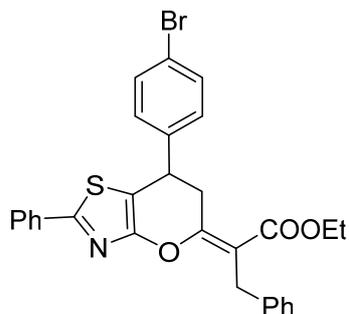
Prepared according to the general procedure as described above in 90% yield (45.0 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 79 – 85 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.91 (m, 2H), 7.52 – 7.40 (m, 4H), 7.36 – 7.11 (m, 7H), 7.03 – 6.97 (m, 1H), 4.95 – 4.86 (m, 1H), 4.15 – 4.03 (m, 3H), 4.00 – 3.89 (m, 2H), 3.54 – 3.42 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 164.3, 157.3, 156.4, 139.9, 138.8, 132.9, 132.7, 130.1, 129.4, 128.6, 128.4, 128.4, 128.3, 127.8, 126.8, 125.5, 125.5, 115.4, 106.6, 60.2, 33.4, 31.7, 30.6, 13.7; IR (film) ν_{max} 3028, 2980, 1705, 1640, 1556, 1495, 1442, 1362, 1275, 1184, 1104, 1078, 1036, 965, 760, 699, 675 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅ClNO₃S⁺ [M+H]⁺ 502.1238, found 502.1235.

Ethyl(*E*)-2-(7-(4-chlorophenyl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate (3ai)



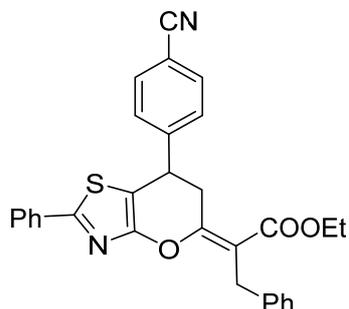
Prepared according to the general procedure as described above in 92% yield (46.2 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 51 – 58 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.87 (m, 2H), 7.48 – 7.40 (m, 3H), 7.32 – 7.25 (m, 6H), 7.21 – 7.10 (m, 3H), 4.36 – 4.26 (m, 1H), 4.15 – 3.90 (m, 4H), 3.74 – 3.56 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 164.1, 156.9, 156.6, 140.3, 139.9, 133.0, 132.9, 130.1, 128.63, 128.60, 128.4, 128.3, 127.8, 125.6, 125.5, 115.0, 107.9, 60.2, 36.4, 32.4, 31.5, 13.7; IR (film) ν_{max} 3028, 2981, 1704, 1640, 1556, 1492, 1454, 1410, 1361, 1256, 1182, 1104, 1031, 1015, 827, 762, 688 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅ClNO₃S⁺ [M+H]⁺ 502.1238, found 502.1245.

Ethyl (*E*)-2-(7-(4-bromophenyl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3- phenylpropanoate (3aj)



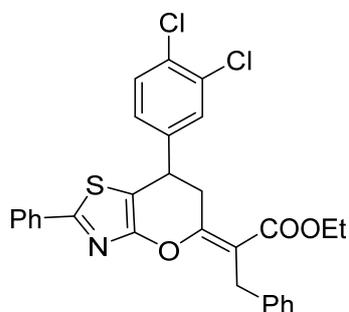
Prepared according to the general procedure as described above in 92% yield (50.1 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 57 – 65 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.88 (m, 2H), 7.47 – 7.40 (m, 5H), 7.31 – 7.23 (m, 4H), 7.21 – 7.14 (m, 1H), 7.11 – 7.05 (m, 2H), 4.35 – 4.26 (m, 1H), 4.15 – 3.91 (m, 4H), 3.74 – 3.56 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 164.1, 156.9, 156.6, 140.8, 139.8, 132.8, 131.6, 130.1, 128.7, 128.6, 128.3, 127.8, 125.5, 125.5, 121.1, 115.0, 107.78, 60.2, 36.5, 32.3, 31.5, 13.7; IR (film) ν_{max} 3028, 2980, 1704, 1640, 1556, 1489, 1454, 1407, 1361, 1274, 1182, 1105, 1074, 1031, 1011, 953, 880, 822, 762, 737, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅BrNO₃S⁺ [M+H]⁺ 546.0733, found 546.0743.

Ethyl (*E*)-2-(7-(4-cyanophenyl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate (3ak)



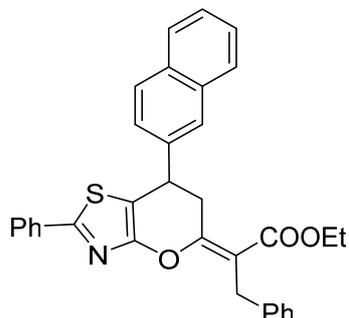
Prepared according to the general procedure as described above in 82% yield (40.4 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 57 – 61 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.88 (m, 2H), 7.61 – 7.54 (m, 2H), 7.48 – 7.41 (m, 3H), 7.31 – 7.24 (m, 6H), 7.23 – 7.14 (m, 1H), 4.45 – 4.35 (m, 1H), 4.15 – 3.88 (m, 4H), 3.84 – 3.73 (m, 1H), 3.64 – 3.52 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.1, 164.6, 156.8, 156.2, 147.0, 139.7, 132.7, 132.2, 130.3, 128.7, 128.3, 127.8, 125.6, 125.5, 118.2, 115.6, 111.1, 106.3, 60.3, 36.9, 31.9, 31.5, 13.7; IR (film) ν_{\max} 2964, 2346, 2229, 1704, 1641, 1608, 1556, 1502, 1454, 1414, 1362, 1260, 1178, 1104, 1030, 800, 763, 690, 661, 555 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₅N₂O₃S⁺ [M+H]⁺ 493.1580, found 493.1581.

Ethyl (*E*)-2-(7-(3,4-dichlorophenyl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate (3al)



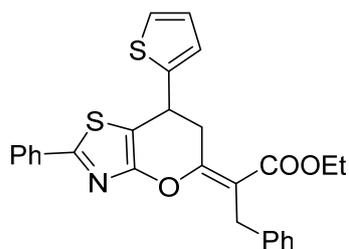
Prepared according to the general procedure as described above in 75% yield (40.1 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 58 – 61 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.87 (m, 2H), 7.51 – 7.41 (m, 3H), 7.39 – 7.32 (m, 2H), 7.29 – 7.14 (m, 5H), 7.05 – 6.99 (m, 1H), 4.36 – 4.26 (m, 1H), 4.15 – 3.89 (m, 4H), 3.75 – 3.57 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 164.5, 156.7, 156.3, 142.0, 139.7, 132.7, 132.5, 131.3, 130.4, 130.2, 129.0, 128.7, 128.2, 127.9, 126.4, 125.6, 125.5, 115.3, 106.9, 60.3, 36.2, 32.1, 31.5, 13.67; IR (film) ν_{\max} 2927, 1704, 1640, 1555, 1495, 1470, 1400, 1361, 1275, 1188, 1104, 1031, 820, 763, 701, 663, 470 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₄Cl₂NO₃S⁺ [M+H]⁺ 536.0848, found 536.0847.

Ethyl(*E*)-2-(7-(naphthalen-2-yl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate (3am)



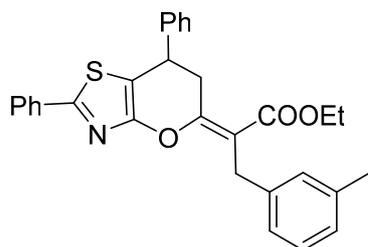
Prepared according to the general procedure as described above in 77% yield (40.0 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 120 – 125 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.97 – 7.90 (m, 2H), 7.88 – 7.75 (m, 3H), 7.69 – 7.66 (m, 1H), 7.54 – 7.47 (m, 2H), 7.47 – 7.41 (m, 3H), 7.40 – 7.35 (m, 1H), 7.32 – 7.15 (m, 5H), 4.57 – 4.45 (m, 1H), 4.14 – 3.94 (m, 4H), 3.90 – 3.80 (m, 1H), 3.78 – 3.68 (m, 1H), 1.11 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 164.0, 157.4, 156.6, 139.9, 139.1, 133.1, 133.0, 132.5, 130.0, 128.6, 128.4, 128.3, 127.8, 127.6, 127.4, 126.0, 125.8, 125.7, 125.5, 125.0, 114.6, 108.6, 60.1, 37.2, 32.4, 31.6, 13.6; IR (film) ν_{max} 3027, 2980, 1704, 1636, 1602, 1556, 1495, 1454, 1358, 1271, 1179, 1104, 1031, 957, 858, 818, 749, 700, 678, 479 cm⁻¹; HRMS (ESI) calcd for C₃₃H₂₈NO₃S⁺ [M+H]⁺ 518.1784, found 518.1784.

Ethyl (*E*)-3-phenyl-2-(2-phenyl-7-(thiophen-2-yl)-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene) propanoate (3an)



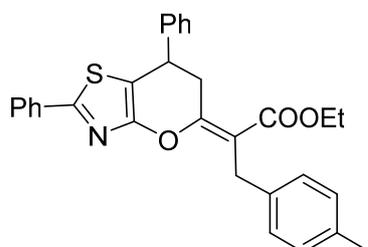
Prepared according to the general procedure as described above in 70% yield (33.1 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 92 – 96 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.99 – 7.90 (m, 2H), 7.51 – 7.42 (m, 3H), 7.35 – 7.16 (m, 6H), 7.02 – 6.91 (m, 2H), 4.75 – 4.61 (m, 1H), 4.25 – 3.95 (m, 4H), 3.88 – 3.71 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 163.9, 156.8, 156.0, 145.1, 139.8, 132.9, 130.0, 128.6, 128.3, 127.8, 126.5, 125.5, 125.5, 124.6, 124.3, 115.0, 108.6, 60.2, 32.7, 32.4, 31.6, 13.7; IR (film) ν_{max} 3062, 3028, 2980, 1704, 1640, 1557, 1495, 1453, 1359, 1271, 1179, 1105, 1031, 960, 915, 849, 762, 699 cm⁻¹; HRMS (ESI) calcd for C₂₇H₂₄NO₃S₂⁺ [M+H]⁺ 474.1153, found 474.1198.

Ethyl (*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-(*m*-tolyl) propanoate (3ba)



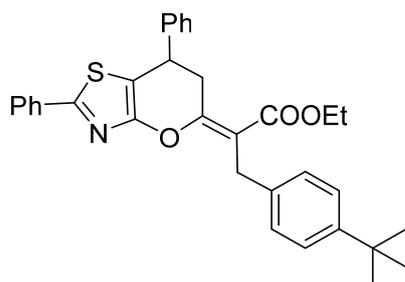
Prepared according to the general procedure as described above in 62% yield (29.9 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 96 – 100 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.97 – 7.86 (m, 2H), 7.47 – 7.39 (m, 3H), 7.37 – 7.28 (m, 3H), 7.26 – 6.96 (m, 6H), 4.37 – 4.29 (m, 1H), 4.13 – 4.03 (m, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.84 – 3.72 (m, 1H), 3.61 – 3.49 (m, 1H), 2.32 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.6, 164.0, 157.4, 156.8, 142.0, 140.0, 137.3, 133.1, 130.1, 129.4, 128.8, 128.6, 127.8, 127.3, 127.1, 126.4, 125.6, 125.6, 114.8, 108.9, 60.2, 37.3, 32.7, 31.6, 21.3, 13.7; IR (film) ν_{\max} 2980, 2379, 2346, 1705, 1636, 1605, 1557, 1494, 1455, 1361, 1258, 1188, 1160, 1105, 1069, 1034, 952, 763, 736, 700, 681 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₈NO₃S⁺ [M+H]⁺ 482.1784, found 482.1799.

Ethyl (*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-(*p*-tolyl) propanoate (3ca)



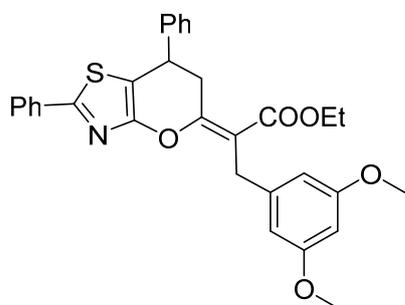
Prepared according to the general procedure as described above in 67% yield (32.3 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a refous solid. mp = 62 – 67 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.87 (m, 2H), 7.47 – 7.38 (m, 3H), 7.38 – 7.28 (m, 3H), 7.27 – 7.17 (m, 4H), 7.12 – 7.03 (m, 2H), 4.38 – 4.29 (m, 1H), 4.15 – 4.04 (m, 2H), 5.02 – 4.92 (m, 2H), 3.84 – 3.76 (m, 1H), 3.56 – 3.48 (m, 1H), 2.32 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.6, 163.9, 157.3, 156.8, 142.0, 137.0, 135.0, 133.1, 130.1, 128.7, 128.6, 128.6, 128.4, 127.4, 127.2, 125.6, 114.9, 108.9, 60.2, 37.3, 32.8, 31.3, 20.8, 13.9; IR (film) ν_{\max} 2980, 2345, 1705, 1641, 1603, 1556, 1514, 1502, 1455, 1362, 1258, 1185, 1108, 1069, 1033, 788, 763, 737, 700 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₈NO₃S⁺ [M+H]⁺ 482.1784, found 482.1791.

Ethyl (*E*)-3-(4-(*tert*-butyl)phenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)propanoate (3da)



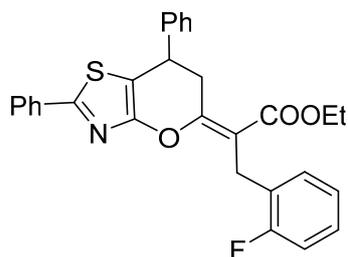
Prepared according to the general procedure as described above in 71% yield (37.2 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 100 – 110 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.85 (m, 2H), 7.48 – 7.39 (m, 3H), 7.37 – 7.28 (m, 5H), 7.28 – 7.37 – 7.27 (m, 4H), 4.33 (m, 1H), 4.16 – 4.06 (m, 2H), 4.06 – 3.90 (m, 2H), 3.85 – 3.75 (m, 1H), 3.55 – 3.45 (m, 1H), 1.32 (s, 9H), 1.18 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.7, 163.9, 157.4, 156.8, 148.4, 142.0, 137.0, 133.2, 130.1, 128.7, 128.6, 128.2, 127.3, 127.2, 125.6, 124.9, 114.9, 109.0, 60.2, 37.3, 34.1, 32.8, 31.24, 31.18, 13.9; IR (film) ν_{max} 3029, 2963, 1705, 1639, 1556, 1502, 1455, 1361, 1258, 1184, 1118, 1101, 1070, 1033, 963, 807, 762, 738, 700, 556 cm⁻¹; HRMS (ESI) calcd for C₃₃H₃₄NO₃S⁺ [M+H]⁺ 524.2254, found 524.2266.

Ethyl (*E*)-3-(3,5-dimethoxyphenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)propanoate (3ea)



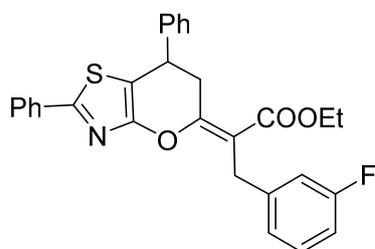
Prepared according to the general procedure as described above in 70% yield (37.0 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 120 – 126 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.92 – 7.83 (m, 2H), 7.45 – 7.37 (m, 3H), 7.34 – 7.26 (m, 3H), 7.22 – 7.16 (m, 2H), 6.54 – 6.49 (m, 2H), 6.31 – 6.27 (m, 1H), 4.35 – 4.26 (m, 1H), 4.15 – 4.05 (m, 2H), 3.98 – 3.86 (m, 2H), 3.83 – 3.76 (m, 1H), 3.76 – 3.70 (m, 6H), 3.53 – 3.43 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 163.8, 160.2, 157.6, 156.5, 142.4, 141.8, 132.92, 130.0, 128.6, 128.5, 127.2, 127.0, 125.4, 114.4, 108.8, 106.5, 98.0, 60.2, 54.9, 37.1, 32.6, 31.8, 13.8; IR (film) ν_{max} 2936, 2837, 1704, 1636, 1596, 1556, 1501, 1459, 1429, 1361, 1290, 1255, 1193, 1156, 1103, 1070, 1032, 830, 763, 701 cm⁻¹; HRMS (ESI) calcd for C₃₁H₃₀NO₅S⁺ [M+H]⁺ 528.1784, found 528.1752.

Ethyl (*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-(2-fluorophenyl)propanoate (3fa)



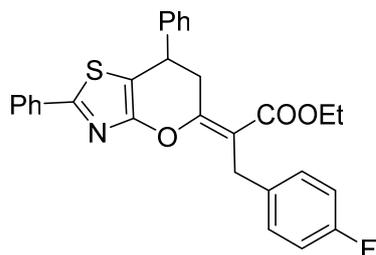
Prepared according to the general procedure as described above in 71% yield (34.5 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 40 – 45 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.86 (m, 2H), 7.48 – 7.40 (m, 3H), 7.40 – 7.28 (m, 4H), 7.26 – 6.97 (m, 5H), 4.41 – 4.32 (m, 1H), 4.15 – 3.98 (m, 4H), 3.86 – 3.77 (m, 1H), 3.67 – 3.57 (m, 1H), 1.12 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 164.0, 160.9 (d, *J* = 243.8 Hz), 158.2, 156.6, 141.9, 133.1, 130.1, 129.9 (d, *J* = 4.5 Hz), 128.8, 128.6, 127.4, 127.3, 127.2, 126.9, 126.7, 125.6, 123.5 (d, *J* = 3.0 Hz), 114.9, 114.6, 113.0, 108.9, 60.3, 37.1, 32.7, 24.8, 13.7; IR (film) ν_{max} 2965, 2345, 1705, 1640, 1586, 1556, 1491, 1455, 1362, 1261, 1230, 1179, 1108, 1033, 801, 760, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅FNO₃S⁺ [M+H]⁺ 486.1534, found 486.1540.

Ethyl (*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-(3-fluorophenyl)propanoate (3ga)



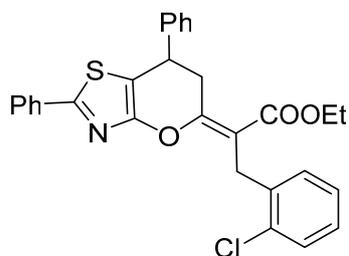
Prepared according to the general procedure as described above in 72% yield (35.0 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 41 – 47 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.99 – 7.84 (m, 2H), 7.49 – 7.40 (m, 3H), 7.38 – 7.29 (m, 3H), 7.26 – 7.05 (m, 4H), 7.05 – 6.82 (m, 2H), 4.39 – 4.29 (m, 1H), 4.16 – 3.89 (m, 4H), 3.85 – 3.73 (m, 1H), 3.66 – 3.55 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 164.1, 162.7 (d, *J* = 243.7 Hz), 158.2, 156.5, 142.8, 142.7, 141.8, 133.1, 130.1, 129.3, 129.2, 128.8, 128.6, 127.4, 127.1, 125.6, 124.1, 115.3 (d, *J* = 13.5 Hz), 113.9, 112.5 (d, *J* = 21.0 Hz), 108.9, 60.3, 37.1, 32.7, 31.5, 13.9; IR (film) ν_{max} 2981, 2381, 1705, 1636, 1615, 1588, 1557, 1487, 1453, 1361, 1300, 1258, 1187, 1136, 1105, 1032, 964, 866, 763, 738, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅FNO₃S⁺ [M+H]⁺ 486.1534, found 486.1540.

Ethyl (*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-(4-fluorophenyl)propanoate (3ha)



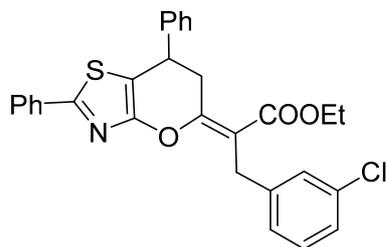
Prepared according to the general procedure as described above in 75% yield (36.4 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 101 – 106 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.99 – 7.84 (m, 2H), 7.49 – 7.40 (m, 3H), 7.38 – 7.29 (m, 3H), 7.26 – 7.05 (m, 4H), 7.05 – 6.82 (m, 2H), 4.39 – 4.29 (m, 1H), 4.16 – 3.89 (m, 4H), 3.85 – 3.73 (m, 1H), 3.66 – 3.55 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 164.1, 158.2, 156.5, 142.8, 142.7, 141.8, 133.1, 129.3, 129.2, 128.77 (d, *J* = 204.0 Hz) 128.75, 128.6, 127.4, 127.1, 125.6, 124.1, 115.3 (d, *J* = 13.5 Hz), 113.9, 112.5 (d, *J* = 21.0 Hz), 108.9, 60.3, 37.1, 32.7, 31.5, 13.6; IR (film) ν_{max} 2981, 2365, 2346, 1705, 1636, 1597, 1557, 1501, 1455, 1431, 1361, 1301, 1260, 1186, 1105, 1033, 763, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅FNO₃S⁺ [M+H]⁺ 486.1534, found 486.1538.

Ethyl (*E*)-3-(2-chlorophenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)propanoate (3ia)



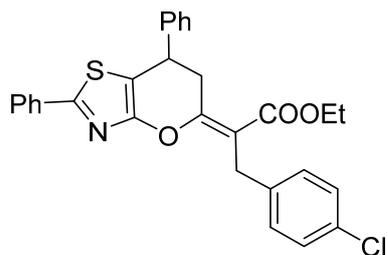
Prepared according to the general procedure as described above in 70% yield (35.0 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 88 – 92 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.91 – 7.84 (m, 2H), 7.43 – 7.38 (m, 3H), 7.38 – 7.29 (m, 4H), 7.29 – 7.24 (m, 2H), 7.15 – 7.04 (m, 3H), 4.41 – 4.30 (m, 1H), 4.19 – 3.96 (m, 4H), 3.84 – 3.73 (m, 1H), 3.72 – 3.59 (m, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 163.9, 158.2, 156.5, 141.6, 137.2, 133.8, 132.9, 130.0, 128.8, 128.6, 128.5, 127.3, 127.0, 126.7, 126.1, 125.4, 112.6, 108.7, 60.1, 36.9, 32.5, 29.2, 13.6; IR (film) ν_{max} 2900, 2379, 2345, 2331, 1705, 1639, 1601, 1557, 1502, 1455, 1443, 1362, 1300, 1264, 1191, 1108, 1069, 1038, 751, 700, 682, 655, 618, 504 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅ClNO₃S⁺ [M+H]⁺ 502.1238, found 502.1247.

Ethyl (*E*)-3-(3-chlorophenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene) propanoate (3ja)



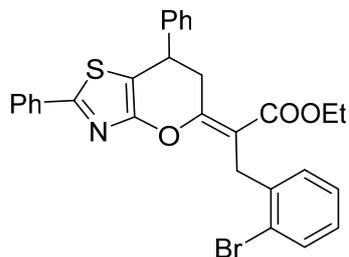
Prepared according to the general procedure as described above in 72% yield (36.0 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 102 – 106 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.86 (m, 2H), 7.49 – 7.39 (m, 3H), 7.39 – 7.28 (m, 4H), 7.27 – 7.17 (m, 5H), 4.39 – 4.30 (m, 1H), 4.14 – 4.04 (m, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.83 – 3.73 (m, 1H), 3.67 – 3.53 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 164.1, 158.3, 156.5, 142.3, 141.8, 133.7, 133.1, 130.2, 129.2, 128.8, 128.7, 128.6, 127.4, 127.1, 126.8, 125.9, 125.6, 113.9, 109.0, 60.4, 37.1, 32.7, 31.5, 13.9; IR (film) ν_{max} 2980, 2378, 2345, 1705, 1635, 1598, 1557, 1503, 1455, 1430, 1362, 1301, 1260, 1185, 1159, 1105, 1032, 763, 700, 681 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅ClNO₃S⁺ [M+H]⁺ 502.1238, found 502.1248.

Ethyl (*E*)-3-(4-chlorophenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene) propanoate (3ka)



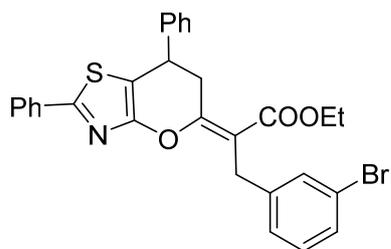
Prepared according to the general procedure as described above in 72% yield (36.0 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 75 – 81 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.94 – 7.87 (m, 2H), 7.47 – 7.40 (m, 3H), 7.36 – 7.28 (m, 3H), 7.25 – 7.18 (m, 6H), 4.33 (dd, *J* = 7.2, 5.6 Hz, 1H), 4.14 – 3.86 (m, 4H), 3.81 – 3.71 (m, 1H), 3.64 – 3.54 (dd, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.1, 164.0, 157.9, 156.4, 141.6, 138.5, 132.9, 131.2, 130.0, 129.7, 128.6, 128.5, 127.9, 127.3, 126.9, 125.5, 114.0, 108.8, 60.2, 36.9, 32.6, 31.0, 13.7; IR (film) ν_{max} 2981, 2365, 2345, 1705, 1639, 1557, 1491, 1455, 1362, 1259, 1185, 1106, 1070, 1016, 804, 763, 738, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅ClNO₃S⁺ [M+H]⁺ 502.1238, found 502.1247.

Ethyl (*E*)-3-(2-bromophenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene) propanoate (3la)



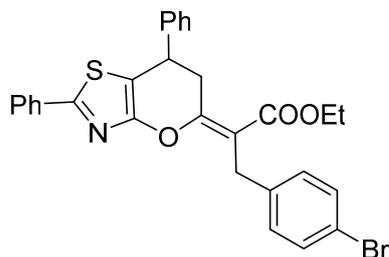
Prepared according to the general procedure as described above in 70% yield (38.2 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 79 – 86 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.91 – 7.81 (m, 2H), 7.58 – 7.51 (m, 1H), 7.43 – 7.40 (m, 3H), 7.39 – 7.28 (m, 4H), 7.27 – 6.99 (m, 4H), 4.42-4.32 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.07 – 3.98 (m, 2H), 3.85 – 3.75 (m, 1H), 3.74 – 65 (m, 1H), 1.07 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 164.1, 158.4, 156.6, 141.8, 139.0, 133.0, 132.3, 130.1, 128.8, 128.7, 128.7, 127.4, 127.2, 127.0, 125.6, 124.5, 112.9, 108.8, 60.3, 37.0, 32.7, 32.1, 13.8; IR (film) ν_{max} 2982, 2870, 2393, 2346, 2321, 1705, 1639, 1601, 1557, 1455, 1427, 1362, 1296, 1263, 1191, 1106, 1068, 1027, 748, 699, 681, 656, 641 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅BrNO₃S⁺ [M+H]⁺ 546.0733, found 546.0744.

Ethyl (*E*)-3-(3-bromophenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene) propanoate (3ma)



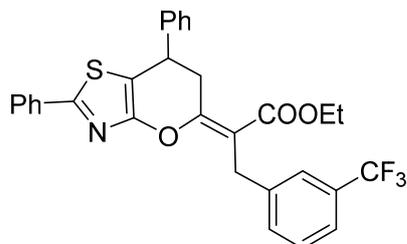
Prepared according to the general procedure as described above in 71% yield (38.8 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 110 – 117 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.87 (m, 2H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.38 – 7.30 (m, 4H), 7.27 – 7.09 (m, 4H), 4.39 – 4.29 (m, 1H), 4.16 – 4.06 (m, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.83 – 3.74 (m, 1H), 3.67 – 3.57 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 164.1, 158.3, 156.5, 142.6, 141.8, 133.1, 131.6, 130.2, 129.5, 128.8, 128.8, 128.7, 127.4, 127.3, 127.1, 125.7, 122.0, 113.9, 109.0, 60.4, 37.1, 32.7, 31.5, 13.9; IR (film) ν_{max} 2870, 2380, 2345, 1704, 1594, 1557, 1455, 1426, 1361, 1302, 1264, 1182, 1159, 1104, 1069, 1033, 763, 746, 699, 680, 656 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅BrNO₃S⁺ [M+H]⁺ 546.0733, found 546.0745.

Ethyl (*E*)-3-(4-bromophenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)propanoate (3na)



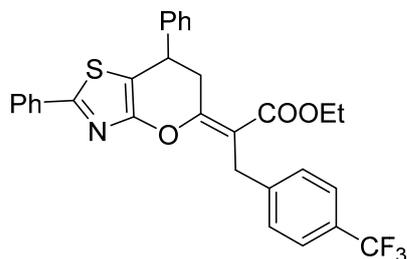
Prepared according to the general procedure as described above in 72% yield (39.3 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 73 – 81 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.97 – 7.87 (m, 2H), 7.60 – 7.50 (m, 2H), 7.50 – 7.39 (m, 5H), 7.38 – 7.28 (m, 3H), 7.27 – 7.20 (m, 2H), 4.39 – 4.31 (m, 1H), 4.16 – 3.98 (m, 4H), 3.85 – 3.75 (m, 1H), 3.71 – 3.61 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.1, 164.0, 158.0, 156.4, 141.6, 139.1, 132.9, 130.8, 130.1, 130.0, 128.6, 128.5, 127.3, 127.0, 125.5, 119.3, 113.9, 108.8, 60.2, 36.9, 32.6, 31.0, 13.8; IR (film) ν_{\max} 2983, 2366, 2345, 1706, 1639, 1557, 1502, 1455, 1420, 1362, 1326, 1278, 1257, 1162, 1109, 1067, 1019, 951, 860, 819, 763, 739, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅BrNO₃S⁺ [M+H]⁺ 546.0733, found 546.0744.

Ethyl (*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-(3-(trifluoromethyl) phenyl)propanoate (3oa)



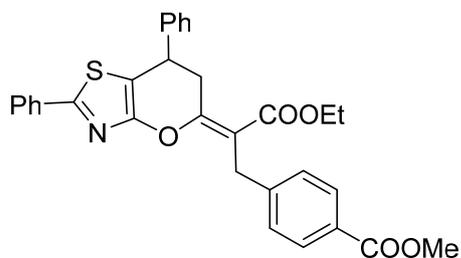
Prepared according to the general procedure as described above in 70% yield (37.5 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 118 – 126 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.87 (m, 2H), 7.61 (s, 1H), 7.53 – 7.41 (m, 5H), 7.40 – 7.28 (m, 4H), 7.27 – 7.18 (m, 2H), 4.38 – 4.31 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.07 – 3.98 (m, 2H), 3.84 – 3.75 (m, 1H), 3.66 – 3.57 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.1, 164.2, 158.5, 156.5, 141.8, 141.2, 133.1, 132.0, 130.20 (q, *J* = 31.9 Hz), 130.17, 128.8, 128.6, 128.4, 127.4, 127.1, 125.6, 125.4 (q, *J* = 3.78 Hz), 122.6 (q, *J* = 3.78 Hz), 113.8, 109.0, 60.4, 37.1, 32.7, 31.6, 13.8; IR (film) ν_{\max} 2982, 2345, 1706, 1637, 1557, 1494, 1452, 1362, 1332, 1276, 1257, 1164, 1122, 1074, 1034, 964, 763, 745, 701, 658 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₅F₃NO₃S⁺ [M+H]⁺ 536.1502, found 536.1507.

Ethyl (*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-(4-(trifluoromethyl) phenyl)propanoate (3pa)



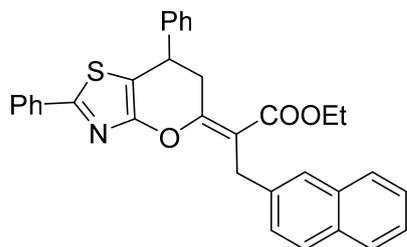
Prepared according to the general procedure as described above in 70% yield (37.5 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 56 – 61 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.87 (m, 2H), 7.55 – 7.48 (m, 2H), 7.48 – 7.37 (m, 5H), 7.37 – 7.29 (m, 3H), 7.26 – 7.18 (m, 2H), 4.41 – 4.31 (m, 1H), 4.17 – 3.94 (m, 4H), 3.84 – 3.74 (m, 1H), 3.69 – 3.58 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 164.2, 158.5, 156.5, 144.4, 141.7, 133.0, 130.2, 128.8, 128.7, 128.6, 127.4, 127.1, 125.6, 124.9 (q, *J* = 3.7 Hz), 113.6, 109.0, 60.4, 37.0, 32.7, 31.6, 13.8; IR (film) ν_{max} 2982, 2345, 1706, 1640, 1557, 1502, 1455, 1419, 1362, 1326, 1278, 1258, 1163, 1109, 1067, 1020, 951, 763, 740, 700 cm⁻¹; HRMS (ESI) calcd for C₃₀H₂₅F₃NO₃S⁺ [M+H]⁺ 536.1502, found 536.1509.

Methyl (*E*)-4-(2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-ethoxy-3-oxopropyl)benzoate (3qa)



Prepared according to the general procedure as described above in 69% yield (36.3 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 122 – 126 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.98 – 7.84 (m, 4H), 7.45 – 7.38 (m, 3H), 7.38 – 7.28 (m, 5H), 7.25 – 7.18 (m, 2H), 4.37 – 4.29 (m, 1H), 4.13 – 3.92 (m, 4H), 3.89 (s, 3H), 3.82 – 3.72 (m, 1H), 3.68 – 3.58 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 167.0, 164.1, 158.4, 156.5, 145.8, 141.7, 133.0, 130.2, 129.4, 128.8, 128.6, 128.4, 127.7, 127.4, 127.1, 125.6, 113.6, 109.0, 60.3, 51.7, 37.0, 32.7, 31.8, 13.9; IR (film) ν_{max} 2982, 2951, 1719, 1639, 1610, 1557, 1501, 1455, 1435, 1361, 1281, 1180, 1106, 1069, 1021, 965, 865, 809, 763, 701 cm⁻¹; HRMS (ESI) calcd for C₃₁H₂₈NO₅S⁺ [M+H]⁺ 526.1683, found 526.1697.

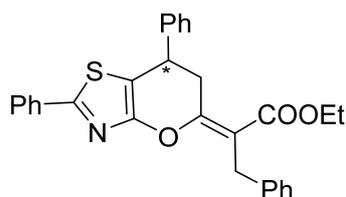
Ethyl (E)-2-(2,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-ylidene)-3-(naphthalen-2-yl) propanoate (3ra)



Prepared according to the general procedure as described above in 63% yield (32.6 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 118 – 124 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.87 (m, 2H), 7.83 – 7.69 (m, 4H), 7.49 – 7.37 (m, 6H), 7.35 – 7.27 (m, 3H), 7.23 (dt, *J* = 7.0, 2.4 Hz, 2H), 4.34 (dd, *J* = 7.4, 5.6 Hz, 1H), 4.25 – 4.01 (m, 4H), 3.81 (dd, *J* = 14.9, 5.6 Hz, 1H), 3.65 – 3.54 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 163.9, 157.6, 156.6, 141.8, 137.5, 133.3, 133.0, 131.8, 130.0, 128.6, 128.5, 127.32, 127.25, 127.2, 127.0, 126.5, 125.5, 125.3, 124.7, 114.4, 108.8, 60.2, 37.1, 32.6, 31.8, 13.7; IR (film) ν_{\max} 3057, 2979, 1704, 1636, 1601, 1555, 1501, 1454, 1361, 1284, 1258, 1184, 1102, 1069, 1031, 950, 860, 795, 762, 700, 474 cm⁻¹; HRMS (ESI) calcd for C₃₃H₂₈NO₃S⁺ [M+H]⁺ 518.1784, found 518.1788.

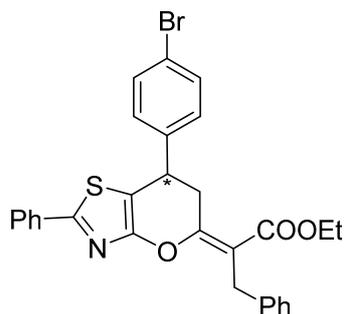
Characterization Data for the Chiral Products (+)-3

(+)-Ethyl (E)-2-(2,7-diphenyl-6,7-dihydro-5H-pyrano[2,3-d]thiazol-5-ylidene)-3-phenyl propanoate ((+)-3aa)



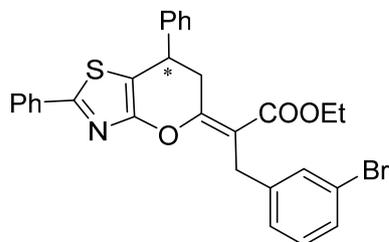
Prepared according to the general procedure as described above in 80% yield (18.8 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 82 – 90 °C; [α]_D²⁵ = + 7.2 (*c* 1.16, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.86 (m, 2H), 7.48 – 7.40 (m, 3H), 7.35 – 7.29 (m, 5H), 7.28 – 7.15 (m, 5H), 4.38 – 4.28 (q, *J* = 7.1 Hz, 1H), 4.14 – 4.04 (m, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.86 – 3.76 (m, 1H), 3.61 – 3.51 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.6, 164.0, 157.6, 156.7, 141.9, 140.1, 133.1, 130.1, 128.8, 128.6, 128.5, 128.0, 127.4, 127.2, 125.7, 125.5, 114.6, 109.0, 60.3, 37.2, 32.7, 31.7, 13.9; IR (film) ν_{\max} 3029, 2981, 2378, 2345, 1704, 1632, 1601, 1556, 1495, 1454, 1361, 1275, 1186, 1155, 1104, 1032, 763, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₆NO₃S⁺ [M+H]⁺ 468.1628, found 468.1638. HPLC analysis: 98% ee (R&C RC-OD, 10% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), *t*_R = 6.2 min (minor), 10.1 min (major).

(+)-Ethyl (*E*)-2-(7-(4-bromophenyl)-2-phenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)-3-phenylpropanoate ((+)-3aj)



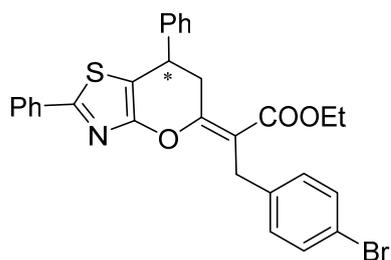
Prepared according to the general procedure as described above in 86% yield (23.4 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 57 – 65 °C; $[\alpha]_D^{25} = +17.8$ (*c* 1.16, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.95 – 7.88 (m, 2H), 7.47 – 7.40 (m, 5H), 7.31 – 7.23 (m, 4H), 7.21 – 7.14 (m, 1H), 7.11 – 7.05 (m, 2H), 4.35 – 4.26 (m, 1H), 4.15 – 3.91 (m, 4H), 3.74 – 3.56 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 164.1, 156.9, 156.6, 140.8, 139.8, 132.8, 131.6, 130.1, 128.7, 128.6, 128.3, 127.8, 125.5, 125.5, 121.1, 115.0, 107.78, 60.2, 36.5, 32.3, 31.5, 13.7; IR (film) ν_{\max} 3028, 2980, 1704, 1640, 1556, 1489, 1454, 1407, 1361, 1274, 1182, 1105, 1074, 1031, 1011, 953, 880, 822, 762, 737, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅BrNO₃S⁺ [M+H]⁺ 546.0733, found 546.0743. HPLC analysis: 95% ee (R&C RC-OD, 10% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), *t*_R = 7.8 min (minor), 12.4 min (major).

(+)-Ethyl (*E*)-3-(3-bromophenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene) Propanoate ((+)-3ma)



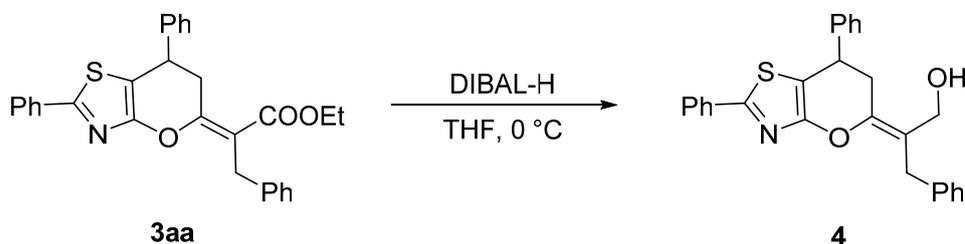
Prepared according to the general procedure as described above in 75% yield (20.4 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford an orange solid. mp = 110 – 117 °C; $[\alpha]_D^{25} = +21.6$ (*c* 1.16, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.87 (m, 2H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.38 – 7.30 (m, 4H), 7.27 – 7.09 (m, 4H), 4.39 – 4.29 (m, 1H), 4.16 – 4.06 (m, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.83 – 3.74 (m, 1H), 3.67 – 3.57 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 164.1, 158.3, 156.5, 142.6, 141.8, 133.1, 131.6, 130.2, 129.5, 128.8, 128.8, 128.7, 127.4, 127.3, 127.1, 125.7, 122.0, 113.9, 109.0, 60.4, 37.1, 32.7, 31.5, 13.9; IR (film) ν_{\max} 2870, 2380, 2345, 1704, 1594, 1557, 1455, 1426, 1361, 1302, 1264, 1182, 1159, 1104, 1069, 1033, 763, 746, 699, 680, 656 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅BrNO₃S⁺ [M+H]⁺ 546.0733, found 546.0745. HPLC analysis: 99% ee (R&C RC-OD, 10% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), *t*_R = 6.9 min (minor), 13.1 min (major).

(+)-Ethyl (*E*)-3-(4-bromophenyl)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene) Propanoate ((+)-3na**)**



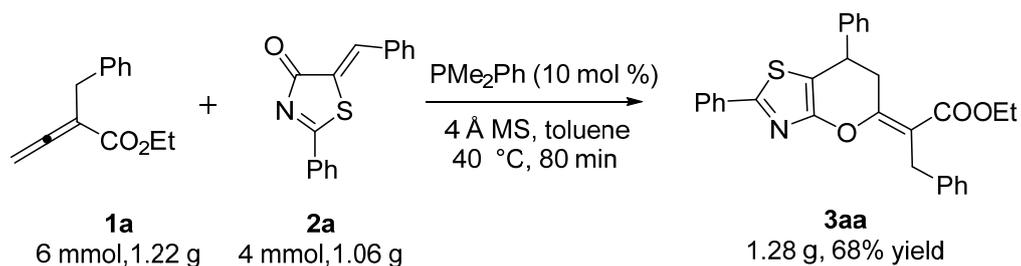
Prepared according to the general procedure as described above in 82% yield (22.3 mg). It was purified by flash chromatography (5.0% EtOAc/PE) to afford a rufous solid. mp = 73 – 81 °C; $[\alpha]_D^{25} = +22.6$ (*c* 1.16, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.97 – 7.87 (m, 2H), 7.60 – 7.50 (m, 2H), 7.50 – 7.39 (m, 5H), 7.38 – 7.28 (m, 3H), 7.27 – 7.20 (m, 2H), 4.39 – 4.31 (m, 1H), 4.16 – 3.98 (m, 4H), 3.85 – 3.75 (m, 1H), 3.71 – 3.61 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.1, 164.0, 158.0, 156.4, 141.6, 139.1, 132.9, 130.8, 130.1, 130.0, 128.6, 128.5, 127.3, 127.0, 125.5, 119.3, 113.9, 108.8, 60.2, 36.9, 32.6, 31.0, 13.8; IR (film) ν_{\max} 2983, 2366, 2345, 1706, 1639, 1557, 1502, 1455, 1420, 1362, 1326, 1278, 1257, 1162, 1109, 1067, 1019, 951, 860, 819, 763, 739, 700 cm⁻¹; HRMS (ESI) calcd for C₂₉H₂₅BrNO₃S⁺ [M+H]⁺ 546.0733, found 546.0744. HPLC analysis: 97% ee (R&C RC-OD, 10% isopropanol/hexane, 1.0 mL/min, UV: 254 nm), *t_R* = 6.5 min (minor), 11.8 min (major).

Transformations of Product 3aa



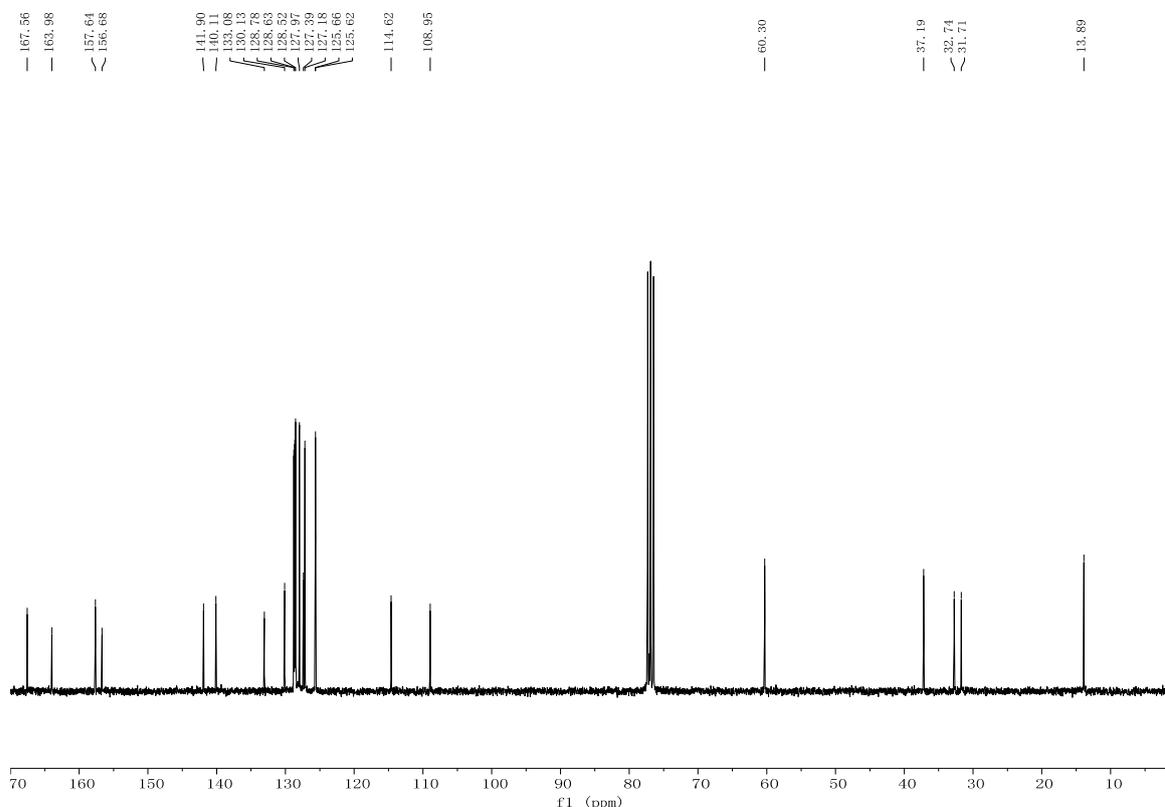
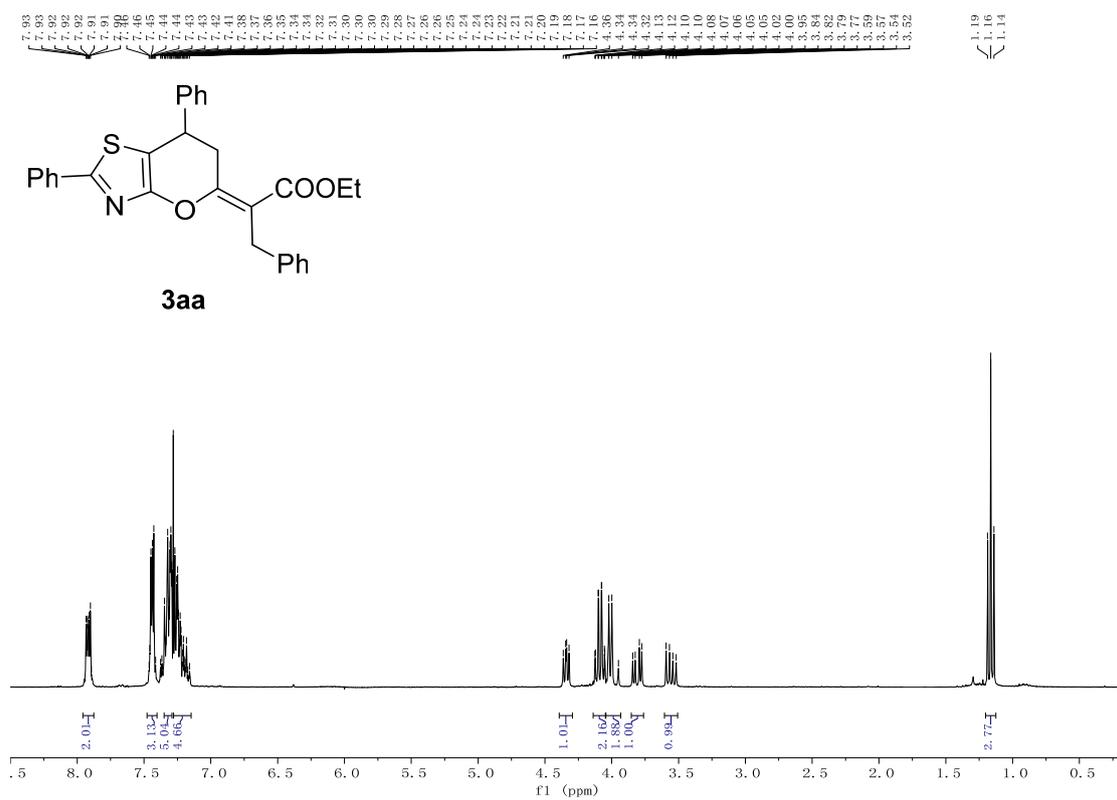
Under N₂ atmosphere, 1 mL of DIBAL-H (1M in Hexane, 10.0 equiv) was dissolved in 1mL of THF, then solution of the cycloaddition product **3aa** (46.8 mg, 0.1 mmol) was dissolved in 1mL of THF was added dropwise. The resulting mixture was stirred at 0 °C for 10 min. The residue was purified through flash column chromatography (30.0% EtOAc/PE) to afford the corresponding product **4** as a rufous solid (32.0 mg, 75% yield). mp = 67 – 71 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.97 – 7.87 (m, 2H), 7.45 – 7.40 (m, 3H), 7.35 – 7.27 (m, 5H), 7.26 – 7.16 (m, 5H), 4.45 – 4.25 (m, 1H), 3.98 – 3.54 (m, 4H), 3.10 (dd, *J* = 14.0, 5.5 Hz, 1H), 2.96 (dd, *J* = 14.1, 5.4 Hz, 1H), 1.27 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 163.9, 158.2, 145.0, 142.6, 139.6, 133.1, 129.9, 128.7, 128.6, 128.4, 128.1, 127.2, 127.1, 127.0, 125.7, 125.5, 120.4, 106.4, 60.3, 37.8, 33.0, 31.9; IR (film) ν_{\max} 3062, 3029, 2922, 1717, 1682, 1601, 1553, 1495, 1454, 1366, 1264, 1180, 1074, 1030, 763, 737, 700 cm⁻¹; HRMS (ESI) calcd for C₂₇H₂₄NO₂S⁺ [M+H]⁺ 426.1483, found 426.1521.

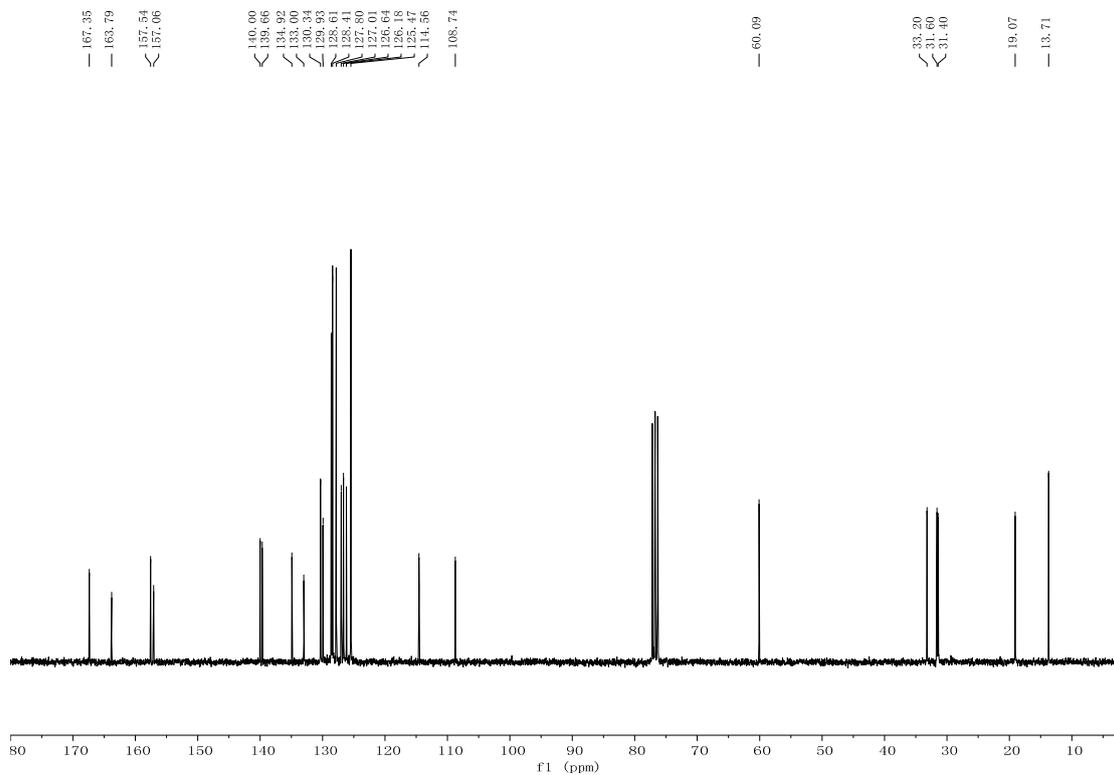
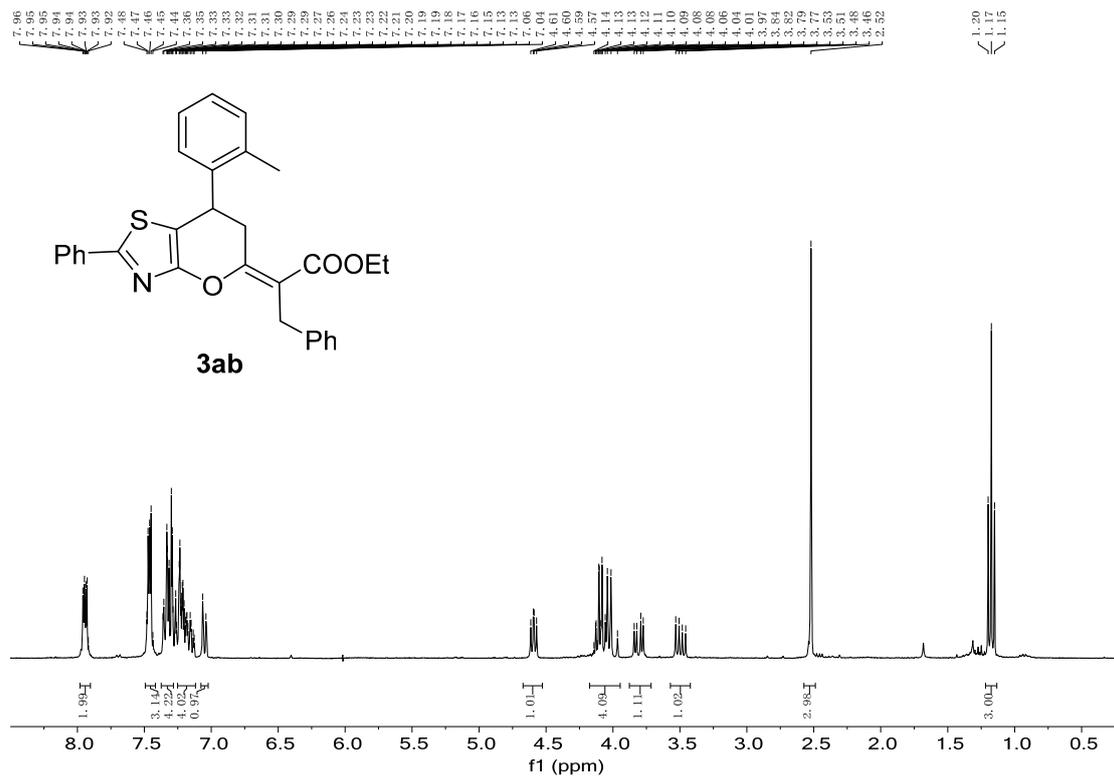
Preparation on the Gram Scale

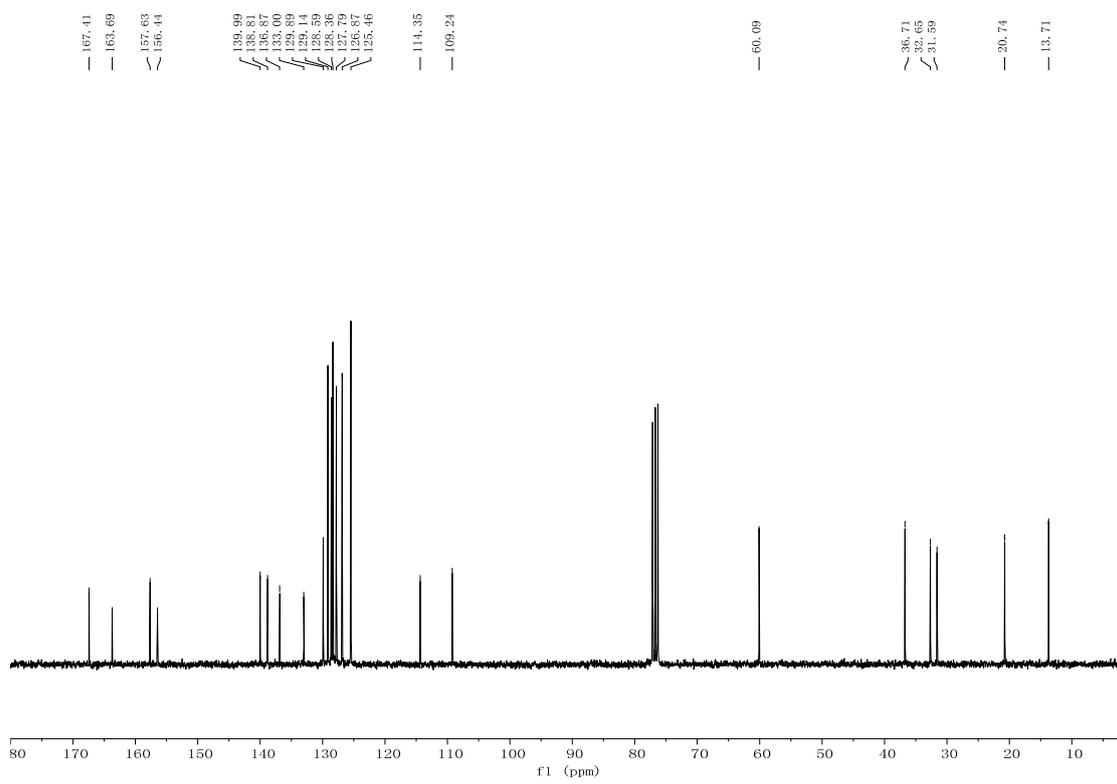
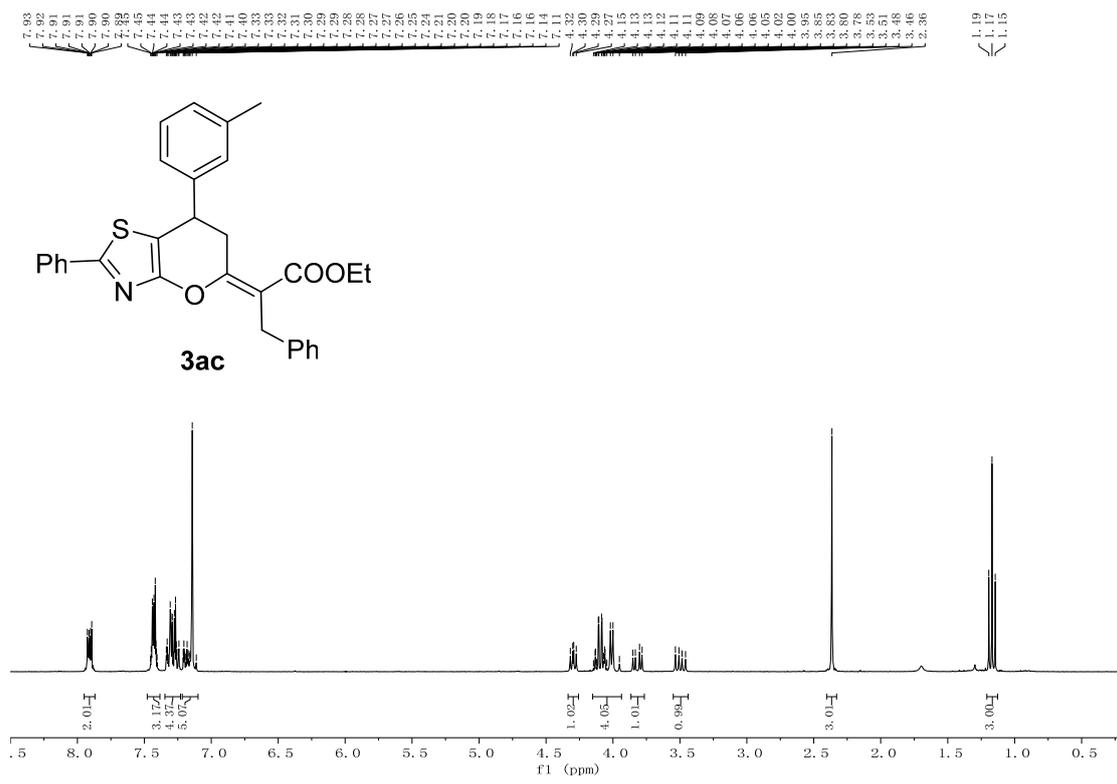


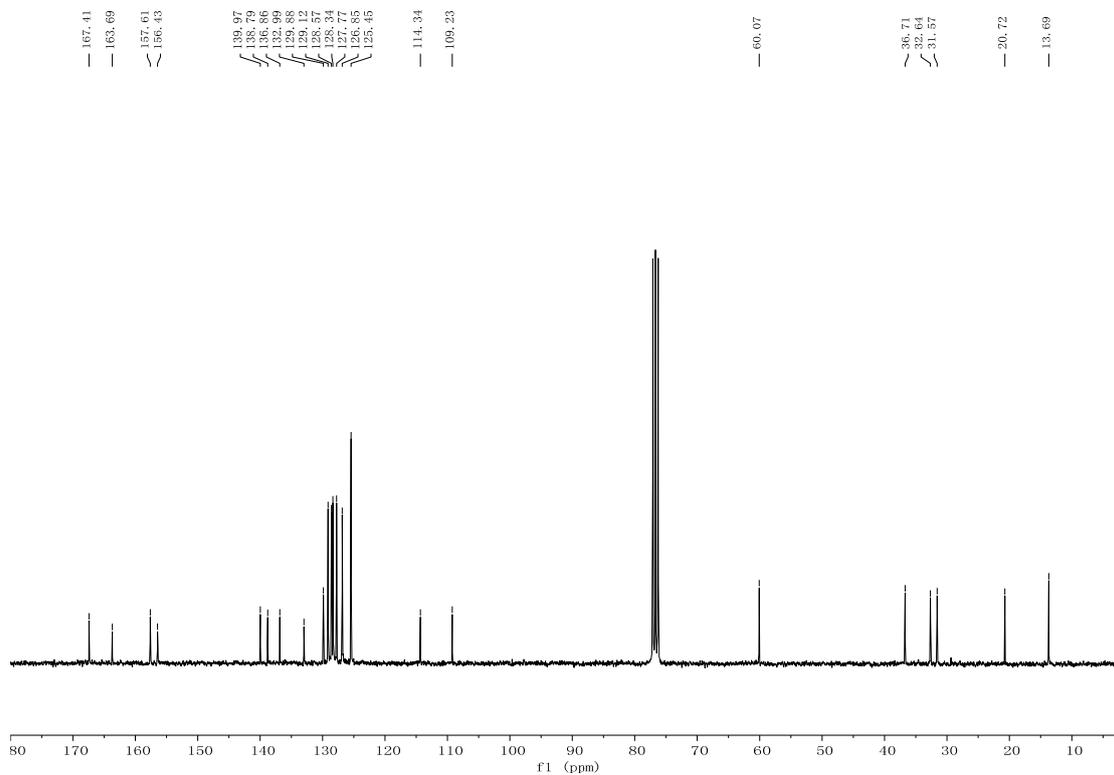
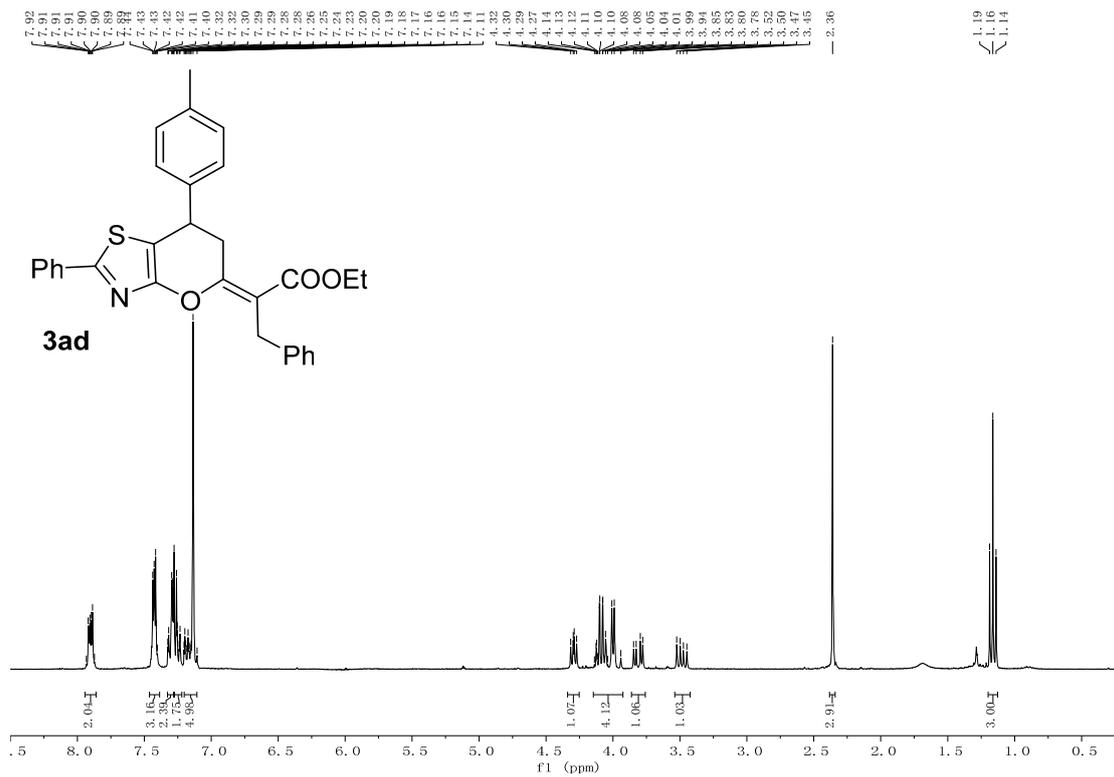
Under nitrogen atmosphere, thiazolone-derived alkene **2a** (1.06 g, 4.0 mmol) and the additive 4 Å MS (4.0 g) in 40.0 mL of toluene, α -benzyl allenotes **1a** (1.22 g, 6.0 mmol) followed with catalyst PMe_2Ph (55.2 mg, 0.40 mmol) were additive in a 100 mL-Shrek tube at 40 °C. The mixture was stirred until starting material was completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (5.0% EtOAc/hexane) to afford the orange product **3aa** (1.28 g, 68% yield).

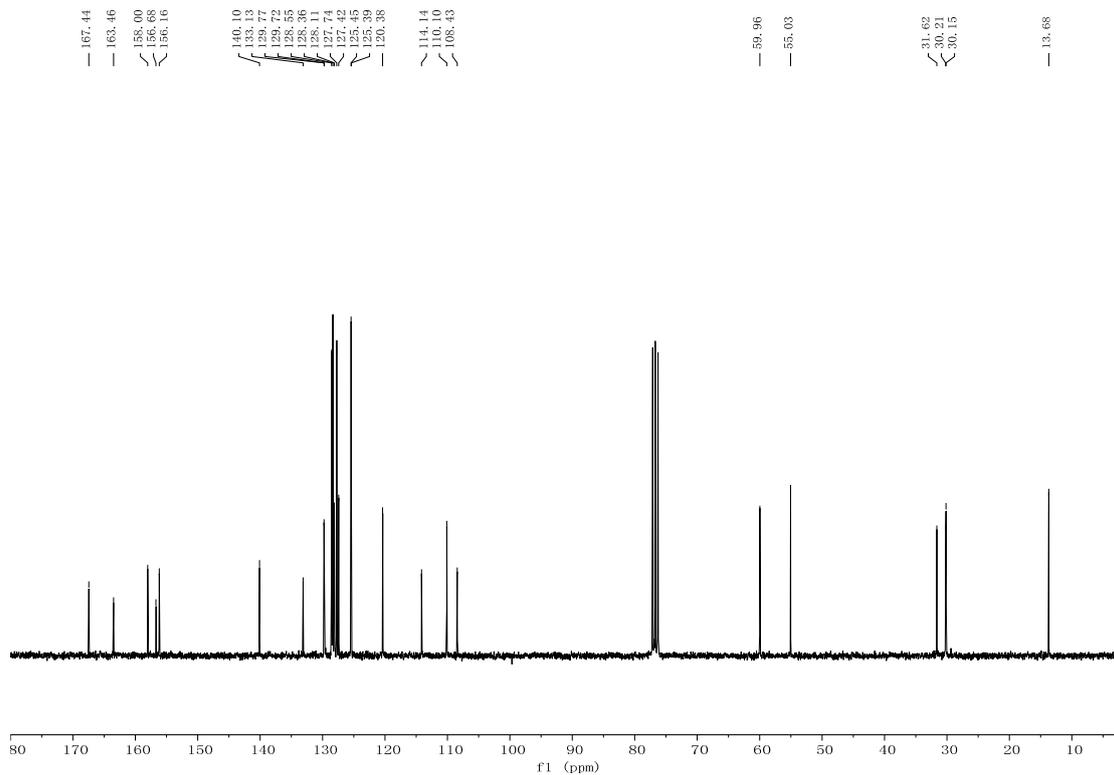
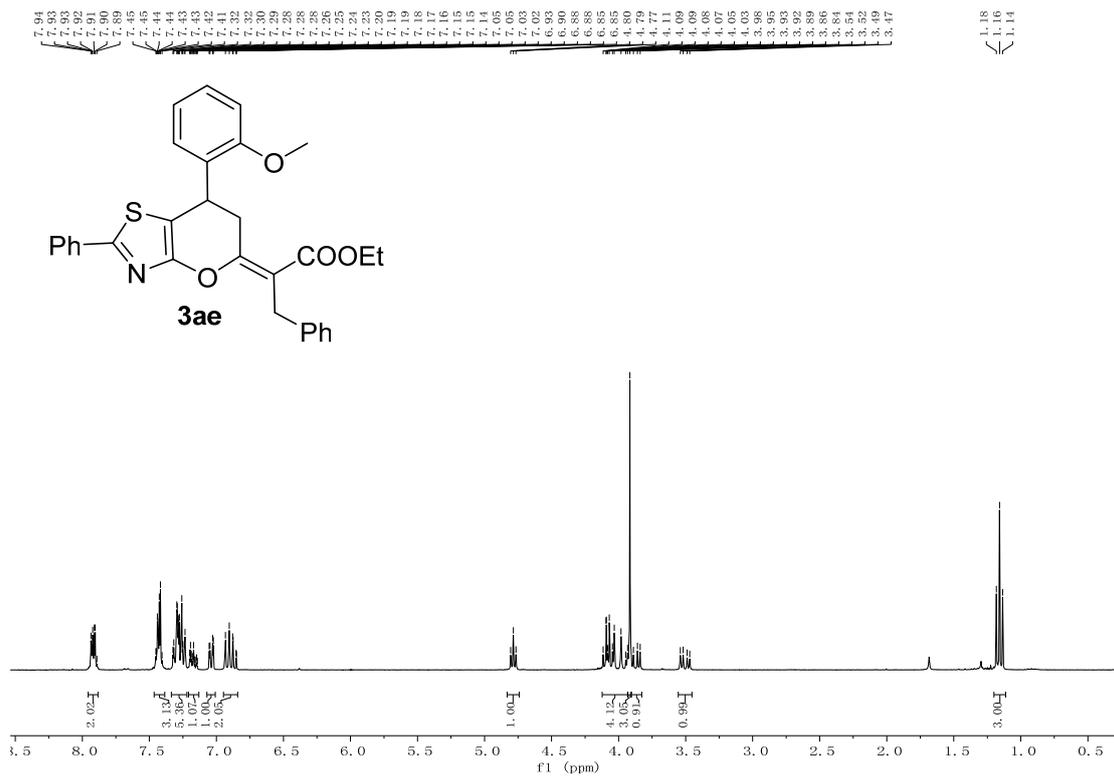
Copies of ^1H and ^{13}C NMR Spectra

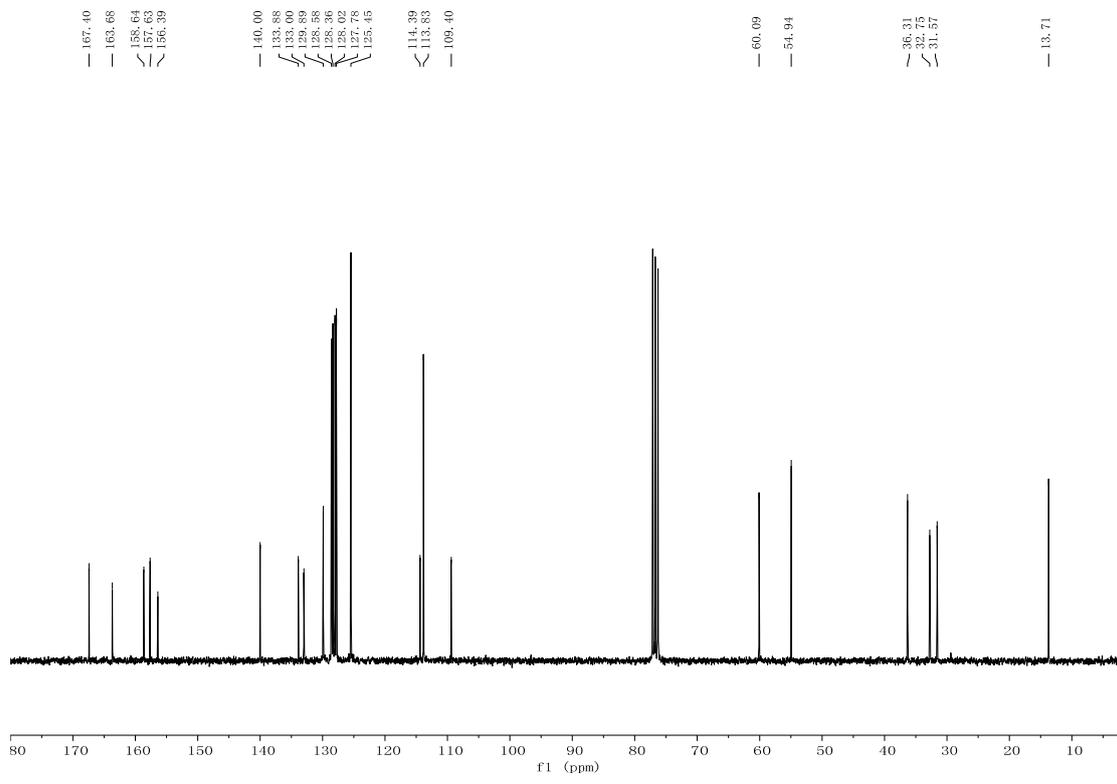
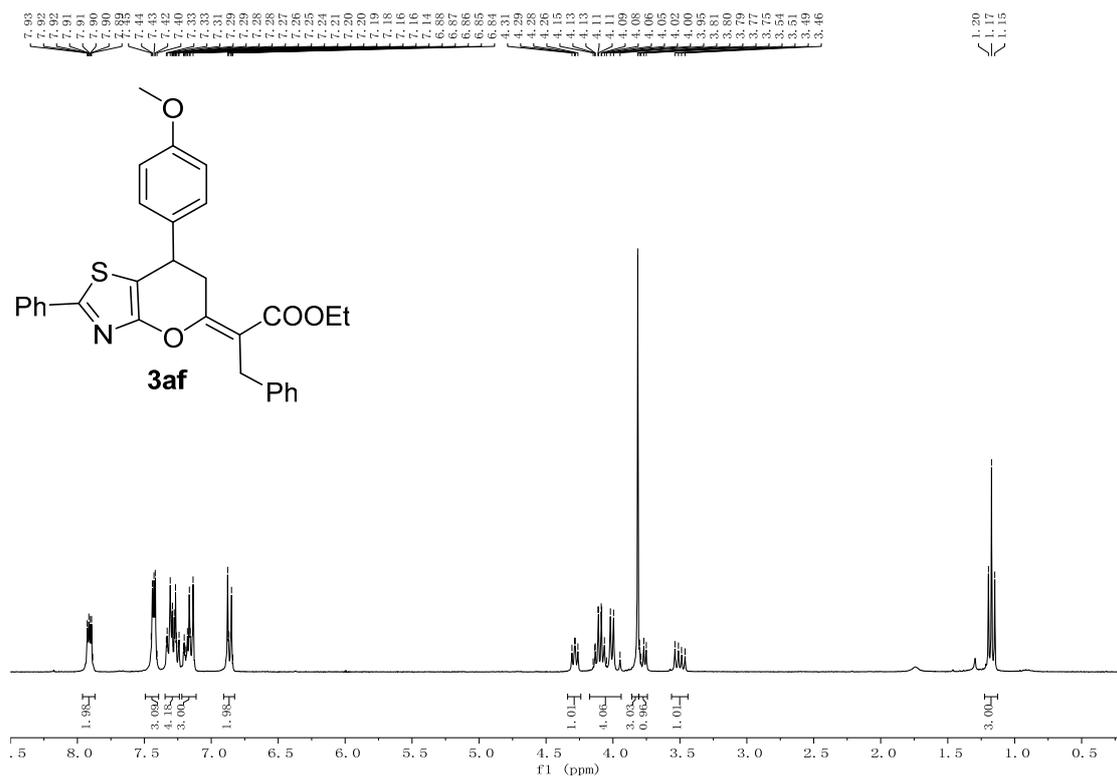


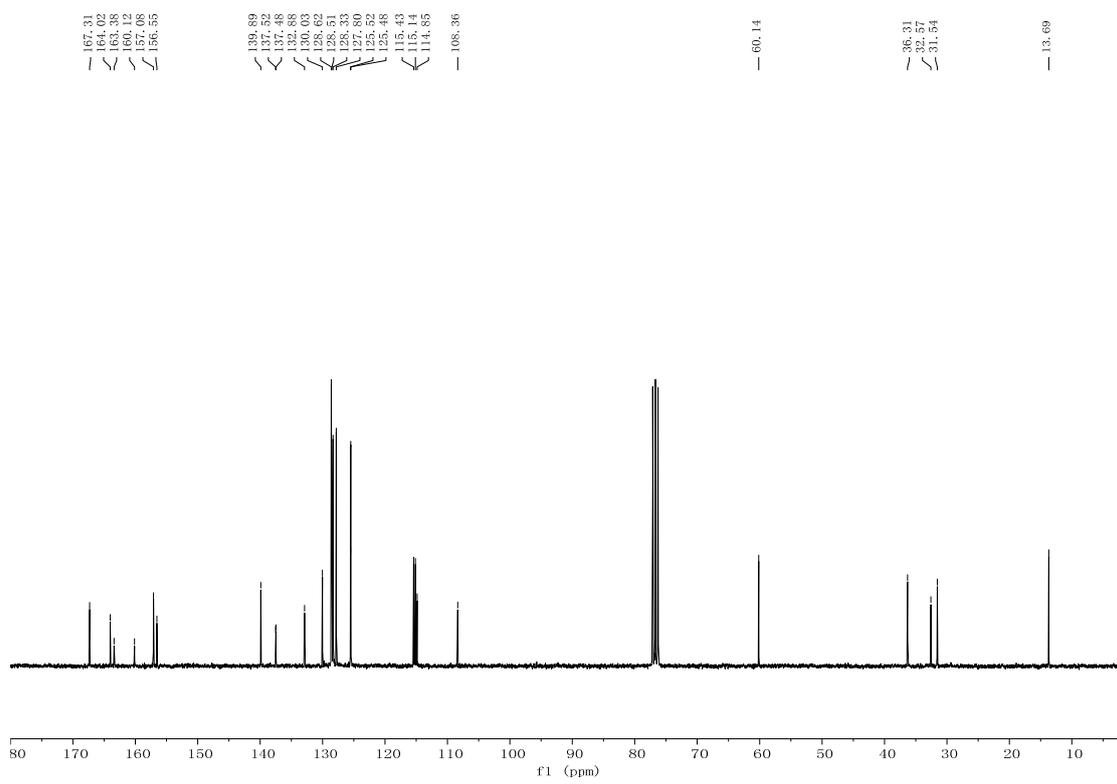
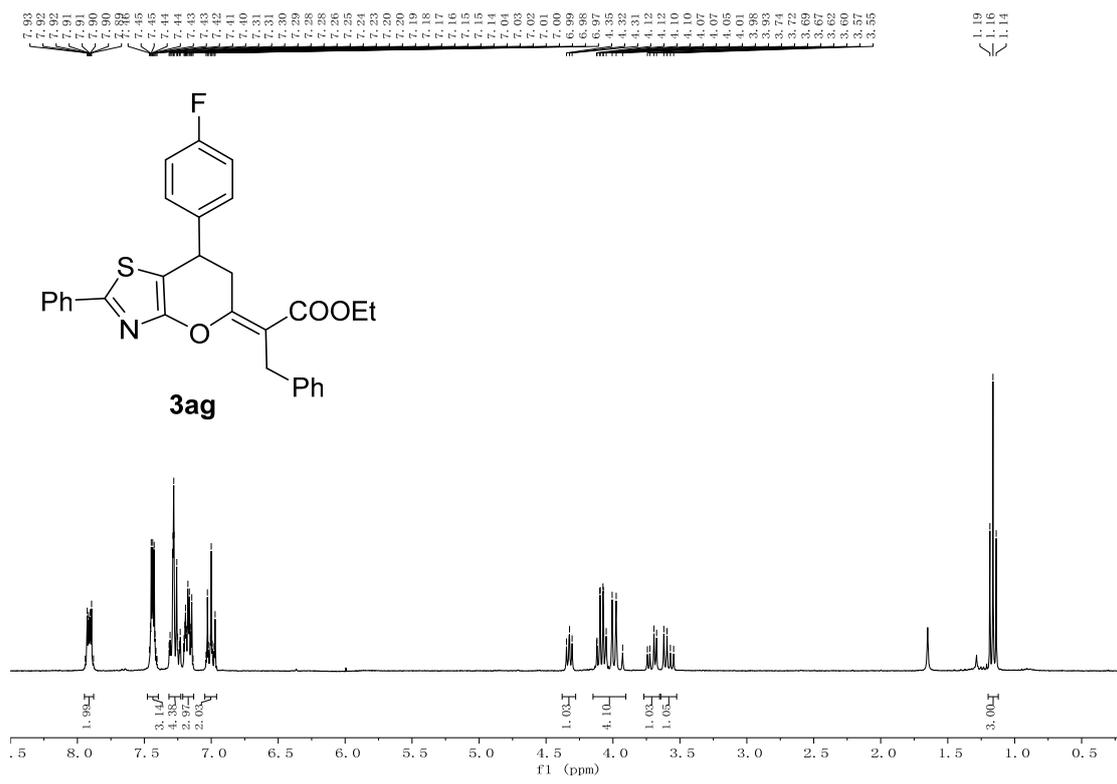


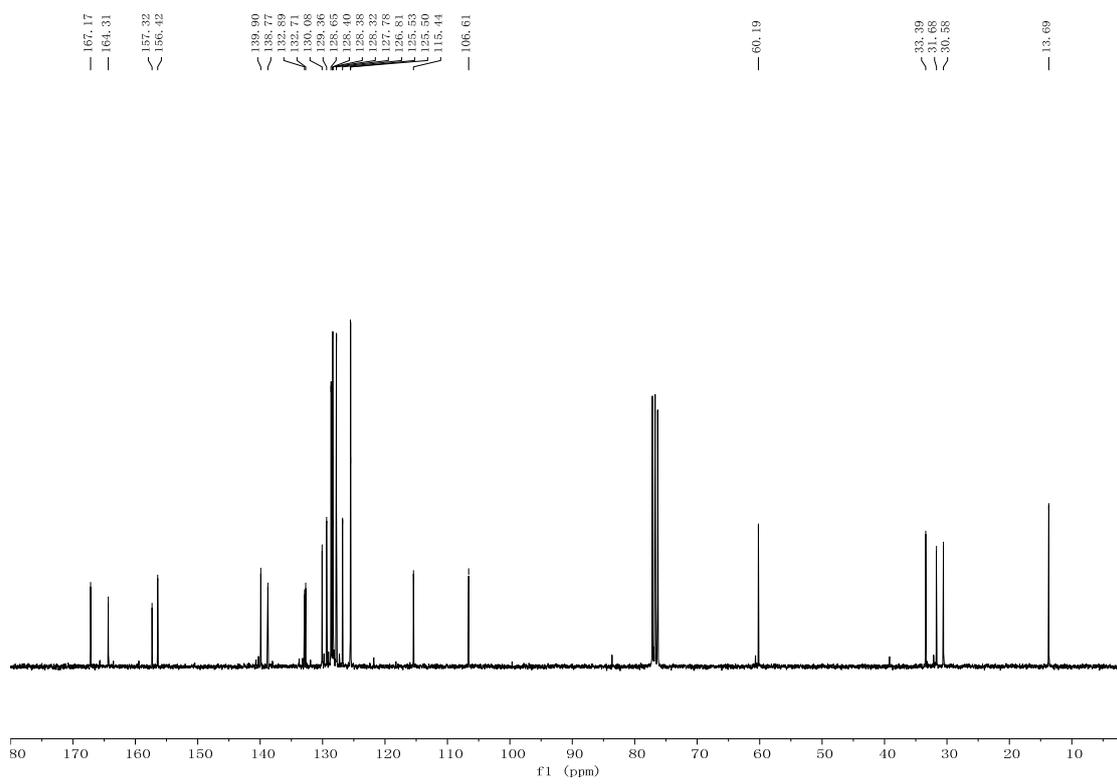
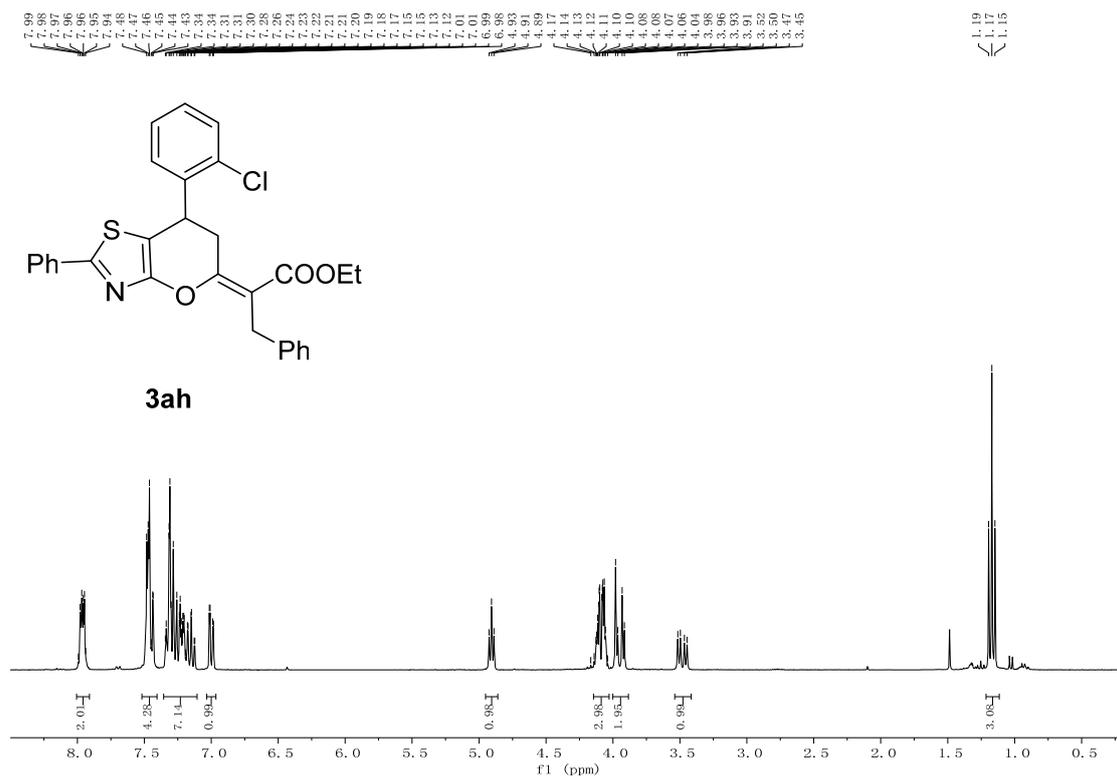


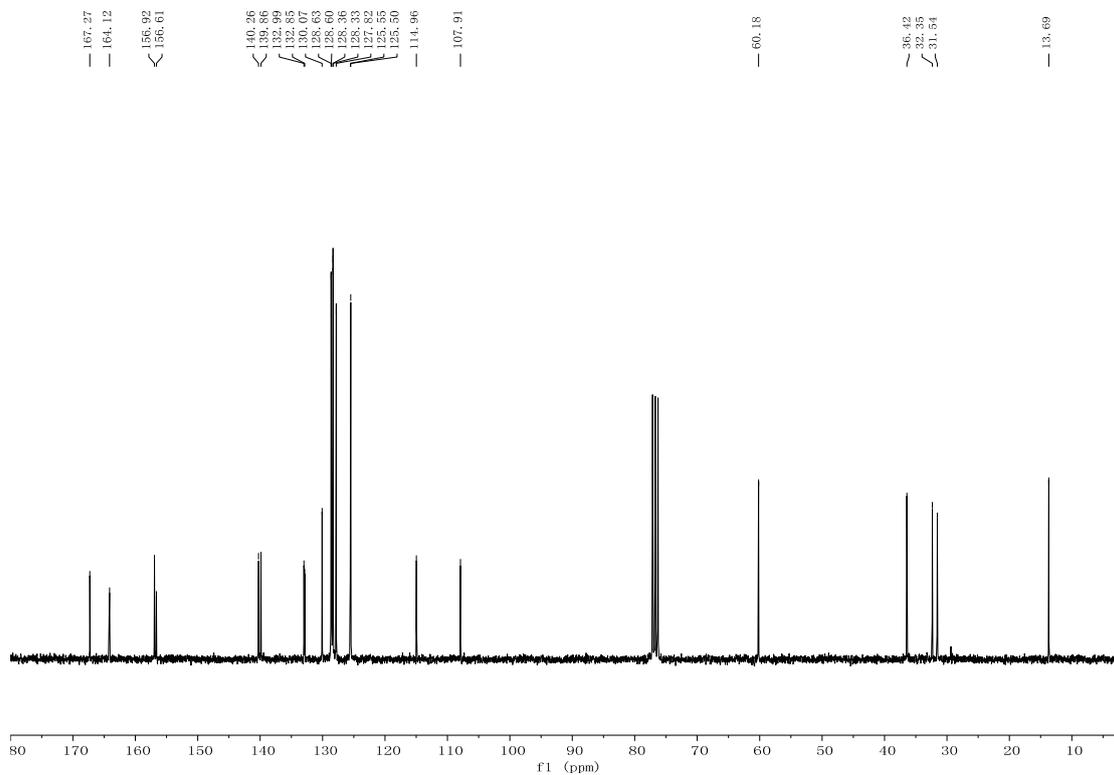
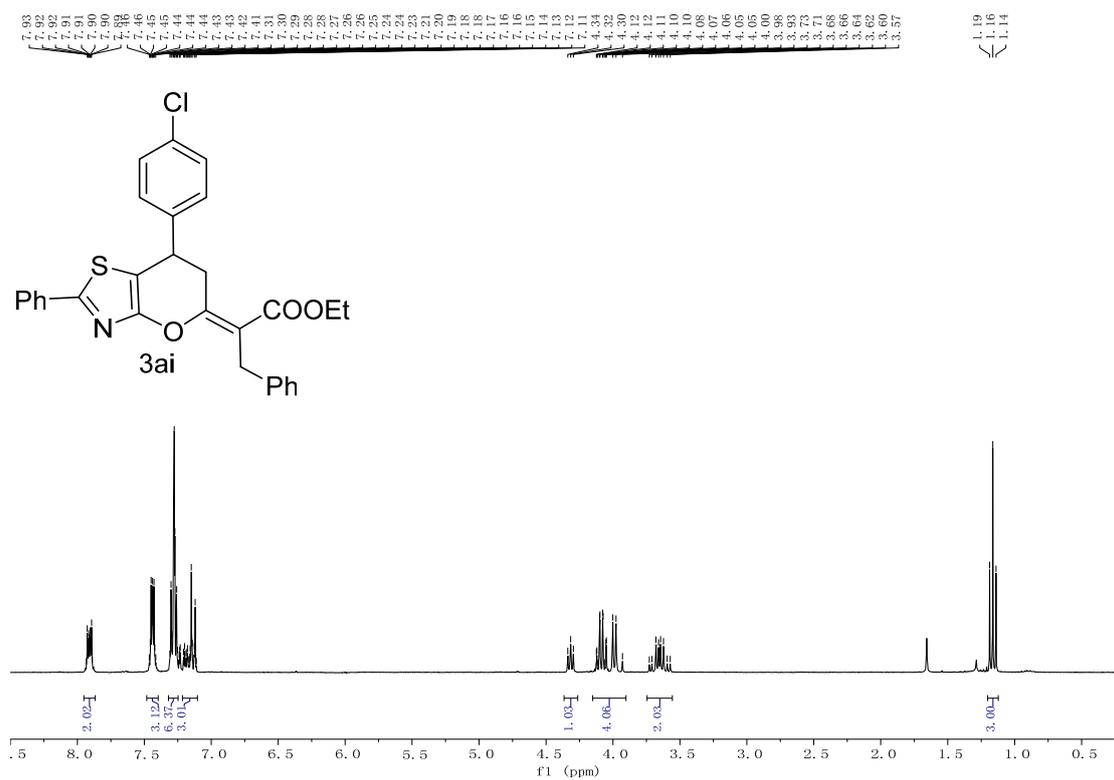


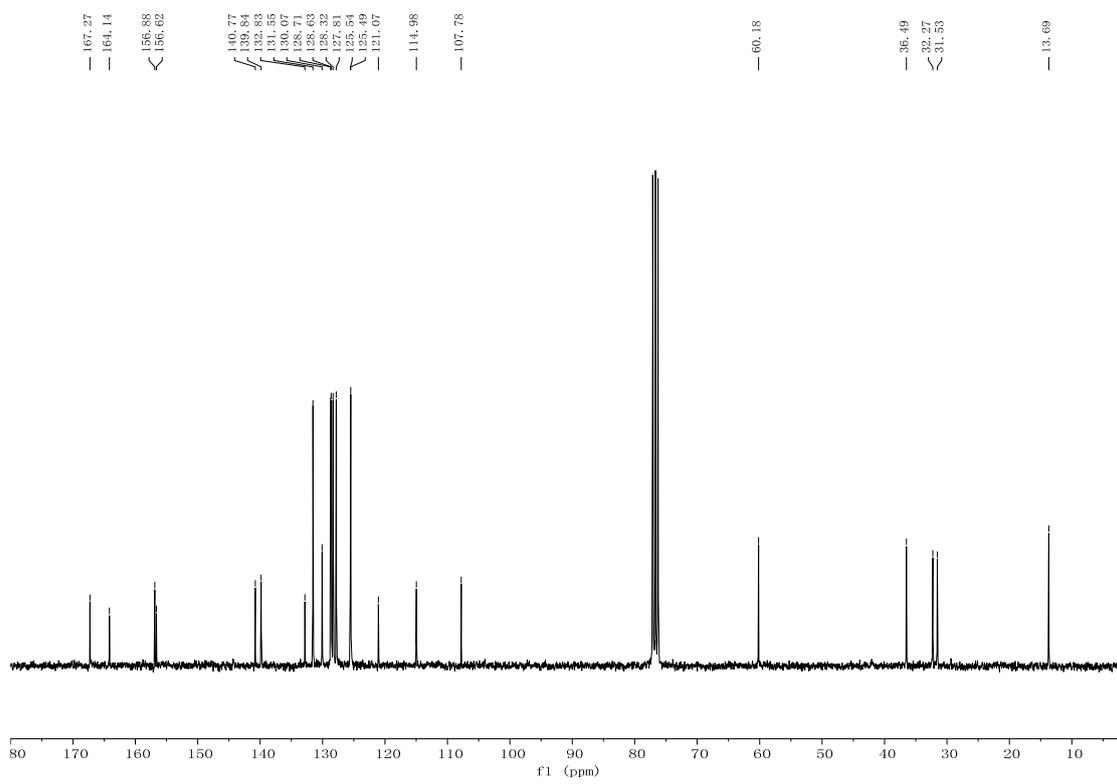
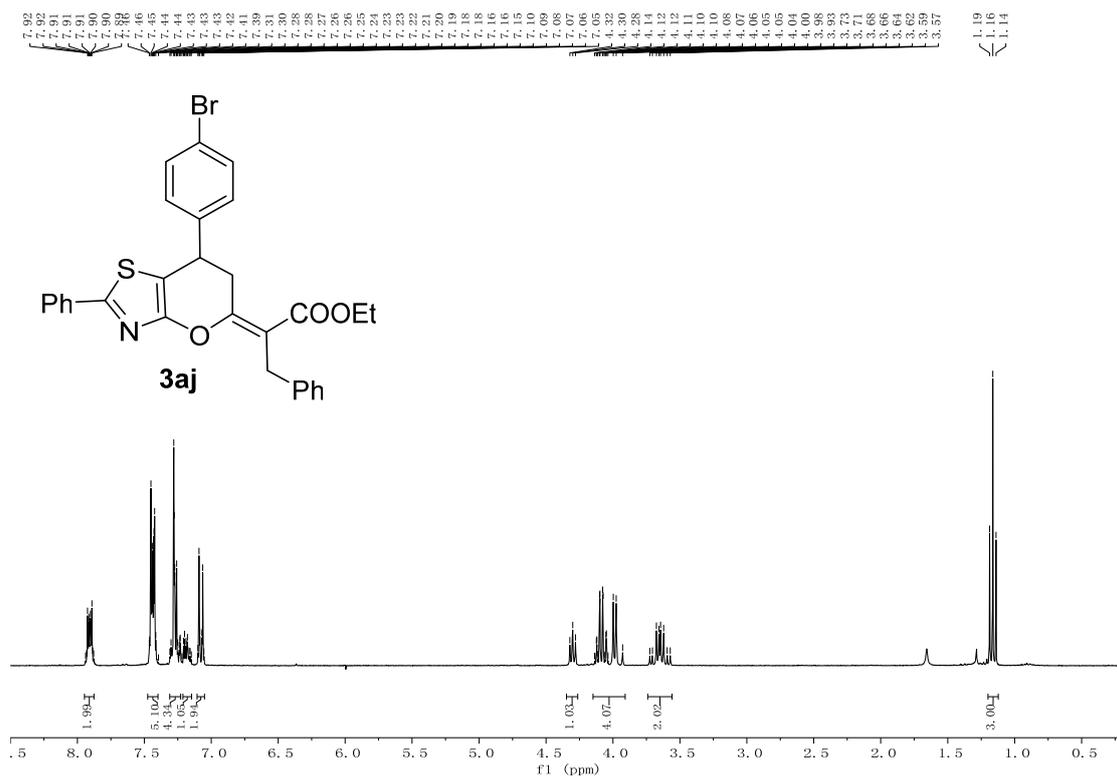


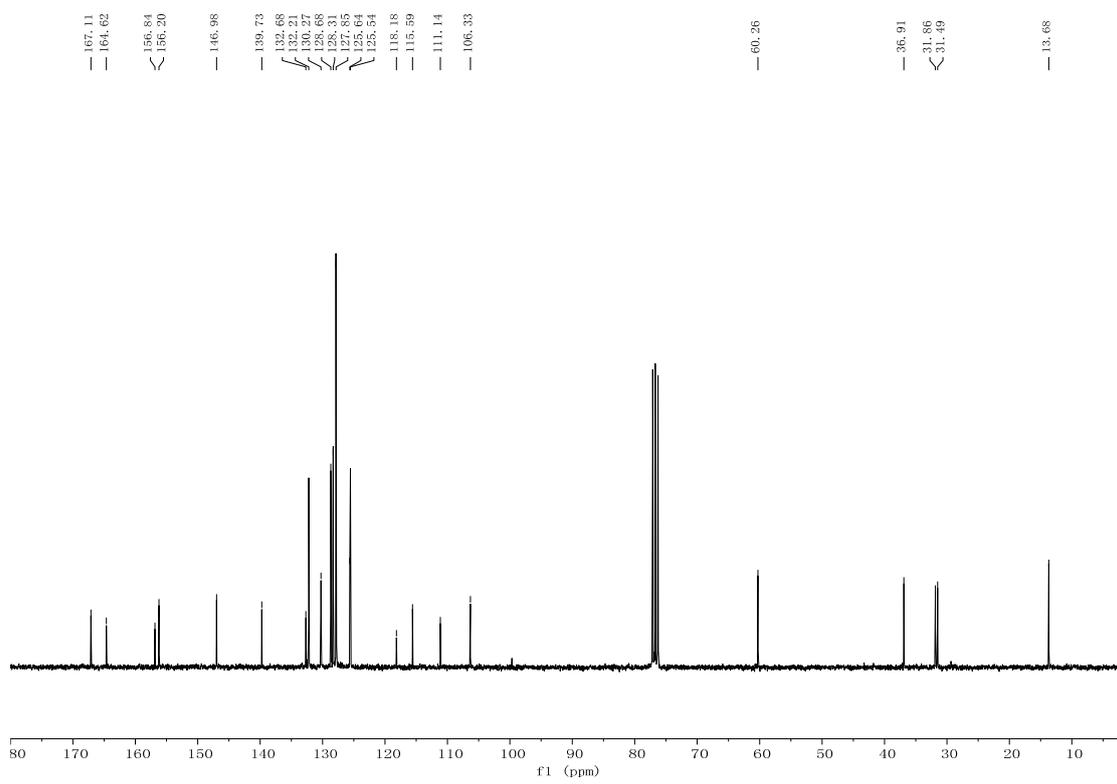
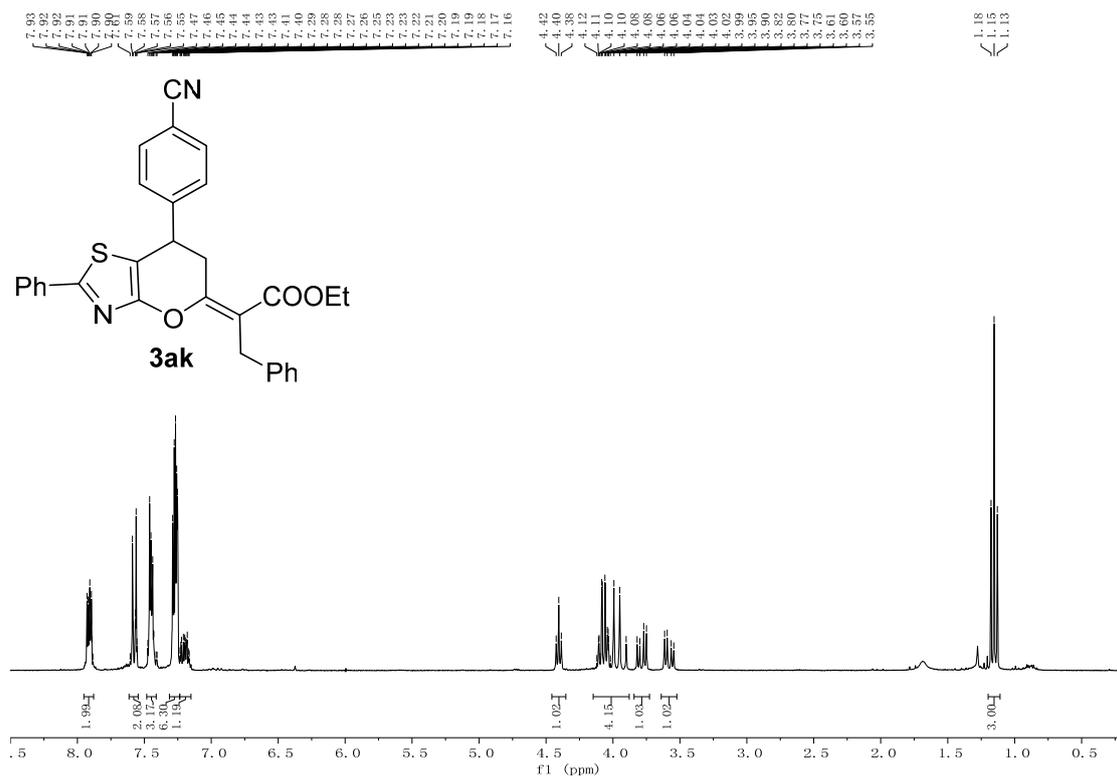


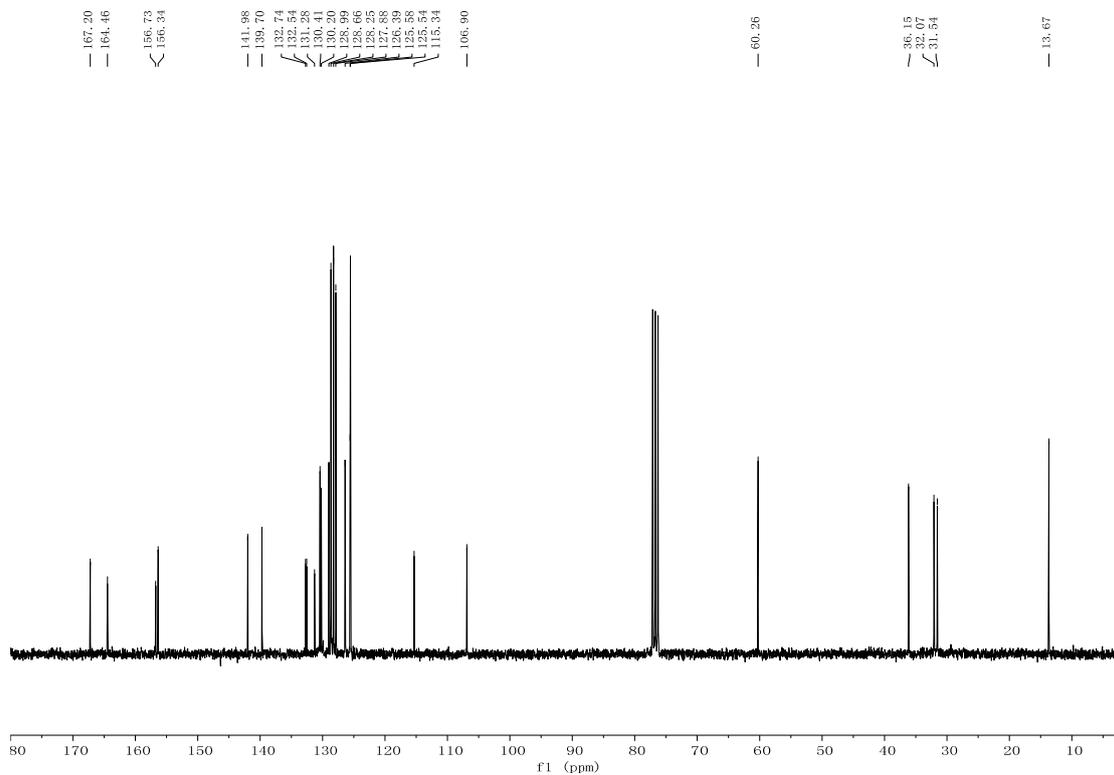
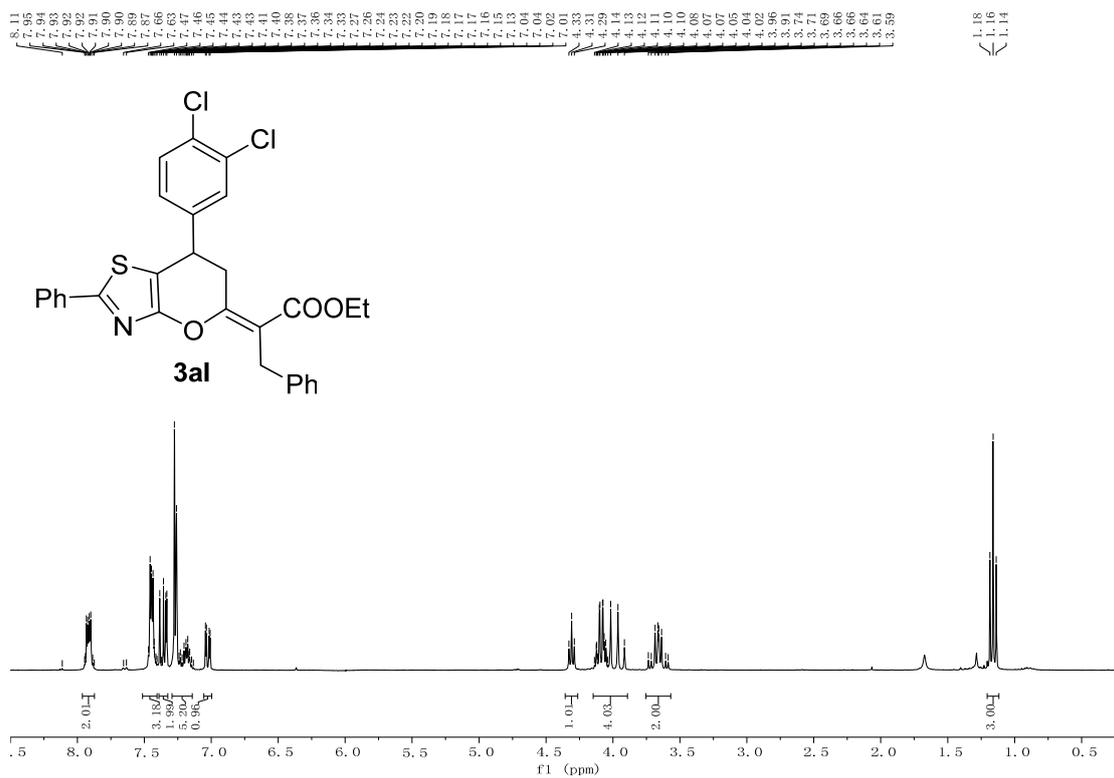




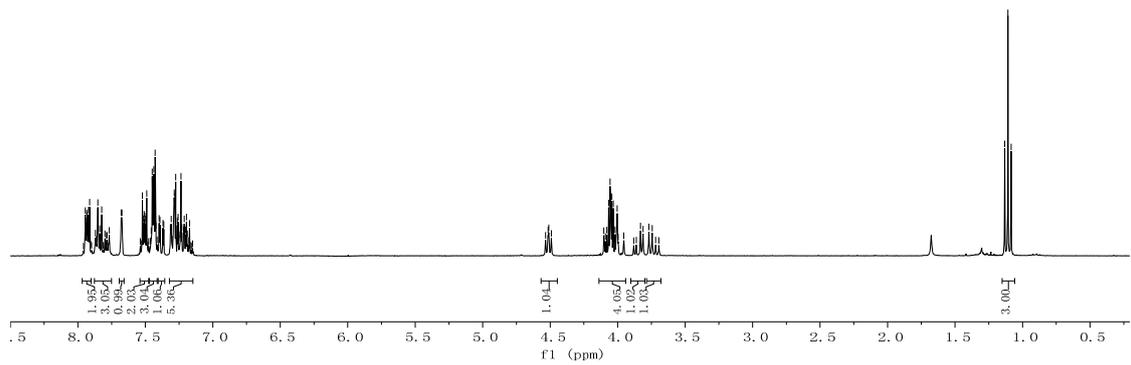
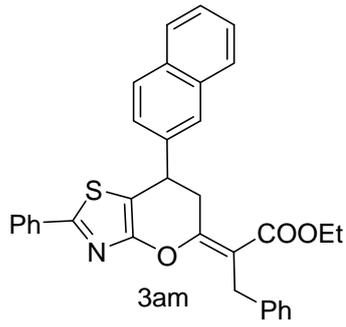




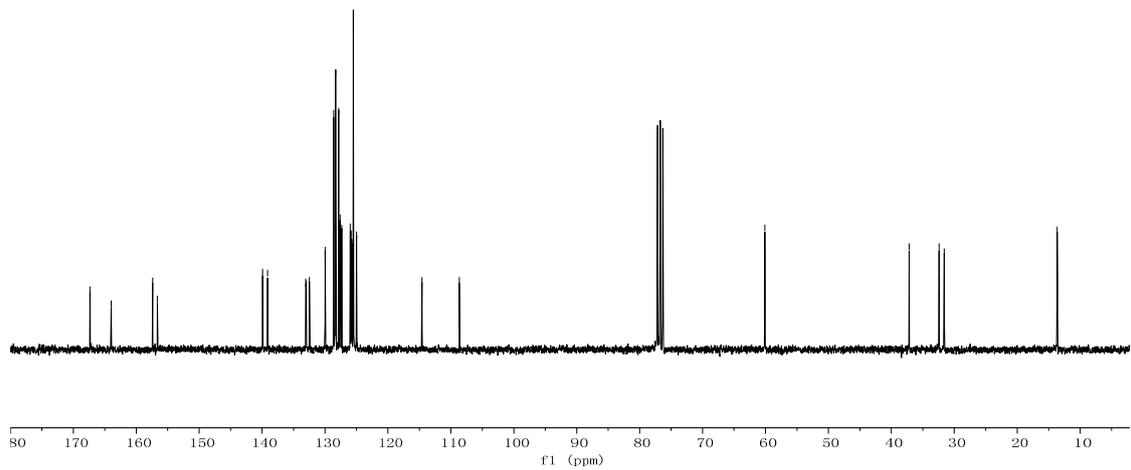


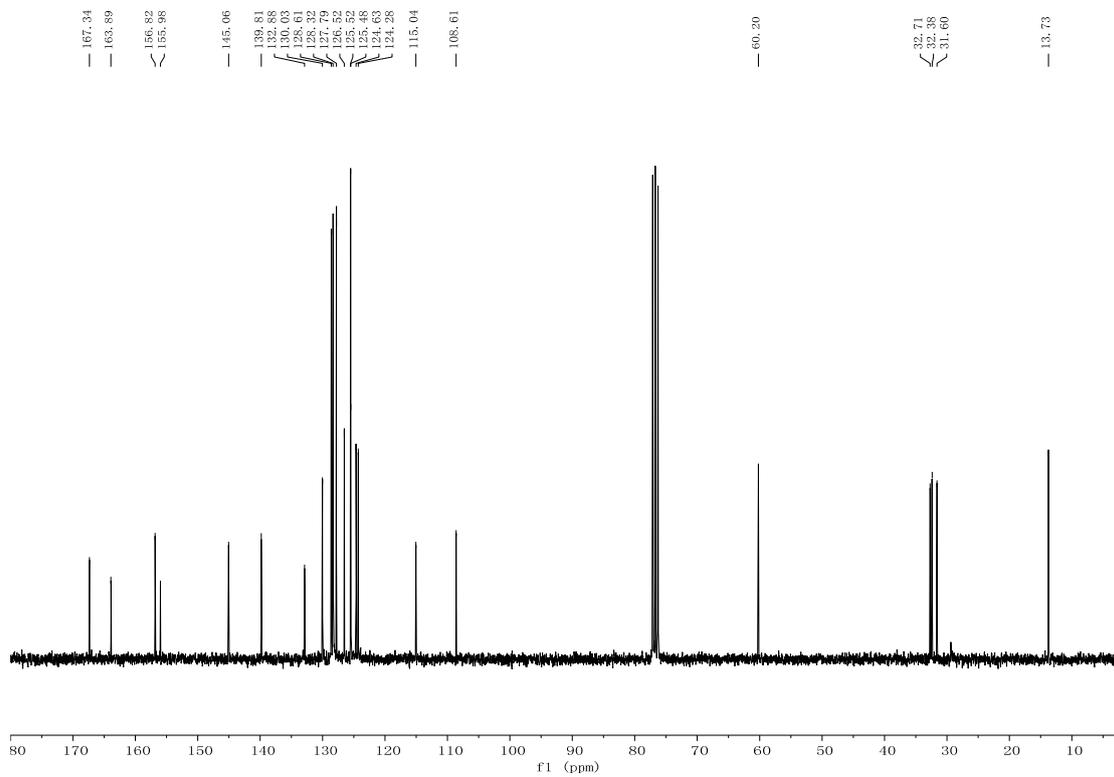
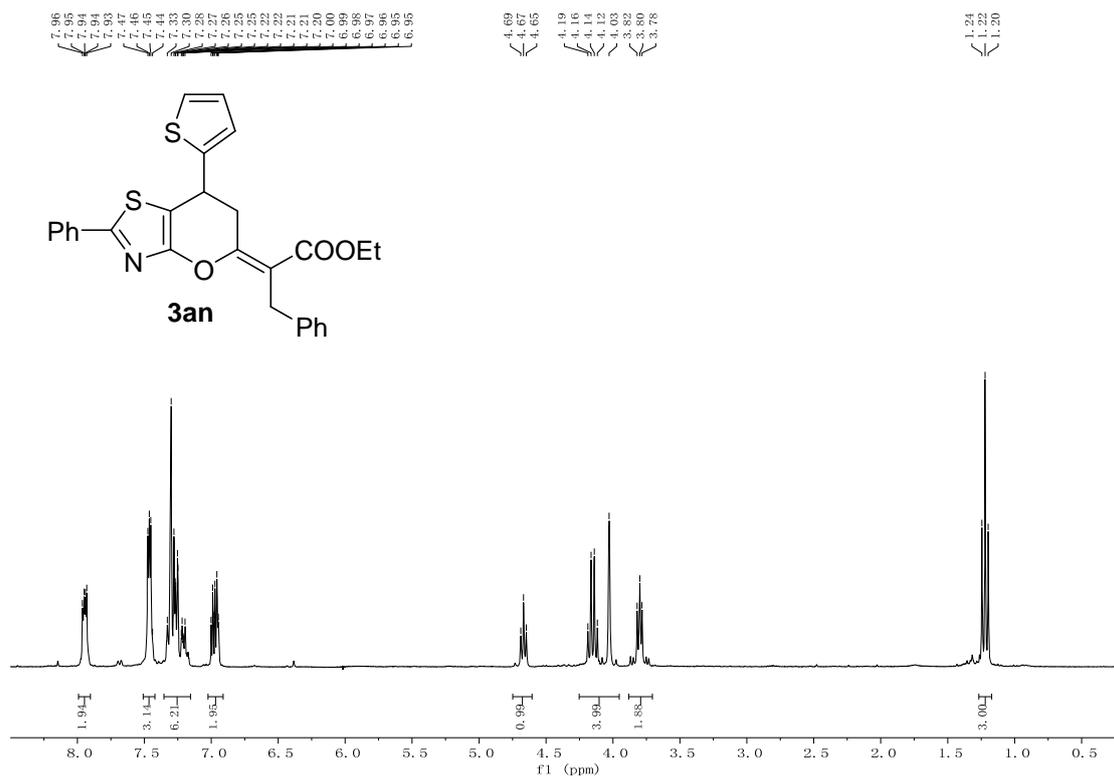


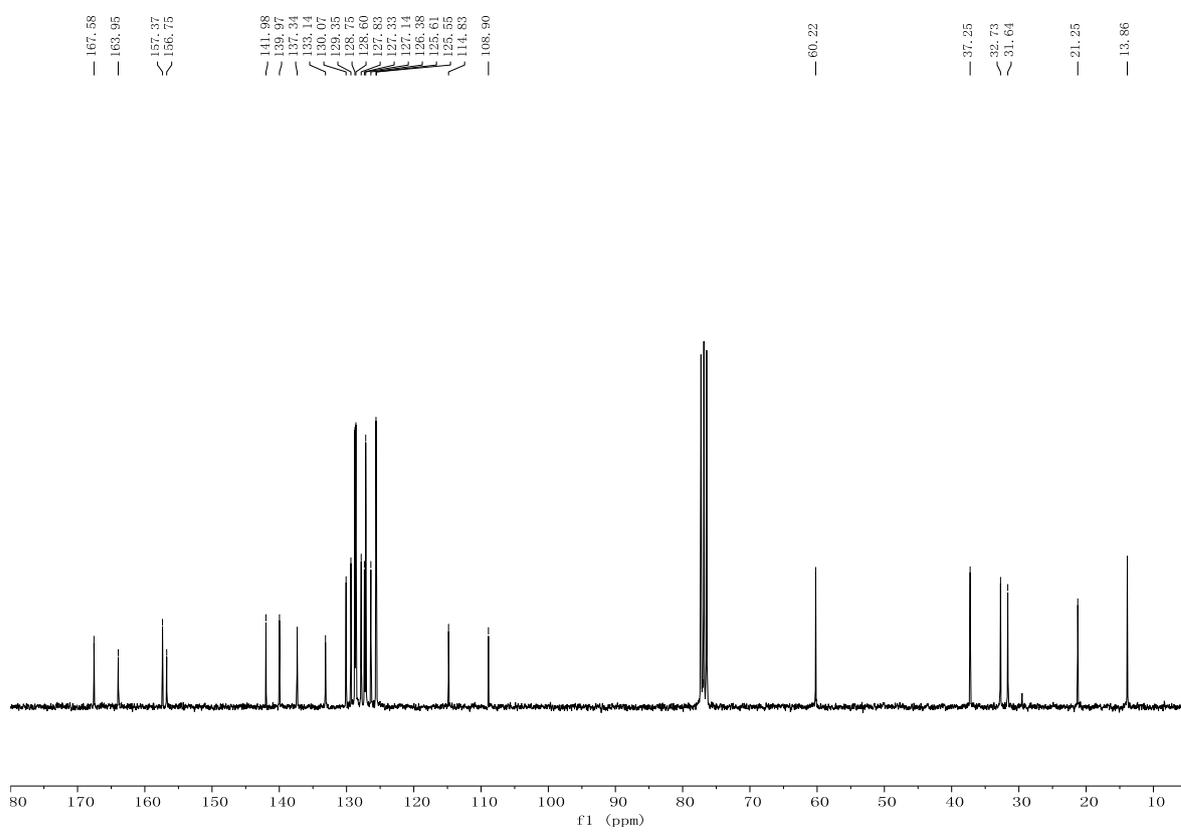
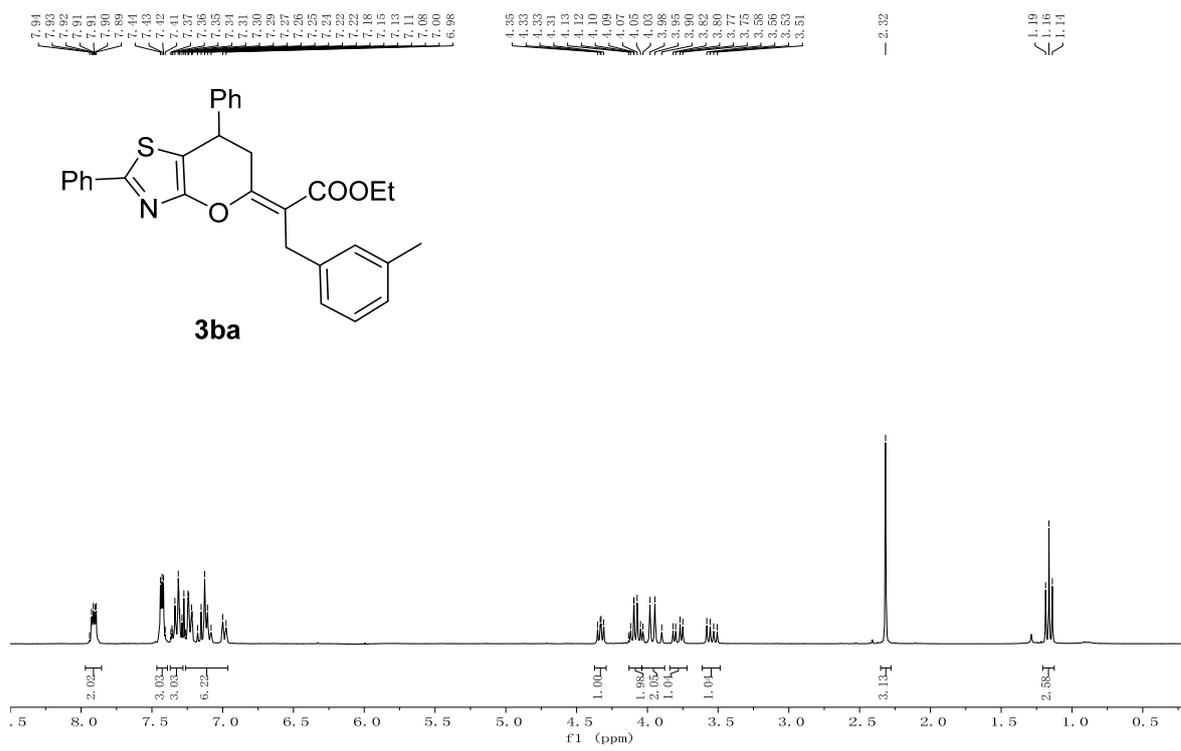
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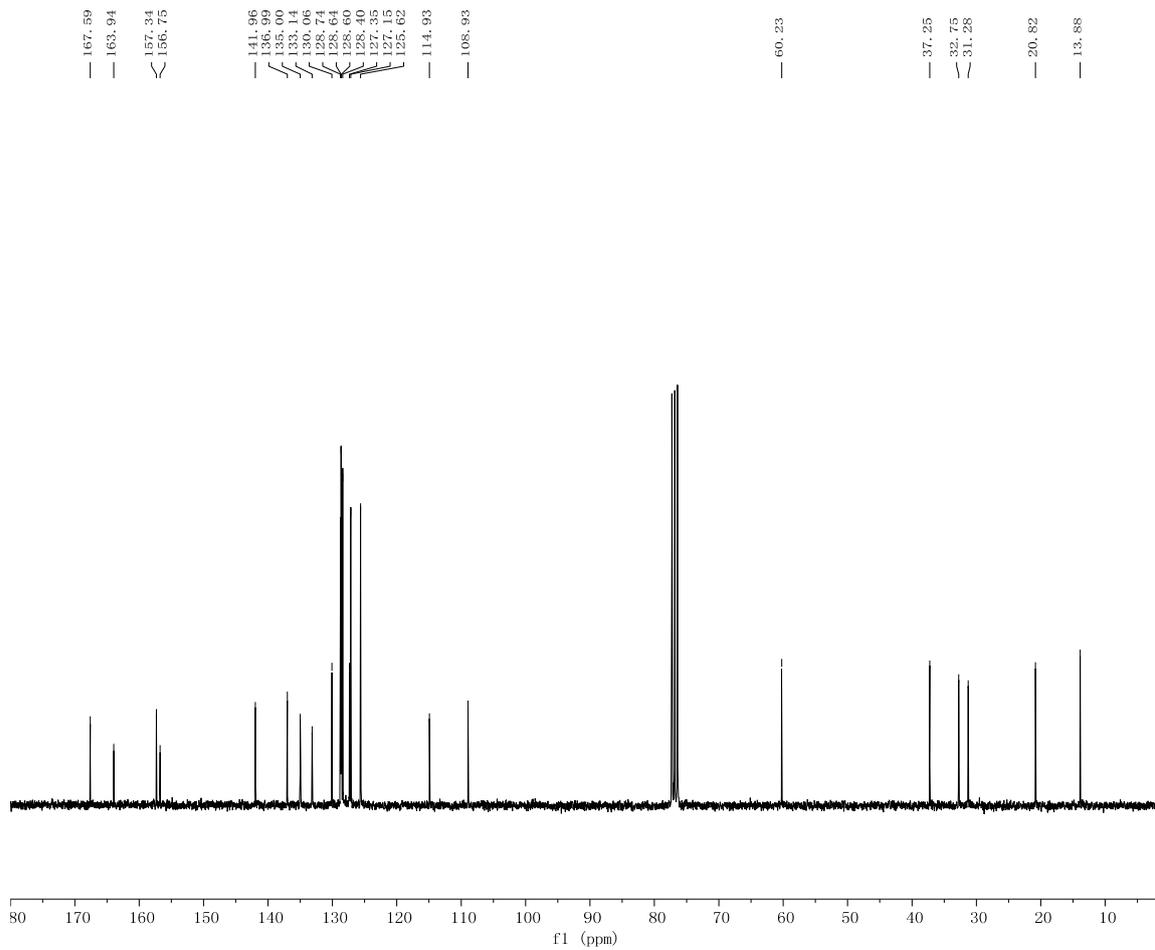
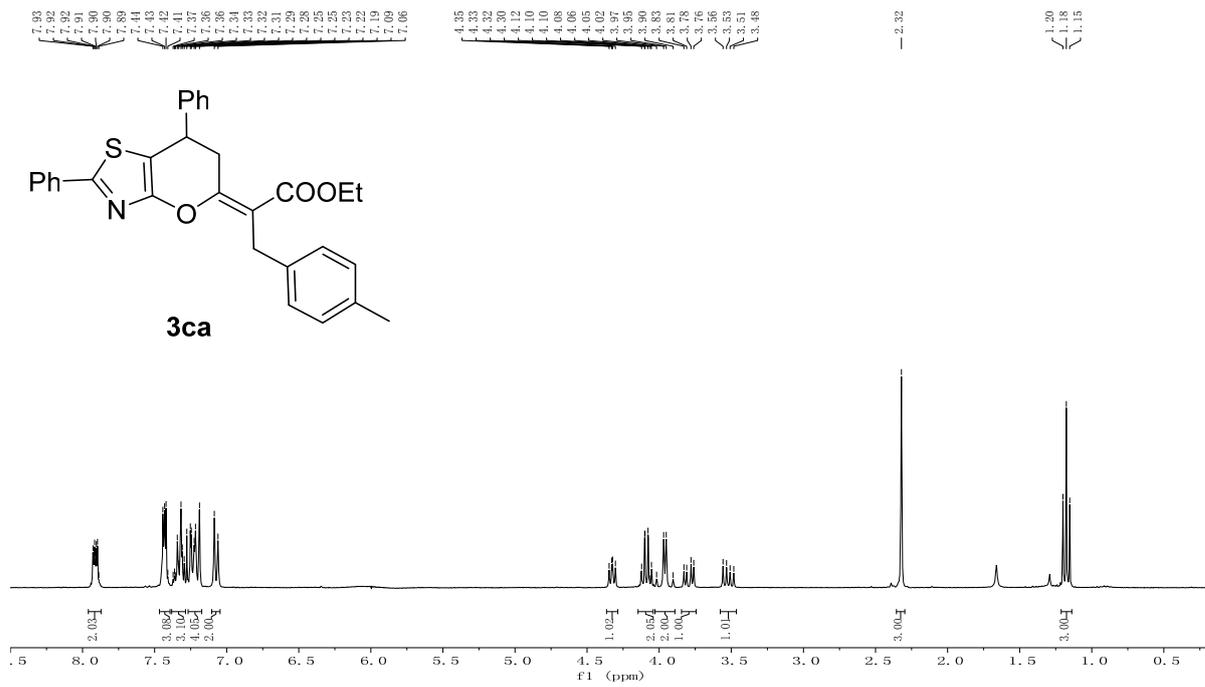


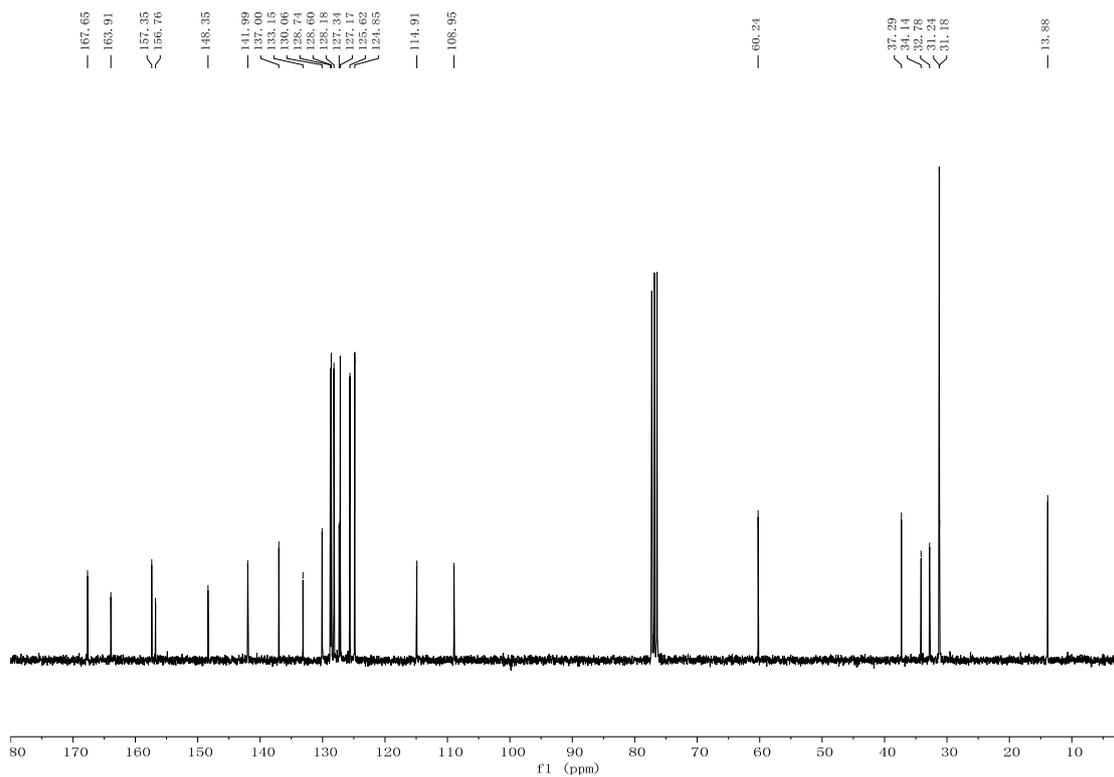
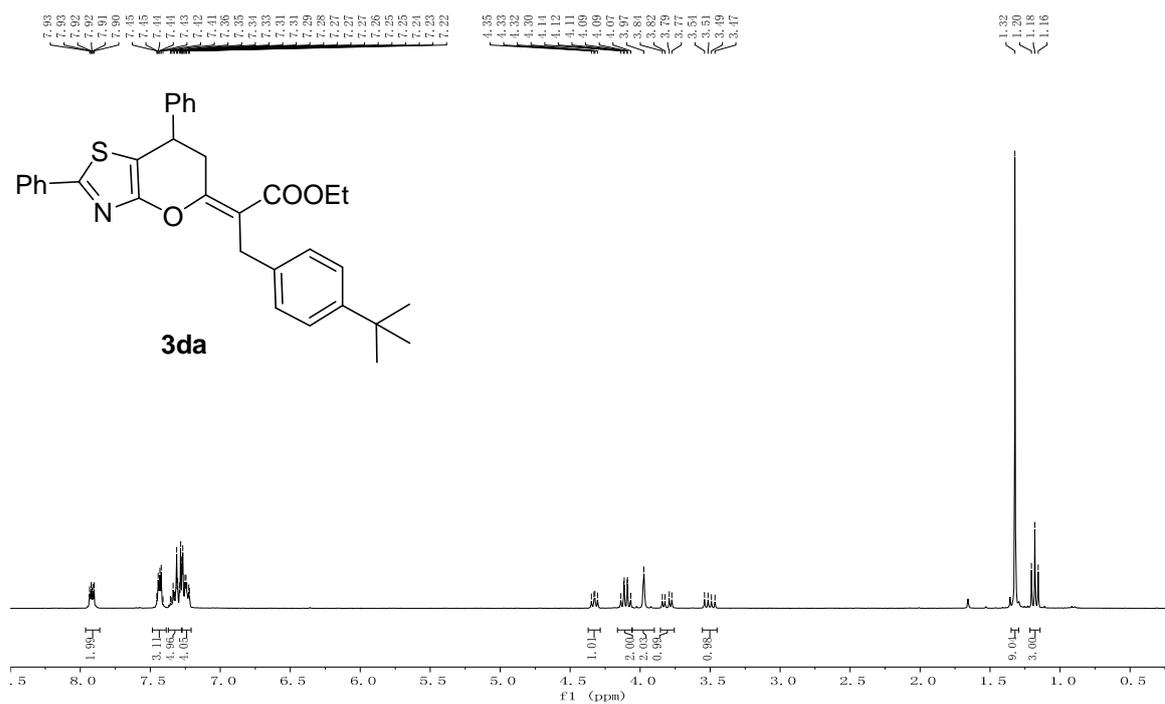
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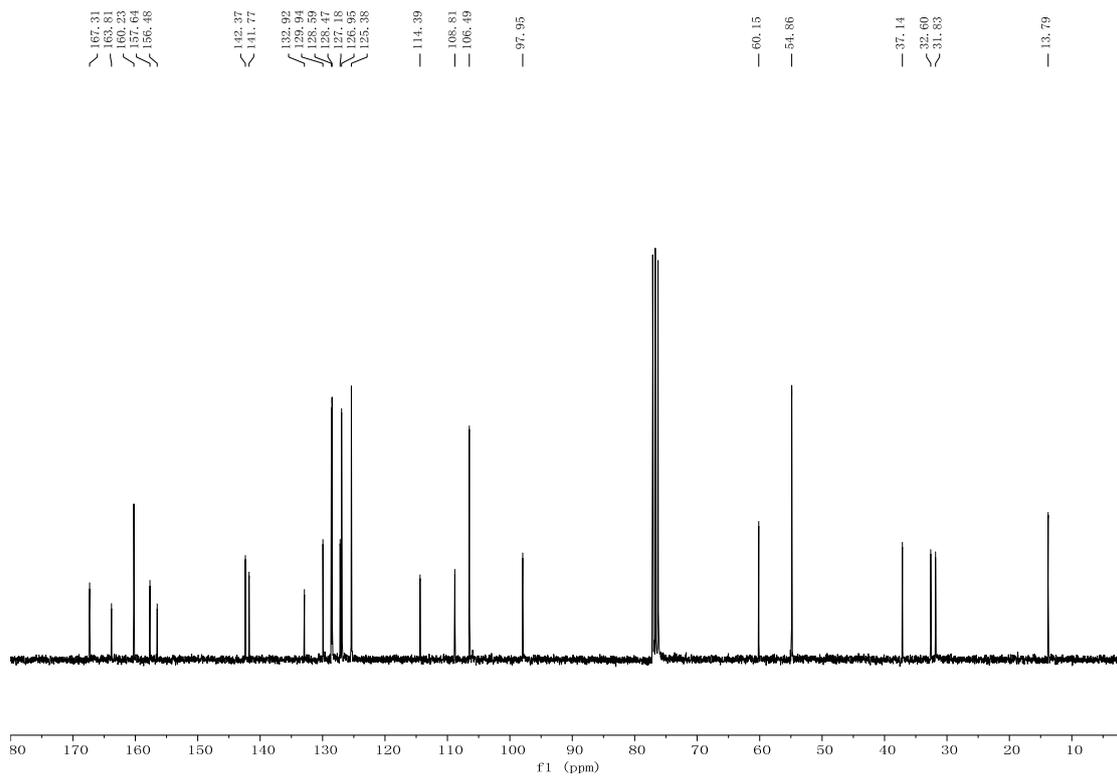
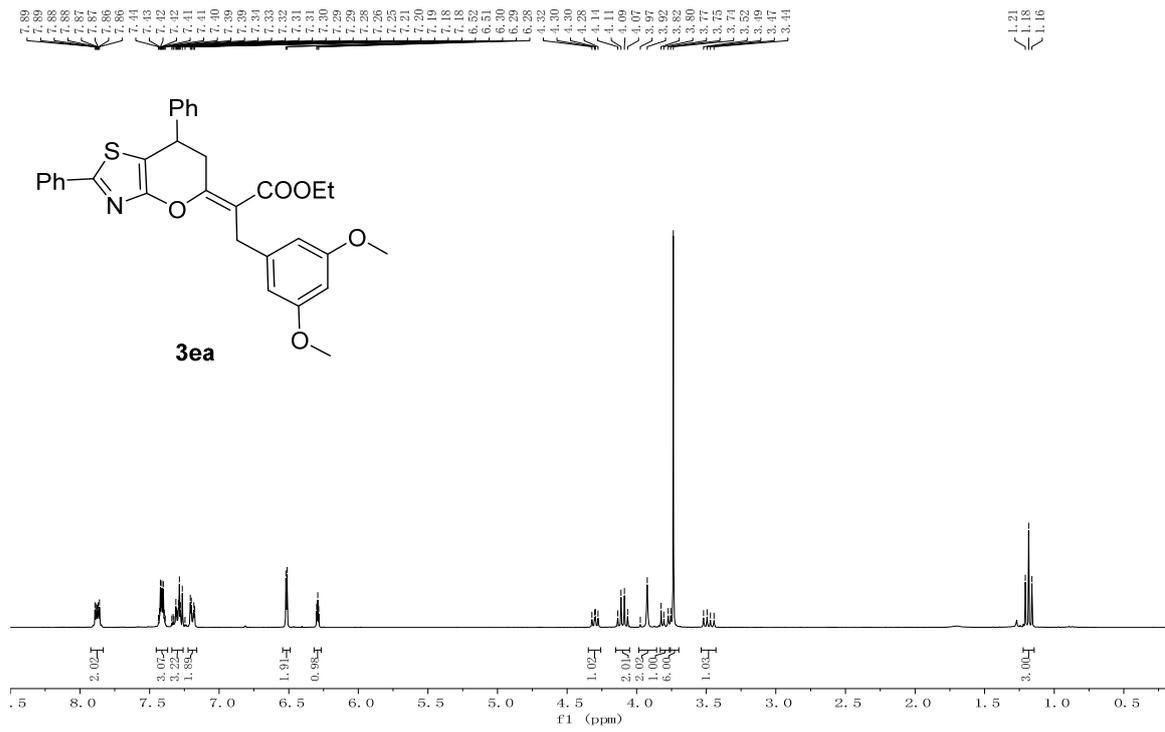


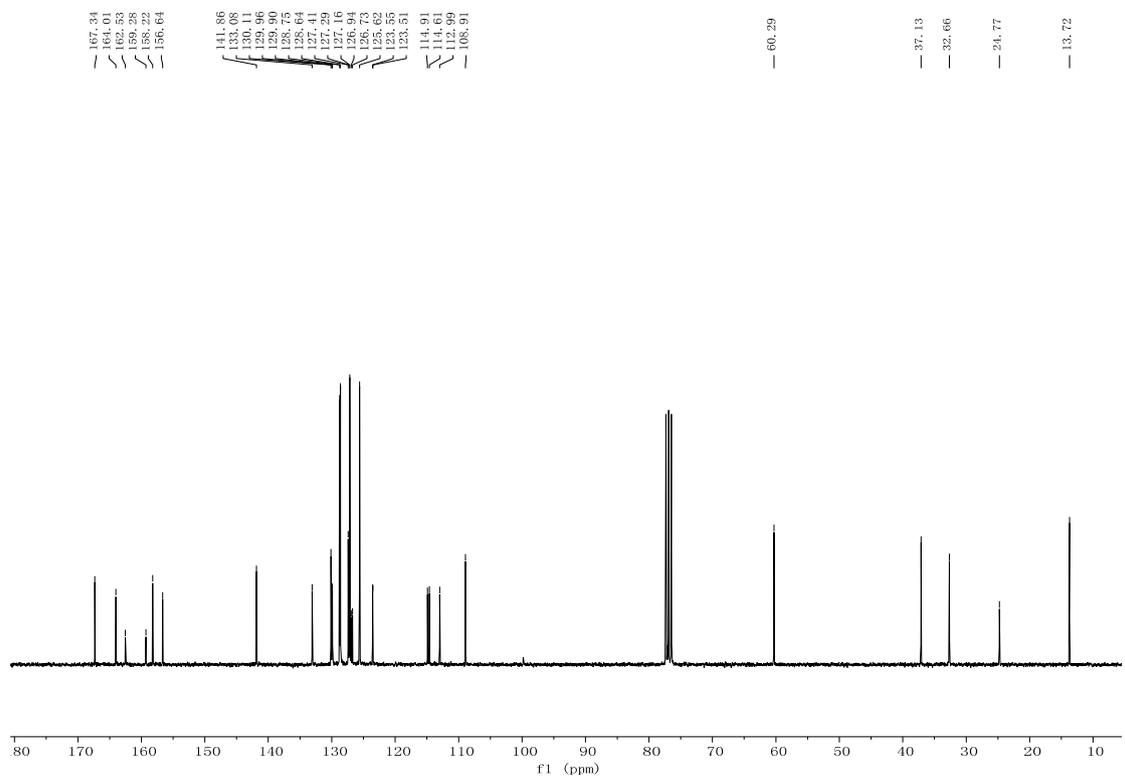
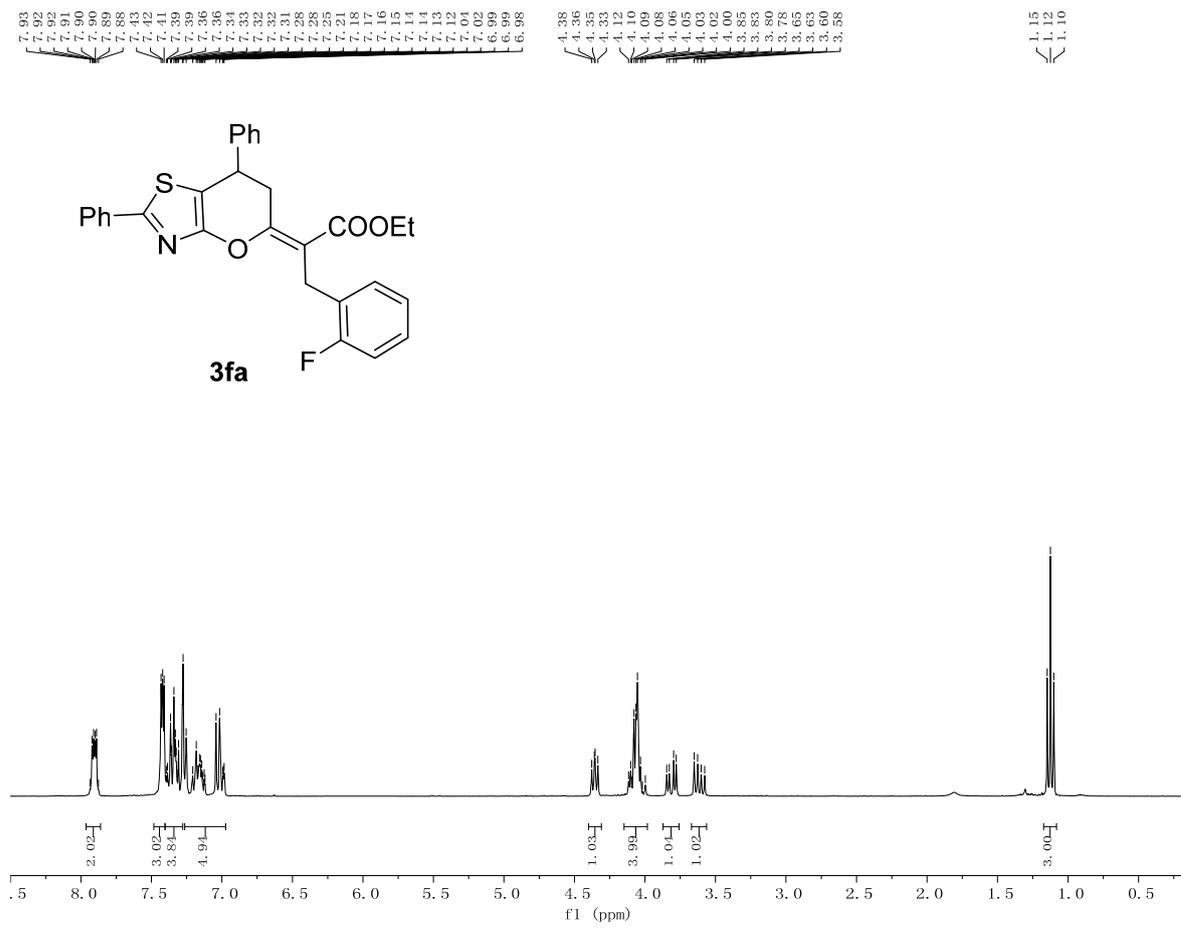


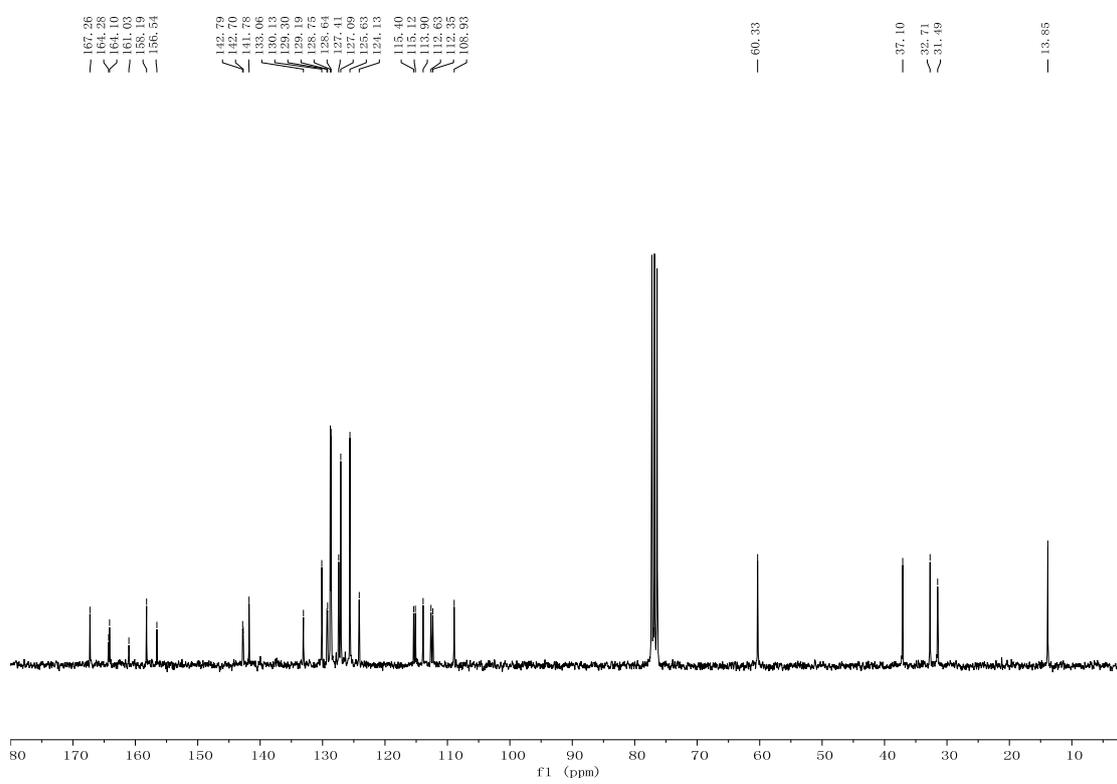
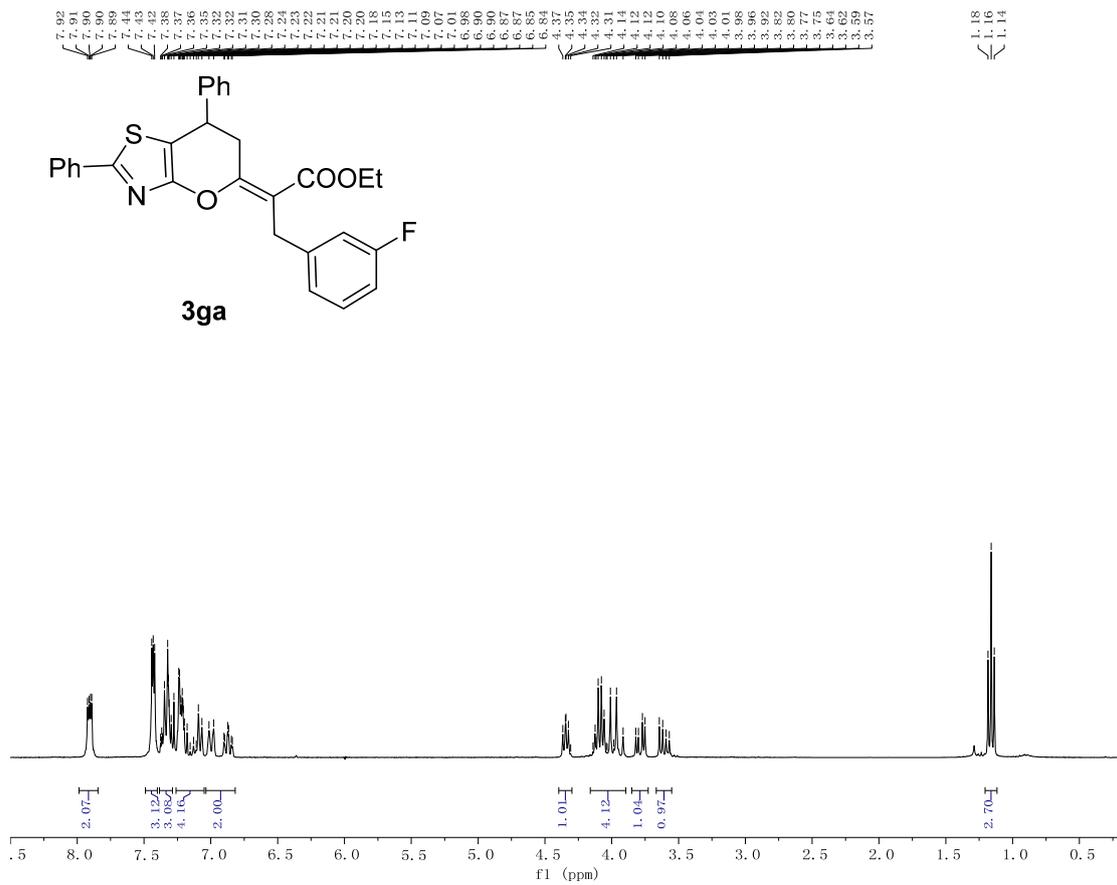






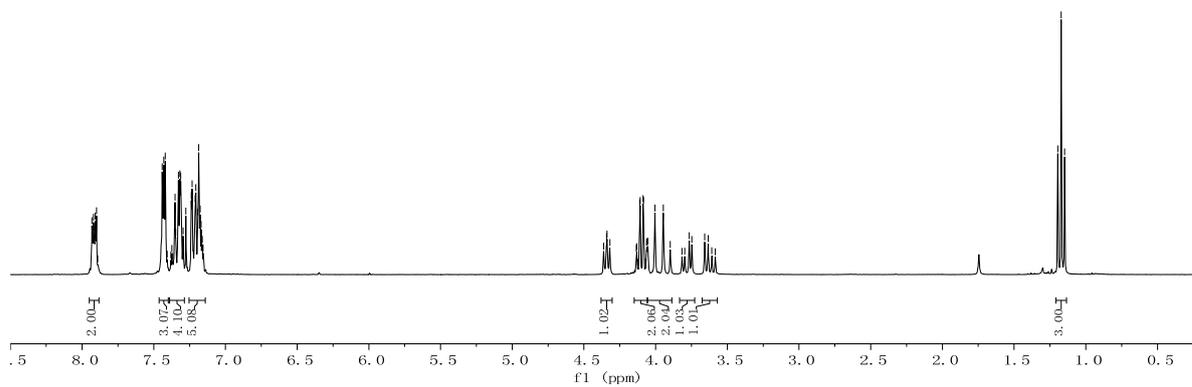
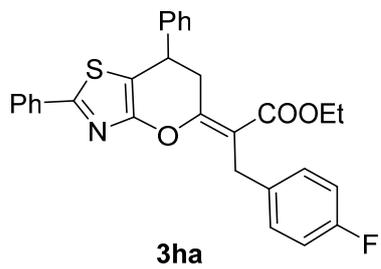






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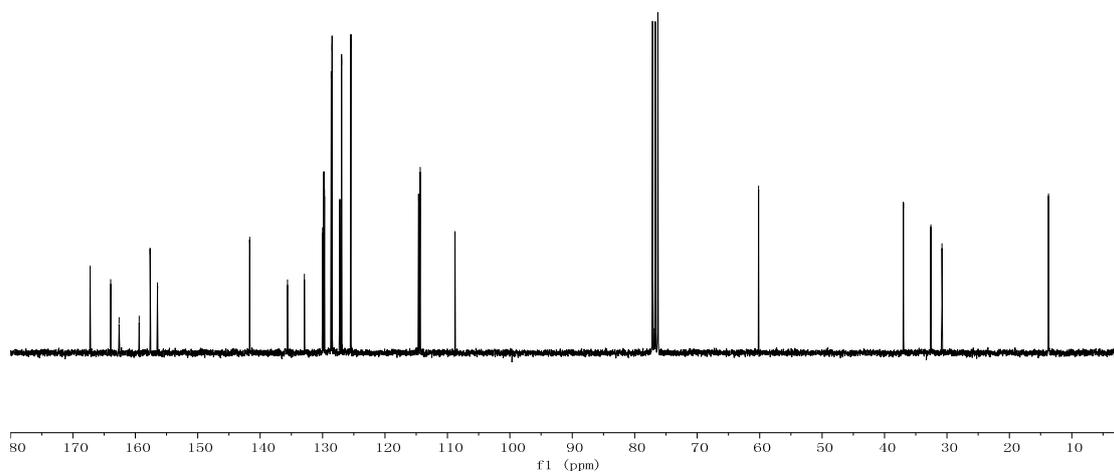
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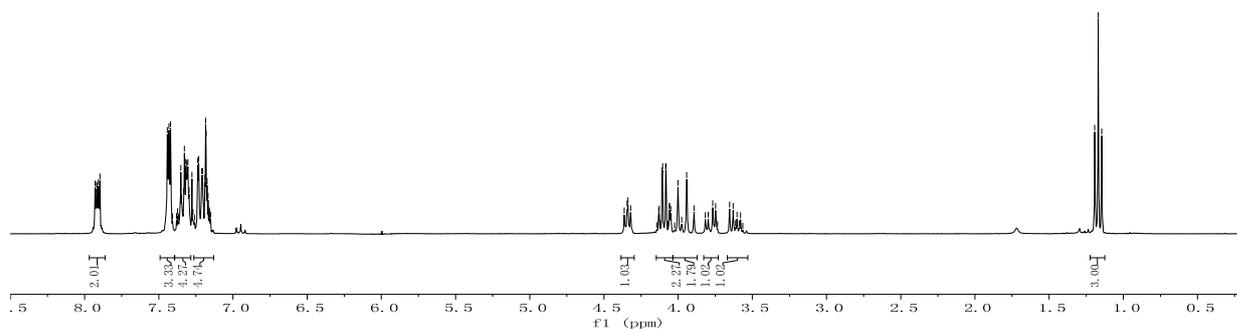
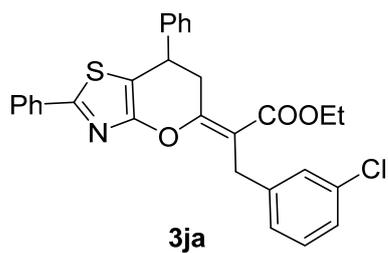
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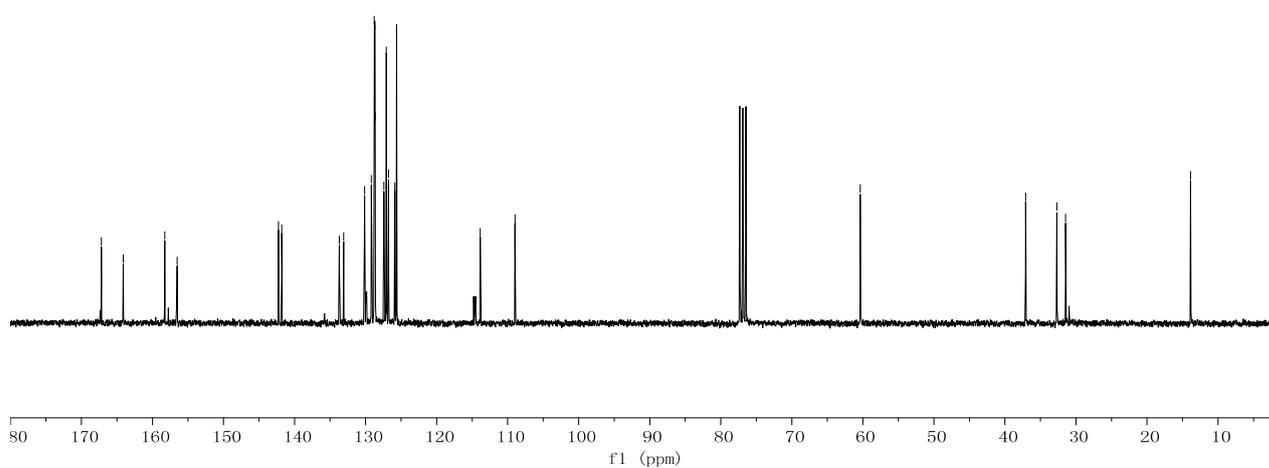
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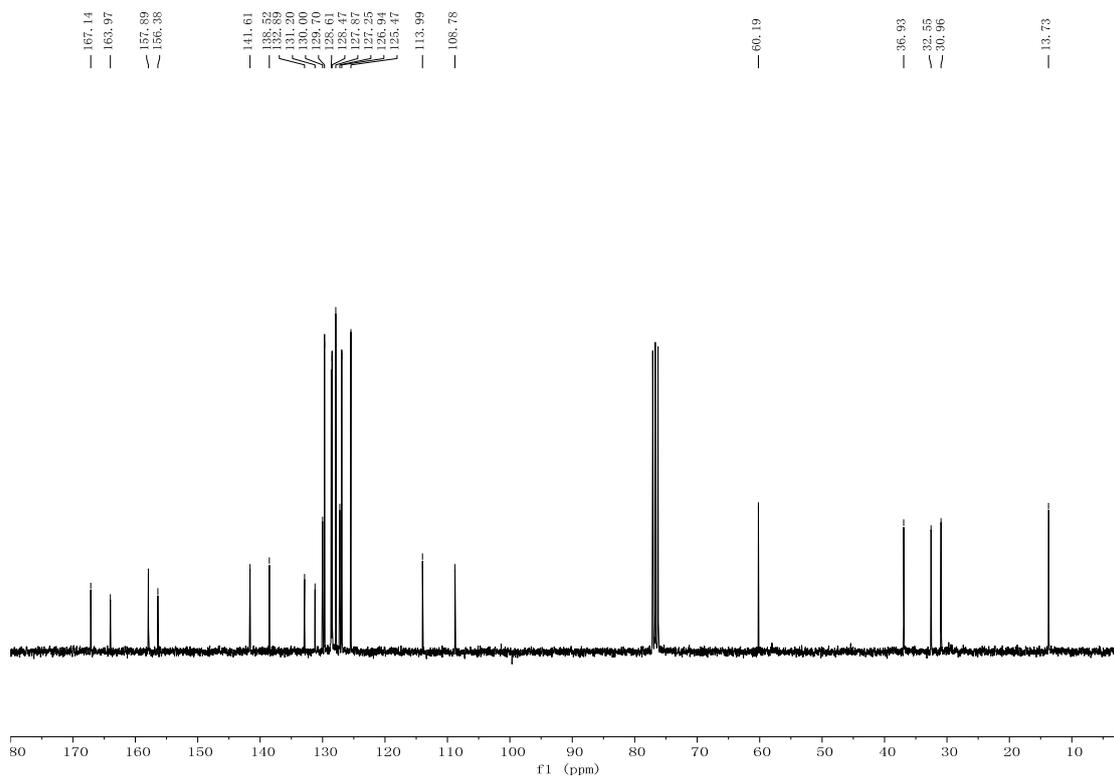
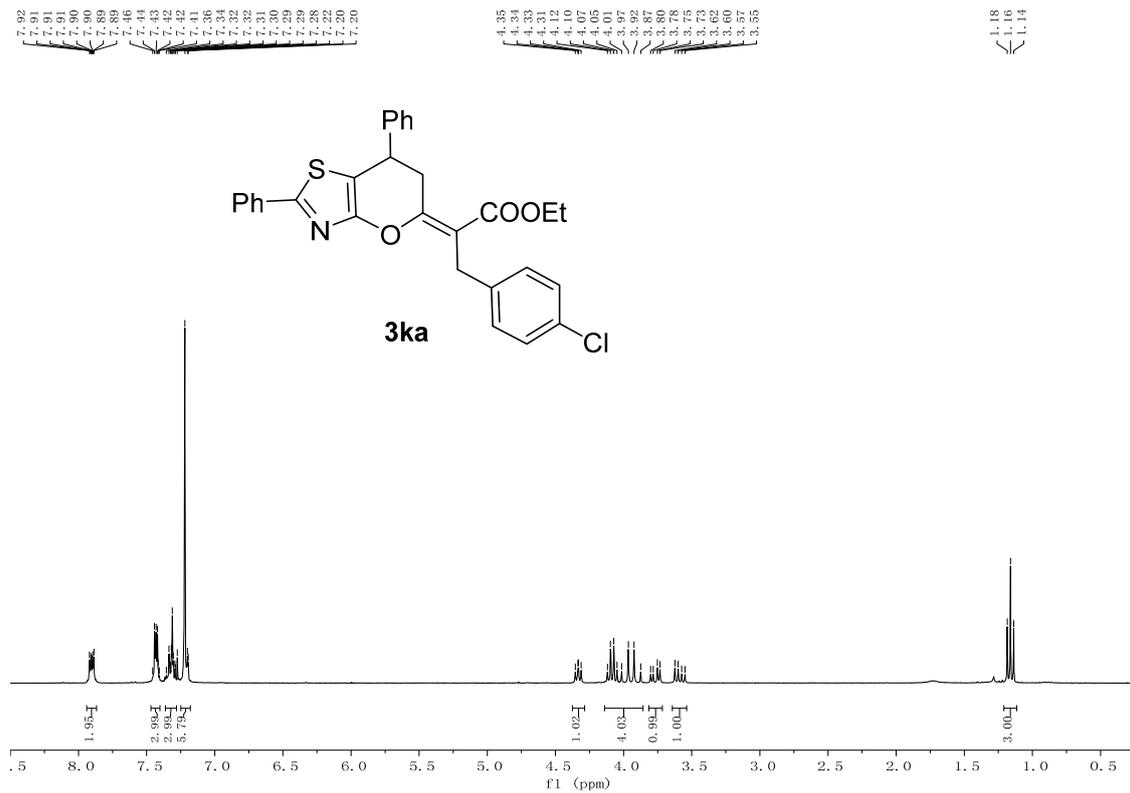


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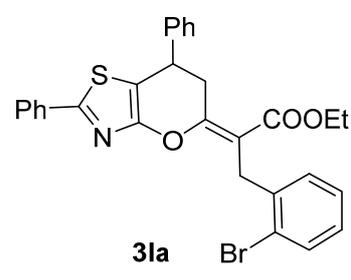


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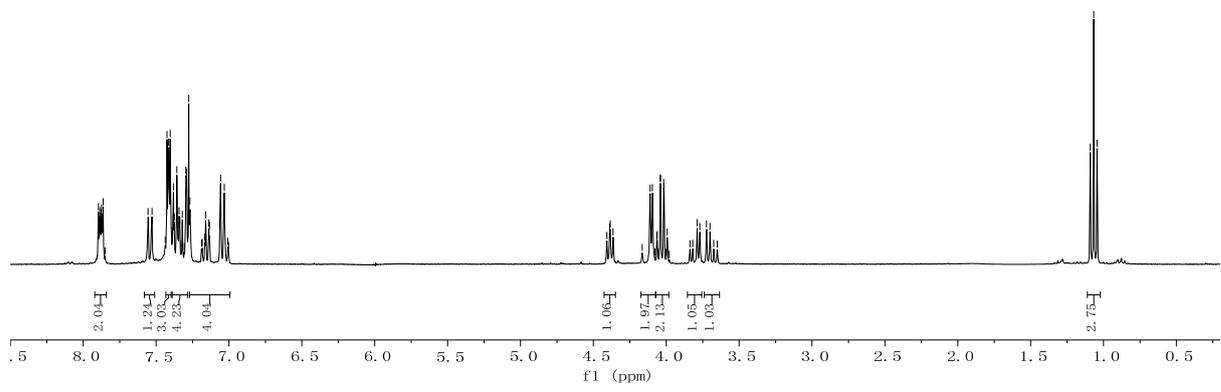




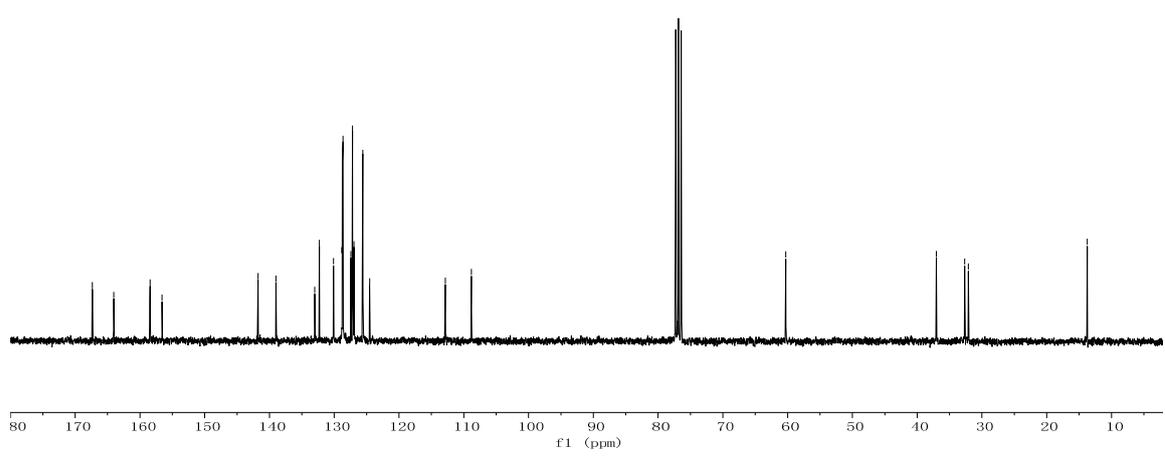
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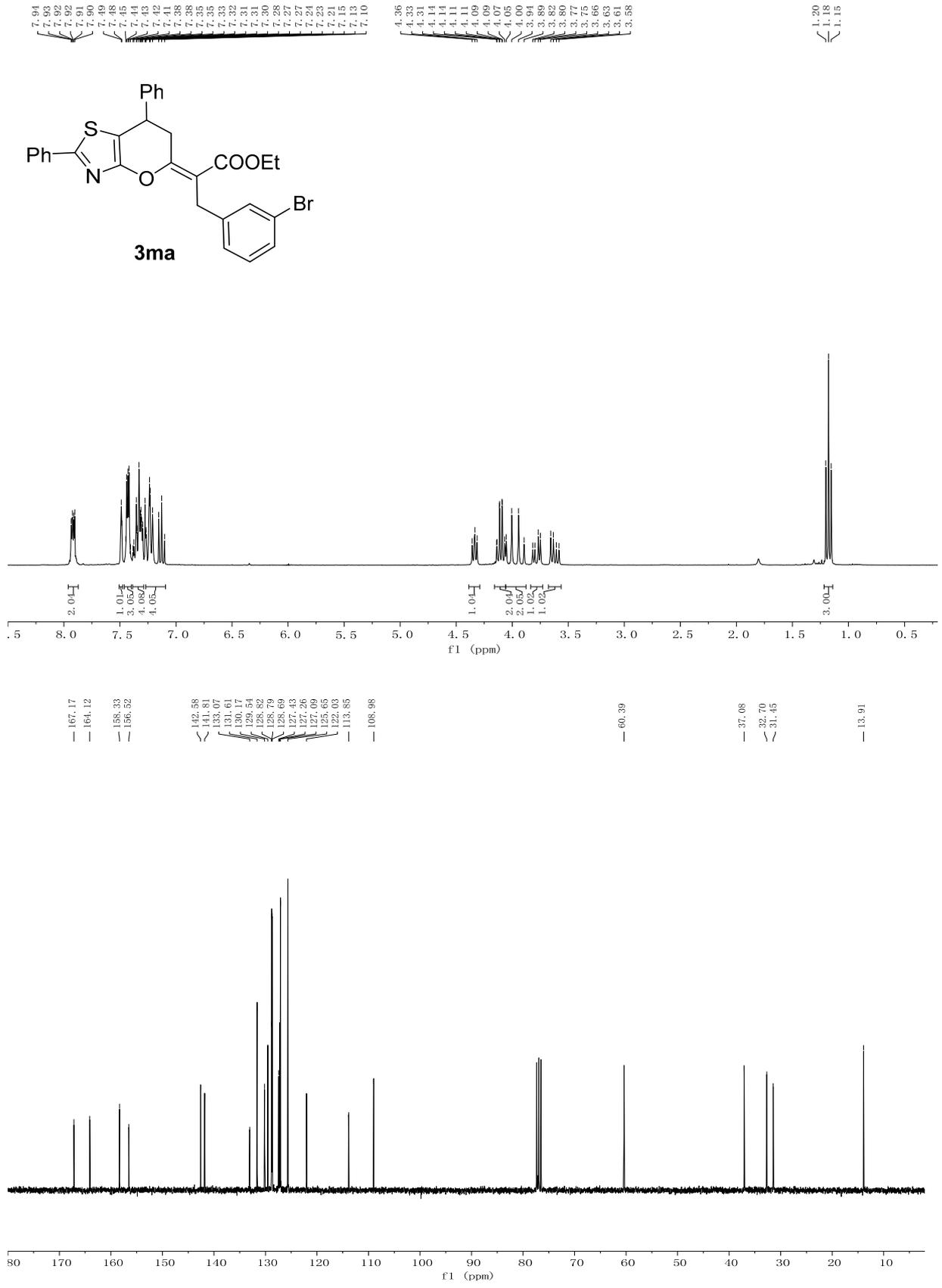


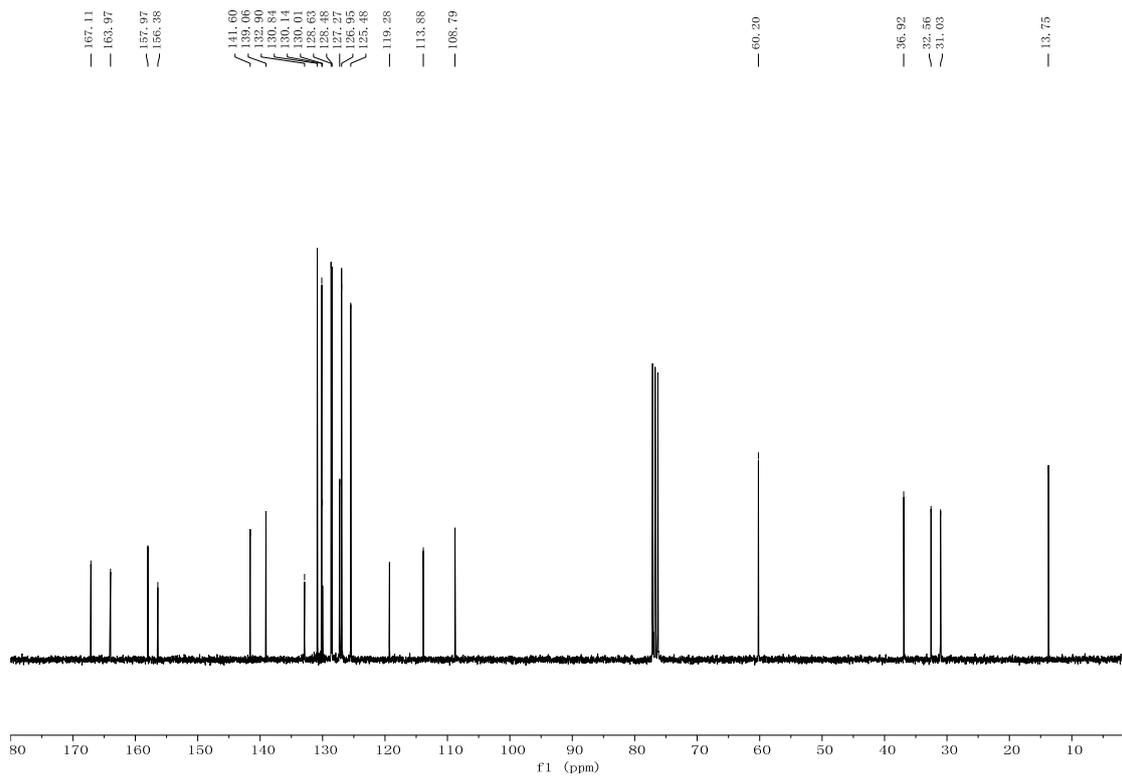
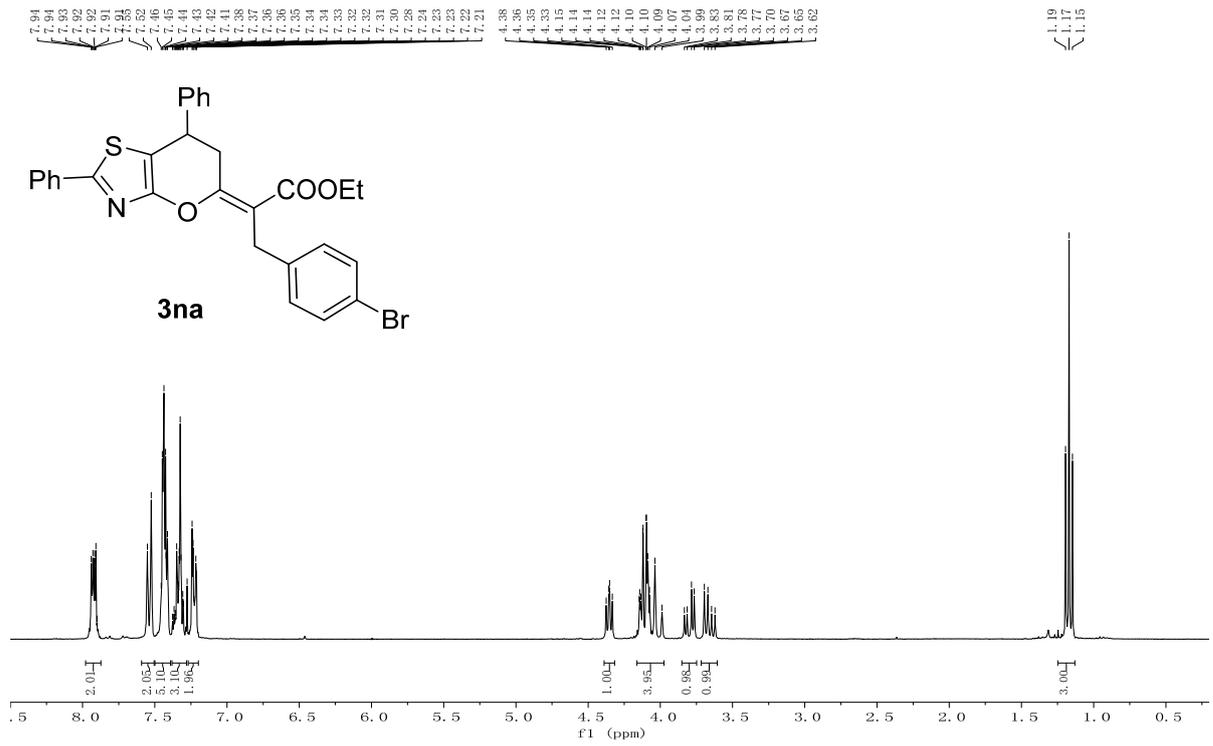
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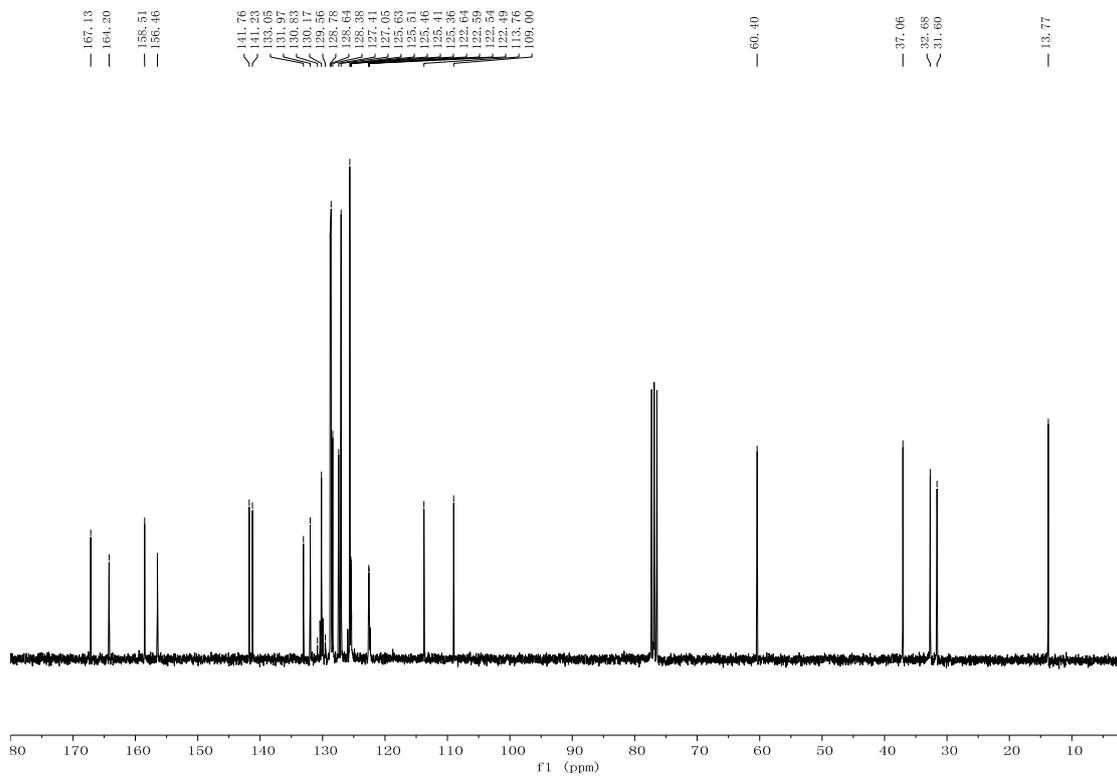
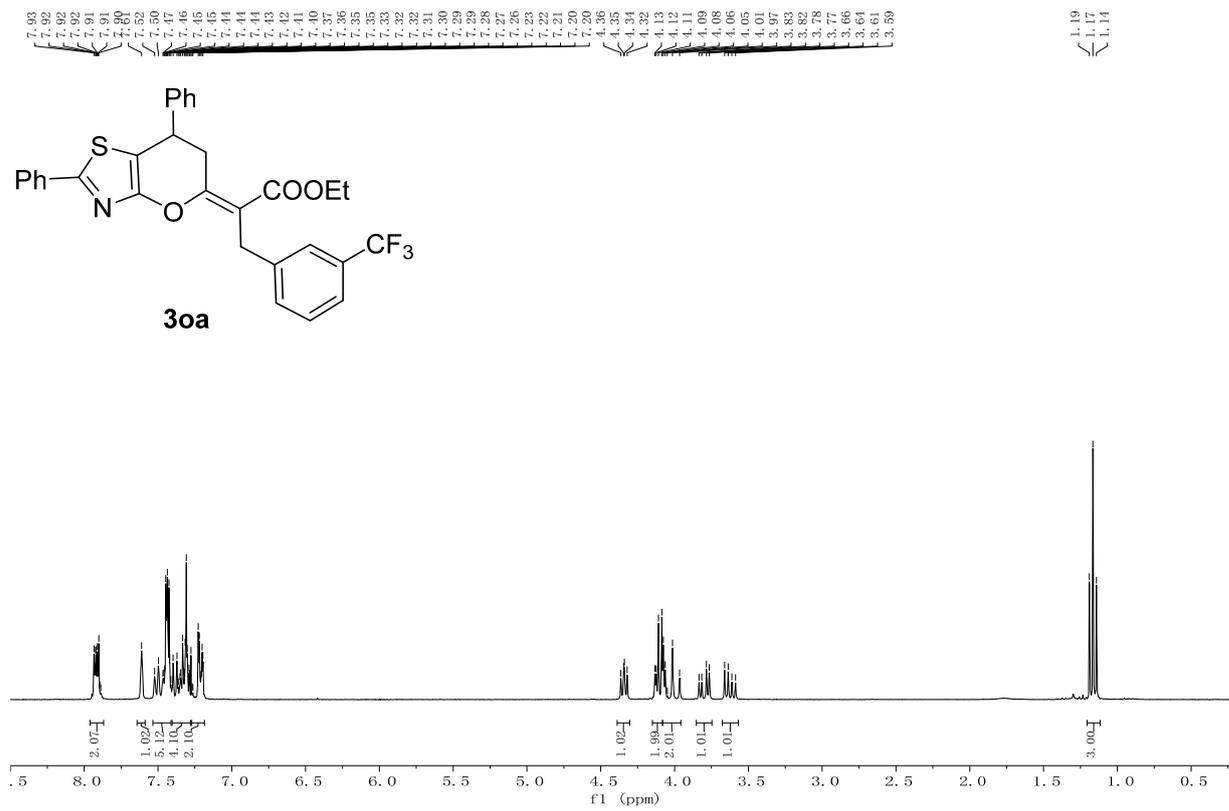


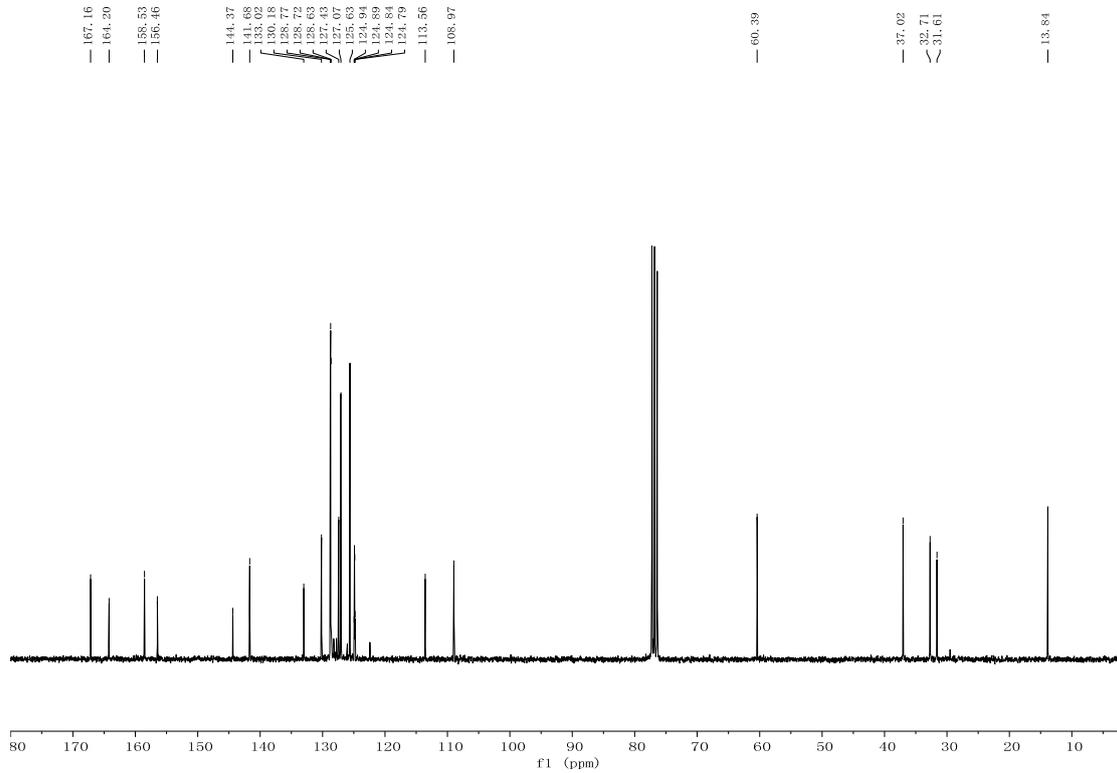
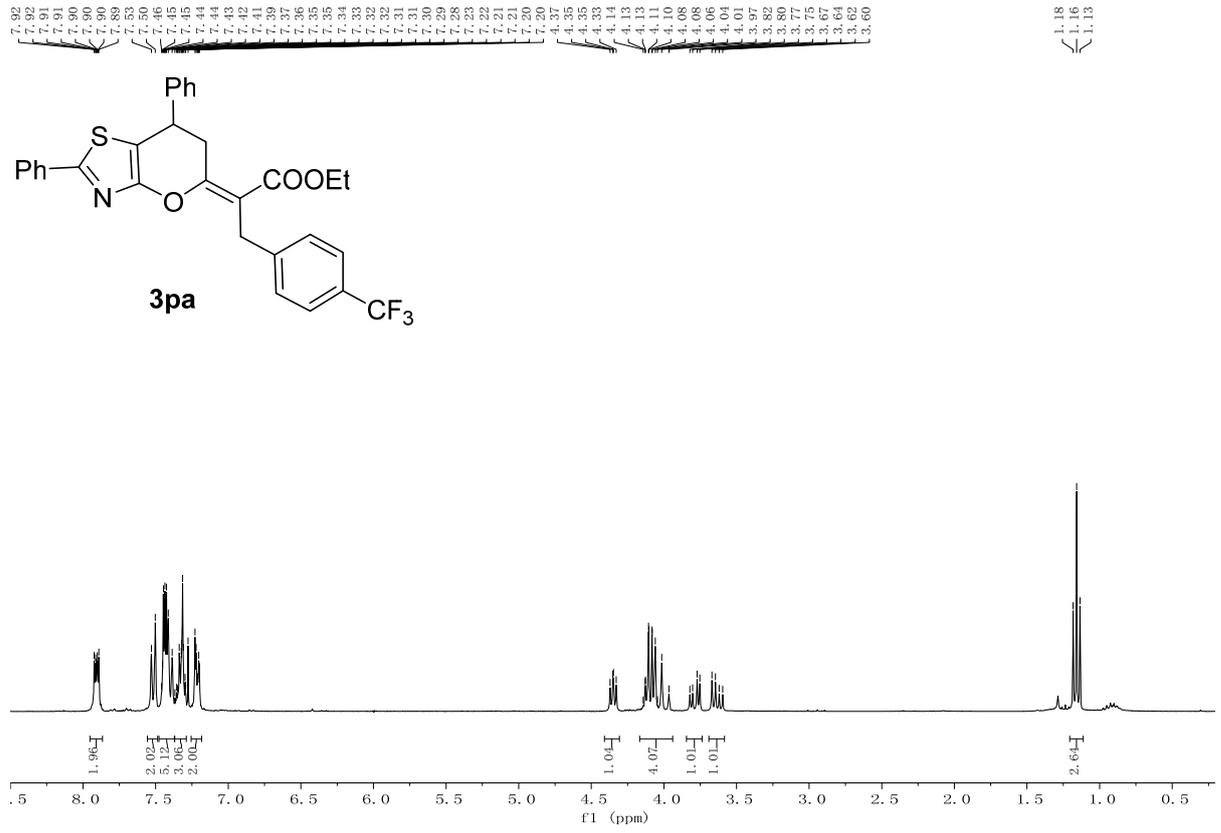
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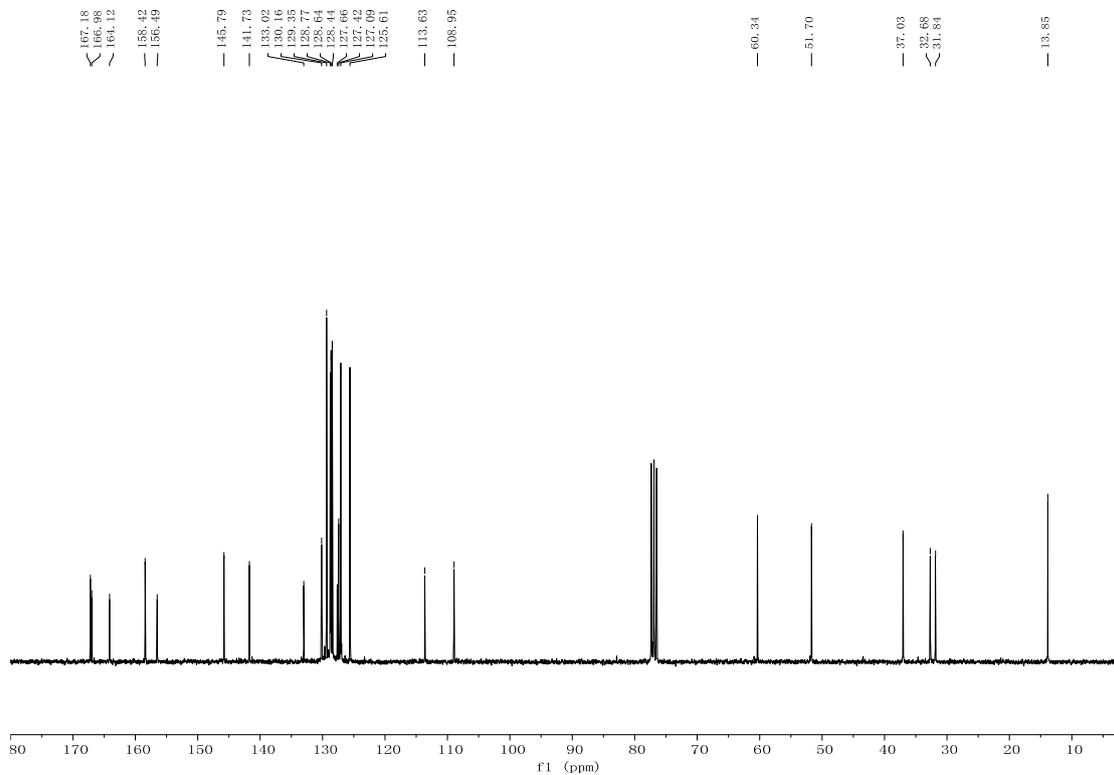
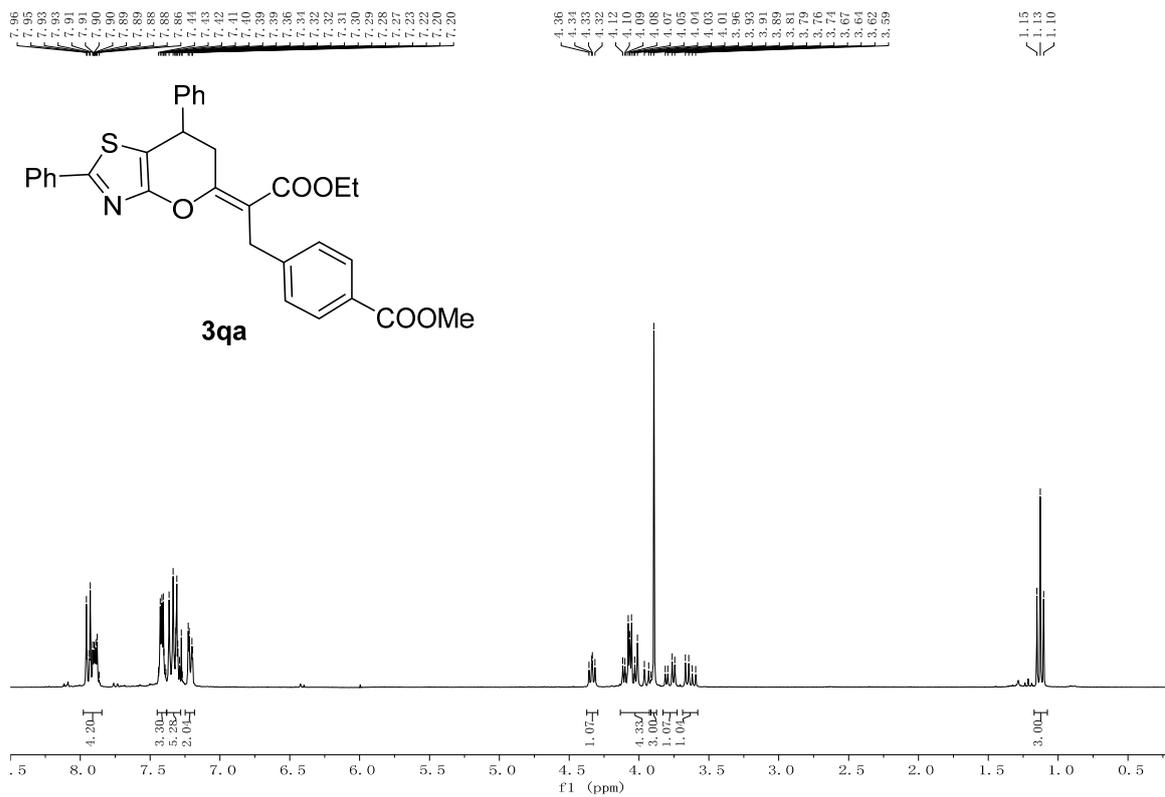




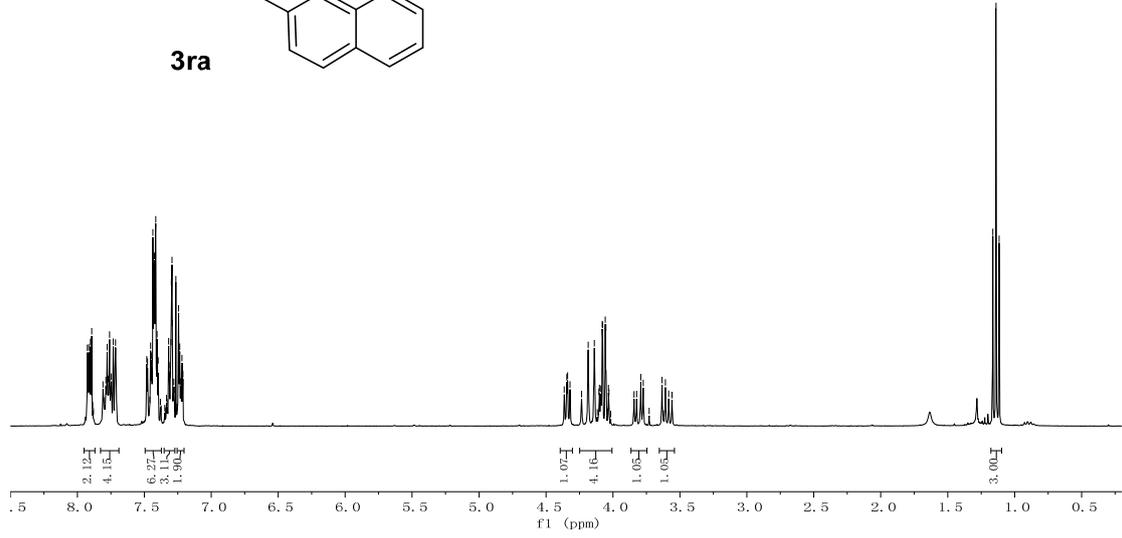
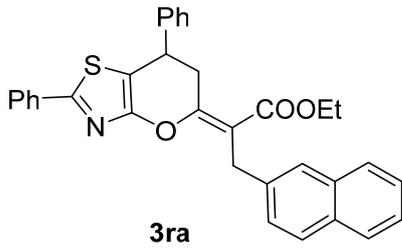




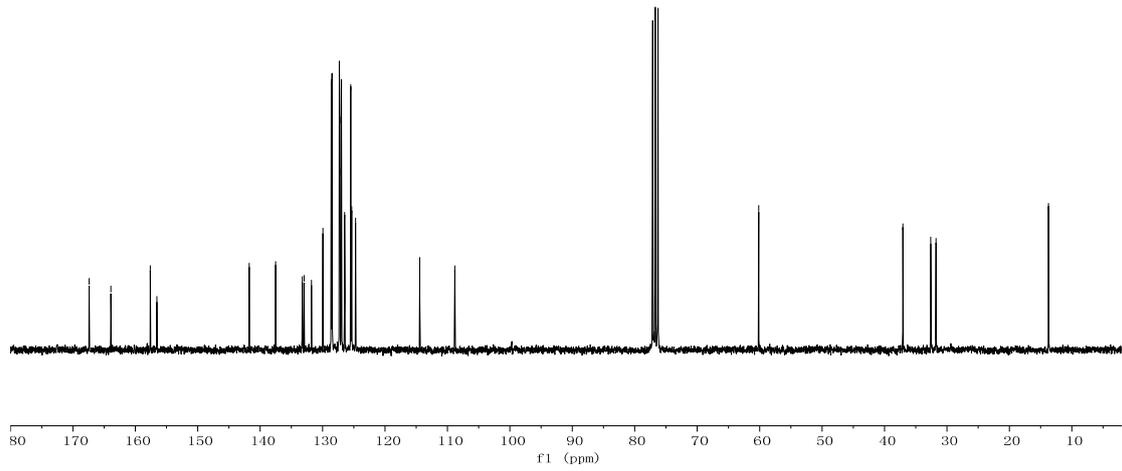


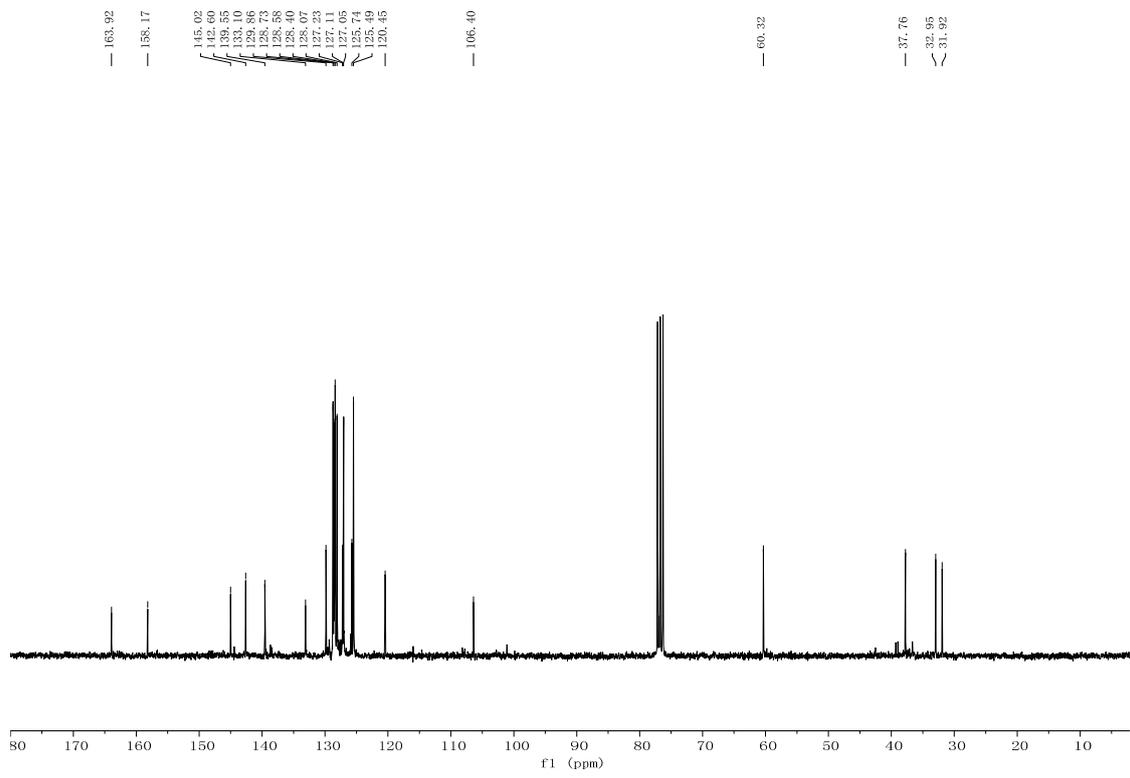
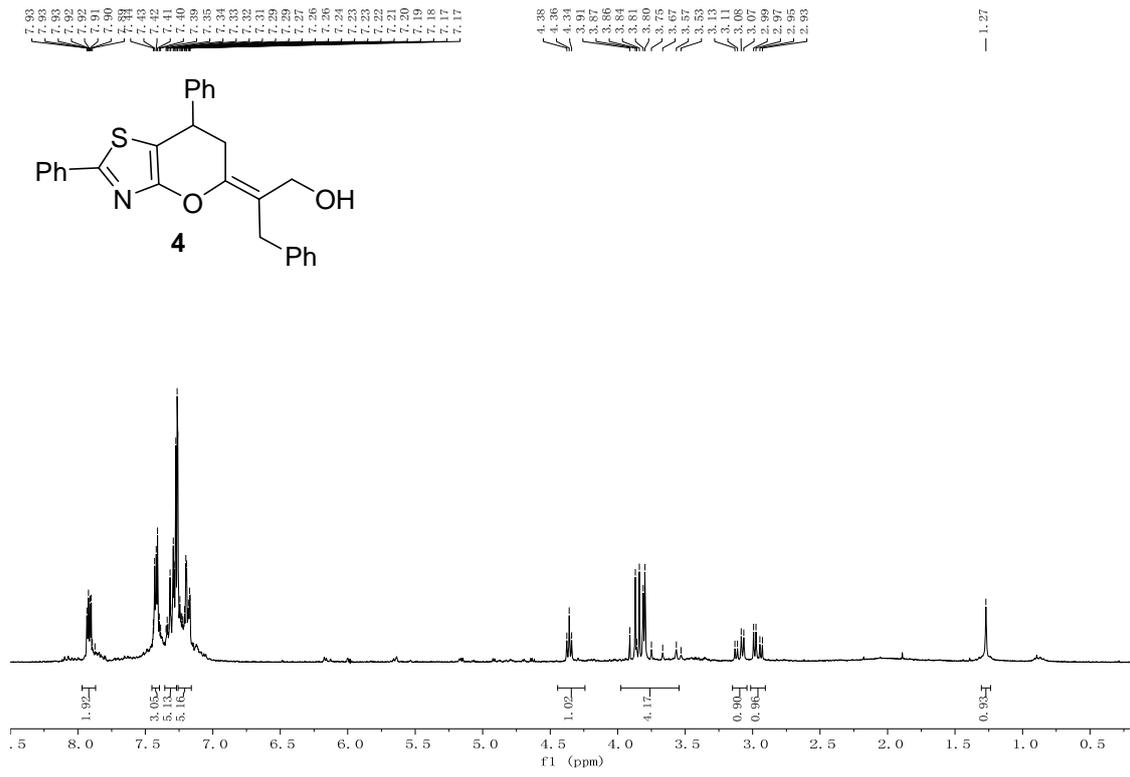


7.93
7.92
7.91
7.90
7.89
7.88
7.87
7.86
7.85
7.75
7.73
7.71
7.68
7.46
7.45
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7.13
7.12



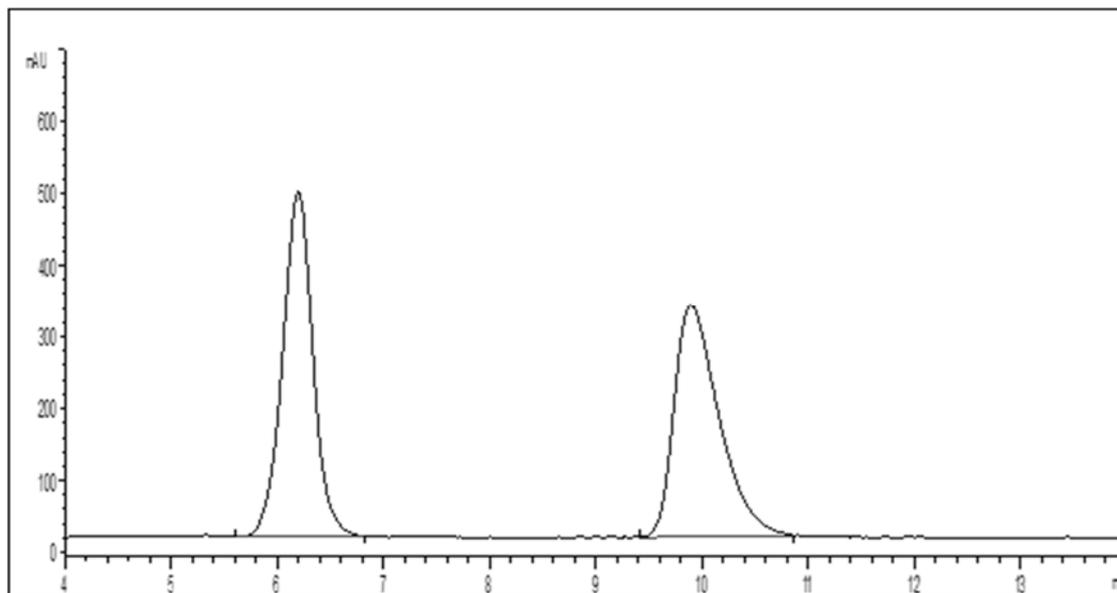
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163.90
157.59
156.55
141.76
137.52
133.26
132.96
132.96
129.96
128.61
128.48
127.32
127.25
126.98
126.47
125.49
125.33
124.43
114.43
108.81
60.15
37.06
32.60
31.76
13.74





HPLC Chromatograms of the Products

HPLC chromatogram of 3aa



Peak RetTime Type Width Area Height Area

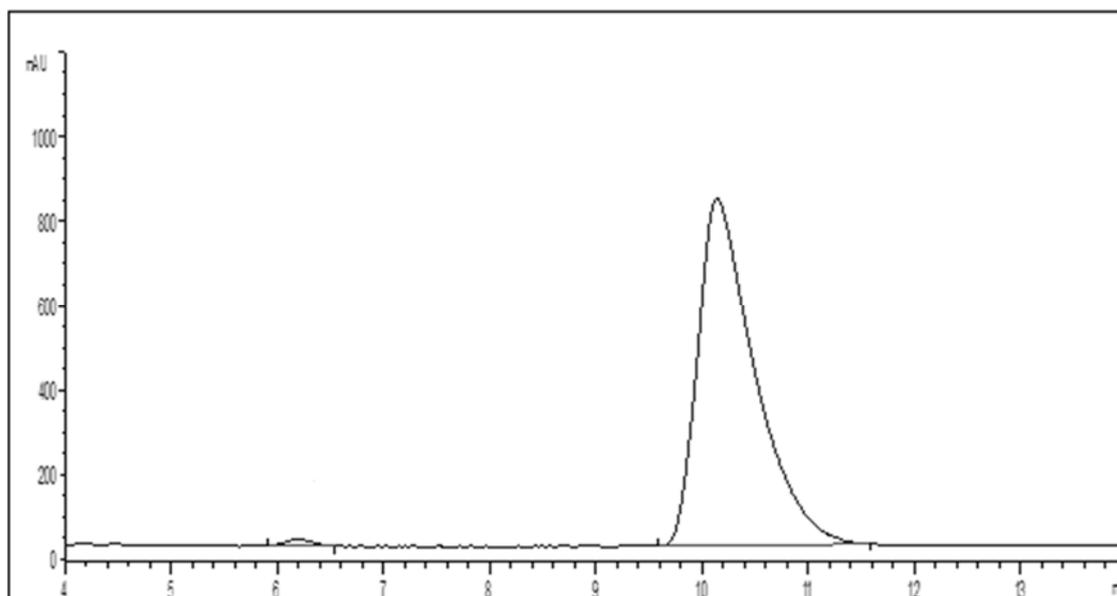
[min] [min] mAU *s [mAU] %

-----|-----|-----|-----|-----|-----|

1 6.200 BB 0.3045 9538.31250 480.32019 50.3986

2 9.896 BB 0.4444 9387.45117 321.19586 49.6014

HPLC chromatogram of (+)-3aa



Peak RetTime Type Width Area Height Area

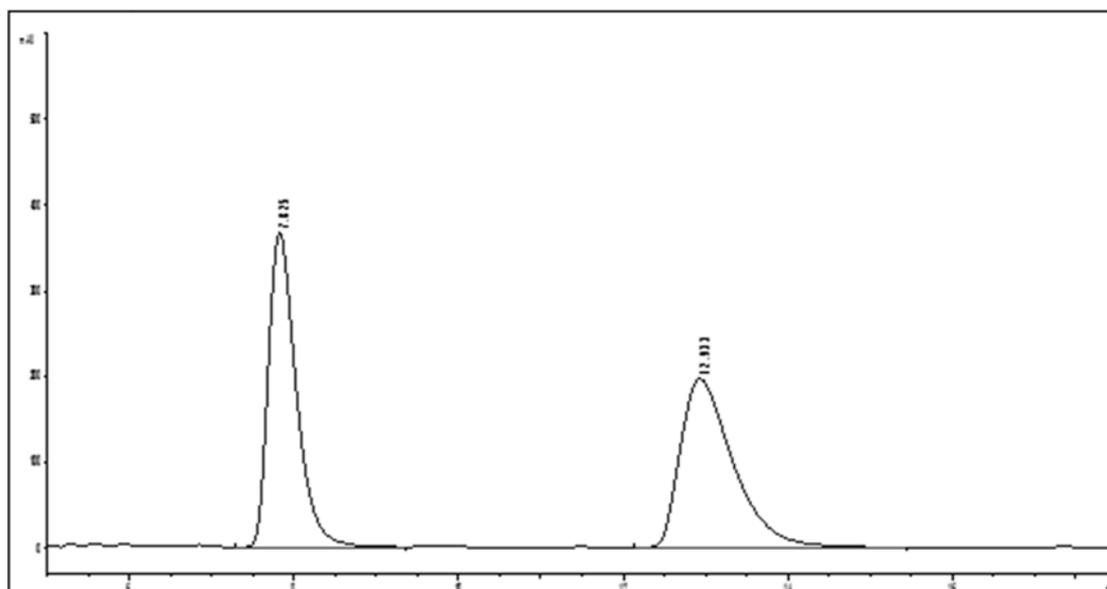
[min] [min] mAU *s [mAU] %

-----|-----|-----|-----|-----|-----|

1 6.192 BB 0.2160 275.45630 15.61180 0.8925

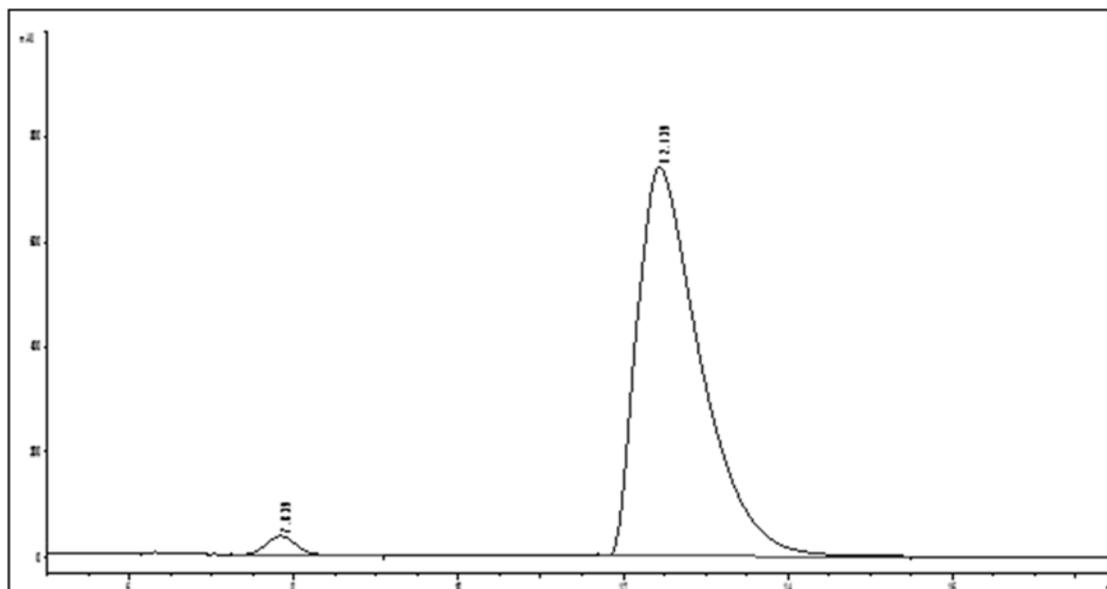
2 10.140 BB 0.5302 3.05892e4 822.05914 99.1075

HPLC chromatogram of 3aj



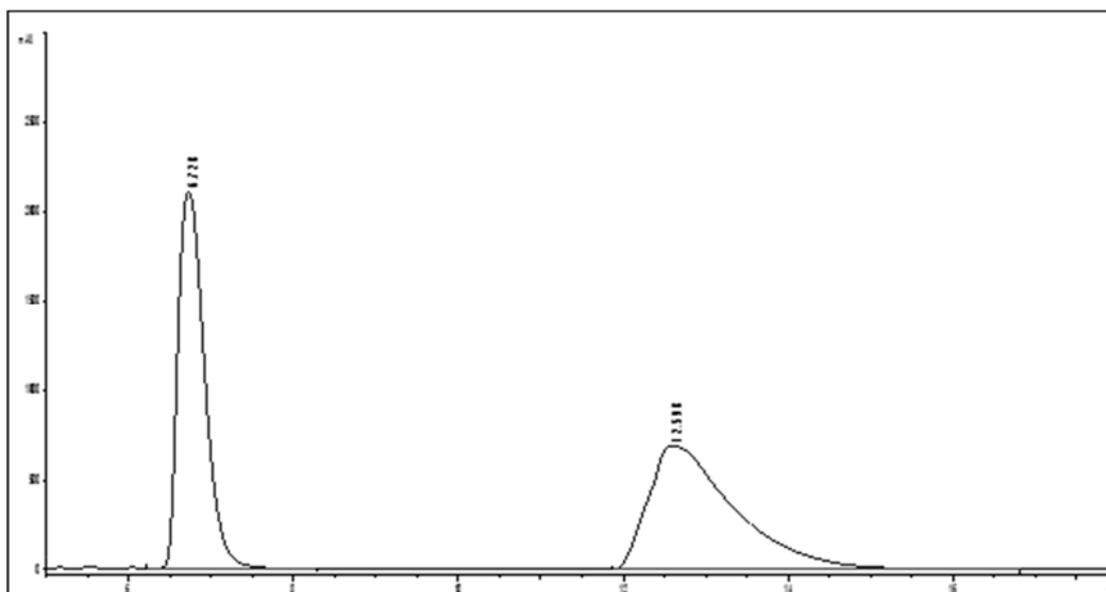
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.825	BB	0.3612	8611.05566	366.80972	49.7399
2	12.933	BB	0.6847	8701.10840	195.68748	50.2601

HPLC chromatogram of (+)-3aj



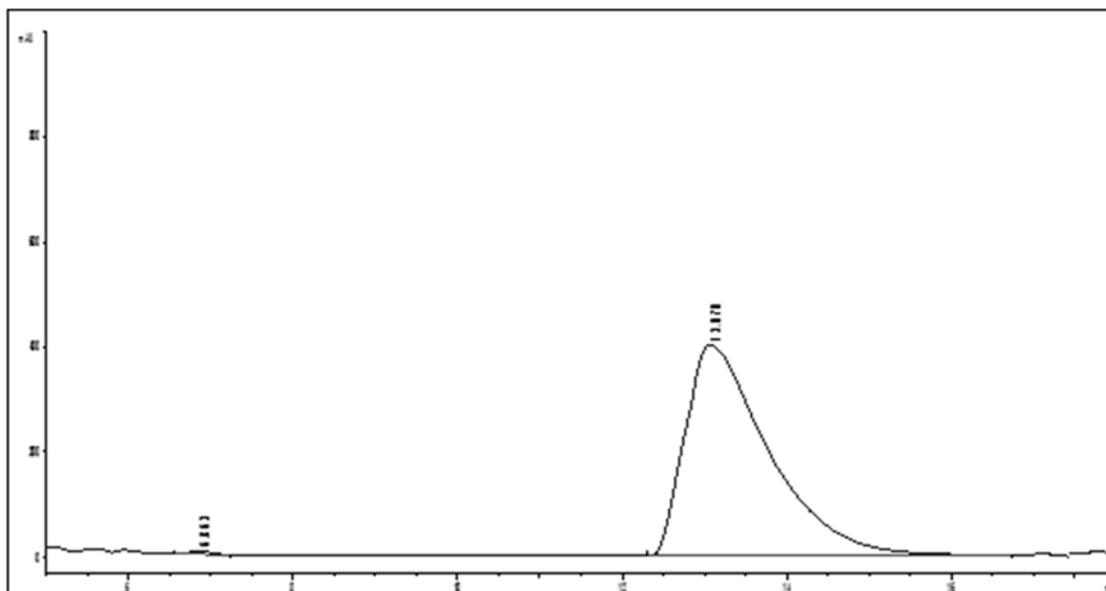
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.839	BB	0.4243	1041.57117	37.19392	2.5775
2	12.439	BB	0.8112	3.93685e4	740.22412	97.4225

HPLC chromatogram of 3ma



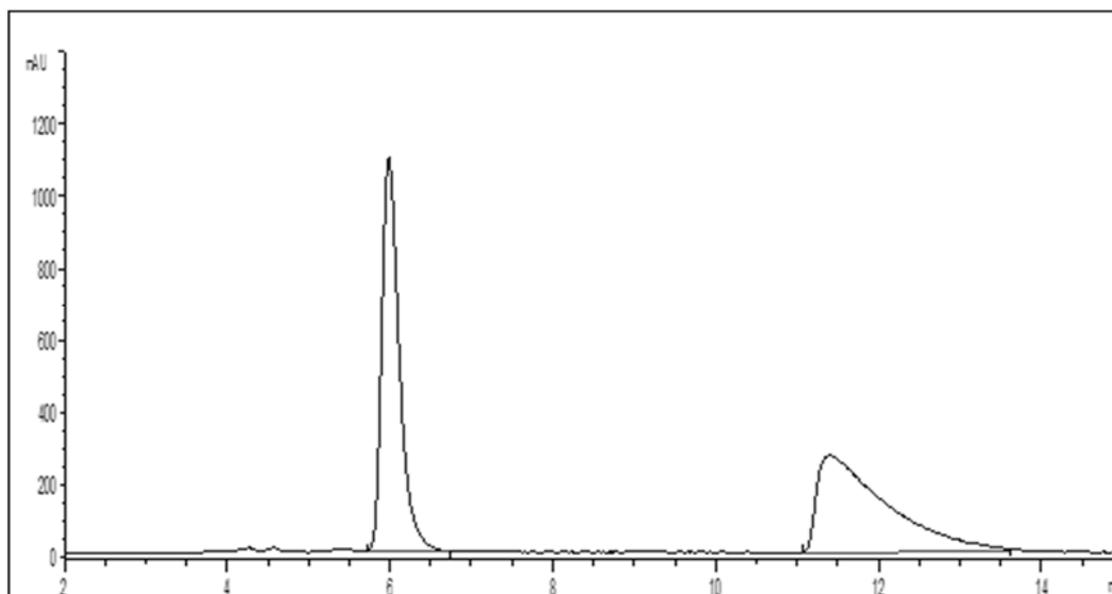
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	6.728	BB	0.3526	4.71176e4	2106.93188	48.6275
2	12.598	BB	1.0159	4.97774e4	685.65204	51.3725

HPLC chromatogram of (+)-3ma



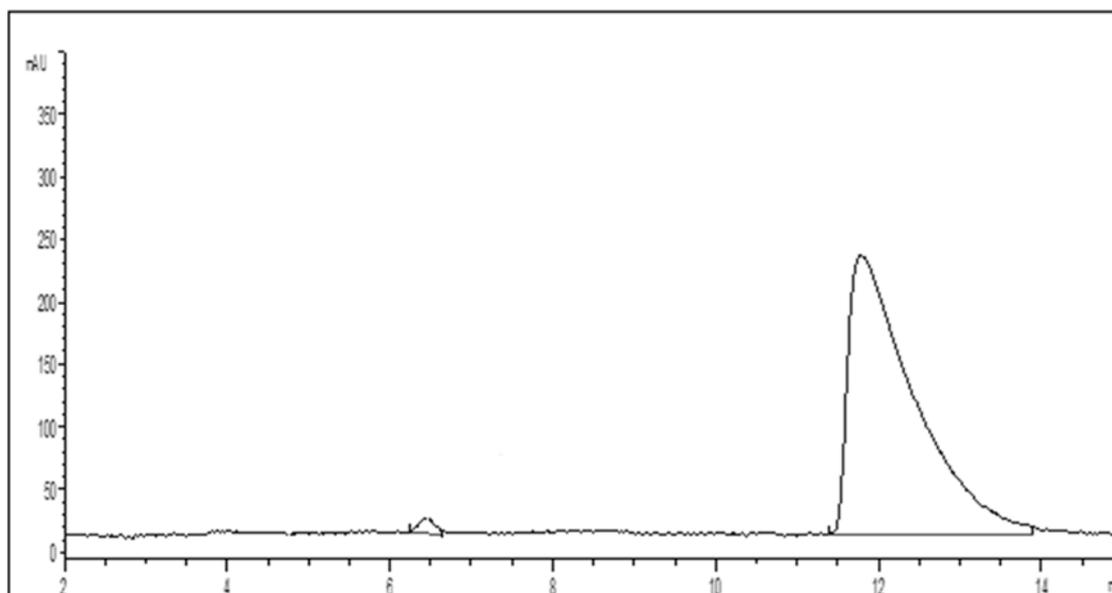
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area [%]
1	6.863	BB	0.2890	104.95959	5.62676	0.3750
2	13.070	BB	0.9917	2.78845e4	397.49524	99.6250

HPLC chromatogram of 3na



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.985	MM	0.2248	1.62344e4	1089.74548	50.4103
2	11.403	MM	0.9841	1.59701e4	270.46375	49.5897

HPLC chromatogram of (+)-3na



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.455	MM	0.2342	175.96973	12.52522	1.3801
2	11.783	MM	0.9345	1.25748e4	224.26157	98.6199

X-Ray Crystallographic Data of 3ma

Crystallographic data for **3ma** have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1482506.

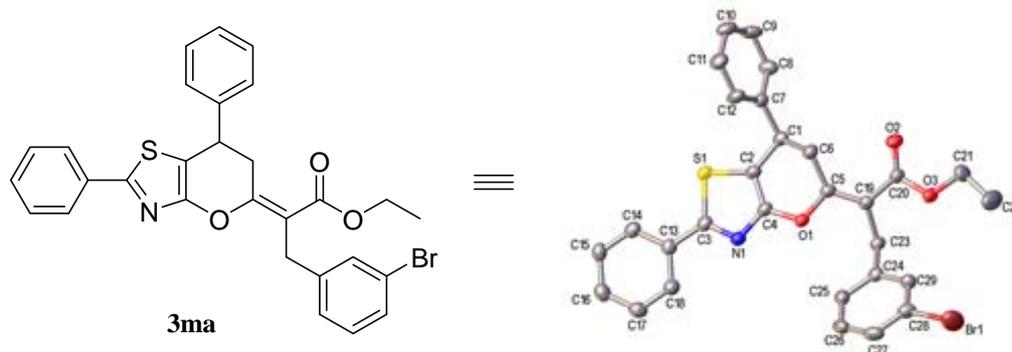


Table 1. Crystal data and structure refinement for **3ma**.

Identification code	mx3974	
Empirical formula	C ₂₉ H ₂₄ Br N O ₃ S	
Formula weight	546.46	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.689(3) Å	a = 90°.
	b = 20.594(10) Å	b = 90°.
	c = 21.431(11) Å	g = 90°.
Volume	2511(2) Å ³	
Z	4	
Density (calculated)	1.446 Mg/m ³	
Absorption coefficient	1.752 mm ⁻¹	
F(000)	1120	
Crystal size	0.26 x 0.08 x 0.04 mm ³	
Theta range for data collection	1.900 to 27.500°.	
Index ranges	-4<=h<=7, -26<=k<=26, -26<=l<=27	
Reflections collected	17429	
Independent reflections	5777 [R(int) = 0.0521]	
Completeness to theta = 26.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6724	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5777 / 0 / 317	
Goodness-of-fit on F ²	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.0987	
R indices (all data)	R1 = 0.0542, wR2 = 0.1029	
Absolute structure parameter	-0.008(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.475 and -0.497 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3ma**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Br1	818(1)	7277(1)	1894(1)	60(1)
S1	8783(2)	4387(1)	5675(1)	32(1)
O1	4902(5)	5192(1)	4433(1)	34(1)
O2	-24(6)	6614(2)	5110(2)	46(1)
O3	-1289(6)	6596(2)	4129(1)	42(1)
N1	8075(6)	4483(2)	4493(2)	29(1)
C1	4874(7)	5291(2)	5792(2)	30(1)
C2	6553(7)	4888(2)	5429(2)	30(1)
C3	9425(7)	4197(2)	4903(2)	29(1)
C4	6487(7)	4865(2)	4799(2)	29(1)
C5	3476(7)	5651(2)	4727(2)	30(1)
C6	4215(8)	5864(2)	5364(2)	33(1)
C7	5761(8)	5517(2)	6422(2)	30(1)
C8	4467(8)	5386(2)	6954(2)	37(1)
C9	5229(10)	5598(2)	7533(2)	44(1)
C10	7290(10)	5940(2)	7590(2)	42(1)
C11	8614(9)	6073(2)	7064(2)	41(1)
C12	7854(8)	5859(2)	6487(2)	39(1)
C13	11371(7)	3762(2)	4732(2)	30(1)
C14	12953(7)	3526(2)	5176(2)	33(1)
C15	14795(8)	3123(2)	5004(2)	36(1)
C16	15094(8)	2964(2)	4383(2)	38(1)
C17	13567(8)	3195(2)	3939(2)	39(1)
C18	11692(8)	3590(2)	4114(2)	34(1)
C19	1640(7)	5854(2)	4375(2)	28(1)
C20	81(7)	6383(2)	4591(2)	30(1)
C21	-2789(9)	7151(2)	4264(2)	45(1)
C22	-3724(14)	7405(3)	3681(3)	77(2)
C23	1155(8)	5542(2)	3745(2)	29(1)
C24	2381(7)	5845(2)	3191(2)	30(1)
C25	4541(7)	5611(2)	2976(2)	36(1)
C26	5586(8)	5872(2)	2450(2)	42(1)
C27	4532(9)	6379(2)	2129(2)	40(1)
C28	2402(9)	6607(2)	2341(2)	37(1)
C29	1305(8)	6348(2)	2864(2)	34(1)

Table 3. Bond lengths [Å] and angles [°] for **3ma**.

Br1-C28	1.907(5)
S1-C2	1.718(4)
S1-C3	1.737(4)
O1-C4	1.371(5)
O1-C5	1.395(5)
O2-C20	1.210(5)
O3-C20	1.335(5)
O3-C21	1.454(5)
N1-C3	1.308(5)
N1-C4	1.366(5)
C1-H1	0.9800
C1-C2	1.487(6)
C1-C6	1.541(6)
C1-C7	1.515(5)
C2-C4	1.351(6)
C3-C13	1.470(6)
C5-C6	1.495(6)
C5-C19	1.355(6)
C6-H6A	0.9700
C6-H6B	0.9700
C7-C8	1.383(6)
C7-C12	1.389(6)
C8-H8	0.9300
C8-C9	1.387(6)
C9-H9	0.9300
C9-C10	1.372(7)
C10-H10	0.9300
C10-C11	1.384(7)
C11-H11	0.9300
C11-C12	1.383(6)
C12-H12	0.9300
C13-C14	1.396(6)
C13-C18	1.384(6)
C14-H14	0.9300
C14-C15	1.386(6)
C15-H15	0.9300
C15-C16	1.381(6)
C16-H16	0.9300
C16-C17	1.374(6)
C17-H17	0.9300
C17-C18	1.393(6)
C18-H18	0.9300

C19-C20	1.479(6)
C19-C23	1.520(5)
C21-H21A	0.9700
C21-H21B	0.9700
C21-C22	1.454(7)
C22-H22A	0.9600
C22-H22B	0.9600
C22-H22C	0.9600
C23-H23A	0.9700
C23-H23B	0.9700
C23-C24	1.513(6)
C24-C25	1.398(6)
C24-C29	1.392(6)
C25-H25	0.9300
C25-C26	1.384(6)
C26-H26	0.9300
C26-C27	1.385(7)
C27-H27	0.9300
C27-C28	1.377(7)
C28-C29	1.389(6)
C29-H29	0.9300
C2-S1-C3	89.9(2)
C4-O1-C5	117.2(3)
C20-O3-C21	116.9(3)
C3-N1-C4	109.0(3)
C2-C1-H1	107.8
C2-C1-C6	105.8(3)
C2-C1-C7	115.1(4)
C6-C1-H1	107.8
C7-C1-H1	107.8
C7-C1-C6	112.1(3)
C1-C2-S1	130.5(3)
C4-C2-S1	107.8(3)
C4-C2-C1	121.6(4)
N1-C3-S1	114.5(3)
N1-C3-C13	123.3(4)
C13-C3-S1	122.2(3)
N1-C4-O1	116.3(3)
C2-C4-O1	124.9(4)
C2-C4-N1	118.7(4)
O1-C5-C6	116.6(3)
C19-C5-O1	114.0(4)
C19-C5-C6	129.4(4)

C1-C6-H6A	109.0
C1-C6-H6B	109.0
C5-C6-C1	112.8(3)
C5-C6-H6A	109.0
C5-C6-H6B	109.0
H6A-C6-H6B	107.8
C8-C7-C1	119.8(4)
C8-C7-C12	118.3(4)
C12-C7-C1	122.0(4)
C7-C8-H8	119.7
C7-C8-C9	120.6(4)
C9-C8-H8	119.7
C8-C9-H9	119.7
C10-C9-C8	120.5(4)
C10-C9-H9	119.7
C9-C10-H10	120.2
C9-C10-C11	119.6(4)
C11-C10-H10	120.2
C10-C11-H11	120.1
C12-C11-C10	119.7(4)
C12-C11-H11	120.1
C7-C12-H12	119.4
C11-C12-C7	121.2(4)
C11-C12-H12	119.4
C14-C13-C3	121.8(4)
C18-C13-C3	119.6(4)
C18-C13-C14	118.6(4)
C13-C14-H14	119.5
C15-C14-C13	121.0(4)
C15-C14-H14	119.5
C14-C15-H15	120.3
C16-C15-C14	119.3(4)
C16-C15-H15	120.3
C15-C16-H16	119.7
C17-C16-C15	120.5(4)
C17-C16-H16	119.7
C16-C17-H17	120.0
C16-C17-C18	120.0(4)
C18-C17-H17	120.0
C13-C18-C17	120.5(4)
C13-C18-H18	119.7
C17-C18-H18	119.7
C5-C19-C20	121.1(4)
C5-C19-C23	120.2(4)

C20-C19-C23	118.7(4)
O2-C20-O3	121.6(4)
O2-C20-C19	127.3(4)
O3-C20-C19	111.1(4)
O3-C21-H21A	109.9
O3-C21-H21B	109.9
O3-C21-C22	109.0(4)
H21A-C21-H21B	108.3
C22-C21-H21A	109.9
C22-C21-H21B	109.9
C21-C22-H22A	109.5
C21-C22-H22B	109.5
C21-C22-H22C	109.5
H22A-C22-H22B	109.5
H22A-C22-H22C	109.5
H22B-C22-H22C	109.5
C19-C23-H23A	108.3
C19-C23-H23B	108.3
H23A-C23-H23B	107.4
C24-C23-C19	116.1(3)
C24-C23-H23A	108.3
C24-C23-H23B	108.3
C25-C24-C23	121.5(4)
C29-C24-C23	120.0(4)
C29-C24-C25	118.5(4)
C24-C25-H25	119.6
C26-C25-C24	120.8(4)
C26-C25-H25	119.6
C25-C26-H26	119.6
C25-C26-C27	120.7(4)
C27-C26-H26	119.6
C26-C27-H27	120.9
C28-C27-C26	118.3(4)
C28-C27-H27	120.9
C27-C28-Br1	119.8(4)
C27-C28-C29	122.1(4)
C29-C28-Br1	118.1(4)
C24-C29-H29	120.2
C28-C29-C24	119.6(4)
C28-C29-H29	120.2

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3ma**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Br1	76(1)	57(1)	46(1)	23(1)	14(1)	13(1)
S1	34(1)	38(1)	25(1)	2(1)	-4(1)	1(1)
O1	36(2)	43(2)	23(2)	-2(1)	-6(1)	11(1)
O2	52(2)	55(2)	30(2)	-11(2)	-8(2)	18(2)
O3	49(2)	49(2)	28(2)	-3(1)	-8(2)	21(2)
N1	33(2)	31(2)	24(2)	0(2)	-2(1)	1(2)
C1	29(2)	35(2)	26(2)	1(2)	-2(2)	-7(2)
C2	31(2)	34(2)	23(2)	2(2)	0(2)	-4(2)
C3	30(2)	29(2)	29(2)	2(2)	-4(2)	-5(2)
C4	30(2)	32(2)	25(2)	1(2)	-4(2)	-3(2)
C5	34(2)	31(2)	23(2)	-1(2)	0(2)	-1(2)
C6	35(2)	36(2)	28(2)	-2(2)	-5(2)	3(2)
C7	30(2)	35(2)	23(2)	1(2)	-1(2)	2(2)
C8	41(2)	40(2)	31(2)	-2(2)	6(2)	-10(2)
C9	63(3)	47(3)	22(2)	-4(2)	10(2)	-7(3)
C10	60(3)	41(3)	25(2)	-6(2)	-6(2)	-1(2)
C11	42(3)	47(3)	34(2)	-6(2)	-7(2)	-7(2)
C12	38(2)	56(3)	23(2)	-2(2)	-1(2)	-8(2)
C13	31(2)	26(2)	33(2)	3(2)	-1(2)	-2(2)
C14	34(2)	32(2)	32(2)	2(2)	-4(2)	-5(2)
C15	31(2)	33(2)	43(3)	7(2)	-4(2)	1(2)
C16	36(2)	34(2)	44(3)	2(2)	4(2)	3(2)
C17	44(3)	37(2)	35(3)	-2(2)	5(2)	1(2)
C18	37(2)	33(2)	31(2)	2(2)	-2(2)	0(2)
C19	30(2)	31(2)	25(2)	2(2)	0(2)	-3(2)
C20	32(2)	34(2)	25(2)	3(2)	-2(2)	2(2)
C21	52(3)	44(3)	40(3)	-1(2)	0(2)	22(2)
C22	109(5)	71(4)	51(4)	-5(3)	-21(4)	53(4)
C23	33(2)	30(2)	23(2)	0(2)	-4(2)	0(2)
C24	30(2)	32(2)	27(2)	-2(2)	-4(2)	-3(2)
C25	32(2)	45(2)	32(2)	-6(2)	-4(2)	5(2)
C26	30(2)	64(3)	31(2)	-10(2)	5(2)	2(2)
C27	45(3)	49(3)	27(2)	-5(2)	10(2)	-12(2)
C28	45(3)	40(2)	27(2)	1(2)	2(2)	-3(2)
C29	33(2)	40(2)	29(2)	1(2)	3(2)	1(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3ma**.

	x	y	z	U(eq)
H1	3452	5033	5862	36
H6A	2943	6108	5555	39
H6B	5557	6153	5327	39
H8	3073	5152	6922	45
H9	4336	5509	7886	53
H10	7794	6080	7980	51
H11	10008	6306	7098	49
H12	8760	5944	6135	47
H14	12768	3640	5593	39
H15	15820	2961	5305	43
H16	16339	2699	4265	46
H17	13786	3088	3521	46
H18	10647	3740	3813	40
H21A	-1889	7485	4476	54
H21B	-4069	7019	4535	54
H22A	-4379	7056	3441	115
H22B	-2482	7608	3449	115
H22C	-4926	7719	3770	115
H23A	1611	5089	3768	35
H23B	-526	5555	3671	35
H25	5285	5276	3189	43
H26	7011	5706	2309	50
H27	5246	6560	1780	49
H29	-138	6510	2996	40

Table 6. Torsion angles [°] for **3ma**.

Br1-C28-C29-C24	178.1(3)
S1-C2-C4-O1	178.5(3)
S1-C2-C4-N1	-0.3(5)
S1-C3-C13-C14	-6.2(6)
S1-C3-C13-C18	175.2(3)
O1-C5-C6-C1	-46.8(5)
O1-C5-C19-C20	-174.3(3)
O1-C5-C19-C23	5.3(5)
N1-C3-C13-C14	172.2(4)
N1-C3-C13-C18	-6.4(6)
C1-C2-C4-O1	-1.0(7)
C1-C2-C4-N1	-179.8(4)
C1-C7-C8-C9	-178.9(4)
C1-C7-C12-C11	178.6(4)
C2-S1-C3-N1	-0.2(3)
C2-S1-C3-C13	178.3(3)
C2-C1-C6-C5	50.2(5)
C2-C1-C7-C8	-125.2(4)
C2-C1-C7-C12	55.0(6)
C3-S1-C2-C1	179.7(4)
C3-S1-C2-C4	0.2(3)
C3-N1-C4-O1	-178.8(3)
C3-N1-C4-C2	0.1(5)
C3-C13-C14-C15	-179.2(4)
C3-C13-C18-C17	178.0(4)
C4-O1-C5-C6	15.3(5)
C4-O1-C5-C19	-166.8(4)
C4-N1-C3-S1	0.1(4)
C4-N1-C3-C13	-178.4(4)
C5-O1-C4-N1	-171.6(3)
C5-O1-C4-C2	9.6(6)
C5-C19-C20-O2	-12.9(7)
C5-C19-C20-O3	167.2(4)
C5-C19-C23-C24	-89.1(5)
C6-C1-C2-S1	151.9(3)
C6-C1-C2-C4	-28.7(5)
C6-C1-C7-C8	113.8(4)
C6-C1-C7-C12	-66.0(5)
C6-C5-C19-C20	3.3(7)
C6-C5-C19-C23	-177.1(4)
C7-C1-C2-S1	27.5(6)

C7-C1-C2-C4	-153.1(4)
C7-C1-C6-C5	176.5(4)
C7-C8-C9-C10	-0.4(7)
C8-C7-C12-C11	-1.2(7)
C8-C9-C10-C11	0.1(7)
C9-C10-C11-C12	-0.3(8)
C10-C11-C12-C7	0.9(8)
C12-C7-C8-C9	1.0(7)
C13-C14-C15-C16	1.3(6)
C14-C13-C18-C17	-0.6(6)
C14-C15-C16-C17	-0.8(6)
C15-C16-C17-C18	-0.3(7)
C16-C17-C18-C13	1.1(7)
C18-C13-C14-C15	-0.6(6)
C19-C5-C6-C1	135.7(4)
C19-C23-C24-C25	93.7(5)
C19-C23-C24-C29	-89.4(5)
C20-O3-C21-C22	167.0(5)
C20-C19-C23-C24	90.5(5)
C21-O3-C20-O2	4.5(6)
C21-O3-C20-C19	-175.5(4)
C23-C19-C20-O2	167.5(4)
C23-C19-C20-O3	-12.4(5)
C23-C24-C25-C26	176.8(4)
C23-C24-C29-C28	-177.5(4)
C24-C25-C26-C27	1.0(7)
C25-C24-C29-C28	-0.6(6)
C25-C26-C27-C28	-1.2(7)
C26-C27-C28-Br1	-177.2(3)
C26-C27-C28-C29	0.5(7)
C27-C28-C29-C24	0.4(7)
C29-C24-C25-C26	-0.1(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3ma** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
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