

A Formal [4+1] Cycloaddition Reaction of Baylis-Hillman Bromides

with Sulfur Ylides: Facile Access to α Alkenyl Lactones

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Supporting Information

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Experimental Section

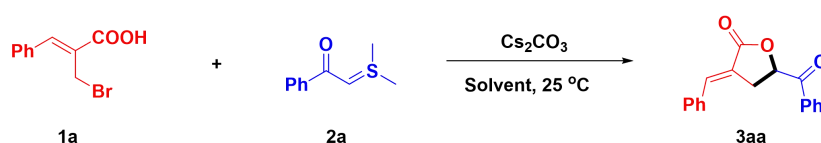
1. General Information

General. Unless otherwise noted, materials were purchased from commercial suppliers and used without purification. Dichloromethane and Xylenes were freshly distilled from calcium hydride. Toluene, tetrahydrofuran (THF) and Et₂O were distilled from sodium/benzophenone. Mesitylene was dried overnight with calcium chloride and then distilled from sodium/benzophenone. Other solvents were also purified before using. Reactions were monitored by thin layer chromatography (TLC), and column chromatography purifications were performed using 200-300 mesh silica gel. ¹H NMR spectra were recorded on 400 MHz spectrophotometers by China Three Gorges University. Solvent for NMR is CDCl₃. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS), relative to the signal of chloroform (δ 7.26, singlet). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets), coupling constants (Hz) and integration; ¹³C NMR spectra were on recorded on 400 (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm relative to the central line of the heptalet at 77.0 ppm for CDCl₃. Melting point was measured with WRR melting point instrument. High resolution mass spectra (HRMS) analyses were taken on a Shimadzu LCMS-IT-TOF mass spectrometer. IR spectra were recorded on a NEXUS FT-IR spectrometer.

Sulfur ylides¹ and Baylis-Hillman bromides² are prepared according to previous report.

2. Reaction Optimization and Result Summary

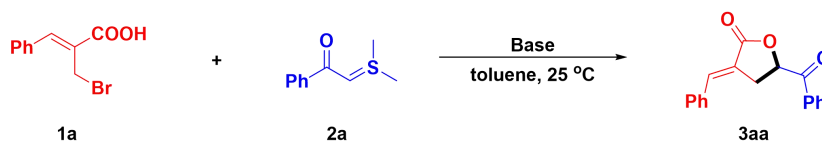
Table S1. The screening of solvents.^[a]



Entry	Solvent	Conc. [M]	Base	Equiv.	Yield ^[b]
1	CH ₂ Cl ₂	0.1	Cs ₂ CO ₃	1.5	49%
2	toluene	0.1	Cs₂CO₃	1.5	69%
3	THF	0.1	Cs ₂ CO ₃	1.5	23%
4	CH ₃ CN	0.1	Cs ₂ CO ₃	1.5	29%
5	Et ₂ O	0.1	Cs ₂ CO ₃	1.5	28%
6	Xylenes	0.1	Cs ₂ CO ₃	1.5	68%
7	Mesitylene	0.1	Cs ₂ CO ₃	1.5	65%

[a] Reaction conditions: **1a** (0.4 mmol, 96.0 mg), **2a** (0.52 mmol, 93.7 mg), Cs₂CO₃ (0.6 mmol, 195.5 mg), solvent (4 mL). [b] Yield of isolated product.

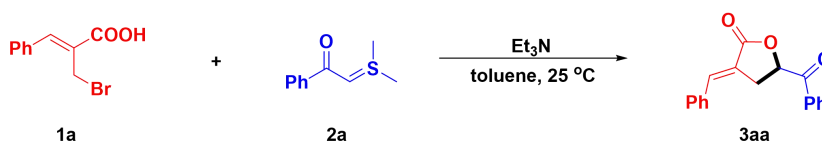
Table S2. The screening of base.^[a]



Entry	Solvent	Conc. [M]	Base	Equiv.	Yield ^[b]
1	toluene	0.1	-	-	49%
2	toluene	0.1	NaOH	1.5	67%
3	toluene	0.1	<i>t</i> -BuOK	1.5	73%
4	toluene	0.1	Cs ₂ CO ₃	1.5	68%
5	toluene	0.1	Et₃N	1.5	81%
6	toluene	0.1	DIPEA	1.5	80%
7	toluene	0.1	Py.	1.5	42%
8	toluene	0.1	DBU	1.5	76%
9	toluene	0.1	DABCO	1.5	Trace
10	toluene	0.1	TMG	1.5	77%

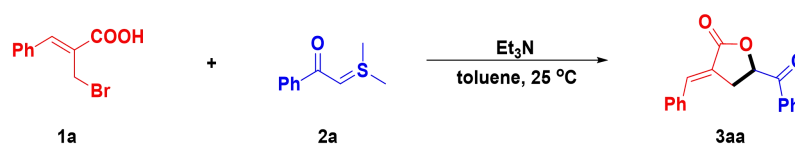
[a] Reaction conditions: **1a** (0.4 mmol, 96.0 mg), **2a** (0.52 mmol, 93.7 mg), base (0.6 mmol) and toluene (4 mL). [b] Yield of isolated product.

Table S3. The screening of the equivalent of Et₃N.^[a]



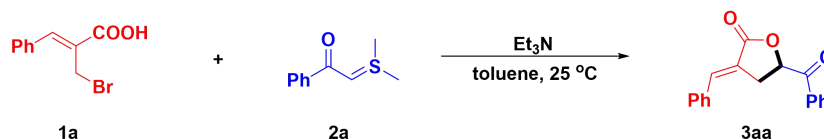
Entry	Solvent	Conc. [M]	Base	Equiv.	Yield ^[b]
1	toluene	0.1	Et ₃ N	1.1	70%
2	toluene	0.1	Et₃N	1.5	81%
3	toluene	0.1	Et ₃ N	2.0	75%

[a] Reaction conditions: **1a** (0.4 mmol, 96.0 mg), **2a** (0.52 mmol, 93.7 mg), Et₃N and toluene (4 mL). [b] Yield of isolated product.

Table S4. The screening of the ratio of substrates.^[a]

Entry	Solvent	Conc. [M]	Base	Equiv.	Ratio (2a)	Yield ^[b]
1	toluene	0.1	Et ₃ N	1.5	1.1	61%
2	toluene	0.1	Et ₃ N	1.5	1.3	81%
3	toluene	0.1	Et₃N	1.5	1.5	87%

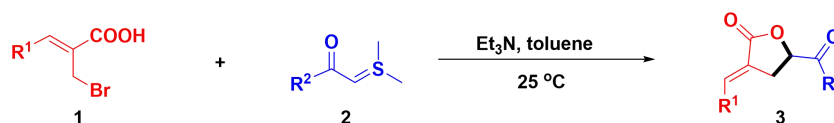
[a] Reaction conditions: **1a** (0.4 mmol, 96.0 mg), **2a**, Et₃N (0.6 mmol, 60.7 mg), toluene (4 mL). [b] Yield of isolated product.

Table S5. The screening of the concentration.^[a]

Entry	Solvent	Conc. [M]	Base	Equiv.	Yield ^[b]
1	toluene	0.2	Et ₃ N	1.5	70%
2	toluene	0.1	Et₃N	1.5	87%
3	toluene	0.05	Et ₃ N	1.5	83%

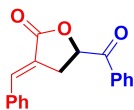
[a] Reaction conditions: **1a** (0.4 mmol, 96.0 mg), **2a** (0.6 mmol, 108.6 mg), Et₃N (0.6 mmol, 60.7 mg), toluene. [b] Yield of isolated product.

3. Experimental Procedures and Characterizations of Products



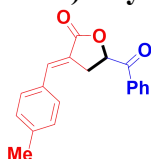
A dry 10 mL flask equipped with a magnetic stirring bar, was sequentially charged with sulfur ylide **2** (0.6 mmol, 1.5 equiv.), toluene (4.0 mL), Et₃N (0.6 mmol, 1.5 equiv.). The reaction mixture was stirred for 15 min at 25°C, then to the above mixture, was added Baylis-Hillman bromides **1** (0.4 mmol, 1.0 equiv.). The reaction was monitored via TLC (Petroleum Ether/Ethyl Acetate = 4:1). Thereafter, the reaction mixture was purified by flash chromatography on silica gel (Petroleum Ether/Ethyl Acetate = 5:1 ~ 15:1) to give the desired product **3**.

(*R,E*)-5-benzoyl-3-benzylidenedihydrofuran-2(3*H*)-one (3aa)



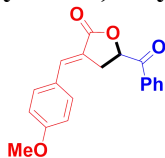
Yellow solid, 97 mg, 87% yield, reaction time for 2 h, mp 127-129 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.09 – 7.99 (m, 2H), 7.70 – 7.60 (m, 2H), 7.53 (dd, *J* = 14.1, 6.9 Hz, 4H), 7.48 – 7.37 (m, 3H), 5.85 (dd, *J* = 8.7, 5.4 Hz, 1H), 3.62 – 3.45 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 193.8, 171.0, 138.0, 134.3, 134.3, 133.8, 130.2, 130.1, 129.1, 129.0, 121.8, 75.9, 29.9; HRMS: C₁₈H₁₄O₃ [M+K⁺]; calculated: 317.0575, found: 317.0598; IR: 2919, 2820, 1751, 1691, 1650, 1449, 1226, 1193, 1182, 1062, 937, 694 cm⁻¹.

(*R,E*)-5-benzoyl-3-(4-methylbenzylidene)dihydrofuran-2(3*H*)-one (3ba)



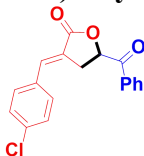
Yellow solid, 98 mg, 84% yield, reaction time for 16 h, mp 161-163 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.04 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.64 (ddt, *J* = 12.6, 5.6, 2.0 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.84 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.59 – 3.47 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 193.9, 171.2, 140.8, 138.1, 134.3, 133.9, 131.6, 130.2, 129.7, 129.1, 129.0, 120.6, 75.9, 29.9, 21.5; HRMS: C₁₉H₁₆O₃ [M+H⁺]; calculated: 293.1172, found: 293.1166; IR: 2936, 2811, 1751, 1686, 1648, 1318, 1228, 1173, 1055, 1019, 691, 525 cm⁻¹.

(*R,E*)-5-benzoyl-3-(4-methoxybenzylidene)dihydrofuran-2(3*H*)-one (3ca)



Yellow solid, 103 mg, 84% yield, reaction time for 8 h, mp 127-129 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 2.7 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.83 (dd, *J* = 8.9, 5.4 Hz, 1H), 3.85 (s, 3H), 3.54 – 3.42 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 194.0, 161.2, 137.8, 134.2, 133.9, 132.0, 129.1, 129.0, 127.0, 118.8, 114.5, 76.9, 66.4, 29.8; HRMS: C₁₉H₁₆O₄ [M+H⁺]; calculated: 309.1121, found: 309.1119; IR: 2923, 2812, 1750, 1693, 1648, 1510, 1262, 1165, 1046, 1023, 926, 805, 728, 694, 524 cm⁻¹.

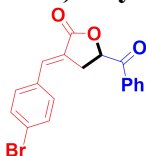
(*R,E*)-5-benzoyl-3-(4-chlorobenzylidene)dihydrofuran-2(3*H*)-one (3da)



Yellow solid, 112 mg, 91% yield, reaction time for 4 h, mp 152-153 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.45 – 7.37 (m, 4H), 5.88 (t, *J* = 7.0 Hz, 1H), 3.55 – 3.42 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 193.6, 170.8, 136.4, 136.1, 134.3, 133.6, 132.6, 131.2, 129.3, 128.9, 122.4, 75.7, 29.8; HRMS: C₁₈H₁₃ClO₃ [M+K⁺]; calculated: 351.0185, found:

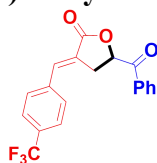
351.0185; IR: 2923, 2845, 1759, 1690, 1651, 1490, 1313, 1221, 1186, 1172, 1054, 930, 830, 742, 694, 665, 517cm⁻¹.

(*R,E*)-5-benzoyl-3-(4-bromobenzylidene)dihydrofuran-2(3*H*)-one (3ea)



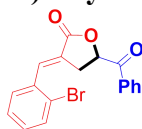
Yellow solid, 128 mg, 90% yield, reaction time for 4 h, mp 162-163 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (dd, *J* = 12.6, 6.9 Hz, 5H), 7.34 (d, *J* = 8.3 Hz, 2H), 5.89 (t, *J* = 7.0 Hz, 1H), 3.47 (dd, *J* = 6.8, 2.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 193.6, 170.8, 136.4, 134.3, 133.6, 133.0, 132.2, 131.4, 129.0, 124.5, 122.6, 75.7, 29.8; HRMS: C₁₈H₁₃BrO₃ [M+Na⁺]; calculated: 378.9940, found: 378.9938; IR: 2976, 2844, 1754, 1688, 1655, 1487, 1320, 1223, 1194, 1175, 1056, 928, 824, 729, 693, 513cm⁻¹.

(*R,E*)-5-benzoyl-3-(4-(trifluoromethyl)benzylidene)dihydrofuran-2(3*H*)-one (3fa)



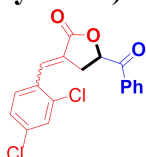
Yellow solid, 129 mg, 93% yield, reaction time for 2 h, mp 142-143 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.08 – 8.00 (m, 2H), 7.65 (ddd, *J* = 17.3, 14.4, 8.2 Hz, 6H), 7.54 (t, *J* = 7.7 Hz, 2H), 5.90 (dd, *J* = 8.7, 5.1 Hz, 1H), 3.64 – 3.45 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 193.4, 170.4, 136.0, 134.5, 133.6, 130.1, 129.1, 125.9, 124.7, 75.7, 29.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.0. HRMS: C₁₉H₁₃F₃O₃ [M+H⁺]; calculated: 347.0890, found: 347.0891; IR: 2943, 2855, 1756, 1681, 1600, 1452, 1417, 1332, 1225, 1117, 1069, 924, 840, 729, 690, 601, 513cm⁻¹.

(*R,E*)-5-benzoyl-3-(2-bromobenzylidene)dihydrofuran-2(3*H*)-one (3ga)



Yellow solid, 121 mg, 85% yield, reaction time for 4 h, mp 119-121 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.92 (s, 1H), 7.65 (t, *J* = 8.9 Hz, 2H), 7.57 – 7.43 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.22 (m, 1H), 5.82 (dd, *J* = 8.7, 5.3 Hz, 1H), 3.56 – 3.34 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 170.1, 136.5, 134.3, 133.7, 131.0, 129.4, 129.0, 127.5, 126.0, 124.8, 75.9, 29.5; HRMS: C₁₈H₁₃BrO₃ [M+H⁺]; calculated: 357.0126, found: 357.0117; IR: 2975, 2670, 1755, 1683, 1634, 1314, 1223, 1154, 1075, 1056, 928, 814, 693, 515cm⁻¹.

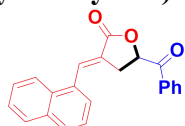
(*R,E*)-5-benzoyl-3-(2,4-dichlorobenzylidene)dihydrofuran-2(3*H*)-one (3ha)



Yellow solid, 119 mg, 86% yield, *trans* : *cis* = 1:1, reaction time for 4 h, mp 141-143 °C. ¹H NMR (400 MHz, CDCl₃): 8.04 (d, *J* = 7.6 Hz, 2H), 7.91 (t, *J* = 2.7 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.61 – 7.46 (m, 3H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.31 (dd,

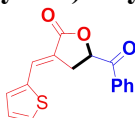
$J = 8.4, 1.7$ Hz, 1H), 5.83 (dd, $J = 8.8, 5.0$ Hz, 1H), 3.51 (ddd, $J = 17.8, 4.7, 3.0$ Hz, 1H), 3.39 (ddd, $J = 17.8, 8.9, 2.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.5, 193.4, 170.1, 136.5, 136.4, 134.4, 134.3, 134.2, 133.7, 133.7, 133.6, 132.6, 131.0, 130.2, 129.9, 129.3, 129.1, 129.1, 129.0, 129.0, 127.5, 127.3, 125.9, 125.2, 124.7, 75.8, 75.8, 29.5, 29.5; HRMS: $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{O}_3$ [$\text{M}+\text{H}^+$]; calculated: 384.9795, found: 384.9795; IR: 2987, 2675, 1745, 1678, 1622, 1332, 1214, 1122, 1034, 1057, 926, 810, 693cm^{-1} .

(*R,E*)-5-benzoyl-3-(naphthalen-1-ylmethylene)dihydrofuran-2(3*H*)-one (3ia)



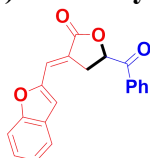
Yellow solid, 106 mg, 88% yield, reaction time for 4 h, mp 143-144 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.36 (s, 1H), 8.11 (d, $J = 8.0$ Hz, 1H), 8.00 (d, $J = 7.6$ Hz, 2H), 7.88 (dd, $J = 7.3, 3.4$ Hz, 2H), 7.66 – 7.45 (m, 7H), 5.85 (t, $J = 7.0$ Hz, 1H), 3.55 – 3.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.9, 171.1, 138.0, 136.1, 134.3, 132.4, 131.4, 131.2, 130.2, 130.2, 129.8, 129.3, 129.0, 129.0, 127.9, 127.2, 124.1, 121.9, 75.9, 30.0; HRMS: $\text{C}_{22}\text{H}_{16}\text{O}_3$ [$\text{M}+\text{H}^+$]; calculated: 351.0992, found: 351.0988; IR: 2965, 2880, 1776, 1695, 1652, 1448, 1337, 1193, 1057, 937, 800, 780, 709, 641cm^{-1} .

(*R,E*)-5-benzoyl-3-(thiophen-2-ylmethylene)dihydrofuran-2(3*H*)-one (3ja)



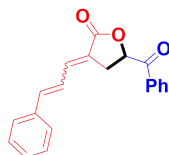
Yellow solid, 87 mg, 77% yield, reaction time for 4 h, mp 143-144 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.04 (s, 2H), 7.81 (s, 1H), 7.66 (t, $J = 7.0$ Hz, 1H), 7.61 – 7.48 (m, 3H), 7.36 (s, 1H), 7.17 (d, $J = 3.8$ Hz, 1H), 5.87 (dd, $J = 8.3, 5.5$ Hz, 1H), 3.54 – 3.33 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.7, 138.6, 134.3, 133.8, 132.8, 130.7, 130.4, 129.0, 128.2, 119.2, 75.7, 29.8; HRMS: $\text{C}_{16}\text{H}_{12}\text{O}_3\text{S}$ [$\text{M}+\text{Na}^+$]; calculated: 307.0399, found: 307.0397; IR: 2924, 2853, 1751, 1686, 1642, 1449, 1416, 1308, 1223, 1176, 1035, 930, 806, 709, 601cm^{-1} .

(*R,E*)-3-(benzofuran-2-ylmethylene)-5-benzoyldihydrofuran-2(3*H*)-one (3ka)



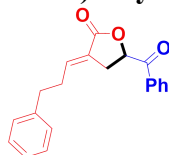
Yellow solid, 130 mg, 77% yield, reaction time for 3 h, mp 153-154 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.10 – 8.01 (m, 2H), 7.61 (ddd, $J = 28.4, 15.1, 7.4$ Hz, 4H), 7.47 (dd, $J = 5.3, 2.2$ Hz, 2H), 7.39 – 7.33 (m, 1H), 7.26 (t, $J = 7.8$ Hz, 1H), 7.03 (s, 1H), 5.90 (t, $J = 7.1$ Hz, 1H), 3.72 (dd, $J = 7.0, 2.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.9, 170.5, 155.9, 152.2, 134.3, 133.8, 129.0, 128.0, 126.6, 124.2, 123.6, 122.5, 122.0, 113.0, 111.5, 76.0, 30.3; HRMS: $\text{C}_{20}\text{H}_{14}\text{O}_4$ [$\text{M}+\text{K}^+$]; calculated: 357.0529, found: 357.0529; IR: 1758, 1699, 1647, 1447, 1316, 1200, 1190, 1178, 1124, 1035, 924, 836, 745, 688cm^{-1} .

(*R,E*)-5-benzoyl-3-((*E*)-3-phenylallylidene)dihydrofuran-2(3*H*)-one (3la)



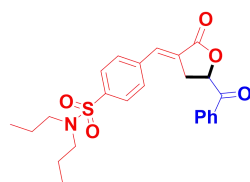
Yellow solid, 91 mg, 75% yield, *trans* : *cis* = 2:1, reaction time for 7 h, mp 134-135 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.07-8.00 (m, 4H), 7.82 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.68-7.62 (m, 2H), 7.51 (ddd, *J* = 11.0, 9.3, 3.8 Hz, 9H), 7.41-7.27 (m, 15H), 6.98 (d, *J* = 15.5 Hz, 2H), 6.82 (dd, *J* = 15.5, 11.4 Hz, 2H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.33 (dd, *J* = 15.7, 10.1 Hz, 1H), 5.84 (dd, *J* = 8.5, 5.8 Hz, 2H), 5.5L9 (dd, *J* = 9.1, 3.1 Hz, 1H), 3.60 (d, *J* = 10.1 Hz, 1H), 3.40-3.36 (m, 3H), 3.00 (dd, *J* = 14.1, 3.1 Hz, 1H), 2.83 (dd, *J* = 14.0, 9.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 194.0, 193.8, 177.4, 170.4, 142.4, 137.2, 136.7, 136.2, 134.0, 133.5, 129.5, 129.0, 129.0, 128.9, 128.8, 128.8, 128.5, 128.1, 127.3, 125.8, 123.4, 122.4, 121.8, 75.8, 50.9, 48.9. HRMS: C₂₀H₁₆O₃ [M+K⁺]; calculated: 343.0737, found: 343.0737; IR:2922, 2849, 1752, 1692, 1648, 1469. 1449, 1384, 1222, 1190, 1121, 1066, 1022, 924, 767, 668, 536 cm⁻¹.

(*R,E*)-5-benzoyl-3-(3-phenylpropylidene)dihydrofuran-2(3*H*)-one (3ma)



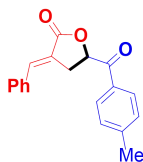
Yellow solid, 78 mg, 64% yield, reaction time for 6 h, mp 65-66 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.99-7.90 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 8.7 Hz, 3H), 6.83 (tt, *J* = 7.6, 2.8 Hz, 1H), 5.67 (t, *J* = 7.2 Hz, 1H), 2.94 – 2.87 (m, 2H), 2.84 – 2.71 (m, 2H), 2.50 (qd, *J* = 7.2, 1.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 193.7, 169.6, 140.8, 140.4, 134.2, 133.6, 128.9, 128.4, 126.3, 124.7, 75.6, 34.0, 32.2, 27.8; HRMS: C₂₀H₁₈O₃ [M+K⁺]; calculated: 357.0529, found: 357.0529; IR:2923, 2850, 1756, 1692, 1595, 1492, 1447, 1371, 1216, 1064, 932, 714, 697, 640, 488 cm⁻¹.

(*R,E*)-4-((5-benzoyl-2-oxodihydrofuran-3(2*H*)-ylidene)methyl)-*N,N*-dipropylbenzenesulfonamide (3na)



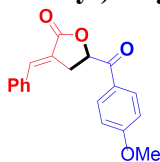
Yellow solid, 153 mg, 87% yield, reaction time for 2 h, mp 116-117 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.06-8.01 (m, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.63-.58 (m, 3H), 7.54 (t, *J* = 7.7 Hz, 2H), 5.92 (dd, *J* = 8.0, 5.7 Hz, 1H), 3.55 (dd, *J* = 7.1, 3.0 Hz, 2H), 3.12-3.06 (m, 4H), 1.55 (dd, *J* = 15.2, 7.5 Hz, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 193.4, 170.3, 141.2, 137.8, 135.7, 134.4, 133.6, 130.3, 129.0, 127.5, 125.0, 75.7, 50.0, 29.8, 22.0, 11.1; HRMS: C₂₄H₂₇NO₅S [M+H⁺]; calculated: 442.1688, found: 442.1678; IR:2959, 2870, 1758, 1689, 1657, 1596, 1335, 1227, 1177, 1154, 1050, 994, 933, 837, 773, 692, 640, 596, 568cm⁻¹.

(*R,E*)-3-benzylidene-5-(4-methylbenzoyl)dihydrofuran-2(3*H*)-one (3ab)



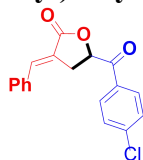
Yellow solid, 104 mg, 89% yield, reaction time for 4 h, mp 150-152 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, J = 8.2 Hz, 2H), 7.63 (t, J = 2.8 Hz, 1H), 7.50 (d, J = 7.4 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.33 (d, J = 8.0 Hz, 2H), 5.83 (dd, J = 8.6, 5.6 Hz, 1H), 3.59 – 3.44 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.3, 171.1, 145.5, 137.9, 134.3, 131.3, 130.1, 129.7, 129.2, 129.0, 122.0, 75.8, 30.0, 21.8; HRMS: $\text{C}_{19}\text{H}_{16}\text{O}_3$ [$\text{M}+\text{H}^+$]; calculated: 293.1172, found: 293.1164; IR: 1756, 1693, 1653, 1494, 1354, 1229, 1179, 1061, 932, 767, 520, 475 cm^{-1} .

(R,E)-3-benzylidene-5-(4-methoxybenzoyl)dihydrofuran-2(3H)-one (3ac)



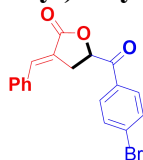
Yellow solid, 105 mg, 85% yield, reaction time for 4 h, mp 140-141 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, J = 8.9 Hz, 2H), 7.63 (t, J = 2.8 Hz, 1H), 7.51 (d, J = 7.3 Hz, 2H), 7.48-7.37 (m, 3H), 7.00 (d, J = 8.9 Hz, 2H), 5.80 (dd, J = 9.0, 5.0 Hz, 1H), 3.90 (s, 3H), 3.53 (dddd, J = 17.7, 12.0, 7.0, 2.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.1, 171.1, 164.4, 137.8, 134.4, 131.6, 130.1, 129.0, 126.9, 122.1, 114.2, 75.8, 55.6, 29.9; HRMS: $\text{C}_{19}\text{H}_{16}\text{O}_4$ [$\text{M}+\text{H}^+$]; calculated: 309.1121, found: 309.1107; IR: 2935, 2848, 1754, 1690, 1602, 1510, 1354, 1283, 1175, 1063, 1023, 927, 843, 768, 592, 516 cm^{-1} .

(R,E)-3-benzylidene-5-(4-chlorobenzoyl)dihydrofuran-2(3H)-one (3ad)



Yellow solid, 106 mg, 85% yield, reaction time for 4 h, mp 127-128 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, J = 8.6 Hz, 2H), 7.64 (t, J = 2.8 Hz, 1H), 7.56-7.38 (m, 6H), 5.76 (dd, J = 9.1, 5.0 Hz, 1H), 3.55 (dddd, J = 17.7, 12.0, 7.1, 2.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.7, 170.8, 141.0, 138.3, 134.2, 132.3, 130.6, 130.3, 130.2, 129.3, 129.0, 121.7, 76.0, 29.5; HRMS: $\text{C}_{18}\text{H}_{13}\text{ClO}_3$ [$\text{M}+\text{Na}^+$]; calculated: 335.0445, found: 335.0457; IR: 2923, 2848, 1761, 1697, 1653, 1589, 1445, 1221, 1181, 1089, 1053, 929, 765, 693, 525, 477 cm^{-1} .

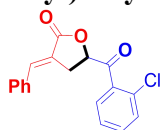
(R,E)-3-benzylidene-5-(4-bromobenzoyl)dihydrofuran-2(3H)-one (3ae)



Yellow solid, 105 mg, 85% yield, reaction time for 4 h, mp 141-142 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.96-7.89 (m, 2H), 7.72 – 7.61 (m, 3H), 7.52 (dd, J = 7.8, 1.6 Hz, 2H), 7.48 – 7.39 (m, 3H), 5.76 (dd, J = 9.1, 5.0 Hz, 1H), 3.55 (dddd, J = 17.7, 12.0, 7.1, 2.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.0, 170.8, 138.3, 134.2,

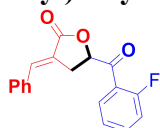
132.7, 132.3, 130.7, 130.3, 130.2, 129.8, 129.0, 121.6, 75.9, 29.5; HRMS: C₁₈H₁₃BrO₃ [M+H⁺]; calculated: 357.0121, found: 357.0094; IR: 2995, 2958, 1754, 1693, 1654, 1586, 1399, 1222, 1178, 1070, 1050, 999, 931, 835, 696, 516, 472 cm⁻¹.

(*R,E*)-3-benzylidene-5-(2-chlorobenzoyl)dihydrofuran-2(3*H*)-one (3af)



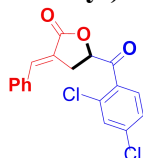
Yellow solid, 106 mg, 85% yield, reaction time for 4 h, mp 140-142 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.61 (t, *J* = 2.8 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.44 (dtd, *J* = 9.7, 4.7, 2.0 Hz, 5H), 7.38 (ddd, *J* = 10.0, 6.9, 3.9 Hz, 1H), 5.75 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.61 – 3.44 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 198.8, 171.0, 138.0, 135.9, 134.2, 132.9, 131.7, 130.6, 130.1, 129.0, 127.2, 121.6, 77.9, 30.3; HRMS: C₁₈H₁₃ClO₃ [M+Na⁺]; calculated: 351.0190, found: 351.0183; IR: 2945, 2812, 1748, 1656, 1573, 1405, 1221, 1043, 1013, 915, 723, 694, 527 cm⁻¹.

(*R,E*)-3-benzylidene-5-(2-fluorobenzoyl)dihydrofuran-2(3*H*)-one (3ag)



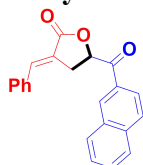
Yellow solid, 102 mg, 86% yield, reaction time for 3 h, mp 133-134 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.10 (ddd, *J* = 8.1, 5.1, 2.4 Hz, 2H), 7.63 (t, *J* = 2.8 Hz, 1H), 7.55-7.49 (m, 2H), 7.48-7.38 (m, 3H), 7.24-7.16 (m, 2H), 5.78 (dd, *J* = 9.1, 5.0 Hz, 1H), 3.62 (ddd, *J* = 17.7, 4.9, 2.9 Hz, 1H), 3.48 (ddd, *J* = 17.7, 9.1, 2.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 192.2, 170.8, 167.6, 165.1, 138.1, 134.2, 132.1, 132.0, 130.2, 129.0, 121.7, 116.3, 116.1, 75.9, 29.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -102.42. HRMS: C₁₈H₁₃ClO₃ [M+Na⁺]; calculated: 351.0190, found: 351.0183; IR: 2923, 2809, 1776, 1648, 1533, 1445, 1232, 1023, 934, 756, 688, 534 cm⁻¹.

(*R,E*)-3-benzylidene-5-(2,4-dichlorobenzoyl)dihydrofuran-2(3*H*)-one (3ah)



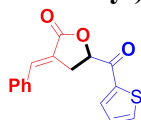
Yellow solid, 112 mg, 81% yield, reaction time for 3 h, mp 104-105 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (t, *J* = 2.7 Hz, 1H), 7.55-7.40 (m, 7H), 7.37 (dd, *J* = 8.3, 1.8 Hz, 1H), 5.73 (dd, *J* = 9.0, 5.3 Hz, 1H), 3.61-3.43 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 197.6, 170.8, 138.8, 138.2, 134.0, 132.8, 131.2, 130.6, 130.2, 129.0, 127.6, 121.3, 77.8, 30.2. HRMS: C₁₈H₁₂Cl₂O₃ [M+K⁺]; calculated: 384.9795, found: 384.9795; IR: 3075, 2964, 1759, 1699, 1651, 1583, 1216, 1180, 1040, 936, 768, 688, 513, 441 cm⁻¹.

(*R,E*)-5-(2-naphthoyl)-3-benzylidenedihydrofuran-2(3*H*)-one (3ai)



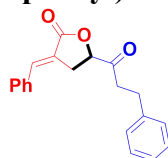
Yellow solid, 106 mg, 81% yield, reaction time for 5 h, mp 143-144 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.58 (s, 1H), 8.08 – 7.97 (m, 2H), 7.91 (dd, *J* = 16.7, 8.4 Hz, 2H), 7.71 – 7.55 (m, 3H), 7.50 (d, *J* = 6.5 Hz, 2H), 7.41 (p, *J* = 6.0 Hz, 3H), 6.00 (dd, *J* = 8.6, 5.5 Hz, 1H), 3.70 – 3.44 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 193.7, 171.1, 138.0, 136.1, 134.3, 132.4, 131.4, 131.2, 130.2, 130.2, 129.8, 129.3, 129.0, 129.0, 127.9, 127.2, 124.1, 121.9, 75.9, 30.0. HRMS: C₂₂H₁₆O₃ [M+Na⁺]; calculated: 351.0992, found: 351.0988; IR: 1746, 1686, 1650, 1446, 1318, 1171, 1123, 1051, 923, 763, 692, 516, 476 cm⁻¹.

(*R,E*)-3-benzylidene-5-(thiophene-2-carbonyl)dihydrofuran-2(3*H*)-one (3aj)



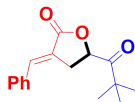
Yellow solid, 89 mg, 78% yield, reaction time for 5 h, mp 139-140 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.03 (dd, *J* = 3.8, 0.8 Hz, 1H), 7.78 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.63 (t, *J* = 2.8 Hz, 1H), 7.51 (d, *J* = 6.5 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.24-7.18 (m, 1H), 5.59 (dd, *J* = 8.2, 6.1 Hz, 1H), 3.66-3.47 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 187.7, 170.9, 140.3, 138.1, 135.8, 134.5, 134.2, 130.2, 129.0, 128.7, 121.6, 77.1, 30.4. HRMS: C₁₆H₁₂O₃S [M+K⁺]; calculated: 323.0144, found: 323.0132; IR: 1748, 1686, 1653, 1443, 1412, 1309, 1221, 1076, 932, 806, 601 cm⁻¹.

(*R,E*)-3-benzylidene-5-(3-phenylpropanoyl)dihydrofuran-2(3*H*)-one (3ak)



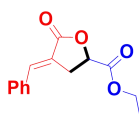
Yellow solid, 78 mg, 64% yield, reaction time for 6 h, mp 105-106 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (t, *J* = 2.9 Hz, 1H), 7.48-7.41 (m, 5H), 7.27-7.22 (m, 2H), 7.19-7.13 (m, 3H), 4.88 (dd, *J* = 9.7, 5.4 Hz, 1H), 3.40 (ddd, *J* = 18.0, 9.7, 2.9 Hz, 1H), 3.11 (ddd, *J* = 18.1, 5.4, 3.0 Hz, 1H), 3.04-2.90 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 207.2, 140.2, 138.2, 134.0, 130.3, 129.0, 128.5, 128.3, 126.3, 79.1, 40.4, 29.7, 28.9. HRMS: C₂₀H₁₈O₃ [M+H⁺]; calculated: 307.1334, found: 307.1328; IR: 3026, 2935, 1744, 1649, 1491, 1367, 1294, 1173, 1049, 940, 771, 690, 545, 518 cm⁻¹.

(*R,E*)-3-benzylidene-5-pivaloyldihydrofuran-2(3*H*)-one (3al)



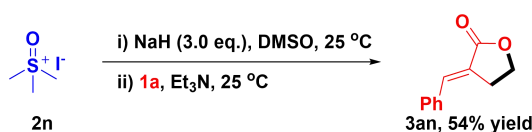
Yellow solid, 47 mg, 46% yield, reaction time for 4 h, mp 123-125 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (t, *J* = 2.7 Hz, 1H), 7.54-7.37 (m, 6H), 5.37 (dd, *J* = 8.9, 5.0 Hz, 1H), 3.36 (ddd, *J* = 17.5, 8.9, 2.8 Hz, 1H), 3.22 (ddd, *J* = 17.6, 4.8, 2.9 Hz, 1H), 1.27 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 171.2, 137.5, 130.1, 129.4, 129.0, 128.9, 122.0, 74.4, 43.8, 30.7, 25.8. HRMS: C₁₆H₁₈O₃ [M+K⁺]; calculated: 297.0893, found: 297.0887; IR: 3033, 2921, 1745, 1652, 1487, 1357, 1283, 1209, 1052, 938, 783, 687, 518 cm⁻¹.

ethyl (*R,E*)-4-benzylidene-5-oxotetrahydrofuran-2-carboxylate (3am)



Yellow solid, 57 mg, **2m** 0.6 mmol were used, 58% yield; but **2m** 1.6 mmol were used, 84% yield, reaction time for 6 h, mp 90-91 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (t, *J* = 2.8 Hz, 1H), 7.51-7.40 (m, 5H), 5.05 (dd, *J* = 9.5, 4.6 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.55 (ddd, *J* = 17.8, 9.5, 2.9 Hz, 1H), 3.29 (ddd, *J* = 17.8, 4.5, 2.8 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 170.8, 169.7, 137.8, 134.1, 130.1, 128.9, 121.4, 73.0, 62.1, 31.2, 14.0. HRMS: C₁₄H₁₄O₄ [M+K⁺]; calculated: 285.0529, found: 285.0523; IR: 2999, 2935, 1759, 1655, 1370, 1210, 1176, 1075, 1019, 771, 698, 522 cm⁻¹.

4. Reaction of dimethylloxosulfonium salt and Baylis-Hillman bromide **1a** to form α-Methylene-γ-butyrolactone derivatives



Under N₂ atmosphere, NaH (70%) (3.0 mmol) was washed with n-hexane for three times. DMSO (10 mL) was added to the flask. Dimethylloxosulfonium iodide **2n** (3.0 mmol) was added to a flask. The mixture was stirred at room temperature for 2 hours. To the above solution, was added the solution of Baylis-Hillman bromides **1a** (1.0 mmol) in DMSO (10 mL). The mixture was stirred at 25 °C. Upon the completion of the reaction, as monitored by TLC, the mixture was quenched by sat. NH₄Cl in ice-bath and then diluted by EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, and dried over MgSO₄. Evaporation of the solvent under reduced pressure. The crude residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to provide (*E*)-3-benzylidenedihydrofuran-2(3*H*)-one **3an** in 54% yield.

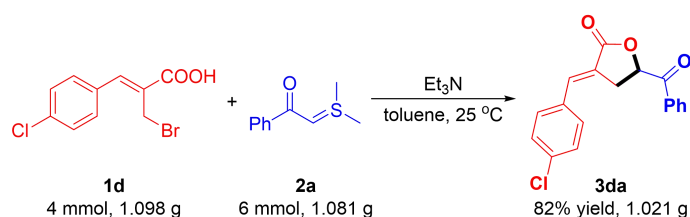
(*E*)-3-benzylidenedihydrofuran-2(3*H*)-one (**3an**)



Yellow solid, 94 mg, 54% yield, reaction time for 3 h, mp 107-109 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (t, *J* = 2.9 Hz, 1H), 7.54-7.49 (m, 2H), 7.48-7.38 (m, 3H), 4.47 (t, *J* = 7.3 Hz, 2H), 3.26 (td, *J* = 7.3, 2.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 172.4, 136.6, 134.6, 129.9, 128.9, 123.5, 65.4, 27.4. HRMS: C₁₁H₁₀O₂ [M+Na⁺]; calculated: 197.0578, found: 197.0572; IR: 3006, 1745, 1621, 1320, 1221, 1106, 1021, 987, 771 cm⁻¹.

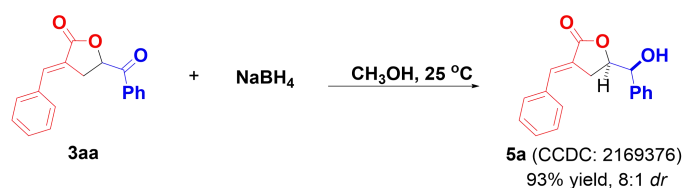
5. Synthetic Transformation

a) Gram-scale synthesis



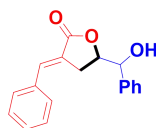
A dry 100 mL flask equipped with a magnetic stirring bar, was sequentially charged with sulfur ylide **2a** (6 mmol, 1.5 equiv.), toluene (40 mL), Et₃N (6 mmol, 1.5 equiv.). The reaction mixture was stirred for 15 min at 25°C, then to the above mixture, was added Baylis-Hillman bromides **1d** (4 mmol, 1.0 equiv.). The reaction was monitored via TLC (Petroleum Ether/Ethyl Acetate = 4:1). Thereafter, the reaction mixture was purified by flash chromatography on silica gel (Petroleum Ether/Ethyl Acetate = 5:1 ~ 15:1) to give the desired product **3da** (1.021 g) in 82% yield.

b) Reduction of **3aa**



To a solution of **3aa** (0.5 mmol) in methanol (1.0 mL), NaBH₄ (0.5 mmol) was added. The reaction was stirring at room temperature for 20 min. The reaction was monitored via TLC (petroleum ether/ethyl acetate = 4:1). Upon consumption of the starting material, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give the desired product **5a** in 93% yield with 8:1 dr value.

(5R)-3-((E)-benzylidene)-5-(hydroxy(phenyl)methyl)dihydrofuran-2(3H)-one (**5a**)



White solid, 93% yield, dr = 8:1, reaction time for 20 min, mp 163-164 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.51 (t, *J* = 2.9 Hz, 1H), 7.47-7.31 (m, 10H), 4.84-4.75 (m, 1H), 4.71 (dd, *J* = 6.5, 2.9 Hz, 1H), 3.06 (ddd, *J* = 17.8, 8.0, 2.8 Hz, 1H), 2.96 (ddd, *J* = 17.8, 5.4, 3.0 Hz, 1H), 2.83 (d, *J* = 3.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 171.6, 138.1, 137.0, 134.4, 130.0, 129.0, 128.7, 127.2, 123.6, 80.2, 29.6; HRMS: C₁₈H₁₆O₃ [M+Na⁺]; calculated: 303.0997, found: 303.0990; IR: 2920, 2854, 1717, 1643, 1496, 1447, 1348, 1240, 1182, 1072, 772, 744, 684, 636, 517 cm⁻¹.

6. Crystal data of **3ad** and **5a**

For the **3ad**: Method for single crystals cultivation: The single crystal for compound **3ad** (CCDC-2078014) were prepared from a mixture solvent of Petroleum Ether/Ethyl Acetate (v/v= 10:1). A pure solid sample (10-20 mg) was dissolved in Ethyl Acetate (0.3 mL) in a vial at room temperature, and Petroleum Ether (2-3 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

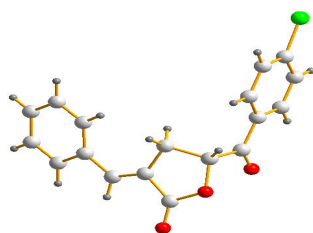


Table S6. Crystal data and structure refinement for 3ad.

Identificaion code	3ad
Formula formula	C ₁₈ H ₁₃ ClO ₃
Formula weight	312.73
Crystal system	Orthorhombic
Temperature (K)	293
Space group	P21 21 21 (19)
<i>a</i> (Å)	5.98719(13)
<i>b</i> (Å)	12.6464(3)
<i>c</i> (Å)	19.9372(4)
α (deg)	90
β (deg)	90
γ (deg)	90
<i>V</i> (Å ³)	1509.58(6)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.376
μ (mm ⁻¹)	2.326
<i>F</i> (000)	648.0
Crystal size (mm)	0.12 x 0.1 x 0.1
$2\theta_{\min}$, $2\theta_{\max}$ (deg)	5.6390, 72.9970
No. of reflns measd (unique)	4707
No. of reflns measd ($I > 2 \sigma(I)$)	0.1058
parameters	200
Goodness-of-fit	1.080
<i>R</i> ₁	0.113
w <i>R</i> ₂ (all data)	0.0382

For the **5a**: Method for single crystals cultivation: The single crystal for compound **5a** (CCDC-2169376) were prepared from a mixture solvent of Dichloromethane/ Hexane (v/v= 1:1). A pure solid sample (5-10 mg) was dissolved in Dichloromethane (2 mL) in a vial at room temperature, and Hexane (2 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

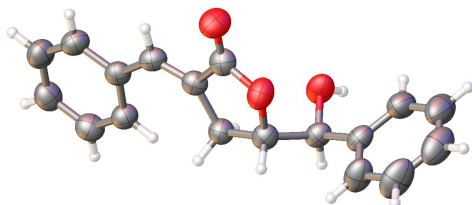


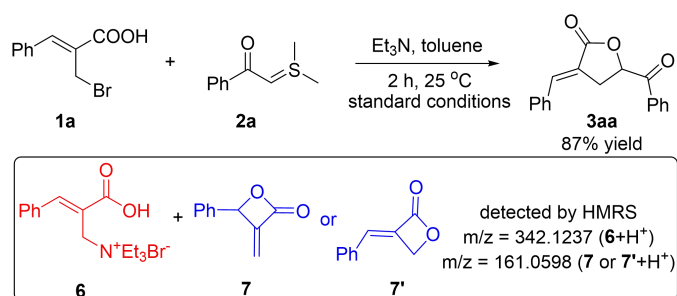
Table S7. Crystal data and structure refinement for 5a.

Identification code	5a
Formula formula	C ₁₈ H ₁₆ O ₃
Formula weight	280.31
Crystal system	Monoclinic
Temperature (K)	293(2)
Space group	P21/n
<i>a</i> (Å)	9.5652(3)
<i>b</i> (Å)	17.1995(4)
<i>c</i> (Å)	9.7794(3)
α (deg)	90
β (deg)	116.893(4)
γ (deg)	90
<i>V</i> (Å ³)	1434.89(9)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.298
μ (mm ⁻¹)	0.708
<i>F</i> (000)	592.0
$2\theta_{\min}$, $2\theta_{\max}$ (deg)	10.286, 139.888
parameters	191
Goodness-of-fit	1.062
<i>R</i> ₁	0.0565

7. Mechanistic Studies

1) Control experiments

a) **Investigation of the reaction mixture:** First, the reaction was performed under the standard basic condition to explore the involving intermediates. HRMS spectrum exhibited peaks at $m/z = 342.1237$ and $m/z = 161.0598$, corresponding to $[6+H^+]$ and $[7$ or $7'+H^+]$, respectively. This result suggested that species **6** and **7** or **7'** may be the intermediates of the title reaction.



A dry 10 mL flask equipped with a magnetic stirring bar, was sequentially charged with sulfur ylide **2a** (0.6 mmol, 1.5 equiv.), toluene (4.0 mL), Et₃N (0.6 mmol, 1.5 equiv.). The reaction mixture was stirred for 15 min at 25°C, then to the above mixture, was added Baylis-Hillman bromide **1a** (0.4 mmol, 1.0 equiv.). The reaction was monitored via TLC (Petroleum Ether/Ethyl Acetate = 4:1). Thereafter, the reaction mixture was then treated with HRMS analysis. HRMS spectrum exhibited peaks at $m/z = 342.1237$ and $m/z = 161.0598$, corresponding to $[6+H^+]$ and $[7$ or $7'+H^+]$, respectively (Figure S1). Lastly, the reaction mixture was purified by flash chromatography on silica gel (Petroleum Ether/Ethyl Acetate = 5:1 ~ 15:1) to give the desired product **3aa** as a white solid.

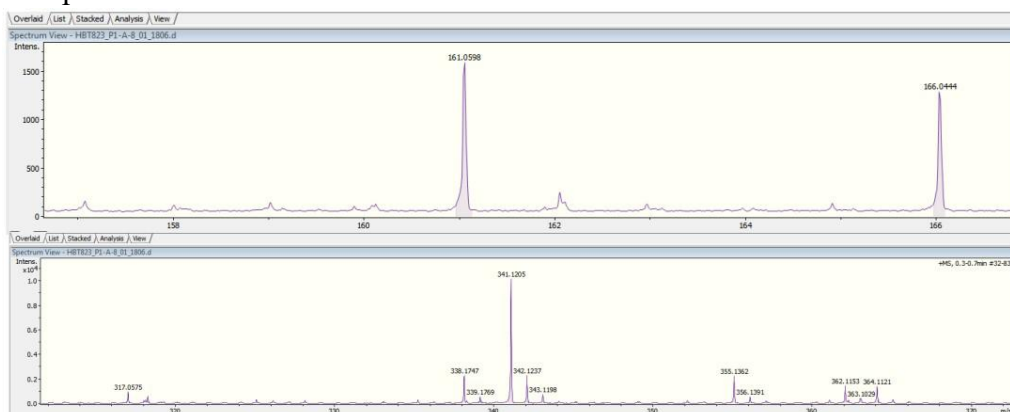


Figure S1. The spectrum of the reaction mixture under standard conditions.

b) **Investigation of addition sequence:** Then we investigated the addition sequence of the substrates. Upon the complete consumption of **1a**, as monitored by TLC, further addition of sulfur ylide **2a** to the above mixture led to a slight decrease in the

yield of this reaction to 62% comparing with the reaction conducted in the standard conditions.

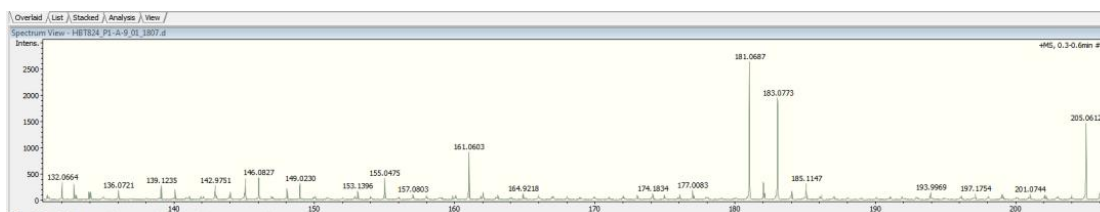
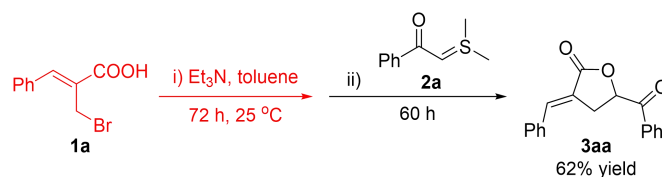


Figure S2. The spectrum of the system of **1a** under basic conditions.

A dry 10 mL flask equipped with a magnetic stirring bar, was sequentially charged with Baylis-Hillman bromides **1a** (0.4 mmol, 1.0 equiv.), toluene (4 mL), Et_3N (0.6 mmol, 1.5 equiv.). The reaction mixture was stirred for 72 h at 25°C. The substrate **1a** was completely consumed and two new points were formed, monitored via TLC (Petroleum Ether/Ethyl Acetate = 4:1). The reaction mixture was then treated with HRMS analysis. HRMS spectrum exhibited a peak at $m/z = 161.0603$, corresponding to $[\mathbf{7} \text{ or } \mathbf{7}^+ + \text{H}^+]$. To the above mixture, was added sulfur ylide **2a** (0.6 mmol, 1.5 equiv.). After 60 h, the reaction mixture was purified by flash chromatography on silica gel (Petroleum Ether/Ethyl Acetate = 1:0 ~ 10:1) to give the desired product **3aa** in 62% yield.

2) DFT calculation

Geometric structures of the reactants, products are optimized at the calculation level of B3LYP/6-31G(d). Transition states on the energy profiles are optimized and the intrinsic reaction coordinate (IRC) approach was used at the calculation level of B3LYP/6-31G to confirm that the transition state indeed connects the intended reactants and products.³ Meanwhile, vibrational frequencies are calculated to make sure that all the geometric structures had no imaginary frequency and the transition state geometries had only one imaginary frequency. The single point energy of corresponding reactants, products and transition states are further calculated at B3LYP/def2tzvpp calculation level. Polarizable continuum model (PCM) was selected to simulated the toluene environment.⁴ All calculations were conducted in Gaussian 16 (version C.01).⁵

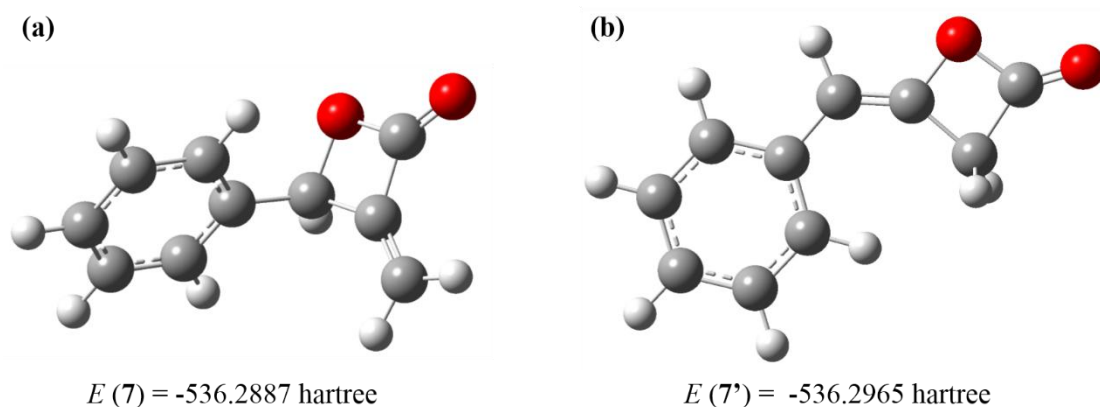


Figure S3. The optimized structures of **7** and **7'** and their corresponding energies at B3LYP/6-31G(d) level

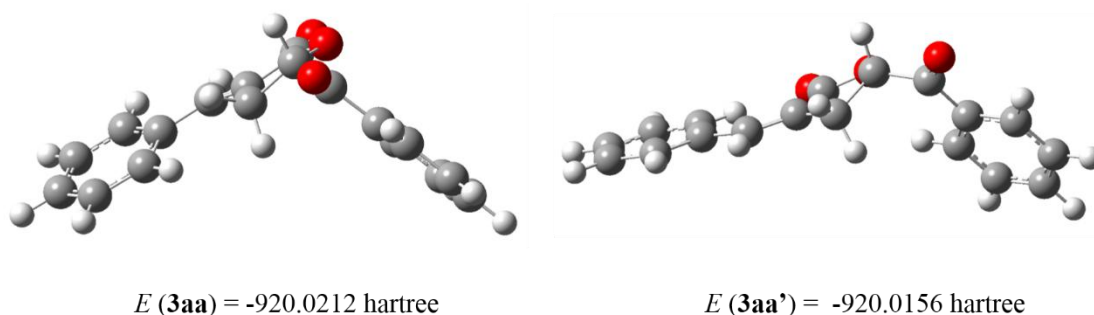


Figure S4. The optimized structures of **3aa** and **3aa'** and their corresponding energies at B3LYP/6-31G(d) level

Table S7. The corresponding energies for (i) in Scheme 4b.

	Raw (hartree)	TS (hartree)	Product (hartree)	ΔE (kcal/mol)	ΔG (kcal/mol)
Path A	-3964.4262	-3964.3859	-3964.4515	25.2612	-15.8527
Path B	-1391.3792	-1391.3347	-1391.3563	27.9546	14.3723

Table S8. The corresponding energies for (ii) in Scheme 4b.

	Raw (hartree)	TS (hartree)	Product (hartree)	ΔE (kcal/mol)	ΔG (kcal/mol)
Path A	-1391.3887	-1391.3481	-1391.4330	25.5122	-27.7607
Path B	-1391.3943	-1391.3420	-1391.4585	32.8188	-40.2995

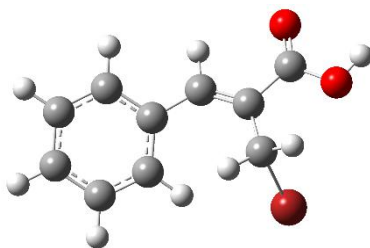


Figure S5 The optimized structure of **1a** at B3LYP/6-31G(d) level

Table S9. The atomic coordination of 1a in toluene.

Atom	x	y	z
C	0.759077	0.955096	0.252223
C	1.849365	1.931822	-0.03329
O	1.714661	2.99822	-0.604863
O	3.05333	1.508055	0.42227
H	3.696448	2.20207	0.184824
C	1.099288	-0.283557	1.001814
H	0.237904	-0.731698	1.490459
H	1.90897	-0.130095	1.709395
Br	1.80981	-1.733997	-0.204449
C	-0.485073	1.315478	-0.152288
C	-1.753785	0.592334	-0.075704
C	-2.9382	1.354952	-0.009816
C	-1.863581	-0.81309	-0.105915
C	-4.18342	0.739397	0.074914
H	-2.869694	2.439857	-0.012945
C	-3.113358	-1.425248	-0.037504
H	-0.976771	-1.424505	-0.233232
C	-4.274455	-0.655135	0.06464
H	-5.082828	1.345267	0.138599
H	-3.180314	-2.508943	-0.074207
H	-5.245877	-1.138462	0.12026
H	-0.550277	2.313923	-0.581141

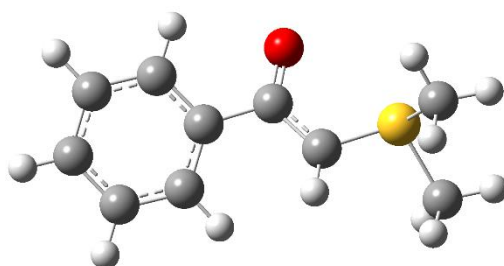
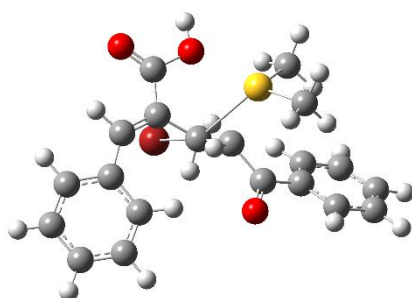


Figure S6. The optimized structure of **2a** at B3LYP/6-31G(d) level.

Table S10. The atomic coordination of 2a in toluene.

Atom	x	y	z
C	0.029966	0.572809	-0.292262
C	1.045035	-0.364581	0.038474
H	0.896463	-1.265207	0.621256
C	3.553665	-1.418233	-0.550959
H	4.621758	-1.198073	-0.618593
H	3.360874	-2.12498	0.260048
H	3.19321	-1.825296	-1.496804
O	0.257338	1.725732	-0.721124
C	-1.407709	0.141091	-0.098802
C	-1.810469	-1.197749	0.015465
C	-2.386142	1.144262	-0.050196
C	-3.156768	-1.523493	0.186237
H	-1.074738	-1.99337	-0.05567
C	-3.730596	0.822224	0.126063
H	-2.063274	2.174595	-0.158518
C	-4.120605	-0.51434	0.246946
H	-3.454233	-2.566209	0.264827
H	-4.476165	1.612437	0.167125
H	-5.168975	-0.768404	0.381199
S	2.649841	0.139539	-0.259649
C	3.464017	0.624794	1.327073
H	4.522993	0.826423	1.141684
H	2.962787	1.535862	1.658426
H	3.340771	-0.16697	2.070153

Figure S7. The structure of **Int-8** by IRC analysis.**Table S11 The atomic coordination of Int-8 in toluene.**

Atom	x	y	z
C	1.436604	0.841386	-0.823741
C	1.45629	2.253693	-1.251045
O	2.416352	2.872568	-1.73384
O	0.222178	2.890186	-1.124348

H	0.332518	3.844967	-1.323102
C	0.199385	0.315268	-0.125027
H	0.508375	-0.351212	0.687555
C	2.593926	0.160487	-1.049307
C	3.04998	-1.181852	-0.696725
C	2.245343	-2.248771	-0.233329
C	4.443132	-1.413826	-0.816067
C	2.816529	-3.472878	0.121413
H	1.172289	-2.153209	-0.161466
C	5.011668	-2.634701	-0.45709
H	5.078234	-0.610013	-1.175573
C	4.198776	-3.670822	0.019842
H	2.176998	-4.274689	0.475525
H	6.083547	-2.777898	-0.545409
H	4.636033	-4.622825	0.302628
H	3.364935	0.760578	-1.52638
C	1.670164	-1.525615	-0.389678
C	0.757818	-0.477312	-1.042397
C	2.712103	2.010929	-1.349331
H	3.143696	2.655777	-2.115322
H	3.475963	1.513574	-0.757485
H	1.992048	2.556543	-0.743738
O	1.328873	-2.70969	-0.603262
C	2.883323	-1.220145	0.399186
C	3.03798	-0.064562	1.191226
C	3.919527	-2.180498	0.3664
C	4.221275	0.133626	1.910997
H	2.227614	0.647795	1.296966
C	5.104216	-1.966337	1.068805
H	3.777526	-3.082533	-0.217912
C	5.258868	-0.804804	1.839029
H	4.323674	1.012104	2.538322
H	5.899851	-2.701926	1.025638
H	6.176163	-0.639145	2.393841
S	1.693629	0.735339	-2.305886
C	3.044656	-0.373798	-3.035507
H	3.560975	0.224834	-3.786351
H	2.538773	-1.21853	-3.503478
H	3.724084	-0.700738	-2.249368
H	0.180677	-1.034699	-1.786686
H	0.288444	1.136415	0.401715
Br	1.434364	1.872749	2.435075

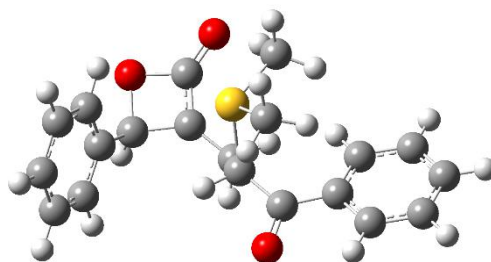


Figure S8. The structure of **Int-10** by IRC analysis.

Table S12 The atomic coordination of Int-10 in toluene.

Atom	x	y	z
C	1.72488	-1.216115	-0.69518
C	0.431752	-0.457357	-0.409491
C	0.988664	1.831126	1.722847
H	0.901997	1.999877	2.797028
H	2.030551	1.79567	1.414056
H	0.386534	2.566567	1.169357
O	1.568925	-2.401364	-1.074127
C	3.089339	-0.645874	-0.576689
C	3.377277	0.733947	-0.586221
C	4.159496	-1.562952	-0.474048
C	4.698111	1.182195	-0.482796
H	2.588537	1.46252	-0.716843
C	5.473261	-1.112666	-0.356351
H	3.935376	-2.623212	-0.486517
C	5.746382	0.262924	-0.358433
H	4.90651	2.246214	-0.50862
H	6.283854	-1.828082	-0.268411
H	6.768971	0.61475	-0.272048
S	0.180153	0.138001	1.449191
C	1.367308	-1.006746	2.40494
H	1.198543	-0.792211	3.45906
H	1.079027	-2.031454	2.174527
H	2.398125	-0.809016	2.117304
H	0.357357	-1.21405	-0.42481
C	1.294201	1.330441	-0.952203
C	1.616759	2.536196	-0.337308
C	2.769222	1.004778	-1.15783
H	3.124794	1.067585	-2.19496
O	3.089653	2.312969	-0.449998
O	1.085959	3.539173	0.206468
C	0.014607	0.711598	-1.355812
H	0.766674	1.476567	-1.413953

H	0.06757	0.245326	-2.353815
C	3.358751	-0.201181	-0.471527
C	3.571988	-1.382526	-1.203125
C	3.664409	-0.190038	0.900808
C	4.056729	-2.536828	-0.574497
H	3.363194	-1.396422	-2.270338
C	4.158205	-1.338834	1.527334
H	3.53222	0.732812	1.453607
C	4.350517	-2.518837	0.794243
H	4.213805	-3.441653	-1.154088
H	4.402831	-1.312513	2.585559
H	4.735979	-3.408977	1.282156

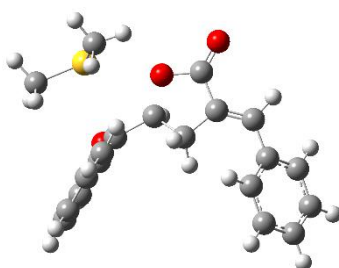


Figure S9 The structure of **Int-9** by IRC analysis.

Table S13 The atomic coordination of **Int-9** in toluene.

Atom	x	y	z
C	1.716647	1.327344	0.306794
C	0.894219	2.547858	0.30617
O	1.219753	3.713546	0.556172
O	-0.427288	2.177962	-0.064573
C	0.797343	0.16185	0.08095
H	1.267122	-0.671633	-0.440281
C	3.062545	1.32021	0.310021
C	3.861256	0.097418	0.207157
C	3.437856	-1.124423	0.776973
C	5.070825	0.123579	-0.513558
C	4.18725	-2.287975	0.603535
H	2.546109	-1.154856	1.390166
C	5.815746	-1.043436	-0.691419
H	5.412706	1.059249	-0.945598
C	5.374843	-2.252306	-0.137656
H	3.85323	-3.216981	1.053924
H	6.740498	-1.011483	-1.258011
H	5.95846	-3.156801	-0.273963
H	3.586979	2.273727	0.321522

C	-1.454093	-0.192222	-1.11766
C	-0.301998	0.804491	-0.753266
C	-3.193098	2.413948	1.432438
H	-4.068451	3.01406	1.686149
H	-3.189124	1.48888	2.013656
H	-2.278733	2.976579	1.615773
O	-1.698491	-0.263368	-2.345373
C	-1.930981	-1.339207	-0.253125
C	-2.0507	-1.305044	1.148137
C	-2.271672	-2.541886	-0.920627
C	-2.498847	-2.429174	1.856913
H	-1.813774	-0.39489	1.68919
C	-2.70508	-3.666047	-0.212161
H	-2.186494	-2.572455	-2.000196
C	-2.823038	-3.61346	1.183366
H	-2.594071	-2.375955	2.936539
H	-2.951504	-4.577545	-0.746931
H	-3.163074	-4.481533	1.738809
S	-3.176032	2.022167	-0.410353
C	-4.700932	0.932637	-0.569076
H	-5.616175	1.519712	-0.478557
H	-4.640844	0.485539	-1.563045
H	-4.67646	0.14279	0.184885
H	0.069142	1.069283	-1.747069
H	0.381151	-0.223293	1.018469

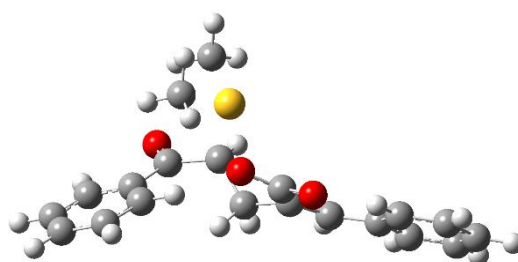


Figure S10. The structure of **Int-9'** by IRC analysis.

Table S14. The atomic coordination of Int-9' in toluene.

Atom	x	y	z
C	-2.433552	0.301271	-1.390171
C	-0.9836	0.635839	-1.019322
C	-2.296413	1.881719	1.671419
H	-2.398842	2.87856	2.103393
H	-3.227254	1.551285	1.212737
H	-1.87775	1.162834	2.370207

O	-2.892798	0.898391	-2.395129
C	-3.25691	-0.671212	-0.636867
C	-2.887915	-1.204985	0.618684
C	-4.488904	-1.05414	-1.214919
C	-3.738581	-2.105629	1.267511
H	-1.958907	-0.911062	1.103076
C	-5.326238	-1.955817	-0.563101
H	-4.763617	-0.634807	-2.175761
C	-4.951034	-2.486136	0.680902
H	-3.451355	-2.50861	2.232709
H	-6.265945	-2.249089	-1.019055
H	-5.602604	-3.190813	1.187729
S	-0.9471	2.065539	0.353134
C	-1.765332	3.443227	-0.68964
H	-1.85074	4.30623	-0.035673
H	-1.077845	3.654856	-1.520117
H	-2.723895	3.121876	-1.069783
H	-0.606123	1.246223	-1.844649
C	1.276984	-0.336323	-0.017788
C	1.051834	-0.206378	1.477364
C	2.437216	-0.395639	-0.730109
H	2.279708	-0.516748	-1.804179
O	1.99323	-0.321342	2.31732
O	-0.197869	0.022192	1.795589
C	-0.032192	-0.556638	-0.77719
H	-0.575772	-1.362168	-0.284298
H	0.19414	-0.907931	-1.794329
C	3.880425	-0.348912	-0.433186
C	4.745953	-0.442182	-1.552338
C	4.471597	-0.231944	0.84612
C	6.133675	-0.414754	-1.408521
H	4.314375	-0.534023	-2.546335
C	5.862401	-0.202026	0.984326
H	3.818709	-0.183677	1.708804
C	6.700943	-0.291563	-0.133719
H	6.76866	-0.487711	-2.286202
H	6.293618	-0.113811	1.977074
H	7.779956	-0.27084	-0.015414

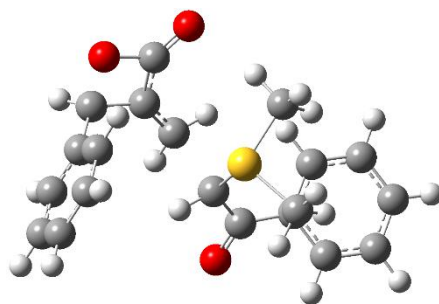


Figure S11 The optimized structure of TS1 in toluene at B3LYP/6-31G level.

Table S15 The atomic coordination of TS1 in toluene.

Atom	x	y	z
C	1.630407	1.020046	-0.605159
C	1.616122	2.38191	-1.187472
O	2.529584	2.916172	-1.834097
O	0.4245	3.062144	-0.977459
H	0.509611	3.979879	-1.314547
C	0.551043	0.656096	0.301162
H	0.599677	-0.242327	0.890568
C	2.732637	0.271269	-0.929445
C	3.164394	-1.06764	-0.557611
C	2.331506	-2.103962	-0.071335
C	4.546374	-1.346396	-0.720956
C	2.872198	-3.347046	0.264511
H	1.259111	-1.984067	0.004477
C	5.081977	-2.583956	-0.371064
H	5.196238	-0.567832	-1.109126
C	4.244587	-3.590841	0.128315
H	2.213003	-4.128649	0.626912
H	6.14488	-2.766356	-0.490007
H	4.655941	-4.55849	0.396922
H	3.454522	0.806345	-1.543364
C	1.567466	-1.435426	-0.279931
C	0.891209	-0.454837	-1.101605
C	2.615041	2.125926	-1.290258
H	3.052097	2.769715	-2.054197
H	3.369325	1.718669	-0.621732
H	1.814846	2.640486	-0.762148
O	0.982399	-2.542549	-0.065848
C	2.877263	-1.181003	0.401525
C	3.104243	-0.035003	1.185202
C	3.865378	-2.18313	0.353972
C	4.30839	0.117898	1.884128

H	2.323728	0.709514	1.295744
C	5.075397	-2.018096	1.032739
H	3.67078	-3.088234	-0.211459
C	5.300411	-0.865682	1.798354
H	4.461598	0.994097	2.505469
H	5.834473	-2.791505	0.978267
H	6.234405	-0.744214	2.337074
S	1.772615	0.722336	-2.245088
C	3.301538	-0.182215	-2.932636
H	3.82268	0.526097	-3.576793
H	2.919645	-1.024044	-3.50834
H	3.924123	-0.514756	-2.103764
H	0.083581	-0.856463	-1.704845
H	0.215062	1.370122	0.528753
Br	1.574065	1.818315	2.416061

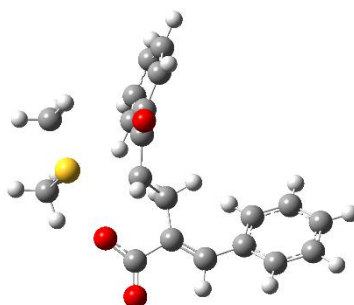


Figure 12. The optimized structure of TS2 in toluene at B3LYP/6-31G level.

Table S16. The atomic coordination of TS2 in toluene.

Atom	x	y	z
C	1.542163	1.501298	0.24262
C	0.96919	2.899829	0.361258
O	1.724306	3.895949	0.549644
O	-0.33267	2.92494	0.24907
C	0.505175	0.414867	0.162484
H	0.956816	-0.519425	-0.219049
C	2.882513	1.340825	0.211778
C	3.68957	0.114517	0.122472
C	3.312057	-1.117564	0.700846
C	4.931886	0.176741	-0.548468
C	4.127467	-2.247679	0.579461
H	2.403025	-1.183957	1.288135
C	5.741405	-0.95345	-0.676081
H	5.250426	1.122061	-0.977679
C	5.339653	-2.173872	-0.116483

H	3.821646	-3.181907	1.040188
H	6.686461	-0.882733	-1.205223
H	5.970797	-3.0518	-0.209385
H	3.442946	2.274778	0.231359
C	-1.482582	-0.443876	-1.254845
C	-0.632626	0.708607	-0.776785
C	-2.958204	2.405511	1.422011
H	-3.868463	2.991165	1.560496
H	-2.992117	1.495647	2.023216
H	-2.061541	2.988179	1.620583
O	-1.715486	-0.478401	-2.488172
C	-1.936736	-1.541999	-0.36472
C	-2.05225	-1.413209	1.033916
C	-2.297878	-2.763167	-0.970457
C	-2.508323	-2.484337	1.806966
H	-1.810761	-0.47682	1.521705
C	-2.74185	-3.834475	-0.195608
H	-2.217509	-2.851562	-2.047583
C	-2.847333	-3.697928	1.195577
H	-2.599934	-2.37177	2.881835
H	-3.006262	-4.772452	-0.671626
H	-3.194433	-4.530279	1.798675
S	-2.821602	1.976202	-0.407644
C	-4.376086	0.91701	-0.625322
H	-5.239187	1.585048	-0.617882
H	-4.291667	0.427008	-1.59577
H	-4.451291	0.176513	0.171368
H	-0.437697	1.410814	-1.578551
H	0.131915	0.146466	1.15943

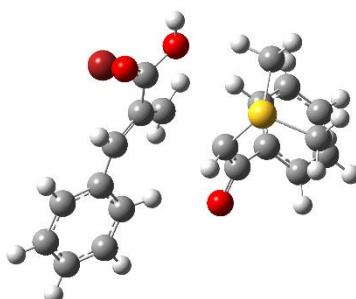


Figure S13. The optimized structure of TS3 in toluene at B3LYP/6-31G level.

Table S17 The atomic coordination of TS3 in toluene.

Atom	x	y	z
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C	1.630407	1.020046	-0.605159
C	1.616122	2.38191	-1.187472
O	2.529584	2.916172	-1.834097
O	0.4245	3.062144	-0.977459
H	0.509611	3.979879	-1.314547
C	0.551043	0.656096	0.301162
H	0.599677	-0.242327	0.890568
C	2.732637	0.271269	-0.929445
C	3.164394	-1.06764	-0.557611
C	2.331506	-2.103962	-0.071335
C	4.546374	-1.346396	-0.720956
C	2.872198	-3.347046	0.264511
H	1.259111	-1.984067	0.004477
C	5.081977	-2.583956	-0.371064
H	5.196238	-0.567832	-1.109126
C	4.244587	-3.590841	0.128315
H	2.213003	-4.128649	0.626912
H	6.14488	-2.766356	-0.490007
H	4.655941	-4.55849	0.396922
H	3.454522	0.806345	-1.543364
C	1.567466	-1.435426	-0.279931
C	0.891209	-0.454837	-1.101605
C	2.615041	2.125926	-1.290258
H	3.052097	2.769715	-2.054197
H	3.369325	1.718669	-0.621732
H	1.814846	2.640486	-0.762148
O	0.982399	-2.542549	-0.065848
C	2.877263	-1.181003	0.401525
C	3.104243	-0.035003	1.185202
C	3.865378	-2.18313	0.353972
C	4.30839	0.117898	1.884128
H	2.323728	0.709514	1.295744
C	5.075397	-2.018096	1.032739
H	3.67078	-3.088234	-0.211459
C	5.300411	-0.865682	1.798354
H	4.461598	0.994097	2.505469
H	5.834473	-2.791505	0.978267
H	6.234405	-0.744214	2.337074
S	1.772615	0.722336	-2.245088
C	3.301538	-0.182215	-2.932636
H	3.82268	0.526097	-3.576793
H	2.919645	-1.024044	-3.50834
H	3.924123	-0.514756	-2.103764

H	0.083581	-0.856463	-1.704845
H	0.215062	1.370122	0.528753
Br	1.574065	1.818315	2.416061

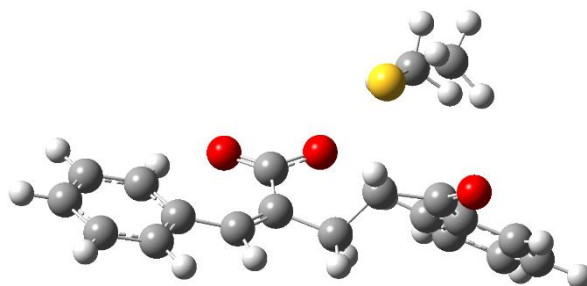


Figure S14. The optimized structure of **TS4** in toluene at B3LYP/6-31G level.

Table S18 The atomic coordination of TS4 in toluene.

Atom	x	y	z
C	-2.279956	0.214014	-1.292618
C	-0.809936	0.321446	-1.023814
C	-2.337658	2.048523	1.839483
H	-2.59709	2.975967	2.352625
H	-3.226354	1.55953	1.439552
H	-1.771228	1.370543	2.47336
O	-2.698055	0.930347	-2.246047
C	-3.173557	-0.718992	-0.579928
C	-2.842792	-1.299577	0.664115
C	-4.42002	-1.013872	-1.176751
C	-3.746043	-2.168796	1.284028
H	-1.905764	-1.040582	1.149998
C	-5.308674	-1.887412	-0.554768
H	-4.664543	-0.555095	-2.12784
C	-4.971611	-2.469229	0.67762
H	-3.492122	-2.608014	2.242806
H	-6.259487	-2.117856	-1.023322
H	-5.664376	-3.149802	1.162116
S	-1.145717	2.47501	0.441414
C	-2.24172	3.583875	-0.625763
H	-2.806832	4.25292	0.025478
H	-1.57691	4.156907	-1.271946
H	-2.910676	2.965574	-1.231154
H	-0.367736	1.127626	-1.600373
C	1.380395	-0.62096	-0.136428
C	1.069045	-0.282211	1.308758

C	2.561628	-0.697115	-0.803134
H	2.450318	-0.924291	-1.864921
O	1.938625	-0.327495	2.227759
O	-0.188371	0.040426	1.480944
C	0.078193	-0.877479	-0.884722
H	-0.460041	-1.717073	-0.439508
H	0.309368	-1.152715	-1.931076
C	3.981224	-0.521266	-0.460324
C	4.890657	-0.558491	-1.546328
C	4.506649	-0.329188	0.83777
C	6.263125	-0.400045	-1.35301
H	4.507205	-0.711194	-2.551975
C	5.882911	-0.172583	1.025399
H	3.820108	-0.313654	1.675439
C	6.766811	-0.204675	-0.060674
H	6.936483	-0.430655	-2.204013
H	6.267425	-0.027441	2.03048
H	7.834103	-0.08287	0.09694

The calculated vibrational frequencies (cm⁻¹) of transition states

Table S19. The calculated vibrational frequencies (cm⁻¹) of transition states at B3LYP/6-31G level level.

Compound	TS1	TS2	TS3	TS4
vibrational frequencies (cm⁻¹)	-302.89	-147.74	-394.69	-202.15
	15.29	15.21	14.11	19.64
	18.09	28.87	27.70	29.97
	29.00	35.68	30.62	34.02
	35.99	48.07	43.36	48.80
	39.91	61.26	50.42	56.87
	68.38	71.53	56.46	82.55
	76.72	77.19	65.57	87.41
	88.18	91.00	66.78	100.95
	98.71	108.63	78.45	123.05
	122.59	116.80	84.51	131.72
	126.49	121.17	95.33	145.14
	140.90	147.34	102.86	153.64
	171.35	162.55	115.73	154.76
	192.01	167.31	130.02	176.12
	199.05	171.50	148.06	177.54
	229.81	184.33	153.97	185.18
	241.05	189.93	174.04	193.92
	245.36	215.14	190.36	219.61
	252.30	243.63	204.43	246.78
	259.81	254.42	236.24	261.40

	270.74	257.08	247.41	294.13
	321.07	301.37	252.09	312.84
	346.46	334.49	276.09	351.46
	362.21	365.33	285.43	375.99
	405.55	407.92	311.63	402.57
	416.78	428.55	344.96	421.48
	424.08	430.23	370.77	429.45
	434.35	445.68	390.77	434.78
	475.46	458.02	420.49	457.35
	492.45	530.87	426.84	530.66
	586.03	546.26	431.16	546.59
	590.68	583.40	457.11	571.01
	607.08	596.39	488.61	607.90
	621.73	619.62	538.12	621.65
	643.73	646.95	564.79	634.18
	648.57	648.96	578.21	647.57
	649.57	659.29	588.57	656.59
	673.02	669.42	603.87	668.72
	704.65	687.59	618.92	688.03
	713.10	706.80	634.94	718.97
	729.79	725.17	648.15	725.07
	733.21	730.87	648.31	739.21
	739.78	734.93	671.67	754.16
	755.30	771.07	675.29	781.02
	778.58	791.55	721.12	795.68
	793.65	817.88	724.89	803.62
	823.39	832.61	737.77	828.45
	857.25	861.00	763.76	868.54
	864.76	874.15	777.73	888.27
	883.71	882.54	794.51	906.10
	891.25	891.55	822.33	926.35
	924.62	950.86	828.82	945.19
	958.64	968.33	852.95	970.98
	973.51	969.45	883.05	979.41
	988.67	980.51	889.35	991.82
	993.13	988.92	927.04	999.89
	1004.09	993.15	935.08	1006.57
	1005.73	1005.24	964.94	1017.82
	1014.13	1013.34	971.87	1023.04
	1020.46	1025.79	979.53	1030.52
	1031.03	1033.05	999.86	1035.03
	1031.97	1033.40	1006.14	1042.57
	1034.55	1036.04	1010.96	1060.39
	1035.22	1051.78	1013.89	1064.05

	1043.24	1058.66	1017.23	1070.76
	1060.24	1065.80	1024.67	1079.12
	1063.19	1081.98	1031.68	1084.70
	1066.20	1087.25	1037.82	1094.68
	1094.39	1092.58	1043.53	1109.90
	1113.14	1126.70	1047.12	1131.12
	1120.86	1130.82	1049.41	1134.97
	1127.33	1149.79	1063.02	1166.51
	1142.82	1221.31	1065.76	1219.35
	1204.51	1224.99	1092.49	1223.92
	1219.07	1230.58	1097.74	1224.17
	1222.08	1237.78	1121.42	1241.78
	1230.31	1247.36	1137.79	1244.79
	1231.95	1257.81	1140.86	1252.09
	1248.06	1275.18	1214.55	1270.26
	1285.08	1303.65	1223.13	1308.67
	1302.94	1333.88	1224.03	1331.68
	1332.00	1353.80	1235.59	1362.13
	1335.33	1368.68	1248.76	1371.58
	1359.34	1371.09	1276.27	1377.52
	1376.39	1387.69	1305.99	1400.69
	1384.40	1388.67	1340.53	1401.59
	1392.67	1392.74	1358.67	1403.64
	1401.30	1394.76	1362.61	1411.49
	1415.54	1422.20	1373.41	1470.63
	1461.30	1463.12	1380.63	1487.22
	1496.69	1493.37	1387.50	1489.77
	1497.35	1502.41	1400.26	1497.54
	1501.90	1504.23	1408.07	1502.59
	1507.50	1504.97	1457.95	1509.54
	1508.40	1508.37	1491.11	1514.87
	1516.14	1522.43	1496.10	1526.06
	1547.25	1549.07	1496.92	1550.02
	1549.36	1552.49	1499.42	1551.39
	1552.49	1607.61	1506.53	1582.46
	1596.63	1610.13	1509.48	1589.81
	1633.10	1628.85	1527.12	1627.40
	1639.30	1640.94	1547.35	1630.80
	1655.03	1657.27	1551.70	1656.04
	1661.02	1657.55	1554.76	1657.42
	1737.41	1715.99	1621.86	1686.11
	3067.39	2976.68	1632.57	2970.09
	3086.00	3063.23	1634.81	3068.39
	3102.46	3084.12	1655.49	3089.27

	3146.33	3085.03	1657.49	3122.12
	3185.17	3168.60	1713.68	3129.20
	3185.39	3188.19	3099.70	3174.29
	3192.96	3191.81	3104.77	3179.89
	3197.15	3192.76	3178.24	3180.53
	3199.18	3197.49	3196.07	3191.39
	3205.11	3204.95	3200.22	3195.91
	3207.86	3206.59	3204.55	3203.14
	3219.30	3208.73	3208.59	3203.34
	3220.12	3216.82	3216.46	3203.40
	3222.15	3219.11	3217.98	3215.60
	3226.82	3227.31	3221.53	3218.75
	3231.73	3228.27	3221.71	3219.44
	3232.15	3235.00	3223.27	3226.68
	3232.96	3239.06	3226.12	3228.36
	3234.35	3242.72	3228.11	3237.84
	3235.94	3258.20	3231.34	3240.01
			3233.16	
			3248.25	
			3255.19	
			3291.54	
			3421.01	
			3620.38	

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9. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compounds 3.

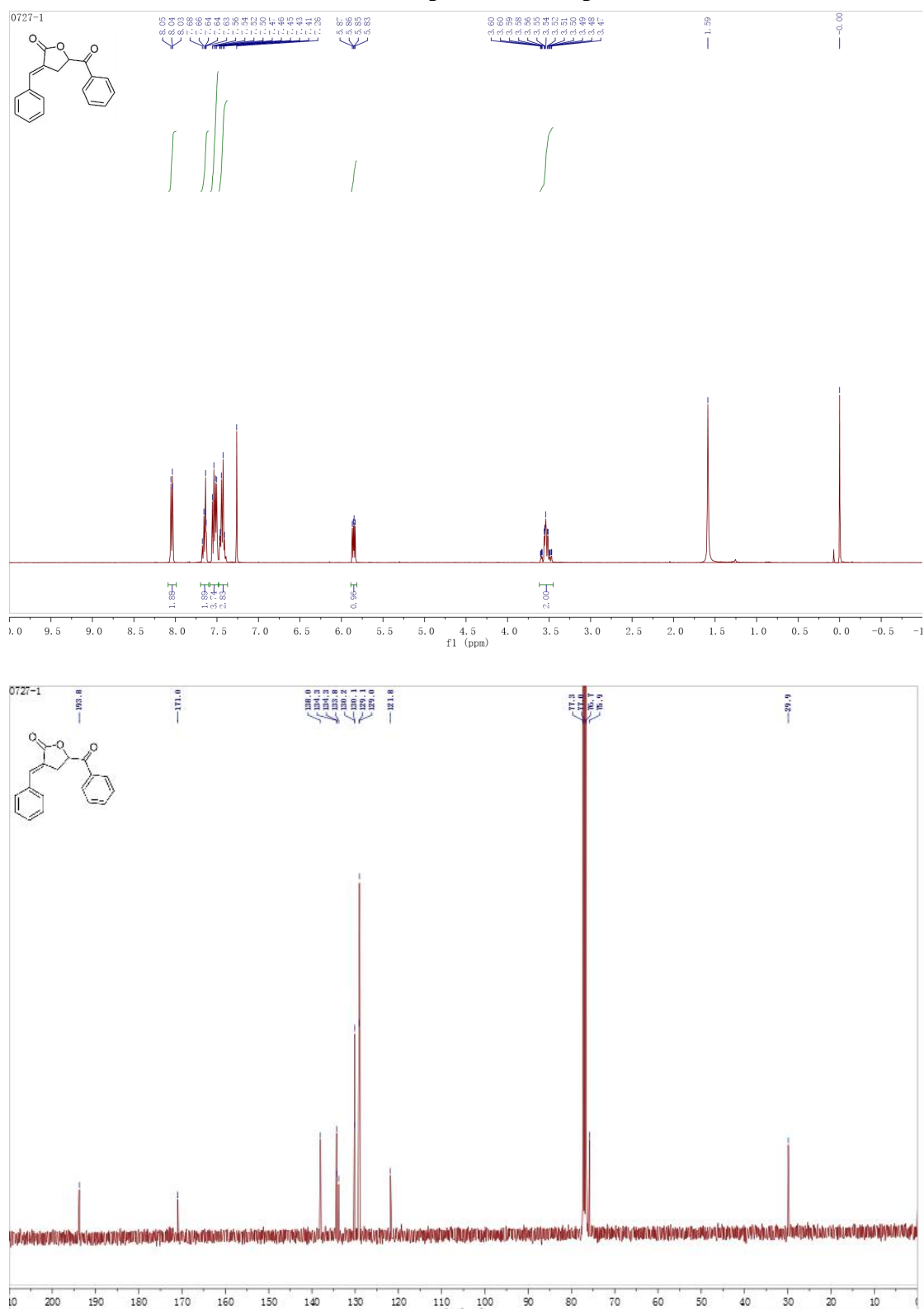


Figure S15. The ^1H NMR and ^{13}C NMR Spectrum of **3aa** in CDCl_3 .

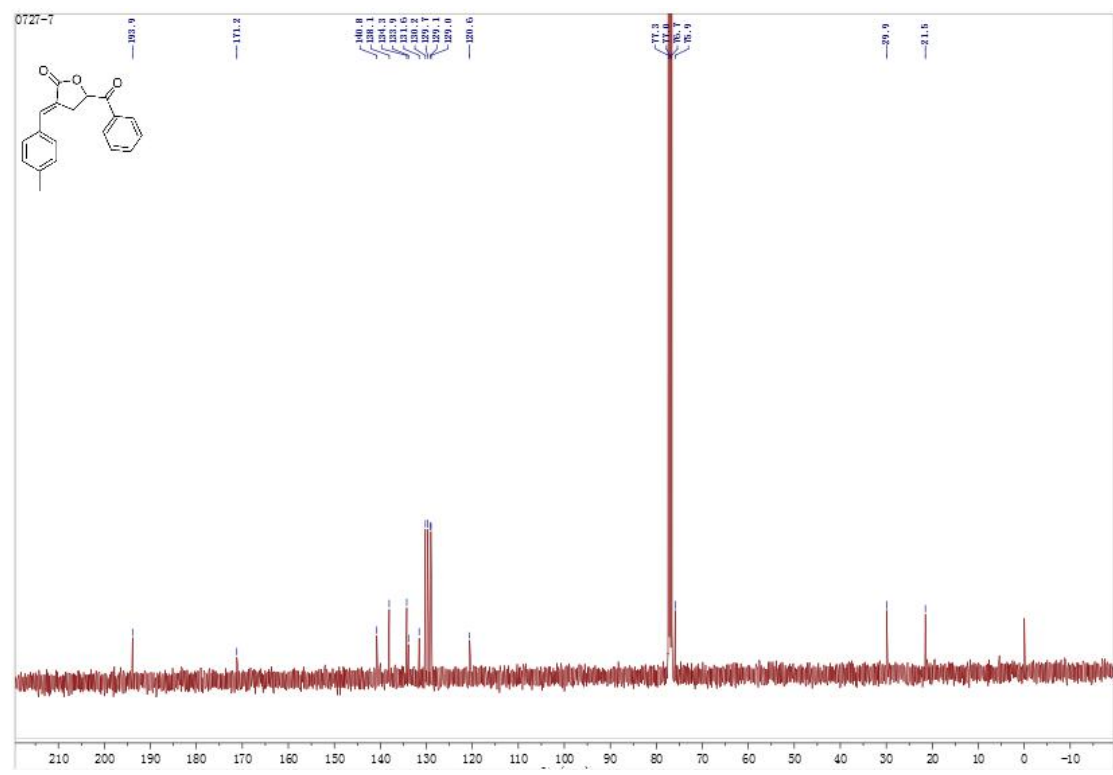
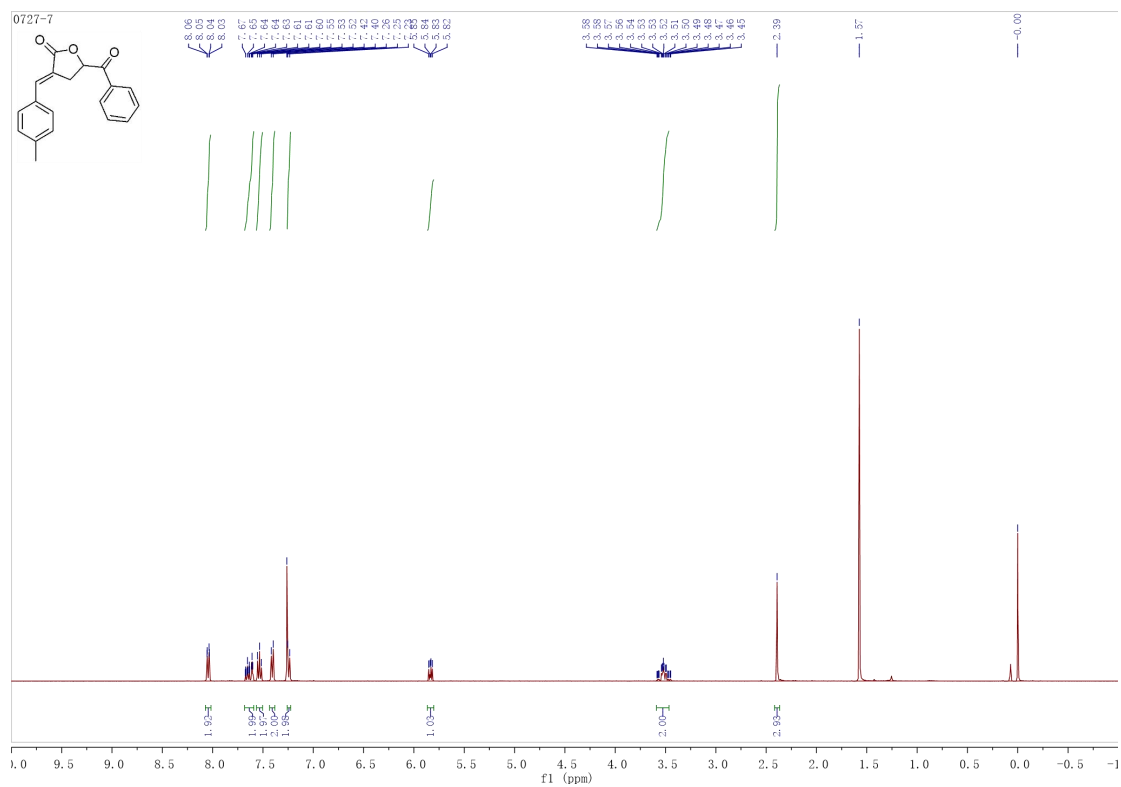


Figure S16. The ^1H NMR and ^{13}C NMR Spectrum of **3ba** in CDCl_3 .

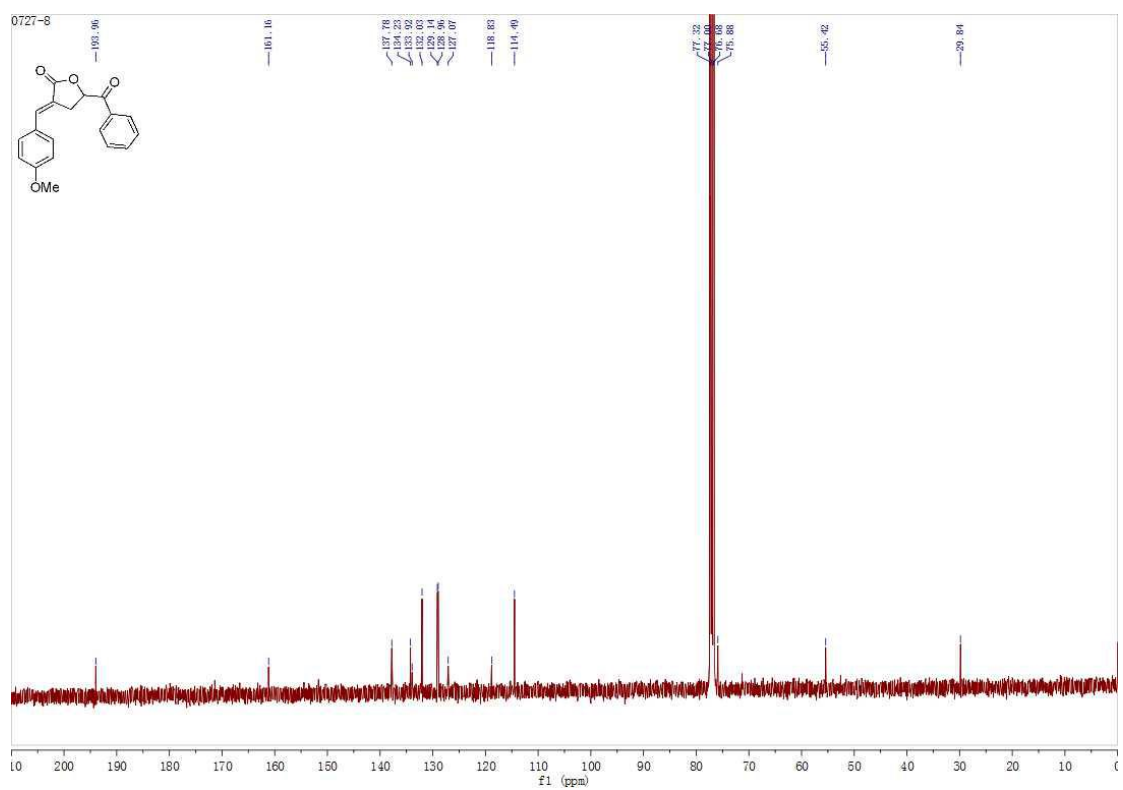
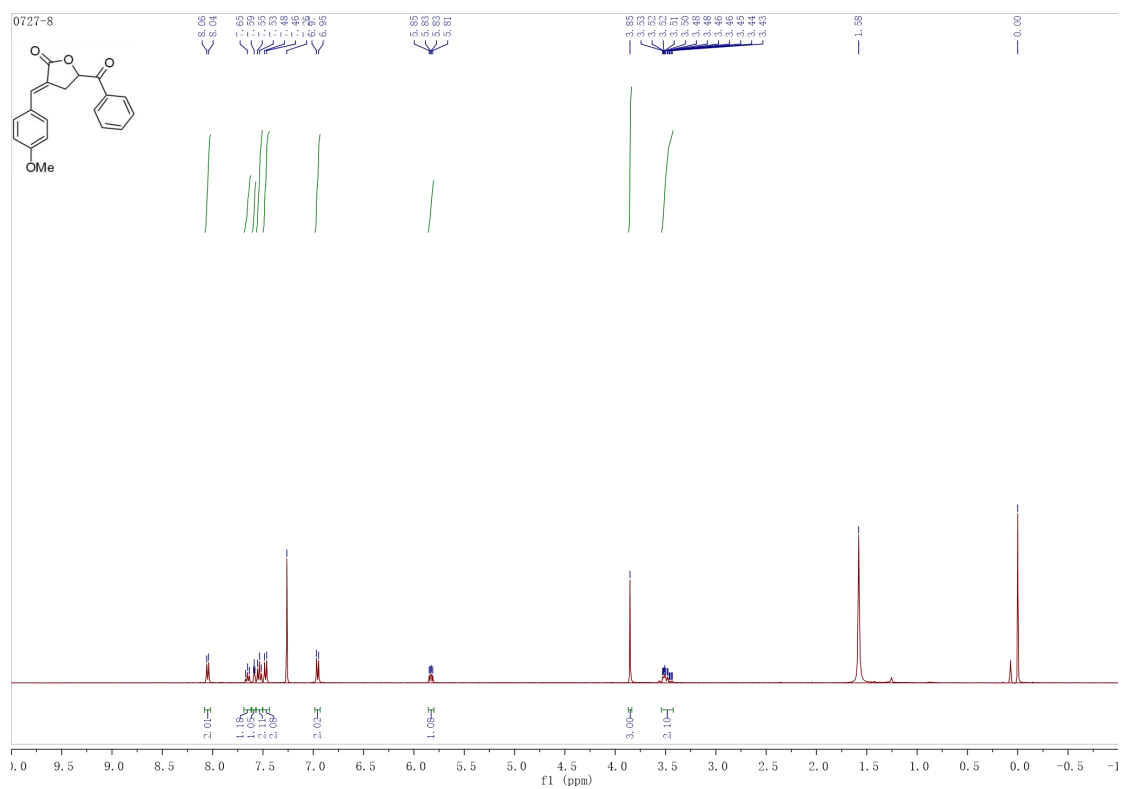


Figure S17. The ¹H NMR and ¹³C NMR Spectrum of **3ca** in CDCl₃.

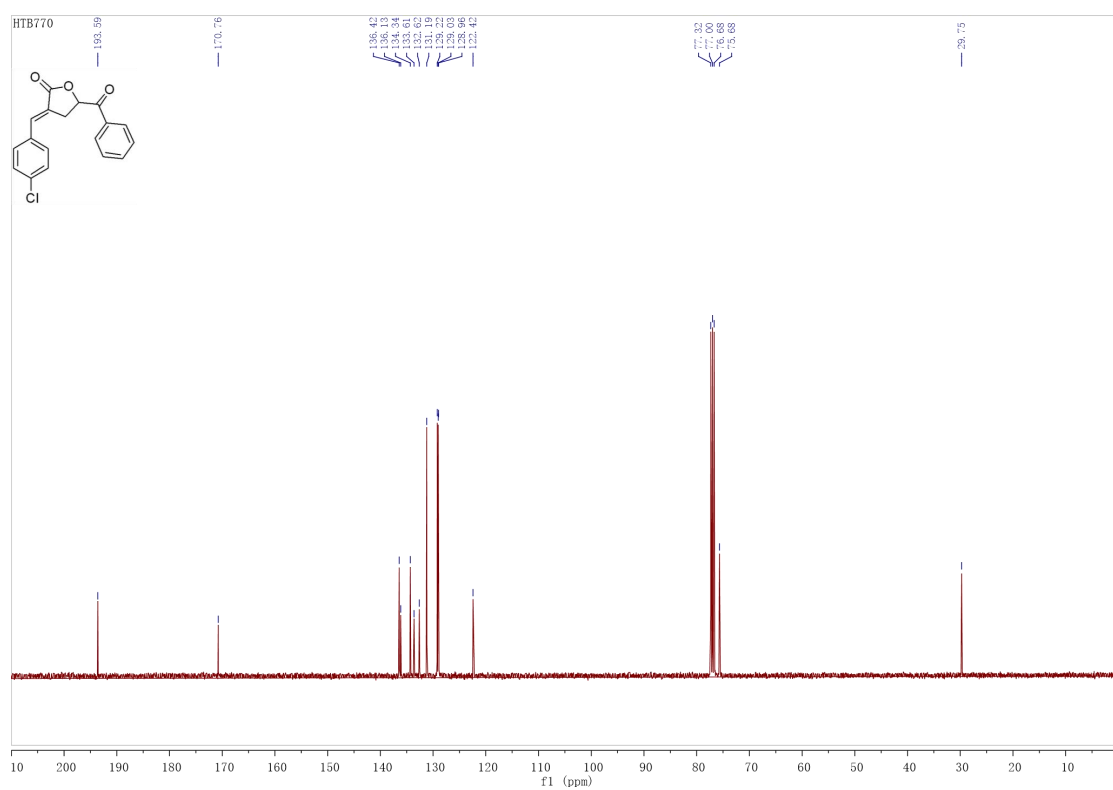
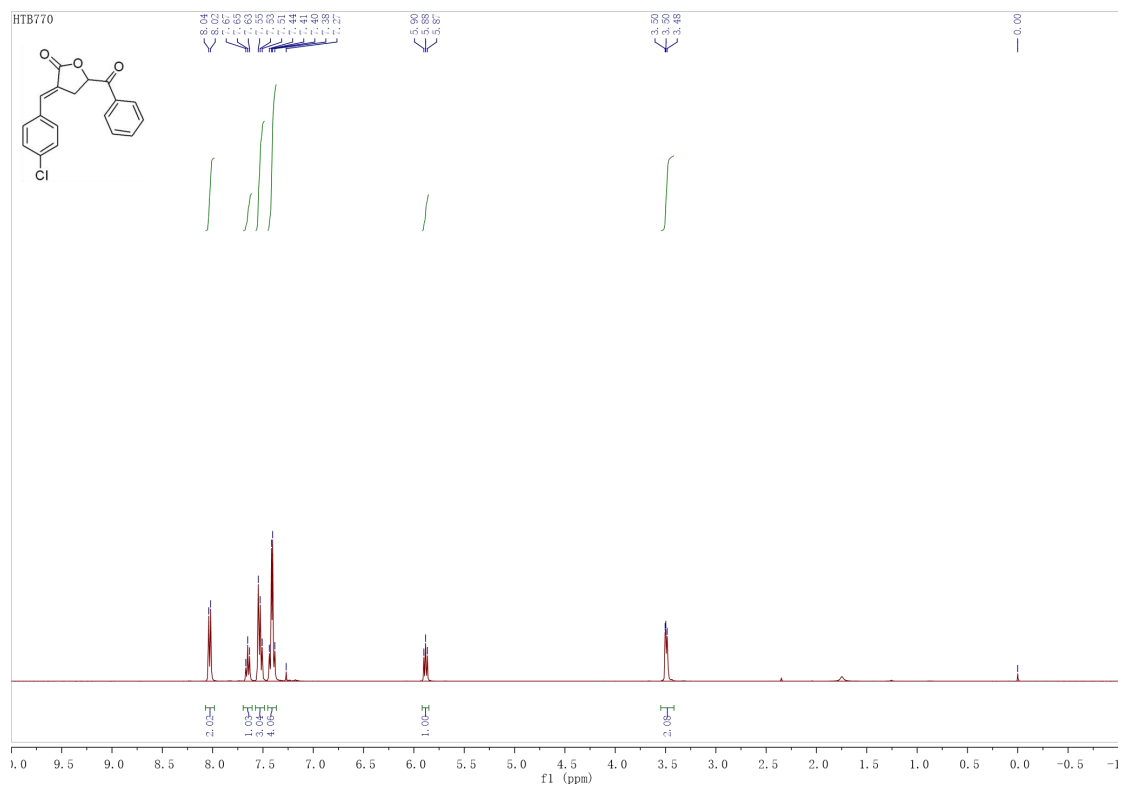


Figure S18. The ^1H NMR and ^{13}C NMR Spectrum of **3da** in CDCl_3 .

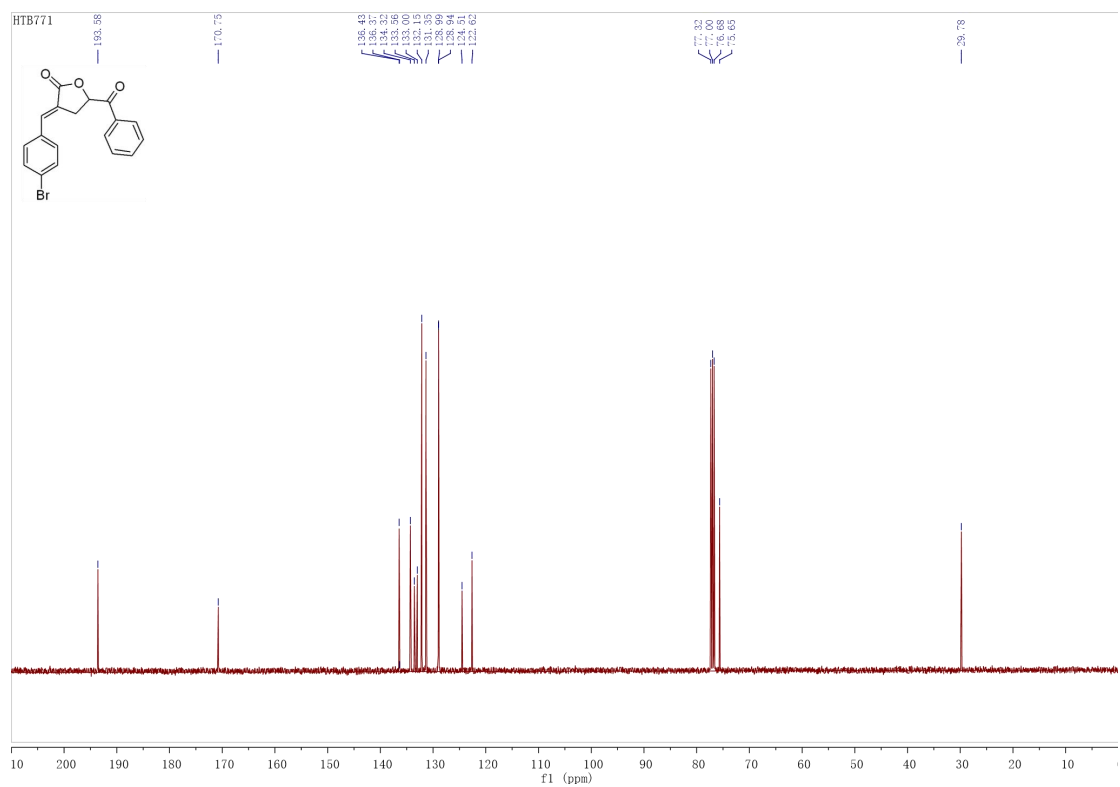
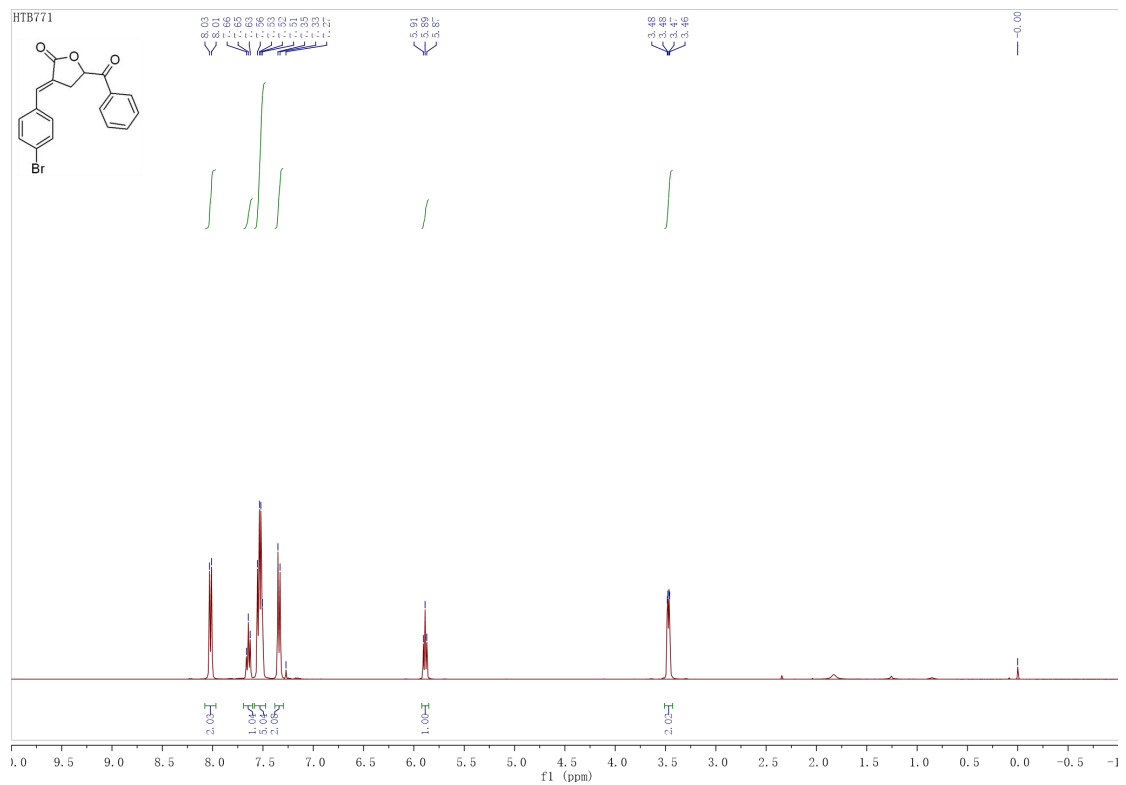


Figure S19. The ^1H NMR and ^{13}C NMR Spectrum of **3ea** in CDCl_3 .

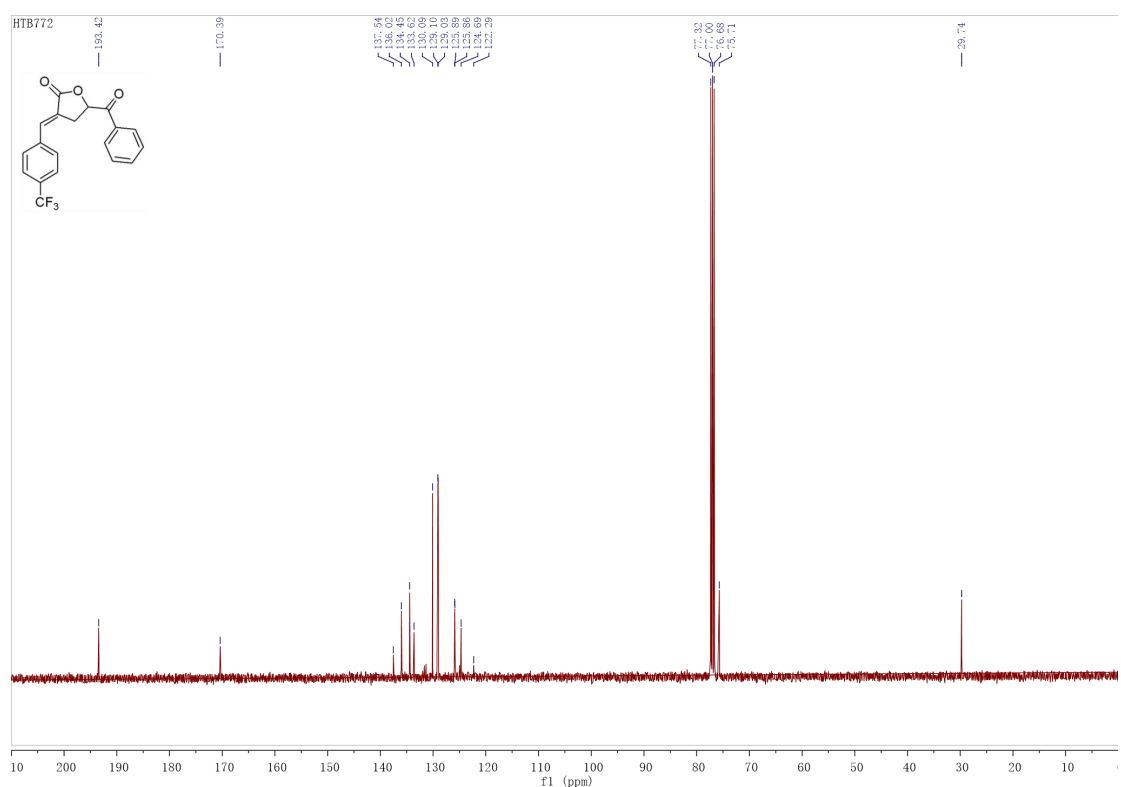
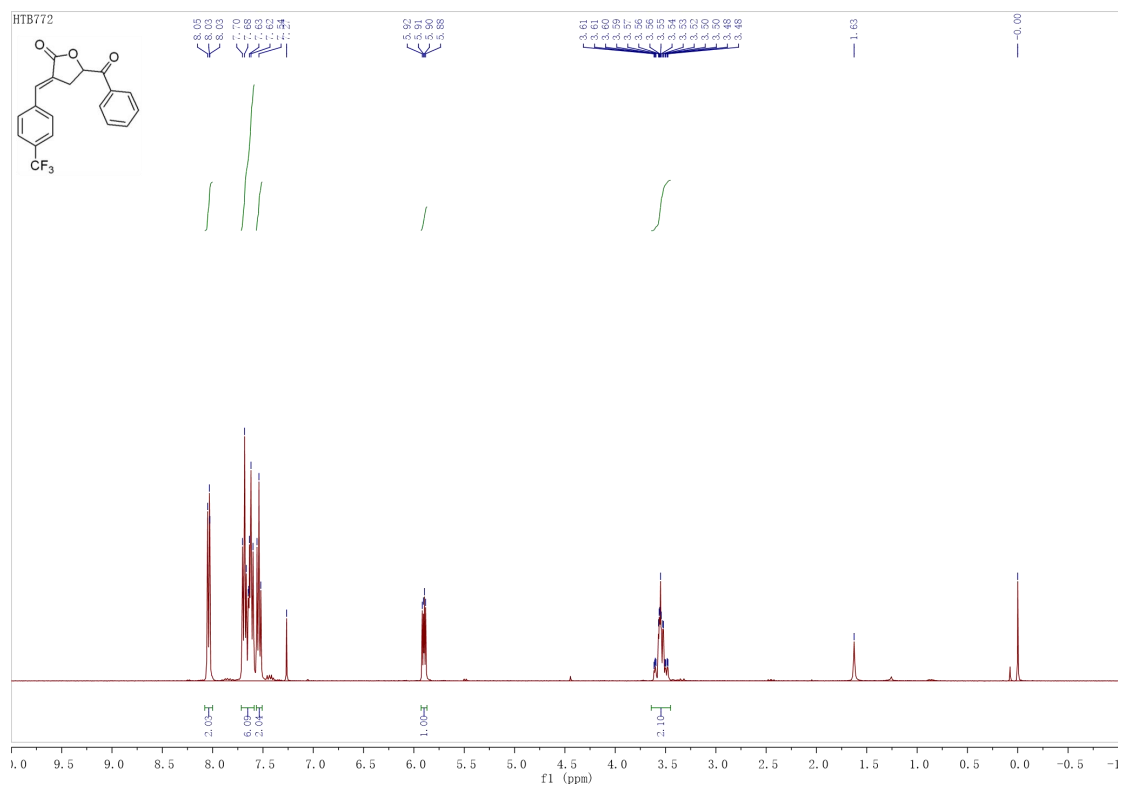


Figure S20-1. The ^1H NMR and ^{13}C NMR Spectrum of **3fa** in CDCl_3 .

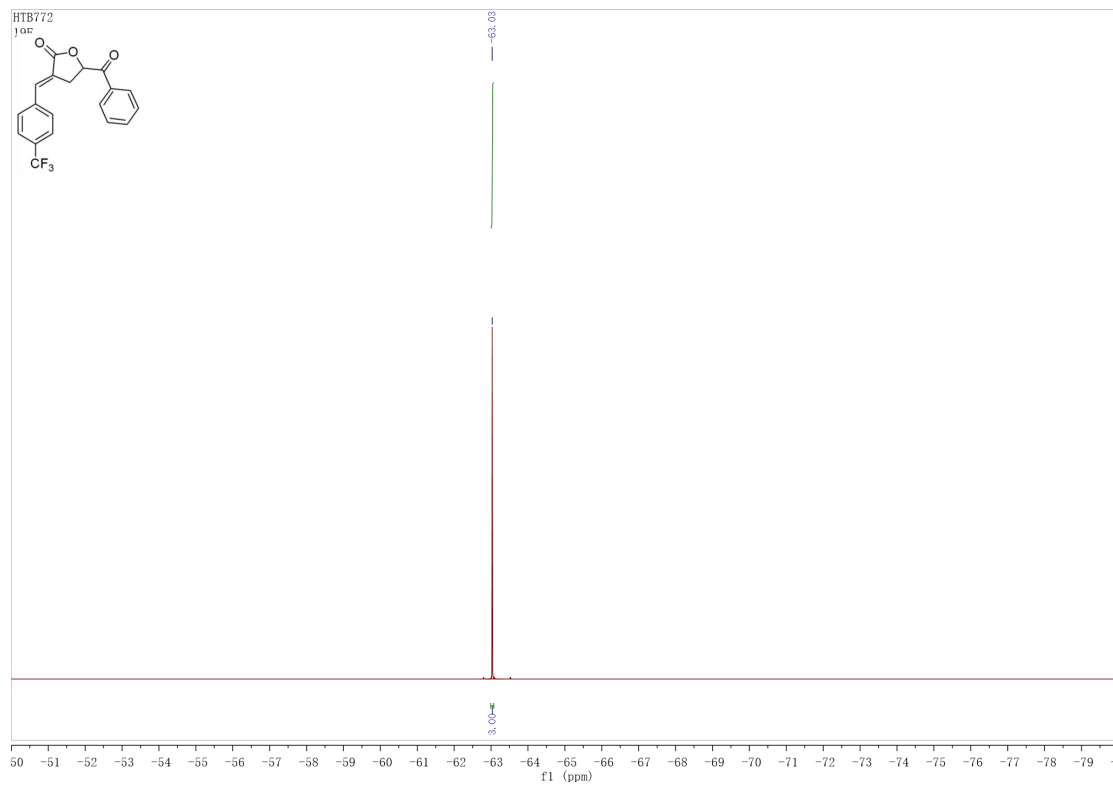


Figure S20-2. The ^{19}F NMR Spectrum of **3fa** in CDCl_3 .

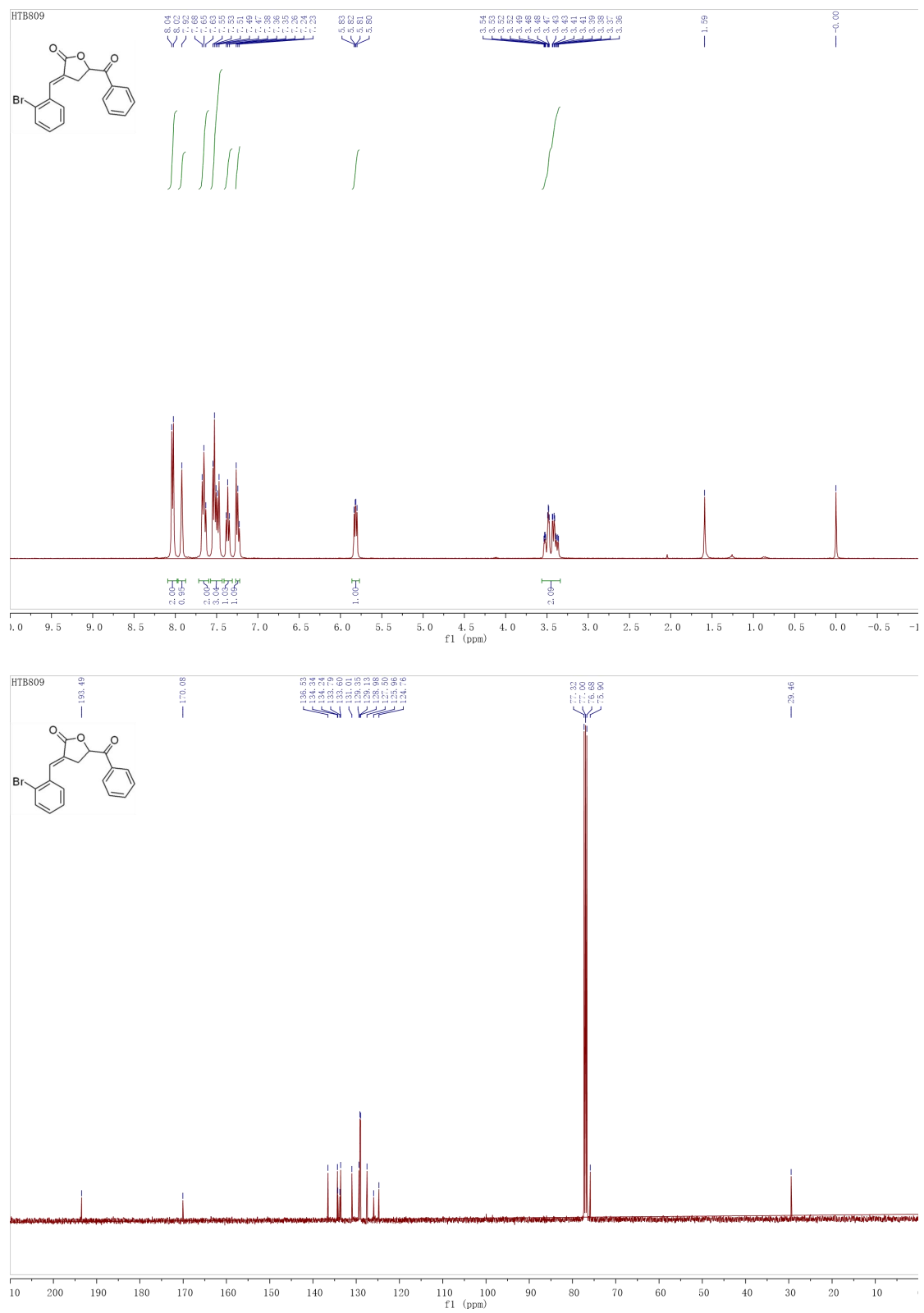


Figure S21. The ¹H NMR and ¹³C NMR Spectrum of **3ga** in CDCl₃.

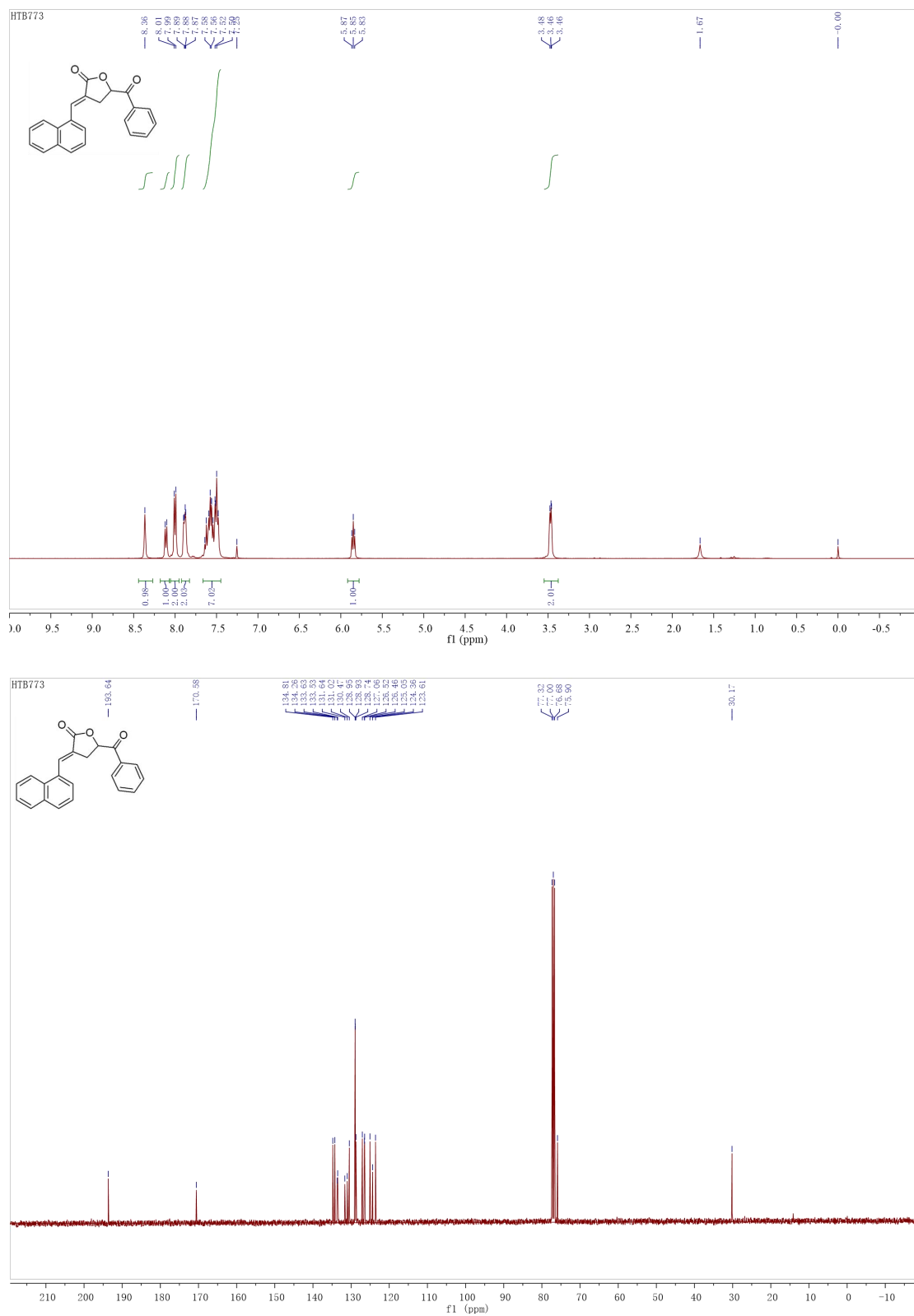


Figure S23. The ^1H NMR and ^{13}C NMR Spectrum of **3ia** in CDCl_3 .

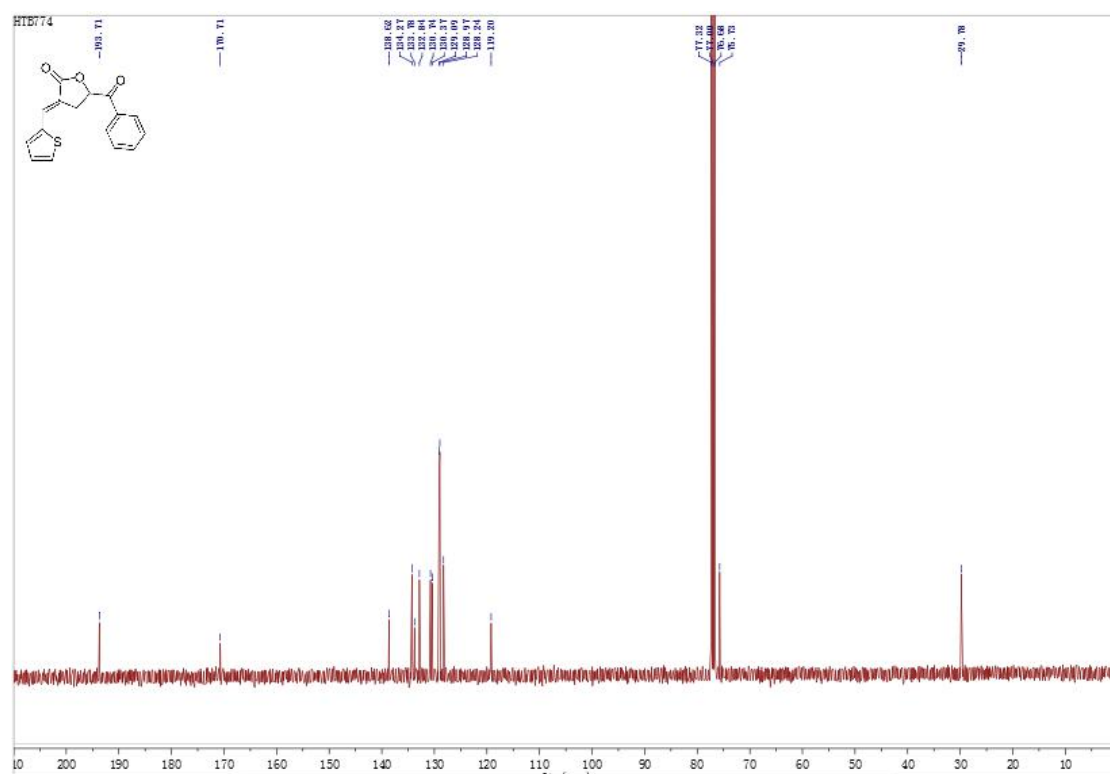
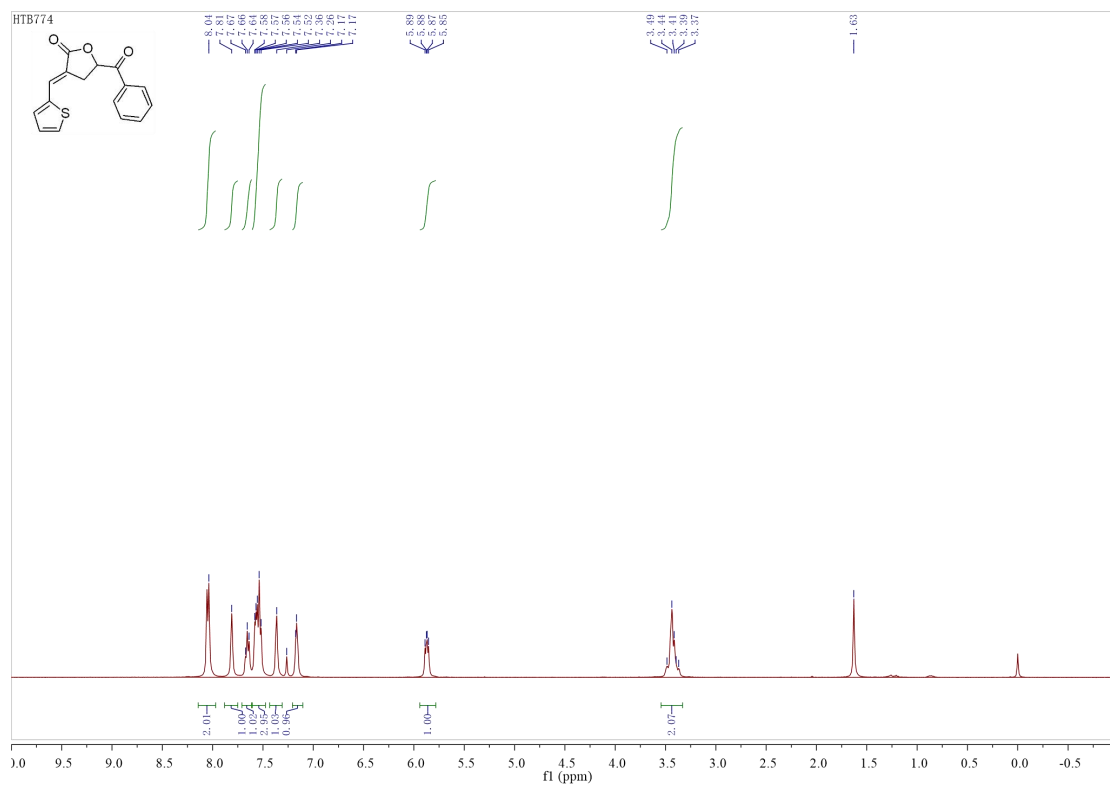


Figure S24. The ^1H NMR and ^{13}C NMR Spectrum of **3ja** in CDCl_3 .

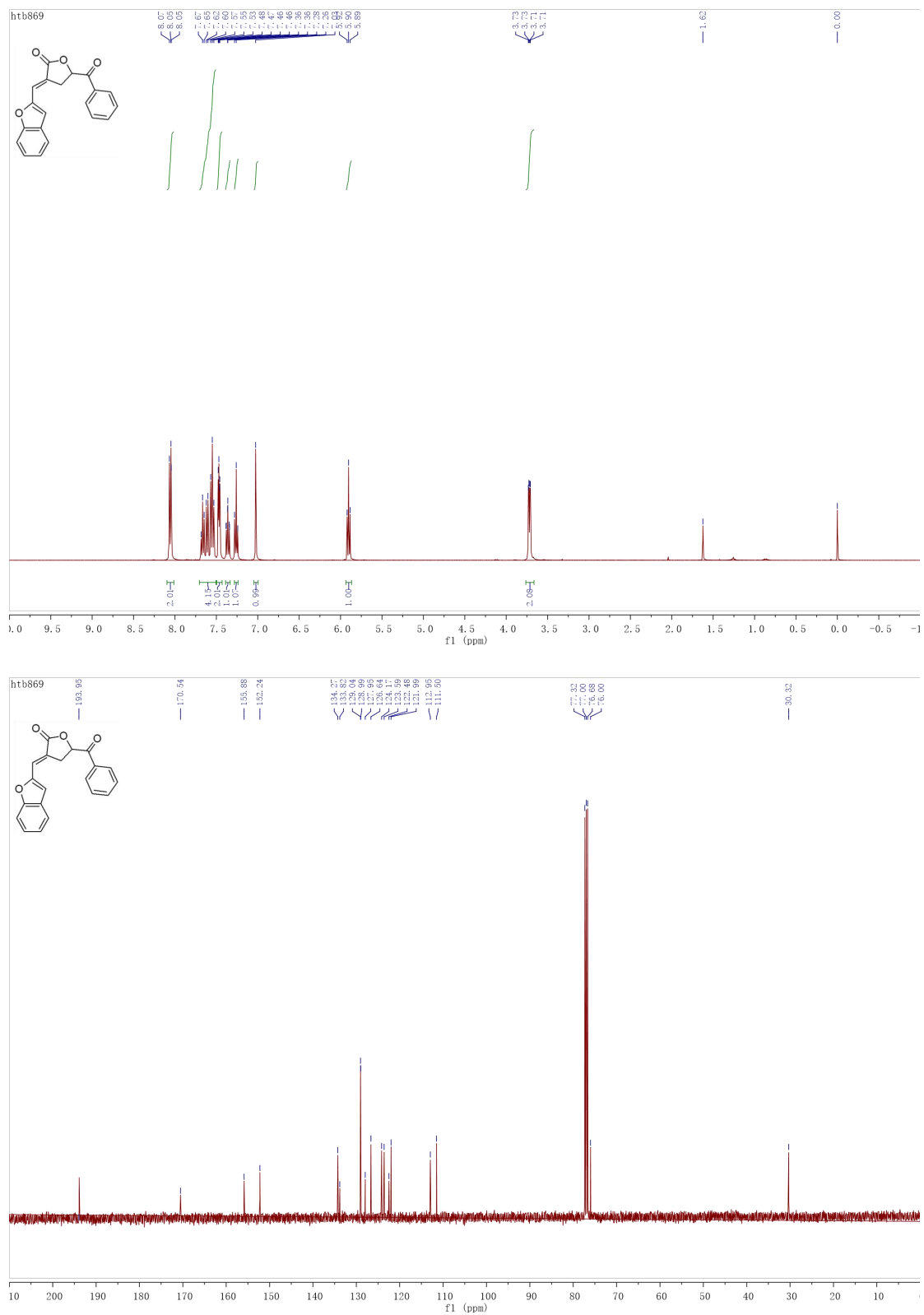


Figure S25. The ^1H NMR and ^{13}C NMR Spectrum of **3ka** in CDCl_3 .

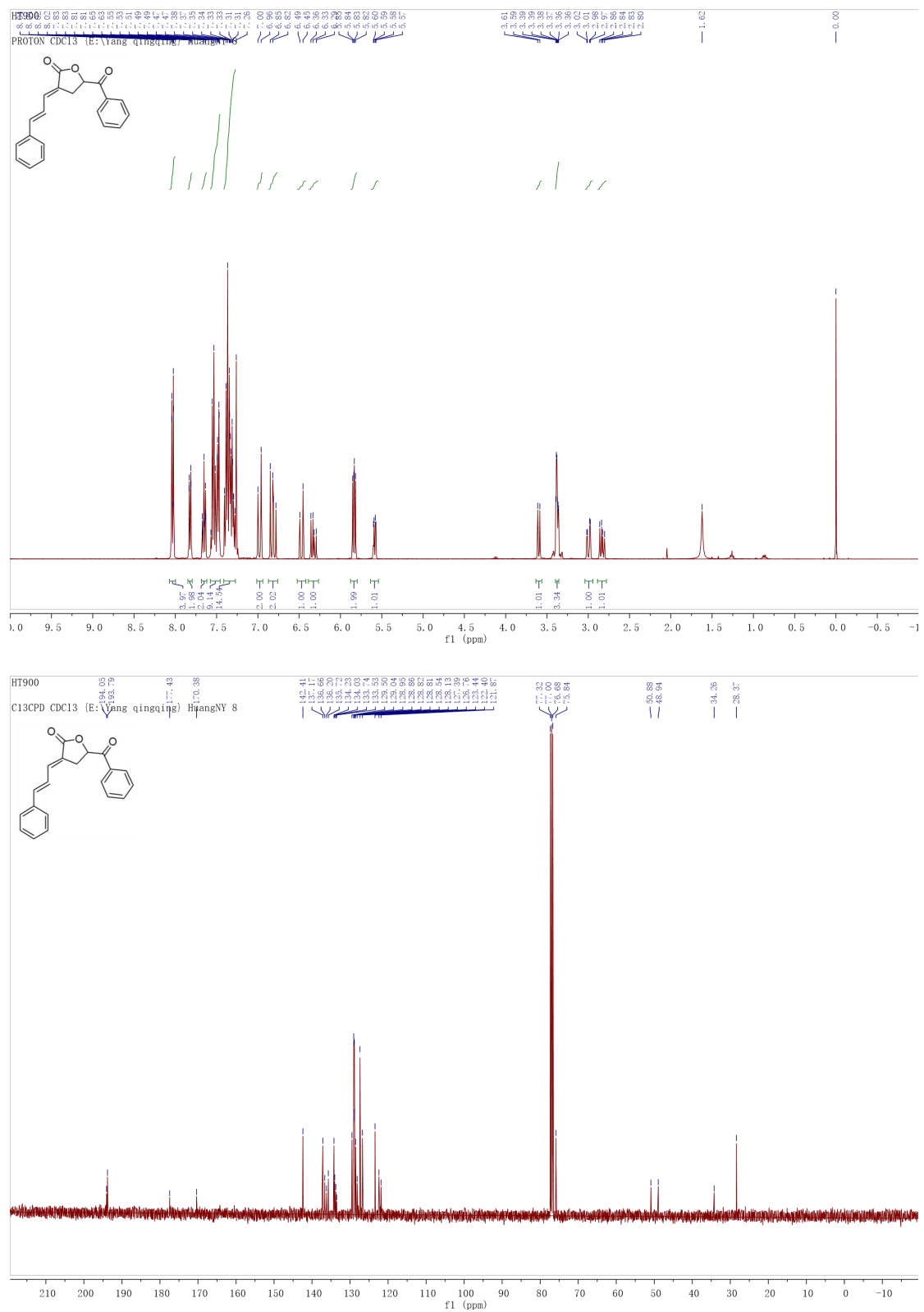


Figure S26. The ¹H NMR and ¹³C NMR Spectrum of **3la** in CDCl₃.

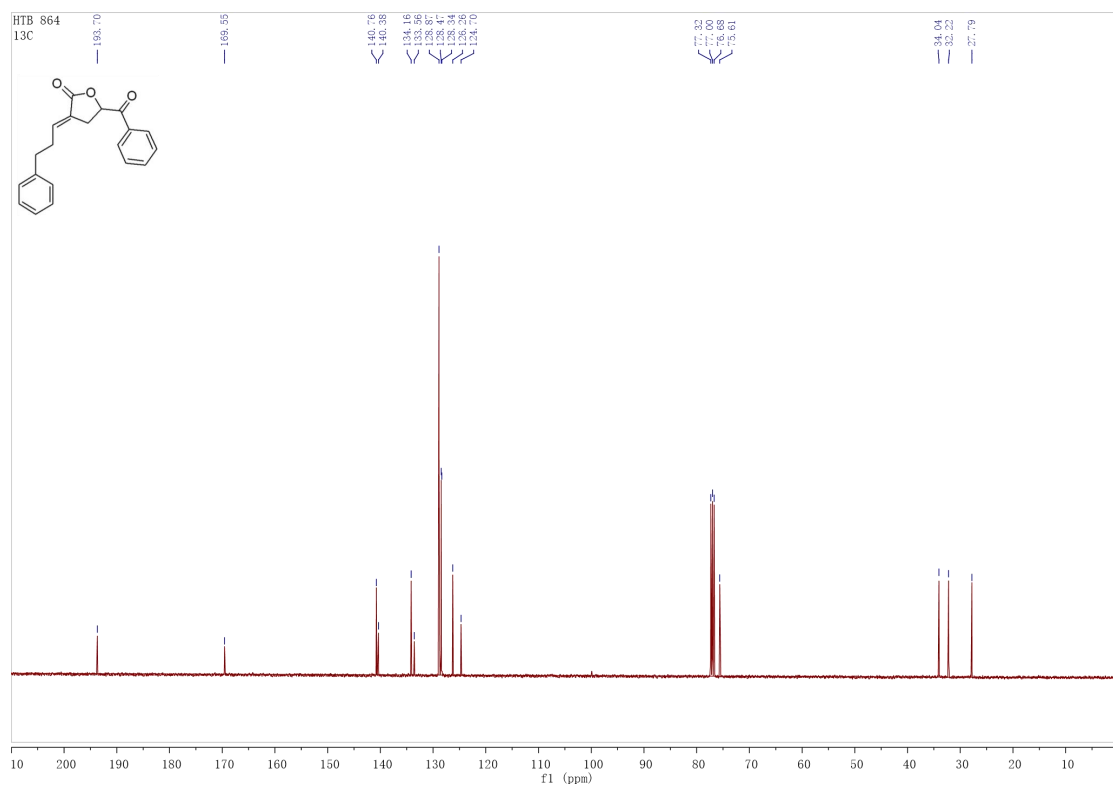
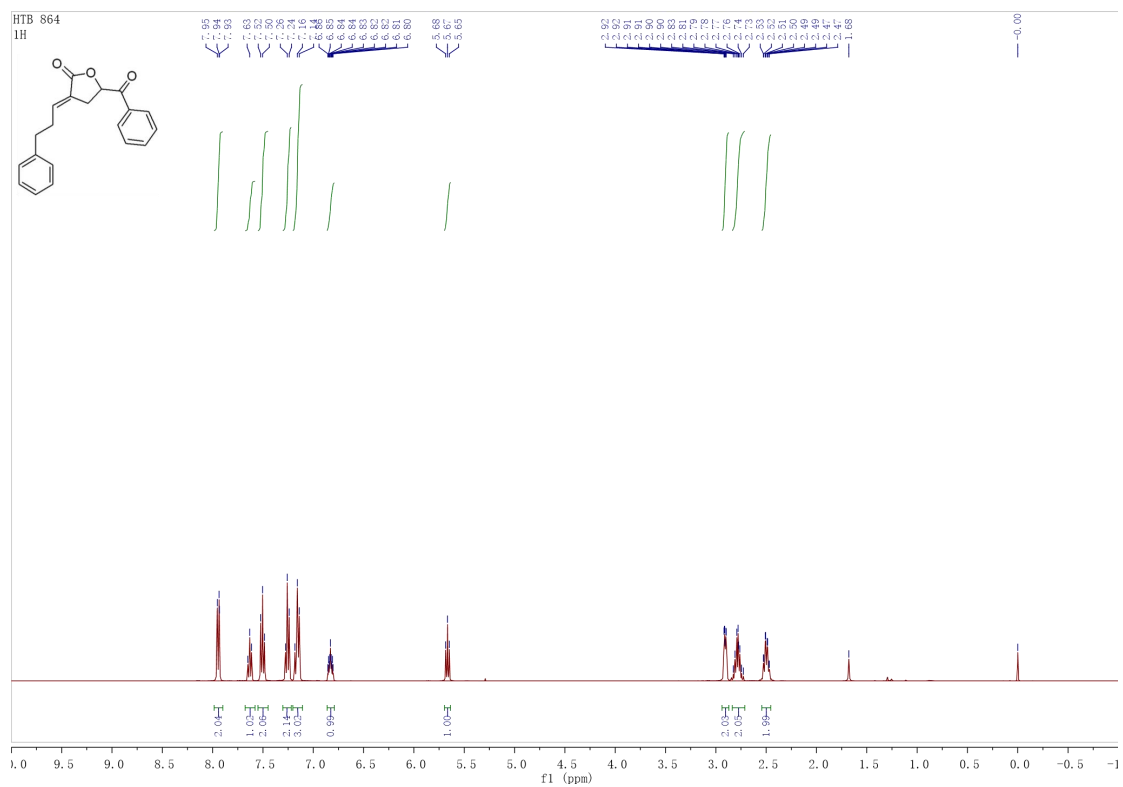


Figure S27. The ^1H NMR and ^{13}C NMR Spectrum of **3ma** in CDCl_3 .

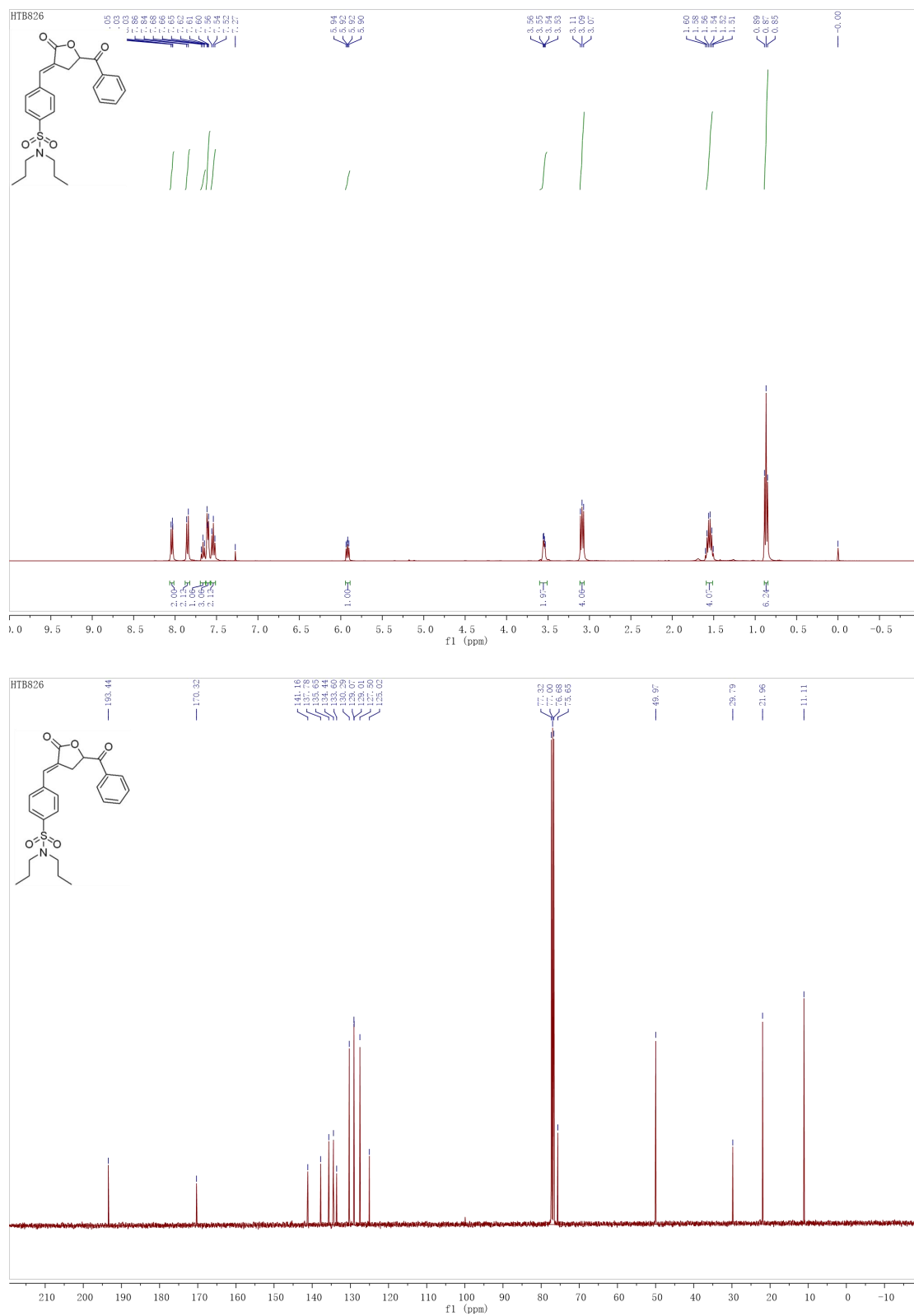


Figure S28. The ¹H NMR and ¹³C NMR Spectrum of **3na** in CDCl₃.

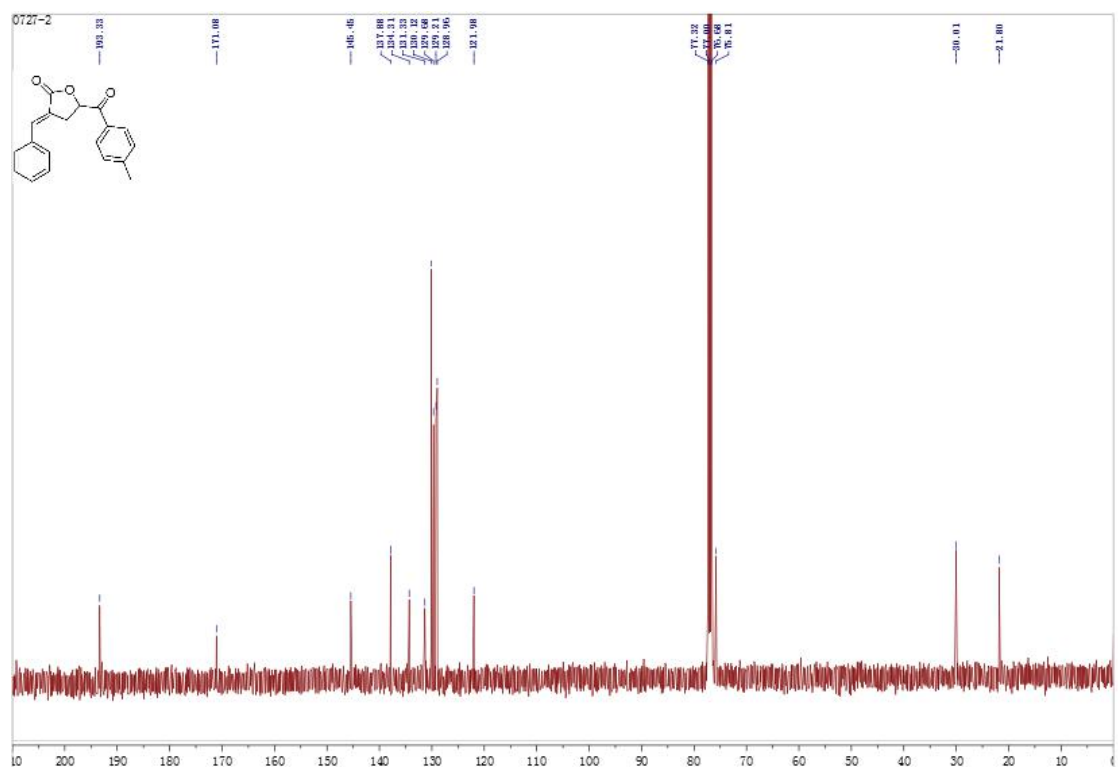
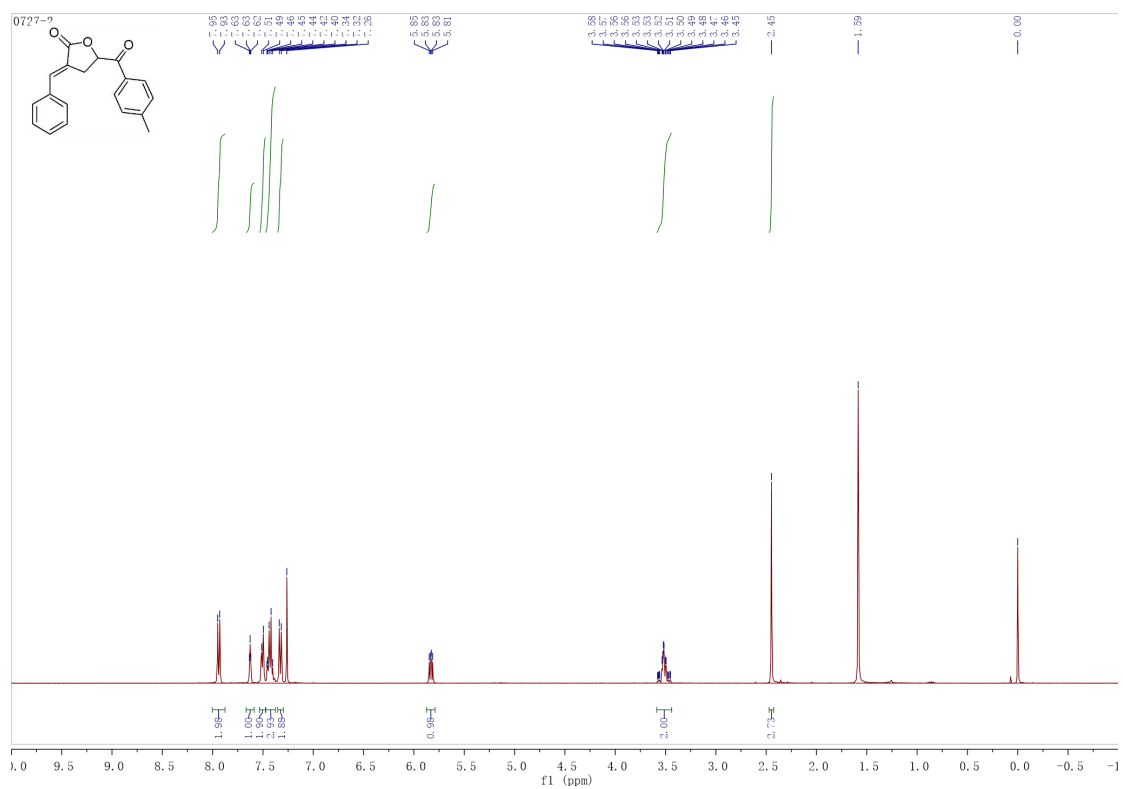


Figure S29. The ^1H NMR and ^{13}C NMR Spectrum of **3ab** in CDCl_3 .

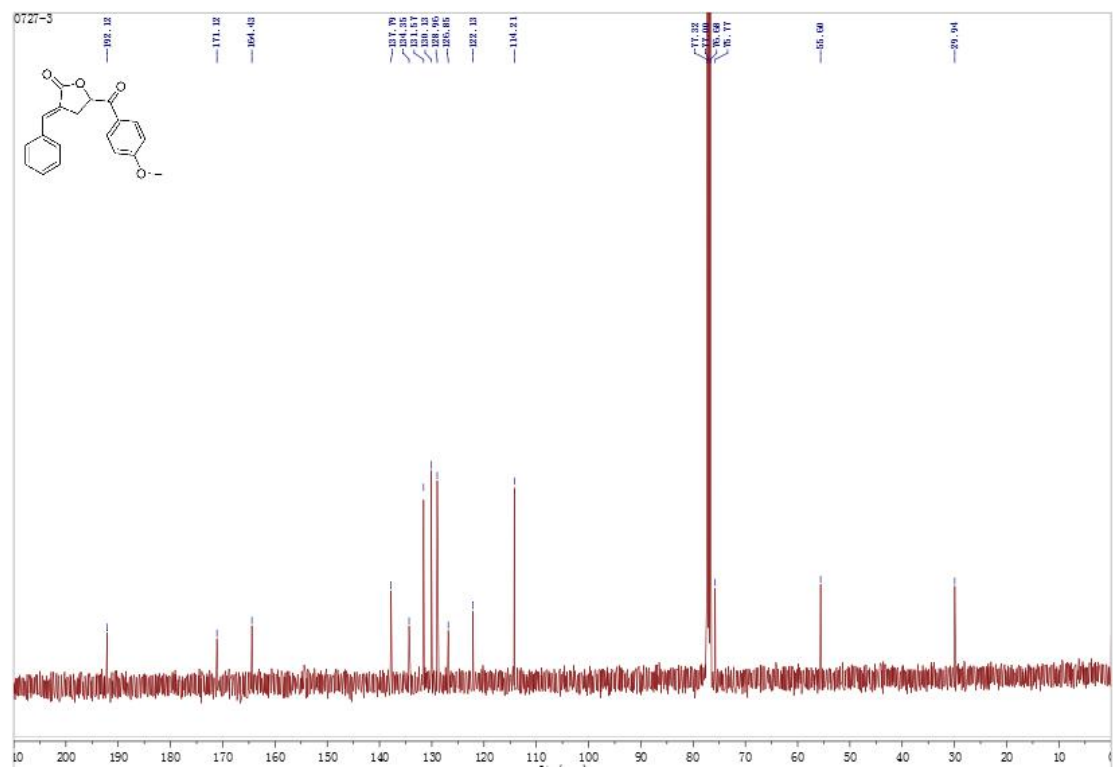
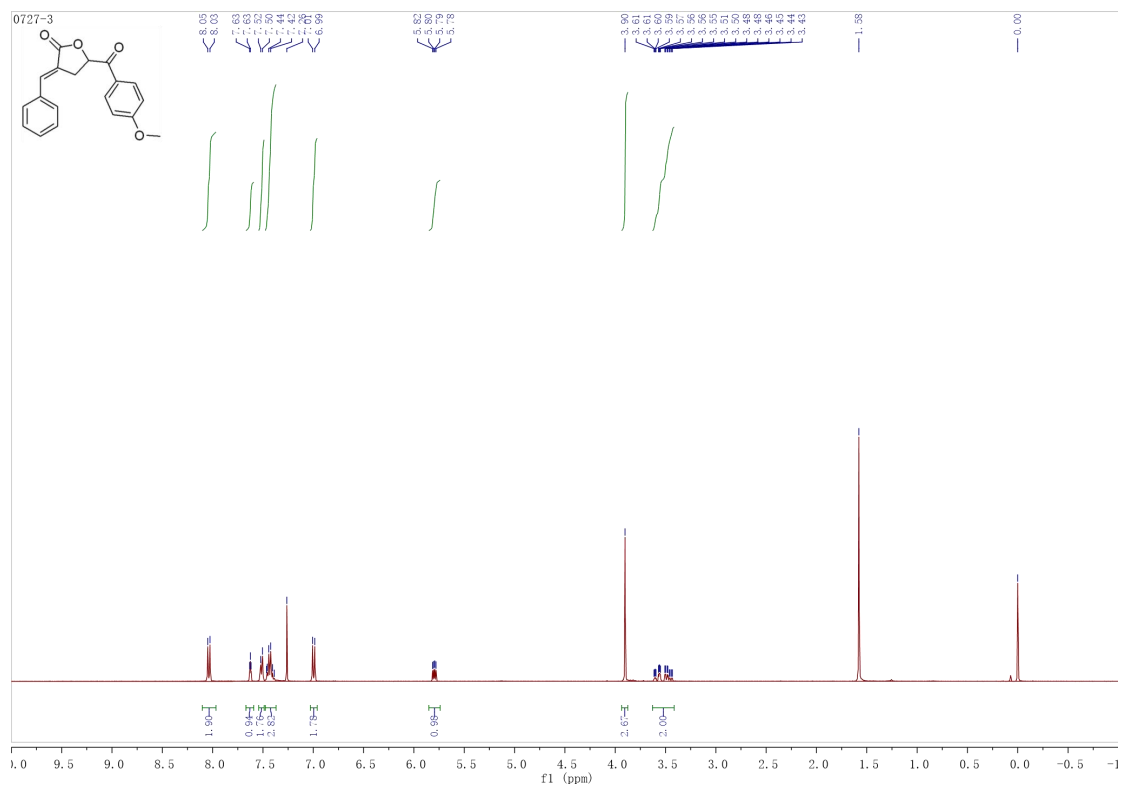


Figure S30. The ^1H NMR and ^{13}C NMR Spectrum of **3ac** in CDCl_3 .

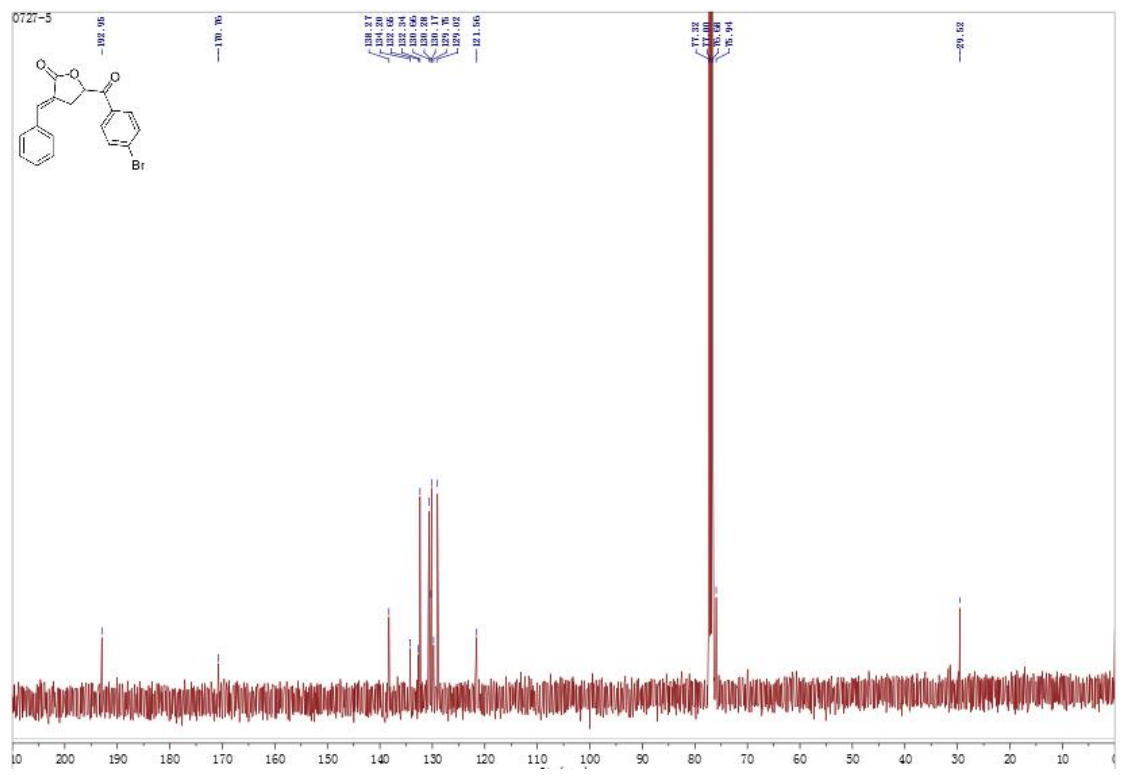
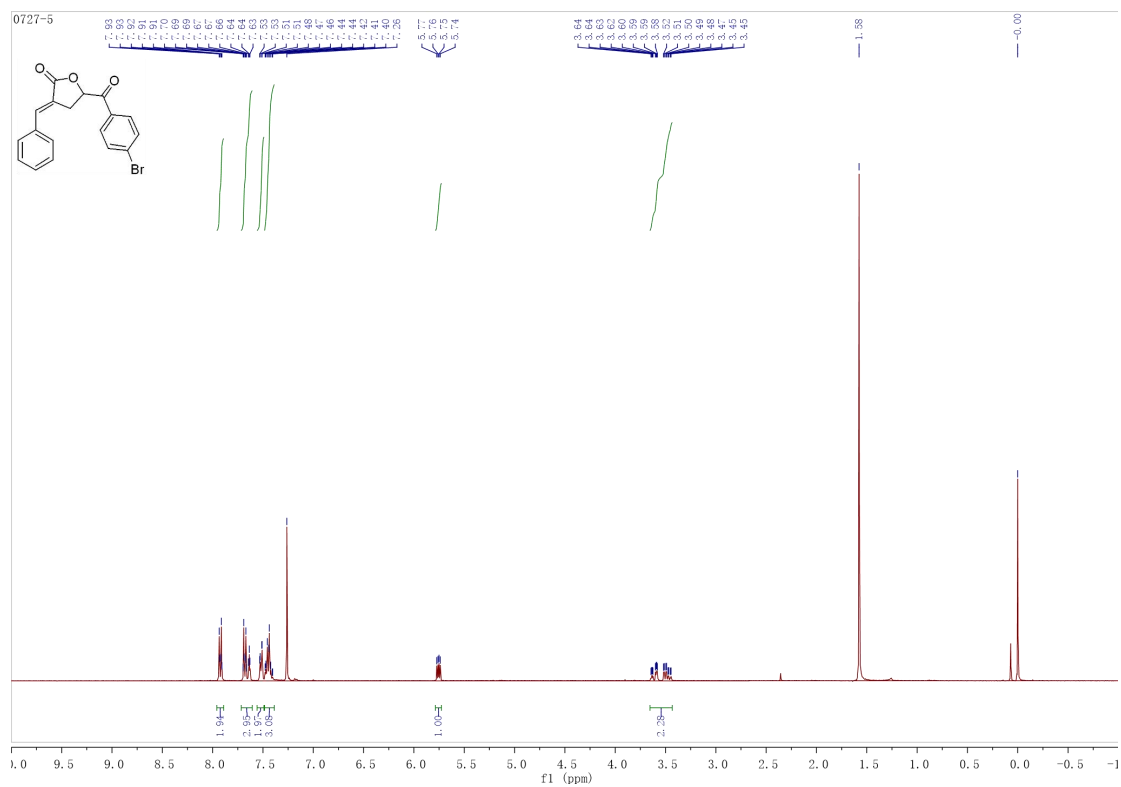


Figure S32. The ^1H NMR and ^{13}C NMR Spectrum of **3ae** in CDCl_3 .

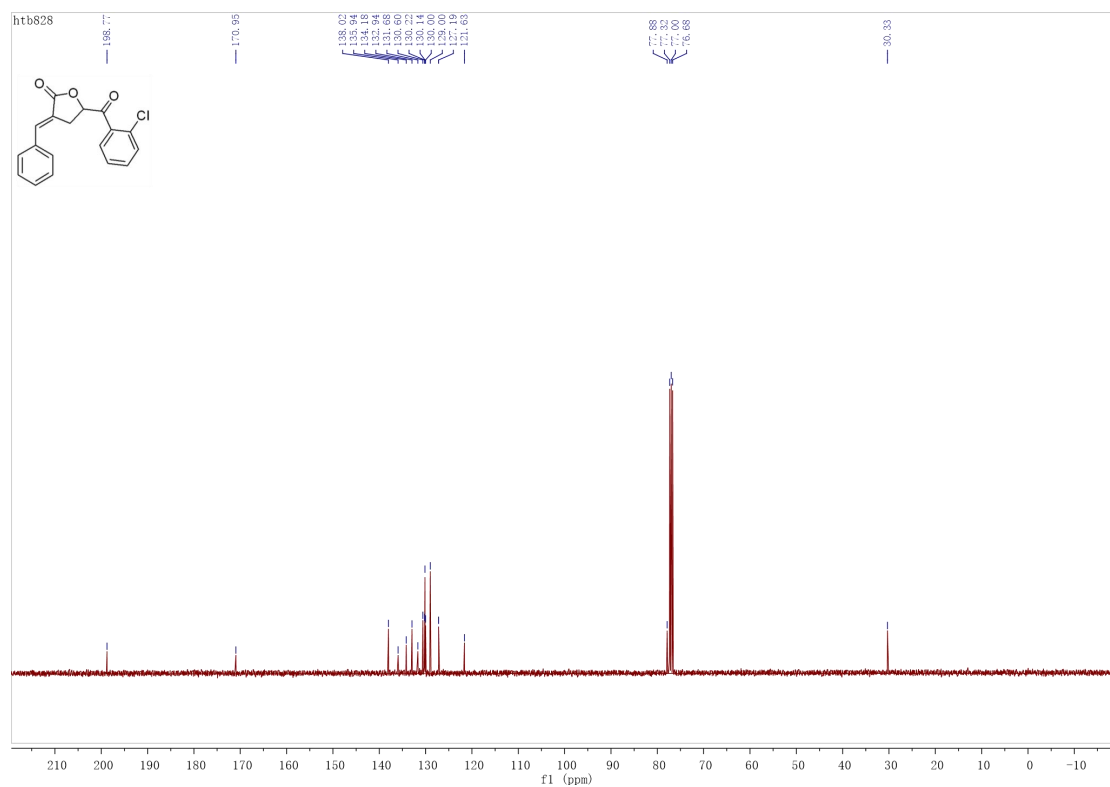
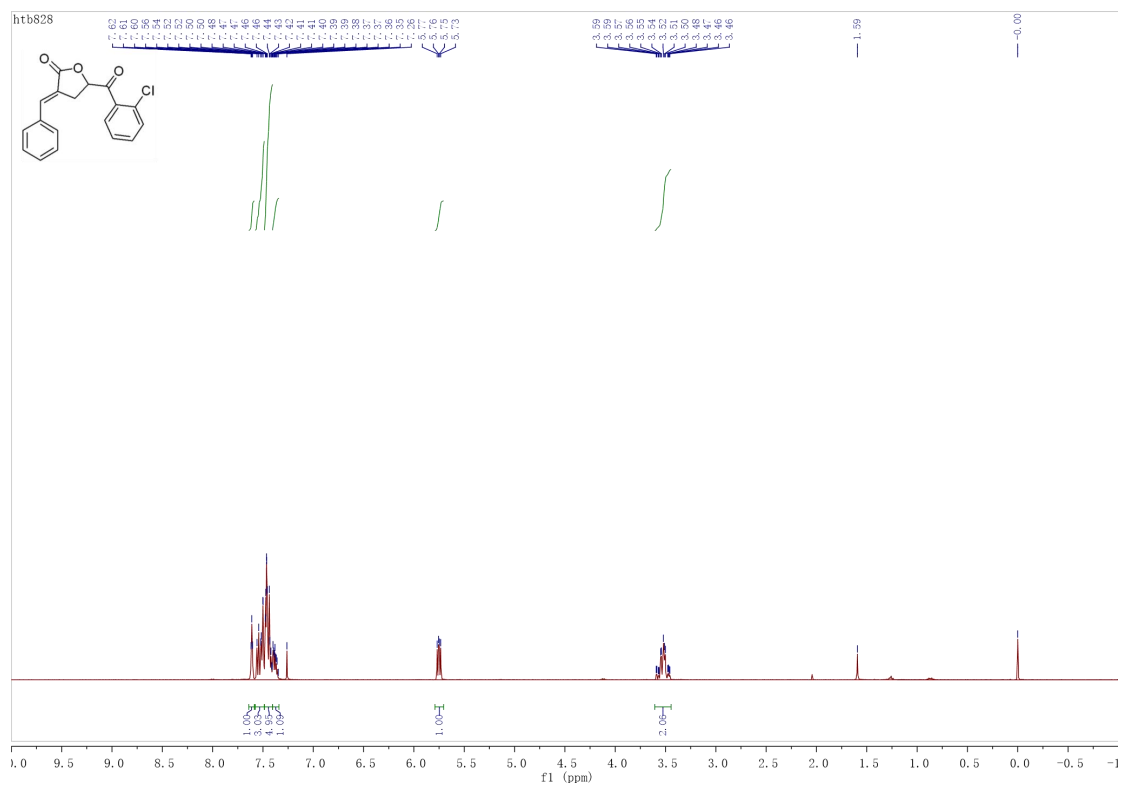


Figure S33. The ^1H NMR and ^{13}C NMR Spectrum of **3af** in CDCl_3 .

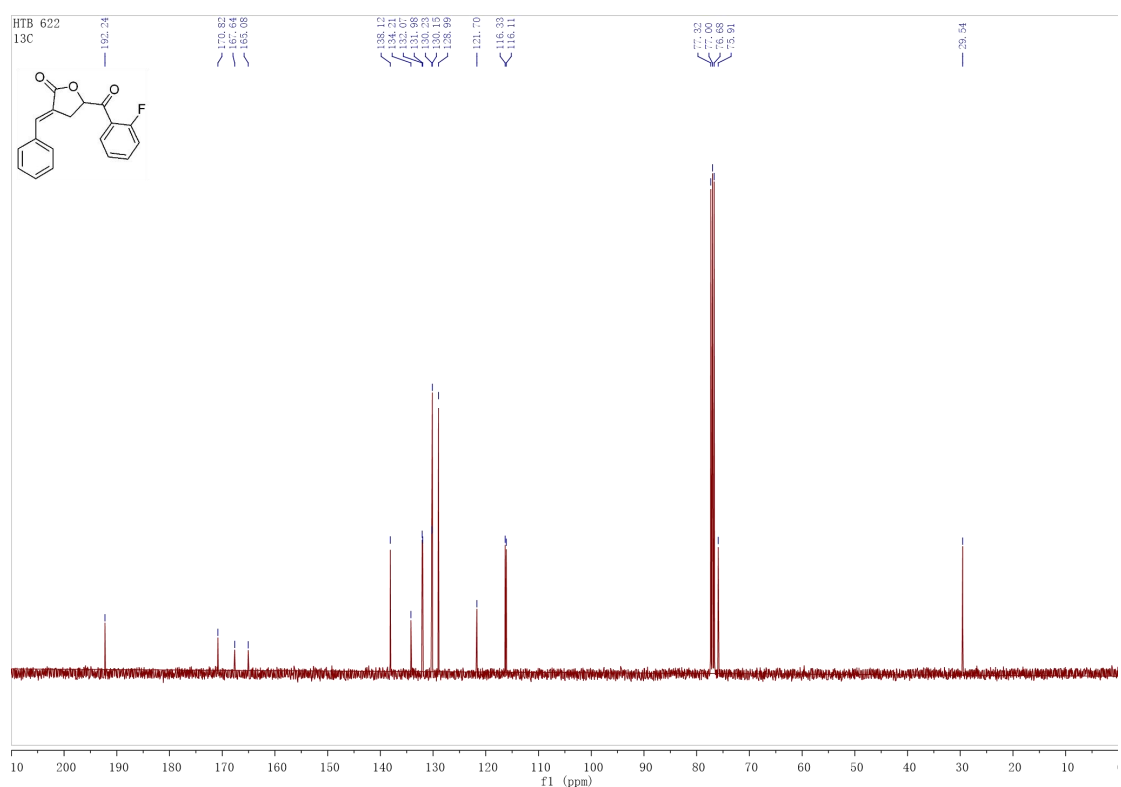
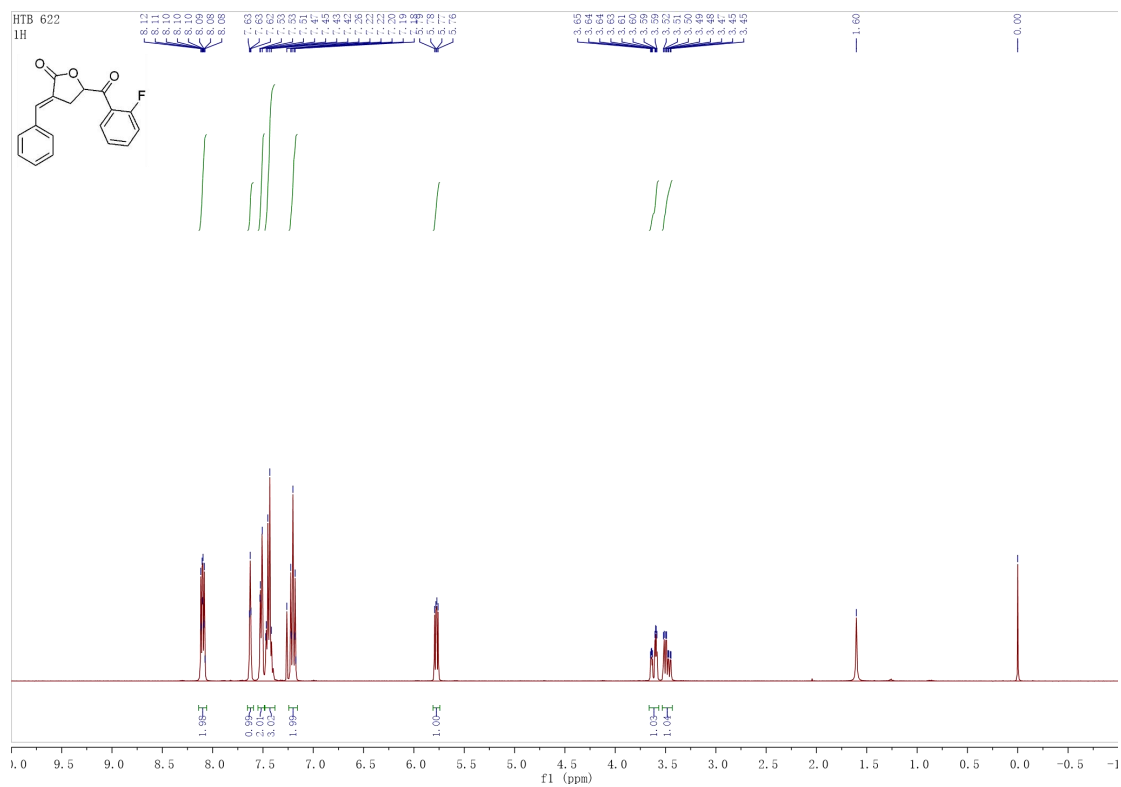


Figure S34-1. The ^1H NMR and ^{13}C NMR Spectrum of **3ag** in CDCl_3 .

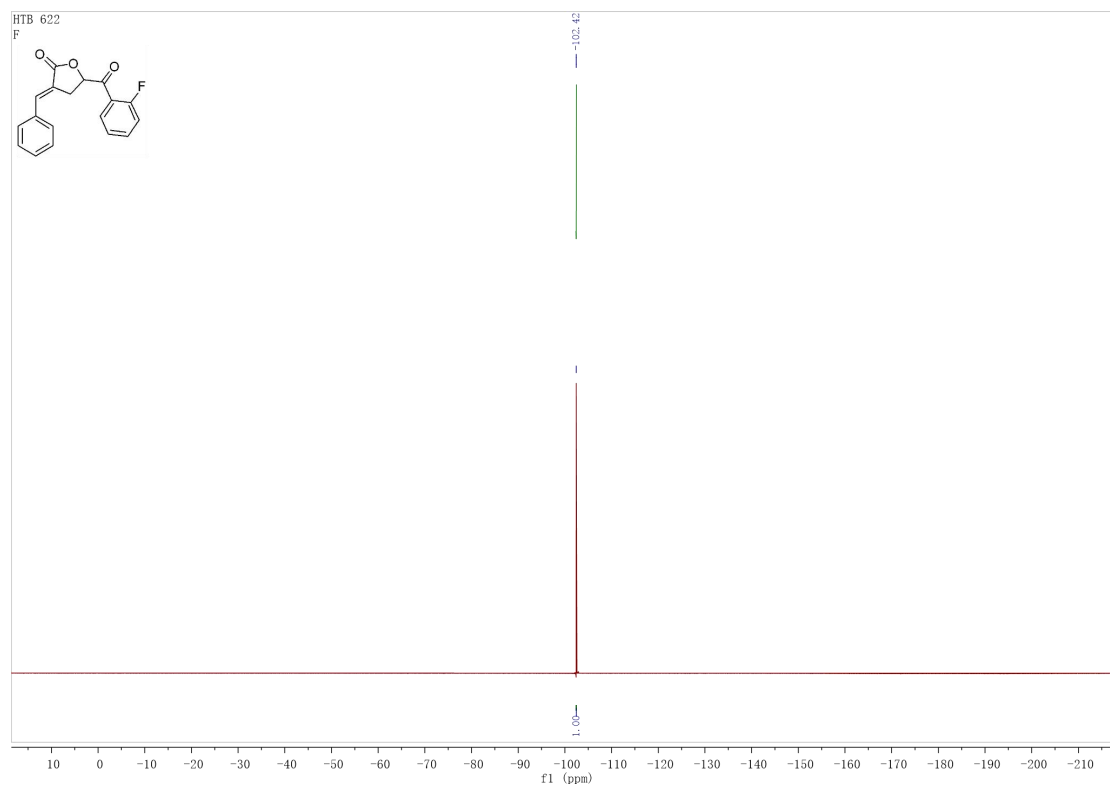


Figure S34-2. The ^{19}F NMR Spectrum of **3ag** in CDCl_3

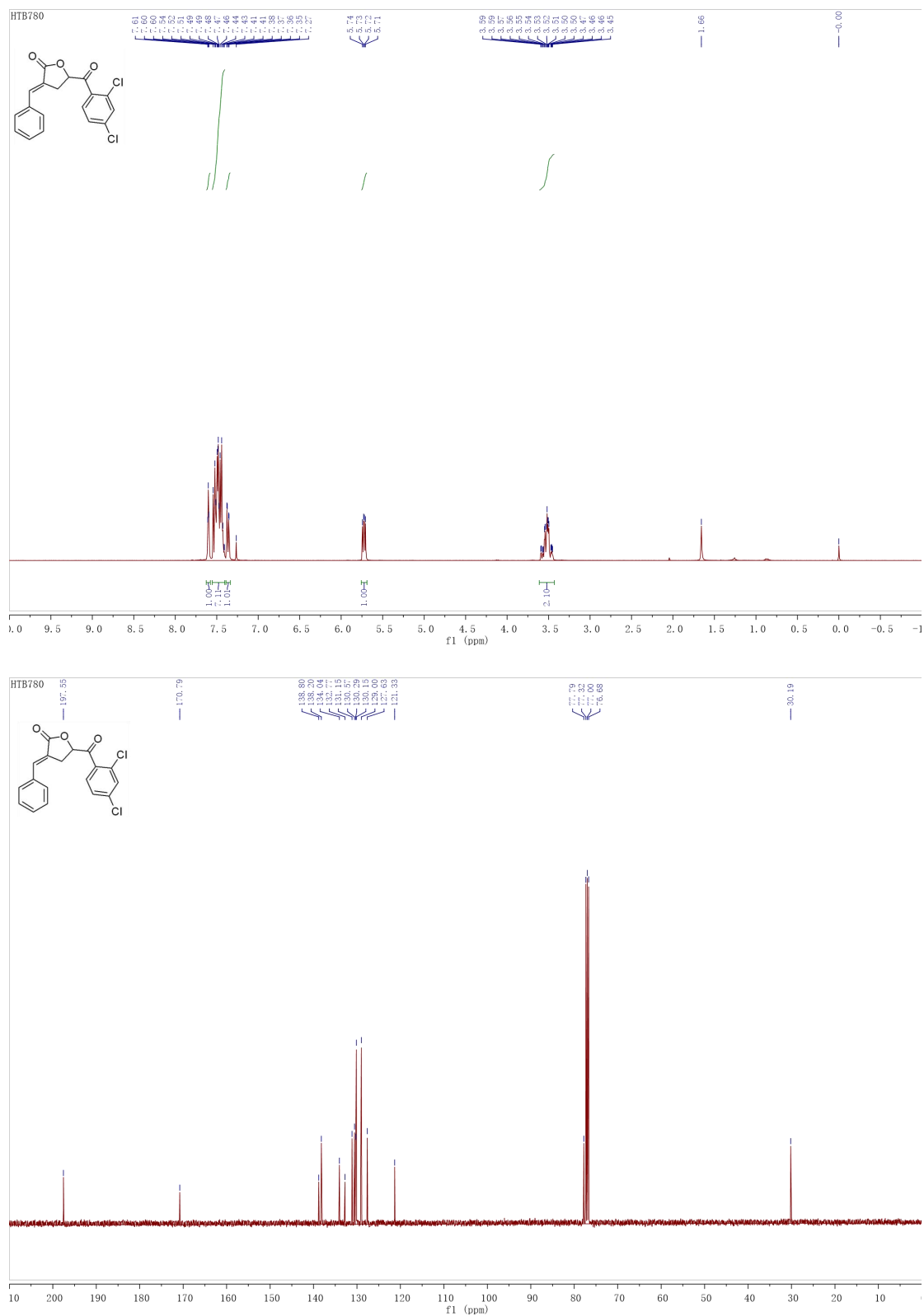


Figure S35. The ^1H NMR and ^{13}C NMR Spectrum of **3ah** in CDCl_3 .

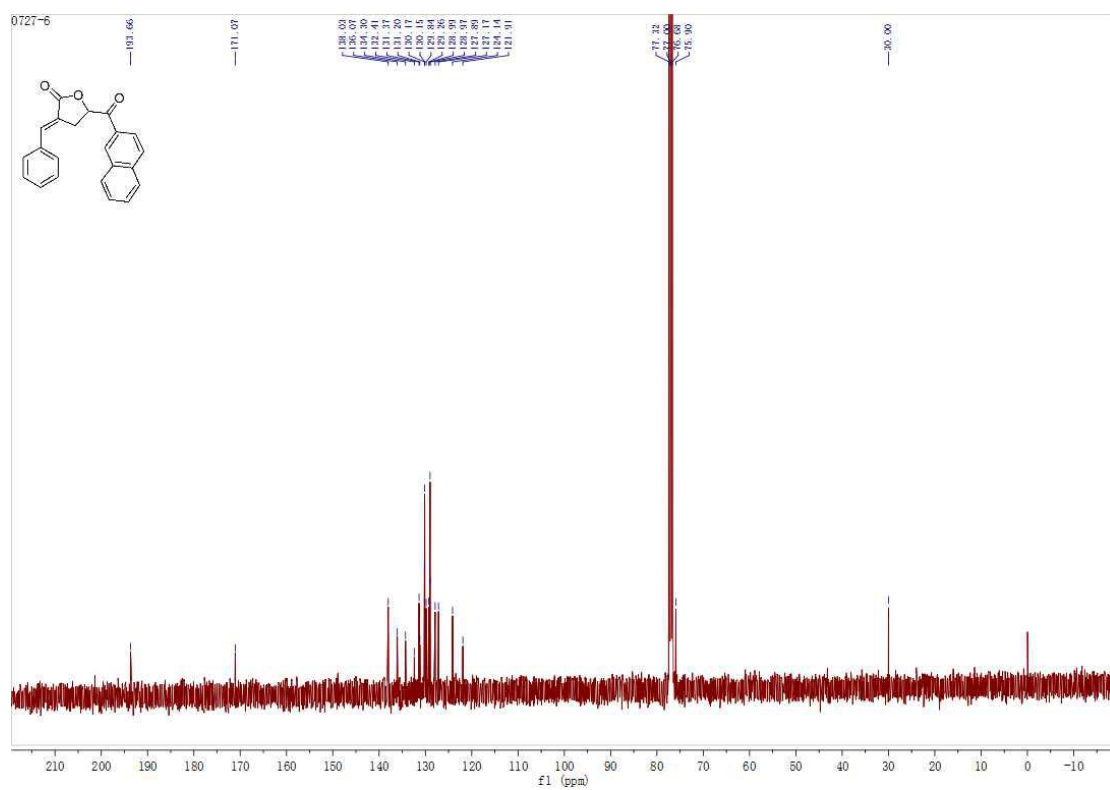
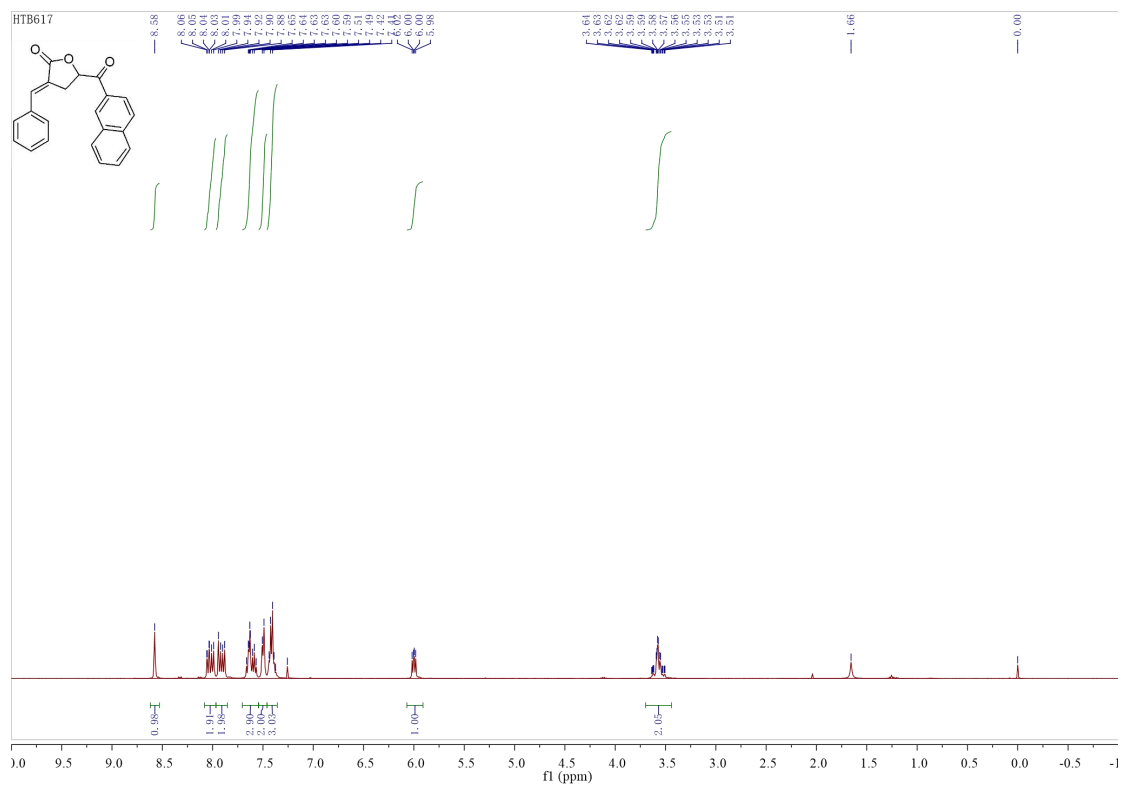


Figure S36. The ^1H NMR and ^{13}C NMR Spectrum of **3ai** in CDCl_3 .

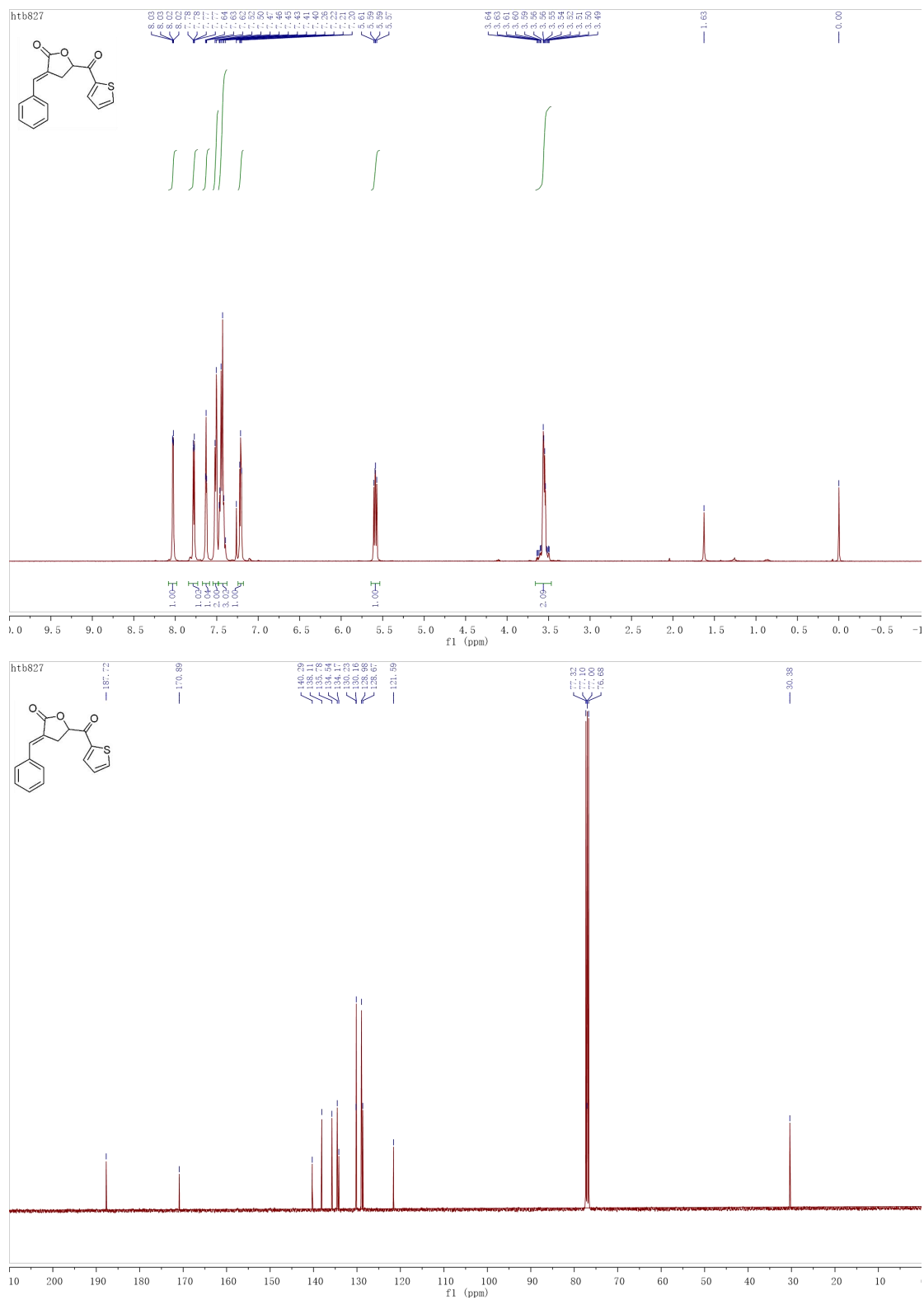


Figure S37. The ¹H NMR and ¹³C NMR Spectrum of **3aj** in CDCl₃.

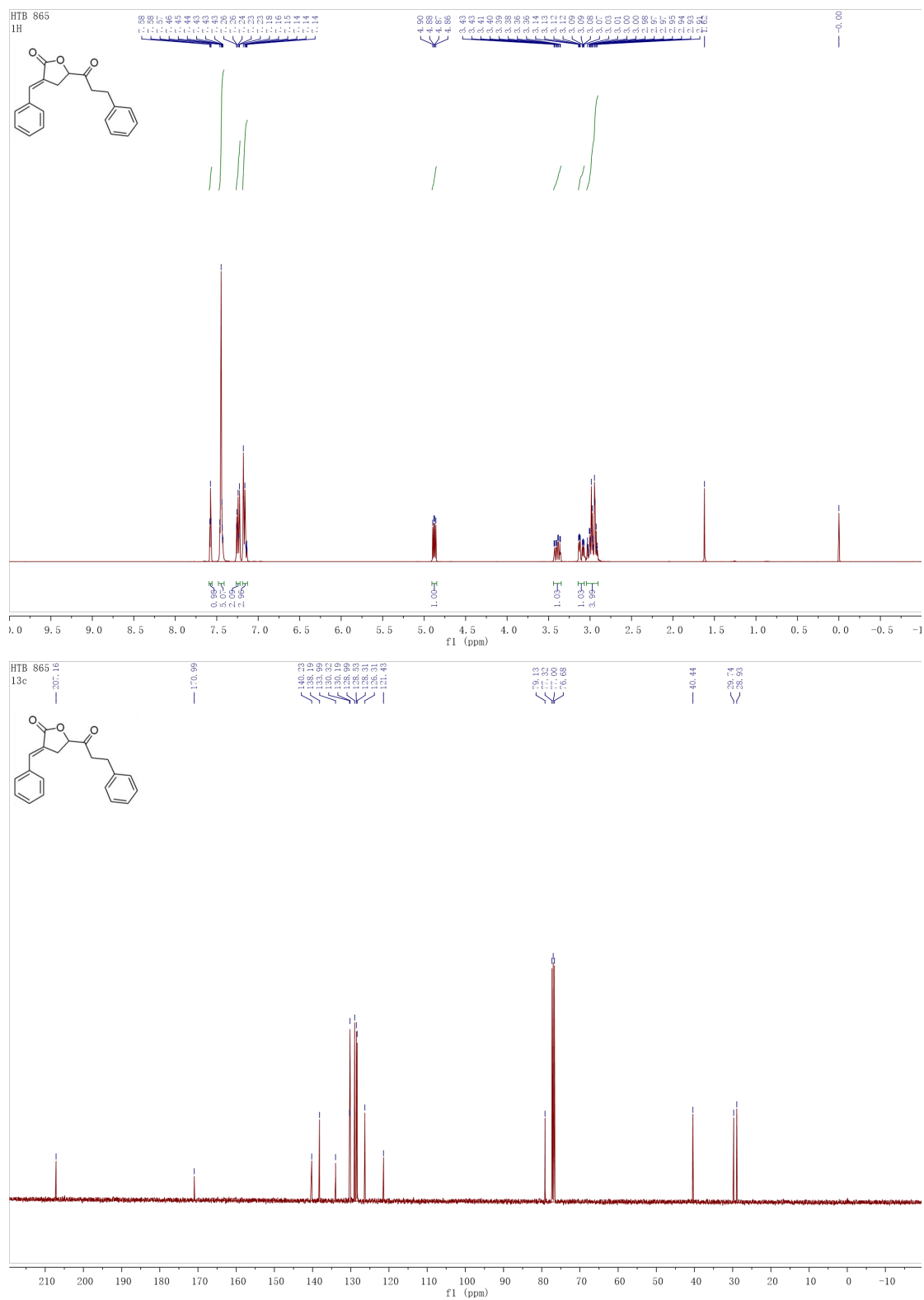
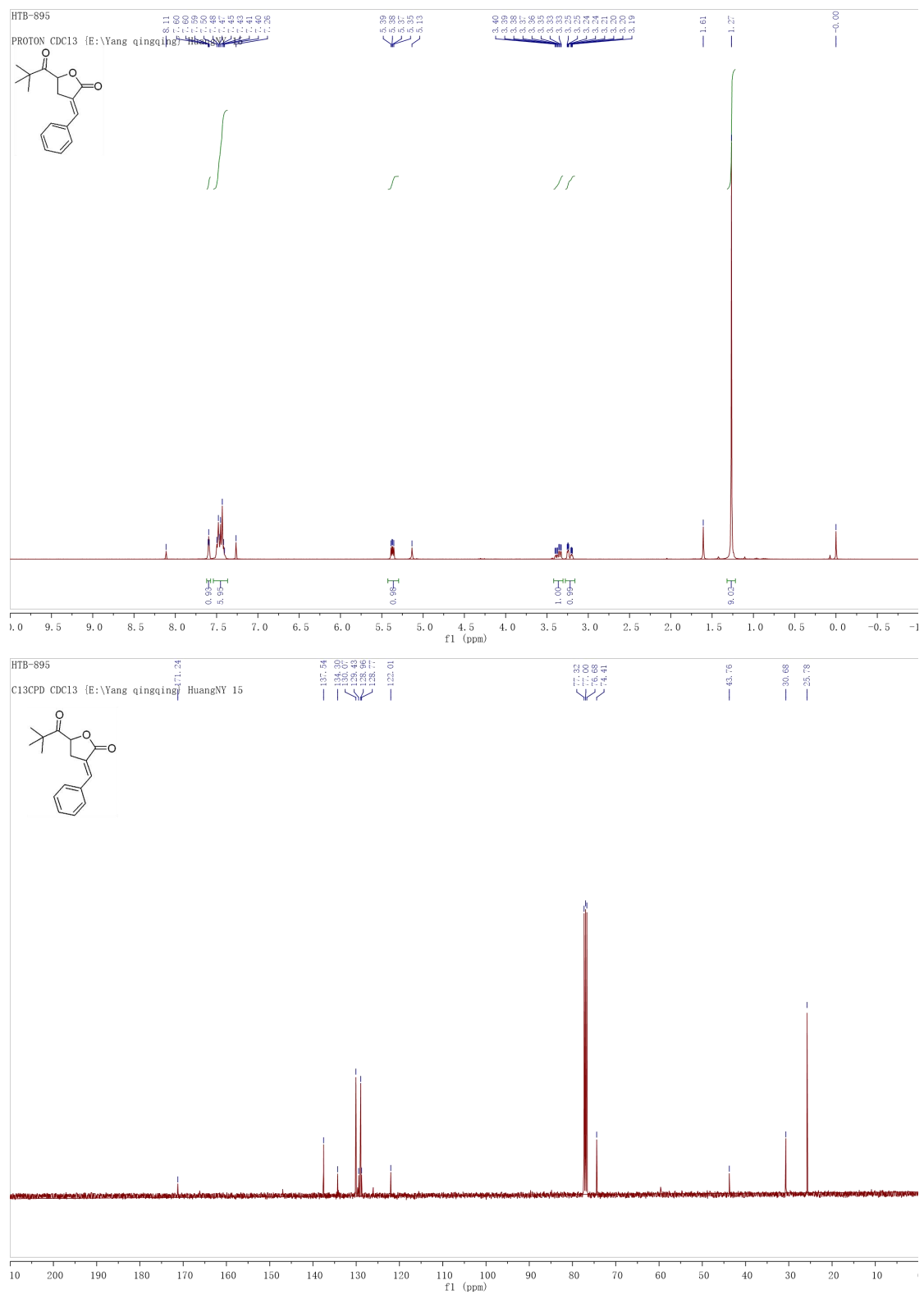


Figure S38. The ^1H NMR and ^{13}C NMR Spectrum of **3ak** in CDCl_3



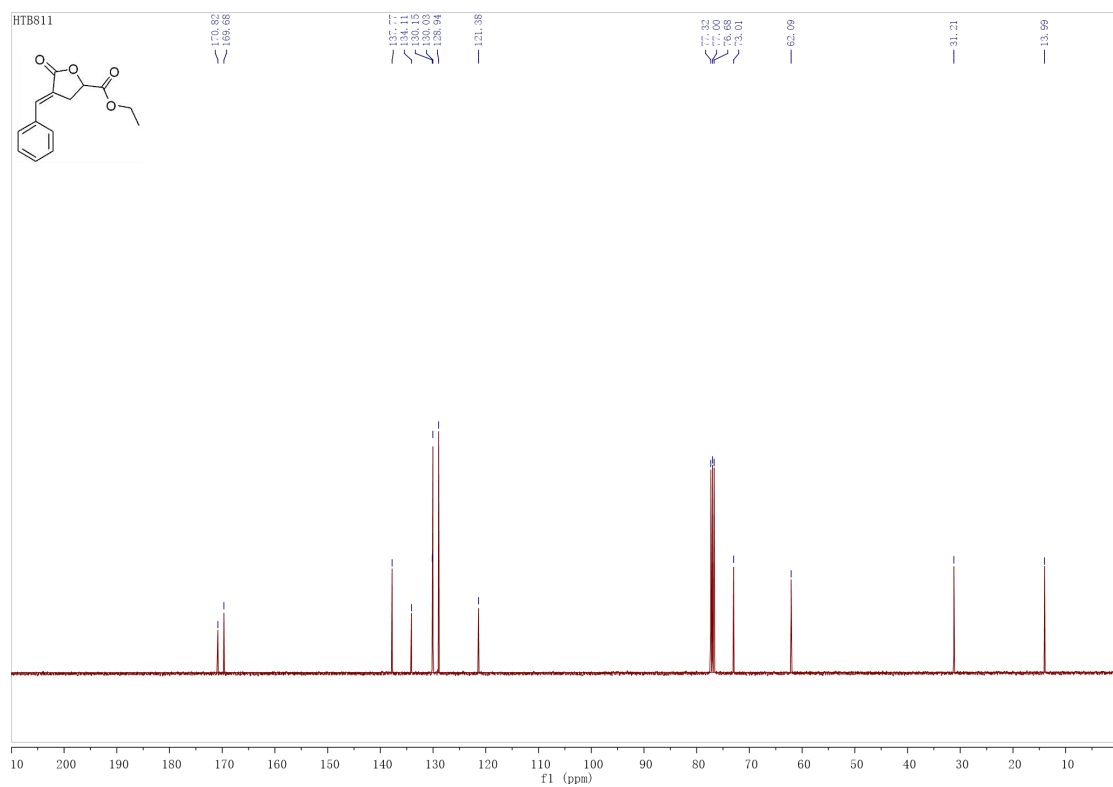
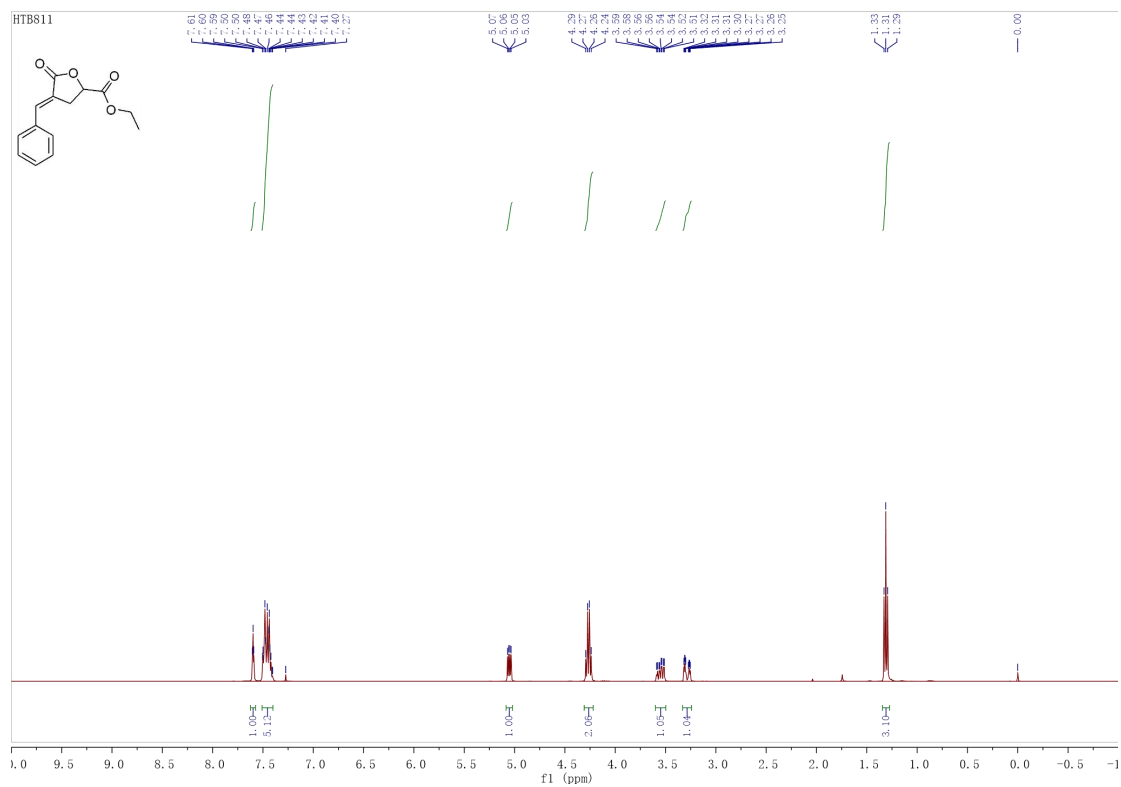


Figure S40. The ^1H NMR and ^{13}C NMR Spectrum of **3am** in CDCl_3

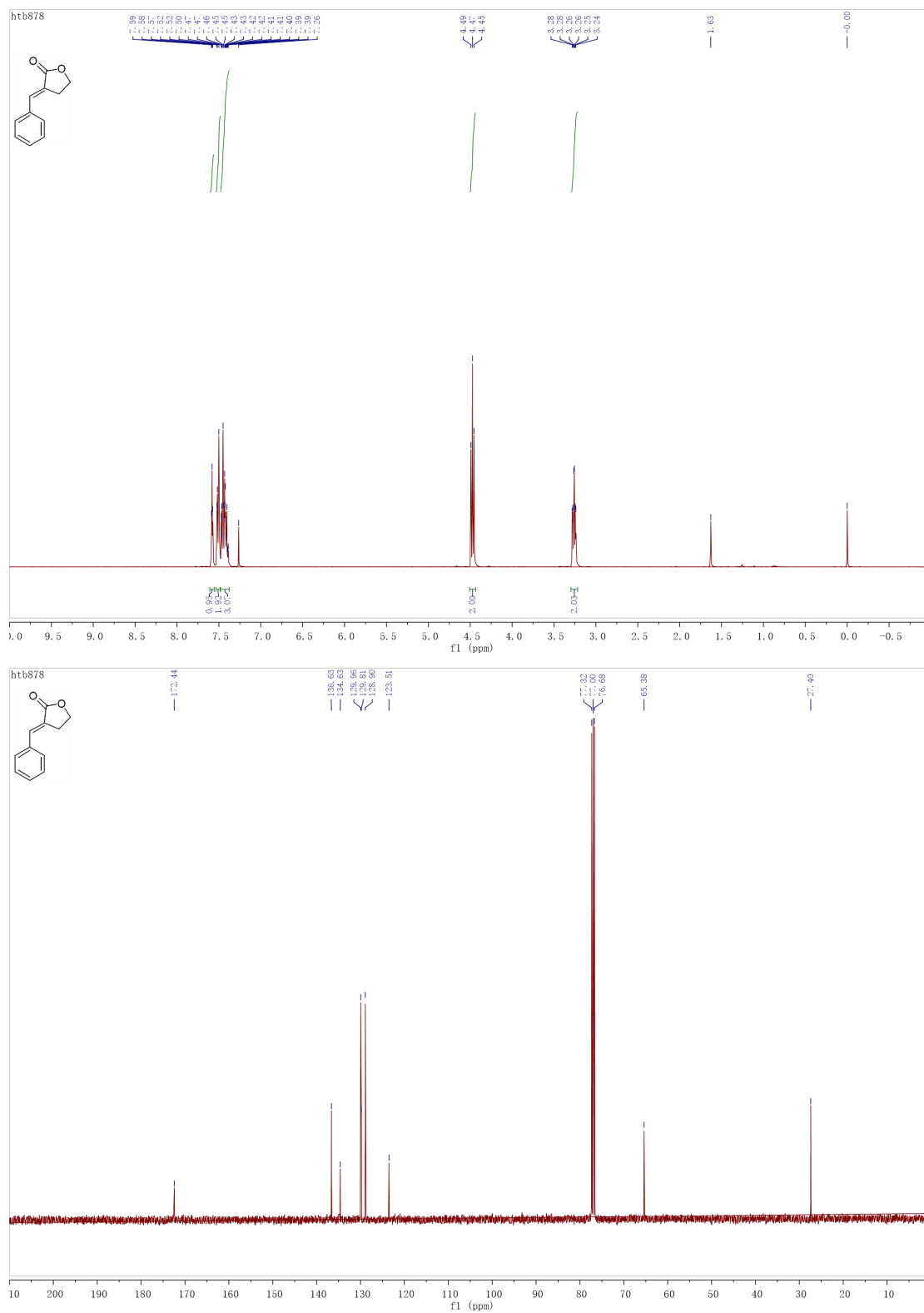


Figure S41. The ^1H NMR and ^{13}C NMR Spectrum of **3an** in CDCl_3 .

9. ^1H NMR and ^{13}C NMR spectra of compounds **5a**.

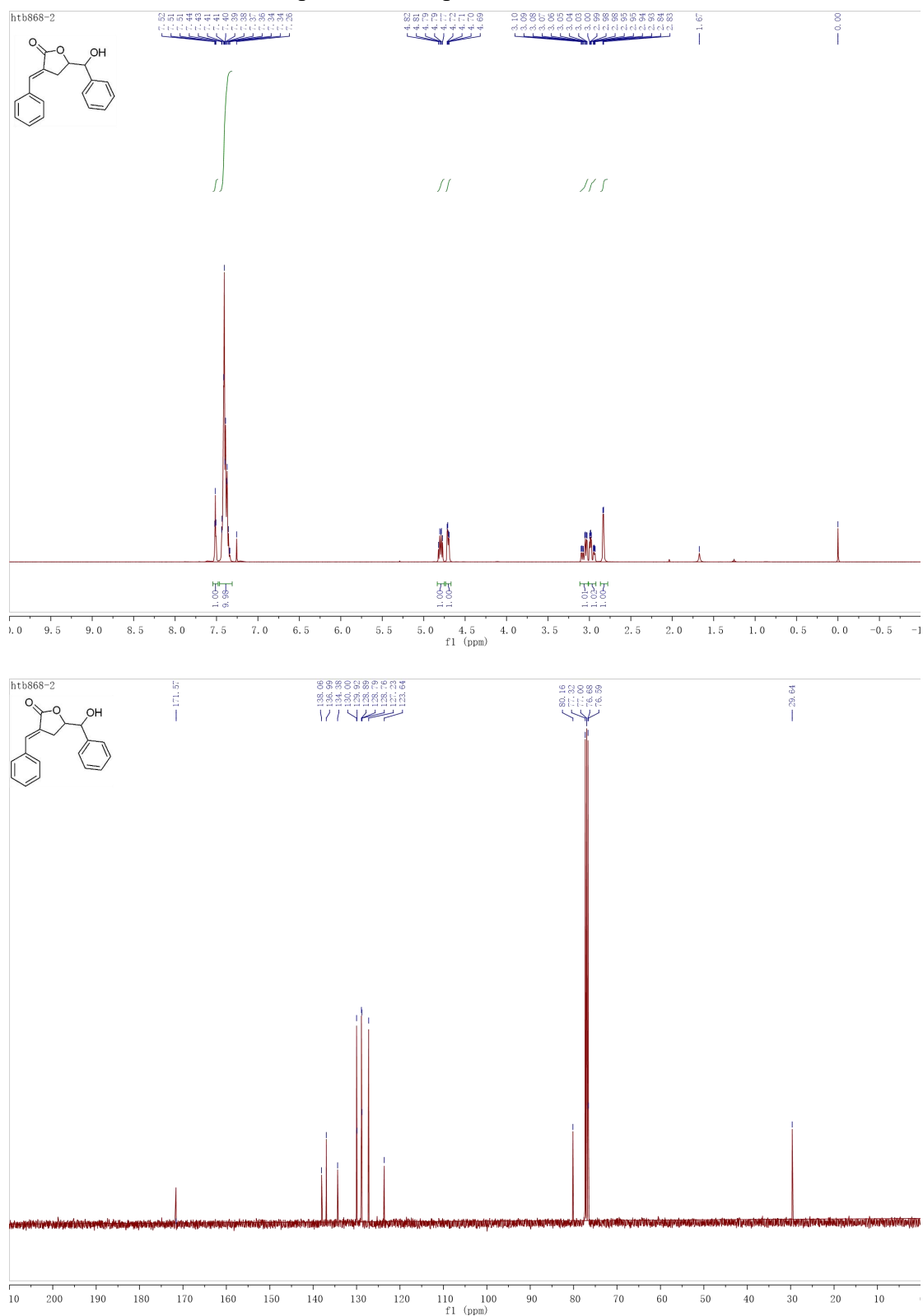


Figure S42. The ^1H NMR and ^{13}C NMR Spectrum of **5a** in CDCl_3 .