Supporting Information

Access to Alkyl Substituted Lactone via Photoredox-Catalyzed Alkylation/Lactonization of Unsaturated Carboxylic Acids

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1. General information

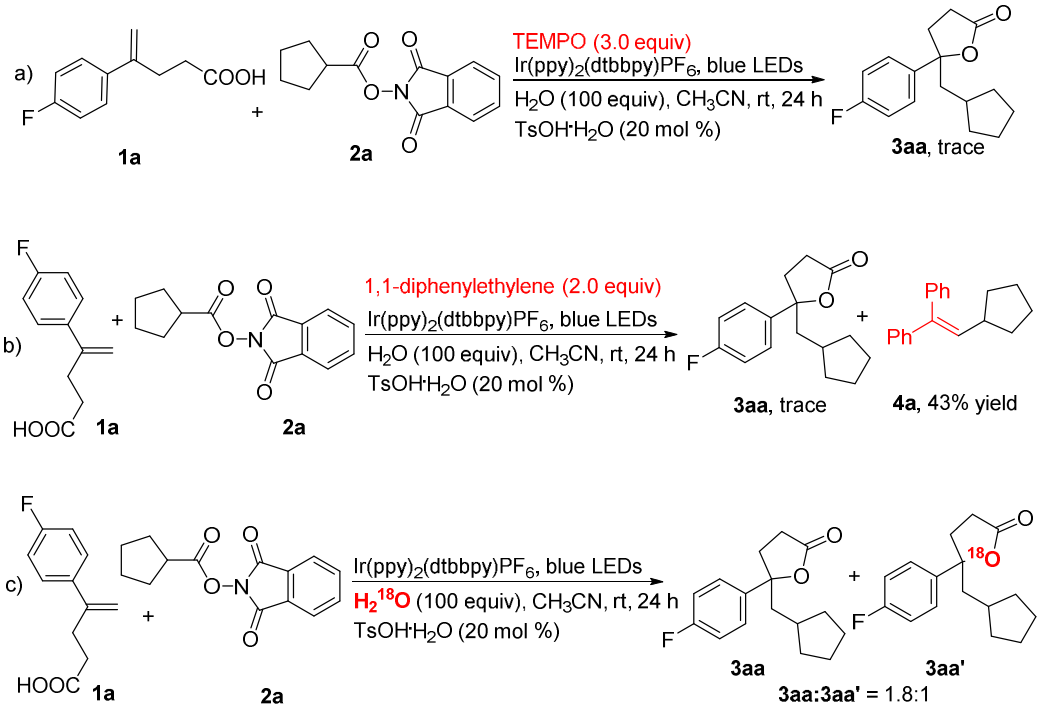
All commercial reagents were used without additional purification unless otherwise specified. The reactions were conducted under an atmosphere of argon and were monitored by TLC unless otherwise noted. Solvents were dried and distilled prior to use. Flash chromatography was performed using silica gel 60 (300–400 mesh). ^{1}H, ^{19}F, ^{13}C and ^{31}P NMR were recorded on a Bruker AVANCE400M spectrometer. Melting points were uncorrected. Infrared spectra were obtained on a Agilent Cary 630 instrument on a diamond plate by way of technology Attenuated Total Reflection (ATR). HRMS were conducted on an Agilent 6540Q-TOF LC/MS equipped with an electrospray ionization (ESI) probe operating in positive ion mode.

2. General procedure for the alkylation/lactonization of unsaturated carboxylic acids

An oven-dried reaction vial containing unsaturated carboxylic acids **1** (0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (0.004 mmol, 0.02 equiv.), **2** (0.4 mmol, 2.0 equiv) and $TsOH{\cdot}H_2O$ (0.04 mmol, 0.2 eq.) was evacuated and purged with argon three times. Then CH_3CN (2 mL) as solution and H_2O (20 mmol, 100 eq.) were added via syringe, respectively. Then the reaction mixture was stirred for 24 hours at room temperature in the presence of 5W blue LED lamps. When the reaction was complete, the reaction mixture was purified by flash chromatography (petroleum ether: dichloromethane = 1: 2) directly to furnish the corresponding product **3**.

1 mmol scale reaction: An oven-dried reaction vial containing unsaturated carboxylic acids **1a** (1.0 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (0.02 mmol, 0.02 equiv.), **2a** (2.0 mmol, 2.0 equiv) and $TsOH{\cdot}H_2O$ (0.2 mmol, 0.2 eq.) was evacuated and purged with argon three times. Then CH_3CN (14 mL) as solution and H_2O (100 mmol, 100 eq.) were added via syringe, respectively. Then the reaction mixture was stirred for 32 hours at room temperature in the presence of 5W blue LED lamps. When the reaction was complete, the reaction mixture was purified by flash chromatography (petroleum ether: dichloromethane = 1: 2) directly to furnish the corresponding product **3aa** in 71% yield (186.2 mg).

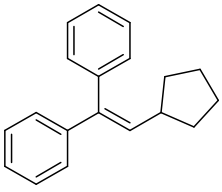
3. Investigation of the mechanism conditions



In condition **a**), a reaction of **1a** and **2a** with the addition of 3 equiv 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as radical-trapping reagent under the standard condition was performed, and the formation of target product **3aa** was suppressed completely detected by TLC.

In condition **b**), the reaction was carried out in the condition of **1a** (0.2 mmol), **2a** (0.4 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (0.004 mmol, 0.02 equiv), $TsOH{\cdot}H_2O$ (0.04 mmol), 1,1-diphenylethylene (0.4 mmol), H_2O (20 mmol) and CH_3CN (2 mL), argon atmosphere, and stirred 24h at room temperature in the presence of 5W blue LED lamps. The formation of target product **3aa** was suppressed. Compound **4a** can be isolated by flash chromatography with 43% yield.

Characterization data of compound **4a:**

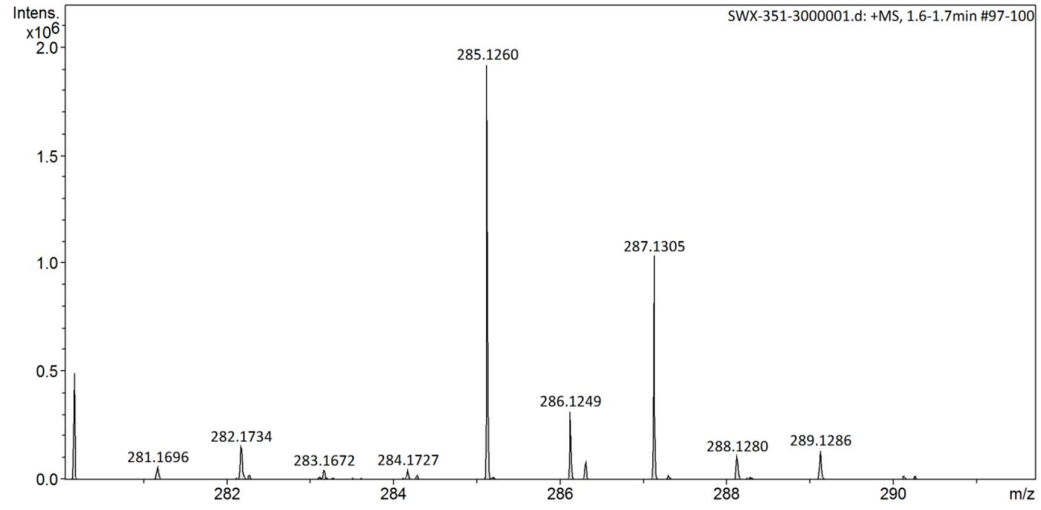


(2-cyclopentylethene-1,1-diyl)dibenzene (**4a**): Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59

– 7.01 (m, 10H), 5.97 (d, J = 10.0 Hz, 1H), 2.63 – 2.32 (m, 1H), 1.84 – 1.73 (m, 2H), 1.73 – 1.62 (m, 2H), 1.57 – 1.45 (m, 2H), 1.45 – 1.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 140.6, 140.0, 135.5, 130.0, 128.1, 128.1, 127.3, 126.8, 126.7, 40.5, 34.3, 25.6. Analytical data for **4a** was consistent with that previously reported.[1]

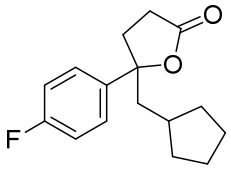
In condition **c**), the reaction was carried out in the condition of **1a** (0.2 mmol), **2a** (0.4 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (0.004 mmol, 0.02 equiv.), $TsOH{\cdot}H_2O$ (0.04 mmol), 1,1-diphenylethylene (0.4 mmol), $H_2{}^{18}O$ (20 mmol) and CH_3CN (2 mL), argon atmosphere, and stirred 24h at room temperature in the presence of 5W blue LED lamps. The formation of target product **3aa** was detected by HRMS (TOF MS ESI): calcd for $C_{16}H_{19}FNaO_2^+$ $[M+Na]^+$ 285.1261, found 285.1260, and **3aa'** was detected by HRMS (TOF MS ESI): calcd for $C_{16}H_{19}FNaO^{18}O^+$ $[M+Na]^+$ 287.1304, found 287.1305.

HRMS for determination of the ratio of **3aa** to **3aa'**



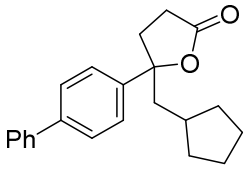
#	m/z	Res.	S/N	I	I %	FWHM	
1	150.1184		9000	107.0	5628	0.3	0.0167
2	159.0669		10712	59.8	3315	0.2	0.0148
3	163.0586		13819	308.1	17444	0.9	0.0118
113	283.6131		16373	26.2	3757	0.2	0.0173
114	283.8497		17327	20.6	2961	0.2	0.0164
115	284.1727		13778	301.4	43384	2.3	0.0206
116	284.2872		14354	123.6	17809	0.9	0.0198
117	285.1260		21605	13288.4	1920900	100.0	0.0132
118	285.1977		11433	67.3	9726	0.5	0.0249
119	285.2966		9603	15.5	2240	0.1	0.0297
120	286.1249		15768	2188.8	318081	16.6	0.0181
121	286.3068		11707	535.4	77800	4.1	0.0245
122	287.1305		19717	7089.1	1033618	53.8	0.0146
123	287.3054		13747	130.5	19025	1.0	0.0209
124	288.1280		12311	719.8	105341	5.5	0.0234

4. Characterization data of products



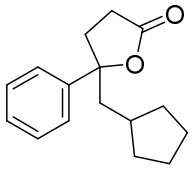
5-(cyclopentylmethyl)-5-(4-fluorophenyl)dihydrofuran-2(3H)-one (3aa)

Yellow liquid, 40.4 mg (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 7.15 – 6.94 (m, 2H), 2.68 – 2.50 (m, 1H), 2.50 – 2.32 (m, 3H), 2.08 (dd, *J* = 14.4, 6.1 Hz, 1H), 1.99 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.84 – 1.69 (m, 1H), 1.59 – 1.29 (m, 6H), 1.10 (ddd, *J* = 17.8, 12.4, 8.7 Hz, 1H), 0.89 (ddt, *J* = 11.5, 8.0, 5.8 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.06 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 162.0 (d, *J* = 246.5 Hz), 139.0 (d, *J* = 3.2 Hz), 126.5 (d, *J* = 8.1 Hz), 115.4 (d, *J* = 21.4 Hz), 89.4, 48.4, 36.0, 36.0, 33.7, 33.7, 28.5, 24.8, 24.8. IR (cm^{-1}): 2946, 1772, 1510, 1185, 1157, 837, 814. HRMS (TOF MS ESI): calcd for $C_{16}H_{19}FNaO_2^+$ $[M+Na]^+$ 285.1261, found 285.1263.



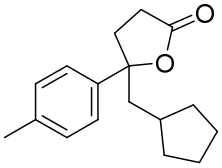
5-([1,1'-biphenyl]-4-yl)-5-(cyclopentylmethyl)dihydrofuran-2(3H)-one (3ba)

Yellow solid, 29.4 mg (46% yield), m.p. 78 - 80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.53 (m, 4H), 7.42 (tt, *J* = 8.6, 1.9 Hz, 4H), 7.38 – 7.31 (m, 1H), 2.66 – 2.52 (m, 1H), 2.52 – 2.35 (m, 3H), 2.15 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.02 (dd, *J* = 14.4, 7.0 Hz, 1H), 1.89 – 1.75 (m, 1H), 1.68 (td, *J* = 9.1, 2.5 Hz, 1H), 1.58 – 1.45 (m, 3H), 1.45 – 1.30 (m, 2H), 1.14 (ddd, *J* = 17.9, 12.3, 8.4 Hz, 1H), 1.02 – 0.84 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 142.2, 140.4, 140.3, 128.8, 127.5, 127.1, 127.0, 125.2, 89.8, 48.4, 36.2, 36.0, 33.8, 33.8, 28.6, 24.9, 24.8. IR (cm^{-1}): 2916, 2850, 1765, 1183, 833, 762, 693. HRMS (TOF MS ESI): calcd for $C_{22}H_{24}NaO_2^+$ $[M+Na]^+$ 343.1669, found 343.1670.



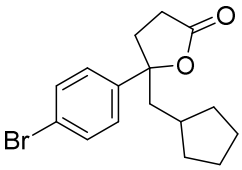
5-(cyclopentylmethyl)-5-phenyldihydrofuran-2(3H)-one (3ca)

Colorless liquid, 37.8 mg (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.11 (m, 5H), 2.56 – 2.41 (m, 1H), 2.41 – 2.24 (m, 3H), 2.04 (dd, *J* = 14.4, 6.0 Hz, 1H), 1.92 (dd, *J* = 14.4, 6.9 Hz, 1H), 1.76 – 1.63 (m, 1H), 1.60 – 1.21 (m, 6H), 1.04 (dq, *J* = 12.5, 8.7 Hz, 1H), 0.83 (tt, *J* = 8.8, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 143.2, 128.5, 127.5, 124.7, 89.8, 48.4, 36.1, 36.0, 33.8, 33.7, 28.6, 24.9, 24.8. IR (cm^{-1}): 2945, 1770, 1191, 928, 766, 703. HRMS (TOF MS ESI): calcd for $C_{16}H_{20}NaO_2^+$ $[M+ Na]^+$ 267.1356, found 267.1354.



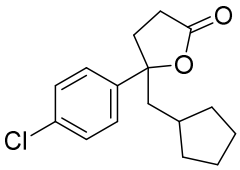
5-(cyclopentylmethyl)-5-(p-tolyl)dihydrofuran-2(3H)-one (3da)

Colorless liquid, 36.3 mg (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 2.60 – 2.46 (m, 1H), 2.46 – 2.36 (m, 3H), 2.35 (s, 3H), 2.10 (dd, *J* = 14.4, 5.9 Hz, 1H), 1.97 (dd, *J* = 14.4, 7.0 Hz, 1H), 1.84 – 1.70 (m, 1H), 1.66 – 1.28 (m, 6H), 1.11 (ddd, *J* = 17.9, 12.4, 8.6 Hz, 1H), 0.99 – 0.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 140.2, 137.1, 129.1, 124.7, 89.9, 48.4, 36.1, 36.1, 33.7, 33.7, 28.6, 24.9, 24.8, 21.0. IR (cm^{-1}): 2945, 1772, 1180, 928, 818. HRMS (TOF MS ESI): calcd for $C_{17}H_{22}NaO_2^+$ $[M+ Na]^+$ 281.1512, found 281.1513.



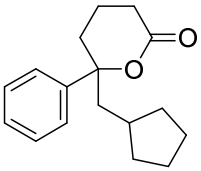
5-(4-bromophenyl)-5-(cyclopentylmethyl)dihydrofuran-2(3H)-one (3ea)

Pale yellow liquid, 44.4 mg (69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.35 (m, 2H), 7.19 – 7.10 (m, 2H), 2.58 – 2.42 (m, 1H), 2.42 – 2.24 (m, 3H), 2.01 (dd, *J* = 14.5, 6.0 Hz, 1H), 1.91 (dd, *J* = 14.5, 7.0 Hz, 1H), 1.75 – 1.64 (m, 1H), 1.57 – 1.22 (m, 6H), 1.03 (ddd, *J* = 17.9, 12.4, 8.6 Hz, 1H), 0.92 – 0.74 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 142.4, 131.6, 126.6, 121.5, 89.3, 48.2, 36.0, 36.0, 33.7, 28.4, 24.9, 24.8. IR (cm^{-1}): 2946, 1772, 1191, 1008, 826, 727. HRMS (TOF MS ESI): calcd for $C_{16}H_{19}BrNaO_2^+$ $[M+ Na]^+$ 345.0461, found 345.0459.



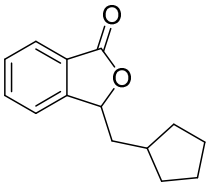
5-(4-chlorophenyl)-5-(cyclopentylmethyl)dihydrofuran-2(3H)-one (3fa)

Colorless liquid, 45.1 mg (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.24 – 7.16 (m, 2H), 2.58 – 2.41 (m, 1H), 2.41 – 2.23 (m, 3H), 2.09 – 1.95 (m, 1H), 1.91 (dd, *J* = 14.5, 6.9 Hz, 1H), 1.77 – 1.62 (m, 1H), 1.57 – 1.22 (m, 6H), 1.03 (ddd, *J* = 17.8, 12.4, 8.6 Hz, 1H), 0.82 (tt, *J* = 8.5, 6.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 141.8, 133.4, 128.7, 126.2, 89.3, 48.2, 36.0, 36.0, 33.7, 33.7, 28.5, 24.9, 24.8. IR (cm^{-1}): 2946, 1772, 1491, 1189, 928, 829. HRMS (TOF MS ESI): calcd for $C_{16}H_{19}ClNaO_2^+$ $[M+ Na]^+$ 301.0966, found 301.0966.



6-(cyclopentylmethyl)-6-phenyltetrahydro-2H-pyran-2-one (3ga)

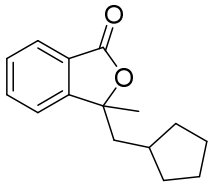
Colorless liquid, 24.1 mg (47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.19 (m, 5H), 2.56 – 2.33 (m, 2H), 2.28 (dt, *J* = 14.1, 4.2 Hz, 1H), 2.11 – 1.92 (m, 3H), 1.87 – 1.69 (m, 3H), 1.61 – 1.45 (m, 3H), 1.45 – 1.28 (m, 3H), 1.19 – 1.00 (m, 1H), 0.96 – 0.75 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 143.6, 128.6, 127.2, 125.1, 88.0, 49.9, 35.4, 34.2, 33.8, 33.6, 29.2, 24.9, 24.8, 16.3. IR (cm^{-1}): 2946, 2866, 1730, 1236, 1034, 762, 701. HRMS (TOF MS ESI): calcd for $C_{17}H_{22}NaO_2^+$ $[M+ Na]^+$ 281.1512, found 281.1513.



3-(cyclopentylmethyl)isobenzofuran-1(3H)-one (3ha)

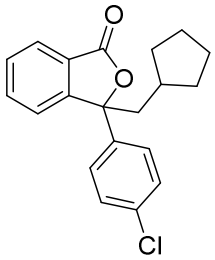
Yellow liquid, 23.7 mg (55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.67 (td, *J* = 7.5, 1.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 7.7, 0.7 Hz, 1H), 5.49 (dd, *J* = 8.9, 3.8 Hz, 1H), 2.24 – 2.05 (m, 1H), 2.03 – 1.87 (m, 2H), 1.87 – 1.73 (m, 2H), 1.68 – 1.46 (m, 4H), 1.33 – 1.05 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 150.5, 133.9, 129.0, 126.0, 125.7,

121.8, 81.2, 41.2, 36.7, 33.2, 32.6, 25.1, 25.0. IR (cm^{-1}): 2946, 1754, 1286, 1060, 742, 695. HRMS (TOF MS ESI): calcd for $C_{14}H_{16}NaO_2^+$ $[M+ Na]^+$ 239.1043, found 239.1044.



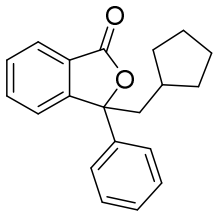
3-(cyclopentylmethyl)-3-methylisobenzofuran-1(3H)-one (3ia)

Yellow oil, 15.0 mg (33% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.80 (m, 1H), 7.65 (td, *J* = 7.5, 1.1 Hz, 1H), 7.50 (td, *J* = 7.5, 0.9 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 2.19 (dd, *J* = 14.6, 6.3 Hz, 1H), 1.94 (dd, *J* = 14.6, 6.7 Hz, 1H), 1.76 – 1.66 (m, 1H), 1.64 (s, 3H), 1.57 – 1.41 (m, 3H), 1.40 – 1.28 (m, 3H), 1.14 (ddd, *J* = 18.0, 12.3, 9.0 Hz, 1H), 0.95 – 0.81 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 154.2, 133.9, 128.8, 126.1, 125.7, 121.1, 88.0, 45.8, 35.7, 33.8, 33.7, 27.0, 25.0, 24.9. IR (cm^{-1}): 2920, 1757, 1286, 1031, 764, 695. HRMS (TOF MS ESI): calcd for $C_{15}H_{18}NaO_2^+$ $[M+ Na]^+$ 253.1199, found 253.1198.



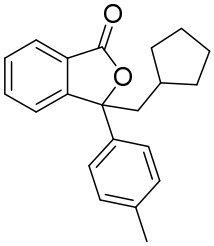
3-(4-chlorophenyl)-3-(cyclopentylmethyl)isobenzofuran-1(3H)-one (3ja)

Colorless oil, 54.9 mg (84% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.58 – 7.42 (m, 4H), 7.36 – 7.29 (m, 2H), 2.57 (dd, *J* = 14.6, 5.7 Hz, 1H), 2.24 (dd, *J* = 14.6, 6.5 Hz, 1H), 1.67 – 1.23 (m, 7H), 1.20 – 1.06 (m, 1H), 1.06 – 0.91 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 152.9, 139.8, 134.3, 134.0, 129.3, 128.8, 126.4, 126.0, 125.4, 122.2, 89.8, 46.3, 36.0, 33.8, 33.7, 24.9, 24.8. IR (cm^{-1}): 2946, 1757, 1493, 1286, 1094, 829, 758. HRMS (TOF MS ESI): calcd for $C_{20}H_{19}ClNaO_2^+$ $[M+ Na]^+$ 349.0966, found 349.0965.



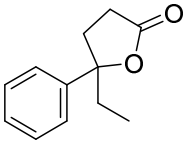
3-(cyclopentylmethyl)-3-phenylisobenzofuran-1(3H)-one (3ka)

Pale yellow oil, 45.5 mg (78% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.64 (td, *J* = 7.7, 1.1 Hz, 1H), 7.54 (dt, *J* = 8.6, 5.4 Hz, 3H), 7.49 (td, *J* = 7.6, 0.9 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.31 – 7.22 (m, 1H), 2.61 (dd, *J* = 14.7, 5.6 Hz, 1H), 2.27 (dd, *J* = 14.7, 6.4 Hz, 1H), 1.70 – 1.57 (m, 2H), 1.57 – 1.22 (m, 5H), 1.22 – 1.06 (m, 1H), 1.05 – 0.89 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 153.4, 141.2, 134.1, 129.1, 128.7, 128.0, 125.8, 125.5, 124.8, 122.4, 90.4, 46.4, 36.0, 33.8, 33.7, 24.9, 24.8. IR (cm^{-1}): 2946, 1754, 1286, 1072, 751, 691. HRMS (TOF MS ESI): calcd for $C_{20}H_{20}NaO_2^+$ $[M+ Na]^+$ 315.1356, found 315.1355.



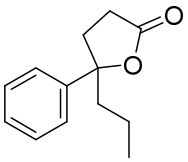
3-(cyclopentylmethyl)-3-(p-tolyl)isobenzofuran-1(3H)-one (3la)

Colorless oil, 50.5 mg (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.55 (td, *J* = 7.7, 1.0 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.51 (dd, *J* = 14.6, 5.6 Hz, 1H), 2.23 (s, 3H), 2.17 (dd, *J* = 14.6, 6.5 Hz, 1H), 1.61 – 1.13 (m, 7H), 1.12 – 0.98 (m, 1H), 0.98 – 0.83 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 153.6, 138.2, 137.8, 134.1, 129.4, 129.0, 125.8, 125.5, 124.8, 122.4, 90.4, 46.3, 36.0, 33.9, 33.7, 24.9, 24.8, 21.0. IR (cm^{-1}): 2946, 1756, 1465, 1286, 1074, 982, 818, 721, 691. HRMS (TOF MS ESI): calcd for $C_{21}H_{22}NaO_2^+$ $[M+ Na]^+$ 329.1512, found 329.1510.



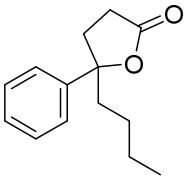
5-ethyl-5-phenyldihydrofuran-2(3H)-one (3cb)

Yellow liquid, 21.3 mg (56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 5H), 2.67 – 2.34 (m, 4H), 2.00 (q, *J* = 7.4 Hz, 2H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 142.7, 128.5, 127.5, 124.8, 89.9, 35.3, 34.6, 28.8, 8.3. Analytical data for **3cb** was consistent with that previously reported.[2]



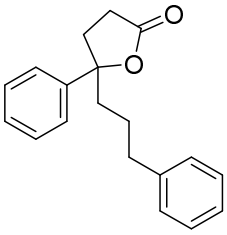
5-phenyl-5-propyldihydrofuran-2(3H)-one (3cc)

Colorless liquid, 29.7 mg (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.17 (m, 5H), 2.69 – 2.51 (m, 1H), 2.51 – 2.35 (m, 3H), 2.04 – 1.81 (m, 2H), 1.48 – 1.28 (m, 1H), 1.20 – 1.00 (m, 1H), 0.84 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 143.0, 128.5, 127.5, 124.6, 89.6, 44.7, 35.1, 28.7, 17.2, 14.1. IR (cm^{-1}): 2960, 1770, 1448, 1191, 762, 701. HRMS (TOF MS ESI): calcd for $C_{13}H_{16}NaO_2^+$ $[M+ Na]^+$ 227.1043, found 227.1044.



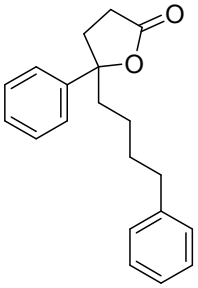
5-butyl-5-phenyldihydrofuran-2(3H)-one (3cd)

Pale yellow oil, 25.5 mg (58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.24 (m, 5H), 2.65 – 2.51 (m, 1H), 2.51 – 2.36 (m, 3H), 2.05 – 1.84 (m, 2H), 1.40 – 1.13 (m, 3H), 1.05 (qdd, J = 16.8, 12.2, 7.6 Hz, 1H), 0.82 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 143.1, 128.5, 127.5, 124.6, 89.6, 42.2, 35.1, 28.7, 25.9, 22.7, 13.9. IR (cm^{-1}): 2935, 1770, 1191, 928, 766, 700. HRMS (TOF MS ESI): calcd for $C_{14}H_{18}NaO_2^+$ $[M+ Na]^+$ 241.1199, found 241.1198.



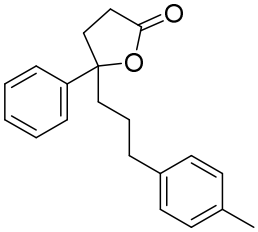
5-phenyl-5-(3-phenylpropyl)dihydrofuran-2(3H)-one (3ce)

Yellow oil, 28.1 mg (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.20 (m, 7H), 7.20 – 7.11 (m, 1H), 7.11 – 7.00 (m, 2H), 2.70 – 2.29 (m, 6H), 2.10 – 1.86 (m, 2H), 1.78 – 1.64 (m, 1H), 1.48 – 1.33 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 142.8, 141.6, 128.6, 128.4, 128.3, 127.6, 125.9, 124.6, 89.4, 41.8, 35.6, 35.3, 28.6, 25.5. IR (cm^{-1}): 2943, 1770, 1191, 934, 749, 699. HRMS (TOF MS ESI): calcd for $C_{19}H_{20}NaO_2^+$ $[M+ Na]^+$ 303.1356, found 303.1355.



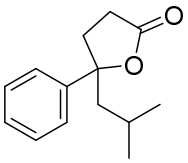
5-phenyl-5-(4-phenylbutyl)dihydrofuran-2(3H)-one (3cf)

Yellow oil, 39.4 mg (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 7.23 (dd, *J* = 9.6, 5.0 Hz, 2H), 7.17 – 7.11 (m, 1H), 7.11 – 7.03 (m, 2H), 2.77 – 2.27 (m, 6H), 2.11 – 1.84 (m, 2H), 1.63 – 1.47 (m, 2H), 1.46 – 1.33 (m, 1H), 1.20 – 1.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 142.9, 142.3, 128.6, 128.3, 127.6, 125.7, 124.7, 89.5, 42.3, 35.7, 35.1, 31.5, 28.7, 23.6. IR (cm^{-1}): 2937, 1770, 1180, 922, 747, 699. HRMS (TOF MS ESI): calcd for $C_{20}H_{22}NaO_2^+$ $[M+ Na]^+$ 317.1512, found 317.1511.



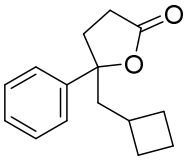
5-phenyl-5-(3-(p-tolyl)propyl)dihydrofuran-2(3H)-one (3cg)

Yellow liquid, 37.2 mg (63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 2.62 – 2.35 (m, 6H), 2.29 (s, 3H), 2.05 – 1.88 (m, 2H), 1.75 – 1.58 (m, 1H), 1.46 – 1.29 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 142.8, 138.5, 135.3, 129.0, 128.6, 128.2, 127.6, 124.6, 89.4, 41.9, 35.2, 35.2, 28.6, 25.6, 21.0. IR (cm^{-1}): 2922, 1772, 1156, 1151, 764, 703. HRMS (TOF MS ESI): calcd for $C_{20}H_{22}NaO_2^+$ $[M+ Na]^+$ 317.1512, found 317.1514.



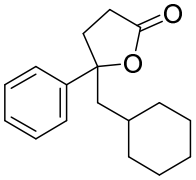
5-isobutyl-5-phenyldihydrofuran-2(3H)-one (3ch)

Yellow oil, 27.4 mg (63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.10 (m, 5H), 2.66 – 2.27 (m, 4H), 2.00 (dd, *J* = 14.6, 5.0 Hz, 1H), 1.83 (dd, *J* = 14.6, 7.4 Hz, 1H), 1.49 (dqd, *J* = 13.5, 6.7, 5.1 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.72 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 142.9, 128.5, 127.5, 124.7, 89.8, 50.8, 36.8, 28.3, 24.5, 24.1, 23.5. IR (cm^{-1}): 2954, 1772, 1191, 1122, 919, 768, 703. HRMS (TOF MS ESI): calcd for $C_{14}H_{18}NaO_2^+$ $[M+ Na]^+$ 241.1199, found 241.1199.



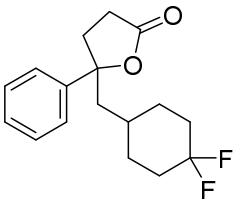
5-(cyclobutylmethyl)-5-phenyldihydrofuran-2(3H)-one (3ci)

Pale yellow oil, 30.2 mg (66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.11 (m, 5H), 2.58 – 2.41 (m, 1H), 2.41 – 2.27 (m, 3H), 2.27 – 2.12 (m, 1H), 2.08 – 1.94 (m, 2H), 1.93 – 1.82 (m, 1H), 1.70 – 1.53 (m, 4H), 1.43 – 1.30 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 143.0, 128.4, 127.5, 124.7, 89.6, 49.3, 35.0, 31.9, 29.6, 29.3, 28.6, 19.1. IR (cm^{-1}): 2932, 1770, 1189, 930, 766, 701. HRMS (TOF MS ESI): calcd for $C_{15}H_{18}NaO_2^+$ $[M+ Na]^+$ 253.1199, found 253.1198.



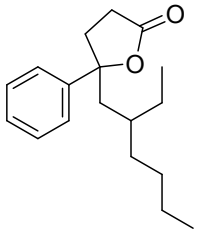
5-(cyclohexylmethyl)-5-phenyldihydrofuran-2(3H)-one (3cj)

Colorless oil, 36.4 mg (71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.15 (m, 5H), 2.61 – 2.46 (m, 1H), 2.46 – 2.30 (m, 3H), 1.95 (dd, *J* = 14.7, 5.0 Hz, 1H), 1.88 – 1.72 (m, 2H), 1.64 – 1.43 (m, 3H), 1.32 (t, *J* = 11.0 Hz, 1H), 1.20 (dddd, *J* = 10.8, 7.1, 5.6, 3.3 Hz, 1H), 1.14 – 0.98 (m, 3H), 0.98 – 0.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 143.1, 128.5, 127.4, 124.7, 89.8, 49.6, 36.6, 34.4, 34.1, 33.7, 28.4, 26.2, 26.1, 26.0. IR (cm^{-1}): 2920, 1772, 1448, 1168, 932, 766, 703. HRMS (TOF MS ESI): calcd for $C_{17}H_{22}NaO_2^+$ $[M+ Na]^+$ 281.1512, found 281.1513.



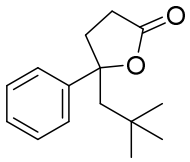
5-((4,4-difluorocyclohexyl)methyl)-5-phenyldihydrofuran-2(3H)-one (3ck)

Yellow solid, 47.7 mg (81% yield), m.p. 103 - 105 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 5H), 2.62 – 2.48 (m, 1H), 2.47 – 2.30 (m, 3H), 2.15 – 1.77 (m, 6H), 1.55 – 1.38 (m, 1H), 1.36 – 1.23 (m, 3H), 1.21 – 1.06 (m, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -92.00 (d, J = 235.9 Hz), -102.15 (d, J = 234.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 142.4, 128.7, 127.8, 124.5, 123.2 (dd, J = 241.5, 239.7 Hz), 89.2, 47.9, 37.2, 34.4 – 32.6 (m), 31.9, 29.8 (dd, J = 47.5, 9.3 Hz), 28.2. IR (cm^{-1}): 2929, 1761, 1176, 1107, 910, 768, 708. HRMS (TOF MS ESI): calcd for $C_{17}H_{20}F_2NaO_2^+$ $[M+Na]^+$ 317.1324, found 317.1323.



5-(2-ethylhexyl)-5-phenyldihydrofuran-2(3H)-one (3cl)

Pale yellow oil, 32.7 mg (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.13 (m, 5H), 2.60 – 2.32 (m, 4H), 1.96 (ddd, J = 14.7, 7.2, 4.2 Hz, 1H), 1.85 (ddd, J = 14.8, 8.6, 6.2 Hz, 1H), 1.42 – 1.12 (m, 5H), 1.12 – 0.94 (m, 4H), 0.84 (t, J = 7.0 Hz, 1.5H), 0.80 – 0.71 (m, 3H), 0.66 (t, J = 7.4 Hz, 1.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 176.8, 143.1, 143.0, 128.4 (overlap, s), 127.5, 127.4, 124.8, 124.8, 90.0, 90.0, 45.9 (overlap, s), 36.5, 36.2, 34.8, 34.6, 33.3, 33.2, 28.5, 28.4, 28.4, 28.3, 26.5, 26.4, 22.9, 22.8, 14.1, 14.0, 10.5, 10.2. IR (cm^{-1}): 2926, 1776, 1180, 924, 766, 703. HRMS (TOF MS ESI): calcd for $C_{18}H_{26}NaO_2^+$ $[M+ Na]^+$ 297.1825, found 297.1826.



5-neopentyl-5-phenyldihydrofuran-2(3H)-one (3cm)

Yellow solid, 34.8 mg (75% yield). m.p. 79 - 80 ^{o}C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 5H), 2.60 – 2.24 (m, 4H), 2.13 (d, J = 14.9 Hz, 1H), 1.99 (d, J = 14.9 Hz, 1H), 0.74 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 143.2, 128.4, 127.4, 125.0, 89.5, 54.4, 39.1, 31.7, 31.0, 27.9. IR

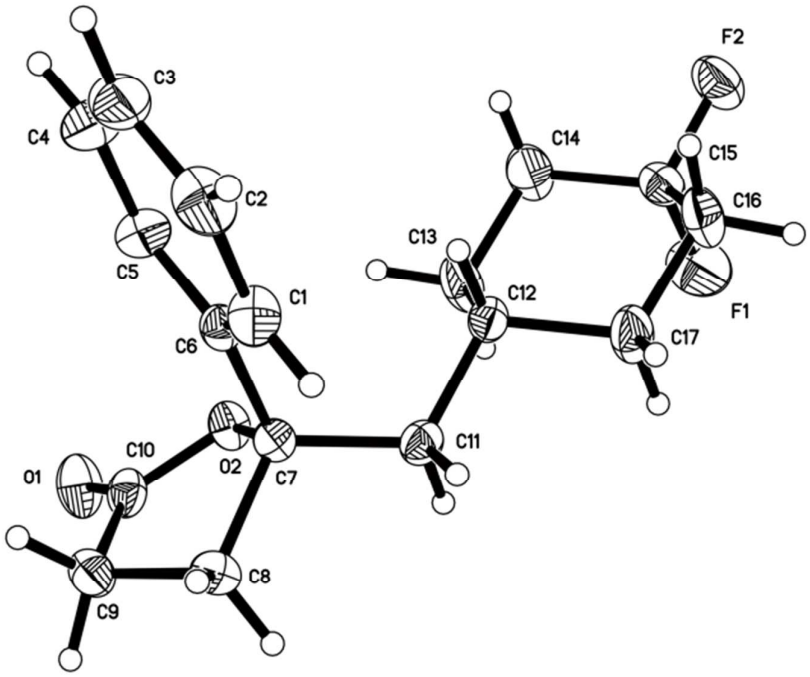
(cm^{-1}): 2941, 1757, 1053, 990, 758, 699. HRMS (TOF MS ESI): calcd for $C_{15}H_{20}NaO_2^+$ $[M+ Na]^+$ 255.1356, found 255.1355.

Reference

1. S. Ni, Y. Zhang, C. Xie, H. Mei, J. Han and Y. Pan, *Org. Lett.*, 2015, **17**, 5524.

2. T. M. Ha, C. Chatalova-Sazepin, Q. Wang and J. Zhu, *Angew. Chem. Int. Ed.*, 2016, **55**, 9249.

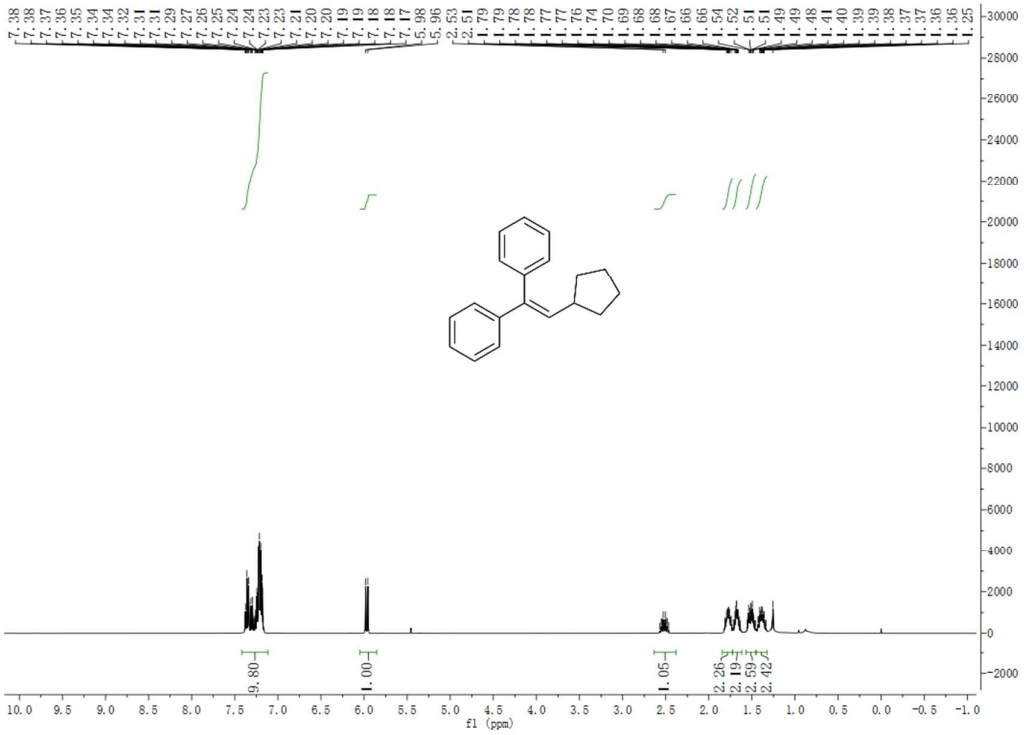
5. X-ray crystallography for 3ck (CCDC number: 1569464)



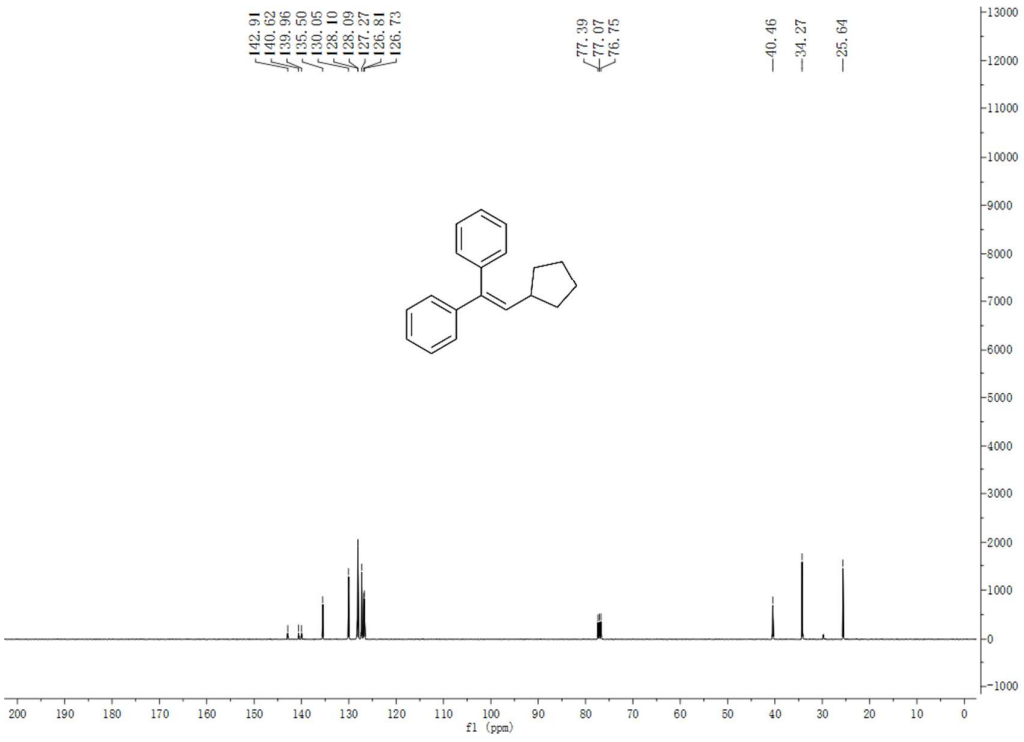
6. NMR spectra

6.1. NMR spectra of compound 4a

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4a**

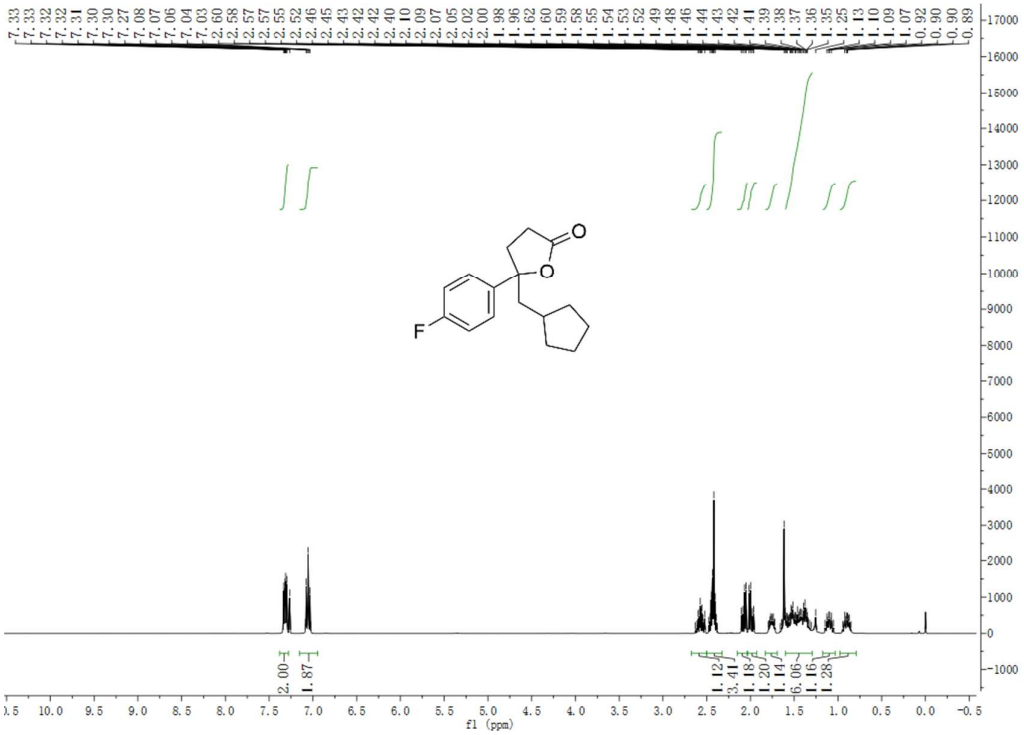


^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4a**

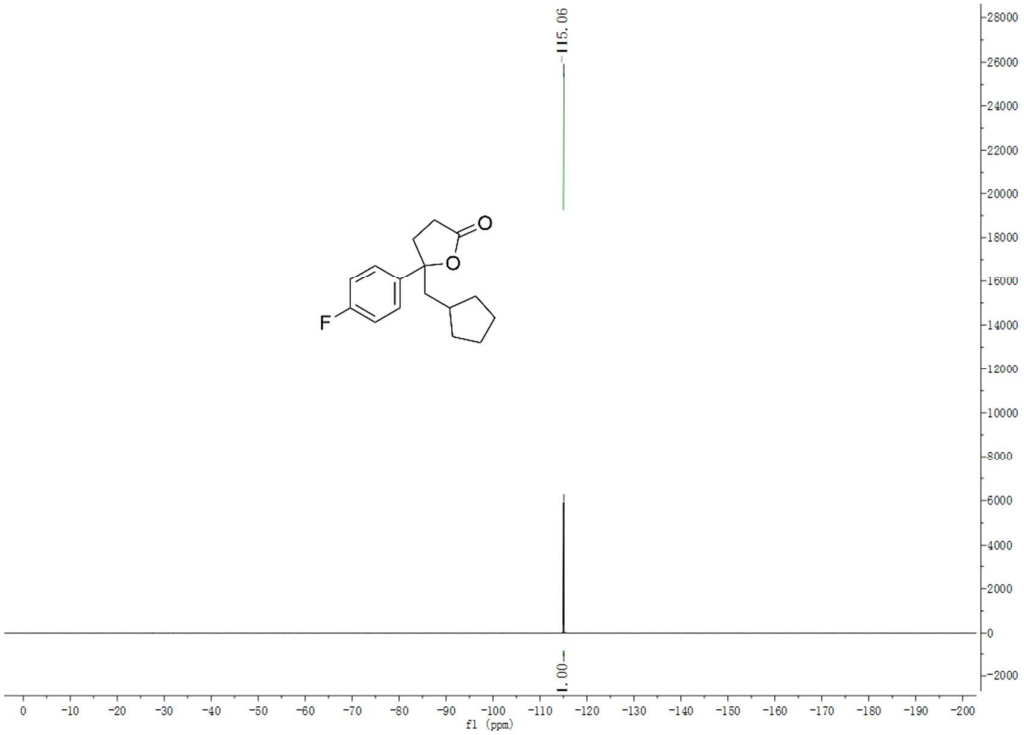


6.2. NMR spectra of products 3

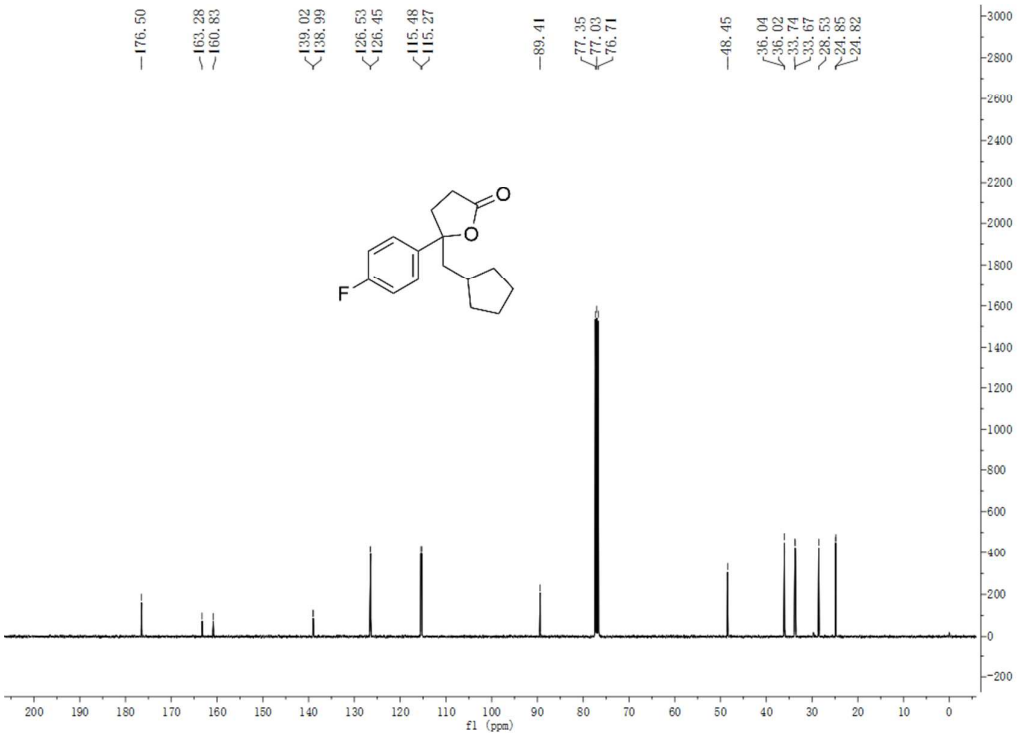
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aa**



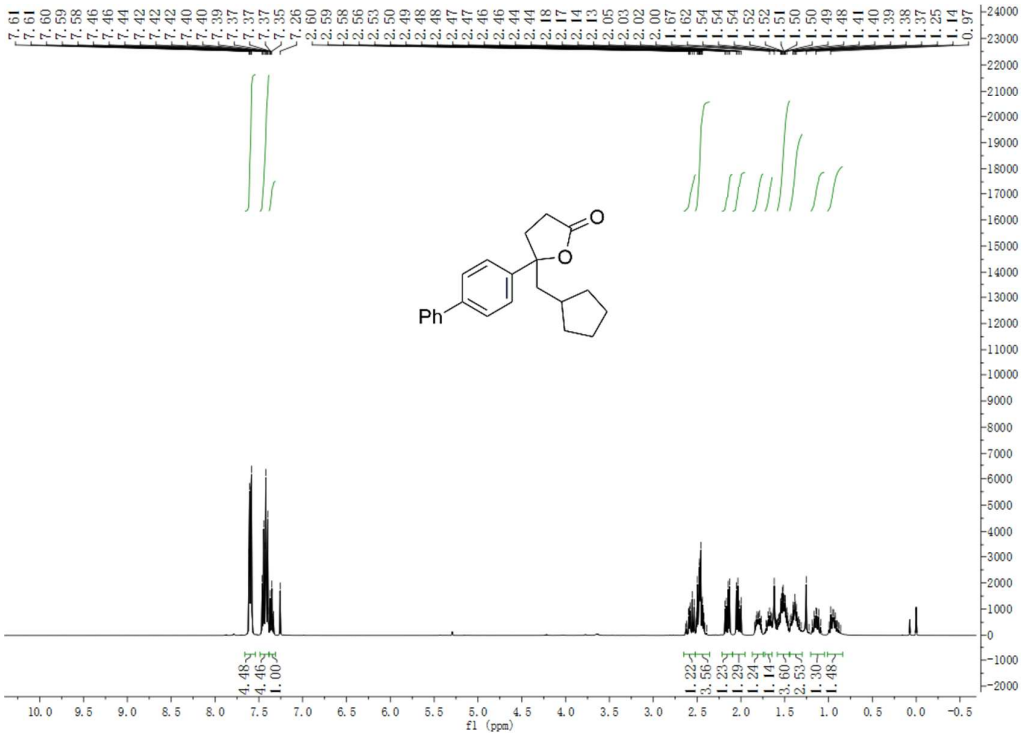
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3aa**



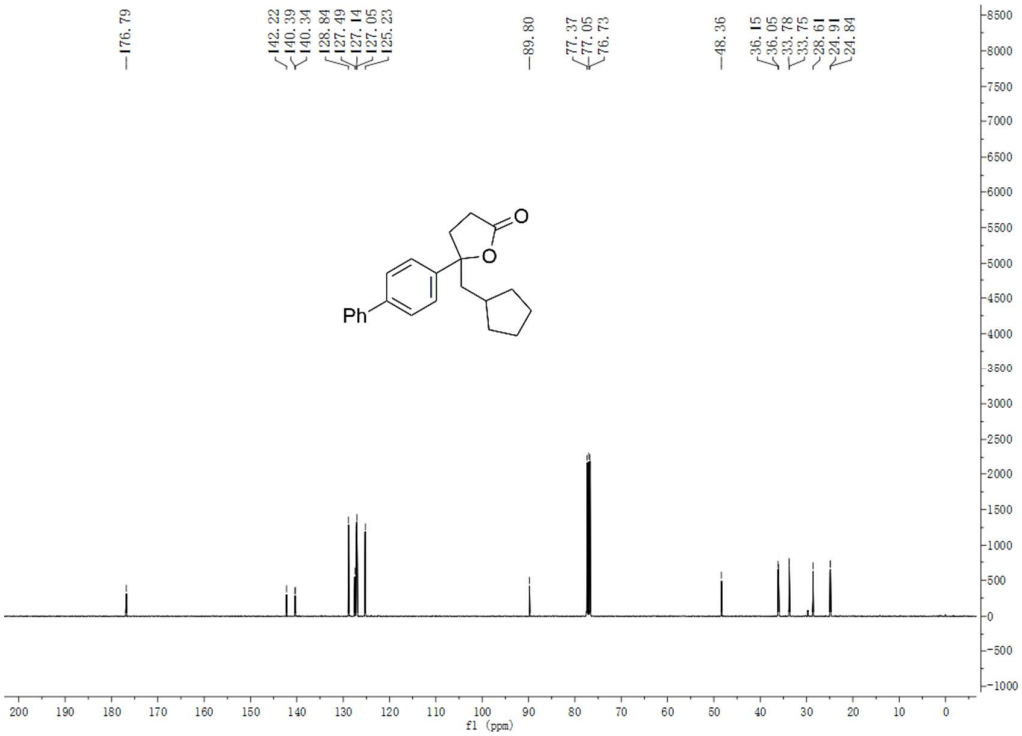
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aa**



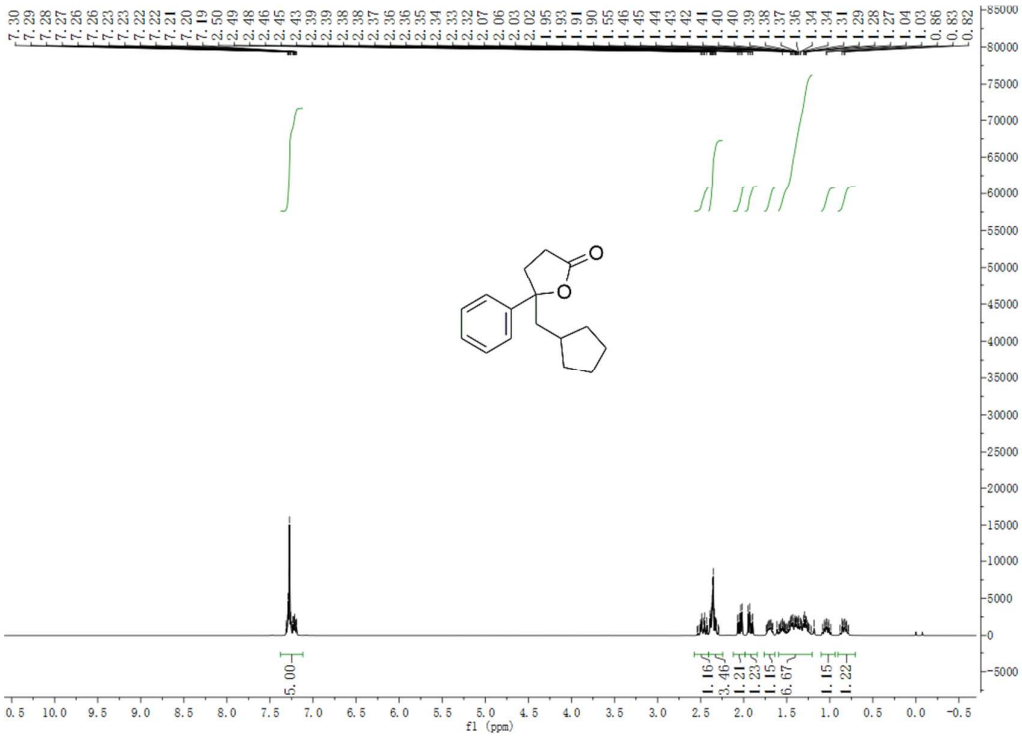
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ba**



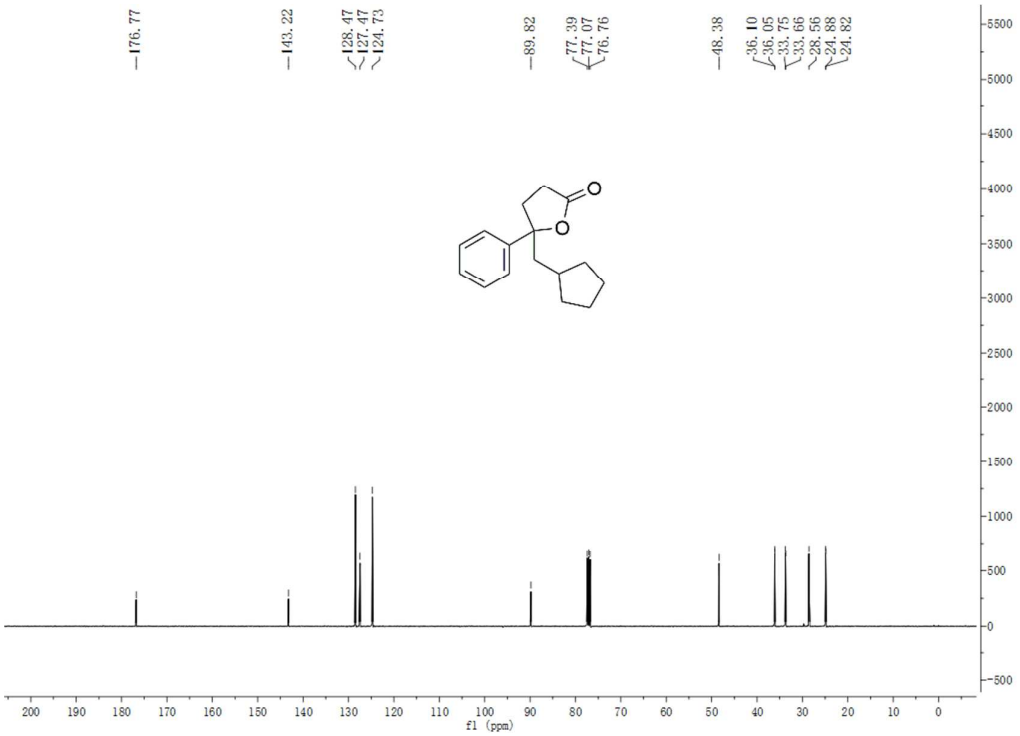
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ba**



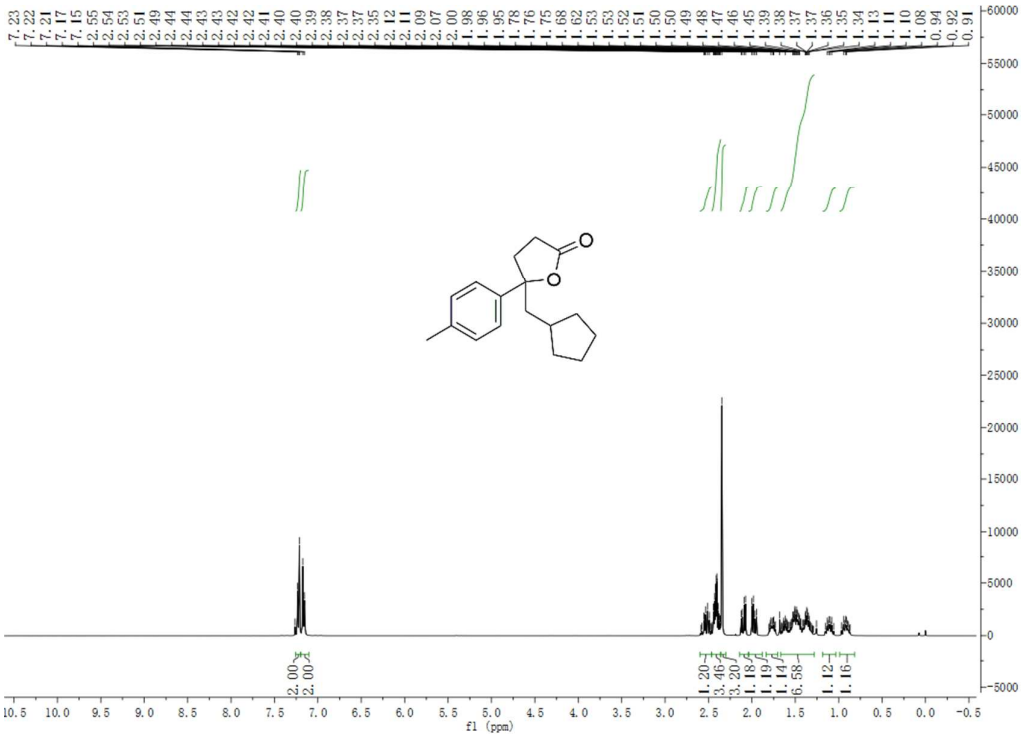
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ca**



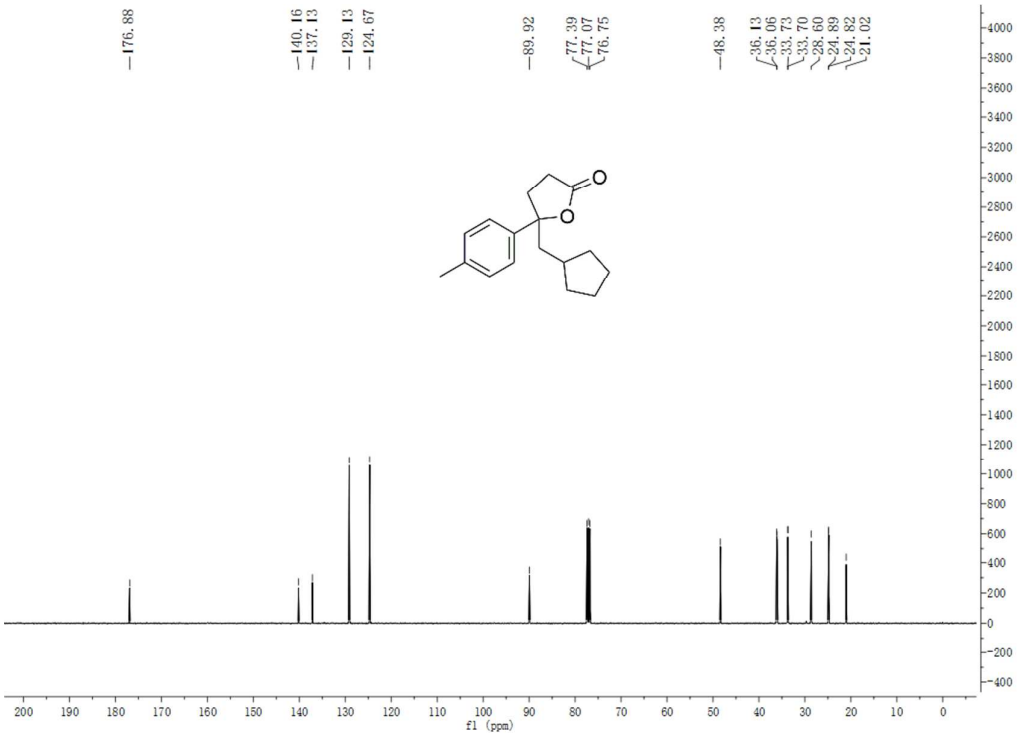
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ca**



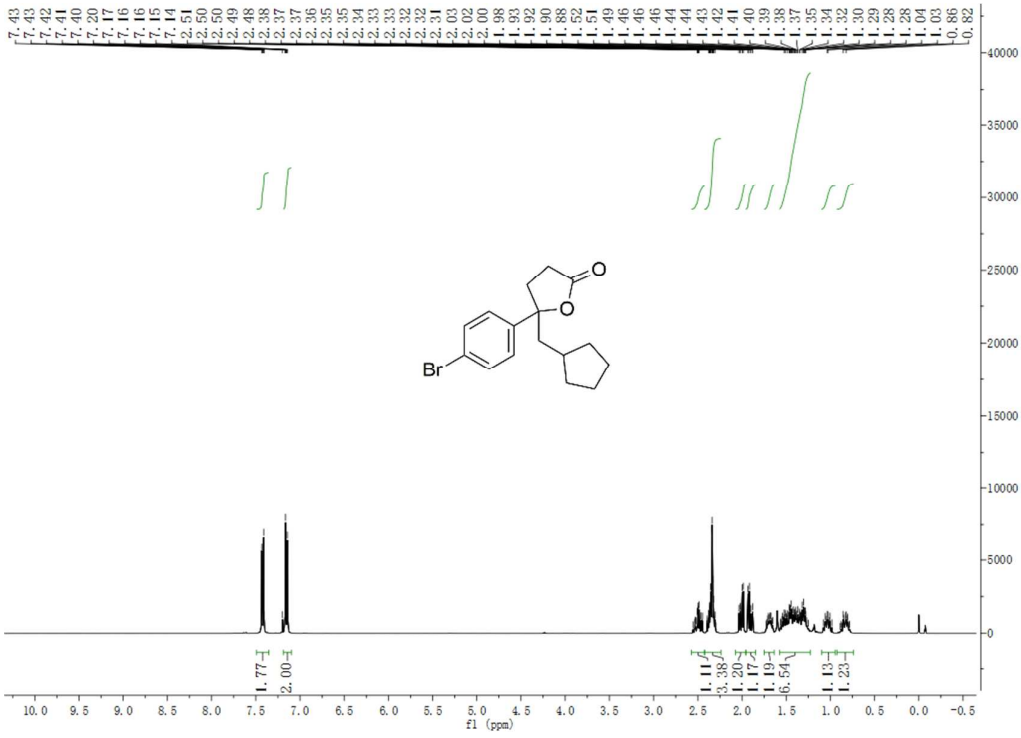
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3da**



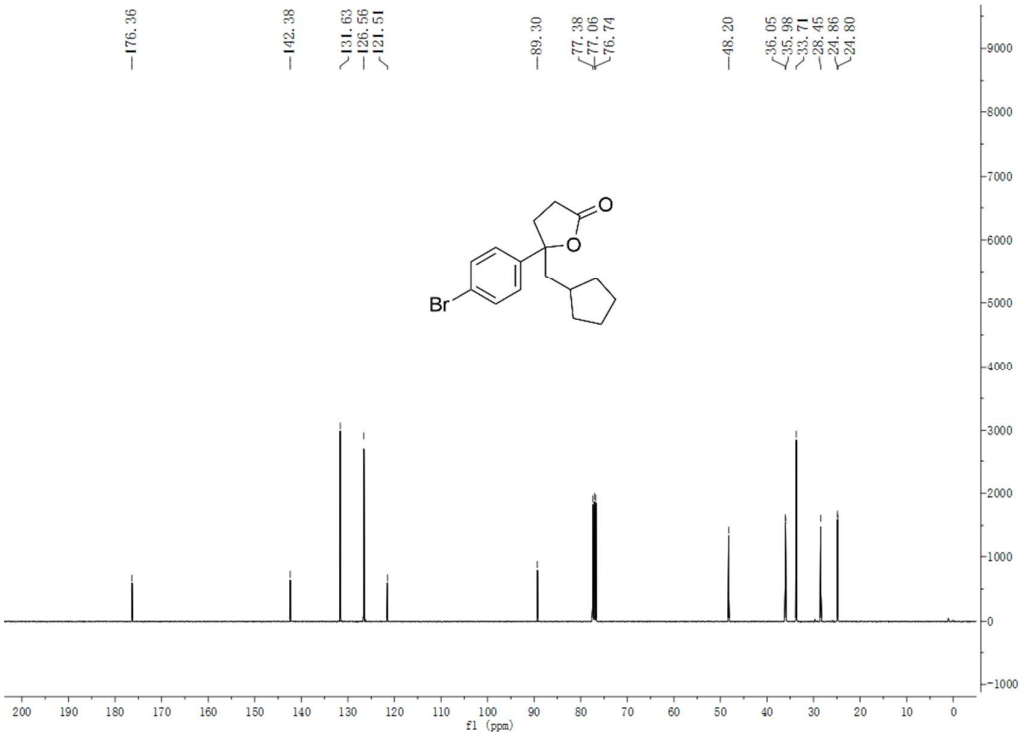
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3da**



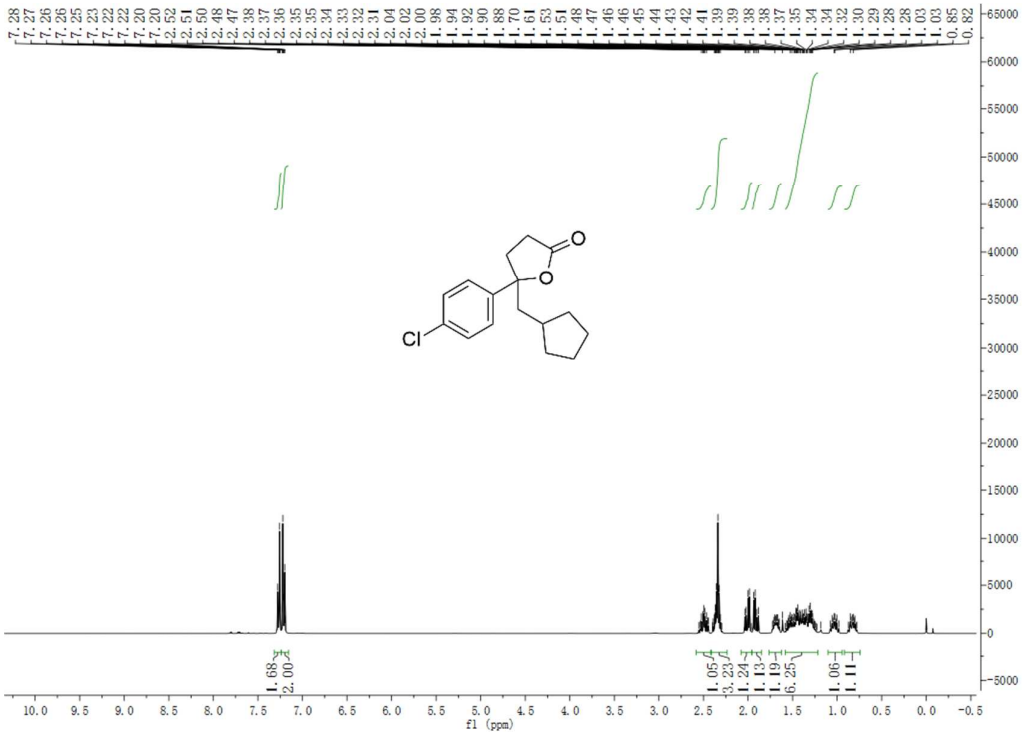
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ea**



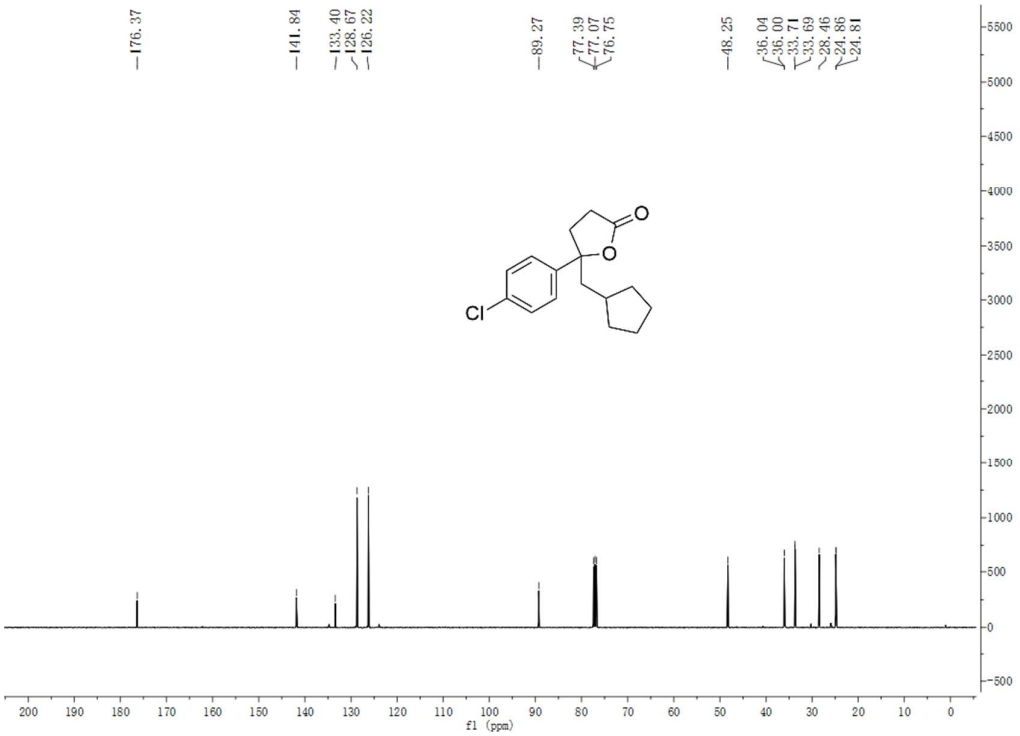
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ea**



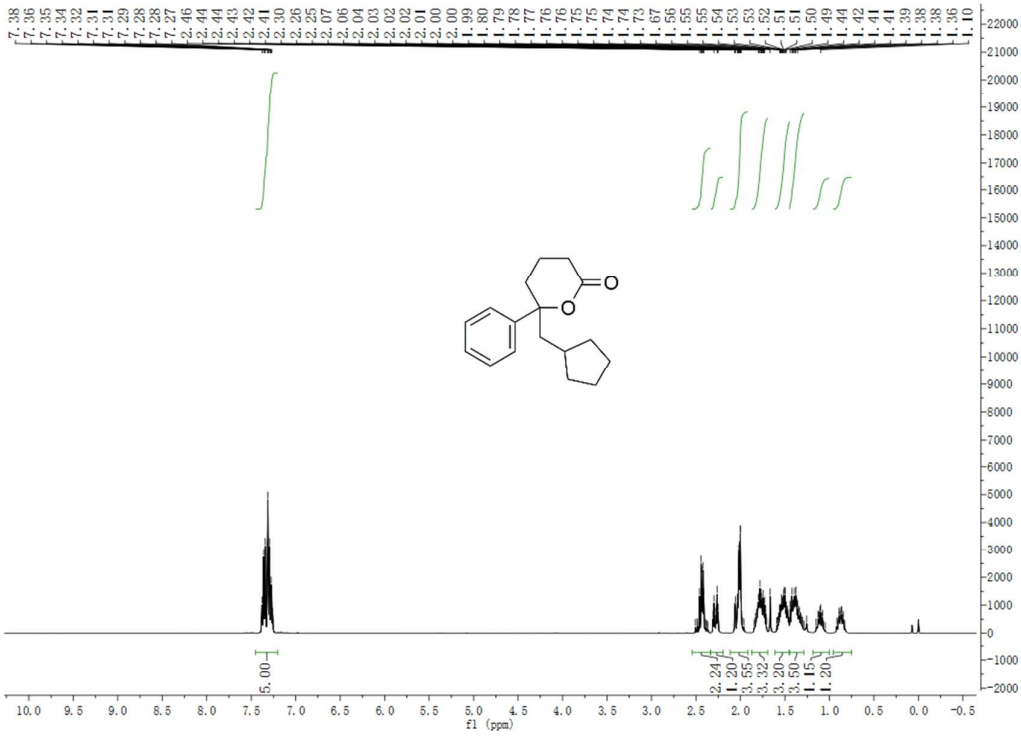
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3fa**



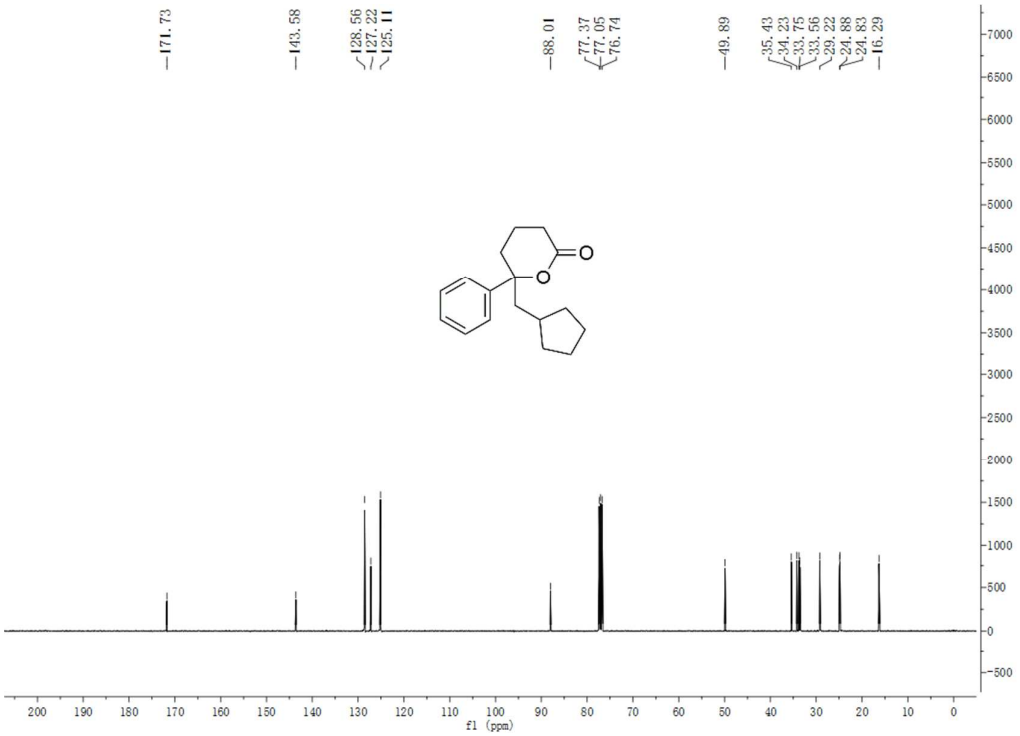
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3fa**



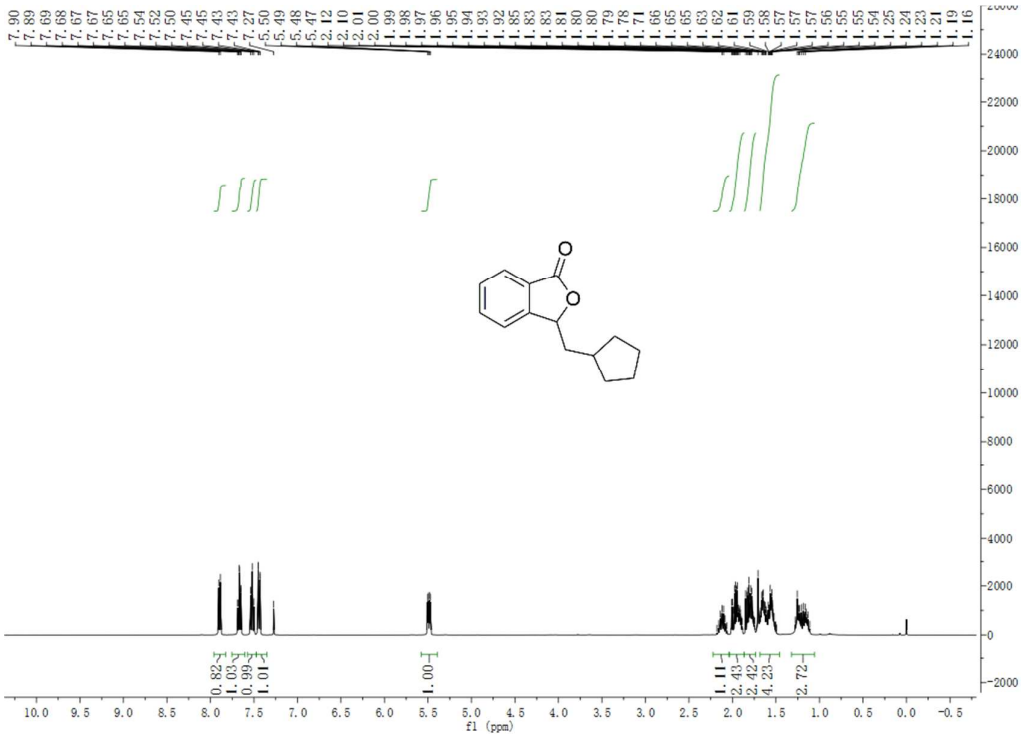
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ga**



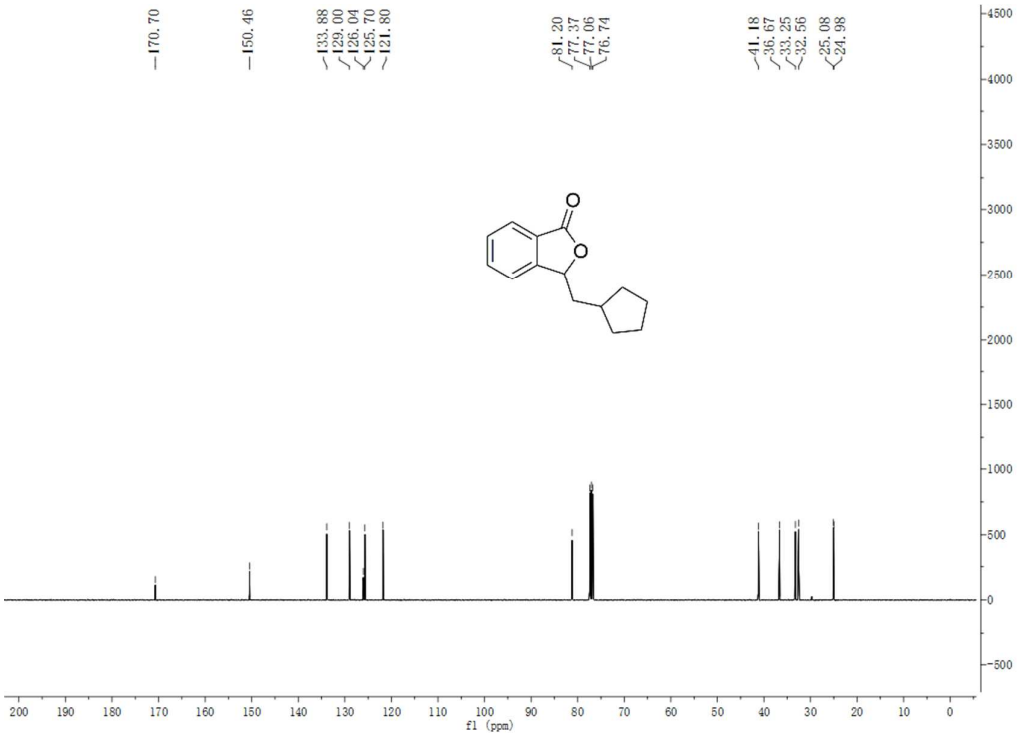
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ga**



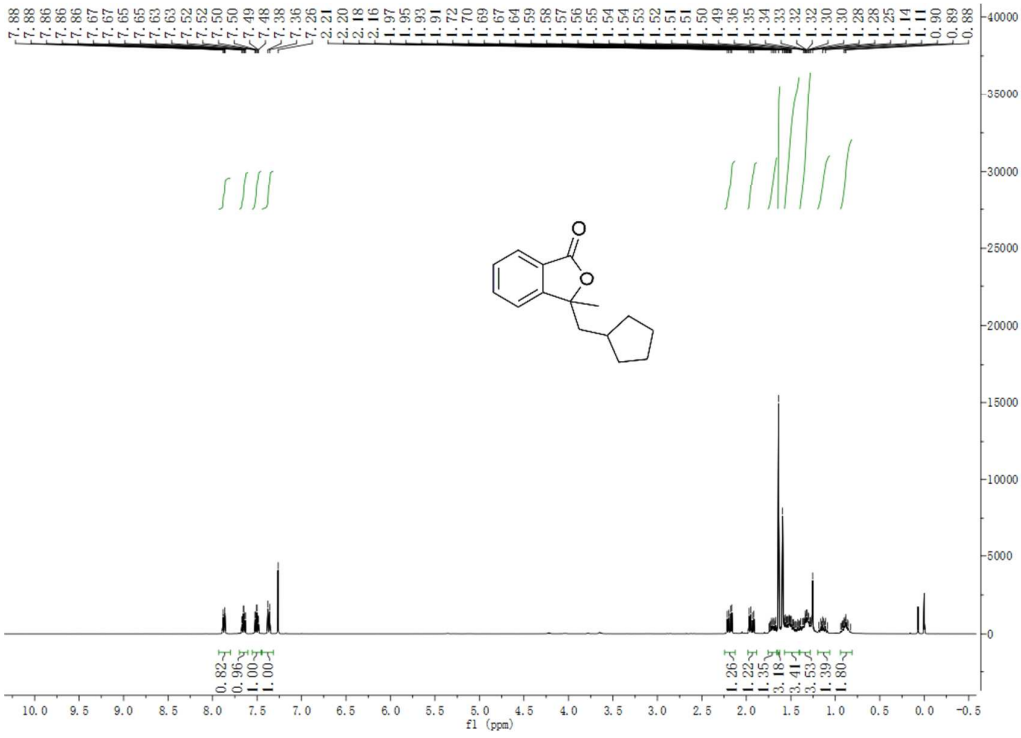
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ha**



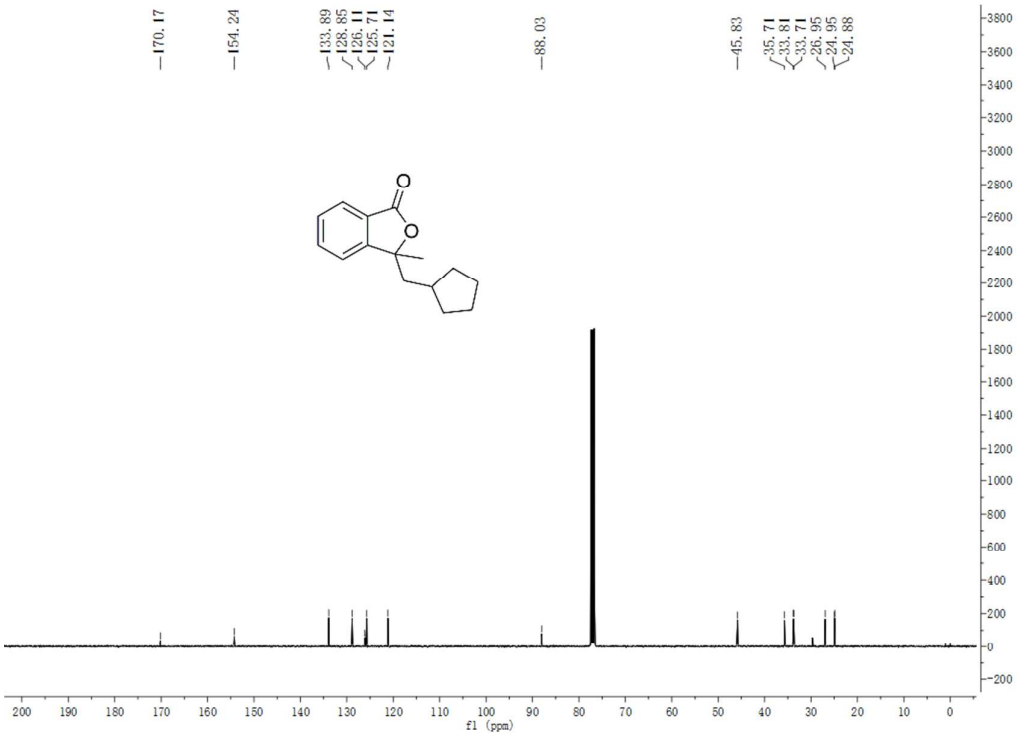
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ha**



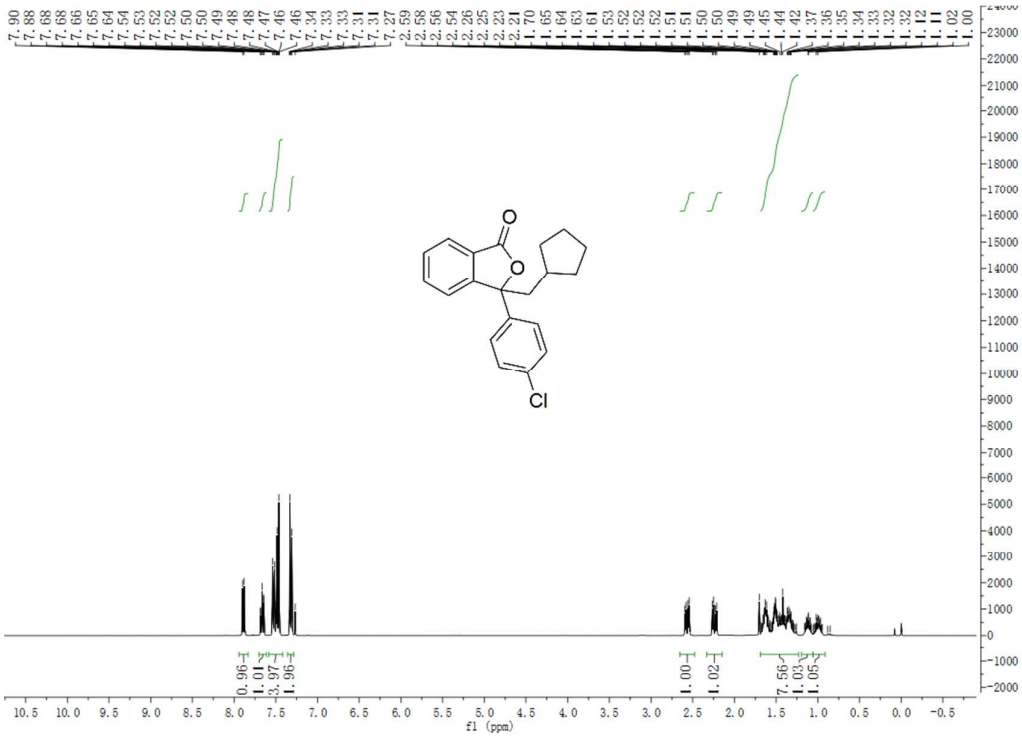
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ia**



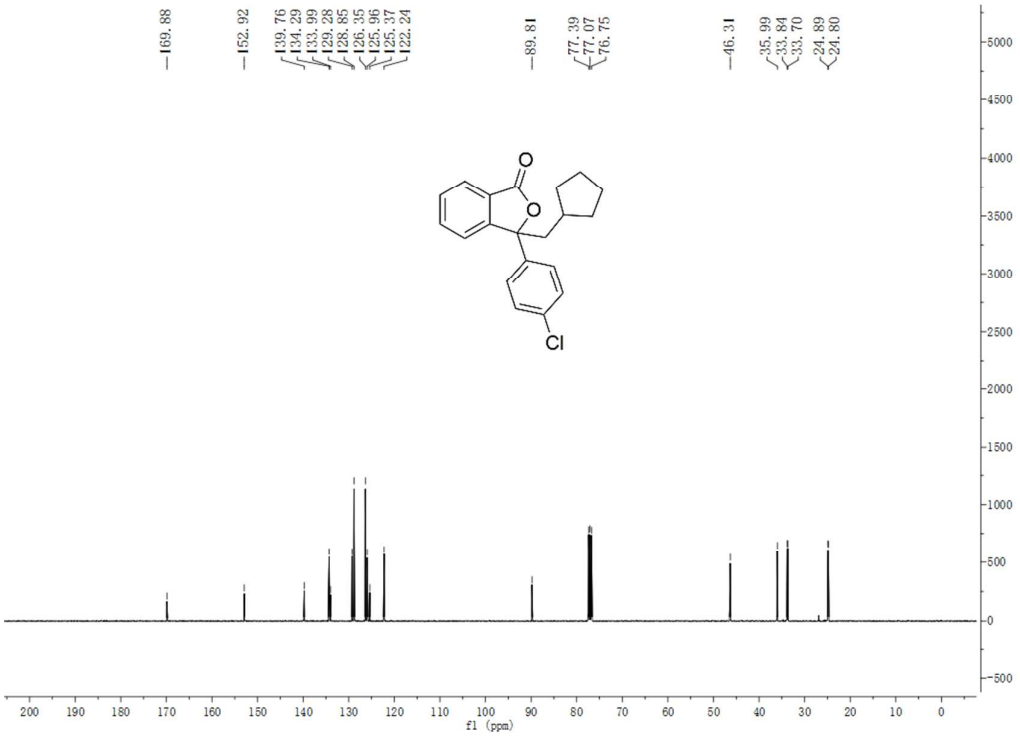
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ia**



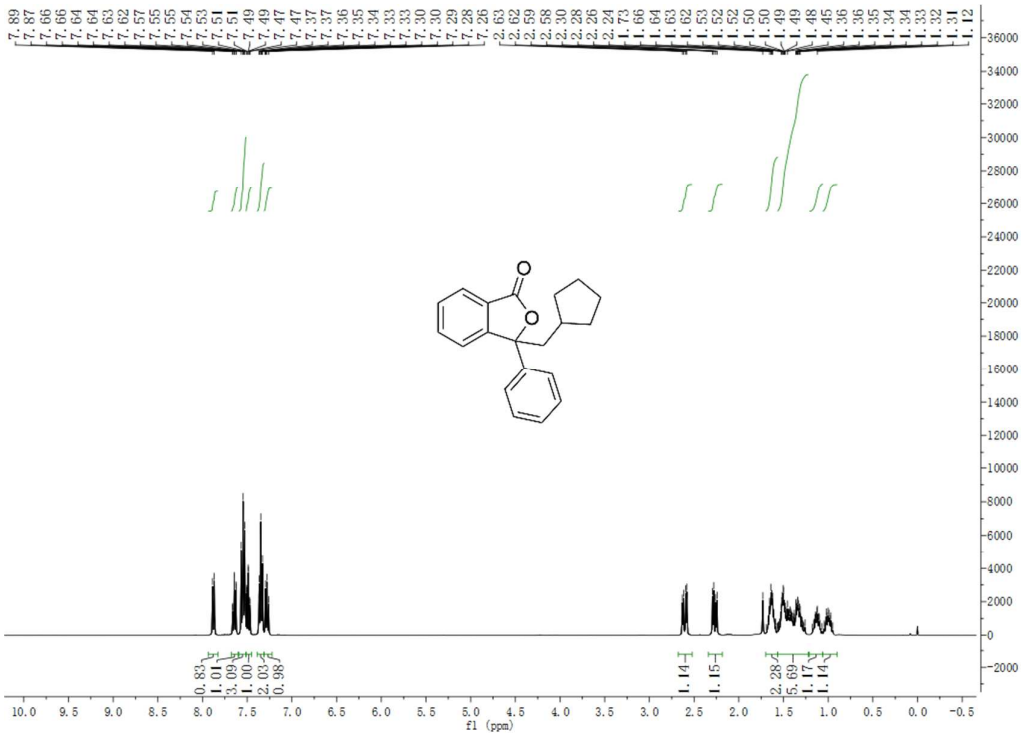
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ja**



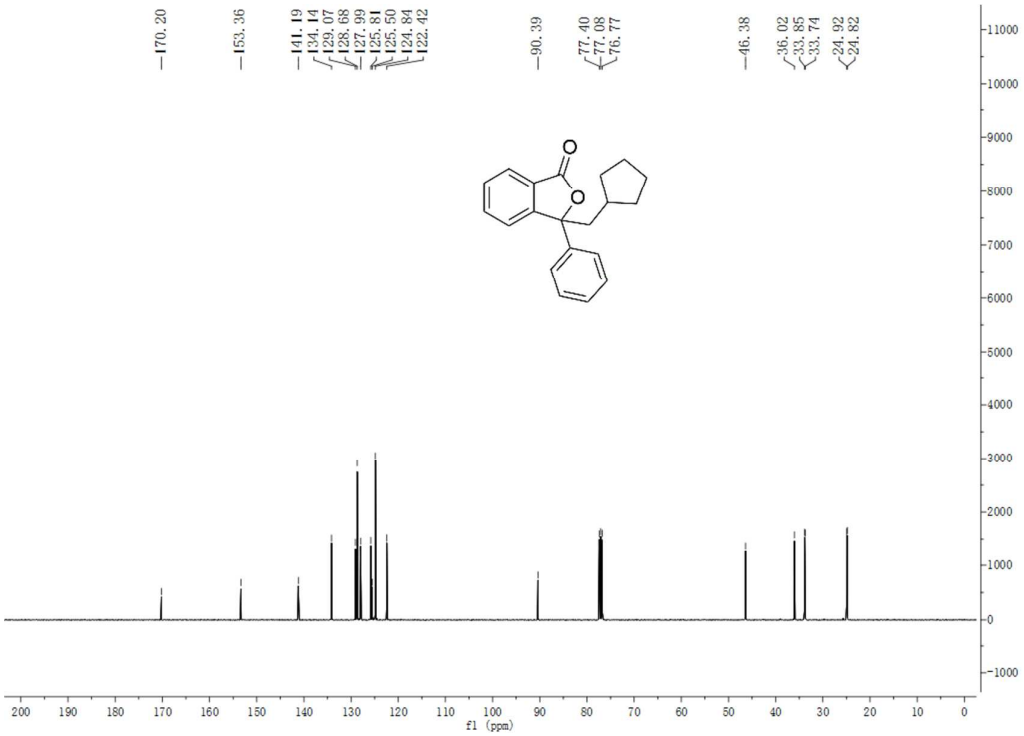
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ja**



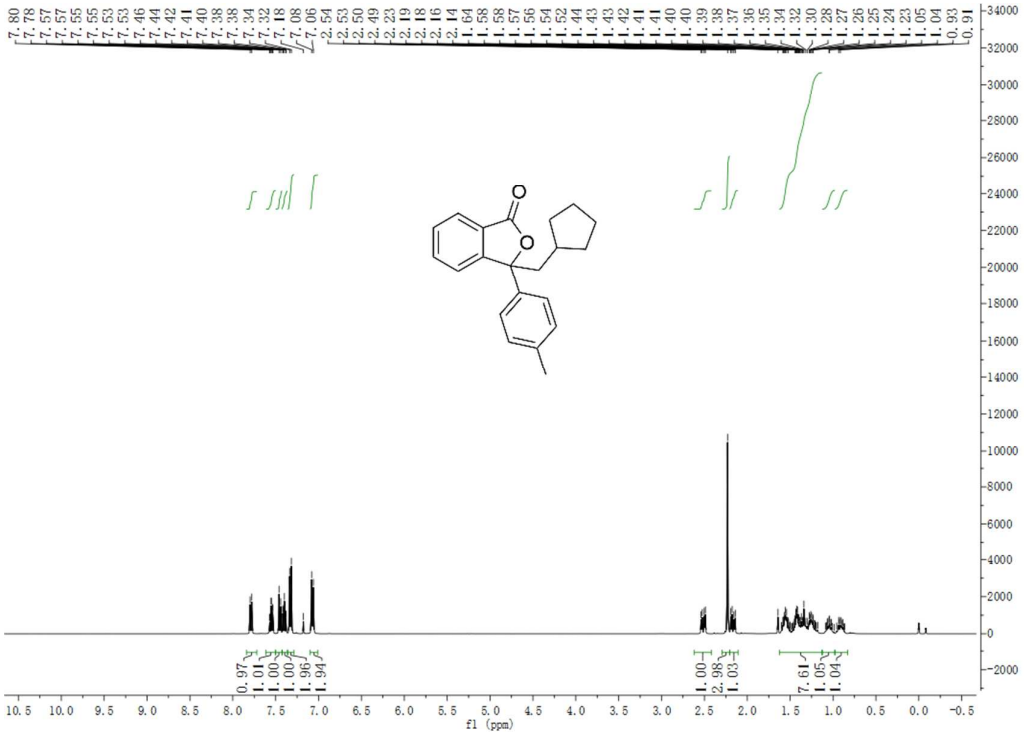
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ka**



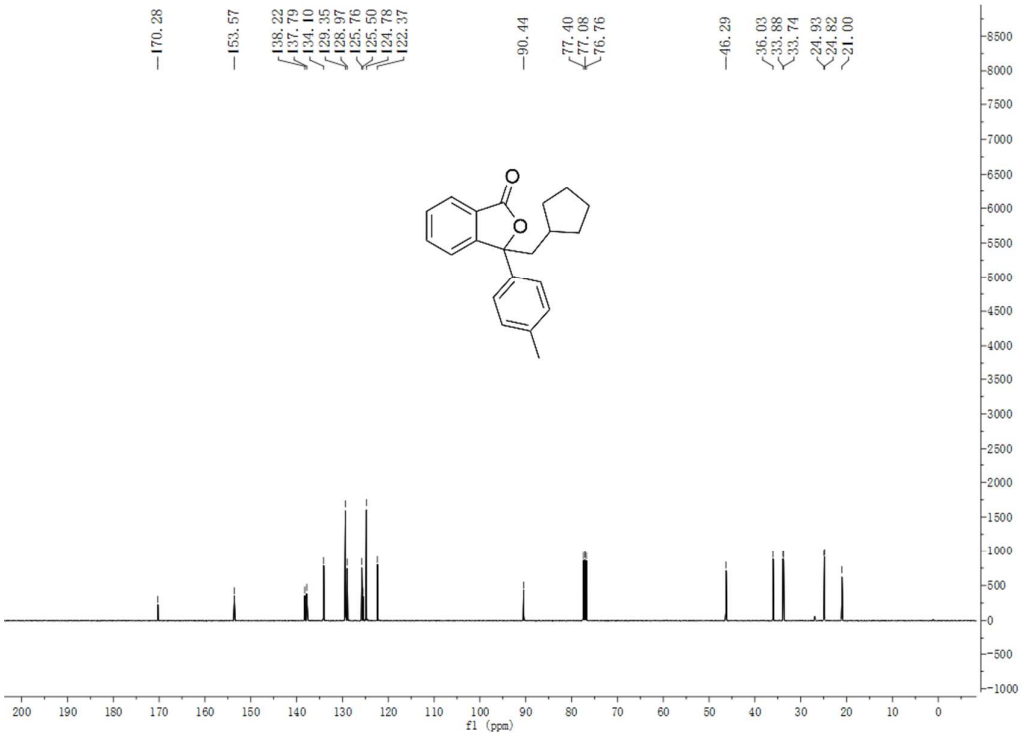
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ka**



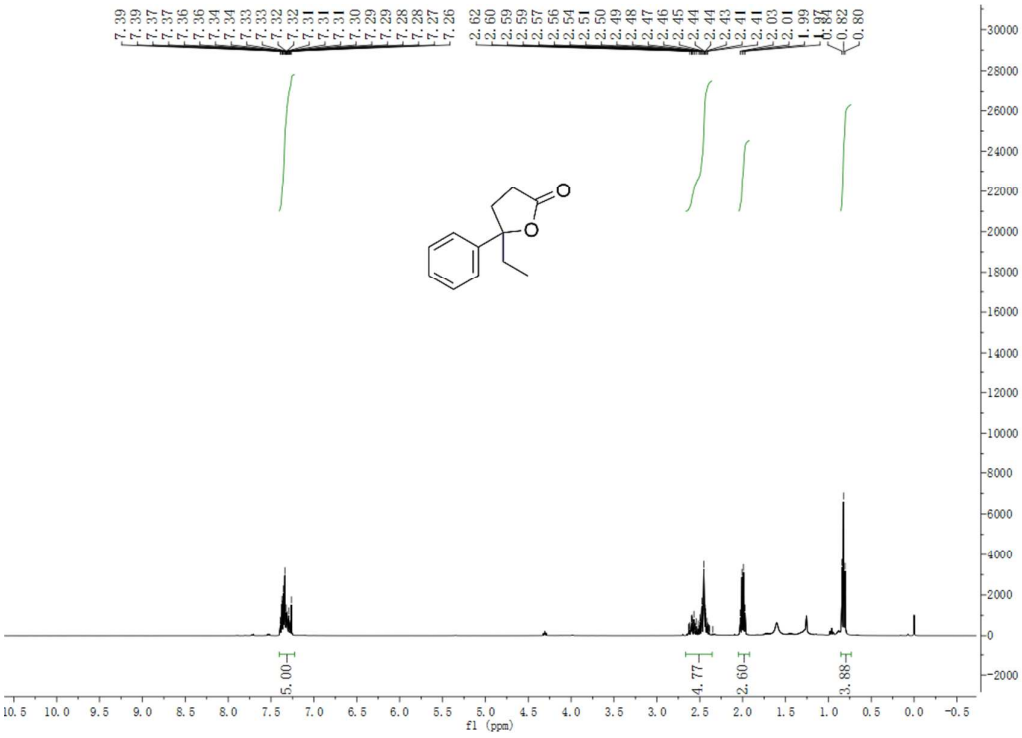
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3la**



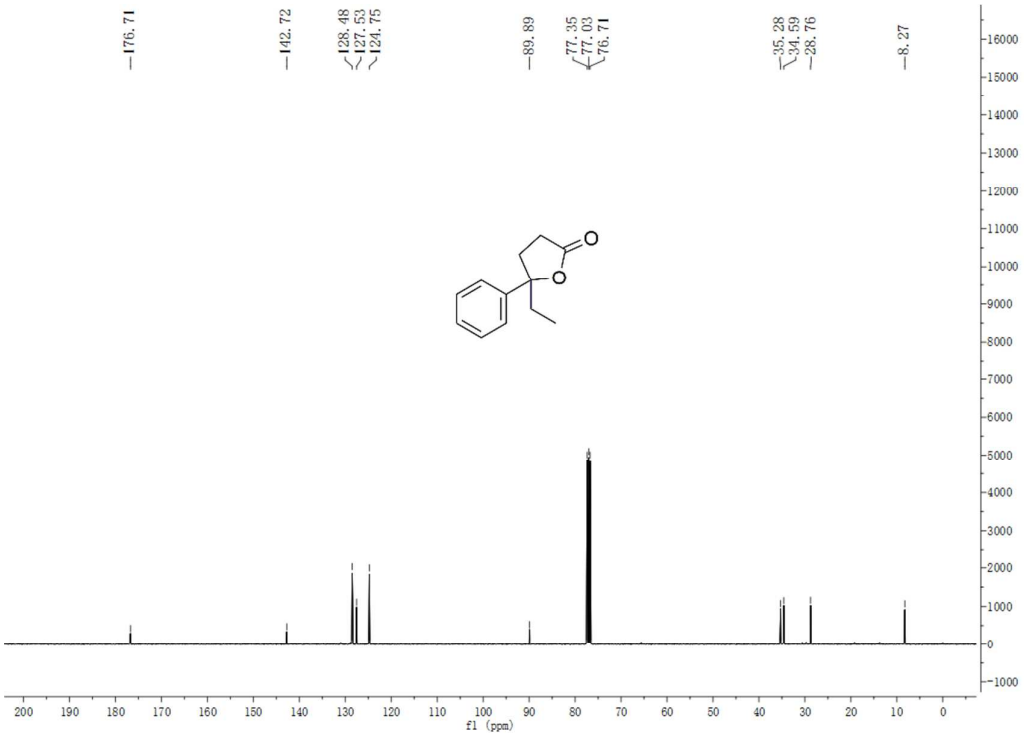
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3la**



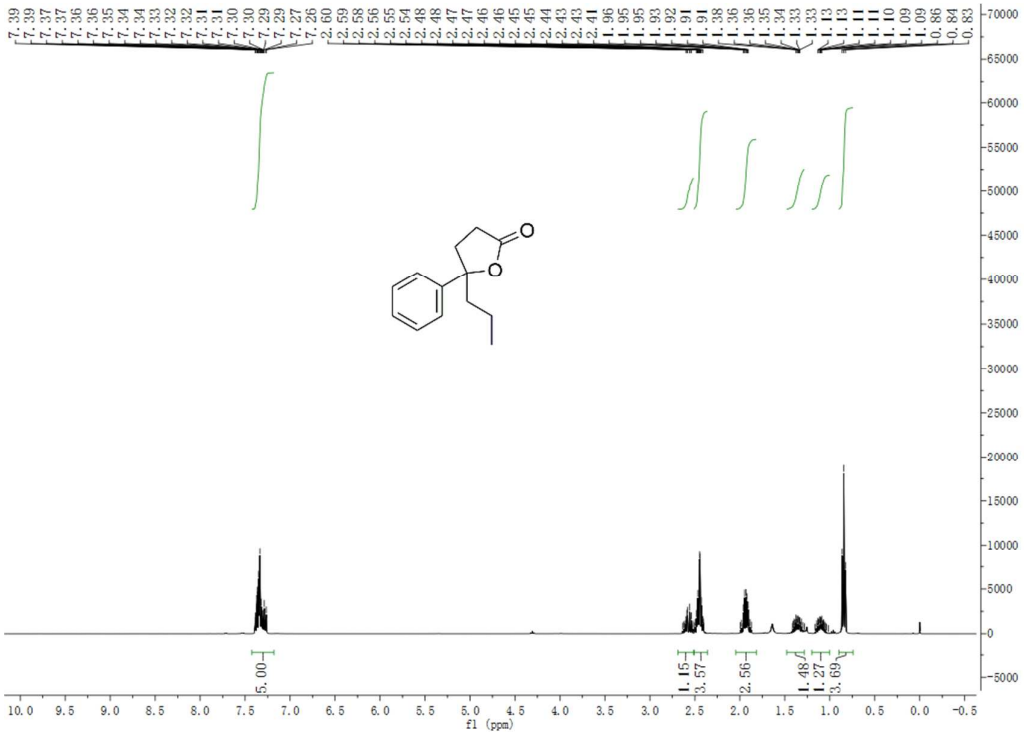
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3cb**



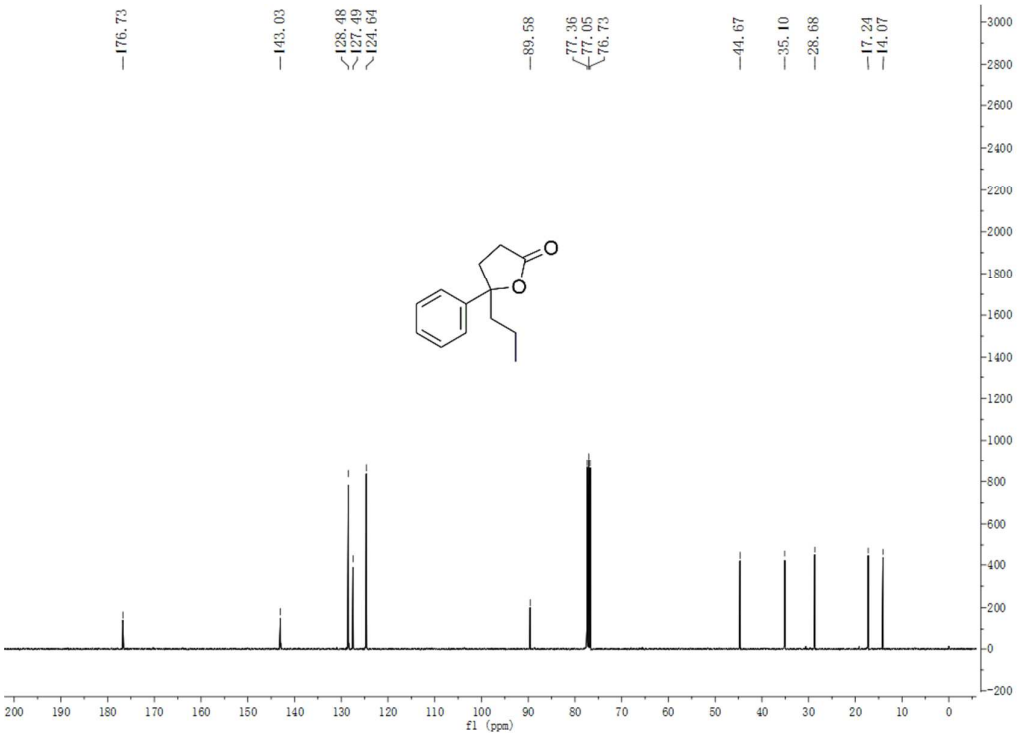
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3cb**



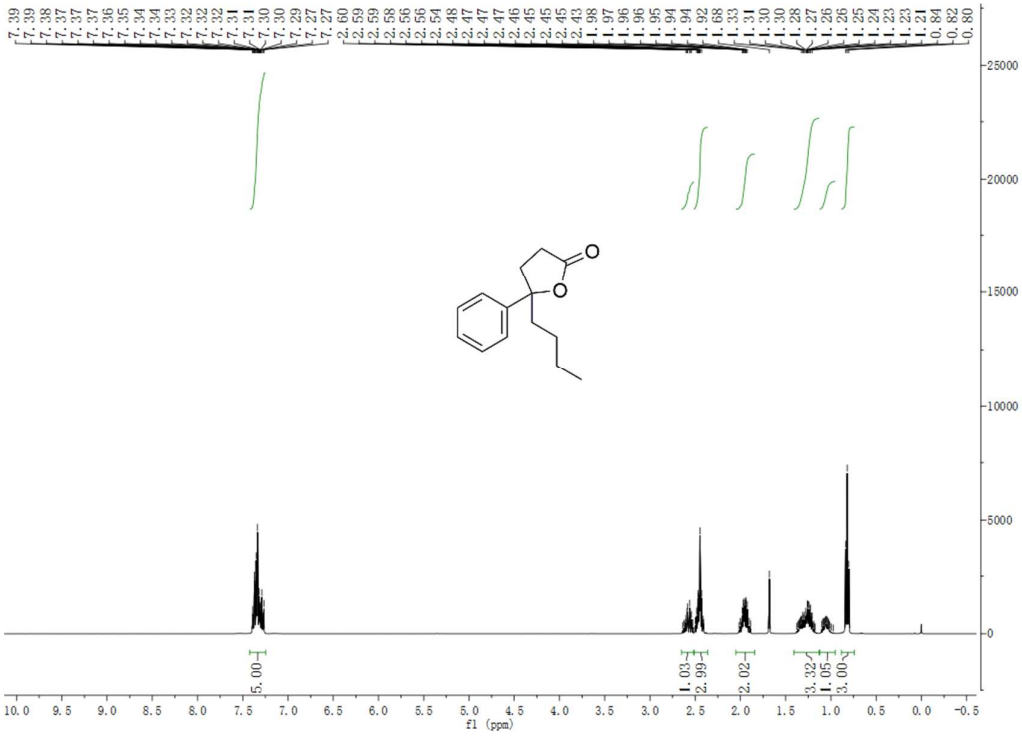
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3cc**



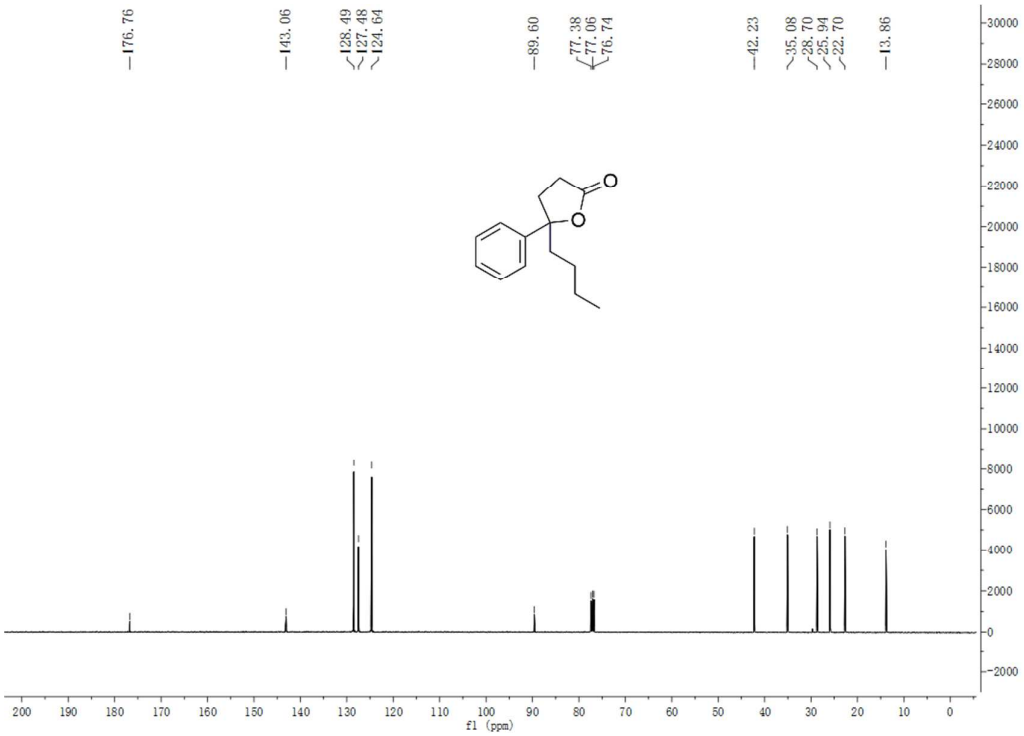
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3cc**



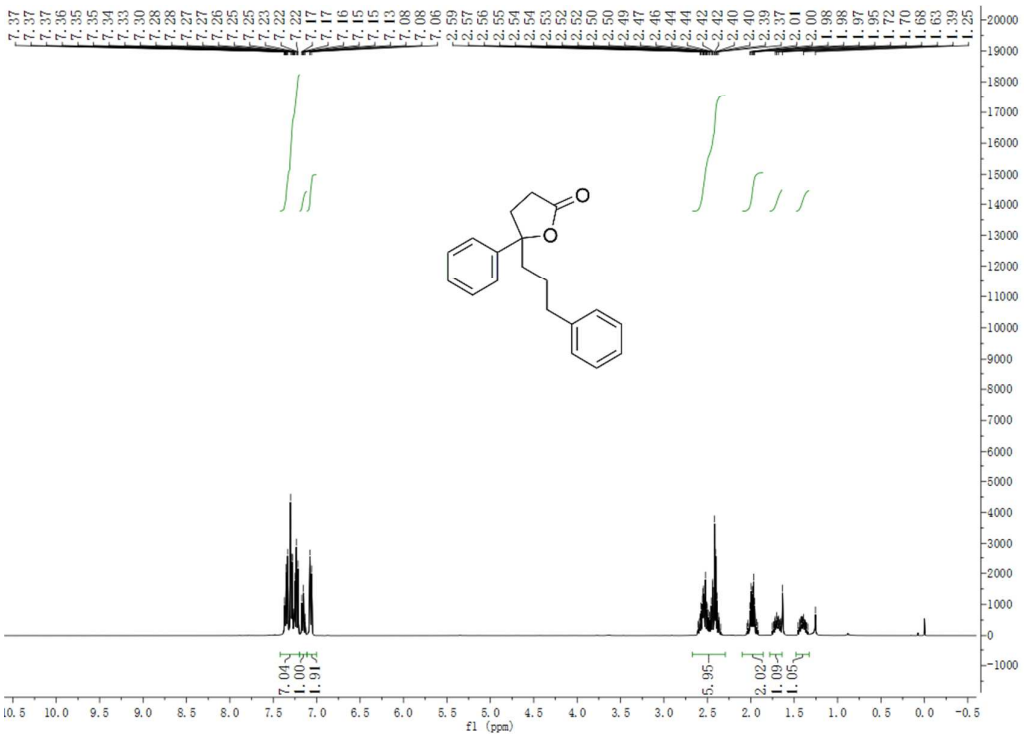
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3cd**



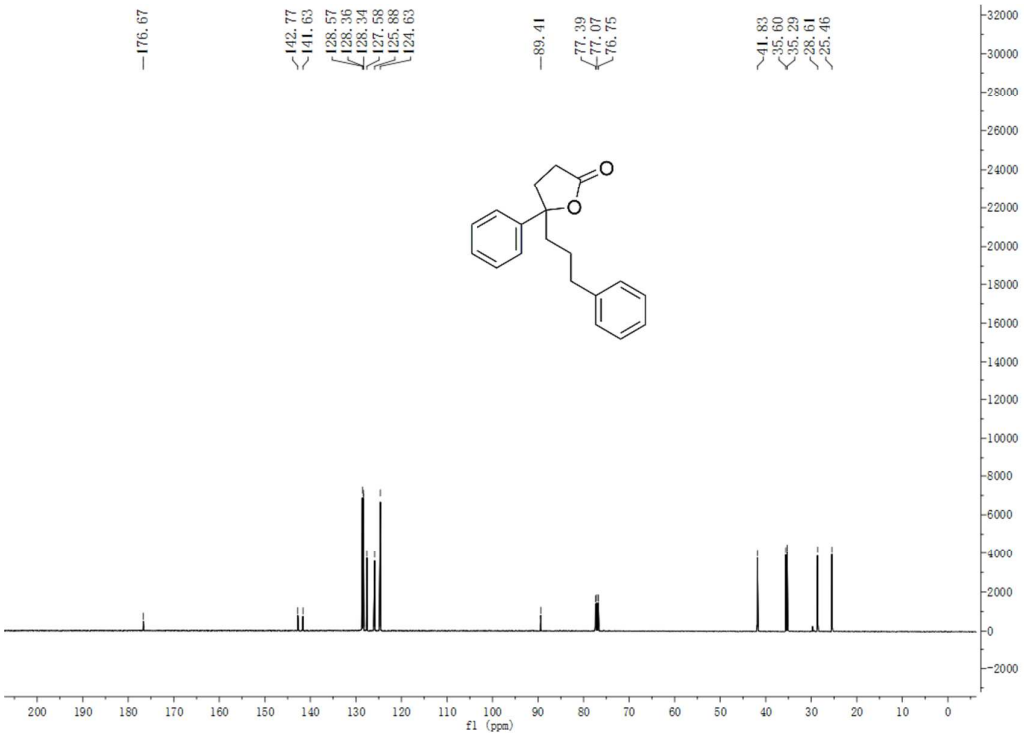
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3cd**



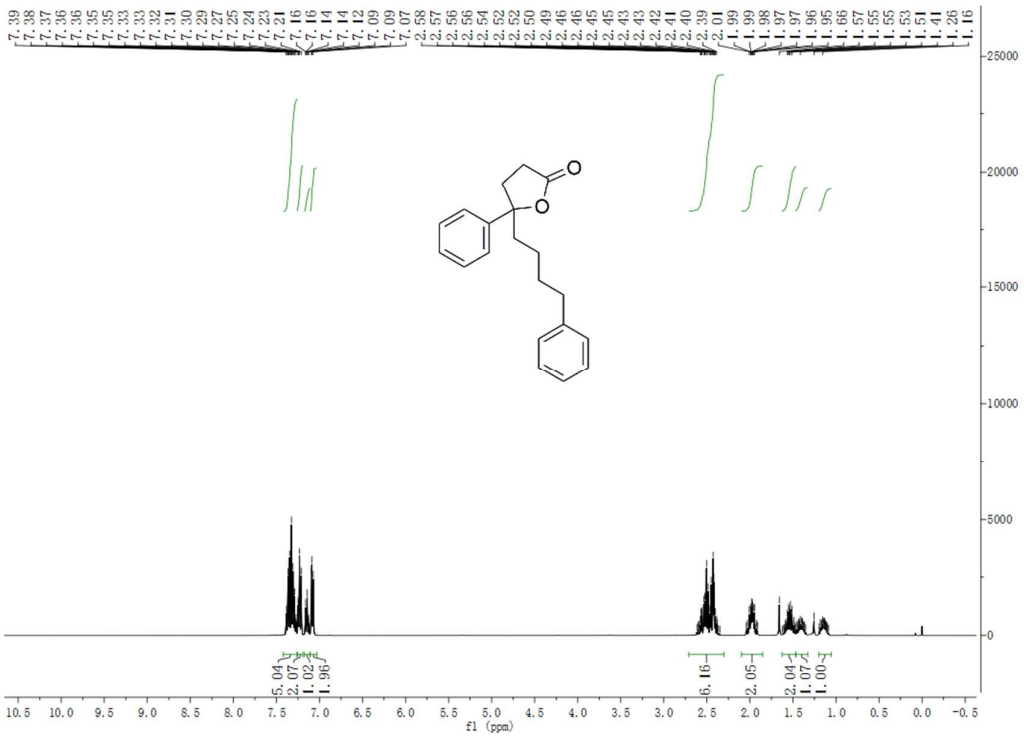
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ce**



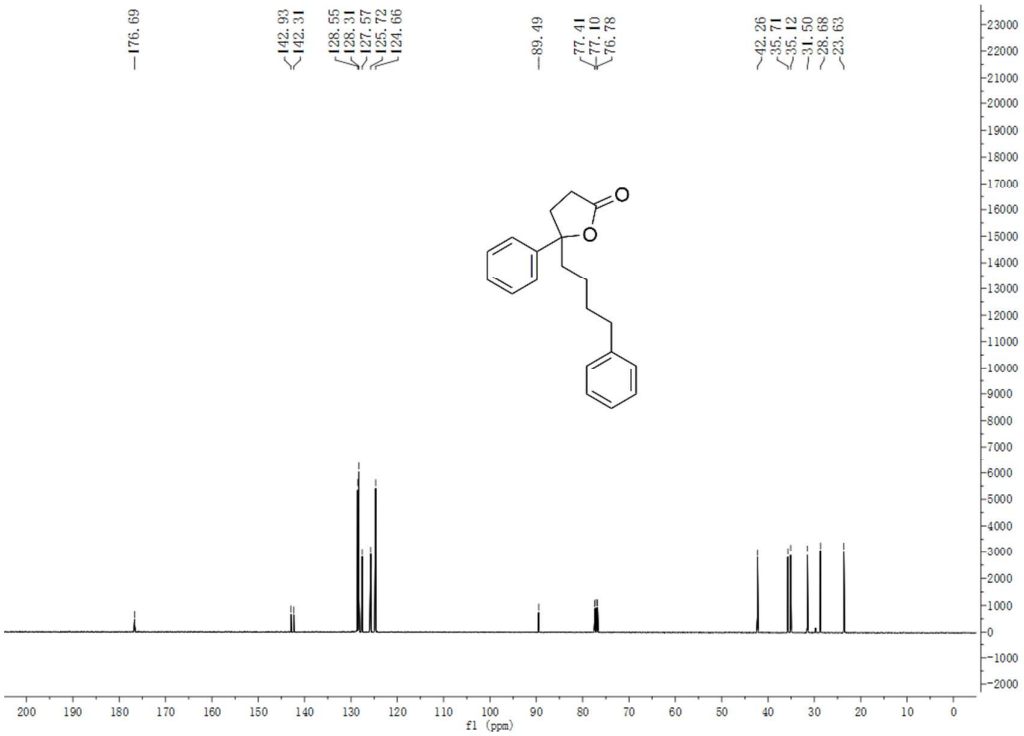
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ce**



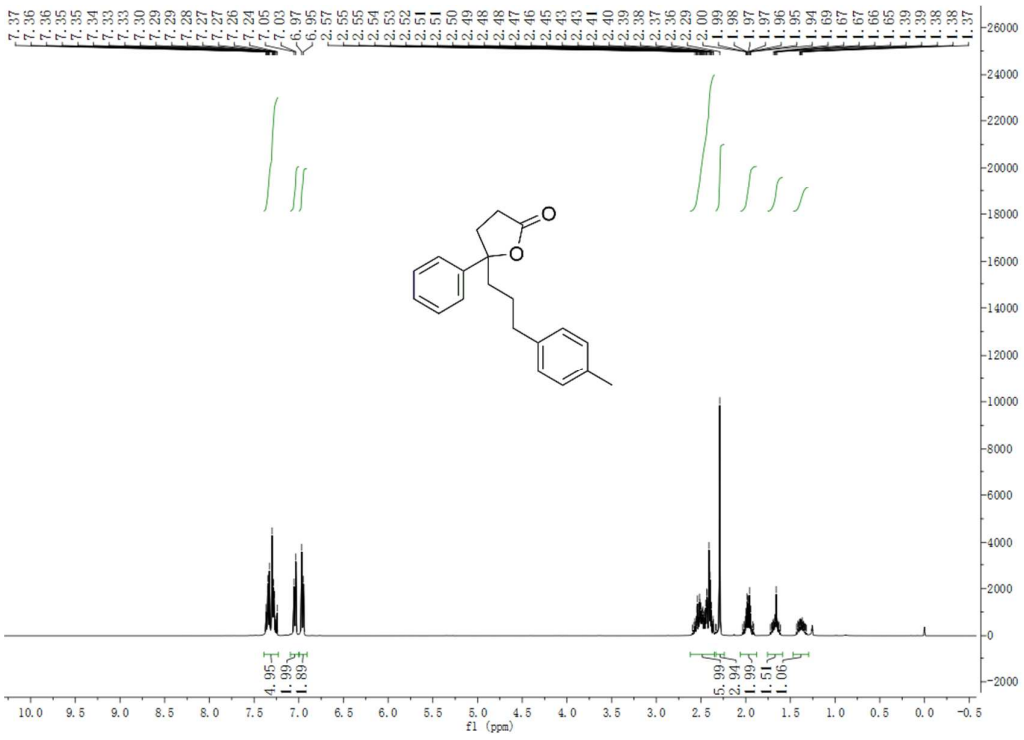
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3cf**



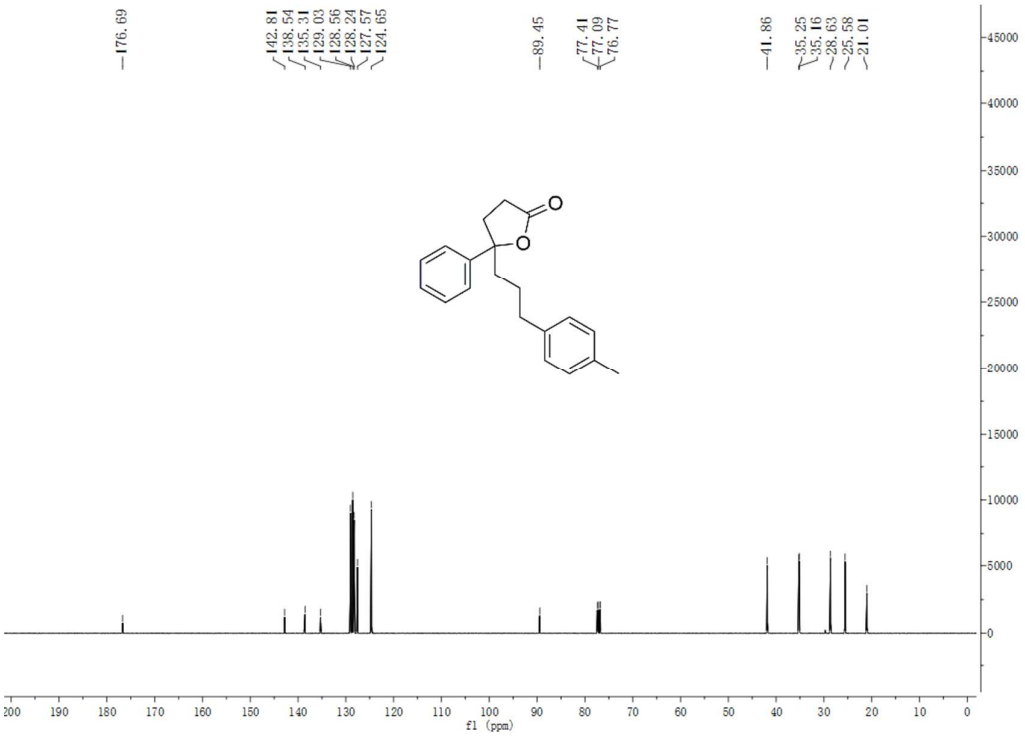
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3cf**



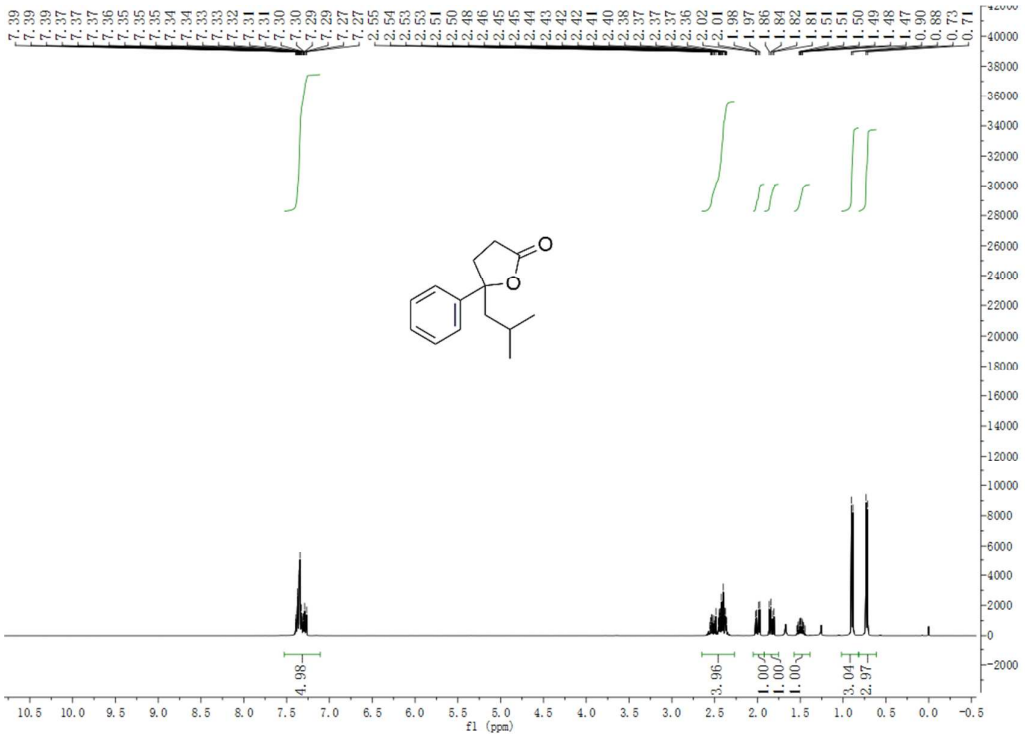
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3cg**



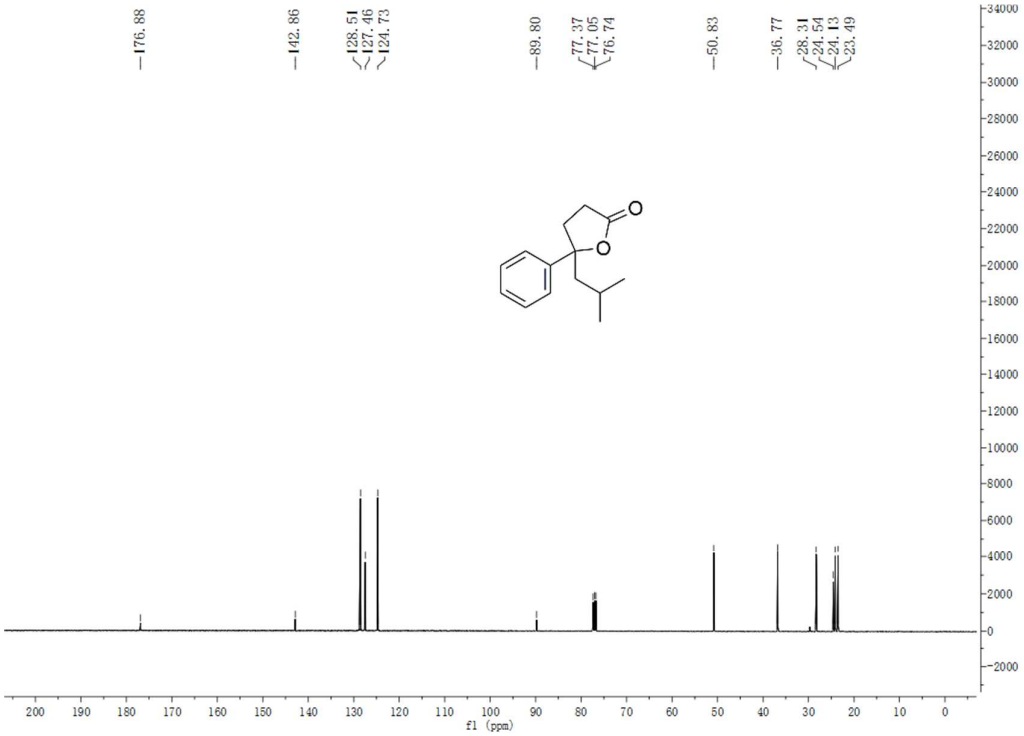
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3cg**



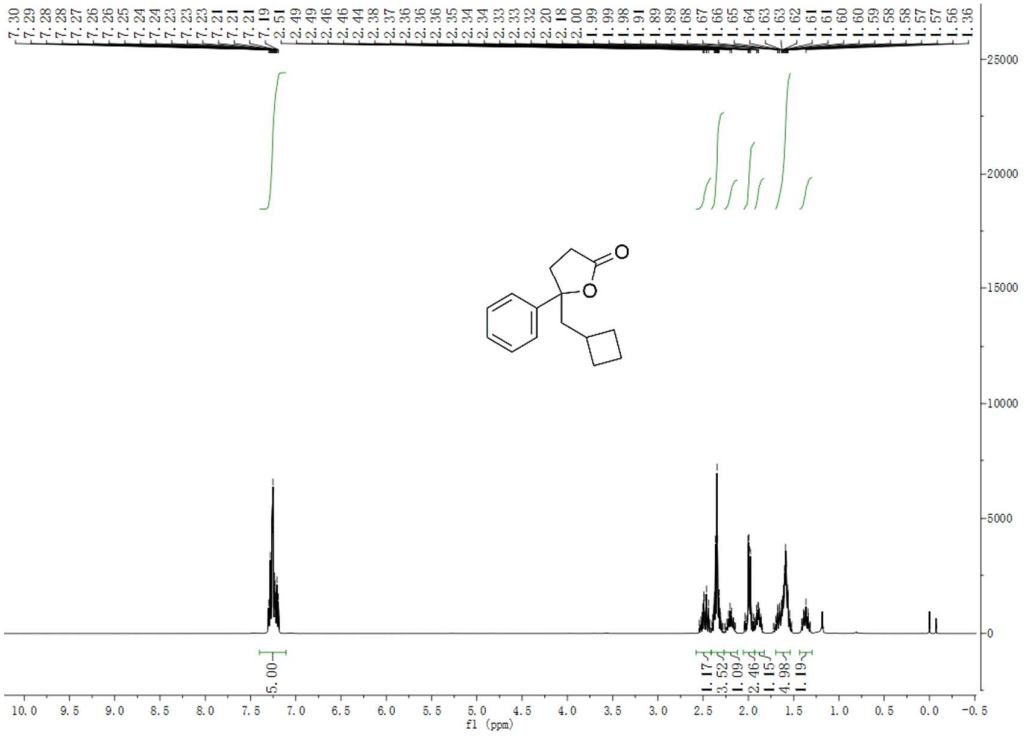
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ch**



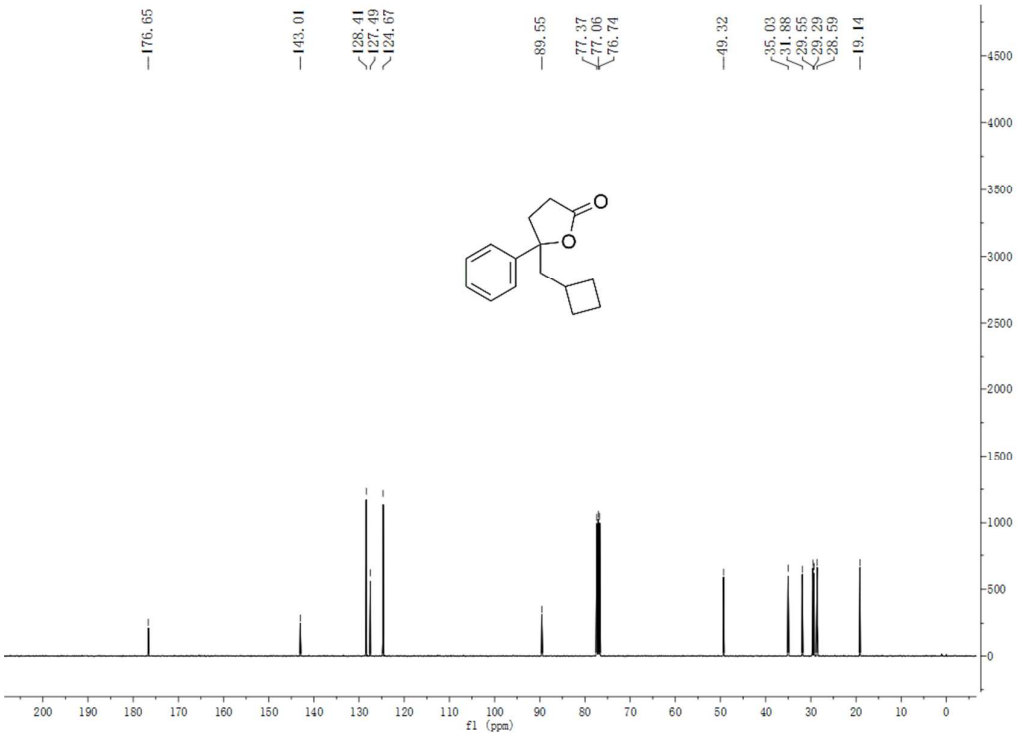
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ch**



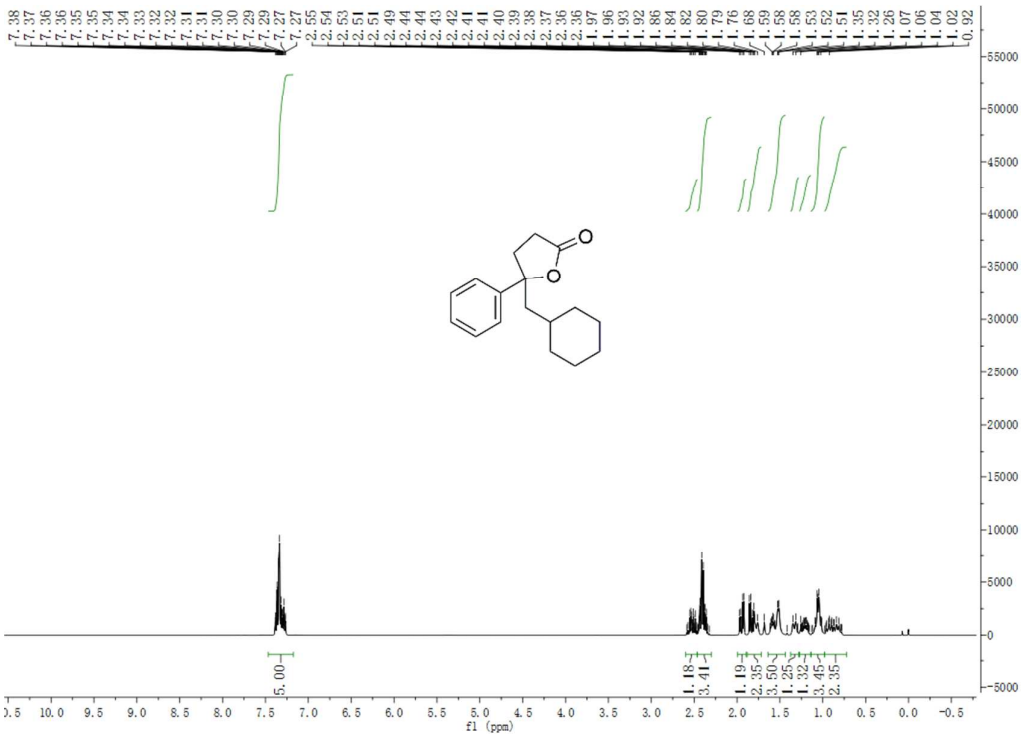
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ci**



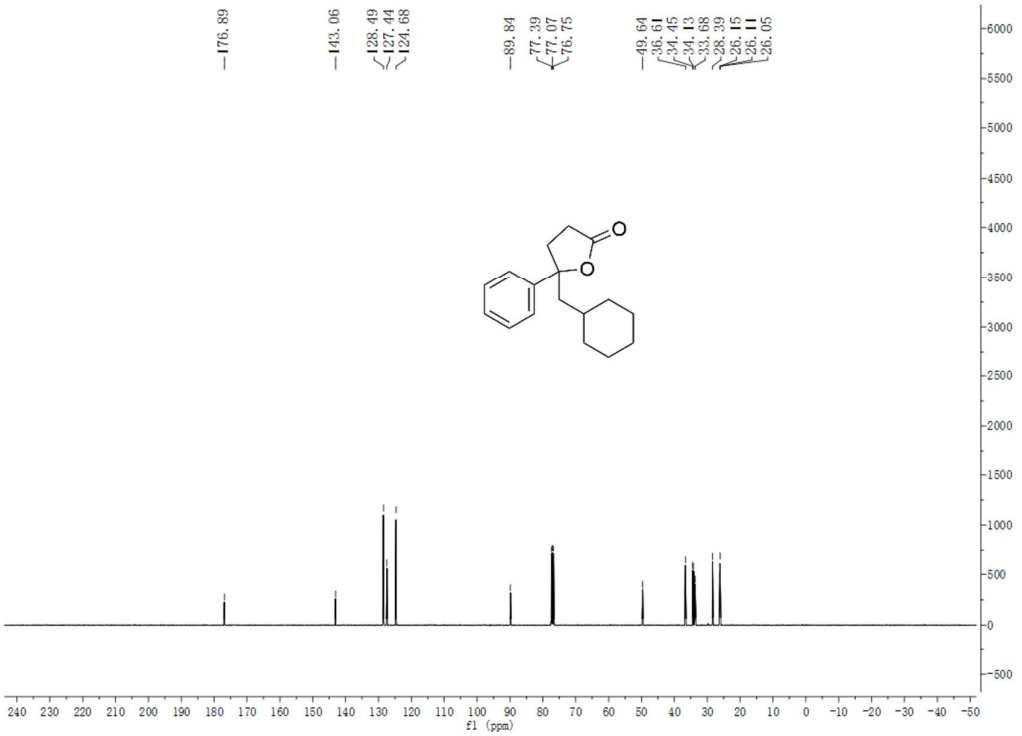
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ci**



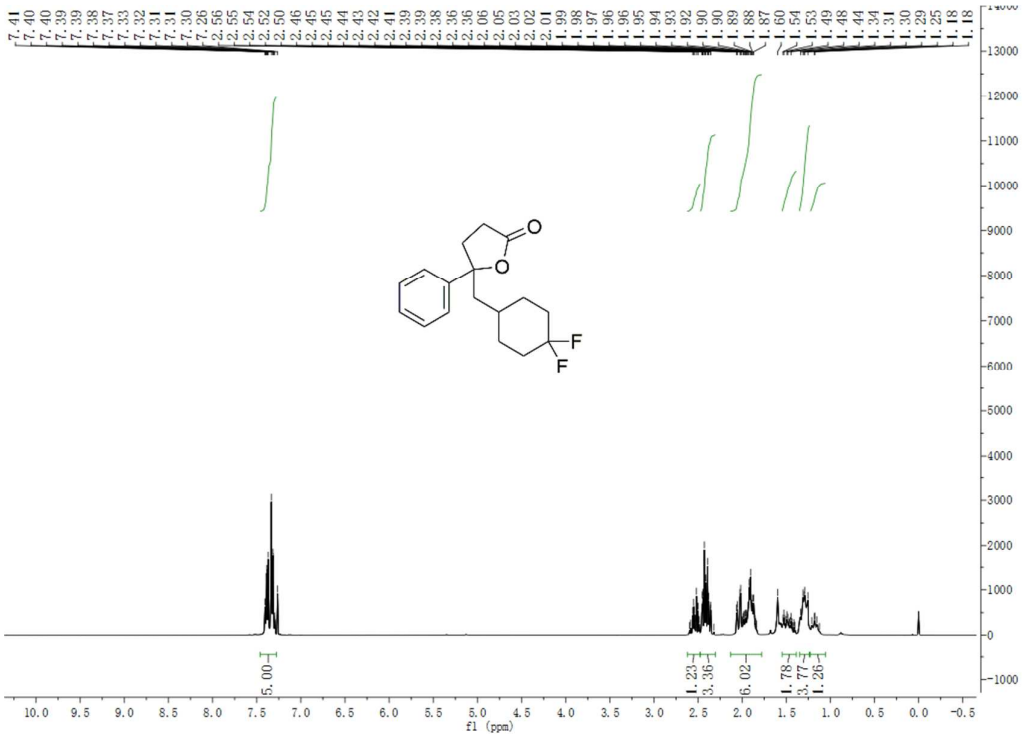
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3cj**



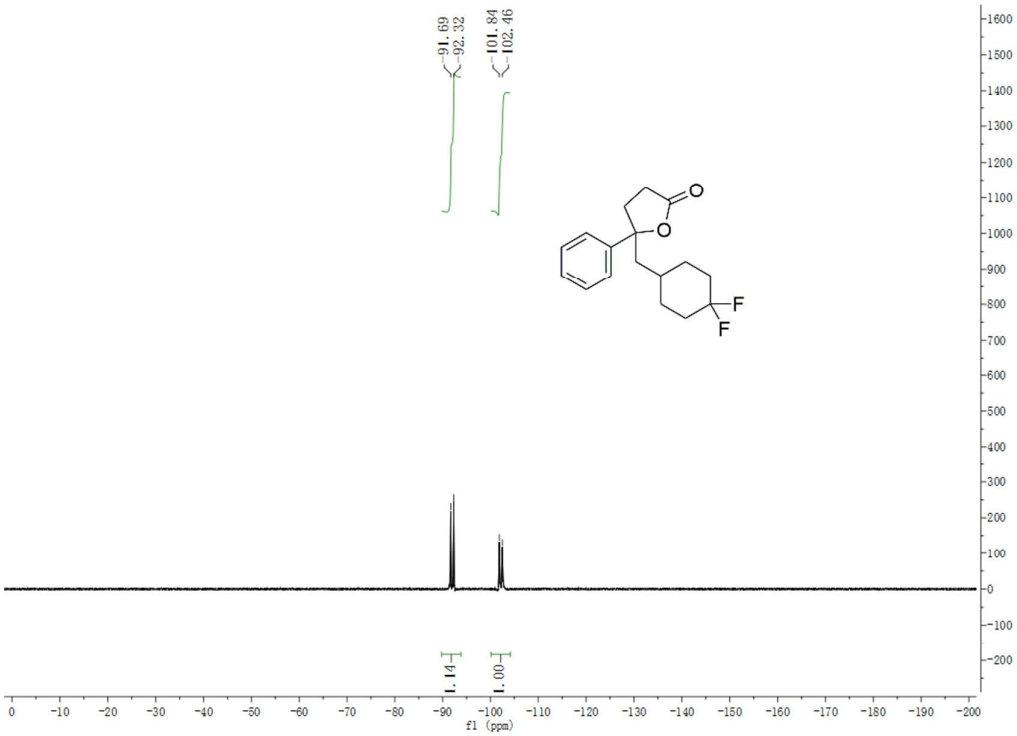
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3cj**



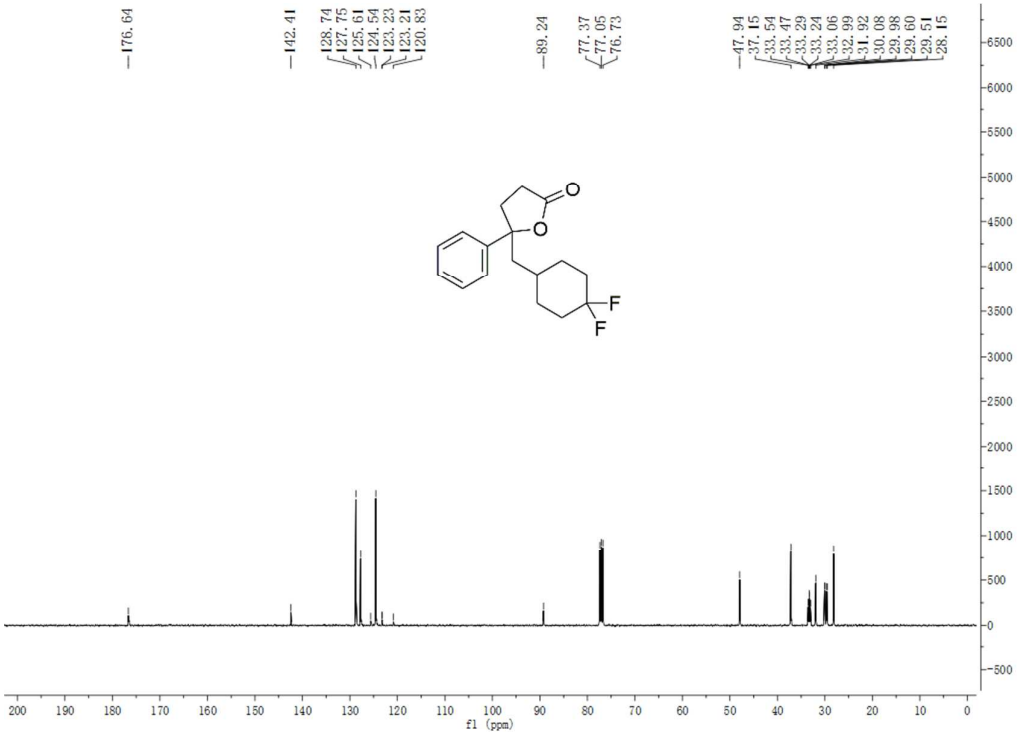
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ck**



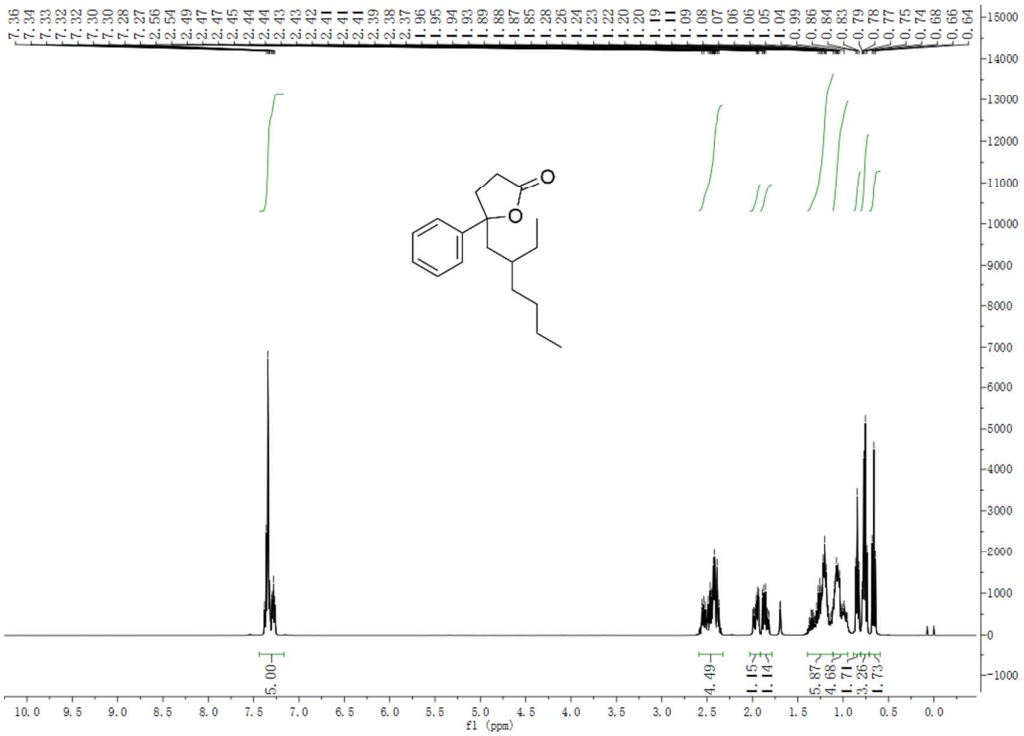
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ck**



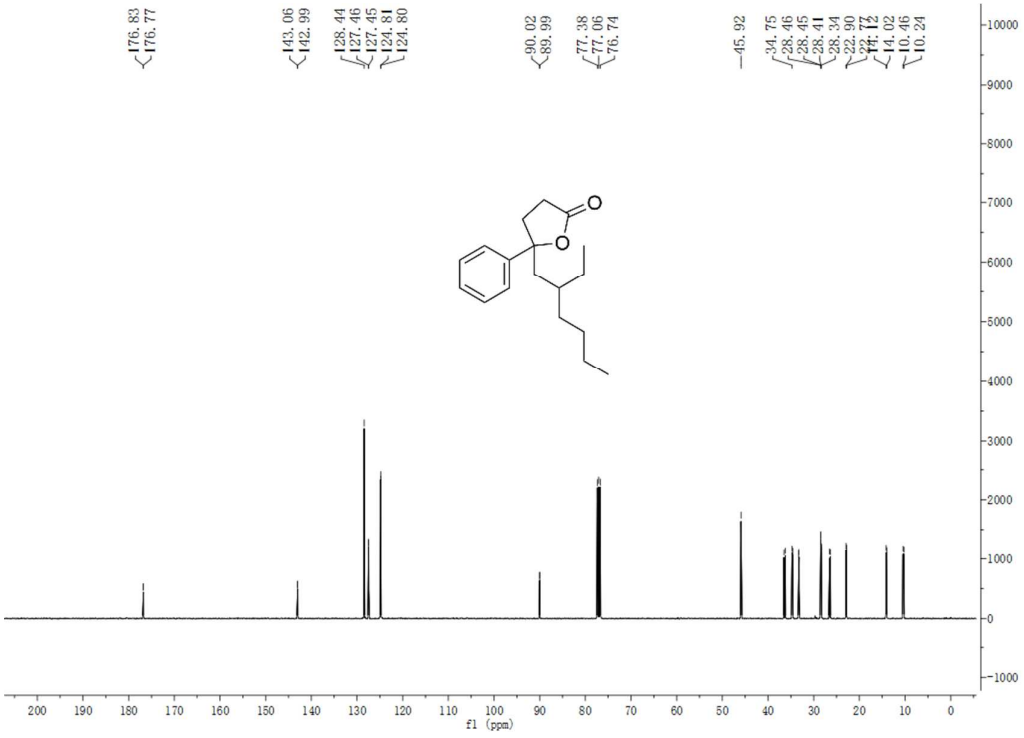
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ck**



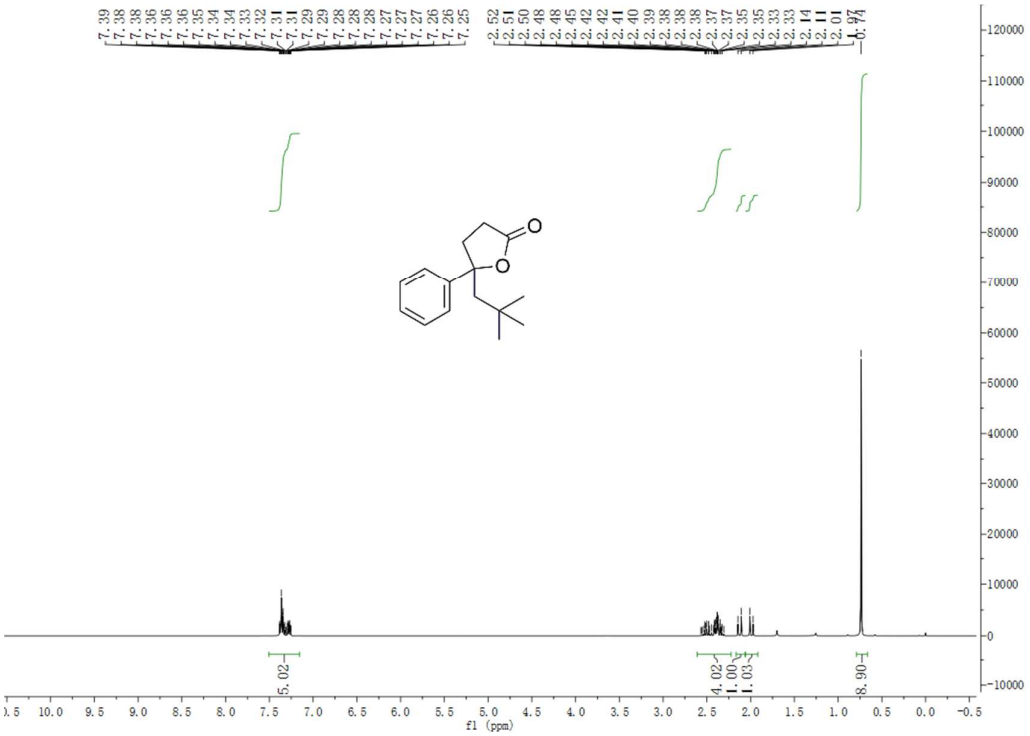
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3cl**



^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3cl**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3cm**



^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3cm**