Supplementary Information

CO_2-induced $ROCO_2Na$/$ROCO_2H$ buffer solution promoted carboxylative cyclization of propargyl alcohol to synthesize cyclic carbonate

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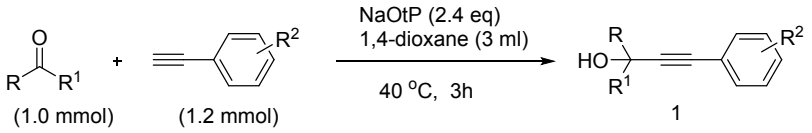
Contents

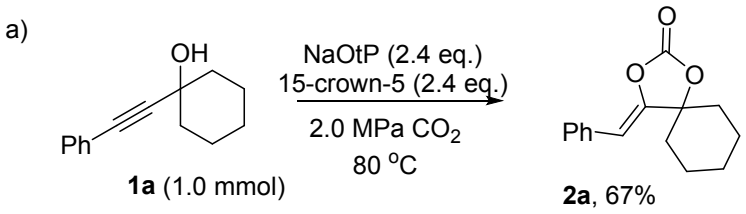
I. General synthetic procedure

Typical procedure for the synthesis of propargyl alcohol:[1, 2] NaOtP (2.4 equiv.) was dissolved in 1,4-dioxane (3 ml) to a schlenk tube, phenylacetylene (1.2 equiv.) was added and stirred for 5 minutes. Ketone (1.0 equiv.) was further added to react at 40 °C for 3 h. The completion of the reaction was examined by thin layer chromatography. **Workup:** The reaction mixture was quenched by saturated ammonium chloride solution and extracted with ethyl acetate three times (20 mL×3). The organic layer was washed with saturated sodium chloride solution and dried with anhydrous Na_2SO_4, then concentrated in vacuum. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1).

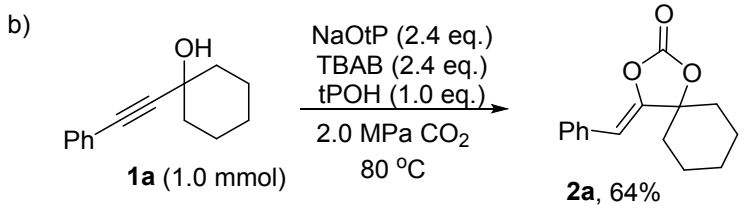


R = alkyl/H/heterocycle
R^1 = alkyl/H/heterocycle
R^2 = F/Br/alkyl/H

Mechanism verification:



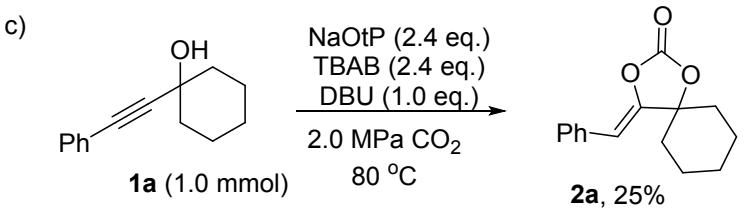
1a (200. 3mg, 1.0 mmol), TBAB (773.7 mg, 2.4 mmol), NaOtP (264.2 mg, 2.4 mmol), 1,4-dioxane (3 ml) were loaded into an inner glass liner in a 50 ml reactor. The autoclave was sealed and CO_2 pressure in the reactor was maintained at 2.0 MPa. The reactor was placed in a constant temperature oil bath at 80 °C and the reaction mixture was stirred for 24 hours. After the reaction time is over, the reactor is cooled in ice water bath for 30 minutes and CO_2 is released slowly. The organic layer obtained by three times extraction with ethyl acetate (20 mL×3) was rinsed with saturated sodium chloride solution, the organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was purified by silica gel chromatography.



1a (200.3mg, 1.0 mmol), TBAB (773.7 mg, 2.4 mmol), NaOtP (264.2 mg, 2.4 mmol), tert-amyl alcohol (88.2mg, 1.0mmol) 1,4-dioxane (3 ml) were loaded into an inner glass liner in a 50 ml reactor. The autoclave was sealed and CO_2 pressure in the reactor was maintained at 2.0 MPa. The reactor was placed in a constant temperature oil bath at 80 °C and the reaction mixture was stirred for 24 hours. After the reaction time is over, the reactor is cooled in ice water bath for 30 minutes and CO_2 is released slowly. The organic layer obtained by three times extraction with ethyl acetate (20 mL × 3) was rinsed with saturated sodium chloride solution, the organic layer was

dried with anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was purified by silica gel chromatography.

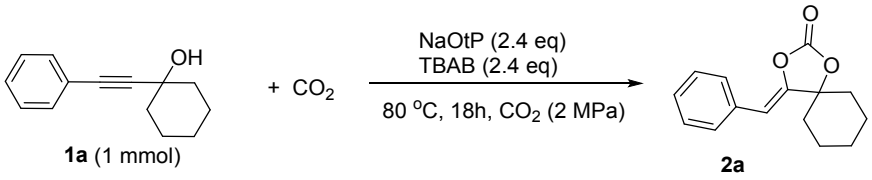
c)



1a (200. 3mg, 1.0 mmol), TBAB (773.7 mg, 2.4 mmol), NaOtP (264.2 mg, 2.4 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (152.2 mg, 1.0mmol) and 1,4-dioxane (3 ml) were loaded into an inner glass liner in a 50 ml reactor. The autoclave was sealed and CO_2 pressure in the reactor was maintained at 2.0 MPa. The reactor was placed in a constant temperature oil bath at 80 °C and the reaction mixture was stirred for 24 hours. After the reaction time is over, the reactor is cooled in ice water bath for 30 minutes and CO_2 is released slowly. The organic layer obtained by three times extraction with ethyl acetate (20 mL×3) was rinsed with saturated sodium chloride solution, the organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was purified by silica gel chromatography.

II Table S1

Table S1. Investigation on the effect of solvent.



Entry	NaOtP	TBAB	Solvent	T/°C	Yield/%
1	2.4eq	2.4eq	THF	80	61
2	2.4eq	2.4eq	Toluene	80	53
3	2.4eq	2.4eq	THF/1,4-dioxane (1:2)	80	49
4	2.4eq	2.4eq	MeCN	80	26
5	2.4eq	2.4eq	DMAc	80	NR
6	2.4eq	2.4eq	NMP	80	NR

Reaction conditions: 1-(phenylethynyl)cyclohexan-1-ol (**1a**) (1.0 mmol, 200.26 mg), NaOtP (2.4 mmol, 264.2 mg), TBAB (2.4 mmol, 773.7 mg), solvent (3 mL), 2.0 MPa CO_2, 80 °C, 18 h; the products are isolated by column chromatography.

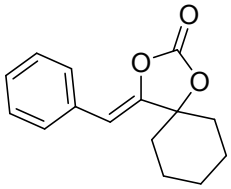
III. Reference

[1] Savarimuthu, S. A.; Thankappan, H.; Thomas, S. A.; Prakash, D. G. L. *ChemistrySelect*, **2018**, *3*(29), 8479-8482.

[2] Qiu, H.; Srinivas, H. D.; Zavalij, P. Y.; Doyle, M. P. *J. Am. Chem. Soc.*, **2016**, *138*(6), 1808-1811.

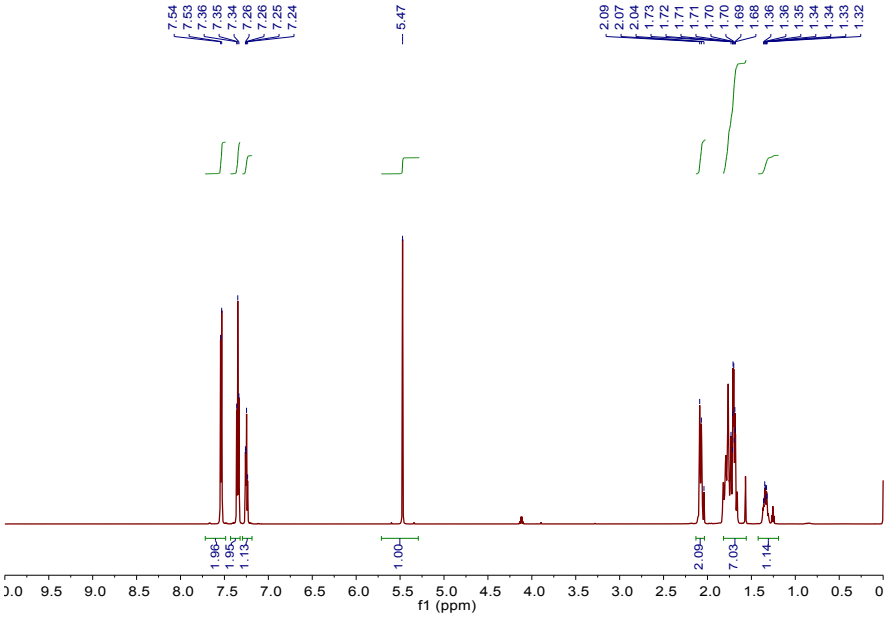
[3] Zhou, H.; Wang, G. X.; Lu, X. B. *Asian. J. Org. Chem.,* **2017**, *6*(9), 1264-1269.
[4] Zhou, Z.; He, C.; Yang, L.; Wang, Y.; Liu, T.; Duan, C. *ACS Catal.*, **2017**, *7*(3), 2248-2256.
[5] Qiu, J.; Zhao, Y.; Li, Z.; Wang, H.; Fan, M.; Wang, J. *ChemSusChem*, **2017**, *10*(6), 1120-1127.

IV. Copies of ^{1}H, ^{13}C NMR spectra of products

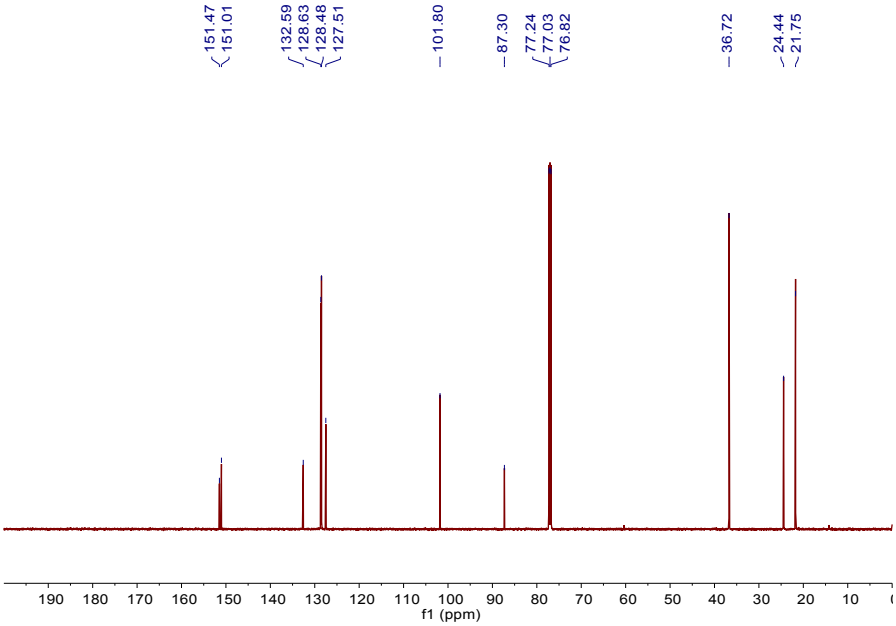


2a

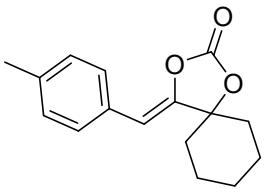
4-benzylidene-1,3-dioxaspiro[4.5]decan-2-one [3] (2a): white solid.



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 7.7 Hz, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.29 - 7.19 (m, 1H), 5.47 (s, 1H), 2.13 - 2.03 (m, 2H), 1.70 (td, J = 12.9, 11.7, 7.8 Hz, 7H), 1.34 (ddd, J = 12.0, 8.2, 3.6 Hz, 1H).

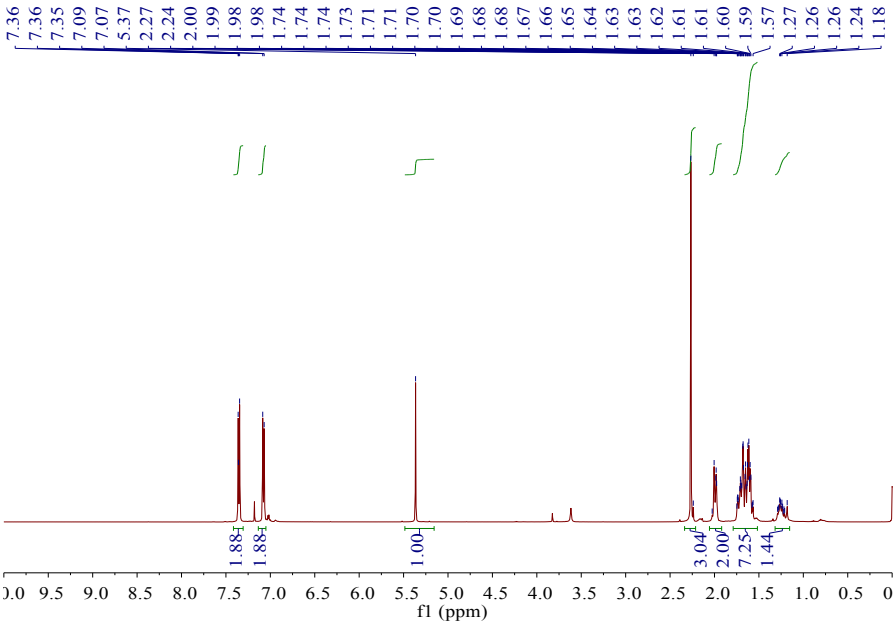


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.47, 151.01, 132.59, 128.63, 128.48, 127.51, 101.80, 87.30, 36.72, 24.44, 21.75.

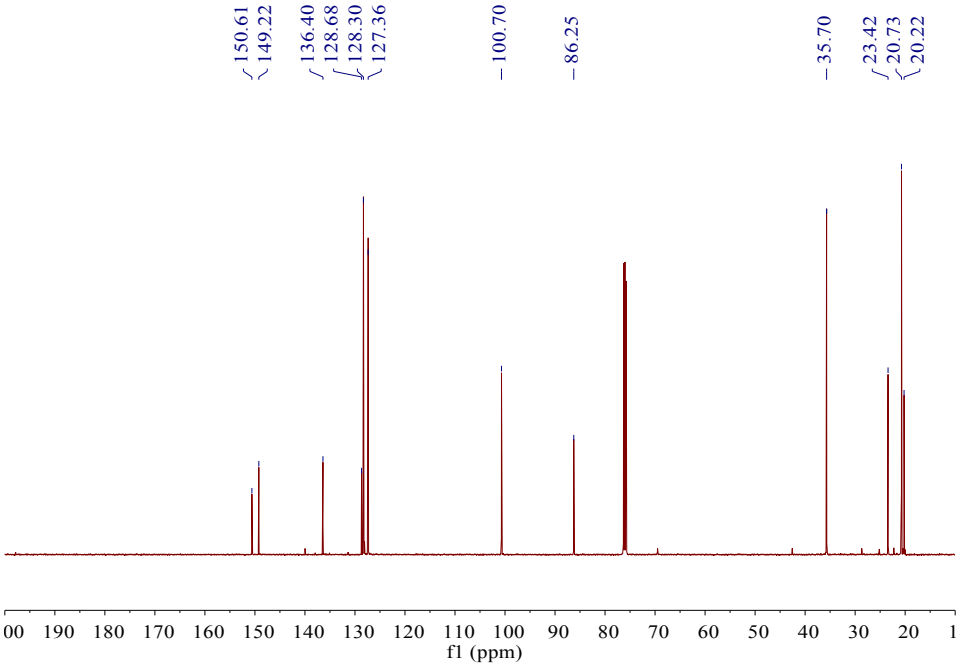


2b

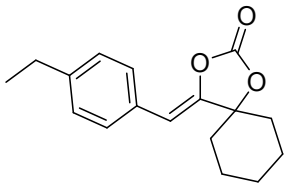
4-(4-methylbenzylidene)-1,3-dioxaspiro[4.5]decan-2-one(2b): pale yellow oil.



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.37 (s, 1H), 2.27 (s, 3H), 2.06 – 1.92 (m, 2H), 1.79 – 1.52 (m, 7H), 1.32 – 1.15 (m, 1H).

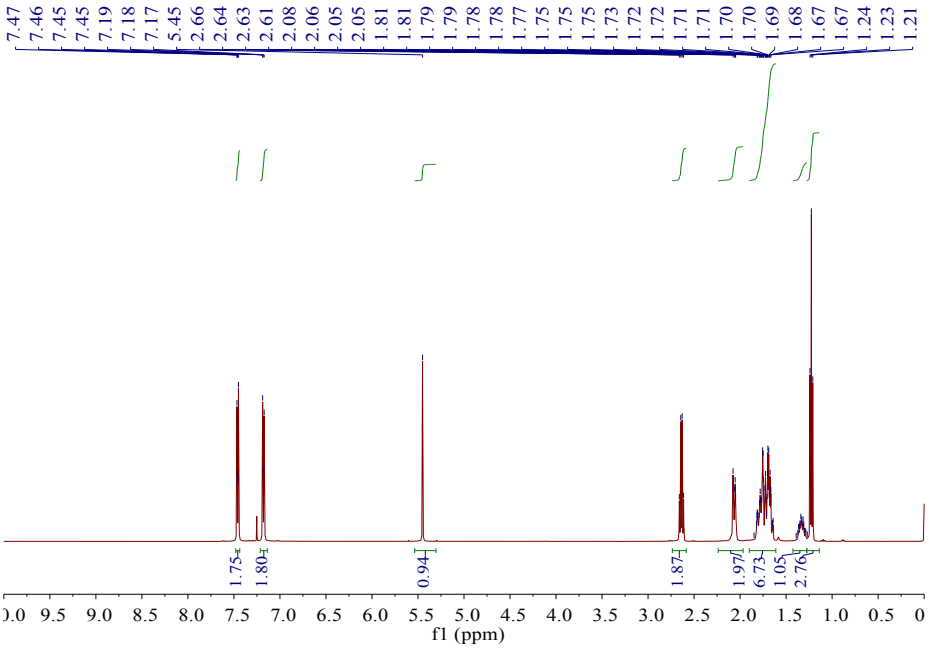


^{13}C NMR (126 MHz, $CDCl_3$) δ 150.61, 149.22, 136.40, 128.68, 128.30, 127.36, 100.70, 86.25, 35.70, 23.42, 20.73, 20.22.

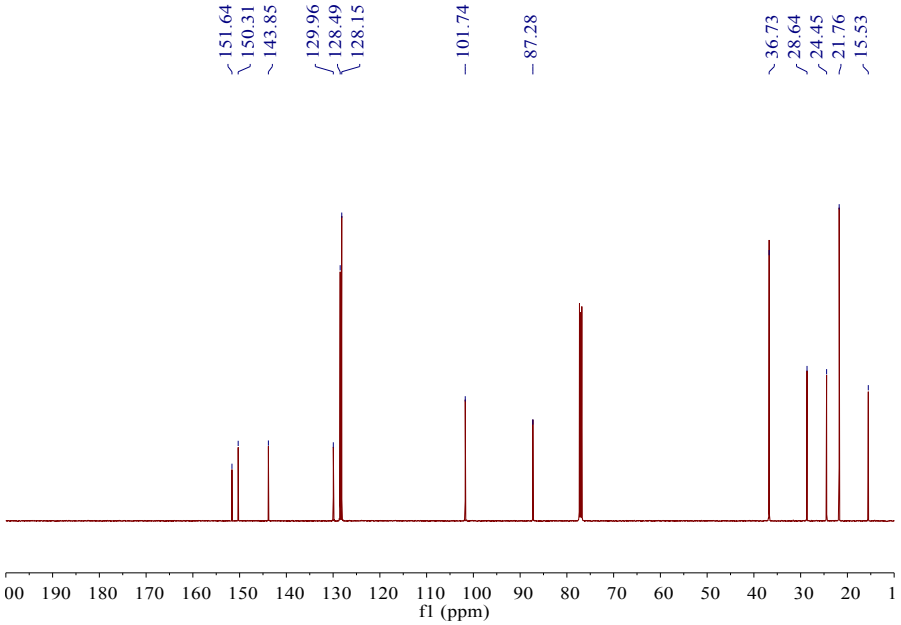


2c

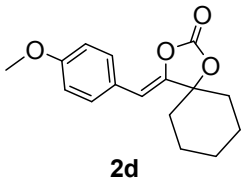
4-(4-ethylbenzylidene)-1,3-dioxaspiro[4.5]decan-2-one (2c): pale yellow solid.



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 – 7.44 (m, 2H), 7.18 (d, J = 8.1 Hz, 2H), 5.45 (s, 1H), 2.64 (q, J = 7.6 Hz, 2H), 2.24 – 1.97 (m, 2H), 1.90 – 1.61 (m, 7H), 1.33 (qt, J = 11.1, 3.8 Hz, 1H), 1.23 (t, J = 7.6 Hz, 3H).

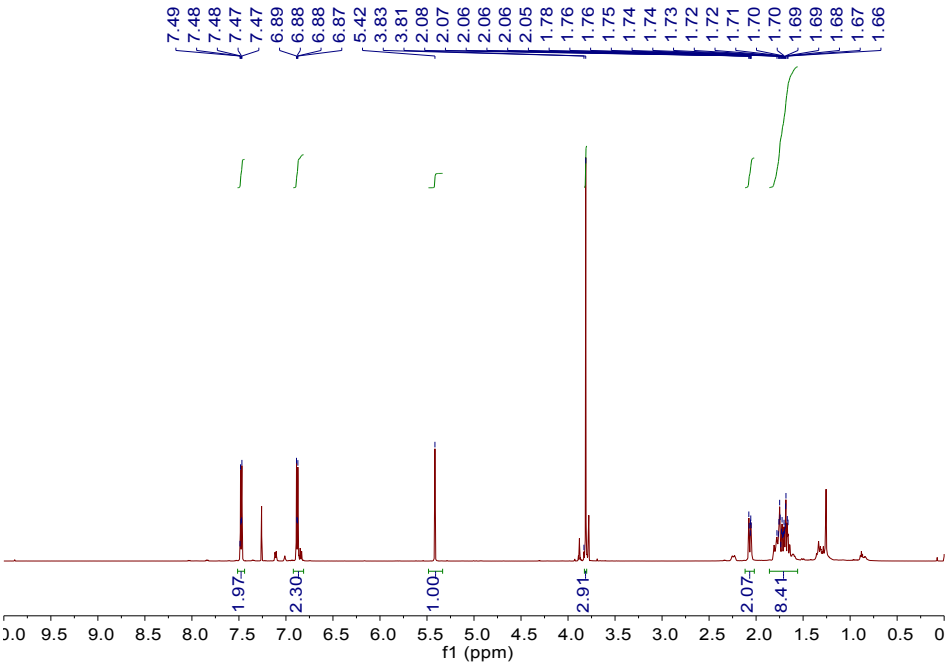


^{13}C NMR (126 MHz, $CDCl_3$) δ 151.64, 150.31, 143.85, 129.96, 128.49, 128.15, 101.74, 87.28, 36.73, 28.64, 24.45, 21.76, 15.53.

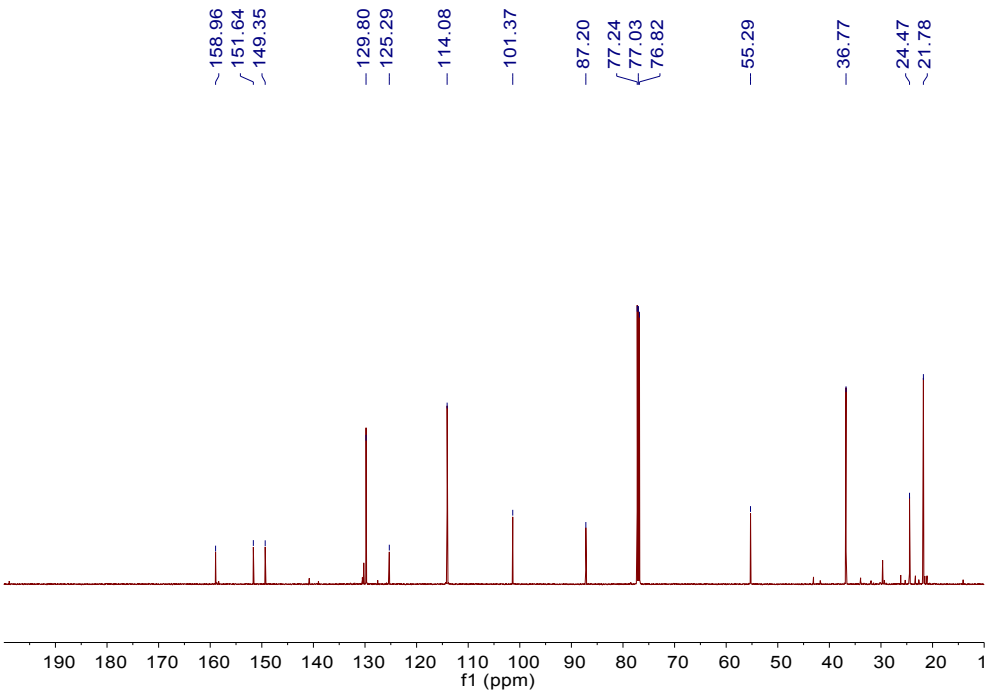


2d

4-(4-methoxybenzylidene)-1,3-dioxaspiro[4.5]decan-2-one (2d): pale yellow solid.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 - 7.44 (m, 2H), 6.92 - 6.81 (m, 2H), 5.42 (s, 1H), 3.81 (s, 3H), 2.12 - 2.02 (m, 2H), 1.77 - 1.66 (m, 8H).



^{13}C NMR (151 MHz, $CDCl_3$): δ 158.96, 151.64, 149.35, 129.80, 125.29, 114.08, 101.37, 87.20, 55.29, 36.77, 24.47, 21.78.

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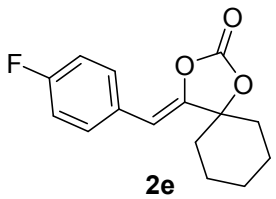
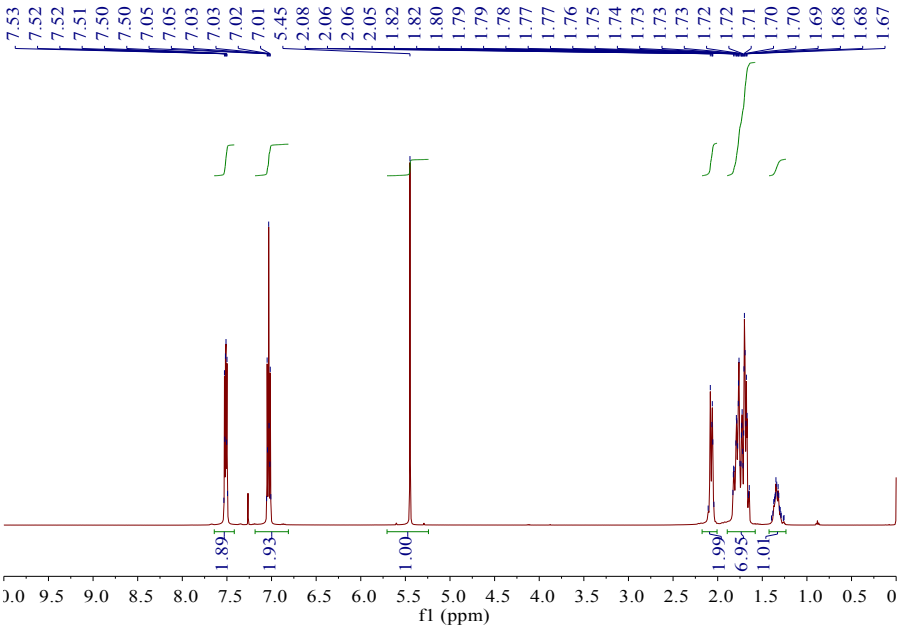
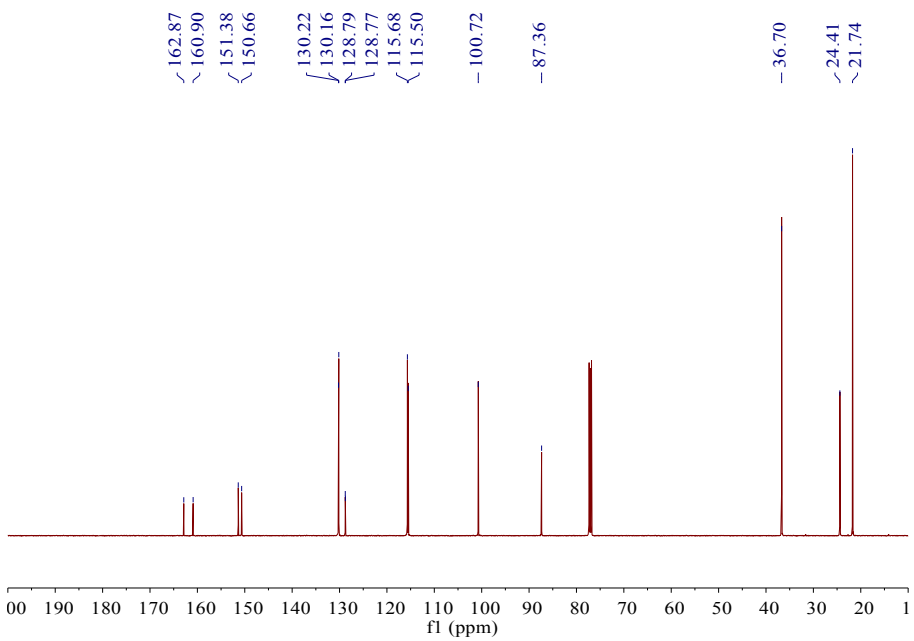


2e

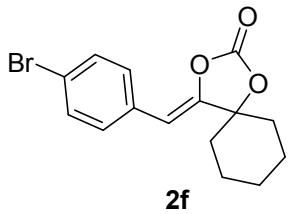
4-(4-fluorobenzylidene)-1,3-dioxaspiro[4.5]decan-2-one (2e): yellow solid.



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.42 (m, 2H), 7.18 – 6.81 (m, 2H), 5.45 (s, 1H), 2.17 – 2.01 (m, 2H), 1.89 – 1.58 (m, 7H), 1.33 (tdd, J = 15.3, 7.7, 3.9 Hz, 1H).

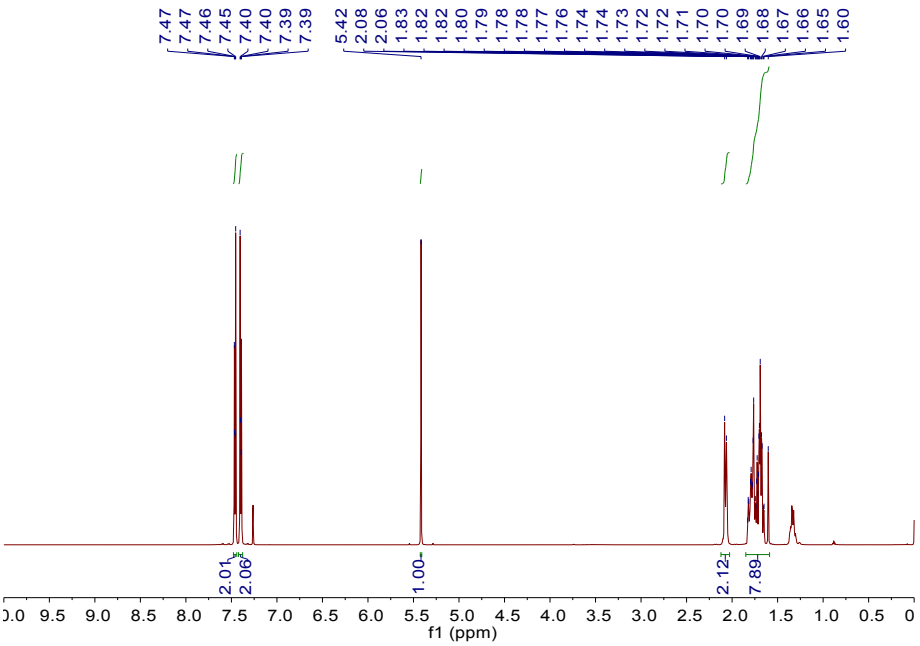


^{13}C NMR (126 MHz, $CDCl_3$) δ 162.87, 160.90, 151.38, 150.66, 130.22, 130.16, 128.79, 128.77, 115.68, 115.50, 100.72, 87.36, 36.70, 24.41, 21.74.

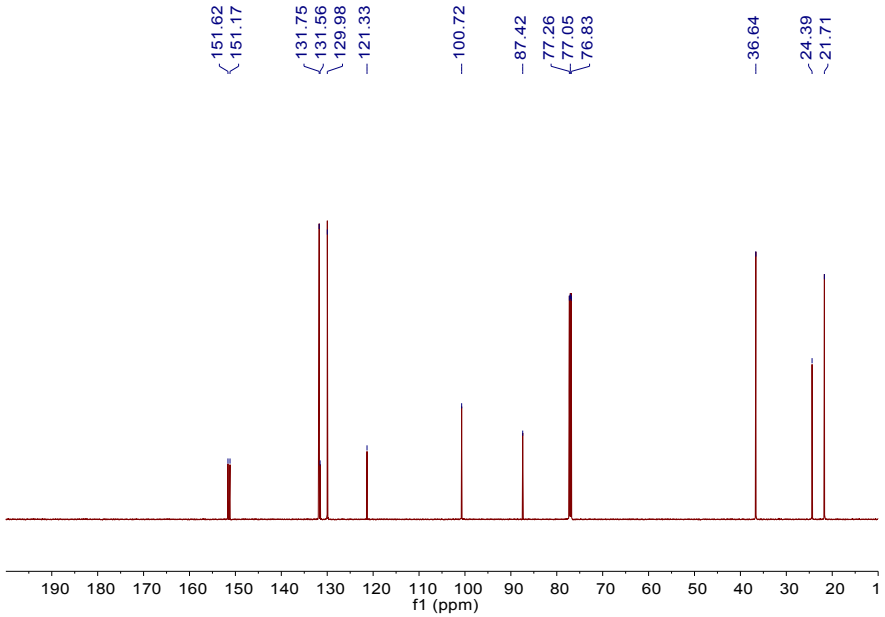


2f

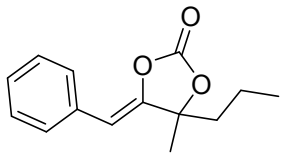
4-(4-bromobenzylidene)-1,3-dioxaspiro[4.5]decan-2-one (2f): white solid.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 - 7.44 (m, 2H), 7.42 - 7.38 (m, 2H), 5.42 (s, 1H), 2.07 (d, J = 11.9 Hz, 2H), 1.85 - 1.59 (m, 8H).

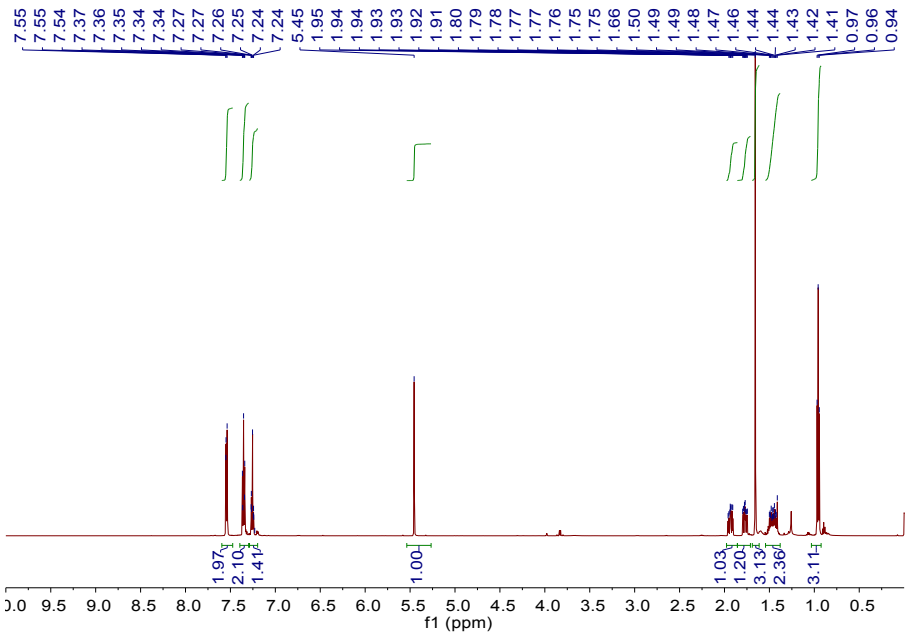


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.62, 151.17, 131.75, 131.56, 129.98, 121.33, 100.72, 87.42, 36.64, 24.39, 21.71.

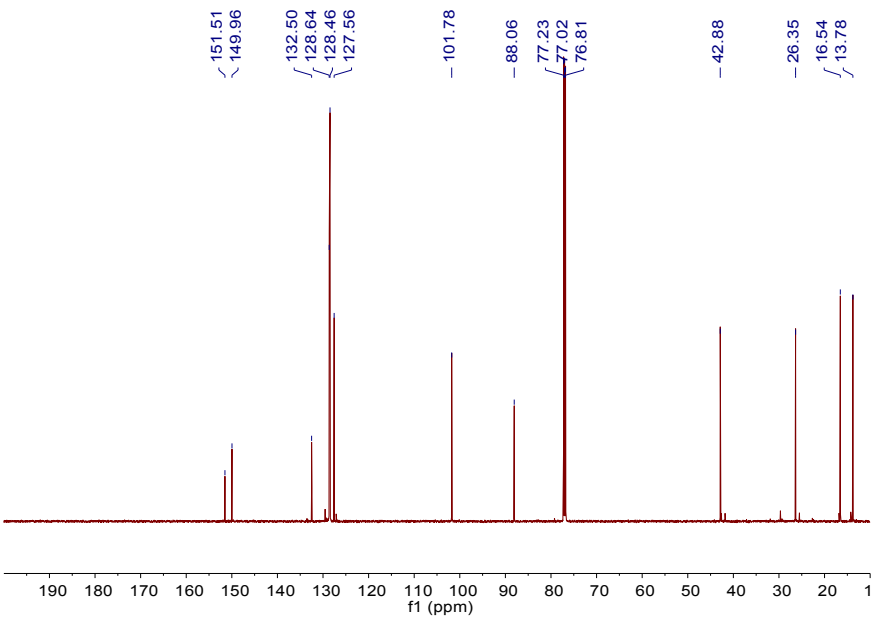


2g

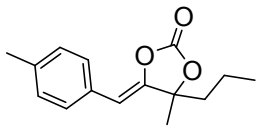
5-benzylidene-4-methyl-4-propyl-1,3-dioxolan-2-one (2g): pale yellow oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 - 7.47 (m, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.29 - 7.20 (m, 1H), 5.45 (s, 1H), 1.93 (ddd, J = 14.3, 11.7, 4.9 Hz, 1H), 1.77 (ddd, J = 14.4, 11.6, 4.9 Hz, 1H), 1.66 (s, 3H), 1.54 - 1.38 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).

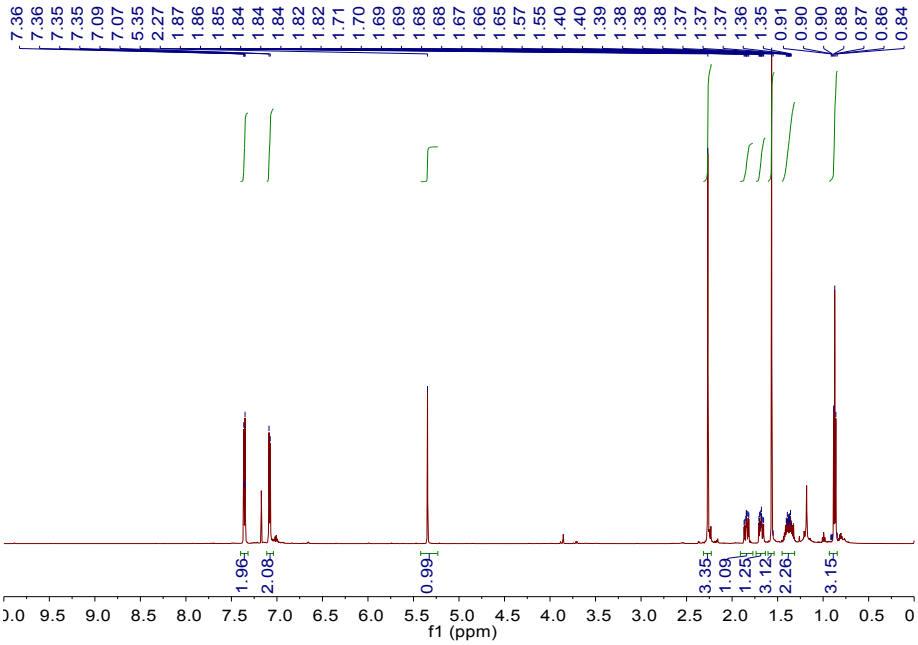


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.51, 149.96, 132.50, 128.64, 128.46, 127.56, 101.78, 88.06, 42.88, 26.35, 16.54, 13.78.

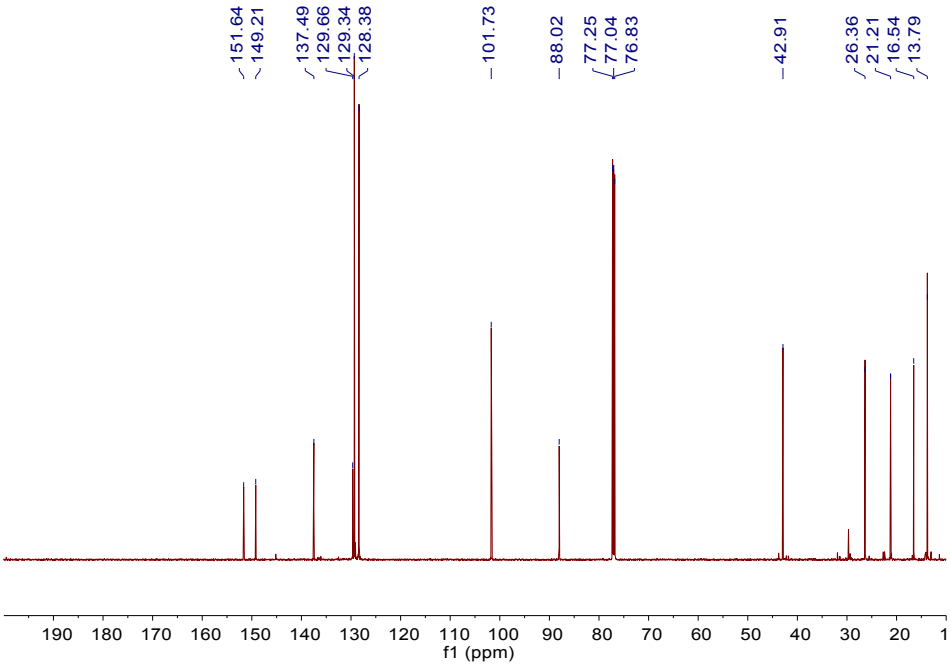


2h

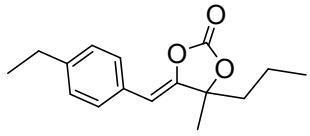
4-methyl-5-(4-methylbenzylidene)-4-propyl-1,3-dioxolan-2-one (2h): pale yellow oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 - 7.32 (m, 2H), 7.08 (d, J = 7.9 Hz, 2H), 5.35 (s, 1H), 2.27 (s, 3H), 1.84 (ddd, J = 14.4, 11.7, 4.9 Hz, 1H), 1.74 - 1.63 (m, 1H), 1.57 (s, 3H), 1.45 - 1.31 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H).

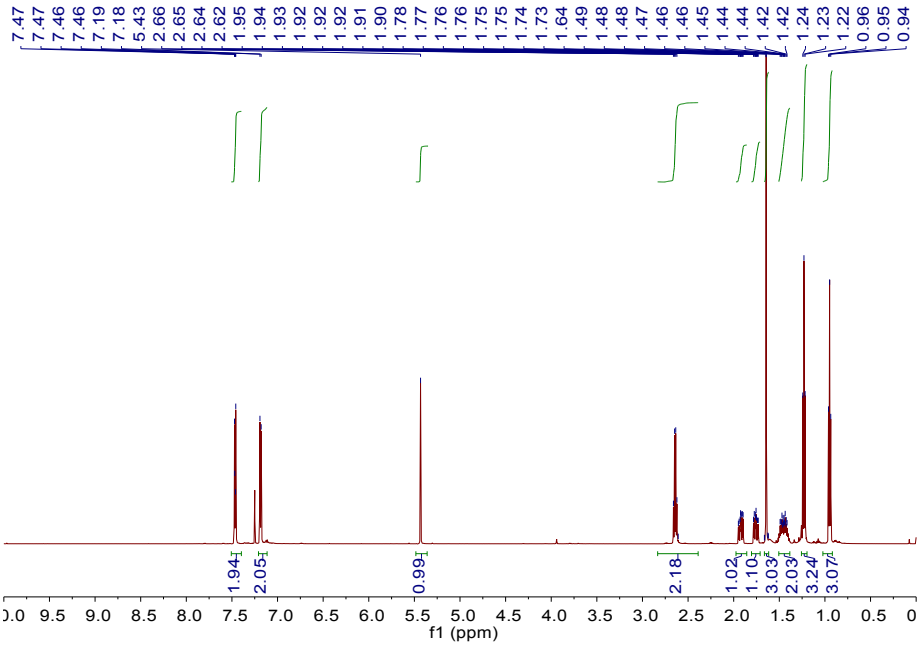


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.64, 149.21, 137.49, 129.66, 129.34, 128.38, 101.73, 88.02, 42.91, 26.36, 21.21, 16.54, 13.79.

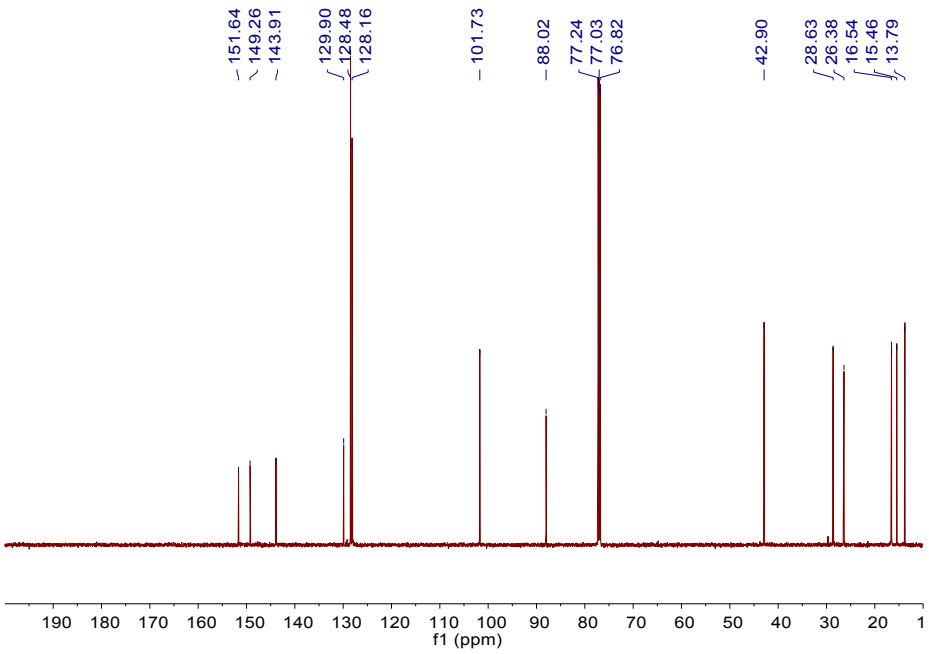


2i

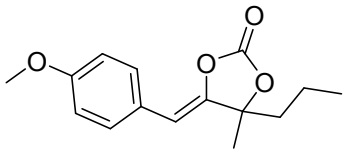
5-(4-ethylbenzylidene)-4-methyl-4-propyl-1,3-dioxolan-2-one (2i): pale yellow oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 - 7.40 (m, 2H), 7.19 (d, J = 8.1 Hz, 2H), 5.43 (s, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.92 (ddd, J = 14.4, 11.6, 4.9 Hz, 1H), 1.76 (ddd, J = 14.5, 11.6, 4.8 Hz, 1H), 1.64 (s, 3H), 1.45 (dddd, J = 21.4, 12.4, 7.8, 5.3 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H).

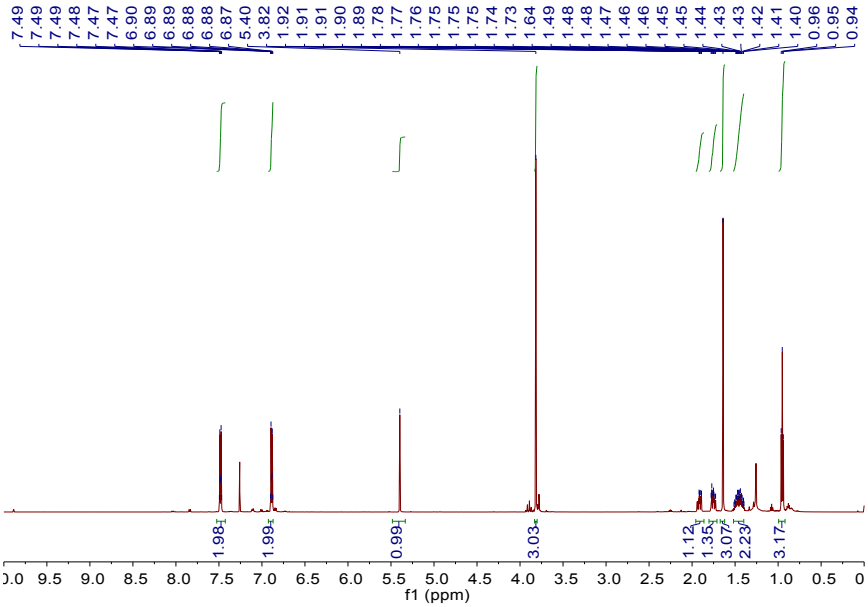


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.64, 149.26, 143.91, 129.90, 128.48, 128.16, 101.73, 88.02, 42.90, 28.63, 26.38, 16.54, 15.46, 13.79.

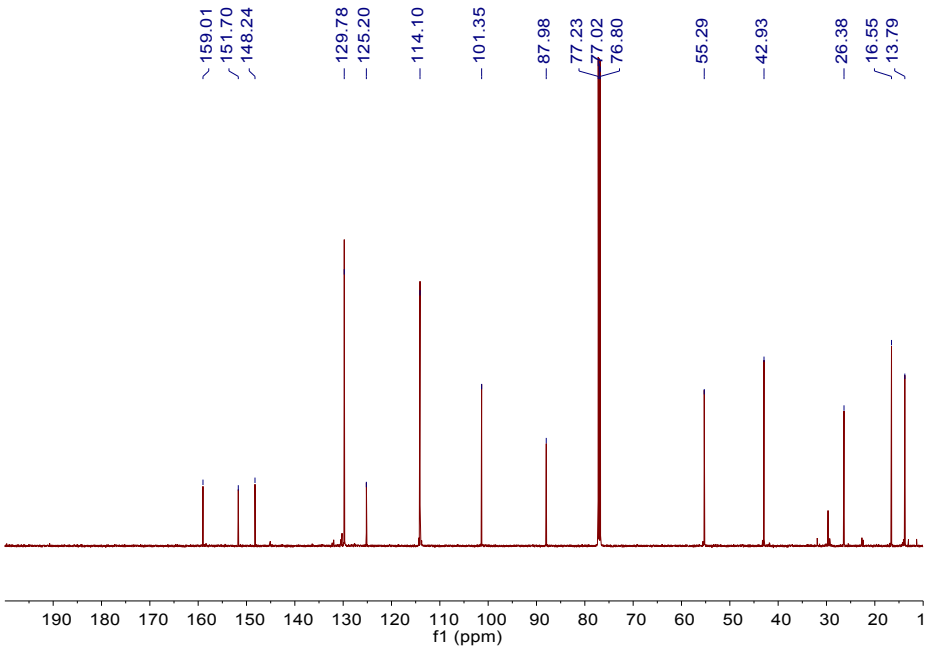


2j

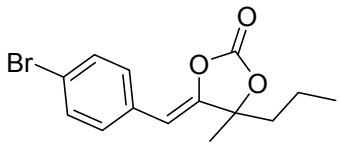
5-(4-methoxybenzylidene)-4-methyl-4-propyl-1,3-dioxolan-2-one (2j): pale yellow oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 - 7.43 (m, 2H), 6.93 - 6.87 (m, 2H), 5.40 (s, 1H), 3.82 (s, 3H), 1.96 - 1.86 (m, 1H), 1.75 (ddd, J = 14.5, 11.6, 4.8 Hz, 1H), 1.64 (s, 3H), 1.52 - 1.40 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H).

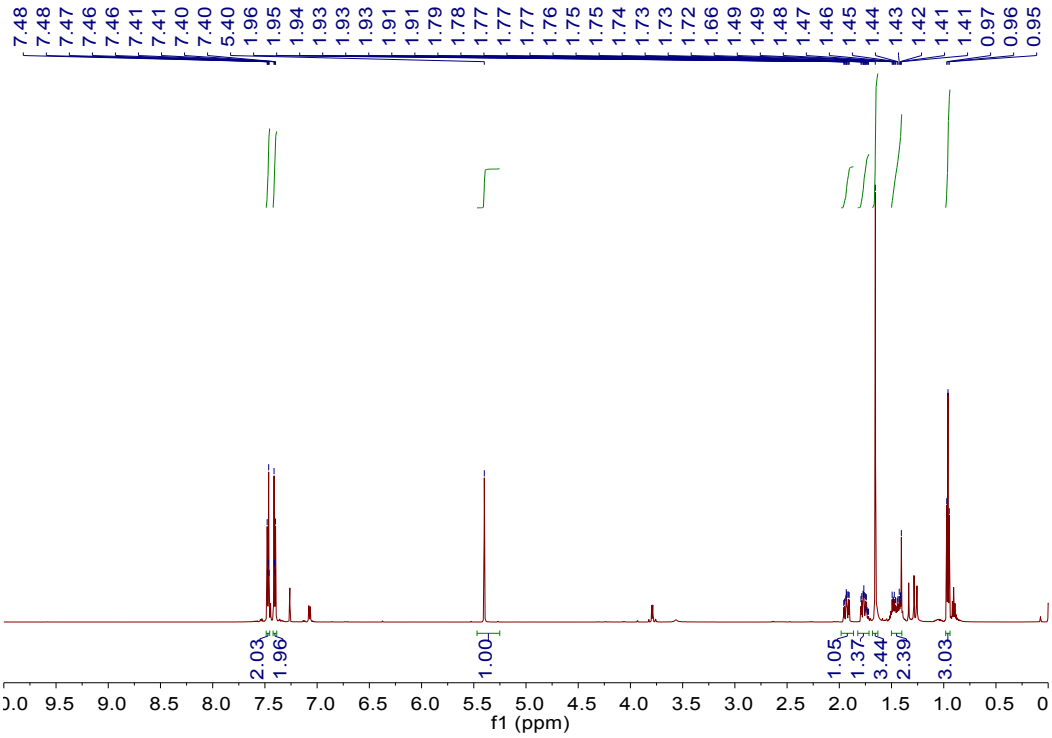


^{13}C NMR (151 MHz, $CDCl_3$): δ 159.01, 151.70, 148.24, 129.78, 125.20, 114.10, 101.35, 87.98, 55.29, 42.93, 26.38, 16.55, 13.79.

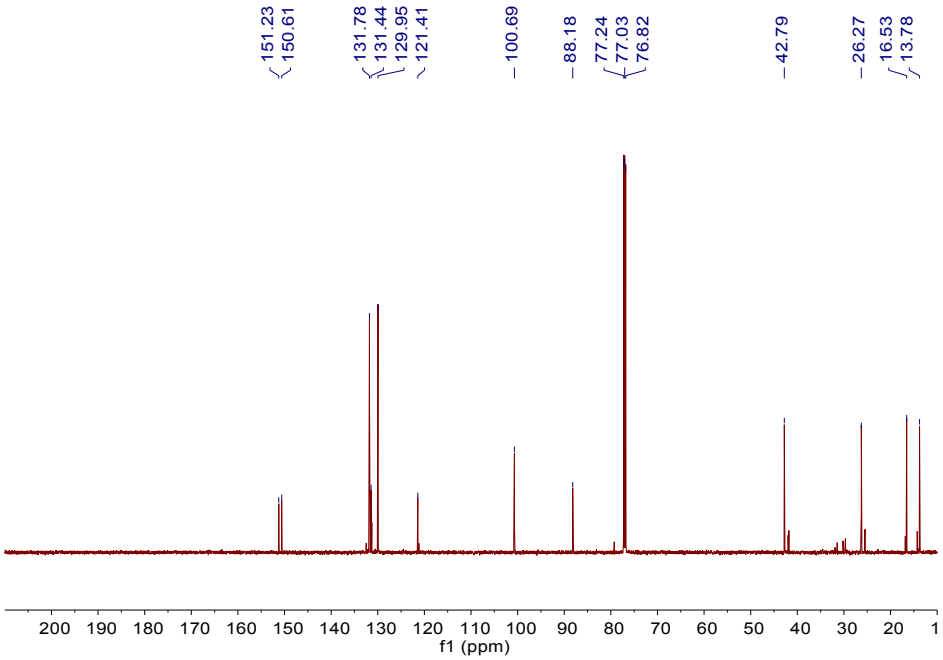


2k

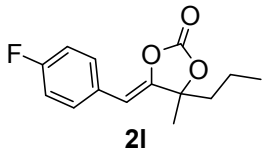
5-(4-bromobenzylidene)-4-methyl-4-propyl-1,3-dioxolan-2-one(2k): pale yellow oil



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 - 7.45 (m, 2H), 7.42 - 7.39 (m, 2H), 5.40 (s, 1H), 1.93 (ddd, J = 14.4, 11.8, 4.8 Hz, 1H), 1.82 - 1.72 (m, 1H), 1.66 (s, 3H), 1.50 - 1.40 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H).

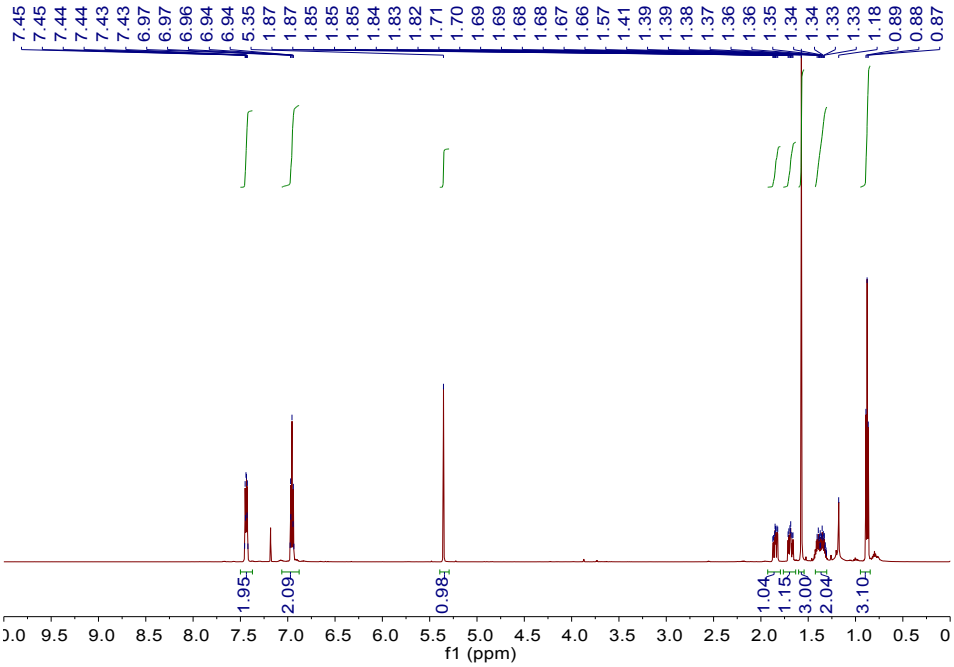


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.23, 150.61, 131.78, 131.44, 129.95, 121.41, 100.69, 88.18, 42.79, 26.27, 16.53, 13.78.

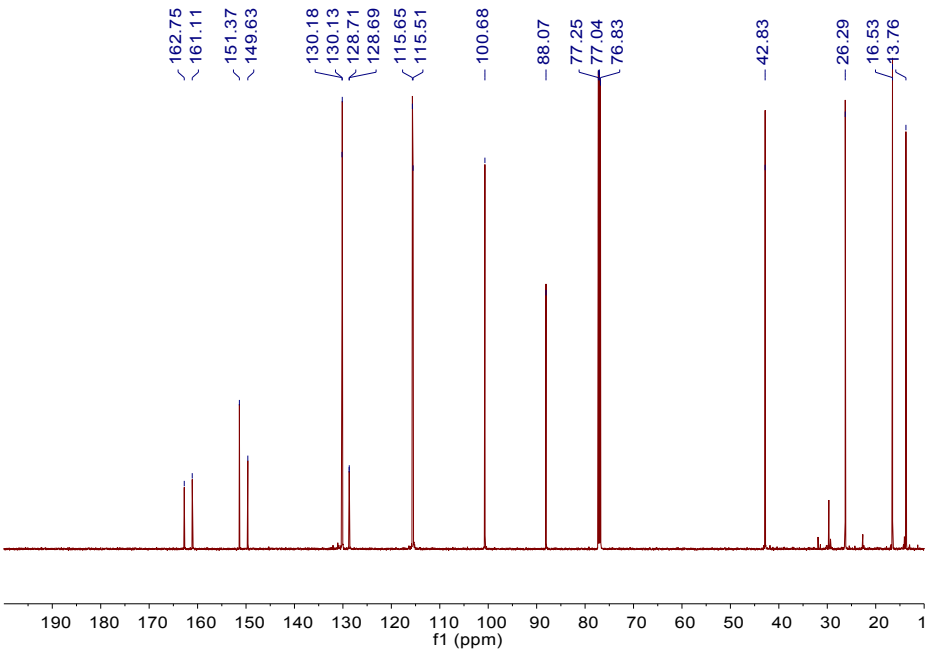


2l

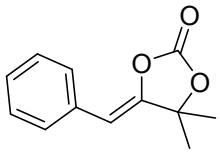
5-(4-fluorobenzylidene)-4-methyl-4-propyl-1,3-dioxolan-2-one (2l): pale yellow solid.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 - 7.37 (m, 2H), 6.96 (t, J = 8.7 Hz, 2H), 5.35 (s, 1H), 1.85 (ddd, J = 14.5, 11.7, 4.9 Hz, 1H), 1.69 (ddd, J = 14.4, 11.6, 4.8 Hz, 1H), 1.57 (s, 3H), 1.42 - 1.30 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H).

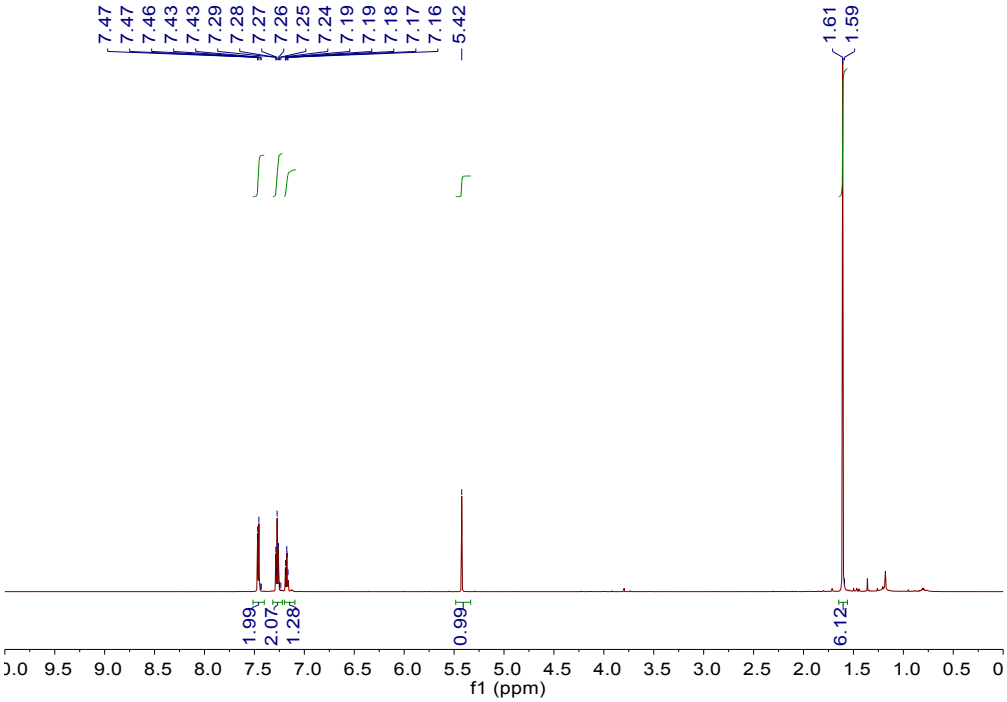


^{13}C NMR (151 MHz, $CDCl_3$): δ 162.75, 161.11, 151.37, 149.63, 130.18, 130.13, 128.71, 128.69, 115.65, 115.51, 100.68, 88.07, 42.83, 26.29, 16.53, 13.76.

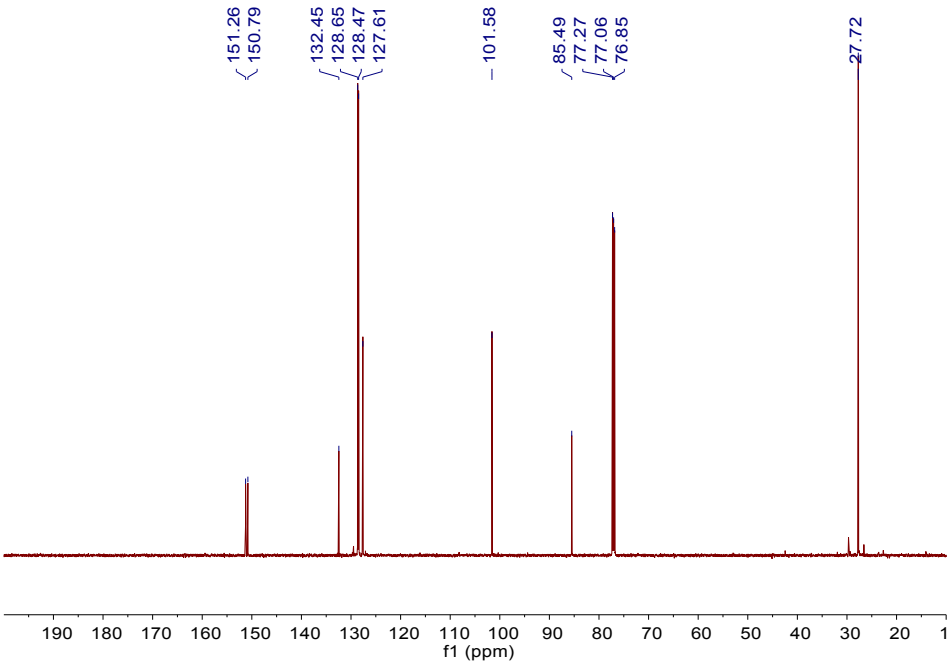


2m

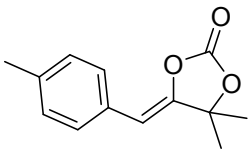
5-benzylidene-4,4-dimethyl-1,3-dioxolan-2-one [4](2m): pale yellow oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 - 7.40 (m, 2H), 7.27 (t, J = 7.7 Hz, 2H), 7.20 - 7.09 (m, 1H), 5.42 (s, 1H), 1.61 (s, 6H).

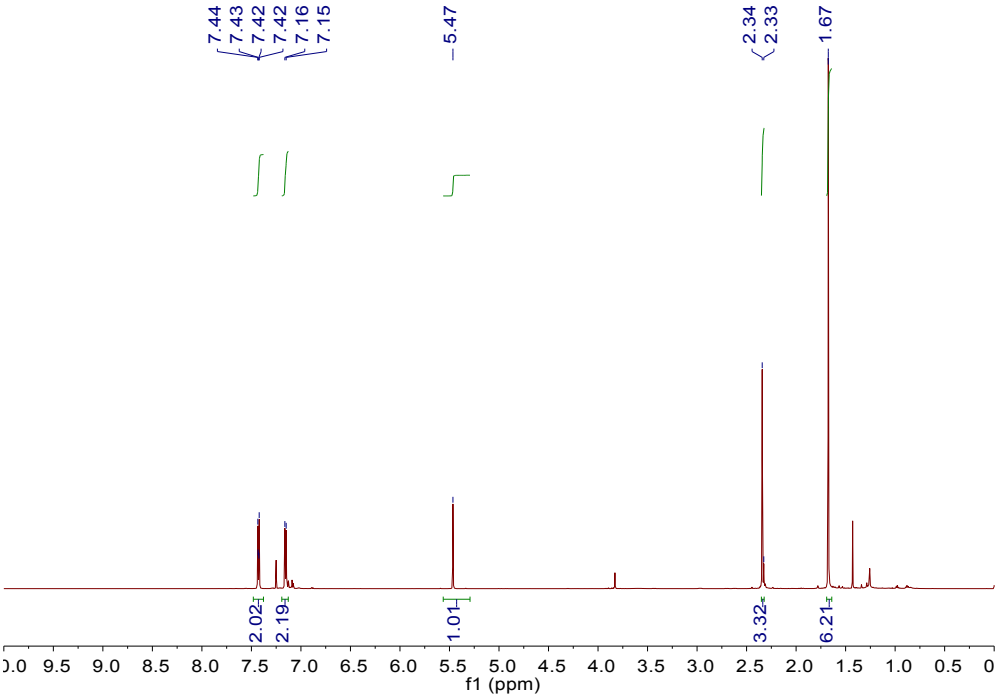


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.26, 150.79, 132.45, 128.65, 128.47, 127.61, 101.58, 85.49, 27.72.

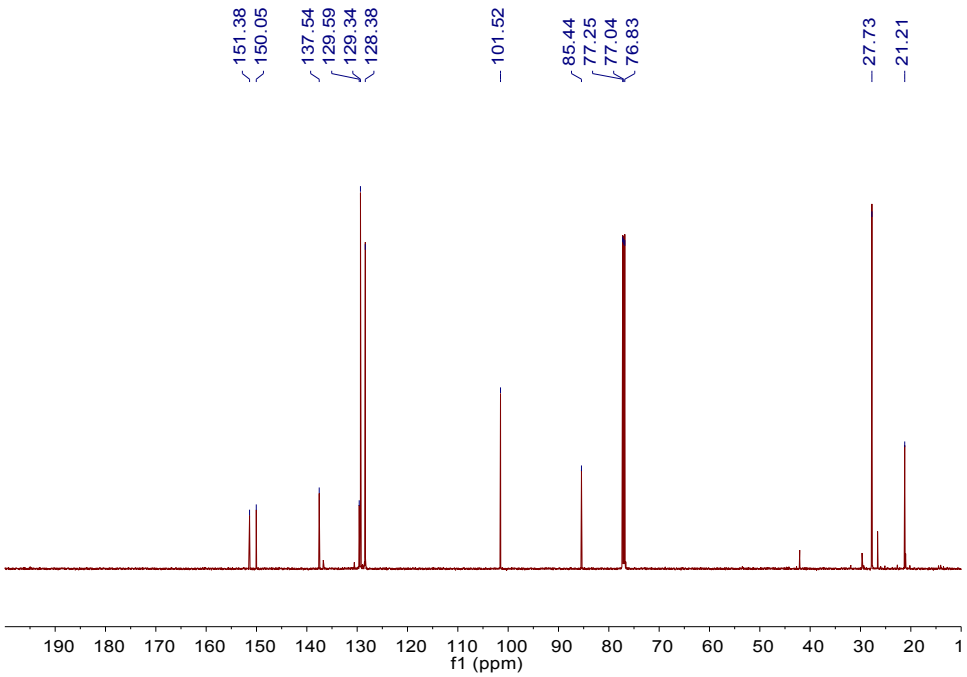


2n

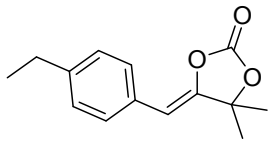
4,4-dimethyl-5-(4-methylbenzylidene)-1,3-dioxolan-2-one [4](2n): pale yellow oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 - 7.38 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 5.47 (s, 1H), 2.34 (s, 3H), 1.67 (s, 6H).

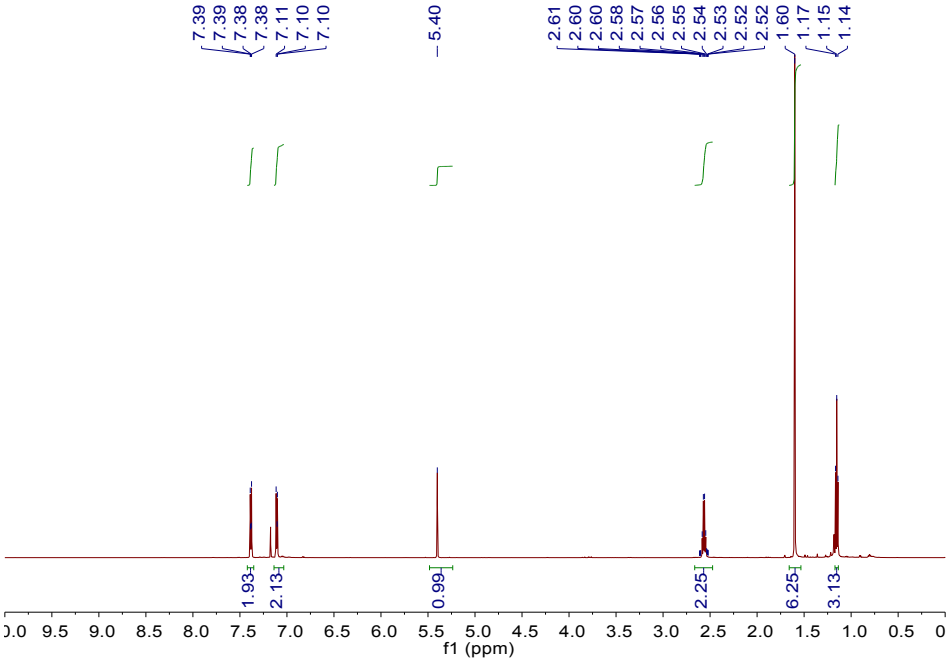


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.38, 150.05, 137.54, 129.59, 129.34, 128.38, 101.52, 85.44, 27.73, 21.21.

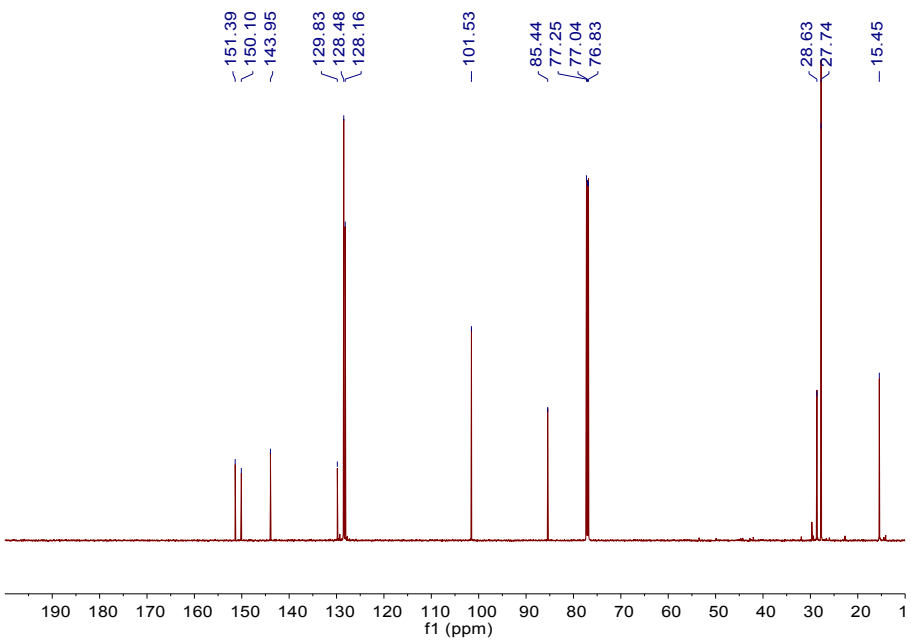


2o

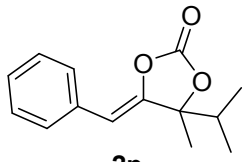
5-(4-ethylbenzylidene)-4,4-dimethyl-1,3-dioxolan-2-one [4](2o): pale yellow oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 - 7.35 (m, 2H), 7.11 (d, J = 8.1 Hz, 2H), 5.40 (s, 1H), 2.56 (q, J = 7.6 Hz, 2H), 1.60 (s, 6H), 1.15 (t, J = 7.6 Hz, 3H).

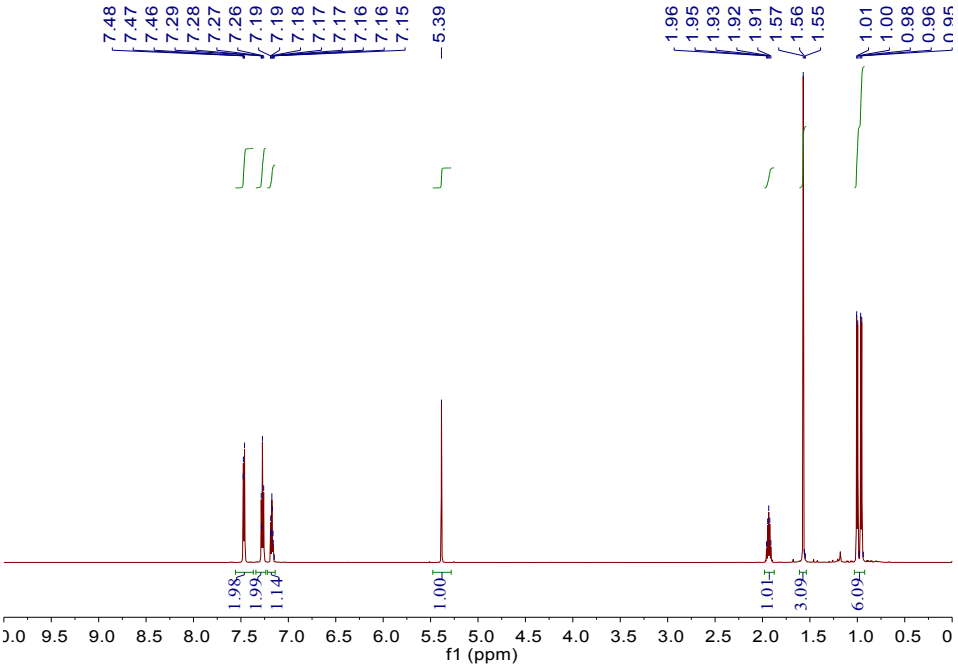


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.39, 150.10, 143.95, 129.83, 128.48, 128.16, 101.53, 85.44, 28.63, 27.74, 15.45.

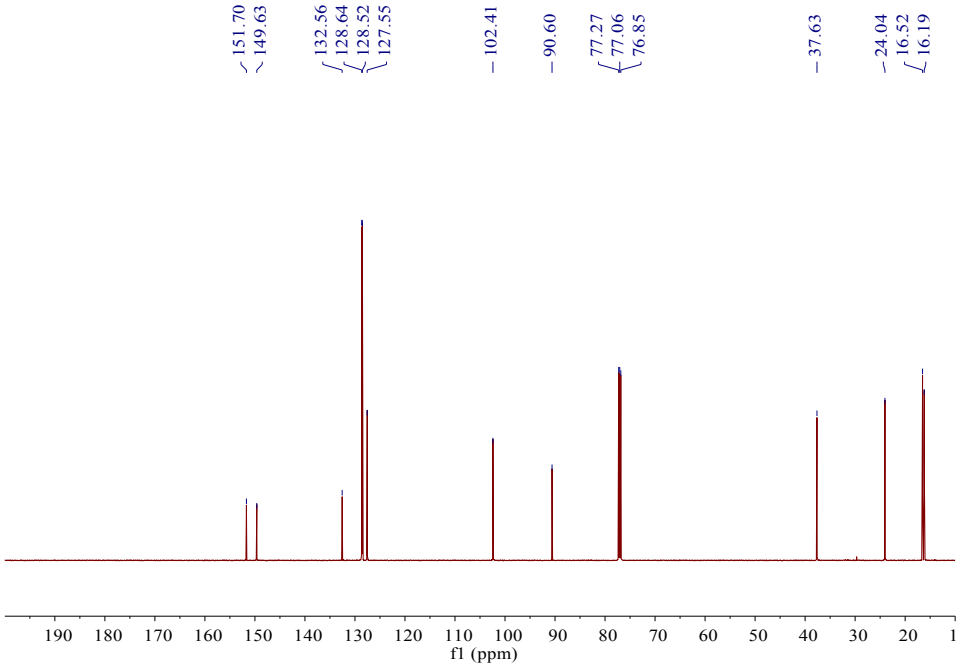


2p

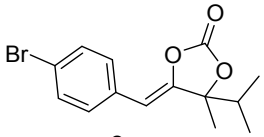
5-benzylidene-4-isopropyl-4-methyl-1,3-dioxolan-2-one [5](2p): pale yellow solid.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 - 7.37 (m, 2H), 7.27 (t, J = 7.7 Hz, 2H), 7.22 - 7.14 (m, 1H), 5.39 (s, 1H), 1.93 (p, J = 6.8 Hz, 1H), 1.57 (s, 3H), 0.98 (dd, J = 25.5, 6.8 Hz, 6H).

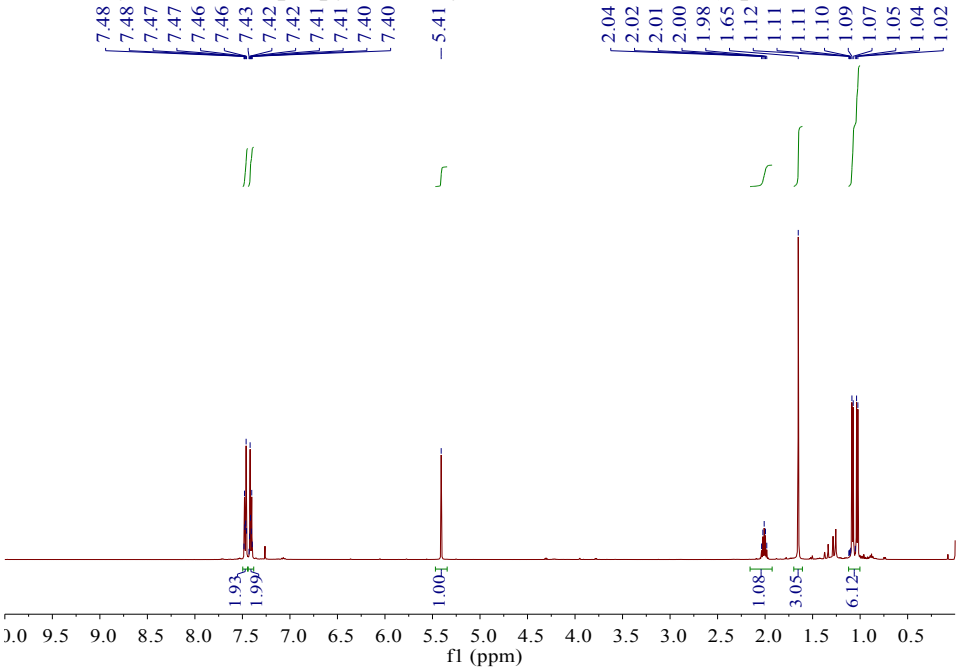


^{13}C NMR (151 MHz, $CDCl_3$): δ 151.70, 149.63, 132.56, 128.64, 128.52, 127.55, 102.41, 90.60, 37.63, 24.04, 16.52, 16.19.

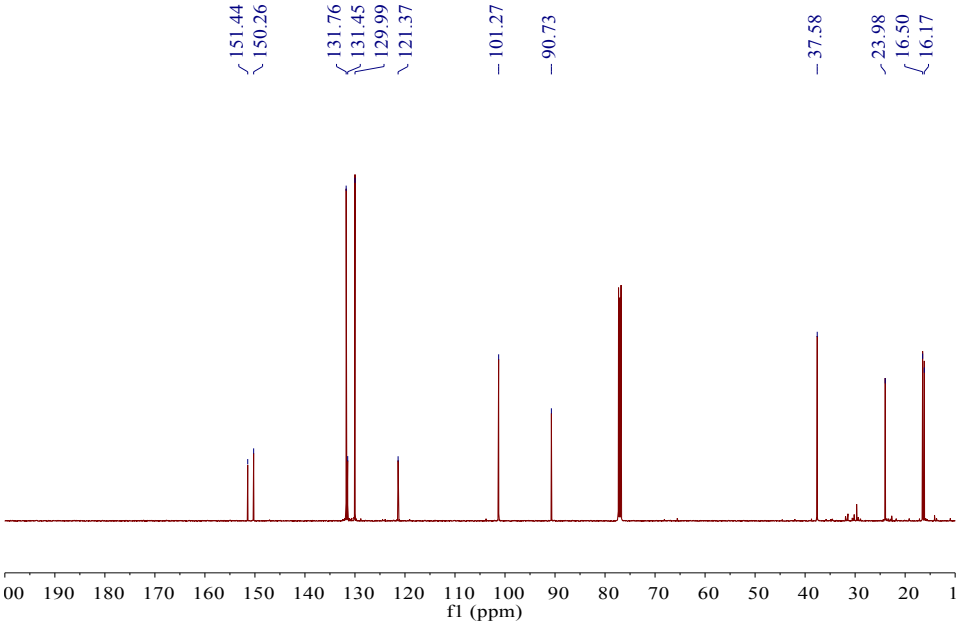


2q

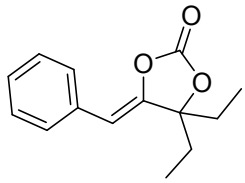
5-(4-bromobenzylidene)-4-isopropyl-4-methyl-1,3-dioxolan-2-one (2q): pale yellow solid.



^{1}H NMR (500 MHz, $CDCl_3$)：δ 7.50 - 7.45 (m, 2H), 7.44 - 7.38 (m, 2H), 5.41 (s, 1H), 2.01 (p, J = 6.8 Hz, 1H), 1.65 (s, 3H), 1.06 (dd, J = 24.5, 6.8 Hz, 6H).

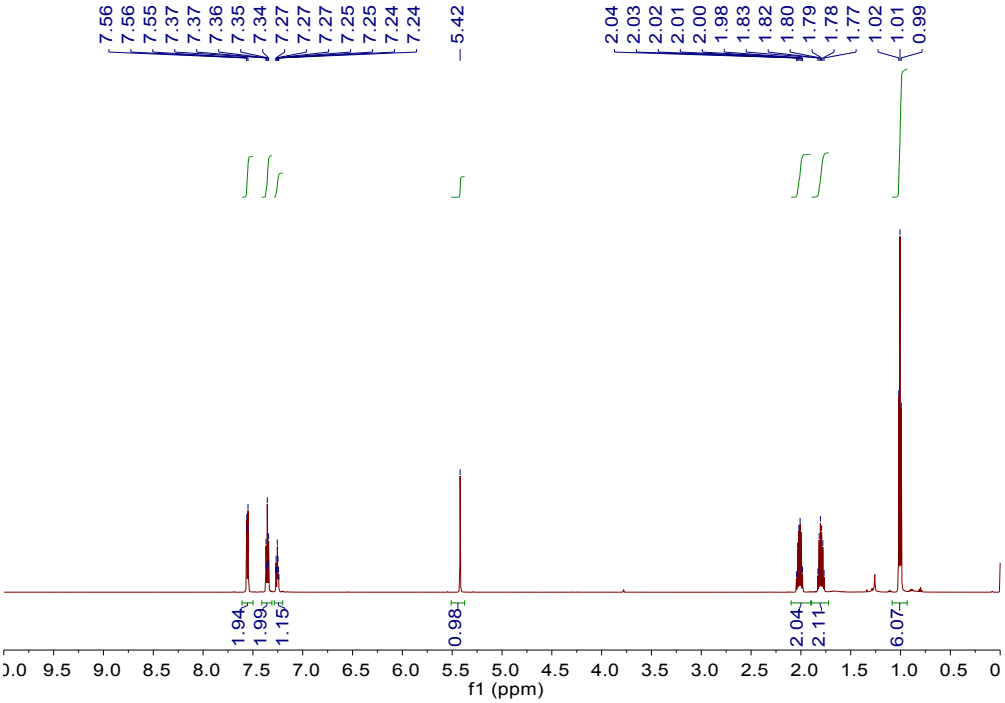


^{13}C NMR (126 MHz, $CDCl_3$) δ 151.44, 150.26, 131.76, 131.45, 129.99, 121.37, 101.27, 90.73, 37.58, 23.98, 16.50, 16.17.

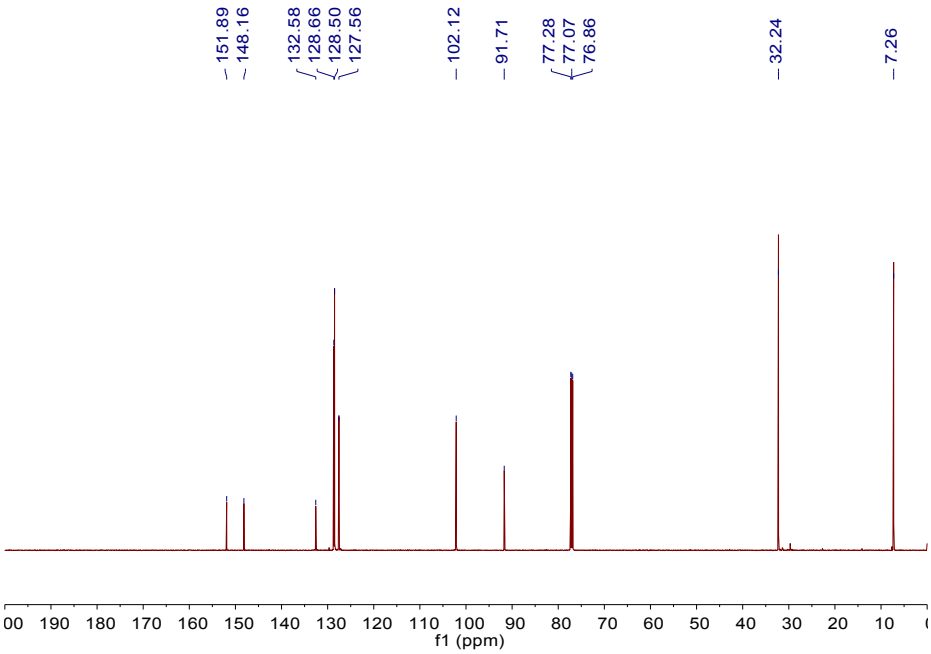


2r

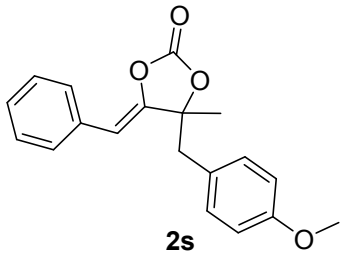
5-benzylidene-4,4-diethyl-1,3-dioxolan-2-one [5](2r): pale yellow oil.



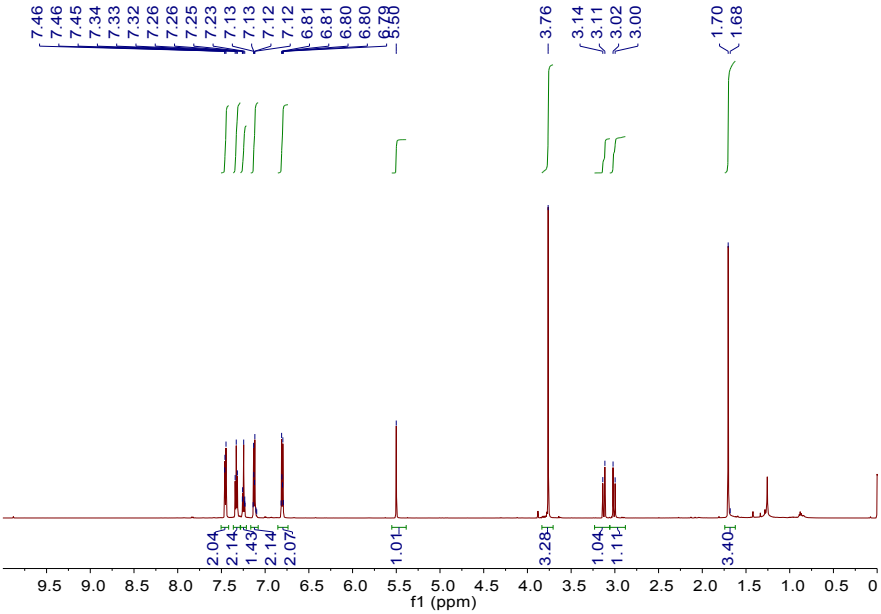
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 - 7.50 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.29 - 7.20 (m, 1H), 5.42 (s, 1H), 2.01 (dq, J = 14.6, 7.3 Hz, 2H), 1.80 (dq, J = 14.8, 7.4 Hz, 2H), 1.01 (t, J = 7.4 Hz, 6H).



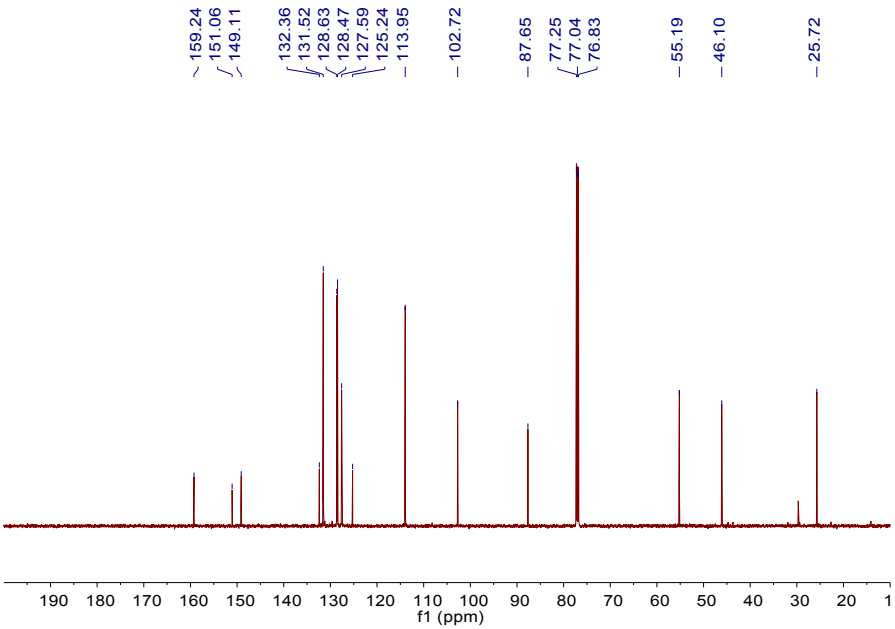
^{13}C NMR (151 MHz, $CDCl_3$): δ 151.89, 148.16, 132.58, 128.66, 128.50, 127.56, 102.12, 91.71, 32.24, 7.26.



5-benzylidene-4-(4-methoxybenzyl)-4-methyl-1,3-dioxolan-2-one (2s): pale yellow oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 - 7.42 (m, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.28 - 7.21 (m, 1H), 7.16 - 7.08 (m, 2H), 6.85 - 6.74 (m, 2H), 5.50 (s, 1H), 3.76 (s, 3H), 3.13 (d, J = 14.3 Hz, 1H), 3.01 (d, J = 14.3 Hz, 1H), 1.70 (s, 3H).



^{13}C NMR (151 MHz, $CDCl_3$): δ 159.24, 151.06, 149.11, 132.36, 131.52, 128.63, 128.47, 127.59, 125.24, 113.95, 102.72, 87.65, 55.19, 46.10, 25.72.