Supplementary Information (SI) for ChemComm.
This journal is © The Royal Society of Chemistry 2024

Supporting Information

CO Insertion Enabled γ-C(sp^3)-H Heteroarylative Carbonylation of Tertiary Alcohols via Heteroaryl Migration

Xin Qi,[a,b] Yuanrui Wang,[a,b] Xiao-Feng Wu[a,b,c]*

[a]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China,

[b]University of Chinese Academy of Sciences, Huairou District, Beijing, 101408, China,

[c]Leibniz-Institut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany

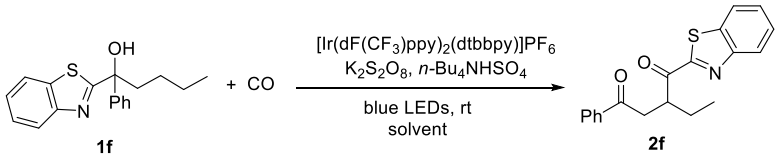
Table Of Contents

1. General Information

Unless otherwise noted, all reactions were carried out under a carbon monoxide or nitrogen atmosphere. All reagents were from commercial sources, all solvents are extra dry solvents and used as received without further purification. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (b.p. 60-90 ^{o}C) and ethyl acetate as the eluents. ^{1}H and ^{13}C NMR spectra were taken on Bruker AVANCE III 400 MHz or 700 MHz spectrometers and spectral data were reported in ppm relative to tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as solvent. All coupling constants (J) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. Gas chromatography (GC) analyses were performed on an Agilent HP-7890A instrument with a FID detector and HP-5 capillary column using argon as carrier gas. Gas chromatography-mass spectrometer (GC-MS) analyses were performed on a Shimadzu QP2020 NX instrument. High resolution mass spectra (HRMS) were recorded on Agilent Q-TOF 6540. Because of the high toxicity of carbon monoxide, all of the reactions should be performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.

2. Optimization of Reaction Conditions

2.1 Optimization of solvent

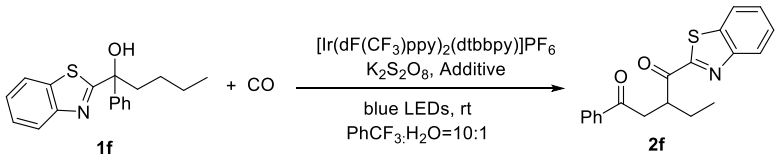


1f 2f

Entry	solvent	Yield (%)[b]
1	$PhCF_3/H_2O$(2mL/100μl)	46
2	$PhCF_3/H_2O$(1.5mL/150μl)	50
3	$DMSO/H_2O$(2mL/100μl)	ND
4	THF/H_2O(2mL/100μl)	ND
5	$toluene/H_2O$(2mL/100μl)	ND
6	acetone(2mL/100μl)	ND
7	CH_3CN(2mL/100μl)	ND
8	para-xylene(2mL/100μl)	ND

[a] Reaction conditions: 1 (0.1 mmol), photocatalyst (3 mol%), $K_2S_2O_8$ (0.25 mmol), Bu_4NHSO_4 (0.05 mmol), at rt for 36 h under CO (50 bar). [b] Yield was determined by GC

2.2 Optimization of additive

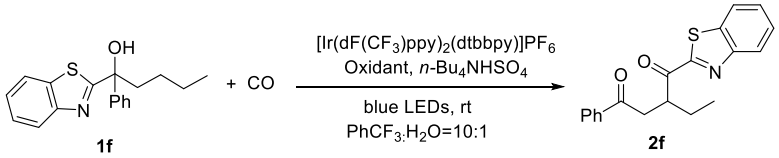


1f 2f

Entry	**Additive (0.5 eq.)**	Yield (%)[b]
1	nBu_4NHSO_4	50(48)[a]
2	$nBu_4N(OCOCH_3)$	30
3	nBu_4NPF_6	ND
4	nBu_4NI	ND
5	nBu_4NF	16
6	nBu_4NBF_4	25
7	CTAB	ND
8	$nBu_4NHSO_4 + K_2CO_3$(2.0 eq.)	20
9	$nBu_4NHSO_4 + KH_2PO_4$(2.0 eq.)	40
10	18-Crown-6	10
11	*n*-Bu_4NCl	45

[a] Reaction conditions: 1 (0.1 mmol), photocatalyst (3 mol%), $K_2S_2O_8$ (0.25 mmol), $PhCF_3$ (1.5 mL), H_2O (150 μl) at rt for 36 h under CO (50 bar). [b] Yield was determined by GC

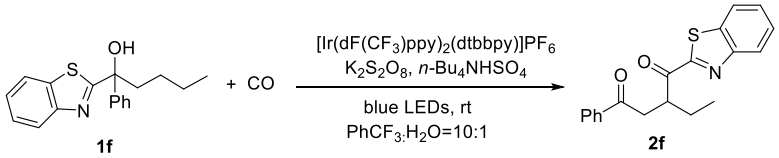
2.3 Optimization of oxidant



1f 2f

entry	Oxidant	Yield (%)[b]
1	$Na_2S_2O_8$ (2.5 equiv.)	46
2	$K_2S_2O_8$ (2.5 equiv.)	50
3	$(NH4)_2S_2O_8$ (2.5 equiv.)	47
4	PIDA (2.0 equiv.)	ND
5	PIFA (2.0 equiv.)	ND
6	BI-OH (2.0 equiv.)	ND
7	BI-OAc (2.0 equiv.)	ND
8	BI-OMe (2.0 equiv.)	ND

[a] Reaction conditions: 1 (0.1 mmol), photocatalyst (3 mol%), $PhCF_3$ (1.5 mL), H_2O (150 µl) at rt for 36 h under CO (50 bar). [b] Yield was determined by GC



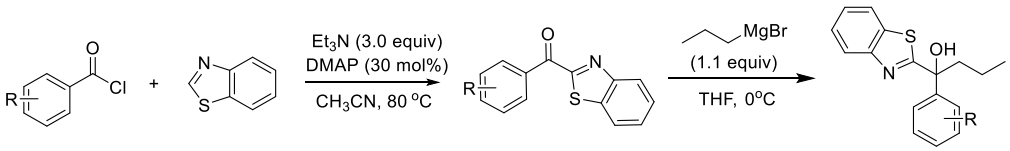
1f 2f

Entry	Variation of reaction conditions	Yield (%)[b]
1	none	50(48)
2	without photocatalyst	0
3	without CO	0
4	without H_2O	0
5	without lights	0

[a] Reaction conditions: 1 (0.1 mmol), photocatalyst (3 mol%), $K_2S_2O_8$ (0.25 mmol), Bu_4NHSO_4 (0.05 mmol), $PhCF_3$ (1.5 mL), H_2O (150 µl) at rt for 36 h under CO (50 bar). [b] Yield was determined by GC the isolated yield is given in parentheses.

3. Preparation of Substrates

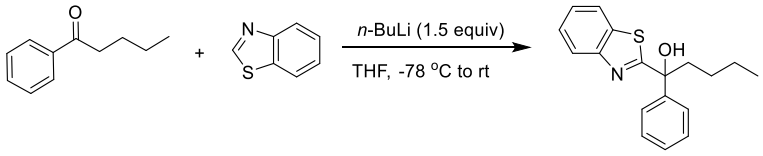
Synthesis of **1a-1e**



Step I[1]: To a solution of 4-dimethylaminopyridine (DMAP, 185 mg, 3.0 mmol) in acetonitrile (10.0 mL) was sequentially added acyl chloride (1.0 equiv., 10.0 mmol), thiazole (1.5 equiv 15.0 mmol), and triethylamine (3.0 equiv., 30mmol) at room temperature. The resulting mixture was heated at 80 °C for 24 h. After cooled to room temperature, the reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (dichloromethane/petroleum ether = 1/5 to 1/1) to afford ketone as white or yellow solid.

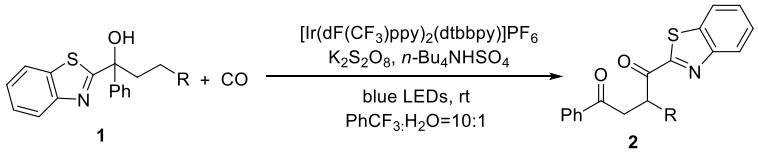
Step II[2]: In an oven-dried 100 mL round-bottomed flask, add n-propylmagnesium bromide (2mol/L in THF, 1.1 equiv.) dropwise to a solution of ketone (1.0 equiv.) in dry THF (0.2 M) under nitrogen at 0 °C. The resulting mixture was gradually brought to room temperature and stirred for 0.5-2 hours. Upon completion of the reaction, the reaction mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate and dried. The reaction mixture was extracted with ethyl acetate and dried, then purified on silica gel column with the eluent being ethyl acetate/petroleum ether (1/20) to give substrate.

Synthesis of **1f**:



To a solution of benzothiazole (1.5 equiv.) in dry THF (15 mL) in a 100 mL nitrogen-filled round-bottomed flask, n-butyllithium (1.5 equiv.) was added dropwise to a solution of benzothiazole (1.5 equiv.) at a dropwise temperature of -78 °C. After 1 h, the ketone was added dropwise, and the reaction was slowly warmed up to room temperature over 2 h. Upon completion of the reaction, the reaction mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate and dried, and then purified on a silica gel column using an ethyl acetate/petroleum ether (1/20) eluent to give a white or yellow solid.

4. General Procedures for Migration

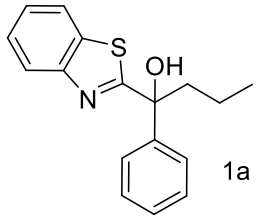


1 2

A 4 mL screw-cap vial was charged with 1 (0.1 mmol), photocatalyst (3 mol%), $K_2S_2O_8$ (0.25 mmol), Bu_4NHSO_4 (0.05 mmol), and an oven-dried stirring bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. Then $PhCF_3$ (1.5 mL), and H_2O (150 μl) were added with a syringe under N_2 atmosphere. The closed autoclave was flushed two times with nitrogen (~ 5 bar), and a pressure of 50 bar CO were charged. The autoclave was then placed on a magnetic stirrer. The reaction mixture was stirred while being irradiated with 45 w blue light at room temperature for 36 h. After irradiation, the light was turned off and the pressure was released carefully. The mixture was concentrated under vacuum. The crude product was purified by column chromatography (PE/EA =20/1 to 3/1) on silica gel to afford the corresponding products.

5. Characterization of Substrates and Products

5.1 substrate



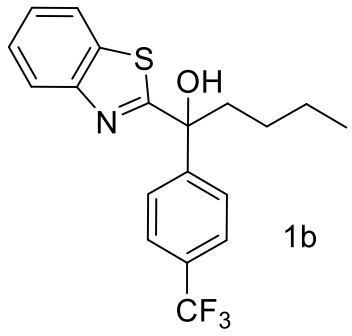
1a

1-(benzo[d]thiazol-2-yl)-1-phenylbutan-1-ol

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.42 – 7.30 (m, 3H), 7.27 (d, *J* = 9.3 Hz, 2H), 3.78 (s, 1H), 2.49 – 2.37 (m, 2H), 1.52 – 1.29 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 152.5, 144.0, 135.7, 128.4, 127.6, 126.0 125.5, 125.0, 123.1, 121.7, 79.0, 44.8, 16.9, 14.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{17}H_{17}NOS$ 284.1104; Found 284.1119.



1b

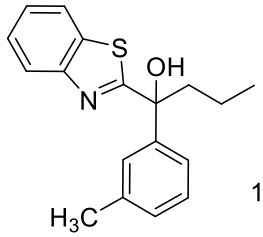
1-(benzo[d]thiazol-2-yl)-1-(4-(trifluoromethyl)phenyl)pentan-1-ol

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 3H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 3.88 (s, 1H), 2.50 – 2.41 (m, 2H), 1.36 (m, *J* = 12.0, 7.4 Hz, 4H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.4, 152.6, 147.8, 135.6, 128.6 (q, *J* = 33.3 Hz), 126.2, 126.0, 124.7 (q, *J* = 4.0 Hz), 123.2, 122.7 (q, *J* = 272.7 Hz), 121.7, 78.8, 42.5, 25.5, 22.8, 13.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.53.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{23}H_{21}NOS$ 366.1134; Found 366.1197.



1c

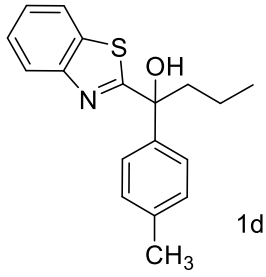
1-(benzo[d]thiazol-2-yl)-1-(m-tolyl)butan-1-ol

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 3.78 (s,

1H), 2.42 (dd, *J* = 9.4, 7.1 Hz, 2H), 2.35 (s, 3H), 1.41 (qt, *J* = 14.6, 6.9 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.6, 152.6, 143.9, 138.0, 135.7, 128.3, 128.2, 126.1, 125.9, 124.9, 123.0, 122.6, 121.6, 78.9, 44.7, 21.6, 16.9, 14.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{18}H_{19}NOS$ 298.1260; Found 298.1278.



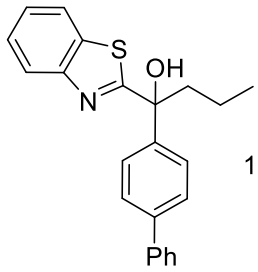
1d

1-(benzo[d]thiazol-2-yl)-1-(p-tolyl)butan-1-ol

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.42 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.35 – 7.26 (m, 1H), 7.14 (d, *J* = 7.1 Hz, 2H), 3.87 (s, 1H), 2.47 – 2.35 (m, 2H), 2.30 (s, 3H), 1.48 – 1.30 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.7, 152.6, 141.1, 137.2, 135.6, 129.0, 125.9, 125., 124.9, 123.0, 121.6, 78.8, 44.6, 21.0, 16.9, 14.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{18}H_{19}NOS$ 298.1260; Found 298.1237.



1e

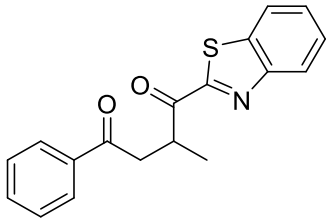
1-([1,1'-biphenyl]-4-yl)-1-(benzo[d]thiazol-2-yl)butan-1-ol

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 13.6 Hz, 4H), 7.50 – 7.28 (m, 5H), 3.86 (s, 1H), 2.53 – 2.40 (m, 2H), 1.55 – 1.31 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.3, 152.6, 143.0, 140.6, 140.4, 135.7, 128.7, 127.3, 127.1, 127.06, 126.0, 125.0, 123.0, 121.7, 78.9, 44.8, 16.9, 14.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{23}H_{21}NOS$ 360.1417; Found 360.1436.

5.2 product



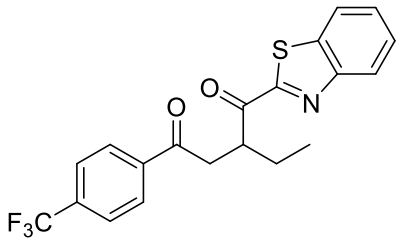
1-(benzo[d]thiazol-2-yl)-2-methyl-4-phenylbutane-1,4-dione(2a)

Yellow viscous oil, 15.1mg, 64% yield, R_f = 0.3 (PE/EA = 15/1) (yield based on the isolated alcohol, alcohol remaining 6.8 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 – 8.19 (m, 1H), 8.02 – 7.95 (m, 3H), 7.62 – 7.44 (m, 5H), 4.60 – 4.47 (m, 1H), 3.80 (dd, *J* = 18.0, 9.4 Hz, 1H), 3.29 (dd, *J* = 18.0, 4.6 Hz, 1H), 1.43 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 197.87, 165.8, 153.7, 137.4, 136.4, 133.3, 128.6, 128.2, 127.5, 126.8, 125.6, 122.4, 42.6, 37.1, 17.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{18}H_{15}NO_2S$ 310.0896; Found 310.0913.



1-(benzo[d]thiazol-2-yl)-2-ethyl-4-(4-(trifluoromethyl)phenyl)butane-1,4-dione(2b)

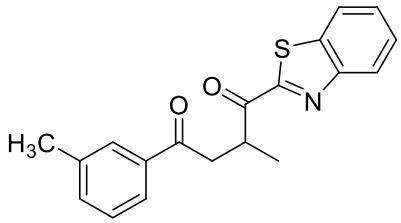
Yellow viscous oil, 16.5mg, 42% yield R_f = 0.3 (PE/EA = 15/1)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.63 – 7.49 (m, 2H), 4.49 (m, *J* = 10.4, 6.6, 3.3 Hz, 1H), 3.79 (dd, *J* = 18.1, 10.2 Hz, 1H), 3.33 (dd, *J* = 18.1, 4.0 Hz, 1H), 1.99 (m, *J* = 14.3, 7.1 Hz, 1H), 1.81 (m, *J* = 14.5, 7.3 Hz, 1H), 1.04 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.5, 197.3, 166.2, 153.7, 139.0, 137.5, 134.5 (q, *J* = 32.7 Hz), 128.5, 127.6, 126.8, 125.78 (q, *J* = 3.0 Hz), 124.9 (q, *J* = 273.7 Hz), 122.4, 43.2, 40.7, 25.2, 11.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.13.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{23}H_{21}NOS$ 392.0927; Found 392.0975.



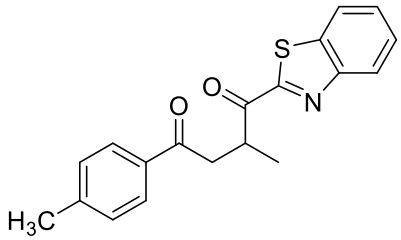
1-(benzo[d]thiazol-2-yl)-2-methyl-4-(m-tolyl)butane-1,4-dione(2c)

Yellow viscous oil, 14.5 mg, 54% yield, R_f = 0.3 (PE/EA = 15/1) (yield based on the isolated alcohol, alcohol remaining 4.8 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.1 Hz, 1H), 8.03 – 7.96 (m, 1H), 7.78 (d, *J* = 6.3 Hz, 2H), 7.62 – 7.46 (m, 2H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.30 (m, 1H), 4.52 (m, *J* = 9.3, 7.1, 4.8 Hz, 1H), 3.78 (dd, *J* = 17.9, 9.3 Hz, 1H), 3.28 (dd, *J* = 18.0, 4.8 Hz, 1H), 2.40 (s, 3H), 1.42 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.1, 198.0, 165.9, 153.7, 138.4, 137.4, 136.4, 134.0, 128.7, 128.5, 127.5, 126.8, 125.6, 125.4, 122.4, 42.8, 37.1, 21.3, 17.3.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{19}H_{17}NO_2S$ 324.1053; Found 324.1070.



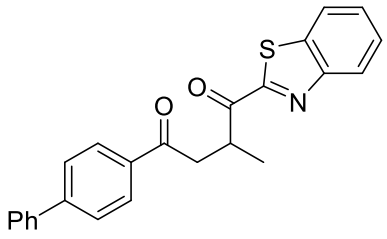
1-(benzo[d]thiazol-2-yl)-2-methyl-4-(p-tolyl)butane-1,4-dione (2d)

Yellow viscous oil, 12.2 mg, 44% yield, R_f = 0.3 (PE/EA = 15/1) (yield based on the isolated alcohol, alcohol remaining 4.1 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.04 – 7.93 (m, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.61 – 7.45 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 4.59 – 4.45 (m, 1H), 3.76 (dd, *J* = 17.9, 9.4 Hz, 1H), 3.27 (dd, *J* = 17.9, 4.7 Hz, 1H), 2.40 (s, 3H), 1.42 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.0, 197.5, 165.9, 153.7, 144.0, 137.4, 133.8, 129.2, 129.0, 128.3, 127.5, 126.8, 125.5, 122.3, 42.6, 37.1, 21.7, 17.3.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{19}H_{17}NO_2S$ 324.1053; Found 324.1039.



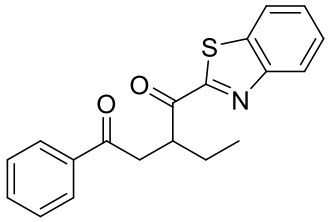
4-([1,1'-biphenyl]-4-yl)-1-(benzo[d]thiazol-2-yl)-2-methylbutane-1,4-dione(2e)

Yellow viscous oil, 15.9 mg, 43% yield, R_f = 0.3 (PE/EA = 15/1) (yield based on the isolated alcohol, alcohol remaining 6.9 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.35 (m, 10H), 4.62 – 4.49 (m, 1H), 3.83 (dd, *J* = 17.9, 9.3 Hz, 1H), 3.32 (dd, *J* = 17.9, 4.7 Hz, 1H), 1.45 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 197.5, 165.8, 153.7, 145.9, 139.8, 137.4, 135.0, 128.9, 128.8, 128.2, 127.5, 127.3, 127.2, 126.8, 125.6, 122.4, 42.7, 37.2, 17.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{24}H_{19}NO_2S$ 386.1209; Found 386.1200.



1-(benzo[d]thiazol-2-yl)-2-ethyl-4-phenylbutane-1,4-dione(2f)

Yellow viscous oil, 15.5 mg, 43% yield, R_f = 0.3 (PE/EA = 15/1)

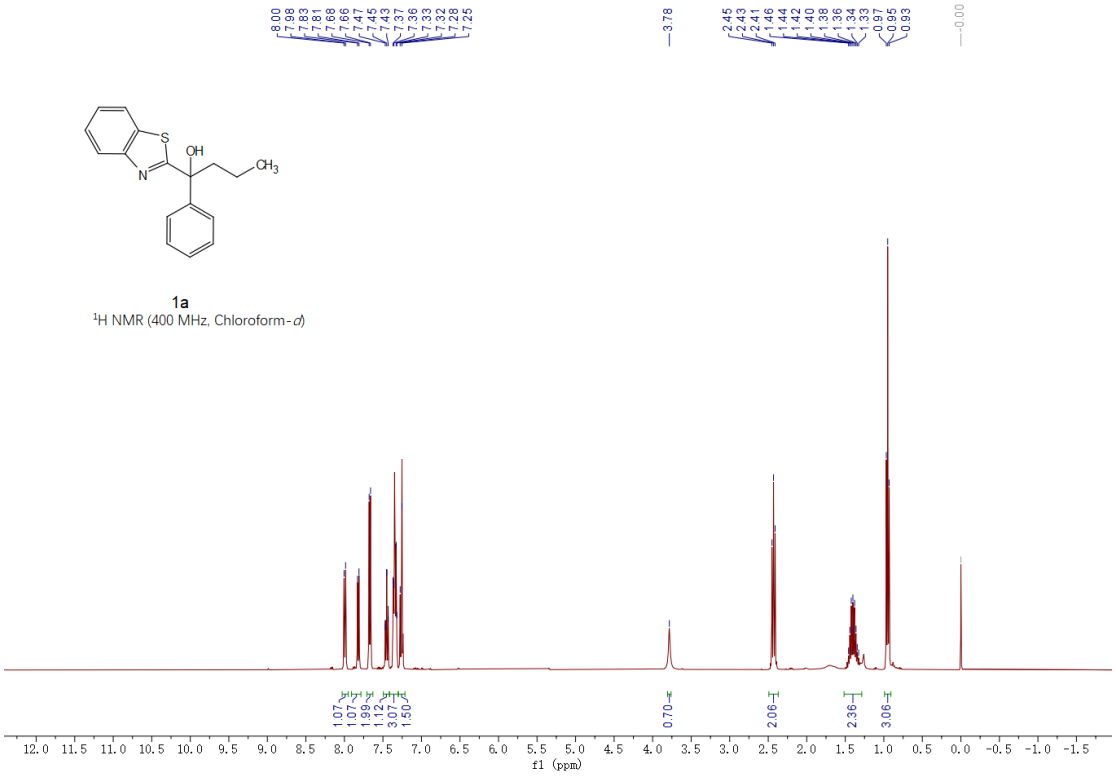
^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.3 Hz, 1H), 7.98 (t, *J* = 7.5 Hz, 3H), 7.59 – 7.53 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 6.9 Hz, 2H), 4.48 (m, *J* = 10.5, 6.7, 3.3 Hz, 1H), 3.77 (dd, *J* = 18.0, 10.1 Hz, 1H), 3.35 (dd, *J* = 18.0, 4.1 Hz, 1H), 1.97 (m, *J* = 14.1, 7.7, 6.6 Hz, 1H), 1.79 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.03 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.1, 197.8, 166.5, 153.8, 137.4, 136.4, 133.2, 128.6, 128.5, 128.1, 127.4, 126.7, 125.6, 122.3, 43.2, 40.7, 25.2, 11.6.

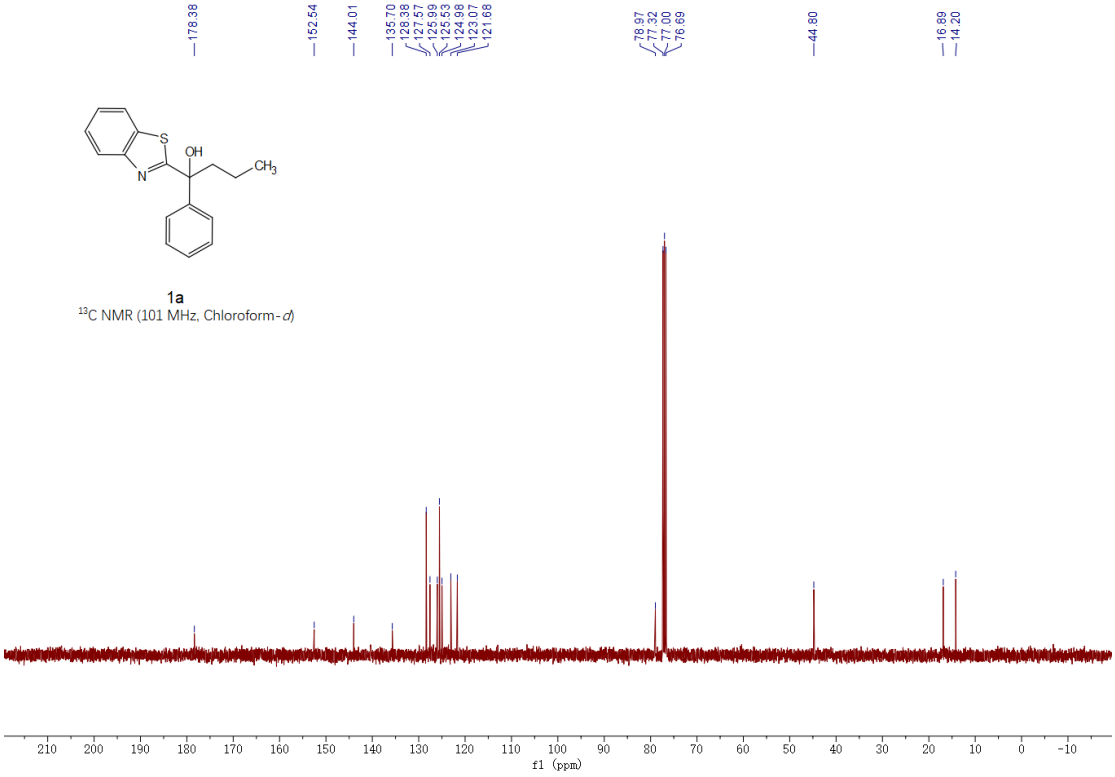
HRMS (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{19}H_{17}NO_2S$ 324.1053; Found 324.1100.

6. NMR Spectra of the Substrates and Products

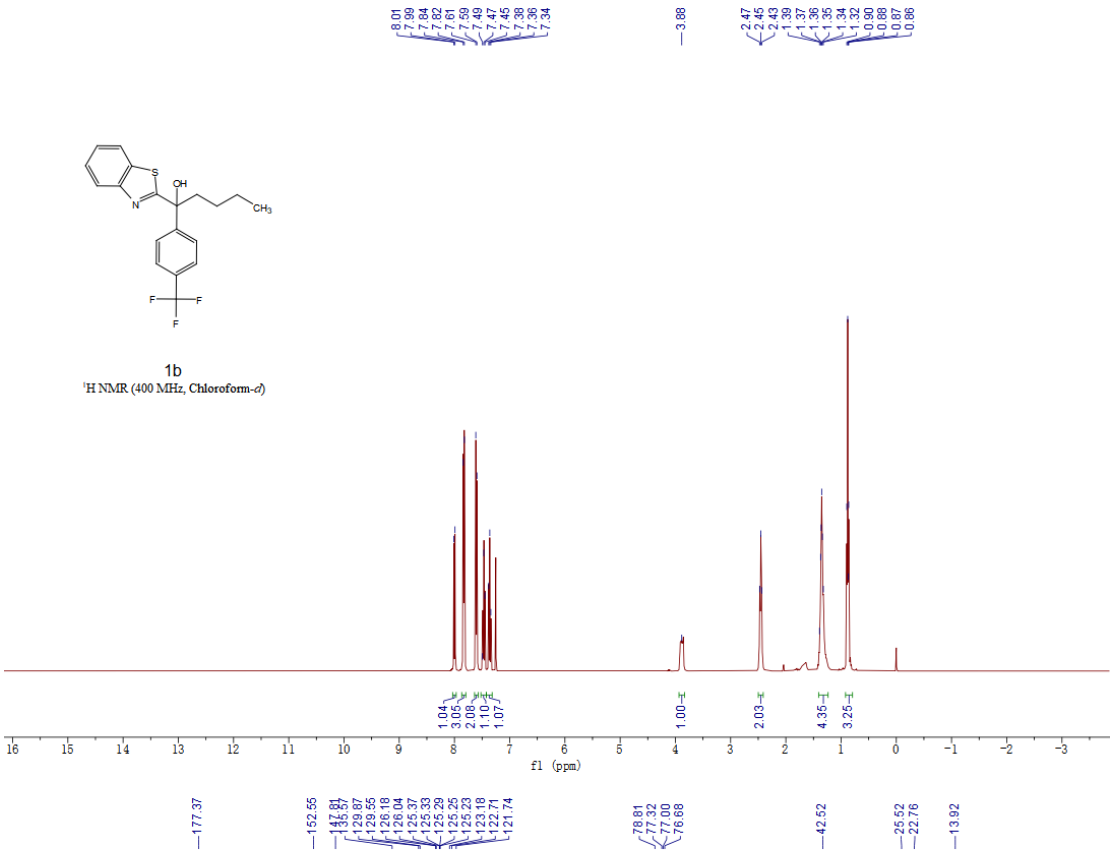
6.1 Substrates

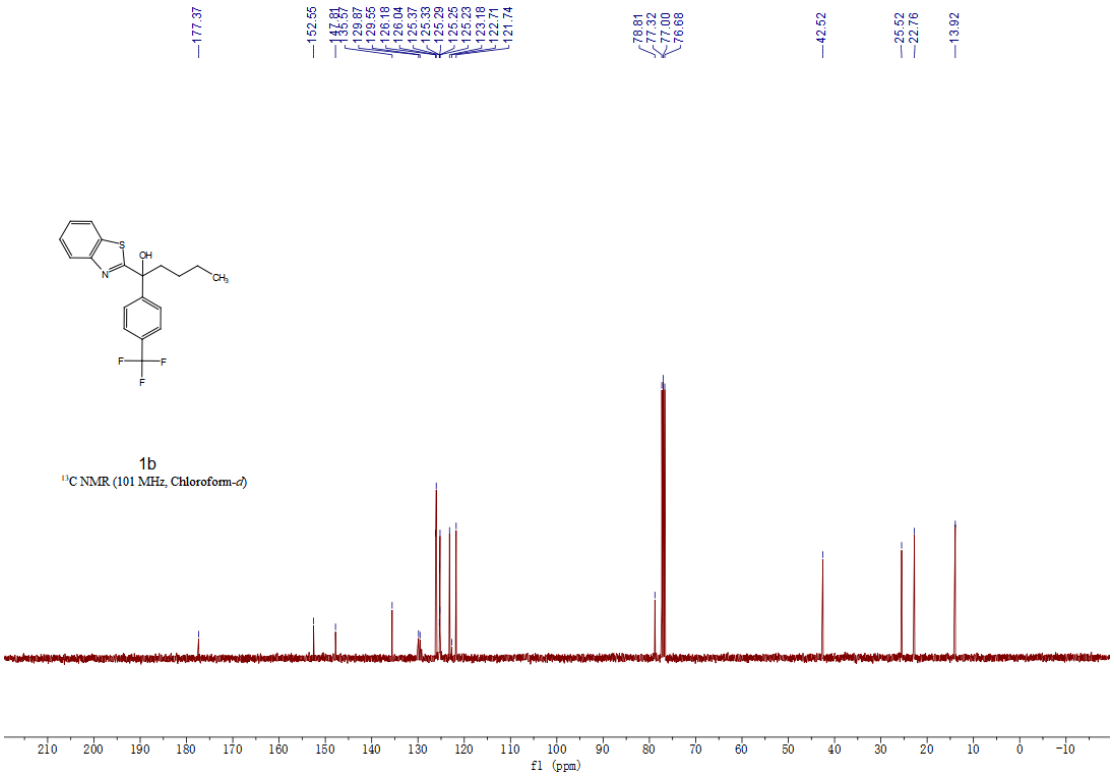


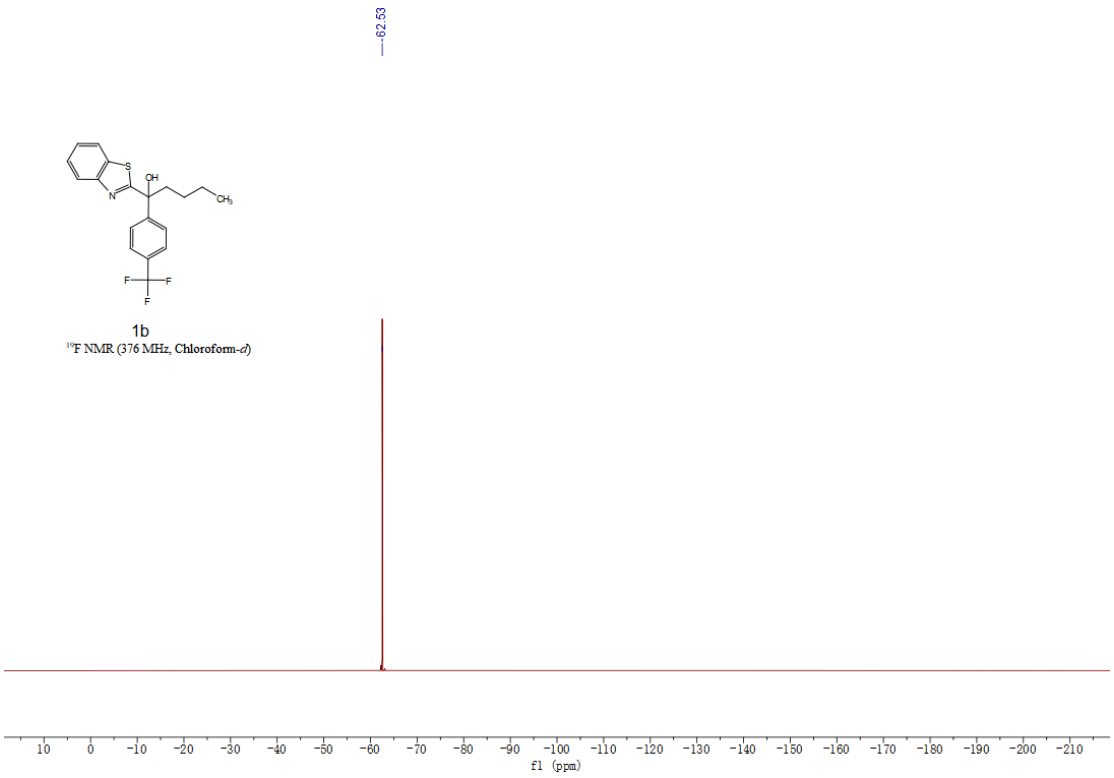
1a
^{1}H NMR (400 MHz, Chloroform-*d*)



1a
^{13}C NMR (101 MHz, Chloroform-*d*)

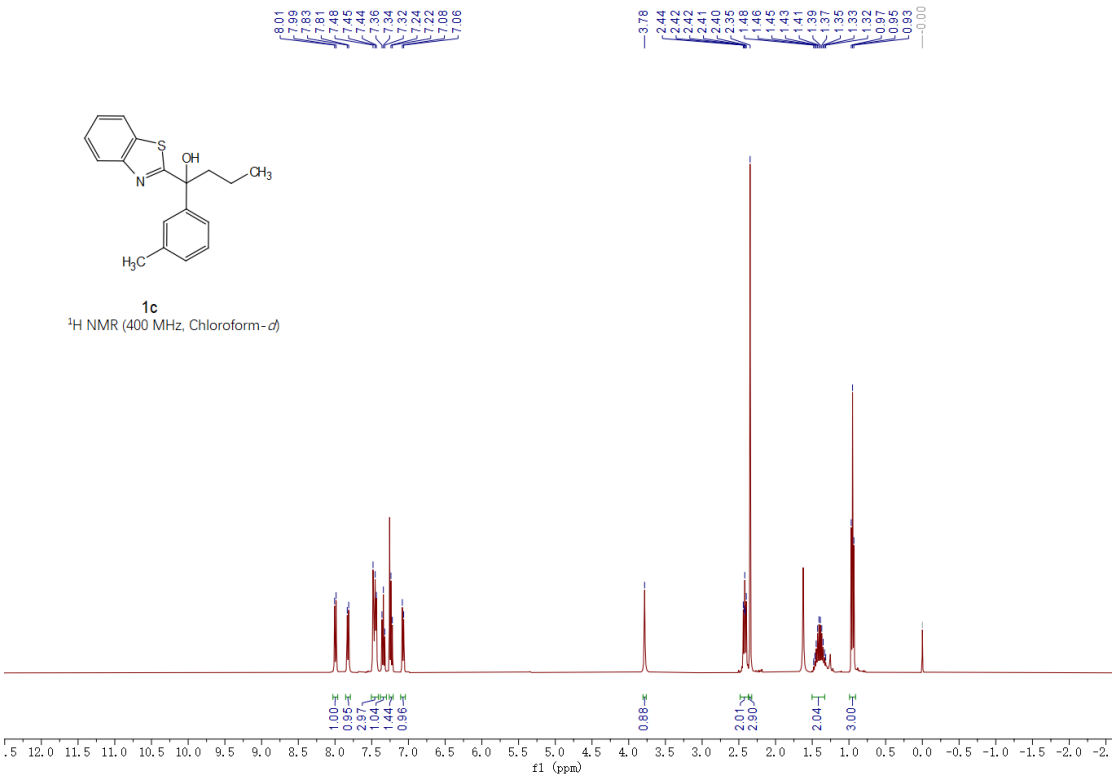

8.01
7.99
7.84
7.82
7.61
7.59
7.49
7.47
7.45
7.38
7.36
7.34
3.88
2.47
2.45
2.43
1.39
1.37
1.36
1.35
1.34
1.32
0.90
0.88
0.87
0.86
OH
CH3
F
F
F
1b
1H NMR (400 MHz, Chloroform-d)
1.04
3.05
2.08
1.10
1.07
1.00
2.03
4.35
3.25
f1 (ppm)


177.37
152.55
147.81
135.57
129.87
129.55
126.18
126.04
125.37
125.33
125.29
125.25
125.23
123.18
122.71
121.74
78.81
77.32
77.00
76.68
42.52
25.52
22.76
13.92
OH
CH3
F
F
F
1b
13C NMR (101 MHz, Chloroform-d)
f1 (ppm)



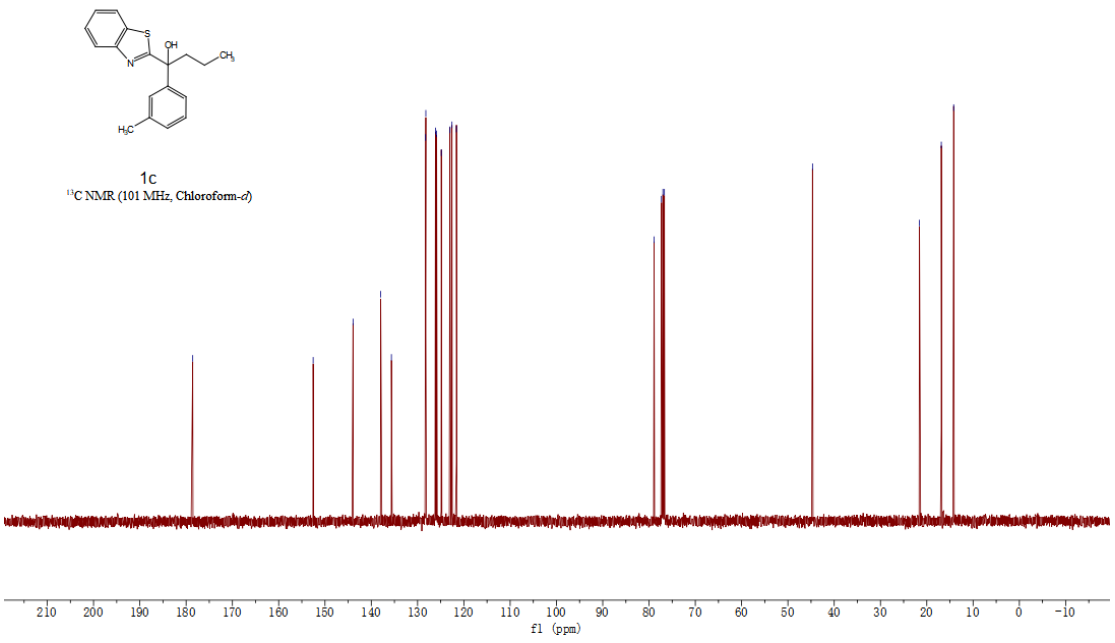
1b

^{19}F NMR (376 MHz, Chloroform-*d*)



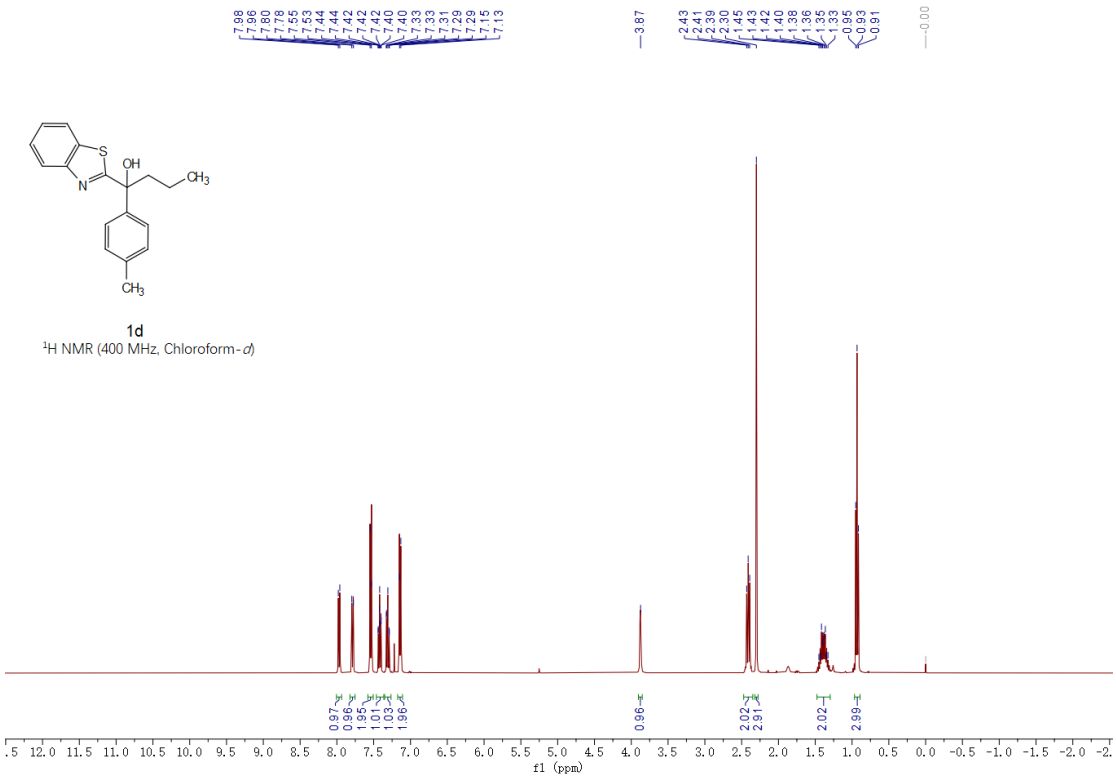
1c

^{1}H NMR (400 MHz, Chloroform-*d*)



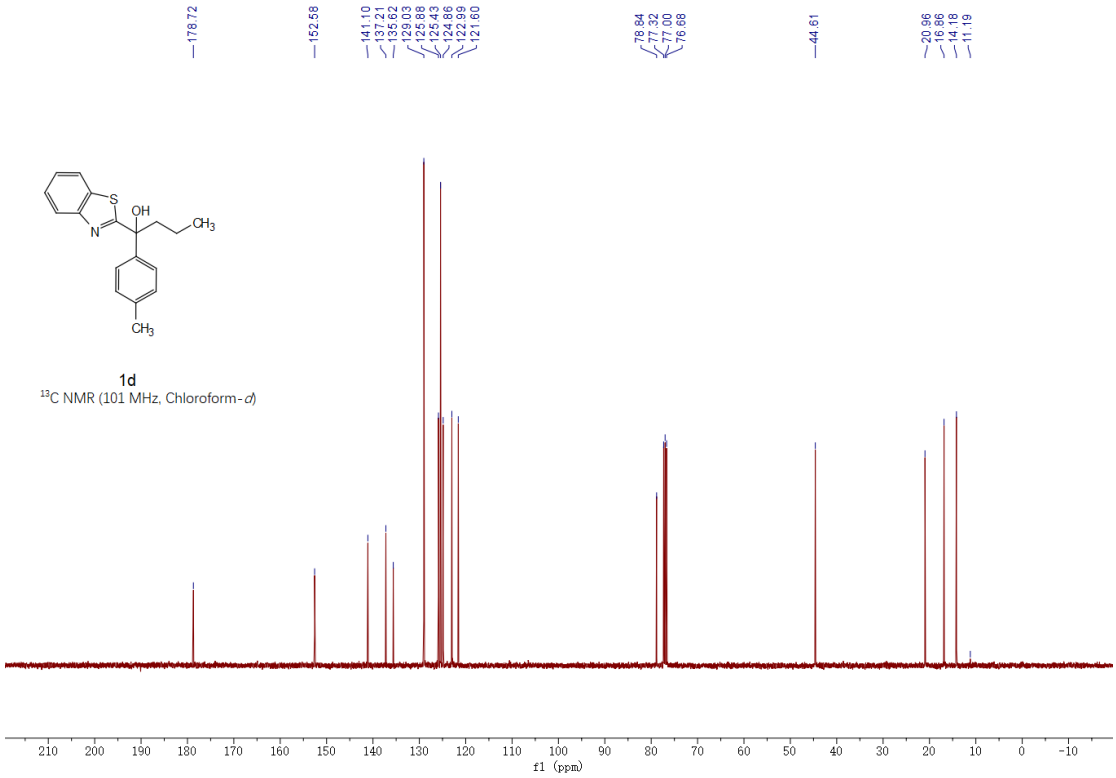
1c

^{13}C NMR (101 MHz, Chloroform-*d*)



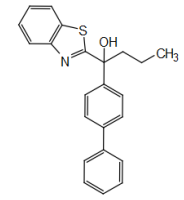
1d

^{1}H NMR (400 MHz, Chloroform-*d*)



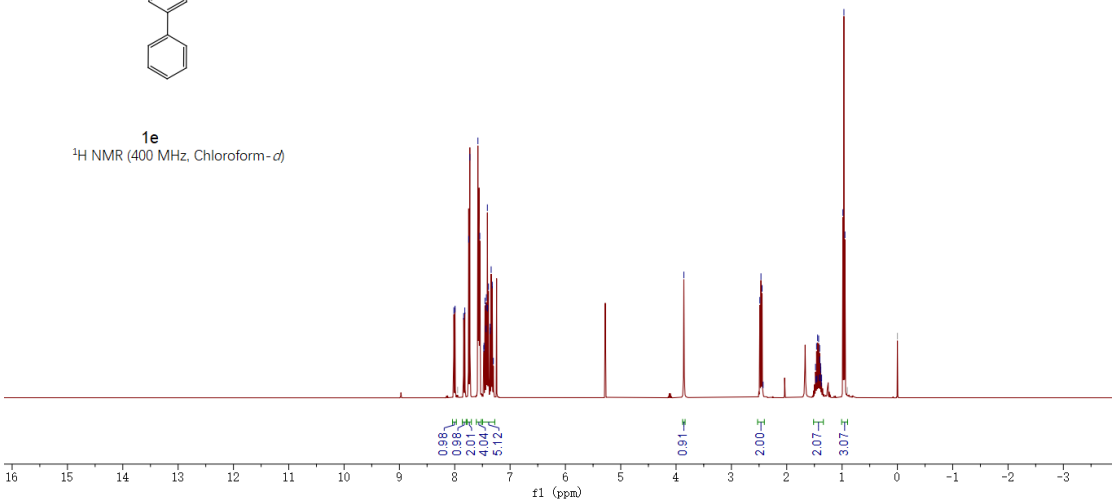
1d

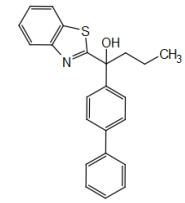
^{13}C NMR (101 MHz, Chloroform-*d*)



1e

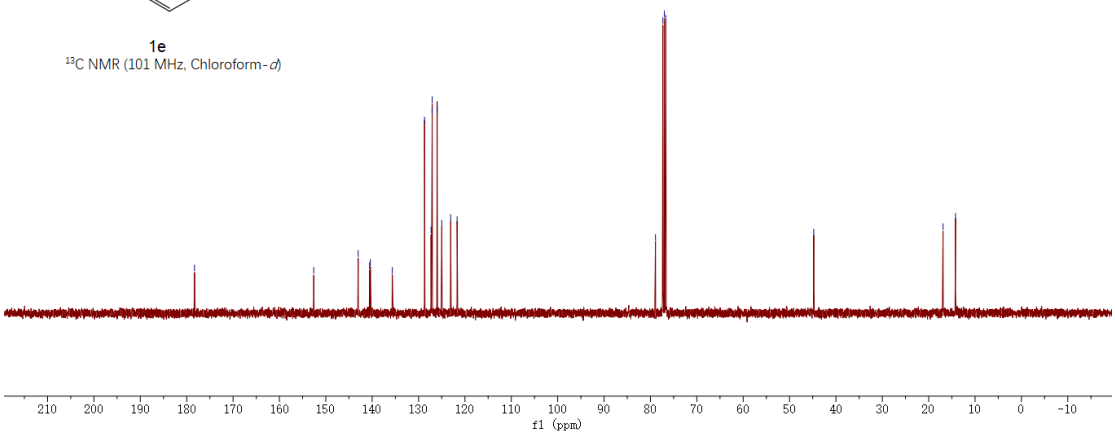
^{1}H NMR (400 MHz, Chloroform-*d*)



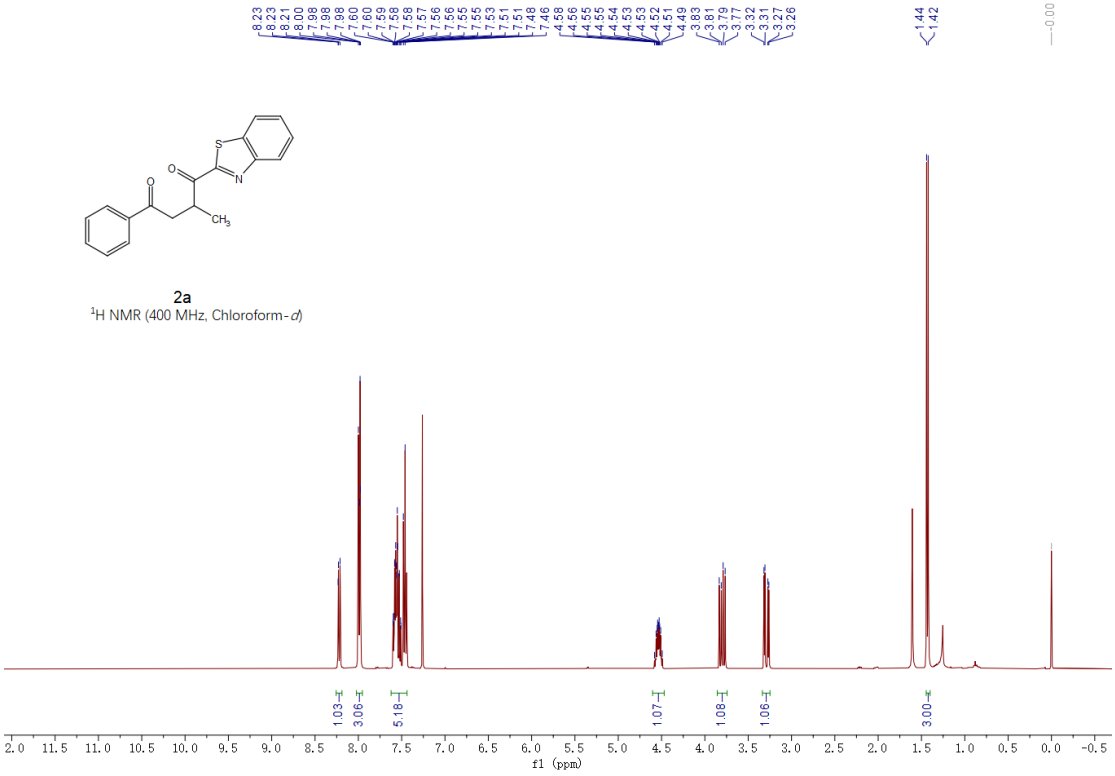


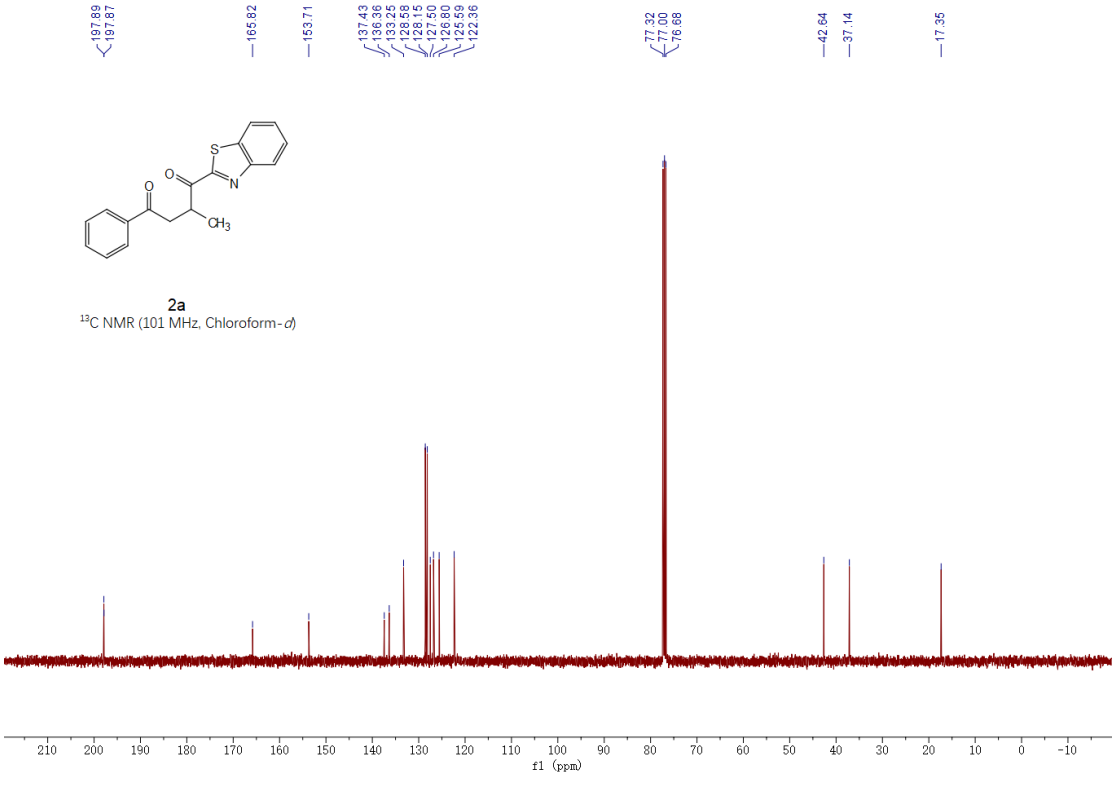
1e

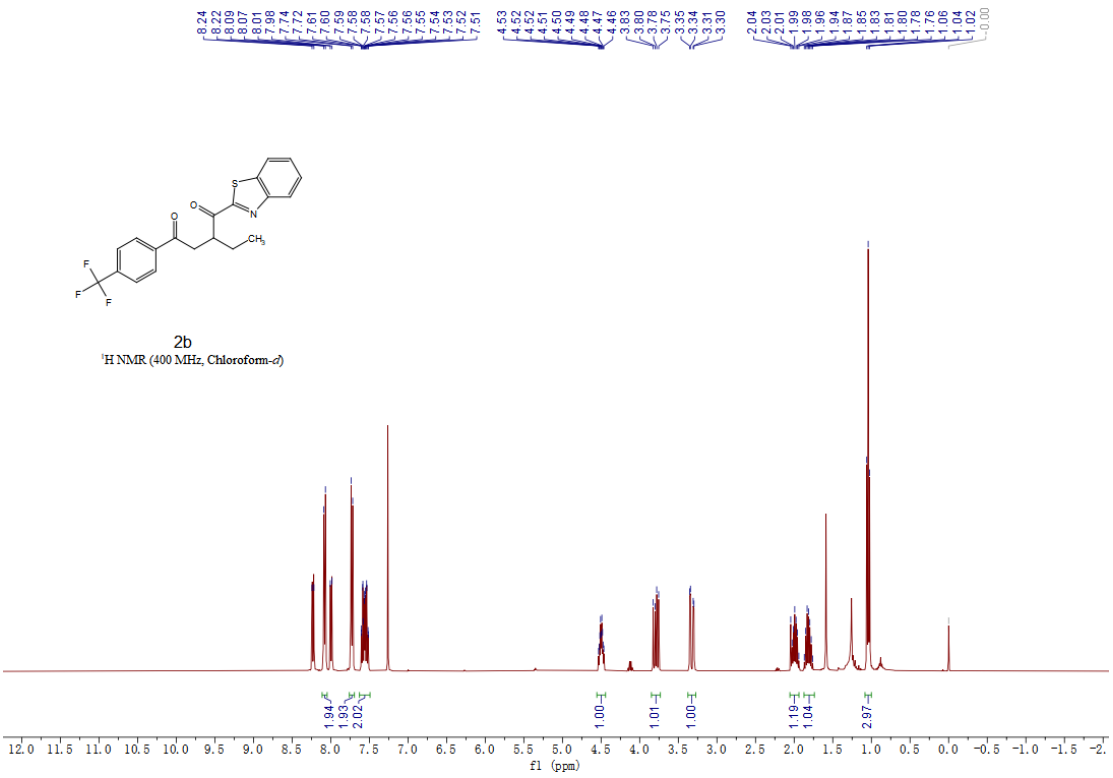
^{13}C NMR (101 MHz, Chloroform-*d*)

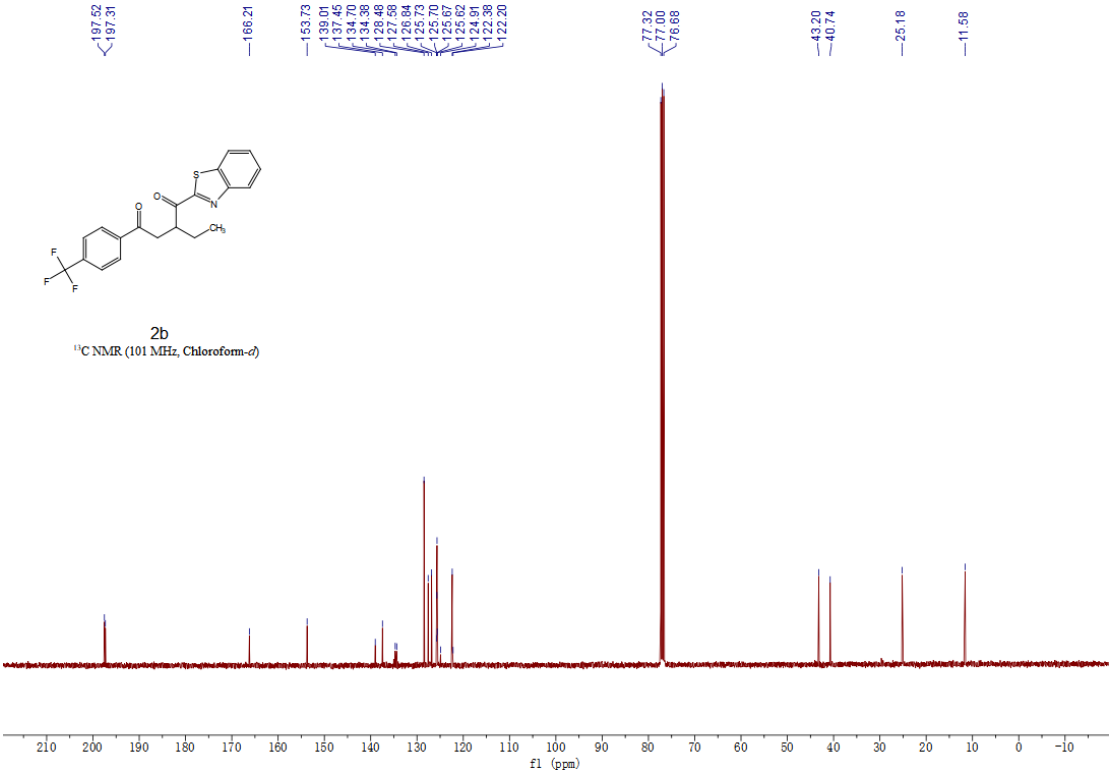


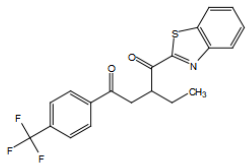
6.2 Products


8.23
8.23
8.21
8.00
7.98
7.98
7.98
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.53
7.51
7.51
7.48
7.46
4.58
4.56
4.55
4.55
4.54
4.53
4.53
4.52
4.51
4.49
3.83
3.81
3.79
3.77
3.32
3.31
3.27
3.26
1.44
1.42
0.00
S
N
O
O
CH3
2a
1H NMR (400 MHz, Chloroform-d)
1.03
3.06
5.18
1.07
1.08
1.06
3.00
f1 (ppm)


197.89
197.87
165.82
153.71
137.43
136.36
133.25
128.58
128.15
127.50
126.80
125.59
122.36
77.32
77.00
76.68
42.64
37.14
17.35
S
N
O
O
CH3
2a
13C NMR (101 MHz, Chloroform-d)
f1 (ppm)

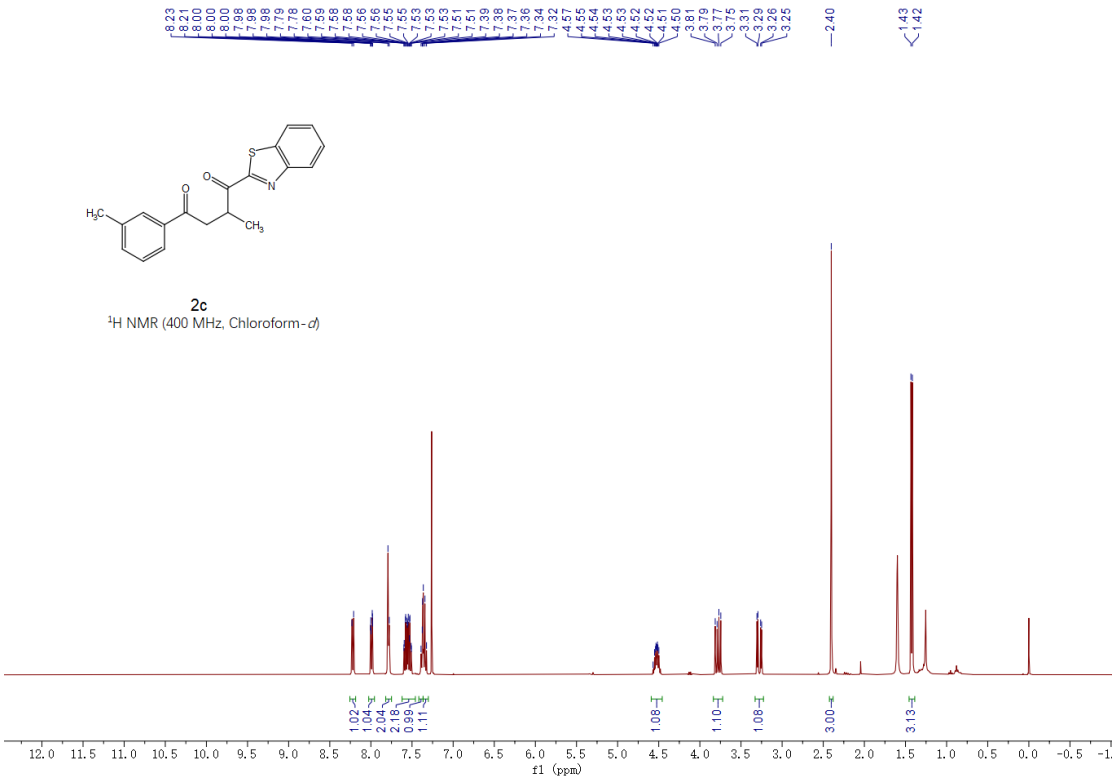

8.24
8.22
8.09
8.07
8.01
7.98
7.74
7.72
7.61
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.54
7.53
7.52
7.51
4.53
4.52
4.52
4.51
4.50
4.49
4.48
4.47
4.46
3.83
3.80
3.78
3.75
3.35
3.34
3.31
3.30
2.04
2.03
2.01
1.99
1.98
1.96
1.94
1.87
1.85
1.83
1.81
1.80
1.78
1.76
1.06
1.04
1.02
0.00
O
S
N
O
CH3
F
F
F
2b
1H NMR (400 MHz, Chloroform-d)
1.94
1.93
2.02
1.00
1.01
1.00
1.19
1.04
2.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.
f1 (ppm)


197.52
197.31
166.21
153.73
139.01
137.45
134.70
134.38
129.48
128.68
126.84
125.73
125.70
125.67
125.62
124.91
122.38
122.20
77.32
77.00
76.68
43.20
40.74
25.18
11.58
O
S
N
O
CH3
F
F
F
2b
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



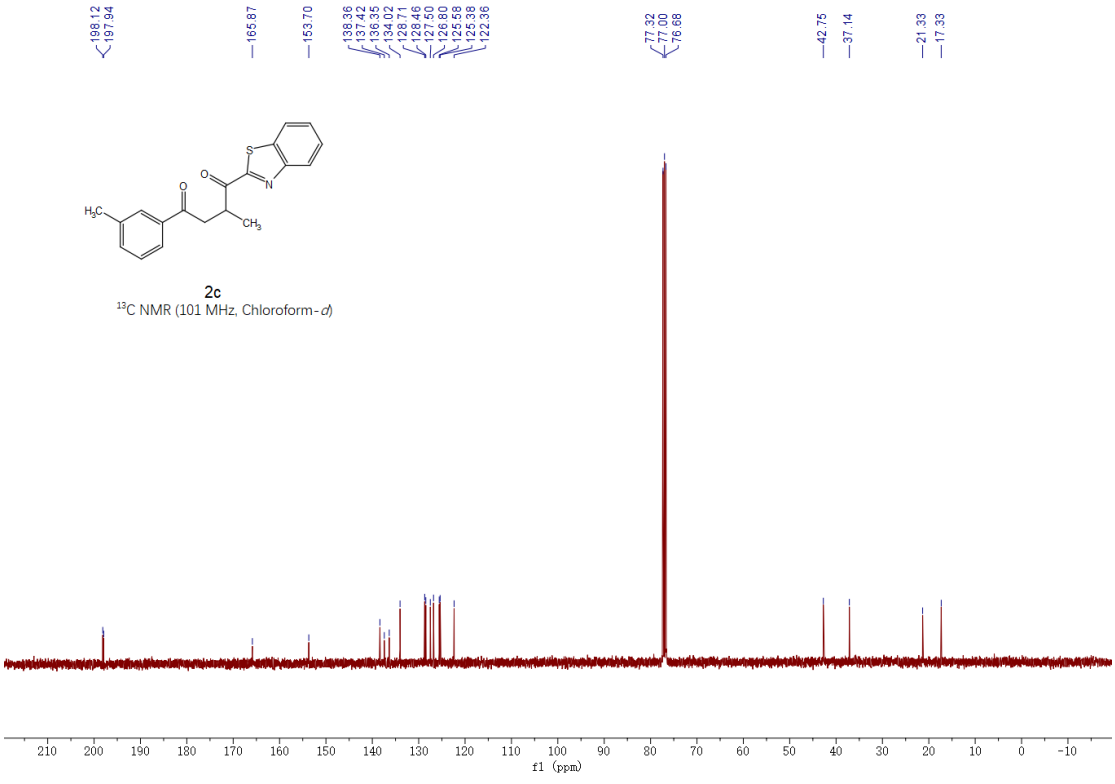
2b

^{19}F NMR (376 MHz, Chloroform-*d*)



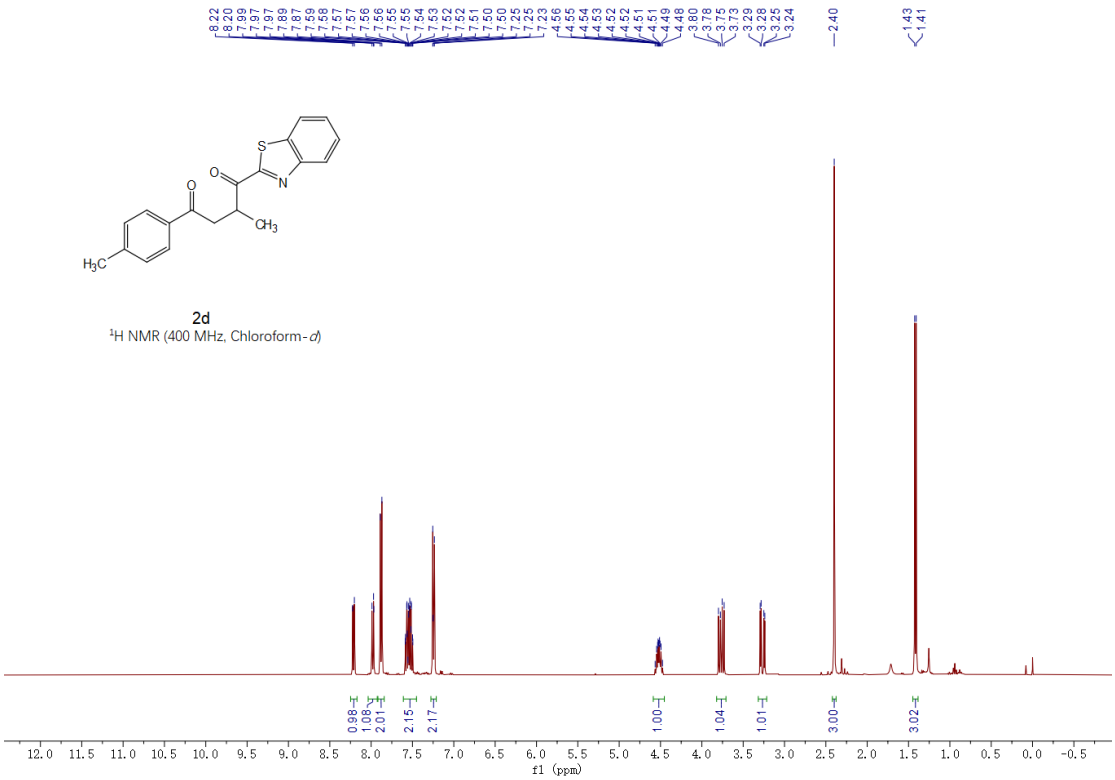
2c

^{1}H NMR (400 MHz, Chloroform-*d*)



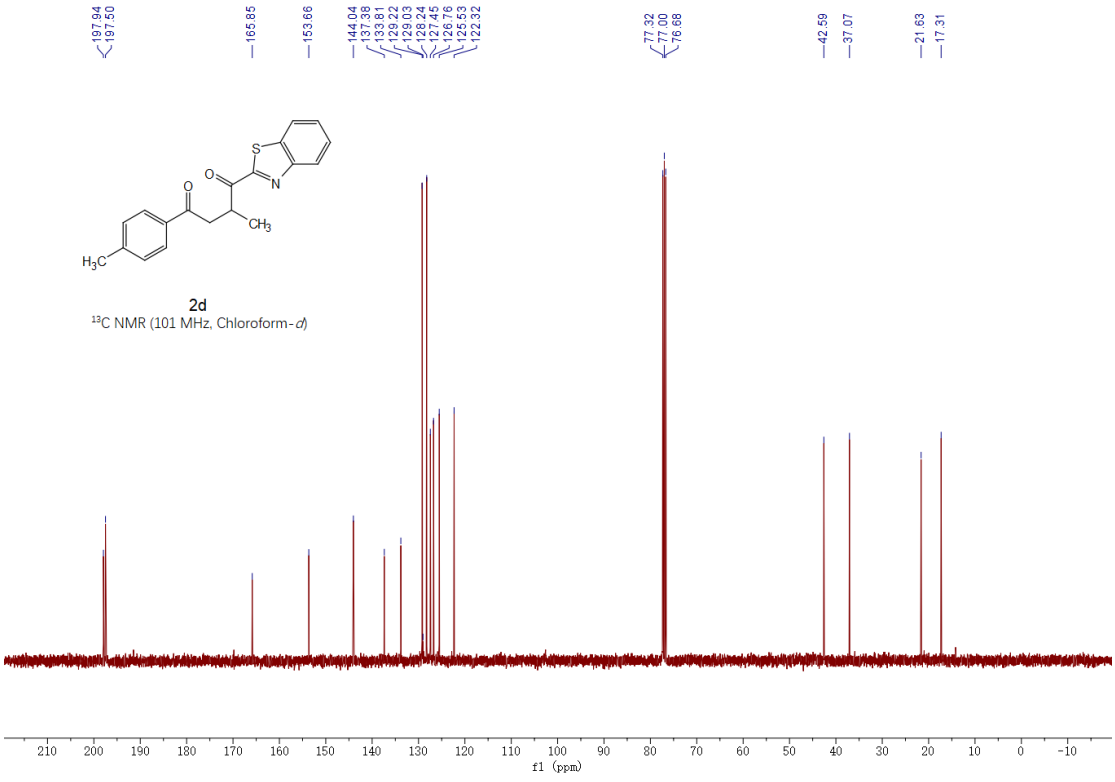
2c

^{13}C NMR (101 MHz, Chloroform-*d*)



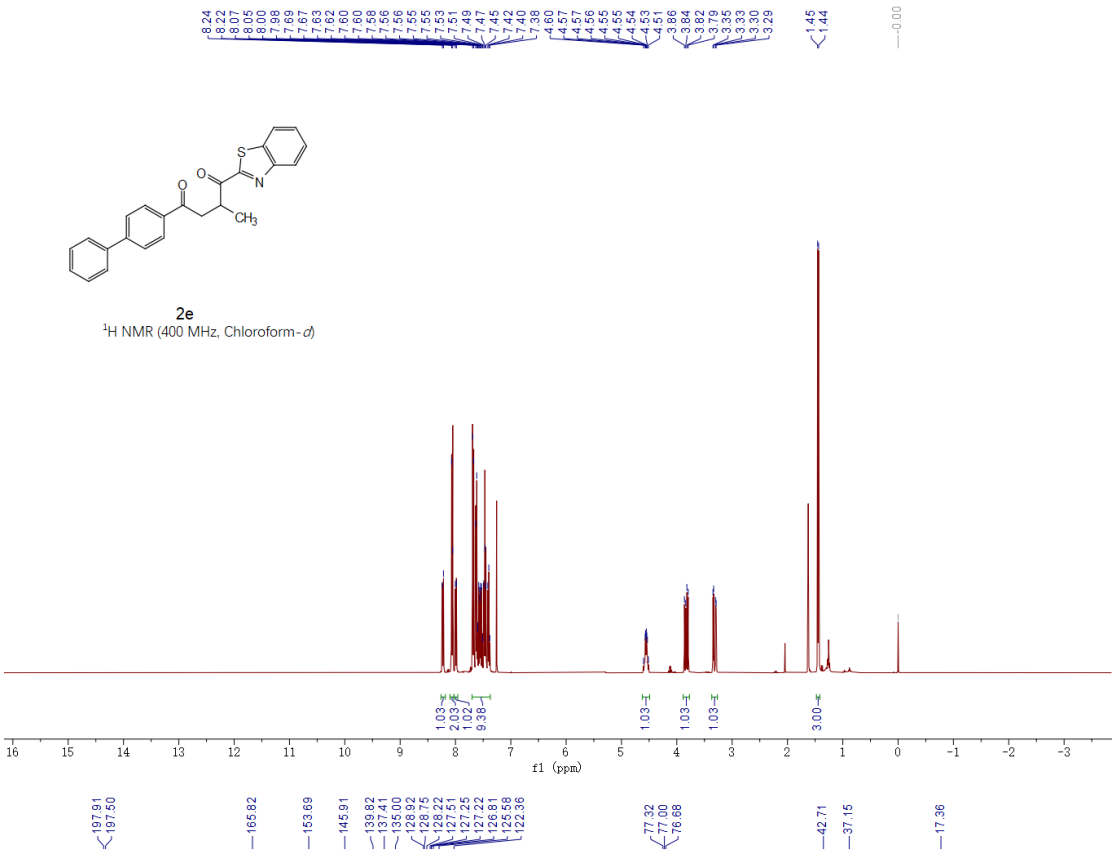
2d

^{1}H NMR (400 MHz, Chloroform-*d*)



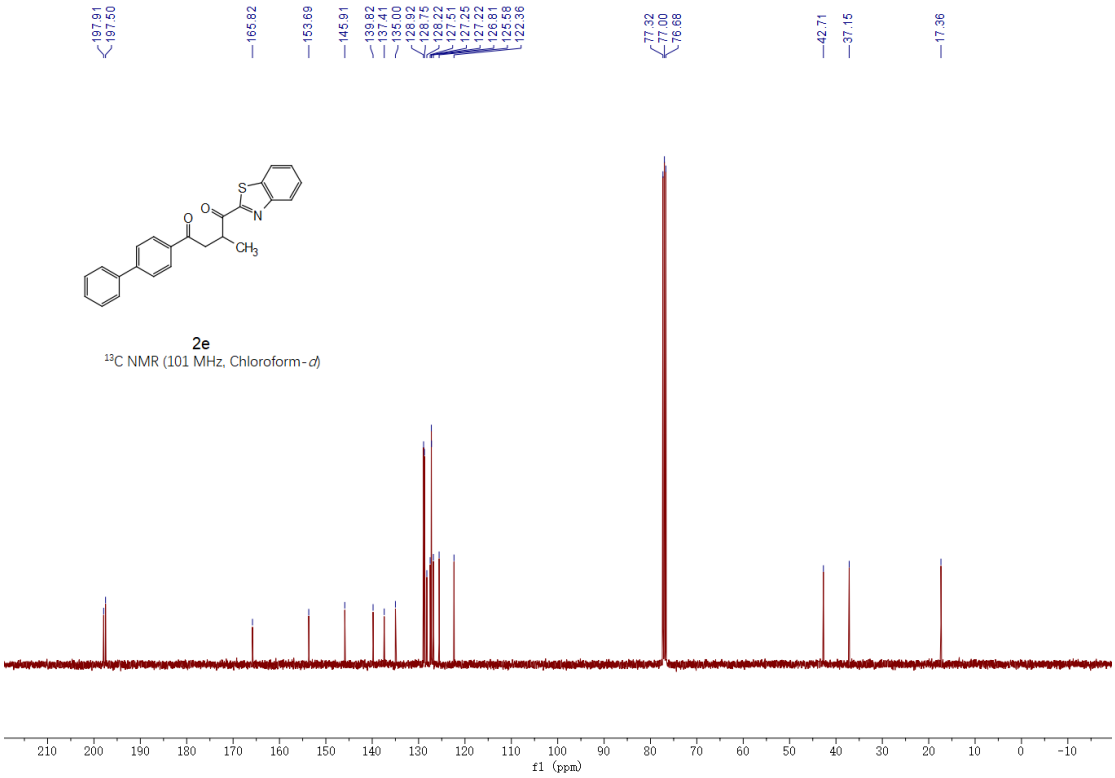
2d

^{13}C NMR (101 MHz, Chloroform-*d*)



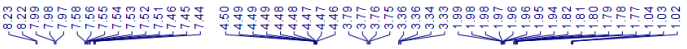
2e

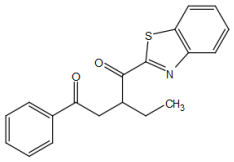
^{1}H NMR (400 MHz, Chloroform-*d*)



2e

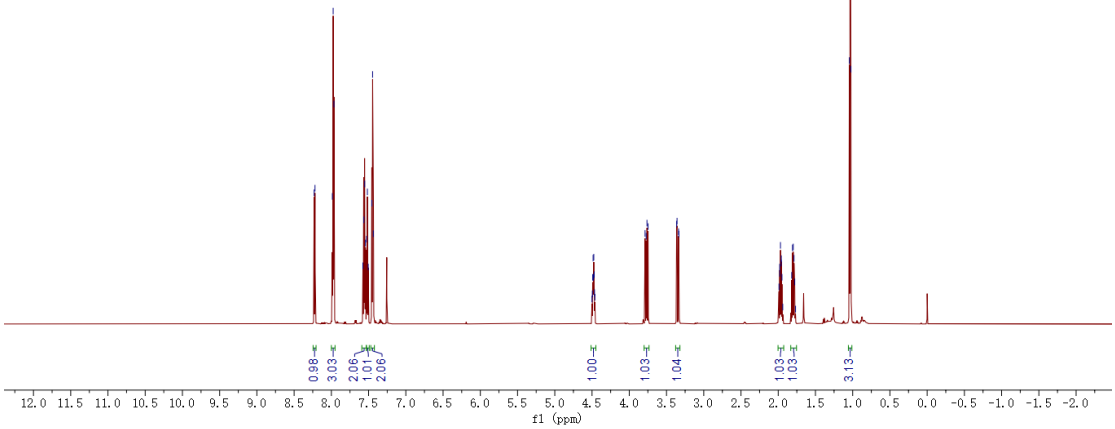
^{13}C NMR (101 MHz, Chloroform-*d*)

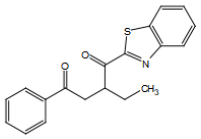




2f

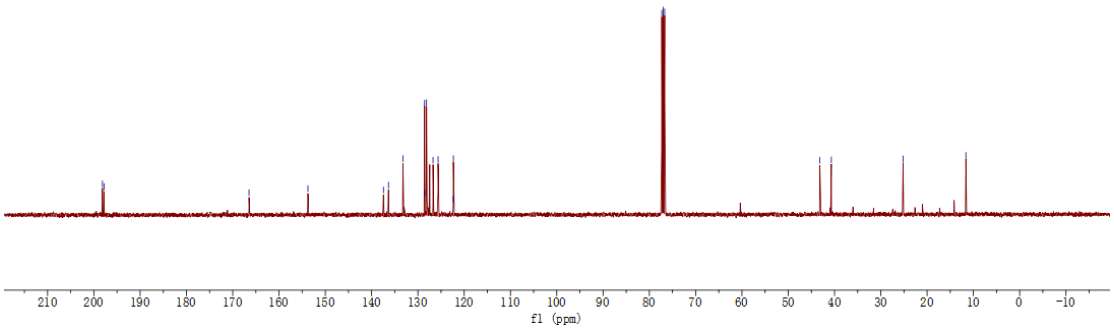
^{1}H NMR (700 MHz, Chloroform-*d*)





2f

^{13}C NMR (101 MHz, Chloroform-*d*)



7. Reference

[1]. Lassalas, P.;Marsais, F.;Hoarau, C., DMAP-Catalyzed Regel-Type Direct C-2 (Hetero)Aroylation of Oxazoles and Thiazoles Derivatives with Acid Chlorides. *Synlett* **2013,** *24*, 2233-2240.

[2]. Wang, Y.;Yang, H.;Zheng, Y., et al., Carbon monoxide enabling synergistic carbonylation and (hetero)aryl migration. *Nature Catalysis* **2024,** in press, https://doi.org/10.1038/s41929-024-01204-6.