Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information (ESI)

Photoswitchable Cu(II)/Cu(I) catalyses assisted by enzyme-like non-covalent interactions in Cu(II)-melamine coordination polymer for installing CO_2/CS_2 and CF_3 groups in heterocycles

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Section I. Synthesis of H_6TDPAT, Cu–TDPAT and Zn–TDPAT:

Synthesis of 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine (H_6TDPAT):

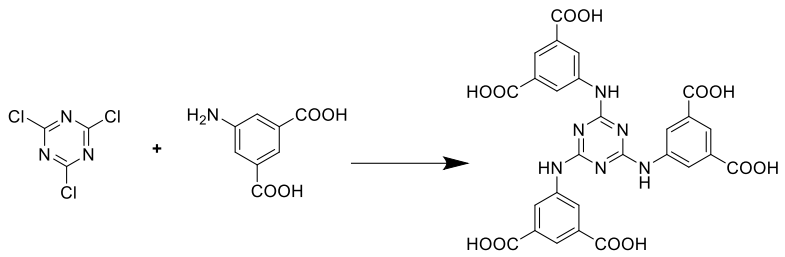


Fig. S1. Diagram of ligand synthesis

H_6TDPAT was synthesized according to the literature with some modification:[1,2,3] NaOH (2.68 g, 0.067 mol), and $NaHCO_3$ (4.37 g, 0.052 mol) were added to 50 mL H_2O. When the system was cooled to room temperature, the 5-aminoisophthalic acid (7.60 g, 0.042 mol) was added into the mixture, and then the mixture was stirred at 0 ℃ for 45 mins. After that, the cyanuric chloride (1.84 g, 0.01 mol), which was suspended in 1,4-dioxane (35 mL), was added dropwise, then the mixture was heated at 100 ℃ for 24h. After cooling down to room temperature, concentrated HCl (aq.) was added into the reaction mixture to adjust pH to 2. The precipitated solid was collected by filtration, and then washed with distilled water for three times and hot methanol for three times successively, and then dried to give pure product H_6TDPAT (5.49 g, 95%). ^{1}H-NMR (d^6-DMSO, 400 MHz): δ 12.84 (br s, 6H), 9.68 (s, 3H), 8.48 (s, 6H), 8.13 (s, 3H). The NMR data were in accordance with the literature.[2]

Synthesis and Activation of Cu–TDPAT:

$[Cu_3(TDPAT)(H_2O)_3]\cdot 10H_2O\cdot 5DMA$: the batch preparation of Cu–TDPAT was in accordance with the literature protocal.[2] 0.6 g (0.98 mmol) of H_6TDPAT was dissolved in the mixture of 20 mL of DMA, 20 mL of DMSO and 2 mL of H_2O. Then, 3.28 g (13.6 mmol) of $Cu(NO_3)_2\cdot 3H_2O$ and 18 mL of HBF_4 were successively added into the solution. The mixture was sonicated until it became homogeneous, and then equally divided into 20 portions, sealed in vials, and heated at 85 ℃ for 3 days. After cooling down to room temperature, blue crystals were collected (0.895 g, 62% yield, calculated based upon ligand).

The sample of Cu–TDPAT was activated according to the literature with some modification.[2] The crystals were washed with methanol three times to remove impurity on surface, then soaked in methanol three days to remove the non-volatile solvents in pores, the fresh methanol was changed every 12 hrs. Following, the crystals were treated with supercritical carbon dioxide, and the sample was then subjected to vacuum heating at 75 ℃ for 6 hrs. After cooling down, the activated sample of Cu–TDPAT was stored in the predried and N_2-filled Schlenk tube away from light.

Synthesis and Activation of Zn–TDPAT:

$Zn_3(TDPAT)(H_2O)\cdot 3.125H_2O\cdot 4DMF$: the batch preparation of Zn–TDPAT was in accordance with the literature protocol.[3] 0.76 g (1.22 mmol) of H_6TDPAT was dissolved in the mixture of 80 mL of DMF, 40 mL of ethylene glycol and 10 mL of H_2O. Then, 1.58 g (5.32 mmol) of $Zn(NO_3)_2\cdot 6H_2O$ and 10 mL of HNO_3 (3.5 mol/L in DMF) were successively added into the solution. The mixture was sonicated until it became homogeneous, and then equally divided into 20 portions, sealed in vials, and heated at 80 ℃ for 3 days. After cooling down to room temperature, purple crystals were collected (0.65 g, 44% yield, calculated based upon ligand).

The crystals were washed with DMF three times to remove impurity on surface, and washed with methanol to remove the residual DMF, then soaked in methanol three days to remove the non-volatile solvents in pores, the fresh methanol was changed every 12 hrs. Following, the crystals were treated with supercritical carbon dioxide, and the sample was then subjected to vacuum at 25 ℃ for 6 hrs. After cooling down, the activated sample of Zn–TDPAT was stored in the predried and N_2-filled Schlenk tube away from light.

Section II Supplementary Figure.

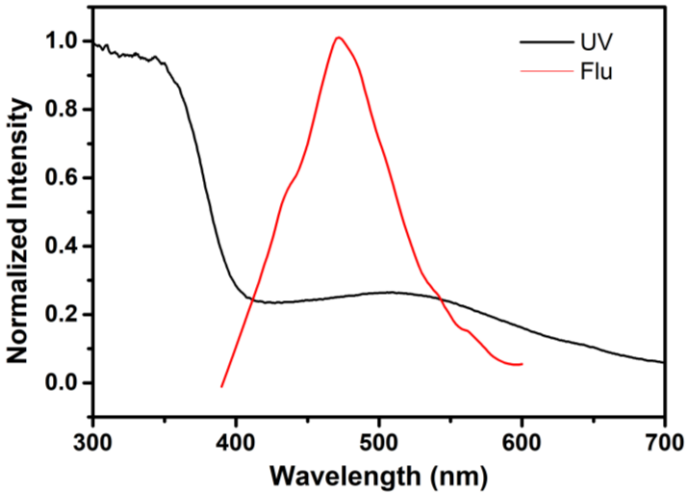


Fig. S2. The UV-vis (black line) and fluorescence (red line) spectra of H_6TDPAT in DMSO solution. Irradiated at 328 nm

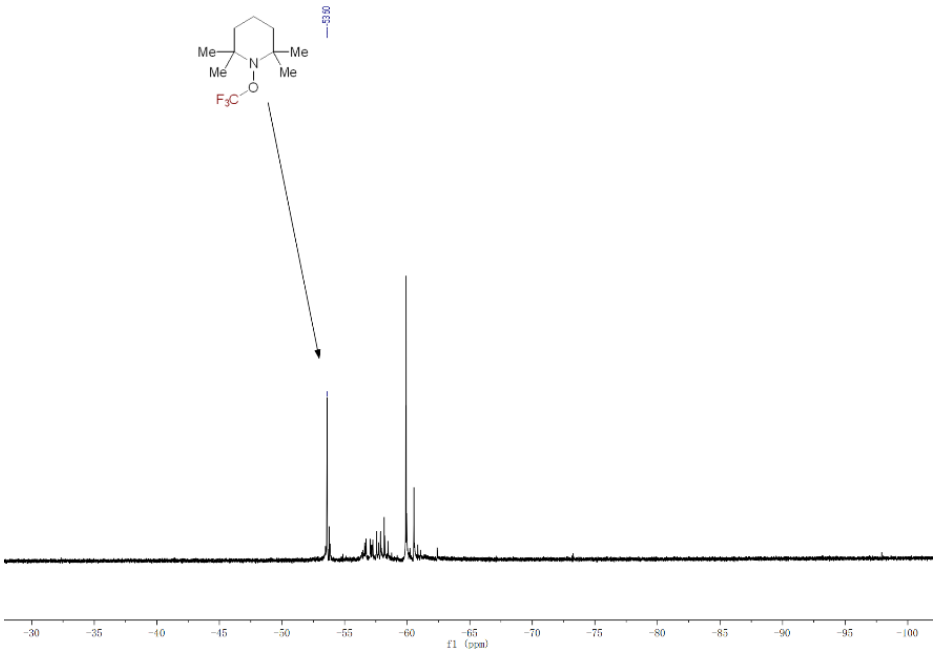


Fig. S3. ^{19}F NMR spectra of TEMPO-CF_3

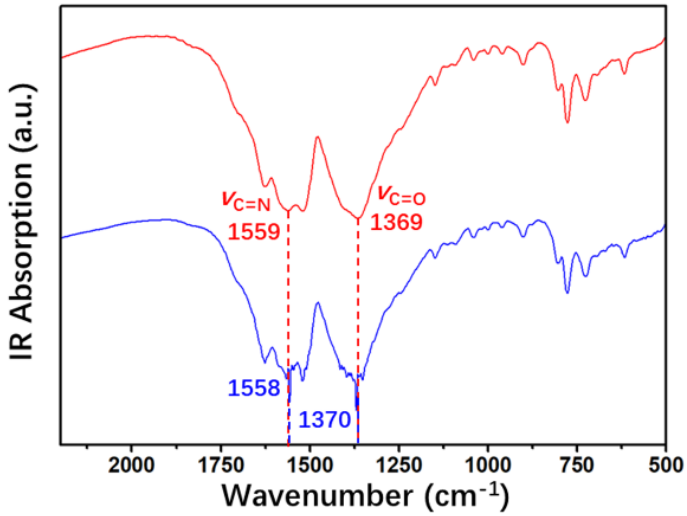


Fig. S4. Comparison of the IR spectra of Zn−TDPAT (red) and Zn−TDPAT encapsulated with CS_2 (blue).

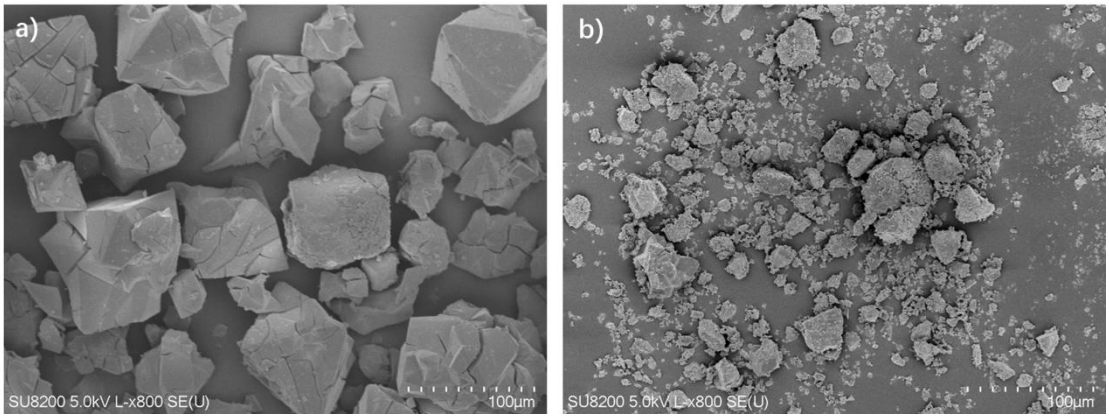
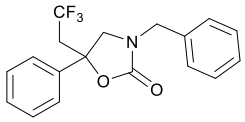


Fig. S5. Comparison of the scanning electron microscope (SEM) images of Cu−TDPAT before (a) and after (b) photocatalysis.

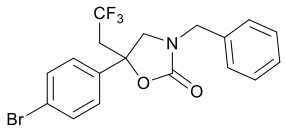
Section III NMR Data of the Products.

3-Benzyl-5-phenyl-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2a**)



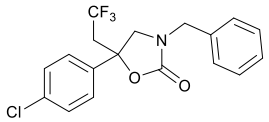
This compound was synthesized according to the general procedure (GP) and isolated by flash chromatography as colorless sticky oil (*ca.* 64.6 mg, 77%) using petroleum ether/ethyl acetate (v:v 10:1~7:1) as the gradient eluent system. Known compound.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43-7.28 (m, 8H), 7.20 (d, J = 7.5 Hz, 2H), 4.44 (dd, J = 47.3, 14.9 Hz, 2H), 3.68 (dd, J = 58.9, 9.1 Hz, 2H), 2.79 (qd, J = 10.1, 2.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.3, 140.9, 135.1, 128.9, 128.9, 128.7, 128.14, 128.07, 124.4 (q, J = 278.4 Hz), 124.3, 78.1 (q, J = 2.2 Hz), 55.2 (q, J = 1.5 Hz), 48.3, 44.4 (q, J = 27.8Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -60.56 (t, J = 10.1 Hz, 3F).

3-Benzyl-5-(4-bromophenyl)-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2b**)



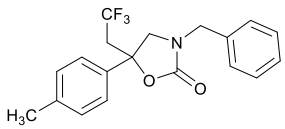
This compound was synthesized according to the general procedure (GP) and isolated by flash chromatography as yellow sticky oil (*ca.* 76.5 mg, 74%) using petroleum ether/ethyl acetate (v:v 7:1~5:1) as the gradient eluent system. Known compound.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.49 (m, 2H), 7.36-7.29 (m, 3H), 7.27-7.16 (m, 4H), 4.43 (dd, J = 37.9, 14.9 Hz, 2H), 3.64 (dd, J = 67.8, 9.2 Hz, 2H), 2.77 (q, J = 10.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.0, 139.8, 134.9, 132.1, 129.0, 128.3, 128.1, 125.2, 124.3 (q, J = 276.7 Hz), 122.9, 77.7 (q, J = 2.1 Hz), 55.0, 48.3, 44.3 (q, J = 28.0 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -60.46 (t, J = 10.0 Hz, 3F).

3-Benzyl-5-(4-chlorophenyl)-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2c**)



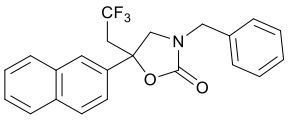
This compound was synthesized according to the general procedure (GP) and isolated by flash chromatography as colorless sticky oil (*ca.* 66.5 mg, 72%) using petroleum ether/ethyl acetate (v:v 7:1~5:1) as the gradient eluent system. Known compound.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.27 (m, 7H), 7.22-7.17 (m, 2H), 4.43 (dd, J = 44.7, 14.9 Hz, 2H), 3.64 (dd, J = 82.8, 9.2 Hz, 2H), 2.77 (q, J = 10.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.0, 139.2, 134.9, 134.8, 129.1, 128.9, 128.3, 128.1, 125.9, 124.3 (q, J = 278.3 Hz), 77.7 (q, J = 2.2 Hz), 55.1 (d, J = 1.4 Hz), 48.3, 44.4 (q, J = 27.8Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -60.48 (t, J = 10.0 Hz, 3F).

3-Benzyl-5-(*p*-tolyl)-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2d**)



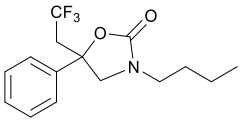
This compound was synthesized according to the general procedure (GP) and isolated by flash chromatography as colorless sticky oil (*ca.* 53.3 mg, 61%) using petroleum ether/ethyl acetate (v:v 5:1) as the eluent system. Known compound.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 3H), 7.25-7.16 (m, 6H), 4.43 (dd, J = 48.7, 14.9 Hz, 2H), 3.66 (dd, J = 55.3, 9.1 Hz, 2H), 2.77 (qd, J = 10.1, 2.8 Hz, 2H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.4, 138.5, 137.9, 135.1, 129.5, 128.90, 128.12, 128.08, 124.5 (q, J = 278.4 Hz), 124.2, 78.1 (q, J = 2.1 Hz), 55.0, 48.3, 44.4 (q, J = 27.6 Hz), 21.1. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -60.57 (t, J = 10.1 Hz, 3F).

3-Benzyl-5-(naphthalen-2-yl)-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2e**)



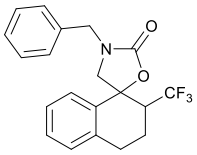
This compound was synthesized according to the general procedure (GP) and isolated by flash chromatography as colorless sticky oil (*ca.* 57.8 mg, 60%) using petroleum ether/ethyl acetate (v:v 7:1~5:1) as the gradient eluent system. Known compound.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.86 (dd, J = 11.9, 7.2 Hz, 3H), 7.56-7.50 (m, 2H), 7.36-7.18 (m, 6H), 4.45 (dd, J = 65.1, 15.0 Hz, 2H), 3.76 (dd, J = 61.4, 9.2 Hz, 2H), 2.95 – 2.83 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.4, 137.9, 135.0, 133.0, 132.9, 129.1, 128.9, 128.4, 128.2, 128.1, 127.7, 126.9, 124.5 (q, J = 278.5 Hz), 123.6, 121.7, 78.2 (q, J = 2.1 Hz), 55.0, 48.4, 44.3 (q, J = 27.9 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -60.51 (t, J = 10.1 Hz, 3F).

3-Butyl-5-phenyl-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2f**)



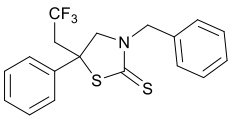
This compound was synthesized according to the general procedure (GP) and isolated by flash chromatography as colorless oil (*ca.* 56.5 mg, 75%) using petroleum ether/ethyl acetate (v:v 7:1~5:1) as the gradient eluent system. Known compound.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.34 (m, 5H), 3.84 (dd, J = 79.0, 9.0 Hz, 2H), 3.26 (dtd, J = 21.4, 14.0, 7.5 Hz, 2H), 2.83 (qd, J = 10.1, 2.4 Hz, 2H), 1.55-1.45 (m, 2H), 1.33-1.27 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.2, 141.2, 128.9, 128.6, 124.5 (q, J = 278.5 Hz), 124.3, 77.8 (q, J = 2.2 Hz), 55.6 (d, J = 1.5 Hz), 44.5 (q, J = 27.7 Hz), 43.9, 29.3, 19.8, 13.7. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -60.59 (t, J = 10.1 Hz, 3F).

3'-Benzyl-2-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,5'-oxazolidin]2'-one (**2g**)



This compound was synthesized according to the general procedure (GP) and isolated by flash chromatography as colorless sticky oil (*ca.* 57.8 mg, 64%) using petroleum ether/ethyl acetate (v:v 5:1~4:1) as the gradient eluent system. Known compound.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.23 (m, 8H), 7.10-7.06 (m, 1H), 4.51 (dd, J = 42.0, 14.8 Hz, 2H), 3.84 (d, J = 9.7 Hz, 1H), 3.32 (d, J = 9.7 Hz, 1H), 2.99 – 2.81 (m, 3H), 2.28-2.21 (m, 1H), 1.84-1.71 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.9, 137.6, 134.2, 133.5, 127.8, 127.7, 127.5, 127.3, 127.1, 125.5, 124.3, 124.2 (q, J = 288.7 Hz), 76.0, 52.4 (q, J = 1.9 Hz), 47.5, 45.4 (q, J = 25.5 Hz), 28.7, 19.1 (d, J = 2.2 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -66.38 (d, J = 8.9 Hz, 3F).

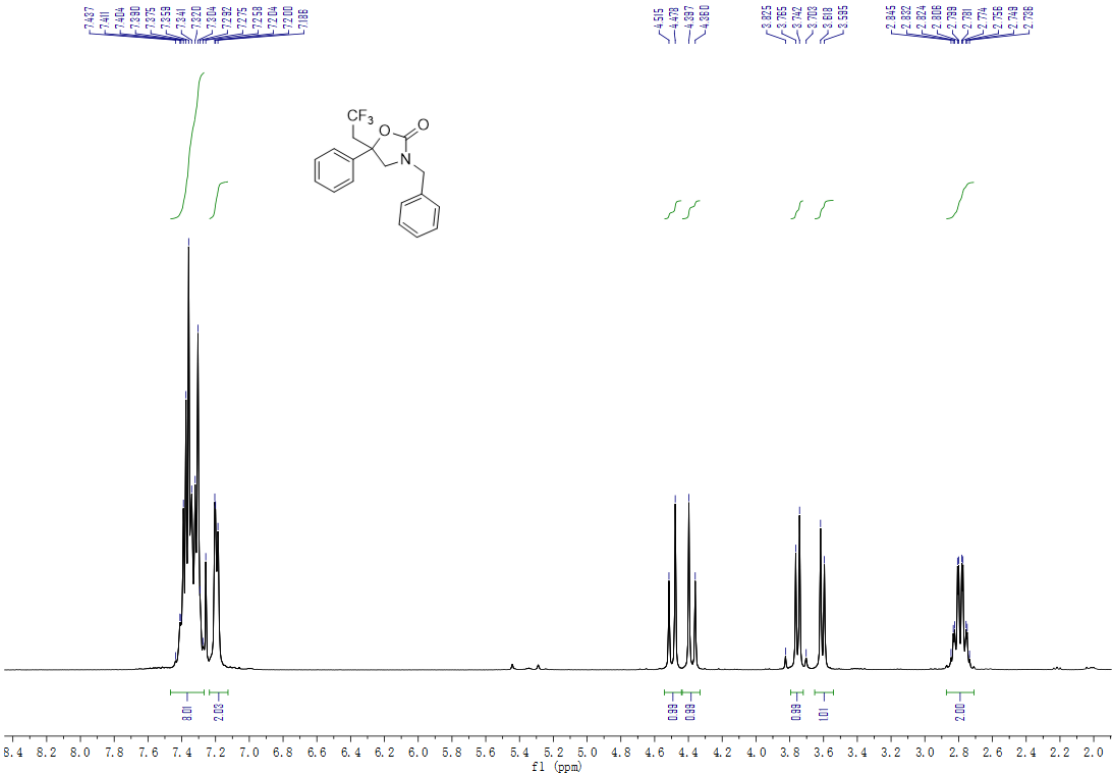
3-Benzyl-5-phenyl-5-(2,2,2-trifluoroethyl)thiazolidine-2-thione (**3a**)

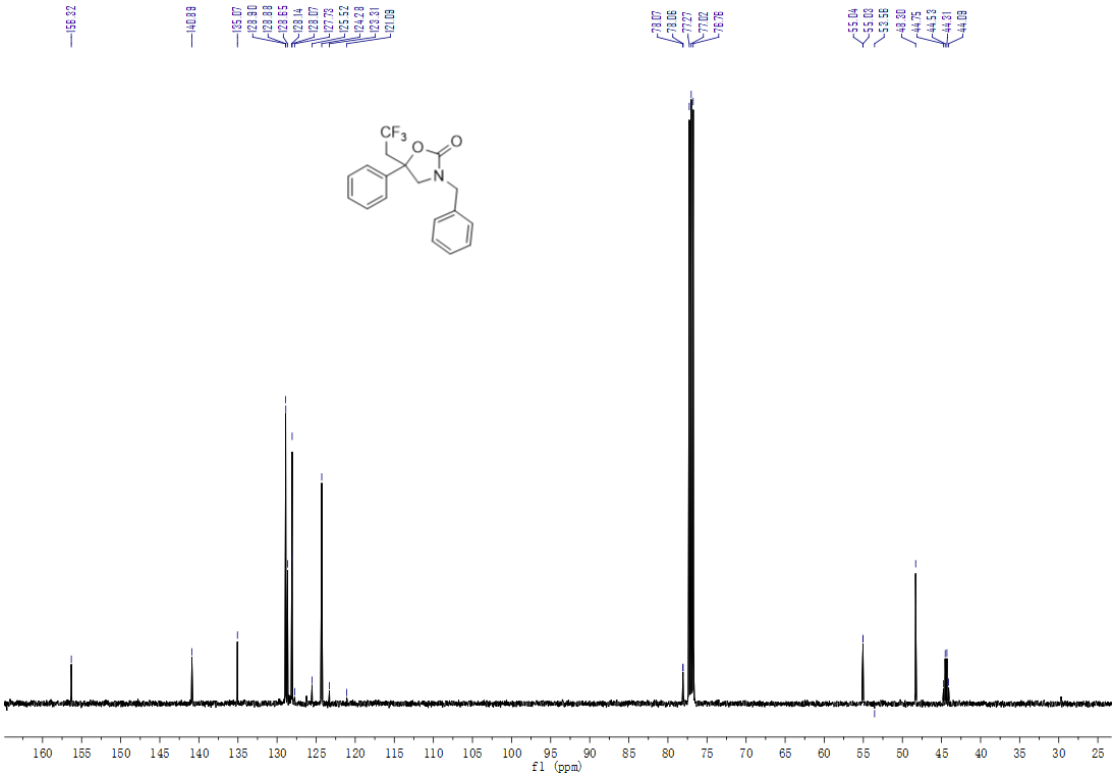


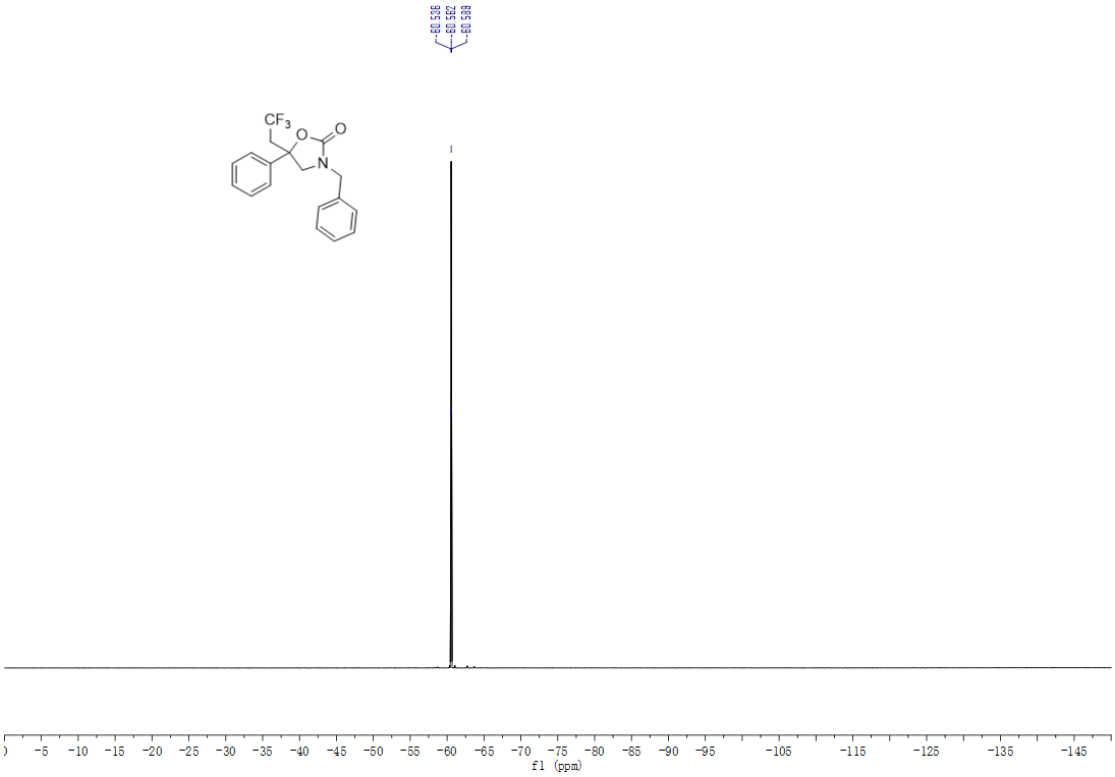
This compound was synthesized according to the general procedure (GP) using CS_2 instead of CO_2, and isolated by flash chromatography as yellow sticky oil (*ca.* 49.6 mg, 54%) using petroleum ether/ethyl acetate (v:v 4:1~3:1) as the gradient eluent system. **^{1}H NMR** (500 MHz, $CDCl_3$) 7.35-7.27 (m, 8H), 7.18-7.16 (m, 2H), 5.02 (dd, J = 36.1, 14.5 Hz, 2H), 4.23 (dd, J = 48.9, 11.9 Hz, 2H), 2.95 (qd, J = 10.0, 3.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.1, 137.0, 133.6, 128.0, 127.9, 127.5 (overlapped), 127.4, 126.8 (q, J = 275.6 Hz), 125.0, 63.0 (d, J = 1.8 Hz), 53.9 (q, J = 1.7 Hz), 51.7, 43.5 (q, J = 27.5 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -60.73 (t, J = 10.1 Hz, 3F). HRMS (ESI^+): calcd for $C_{18}H_{17}F_3NS_2^+$ $[M+H]^+$ 368.0749, found 368.0741.

Section IV NMR Spectra of the Products.

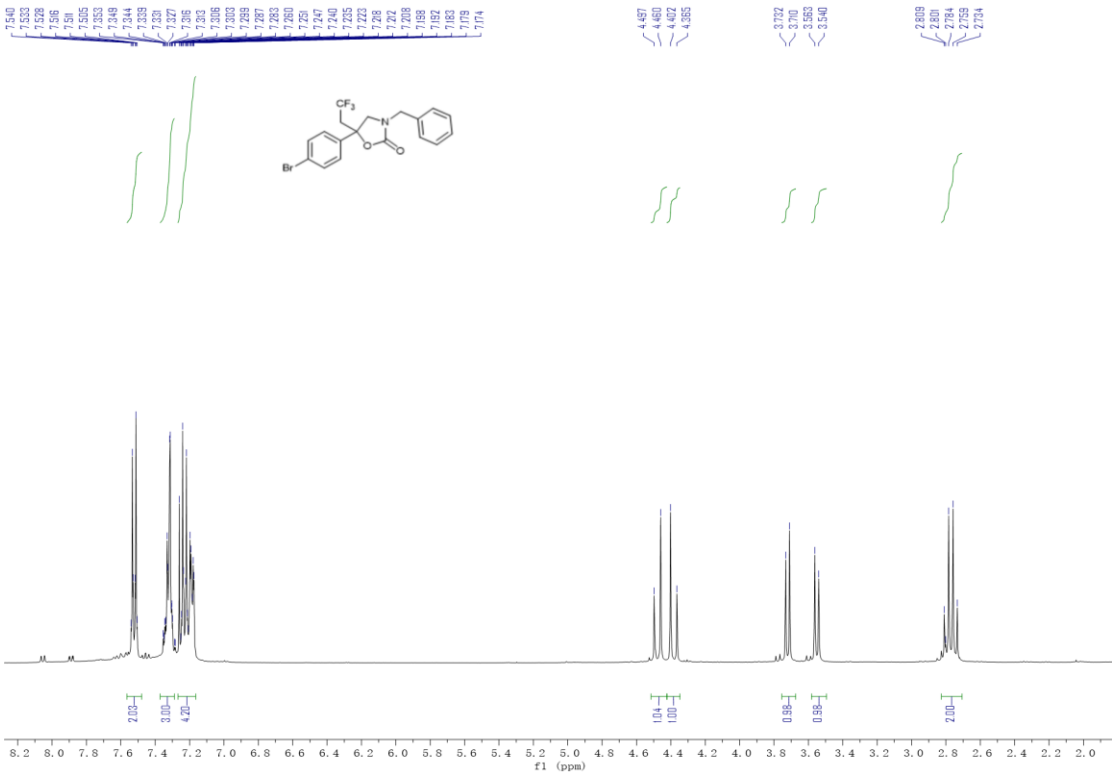
3-Benzyl-5-phenyl-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2a**)

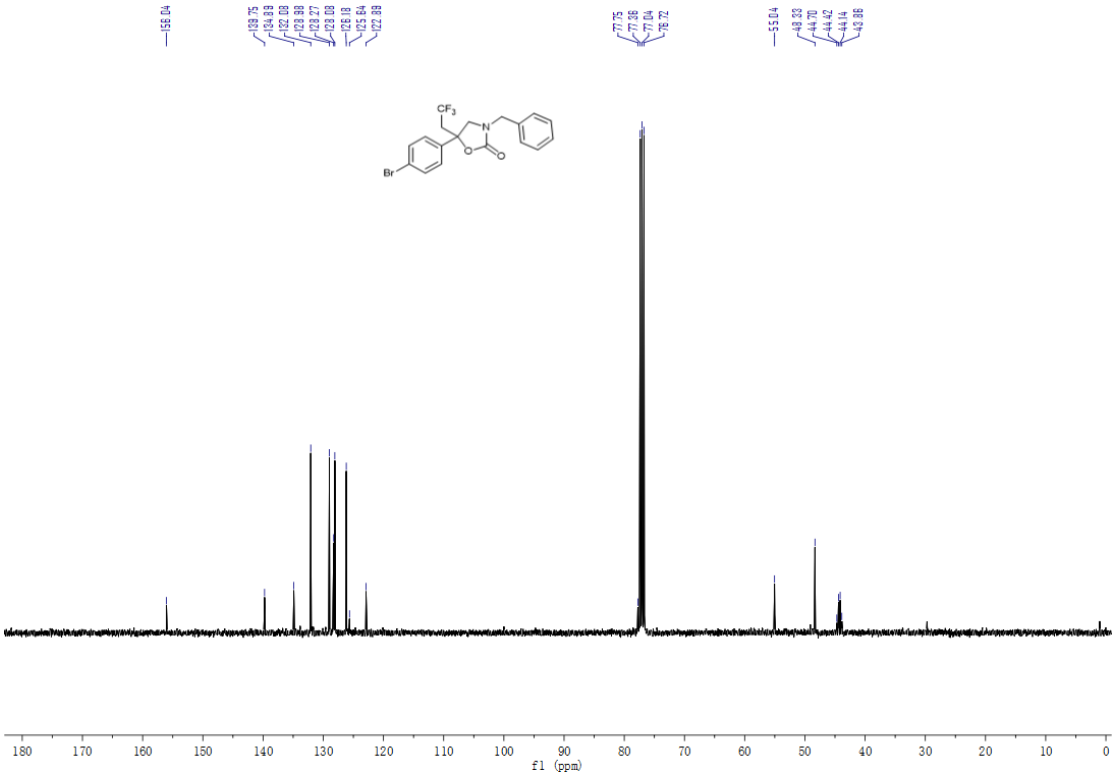






3-Benzyl-5-(4-bromophenyl)-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2b**)

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132.08
129.88
128.27
128.08
126.18
125.64
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77.73
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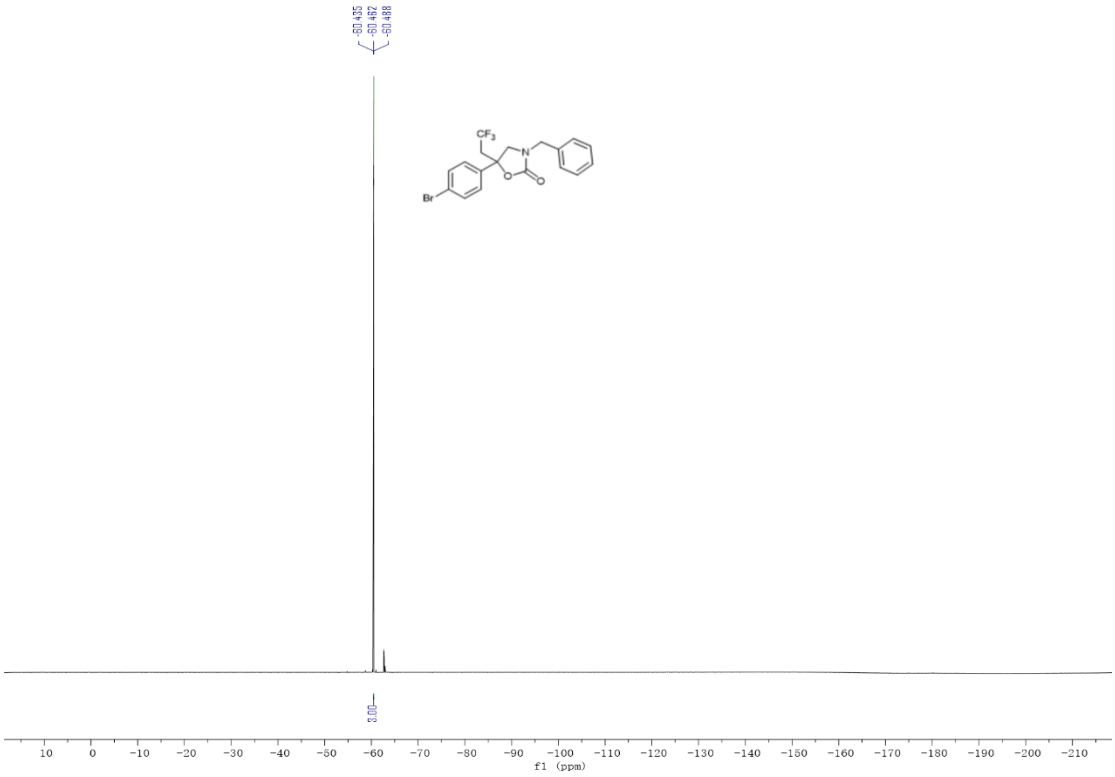
77.04
76.72
55.04
48.33
44.70
44.42
44.14
43.86
CF3
N
O
O
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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CF3
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O
O
Br
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-10
-20
-30
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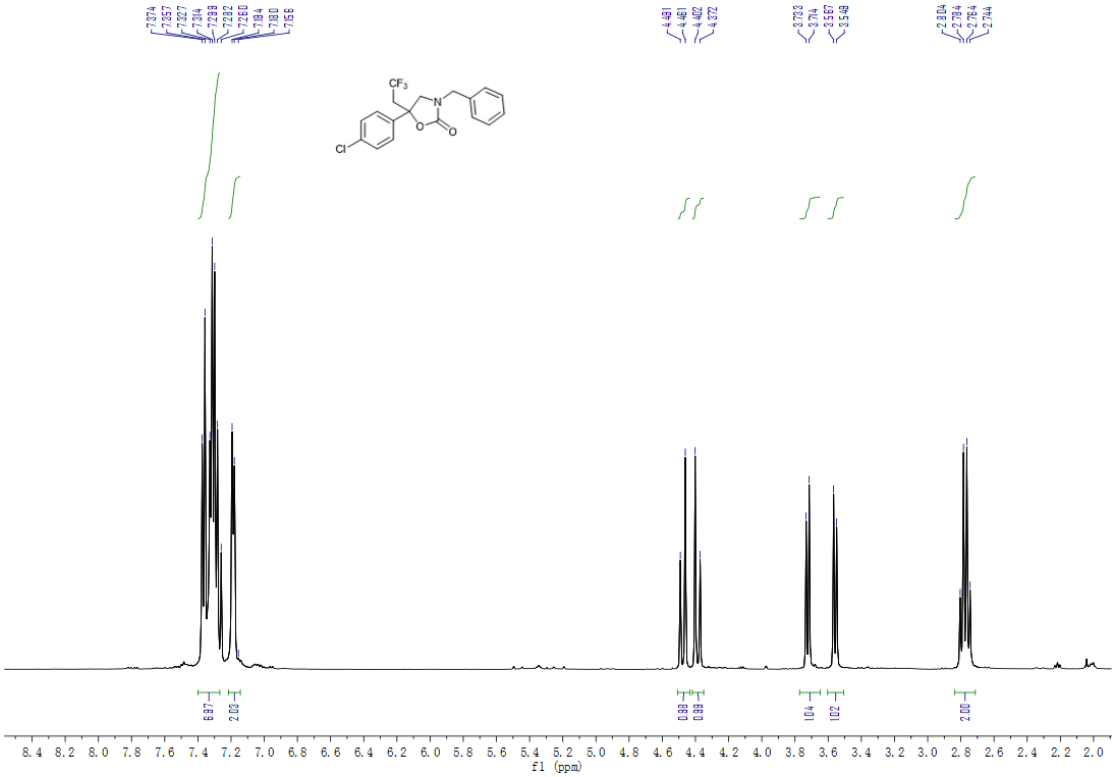
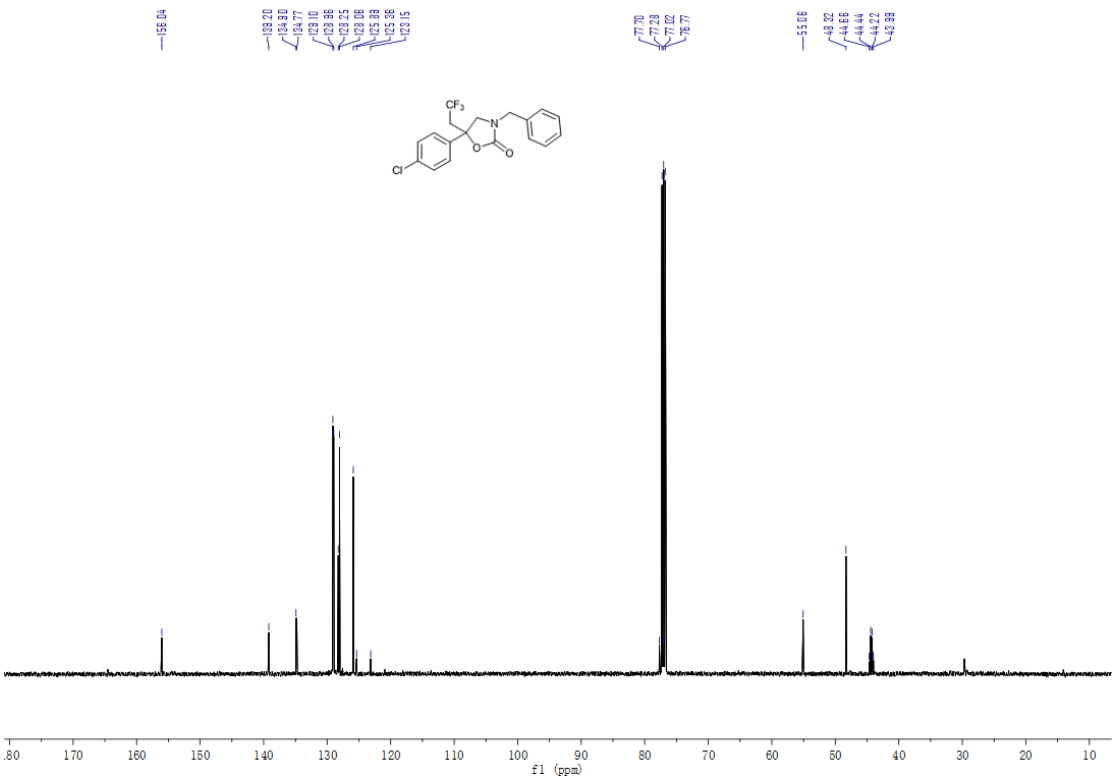
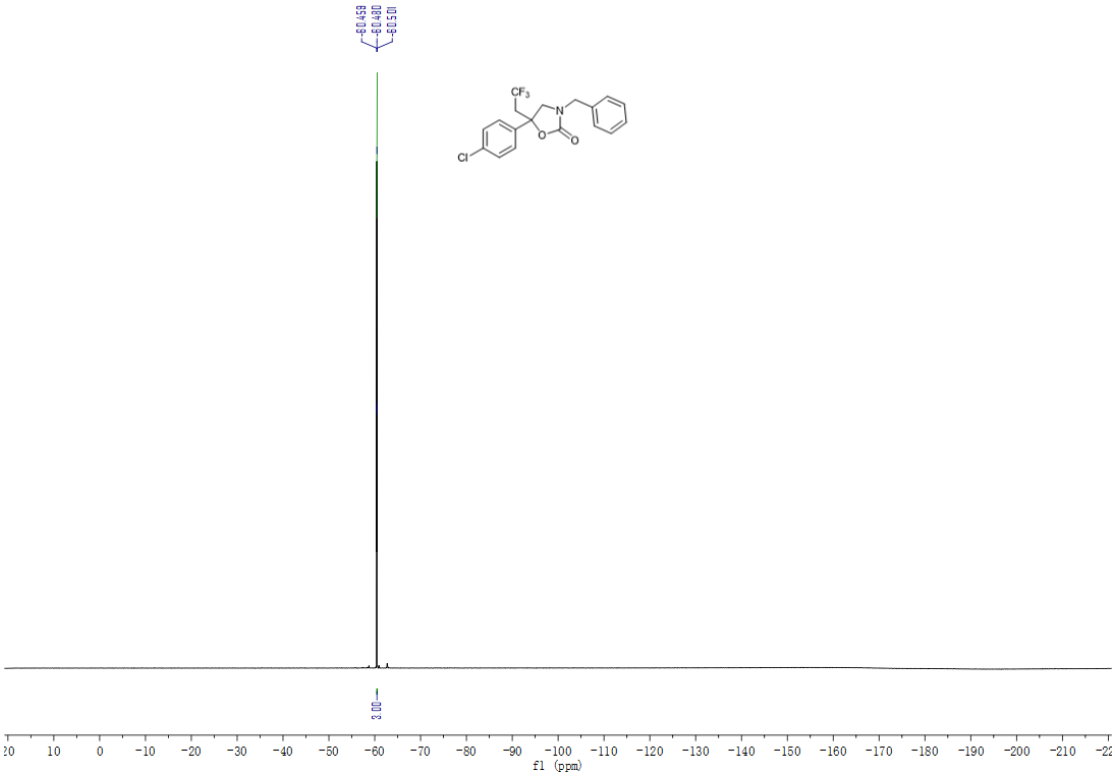
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

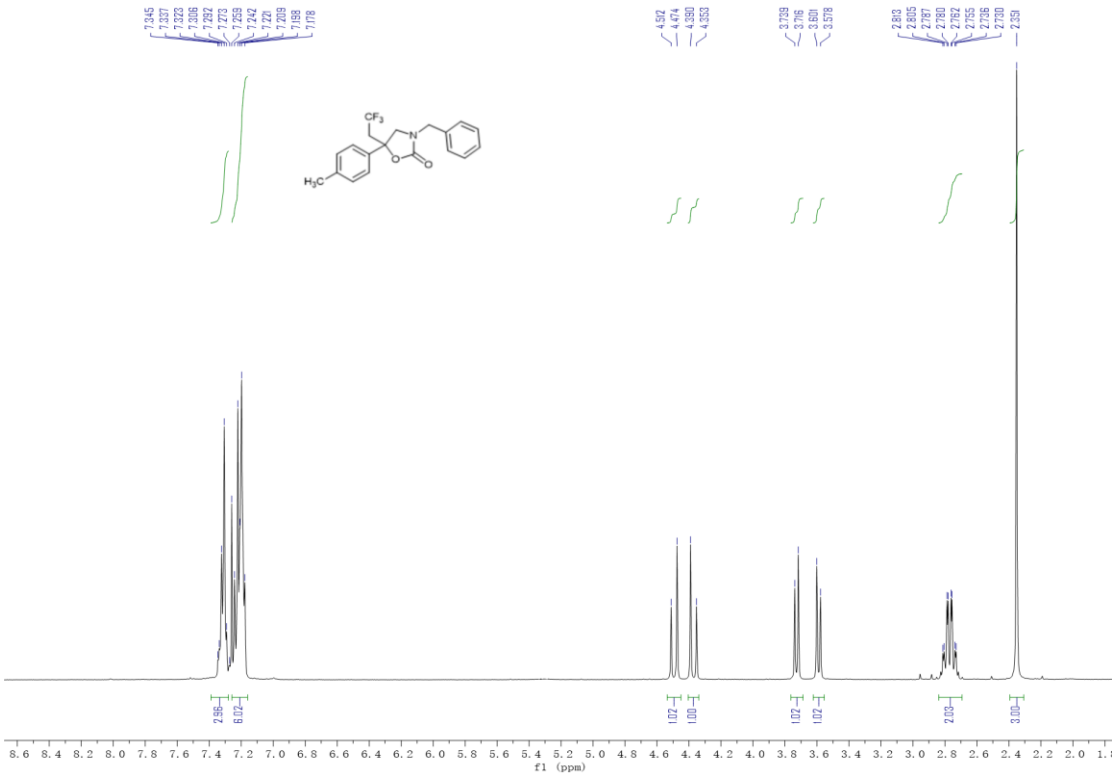
3-Benzyl-5-(4-chlorophenyl)-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2c**)

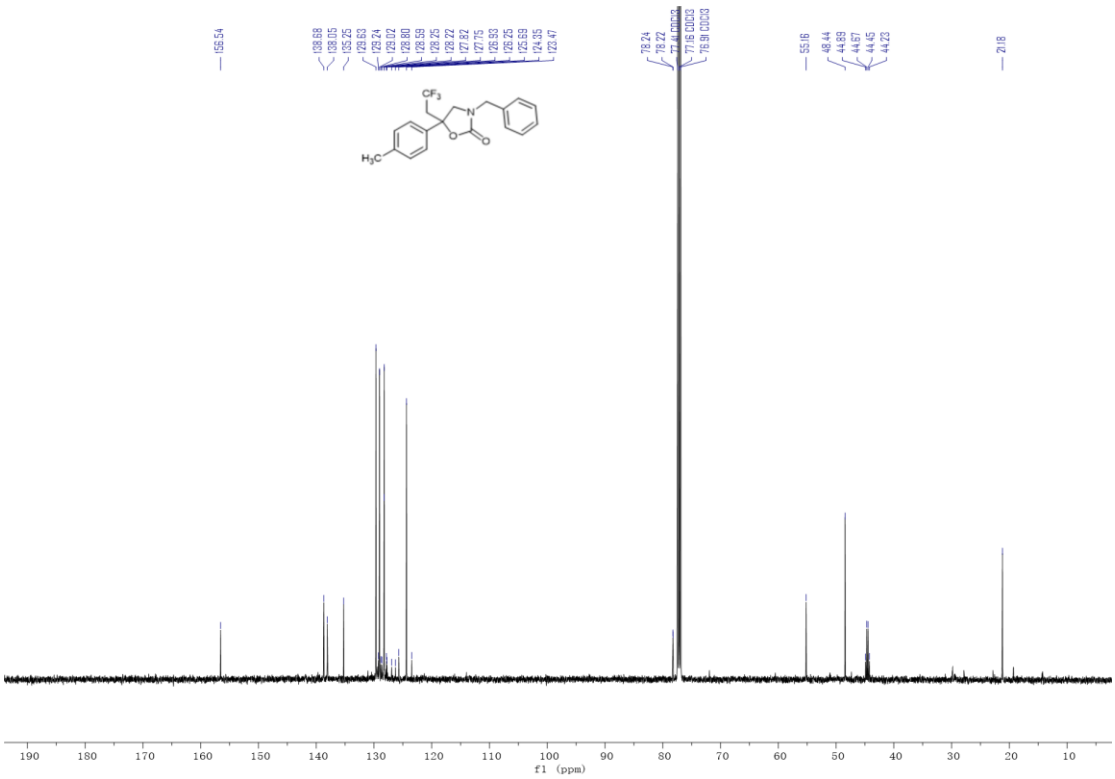


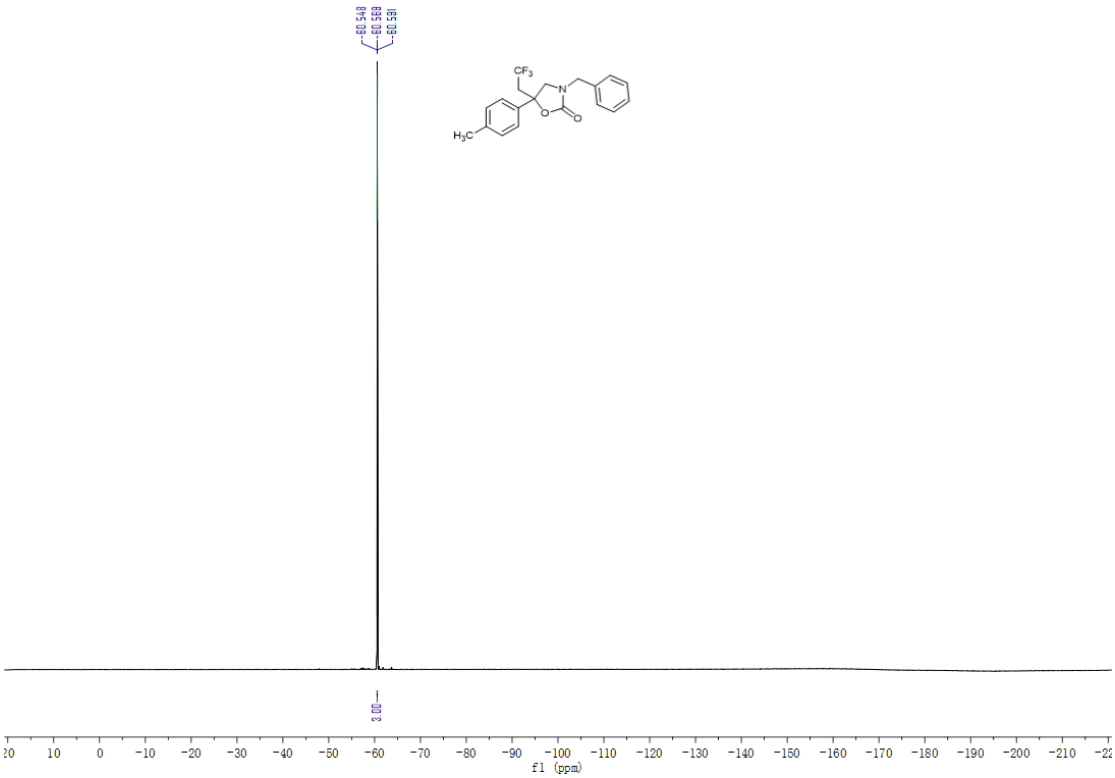




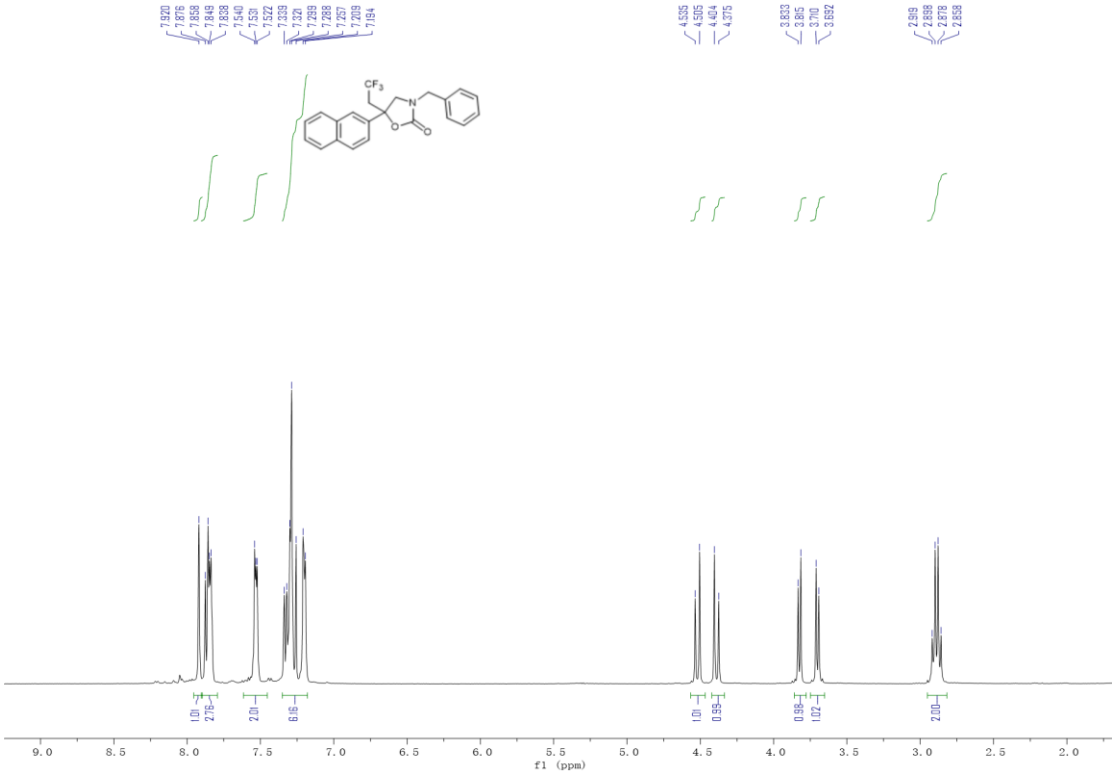
3-Benzyl-5-(*p*-tolyl)-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2d**)

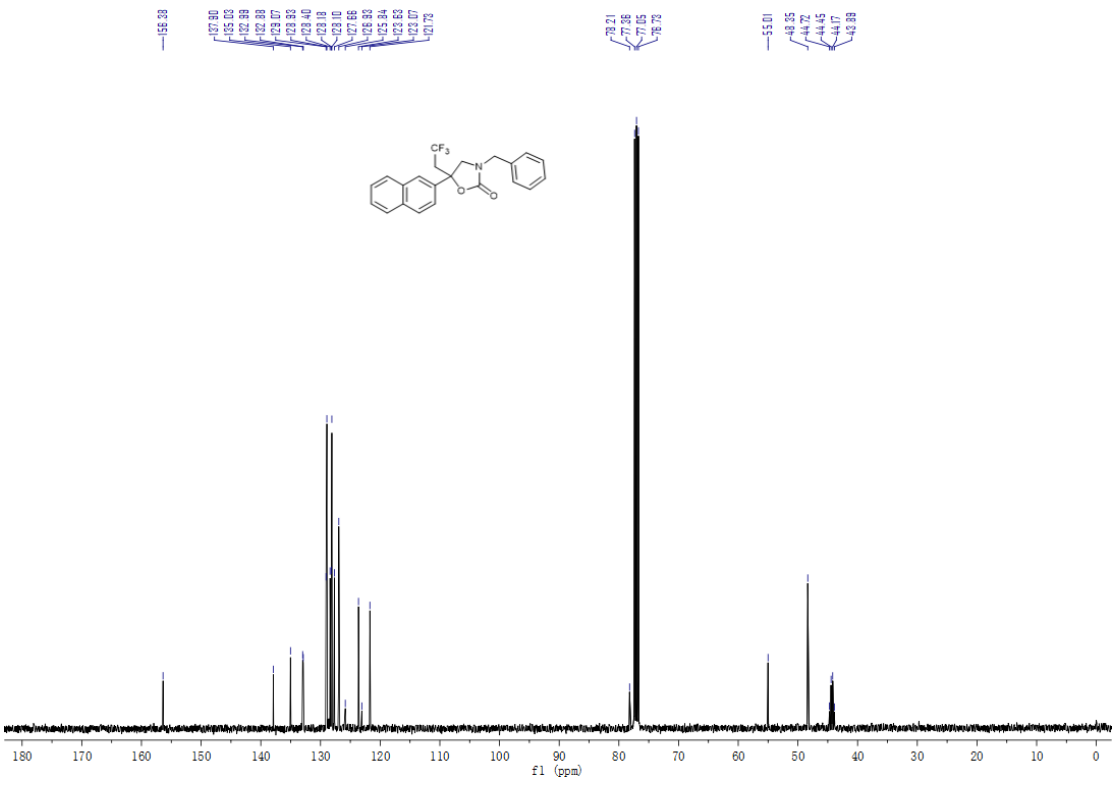


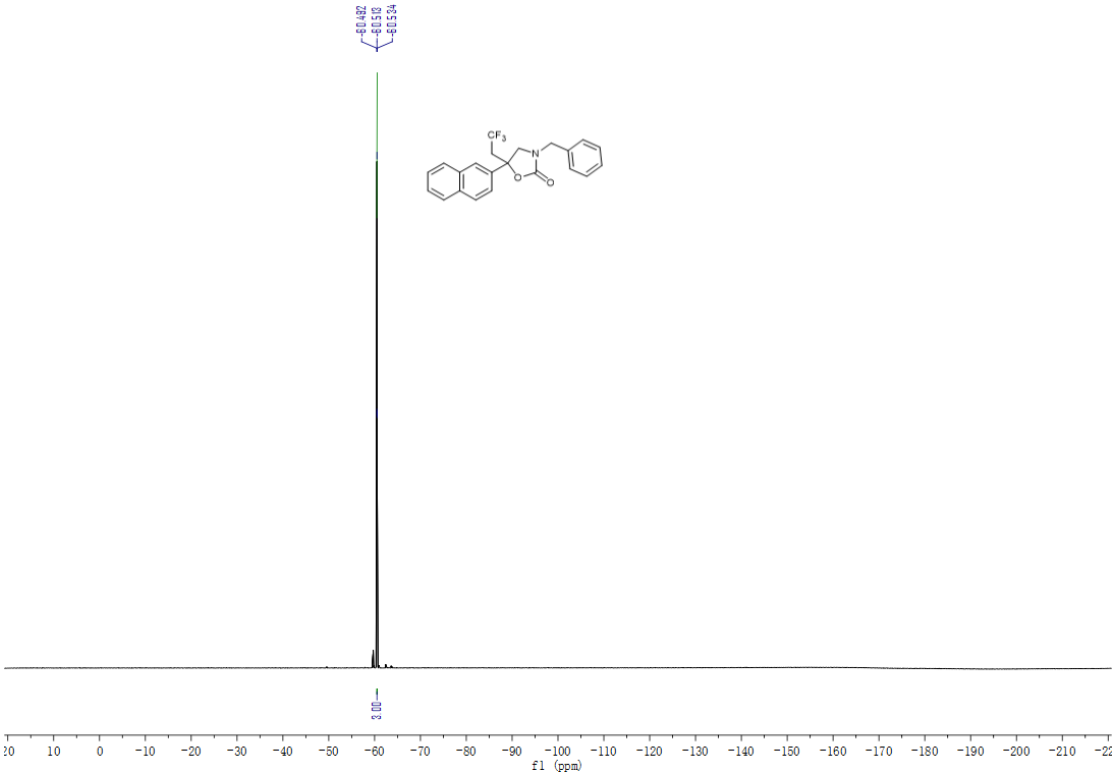

156.54
138.68
138.05
135.25
129.63
129.24
129.02
128.80
128.59
128.25
128.22
127.82
127.75
126.83
126.25
125.69
124.35
123.47
78.24
77.82
77.41 CDCl3
77.16 CDCl3
76.99 CDCl3
55.16
48.44
44.89
44.67
44.45
44.23
21.18
CF3
N
O
O
H3C
f1 (ppm)


-60.548
-60.569
-60.591
CF3
N
O
O
H3C
3.00
f1 (ppm)

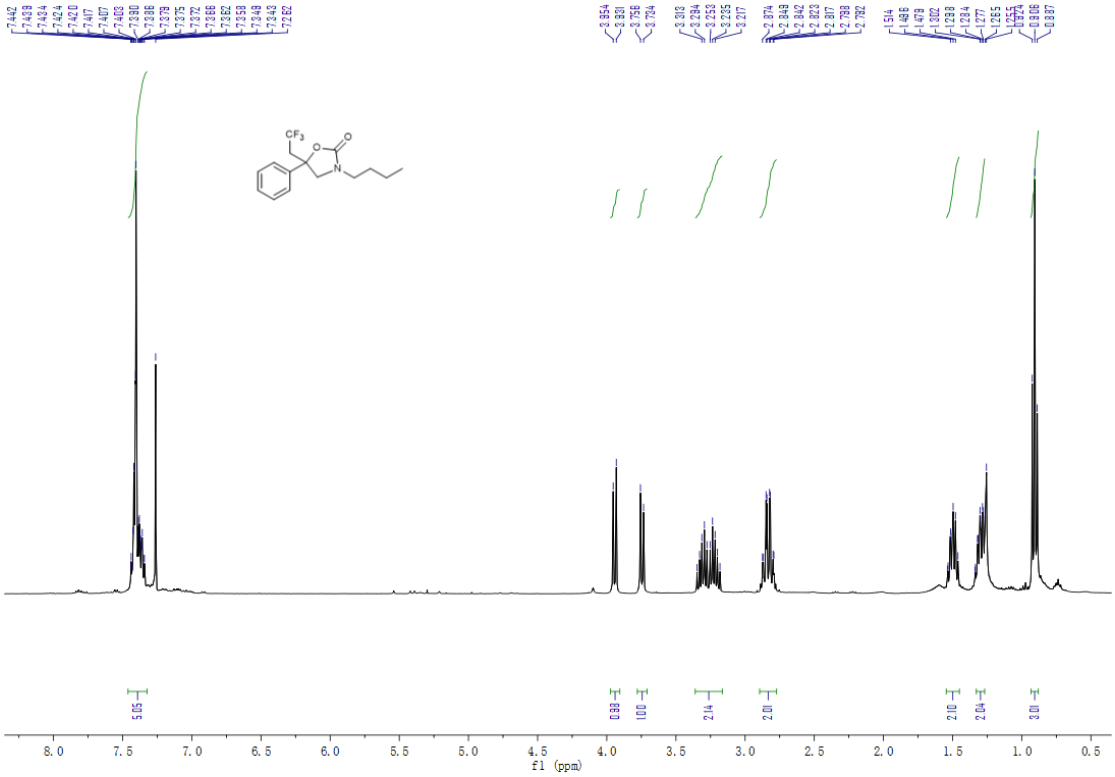
3-Benzyl-5-(naphthalen-2-yl)-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2e**)

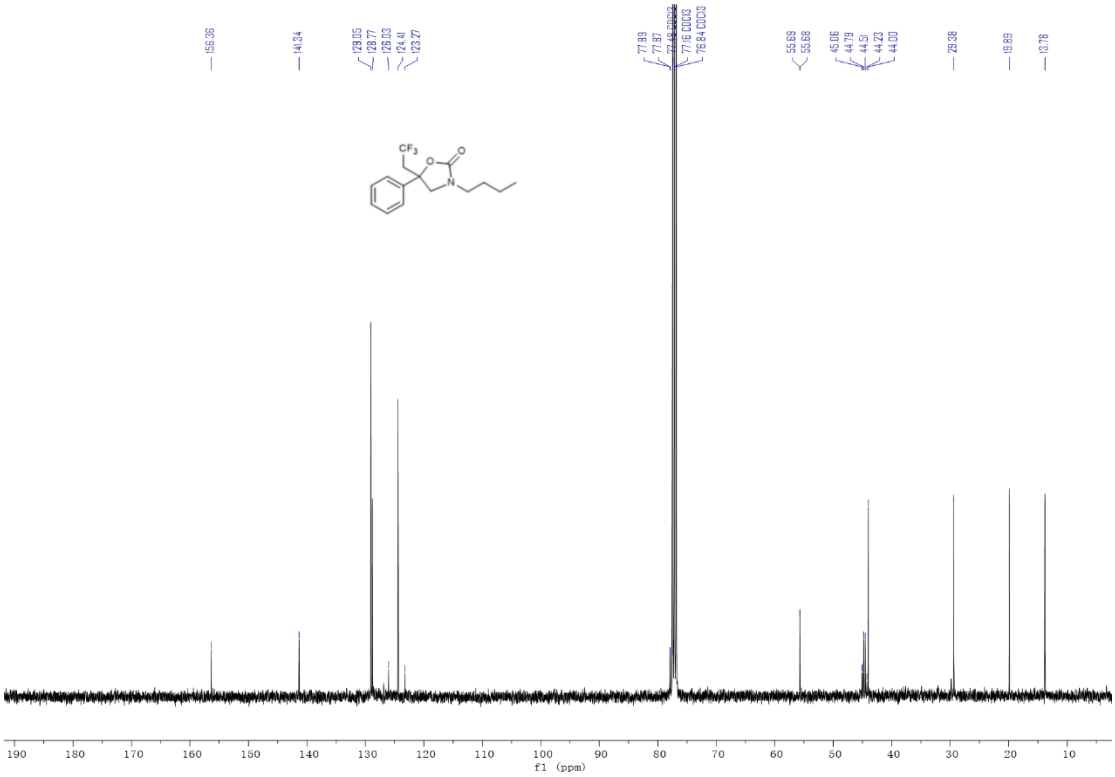


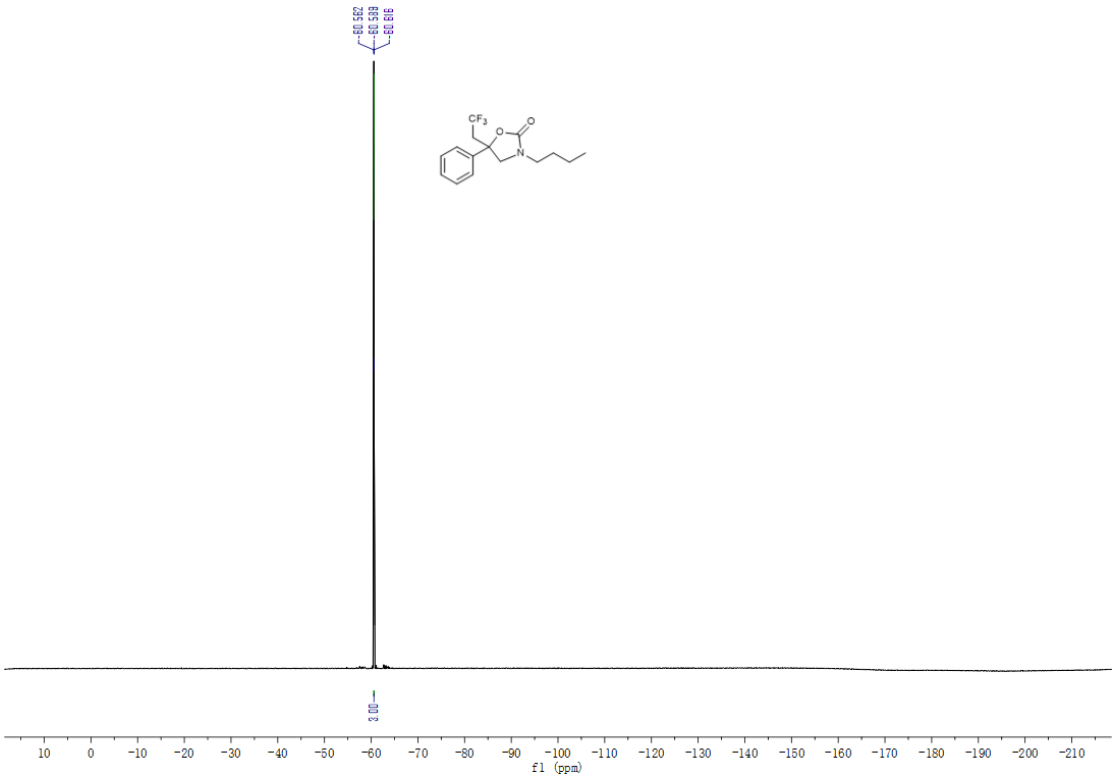




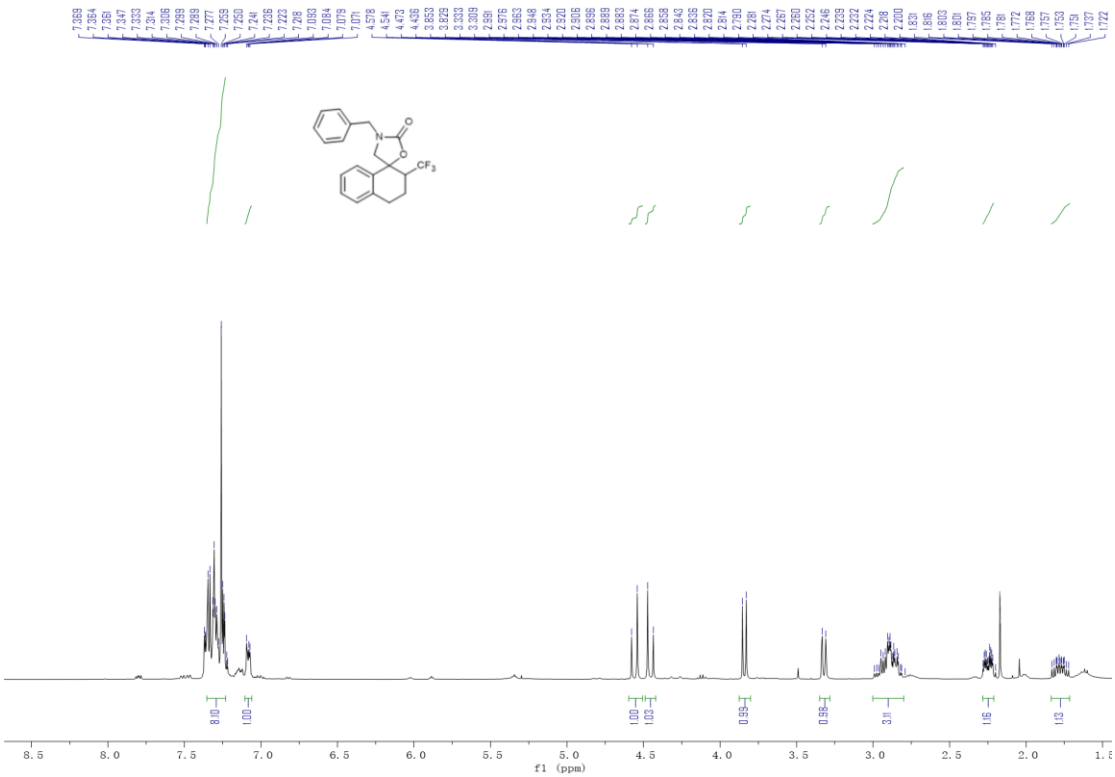
3-Butyl-5-phenyl-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (**2f**)

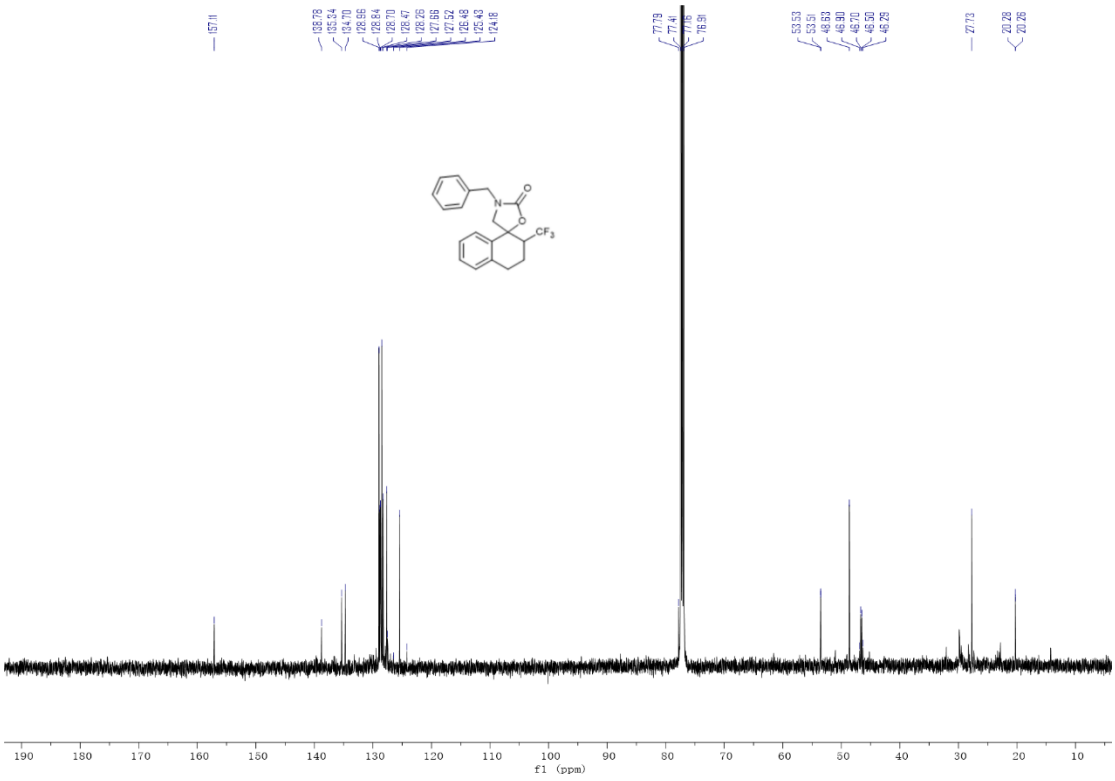


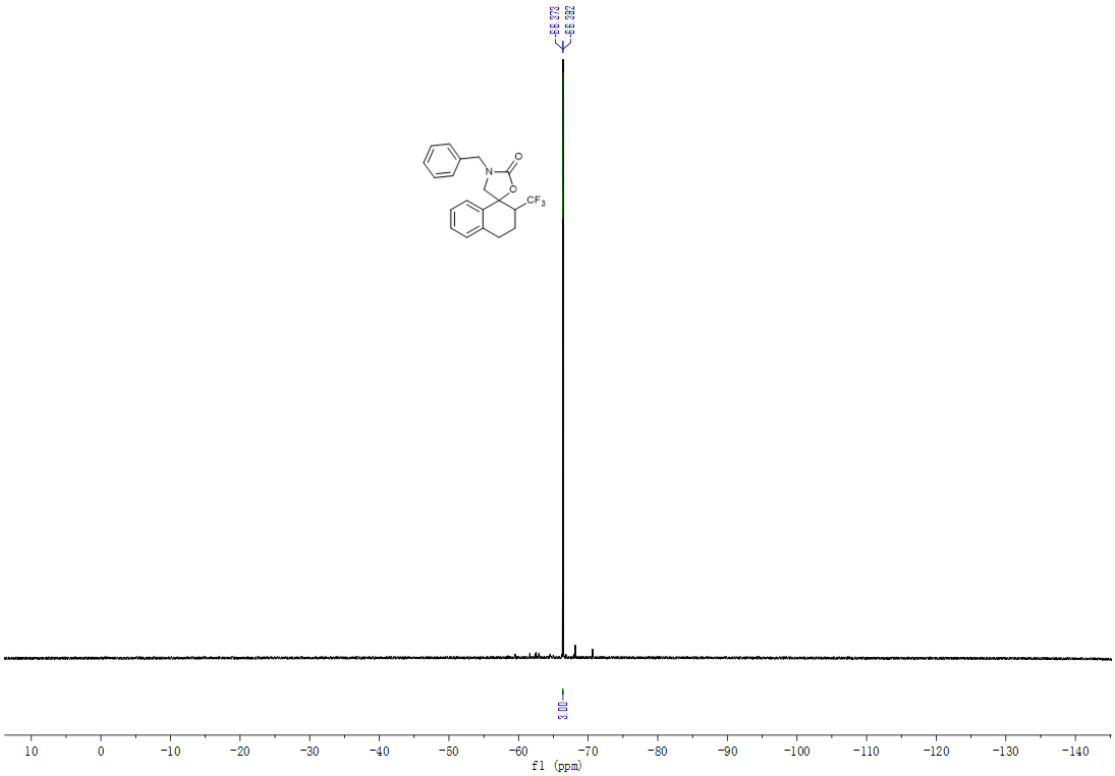

156.96
144.54
129.05
128.77
126.03
124.41
123.27
77.89
77.87
77.16
76.84
55.69
55.68
45.06
44.79
44.51
44.23
44.00
29.38
19.89
13.78
CF3
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-60.562
-60.589
-60.616
CF3
O
O
N
3.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

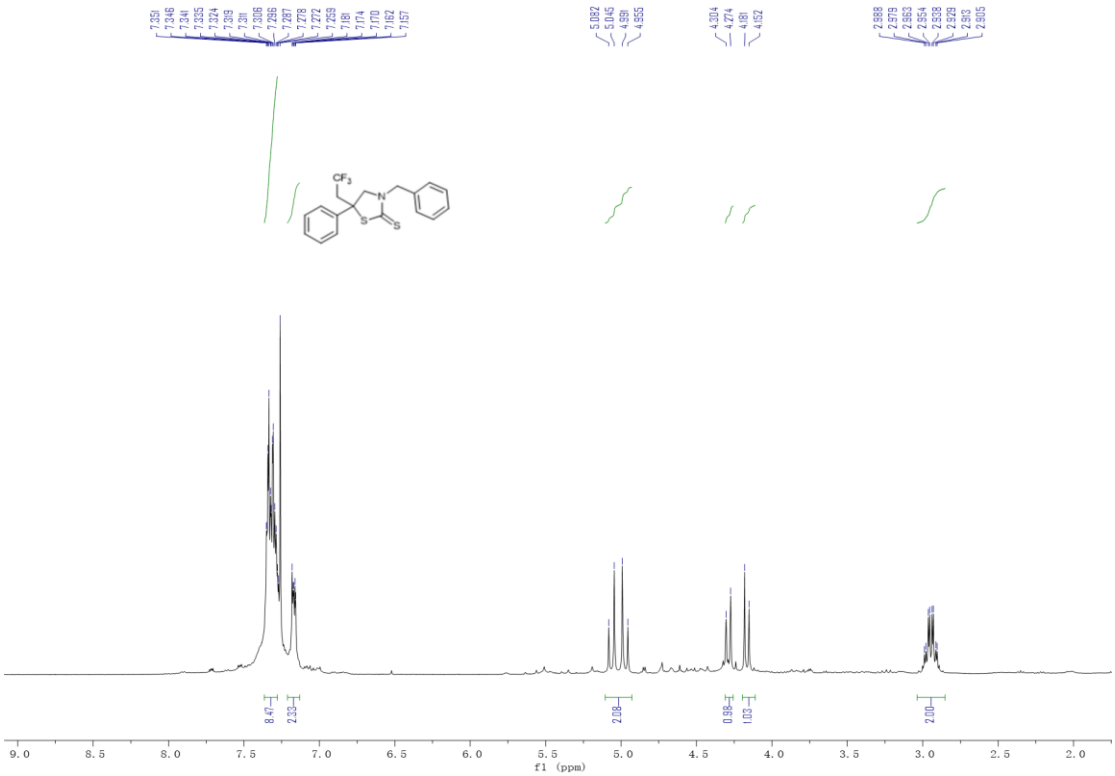
3'-Benzyl-2-(trifluoromethyl)-3,4-dihydro-2*H*-spiro[naphthalene-1,5'-oxazolidin]2'-one (**2g**)

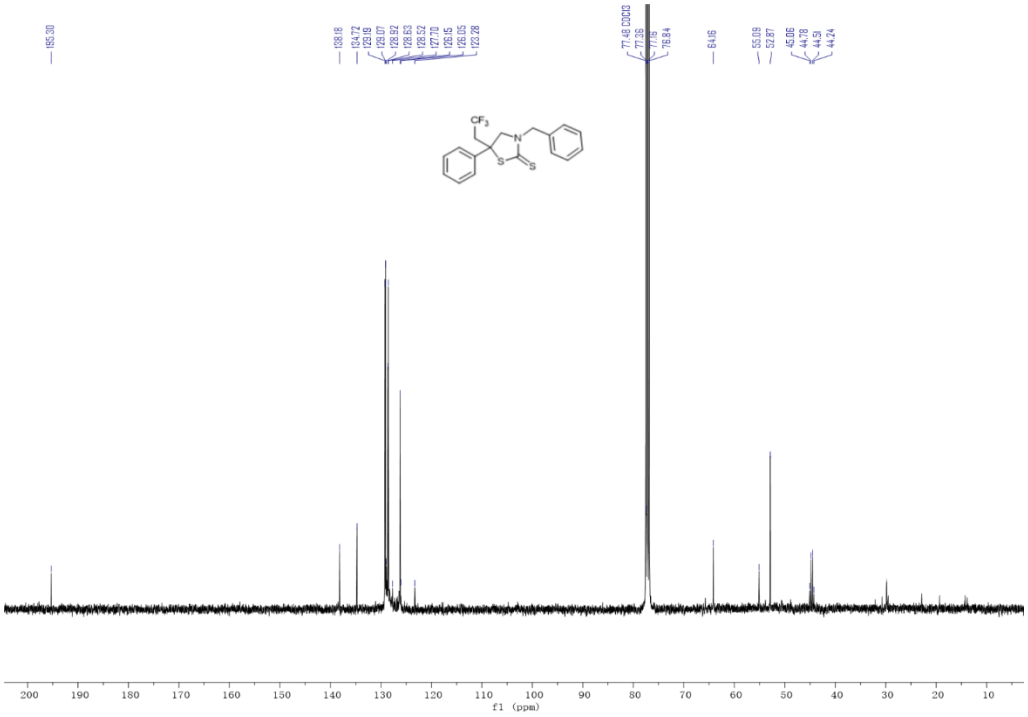


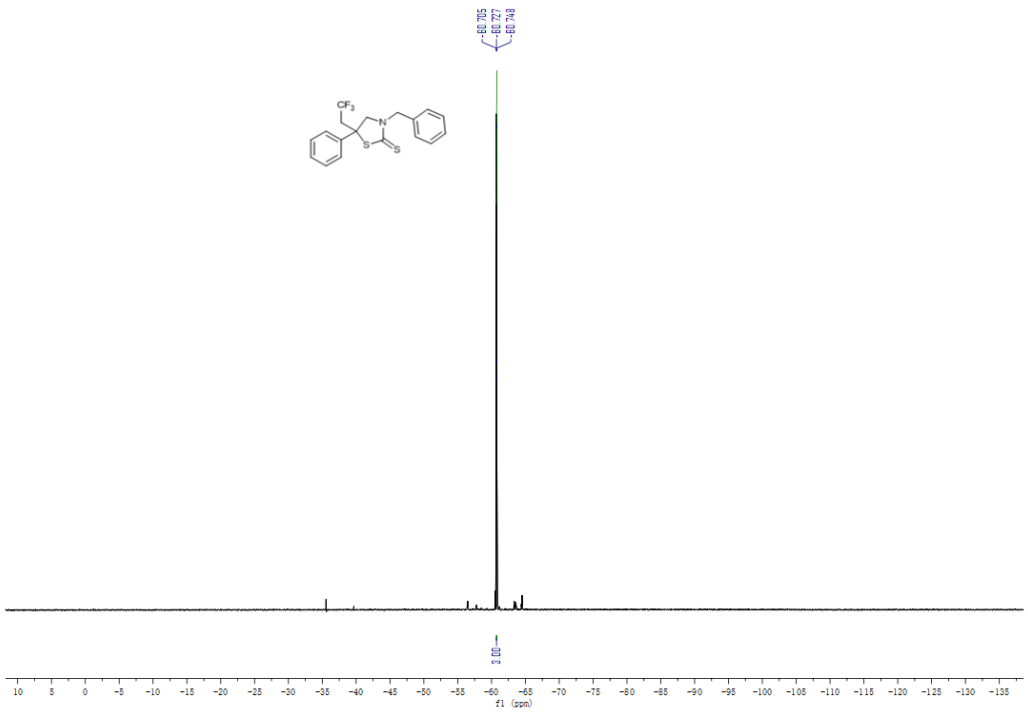




3-Benzyl-5-phenyl-5-(2,2,2-trifluoroethyl)thiazolidine-2-thione (**3a**)







Notes and references

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