Supporting Information

$PhI(OAc)_2$-Mediated 1,2-Haloamination of Alkynes: A General Access to (*E*)-4-(Halomethylene)oxazolidin-2-ones

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1. General

All the reactions were carried out under an air atmosphere using 10 ml round-bottom flask under reflux. For thin layer chromatography (TLC) analyses throughout this work, Flash column chromatography was performed using Qingdao Haiyang silica gel (300-400) with distilled solvents. ^{1}H NMR (400MHz) spectra were recorded on Bruker Avance 400/300 spectrometers in $CDCl_3$/DMSO-d6. ^{13}C NMR (100/75 MHz) spectra on Bruker Avance 400/300 spectrometers in $CDCl_3$/DMSO-d6. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiple. Chemical shifts (δ) are in parts per million relative to $CDCl_3$ at 7.26 ppm for ^{1}H and at 77.03 ppm for $^{13}C\{^{1}H\}$, and relative to DMSO-d6 at 3.39 ppm for ^{1}H and at 39.5 ppm for $^{13}C\{^{1}H\}$, respectively. The NMR yields were determined by ^{1}H NMR spectra with methyl tert-butyl ether as an internal standard.

2. Experimental Section

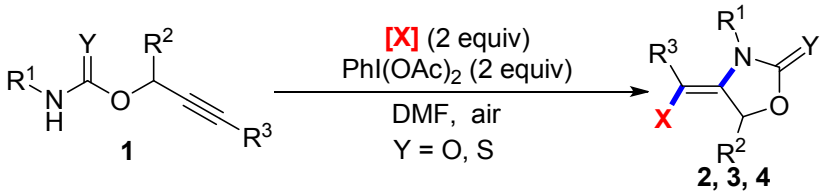
2.1 Synthesis of products via copper halides promoted

CuI (DMSO, 1 ml)/$CuBr_2$, $CuCl_2$ (DMF, 1 ml) (0.4 mmol) were added to a round-bottom flask (10 ml) and stirred at room temperature for 5 min. Then, DIB (0.4 mmol) and *O*-propargyl carbamates **1** (0.2 mmol) were separately dissolved in DMSO/DMF (1 ml) for sequential addition to the system at room temperature. The reaction mixture was heated with stirring at 80°C for 10 min. Upon completion, the mixture was cooled to room temperature and quenched with an aqueous solution of saturated $Na_2S_2O_3$ (5 ml). After extraction with CH_2Cl_2 (3 × 10 ml), the organic phases were washed with water (2 × 10 ml) and brine, dried over anhydrous Na_2SO_4, and then evaporated in vacuo to give the residual crude product. The residual crude product was purified by flash column chromatography with a mixture of n-hexane and ethyl acetate to give the desired product in the noted yields.

2.2 Synthesis of products under metal free-conditions

CBr_4/I_2 (0.4 mmol), *O*-propargyl carbamates **1** (0.2 mmol), DMF (2 ml) were sequentially added to a round-bottom flask (10 ml) and stirred at room temperature. Then, DIB (0.4 mmol) was dissolved in DMF (1 ml) for addition to the system. The reaction mixture was heated with stirring at 100°C for 15 min. Upon completion, the mixture was cooled to room temperature and quenched with an aqueous solution of saturated $Na_2S_2O_3$ (5 ml). After extraction with CH_2Cl_2 (3 × 10 ml), the organic phases were washed with water (2 × 10 ml) and brine, dried over anhydrous Na_2SO_4, and then evaporated in vacuo to give the residual crude product. The residual crude product was purified by flash column chromatography with a mixture of n-hexane and ethyl acetate to give the desired product in the noted yields.

2.3 Optimization of the Reaction Conditions[a]



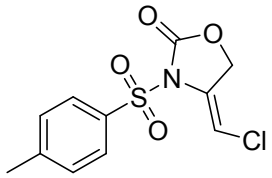
Entry	Halogen sources (equiv)	Substrate	Temp (°C)/Time (h)	Isolated yield
1	NaBr (2)	**1a**	60°C/1h	20% (**3a**)
2	LiBr (2)	**1a**	60°C/1h	14% (**3a**)
3	NBS (2)	**1a**	60°C/1h	12% (**3a**)

4	NH_4Br (2)	**1a**	60°C/1h	21% (**3a**)
5	CBr_4 (2)	**1a**	60°C/1h	54% (**3a**)
6	CBr_4 (2)	**1a**	80°C/1h	65% (**3a**)
7	**CBr_4 (2)**	**1a**	**100°C/15min**	**75% (3a)**
8	CBr_4 (3)	**1a**	100°C/1h	71% (**3a**)
9	CBr_4 (1)	**1a**	100°C/1h	58% (**3a**)
10	**I_2 (2)**	**1b**	**100°C/15min**	**48% (4b)**
11	KI (2)	**1b**	100°C/1h	20% (**4a**)
12	NIS (2)	**1b**	100°C/1h	13% (**4a**)
13	NaCl (2)	**1a**	100°C/1h	trace (**2a**)
14	$MgCl_2$ (2)	**1a**	100°C/1h	trace (**2a**)
15	CCl_4 (2)	**1a**	100°C/1h	trace (**2a**)
16	Py·HCl (2)	**1a**	100°C/1h	trace (**2a**)
17	LiCl(2)	**1a**	100°C/1h	trace (**2a**)
18	NCS (2)	**1a**	100°C/1h	trace (**2a**)

[a] Reaction conditions: **1** (0.2 mmol), halogen sources, DIB (0.4 mmol) in DMF (3 mL) under air.

3. Spectra data

(E)-4-(chloromethylene)-3-tosyloxazolidin-2-one (2a)

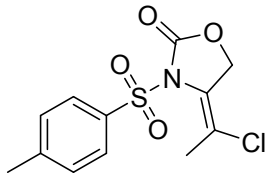


Follow the general procedure **2.1**, **2a** was obtained 52.2 mg (91%) or as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 142~144 °C.

^{1}H NMR (400 MHz, DMSO) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 6.64 (s, 1H), 5.03 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 151.0, 146.7, 133.1, 132.2, 130.2, 128.0, 97.3, 66.3, 21.2.
HRMS (ESI): [$C_{11}H_{10}ClNO_4S$+H^+] calcd. For 288.0092; found 288.0083.

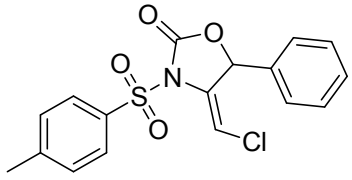
(E)-4-(1-chloroethylidene)-3-tosyloxazolidin-2-one (2b)



Follow the general procedure **2.1**, **2b** was obtained 10.8 mg (18%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.75 (s, 2H), 2.46 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 146.3, 134.5, 130.0, 128.4, 125.2, 122.8, 68.6, 24.3, 21.7.
HRMS (ESI): [$C_{12}H_{12}ClNO_4S$+H^+] calcd. For 302.0248; found 302.0250.

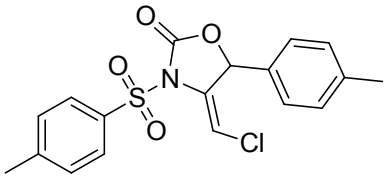
(E)-4-(chloromethylene)-5-phenyl-3-tosyloxazolidin-2-one (2c)



Follow the general procedure **2.1**, **2c** was obtained 58.0 mg (80%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 5.96 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 146.8, 134.0, 133.8, 133.7, 130.1, 130.0, 128.9, 128.4, 127.3, 102.3, 79.2, 21.8.
HRMS (ESI): [$C_{17}H_{14}ClNO_4S$+H^+] calcd. For 364.0405; found 364.0366.

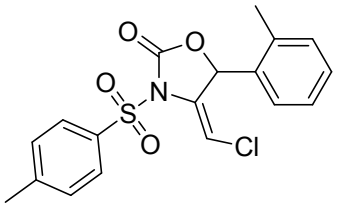
(E)-4-(chloromethylene)-5-(p-tolyl)-3-tosyloxazolidin-2-one (2d)



Follow the general procedure **2.1**, **2d** was obtained 67.8 mg (90%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 4.0 Hz, 2H), 6.79 (s, 1H), 5.93 (s, 1H), 2.50 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 146.7, 140.1, 134.1, 133.7, 130.8, 130.1, 129.6, 128.3, 127.3, 102.0, 79.1, 21.8, 21.2.
HRMS (ESI): [$C_{18}H_{16}ClNO_4S$+H^+] calcd. For 378.0561; found 378.0570.

(E)-4-(chloromethylene)-5-(o-tolyl)-3-tosyloxazolidin-2-one (2e)

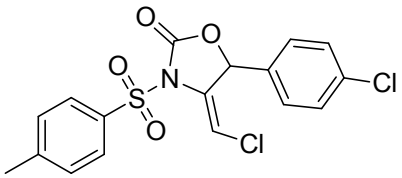


Follow the general procedure **2.1**, **2e** was obtained 65.6 mg (87%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 106~108 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 4.0 Hz, 1H), 6.81 (s, 1H), 6.17 (s, 1H), 2.46 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 146.8, 137.6, 133.8, 133.7, 131.4, 131.0, 130.1, 128.4, 126.5, 126.4, 101.8, 76.8, 21.8, 18.9.
HRMS (ESI): [$C_{18}H_{16}ClNO_4S$+H^+] calcd. For 378.0561; found 378.0559.

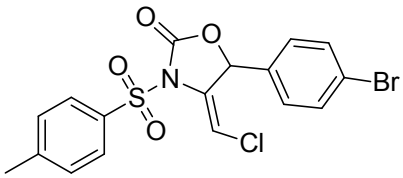
(E)-4-(chloromethylene)-5-(4-chlorophenyl)-3-tosyloxazolidin-2-one (2f)



Follow the general procedure **2.1**, **2f** was obtained 70.6 mg (89%) as white viscous oil with *n*-hexane/ethyl acetate (10/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 5.94 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.9, 136.0, 133.6, 133.5, 132.3, 130.1, 129.2, 128.7, 128.3, 102.5, 78.2, 21.8.
HRMS (ESI): [$C_{17}H_{13}Cl_2NO_4S$+H^+] calcd. For 398.0015; found 398.0009.

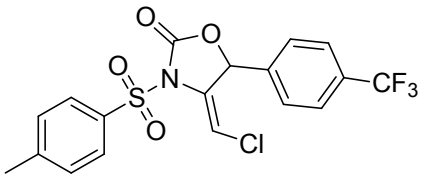
(E)-5-(4-bromophenyl)-4-(chloromethylene)-3-tosyloxazolidin-2-one (2g)



Follow the general procedure **2.1**, **2g** was obtained 74.9 mg (85%) as white viscous oil with *n*-hexane/ethyl acetate (10/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 5.92 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.9, 133.5, 132.8, 132.2, 130.1, 128.9, 128.3, 124.2, 102.5, 78.3, 21.85.
HRMS (ESI): [$C_{17}H_{13}BrClNO_4S$+H^+] calcd. For 441.9510; found 441.9510.

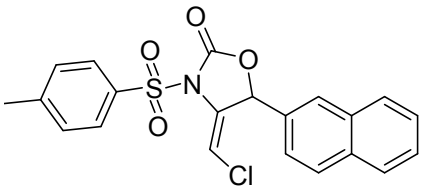
(E)-4-(chloromethylene)-3-tosyl-5-(4-(trifluoromethyl)phenyl)oxazolidin-2-one (2h)



Follow the general procedure **2.1**, **2h** was obtained 75.8 mg (88%) as white viscous oil with *n*-hexane/ethyl acetate (10/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 4.0 Hz, 2H), 6.84 (s, 1H), 6.02 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 147.0, 137.5, 133.5, 133.4, 130.2, 128.4, 127.7, 126.0, 125.9, 102.8, 78.0, 21.8.
HRMS (ESI): [$C_{18}H_{13}ClF_3NO_4S$+Na^+] calcd. For 454.0098; found 454.0092.

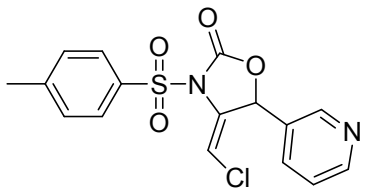
(E)-4-(chloromethylene)-5-(naphthalen-2-yl)-3-tosyloxazolidin-2-one (2i)



Follow the general procedure **2.1**, **2i** was obtained 72.6 mg (88%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.54 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 6.77 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.8, 134.0, 133.8, 133.2, 131.2, 131.0, 130.1, 129.0, 128.4, 128.0, 127.2, 126.3, 124.9, 124.7, 122.7, 102.9, 76.5, 21.8.
HRMS (ESI): [$C_{21}H_{16}ClNO_4S$+H^+] calcd. For 414.0561; found 414.0570.

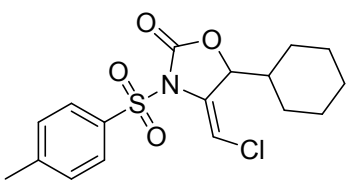
(E)-4-(chloromethylene)-5-(pyridin-3-yl)-3-tosyloxazolidin-2-one (2j)



Follow the general procedure **2.1**, **2j** was obtained 50.9 mg (70%) as white viscous oil with *n*-hexane/ethyl acetate (1/1) used as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.52 (s, 1H), 7.98 (d, *J* = 12.0 Hz, 2H), 7.44 (dd, *J* = 16.0, 8.0 Hz, 3H), 7.30 (s, 1H), 6.85 (s, 1H), 6.01 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 150.0, 149.0, 147.1, 134.6, 133.5, 133.1, 130.2, 128.4, 102.6, 76.9, 21.8.
HRMS (ESI): [$C_{16}H_{13}ClN_2O_4S$+H^+] calcd. For 365.0357; found 365.0360.

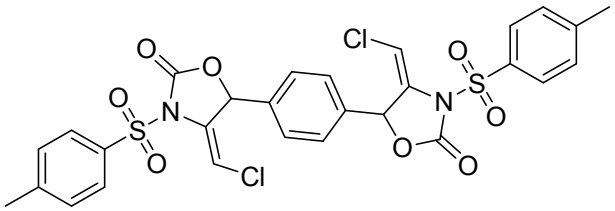
(E)-4-(chloromethylene)-5-cyclohexyl-3-tosyloxazolidin-2-one (2k)



Follow the general procedure **2.1**, **2k** was obtained 60.5 mg (82%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 4.97 (s, 1H), 2.46 (s, 3H), 2.03 (t, *J* = 12.0 Hz, 1H), 1.75 (d, *J* = 12.0 Hz, 1H), 1.61 (s, 3H), 1.33 – 1.01 (m, 5H), 0.87 – 0.77 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 146.5, 133.99, 133.92, 129.9, 128.3, 100.4, 81.8, 39.6, 28.7, 26.0, 25.6, 25.4, 23.8, 21.7.
HRMS (ESI): [$C_{17}H_{20}ClNO_4S+H^+$] calcd. For 370.0874; found 370.0873.

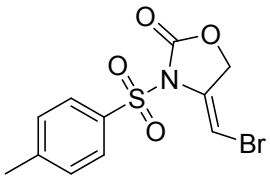
(4E,4'E)-5,5'-(1,4-phenylene)bis(4-(chloromethylene)-3-tosyloxazolidin-2-one) (2o)



Follow the general procedure **2.1**, **2o** was obtained 106.2 mg (82%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 4H), 7.41 (d, *J* = 8.0 Hz, 4H), 7.13 (s, 4H), 6.81 (s, 2H), 5.96 (s, 2H), 2.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 147.08, 147.04, 135.5, 133.5, 130.2, 128.4, 127.9, 102.6, 78.2, 21.8.
HRMS (ESI): [$C_{28}H_{22}Cl_2N_2O_8S_2+Na^+$] calcd. For 671.0087; found 671.0062.

(E)-4-(bromomethylene)-3-tosyloxazolidin-2-one (3a)

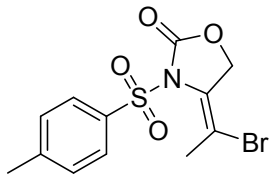


Follow the general procedure **2.1 or 2.2**, **3a** was obtained 60.8 mg (92%) or 49.6 mg (75%) as white solid with *n*-hexane/ethyl acetate (10/1) used as eluent.

Melting point: 130 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 4.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.66 (s, 1H), 4.78 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 146.8, 133.6, 131.7, 130.0, 128.4, 86.3, 67.9, 21.8.
HRMS (ESI): [$C_{11}H_{10}BrNO_4S+H^+$] calcd. For 331.9587; found 331.9565.

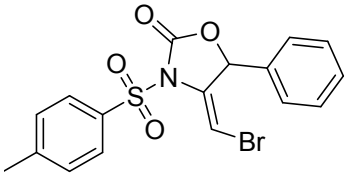
(E)-4-(1-bromoethylidene)-3-tosyloxazolidin-2-one (3b)



Follow the general procedure **2.1**, **3b** was obtained 61.4 mg (89%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.70 (s, 2H), 2.53 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 146.3, 134.5, 130.0, 128.4, 126.3, 113.1, 70.5, 26.7, 21.7.
HRMS (ESI): [$C_{12}H_{12}BrNO_4S$+H^+] calcd. For 345.9743; found 345.9743.

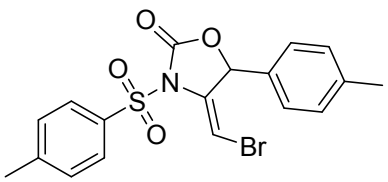
(E)-4-(bromomethylene)-5-phenyl-3-tosyloxazolidin-2-one (3c)



Follow the general procedure **2.1**, **3c** was obtained 59.4 mg (73%) as white viscous oil with *n*-hexane/ethyl acetate (10/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 12.0, 8.0 Hz, 3H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 5.88 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 146.8, 134.6, 133.8, 133.6, 130.1, 130.0, 129.0, 128.4, 127.7, 89.8, 80.6, 21.8.
HRMS (ESI): [$C_{17}H_{14}BrNO_4S$+H^+] calcd. For 407.9900; found 407.9893.

(E)-4-(bromomethylene)-5-(p-tolyl)-3-tosyloxazolidin-2-one (3d)

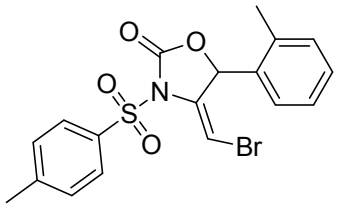


Follow the general procedure **2.1** or **2.2**, **3d** was obtained 64.8 mg (77%) or 61.4 mg (73%) as white solid with *n*-hexane/ethyl acetate (5/1) used as eluent.

Melting point: 122~124 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.86 (s, 1H), 5.84 (s, 1H), 2.50 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 146.7, 140.1, 134.7, 133.8, 130.7, 130.1, 129.6, 128.4, 127.6, 89.6, 80.5, 21.8, 21.3.
HRMS (ESI): [$C_{18}H_{16}BrNO_4S+H^+$] calcd. For 422.0056; found 422.0043.

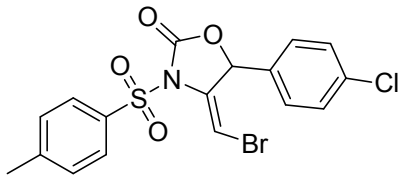
(E)-4-(bromomethylene)-5-(o-tolyl)-3-tosyloxazolidin-2-one (3e)



Follow the general procedure **2.1**, **3e** was obtained 59.7 mg (71%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 6.12 (s, 1H), 2.49 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 146.8, 137.7, 134.6, 133.8, 131.3, 131.0, 130.1, 128.4, 126.6, 126.4, 89.4, 78.1, 21.8, 19.0.
HRMS (ESI): [$C_{18}H_{16}BrNO_4S+H^+$] calcd. For 422.0056; found 422.0053.

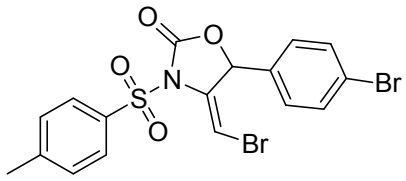
(E)-4-(bromomethylene)-5-(4-chlorophenyl)-3-tosyloxazolidin-2-one (3f)



Follow the general procedure **2.1**, **3f** was obtained 71.4 mg (81%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 4.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 5.85 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.9, 136.0, 134.2, 133.6, 132.1, 130.1, 129.2, 129.0, 128.4, 90.1, 79.6, 21.8.
HRMS (ESI): [$C_{17}H_{13}BrClNO_4S+H^+$] calcd. For 441.9510; found 441.9510.

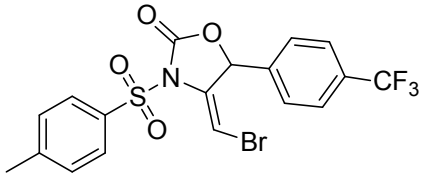
(E)-4-(bromomethylene)-5-(4-bromophenyl)-3-tosyloxazolidin-2-one (3g)



Follow the general procedure **2.1**, **3g** was obtained 69.8 mg (72%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 5.84 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.9, 134.2, 133.6, 132.6, 132.2, 130.1, 129.2, 128.4, 124.3, 90.1, 79.7, 21.8. HRMS (ESI): [$C_{17}H_{13}Br_2NO_4S+H^+$] calcd. For 485.9005; found 485.9001.

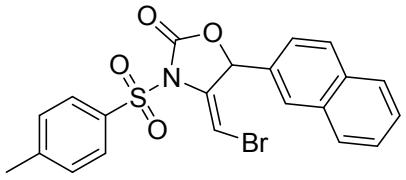
(E)-4-(bromomethylene)-3-tosyl-5-(4-(trifluoromethyl)phenyl)oxazolidin-2-one (3h)



Follow the general procedure **2.1**, **3h** was obtained 75.9 mg (80%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.91 (s, 1H), 5.93 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 147.0, 137.3, 134.0, 133.5, 130.2, 128.4, 128.0, 126.05, 126.01, 90.4, 79.4, 21.8. HRMS (ESI): [$C_{18}H_{13}BrF_3NO_4S+Na^+$] calcd. For 497.9593; found 497.9577.

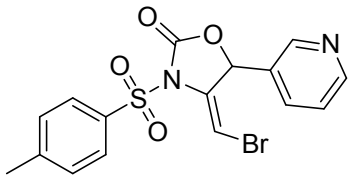
(E)-4-(bromomethylene)-5-(naphthalen-2-yl)-3-tosyloxazolidin-2-one (3i)



Follow the general procedure **2.1** or **2.2**, **3i** was obtained 74.0 mg (81%) or 57.5 mg (63%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, *J* = 12.0 Hz, 3H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 6.69 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.8, 134.0, 133.8, 131.2, 131.0, 130.1, 129.0, 128.4, 127.9, 127.2, 126.3, 124.9, 124.8, 122.7, 90.6, 77.8, 21.8.
HRMS (ESI): [$C_{21}H_{16}BrNO_4S$+H^+] calcd. For 458.0056; found 458.0043.

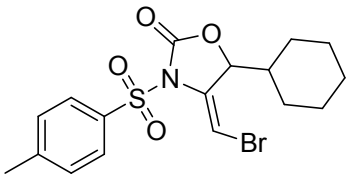
(E)-4-(bromomethylene)-5-(pyridin-3-yl)-3-tosyloxazolidin-2-one (3j)



Follow the general procedure **2.1**, **3j** was obtained 55.4 mg (68%) as white viscous oil with *n*-hexane/ethyl acetate (1/1) used as eluent.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.54 (s, 1H), 7.99 (d, *J* = 12.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 12.0 Hz, 2H), 7.32 – 7.28 (m, 1H), 6.91 (s, 1H), 5.93 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 150.0, 149.2, 147.1, 134.9, 133.7, 133.5, 130.2, 129.7, 128.4, 123.9, 90.1, 78.2, 21.8.
HRMS (ESI): [$C_{16}H_{13}BrN_2O_4S$+H^+] calcd. For 408.9852; found 408.9844.

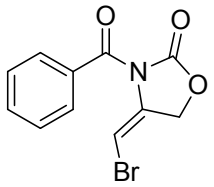
(E)-4-(bromomethylene)-5-cyclohexyl-3-tosyloxazolidin-2-one (3k)



Follow the general procedure **2.1**, **3k** was obtained 60.3 mg (73%) or 52.0 mg (63%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 4.88 (s, 1H), 2.46 (s, 3H), 2.12 (t, *J* = 12.0 Hz, 1H), 1.76 (d, *J* = 12.0 Hz, 1H), 1.61 (s, 3H), 1.35 – 1.02 (m, 5H), 0.83 – 0.77 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 146.5, 134.7, 133.9, 129.9, 128.3, 87.5, 83.0, 39.5, 28.7, 26.0, 25.5, 25.4, 23.7, 21.7.
HRMS (ESI): [$C_{17}H_{20}BrNO_4S$+H^+] calcd. For 414.0369; found 414.0363.

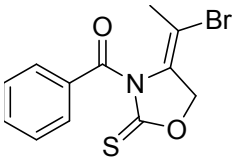
(E)-3-benzoyl-4-(bromomethylene)oxazolidin-2-one (3l)



Follow the general procedure **2.1**, **3l** was obtained 39.3 mg (70%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 5.73 (s, 1H), 4.98 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 153.7, 134.6, 134.3, 132.2, 130.9, 128.6, 83.7, 68.4.
HRMS (ESI): [$C_{11}H_8BrNO_3$+Na^+] calcd. For 303.9580; found 303.9571.

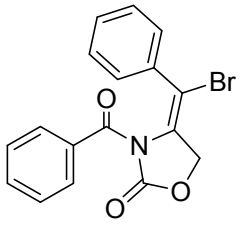
(E)-(4-(1-bromoethylidene)-2-thioxooxazolidin-3-yl)(phenyl)methanone (3m)



Follow the general procedure **2.1** or **2.2**, **3m** was obtained 48.5 mg (78%) or 42.2 mg (68%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 5.05 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 176.8, 134.5, 133.4, 130.1, 128.6, 128.4, 108.5, 73.3, 26.7.
HRMS (ESI): [$C_{12}H_{10}BrNO_2S$+Na^+] calcd. For 333.9508; found 333.9499.

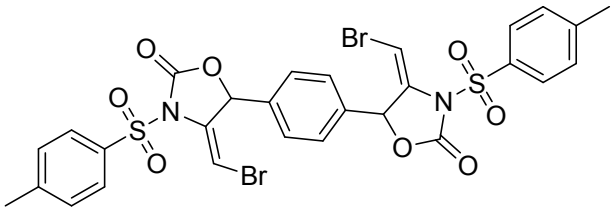
(E)-3-benzoyl-4-(bromo(phenyl)methylene)oxazolidin-2-one (3n)



Follow the general procedure **2.1** or **2.2**, **3n** was obtained 48.5 mg (68%) or 42.8 mg (60%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 3H), 7.16 (s, 2H), 7.12 (s, 3H), 5.12 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 154.1, 137.1, 134.1, 131.9, 130.0, 129.0, 128.6, 128.4, 128.1, 102.3, 69.6.
HRMS (ESI): [$C_{17}H_{12}BrNO_3$+H^+] calcd. For 358.0073; found 358.0064.

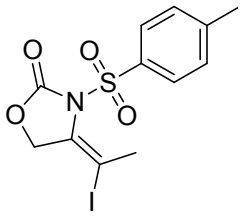
(4E,4'E)-5,5'-(1,4-phenylene)bis(4-(bromomethylene)-3-tosyloxazolidin-2-one) (3o)



Follow the general procedure **2.1**, **3o** was obtained 105.9 mg (72%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 4H), 7.42 (d, *J* = 8.0 Hz, 4H), 7.17 (s, 4H), 6.88 (s, 2H), 5.87 (s, 2H), 2.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 147.0, 135.4, 134.1, 133.6, 130.2, 128.4, 128.3, 90.2, 79.6, 21.8.
HRMS (ESI): [$C_{28}H_{22}Br_2N_2O_8S_2$+$Na^+$] calcd. For 758.9077; found 758.9052.

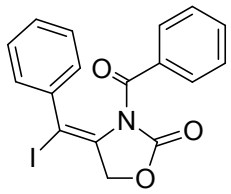
(E)-4-(1-iodoethylidene)-3-tosyloxazolidin-2-one (4b)



Follow the general procedure **2.1** or **2.2**, **4b** was obtained 43.2 mg (55%) or as 37.7 mg (48%) white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.64 (s, 2H), 2.70 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 146.2, 134.6, 130.0, 128.9, 128.4, 87.6, 74.3, 31.0, 21.7.
HRMS (ESI): [$C_{12}H_{12}INO_4S$+H^+] calcd. For 393.9604; found 393.9601.

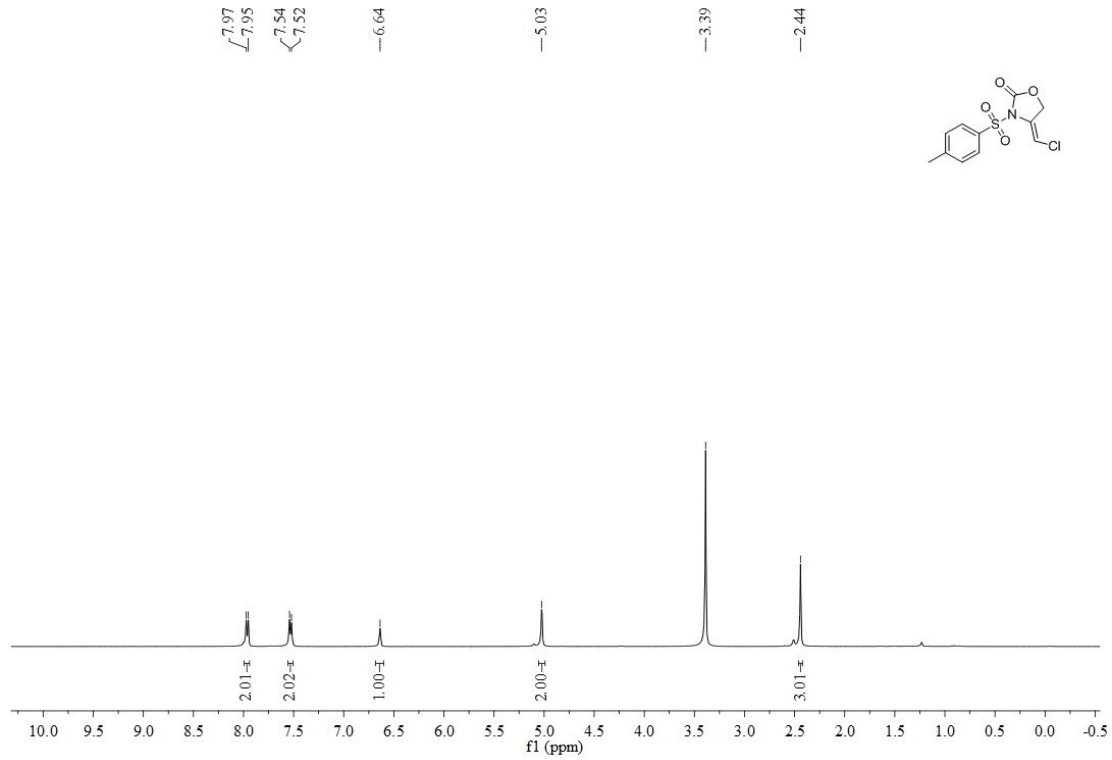
(E)-3-benzoyl-4-(iodo(phenyl)methylene)oxazolidin-2-one (4n)

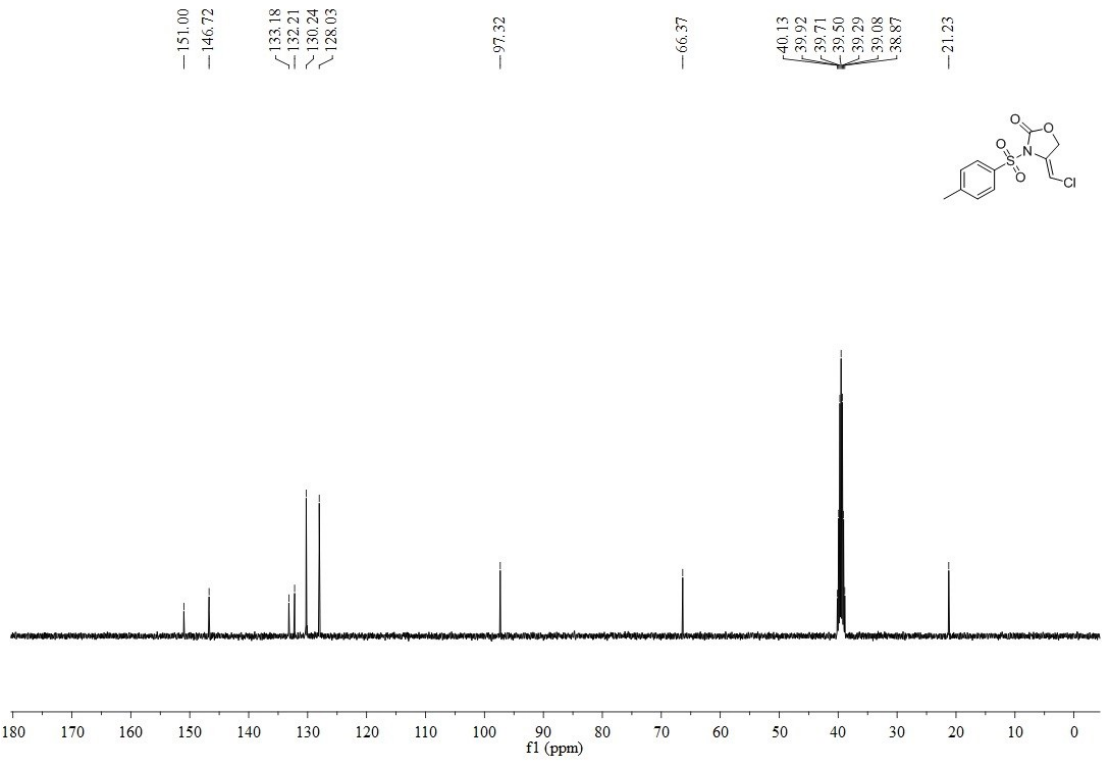


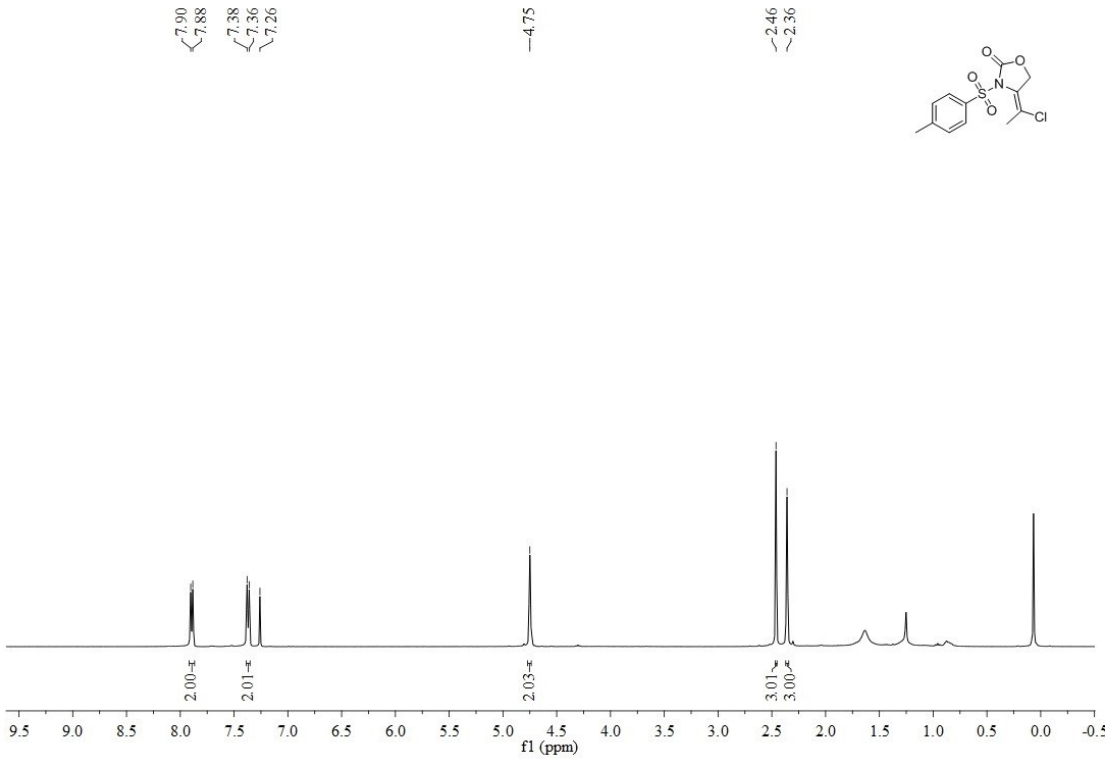
Follow the general procedure **2.1** or **2.2**, **4n** was obtained 56.6 mg (70%) or 52.6 mg (65%) as white viscous oil with *n*-hexane/ethyl acetate (5/1) used as eluent.

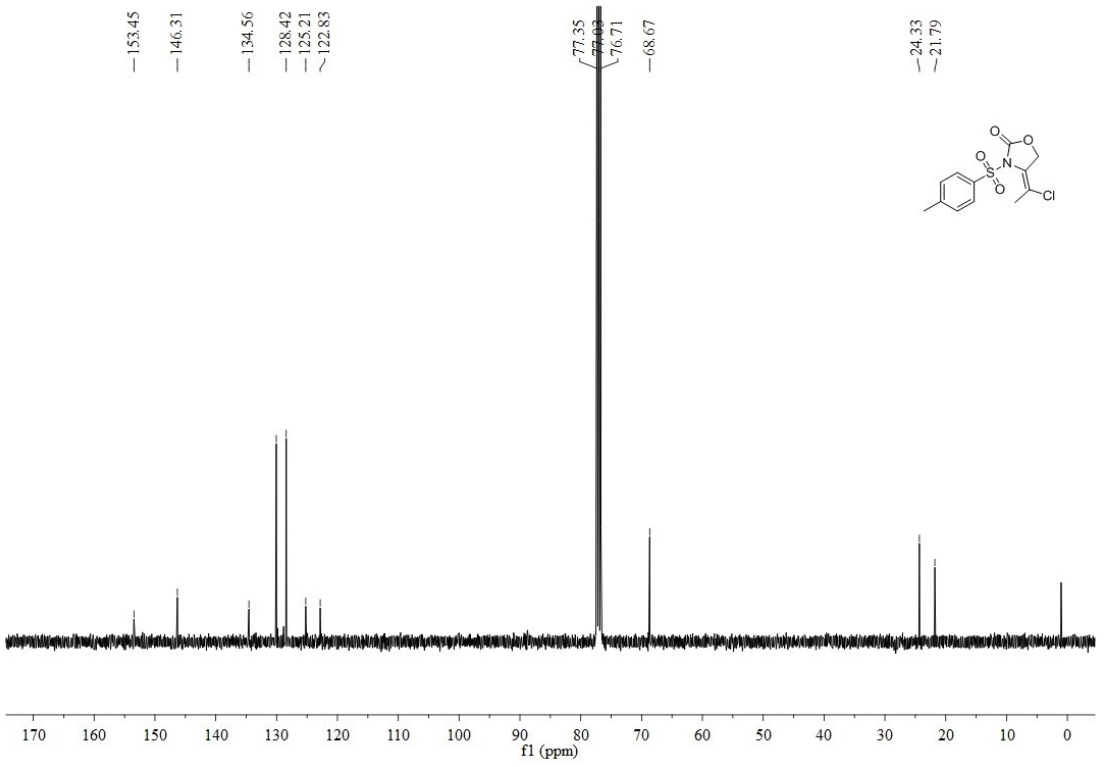
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, *J* = 8.0 Hz, 3H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 16.0 Hz, 5H), 5.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 154.6, 140.0, 134.1, 132.3, 131.7, 129.9, 128.5, 128.4, 128.2, 75.0, 73.3.
HRMS (ESI): [$C_{17}H_{12}INO_3$+H^+] calcd. For 405.9935; found 405.9921.

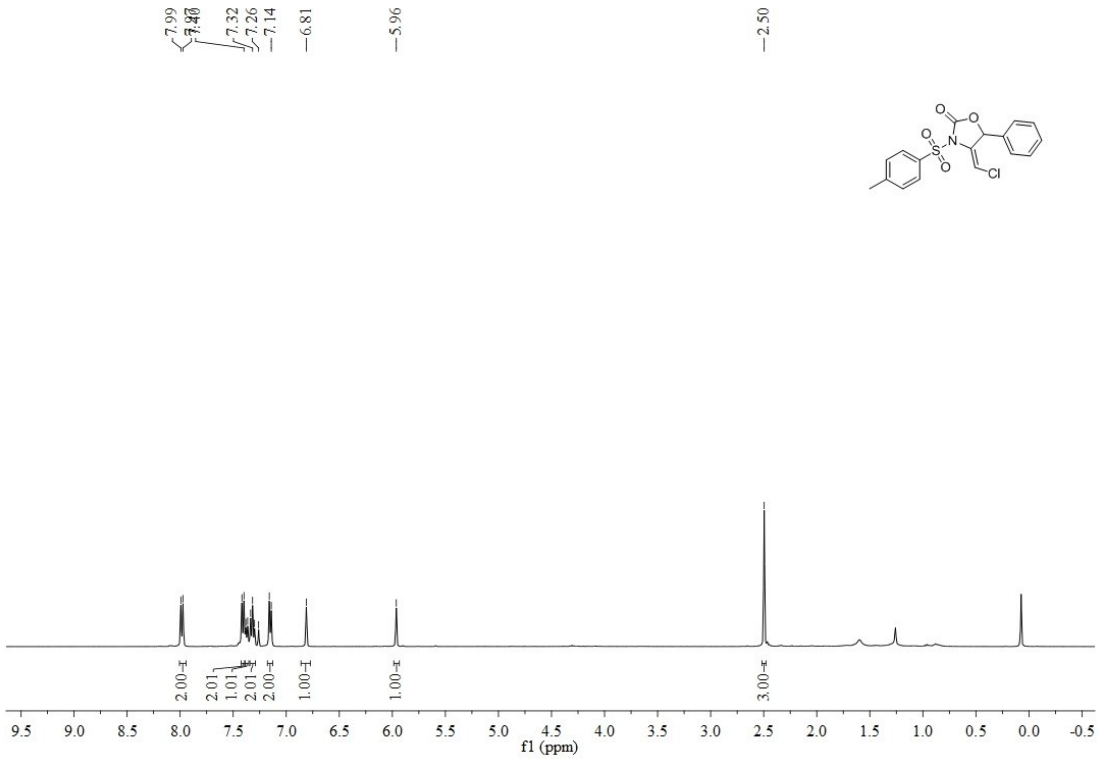
4 Spectra


7.97
7.95
7.54
7.52
6.64
5.03
3.39
2.44
Cl
2.01
2.02
1.00
2.00
3.01
f1 (ppm)


151.00
146.72
133.18
132.21
130.24
128.03
97.32
66.37
40.13
39.92
39.71
39.50
39.29
39.08
38.87
21.23
Cl
f1 (ppm)


7.90
7.88
7.38
7.36
7.26
4.75
2.46
2.36
Cl
2.00
2.01
2.03
3.01
3.00
f1 (ppm)


153.45
146.31
134.56
128.42
125.21
122.83
77.35
77.03
76.71
68.67
24.33
21.79
Cl
f1 (ppm)


7.99
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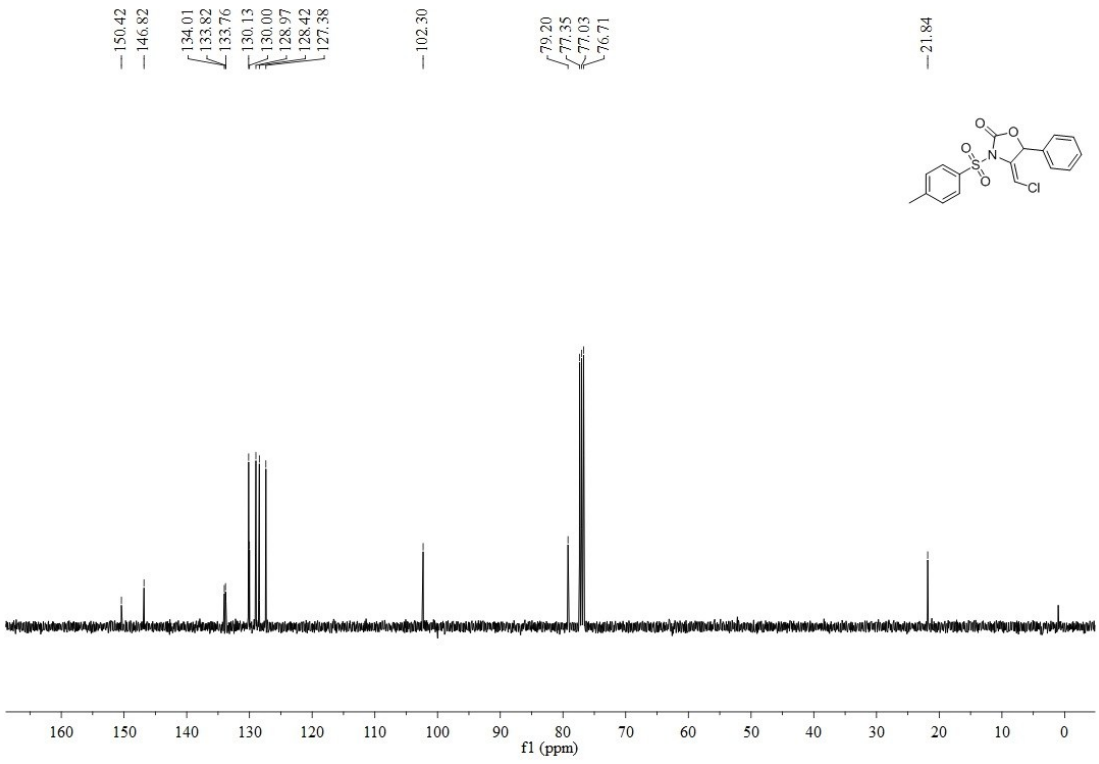
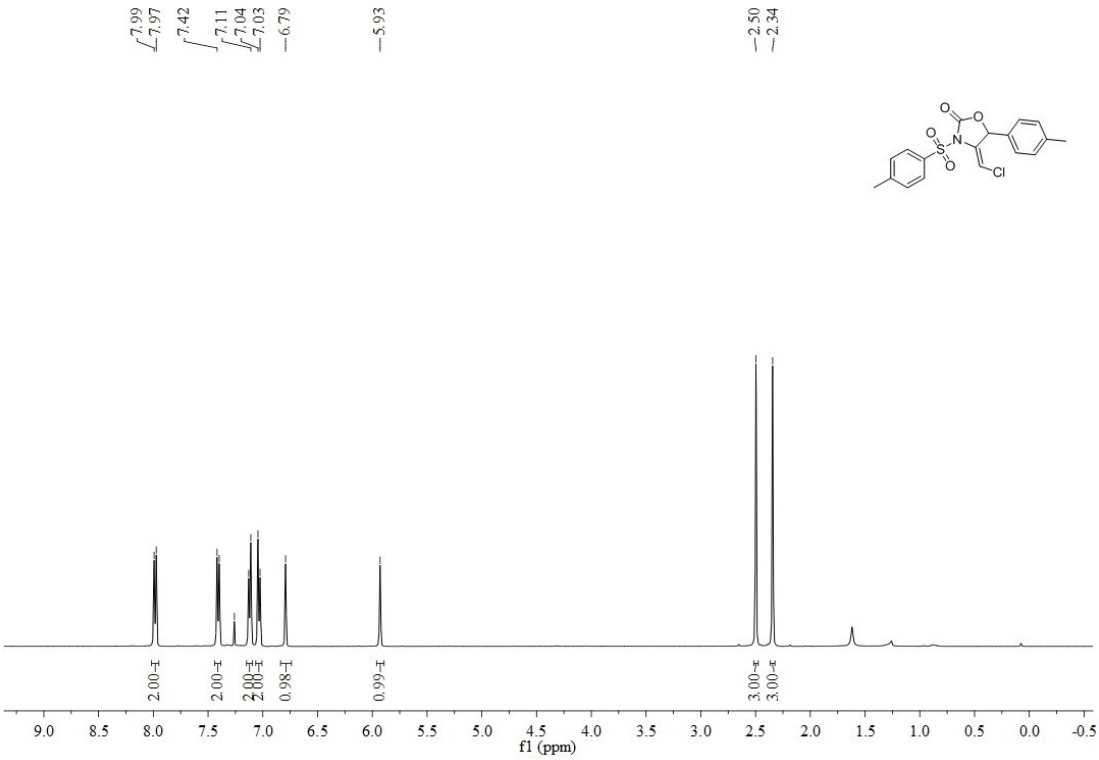
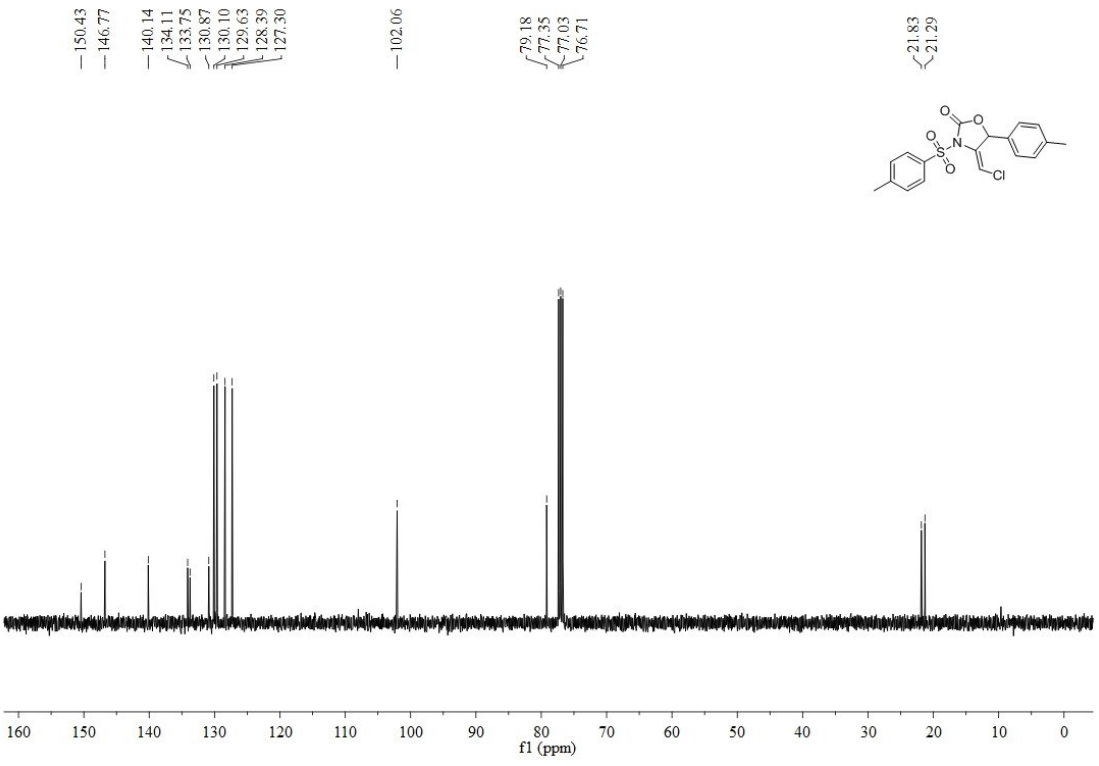
7.26
7.14
6.81
5.96
2.50
Cl
2.00
2.01
1.01
2.01
2.00
1.00
1.00
3.00
f1 (ppm)


150.42
146.82
134.01
133.82
133.76
130.13
130.00
128.97
128.42
127.38
102.30
79.20
77.35
77.03
76.71
21.84
Cl
f1 (ppm)


7.99
7.97
7.42
7.11
7.04
7.03
6.79
5.93
2.50
2.34
Cl
2.00
2.00
2.00
2.00
0.98
0.99
3.00
3.00
f1 (ppm)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130.87
130.10
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127.30
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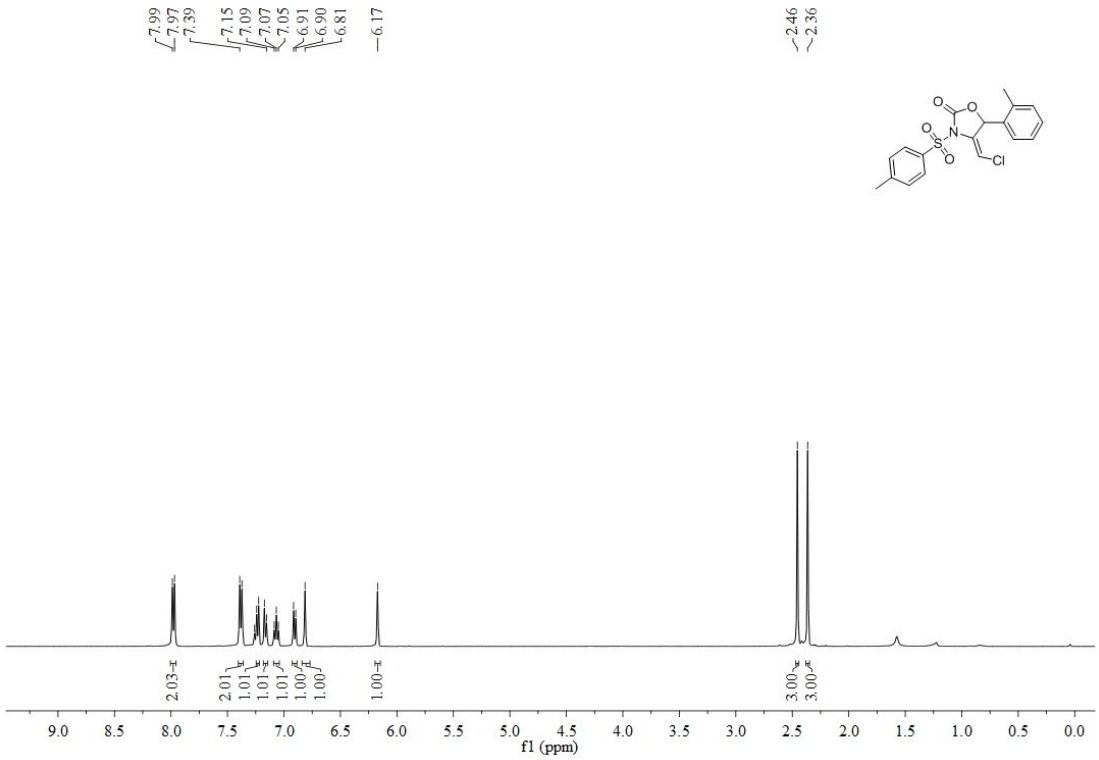
77.35
77.03
76.71
21.83
21.29
Cl
f1 (ppm)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7.07
7.05
6.91
6.90
6.81
6.17
2.46
2.36
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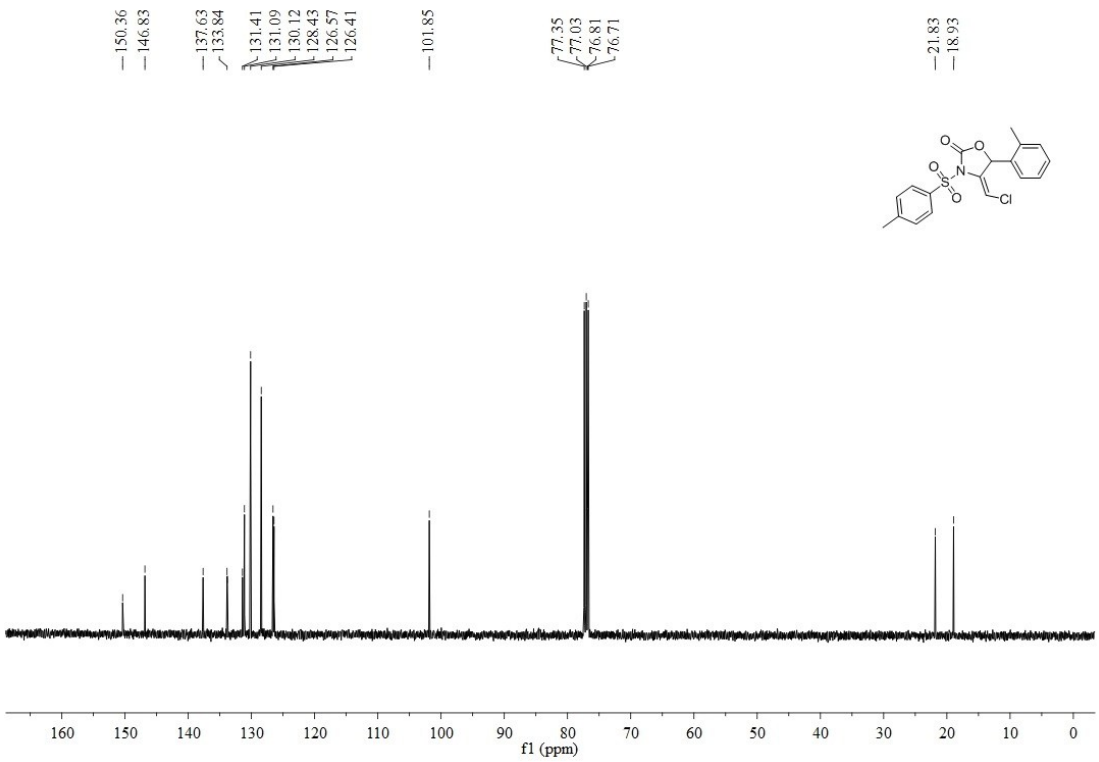
1.01
1.01
1.01
1.00
1.00
1.00
3.00
3.00
f1 (ppm)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131.09
130.12
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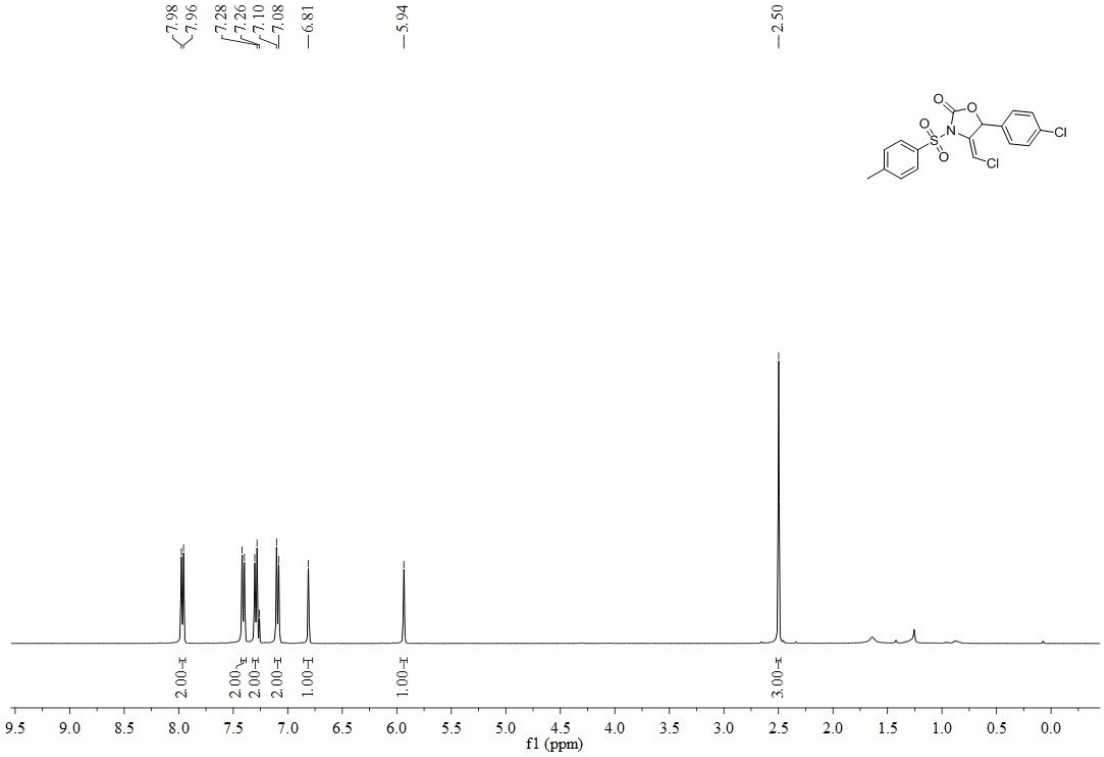
126.41
101.85
77.35
77.03
76.81
76.71
21.83
18.93
Cl
f1 (ppm)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7.26
7.10
7.08
6.81
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Cl
Cl
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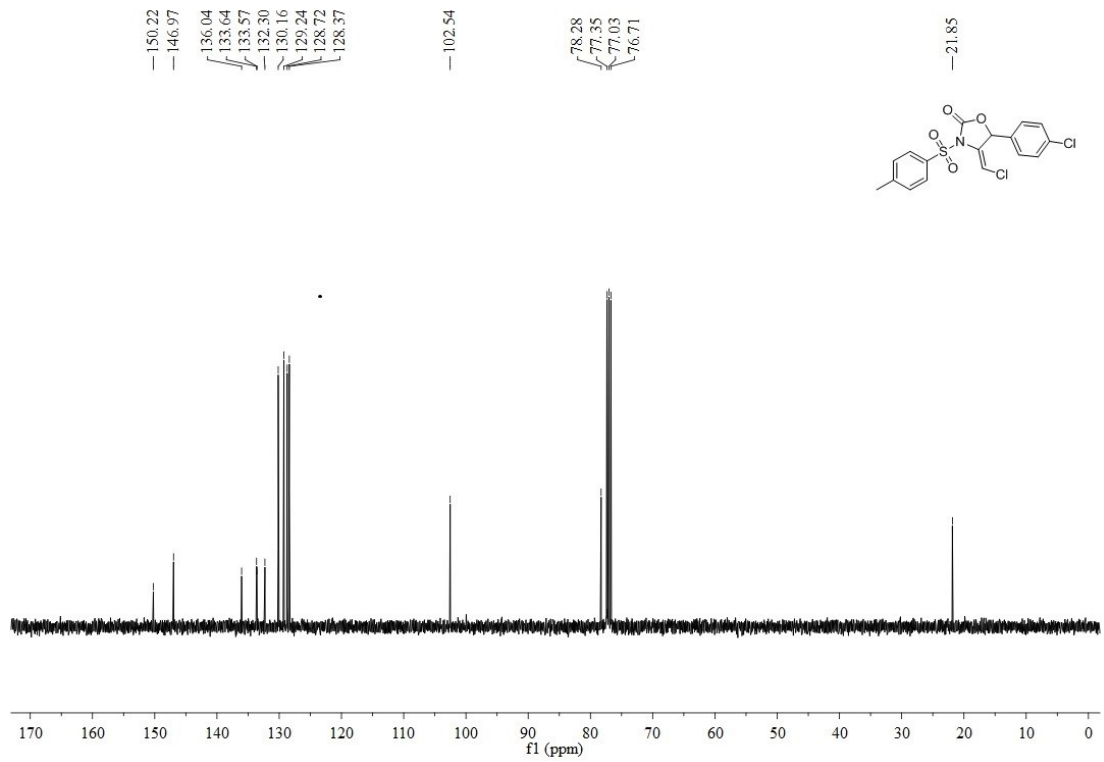
3.00
f1 (ppm)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132.30
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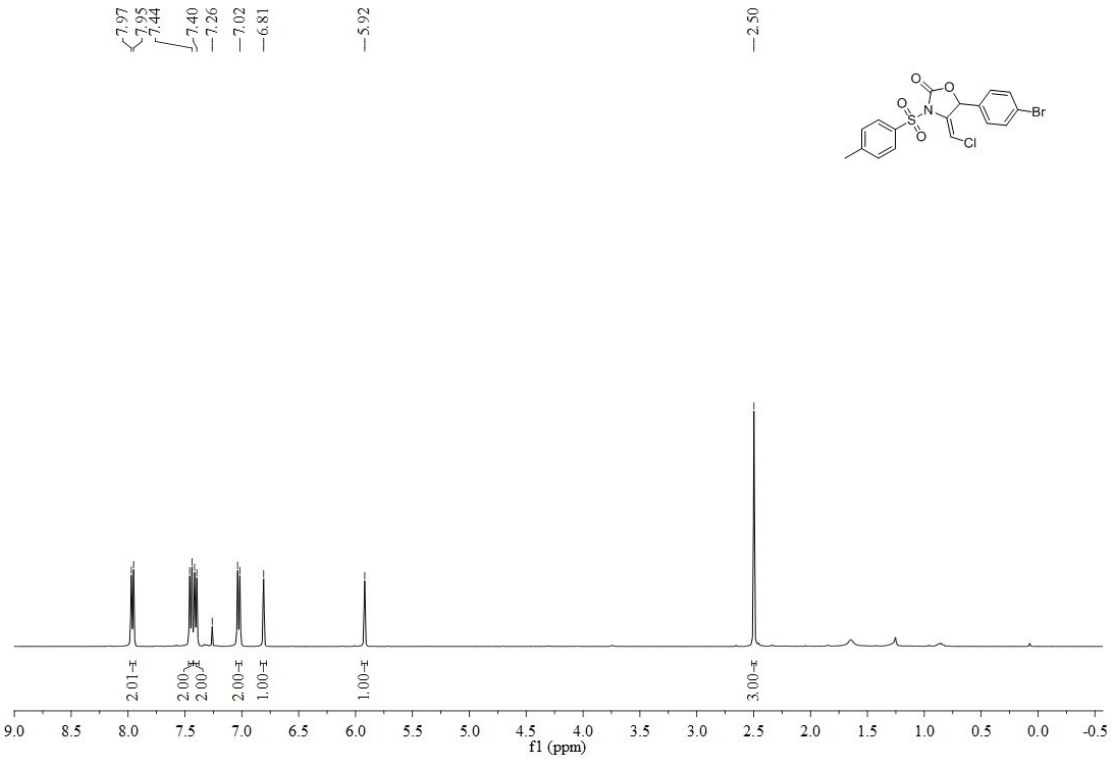
78.28
77.35
77.03
76.71
21.85
Cl
Cl
f1 (ppm)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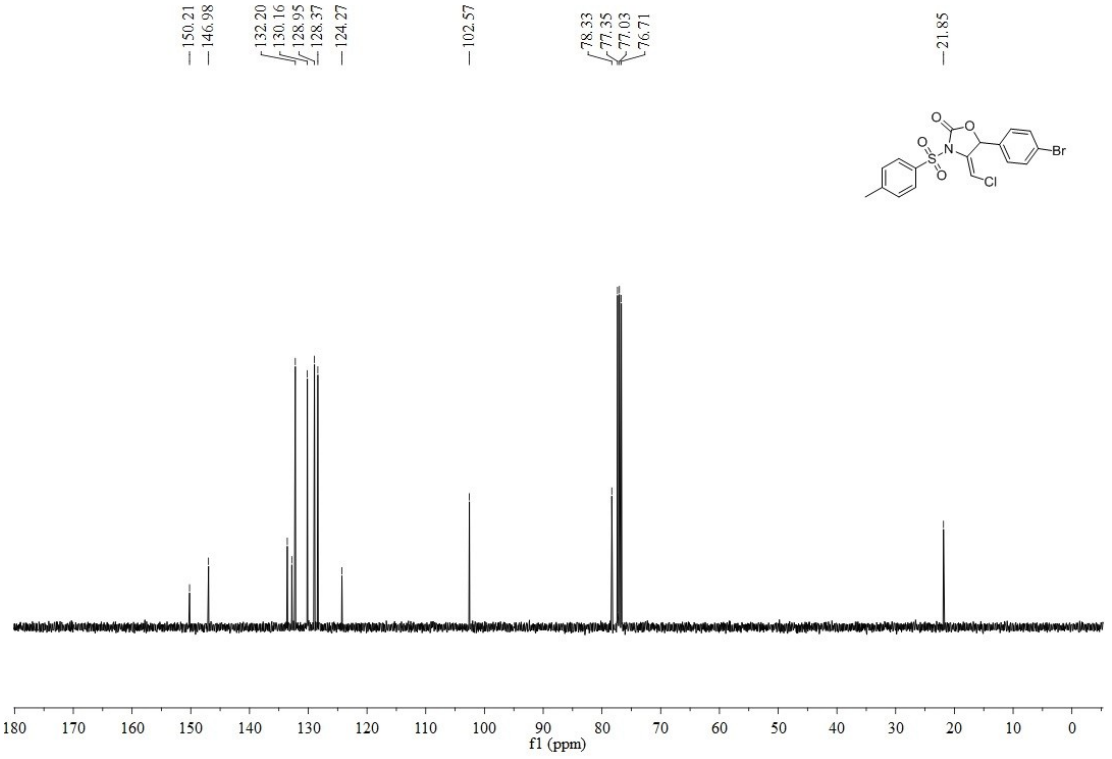
1.00
3.00
f1 (ppm)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78.33
77.35
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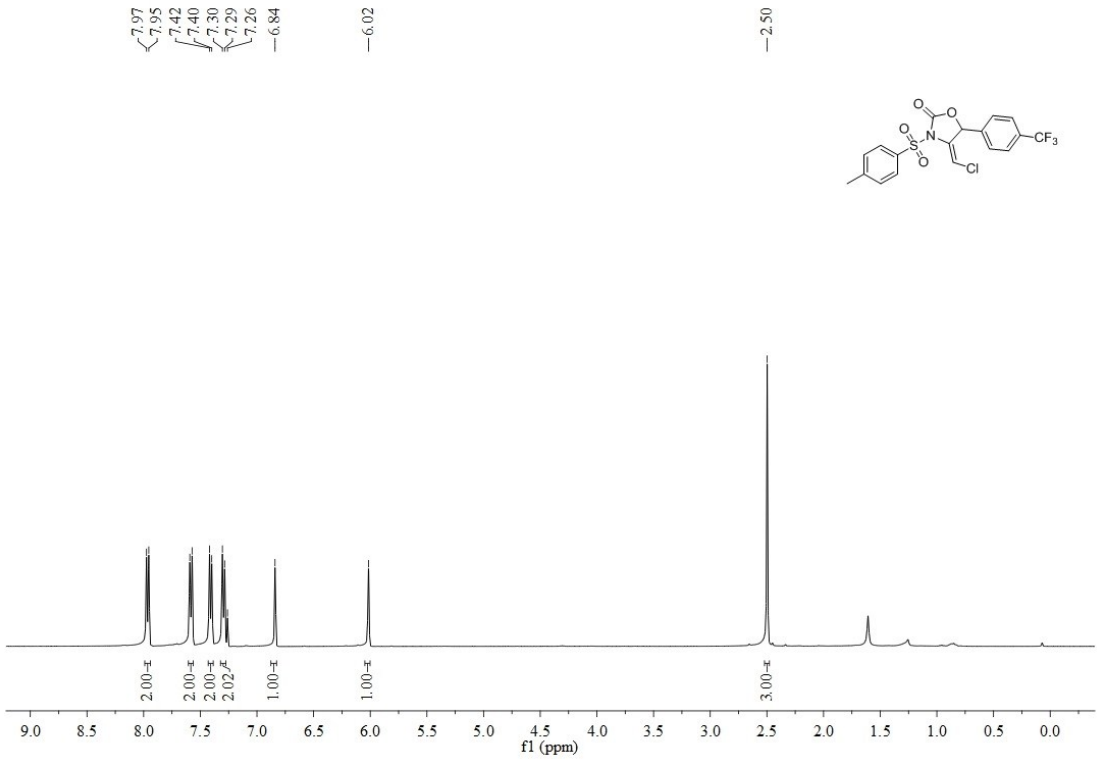
76.71
21.85
Br
Cl
f1 (ppm)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7.30
7.29
7.26
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CF3
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2.00
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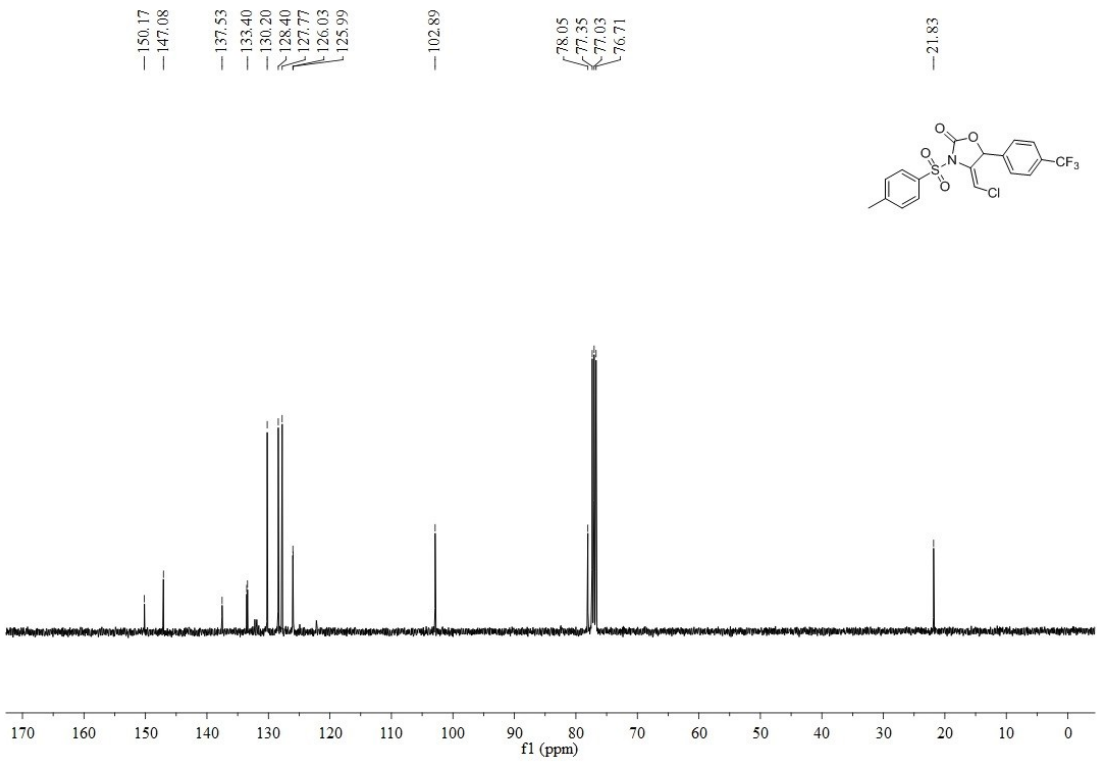
1.00
1.00
3.00
f1 (ppm)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102.89
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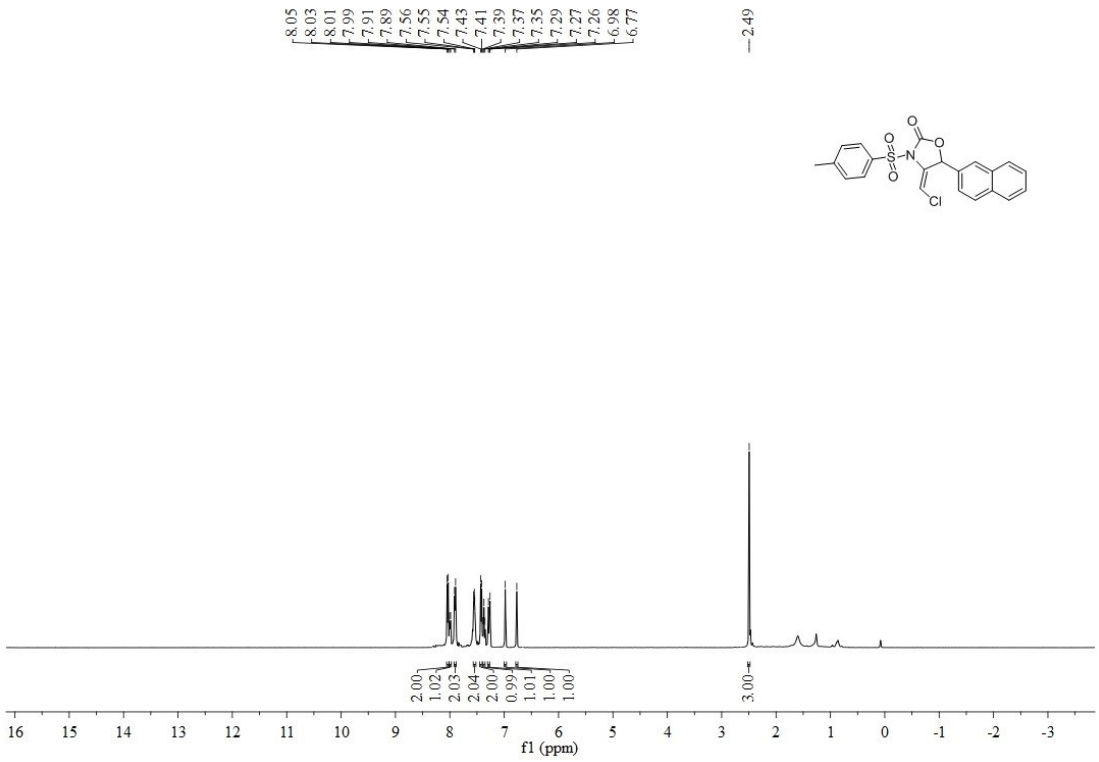
77.35
77.03
76.71
21.83
CF3
Cl
f1 (ppm)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7.89
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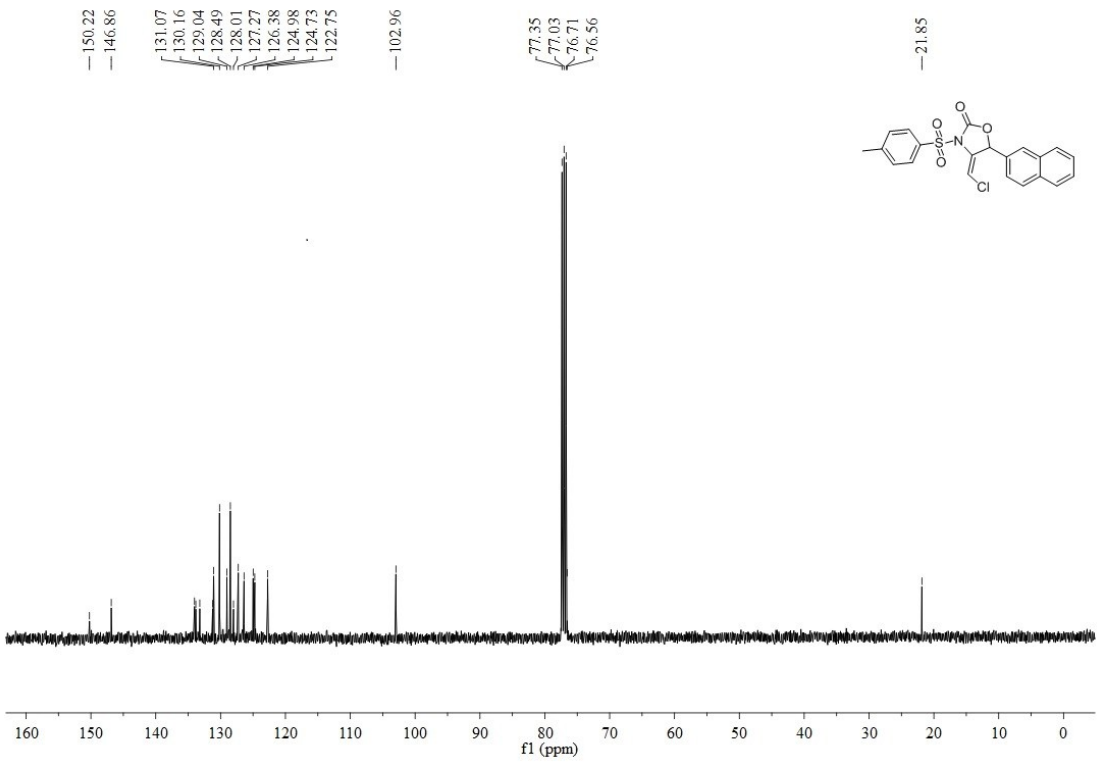
7.55
7.54
7.43
7.41
7.39
7.37
7.35
7.29
7.27
7.26
6.98
6.77
2.49
Cl
2.00
1.02
2.03
2.04
2.00
0.99
1.01
1.00
1.00
3.00
f1 (ppm)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129.04
128.49
128.01
127.27
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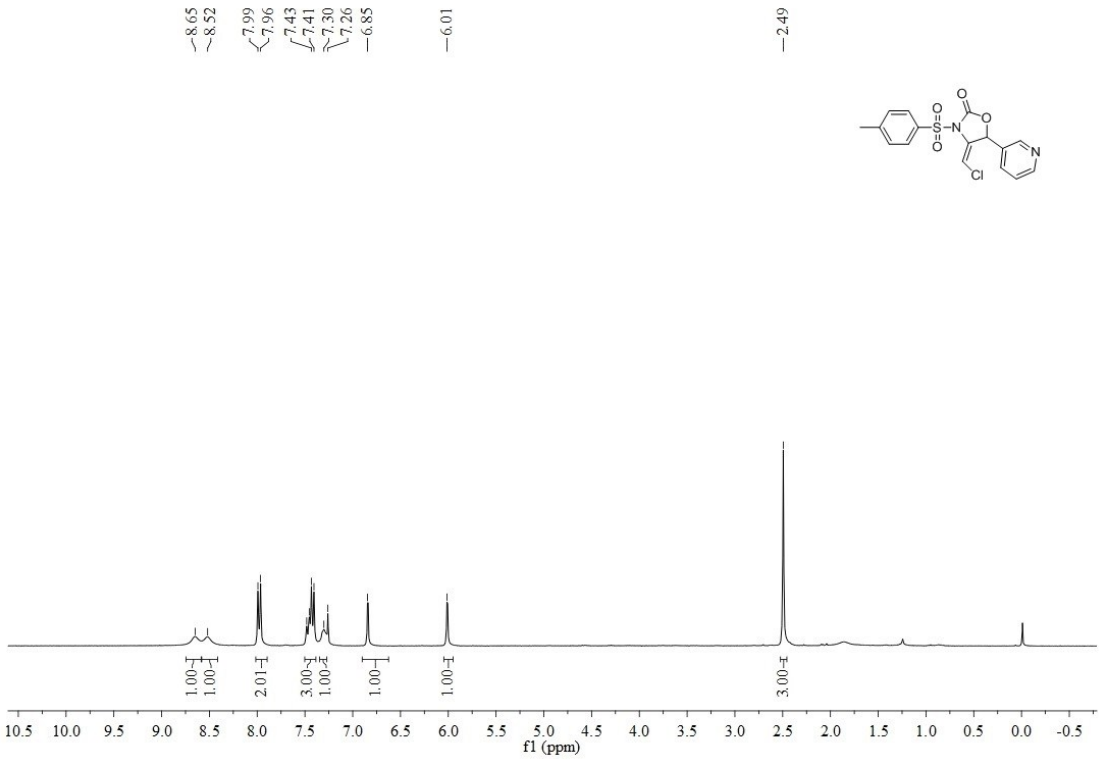
124.73
122.75
102.96
77.35
77.03
76.71
76.56
21.85
Cl
f1 (ppm)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7.96
7.43
7.41
7.30
7.26
6.85
6.01
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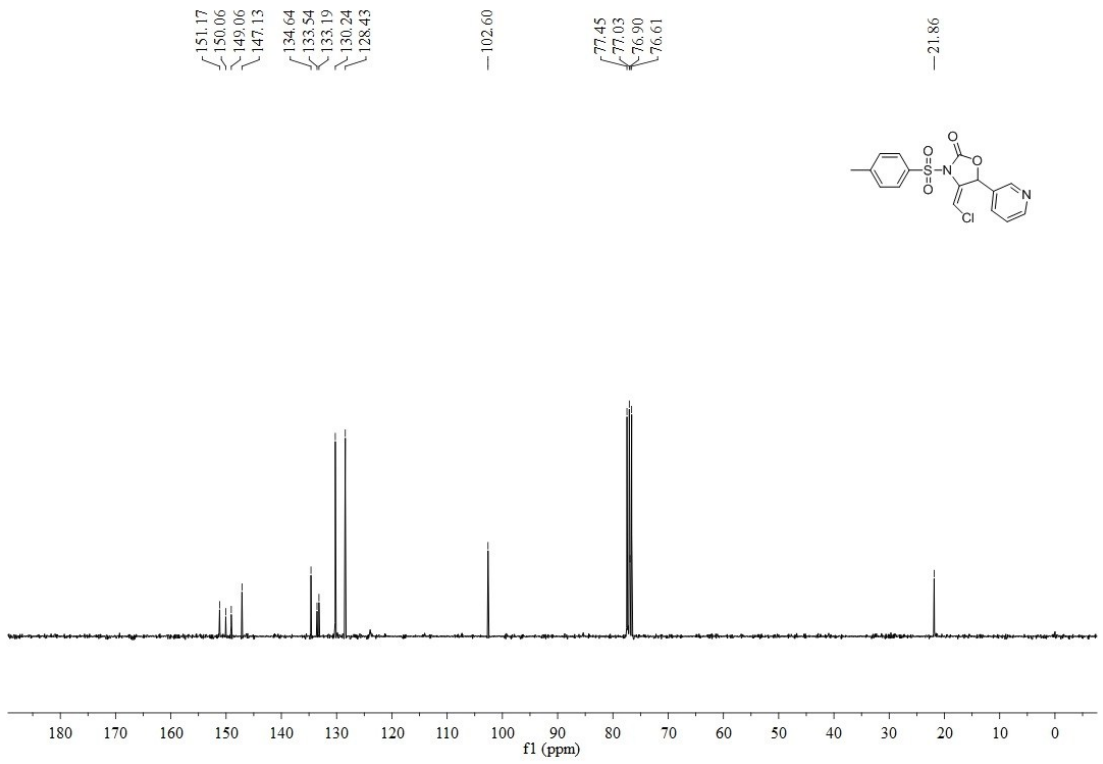
1.00
3.00
f1 (ppm)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149.06
147.13
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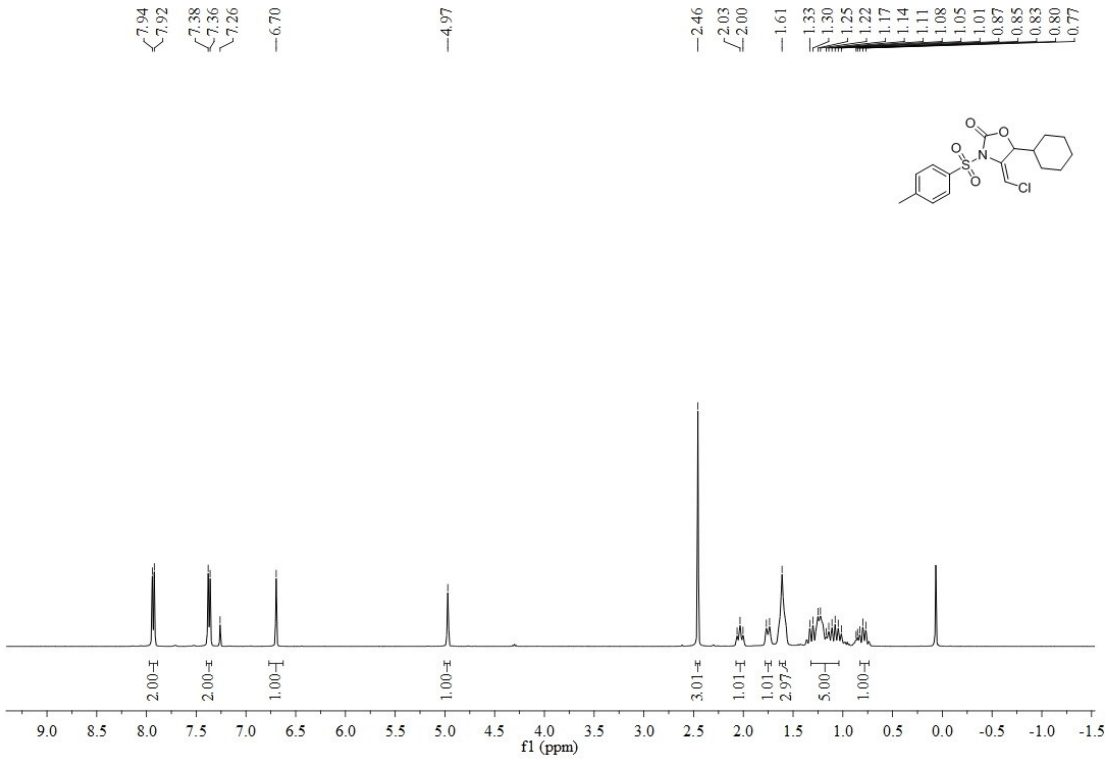
130.24
128.43
102.60
77.45
77.03
76.90
76.61
21.86
f1 (ppm)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7.92
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7.36
7.26
6.70
4.97
2.46
2.03
2.00
1.61
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1.30
1.25
1.22
1.17
1.14
1.11
1.08
1.05
1.01
0.87
0.85
0.83
0.80
0.77
Cl
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1.00
3.01
1.01
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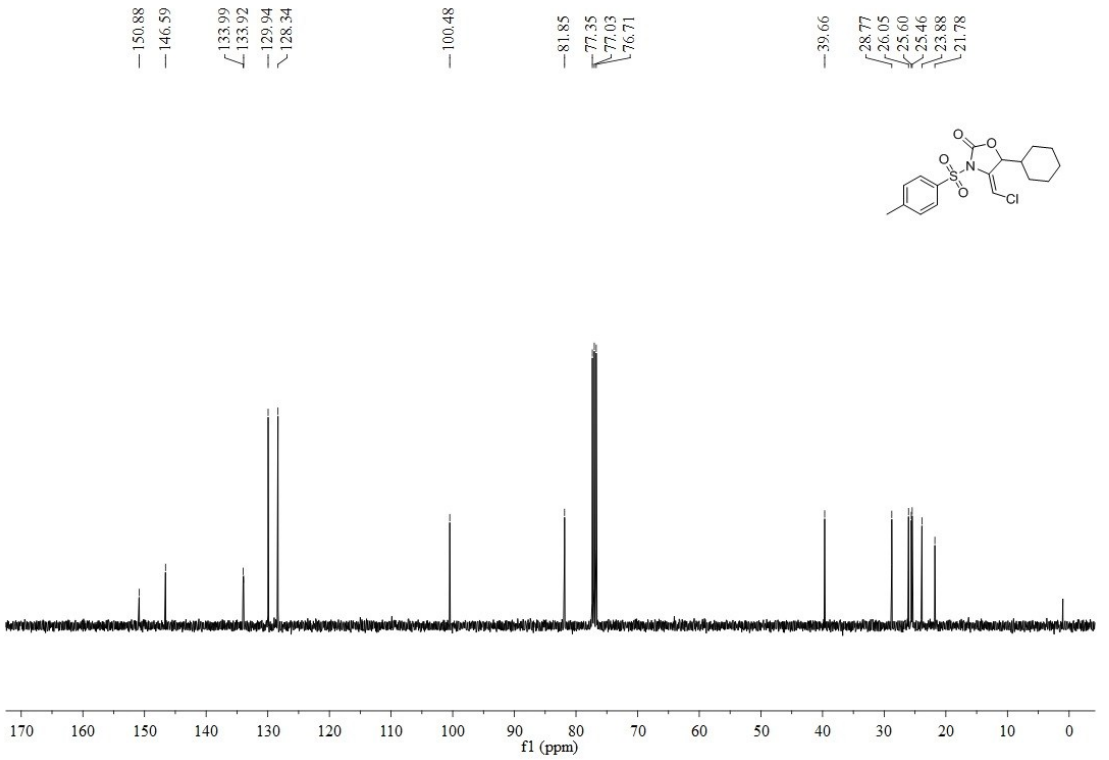
2.97
5.00
1.00
f1 (ppm)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39.66
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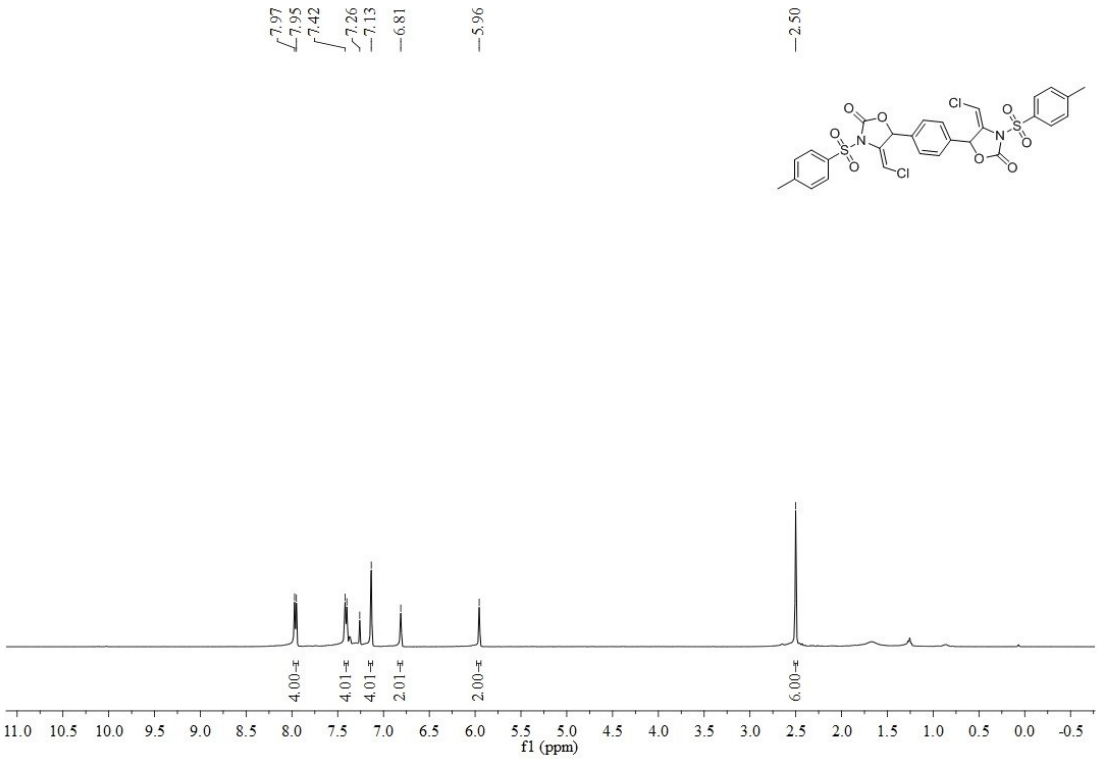
26.05
25.60
25.46
23.88
21.78
Cl
f1 (ppm)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7.95
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7.26
7.13
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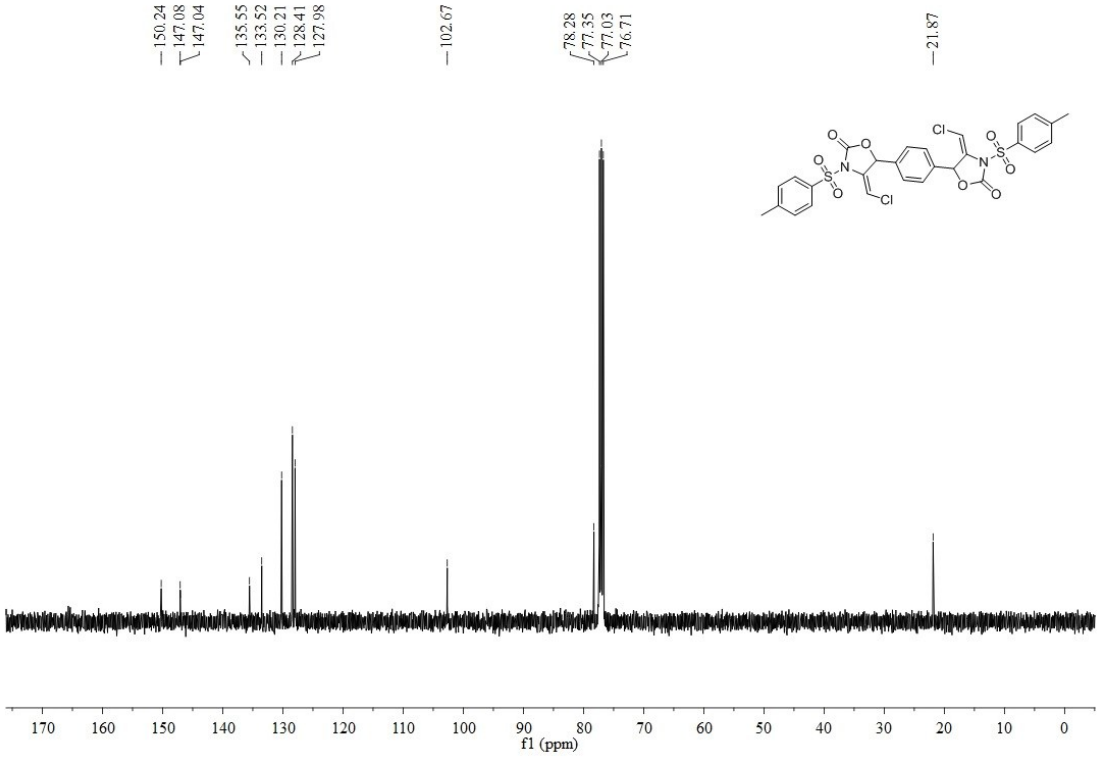
Cl
Cl
4.00
4.01
4.01
2.01
2.00
6.00
f1 (ppm)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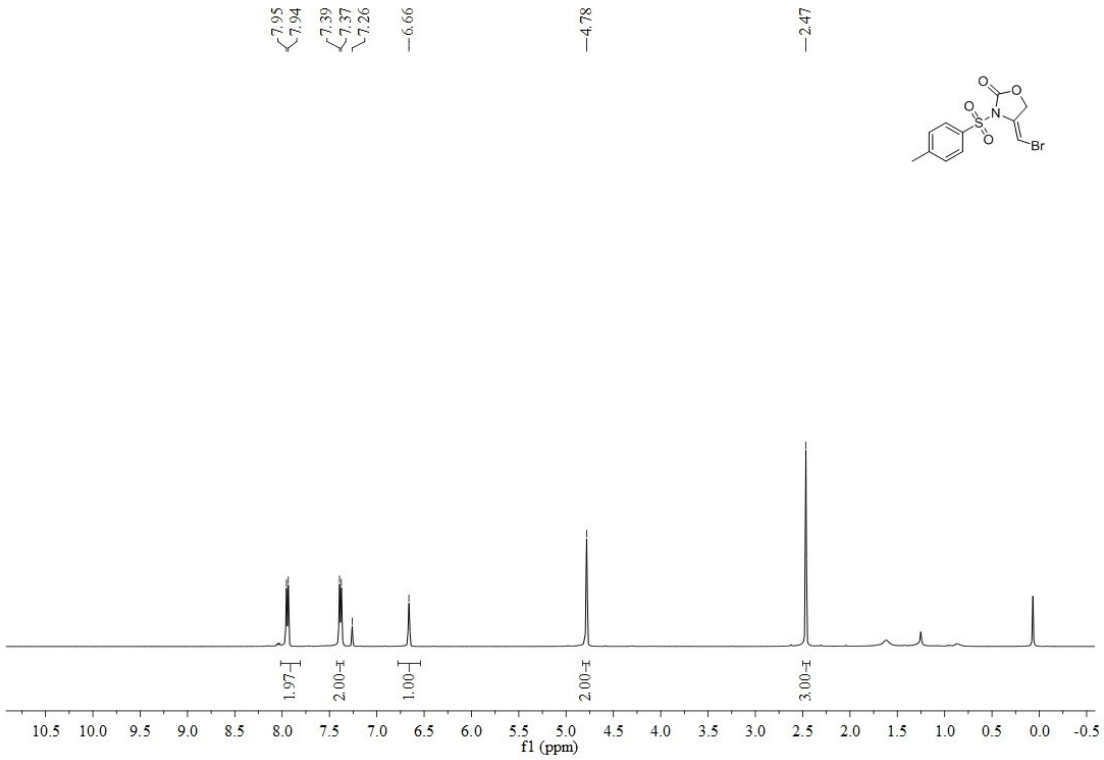
76.71
21.87
Cl
Cl
f1 (ppm)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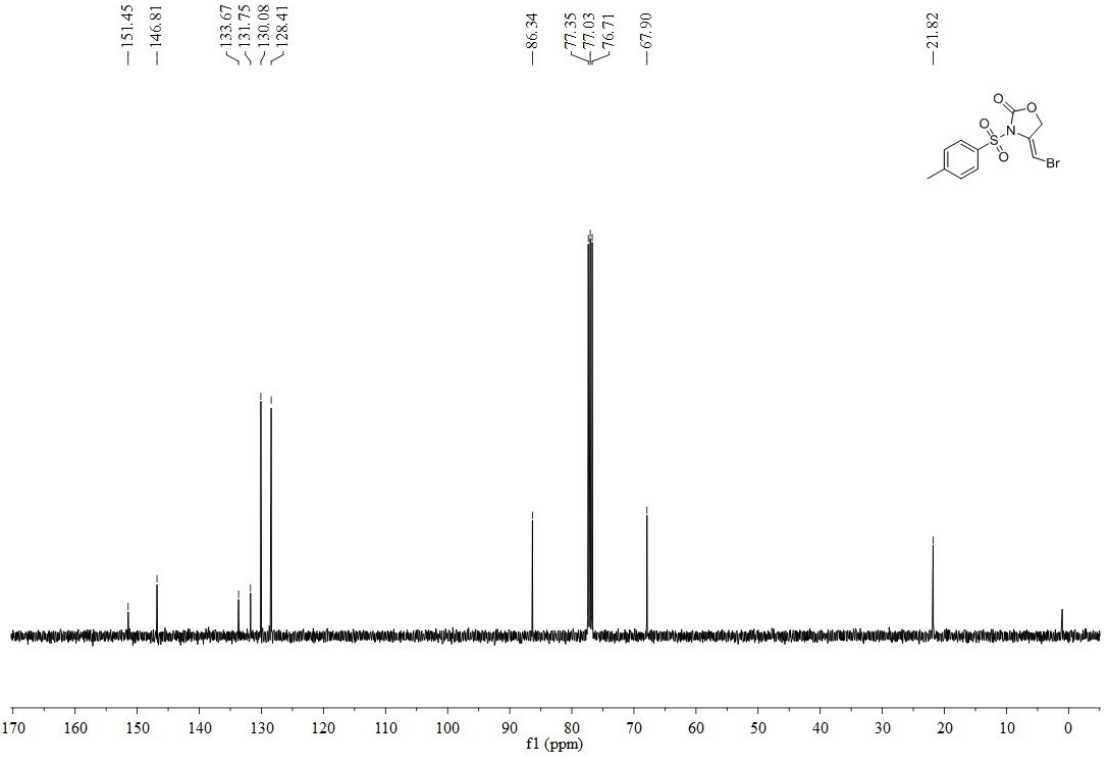
7.94
7.39
7.37
7.26
6.66
4.78
2.47
Br
1.97
2.00
1.00
2.00
3.00
f1 (ppm)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77.03
76.71
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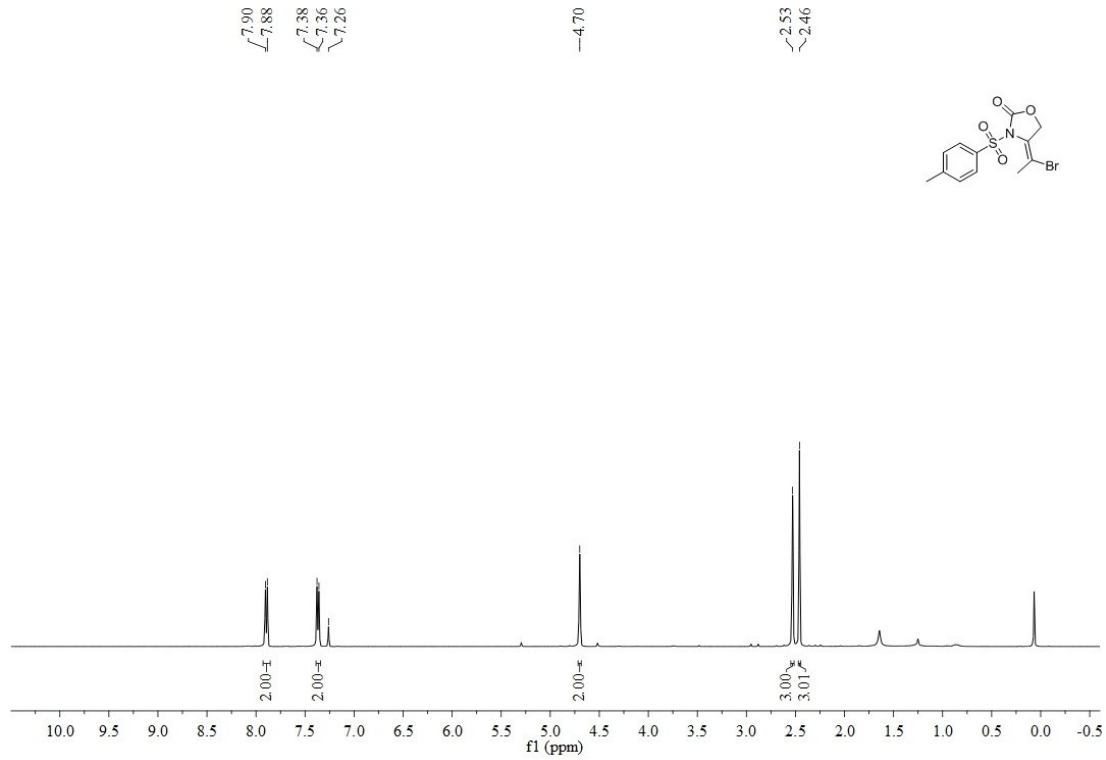
21.82
Br
f1 (ppm)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7.88
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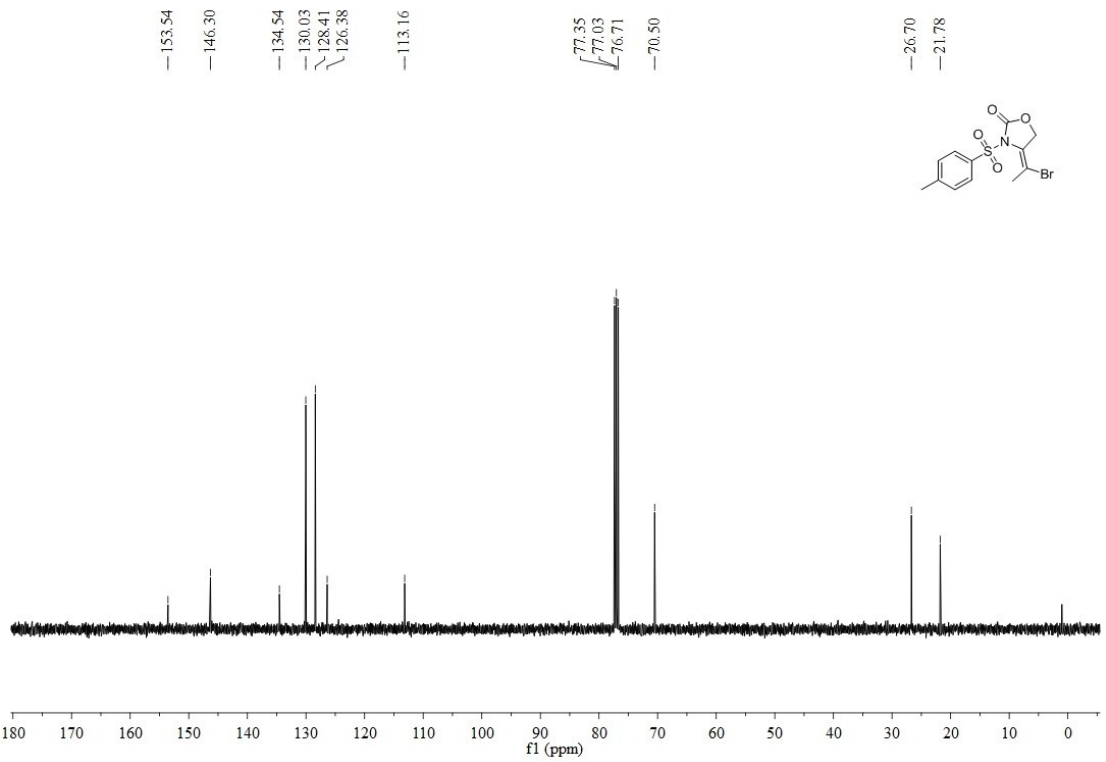
7.36
7.26
4.70
2.53
2.46
Br
2.00
2.00
2.00
3.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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134.54
130.03
128.41
126.38
113.16
77.35
77.03
76.71
70.50
26.70
21.78
Br
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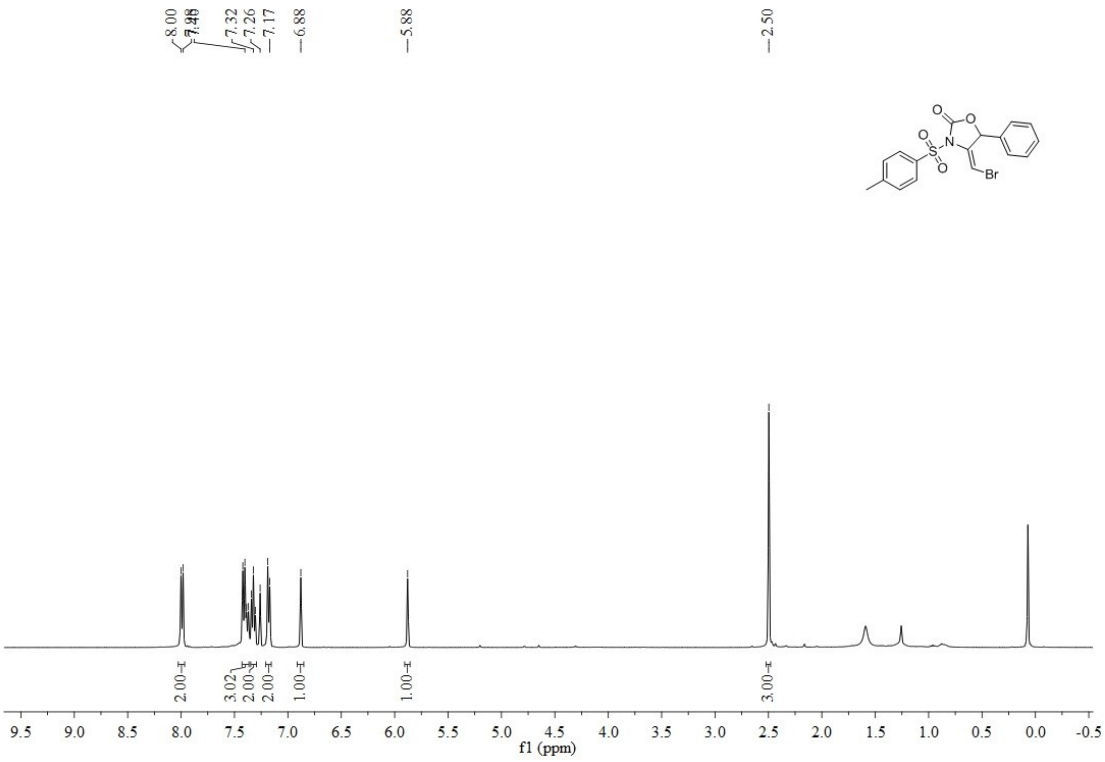
f1 (ppm)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7.17
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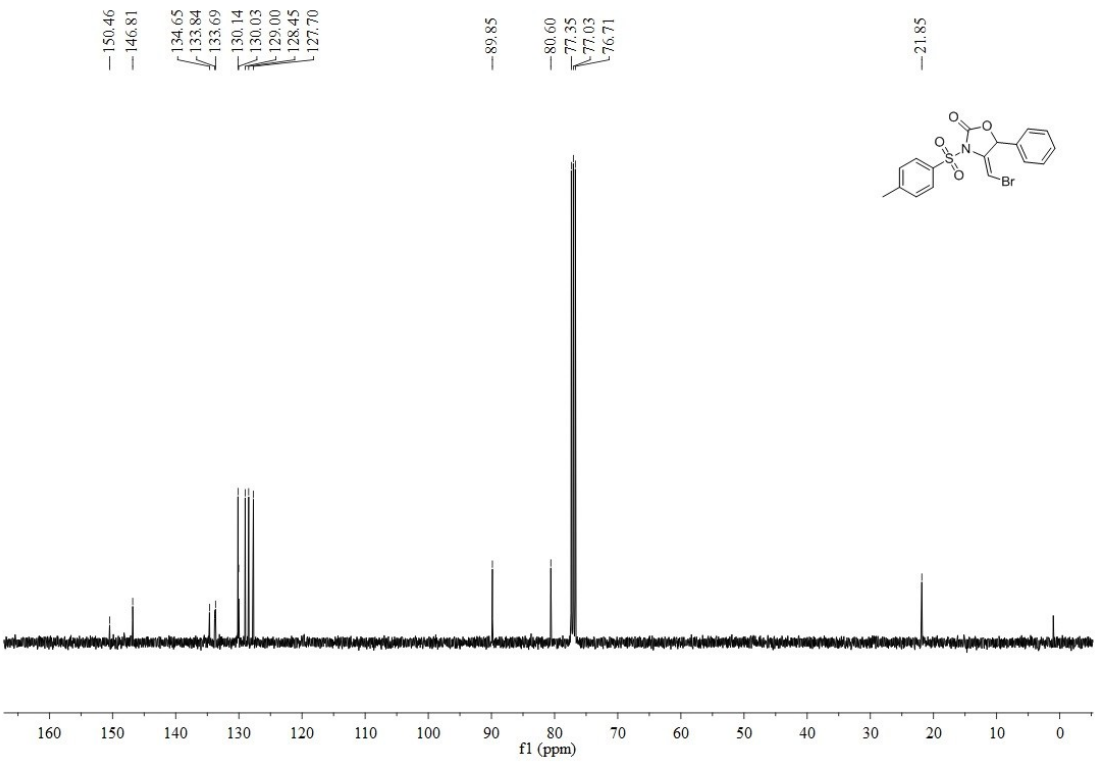
5.88
2.50
Br
2.00
3.02
2.00
2.00
1.00
1.00
3.00
f1 (ppm)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130.14
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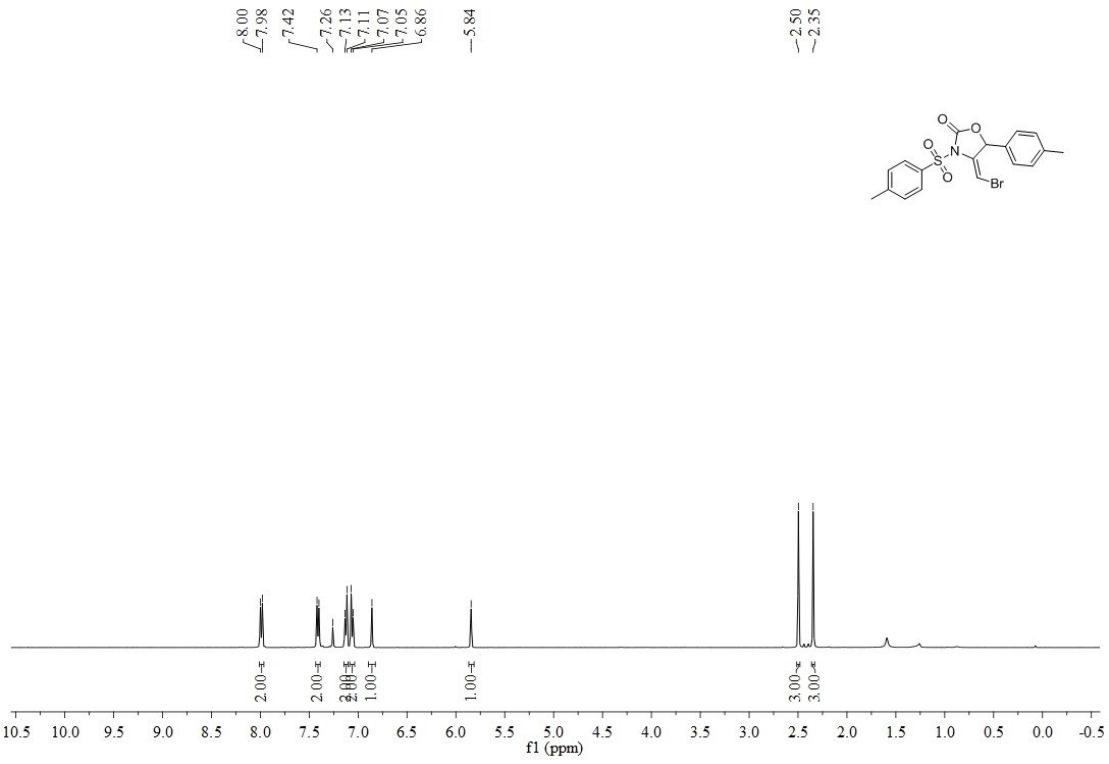
127.70
89.85
80.60
77.35
77.03
76.71
21.85
Br
f1 (ppm)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7.07
7.05
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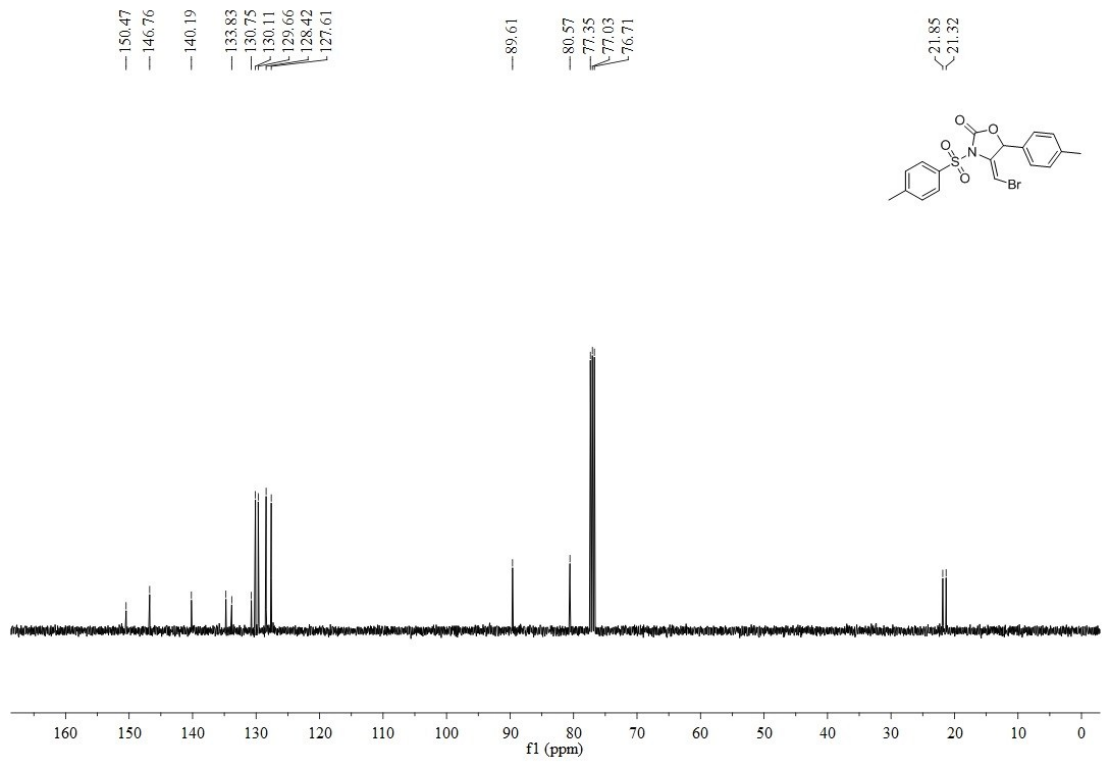
2.35
Br
2.00
2.00
1.00
1.00
3.00
3.00
f1 (ppm)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89.61
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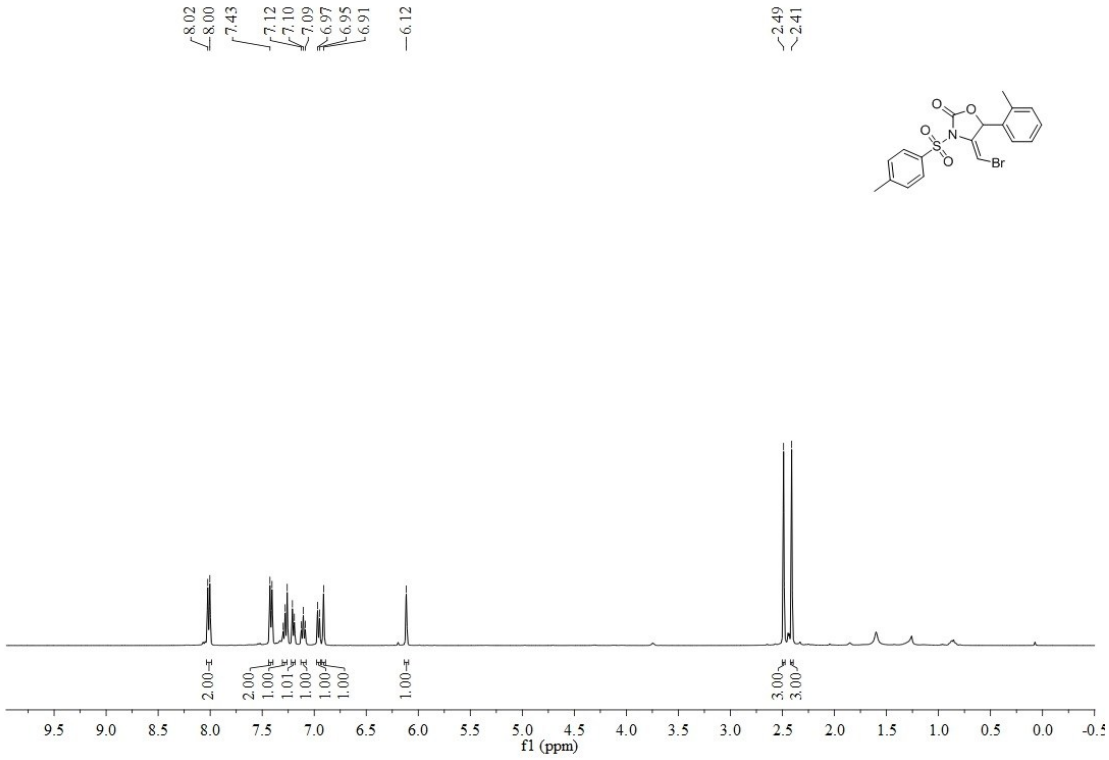
77.35
77.03
76.71
21.85
21.32
Br
f1 (ppm)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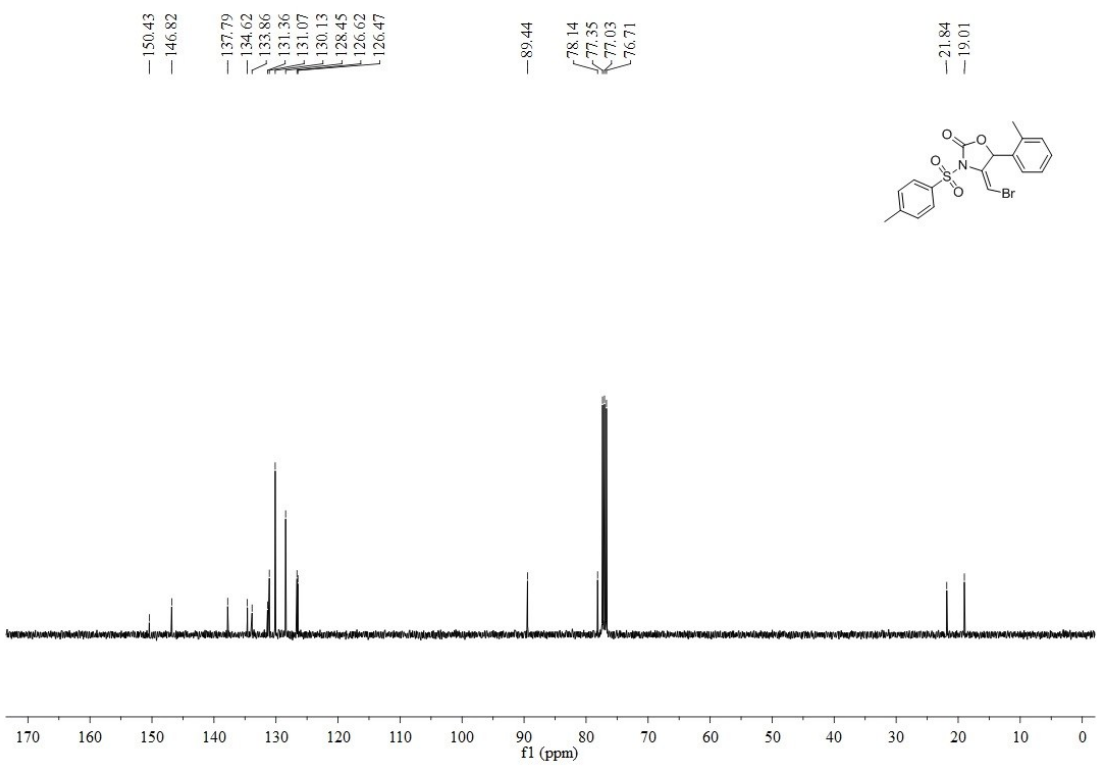
6.95
6.91
6.12
2.49
2.41
Br
2.00
2.00
1.00
1.01
1.00
1.00
1.00
1.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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126.62
126.47
89.44
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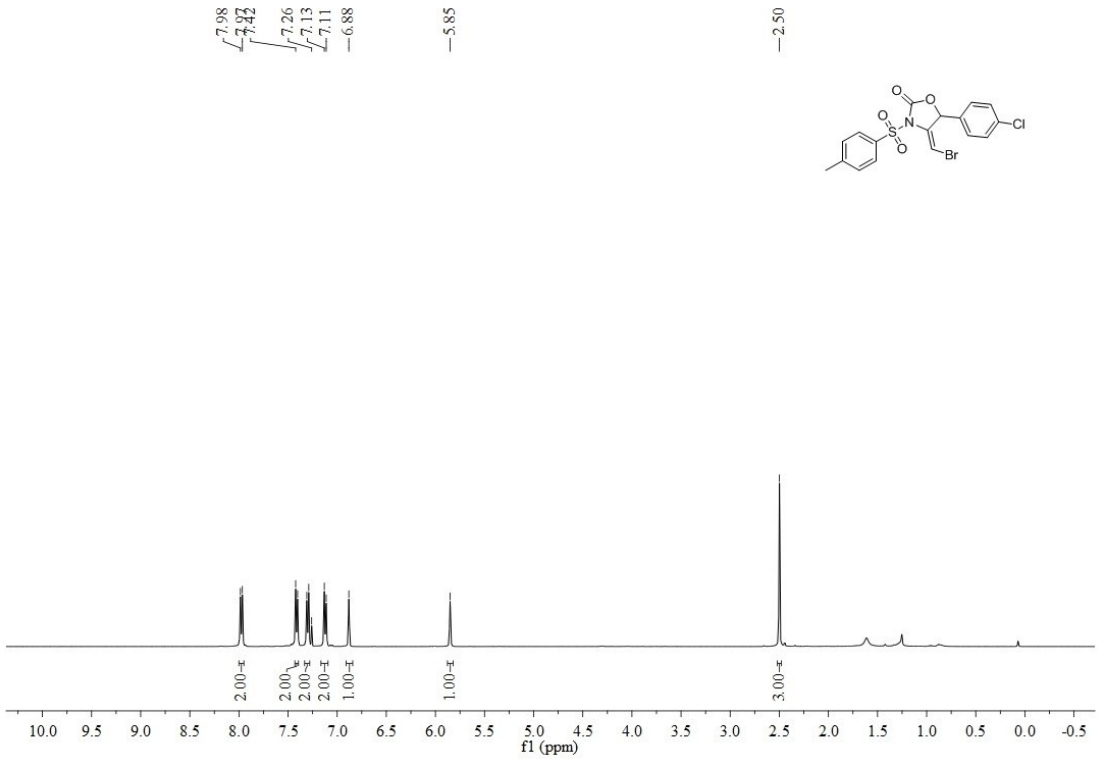
77.03
76.71
21.84
19.01
Br
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.98
7.97
7.42
7.26
7.13
7.11
6.88
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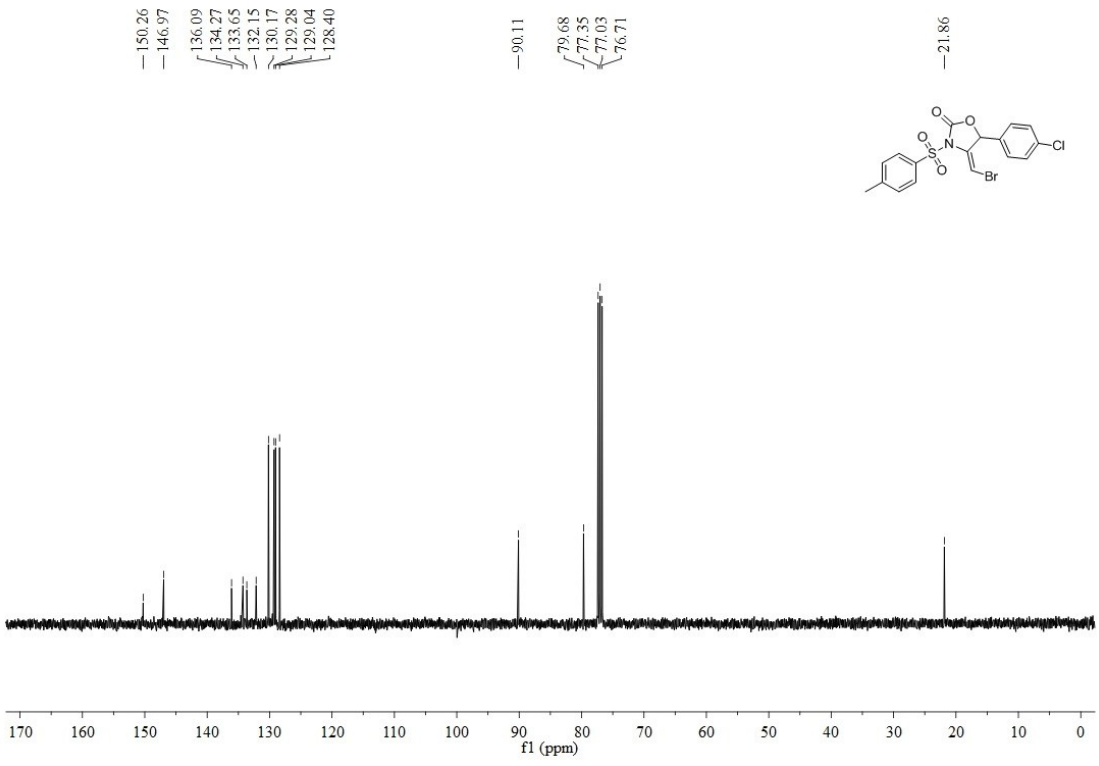
2.50
2.00
2.00
2.00
2.00
1.00
1.00
3.00
f1 (ppm)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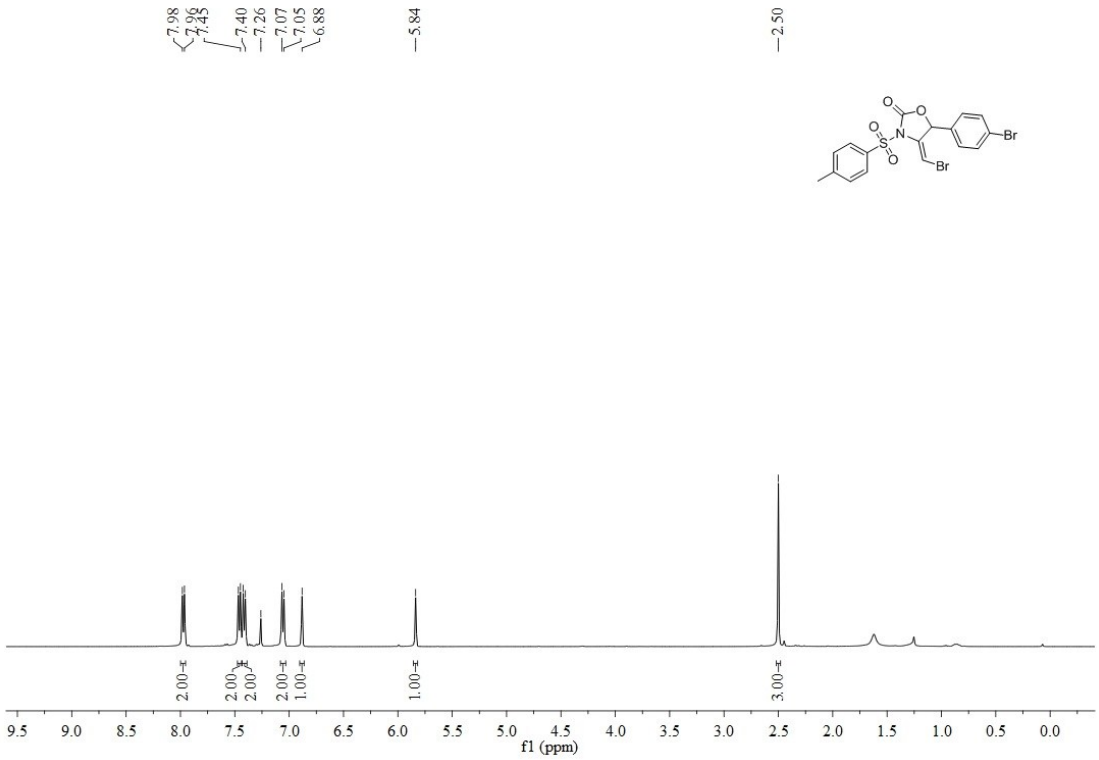
129.04
128.40
90.11
79.68
77.35
77.03
76.71
21.86
f1 (ppm)


7.98
7.96
7.45
7.40
7.26
7.07
7.05
6.88
5.84
2.50
Br
Br
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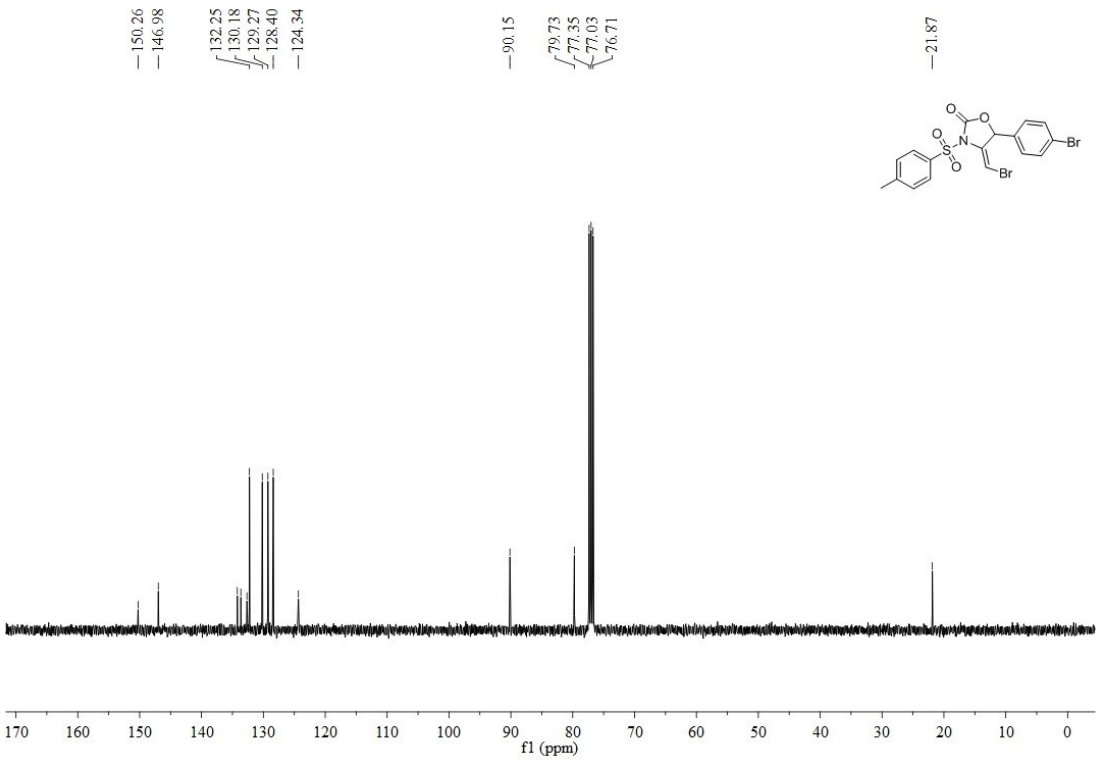
2.00
1.00
1.00
3.00
f1 (ppm)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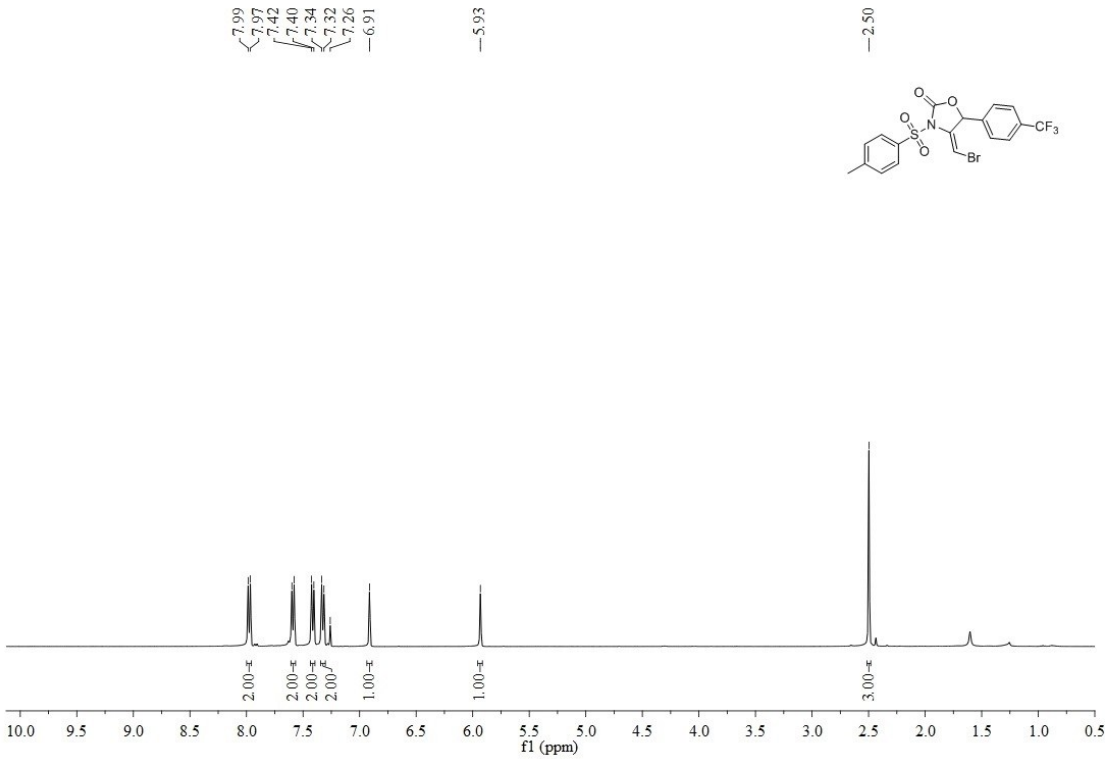
124.34
90.15
79.73
77.35
77.03
76.71
21.87
Br
Br
f1 (ppm)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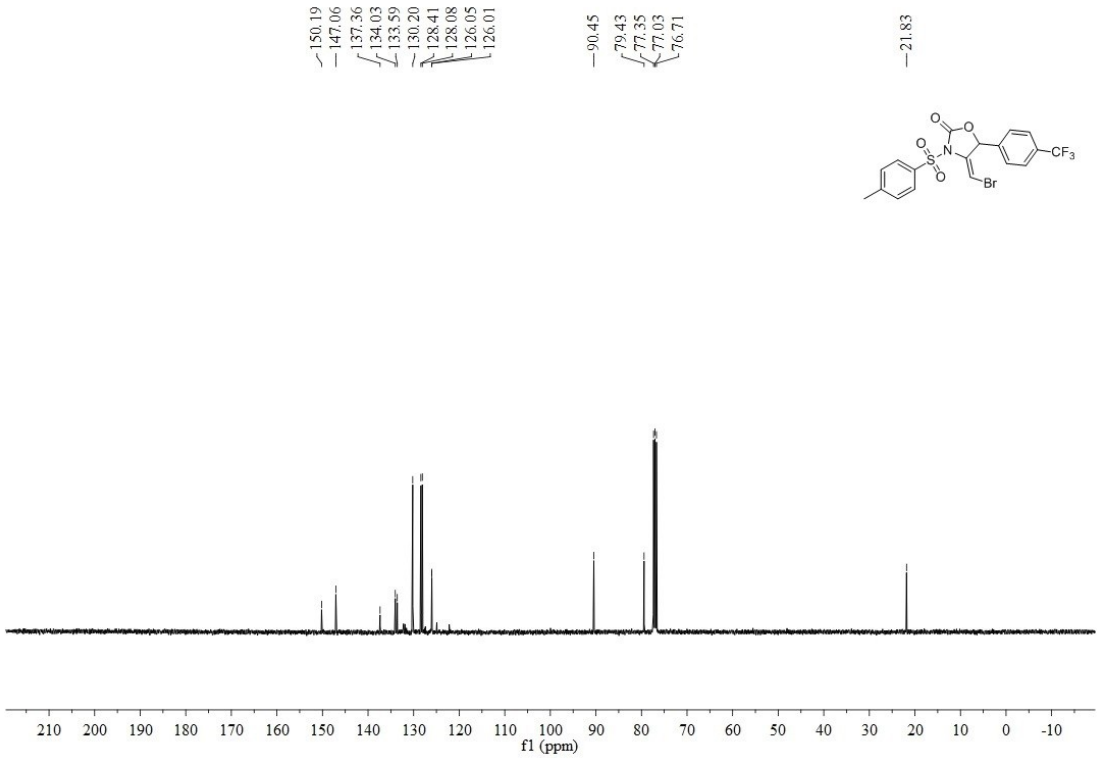
7.97
7.42
7.40
7.34
7.32
7.26
6.91
5.93
2.50
Br
CF3
2.00
2.00
2.00
1.00
1.00
3.00
f1 (ppm)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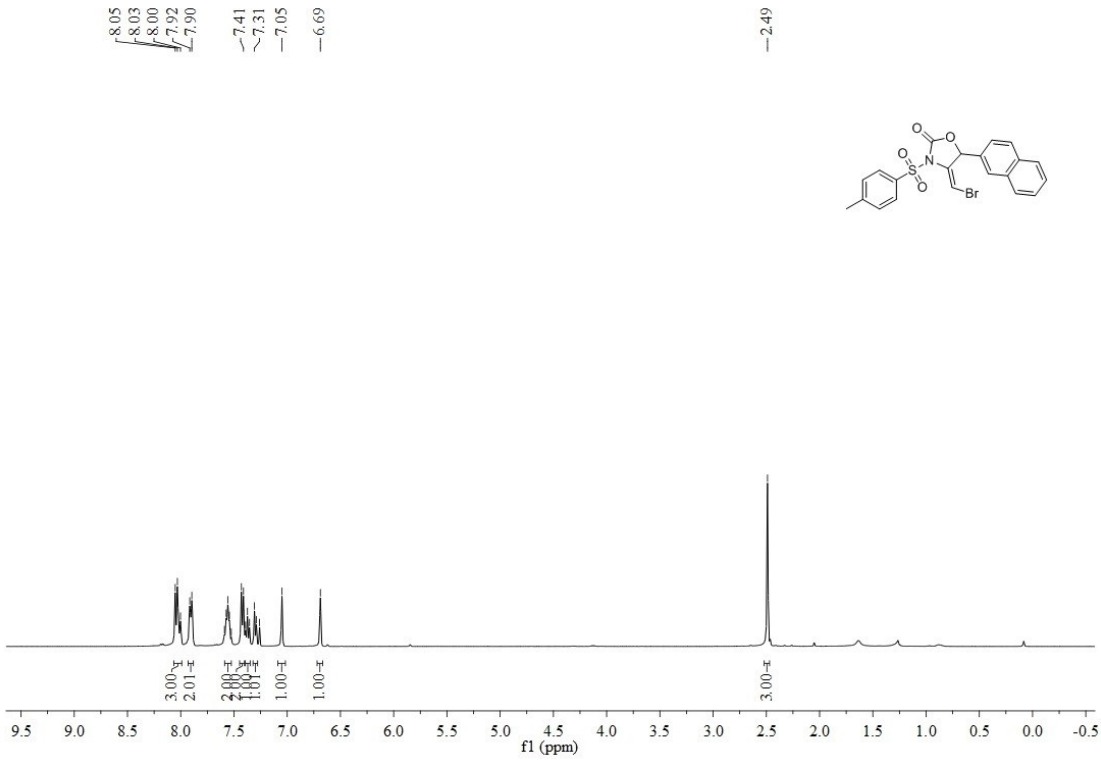
126.01
90.45
79.43
77.35
77.03
76.71
21.83
Br
CF3
f1 (ppm)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8.00
7.92
7.90
7.41
7.31
7.05
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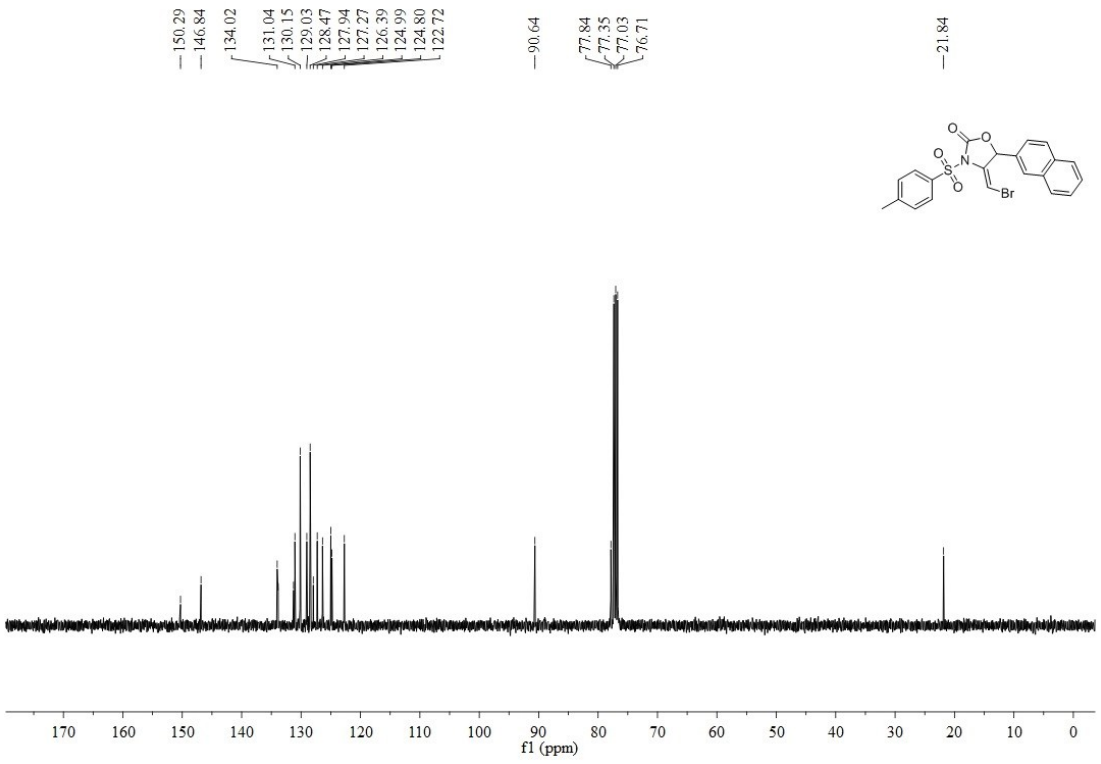
2.49
Br
3.00
2.01
2.00
2.00
1.01
1.00
1.00
3.00
f1 (ppm)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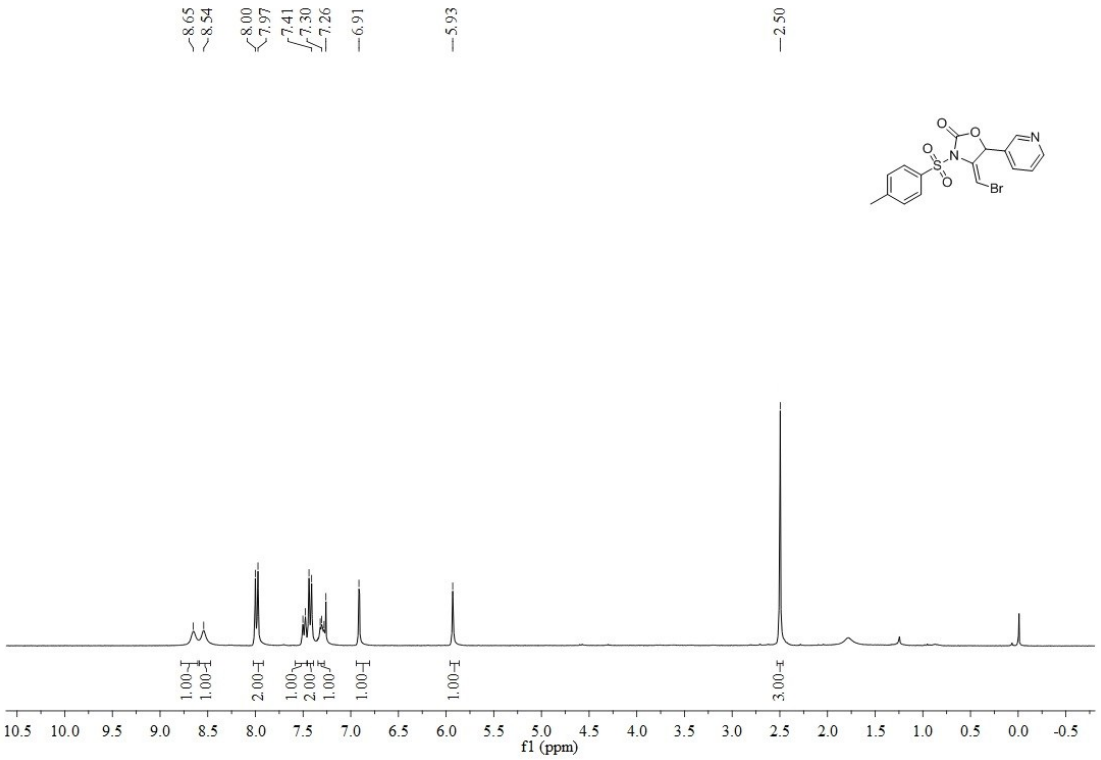
128.47
127.94
127.27
126.39
124.99
124.80
122.72
90.64
77.84
77.35
77.03
76.71
21.84
Br
f1 (ppm)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8.54
8.00
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7.26
6.91
5.93
2.50
Br
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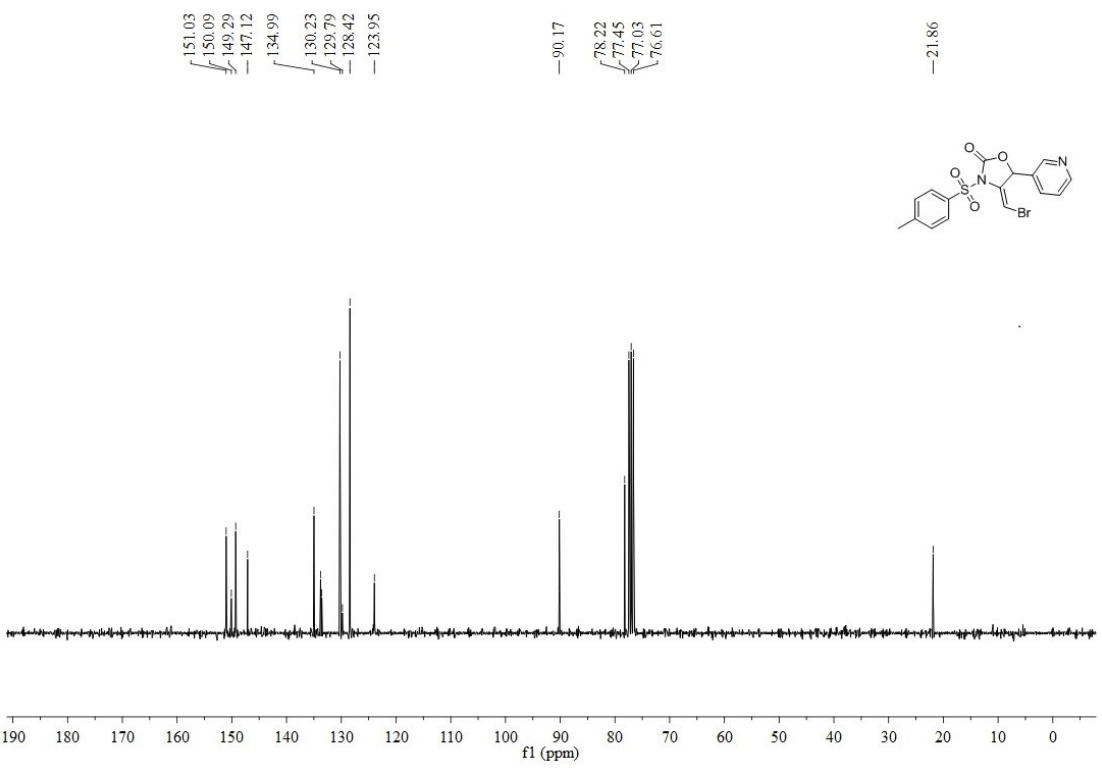
1.00
2.00
1.00
2.00
1.00
1.00
1.00
3.00
f1 (ppm)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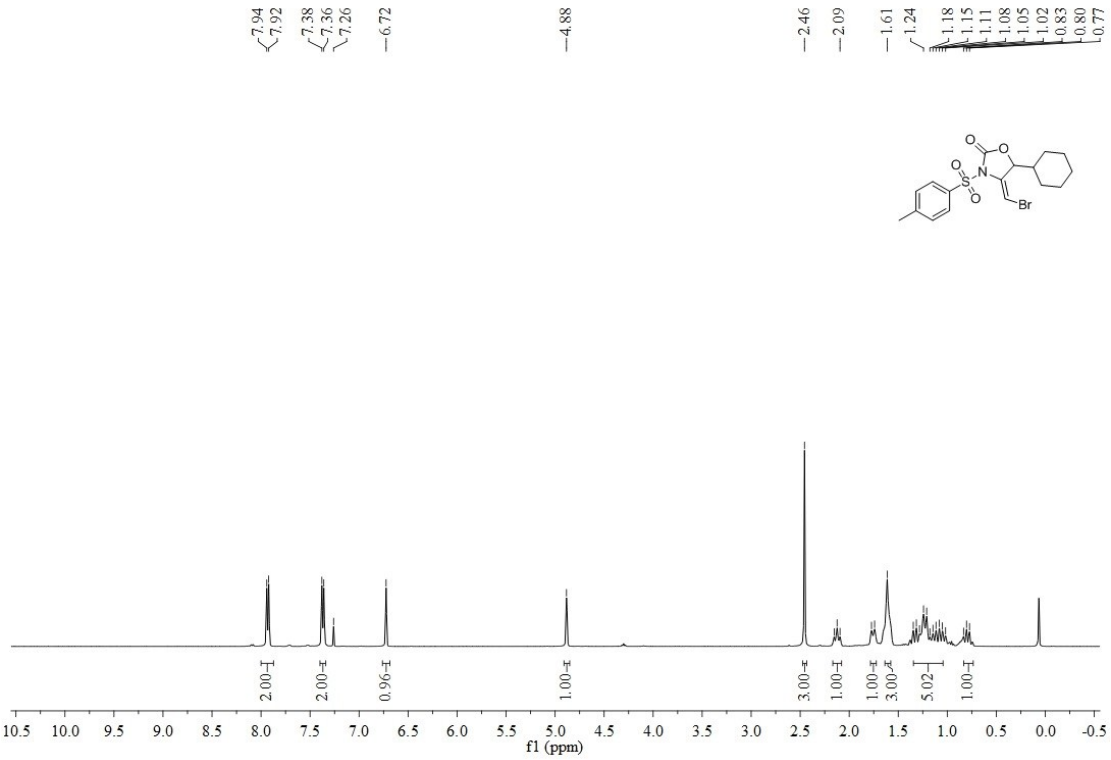
150.09
149.29
147.12
134.99
130.23
129.79
128.42
123.95
90.17
78.22
77.45
77.03
76.61
21.86
Br
f1 (ppm)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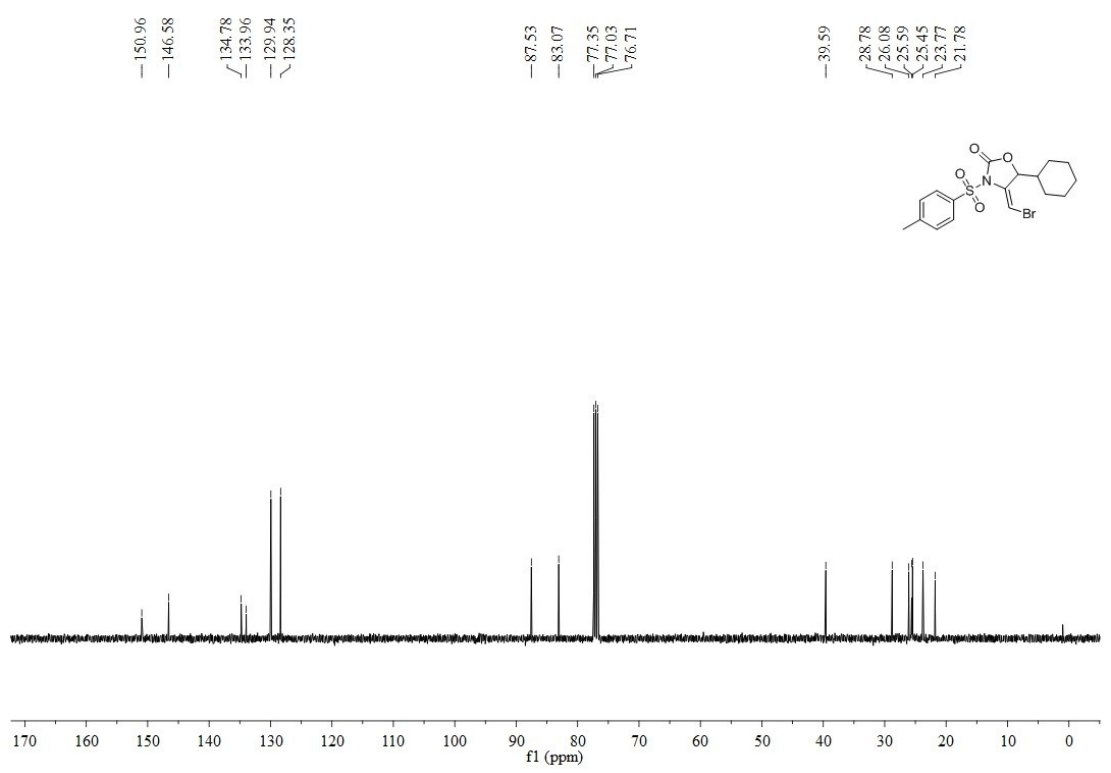
7.92
7.38
7.36
7.26
6.72
4.88
2.46
2.09
1.61
1.24
1.18
1.15
1.11
1.08
1.05
1.02
0.83
0.80
0.77
Br
2.00
2.00
0.96
1.00
3.00
1.00
1.00
3.00
5.02
1.00
f1 (ppm)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133.96
129.94
128.35
87.53
83.07
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77.03
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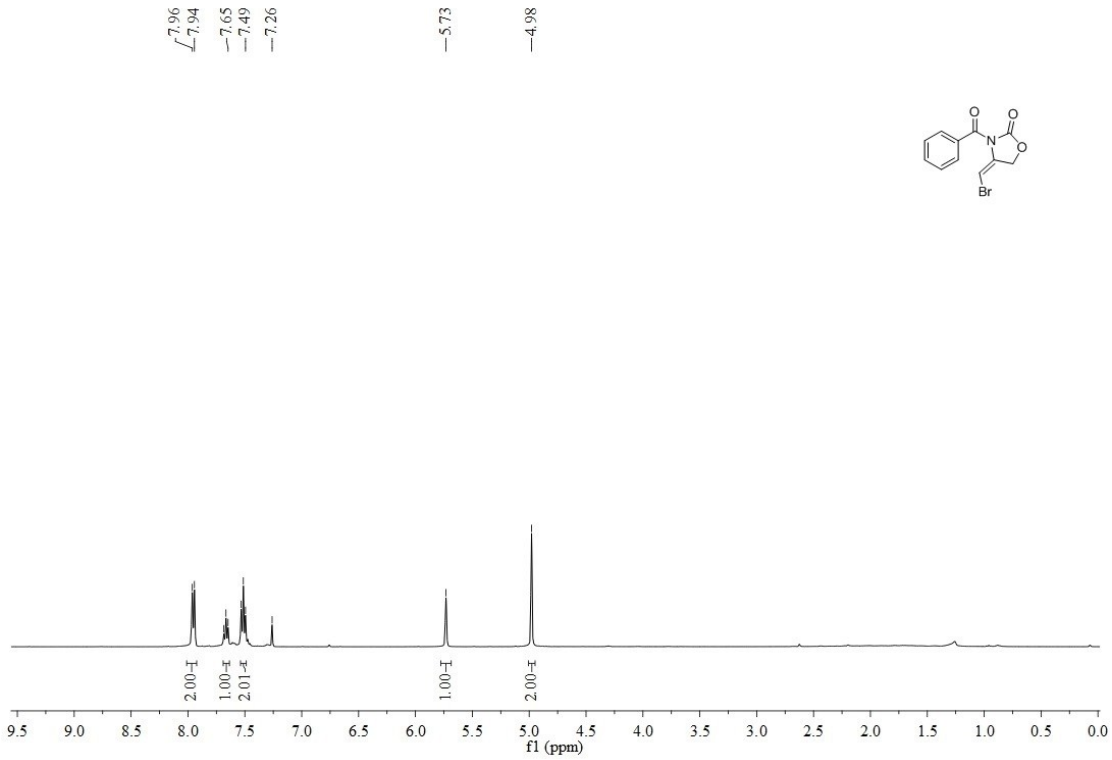
26.08
25.59
25.45
23.77
21.78
Br
f1 (ppm)


7.96
7.94
7.65
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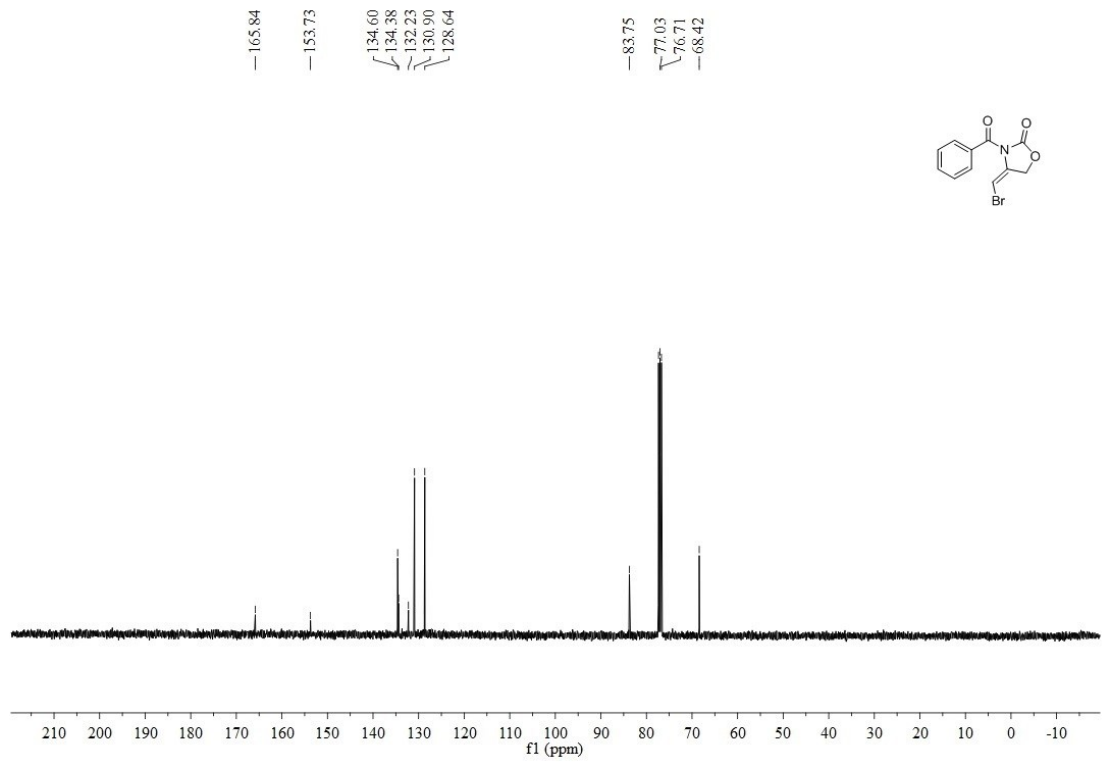
5.73
4.98
Br
2.00
1.00
2.01
1.00
2.00
f1 (ppm)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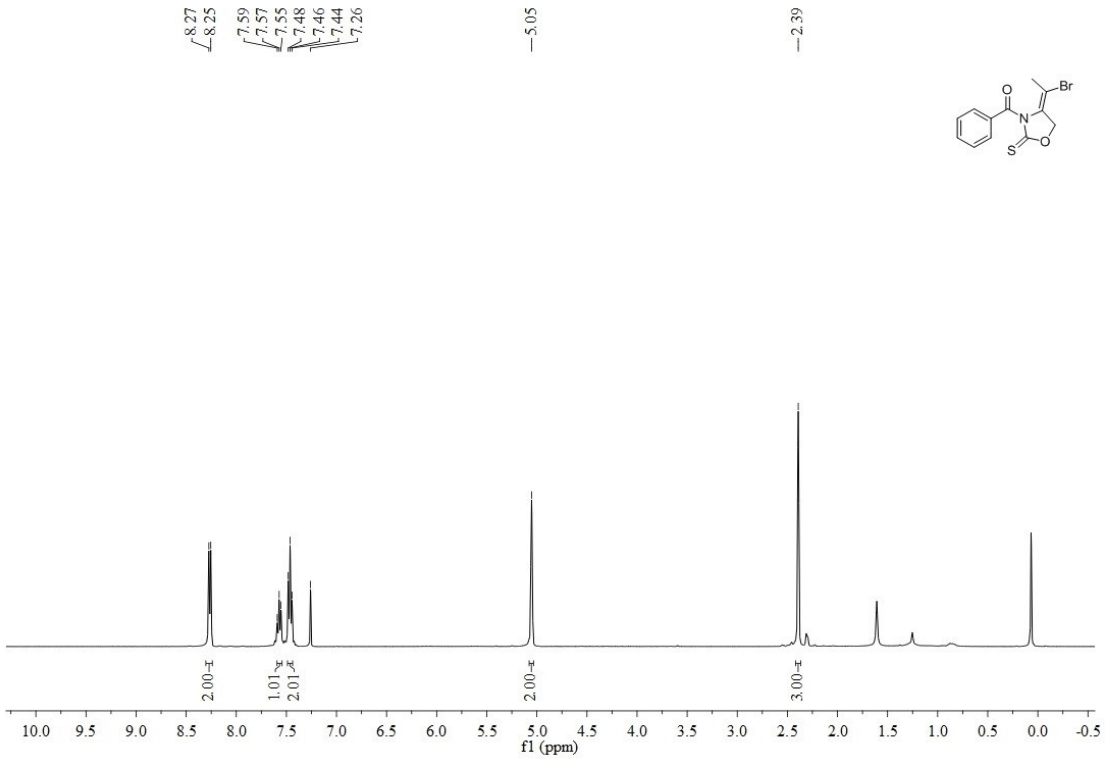
130.90
128.64
83.75
77.03
76.71
68.42
Br
f1 (ppm)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8.25
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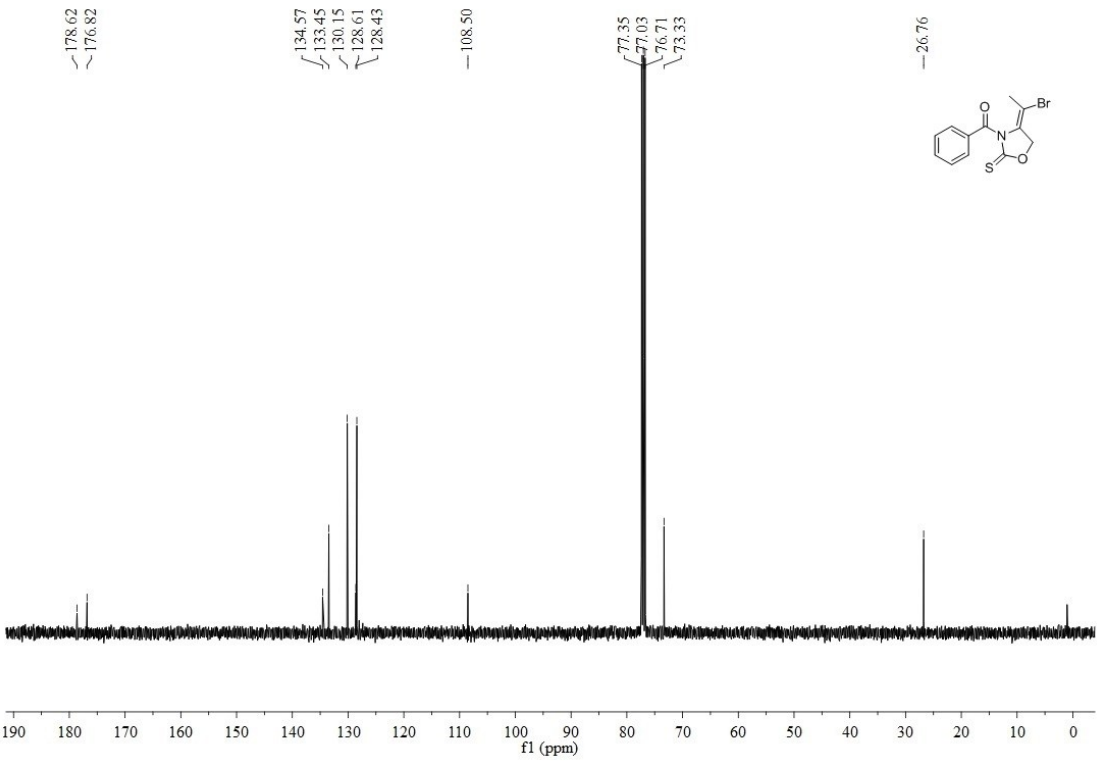
7.57
7.55
7.48
7.46
7.44
7.26
5.05
2.39
Br
O
N
S
O
2.00
1.01
2.01
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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176.82
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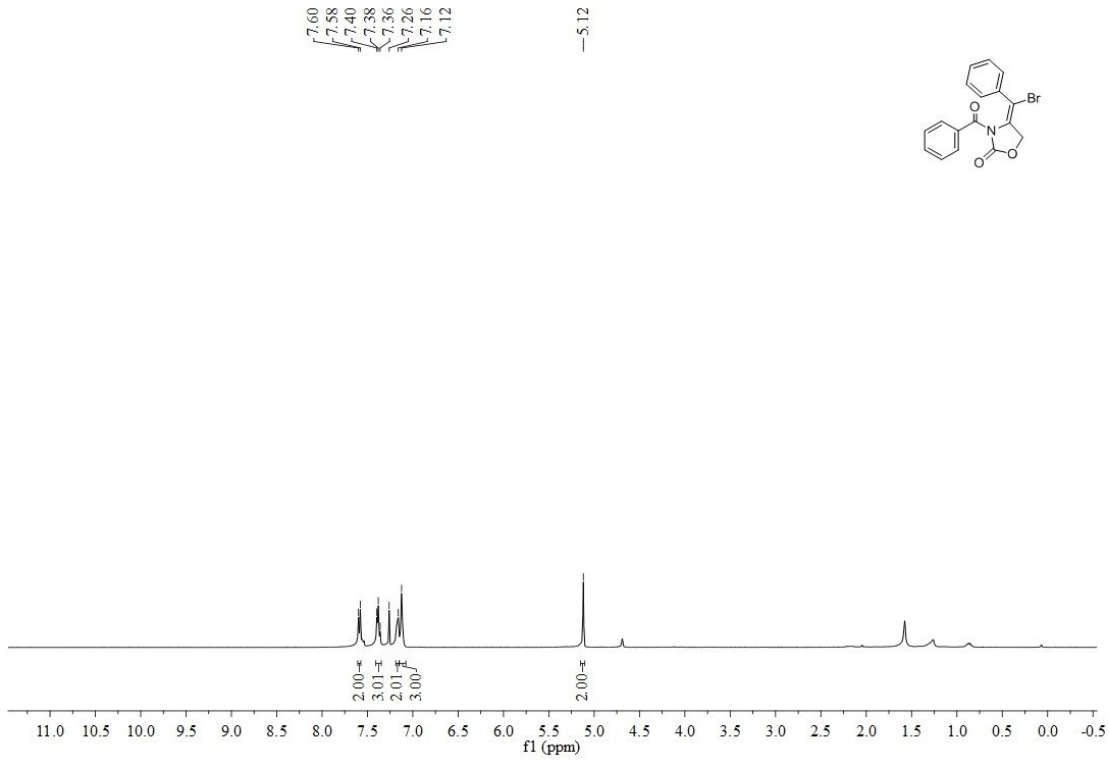
133.45
130.15
128.61
128.43
108.50
77.35
77.03
76.71
73.33
26.76
Br
O
N
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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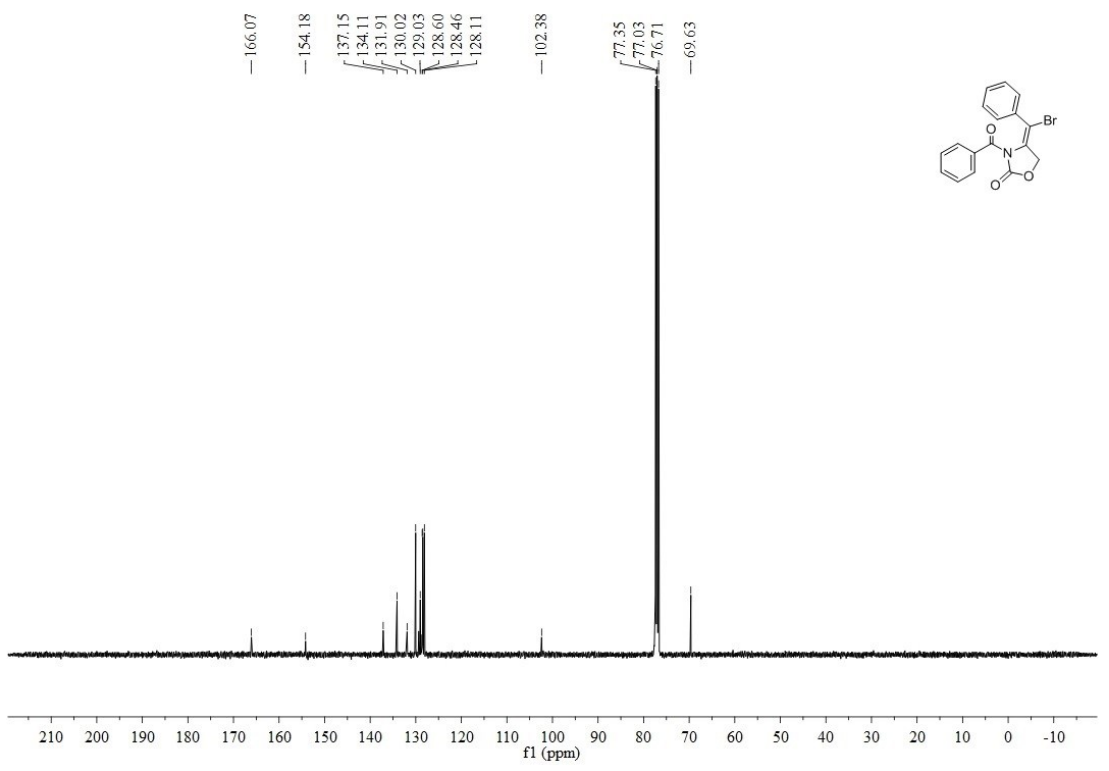
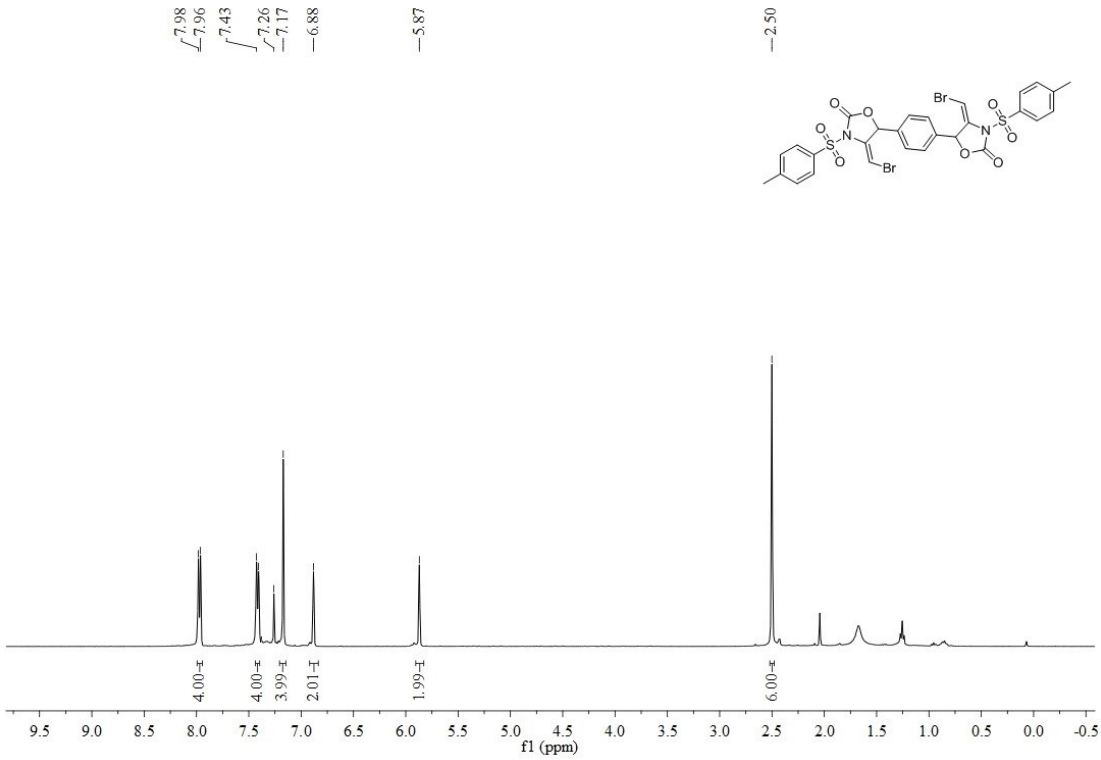
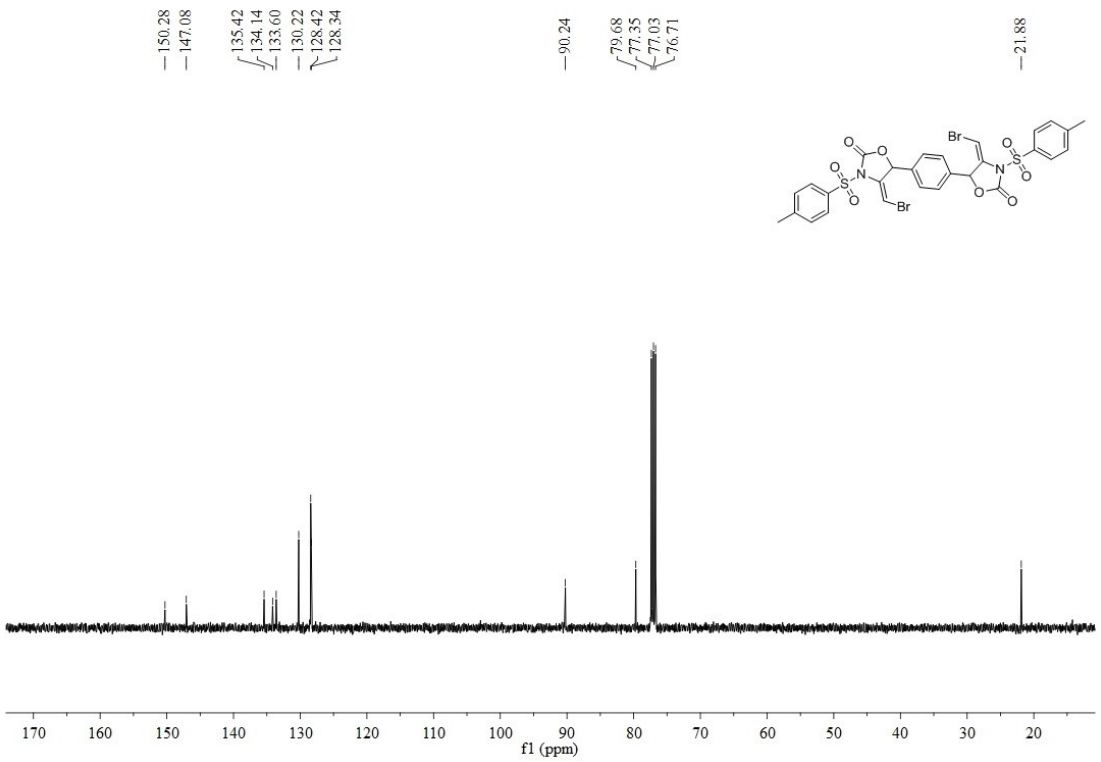
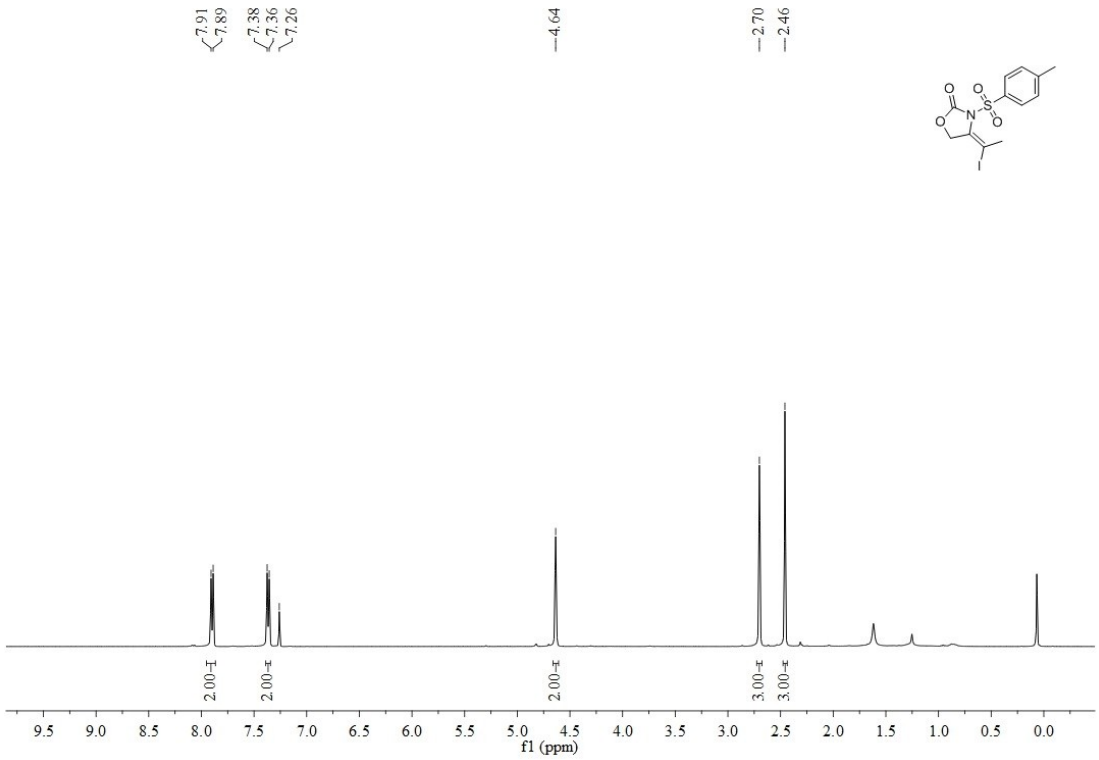
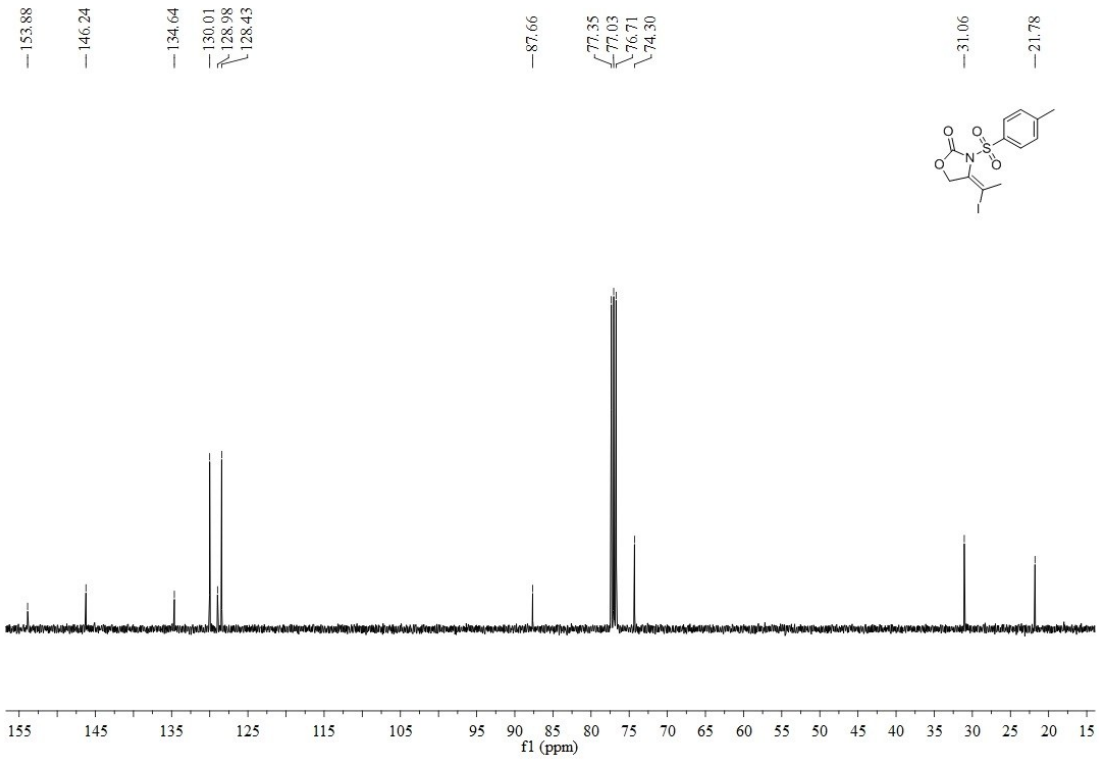
7.40
7.38
7.36
7.26
7.16
7.12
5.12
Br
O
N
O
O
2.00
3.01
2.01
3.00
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

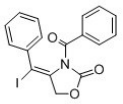

166.07
154.18
137.15
134.11
131.91
130.02
129.03
128.60
128.46
128.11
102.38
77.35
77.03
76.71
69.63
Br
O
N
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

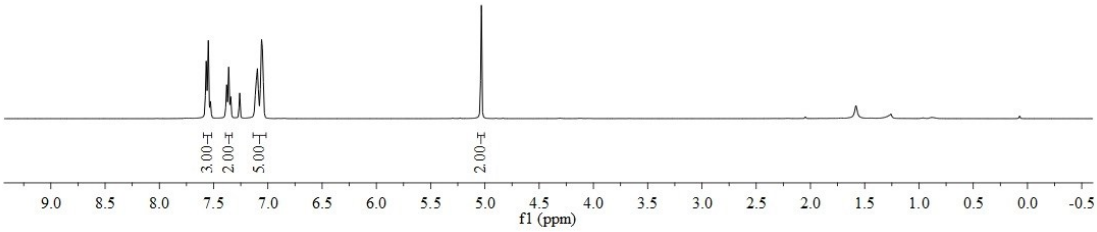

7.98
7.96
7.43
7.26
7.17
6.88
5.87
2.50
Br
Br
4.00
4.00
3.99
2.01
1.99
6.00
f1 (ppm)

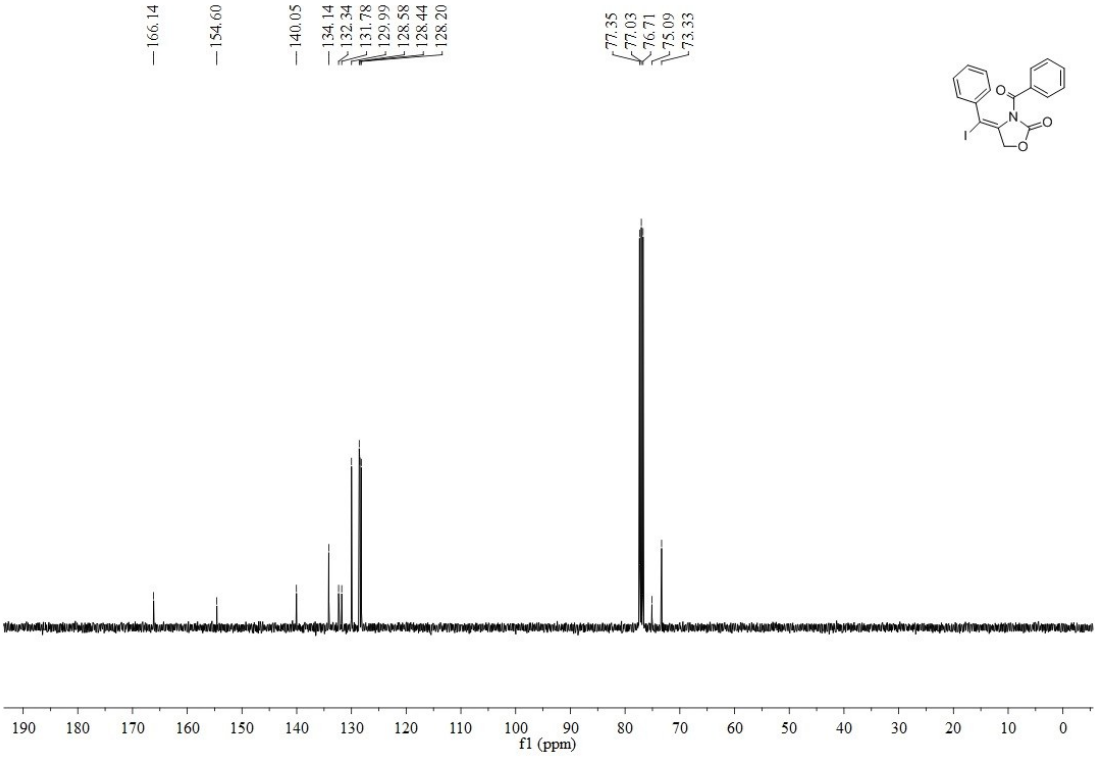

150.28
147.08
135.42
134.14
133.60
130.22
128.42
128.34
90.24
79.68
77.35
77.03
76.71
21.88
Br
Br
f1 (ppm)


7.91
7.89
7.38
7.36
7.26
4.64
2.70
2.46
2.00-H
2.00-H
2.00-H
3.00-H
3.00-H
f1 (ppm)


153.88
146.24
134.64
130.01
128.98
128.43
87.66
77.35
77.03
76.71
74.30
31.06
21.78
f1 (ppm)




3.00
2.00
5.00
2.00
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
f1 (ppm)


166.14
154.60
140.05
134.14
132.34
131.78
129.99
128.58
128.44
128.20
77.35
77.03
76.71
75.09
73.33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5. Crystallographic spectrum for *3a*

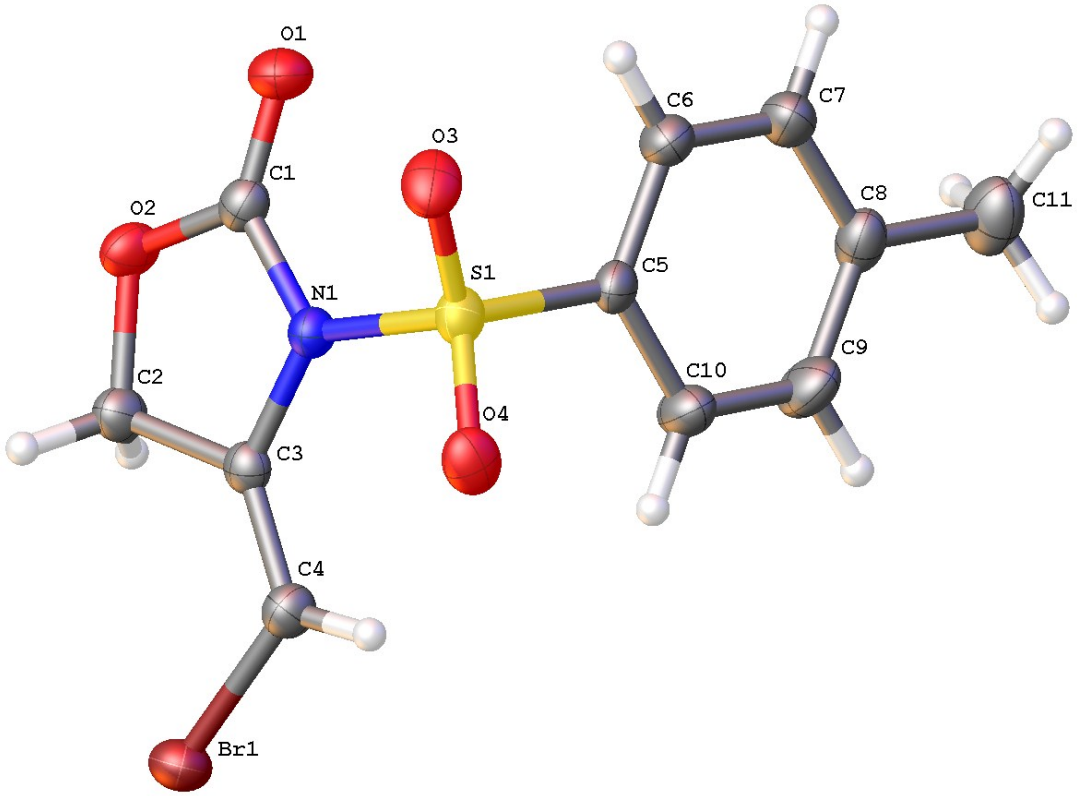


Table 1. Crystal data and structure refinement for mo_dm16821_0m.

Identification code	mo_dm16821_0m	
Empirical formula	C11 H10 Br N O4 S	
Formula weight	332.17	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.1512(10) Å	α= 90°.
	b = 16.7902(19) Å	β= 97.105(2)°.
	c = 9.2892(11) Å	γ = 90°.
Volume	1261.6(3) $Å^3$	
Z	4	
Density (calculated)	1.749 Mg/m^3	
Absorption coefficient	3.429 mm^{-1}	
F(000)	664	
Crystal size	0.22 x 0.2 x 0.15 mm^3	
Theta range for data collection	2.426 to 30.616°.	
Index ranges	-11<=h<=10, -20<=k<=24, -12<=l<=13	

Reflections collected	12685
Independent reflections	3898 [R(int) = 0.0311]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.5063
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3898 / 0 / 164
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.0979
R indices (all data)	R1 = 0.0719, wR2 = 0.1101
Extinction coefficient	n/a
Largest diff. peak and hole	0.443 and -1.175 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_dm16821_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	8094(1)	2379(1)	6832(1)	55(1)
S(1)	2045(1)	3398(1)	6027(1)	41(1)
O(1)	2764(2)	4655(1)	3817(2)	55(1)
O(2)	5355(2)	4215(1)	3827(2)	48(1)
O(3)	704(2)	3510(1)	4912(2)	56(1)
O(4)	2333(3)	2641(1)	6694(2)	52(1)
N(1)	3789(2)	3590(1)	5270(2)	36(1)
C(1)	3858(3)	4204(1)	4254(3)	40(1)
C(2)	6424(3)	3628(2)	4606(3)	45(1)
C(3)	5369(3)	3239(1)	5618(2)	35(1)
C(4)	5862(3)	2700(2)	6621(3)	44(1)
C(5)	2031(3)	4130(2)	7354(3)	39(1)
C(6)	1118(3)	4822(2)	7063(3)	50(1)
C(7)	1139(4)	5396(2)	8111(3)	57(1)
C(8)	2043(4)	5305(2)	9460(3)	51(1)
C(9)	2939(5)	4602(2)	9741(3)	63(1)
C(10)	2942(4)	4016(2)	8700(3)	55(1)
C(11)	2069(5)	5944(2)	10601(4)	72(1)

Table 3. Bond lengths [Å] and angles [°] for mo_dm16821_0m.

Br(1)-C(4)	1.884(3)
S(1)-O(3)	1.422(2)
S(1)-O(4)	1.420(2)
S(1)-N(1)	1.693(2)
S(1)-C(5)	1.742(3)
O(1)-C(1)	1.203(3)
O(2)-C(1)	1.328(3)
O(2)-C(2)	1.448(3)
N(1)-C(1)	1.403(3)
N(1)-C(3)	1.417(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(2)-C(3)	1.501(3)
C(3)-C(4)	1.325(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.388(4)
C(5)-C(10)	1.386(4)
C(6)-H(6)	0.9300
C(6)-C(7)	1.369(4)
C(7)-H(7)	0.9300
C(7)-C(8)	1.382(4)
C(8)-C(9)	1.395(4)
C(8)-C(11)	1.507(4)
C(9)-H(9)	0.9300
C(9)-C(10)	1.379(4)
C(10)-H(10)	0.9300
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600

O(3)-S(1)-N(1)	106.34(11)
O(3)-S(1)-C(5)	110.47(12)
O(4)-S(1)-O(3)	120.52(13)
O(4)-S(1)-N(1)	104.45(11)
O(4)-S(1)-C(5)	109.73(12)
N(1)-S(1)-C(5)	103.79(11)

C(1)-O(2)-C(2)	111.04(19)
C(1)-N(1)-S(1)	121.66(17)
C(1)-N(1)-C(3)	110.35(19)
C(3)-N(1)-S(1)	127.76(16)
O(1)-C(1)-O(2)	124.1(2)
O(1)-C(1)-N(1)	126.9(2)
O(2)-C(1)-N(1)	109.1(2)
O(2)-C(2)-H(2A)	110.8
O(2)-C(2)-H(2B)	110.8
O(2)-C(2)-C(3)	104.7(2)
H(2A)-C(2)-H(2B)	108.9
C(3)-C(2)-H(2A)	110.8
C(3)-C(2)-H(2B)	110.8
N(1)-C(3)-C(2)	104.52(19)
C(4)-C(3)-N(1)	129.2(2)
C(4)-C(3)-C(2)	126.2(2)
Br(1)-C(4)-H(4)	120.9
C(3)-C(4)-Br(1)	118.2(2)
C(3)-C(4)-H(4)	120.9
C(6)-C(5)-S(1)	120.2(2)
C(10)-C(5)-S(1)	119.4(2)
C(10)-C(5)-C(6)	120.4(2)
C(5)-C(6)-H(6)	120.3
C(7)-C(6)-C(5)	119.5(3)
C(7)-C(6)-H(6)	120.3
C(6)-C(7)-H(7)	119.2
C(6)-C(7)-C(8)	121.6(3)
C(8)-C(7)-H(7)	119.2
C(7)-C(8)-C(9)	118.2(3)
C(7)-C(8)-C(11)	121.2(3)
C(9)-C(8)-C(11)	120.6(3)
C(8)-C(9)-H(9)	119.4
C(10)-C(9)-C(8)	121.2(3)
C(10)-C(9)-H(9)	119.4
C(5)-C(10)-H(10)	120.4
C(9)-C(10)-C(5)	119.1(3)
C(9)-C(10)-H(10)	120.4
C(8)-C(11)-H(11A)	109.5

C(8)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_dm16821_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	54(1)	54(1)	56(1)	6(1)	4(1)	16(1)
S(1)	37(1)	47(1)	39(1)	-2(1)	10(1)	-4(1)
O(1)	56(1)	57(1)	53(1)	11(1)	2(1)	13(1)
O(2)	46(1)	52(1)	48(1)	14(1)	10(1)	-2(1)
O(3)	38(1)	80(1)	49(1)	-7(1)	1(1)	-5(1)
O(4)	53(1)	45(1)	63(1)	2(1)	21(1)	-9(1)
N(1)	35(1)	40(1)	34(1)	2(1)	8(1)	1(1)
C(1)	46(1)	38(1)	35(1)	0(1)	7(1)	-2(1)
C(2)	42(1)	46(1)	48(1)	6(1)	11(1)	2(1)
C(3)	38(1)	32(1)	34(1)	-4(1)	6(1)	-1(1)
C(4)	46(1)	45(1)	41(1)	5(1)	9(1)	0(1)
C(5)	40(1)	49(1)	32(1)	3(1)	12(1)	4(1)
C(6)	56(2)	57(2)	38(1)	6(1)	5(1)	13(1)
C(7)	73(2)	51(2)	48(2)	5(1)	14(1)	18(1)
C(8)	68(2)	47(2)	40(1)	-1(1)	18(1)	-3(1)
C(9)	88(2)	65(2)	35(1)	1(1)	-2(1)	7(2)
C(10)	72(2)	52(2)	39(1)	3(1)	2(1)	16(1)
C(11)	106(3)	56(2)	57(2)	-10(2)	23(2)	-6(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for mo_dm16821_0m.

	x	y	z	U(eq)
H(2A)	7381	3881	5142	53
H(2B)	6798	3242	3942	53
H(4)	5125	2485	7205	52
H(6)	497	4894	6164	60
H(7)	529	5860	7909	68
H(9)	3546	4528	10646	76
H(10)	3547	3551	8899	66
H(11A)	2854	6348	10423	108
H(11B)	2381	5715	11542	108
H(11C)	990	6178	10566	108