Supporting Information

Highly Selective Catalyst- and Additive-Free Iodosulfonylation of Cyclopropenes in Water

Chuxiong Peng,[a]† Fengyan Gu,[a]† Xiaofeng Lin,[a] Ning Ding,[a] Qichen Zhan,[a] Peng Cao*[a,b,c,d] and Tao Cao*[a]

[a] School of Pharmacy, Nanjing University of Chinese Medicine, Nanjing 210023, P. R. China.

[b] Affiliated Hospital of Integrated Traditional Chinese and Western Medicine, Nanjing University of Chinese Medicine, Nanjing 210028, P. R. China.

[c] Zhenjiang Hospital of Chinese Traditional and Western Medicine, Zhenjiang 212002, P. R. China.

[d] Gaoyou Hospital of Traditional Chinese Medicine, Yangzhou 225600, P. R. China

E-mail: caot@njucm.edu.cn, cao_peng@njucm.edu.cn

† These authors contributed equally to this work.

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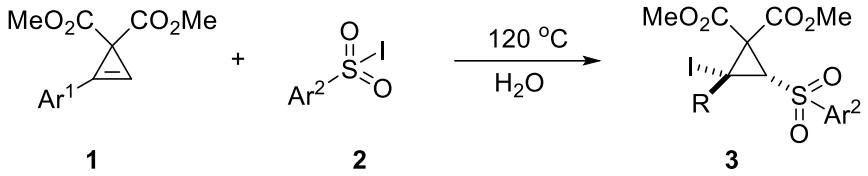
General Information: All the temperatures are referred to the preheated oil baths used. The reaction under microwave conditions was performed on a microwave reactor (Discover 2.0, CEM Corporation, USA). Commercially available reagents and solvents were purchased from Adamas, Sinopharm, and Sigma-Aldrich. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer in $CDCl_3$ (δ 7.26 ppm) or DMSO-d_6 (δ 2.50 ppm). The data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets), coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer and data are reported in terms of chemical shift relative to $CDCl_3$ (77.10 ppm) or DMSO-d_6 (δ 39.60 ppm).

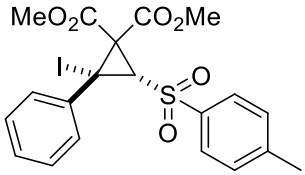
1. Iodosulfonylation of cyclopropenes.



1 **2** **3**

General Procedure I: To a 10 mL reaction tube equipped with a stirring bar was added **1** (1.0 equiv), **2** (1.2 equiv), and H_2O (*c* = 0.1 mol/L for **1**) successively, and the tube was sealed with a septum. The mixture was heated at 120 °C for indicated time. After the reaction was complete, the mixture was filtered and triturated with a mixture of ethyl acetate and petroleum ether to afford corresponding product.

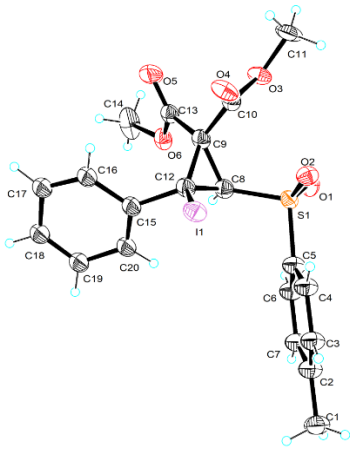
(1) Dimethyl (2*R,3*S**)-2-iodo-2-phenyl-3-tosylcyclopropane-1,1-dicarboxylate (3a) (pcx-2-41, pcx-7-38, pcx-9-11).**



3a

Following General Procedure I, after being stirred for 2 h, **3a** was afforded as a white solid (0.2 mmol scale, 85.6 mg, 83%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 172.0 °C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2 H), 7.43 (d, *J* = 8.1 Hz, 2 H), 7.22 (t, *J* = 7.5 Hz, 2 H), 7.14 (t, *J* = 7.4 Hz, 1 H), 7.07 (d, *J* = 7.6 Hz, 2 H), 3.97 (s, 3 H), 3.73 (s, 1 H), 3.51 (s, 3 H), 2.50 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.19, 162.20, 145.59, 143.06, 136.87, 130.08, 128.81, 128.71, 128.63, 126.85, 53.86, 53.52, 51.31, 44.87, 21.84, 6.94; HRMS calcd for $C_{20}H_{19}INaO_6S$ ($[M+Na]^+$): 536.9839; found: 536.9840.

Crystal data and structure refinement of 3a:



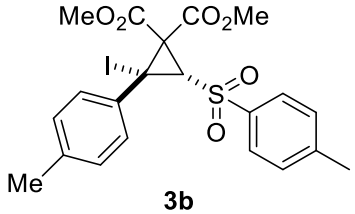
Bond precision:	C-C = 0.0474 A	Wavelength=1.54184	
Cell:	a=6.8727(9)	b=7.4757(10)	c=10.7012(13)
	alpha=75.161(12)	beta=88.164(11)	gamma=77.878(12)
Temperature:	293 K		
	Calculated	Reported	
Volume	519.48(12)	519.48(12)	
Space group	P 1	P 1	
Hall group	P 1	P 1	
Moiety formula	C20 H19 I O6	C20 H19 I O6	
Sum formula	C20 H19 I O6	C20 H19 I O6	
Mr	514.31	514.31	
Dx,g cm-3	1.644	1.644	
Z	1	1	
Mu (mm-1)	13.341	13.341	
F000	256.0	256.0	
F000’	256.76		
h,k,lmax	7,8,12	7,8,12	
Nref	3416[1708]	1979	
Tmin,Tmax	0.472,0.586	0.338,1.000	
Tmin’	0.428		

Correction method= # Reported T Limits: Tmin=0.338 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.16/0.58	Theta(max)= 63.656
R(reflections)= 0.0875(1636)	wR2(reflections)= 0.2652(1979)
S = 1.056	Npar= 257

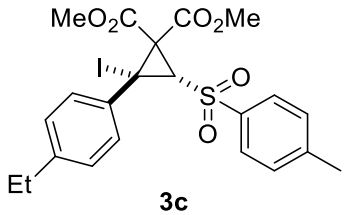
(2) Dimethyl (2*R,3*S**)-2-iodo-2-(*p*-tolyl)-3-tosylcyclopropane-1,1-dicarboxylate (3b) (pcx-2-45, pcx-11-3).**



3b

Following General Procedure I, after being stirred for 10 h, **3b** was afforded as a white solid (0.2 mmol scale, 81.5 mg, 77%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 193.7-194.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.02 (d, *J* = 7.9 Hz, 2 H), 6.96 (d, *J* = 7.9 Hz, 2 H), 3.96 (s, 3 H), 3.70 (s, 1 H), 3.53 (s, 3 H), 2.49 (s, 3 H), 2.28 (s, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.01, 161.75, 145.39, 140.28, 137.72, 136.62, 130.01, 129.23, 128.51, 126.71, 53.93, 53.16, 50.08, 44.32, 21.27, 20.67, 5.99; HRMS calcd for $C_{21}H_{21}INaO_6S$ ($[M+Na]^+$): 550.9996; found: 550.9996.

(3) Dimethyl (2*R,3*S**)-2-(4-ethylphenyl)-2-iodo-3-tosylcyclopropane-1,1-dicarboxylate (3c) (pcx-4-49, pcx-11-37).**

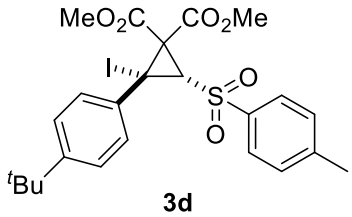


3c

Following General Procedure I, after being stirred for 2.5 h, **3c** was afforded as a white solid (0.1 mmol scale, 37.9 mg, 70%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 161.8 °C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.97 (d, *J* = 7.8 Hz, 2 H), 3.96 (s, 3 H), 3.71 (s, 1 H), 3.52 (s, 3 H), 2.57 (q, *J* = 7.6 Hz, 2 H), 2.49 (s, 3 H), 1.16 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.27, 162.30, 145.55, 144.85, 140.38, 137.00, 130.07, 128.76, 128.28, 126.81, 53.84, 53.51,

51.41, 45.00, 28.47, 21.85, 15.18, 7.04; HRMS calcd for $C_{22}H_{23}INaO_6S$ ($[M+Na]^+$): 565.0152; found: 565.0158.

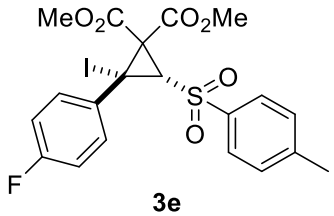
(4) Dimethyl (2*R,3*S**)-2-(4-(*tert*-butyl)phenyl)-2-iodo-3-tosylcyclopropane-1,1-dicarboxylate (3d) (pcx-4-48, pcx-11-4).**



3d

Following General Procedure I, after being stirred for 2 h, **3d** was afforded as a white solid (0.2 mmol scale, 65.4 mg, 57%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 179.4-181.0 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 3.97 (s, 3 H), 3.71 (s, 1 H), 3.50 (s, 3 H), 2.50 (s, 3 H), 1.23 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.23, 162.30, 151.77, 145.55, 140.02, 136.96, 130.07, 128.78, 126.54, 125.72, 53.77, 53.52, 51.31, 44.90, 34.65, 31.25, 21.86, 7.05; HRMS calcd for $C_{24}H_{27}INaO_6S$ ($[M+Na]^+$): 593.0465; found: 593.0464.

(5) Dimethyl (2*R,3*S**)-2-(4-fluorophenyl)-2-iodo-3-tosylcyclopropane-1,1-dicarboxylate (3e) (pcx-3-48).**

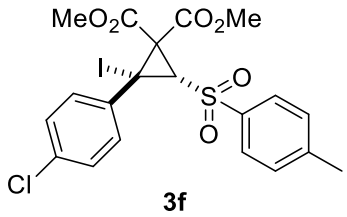


3e

Following General Procedure I, after being stirred for 2 h, **3e** was afforded as a white solid (0.2 mmol scale, 76.1 mg, 71% yield) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 166.4-168.0 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.7 Hz, 2 H), 7.43 (d, *J* = 8.2 Hz, 2 H), 7.10-7.04 (m, 2 H), 6.92 (t, *J* = 8.7 Hz, 2 H), 3.97 (s, 3 H), 3.68 (s, 1 H), 3.54 (s, 3 H), 2.50 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.19 (d, *J* = 6.8 Hz), 162.08, 161.23, 145.71, 139.18 (d, *J* = 3.4 Hz), 136.84, 130.14, 128.84 (d, *J* = 8.5 Hz), 128.69, 115.93 (d, *J* = 22.2 Hz), 53.99, 53.58, 51.45,

44.99, 21.86, 5.66; ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.78; HRMS calcd for $C_{20}H_{18}FINaO_6S$ ([M+Na]$^+$): 554.9745; found: 554.9747.

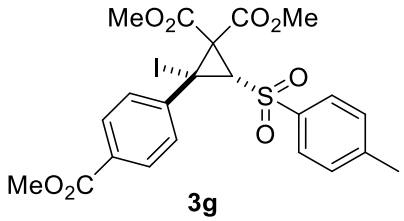
(6) Dimethyl (2*R,3*S**)-2-(4-chlorophenyl)-2-iodo-3-tosylcyclopropane-1,1-dicarboxylate (3f) (pcx-2-47).**



3f

Following General Procedure I, after being stirred for 3.5 h, **3f** was afforded as a white solid (0.2 mmol scale, 76.8 mg, 70%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 181.7 °C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2 H), 7.43 (d, *J* = 8.1 Hz, 2 H), 7.20 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.2 Hz, 2 H), 3.97 (s, 3 H), 3.66 (s, 1 H), 3.55 (s, 3 H), 2.50 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.14, 162.02, 145.74, 141.66, 136.81, 134.51, 130.14, 129.10, 128.69, 128.29, 54.05, 53.59, 51.33, 44.90, 21.86, 5.70; HRMS calcd for $C_{20}H_{18}{}^{35}ClINaO_6S$ ([M+Na]$^+$): 570.9450; found: 570.9451.

(7) Dimethyl (2*R,3*S**)-2-iodo-2-(4-(methoxycarbonyl)phenyl)-3-tosylcyclopropane-1,1-dicarboxylate (3g) (pcx-2-48).**

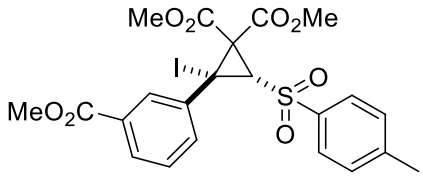


3g

Following General Procedure I, after being stirred for 2 h, **3g** was afforded as a white solid (0.2 mmol scale, 91.8 mg, 80%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 190.7-191.9 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.07 (d, *J* = 7.9 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 7.9 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 4.14 (s, 1 H), 3.83 (s, 6 H), 3.43 (s, 3 H), 2.45 (s, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.50, 163.03, 161.62, 147.85, 145.49, 136.53, 130.03, 129.66,

129.23, 128.52, 127.35, 54.07, 53.25, 52.34, 49.84, 44.14, 21.28, 5.43; HRMS calcd for $C_{22}H_{21}INaO_8S$ ($[M+Na]^+$): 594.9894; found: 594.9896.

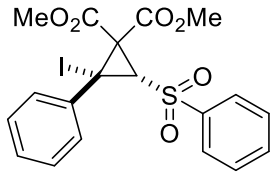
(8) Dimethyl (2*R,3*S**)-2-iodo-2-(3-(methoxycarbonyl)phenyl)-3-tosylcyclopropane-1,1-dicarboxylate (3h) (pcx-6-25, pcx-11-7).**



3h

Following General Procedure I, after being stirred for 2 h, **3h** was afforded as a white solid (0.2 mmol scale, 97.8 mg, 85%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 173.2-175.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2 H), 7.83 (d, *J* = 7.6 Hz, 1 H), 7.70 (s, 1 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.32 (t, *J* = 7.7 Hz, 1 H), 7.28 (s, 1 H), 3.98 (s, 3 H), 3.89 (s, 3 H), 3.71 (s, 1 H), 3.55 (s, 3 H), 2.50 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.02, 163.25, 162.08, 145.74, 143.66, 136.83, 131.46, 130.89, 130.14, 129.74, 129.11, 128.75, 127.79, 54.02, 53.61, 52.35, 51.31, 44.84, 21.87, 6.07; HRMS calcd for $C_{22}H_{21}INaO_8S$ ($[M+Na]^+$): 594.9894; found: 594.9899.

(9) Dimethyl (2*R,3*S**)-2-iodo-2-phenyl-3-(phenylsulfonyl)cyclopropane-1,1-dicarboxylate (3j) (pcx-2-42, pcx-11-17).**

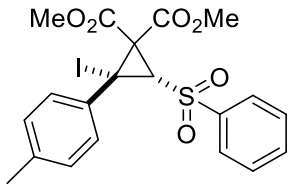


3j

Following General Procedure I, after being stirred for 3 h, **3j** was afforded as a white solid (0.2 mmol scale, 81.1 mg, 81%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 166.5 °C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.1 Hz, 2 H), 7.75 (t, *J* = 7.5 Hz, 1 H), 7.65 (t, *J* = 7.8 Hz, 2 H), 7.22 (t, *J* = 7.8 Hz, 2 H), 7.15 (t, *J* = 7.4 Hz, 1 H), 7.06 (d, *J* = 6.6 Hz, 2 H), 3.98 (s, 3 H), 3.74 (s, 1 H), 3.52 (s, 3 H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.13, 162.15, 142.99,

139.81, 134.48, 129.48, 128.83, 128.67, 128.66, 126.82, 53.90, 53.56, 51.30, 45.00, 6.81; HRMS calcd for $C_{19}H_{17}INaO_6S$ ($[M+Na]^+$): 522.9683; found: 522.9684.

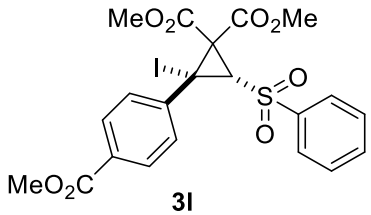
(10) Dimethyl (2*R,3*S**)-2-iodo-3-(phenylsulfonyl)-2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate (3k) (pcx-2-49, pcx-11-16).**



3k

Following General Procedure I, after being stirred for 2 h, **3k** was afforded as a white solid (0.2 mmol scale, 80.4 mg, 78%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 180.1 °C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 7.7 Hz, 2 H), 7.74 (t, J = 7.5 Hz, 1 H), 7.65 (t, J = 7.7 Hz, 2 H), 7.02 (d, J = 7.8 Hz, 2 H), 6.95 (d, J = 7.8 Hz, 2 H), 3.97 (s, 3 H), 3.71 (s, 1 H), 3.54 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.19, 162.22, 140.14, 139.86, 138.68, 134.43, 129.53, 129.45, 128.66, 126.68, 53.91, 53.53, 51.37, 45.07, 21.20, 6.79; HRMS calcd for $C_{20}H_{19}INaO_6S$ ($[M+Na]^+$): 536.9839; found: 536.9839.

(11) Dimethyl (2*R,3*S**)-2-iodo-2-(4-(methoxycarbonyl)phenyl)-3-(phenylsulfonyl)cyclopropane-1,1-dicarboxylate (3l) (pcx-3-9).**

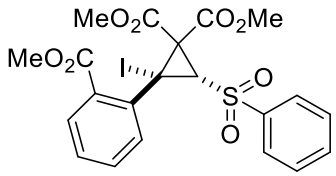


3l

Following General Procedure I, after being stirred for 4.5 h, **3l** was afforded as a white solid (0.2 mmol scale, 100.8 mg, 90%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 179.0-180.8 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.21 (d, *J* = 7.1 Hz, 2 H), 7.87 (d, *J* = 8.5 Hz, 2 H), 7.84 (d, *J* = 7.4 Hz, 1 H), 7.75 (t, *J* = 7.9 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 4.21 (s, 1 H), 3.83 (d, *J* = 5.6 Hz, 6 H), 3.43 (s, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.51, 163.00, 161.62, 147.80, 139.35,

134.79, 129.66, 129.60, 129.26, 128.49, 127.36, 54.11, 53.30, 52.35, 49.74, 44.22, 5.36; HRMS calcd for $C_{21}H_{19}INaO_8S$ ($[M+Na]^+$): 580.9738; found: 580.9740.

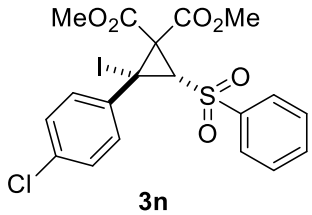
(12) Dimethyl (2*R,3*S**)-2-iodo-2-(2-(methoxycarbonyl)phenyl)-3-(phenylsulfonyl)cyclopropane-1,1-dicarboxylate (3m) (pcx-5-33).**



3m

Following General Procedure I, after being stirred for 2 h, **3m** was afforded as a white solid (0.2 mmol scale, 70.7 mg, 63%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 162.5-164.2 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 2 H), 7.89 (d, *J* = 7.8 Hz, 1 H), 7.77 (t, *J* = 7.5 Hz, 1 H), 7.67 (t, *J* = 7.6 Hz, 2 H), 7.39 (t, *J* = 7.6 Hz, 1 H), 7.27 (t, *J* = 7.4 Hz, 1 H), 7.00 (d, *J* = 7.8 Hz, 1 H), 3.98 (d, *J* = 4.5 Hz, 6 H), 3.71 (s, 1 H), 3.56 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.65, 164.06, 162.07, 142.95, 139.85, 134.54, 132.90, 131.79, 129.52, 129.33, 128.84, 128.68, 128.22, 54.05, 53.97, 53.28, 52.63, 44.79, 7.36; HRMS calcd for $C_{21}H_{19}INaO_8S$ ($[M+Na]^+$): 580.9738; found: 580.9741.

(13) Dimethyl (2*R,3*S**)-2-(4-chlorophenyl)-2-iodo-3-(phenylsulfonyl)cyclopropane-1,1-dicarboxylate (3n) (pcx-3-47, pcx-11-9).**

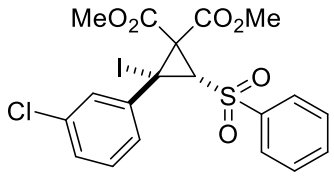


3n

Following General Procedure I, after being stirred for 2 h, **3n** was afforded as a white solid (0.2 mmol scale, 96.6 mg, 90%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 168.5-170.4 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.0 Hz, 2 H), 7.75 (t, *J* = 7.4 Hz, 1 H), 7.65 (t, *J* = 7.7 Hz, 2 H), 7.20 (d, *J* = 8.3 Hz, 2 H), 7.01 (d, *J* = 8.1 Hz, 2 H), 3.98 (s, 3 H), 3.68 (s, 1 H), 3.56 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.07, 161.98, 141.57, 139.72, 134.58, 134.55, 129.54,

129.12, 128.64, 128.25, 54.09, 53.63, 51.30, 45.01, 5.56; HRMS calcd for $C_{19}H_{16}{}^{35}ClINaO_6S$ ($[M+Na]^+$): 556.9293; found:556.9294.

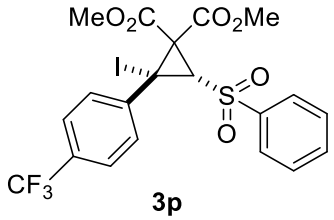
(14) Dimethyl (2*R,3*S**)-2-(3-chlorophenyl)-2-iodo-3-(phenylsulfonyl)cyclopropane-1,1-dicarboxylate (3o) (pcx-4-2, pcx-11-10).**



3o

Following General Procedure I, after being stirred for 2 h, **3o** was afforded as a white solid (0.2 mmol scale, 101.8 mg, 95%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 178.8-180.0 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19-8.15 (m, 2 H), 7.76 (t, *J* = 7.5 Hz, 1 H), 7.66 (t, *J* = 7.8 Hz, 2 H), 7.17 (t, *J* = 7.8 Hz, 1 H), 7.14-7.10 (m, 1 H), 7.04 (s, 1 H), 6.96 (d, *J* = 7.6 Hz, 1 H), 3.98 (s, 3 H), 3.69 (s, 1 H), 3.57 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.06, 161.93, 144.76, 139.68, 134.61, 134.39, 130.15, 129.55, 128.93, 128.64, 127.09, 125.05, 54.09, 53.65, 51.23, 44.96, 5.28; HRMS calcd for $C_{19}H_{16}{}^{35}ClINaO_6S$ ($[M+Na]^+$): 556.9293; found: 556.9290.

(15) Dimethyl (2*R,3*S**)-2-iodo-3-(phenylsulfonyl)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate (3p) (pcx-3-46).**

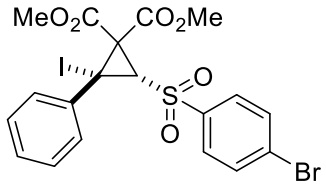


3p

Following General Procedure I, after being stirred for 2.5 h, **3p** was afforded as a white solid (0.2 mmol scale, 104.7 mg, 92%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 148.4 ^oC (decomposition); ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.1 Hz, 2 H), 7.76 (t, *J* = 7.5 Hz, 1 H), 7.66 (t, *J* = 7.8 Hz, 2 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 3.99 (s, 3 H), 3.71 (s, 1 H), 3.56 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.09, 161.91, 146.65, 139.65, 134.68, 130.68

(q, *J* = 32.7 Hz), 129.60, 128.68, 127.35, 125.96 (q, *J* = 3.7 Hz), 123.53 (q, *J* = 272.5 Hz), 54.17, 53.71, 51.20, 44.84, 5.65; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.79; HRMS calcd for $C_{20}H_{16}F_3INaO_6S$ ($[M+Na]^+$): 590.9557; found: 590.9559.

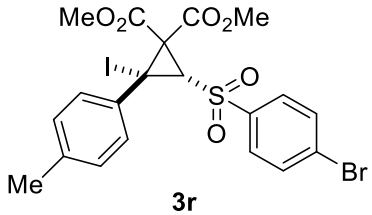
(16) Dimethyl (2*R,3*S**)-3-((4-bromophenyl)sulfonyl)-2-iodo-2-phenylcyclopropane-1,1-dicarboxylate (3q) (pcx-2-43).**



3q

Following General Procedure I, after being stirred overnight, **3q** was afforded as a white solid (0.2 mmol scale, 115.1 mg, 99%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 165.5-167.3 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 2 H), 7.78 (d, *J* = 8.6 Hz, 2 H), 7.24 (t, *J* = 8.6 Hz, 2 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 7.09 (d, *J* = 7.0 Hz, 2 H), 3.97 (s, 3 H), 3.73 (s, 1 H), 3.52 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.03, 162.06, 142.82, 138.78, 132.85, 130.23, 130.02, 128.92, 128.80, 126.82, 54.00, 53.62, 51.33, 45.20, 6.45; HRMS calcd for $C_{19}H_{16}{}^{79}BrINaO_6S$ ($[M+Na]^+$): 600.8788; found: 600.8790.

(17) Dimethyl (2*R,3*S**)-3-((4-bromophenyl)sulfonyl)-2-iodo-2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate (3r) (pcx-2-50).**

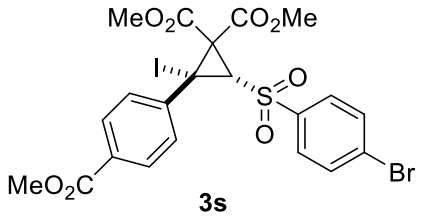


3r

Following General Procedure I, after being stirred for 4 h, **3r** was afforded as a white solid (0.2 mmol scale, 103.6 mg, 87%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 199.1-200.7 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2 H), 7.78 (d, *J* = 8.3 Hz, 2 H), 7.04 (d, *J* = 7.9 Hz, 2 H), 6.98 (d, *J* = 7.8 Hz, 2 H), 3.97 (s, 3 H), 3.70 (s, 1 H), 3.54 (s, 3 H), 2.29 (s, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.86, 161.68, 140.06, 138.62, 137.78, 132.66, 130.54, 129.21,

129.03, 126.79, 53.96, 53.24, 49.77, 44.50, 20.67, 5.75; HRMS calcd for $C_{20}H_{18}{}^{79}BrINaO_6S$ ([M+Na]$^+$): 614.8944; found: 614.8944.

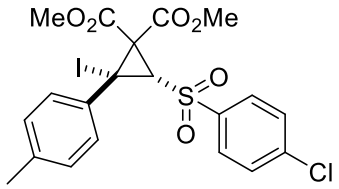
(18) Dimethyl (2*R,3*S**)-3-((4-bromophenyl)sulfonyl)-2-iodo-2-(4-(methoxycarbonyl)phenyl)cyclopropane-1,1-dicarboxylate (3s) (pcx-3-10).**



3s

Following General Procedure I, after being stirred for 3.5 h, **3s** was afforded as a white solid (0.2 mmol scale, 111.3 mg, 87%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 202.4-204.2 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2 H), 7.92 (d, *J* = 8.0 Hz, 2 H), 7.79 (d, *J* = 8.2 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 3.98 (s, 3 H), 3.88 (s, 3 H), 3.70 (s, 1 H), 3.54 (s, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.53, 162.91, 161.58, 147.67, 138.54, 132.71, 130.56, 129.66, 129.28, 129.15, 127.45, 54.13, 53.35, 52.37, 49.53, 44.31, 5.20; HRMS calcd for $C_{21}H_{18}{}^{79}BrINaO_8S$ ([M+Na]$^+$): 658.8843; found: 658.8843.

(19) Dimethyl (2*R,3*S**)-3-((4-chlorophenyl)sulfonyl)-2-iodo-2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate (3t) (pcx-3-2).**

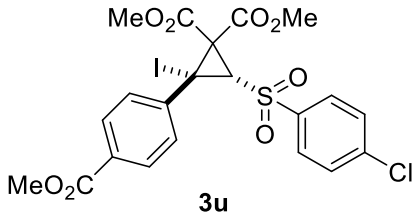


3t

Following General Procedure I, after being stirred for 2 h, **3t** was afforded as a white solid (0.2 mmol scale, 89.0 mg, 81%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 195.5 ^{o}C (decomposition); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 (d, *J* = 8.7 Hz, 2 H), 7.83 (d, *J* = 8.6 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 6.98 (d, *J* = 8.2 Hz, 2 H), 4.19 (s, 1 H), 3.81 (s, 3 H), 3.44 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.87, 161.69, 140.07, 139.83, 138.20, 137.78,

130.55, 129.72, 129.22, 126.79, 53.97, 53.25, 49.81, 44.51, 20.68, 5.80; HRMS calcd for $C_{20}H_{18}{}^{35}ClINaO_6S$ ($[M+Na]^+$): 570.9450; found: 570.9447.

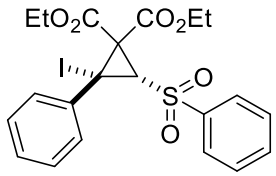
(20) Dimethyl (2*R,3*S**)-3-((4-chlorophenyl)sulfonyl)-2-iodo-2-(4-(methoxycarbonyl)phenyl)cyclopropane-1,1-dicarboxylate (3u) (pcx-3-11).**



3u

Following General Procedure I, after being stirred for 2 h, **3u** was afforded as a white solid (0.2 mmol scale, 115.4 mg, 97%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 185.4-186.5 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.23 (d, *J* = 8.7 Hz, 2 H), 7.89 (d, *J* = 8.5 Hz, 2 H), 7.84 (d, *J* = 8.7 Hz, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 4.36 (s, 1 H), 3.83 (s, 6 H), 3.43 (s, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.53, 162.91, 161.59, 147.67, 139.92, 138.11, 130.57, 129.76, 129.66, 129.28, 127.44, 54.13, 53.35, 52.37, 49.57, 44.31, 5.24; HRMS calcd for $C_{21}H_{18}{}^{35}ClINaO_8S$ ($[M+Na]^+$): 614.9348; found: 614.9352.

(21) Diethyl (2*R,3*S**)-2-iodo-2-phenyl-3-(phenylsulfonyl)cyclopropane-1,1-dicarboxylate (3v) (pcx-5-42).**

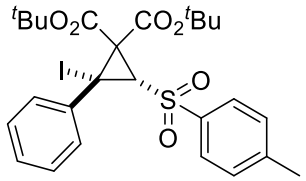


3v

Following General Procedure I, after being stirred for 2 h, **3v** was afforded as a white solid (0.2 mmol scale, 80.4 mg, 76%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 126.8-128.0 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.7 Hz, 2 H), 7.74 (t, *J* = 7.5 Hz, 1 H), 7.65 (t, *J* = 7.7 Hz, 2 H), 7.21 (t, *J* = 7.6 Hz, 2 H), 7.14 (t, *J* = 7.2 Hz, 1 H), 7.07 (d, *J* = 7.6 Hz, 2 H), 4.55-4.38 (m, 2 H), 4.04-3.90 (m, 2 H), 3.73 (s, 1 H), 1.42 (t, *J* = 7.1 Hz, 3 H), 1.05 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.73, 161.74, 143.14, 140.05, 134.40, 129.45, 128.77,

128.69, 128.62, 127.02, 63.26, 62.96, 51.27, 45.00, 13.93, 13.80, 7.01; HRMS calcd for $C_{21}H_{21}INaO_6S$ ([M+Na]$^+$): 550.9996; found: 550.9997.

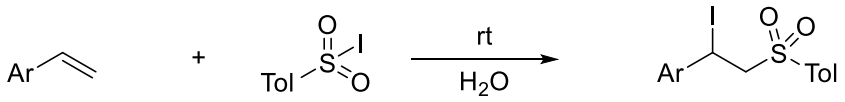
(22) Di-*tert*-butyl (2*R,3*S**)-2-iodo-2-phenyl-3-tosylcyclopropane-1,1-dicarboxylate (3w) (pcx-3-32).**



3w

Following General Procedure I, after being stirred for 2.5 h, **3w** was afforded as a white solid (0.15 mmol scale, 67.5 mg, 75%) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 160.7-161.9 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2 H), 7.42 (d, *J* = 8.1 Hz, 2 H), 7.19 (t, *J* = 7.5 Hz, 2 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 7.05 (d, *J* = 7.5 Hz, 2 H), 3.62 (s, 1 H), 2.49 (s, 3 H), 1.63 (s, 9 H), 1.28 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.64, 160.58, 145.25, 143.28, 137.52, 130.00, 128.61, 128.57, 128.41, 127.35, 84.29, 83.91, 50.99, 45.98, 27.90, 27.73, 21.85, 7.77; HRMS calcd for $C_{26}H_{31}INaO_6S$ ([M+Na]$^+$): 621.0778; found: 621.0778.

2. Iodosulfonylation of styrenes.

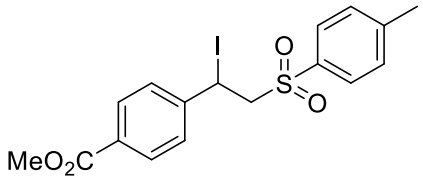


4 **2a** **6**

General Procedure II: To a 10 mL reaction tube equipped with a stirring bar was added **4** (1.0 equiv), **2a** (1.2 equiv), and H_2O (*c* = 0.1 mol/L for **4**) successively, and the tube was sealed with a septum. The mixture was stirred at room temperature overnight until completion of the reaction. In case that a solid was formed, filtration was performed to give the crude product. Otherwise the mixture was extracted with ethyl acetate (5 mL × 3), washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to give the crude product. Further recrystallization of the

crude product with a mixture of ethyl acetate and petroleum ether afforded the pure product.

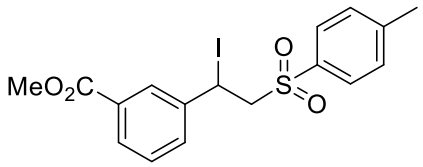
(1) Methyl 4-(1-iodo-2-tosylethyl)benzoate (6a) (pcx-9-44).



6a

Following General Procedure II, **6a** was afforded as a white solid (0.2 mmol scale, 89.9 mg, >99%) by extraction with ethyl acetate and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 103.4-104.7 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.3 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.10 (d, *J* = 7.5 Hz, 2 H), 5.53 (dd, *J* = 11.5, 4.1 Hz, 1 H), 4.28 (dd, *J* = 14.7, 11.5 Hz, 1 H), 4.04 (dd, *J* = 14.6, 4.0 Hz, 1 H), 3.90 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.27, 145.32, 145.09, 135.87, 130.05, 129.99, 129.80, 128.03, 127.22, 65.48, 52.31, 21.57, 16.41; HRMS calcd for $C_{17}H_{17}INaO_4S$ ($[M+Na]^+$): 466.9784; found: 466.9783.

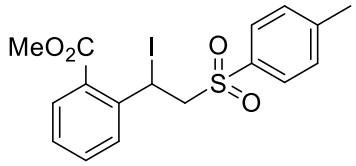
(2) Methyl 3-(1-iodo-2-tosylethyl)benzoate (6b) (pcx-10-44).



6b

Following General Procedure II, **6b** was afforded as a white solid (0.2 mmol scale, 69.1 mg, 79%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 128.2 ºC (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1 H), 7.77 (s, 1 H), 7.43 (d, *J* = 7.9 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 5.56 (dd, *J* = 11.6, 4.0 Hz, 1 H), 4.34 (dd, *J* = 14.7, 11.6 Hz, 1 H), 4.06 (dd, *J* = 14.7, 4.0 Hz, 1 H), 3.89 (s, 3 H), 2.32 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.00, 144.80, 140.93, 136.02, 131.62, 130.72, 129.77, 129.52, 128.91, 128.19, 127.95, 65.53, 52.31, 21.54, 16.71; HRMS calcd for $C_{17}H_{17}INaO_4S$ ($[M+Na]^+$): 466.9784; found: 466.9873.

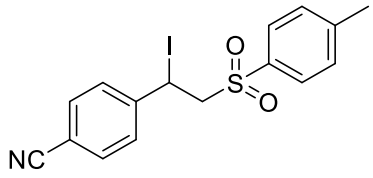
(3) Methyl 2-(1-iodo-2-tosylethyl)benzoate (6c) (pcx-10-43).



6c

Following General Procedure II, **6c** was afforded as a white solid (0.2 mmol scale, 78.4 mg, 73%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 85.4-86.6 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1 H), 7.47 (d, *J* = 8.3 Hz, 3 H), 7.28 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.23 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.72 (s, 1 H), 4.36 (t, *J* = 13.2 Hz, 1 H), 4.07 (dd, *J* = 14.7, 4.3 Hz, 1 H), 3.94 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.12, 144.82, 141.96, 135.96, 132.52, 130.92, 129.84, 129.10, 128.12, 128.05, 65.66, 52.56, 21.67, 13.21; HRMS calcd for $C_{17}H_{17}INaO_4S$ ($[M+Na]^+$): 466.9784; found: 466.9785.

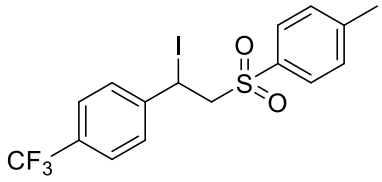
(4) 4-(1-Iodo-2-tosylethyl)benzonitrile (6d) (pcx-11-50).



6d

Following General Procedure II, **6d** was afforded as a white solid (0.2 mmol scale, 70.6 mg, 86%) by extraction with ethyl acetate and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 118.8 ºC (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 2 H), 7.43 (d, *J* = 7.8 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 5.51 (dd, *J* = 11.6, 3.9 Hz, 1 H), 4.24 (dd, *J* = 14.6, 11.7 Hz, 1 H), 4.02 (dd, *J* = 14.6, 4.0 Hz, 1 H), 2.41 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.74, 145.44, 135.89, 132.47, 129.96, 128.02, 118.13, 112.15, 65.28, 21.69, 15.25; HRMS calcd for $C_{16}H_{14}INNaO_2S$ ($[M+Na]^+$): 433.9682; found: 433.9686.

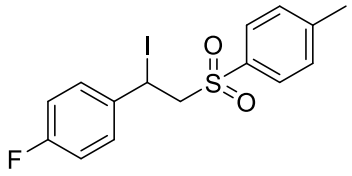
(5) 1-((2-Iodo-2-(4-(trifluoromethyl)phenyl)ethyl)sulfonyl)-4-methylbenzene (6e) (pcx-10-29).



6e

Following General Procedure II, **6e** was afforded as a white solid (0.2 mmol scale, 72.6 mg, 81%) by extraction with ethyl acetate and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 132.0-134.0 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 5.55 (dd, *J* = 11.9, 3.8 Hz, 1 H), 4.30 (dd, *J* = 14.7, 11.9 Hz, 1 H), 4.06 (dd, *J* = 14.8, 3.8 Hz, 1 H), 2.34 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.06, 144.28, 135.91, 130.42 (q, *J* = 32.7 Hz), 129.77, 127.93, 127.63, 125.65 (q, *J* = 3.7 Hz), 123.71 (q, *J* = 272.1 Hz), 65.58, 21.44, 15.92; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.85; HRMS calcd for $C_{16}H_{14}F_3INaO_2S$ ($[M+Na]^+$): 476.9603; found: 476.9604.

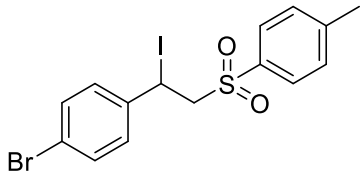
(6) 1-Fluoro-4-(1-iodo-2-tosylethyl)benzene (6f) (pcx-10-28).



6f

Following General Procedure II, **6f** was afforded as a white solid (0.2 mmol scale, 63.3 mg, 73%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 122.6-123.3 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2 H), 7.20 (dd, *J* = 8.8, 5.1 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.80 (t, *J* = 8.6 Hz, 2 H), 5.54 (dd, *J* = 11.6, 4.1 Hz, 1 H), 4.25 (dd, *J* = 14.6, 11.5 Hz, 1 H), 4.04 (dd, *J* = 14.6, 4.1 Hz, 1 H), 2.39 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.35 (d, *J* = 249.3 Hz), 144.96, 136.55 (d, *J* = 3.2 Hz), 136.16, 129.78, 129.07 (d, *J* = 8.3 Hz), 128.03, 115.75 (d, *J* = 21.9 Hz), 66.19, 21.63, 17.09; ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.10; HRMS calcd for $C_{15}H_{14}FINaO_2S$ ($[M+Na]^+$): 426.9635; found: 426.9638.

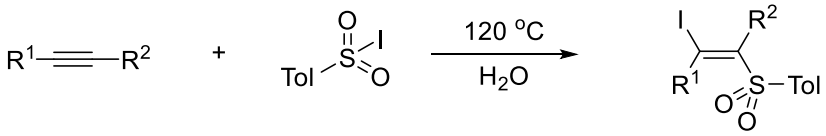
(7) 1-Bromo-4-(1-iodo-2-tosylethyl)benzene (6g) (pcx-10-30).



6g

Following General Procedure II, **6g** was afforded as a white solid (0.2 mmol scale, 82.1 mg, 87%) by extraction with ethyl acetate and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 107.1-108.5 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2 H), 7.20 (d, *J* = 8.5 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 8.5 Hz, 2 H), 5.48 (dd, *J* = 11.7, 3.9 Hz, 1 H), 4.25 (dd, *J* = 14.6, 11.7 Hz, 1 H), 4.02 (dd, *J* = 14.6, 4.0 Hz, 1 H), 2.41 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.07, 139.49, 131.84, 129.80, 128.80, 127.98, 122.51, 65.84, 21.71, 16.79; HRMS calcd for $C_{15}H_{14}{}^{79}BrINaO_2S$ ([M+Na]$^{+}$): 486.8835; found: 486.8835.

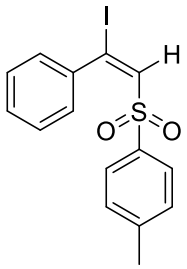
3. Iodosulfonylation of alkynes.



5 **2a** **7**

General Procedure III: To a 10 mL reaction tube equipped with a stirring bar was added **5** (1.0 equiv), **2a** (1.2 equiv), and H_2O (*c* = 0.1 mol/L for **5**) successively, and the tube was sealed with a septum. The mixture was stirred at 120 ^{o}C for indicated time until completion of the reaction. In case that a solid was formed, filtration was performed to give the crude product. Otherwise the mixture was extracted with ethyl acetate (5 mL × 3), washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to give the crude product. Further recrystallization of the crude product with a mixture of ethyl acetate and petroleum ether afforded the pure product unless otherwise stated.

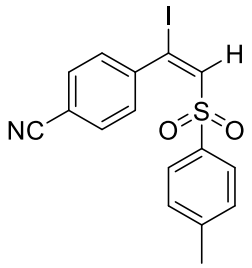
(1) (*E*)-1-((2-Iodo-2-phenylvinyl)sulfonyl)-4-methylbenzene (7a) (pcx-9-33).



7a

Following General Procedure III, after being stirred for 3.5 h, **7a** was afforded as a white solid (0.2 mmol scale, 61.4 mg, 77%) by extraction with ethyl acetate and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 80.7-82.1 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2 H), 7.36 (s, 1 H), 7.34-7.26 (m, 3 H), 7.24-7.21 (m, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 2.39 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.63, 141.33, 139.73, 137.39, 129.85, 129.73, 127.98, 127.95, 127.77, 114.23, 21.71; HRMS calcd for $C_{15}H_{13}INaO_2S$ ($[M+Na]^+$): 406.9573; found: 406.9572.

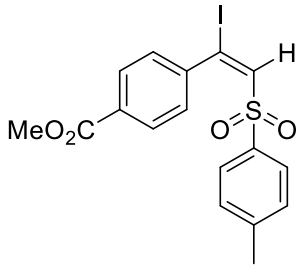
(2) (*E*)-4-(1-Iodo-2-tosylvinyl)benzonitrile (7b) (pcx-10-2).



7b

Following General Procedure III, after being stirred for 2 h, **7b** was afforded as a white solid (0.2 mmol scale, 60.6 mg, 73%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 188.1 ^{o}C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 7.38-7.33 (m, 3 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.38, 144.19, 142.36, 136.92, 131.81, 130.10, 128.33, 127.92, 118.08, 113.42, 109.86, 21.78; HRMS calcd for $C_{16}H_{14}INNaO_2S$ ($[M+Na]^+$): 431.9526; found: 431.9523.

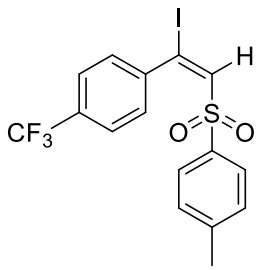
(3) Methyl (E)-4-(1-iodo-2-tosylvinyl)benzoate (7c) (pcx-9-28).



7c

Following General Procedure III, after being stirred for 2 h, **7c** was afforded as a white solid (0.2 mmol scale, 65.6 mg, 73%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 158.1-160.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 7.8 Hz, 2 H), 7.37 (s, 1 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 7.9 Hz, 2 H), 3.94 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.24, 145.06, 144.07, 141.91, 137.18, 131.08, 129.94, 129.26, 127.97, 127.64, 111.93, 52.44, 21.74; HRMS calcd for $C_{17}H_{15}INaO_4S$ ($[M+Na]^+$): 464.9628; found: 464.9627.

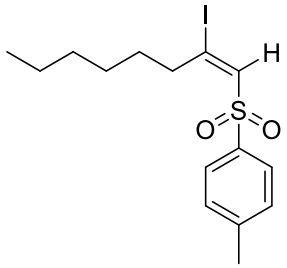
(4) (*E*)-1-((2-Iodo-2-(4-(trifluoromethyl)phenyl)vinyl)sulfonyl)-4-methylbenzene (7d) (pcx-10-7, pcx-10-39).



7d

Following General Procedure III, after being stirred for 3 h, **7d** was afforded as a white solid (0.2 mmol scale, 53.9 mg, 57%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 145.8-146.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2 H), 7.47 (d, *J* = 8.3 Hz, 2 H), 7.40 (s, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 2.40 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.11, 143.19, 142.55, 136.94, 131.51 (q, *J* = 33.0 Hz), 129.91, 128.01, 127.97, 125.05 (q, *J* = 3.8 Hz), 123.64 (q, *J* = 272.9 Hz), 110.75, 21.69; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.91; HRMS calcd for $C_{16}H_{12}F_3INaO_2S$ ($[M+Na]^+$): 474.9447; found: 474.9447.

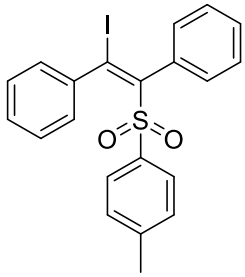
(5) (*E*)-1-((2-Iodooct-1-en-1-yl)sulfonyl)-4-methylbenzene (7e) (pcx-10-40).



7e

Following General Procedure III, after being stirred for 2 h, **7e** was afforded as a white solid (0.2 mmol scale, 41.8 mg, 52%) by extraction with ethyl acetate and chromatography on silica gel (0-8% ethyl acetate in petroleum ether): m.p. 51.5-52.9 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.00 (s, 1 H), 3.01 (t, *J* = 7.5 Hz, 2 H), 2.44 (s, 3 H), 1.55-1.47 (m, 2 H), 1.34-1.26 (m, 6 H), 0.88 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.88, 138.98, 138.16, 130.16, 127.58, 125.83, 40.06, 31.59, 29.92, 28.23, 22.56, 21.75, 14.12; HRMS calcd for $C_{15}H_{21}INaO_2S$ ($[M+Na]^+$): 415.0199; found: 415.0200.

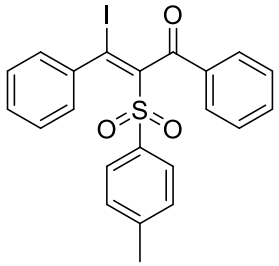
(6) (*E*)-(1-Iodo-2-tosylethene-1,2-diyl)dibenzene (7f) (pcx-9-34).



7f

Following General Procedure III, after being stirred for 2 h, **7f** was afforded as a white solid (0.2 mmol scale, 68.7 mg, 74%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 188.5-190.2 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.30 (m, 8 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 7.17 (d, *J* = 7.2 Hz, 2 H), 7.10 (d, *J* = 7.9 Hz, 2 H), 2.37 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.15, 144.32, 142.59, 139.45, 136.84, 130.36, 129.27, 129.07, 128.62, 128.40, 127.93, 127.44, 118.13, 21.70; HRMS calcd for $C_{21}H_{17}INaO_2S$ ($[M+Na]^+$): 482.9886; found: 482.9884.

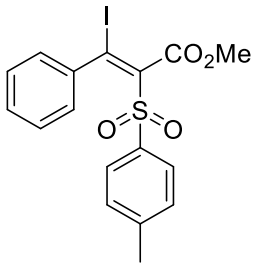
(7) (*E*)-3-Iodo-1,3-diphenyl-2-tosylprop-2-en-1-one (7g) (pcx-9-31).



7g

Following General Procedure III, after being stirred for 2 h, **7g** was afforded as a white solid (0.2 mmol scale, 54.8 mg, 55%) by extraction with ethyl acetate and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 117.3-118.9 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.3 Hz, 2 H), 7.70 (t, *J* = 7.4 Hz, 1 H), 7.60 (t, *J* = 7.7 Hz, 2 H), 7.33 (d, *J* = 8.3 Hz, 2 H), 7.32-7.26 (m, 3 H), 7.18 (d, *J* = 7.2 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 2.38 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.71, 149.40, 144.95, 140.08, 137.44, 134.69, 133.88, 130.35, 129.61, 129.43, 129.27, 128.53, 127.99, 127.52, 113.82, 21.76; HRMS calcd for $C_{22}H_{17}INaO_3S$ ($[M+Na]^+$): 510.9835; found: 510.9831.

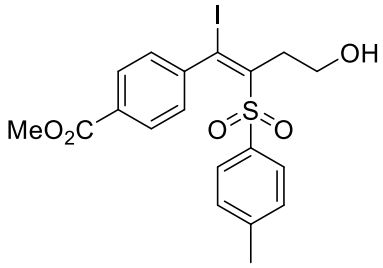
(8) Methyl (*E*)-3-iodo-3-phenyl-2-tosylacrylate (7h) (pcx-9-21).



7h

Following General Procedure III, after being stirred for 2.5 h, **7h** was afforded as a white solid (0.2 mmol scale, 71.4 mg, 80%) by extraction with ethyl acetate and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 126.6-128.4 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 7.1 Hz, 1 H), 7.22 (t, *J* = 7.5 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 7.6 Hz, 2 H), 3.96 (s, 3 H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.10, 146.53, 144.93, 139.45, 136.99, 129.63, 129.35, 128.18, 127.80, 127.25, 114.44, 53.72, 21.64; HRMS calcd for $C_{17}H_{15}INaO_4S$ ($[M+Na]^+$): 464.9628; found: 464.9627.

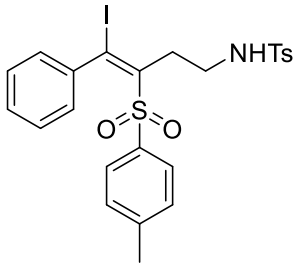
(9) Methyl (*E*)-4-(4-hydroxy-1-iodo-2-tosylbut-1-en-1-yl)benzoate (7i) (pcx-10-15).



7i

Following General Procedure III, after being stirred for 2 h, **7i** was afforded as a white solid (0.2 mmol scale, 80.8 mg, 84%): by extraction with ethyl acetate and recrystallization (ethyl acetate/petroleum ether = 1:20) m.p. 146.6 ^{o}C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 8.1 Hz, 2 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 4.05 (t, *J* = 6.5 Hz, 2 H), 3.93 (s, 3 H), 3.23 (t, *J* = 6.5 Hz, 2 H), 2.37 (s, 3 H), 1.25 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.32, 146.96, 146.89, 144.69, 137.08, 130.08, 129.61, 128.98, 127.85, 127.68, 115.51, 61.00, 52.40, 42.15, 21.69; HRMS calcd for $C_{19}H_{19}INaO_5S$ ($[M+Na]^+$): 508.9890; found: 508.9889.

(10) (*E*)-*N*-(4-Iodo-4-phenyl-3-tosylbut-3-en-1-yl)-4-methylbenzenesulfonamide (7j) (pcx-9-43).

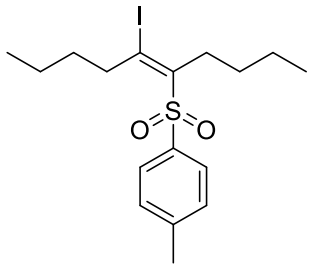


7j

Following General Procedure III, after being stirred for 2 h, **7j** was afforded as a white solid (0.2 mmol scale, 100.5 mg, 86%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 192.4-193.0 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.24 (s, 1 H), 7.20-7.16 (m, 1 H), 7.16-7.09 (m, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.95-6.90 (m, 2 H), 5.16 (s, 1 H), 3.42 (q, *J* = 6.6 Hz, 2 H), 3.11 (t, *J* = 7.2 Hz, 2 H), 2.45 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.57, 144.31, 143.59, 142.42, 137.06, 136.94, 129.88, 129.53, 128.84,

127.83, 127.73, 127.58, 127.35, 118.35, 41.40, 39.32, 21.65; HRMS calcd for $C_{24}H_{24}INNaO_4S_2$ ($[M+Na]^+$): 604.0084; found: 604.0084.

(11) (*E*)-1-((6-Iododec-5-en-5-yl)sulfonyl)-4-methylbenzene (7k) (pcx-10-9).

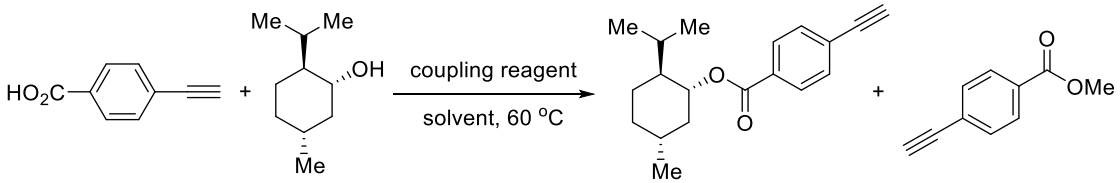


7k

Following General Procedure III, after being stirred for 2 h, **7k** was afforded by extraction with ethyl acetate and chromatography on silica gel (0-8% ethyl acetate in petroleum ether) as a white solid (0.2 mmol scale, 34.5 mg, 40%): m.p. 52.3-53.6 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 3.13 (t, *J* = 7.7 Hz, 2 H), 2.59 (t, *J* = 8.3 Hz, 2 H), 2.44 (s, 3 H), 1.56-1.48 (m, 2 H), 1.46-1.38 (m, 2 H), 1.32 (tt, *J* = 15.2, 7.6 Hz, 4 H), 0.88 (q, *J* = 7.5 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.59, 144.42, 138.72, 129.90, 127.77, 127.39, 43.49, 40.36, 32.53, 30.33, 22.73, 21.94, 21.68, 13.98, 13.72; HRMS calcd for $C_{17}H_{25}INaO_2S$ ($[M+Na]^+$): 443.0512; found: 443.0512.

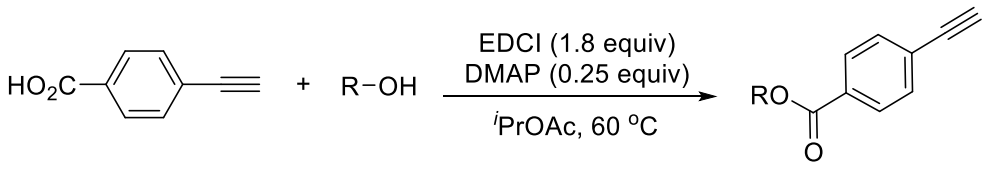
4. Synthesis of alkynes 9.

Table S1 Screening the conditions for esterification.



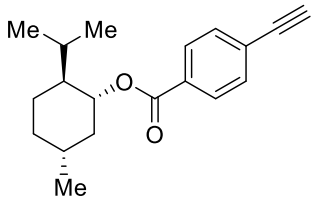
8 *L*-menthol **9a** **8-Me**

Entry	Coupling reagent (equiv)	Solvent	Yield (%)
1	Muk (1.05) + 2,6-lutidine (2)	DMC	Complicated mixture
2	EDC-HCl (1.8) + DMAP (0.25)	DMC	23% (**9a**) + 50% (**8-Me**)
3	Muk (1.05) + 2,6-lutidine (2)	^{i}PrOAc	Complicated mixture
4	**EDC-HCl (1.8)+ DMAP (0.25)**	**^{i}PrOAc**	**65% (9a)**

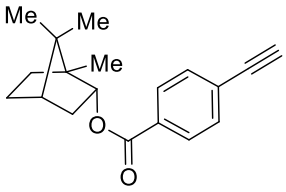


8 **9**

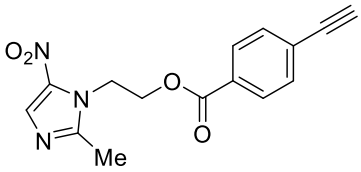
General Procedure IV:[1] To a round bottom flask were added corresponding alcohol (1.0 equiv), 4-ethynylbenzoic acid **8** (1.5 equiv), EDC-HCl (1.8 equiv), DMAP (0.25 equiv), and ^{i}PrOAc (0.25 M for alcohol). The mixture was stirred at 60 ^{o}C overnight until the completion of the reaction as monitored by TLC. Then the mixture was concentrated in vacuo. Alkynes **9** were obtained via chromatography on silica gel (0-30% ethyl acetate in petroleum ether).



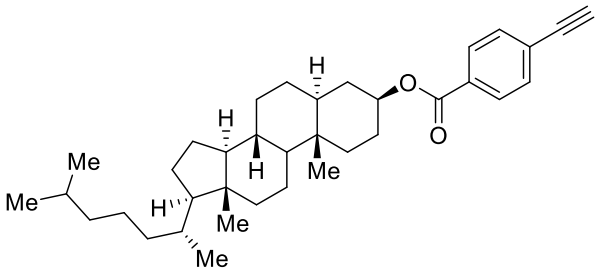
9a, 65%



9b, 71%

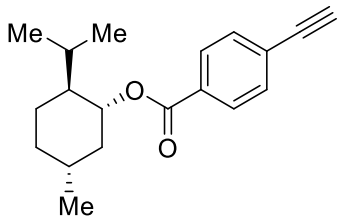


9c, 73%



9d, 51%

(1) (1*R*,2*S*,5*R*)-2-*Iso*propyl-5-methylcyclohexyl 4-((*E*)-1-iodo-2-tosylvinyl) benzoate (9a) (pcx-11-35, pcx-11-47).

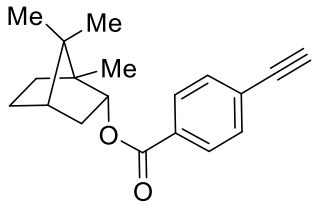


9a

Following General Procedure IV, **9a** was afforded as a colorless oil (3.0 mmol scale, 552.6 mg, 65%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 2 H), 7.54

(d, *J* = 8.2 Hz, 2 H), 4.99-4.88 (m, 1 H), 3.22 (s, 1 H), 2.12 (d, *J* = 12.0 Hz, 1 H), 1.97-1.89 (m, 1 H), 1.72 (d, *J* = 12.3 Hz, 2 H), 1.60-1.50 (m, 2 H), 1.18-1.04 (m, 2 H), 0.96-0.88 (m, 7 H), 0.79 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.46, 132.08, 130.93, 129.49, 126.58, 82.97, 79.95 , 75.23, 47.32, 41.01, 34.37, 31.52, 26.60, 23.72, 22.10, 20.82, 16.60; HRMS calcd for $C_{19}H_{24}NaO_2$ ($[M+Na]^+$): 307.1669; found: 307.1665.

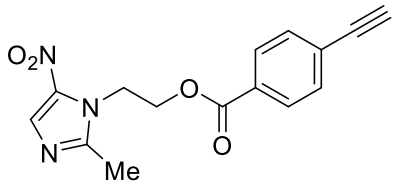
(2) (1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-ethynylbenzoate (9b) (pcx-11-36).



9b

Following General Procedure IV, **9b** was afforded as a white solid (3.0 mmol scale, 600.1 mg, 71%): m.p. 103.8-105.6 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2 H), 7.55 (d, *J* = 8.3 Hz, 2 H), 5.14-5.08 (m, 1 H), 3.23 (s, 1 H), 2.52-2.43 (m, 1 H), 2.14-2.07 (m, 1 H), 1.84-1.76 m, 1 H), 1.73 (t, *J* = 4.5 Hz, 1 H), 1.44-1.37 (m, 1 H), 1.33-1.27 (m, 1 H), 1.13-1.09 (m, 1 H), 0.96 (s, 3 H), 0.90 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.12, 132.08, 130.90, 129.41, 126.60, 82.92, 80.87, 80.02, 49.15, 47.94, 45.01, 36.92, 28.13, 27.44, 19.76, 18.95, 13.67; HRMS calcd for $C_{19}H_{22}NaO_2$ ($[M+Na]^+$): 305.1512; found: 305.1528.

(3) 2-(2-Methyl-5-nitro-1*H*-imidazol-1-yl)ethyl 4-ethynylbenzoate (9c) (pcx-11-22).

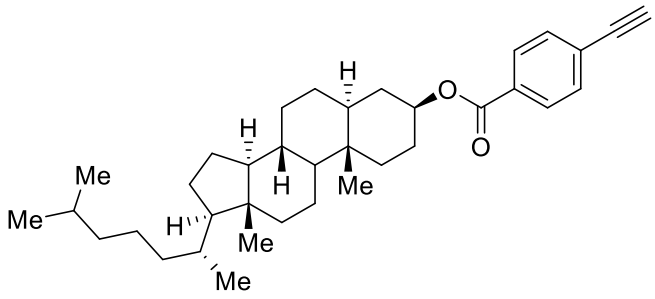


9c

Following General Procedure IV, **9c** was afforded as a white solid (1.0 mmol scale, 221.2 mg, 73%): m.p. 126.6-128.3 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.5 Hz, 2 H), 4.74-4.64 (m, 4 H), 3.26 (s, 1 H),

2.47 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.43, 150.78, 138.62, 133.34, 132.39, 129.48, 128.97, 127.61, 82.55, 80.78, 63.08, 45.28, 14.41; HRMS calcd for $C_{15}H_{13}N_3NaO_4$ ([M+Na]$^+$): 322.0798; found: 322.0798.

(4) (3*S*,5*S*,8*R*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 4-ethynylbenzoate (9d) (pcx-11-31).

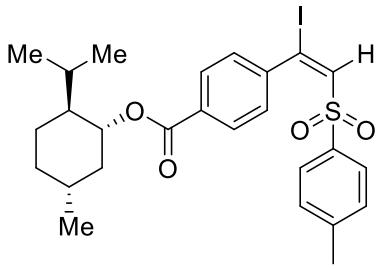


9d

Following General Procedure IV, **9d** was afforded as a white solid (1.0 mmol scale, 263.7 mg, 51%): m.p. 147.4-149.3 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2 H), 7.53 (d, *J* = 8.1 Hz, 2 H), 4.94 (tt, *J* = 10.9, 4.9 Hz, 1 H), 3.21 (s, 1 H), 2.00-1.90 (m, 2 H), 1.83-1.75 (m, 2 H), 1.73-1.61 (m, 3 H), 1.53-1.47 (m, 3 H), 1.38-1.22 (m, 10 H), 1.17-1.07 (m, 7 H), 1.04-0.97 (m, 3 H), 0.90 (d, *J* = 6.5 Hz, 4 H), 0.88-0.84 (m, 9 H), 0.66 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.50, 132.04, 131.05, 129.48, 126.52, 83.01, 79.90, 74.80, 56.51, 56.37, 54.33, 44.80, 42.69, 40.08, 39.61, 36.88, 36.27, 35.90, 35.61, 35.59, 34.19, 32.09, 28.73, 28.34, 28.10, 27.66, 24.31, 23.94, 22.91, 22.66, 21.32, 18.77, 12.38, 12.17; HRMS calcd for $C_{36}H_{52}NaO_2$ ([M+Na]$^+$): 539.3860; found: 539.3861.

5. Iodosulfonylation of alkynes 9.

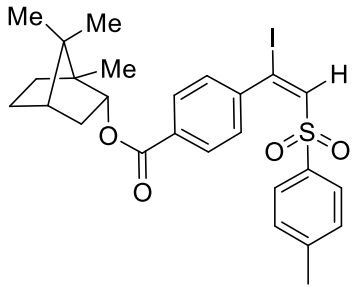
(1) (1*R*,2*S*,5*R*)-2-*Iso*propyl-5-methylcyclohexyl 4-ethynylbenzoate (10a) (pcx-10-8).



10a

Following General Procedure III, after being stirred for 2 h, **10a** was afforded as a white solid (0.2 mmol scale, 124.8 mg, 99%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 121.0-122.9 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2 H), 7.50 (d, *J* = 8.2 Hz, 2 H), 7.36 (s, 1 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 4.95 (td, *J* = 10.9, 4.4 Hz, 1 H), 2.41 (s, 3 H), 2.12 (d, *J* = 12.2 Hz, 1 H), 2.00-1.93 (m, 1 H), 1.77-1.71 (m, 2 H), 1.59-1.53 (m, 2 H), 1.19-1.14 (m, 1 H), 1.13-1.06 (m, 1 H), 0.99-0.89 (m, 7 H), 0.81 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.20, 145.01, 143.88, 141.80, 137.16, 131.80, 129.92, 129.23, 128.00, 127.56, 112.01, 75.32, 47.35, 41.02, 34.36, 31.55, 26.56, 23.64, 22.13, 21.73, 20.89, 16.55; HRMS calcd for $C_{26}H_{31}INaO_4S$ ($[M+Na]^+$): 589.0880; found: 589.0879.

(2) (1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-((*E*)-1-iodo-2-tosylvinyl) benzoate (10b) (pcx-10-31).

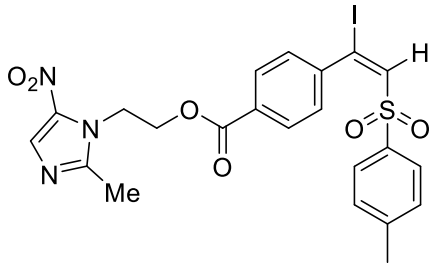


10b

Following General Procedure III, after being stirred for 2 h, **10b** was afforded as a white solid (0.2 mmol scale, 62.2 mg, 55%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 158.3-159.4 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2 H), 7.51 (d, *J* = 8.1 Hz, 2 H), 7.36 (s, 1 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 5.12 (d, *J* = 9.7 Hz, 1 H), 2.53-2.45 (m, 1 H), 2.41 (s, 3 H), 2.14-2.08 (m, 1 H), 1.86-1.78 (m, 1 H), 1.75 (t, *J* = 4.5 Hz, 1 H), 1.46-1.39 (m, 1

H), 1.35-1.28 (m, 1 H), 1.12 (dd, *J* = 13.8, 3.6 Hz, 1 H), 0.97 (s, 3 H), 0.92 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.88, 145.02, 143.95, 141.70, 137.13, 131.77, 129.94, 129.16, 127.95, 127.54, 111.95, 81.01, 49.17, 47.98, 45.02, 36.96, 28.15, 27.45, 21.72, 19.78, 18.98, 13.69; HRMS calcd for $C_{26}H_{29}INaO_4S$ ($[M+Na]^+$): 587.0723; found: 587.0723.

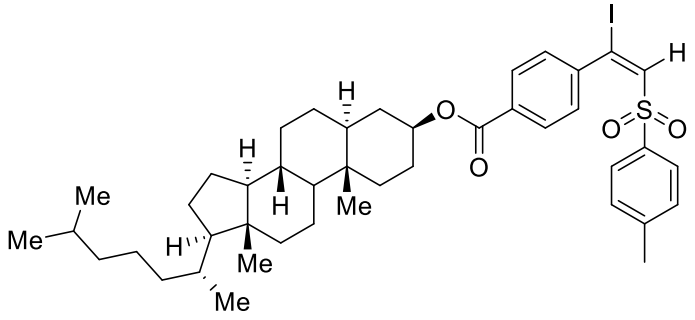
(3) 2-(2-Methyl-5-nitro-1H-imidazol-1-yl)ethyl (*E*)-4-(1-iodo-2-tosylvinyl) benzoate (10c) (pcx-11-24).



10c

Following General Procedure III, after being stirred for 2 h, **10c** was afforded as a white solid (0.2 mmol scale, 82.4 mg, 71%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 205.9-207.8 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08 (s, 1 H), 7.83 (s, 1 H), 7.79 (d, *J* = 8.2 Hz, 2 H), 7.53 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 4.76 (t, *J* = 5.1 Hz, 2 H), 4.67 (t, *J* = 5.1 Hz, 2 H), 2.39 (s, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 164.78, 151.58, 145.42, 144.83, 140.48, 138.70, 137.15, 133.33, 130.10, 129.35, 128.67, 127.57, 127.40, 113.48, 63.28, 44.82, 21.22, 14.09; HRMS calcd for $C_{43}H_{59}INaO_4S$ ($[M+Na]^+$): 604.0010; found: 604.0009.

(4) (3*S*,5*S*,8*R*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*E*)-1-iodo-2-tosylvinyl) benzoate (10d) (pcx-11-33).

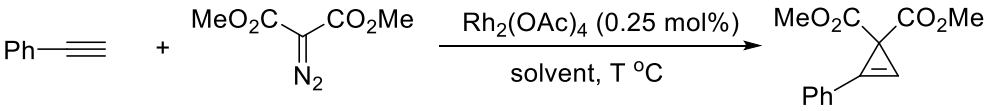


10d

Following General Procedure III, after being stirred for 2 h, **10d** was afforded as a white solid (0.2 mmol scale, 63.9 mg, 40%) by filtration and recrystallization (ethyl acetate/petroleum ether = 1:20): m.p. 186.2-187.8 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2 H), 7.50 (d, *J* = 7.9 Hz, 2 H), 7.35 (s, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 7.9 Hz, 2 H), 4.96 (tt, *J* = 10.9, 5.0 Hz, 1 H), 2.41 (s, 3 H), 2.00-1.92 (m, 2 H), 1.85-1.77 (m, 2 H), 1.72-1.62 (m, 3 H), 1.54-1.47 (m, 3 H), 1.38-1.21 (m, 10 H), 1.17-1.06 (m, 7 H), 1.04-0.98 (m, 3 H), 0.91 (d, *J* = 6.5 Hz, 4 H), 0.88 (s, 6 H), 0.86 (s, 3 H), 0.66 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.25, 145.03, 143.85, 141.77, 137.22, 131.94, 129.96, 129.22, 128.00, 127.51, 112.11, 74.86, 56.52, 56.37, 54.34, 44.81, 42.70, 40.08, 39.61, 36.88, 36.26, 35.89, 35.61, 35.59, 34.19, 32.10, 28.74, 28.34, 28.10, 27.67, 24.31, 23.93, 22.91, 22.65, 21.75, 21.32, 18.76, 12.39, 12.17; HRMS calcd for $C_{43}H_{59}INaO_4S$ ($[M+Na]^+$): 821.3071; found: 821.3074.

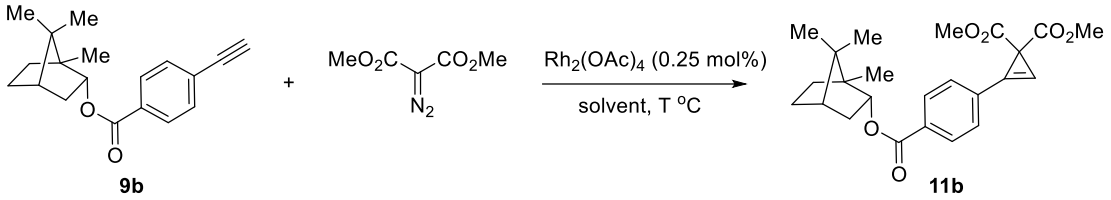
6. Synthesis of cyclopropenes 11.

Table S2 Screening the conditions for cyclopropenation of phenylacetylene.

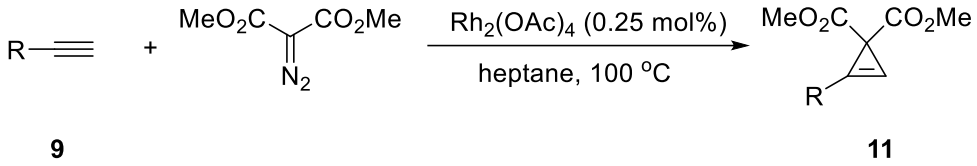


Entry	Solvent	Temperature (^{o}C)	Yield (%)
1	dichloromethane	40	45
2	^{i}PrOAc	60	0
3	dimethyl carbonate	60	0
4	**anisole**	**60**	**31**
5	**heptane**	**100**	**32**

Table S3 Screening the conditions for cyclopropenation of 9b.



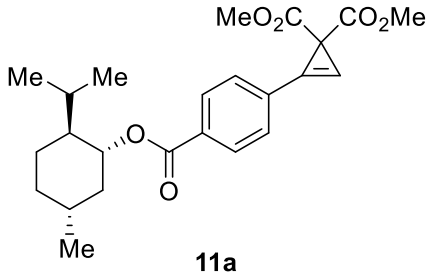
Entry	Solvent	Temperature (°C)	Yield (%)
1	anisole	100	0
2	**heptane**	**100**	**29**



9 **11**

General Procedure V: Under nitrogen atmosphere, to a three-neck flask equipped with a stirring bar were added anhydrous $Rh_2(OAc)_4$ (0.25 mol%), and a solution of alkyne **9** (1 equiv) in heptane (0.025 M). The mixture was then heated at 100 °C. After that, a solution of dimethyl 2-diazomalonate (3 equiv) in heptane (0.05 M) was added via a syringe pump over a period of 2 h. After complete conversion of the starting material as monitored by TLC, the mixture was concentrated in vacuo. Cyclopropene **11** was obtained via chromatography on silica gel (0-20% ethyl acetate in petroleum ether).

(1) Dimethyl 2-(4-((((*1R*,*2S*,*5R*)-2-isopropyl-5-methylcyclohexyl)oxy) carbonyl)phenyl)cycloprop-2-ene-1,1-dicarboxylate (11a) (pcx-7-4, pcx-7-7-2)

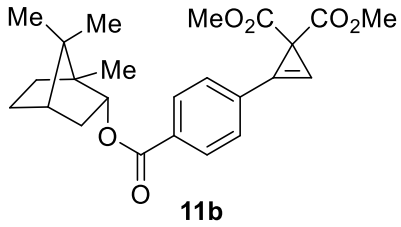


11a

Following General Procedure V, **11a** was afforded as a colorless oil (0.4 mmol scale, 16.6 mg, 10%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 2 H), 7.69 (d,

J = 8.3 Hz, 2 H), 7.04 (s, 1 H), 4.94 (td, *J* = 10.9, 4.5 Hz, 1 H), 3.74 (d, *J* = 2.3 Hz, 6 H), 2.14-2.09 (m, 1 H), 1.95-1.90 (m, 1 H), 1.76-1.71 (m, 2 H), 1.59-1.52 (m, 2 H), 1.15-1.07 (m, 2 H), 0.96-0.89 (m, 7 H), 0.79 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.73, 170.72, 165.17, 132.39, 130.11, 129.98, 127.84, 111.71, 97.98, 75.28, 52.41, 52.39, 47.18, 40.84, 34.20, 32.88, 31.37, 26.53, 23.62, 21.95, 20.64, 16.49; HRMS calcd for $C_{24}H_{30}NaO_6$ ([M+Na]$^+$): 437.1935; found: 437.1936.

(2) Dimethyl 2-(4-((((*1S*,*2R*,*4S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)phenyl)cycloprop-2-ene-1,1-dicarboxylate (11b) (pcx-7-18, pcx-7-23, pcx-11-42).

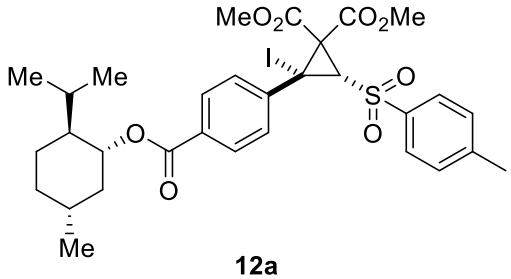


11b

Following General Procedure V, **11b** was afforded as a pale yellow oil (0.2 mmol scale, 11.9 mg, 29%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.04 (s, 1 H), 5.15-5.10 (m, 1 H), 3.73 (s, 6 H), 2.51-2.44 (m, 1 H), 2.13-2.06 (m, 1 H), 1.84-1.77 (m, 1 H), 1.74 (t, *J* = 4.5 Hz, 1 H), 1.45-1.38 (m, 1 H), 1.31-1.29 (m, 1 H), 1.11 (dd, *J* = 13.8, 3.5 Hz, 1 H), 0.96 (s, 3 H), 0.91 (s, 3 H), 0.90 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.84, 166.03, 132.58, 130.28, 130.05, 128.00, 111.93, 98.08, 81.09, 52.56, 49.21, 47.99, 45.05, 36.96, 33.04, 28.15, 27.46, 19.77, 18.97, 13.66; HRMS calcd for $C_{24}H_{28}NaO_6$ ([M+Na]$^+$): 435.1778; found: 435.1783.

7. Iodosulfonylation of cyclopropenes 11.

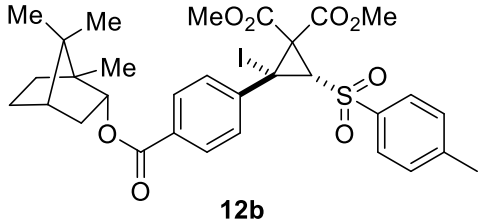
(1) Dimethyl (2*R,3*S**)-2-iodo-2-(4-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)-3-tosylcyclopropane-1,1-dicarboxylate (12a) (pcx-7-10).**



12a

Following General Procedure I, after being stirred for 3 h, **12a** was afforded as a white solid (0.1 mmol scale, 47.5 mg, 74%, 1:1 dr based on original chiral centres of the substrate) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 181.1-182.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.4, 2.4 Hz, 2 H), 7.90 (dd, *J* = 8.8, 1.9 Hz, 2 H), 7.44 (dd, *J* = 8.1, 2.1 Hz, 2 H), 7.13-7.10 (d, *J* = 7.1 Hz, 2 H), 4.89 (tt, *J* = 10.8, 4.0 Hz, 1 H), 3.98 (s, 3 H), 3.70 (s, 1 H), 3.57 (d, *J* = 3.2 Hz, 3 H), 2.50 (s, 3 H), 2.08-2.03 (m, 1 H), 1.92-1.87 (m, 1 H), 1.71 (d, *J* = 12.3 Hz, 2 H), 1.50 (d, *J* = 10.9 Hz, 2 H), 1.11 (d, *J* = 11.6 Hz, 1 H), 1.04 (dd, *J* = 11.3, 3.3 Hz, 1 H), 0.92-0.88 (m, 7 H), 0.76 (dd, *J* = 7.0, 1.8 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.11, 163.25, 162.06, 147.35, 147.32, 145.81, 136.79, 130.99, 130.96, 130.19, 130.17, 129.96, 128.77, 126.91, 75.27, 54.14, 53.64, 51.31, 51.28, 47.32, 47.29, 44.80, 44.75, 40.99, 34.33, 31.50, 26.48, 26.47, 23.58, 22.08, 21.88, 20.86, 20.84, 16.48, 16.46, 6.51, 6.44; HRMS calcd for $C_{31}H_{37}INaO_8S$ ($[M+Na]^+$): 719.1146; found: 719.1155.

(2) Dimethyl (2*R,3*S**)-2-iodo-3-tosyl-2-(4-((((1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)phenyl)cyclopropane-1,1-dicarboxylate (12b) (pcx-7-25).**



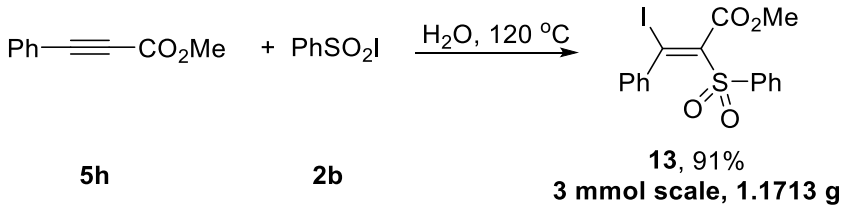
12b

Following General Procedure I, after being stirred for 2 h, **12b** was afforded as a white solid (0.25 mmol scale, 129.9 mg, 75%, 1:1 dr based on original chiral centres of the substrate) by filtration and trituration (ethyl acetate/petroleum ether = 1:20): m.p. 188.2 °C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2 H), 7.92 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 5.08-5.03

(m, 1 H), 3.98 (s, 3 H), 3.71 (s, 1 H), 3.57 (d, *J* = 4.0 Hz, 3 H), 2.51 (s, 3 H), 2.48-2.40 (m, 1 H), 2.08-2.01 (m, 1 H), 1.83-1.75 (m, 1 H), 1.72 (t, *J* = 4.5 Hz, 1 H), 1.42-1.35 (m, 1 H), 1.31-1.23 (m, 1 H), 1.10-1.03 (m, 1 H), 0.94 (s, 3 H), 0.90 (s, 3 H), 0.88 (d, *J* = 4.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.78, 163.27, 162.03, 147.43, 145.80, 136.81, 131.00, 130.19, 130.15, 128.77, 126.96, 81.01, 80.98, 54.15, 53.62, 51.31, 51.29, 49.17, 49.13, 47.98, 45.03, 44.75, 36.96, 36.90, 28.14, 27.45, 21.89, 19.78, 18.96, 13.67, 13.65, 6.46, 6.44; HRMS calcd for $C_{31}H_{35}INaO_8S$ ($[M+Na]^+$): 717.0990; found: 717.0997.

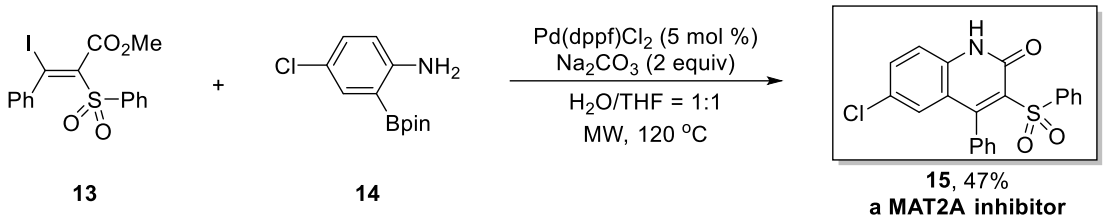
8. Synthesis of a MAT2A inhibitor 15.

(1) Gram-scale synthesis of 13 (pcx-11-5).



To a 50 mL reaction tube equipped with a stirring bar was added **5a** (0.44 mL, 3.0 mmol, 1.0 equiv), **2b** (964.9 mg, 3.6 mmol, 1.2 equiv), and H_2O (30 mL) successively, and the tube was sealed with a septum. The mixture was heated at 120 °C for 2 hours. After the reaction was complete, the aqueous layer was extracted with EtOAc (10 mL × 3), washed with brine (15 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. After that, the mixture triturated with a mixture of ethyl acetate and petroleum ether (1:15) to afford **13** (1.1713g, 91%) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.4 Hz, 1 H), 7.41 (d, *J* = 7.2 Hz, 2 H), 7.29 (t, *J* = 7.8 Hz, 2 H), 7.24 (d, *J* = 7.0 Hz, 1 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.00 (d, *J* = 7.3 Hz, 2 H), 3.95 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.94, 146.35, 139.89, 139.27, 133.73, 129.65, 128.71, 127.99, 127.84, 127.18, 114.90, 53.76; HRMS calcd for $C_{21}H_{14}ClNNaO_3S$ ($[M+Na]^+$): 450.9471; found: 450.9472.

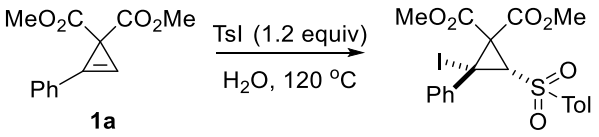
(2) 6-Chloro-4-phenyl-3-(phenylsulfonyl)quinolin-2(1*H*)-one (15) (pcx-11-34-4).



To a 10 mL microwave reaction tube equipped with a stirring bar was added **13** (85.9 mg, 0.2 mmol, 1.0 equiv), **14** (107.4 mg, 0.3 mmol, 1.5 equiv), Pd(dppf)Cl_2 (7.6 mg, 0.01mmol, 5 mol%), Na_2CO_3 (43.5 mg, 0.4mmol, 2.0 equiv), and THF/H_2O (1:1, 2 mL) successively and the tube was sealed with a septum and heated at 120 ℃ for 1h under 120 W of microwave irradiation. The mixture was cooled to room temperature. The mixture was extracted with EtOAc (5 mL × 3), washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The residual was purification by chromatography on silica gel (0-50% ethyl acetate in petroleum ether) to afford the product **15** as an oil (0.2 mmol scale, 37.4 mg, 47%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.82 (s, 1 H), 8.03 (d, *J* = 7.6 Hz, 2 H), 7.62-7.59 (m, 1 H), 7.58 (s, 2 H), 7.56 (d, *J* = 7.1 Hz, 2 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.38-7.33 (m, 2 H), 7.23 (d, *J* = 8.5 Hz, 1 H), 7.06 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.34, 141.47, 137.82, 133.79, 133.40, 133.29, 129.15, 129.05, 128.83, 128.53, 128.38, 128.34, 127.86, 121.68, 117.73; HRMS calcd for $C_{21}H_{14}ClNNaO_3S$ ($[M+Na]^+$): 418.0275; found: 418.0273.

9. Formal synthesis of a dipeptide renin inhibitor 20.

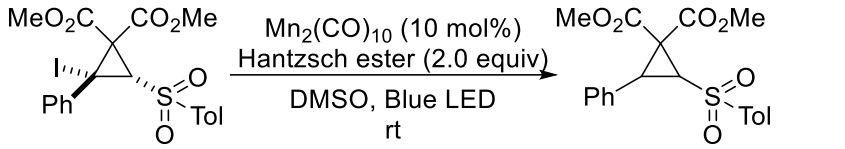
(1) Gram-scale synthesis of 3a (pcx-5-49).



3a, 88%
2 mmol scale, 0.9097 g

To a 50 mL reaction tube equipped with a stirring bar was added **1a** (464.4 mg, 2.0 mmol, 1.0 equiv), **2a** (680.7 mg, 2.4 mmol, 1.2 equiv), and H_2O (20.0 mL) successively, and the tube was sealed with a septum. The mixture was heated at 120 °C for 2 hours. After that, the mixture was filtered and triturated with a mixture of ethyl acetate and petroleum ether (1:15) to afford **3a** (909.7 mg, 88%) as a solid.

(2) Dimethyl 2-phenyl-3-tosylcyclopropane-1,1-dicarboxylate (16) (pcx-7-33).



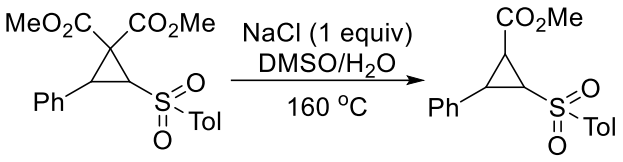
3a **16**, 98%, *cis*/*trans* = 71:29

To a flame-dried Schlenk tube was added $Mn_2(CO)_{10}$ (7.8 mg, 0.02 mmol) and Hantzsch ester (113.1 mg, 0.4 mmol). Compound **3a** (102.9 mg, 0.2 mmol) and anhydrous DMSO (2 mL) were sequentially added under nitrogen. After that, the Schlenk tube was irradiated using a Blue LED light. A fan was used to maintain room temperature. After being stirred overnight, the reaction was complete as monitored by TLC. 3 M HCl (3 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (5 mL × 3) and the combined organic layer was washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. **16** was obtained via chromatography (0-25% ethyl acetate in petroleum ether) as a white solid (76.4 mg, 98%, *cis*/*trans* = 71:29): m.p. 134.4-136.0 °C.

The following signals are discernible for the *cis*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.63 (m, 2 H), 7.62 (d, *J* = 8.3 Hz, 2 H), 7.40 (d, *J* = 8.1 Hz, 1 H), 7.32 (d, *J* = 1.9 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 3.61 (d, *J* = 10.2 Hz, 1 H), 3.28 (d, *J* = 10.1 Hz, 1 H), 2.44 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.83, 163.50, 144.85, 137.80, 131.01, 130.04, 129.60，127.84, 127.74, 127.62，53.88, 52.82, 47.85，39.29, 36.22，21.61.

The following signals are discernible for the *trans*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 4.6 Hz, 1 H), 7.33 (d, *J* = 2.2 Hz, 2 H), 7.26 (d, *J* = 2.3 Hz, 2 H), 7.14-7.11 (m, 2 H), 3.98 (d, *J* = 7.8 Hz, 1 H), 3.92 (s, 3 H), 3.92 (d, *J* = 7.5 Hz, 1 H), 3.48 (s, 3 H), 2.47 (s, 3 H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.88, 164.69, 145.27, 136.68, 131.58, 129.27, 128.51, 128.25, 128.13, 127.94, 53.56, 53.14, 48.53, 44.08, 33.78, 21.67; HRMS calcd for $C_{20}H_{20}NaO_6S$ ($[M+Na]^+$): 411.0873; found: 411.0876.

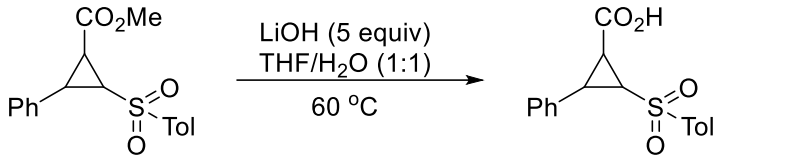
(3) Methyl 2-phenyl-3-tosylcyclopropane-1-carboxylate (17) (pcx-8-48).



16, *cis*/*trans* = 71:29 **17**, 99%, dr = 61:23:16

To a flame-dried Schlenk tube were added NaCl (26.0 mg, 0.41 mmol), Compound **16** (176.1 mg, 0.41 mmol) in anhydrous DMSO (2 mL), and H_2O sequentially under nitrogen. After the reaction mixture was heated at 160 °C for 2 hours, H_2O (3 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (5 mL × 3) and the combined organic layer was washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. **17** (133.9 mg, 99%, dr = 61:23:16) was obtained via chromatography on silica gel (0-25% ethyl acetate in petroleum ether) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.83 (m, 1.51 H), 7.43-7.37 (m, 1.52 H), 7.32-7.24 (m, 3.61 H), 7.21-7.17 (m, 0.94 H), 7.13-7.08 (m, 1.50 H), 3.83 (s, 0.48 H), 3.79 (0.68 H), 3.59 (dd, *J* = 6.3, 4.9 Hz, 0.73 H), 3.51 (s, 1.82 H), 3.41 (dd, *J* = 10.4, 6.5 Hz, 0.61 H), 3.32 (d, *J* = 8.1 Hz, 0.44 H), 3.10 (t, *J* = 8.1 Hz, 0.25 H), 3.05-3.01 (m, 0.15 H), 2.94 (dd, *J* = 10.4, 4.9 Hz, 0.58 H), 2.59 (dd, *J* = 9.3, 7.2 Hz, 0.20 H), 2.49 (s, 1.68 H), 2.48 (s, 0.63 H), 2.43 (s, 0.64 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.87, 167.53, 167.10, 145.12, 144.92, 144.58, 137.43, 137.09, 136.75, 135.71, 132.43, 130.41, 130.25, 130.01, 129.93, 129.57, 129.53, 128.87, 128.71, 128.49, 128.12, 127.93, 127.88, 127.83, 127.78, 127.72, 127.44, 126.88, 52.88, 52.81, 52.34, 47.57, 46.56, 44.68, 44.21, 32.26, 31.51, 30.69, 30.27, 29.76, 28.27, 27.43, 23.74, 21.76, 21.68; HRMS calcd for $C_{18}H_{18}NaO_4S$ ($[M+Na]^+$): 353.0818; found: 353.0823.

(4) 2-Phenyl-3-tosylcyclopropane-1-carboxylic acid (18) (pcx-8-49).

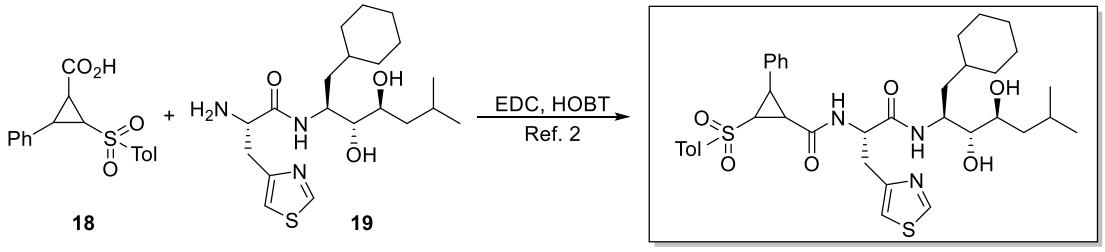


17, dr = 61:23:16 **18**, 89%, dr = 74:22:<4

To a round bottom flask was added LiOH (42.0 mg, 1.7 mmol) and compound **17** (112.0 mg, 0.34 mmol) in THF/H_2O (1:1, 4.0 mL). The mixture was stirred at 60 °C stirred overnight until the reaction was complete as monitored by TLC. 3 M HCl (2 mL)

was added to quench the reaction. The aqueous layer was extracted with EtOAc (5 mL × 3) and the combined organic layer was washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. **18** (95.7 mg, 89%, dr = 74:22:<4) was obtained via chromatography on silica gel (eluent: petroleum ether/diethyl ether = 3/1) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1.48 H), 7.80 (d, *J* = 8.2 Hz, 0.08 H), 7.54 (d, *J* = 8.5 Hz, 0.10 H), 7.40 (d, *J* = 8.1 Hz, 1.50 Hz), 7.33-7.27 (m, 1.57 H), 7.26-7.22 (m, 2.12 H), 7.21-7.15 (m, 1.04 H), 7.10-7.05 (m, 1.45 H), 3.54 (dd, *J* = 6.3, 5.1 Hz, 0.74 H), 3.44 (dd, *J* = 10.3, 6.7 Hz), 3.29 (dd, *J* = 9.3, 4.8 Hz, 0.22 H), 3.23 (t, *J* = 5.8 Hz, 0.22 H), 3.09 (dd, *J* = 9.0, 7.2 Hz, 0.24 H), 2.87 (dd, *J* = 10.4, 4.8 Hz, 0.72 H), 2.49 (s, 2.15 H), 2.45 (s, 0.12 H), 2.43 (s, 0.67 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.53, 172.34, 145.27, 144.75, 136.86, 136.46, 131.86, 130.29, 130.12, 129.98, 129.64, 129.44, 128.90, 128.70, 128.52, 128.16, 127.97, 127.93, 127.89, 127.81, 127.71, 126.83, 46.70, 44.48, 32.63, 31.49, 31.27, 30.25, 29.75, 29.41, 27.11, 23.74, 22.74, 21.75, 21.67, 14.17; HRMS calcd for $C_{17}H_{15}O_4S$ ($[M-H]^-$): 315.0697; found: 315.0699.

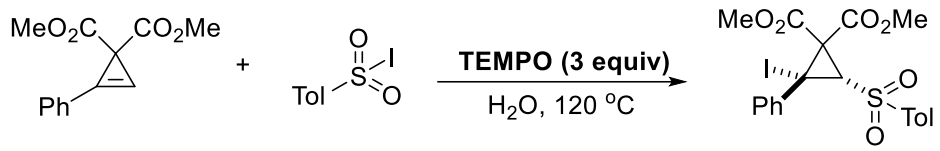
According to literature,[2] condensation of acid 18 with amine 19 will give the final renin inhibitor 20.



18 **19** **20**, a renin inhibitor

10. Control experiment (pcx-8-31).

To a 10 mL reaction tube equipped with a stirring bar was added **1** (24.8 mg, 0.1 mmol, 1.0 equiv), **2** (36.0 mg, 0.12 mmol, 1.2 equiv), TEMPO (46.9 mg, 0.3 mmol, 3.0 equiv), and H_2O (1.0 mL) successively and the tube was sealed with a septum. The mixture was stirred at 120 °C for 2 h. **3a** was not observed in this reaction.

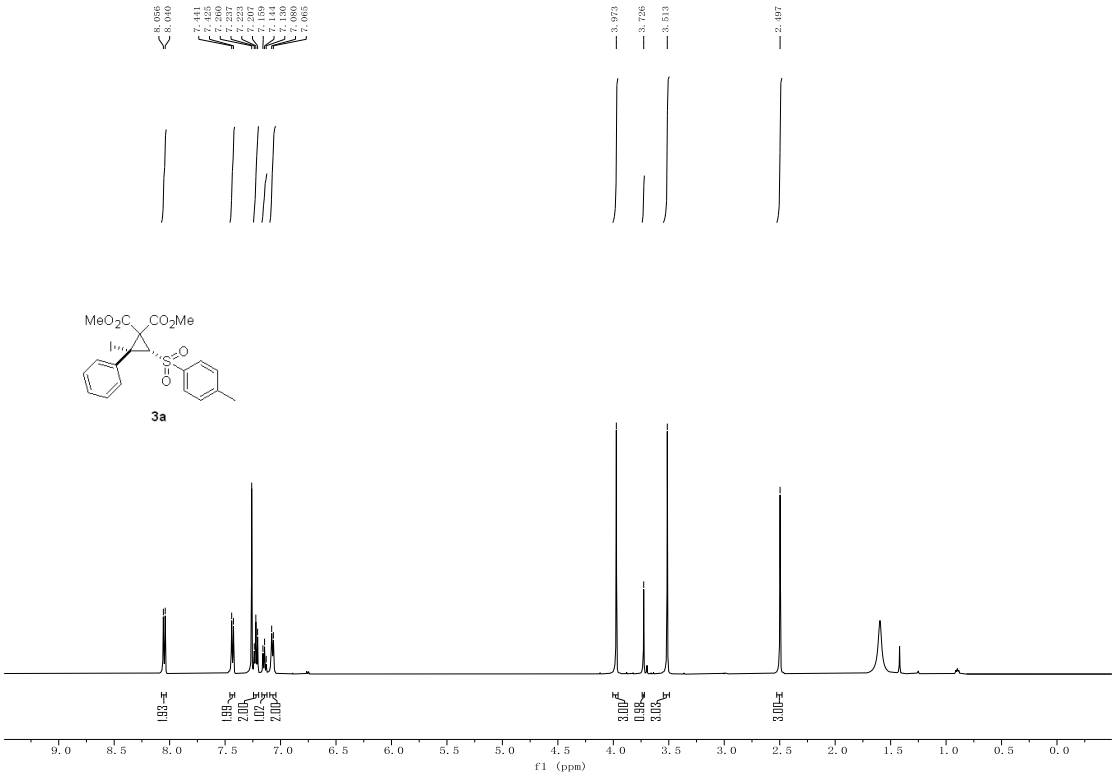


1a **2a** **3a**, 0%

References

1 A. Jordan, K. D. Whymark, J. Sydenham, H. F. Sneddon, *Green Chem.*, 2021, **23**, 6405.

2 W. R. Baker, H.-S. Jae, S. R. Martin, S. L. Condon, H. H. Stein, J. Cohen, H. D. Kleinert, *Bioorg*. *Med*. *Chem*. *Lett*., 1992, **2**, 1405.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7.300
7.237
7.233
7.207
7.159
7.144
7.100
7.080
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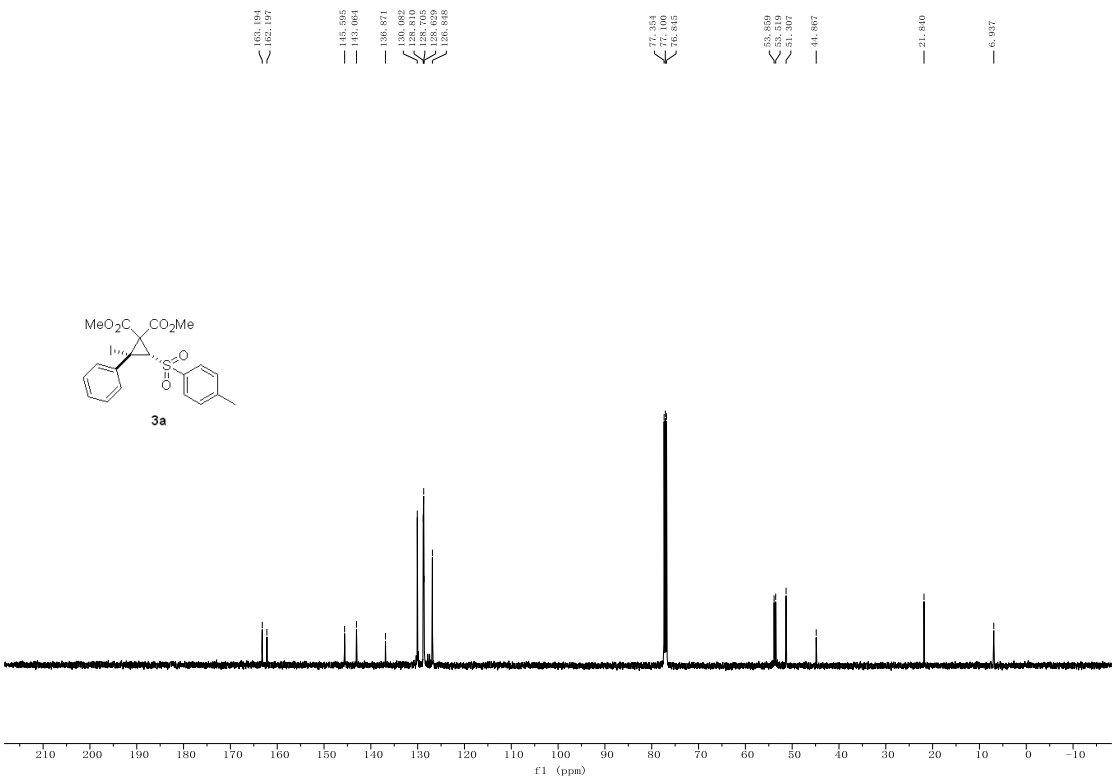
3.973
3.726
3.513
2.497
MeO2C
CO2Me
I
S
O
O
3a
1.93
1.93
2.00
1.02
2.00
3.00
0.98
3.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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53.859
53.519
51.307
44.867
21.840
6.937
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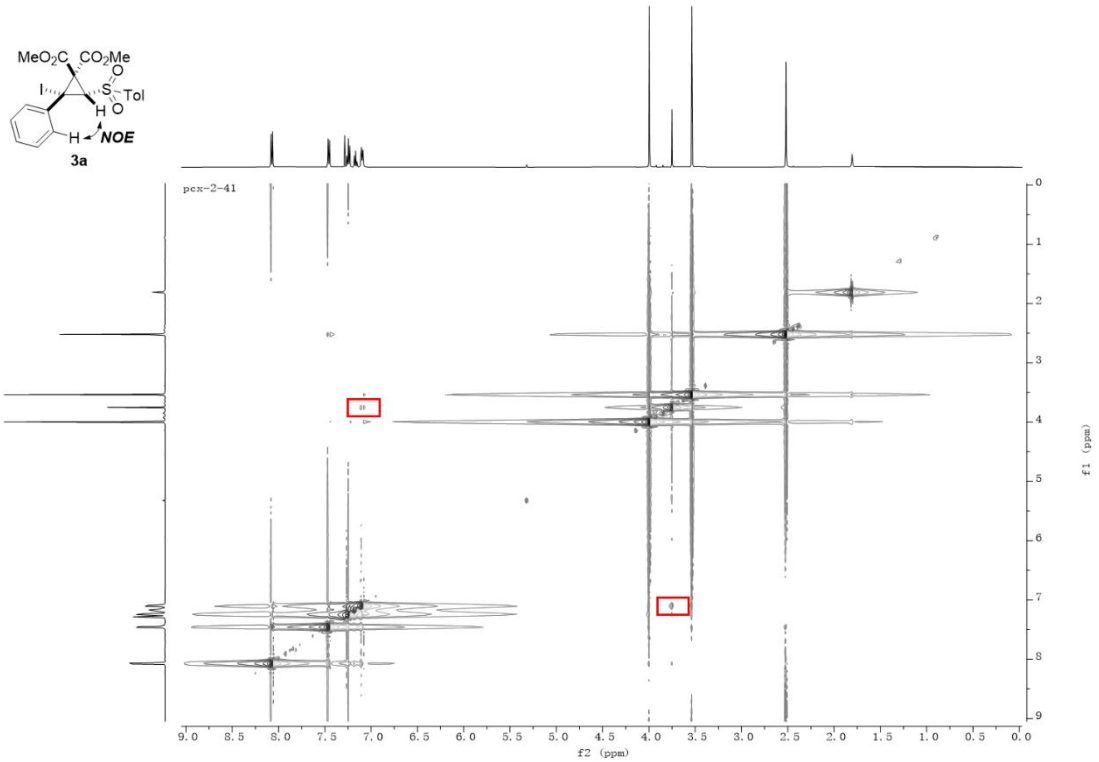
I
S
O
O
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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CO2Me
I
S
O
Tol
H
O
H
NOE
3a
pcx-2-41
f2 (ppm)
f1 (ppm)


8.052
8.036
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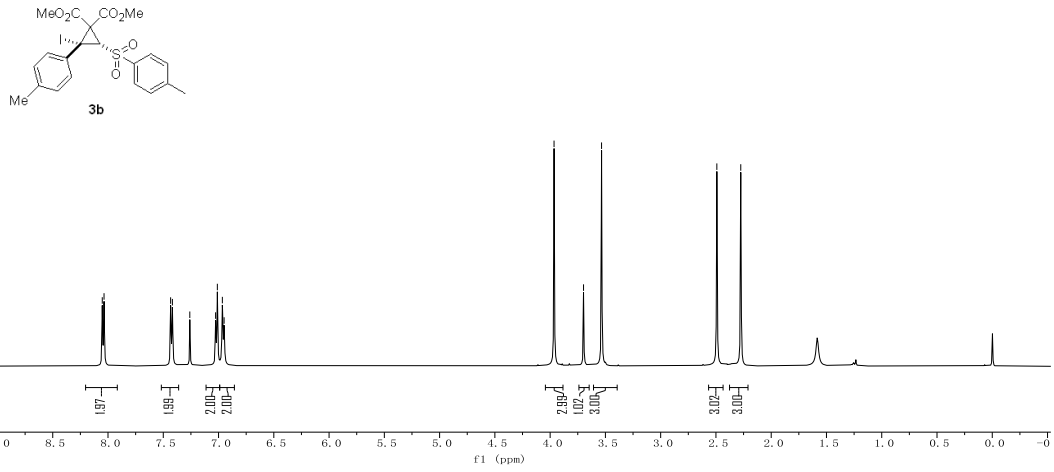
6.950
3.965
3.698
3.535
2.492
2.275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CO2Me
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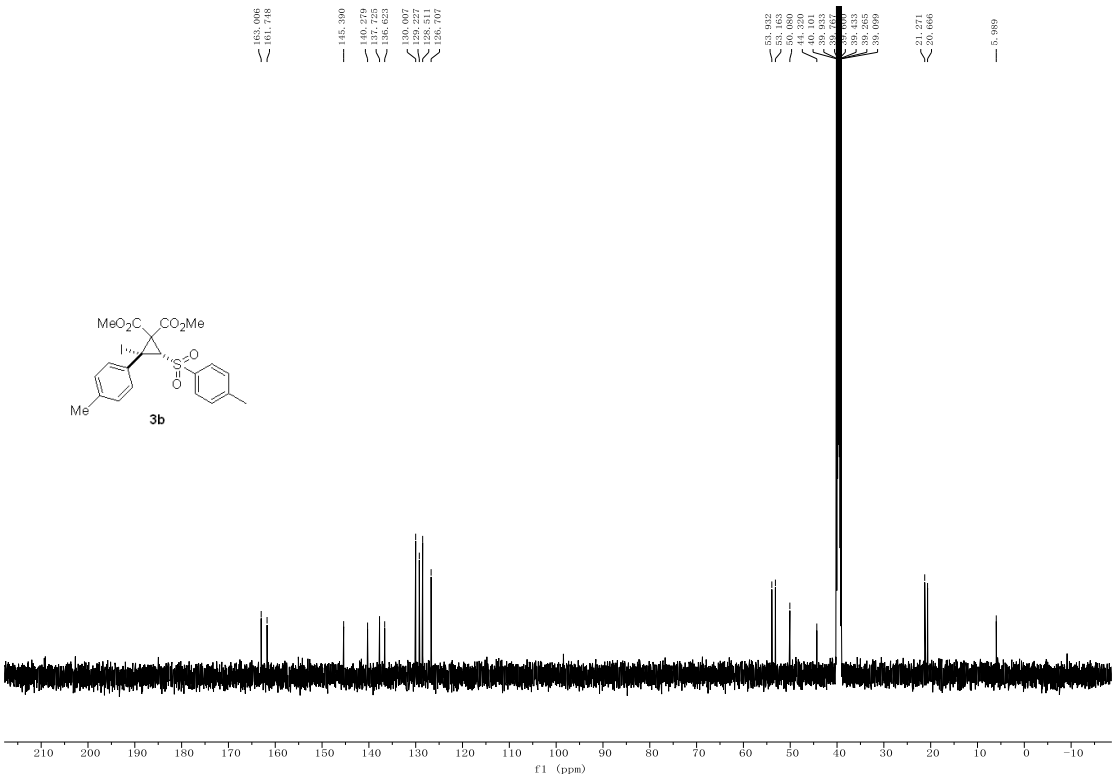
3.02
3.00
f1 (ppm)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39.767
39.600
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I
S
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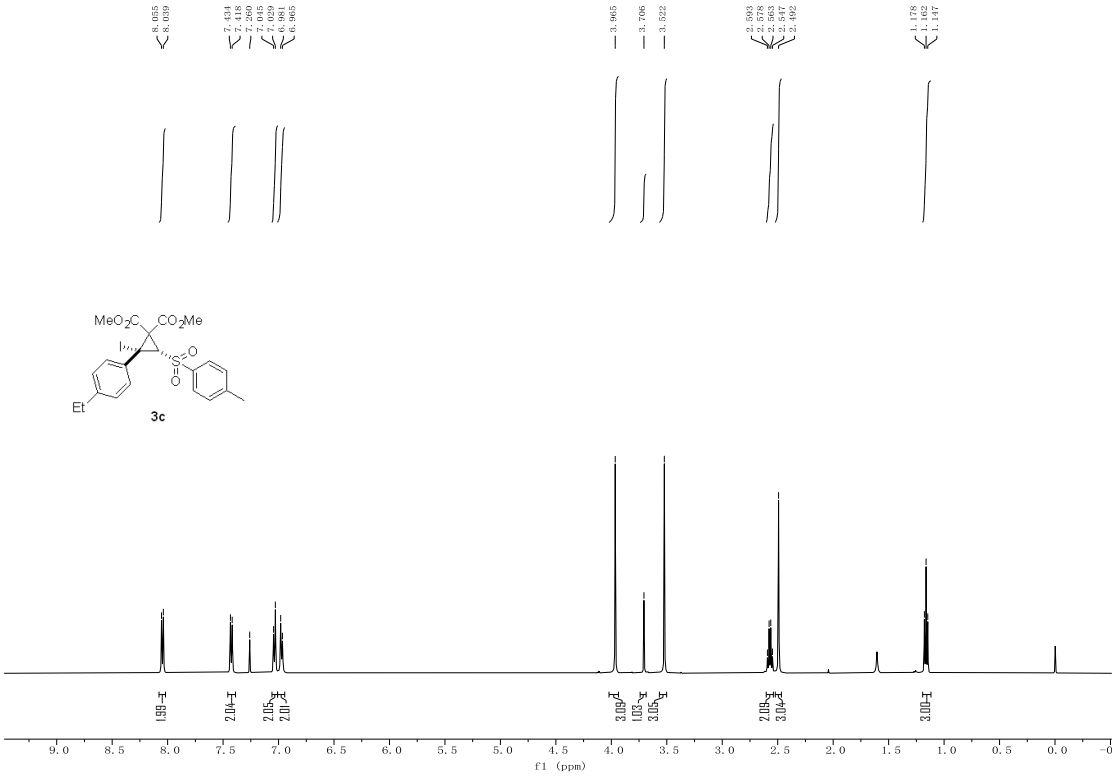
O
Me
3b
f1 (ppm)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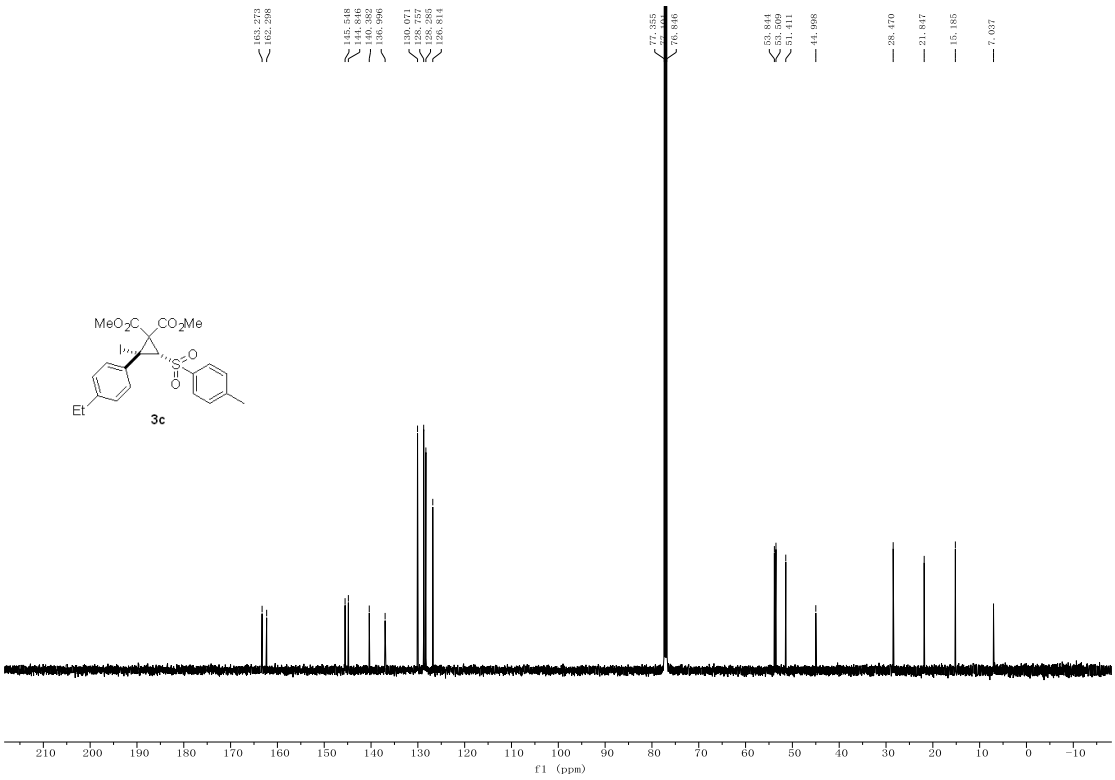
1.162
1.147
MeO2C
CO2Me
I
S
O
O
Et
3c
1.93
2.04
2.05
2.01
3.09
1.03
3.05
2.19
3.04
3.00
f1 (ppm)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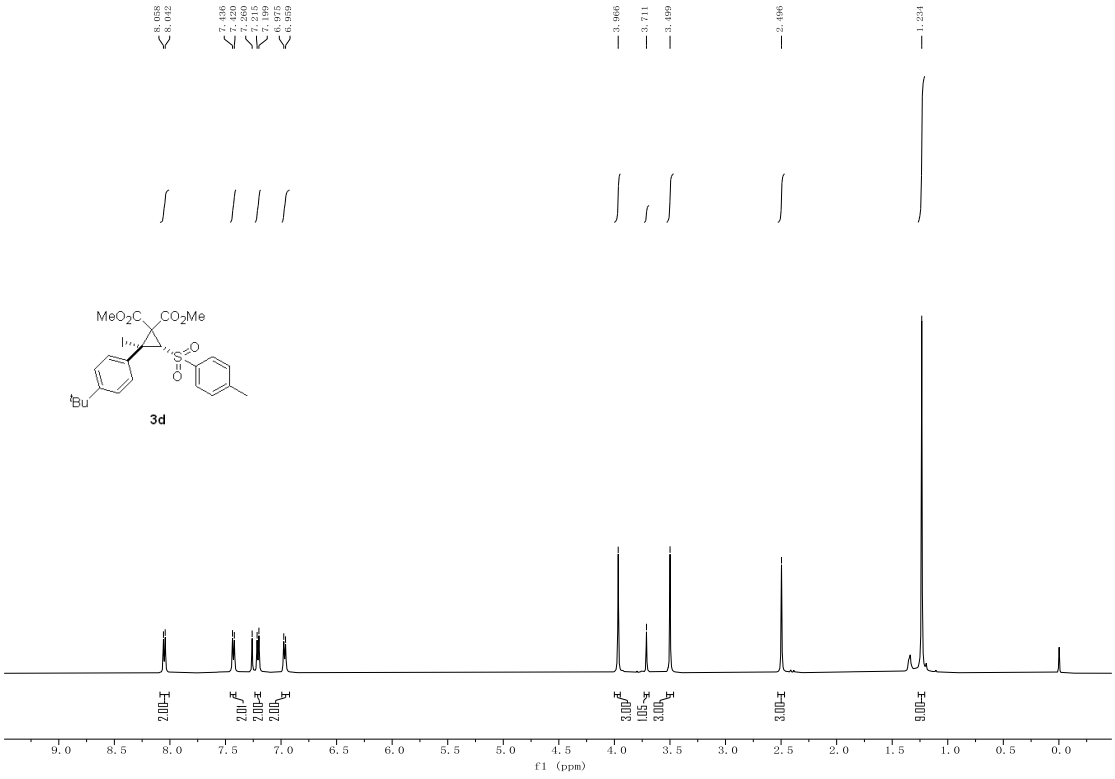
145.548
144.846
140.382
136.966
130.071
128.757
128.285
126.814
77.355
77.044
76.846
53.844
53.509
51.411
44.998
28.470
21.847
15.185
7.037
MeO2C
CO2Me
Et
3c
f1 (ppm)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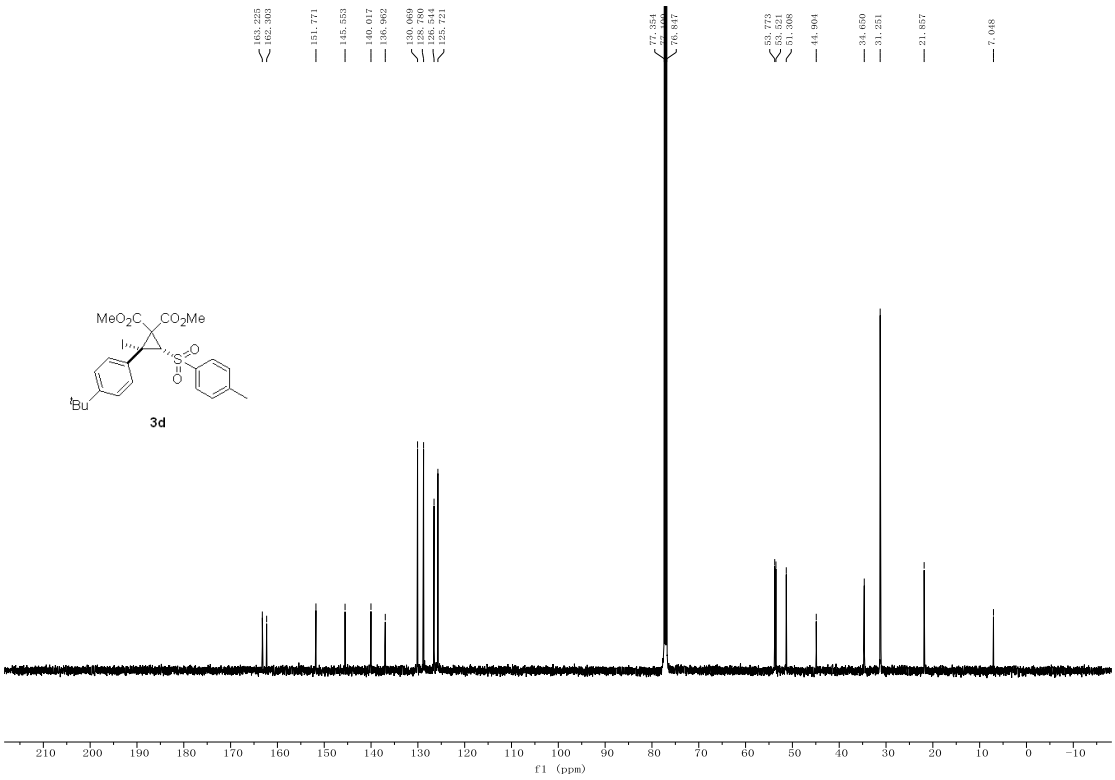
8.042
7.436
7.420
7.260
7.245
7.198
6.975
6.959
3.966
3.711
3.499
2.496
1.234
MeO2C
CO2Me
tBu
3d
2.00
2.01
2.00
2.00
3.00
1.05
3.00
3.00
9.00
f1 (ppm)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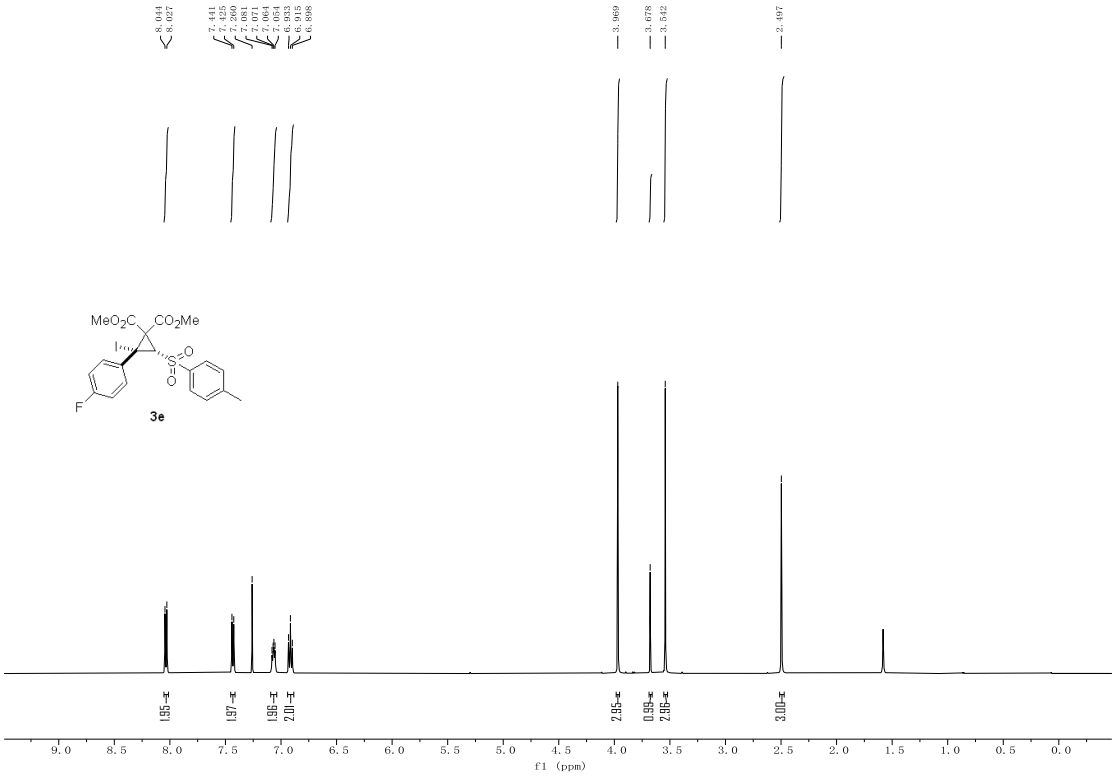
77.354
77.040
76.847
53.773
53.521
51.308
44.904
34.650
31.251
21.857
7.048
MeO2C
CO2Me
tBu
3d
f1 (ppm)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7.435
7.260
7.081
7.071
7.064
7.054
6.933
6.915
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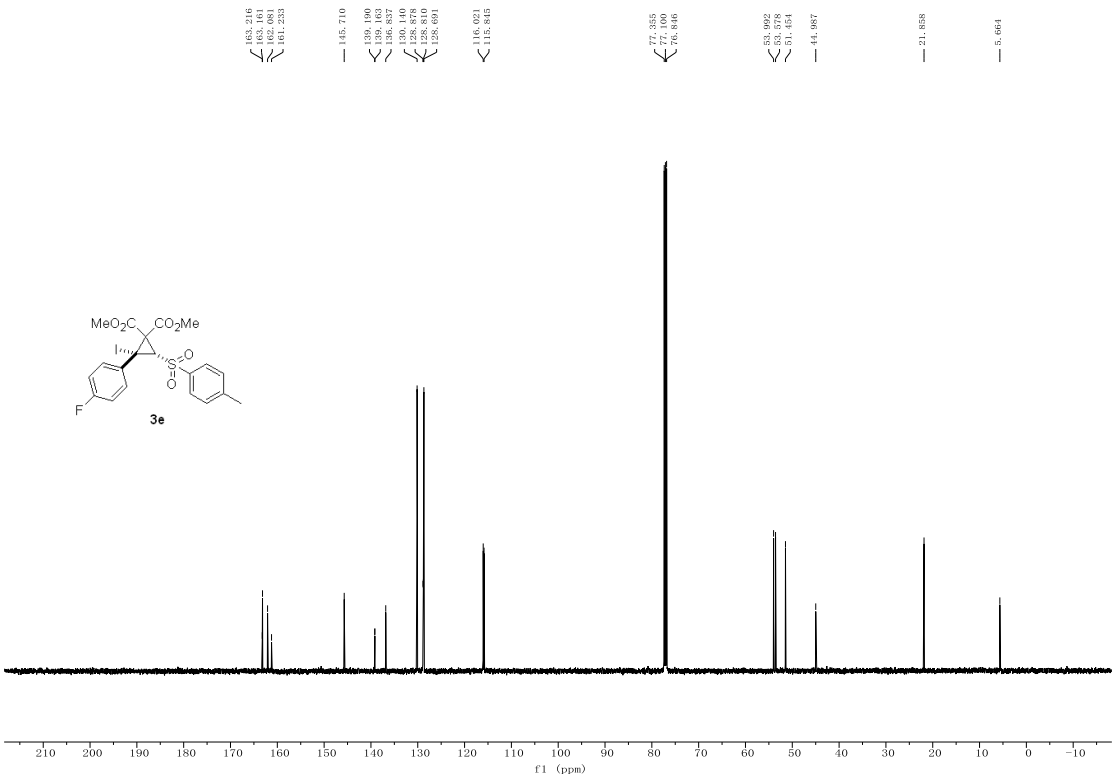
3.969
3.678
3.542
2.497
MeO2C
CO2Me
F
3e
1.95
1.97
1.96
2.01
2.95
0.99
2.95
3.00
f1 (ppm)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128.878
128.810
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116.021
115.845
77.355
77.100
76.846
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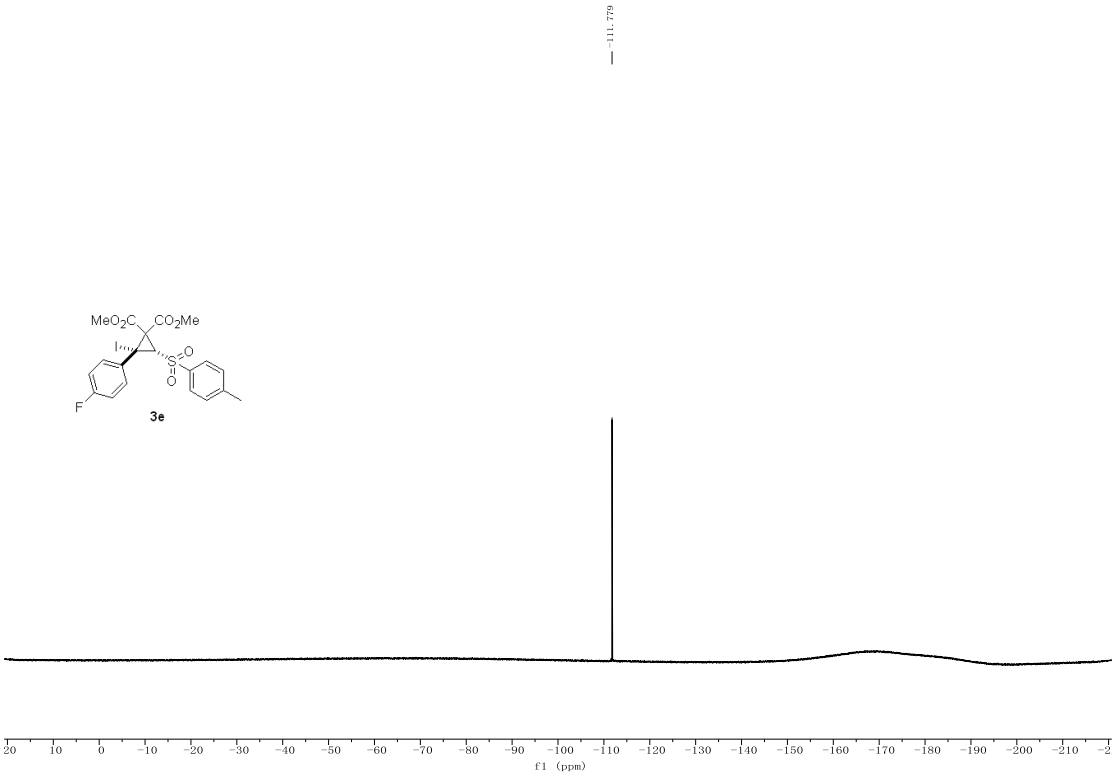
53.578
51.454
44.987
21.858
5.664
MeO2C
CO2Me
F
3e
f1 (ppm)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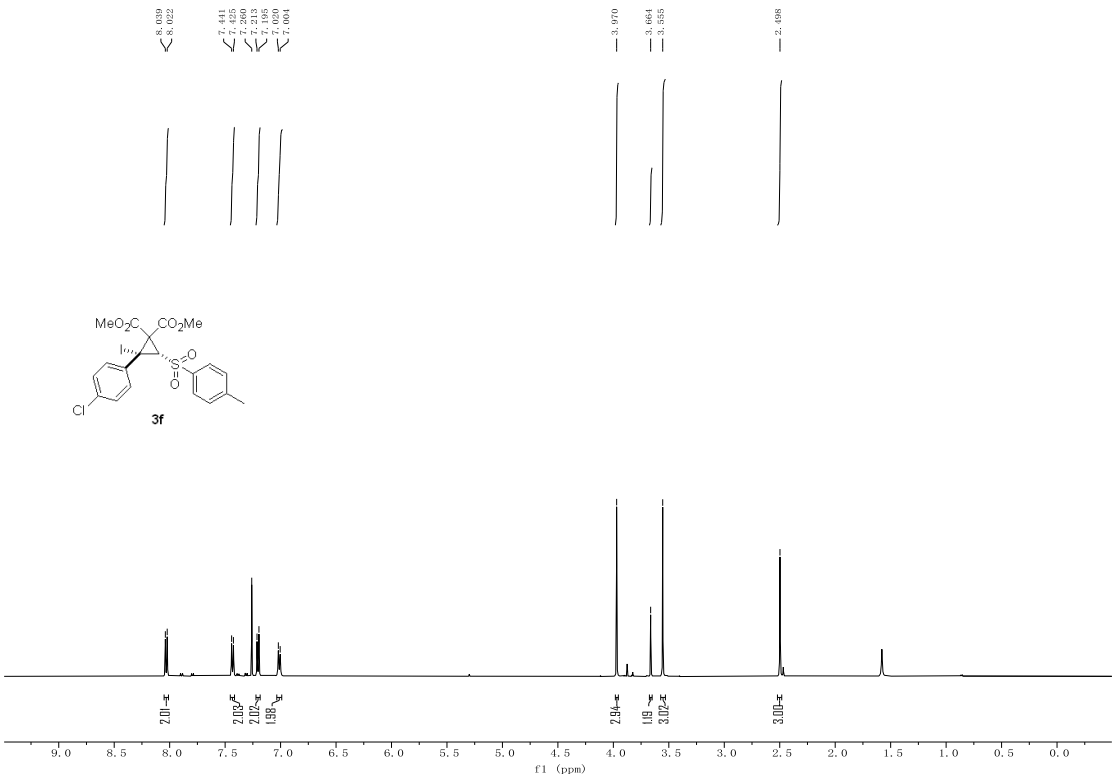
CO2Me
F
3e
f1 (ppm)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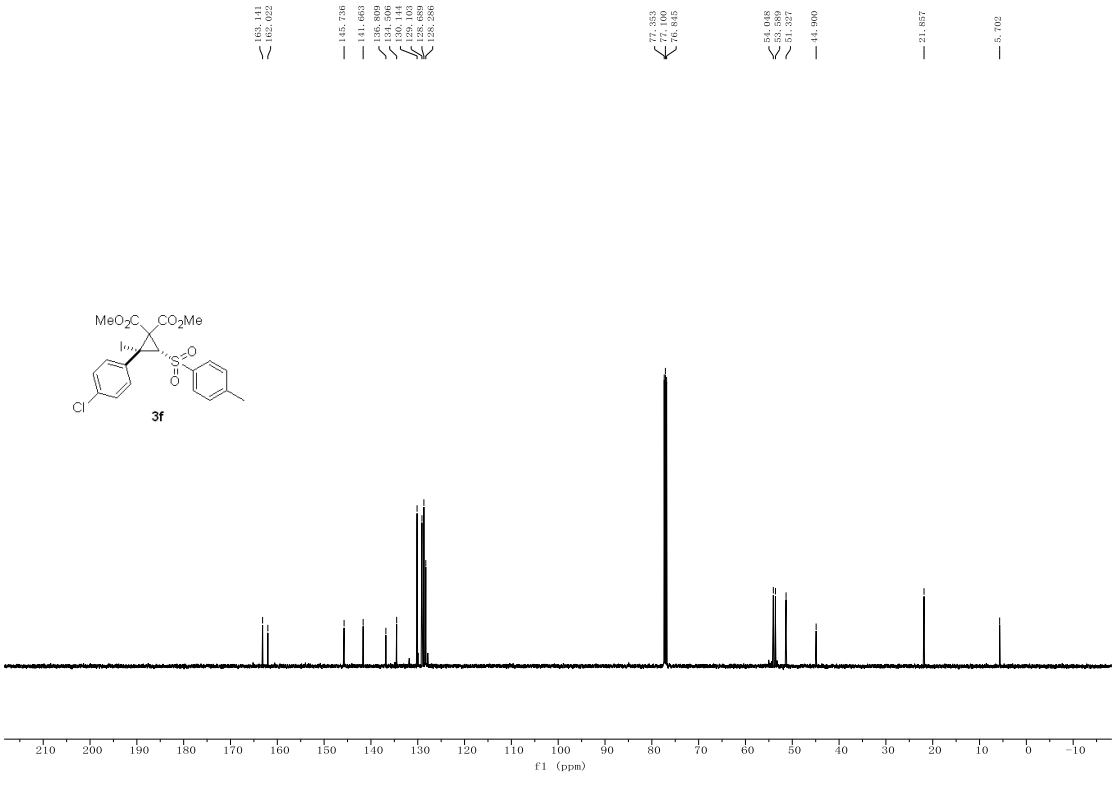
8.022
7.441
7.425
7.260
7.213
7.195
7.030
7.004
3.970
3.664
3.555
2.498
MeO2C
CO2Me
Cl
3f
2.11
2.03
2.02
1.98
2.94
1.19
3.02
3.00
f1 (ppm)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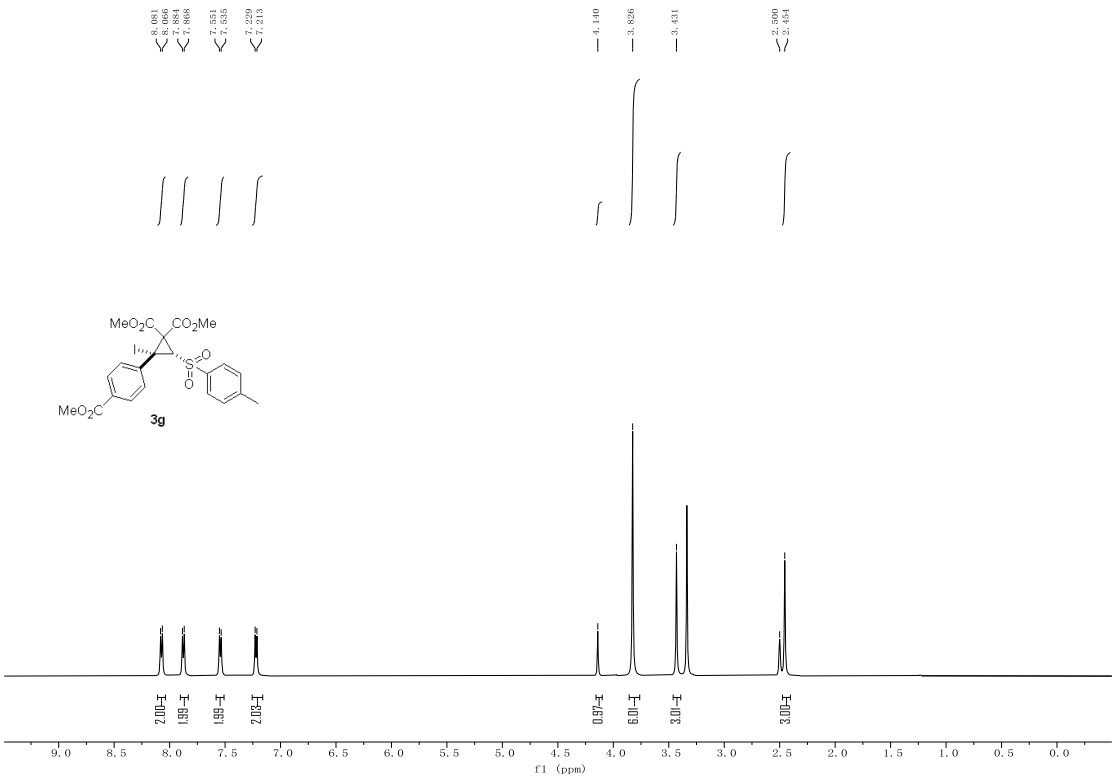
136.809
134.506
130.144
129.403
128.668
128.286
77.353
77.100
76.845
54.048
53.589
51.327
44.900
21.857
5.702
MeO2C
CO2Me
Cl
3f
f1 (ppm)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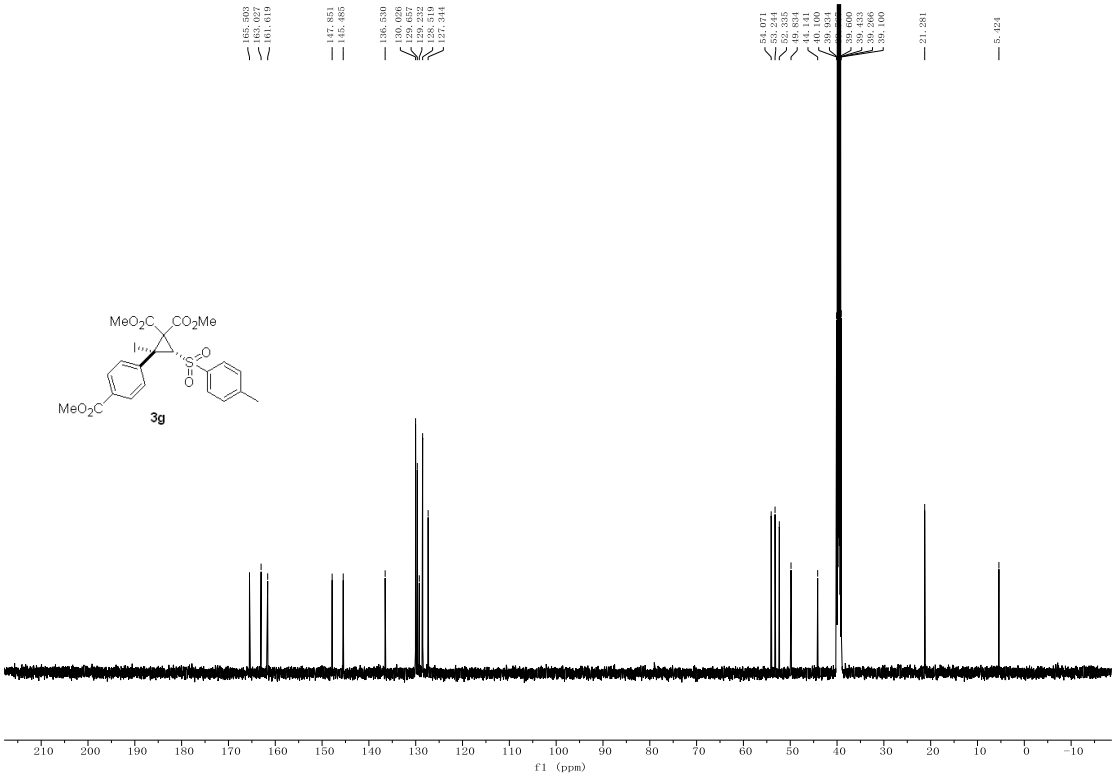
8.066
7.884
7.868
7.551
7.535
7.229
7.213
4.140
3.836
3.431
2.590
2.454
MeO2C
CO2Me
I
S
O
O
MeO2C
3g
2.00
1.98
1.59
2.02
0.97
6.00
3.00
3.00
f1 (ppm)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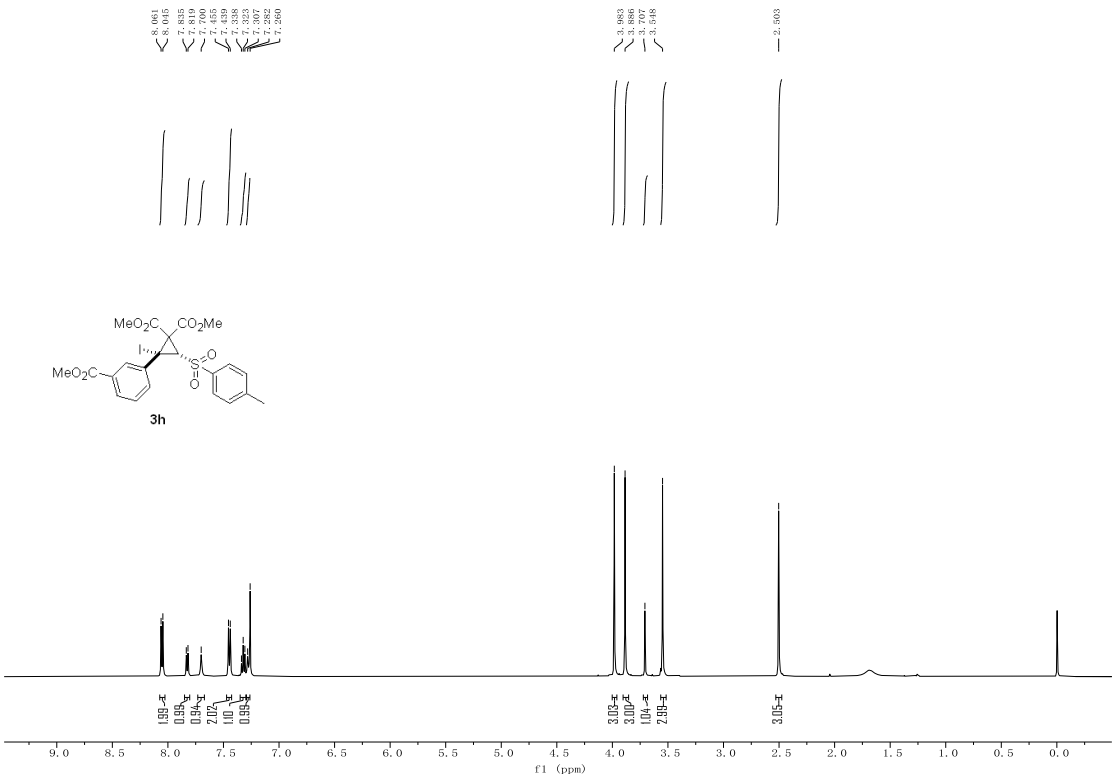
163.027
161.619
147.851
145.485
136.530
130.026
129.657
129.252
128.519
127.344
54.071
53.244
52.835
49.834
44.141
40.100
39.904
39.600
39.433
39.266
39.100
21.281
5.424
MeO2C
CO2Me
I
S
O
O
MeO2C
3g
f1 (ppm)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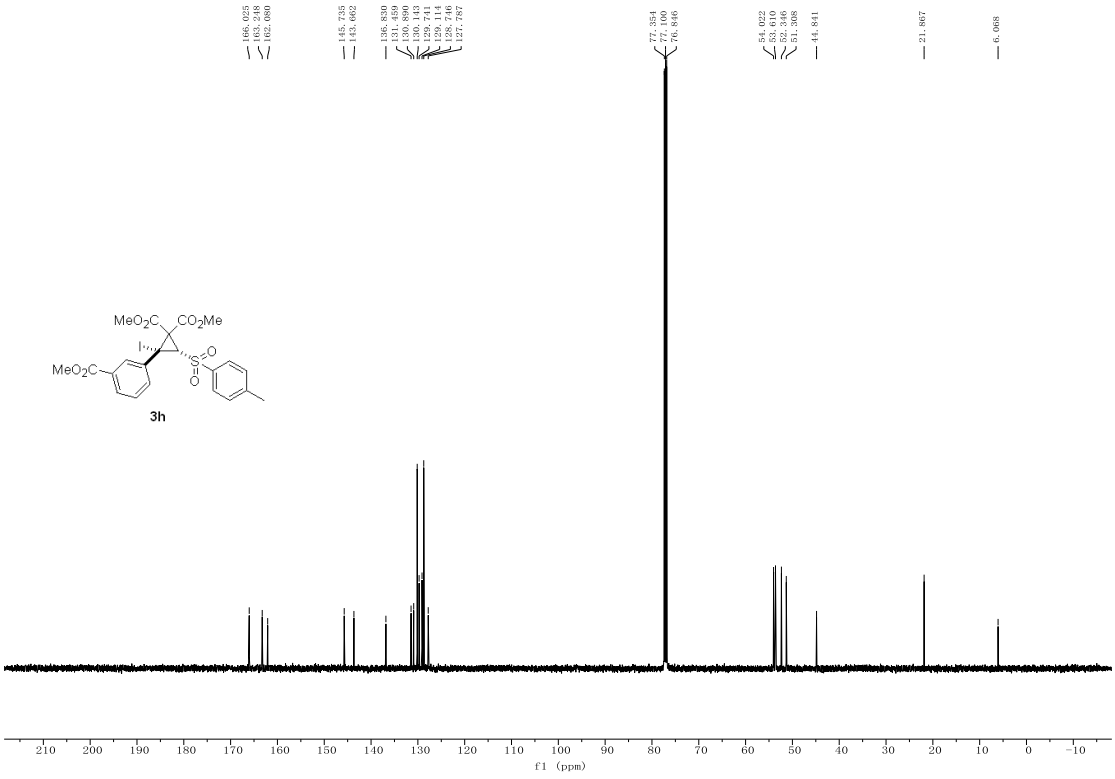
8.045
7.835
7.819
7.700
7.455
7.434
7.338
7.323
7.307
7.282
7.260
3.983
3.966
3.707
3.548
2.503
MeO2C
CO2Me
I
S
O
O
MeO2C
3h
1.98
0.99
0.94
2.02
1.00
0.99
3.03
3.00
1.04
2.89
3.05
f1 (ppm)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162.080
145.735
143.662
136.830
131.459
130.890
130.143
129.741
129.114
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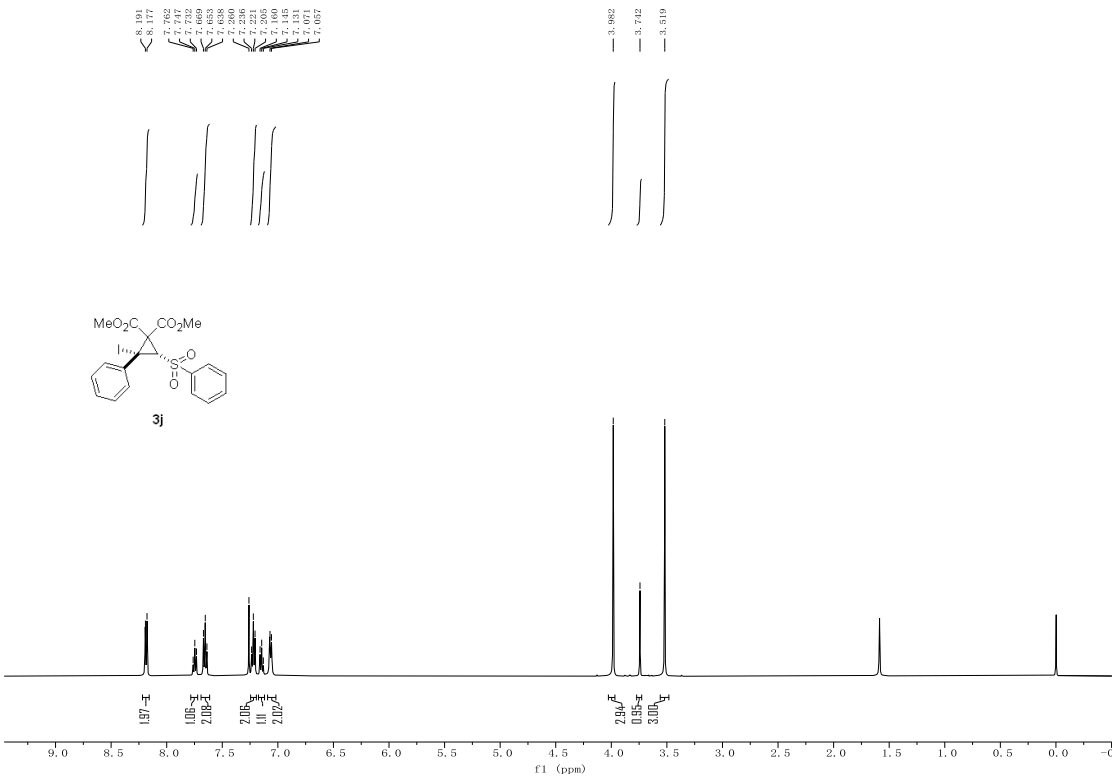
127.787
77.354
77.100
76.846
54.022
53.040
52.346
51.308
44.841
21.867
6.068
MeO2C
CO2Me
I
S
O
O
MeO2C
3h
f1 (ppm)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8.177
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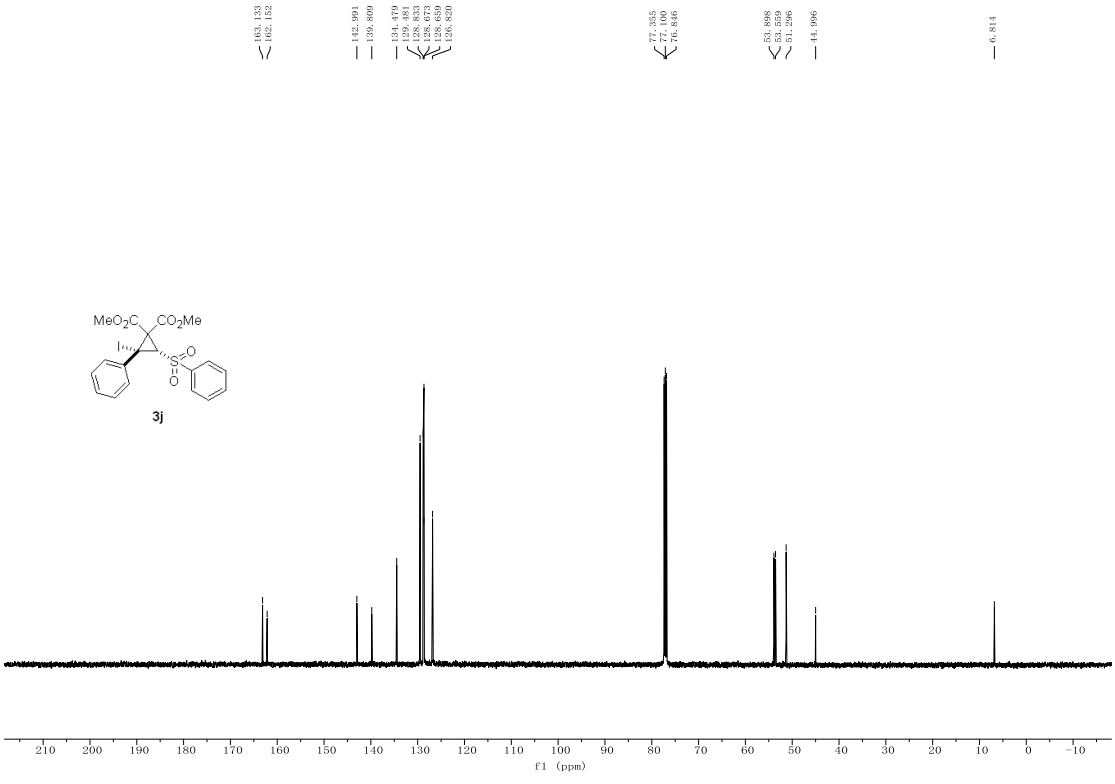
7.747
7.732
7.669
7.655
7.638
7.260
7.236
7.221
7.205
7.160
7.145
7.131
7.071
7.057
3.982
3.742
3.519
MeO2C
CO2Me
3j
1.97
1.06
2.08
2.05
1.11
2.02
2.94
0.95
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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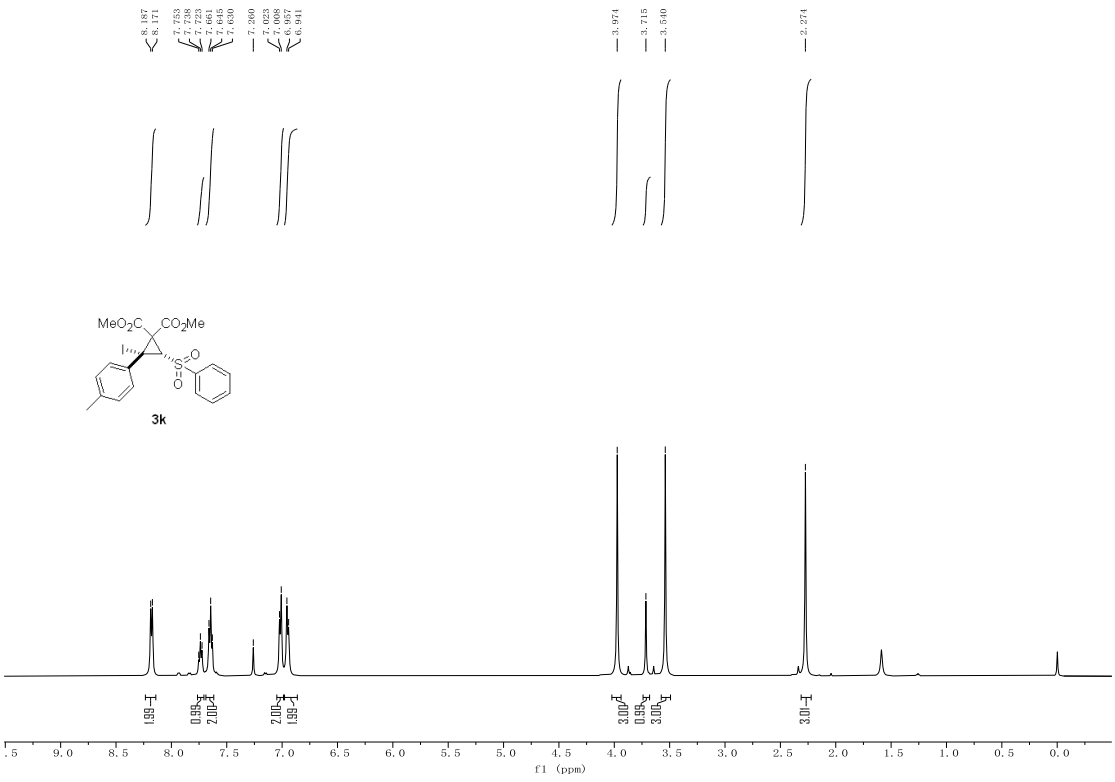
142.991
139.809
134.479
129.481
128.833
128.673
128.659
126.850
77.355
77.100
76.846
53.898
53.559
51.296
44.996
6.814
MeO2C
CO2Me
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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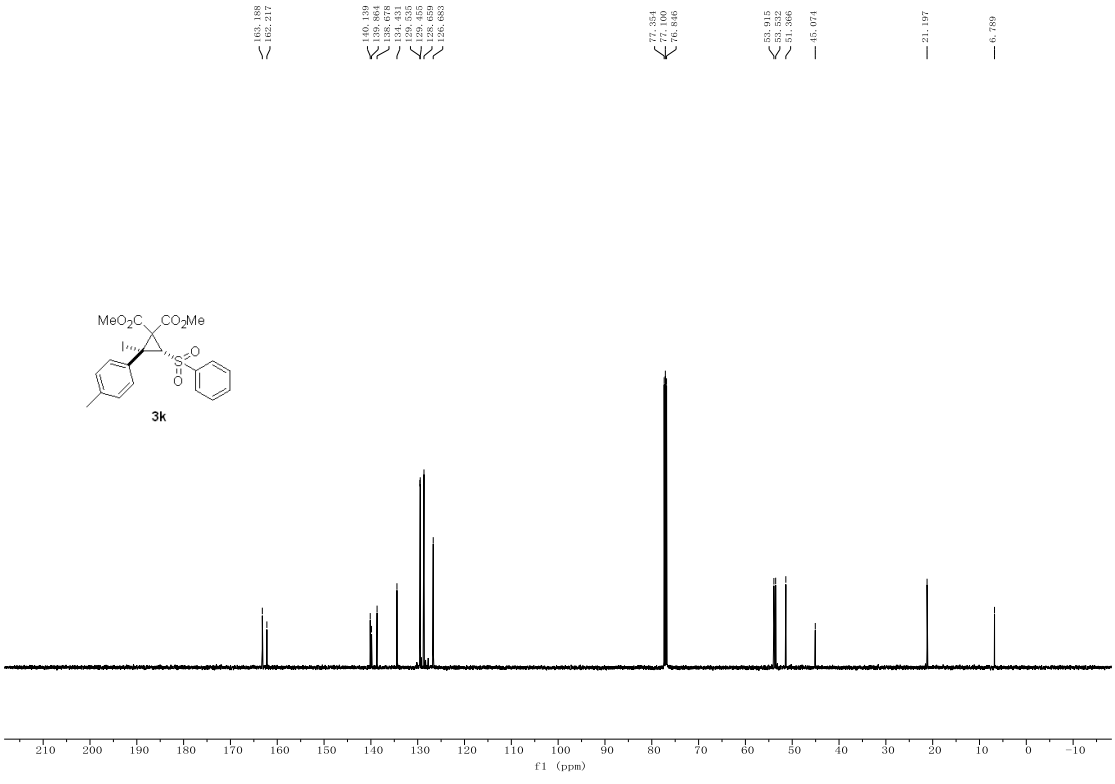
8.171
7.753
7.738
7.723
7.661
7.645
7.630
7.290
7.023
7.008
6.957
6.941
3.974
3.715
3.540
2.274
MeO2C
CO2Me
3k
1.98
0.89
2.00
2.00
1.99
3.00
0.95
3.00
3.01
f1 (ppm)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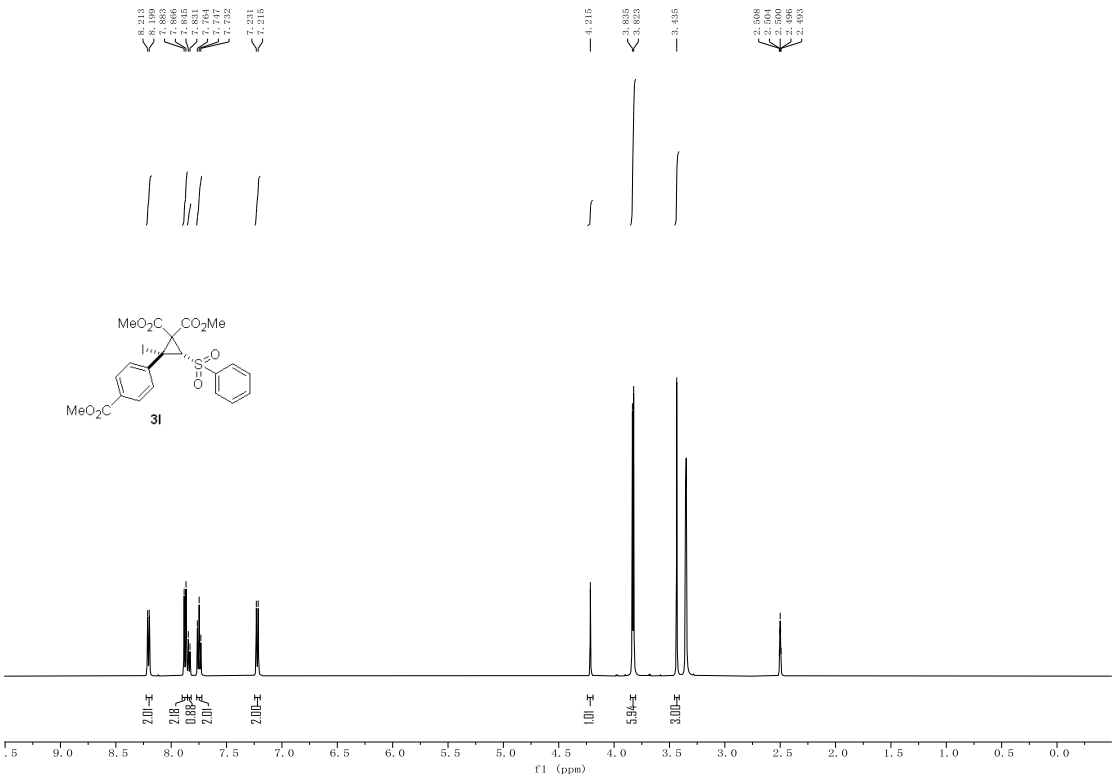
162.247
140.139
139.864
138.678
134.431
130.535
129.455
128.659
126.683
77.354
77.100
76.846
53.915
53.532
51.366
45.074
21.197
6.789
MeO2C
CO2Me
3k
f1 (ppm)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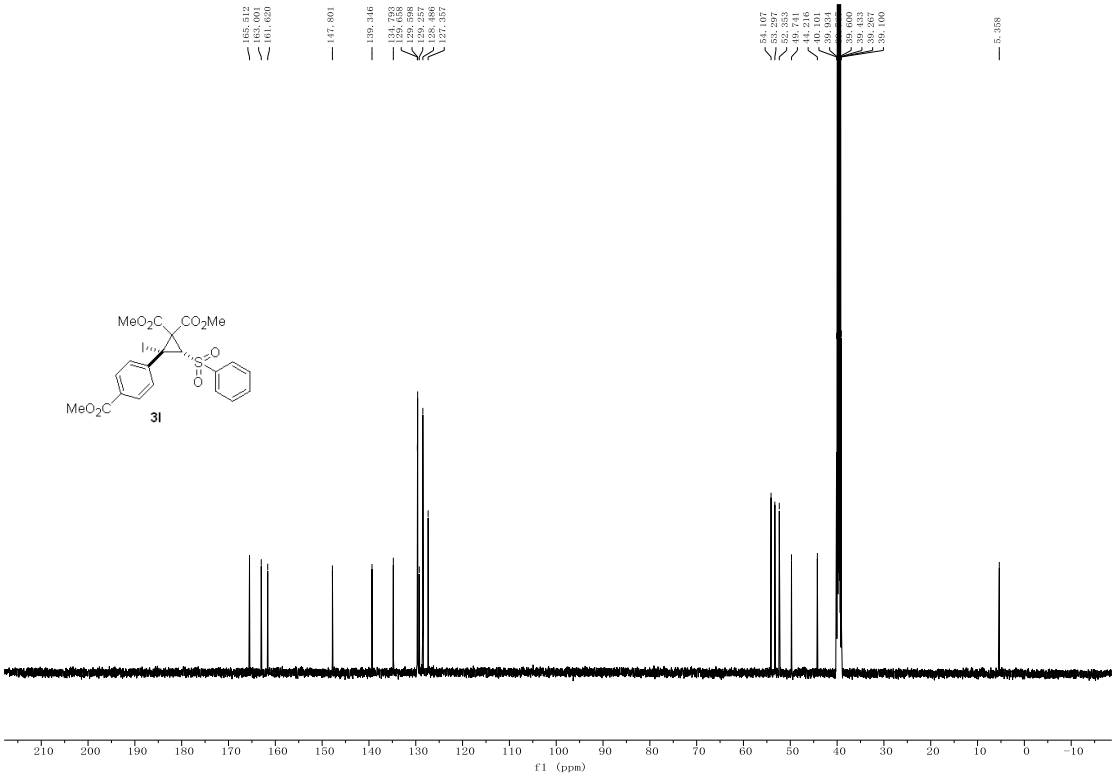
8.199
7.883
7.866
7.845
7.831
7.764
7.747
7.732
7.231
7.215
4.215
3.835
3.823
3.435
2.508
2.504
2.500
2.496
2.493
MeO2C
CO2Me
I
O
O
O
MeO2C
3l
2.01
2.08
0.88
2.01
2.00
1.01
5.64
3.00
f1 (ppm)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127.357
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53.297
52.953
49.741
44.216
40.101
39.964
39.600
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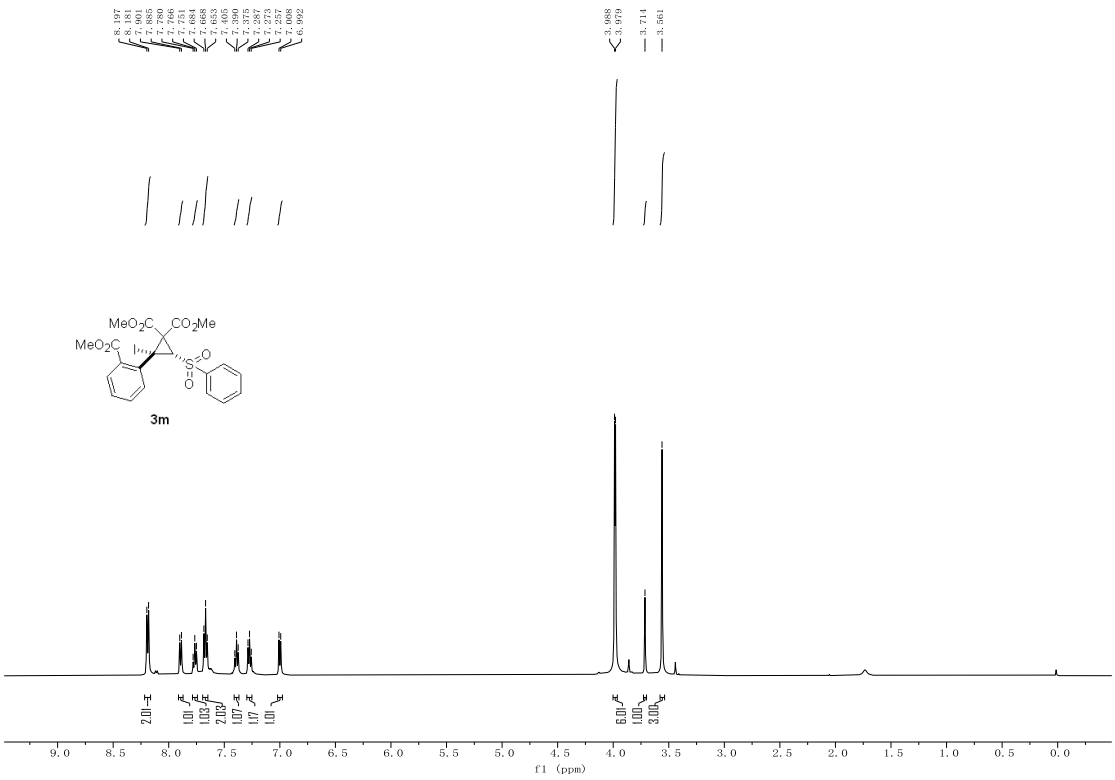
39.267
39.100
5.358
MeO2C
CO2Me
I
O
O
O
MeO2C
3l
f1 (ppm)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7.684
7.668
7.653
7.605
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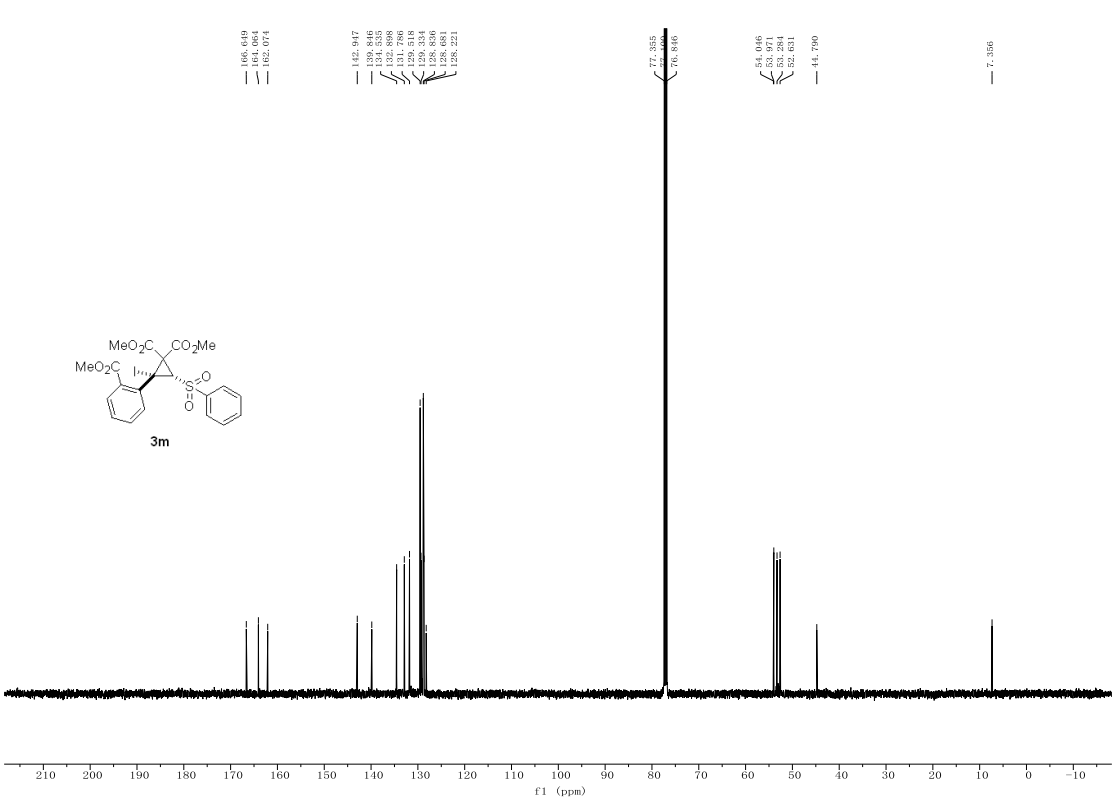
7.375
7.287
7.273
7.257
7.008
6.992
3.988
3.979
3.714
3.561
MeO2C
CO2Me
MeO2C
S
O
O
3m
2.01
1.01
1.03
2.02
1.07
1.17
1.01
6.01
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.254
128.856
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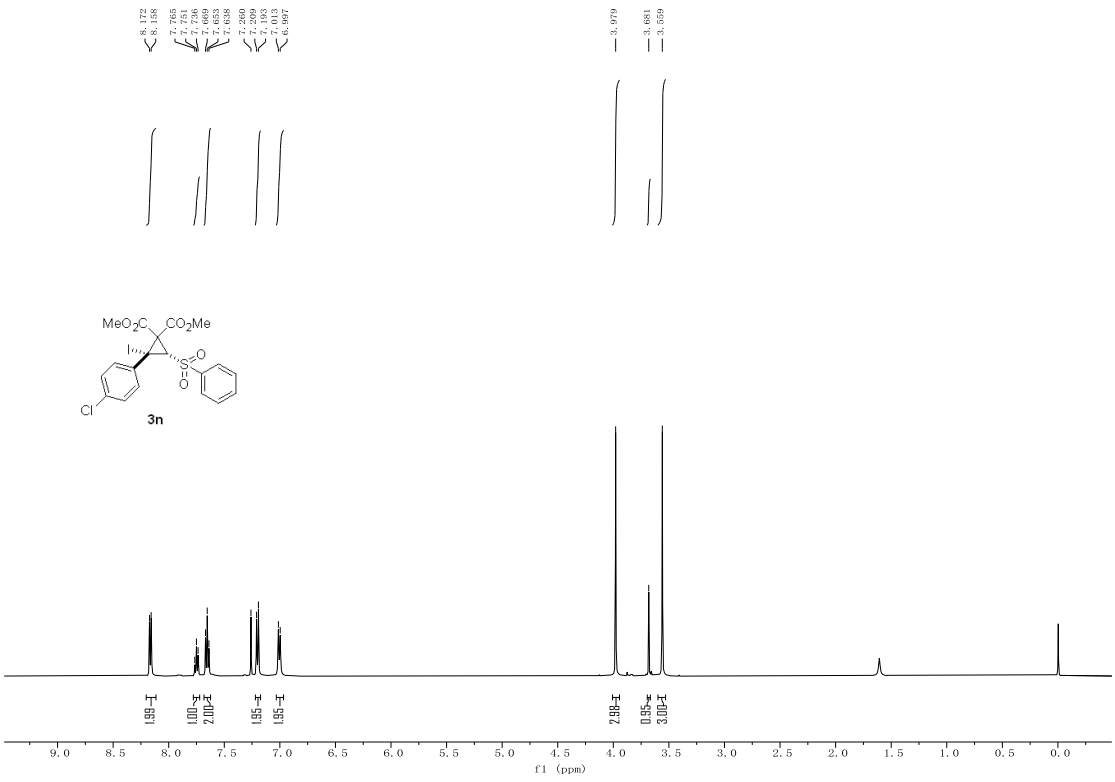
128.221
77.355
77.046
76.846
54.046
53.971
53.284
52.631
44.790
7.356
MeO2C
CO2Me
MeO2C
S
O
O
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.669
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7.638
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7.193
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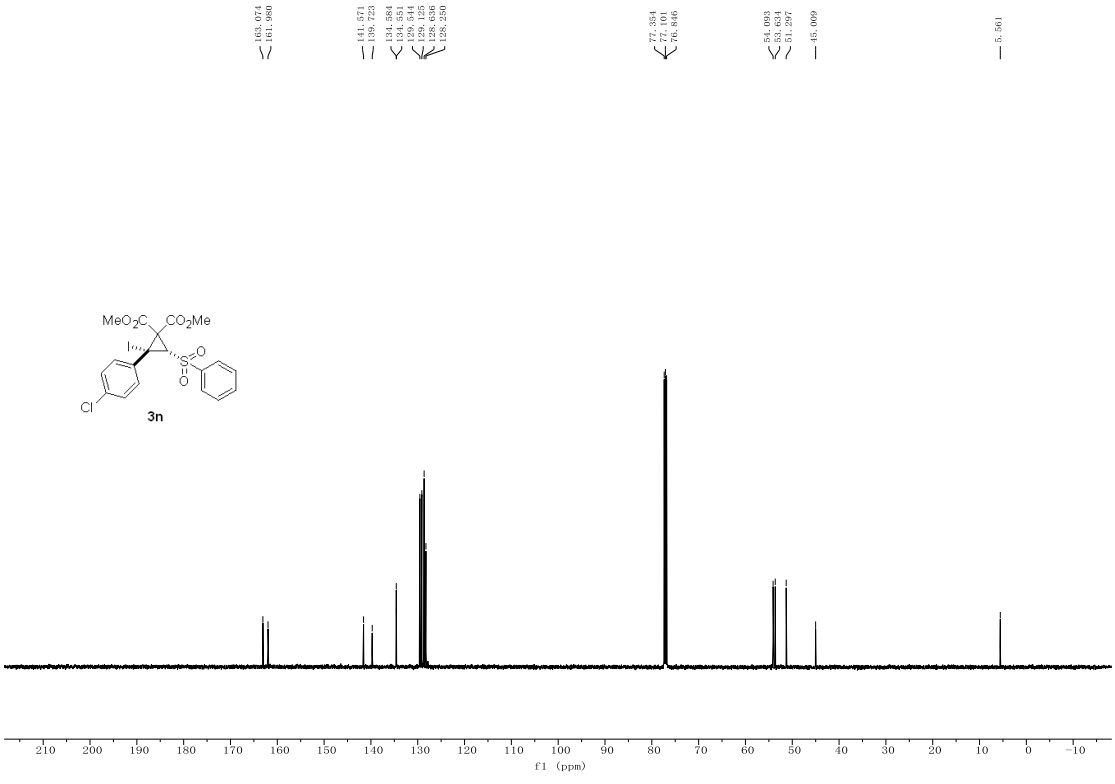
6.997
3.979
3.681
3.559
MeO2C
CO2Me
Cl
3n
1.98
1.00
2.00
1.95
1.95
2.98
0.95
3.00
f1 (ppm)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129.175
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128.250
77.354
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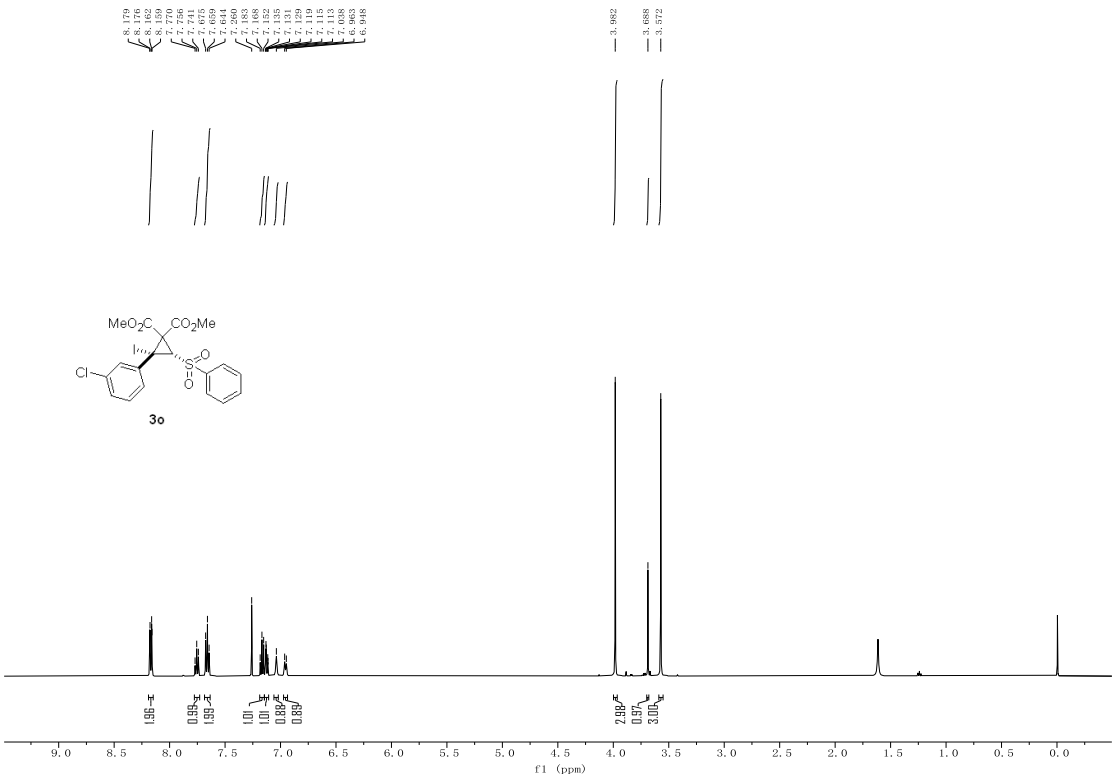
76.846
54.093
53.634
51.297
45.009
5.861
MeO2C
CO2Me
Cl
3n
f1 (ppm)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7.741
7.675
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7.644
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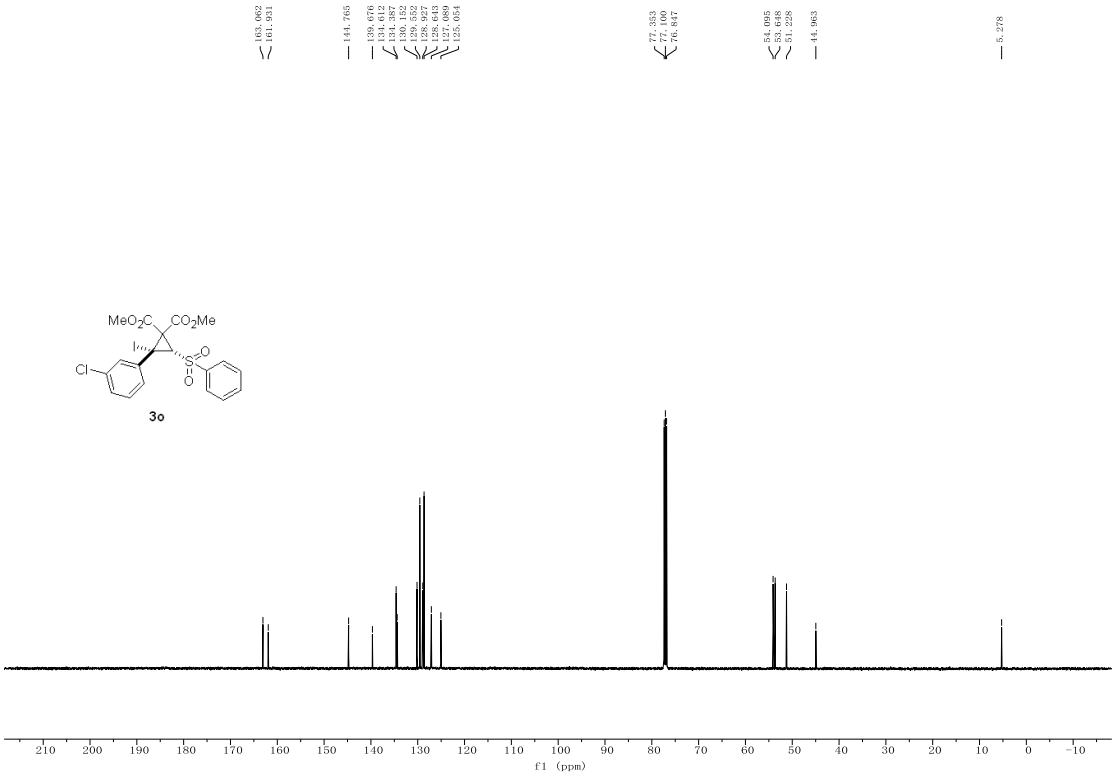
7.183
7.168
7.152
7.135
7.131
7.129
7.119
7.115
7.113
7.038
6.993
6.948
3.982
3.688
3.672
MeO2C
CO2Me
Cl
S
O
O
3o
1.96
0.99
1.99
1.01
1.01
0.88
0.89
2.98
0.97
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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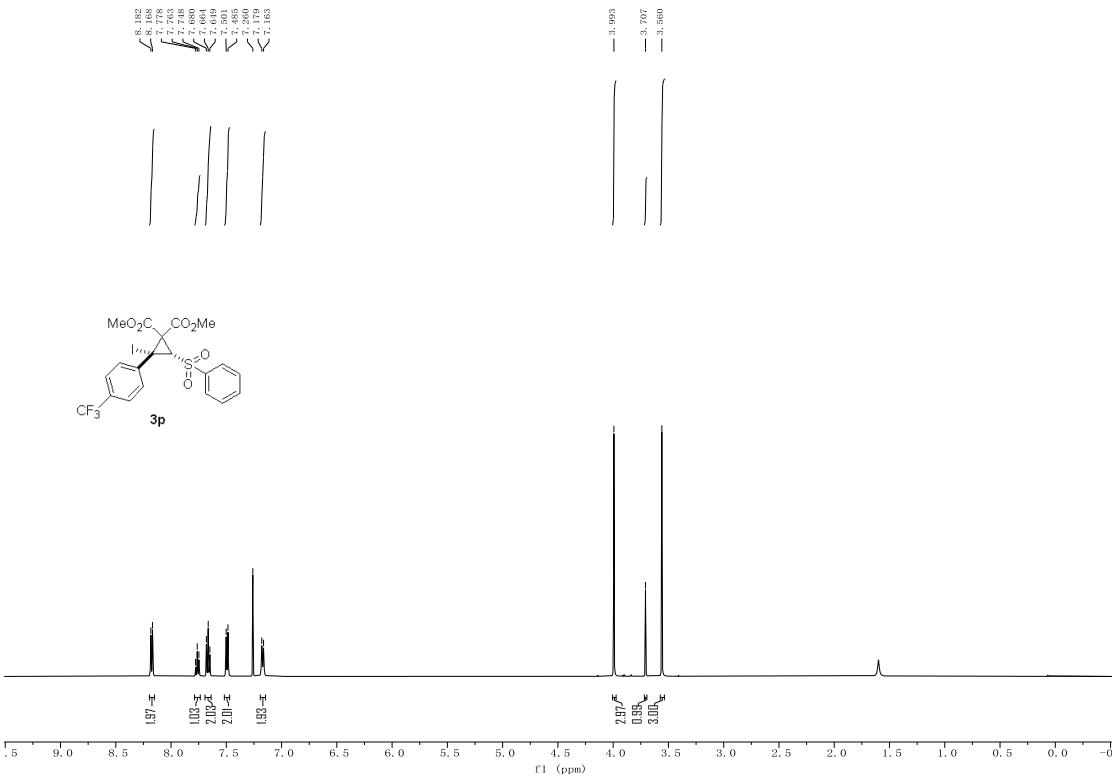
129.552
128.927
128.643
127.089
125.054
77.353
77.100
76.847
54.095
53.648
51.228
44.963
5.278
MeO2C
CO2Me
Cl
S
O
O
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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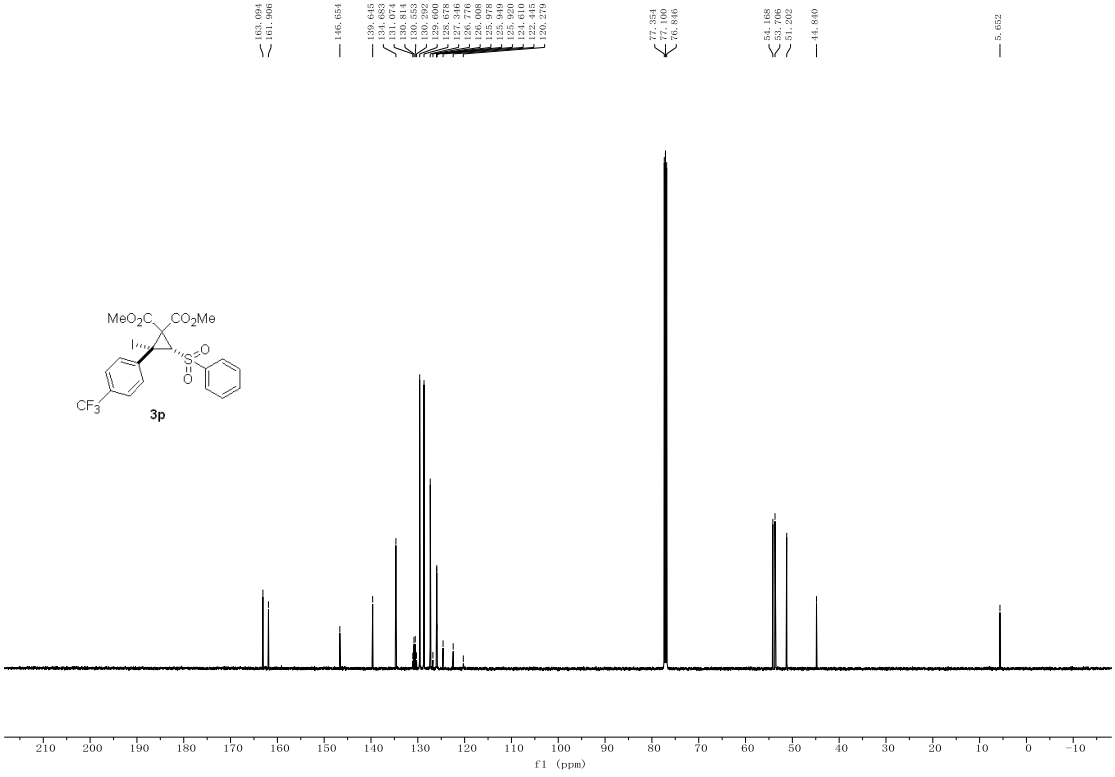
7.680
7.664
7.649
7.631
7.485
7.260
7.179
7.163
3.993
3.707
3.560
MeO2C
CO2Me
O=S=O
CF3
3p
1.97
1.03
2.02
2.01
1.93
2.97
0.95
3.00
f1 (ppm)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130.553
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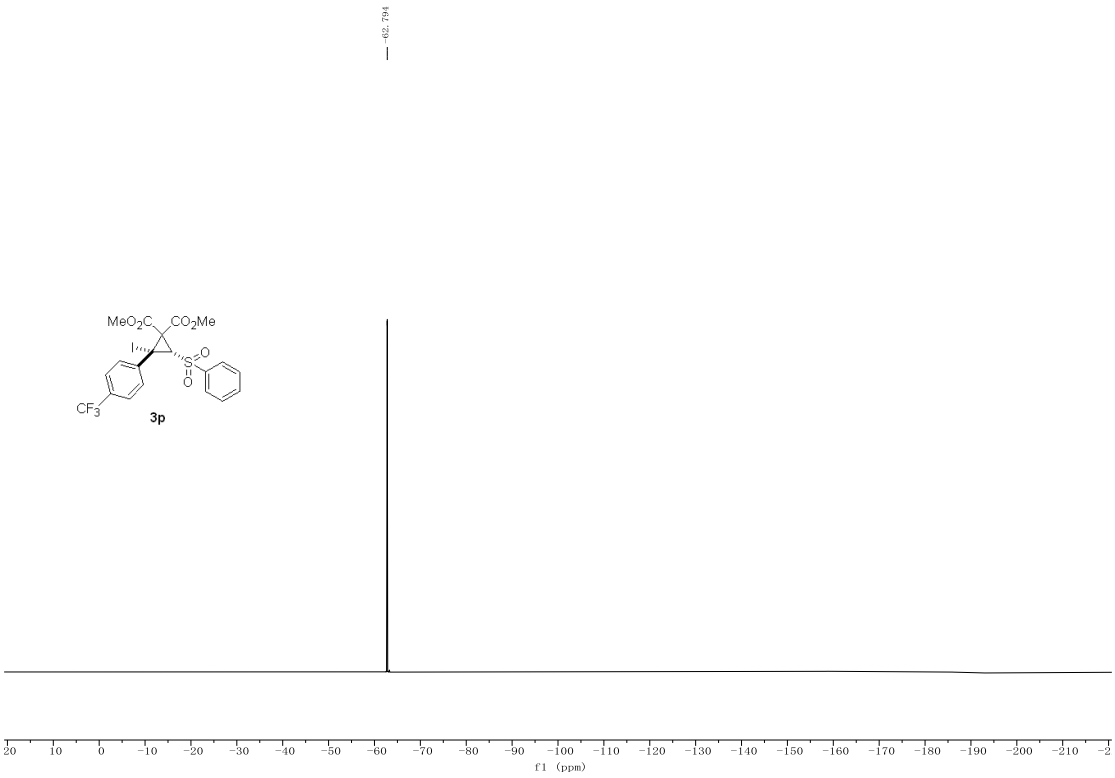
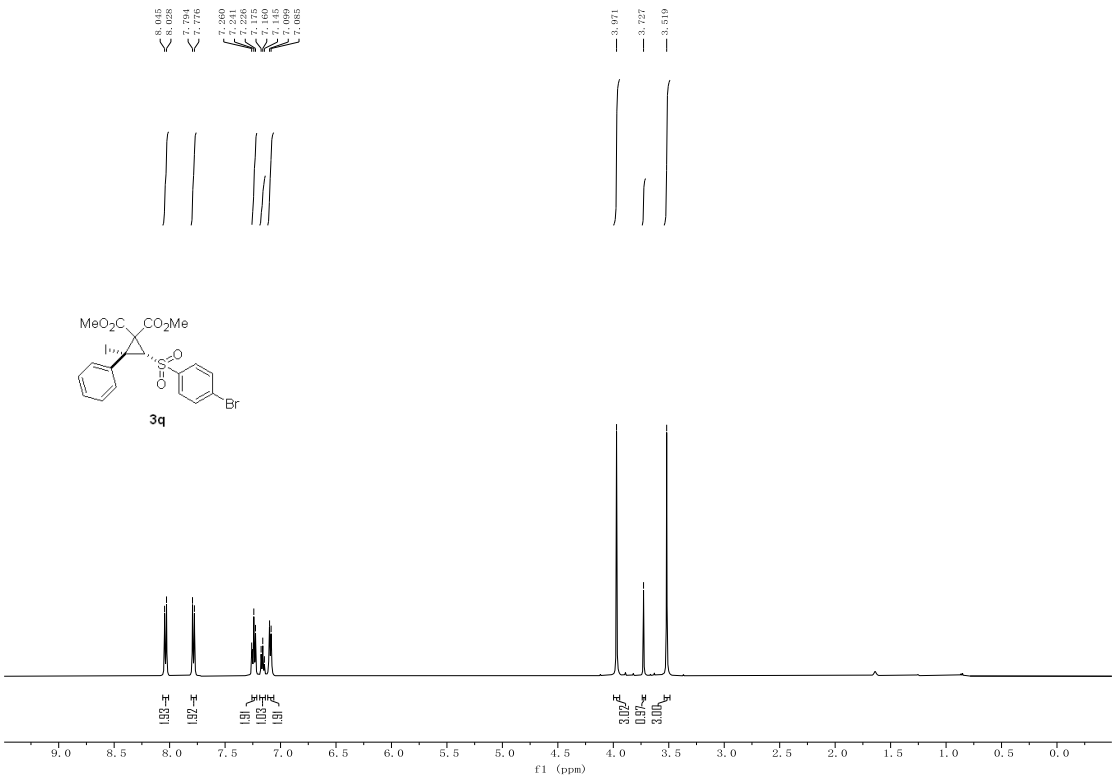
127.346
126.776
126.098
125.978
125.949
125.920
124.610
122.445
120.279
77.354
77.100
76.846
54.168
53.706
51.202
44.840
5.652
MeO2C
CO2Me
O=S=O
CF3
3p
f1 (ppm)


-62.794
MeO2C
CO2Me
CF3
3p
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)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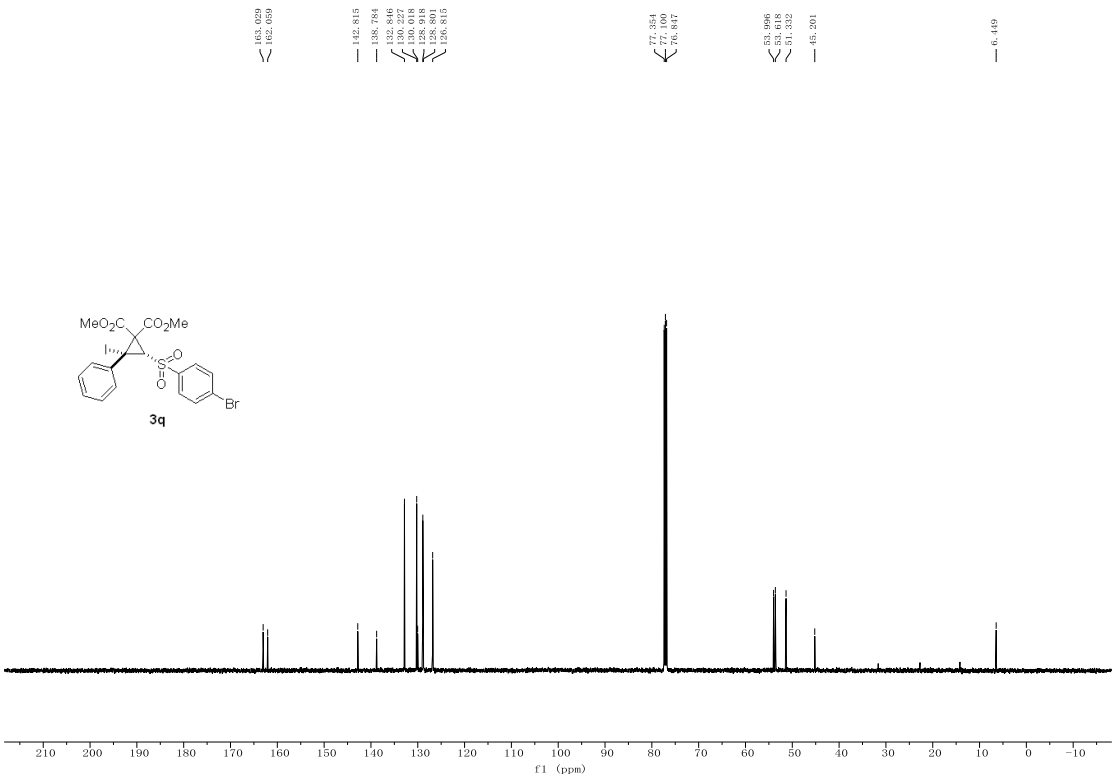
7.794
7.776
7.260
7.241
7.226
7.175
7.165
7.145
7.099
7.085
3.971
3.727
3.519
MeO2C
CO2Me
Br
3q
1.93
1.92
1.91
1.03
1.91
3.02
0.97
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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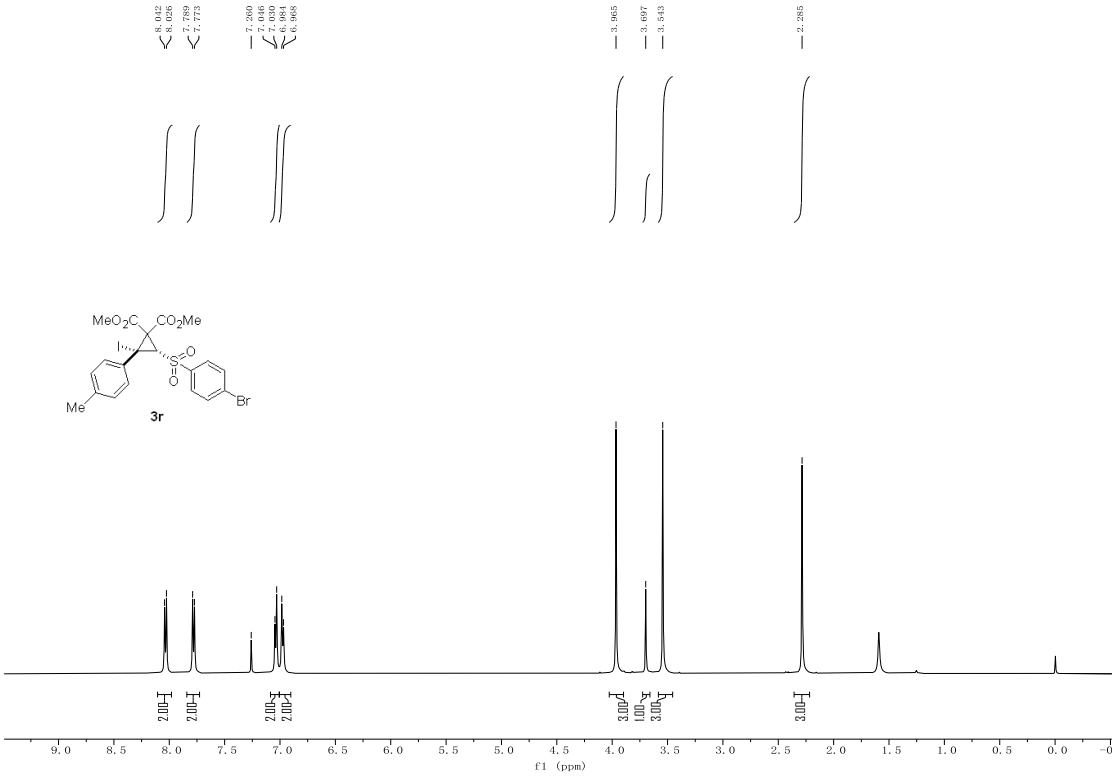
162.059
142.815
138.784
132.846
130.227
130.018
128.918
128.801
126.815
77.354
77.100
76.847
53.996
53.618
51.332
45.201
6.449
MeO2C
CO2Me
O
S
O
Br
3q
f1 (ppm)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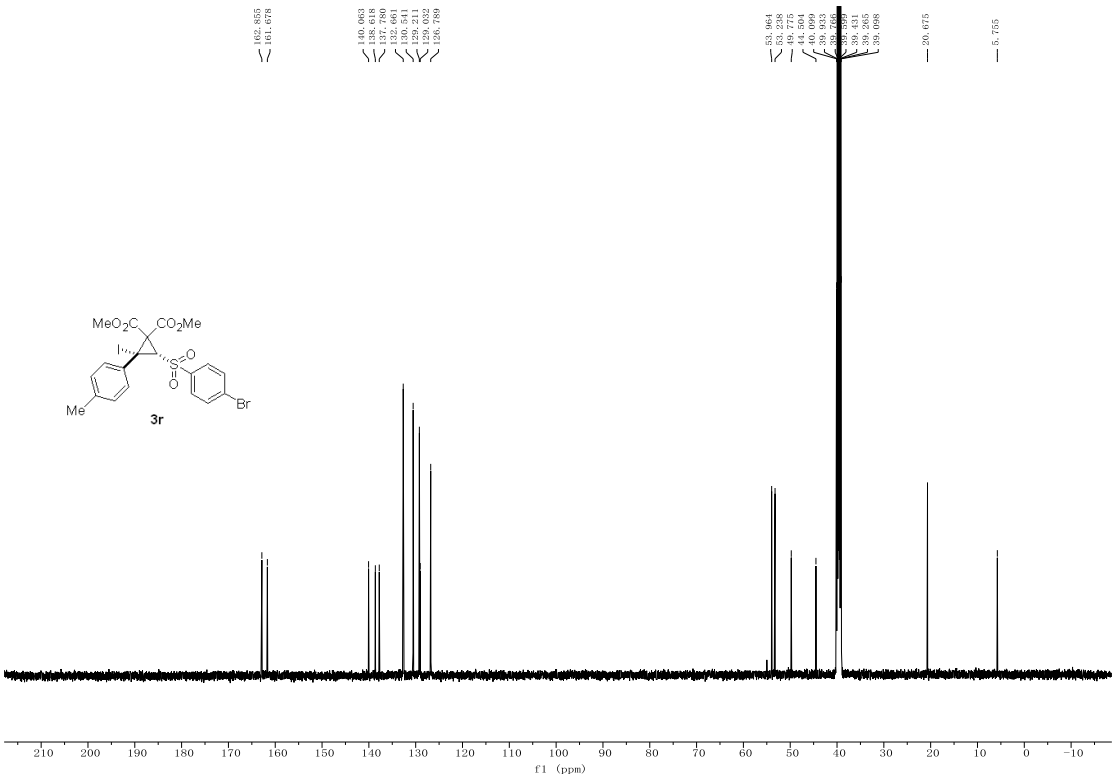
8.026
7.789
7.773
7.260
7.046
7.030
6.984
6.968
3.965
3.697
3.543
2.285
MeO2C
CO2Me
O
S
O
Br
Me
3r
2.00
2.00
2.00
2.00
3.00
1.00
3.00
3.00
f1 (ppm)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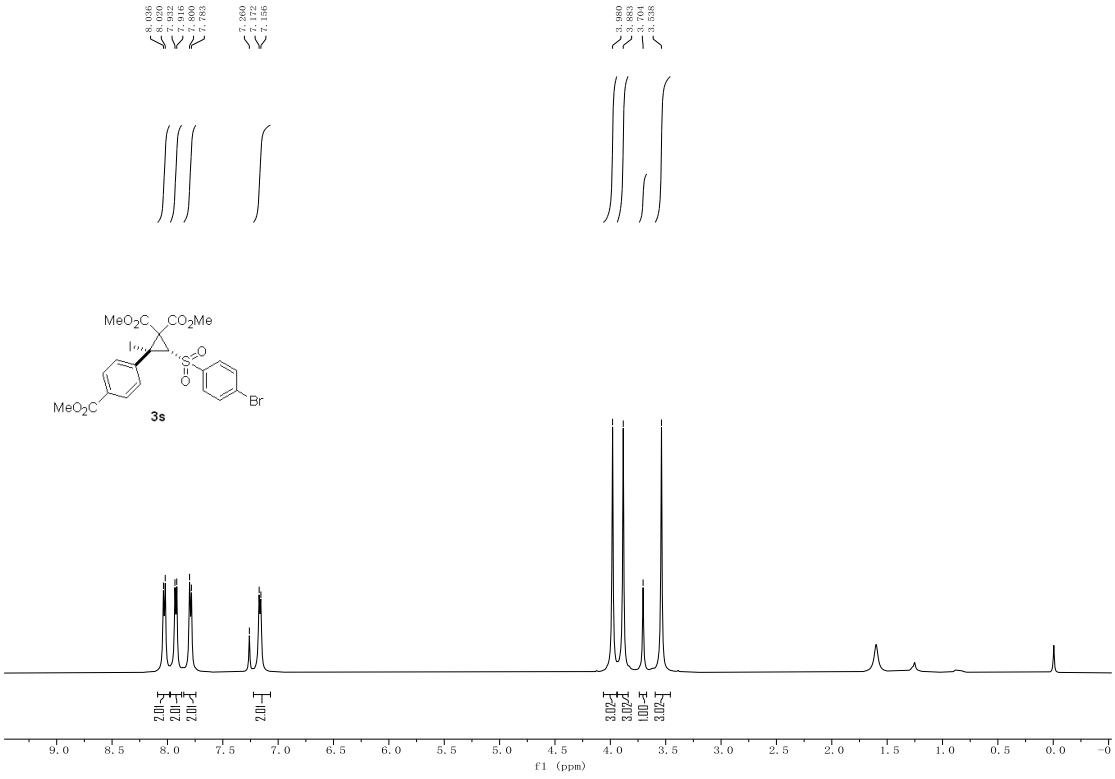
140.063
138.618
137.780
132.661
130.541
129.211
129.032
126.789
53.964
53.238
49.775
41.694
40.069
39.933
39.797
39.661
39.525
39.389
39.253
39.098
20.675
5.755
MeO2C
CO2Me
Me
Br
3r
f1 (ppm)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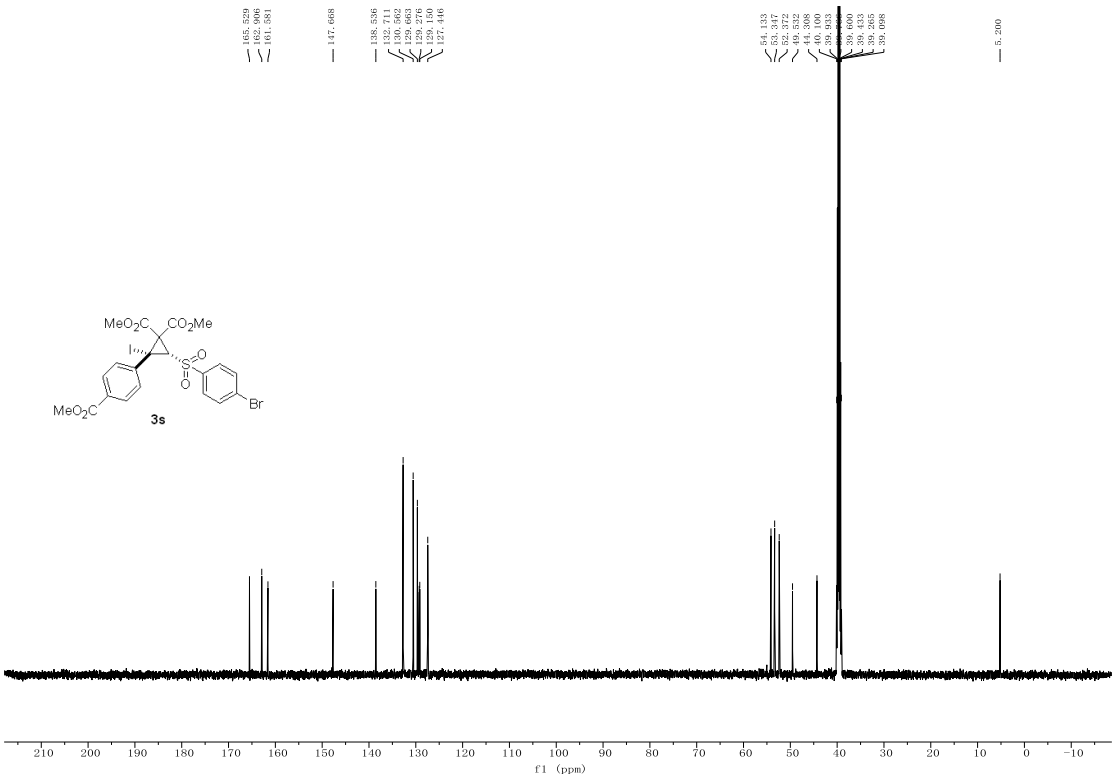
8.020
7.932
7.915
7.800
7.783
7.260
7.172
7.156
3.980
3.885
3.704
3.538
MeO2C
CO2Me
MeO2C
Br
3s
2.01
2.01
2.01
2.01
3.02
3.02
1.00
3.02
f1 (ppm)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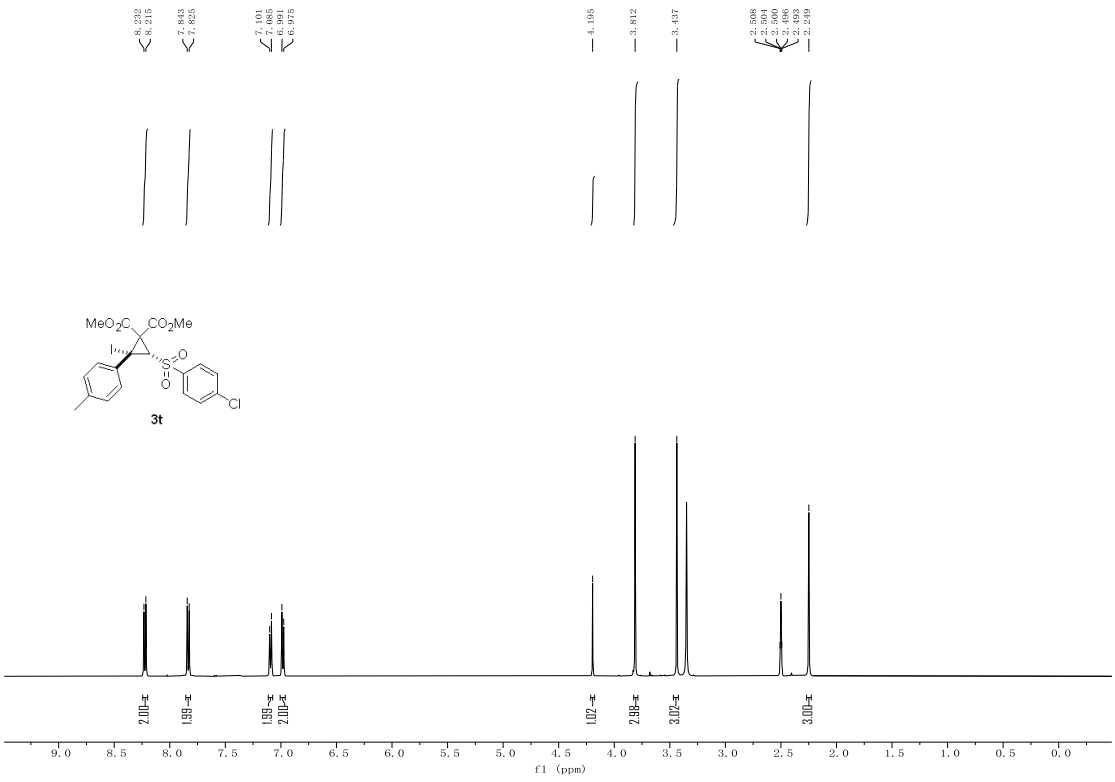
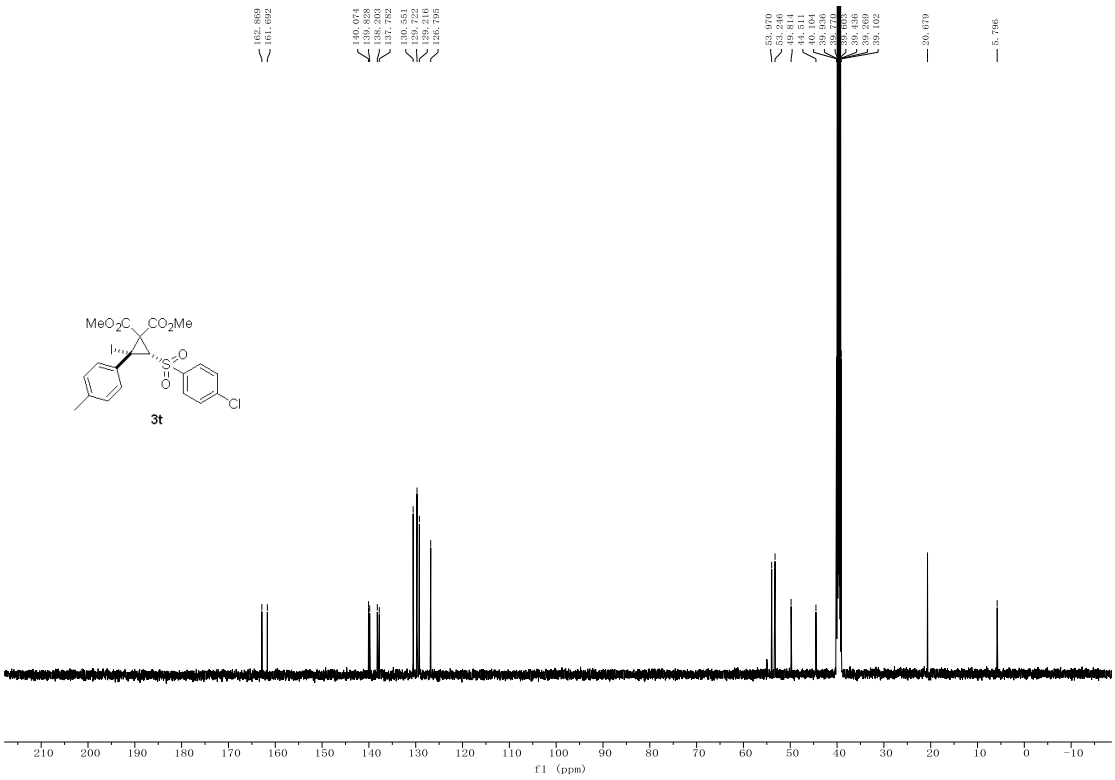
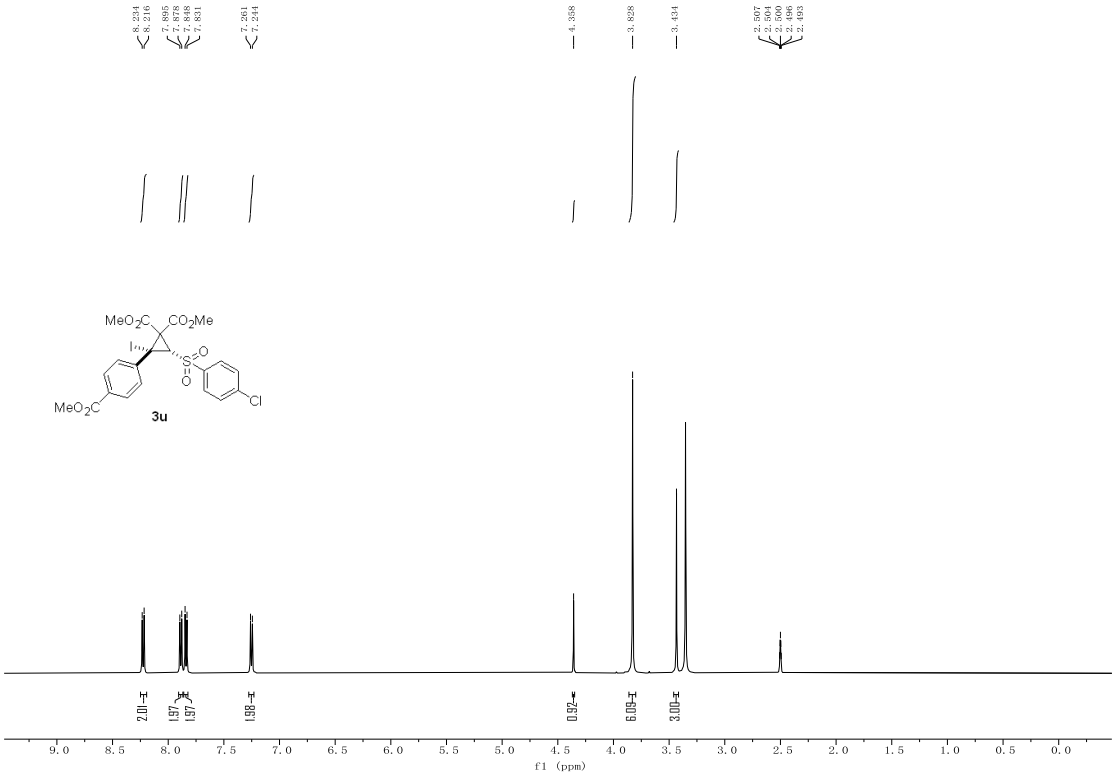
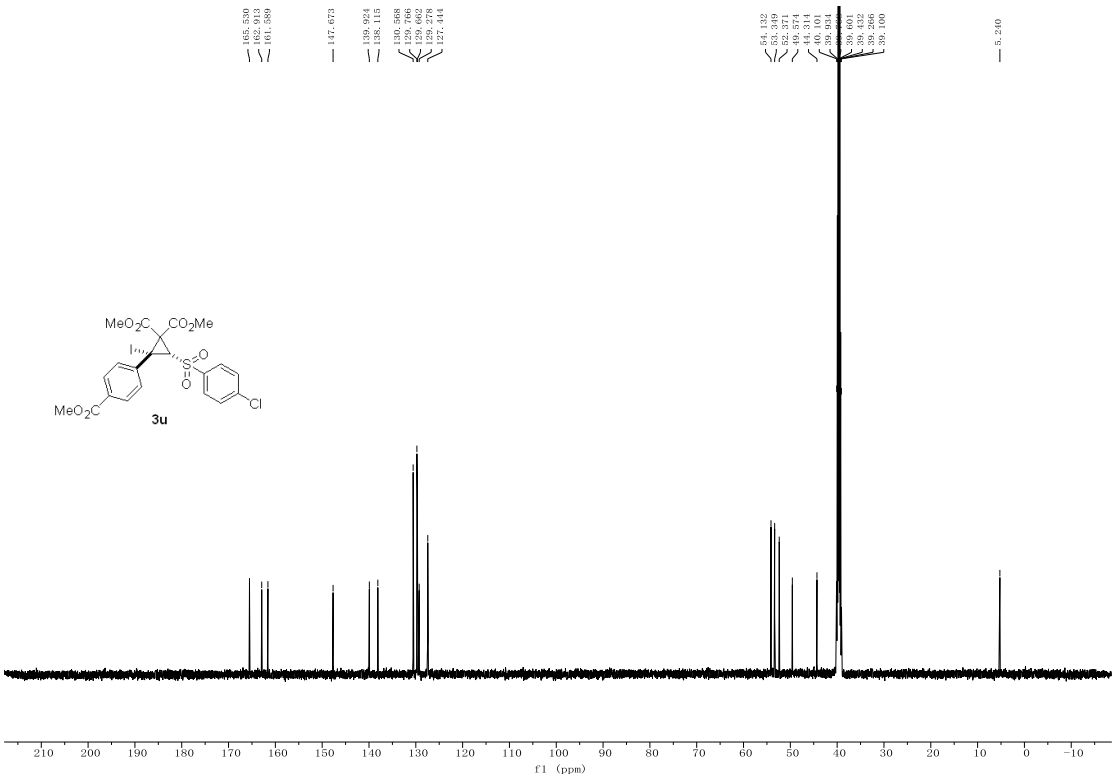
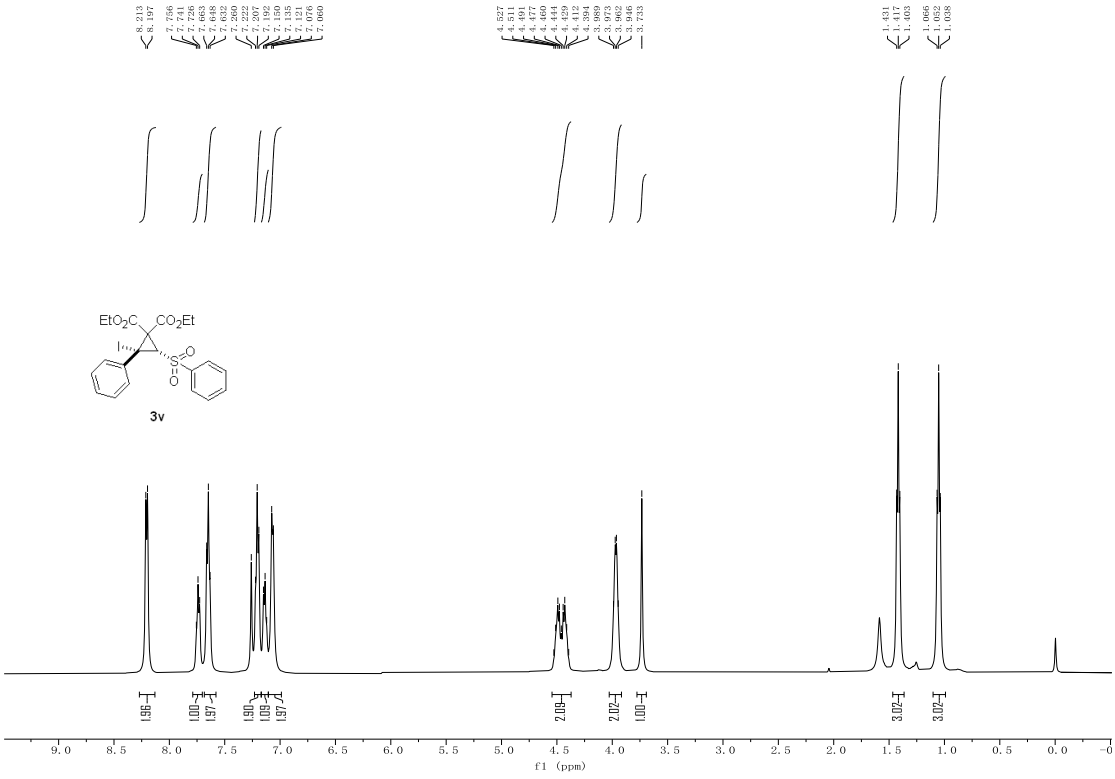
162.906
161.581
147.668
138.536
132.711
130.562
130.468
129.276
129.150
127.446
54.133
53.347
53.272
49.532
44.308
40.100
39.933
39.600
39.433
39.265
38.098
5.200
MeO2C
CO2Me
I
O
S
O
Br
MeO2C
3s
f1 (ppm)

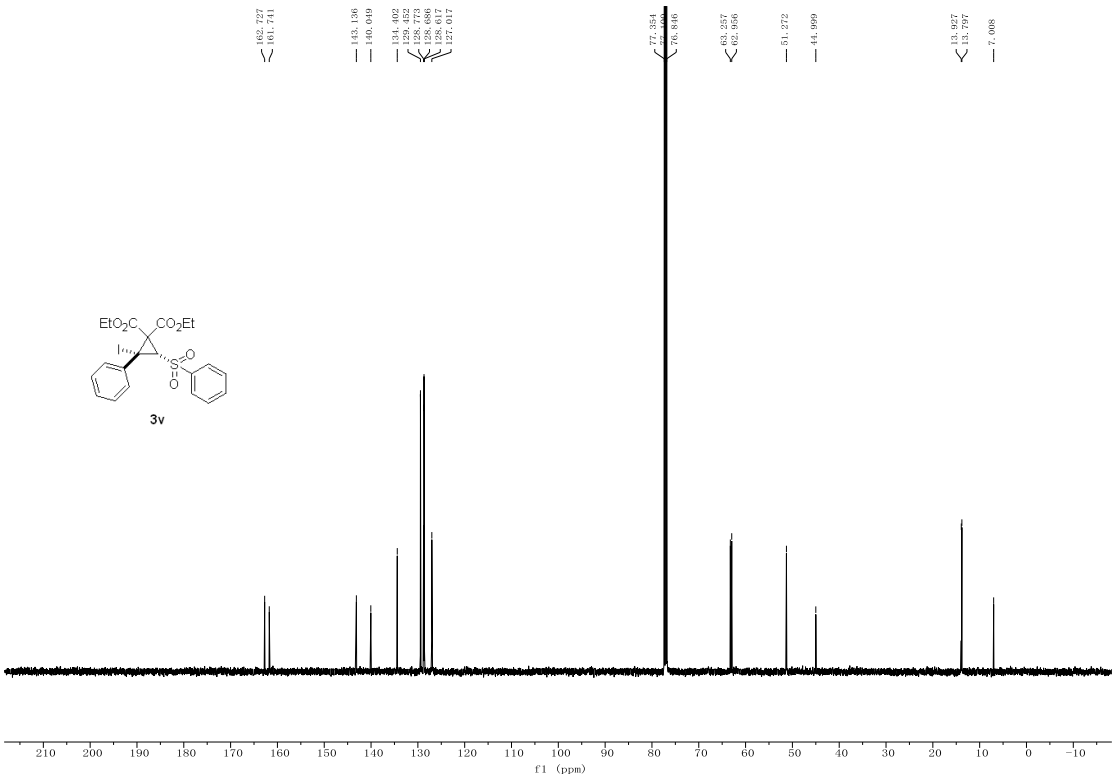

8.232
8.215
7.843
7.825
7.101
7.085
6.991
6.975
4.195
3.812
3.437
2.508
2.504
2.500
2.496
2.493
2.249
MeO2C
CO2Me
I
O
S
O
Cl
3t
2.00
1.99
1.99
2.01
1.02
2.98
3.02
3.00
f1 (ppm)


162.869
161.692
140.074
136.938
135.506
137.782
130.551
129.722
129.216
126.795
53.970
53.246
49.814
41.511
40.404
39.936
39.770
39.603
39.436
39.269
39.102
20.679
5.796
MeO2C
CO2Me
I
S
O
O
Cl
3t
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)


8.234
8.216
7.895
7.878
7.848
7.831
7.261
7.244
4.358
3.828
3.434
2.507
2.504
2.500
2.496
2.493
MeO2C
CO2Me
I
S
O
O
Cl
MeO2C
3u
2.01
1.97
1.97
1.98
0.92
6.09
3.00
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
f1 (ppm)


MeO2C
CO2Me
MeO2C
Cl
3u
f1 (ppm)


EtO2C
CO2Et
3v
f1 (ppm)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143.136
140.049
134.402
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128.686
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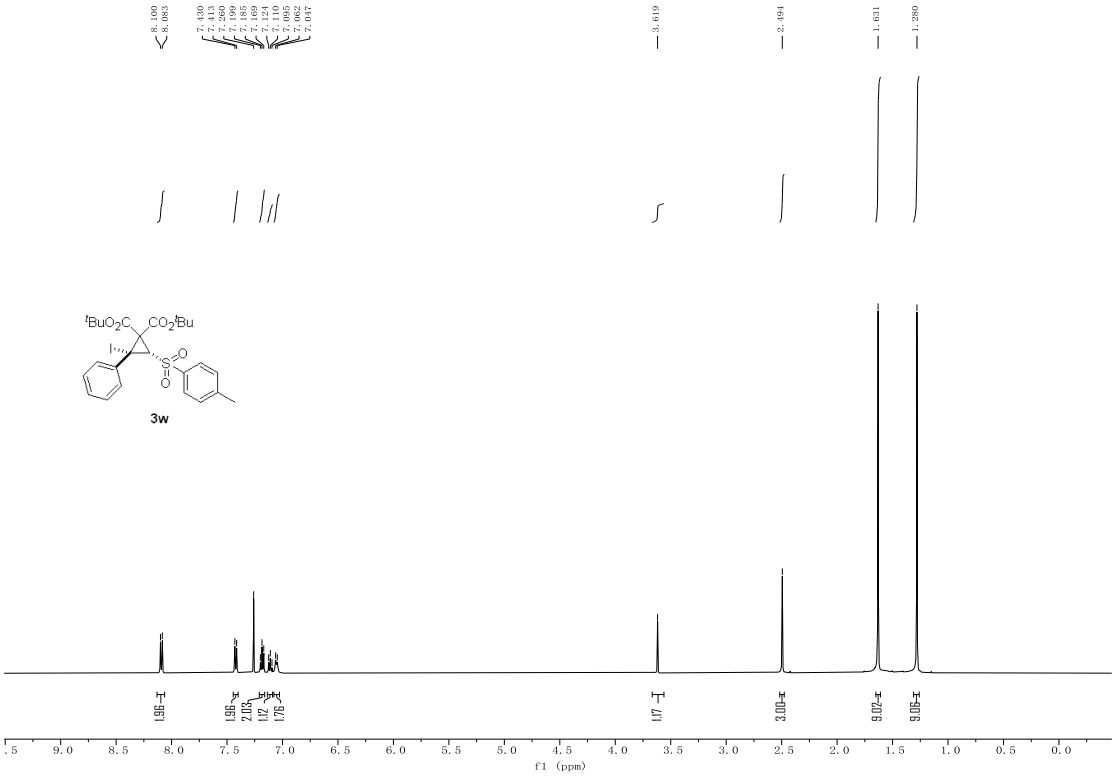
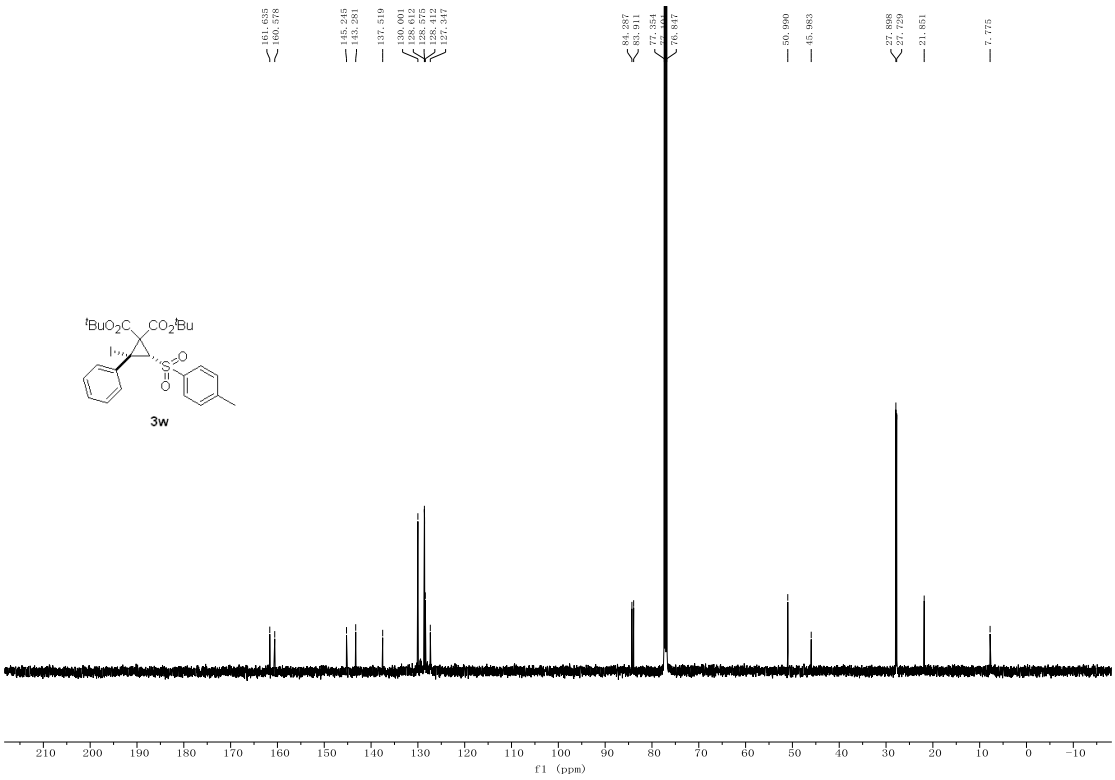
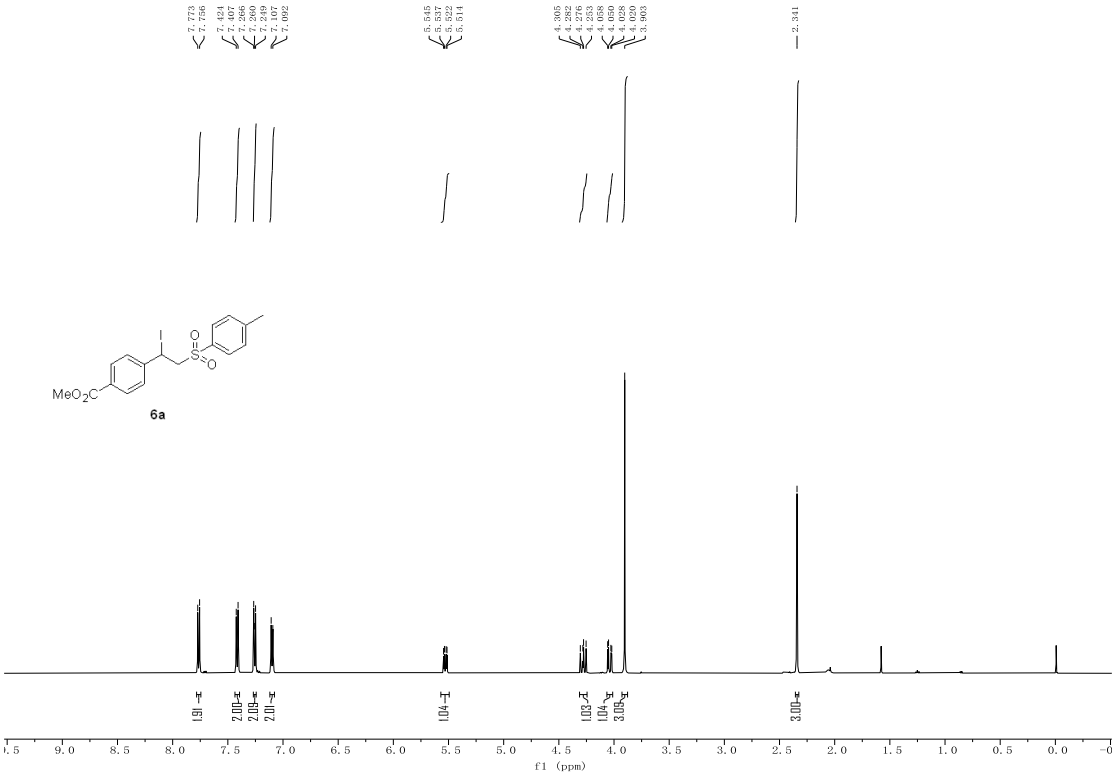
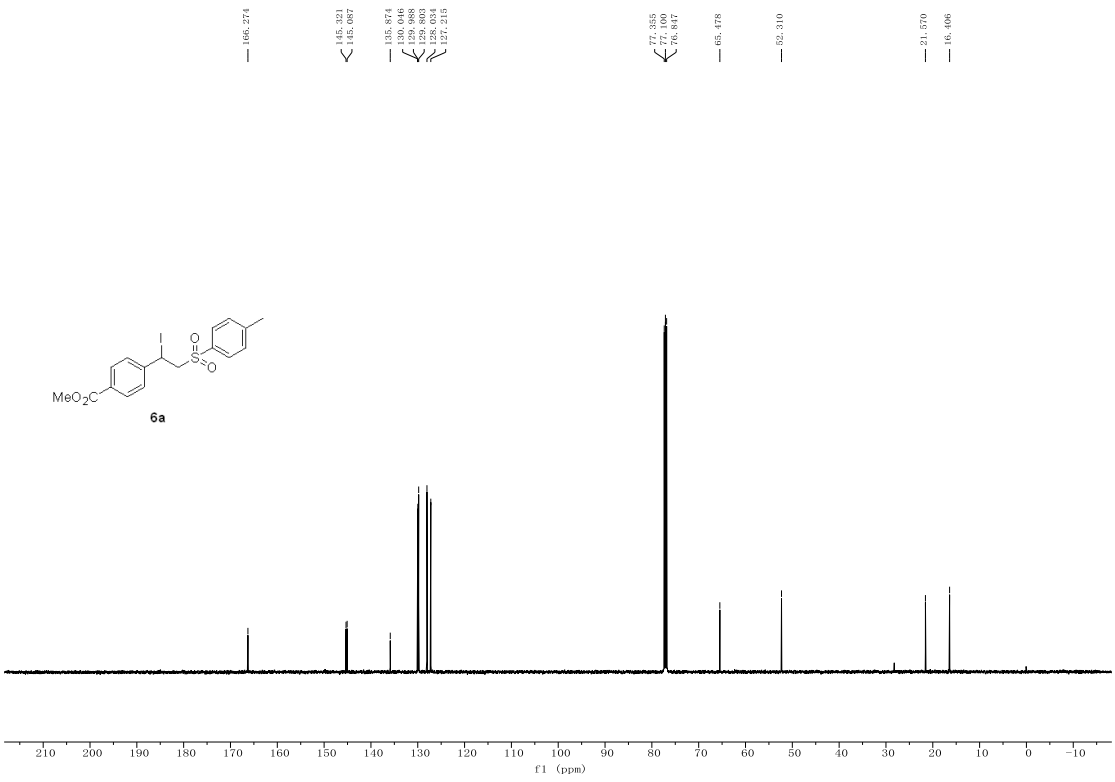
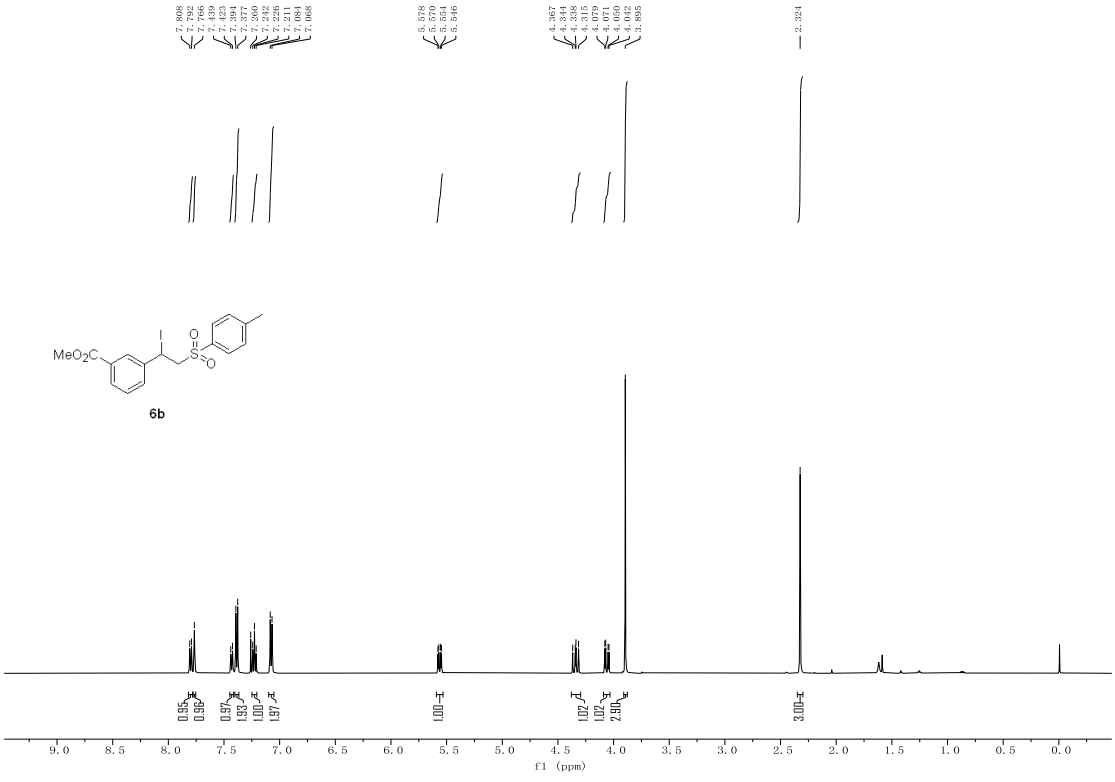
127.017
77.354
77.040
76.846
63.257
62.956
51.272
44.999
13.927
13.797
7.008
EtO2C
CO2Et
I
S
O
O
3v
f1 (ppm)

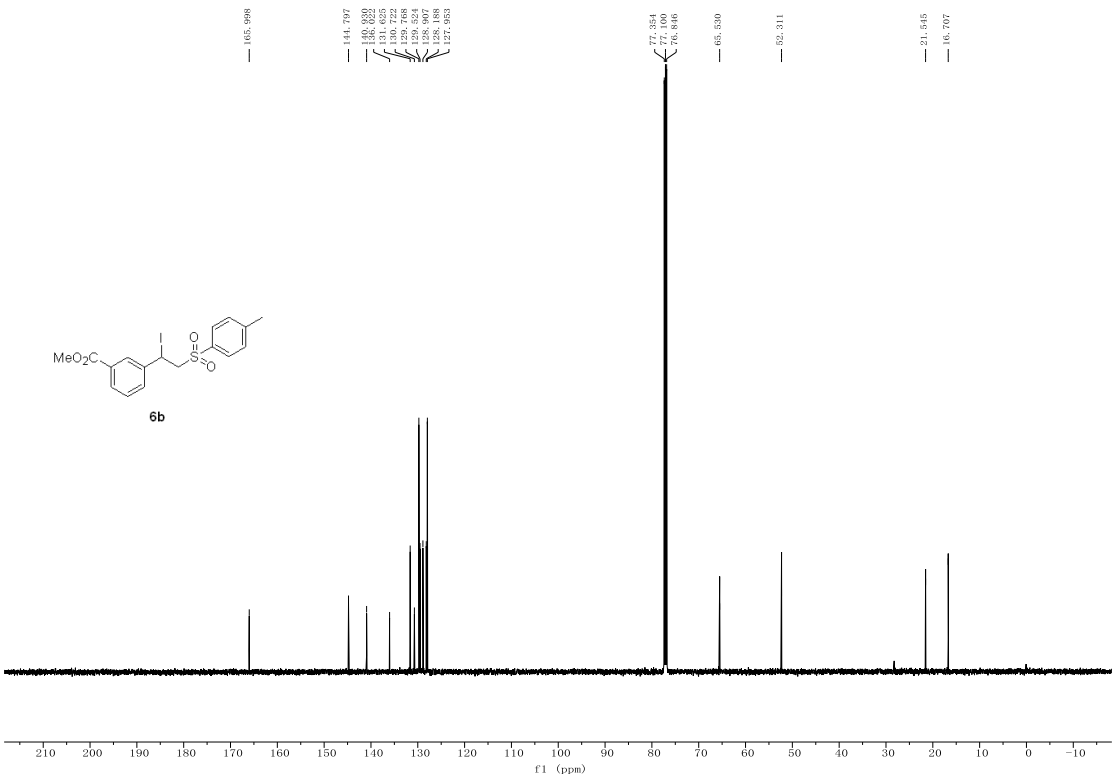

8.100
8.083
7.430
7.413
7.260
7.199
7.185
7.169
7.124
7.110
7.095
7.062
7.047
3.619
2.494
1.631
1.280
tBuO2C
CO2tBu
I
S
O
O
3w
1.96
1.96
2.03
1.12
1.76
1.17
3.00
9.02
9.06
f1 (ppm)


161.635
160.578
145.245
143.281
137.519
130.001
128.612
128.575
128.412
127.347
84.287
83.911
77.354
77.042
76.847
50.990
45.983
27.898
27.729
21.851
7.775
3w
f1 (ppm)


7.773
7.756
7.424
7.407
7.266
7.249
7.107
7.092
5.545
5.537
5.522
5.514
4.305
4.282
4.276
4.253
4.058
4.050
4.028
4.009
3.965
2.341
6a
1.91
2.00
2.09
2.01
1.04
1.03
1.04
3.09
3.00
f1 (ppm)


166.274
145.321
145.067
135.874
130.046
129.988
129.903
128.034
127.215
77.355
77.100
76.844
65.478
52.310
21.570
16.406
6a
f1 (ppm)


7.808
7.792
7.766
7.649
7.423
7.394
7.377
7.369
7.242
7.226
7.211
7.084
7.068
5.578
5.570
5.554
5.546
4.367
4.344
4.338
4.315
4.079
4.071
4.050
4.042
3.895
2.324
0.95
0.92
0.87
1.83
1.00
1.97
1.00
1.02
1.02
2.93
3.00
6b
f1 (ppm)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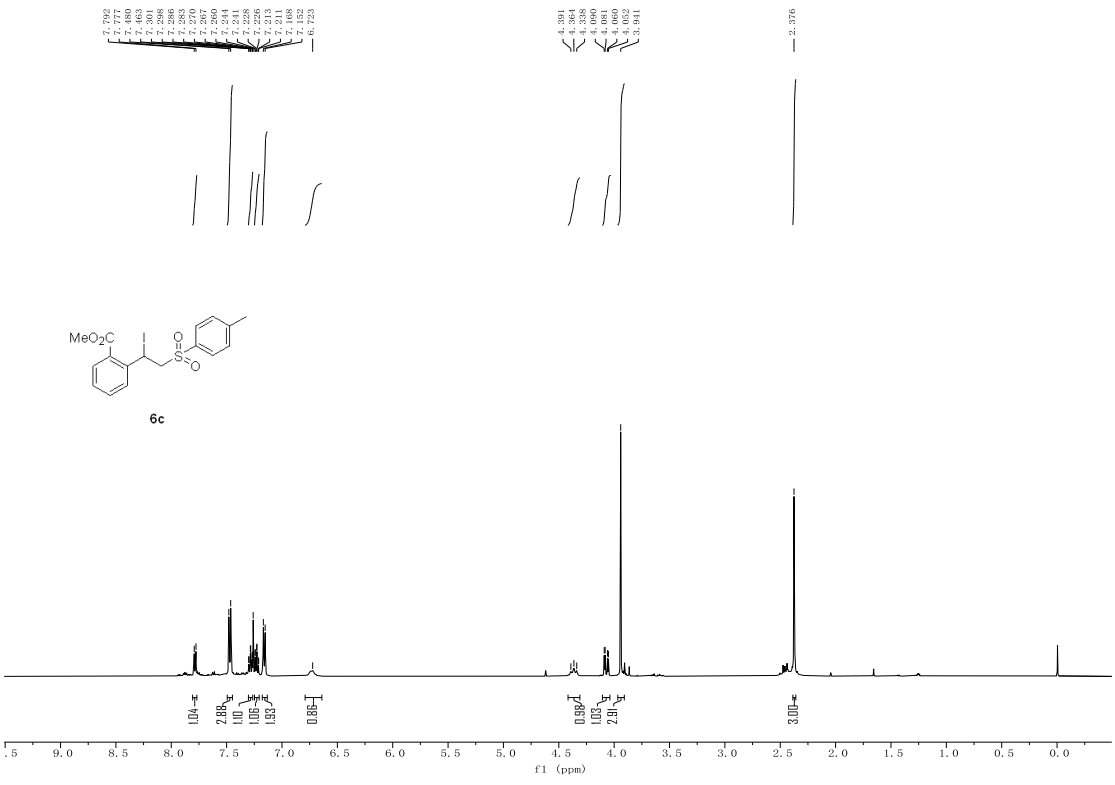
144.797
140.930
136.622
131.625
130.722
129.768
129.524
128.997
128.188
127.953
77.354
77.100
76.846
65.530
52.311
21.545
16.707
MeO2C
I
O
S
O
6b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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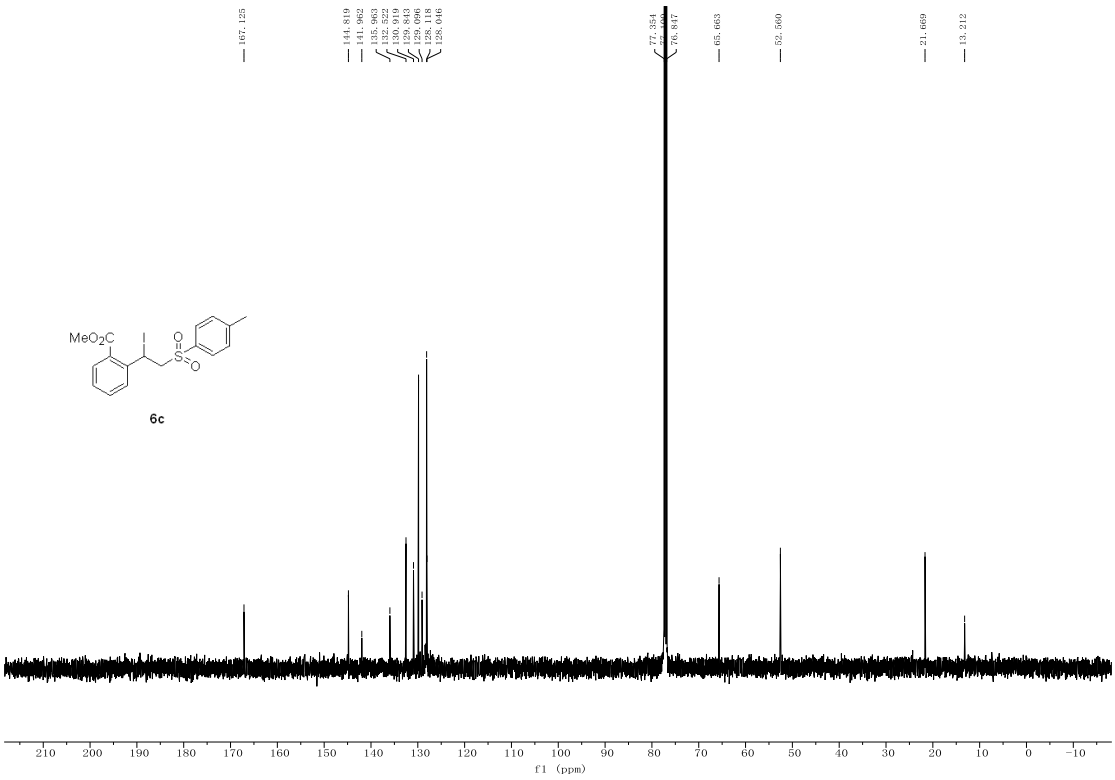
7.301
7.298
7.285
7.275
7.270
7.267
7.260
7.244
7.241
7.228
7.213
7.211
7.168
7.152
6.723
4.391
4.364
4.338
4.090
4.061
4.060
4.052
3.941
2.376
MeO2C
I
O
S
O
6c
1.04
2.88
1.10
1.06
1.93
0.86
0.59
1.03
2.91
3.00
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.125
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141.962
135.963
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130.919
129.845
129.096
128.118
128.046
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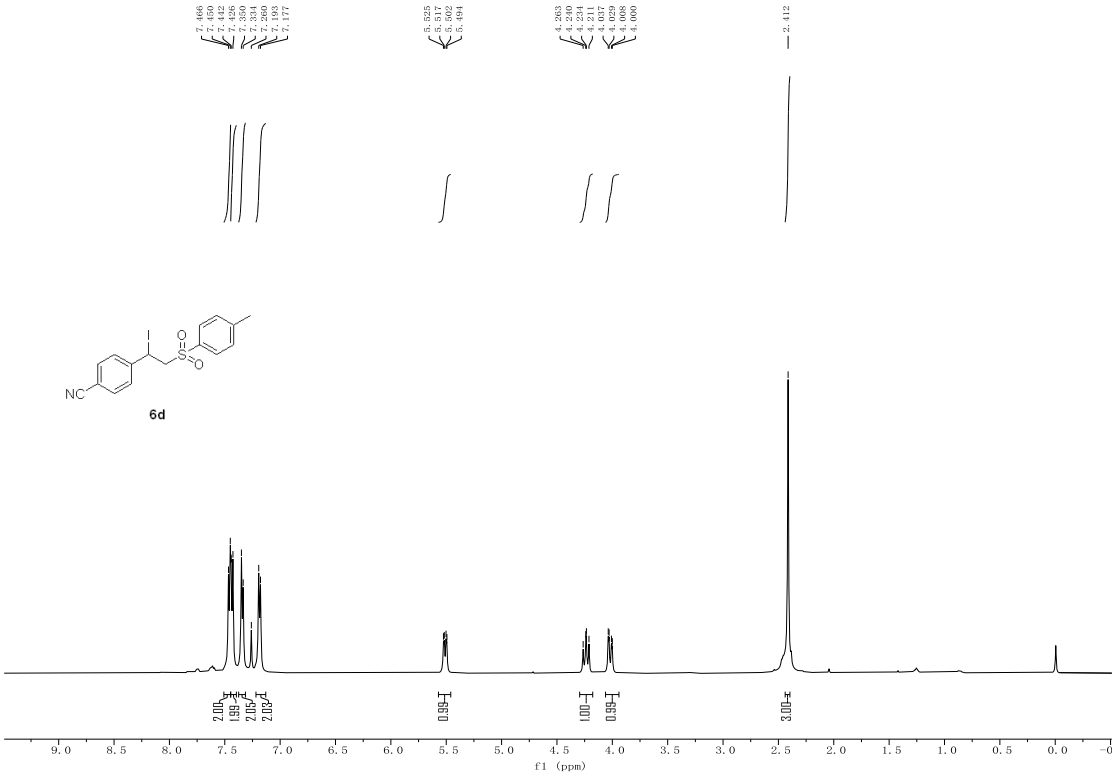
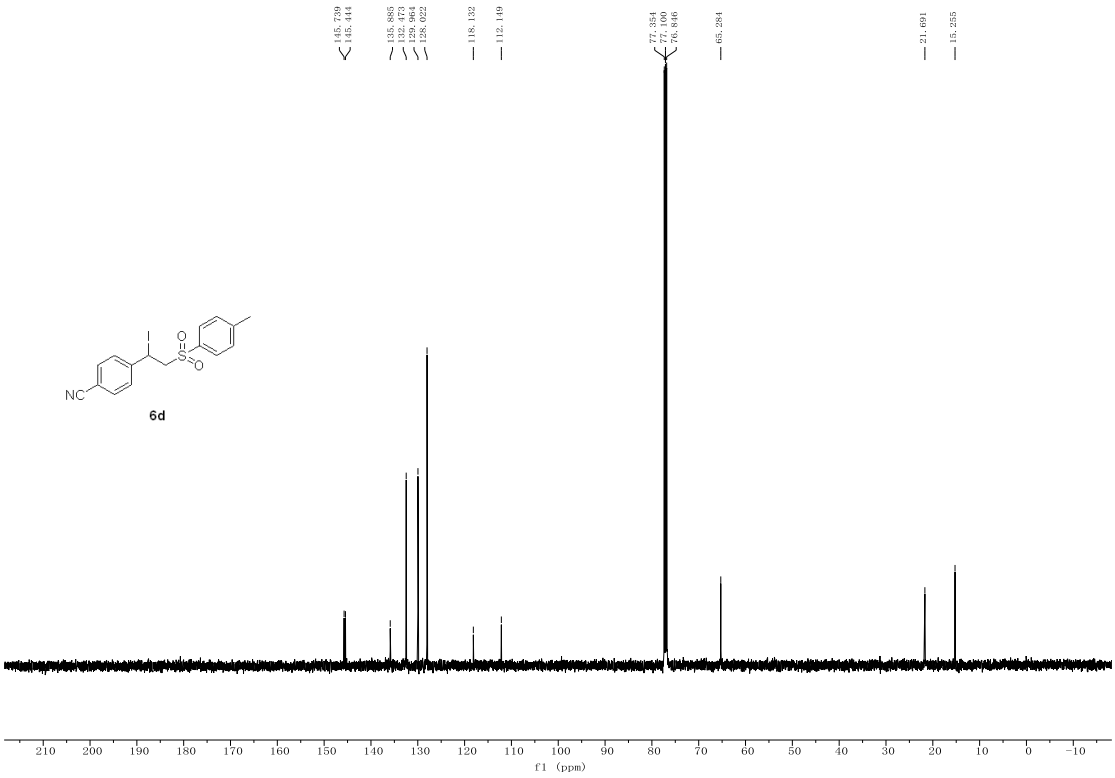
77.046
76.847
65.663
52.560
21.669
13.212
MeO2C
O
S
O
6c
f1 (ppm)


7.466
7.459
7.442
7.426
7.350
7.334
7.260
7.193
7.177
5.525
5.517
5.502
5.494
4.263
4.240
4.234
4.211
4.017
4.029
4.008
4.000
2.412
NC
O
S
O
6d
2.00
1.99
2.05
2.02
0.99
1.00
0.59
3.00
f1 (ppm)


145.739
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135.885
132.473
129.964
128.022
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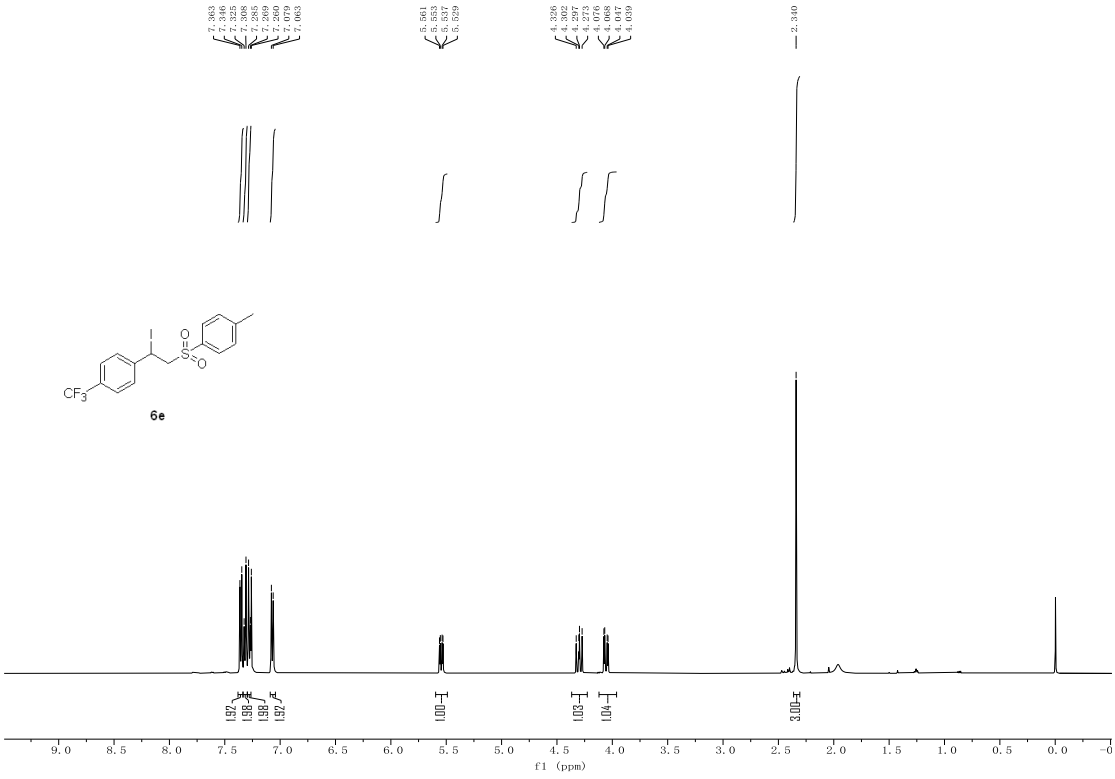
112.149
77.354
77.100
76.846
65.284
21.691
15.255
NC
6d
f1 (ppm)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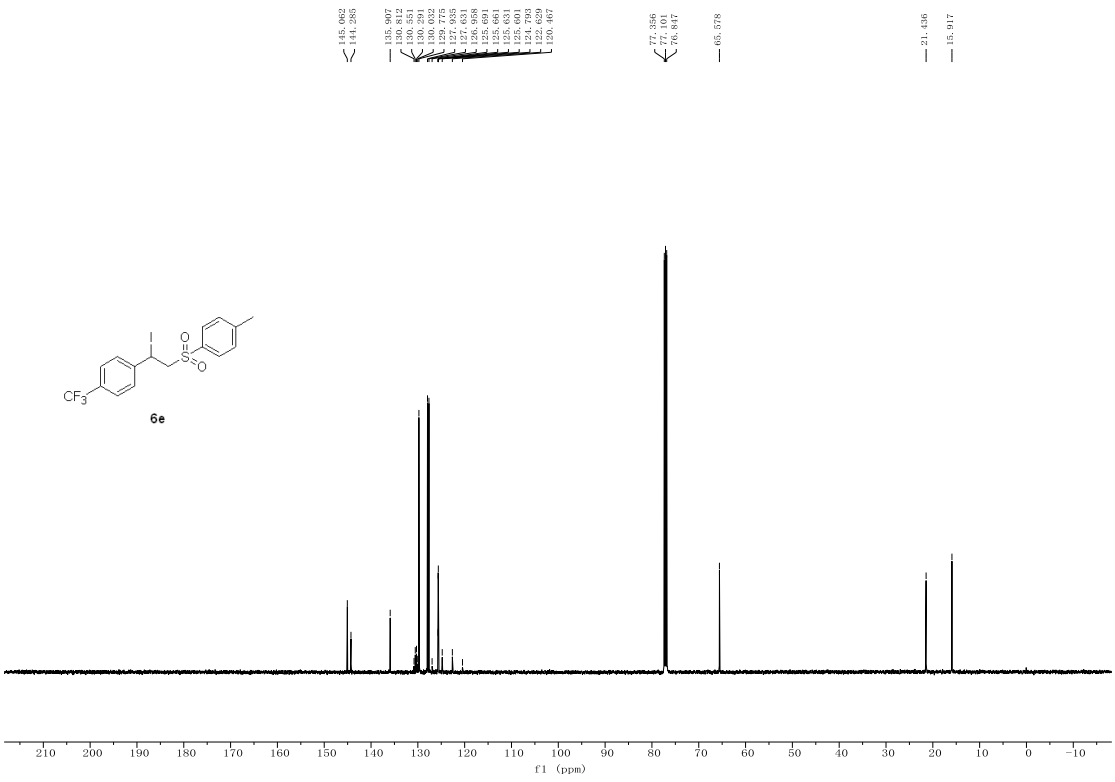
7.346
7.325
7.308
7.285
7.268
7.260
7.079
7.063
5.561
5.553
5.537
5.529
4.326
4.302
4.297
4.273
4.076
4.068
4.047
4.039
2.340
CF3
6e
1.92
1.98
1.98
1.92
1.00
1.03
1.04
3.00
f1 (ppm)


145.062
144.265
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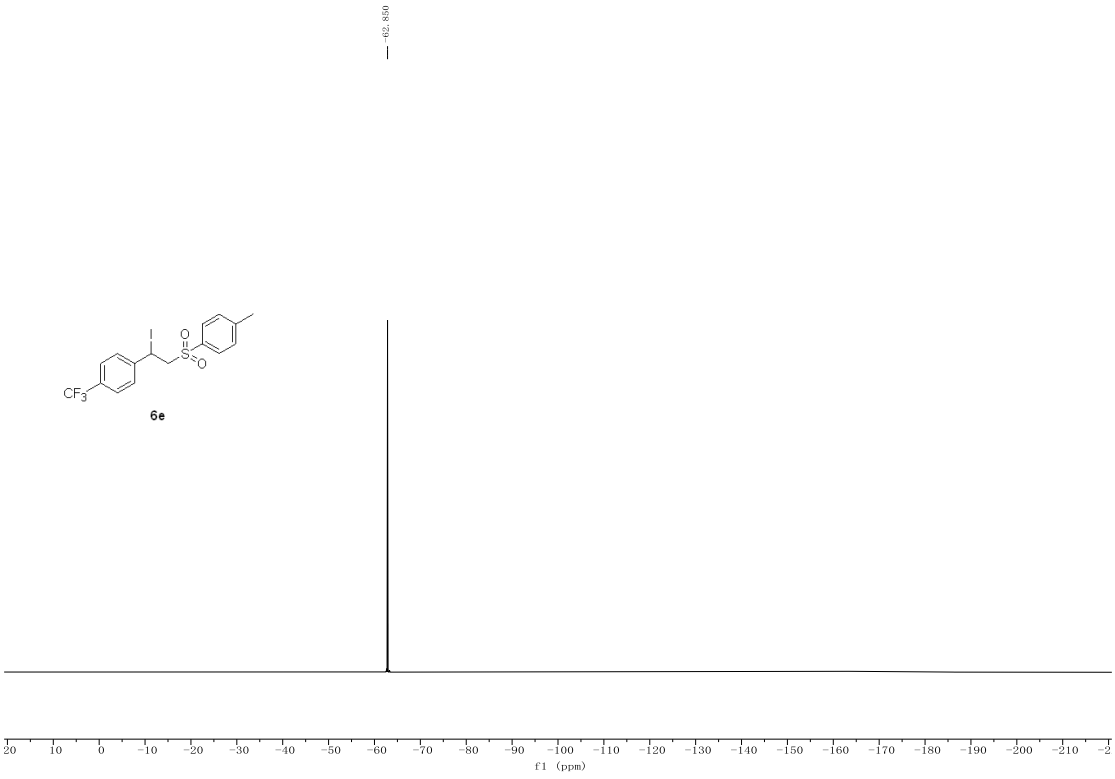
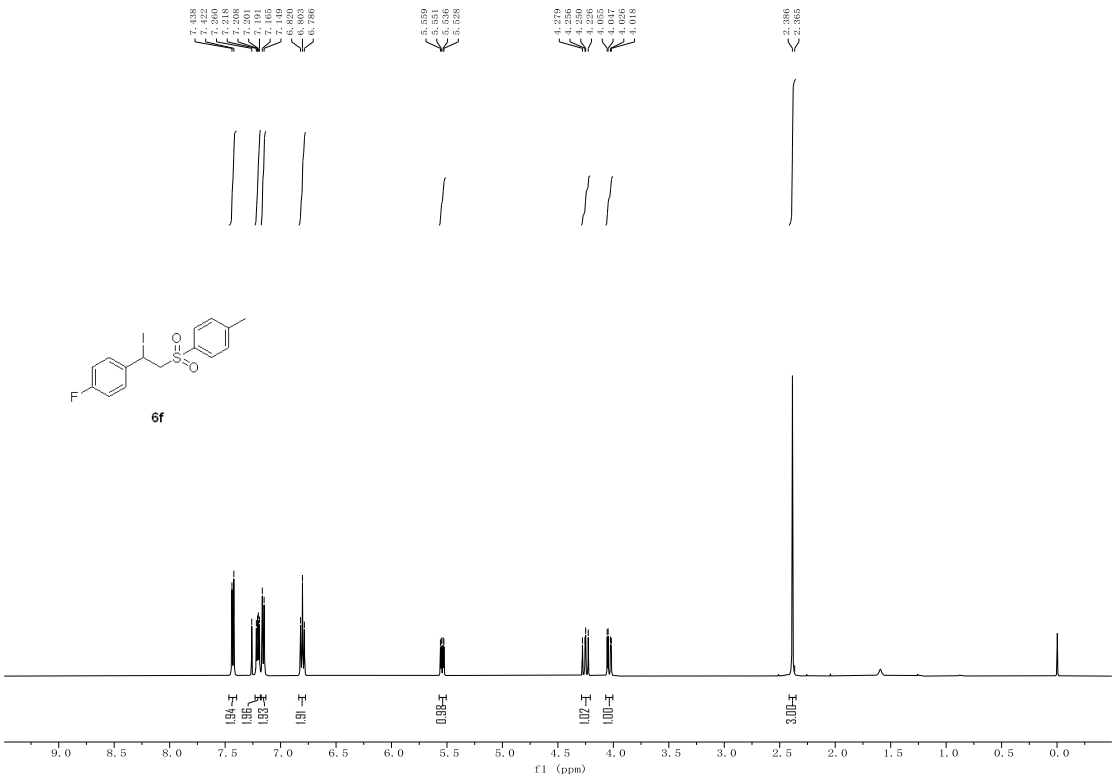
130.812
130.351
130.201
130.032
129.775
127.935
127.661
126.958
125.691
125.661
125.651
125.601
124.793
122.629
120.467
77.356
77.101
76.847
65.578
21.436
15.917
6e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-62.850
6e
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)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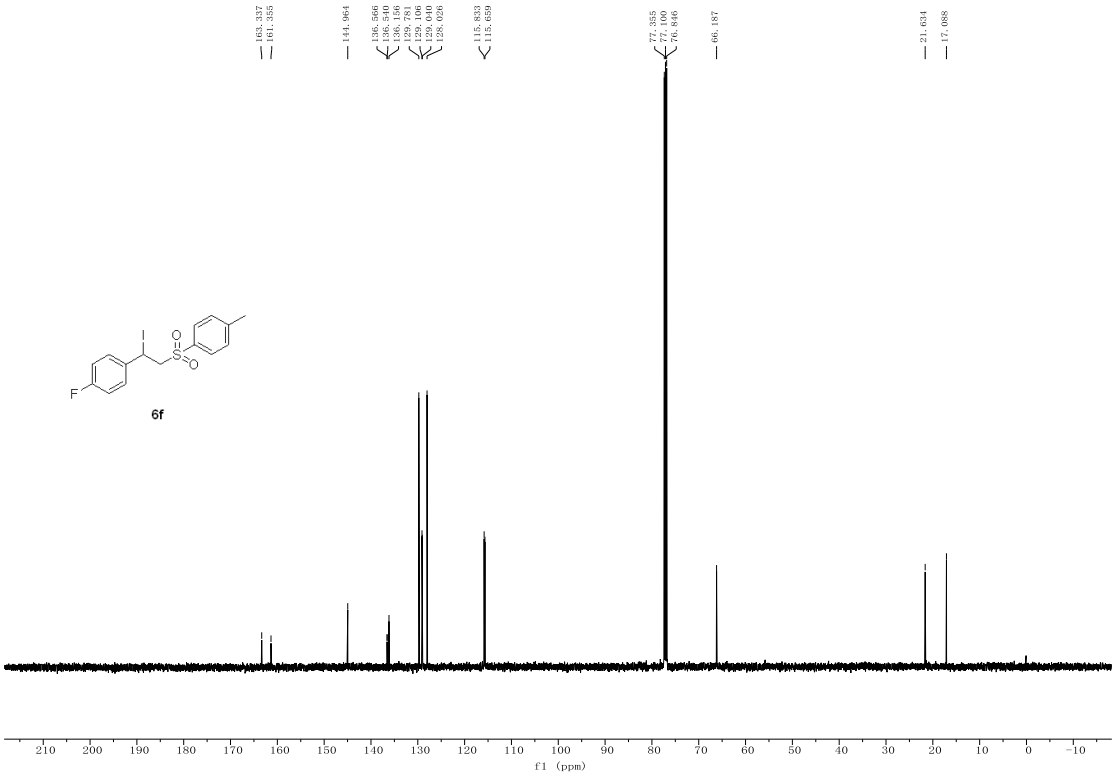
6.803
6.786
5.559
5.551
5.536
5.528
4.279
4.256
4.250
4.236
4.055
4.047
4.026
4.018
2.386
2.365
6f
1.94
1.96
1.93
1.91
0.98
1.02
1.00
3.00
f1 (ppm)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136.091
129.106
129.040
128.026
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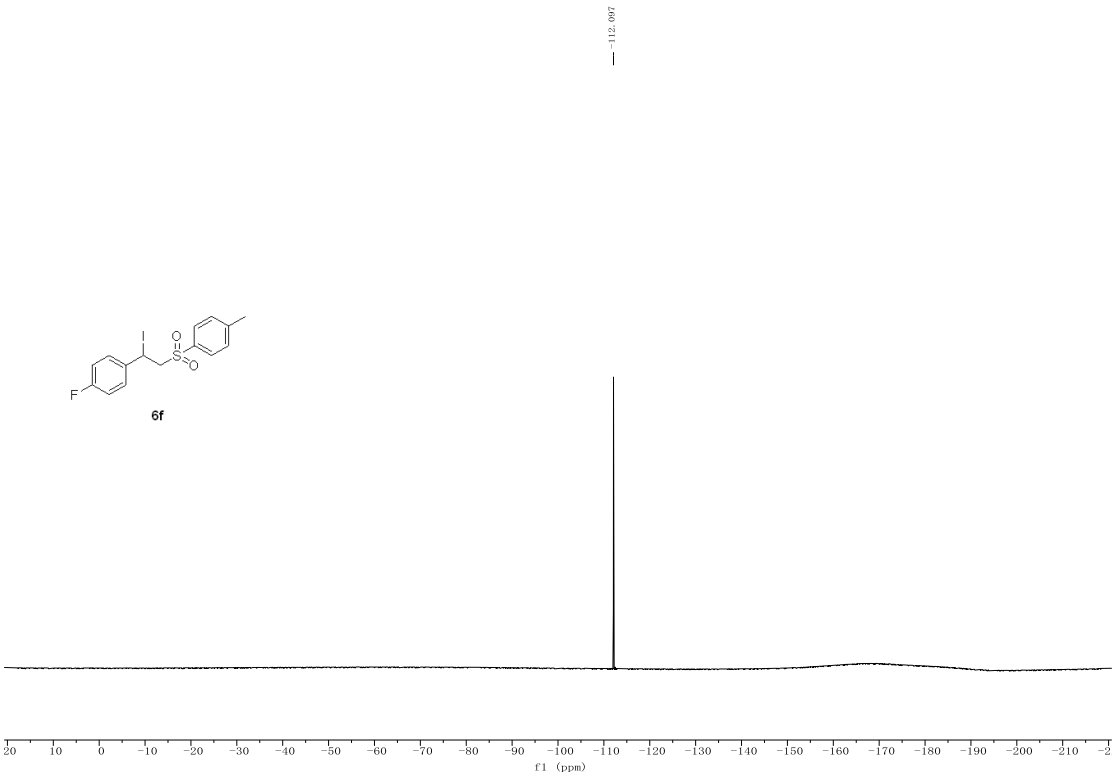
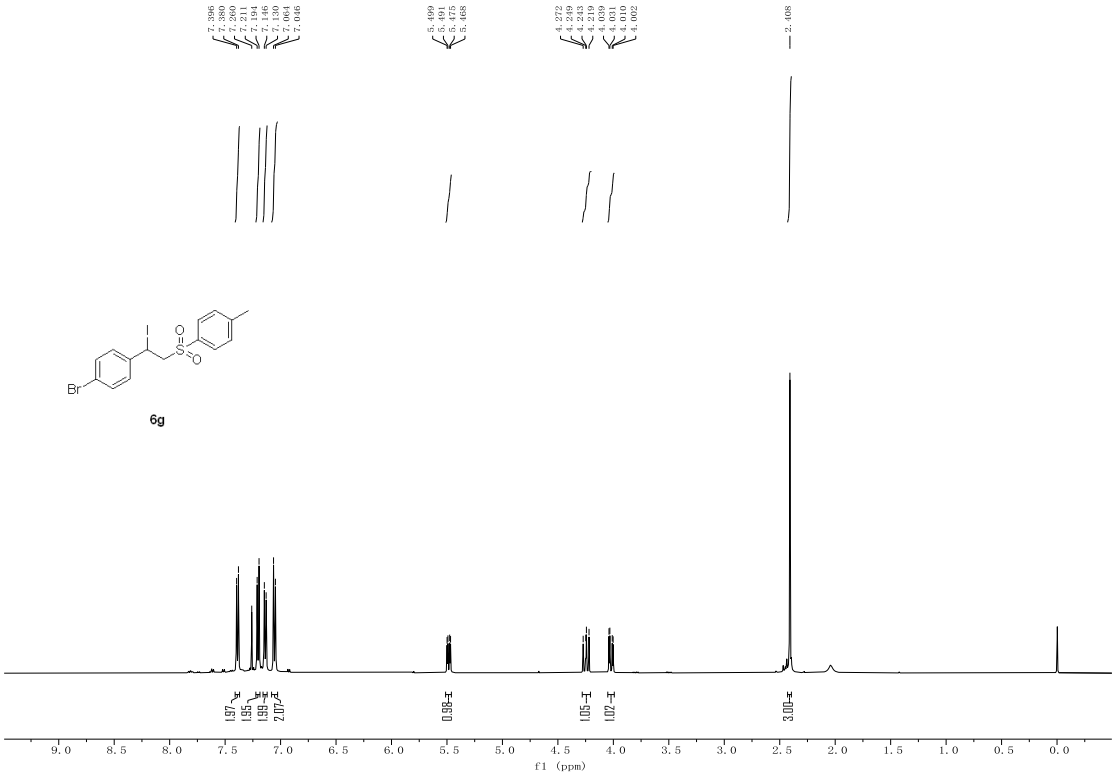
66.187
21.634
17.088
6f
f1 (ppm)


-112.097
6f
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)


7.396
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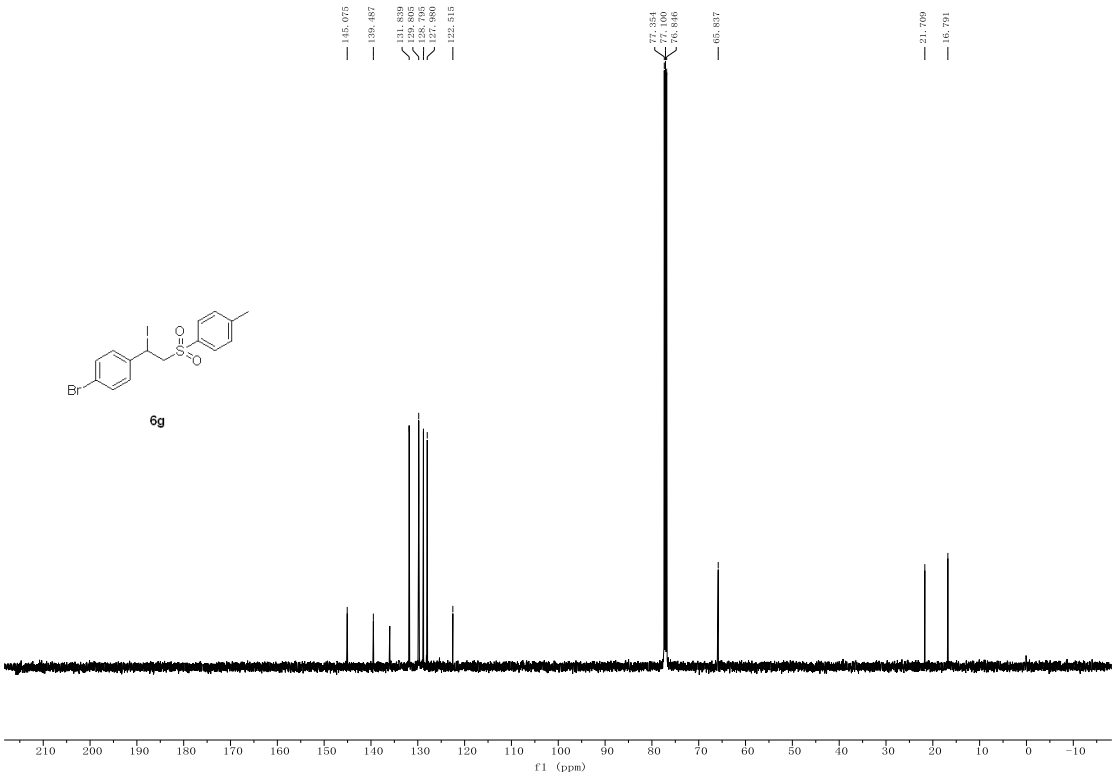
7.211
7.194
7.146
7.130
7.064
7.046
5.499
5.491
5.475
5.468
4.272
4.249
4.243
4.219
4.059
4.031
4.010
4.002
2.408
6g
1.97
1.95
1.99
2.07
0.98
1.05
1.02
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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139.487
131.839
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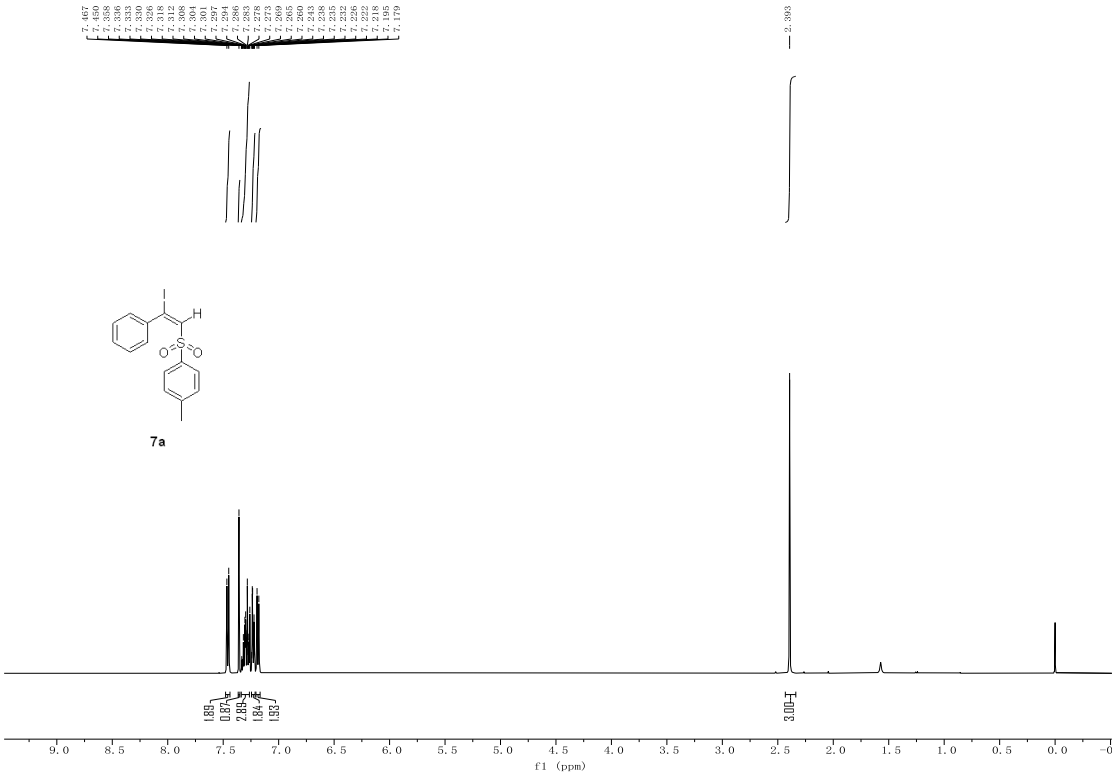
122.515
77.354
77.100
76.846
65.837
21.709
16.791
6g
f1 (ppm)


7.467
7.450
7.358
7.336
7.333
7.330
7.326
7.318
7.312
7.306
7.304
7.301
7.297
7.294
7.286
7.283
7.278
7.273
7.269
7.265
7.260
7.243
7.238
7.235
7.232
7.226
7.223
7.218
7.195
7.179
2.393
7a
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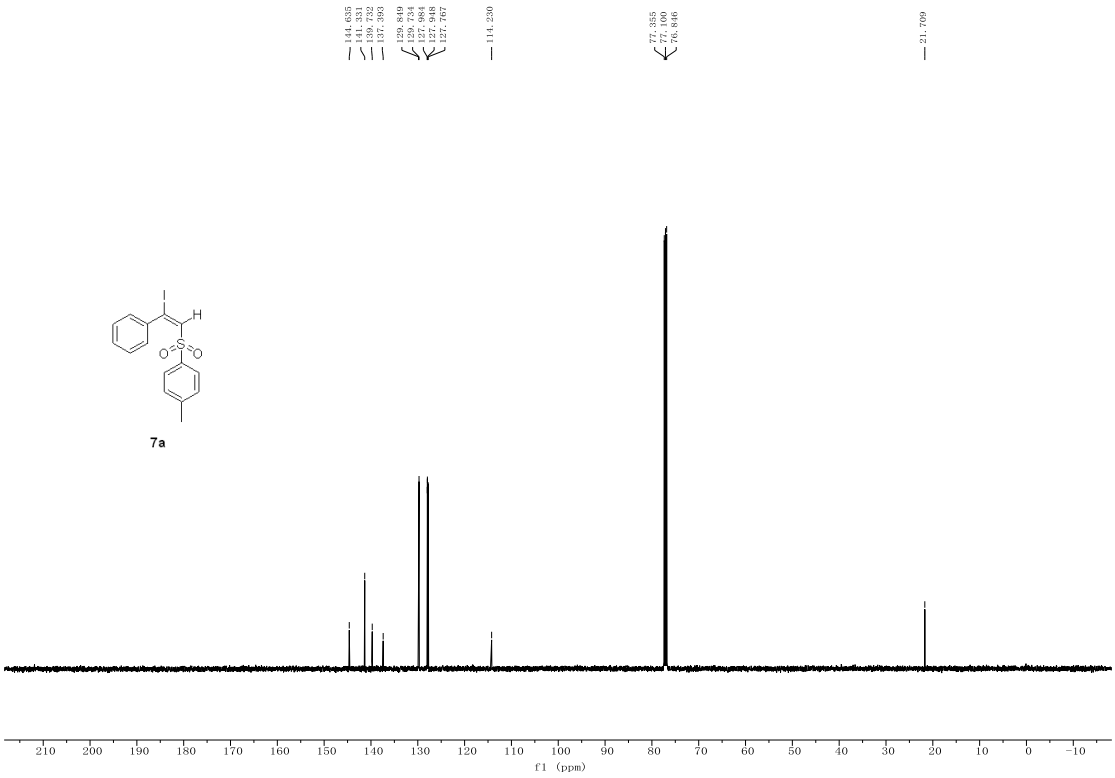
0.87
2.89
1.84
1.53
3.00
f1 (ppm)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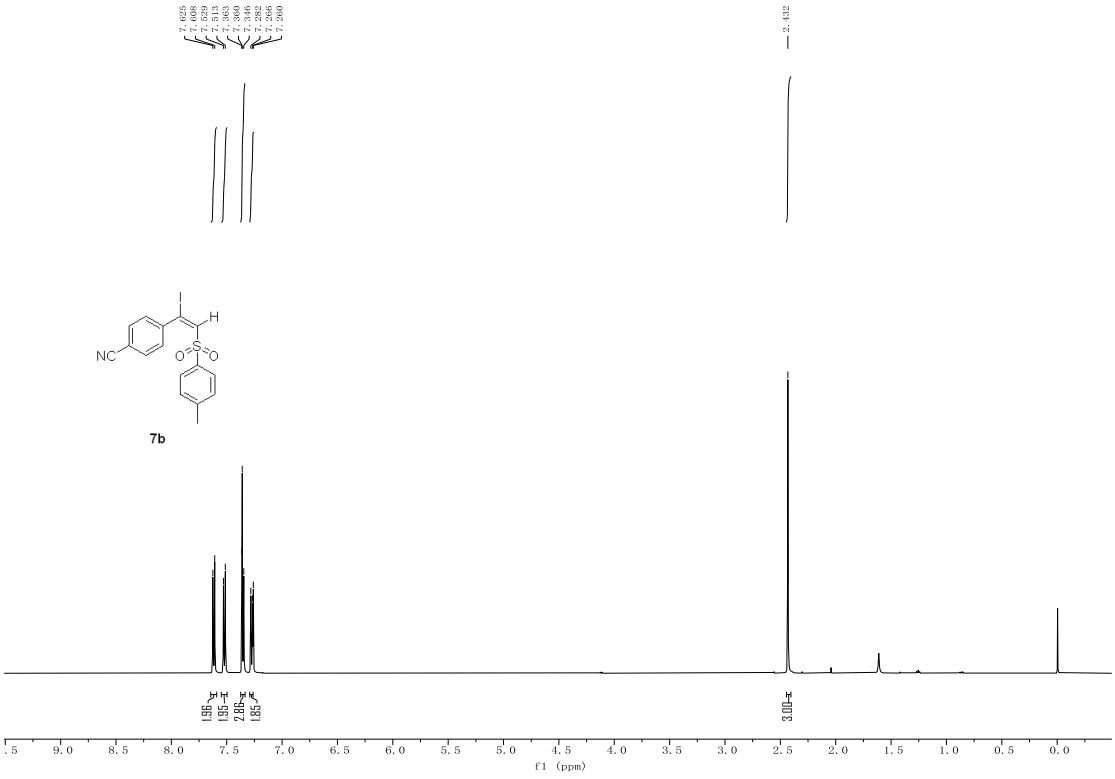
141.331
139.732
137.393
129.849
129.734
127.964
127.948
127.767
114.230
77.355
77.100
76.846
21.709
7a
f1 (ppm)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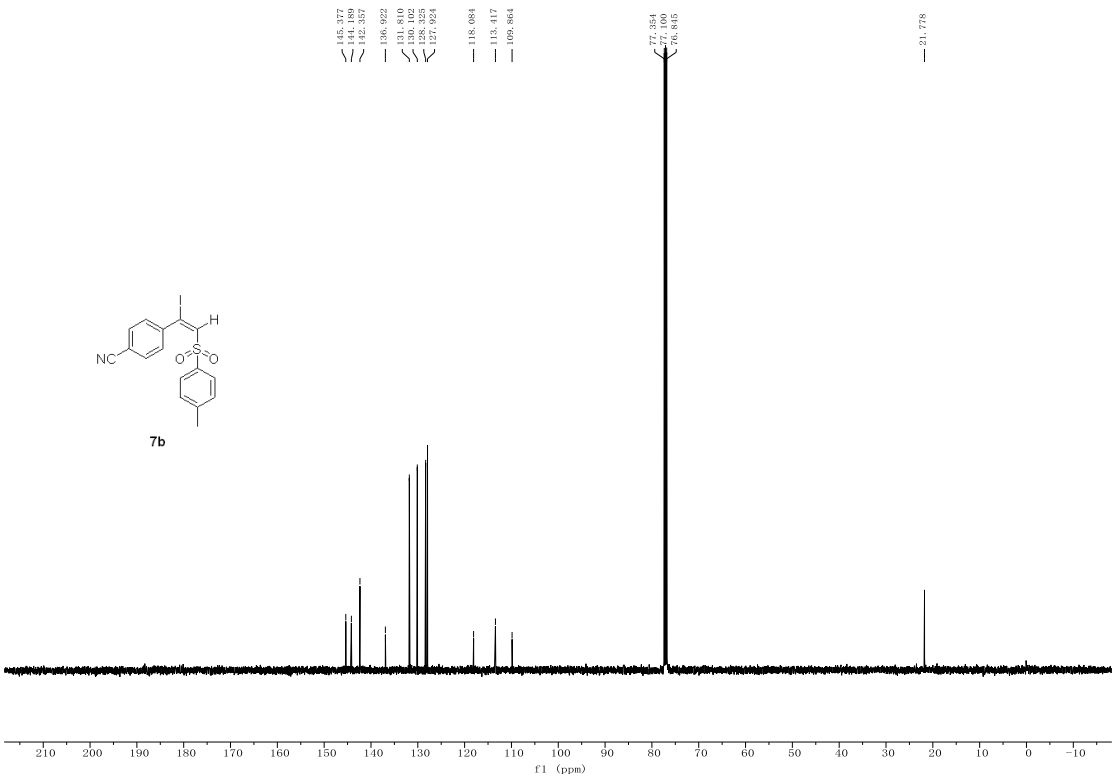
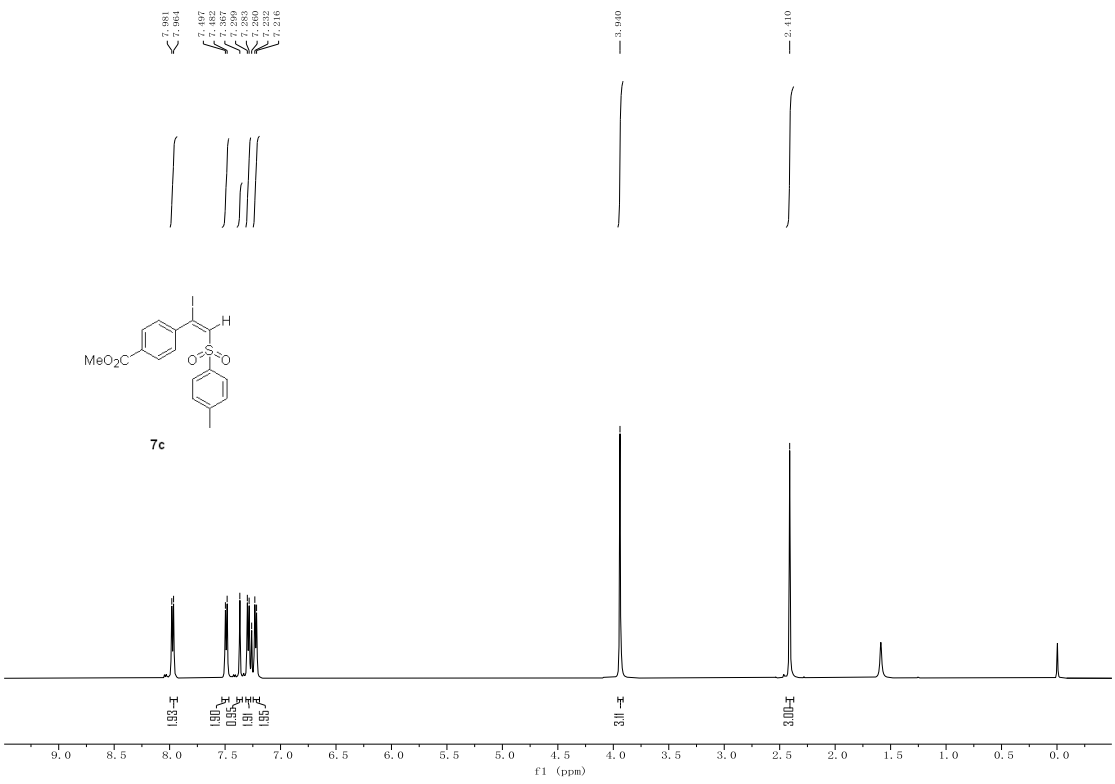
7.608
7.529
7.513
7.363
7.360
7.346
7.282
7.266
7.260
2.432
NC
7b
1.96
1.95
2.08
1.85
3.00
f1 (ppm)


145.377
144.199
142.357
136.922
131.810
130.102
128.235
127.924
118.084
113.417
109.864
77.354
77.100
76.845
21.778
NC
I
H
O
S
O
7b
f1 (ppm)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7.964
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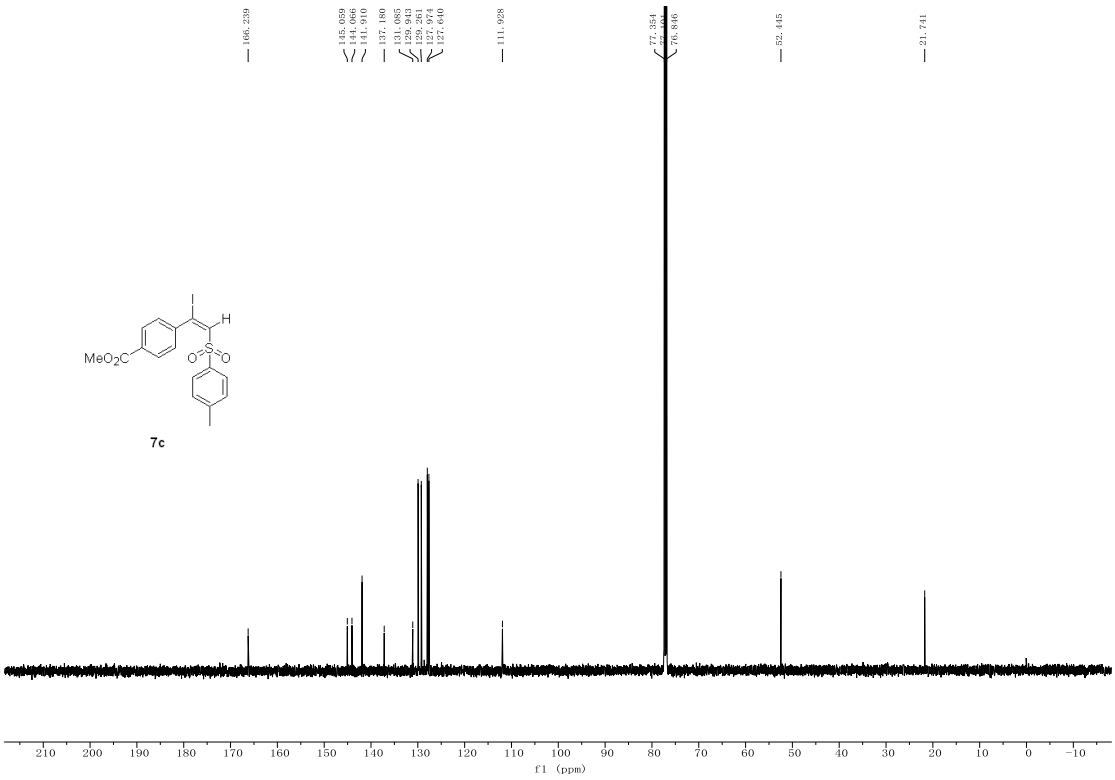
7.483
7.367
7.299
7.283
7.269
7.232
7.216
3.940
2.410
MeO2C
I
H
O
S
O
7c
1.93
1.90
0.95
1.91
1.95
3.11
3.00
f1 (ppm)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129.381
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127.640
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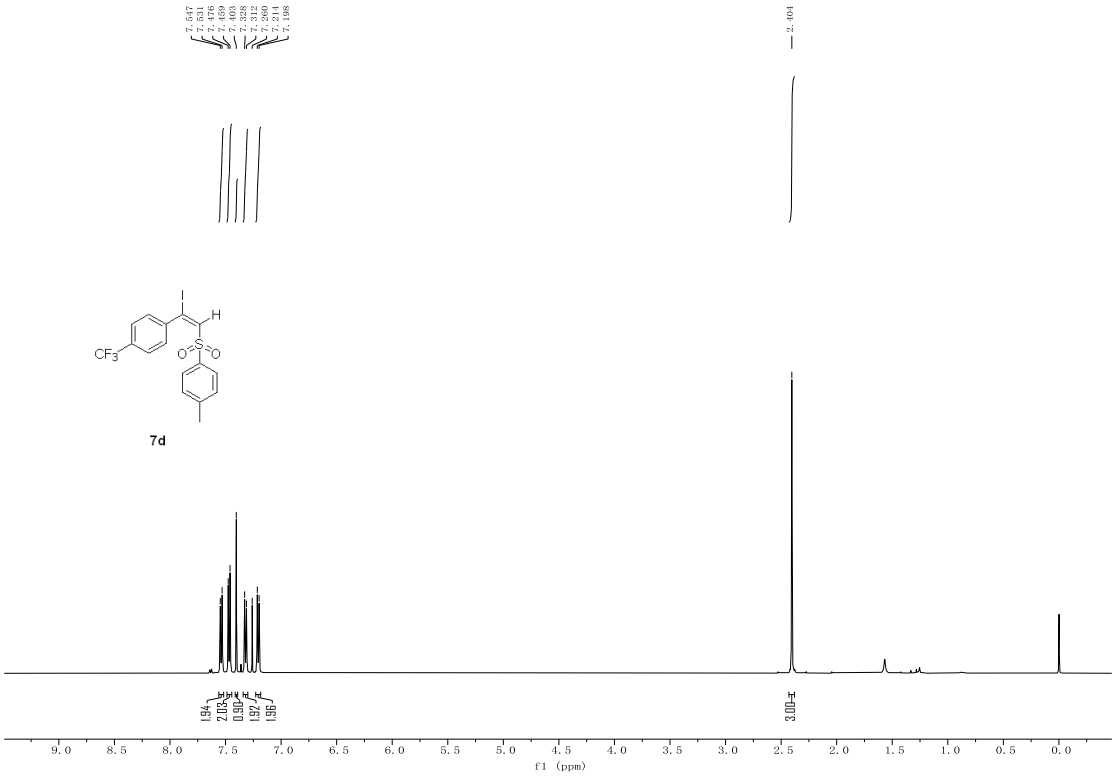
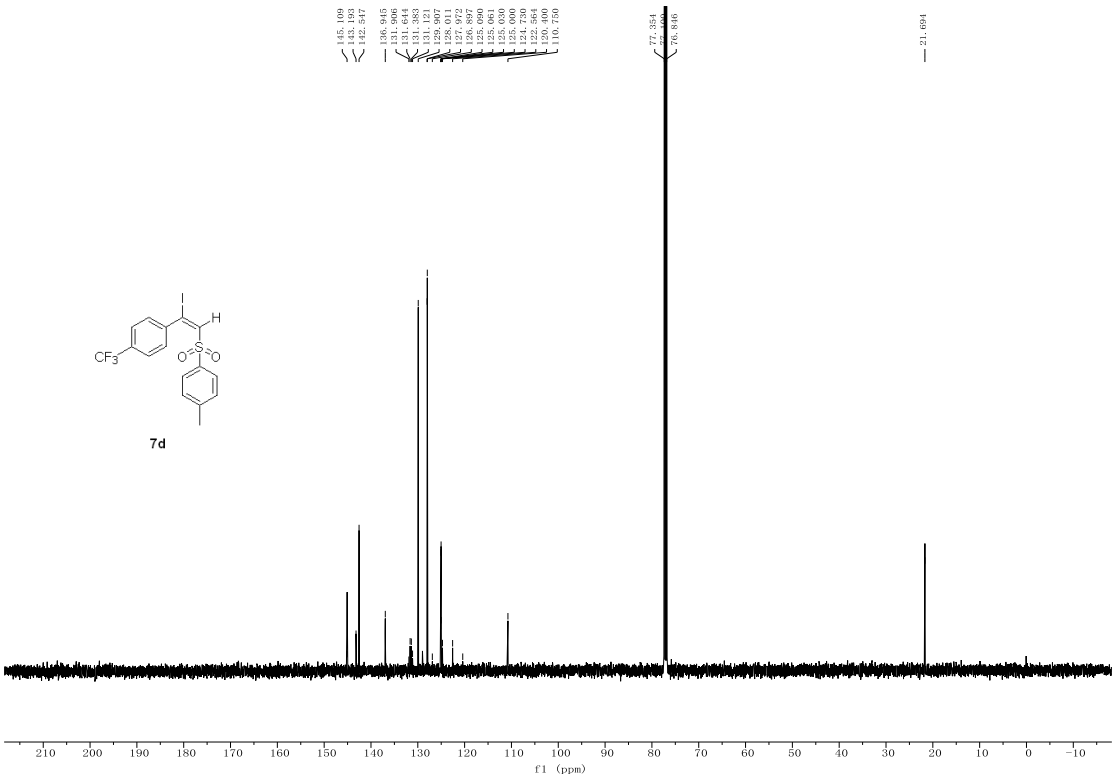
77.044
76.846
52.445
21.741
MeO2C
I
H
O
S
O
7c
f1 (ppm)


7.547
7.531
7.495
7.459
7.403
7.328
7.312
7.293
7.269
7.214
7.198
2.404
CF3
I
H
O
S
O
7d
1.94
2.03
0.90
1.92
1.96
3.00
f1 (ppm)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143.193
142.547
136.945
131.996
131.644
131.383
131.121
129.907
129.011
127.972
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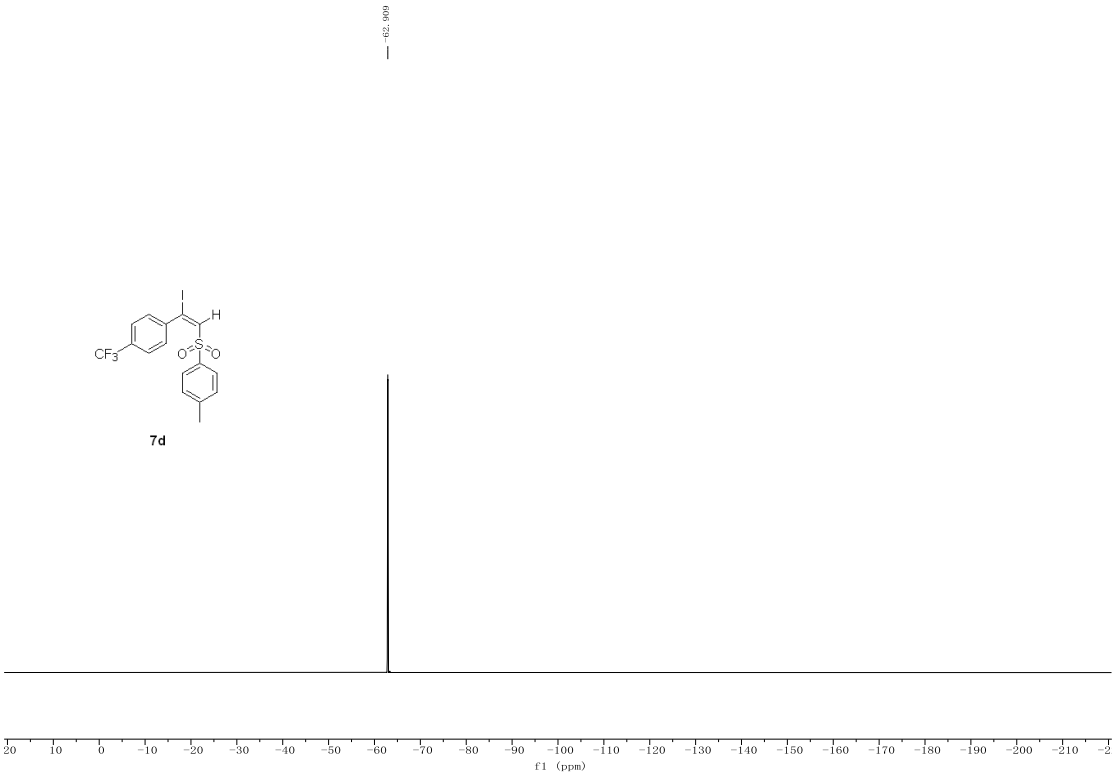
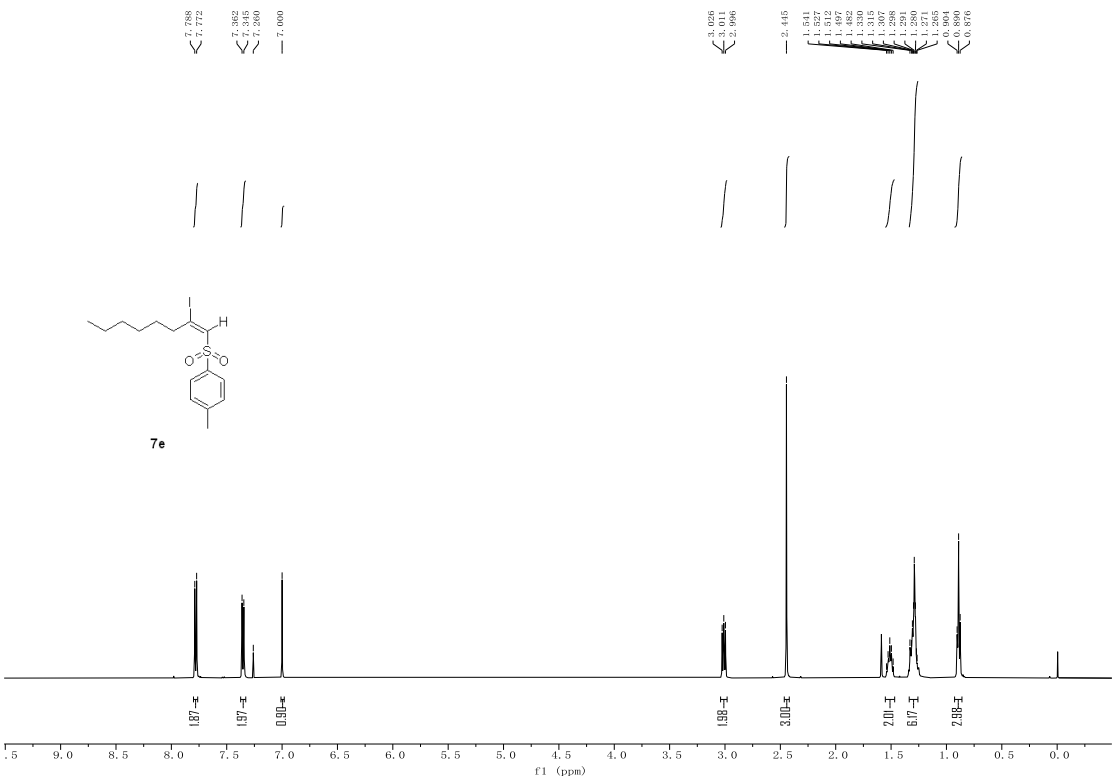
125.090
125.061
125.030
125.000
124.730
123.564
120.400
110.750
77.354
77.146
76.940
21.694
I
H
CF3
S
O
O
7d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.909
I
H
CF3
S
O
O
7d
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)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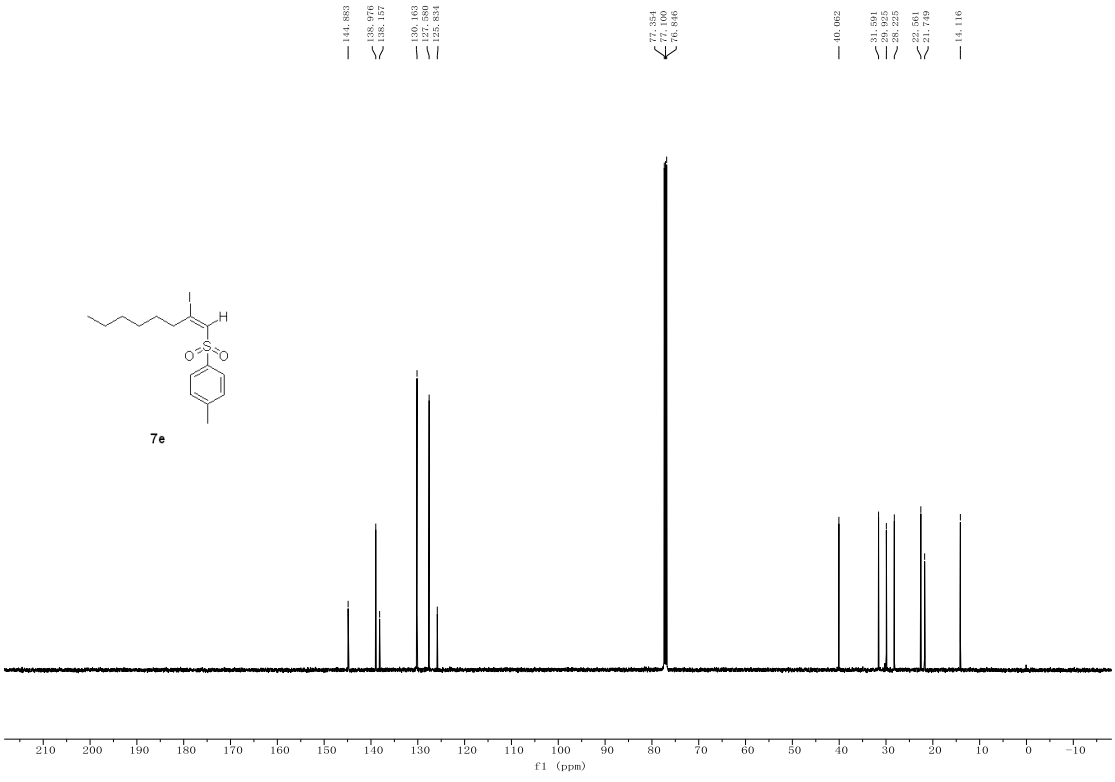
7.362
7.345
7.260
7.000
3.026
3.011
2.996
2.445
1.541
1.527
1.513
1.497
1.482
1.330
1.315
1.298
1.291
1.280
1.271
1.265
0.904
0.890
0.876
I
H
O
S
O
7e
1.87
1.97
0.90
1.98
3.00
2.01
6.07
2.98
f1 (ppm)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138.976
138.157
130.163
127.580
125.834
77.354
77.100
76.846
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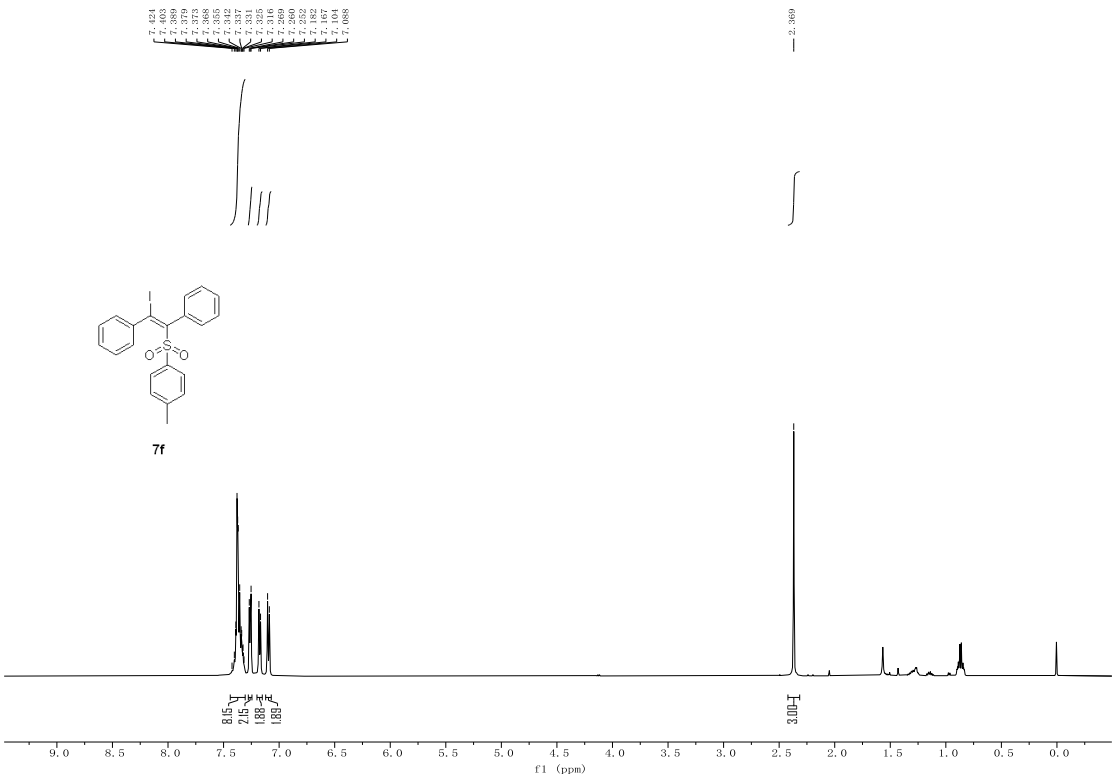
31.591
29.075
28.225
22.561
21.749
14.116
I
H
O
S
O
7e
f1 (ppm)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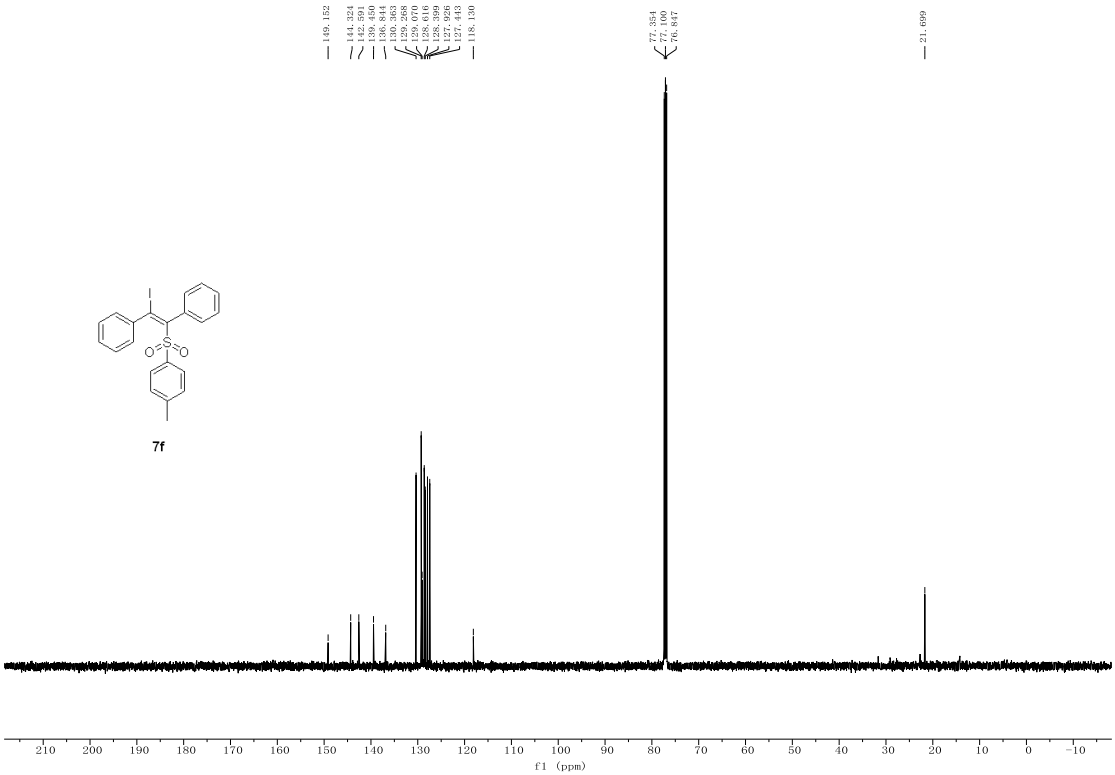
7.403
7.389
7.379
7.373
7.368
7.355
7.342
7.337
7.331
7.325
7.316
7.309
7.260
7.252
7.182
7.167
7.104
7.088
2.369
7f
8.15
2.15
1.88
1.89
3.00
f1 (ppm)


149.152
144.324
142.591
139.450
136.844
130.963
129.268
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128.616
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127.926
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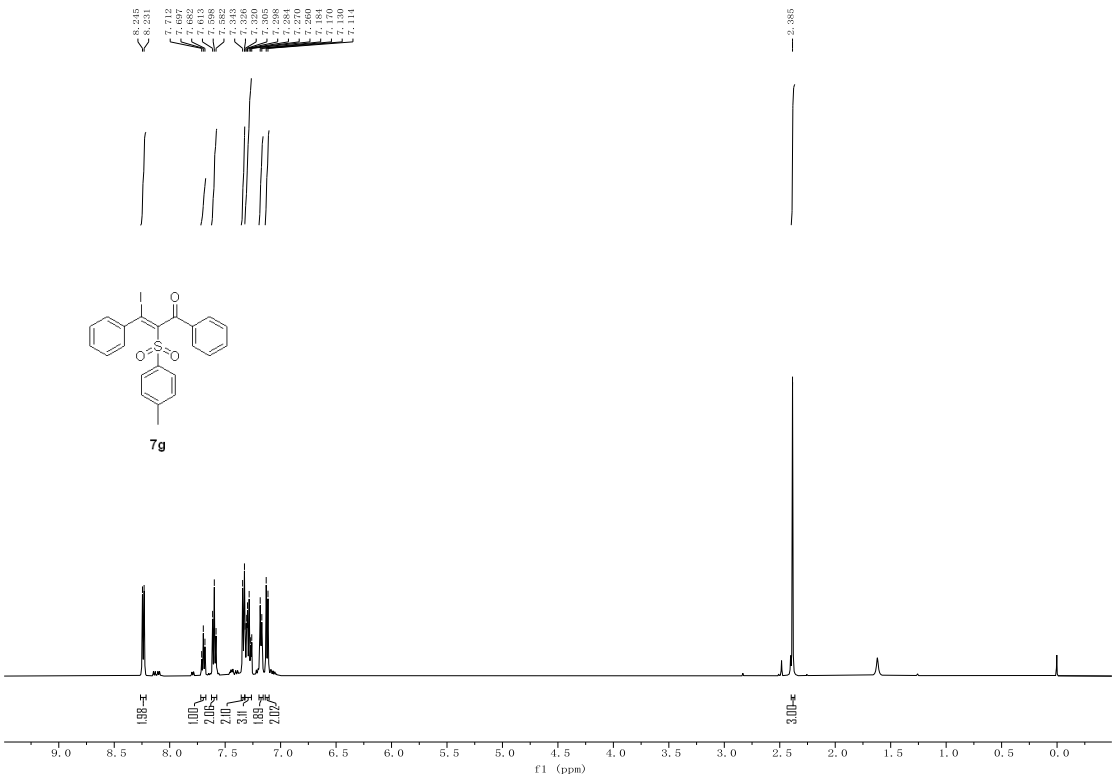
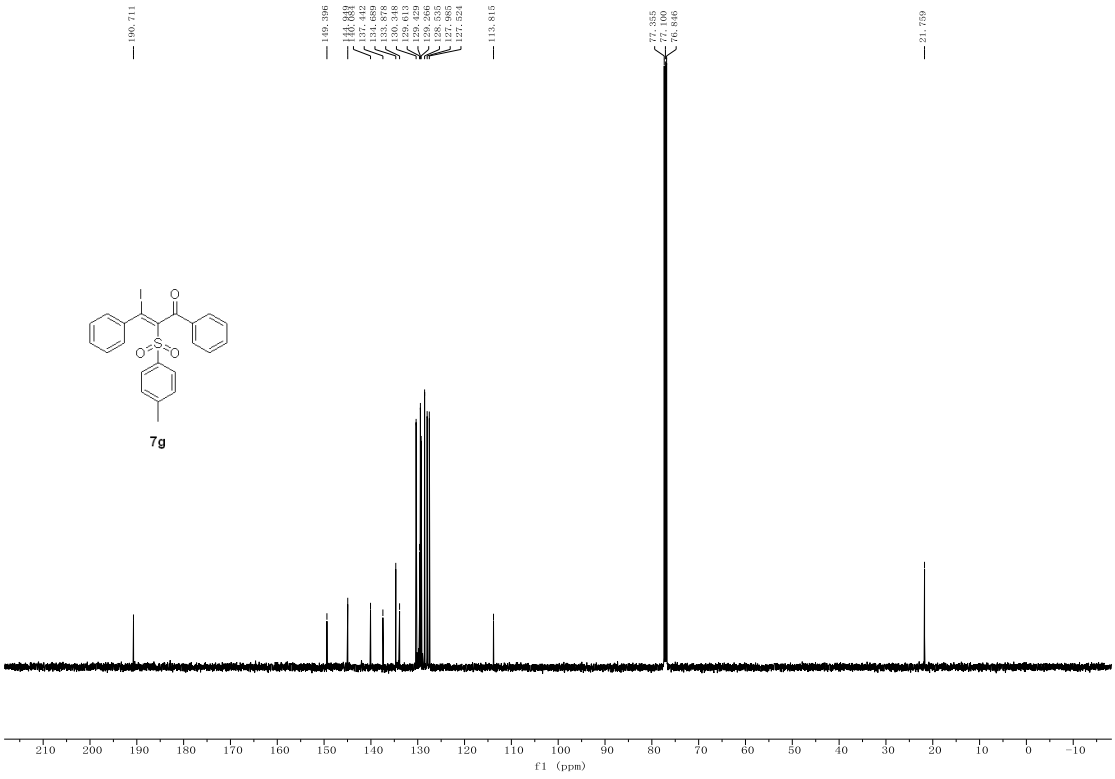
77.100
76.847
21.699
7f
f1 (ppm)


8.245
8.231
7.712
7.697
7.682
7.613
7.598
7.582
7.343
7.336
7.329
7.305
7.298
7.284
7.270
7.266
7.184
7.170
7.130
7.114
2.385
7g
1.98
1.00
2.05
2.10
3.11
1.89
2.02
3.00
f1 (ppm)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134.689
133.878
130.348
129.815
129.429
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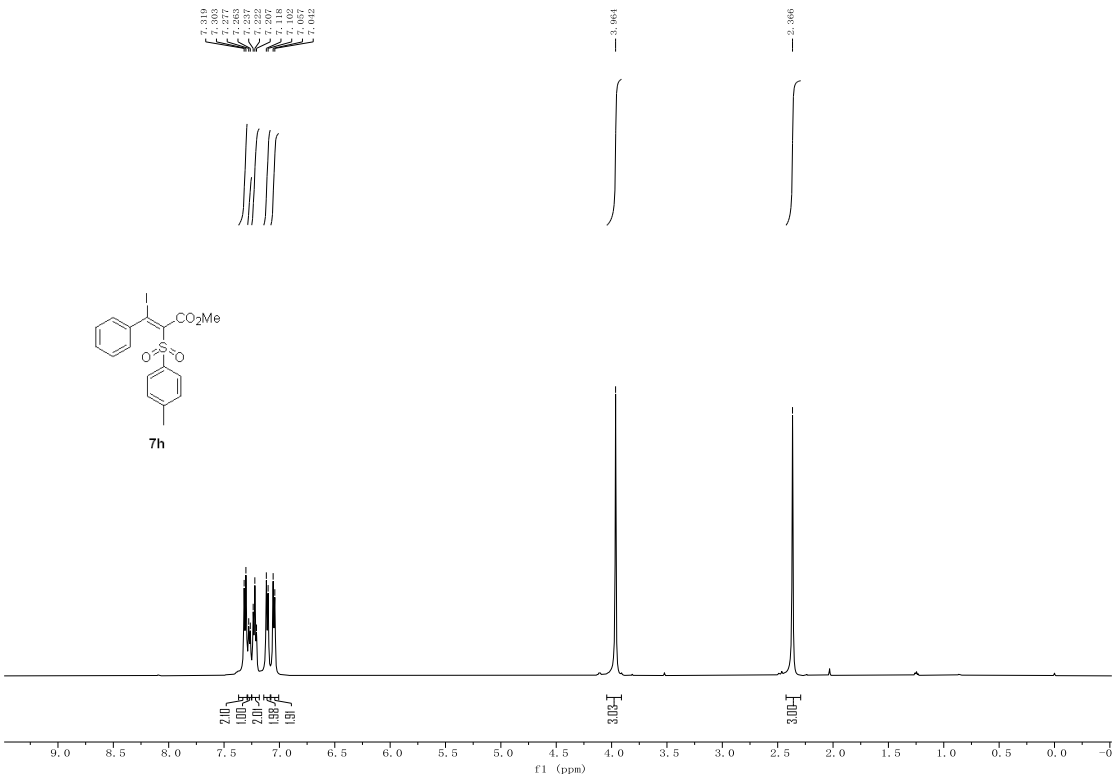
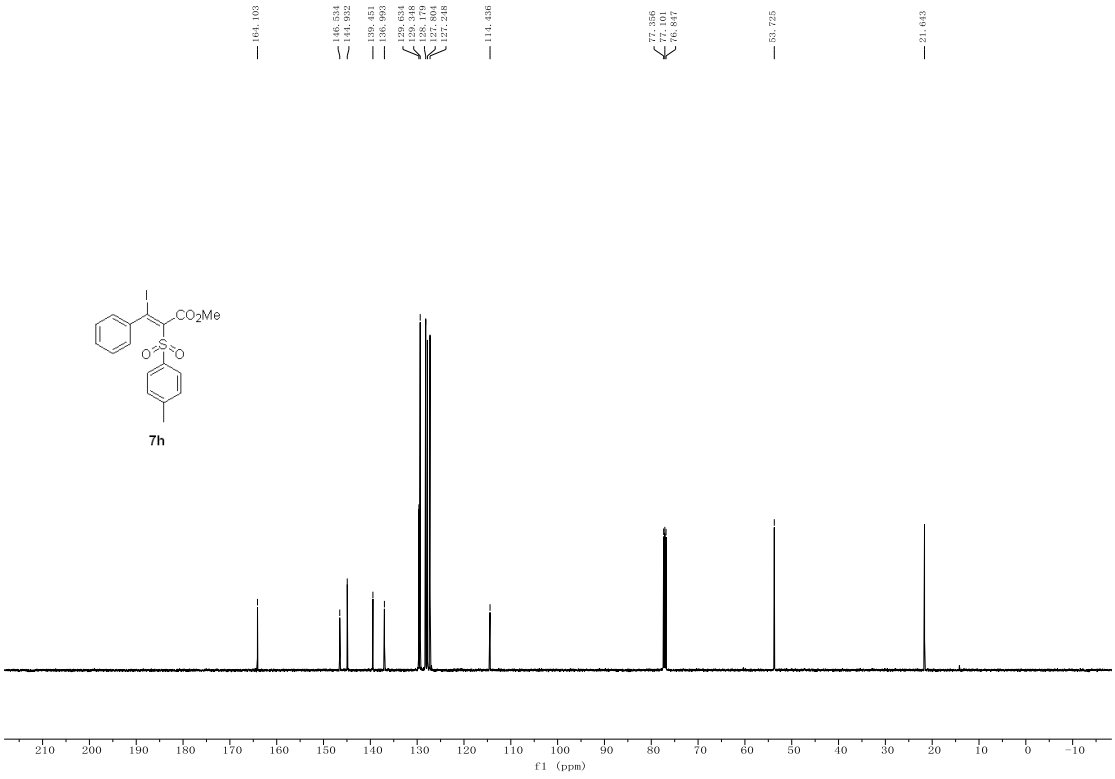
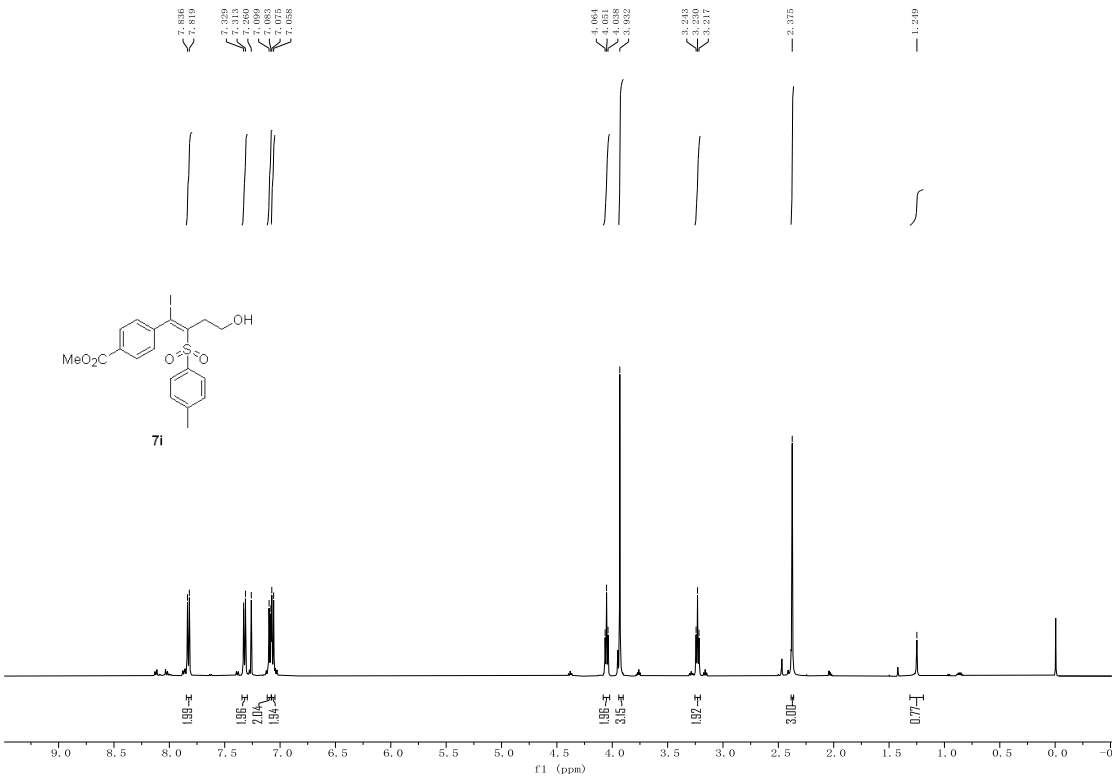
127.985
127.524
113.815
77.355
77.100
76.846
21.739
7g
f1 (ppm)


7.319
7.303
7.277
7.263
7.237
7.222
7.118
7.102
7.057
7.042
3.964
2.366
7h
2.10
1.00
2.10
1.98
1.91
3.03
3.00
f1 (ppm)


164.103
146.534
144.932
139.451
136.993
129.634
129.348
128.179
127.804
127.248
114.436
77.356
77.101
76.847
53.725
21.643
7h
f1 (ppm)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7.339
7.313
7.260
7.099
7.096
7.075
7.058
4.064
4.051
4.038
3.932
3.243
3.230
3.217
2.375
1.249
I
OH
MeO2C
O
S
O
1.99
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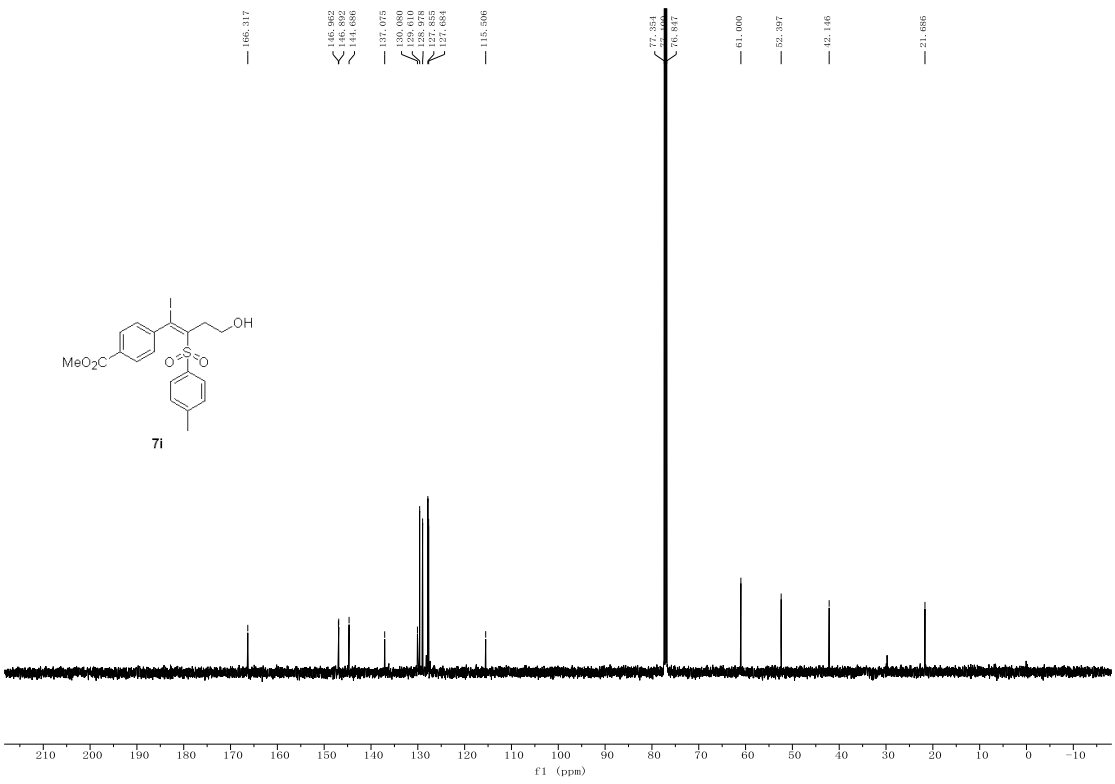
2.04
1.94
1.96
3.15
1.92
3.00
0.77
f1 (ppm)

7i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129.610
128.578
127.855
127.684
115.506
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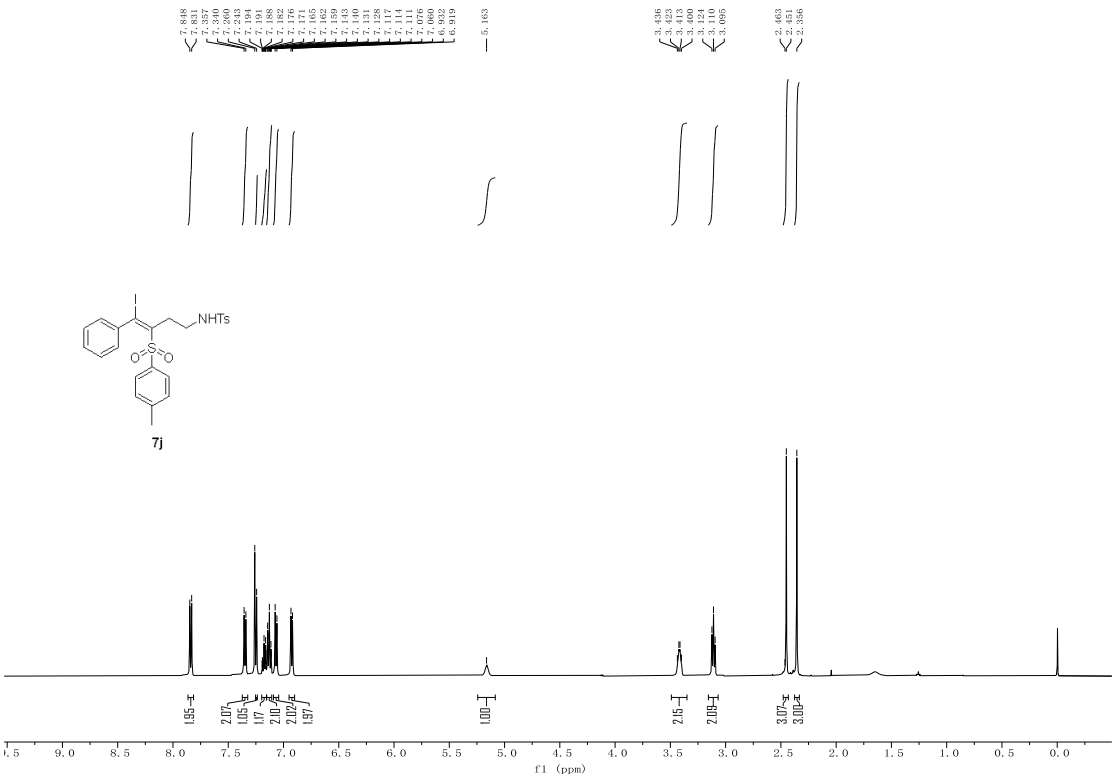
61.000
52.397
42.146
21.686
I
OH
MeO2C
O
S
O
f1 (ppm)

7i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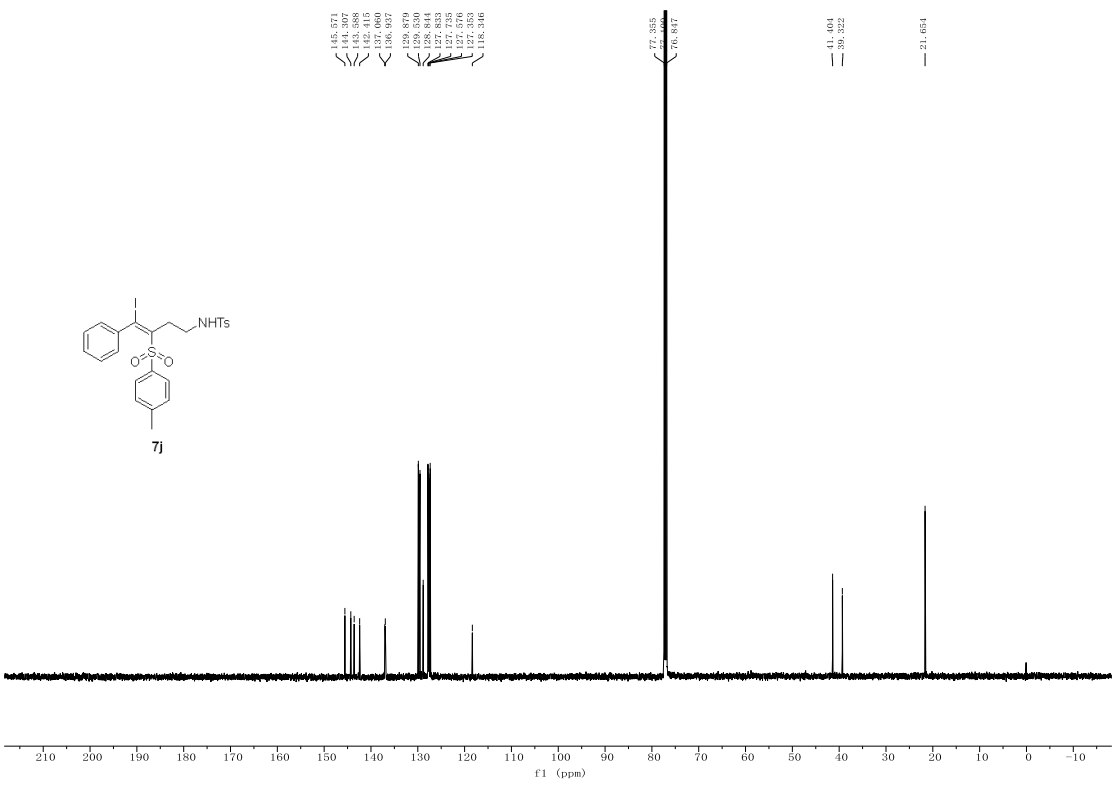
7.191
7.188
7.182
7.176
7.171
7.165
7.162
7.159
7.143
7.140
7.131
7.128
7.117
7.114
7.111
7.076
7.060
6.932
6.919
5.163
3.436
3.423
3.413
3.400
3.124
3.110
3.095
2.463
2.451
2.356
NHTs
7j
1.95
2.07
1.05
1.17
2.10
2.02
1.97
1.00
2.15
2.09
3.07
3.00
f1 (ppm)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127.833
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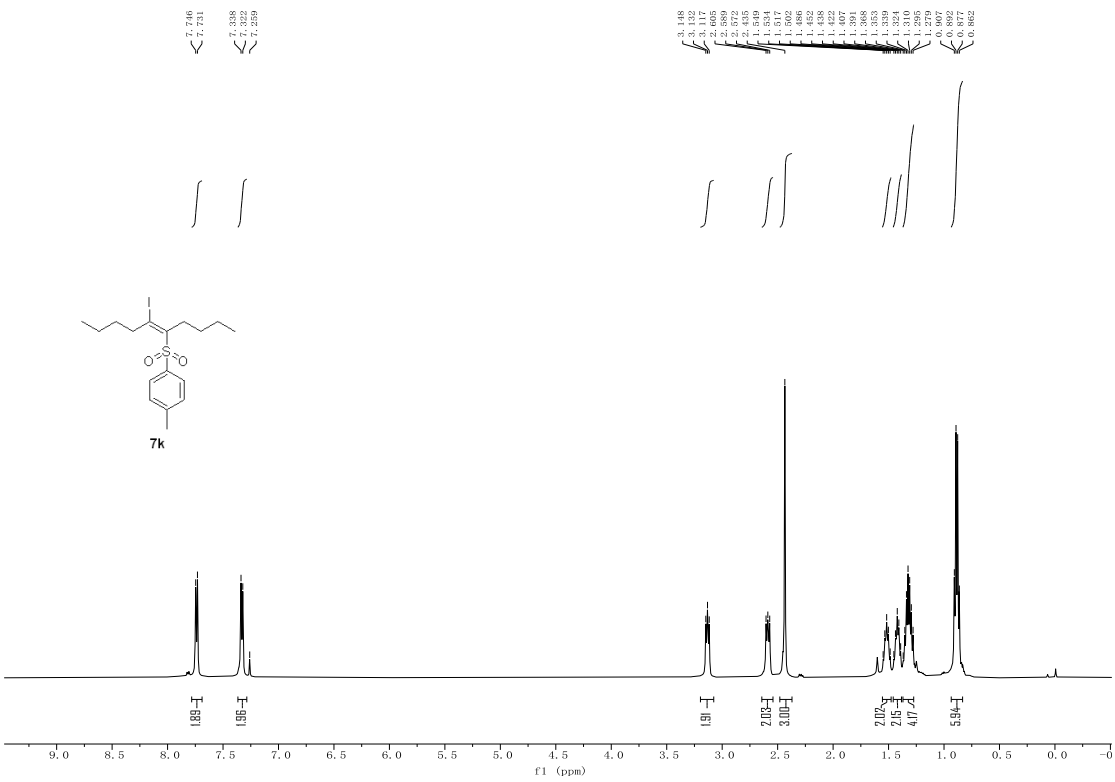
77.355
77.146
76.847
41.404
39.322
21.654
NHTs
7j
f1 (ppm)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3.117
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2.589
2.572
2.435
2.419
1.534
1.517
1.502
1.486
1.452
1.438
1.422
1.407
1.391
1.368
1.353
1.339
1.324
1.310
1.295
1.279
0.906
0.892
0.877
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7k
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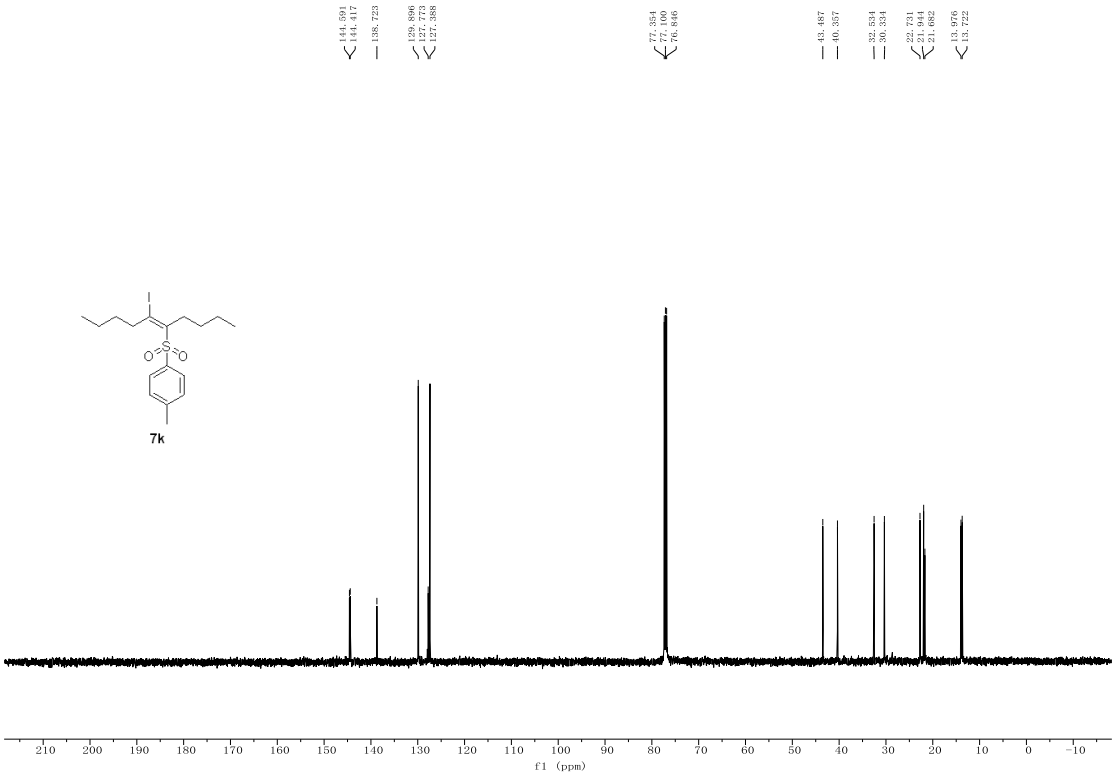
1.96
1.91
2.03
3.00
2.02
2.15
4.17
5.94
f1 (ppm)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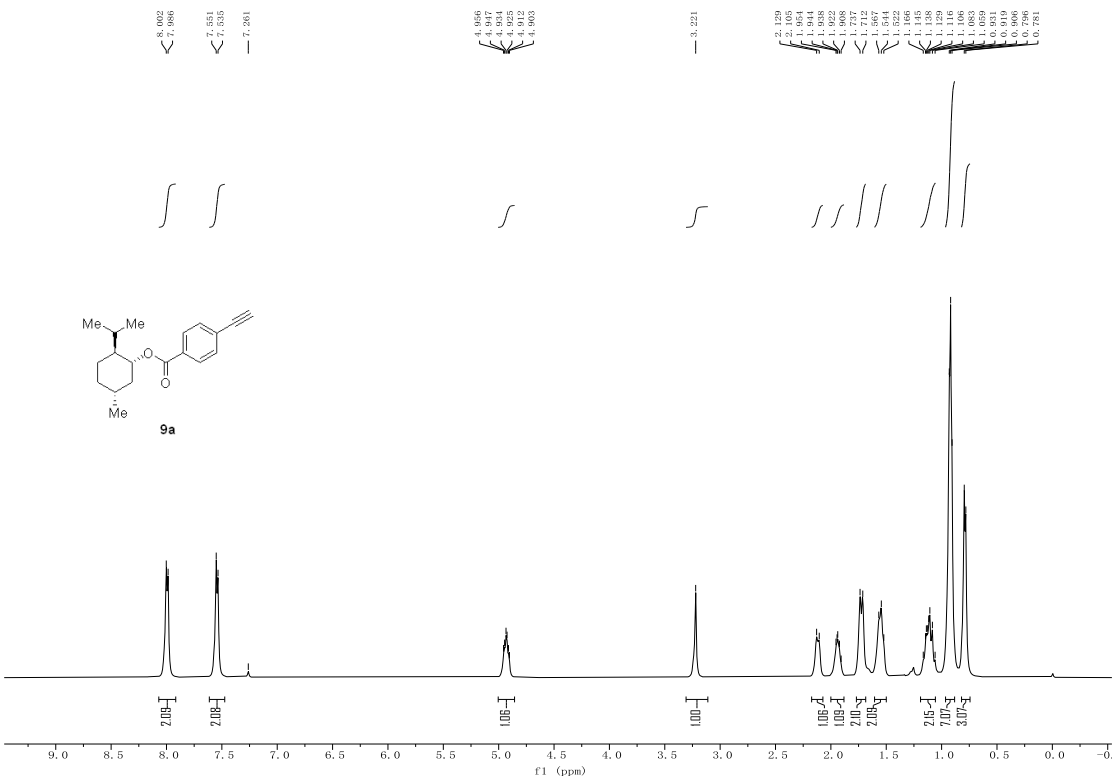
7k
f1 (ppm)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4.934
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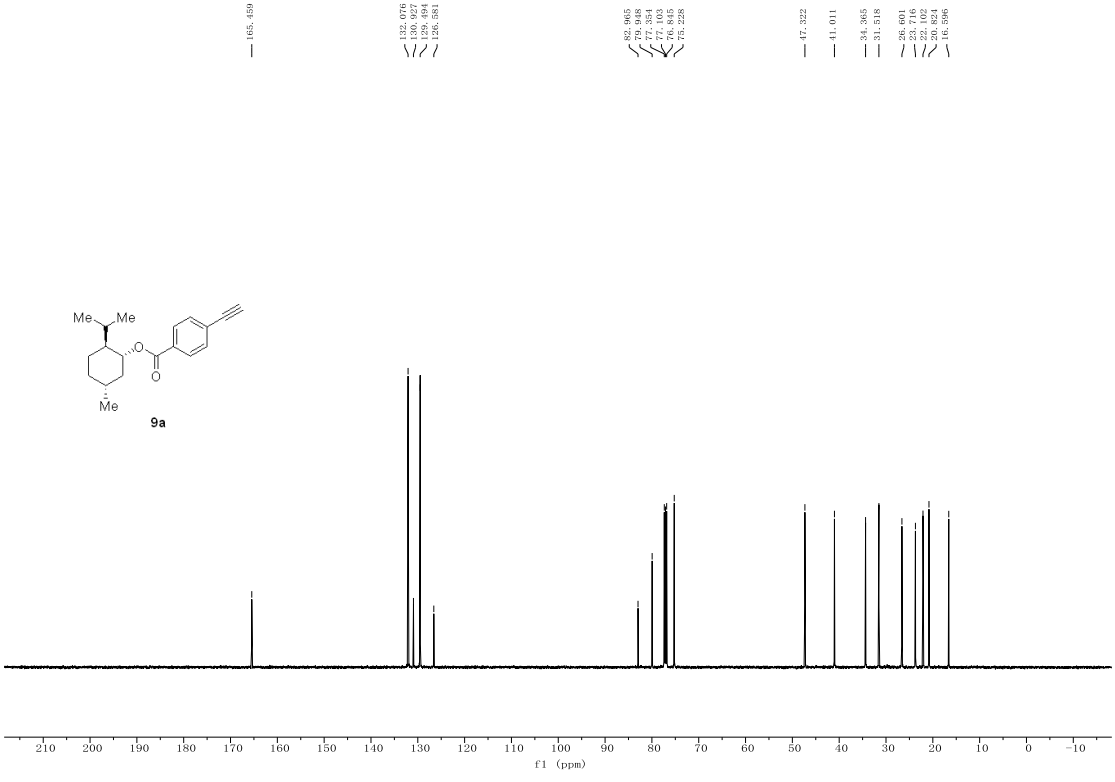
3.221
2.129
2.105
1.964
1.944
1.938
1.922
1.908
1.737
1.712
1.567
1.544
1.522
1.166
1.145
1.138
1.129
1.116
1.106
1.083
1.059
0.931
0.919
0.906
0.796
0.791
Me
Me
O
O
Me
9a
2.09
2.08
1.06
1.00
1.06
1.09
2.10
2.08
2.15
7.07
3.07
f1 (ppm)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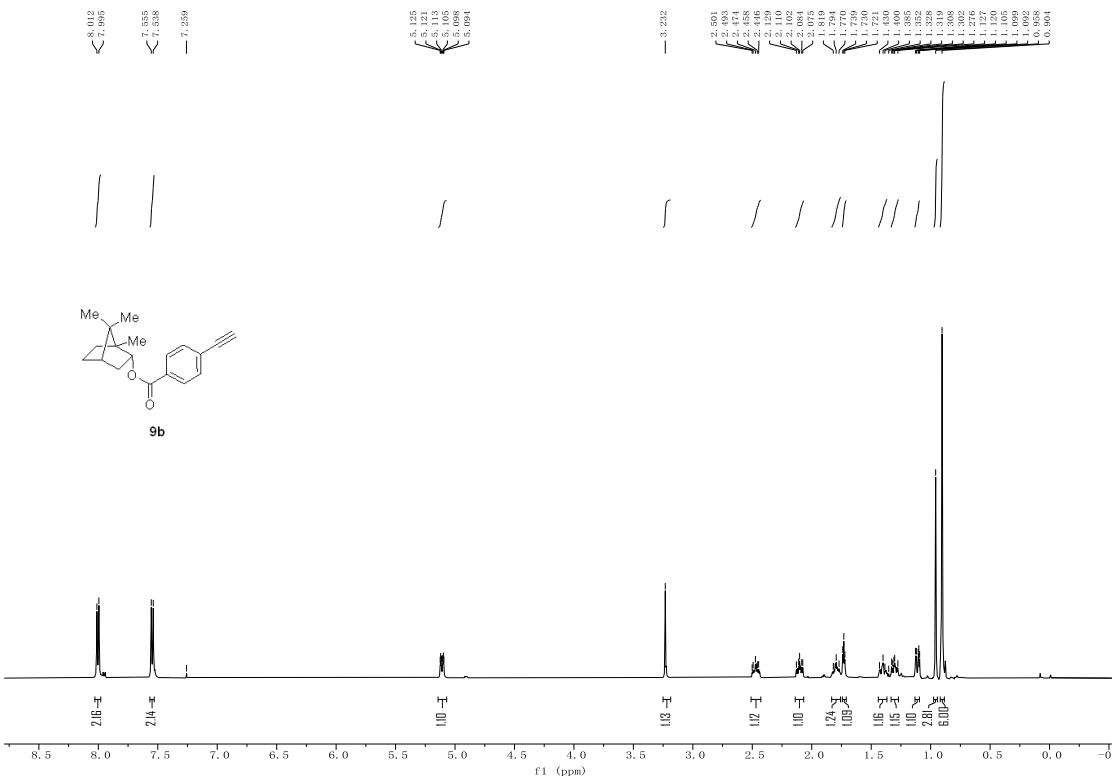
77.354
77.040
76.845
75.228
47.322
41.011
34.365
31.518
26.601
23.776
22.162
20.824
16.596
Me
Me
O
O
Me
9a
f1 (ppm)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5.094
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2.493
2.474
2.438
2.446
2.129
2.110
2.102
2.084
2.075
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1.794
1.770
1.739
1.730
1.721
1.430
1.409
1.385
1.352
1.328
1.319
1.308
1.302
1.276
1.237
1.150
1.105
1.099
1.092
1.058
0.904
Me
Me
Me
O
O
9b
2.16
2.14
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1.13
1.12
1.10
1.24
1.09
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1.15
1.10
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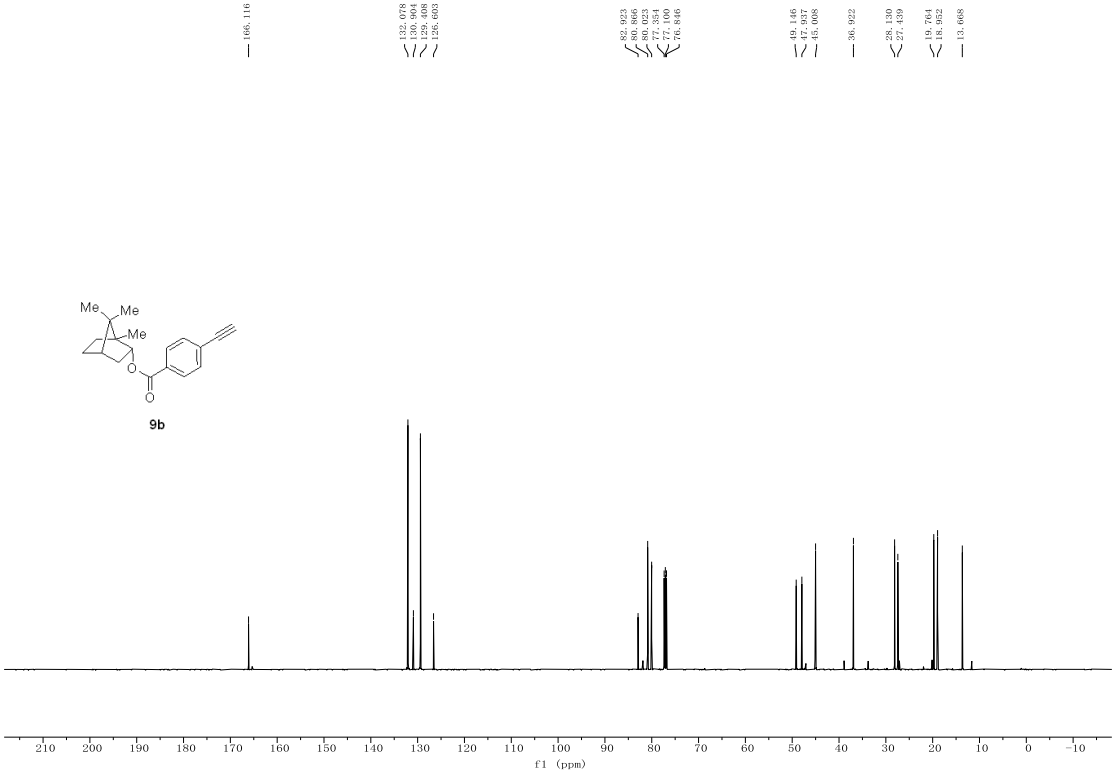
6.00
f1 (ppm)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80.072
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77.106
76.846
49.146
47.937
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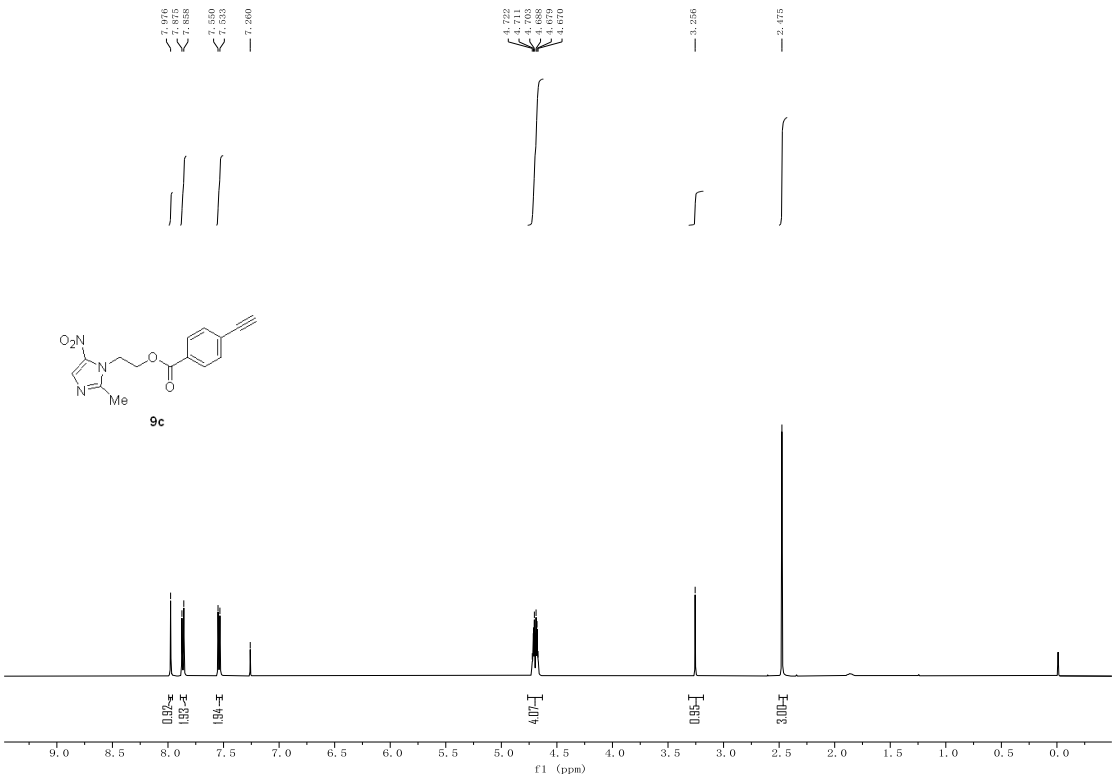
27.439
19.764
18.952
13.668
Me
Me
Me
O
O
9b
f1 (ppm)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4.732
4.711
4.703
4.688
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2.475
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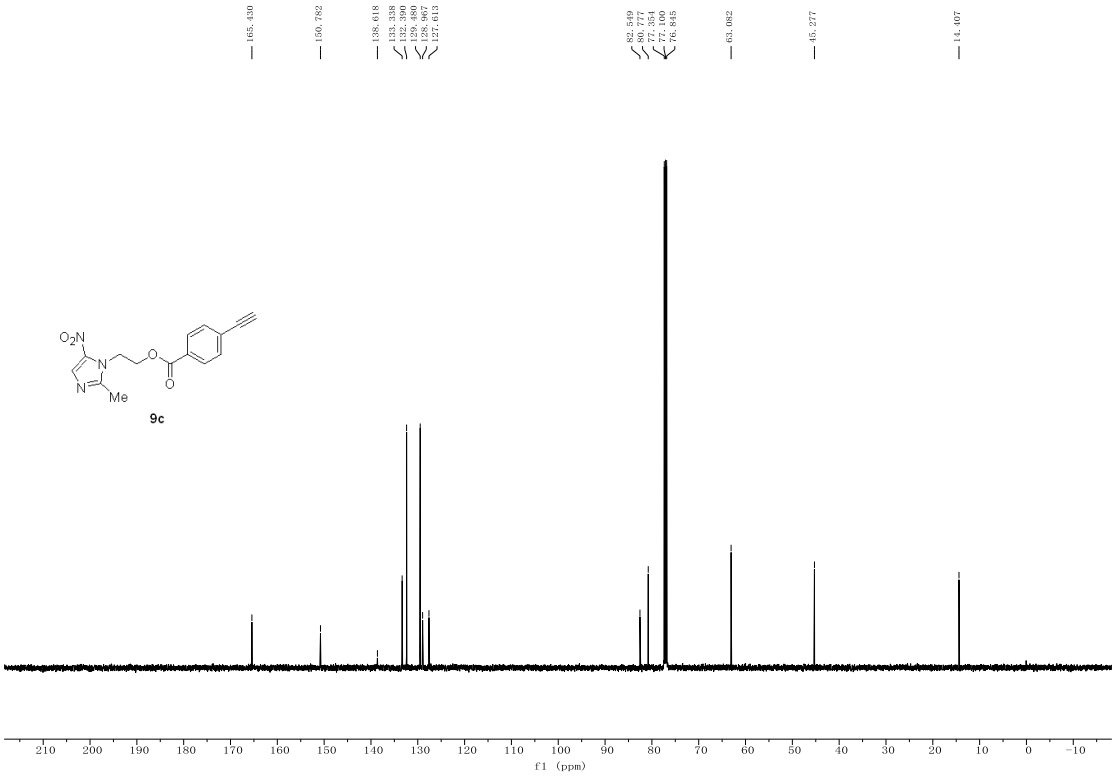
1.94
4.07
0.95
3.00
f1 (ppm)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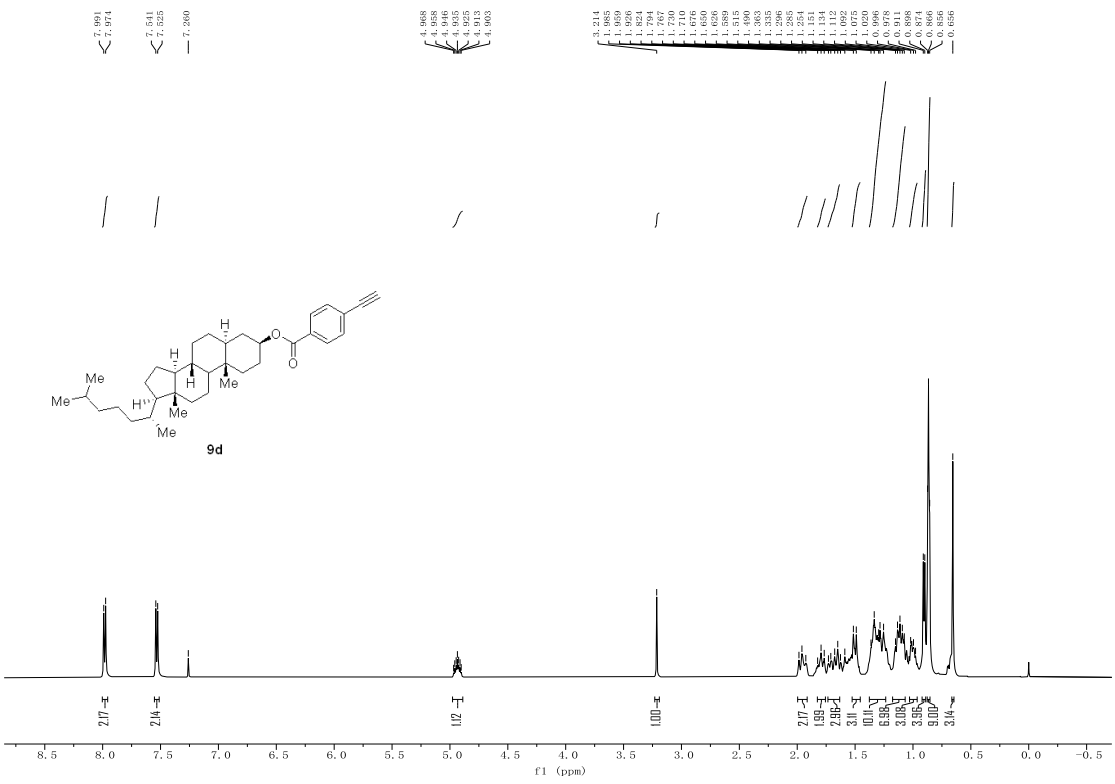
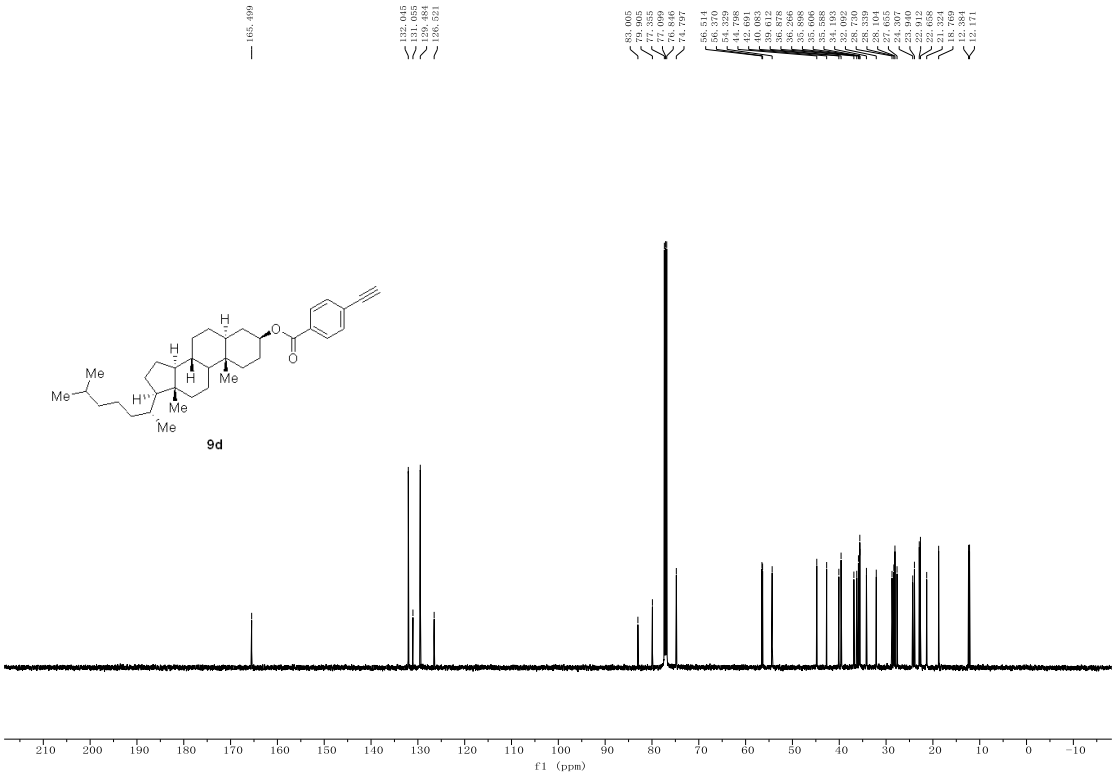
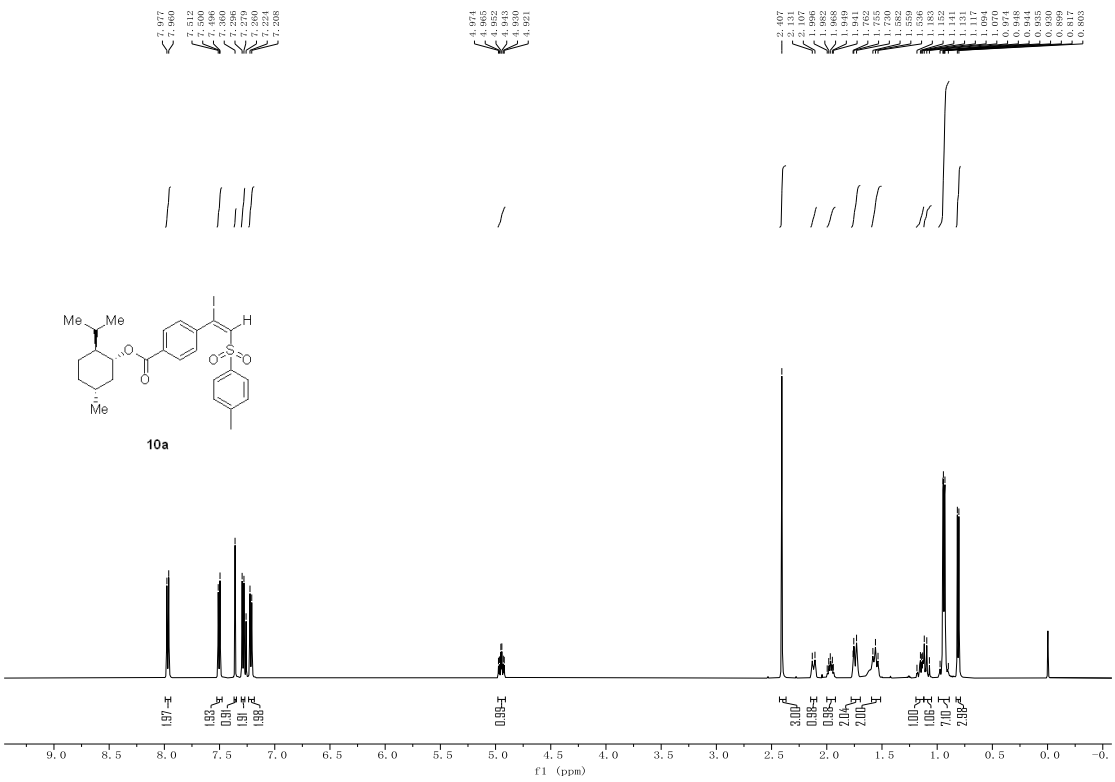
14.407
9c
f1 (ppm)


9d
f1 (ppm)


9d
f1 (ppm)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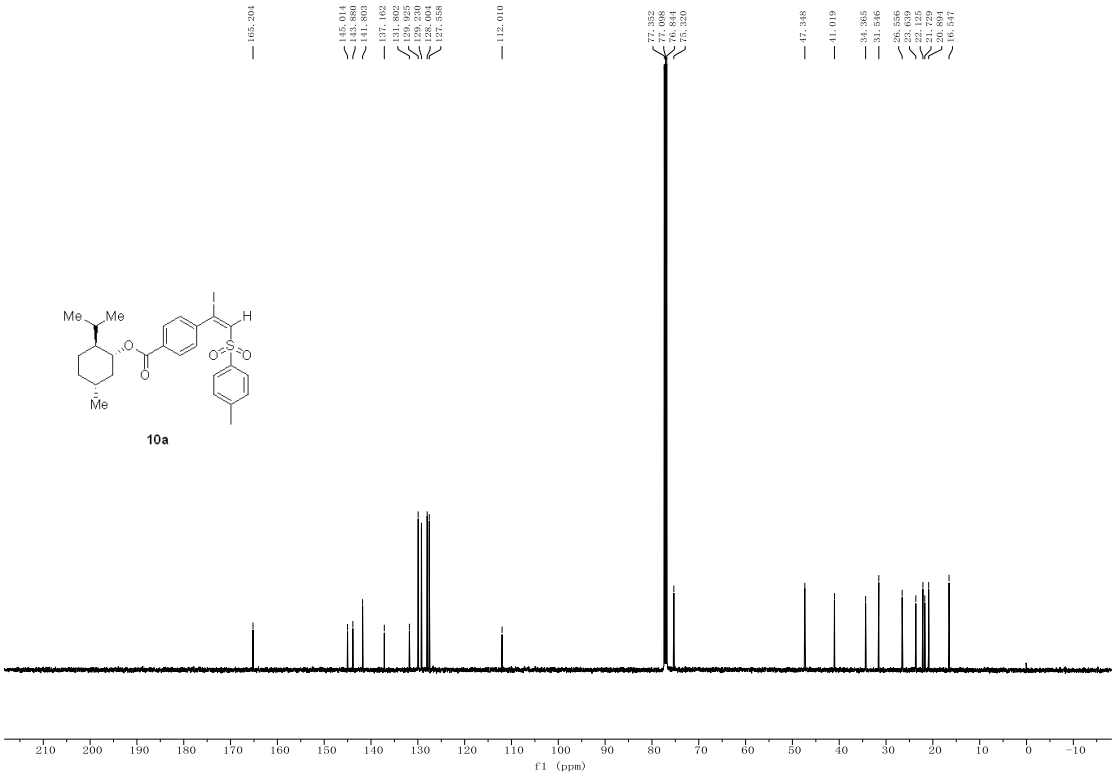
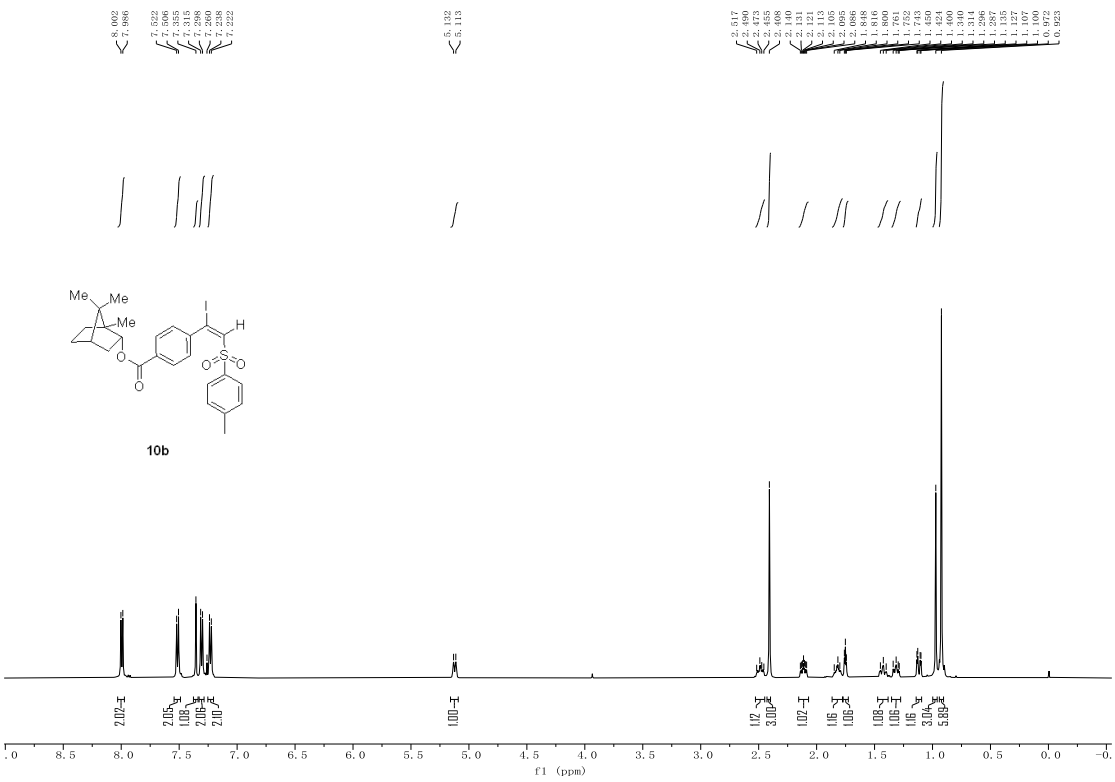
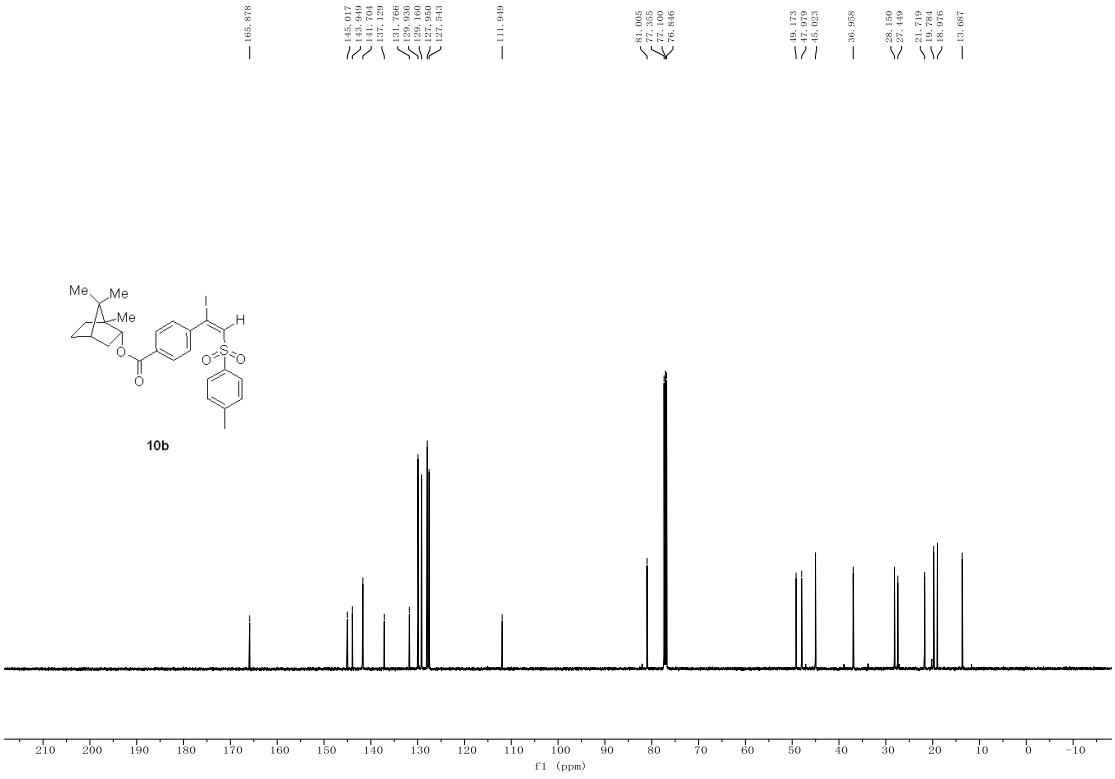
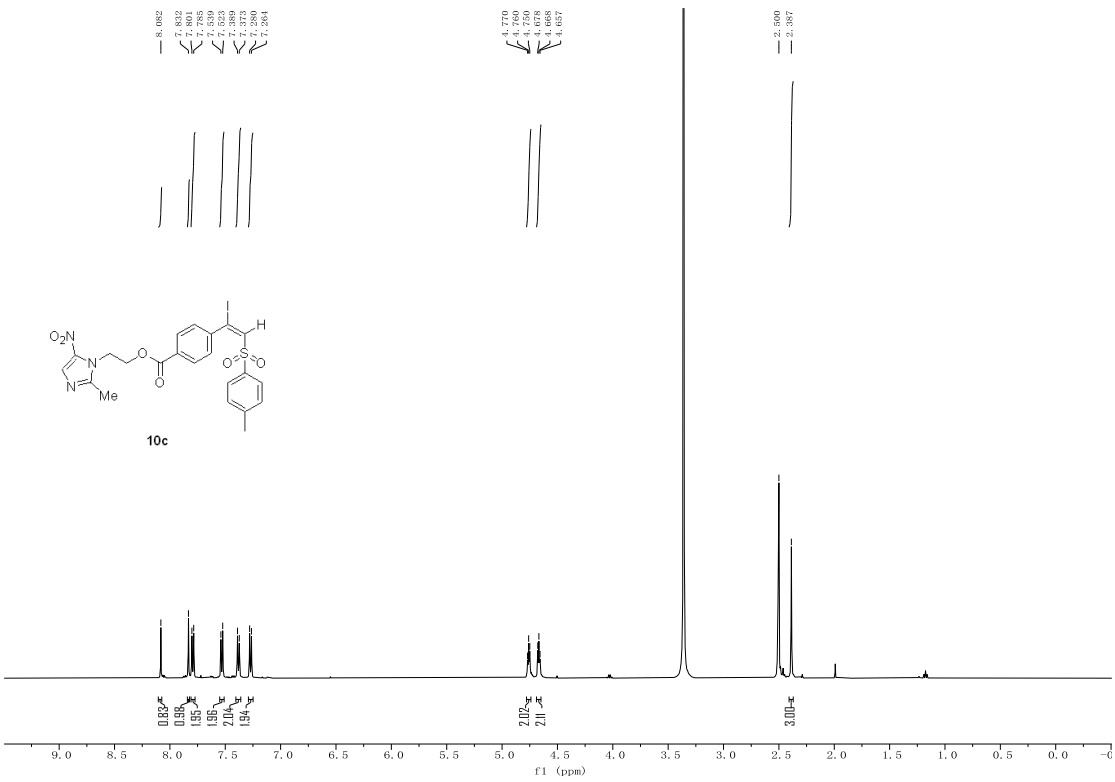
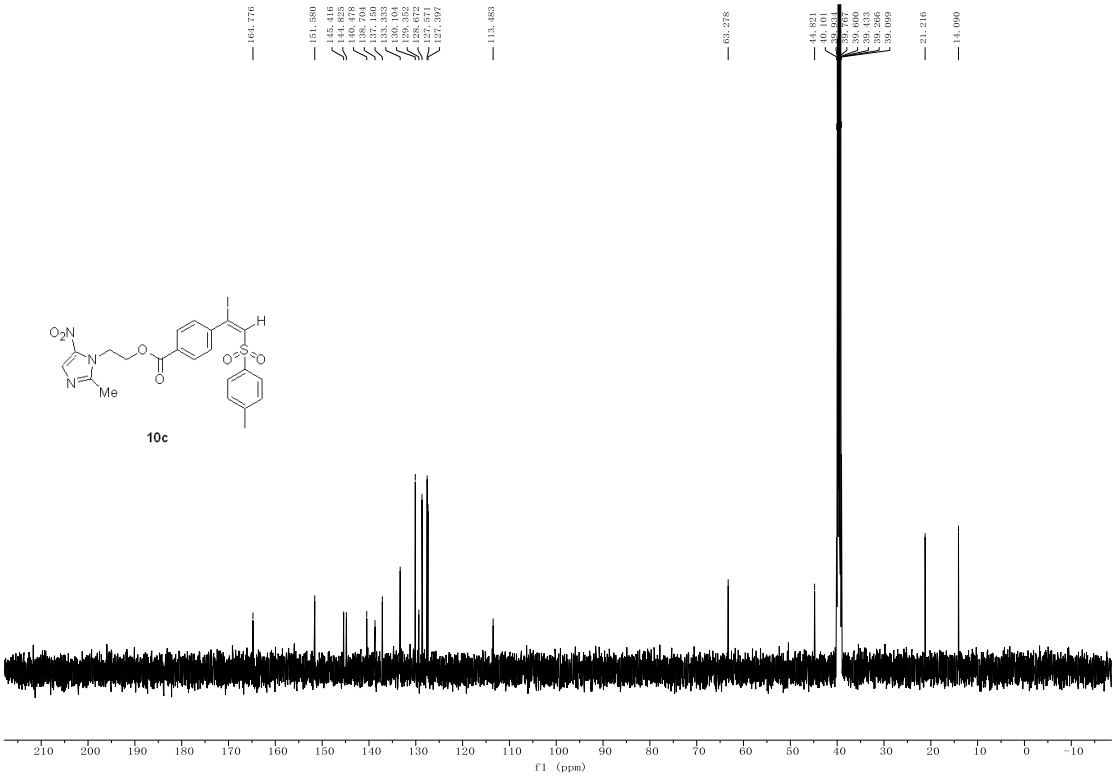
7.960
7.512
7.490
7.486
7.360
7.296
7.279
7.260
7.224
7.208
4.974
4.965
4.952
4.943
4.930
4.921
2.407
2.131
2.097
1.998
1.982
1.968
1.949
1.941
1.762
1.755
1.730
1.582
1.559
1.536
1.183
1.152
1.141
1.131
1.117
1.094
1.070
0.974
0.948
0.944
0.935
0.930
0.899
0.817
0.803
Me
Me
Me
O
O
I
H
S
O
O
10a
1.97
1.93
0.91
1.91
1.98
0.89
3.09
0.98
0.98
2.04
2.04
1.00
1.06
7.10
2.89
f1 (ppm)

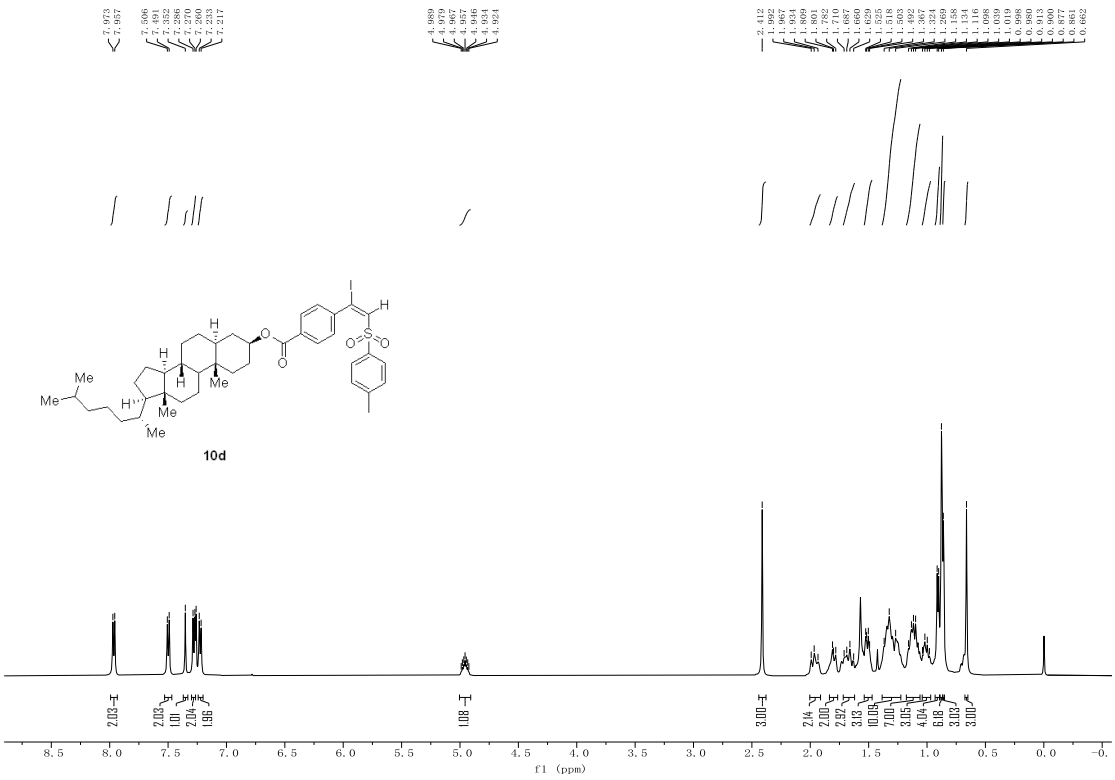

165.204
145.014
143.880
141.605
137.162
131.802
130.955
129.230
128.064
127.538
112.010
77.352
77.098
76.844
75.320
47.348
41.019
34.365
31.546
26.556
23.639
22.125
21.729
20.964
16.547
Me
Me
Me
O
O
I
H
S
O
O
10a
f1 (ppm)

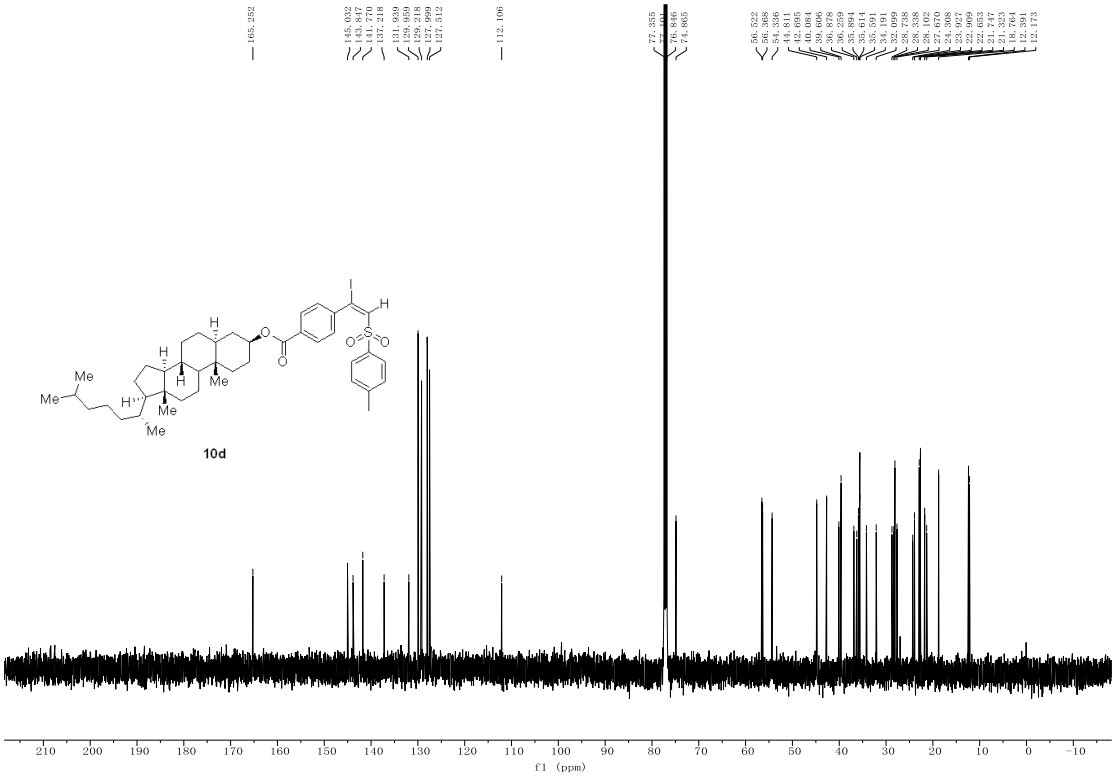

8.002
7.986
7.622
7.606
7.355
7.315
7.298
7.260
7.238
7.222
5.132
5.113
2.517
2.490
2.475
2.455
2.408
2.140
2.131
2.121
2.113
2.105
2.095
2.085
1.848
1.816
1.800
1.791
1.752
1.743
1.490
1.454
1.400
1.340
1.314
1.306
1.287
1.135
1.127
1.107
1.100
0.972
0.923
Me
Me
Me
O
O
I
H
S
O
O
10b
2.02
2.05
1.08
2.08
2.10
1.00
1.12
3.00
1.02
1.16
1.08
1.08
1.06
1.16
3.04
5.88
f1 (ppm)

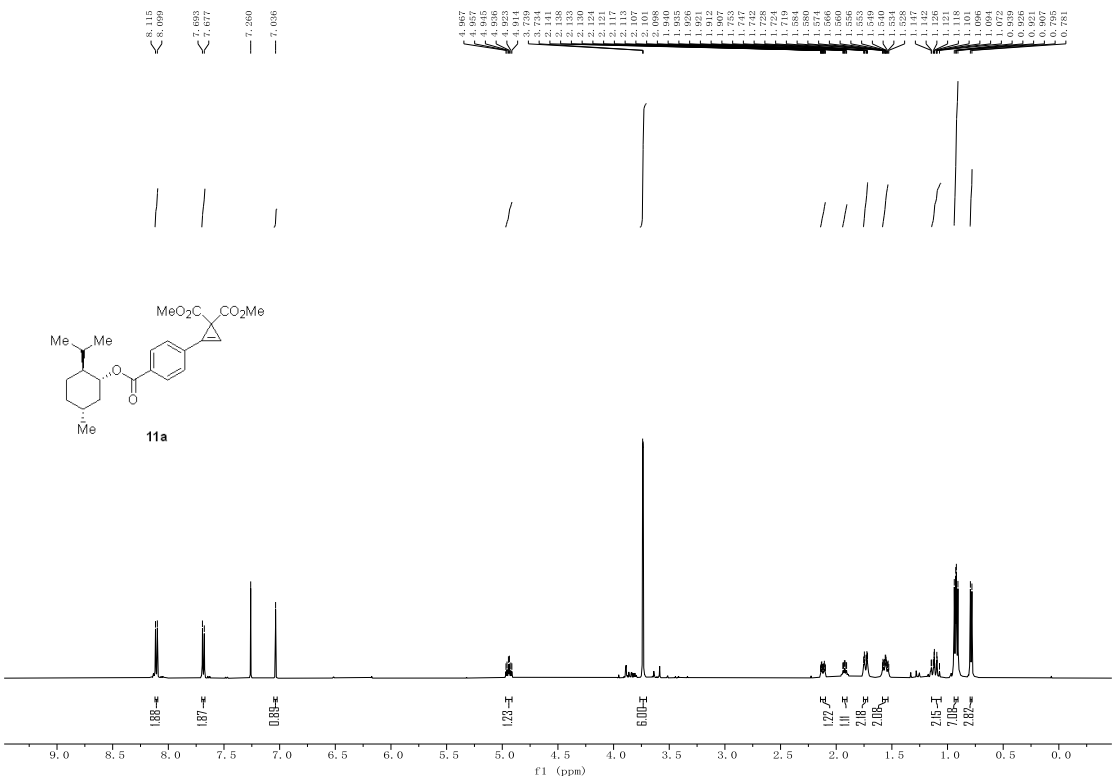

165.878
145.017
143.949
141.704
137.129
131.766
130.936
129.160
127.950
127.543
111.949
81.005
77.355
77.000
76.646
49.173
47.979
45.023
36.958
28.150
27.449
21.719
19.784
18.976
13.687
Me
Me
Me
O
O
I
H
S
O
O
10b
f1 (ppm)

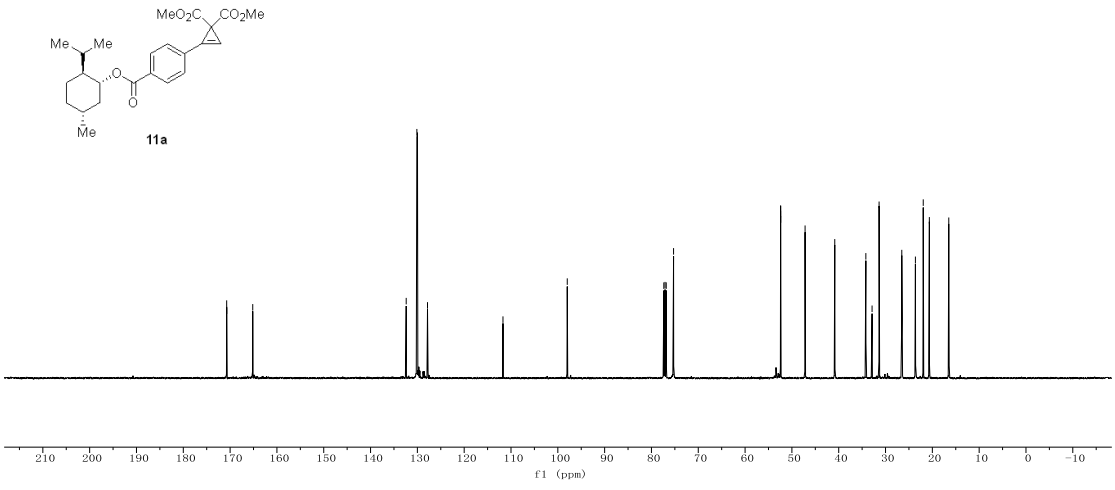

8.082
7.832
7.801
7.785
7.536
7.523
7.389
7.373
7.360
7.264
4.770
4.760
4.750
4.678
4.668
4.657
2.590
2.387
0.83
0.98
1.95
1.96
2.04
1.94
2.02
2.11
3.00
f1 (ppm)
10c

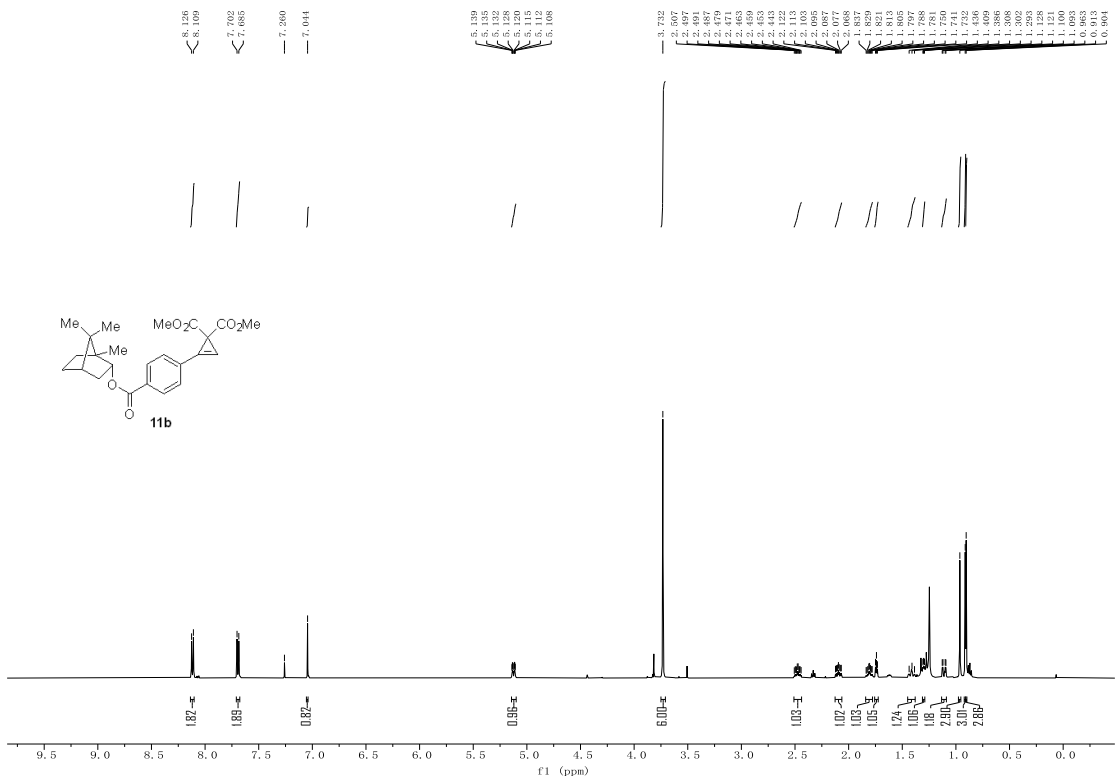

164.776
151.580
145.416
144.825
140.678
138.704
137.150
133.333
130.014
129.352
128.672
127.571
127.397
113.483
63.278
44.821
40.101
39.934
39.767
39.600
39.433
39.266
39.099
21.216
14.090
f1 (ppm)
10c

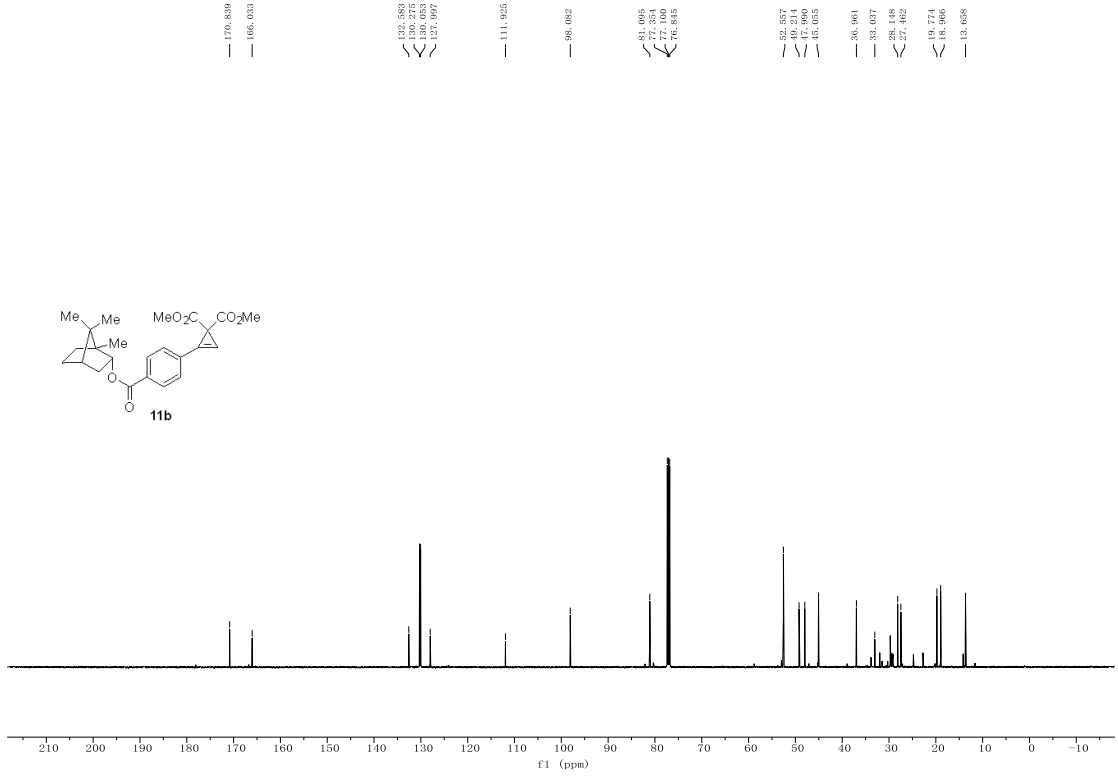

10d
f1 (ppm)

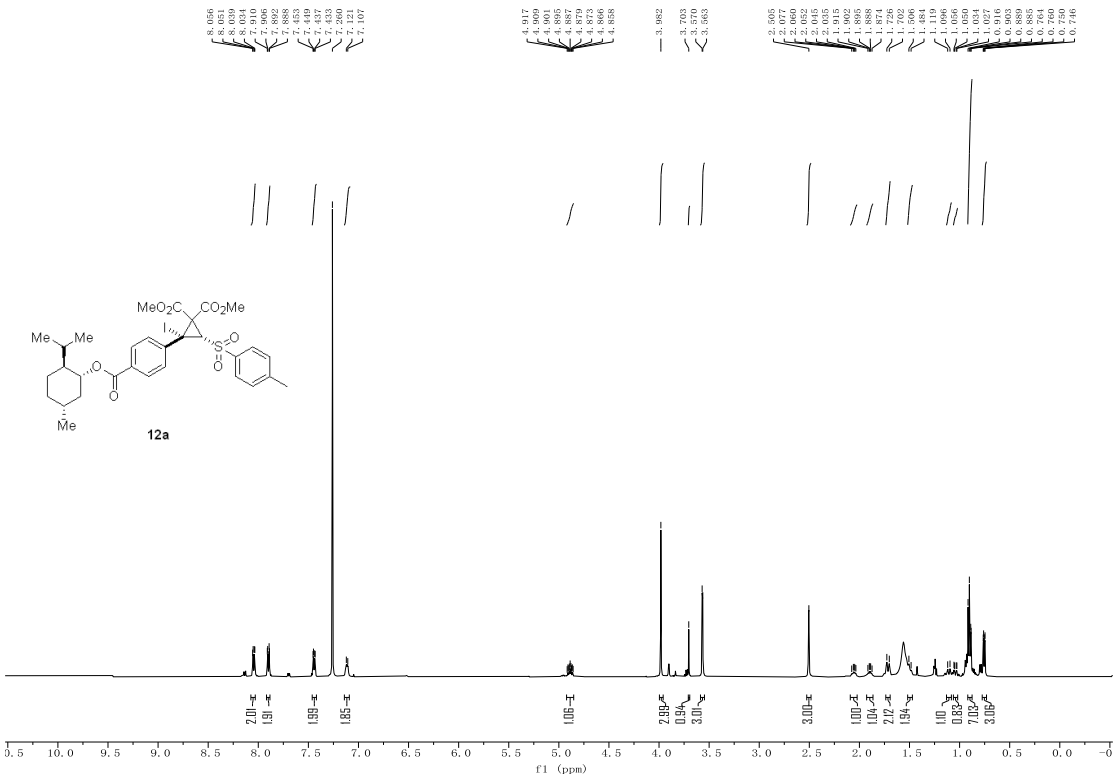

10d
f1 (ppm)

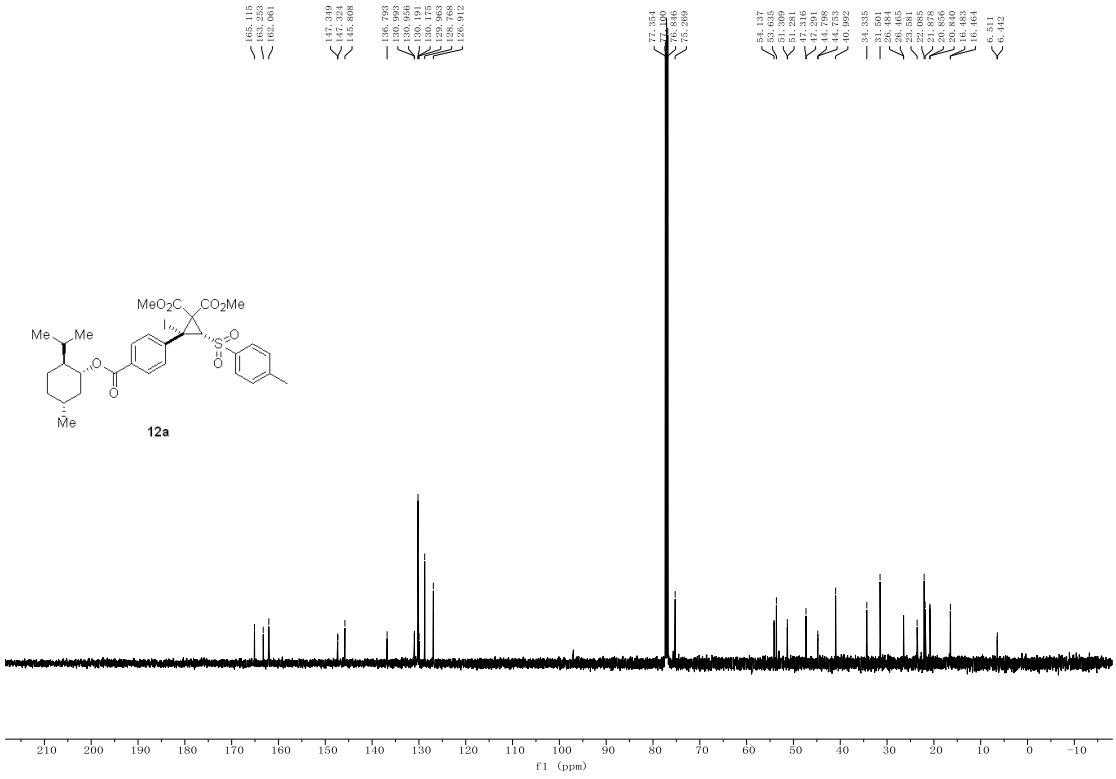

MeO2C
CO2Me
Me
Me
O
O
Me
11a
f1 (ppm)

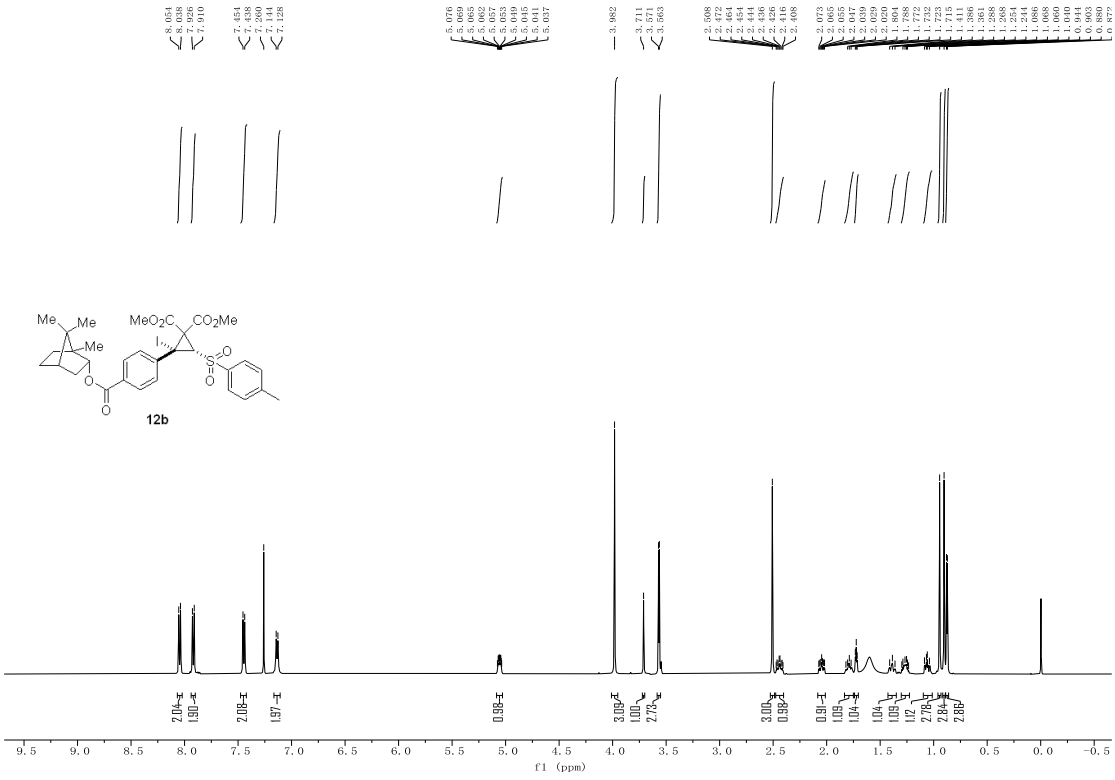

MeO2C
CO2Me
Me
Me
O
O
Me
11a
f1 (ppm)

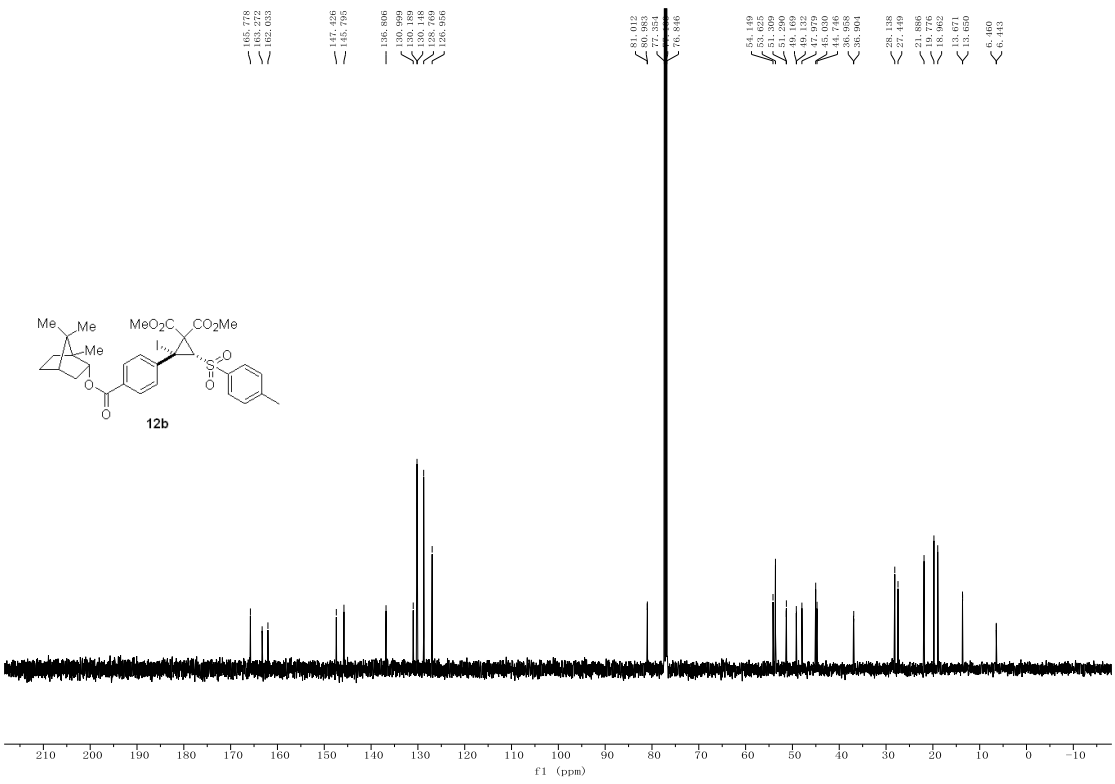

8.136
8.109
7.792
7.685
7.290
7.044
5.139
5.135
5.132
5.128
5.120
5.115
5.112
5.108
3.732
2.507
2.497
2.491
2.487
2.474
2.471
2.463
2.459
2.455
2.443
2.122
2.113
2.095
2.085
2.087
2.077
2.068
1.857
1.829
1.821
1.813
1.805
1.797
1.788
1.781
1.750
1.741
1.732
1.436
1.429
1.398
1.308
1.302
1.293
1.258
1.121
1.100
1.093
0.985
0.913
0.904
Me
Me
Me
O
O
MeO2C
CO2Me
11b
1.82
1.89
0.87
0.95
6.00
1.03
1.02
1.03
1.05
1.24
1.06
1.18
2.94
3.01
2.89
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)

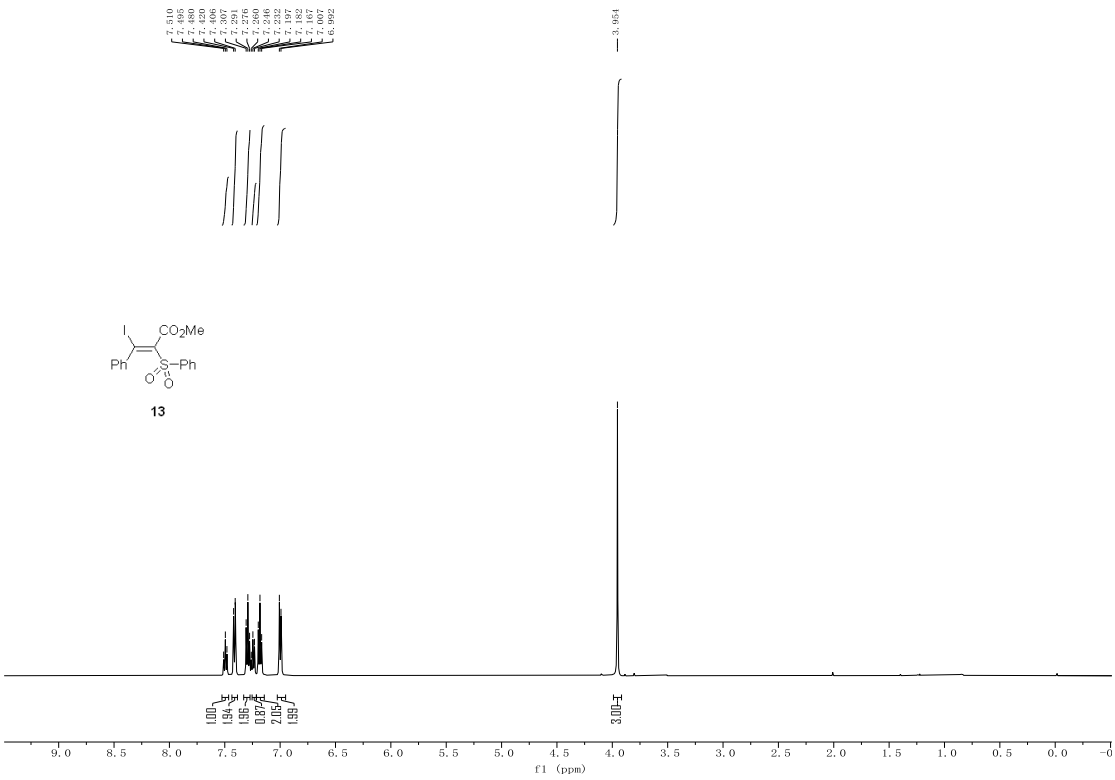

170.839
166.033
132.583
130.275
130.058
127.997
111.925
98.082
81.095
77.354
77.000
76.645
52.557
49.214
47.590
45.695
36.961
33.037
28.148
27.462
19.774
18.966
13.658
Me
Me
Me
O
O
MeO2C
CO2Me
11b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

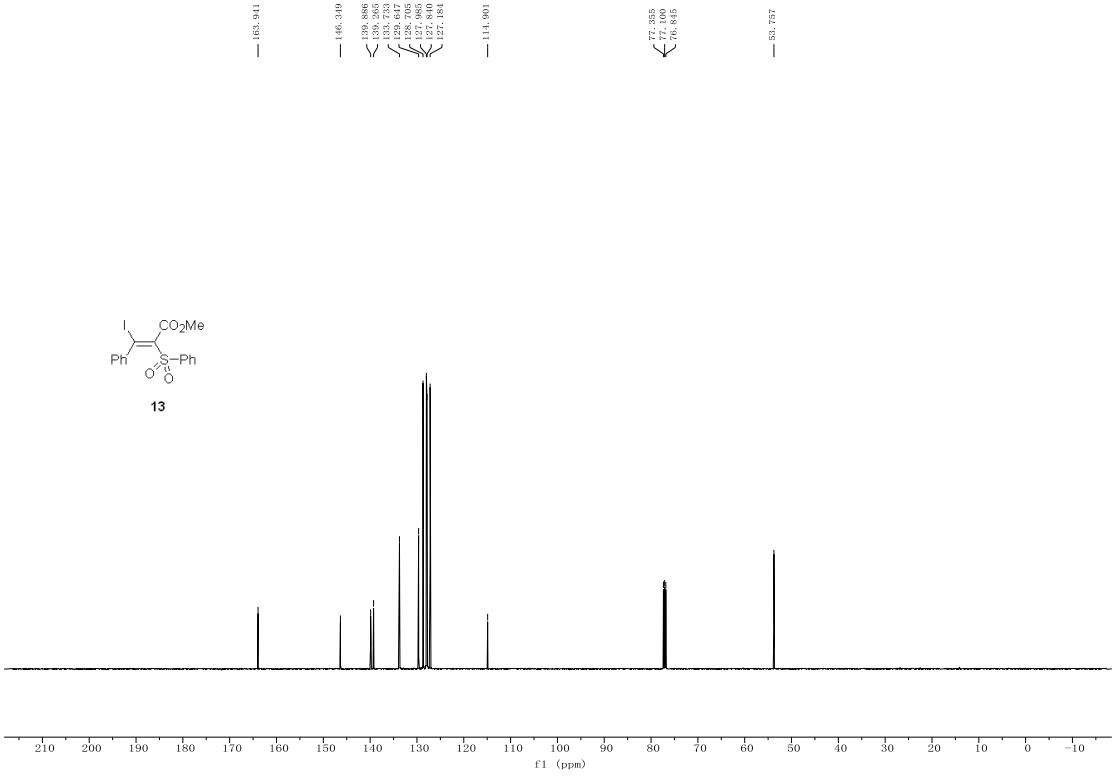

MeO2C
CO2Me
Me
Me
Me
O
O
S
O
O
12a
f1 (ppm)

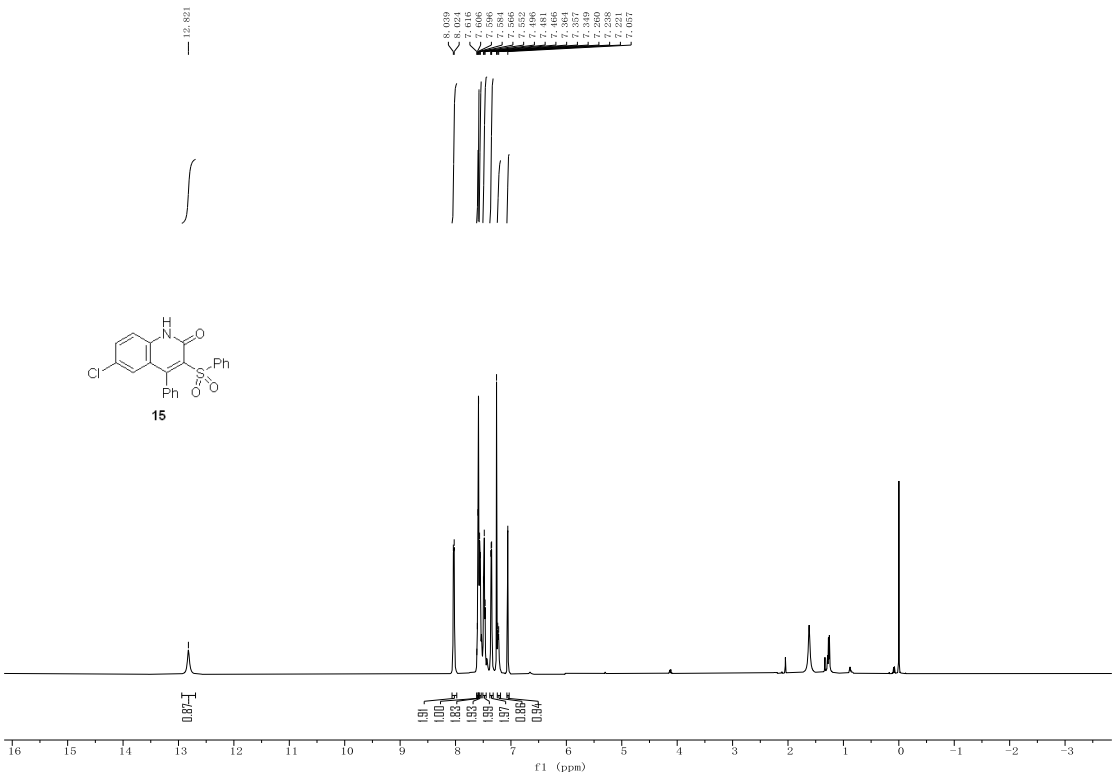

MeO2C
CO2Me
Me
Me
Me
O
O
S
O
O
12a
f1 (ppm)

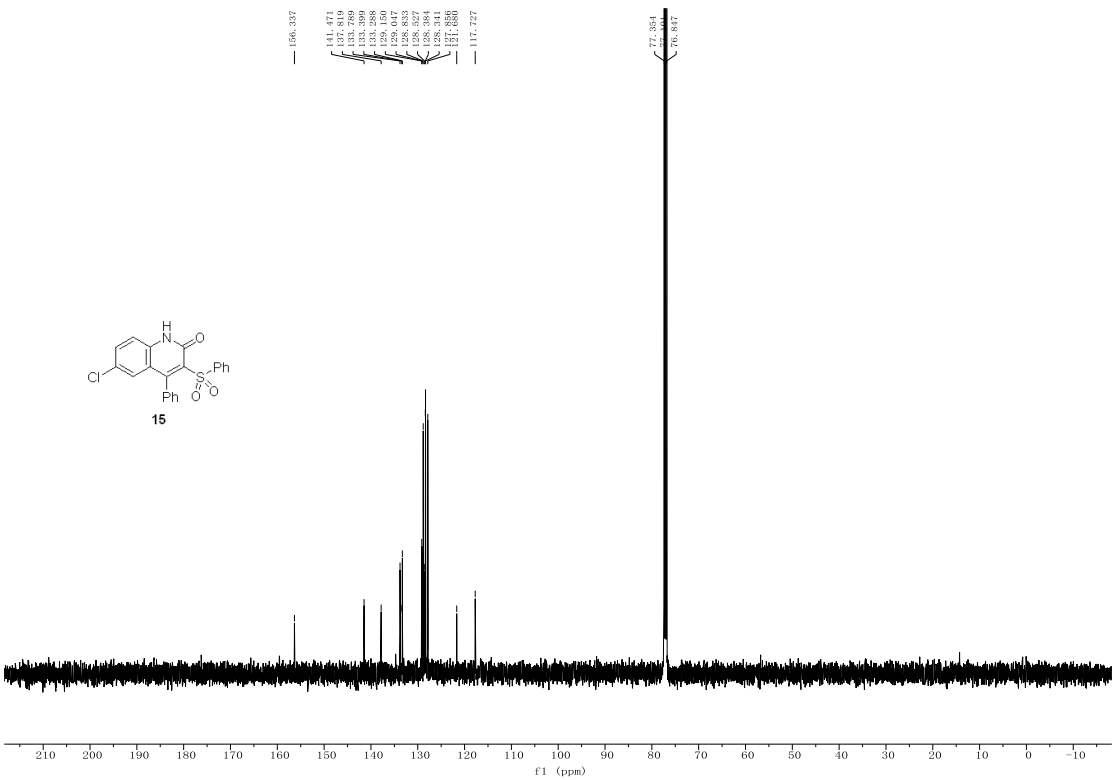

12b
f1 (ppm)


12b
f1 (ppm)


7.510
7.495
7.480
7.420
7.406
7.307
7.291
7.276
7.260
7.246
7.232
7.197
7.182
7.167
7.007
6.992
3.954
I
CO2Me
Ph
S
Ph
O
O
13
1.00
1.94
1.96
0.87
2.05
1.99
3.00
f1 (ppm)


163.941
146.349
139.886
139.265
133.723
129.647
128.705
128.595
127.985
127.840
127.184
114.901
77.355
77.100
76.845
53.757
I
CO2Me
Ph
S
Ph
O
O
13
f1 (ppm)


12.821
8.039
8.024
7.616
7.598
7.596
7.584
7.566
7.552
7.466
7.481
7.466
7.364
7.357
7.349
7.260
7.238
7.231
7.057
15
0.87
1.91
1.00
1.83
1.53
1.99
1.97
0.89
0.94
f1 (ppm)


156.337
141.471
137.819
133.799
133.399
133.288
129.150
129.047
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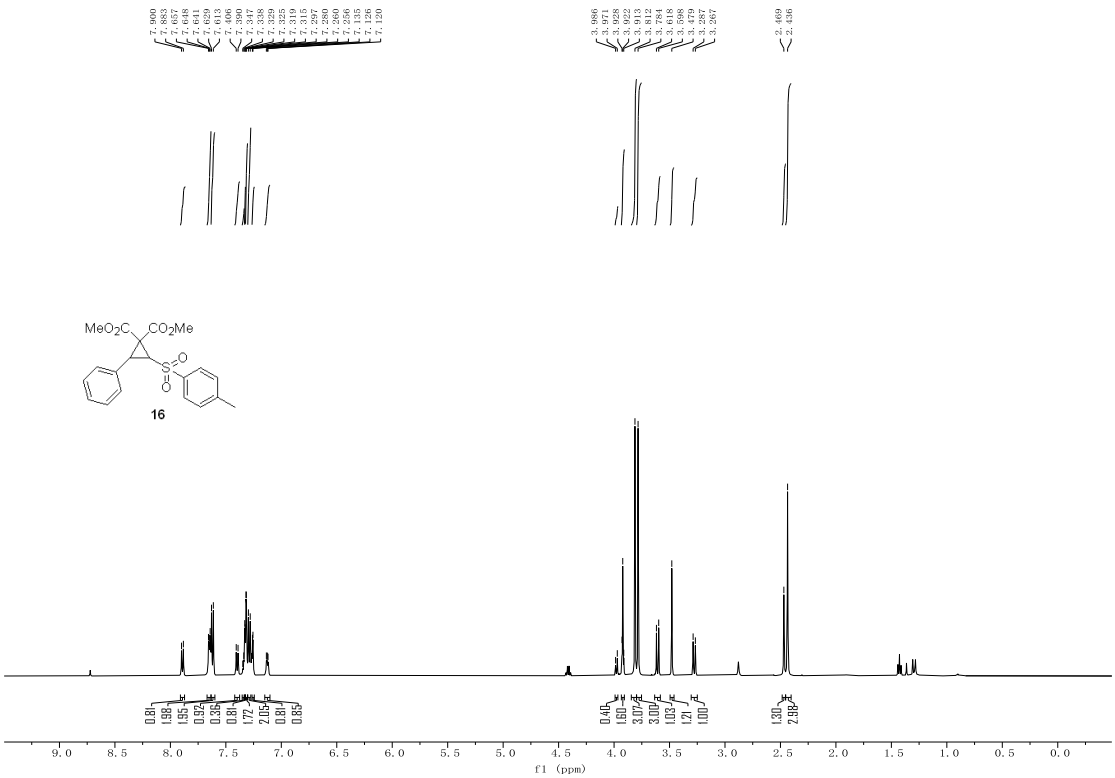
128.384
128.341
127.895
121.680
117.727
77.354
77.042
76.847
15
f1 (ppm)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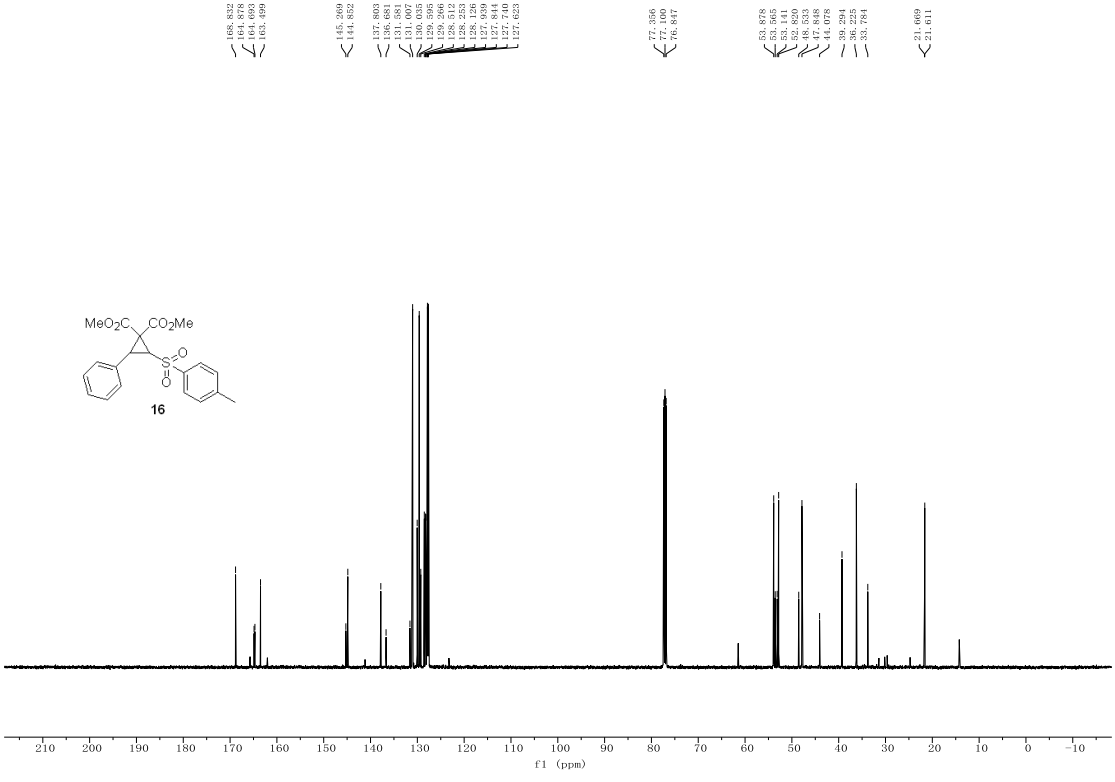
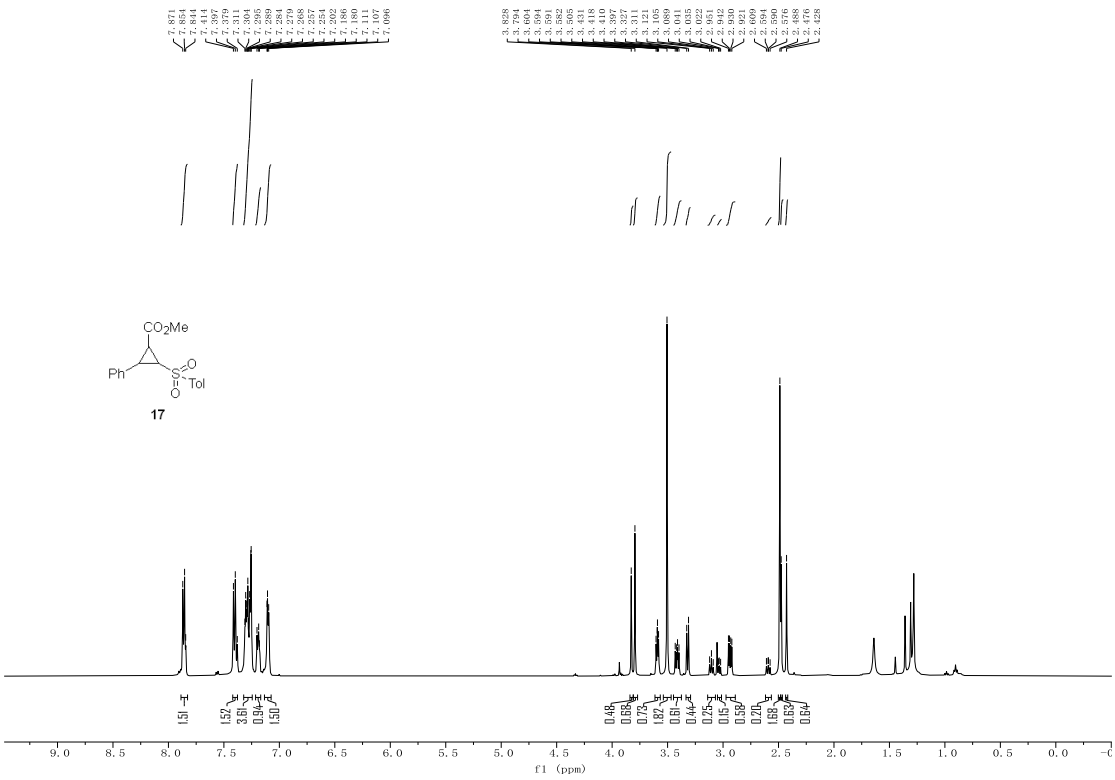
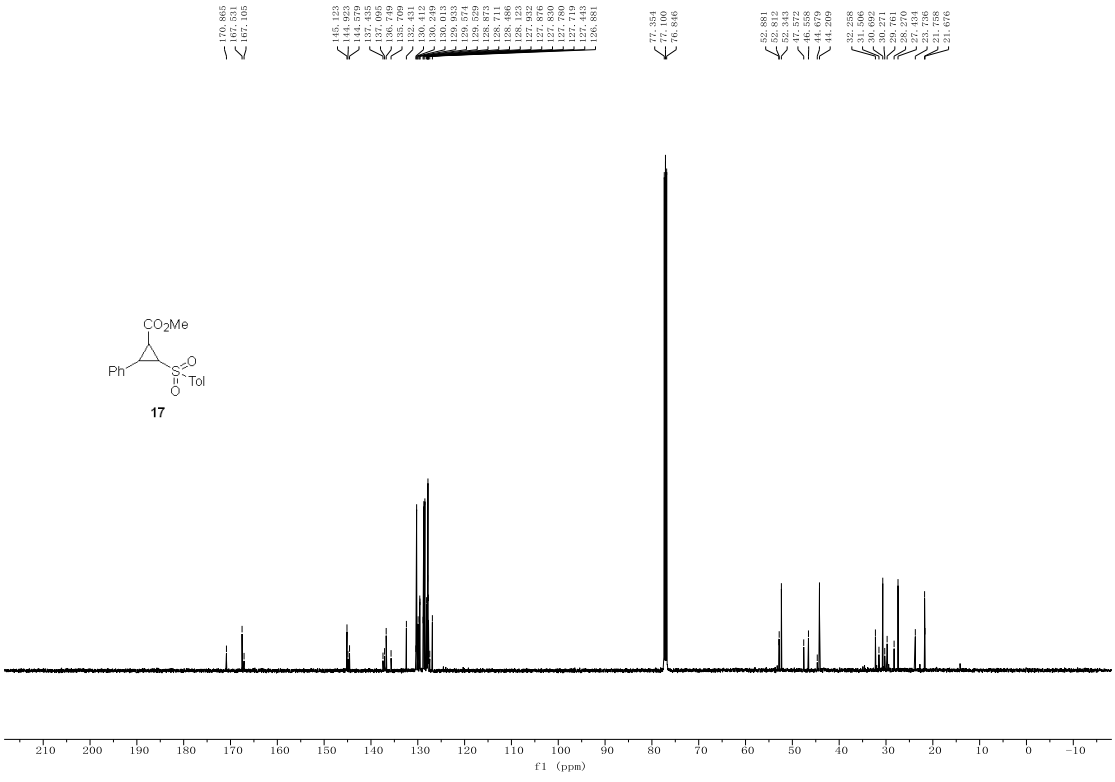
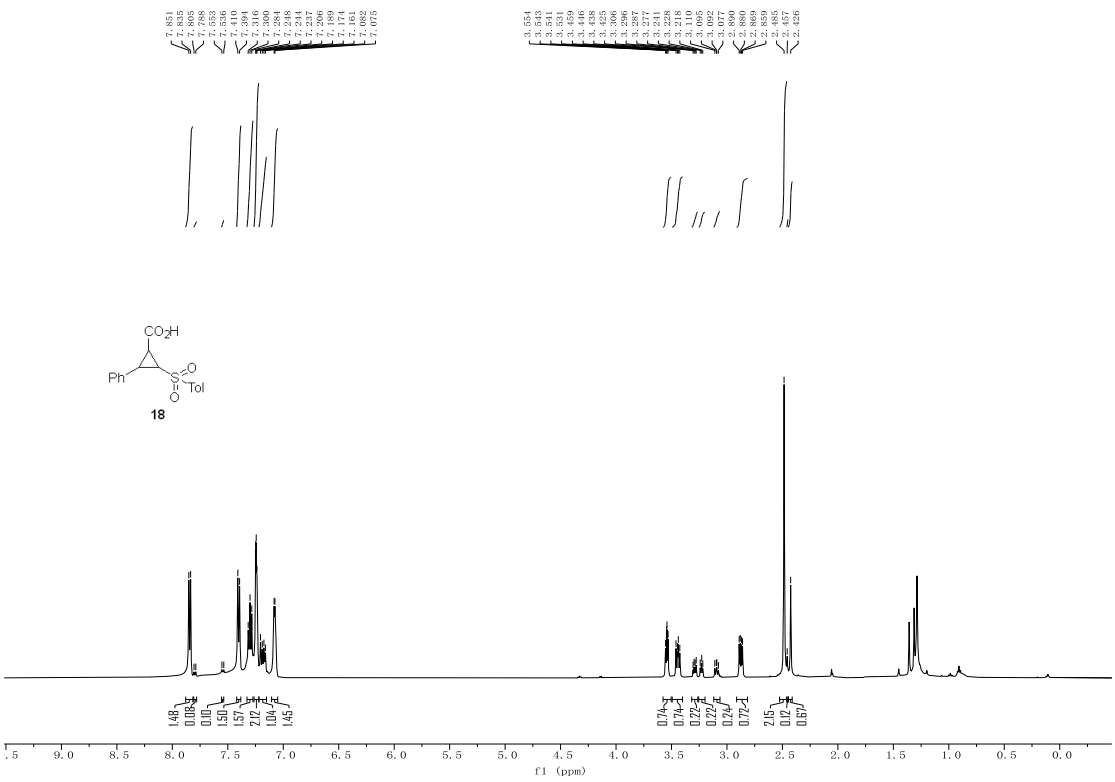
7.629
7.613
7.406
7.390
7.347
7.338
7.329
7.325
7.319
7.315
7.297
7.280
7.264
7.256
7.135
7.120
3.986
3.971
3.958
3.922
3.913
3.812
3.794
3.618
3.598
3.479
3.387
3.367
2.469
2.436
MeO2C
CO2Me
S
O
O
16
0.81
1.98
1.95
0.92
0.36
0.81
1.72
2.05
0.81
0.65
0.41
1.60
3.07
3.09
1.03
1.21
1.00
1.30
2.98
f1 (ppm)


168.832
164.878
164.695
163.499
145.269
144.852
137.803
136.681
131.381
130.697
130.055
129.595
129.246
128.512
128.253
128.126
127.939
127.844
127.740
127.623
77.356
77.100
76.847
53.878
53.565
53.141
52.820
48.533
47.848
44.676
34.294
33.225
33.784
21.669
21.611
MeO2C
CO2Me
S
O
O
16
f1 (ppm)


CO2Me
Ph
S
O
O
Tol
17
f1 (ppm)


CO2Me
Ph
S
O
O
Tol
17
f1 (ppm)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7.410
7.394
7.316
7.300
7.284
7.248
7.244
7.237
7.206
7.189
7.174
7.161
7.082
7.075
3.554
3.543
3.531
3.521
3.459
3.446
3.438
3.425
3.306
3.296
3.287
3.277
3.241
3.228
3.218
3.110
3.095
3.092
3.077
2.890
2.880
2.869
2.859
2.485
2.457
2.426
CO2H
Ph
S
O
O
Tol
18
1.48
0.08
0.10
1.50
1.57
2.12
1.04
1.45
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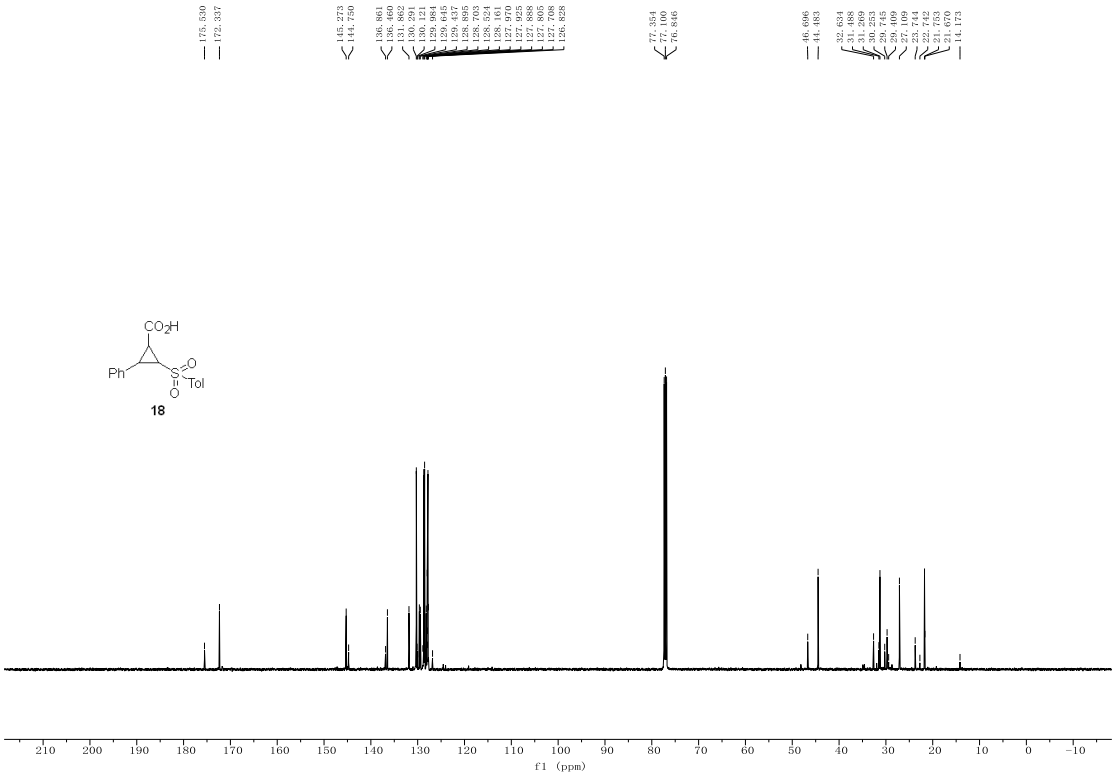
0.74
0.22
0.22
0.74
0.72
2.15
0.12
0.67
f1 (ppm)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145.273
144.750
136.861
136.460
131.862
130.291
130.171
129.984
129.645
129.437
128.895
128.705
128.524
128.161
127.970
127.895
127.888
127.805
127.708
126.828
77.354
77.100
76.846
46.696
44.483
32.634
31.488
31.269
30.253
29.745
29.409
27.109
23.744
22.842
21.755
21.670
14.173
CO2H
Ph
S
O
O
Tol
18
f1 (ppm)