

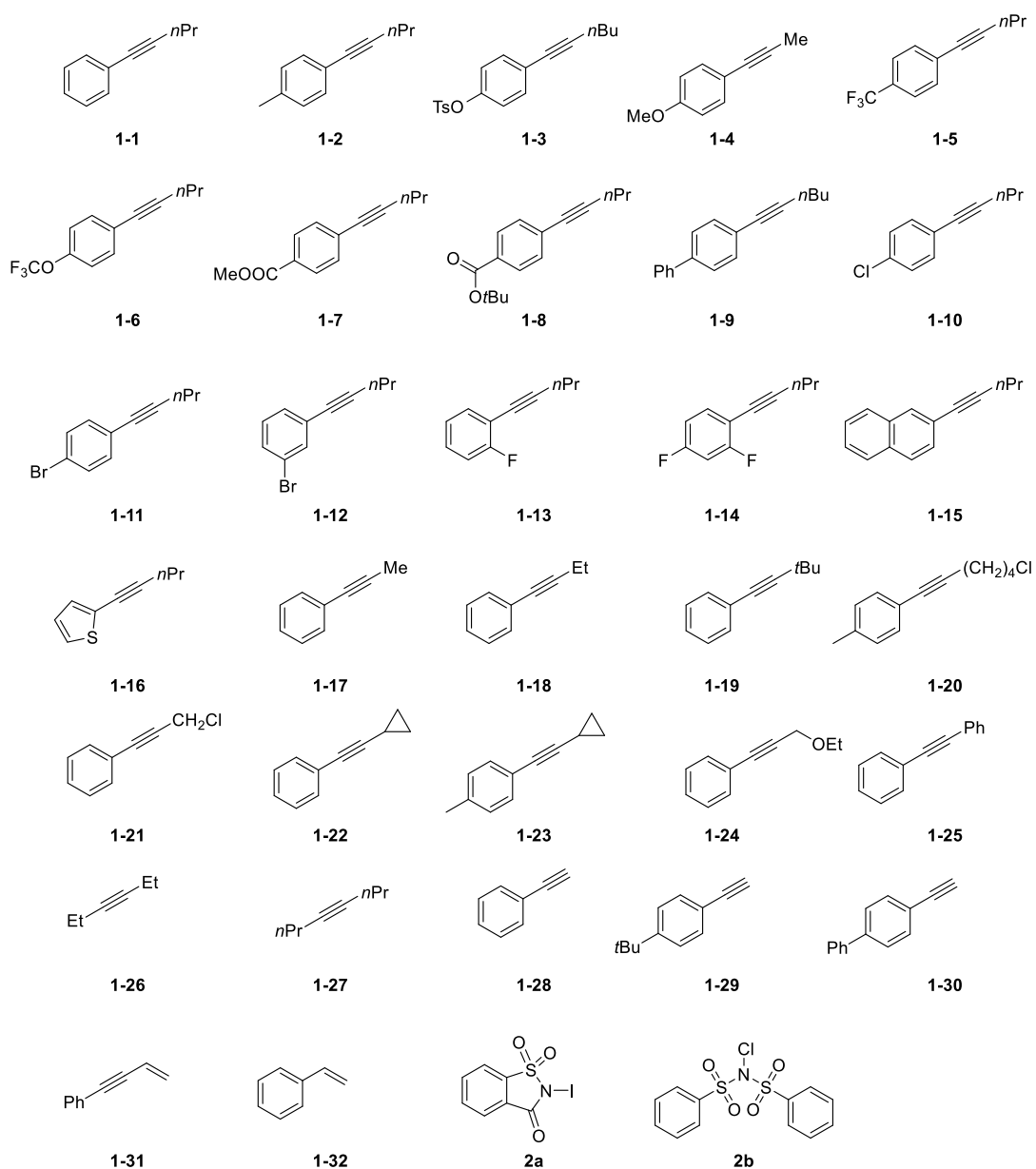
Catalyst-free Trans-selective Oxyiodination and Oxychlorination of Alkynes Employing N–X (Halogen) Reagents

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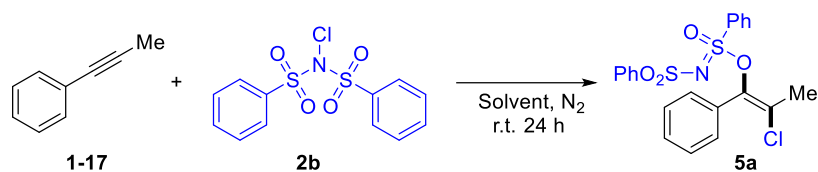
I. List for the Starting Materials



Scheme S1 List for the Starting Materials.

II. Optimization Conditions

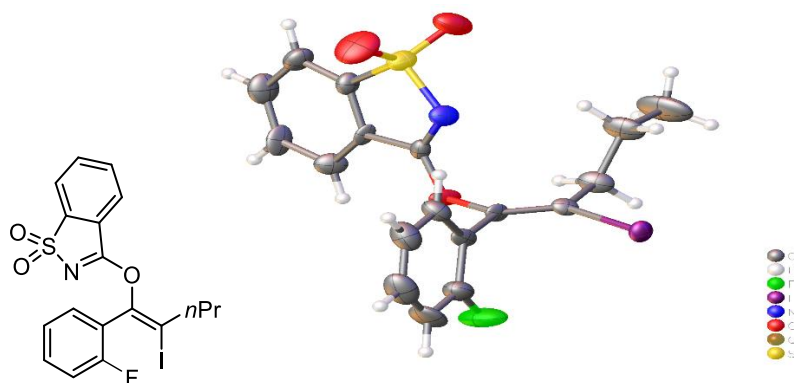
Table S1. Optimization of intermolecular oxyiodination of alkynes.



Entry	Solvent	T (°C)	Yield (%) ^a
1	DCM	25	66
2	DCE	25	70
3	CHCl ₃	25	86
4	THF	25	16
5	Dioxane	25	22
6	Toluene	25	35
7	CH ₃ CN	25	29
8	CHCl ₃	50	70
9	CHCl ₃	70	33
10 ^b	CHCl ₃	25	77
11 ^c	CHCl ₃	25	85

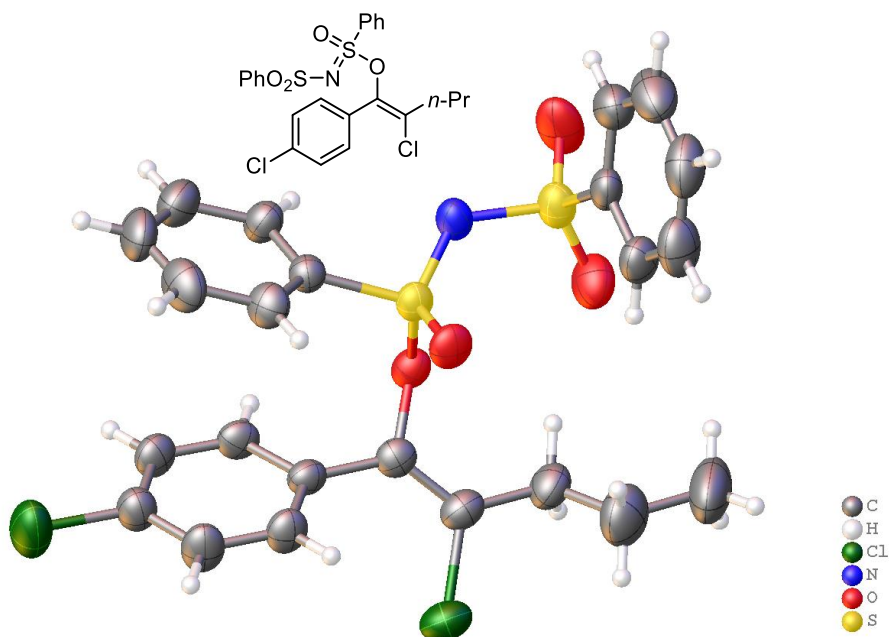
Reaction conditions: **1-17** (0.2 mmol), **2b** (2.0 equiv), Solvents (2 mL), 25 °C, under N₂ atmosphere (g) for 24 h. ^aYield of the isolated product based on **1-17**. ^b **2b** (1.5 equiv) was employed. ^c Employing Schlenk technical instead of glove box.

III. X-ray Crystallographic Data



Crystal data and structure refinement for 3i

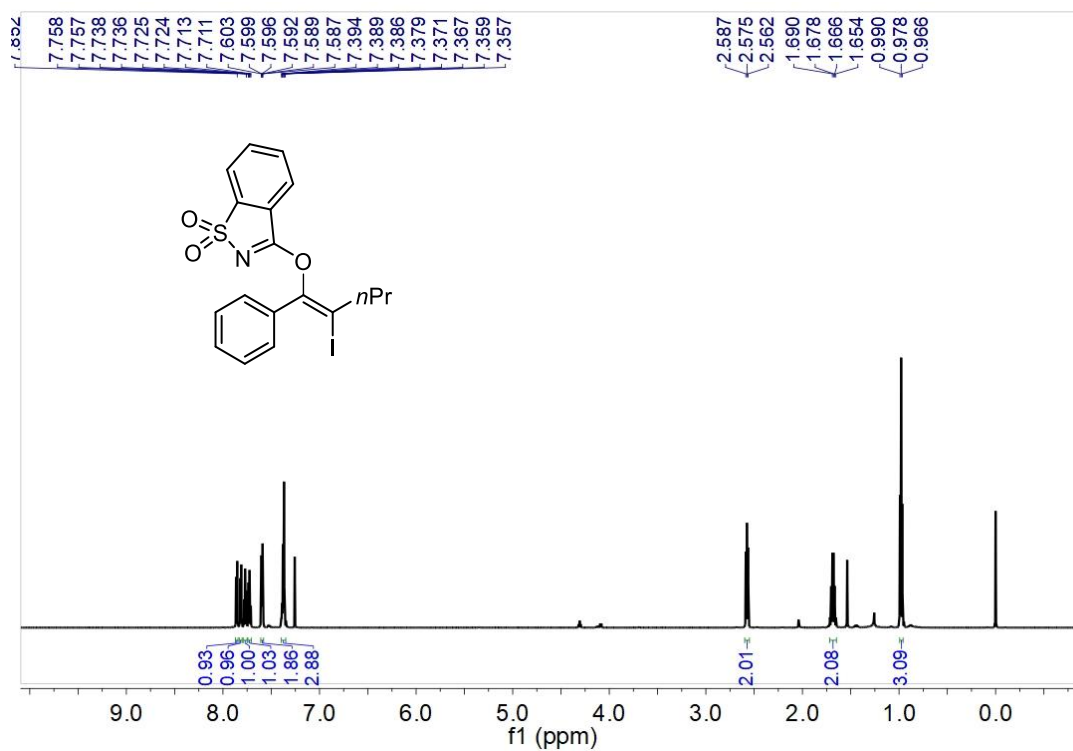
Identification code	CCDC_2304082
Empirical formula	C ₁₈ H ₁₆ FINO ₃ S
Formula weight	472.28
Temperature/K	293.01
Crystal system	triclinic
Space group	P-1
a/Å	9.532(3)
b/Å	9.899(4)
c/Å	10.483(4)
α/°	111.72(3)
β/°	90.99(2)
γ/°	95.57(3)
Volume/Å ³	913.1(6)
Z	2
ρ _{calc} /g/cm ³	1.718
μ/mm ⁻¹	15.088
F(000)	466.0
Crystal size/mm ³	0.21 × 0.21 × 0.15
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	9.096 to 127.34
Index ranges	-8 ≤ h ≤ 11, -11 ≤ k ≤ 11, -12 ≤ l ≤ 12
Reflections collected	5908
Independent reflections	2868 [R _{int} = 0.0636, R _{sigma} = 0.0773]
Data/restraints/parameters	2868/72/227
Goodness-of-fit on F ²	1.131
Final R indexes [I > 2σ (I)]	R ₁ = 0.0996, wR ₂ = 0.2432
Final R indexes [all data]	R ₁ = 0.1033, wR ₂ = 0.2494
Largest diff. peak/hole / e Å ⁻³	2.35/-4.73



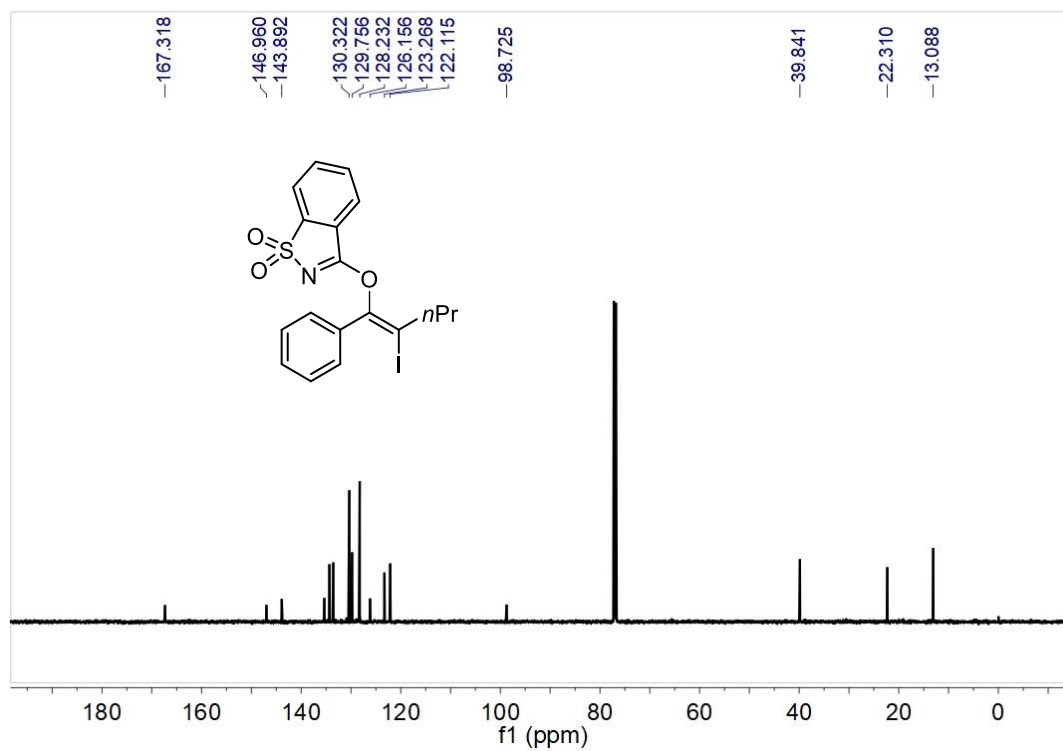
Crystal data and structure refinement for 5j

CCDC number	1829383
Empirical formula	C ₂₇ H ₂₀ Br N O ₃ S
Formula weight	518.41
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 ₁ /C
Unit cell dimensions	a = 12.857 Å alpha = 90 deg. b = 15.123 Å beta = 102.04 deg. c = 12.073 Å gamma = 90 deg.
Volume	2295.8 Å ³
Z, Calculated density	4, 1.500 Mg/m ³
Reflections collected / unique	12707 / 4058 [R(int) = 0.0561]
F(000)	1056
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7625 and 0.5626
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4058 / 0 / 298
Goodness-of-fit on F ²	1.007
Final R indices [I > 2sigma(I)]	R ₁ = 0.0490, wR ₂ = 0.1117
R indices (all data)	R ₁ = 0.0805, wR ₂ = 0.1268
Largest diff. peak and hole	0.540 and -0.288 e.Å ⁻³
$R_1 = \sum F_o - F_c / \sum F_o $; $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$	

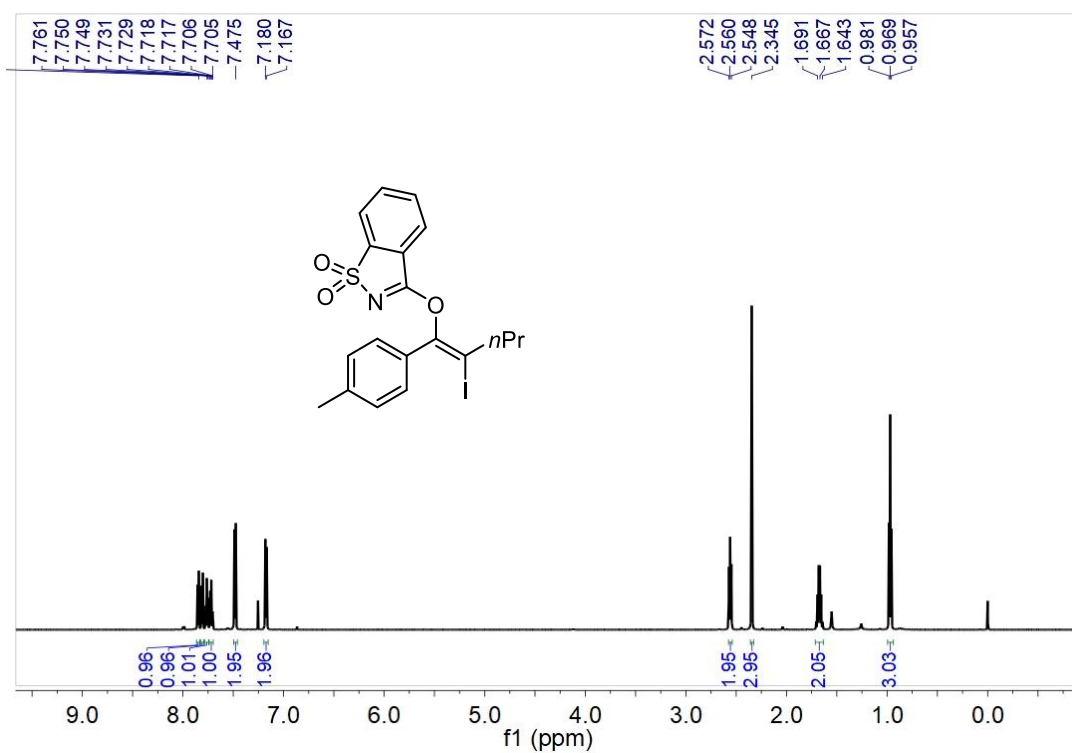
IV. NMR Spectra of New Compounds



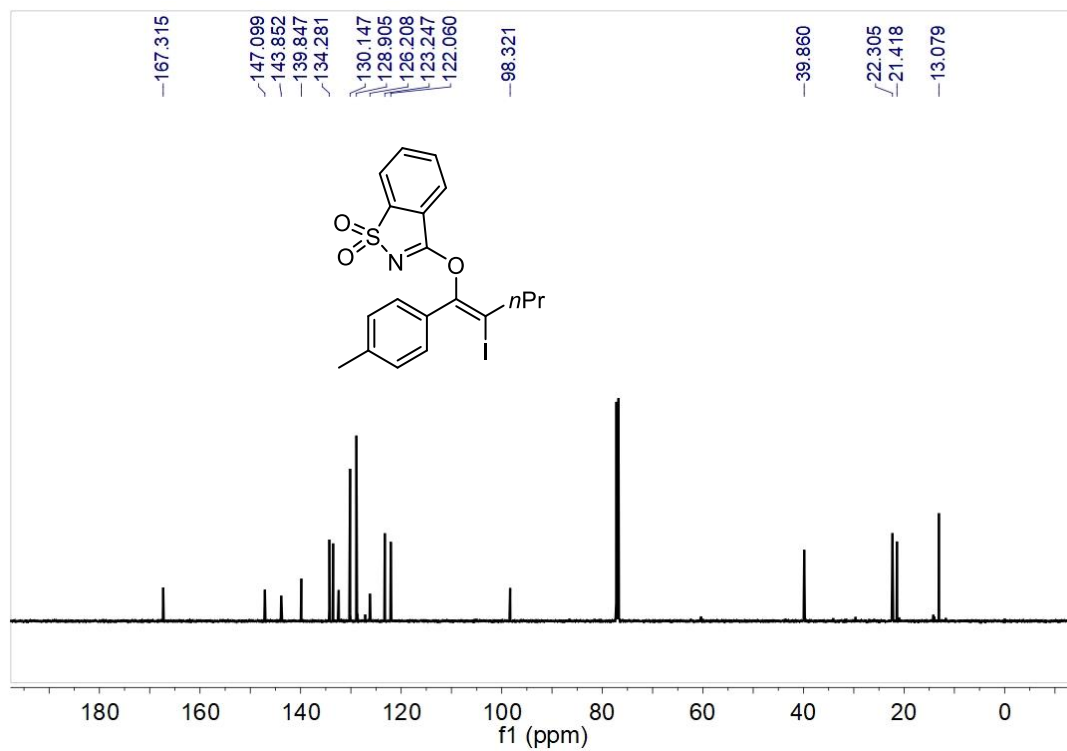
¹H NMR (600 MHz, CDCl₃) spectrum of 3a.



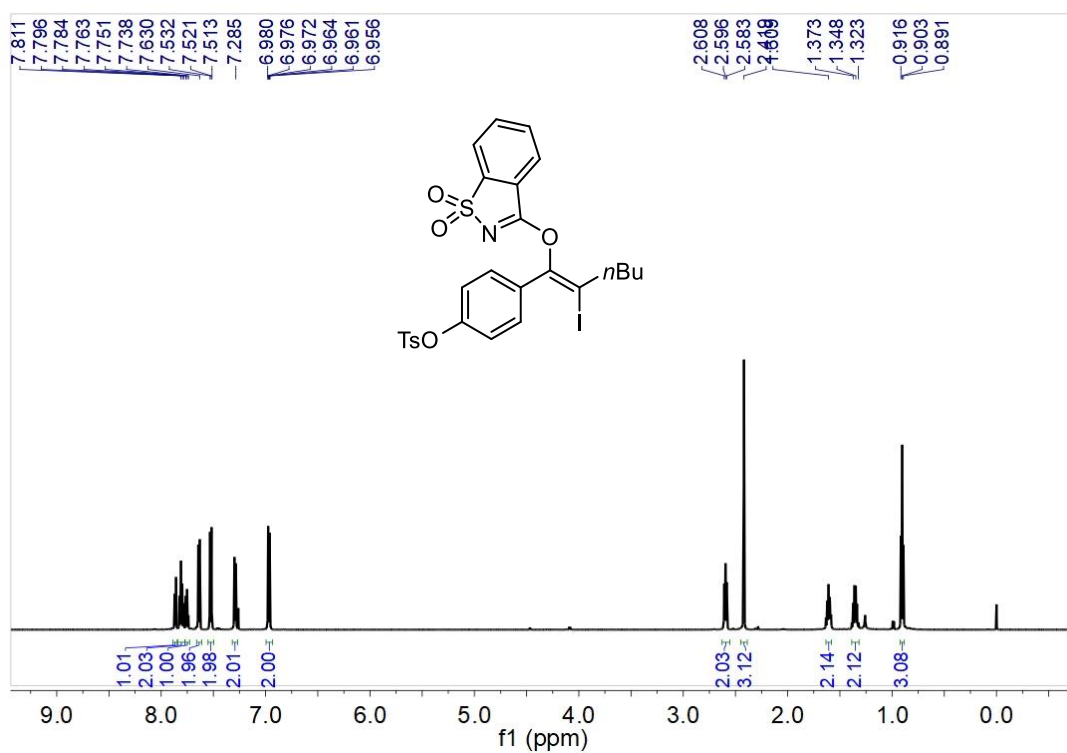
¹³C NMR (150 MHz, CDCl₃) spectrum of 3a.



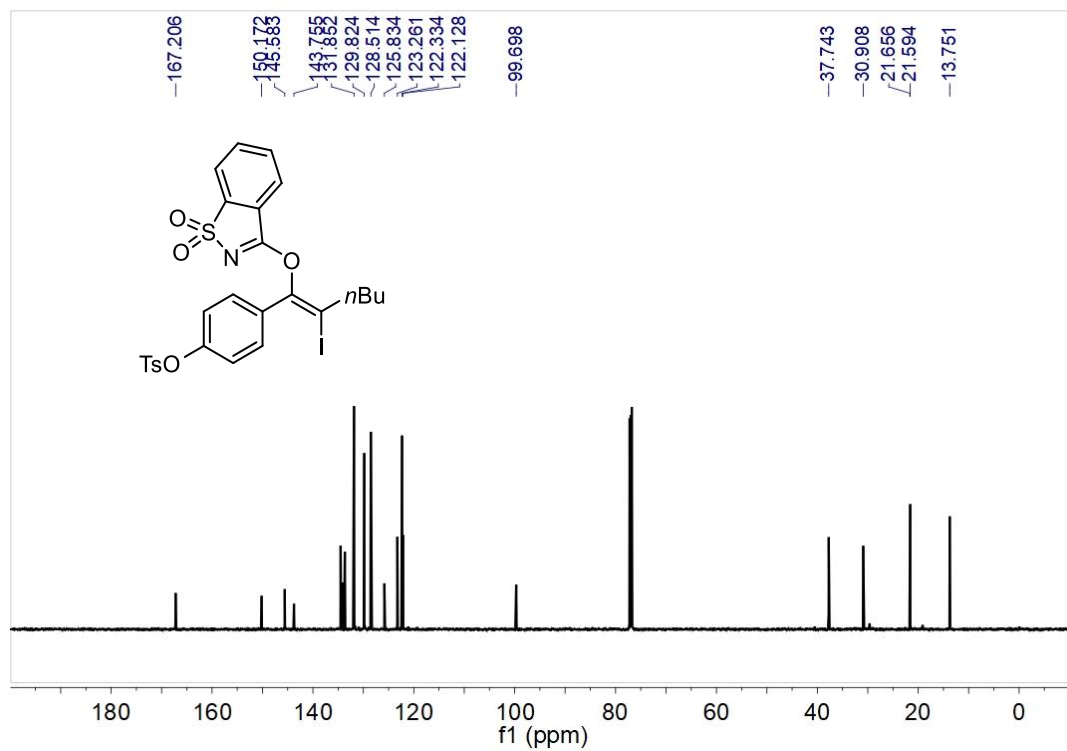
¹H NMR (600 MHz, CDCl₃) spectrum of 3b.



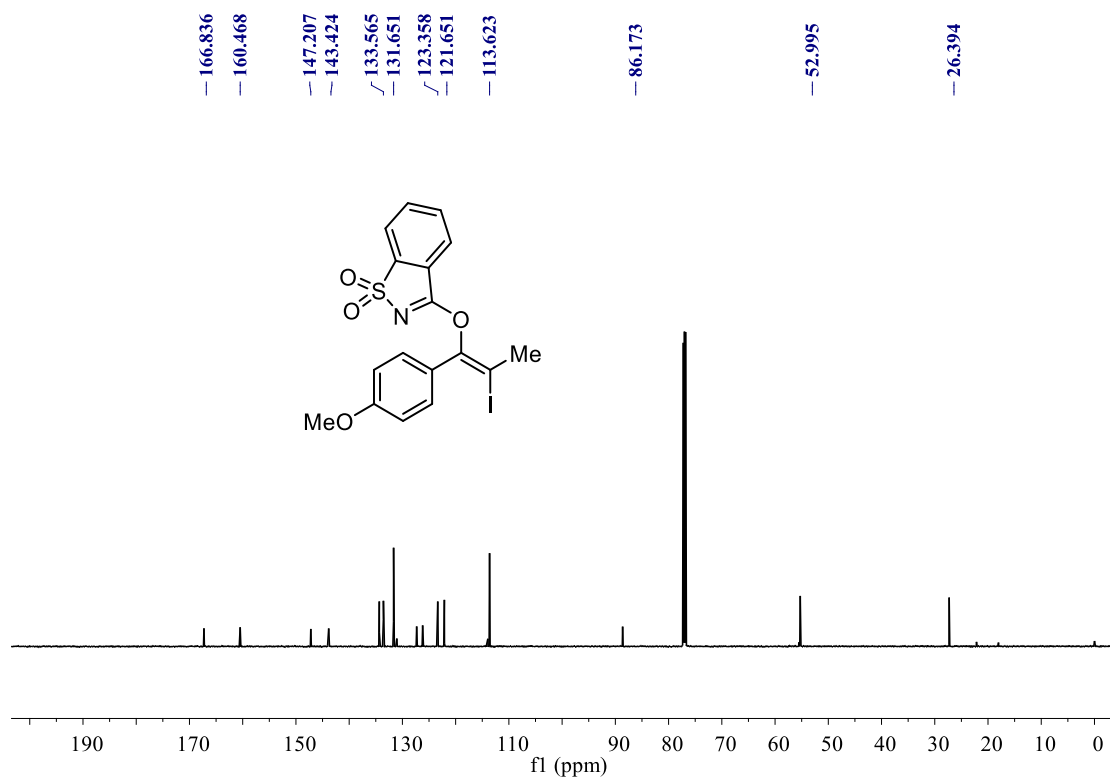
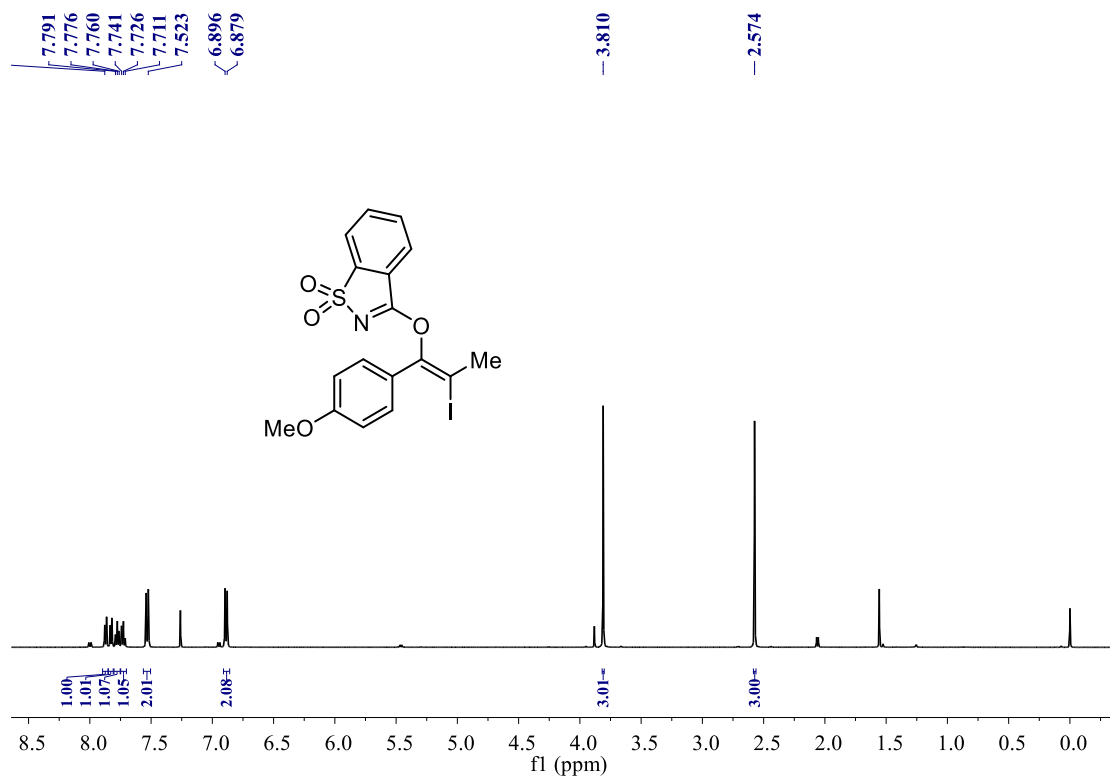
¹³C NMR (150 MHz, CDCl₃) spectrum of 3b.

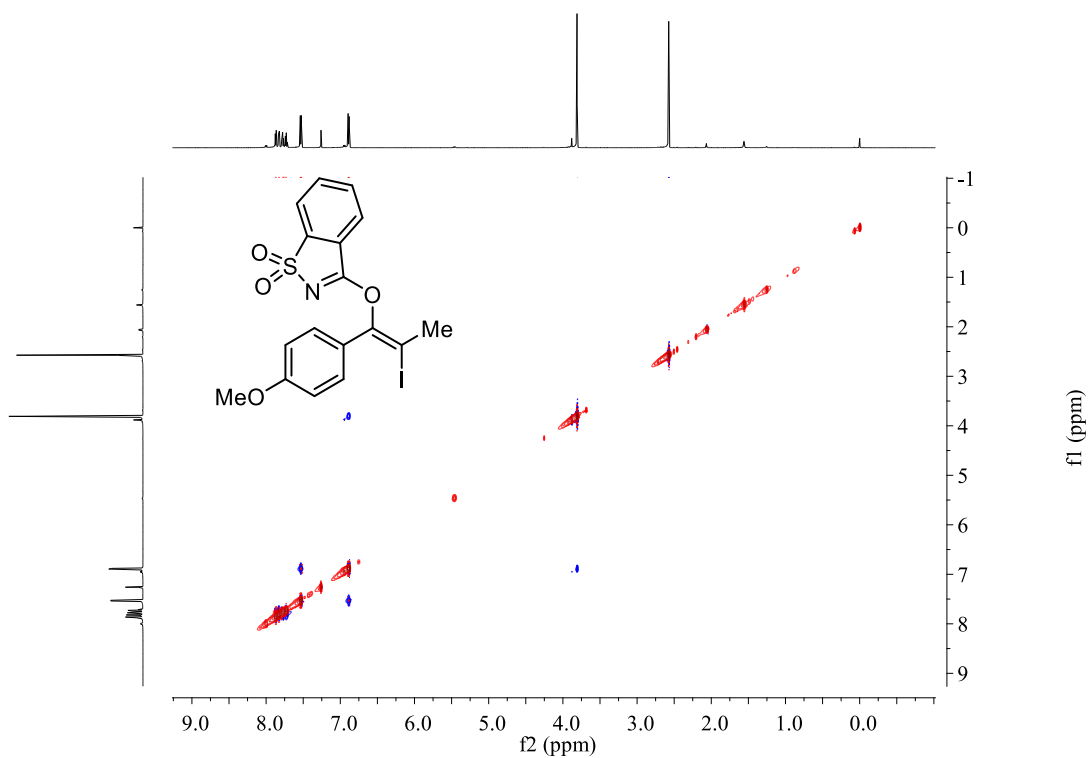


¹H NMR (600 MHz, CDCl₃) spectrum of 3c.

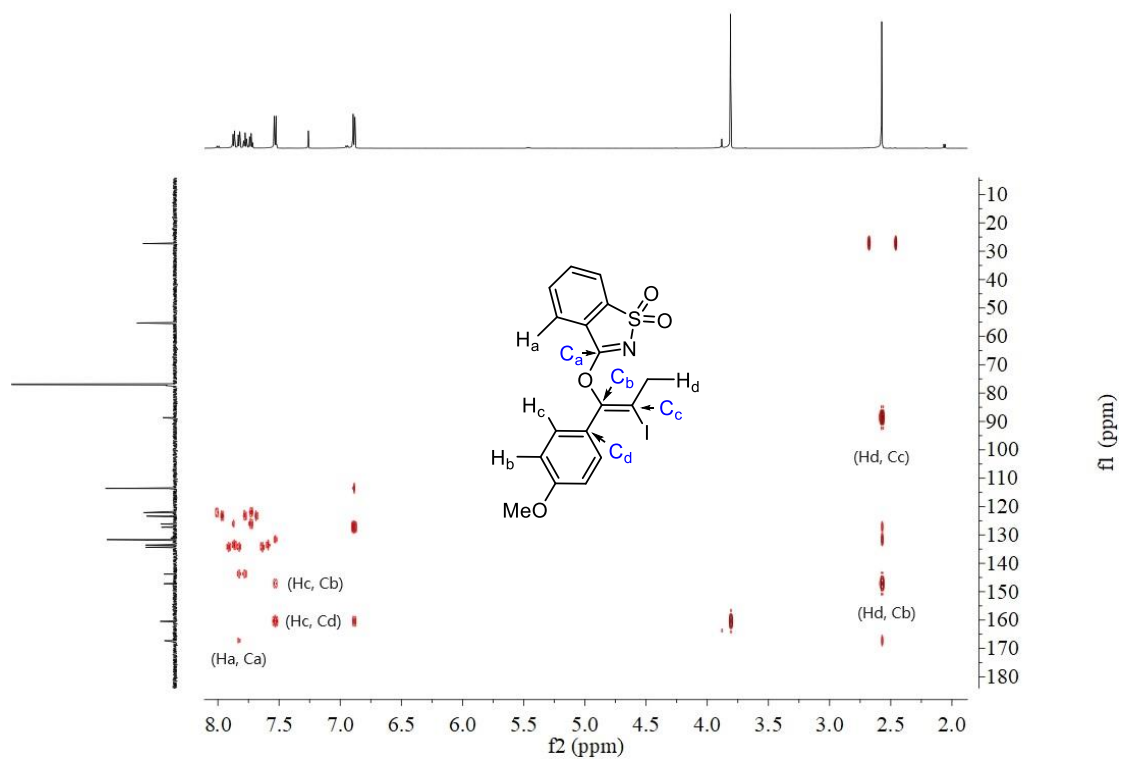


¹³C NMR (150 MHz, CDCl₃) spectrum of 3c.

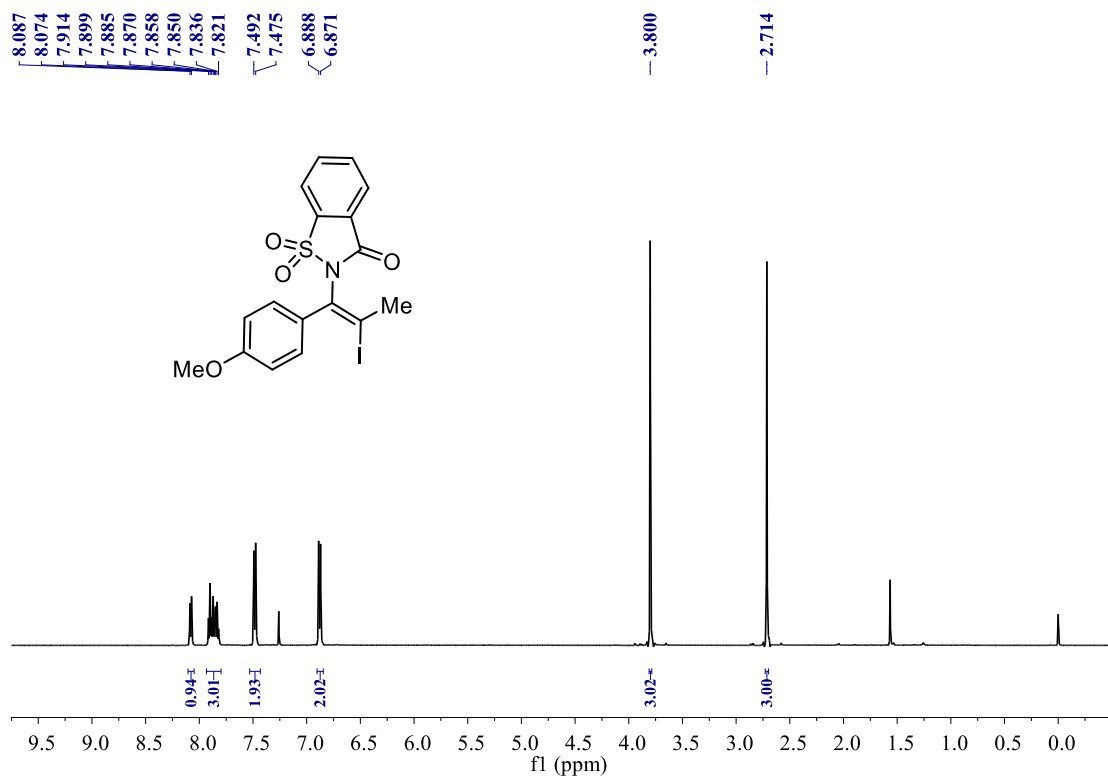




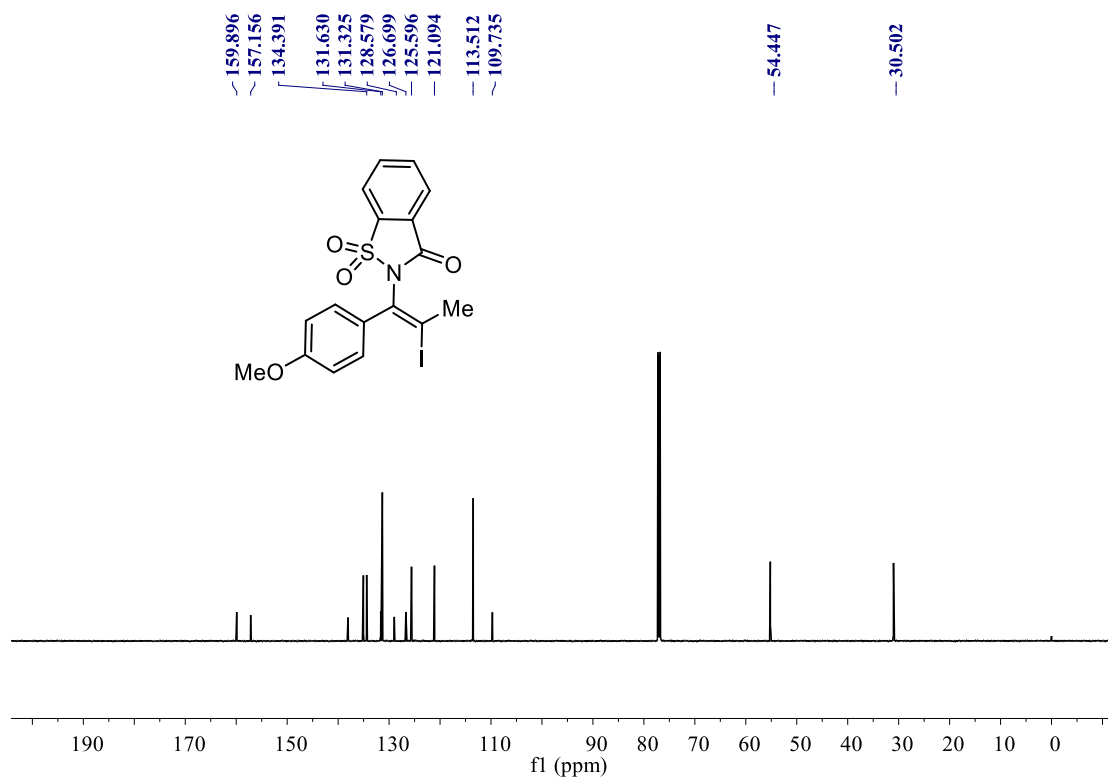
^1H - ^1H NOE spectrum of **3d.**



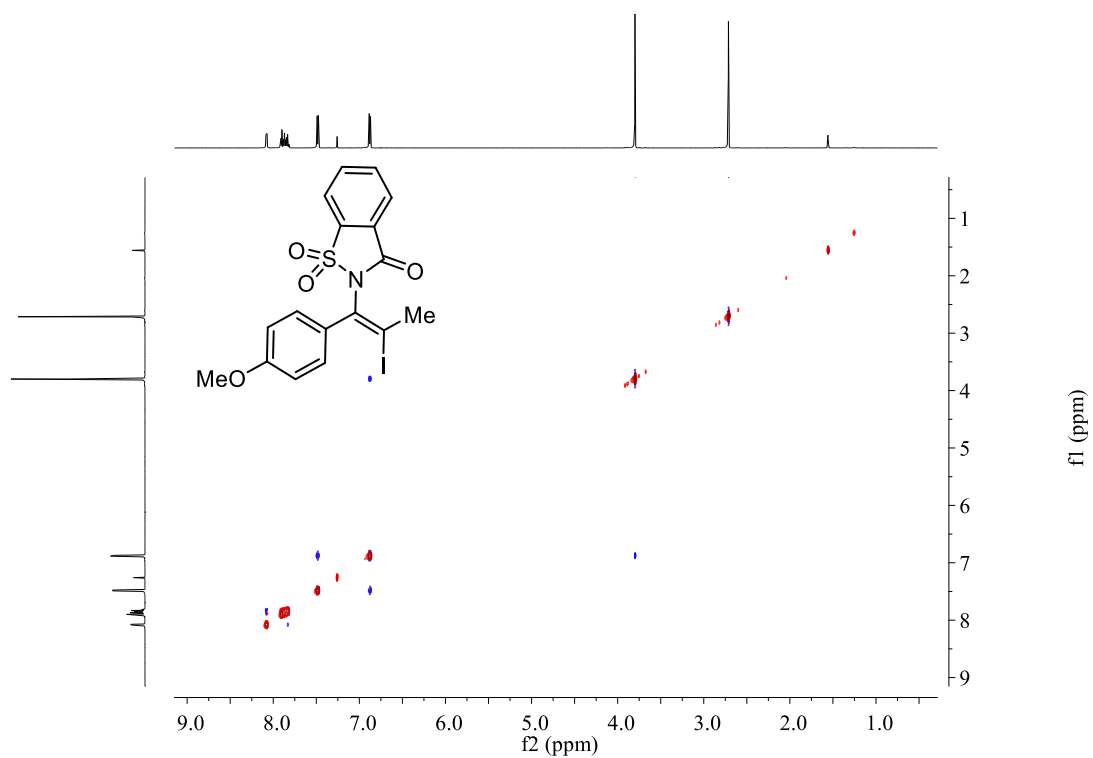
^1H - ^{13}C HMQC spectrum of **3d.**



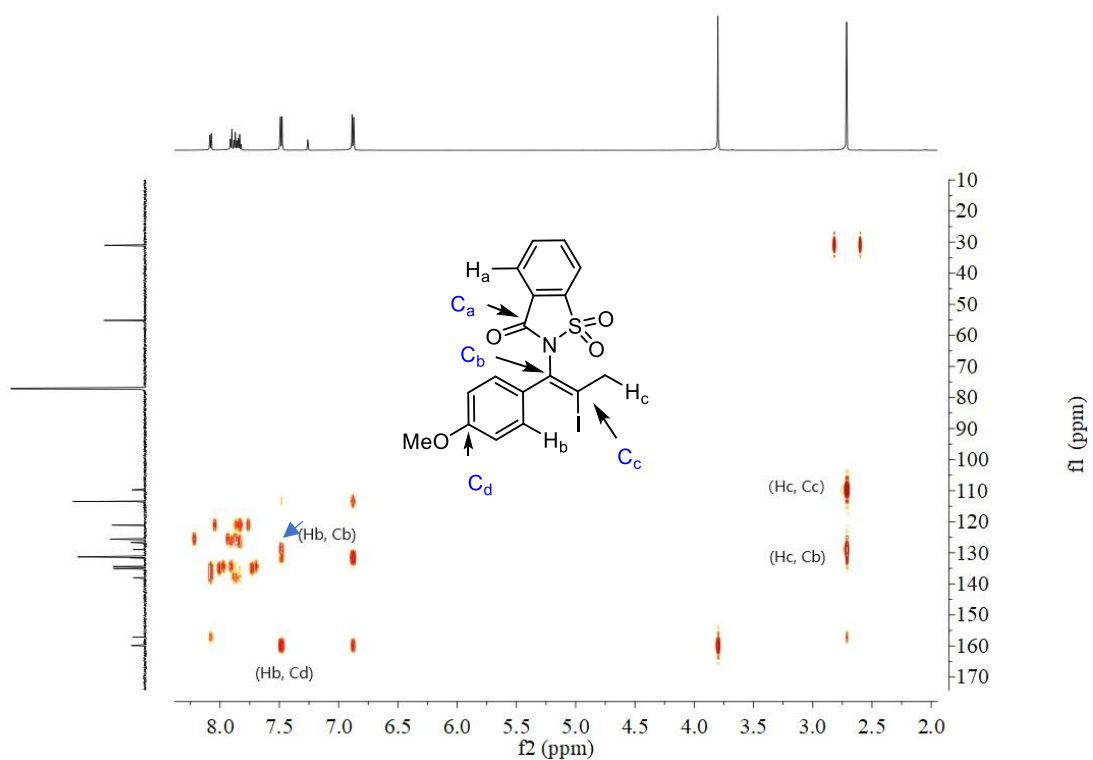
¹H NMR (500 MHz, CDCl₃) spectrum of **3d'.**



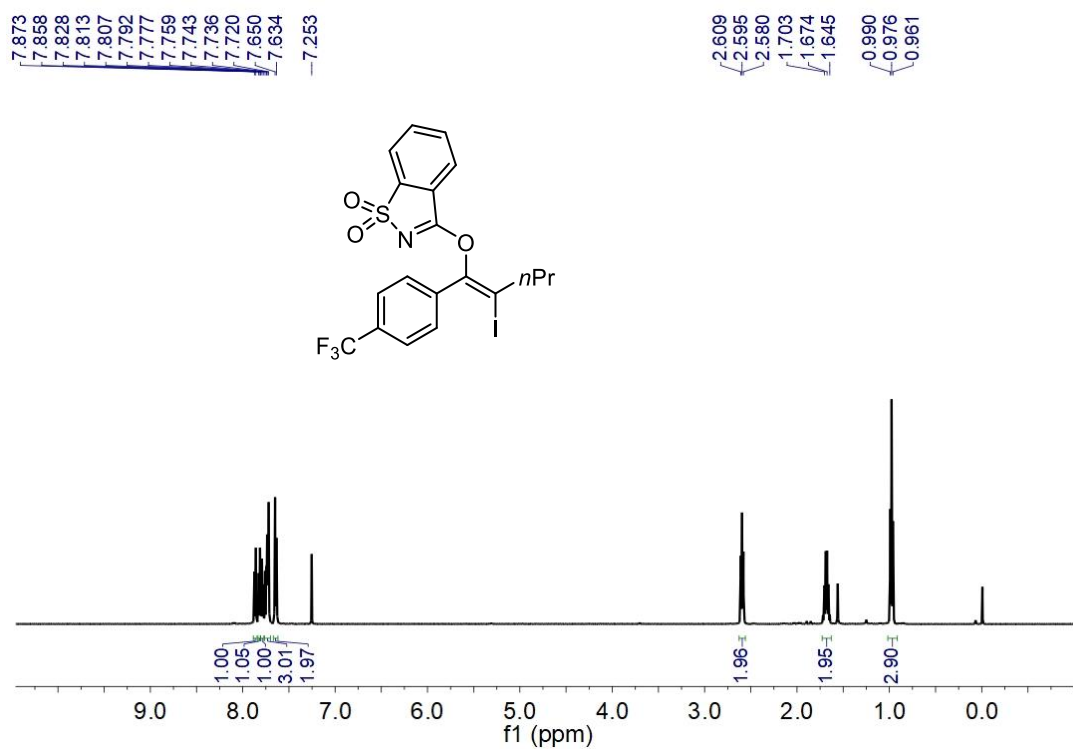
¹³C NMR (150 MHz, CDCl₃) spectrum of **3d'.**



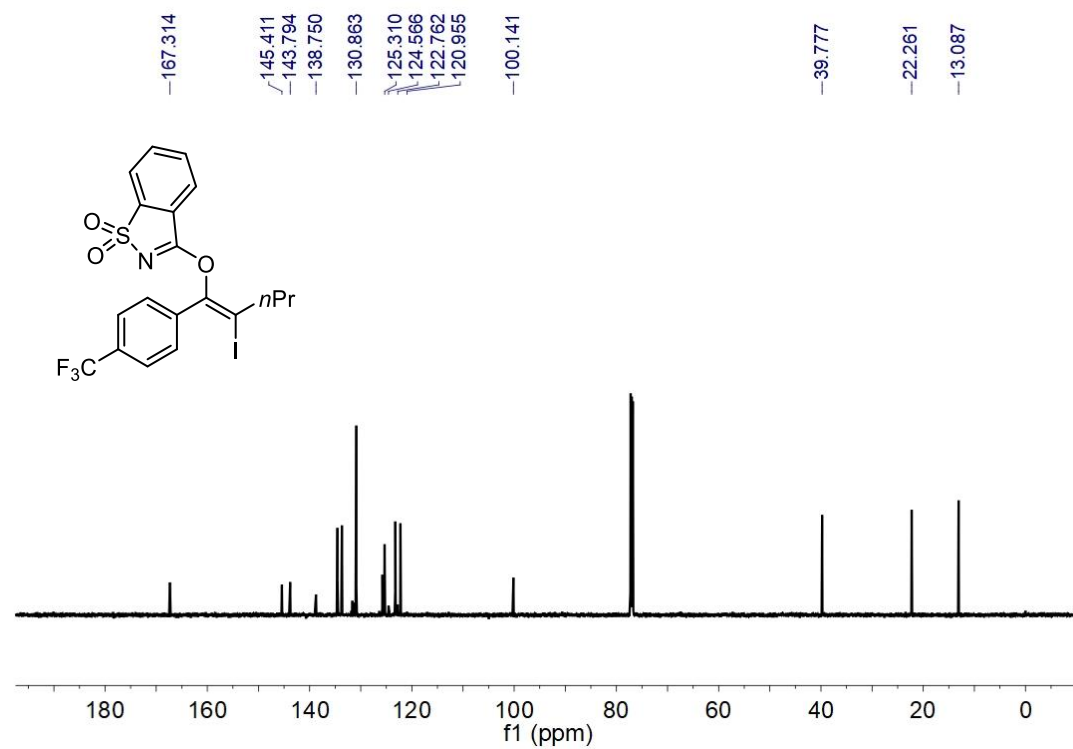
^1H - ^1H NOESY spectrum of **3d'.**



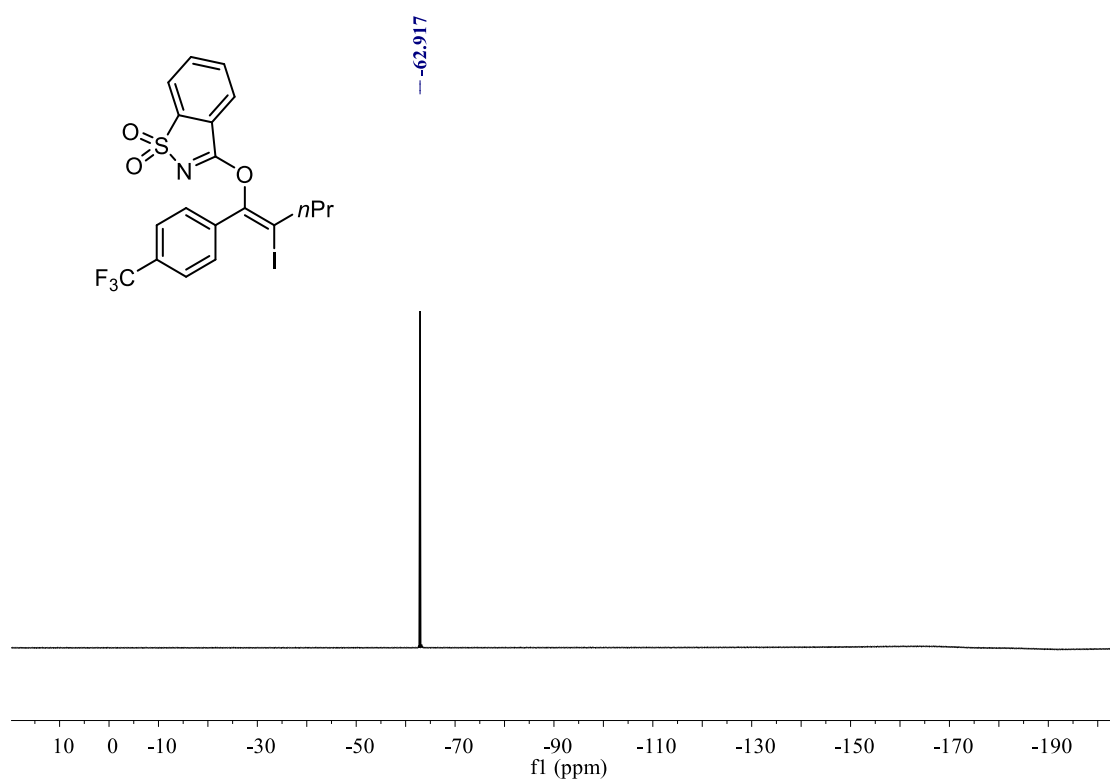
^1H - ^{13}C HMQC spectrum of **3d'.**



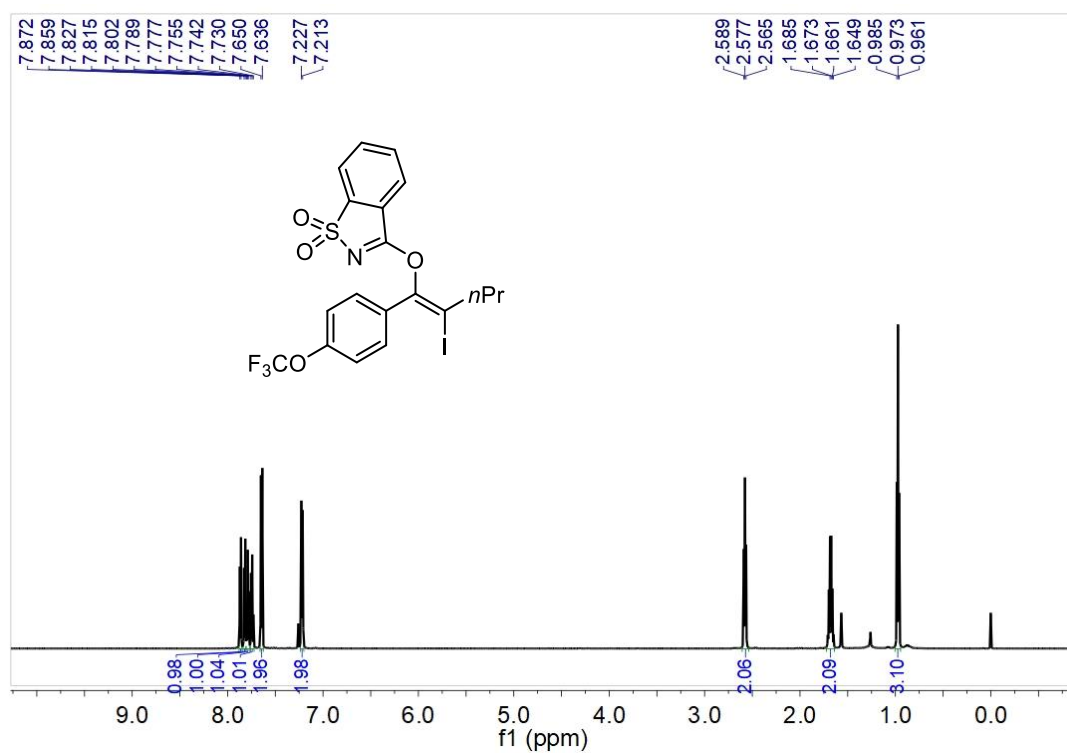
¹H NMR (500 MHz, CDCl₃) spectrum of 3e.



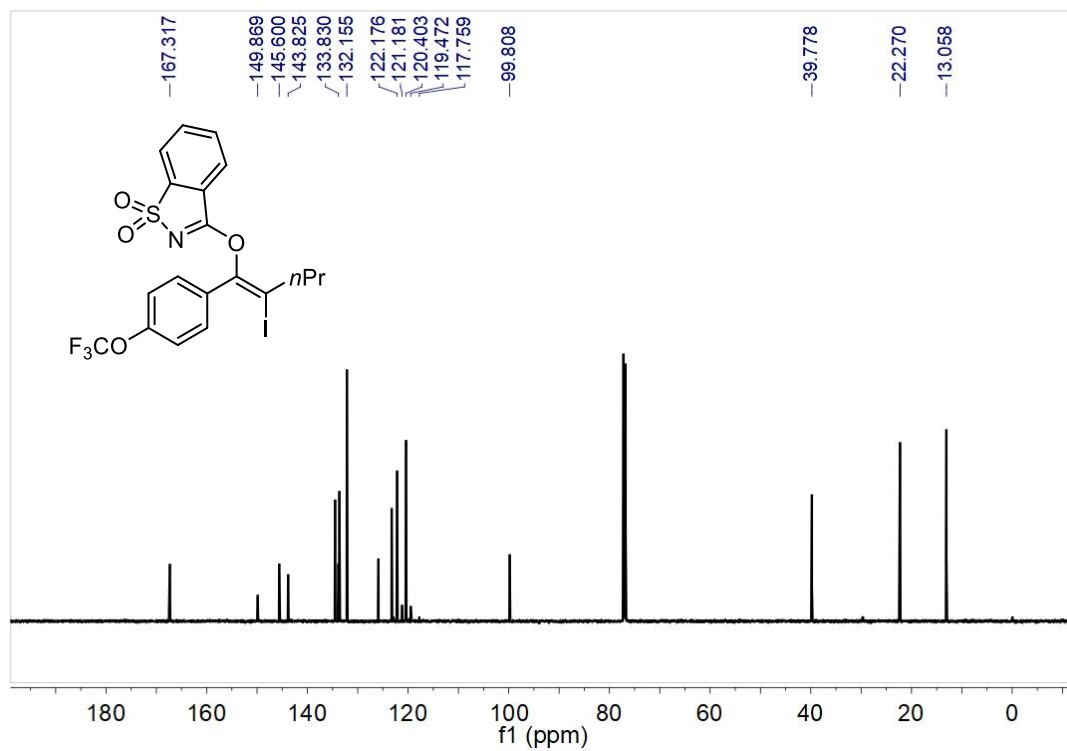
¹³C NMR (150 MHz, CDCl₃) spectrum of 3e.



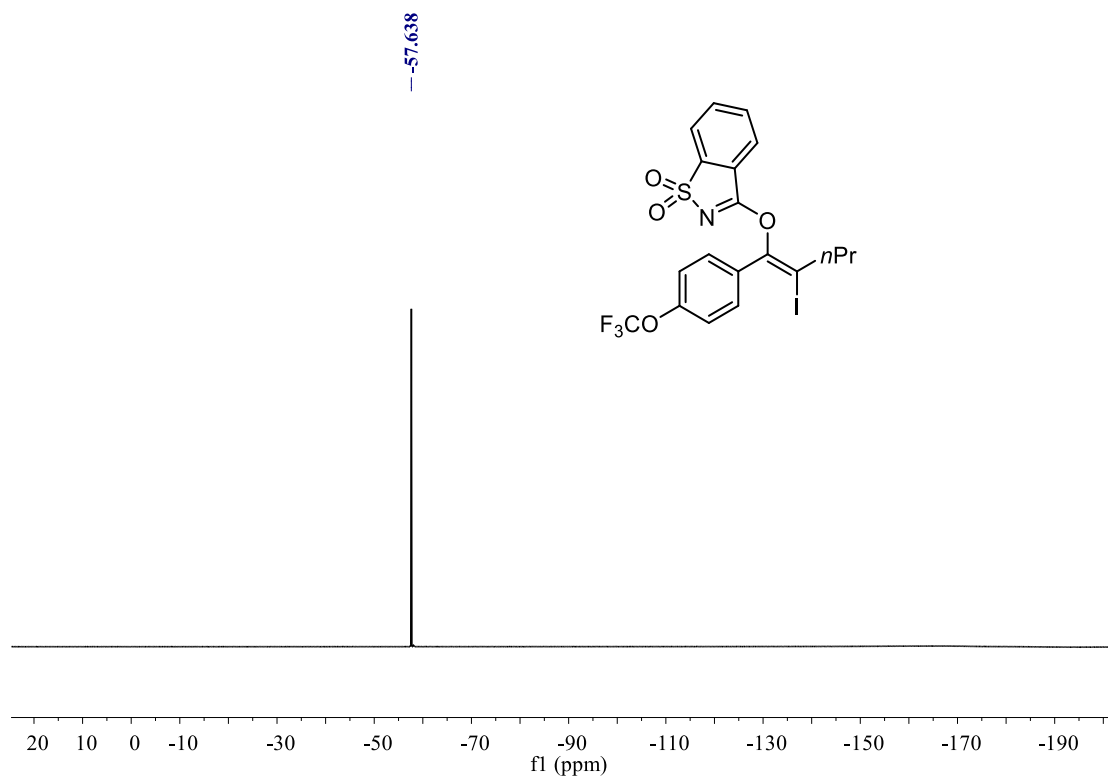
^{19}F NMR (565 MHz, CDCl_3) spectrum of 3e.



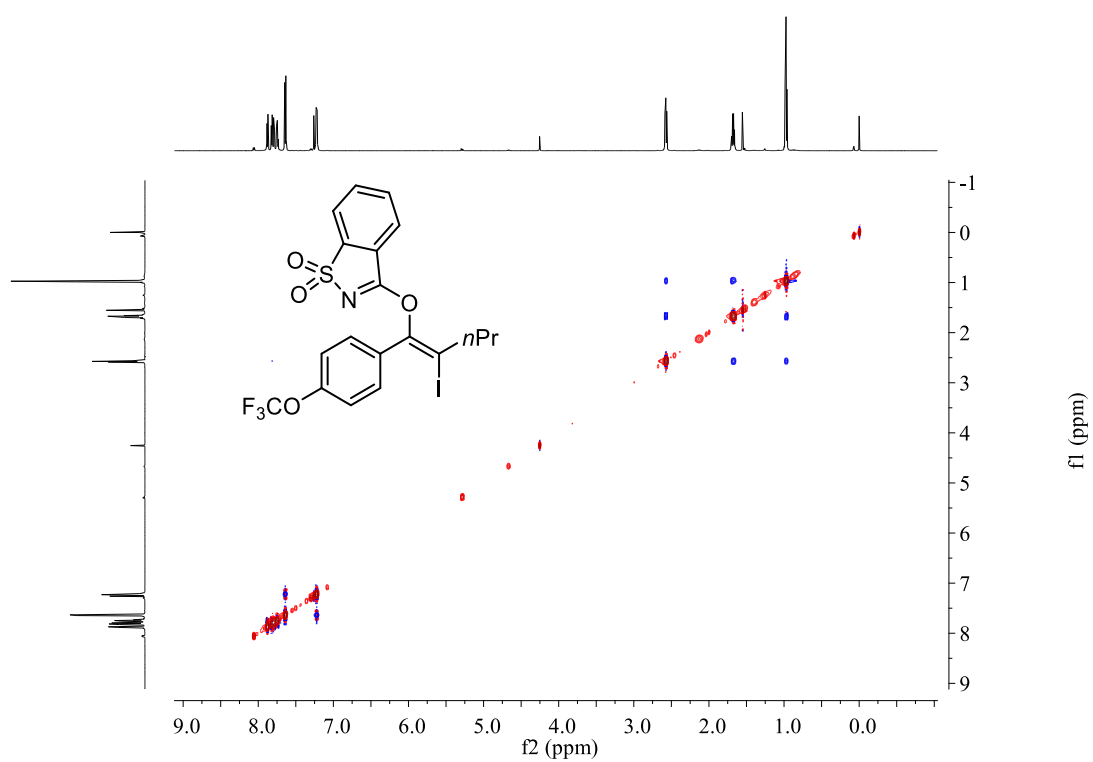
¹H NMR (600 MHz, CDCl₃) spectrum of 3f.



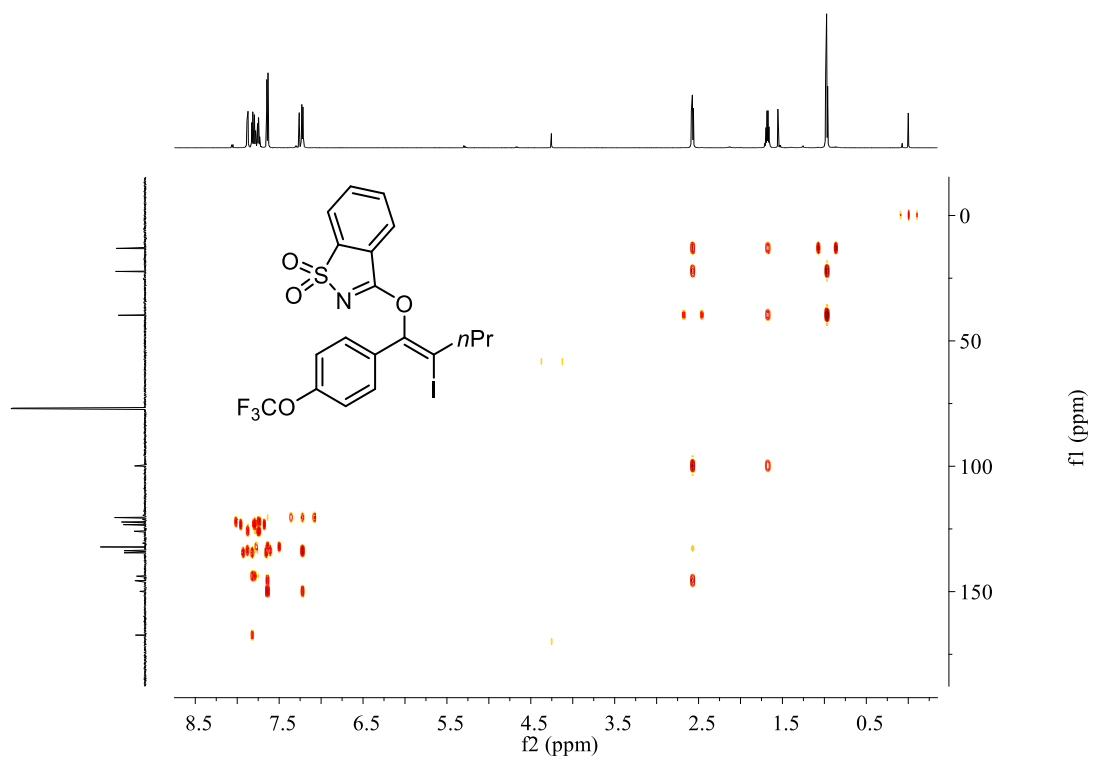
¹³C NMR (150 MHz, CDCl₃) spectrum of 3f.



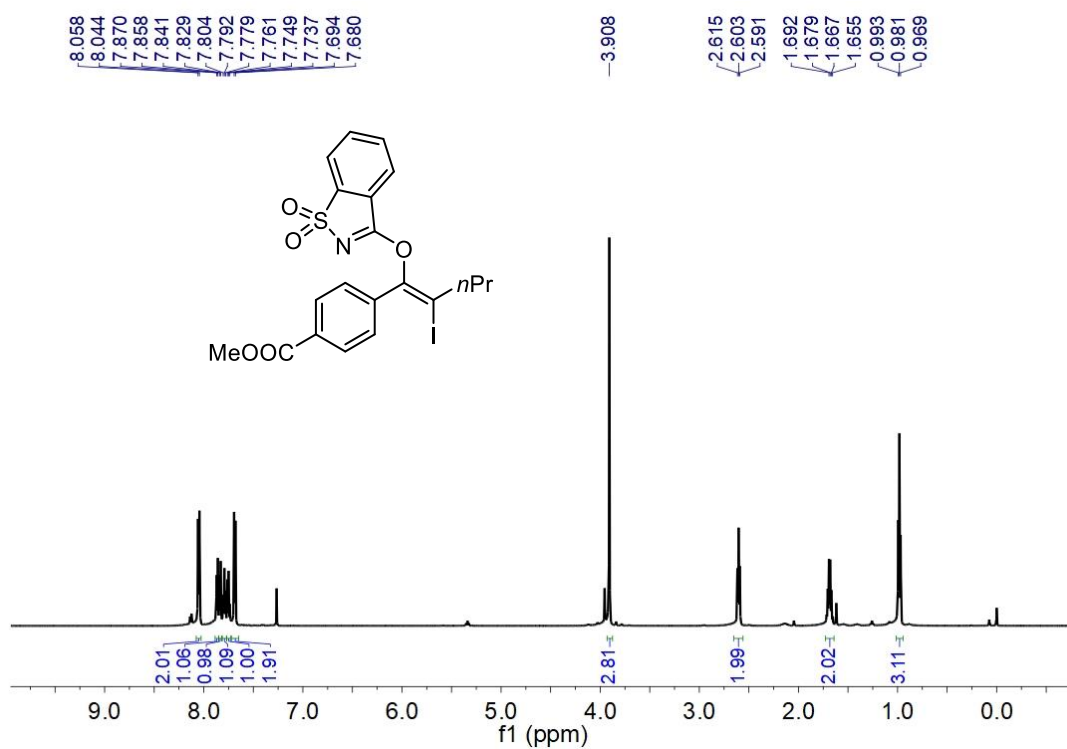
^{19}F NMR (565 MHz, CDCl_3) spectrum of 3f.



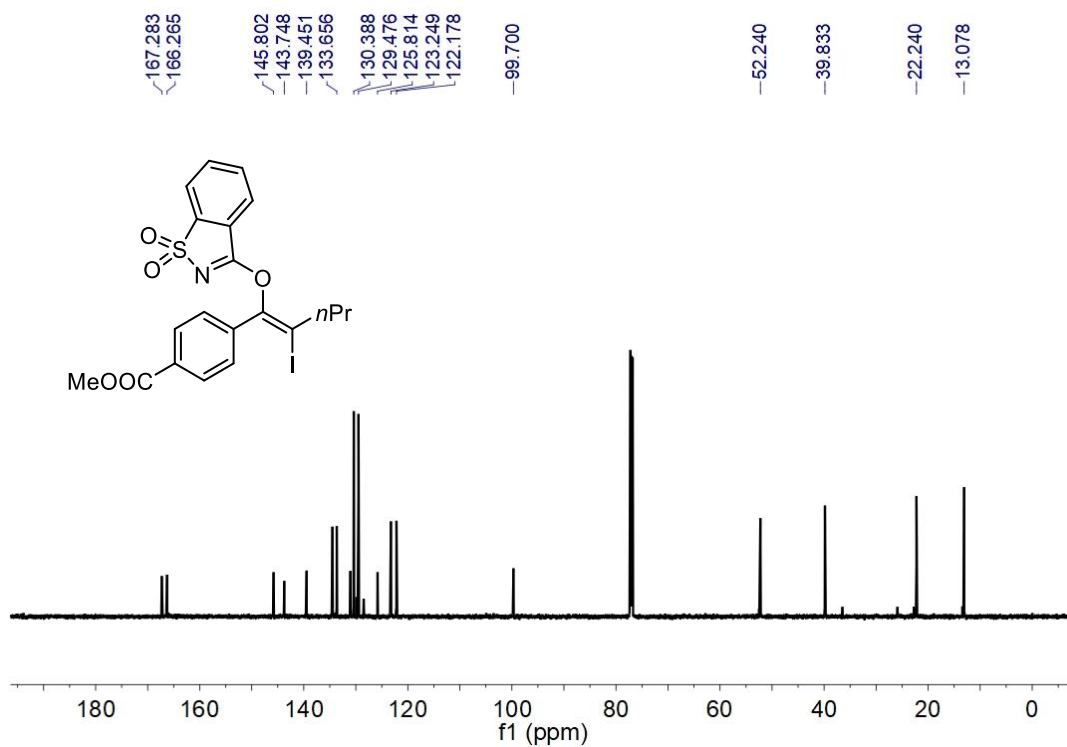
^1H - ^1H NOESY spectrum of 3f.



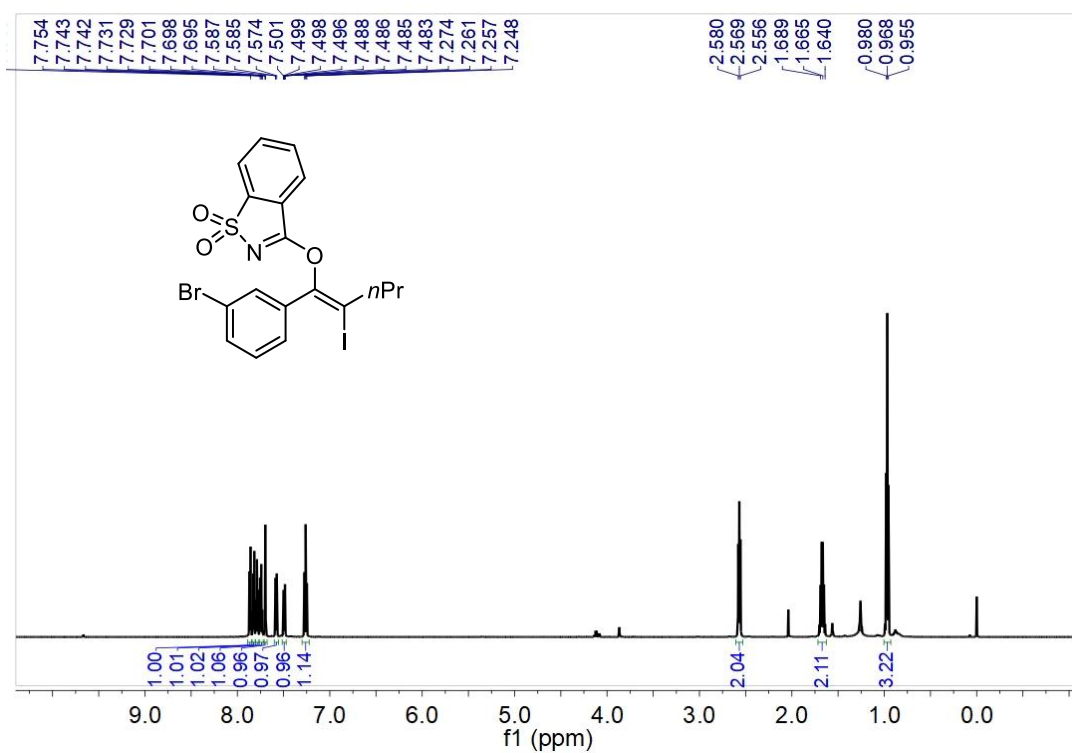
^1H - ^{13}C HMQC spectrum of **3f.**



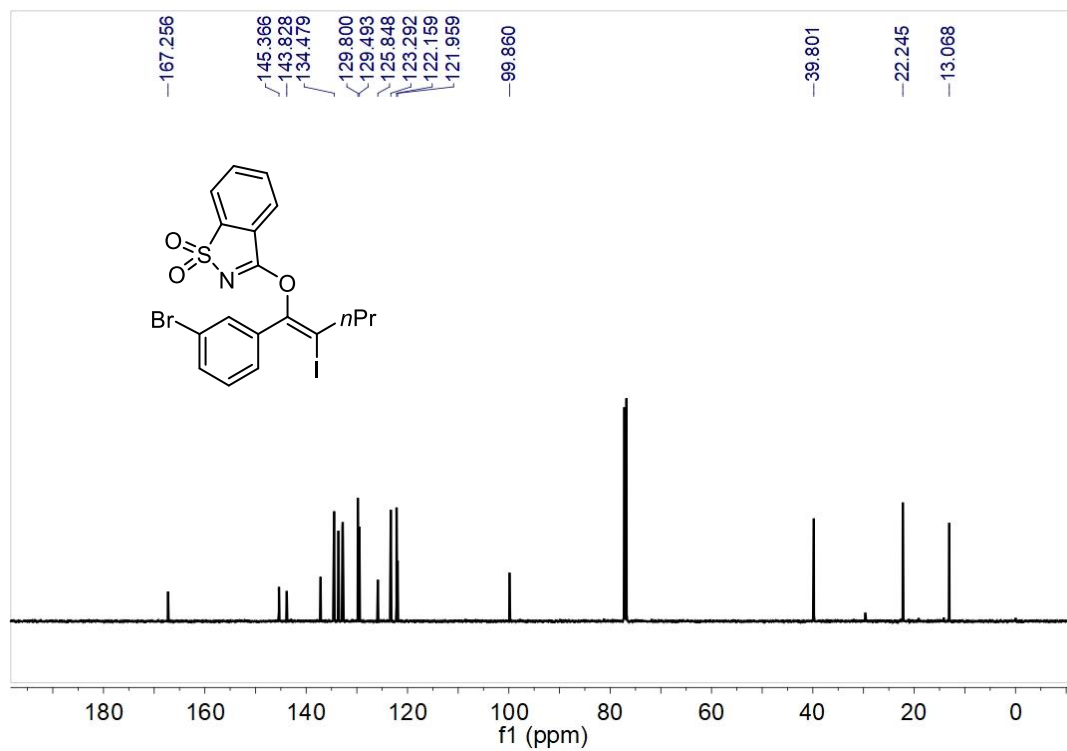
¹H NMR (600 MHz, CDCl₃) spectrum of 3g.



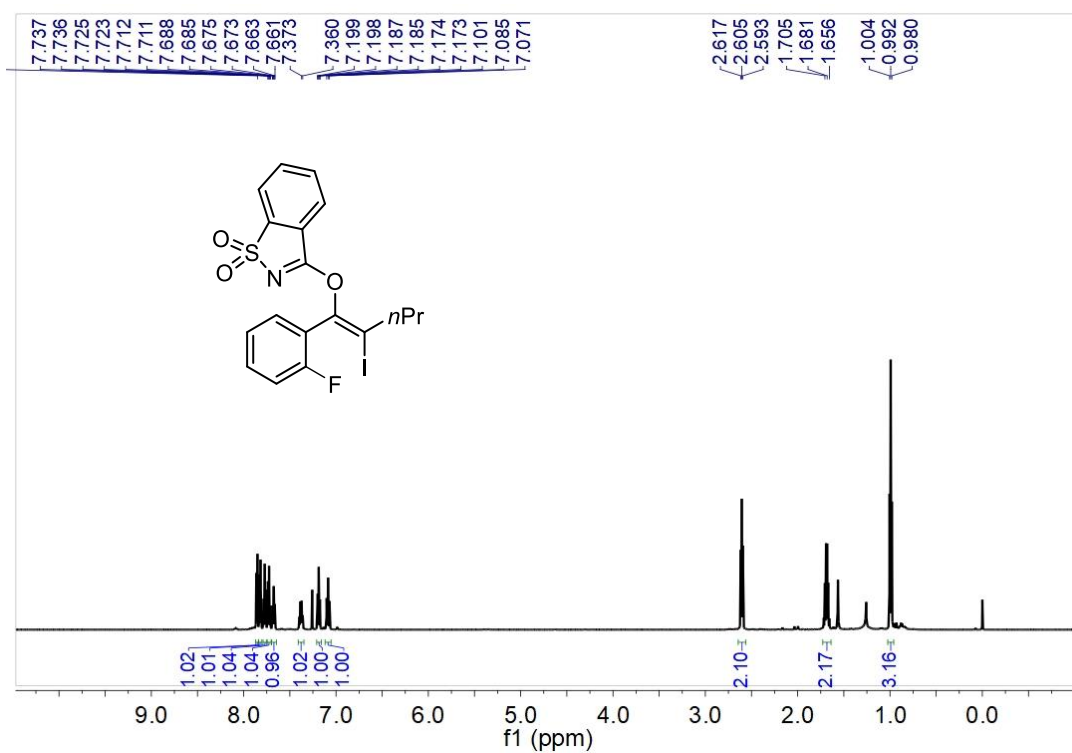
¹³C NMR (150 MHz, CDCl₃) spectrum of 3g.



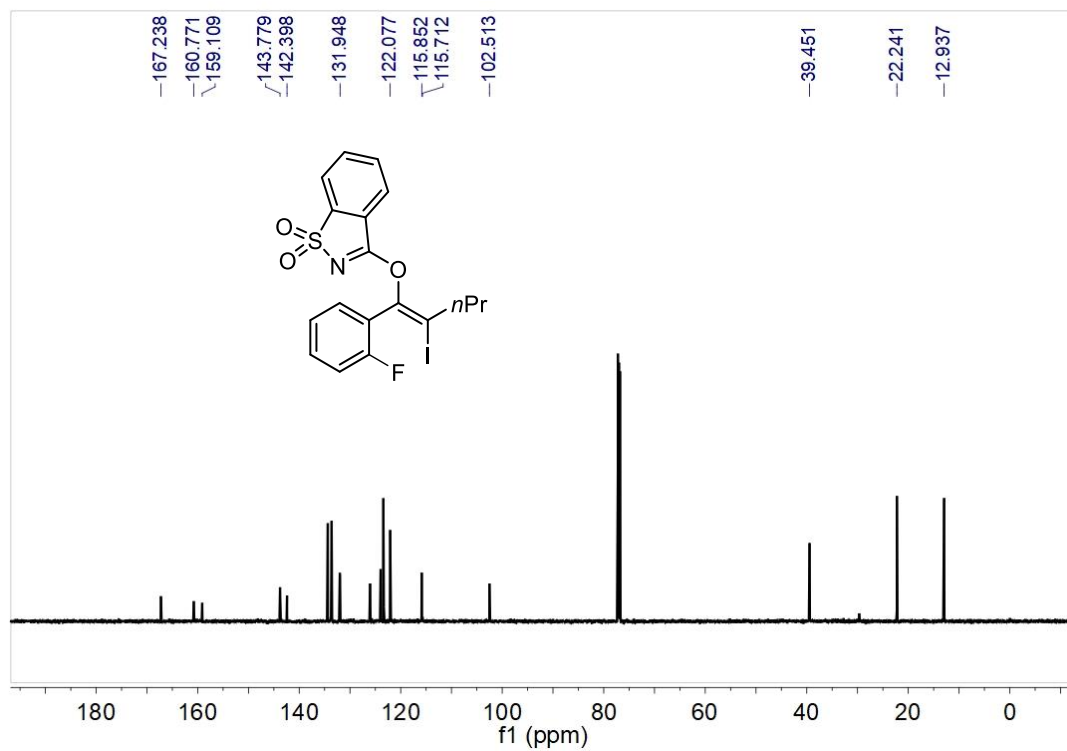
¹H NMR (600 MHz, CDCl₃) spectrum of 3h.



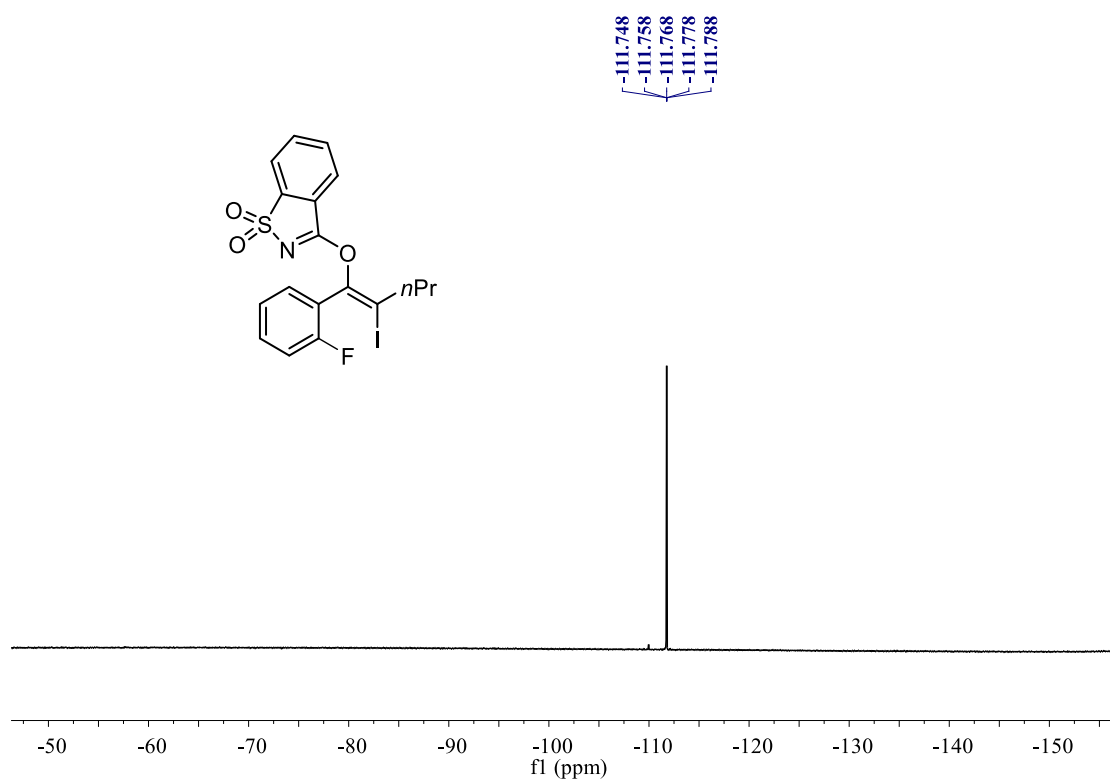
¹³C NMR (150 MHz, CDCl₃) spectrum of 3h.



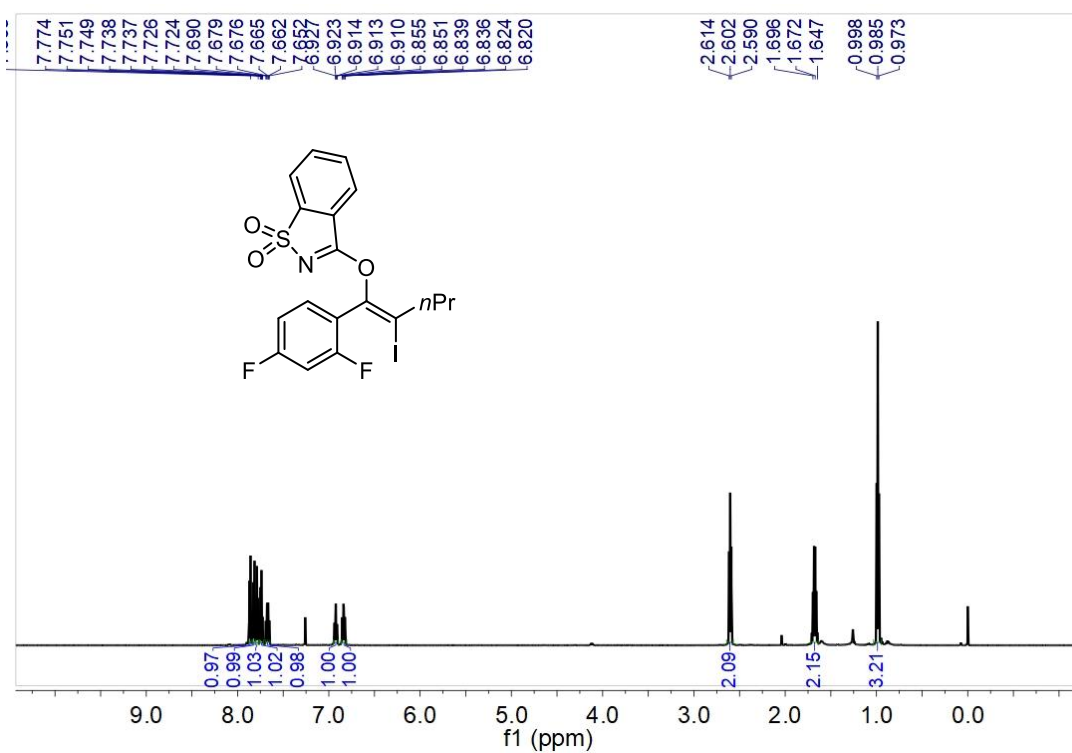
¹H NMR (600 MHz, CDCl₃) spectrum of 3i.



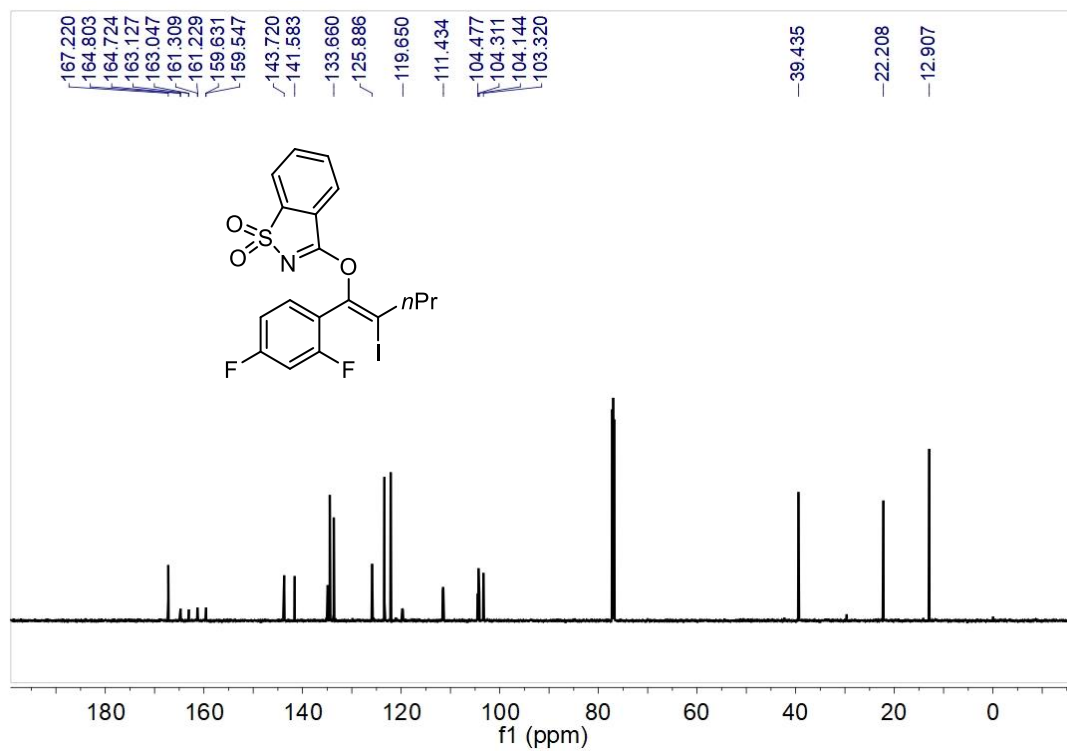
¹³C NMR (150 MHz, CDCl₃) spectrum of 3i.



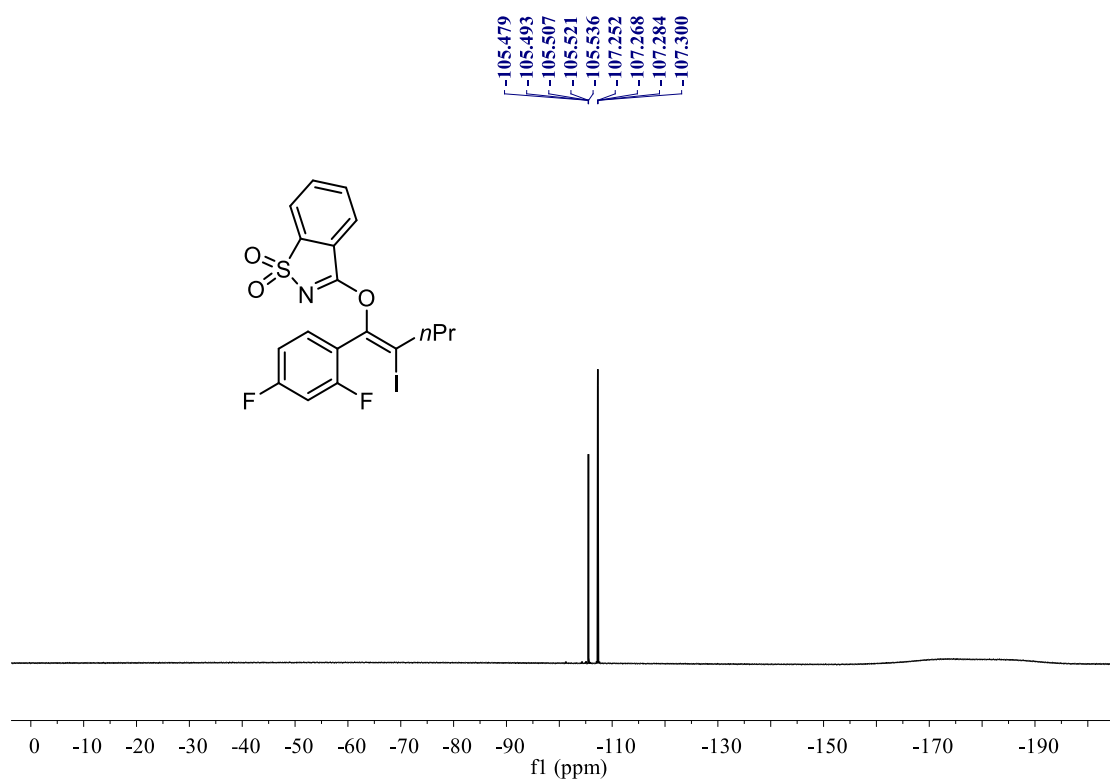
^{19}F NMR (565 MHz, CDCl_3) spectrum of **3i.**



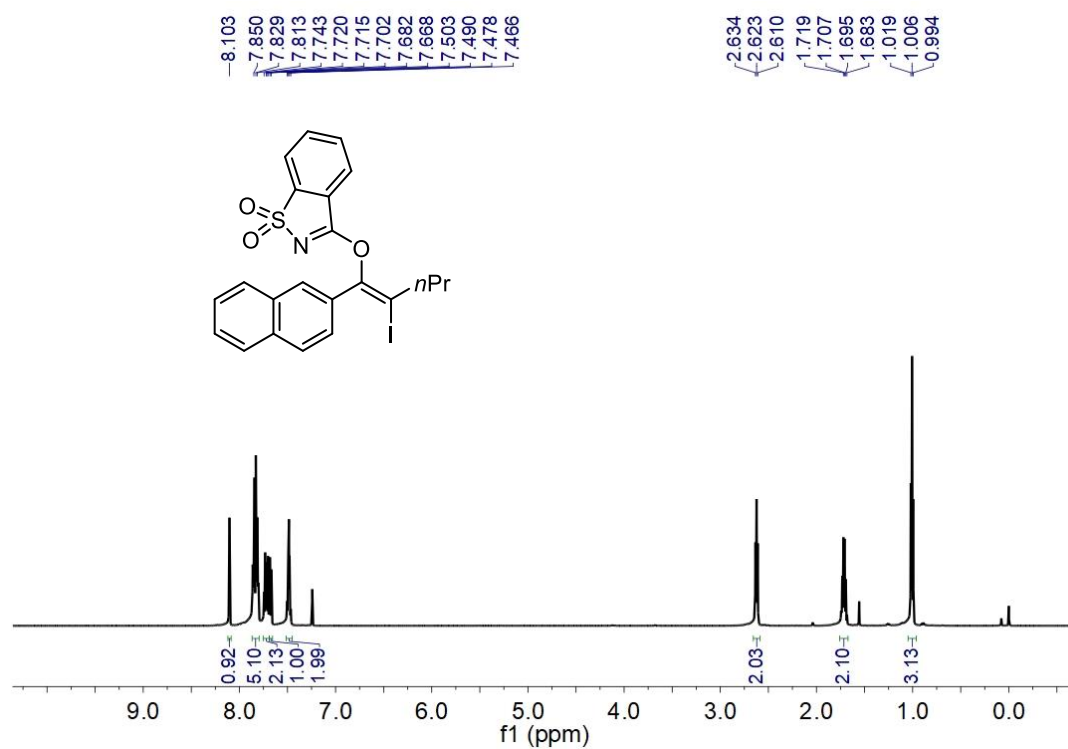
¹H NMR (600 MHz, CDCl₃) spectrum of 3j.



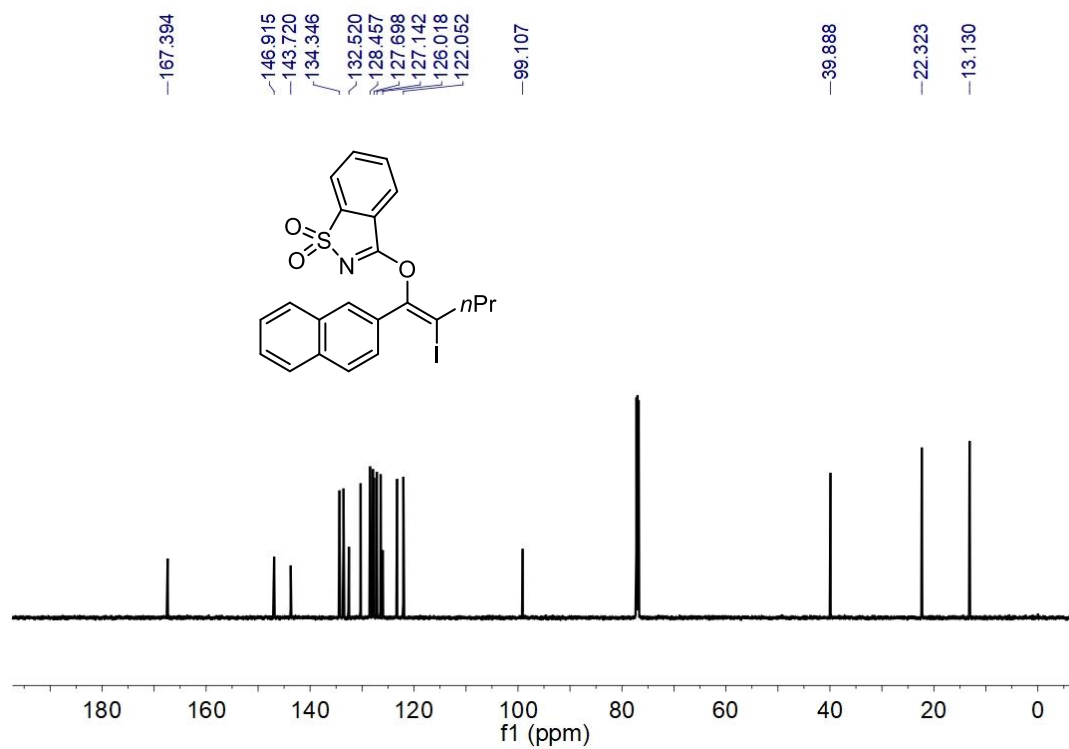
¹³C NMR (150 MHz, CDCl₃) spectrum of 3j.



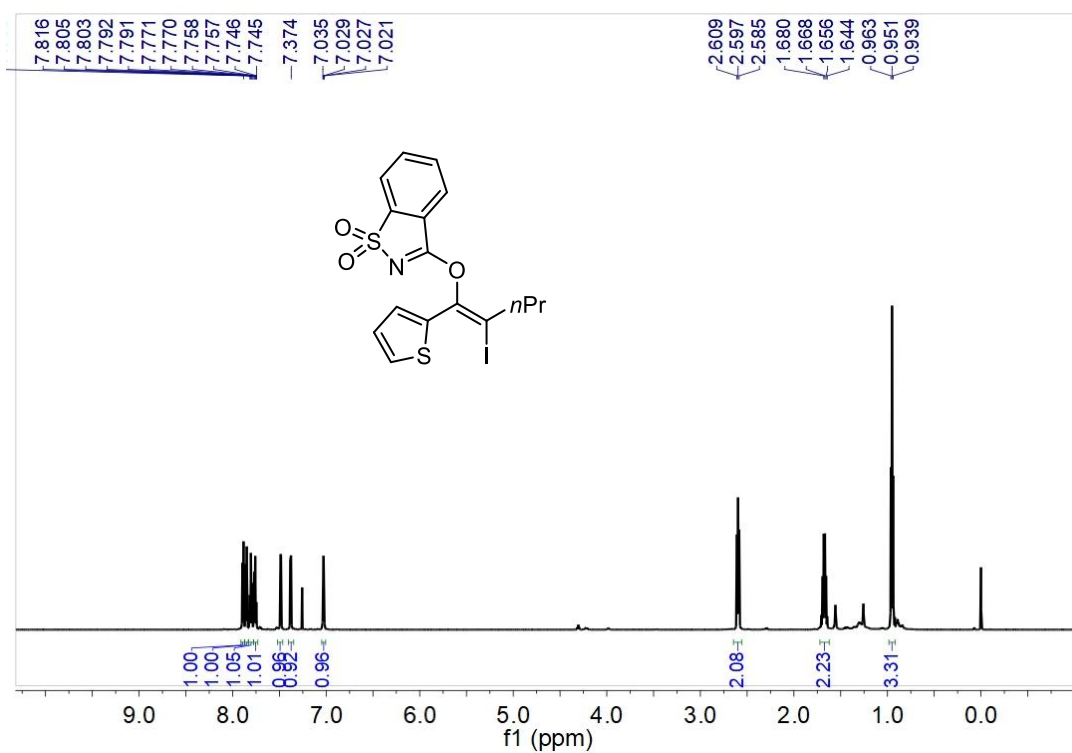
¹⁹F NMR (565 MHz, CDCl₃) spectrum of 3j.



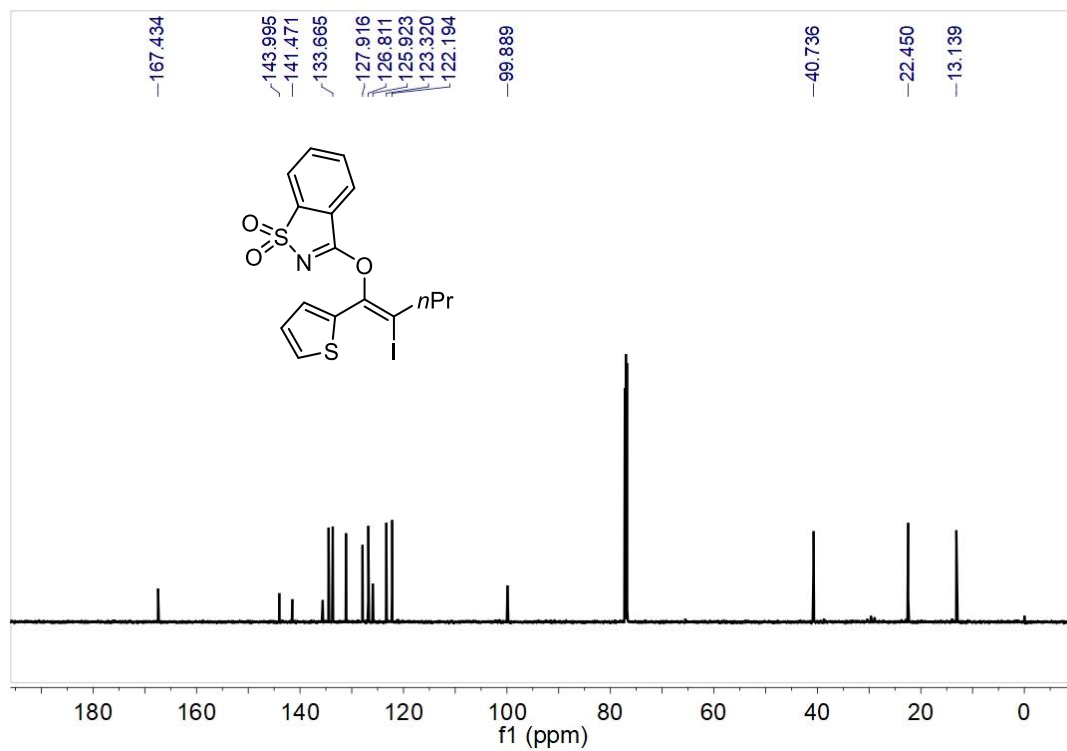
¹H NMR (600 MHz, CDCl₃) spectrum of 3k.



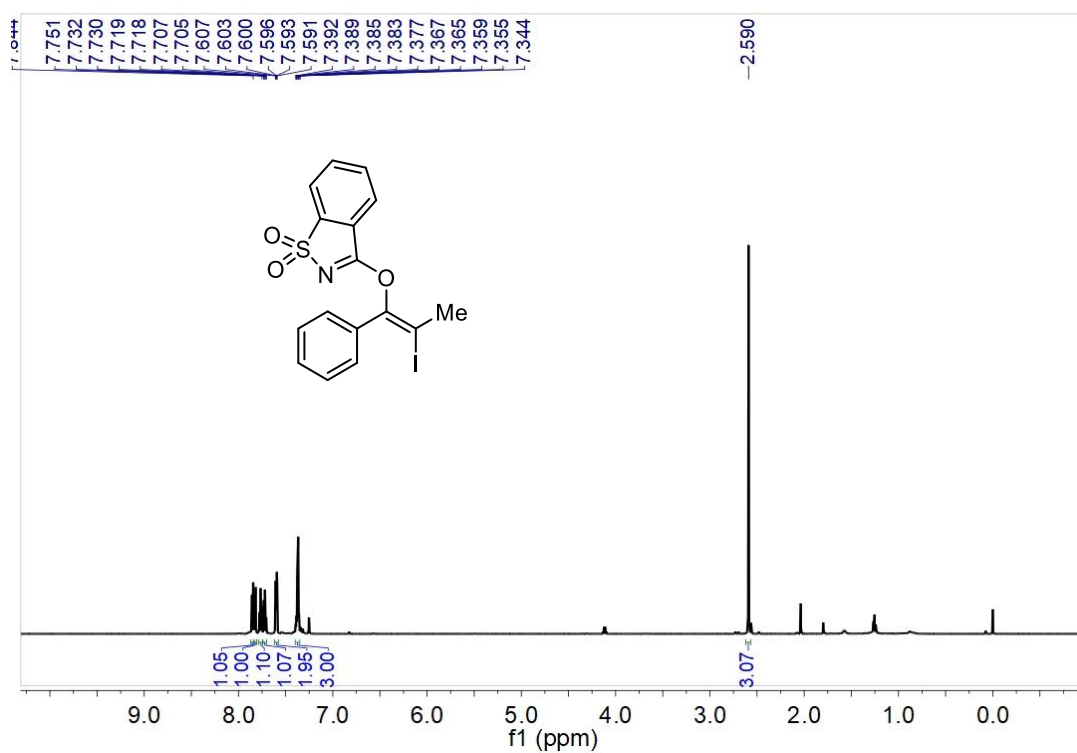
¹³C NMR (150 MHz, CDCl₃) spectrum of 3k.



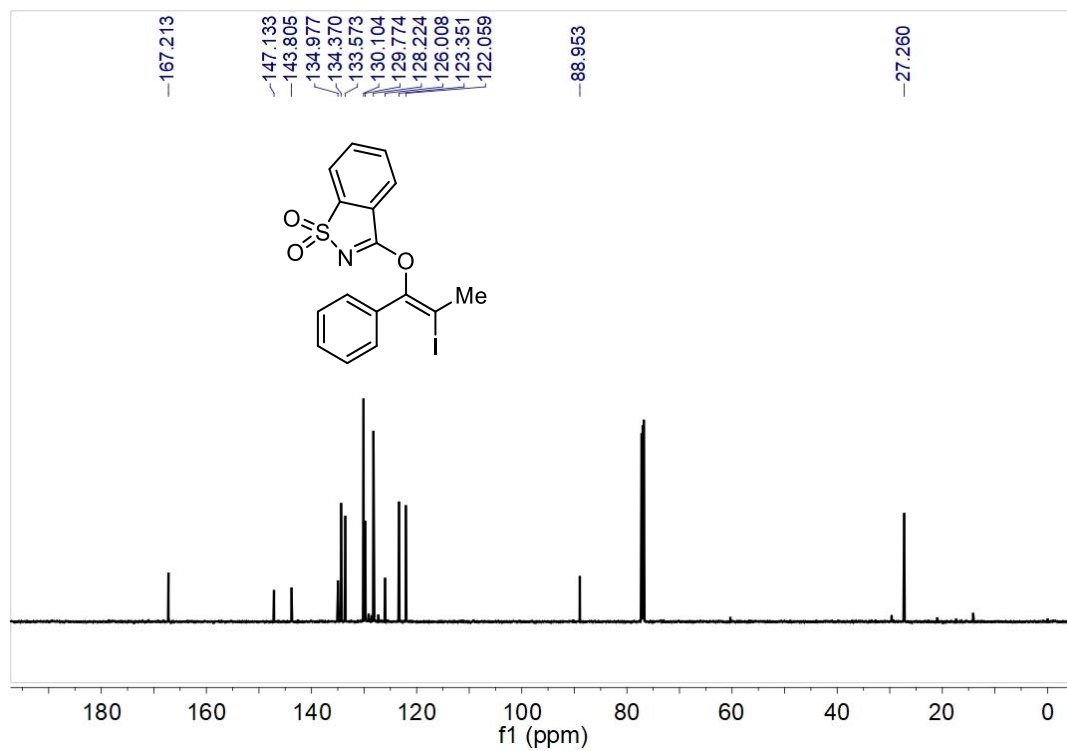
¹H NMR (600 MHz, CDCl₃) spectrum of 3l.



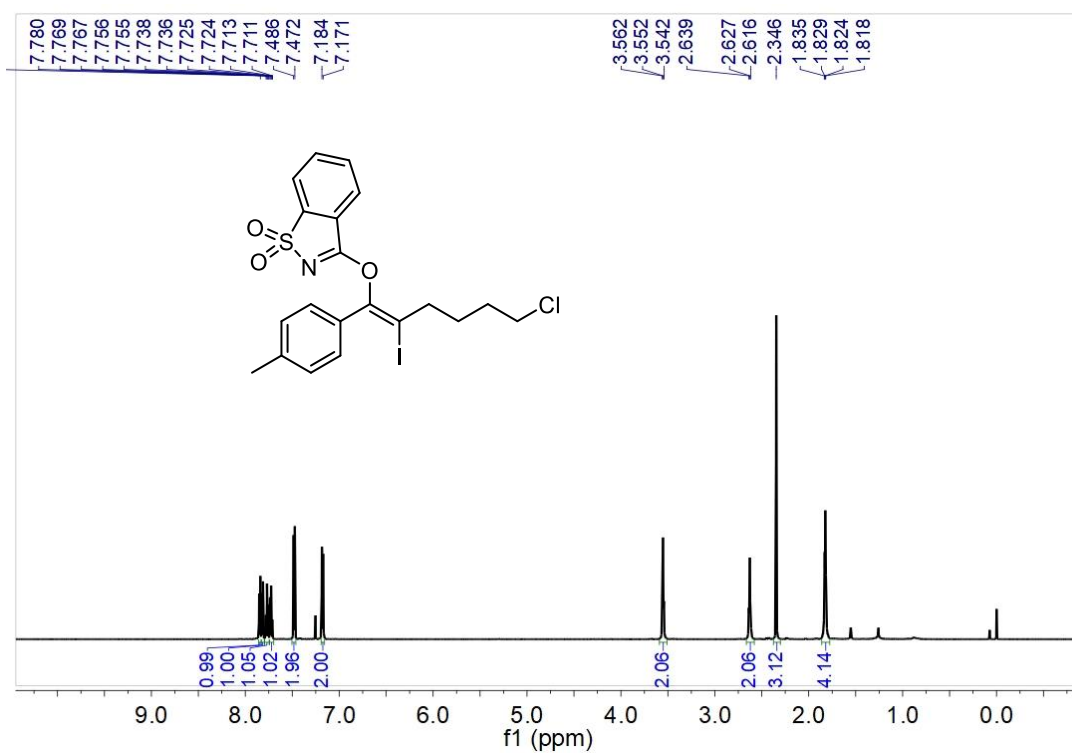
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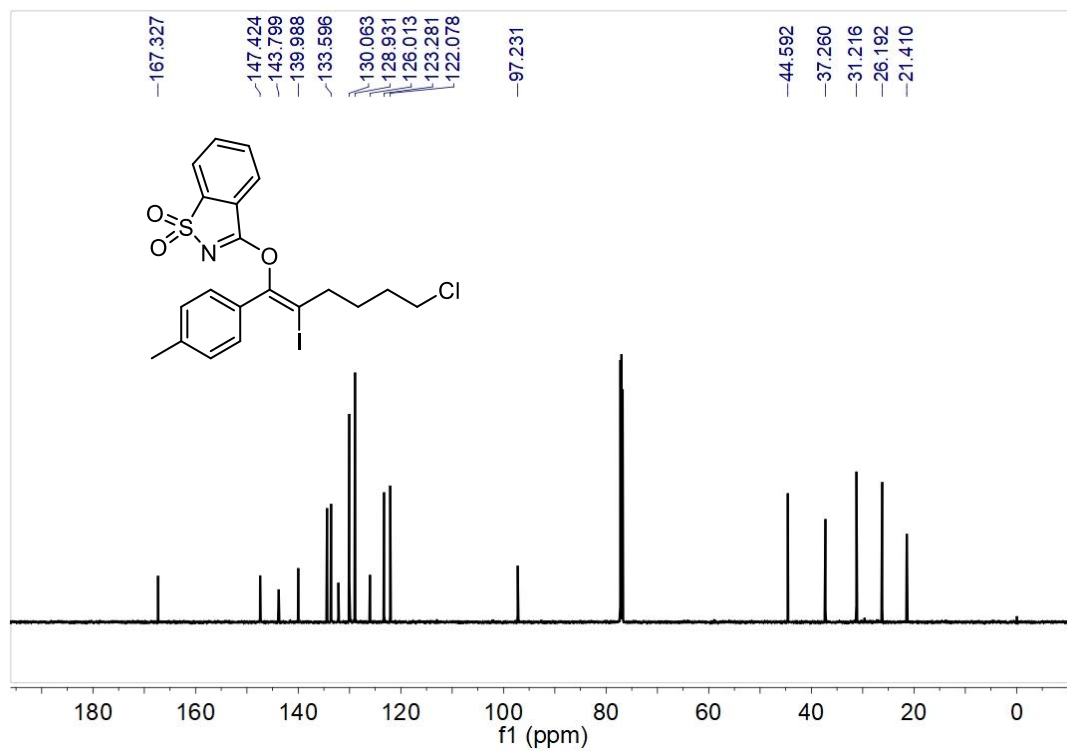
¹H NMR (600 MHz, CDCl₃) spectrum of 3m.



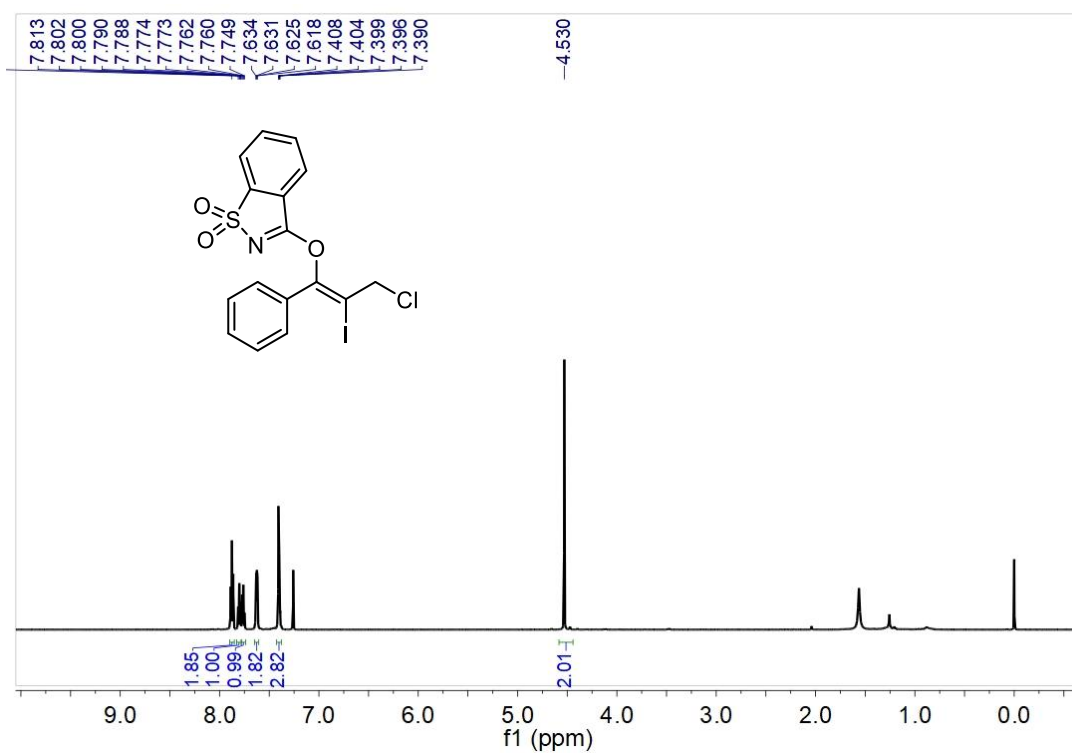
¹³C NMR (150 MHz, CDCl₃) spectrum of 3m.



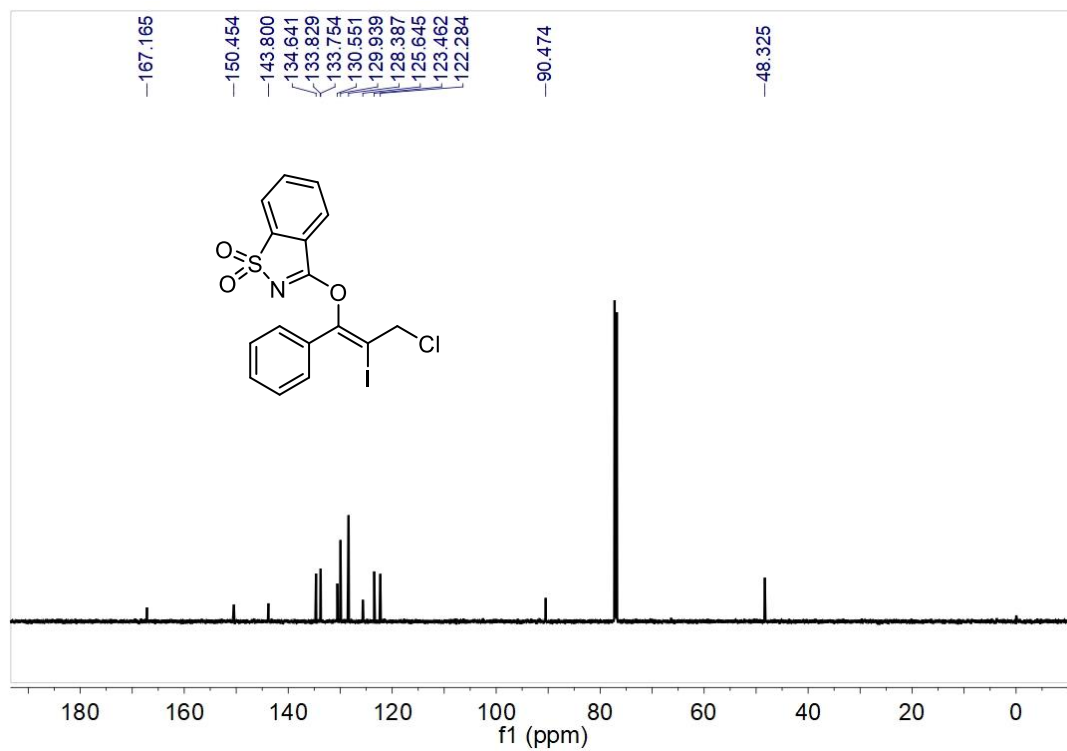
¹H NMR (600 MHz, CDCl₃) spectrum of 3n.



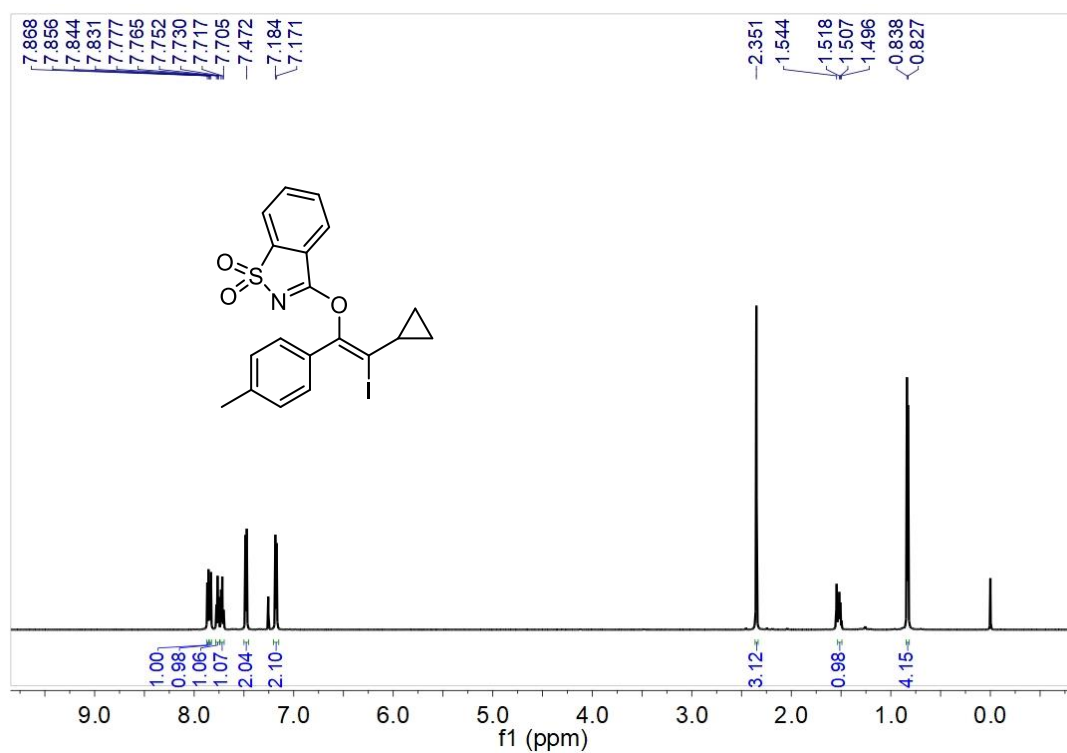
¹³C NMR (150 MHz, CDCl₃) spectrum of 3n.



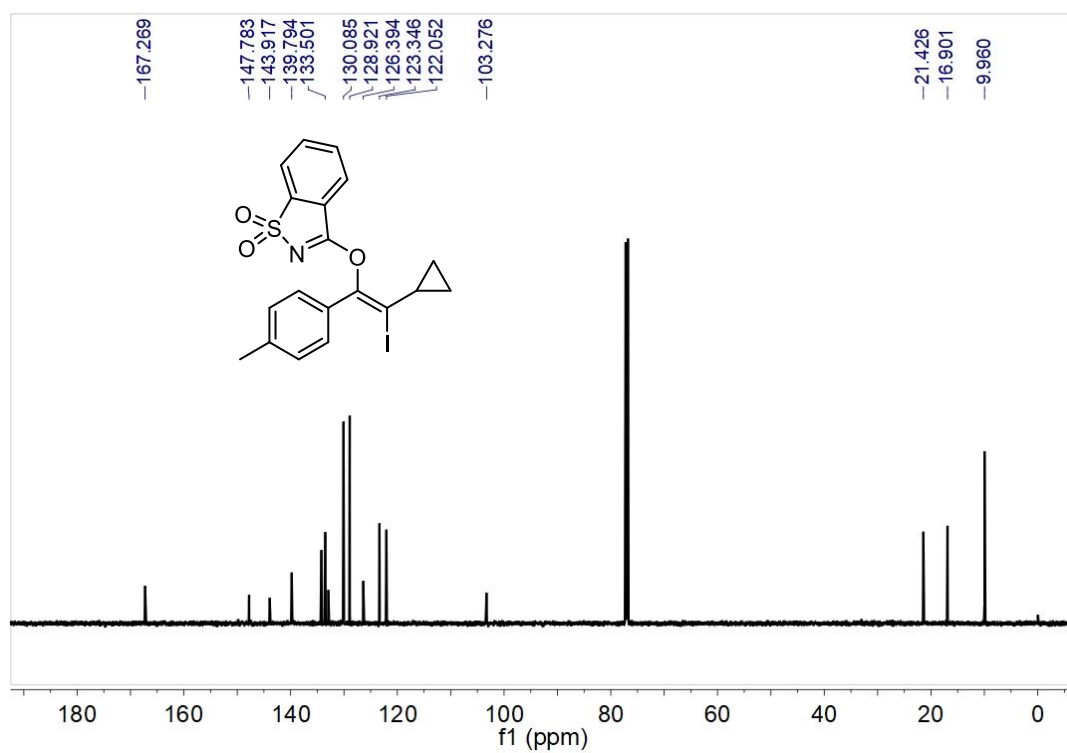
¹H NMR (600 MHz, CDCl₃) spectrum of 3o.



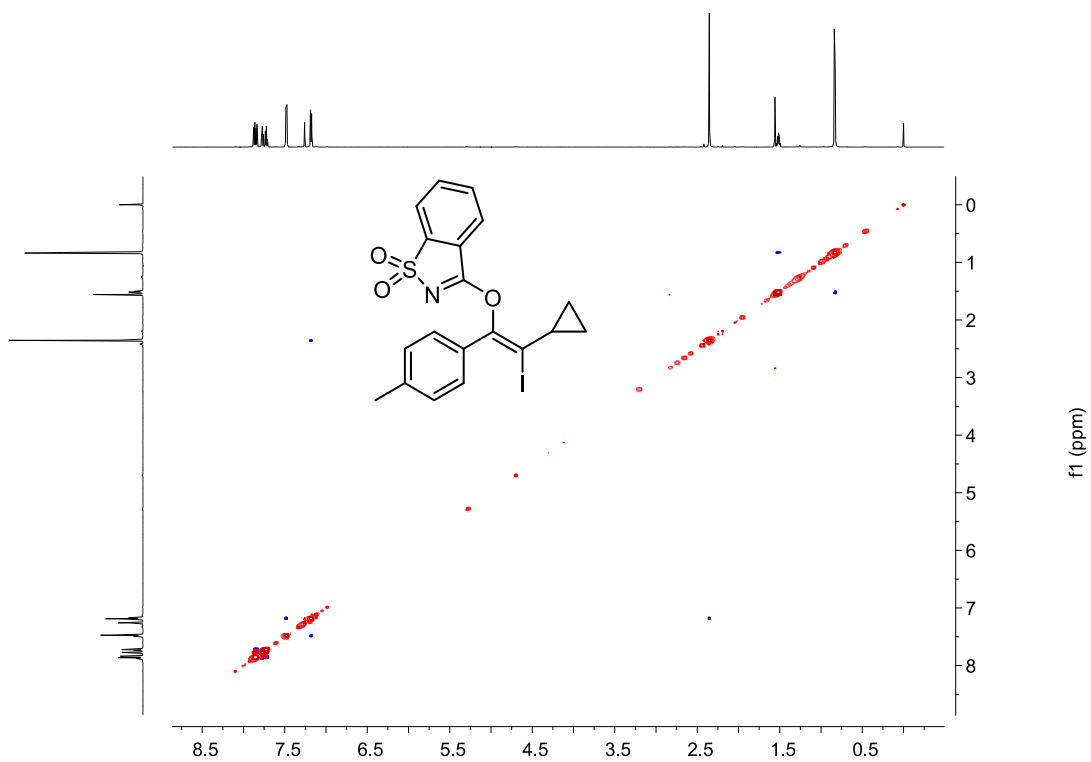
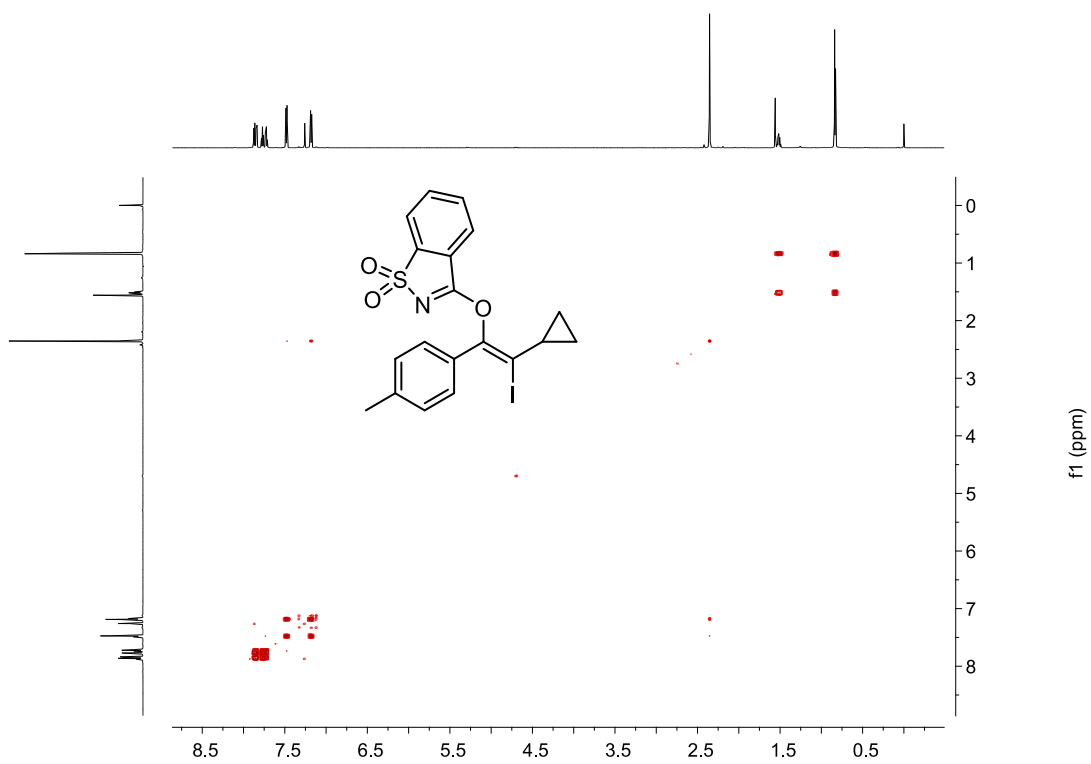
¹³C NMR (150 MHz, CDCl₃) spectrum of 3o.

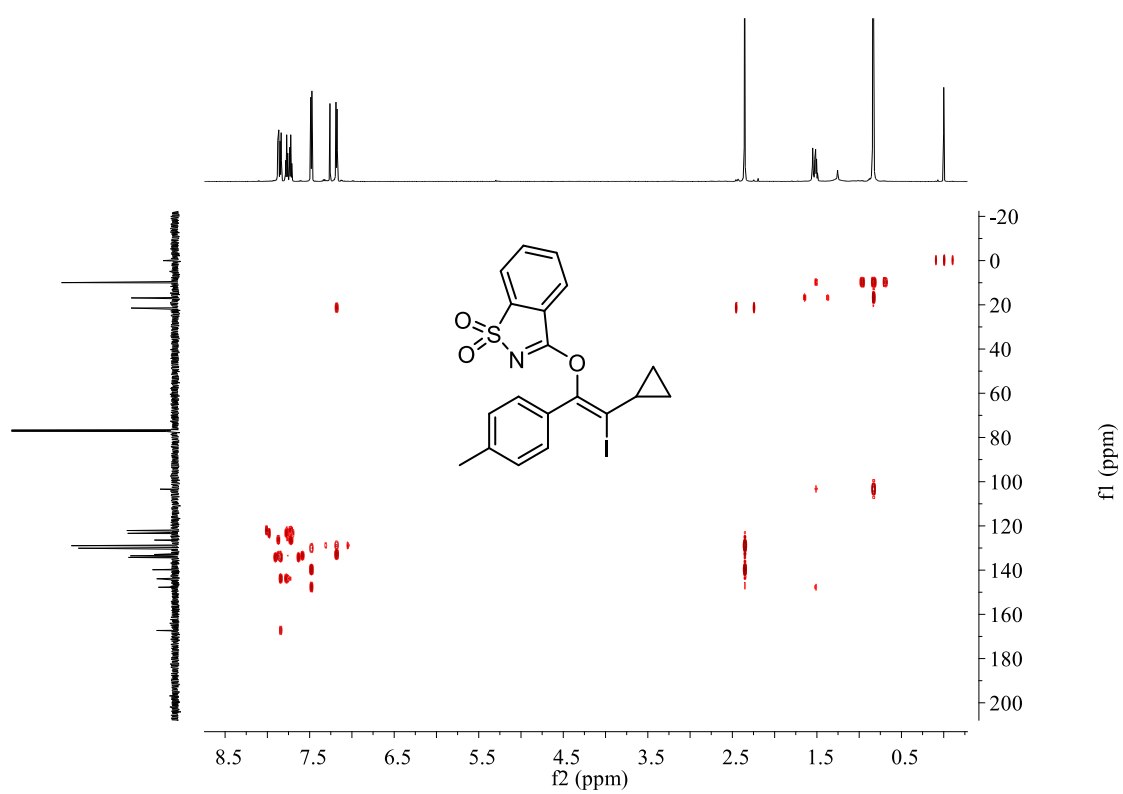


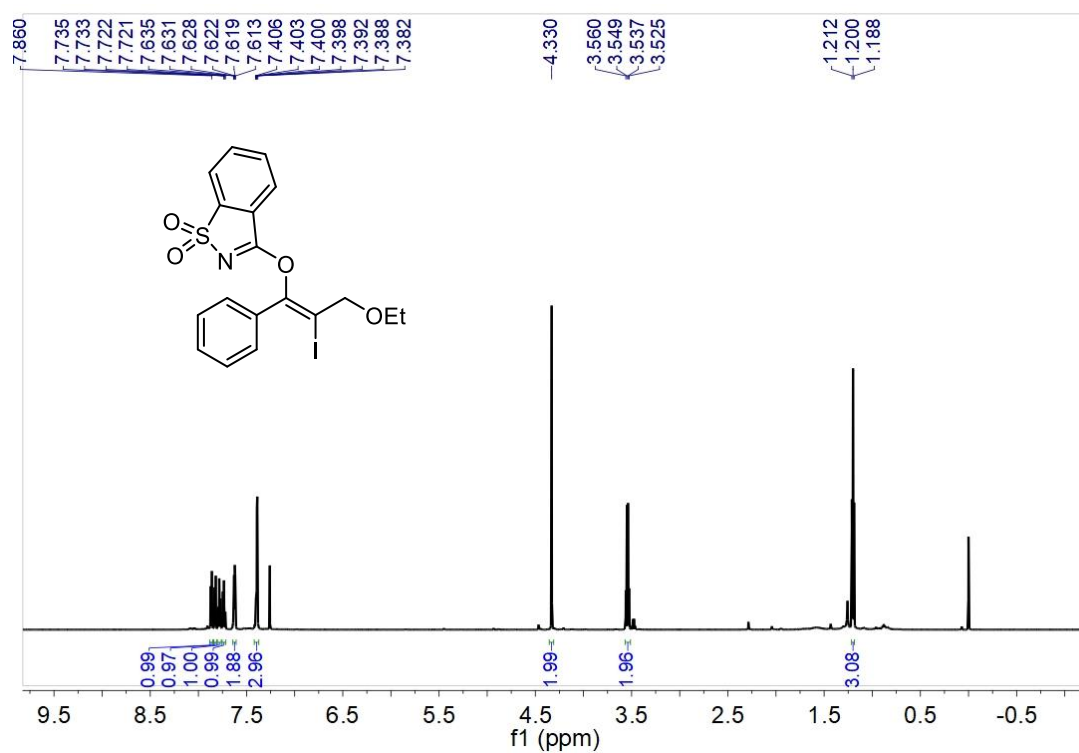
¹H NMR (600 MHz, CDCl₃) spectrum of 3p.



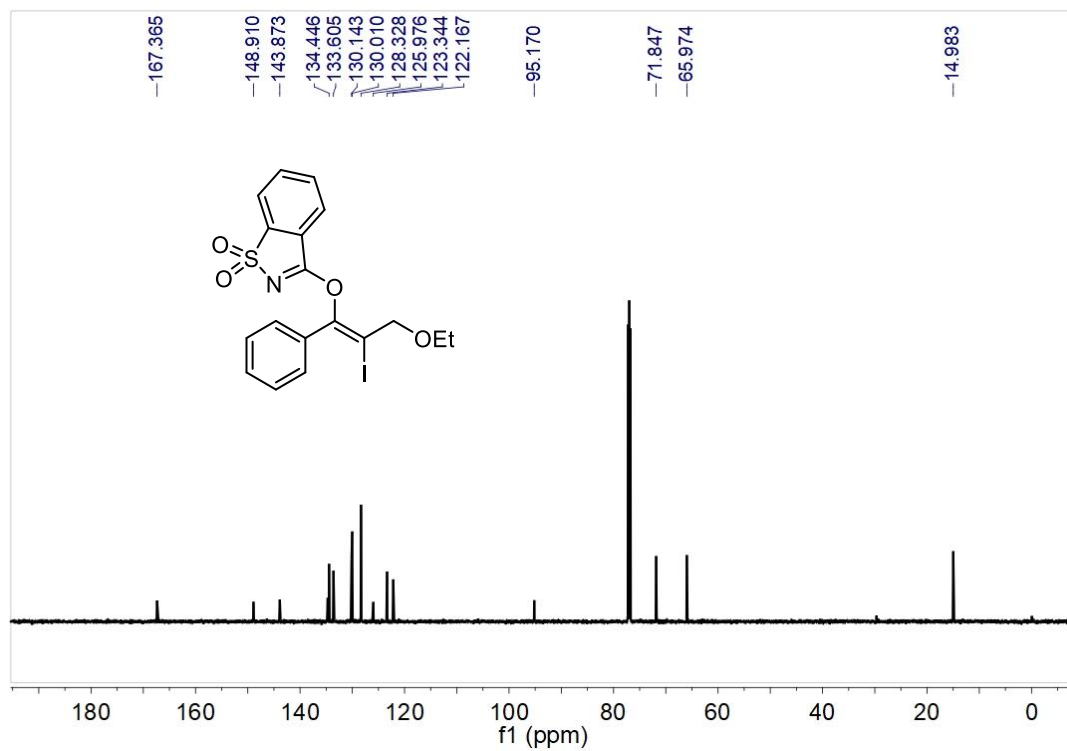
¹³C NMR (150 MHz, CDCl₃) spectrum of 3p.



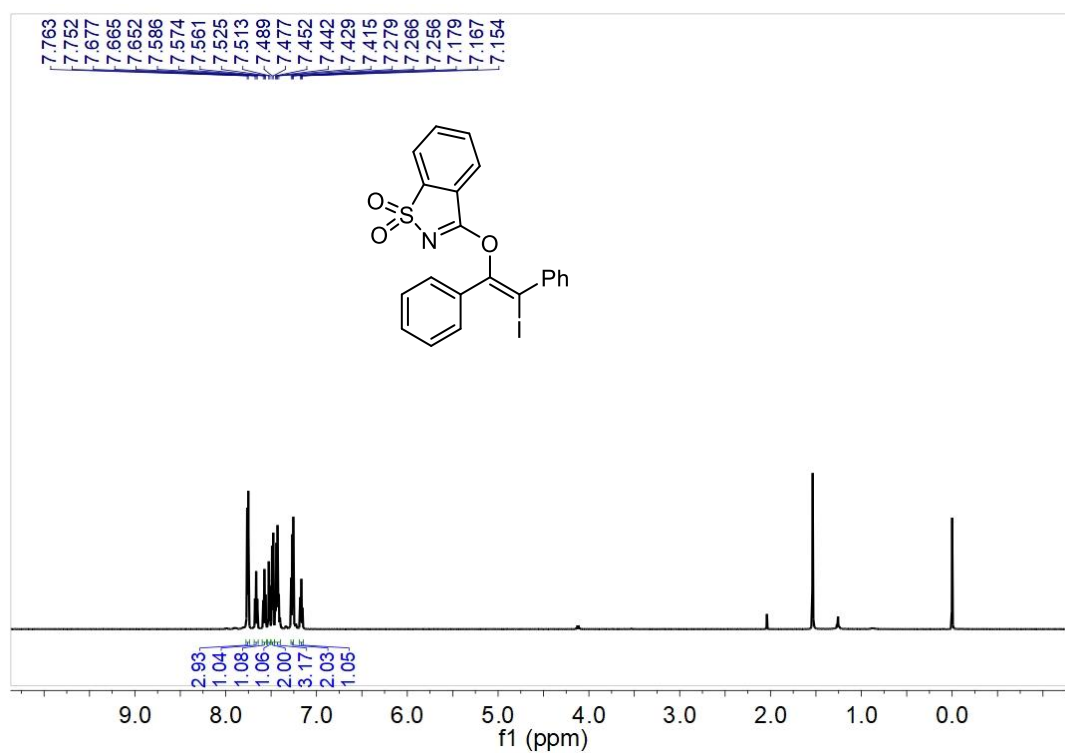




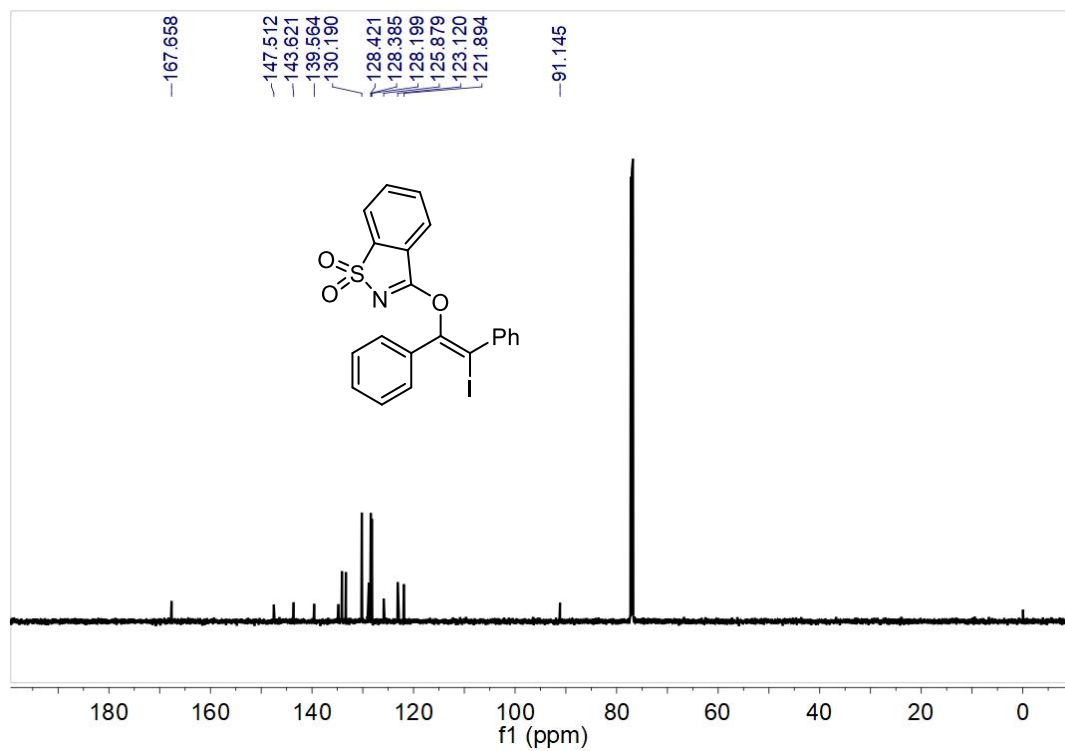
¹H NMR (600 MHz, CDCl₃) spectrum of 3q.



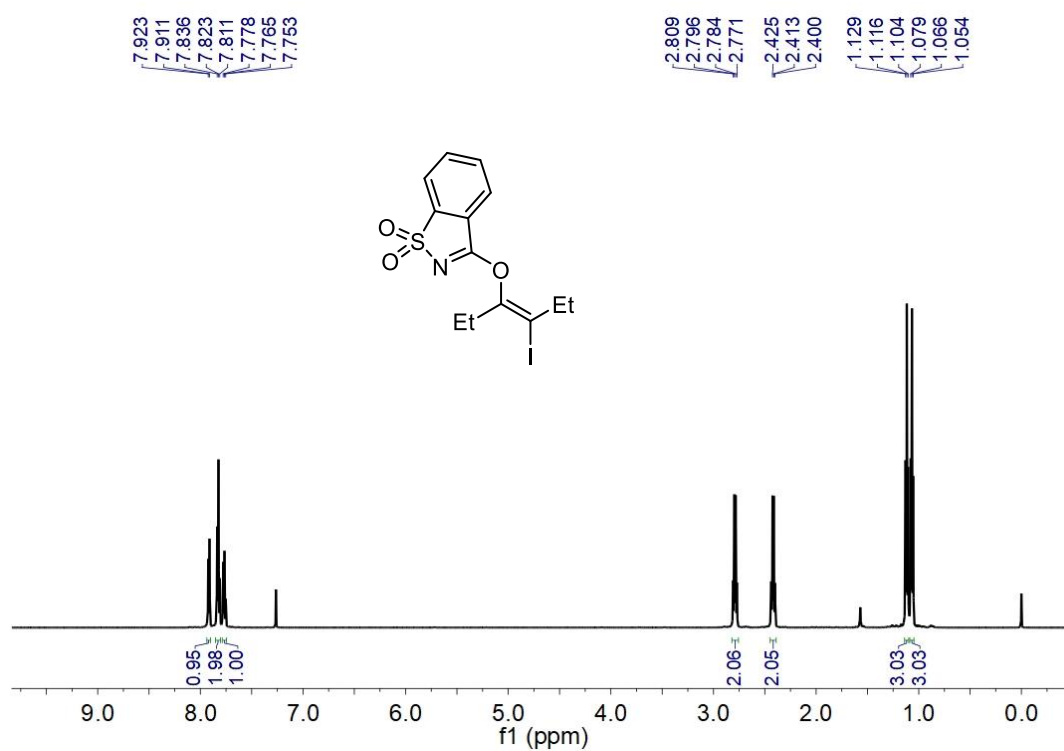
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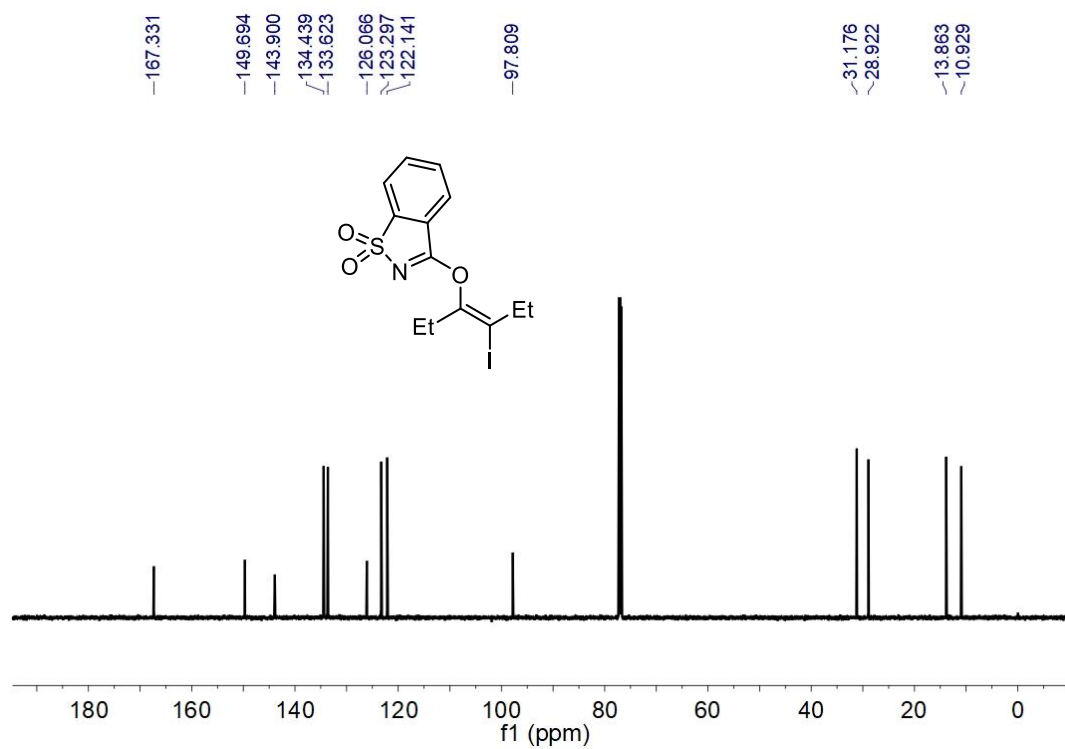
¹H NMR (600 MHz, CDCl₃) spectrum of 3r.



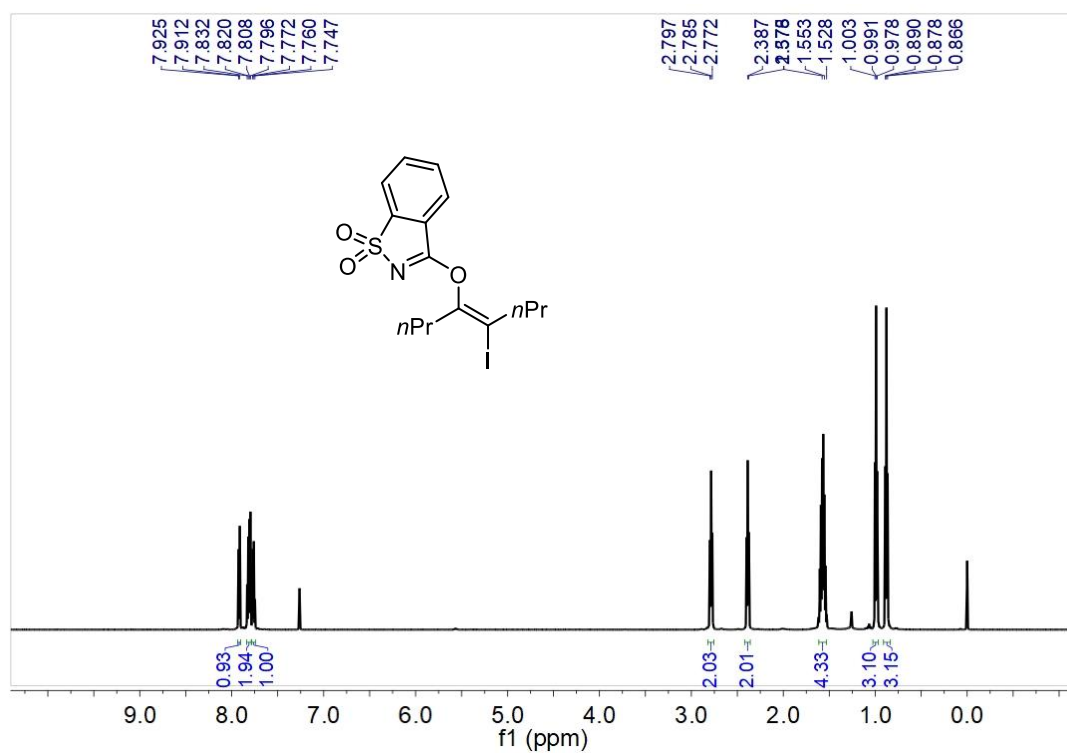
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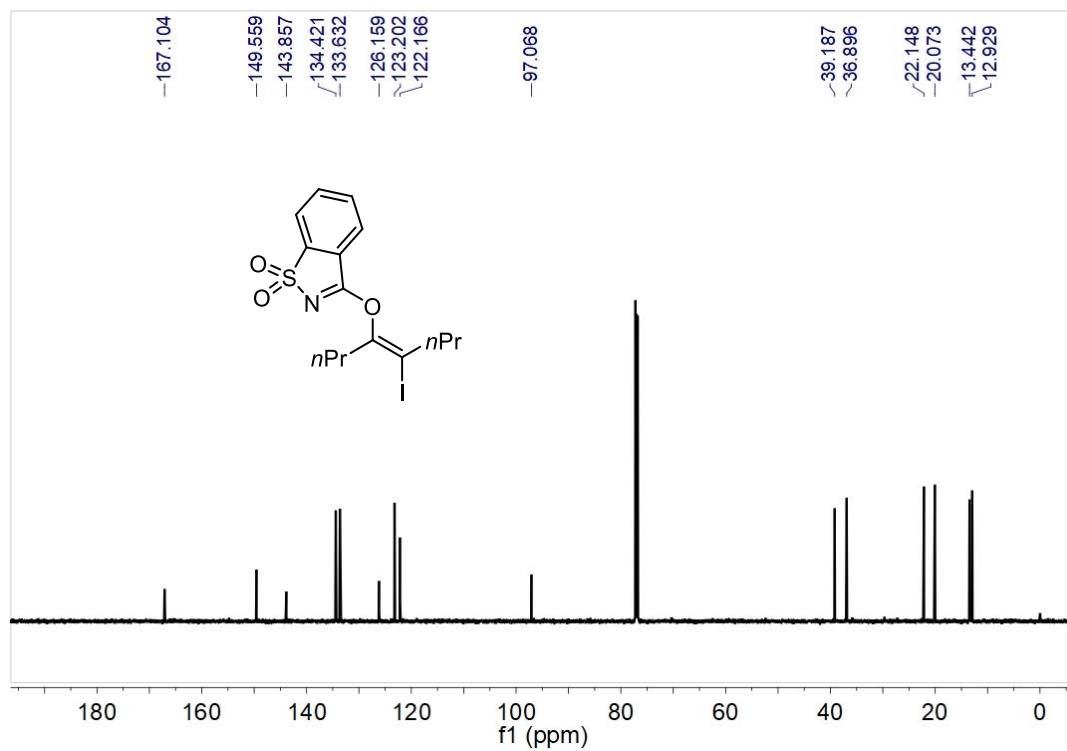
¹H NMR (600 MHz, CDCl₃) spectrum of 3s.



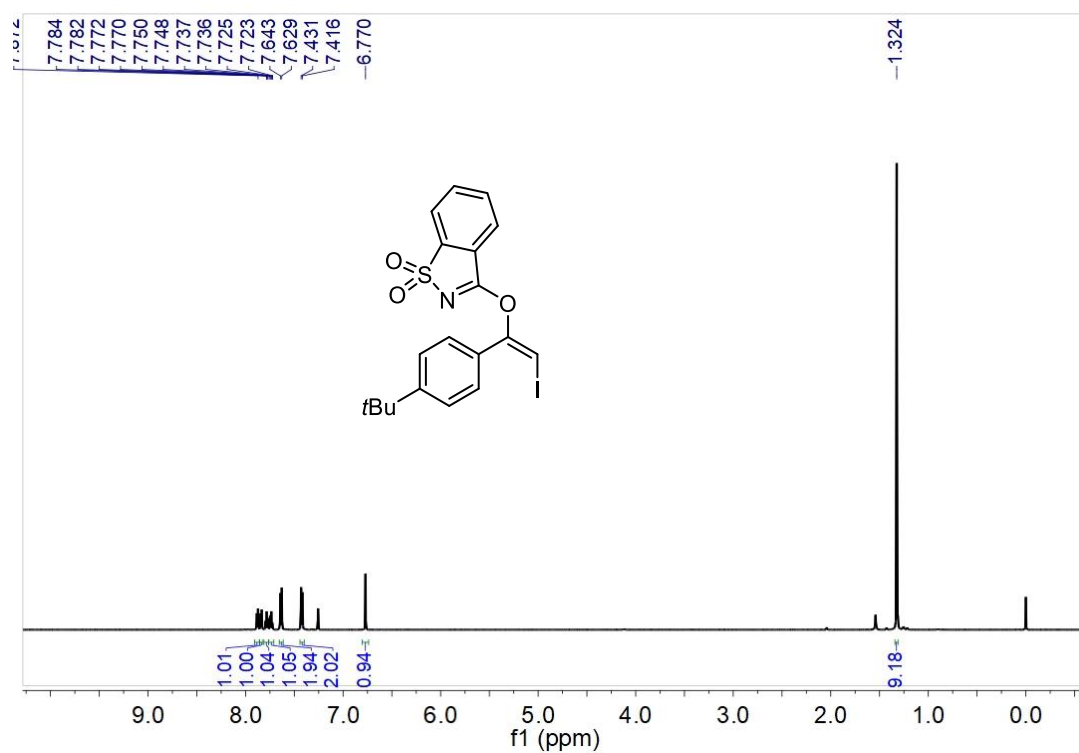
¹³C NMR (150 MHz, CDCl₃) spectrum of 3s.



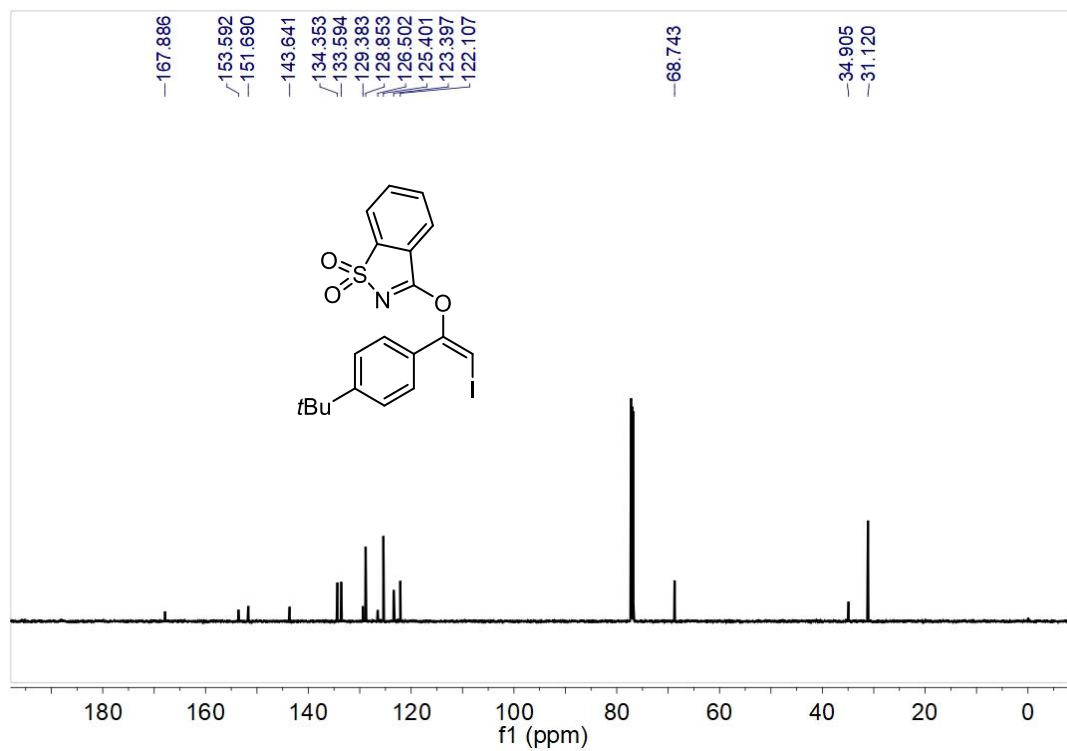
¹H NMR (600 MHz, CDCl₃) spectrum of 3t.



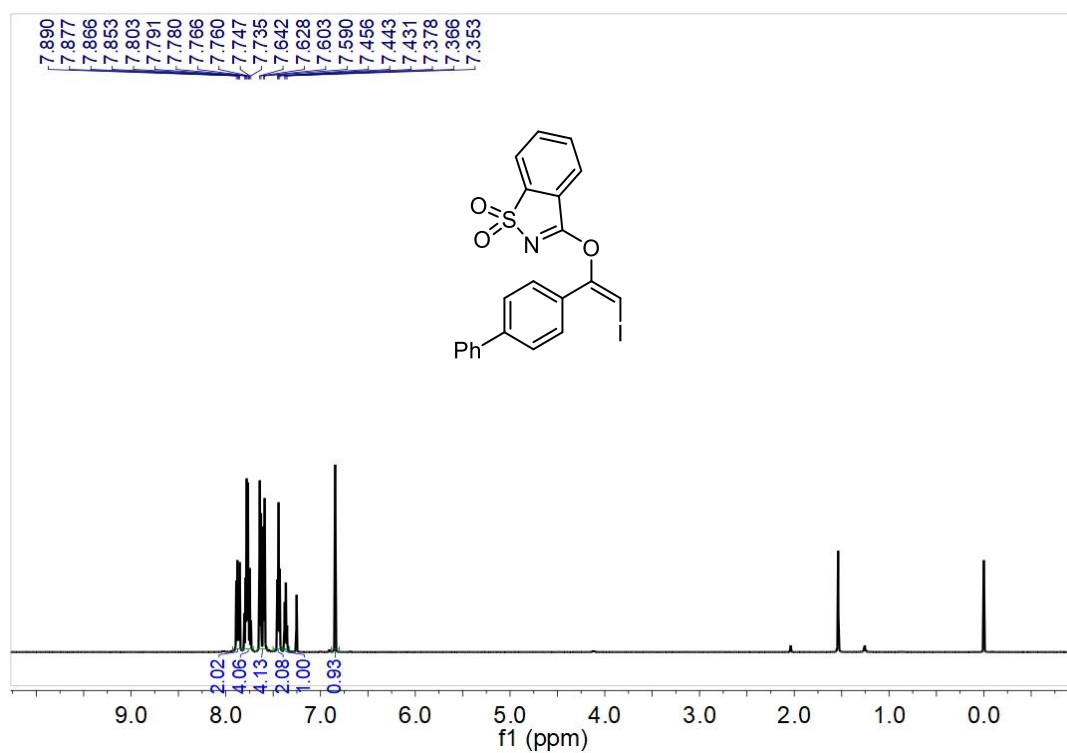
¹³C NMR (150 MHz, CDCl₃) spectrum of 3t.



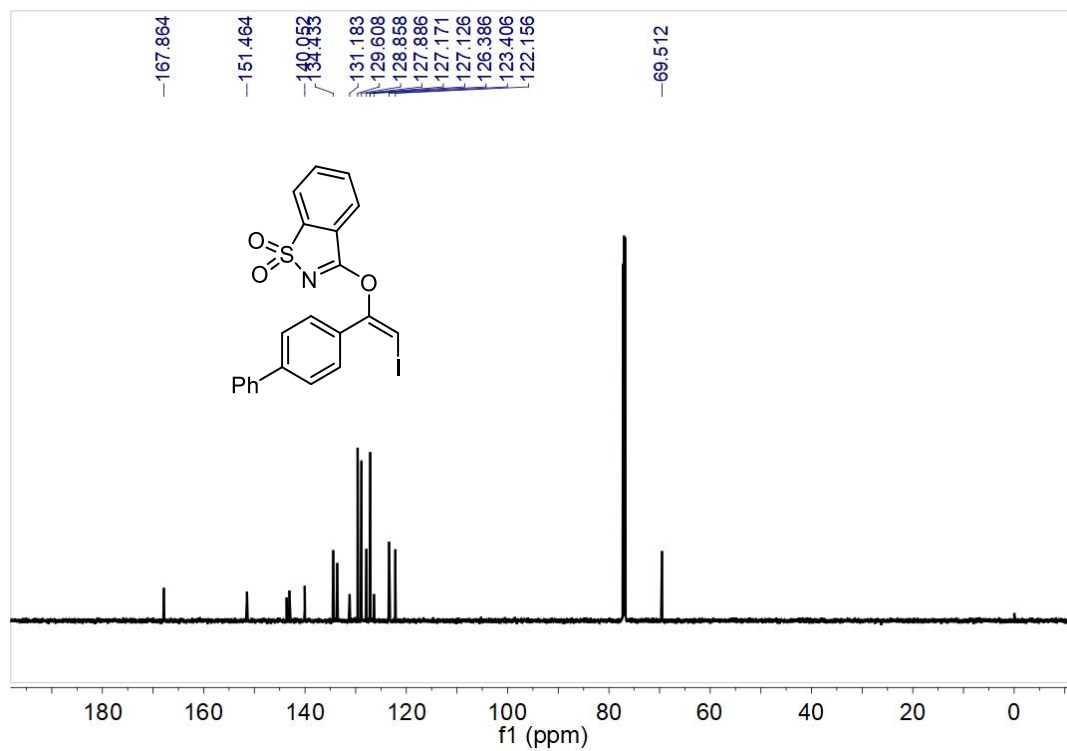
¹H NMR (600 MHz, CDCl₃) spectrum of 3u.



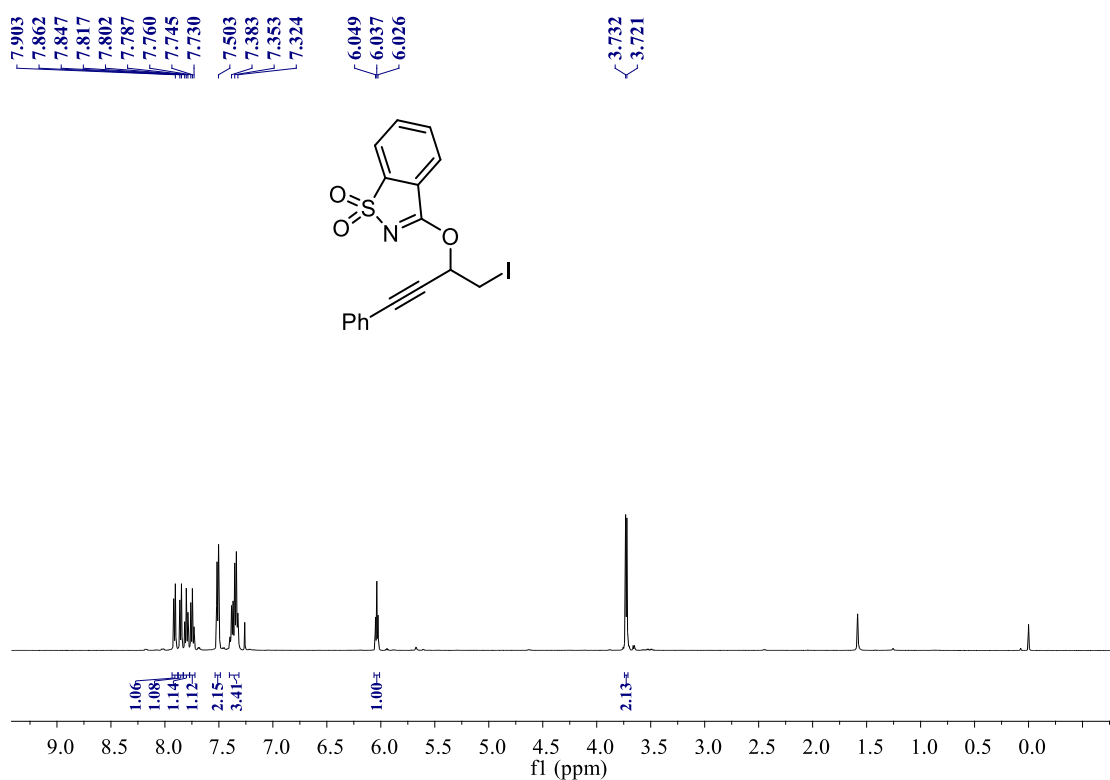
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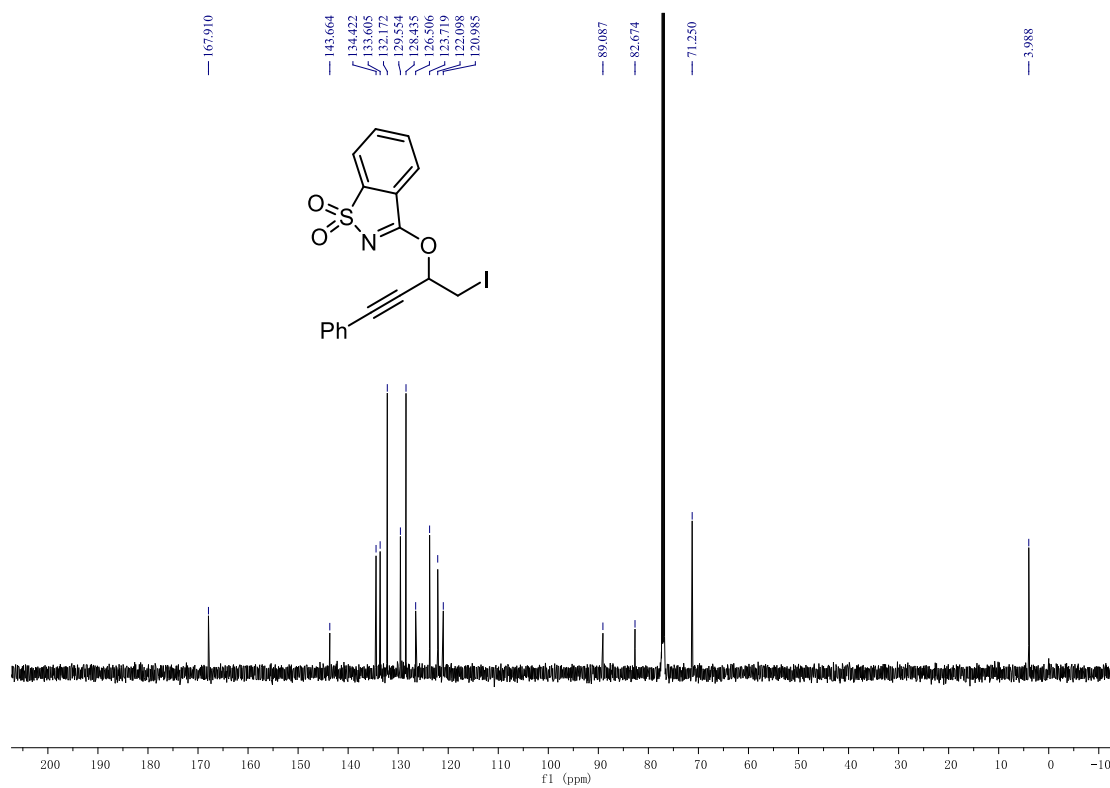
¹H NMR (600 MHz, CDCl₃) spectrum of 3v.



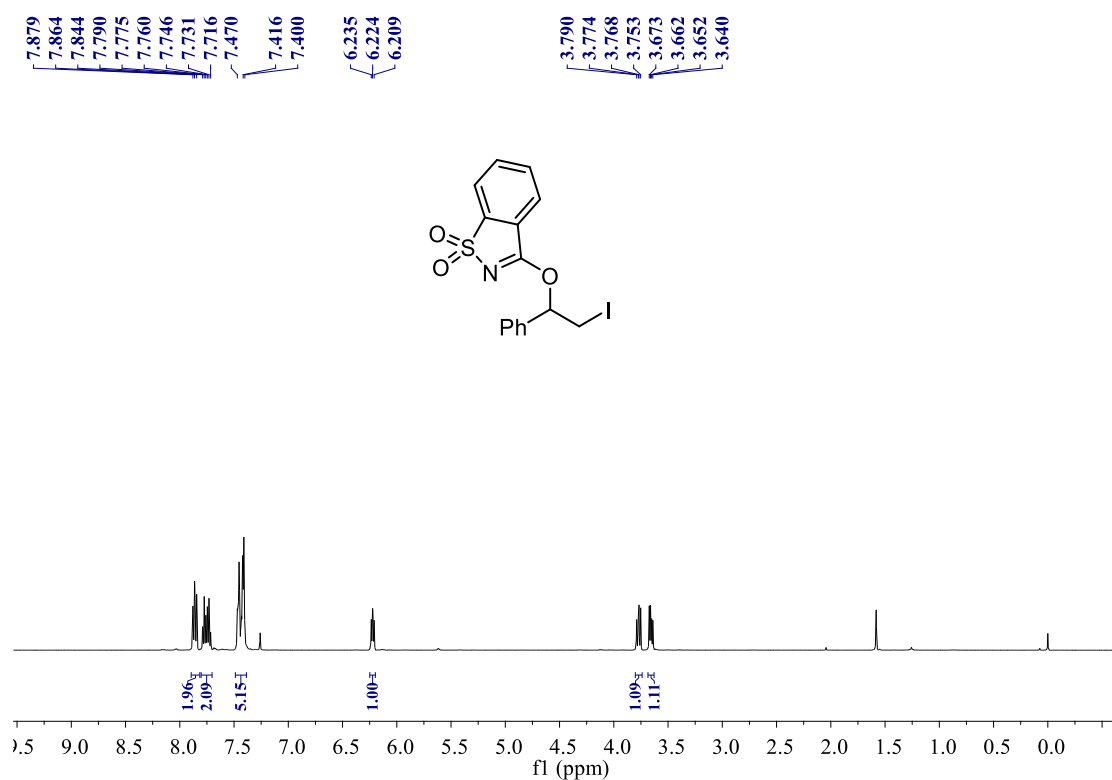
¹³C NMR (150 MHz, CDCl₃) spectrum of 3v.



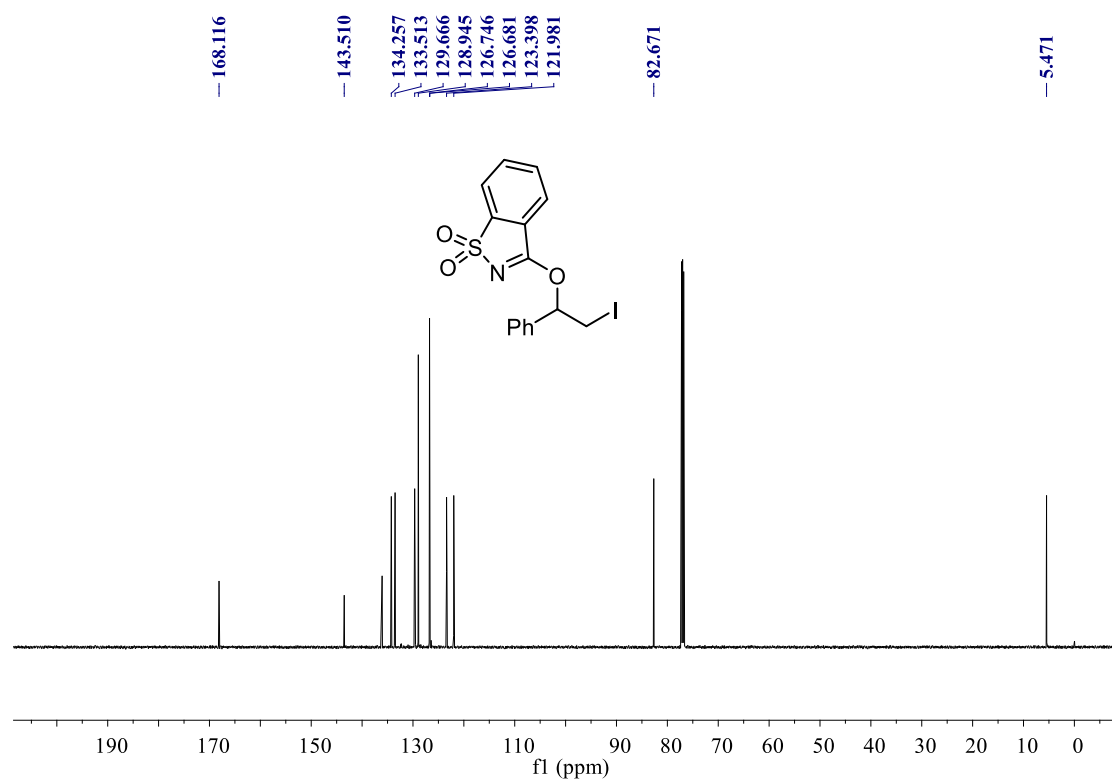
¹H NMR (500 MHz, CDCl₃) spectrum of 4a.



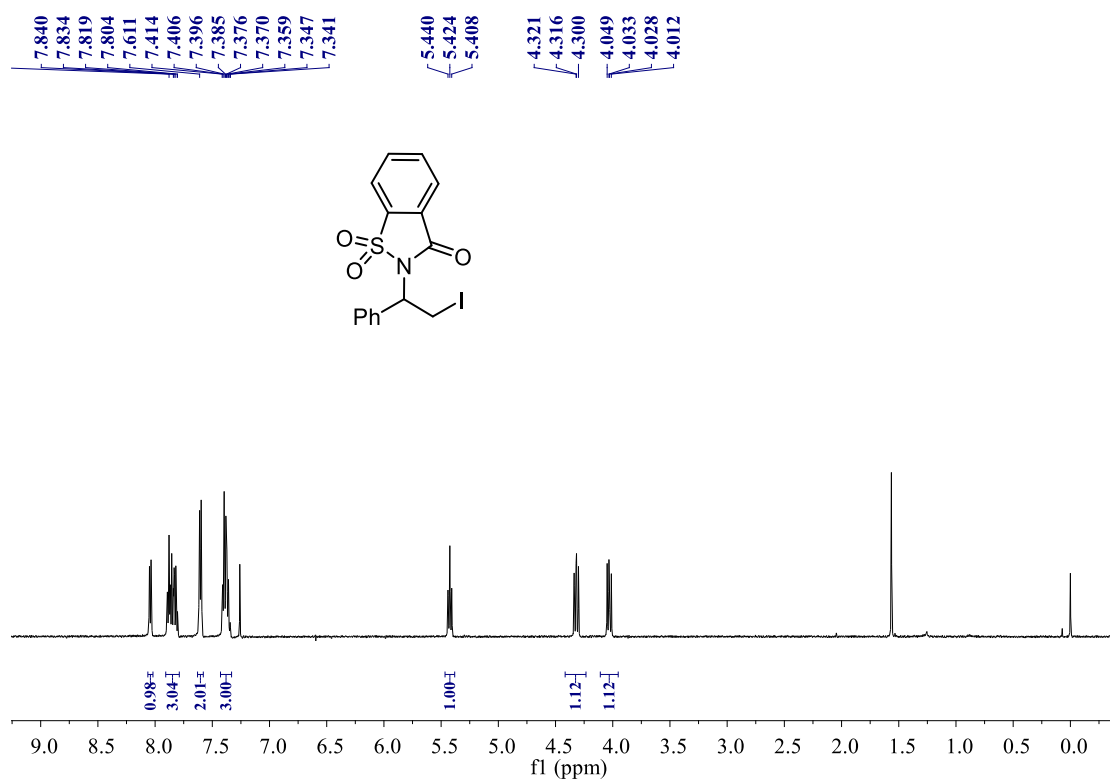
¹³C NMR (150 MHz, CDCl₃) spectrum of 4a.



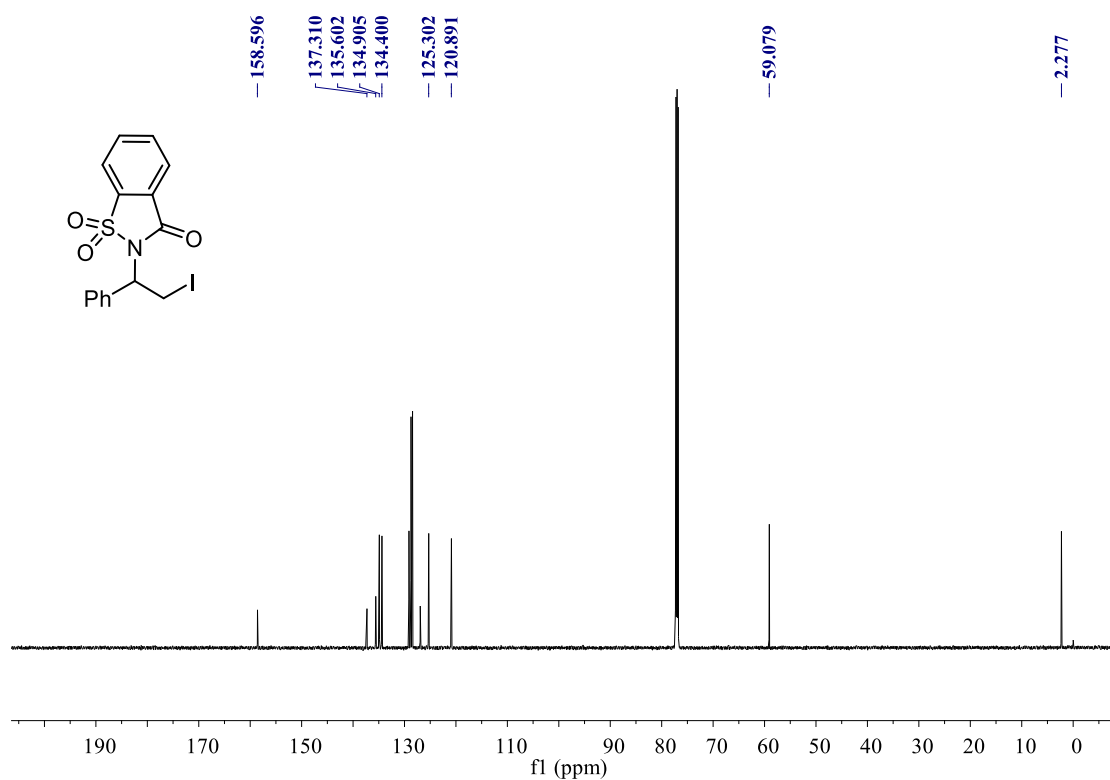
¹H NMR (500 MHz, CDCl₃) spectrum of 4b.



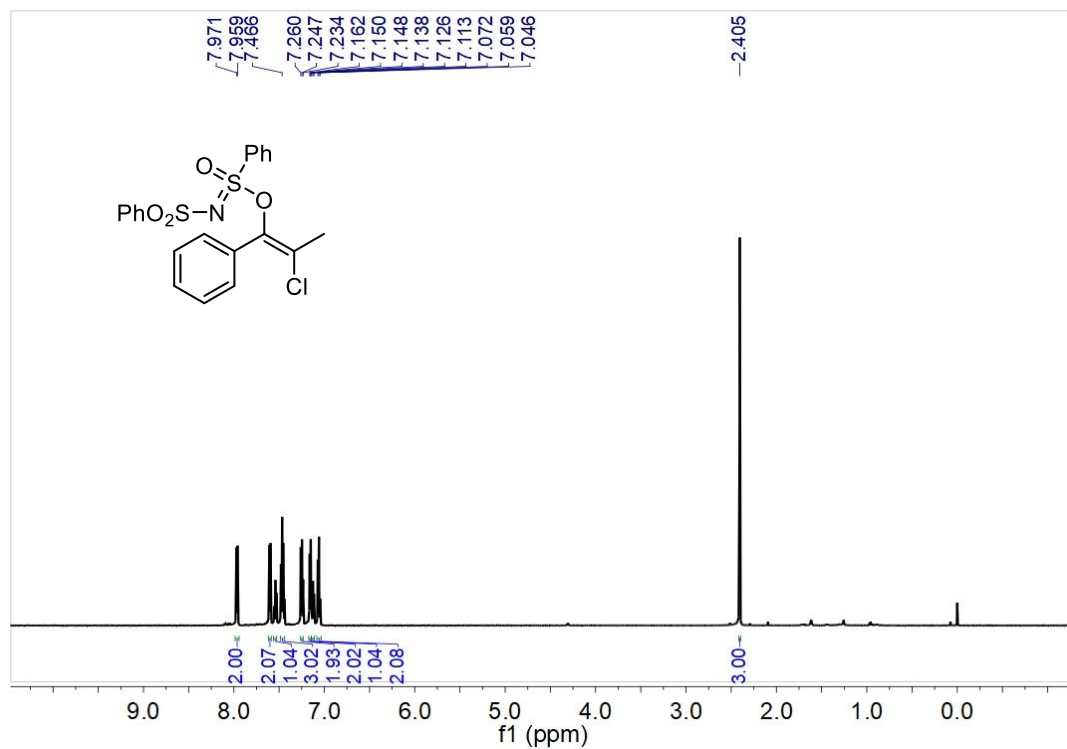
¹³C NMR (500 MHz, CDCl₃) spectrum of 4b.



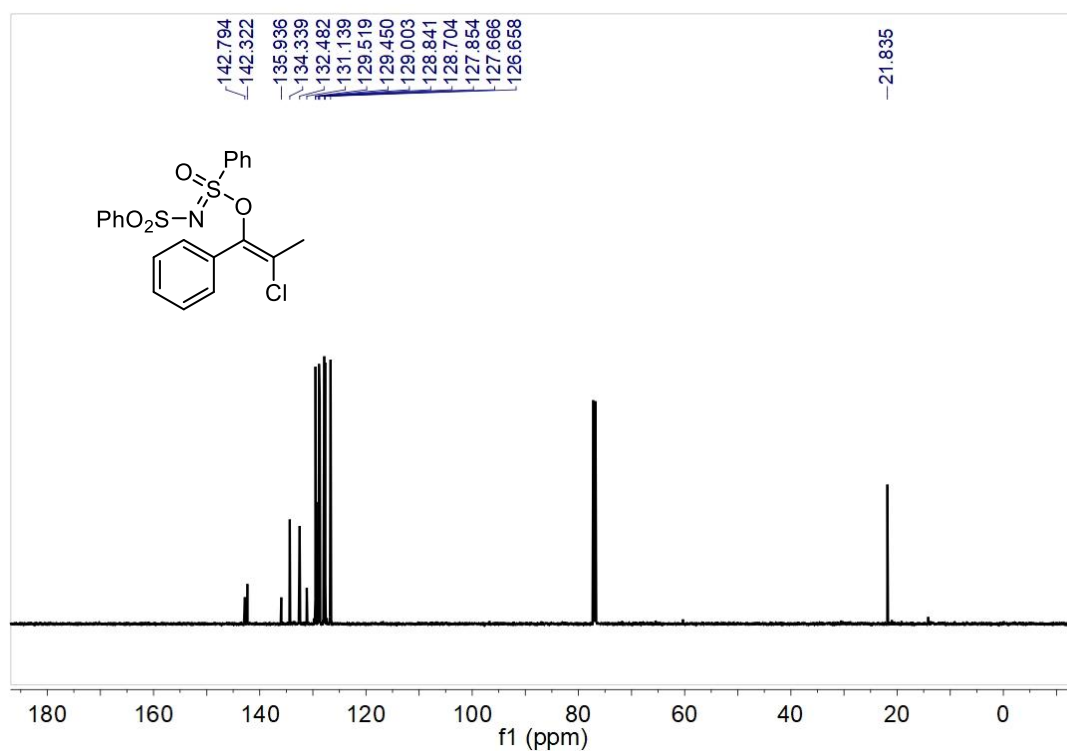
¹H NMR (500 MHz, CDCl₃) spectrum of 4b'.



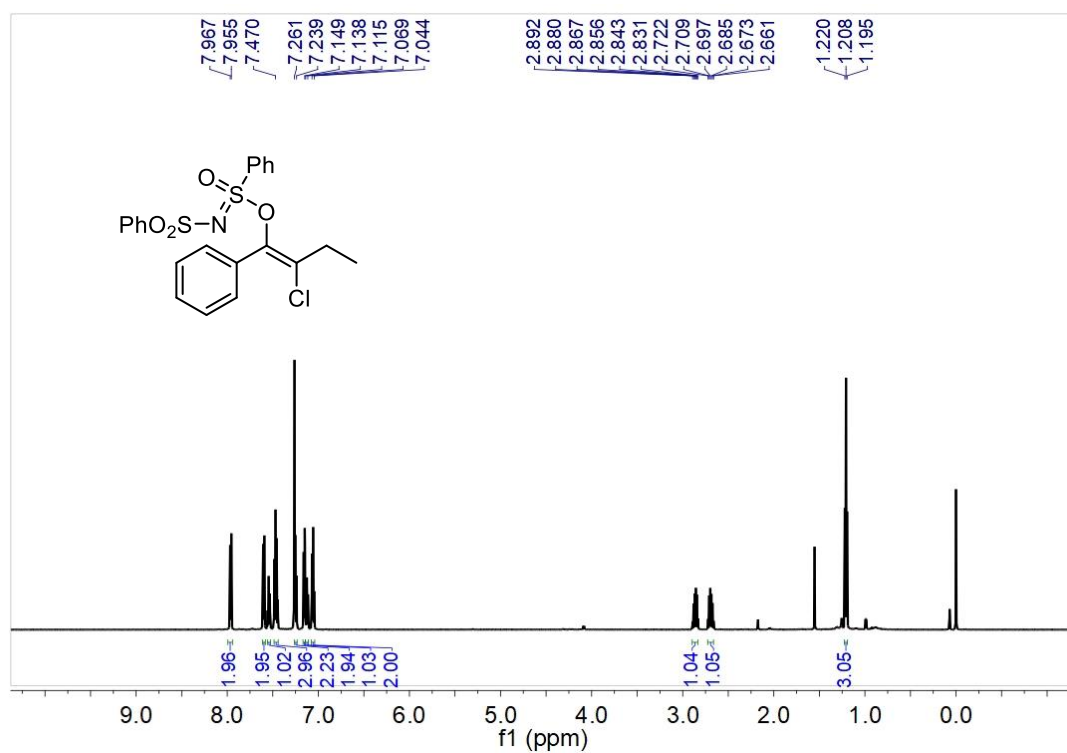
¹³C NMR (150 MHz, CDCl₃) spectrum of 4b'.



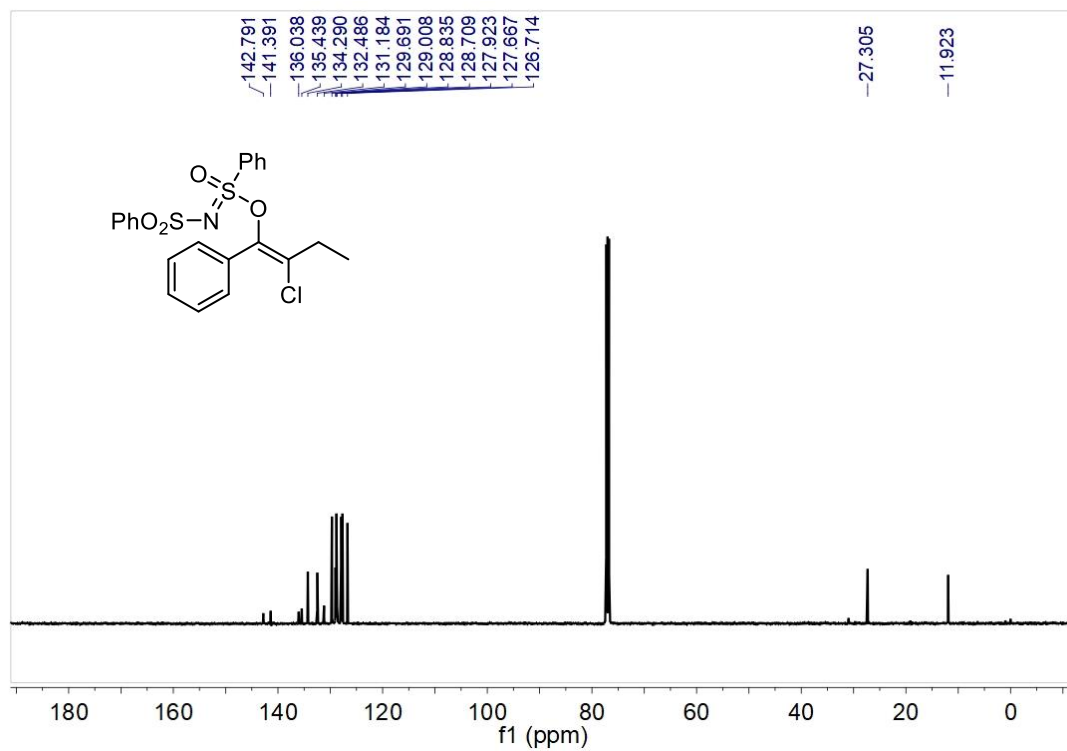
¹H NMR (600 MHz, CDCl₃) spectrum of 5a.



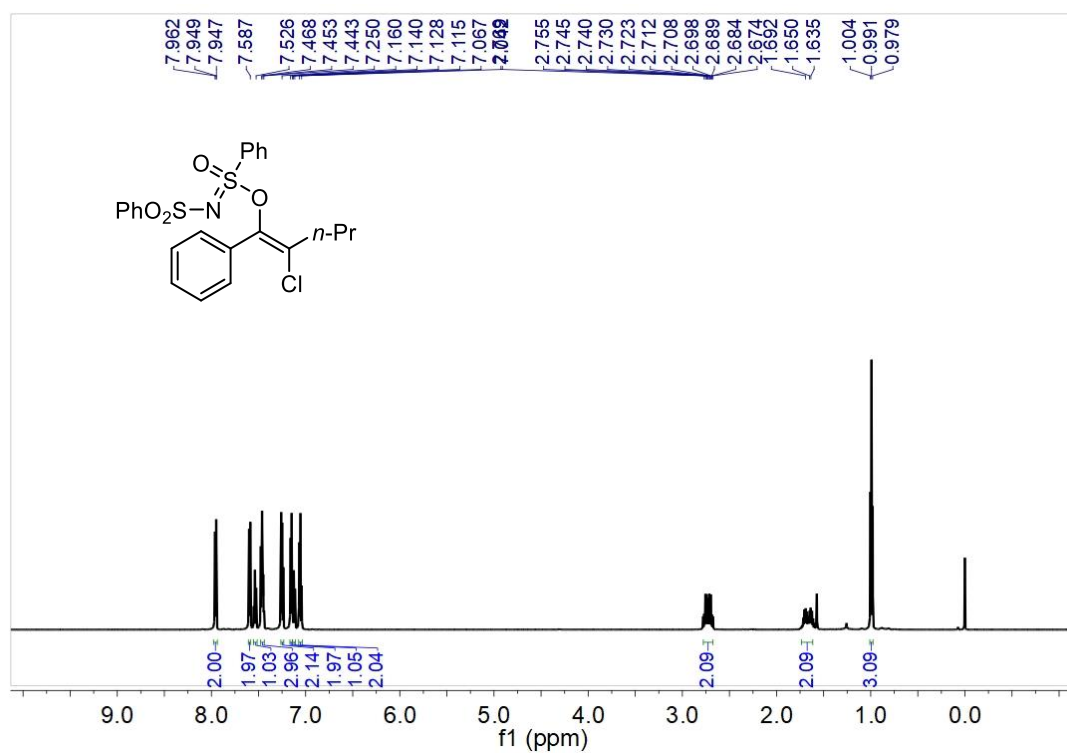
¹³C NMR (150 MHz, CDCl₃) spectrum of 5a.



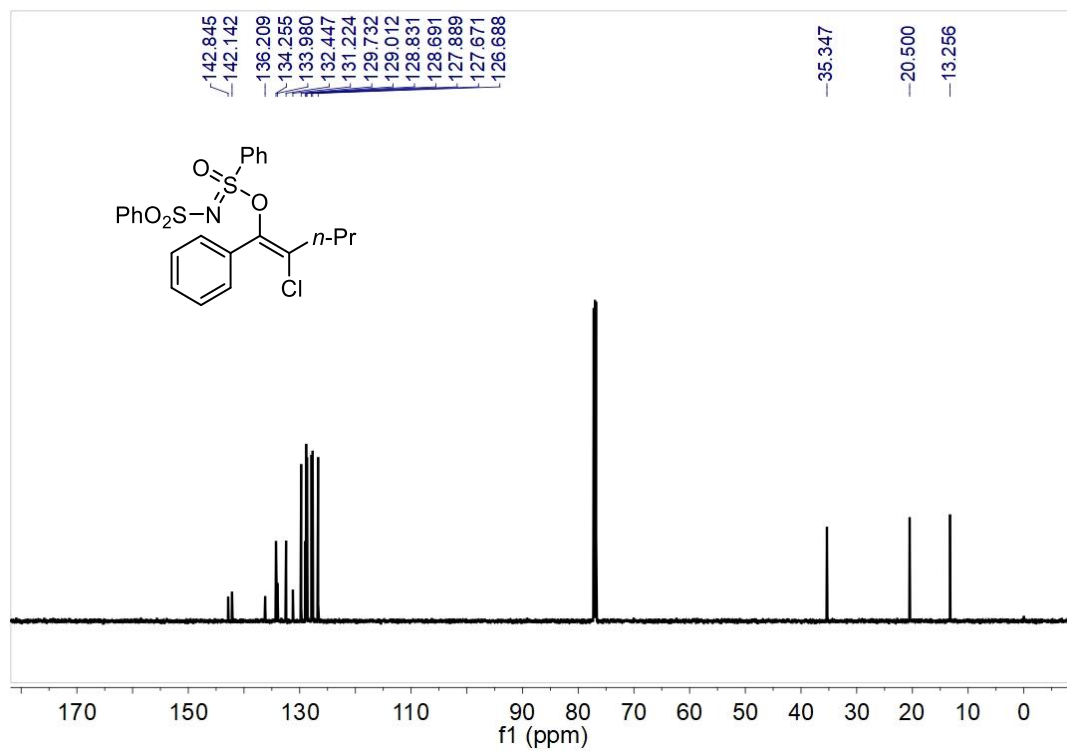
¹H NMR (600 MHz, CDCl₃) spectrum of 5b.



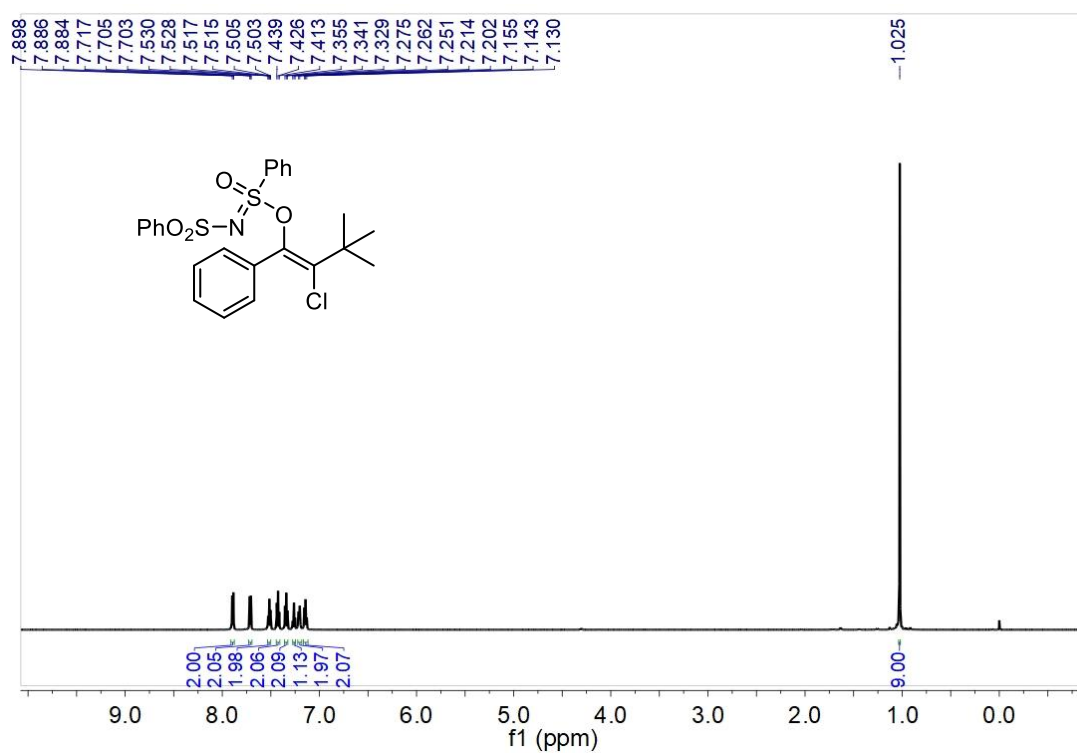
¹³C NMR (125 MHz, CDCl₃) spectrum of 5b.



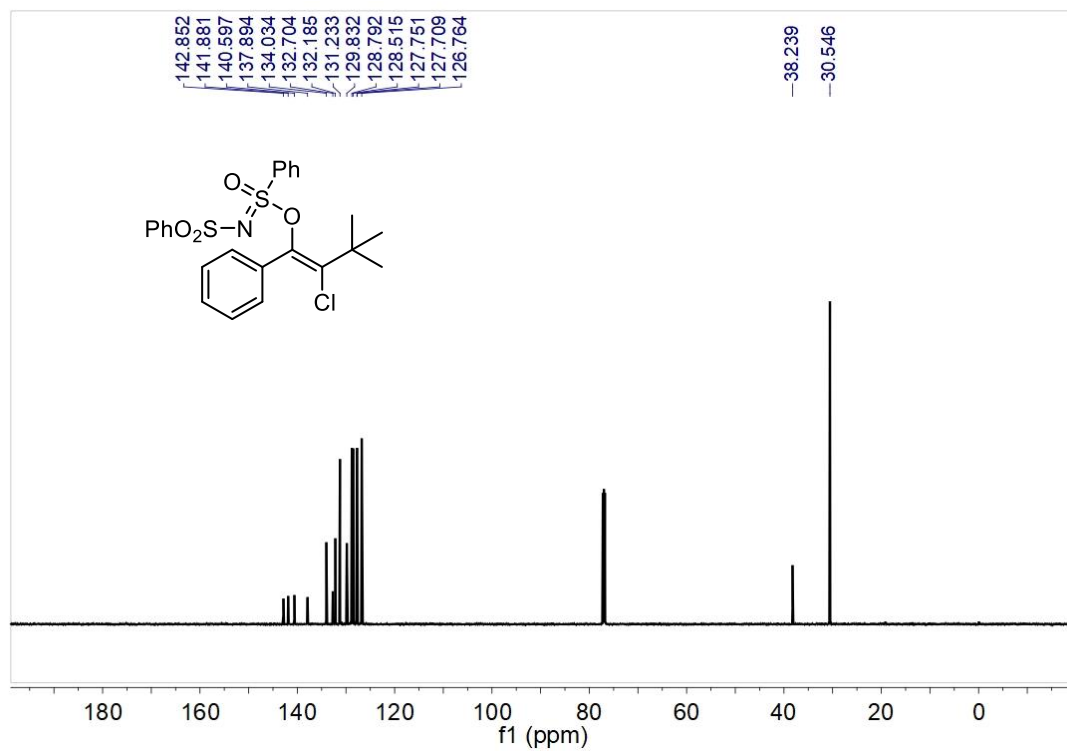
¹H NMR (600 MHz, CDCl₃) spectrum of 5c.



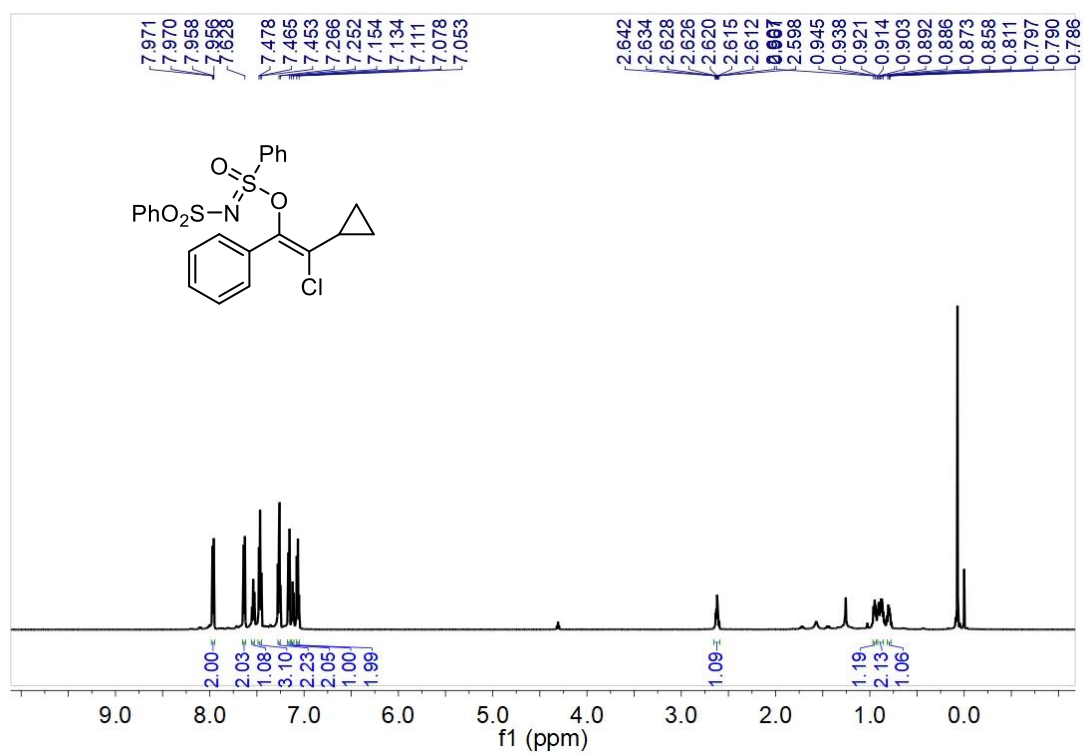
¹³C NMR (150 MHz, CDCl₃) spectrum of 5c.



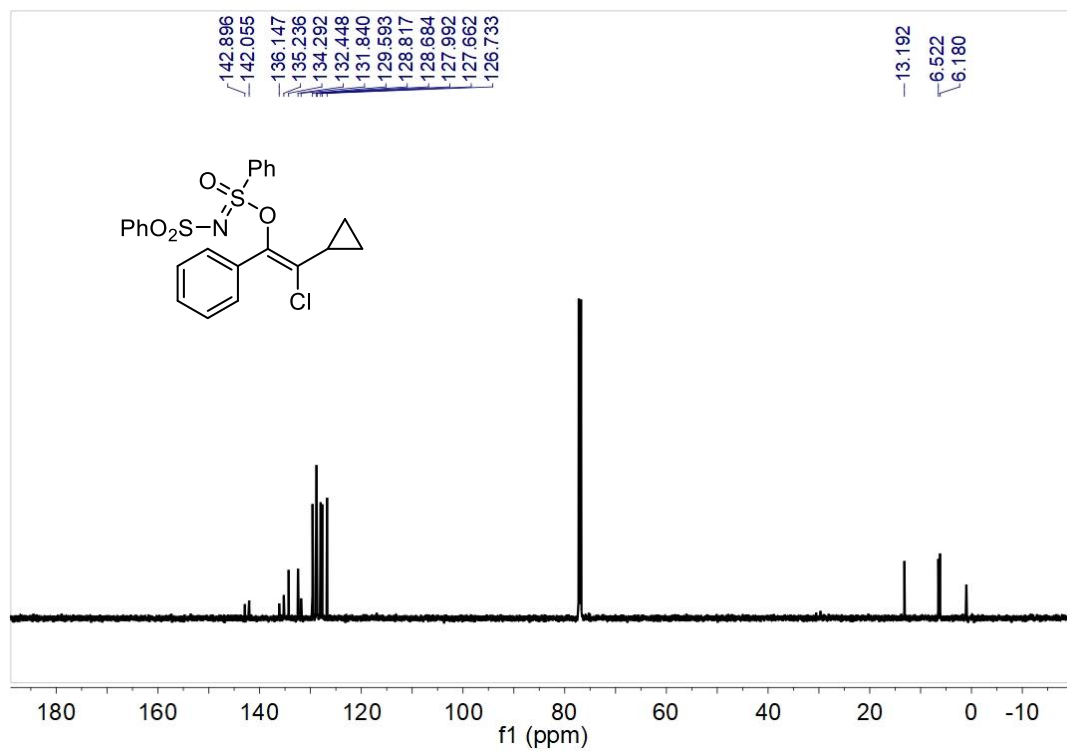
¹H NMR (600 MHz, CDCl₃) spectrum of 5d.



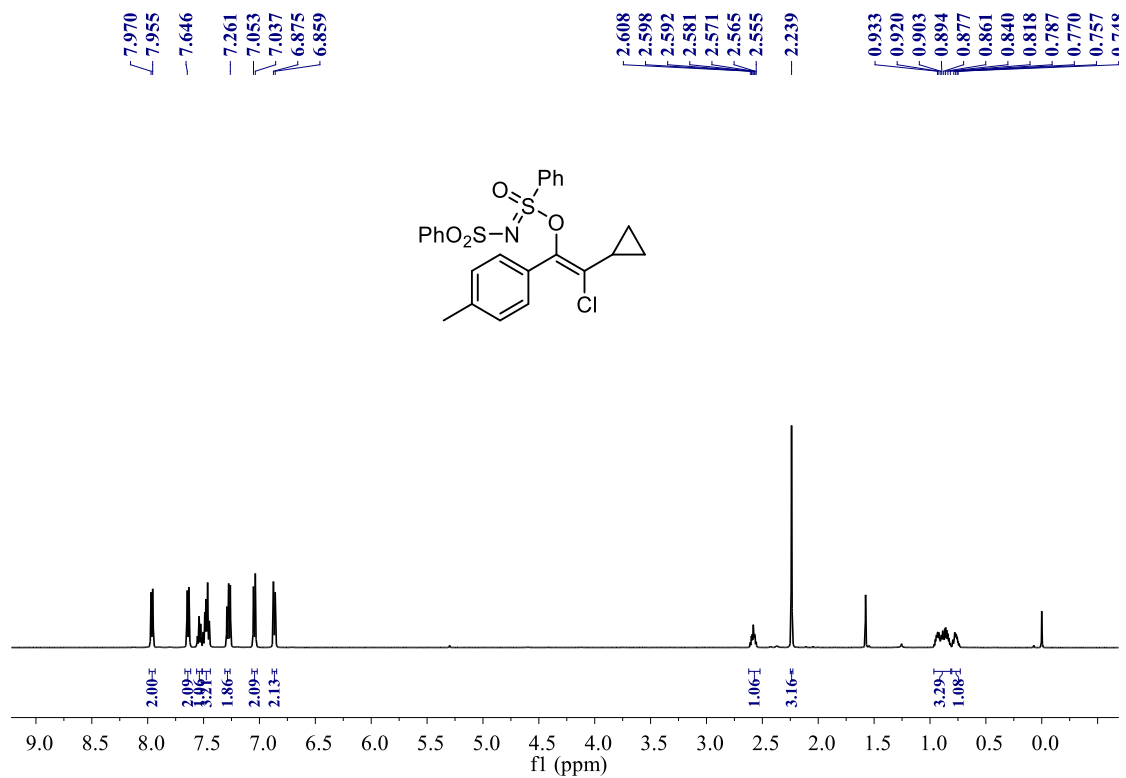
¹³C NMR (150 MHz, CDCl₃) spectrum of 5d.



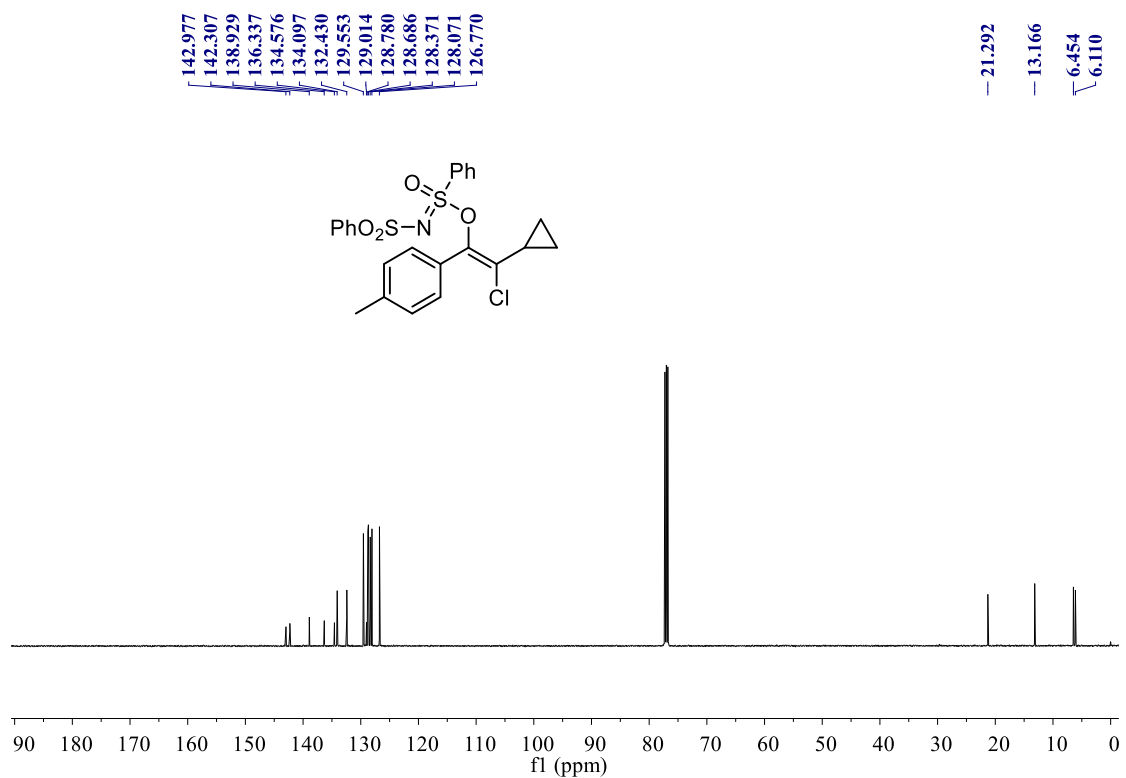
¹H NMR (600 MHz, CDCl₃) spectrum of 5e.



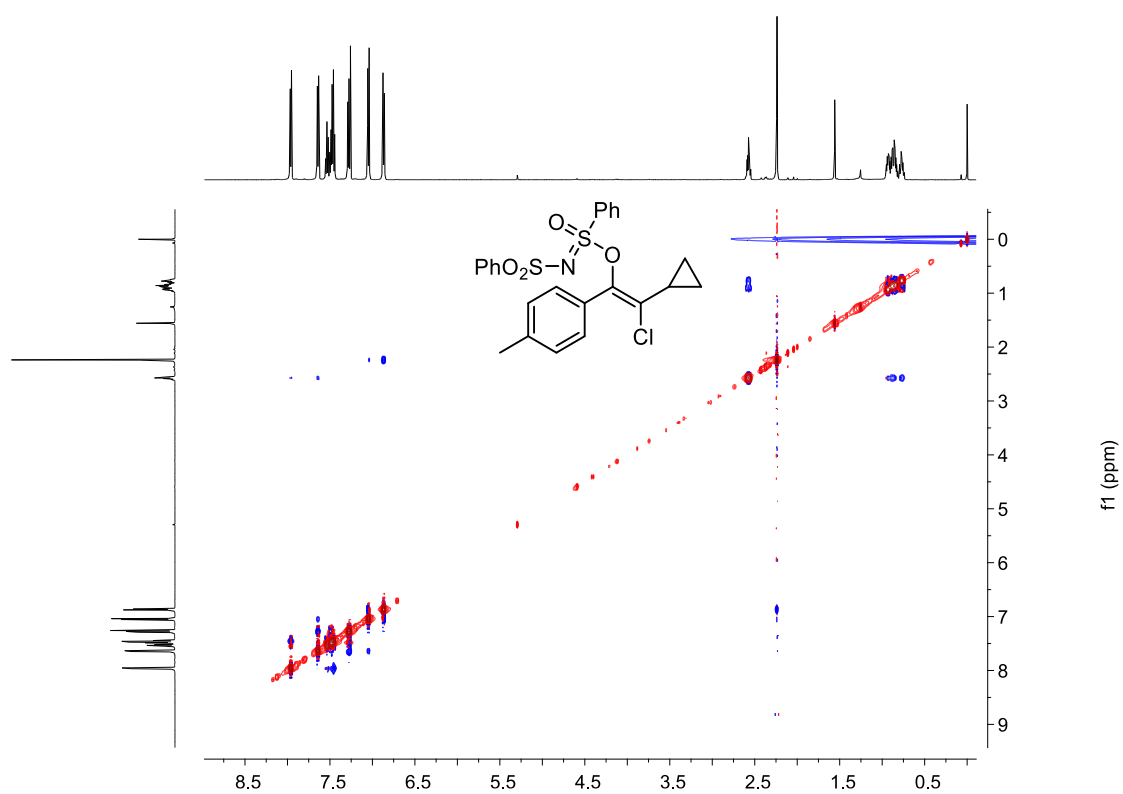
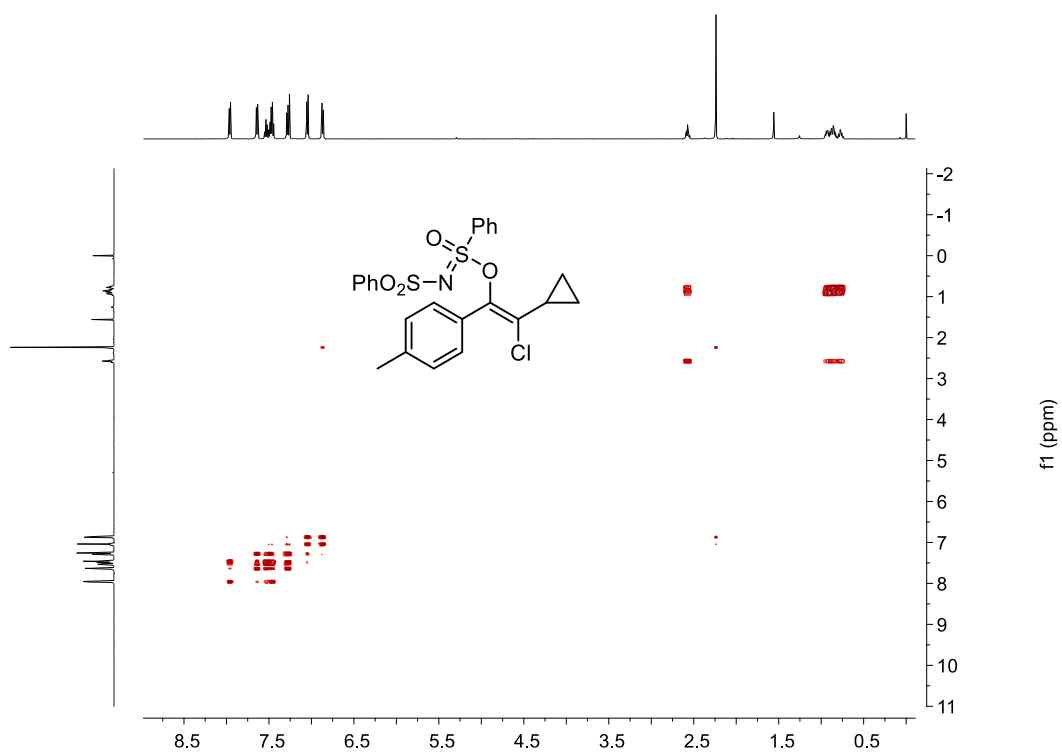
¹³C NMR (150 MHz, CDCl₃) spectrum of 5e.

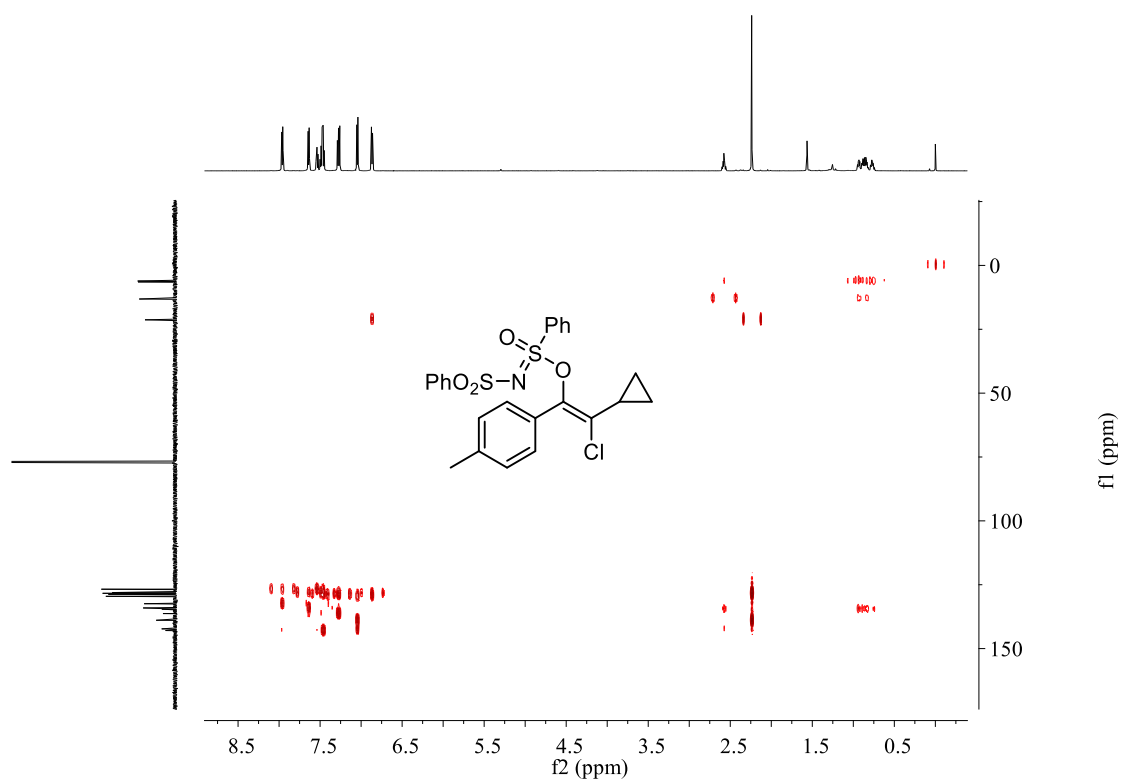


¹H NMR (500 MHz, CDCl₃) spectrum of 5f.

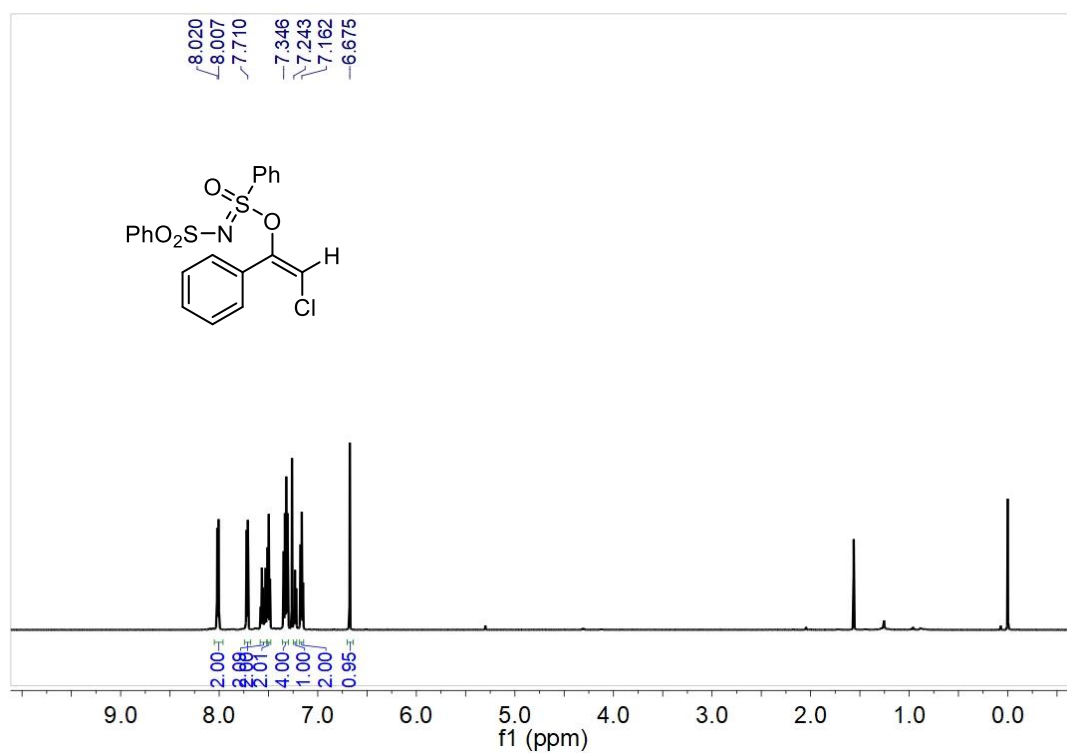


¹³C NMR (150 MHz, CDCl₃) spectrum of 5f.

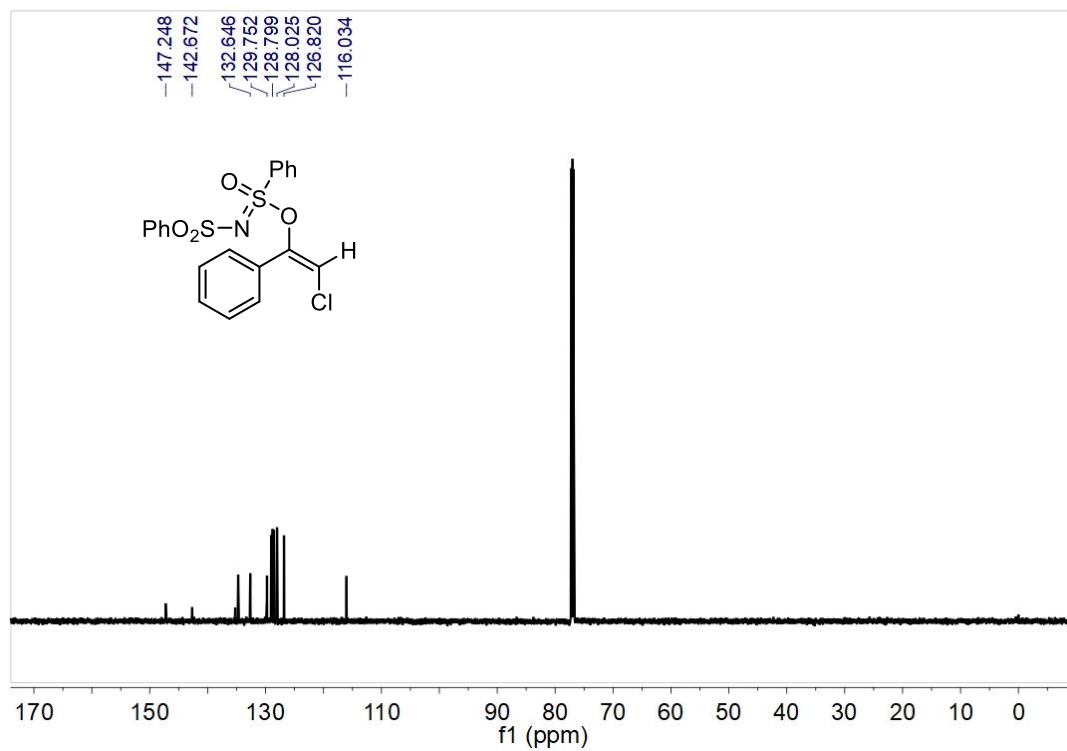




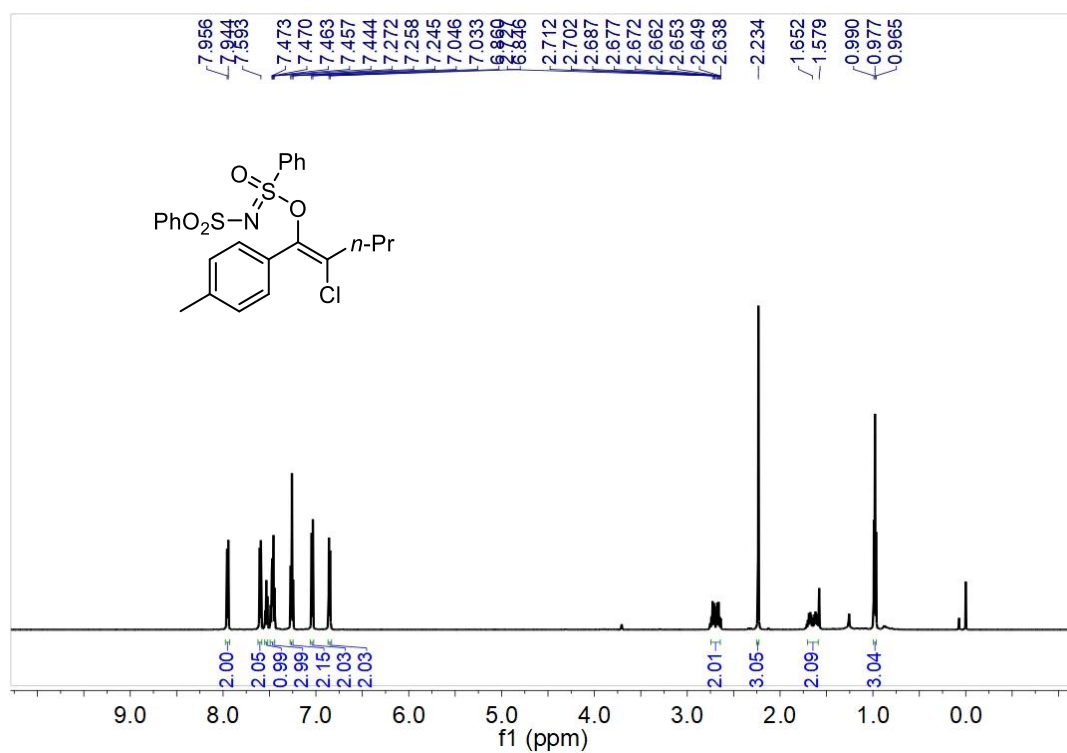
^1H - ^{13}C HMQC spectrum of 5f.



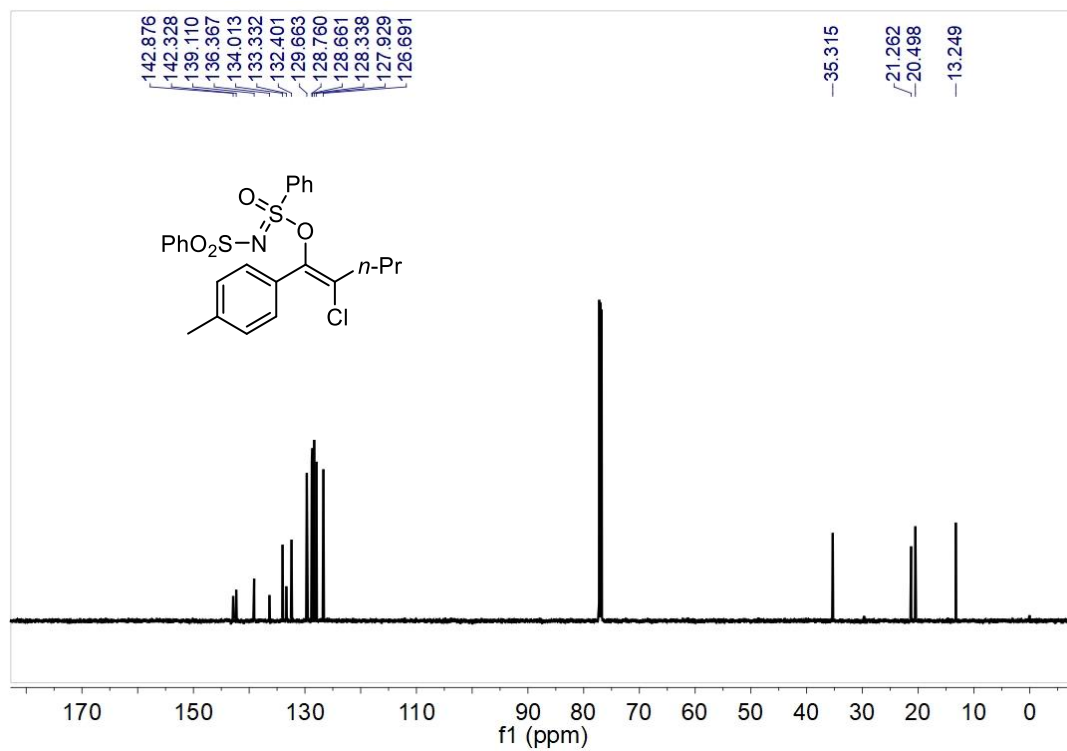
¹H NMR (600 MHz, CDCl₃) spectrum of 5g.



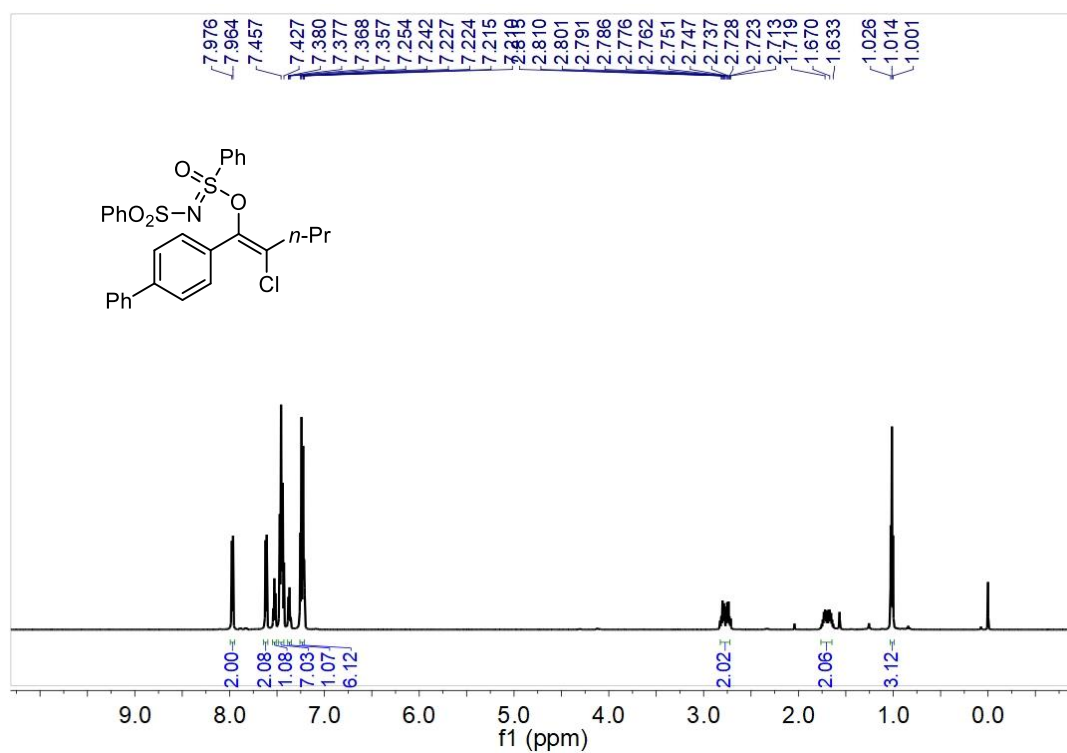
¹³C NMR (150 MHz, CDCl₃) spectrum of 5g.



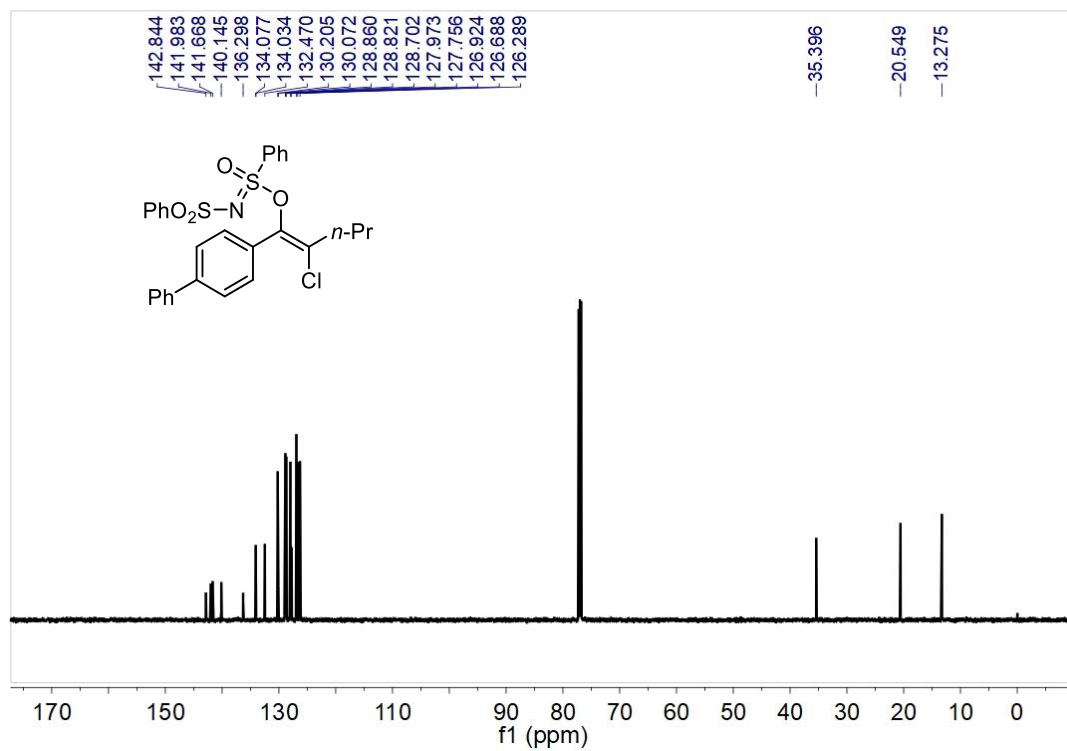
¹H NMR (600 MHz, CDCl₃) spectrum of 5h.



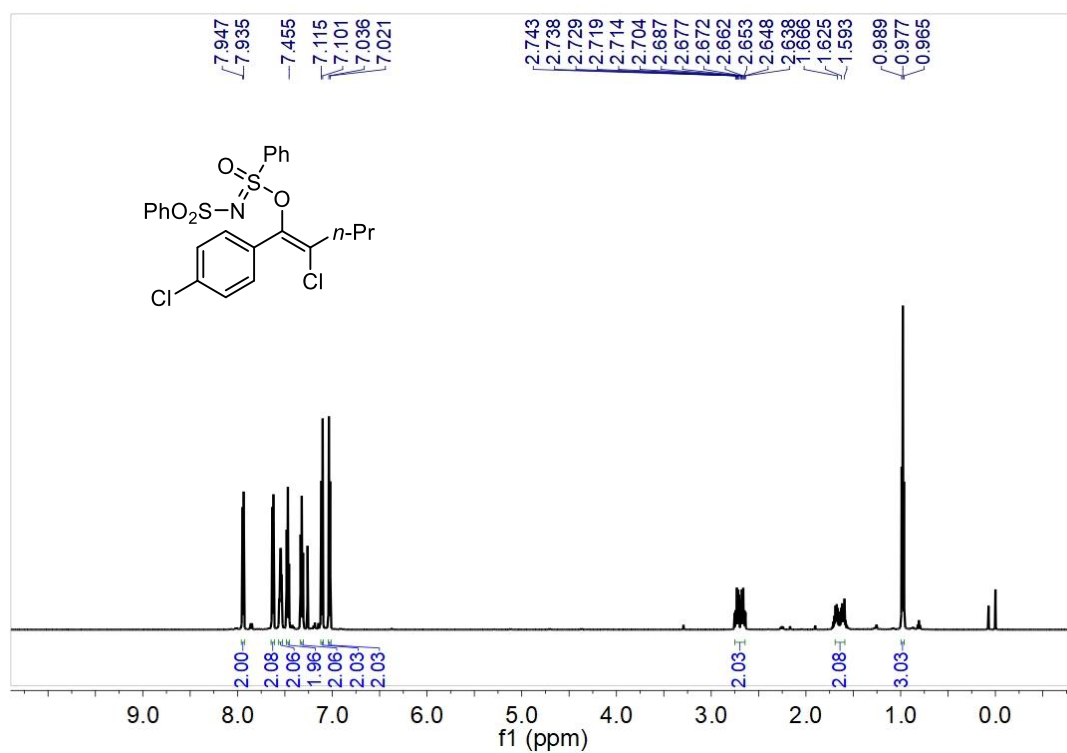
¹³C NMR (150 MHz, CDCl₃) spectrum of 5h.



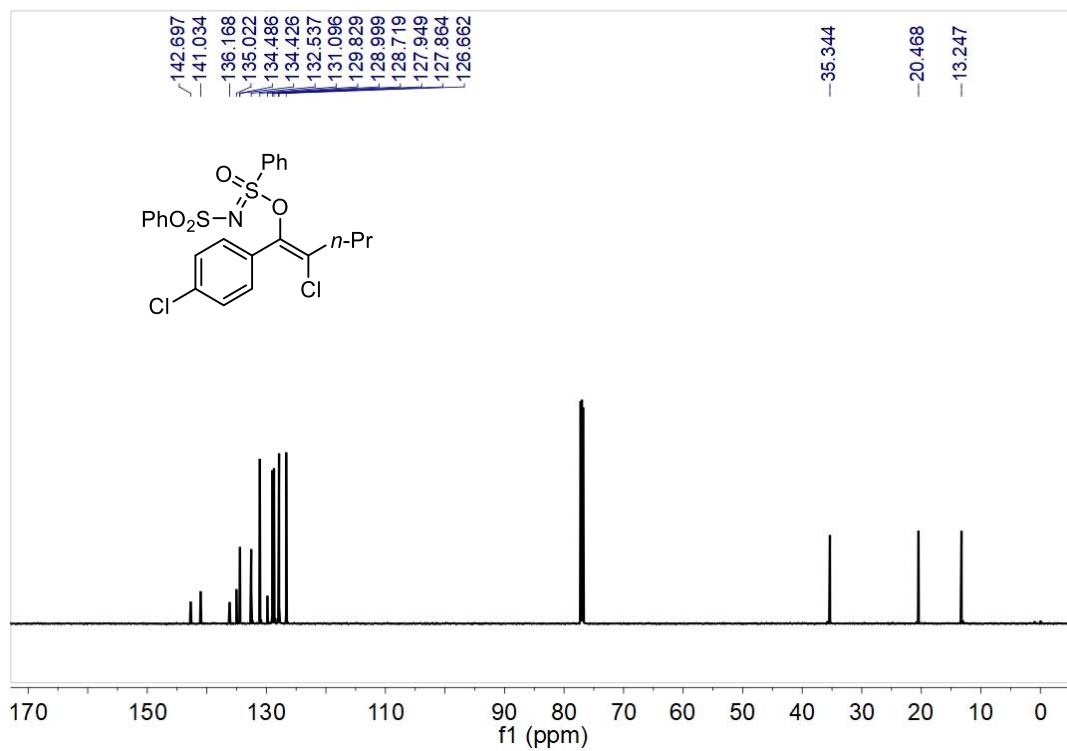
¹H NMR (600 MHz, CDCl₃) spectrum of 5i.



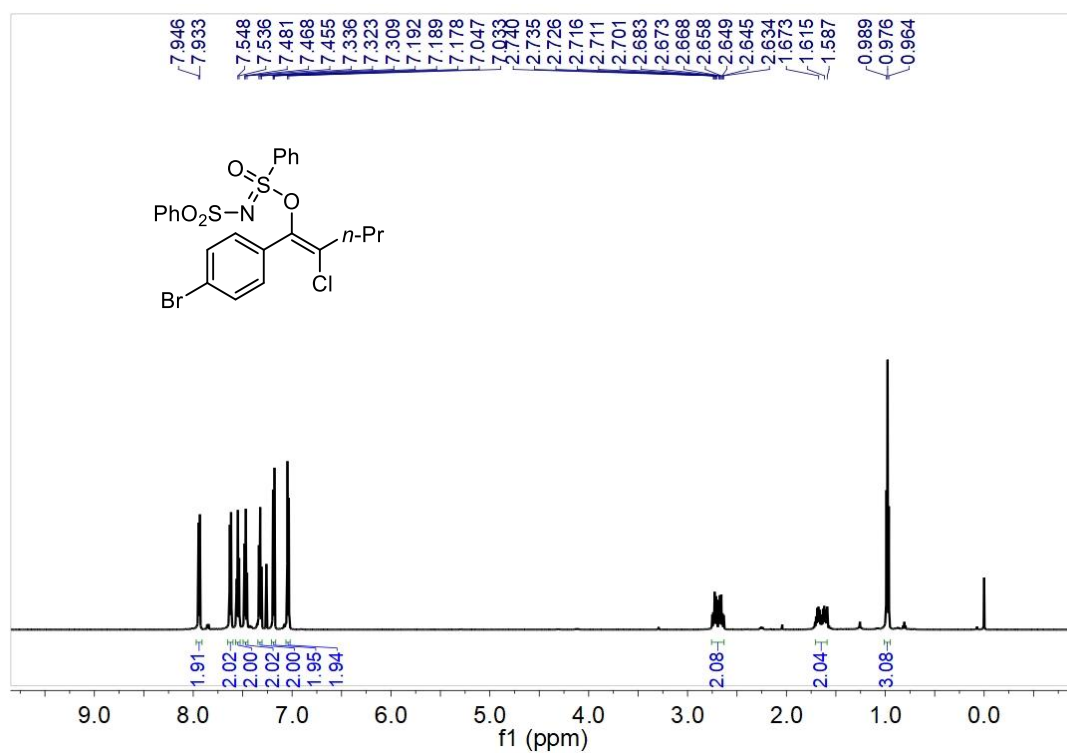
^{13}C NMR (150 MHz, CDCl_3) spectrum of 5i.



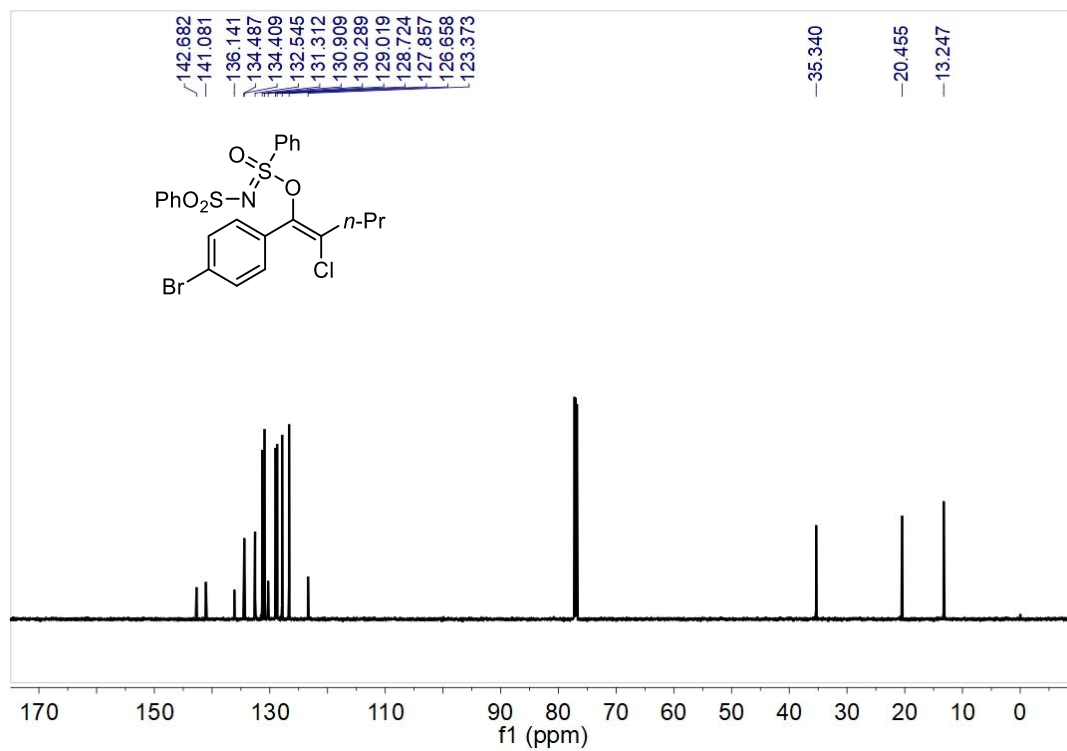
¹H NMR (600 MHz, CDCl₃) spectrum of 5j.



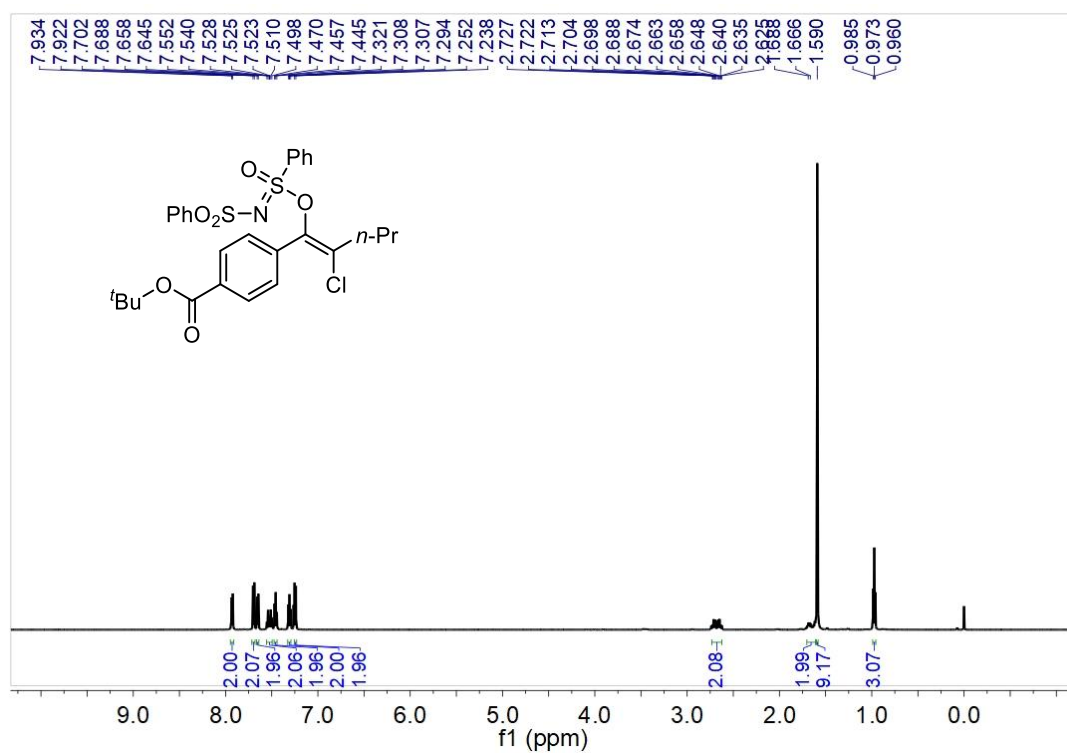
¹³C NMR (150 MHz, CDCl₃) spectrum of 5j.



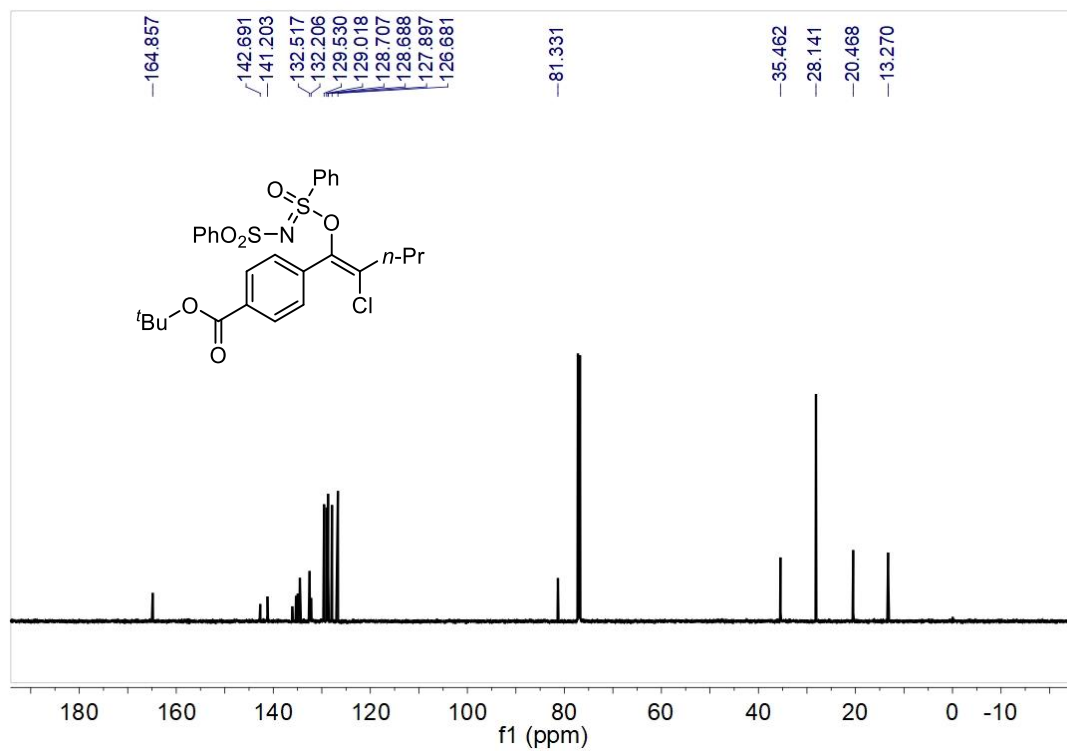
¹H NMR (600 MHz, CDCl₃) spectrum of 5k.



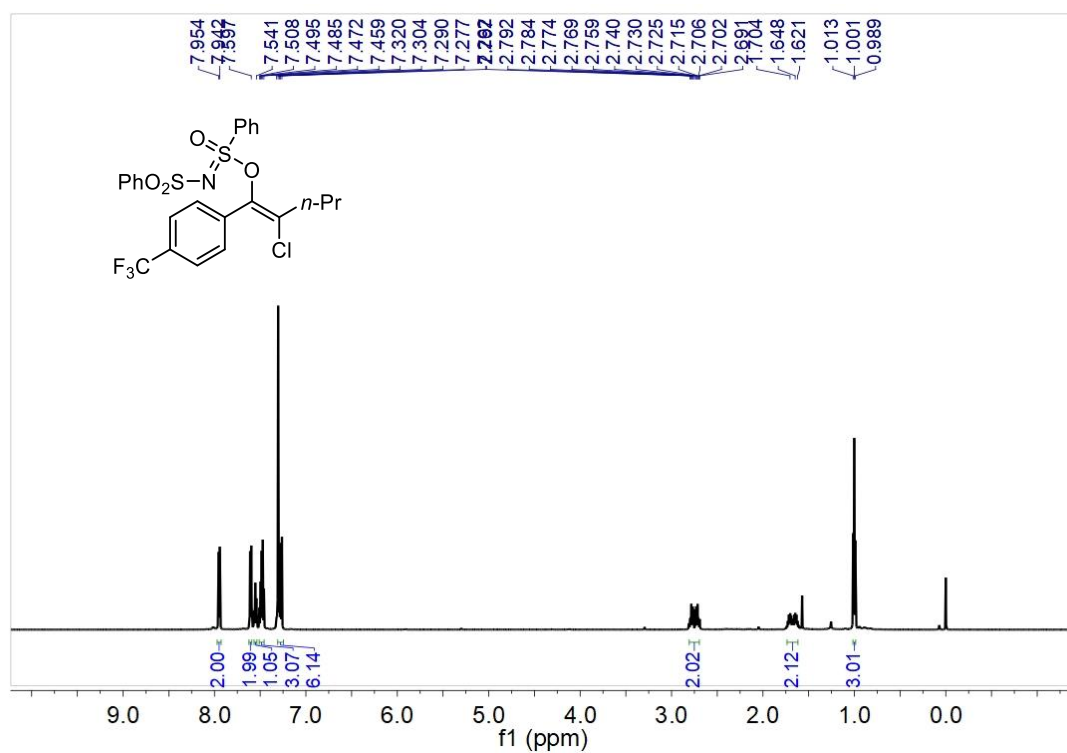
¹³C NMR (150 MHz, CDCl₃) spectrum of 5k.



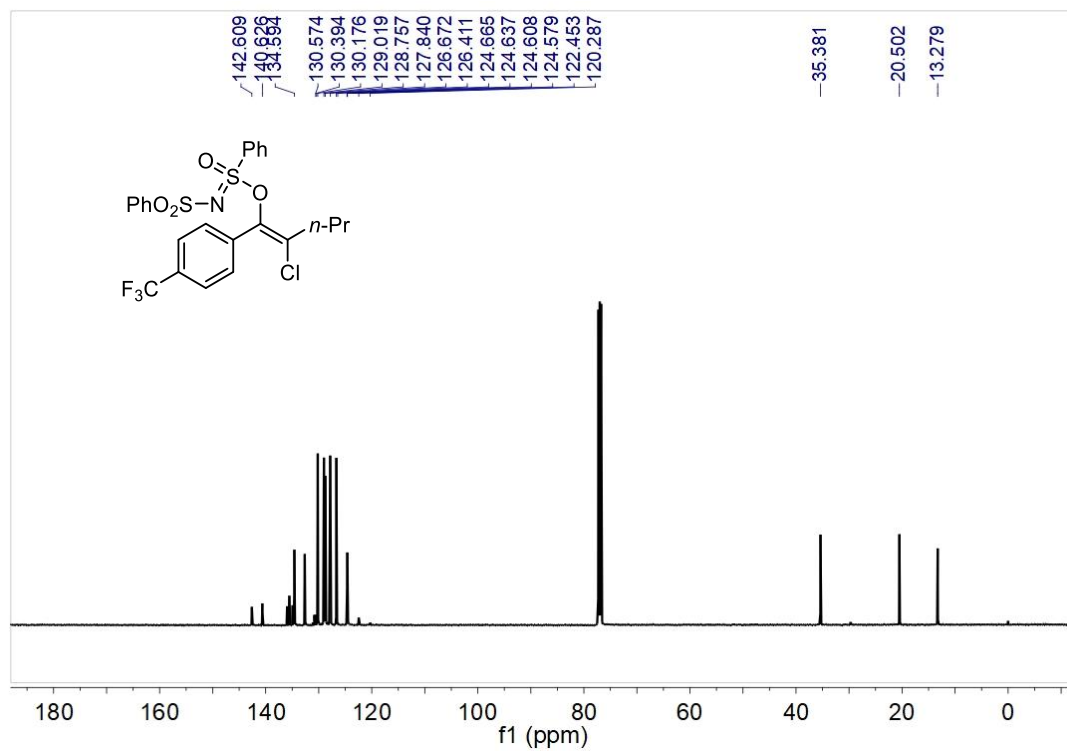
¹H NMR (600 MHz, CDCl₃) spectrum of 5l.



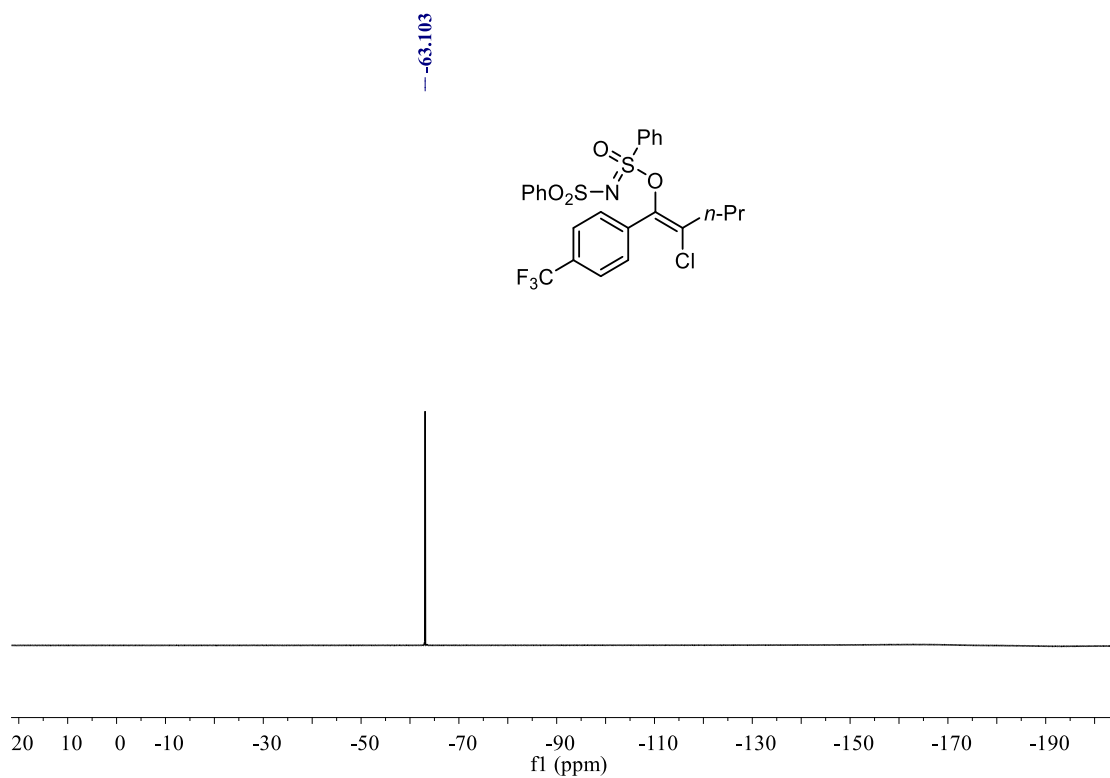
¹³C NMR (150 MHz, CDCl₃) spectrum of 5l.



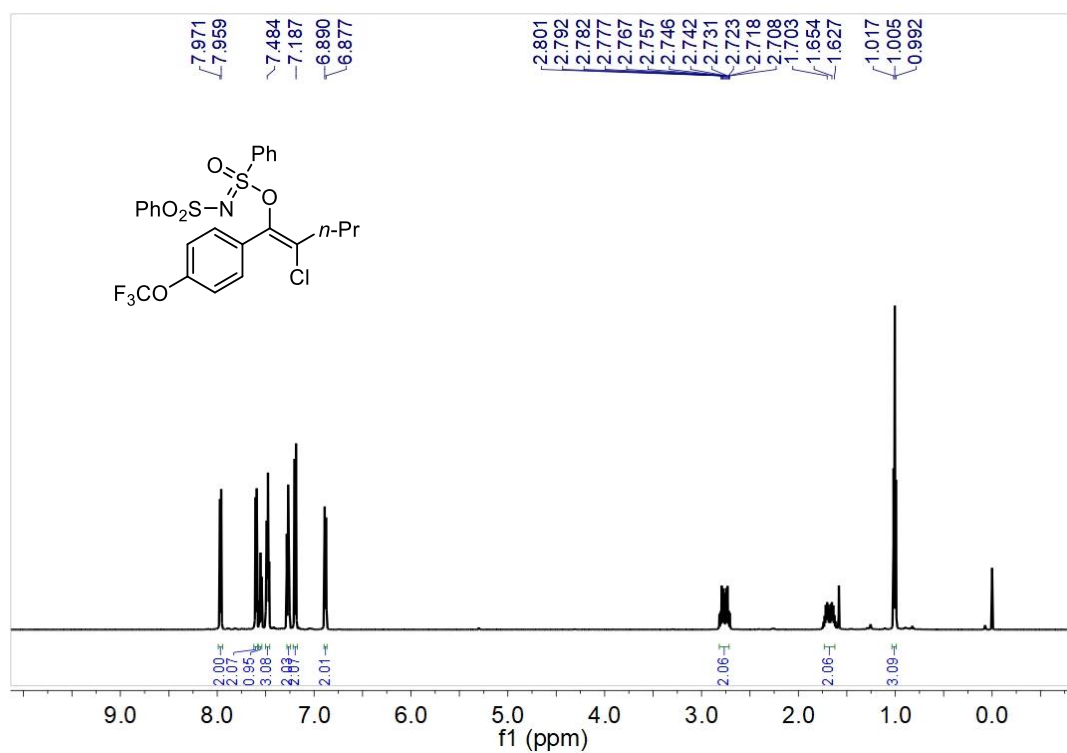
¹H NMR (600 MHz, CDCl₃) spectrum of 5m.



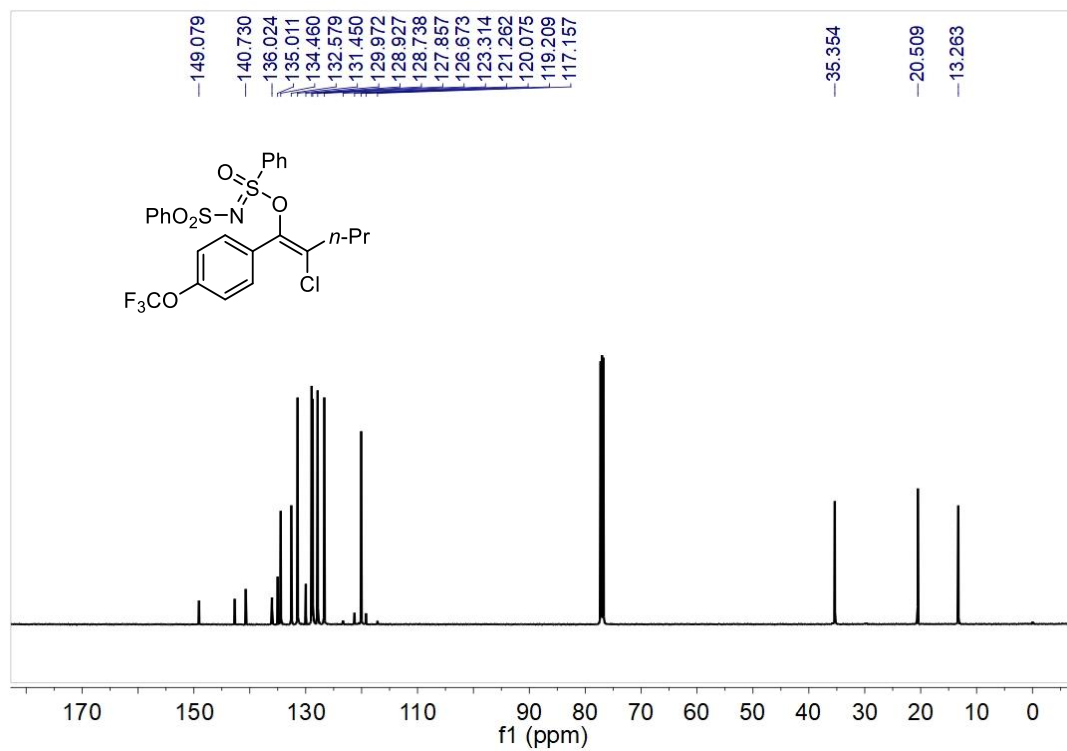
¹³C NMR (125 MHz, CDCl₃) spectrum of 5m.



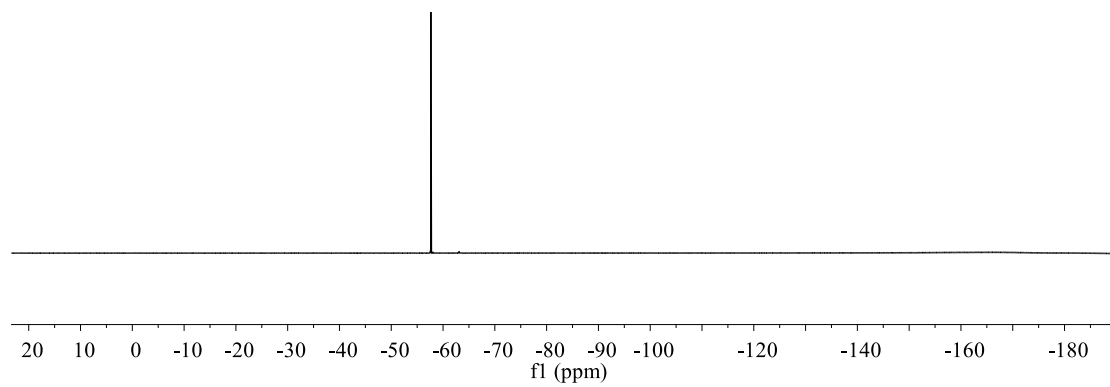
^{19}F NMR (565 MHz, CDCl_3) spectrum of **5m.**



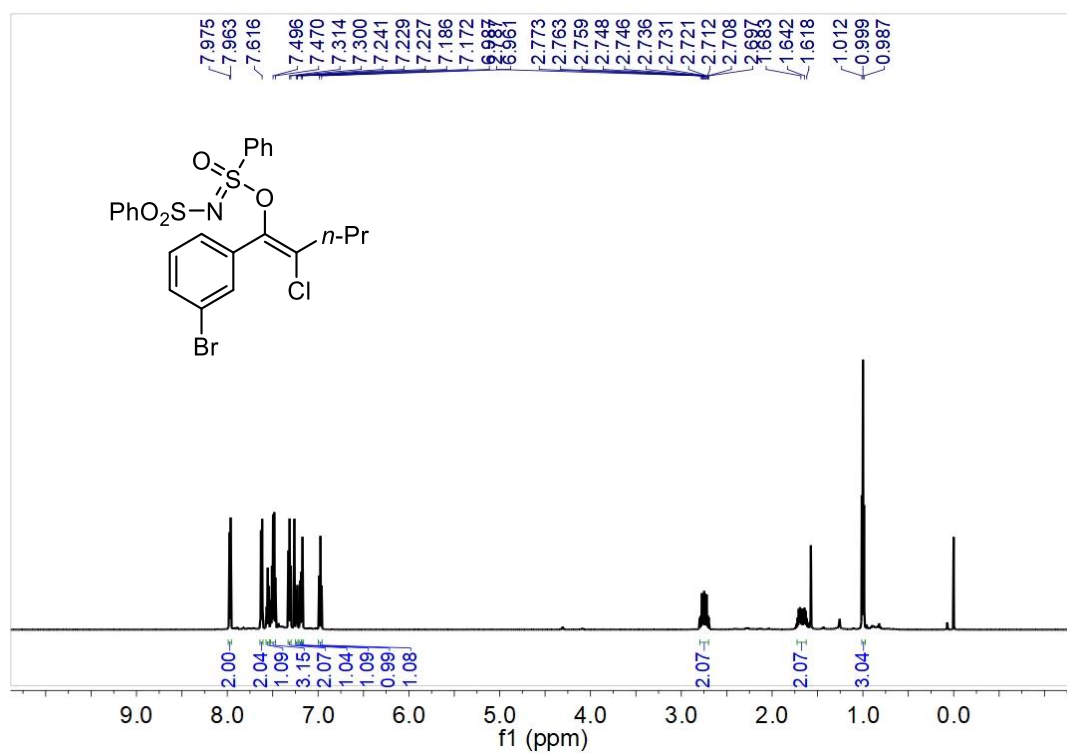
¹H NMR (600 MHz, CDCl₃) spectrum of 5n.



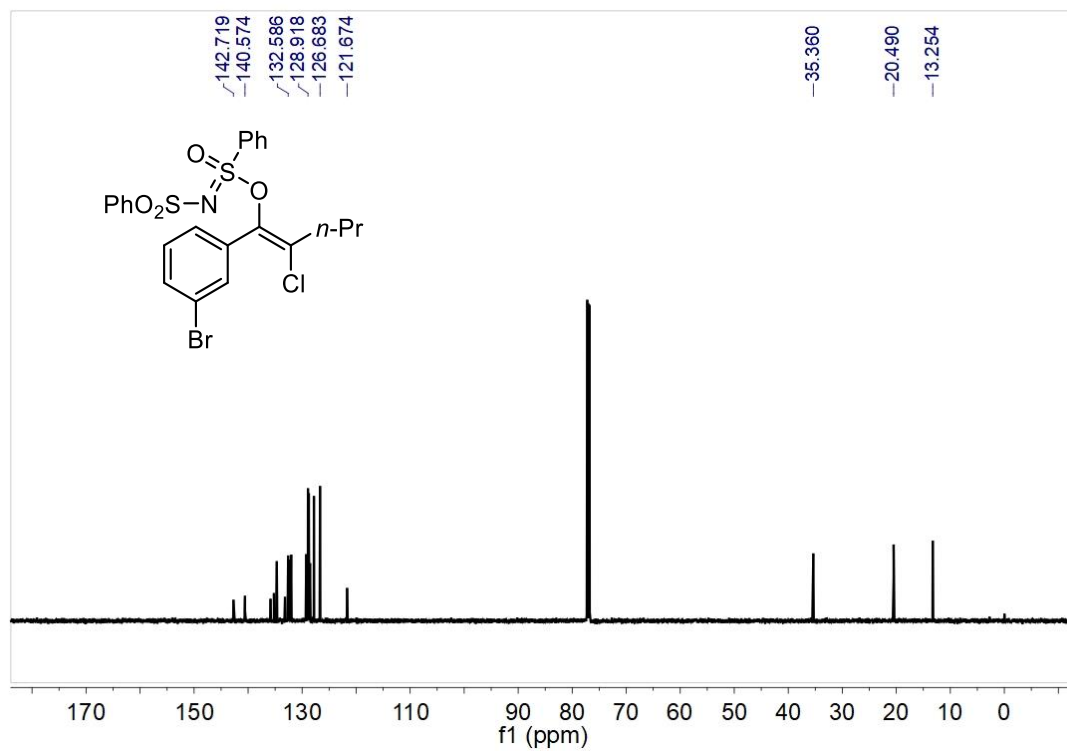
¹³C NMR (125 MHz, CDCl₃) spectrum of 5n.

CC(=C(Cl)C1=CC=C(C=C1)C(=O)N(S(=O)(=O)c2ccccc2)C(=O)c3ccccc3)C(F)(F)F

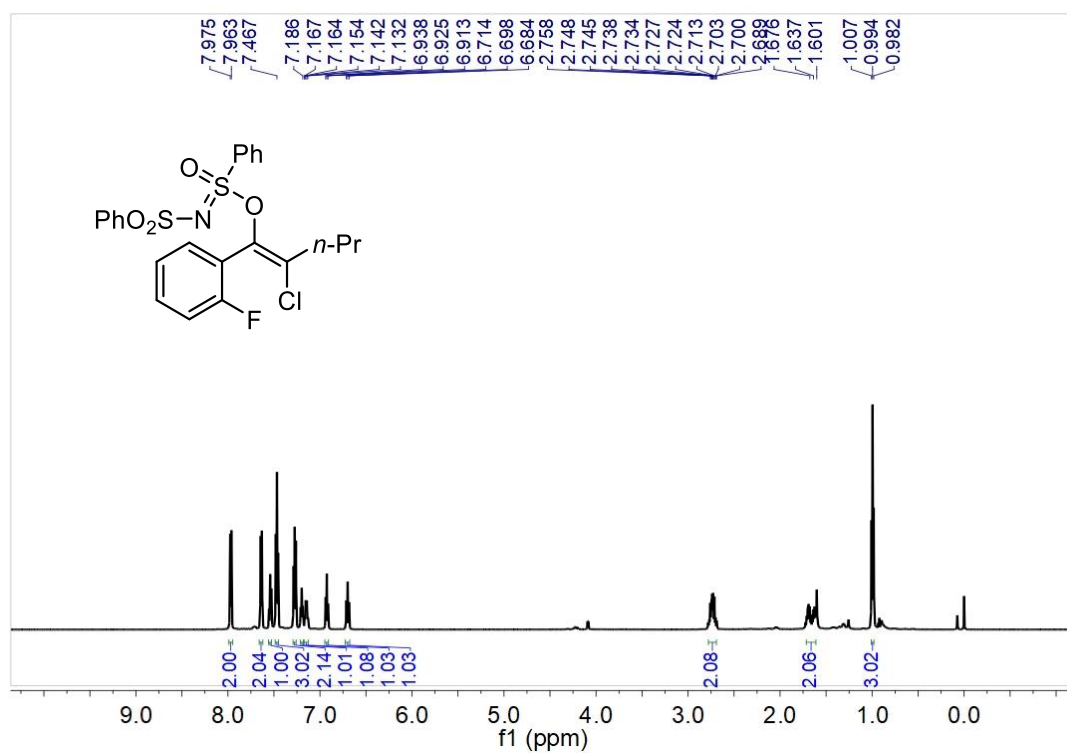
¹⁹F NMR (565 MHz, CDCl₃) spectrum of 5n.



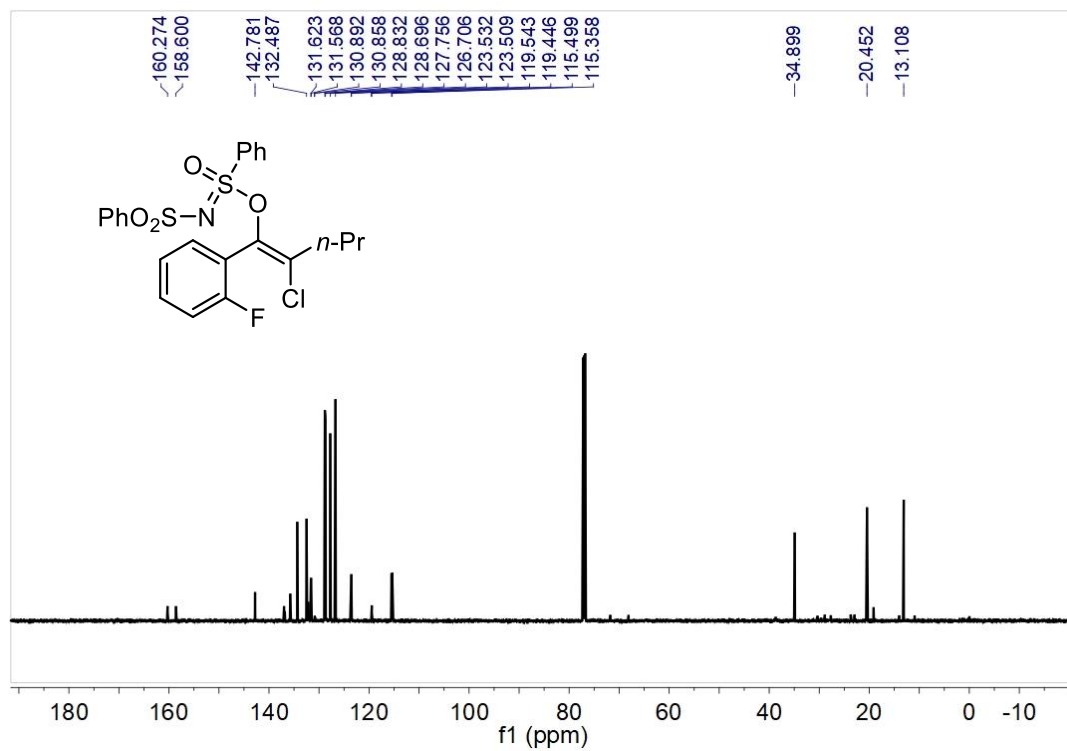
¹H NMR (600 MHz, CDCl₃) spectrum of 5o.



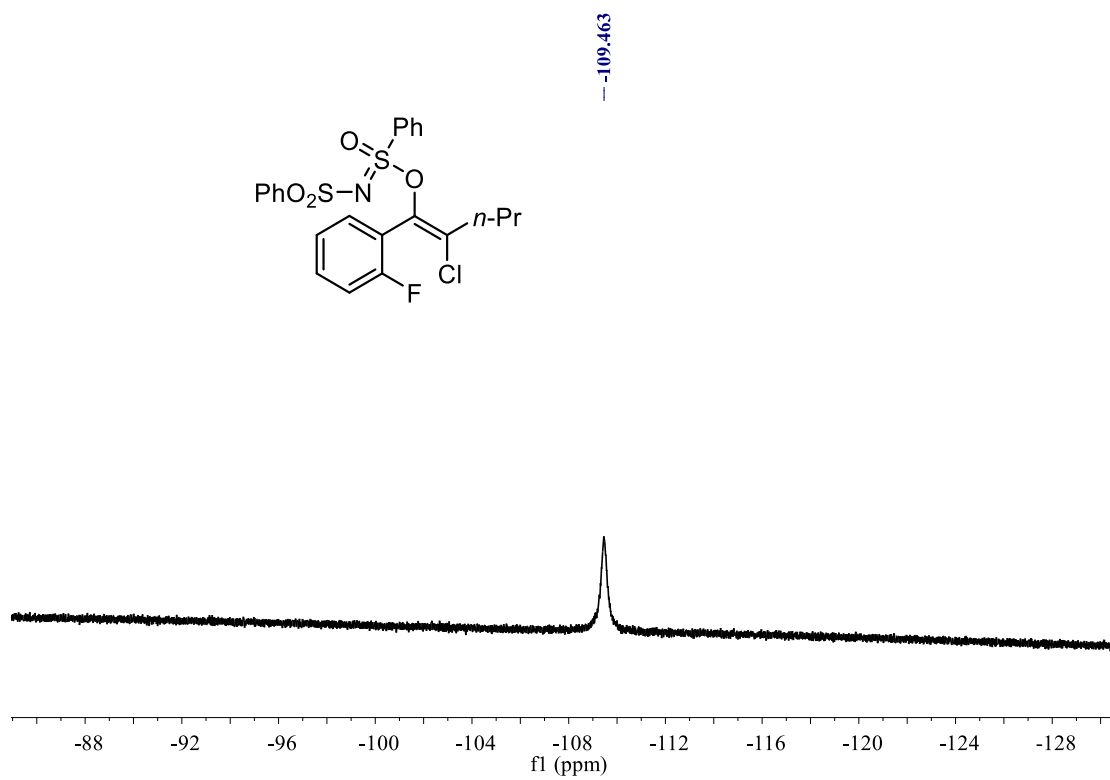
¹³C NMR (150 MHz, CDCl₃) spectrum of 5o.



¹H NMR (600 MHz, CDCl₃) spectrum of 5p.



¹³C NMR (150 MHz, CDCl₃) spectrum of 5p.



¹⁹F NMR (565 MHz, CDCl₃) spectrum of 5p.