

Supplementary Information:

Pyridine-*N*-oxide catalyzed asymmetric *N*-acylative desymmetrization of sulfonimidamides

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General information

¹H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet; t = triplet; q = quartet; dd = doublet of doublets; td = triplets of doublet; m = multiplet; br = broad), coupling constants (Hz), integration. ¹³C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. ¹⁹F NMR data were collected on Bruker Avance III HD 565 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IA/ID/IE in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity. Optical rotations were reported as follows: $[\alpha]_{\text{D}}^{\text{T}}$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI-TOF). CHCl₃ was obtained by adding spherical molecular sieve. Other solvents used for work-up and purification purposes were purchased in technical grade quality and distilled by rotary evaporator before use. Single crystal X-ray crystallography data were obtained on Supernova Atlas S2 CCD detector. Chloroformates **2a-2o** and **2p-2t** are commercially available. Catalysts (**C1-C4**) and *ent*-**C4** were prepared by previous reported methods^[1]. Sulfonimidamides were prepared according to the literature^[2].

Optimization of the reaction conditions

Table S1 Screening of solvents^a

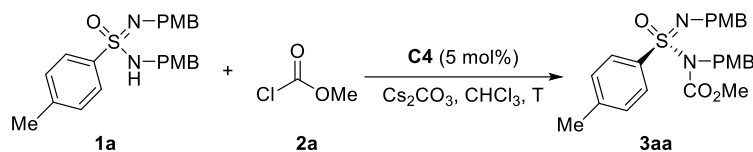
entry	solvent	yield (%) ^b	ee (%) ^c
1	THF	34	61
2	EA	48	70
3	Toluene	50	67
4	DCE	49	56
5	CHCl ₃	51	82

^aReactions were carried out with **1a** (0.05 mmol), **2a** (0.075 mmol), **C4** (5 mol%) in solvent (0.5 mL) at -20 °C for 48 h. ^bThe yield was determined by ¹H NMR spectra of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cThe ee value was determined by chiral HPLC analysis.

Table S2 Screening of bases^a

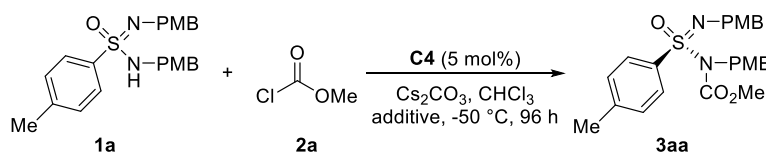
entry	base	yield (%) ^b	ee (%) ^c
1	-	51	82
2	KOH	71	55
3	K ₂ CO ₃	63	62
4	Na ₂ CO ₃	95	83
5	Cs ₂ CO ₃	94	84
6	Et ₃ N	38	79
7	DIPEA	69	41

^aReactions were carried out with **1a** (0.05 mmol), **2a** (0.075 mmol), **C4** (5 mol%), base (1.0 equiv.) in CHCl₃ (0.5 mL) at -20 °C for 48 h. ^bThe yield was determined by ¹H NMR spectra of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cThe ee value was determined by chiral HPLC analysis.

Table S3 Screening of temperatures^a

entry	T (°C)	time (h)	yield (%) ^b	ee (%) ^c
1	-20	48	94	84
2	-30	96	85	86
3	-40	96	69	90
4	-50	96	51	92
5	-60	96	36	92

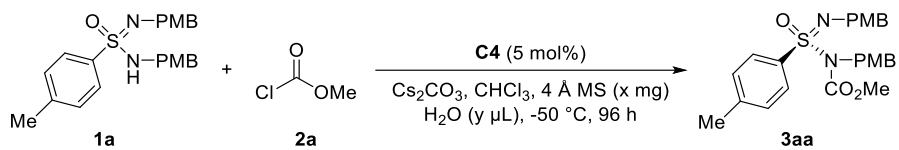
^aReactions were carried out with **1a** (0.05 mmol), **2a** (0.075 mmol), **C4** (5 mol%), Cs_2CO_3 (1.0 equiv.) in CHCl_3 (0.5 mL). ^bThe yield was determined by ^1H NMR spectra of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cThe ee value was determined by chiral HPLC analysis.

Table S4 Screening of additives^a

entry	additive	amount (mg)	yield (%) ^b	ee (%) ^c
1	3 Å MS	10	71	92
2	4 Å MS	10	80	92
3	5 Å MS	10	38	85
4	4 Å MS	15	85	92
5	4 Å MS	20	88	92
6	4 Å MS	25	90	92

^aReactions were carried out with **1a** (0.05 mmol), **2a** (0.075 mmol), **C4** (5 mol%), Cs_2CO_3 (1.0 equiv.) and additive in CHCl_3 (0.5 mL) at $-50\text{ }^\circ\text{C}$ for 96 h. ^bThe yield was determined by ^1H NMR spectra of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cThe ee value was determined by chiral HPLC analysis.

Table S5 Screening of the amount of 4 Å MS and water^a



entry	x (mg)	y (μL)	yield (%) ^b	ee (%) ^c
1	25	-	90	92
2	25	5	90	92
3	25	15	89	92
4	25	20	83	92
5	25	25	75	92
6	25	30	70	91
7	50	25	88	92
8	50	30	80	91

^aReactions were carried out with **1a** (0.05 mmol), **2a** (0.075 mmol), **C4** (5 mol%), Cs_2CO_3 (1.0 equiv.) 4 Å MS and H_2O in CHCl_3 (0.5 mL) at $-50\text{ }^\circ\text{C}$ for 96 h. ^bThe yield was determined by ^1H NMR spectra of the chiral HPLC analysis.

^1H NMR Studies on tautomerization

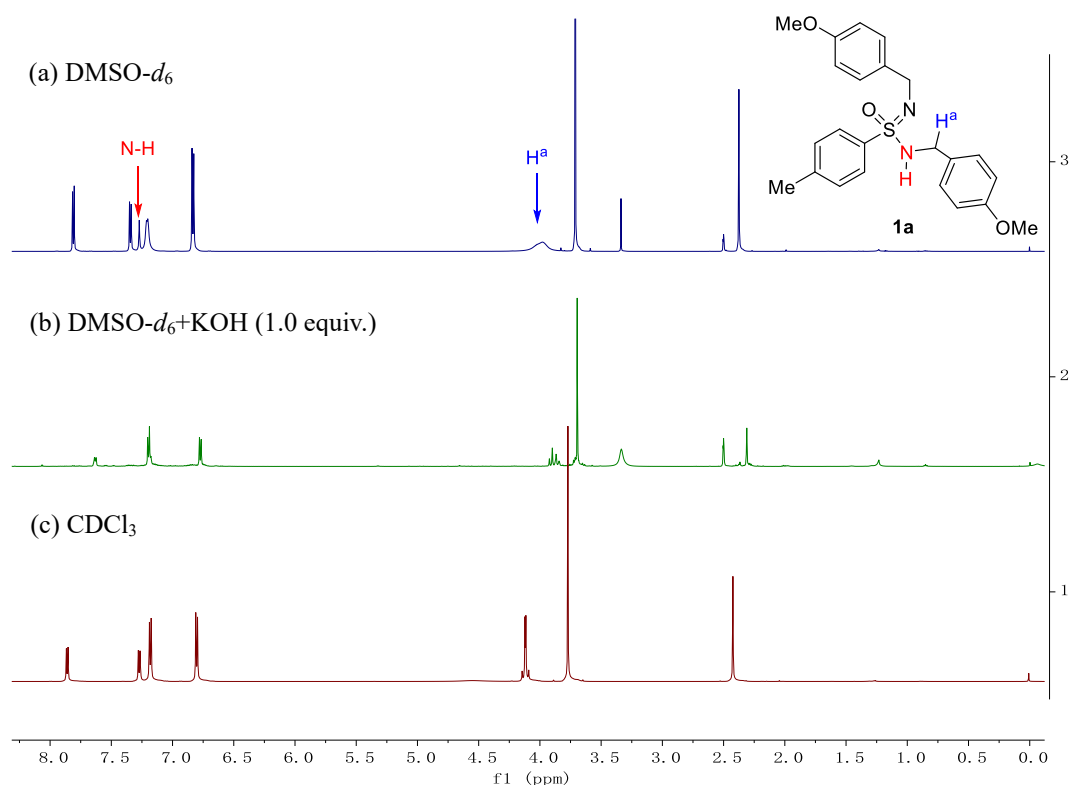


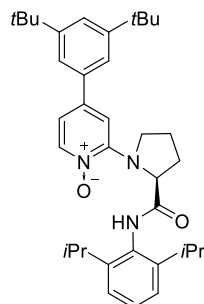
Fig. S1. ^1H NMR spectrum of compound **1a** at 600 MHz and 298 K analysing the tautomerization process

(a) In $\text{DMSO-}d_6$ the PMB groups are observed to be chemically and magnetically inequivalent on the NMR timescale. (b) Addition of KOH produced a variety of changes to the spectrum, firstly the NH proton is no longer observable and secondly the methylene peaks can now be observed as two distinct diastereotopic protons. (c) The ^1H NMR spectrum of **1a** in CDCl_3 showed there is no observable NH environment and two PMB groups are observed to be chemically and magnetically equivalent on the NMR timescale.

Characterization of compounds

(S)-4-(3,5-Di-*tert*-butylphenyl)-2-(2-((2,6-diisopropylphenyl)carbamoyl)pyrrolidin-1-yl)pyridine

1-oxide (C4)



white solid, m.p.: 195.8-196.4 °C, R_f = 0.27 (DCM/MeOH, 20/1, v/v); $[\alpha]_D^{25.0}$ = -37.4 (c = 0.25, CHCl₃).

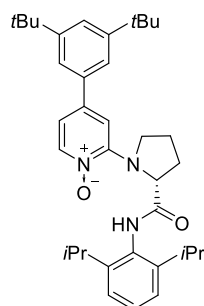
¹H NMR (600 MHz, CDCl₃) δ 9.06 (s, 1H), 8.12 (d, J = 7.2 Hz, 1H), 7.52 (t, J = 1.8 Hz, 1H), 7.36 (d, J = 1.8 Hz, 2H), 7.21 (t, J = 7.8 Hz, 1H), 7.08-7.03 (m, 4H), 5.65 (dd, J = 7.8, 5.4 Hz, 1H), 4.13-4.08 (m, 1H), 3.48-3.44 (m, 1H), 2.74 (s, 2H), 2.51-2.39 (m, 2H), 2.33-2.27 (m, 1H), 2.09-2.02 (m, 1H), 1.37 (s, 18H), 1.02 (d, J = 6.6 Hz, 12H).

¹³C NMR (150 MHz, CDCl₃) δ 171.3, 152.0, 150.9, 146.1, 143.3, 140.5, 136.9, 131.3, 128.1, 123.5, 123.3, 121.2, 114.9, 112.5, 63.3, 51.2, 35.1, 31.6, 29.5, 28.8, 24.3, 23.8.

HRMS (ESI-TOF): exact mass calcd for C₃₆H₄₉N₃NaO₂⁺ (M+Na)⁺ required m/z 578.3717, found m/z 578.3718 (Δ = +1 ppm).

(R)-4-(3,5-Di-*tert*-butylphenyl)-2-(2-((2,6-diisopropylphenyl)carbamoyl)pyrrolidin-1-yl)pyridine

1-oxide (*ent*-C4)



light yellow solid, m.p.: 198.8-199.5 °C, R_f = 0.27 (DCM/MeOH, 20/1, v/v); $[\alpha]_D^{25.0}$ = +28.0 (c = 0.28, CHCl₃).

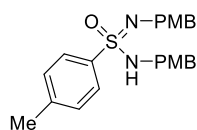
¹H NMR (400 MHz, CDCl₃) δ 9.07 (s, 1H), 8.12 (d, J = 6.8 Hz, 1H), 7.52 (t, J = 1.6 Hz, 1H), 7.36 (d, J = 1.6 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.08-7.03 (m, 4H), 5.66 (dd, J = 7.6, 5.6 Hz, 1H), 4.09 (dd, J =

16.8, 8.0 Hz, 1H), 3.49-3.44 (m, 1H), 2.78-2.71 (m, 2H), 2.53-2.37 (m, 2H), 2.34-2.25 (m, 1H), 2.09-2.02 (m, 1H), 1.38 (s, 18H), 1.02 (d, $J = 6.8$ Hz, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 152.0, 150.9, 146.0, 143.2, 140.5, 136.9, 131.3, 128.1, 123.5, 123.3, 121.2, 115.0, 112.4, 63.2, 51.2, 35.1, 31.6, 29.5, 28.8, 24.3, 23.7.

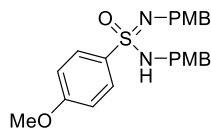
HRMS (ESI-TOF): exact mass calcd for $\text{C}_{36}\text{H}_{49}\text{N}_3\text{NaO}_2^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 578.3717, found m/z 578.3717 ($\Delta = 0$ ppm).

***N,N'*-Bis(4-methoxybenzyl)-4-methylbenzenesulfonimidamide (1a)**



^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 4H), 6.78 (d, $J = 8.4$ Hz, 4H), 4.09 (t, $J = 14.8$ Hz, 4H), 3.75 (s, 6H), 2.40 (s, 3H).

4-Methoxy-*N,N'*-bis(4-methoxybenzyl)benzenesulfonimidamide (1b)



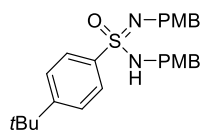
white solid, m.p.: 108.3-109.0 °C, $R_f = 0.56$ (Pet/EtOAc, 2/1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.8$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 4H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 4H), 5.18 (br, 1H), 4.09 (d, $J = 14.0$ Hz, 2H), 4.06 (d, $J = 14.0$ Hz, 2H), 3.84 (s, 3H), 3.76 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 162.4, 158.6, 131.7, 131.6, 129.7, 128.9, 113.9, 113.8, 55.6, 55.3, 46.2.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ required m/z 427.1686, found m/z 427.1688 ($\Delta = +2$ ppm).

4-(*Tert*-butyl)-*N,N'*-bis(4-methoxybenzyl)benzenesulfonimidamide (1c)



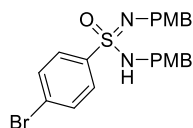
white solid, m.p.: 142.5-143.3 °C, $R_f = 0.47$ (Pet/EtOAc, 4/1, v/v).

¹H NMR (600 MHz, CDCl₃) δ 7.88 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 4H), 6.80 (d, *J* = 8.4 Hz, 4H), 4.16 (d, *J* = 14.4 Hz, 2H), 4.13 (d, *J* = 14.4 Hz, 2H), 3.77 (s, 6H), 1.34 (s, 9H).

¹³C NMR (150 MHz, CDCl₃) δ 158.8, 155.8, 137.2, 131.7, 129.0, 127.5, 126.0, 114.0, 55.4, 46.4, 35.2, 31.3.

HRMS (ESI-TOF): exact mass calcd for C₂₆H₃₃N₂O₃S⁺ (M+H)⁺ required m/z 453.2206, found m/z 453.2203 (Δ = -3 ppm).

4-Bromo-*N,N'*-bis(4-methoxybenzyl)benzenesulfonimidamide (1e)



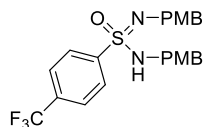
white solid, m.p.: 119.0-120.4 °C, R_f = 0.50 (Pet/EtOAc, 3/1, v/v).

¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 4H), 6.79 (d, *J* = 8.4 Hz, 4H), 4.10 (d, *J* = 14.0 Hz, 2H), 4.04 (d, *J* = 14.0 Hz, 2H), 3.77 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 158.9, 139.5, 132.1, 131.2, 129.3, 129.0, 126.9, 113.9, 55.4, 46.3.

HRMS (ESI-TOF): exact mass calcd for C₂₂H₂₃BrN₂NaO₃S⁺ (M+Na)⁺ required m/z 497.0505, found m/z 497.0505 (Δ = 0 ppm).

***N,N'*-Bis(4-methoxybenzyl)-4-(trifluoromethyl)benzenesulfonimidamide (1f)**



white solid, m.p.: 118.3-119.9 °C, R_f = 0.49 (Pet/EtOAc, 4/1, v/v).

¹H NMR (600 MHz, CDCl₃) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 4H), 6.79 (d, *J* = 9.0 Hz, 4H), 4.14 (d, *J* = 14.4 Hz, 2H), 4.11 (d, *J* = 14.4 Hz, 2H), 3.77 (s, 6H).

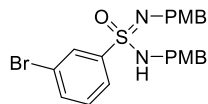
¹³C NMR (150 MHz, CDCl₃) δ 158.9, 144.2, 133.8, 133.6, 131.0, 129.0, 128.2, 126.0, 128.2, 125.9, 124.4, 122.6, 55.4, 46.3.

¹⁹F NMR (565 MHz, CDCl₃) δ 62.9.

HRMS (ESI-TOF): exact mass calcd for C₂₃H₂₃F₃N₂NaO₃S⁺ (M+Na)⁺ required m/z 487.1274, found m/z

487.1278 ($\Delta = +4$ ppm).

3-Bromo-*N,N'*-bis(4-methoxybenzyl)benzenesulfonimidamide (1h)



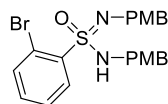
colorless oil, $R_f = 0.53$ (Pet/EtOAc, 2/1, v/v).

^1H NMR (600 MHz, CDCl_3) δ 8.04 (t, $J = 1.8$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.27-7.23 (m, 1H), 7.12 (d, $J = 8.4$ Hz, 4 H), 6.76 (d, $J = 9.0$ Hz, 4 H), 4.06 (d, $J = 13.8$ Hz, 2H), 4.04 (d, $J = 13.8$ Hz, 2H), 3.73 (s, 6H).

^{13}C NMR (150 MHz, CDCl_3) δ 158.7, 142.4, 134.9, 131.1, 130.6, 130.3, 128.9, 126.1, 122.8, 113.8, 55.3, 46.1.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{22}\text{H}_{23}\text{BrKN}_2\text{O}_3\text{S}^+(\text{M}+\text{K})^+$ required m/z 513.0244, found m/z 513.0246 ($\Delta = +2$ ppm).

2-Bromo-*N,N'*-bis(4-methoxybenzyl)benzenesulfonimidamide (1i)



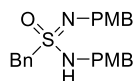
colorless oil, $R_f = 0.32$ (Pet/EtOAc, 2/1, v/v).

^1H NMR (600 MHz, CDCl_3) δ 8.13 (d, $J = 7.8$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 1H), 7.26 (t, $J = 7.2$ Hz, 1H), 7.17 (t, $J = 7.2$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 4H), 6.65 (d, $J = 8.4$ Hz, 4H), 4.05 (d, $J = 13.8$ Hz, 2H), 3.98 (d, $J = 14.4$ Hz, 2H), 3.61 (s, 6H).

^{13}C NMR (150 MHz, CDCl_3) δ 157.6, 137.5, 133.9, 131.9, 131.4, 129.9, 128.1, 126.6, 118.9, 112.7, 54.2, 45.5.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{22}\text{H}_{23}\text{BrN}_2\text{NaO}_3\text{S}^+(\text{M}+\text{Na})^+$ required m/z 497.0505, found m/z 497.0502 ($\Delta = -3$ ppm).

***N,N'*-Bis(4-methoxybenzyl)-1-phenylmethanesulfonimidamide (1k)**



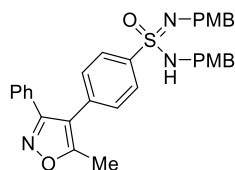
white solid, m.p.: 88.7-90.4 °C, $R_f = 0.50$ (Pet/EtOAc, 2/1, v/v).

¹H NMR (600 MHz, CDCl₃) δ 7.35 (s, 5H), 7.18 (d, *J* = 8.4 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 4H), 4.32 (s, 2H), 4.11 (d, *J* = 14.4 Hz, 2H), 4.05 (d, *J* = 13.8 Hz, 2H), 3.78 (s, 6H).

¹³C NMR (150 MHz, CDCl₃) δ 158.9, 131.9, 131.2, 129.8, 129.0, 128.7, 128.6, 114.0, 60.2, 55.4, 46.5.

HRMS (ESI-TOF): exact mass calcd for C₂₃H₂₆N₂NaO₃S⁺(M+Na)⁺ required *m/z* 433.1556, found *m/z* 433.1551 (Δ = -5 ppm).

***N,N'*-Bis(4-methoxybenzyl)-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfonimidamide (1m)**

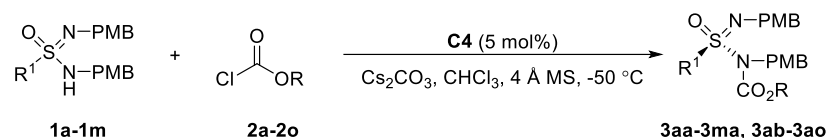


white solid, m.p.:140.0-141.8 °C, *R_f* = 0.54 (Pet/EtOAc, 1/1, v/v).

¹H NMR (600 MHz, CDCl₃) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.40-7.39 (m, 3H), 7.35-7.32 (m, 2H), 7.27-7.26 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 4H), 6.81 (d, *J* = 8.4 Hz, 4H), 4.21 (d, *J* = 13.8 Hz, 2H), 4.16 (d, *J* = 13.8 Hz, 2H), 3.77 (s, 6H), 2.48 (s, 3H).

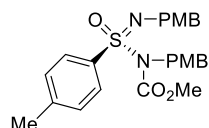
¹³C NMR (150 MHz, CDCl₃) δ 167.3, 161.2, 158.9, 139.7, 134.6, 131.4, 130.2, 129.8, 129.0, 128.8, 128.7, 128.6, 128.0, 114.8, 114.0, 55.4, 46.4, 11.8.

HRMS (ESI-TOF): exact mass calcd for C₃₂H₃₁N₃NaO₄S⁺(M+Na)⁺ required *m/z* 576.1927, found *m/z* 576.1924 (Δ = -3 ppm).



General procedure A In a dry test tube, chiral ArPNO **C4** (0.005 mmol, 5 mol%), sulfonimidamide **1** (0.1 mmol), Cs₂CO₃ (0.1 mmol) and 4 Å MS (50 mg) were added. Then, CHCl₃ (1 mL) was added and the reaction was stirred for 30 min at -50 °C. Afterwards, chloroformate **2** (0.15 mmol) was added and the reaction was stirred for 96 h at -50 °C. Then, the reaction mixture was purified by silica gel chromatography using Pet/EtOAc system (Pet/EtOAc, 4/1, v/v) to afford the desired product **3**.

Methyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate (3aa**)**



colourless oil, 42.2 mg, 90% yield, 92% ee; *R*_f = 0.25 (Pet/EtOAc, 4/1, v/v); [*α*]_D^{25.0} = +20.6 (*c* = 0.43, CHCl₃).

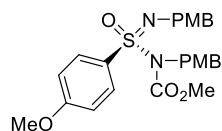
HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, λ = 254 nm, retention time: 9.553 min (major), 17.020 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.86-6.83 (m, 4H), 4.93 (d, *J* = 15.2 Hz, 1H), 4.87 (d, *J* = 14.8 Hz, 1H), 4.26 (d, *J* = 14.4 Hz, 1H), 4.07 (d, *J* = 14.4 Hz, 1H), 3.78 (d, *J* = 7.6 Hz, 6H), 3.55 (s, 3H), 2.37 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.1, 158.4, 153.9, 143.5, 137.1, 132.6, 130.4, 130.2, 128.9, 128.7, 128.6, 113.7, 113.6, 55.3, 53.2, 50.2, 45.7, 21.5.

HRMS (ESI): exact mass calcd for C₂₅H₂₈N₂NaO₅S⁺ (*M*+Na)⁺ required *m/z* 491.1611, found *m/z* 491.1610 (Δ = -1 ppm).

Methyl (*R*)-(4-methoxy-*N*-(4-methoxybenzyl)phenylsulfonimidoyl)(4-methoxybenzyl)carbamate (3ba**)**



colourless oil, 43.6 mg, 90% yield, 92% ee; $R_f = 0.46$ (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0} = +22.7$ ($c = 0.86$, CHCl_3).

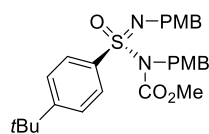
HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 12.568 min (major), 19.113 min (minor).

^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 7.8$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 6.87-6.83 (m, 6H), 4.92 (d, $J = 15.0$ Hz, 1H), 4.86 (d, $J = 15.0$ Hz, 1H), 4.24 (d, $J = 14.4$ Hz, 1H), 4.05 (d, $J = 14.4$ Hz, 1H), 3.83 (s, 3H), 3.79 (d, $J = 10.2$ Hz, 6H), 3.57 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 163.1, 159.2, 158.5, 154.0, 132.8, 131.6, 130.9, 130.4, 130.3, 128.8, 113.8, 113.7, 113.5, 55.7, 55.4, 53.3, 50.3, 45.9.

HRMS (ESI): exact mass calcd for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{NaO}_6\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 507.1560, found m/z 507.1557 ($\Delta = -3$ ppm).

Methyl (*R*)-(4-(*tert*-butyl)-*N*-(4-methoxybenzyl)phenylsulfonimidoyl)(4-methoxybenzyl) carbamate (3ca)



colourless oil, 39.8 mg, 78% yield, 90% ee; $R_f = 0.47$ (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0} = +18.5$ ($c = 0.84$, CHCl_3).

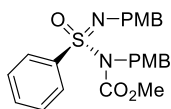
HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 7.838 min (major), 11.323 min (minor).

^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 9.0$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 6.85-6.83 (m, 4H), 4.92 (d, $J = 15.0$ Hz, 1H), 4.87 (d, $J = 15.0$ Hz, 1H), 4.26 (d, $J = 14.4$ Hz, 1H), 4.06 (d, $J = 14.4$ Hz, 1H), 3.79 (d, $J = 12.6$ Hz, 6H), 3.57 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (150 MHz, CDCl_3) δ 159.2, 158.5, 156.5, 154.1, 137.1, 132.8, 130.5, 130.4, 128.8, 128.4, 125.5, 113.8, 113.7, 55.4, 53.3, 50.3, 45.8, 35.2, 31.2.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{28}\text{H}_{34}\text{N}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 533.2081, found m/z 533.2082 ($\Delta = +1$ ppm).

Methyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)phenylsulfonimidoyl)carbamate (3da)



colourless oil, 41.8 mg, 92% yield, 93% ee; R_f = 0.56 (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0}$ = +22.2 (c = 0.82, CHCl_3).

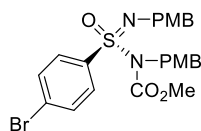
HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, λ = 254 nm, retention time: 7.945 min (major), 9.678 min (minor).

^1H NMR (600 MHz, CDCl_3) δ 7.95 (d, J = 7.8 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.42-7.38 (m, 4H), 7.25 (d, J = 8.4 Hz, 2H), 6.86-6.84 (m, 4H), 4.95 (d, J = 15.0 Hz, 1H), 4.89 (d, J = 15.0 Hz, 1H), 4.27 (d, J = 13.8 Hz, 1H), 4.08 (d, J = 14.4 Hz, 1H), 3.79 (d, J = 10.8 Hz, 6H), 3.56 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 159.2, 158.5, 153.9, 140.1, 132.7, 132.6, 130.5, 130.2, 128.8, 128.6, 128.4, 55.4, 53.3, 50.3, 45.8.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{24}\text{H}_{26}\text{N}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 477.1455, found m/z 477.1457 (Δ = +2 ppm).

Methyl (*R*)-(4-bromo-*N*-(4-methoxybenzyl)phenylsulfonimidoyl)(4-methoxybenzyl)carbamate (3ea)



colourless oil, 49.5 mg, 93% yield, 96% ee; R_f = 0.72 (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0}$ = +26.9 (c = 0.84, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.267 min (major), 14.798 min (minor).

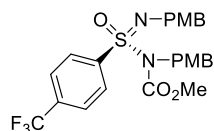
^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H), 7.34 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 6.85-6.83 (m, 4H), 4.93 (d, J = 15.0 Hz, 1H), 4.85 (d, J = 15.0 Hz, 1H), 4.24 (d, J = 14.4 Hz, 1H), 4.06 (d, J = 14.4 Hz, 1H), 3.79 (d, J = 12.0 Hz, 6H), 3.58 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 159.3, 158.6, 153.8, 139.2, 132.4, 131.6, 130.5, 130.3, 130.0, 128.9, 127.9, 113.9, 113.8, 55.4, 53.5, 50.3, 45.9.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{24}\text{H}_{25}\text{BrN}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 555.0560, found m/z

555.0564 ($\Delta = +4$ ppm).

Methyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-(trifluoromethyl)phenylsulfonimidoyl)carbamate (3fa)



colourless oil, 43.3 mg, 83% yield, 95% ee; $R_f = 0.44$ (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0} = +18.7$ ($c = 0.79$, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 7.985 min (major), 9.655 min (minor).

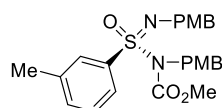
^1H NMR (600 MHz, CDCl_3) δ 8.02 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 6.86-6.84 (m, 4H), 4.97 (d, $J = 15.0$ Hz, 1H), 4.87 (d, $J = 15.6$ Hz, 1H), 4.28 (d, $J = 14.4$ Hz, 1H), 4.11 (d, $J = 14.4$ Hz, 1H), 3.80 (d, $J = 11.4$ Hz, 6H), 3.58 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 159.4, 158.7, 153.7, 143.6, 134.2 (q, $J = 33.0$ Hz), 132.2, 130.5, 129.9, 129.2, 128.9, 125.5 (q, $J = 3.0$ Hz), 124.4, 122.5, 113.9, 113.8, 55.4, 53.5, 50.4, 45.9.

^{19}F NMR (565 MHz, CDCl_3) δ 63.1.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{25}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}_5\text{S}^+ (\text{M}+\text{Na})^+$ required m/z 545.1328, found m/z 545.1325 ($\Delta = -3$ ppm).

Methyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-3-methylphenylsulfonimidoyl)carbamate (3ga)



colourless oil, 41.7 mg, 89% yield, 84% ee; $R_f = 0.62$ (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0} = +22.5$ ($c = 0.56$, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 7.213 min (major), 8.773 min (minor).

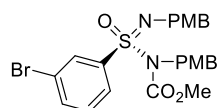
^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 6.8$ Hz, 1H), 7.58 (s, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.29-7.24 (m, 4H), 6.84 (d, $J = 8.0$ Hz, 4H), 4.96 (d, $J = 14.8$ Hz, 1H), 4.86 (d, $J = 15.2$ Hz, 1H), 4.28 (d, $J = 14.4$

Hz, 1H), 4.09 (d, $J = 14.4$ Hz, 1H), 3.79 (d, $J = 6.8$ Hz, 6H), 3.57 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.3, 158.6, 154.1, 140.0, 138.6, 133.5, 132.7, 130.6, 130.3, 128.9, 128.6, 128.2, 125.9, 113.8, 113.7, 55.4, 55.4, 53.3, 50.3, 45.9, 21.4.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 491.1611, found m/z 491.1612 ($\Delta = +1$ ppm).

Methyl (*R*)-(3-bromo-*N*-(4-methoxybenzyl)phenylsulfonimidoyl)(4-methoxybenzyl)carbamate (3ha)



colourless oil, 47.3 mg, 89% yield, 91% ee; $R_f = 0.54$ (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{25.0} = +20.4$ ($c = 0.35$, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 7.262 min (major), 8.538 min (minor).

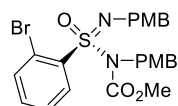
^1H NMR (600 MHz, CDCl_3) δ 7.87-7.85 (m, 2H), 7.61-7.59 (m, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.25-7.22 (m, 3H), 6.85-6.83 (m, 4H), 4.96 (d, $J = 15.0$ Hz, 1H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.26 (d, $J = 14.4$ Hz, 1H), 4.09 (d, $J = 14.4$ Hz, 1H), 3.79 (d, $J = 11.4$ Hz, 6H), 3.59 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 159.4, 158.6, 153.8, 141.8, 135.7, 132.3, 131.4, 130.5, 129.9, 129.7, 128.9, 127.4, 127.4, 122.2, 113.9, 113.8, 55.4, 55.4, 53.5, 50.4, 45.9.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{24}\text{H}_{25}\text{BrN}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 555.0560, found m/z 555.0563 ($\Delta = +3$ ppm).

Methyl (*R*)-(2-bromo-*N*-(4-methoxybenzyl)phenylsulfonimidoyl)(4-methoxybenzyl)carbamate

(3ia)



colourless oil, 47.3 mg, 89% yield, 19% ee; $R_f = 0.47$ (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{25.0} = -1.88$ ($c = 0.37$, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 12.927 min (major), 15.293 min (minor).

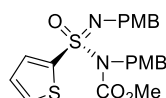
^1H NMR (400 MHz, CDCl_3) δ 8.51 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 1H), 7.48 (d, $J = 28.8$ Hz,

2H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H), 5.08 (s, 2H), 3.98 (d, $J = 14.4$ Hz, 1H), 3.81-3.74 (m, 7H), 3.52 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 158.3, 153.5, 139.6, 135.4, 133.9, 133.2, 132.6, 130.6, 130.2, 128.4, 127.1, 113.8, 113.5, 55.3, 55.4, 53.4, 50.9, 45.6.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{24}\text{H}_{25}\text{BrN}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 555.0560, found m/z 555.0560 ($\Delta = 0$ ppm).

Methyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)thiophene-2-sulfonimidoyl)carbamate (3ja)



colourless oil, 31.3 mg, 68% yield, 76% ee; $R_f = 0.32$ (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0} = +19.3$ ($c = 0.64$, CHCl_3).

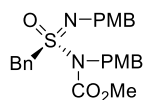
HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 13.902 min (major), 16.460 min (minor).

^1H NMR (400 MHz, CDCl_3) δ 7.53 (dd, $J = 5.2, 1.6$ Hz, 1H), 7.44 (dd, $J = 4.0, 1.2$ Hz, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.8$ Hz, 2H), 6.97-6.94 (m, 1H), 6.84 (d, $J = 8.0$ Hz, 4H), 4.95 (d, $J = 15.2$ Hz, 1H), 4.88 (d, $J = 15.2$ Hz, 1H), 4.22 (d, $J = 14.4$ Hz, 1H), 4.06 (d, $J = 14.4$ Hz, 1H), 3.79 (d, $J = 5.2$ Hz, 6H), 3.63 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 158.5, 153.9, 141.4, 133.3, 133.2, 132.3, 130.5, 129.9, 128.7, 126.9, 113.8, 113.7, 55.4, 55.3, 53.5, 50.6, 46.2.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{NaO}_5\text{S}_2^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 483.1019, found m/z 483.1019 ($\Delta = 0$ ppm).

Methyl (*R*)-(S-benzyl-*N*-(4-methoxybenzyl)sulfonimidoyl)(4-methoxybenzyl)carbamate (3ka)



colourless oil, 39.9 mg, 85% yield, 97% ee; $R_f = 0.49$ (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{25.0} = -28.2$ ($c = 0.65$, CHCl_3).

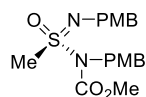
HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 9.285 min (major), 12.720 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 7.36-7.31 (m, 5H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.82 (d, *J* = 13.6 Hz, 1H), 4.64 (d, *J* = 14.0 Hz, 1H), 4.41 (d, *J* = 14.8 Hz, 1H), 4.17 (d, *J* = 15.2 Hz, 1H), 4.07 (d, *J* = 14.0 Hz, 1H), 3.89 (d, *J* = 14.4 Hz, 1H), 3.77 (d, *J* = 3.2 Hz, 6H), 3.76 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.1, 158.5, 154.6, 132.6, 131.4, 130.3, 130.1, 129.2, 128.9, 128.8, 128.2, 113.7, 113.7, 60.8, 55.4, 53.7, 50.3, 46.1.

HRMS (ESI-TOF): exact mass calcd for C₂₅H₂₈N₂NaO₅S⁺ (M+Na)⁺ required *m/z* 491.1611, found *m/z* 491.1615 (Δ = +4 ppm).

Methyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-*S*-methylsulfonimidoyl)carbamate (3la)



colourless oil, 32.1 mg, 82% yield, 95% ee; *R_f* = 0.44 (Pet/EtOAc, 1/3, v/v); [α]_D^{25.0} = +5.3 (*c* = 0.31, CHCl₃).

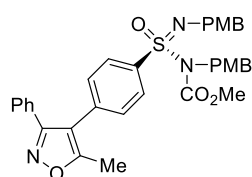
HPLC CHIRALPAK IA, n-hexane/2-propanol = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.510 min (major), 20.940 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.85-6.81 (m, 4H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.71 (d, *J* = 15.2 Hz, 1H), 4.09 (d, *J* = 14.0 Hz, 1H), 3.92 (d, *J* = 14.0 Hz, 1H), 3.79 (d, *J* = 3.6 Hz, 6H), 3.73 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.3, 158.6, 154.4, 132.3, 130.3, 129.9, 129.1, 113.9, 113.8, 55.4, 55.4, 53.7, 49.6, 46.1, 44.2.

HRMS (ESI-TOF): exact mass calcd for C₁₉H₂₄N₂NaO₅S⁺ (M+Na)⁺ required *m/z* 415.1298, found *m/z* 415.1299 (Δ = +1 ppm).

Methyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-(5-methyl-3-phenylisoxazol-4-yl)phenylsulfonimidoyl)carbamate (3ma)



colourless oil, 46.4 mg, 76% yield, 91% ee; $R_f = 0.49$ (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{25.0} = +23.5$ ($c = 0.75$, CHCl_3).

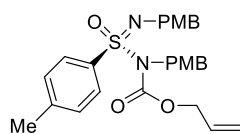
HPLC CHIRALPAK IE, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 20.577 min (major), 30.698 min (minor).

^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.4$ Hz, 2H), 7.41-7.31 (m, 7H), 7.26-7.19 (m, 4H), 6.85 (d, $J = 2.4$ Hz, 2H), 6.83 (d, $J = 2.4$ Hz, 2H), 4.95 (d, $J = 15.2$ Hz, 2H), 4.90 (d, $J = 14.8$ Hz, 2H), 4.26 (d, $J = 14.4$ Hz, 1H), 4.08 (d, $J = 14.4$ Hz, 1H), 3.77 (d, $J = 0.8$ Hz, 6H), 3.58 (s, 3H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 161.2, 159.3, 158.6, 154.0, 139.2, 135.2, 132.4, 130.5, 130.1, 129.8, 129.6, 129.1, 128.9, 128.8, 128.7, 128.6, 114.6, 113.8, 113.7, 77.4, 77.2, 77.0, 55.4, 55.4, 53.3, 50.4, 45.9, 11.9.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{34}\text{H}_{33}\text{N}_3\text{NaO}_6\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 634.1982, found m/z 634.1981 ($\Delta = -1$ ppm).

Allyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate (3ab)



colourless oil, 42.5 mg, 86% yield, 90% ee; $R_f = 0.39$ (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0} = +20.6$ ($c = 0.39$, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 8.780 min (major), 12.487 min (minor).

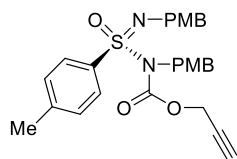
^1H NMR (600 MHz, CDCl_3) δ 7.82 (d, $J = 7.8$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.86-6.83 (m, 4H), 5.76-5.69 (m, 1H), 5.19-5.16 (m, 2H), 4.96 (d, $J = 15.0$ Hz, 1H), 4.90 (d, $J = 15.0$ Hz, 1H), 4.48-4.41 (m, 2H), 4.26 (d, $J = 14.4$ Hz, 1H), 4.07 (d, $J = 14.4$ Hz, 1H), 3.80 (d, $J = 12.0$ Hz, 6H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 159.2, 158.5, 153.3, 143.5, 137.2, 132.7, 131.6, 130.5, 130.4, 128.9, 128.8, 128.7, 118.9, 113.8, 113.7, 67.3, 55.4, 50.2, 45.8, 21.6.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{27}\text{H}_{30}\text{N}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 517.1768, found m/z 517.1767 ($\Delta = -1$ ppm).

Prop-2-yn-1-yl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)

carbamate(3ac)



colourless oil, 39.4 mg, 80% yield, 93% ee; $R_f = 0.46$ (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{25.0} = +22.2$ ($c = 0.82$, CHCl_3).

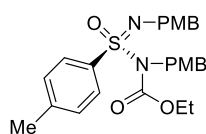
HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 10.185 min (major), 15.918 min (minor).

^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.26-7.25 (m, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.85-6.83 (m, 4H), 4.93 (d, $J = 15.0$ Hz, 1H), 4.87 (d, $J = 15.0$ Hz, 1H), 4.57-4.47 (m, 2H), 4.25 (d, $J = 14.4$ Hz, 1H), 4.07 (d, $J = 14.4$ Hz, 1H), 3.79 (d, $J = 11.4$ Hz, 6H), 2.46 (t, $J = 2.4$ Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 159.3, 158.5, 152.7, 143.7, 136.8, 132.5, 130.7, 130.1, 129.1, 128.9, 128.8, 113.8, 113.7, 75.6, 55.4, 53.9, 50.4, 45.9, 21.6.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{27}\text{H}_{28}\text{N}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 515.1611, found m/z 515.1607 ($\Delta = -4$ ppm).

Ethyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate (3ad)



colourless oil, 34.7 mg, 78% yield, 87% ee; $R_f = 0.29$ (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0} = +21.7$ ($c = 0.67$, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 9.323 min (major), 13.448 min (minor).

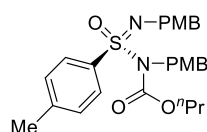
^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.8$ Hz, 2H), 7.25 (d, $J = 8.8$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.86-6.83 (m, 4H), 4.95 (d, $J = 15.2$ Hz, 1H), 4.88 (d, $J = 15.2$ Hz, 1H), 4.25 (d, $J = 14.4$ Hz, 1H), 4.07-3.94 (m, 3H), 3.79 (d, $J = 8.8$ Hz, 6H), 2.39 (s, 3H), 1.11 (q, $J = 6.8$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.2, 158.5, 153.6, 143.5, 137.4, 132.8, 130.6, 130.5, 128.9, 128.8, 128.7, 113.8, 113.7, 62.8, 55.4, 50.2, 45.8, 21.6, 14.2.

HRMS (ESI-TOF): exact mass calcd for C₂₆H₃₀N₂NaO₅S⁺ (M+Na)⁺ required m/z 505.1768, found m/z 505.1769 (Δ = +1 ppm).

Propyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate

(3ae)



colourless oil, 34.7 mg, 70% yield, 88% ee; R_f = 0.39 (Pet/EtOAc, 4/1, v/v). [α]_D^{25.0} = +21.3 (*c* = 0.40, CHCl₃).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, λ = 254 nm, retention time: 8.482 min (major), 10.588 min (minor).

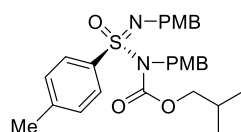
¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.84 (t, *J* = 9.0, 4H), 4.95 (d, *J* = 15.0 Hz, 1H), 4.89 (d, *J* = 15.0 Hz, 1H), 4.25 (d, *J* = 14.4 Hz, 1H), 4.05 (d, *J* = 14.4 Hz, 1H), 3.95-3.84 (m, 2H), 3.79 (d, *J* = 13.2 Hz, 6H), 2.38 (s, 3H), 1.49 (q, *J* = 7.2 Hz, 2H), 0.78 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 159.2, 158.5, 153.7, 143.4, 137.4, 132.8, 130.5, 130.5, 129.0, 128.9, 128.7, 113.8, 113.7, 68.5, 55.4, 50.2, 45.8, 21.9, 21.6, 10.3.

HRMS (ESI-TOF): exact mass calcd for C₂₇H₃₂N₂NaO₅S⁺ (M+Na)⁺ required m/z 519.1924, found m/z 519.1926 (Δ = +2 ppm).

Isobutyl(*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate

(3af)



colourless oil, 38.3 mg, 75% yield, 80% ee; R_f = 0.39 (Pet/EtOAc, 4/1, v/v), [α]_D^{25.0} = +22.9 (*c* = 0.45, CHCl₃).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.357 min (major), 12.127 min (minor).

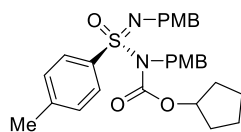
¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.84 (t, J = 7.2 Hz, 4H), 4.96 (d, J = 15.2 Hz, 1H), 4.90 (d, J = 15.2 Hz, 1H), 4.26 (d, J = 14.4 Hz, 1H), 4.06 (d, J = 14.0 Hz, 1H), 3.80-3.68 (m, 8H), 2.38 (s, 3H), 1.81-1.71 (m, 1H), 0.77 (dd, J = 10.0, 6.8 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 159.1, 158.5, 153.7, 148.4, 137.5, 132.7, 130.5, 130.4, 129.0, 128.9, 128.5, 73.1, 55.4, 50.2, 45.8, 27.7, 21.6, 19.1, 19.0.

HRMS (ESI-TOF): exact mass calcd for C₂₈H₃₄N₂NaO₅S⁺ (M+Na)⁺ required m/z 533.2081, found m/z 533.2083 (Δ = +2 ppm).

Cyclopentyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)

carbamate (3ag)



colourless oil, 21.4 mg, 45% yield, 65% ee; R_f = 0.49 (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0}$ = +11.7 (c = 0.06, CHCl₃).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.025 min (major), 13.995 min (minor).

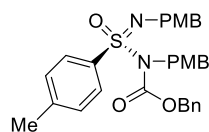
¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.86-6.82 (m, 4H), 5.01-4.87 (m, 3H), 4.24 (d, J = 14.0 Hz, 1H), 4.02 (d, J = 14.4 Hz, 1H), 3.79 (d, J = 8.8 Hz, 6H), 2.39 (s, 3H), 1.75-1.54 (m, 5H), 1.48-1.43 (m, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.1, 158.5, 153.4, 143.3, 137.7, 132.8, 130.7, 130.5, 128.9, 128.8, 128.5, 113.8, 113.7, 80.2, 55.4, 50.2, 45.7, 32.6, 32.5, 23.7, 23.6, 21.6.

HRMS (ESI-TOF): exact mass calcd for C₂₉H₃₄N₂NaO₅S⁺ (M+Na)⁺ required m/z 545.2081, found m/z 545.2083 (Δ = +2 ppm).

Benzyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate

(3ah)



colourless oil, 43.5 mg, 80% yield, 87% ee; $R_f = 0.41$ (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0} = +16.8$ ($c = 0.50$, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 10.103 min (major), 13.962 min (minor).

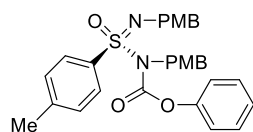
^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.30-7.24 (m, 3H), 7.20 (d, $J = 8.4$ Hz, 2H), 7.11-7.06 (m, 4H), 6.82 (d, $J = 8.0$ Hz, 4H), 5.00-4.87 (m, 4H), 4.23 (d, $J = 14.4$ Hz, 1H), 4.01 (d, $J = 14.4$ Hz, 1H), 3.79 (d, $J = 7.6$ Hz, 6H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 158.5, 153.5, 143.4, 137.2, 135.1, 132.7, 130.6, 130.4, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 113.8, 113.7, 68.5, 55.4, 50.3, 45.8, 21.6.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{31}\text{H}_{32}\text{N}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 567.1924, found m/z 567.1924 ($\Delta = 0$ ppm).

Phenyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate

(3ai)



colourless oil, 41.3 mg, 78% yield, 78% ee; $R_f = 0.44$ (Pet/EtOAc, 4/1, v/v); $[\alpha]_D^{25.0} = +10.2$ ($c = 0.46$, CHCl_3).

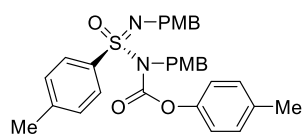
HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 13.358 min (major), 16.032 min (minor).

^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, $J = 9.0$ Hz, 2H), 7.46 (d, $J = 9.0$ Hz, 2H), 7.27-7.25 (m, 4H), 7.20 (d, $J = 8.4$ Hz, 2H), 7.16 (t, $J = 7.2$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 2H), 6.82 (d, $J = 7.2$ Hz, 2H), 6.72 (d, $J = 7.2$ Hz, 2H), 5.04 (d, $J = 15.0$ Hz, 1H), 5.00 (d, $J = 15.0$ Hz, 1H), 4.32 (d, $J = 14.4$ Hz, 1H), 4.16 (d, $J = 14.4$ Hz, 1H), 3.79 (d, $J = 22.8$ Hz, 6H), 2.39 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 159.3, 158.6, 152.2, 150.4, 143.8, 137.0, 132.5, 130.8, 130.2, 129.4, 129.2, 128.9, 128.8, 126.0, 55.4, 50.6, 45.9, 21.7.

HRMS (ESI-TOF): exact mass calcd for C₃₀H₃₀N₂NaO₅S⁺ (M+Na)⁺ required m/z 553.1768, found m/z 553.1770 (Δ = +2 ppm).

***P*-tolyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate (3aj)**



colourless oil, 50.1 mg, 92% yield, 86% ee; R_f = 0.47 (Pet/EtOAc, 4/1, v/v); [α]_D^{25.0} = +6.4 (*c* = 0.52, CHCl₃).

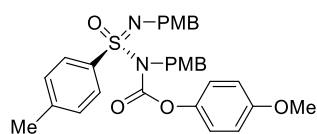
HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 15.742 min (major), 18.870 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 5.06 (d, *J* = 14.8 Hz, 1H), 5.01 (d, *J* = 15.2 Hz, 1H), 4.34 (d, *J* = 14.4 Hz, 1H), 4.18 (d, *J* = 14.4 Hz, 1H), 3.81 (d, *J* = 12.4 Hz, 6H), 2.41 (s, 3H), 2.31 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.3, 158.6, 152.33, 148.2, 143.7, 137.0, 135.7, 132.5, 130.7, 130.2, 129.9, 129.1, 128.9, 121.2, 113.9, 113.8, 55.4, 50.6, 45.9, 21.6, 20.9.

HRMS (ESI-TOF): exact mass calcd for C₃₁H₃₂N₂NaO₅S⁺ (M+Na)⁺ required m/z 567.1924, found m/z 567.1922 (Δ = -2 ppm).

4-Methoxyphenyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate (3ak)



colourless oil, 50.9 mg, 91% yield, 83% ee; R_f = 0.38 (Pet/EtOAc, 4/1, v/v); [α]_D^{25.0} = +3.8 (*c* = 0.55, CHCl₃).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 21.610 min (major), 25.392 min (minor).

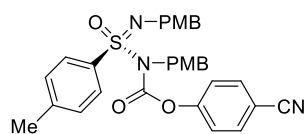
¹H NMR (600 MHz, CDCl₃) δ 7.87 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 7.8 Hz, 2H), 6.76 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 5.02 (d, J = 15.0 Hz, 1H), 4.99 (d, J = 15.0 Hz, 1H), 4.31 (d, J = 14.4 Hz, 1H), 4.15 (d, J = 14.4 Hz, 1H), 3.79 (d, J = 19.2 Hz, 6H), 3.74 (s, 3H), 2.38 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 159.3, 158.6, 157.4, 152.5, 143.9, 143.7, 137.0, 132.5, 130.7, 130.2, 129.1, 128.9, 122.3, 114.4, 113.9, 113.8, 55.7, 55.4, 50.6, 45.9, 21.6.

HRMS (ESI-TOF): exact mass calcd for C₃₁H₃₂N₂NaO₆S⁺ (M+Na)⁺ required m/z 583.1873, found m/z 583.1873 (Δ = +0 ppm).

4-Cyanophenyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)

carbamate (3al)



colourless oil, 49.9 mg, 90% yield, 71% ee; R_f = 0.59 (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{25.0}$ = -3.5 (c = 0.40, CHCl₃).

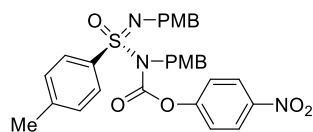
HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 34.030 min (major), 46.733 min (minor).

¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.22 (dd, J = 7.8, 6.0 Hz, 4H), 6.89 (d, J = 8.4 Hz, 2H), 6.80 (dd, J = 8.4, 7.2 Hz, 4H), 5.03 (d, J = 15.0 Hz, 1H), 4.99 (d, J = 15.0 Hz, 1H), 4.33 (d, J = 14.4 Hz, 1H), 4.15 (d, J = 14.4 Hz, 1H), 3.80 (d, J = 26.4 Hz, 6H), 2.41 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 159.5, 158.7, 153.5, 151.1, 144.1, 136.8, 133.6, 132.1, 130.7, 129.7, 129.2, 128.9, 128.7, 122.5, 118.2, 113.9, 113.8, 109.8, 55.4, 55.3, 50.7, 45.8, 21.7.

HRMS (ESI-TOF): exact mass calcd for C₃₁H₂₉N₃NaO₅S⁺ (M+Na)⁺ required m/z 578.1720, found m/z 578.1717 (Δ = -3 ppm).

4-Nitrophenyl (*R*)-(4-methoxybenzyl)(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl) carbamate (3am)



colourless oil, 51.2 mg, 89% yield, 59% ee; $R_f = 0.56$ (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{25.0} = -0.1$ ($c = 0.83$, CHCl_3).

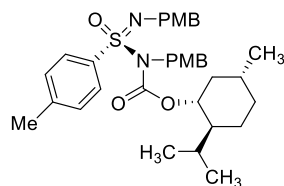
HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 28.693 min (major), 38.877 min (minor).

^1H NMR (600 MHz, CDCl_3) δ 8.12 (d, $J = 9.0$ Hz, 2H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.24-7.21 (m, 4H), 6.89 (d, $J = 8.4$ Hz, 2H), 6.84-6.80 (m, 4H), 5.03 (d, $J = 15.0$ Hz, 1H), 5.00 (d, $J = 15.0$ Hz, 1H), 4.33 (d, $J = 14.4$ Hz, 1H), 4.16 (d, $J = 14.4$ Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 159.5, 158.7, 154.9, 150.9, 145.3, 144.2, 136.8, 132.1, 130.7, 129.7, 129.3, 128.9, 128.7, 125.1, 122.2, 114.0, 113.8, 55.4, 55.4, 50.8, 45.9, 21.7.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{30}\text{H}_{29}\text{N}_3\text{NaO}_7\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 598.1618, found m/z 598.1620 ($\Delta = +2$ ppm).

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (4-methoxybenzyl)((*S*)-*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate (3an)



colourless oil, 49.1 mg, 83% yield, dr: 4.9:1; $R_f = 0.46$ (Pet/EtOAc, 5/1, v/v); $[\alpha]_D^{25.0} = +8.2$ ($c = 0.27$, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 19.487 min (minor), 22.737 min (major).

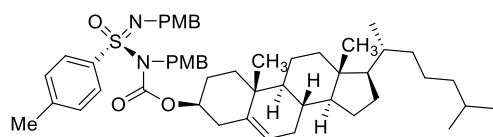
^1H NMR (600 MHz, CDCl_3) δ 7.81-7.78 (m, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.26-7.24 (m, 2H), 7.21-7.17 (m, 2H), 6.84 (dd, $J = 13.2, 8.4$ Hz, 4H), 5.05-4.91 (m, 2H), 4.48 (td, $J = 10.8, 4.2$ Hz, 1H), 4.22 (d, $J = 14.4$ Hz, 1H), 3.95 (dd, $J = 14.4, 6.6$ Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 2.39 (s, 3H), 1.72-1.57 (m, 5H),

1.37-1.32 (m, 1H), 1.23-1.19 (m, 1H), 0.94-0.84 (m, 2H), 0.81-0.79 (m, 3H), 0.74-0.71 (m, 3H), 0.57-0.54 (m, 3H), 0.41 (q, $J = 12.0$ Hz, 1H).

^{13}C NMR (150 MHz, CDCl_3) δ 159.1, 158.4, 153.3, 143.2, 137.9, 132.9, 130.8, 130.4, 128.9, 128.7, 128.6, 113.8, 113.7, 55.4, 50.0, 47.1, 45.6, 40.4, 34.2, 31.4, 25.5, 22.9, 22.0, 21.6, 21.0.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{34}\text{H}_{44}\text{N}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 615.2863, found m/z 615.2861 ($\Delta = -2$ ppm).

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl(4-methoxybenzyl)((*S*)-*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate (3ao)



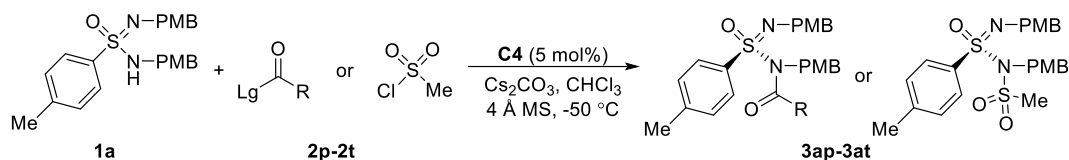
colourless oil, 69.8 mg, 85% yield, dr: 4.3:1; $R_f = 0.49$ (Pet/EtOAc, 5:1, v/v); $[\alpha]_D^{25.0} = -10.2$ ($c = 0.68$, CHCl_3).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 7.945 min (major), 9.678 min (minor).

^1H NMR (600 MHz, CDCl_3) δ 7.82-7.79 (m, 2H), 7.41-7.39 (m, 2H), 7.27-7.25 (m, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.85-6.82 (m, 4H), 5.28 (d, $J = 4.2$ Hz, 1H), 4.97-4.88 (m, 2H), 4.40-4.35 (m, 1H), 4.23 (d, $J = 14.4$ Hz, 1H), 4.03 (d, $J = 14.4$ Hz, 1H), 3.79 (d, $J = 16.2$ Hz, 6H), 2.38 (s, 3H), 2.22 (d, $J = 7.8$ Hz, 2H), 2.00-1.92 (m, 2H), 1.85-1.79 (m, 1H), 1.76-1.72 (m, 1H), 1.62-1.44 (m, 4H), 1.44-1.31 (m, 6H), 1.28-1.19 (m, 3H), 1.16-1.05 (m, 6H), 1.02-0.95 (m, 3H), 0.91 (t, $J = 6.0$ Hz, 6H), 0.86 (dd, $J = 7.2, 3.0$ Hz, 6H), 0.67 (s, 3H).

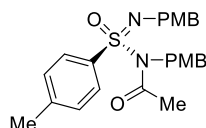
^{13}C NMR (150 MHz, CDCl_3) δ 159.2, 158.5, 153.0, 143.3, 139.4, 137.6, 132.9, 130.6, 128.9, 128.8, 128.8, 128.7, 123.0, 113.8, 113.7, 56.8, 56.3, 55.4, 55.4, 50.1, 50.0, 45.8, 42.4, 39.8, 39.6, 37.8, 36.9, 36.6, 36.3, 35.9, 32.0, 31.9, 28.3, 28.1, 27.6, 24.4, 24.0, 23.0, 22.7, 21.6, 21.1, 19.3, 18.8, 11.9.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{51}\text{H}_{70}\text{N}_2\text{NaO}_5\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 845.4898, found m/z 845.4897 ($\Delta = -1$ ppm).



General procedure B In a dry test tube, chiral ArPNO **C4** (0.005 mmol, 5 mol%), sulfonimidamide **1a** (0.1 mmol), Cs_2CO_3 (0.1 mmol) and 4 Å MS (50 mg) were added. Then, CHCl_3 (1 mL) was added and the reaction was stirred for 30 min at $-50\text{ }^\circ\text{C}$. Afterwards, electrophiles **2p-2t** (0.15 mmol) was added and the reaction was stirred for 96 h at $-50\text{ }^\circ\text{C}$. Then, the reaction mixture was purified by silica gel chromatography using Pet/EtOAc system (Pet/EtOAc, 2/1, v/v) to afford the desired product **3ap-3at**.

***N*-(4-Methoxybenzyl)-*N*-(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)acetamide (**3ap**)**



colourless oil, 9.4 mg, 21% yield, 0% ee; $R_f = 0.60$ (Pet/EtOAc, 2/1, v/v).

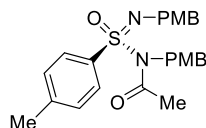
HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, $\lambda = 254\text{ nm}$, retention time: 12.322 min, 15.772 min.

^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 7.8\text{ Hz}$, 2H), 7.38 (d, $J = 8.4\text{ Hz}$, 2H), 7.23 (dd, $J = 8.4, 5.4\text{ Hz}$, 4H), 6.85 (dd, $J = 8.4, 2.4\text{ Hz}$, 4H), 5.04 (t, $J = 15.6\text{ Hz}$, 2H), 4.31 (d, $J = 14.4\text{ Hz}$, 1H), 3.98 (d, $J = 14.4\text{ Hz}$, 1H), 3.79 (d, $J = 6.6\text{ Hz}$, 6H), 2.40 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 171.7, 159.1, 158.7, 143.9, 137.6, 132.2, 130.5, 130.4, 129.6, 128.8, 127.8, 113.9, 113.8, 55.4, 49.1, 45.4, 24.7, 21.6.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{NaO}_4\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 475.1662, found m/z 475.1665 ($\Delta = +3\text{ ppm}$).

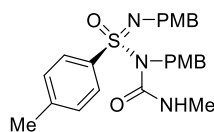
***N*-(4-Methoxybenzyl)-*N*-(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)acetamide (**3aq**)**



32.5 mg, 72% yield, 0% ee.

HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, $\lambda = 254\text{ nm}$, retention time: 12.478 min, 15.963 min.

***N,N'*-Bis(4-methoxybenzyl)-4-methyl-*N*-(methylcarbamoyl)benzenesulfonimidamide (3ar)**



colourless oil, 24.8 mg, 53% yield, 0% ee; R_f = 0.39 (Pet/EtOAc, 2/1, v/v).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, λ = 254 nm, retention time: 8.485 min, 10.620 min.

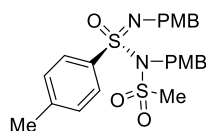
^1H NMR (400 MHz, DMSO- d_6) δ 7.86 (d, J = 8.4 Hz, 2H), 7.69 (q, J = 4.4 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 6.93-6.88 (m, 4H), 4.79 (d, J = 15.2 Hz, 1H), 4.71 (d, J = 15.2 Hz, 1H), 4.31 (d, J = 14.4 Hz, 1H), 4.07 (d, J = 14.4 Hz, 1H), 3.77 (d, J = 1.6 Hz, 6H), 2.63 (d, J = 4.4 Hz, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 158.4, 158.1, 154.2, 143.6, 136.3, 132.1, 130.2, 129.6, 129.2, 128.6, 127.0, 113.6, 113.5, 55.0, 48.3, 44.6, 27.4, 20.9.

HRMS (ESI-TOF): exact mass calcd for $\text{C}_{25}\text{H}_{29}\text{N}_3\text{NaO}_4\text{S}^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 490.1771, found m/z 490.1773 (Δ = +2 ppm).

***N*-(4-Methoxybenzyl)-*N*-(*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)**

methanesulfonamide (3at)



colourless oil, 13.7 mg, 28% yield, 0% ee; R_f = 0.53 (Pet/EtOAc, 2/1, v/v).

HPLC CHIRALPAK IA, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 20.715 min, 30.642 min.

^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, J = 7.8 Hz, 2H), 7.27-7.25 (m, 2H), 7.20 (d, J = 6.0 Hz, 2H), 7.19 (d, J = 6.6 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 4.74 (d, J = 16.2 Hz, 1H), 4.57 (d, J = 15.6 Hz, 1H), 4.41 (d, J = 14.4 Hz, 1H), 3.92 (d, J = 14.4 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.26 (s, 3H), 2.39 (s, 3H).

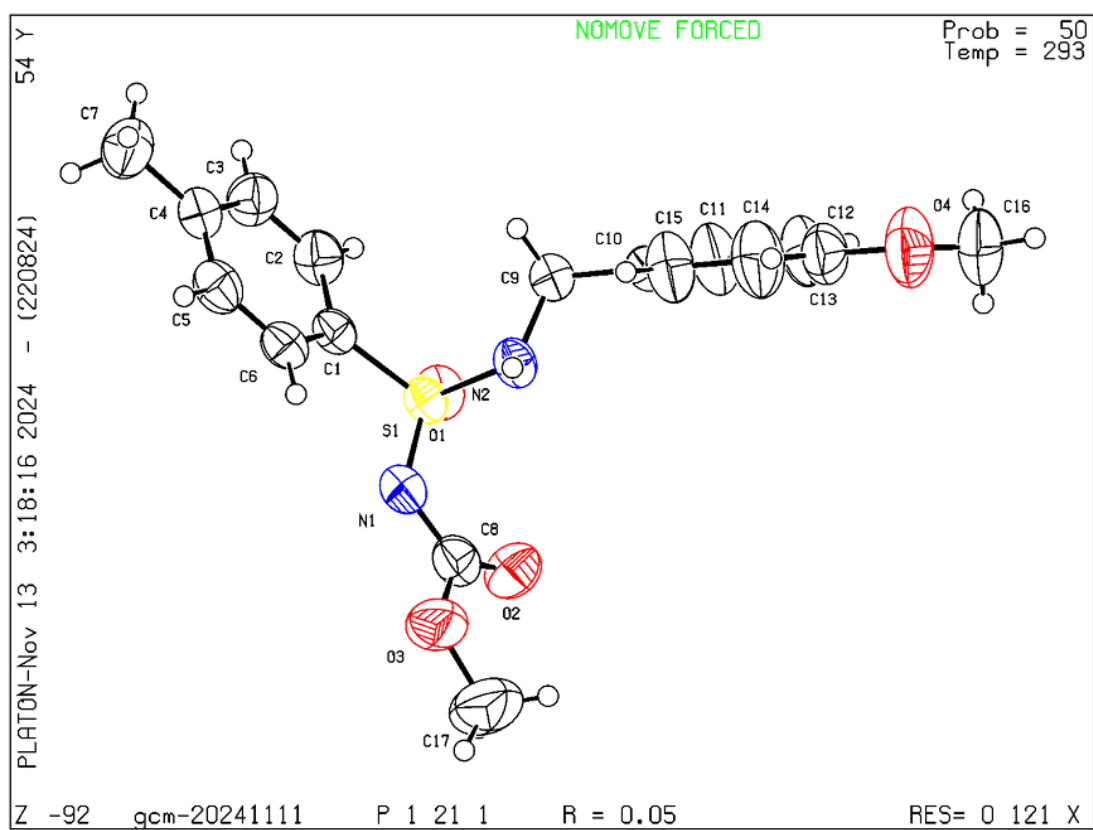
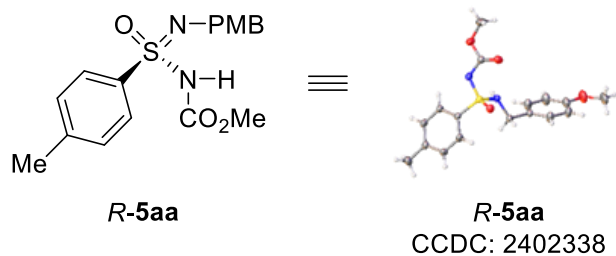
^{13}C NMR (150 MHz, CDCl_3) δ 159.3, 158.7, 144.1, 136.1, 132.1, 130.0, 129.4, 128.7, 128.5, 128.4, 113.8, 113.8, 55.4, 55.4, 50.7, 45.8, 44.7, 21.6.

HRMS (ESI): exact mass calcd for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{NaO}_5\text{S}_2^+$ ($\text{M}+\text{Na}$) $^+$ required m/z 511.1332, found m/z

511.1334 ($\Delta = +2$ ppm).

X-ray data of *R*-5aa

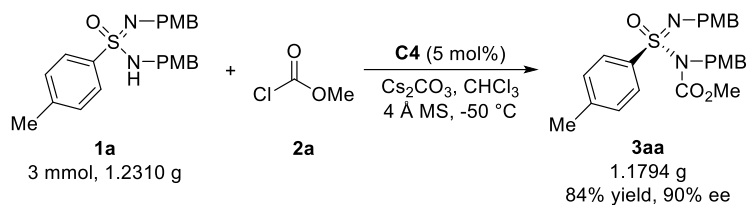
X-Ray crystal structure of *R*-5aa. The crystal was obtained by slow evaporation of *R*-5aa in a mixture of CH₂Cl₂/petroleum ether). (CCDC: 2402338):



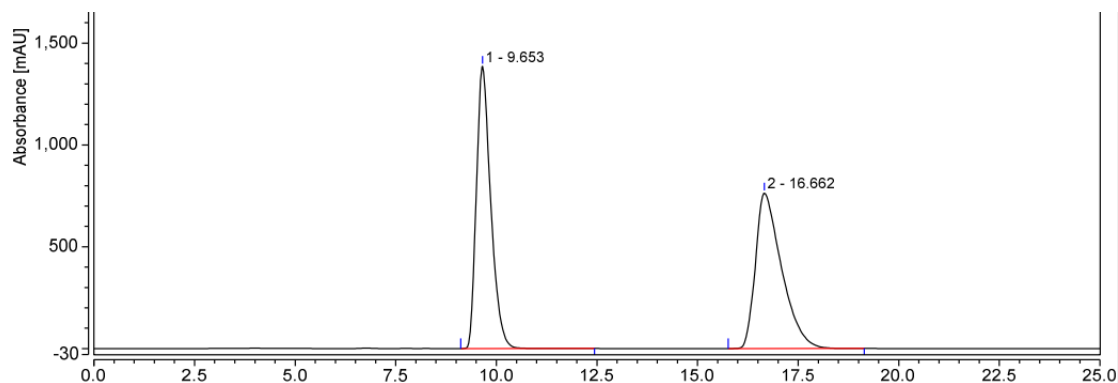
Crystal data and structure refinement for *R*-5aa

Identification code	<i>R</i> -5aa
Empirical formula	C ₁₇ H ₂₀ N ₂ O ₄ S
Formula weight	348.41
Temperature/K	293.15
Crystal system	monoclinic
Space group	P2 ₁
<i>a</i> /Å	4.99040(10)
<i>b</i> /Å	10.6896(2)
<i>c</i> /Å	16.6446(3)
α /°	90
β /°	94.504(2)
γ /°	90
Volume/Å ³	885.17(3)
<i>Z</i>	2
ρ_{calc} /cm ³	1.307
μ /mm ⁻¹	1.824
<i>F</i> (000)	368.0
Crystal size/mm ³	0.15 × 0.13 × 0.11
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	9.842 to 142.828
Index ranges	-6 ≤ <i>h</i> ≤ 6, -13 ≤ <i>k</i> ≤ 13, -20 ≤ <i>l</i> ≤ 20
Reflections collected	22527
Independent reflections	3402 [<i>R</i> _{int} = 0.0696, <i>R</i> _{sigma} = 0.0410]
Data/restraints/parameters	3402/1/224
Goodness-of-fit on <i>F</i> ²	1.042
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0455, <i>wR</i> ₂ = 0.1191
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0568, <i>wR</i> ₂ = 0.1220
Largest diff. peak/hole / e Å ⁻³	0.34/-0.22
Flack parameter	-0.035(15)

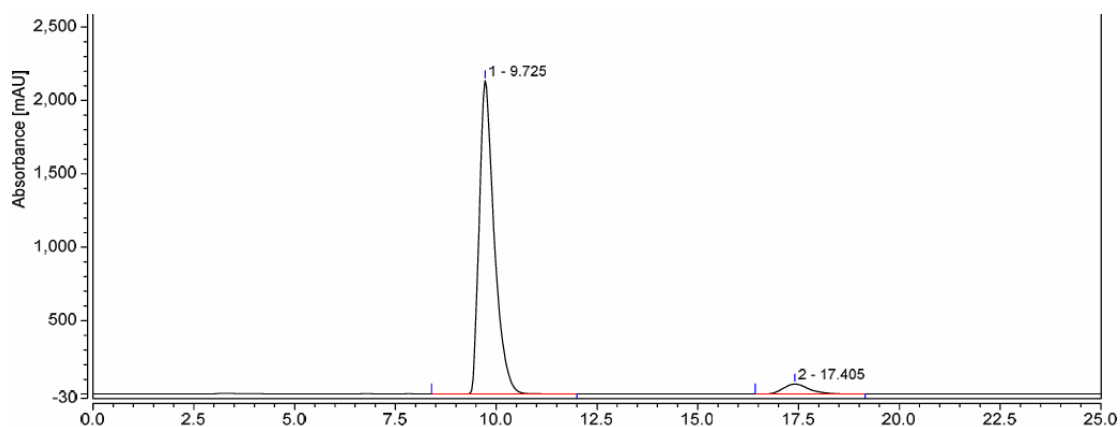
Gram-scale synthesis of **3aa**



In a dry test tube, chiral ArPNO **C4** (0.15 mmol, 5 mol%), sulfonimidamide **1a** (1.2310 g, 3 mmol), Cs_2CO_3 (0.3 mmol) and 4 Å MS (1.5 g) were added. Then, CHCl_3 (30 mL) was added and the reaction was stirred for 50 min at -50°C . Afterwards, chloroformate (348 μL , 4.5 mmol) was added and the reaction was stirred for 8 days at -50°C . Then, the reaction mixture was purified by silica gel chromatography using Pet/EtOAc system (Pet/EtOAc, 4/1, v/v) to give the product *R*-**3aa** as a colorless oil (1.1794 g, 84% yield, 90% ee).

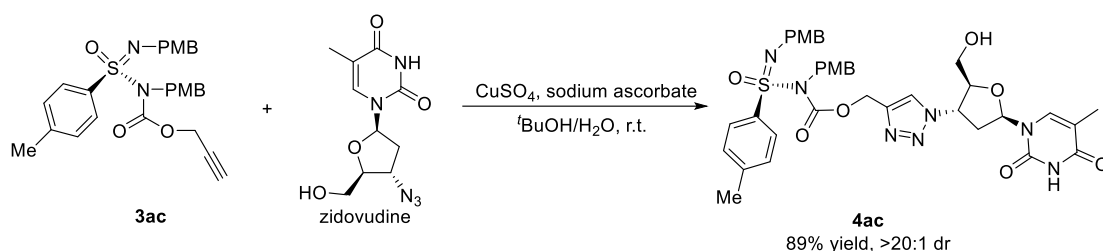


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.653	571.875	1386.089	49.92	64.46
2	16.662	573.771	764.163	50.08	35.54
Total:		1145.647	2150.252	100.00	100.00



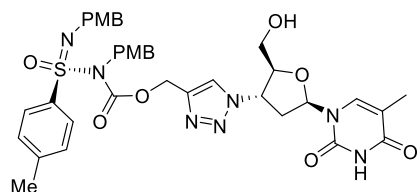
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.725	916.041	2133.929	94.84	96.93
2	17.405	49.822	67.657	5.16	3.07
Total:		965.864	2201.585	100.00	100.00

Transformations



In a dry test tube, **3ac** (49.2 mg, 0.1 mmol), zidovudine (40.1 mg, 0.15 mmol), CuSO₄ (20 mol%) and sodium ascorbate (60 mol%) were added. Then, ^tBuOH/H₂O (1:1, v/v, 1 mL) was added and the reaction was stirred for 12 hours at room temperature. Water and EtOAc were added to the solution, the organic layer was extracted, and the aqueous phase further extracted with EtOAc × 2 (50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated under vacuo. The residue was purified by column chromatography on silica gel (Pet/EtOAc = 1/8 as eluant) to afford **4ac** (67.6 mg, 89% yield).

(1-((2*S*,3*S*,5*R*)-2-(Hydroxymethyl)-5-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*))-yl)tetrahydrofuran-3-yl)-1*H*-1,2,3-triazol-4-yl)methyl (4-methoxybenzyl)((*R*)-*N*-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate (4ac**)**



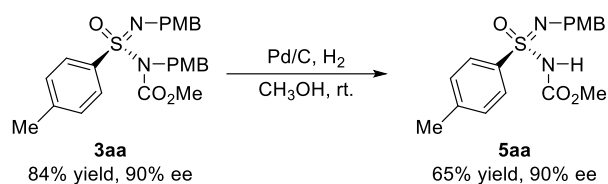
white solid, m.p.: 123.1-125.2 °C; 67.5 mg, 89% yield, > 20:1 dr; *R*_f = 0.28 (EtOAc); [*α*]_D^{25.0} = -2.9 (*c* = 0.35, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 9.71 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.46 (s, 1H), 7.43 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 4H), 6.19 (t, *J* = 6.0 Hz, 1H), 5.27-5.19 (m, 1H), 5.11 (s, 2H), 4.89 (q, *J* = 15.0 Hz, 2H), 4.25-4.20 (m, 2H), 3.96 (d, *J* = 14.4 Hz, 1H), 3.91 (d, *J* = 12.0 Hz, 1H), 3.76 (d, *J* = 13.2 Hz, 6H), 3.70-3.62 (m, 2H), 2.84-2.76 (m, 2H), 2.35 (s, 3H), 1.87 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 163.2, 158.1, 157.4, 152.2, 149.6, 142.8, 141.8, 135.7, 131.5, 129.4, 129.0, 128.1, 127.8, 127.5, 122.7, 112.8, 112.7, 110.2, 86.9, 84.1, 60.3, 58.5, 58.2, 54.4, 54.3, 49.3, 44.6, 36.6, 28.7, 20.5, 11.5.

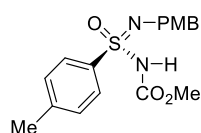
HRMS (ESI): exact mass calcd for C₃₇H₄₁N₇NaO₉S⁺ (*M*+*Na*)⁺ requires *m/z* 782.2579, found *m/z*

782.2578 ($\Delta = -1$ ppm).



To a 10 mL dry flask equipped with a magnetic stir bar, was added **3aa** (46.8 mg, 0.1 mmol), wet 5% Pd/C (3.0 equiv.), and CH₃OH (1 mL). The reactor was filled with H₂ using balloon and stirred at room temperature for 48 hours. The reaction mixture was then passed through a short pad of celite, and then washed with EA extensively. The filtrate was concentrated under reduced pressure and the residual was purified by a short flash column chromatography on silica gel (Pet/EtOAc = 1:1) to afford **5aa** (22.6 mg, 65% yield, 90% ee).

Methyl (*R*)-(N-(4-methoxybenzyl)-4-methylphenylsulfonimidoyl)carbamate (5aa**)**



white solid, m.p.: 125.3-126.9 °C; 22.6 mg, 65% yield, 90% ee; $R_f = 0.34$ (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{25.0} = -10.1$ ($c = 0.35$, CHCl₃).

HPLC CHIRALPAK ID, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 19.913 min (minor), 25.445 min (major).

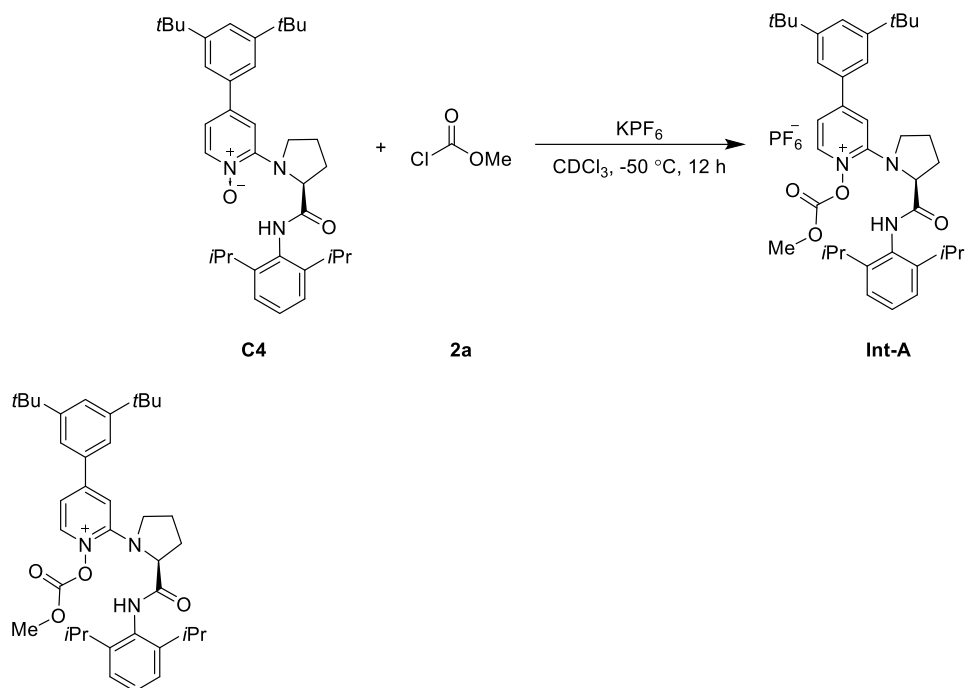
¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 7.10 (d, $J = 8.4$ Hz, 2H), 6.94 (s, 1H), 6.77 (d, $J = 7.8$ Hz, 2H), 4.14 (d, $J = 13.8$ Hz, 1H), 3.90 (d, $J = 13.8$ Hz, 1H), 3.76 (s, 3H), 3.57 (s, 3H), 2.42 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 159.3, 158.7, 144.3, 135.2, 129.9, 129.4, 128.1, 128.0, 114.1, 55.3, 53.1, 45.0, 21.7.

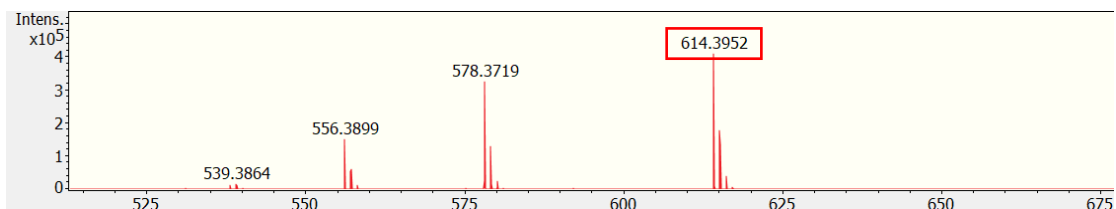
HRMS (ESI): exact mass calcd for C₁₇H₂₀N₂NaO₄S⁺ (M+Na)⁺ requires m/z 371.1036, found m/z 371.1039 ($\Delta = +3$ ppm).

HRMS experiment

In a dry test tube, chiral **C4** (0.02 mmol) and KPF_6 (0.024 mmol) were added. Then, CDCl_3 (0.2 mL) was added and the reaction was stirred for 12 hours at -50°C .



Exact Mass: 614.3952
Found: 614.3952



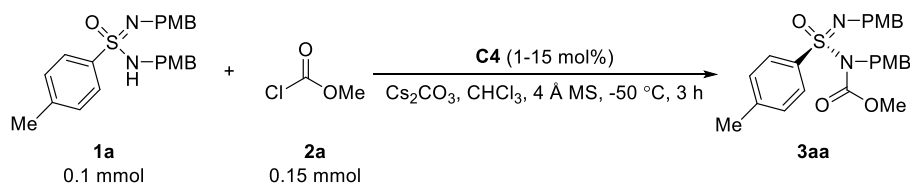
Kinetic experiments

1. General Procedure for Kinetic Experiments

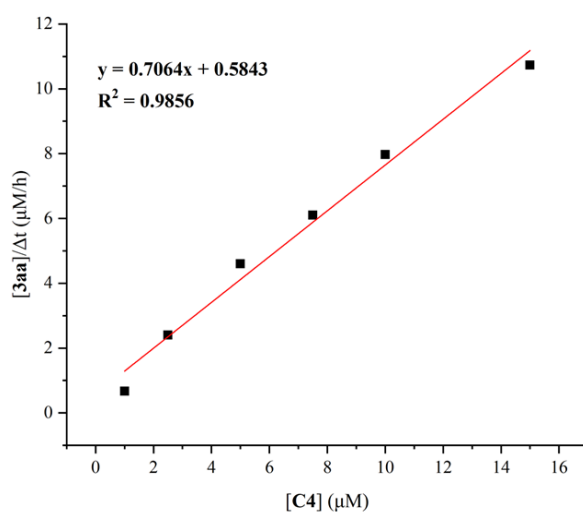
Kinetic experiments were run in test tubes. The data ([product] versus time) was analyzed using the initial rates method. For each reaction, the total amount of solvent CHCl_3 is 1 mL. Purification by flash column chromatography using gradient elution. The conversion data were determined by crude ^1H NMR spectra.

1) Order in catalyst **C4**

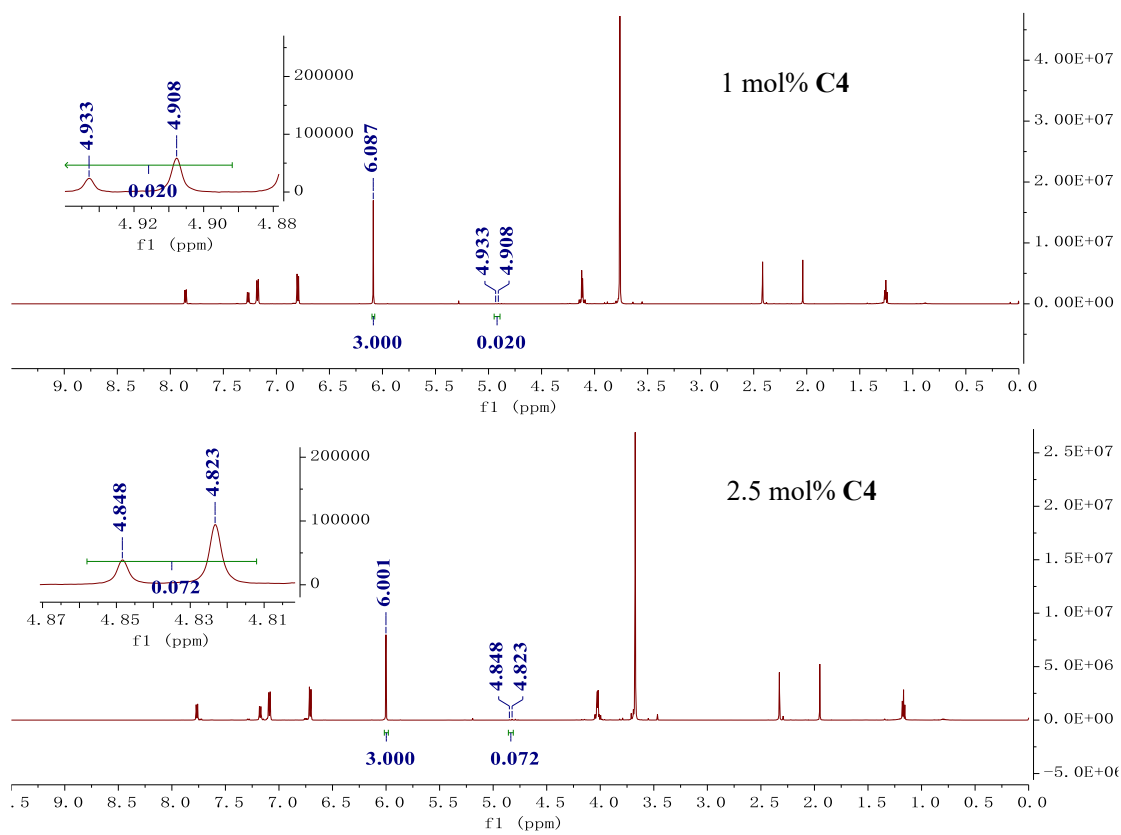
In a dry test tube, chiral **C4** (1-15 mol%), sulfonimidamide **1a** (41.0 mg, 0.1 mmol), Cs_2CO_3 (32.6 mg, 0.1 mmol) and 4 Å MS (50.0 mg) were added. Then, CHCl_3 (1 mL) was added and the reaction was stirred for 30 min at $-50\text{ }^\circ\text{C}$. Afterwards, chloroformate **2a** (11.6 μL , 0.15 mmol) was added and the reaction was stirred for 3 h at $-50\text{ }^\circ\text{C}$. Purification by flash column chromatography directly on silica gel using gradient elution to give the title product **3aa**. The conversion data were determined by crude ^1H NMR spectra by taking the reaction solution. The eluents were pure Pet and Pet/EtOAc (4/1, v/v).

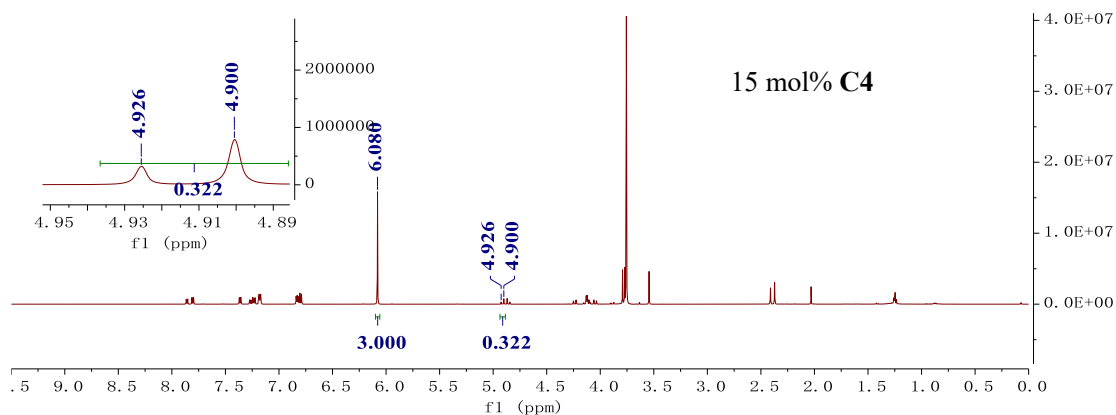
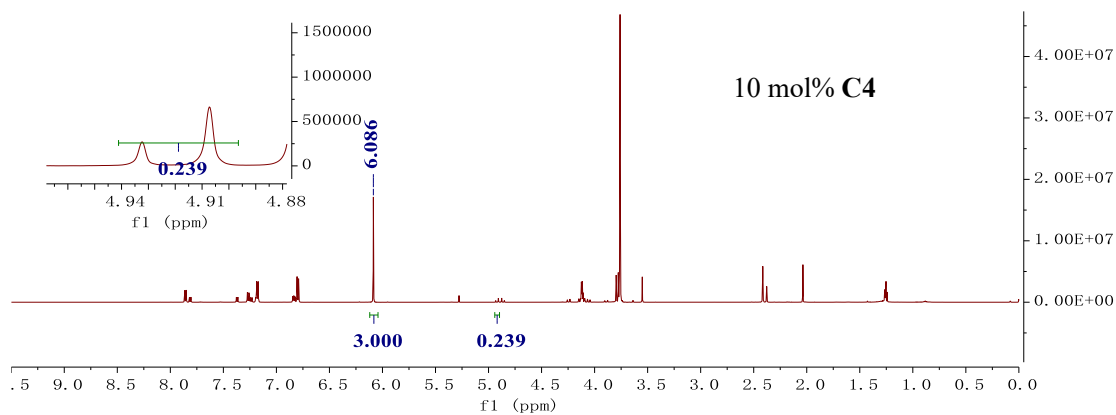
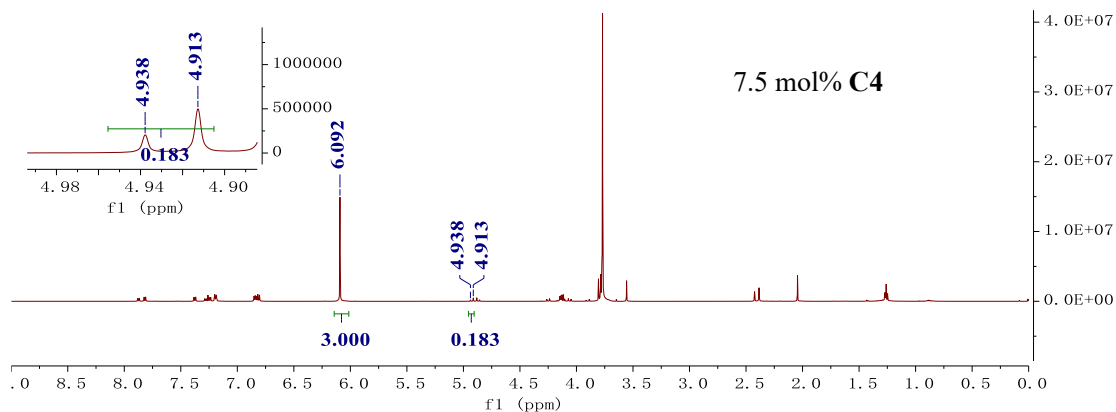
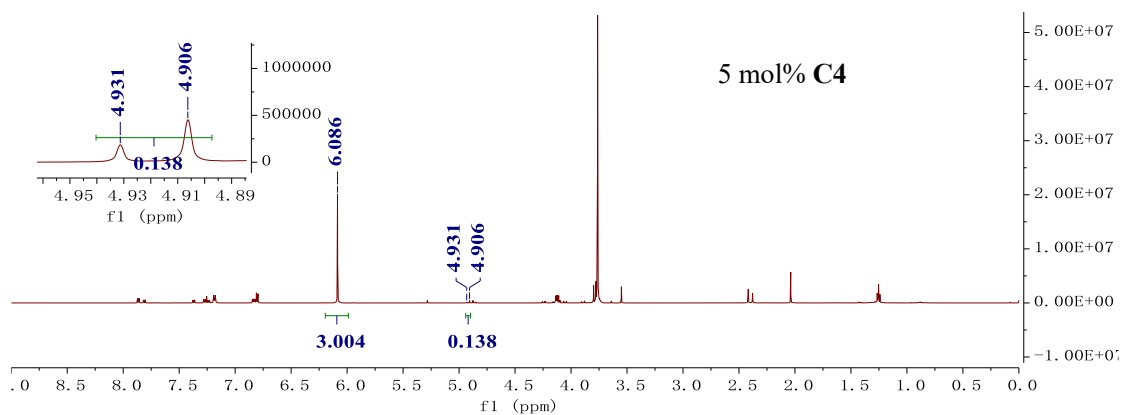


Entry	C4 (mol %)	[C4] μM	Conversion (3aa) (%)	Initial rate [$\mu\text{M}/\text{h}$]
1	1	1	2.0	0.67
2	2.5	2.5	7.2	2.40
3	5	5	13.8	4.60
4	7.5	7.5	18.3	6.10
5	10	10	23.9	7.97
6	15	15	32.2	10.73



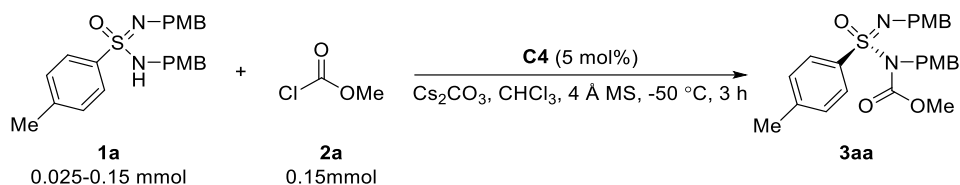
Plot of initial rates versus concentration of C4



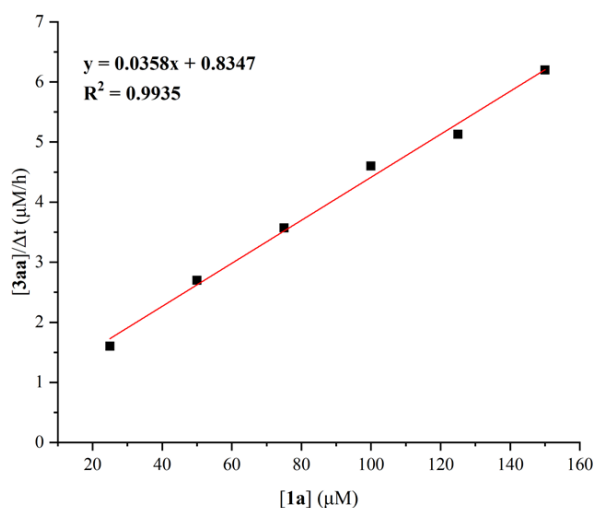


2) Order in sulfonimidamide **1a**

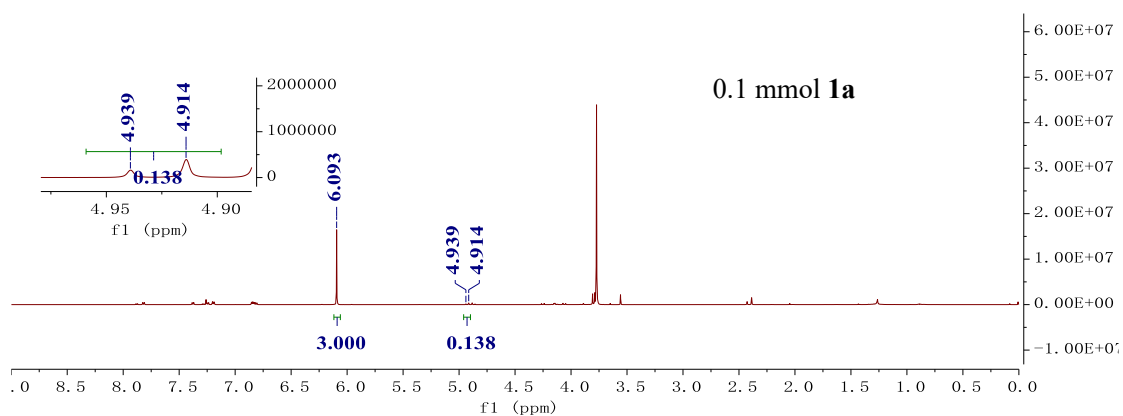
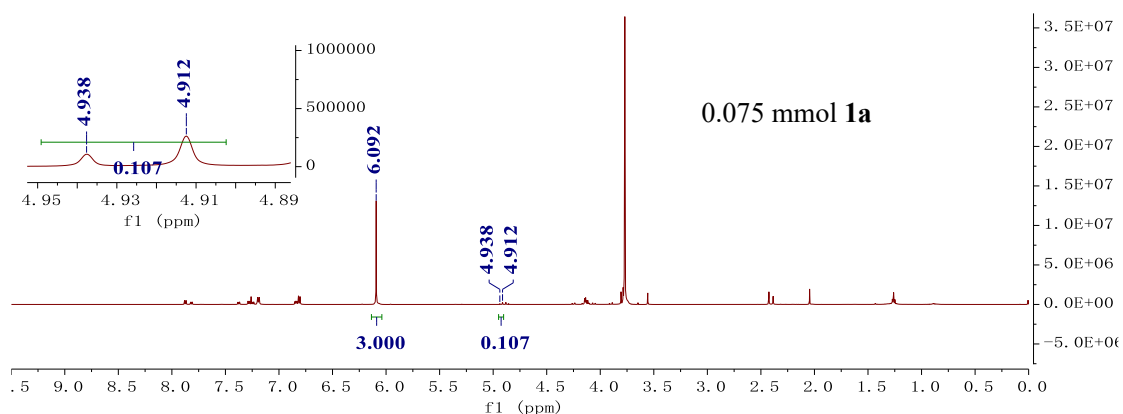
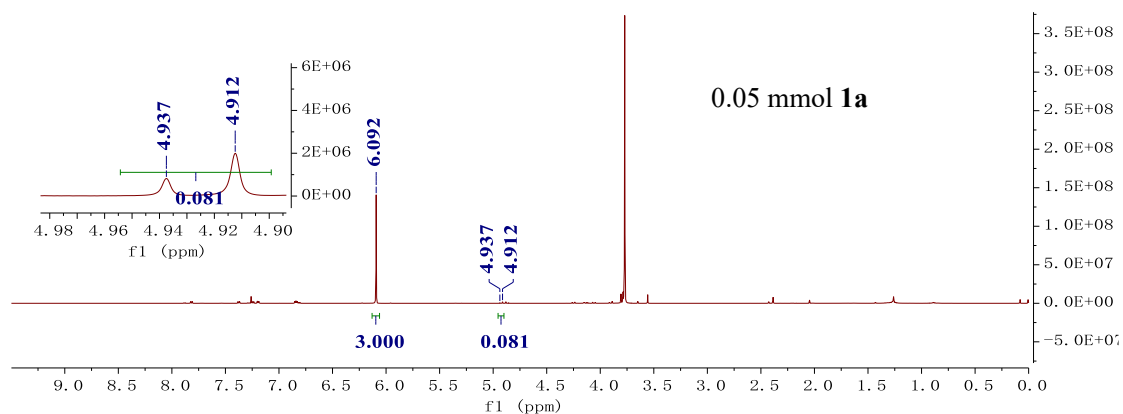
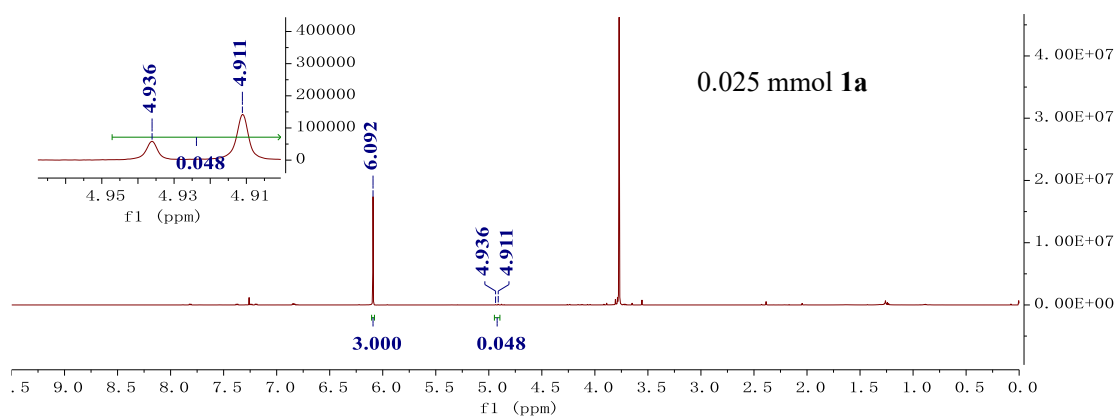
In a dry test tube, chiral **C4** (2.8 mg, 5 mol%), sulfonimidamide **1a** (10.3-61.5 mg, 0.025-0.15 mmol), Cs₂CO₃ (32.6 mg, 0.1 mmol) and 4 Å MS (50.0 mg) were added. Then, CHCl₃ (1 mL) was added and the reaction was stirred for 30 min at -50 °C. Afterwards, chloroformate **2a** (11.6 µL, 0.15 mmol) was added and the reaction was stirred for 3 h at -50 °C. Purification by flash column chromatography directly on silica gel using gradient elution to give the title product **3aa**. The conversion data were determined by crude ¹H NMR spectra by taking the reaction solution. The eluents were pure Pet and Pet/EtOAc (4/1, v/v).

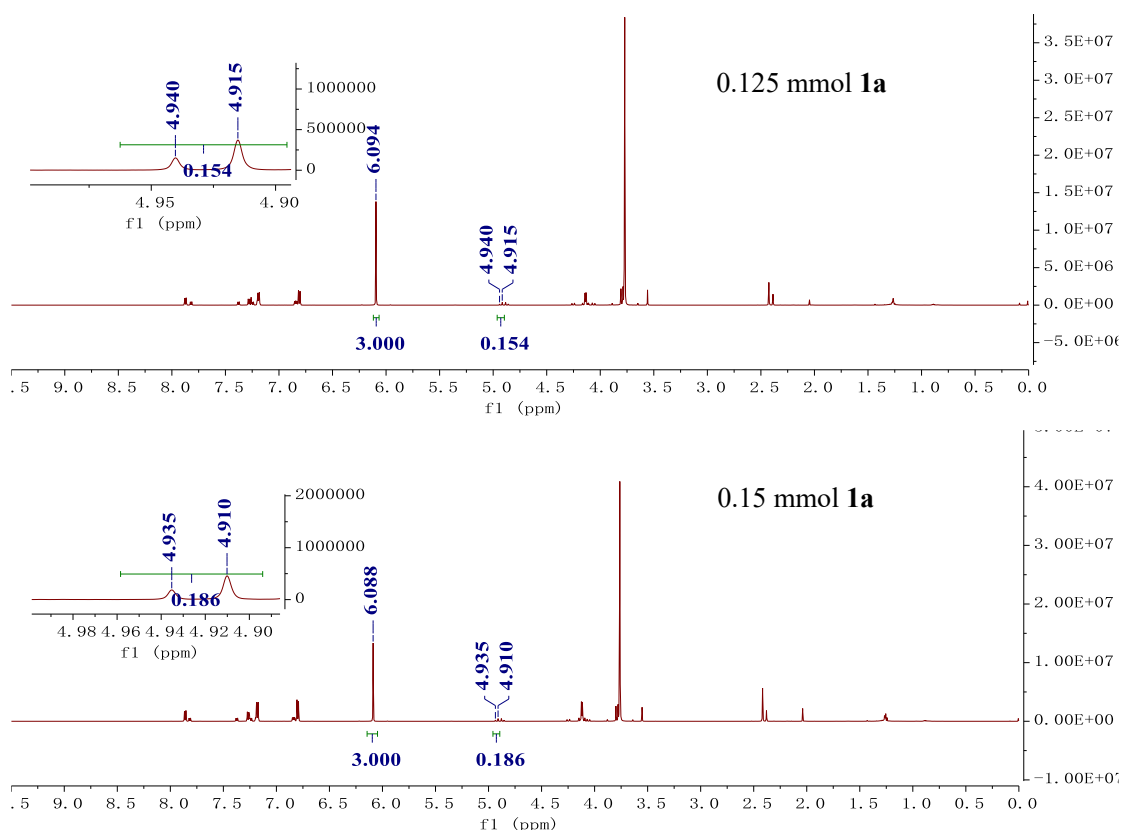


Entry	1a (mmol)	[1a] µM	Conversion (3aa) (%)	Initial rate [µM/h]
1	0.025	25	4.8	1.6
2	0.05	50	8.1	2.7
3	0.075	75	10.7	3.57
4	0.10	100	13.8	4.6
5	0.125	125	15.4	5.13
6	0.15	150	18.6	6.2



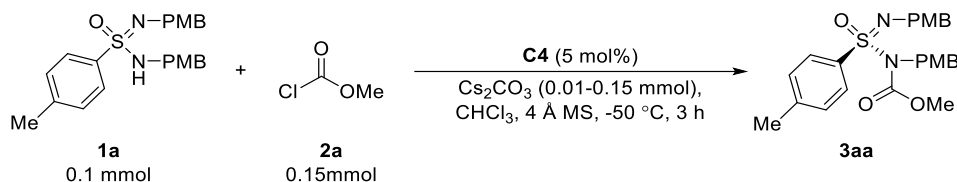
Plot of initial rates versus concentration of **1a**



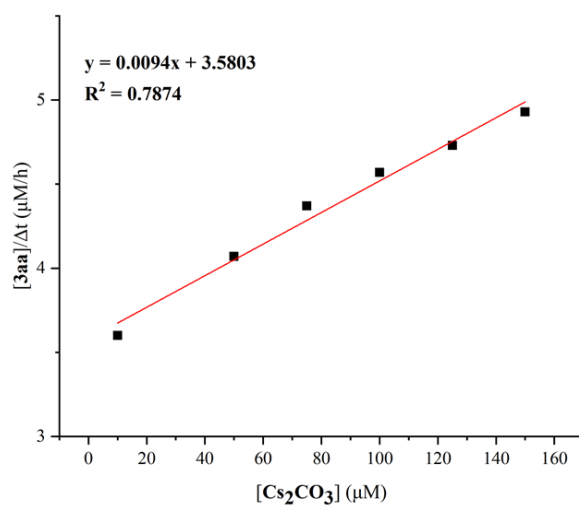


3) Order in Cs₂CO₃

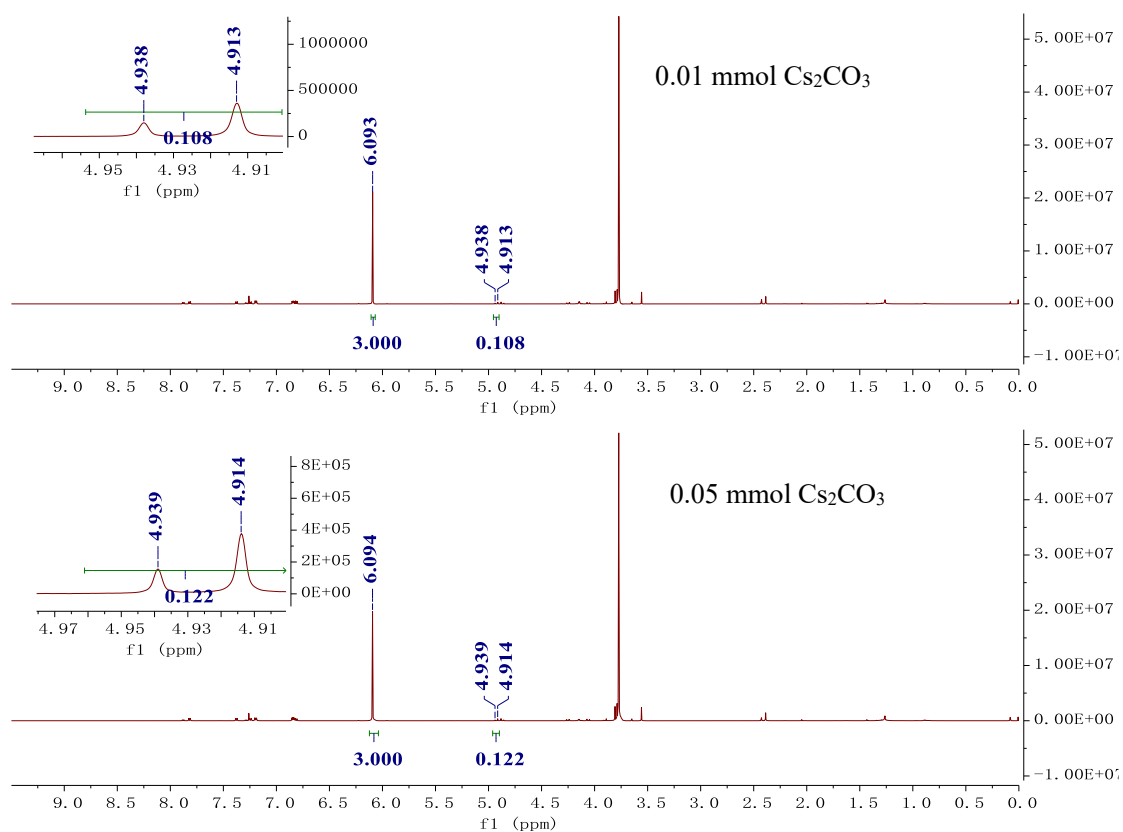
In a dry test tube, chiral **C4** (2.8 mg, 5 mol%), sulfonimidamide **1a** (41.0 mg, 0.1 mmol), Cs₂CO₃ (3.3-48.9 mg, 0.01-0.15 mmol) and 4 Å MS (50.0 mg) were added. Then, CHCl₃ (1 mL) was added and the reaction was stirred for 30 min at -50 °C. Afterwards, chloroformate **2a** (11.6 μL, 0.15 mmol) was added and the reaction was stirred for 3 h at -50 °C. Purification by flash column chromatography directly on silica gel using gradient elution to give the title product **3aa**. The conversion data were determined by crude ¹H NMR spectra by taking the reaction solution. The eluents were pure Pet and Pet/EtOAc (4/1, v/v).

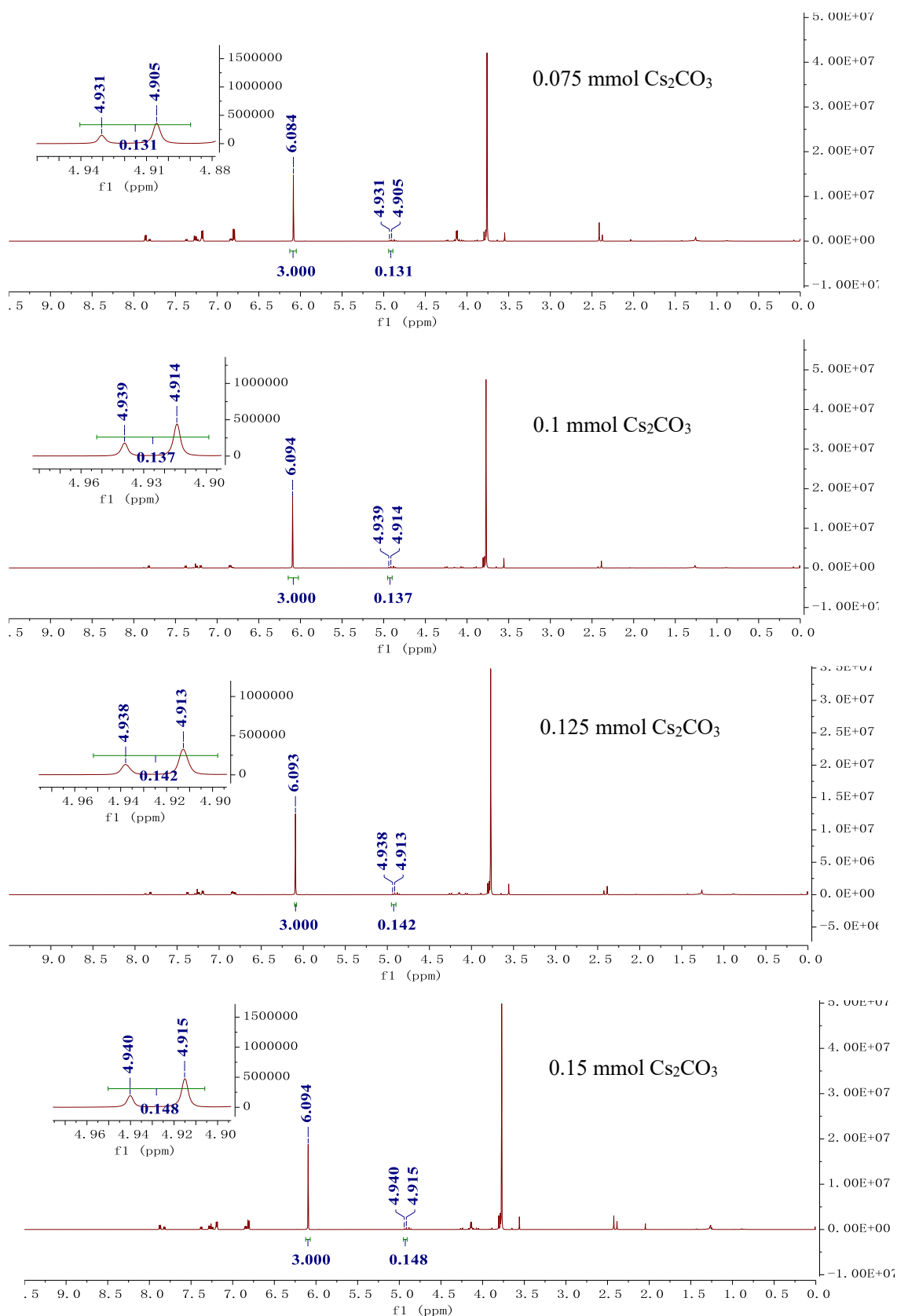


Entry	Cs ₂ CO ₃ (mmol)	[Cs ₂ CO ₃] μM	Conversion (3aa) (%)	Initial rate [μM/h]
1	0.01	10	10.8	3.6
2	0.05	50	12.2	4.07
3	0.075	75	13.1	4.37
4	0.1	100	13.7	4.57
5	0.125	125	14.2	4.73
6	0.15	150	14.8	4.93



Plot of initial rates versus concentration of Cs_2CO_3

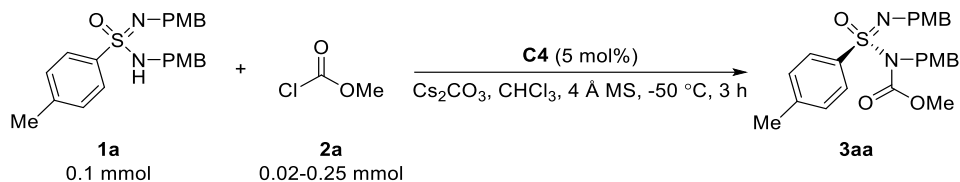




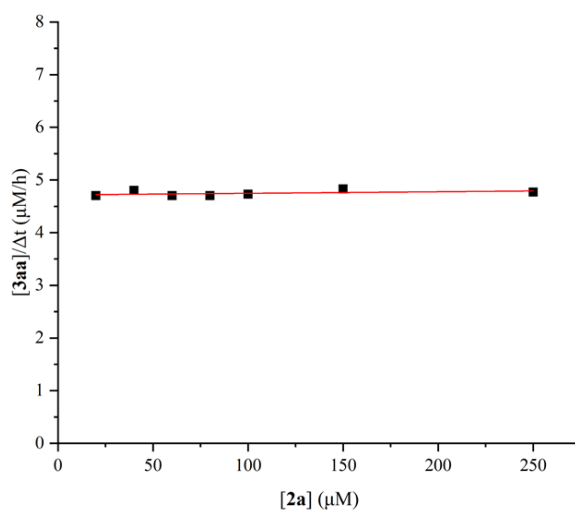
4) Order in chloroformate **2a**

In a dry test tube, chiral **C4** (2.8 mg, 5 mol%), sulfonimidamide **1a** (41.0 mg, 0.1 mmol), Cs_2CO_3 (32.6 mg, 0.1 mmol) and 4 Å MS (50.0 mg) were added. Then, CHCl_3 (1 mL) was added and the reaction was

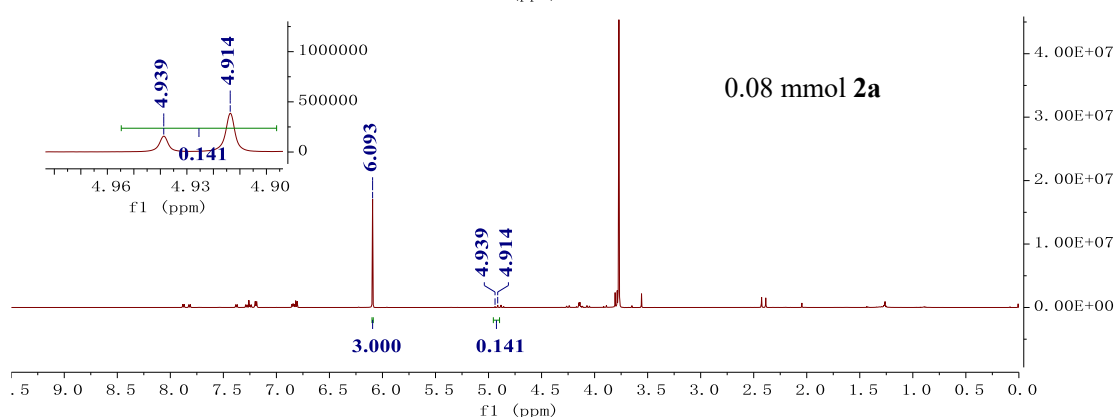
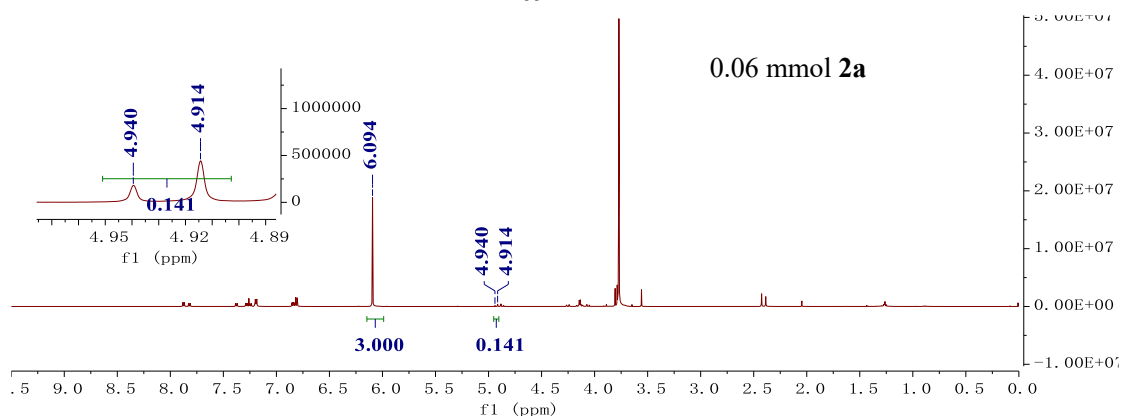
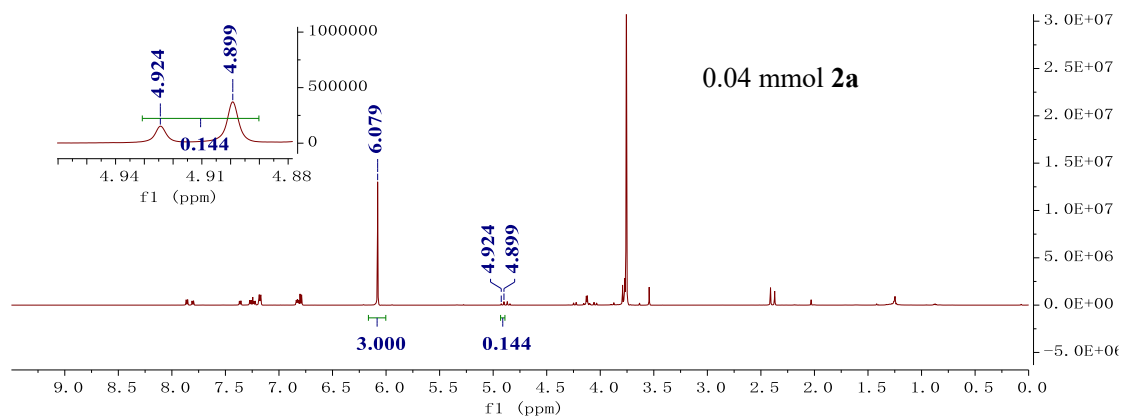
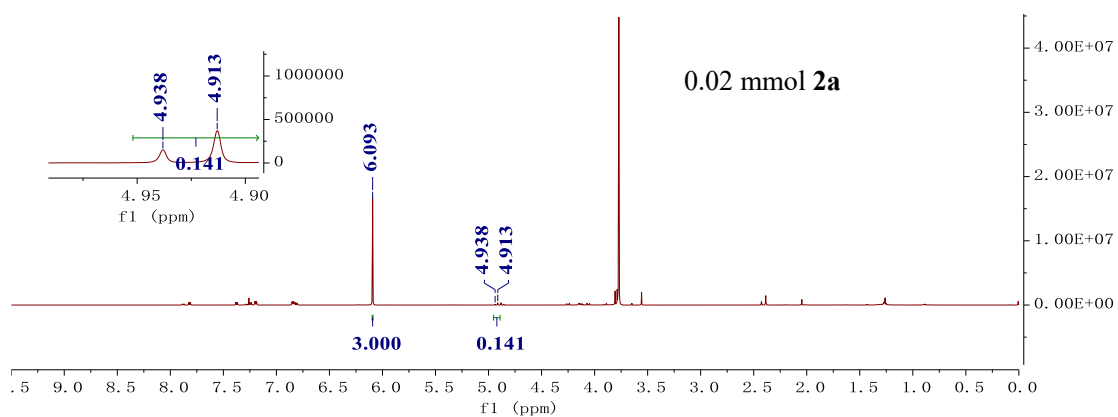
stirred for 30 min at -50 °C. Afterwards, chloroformate **2a** (1.6-19.4 μL , 0.02-0.25 mmol) was added and the reaction was stirred for 3 h at -50 °C. Purification by flash column chromatography directly on silica gel using gradient elution to give the title product **3aa**. The conversion data were determined by crude ^1H NMR spectra by taking the reaction solution. The eluents were pure Pet and Pet/EtOAc (4/1, v/v).

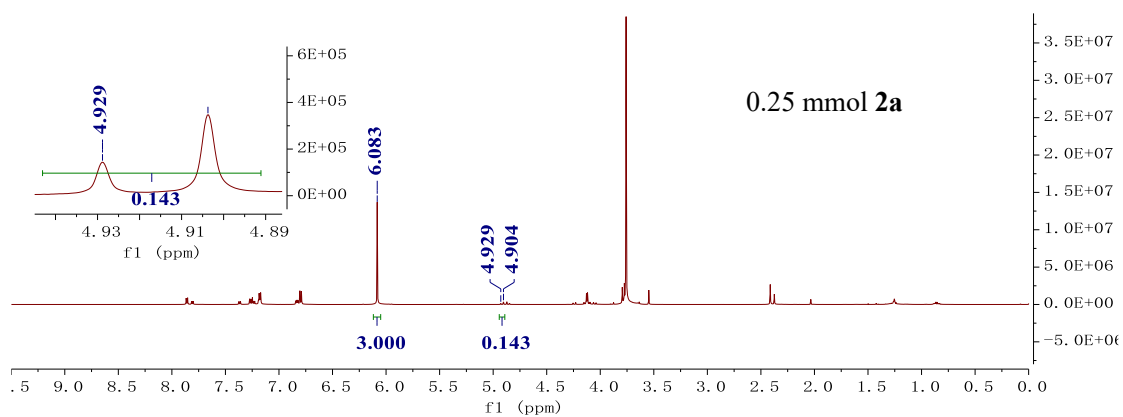
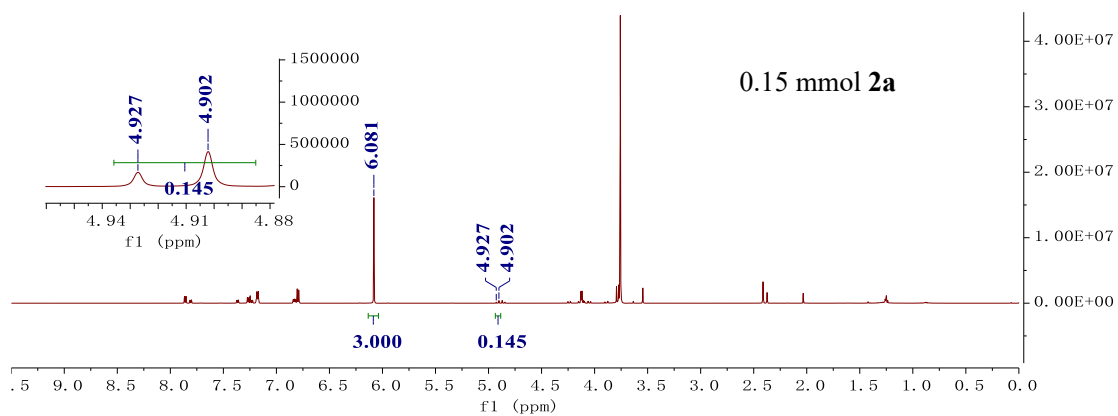
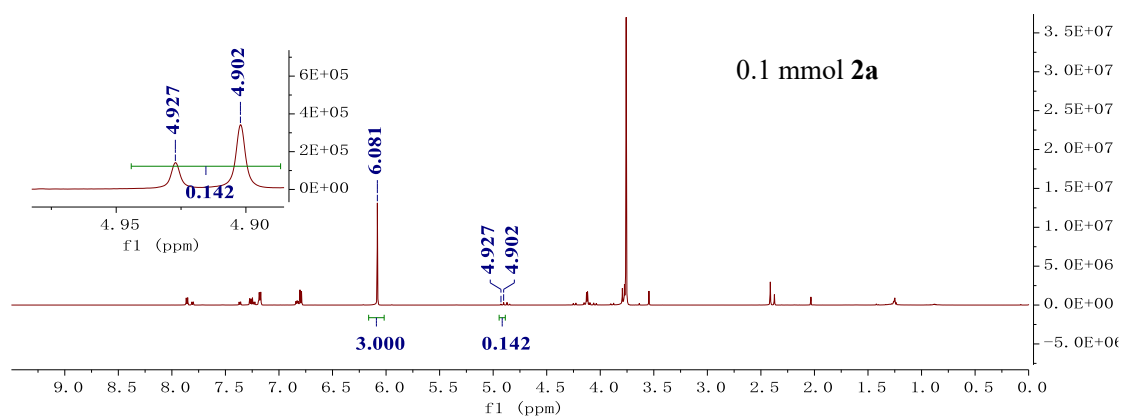


Entry	2a (mmol)	[2a] μM	Conversion (3aa) (%)	Initial rate [$\mu\text{M}/\text{h}$]
1	0.02	20	14.1	4.70
2	0.04	40	14.4	4.80
3	0.06	60	14.1	4.70
4	0.08	80	14.1	4.70
5	0.10	100	14.2	4.73
6	0.15	150	14.5	4.83
7	0.25	250	14.3	4.77



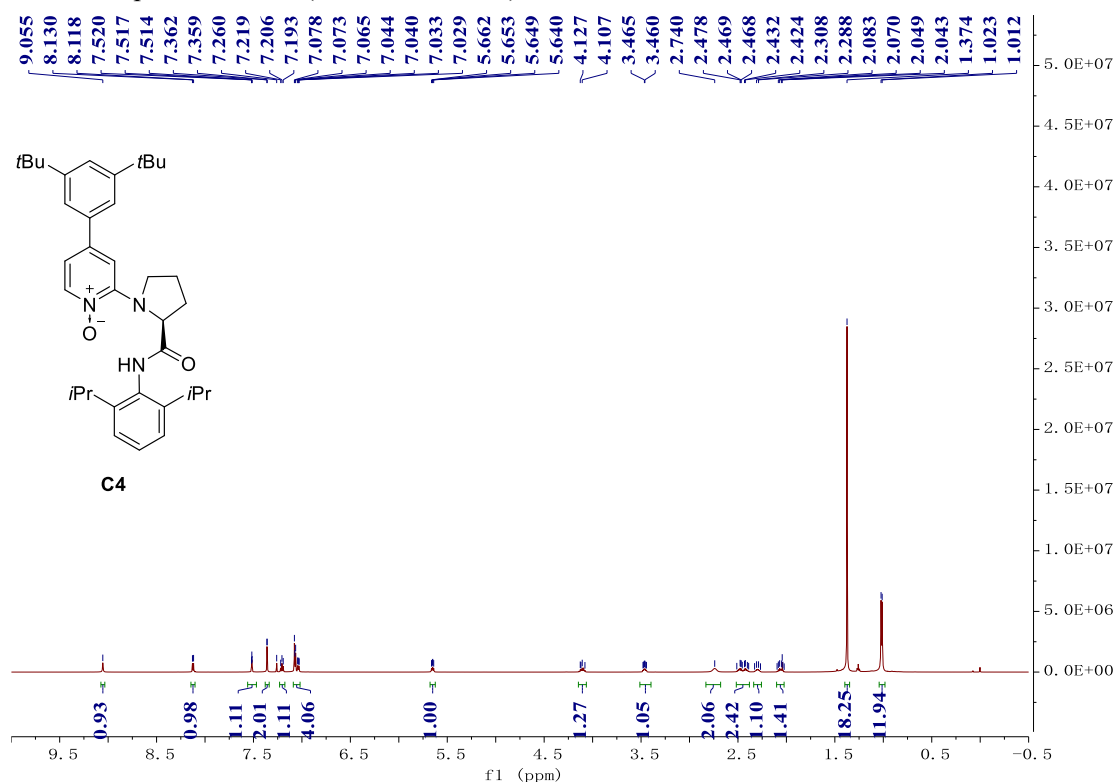
Plot of initial rates versus concentration of **2a**



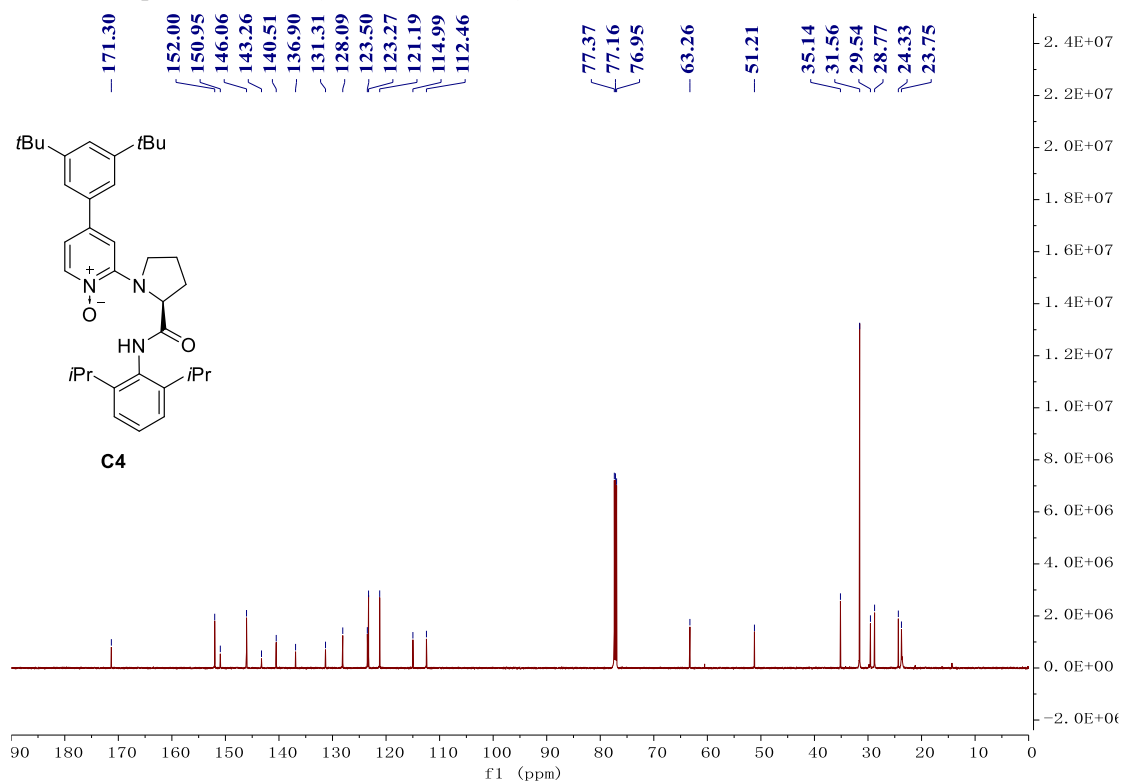


NMR Spectra

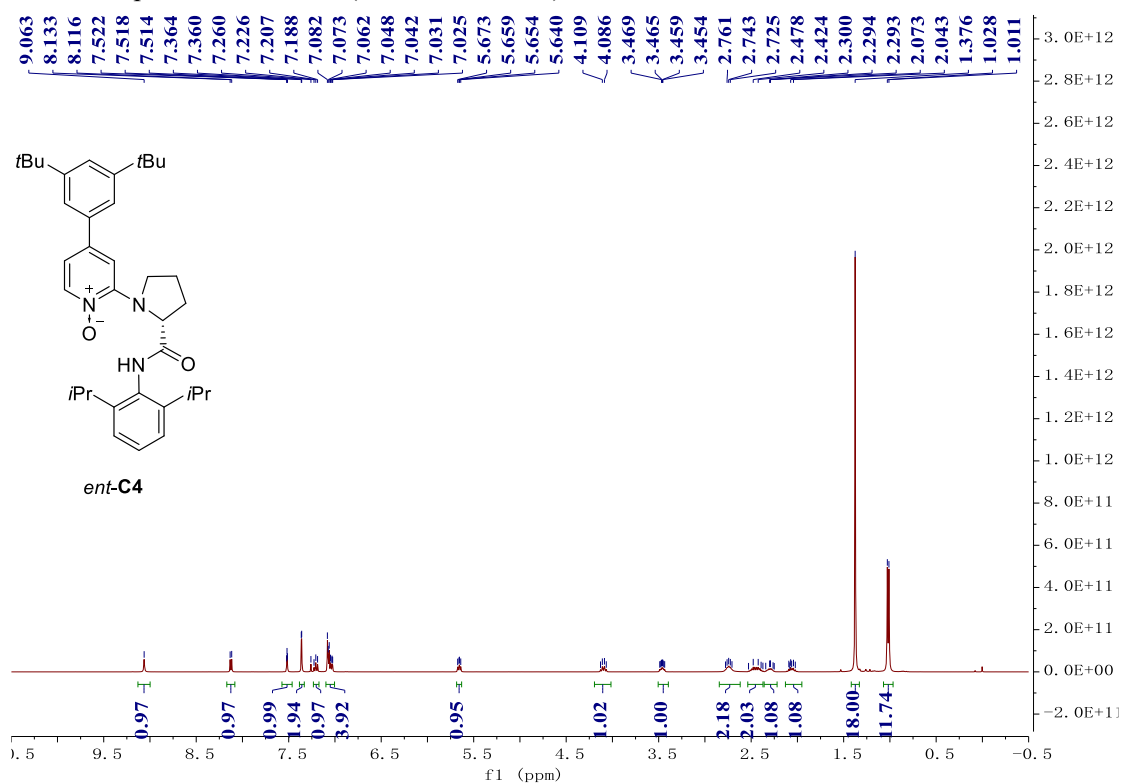
¹H NMR Spectrum of C4 (600 MHz, CDCl₃)



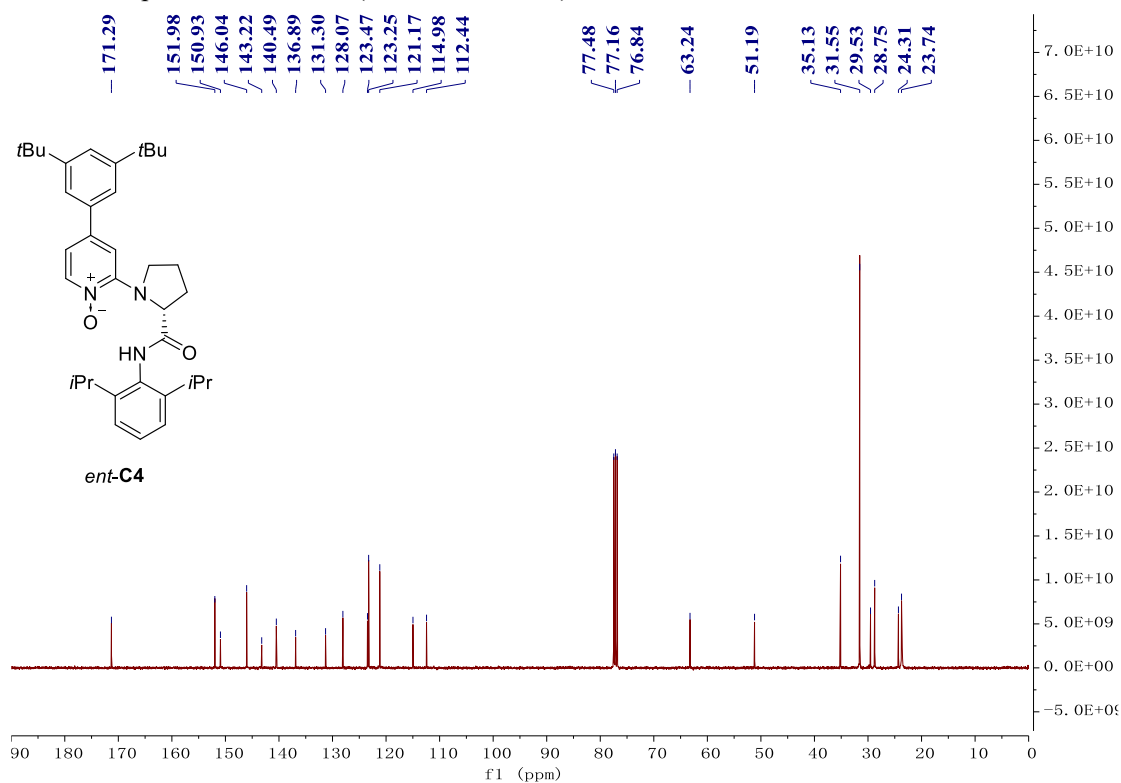
¹³C NMR Spectrum of C4 (150 MHz, CDCl₃)



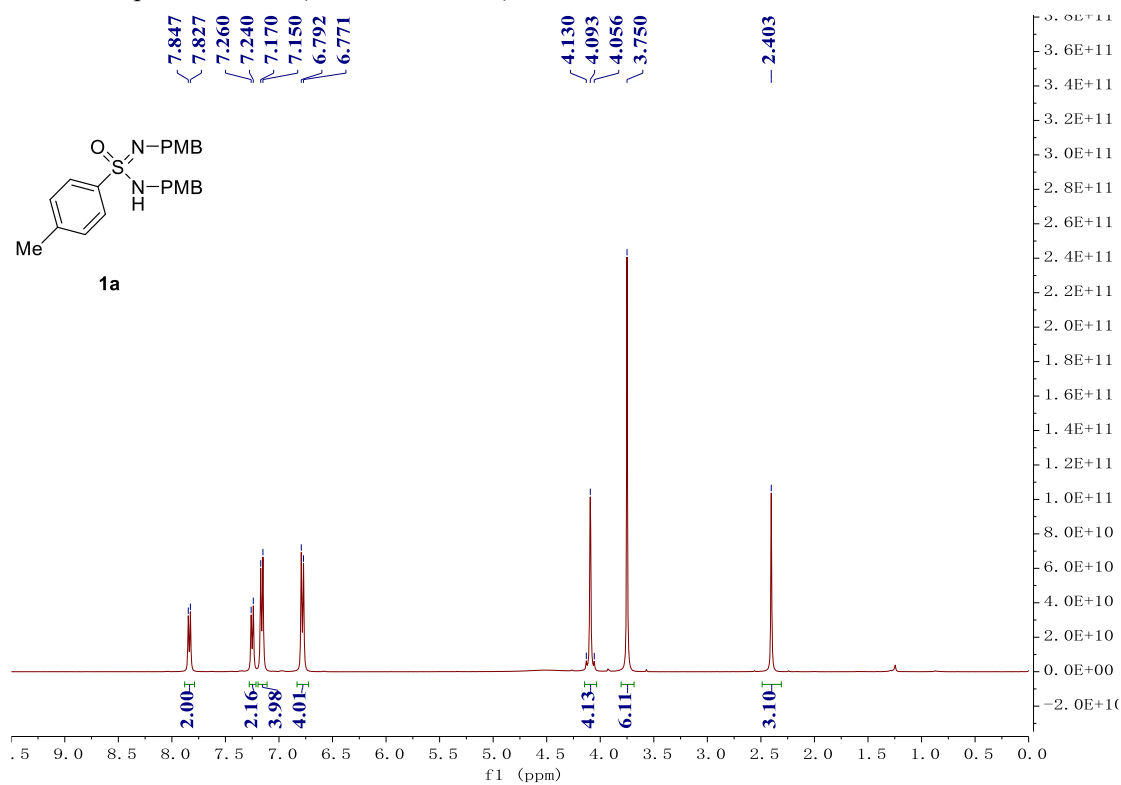
¹H NMR Spectrum of *ent*-C4 (400 MHz, CDCl₃)



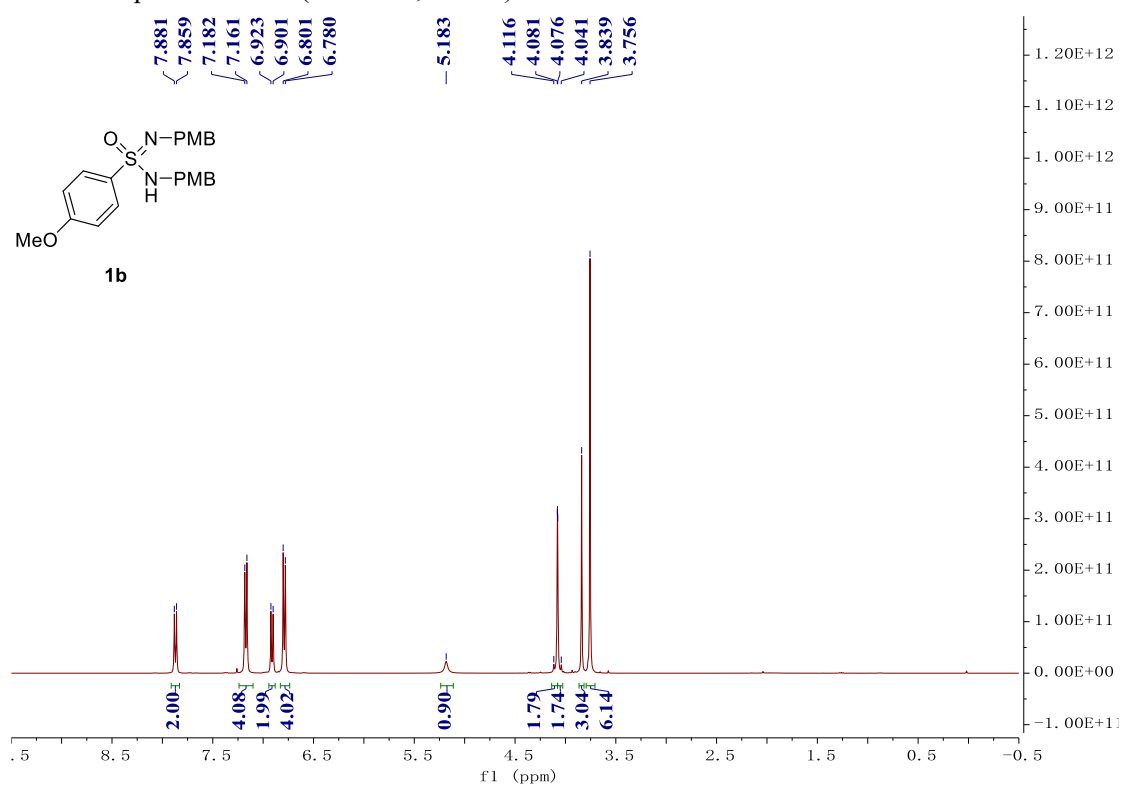
¹³C NMR Spectrum of *ent*-C4 (100 MHz, CDCl₃)



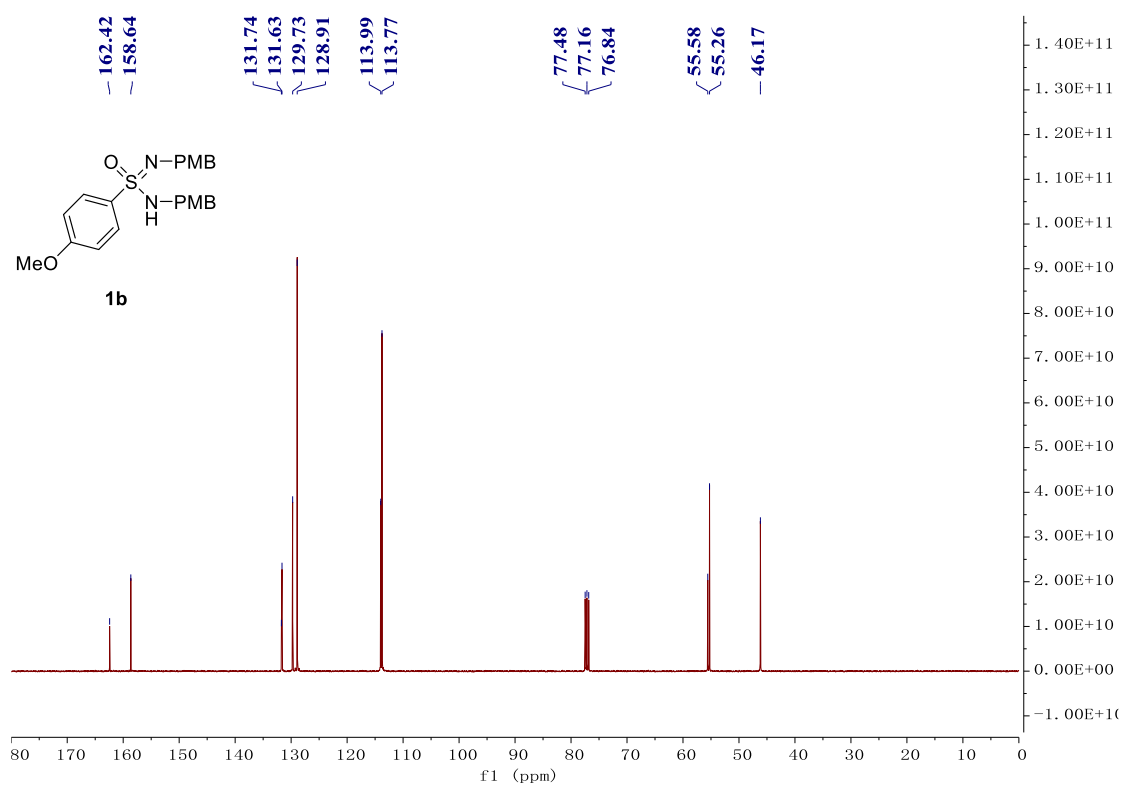
¹H NMR Spectrum of **1a** (400 MHz, CDCl₃)



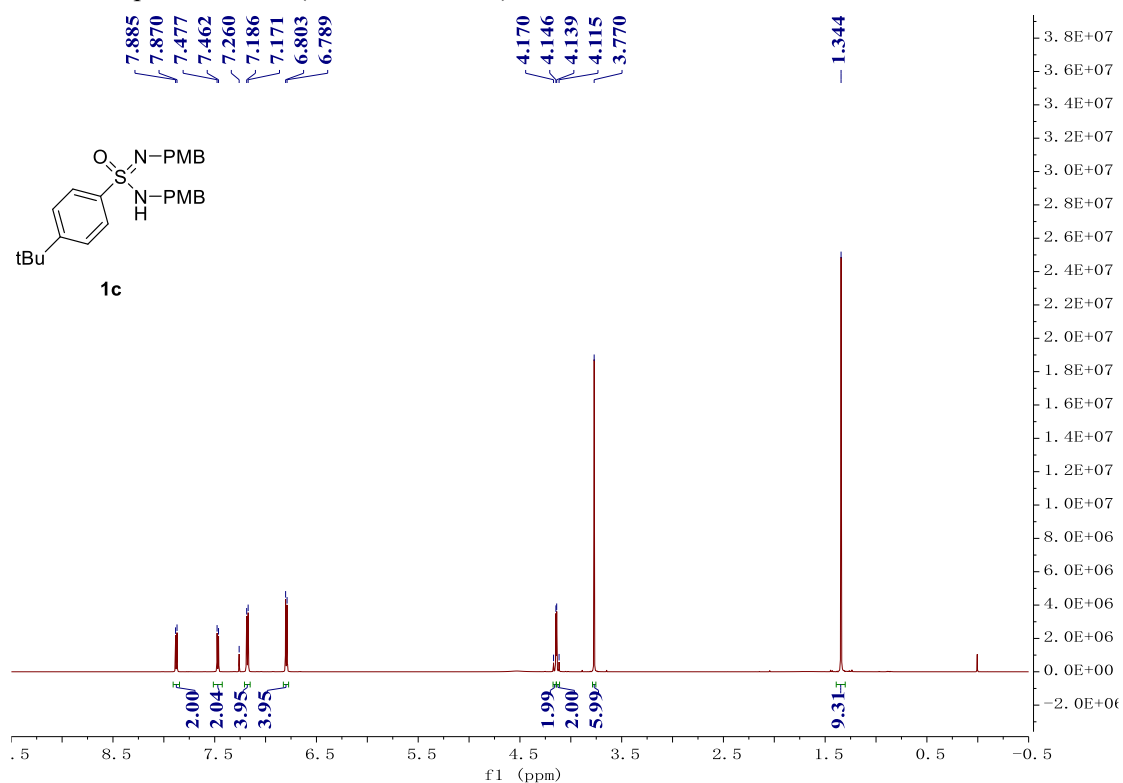
¹H NMR Spectrum of **1b** (400 MHz, CDCl₃)



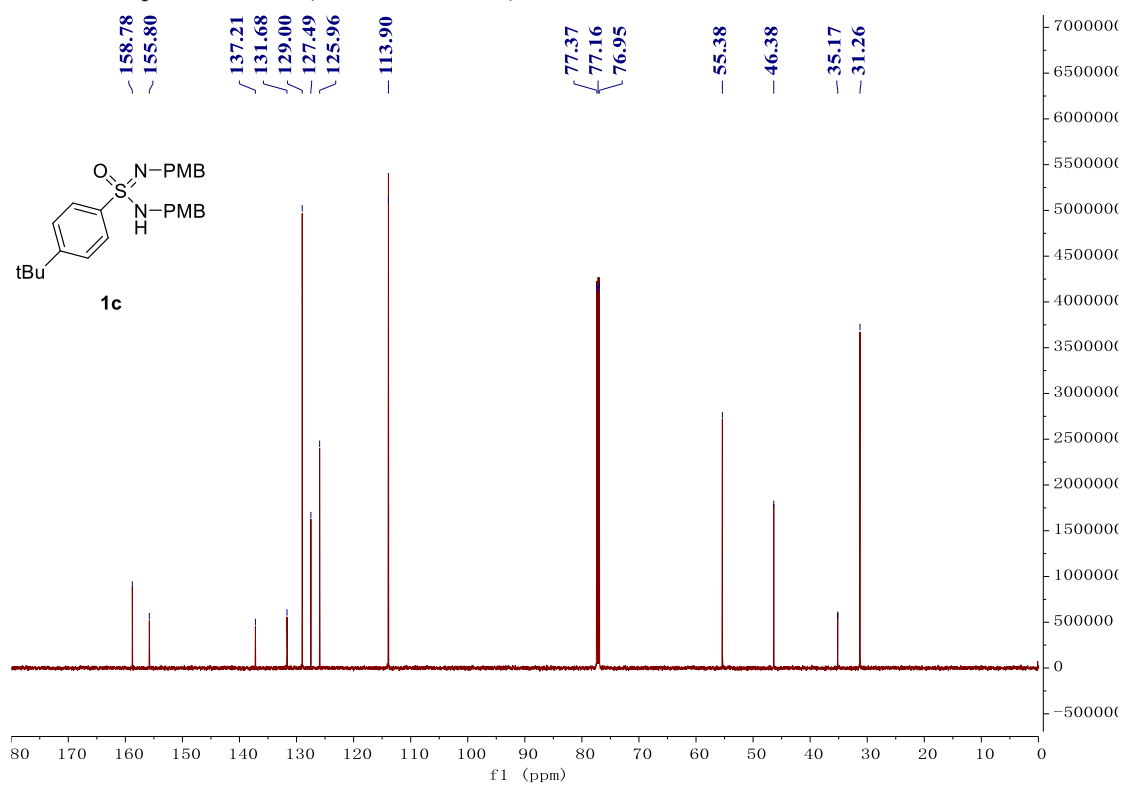
^{13}C NMR Spectrum of **1b** (100 MHz, CDCl_3)



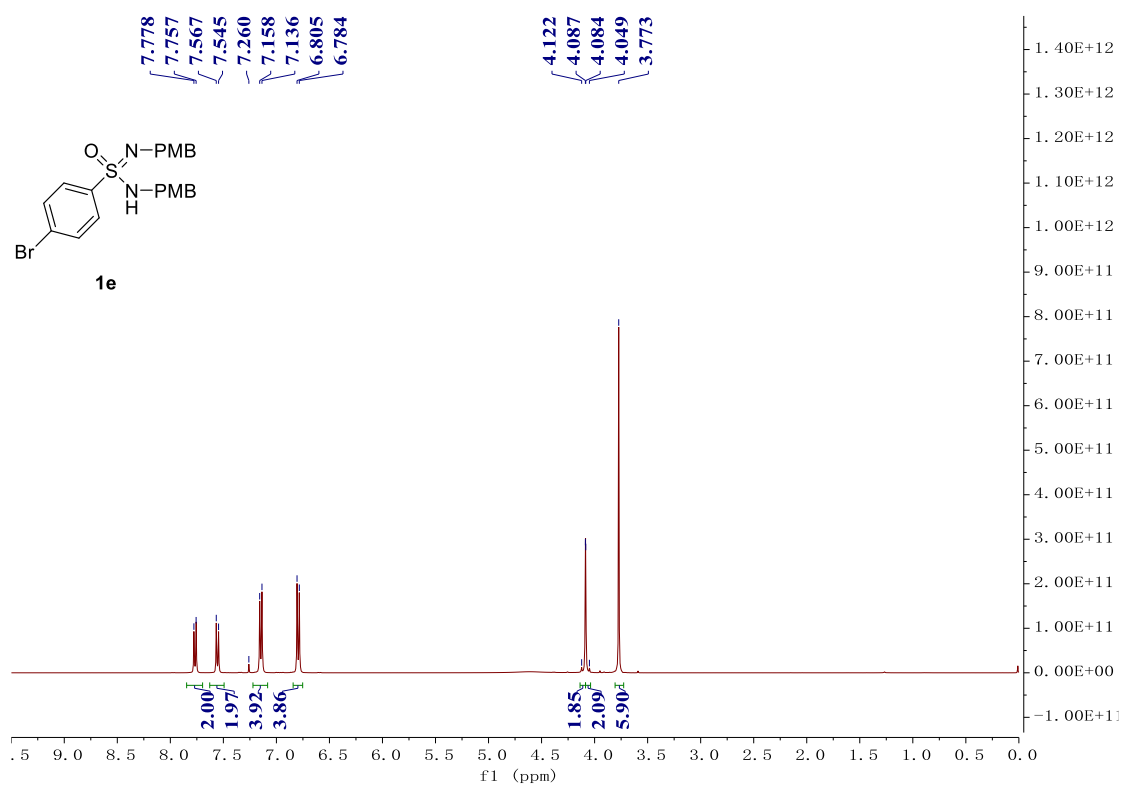
^1H NMR Spectrum of **1c** (600 MHz, CDCl_3)



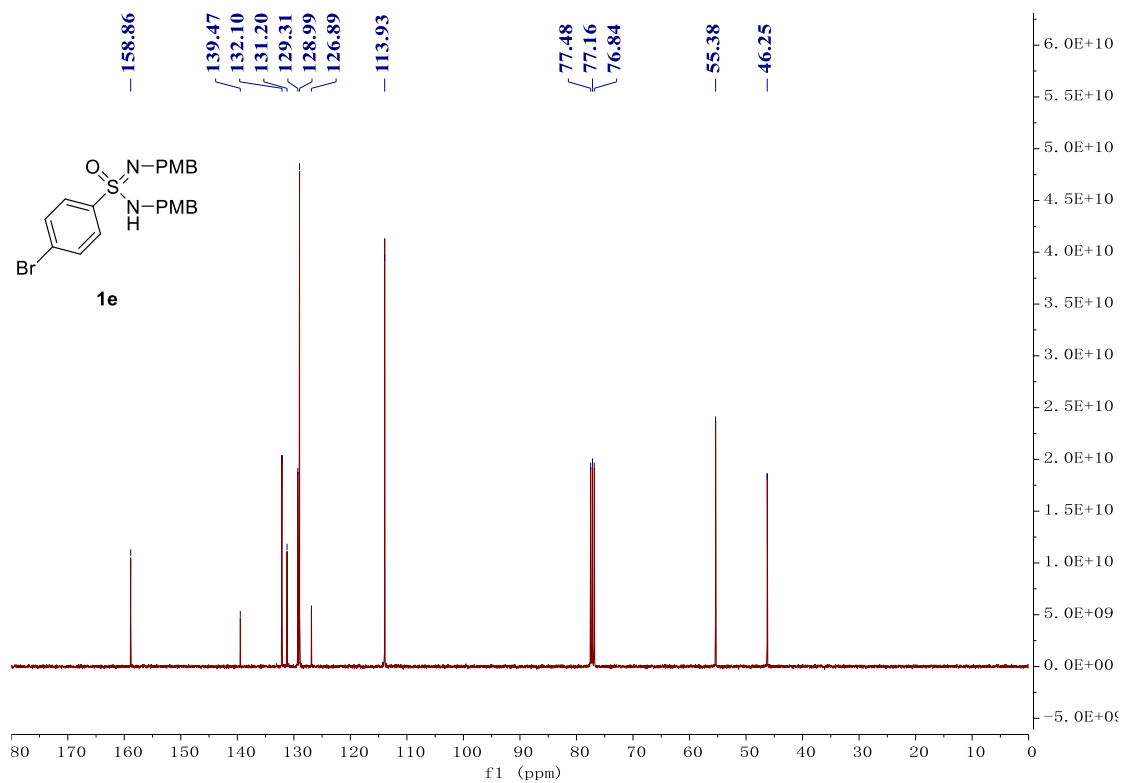
^{13}C NMR Spectrum of **1c** (150 MHz, CDCl_3)



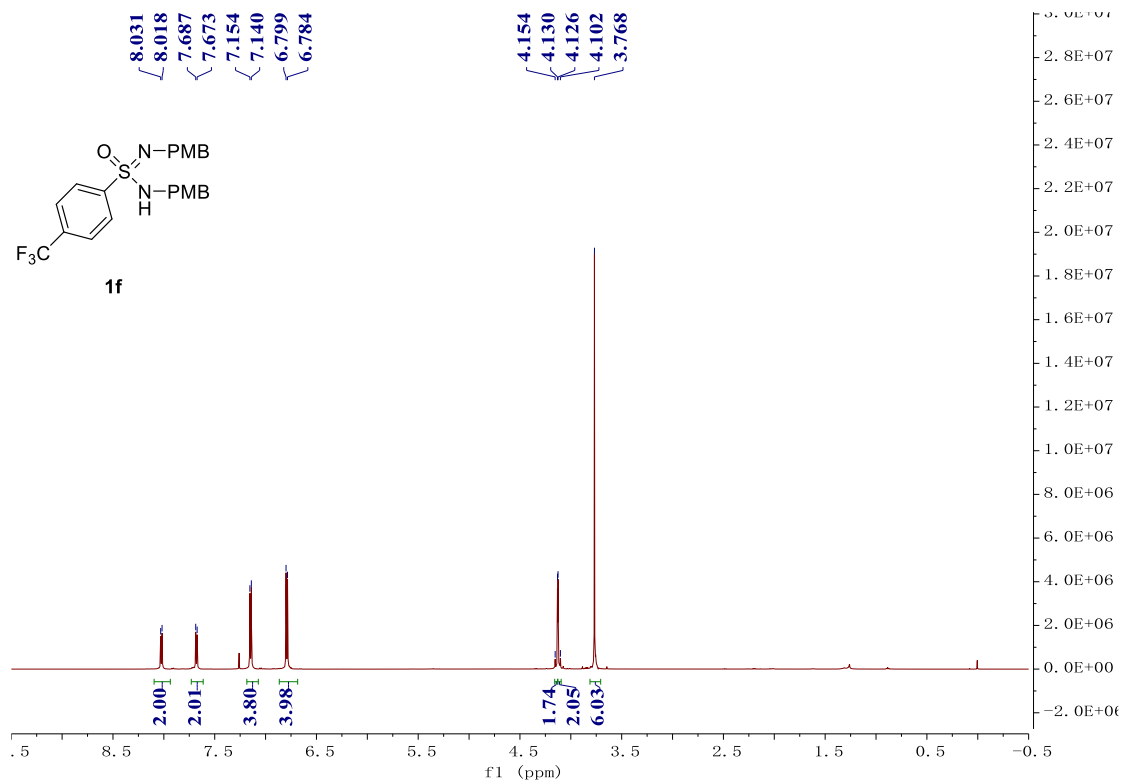
^1H NMR Spectrum of **1e** (400 MHz, CDCl_3)



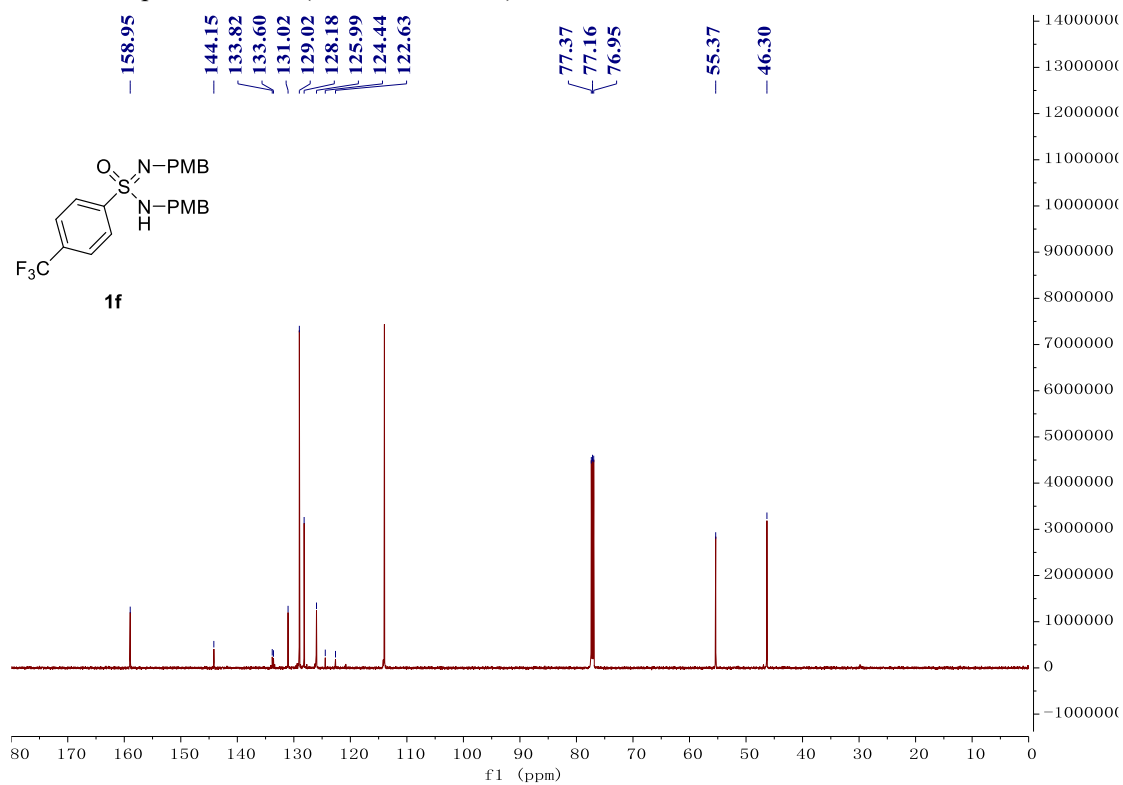
^{13}C NMR Spectrum of **1e** (100 MHz, CDCl_3)



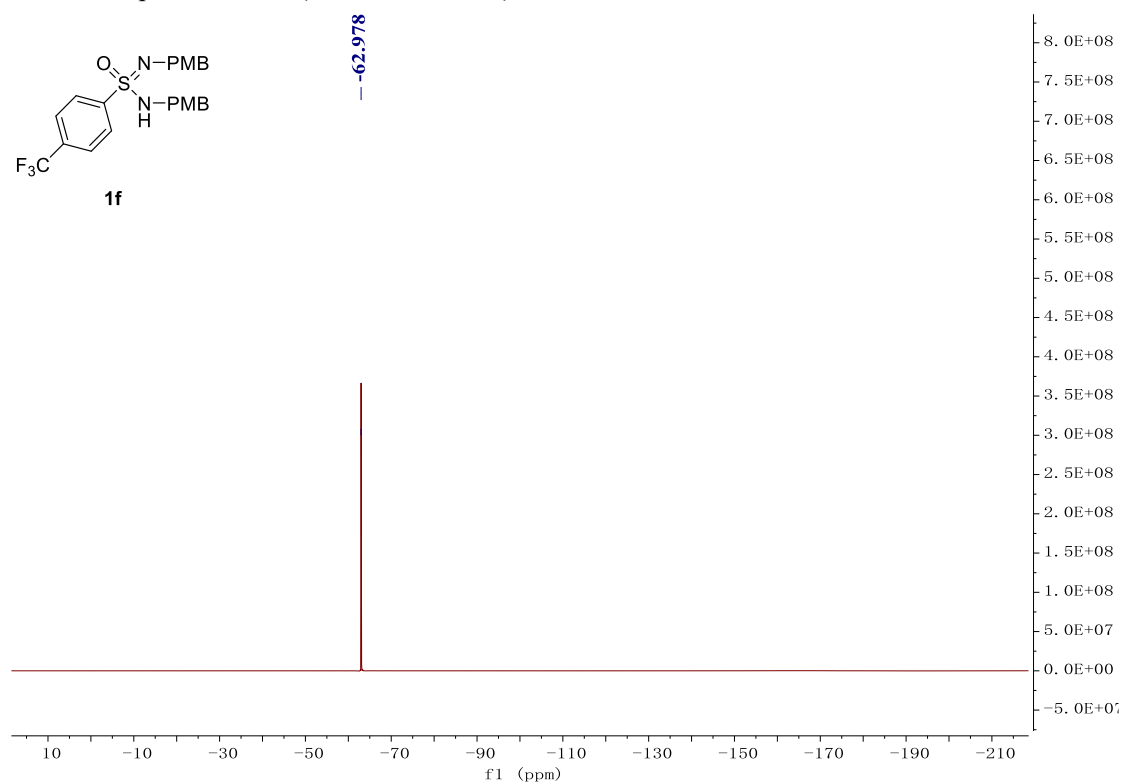
^1H NMR Spectrum of **1f** (600 MHz, CDCl_3)



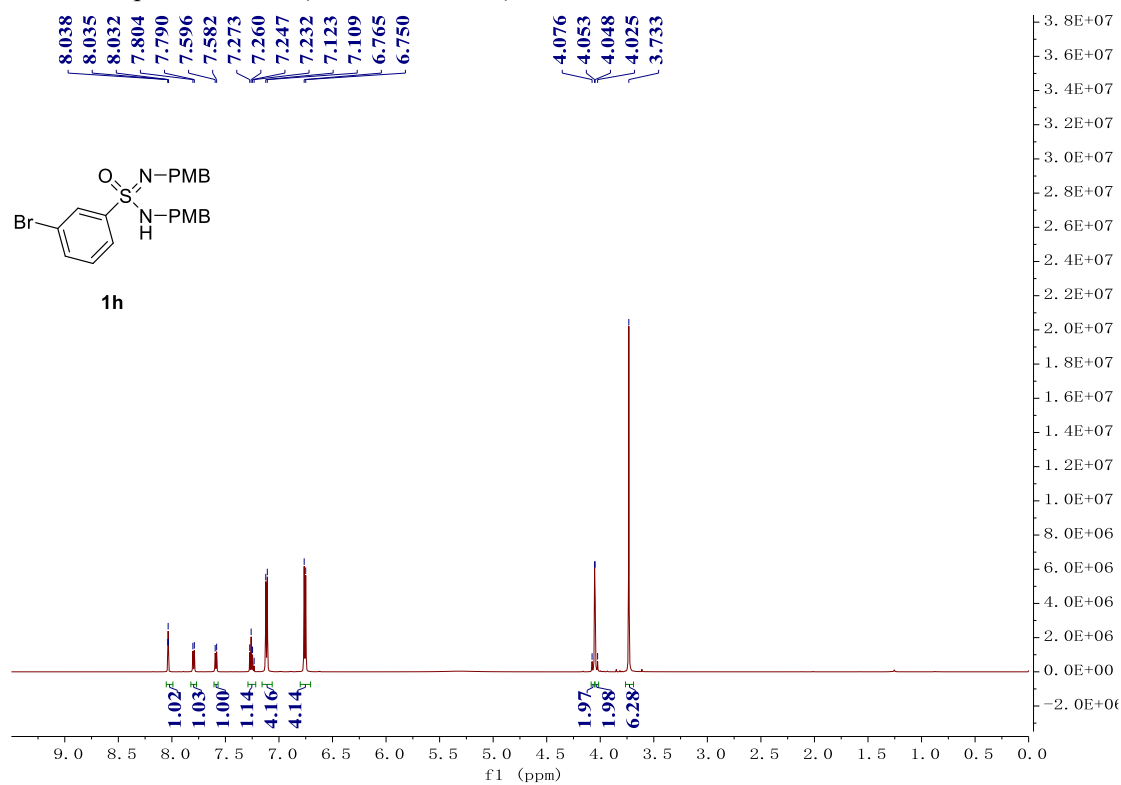
^{13}C NMR Spectrum of **1f** (150 MHz, CDCl_3)



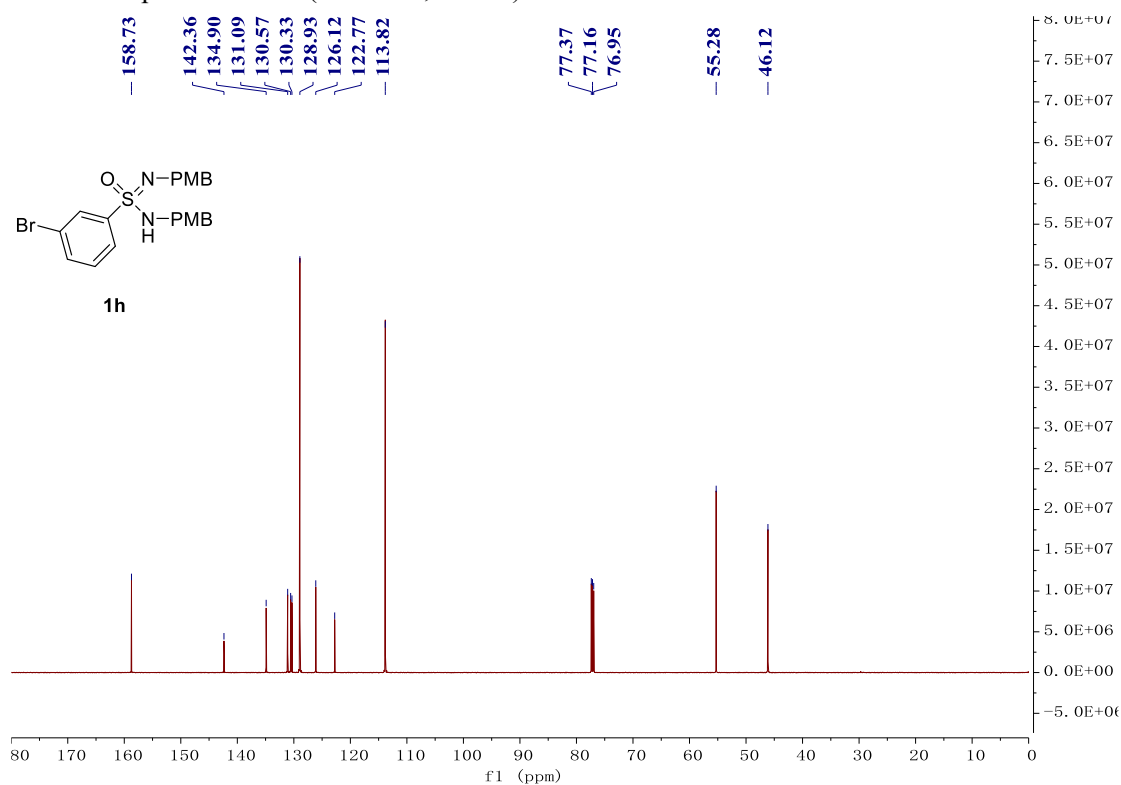
^{19}F NMR Spectrum of **1f** (565 MHz, CDCl_3)



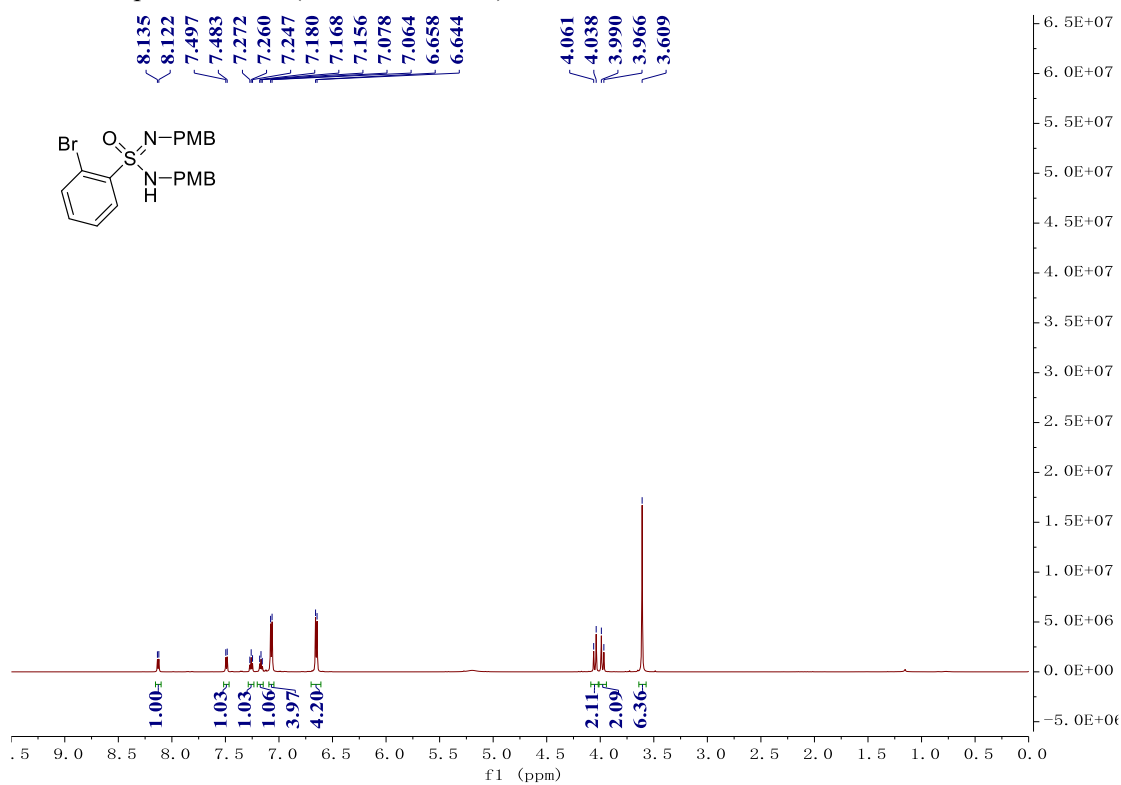
^1H NMR Spectrum of **1h** (600 MHz, CDCl_3)



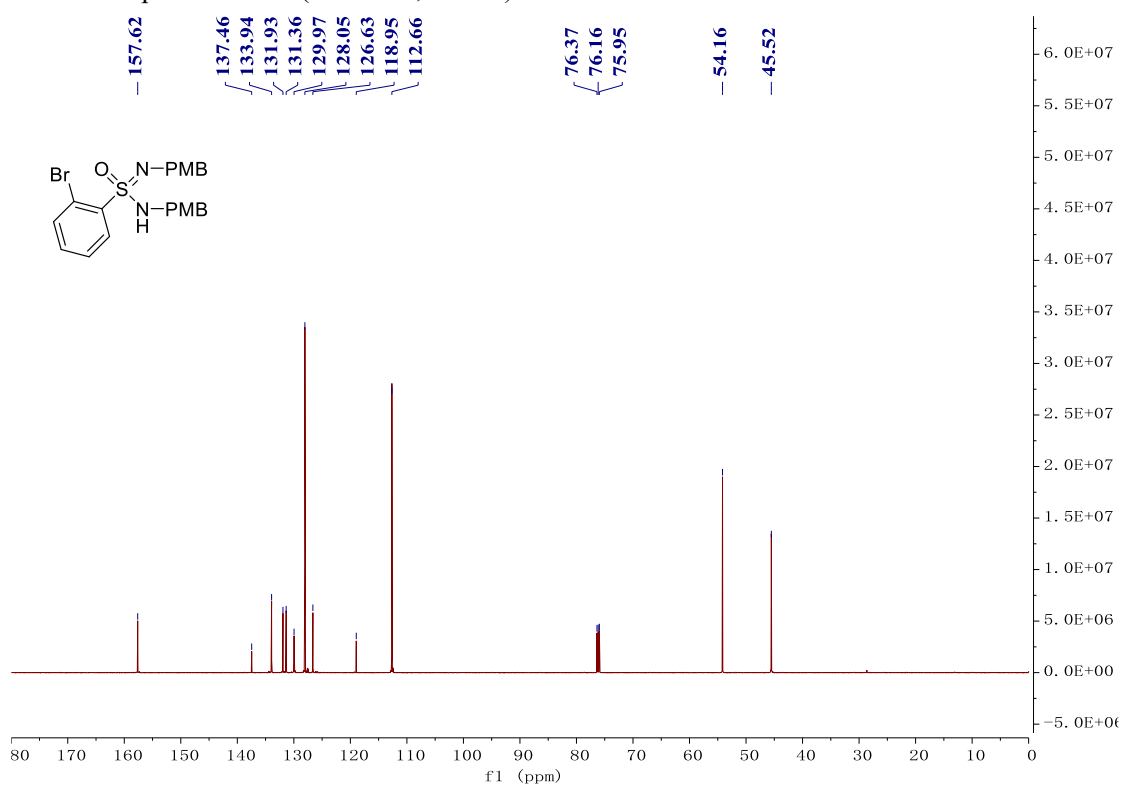
^{13}C NMR Spectrum of **1h** (150 MHz, CDCl_3)



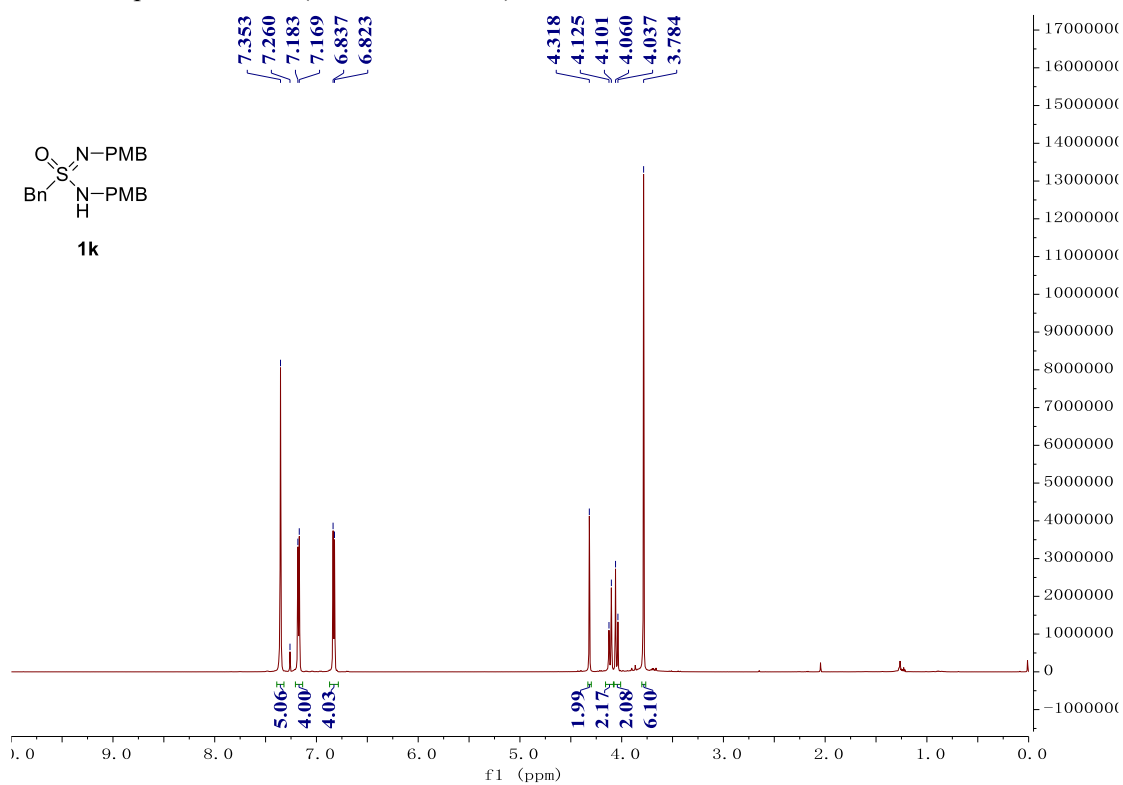
¹H NMR Spectrum of **1i** (600 MHz, CDCl₃)



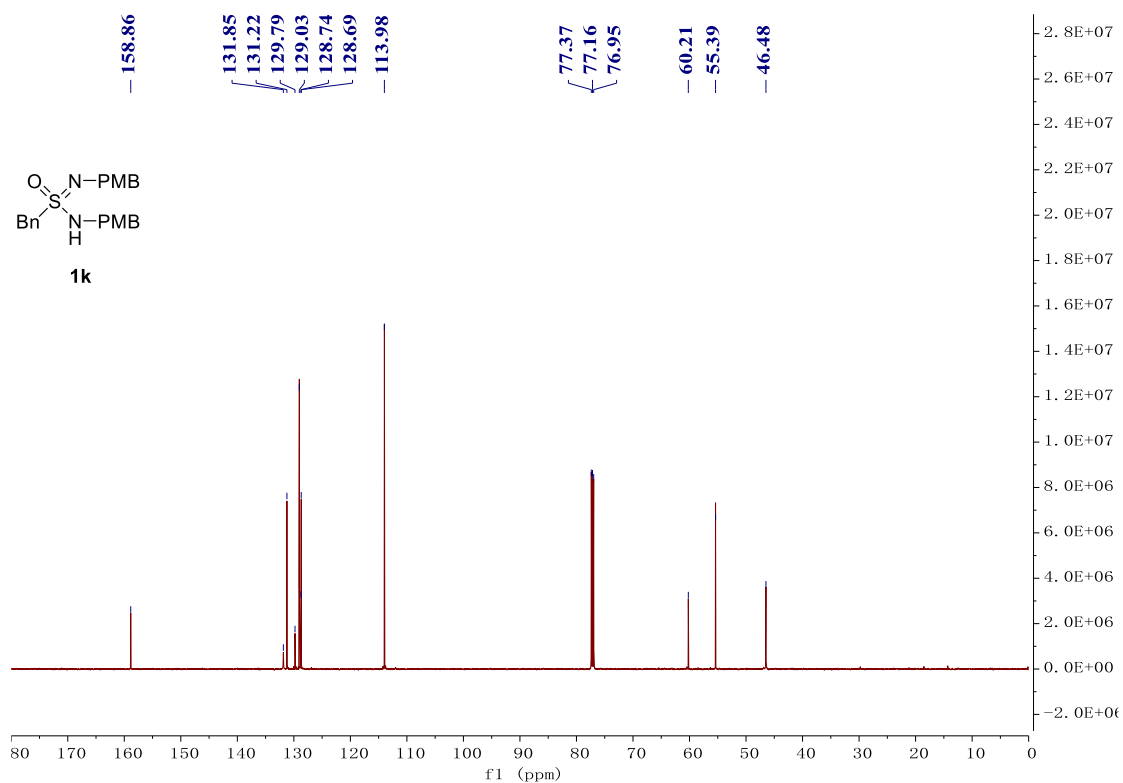
¹³C NMR Spectrum of **1i** (150 MHz, CDCl₃)



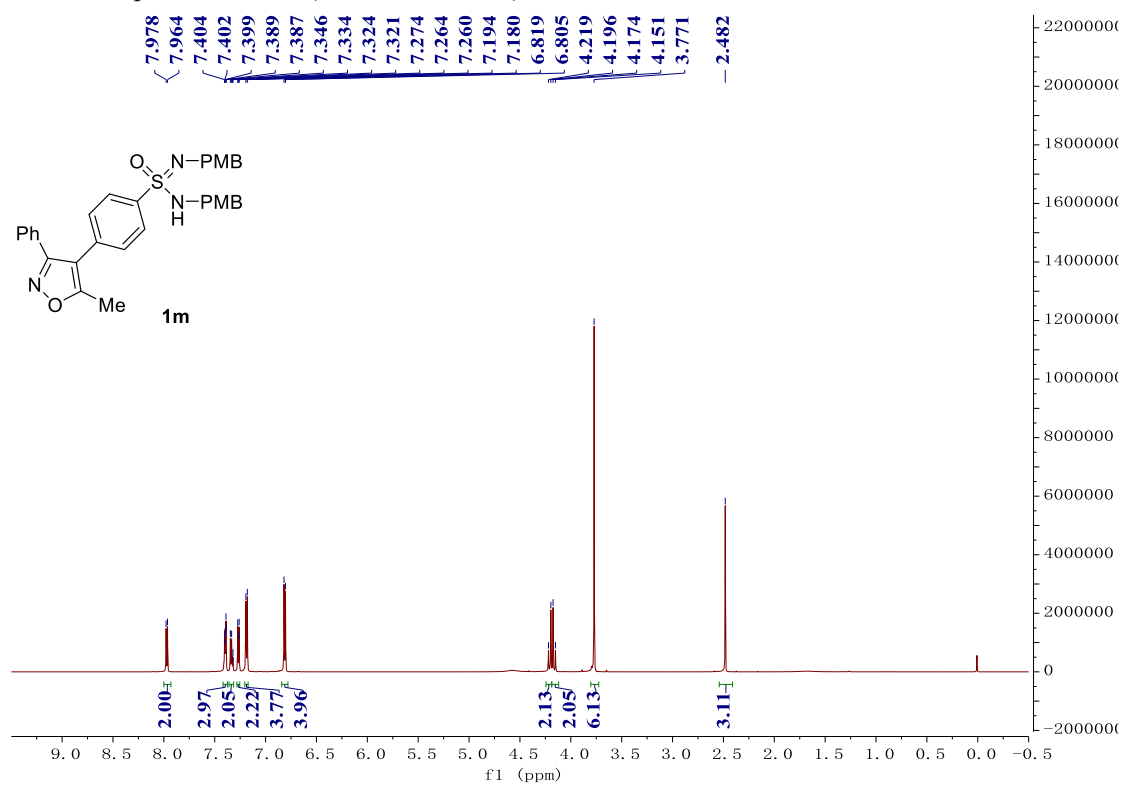
^1H NMR Spectrum of **1k** (600 MHz, CDCl_3)



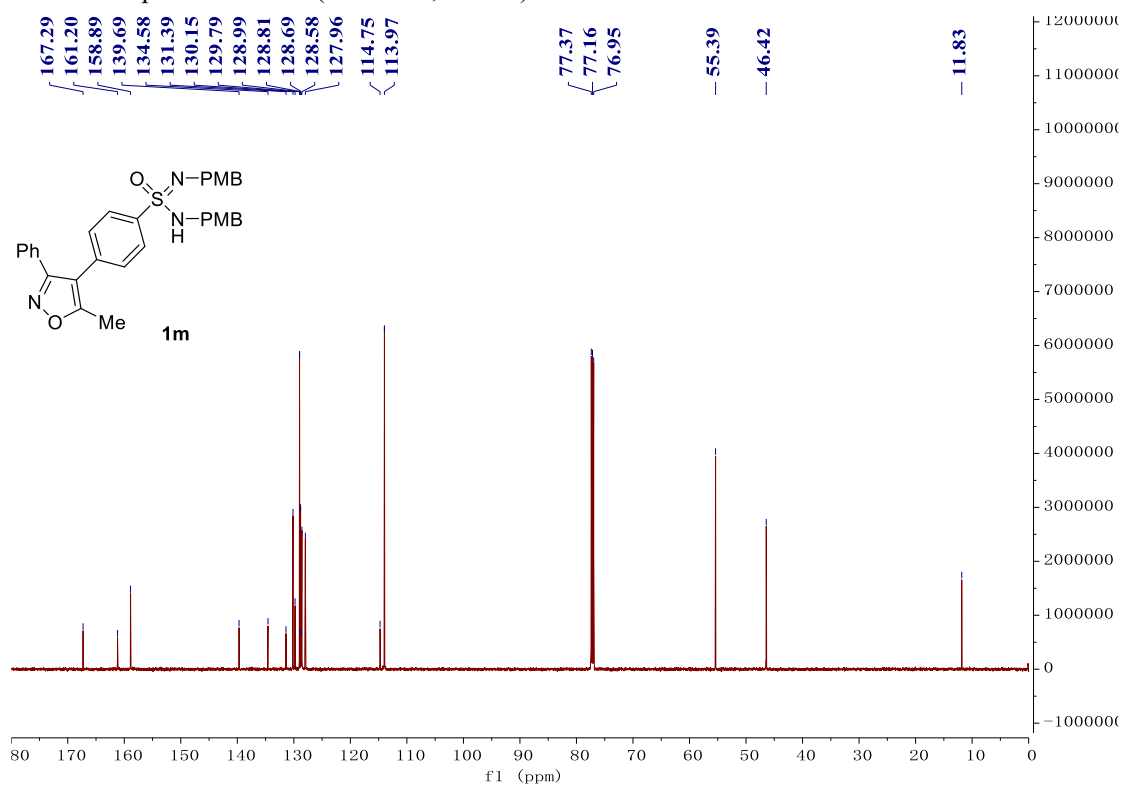
^{13}C NMR Spectrum of **1k** (150 MHz, CDCl_3)



¹H NMR Spectrum of **1m** (600 MHz, CDCl₃)



¹³C NMR Spectrum of **1m** (150 MHz, CDCl₃)



3aa

CN(C)S(=O)(c1ccc(C)cc1)C(=O)OC

¹H NMR spectrum (CDCl₃) of compound **3aa**. The x-axis represents the chemical shift in ppm (f1), ranging from 0.0 to 10.0. The y-axis represents the intensity, ranging from -5.0E+10 to 7.5E+11. The spectrum shows several peaks corresponding to the protons in the molecule. The chemical structure of **3aa** is shown above the spectrum.

Chemical structure of **3aa**: CN(C)S(=O)(c1ccc(C)cc1)C(=O)OC

Peak list (ppm):

Chemical Shift (ppm)
7.836
7.815
7.395
7.374
7.260
7.238
7.201
7.181
6.858
6.849
6.843
6.837
6.828
4.953
4.915
4.889
4.852
4.275
4.239
4.085
4.049
3.791
3.772
3.554
2.371

Integration values:

Integration Value
2.00
2.02
2.07
2.11
4.12
1.02
1.01
1.08
1.08
6.13
3.11
3.25

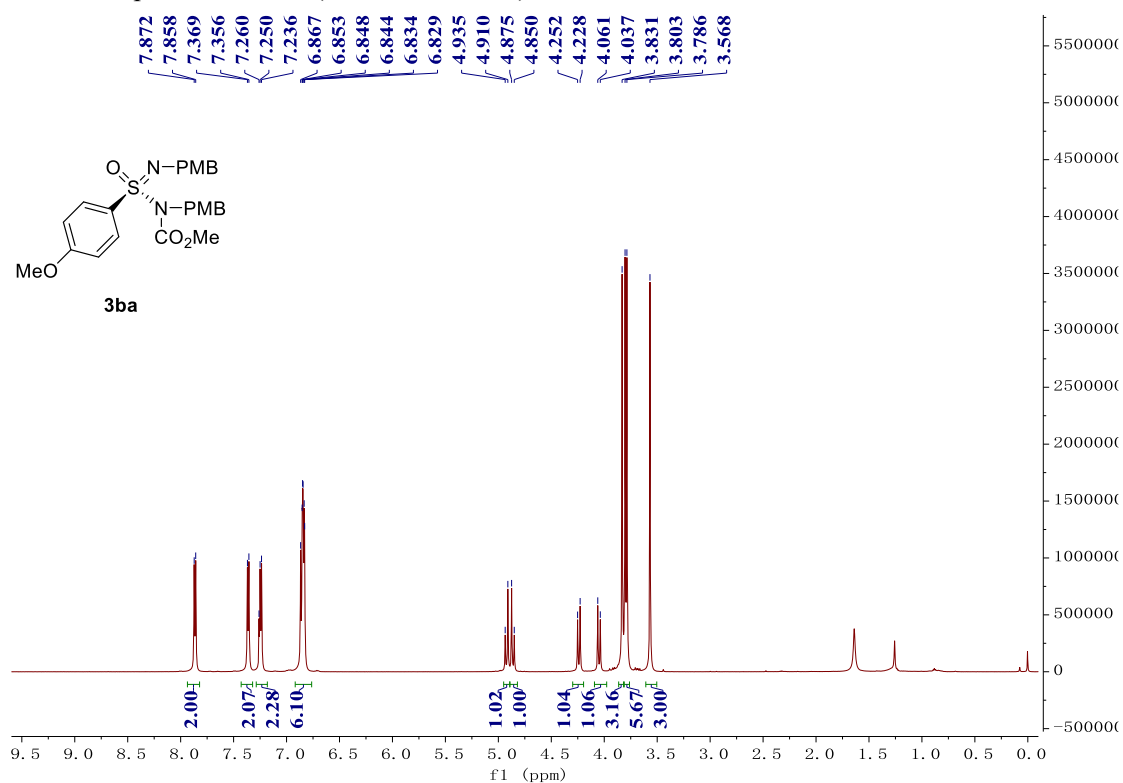
Chemical structure of **3aa** is shown: COC(=O)N(C1=CC=C(C)C1)S(=O)(C2=CC=C(C)C2)C3=CC=C(C)C3.

¹³C NMR spectrum (CDCl₃) of **3aa** is displayed, showing peaks corresponding to the structure. The x-axis represents the chemical shift in ppm (f1), ranging from 0 to 200. The y-axis represents intensity, ranging from -5.0E+08 to 7.5E+10.

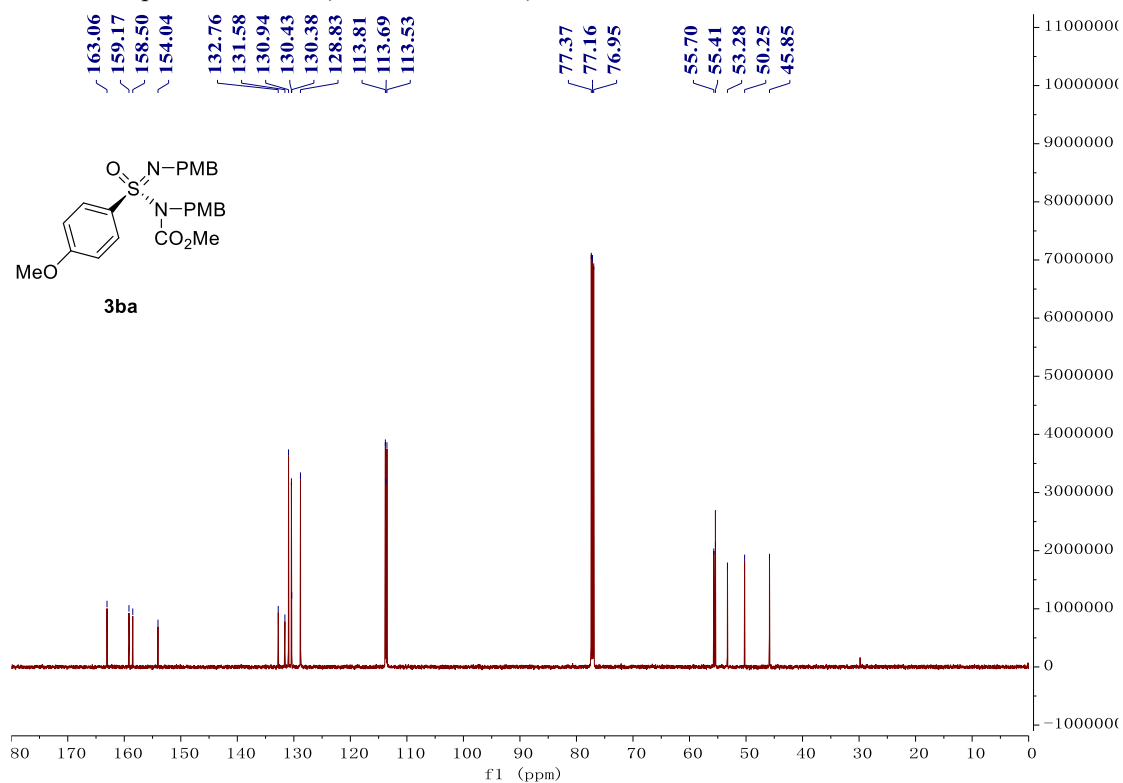
Key peaks are labeled with their chemical shifts (ppm):

- 159.08, 158.39, 153.90, 143.45, 137.06, 132.59, 130.38, 130.23, 128.94, 128.72, 128.56, 113.69, 113.57 (aromatic and carbonyl carbons)
- 77.48, 77.16, 76.84 (CDCl₃ solvent triplet)
- 55.27, 53.18, 50.16, 45.69 (methoxy and methyl carbons)
- 21.52 (aromatic methyl carbon)

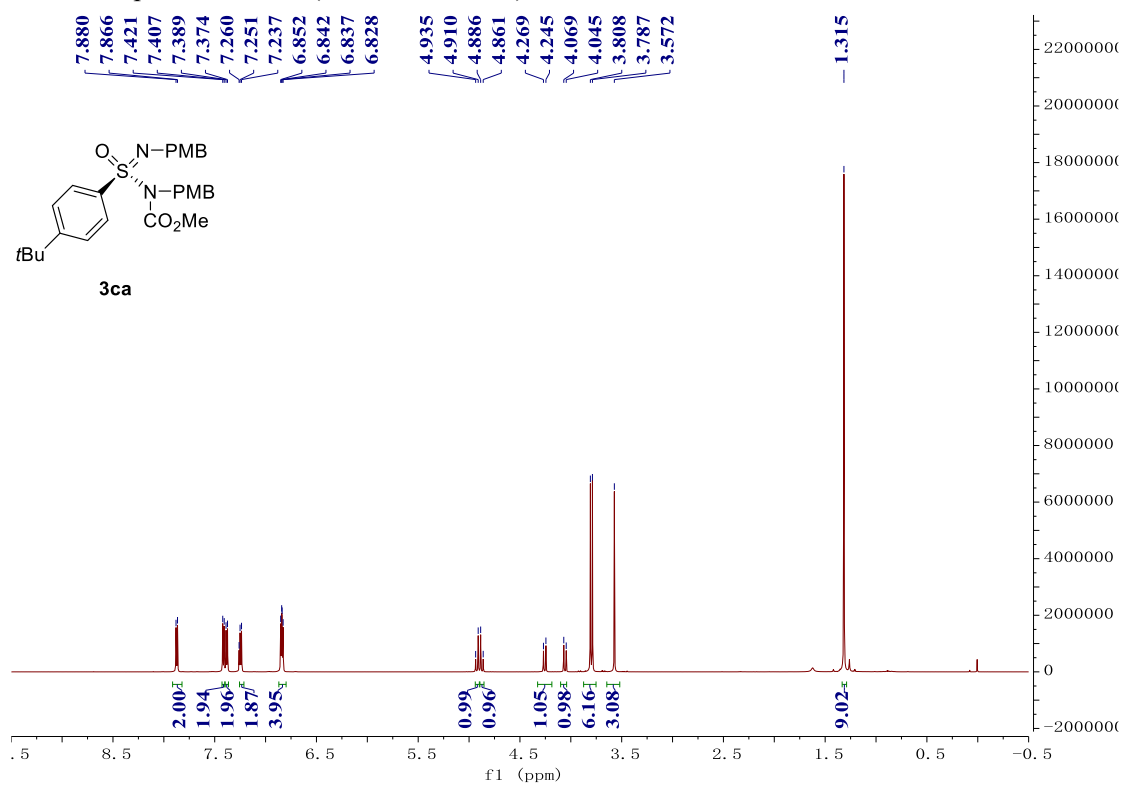
¹H NMR Spectrum of **3ba** (600 MHz, CDCl₃)



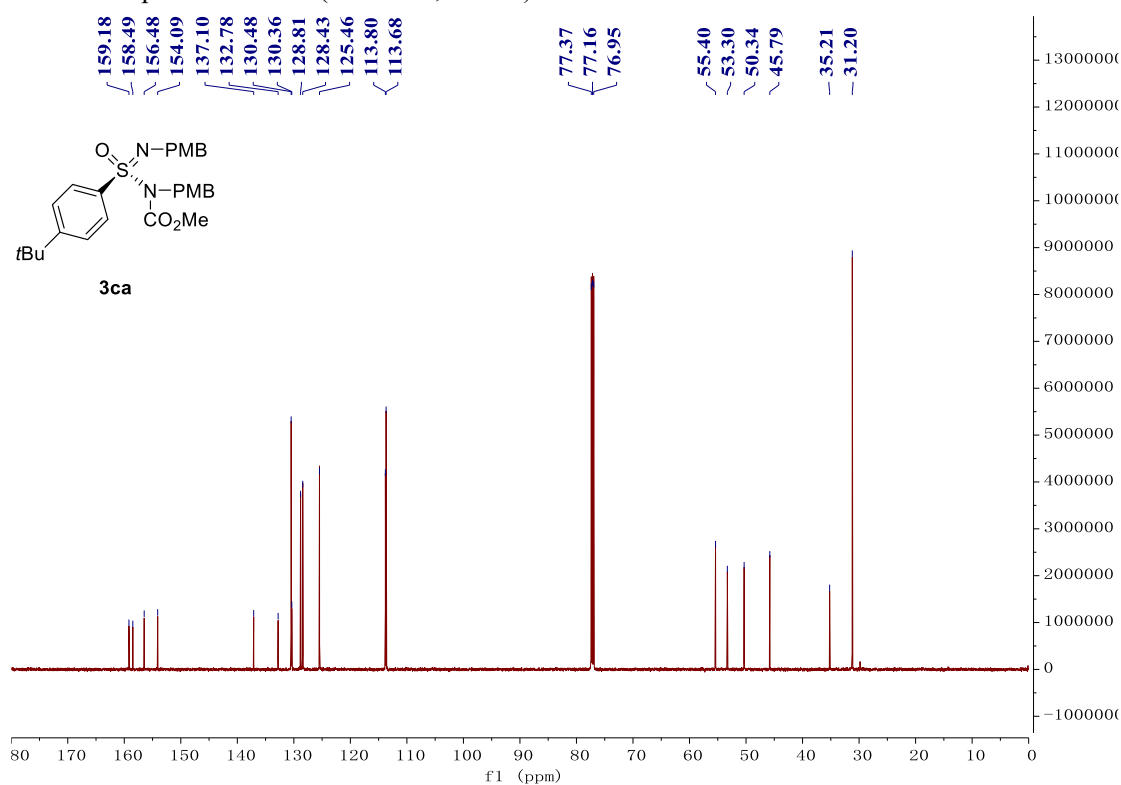
¹³C NMR Spectrum of **3ba** (150 MHz, CDCl₃)



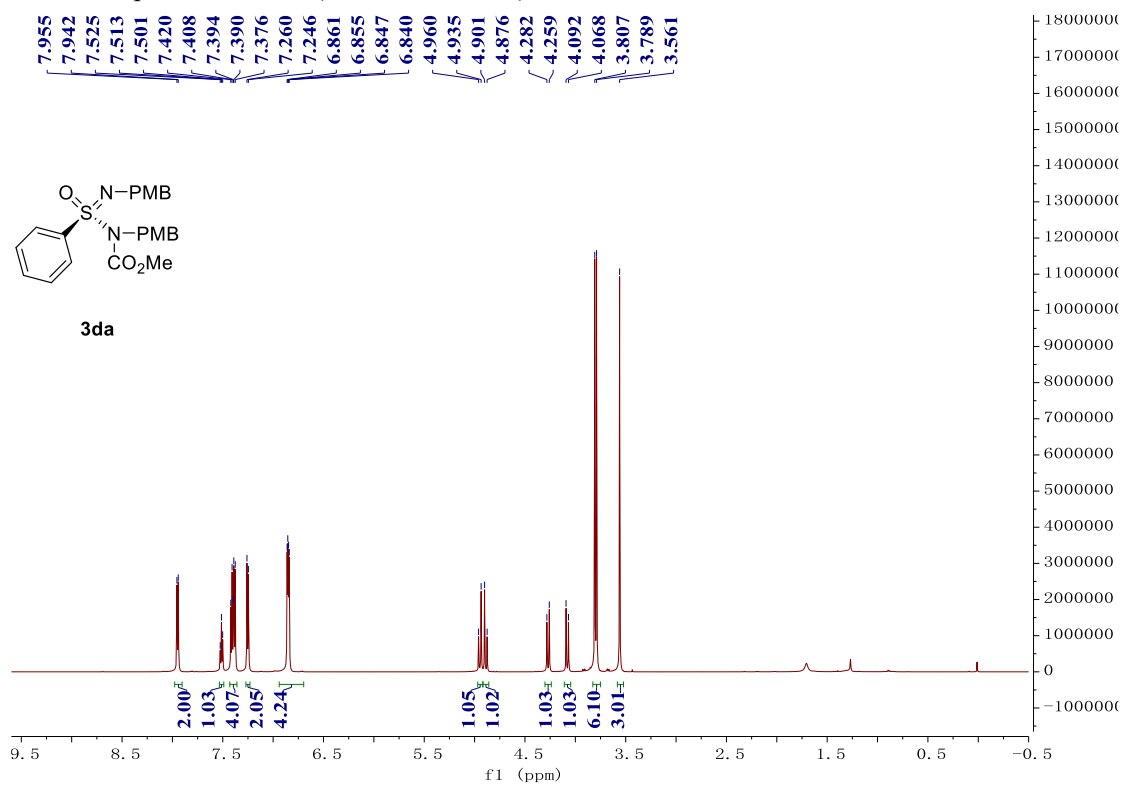
¹H NMR Spectrum of **3ca** (600 MHz, CDCl₃)



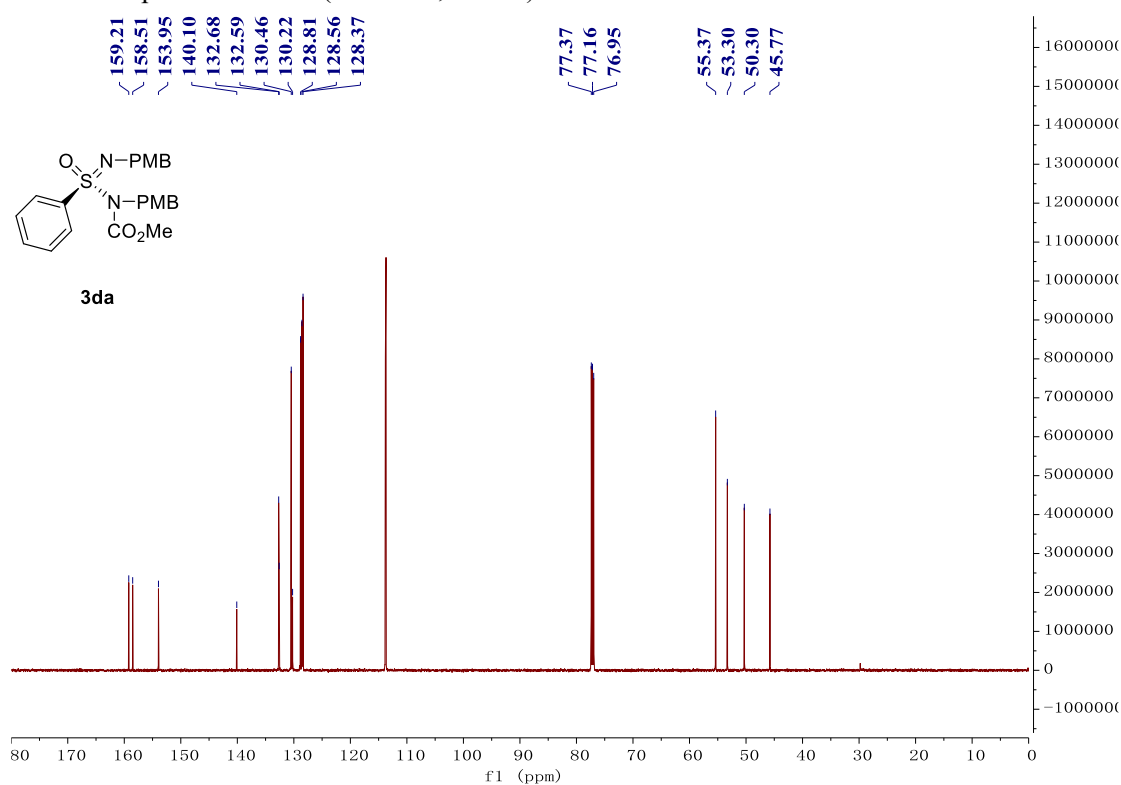
¹³C NMR Spectrum of **3ca** (150 MHz, CDCl₃)



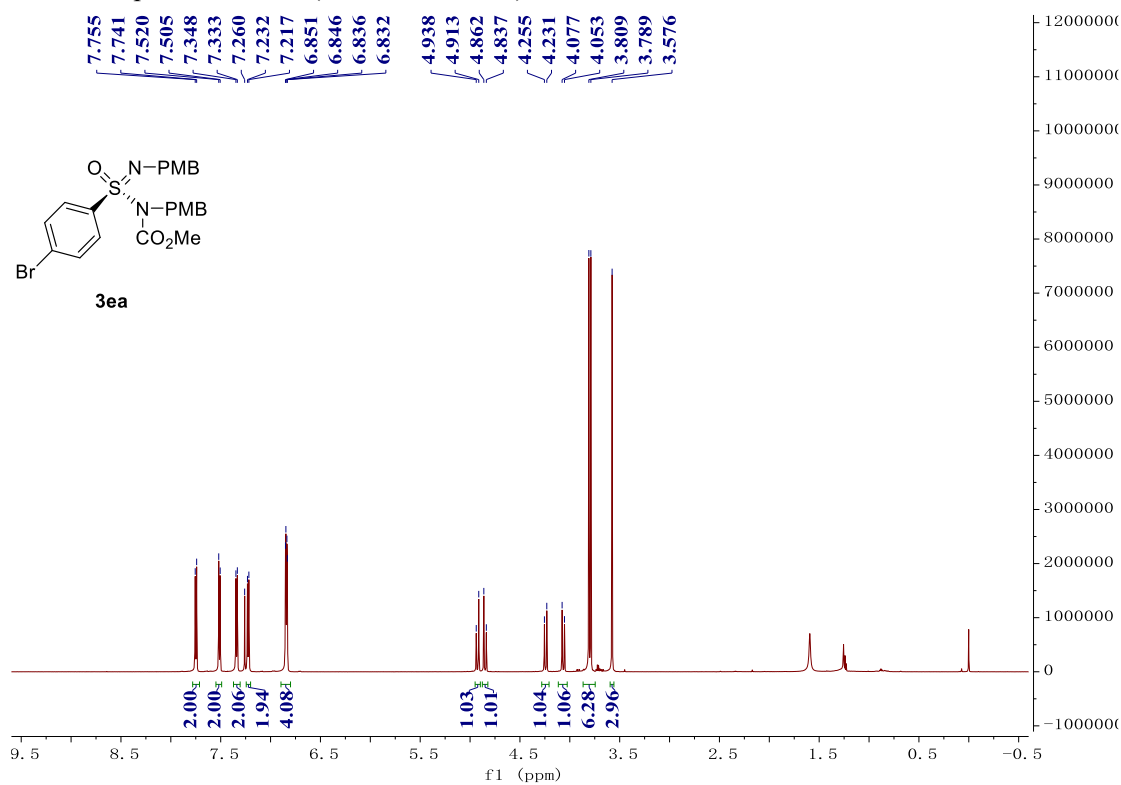
¹H NMR Spectrum of **3da** (600 MHz, CDCl₃)



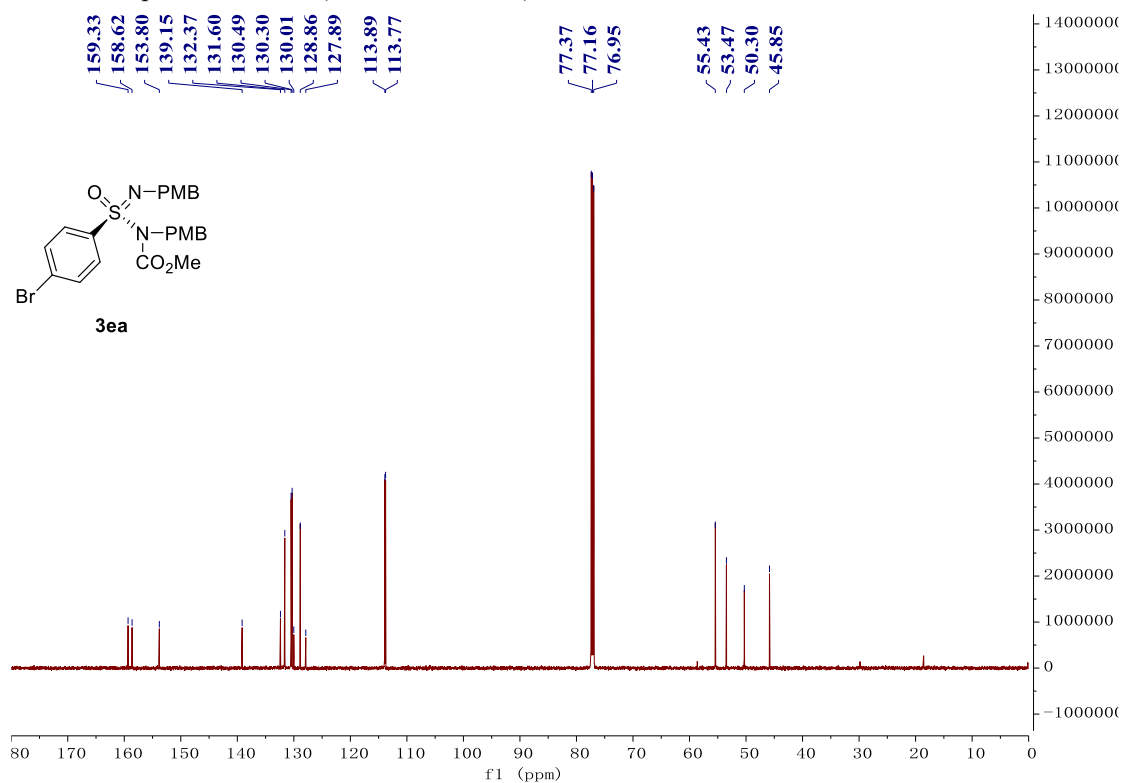
¹³C NMR Spectrum of **3da** (150 MHz, CDCl₃)



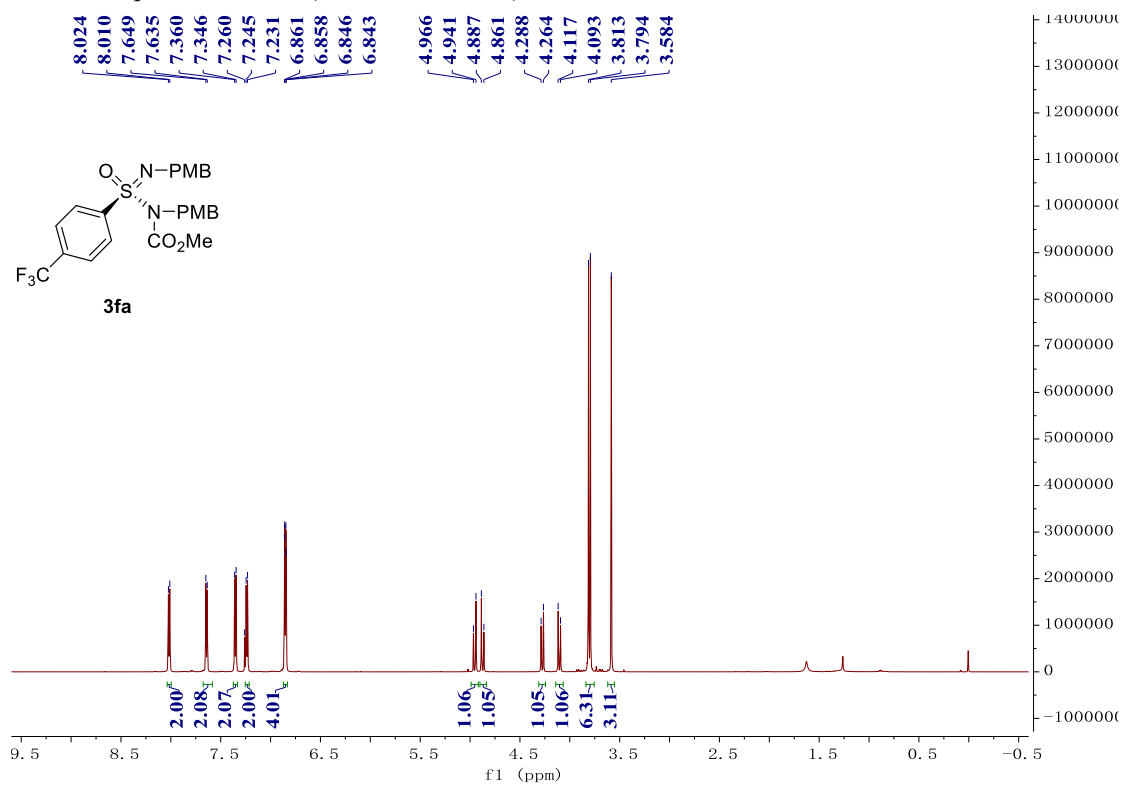
¹H NMR Spectrum of **3ea** (600 MHz, CDCl₃)



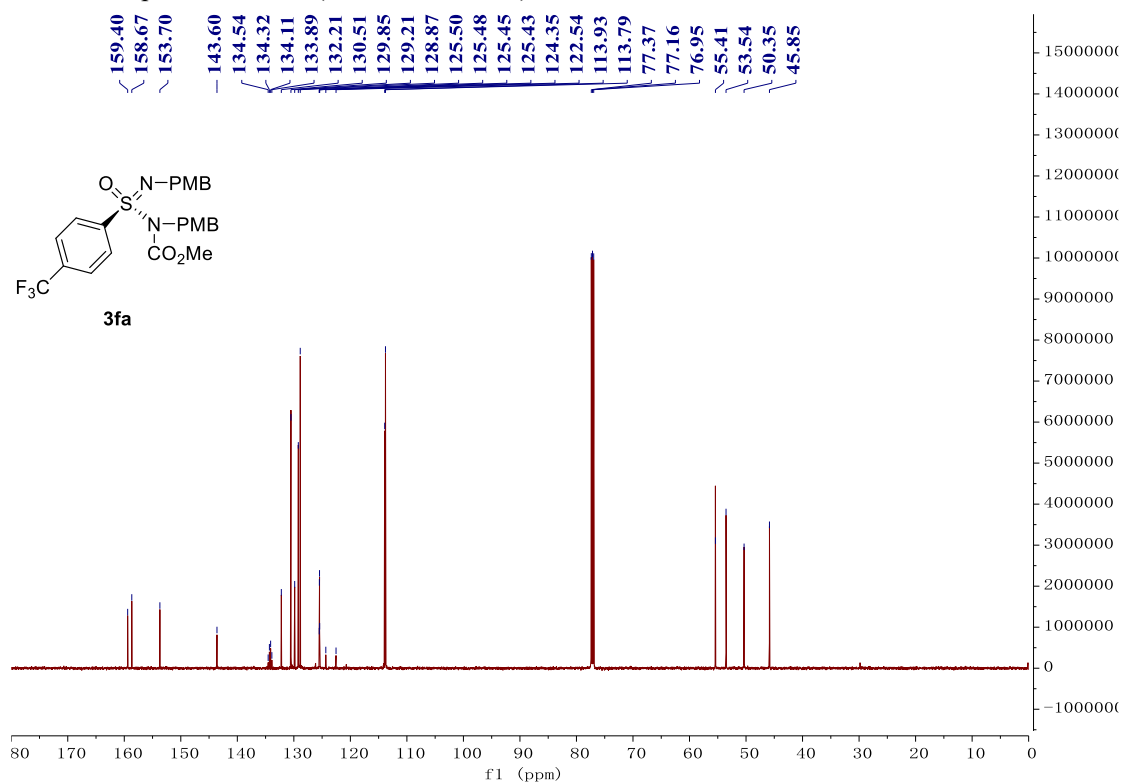
¹³C NMR Spectrum of **3ea** (150 MHz, CDCl₃)



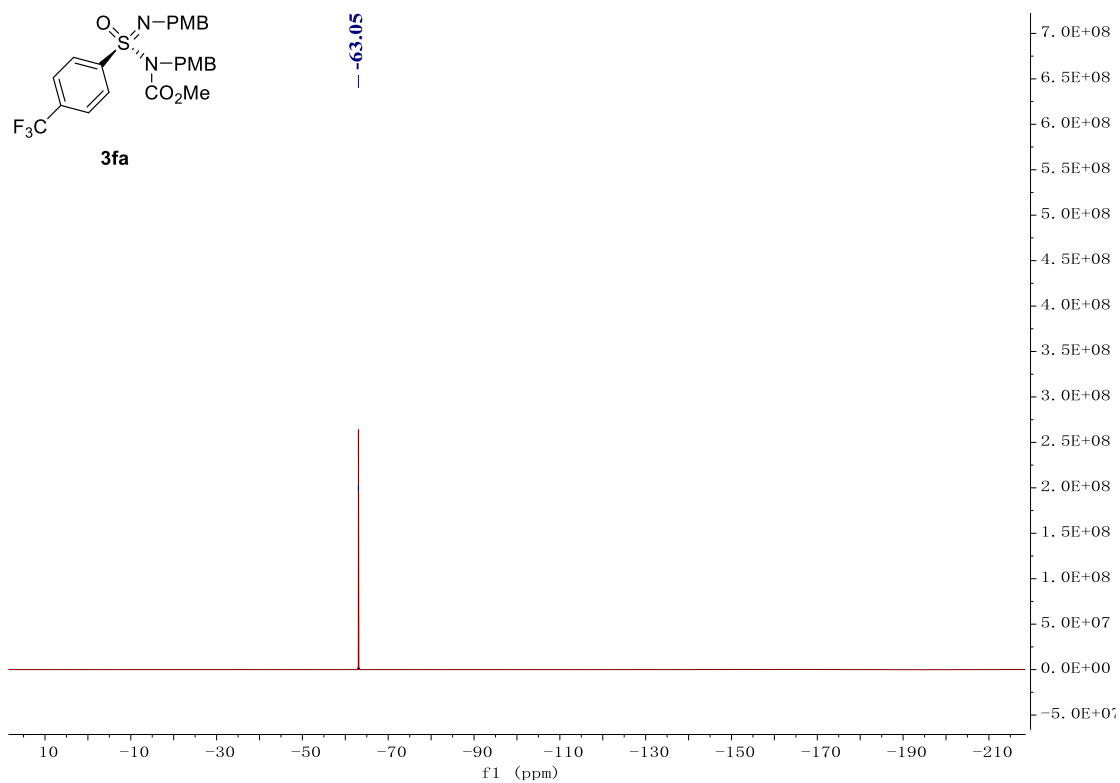
¹H NMR Spectrum of **3fa** (600 MHz, CDCl₃)



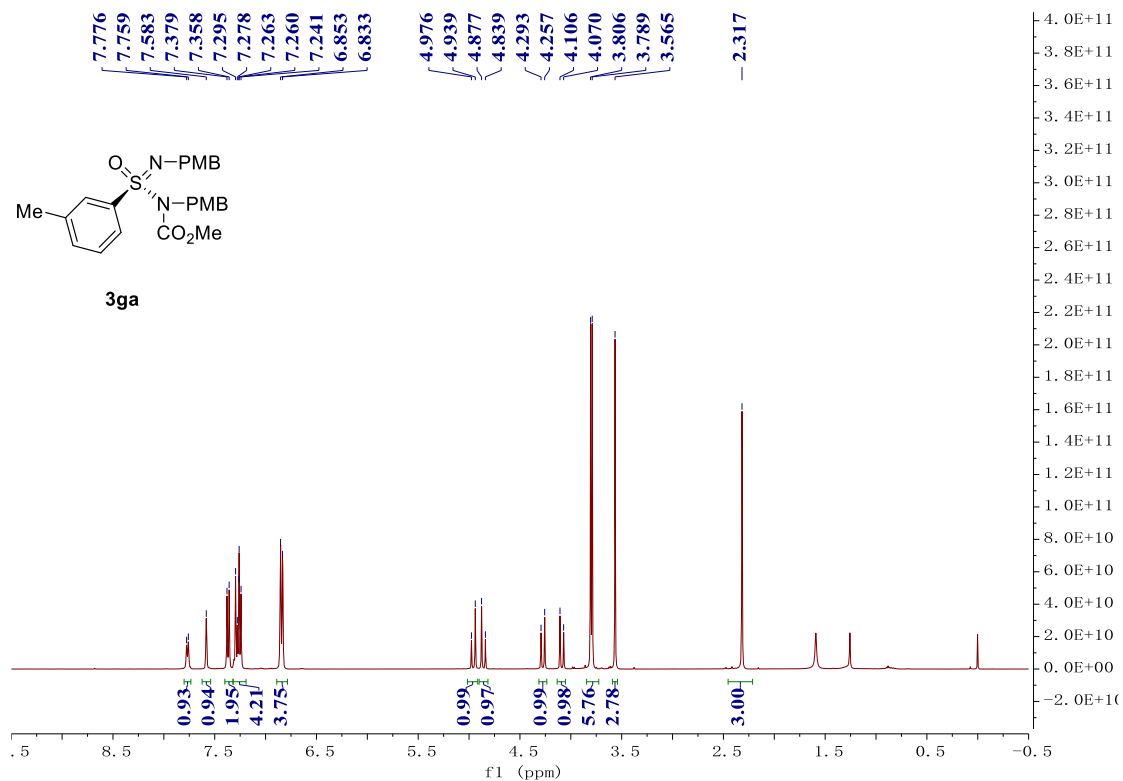
¹³C NMR Spectrum of **3fa** (150 MHz, CDCl₃)



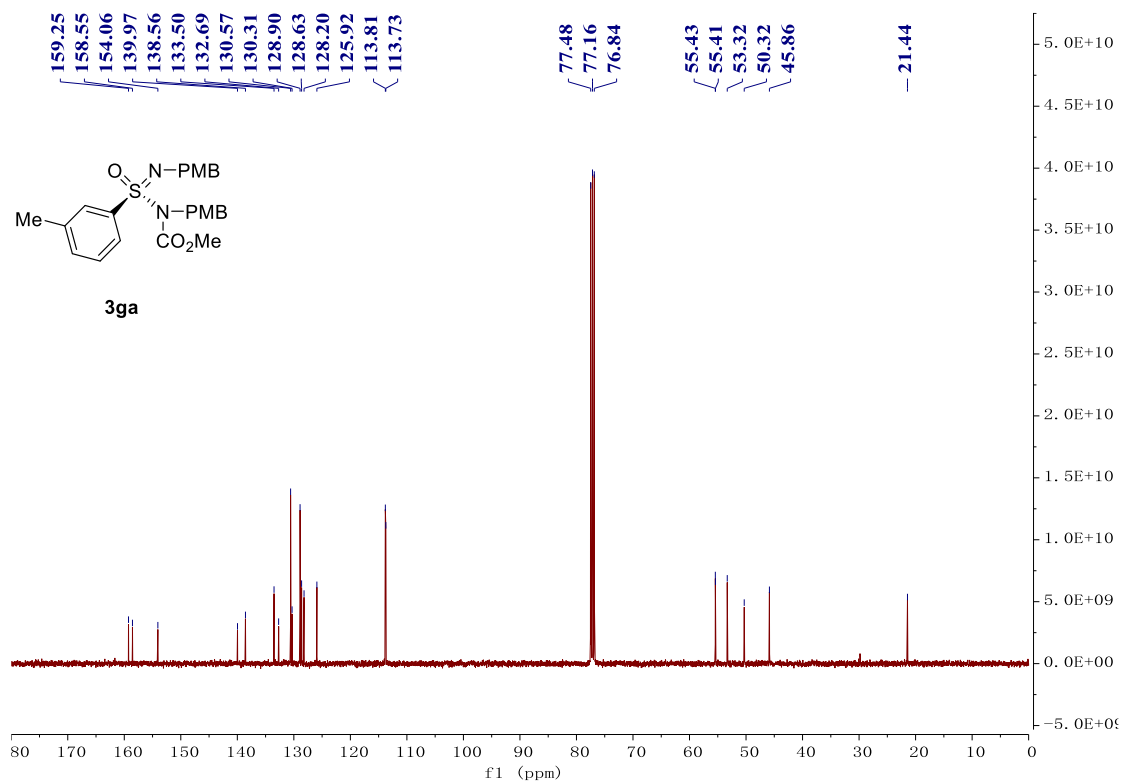
^{19}F NMR Spectrum of **3fa** (565 MHz, CDCl_3)



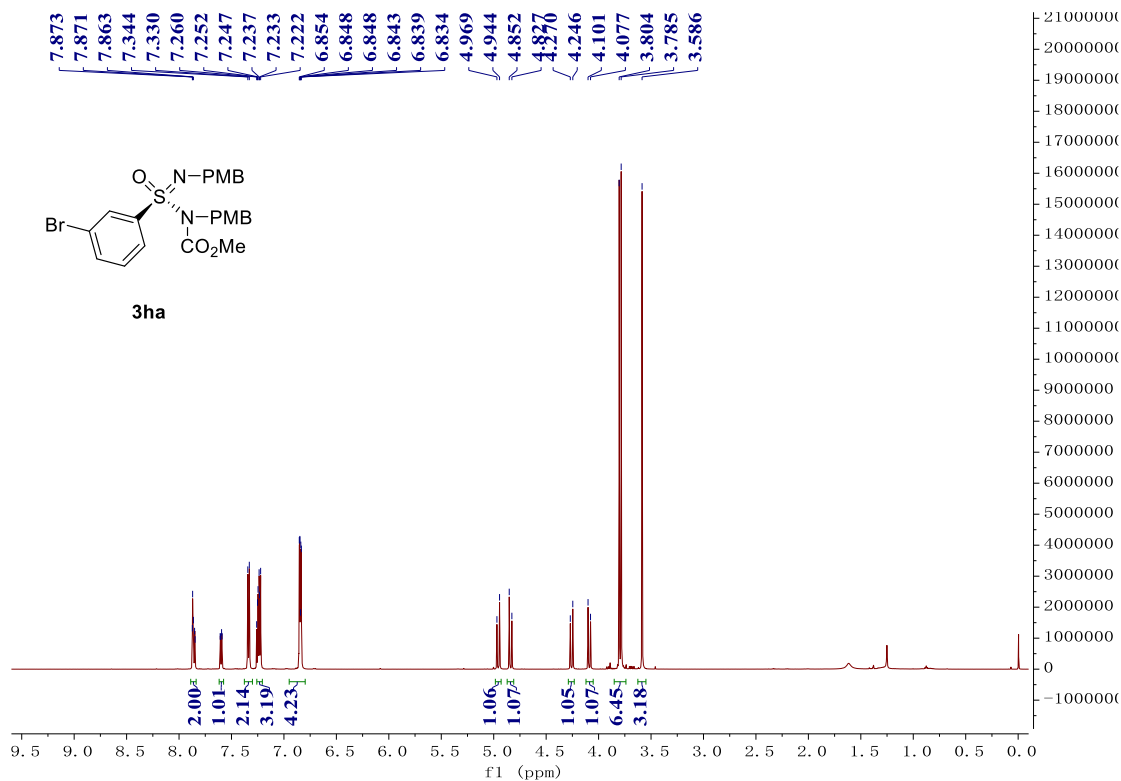
^1H NMR Spectrum of **3ga** (400 MHz, CDCl_3)



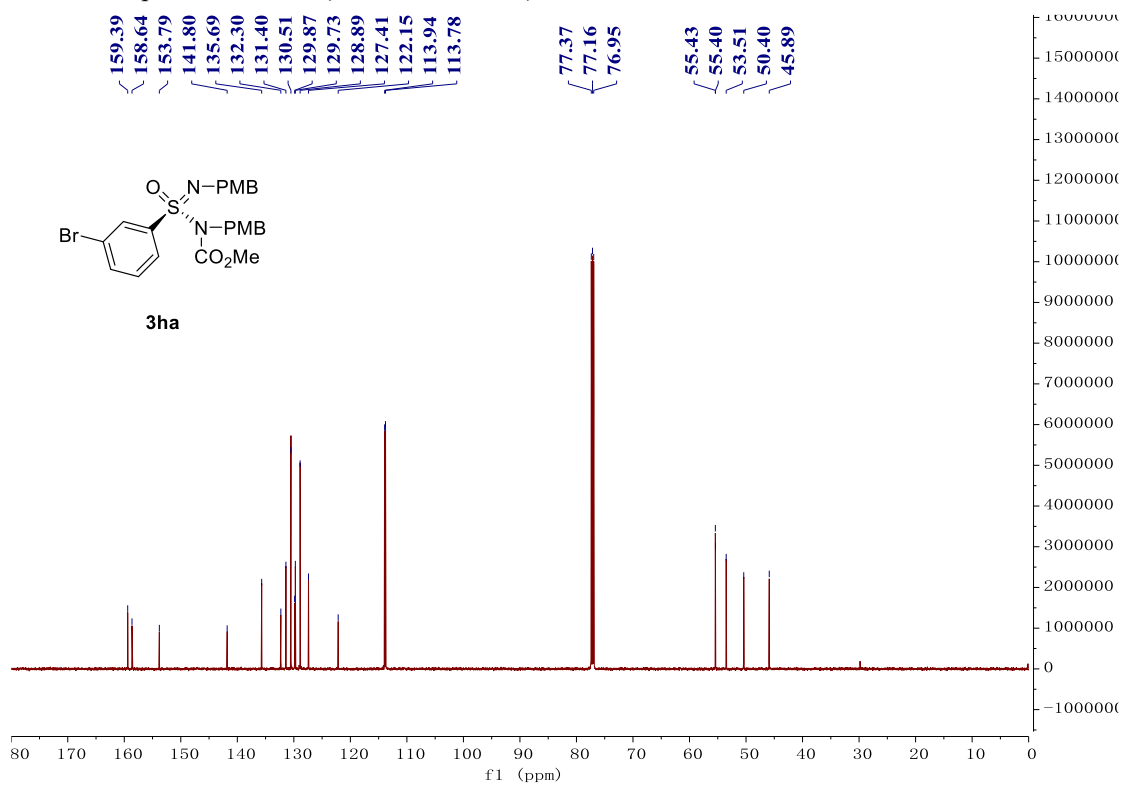
^{13}C NMR Spectrum of **3ga** (100 MHz, CDCl_3)



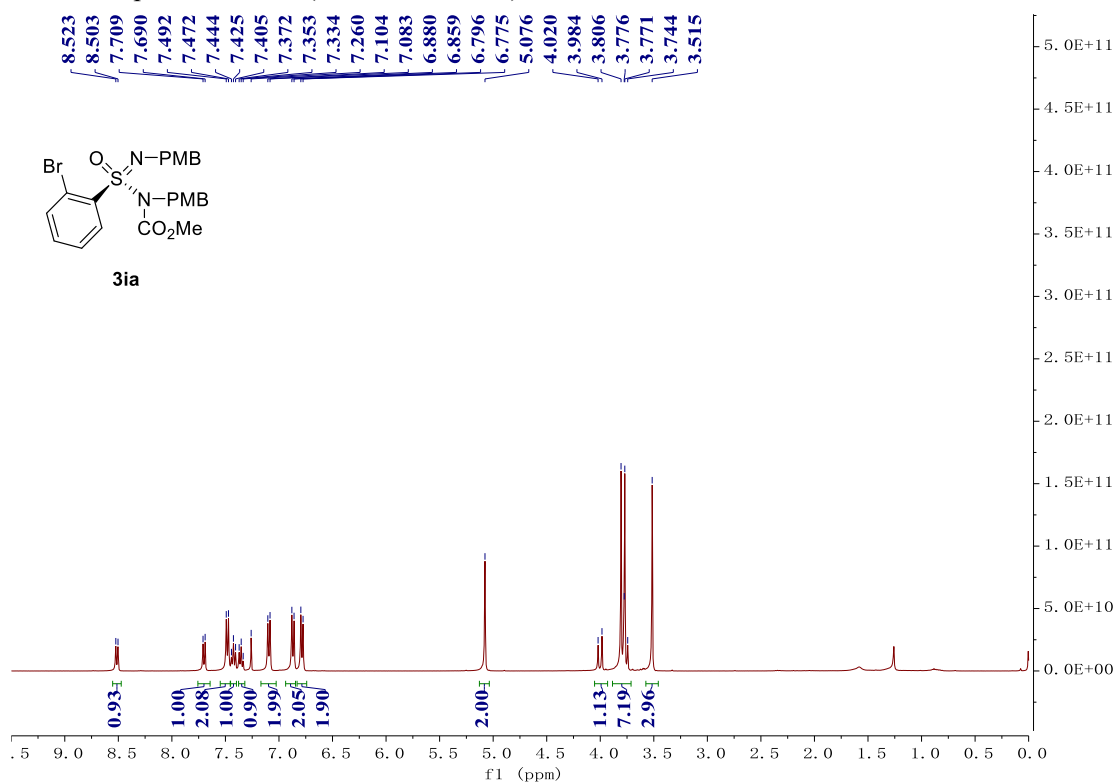
^1H NMR Spectrum of **3ha** (600 MHz, CDCl_3)



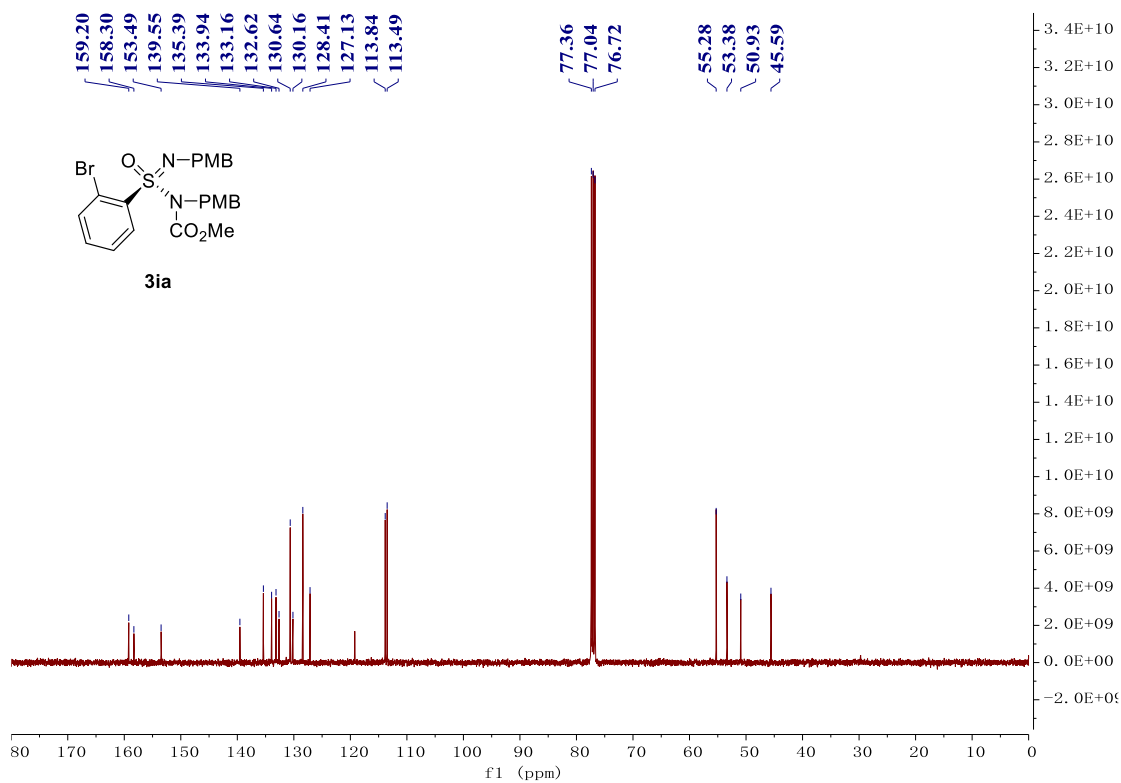
¹³C NMR Spectrum of **3ha** (150 MHz, CDCl₃)



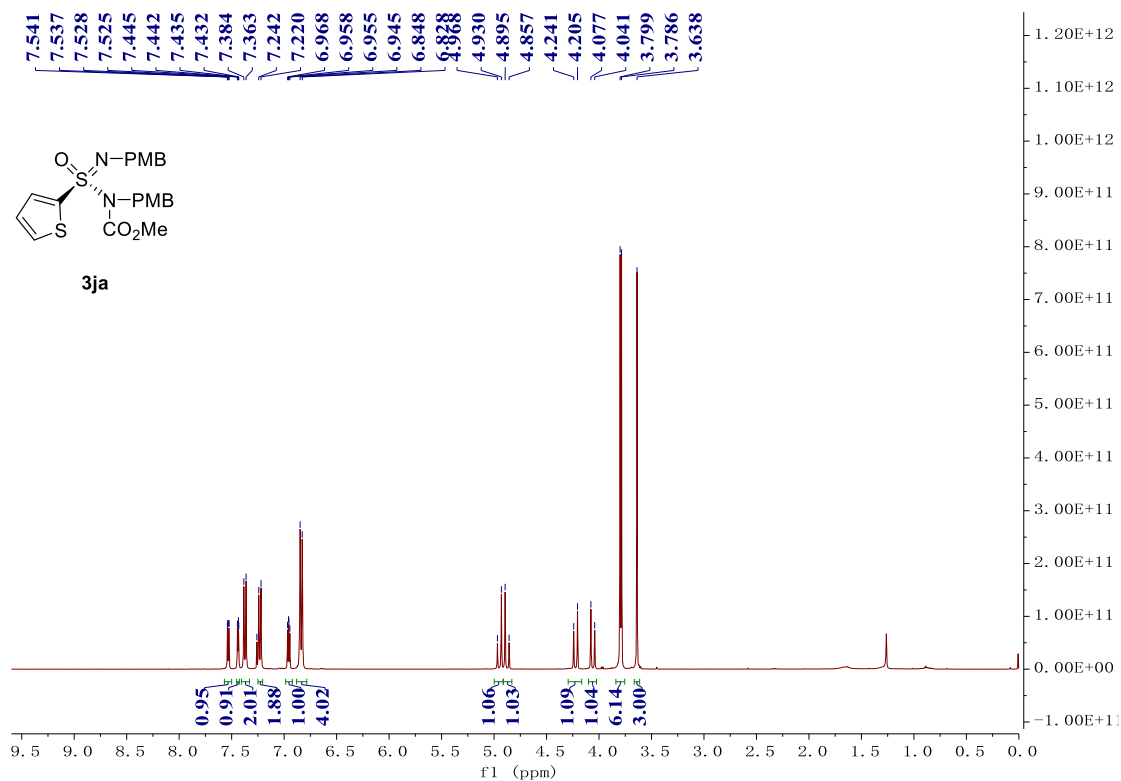
¹H NMR Spectrum of **3ia** (400 MHz, CDCl₃)



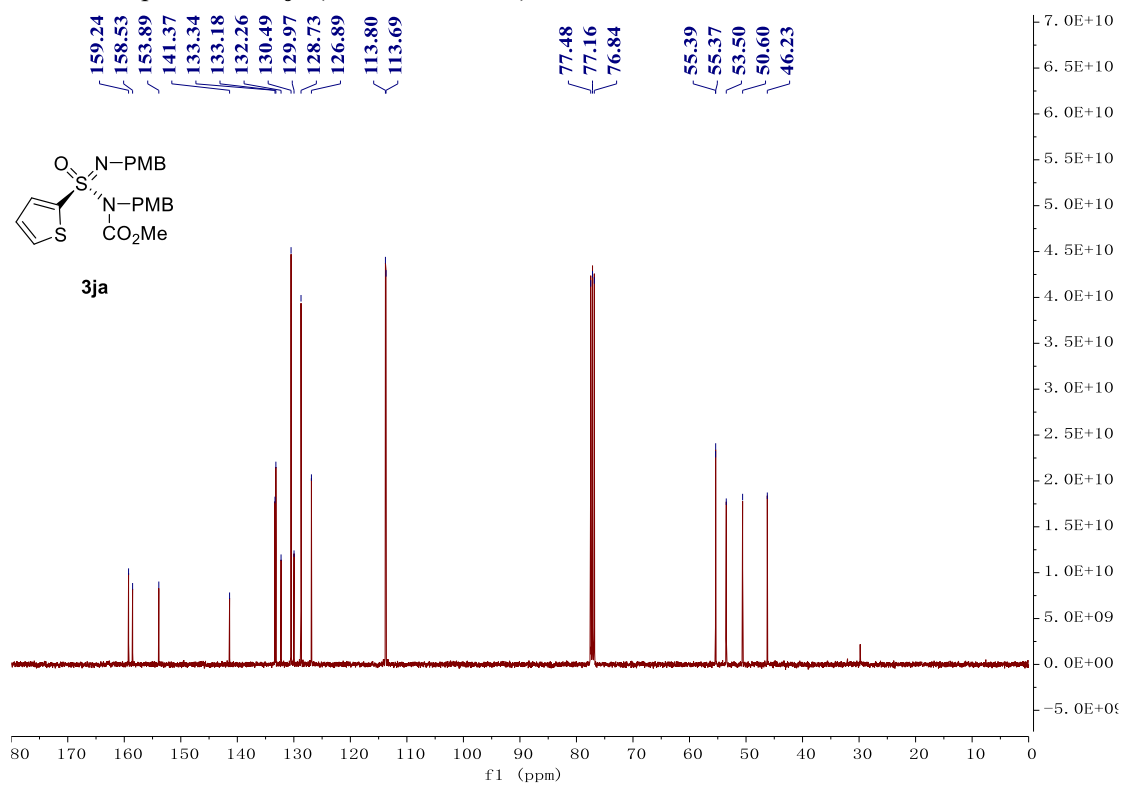
¹³C NMR Spectrum of **3ia** (100 MHz, CDCl₃)



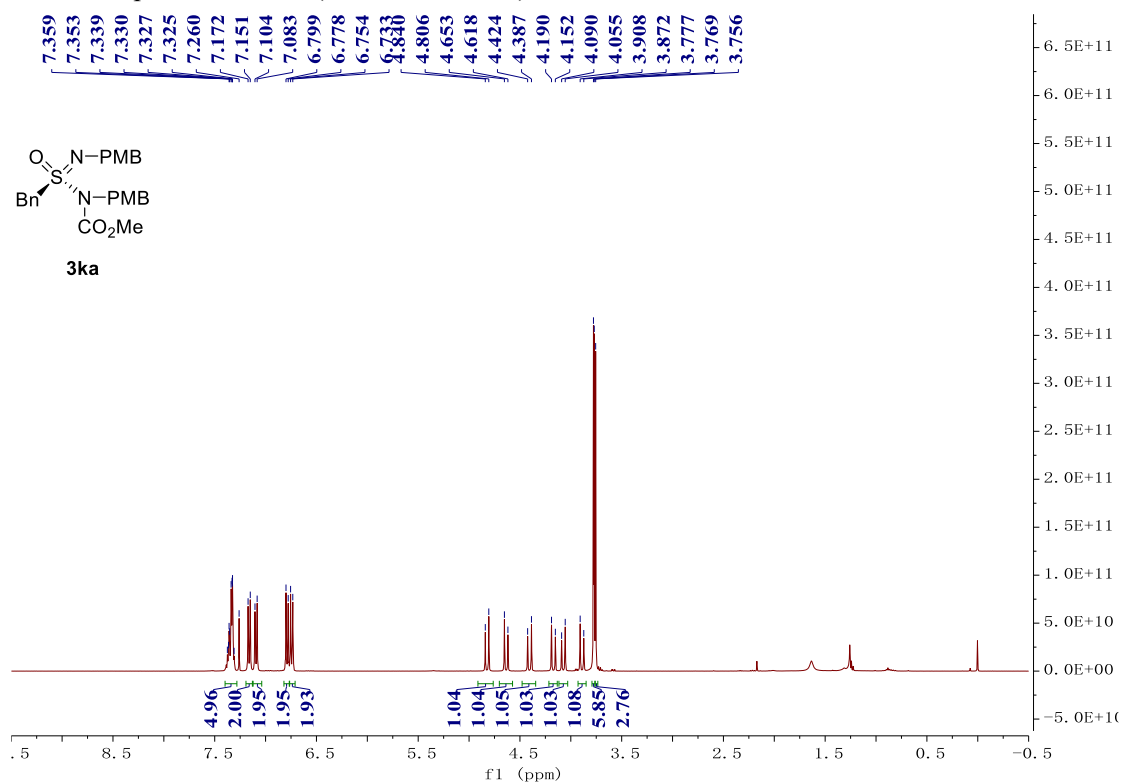
¹H NMR Spectrum of **3ja** (400 MHz, CDCl₃)



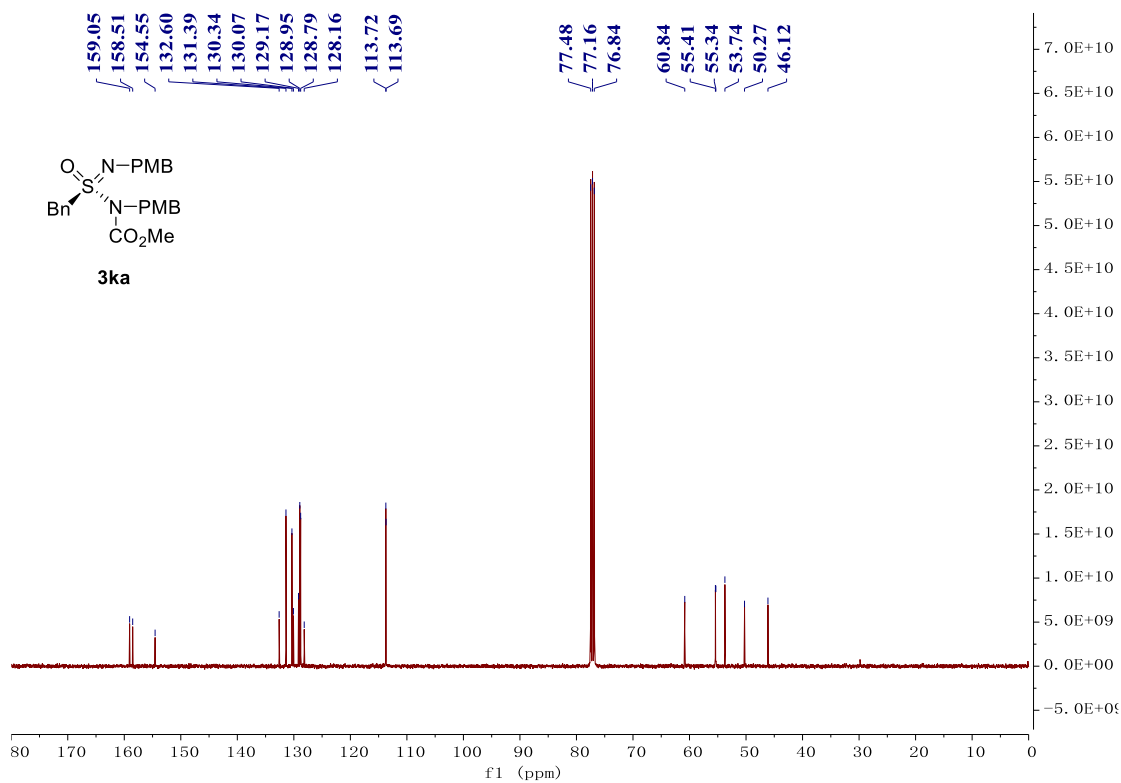
^{13}C NMR Spectrum of **3ja** (100 MHz, CDCl_3)



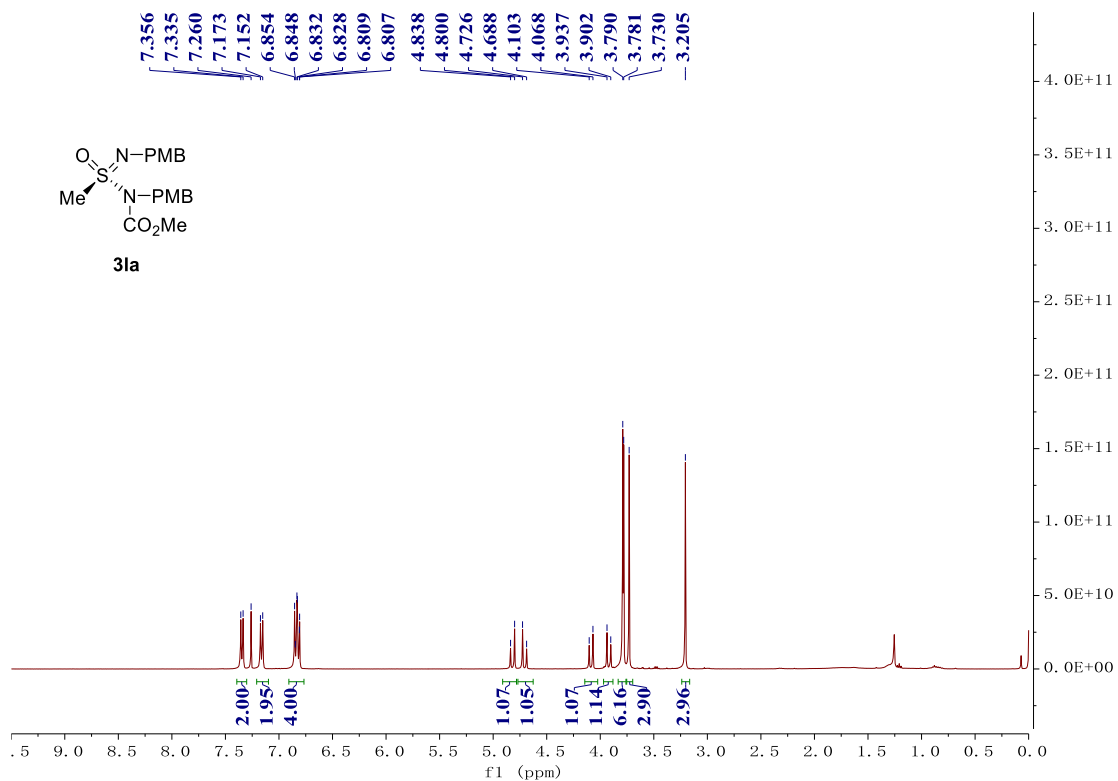
^1H NMR Spectrum of **3ka** (400 MHz, CDCl_3)



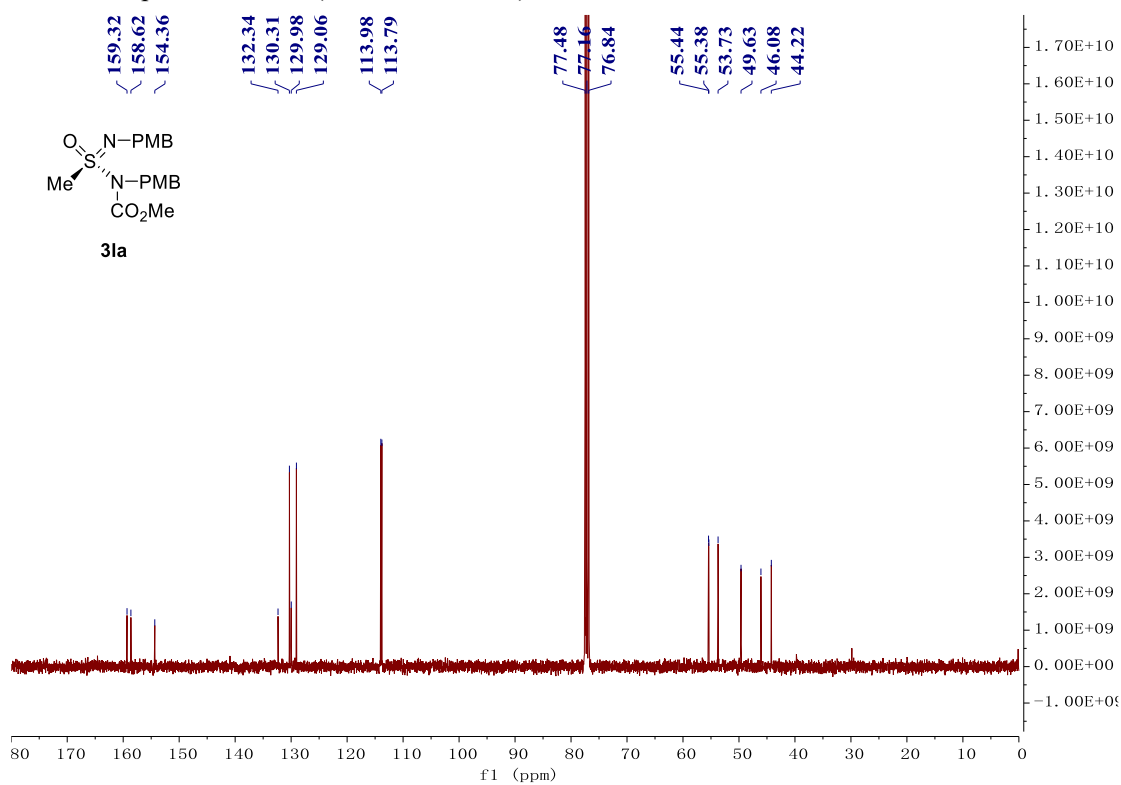
¹³C NMR Spectrum of **3ka** (100 MHz, CDCl₃)



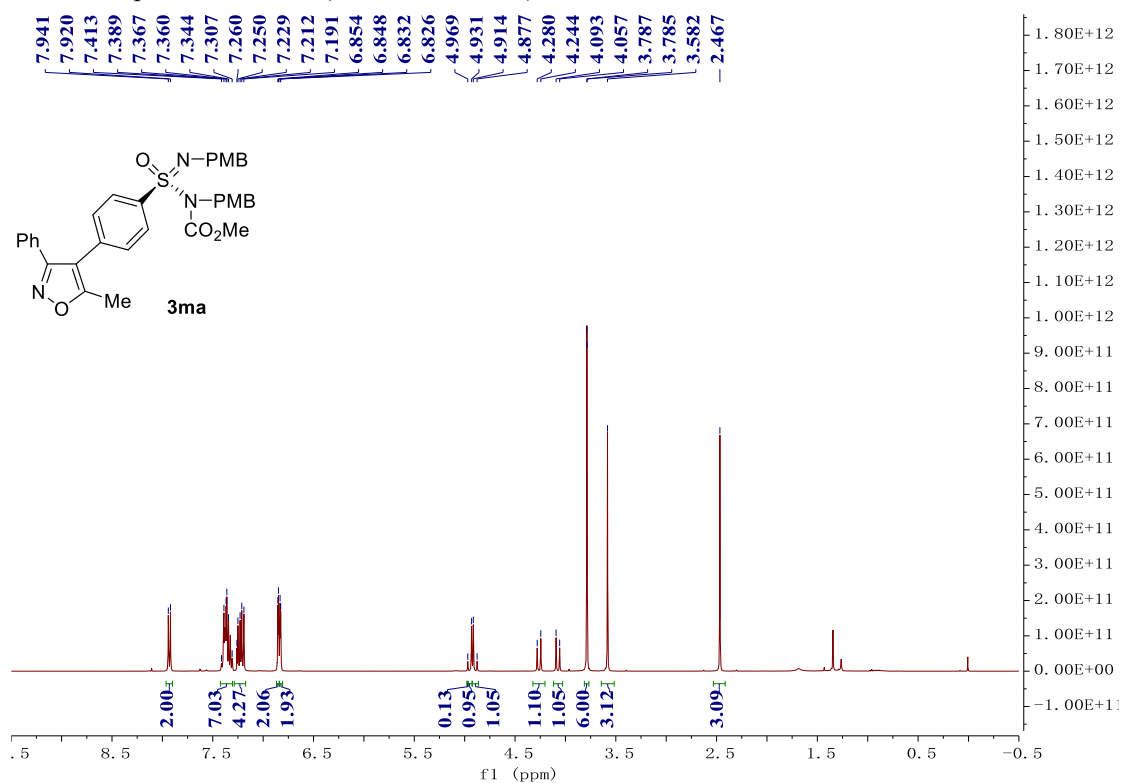
¹H NMR Spectrum of **3la** (400 MHz, CDCl₃)



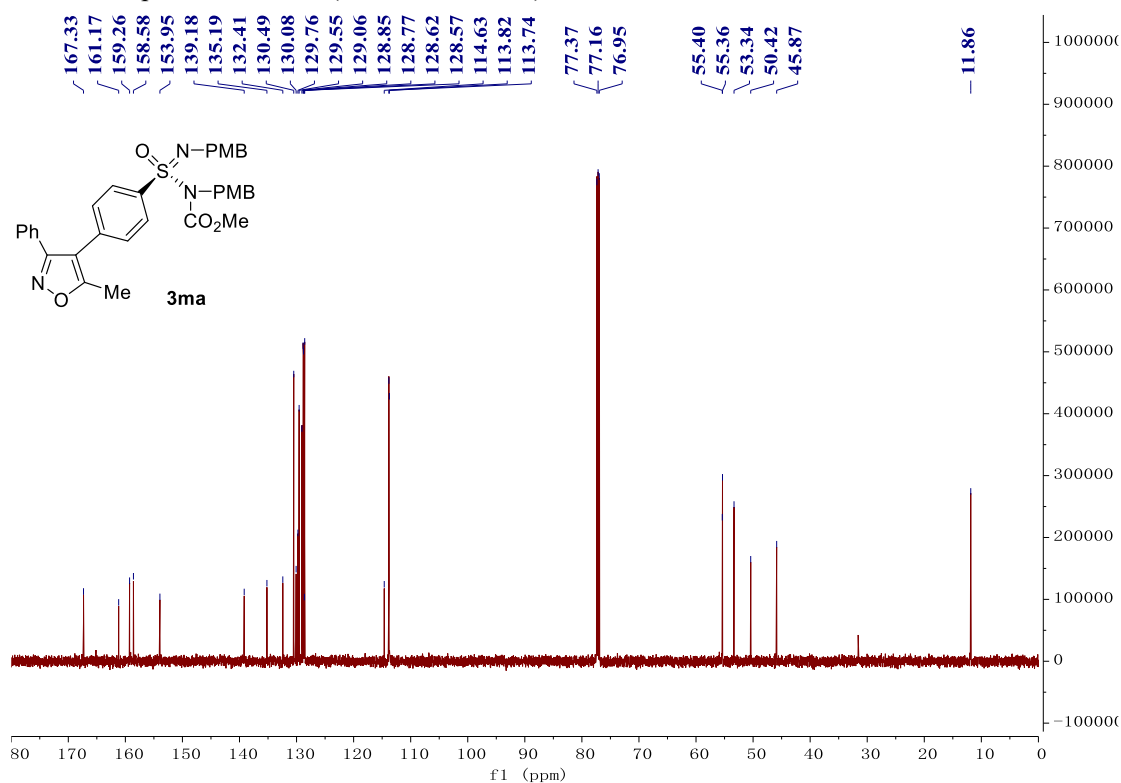
^{13}C NMR Spectrum of **3la** (100 MHz, CDCl_3)



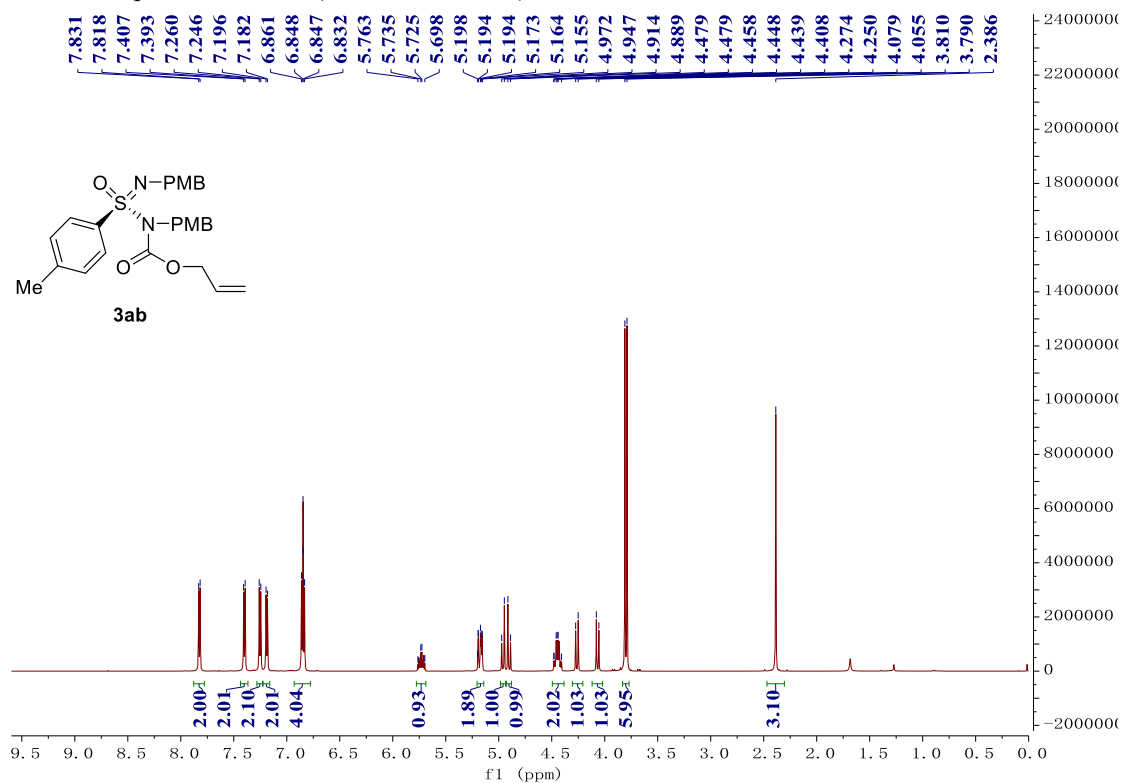
^1H NMR Spectrum of **3ma** (400 MHz, CDCl_3)



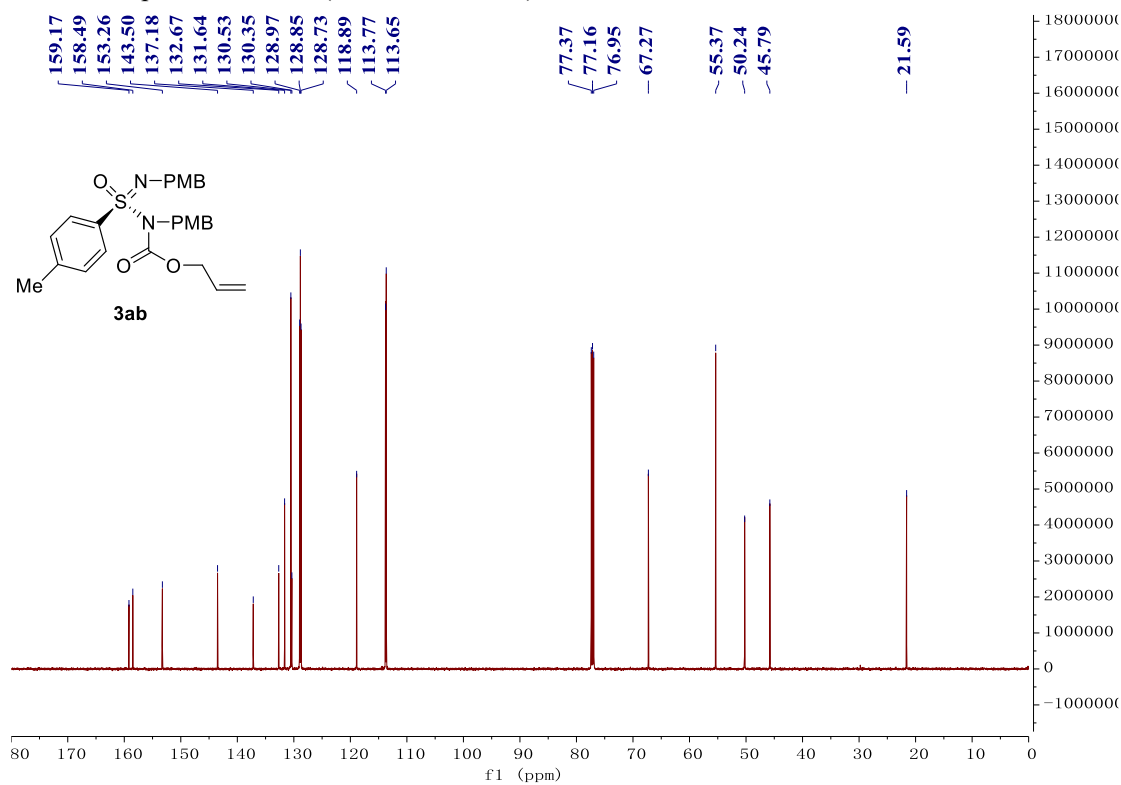
^{13}C NMR Spectrum of **3ma** (100 MHz, CDCl_3)



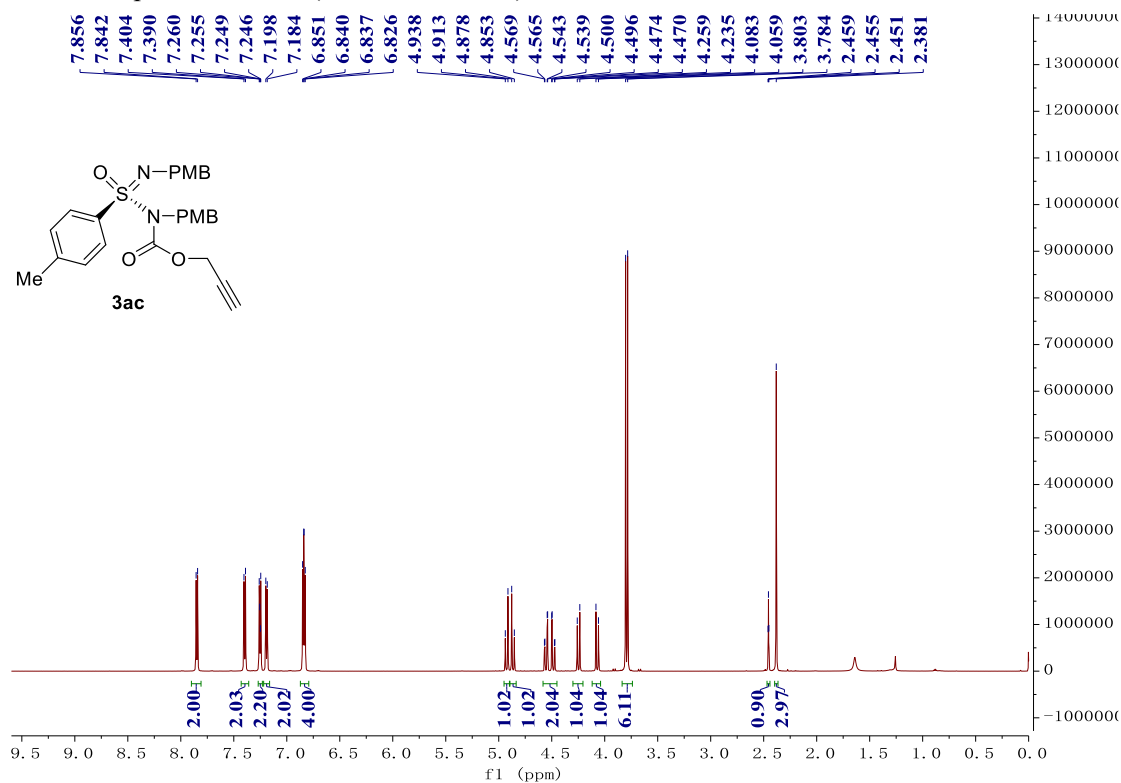
^1H NMR Spectrum of **3ab** (600 MHz, CDCl_3)



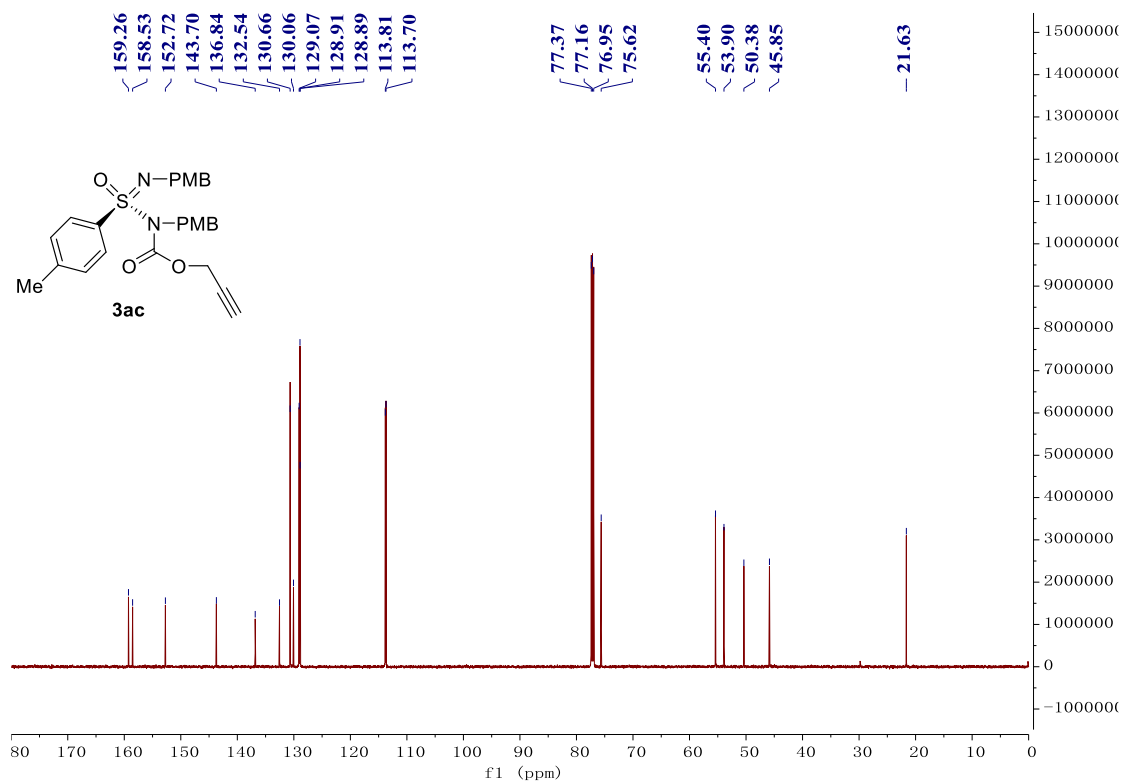
^{13}C NMR Spectrum of **3ab** (150 MHz, CDCl_3)



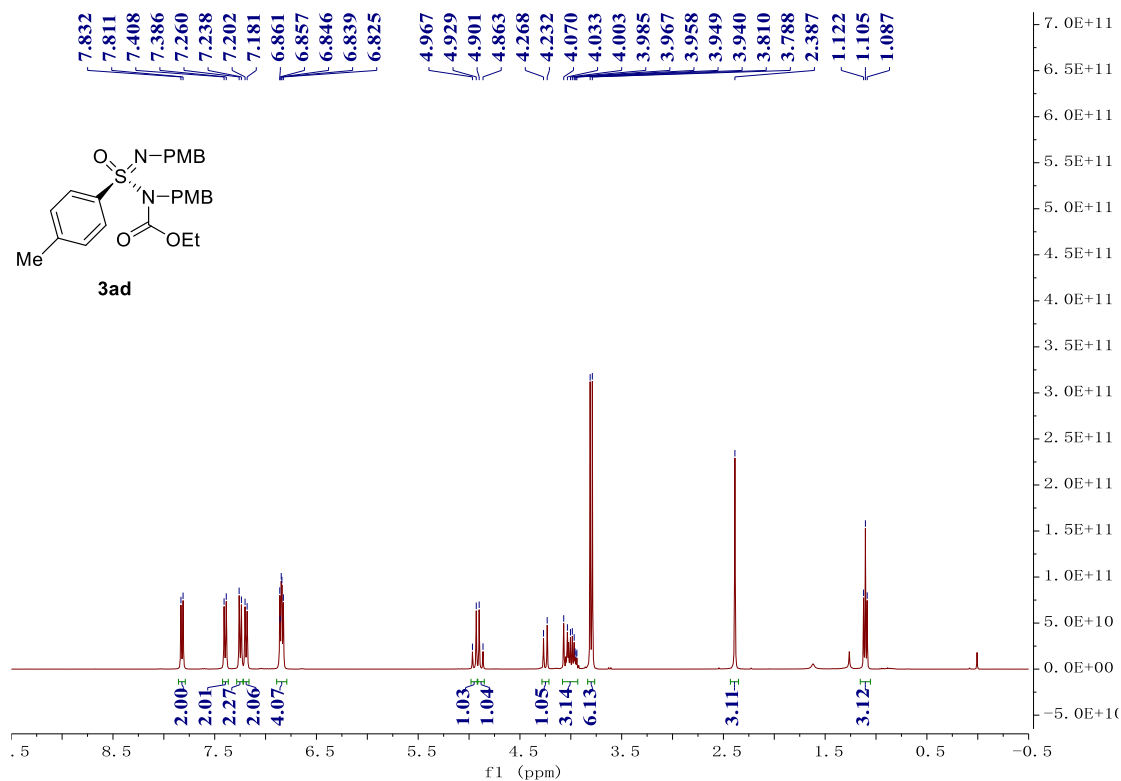
^1H NMR Spectrum of **3ac** (600 MHz, CDCl_3)



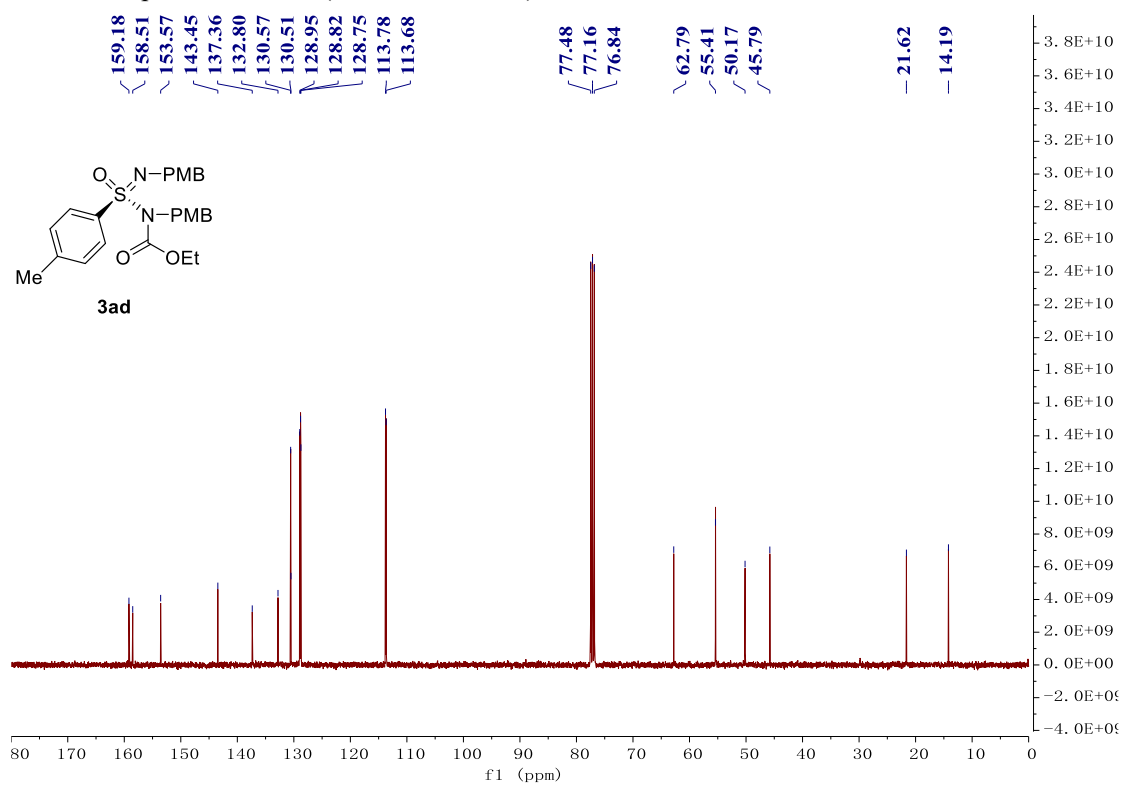
¹³C NMR Spectrum of **3ac** (150 MHz, CDCl₃)



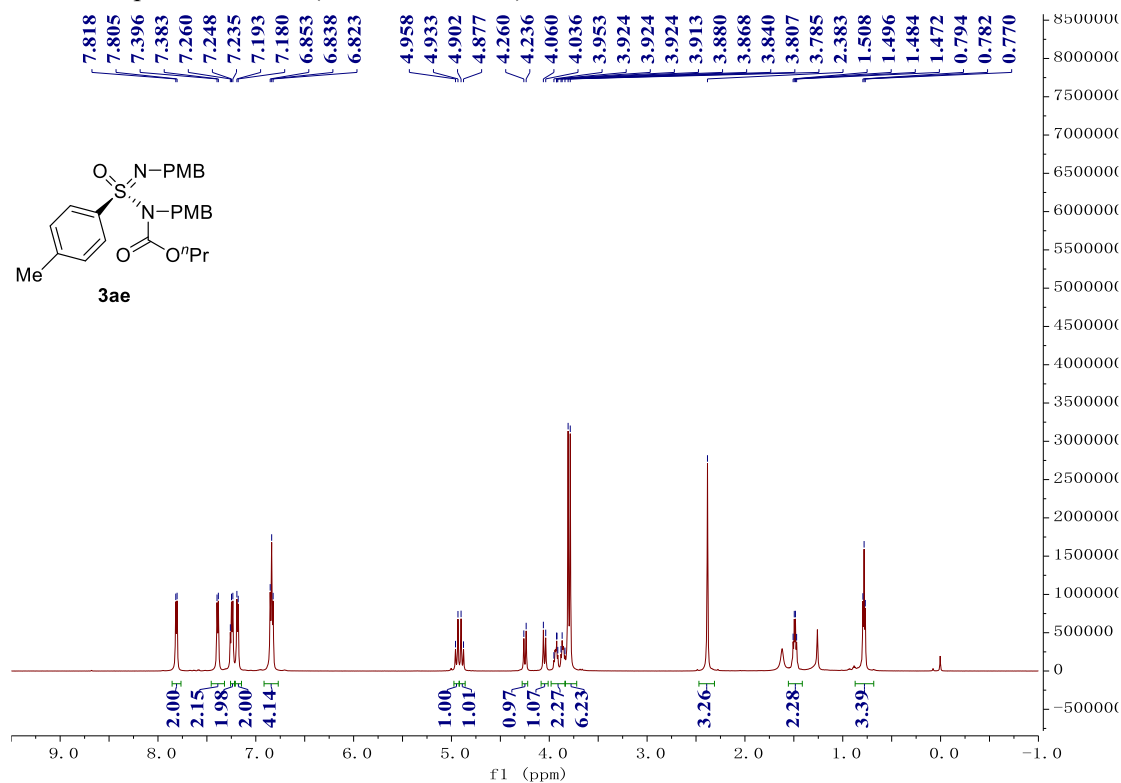
¹H NMR Spectrum of **3ad** (400 MHz, CDCl₃)



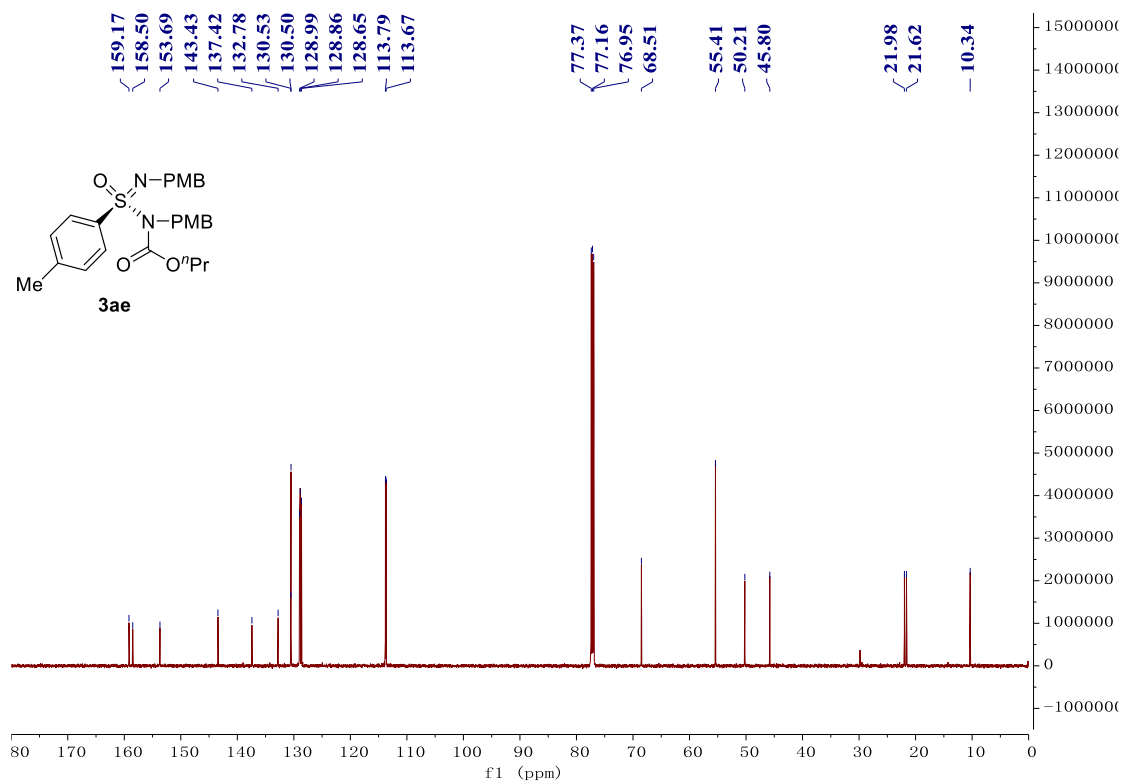
^{13}C NMR Spectrum of **3ad** (100 MHz, CDCl_3)



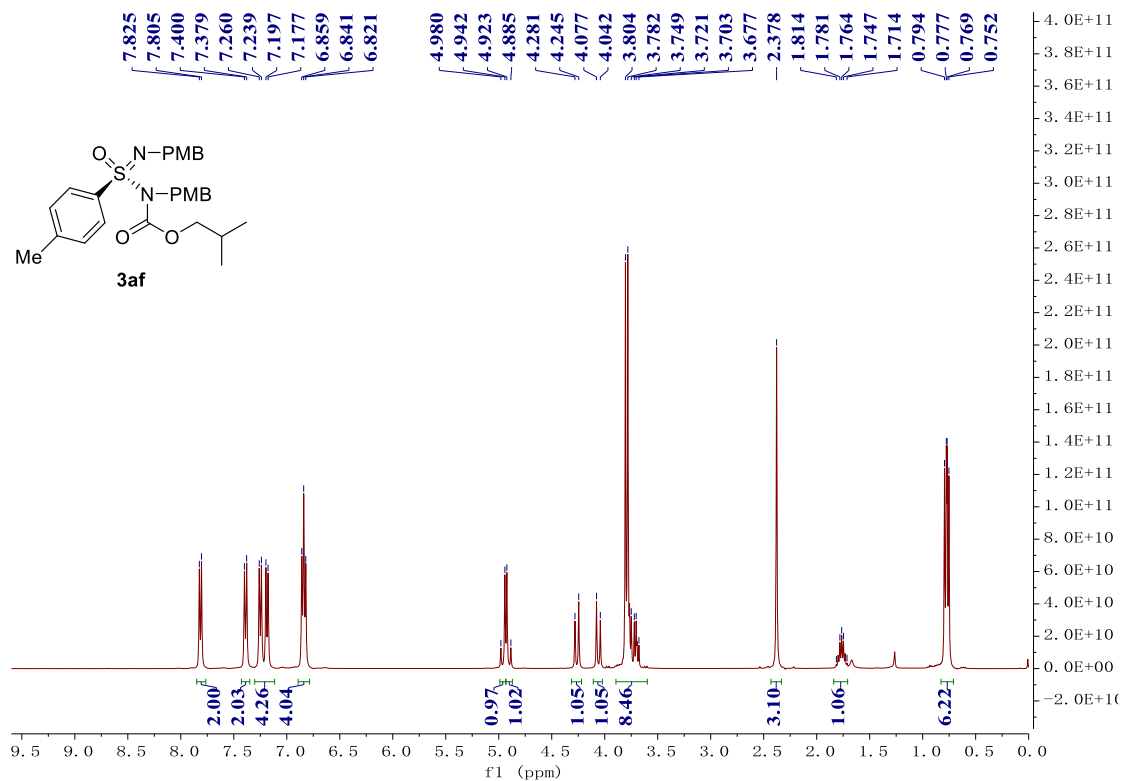
^1H NMR Spectrum of **3ae** (600 MHz, CDCl_3)



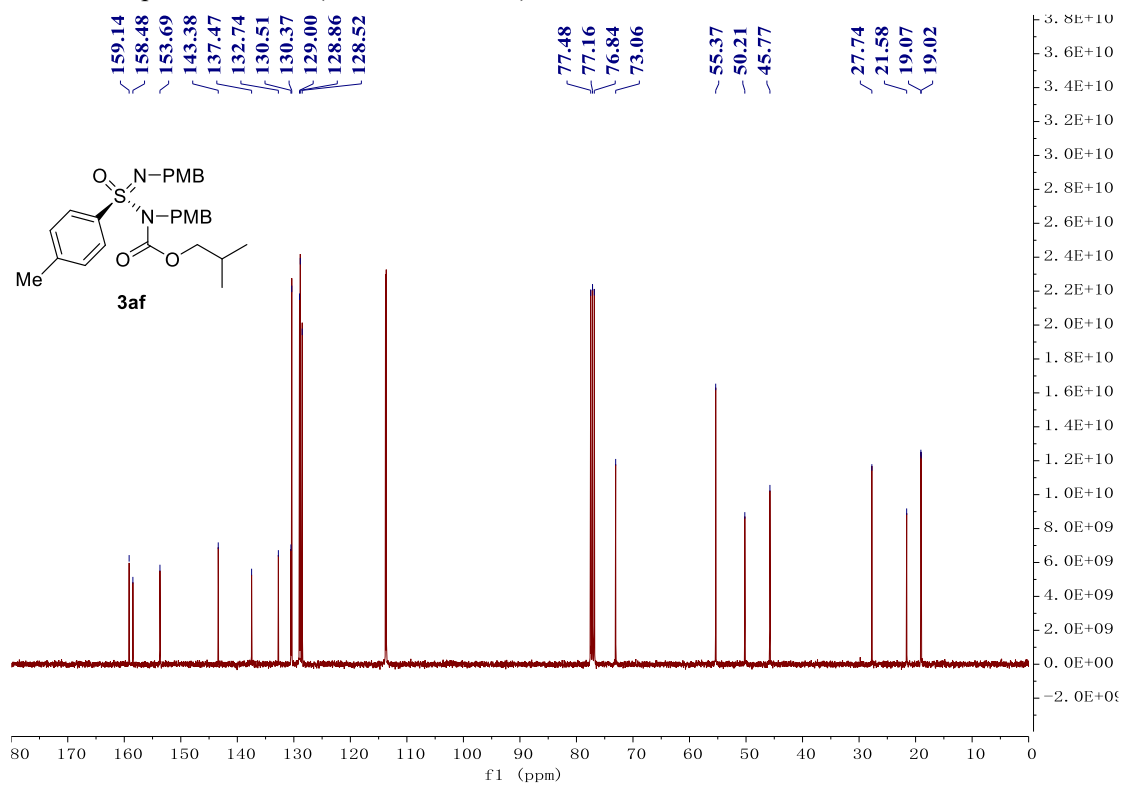
^{13}C NMR Spectrum of **3ae** (150 MHz, CDCl_3)



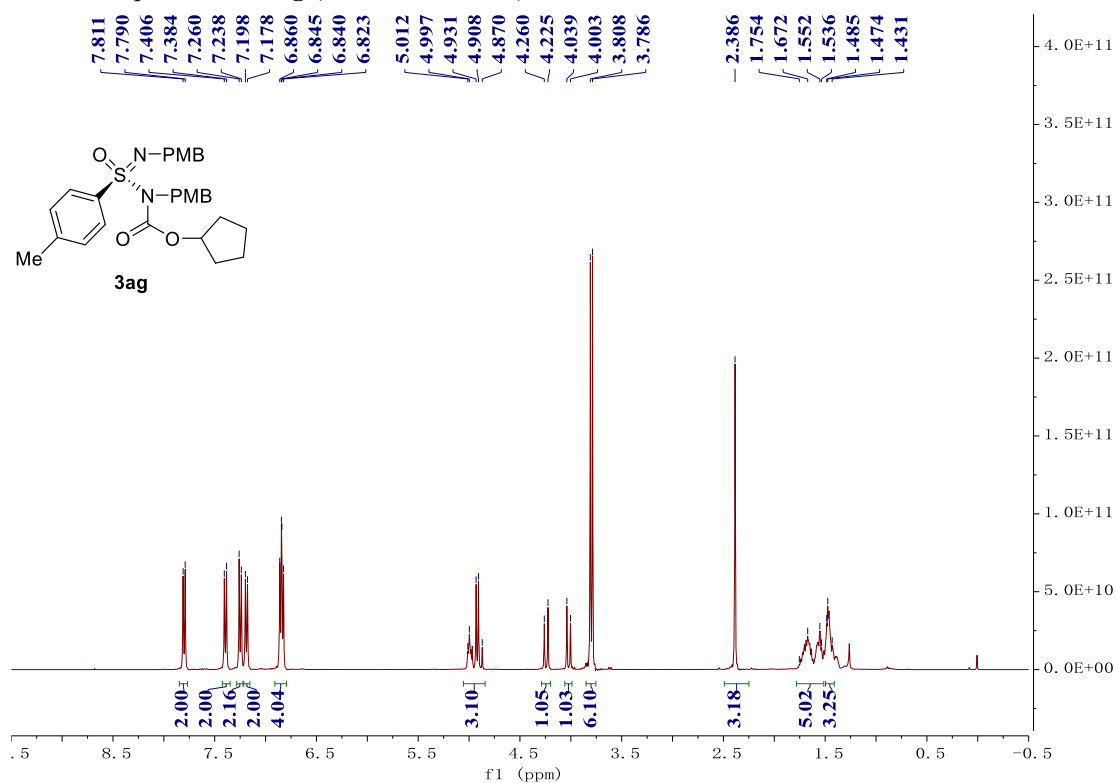
^1H NMR Spectrum of **3af** (400 MHz, CDCl_3)



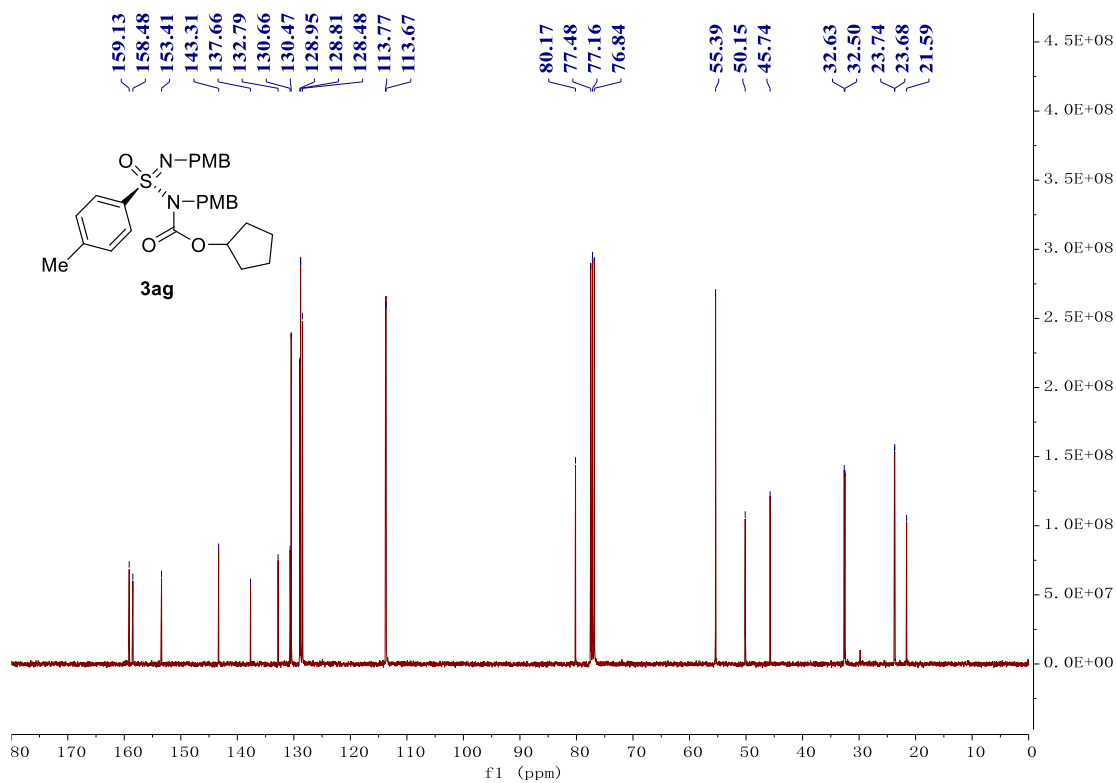
^{13}C NMR Spectrum of **3af** (100 MHz, CDCl_3)



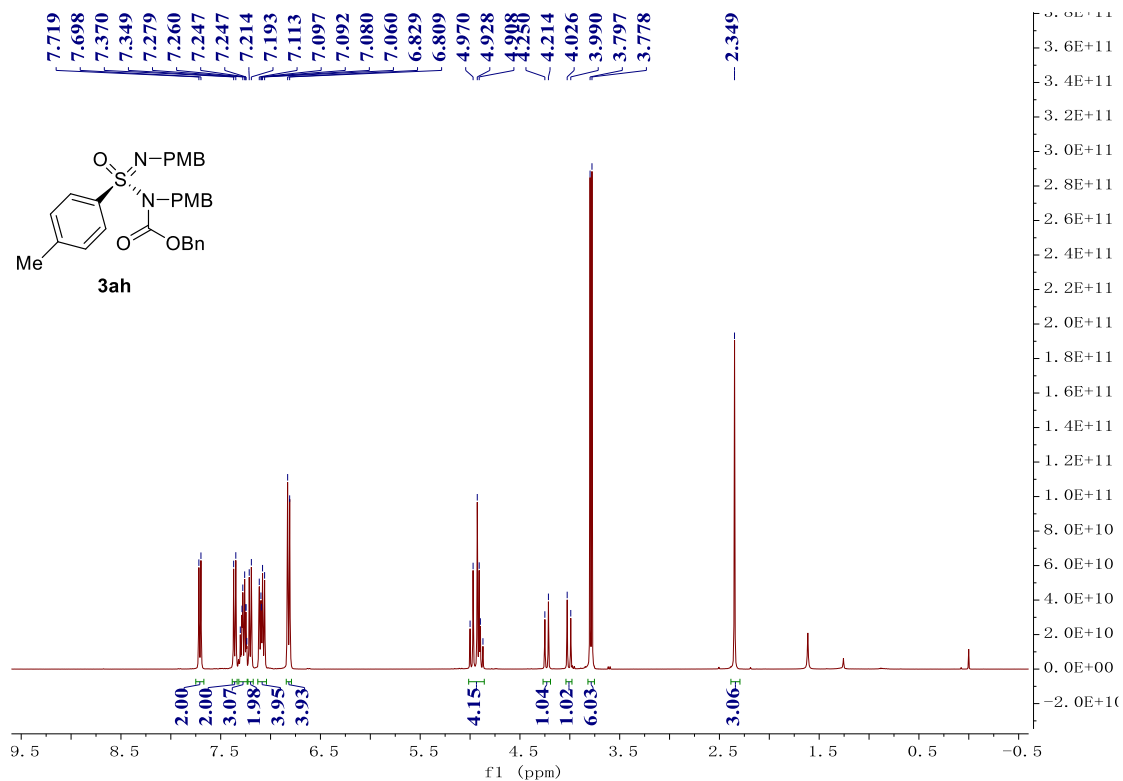
^1H NMR Spectrum of **3ag** (400 MHz, CDCl_3)



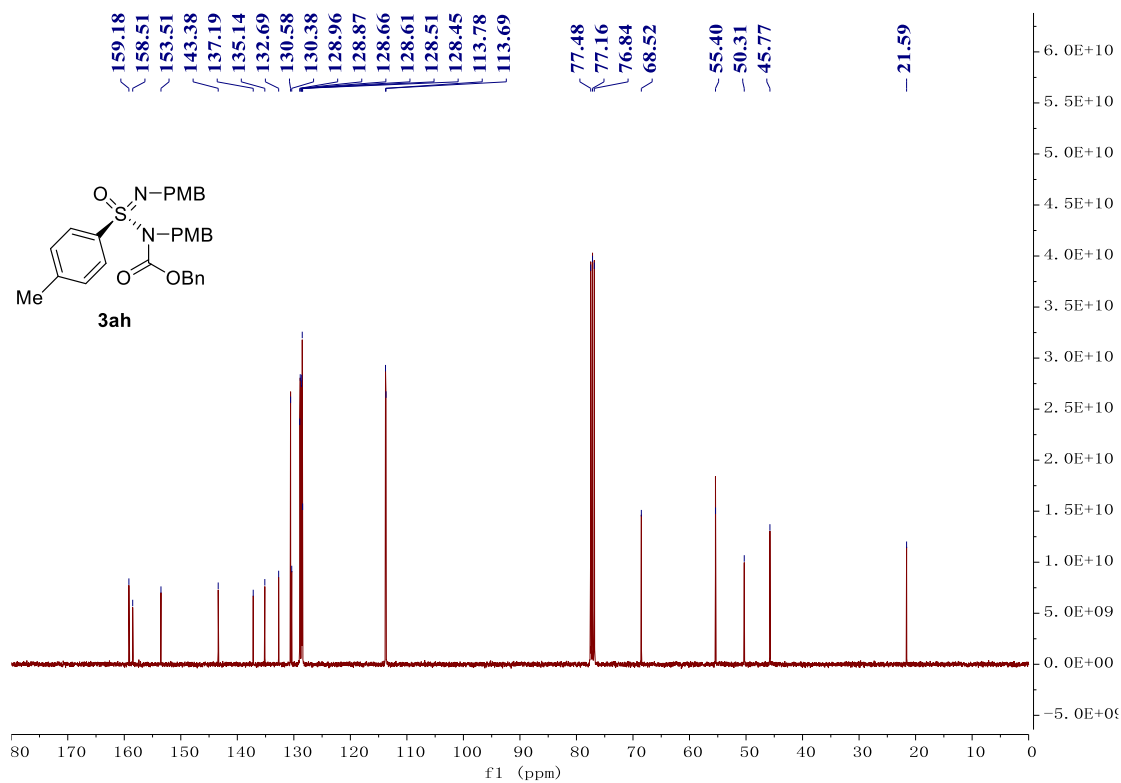
^{13}C NMR Spectrum of **3ag** (100 MHz, CDCl_3)



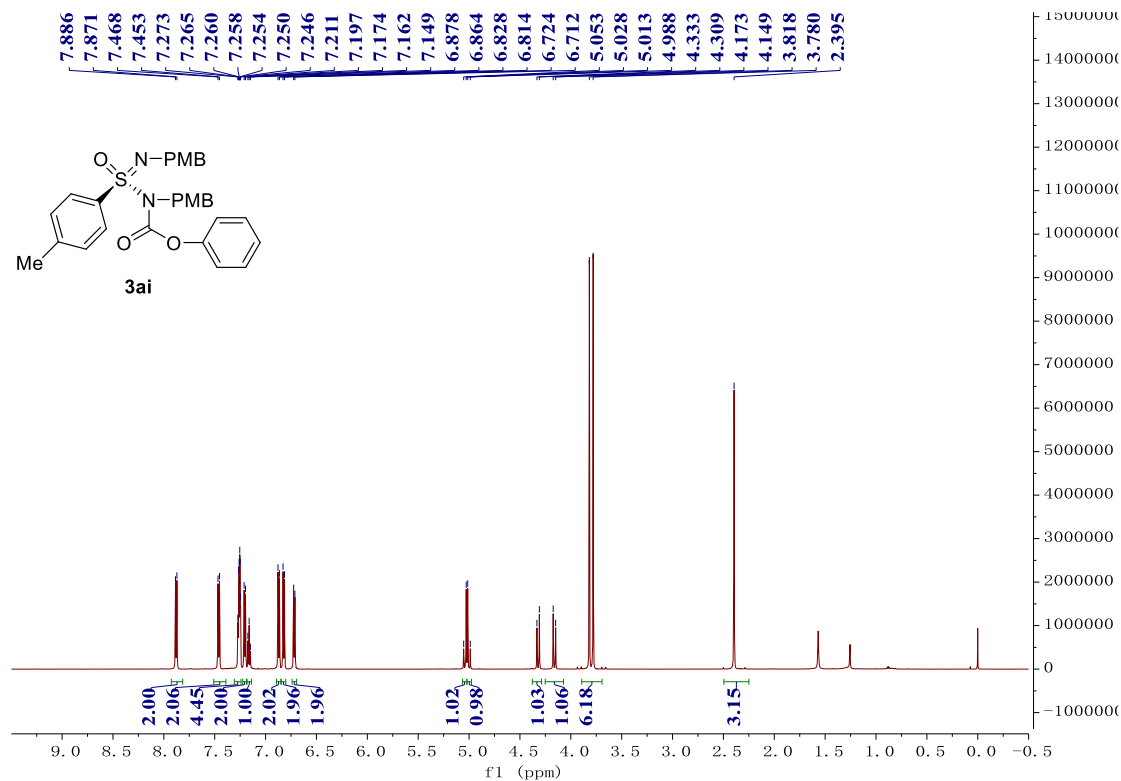
^1H NMR Spectrum of **3ah** (400 MHz, CDCl_3)



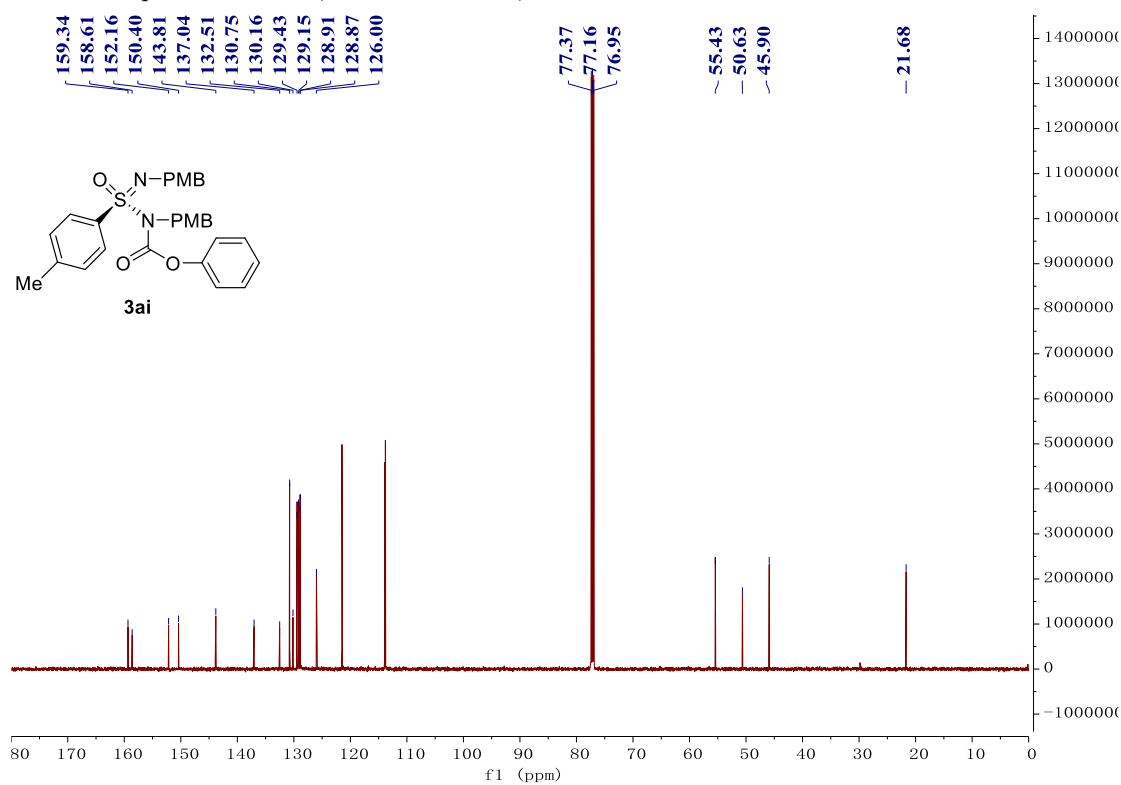
^{13}C NMR Spectrum of **3ah** (100 MHz, CDCl_3)



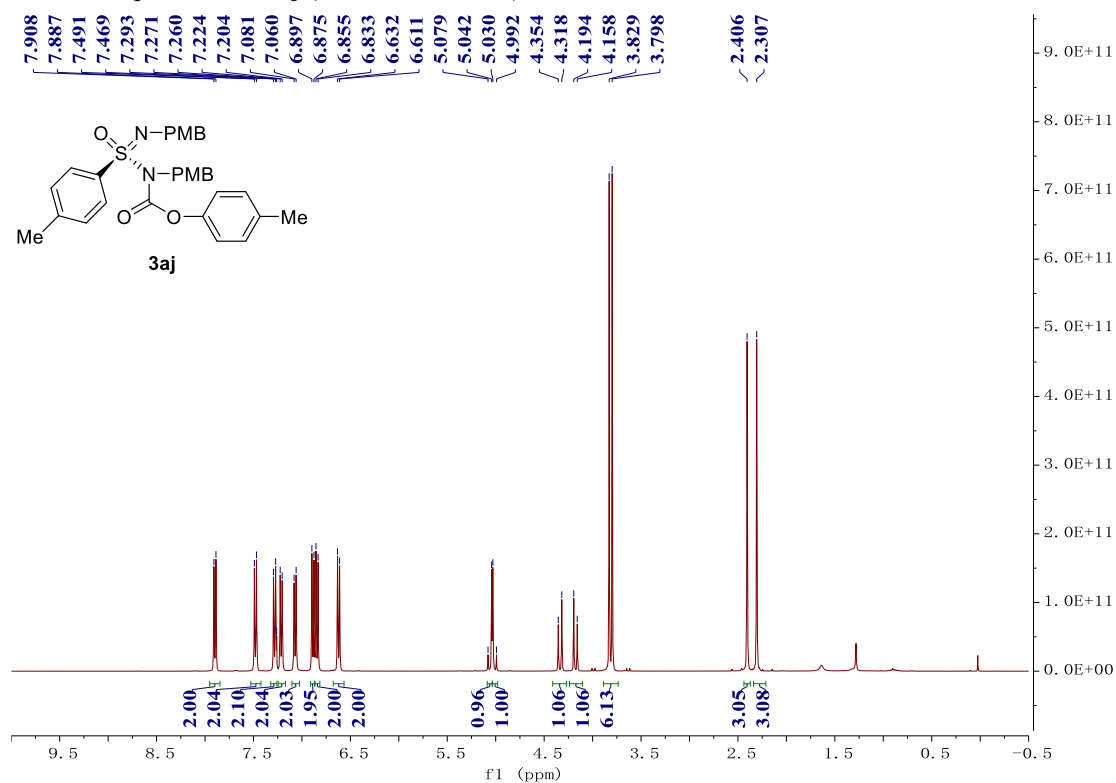
^1H NMR Spectrum of **3ai** (600 MHz, CDCl_3)



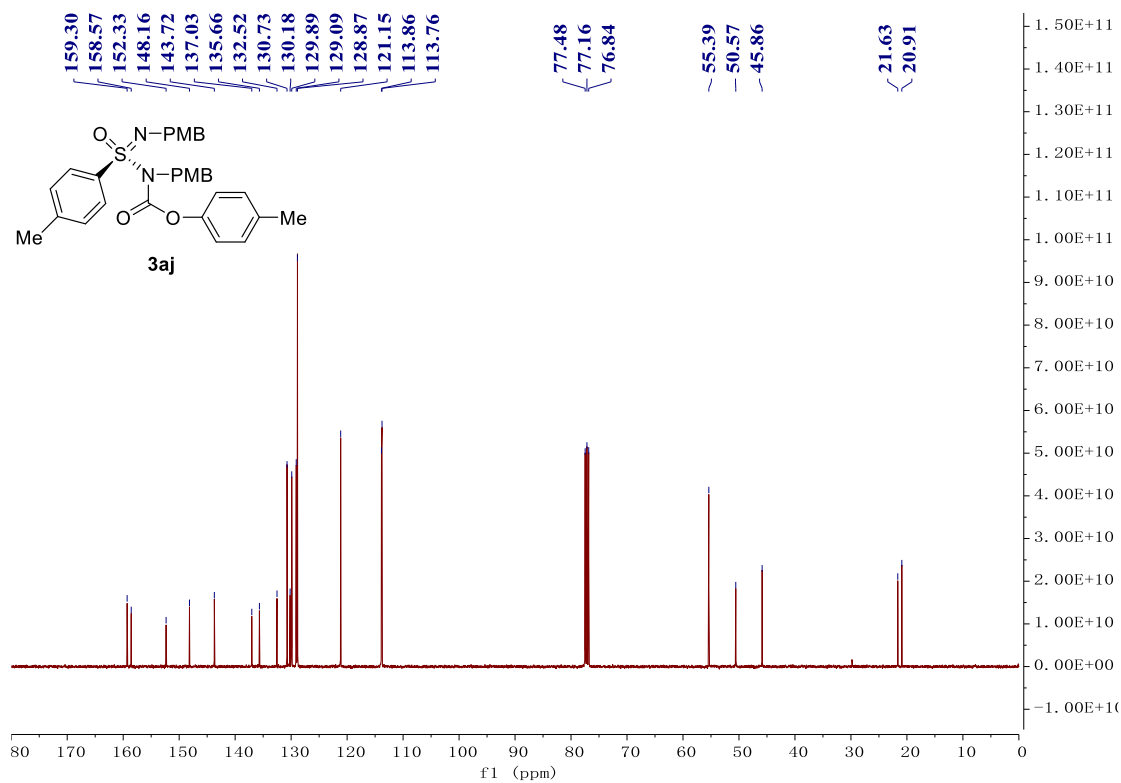
^{13}C NMR Spectrum of **3ai** (150 MHz, CDCl_3)



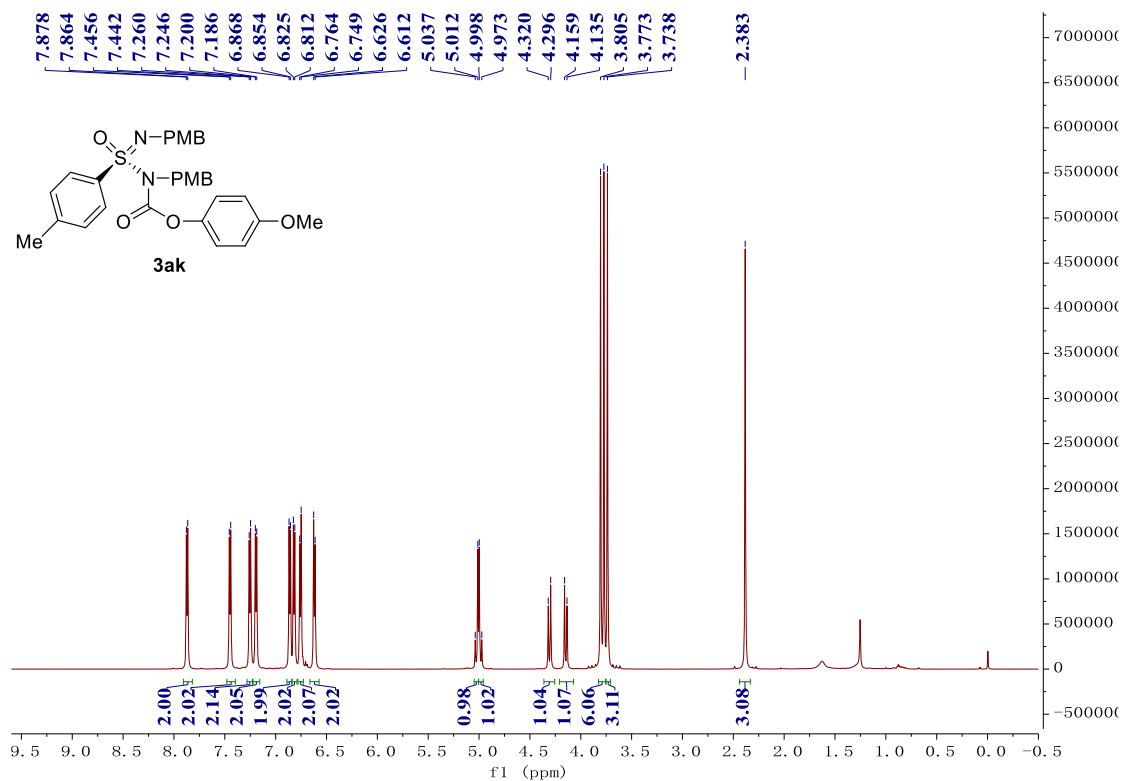
^1H NMR Spectrum of **3aj** (400 MHz, CDCl_3)



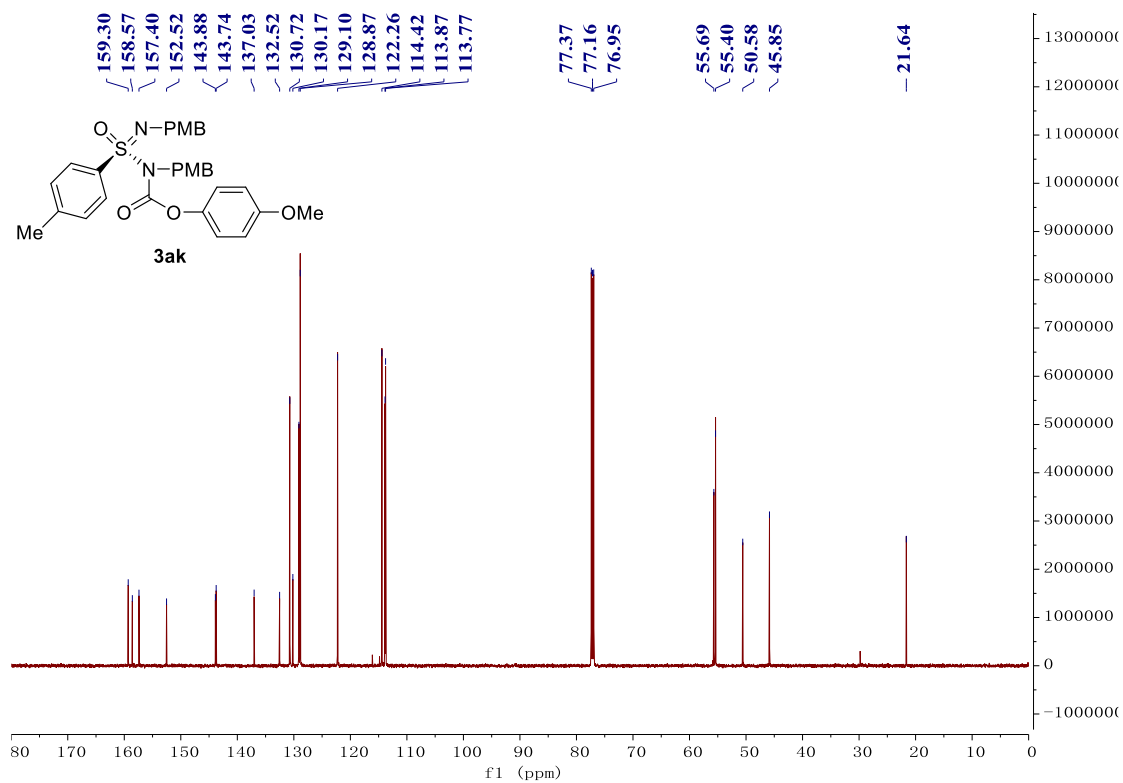
^{13}C NMR Spectrum of **3aj** (100 MHz, CDCl_3)



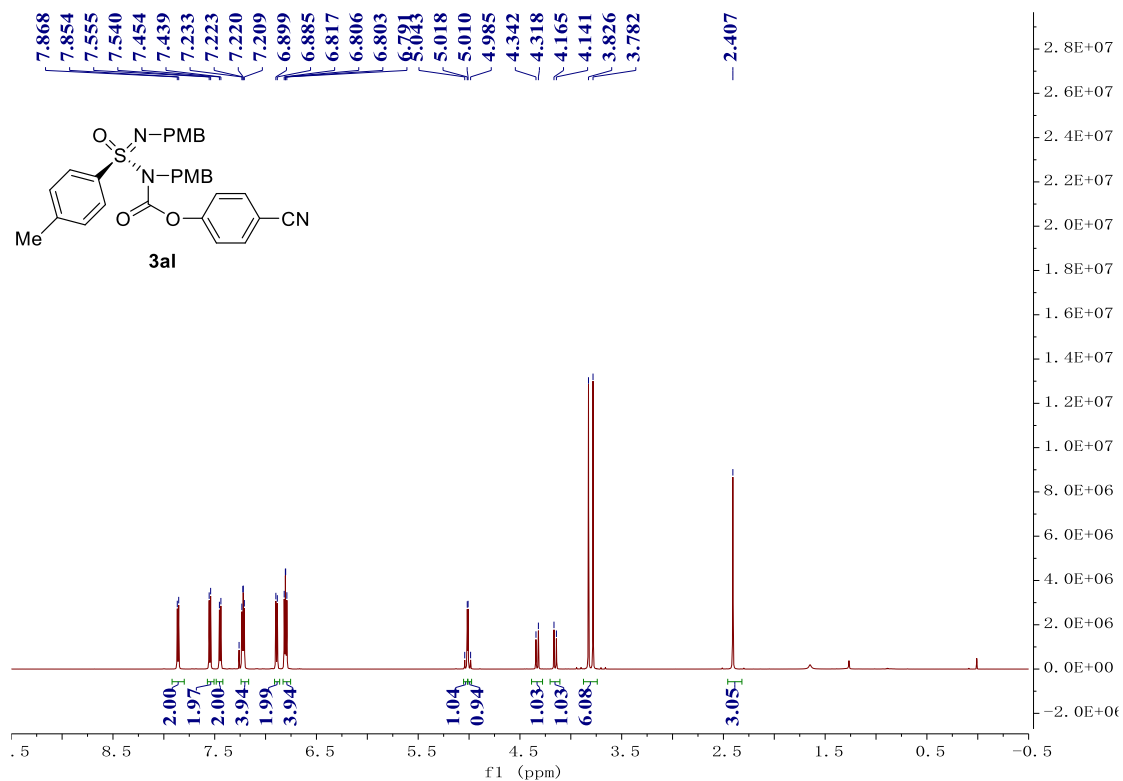
^1H NMR Spectrum of **3ak** (600 MHz, CDCl_3)



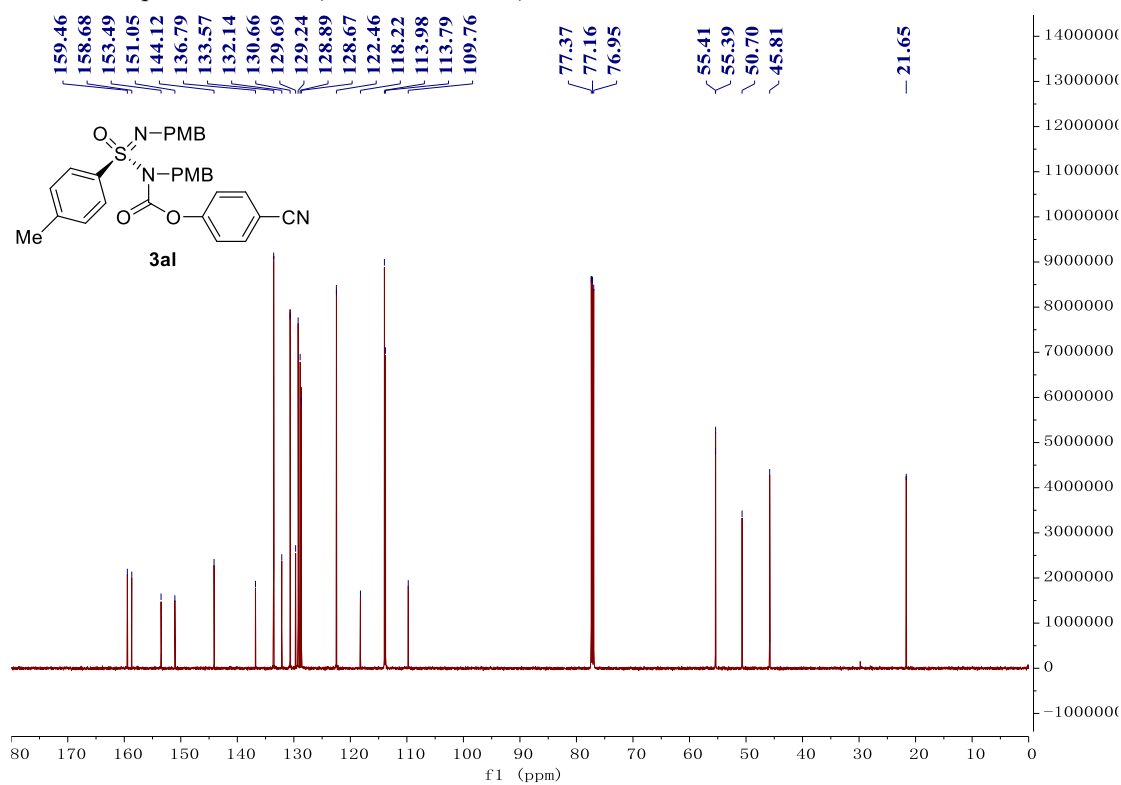
^{13}C NMR Spectrum of **3ak** (150 MHz, CDCl_3)



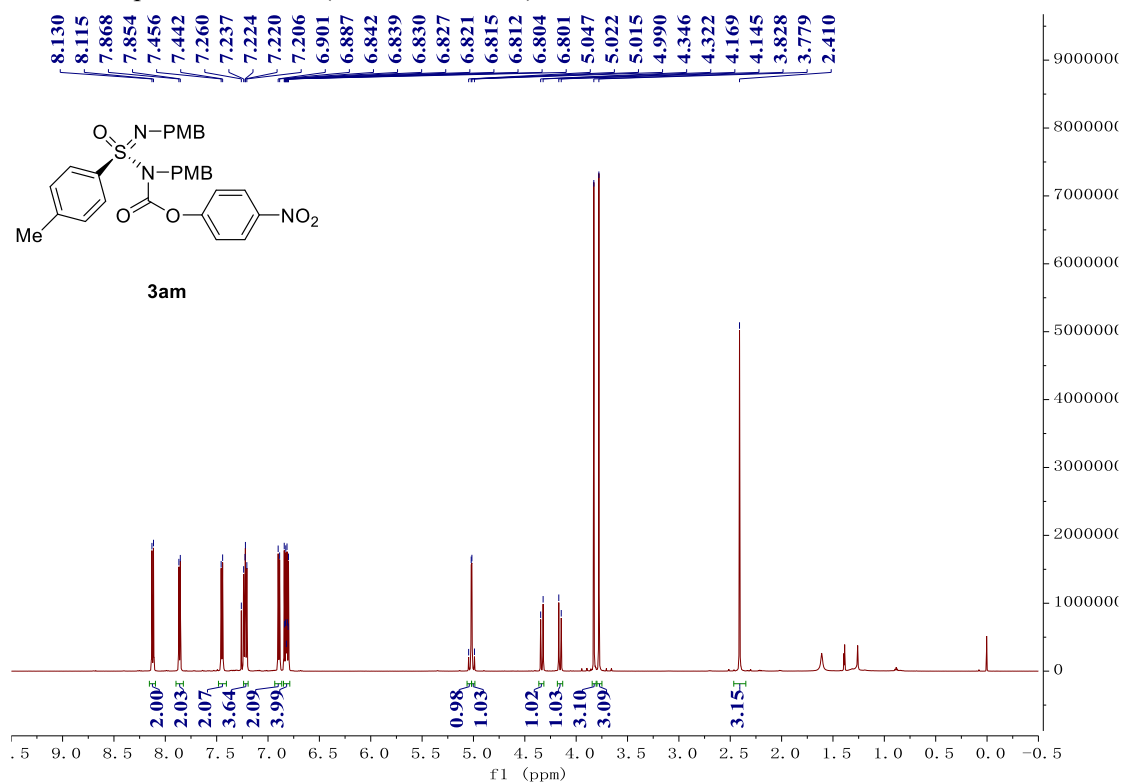
^1H NMR Spectrum of **3al** (600 MHz, CDCl_3)



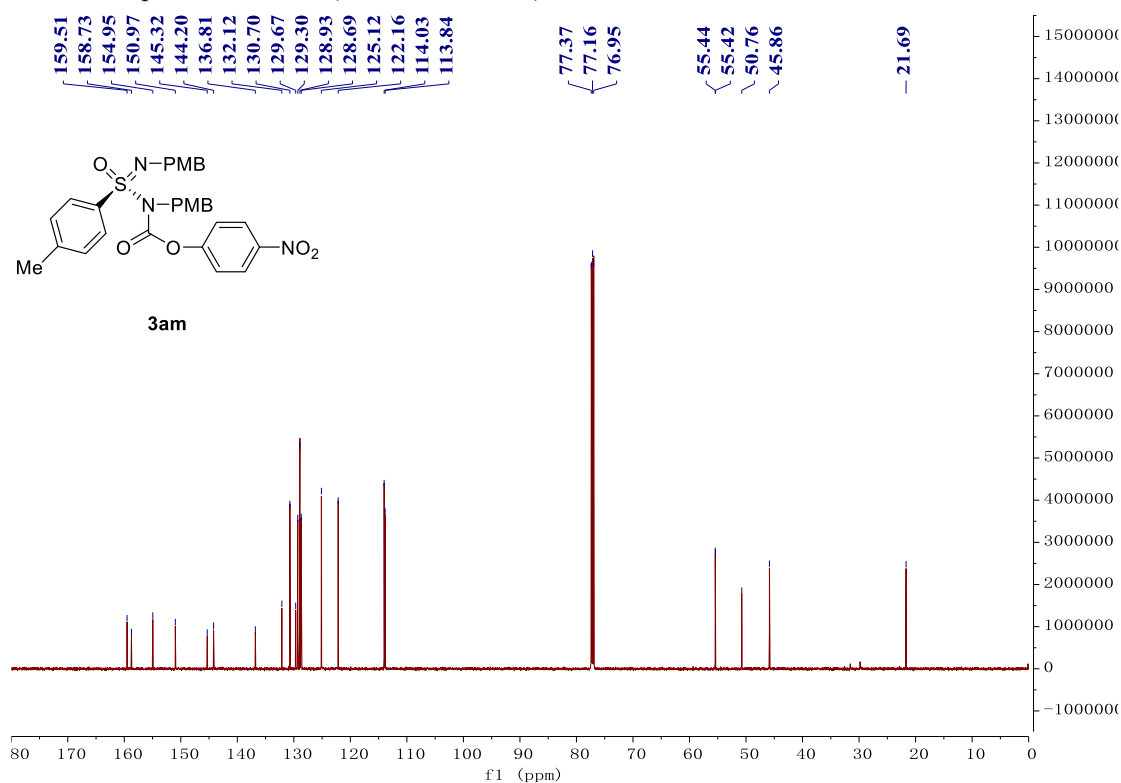
^{13}C NMR Spectrum of **3al** (150 MHz, CDCl_3)



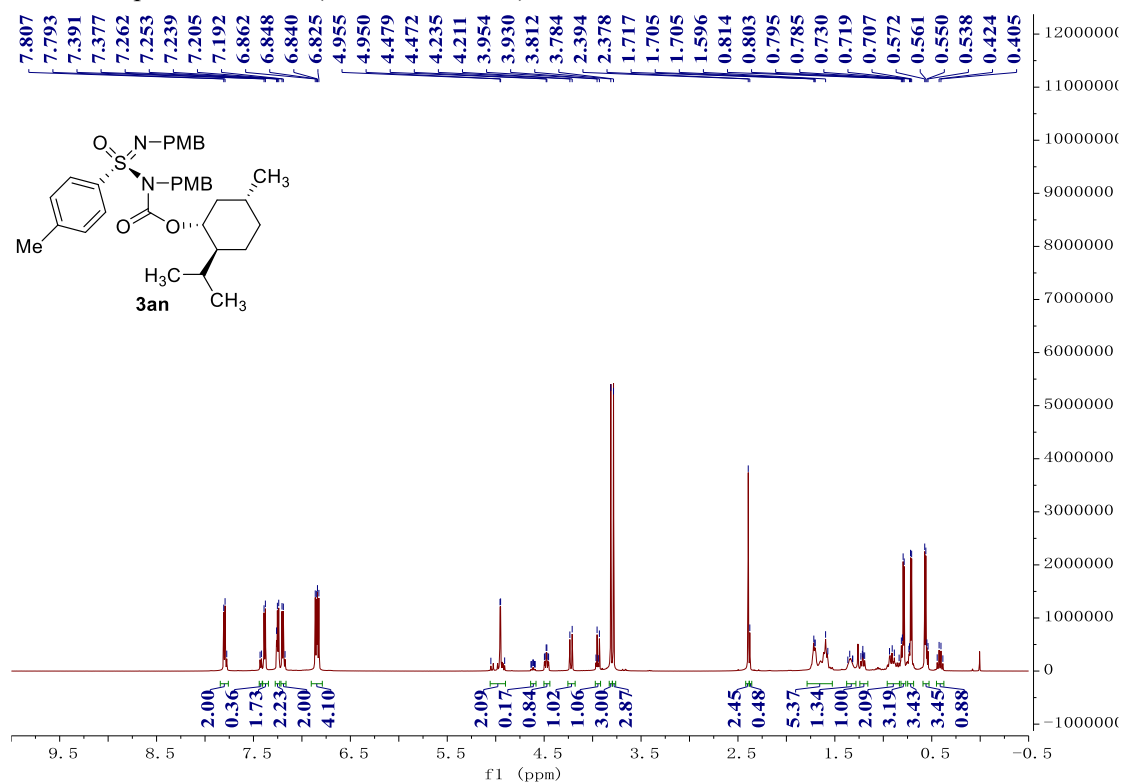
^1H NMR Spectrum of **3am** (600 MHz, CDCl_3)



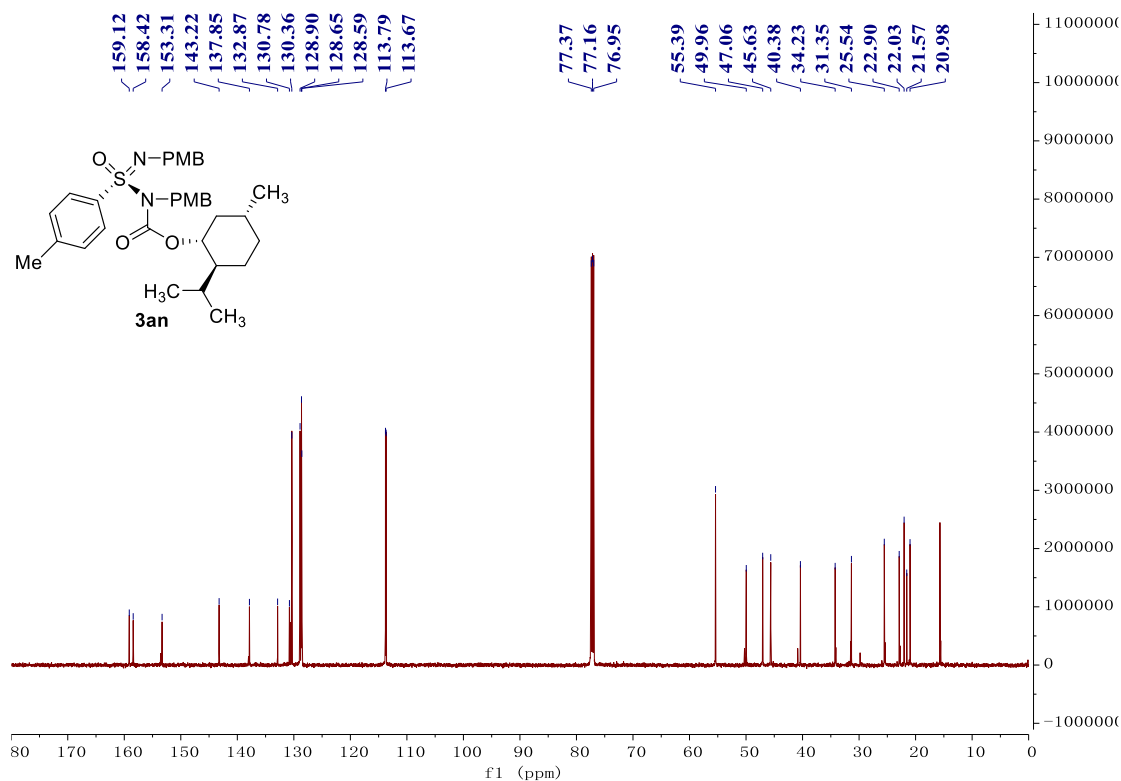
¹³C NMR Spectrum of **3am** (150 MHz, CDCl₃)



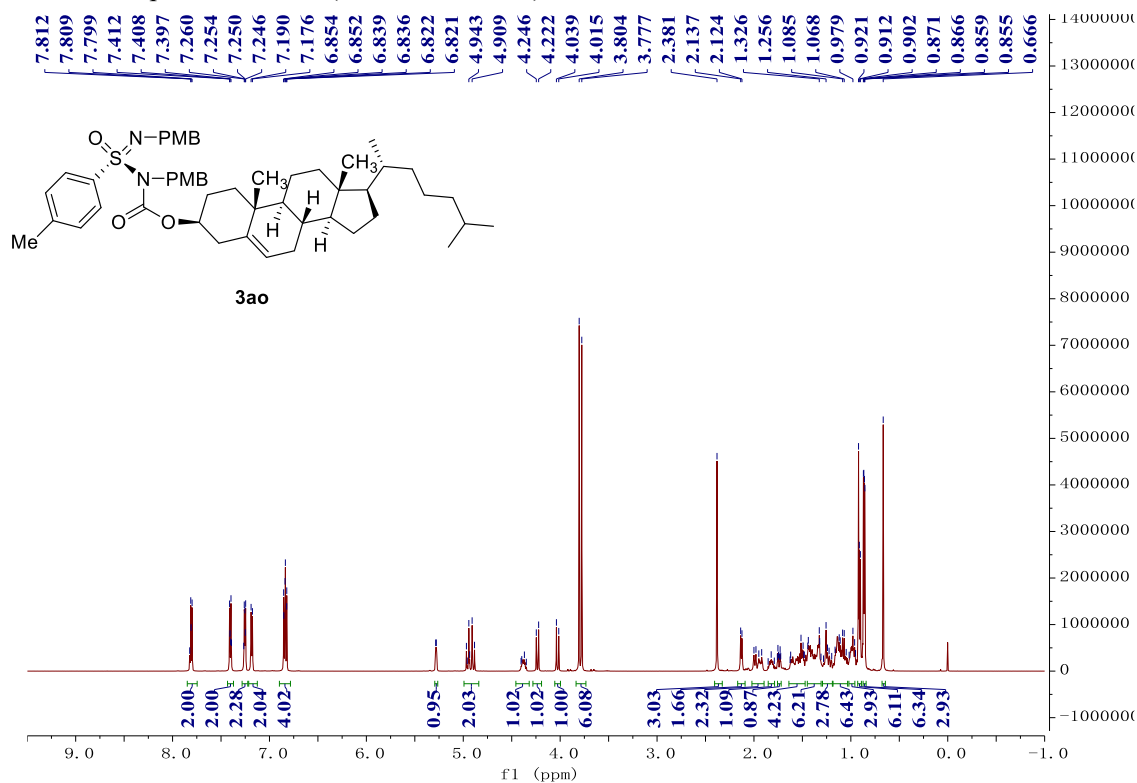
¹H NMR Spectrum of **3an** (600 MHz, CDCl₃)



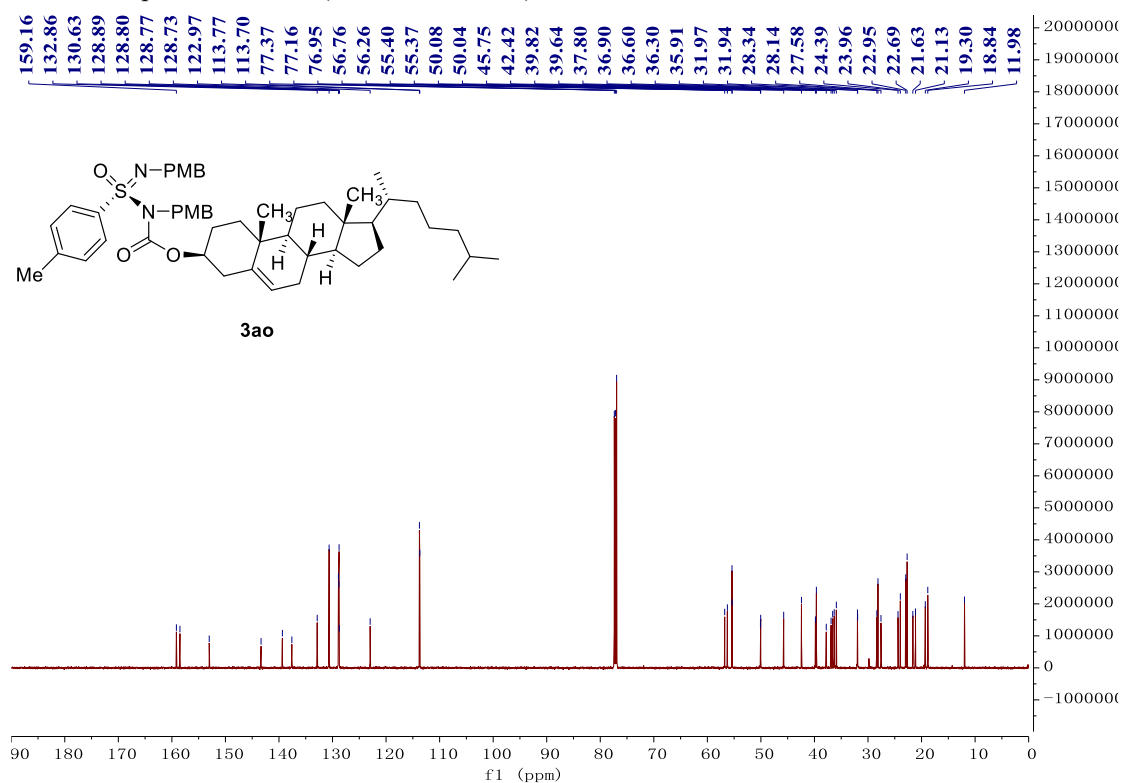
¹³C NMR Spectrum of **3an** (150 MHz, CDCl₃)



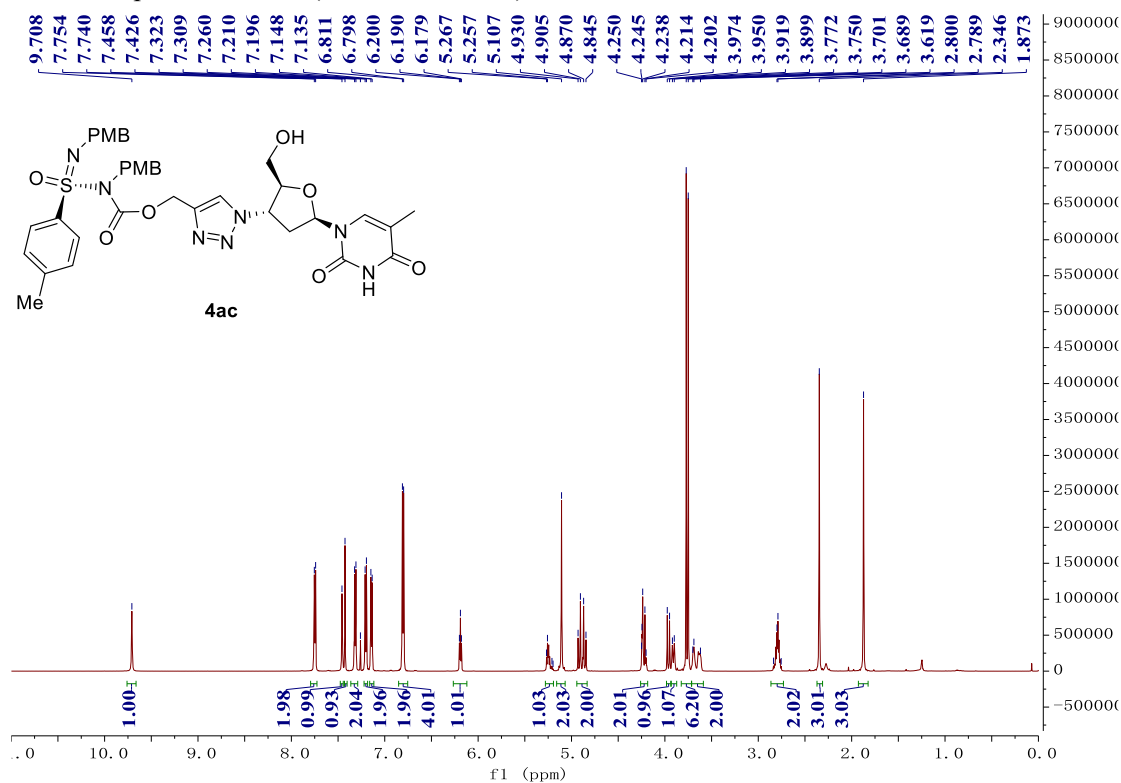
¹H NMR Spectrum of **3ao** (400 MHz, CDCl₃)



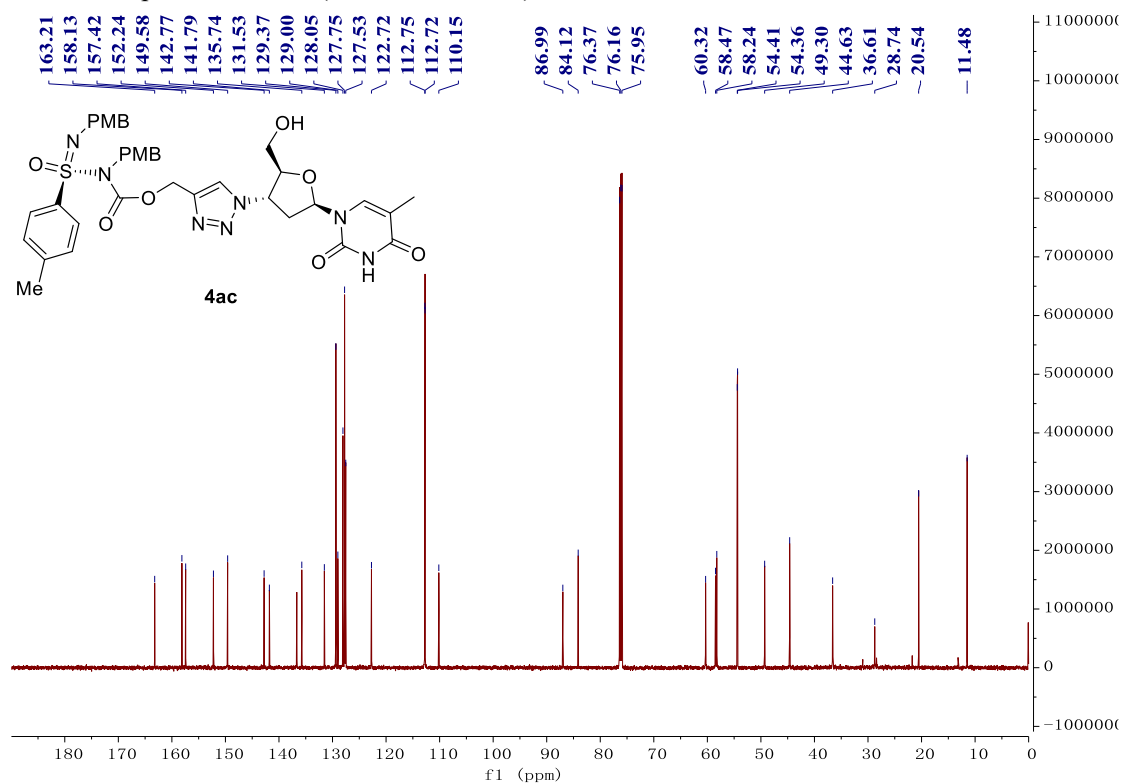
^{13}C NMR Spectrum of **3ao** (100 MHz, CDCl_3)



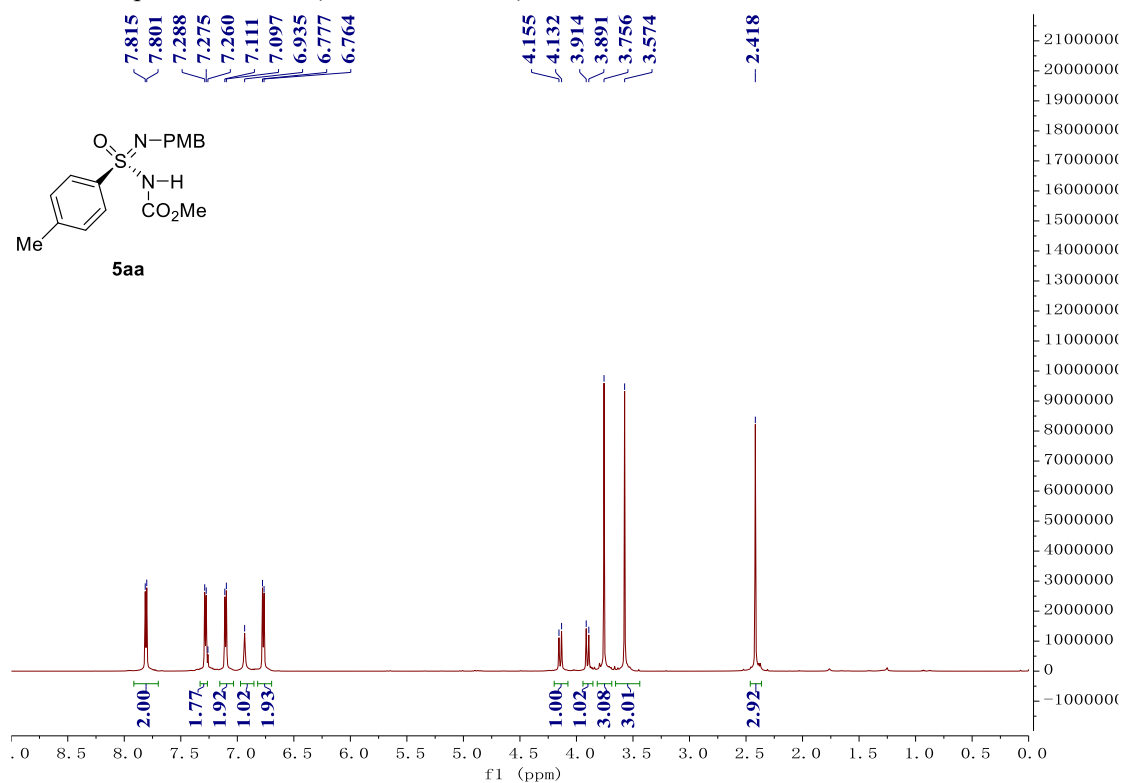
^1H NMR Spectrum of **4ac** (600 MHz, CDCl_3)



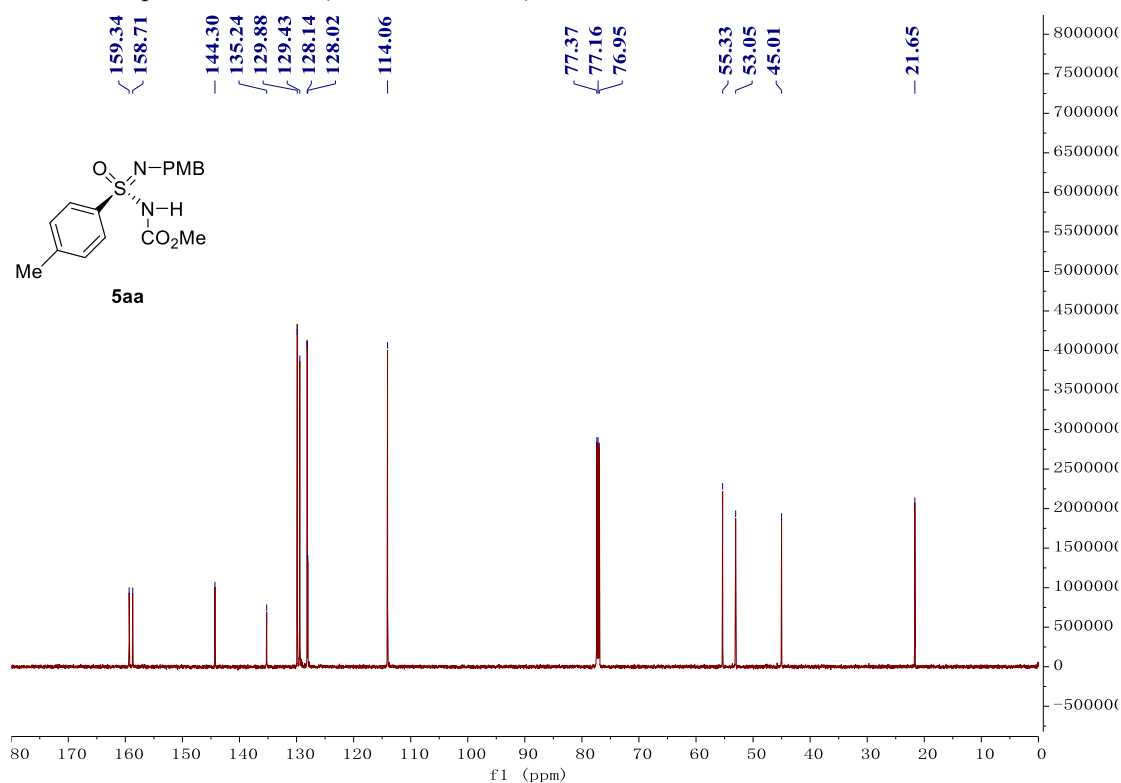
^{13}C NMR Spectrum of **4ac** (150 MHz, CDCl_3)



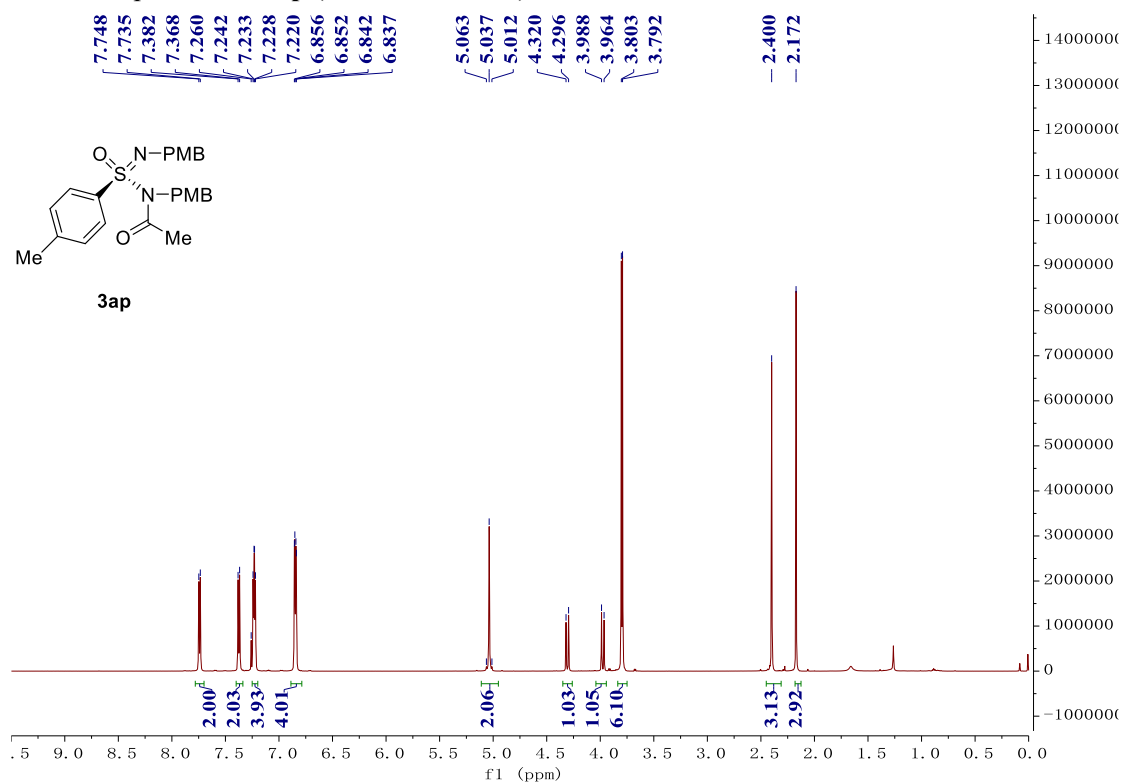
^1H NMR Spectrum of **5aa** (600 MHz, CDCl_3)



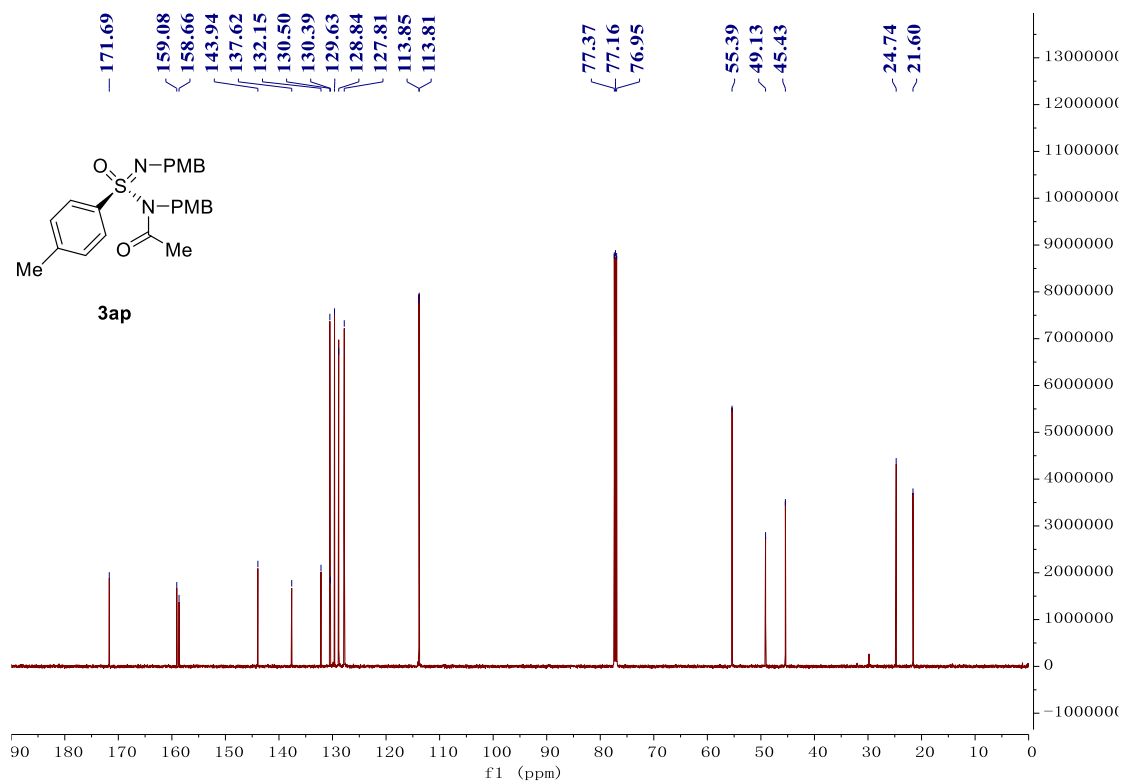
^{13}C NMR Spectrum of **5aa** (150 MHz, CDCl_3)



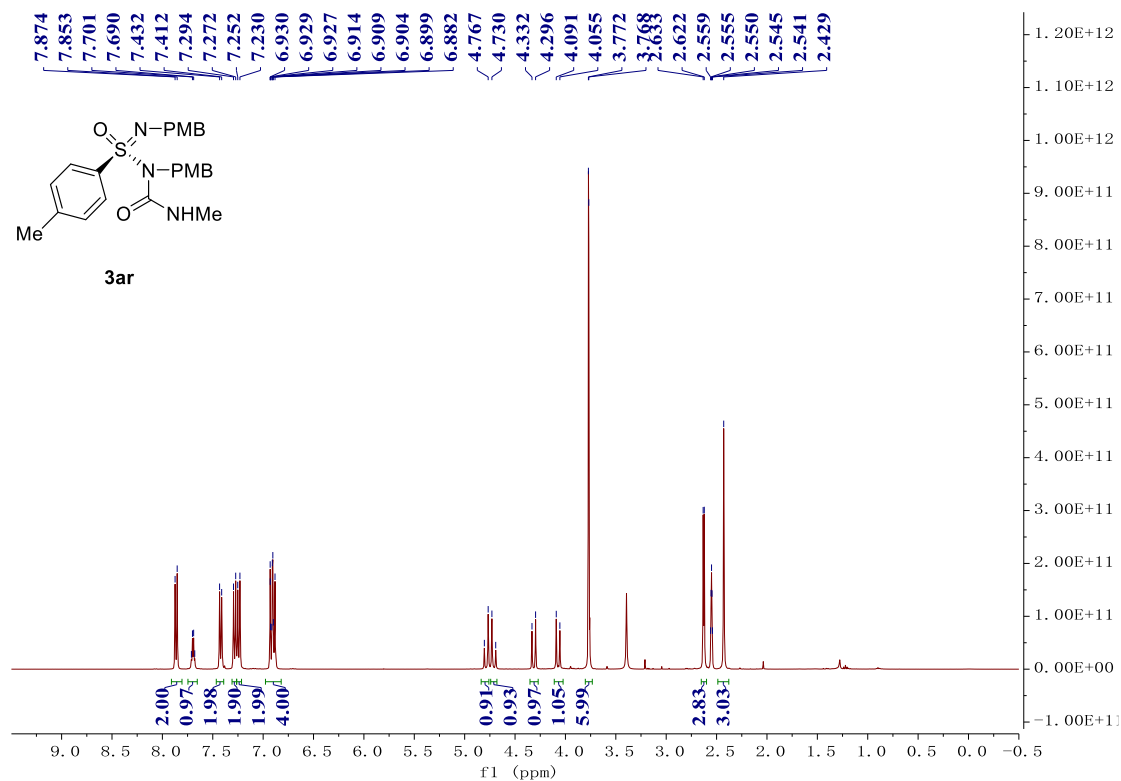
^1H NMR Spectrum of **3ap** (600 MHz, CDCl_3)



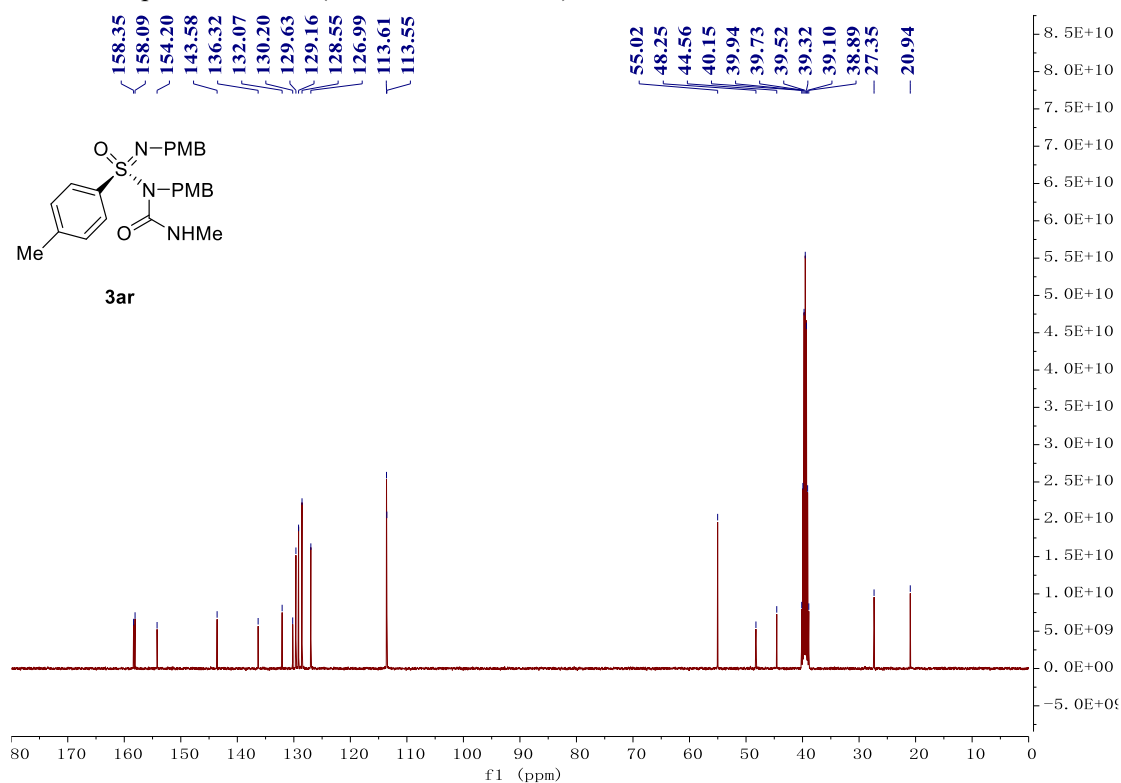
^{13}C NMR Spectrum of **3ap** (150 MHz, CDCl_3)



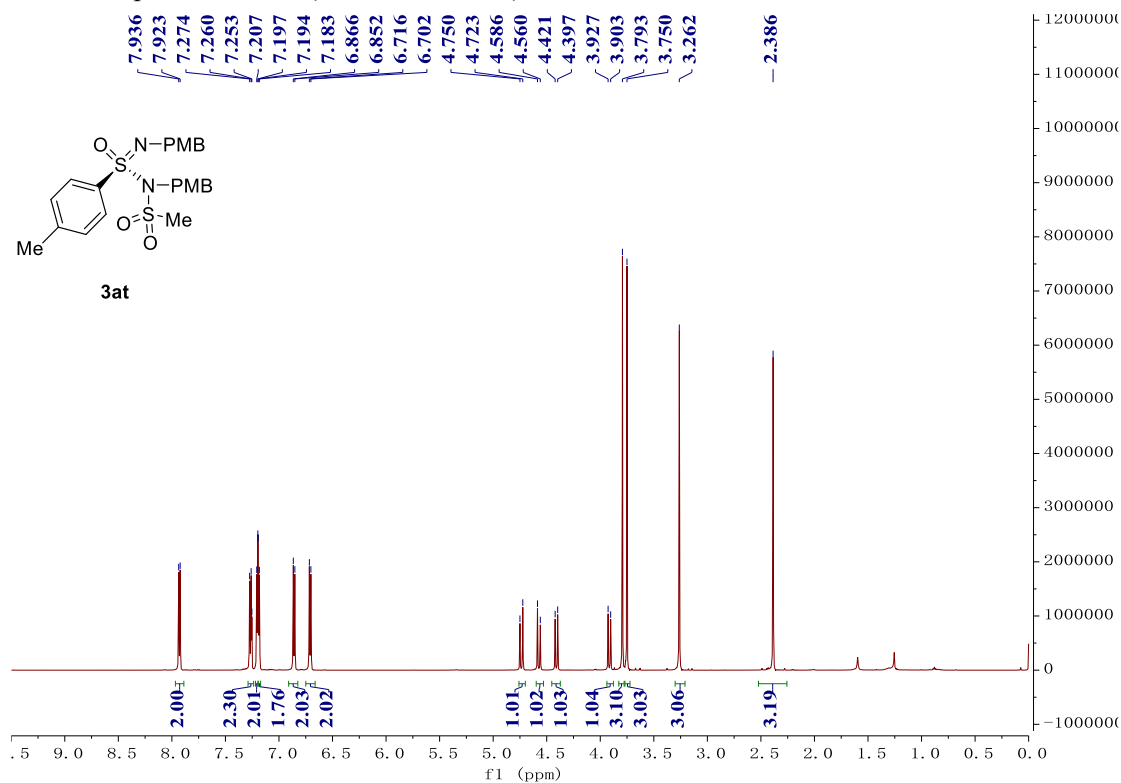
^1H NMR Spectrum of **3ar** (400 MHz, $\text{DMSO}-d_6$)



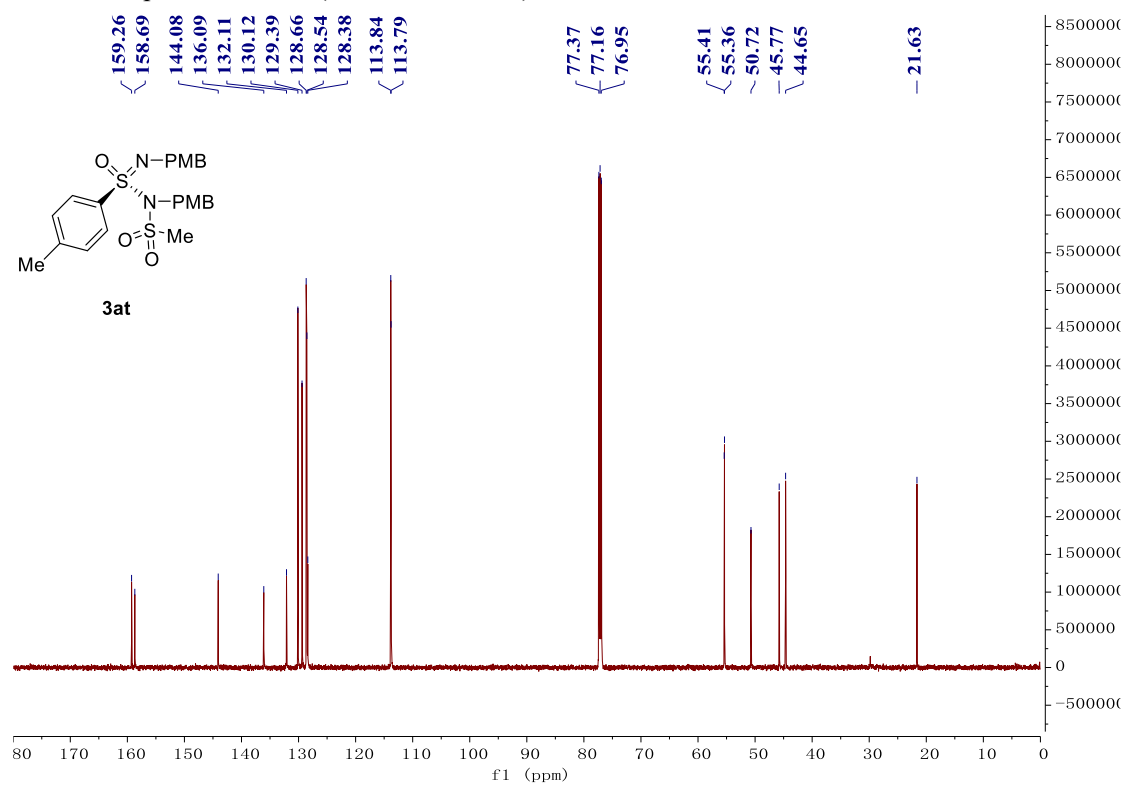
¹³C NMR Spectrum of **3ar** (100 MHz, DMSO-*d*₆)



¹H NMR Spectrum of **3at** (600 MHz, CDCl₃)

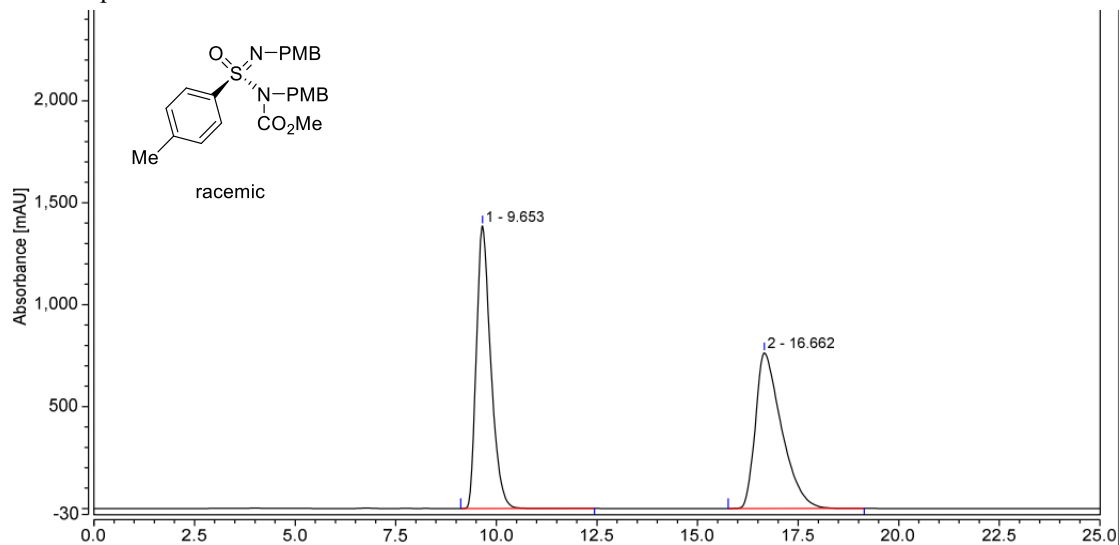


^{13}C NMR Spectrum of **3at** (150 MHz, CDCl_3)

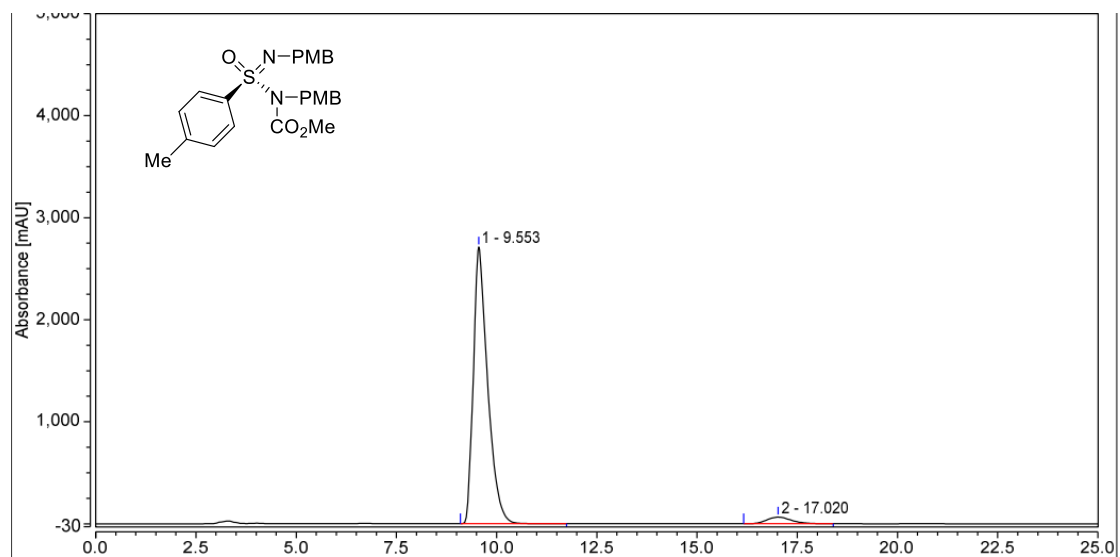


HPLC spectra

HPLC Spectrum of **3aa**

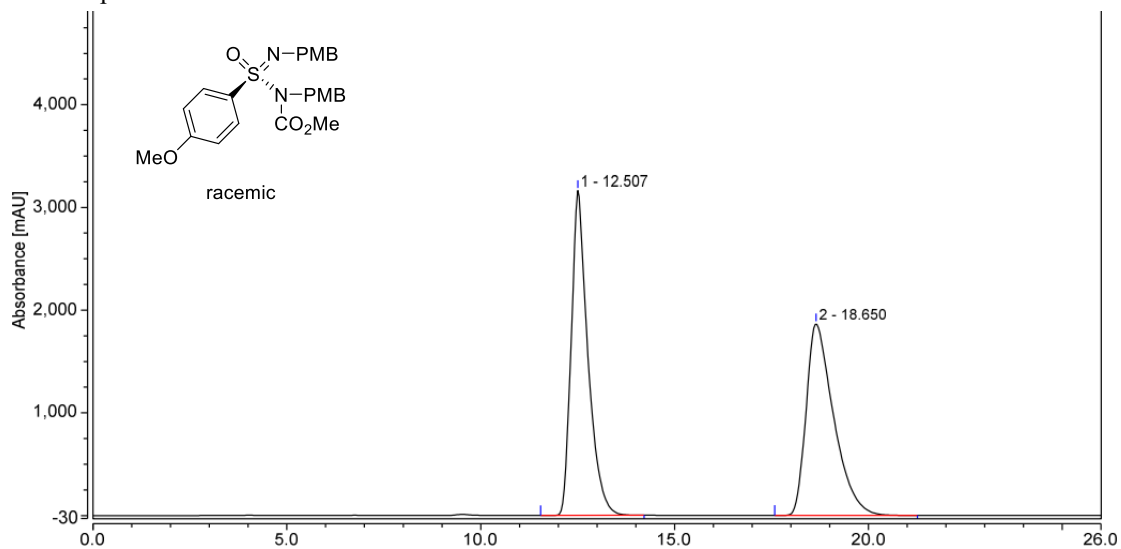


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.653	571.875	1386.089	49.92	64.46
2	16.662	573.771	764.163	50.08	35.54
Total:		1145.647	2150.252	100.00	100.00

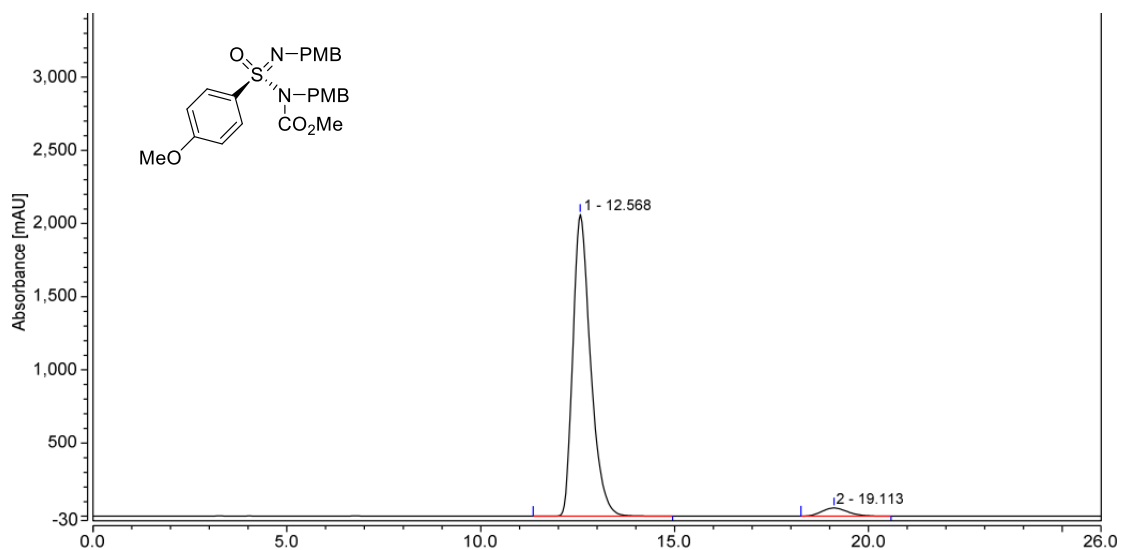


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.553	1117.768	2712.994	96.00	97.65
2	17.020	46.547	65.214	4.00	2.35
Total:		1164.315	2778.209	100.00	100.00

HPLC Spectrum of **3ba**

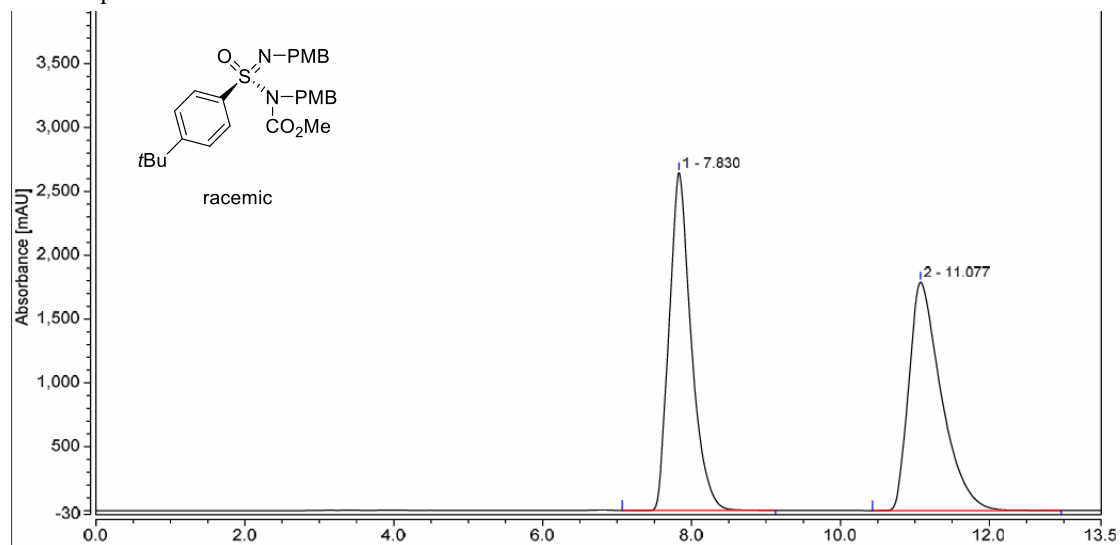


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.507	1571.146	3162.522	50.59	62.90
2	18.650	1534.509	1865.732	49.41	37.10
Total:		3105.656	5028.254	100.00	100.00

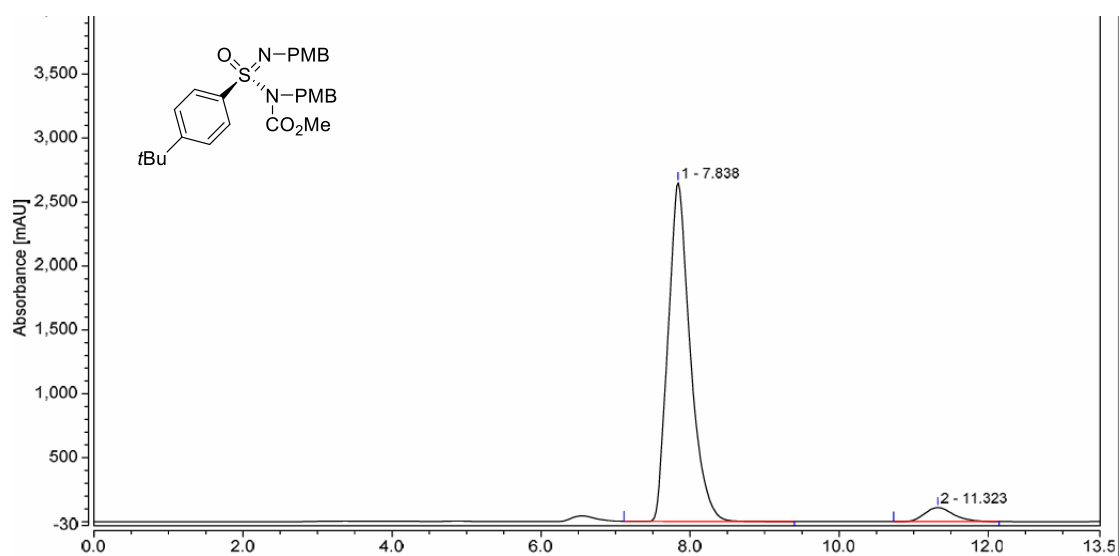


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.568	1092.178	2062.265	96.10	97.34
2	19.113	44.267	56.365	3.90	2.66
Total:		1136.445	2118.630	100.00	100.00

HPLC Spectrum of **3ca**

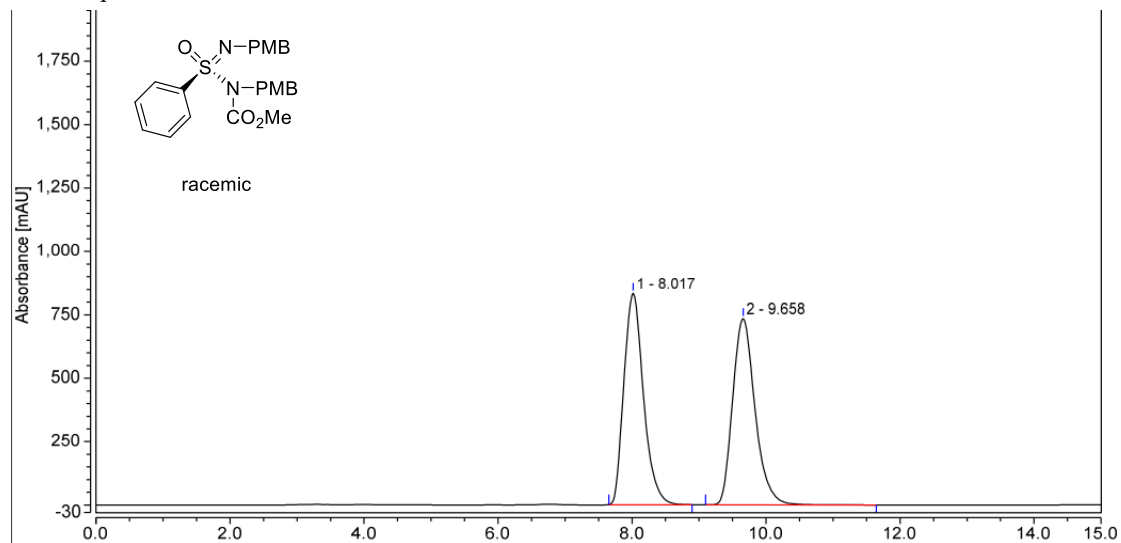


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.830	906.968	2647.029	50.15	59.65
2	11.077	901.603	1790.819	49.85	40.35
Total:		1808.571	4437.847	100.00	100.00

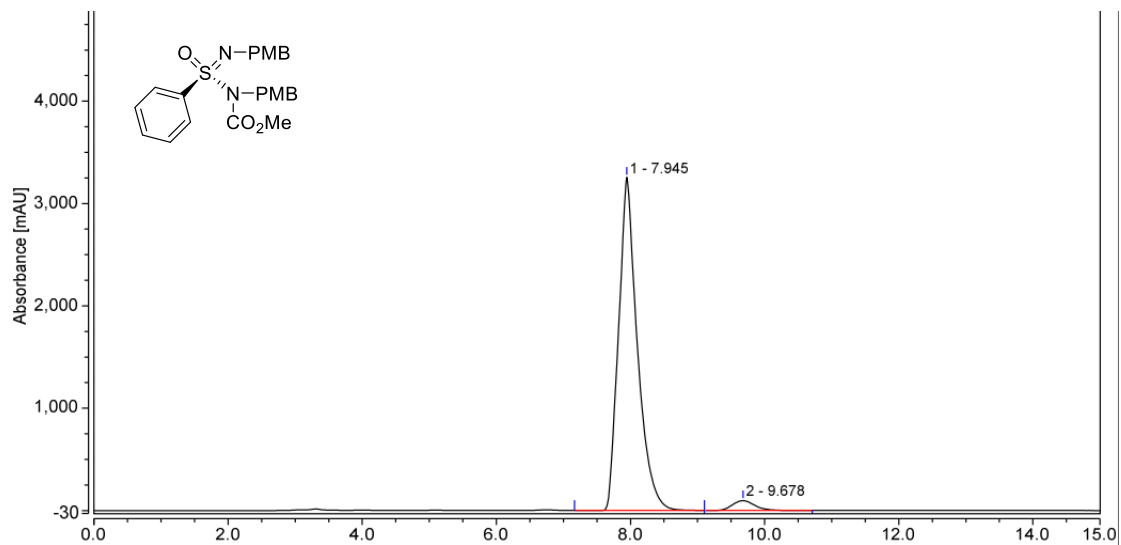


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.838	910.832	2650.387	94.78	96.00
2	11.323	50.116	110.380	5.22	4.00
Total:		960.948	2760.767	100.00	100.00

HPLC Spectrum of **3da**

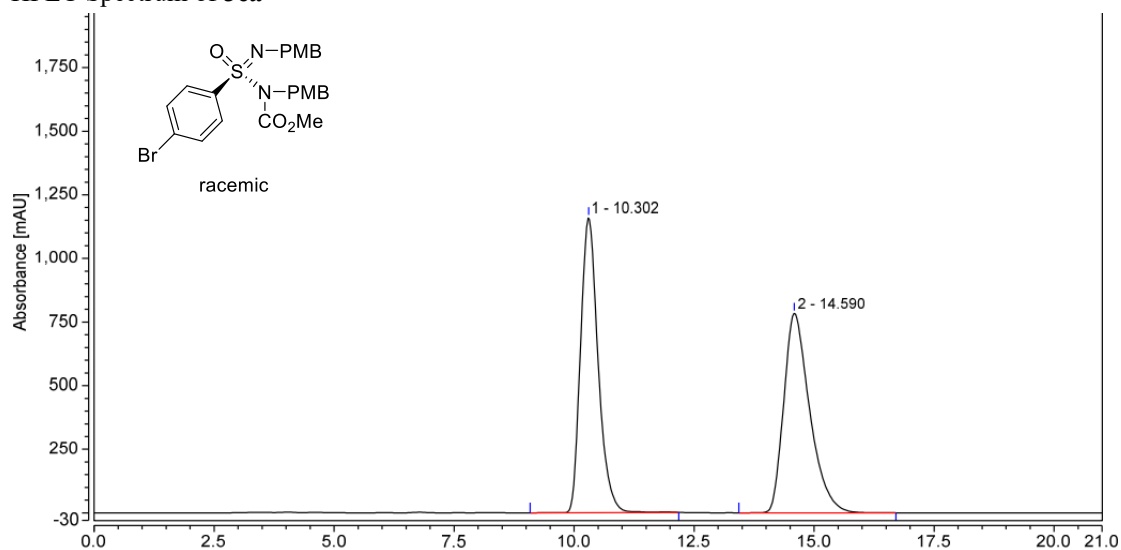


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.017	282.373	834.108	49.88	53.15
2	9.658	283.734	735.239	50.12	46.85
Total:		566.107	1569.346	100.00	100.00

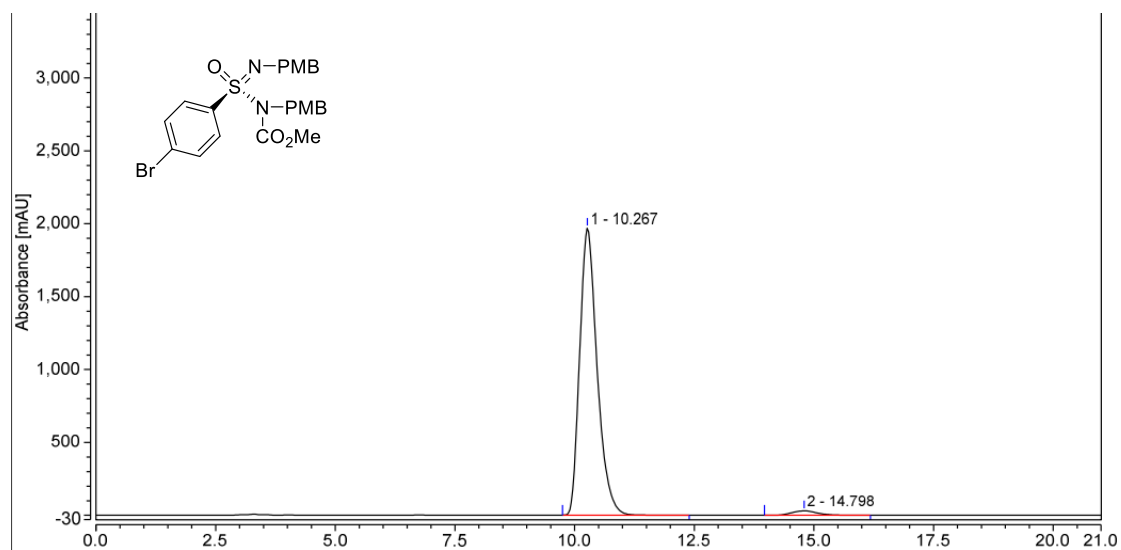


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.945	1056.078	3255.406	96.55	97.12
2	9.678	37.720	96.398	3.45	2.88
Total:		1093.798	3351.804	100.00	100.00

HPLC Spectrum of **3ea**

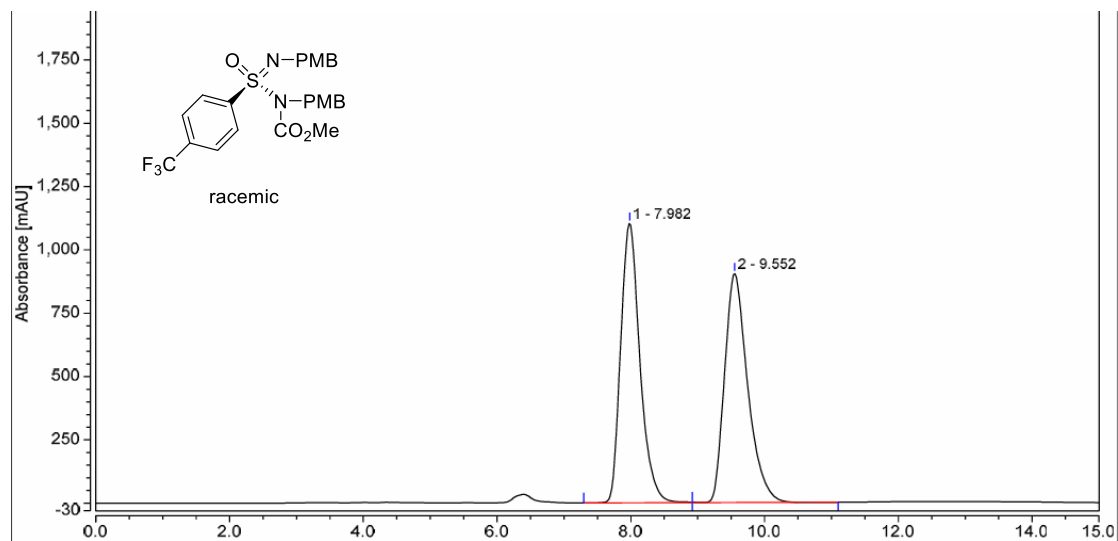


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.302	491.062	1160.607	49.99	59.66
2	14.590	491.301	784.690	50.01	40.34
Total:		982.363	1945.297	100.00	100.00

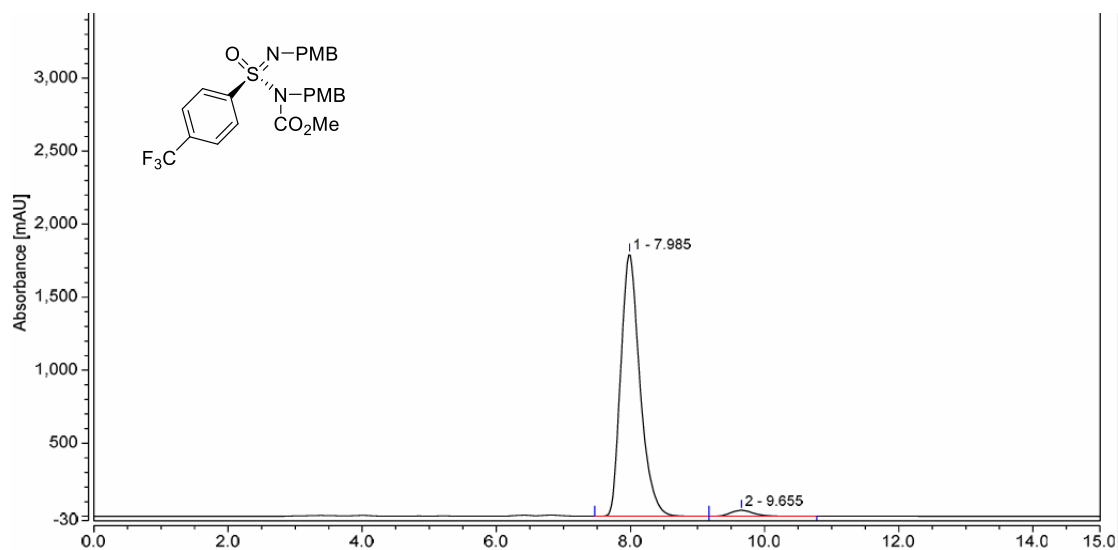


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.267	831.648	1969.163	97.78	98.48
2	14.798	18.916	30.370	2.22	1.52
Total:		850.564	1999.533	100.00	100.00

HPLC Spectrum of 3fa

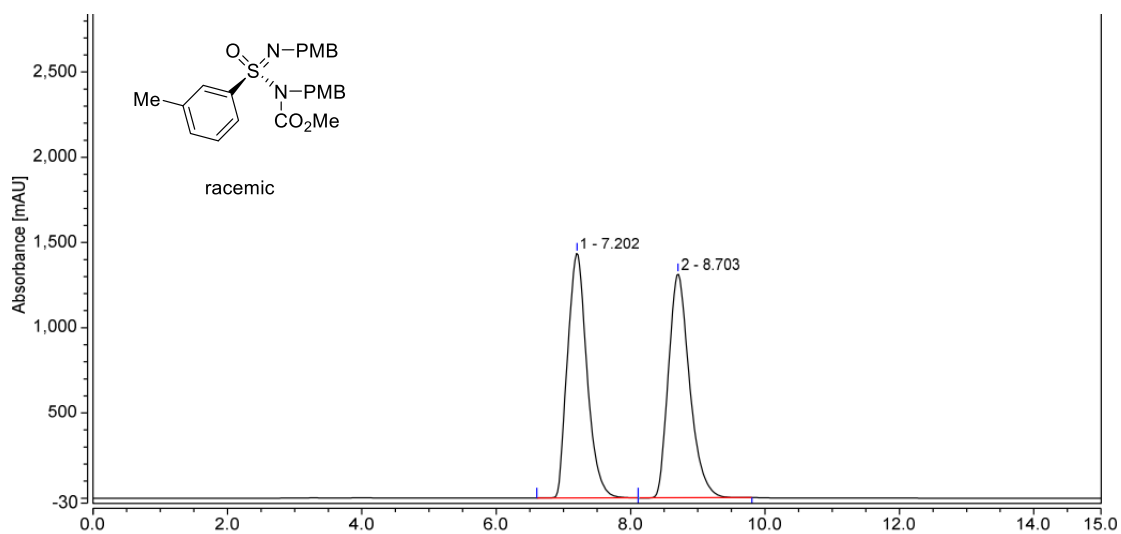


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.982	367.534	1104.970	50.42	54.97
2	9.552	361.475	905.131	49.58	45.03
Total:		729.009	2010.101	100.00	100.00

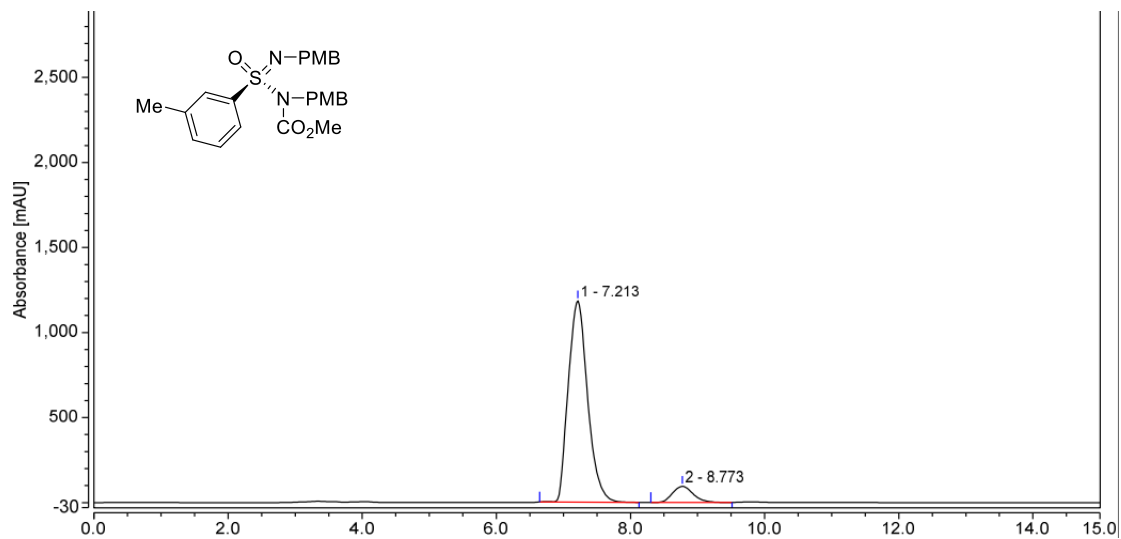


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.985	594.013	1796.248	97.32	97.78
2	9.655	16.334	40.825	2.68	2.22
Total:		610.347	1837.073	100.00	100.00

HPLC Spectrum of **3ga**

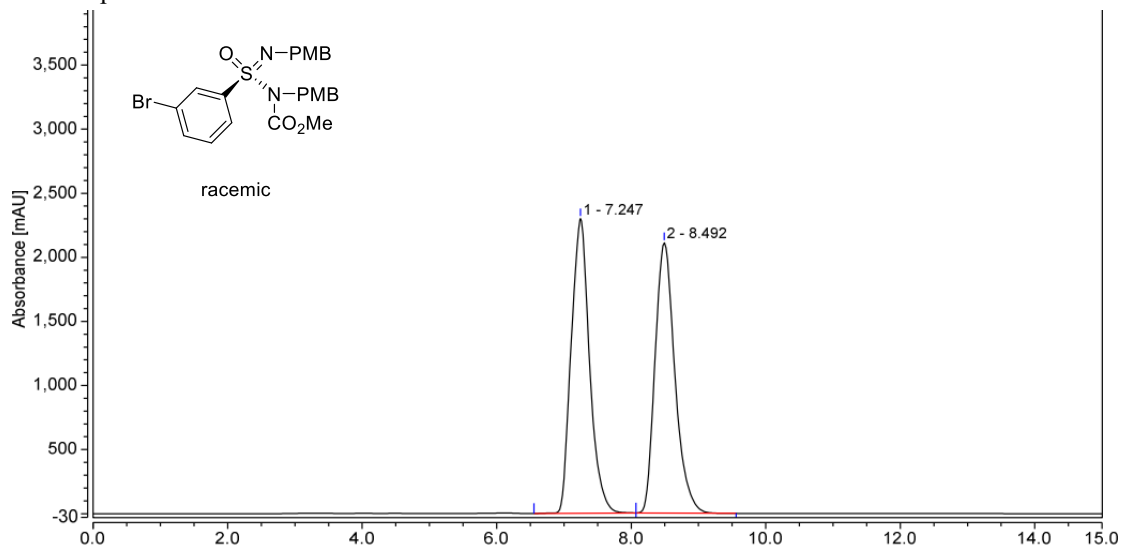


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.202	479.568	1435.739	50.15	52.24
2	8.703	476.697	1312.822	49.85	47.76
Total:		956.265	2748.561	100.00	100.00

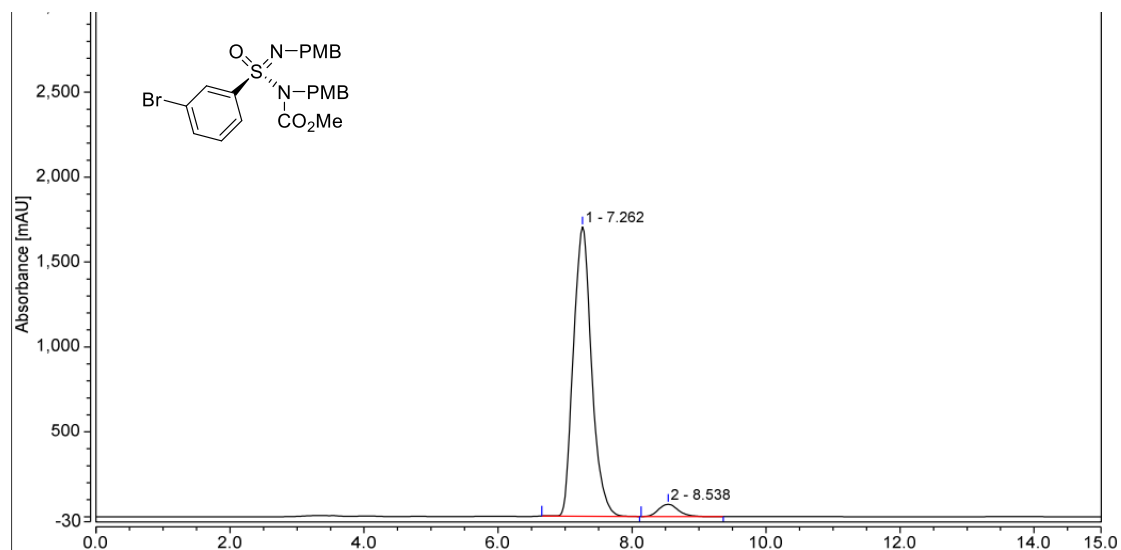


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.213	394.051	1183.438	92.12	92.61
2	8.773	33.722	94.387	7.88	7.39
Total:		427.773	1277.825	100.00	100.00

HPLC Spectrum of **3ha**

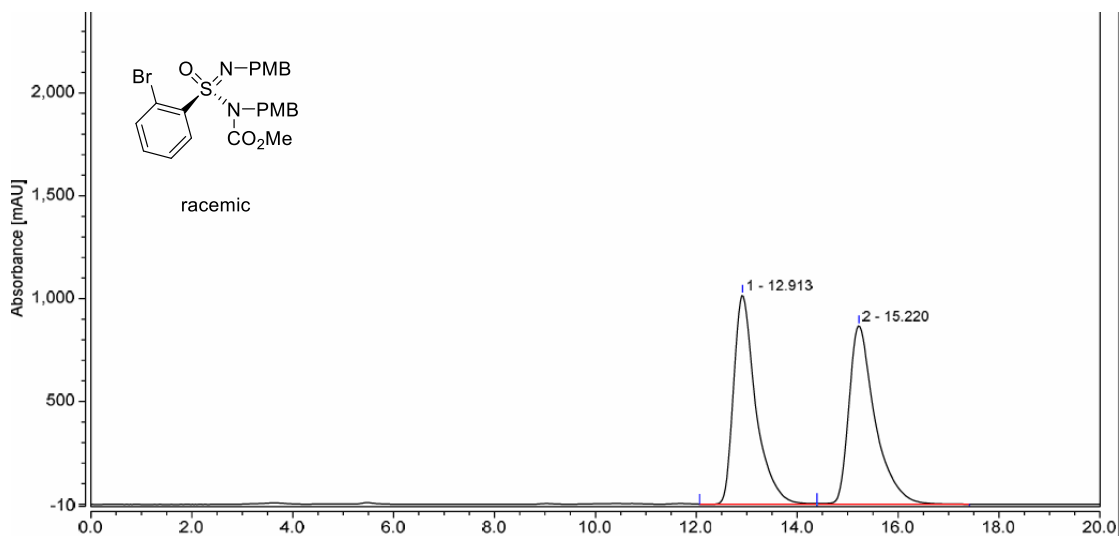


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.247	724.460	2298.491	50.22	52.14
2	8.492	718.073	2110.010	49.78	47.86
Total:		1442.533	4408.501	100.00	100.00

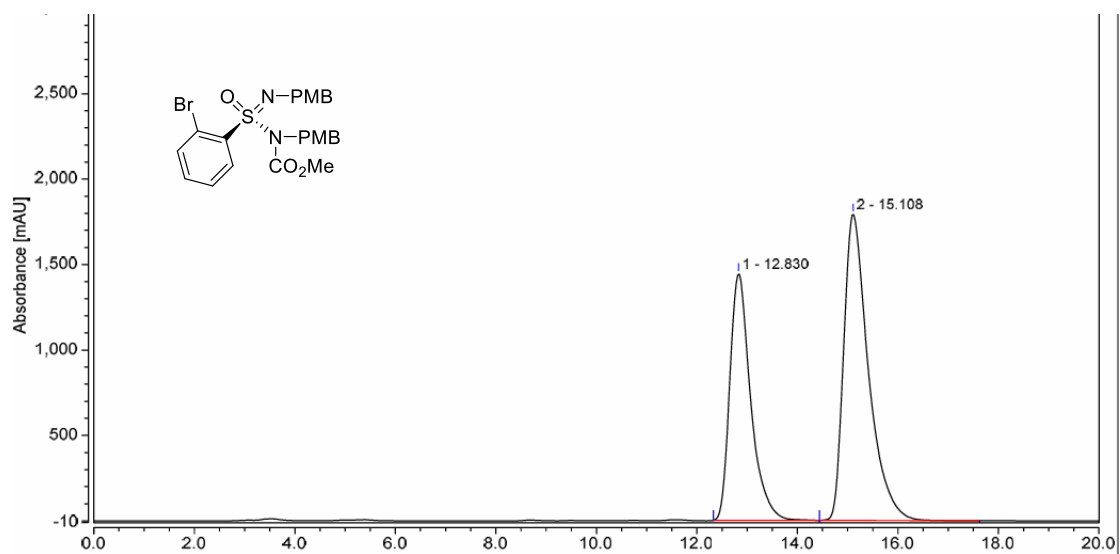


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.262	534.496	1703.983	95.61	95.94
2	8.538	24.524	72.093	4.39	4.06
Total:		559.019	1776.076	100.00	100.00

HPLC Spectrum of **3ia**

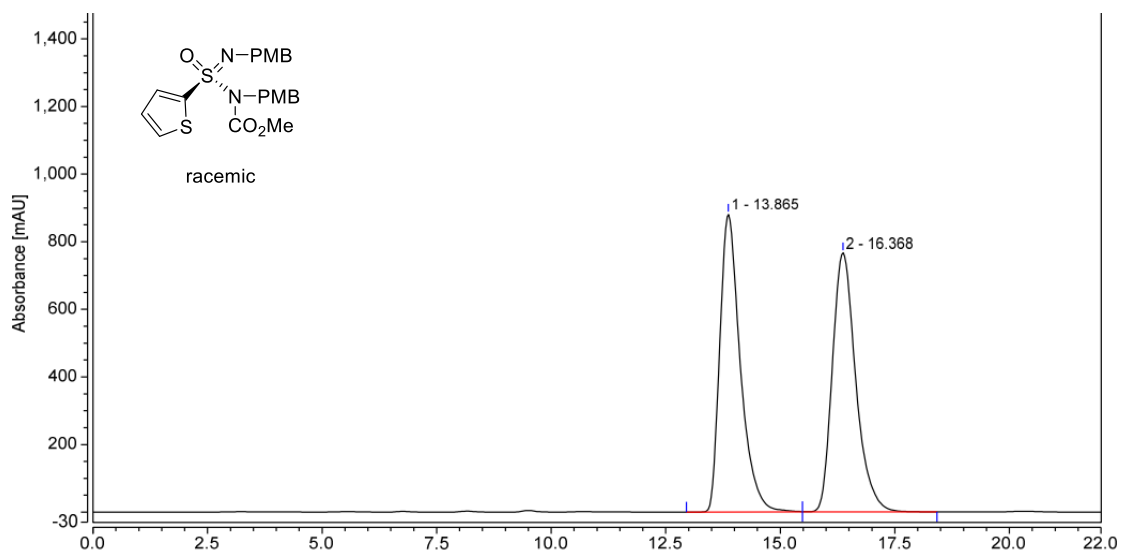


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.913	516.929	1016.134	49.91	53.95
2	15.220	518.875	867.214	50.09	46.05
Total		1035.804	1883.347	100.00	100.00

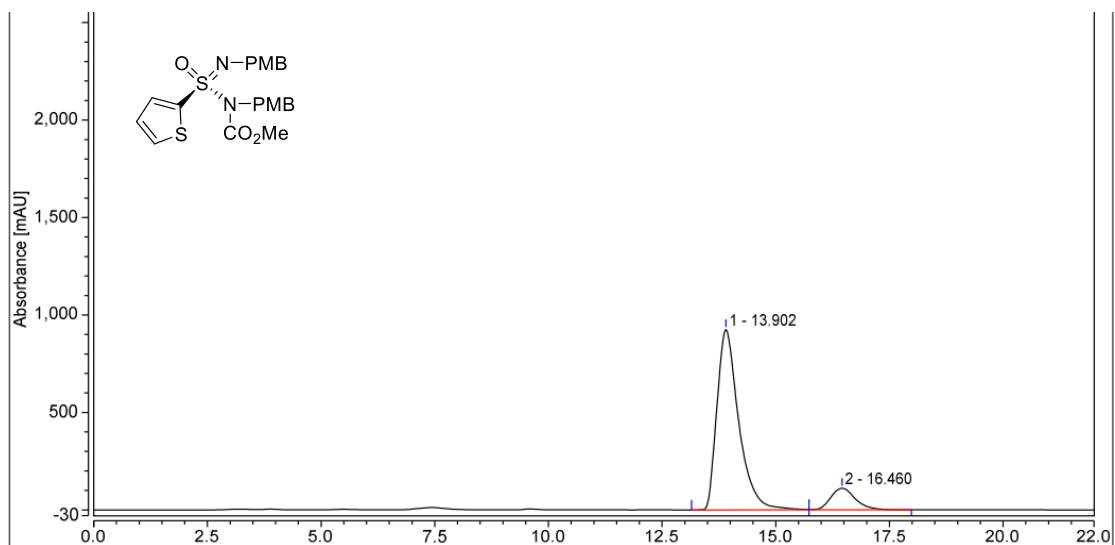


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.830	692.849	1444.535	40.49	44.60
2	15.108	1018.277	1794.263	59.51	55.40
Total		1711.126	3238.797	100.00	100.00

HPLC Spectrum of 3ja

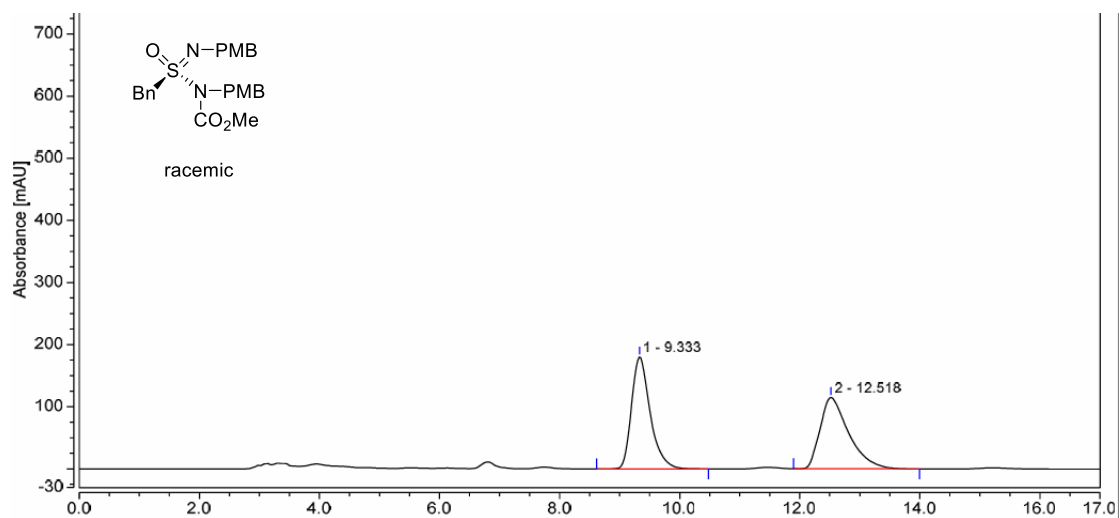


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.865	455.956	881.320	50.10	53.49
2	16.368	454.196	766.363	49.90	46.51
Total:		910.153	1647.683	100.00	100.00

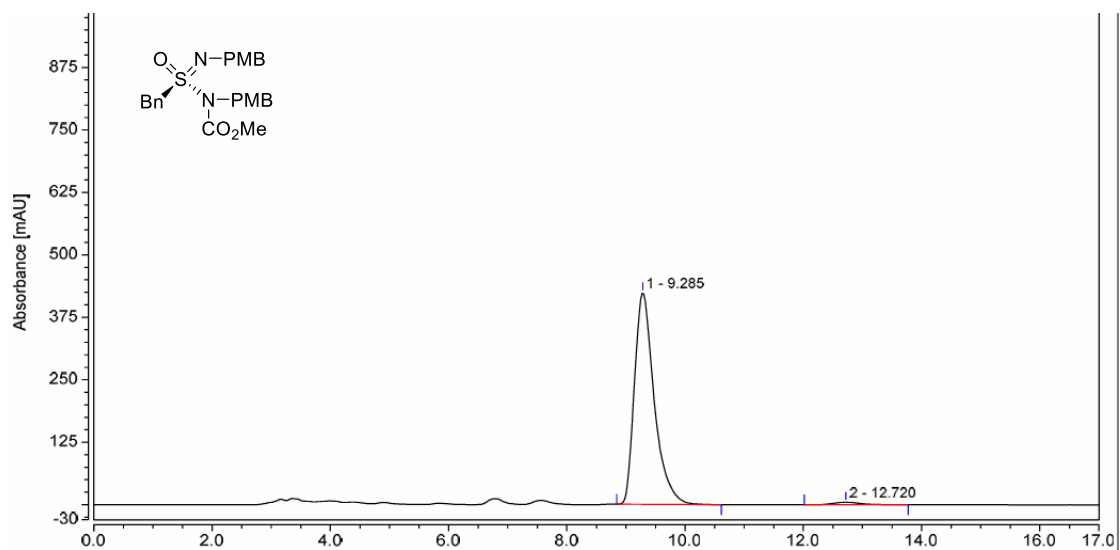


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.902	514.341	924.729	88.05	89.30
2	16.460	69.819	110.744	11.95	10.70
Total:		584.160	1035.473	100.00	100.00

HPLC Spectrum of **3ka**

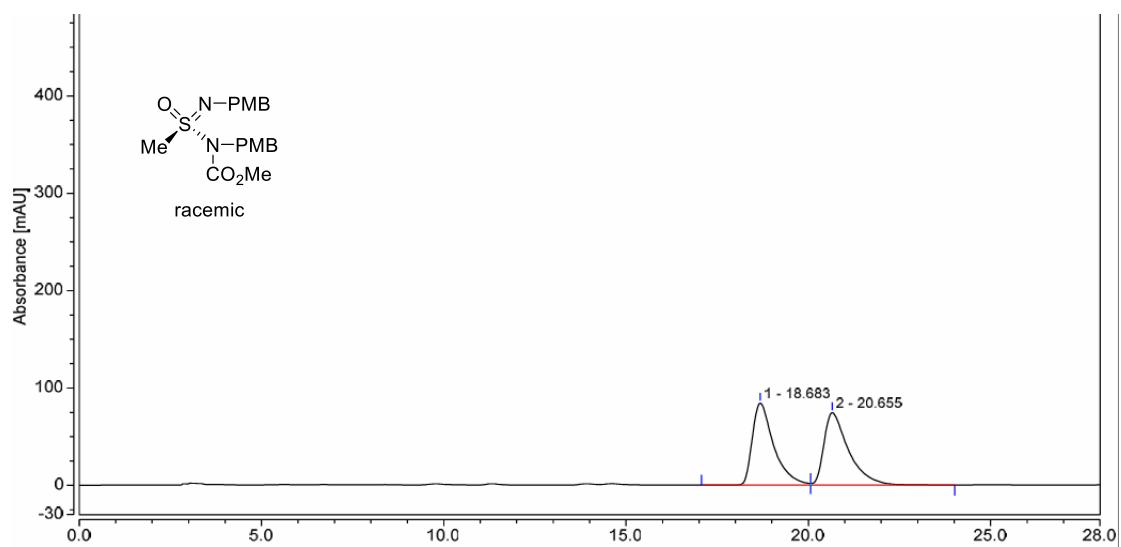


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.333	64.902	180.159	50.68	61.10
2	12.518	63.163	114.722	49.32	38.90
Total:		128.065	294.881	100.00	100.00

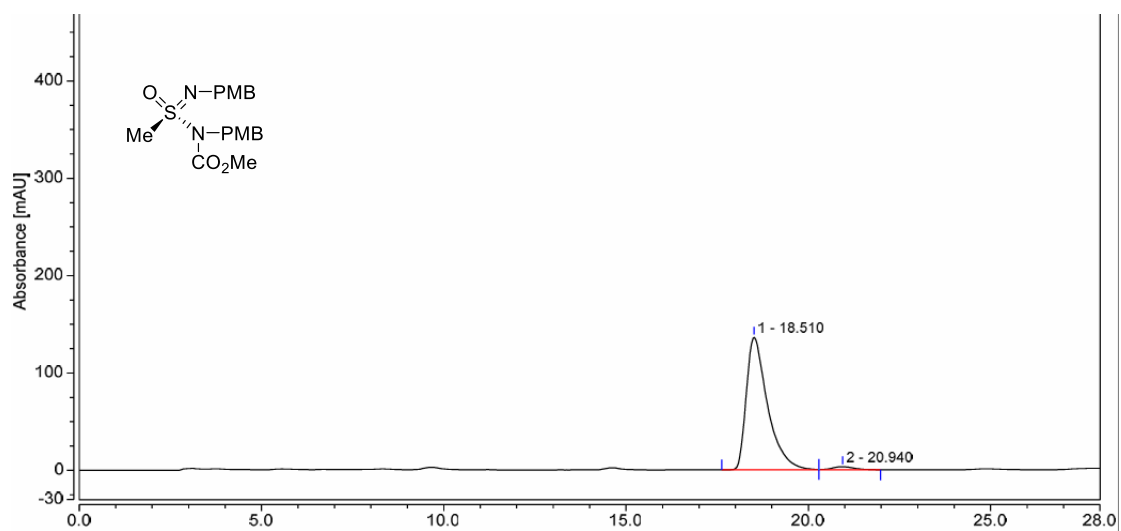


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.285	163.688	423.641	98.39	98.82
2	12.720	2.682	5.056	1.61	1.18
Total:		166.370	428.697	100.00	100.00

HPLC Spectrum of **3la**

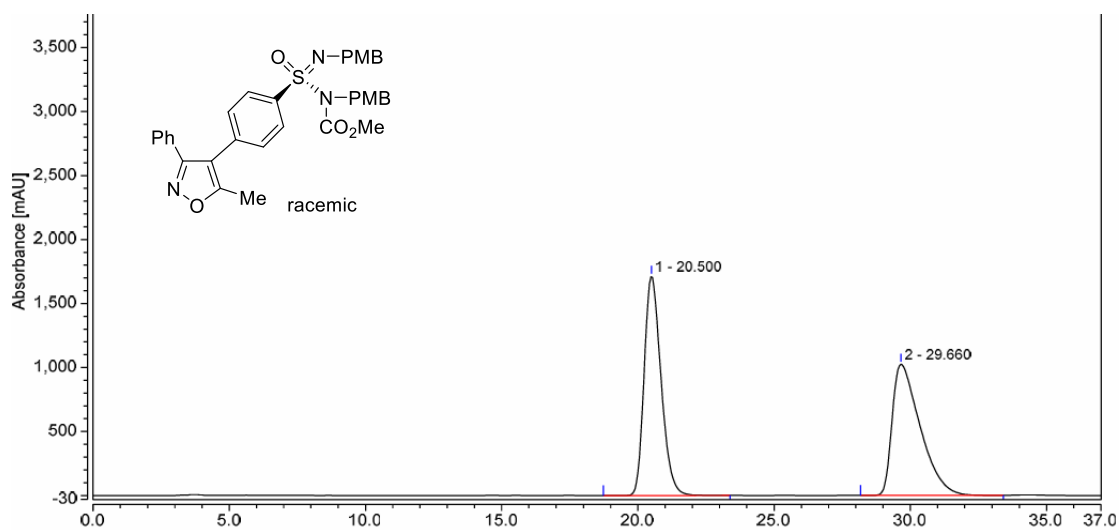


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	18.683	57.292	84.200	49.59	53.11
2	20.655	58.231	74.349	50.41	46.89
Total		115.524	158.549	100.00	100.00

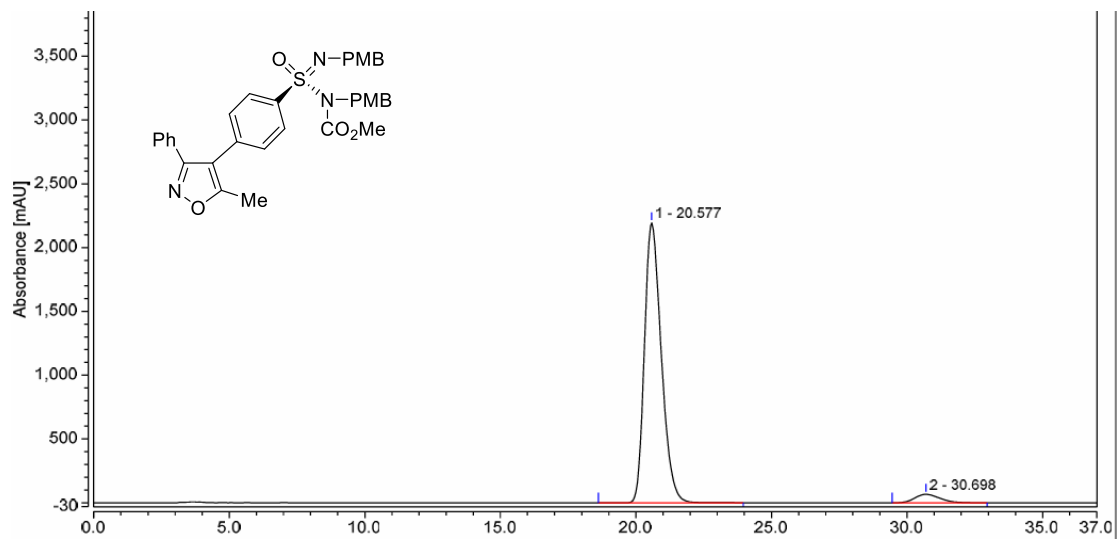


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	18.510	92.319	136.273	97.58	97.68
2	20.940	2.292	3.243	2.42	2.32
Total		94.611	139.516	100.00	100.00

HPLC Spectrum of **3ma**

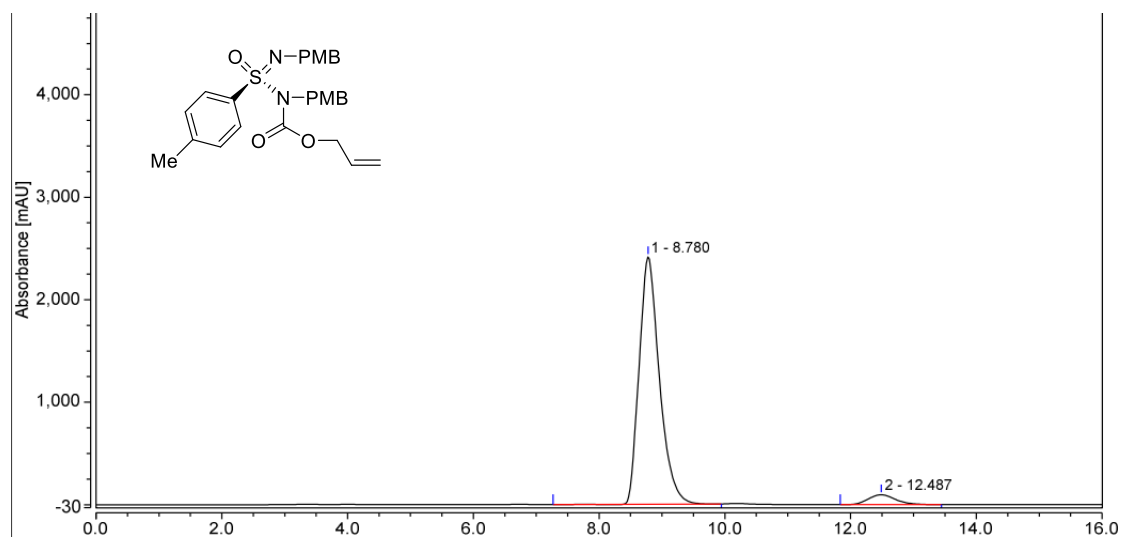
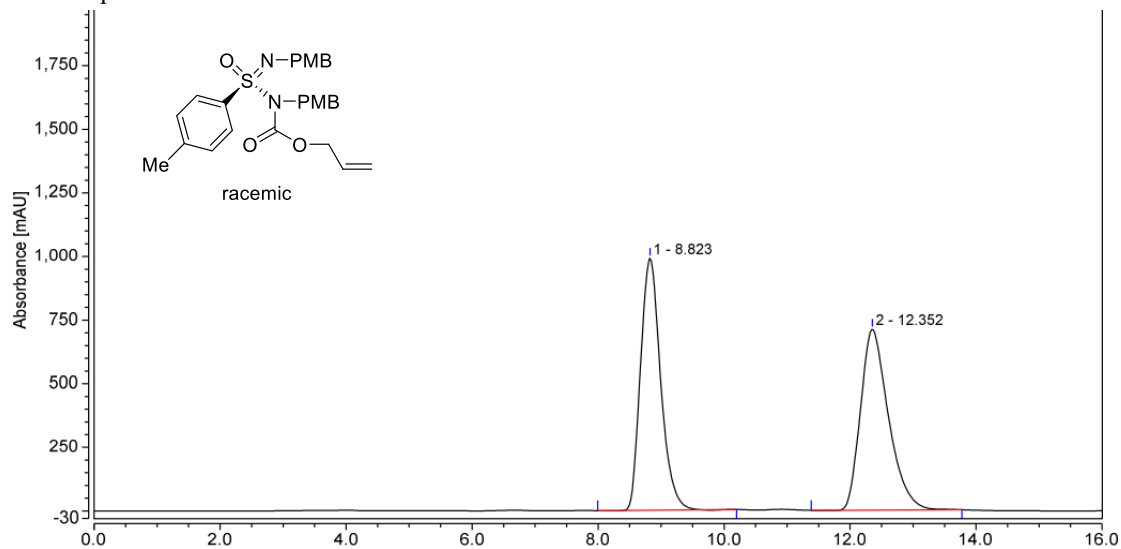


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	20.500	1231.014	1715.228	50.25	62.60
2	29.660	1218.669	1024.546	49.75	37.40
Total:		2449.682	2739.773	100.00	100.00

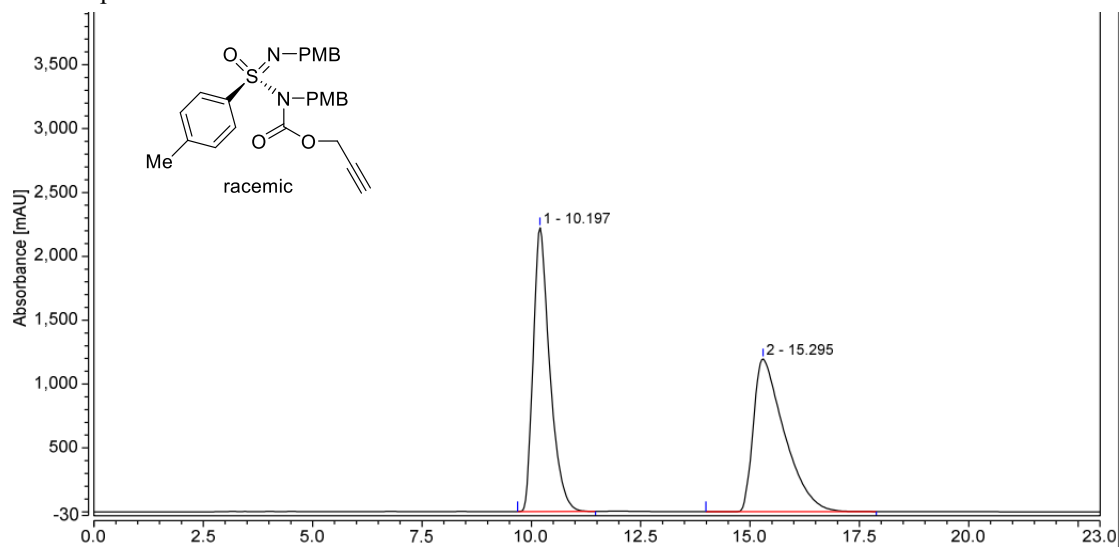


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	20.577	1580.630	2197.372	95.50	97.00
2	30.698	74.522	67.970	4.50	3.00
Total:		1655.152	2265.343	100.00	100.00

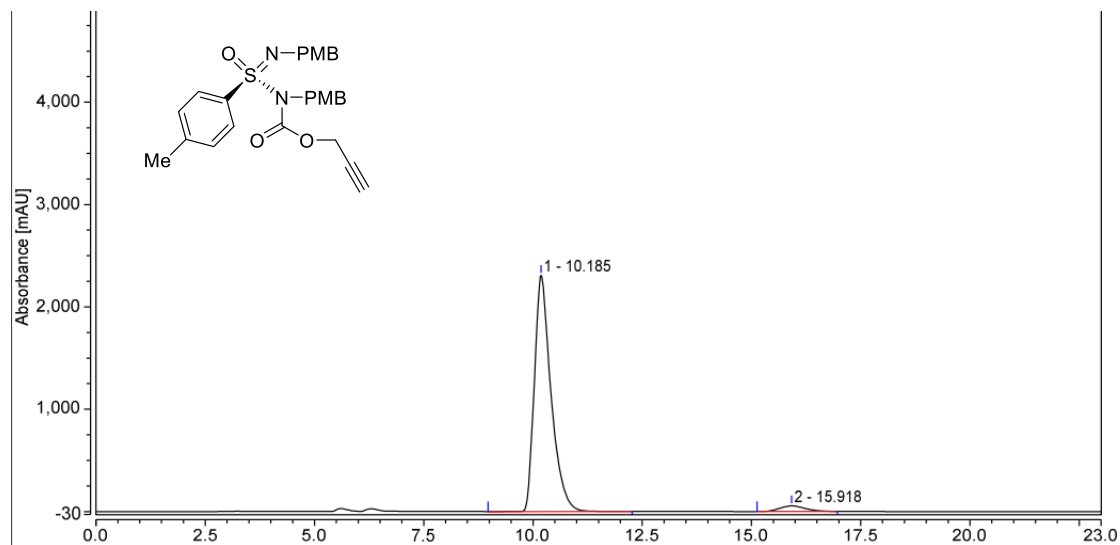
HPLC Spectrum of **3ab**



HPLC Spectrum of 3ac

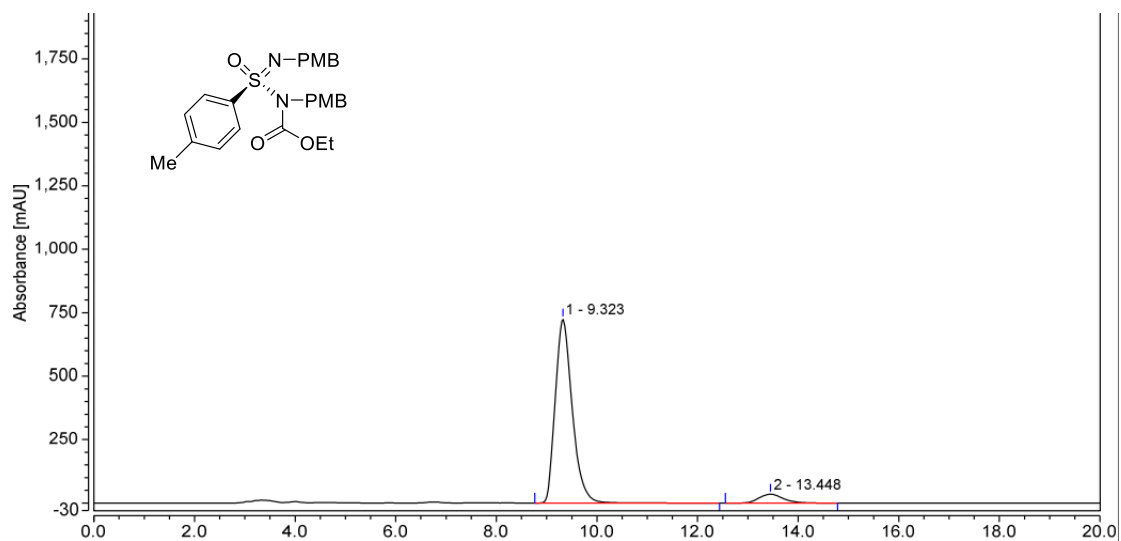
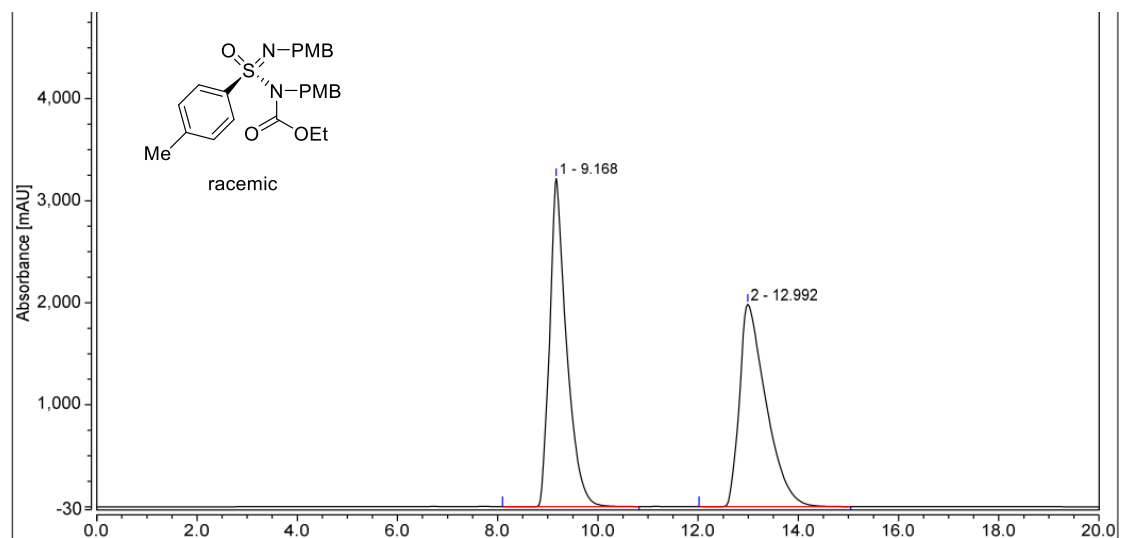


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.197	976.829	2222.960	49.89	65.03
2	15.295	981.084	1195.454	50.11	34.97
Total:		1957.913	3418.414	100.00	100.00

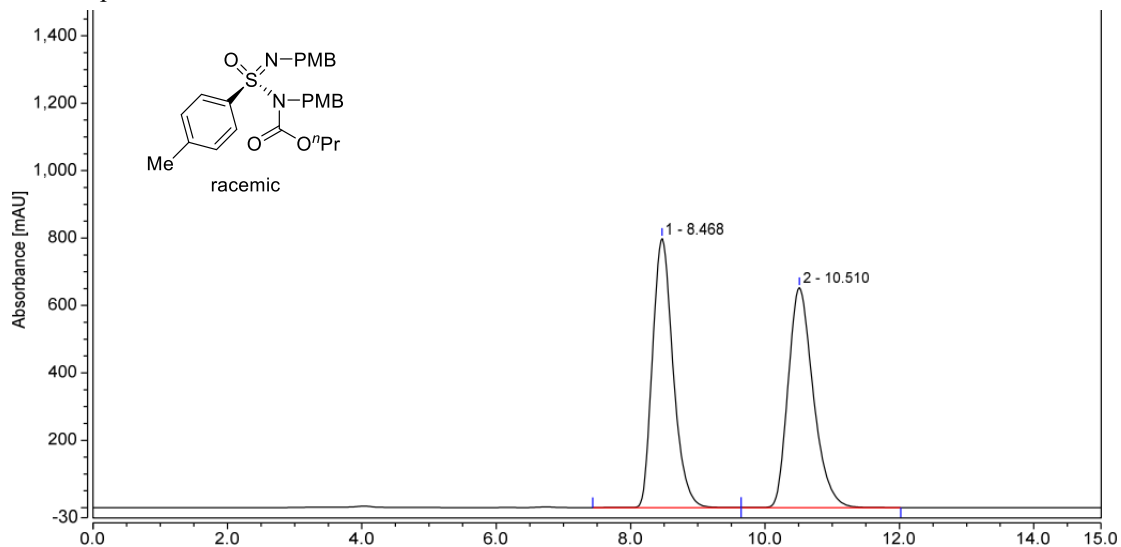


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.185	1016.380	2307.604	96.44	97.67
2	15.918	37.535	54.955	3.56	2.33
Total:		1053.915	2362.560	100.00	100.00

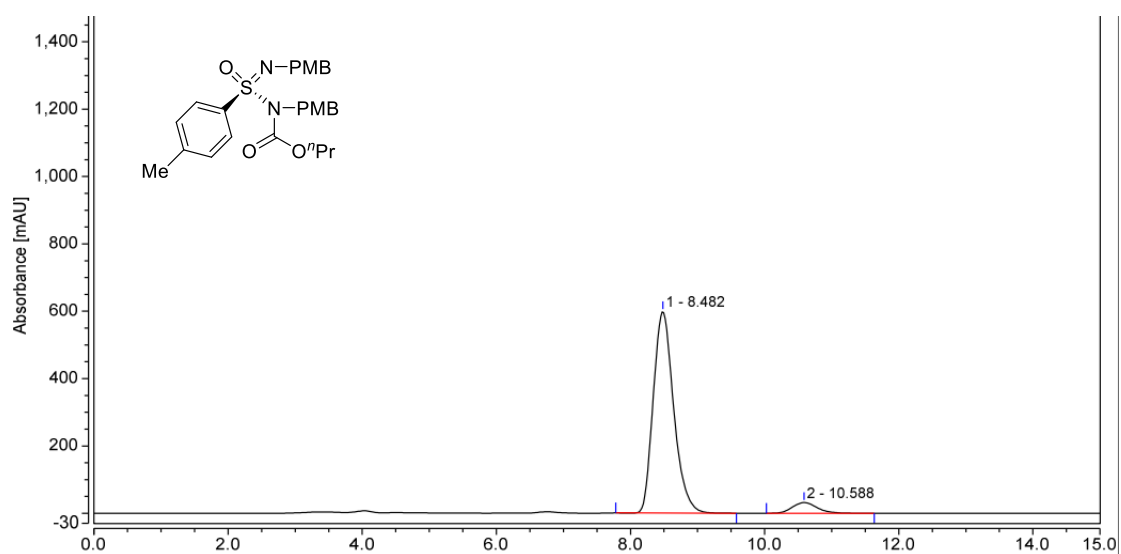
HPLC Spectrum of 3ad



HPLC Spectrum of **3ae**

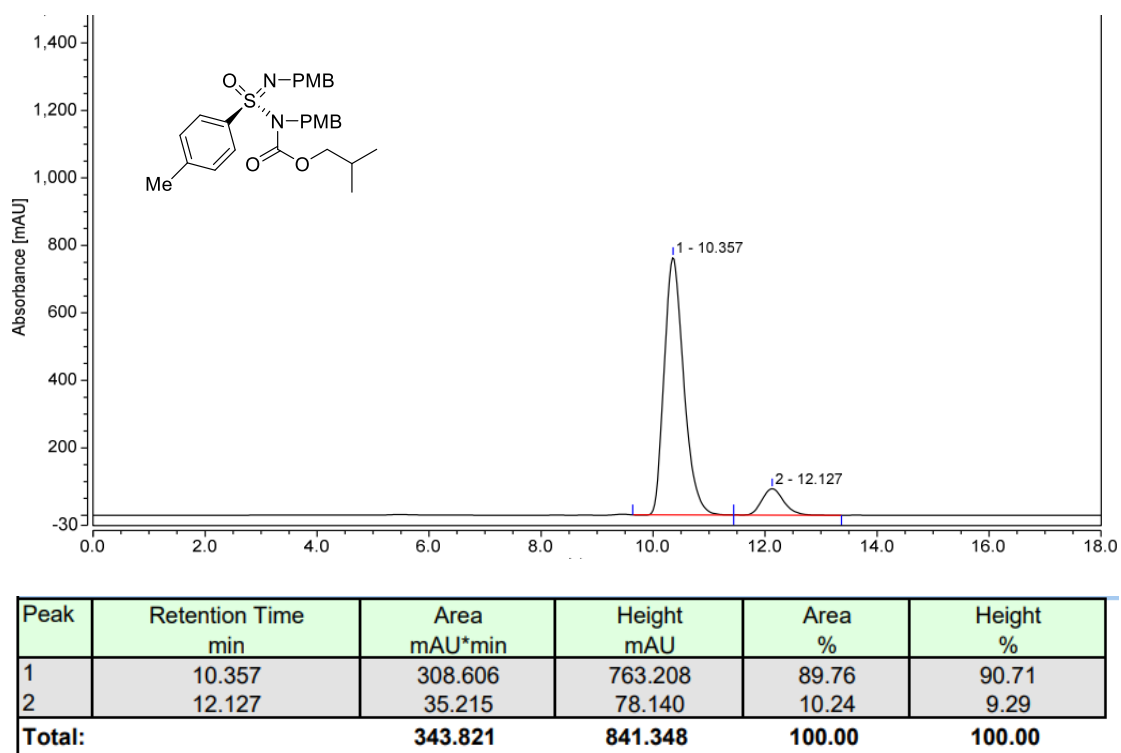
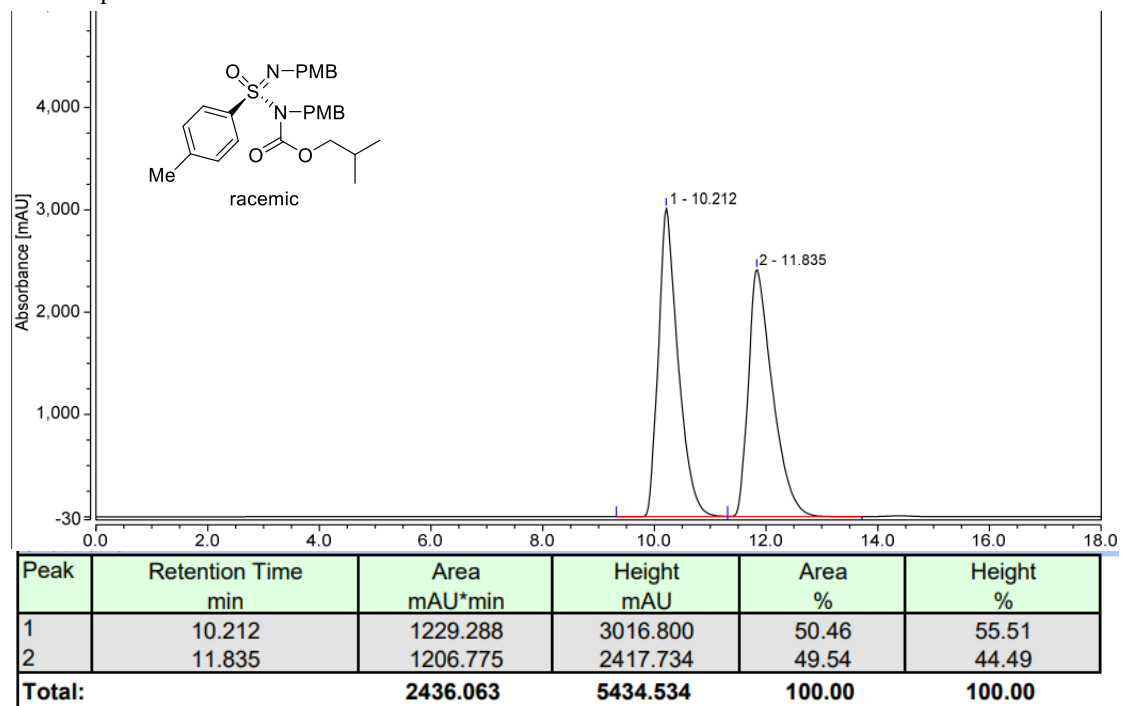


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.468	282.878	798.633	49.99	55.03
2	10.510	282.981	652.624	50.01	44.97
Total:		565.859	1451.257	100.00	100.00

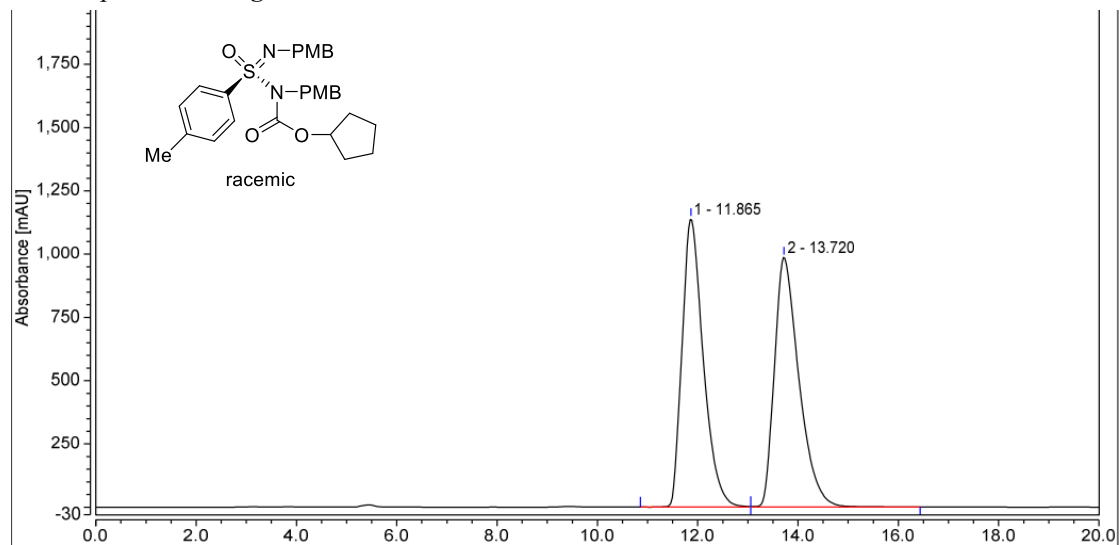


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.482	210.570	598.254	93.94	94.98
2	10.588	13.575	31.645	6.06	5.02
Total:		224.145	629.899	100.00	100.00

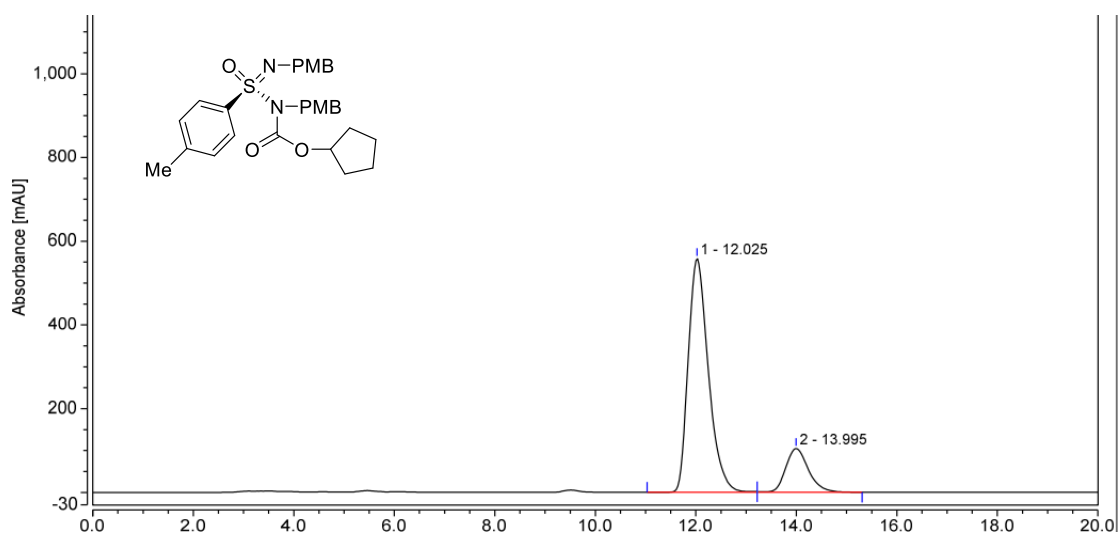
HPLC Spectrum of 3af



HPLC Spectrum of **3ag**

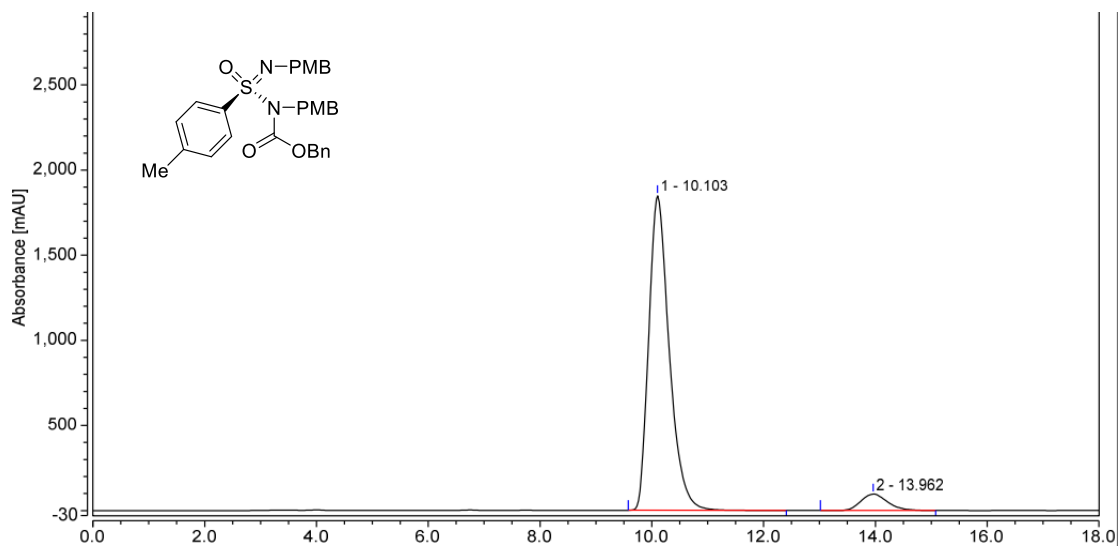
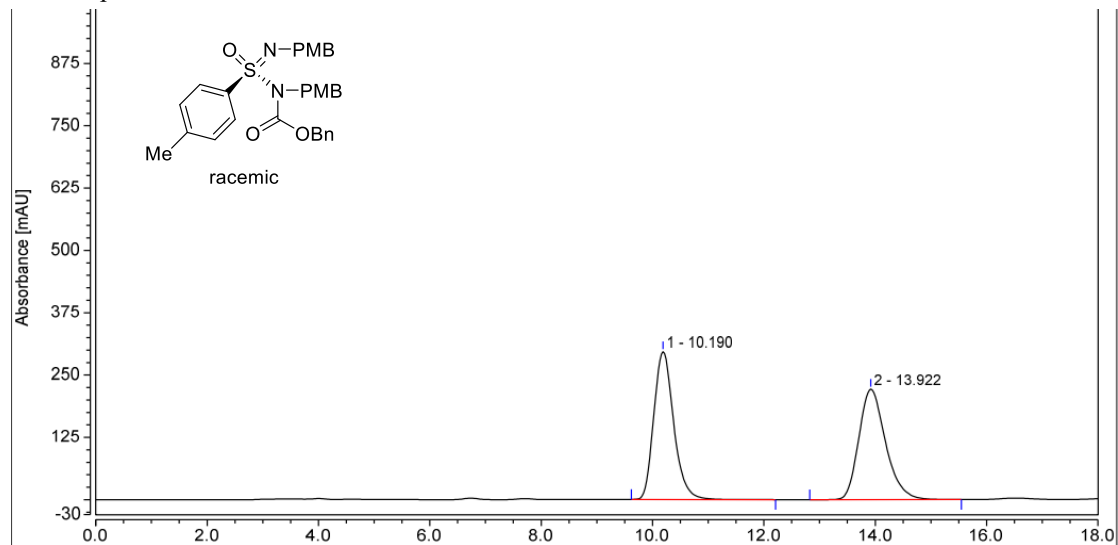


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	11.865	556.774	1140.326	49.92	53.59
2	13.720	558.647	987.576	50.08	46.41
Total:		1115.421	2127.902	100.00	100.00

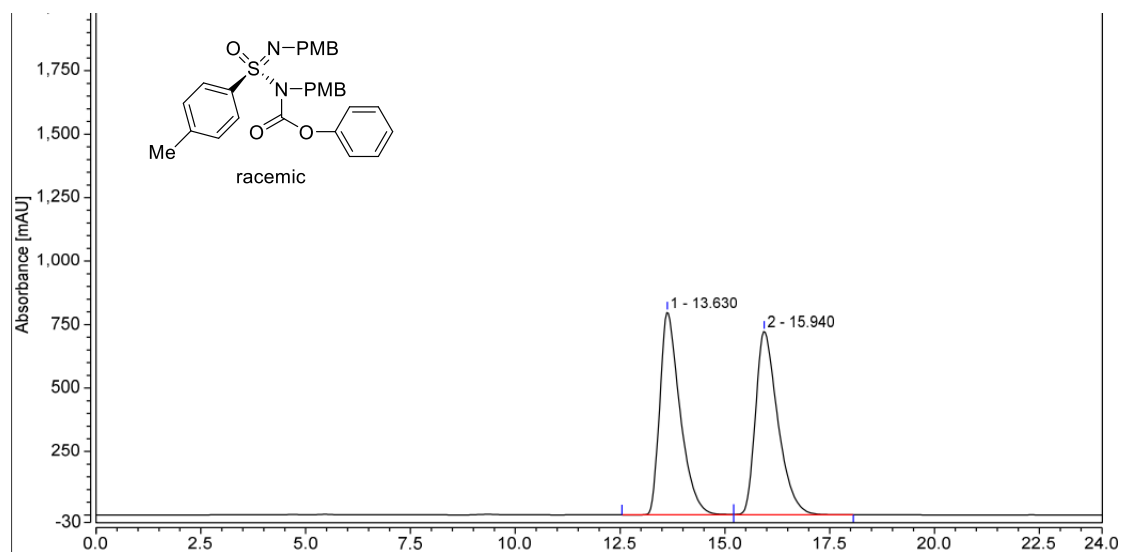


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.025	259.253	558.339	82.58	84.25
2	13.995	54.686	104.399	17.42	15.75
Total:		313.939	662.738	100.00	100.00

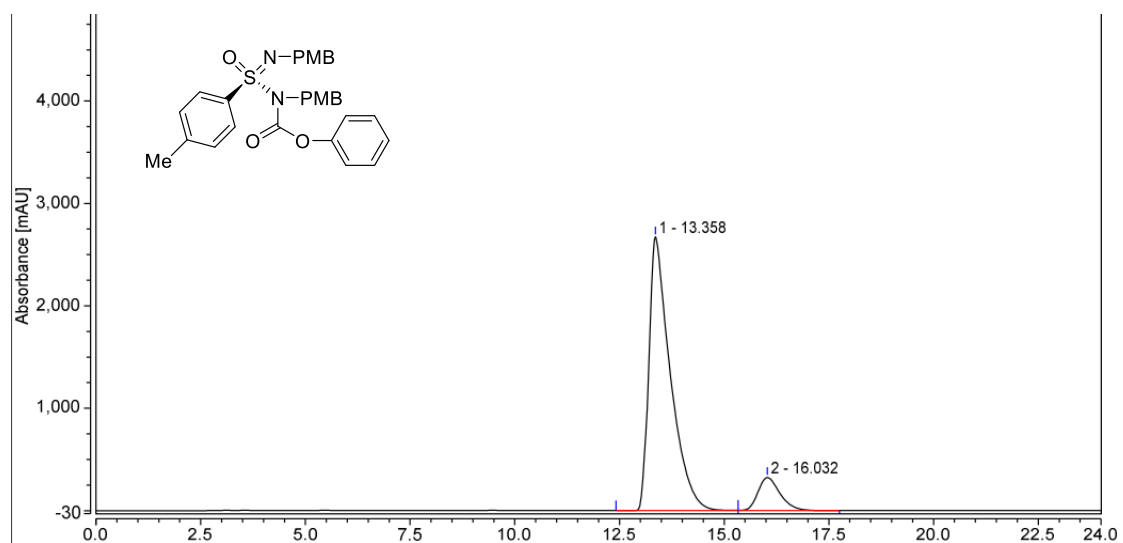
HPLC Spectrum of **3ah**



HPLC Spectrum of 3ai

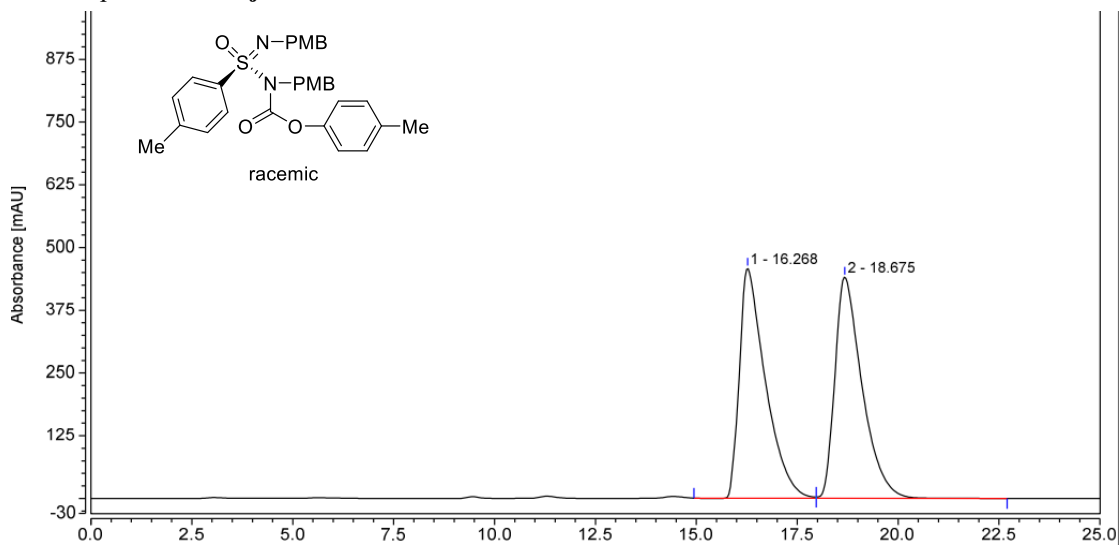


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.630	446.712	798.372	50.03	52.49
2	15.940	446.240	722.613	49.97	47.51
Total:		892.952	1520.985	100.00	100.00

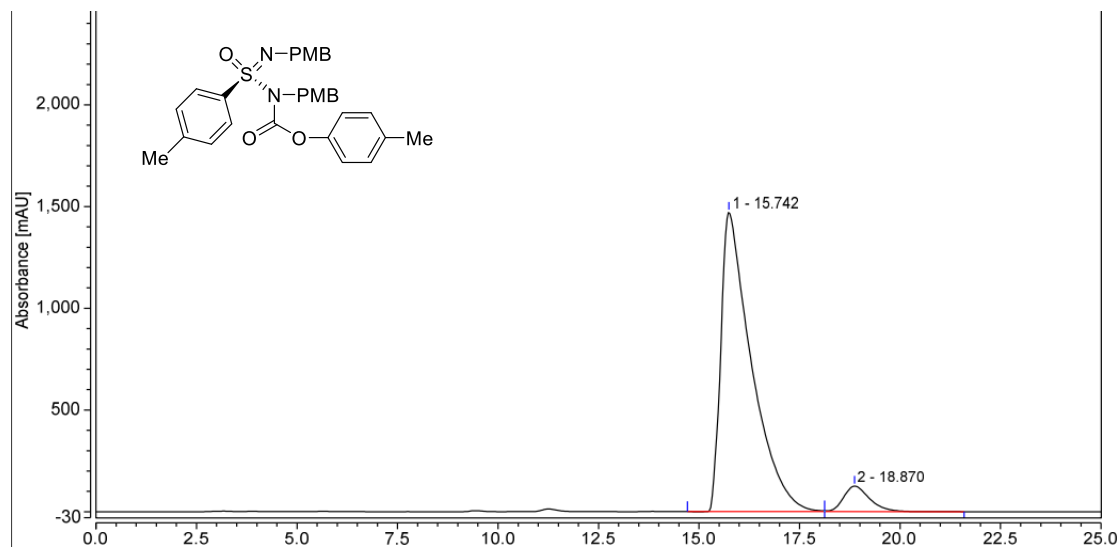


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.358	1582.437	2673.359	88.91	89.20
2	16.032	197.293	323.604	11.09	10.80
Total:		1779.729	2996.963	100.00	100.00

HPLC Spectrum of 3aj

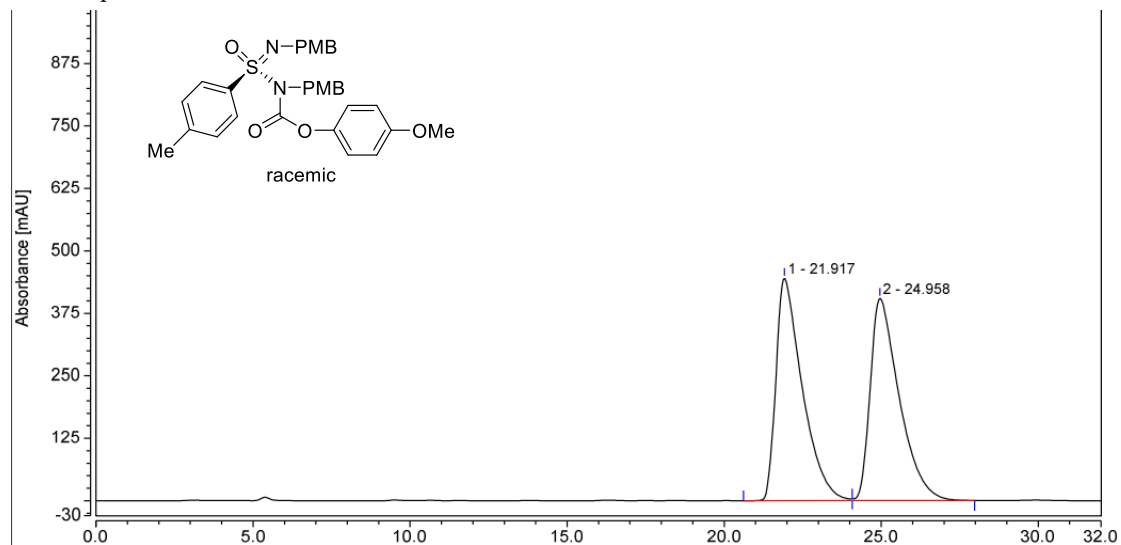


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	16.268	341.657	458.162	49.87	50.97
2	18.675	343.408	440.765	50.13	49.03
Total:		685.065	898.927	100.00	100.00

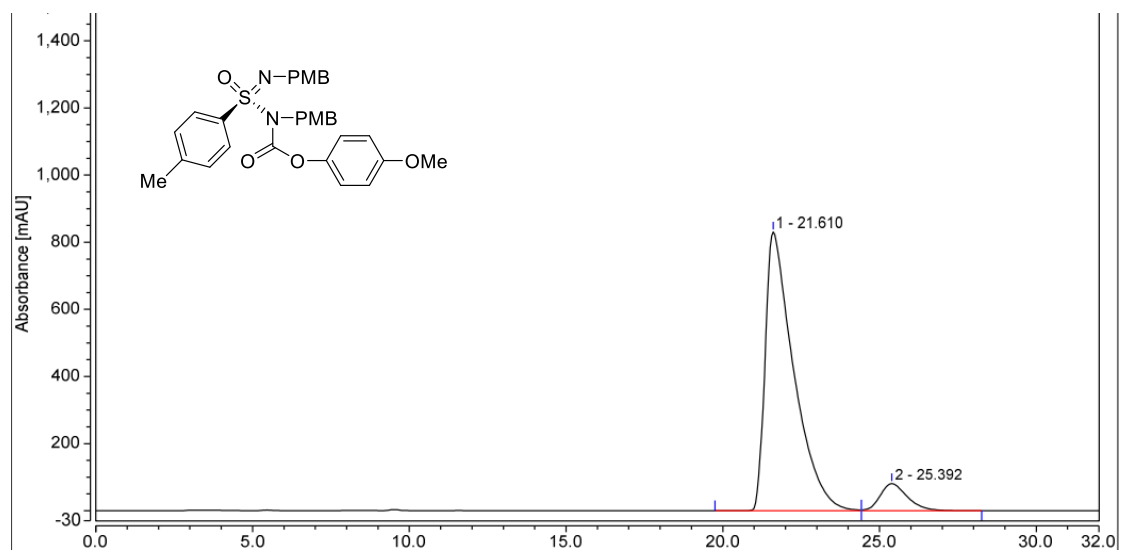


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	15.742	1293.911	1471.543	93.16	92.12
2	18.870	94.954	125.848	6.84	7.88
Total:		1388.866	1597.391	100.00	100.00

HPLC Spectrum of **3ak**

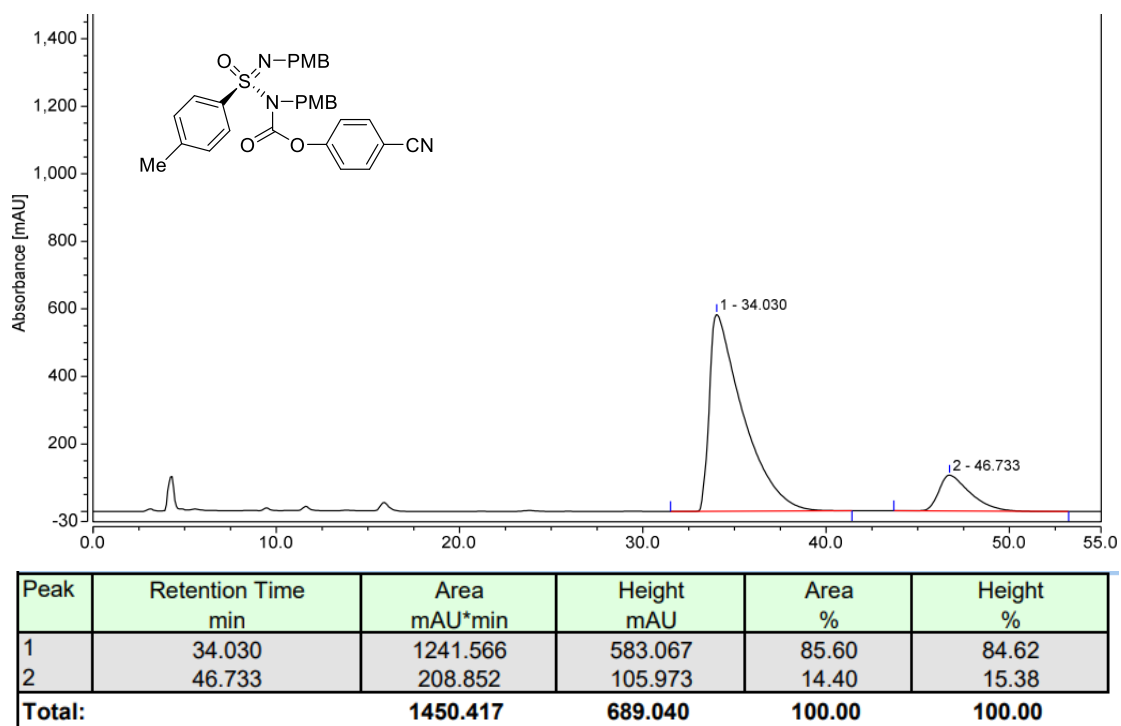
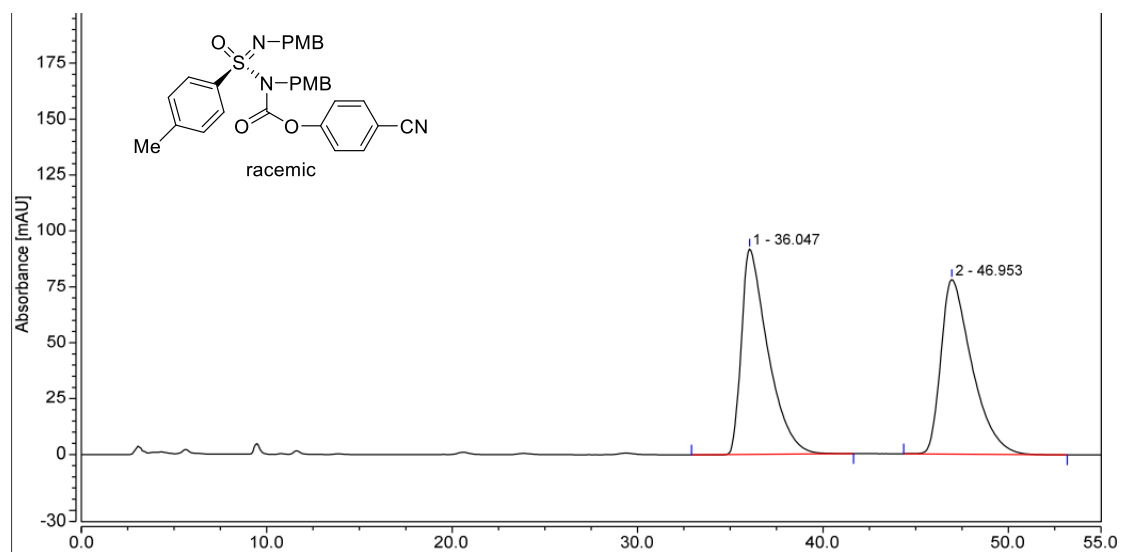


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	21.917	431.983	445.185	49.98	52.36
2	24.958	432.268	405.021	50.02	47.64
Total:		864.251	850.206	100.00	100.00

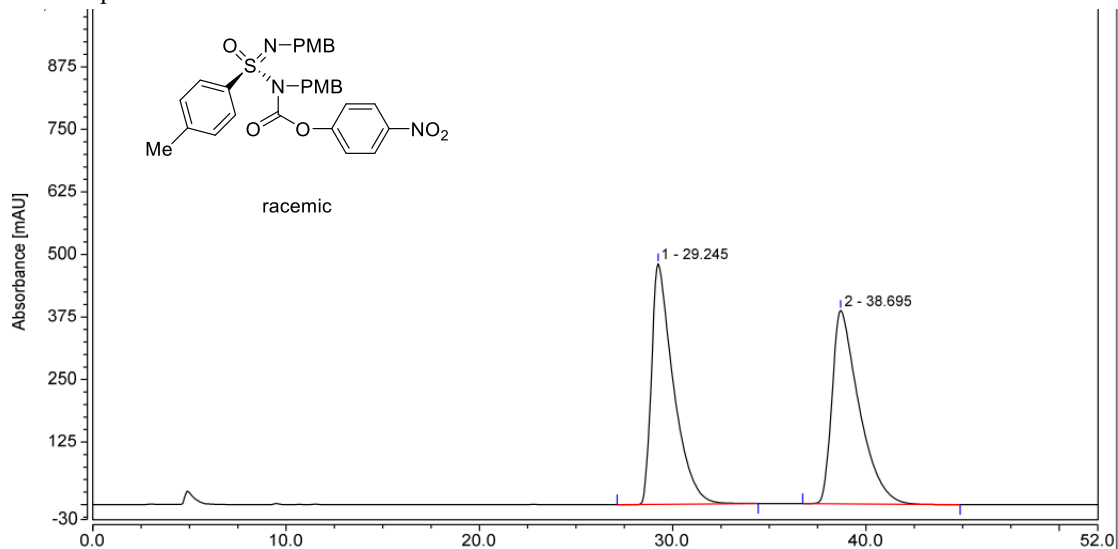


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	21.610	874.573	830.063	91.49	91.15
2	25.392	81.394	80.610	8.51	8.85
Total:		955.968	910.672	100.00	100.00

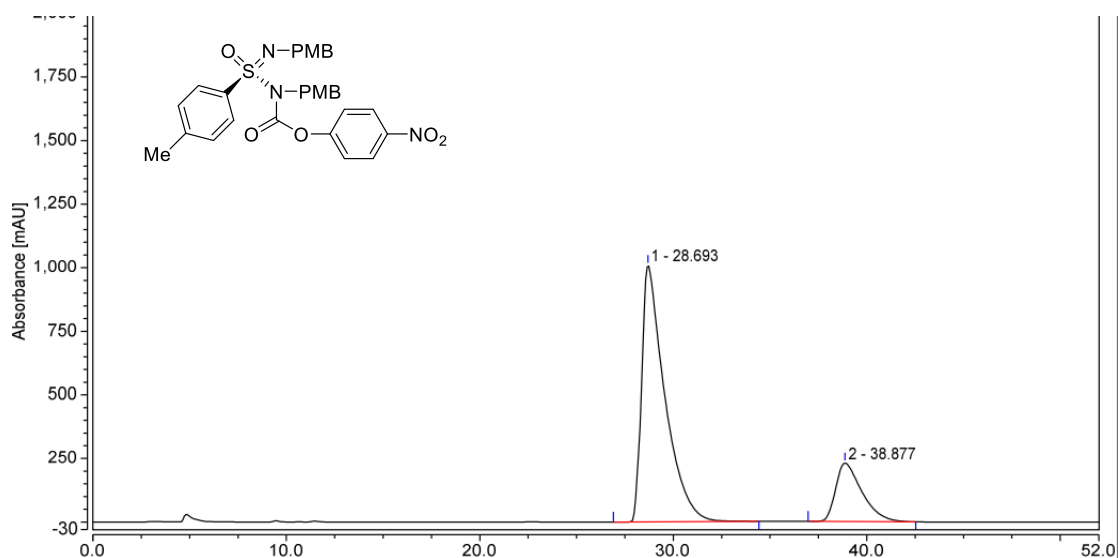
HPLC Spectrum of **3al**



HPLC Spectrum of **3am**

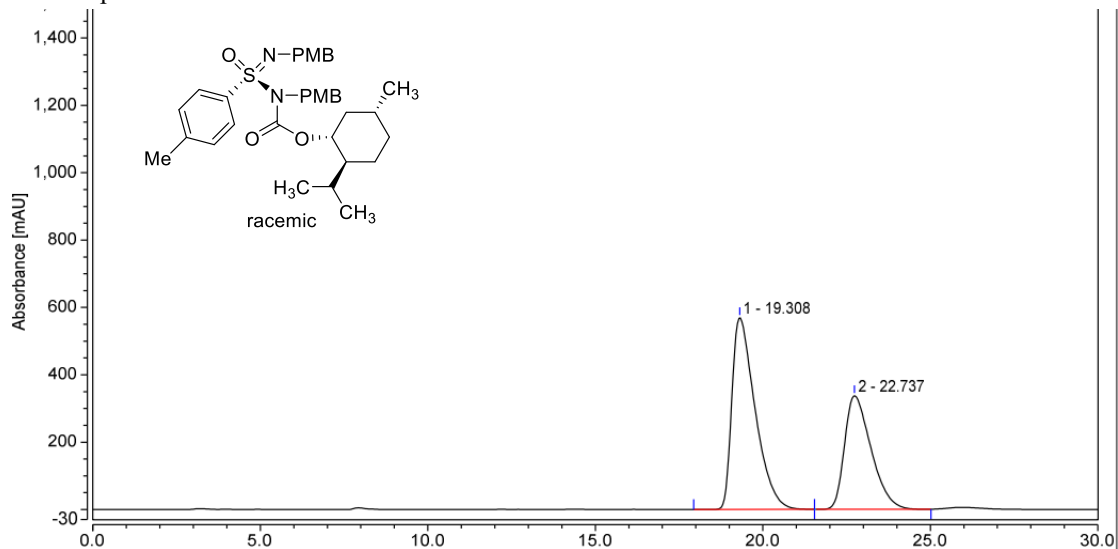


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	29.245	630.749	480.900	50.20	55.45
2	38.695	625.637	386.437	49.80	44.55
Total:		1256.386	867.336	100.00	100.00

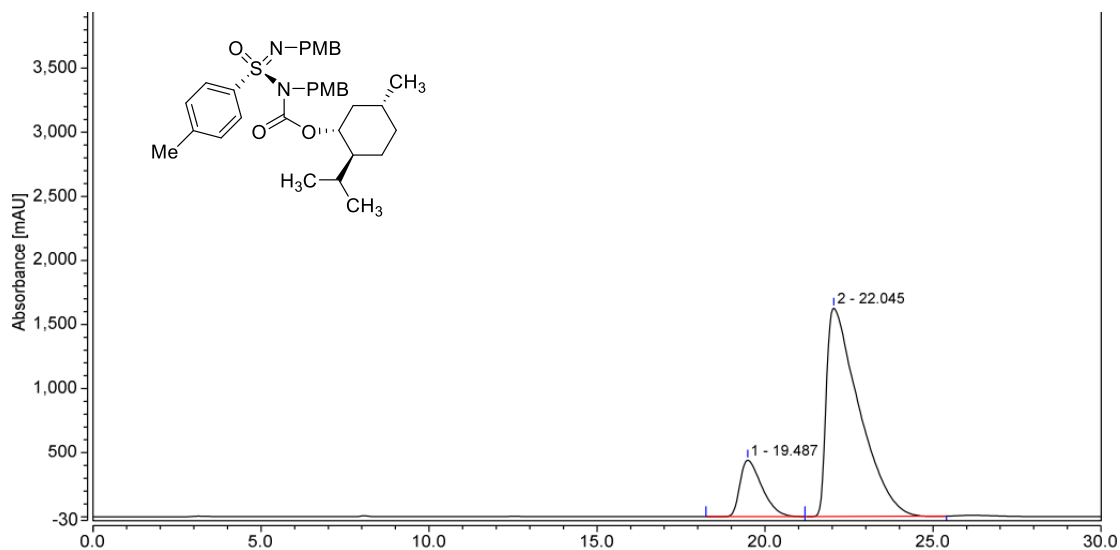


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	28.693	1392.086	1009.039	79.45	81.45
2	38.877	360.066	229.794	20.55	18.55
Total:		1752.152	1238.833	100.00	100.00

HPLC Spectrum of **3an**

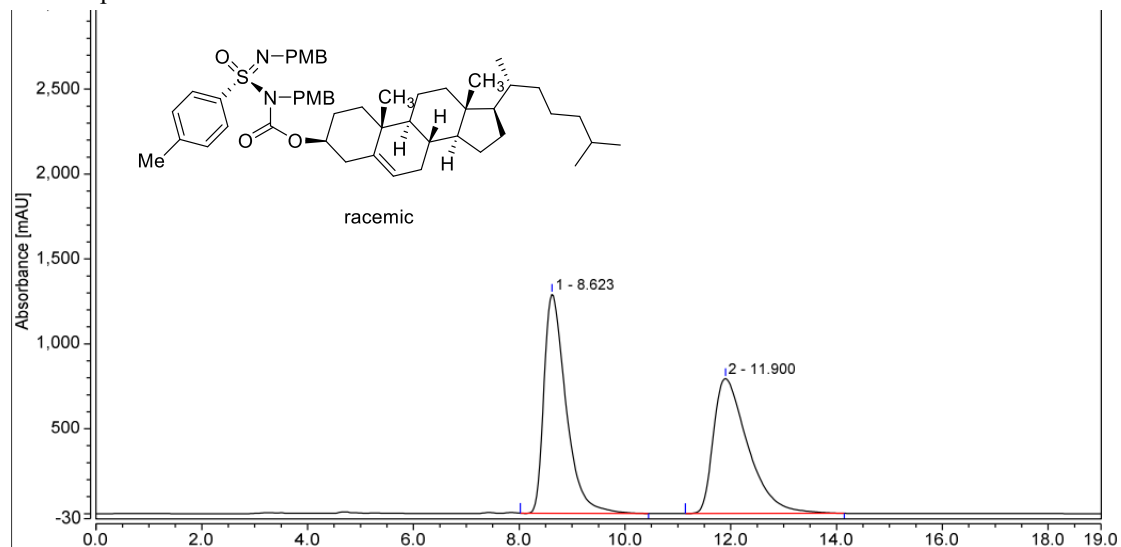


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	19.308	458.717	569.738	59.70	62.81
2	22.737	309.607	337.413	40.30	37.19
Total		768.324	907.151	100.00	100.00

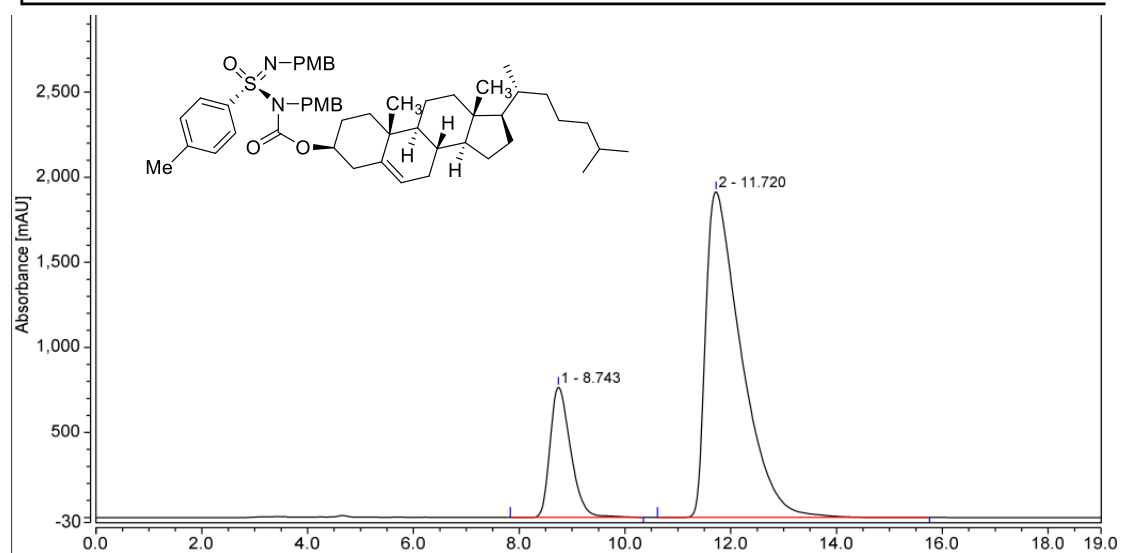


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	19.487	332.691	440.714	15.37	21.33
2	22.045	1831.990	1625.926	84.63	78.67
Total		2164.681	2066.640	100.00	100.00

HPLC Spectrum of 3ao

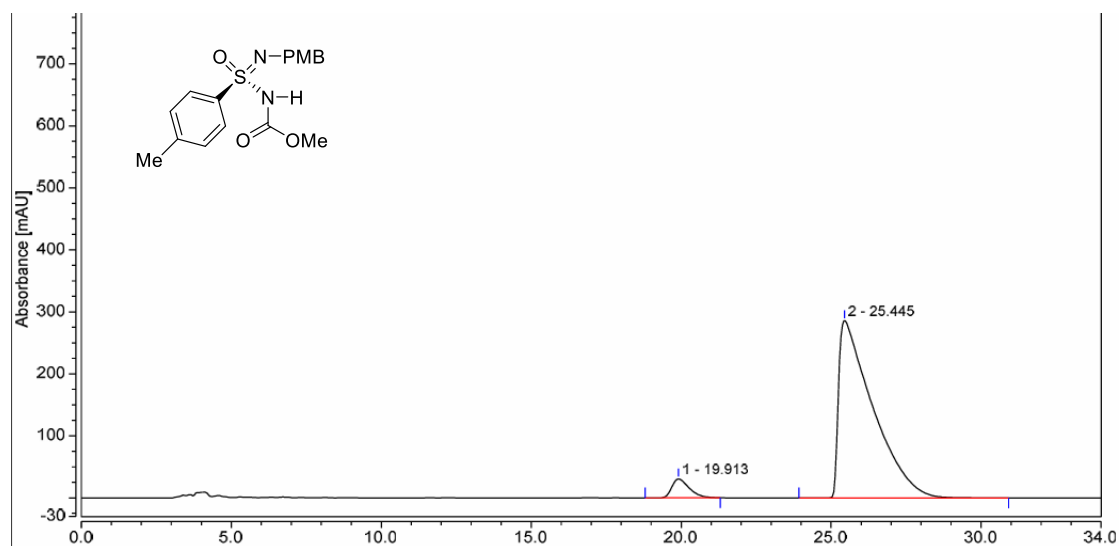
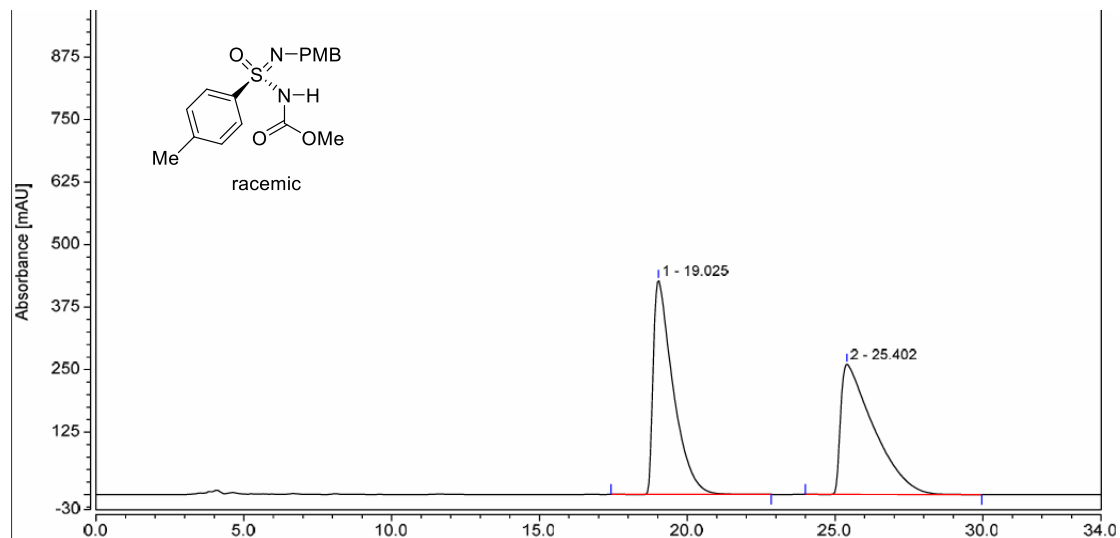


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.623	623.372	1289.729	50.97	61.89
2	11.900	599.697	794.158	49.03	38.11
Total		1223.069	2083.887	100.00	100.00

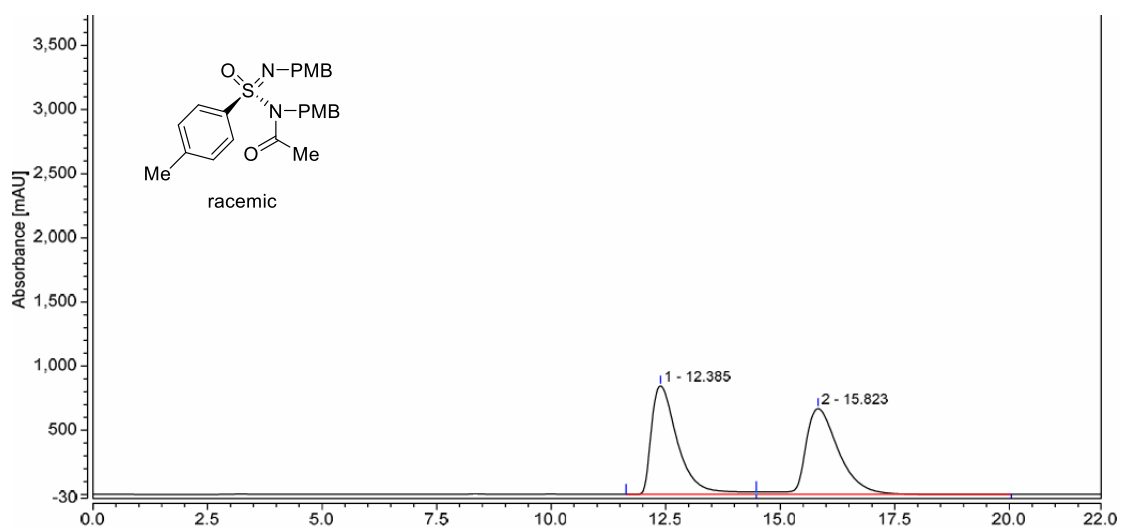


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.743	344.274	765.373	18.79	28.56
2	11.720	1487.474	1914.445	81.21	71.44
Total		1831.748	2679.818	100.00	100.00

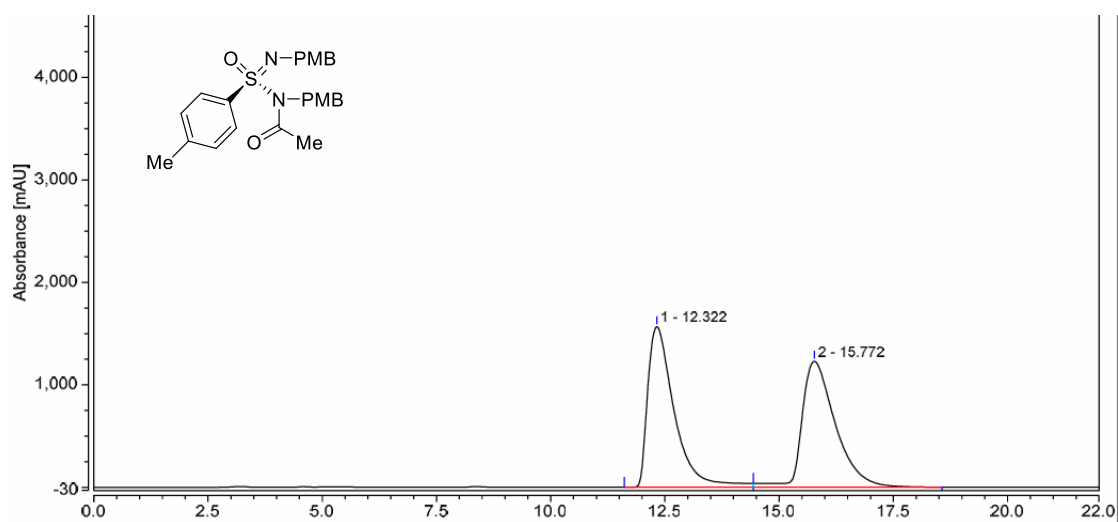
HPLC Spectrum of **5aa**



HPLC Spectrum of **3ap**

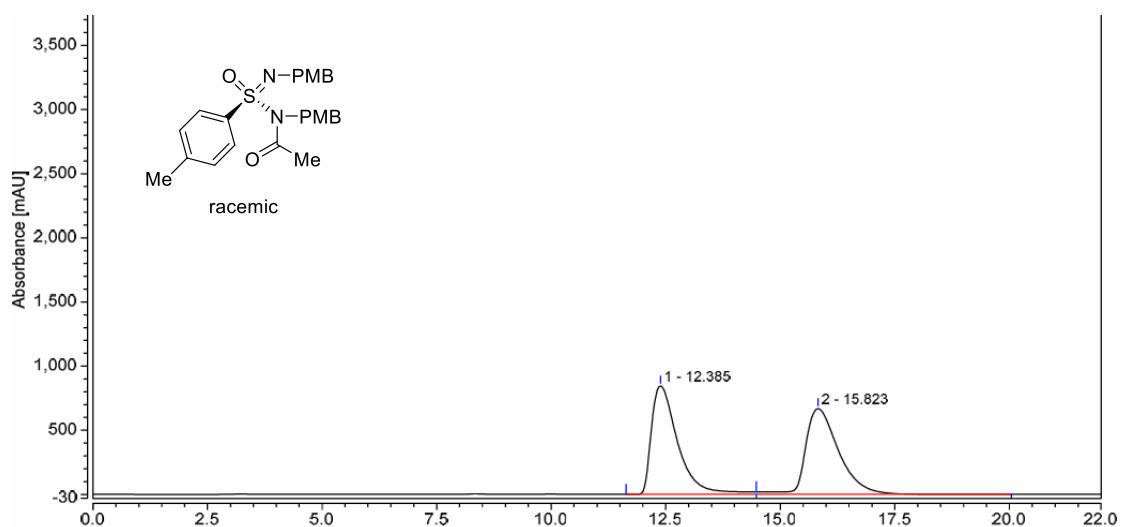


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.385	568.921	846.460	50.20	55.86
2	15.823	564.372	668.857	49.80	44.14
Total:		1133.293	1515.317	100.00	100.00

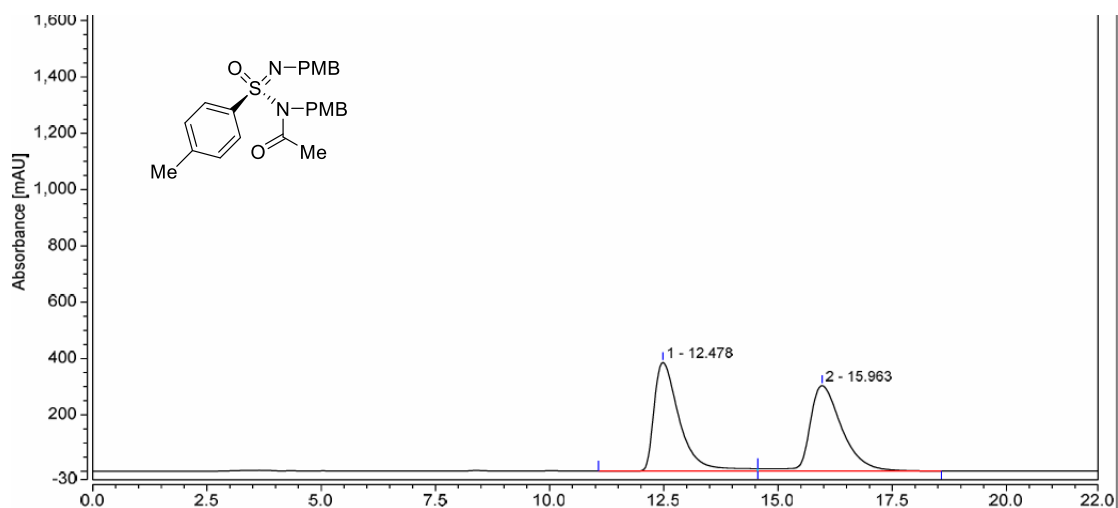


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.322	1056.262	1568.628	50.31	56.08
2	15.772	1043.238	1228.607	49.69	43.92
Total:		2099.500	2797.234	100.00	100.00

HPLC Spectrum of **3aq**

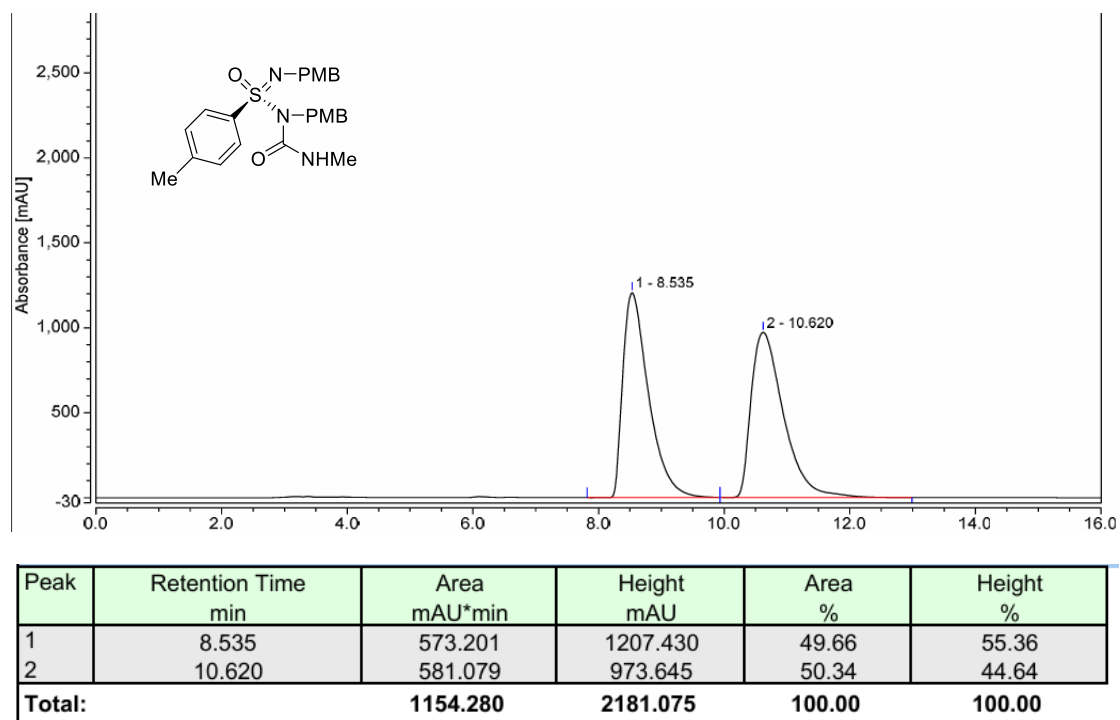
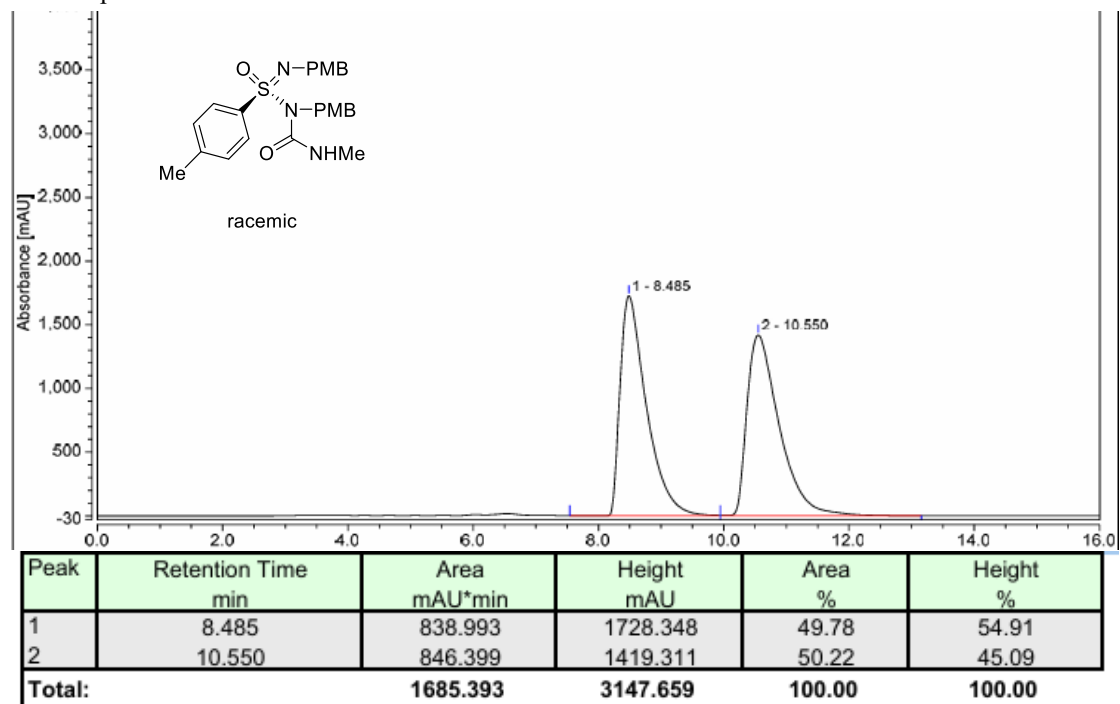


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.385	568.921	846.460	50.20	55.86
2	15.823	564.372	668.857	49.80	44.14
Total:		1133.293	1515.317	100.00	100.00

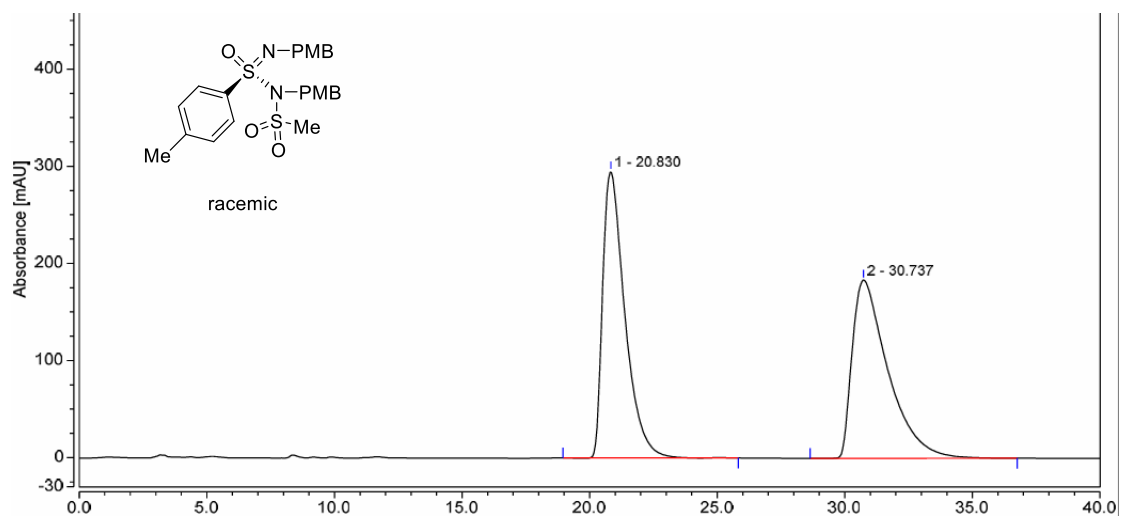


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.478	249.601	385.635	50.26	55.96
2	15.963	247.017	303.456	49.74	44.04
Total:		496.618	689.091	100.00	100.00

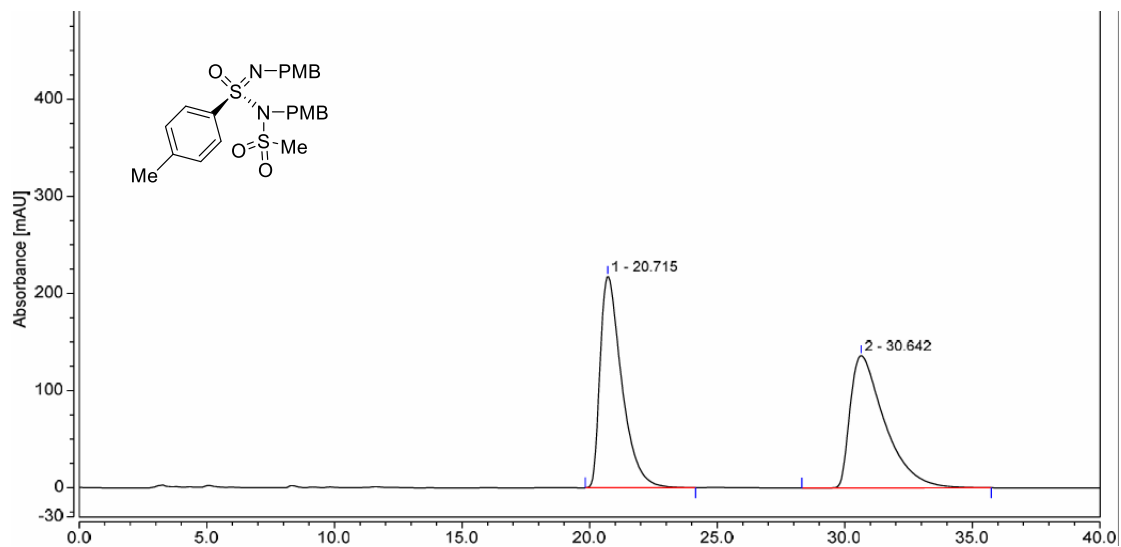
HPLC Spectrum of 3ar



HPLC Spectrum of **3at**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	20.830	296.696	294.927	49.89	61.64
2	30.737	297.986	183.568	50.11	38.36
Total:		594.683	478.494	100.00	100.00



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	20.715	213.910	217.798	49.97	61.52
2	30.642	214.125	136.225	50.03	38.48
Total:		428.035	354.022	100.00	100.00

Quantum chemical calculations

The exchange and correlation electronic effects were considered by employing the density functional theory (DFT)^[3,4] at the M06-2X level^[5], which included dispersion-like and steric exchange repulsion effects implicitly^[5,6]. The ultrafine grid (99,590), having 99 radial shells and 590 angular points per shell, was used to evaluate the numerical integration accuracy. Geometry optimizations were performed with the double-zeta basis set 6-31G(d,p) in the trichloromethane medium while using Truhlar's SMD solvation model^[7]. The temperature was set to 223.15 K for thermochemistry analysis. The chiral catalyst **C4** were optimized based on single-crystal structure, and the crystal conformation of catalyst was utilized to explore catalyzed reaction pathway. Based on the optimized structures, the electronic energy (E_{electron}) and solvation free energy (ΔG_{solv}) were calculated at the same level of theory. The harmonic vibrational frequencies were analyzed after the geometry optimizations to characterize the nature of the stationary point as a minimum with all positive frequencies or as a transition state with only one imaginary frequency and to provide the zero-point energy (E_{ZPE}), total entropy (S_{tot}) and thermal correction to enthalpy (H_{corr}) at the same theoretical level. The Gibbs free energy of free catalyst and substrate were defined as reference-point. In addition, the intrinsic reaction coordinate (IRC)^[8,9] calculations were carried out to verify the transition state (TS) associated with the correct reactant complexes (RC) and intermediates (IM) at the same level of theory. All calculations were carried out with Gaussian 16 program^[10]. And the visual analysis of noncovalent interactions (NCI)^[11] was performed by independent gradient model based on Hirshfeld partition (IGMH)^[12,13].

$$G = E_{\text{electron}} + \Delta G_{\text{solv}} + E_{\text{ZPE}} + H_{\text{corr}} - TS_{\text{tot}} \quad (1)$$

$$\Delta G = G - (G_{\text{catalyst}} + G_{\text{substrate}}) \quad (2)$$

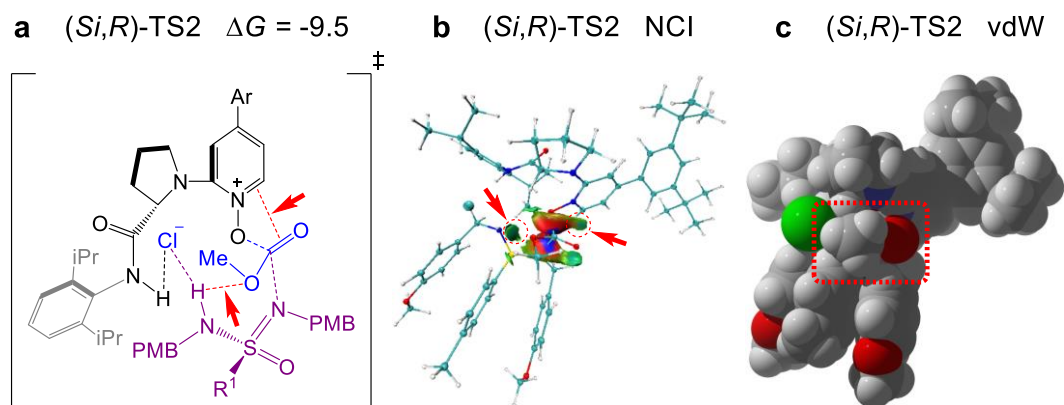


Fig. S2 (a) DFT-computed relative free energy (kcal/mol), (b) non-covalent interactions (NCI) and (c) van der Waals (vdW) radii structure of the key transition state (*Si,R*)-TS2.

As shown in Fig. S2(b), the π - π interaction between pyridinium cation of **C4** and C=O of *O*-acyloxypyridinium cation are displayed. Meanwhile, the electrostatic interactions between N-H of sulfonimidamide **1a** and O-Me in *O*-acyloxypyridinium cation are also displayed. Therefore, the oxygen of methoxyl in *O*-acyloxypyridinium cation is very important, which serve as electron donor. As shown in Fig. S2(c), the cavity between catalyst **C4** and substrate sulfonimidamide **1a** can only accommodate the sheet structure due to the large steric hindrance. So, according to the above two points, the high-electronegative and low-substitution atom in this position are more favorable to this system, namely, the order is oxygen > nitrogen > carbon. Meanwhile, the small steric hindrance of substituents on oxygen atoms is more favorable, which shows good agreement with Scheme 4.

Cartesian coordinate for theoretical calculation

1. DFT-computed reaction pathway in Figure 3.

C4			
H	-1.47943900	-0.93155100	-2.71619300
O	2.33255200	1.29781000	-2.70547100
N	1.58556500	2.70757000	-0.53692500
O	3.27576500	1.03938700	1.62905700
N	1.16288000	1.06494400	-2.17000600
N	3.41542600	0.09216500	-0.43712500
H	3.31896400	0.29791600	-1.43782700
C	-0.53179700	1.49410000	-0.54952900
C	3.26103100	1.13776700	0.40622100
C	3.03920700	2.49136000	-0.30412700
H	3.55518800	2.48774200	-1.26163700
C	-1.37328500	0.54921400	-1.12591200
C	0.74812200	1.75863400	-1.06099100
H	-0.85801300	2.04892000	0.32110300
C	3.67987000	-1.24026300	0.01386500
C	0.36456800	0.11864000	-2.72215500
H	0.81648800	-0.37860200	-3.57044700
C	5.01008600	-1.70016200	-0.02706700
C	-0.89362200	-0.15310700	-2.24197300
C	3.44954700	3.66927100	0.59842500
H	3.65403100	3.28551100	1.59993200
H	4.34891700	4.15886900	0.22144200
C	1.19139900	-1.57311000	0.50002400
H	1.12683700	-0.69217600	-0.14410600
C	2.63065100	-2.05655400	0.46802400
C	6.12868200	-0.78067100	-0.49034800
H	5.71505700	-0.11544500	-1.25563500
C	2.23314600	4.60118400	0.63118500
H	2.17045600	5.18174000	1.55331000
H	2.24441500	5.29032500	-0.21795100
C	5.27654100	-2.99512100	0.41875700
H	6.29347700	-3.37349300	0.39717800
C	2.94660600	-3.34182900	0.91967700
H	2.15473200	-3.98630600	1.29017200
C	1.07104400	3.63111400	0.47690600
H	0.86264100	3.11396500	1.42638600
H	0.15126300	4.10242500	0.12116500
C	4.25404900	-3.80834500	0.89741200
H	4.47875500	-4.81079600	1.24921500
C	0.20597200	-2.61265600	-0.04138500
H	0.47571300	-2.93589400	-1.05171900
H	-0.80139300	-2.18354900	-0.07568700
H	0.16055100	-3.49918100	0.59946200
C	0.79003300	-1.14504600	1.91660700
H	0.81125800	-2.00391100	2.59760300
H	-0.23075400	-0.74532500	1.91061300
H	1.46870300	-0.37993900	2.30121400
C	6.60180600	0.09050200	0.68231500
H	5.77292300	0.63543200	1.14255000
H	7.35363400	0.81294300	0.34795500
H	7.05500100	-0.53907700	1.45619300
C	7.31301700	-1.52289600	-1.11069300
H	7.86648400	-2.09913100	-0.36223000
H	8.01228300	-0.80301100	-1.54635300
H	6.99261800	-2.20802800	-1.90132500
C	-2.71376400	0.26090600	-0.56028000
C	-3.77232600	-0.08675000	-1.40380500
C	-2.93167200	0.31913800	0.81904100
C	-5.04004200	-0.37382500	-0.89323000
H	-3.60513500	-0.10760100	-2.47730900
C	-4.18505800	0.03515000	1.36602300
H	-2.10123100	0.56835800	1.47410200
C	-5.22315100	-0.30791900	0.49270400
H	-6.19950600	-0.53065600	0.90307600
C	-6.17321600	-0.73902500	-1.85955900

C	-4.37161000	0.09650300	2.88656300
C	-7.48644100	-1.03706900	-1.12961900
H	-8.25758500	-1.29593300	-1.86167800
H	-7.38434800	-1.88122400	-0.43984300
H	-7.84202800	-0.16966300	-0.56409400
C	-6.41220500	0.43227300	-2.82671800
H	-6.69518100	1.33758100	-2.28003500
H	-5.51909700	0.65822800	-3.41680000
H	-7.22109100	0.18590700	-3.52301900
C	-5.77385800	-1.98767900	-2.66350800
H	-5.58979800	-2.83750800	-1.99836300
H	-6.57753200	-2.26192400	-3.35529800
H	-4.86869900	-1.81688000	-3.25396600
C	-3.42511300	-0.91441800	3.55510600
H	-2.37571600	-0.69010000	3.34075900
H	-3.55668200	-0.89038000	4.64226200
H	-3.63188900	-1.93171000	3.20744800
C	-4.03455000	1.51187400	3.38432100
H	-4.16559700	1.56946900	4.47020700
H	-2.99918900	1.78392400	3.15815900
H	-4.69062900	2.25545900	2.92037700
C	-5.80628600	-0.23393400	3.30916100
H	-6.52755100	0.46879200	2.87936600
H	-6.09290400	-1.24815300	3.01273800
H	-5.88732700	-0.17019200	4.39859800

1a			
S	0.20407100	-2.30463300	0.13742200
O	0.90023900	-2.54141300	1.41638600
N	-1.09706700	-3.05672200	-0.20639900
C	0.06578900	-0.52600700	-0.01732800
C	-0.62198700	-0.01091600	-1.11492800
C	0.56930100	0.30129400	0.97597200
C	-0.81220300	1.35955700	-1.20360100
H	-1.01492100	-0.68119400	-1.87376100
C	0.37791000	1.67766200	0.86499000
H	1.10180900	-0.12898200	1.81717800
C	-0.32280900	2.22232200	-0.21197800
H	-1.36013600	1.77285000	-2.04677000
H	0.77175100	2.33650300	1.63432700
C	-0.58945500	3.70061700	-0.30135600
H	-0.35889000	4.08446300	-1.29923400
H	-1.64805200	3.90512400	-0.10675000
H	0.00260400	4.25717900	0.42834300
N	1.14854000	-2.71075700	-1.18156100
H	0.80570200	-3.61192700	-1.51438400
C	2.60556800	-2.69462500	-0.94866800
H	3.04193000	-3.10804400	-1.86278500
H	2.88837300	-3.34212900	-0.11111400
C	-2.21270600	-2.91656400	0.75001800
H	-2.90723300	-3.72457600	0.50327200
H	-1.88280500	-3.08214700	1.78444800
C	-2.92066900	-1.58213000	0.65178900
C	-2.71066800	-0.58093600	1.60570800
C	-3.70711200	-1.27872400	-0.45704300
C	-3.24162200	0.68974400	1.44200800
H	-2.09498000	-0.79448200	2.47689100
C	-4.25870800	-0.01063000	-0.63867900
H	-3.87542400	-2.04197300	-1.21349700
C	-4.01103900	0.98383400	0.31104100
H	-3.06196700	1.47709400	2.16727300
H	-4.86177000	0.19155400	-1.51602100
O	-4.46785400	2.26197000	0.22154600
C	-5.19769900	2.61358400	-0.93857800
H	-5.44512400	3.67019700	-0.83382400
H	-4.59779000	2.47014100	-1.84530300
H	-6.12371800	2.03322200	-1.02195600
C	3.10496800	-1.29272700	-0.70013600
C	2.88729300	-0.28121300	-1.64592800

C	3.72888600	-0.96037800	0.49549300
C	3.26973600	1.02291400	-1.39093200
H	2.38102800	-0.52187600	-2.57744600
C	4.13333700	0.34910500	0.76825500
H	3.88338600	-1.72961000	1.24750200
C	3.89130900	1.34668200	-0.17548300
H	3.08952600	1.81755400	-2.10768600
H	4.61164000	0.57490800	1.71381400
O	4.21295000	2.65497400	-0.00958000
C	4.80451300	3.03037500	1.22048400
H	4.96889600	4.10646400	1.16293800
H	4.14105900	2.80924300	2.06487300
H	5.76537900	2.52564100	1.37309500
2a			
C	0.03212500	0.30736000	0.00025200
O	-0.22147900	1.47107700	-0.00004100
O	-0.80075800	-0.70986000	0.00012100
C	-2.19522500	-0.33437100	-0.00010800
H	-2.74301800	-1.27369900	-0.00058300
H	-2.42230900	0.24634200	0.89503100
H	-2.42187400	0.24700200	-0.89492500
Cl	1.69080600	-0.30278300	-0.00006000
(R)-3aa·HCl			
S	-0.36785400	-0.96020300	-1.11824800
O	-1.30803300	-1.13706300	-2.21591800
N	1.13558500	-1.35946000	-1.34582100
C	-0.46851300	0.72351400	-0.58248000
C	0.56855600	1.31791700	0.13345400
C	-1.65459800	1.40475400	-0.87178500
C	0.41184800	2.63613200	0.54795900
H	1.47553000	0.76944200	0.35687400
C	-1.79027300	2.71144300	-0.43097600
H	-2.44995600	0.91484100	-1.42412500
C	-0.76149200	3.34632600	0.27897900
H	1.21874300	3.11825200	1.09128700
H	-2.70946300	3.25109000	-0.64133800
C	-0.93358200	4.76561100	0.74306500
H	-1.76436000	4.83751600	1.45196300
H	-0.03137100	5.13759300	1.23178800
H	-1.16773200	5.42204400	-0.10018000
N	-0.83913300	-1.99781200	0.10090200
C	-2.21486000	-2.55018400	-0.01555900
H	-2.25336400	-3.32321100	0.75266900
H	-2.31179900	-3.02654800	-0.99033600
C	2.03261300	-0.61606300	-2.24984600
H	2.46466500	-1.36643900	-2.91893300
H	1.45010600	0.07003900	-2.87264800
C	3.10736700	0.12802100	-1.49324200
C	3.41302800	1.45551400	-1.80318700
C	3.78978000	-0.49155200	-0.44677800
C	4.37759800	2.14943400	-1.08674900
H	2.88072800	1.95831300	-2.60674200
C	4.75846800	0.19330400	0.28570600
H	3.55268600	-1.52237000	-0.18530200
C	5.05463600	1.52191700	-0.03538200
H	4.61836700	3.18208100	-1.31717100
H	5.27341700	-0.31596400	1.09182400
O	5.97199200	2.28058700	0.61543500
C	6.69138800	1.67520200	1.67538200
H	7.37168300	2.43817900	2.05382700
H	6.02103800	1.35608200	2.48169700
H	7.27156300	0.81484300	1.32338100
C	-3.26539300	-1.48624300	0.18583600
C	-3.30269300	-0.74239900	1.37321700
C	-4.17267600	-1.17995900	-0.82215900
C	-4.21200600	0.28785000	1.53509500
H	-2.60364000	-0.97052700	2.17486100

C	-5.10566200	-0.15160800	-0.67261000
H	-4.14302800	-1.73779300	-1.75423000
C	-5.11777300	0.59260800	0.50851300
H	-4.24452900	0.87562600	2.44650500
H	-5.79824400	0.06199700	-1.47779700
O	-5.96113200	1.62500400	0.75555300
C	-6.89020500	1.97018000	-0.25703900
H	-7.46502900	2.81006200	0.13304200
H	-6.37968000	2.27605300	-1.17771000
H	-7.56811400	1.13790100	-0.47691800
C	-0.16559100	-2.13398300	1.33549400
O	-0.56440200	-2.87140300	2.19983000
O	0.88616600	-1.33684100	1.41128200
C	1.75451800	-1.57062200	2.53062100
H	2.17017000	-2.57680400	2.45487900
H	2.54092000	-0.82184900	2.44463800
H	1.20516900	-1.44723600	3.46511800
H	1.45618200	-2.31598000	-0.94513900
Cl	2.12389400	-3.90400200	-0.22247000
RC			
H	2.31812400	1.66919400	2.04047300
O	-1.64375100	1.80102400	0.08656300
N	-0.81044000	0.17598800	-1.87209600
O	-2.03549100	-1.36799400	0.10911900
N	-0.42739500	1.33546700	0.13819000
N	-4.02501800	-0.28772300	-0.17346100
H	-4.46516700	0.49238700	-0.64611900
C	1.34340700	0.01575700	-0.75402900
C	-2.73820300	-0.57230500	-0.49961000
C	-2.27680100	0.07484500	-1.79794400
H	-2.72498200	1.06439400	-1.90917800
C	2.20578200	0.42976500	0.25791900
C	0.01786600	0.46444700	-0.82517600
H	1.70102200	-0.66070700	-1.51941700
C	-4.70924100	-0.88781500	0.93199000
C	0.39993100	1.74154800	1.12832400
H	-0.06745800	2.43326900	1.81628100
C	-5.42289600	-2.08032000	0.71738400
C	1.70768400	1.32057100	1.21629900
C	-2.63393600	-0.84355200	-2.98497600
H	-2.65621000	-1.88677600	-2.64806200
H	-3.60979900	-0.59344100	-3.40566800
C	-3.86130900	1.00398900	2.41019000
H	-3.71800700	1.49340200	1.44334400
C	-4.67028400	-0.26138500	2.18860300
C	-5.43633000	-2.75417200	-0.64466300
H	-5.24143700	-1.97992200	-1.39406300
C	-1.47168300	-0.64304400	-3.95512300
H	-1.37767100	-1.44576600	-4.68849300
H	-1.57851700	0.30881000	-4.48605800
C	-6.08683800	-2.65411700	1.80394500
H	-6.63957700	-3.57862800	1.66821500
C	-5.35378300	-0.86774700	3.24583400
H	-5.33505900	-0.40762800	4.22922800
C	-0.28063200	-0.58042000	-3.00831400
H	0.02862300	-1.59196000	-2.70595900
H	0.58761700	-0.06569300	-3.43305000
C	-6.05258600	-2.05436800	3.05790100
H	-6.57512500	-2.51345900	3.89187900
C	-4.54387200	1.99437400	3.35627800
H	-5.57295600	2.20515000	3.04914500
H	-3.99077100	2.93856800	3.36155600
H	-4.56619600	1.62516500	4.38697700
C	-2.46336500	0.63830800	2.92465300
H	-2.53472000	0.11571500	3.88619400
H	-1.86746800	1.54468700	3.07097900
H	-1.94400700	-0.00999700	2.21325200
C	-4.30275600	-3.78602700	-0.73024000

H	-3.33557800	-3.33172900	-0.49770200
H	-4.25717700	-4.22746000	-1.73181000
H	-4.47607400	-4.59533100	-0.01168000
C	-6.77961800	-3.40506200	-0.98170200
H	-6.97632900	-4.27797000	-0.35121800
H	-6.77399100	-3.75136500	-2.01978400
H	-7.61037100	-2.70346100	-0.86042600
C	3.60290600	-0.06492800	0.31622600
C	4.63072600	0.77473800	0.75366300
C	3.90807600	-1.37440000	-0.06373600
C	5.95295300	0.32894700	0.81503000
H	4.39078600	1.79893300	1.02691200
C	5.21865100	-1.85457000	-0.01794000
H	3.10099300	-2.03330800	-0.37251200
C	6.22393300	-0.98721600	0.42392900
H	7.24382400	-1.34680800	0.46695600
C	7.04944200	1.28936400	1.29127600
C	5.50292400	-3.30123100	-0.43919300
C	8.42850200	0.62374900	1.32933400
H	9.17003000	1.34556500	1.68541800
H	8.44537200	-0.23486500	2.00846600
H	8.74357000	0.28542500	0.33686800
C	7.12020100	2.49280400	0.33657500
H	7.35535000	2.16868400	-0.68239300
H	6.17449200	3.04207500	0.30751600
H	7.90159500	3.18729300	0.66376100
C	6.71368000	1.78460300	2.70778500
H	6.65185100	0.94659000	3.40947900
H	7.49170500	2.47008900	3.06070900
H	5.75990900	2.31978100	2.73425300
C	4.71656300	-4.25961800	0.47054500
H	3.63817100	-4.08870100	0.40302300
H	4.91107100	-5.29790200	0.18057000
H	5.01376500	-4.13512400	1.51677000
C	5.05504000	-3.50296200	-1.89649500
H	5.25288800	-4.53313300	-2.21180800
H	3.98422200	-3.31527800	-2.02019000
H	5.59758400	-2.82950200	-2.56797200
C	6.99010100	-3.65400100	-0.34035700
H	7.60211800	-3.01651800	-0.98688400
H	7.36097800	-3.56251400	0.68564400
H	7.13902500	-4.69094600	-0.65695900
C	-1.51065800	3.93194900	-1.33245500
Cl	-3.23215200	4.18346900	-0.99817500
O	-1.38894500	3.23637900	-2.44602300
O	-0.64918700	4.43589100	-0.68249600
C	-0.03022100	3.08062100	-2.89536600
H	0.59345900	2.66889300	-2.10074300
H	-0.08084300	2.39749300	-3.74132400
H	0.36272800	4.05011100	-3.20932700

(Si)-TS1

H	2.35655600	-2.00199200	-1.63057600
O	-1.62418300	-1.67441800	0.26271900
N	-0.75992900	0.37206700	1.83789300
O	-2.29071000	1.65156400	-0.18908600
N	-0.38328400	-1.21651000	0.13274600
N	-3.96745100	0.14288300	0.16223200
H	-4.13355100	-0.75723300	0.59861600
C	1.40515800	0.20488200	0.76856600
C	-2.80039300	0.76155200	0.47675500
C	-2.23190200	0.36892000	1.83677500
H	-2.60759700	-0.60404100	2.15833900
C	2.25501500	-0.42742900	-0.12643200
C	0.05826400	-0.18470700	0.91697200
H	1.77642900	1.01647500	1.37953900
C	-4.76159400	0.50890400	-0.96716400
C	0.43180600	-1.84502700	-0.74772500
H	-0.05851800	-2.64379700	-1.28714600

C	-5.52667500	1.68517100	-0.90933000
C	1.74586600	-1.48705200	-0.89991000
C	-2.58432400	1.46907500	2.85821400
H	-2.66817400	2.43034500	2.33907100
H	-3.52924300	1.25528800	3.36087300
C	-3.84415100	-1.52679500	-2.17579600
H	-3.69370200	-1.92437200	-1.16746300
C	-4.77506500	-0.32970200	-2.09675900
C	-5.51129400	2.60411100	0.30036800
H	-4.98284500	2.08638900	1.10651700
C	-1.37794800	1.49237200	3.79302600
H	-1.29709600	2.41626500	4.36807200
H	-1.41493400	0.64634800	4.48655700
C	-6.30901300	2.01525500	-2.02019900
H	-6.89943200	2.92727600	-2.00320100
C	-5.59185900	0.02506000	-3.17097300
H	-5.62537000	-0.60809300	-4.05196600
C	-0.21668900	1.31383700	2.82395000
H	0.05294500	2.26587000	2.34620400
H	0.67451100	0.89287700	3.29815800
C	-6.35072100	1.19114200	-3.13685600
H	-6.97264300	1.45801700	-3.98605200
C	-4.37137900	-2.66039100	-3.05533800
H	-5.38762400	-2.95297600	-2.77372300
H	-3.72503100	-3.53679000	-2.95014100
H	-4.37679700	-2.38525100	-4.11525800
C	-2.47221100	-1.05017400	-2.67142500
H	-2.56010000	-0.63294000	-3.68143400
H	-1.76814200	-1.88742100	-2.70618300
H	-2.06246200	-0.27672300	-2.01465700
C	-4.74858700	3.89643600	-0.01527300
H	-3.73461000	3.67311000	-0.35647000
H	-4.68853100	4.53341200	0.87385200
H	-5.26166500	4.46357300	-0.80021800
C	-6.92517100	2.91637800	0.80153300
H	-7.49205200	3.49731900	0.06687400
H	-6.87633300	3.50855400	1.72090700
H	-7.48528400	2.00101500	1.01399800
C	3.66405800	0.01098300	-0.27445100
C	4.66371000	-0.92879100	-0.53728800
C	4.00505500	1.36092200	-0.15830800
C	5.99790400	-0.54232200	-0.68054800
H	4.39328200	-1.97900600	-0.60674000
C	5.32861400	1.78436000	-0.29686400
H	3.21795500	2.09052600	0.01203300
C	6.30624700	0.81705800	-0.55597100
H	7.33575400	1.13178200	-0.66694900
C	7.06339700	-1.60813600	-0.96253700
C	5.65714300	3.27716600	-0.17543000
C	8.46525500	-1.00631700	-1.09942400
H	9.18448300	-1.80571900	-1.30236700
H	8.52023300	-0.29055400	-1.92609800
H	8.78070600	-0.49954000	-0.18158900
C	7.08391300	-2.62445900	0.19121100
H	7.32377900	-2.13276100	1.13951200
H	6.11906900	-3.12748500	0.30472800
H	7.84208100	-3.39206500	0.00234600
C	6.71981500	-2.33470400	-2.27375600
H	6.69328500	-1.63253300	-3.11321400
H	7.47540500	-3.09778400	-2.48934100
H	5.74762200	-2.83356000	-2.21839500
C	4.90489600	4.05250500	-1.26978200
H	3.82136500	3.93195700	-1.17921700
H	5.13111400	5.12169300	-1.19579000
H	5.20183400	3.70797900	-2.26551900
C	5.21076700	3.78657900	1.20514200
H	5.44405200	4.85195500	1.30575300
H	4.13326100	3.66604400	1.35205600
H	5.72594400	3.24637500	2.00603000

C	7.15541300	3.55635300	-0.32883800
H	7.74372500	3.04423300	0.43960200
H	7.52717100	3.24848900	-1.31147300
H	7.33632900	4.63075700	-0.22663800
C	-1.50711100	-3.22369100	1.46236500
Cl	-3.33902900	-3.40735600	1.43700200
O	-1.20184500	-2.56830600	2.59666400
O	-0.80647200	-4.02157800	0.90275600
C	0.15253200	-2.75592000	3.02736200
H	0.86284800	-2.47213400	2.24688500
H	0.27171400	-2.11214700	3.89842000
H	0.31964300	-3.79956800	3.30414500
IM1			
H	2.45073900	-1.90091800	-1.88007700
O	-1.53894100	-1.61859200	-0.02422400
N	-0.57421600	0.32298200	1.77695300
O	-1.91976700	1.37797900	-0.40717200
N	-0.22746000	-1.19247800	-0.01289900
N	-3.90093400	0.44188000	0.26410000
H	-4.28293900	-0.24675600	0.92720900
C	1.59814200	0.07168300	0.75891500
C	-2.60036500	0.77067500	0.41062300
C	-2.04835800	0.37361000	1.77787400
H	-2.47245100	-0.58023100	2.10510900
C	2.41448500	-0.50483000	-0.18701000
C	0.21271900	-0.23868400	0.86549900
H	2.00515000	0.79627400	1.45044900
C	-4.63976400	0.73663300	-0.92153300
C	0.54538700	-1.76239300	-0.98360100
H	0.01203800	-2.45179700	-1.62705600
C	-5.03474300	2.06009700	-1.18319400
C	1.86027000	-1.45323200	-1.09152100
C	-2.36269900	1.46796800	2.81127400
H	-2.38304400	2.44631600	2.31750700
H	-3.33097400	1.28547700	3.27976000
C	-4.48702500	-1.73498600	-1.54818600
H	-4.03435900	-1.78176400	-0.55565300
C	-4.97120800	-0.31642900	-1.79170600
C	-4.68966500	3.21001800	-0.25212400
H	-4.23510300	2.78706800	0.64840700
C	-1.18184800	1.39337500	3.77418300
H	-1.06059800	2.29338100	4.37879700
H	-1.28834900	0.53159200	4.43938300
C	-5.76356000	2.31172700	-2.34823100
H	-6.07057100	3.32972900	-2.57322600
C	-5.71648100	-0.02040300	-2.93512700
H	-5.98000700	-0.82276000	-3.61927900
C	-0.00129100	1.18076700	2.83492800
H	0.34124700	2.12773800	2.40036500
H	0.84158300	0.67546500	3.31106100
C	-6.10866800	1.28290300	-3.21682600
H	-6.68170800	1.49780100	-4.11383400
C	-5.62810300	-2.75420400	-1.56011000
H	-6.39316900	-2.49409500	-0.82303300
H	-5.24078100	-3.74616800	-1.30681900
H	-6.10570100	-2.82014400	-2.54392600
C	-3.40785900	-2.10101200	-2.57388700
H	-3.82619300	-2.13321600	-3.58671300
H	-2.98616700	-3.08472700	-2.34364500
H	-2.59784600	-1.36456300	-2.56680800
C	-3.67047400	4.15020200	-0.90567500
H	-2.77241600	3.60015300	-1.19648600
H	-3.38439800	4.94821800	-0.21200300
H	-4.09614100	4.62061400	-1.79923500
C	-5.94073500	3.98109900	0.18240200
H	-6.41858500	4.47939400	-0.66749500
H	-5.67404300	4.75429700	0.91016600
H	-6.67733700	3.31686600	0.64343000

C	3.84493700	-0.13427200	-0.27994600
C	4.79364200	-1.10431400	-0.61345100
C	4.25375100	1.17916600	-0.03587200
C	6.15026400	-0.78378100	-0.69301900
H	4.46705200	-2.12653000	-0.78435500
C	5.60091100	1.53711700	-0.11693400
H	3.50332500	1.93357800	0.18474800
C	6.52794500	0.54030700	-0.44283800
H	7.57555500	0.80386800	-0.50781500
C	7.16370800	-1.87938900	-1.04360400
C	6.00980600	2.99195200	0.14127500
C	8.59851000	-1.34621700	-1.09834500
H	9.27874400	-2.16415800	-1.35422400
H	8.71314500	-0.56720900	-1.85904900
H	8.91689600	-0.93781000	-0.13370500
C	7.09998800	-2.98861100	0.01953200
H	7.33930200	-2.59250100	1.01162500
H	6.10792000	-3.44756500	0.06773900
H	7.82221800	-3.77696400	-0.21766100
C	6.81504900	-2.47250600	-2.41890000
H	6.84938200	-1.70236900	-3.19609900
H	7.53282500	-3.25669300	-2.68188200
H	5.81584200	-2.91838200	-2.42679200
C	5.30817200	3.90462100	-0.87808800
H	4.21900500	3.83715200	-0.80092600
H	5.59249500	4.94790800	-0.70465700
H	5.59260400	3.63790900	-1.90096200
C	5.58331900	3.39427200	1.56290500
H	5.87141800	4.43200300	1.76133200
H	4.50030100	3.31723000	1.69841800
H	6.06577100	2.75636600	2.31048000
C	7.52188700	3.20105000	0.01536900
H	8.07737900	2.59348100	0.73723600
H	7.88229500	2.96032100	-0.98996600
H	7.75930800	4.25102800	0.21137800
C	-1.75773100	-2.79165600	0.72477300
Cl	-4.49392300	-1.94686500	2.36092300
O	-1.13363500	-2.72227300	1.87433400
O	-2.43311800	-3.65832900	0.26868600
C	-1.42188500	-3.81835700	2.77155900
H	-1.10132900	-4.75760000	2.31830900
H	-0.84936900	-3.60744400	3.67199500
H	-2.49389800	-3.82291700	2.97442800
IM2			
H	-3.38257700	2.04939400	-1.22782500
O	-0.53431700	-0.28793700	1.24295900
N	-2.51515500	-1.58413000	2.44262200
O	-2.46741600	-3.24742600	0.21110900
N	-1.81549800	-0.01390000	0.85716400
N	-0.18318700	-3.17370700	0.24817500
H	0.63403500	-2.99094300	0.85007300
C	-4.12409800	-0.20408300	1.22275300
C	-1.40485900	-3.02611700	0.78523800
C	-1.42110600	-2.58033300	2.25533300
H	-0.45603800	-2.17535700	2.56526600
C	-4.34765500	0.75944600	0.25507000
C	-2.82015300	-0.64284200	1.53339300
H	-4.95444800	-0.64877600	1.75499500
C	0.05248100	-3.71747900	-1.05339600
C	-1.98345600	0.92555800	-0.10937600
H	-1.05019700	1.27130500	-0.54605500
C	0.68053500	-4.97741100	-1.12441300
C	-3.24296300	1.32534900	-0.43531500
C	-1.84947600	-3.75353700	3.15743700
H	-2.38725400	-4.49509400	2.55902500
H	-0.97811000	-4.22914200	3.61061600
C	-0.94414300	-1.62518900	-2.15373400
H	-0.86237100	-1.27234000	-1.12145100

C	-0.28101800	-2.99051400	-2.20765800
C	0.95180000	-5.76033900	0.15080500
H	1.26305300	-5.04827400	0.92265500
C	-2.81025800	-3.12236300	4.16576000
H	-3.46956600	-3.85190800	4.63834000
H	-2.26073600	-2.58494700	4.94406300
C	0.97912000	-5.49710700	-2.38327400
H	1.47345000	-6.45952300	-2.46521200
C	0.01512400	-3.56479400	-3.44919500
H	-0.24233700	-3.02571500	-4.35665500
C	-3.57880700	-2.13624500	3.29823400
H	-4.32569500	-2.65627500	2.68403200
H	-4.06202200	-1.33290400	3.85887900
C	0.64480300	-4.79815800	-3.54018600
H	0.87799300	-5.21860000	-4.51382900
C	-0.24110800	-0.59744900	-3.04580600
H	0.82872000	-0.53380100	-2.83684200
H	-0.67226600	0.39684000	-2.87725800
H	-0.37582500	-0.82991600	-4.10775200
C	-2.42504600	-1.72436500	-2.54218800
H	-2.51887700	-2.07207800	-3.57766900
H	-2.90436300	-0.74094000	-2.47899800
H	-2.95590700	-2.41842200	-1.88916800
C	-0.34815100	-6.43360600	0.61586500
H	-1.17312100	-5.71734700	0.68182400
H	-0.21374300	-6.90132900	1.59678900
H	-0.64484500	-7.21171100	-0.09659500
C	2.06774700	-6.79435000	0.01315100
H	1.78415000	-7.61438200	-0.65513600
H	2.28562700	-7.23156800	0.99199600
H	2.98855700	-6.34187300	-0.36718600
C	-5.72711300	1.18194300	-0.07581100
C	-5.98920200	2.51873900	-0.38665100
C	-6.77128200	0.25340600	-0.07396700
C	-7.28487300	2.94465400	-0.68454300
H	-5.17455400	3.23775400	-0.36440500
C	-8.07737800	0.64368000	-0.37573200
H	-6.55163800	-0.79082900	0.13166600
C	-8.30934900	1.99134600	-0.67403800
H	-9.31743600	2.30749600	-0.90872300
C	-7.53440500	4.42293600	-1.00367100
C	-9.19302300	-0.40762500	-0.38256700
C	-9.00563200	4.70806700	-1.31942600
H	-9.12798300	5.77196900	-1.54411600
H	-9.35060600	4.14142100	-2.19038100
H	-9.65605600	4.46993400	-0.47151700
C	-7.12261400	5.27854900	0.20576200
H	-7.70515000	5.00765200	1.09216500
H	-6.06235500	5.15513400	0.44569300
H	-7.29705100	6.33846700	-0.00776600
C	-6.68975800	4.82747700	-2.22328700
H	-6.96012200	4.23118400	-3.10062700
H	-6.85703400	5.88317800	-2.46179400
H	-5.62002200	4.69217800	-2.03733800
C	-8.87904300	-1.46888000	-1.45011600
H	-7.92898500	-1.97343100	-1.25054200
H	-9.66679700	-2.22958900	-1.46633900
H	-8.81984500	-1.01591700	-2.44491300
C	-9.26617800	-1.08235800	0.99728800
H	-10.06485800	-1.83153000	1.00576100
H	-8.33068400	-1.59047000	1.24987100
H	-9.47770000	-0.34792400	1.78114500
C	-10.56302600	0.20239100	-0.69354500
H	-10.84766700	0.95832300	0.04574100
H	-10.58612100	0.66312800	-1.68636000
H	-11.32255100	-0.58503100	-0.67503900
C	-0.05313200	0.69179300	2.11532600
Cl	2.33164600	-2.71548000	2.17159500
O	-0.60256000	1.73455200	2.32026100

S	2.47691100	0.77237500	-0.78788600
O	2.74615400	0.95074800	-2.22478900
N	2.17144300	-0.82494900	-0.50405300
C	4.01287400	1.14766200	0.07038000
C	4.12117000	0.79929900	1.41297100
C	5.04320000	1.80617800	-0.58847000
C	5.27005000	1.14804500	2.11336800
H	3.33597700	0.22201500	1.89517500
C	6.18854000	2.14434000	0.12624300
H	4.94399800	2.04565600	-1.64185000
C	6.31418100	1.83343000	1.48373400
H	5.36397400	0.87204800	3.16031400
H	7.00128700	2.66158000	-0.37877400
C	7.55984100	2.22419600	2.23307800
H	7.50754400	1.91917100	3.28046600
H	8.44317500	1.75781900	1.78497500
H	7.70576300	3.30881400	2.19830700
N	1.27787800	1.49202400	-0.12319800
H	2.08173100	-1.06216000	0.49362600
C	1.10437700	2.92105800	-0.45017600
H	0.24770500	3.24110700	0.15451200
H	0.82279400	3.03886100	-1.50583600
C	2.96234200	-1.81657700	-1.26911200
H	2.68548300	-2.77207900	-0.81367100
H	2.59629100	-1.81863400	-2.29977400
C	4.46312400	-1.63582100	-1.25091800
C	5.14093000	-1.19893500	-2.38328800
C	5.19104200	-1.83478600	-0.06961400
C	6.51339700	-0.93812500	-2.35884500
H	4.58584600	-1.02928700	-3.30205900
C	6.54751600	-1.56587100	-0.02121500
H	4.66642500	-2.17037000	0.82348200
C	7.21425500	-1.10389700	-1.16448800
H	7.00903800	-0.59150500	-3.25788300
H	7.11688600	-1.69089700	0.89461300
O	8.53910900	-0.83926100	-1.00767900
C	9.23471200	-0.32176700	-2.12500000
H	10.26094500	-0.15653900	-1.79569700
H	9.23474600	-1.02982600	-2.96183500
H	8.80285000	0.62995200	-2.45735500
C	2.29111000	3.81441600	-0.16413600
C	2.73555900	3.99732400	1.15193000
C	3.01667400	4.40461300	-1.19189300
C	3.88796100	4.71075800	1.42542800
H	2.16287500	3.55795000	1.96482800
C	4.17356100	5.14809400	-0.93812200
H	2.69212900	4.26715300	-2.22065100
C	4.62196500	5.28179000	0.37485200
H	4.25112700	4.83855200	2.44031900
H	4.71926100	5.58890200	-1.76400300
O	5.75433100	5.93926200	0.73888600
C	6.52929000	6.52089600	-0.29246700
H	7.38496800	6.98749100	0.19603700
H	6.88527900	5.76315600	-1.00045300
H	5.96273400	7.28550200	-0.83647100
O	1.01040600	0.17591500	2.66577300
C	1.63376200	0.97675000	3.68361000
H	2.36278200	0.31873800	4.15333400
H	2.12864900	1.83602400	3.22914200
H	0.88665400	1.30472400	4.40781600
(Si,R)-TS2			
H	3.87900200	1.76879700	1.81054600
O	0.56160700	-0.21469800	-0.34872300
N	2.28430000	-1.32179300	-2.10413300
O	2.15687600	-3.09148800	0.03041000
N	1.89399700	0.00506700	-0.20641900
N	-0.11591200	-3.24155500	-0.16977100
H	-0.89571600	-3.06170700	-0.81368500

C	4.10212900	-0.13661500	-1.00403800
C	1.11665200	-2.89483900	-0.58800500
C	1.13690500	-2.25567600	-1.97785900
H	0.19288300	-1.74771600	-2.18341300
C	4.52864700	0.67990900	0.02549100
C	2.74738000	-0.52359200	-1.13020800
H	4.81057400	-0.50433400	-1.73405500
C	-0.39070500	-3.94970400	1.03864800
C	2.27533600	0.80751700	0.81845300
H	1.46101500	1.11515700	1.46437900
C	-1.01037800	-5.21185000	0.92128100
C	3.58250100	1.15543500	0.96963400
C	1.42601200	-3.31860000	-3.05171400
H	2.01878500	-4.13131000	-2.61806600
H	0.49346300	-3.72876900	-3.44372600
C	0.55749200	-2.02309400	2.45793600
H	0.60965400	-1.55740600	1.47314000
C	-0.10293200	-3.38226900	2.29176200
C	-1.22379000	-5.82505500	-0.45481700
H	-1.54885900	-5.03112800	-1.13656600
C	2.26558900	-2.56638600	-4.08218300
H	2.82690900	-3.22695400	-4.74477800
H	1.63339400	-1.91016100	-4.68809000
C	-1.35060100	-5.89405100	2.08827600
H	-1.83886000	-6.86078200	2.02401900
C	-0.43822500	-4.11941700	3.43383500
H	-0.21331500	-3.70611200	4.41343300
C	3.18274300	-1.73385700	-3.19682000
H	4.00408500	-2.34612500	-2.80118600
H	3.59674300	-0.85312400	-3.69327500
C	-1.06272800	-5.35459800	3.33940700
H	-1.32644800	-5.90146200	4.23968400
C	-0.25455500	-1.08841300	3.36057600
H	-1.26973300	-0.93629800	2.98801900
H	0.22662500	-0.10424900	3.40897900
H	-0.31603100	-1.46808400	4.38624300
C	1.98085900	-2.17950300	3.00716800
H	1.95926100	-2.60575300	4.01696700
H	2.47632500	-1.20372500	3.07043500
H	2.57456500	-2.82893800	2.36216900
C	0.11136800	-6.37899500	-0.97444500
H	0.90385200	-5.62552300	-0.93380400
H	0.01183800	-6.72182000	-2.00963900
H	0.43020800	-7.22909300	-0.36083500
C	-2.29636900	-6.91240600	-0.48694300
H	-1.98927900	-7.80394400	0.07019700
H	-2.47569000	-7.21942800	-1.52143700
H	-3.24380900	-6.55584000	-0.07161600
C	5.95945400	1.04139400	0.15488500
C	6.31957700	2.31431900	0.60433600
C	6.95473500	0.11706900	-0.17244700
C	7.66172400	2.68169000	0.72031400
H	5.53872100	3.03318400	0.83750500
C	8.30655800	0.44794000	-0.06082400
H	6.66472100	-0.88198800	-0.48617400
C	8.63467100	1.73392800	0.38331700
H	9.67885100	2.00423700	0.47187200
C	8.01609100	4.09296400	1.20271300
C	9.36909700	-0.60018600	-0.41092600
C	9.52924500	4.31542600	1.28404700
H	9.72734300	5.33256900	1.63550000
H	10.00362900	3.62184100	1.98593200
H	10.00951500	4.20115200	0.30688700
C	7.42562100	5.12569000	0.22836800
H	7.83037600	4.98728800	-0.77930800
H	6.33584000	5.04966600	0.16930400
H	7.67340300	6.13947900	0.56062700
C	7.41947000	4.31503600	2.60243800
H	7.82002200	3.58887700	3.31705600

H	7.66692600	5.32009000	2.96040000
H	6.32941200	4.22112900	2.59815000
C	9.21603400	-1.80877500	0.52760100
H	8.23191200	-2.27630700	0.42867000
H	9.97212600	-2.56519500	0.29143900
H	9.34567100	-1.50979000	1.57265100
C	9.17291100	-1.05816900	-1.86567200
H	9.92821000	-1.80650000	-2.12816800
H	8.18846100	-1.51050600	-2.01889300
H	9.27146300	-0.21527500	-2.55731000
C	10.79263100	-0.05370400	-0.26617600
H	10.96687300	0.80377400	-0.92438900
H	11.00795100	0.25063800	0.76321400
H	11.50935900	-0.83443900	-0.53837100
C	-0.05850300	0.86167500	-1.14273800
Cl	-2.45543700	-2.59312700	-2.36117600
O	0.60089700	1.83158200	-1.44675900
S	-2.55189300	0.70152700	0.74232800
O	-2.85159000	0.85229700	2.16951100
N	-2.31164100	-0.87957400	0.38553200
C	-3.99256600	1.25502900	-0.17030400
C	-4.07536000	0.96671300	-1.52914000
C	-4.97966800	1.98500000	0.48064700
C	-5.15821200	1.45139800	-2.25314900
H	-3.33544300	0.33081600	-2.00776000
C	-6.05748400	2.45703800	-0.26100700
H	-4.90075900	2.17587900	1.54542100
C	-6.15678700	2.20987800	-1.63405500
H	-5.23582500	1.22414600	-3.31257100
H	-6.83663300	3.03071500	0.23543400
C	-7.32631300	2.74866500	-2.41259700
H	-7.27901700	2.44848800	-3.46141300
H	-8.27001800	2.38551300	-1.99359300
H	-7.34437800	3.84263300	-2.36909900
N	-1.25157200	1.42851300	0.22562700
H	-2.17903600	-1.07353000	-0.62069900
C	-1.02917200	2.79331500	0.72886100
H	-0.07076200	3.07851400	0.28187000
H	-0.90702300	2.78022400	1.81818500
C	-3.20769900	-1.86285000	1.05292900
H	-2.98015900	-2.79926600	0.53576400
H	-2.88605300	-1.96451900	2.09200500
C	-4.68637200	-1.56162500	0.98813300
C	-5.36699100	-1.10607800	2.11200200
C	-5.38098000	-1.65548700	-0.22563700
C	-6.70762000	-0.72026200	2.04644200
H	-4.83698800	-1.02115300	3.05697300
C	-6.70456500	-1.26202300	-0.31357500
H	-4.85346900	-2.00692000	-1.11082800
C	-7.37137400	-0.77809000	0.82064700
H	-7.20634800	-0.36170400	2.93897200
H	-7.24595400	-1.30427100	-1.25345100
O	-8.65690000	-0.38394900	0.62440000
C	-9.34721600	0.16138900	1.73239300
H	-10.33790100	0.43560100	1.36901700
H	-9.45005800	-0.57067200	2.54155600
H	-8.84096200	1.05548800	2.11565100
C	-2.10172000	3.78922800	0.34956000
C	-2.39901800	4.01666600	-1.00101100
C	-2.86099600	4.43874400	1.31413000
C	-3.44844400	4.83760300	-1.36944900
H	-1.79986800	3.52053300	-1.76131000
C	-3.91380200	5.28998900	0.96340300
H	-2.64925300	4.26547500	2.36670600
C	-4.22047400	5.47215100	-0.38400100
H	-3.70242000	5.00265600	-2.41176300
H	-4.49133700	5.77629100	1.74059700
O	-5.24574900	6.23607600	-0.84347400
C	-6.06059700	6.87950000	0.11825400

H	-6.81834800	7.42716900	-0.44241400
H	-6.55147600	6.15227600	0.77586000
H	-5.48152700	7.58359300	0.72678200
O	-0.90992200	0.19539000	-1.95205200
C	-1.16101600	0.81944600	-3.21101700
H	-1.74182900	0.08907400	-3.77483900
H	-1.73319600	1.74307300	-3.08438000
H	-0.21863500	1.03474600	-3.71969700
PC			
H	3.98210800	2.00486600	1.18226600
O	0.70619400	-0.40227400	-0.55628600
N	2.41991800	-1.84891700	-1.99307700
O	2.14745400	-3.11808300	0.51991500
N	1.97884200	-0.13967300	-0.44749100
N	-0.11981300	-3.20855600	0.23181300
H	-0.85556200	-3.09220700	-0.46924800
C	4.24386200	-0.51430400	-1.07224100
C	1.15179800	-3.00745800	-0.18559400
C	1.26332500	-2.72006900	-1.67846000
H	0.33742500	-2.26813700	-2.03570400
C	4.67424900	0.52149400	-0.24899900
C	2.89088000	-0.86890500	-1.16682700
H	4.96417400	-1.06453200	-1.66356800
C	-0.50337100	-3.59790200	1.54551900
C	2.38663800	0.85048500	0.37810000
H	1.56993100	1.32177000	0.91090100
C	-1.24247600	-4.79440800	1.67363300
C	3.70927600	1.21128400	0.49705500
C	1.57346200	-4.02174700	-2.44149100
H	2.12094600	-4.71015000	-1.78791500
H	0.65469700	-4.50950100	-2.77458700
C	0.51853500	-1.46204900	2.54984400
H	0.62193100	-1.21779700	1.48948700
C	-0.22045600	-2.78620300	2.65789600
C	-1.49192600	-5.66357900	0.44931600
H	-1.71300100	-5.00278900	-0.39692700
C	2.48822300	-3.56421800	-3.57603500
H	3.06864800	-4.37660300	-4.01712100
H	1.90802500	-3.07544100	-4.36491200
C	-1.68704200	-5.16985700	2.94024300
H	-2.26602000	-6.07957100	3.06077500
C	-0.65931000	-3.22405200	3.91382600
H	-0.43628600	-2.62079100	4.78992300
C	3.36869200	-2.54283700	-2.86932500
H	4.15039400	-3.04936300	-2.28315100
H	3.84735600	-1.83145000	-3.54858200
C	-1.38820600	-4.39555800	4.05881200
H	-1.73026900	-4.70665400	5.04137600
C	-0.26742300	-0.31800100	3.20103900
H	-1.27622500	-0.22825600	2.78760300
H	0.25680000	0.63053600	3.03324100
H	-0.35712800	-0.44801400	4.28538400
C	1.91039300	-1.56070500	3.18634200
H	1.83047100	-1.75982800	4.26200400
H	2.45516100	-0.61780900	3.06183900
H	2.49073600	-2.35790400	2.72048200
C	-0.21716300	-6.45018100	0.11230200
H	0.64750300	-5.78712600	0.01489300
H	-0.33813900	-7.00180700	-0.82582600
H	0.00157200	-7.17084200	0.90823300
C	-2.68015200	-6.61232000	0.59895700
H	-2.48896400	-7.38983000	1.34616800
H	-2.87082800	-7.11509300	-0.35368000
H	-3.59009800	-6.07589800	0.88665000
C	6.11270600	0.87079600	-0.15361100
C	6.50513500	2.20373300	-0.00652500
C	7.09090200	-0.12539900	-0.20750600
C	7.85365000	2.55586200	0.08303700

H	5.74122900	2.97654000	0.01159200
C	8.44903800	0.18863000	-0.12189900
H	6.77902600	-1.16309600	-0.28974600
C	8.80755600	1.53370700	0.02215500
H	9.85643100	1.79161100	0.09040200
C	8.23567000	4.03318800	0.23398700
C	9.48512200	-0.94044200	-0.17559000
C	9.75119100	4.23555800	0.32588800
H	9.96900000	5.30243600	0.43569100
H	10.17767700	3.71729500	1.19089800
H	10.26263900	3.88211500	-0.57532800
C	7.71574900	4.81968100	-0.98079500
H	8.15349400	4.43764600	-1.90866800
H	6.62724500	4.75499700	-1.06862200
H	7.98286200	5.87787800	-0.88642400
C	7.59512000	4.59556800	1.51394600
H	7.94388800	4.05007000	2.39673000
H	7.86168400	5.65102800	1.63595400
H	6.50349900	4.52773100	1.48324400
C	9.24939400	-1.90186200	1.00115800
H	8.25211600	-2.34991300	0.96387000
H	9.98389900	-2.71418200	0.97629200
H	9.34974900	-1.37872800	1.95760600
C	9.33096500	-1.71016600	-1.49790400
H	10.06686500	-2.51980200	-1.55013500
H	8.33641900	-2.15615000	-1.59272700
H	9.48924900	-1.04801400	-2.35535100
C	10.92155200	-0.41575500	-0.08927500
H	11.15577500	0.26238100	-0.91640100
H	11.10452000	0.11176300	0.85248700
H	11.61920000	-1.25743200	-0.14009500
C	-0.81985600	1.54085500	-1.14472500
Cl	-2.34960300	-2.65787500	-2.10013000
O	0.07927700	2.26160100	-1.49505700
S	-2.82353100	0.81502300	0.49191200
O	-3.20139500	1.19691400	1.84414700
N	-2.47753100	-0.75863700	0.41345600
C	-4.10282800	1.27753900	-0.64817300
C	-4.42279400	0.44332100	-1.71828000
C	-4.82018600	2.43573000	-0.35594500
C	-5.50961800	0.79031700	-2.50713800
H	-3.85785400	-0.46513000	-1.91980900
C	-5.89815800	2.76093600	-1.17133600
H	-4.56080500	3.05633500	0.49712900
C	-6.26254200	1.94253300	-2.24518500
H	-5.79075100	0.14267500	-3.33271100
H	-6.47239700	3.65764100	-0.95761100
C	-7.45538400	2.26587200	-3.10152500
H	-7.15329600	2.42731100	-4.14090800
H	-8.16471200	1.43201000	-3.09508800
H	-7.96901100	3.16255600	-2.74951400
N	-1.43144000	1.64868400	0.11934100
H	-2.20043800	-1.11421700	-0.52446300
C	-1.05514500	2.76673400	1.02135500
H	-0.04340000	3.02300600	0.70093700
H	-1.01469500	2.38429200	2.04145000
C	-3.39459600	-1.67319400	1.17420100
H	-2.97023100	-2.66100700	0.98212900
H	-3.26403700	-1.44732700	2.23516300
C	-4.84411200	-1.61238400	0.75940300
C	-5.71454500	-0.69716700	1.34917600
C	-5.32129600	-2.40547000	-0.29269000
C	-7.01180300	-0.51474500	0.87133800
H	-5.37069300	-0.08802800	2.18093500
C	-6.61117600	-2.24582100	-0.77187400
H	-4.65446800	-3.12252900	-0.76256000
C	-7.45390400	-1.27659700	-0.21213200
H	-7.65468000	0.22046000	1.34009600
H	-6.98392400	-2.84399800	-1.59709800

O	-8.67674900	-1.14966800	-0.78640600
C	-9.54497700	-0.16041700	-0.26364300
H	-10.44496100	-0.19128100	-0.87799000
H	-9.81112400	-0.37279900	0.77812500
H	-9.09637500	0.83817800	-0.32598900
C	-1.99210700	3.94294900	0.91022700
C	-2.15033600	4.61137700	-0.31193500
C	-2.75941900	4.34634700	1.99753300
C	-3.06263900	5.64391900	-0.43932400
H	-1.55723700	4.30827800	-1.17140000
C	-3.67800600	5.39274500	1.89011500
H	-2.65947400	3.82421200	2.94523700
C	-3.83534200	6.03976200	0.66264200
H	-3.19857300	6.16484600	-1.38134000
H	-4.26076900	5.68201900	2.75624700
O	-4.70362400	7.05547400	0.43798700
C	-5.49823800	7.49402600	1.52646500
H	-6.11416600	8.30719500	1.14278500
H	-6.14610200	6.69053500	1.89509600
H	-4.87655900	7.86649400	2.34838500
O	-1.43987300	0.61838900	-1.86329900
C	-0.81428100	0.29474100	-3.11786400
H	-1.42311400	-0.50068100	-3.54118300
H	-0.80100800	1.17842700	-3.75831100
H	0.19908200	-0.05655600	-2.91368800

2. DFT-computed enantio-determining transition state **TS2** in Figure 4.
(*Si,R*)-**TS2**

H	3.87900200	1.76879700	1.81054600
O	0.56160700	-0.21469800	-0.34872300
N	2.28430000	-1.32179300	-2.10413300
O	2.15687600	-3.09148800	0.03041000
N	1.89399700	0.00506700	-0.20641900
N	-0.11591200	-3.24155500	-0.16977100
H	-0.89571600	-3.06170700	-0.81368500
C	4.10212900	-0.13661500	-1.00403800
C	1.11665200	-2.89483900	-0.58800500
C	1.13690500	-2.25567600	-1.97785900
H	0.19288300	-1.74771600	-2.18341300
C	4.52864700	0.67990900	0.02549100
C	2.74738000	-0.52359200	-1.13020800
H	4.81057400	-0.50433400	-1.73405500
C	-0.39070500	-3.94970400	1.03864800
C	2.27533600	0.80751700	0.81845300
H	1.46101500	1.11515700	1.46437900
C	-1.01037800	-5.21185000	0.92128100
C	3.58250100	1.15543500	0.96963400
C	1.42601200	-3.31860000	-3.05171400
H	2.01878500	-4.13131000	-2.61806600
H	0.49346300	-3.72876900	-3.44372600
C	0.55749200	-2.02309400	2.45793600
H	0.60965400	-1.55740600	1.47314000
C	-0.10293200	-3.38226900	2.29176200
C	-1.22379000	-5.82505500	-0.45481700
H	-1.54885900	-5.03112800	-1.13656600
C	2.26558900	-2.56638600	-4.08218300
H	2.82690900	-3.22695400	-4.74477800
H	1.63339400	-1.91016100	-4.68809000
C	-1.35060100	-5.89405100	2.08827600
H	-1.83886000	-6.86078200	2.02401900
C	-0.43822500	-4.11941700	3.43383500
H	-0.21331500	-3.70611200	4.41343300
C	3.18274300	-1.73385700	-3.19682000
H	4.00408500	-2.34612500	-2.80118600
H	3.59674300	-0.85312400	-3.69327500
C	-1.06272800	-5.35459800	3.33940700
H	-1.32644800	-5.90146200	4.23968400
C	-0.25455500	-1.08841300	3.36057600
H	-1.26973300	-0.93629800	2.98801900

H	0.22662500	-0.10424900	3.40897900
H	-0.31603100	-1.46808400	4.38624300
C	1.98085900	-2.17950300	3.00716800
H	1.95926100	-2.60575300	4.01696700
H	2.47632500	-1.20372500	3.07043500
H	2.57456500	-2.82893800	2.36216900
C	0.11136800	-6.37899500	-0.97444500
H	0.90385200	-5.62552300	-0.93380400
H	0.01183800	-6.72182000	-2.00963900
H	0.43020800	-7.22909300	-0.36083500
C	-2.29636900	-6.91240600	-0.48694300
H	-1.98927900	-7.80394400	0.07019700
H	-2.47569000	-7.21942800	-1.52143700
H	-3.24380900	-6.55584000	-0.07161600
C	5.95945400	1.04139400	0.15488500
C	6.31957700	2.31431900	0.60433600
C	6.95473500	0.11706900	-0.17244700
C	7.66172400	2.68169000	0.72031400
H	5.53872100	3.03318400	0.83750500
C	8.30655800	0.44794000	-0.06082400
H	6.66472100	-0.88198800	-0.48617400
C	8.63467100	1.73392800	0.38331700
H	9.67885100	2.00423700	0.47187200
C	8.01609100	4.09296400	1.20271300
C	9.36909700	-0.60018600	-0.41092600
C	9.52924500	4.31542600	1.28404700
H	9.72734300	5.33256900	1.63550000
H	10.00362900	3.62184100	1.98593200
H	10.00951500	4.20115200	0.30688700
C	7.42562100	5.12569000	0.22836800
H	7.83037600	4.98728800	-0.77930800
H	6.33584000	5.04966600	0.16930400
H	7.67340300	6.13947900	0.56062700
C	7.41947000	4.31503600	2.60243800
H	7.82002200	3.58887700	3.31705600
H	7.66692600	5.32009000	2.96040000
H	6.32941200	4.22112900	2.59815000
C	9.21603400	-1.80877500	0.52760100
H	8.23191200	-2.27630700	0.42867000
H	9.97212600	-2.56519500	0.29143900
H	9.34567100	-1.50979000	1.57265100
C	9.17291100	-1.05816900	-1.86567200
H	9.92821000	-1.80650000	-2.12816800
H	8.18846100	-1.51050600	-2.01889300
H	9.27146300	-0.21527500	-2.55731000
C	10.79263100	-0.05370400	-0.26617600
H	10.96687300	0.80377400	-0.92438900
H	11.00795100	0.25063800	0.76321400
H	11.50935900	-0.83443900	-0.53837100
C	-0.05850300	0.86167500	-1.14273800
Cl	-2.45543700	-2.59312700	-2.36117600
O	0.60089700	1.83158200	-1.44675900
S	-2.55189300	0.70152700	0.74232800
O	-2.85159000	0.85229700	2.16951100
N	-2.31164100	-0.87957400	0.38553200
C	-3.99256600	1.25502900	-0.17030400
C	-4.07536000	0.96671300	-1.52914000
C	-4.97966800	1.98500000	0.48064700
C	-5.15821200	1.45139800	-2.25314900
H	-3.33544300	0.33081600	-2.00776000
C	-6.05748400	2.45703800	-0.26100700
H	-4.90075900	2.17587900	1.54542100
C	-6.15678700	2.20987800	-1.63405500
H	-5.23582500	1.22414600	-3.31257100
H	-6.83663300	3.03071500	0.23543400
C	-7.32631300	2.74866500	-2.41259700
H	-7.27901700	2.44848800	-3.46141300
H	-8.27001800	2.38551300	-1.99359300
H	-7.34437800	3.84263300	-2.36909900

N	-1.25157200	1.42851300	0.22562700
H	-2.17903600	-1.07353000	-0.62069900
C	-1.02917200	2.79331500	0.72886100
H	-0.07076200	3.07851400	0.28187000
H	-0.90702300	2.78022400	1.81818500
C	-3.20769900	-1.86285000	1.05292900
H	-2.98015900	-2.79926600	0.53576400
H	-2.88605300	-1.96451900	2.09200500
C	-4.68637200	-1.56162500	0.98813300
C	-5.36699100	-1.10607800	2.11200200
C	-5.38098000	-1.65548700	-0.22563700
C	-6.70762000	-0.72026200	2.04644200
H	-4.83698800	-1.02115300	3.05697300
C	-6.70456500	-1.26202300	-0.31357500
H	-4.85346900	-2.00692000	-1.11082800
C	-7.37137400	-0.77809000	0.82064700
H	-7.20634800	-0.36170400	2.93897200
H	-7.24595400	-1.30427100	-1.25345100
O	-8.65690000	-0.38394900	0.62440000
C	-9.34721600	0.16138900	1.73239300
H	-10.33790100	0.43560100	1.36901700
H	-9.45005800	-0.57067200	2.54155600
H	-8.84096200	1.05548800	2.11565100
C	-2.10172000	3.78922800	0.34956000
C	-2.39901800	4.01666600	-1.00101100
C	-2.86099600	4.43874400	1.31413000
C	-3.44844400	4.83760300	-1.36944900
H	-1.79986800	3.52053300	-1.76131000
C	-3.91380200	5.28998900	0.96340300
H	-2.64925300	4.26547500	2.36670600
C	-4.22047400	5.47215100	-0.38400100
H	-3.70242000	5.00265600	-2.41176300
H	-4.49133700	5.77629100	1.74059700
O	-5.24574900	6.23607600	-0.84347400
C	-6.06059700	6.87950000	0.11825400
H	-6.81834800	7.42716900	-0.44241400
H	-6.55147600	6.15227600	0.77586000
H	-5.48152700	7.58359300	0.72678200
O	-0.90992200	0.19539000	-1.95205200
C	-1.16101600	0.81944600	-3.21101700
H	-1.74182900	0.08907400	-3.77483900
H	-1.73319600	1.74307300	-3.08438000
H	-0.21863500	1.03474600	-3.71969700
(Si,S)-TS2			
H	-2.68825900	-2.05778100	0.88066900
O	-0.06665600	0.81664600	-1.22582000
N	-2.18419600	2.31294800	-1.95156900
O	-1.88655000	3.47935000	0.52821800
N	-1.30689600	0.47839200	-0.78968400
N	0.36611900	3.66342800	0.20162300
H	1.09721600	3.70248800	-0.52385200
C	-3.65131800	0.66843300	-0.91800500
C	-0.90305300	3.46847700	-0.20602600
C	-1.07788900	3.27520500	-1.71477700
H	-0.15270000	2.95117300	-2.19192700
C	-3.79018300	-0.48495500	-0.17194900
C	-2.37842700	1.19773500	-1.23452100
H	-4.52589600	1.19645400	-1.27407800
C	0.68861200	4.04661000	1.53904300
C	-1.40526800	-0.66654400	-0.06758800
H	-0.44948300	-1.11187700	0.18345400
C	1.22600300	5.33367400	1.74392000
C	-2.62495100	-1.16453300	0.27260500
C	-1.59971300	4.57834100	-2.35182200
H	-2.09258400	5.19004700	-1.58933300
H	-0.77637600	5.14869100	-2.78522700
C	-0.08183500	1.75837300	2.41648700
H	-0.11840100	1.55871400	1.34024300

C	0.47073600	3.16138000	2.60698500
C	1.34792000	6.29901700	0.57559000
H	1.64729600	5.72902700	-0.31025200
C	-2.63733400	4.10270300	-3.36821200
H	-3.34063700	4.88476900	-3.65875300
H	-2.14890500	3.71183900	-4.26562000
C	1.55384400	5.71513900	3.04415500
H	1.97703600	6.69782500	3.22527400
C	0.78824600	3.59944700	3.89761600
H	0.61367700	2.93592700	4.74038300
C	-3.32040100	2.96787600	-2.61738800
H	-4.02600500	3.35979500	-1.87232500
H	-3.83473200	2.25434700	-3.26538200
C	1.33007400	4.85750500	4.11794300
H	1.57890900	5.17378400	5.12649500
C	0.82791300	0.70431700	3.05788700
H	1.85646000	0.77560900	2.69147400
H	0.44886000	-0.30006500	2.83288200
H	0.84895300	0.80477500	4.14805300
C	-1.49946300	1.63288300	2.98714300
H	-1.48758400	1.78213300	4.07304000
H	-1.90144000	0.63142500	2.79447200
H	-2.16480100	2.36986300	2.53651300
C	-0.02810400	6.92160400	0.29499200
H	-0.80114700	6.15509900	0.18262600
H	-0.00193000	7.52374600	-0.61922000
H	-0.32511900	7.57125500	1.12625400
C	2.39248600	7.39421200	0.78539700
H	2.09610900	8.09610900	1.57228900
H	2.50986800	7.96960500	-0.13757900
H	3.36826600	6.97484900	1.04826300
C	-5.13425200	-1.00314700	0.17270300
C	-5.35972300	-2.38124200	0.22240000
C	-6.18393400	-0.12161900	0.44277800
C	-6.62348700	-2.89175000	0.52529000
H	-4.54360300	-3.06028100	-0.00945900
C	-7.45876800	-0.59730900	0.75562000
H	-5.99035700	0.94749200	0.43758000
C	-7.65460100	-1.98272900	0.78803800
H	-8.63846400	-2.36502300	1.02707700
C	-6.83358700	-4.41006600	0.55618600
C	-8.58019100	0.40292200	1.05929800
C	-8.27796700	-4.78912500	0.89635100
H	-8.37413200	-5.87910200	0.90467000
H	-8.57228000	-4.42115700	1.88462800
H	-8.98442400	-4.39791500	0.15709800
C	-6.48966800	-4.99993300	-0.82158800
H	-7.12898000	-4.57143400	-1.60003000
H	-5.44786600	-4.80938100	-1.09571500
H	-6.64080700	-6.08466100	-0.81319700
C	-5.90850900	-5.02713000	1.61837600
H	-6.13117800	-4.62377300	2.61146800
H	-6.04587800	-6.11321000	1.65105300
H	-4.85459600	-4.82945700	1.40048500
C	-8.19435000	1.23640300	2.29266100
H	-7.26967600	1.79780100	2.12912500
H	-8.98770500	1.95575700	2.52217700
H	-8.05092600	0.59430000	3.16763100
C	-8.76878000	1.33765600	-0.14707500
H	-9.56986000	2.05591700	0.05718100
H	-7.85966500	1.90565300	-0.36612800
H	-9.03908000	0.76936300	-1.04292400
C	-9.91578700	-0.29116000	1.34314500
H	-10.25094300	-0.88969400	0.48972800
H	-9.85674400	-0.94276200	2.22096300
H	-10.68156700	0.46488300	1.54146600
C	0.16220300	0.20921300	-2.56929200
S	2.91940700	-0.76417400	-1.71774300
O	3.90788000	-1.14128300	-2.73685800

N	1.38342900	-1.04443500	-2.07335700
C	3.30244200	-1.64700600	-0.21531800
C	2.50598200	-1.41106600	0.90124000
C	4.35170500	-2.55207600	-0.19375700
C	2.78622800	-2.09414100	2.07538800
H	1.70433500	-0.67920800	0.84884900
C	4.61402000	-3.23231100	0.99398500
H	4.95148500	-2.71365300	-1.08294600
C	3.84802600	-3.00769500	2.13970600
H	2.18877500	-1.90548100	2.96349100
H	5.43525000	-3.94325600	1.02927300
C	4.19158500	-3.69019000	3.43580800
H	4.72057500	-4.63039000	3.26266400
H	4.84814600	-3.04740100	4.03325700
H	3.29753400	-3.89417400	4.03057200
N	2.98013000	0.81309800	-1.24928000
C	4.35363700	1.39634100	-1.23827900
H	4.17186000	2.44916100	-1.01395700
H	4.79662700	1.34073100	-2.23837700
C	1.19036400	-2.31357000	-2.81861200
H	0.11333600	-2.34415600	-2.99324600
H	1.68502800	-2.26633900	-3.79649600
C	1.65414400	-3.54522600	-2.07852700
C	2.70263400	-4.32418400	-2.57432600
C	1.08768600	-3.89929400	-0.85531900
C	3.17930400	-5.41764900	-1.86466500
H	3.16484100	-4.05561200	-3.52073200
C	1.56019900	-4.98166600	-0.11909000
H	0.27420600	-3.29862500	-0.45305900
C	2.62087700	-5.74152900	-0.62475800
H	3.99820900	-6.02276200	-2.23988300
H	1.10946200	-5.21852000	0.83737300
O	3.17457400	-6.80113800	0.01855300
C	2.64626500	-7.14545100	1.28588300
H	3.23049200	-7.99589500	1.63761200
H	2.74562300	-6.31759400	1.99811800
H	1.59184800	-7.43628400	1.21398700
C	5.26322500	0.75092400	-0.22806600
C	4.94575700	0.78686900	1.13655000
C	6.40681000	0.06972200	-0.62657000
C	5.72786700	0.12435700	2.06403600
H	4.05637700	1.32269700	1.46066500
C	7.22036000	-0.59253100	0.29680700
H	6.66213300	0.02894400	-1.68240100
C	6.86481300	-0.58323500	1.64489200
H	5.47885100	0.12646500	3.12069200
H	8.10005000	-1.12270900	-0.04793000
O	7.54572600	-1.23210600	2.62457600
C	8.68672900	-1.97707700	2.24108900
H	9.07768000	-2.42629200	3.15416900
H	8.42424300	-2.76967000	1.53037900
H	9.45469400	-1.33291600	1.79793700
Cl	2.39892200	3.94312200	-2.27542900
H	2.35397100	1.41029700	-1.81156500
O	-0.75570700	-0.38180700	-3.10472400
O	0.91650500	1.17688700	-3.15860600
C	1.35234700	0.87292600	-4.47977100
H	1.81513600	1.78583200	-4.85205200
H	2.09319700	0.06448300	-4.46275400
H	0.50264000	0.58796400	-5.10415700
(Re,R)-TS2			
H	3.91802900	-1.83054800	-1.74574000
O	0.55909500	0.22565800	0.28016400
N	2.27166100	1.46492800	1.97130600
O	2.09953300	3.01327400	-0.31132500
N	1.89872300	0.00690200	0.16909800
N	-0.15538800	3.28873600	-0.04712300
H	-0.91353600	3.20926500	0.64485000

C	4.10090100	0.21191200	0.97239400
C	1.07396400	2.91008300	0.35363100
C	1.11085300	2.37059900	1.78413000
H	0.17586400	1.86425200	2.03405400
C	4.54187500	-0.65763900	-0.00473800
C	2.74301600	0.60617800	1.05870600
H	4.79825700	0.62172800	1.69059400
C	-0.42671400	3.95682900	-1.27902100
C	2.29805400	-0.83617500	-0.81601400
H	1.49354100	-1.18401000	-1.45341900
C	-0.93696900	5.27050900	-1.20814300
C	3.60798300	-1.18153700	-0.93729500
C	1.38876900	3.50904300	2.78052800
H	1.97894200	4.29352600	2.29400500
H	0.44855100	3.93505500	3.13554200
C	0.31217900	1.89320300	-2.62329100
H	0.34277400	1.46731900	-1.61792700
C	-0.22805500	3.30960000	-2.51016700
C	-1.04848600	5.96799800	0.13898200
H	-1.39407200	5.23502300	0.87605500
C	2.22538300	2.83521900	3.86553800
H	2.77807400	3.54286700	4.48551300
H	1.59141500	2.21843900	4.50936800
C	-1.25570300	5.92312500	-2.39789900
H	-1.65823900	6.93031400	-2.36813700
C	-0.53871800	4.01613300	-3.67818100
H	-0.38180300	3.53849100	-4.64162800
C	3.15516800	1.94927600	3.04723200
H	3.98068500	2.53552800	2.62236200
H	3.56443300	1.10368200	3.60528900
C	-1.05355100	5.30334600	-3.62825900
H	-1.29900800	5.82774600	-4.54694900
C	-0.59416400	0.99701500	-3.47381100
H	-1.61688200	0.96624200	-3.09199200
H	-0.21407300	-0.03131700	-3.46910600
H	-0.62322400	1.32810200	-4.51765500
C	1.73153800	1.90212900	-3.20585700
H	1.72437700	2.30325600	-4.22619400
H	2.13310100	0.88330500	-3.25573100
H	2.39822500	2.50994300	-2.59221000
C	0.34303700	6.45626900	0.56919100
H	1.08364100	5.65199000	0.52448500
H	0.31781000	6.84807400	1.59150800
H	0.68346100	7.25715400	-0.09708300
C	-2.04406300	7.12679100	0.15550600
H	-1.70363100	7.96647500	-0.45994400
H	-2.15755500	7.49700900	1.17863800
H	-3.03021400	6.81519400	-0.20173200
C	5.97292900	-1.03098200	-0.09264400
C	6.33302000	-2.32385500	-0.48180900
C	6.96865100	-0.10086700	0.21661500
C	7.67427500	-2.70523300	-0.55394400
H	5.55252600	-3.04709800	-0.70289800
C	8.31985800	-0.44576300	0.14818100
H	6.68053600	0.91269500	0.48193400
C	8.64730000	-1.75133600	-0.23538300
H	9.69090500	-2.03253000	-0.29020900
C	8.02741500	-4.13800800	-0.96935200
C	9.38311800	0.60780500	0.47924300
C	9.53999900	-4.37604900	-1.00265500
H	9.73769600	-5.40846200	-1.30654200
H	10.03823300	-3.71604300	-1.72015500
H	9.99638600	-4.22519100	-0.01898900
C	7.40328600	-5.12465400	0.03133100
H	7.78489800	-4.94876600	1.04220800
H	6.31318100	-5.03609400	0.06006900
H	7.64874600	-6.15344100	-0.25307600
C	7.46387500	-4.41289500	-2.37341200
H	7.88839600	-3.71978000	-3.10670900

H	7.71117600	-5.43370900	-2.68368600
H	6.37488000	-4.30997700	-2.40018300
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C	9.16092600	1.12269500	1.91109400
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H	11.03800600	-0.30184700	-0.62636400
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H	-5.16926100	1.11139300	-2.63995000
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O	-5.45888900	-6.24259000	-0.10558700
C	-6.26243900	-6.57134700	-1.22389900
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C	0.35169000	-2.40376100	2.69407700
H	-0.71896200	-2.61328300	2.73958400
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H	0.63435500	-1.79629100	3.55677400
(Re,S)-TS2			
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O	2.25626000	3.41532900	-0.30686000
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C	1.21233000	3.27269100	1.84214800
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O	-1.13916700	1.20140200	3.30034400
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H	0.79098800	0.75690700	4.98024500

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