Supporting Information for

Synthesis of Axially Chiral Vinyl Halides via Cu(I)-Catalyzed Enantioselective Radical 1,2-Halofunctionalization of Terminal Alkynes

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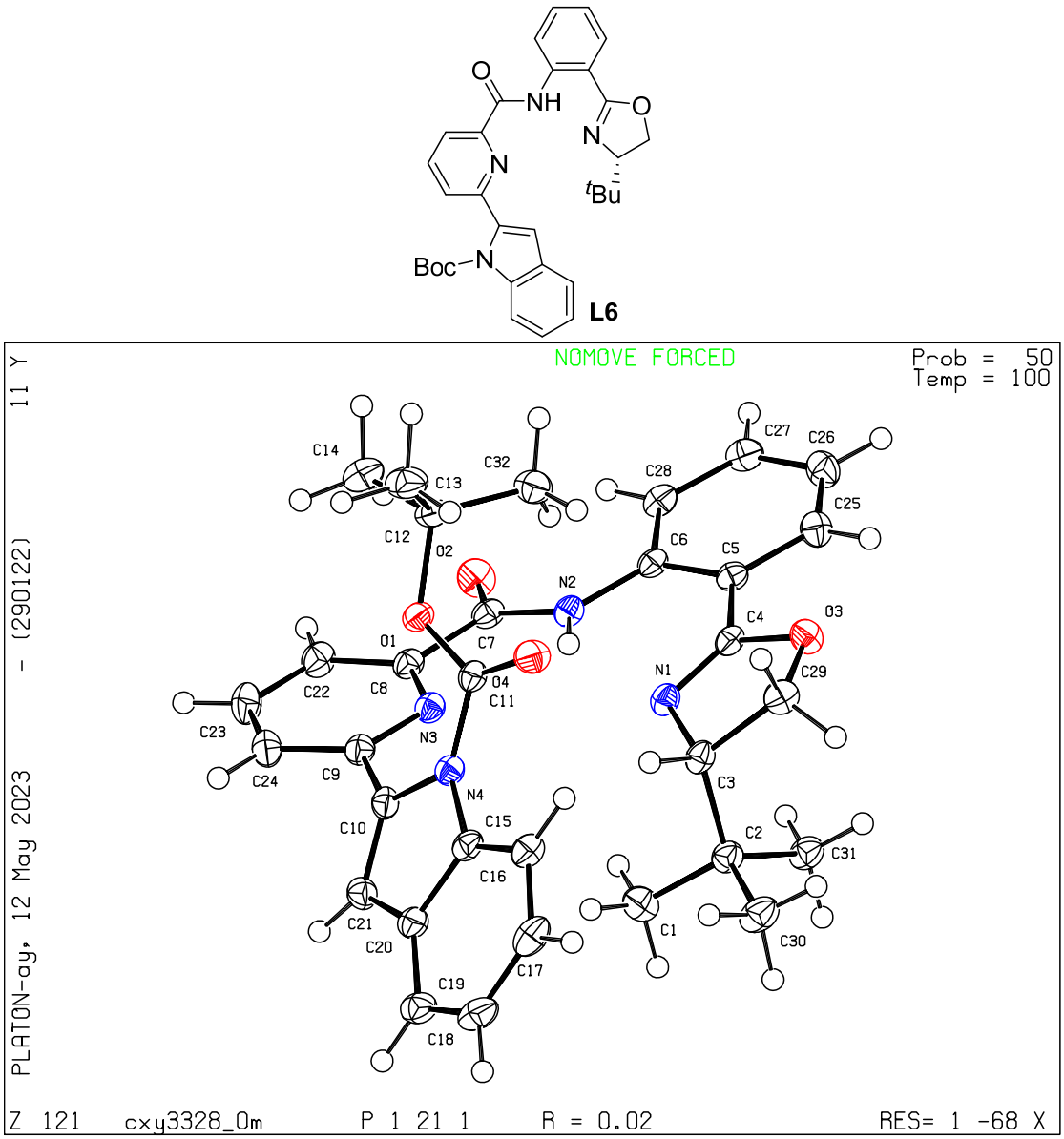


Figure S1. The X-ray structure of **L6** (CCDC 2259801, 50% probability ellipsoids). Boc, *tert*-butoxycarbonyl; ^{t}Bu, *tert*-butyl.

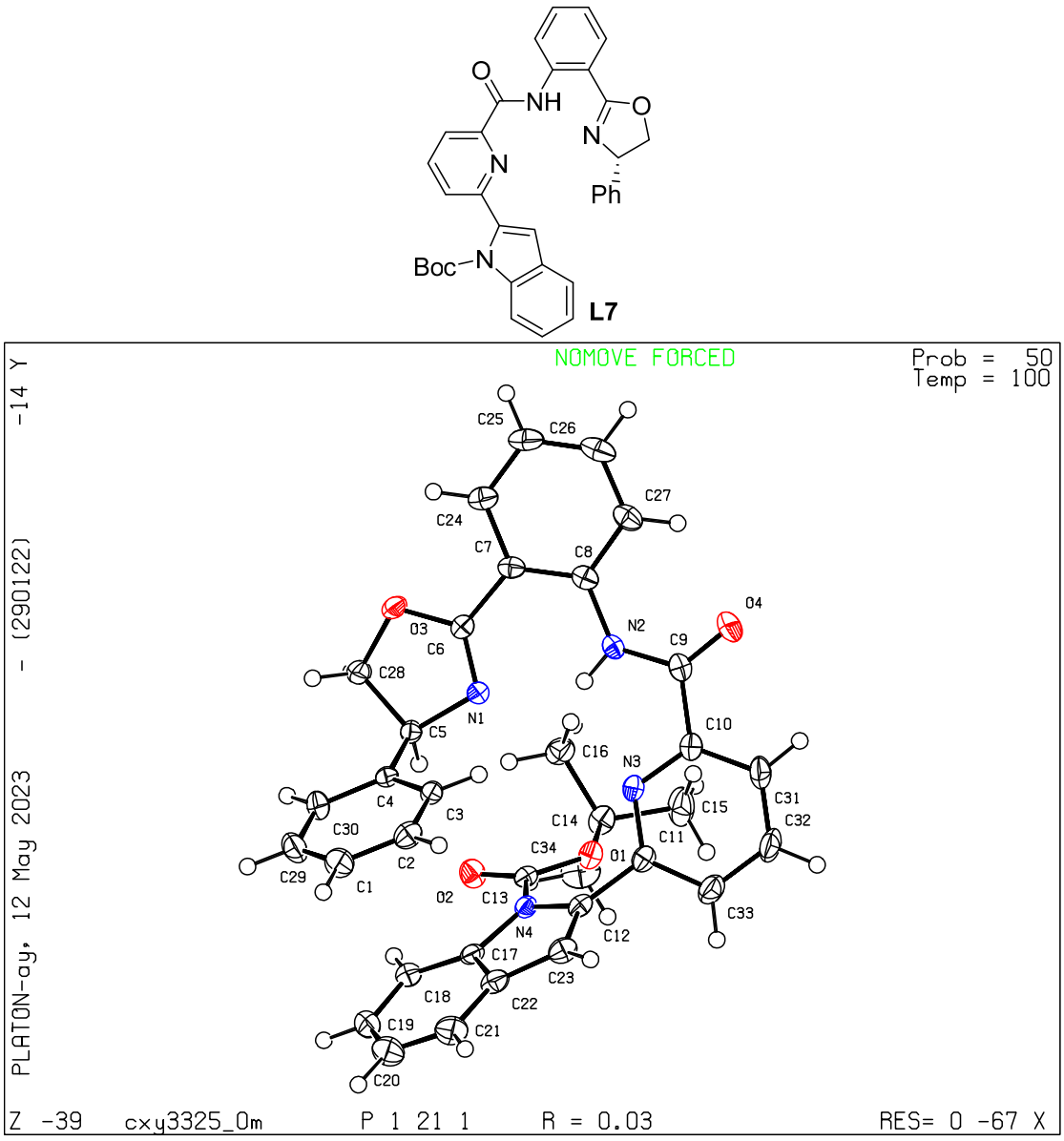
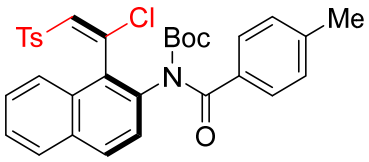


Figure S2. The X-ray structure of **L7** (CCDC 2259802, 50% probability ellipsoids). Ph, phenyl.



N1

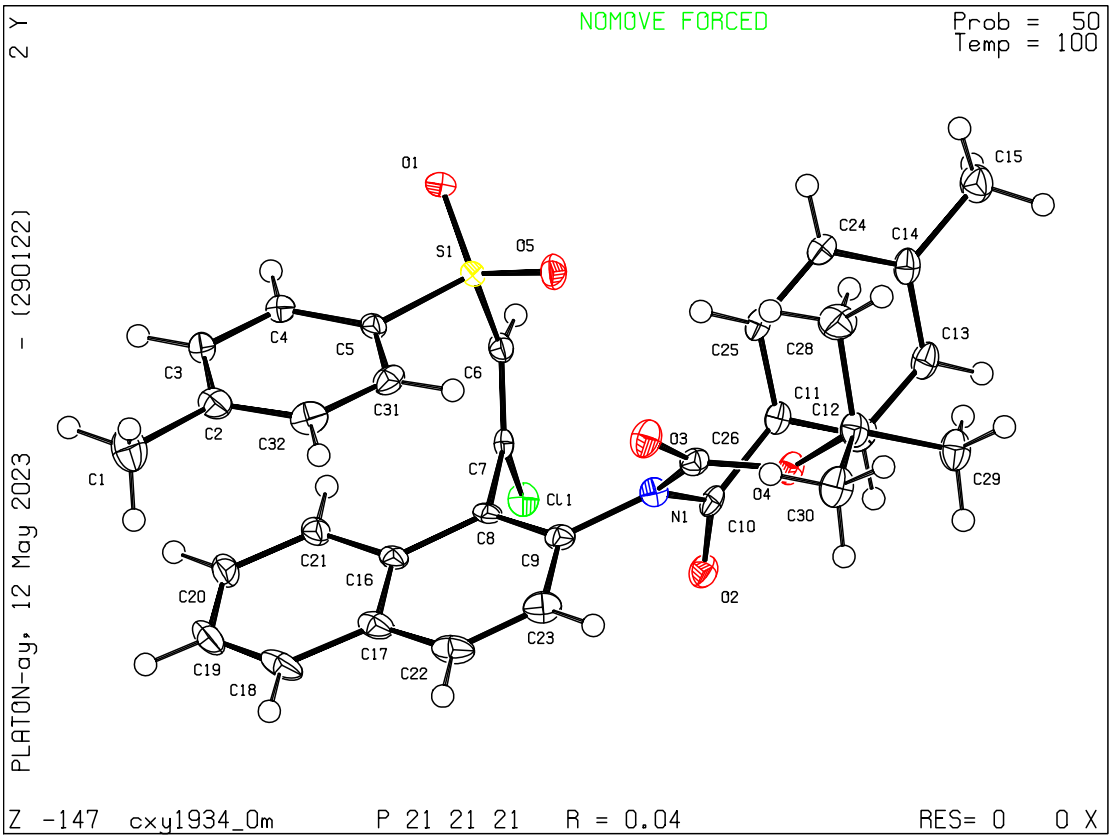


Figure S3. The X-ray structure of product **N1** (CCDC 2259803, 50% probability ellipsoids). Ts, *p*-methylbenzenesulfonyl.

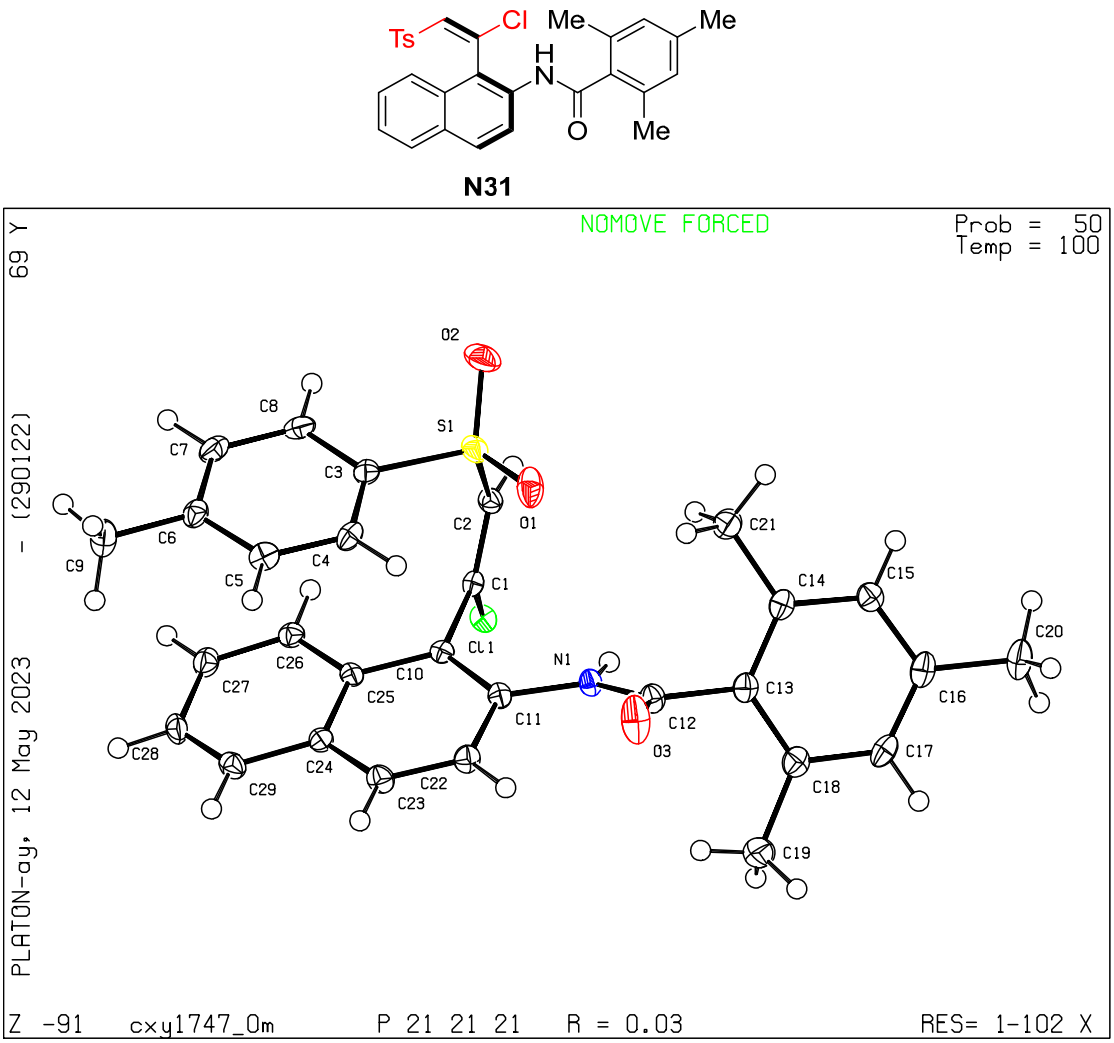
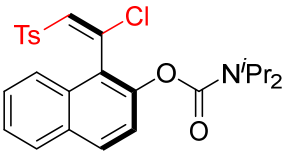


Figure S4. The X-ray structure of product **N31** (CCDC 2259804, 50% probability ellipsoids).



O1

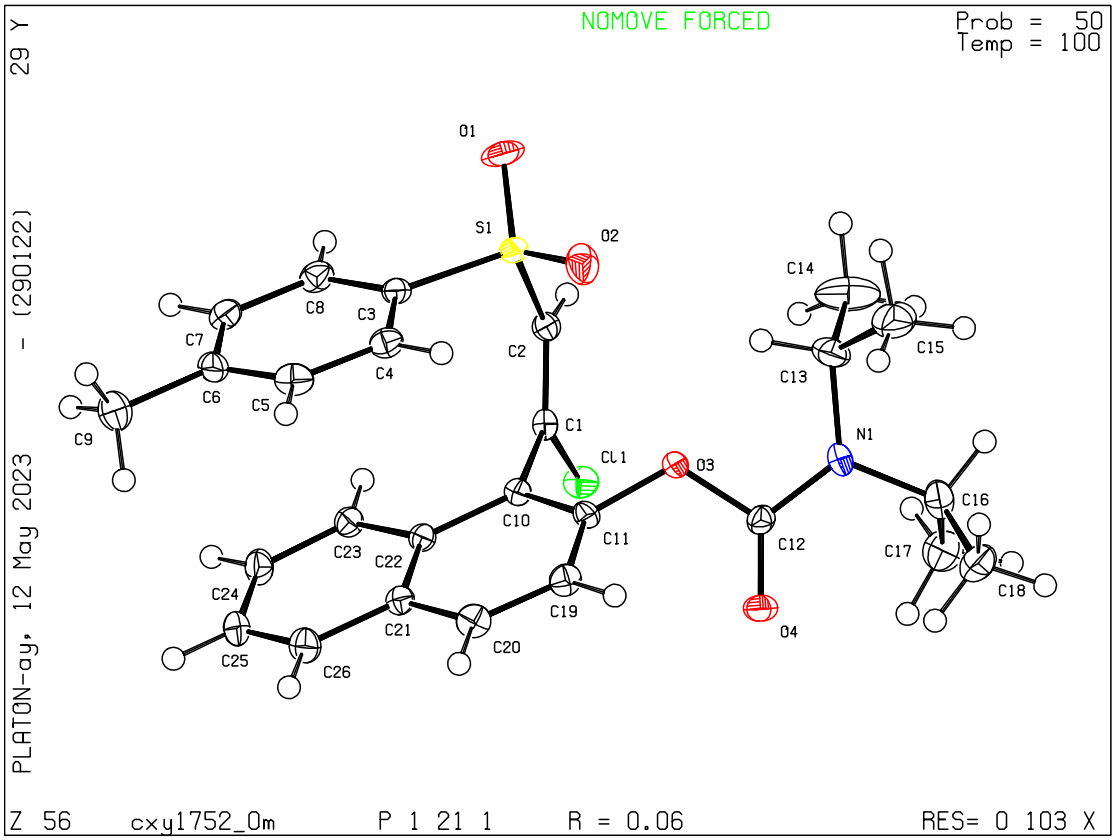


Figure S5. The X-ray structure of product **O1** (CCDC 2259805, 50% probability ellipsoids). ^{i}Pr, isopropyl.

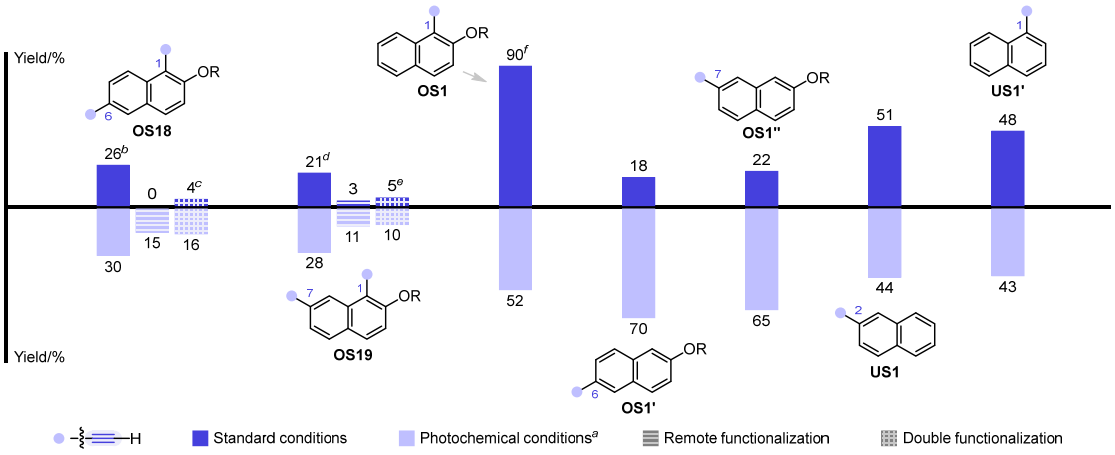
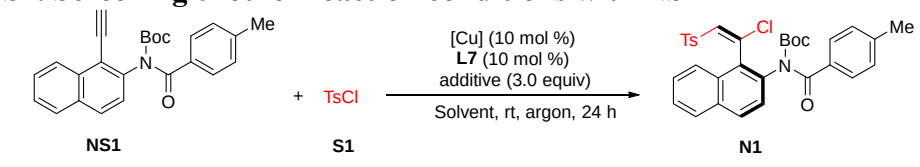
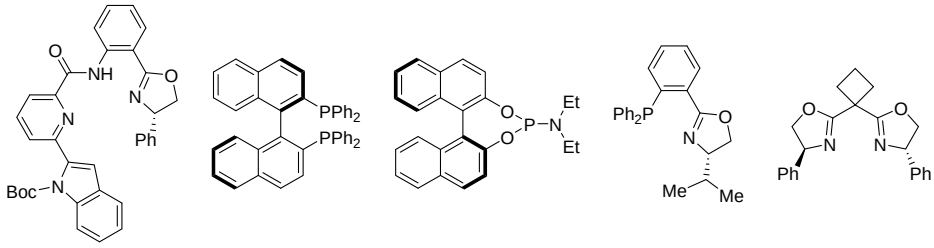


Figure S6. The results of bis- and mono-alkyne substrates. R = C(O)N^{i}Pr$_2$. [a][Cu(MeCN)$_4$]BF$_4$ (5.0 mol %), 2,9-dimethylphenanthroline (10 mol %), blue LEDs (light-emitting diodes, 450 nm), $CHCl_3$, rt, argon, 4 d. [b]90% ee. [c]88%. [d]54% ee. [e]35% ee. [f]92% ee. Rt, room temperature; Ee, enantiomeric excess.

Table S1. Screening of other reaction conditions with NS1[a]



NS1 S1 N1

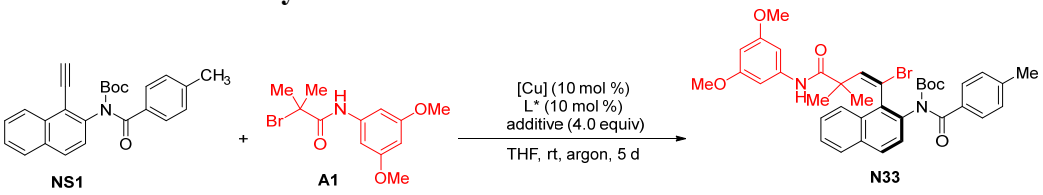


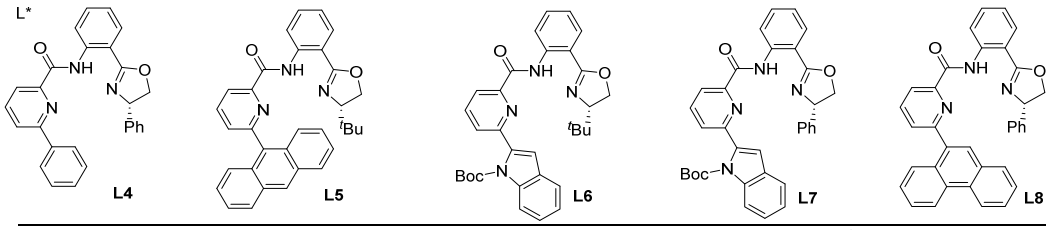
L7 L9 L10 L11 L12

Entry	[Cu]	ligand	Additive	Solvent	Yield (%)[b]	Ee (%)[c]
1	$Cu(CH_3CN)_4PF_6$	**L9**	K_3PO_4	DME	Trace	N.d.
2	$Cu(CH_3CN)_4PF_6$	**L10**	K_3PO_4	DME	0	N.d.
3	$Cu(CH_3CN)_4PF_6$	**L11**	K_3PO_4	DME	0	N.d.
4	$Cu(CH_3CN)_4PF_6$	**L12**	K_3PO_4	DME	0	N.d.
5	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	1,4-Dioxane	50	92
6	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	THF	55	94
7	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	PhCl	0	N.d.
8	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DMF	0	N.d.
9	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	CH_3CN	0	N.d.
10	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	MTBE	84	90
11	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DCM	65	92
12	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	Toluene	50	92
13[d]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DME/MTBE	73	94
14[e]	$Cu(CH_3CN)_4PF_6$	**L7**	Na_3PO_4	DME/MTBE	65	91
16[e]	$Cu(CH_3CN)_4PF_6$	**L7**	Li_3PO_4	DME/MTBE	60	92
16[e]	$Cu(CH_3CN)_4PF_6$	**L7**	K_2CO_3	DME/MTBE	55	92
17[e]	$Cu(CH_3CN)_4PF_6$	**L7**	^{t}BuOK	DME/MTBE	0	N.d.
18[e]	$Cu(CH_3CN)_4BF_4$	**L7**	K_3PO_4	DME/MTBE	60	93
19[e]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DME/MTBE	78	93
20[e]	CuCl	**L7**	K_3PO_4	DME/MTBE	75	90
21[e]	CuCN	**L7**	K_3PO_4	DME/MTBE	0	N.d.
22[e]	$CuCF_3{\cdot}PPh_3{\cdot}$Phen	**L7**	K_3PO_4	DME/MTBE	0	N.d.
23[e,f]	$Cu(CH_3CN)_4PF_6$	**L7**	–	DME/MTBE	10	93
24[e,g]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DME/MTBE	24	93
25[e,h]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DME/MTBE	30	93
26[e,i]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DME/MTBE	43	93
27[e,j]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DME/MTBE	51	92

[a]Reaction conditions: **NS1** (19.3 mg, 0.050 mmol, 1.0 equiv), **S1** (14.3 mg, 0.075 mmol, 1.5 equiv), [Cu] (10 mol %), **L7** (2.79 mg, 10 mol %), additive (0.15 mmol, 3.0 equiv) in dry solvent (1.0 mL) at rt for 24 h under argon. [b]Yield based on ^{1}H NMR (nuclear magnetic resonance) analysis of the crude product using CH_2Br_2 as an internal standard. [c]Ee values based on HPLC (high-performance liquid chromatography) analysis. [d]DME/MTBE = 1/1. [e]DME/MTBE = 1/3. [f]Without K_3PO_4. [g]K_3PO_4 (0.5 equiv). [h]K_3PO_4 (1.0 equiv). [i]K_3PO_4 (2.0 equiv). [j]K_3PO_4 (4.0 equiv). THF, tetrahydrofuran; DMF, *N*,*N*-dimethylformamide; MTBE, methyl *tert*-butyl ether; DCM, dichloromethane; DME, dimethoxyethane; Phen, 1,10-phenanthroline.

Table S2. Screening of reaction conditions for asymmetric bromide atom Transfer radical addition of alkyne[a]

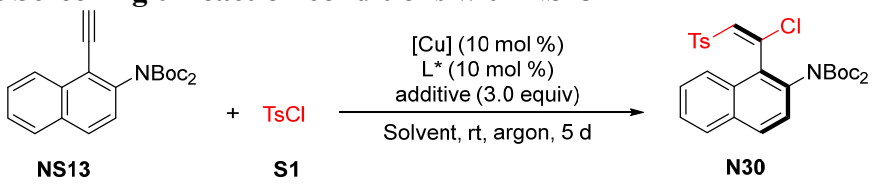




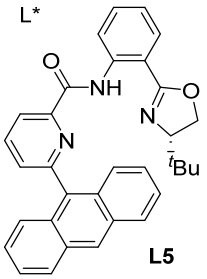
Entry	[Cu]	L*	Additive	Yield(%)[b]	Ee(%)[c]
1	$Cu(CH_3CN)_4PF_6$	**L4**	K_3PO_4	23	46
2	$Cu(CH_3CN)_4PF_6$	**L5**	K_3PO_4	0	N.d.
3	$Cu(CH_3CN)_4PF_6$	**L6**	K_3PO_4	0	N.d.
4	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	53	80
5	$Cu(CH_3CN)_4PF_6$	**L8**	K_3PO_4	Trace	N.d.
6	CuCN	**L7**	K_3PO_4	60	81
7	CuTc	**L7**	K_3PO_4	0	N.d.
8	$CuBH_4(PPh_3)_2$	**L7**	K_3PO_4	70	75
9	$CuCF_3PPh_3$•Phen	**L7**	K_3PO_4	60	20
10	$CuBr•CH_3SCH_3$	**L7**	K_3PO_4	10	73
11	CuBr	**L7**	K_3PO_4	64	87
12	CuBr	**L7**	Na_3PO_4	56	83
13	CuBr	**L7**	Li_3PO_4	0	N.d.
14	CuBr	**L7**	$(^tBuO)_2Mg$	70	83
15[d]	CuBr	**L7**	K_3PO_4	21	88
16[d]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	13	90

[a]Reaction conditions: **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv), **A1** (90.7 mg, 0.30 mmol, 1.5 equiv), [Cu] (10 mol %), **L*** (10 mol %), additive (4.0 equiv) in dry THF (4.0 mL) at rt for 5 d under argon. [b]Isolated yield. [c]Ee values based on HPLC analysis. [d]Conducted at 0 °C. Me, methyl; Tc, thiophene-2-carboxylate; N,d., not determined.

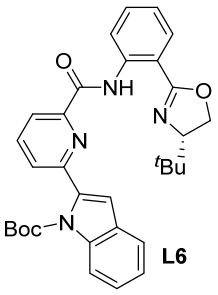
Table S3. Screening of reaction conditions with NS13[a]



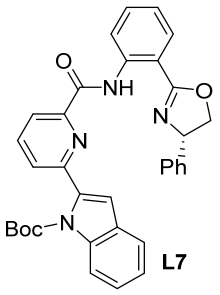
NS13 **S1** **N30**



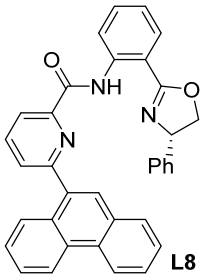
L5



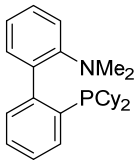
L6



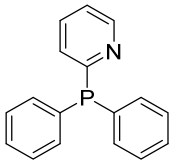
L7



L8



L9-rac

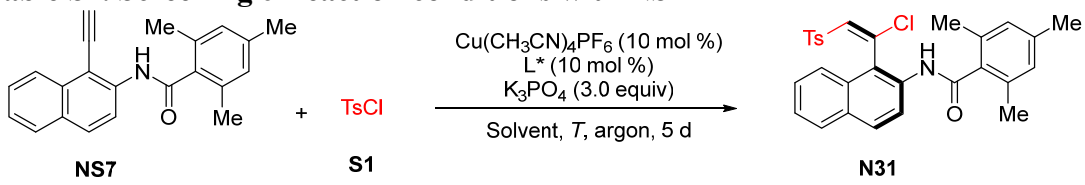


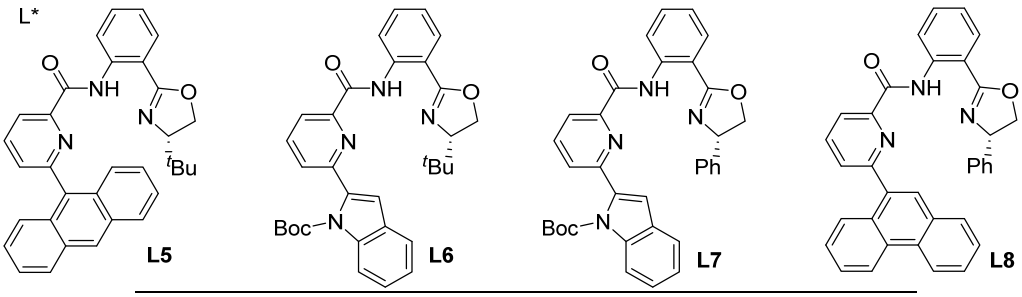
L10-rac

Entry	[Cu]	L*	Solvent	Yield (%)[b]	Ee (%)[c]
1	$Cu(CH_3CN)_4PF_6$	**L5**	DCM	35	82
2	$Cu(CH_3CN)_4PF_6$	**L6**	DCM	0	N.d.
3	$Cu(CH_3CN)_4PF_6$	**L7**	DCM	0	N.d.
4	$Cu(CH_3CN)_4PF_6$	**L8**	DCM	62	86
5	$Cu(CH_3CN)_4PF_6$	**L8**	Toluene	60	86
6	$Cu(CH_3CN)_4PF_6$	**L8**	EtOAc	50	86
7	$Cu(CH_3CN)_4PF_6$	**L8**	1,4-Dioxane	45	86
8	$Cu(CH_3CN)_4PF_6$	**L8**	DME	56	88
9	$Cu(CH_3CN)_4PF_6$	**L8**	THF	70	87
10	$Cu(CH_3CN)_4BF_4$	**L8**	THF	68	86
11	CuCN	**L8**	THF	0	N.d.
12	CuCl	**L8**	THF	80	88
13[d]	CuCl	**L8**	THF	26	92
14[d,e]	CuCl	**L8**	THF	22	92
15[d,f]	CuCl	**L8**	THF	67	90

[a]Reaction conditions: **NS13** (73.5 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), [Cu] (10 mol %), **L*** (10 mol %), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv) in dry solvent (4.0 mL) at rt for 5 d under argon. [b]Isolated yield. [c]Ee values based on HPLC analysis. [d]Conducted at 0 °C. [e]10 mol % **L9-rac** as additional additive. [f]10 mol % **L10-rac** as additional additive. Cy, cyclohexyl; Et, ethyl; Ac, acetyl.

Table S4. Screening of reaction conditions with NS7[a]

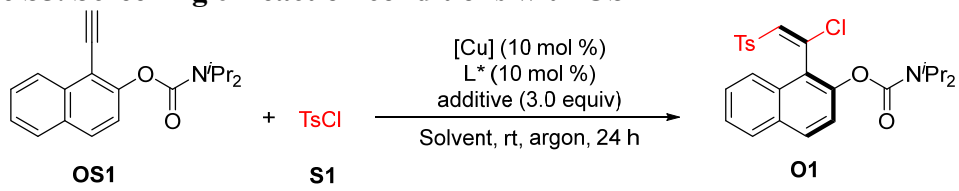


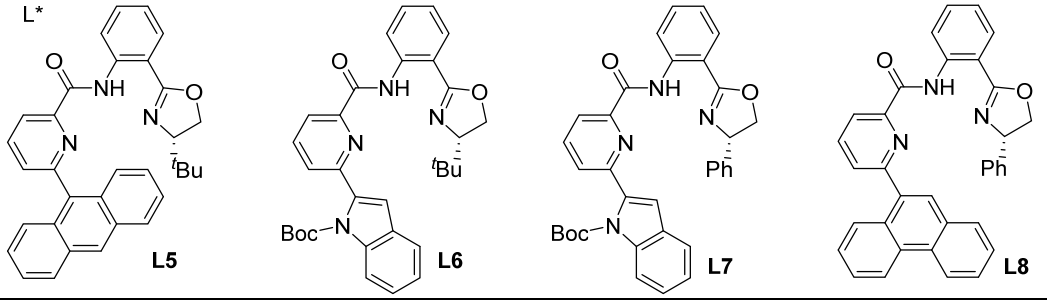


Entry	L*	Solvent	Yield (%)[b]	Ee (%)[c]
1	**L5**	DCM	0	N.d.
2	**L6**	DCM	88	81
3	**L7**	DCM	70	73
4	**L8**	DCM	73	66
5	**L6**	Toluene	65	84
6	**L6**	DME	60	80
7	**L6**	EtOAc	45	80
8[d]	**L6**	DCM/toluene	93	82
9[d,e]	**L6**	DCM/toluene	85	82
10[d,f]	**L6**	DCM/toluene	80	86

[a]Reaction conditions: **NS7** (62.7 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (7.45 mg, 10 mol %), **L*** (10 mol %), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv) in dry solvent (4.0 mL) at rt for 5 d under argon. [b]Isolated yield. [c]Ee values based on HPLC analysis. [d]DCM/toluene = 1/3. [e]Conducted at 0 °C. [f]Conducted at −10 °C. *T*, reaction temperature.

Table S5. Screening of reaction conditions with OS1[a]

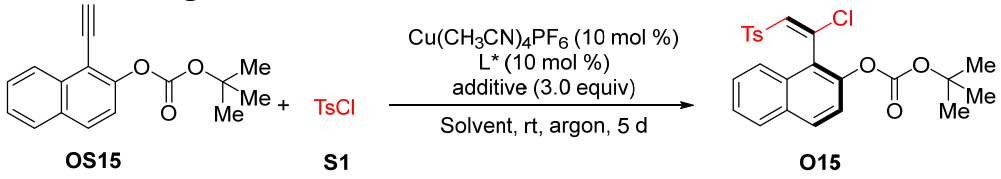


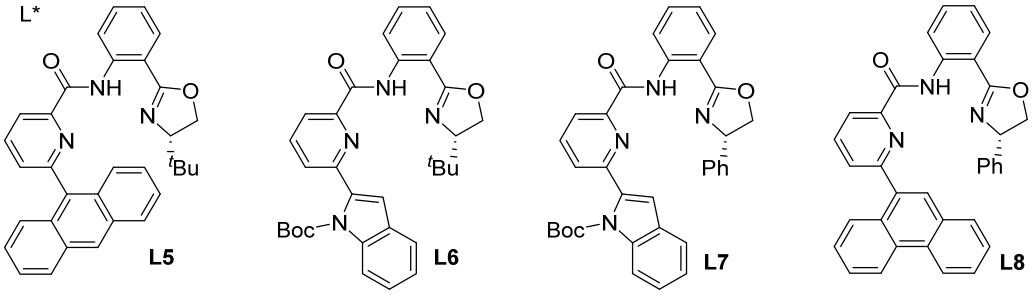


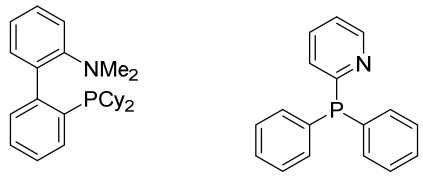
Entry	[Cu]	L*	Additive	Solvent	Yield (%)[b]	Ee (%)[c]
1	$Cu(CH_3CN)_4PF_6$	**L5**	K_3PO_4	DME	60	67
2	$Cu(CH_3CN)_4PF_6$	**L6**	K_3PO_4	DME	40	88
3	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DME	46	92
4	$Cu(CH_3CN)_4PF_6$	**L8**	K_3PO_4	DME	50	77
5	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	THF	61	90
6	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	MTBE	65	89
7	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	Toluene	50	89
8	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	DCM	26	89
9	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	EtOAc	84	92
10	$Cu(CH_3CN)_4BF_4$	**L7**	K_3PO_4	EtOAc	75	92
11	CuCN	**L7**	K_3PO_4	EtOAc	60	90
12	$CuCF_3{\cdot}PPh_3{\cdot}$Phen	**L7**	K_3PO_4	EtOAc	0	N.d.
13	$Cu(CH_3CN)_4PF_6$	**L7**	K_2CO_3	EtOAc	65	92
14	$Cu(CH_3CN)_4PF_6$	**L7**	^{t}BuOK	EtOAc	0	N.d.
15[d]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	EtOAc	90	92
16[e,f]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	EtOAc	59	80
17[e,g]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	EtOAc	45	85
18[e,h]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	EtOAc	40	90
19[e,i]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	EtOAc	39	92
20[e,j]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	EtOAc	35	91
21[e,k]	$Cu(CH_3CN)_4PF_6$	**L7**	K_3PO_4	EtOAc	29	92

[a]Reaction conditions: **OS1** (14.8 mg, 0.050 mmol, 1.0 equiv), **S1** (14.3 mg, 0.075 mmol, 1.5 equiv), [Cu] (10 mol %), **L*** (10 mol %), additive (0.15 mmol, 3.0 equiv) in dry solvent (1.0 mL) at rt for 24 h under argon. [b]Yield based on ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard. [c]Ee values based on HPLC analysis. [d]**OS1** (59.2 mg, 0.20 mmol, 1.0 equiv), **S1** (14.3 mg, 0.30 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (10 mol %), **L7** (10 mol %), K_3PO_4 (0.60 mmol, 3.0 equiv) in dry EtOAc (4.0 mL) at rt for 5 d under argon. [e]**OS1** (59.2 mg, 0.20 mmol, 1.0 equiv), **S1** (14.3 mg, 0.30 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (10 mol %), **L7** (10 mol %), K_3PO_4 (0.60 mmol, 3.0 equiv) in dry EtOAc at rt for 24 h under argon. [f]EtOAc (1.0 mL). [g]EtOAc (2.0 mL). [h]EtOAc (3.0 mL). [i]EtOAc (4.0 mL). [j]EtOAc (4.0 mL), 4Å MS (50 mg). [k]EtOAc (4.0 mL), H_2O (1.0 equiv).

Table S6. Screening of reaction conditions with OS15[a]



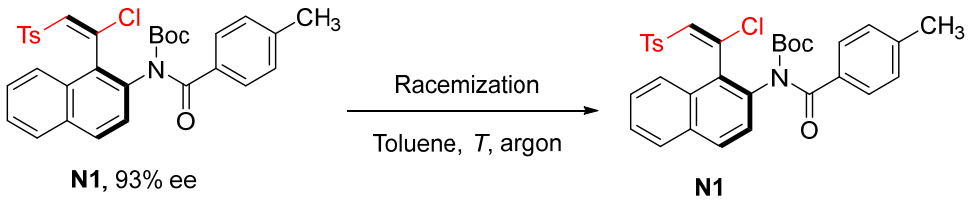




Entry	L*	Solvent	Yield (%)[b]	Ee (%)[c]
1	**L5**	DCM	35	55
2	**L6**	DCM	40	86
3	**L7**	DCM	33	82
4	**L8**	DCM	39	68
5	**L6**	Toluene	62	87
6	**L6**	EtOAc	56	87
7	**L6**	1,4-Dioxane	Trace	N.d.
8	**L6**	DME	81	87
9	**L6**	THF	80	86
10[d]	**L6**	DME	24	90
11[d,e]	**L6**	DME	22	92
12[d,f]	**L6**	DME	44	91

[a]Reaction conditions: **OS15** (53.6 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (7.45 mg, 10 mol %), **L*** (10 mol %), K_3PO_4 (127. 4 mg, 0.60 mmol, 3.0 equiv) in dry solvent (4.0 mL) at rt for 5 d under argon. [b]Isolated yield. [c]Ee values based on HPLC analysis. [d]Conducted at 0 °C. [e]10 mol % **L9-rac** as additional additive. [f]10 mol % **L10-rac** as additional additive.

Table S7. Racemization experiments with N1[a]



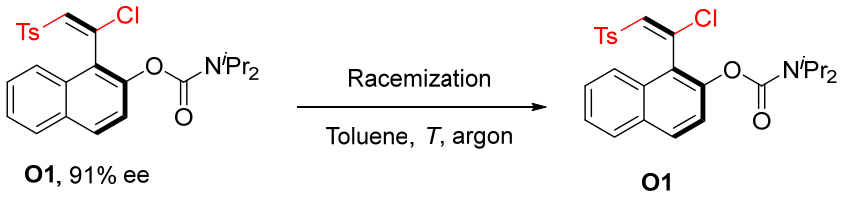
N1, 93% ee

N1

T	24 h	48 h	72 h	96 h	120 h
60 °C	93% ee	93% ee	93% ee	93% ee	93% ee
80 °C	90% ee	88% ee	88% ee	82% ee	78% ee
100 °C	78% ee	66% ee	54% ee	45% ee	34% ee

[a]Reaction conditions: **N1** (57.6 mg, 0.10 mmol) in dry toluene (2.0 mL) at corresponding reaction temperature (*T*) under argon. Ee values based on HPLC analysis.

Table S8. Racemization experiments with O1[a]



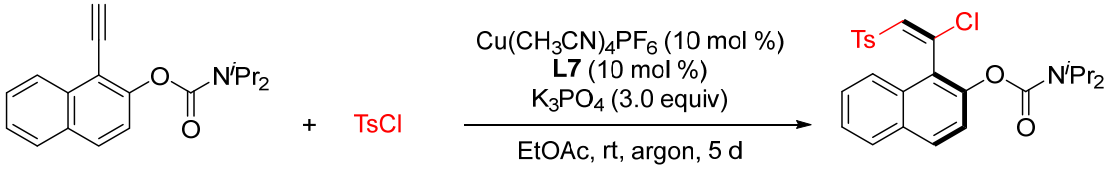
O1, 91% ee

O1

T	24 h	48 h	72 h	96 h	120 h
60 °C	91% ee	91% ee	91% ee	91% ee	90% ee
80 °C	83% ee	83% ee	77% ee	75% ee	70% ee

[a]Reaction conditions: Dissolved **O1** (48.6 mg, 0.10 mmol) in dry toluene (2.0 mL) at corresponding reaction temperature (*T*) under argon. Ee values based on HPLC analysis.

Table S9. Control experiments with OS1[a]

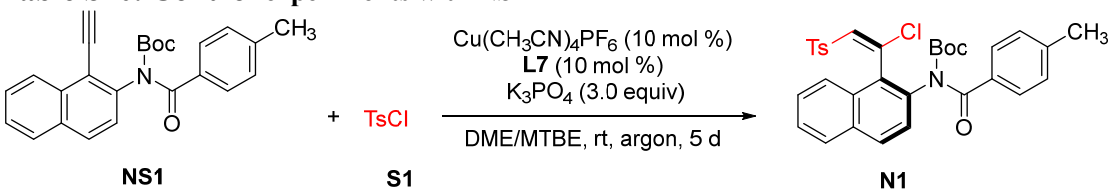


OS1, 1.0 equiv **S1**, 1.5 equiv **O1**

Entry	[Cu]	**L7**	K_3PO_4	TEMPO	Yield (%)[b]	Ee (%)[c]
1	−	+	+	−	0	N.d.
2	+	−	+	−	0	N.d.
3	+	+	−	−	6	91
4	+	+	+	1.0 equiv	0	N.d.

[a]Reaction conditions: **OS1** (59.1 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.075 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (7.45 mg, 10 mol %), **L7** (11.2 mg, 10 mol %), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv) in dry EtOAc (4.0 mL) at rt for 5 d. [b]Isolated yield. [c]Ee values based on HPLC analysis.

Table S10. Control experiments with NS1[a]

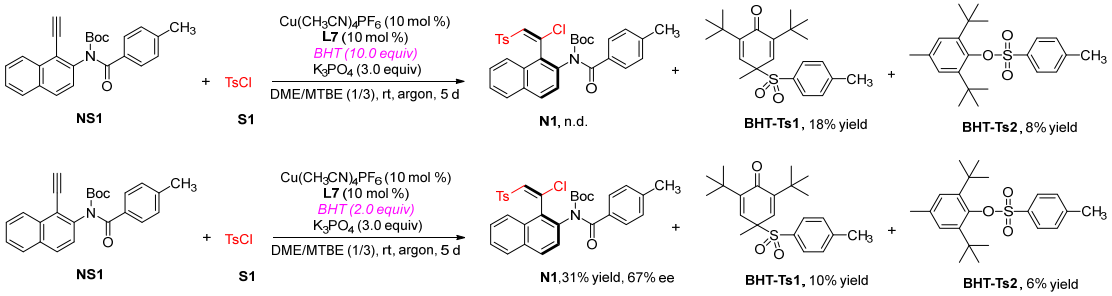


NS1 **S1** **N1**

Entry	[Cu]	**L7**	K_3PO_4	TEMPO	Yield (%)[b]	Ee (%)[c]
1	−	+	+	−	0	N.d.
2	+	−	+	−	0	N.d.
3	+	+	−	−	12	93
4	+	+	+	1.0 equiv	0	N.d.

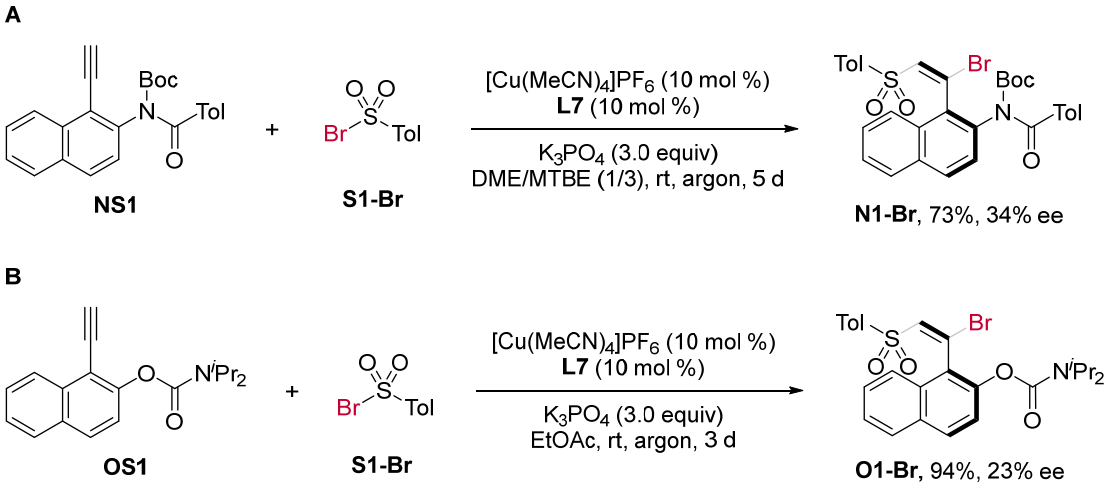
[a]Reaction conditions: **NS1** (77.1 mg, 0.20 mmol), **S1** (57.2 mg, 0.075 mmol), $Cu(CH_3CN)_4PF_6$ (7.45 mg, 10 mol %), **L7** (11.2 mg, 10 mol %), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv) in dry DME (1.0 mL) and MTBE (3.0 mL) at rt for 5 d. [b]Isolated yield. [c]Ee values based on HPLC analysis.

Table S11. Control experiments of NS1 with BHT



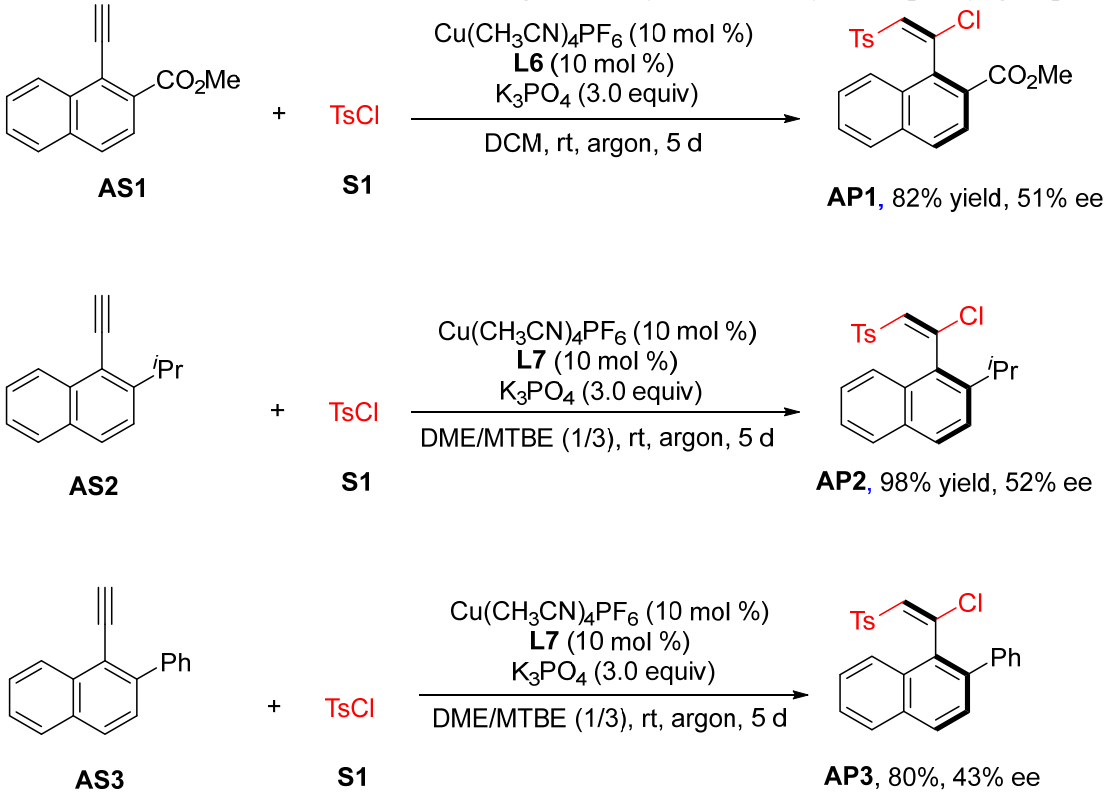
BHT, butylated hydroxytoluene.

Scheme S1. The results with tosyl bromide (S1-Br).

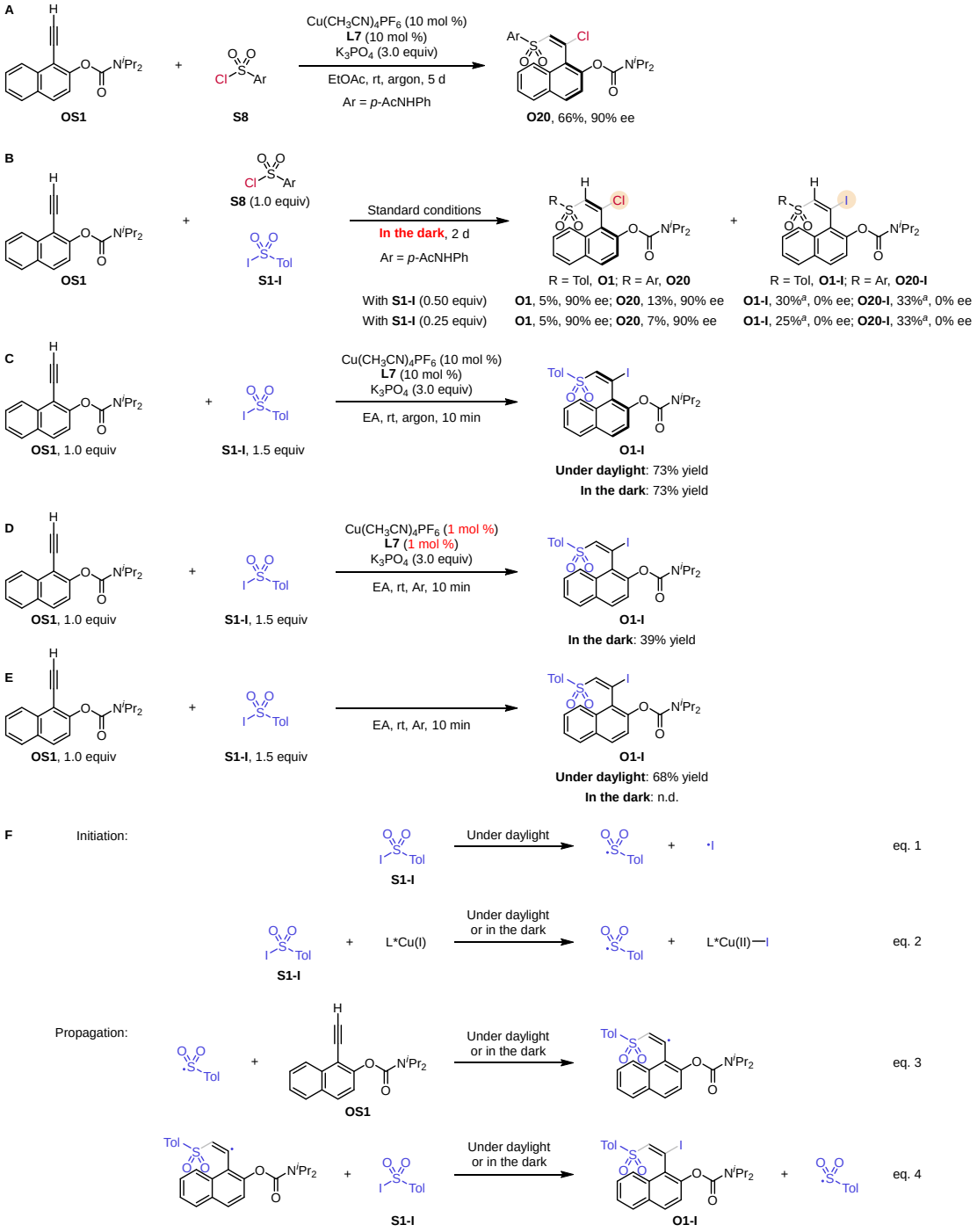


Tol, *p*-tolyl.

Scheme S2. The results of substrates bearing 2-carboxylic ester, -alkyl, and -phenyl groups.



Scheme S3. The results of OS1 with S8 or S1-I under standard conditions.



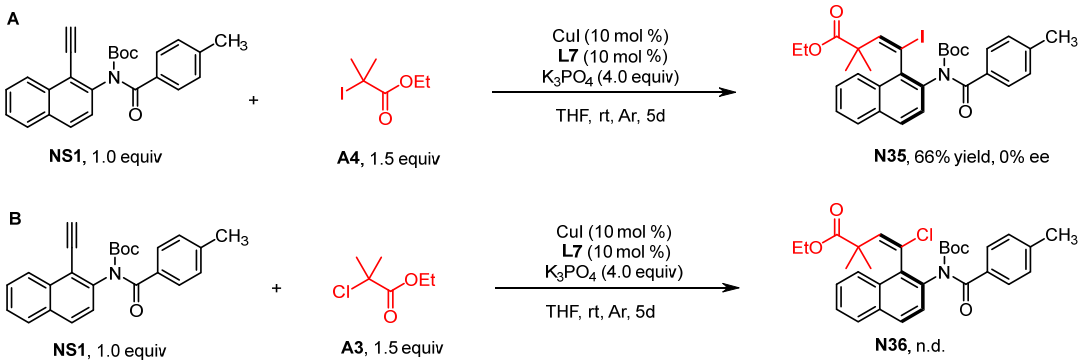
[a]The yield was calculated based on the amount of **S1-I**. To express the yield relative to **OS1**, the value should be divided by 2 or 4 for reactions using 0.50 or 0.25 equiv of **S1-I**, respectively.

The reaction of **S1-1** in the absence of a copper catalyst showed comparable efficiency under daylight conditions (Scheme S3E). This observation strongly suggests the existence of a copper-independent reaction pathway. Interestingly, this pathway was completely suppressed when the reaction was carried out in the dark (Scheme S3E), resembling a previously reported light-initiated radical chain iodosulfonylation reaction.[1]

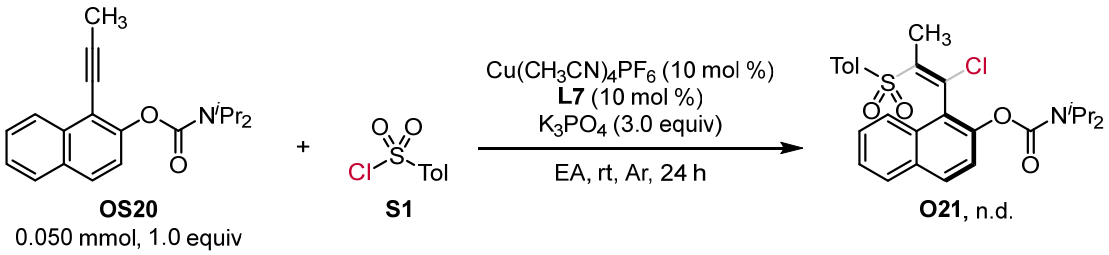
When the reaction was performed in the dark with the addition of the copper catalyst, the reaction efficiency was fully restored in terms of both reaction time and yield (Scheme S3C). This result suggests the presence of a copper-initiated radical chain iodosulfonylation pathway. Further evidence for this pathway comes from the observation that the reaction efficiency was largely retained even with a significant reduction in copper catalyst loading (Scheme S3D). Based on these findings, we propose that the reaction of **S1-1** proceeds via a radical chain mechanism that can be initiated by either copper salts or light (Scheme S3F).

To further investigate the light-initiated radical chain pathway, we conducted a cross-over experiment in the dark, which yielded results comparable to those obtained under daylight (Scheme S3B). This indicates that the fast iodine atom transfer from **S1-I** to vinyl radicals occurs under both conditions, leading to racemic vinyl iodide products. These findings confirm the racemic nature of the vinyl radical species formed in situ.

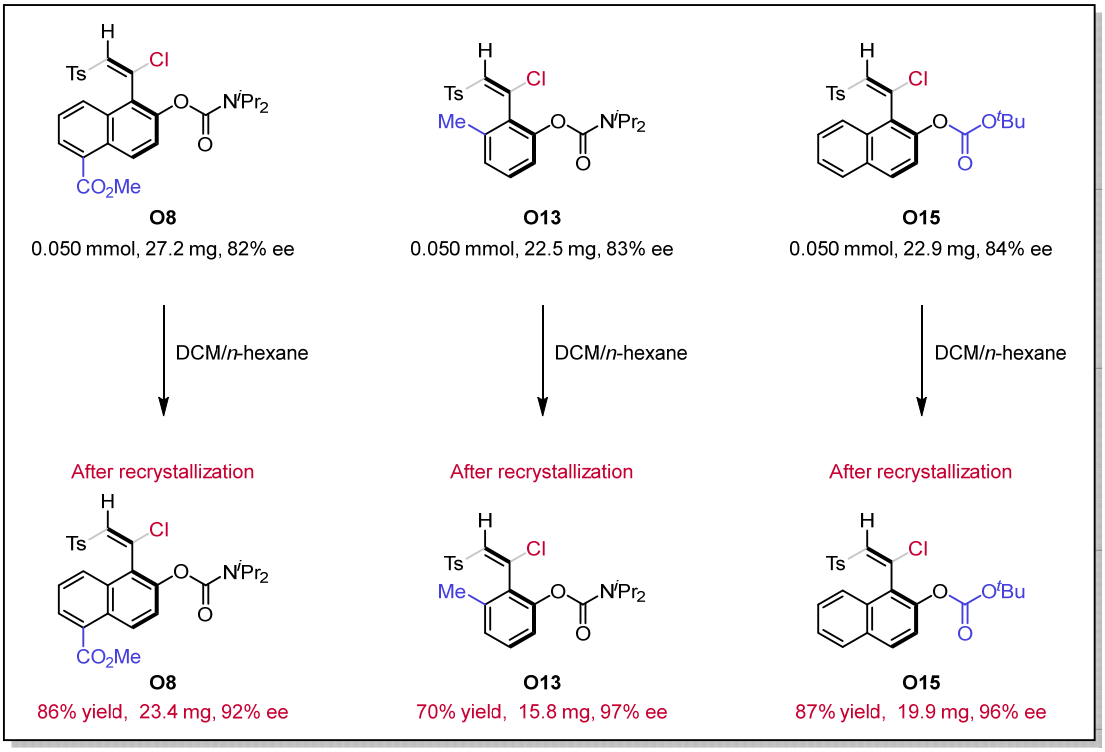
Scheme S4. The results of NS1 with A3 or A4 under standard conditions.



Scheme S5. Reactivity of Internal Alkyne O20

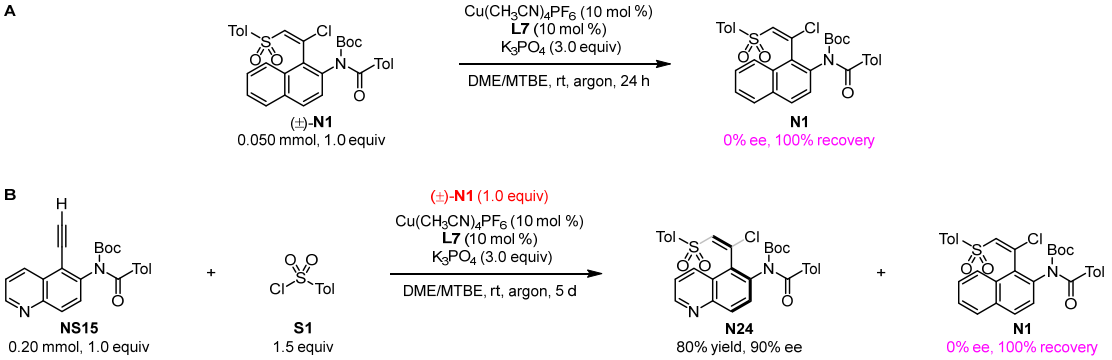


Scheme S6. Recrystallization Experiment Results[a]

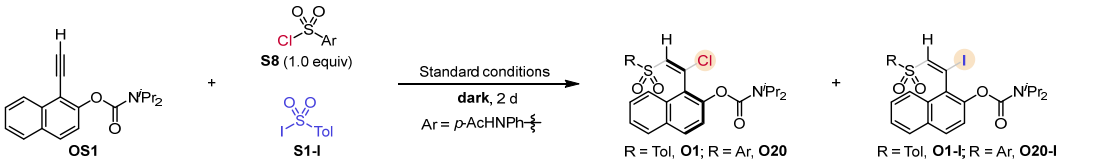


[a]Recrystallization method: The axially chiral vinyl halide product (0.050 mmol) was dissolved in DCM (0.20 mL). *n*-Hexane (5.0 mL) was then added to the solution. The resulting mixture was stored in a refrigerator at –30 °C for 4 h. After recrystallization, the solid was collected by filtration, and the ee value was determined using chiral HPLC analysis.

Scheme S7. Control Experiments with Racemic N1



Scheme S8. The results of the crossover experiment of OS1 with TsI and S8 under dark condition



[a]The yield was based on the amount of TsI.

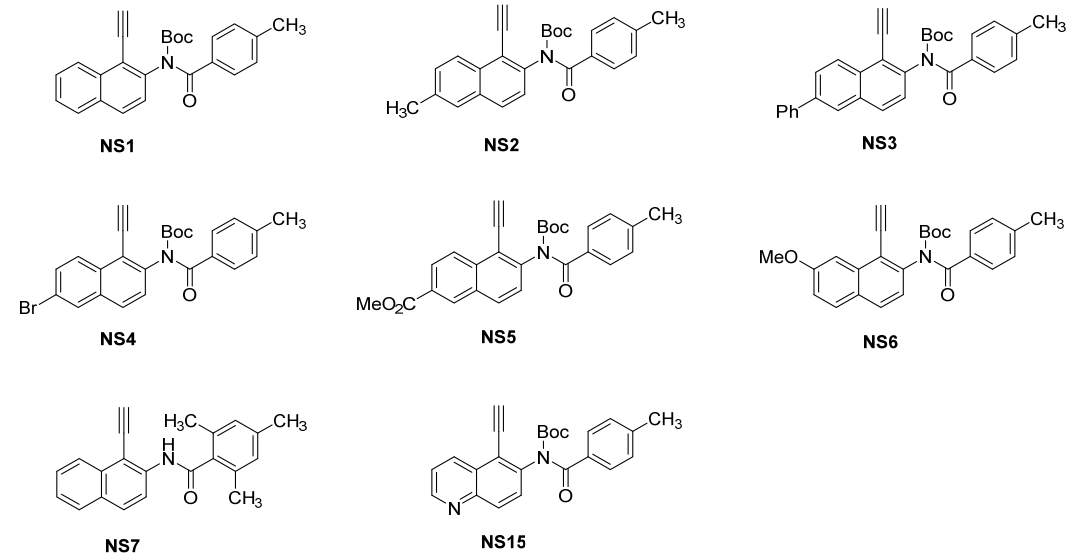
General information

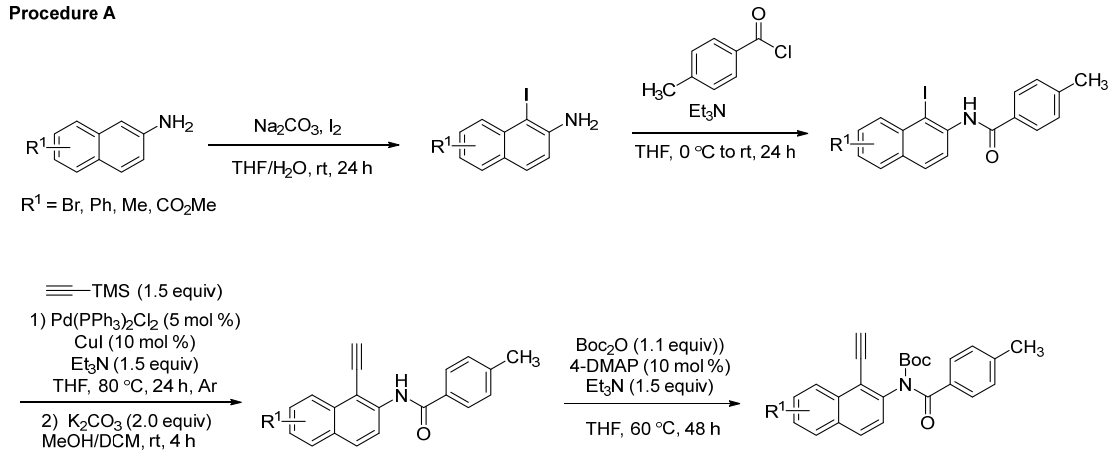
All reactions were carried out under an argon atmosphere using Schlenk techniques unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification unless otherwise stated. $Cu(CH_3CN)_4PF_6$, $Cu(CH_3CN)_4BF_4$, and CuCl were purchased from Bide Pharmatech Ltd. K_3PO_4 was purchased from Accela ChemBio Co., Ltd. Anhydrous 1,2-dimethoxyethane (DME), 2-methoxy-2-methylpropane (MTBE), and ethyl acetate (EtOAc) were purchased from Shanghai Energy-Chemical Reagent Co. Ltd, which were directly used without further treatment. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were purified and dried using a solvent-purification system that contained activated alumina under argon. Anhydrous toluene (Tol) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd, which was treated by 4 Å Molecular sieves and distilled after refluxing with sodium and benzophenone. Other solvents and reagents were purchased from Aladdin, J&K Scientific, Tansoole, and Bidepharm. An oil bath was employed for reactions that needed heating, and the temperature of the oil bath was denoted. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved using UV light (254 nm), iodine, or basic $KMnO_4$ indicator.

NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ^1H NMR and 100 or 150 MHz for ^{13}C NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. The chemical shifts were expressed in ppm, and coupling constants were given in Hz. Data for ^1H NMR were recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR were reported as chemical shifts (δ, ppm). HRMS measurements were performed with a Thermo Q Exactive mass spectrometer with an orbitrap mass analyzer. X-ray diffraction was measured on a Bruker D8 VENTURE diffractometer with MoKα (λ = 0.71073) radiation.

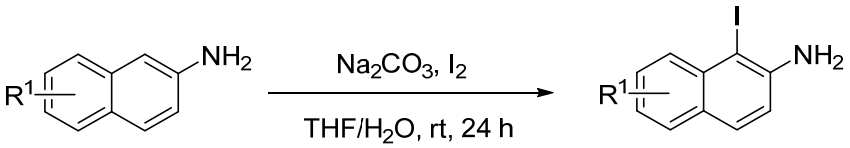
Procedures for the synthesis of substrates

Procedure A for the synthesis of naphthylamine-derived alkynes ***NS1–7****:*





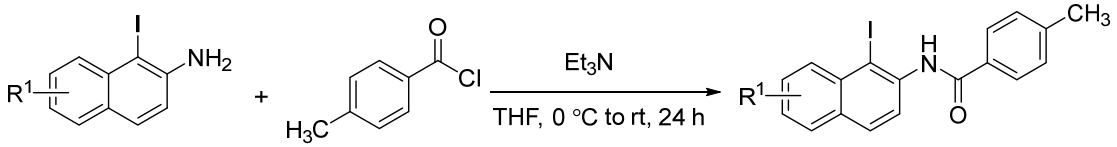
Synthesis of 1-iodonaphthalen-2-amine[2]



To a mixture of substituted naphthalen-2-amine (10 mmol, 1.0 equiv) and Na_2CO_3 (2.12 g, 20 mmol, 2.0 equiv) in THF/H_2O (20 mL/2 mL) was added I_2 (5.58 g, 22 mmol, 1.1 equiv). The mixture was stirred at room temperature overnight and then extracted with EtOAc (10 mL × 3). The combined organic layers were washed with saturated $Na_2S_2O_3$ solution (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give substituted

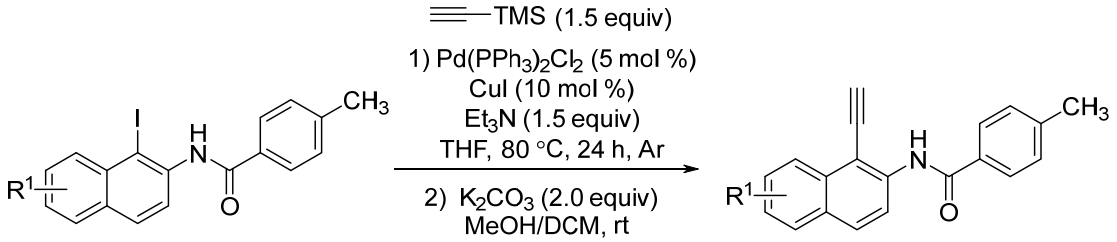
1-iodo-naphthalen-2-amine.

Synthesis of acyl-protected substituted 2-iodonamide[3]



To a solution of substituted 2-iodoaniline (10.5 mmol, 1.05 equiv) and triethylamine (2.04 mL, 15 mmol, 1.5 equiv) in THF (15 mL) was slowly added a solution of 4-methylbenzoyl chloride (1.55 g, 10.0 mmol, 1.0 equiv) in THF (5 mL) at 0 °C, which resulted in a colorless precipitate. After the reaction mixture was stirred for 24 h at room temperature, the formed triethylammonium chloride was removed by filtration. The combined organic layers were concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give substituted acyl-protected 2-iodonamide.

Synthesis of substituted *N*-(1-ethynylnaphthalen-2-yl)-4-methylbenzamide[4]

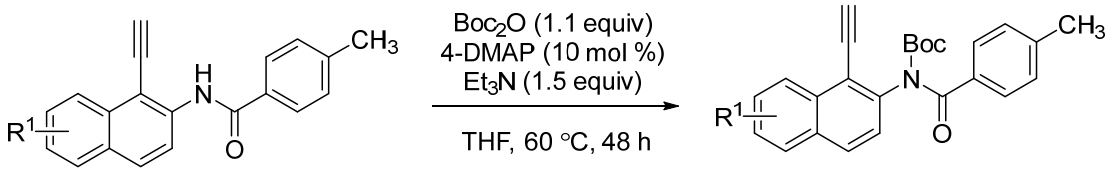


To a mixture of acyl-protected substituted 2-iodonamide (5.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (175 mg, 0.25 mmol, 5.0 mol %), CuI (96.0 mg, 0.50 mmol, 10 mol %), and Et_3N (1.04 mL, 7.5 mmol, 1.5 equiv) in dry THF (15 mL) was slowly added trimethylsilylacetylene (1.04 mL, 7.5 mmol, 1.5 equiv) under argon. After the reaction mixture was stirred at 80 °C for 24 h, it was treated with standard aqueous work-up and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography to afford the silylated arylacetylenes.

The mixture of silylated arylacetylenes and K_2CO_3 (1.38 g, 10 mmol, 2.0 equiv) dissolved in MeOH (10 mL) and DCM (5 mL) was stirred at room temperature until the starting silylated acetylenes disappeared. Then, the mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration of the solid, the organic layer was concentrated under reduced pressure. The residue was purified by silica gel

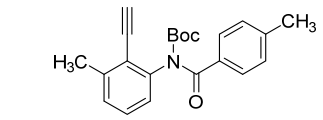
chromatography to provide the substituted *N*-(1-ethynylnaphthalen-2-yl)-4-methylbenzamide.

Synthesis of substituted *tert*-butyl (1-ethynylnaphthalen-2-yl)(4-methylbenzoyl)carbamate[5]

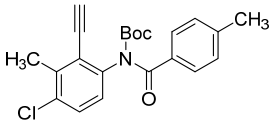


A solution of substituted *N*-(1-ethynylnaphthalen-2-yl)-4-methylbenzamide (2.0 mmol, 1.0 equiv) in THF (10 mL) was treated with Et_3N (0.4 mL, 3.0 mmol, 1.5 equiv), 4-DMAP (49.6 mg, 0.20 mmol, 10 mol %), and Boc_2O (0.70 mL, 2.75 mmol, 1.1 equiv), and the reaction mixture was stirred at 60 °C for 48 h. The reaction mixture was cooled to room temperature, washed with aqueous $KHSO_4$, and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography to provide the Boc-protected substituted naphthylamine-derived alkynes.

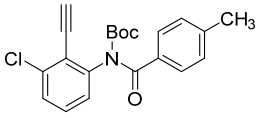
Procedure B for the synthesis of alkynes ***NS8–12****:*



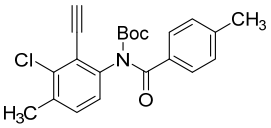
NS8



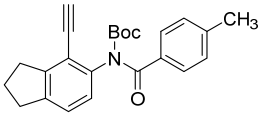
NS9



NS10

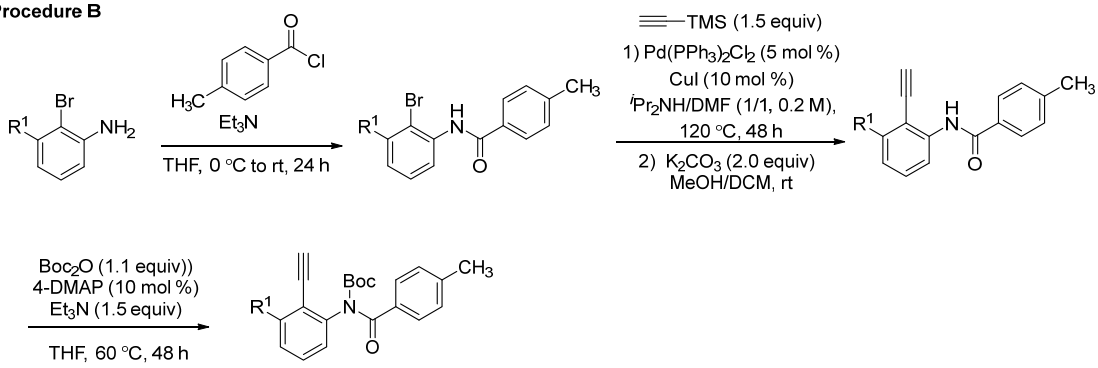


NS11

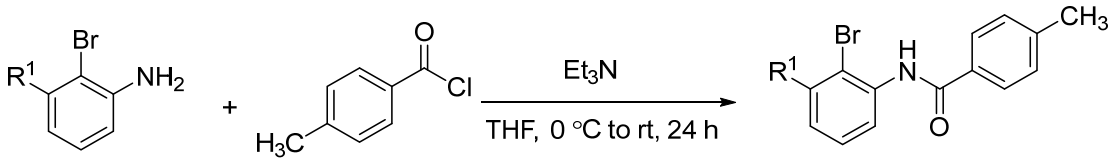


NS12

Procedure B

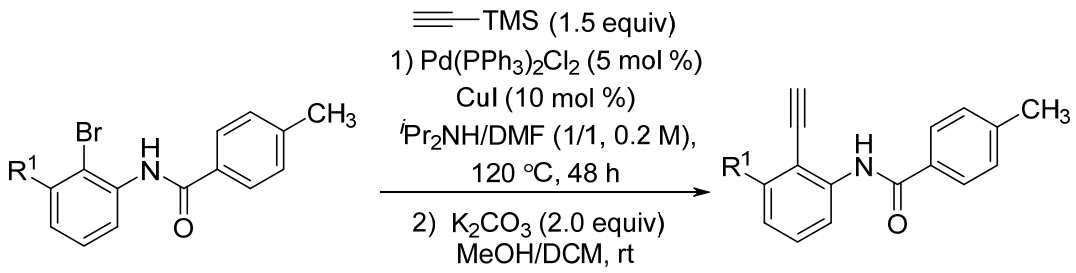


Synthesis of acyl-protected substituted *N*-(2-bromophenyl)-4-methylbenzamide



To a solution of substituted 2-bromoaniline (10.5 mmol, 1.05 equiv) and triethylamine (2.04 mL, 15 mmol, 1.5 equiv) in THF (15 mL) was slowly added a solution of 4-methylbenzoyl chloride (1.55 g, 10.0 mmol, 1.0 equiv) in THF (5 mL) at 0 °C, which resulted in a colorless precipitate. After the reaction mixture was stirred for 24 h at room temperature, the formed triethylammonium chloride was removed by filtration. The combined organic layers were concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give substituted *N*-(2-bromophenyl)-4-methylbenzamide.

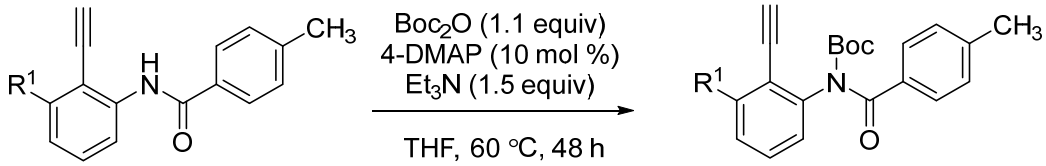
Synthesis of substituted *N*-(2-ethynylphenyl)-4-methylbenzamide[5]



To a mixture of substituted *N*-(2-bromophenyl)-4-methylbenzamide (5.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (175 mg, 0.25 mmol, 5.0 mol %), CuI (96.0 mg, 0.50 mmol, 10 mol %), and $^{i}Pr_2NH$ (10 mL) in dry DMF (10 mL) was slowly added trimethylsilylacetylene (1.04 mL, 7.5 mmol, 1.5 equiv) under argon. After the reaction mixture was stirred at 120 °C for 48 h, it was treated with standard aqueous work-up and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography to afford the silylated arylacetylenes.

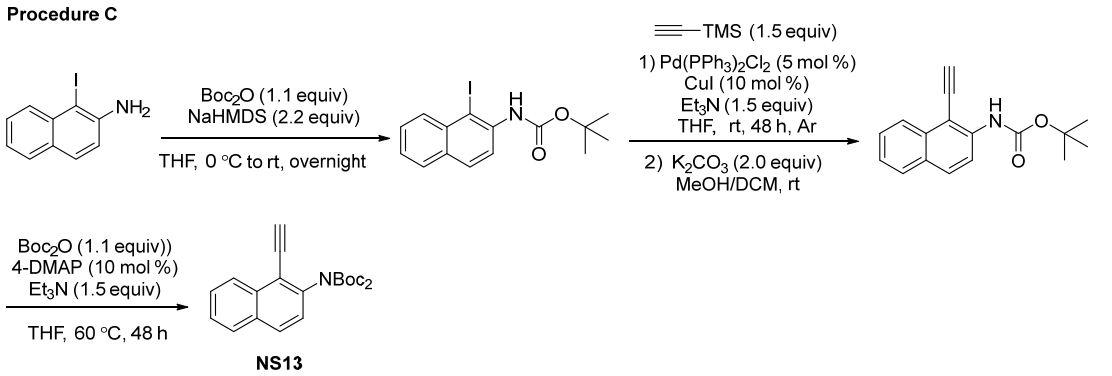
The mixture of silylated arylacetylenes and K_2CO_3 (1.38 g, 10 mmol, 2.0 equiv) dissolved in MeOH (10 mL) and DCM (5 mL) was stirred at room temperature until the starting silylated acetylenes disappeared. Then, the mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by silica gel chromatography to provide the substituted *N*-(2-ethynylphenyl)-4-methylbenzamide.

Synthesis of substituted *tert*-butyl (2-ethynylphenyl)(4-methylbenzoyl)carbamate

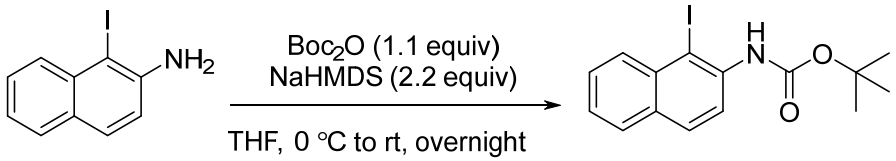


A solution of substituted *N*-(2-ethynylphenyl)-4-methylbenzamide (2.0 mmol, 1.0 equiv) in THF (10 mL) was treated with Et_3N (0.40 mL, 3.0 mmol, 1.5 equiv), 4-DMAP (49.6 mg, 0.20 mmol, 10 mol %), and Boc_2O (0.70 mL, 2.75 mmol, 1.1 equiv) and the reaction mixture was stirred at 60 °C for 48 h. Upon completion, the reaction mixture was cooled to room temperature, washed with aqueous $KHSO_4$, and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated. The residue was purified by silica gel chromatography to provide the Boc-protected alkynes.

Procedure C for the synthesis of tert-butyl (tert-butoxycarbonyl)(1-ethynylnaphthalen-2-yl)carbamate ***NS13****:*

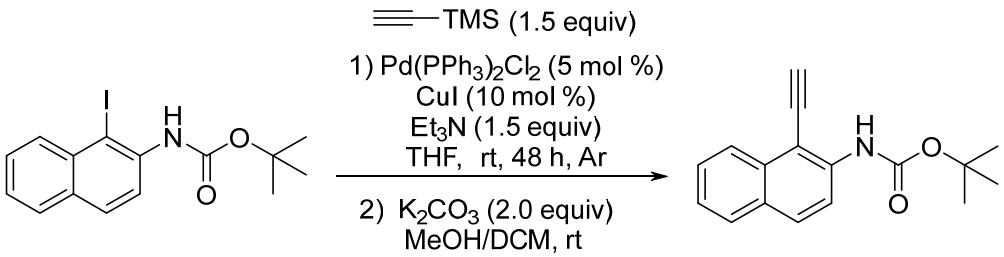


Synthesis of *tert*-butyl (1-iodonaphthalen-2-yl)carbamate[7]



To a solution of 1-iodonaphthalen-2-amine (5.38 g, 20 mmol, 1.0 equiv) in THF (2.0 M) was added NaHMDS (22.0 mL, 44.0 mmol, 2.2 equiv) at 0 °C. The reaction was stirred at 0 °C for 30 min before a solution of Boc_2O (5.05 mL, 22 mmol, 1.1 equiv) in THF (1.0 M) was added dropwise. The reaction mixture was stirred at 0 °C for 15 min before warming to room temperature over 30 min. The reaction mixture was then concentrated in vacuo before being partitioned between EtOAc and 1.0 N HCl (aq). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude *N*-Boc aniline. The residue was purified by flash silica gel column chromatography to give *tert*-butyl (1-iodonaphthalen-2-yl)carbamate.

Synthesis of *tert*-butyl (1-ethynylnaphthalen-2-yl)carbamate

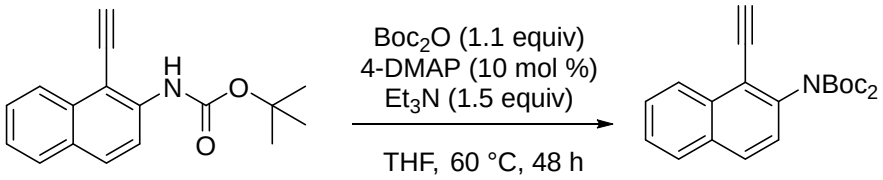


To a mixture of *tert*-butyl (1-iodonaphthalen-2-yl)carbamate (1.85 g, 5.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (175 mg, 0.25 mmol, 5.0 mol %), CuI (96.0 mg, 0.50 mmol, 10 mol %), and Et_3N (1.04 mL, 7.5 mmol, 1.5 equiv) in dry THF (15 mL) was slowly

added trimethylsilylacetylene (1.04 mL, 7.5 mmol, 1.5 equiv). After the reaction mixture was stirred at room temperature for 48 h, it was treated with standard aqueous work-up and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography to afford the silylated arylacetylenes.

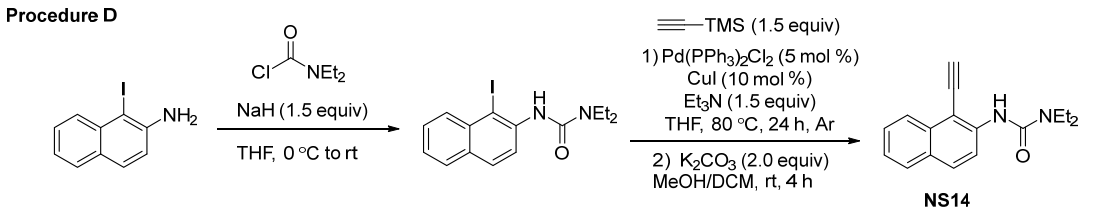
The mixture of silylated arylacetylenes and K_2CO_3 (1.38 g, 10 mmol, 2.0 equiv) dissolved in MeOH (10 mL) and DCM (5 mL) was stirred at room temperature until the starting silylated acetylenes disappeared. Then, the mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by silica gel chromatography to provide the *tert*-butyl (1-ethynylnaphthalen-2-yl)carbamate.

Synthesis of *tert*-butyl (*tert*-butoxycarbonyl)(1-ethynylnaphthalen-2-yl)carbamate

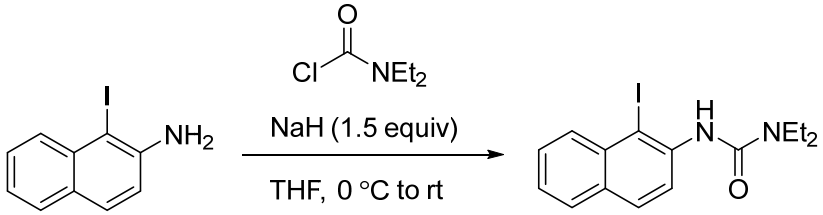


A solution of *tert*-butyl (1-ethynylnaphthalen-2-yl)carbamate (534.0 mg, 2.0 mmol, 1.0 equiv) in THF (10 mL) was treated with Et_3N (0.40 mL, 3.0 mmol, 1.5 equiv), 4-DMAP (49.6 mg, 0.20 mmol, 10 mol %), and Boc_2O (0.70 mL, 2.2 mmol, 1.1 equiv) and the reaction mixture was stirred at 60 °C for 48 h. The reaction mixture was cooled to room temperature, washed with aqueous $KHSO_4$, and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography to provide the Boc-protected alkyne **NS13**.

Procedure D for the synthesis of tert-butyl (tert-butoxycarbonyl)(1-ethynylnaphthalen-2-yl)carbamate ***NS14****:*



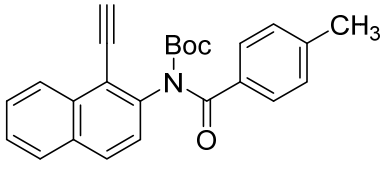
Synthesis of 1,1-diethyl-3-(1-iodonaphthalen-2-yl)urea[8]



To a solution of 1-iodonaphthalen-2-amine (2.69 g, 10.0 mmol, 1.0 equiv) in THF (20.0 mL) was slowly added NaH (60% dispersion in oil, 600 mg, 15.0 mmol, 1.5 equiv,) at 0 °C and the resulting solution was stirred at 0 °C for 30 min. Then, a solution of diethylcarbamoyl chloride (1.63 g, 12.0 mmol, 1.2 equiv) in THF (10 mL) was added dropwise via cannula to the reaction vessel. The reaction was warmed to room temperature, stirred overnight, and quenched with several drops of water. Then, the mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give the desired product.

Further transformation of this product to alkyne **NS14** was conducted according to general procedure A.

***tert*-Butyl (1-ethynylnaphthalen-2-yl)(4-methylbenzoyl)carbamate (NS1)**



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS1** (0.62 g, 80% yield) as a pale-yellow solid.

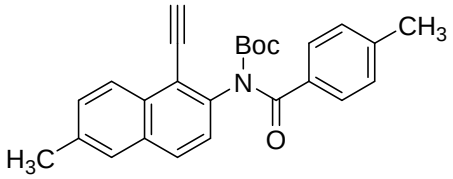
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 8.2 Hz, 1H), 7.94 – 7.83 (m, 2H), 7.78 – 7.71 (m, 2H), 7.60 – 7.51 (m, 2H), 7.34 (d, J = 8.7 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H),

3.63 (s, 1H), 2.40 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 152.9, 142.4, 140.4, 134.1, 134.0, 132.4, 130.0, 128.8(2), 128.7(7), 128.3, 127.5, 127.1, 126.6, 126.3, 118.8, 87.8, 83.6, 78.4, 27.7, 21.8.

HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{24}NO_3$ $[M + H]^+$ 386.1751, found 386.1747.

tert-Butyl (1-ethynyl-6-methylnaphthalen-2-yl)(4-methylbenzoyl)carbamate (NS2)



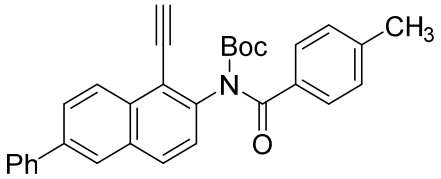
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS2** (0.66 g, 82% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.63 (s, 1H), 7.42 (dd, J = 8.6, 1.8 Hz, 1H), 7.30 (d, J = 8.7 Hz, 1H), 7.23 (d, J = 7.9 Hz, 2H), 3.62 (s, 1H), 2.53 (s, 3H), 2.41 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 153.0, 142.3, 139.7, 136.9, 134.1, 132.6, 132.4, 129.7, 129.3, 128.8(1), 128.7(8), 127.3, 126.4, 126.3, 118.6, 87.4, 83.5, 78.6, 27.7, 21.7(4), 21.7(1).

HRMS (ESI) *m*/*z* calcd. for $C_{26}H_{25}NO_3Na$ $[M + Na]^+$ 422.1727, found 422.1722.

tert-Butyl (1-ethynyl-6-phenylnaphthalen-2-yl)(4-methylbenzoyl)carbamate (NS3)



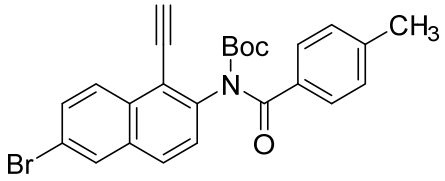
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS3** (637.0 mg, 69% yield) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.7 Hz, 1H), 8.04 (d, J = 1.8 Hz, 1H), 7.96 – 7.66 (m, 6H), 7.48 (t, J = 7.7 Hz, 2H), 7.43 – 7.32 (m, 2H), 7.25 – 7.19 (m, 2H), 3.65 (s, 1H), 2.40 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 152.9, 142.4, 140.6, 140.3, 139.8, 133.9, 133.3, 132.6, 130.2, 129.0, 128.8(2), 128.7(8), 127.8, 127.5, 127.2, 127.1, 126.8, 126.0, 118.7, 87.8, 83.6, 78.3, 27.7, 21.8.

HRMS (ESI) *m*/*z* calcd. for $C_{31}H_{27}NO_3Na$ $[M + Na]^+$ 484.1883, found 484.1882.

tert-Butyl (6-bromo-1-ethynylnaphthalen-2-yl)(4-methylbenzoyl)carbamate (NS4)



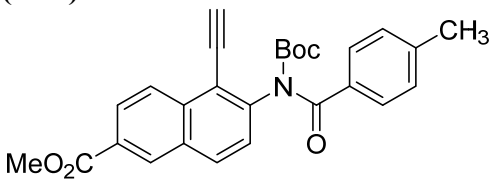
The Sonogashira coupling for the synthesis of **NS4** was conducted at room temperature. The final product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS4** (0.65 g, 70% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.9 Hz, 1H), 8.02 (d, J = 2.0 Hz, 1H), 7.82 – 7.72 (m, 3H), 7.65 (dd, J = 8.9, 2.0 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.28 – 7.19 (m, 2H), 3.65 (s, 1H), 2.41 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 152.8, 142.5, 140.7, 133.8, 132.6, 130.8, 130.2, 128.9(2), 128.8(9), 128.8(6), 128.8, 128.4, 127.6, 121.4, 119.1, 88.3, 83.8, 77.9, 27.7, 21.8.

HRMS (ESI) m/z calcd. for $C_{25}H_{23}NO_3Br$ $[M + H]^+$ 464.0856 found 464.0852.

Methyl 6-(*N*-(*tert*-butoxycarbonyl)-4-methylbenzamido)-5-ethynyl-2-naphthoate (NS5)



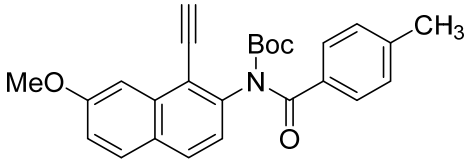
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **NS5** (0.51g, 57% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 1.6 Hz, 1H), 8.41 (d, J = 8.8 Hz, 1H), 8.16 (dd, J = 8.8, 1.7 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.7 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 3.99 (s, 3H), 3.67 (s, 1H), 2.42 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 167.0, 152.7, 142.6, 142.4, 136.4, 133.8, 131.6, 131.2, 128.9, 128.8, 128.6, 127.3, 127.0, 126.9, 119.0, 88.4, 83.9, 77.9, 52.5, 27.7, 21.8.

HRMS (ESI) m/z calcd. for $C_{27}H_{25}NO_5Na$ $[M + Na]^+$ 466.1625, found 466.1625.

***tert*-Butyl (1-ethynyl-7-methoxynaphthalen-2-yl)(4-methylbenzoyl)carbamate (NS6)**



The reaction mixture was purified by silica gel column chromatography (petroleum

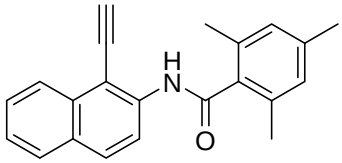
ether/ethyl acetate = 8/1) to afford **NS6** (556.8 mg, 67% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.6 Hz, 1H), 7.75 (d, J = 8.2 Hz, 3H), 7.65 (d, J = 2.6 Hz, 1H), 7.25 – 7.17 (m, 4H), 3.96 (s, 3H), 3.66 (s, 1H), 2.41 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 159.1, 153.0, 142.3, 140.9, 135.7, 134.0, 129.8, 129.7, 128.8, 128.7, 127.8, 123.9, 119.8, 117.5, 104.8, 87.6, 83.5, 78.7, 55.5, 27.7, 21.7.

HRMS (ESI) m/z calcd. for $C_{26}H_{25}NO_4Na$ $[M + Na]^+$ 438.1676, found 438.1673.

_N_-(1-Ethynylnaphthalen-2-yl)-2,4,6-trimethylbenzamide (NS7)



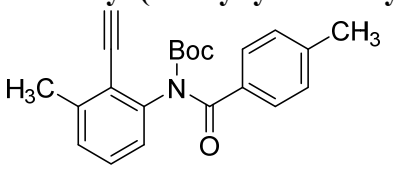
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS7** (1.41 g, 90% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, J = 9.0 Hz, 1H), 8.33 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 9.1 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.70 – 7.53 (m, 1H), 7.48 (t, J = 7.5 Hz, 1H), 6.94 (s, 2H), 3.84 (s, 1H), 2.45 (s, 6H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 139.4, 139.2, 134.9, 134.5, 133.5, 130.3, 130.2, 128.6, 128.3, 127.7, 125.6, 125.6, 119.4, 106.4, 89.9, 77.7, 21.3, 19.5.

HRMS (ESI) m/z calcd. for $C_{22}H_{20}NO$ $[M + H]^+$ 314.1539, found 314.1537.

***tert*-Butyl (2-ethynyl-3-methylphenyl)(4-methylbenzoyl)carbamate (NS8)**



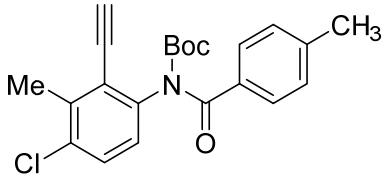
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS8** (0.55 g, 78% yield) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.31 – 7.23 (m, 1H), 7.23 – 7.17 (m, 3H), 7.07 (d, J = 7.8 Hz, 1H), 3.41 (s, 1H), 2.48 (s, 3H), 2.39 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 152.9, 142.5, 142.1, 141.6, 134.1, 129.2, 129.0, 128.7, 128.6, 126.1, 121.7, 86.3, 83.3, 78.9, 27.6, 21.7, 20.9.

HRMS (ESI) m/z calcd. for $C_{22}H_{23}NO_3Na$ $[M + Na]^+$ 372.1570, found 372.1568.

***tert*-Butyl (4-chloro-2-ethynyl-3-methylphenyl)(4-methylbenzoyl)carbamate (NS9)**



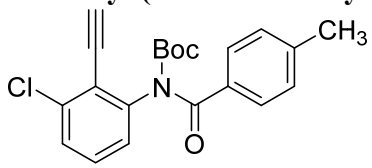
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS9** (0.70 g, 90% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.5 Hz, 1H), 7.23 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 8.5 Hz, 1H), 3.48 (s, 1H), 2.57 (s, 3H), 2.41 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 152.6, 142.3, 140.3, 140.1, 134.2, 133.7, 130.0, 128.7, 128.6, 127.2, 123.5, 87.0, 83.6, 78.5, 27.5, 21.7, 18.8.

HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{22}ClNO_3Na$ $[M + Na]^+$ 406.1180, found 406.1176.

***tert*-Butyl (3-chloro-2-ethynylphenyl)(4-methylbenzoyl)carbamate (NS10)**



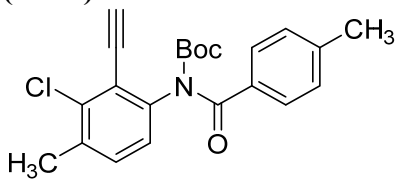
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS10** (0.55 g, 74% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.39 (dd, J = 8.1 Hz, 1.1 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.16 (dd, J = 7.9, 1.1 Hz, 1H), 3.51 (s, 1H), 2.39 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 152.3, 142.9, 142.4, 137.3, 133.5, 129.7, 128.8, 128.7, 128.6, 127.4, 122.1, 87.6, 83.7, 77.0, 27.5, 21.6.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{20}ClNO_3Na$ $[M + Na]^+$ 392.1024, found 392.1021.

***tert*-Butyl (3-chloro-2-ethynyl-4-methylphenyl)(4-methylbenzoyl)carbamate (NS11)**



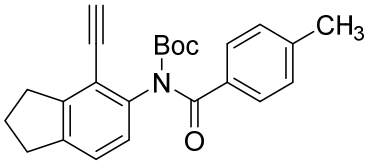
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS11** (0.54 g, 70% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.65 (m, 2H), 7.28 – 7.17 (m, 3H), 7.06 (d, J = 8.1 Hz, 1H), 3.49 (s, 1H), 2.39 (s, 6H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 152.6, 142.4, 140.6, 137.1, 136.7, 133.7, 131.1, 128.8, 128.6, 126.9, 122.1, 87.1, 83.7, 77.6, 27.6, 21.7, 20.6.

HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{22}ClNO_3Na$ $[M + Na]^+$ 406.1180, found 406.1176.

tert-Butyl (4-ethynyl-2,3-dihydro-1*H*-inden-5-yl)(4-methylbenzoyl)carbamate (NS12)



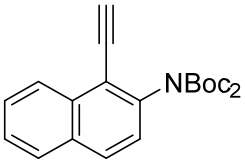
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **NS12** (0.54 g, 72% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.67 (m, 2H), 7.23 (dd, J = 7.9, 4.7 Hz, 3H), 7.01 (d, J = 7.9 Hz, 1H), 3.31 (s, 1H), 3.03 (t, J = 7.5 Hz, 2H), 2.94 (t, J = 7.6 Hz, 2H), 2.41 (s, 3H), 2.16 – 2.08 (m, 2H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 153.2, 149.1, 144.3, 142.1, 139.2, 134.3, 128.8, 128.7, 126.7, 125.3, 117.9, 84.6, 83.3, 79.0, 33.2, 33.0, 27.6, 25.1, 21.7.

HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{25}NO_3Na$ $[M + Na]^+$ 398.1727, found 398.1723.

tert-Butyl (_tert_-butoxycarbonyl)(1-ethynylnaphthalen-2-yl)carbamate (NS13)



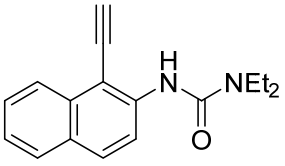
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to afford **NS13** (0.63 g, 85% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, J = 8.2 Hz, 1H), 7.84 (t, J = 8.7 Hz, 2H), 7.70 – 7.47 (m, 2H), 7.27 (d, J = 8.6 Hz, 1H), 3.65 (s, 1H), 1.37 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 140.6, 133.7, 132.1, 129.3, 128.2, 127.2, 126.8, 126.5, 126.3, 118.4, 87.4, 82.8, 77.8, 27.9.

HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{25}NO_4Na$ $[M + Na]^+$ 390.1676, found 390.1673.

1,1-Diethyl-3-(1-ethynylnaphthalen-2-yl)urea (NS14)



The reaction mixture was purified by silica gel column chromatography (petroleum

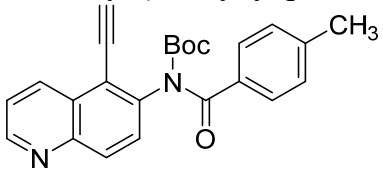
ether/ethyl acetate = 10/1) to afford **NS14** (0.93 g, 70% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 9.2 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.80 (dd, J = 18.0, 8.6 Hz, 2H), 7.67 (s, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 3.93 (s, 1H), 3.45 (q, J = 7.2 Hz, 4H), 1.30 (t, J = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 141.9, 133.6, 130.2, 129.1, 128.3, 127.4, 125.1, 124.6, 118.8, 103.7, 88.9, 78.9, 42.0, 14.0.

HRMS (ESI) m/z calcd. for $C_{17}H_{19}N_2O$ $[M + H]^+$ 267.1492, found 267.1489.

***tert*-Butyl (5-ethynylquinolin-6-yl)(4-methylbenzoyl)carbamate (NS15)**



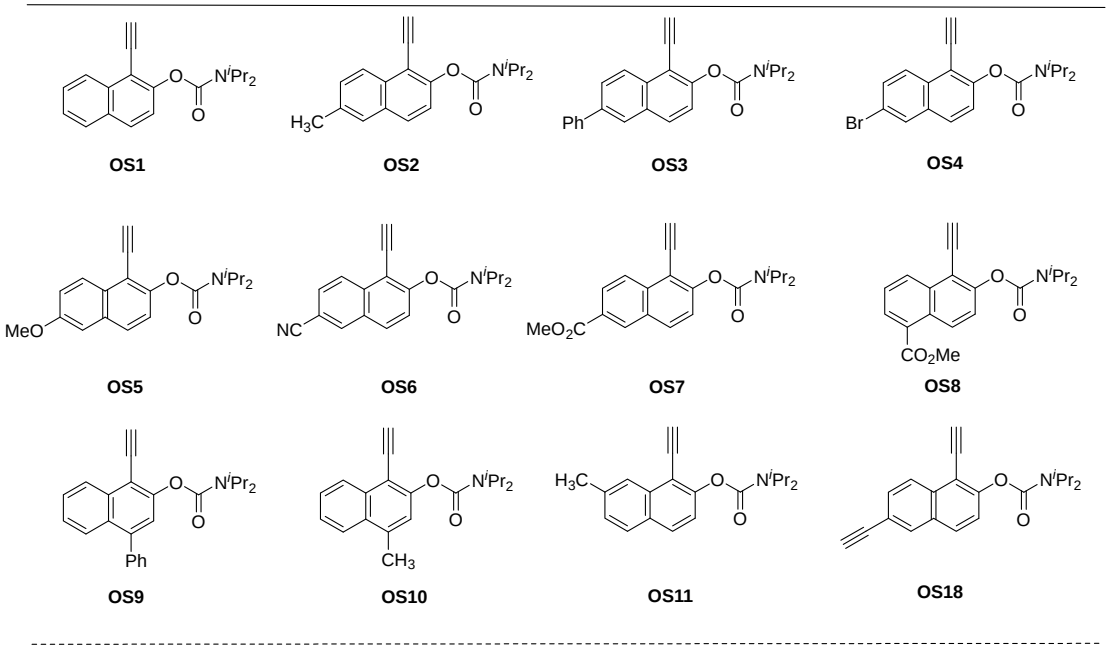
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford **NS15** (0.39 g, 51% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (dd, J = 4.3, 1.7 Hz, 1H), 8.65 (d, J = 8.6 Hz, 1H), 8.16 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 9.0 Hz, 1H), 7.50 (dd, J = 8.5, 4.2 Hz, 1H), 7.34 – 7.17 (m, 2H), 3.66 (s, 1H), 2.42 (s, 3H), 1.28 (s, 9H).

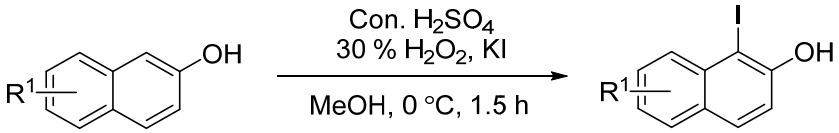
^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 152.7, 151.4, 147.1, 142.6, 140.8, 134.9, 133.8, 131.6, 130.1, 129.4, 128.9, 128.8, 122.3, 119.1, 88.3, 83.9, 77.3, 27.7, 21.8.

HRMS (ESI) m/z calcd. For $C_{24}H_{22}N_2O_3Na$ $[M + Na]^+$ 409.1523, found 409.1524.

Procedure E for the synthesis of naphthol-derived alkynes ***OS1–11*** *and* ***OS18****:*



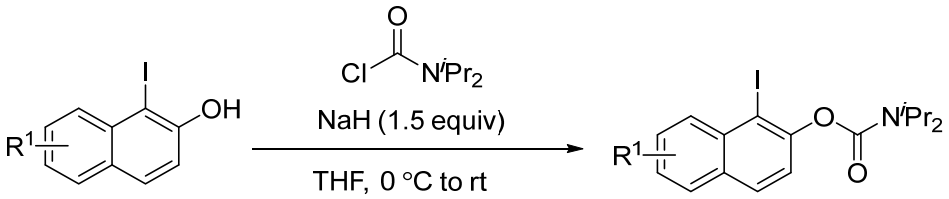
Synthesis of substituted 1-iodo-2-naphthol[9]



To a stirred solution of conc. H_2SO_4 (1.1 mL, 21 mmol, 1.5 equiv) in MeOH (40 mL) were sequentially added substituted naphthalen-2-ol (13.8 mmol, 1.0 equiv), KI (2.54 g, 15 mmol, 1.1 equiv), and H_2O_2 (30% aq. solution, 7.50 mL, 28 mmol, 2.0 equiv) at 0 °C. The mixture was stirred for an additional 75 min at 0 °C and poured into DCM (100 mL). The organic layer was separated, washed with sat. aq. $NaHSO_3$ solution (10 mL) and H_2O (80 mL), dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The crude product was then purified by flash column chromatography to

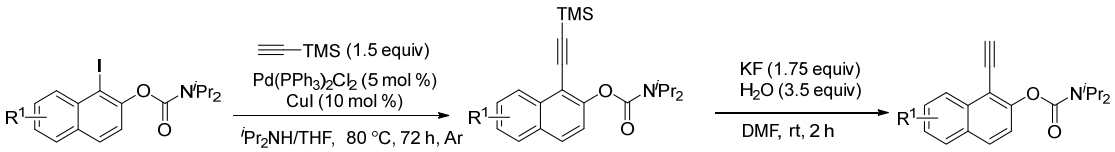
afford the desired substituted 1-iodo-2-naphthol.

Synthesis of substituted 1-iodonaphthalen-2-yl diisopropylcarbamate[8]



To a solution of substituted 1-iodo-2-naphthol (10.0 mmol, 1.0 equiv) in THF (20.0 mL) was slowly added NaH (60% dispersion in oil, 600 mg, 15.0 mmol, 1.5 equiv) at 0 °C and the resulting solution was stirred at 0 °C for 30 min. Then, a solution of diisopropylcarbamic chloride (1.96 g, 12.0 mmol, 1.2 equiv) in THF (10 mL) was added dropwise via cannula to the reaction vessel. The reaction mixture was warmed to room temperature, stirred overnight, and quenched with several drops of water. Then, the mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give substituted 1-iodonaphthalen-2-yl diisopropylcarbamate.

Synthesis of substituted 1-ethynylnaphthalen-2-yl diisopropylcarbamate[4,10]

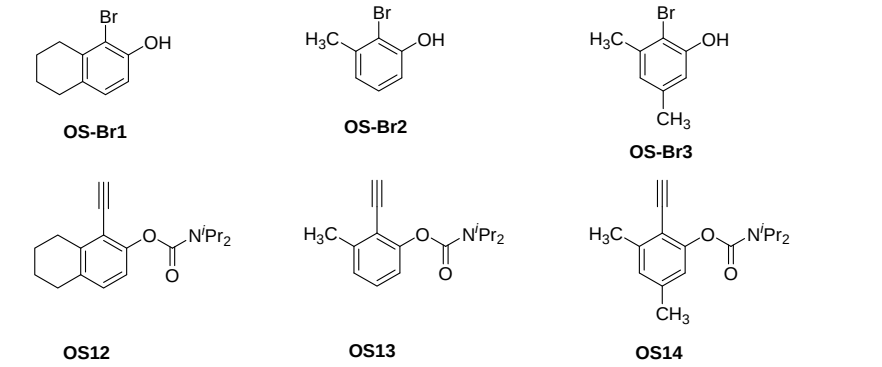


To a mixture of substituted 1-iodonaphthalen-2-yl diisopropylcarbamate (5.0 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (175 mg, 0.25 mmol, 5 mol %), CuI (48 mg, 0.50 mmol, 10 mol %), and $^iPr_2NH$ (7.5 mL) in dry THF (7.5 mL) was slowly added trimethylsilylacetylene (1.04 mL, 7.5 mmol, 1.5 equiv) under argon atmosphere. Then, the reaction mixture was stirred at 80 °C for 72 h, treated with a saturated NH_4Cl aqueous solution, and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified by silica gel column chromatography to afford the silylated arylacetylenes.

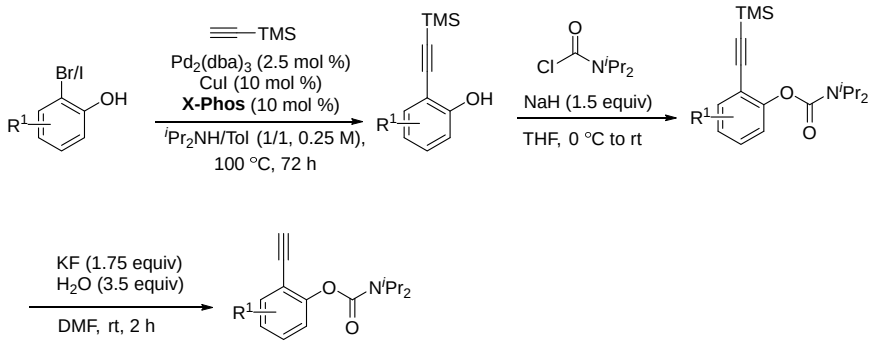
The mixture of silylated arylacetylenes and KF (580 mg, 10.0 mmol, 2.0 equiv) dissolved in DMF (15.0 mL) and H_2O (0.3 mL) was stirred at room temperature until the starting silylated acetylenes disappeared. Then, the mixture was extracted with EtOAc and dried over anhydrous Na_2SO_4. After filtration, the organic layer was

concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give alkynes.

Procedure F for the synthesis of naphthol-derived alkynes ***OS12–14****:*

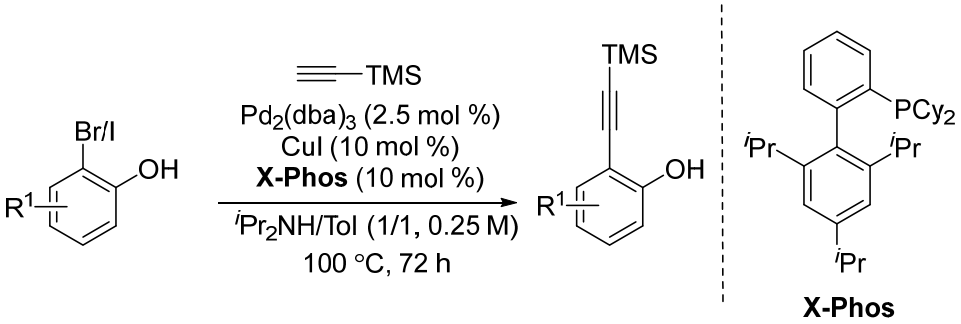


Procedure F



OS-Br1 is commercially available. **OS-Br2** and **OS-Br3** were synthesized according to the literature.[11]

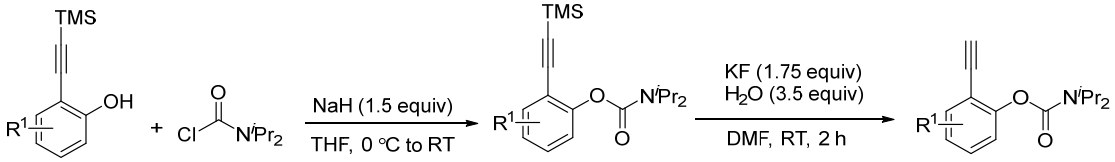
Synthesis of substituted 2-((trimethylsilyl)ethynyl)phenol[12]



To a solution of substituted 2-bromophenol (10 mmol, 1.0 equiv), $Pd_2(dba)_3$ (229 mg, 0.25 mmol, 2.5 mol %), CuI (192 mg, 0.10 mmol, 10 mol %), and X-Phos (477 mg, 0.10 mmol, 10 mol %) in a mixture of toluene/$^{i}Pr_2NH$ (1/1 v/v, 40 mL) placed in a sealed tube was slowly added trimethylsilylacetylene (2.08 mL, 15 mmol, 1.5 equiv).

The resulting solution was stirred at 100 °C for 72 h until the starting material disappeared. The catalyst was removed by filtration over silica gel using DCM as the eluent, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography to afford the silylated arylacetylenes.

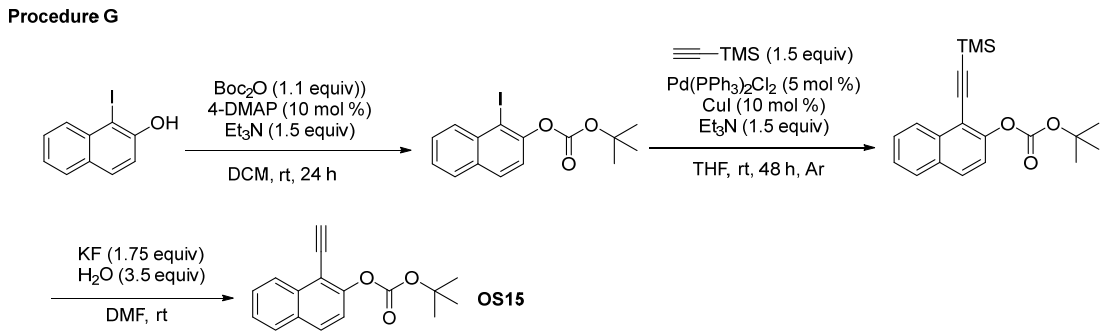
Synthesis of substituted 2-((trimethylsilyl)ethynyl)phenol



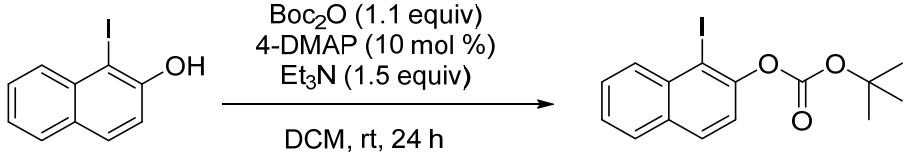
To a solution of substituted 2-((trimethylsilyl)ethynyl)phenol (5.0 mmol, 1.0 equiv) in THF (10.0 mL) was slowly added NaH (60% dispersion in oil, 300 mg, 7.5 mmol, 1.5 equiv) at 0 °C and the resulting solution was stirred at 0 °C for 30 min. Then, a solution of diisopropylcarbamic chloride (981 mg, 6.0 mmol, 1.2 equiv) in THF (5 mL) was added dropwise via cannula to the reaction vessel. The reaction was warmed to room temperature, stirred overnight, and quenched with several drops of water. Then, the mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give substituted 2-((trimethylsilyl)ethynyl)phenyl diisopropylcarbamate.

The mixture of silylated arylacetylenes (5.0 mmol, 1.0 equiv) and KF (508.3 mg, 8.75 mmol, 1.75 equiv) dissolved in DMF (15.0 mL) and H_2O (0.32 mL, 17.5 mmol, 3.50 equiv) was stirred at room temperature until the starting silylated acetylenes disappeared. Then, the mixture was extracted with EtOAc and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give alkynes.

Procedure G for the synthesis of alkyne ***OS15****:*

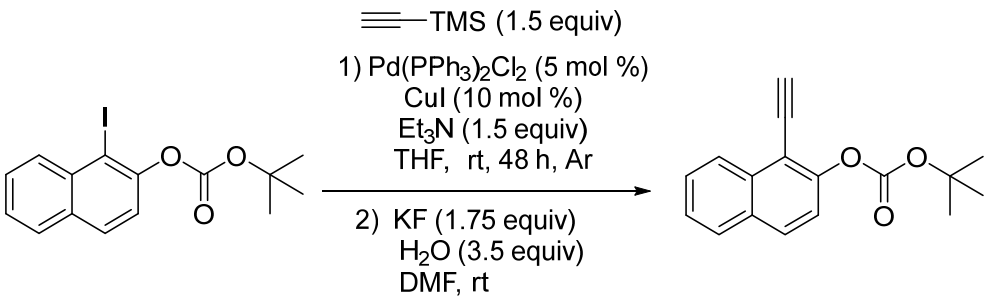


Synthesis of *tert*-butyl (1-iodonaphthalen-2-yl) carbonate[8]



A round bottom flask was charged with 1-iodo-2-naphthol (2.70 g, 10.0 mmol, 1.0 equiv), 4-DMAP (122.2 mg, 1.0 mmol, 10 mol %), DCM (30 mL), and Et_3N (2.08 mL, 15.0 mmol, 1.5 equiv). Boc_2O (2.53 mL, 11.0 mmol, 1.1 equiv) was added to the reaction vessel, and the reaction was stirred until the bubbling subsided (about 15 min). The solution was transferred to a separatory funnel, and $KHSO_4$ solution (0.5 M, 20 mL) was added. The layers were separated, and the aqueous layer was extracted with DCM (3x20 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by flash chromatography to give *tert*-butyl (1-iodonaphthalen-2-yl) carbonate.

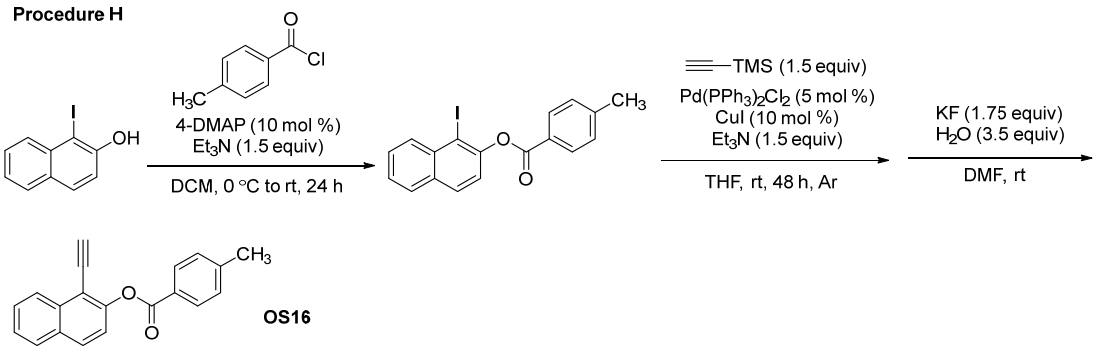
Synthesis of *tert*-butyl (1-ethynylnaphthalen-2-yl) carbonate



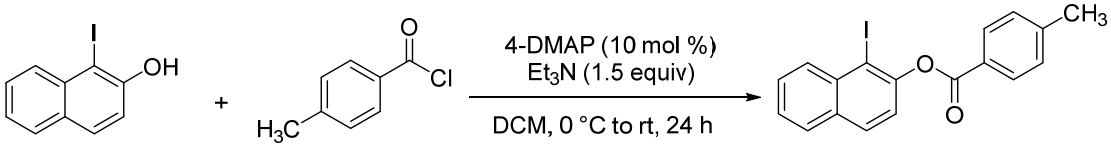
To a mixture of *tert*-butyl (1-iodonaphthalen-2-yl) carbonate (1.85 g, 5.0 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (175 mg, 0.25 mmol, 5 mol %), CuI (48 mg, 0.10 mmol, 10 mol %), and Et_3N (1.04 mL, 7.5 mmol, 1.5 equiv) in dry THF (7.5 mL) was slowly added trimethylsilylacetylene (1.04 mL, 7.5 mmol, 1.5 equiv) under argon atmosphere.

Then, the reaction mixture was stirred at room temperature for 48 h. Upon completion, the reaction mixture was treated with saturated NH_4Cl aqueous solution and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified by silica gel column chromatography to afford the silylated arylacetylenes. The mixture of silylated arylacetylenes and KF (580 mg, 10.0 mmol, 2.0 equiv) dissolved in DMF (15.0 mL) and H_2O (0.3 mL) was stirred at room temperature until the starting silylated acetylenes disappeared. Then, the mixture was extracted with EtOAc and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give *tert*-butyl (1-ethynylnaphthalen-2-yl) carbonate.

*Procedure H for the synthesis of alkyne **OS16**:*



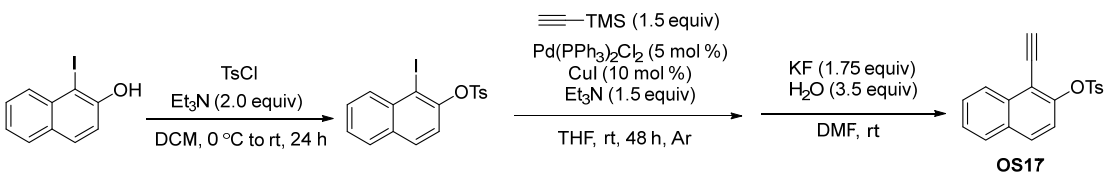
Synthesis of 1-iodonaphthalen-2-yl 4-methylbenzoate[13]



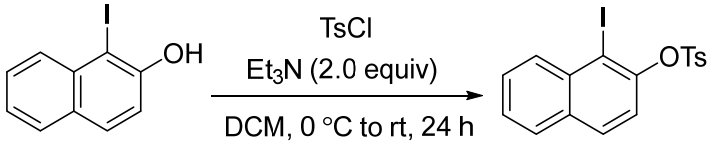
A round bottom flask was charged with 1-iodo-2-naphthol (2.70 g, 10.0 mmol, 1.0 equiv), 4-DMAP (122.2 mg, 1.0 mmol, 10 mol %), DCM (20 mL), and Et_3N (2.08 mL, 15.0 mmol, 1.5 equiv). Then, the resulting solution was stirred at 0 °C, and a solution of 4-methylbenzoyl chloride (12.0 mmol, 1.2 equiv) in DCM (10 mL) was added dropwise via cannula to the reaction vessel. The reaction was warmed to room temperature and stirred overnight. Then, the mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give the acyl-protected product. Then, alkyne **OS16** was prepared by following procedure

G.

Procedure I for the synthesis of alkyne ***OS17****:*

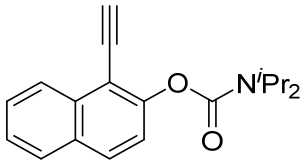


Synthesis of 1-iodonaphthalen-2-yl 4-methylbenzenesulfonate[14a]



A round-bottom flask was charged with 1-iodo-2-naphthol (2.70 g, 10.0 mmol, 1.0 equiv), DCM (20 mL), and Et_3N (3.0 mL, 15.0 mmol, 1.5 equiv). Then, the reaction mixture was stirred at 0 °C, and a solution of 4-methylbenzenesulfonyl chloride (2.28 g, 12.0 mmol, 1.2 equiv) in DCM (10 mL) was added dropwise via cannula to the reaction vessel. The reaction was warmed to room temperature and stirred overnight. Upon completion, the reaction mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give the desired product. Subsequently, alkyne **OS17** was prepared by following procedure G.

1-Ethynylnaphthalen-2-yl diisopropylcarbamate (OS1)



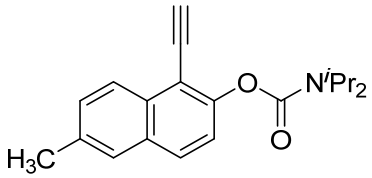
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS1** (1.30 g, 88% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 8.4 Hz, 1H), 7.89 – 7.78 (m, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.9 Hz, 1H), 4.31 – 3.95 (m, 2H), 3.62 (s, 1H), 1.52 – 1.21 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 152.3, 134.3, 130.9, 130.0, 128.2, 127.4, 126.0, 125.9, 122.1, 112.0, 86.8, 77.7, 46.9, 21.6, 20.6.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{22}NO_2$ $[M + H]^+$ 296.1645, found 296.1643.

1-Ethynyl-6-methylnaphthalen-2-yl diisopropylcarbamate (OS2)



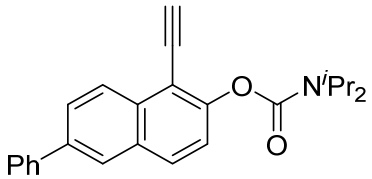
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS2** (1.40 g, 90% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.58 (s, 1H), 7.38 (dd, J = 8.5, 1.7 Hz, 1H), 7.27 (d, J = 8.9 Hz, 1H), 4.22 – 3.98 (m, 2H), 3.58 (s, 1H), 2.49 (s, 3H), 1.40 – 1.31 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 151.7, 135.6, 132.5, 131.1, 129.6, 129.3, 127.3, 125.8, 122.0, 111.8, 86.4, 77.9, 46.9, 21.6, 20.7.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NO_2$ $[M + H]^+$ 310.1802, found 310.1798.

1-Ethynyl-6-phenylnaphthalen-2-yl diisopropylcarbamate (OS3)



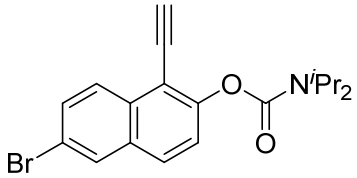
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS3** (1.54 g, 83% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 8.7 Hz, 1H), 8.02 (d, J = 2.0 Hz, 1H), 7.88 (d, J = 8.9 Hz, 1H), 7.82 (dd, J = 8.7, 1.9 Hz, 1H), 7.71 (dd, J = 7.4, 1.7 Hz, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.41 – 7.32 (m, 2H), 4.24 – 3.95 (m, 2H), 3.62 (s, 1H), 1.47 – 1.28 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 152.4, 140.8, 138.7, 133.6, 131.2, 130.2, 129.0, 127.6, 127.5, 127.0, 126.6, 126.1, 122.5, 112.0, 86.7, 77.7, 46.9, 21.6, 20.7.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}NO_2$ $[M + H]^+$ 372.1958, found 372.1953.

6-Bromo-1-ethynylnaphthalen-2-yl diisopropylcarbamate (OS4)



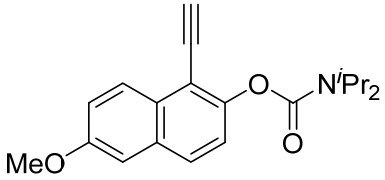
The Sonogashira coupling for the synthesis of **OS4** was conducted at room temperature. The final product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS4** (1.46 g, 78% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.9 Hz, 1H), 7.99 (d, J = 2.0 Hz, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.62 (dd, J = 8.9, 2.0 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 4.17 – 3.93 (m, 2H), 3.62 (s, 1H), 1.51 – 1.23 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 152.5, 132.9, 132.0, 130.7, 130.2, 128.9, 127.8, 123.3, 120.0, 112.4, 87.2, 77.2, 47.0, 21.6, 20.6.

HRMS (ESI) m/z calcd. for $C_{19}H_{21}BrNO_2$ $[M + H]^+$ 374.0750, found 374.0748.

1-Ethynyl-6-methoxynaphthalen-2-yl diisopropylcarbamate (OS5)



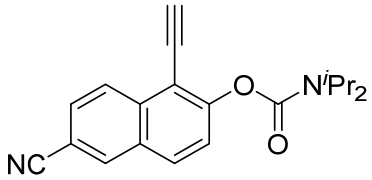
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **OS5** (1.31 g, 80% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 9.1 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.28 (d, J = 8.9 Hz, 1H), 7.23 (dd, J = 9.1, 2.6 Hz, 1H), 7.12 (d, J = 2.6 Hz, 1H), 4.16 – 4.01 (m, 2H), 3.90 (s, 3H), 3.59 (s, 1H), 1.41 – 1.26 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 153.3, 150.6, 132.1, 129.6, 128.7, 127.5, 122.4, 120.0, 112.0, 106.3, 86.4, 77.8, 55.4, 46.9, 46.7, 21.6, 20.6.

HRMS (ESI) m/z calcd. for $C_{20}H_{24}NO_3$ $[M + H]^+$ 326.1751, found 326.1746.

6-Cyano-1-ethynylnaphthalen-2-yl diisopropylcarbamate (OS6)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15/1) to afford **OS6** (1.28 g, 80% yield) as a white solid.

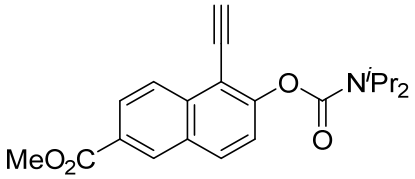
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (dd, J = 8.7, 2.9 Hz, 1H), 8.20 (s, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.67 (dd, J = 8.7, 1.7 Hz, 1H), 7.46 (d, J = 8.9 Hz, 1H), 4.19 – 3.99 (m, 2H), 3.68 (s, 1H), 1.50 – 1.23 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 152.4, 135.9, 134.2, 130.2, 129.8, 127.9, 127.4,

124.1, 119.0, 112.7, 109.6, 88.0, 76.6, 47.1, 21.6, 20.6.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}N_2O_2$ $[M + H]^+$ 321.1598, found 321.1593.

Methyl 6-((diisopropylcarbamoyl)oxy)-5-ethynyl-2-naphthoate (OS7)



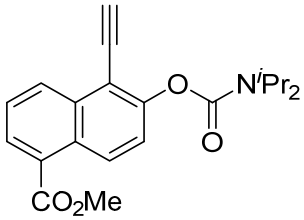
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **OS7** (1.48 g, 84% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.34 (d, J = 8.8 Hz, 1H), 8.13 (dd, J = 8.8, 1.7 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.40 (d, J = 8.9 Hz, 1H), 4.29 – 4.00 (m, 2H), 3.98 (s, 3H), 3.65 (s, 1H), 1.50 – 1.26 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 154.1, 152.7, 136.7, 131.3, 131.2, 130.0, 127.6, 126.8, 126.3, 123.0, 112.3, 87.3, 77.2, 52.4, 47.0, 21.6, 20.6.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}NO_4$ $[M + H]^+$ 354.1700, found 354.1696.

Methyl 6-((diisopropylcarbamoyl)oxy)-5-ethynyl-1-naphthoate (OS8)



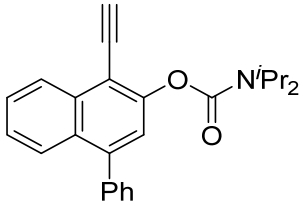
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **OS8** (1.45 g, 82% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (d, J = 9.5 Hz, 1H), 8.56 (d, J = 8.4 Hz, 1H), 8.18 (dd, J = 7.2, 1.3 Hz, 1H), 7.58 (dd, J = 8.4, 7.3 Hz, 1H), 7.45 (d, J = 9.4 Hz, 1H), 4.23 – 4.03 (m, 2H), 3.99 (s, 3H), 3.64 (s, 1H), 1.49 – 1.23 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 152.8, 152.6, 135.0, 131.2, 130.2, 129.0, 128.2, 127.5, 126.1, 123.7, 112.5, 87.3, 77.5, 52.4, 47.0, 46.9, 21.6, 20.6.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}NO_4$ $[M + H]^+$ 354.1700, found 354.1694.

1-Ethynyl-4-phenylnaphthalen-2-yl diisopropylcarbamate (OS9)



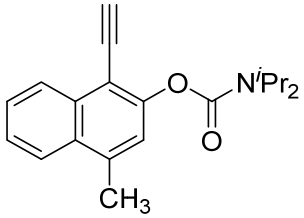
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS9** (1.45 g, 78% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H)., 7.62 – 7.55 (m, 1H), 7.55 – 7.40 (m, 6H), 7.31 (s, 1H), 4.18 – 4.04 (m, 2H), 3.66 (s, 1H), 1.51 – 1.27 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 151.7, 142.6, 139.7, 134.8, 130.1, 129.4, 128.4, 127.8, 127.3, 126.6, 126.4, 126.0, 123.0, 111.5, 86.9, 77.8, 47.0, 46.7, 21.7, 20.7.

HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{26}NO_2$ $[M + H]^+$ 372.1958, found 372.1956.

1-Ethynyl-4-methylnaphthalen-2-yl diisopropylcarbamate (OS10)



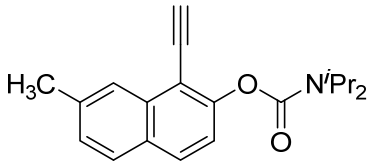
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS10** (1.25 g, 81% yield) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.52 (td, J = 7.6, 6.9, 1.2 Hz, 1H), 7.20 (s, 1H), 4.16 – 3.92 (m, 2H), 3.59 (s, 1H), 2.70 (s, 3H), 1.38 (d, J = 21.4 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 151.8, 137.4, 134.3, 130.2, 127.0, 126.5, 125.7, 124.4, 122.7, 110.1, 86.1, 77.8, 46.8, 46.7, 21.5, 20.6, 19.7.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{24}NO_2$ $[M + H]^+$ 310.1802, found 310.1799.

1-Ethynyl-7-methylnaphthalen-2-yl diisopropylcarbamate (OS11)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS11** (1.24 g, 80% yield) as a white solid.

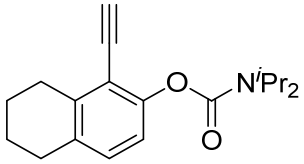
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.71 (d, J = 8.3

Hz, 1H), 7.29 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 1H), 4.15 – 3.97 (m, 2H), 3.60 (s, 1H), 2.53 (s, 3H), 1.55 – 1.18 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 152.5, 137.4, 134.5, 129.7, 129.1, 128.2, 128.0, 125.0, 121.0, 111.3, 86.5, 77.9, 46.8, 22.0, 21.6, 20.7.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{24}NO_2$ $[M + H]^+$ 310.1802, found 310.1796.

1-Ethynyl-5,6,7,8-tetrahydronaphthalen-2-yl diisopropylcarbamate (OS12)



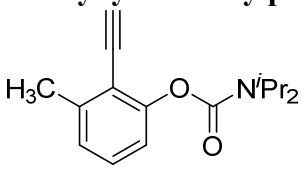
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS12** (1.14 g, 76% yield) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 4.20 – 3.98 (m, 2H), 3.40 (s, 1H), 2.94 – 2.61 (m, 4H), 1.83 – 1.69 (m, 4H), 1.45 – 1.17 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 151.2, 141.0, 134.2, 130.2, 119.6, 116.0, 86.0, 78.2, 46.6, 29.4, 28.3, 22.8, 21.5, 20.6.

HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{26}NO_2$ $[M + H]^+$ 300.1958, found 300.1955.

2-Ethynyl-3-methylphenyl diisopropylcarbamate (OS13)



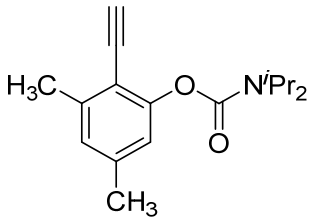
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS13** (0.97 g, 75% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 15.2, 7.3 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 4.20 – 3.91 (m, 2H), 3.40 (s, 1H), 2.45 (s, 3H), 1.40 – 1.24 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 142.7, 129.1, 127.5, 126.3, 120.1, 116.7, 85.6, 78.3, 46.8, 21.6, 20.8, 20.6.

HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{22}NO_2$ $[M + H]^+$ 260.1645, found 260.1643.

2-Ethynyl-3,5-dimethylphenyl diisopropylcarbamate (OS14)



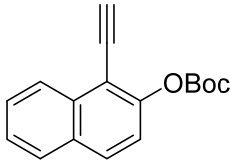
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS14** (0.98 g, 72% yield) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (s, 1H), 6.80 (s, 1H), 4.20 – 3.91 (m, 2H), 3.34 (s, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 1.42 – 1.18 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2(0), 153.1(6), 142.2, 139.6, 127.3, 120.7, 113.6, 84.8, 78.5, 46.7, 21.5, 20.6.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{24}NO_2$ $[M + H]^+$ 274.1802, found 274.1799.

1-Ethynylnaphthalen-2-yl diisopropylcarbamate (OS15)



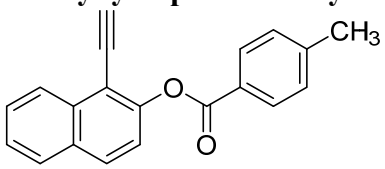
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS15** (1.24 g, 92% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 8.4 Hz, 1H), 7.86 (t, J = 8.0 Hz, 2H), 7.60 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.51 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.33 (d, J = 8.9 Hz, 1H), 3.72 (s, 1H), 1.60 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 151.4, 134.1, 131.2, 130.4, 128.3, 127.7, 126.4, 126.1, 120.9, 112.3, 87.7, 84.2, 76.6, 27.8.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{16}O_3Na$ $[M + Na]^+$ 291.0992, found 291.0990.

1-Ethynylnaphthalen-2-yl 4-methylbenzoate (OS16)



The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS16** (1.03 g, 72% yield) as a yellow solid.

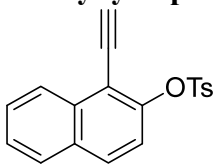
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 8.1 Hz, 2H), 7.90 (dd, J = 11.3, 8.5 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 8.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 3.58 (s, 1H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 151.8, 144.7, 134.3, 131.3, 130.6, 130.3, 129.5,

128.4, 127.7, 126.7, 126.4, 126.1, 121.5, 112.3, 87.4, 76.8, 22.0.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{15}O_2$ $[M + H]^+$ 287.1067, found 287.1065.

1-Ethynylnaphthalen-2-yl 4-methylbenzenesulfonate (OS17)



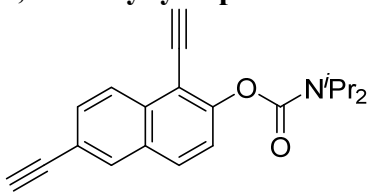
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS17** (1.37 g, 85% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.3 Hz, 1H), 7.88 – 7.77 (m, 4H), 7.62 – 7.49 (m, 2H), 7.42 (d, J = 9.0 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 3.43 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 145.6, 134.1, 132.9, 131.5, 130.4, 129.9, 129.0, 128.3, 127.9, 126.9, 126.4, 121.3, 113.4, 87.5, 76.1, 21.9.

HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{15}O_3S$ $[M + H]^+$ 323.0736, found 323.0735.

1,6-Diethynylnaphthalen-2-yl diisopropylcarbamate (OS18)



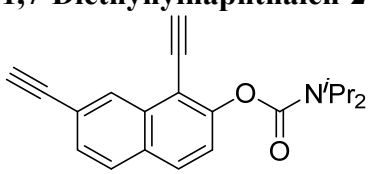
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to afford **OS18** (1.24 g, 90% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 1.5 Hz, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.61 (dd, J = 8.7, 1.7 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 4.26 – 3.97 (m, 2H), 3.62 (s, 1H), 3.16 (s, 1H), 1.49 – 1.21 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 152.8, 134.1, 132.5, 130.3, 130.1, 129.8, 126.2, 122.9, 119.6, 112.3, 87.1, 83.7, 78.0, 77.3, 47.0, 21.6, 20.6.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{22}NO_2$ $[M + H]^+$ 320.1645, found 320.1640.

1,7-Diethynylnaphthalen-2-yl diisopropylcarbamate (OS19)



The reaction mixture was purified by silica gel column chromatography (petroleum

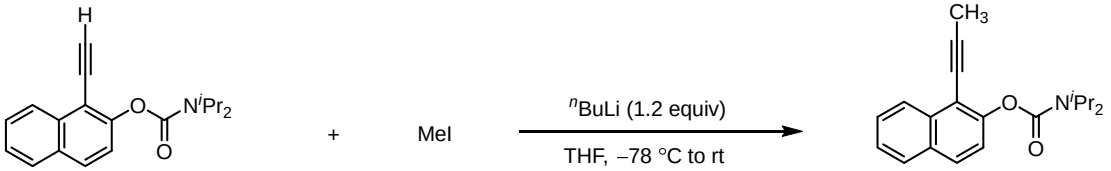
ether/ethyl acetate = 10/1) to afford **OS19** (0.81 g, 50% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.79 (dd, J = 11.7, 8.7 Hz, 2H), 7.52 (dd, J = 8.4, 1.6 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 4.29 – 3.83 (m, 2H), 3.65 (s, 1H), 3.19 (s, 1H), 1.52 – 1.14 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 152.9, 133.9, 130.5, 130.3, 129.7, 128.7, 128.4, 123.1, 121.1, 112.0, 87.4, 84.0, 78.3, 47.0, 21.6, 20.7.

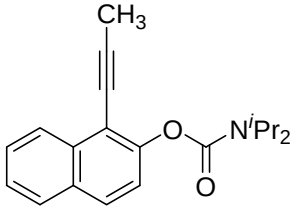
HRMS (ESI) m/z calcd. for $C_{21}H_{22}NO_2$ $[M + H]^+$ 320.1645, found 320.1640.

The internal alkyne **OS20** was synthesized according to the reported literature.[14b]



OS1, 1.0 equiv 1.25 equiv **OS20**

1-(Prop-1-yn-1-yl)naphthalen-2-yl diisopropylcarbamate (OS20)



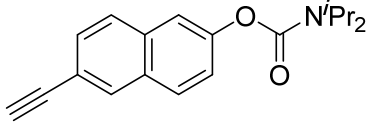
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **OS20** as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.60 (s, 1H), 7.53 (t, J = 7.0 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.20 (s, 1H), 3.93–3.48 (m, 2H), 2.29 (s, 3H), 1.53–1.20 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 153.2, 134.2, 128.6, 127.8(0), 127.7(9), 126.3, 125.8, 125.1, 124.5, 105.1, 97.9, 72.4, 20.8, 5.1.

HRMS (ESI) m/z calcd. for $C_{20}H_{24}NO_2$ $[M + H]^+$ 310.1802, found 310.1800.

6-Ethynylnaphthalen-2-yl diisopropylcarbamate (OS1')



The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS1'** (1.23 g, 83% yield) as a white solid.

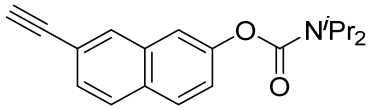
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.57 (d, J = 2.3 Hz, 1H), 7.51 (dd, J = 8.5, 1.6 Hz, 1H), 7.31 (dd, J = 8.9, 2.3

Hz, 1H), 4.26 – 3.90 (m, 2H), 3.14 (s, 1H), 1.52 – 1.15 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.1, 133.7, 132.2, 130.6, 129.2, 129.1, 127.8, 122.7, 118.9, 118.5, 84.1, 77.5, 47.1, 46.4, 21.7, 20.6.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}NO_2Na$ $[M + Na]^+$ 318.1465, found 318.1461.

7-Ethynylnaphthalen-2-yl diisopropylcarbamate (OS1'')



The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **OS1''** (1.24 g, 84% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.78 (dd, J = 14.7, 8.7 Hz, 2H), 7.60 – 7.43 (m, 2H), 7.31 (dd, J = 8.8, 2.3 Hz, 1H), 4.30 – 3.85 (m, 2H), 3.15 (s, 1H), 1.51 – 0.97 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 149.8, 133.5, 131.9, 130.8, 129.1, 128.1, 127.9, 123.0, 120.0, 118.4, 84.1, 77.8, 47.1, 46.4, 21.7, 20.6.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}NO_2Na$ $[M + Na]^+$ 318.1465, found 318.1461.

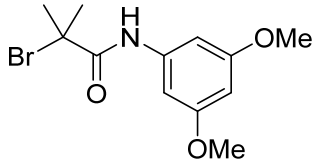
The radical precursors **A1** and **A2** were synthesized according to the reported literature.[15] The radical precursors **A3** and **A4** were commercially available.

For the synthesis of **A1**: To a stirred solution of 3,5-dimethoxyaniline (1.53 g, 10 mmol, 1.0 equiv) and triethylamine (4.17 mL, 3.03 g, 30 mmol, 3.0 equiv) in anhydrous DCM (100 mL) was added 2-bromoisobutyryl bromide (1.23 mL, 2.29 g, 10 mmol, 1.0 equiv) dropwise at 0 °C. After the addition was completed, the reaction was allowed to return to room temperature and stirred overnight. Then, the mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **A1** as a white solid.

For the synthesis of **A2**: To a solution of 3,5-dichlorophenol (1.62 g, 10 mmol, 1.0 equiv) and Et_3N (2.08 mL, 15 mmol, 1.5 equiv) in THF (30 mL) was added 2-bromoisobutyryl bromide (1.8 mL, 15 mmol, 1.5 equiv) dropwise under argon for 5 min at 0 °C. The reaction mixture was stirred at room temperature for 12 h and then filtrated through a short pad of silica. The filtrate was concentrated in vacuo, and the residue was diluted in DCM (60 mL) and washed with 0.1 M HCl aq. solution (40 mL) and sat. $NaHCO_3$ solution (40 mL) sequentially. The organic layer was dried over anhydrous Na_2SO_4,

filtrated, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to afford **A2** as a white solid.

2-Bromo-*N*-(3,5-dimethoxyphenyl)-2-methylpropanamide (A1)

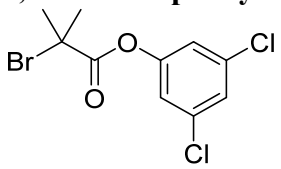


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 6.78 (d, J = 2.3 Hz, 2H), 6.26 (t, J = 2.2 Hz, 1H), 3.77 (s, 6H), 2.03 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 161.1, 139.2, 98.1, 97.5, 63.1, 55.5, 32.6.

HRMS (ESI) m/z calcd. for $C_{12}H_{17}BrNO_3$ $[M + H]^+$ 302.0386, found 302.0388.

3,5-Dichlorophenyl 2-bromo-2-methylpropanoate (A2)



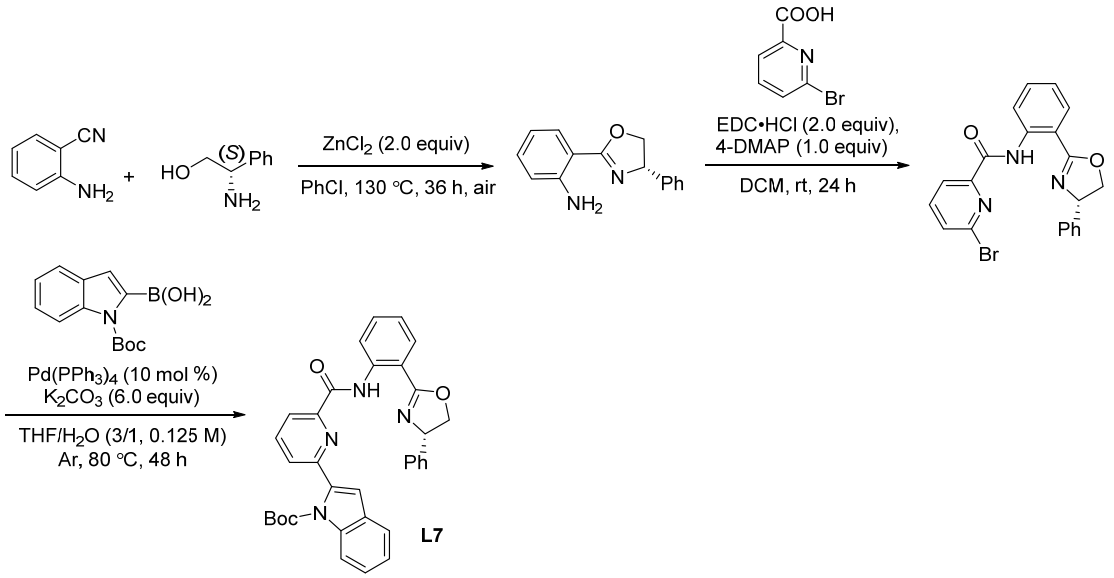
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (t, J = 1.9 Hz, 1H), 7.10 (d, J = 1.9 Hz, 2H), 2.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 151.4, 135.5, 126.8, 120.5, 54.8, 30.6.

HRMS (ESI) m/z calcd. for $C_{10}H_{10}BrCl_2O_2$ $[M + H]^+$ 310.9236, found 310.9236.

Procedures for the synthesis of chiral ligands

Procedures for the synthesis of chiral ligand L7



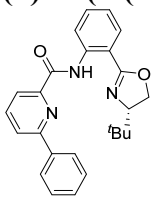
Synthesis of *(S)*-2-(4-phenyl-4,5-dihydrooxazol-2-yl)aniline: Under argon atmosphere, a dry 100 mL round-bottom flask equipped with a magnetic stir bar was charged with 2-aminobenzonitrile (1.18 g, 10 mmol, 1.0 equiv), *(S)*-2-amino-2-phenylethan-1-ol (1.65 g, 12 mmol, 1.2 equiv), dry $ZnCl_2$ (2.72 g, 20 mmol, 2.0 equiv), and chlorobenzene (40 mL). Then, the reaction mixture was refluxed for 36 h before being quenched with H_2O, EtOAc, and 2 mL ethylenediamine. The reaction mixture was extracted with EtOAc and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired amine as a white solid.

Synthesis of *(S)*-6-bromo-*N*-(2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenyl)picolinamide: Under atmospheric condition, a dry 50 mL round-bottom flask equipped with a magnetic stir bar was charged with *(S)*-2-(4-phenyl-4,5-dihydrooxazol-2-yl)aniline (1.19 g, 5.0 mmol, 1.0 equiv), 6-bromopicolinic acid (1.52 g, 7.5 mmol, 1.5 equiv), EDCI (1.92 g, 10 mmol, 2.0 equiv), 4-DMAP (0.61 g, 5.0 mmol, 1.0 equiv), and DCM (20 mL), and then the mixture was stirred at room temperature for 24 h. Upon completion, the reaction mixture was extracted with DCM and dried over anhydrous Na_2SO_4. After filtration, the organic layer was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired product as a white solid.

Synthesis of L7 (Suzuki-Miyaura coupling): A flame-dried 100 mL Schlenk tube

equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (432 mg, 0.40 mmol, 10 mol %), *(S)*-6-bromo-N-(2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenyl)picolinamide (1.60 g, 4.0 mmol, 1.0 equiv), (1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)boronic acid (1.68 g, 6.4 mmol, 1.6 equiv), and K_2CO_3 (3.32 g, 24.0 mmol, 6.0 equiv). The tube was evacuated and backfilled with argon three times, then analytically pure THF (24.0 mL) and H_2O (8 mL) were added into the mixture, and the reaction mixture was stirred at 80 °C for 48 h. Upon completion, the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired chiral ligand **L7** as a white solid. Chiral ligands **L4**, **L5**, **L6**, and **L8** were prepared following procedures similar to those of chiral ligand **L7**, using corresponding chiral amino alcohols and aryl boronic acids.

(*S*)-*N*-(2-(4-(*tert*-Butyl)-4,5-dihydrooxazol-2-yl)phenyl)-6-phenylpicolinamide (L4)



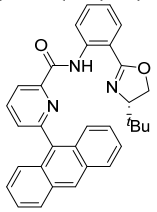
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **L4** (1.44 g, 90% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.64 (s, 1H), 8.99 (dd, J = 8.5, 1.1 Hz, 1H), 8.22 (dd, J = 7.3, 1.2 Hz, 1H), 8.19 – 8.08 (m, 2H), 8.02 – 7.81 (m, 3H), 7.65 – 7.40 (m, 4H), 7.15 (td, J = 7.6, 1.2 Hz, 1H), 4.34 – 4.17 (m, 2H), 4.11 (dd, J = 10.0, 6.3 Hz, 1H), 0.54 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 162.7, 156.2, 151.4, 139.8, 138.7, 138.1, 132.3, 129.6, 129.4, 128.7, 127.7, 122.9, 122.8, 121.4, 120.6, 114.9, 76.1, 67.4, 34.2, 25.4.

HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{26}N_3O_2$ $[M + H]^+$ 400.2020, found 400.2015.

(*S*)-*N*-(2-(4-(*tert*-Butyl)-4,5-dihydrooxazol-2-yl)phenyl)-6-phenylpicolinamide (L5)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **L5** (1.48 g, 74% yield) as a white solid.

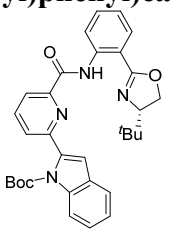
^{1}H NMR (400 MHz, $CDCl_3$): δ 13.29 (s, 1H), 9.01 (dd, J = 8.6, 1.1 Hz, 1H), 8.58 (s, 1H), 8.50 (dd, J = 7.9, 1.1 Hz, 1H), 8.18 – 8.02 (m, 3H), 7.76 (dd, J = 7.8, 1.7 Hz, 1H),

7.72 – 7.62 (m, 3H), 7.55 – 7.44 (m, 3H), 7.43 – 7.32 (m, 2H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 3.69 – 3.51 (m, 2H), 2.68 (dd, *J* = 9.8, 6.8 Hz, 1H), 0.00 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 161.9, 156.9, 151.3, 139.0, 137.6, 134.9, 132.0, 131.5(8), 131.5(6), 130.4, 130.3, 129.9, 129.3, 128.6, 128.4, 127.8, 126.7, 126.2, 126.0, 125.9, 125.4, 125.3, 123.0, 121.8, 120.8, 115.9, 75.2, 67.4, 33.2, 24.7.

HRMS (ESI) *m*/*z* calcd. for $C_{33}H_{30}N_3O_2$ $[M + H]^+$ 500.2333, found 500.2328.

tert-Butyl (*S*)-2-(6-((2-(4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)pyridin-2-yl)-1*H*-indole-1-carboxylate (L6)



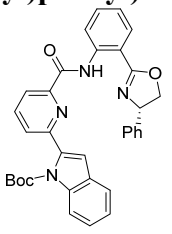
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **L6** (2.07 g, 96% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.82 (s, 1H), 9.07 (d, *J* = 9.7 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.22 (d, *J* = 9.5 Hz, 1H), 7.95 (t, *J* = 7.8 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.72 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.51 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.39 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.29 (td, *J* = 7.5, 1.1 Hz, 1H), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H), 6.84 (s, 1H), 4.22 (dd, *J* = 9.9, 8.5 Hz, 1H), 4.13 (dd, *J* = 8.5, 6.2 Hz, 1H), 3.97 (dd, *J* = 9.9, 6.2 Hz, 1H), 1.19 (s, 9H), 0.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 162.2, 151.9, 150.6, 150.0, 139.5, 139.0, 138.1, 137.7, 132.1, 129.4, 128.9, 125.3, 125.2, 123.2, 122.8, 121.4, 121.3, 120.2, 115.1, 114.9, 111.5, 83.6, 75.4, 67.7, 33.7, 27.6, 25.0.

HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{35}N_4O_4$ $[M + H]^+$ 539.2653, found 539.2652.

tert-Butyl (*S*)-2-(6-((2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenyl)carbamoyl)pyridin-2-yl)-1*H*-indole-1-carboxylate (L7)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **L7** (2.10 g, 94% yield) as a white solid.

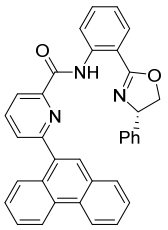
^{1}H NMR (400 MHz, $CDCl_3$): δ 14.21 (s, 1H), 9.15 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 6.8

Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 8.01 – 7.87 (m, 2H), 7.64 – 7.52 (m, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.0 Hz, 1H), 6.93 – 6.74 (m, 3H), 6.60 (d, *J* = 7.3 Hz, 2H), 6.53 (s, 1H), 5.49 (dd, *J* = 10.1, 7.3 Hz, 1H), 4.69 (dd, *J* = 10.2, 8.1 Hz, 1H), 4.06 (dd, *J* = 8.1, 7.3 Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 163.7, 152.1, 150.2, 150.0, 142.0, 139.8, 138.4, 137.8, 137.5, 132.6, 129.7, 128.8, 127.9, 126.5, 125.6, 125.4, 125.1, 122.9, 122.8, 121.2, 121.2, 120.2, 114.8, 114.7, 111.5, 83.5, 73.7, 69.4, 27.6.

HRMS (ESI) *m*/*z* calcd. for $C_{34}H_{31}N_4O_4$ $[M + H]^+$ 559.2340, found 559.2340.

(S)-6-(Phenanthren-9-yl)-*N*-(2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenyl)picolinamide (L8)



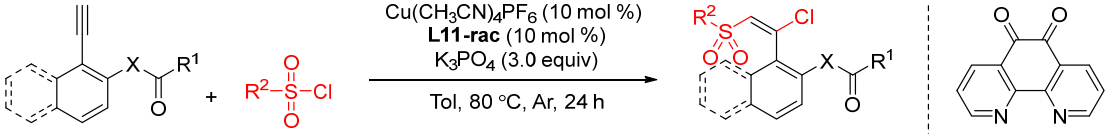
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **L8** (1.45 g, 70% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 14.20 (s, 1H), 9.19 (d, *J* = 8.5 Hz, 1H), 8.70 (d, *J* = 8.3 Hz, 1H), 8.65 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 7.7 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 8.01 (t, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.74 – 7.53 (m, 6H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.61 – 6.44 (m, 3H), 6.40 – 6.29 (m, 2H), 4.29 (ddd, *J* = 34.0, 10.2, 7.5 Hz, 2H), 3.82 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 163.5, 158.1, 150.6, 141.5, 139.9, 137.9, 136.5, 132.6, 131.4, 130.8, 130.6, 130.4, 129.5, 129.0, 128.8, 127.7, 127.5, 127.1, 126.9, 126.8, 126.5, 126.5, 126.2, 125.2, 122.8(2), 122.7(6), 122.6, 121.2, 120.3, 114.8, 73.3, 69.1.

HRMS (ESI) *m*/*z* calcd. for $C_{35}H_{26}N_3O_2$ $[M + H]^+$ 520.2020, found 520.2019.

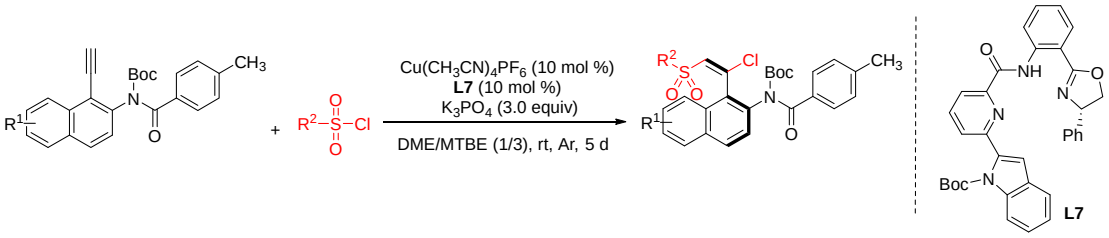
General procedure for the synthesis of racemates



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (3.73 mg, 0.010 mmol, 10 mol %), **L11-rac** (2.10 mg, 0.010 mmol, 10 mol %), alkyne (0.10 mmol, 1.0 equiv), sulfonyl chloride (0.15 mmol, 1.5 equiv), and K_3PO_4 (63.7 mg, 0.30 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Toluene (2.0 mL) was added to the mixture, and the reaction mixture was stirred at 80 °C for 24 h. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

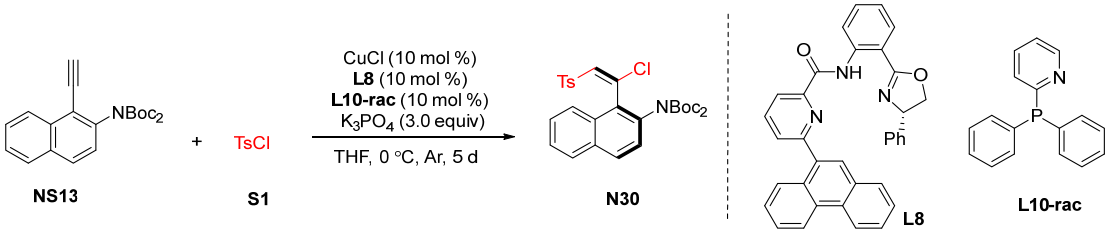
Procedures for the asymmetric chlorine atom transfer radical addition of alkynes

Procedure I:



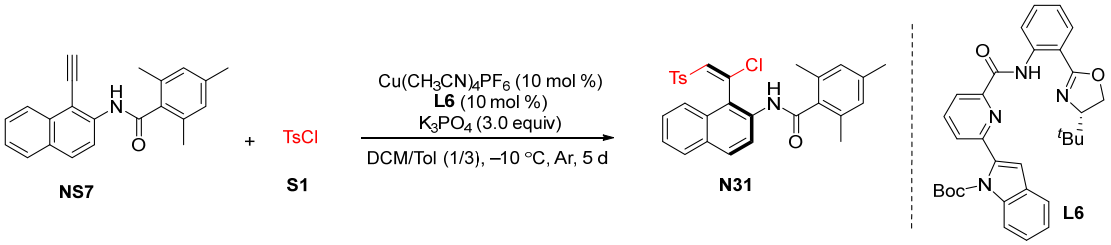
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L7** (11.2 mg, 0.020 mmol, 10 mol %), alkyne (0.20 mmol, 1.0 equiv), sulfonyl chloride (0.30 mmol, 1.5 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Anhydrous DME (1.0 mL) and MTBE (3.0 mL) were added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Procedure II:



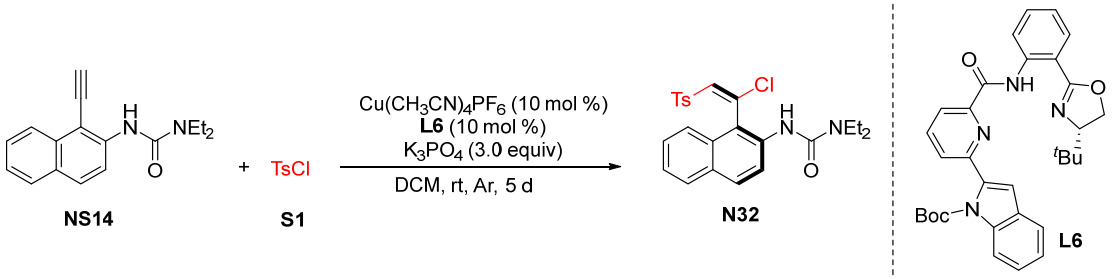
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuCl (1.97 mg, 0.020 mmol, 10 mol %), **L8** (10.4 mg, 0.020 mmol, 10 mol %), **L10-rac** (5.26 mg, 0.020 mmol, 10 mol %), **NS13** (73.5 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Anhydrous THF (4.0 mL) was added to the mixture, and the reaction mixture was stirred at 0 °C for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Procedure III:



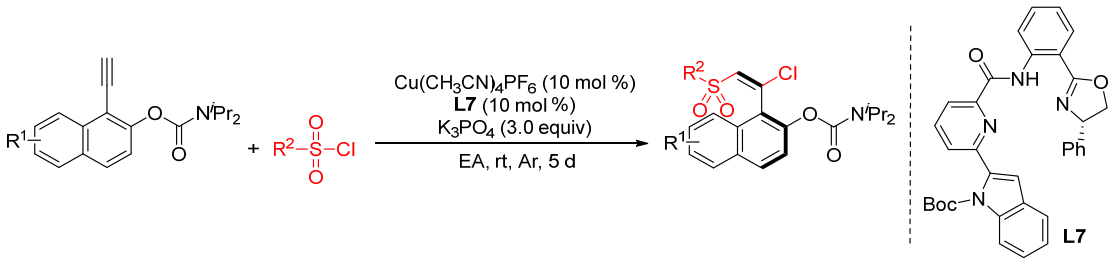
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L6** (10.8 mg, 0.020 mmol, 10 mol %), **NS7** (62.7 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.30 mmol, 1.5 equiv) and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Anhydrous DCM (1.0 mL) and toluene (3.0 mL) were added to the mixture, and the reaction mixture was stirred at −10 °C for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Procedure IV:



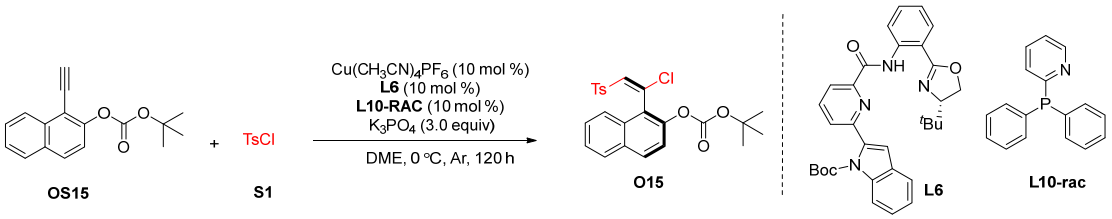
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L6** (10.8 mg, 0.020 mmol, 10 mol %), **NS14** (53.3 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Anhydrous DCM (4.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Procedure V:



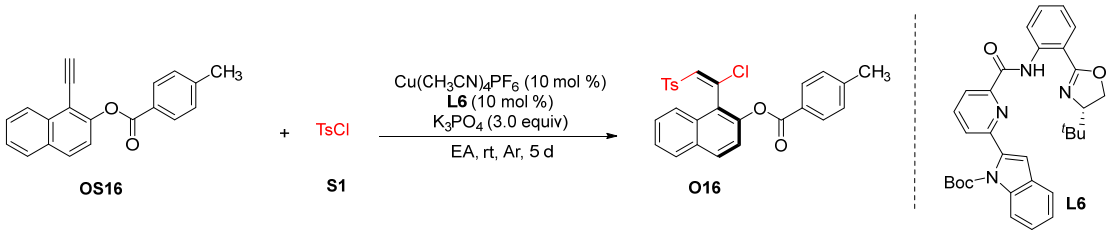
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L7** (11.2 mg, 0.020 mmol, 10 mol %), alkyne (0.20 mmol, 1.0 equiv), sulfonyl chloride (0.30 mmol, 1.5 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Anhydrous EtOAc (4.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Procedure VI:



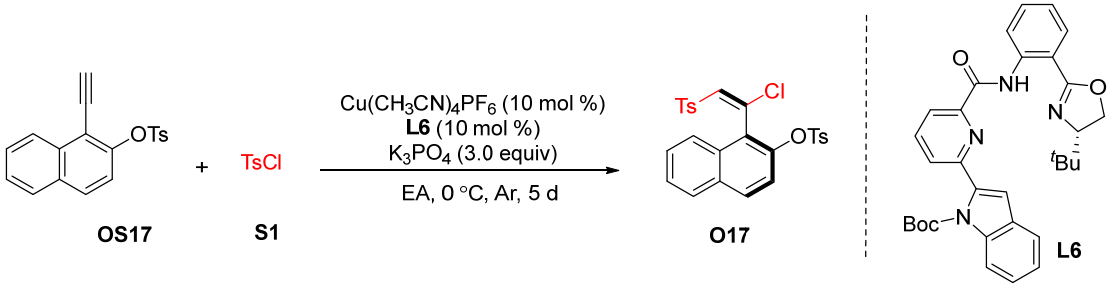
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L6** (10.8 mg, 0.020 mmol, 10 mol %), **OS15** (53.7 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Anhydrous DME (4.0 mL) was added to the mixture, and the reaction mixture was stirred at 0 °C for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Procedure VII:



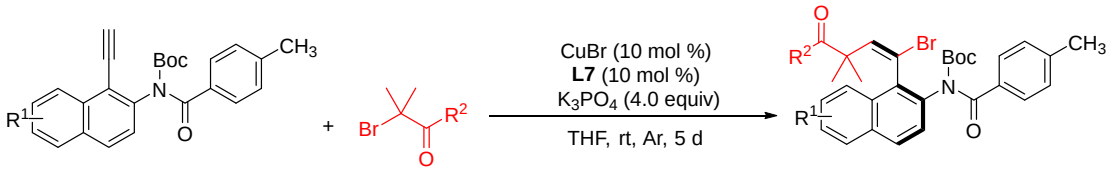
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L6** (10.8 mg, 0.020 mmol, 10 mol %), **OS16** (57.2 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Anhydrous EtOAc (4.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Procedure VIII:



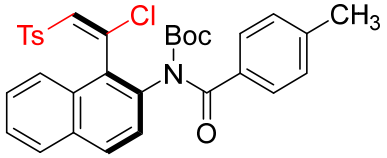
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L6** (10.8 mg, 0.020 mmol, 10 mol %), **OS17** (64.4 mg, 0.20 mmol, 1.0 equiv), **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Anhydrous EtOAc (4.0 mL) was added to the mixture, and the reaction mixture was stirred at 0 °C for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Procedure IX:



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuBr (2.84 mg, 0.020 mmol, 10 mol %), **L7** (11.2 mg, 0.020 mmol, 10 mol %), alkyne (0.20 mmol, 1.0 equiv), radical precursor (0.30 mmol, 1.5 equiv), and K_3PO_4 (169.4 mg, 0.80 mmol, 4.0 equiv). The tube was evacuated and backfilled with argon three times. Anhydrous THF (4.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

***tert*-Butyl (S_a,*E*)-(1-(1-chloro-2-tosylvinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N1)**



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column

chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N1** (92.2 mg, 80% yield, 93% ee) as a pale-yellow solid.

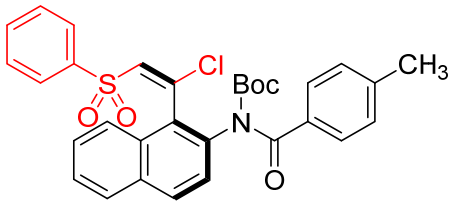
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 – 7.57 (m, 5H), 7.57 – 7.33 (m, 5H), 7.33 – 7.03 (m, 3H), 6.85 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H), 2.18 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 172.6, 152.7, 144.4, 143.1, 141.2, 137.1, 136.0, 135.5, 133.8, 133.7, 132.5, 129.7, 129.5, 129.3, 128.9, 128.5, 128.3, 127.9, 127.0, 126.8(1), 126.7(6), 125.0, 84.0, 28.1, 27.7, 21.5.

HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{31}ClNO_5S$ $[M + H]^+$ 576.1606, found 576.1605.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 11.00 min, t_R (major) = 15.83 min, 93% ee.

tert-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-(phenylsulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N2)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S2** (53.0 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N2** (84.3 mg, 75% yield, 95% ee) as a pale-yellow solid.

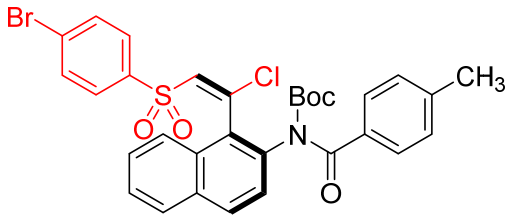
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 7.72 (m, 4H), 7.71 – 7.36 (m, 6H), 7.36 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.21 – 7.05 (m, 3H), 2.44 (s, 3H), 1.44 – 1.22 (br, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 152.7, 143.0, 142.1, 138.9, 136.1, 134.7, 133.6, 133.3, 132.4, 131.2, 129.3, 128.9, 128.6, 128.4, 128.3, 127.8, 127.2, 126.9, 124.8, 83.9, 27.7, 21.8.

HRMS (ESI) *m*/*z* calcd. for $C_{31}H_{29}ClNO_5S$ $[M + H]^+$ 562.1449, found 562.1446.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 19.14 min, t_R (minor) = 24.80 min, 95% ee.

tert-Butyl (*S*$_a$,*E*)-(1-(2-((4-bromophenyl)sulfonyl)-1-chlorovinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N3)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S3** (76.7 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 7/1) to afford **N3** (95.0 mg, 74% yield, 93% ee) as a pale-yellow solid.

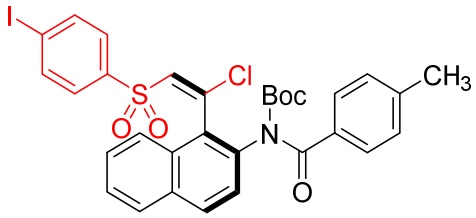
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 – 7.58 (m, 5H), 7.58 – 7.46 (m, 3H), 7.46 – 7.26 (m, 4H), 7.20 – 6.99 (m, 3H), 2.44 (s, 3H), 1.27 (br, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 152.6, 143.2, 142.4, 137.2, 136.3, 135.2, 133.6, 132.4, 131.7, 131.3, 129.9, 129.5, 128.9, 128.8, 128.5, 127.8, 127.4, 127.1, 124.7, 84.1, 27.7, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{28}BrClNO_5S$ $[M + H]^+$ 640.0555, found 640.0550.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 11.55 min, t_R (major) = 17.57 min, 93% ee.

tert-Butyl (S_a,*E*)-(1-(1-chloro-2-((4-iodophenyl)sulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N4)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S4** (90.8 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **N4** (88.1 mg, 64% yield, 92% ee) as a pale-yellow solid.

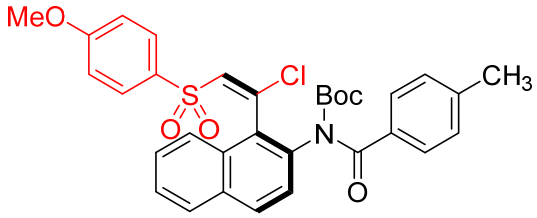
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.51 (m, 6H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.47 – 7.27 (m, 5H), 7.25 – 7.05 (m, 3H), 2.46 (s, 3H), 1.37 – 1.20 (br, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 152.6, 143.2, 142.2, 137.6, 136.5, 135.3, 133.6, 132.3, 131.3, 129.6, 129.0, 128.6, 127.8, 127.5, 127.2, 124.7, 101.7, 84.0, 27.7, 21.9.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{28}ClNIO_5S$ $[M + H]^+$ 688.0416 found 688.0412

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 12.96 min, t_R (major) = 19.53 min, 92% ee.

***tert*-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-((4-methoxyphenyl)sulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N5)**



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S5** (62.0 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **N5** (99.5 mg, 84% yield, 94% ee) as a pale-yellow solid.

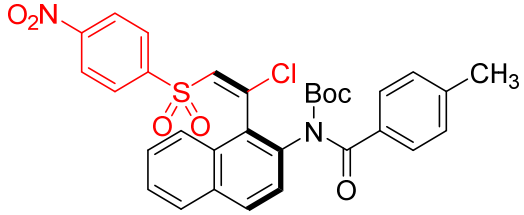
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 7.63 (m, 4H), 7.62 – 7.38 (m, 5H), 7.29 (s, 2H), 7.16 (s, 2H), 6.47 (d, J = 8.9 Hz, 2H), 3.67 (s, 3H), 2.43 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 163.4, 152.7, 143.1, 141.0, 140.2, 136.3, 135.8, 134.9, 133.7, 132.5, 131.1, 130.7, 130.2, 129.4, 128.9, 128.2, 127.9, 127.1, 126.8, 125.0, 113.7, 84.0, 55.5, 27.7, 21.8.

HRMS (ESI) m/z calcd. for $C_{32}H_{31}ClNO_6S$ $[M + H]^+$ 592.1555, found 592.1550.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 13.26 min, t_R (major) = 21.33 min, 94% ee.

***tert*-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-((4-nitrophenyl)sulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N6)**



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S6** (66.5 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N6** (48.0 mg, 40% yield, 91% ee) as a pale-yellow solid.

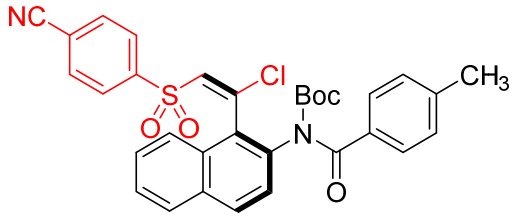
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 7.55 (m, 8H), 7.50 (d, J = 8.6 Hz, 1H), 7.42 – 7.11 (m, 6H), 2.45 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 152.8, 149.5, 143.5, 137.0, 135.3, 133.6, 132.2, 131.6, 130.0, 129.6, 129.0, 128.3, 127.9, 127.3, 124.6, 123.4, 123.0, 84.3, 27.7, 21.8.

HRMS (ESI) m/z calcd. for $C_{31}H_{28}ClN_2O_7S$ $[M + H]^+$ 607.1300, found 607.1298.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 15.61 min, t_R (major) = 25.33 min, 91% ee.

tert-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-((4-cyanophenyl)sulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N7)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S7** (60.5 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **N7** (63.0 mg, 54% yield, 92% ee) as a pale-yellow solid.

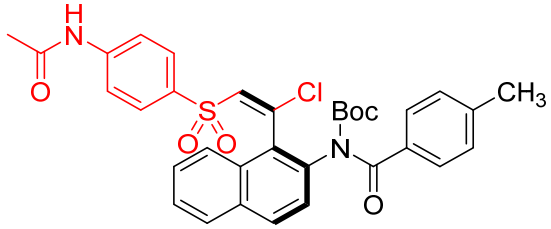
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 7.73 (m, 4H), 7.73 – 7.51 (m, 4H), 7.49 (d, J = 8.6 Hz, 1H), 7.46 – 7.26 (m, 3H), 7.23 – 7.06 (m, 3H), 2.45 (s, 3H), 1.27 (br, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 152.5, 143.4, 142.3, 141.9, 136.8, 135.0, 133.6, 133.0, 132.2, 131.7, 131.5, 129.4, 129.1, 129.0, 128.5, 127.9, 127.3, 124.6, 117.0, 116.4, 84.3, 27.7, 21.8.

HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{28}ClN_2O_5S$ $[M + H]^+$ 587.1402, found 587.1395.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 17.13 min, t_R (major) = 38.43 min, 92% ee.

tert-Butyl (*S*$_a$,*E*)-(1-(2-((4-acetamidophenyl)sulfonyl)-1-chlorovinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N8)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S8** (70.1 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/2) to afford **N8** (85.0 mg, 69% yield, 94% ee) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26– 7.99 (m, 1H), 7.98 – 7.60 (m, 4H), 7.60 – 7.27 (m, 5H), 7.26 – 6.95 (m, 5H), 2.63 – 2.27 (m, 3H), 1.92 (s, 3H), 1.44 – 1.08 (m, 9H).

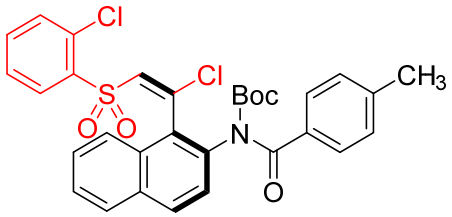
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 172.5, 169.4, 152.6, 143.4, 141.2, 135.8, 134.8,

133.8, 133.5, 132.5, 131.3, 130.1, 129.3, 129.0, 128.4, 127.6, 127.1, 124.7, 118.9, 84.3, 27.6, 24.5, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{33}H_{32}ClN_2O_6S$ $[M + H]^+$ 619.1664, found 619.1661.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 21.39 min, t_R (major) = 23.70 min, 94% ee.

tert-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-((2-chlorophenyl)sulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N9)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S9** (63.3 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N9** (47.7 mg, 40% yield, 92% ee) as a pale-yellow solid.

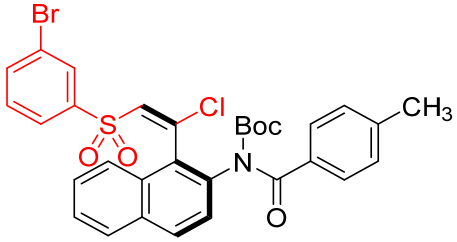
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 – 7.27 (m, 11H), 7.25 – 7.15 (m, 1H), 7.04 (s, 2H), 6.84 (s, 1H), 2.44 (s, 3H), 1.38 – 1.16 (br, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 152.5, 144.2, 143.2, 136.5, 134.0, 132.3, 131.9, 131.0, 129.6, 128.9, 128.2, 127.7, 127.1, 126.9, 126.3, 124.9, 83.8, 27.7, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{28}Cl_2NO_5S$ $[M + H]^+$ 596.1060, found 596.1054.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 16.66 min, t_R (minor) = 19.04 min, 92% ee.

tert-Butyl (*S*$_a$,*E*)-(1-(2-((3-bromophenyl)sulfonyl)-1-chlorovinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N10)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S10** (76.7 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N10** (97.5mg, 76% yield, 91% ee) as a pale-yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 7.71 (m, 4H), 7.68 (s, 1H), 7.65 – 7.35 (m, 5H),

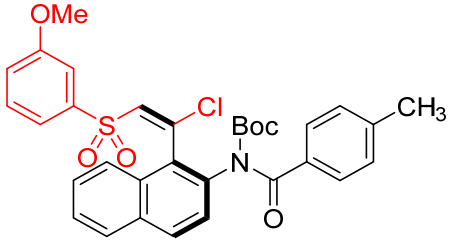
7.35 – 7.26 (m, 2H), 7.23 – 7.07 (m, 2H), 6.86 (s, 1H), 2.43 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 152.6, 143.1, 140.3, 136.3, 134.8, 133.6, 132.3, 131.6, 131.2, 129.8, 129.4, 128.9, 128.4, 127.7, 127.4, 127.1, 124.4, 122.6, 84.0, 27.7, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{28}BrClNO_5S$ $[M + H]^+$ 640.0555, found 640.0552.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 11.30 min, t_R (major) = 16.04 min, 91% ee.

tert-Butyl (S_a,*E*)-(1-(1-chloro-2-((3-methoxyphenyl)sulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N11)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S11** (62.0 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N11** (83.0mg, 70% yield, 94% ee) as a pale-yellow solid.

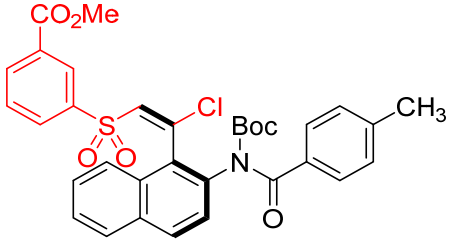
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 7.60 (m, 5H), 7.59 – 7.26 (m, 5H), 7.24 – 7.01 (m, 3H), 6.96 (t, J = 7.6 Hz, 1H), 6.71 (s, 1H), 3.65 (s, 3H), 2.42 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 159.3, 152.6, 142.9, 142.1, 139.9, 136.1, 134.9, 133.6, 132.4, 131.2, 129.6, 129.4, 128.9, 128.3, 127.8, 127.1, 126.9, 124.8, 120.6, 120.3, 112.4, 83.9, 55.5, 27.6, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{32}H_{31}ClNO_6S$ $[M + H]^+$ 592.1555, found 592.1551.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 12.29 min, t_R (major) = 16.88 min, 94% ee.

Methyl (S_a,*E*)-3-((2-(2-(*N*-(*tert*-butoxycarbonyl)-4-methylbenzamido)naphthalen-1-yl)-2-chlorovinyl)sulfonyl)benzoate (N12)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S12** (70.4 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column

chromatography (petroleum ether/ethyl acetate = 4/1) to afford **N12** (85.6mg, 69% yield, 91% ee) as a pale-yellow oil.

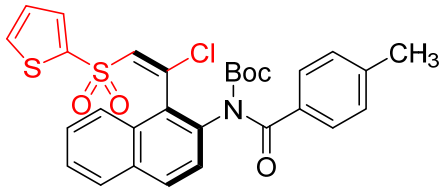
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.10 –7.58(m, 6H), 7.57 – 7.27 (m, 5H), 7.24 – 7.02 (m, 3H), 3.90 (s, 3H), 2.43 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 165.0, 152.6, 143.2, 142.7, 139.2, 136.3, 134.8, 134.0, 133.6, 132.7, 132.3, 131.3, 130.7, 129.4, 128.9, 128.5, 128.3, 127.8, 127.2, 127.0, 124.6, 84.0, 52.5, 27.6, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{33}H_{31}ClNO_7S$ $[M + H]^+$ 620.1504, found 620.1500.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 12.66 min, t_R (major) = 17.51 min, 91% ee.

tert-Butyl (S_a,*E*)-(1-(1-chloro-2-(thiophen-2-ylsulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N13)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S13** (54.8 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **N13** (91.5 mg, 81% yield, 94% ee) as a pale-yellow solid.

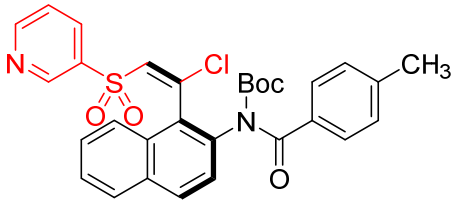
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz, 1H), 7.97 – 7.72 (m, 3H), 7.72 – 7.59 (m, 1H), 7.59 – 7.43 (m, 3H), 7.39 (d, *J* = 5.0 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.13 (m, 1H), 6.69 (s, 1H), 2.44 (s, 3H), 1.32 (br, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 152.7, 143.0, 142.1, 140.0, 135.8, 135.4, 134.4, 133.5, 132.5, 131.2, 129.9, 129.2, 128.9, 128.4, 127.8, 127.7, 127.4, 127.0, 124.8, 84.0, 27.7, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{27}ClNO_5S_2$ $[M + H]^+$ 568.1014, found 568.1006.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 70/30, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 14.64 min, t_R (major) = 17.01 min, 94% ee.

tert-Butyl (S_a,*E*)-(1-(1-chloro-2-(pyridin-3-ylsulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N14)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S14** (53.3 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford **N14** (52.0 mg, 46% yield, 92% ee) as a pale-yellow solid.

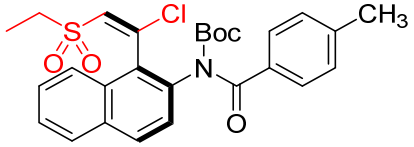
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.33 (s, 1H), 8.09 – 7.62 (m, 5H), 7.61 – 7.36 (m, 4H), 7.36 – 7.28 (m, 1H), 7.24 – 7.09 (s, 1H), 6.87 (s, 1H), 2.44 (s, 3H), 1.36 – 1.16 (br, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 153.3, 152.6, 149.3, 143.3, 136.2, 135.2, 134.8, 133.5, 132.3, 131.6, 129.3, 129.0, 128.4, 127.8, 127.2, 124.4, 122.8, 84.1, 27.7, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{27}ClN_2O_5SNa$ $[M+Na]^+$ 585.1221, found 585.1222.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 11.69 min, t_R (major) = 15.36 min, 92% ee.

tert-Butyl (S_a,*E*)-(1-(1-chloro-2-(ethylsulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N15)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S15** (38.6 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **N15** (83 mg, 81% yield, 93% ee) as a pale-yellow oil.

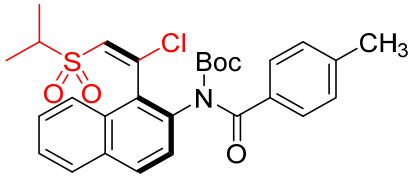
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J = 8.7 Hz, 1H), 8.00 – 7.93 (m, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.7 Hz, 2H), 7.66 – 7.55 (m, 2H), 7.44 (d, J = 8.7 Hz, 1H), 7.32 (d, J = 7.9 Hz, 2H), 7.20 – 6.94 (m, 1H), 3.07 – 2.53 (m, 2H), 2.46 (s, 3H), 1.28 (s, 10H), 1.14 – 0.81 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 152.7, 143.1, 134.9, 133.5, 132.5, 131.4, 129.9, 129.0, 128.9, 128.4, 127.8, 127.3, 127.1, 124.9, 83.9, 49.0, 27.6, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{29}ClNO_5S$ $[M+H]^+$ 514.1449, found 514.1447.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 19.60 min, t_R (minor) = 35.09 min, 93% ee.

***tert*-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-(isopropylsulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N16)**



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S16** (42.8 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **N16** (44.5 mg, 42% yield, 96% ee) as a pale-yellow oil.

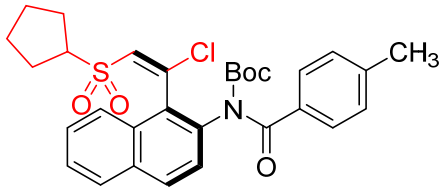
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.79 (m, 5H), 7.66 – 7.52 (m, 2H), 7.43 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 7.03 (s, 1H), 3.03 (d, J = 80.9 Hz, 1H), 2.45 (s, 3H), 1.34 – 1.22 (br, 11H), 1.14 – 0.68 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 152.8, 144.0, 143.2, 133.5(4), 133.5(0), 132.5, 131.4, 130.1, 129.1, 128.5, 127.6, 127.1, 125.1, 83.9, 54.8, 27.7, 21.8, 15.5, 13.5.

HRMS (ESI) *m*/*z* calcd. for $C_{28}H_{31}ClNO_5S$ $[M + H]^+$ 528.1606, found 528.1603.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 15.22 min, t_R (minor) = 20.72 min, 96% ee.

***tert*-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-(cyclopentylsulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N17)**



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S17** (50.6 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **N17** (60.0 mg, 54% yield, 96% ee) as a pale-yellow oil.

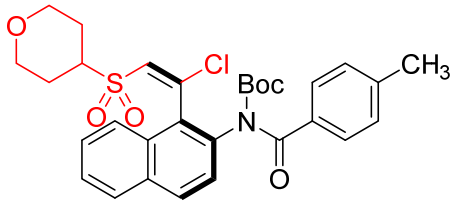
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.88 (m, 3H), 7.86 (d, J = 7.9 Hz, 2H), 7.65 – 7.53 (m, 2H), 7.43 (d, J = 8.7 Hz, 1H), 7.32 (d, J = 7.8 Hz, 2H), 7.10 – 6.92 (m, 1H), 3.53 – 2.97 (m, 1H), 2.46 (s, 3H), 2.13 – 1.35 (m, 8H), 1.28 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 152.7, 143.3, 134.8, 133.6, 132.5, 131.3, 131.2, 129.1, 129.0, 128.4, 127.6, 127.4, 127.1, 125.1, 83.8, 63.0, 27.7, 27.4, 25.9, 25.5, 24.9, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{33}ClNO_5S$ $[M + H]^+$ 554.1762, found 554.1760.

HPLC condition: Chiralcel IG, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 22.79 min, t_R (minor) = 31.31 min, 96% ee.

tert-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-((tetrahydro-2*H*-pyran-4-yl)sulfonyl)vinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N18)



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S18** (55.4 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford **N18** (51.3mg, 45% yield, 95% ee) as a pale-yellow solid.

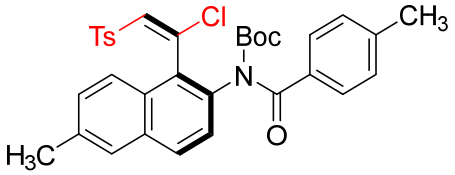
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.89 (m, 3H), 7.84 (d, J = 7.8 Hz, 2H), 7.66 – 7.54 (m, 2H), 7.43 (d, J = 8.7 Hz, 1H), 7.33 (d, J = 7.7 Hz, 2H), 7.01 (s, 1H), 3.87 (s, 1H), 3.56 (s, 1H), 3.06 (td, J = 11.5, 2.7 Hz, 1H), 2.94 (s, 1H), 2.45 (s, 1H), 1.92 – 1.48 (m, 4H), 1.27 (s, 9H), 1.05 (d, J = 12.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 152.5, 144.6, 143.5, 134.5, 133.7, 132.4, 131.6, 129.9, 129.5, 129.2, 128.9, 128.4, 127.8, 127.2, 127.1, 125.1, 84.0, 66.4, 65.4, 59.6, 27.7, 26.3, 22.6, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{33}ClNO_6S$ $[M + H]^+$ 570.1712, found 570.1707.

HPLC condition: Chiralcel IH, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 15.80 min, t_R (major) = 23.35 min, 95% ee.

tert-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-tosylvinyl)-6-methylnaphthalen-2-yl)(4-methylbenzoyl)carbamate (N19)



According to **Procedure I** with **NS2** (79.9 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N19** (76.7 mg, 65% yield, 95% ee) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.54 (m, 5H), 7.46 (d, J = 8.7 Hz, 3H), 7.38 –

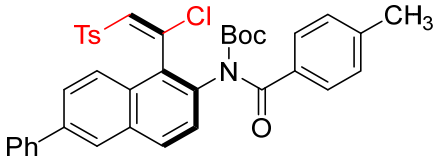
7.27 (m, 2H), 7.25 – 7.04 (m, 2H), 6.86 (d, J = 8.0 Hz, 2H), 2.51 (s, 3H), 2.44 (s, 3H), 2.19 (s, 3H), 1.41 – 1.18 (br, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 152.8, 144.3, 143.1, 141.9, 136.7, 136.0, 135.2, 134.4, 133.8, 132.7, 130.5, 129.4, 129.2, 128.9, 128.5, 127.9, 127.3, 124.8, 83.9, 29.8, 27.7, 21.8, 21.6, 21.5.

HRMS (ESI) m/z calcd. for $C_{33}H_{32}ClNO_5SNa$ $[M + Na]^+$ 612.1582, found 612.1579.

HPLC condition: Chiralcel IE, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 31.03 min, t_R (minor) = 54.59 min, 95% ee.

tert-Butyl (S_a,E)-(1-(1-chloro-2-tosylvinyl)-6-phenylnaphthalen-2-yl)(4-methylbenzoyl)carbamate (N20)



According to **Procedure I** with **NS3** (92.3 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N20** (85.0 mg, 65% yield, 94% ee) as a yellow oil.

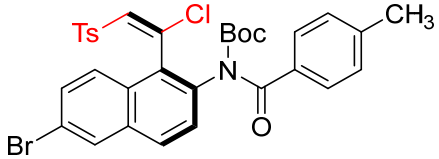
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 7.76 (m, 4H), 7.71 (d, J = 7.6 Hz, 3H), 7.59 – 7.46 (m, 5H), 7.46 – 7.36 (m, 2H), 7.36 – 7.27 (m, 2H), 7.19 (s, 1H), 6.87 (d, J = 8.1 Hz, 2H), 2.45 (s, 3H), 2.14 (s, 3H), 1.47 – 1.18 (br, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1, 152.7, 144.4, 143.1, 141.5, 140.4, 139.6, 135.9, 135.5, 13378, 131.3, 129.4, 129.2, 129.1, 128.9, 128.5, 127.9, 127.5, 126.8, 126.0, 125.6, 84.0, 27.7, 21.8, 21.5.

HRMS (ESI) m/z calcd. for $C_{38}H_{34}ClNO_5SNa$ $[M +Na]^+$ 674.1738, found 674.1738.

HPLC condition: Chiralcel IH, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 16.67 min, t_R (major) = 23.83 min, 94% ee.

tert-Butyl (S_a,E)-(6-bromo-1-(1-chloro-2-tosylvinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N21)



According to **Procedure I** with **NS4** (92.9 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column

chromatography (petroleum ether/ethyl acetate = 6/1) to afford **N21** (70.7 mg, 54% yield, 92% ee) as a yellow oil.

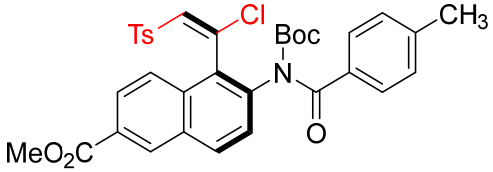
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 7.79 (m, 5H), 7.53 (d, J = 8.8 Hz, 1H), 7.51 – 7.38 (m, 3H), 7.35 – 7.27 (m, 2H), 7.15 (s, 1H), 6.88 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H), 2.24 (s, 3H), 1.33 – 1.19 (br, 9H).

^{13}C NMR (126MHz, $CDCl_3$) δ 172.9, 152.5, 148.2, 144.6, 143.2, 140.9, 135.7, 133.5, 131.6, 130.5, 130.2, 130.0, 129.3, 128.9, 128.4, 126.6, 121.1, 84.1, 27.7, 21.8, 21.6.

HRMS (ESI) m/z calcd. for $C_{32}H_{29}BrClNO_5SNa$ $[M + Na]^+$ 676.0531, found 676.0528.

HPLC condition: Chiralcel IE, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 21.94 min, t_R (minor) = 34.27 min, 92% ee.

Methyl (*S*$_a$,*E*)-6-(*N*-(*tert*-butoxycarbonyl)-4-methylbenzamido)-5-(1-chloro-2-tosylvinyl)-2-naphthoate (N22)



According to **Procedure I** with **NS5** (88.6 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **N22** (63.4 mg, 50% yield, 88% ee) as a pale-yellow oil.

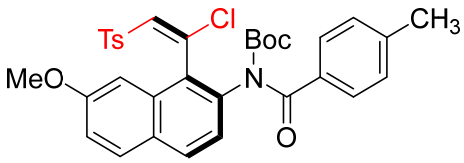
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.22 – 7.60 (m, 5H), 7.57 (d, J = 8.7 Hz, 1H), 7.53 – 7.27 (m, 4H), 7.15 (s, 1H), 6.89 (d, J = 7.8 Hz, 2H), 4.00 (s, 3H), 2.43 (s, 3H), 2.18 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7, 166.7, 152.5, 144.6, 143.2, 140.8, 138.3, 135.9, 135.4, 133.4, 132.2, 131.7, 131.1, 129.4, 128.9, 128.3, 126.6, 125.3, 84.2, 52.5, 27.7, 21.8, 21.5.

HRMS (ESI) m/z calcd. for $C_{34}H_{32}ClNO_7SNa$ $[M + Na]^+$ 656.1480, found 656.1479.

HPLC condition: Chiralcel IND, n-hexane/i-PrOH = 50/50, flow rate 0.8 mL/min. λ = 254 nm, t_R (minor) = 21.10 min, t_R (major) = 40.72 min, 88% ee.

***tert*-Butyl (*S*$_a$,*E*)-(1-(1-chloro-2-tosylvinyl)-7-methoxynaphthalen-2-yl)(4-methylbenzoyl)carbamate (N23)**



According to **Procedure I** with **NS6** (83.0 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg,

0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **N23** (84.9 mg, 70% yield, 56% ee) as a pale-yellow oil.

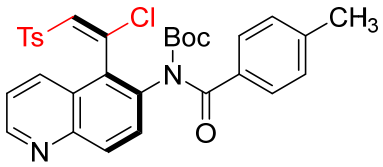
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 – 7.58 (m, 4H), 7.56 – 6.96 (m, 7H), 6.85 (d, J = 8.1 Hz, 2H), 3.79 (s, 3H), 2.43 (s, 3H), 2.19 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 173.5, 158.4, 152.7, 144.5, 143.0, 142.3, 137.3, 135.38, 134.5, 133.8, 130.8, 129.8, 129.4, 129.2, 129.0, 128.9, 128.5, 119.4, 103.5, 83.9, 55.4, 27.7, 21.8, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{33}H_{33}ClNO_6S$ $[M + H]^+$ 606.1712 found 606.1709.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 25.70 min, t_R (minor) = 33.23 min, 56% ee.

tert-Butyl (*Sa,E*)-(5-(1-chloro-2-tosylvinyl)quinolin-6-yl)(4-methylbenzoyl)carbamate (N24)



According to **Procedure I** with **NS15** (77.3 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to afford **N24** (83.7 mg, 82% yield, 90% ee) as a yellow solid.

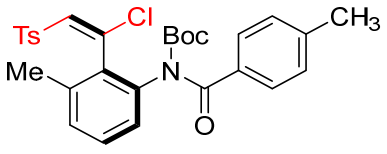
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.92 (s, 1H), 8.52 – 8.01 (m, 1H), 8.04 – 7.49 (m, 4H), 7.50 – 7.00 (m, 6H), 6.87 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H), 2.20 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.8, 152.4, 150.9, 146.9, 144.7, 143.2, 139.8, 136.3, 135.8, 133.4, 133.1, 132.5, 131.8, 129.4, 128.9, 128.4, 125.5, 121.9, 84.2, 27.7, 21.8, 21.5.

HRMS (ESI) *m/z* calcd. For $C_{31}H_{30}ClN_2O_5S$ $[M + H]^+$ 577.1558, found 577.1568.

HPLC condition: Chiralcel IH, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 11.27 min, t_R (major) = 19.26 min, 90% ee.

tert-Butyl (S_a,*E*)-(2-(1-chloro-2-tosylvinyl)-3-methylphenyl)(4-methylbenzoyl)carbamate (N25)



According to **Procedure I** with **NS8** (69.8 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to afford **N25** (87.5mg, 81% yield, 92% ee) as a pale-yellow solid.

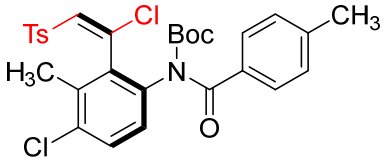
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.38 (m, 5H), 7.38 – 7.27 (m, 1H), 7.24 (d, J = 8.1 Hz, 2H), 7.21 – 6.73 (m, 4H), 2.68 – 2.06 (m, 9H), 1.38 – 1.10 (m, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.8, 152.8, 144.9, 144.2, 142.7, 142.4, 142.0, 137.9, 137.1, 136.2, 133.7, 132.6, 130.4, 129.8, 129.4, 128.8, 128.5, 128.0, 83.3, 27.6, 21.7, 20.0.

HRMS (ESI) m/z calcd. for $C_{29}H_{30}ClNO_5SNa$ $[M + Na]^+$ 562.1425, found562.1422.

HPLC condition: Chiralcel IG, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 20.82 min, t_R (minor) = 32.27 min, 92% ee.

***tert*-Butyl (*S*$_a$,*E*)-(4-chloro-2-(1-chloro-2-tosylvinyl)-3-methylphenyl)(4-methylbenzoyl)carbamate (N26)**



According to **Procedure I** with **NS9** (76.8 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **N26** (100.0 mg, 87% yield, 90% ee) as a pale-yellow oil.

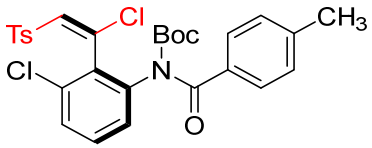
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.65 (m, 2H), 7.65 – 7.38 (m, 3H), 7.35 – 7.27 (m, 1H), 7.22 (d, J = 8.5 Hz, 2H), 7.12 (s, 1H), 7.04 – 6.78 (m, 2H), 2.58 – 2.32 (m, 6H), 2.27 (s, 1H), 2.04 (s, 1H), 1.63 (s, 1H), 1.37 – 1.11 (br, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 152.6, 145.4, 144.6, 143.2, 142.6, 141.7, 141.2, 136.6, 136.4, 136.0, 135.1, 134.5, 133.9, 133.5, 131.2, 129.8, 129.5, 129.3, 128.9, 128.6, 128.1, 84.1, 27.7, 21.8, 17.9.

HRMS (ESI) m/z calcd. for $C_{29}H_{29}Cl_2NO_5SNa$ $[M + Na]^+$ 596.1036, found 596.1032.

HPLC condition: Chiralcel IE, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 19.31 min, t_R (major) = 25.18 min, 90% ee.

***tert*-Butyl (*S*$_a$,*E*)-(3-chloro-2-(1-chloro-2-tosylvinyl)phenyl)(4-methylbenzoyl)carbamate (N27)**



According to **Procedure I** with **NS10** (74.0 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to afford **N27** (78.5 mg, 70% yield, 90% ee) as a pale-yellow oil.

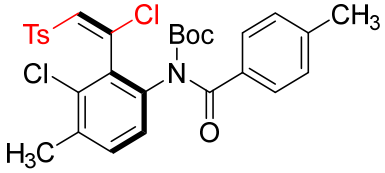
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.53 (m, 4H), 7.48 (d, J = 6.9 Hz, 2H), 7.40 – 7.27 (m, 2H), 7.25 – 6.89 (m, 3H), 6.85 (s, 1H), 2.41 (s, 6H), 1.47-1.06 (br, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 152.5, 145.1, 143.0, 139.8, 139.3, 136.7, 133.2, 131.1, 129.8, 129.3, 129.1, 128.9, 128.4, 84.1, 27.6, 21.8, 21.7.

HRMS (ESI) *m*/*z* calcd. for $C_{28}H_{27}Cl_2NO_5SNa$ $[M + Na]^+$ 582.0879, found 582.0878.

HPLC condition: Chiralcel IG, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 20.70 min, t_R (minor) = 38.73 min, 90% ee.

tert-Butyl (S_a,*E*)-(3-chloro-2-(1-chloro-2-tosylvinyl)-4-methylphenyl)(4-methylbenzoyl)carbamate (N28)



According to **Procedure I** with **NS11** (76.8 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N28** (72.2 mg, 73% yield, 84% ee) as a pale-yellow oil.

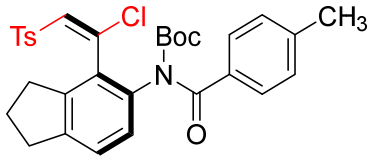
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 – 7.45 (m, 4H), 7.46 – 6.96 (m, 6H), 6.85 (s, 1H), 2.68 – 2.10 (m, 9H), 1.30 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 173.0, 152.6, 144.9, 143.0, 140.6, 136.8, 133.4, 133.2, 132.4, 131.6, 129.7, 129.2, 128.9, 128.6, 128.4, 84.1, 27.6, 21.8, 21.7, 20.5.

HRMS (ESI) *m*/*z* calcd. for $C_{29}H_9Cl_2NO_5SNa$ $[M + Na]^+$ 596.1036, found 596.1031.

HPLC condition: Chiralcel INB, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 254 nm, t_R (major) = 12.32 min, t_R (minor) = 14.35 min, 84% ee.

tert-Butyl (S_a,*E*)-(4-(1-chloro-2-tosylvinyl)-2,3-dihydro-1H-inden-5-yl)(4-methylbenzoyl)carbamate (N29)



According to **Procedure I** with **NS12** (75.1 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N29** (95.8 mg, 84% yield, 86% ee) as a colorless oil.

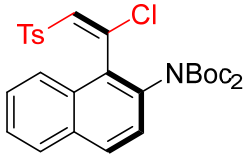
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 – 7.39 (m, 4H), 7.34 (s, 1H), 7.29 – 7.02 (m, 4H), 7.02 – 6.65 (m, 2H), 2.92 (s, 3H), 2.56 – 1.77 (m, 9H), 1.22 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 172.2, 153.0, 144.5, 142.4, 136.7, 134.1, 132.5, 131.6, 130.5, 129.5, 128.9, 128.7, 128.4, 126.7, 83.4, 33.0, 32.1, 27.6, 25.1, 21.7, 21.6.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{33}ClNO_5S$ $[M + H]^+$ 566.1762, found 566.1761.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 26.90 min, t_R (major) = 29.34 min, 86% ee.

tert-Butyl (*S*$_a$,*E*)-(*tert*-butoxycarbonyl)(1-(1-chloro-2-tosylvinyl)naphthalen-2-yl)carbamate (N30)



According to **Procedure II** with **NS13** (73.5 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **N30** (0 °C: 74.8 mg, 67% yield, 91% ee; rt: 52.4 mg, 47% yield, 92% ee, according to **Procedure I**) as a pale-yellow solid.

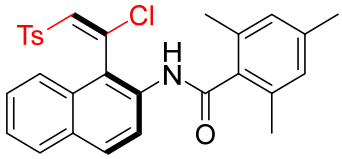
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.65 – 7.34 (m, 6H), 7.13 (d, J = 8.1 Hz, 2H), 7.08 (s, 1H), 2.34 (s, 3H), 1.50 (s, 9H), 1.44 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 144.8, 141.1, 136.9, 135.4, 133.7, 132.4, 130.8, 130.1, 129.6, 129.4, 128.3(9), 128.3(6), 127.8, 127.0, 126.7, 125.1, 83.8, 83.4, 77.4, 28.0, 21.6.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{32}ClNO_6SNa$ $[M + Na]^+$ 580.1531, found 580.1529.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 16.92 min, t_R (minor) = 24.46 min, 91% ee.

(*S*$_a$,*E*)-*N*-(1-(1-chloro-2-tosylvinyl)naphthalen-2-yl)-2,4,6-trimethylbenzamide (N31)



According to **Procedure III** with **NS7** (62.7 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N31** (–10 °C: 81.0 mg, 80% yield, 86% ee; rt: 23.2 mg, 23% yield, 71% ee, according to **Procedure I**) as a pale-yellow solid.

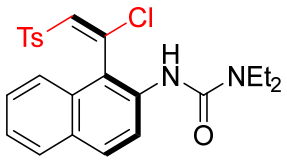
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.9 Hz, 1H), 8.10 (s, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.37 (s, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.12 (t, J = 7.7 Hz, 1H), 7.03 (dd, J = 8.4, 1.1 Hz, 1H), 7.00 – 6.90 (m, 4H), 6.61 (d, J = 8.4 Hz, 2H), 2.49 (s, 6H), 2.34 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 144.7, 139.0, 137.4, 134.7, 134.4, 134.4, 133.2, 131.6, 130.9, 129.1, 129.0, 128.6, 128.1, 127.7, 127.1, 125.6, 123.8, 123.5, 122.5, 21.3, 21.2, 19.3.

HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{27}ClNO_3S$ $[M + H]^+$ 504.1395, found 504.1394.

HPLC condition: Chiralcel INA, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 9.52 min, t_R (major) = 17.98 min, 86% ee.

(*S*$_a$,*E*)-3-(1-(1-chloro-2-tosylvinyl)naphthalen-2-yl)-1,1-diethylurea (N32)



According to **Procedure IV** with **NS14** (53.3 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford **N32** (36.6 mg, 40% yield, 77% ee; 21.9 mg, 24% yield, 44% ee, according to **Procedure I**) as a yellow oil.

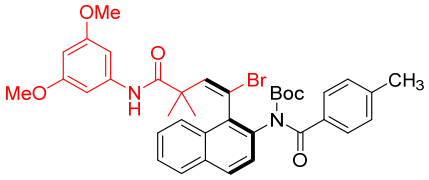
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.45 (s, 1H), 7.30 – 7.23 (m, 2H), 7.11 (t, J = 7.5 Hz, 1H), 7.05 – 6.97 (m, 3H)6.60 (d, J = 8.1 Hz, 2H), 3.57 (dq, J = 14.4, 7.1 Hz, 2H), 3.36 (dq, J = 14.5, 7.2 Hz, 2H), 2.05 (s, 3H), 1.30 (t, J = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.6, 146.0, 144.7, 137.3, 135.4, 134.4, 131.2, 129.9, 129.2, 129.0, 128.0, 127.9, 126.8, 124.8, 123.6, 123.5, 120.2, 41.8, 21.4, 14.0.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}ClN_2O_3S$ $[M + H]^+$ 457.1347, found 457.1342.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.7 mL/min. λ = 254 nm, t_R (minor) = 17.80 min, t_R (major) = 44.14 min, 77% ee.

tert-Butyl (*Sa,E*)-(1-(1-bromo-4-((3,5-dimethoxyphenyl)amino)-3,3-dimethyl-4-oxobut-1-en-1-yl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N33)



According to **Procedure IX** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **A1** (90.7 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N33** (88.0 mg, 64% yield, 87% ee) as a colorless oil.

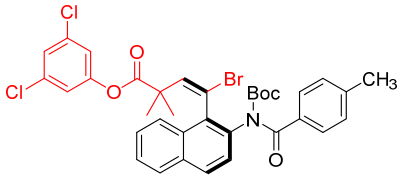
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, J = 8.4, 1.2 Hz, 1H), 7.97 – 7.52 (m, 7H), 7.33 (d, J = 8.7 Hz, 1H), 7.04 (s, 2H), 6.68 (s, 1H), 6.43 (s, 2H), 6.14 (t, J = 2.3 Hz, 1H), 3.70 (s, 6H), 2.32 (s, 3H), 1.24 (s, 3H), 1.19 (s, 9H), 0.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 160.5, 152.4, 142.8, 142.4, 139.6, 135.2, 133.9, 133.3, 132.9, 131.6, 130.2, 128.7, 128.4(6), 128.4(2), 127.5(2), 127.4(8), 127.1, 125.8, 98.4, 97.0, 84.0, 55.4, 49.0, 27.6, 25.7, 21.7.

HRMS (ESI) *m/z* calcd. For $C_{37}H_{40}BrN_2O_6$ $[M + H]^+$ 687.2064, found 687.2061.

HPLC condition: Chiralcel IF, n-hexane/i-PrOH = 60/50, flow rate 0.5 mL/min. λ = 254 nm, t_R (major) = 16.48 min, t_R (minor) = 19.16min, 87% ee.

3,5-Dichlorophenyl (*Sa,E*)-4-bromo-4-(2-(N-(*tert*-butoxycarbonyl)-4-methylbenzamido)naphthalen-1-yl)-2,2-dimethylbut-3-enoate (N34)



According to **Procedure IX** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **A2** (93.6 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **N34** (83.7 mg, 60% yield, 84% ee) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.1 Hz, 1H), 8.01 – 7.74 (m, 4H), 7.66 – 7.52 (m, 2H), 7.38 (d, J = 8.7 Hz, 1H), 7.30 – 7.10 (m, 4H), 6.75 (d, J = 10.9 Hz, 2H),

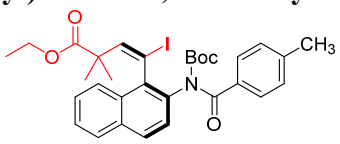
2.36 (s, 3H), 1.21 (s, 9H), 1.09 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 152.5, 151.3, 142.5, 140.4, 135.7, 135.3, 134.8, 134.0, 133.9, 132.8, 131.6, 130.2, 128.8, 128.7, 128.5, 128.0, 127.5, 127.1, 126.0, 125.7, 120.7, 115.1, 114.6, 83.6, 47.7, 27.7, 25.0, 22.4, 21.8.

HRMS (ESI) *m/z* calcd. For $C_{35}H_{32}BrCl_2NO_5Na$ $[M + Na]^+$ 718.0733, found 718.0730.

HPLC condition: Chiralcel IC, n-hexane/i-PrOH = 80/20, flow rate 0.5 mL/min. λ = 254 nm, t_R (major) = 12.15 min, t_R (minor) = 15.15 min, 84% ee.

Ethyl (*Sa,E*)-4-(2-(N-(tert-butoxycarbonyl)-4-methylbenzamido)naphthalen-1-yl)-4-iodo-2,2-dimethylbut-3-enoate (N35)



According to **Procedure IX** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **A4** (72.6 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **N35** (82.8 mg, 66% yield, 0% ee) as a colorless oil.

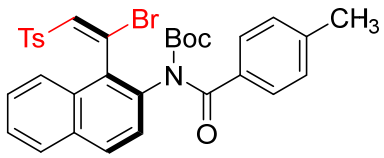
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.8 Hz, 2H), 7.89 (dd, J = 8.5, 3.2 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.35 – 7.27 (m, 3H), 6.89 (s, 1H), 4.02 – 3.61 (m, 2H), 2.45 (s, 3H), 1.26 (s, 9H), 1.14 (t, J = 7.1 Hz, 3H), 0.73 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 172.5, 152.4, 149.9, 142.8, 136.9, 134.6, 134.1, 132.9, 130.8, 129.4, 128.9, 128.3, 128.2, 127.0, 126.3, 88.4, 83.5, 61.0, 49.6, 27.9, 23.7, 22.6, 21.9, 14.2.

HRMS (ESI) *m/z* calcd. For $C_{31}H_{34}INO_5Na$ $[M + Na]^+$ 650.1374, found 650.1376.

HPLC condition: Chiralcel IE, n-hexane/i-PrOH = 90/10, flow rate 0.5 mL/min. λ = 238 nm, t_R (major) = 19.77 min, t_R (minor) = 23.61 min, 0% ee.

***tert*-Butyl-(*Sa,E*)-(1-(1-bromo-2-tosylvinyl)naphthalen-2-yl)(4-methylbenzoyl)carbamate (N1-Br)**



According to **Procedure I** with **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv) and **S1-Br** (70.5 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N1-Br** (90.7 mg, 73%

yield, 34% ee) as a yellow solid.

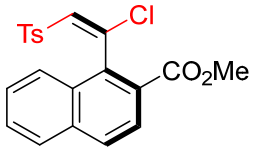
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 – 7.64 (m, 4H), 7.62 – 7.16 (m, 9H), 6.85 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H), 2.18 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.1, 152.7, 144.4, 143.2, 138.4, 137.6, 135.8, 133.9, 132.5, 131.0, 129.5, 129.3, 128.9, 128.5, 128.0, 126.9, 125.1, 84.0, 27.7, 21.8, 21.6.

HRMS (ESI) m/z calcd. For $C_{32}H_{30}BrNSO_5Na$ $[M + Na]^+$ 642.0920, found 642.0931.

HPLC condition: Chiralcel IE, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 11.43 min, t_R (major) = 20.74 min, 34% ee.

Methyl (*Sa,E*)-1-(1-chloro-2-tosylvinyl)-2-naphthoate (AP1)



According to **Procedure IV** with **AS1** (42.0 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **AP1** (65.8 mg, 82% yield, 51% ee) as a white solid.

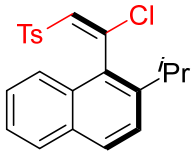
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 8.7 Hz, 1H), 7.84 (dd, J = 8.3, 1.2 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.56 (t, J = 7.0 Hz, 1H), 7.44 (t, J = 8.3 Hz, 1H), 7.21 – 7.13 (m, 3H), 6.92 (d, J = 7.8 Hz, 2H), 3.89 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 146.2, 144.4, 136.7, 135.0, 133.6, 132.3, 130.6, 129.5, 129.4, 128.2(9), 128.2(7), 127.8, 127.7, 126.5, 126.0, 125.6, 52.5, 21.6.

HRMS (ESI) m/z calcd. For $C_{21}H_{17}ClO_4Na$ $[M + Na]^+$ 423.0428, found 423.0431.

HPLC condition: Chiralcel IE, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 19.87 min, t_R (major) = 22.04 min, 51% ee.

(*Sa,E*)-1-(1-Chloro-2-tosylvinyl)-2-isopropylnaphthalene (AP2)



According to **Procedure I** with **AS2** (38.8 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford **AP2** (75.4 mg, 98% yield, 52% ee) as a white solid.

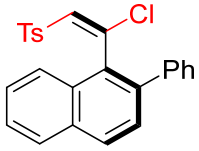
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.7 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 8.7 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.32 – 7.17 (m, 3H), 7.17 – 7.09 (m, 2H), 6.85 (d, J = 8.0 Hz, 2H), 3.37 (p, J = 6.8 Hz, 1H), 2.23 (s, 3H), 1.50 (d, J = 6.7 Hz, 3H), 1.27 (d, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 145.2, 144.5, 136.3, 134.0, 131.8, 130.8, 129.3, 129.2, 128.2, 128.0, 126.8, 125.4, 124.5, 123.7, 31.7, 24.7, 22.4, 21.6.

HRMS (ESI) m/z calcd. for $C_{22}H_{21}ClO_2SNa$ $[M + Na]^+$ 407.0843, found 407.0848.

HPLC condition: Chiralcel AD-H, n-hexane/i-PrOH = 90/10, flow rate 0.3 mL/min. λ = 254 nm, t_R (minor) = 20.33 min, t_R (major) = 22.80 min, 52% ee.

(*Sa,E*)-1-(1-Chloro-2-tosylvinyl)-2-phenylnaphthalene (AP3)



According to **Procedure I** with **AS3** (45.7 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to afford **AP3** (67.1 mg, 80% yield, 43% ee) as a white solid.

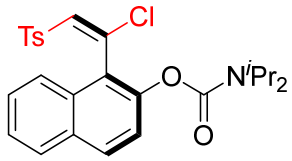
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.64 (dt, J = 7.7, 1.5 Hz, 3H), 7.56 – 7.36 (m, 6H), 7.19 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.87 (s, 1H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 144.7, 140.5, 139.5, 136.9, 133.2, 132.5, 130.4, 129.7, 129.6, 129.4, 128.5, 128.3, 128.2, 127.8(4), 127.8(0), 127.3, 126.2, 125.0, 21.7.

HRMS (ESI) m/z calcd. for $C_{25}H_{19}ClO_2SNa$ $[M + Na]^+$ 441.0686, found 441.0690.

HPLC condition: Chiralcel AD-H, n-hexane/i-PrOH = 70/30, flow rate 0.5 mL/min. λ = 254 nm, t_R (minor) = 17.88 min, t_R (major) = 19.13 min, 43% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O1)



According to **Procedure V** with **OS1** (59.1 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O1** (87.5 mg, 90% yield, 92% ee) as a yellow solid.

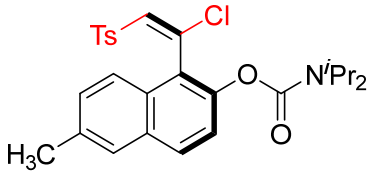
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 7.4 Hz, 1H), 7.52 – 7.32 (m, 4H), 7.29 – 7.24 (m, 2H), 7.22 (s, 1H), 6.89 (d, J = 8.0 Hz, 2H), 4.12 (p, J = 6.8 Hz, 1H), 3.89 (p, J = 7.1 Hz, 1H), 2.23 (s, 3H), 1.47 – 1.09 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 146.6, 144.5, 142.6, 136.2, 134.9, 131.6, 131.26, 130.7, 130.5, 130.2, 129.3, 128.3, 128.2, 127.2, 125.7, 124.2, 122.5, 121.9, 47.09, 46.6, 21.6, 21.3, 21.2, 20.6, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{29}ClNO_4S$ $[M + H]^+$ 486.1500, found 486.1501.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 230 nm, t_R (major) = 15.86 min, t_R (minor) = 17.83 min, 92% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)-6-methylnaphthalen-2-yl diisopropylcarbamate (O2)



According to **Procedure V** with **OS2** (61.9 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O2** (77.0 mg, 77% yield, 90% ee) as a pale-yellow solid.

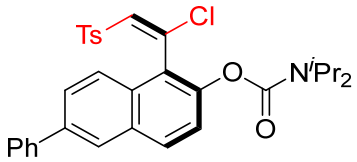
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 9.0 Hz, 1H), 7.55 (s, 1H), 7.38 (dd, J = 8.8, 5.4 Hz, 2H), 7.28 – 7.27 (m, 1H), 7.26 (s, 1H), 7.22 – 7.17 (m, 2H), 6.90 (d, J = 8.0 Hz, 2H), 4.18 – 4.04 (m, 1H), 3.94 – 3.81 (m, 1H), 2.48 (s, 3H), 2.24 (s, 3H), 1.37 – 1.25 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 145.9, 144.4, 142.9, 136.3, 135.4, 134.8, 130.9, 130.6, 129.4, 129.2, 128.3, 128.2, 127.2, 124.1, 122.4, 121.8, 47.1, 46.5, 21.5(6), 21.5(5), 21.3, 21.2, 20.6, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{31}ClNO_4S$ $[M + H]^+$ 500.1657, found 500.1654.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 19.61 min, t_R (minor) = 24.68 min, 90% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)-6-phenylnaphthalen-2-yl diisopropylcarbamate (O3)



According to **Procedure V** with **OS3** (74.3 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O3** (78.7 mg, 70% yield, 92% ee) as a pale-yellow oil.

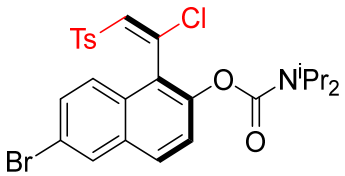
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 1.8 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.63 (dd, J = 8.7, 1.9 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.43 – 7.37 (m, 1H), 7.34 – 7.28 (m, 2H), 7.26 (s, 1H), 6.90 (d, J = 8.1 Hz, 2H), 4.25 – 4.04 (m, 1H), 4.00 – 3.83 (m, 1H), 2.18 (s, 3H), 1.40 – 1.28 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 146.7, 144.5, 142.5, 140.5, 138.5, 136.2, 135.1, 131.5, 131.0, 129.3, 129.1, 128.2, 127.7, 127.4, 126.8, 126.0, 124.8, 122.9, 121.9, 47.1, 46.6, 21.6, 21.3, 21.2, 20.6, 20.5.

HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{33}ClNO_4S$ $[M + H]^+$ 562.1813, found 562.1810.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 23.70 min, t_R (minor) = 35.11 min, 92% ee.

(S_a,*E*)-6-Bromo-1-(1-chloro-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O4)



According to **Procedure V** with **OS4** (74.8 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **O4** (104.2 mg, 92% yield, 92% ee) as a white solid.

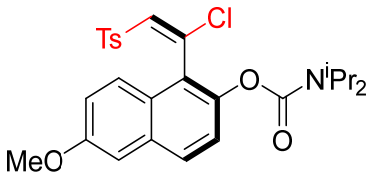
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 2.0 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 9.0 Hz, 1H), 7.40 (dd, J = 8.9, 2.0 Hz, 1H), 7.32 – 7.20 (m, 4H), 6.92 (d, J = 8.1 Hz, 2H), 4.15 – 3.87 (m, 2H), 2.28 (s, 3H), 1.35 – 1.26 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 147.0, 144.8, 142.0, 136.2, 135.4, 131.7, 130.5, 130.2, 130.2, 129.4, 128.7, 128.2, 125.9, 123.8, 122.2, 119.7, 47.2, 46.7, 21.6, 21.3, 21.2, 20.6, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}ClNO_4SBr$ $[M + H]^+$ 564.0605, found 564.0600.

HPLC condition: Chiralcel IG, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 30.51 min, t_R (minor) = 35.68 min, 92% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)-6-methoxynaphthalen-2-yl diisopropylcarbamate (O5)



According to **Procedure V** with **OS5** (65.0 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **O5** (68.1 mg, 64% yield, 92% ee) as a colorless oil.

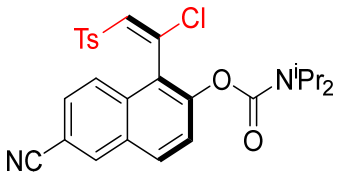
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 9.0 Hz, 1H), 7.39 (dd, J = 10.3, 9.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.22 (s, 1H), 7.11 (d, J = 2.6 Hz, 1H), 7.05 (dd, J = 9.1, 2.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 4.19 – 4.04 (m, 1H), 3.98 – 3.84 (m, 4H), 2.28 (s, 4H), 1.40 – 1.23 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 152.4, 144.9, 144.5, 142.8, 136.3, 134.8, 132.0, 130.0, 129.3, 128.2, 125.7, 125.3, 123.0, 122.0, 119.9, 106.3, 55.5, 47.0, 46.5, 21.6, 21.3, 21.2, 20.6, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{31}ClNO_5S$ $[M + H]^+$ 516.1606, found 516.1605.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 28.95 min, t_R (minor) = 34.97 min, 92% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)-6-cyanonaphthalen-2-yl diisopropylcarbamate (O6)



According to **Procedure V** with **OS6** (64.0 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **O6** (98.1 mg, 95% yield, 87% ee) as a white solid.

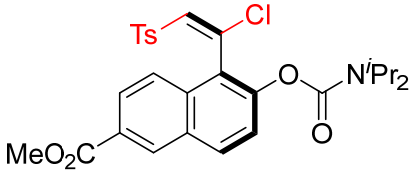
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.54 – 7.50 (m, 1H), 7.34 – 7.22 (m, 3H), 7.01 (d, J = 8.0 Hz, 2H), 4.13 – 3.86 (m, 2H), 2.31 (s, 3H), 1.45 – 1.15 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 149.1, 145.0, 141.3, 136.4, 135.4, 134.1, 132.0, 131.5, 129.6(0), 129.5(5), 128.1, 127.8, 125.6, 124.6, 122.6, 109.3, 47.3, 46.8, 21.6, 21.3, 21.2, 20.6, 20.4.

HRMS (ESI) m/z calcd. for $C_{27}H_{28}ClN_2O_4S$ $[M + H]^+$ 511.1453, found 511.1451.

HPLC condition: Chiralcel IH, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 16.42 min, t_R (major) = 21.38 min, 87% ee.

Methyl (S_a,E)-5-(1-chloro-2-tosylvinyl)-6-((diisopropylcarbamoyl)oxy)-2-naphthoate (O7)



According to **Procedure V** with **OS7** (70.6 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **O7** (101.0 mg, 93% yield, 80% ee) as a yellow oil.

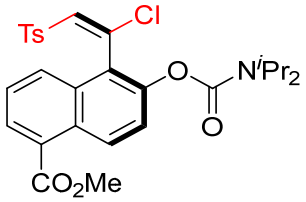
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 1.6 Hz, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.93 (dd, J = 8.8, 1.7 Hz, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.27 (s, 1H), 7.24 (d, J = 5.3 Hz, 2H), 6.92 (d, J = 8.1 Hz, 2H), 4.21 – 4.08 (m, 1H), 3.99 (s, 3H), 3.95 – 3.84 (m, 1H), 2.23 (s, 3H), 1.36 – 1.24 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 151.9, 148.6, 144.8, 142.0, 136.3, 135.3, 132.5(4), 132.5(0), 131.2, 129.8, 129.4, 128.2, 127.3, 126.6, 124.5, 123.5, 122.2, 52.5, 47.3, 46.7, 21.5, 21.3, 21.2, 20.6, 20.5.

HRMS (ESI) m/z calcd. for $C_{28}H_{31}ClNO_6S$ $[M + H]^+$ 544.1555, found 544.1555.

HPLC condition: Chiralcel IE, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 33.96 min, t_R (minor) = 41.15 min, 80% ee.

Methyl (S_a,E)-5-(1-chloro-2-tosylvinyl)-6-((diisopropylcarbamoyl)oxy)-1-naphthoate (O8)



According to **Procedure V** with **OS8** (70.6 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **O8** (98.0 mg, 90% yield, 82% ee) as a pale-yellow solid.

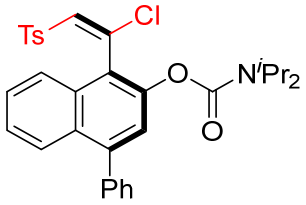
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 9.5 Hz, 1H), 8.10 (dd, J = 7.3, 1.2 Hz, 1H), 7.69 (d, J = 8.4, 1H), 7.55 (d, J = 9.5 Hz, 1H), 7.39 (dd, J = 8.5, 7.3 Hz, 1H), 7.25 (d, J = 7.5 Hz, 3H), 6.89 (d, J = 8.0 Hz, 2H), 4.16 – 4.04 (m, 1H), 4.01 (s, 3H), 3.96 – 3.83 (m, 1H), 2.21 (s, 3H), 1.39 – 1.22 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 152.0, 146.9, 144.6, 142.0, 136.0, 135.5, 130.9, 129.7, 129.4, 129.3, 129.2, 128.7, 128.2, 127.6, 126.0, 124.1, 122.2, 52.5, 47.1, 46.7, 21.5, 21.3, 21.2, 20.6, 20.5.

HRMS (ESI) m/z calcd. for $C_{28}H_{31}ClNO_6S$ $[M + H]^+$ 544.1555, found 544.1555.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 32.94 min, t_R (minor) = 40.17 min, 82% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)-4-phenylnaphthalen-2-yl diisopropylcarbamate (O9)



According to **Procedure V** with **OS9** (74.2 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O9** (90.0 mg, 80% yield, 92% ee) as a pale-yellow oil.

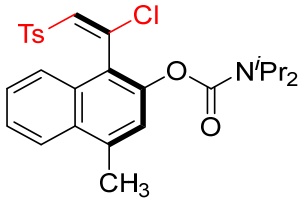
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 1H), 7.56 – 7.42 (m, 6H), 7.41 – 7.30 (m, 5H), 7.25 (s, 1H), 6.88 (d, J = 8.0 Hz, 2H), 4.21 – 4.06 (m, 1H), 4.00 – 3.84 (m, 1H), 2.19 (s, 3H), 1.31 (d, J = 6.7 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 146.0, 144.5, 143.9, 142.4, 139.4, 136.0, 135.2, 130.6, 130.1, 129.2, 128.4, 128.3, 128.0, 127.1, 126.5, 125.7, 124.6, 123.3, 121.2, 47.0, 46.6, 21.6, 21.4, 21.3, 20.6, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{32}H_{33}ClNO_4S$ $[M + H]^+$ 562.1813, found 562.1809.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 32.63 min, t_R (major) = 34.32 min, 92% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)-4-methylnaphthalen-2-yl diisopropylcarbamate (O10)



According to **Procedure V** with **OS10** (61.8 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O10** (82.0 mg, 82% yield, 91% ee) as a pale-yellow solid.

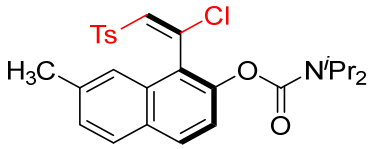
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.42 – 7.32 (m, 1H), 7.31 – 7.24 (m, 3H), 7.20 (s, 1H), 6.88 (d, J = 8.1 Hz, 2H), 4.18 – 4.03 (m, 1H), 3.98 – 3.83 (m, 1H), 2.71 (s, 3H), 2.23 (s, 3H), 1.39 – 1.24 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 146.1, 144.3, 142.8, 138.7, 136.1, 134.7, 130.2, 130.0, 129.1, 128.1, 126.9, 125.4, 124.8, 124.4, 122.9, 120.2, 47.0, 46.5, 21.5, 21.2, 21.1, 20.6, 20.4, 19.8.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{31}ClNO_4S$ $[M + H]^+$ 500.1657, found 500.1655.

HPLC condition: Chiralcel IF, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 254 nm, t_R (minor) = 14.7 1min, t_R (major) = 18.60 min, 91% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)-7-methylnaphthalen-2-yl diisopropylcarbamate (O11)



According to **Procedure V** with **OS11** (61.8 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **O11** (30 mg, 30% yield, 60% ee) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.9 Hz, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.38 (d, J = 9.0 Hz, 1H), 7.24 – 7.19 (m, 4H), 7.07 (s, 1H), 6.86 (d, J = 8.1 Hz, 2H), 4.21 –

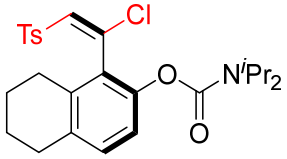
4.06 (m, 1H), 4.02 – 3.48 (m, 1H), 2.36 (s, 3H), 2.23 (s, 3H), 1.37 – 1.30 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 146.9, 144.3, 143.3, 137.0, 136.3, 135.0, 131.0, 130.2, 129.1, 129.0, 128.2, 128.1, 127.8, 123.2, 121.5, 121.2, 47.1, 46.6, 21.9, 21.6, 21.4, 21.3, 20.7, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{31}ClNO_4S$ $[M + H]^+$ 500.1657, found 500.1657.

HPLC condition: Chiralcel IG, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 18.38 min, t_R (major) = 22.40 min, 60% ee.

(*S*$_a$,*E*)-1-(1-Chloro-2-tosylvinyl)-5,6,7,8-tetrahydronaphthalen-2-yl diisopropylcarbamate (O12)



According to **Procedure V** with **OS12** (59.9 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **O12** (83.2 mg, 84% yield, 74% ee) as a colorless oil.

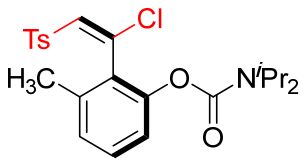
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.45 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.96 (s, 1H), 3.93 – 3.62 (m, 1H), 2.73 – 2.67 (m, 2H), 2.64 – 2.45 (m, 2H), 2.41 (s, 3H), 1.76 – 1.60 (m, 4H), 1.32 – 1.21 (m, 6H), 1.16 – 1.08 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 145.7, 144.9, 144.7, 137.1, 136.1, 134.2, 132.9, 131.7, 129.7, 128.4, 126.2, 120.6, 46.9, 46.1, 29.4, 26.5, 22.6, 22.4, 21.8, 21.0, 20.9, 20.7, 20.4.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{33}ClNO_4S$ $[M + H]^+$ 490.1813, found 490.1808.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 254 nm, t_R (minor) = 19.55 min, t_R (major) = 21.44 min, 74% ee.

(*S*$_a$,*E*)-2-(1-Chloro-2-tosylvinyl)-3-methylphenyl diisopropylcarbamate (O13)



According to **Procedure V** with **OS13** (51.9 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O13** (72.0 mg, 80%

yield, 83% ee) as a white solid.

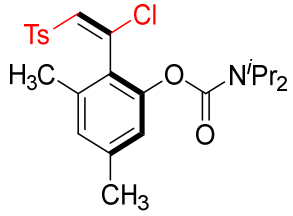
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H), 7.32 (t, J = 7.9 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.05 (dd, J = 16.4, 7.9 Hz, 2H), 6.97 (s, 1H), 3.91 – 3.78 (m, 1H), 3.78 – 3.65 (m, 1H), 2.40 (s, 3H), 2.22 (s, 3H), 1.33 – 1.19 (m, 6H), 1.19 – 1.02 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 148.1, 144.9, 144.7, 137.8, 137.2, 132.9, 130.6, 129.8, 128.2, 126.9, 126.6, 120.8, 47.0, 46.1, 21.8, 21.0, 20.9, 20.6, 20.4, 19.3.

HRMS (ESI) m/z calcd. for $C_{23}H_{29}ClNO_4S$ $[M + H]^+$ 450.1500, found 450.1496.

HPLC condition: Chiralcel IG, n-hexane/i-PrOH = 60/40, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 12.52 min, t_R (minor) = 14.82 min, 83% ee.

(S_a,*E*)-2-(1-Chloro-2-tosylvinyl)-3,5-dimethylphenyl diisopropylcarbamate (O14)



According to **Procedure V** with **OS14** (54.7 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford **O14** (82.1 mg, 88% yield, 81% ee) as a colorless oil.

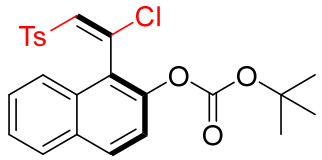
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.94 (s, 1H), 6.87 (d, J = 16.0 Hz, 2H), 3.89 – 3.64 (m, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 2.19 (s, 3H), 1.33 – 1.20 (m, 6H), 1.11 – 1.07 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 147.9, 145.1, 144.8, 141.2, 137.4, 137.3, 132.8, 129.7, 128.3, 127.6, 124.1, 121.3, 46.9, 46.1, 21.8, 21.5, 21.0, 20.9, 20.7, 20.4, 19.2.

HRMS (ESI) m/z calcd. for $C_{24}H_{31}ClNO_4S$ $[M + H]^+$ 464.1657, found 464.1652.

HPLC condition: Chiralcel IH, n-hexane/i-PrOH = 60/40, flow rate 0.5 mL/min. λ = 254 nm, t_R (major) = 10.41 min, t_R (minor) = 12.37 min, 81% ee.

(S_a,*E*)-*tert*-Butyl (1-(1-chloro-2-tosylvinyl)naphthalen-2-yl) carbonate (O15)



According to **Procedure VI** with **OS15** (53.7 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O15** (0 °C: 40.4 mg, 44% yield, 90% ee; rt: 60.0 mg, 61% yield, 84% ee, according to **Procedure V**) as a pale-yellow solid.

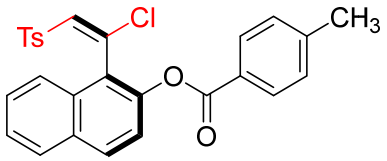
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 7.2 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.48 – 7.34 (m, 5H), 7.23 (s, 1H), 6.92 (d, J = 7.7 Hz, 2H), 2.23 (s, 3H), 1.58 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 145.7, 144.5, 140.9, 136.1, 134.9, 131.5, 130.9, 130.0, 129.3, 128.3, 128.1, 127.5, 126.0, 124.4, 122.1, 121.2, 84.1, 27.7, 21.5.

HRMS (ESI) m/z calcd. For $C_{24}H_{23}ClO_4SNa$ $[M + Na]^+$ 481.0847, found 481.0845.

HPLC condition: Chiralcel IE, n-hexane/i-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 12.61 min, t_R (minor) = 16.26 min, 90% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)naphthalen-2-yl 4-methylbenzoate (O16)



According to **Procedure VII** with **OS16** (57.2 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **O16** (rt: 66.8 mg, 70% yield, 80% ee; 63.9 mg, 67% yield, 78% ee, according to **Procedure V**) as a white solid.

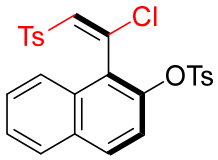
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.55 (dd, J = 17.1, 8.6 Hz, 2H), 7.51 – 7.41 (m, 2H), 7.32 (dd, J = 10.5, 8.2 Hz, 4H), 7.24 (s, 1H), 6.95 (d, J = 8.0 Hz, 2H), 2.47 (s, 1H), 2.25 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 145.9, 144.9, 144.7, 141.7, 136.3, 134.9, 131.7, 131.1, 130.6, 130.3, 129.5, 129.4(7), 128.4, 128.1, 127.6, 126.2, 126.1, 124.4, 122.5, 121.6, 22.0, 21.6.

HRMS (ESI) m/z calcd. for $C_{27}H_{22}ClO_4S$ $[M + H]^+$ 477.0922, found 477.0919.

HPLC condition: Chiralcel IF, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 17.96 min, t_R (major) = 25.87 min, 80% ee.

(S_a,*E*)-1-(1-Chloro-2-tosylvinyl)naphthalen-2-yl 4-methylbenzenesulfonate (O17)



According to **Procedure VIII** with **OS17** (64.4 mg, 0.20 mmol, 1.0 equiv) and **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **O17** (0 °C: 35.6 mg, 34% yield, 83% ee; rt: 21.5 mg, 21% yield, 60% ee, according to **Procedure V**) as a pale-yellow oil.

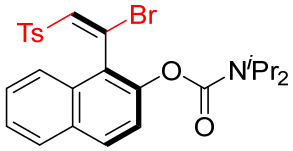
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 9.1 Hz, 1H), 7.88 – 7.78 (m, 3H), 7.69 – 7.62 (m, 1H), 7.58 – 7.46 (m, 3H), 7.43 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.08 (t, J = 4.1 Hz, 3H), 2.43 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 144.9, 144.2, 140.4, 136.5, 134.6, 133.3, 132.3, 131.5, 130.6, 130.0, 129.7, 128.5(3), 128.4(8), 128.1(1), 128.0(7), 126.6, 124.9, 123.1, 119.7, 21.9, 21.7.

HRMS (ESI) m/z calcd. for $C_{26}H_{22}ClO_5S_2$ $[M + H]^+$ 513.0592, found 513.0589.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 230 nm, t_R (major) = 37.81 min, t_R (minor) = 41.24 min, 83% ee.

(*Sa,E*)-1-(1-Bromo-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O1-Br)



According to **Procedure V** with **OS1** (59.1 mg, 0.20 mmol, 1.0 equiv) and **S1-Br** (70.5 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O1-Br** (99.7 mg, 94% yield, 23% ee) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 9.0 Hz, 1H), 7.77 (dd, J = 7.8, 1.5 Hz, 1H), 7.52 – 7.32 (m, 5H), 7.30 – 7.22 (m, 2H), 6.88 (d, J = 8.0 Hz, 2H), 4.29 – 3.68 (m, 2H), 2.22 (s, 3H), 1.47 – 1.15 (m, 12H).

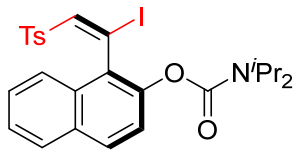
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 146.1, 144.5, 138.0, 136.1, 132.3, 131.1, 130.8, 129.9, 129.3, 128.3, 128.2, 127.1, 125.7, 124.4, 123.3, 122.6, 47.2, 46.6, 21.6, 21.4, 21.2, 20.7, 20.5.

HRMS (ESI) m/z calcd. for $C_{26}H_{29}BrNO_4S$ $[M + H]^+$ 530.0995, found 530.0991.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ =

238 nm, t_R (major) = 22.03 min, t_R (minor) = 25.25 min, 23% ee.

(*Sa,E*)-1-(1-Iodo-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O1-I)



According to **Procedure V** with **OS1** (59.1 mg, 0.20 mmol, 1.0 equiv) and **S1-I** (84.6 mg, 0.30 mmol, 1.5 equiv) in place of sulfonyl chloride, the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O1-I** (103.9 mg, 90% yield, 0% ee) as a yellow solid.

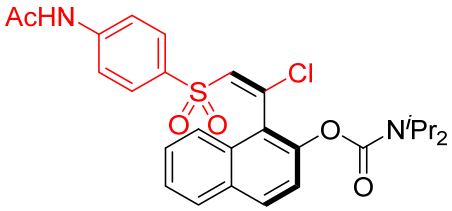
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 9.0 Hz, 1H), 7.77 (dd, J = 6.9, 2.2 Hz, 1H), 7.66 (s, 1H), 7.53 – 7.34 (m, 4H), 7.30 – 7.18 (m, 2H), 6.86 (d, J = 8.1 Hz, 2H), 4.29 – 3.74 (m, 2H), 2.21 (s, 3H), 1.48 – 1.25 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 144.7, 144.5, 144.3, 135.9, 130.9, 130.5, 129.3, 129.1, 128.3, 128.1, 126.8, 126.3, 125.7, 124.5, 122.8, 107.0, 47.3, 46.5, 21.6, 21.5, 21.3, 20.8, 20.6.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{29}INO_4S$ $[M + H]^+$ 578.0856, found 578.0856.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 238 nm, t_R (major) = 24.60 min, t_R (minor) = 29.87 min, 0% ee.

(*Sa,E*)-1-(2-((4-Acetamidophenyl)sulfonyl)-1-chlorovinyl)naphthalen-2-yl diisopropylcarbamate (O20)



According to **Procedure V** with **OS1** (59.1 mg, 0.20 mmol, 1.0 equiv) and **S8** (70.1 mg, 0.30 mmol, 1.5 equiv), the product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to afford **O20** (69.8 mg, 66% yield, 90% ee) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 9.0 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.51 – 7.28 (m, 4H), 7.25 – 7.14 (m, 5H), 4.31 – 3.68 (m, 2H), 2.03 (s, 3H), 1.46 – 1.23 (m, 12H).

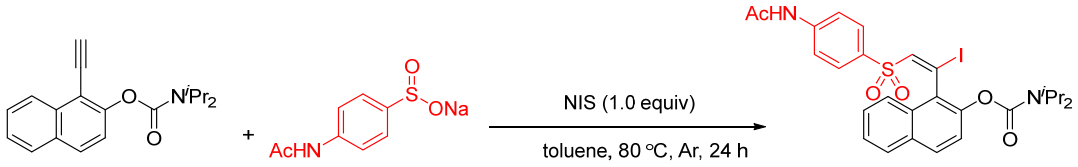
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 152.5, 146.5, 143.1, 142.7, 134.6, 133.3, 131.4, 130.7, 130.2, 129.3, 128.3, 127.5, 125.9, 124.1, 122.3, 122.1, 118.8, 47.1, 46.7, 24.7,

21.4, 21.2, 20.7, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{30}ClN_2O_5S$ $[M + H]^+$ 529.1558, found 529.1555.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 238 nm, t_R (minor) = 21.09 min, t_R (major) = 27.43 min, 90% ee.

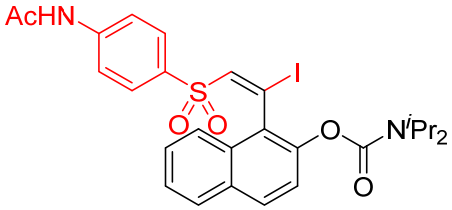
Synthesis of racemic O20-I



OS1, 1.0 equiv, 0.20 mmol 1.0 equiv **O20-I**, 23% yield

A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with alkyne **OS1** (59.1 mg, 0.20 mmol, 1.0 equiv) and sodium 4-acetamidobenzenesulfinate (44.2 mg, 0.20 mmol, 1.0 equiv). The tube was evacuated and backfilled with argon three times, toluene (1.0 mL) was added to the mixture, and the reaction mixture was stirred at 80 °C for 24 h. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(*E*)-1-(2-((4-Acetamidophenyl)sulfonyl)-1-iodovinyl)naphthalen-2-yl diisopropylcarbamate (O20-I)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to afford **O20-I** (28.5 mg, 23% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.9 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.63 (s, 1H), 7.50 – 7.32 (m, 5H), 7.28 – 7.16 (m, 4H), 4.35 – 3.71 (m, 2H), 2.13 (s, 3H), 1.46 – 1.25 (m, 12H).

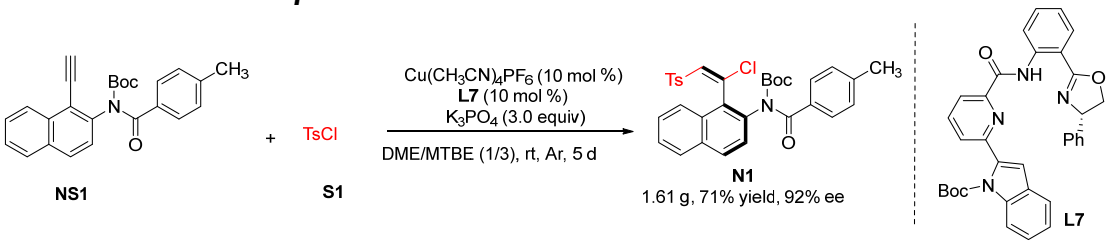
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 151.7, 147.8, 145.2, 144.7, 144.1, 142.8, 133.4, 130.9, 130.7, 129.6, 129.2, 128.2, 127.0, 126.3, 125.9, 124.5, 122.8, 107.2, 47.3, 46.6, 24.8, 21.5, 21.3, 20.8, 20.7.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{30}IN_2O_5S$ $[M + H]^+$ 621.0915, found 621.0913.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 238 nm, t_{R1} = 23.24 min, t_{R2} = 29.31 min.

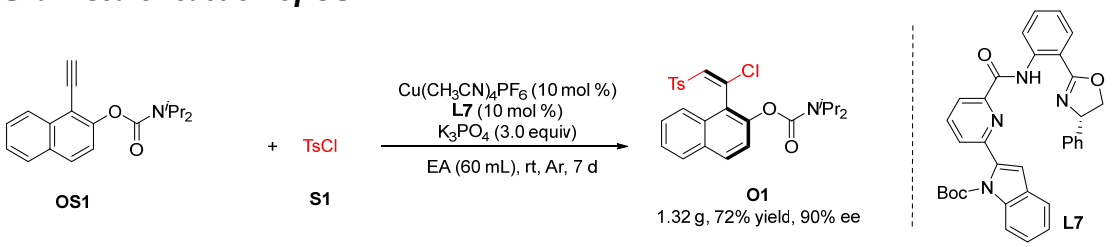
Gram-scale reactions and procedures for synthetic applications

Gram-scale reaction of NS1



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (149.0 mg, 0.40 mmol, 10 mol %), **L7** (224.0 mg, 0.40 mmol, 10 mol %), alkyne **NS1** (1.54 g, 4.0 mmol, 1.0 equiv), sulfonyl chloride **S1** (1.15 g, 6.0 mmol, 1.5 equiv), and K_3PO_4 (2.55 g, 12.0 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous DME (15 mL) and MTBE (45 mL) were added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **N1** in 71% yield and 92% ee.

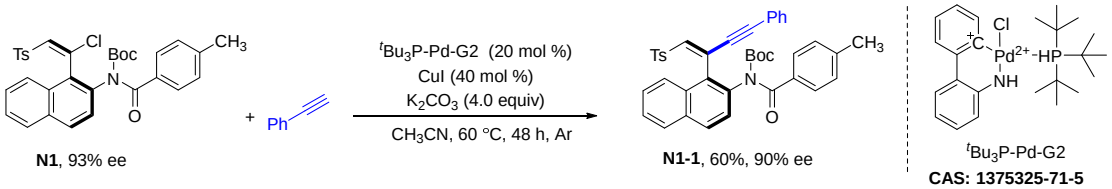
Gram-scale reaction of OS1



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (149.0 mg, 0.40 mmol, 10 mol %), **L7** (224.0 mg, 0.40 mmol, 10 mol %), alkyne **OS1** (1.18 g, 4.0 mmol, 1.0 equiv), sulfonyl chloride **S1** (1.15 g, 6.0 mmol, 1.5 equiv), and K_3PO_4 (2.55 g, 12.0 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous EtOAc (60 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 7 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated, and the residue was purified by column chromatography on silica gel to afford the desired product **O1** in 72% yield and 90% ee.

Sonogashira coupling of axially chiral sulfone-containing styrene

Procedure a: *Sonogashira coupling of* ***N1***



N1, 93% ee

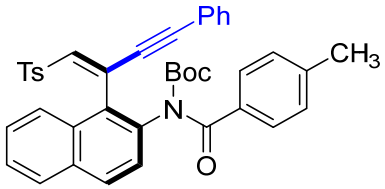
N1-1, 60%, 90% ee

^{t}Bu$_3$P-Pd-G2

CAS: 1375325-71-5

To a mixture of chiral sulfone-containing styrene **N1** (115.2 mg, 0.20 mmol, 1.0 equiv, 93% ee), ^{t}Bu$_3$P-Pd-G2 (20.5 mg, 0.040 mmol, 20 mol %), CuI (15.2 mg, 0.080 mmol, 40 mol %), and K_2CO_3 (110.5 mg, 0.80 mmol, 4.0 equiv) in dry CH_3CN (4 mL) was added ethynylbenzene (44 μL, 0.40 mmol, 2.0 equiv). After the reaction mixture was stirred at 60 °C under argon for 48 h, it was treated with standard aqueous work-up and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography to afford the desired product **N1-1**.

***tert*-Butyl (S_a,*Z*)-(4-methylbenzoyl)(1-(4-phenyl-1-tosylbut-1-en-3-yn-2-yl)naphthalen-2-yl)carbamate (N1-1)**



The product mixture was purified by silica gel column chromatography (petroleum ether/dichloromethane/ethyl acetate = 10/10/1) to afford **N1-1** (75.0 mg, 60% yield, 90% ee) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 – 7.71 (m, 4H), 7.68 – 7.01 (m, 14H), 6.99 – 6.84 (m, 2H), 2.37 (s, 3H), 2.23 (s, 3H), 1.35 (br, 9H).

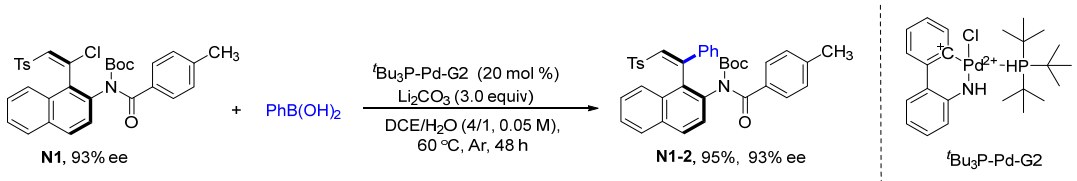
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.0, 153.0, 144.1, 142.7, 138.5, 136.5, 133.8, 132.6, 132.0, 129.8, 129.5, 129.3, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.0, 126.6, 125.6, 121.5, 86.7, 83.8, 83.7, 27.7, 27.0, 21.8, 21.6.

HRMS (ESI) *m*/*z* calcd. for $C_{40}H_{36}NO_5S$ $[M + H]^+$ 642.2309, found 642.2307.

HPLC condition: Chiralcel INA, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 12.60 min, t_R (major) = 15.26 min, 90% ee.

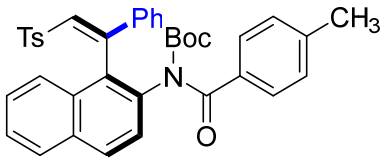
Suzuki-Miyaura coupling of axially chiral sulfone-containing styrene

Procedure b: *Suzuki-Miyaura coupling of* ***N1***



To a mixture of chiral sulfone-containing styrene **N1** (922 mg, 1.6 mmol, 1.0 equiv, 93% ee), phenylboronic acid (392 mg, 3.2 mmol, 2.0 equiv), ^{t}Bu$_3$P-Pd-G2 (164 mg, 0.32 mmol, 20 mol%), and Li_2CO_3 (355 mg, 4.8 mmol, 3.0 equiv) was added DCE/H_2O (4/1, 32 mL). The reaction was stirred at 60 °C under argon for 48 h. Upon completion, the reaction mixture was extracted with EtOAc. The organic layer was dried over Na_2SO_4 and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography to afford the desired product **N1-2**.

***tert*-Butyl (*S*$_a$,*Z*)-(4-methylbenzoyl)(1-(1-phenyl-2-tosylvinyl)naphthalen-2-yl)carbamate (N1-2)**



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N1-2** (940 mg, 95% yield, 93% ee) as a yellow solid.

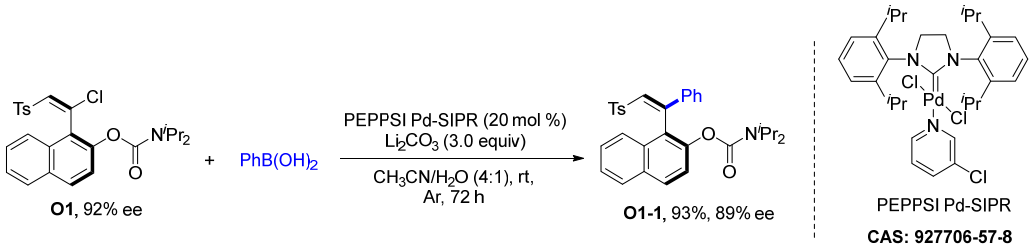
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, J = 8.2 Hz, 1H), 7.92 – 7.76 (m, 1H), 7.57 (s, 2H), 7.50 (d, J = 8.7 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.38 – 6.96 (m, 9H), 6.96 – 6.90 (m, 3H), 2.37 (s, 3H), 2.22 (s, 3H), 1.47 – 0.82 (br, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 172.0, 152.7, 146.2, 143.7, 142.6, 137.2, 135.2, 133.2, 132.3, 130.6, 130.2, 129.5, 129.4, 128.5, 128.4, 128.2, 128.1, 127.9, 126.7, 126.4, 126.1, 83.2, 77.4, 27.5, 21.7, 21.5.

HRMS (ESI) m/z calcd. for $C_{38}H_{36}NO_5S$ $[M + H]^+$ 618.2309, found 618.2308.

HPLC condition: Chiralcel INA, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 11.92 min, t_R (minor) = 14.46 min, 93% ee.

Procedure c: *Suzuki-Miyaura coupling of product* ***O1***



O1, 92% ee

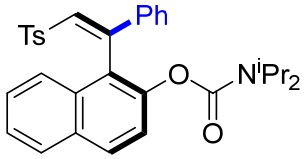
O1-1, 93%, 89% ee

PEPPSI Pd-SIPR

CAS: 927706-57-8

To a mixture of chiral sulfone-containing styrene **O1** (97.2 mg, 0.20 mmol, 1.0 equiv, 92% ee), phenylboronic acid (49 mg, 0.40 mmol, 2.0 equiv), PEPPSI Pd-SIPR (27.3 mg, 0.040 mmol, 20 mol %), and Li_2CO_3 (44.3 mg, 0.60 mmol, 3.0 equiv) was added CH_3CN/H_2O (4/1, 4.0 mL) under argon. Then, the reaction was stirred at room temperature for 72 h. Upon completion, the reaction mixture was extracted with EtOAc. The organic layer was dried over Na_2SO_4 and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography to afford the desired product **O1-1**.

(*S*$_a$,*Z*)-1-(1-Phenyl-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O1-1)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **O1-1** (98.0 mg, 93% yield, 89% ee) as a yellow solid.

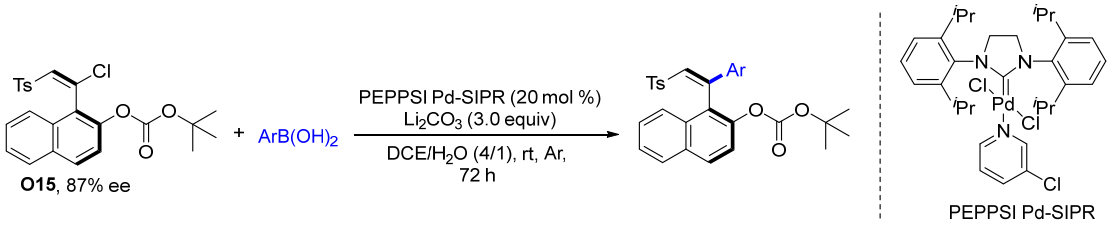
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 9.4 Hz, 1H), 7.45 (d, J = 9.0 Hz, 1H), 7.42 – 7.25 (m, 5H), 7.28 – 7.18 (m, 5H), 7.15 (ddd, J = 8.2, 6.7, 1.3 Hz, 1H), 6.86 (d, J = 8.2 Hz, 2H), 4.01 (p, J = 6.8 Hz, 1H), 3.58 (p, J = 6.8 Hz, 1H), 2.22 (s, 3H), 1.18 (dd, J = 17.9, 6.8 Hz, 6H), 1.00 (dd, J = 15.8, 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 148.4, 146.7, 143.7, 137.2, 136.7, 131.8, 130.85, 130.7, 130.5, 129.8, 129.0, 128.8, 128.0, 127.9, 127.5, 126.6, 125.1(8), 125.1(5), 122.9, 122.8, 47.0, 45.9, 21.5, 21.0, 20.9, 20.5, 20.1.

HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{34}NO_4S$ $[M + H]^+$ 528.2203, found 528.2203.

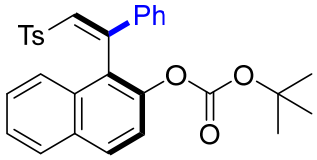
HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 19.87 min, t_R (major) = 24.75 min, 89% ee.

Procedure d: *Suzuki-Miyaura coupling of* ***O15***



To a mixture of chiral sulfone-containing styrene **O15** (91.8 mg, 0.20 mmol, 1.0 equiv, 87% ee), aryl boronic acid (0.40 mmol, 2.0 equiv), PEPPSI Pd-SIPR (27.3 mg, 0.040 mmol, 20 mol %), and Li_2CO_3 (44.3 mg, 0.60 mmol, 3.0 equiv) was added DCE/H_2O (4/1, 4.0 mL) under argon. The reaction was stirred at room temperature under argon for 72 h. Upon completion, the reaction mixture was extracted with EtOAc. The organic layer was dried over Na_2SO_4 and filtered. After evaporation of the solvent, the crude was purified by silica gel column chromatography to afford **the** desired product.

(*S*$_a$,*Z*)-*tert*-Butyl (1-(1-phenyl-2-tosylvinyl)naphthalen-2-yl) carbonate (O15-1)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **O15-1** (80.2 mg, 80% yield, 86% ee) as a yellow solid.

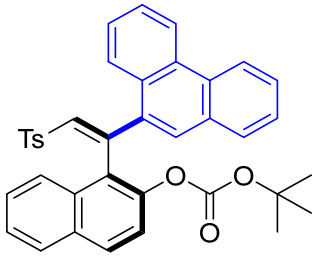
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.45 (d, J = 9.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.34 – 7.15 (m, 10H), 6.88 (d, J = 8.0 Hz, 2H), 2.23 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 146.8, 146.1, 143.7, 137.3, 137.1, 131.7, 131.0(9), 131.0(8), 130.4, 130.1, 129.1, 128.9, 128.1, 128.0, 127.5, 126.9, 125.6, 125.4, 123.2, 121.6, 83.5, 27.6, 21.6.

HRMS (ESI) *m*/*z* calcd. for $C_{30}H_{28}O_5SNa$ $[M + Na]^+$ 523.1550, found 523.1551.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 18.03min, t_R (minor) = 24.96 min, 86% ee.

(*S*$_a$,*Z*)-*tert*-Butyl (1-(1-(phenanthren-9-yl)-2-tosylvinyl)naphthalen-2-yl) carbonate (O15-2)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O15-2** (85.0 mg, 70% yield, 86% ee) as a white solid.

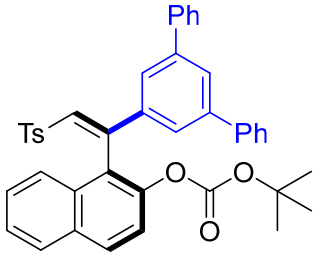
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (ddd, J = 8.0, 6.4, 2.1 Hz, 2H), 8.59 (d, J = 8.4 Hz, 1H), 7.95 – 7.83 (m, 2H), 7.80 (d, J = 8.4 Hz, 1H), 7.70 (tt, J = 7.1, 5.3 Hz, 2H), 7.64 – 7.52 (m, 2H), 7.50 – 7.42 (m, 5H), 7.42 – 7.34 (m, 2H), 7.19 (s, 1H), 7.03 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H), 1.09 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 146.2, 144.2, 144.0, 137.2, 136.2, 134.7, 132.6, 131.4, 131.3, 130.6, 130.5, 130.1, 129.6, 129.3(4), 129.3(1), 128.9, 128.3, 128.1, 127.9, 127.3(4), 127.3(1), 127.0, 126.9, 126.3, 125.7(9), 125.7(5), 125.5, 123.4, 122.4, 121.6, 83.3, 27.2, 21.7.

HRMS (ESI) m/z calcd. for $C_{38}H_{32}O_5SNa$ $[M + Na]^+$ 623.1863, found 623.1861.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 23.43 min, t_R (minor) = 33.93 min, 86% ee.

(S_a,*Z*)-1-(1-([1,1':3',1''-Terphenyl]-5'-yl)-2-tosylvinyl)naphthalen-2-yl *tert*-butyl carbonate (O15-3)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O15-3** (116.8 mg, 90% yield, 86% ee) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 1.7 Hz, 1H), 7.55 – 7.45 (m, 8H), 7.44 – 7.38 (m, 5H), 7.38 – 7.32 (m, 5H), 7.22 (t, J = 7.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 2H), 2.26 (s, 3H), 1.34 (s, 9H).

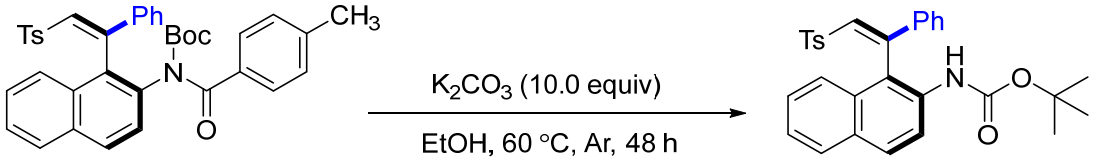
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 146.7, 146.2, 143.8, 142.5, 140.4, 138.5, 137.0, 131.8, 131.6, 131.2, 130.3, 129.2, 129.0, 128.3, 128.2, 128.1, 127.9, 127.4, 127.1, 125.7,

125.43, 125.2, 123.1, 121.7, 83.6, 27.6, 21.6.

HRMS (ESI) *m*/*z* calcd. for $C_{42}H_{36}O_5SNa$ $[M + Na]^+$ 675.2176, found 675.2176.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 21.77 min, t_R (major) = 23.49 min, 86% ee.

Procedure e: *Removal of the protecting group from axially chiral sulfone-containing styrene*

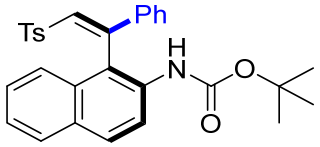


N1-2, 93% ee

N1-2-Boc, 91%, 91% ee

To a 25 mL Schlenk bottle containing a mixture of **N1-2** (988.4 mg, 1.6 mmol, 1.0 equiv, 93% ee) and K_2CO_3 (2.21 g, 16 mmol, 10.0 equiv) was added EtOH (32 mL) under argon. Then, the reaction bottle was sealed and heated to 60 °C for 48 h. Upon completion, the solvent was removed, and the residue was dissolved in water. The aqueous solution was extracted with DCM. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by silica-gel column chromatography to afford **N1-2-Boc**.

***tert*-Butyl (*S*$_a$,*Z*)-(1-(1-phenyl-2-tosylvinyl)naphthalen-2-yl)carbamate (N1-2-Boc)**



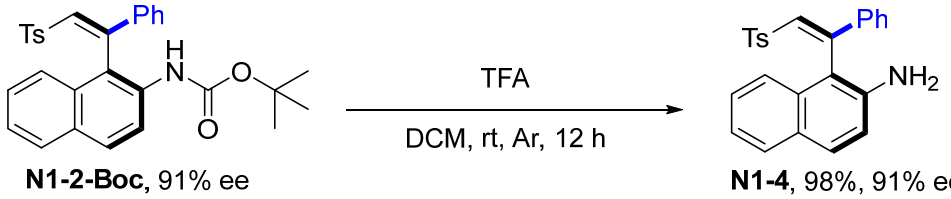
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N1-2-Boc** (723 mg, 91% yield, 91% ee) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.51 (s, 1H), 7.36 – 7.21 (m, 5H), 7.18 (t, J = 7.5 Hz, 1H), 7.06 (s, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.88 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 8.1 Hz, 2H), 2.06 (s, 3H), 1.45 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 150.2, 143.8, 136.5, 135.7, 134.2, 133.1, 130.8, 130.5, 130.4, 129.8, 129.1, 128.8, 127.8, 127.6, 127.2, 126.3, 124.6, 124.6, 80.6, 28.3, 21.3.

HRMS (ESI) *m*/*z* calcd. for $C_{30}H_{30}NO_4S$ $[M + H]^+$ 500.1890, found 500.1890.

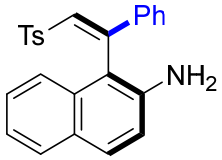
HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 24.50 min, t_R (minor) = 27.84 min, 91% ee.



N1-2-Boc, 91% ee **N1-4**, 98%, 91% ee

To a 50 mL Schlenk bottle containing a mixture of **N1-2-Boc** (500.0 mg, 1.0 mmol, 1.0 equiv, 91% ee) and DCM (8.0 mL) was added TFA (8.0 mL) under argon. Then, the reaction bottle was sealed and stirred at room temperature for 12 h. Upon completion, the reaction mixture was poured into a saturated $NaHCO_3$ solution. The mixture was extracted with DCM. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by silica-gel column chromatography to afford **N1-4**.

(*S*$_a$,*Z*)-1-(1-Phenyl-2-tosylvinyl)naphthalen-2-amine (N1-4)



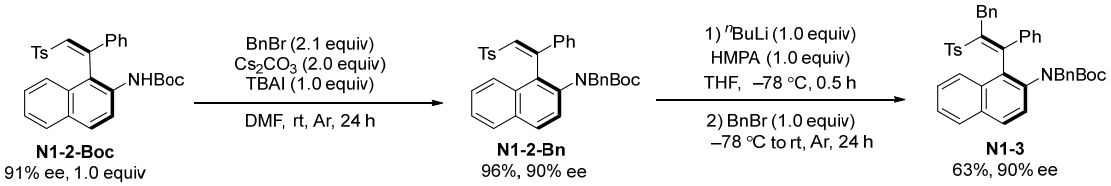
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **N1-4** (392.3 mg, 98% yield, 91% ee) as a yellow solid.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.3 Hz, 1H), 7.55 (d, J = 8.6 Hz, 1H), 7.47 (s, 1H), 7.37 – 7.30 (m, 3H), 7.30 – 7.24 (m, 2H), 7.10 (d, J = 8.3 Hz, 2H), 7.08 – 6.99 (m, 2H), 6.86 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 6.65 (dd, J = 8.3, 2.4 Hz, 3H), 4.06 (s, 2H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 143.6, 142.4, 136.6, 136.1, 132.6, 131.7, 130.7, 130.4, 129.1, 128.8, 127.8, 127.7, 127.6, 127.3, 126.5, 123.3, 122.1, 118.6, 112.9, 21.41.

HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{22}NO_2S$ $[M + H]^+$ 400.1366, found 400.1364.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 21.65 min, t_R (minor) = 23.00 min, 91% ee.

Procedure f: *Preparation of chiral tetrasubstituted alkene*

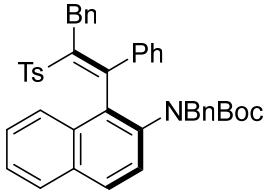


N1-2-Boc 91% ee, 1.0 equiv **N1-2-Bn** 96%, 90% ee **N1-3** 63%, 90% ee

To a mixture of chiral sulfone-containing styrene **N1-2-Boc** (499.0 mg, 0.10 mmol, 1.0 equiv), Cs_2CO_3 (652.0 mg, 0.20 mmol, 2.0 equiv), and TBAI (36.8 mg, 0.10 mmol, 1.0 equiv) in anhydrous DMF (5.0 mL) was added BnBr (0.25 mL, 0.21 mmol, 2.1 equiv) under argon. The reaction was stirred at room temperature for 24 h. Upon completion, the mixture was diluted with EtOAc and subsequently washed with water, followed by brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography on silica gel to afford the desired product **N1-2-Bn** (96% yield, 90% ee) as a yellow solid.[16]

Chiral sulfone-containing styrene **N1-2-Bn** (58.9 mg, 0.10 mmol, 1.0 equiv) was dissolved in THF (2.0 mL) under argon. The solution was cooled to –78 °C, and ^{n}BuLi (1.0 M in THF, 100 μL, 0.10 mmol, 1.0 equiv) was added dropwise at –78 °C. After 15 min, HMPA (18 μL, 0.10 mmol, 1.0 equiv) was added dropwise, followed by BnBr (12 μL, 0.10 mmol, 1.0 equiv) added all at once. The mixture was allowed to warm to room temperature and stirred for 24 h. Upon completion, the reaction was quenched with brine, followed by extraction with EtOAc three times. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **N1-3**.[17]

***tert*-Butyl (*Sa,Z*)-benzyl(1-(1,3-diphenyl-2-tosylprop-1-en-1-yl)naphthalen-2-yl)carbamate (N1-3)**



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **N1-3** (42.8 mg, 63% yield, 90% ee) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.60 – 7.43 (m, 4H), 7.41 – 7.37 (m, 1H), 7.33 – 7.23 (m, 4H), 7.21 – 7.08 (m, 9H), 7.04 (d, J = 8.0 Hz, 2H), 6.86 (dd, J = 6.7, 2.9 Hz, 2H), 6.52 (d, J = 8.6 Hz, 1H), 5.52 (d, J = 14.1 Hz, 1H), 4.92 (d, J = 14.1 Hz, 1H), 4.24 (d, J = 16.3 Hz, 1H), 3.93 (d, J = 16.4 Hz, 1H), 2.34 (s, 3H), 1.31 (s, 3H), 0.82 (s, 6H).

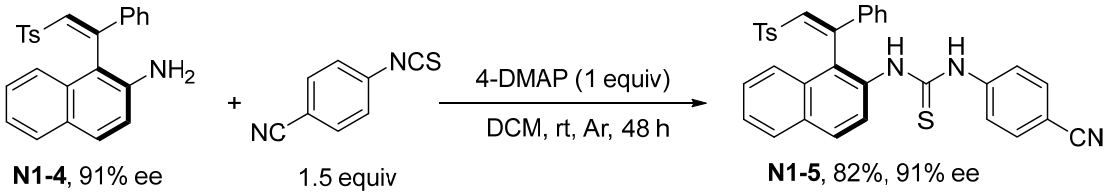
^{13}C NMR (126 MHz, $CDCl_3$): δ 154.9, 149.1, 144.5, 142.3, 139.7, 138.7, 138.5, 136.5, 135.3, 132.5, 132.4, 130.1, 129.9, 129.4, 129.3, 128.7, 128.4(0), 128.3(6), 128.3(3), 128.2(9), 128.2, 128.0(0), 127.9(7), 127.3, 126.5, 126.2, 126.0, 125.8, 79.5, 51.2, 36.52,

27.9, 21.7

HRMS (ESI) *m/z* calcd. for $C_{44}H_{41}NO_4NaS$ $[M + Na]^+$ 702.2649, found 702.2648.

HPLC condition: Chiralcel IA, *n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min. λ = 254 nm, t_R (minor) = 13.94 min, t_R (major) = 16.29 min, 90% ee.

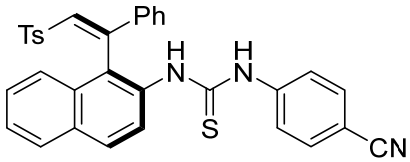
Procedure g: *Transformations of the amino group on axially chiral sulfone-containing styrene*



N1-4, 91% ee 1.5 equiv **N1-5**, 82%, 91% ee

To a 10 mL Schlenk bottle containing a mixture of (*Sa,Z*)-1-(1-phenyl-2-tosylvinyl)naphthalen-2-amine **N1-4** (79.9 mg, 0.20 mmol, 1.0 equiv, 91% ee), 4-isothiocyanatobenzonitrile (48.0 mg, 0.30 mmol, 1.5 equiv), and 4-DMAP (24.4 mg, 0.20 mmol, 1.0 equiv) was added DCM (4.0 mL) under argon. Then, the reaction bottle was sealed and stirred at room temperature for 48 h. Upon completion, the reaction mixture was concentrated. The crude residue was purified by silica-gel column chromatography to afford the desired product **N1-5**.

(*S*$_a$,*Z*)-1-(4-Cyanophenyl)-3-(1-(1-phenyl-2-tosylvinyl)naphthalen-2-yl)thiourea (N1-5)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford **N1-5** (91.8 mg, 82% yield, 91% ee) as a white solid.

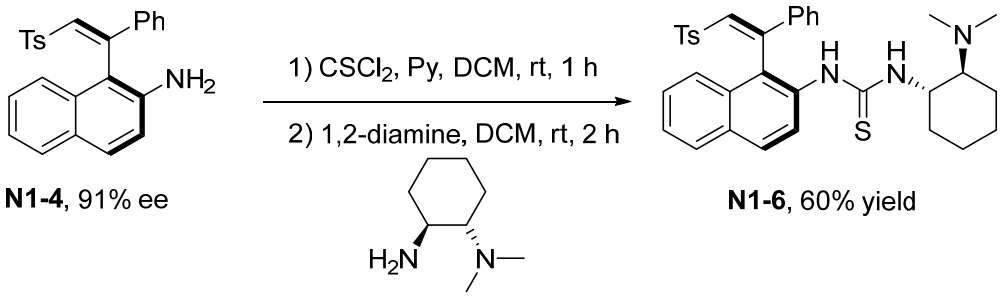
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.31 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.77 (t, *J* = 8.1 Hz, 2H), 7.59 (s, 4H), 7.49 – 7.38 (m, 3H), 7.40 – 7.31 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.05 – 6.94 (m, 3H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.7, 150.9, 144.5, 142.2, 136.1, 135.9, 133.9, 133.2, 132.2, 131.4, 130.8, 130.5, 130.2, 129.4, 129.3, 129.1, 128.2, 127.6, 127.4, 127.0, 126.5, 126.3, 125.3, 123.4, 118.8, 108.5, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{33}H_{26}N_3O_2S_2$ $[M + H]^+$ 560.1461, found 560.1458.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ =

254 nm, t_R (minor) = 38.15 min, t_R (major) = 47.28 min, 91% ee.

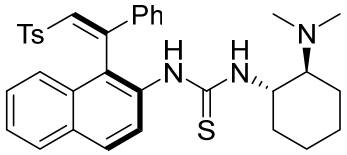


N1-4, 91% ee

N1-6, 60% yield

To a solution of (*Sa,Z*)-1-(1-phenyl-2-tosylvinyl)naphthalen-2-amine **N1-4** (80.0 mg, 0.20 mmol, 1.0 equiv, 91% ee) and pyridine (49 μL, 0.60 mmol, 3.0 equiv) in DCM (4 mL) was added $CSCl_2$ (55.2 mg, 0.48 mmol, 2.4 equiv). The reaction mixture was stirred at room temperature for 1 h. Upon completion, DCM and $CSCl_2$ were removed under high vacuum. To a solution of the resulting residue in DCM (4 mL) was added (1*S*,2*S*)-*N*1,*N*1-dimethylcyclohexane-1,2-diamine (85.3 mg, 0.60 mmol, 3.0 equiv). The mixture was stirred at room temperature for 2 h. Upon completion, DCM was removed and the residue was purified by silica gel column chromatography to afford the desired product **N1-6**.

1-((*1S,2S*)-2-(Dimethylamino)cyclohexyl)-3-(1-((*Sa,Z*)-1-phenyl-2-tosylvinyl)naphthalen-2-yl)thiourea (N1-6)

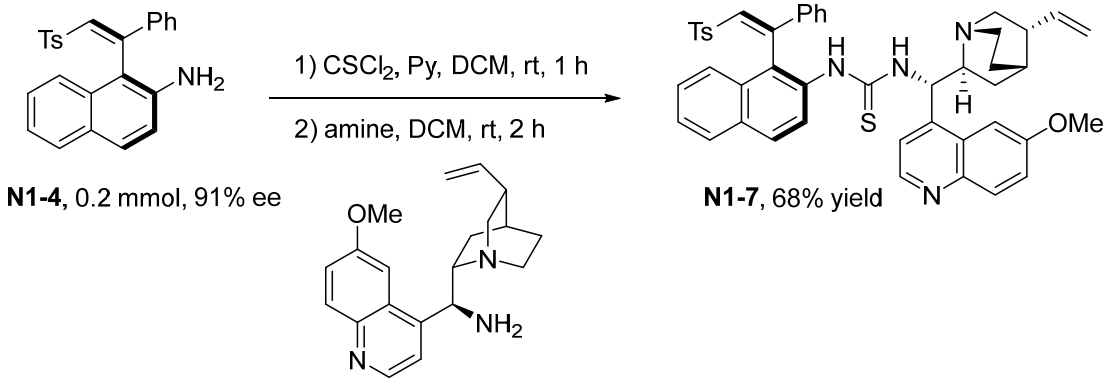


The product mixture was purified by silica gel column chromatography (DCM/MeOH = 40:1 to 20:1) to afford **N1-6** (71.0 mg, 60% yield) as a single optically pure diastereomer and white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.95 – 7.79 (m, 2H), 7.70 (d, J = 8.2 Hz, 1H), 7.46 – 7.34 (m, 3H),7.35 – 7.21 (m, 3H), 7.08 (d, J = 7.9 Hz, 2H), 7.01 – 6.91 (m, 1H), 6.88 (d, J = 8.6 Hz, 1H), 6.71 (d, J = 7.9 Hz, 2H), 3.86 (s, 1H), 2.65 – 2.36 (m, 2H), 2.20 (s, 6H), 2.12 (s, 3H), 1.90 – 1.76 (m, 2H), 1.73 – 1.62 (m, 1H), 1.46 – 1.31 (m, 1H), 1.31 – 1.11 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0, 144.0, 136.5, 136.0, 134.7, 131.6, 131.2, 131.0, 130.8, 129.4, 129.1, 129.1, 128.0, 127.6, 127.5, 127.3, 126.5, 125.6, 125.2, 66.7, 55.8, 40.0, 32.4, 25.1, 24.6, 21.8, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{34}H_{38}N_3O_2S_2$ $[M + H]^+$ 584.2400, found 584.2405.

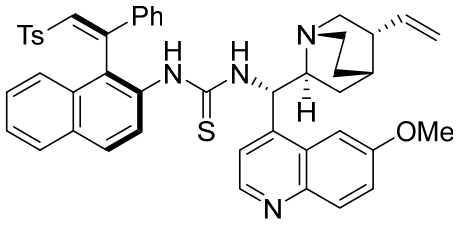


N1-4, 0.2 mmol, 91% ee

N1-7, 68% yield

To a solution of (*Sa,Z*)-1-(1-phenyl-2-tosylvinyl)naphthalen-2-amine **N1-4** (80.0 mg, 0.20 mmol, 1.0 equiv) and pyridine (49 μL, 0.60 mmol, 3.0 equiv) in DCM (4 mL) was added $CSCl_2$ (55.2 mg, 0.48 mmol, 2.4 equiv). The reaction mixture was stirred at room temperature for 1 h. Upon completion, DCM and $CSCl_2$ were removed under high vacuum. To a solution of the resulting residue in DCM (4 mL) was added (*S*)-(6-methoxyquinolin-4-yl)((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methanamine (194.0 mg, 0.60 mmol, 3.0 equiv). The mixture was stirred at room temperature for 2 h. Upon completion, DCM was removed, and the residue was purified by silica gel column chromatography to afford the desired product **N1-7**.

1-((1*S*)-(6-Methoxyquinolin-4-yl)((5S)-5-vinylquinuclidin-2-yl)methyl)-3-(1-((*Sa,Z*)-1-phenyl-2-tosylvinyl)naphthalen-2-yl)thiourea (N1-7)

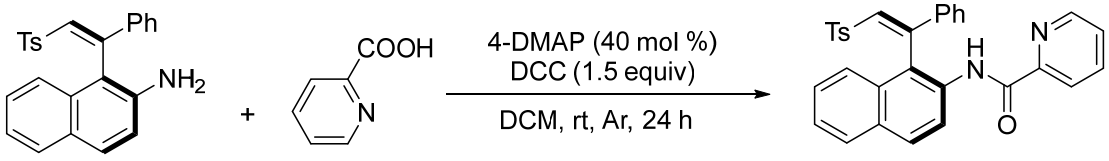


The product mixture was purified by silica gel column chromatography (DCM/MeOH = 40:1 to 20:1) to afford **N1-7** (104.1 mg, 68% yield) as a single optically pure diastereomer and pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.26 – 7.57 (m, 6H), 7.51 – 6.78 (m, 13H), 6.64 (d, J = 7.9 Hz, 2H), 6.01 (s, 1H), 5.78 – 5.53 (m, 1H), 5.10 – 4.78 (m, 2H), 3.98 (s, 3H), 3.66 – 2.23 (m, 8H), 2.12 (s, 3H), 1.40 (t, J = 11.9 Hz, 1H), 0.94 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 182.0, 157.8, 150.5, 147.7, 144.7, 144.0, 140.7, 136.2, 136.1, 134.6, 131.7, 131.5, 130.9, 129.4, 129.1, 128.9, 128.0, 127.6, 127.4(5), 127.4(2), 126.6, 125.7, 125.3, 121.9, 115.1, 102.9, 61.7, 56.0, 55.6, 53.6, 41.9, 39.3, 27.4, 25.8, 21.4.

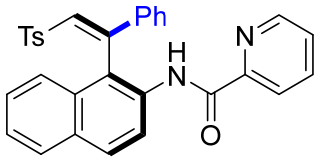
HRMS (ESI) *m/z* calcd. for $C_{46}H_{45}N_4O_3S_2$ $[M + H]^+$ 765.2928, found 765.2934.



N1-4, 91% ee 1.5 equiv **N1-8**, 96%, 91% ee

To a 10 mL Schlenk bottle containing a mixture of (*Sa,Z*)-1-(1-phenyl-2-tosylvinyl)naphthalen-2-amine **N1-4** (79.9 mg, 0.20 mmol, 1.0 equiv, 91% ee), picolinic acid (36.9 mg, 0.30 mmol, 1.5 equiv), DCC (61.9 mg, 0.30 mmol, 1.5 equiv), and 4-DMAP (9.8 mg, 0.080 mmol, 40 mol %) was added DCM (4.0 mL) under argon. Then, the reaction bottle was sealed and stirred at room temperature for 24 h. Upon completion, the reaction mixture was concentrated. The crude residue was purified by silica-gel column chromatography to afford the desired product **N1-8**.

(S_a,*Z*)-*N*-(1-(1-Phenyl-2-tosylvinyl)naphthalen-2-yl)picolinamide (N1-8)



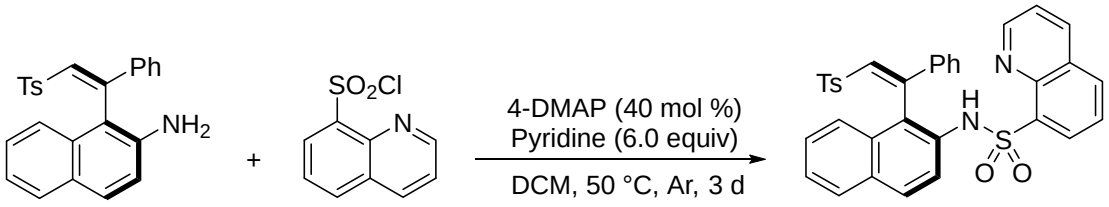
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford **N1-8** (96.8 mg, 96% yield, 91% ee) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.38 (s, 1H), 8.55 (d, J = 4.7 Hz, 1H), 8.48 (d, J = 9.0 Hz, 1H), 8.20 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H), 7.82 (td, J = 7.7, 1.7 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.61 (s, 1H), 7.44 – 7.18 (m, 7H), 7.14 – 7.04 (m, 4H), 6.64 (d, J = 8.1 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 149.7, 149.7, 148.3, 143.9, 137.4, 136.7, 136.2, 133.5, 133.1, 131.0, 130.8, 130.7, 130.1, 129.1, 128.9, 127.9, 127.8, 127.4, 126.7, 126.4, 125.1, 125.0, 122.3(3), 122.2(5), 121.6, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{31}H_{25}N_2O_3S$ $[M + H]^+$ 505.1580, found 505.1577.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (minor) = 46.85 min, t_R (major) = 56.67 min, 91% ee.

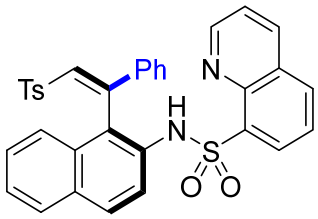


N1-4, 91% ee 1.5 equiv **N1-9**, 60%, 90% ee

To a 10 mL Schlenk bottle containing a mixture of (*Sa,Z*)-1-(1-phenyl-2-

tosylvinyl)naphthalen-2-amine **N1-4** (79.9 mg, 0.20 mmol, 1.0 equiv, 91% ee), quinoline-8-sulfonyl chloride (68.0 mg, 0.30 mmol, 1.5 equiv), 4-DMAP (9.8 mg, 0.080 mmol, 40 mol %), and pyridine (100 μL, 1.2 mmol, 6.0 equiv) was added DCM (4.0 mL) under argon. Then, the reaction bottle was sealed and stirred at 50 °C for 72 h. Upon completion, the reaction mixture was quenched with saturated NH_4Cl solution, extracted with DCM, dried over Na_2SO_4, and concentrated in vacuo. The crude residue was purified by silica-gel column chromatography to afford the desired product **N1-9**.

(*S*$_a$,*Z*)-*N*-(1-(1-Phenyl-2-tosylvinyl)naphthalen-2-yl)quinoline-8-sulfonamide (N1-9)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to afford **N1-9** (70.9 mg, 60% yield, 90% ee) as a white solid.

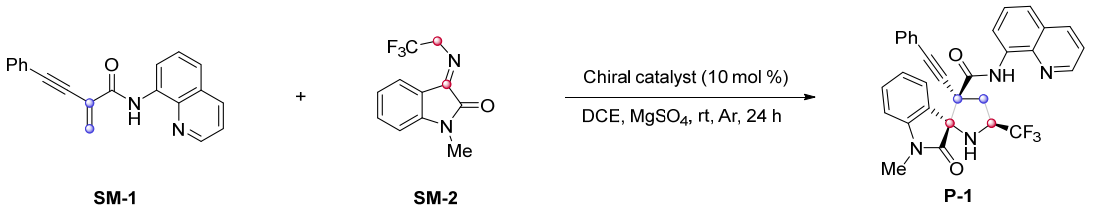
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 9.13 (dd, J = 4.2, 1.7 Hz, 1H), 8.12 (dd, J = 7.2, 1.4 Hz, 1H), 8.04 (dd, J = 8.4, 1.8 Hz, 1H), 7.92 – 7.82 (m, 2H), 7.70 (dd, J = 8.3, 1.4 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.52 (dd, J = 8.3, 4.3 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.05 – 6.92 (m, 4H), 6.82 – 6.74 (m, 3H), 6.59 (t, J = 7.5 Hz, 4H), 6.47 (d, J = 8.5 Hz, 1H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 148.4, 143.9, 143.2, 138.6, 136.5, 135.9, 135.7, 133.9, 133.1, 131.8, 131.3, 130.6, 130.2, 130.1, 129.0, 128.9, 128.5, 128.4, 127.8, 127.6, 126.4, 126.3, 126.1, 125.4, 125.3, 125.2, 122.4, 21.4.

HRMS (ESI) *m*/*z* calcd. for $C_{34}H_{27}N_2O_4S_2$ $[M + H]^+$ 591.1407, found 591.1403.

HPLC condition: Chiralcel OD-3, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 14.48 min, t_R (minor) = 20.42 min, 90% ee.

Application of chiral organocatalysts in the enantioselective tandem Michael addition and cyclization reaction of enynamide and ketimine[18]

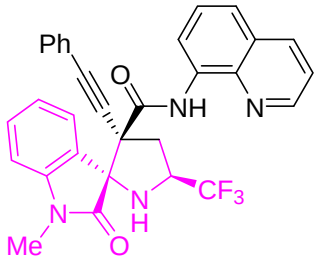


SM-1 **SM-2** **P-1**

With catalyst **N1-5**, 65%, >20:1 dr, 92% ee
With catalyst **N1-6**, 76%, >20:1 dr, 94% ee
With catalyst **N1-7**, 93%, >20:1 dr, 98% ee

A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with 2-methylene-4-phenyl-N-(quinolin-8-yl)but-3-ynamide **SM-1** (29.8 mg, 0.10 mmol, 1.0 equiv), 1-methyl-3-((2,2,2-trifluoroethyl)imino)indolin-2-one **SM-2** (36.3 mg, 0.15 mmol, 1.5 equiv), $MgSO_4$ (30.0 mg, 0.25 mmol, 2.5 equiv), and chiral catalyst (0.010 mmol, 10 mol %). Then, DCE (1.0 mL) was added to the mixture. The reaction mixture was stirred at room temperature for 24 h. Upon completion, it was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the desired product.

(*3R,3'R,5'S*)-1-Methyl-2-oxo-3'-(phenylethynyl)-N-(quinolin-8-yl)-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3'-carboxamide (P-1)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford **P-1** (50.3 mg, 93% yield, 98% ee) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.59 (dd, J = 5.6, 3.4 Hz, 1H), 8.49 (dd, J = 4.2, 1.7 Hz, 1H), 8.08 (dd, J = 8.3, 1.7 Hz, 1H), 7.88 (d, J = 6.3 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.51 – 7.41 (m, 2H), 7.42 – 7.32 (m, 5H), 7.16 (t, J = 7.6 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 4.61 – 4.41 (m, 1H), 3.97 (t, J = 12.0 Hz, 1H), 2.95 (s, 3H), 2.77 (dd, J = 12.2, 6.0 Hz, 1H), 2.67 (d, J = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 164.5, 148.0, 145.4, 138.4, 136.2, 134.0 131.9, 130.8, 129.3, 128.7, 127.8, 127.3, 125.8 (q, J = 280.0 Hz), 125.31, 122.3, 121.9, 121.6, 116.5, 108.6, 89.7, 86.9, 77.4, 71.3, 59.5, 58.5 (q, J = 32.2 Hz), 35.3, 26.3.

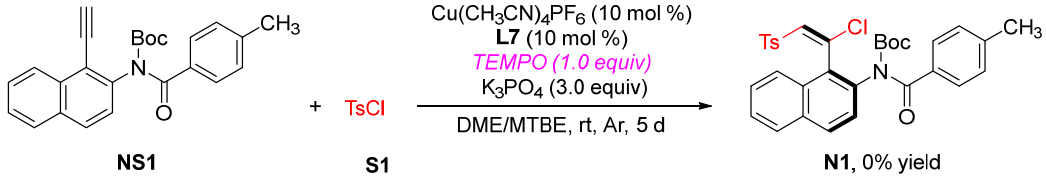
^{19}F NMR (376 MHz, $CDCl_3$): δ –74.9.

HRMS (ESI) m/z calcd. for $C_{31}H_{23}F_3N_4O_2Na$ $[M + Na]^+$ 563.1665, found 563.1670.

HPLC condition: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min. λ = 254 nm, t_R (minor) = 8.05 min, t_R (major) = 16.67 min, 98% ee.

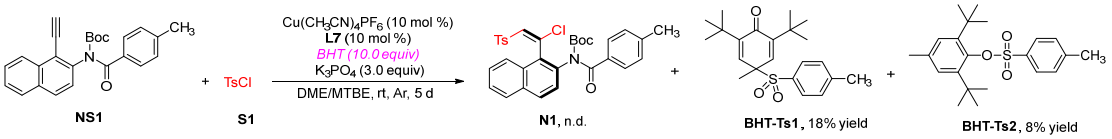
Mechanism experiments

*Procedures for the trapping experiment of **NS1** with TEMPO:*



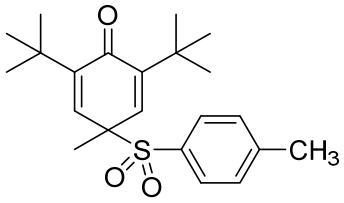
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L7** (11.2 mg, 0.020 mmol, 10 mol %), alkyne **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv), sulfonyl chloride **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), TEMPO (31.2 mg, 0.20 mmol, 1.0 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous DME (1.0 mL) and MTBE (3.0 mL) were added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. No formation of **N1** was detected through TLC monitoring.

*Procedures for the trapping experiment of **NS1** with BHT:*



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L7** (11.2 mg, 0.020 mmol, 10 mol %), alkyne **NS1** (77.1 mg, 0.20 mmol, 1.0 equiv), sulfonyl chloride **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), BHT (220.0 mg, 2.0 mmol, 10.0 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous DME (1.0 mL) and MTBE (3.0 mL) were added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford **BHT-Ts1** (18% yield) and **BHT-Ts2** (8% yield). No formation of **N1** was detected through TLC monitoring.

2,6-di-*tert*-Butyl-4-methyl-4-tosylcyclohexa-2,5-dien-1-one (BHT-Ts1)



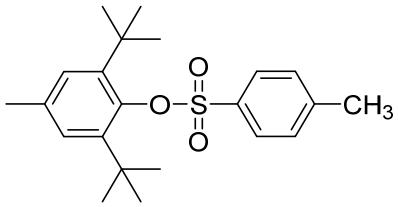
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford **BHT-Ts1** (13.4 mg, 18% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.64 (s, 2H), 2.36 (s, 3H), 1.81 (s, 3H), 1.10 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.8, 151.3, 145.4, 135.8, 130.7, 130.4, 128.9, 65.9, 35.3, 29.1, 21.8, 18.6.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{30}SO_3Na$ $[M + Na]^+$ 397.1808, found 397.1804.

2,6-di-*tert*-Butyl-4-methylphenyl 4-methylbenzenesulfonate (BHT-Ts2)



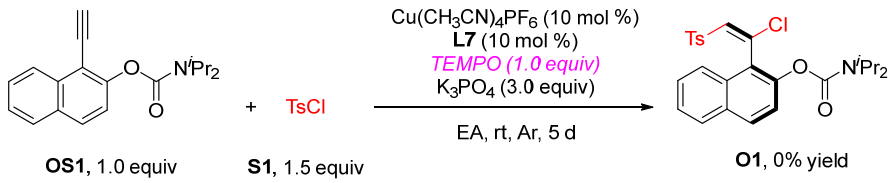
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **BHT-Ts2** (6.0 mg, 8% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.08 (s, 2H), 2.45 (s, 3H), 2.31 (s, 3H), 1.34 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8(0), 144.7(6), 140.8, 134.8, 134.3, 129.7, 128.8, 128.6, 36.9, 32.9, 21.8, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{30}SO_3Na$ $[M + Na]^+$ 397.1808, found 397.1803.

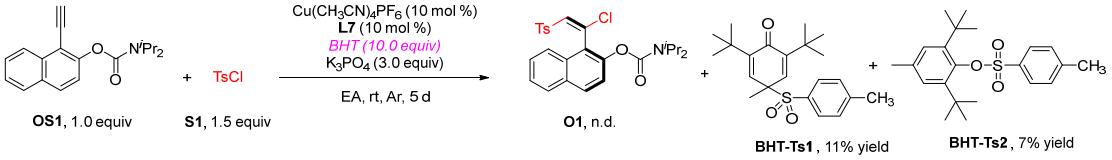
*Procedures for the trapping experiment of **OS1** with TEMPO:*



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L7** (11.2 mg, 0.020 mmol, 10 mol %), alkyne **OS1** (59.1 mg, 0.20 mmol, 1.0 equiv), sulfonyl chloride **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), TEMPO (31.2 mg, 0.20 mmol, 1.0 equiv), and K_3PO_4 (127.4

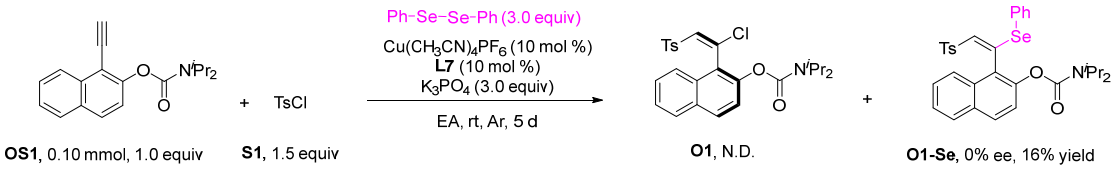
mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous EtOAc (4.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. No formation of **O1** was detected through TLC monitoring.

*Procedures for the trapping experiment of **OS1** with BHT:*



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L7** (11.2 mg, 0.020 mmol, 10 mol %), alkyne **OS1** (59.1 mg, 0.20 mmol, 1.0 equiv), sulfonyl chloride **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), BHT (220.0 mg, 2.0 mmol, 10.0 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous EtOAc (4.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated, and the residue was purified by column chromatography on silica gel to afford the **BHT-Ts1** (8.2 mg, 11% yield) and **BHT-Ts2** (5.2 mg, 7% yield). No formation of **O1** was detected through TLC monitoring.

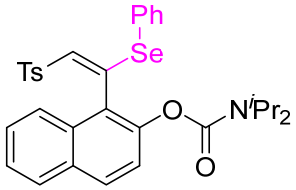
*Procedures for the trapping experiment of **OS1** with Ph-Se-Se-Ph:*



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L7** (11.2 mg, 0.020 mmol, 10 mol %), alkyne **OS1** (59.1 mg, 0.20 mmol, 1.0 equiv), sulfonyl chloride **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), Ph-Se-Se-Ph (187.3 mg, 0.60 mmol, 3.0 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous EtOAc (4.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the **O1-Se**. No formation of

O1 was detected through TLC monitoring.

(*E*)-1-(1-(Phenylselanyl)-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O1-Se)



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O1-Se** (9.7 mg, 16% yield, 0% ee) as a yellow solid.

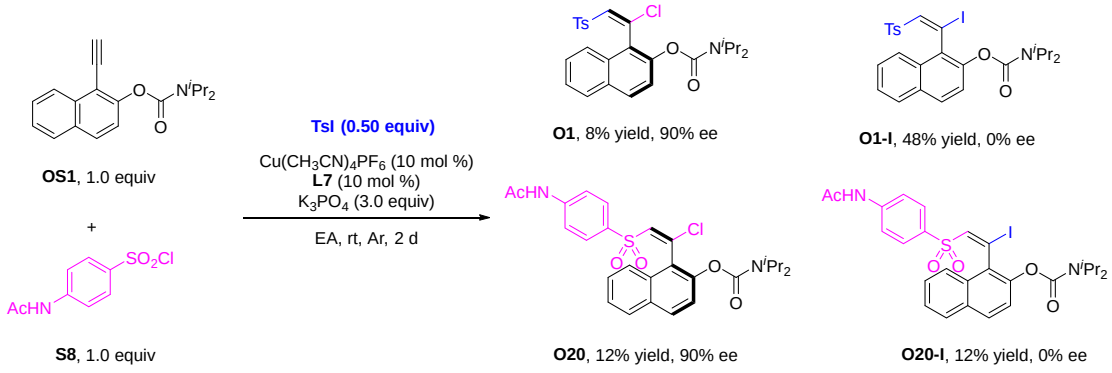
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.51 (d, J = 8.3 Hz, 1H), 7.45 – 7.31 (m, 5H), 7.30 – 7.26 (m, 1H), 7.16 – 7.06 (m, 2H), 6.80 (d, J = 8.0 Hz, 2H), 6.46 (s, 1H), 4.21 – 3.85 (m, 2H), 2.19 (s, 3H), 1.58 – 1.14 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 151.3, 145.7, 143.5, 137.4, 137.0, 130.7, 130.6, 130.3, 130.2, 129.0, 128.1, 127.9, 127.8, 126.6, 126.3, 125.3, 125.0, 122.5, 121.8, 47.0, 46.5, 21.5(1), 21.4(9), 21.3, 20.8, 20.7.

HRMS (ESI) *m/z* calcd. for $C_{32}H_{34}NO_4SSe$ $[M + H]^+$ 608.1368, found 608.1366.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 50/50, flow rate 0.6 mL/min. λ = 254 nm, t_R (major) = 9.07 min, t_R (minor) = 14.49 min, 0% ee.

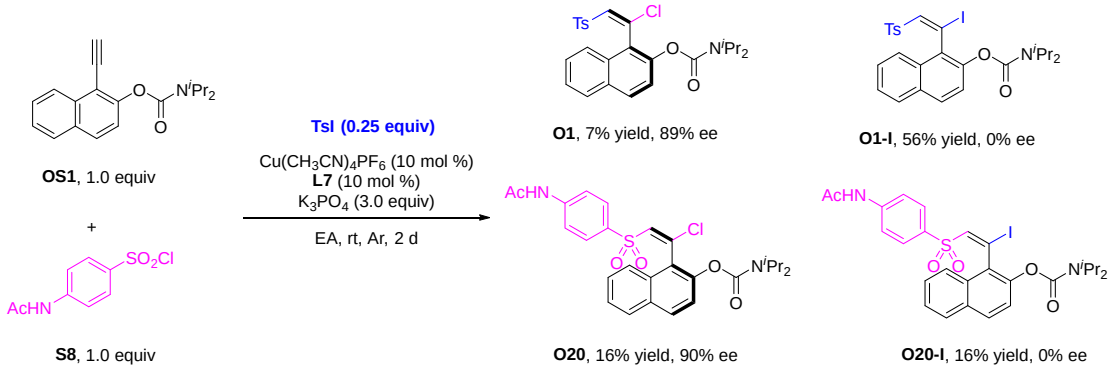
*Experimental procedures for the crossover experiment of **OS1** with **TsI** (**S1-I**, 0.50 equiv) and **S8** (1.0 equiv):*



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (3.68 mg, 0.010 mmol, 10 mol %), **L7** (5.60 mg, 0.010 mmol, 10 mol %), alkyne **OS1** (29.6 mg, 0.10 mmol, 1.0 equiv), 4-methylbenzenesulfonyl iodide (**TsI**, **S1-I**) (14.1 mg, 0.050 mmol, 0.5 equiv), **S8** (23.4 mg, 0.10 mmol, 1.0 equiv), and

K_3PO_4 (63.6 mg, 0.30 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous EtOAc (2.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 2 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated, and the reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the **O1** and **O1-I** mixture. The remaining reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to afford the **O20** and **O20-I** mixture. The yield was determined based on the ^{1}H NMR analysis of the product mixtures using CH_2Br_2 as an internal standard. HPLC conditions for the **O1** and **O1-I** mixture: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 238 nm, t_R (major **O1**) = 22.70 min, t_R (minor **O1**) = 25.89 min, 90% ee; t_R (major **O1-I**) = 24.40 min, t_R (minor **O1-I**) = 29.58 min, 0% ee.
HPLC conditions for the **O20** and **O20-I** mixture: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 238 nm, t_R (minor **O20**) = 20.91min, t_R (major **O20**) = 27.07 min, 90% ee; t_R (major **O20-I**) = 23.23 min, t_R (minor **O20-I**) = 29.30 min, 0% ee.

*Experimental procedures for the crossover experiment of **OS1** with **TsI** (**S1-I**, 0.25 equiv) and **S8** (1.0 equiv):*

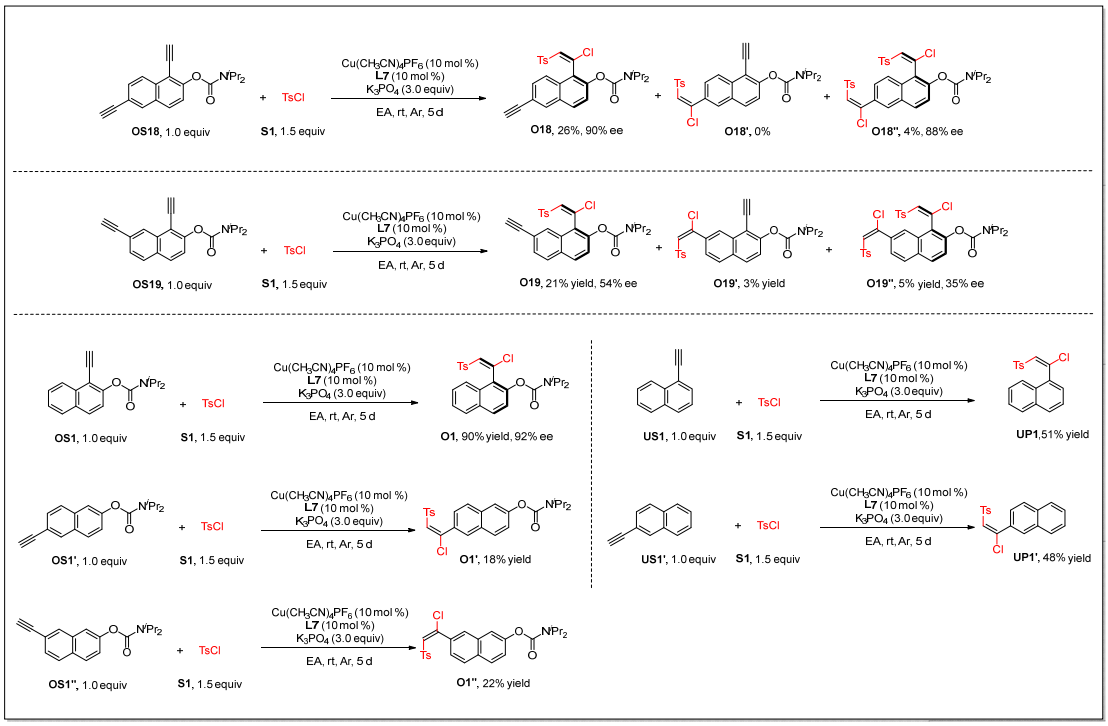


A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (3.68 mg, 0.010 mmol, 10 mol %), **L7** (5.60 mg, 0.010 mmol, 10 mol %), alkyne **OS1** (29.6 mg, 0.10 mmol, 1.0 equiv), 4-methylbenzenesulfonyl iodide (**TsI**, **S1-I**) (7.0 mg, 0.025 mmol, 0.25 equiv), **S8** (23.4 mg, 0.10 mmol, 1.0 equiv), and K_3PO_4 (63.6 mg, 0.30 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous EtOAc (2.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 2 d. Upon completion, the

precipitate was filtered off and washed by DCM. The filtrate was evaporated, and the reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the **O1** and **O1-I** mixture. The remaining reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to afford the **O20** and **O20-I** mixture. The yield was determined based on the ^{1}H NMR analysis of the product mixtures using CH_2Br_2 as an internal standard. HPLC conditions for the **O1** and **O1-I** mixture: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 238 nm, t_R (major **O1**) = 23.35 min, t_R (minor **O1**) = 26.67 min, 89% ee; t_R (major **O1-I**) = 25.08 min, t_R (minor **O1-I**) = 30.53 min, 0% ee.

HPLC condition of **O20** and **O20-I** mixture: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 238 nm, t_R (minor **O20**) = 21.23min, t_R (major **O20**) = 27.65 min, 90% ee; t_R (major **O20-I**) = 23.63 min, t_R (minor **O20-I**) = 29.97 min, 0% ee.

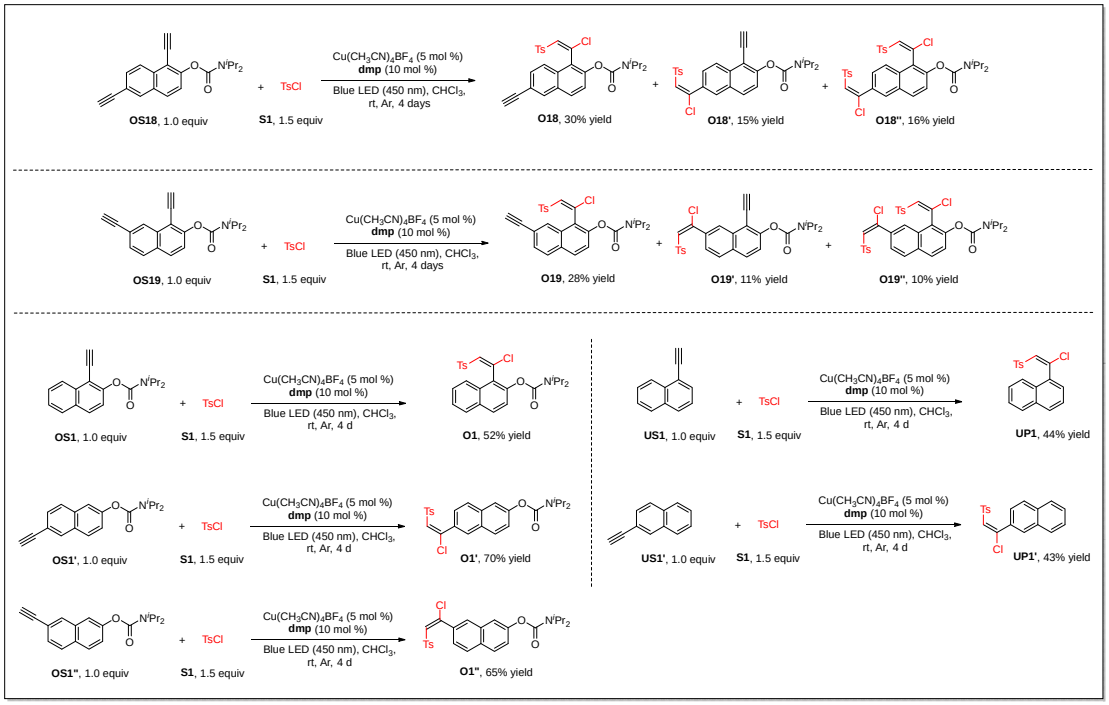
Control experiments of alkynes with TsCl under standard reaction conditions



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4PF_6$ (7.45 mg, 0.020 mmol, 10 mol %), **L7** (11.2 mg, 0.020 mmol, 10 mol %), alkyne (0.20 mmol, 1.0 equiv), sulfonyl chloride **S1** (57.2 mg, 0.30 mmol, 1.5 equiv), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times, anhydrous EtOAc (4.0 mL) was added to the mixture, and the reaction mixture was stirred at room temperature for 5 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the

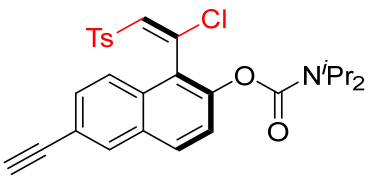
residue was purified by column chromatography on silica gel to afford the product.

Control experiments of alkynes with TsCl under photocatalytic conditions



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(CH_3CN)_4BF_4$ (3.14 mg, 0.010 mmol, 5 mol %), 2,9-dimethyl-1,10-phenanthroline (**dmp**) (4.17 mg, 0.020 mmol, 10 mol %), alkyne (0.20 mmol, 1.0 equiv), and sulfonyl chloride **S1** (57.2 mg, 0.30 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon three times, and anhydrous $CHCl_3$ (2.0 mL) was added to the mixture. The reaction mixture was irradiated with Blue LEDs (450 nm) and stirred at room temperature for 4 d. Upon completion, the precipitate was filtered off and washed by DCM. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(*S*$_a$,*E*)-1-(1-Chloro-2-tosylvinyl)-6-ethynylnaphthalen-2-yl diisopropylcarbamate (O18)



The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O18** (27.2 mg, 26% yield, 90% ee) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 9.0

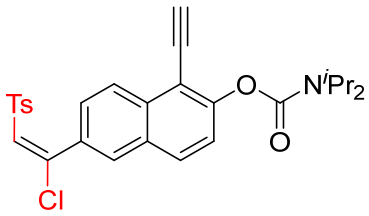
Hz, 1H), 7.36 (d, J = 1.7 Hz, 2H), 7.28 – 7.20 (m, 3H), 6.90 (d, J = 8.0 Hz, 2H), 4.21 – 3.79 (m, 2H), 2.26 (s, 3H), 3.17 (s, 1H), 1.39 – 1.20 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 147.5, 144.8, 142.1, 136.1, 135.3, 132.3, 131.0, 130.1, 129.9, 129.8, 129.3, 128.1, 124.3, 123.4, 122.0, 119.4, 83.4, 78.2, 47.1, 46.6, 21.5, 21.3, 21.2, 20.6, 20.4.

HRMS (ESI) m/z calcd. for $C_{28}H_{29}ClNO_4S$ $[M + H]^+$ 510.1500, found 515.1498.

HPLC condition: Chiralcel IE, n-hexane/i-PrOH = 60/40, flow rate 0.5 mL/min. λ = 254 nm, t_R (major) = 23.27 min, t_R (minor) = 28.16 min, 90% ee.

(*E*)-6-(1-Chloro-2-tosylvinyl)-1-ethynylnaphthalen-2-yl diisopropylcarbamate (O18')



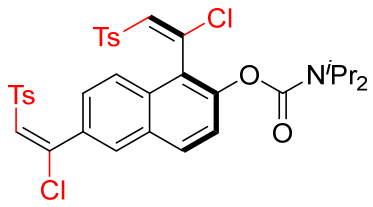
The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O18'** (15.3 mg, 15% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 1.8 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.50 – 7.34 (m, 4H), 7.10 (d, J = 8.1 Hz, 2H), 7.04 (s, 1H), 4.29 – 3.92 (m, 2H), 3.64 (s, 1H), 2.35 (s, 3H), 1.47 – 1.28 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 152.8, 147.6, 144.9, 137.5, 135.1, 132.0, 131.6, 130.7, 129.7, 129.6, 127.9, 126.6, 126.1, 123.2, 112.3, 87.3, 77.4, 47.1, 46.9, 21.7, 20.7.

HRMS (ESI) m/z calcd. for $C_{28}H_{29}ClNO_4S$ $[M + H]^+$ 510.1500, found 515.1500.

1,6-Bis((*S*$_a$,*E*)-1-chloro-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O18'')



The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **O18''** (5.6 mg, 4% yield, 88% ee) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.54 (d, J = 9.0 Hz, 1H), 7.47 – 7.25 (m, 6H), 7.22 (s, 1H), 7.10 (d, J = 8.1 Hz, 2H), 7.06 (s, 1H), 7.03 (d, J = 8.1 Hz,

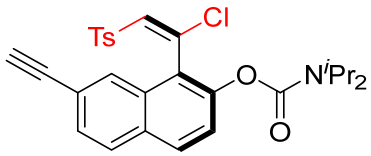
2H), 4.20 – 3.82 (m, 2H), 2.31 (s, 3H), 2.30 (s, 3H), 1.38 – 1.24 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 148.2, 147.3, 145.0, 141.7, 137.3, 136.3, 135.0, 132.4, 131.9, 131.4, 131.0, 129.8, 129.7(4), 129.6(8), 129.4, 128.3, 127.9, 126.6, 124.3, 123.6, 122.3, 47.2, 46.8, 21.7(3), 21.7(0), 21.4, 21.3, 20.6, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{35}H_{36}Cl_2NO_6S_2$ $[M + H]^+$ 700.1361, found 700.1354.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 254 nm, t_R (major) = 99.39 min, t_R (minor) = 122.68 min, 88% ee.

(*Sa,E*)-1-(1-Chloro-2-tosylvinyl)-7-ethynylnaphthalen-2-yl diisopropylcarbamate (O19)



The reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O19** (21.5 mg, 21% yield, 54% ee) as a yellow solid.

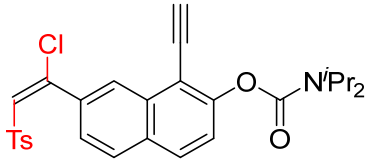
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.43 (dd, J = 8.4, 1.5 Hz, 1H), 7.40 (s, 1H), 7.26 (d, J = 3.3 Hz, 1H), 7.22 (d, J = 8.3 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 4.39 – 3.77 (m, 2H), 3.15 (s, 1H), 2.25 (s, 3H), 1.41 – 1.23 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 147.6, 144.7, 142.4, 136.1, 135.6, 131.0, 130.2, 129.5, 129.4, 128.4, 128.3(3), 128.3(1),128.1, 123.6, 121.7, 120.9, 83.6, 78.5, 47.2, 46.8, 21.6, 21.4, 21.3, 20.6, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{29}ClNO_4S$ $[M + H]^+$ 510.1500, found 515.1499.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 254 nm, t_R (major) = 17.79 min, t_R (minor) = 18.86 min, 54% ee.

(*E*)-7-(1-Chloro-2-tosylvinyl)-1-ethynylnaphthalen-2-yl diisopropylcarbamate (O19')



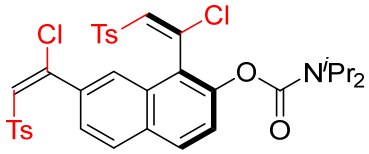
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O19'** (3.2 mg, 3% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.82 (dd, J = 13.9, 8.7 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.06 (d, J = 9.0 Hz, 3H), 4.25 – 3.98 (m, 2H), 3.63 (s, 1H), 2.31 (s, 3H), 1.47 – 1.24 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.0, 152.8, 147.6, 144.9, 137.3, 133.3, 133.2, 132.2, 131.3, 129.7(1), 129.6(8), 128.3, 128.0, 126.9, 125.6, 124.0, 112.9, 87.7, 47.1, 46.9, 29.8, 21.7, 20.6.

HRMS (ESI) m/z calcd. for $C_{28}H_{29}ClNO_4S$ $[M + H]^+$ 510.1500, found 515.1500.

1,7-Bis((*Sa,E*)-1-chloro-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O19'')



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **O19''** (7.0 mg, 5% yield, 35% ee) as a white solid.

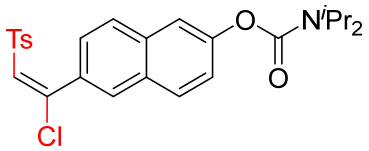
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 9.0 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.21 (s, 1H), 7.06 (d, J = 8.1 Hz, 2H), 6.99 (s, 1H), 6.92 (d, J = 8.0 Hz, 2H), 4.35 – 3.69 (m, 2H), 2.30 (s, 3H), 2.21 (s, 3H), 1.40 – 1.27 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 147.6, 146.9, 144.9, 144.6, 140.9, 137.2, 136.0, 135.4, 132.9, 132.2, 131.2, 130.8, 129.7, 129.5, 129.2, 128.2, 128.1, 127.9, 125.5, 125.3, 124.5, 122.8, 47.3, 46.7, 21.7, 21.6, 21.4, 21.2, 20.6, 20.5.

HRMS (ESI) m/z calcd. for $C_{35}H_{36}Cl_2NO_6S_2$ $[M + H]^+$ 700.1361, found 700.1354.

HPLC condition: Chiralcel IE, *n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min. λ = 254 nm, t_R (major) = 65.66 min, t_R (minor) = 74.5 min, 35% ee.

(*E*)-6-(1-Chloro-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O1')



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O1'** (17.5 mg, 18% yield) as a white solid.

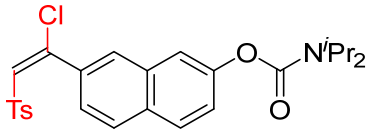
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 2.3 Hz, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.02 (s, 1H), 4.25 – 3.89 (m, 2H), 2.32 (s, 3H), 1.63 – 1.09 (m,

12H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.6, 150.8, 148.1, 144.7, 137.6, 134.7, 131.6, 130.9, 130.0, 129.7, 129.6, 129.4, 127.9, 127.6, 125.7, 122.9, 118.4, 47.1, 46.3, 21.7, 21.6, 20.6.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}ClNNaO_4S$ $[M + Na]^+$ 508.1320, found 508.1322.

(*E*)-7-(1-Chloro-2-tosylvinyl)naphthalen-2-yl diisopropylcarbamate (O1'')



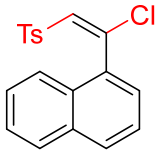
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **O1''** (21.4 mg, 22% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 – 7.79 (m, 2H), 7.76 (d, J = 8.5 Hz, 1H), 7.57 (d, J = 2.3 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.39 (dd, J = 8.8, 2.3 Hz, 1H), 7.32 (dd, J = 8.5, 1.8 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.02 (s, 1H), 4.30 – 3.86 (m, 2H), 2.32 (s, 3H), 1.49 – 1.18 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.7, 150.0, 147.9, 144.7, 137.6, 132.7, 132.1, 131.8, 131.6, 129.6, 129.0(3), 128.9(7), 127.9, 127.8, 124.7, 124.0, 119.3, 47.1, 46.4, 21.7, 21.6, 20.6.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}ClNNaO_4S$ $[M + Na]^+$ 508.1320, found 508.1322.

(*E*)-1-(1-Chloro-2-tosylvinyl)naphthalene (UP1)



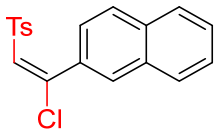
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to afford **UP1** (35.1 mg, 51% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, J = 6.0, 3.5 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.52 – 7.39 (m, 4H), 7.33 (t, J = 6.9, 1H), 7.15 (d, J = 8.3 Hz, 2H), 6.79 (d, J = 8.0 Hz, 2H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 144.3, 136.4, 134.8, 133.3, 131.3, 131.0, 129.2, 129.1, 128.4, 127.8(8), 127.8(5), 126.8, 126.3, 124.9, 124.6, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{15}ClNaO_2S$ $[M + Na]^+$ 365.0373, found 365.0372.

(*E*)-2-(1-Chloro-2-tosylvinyl)naphthalene (UP1')



The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to afford **UP1'** (33.0 mg, 48% yield) as a white solid.

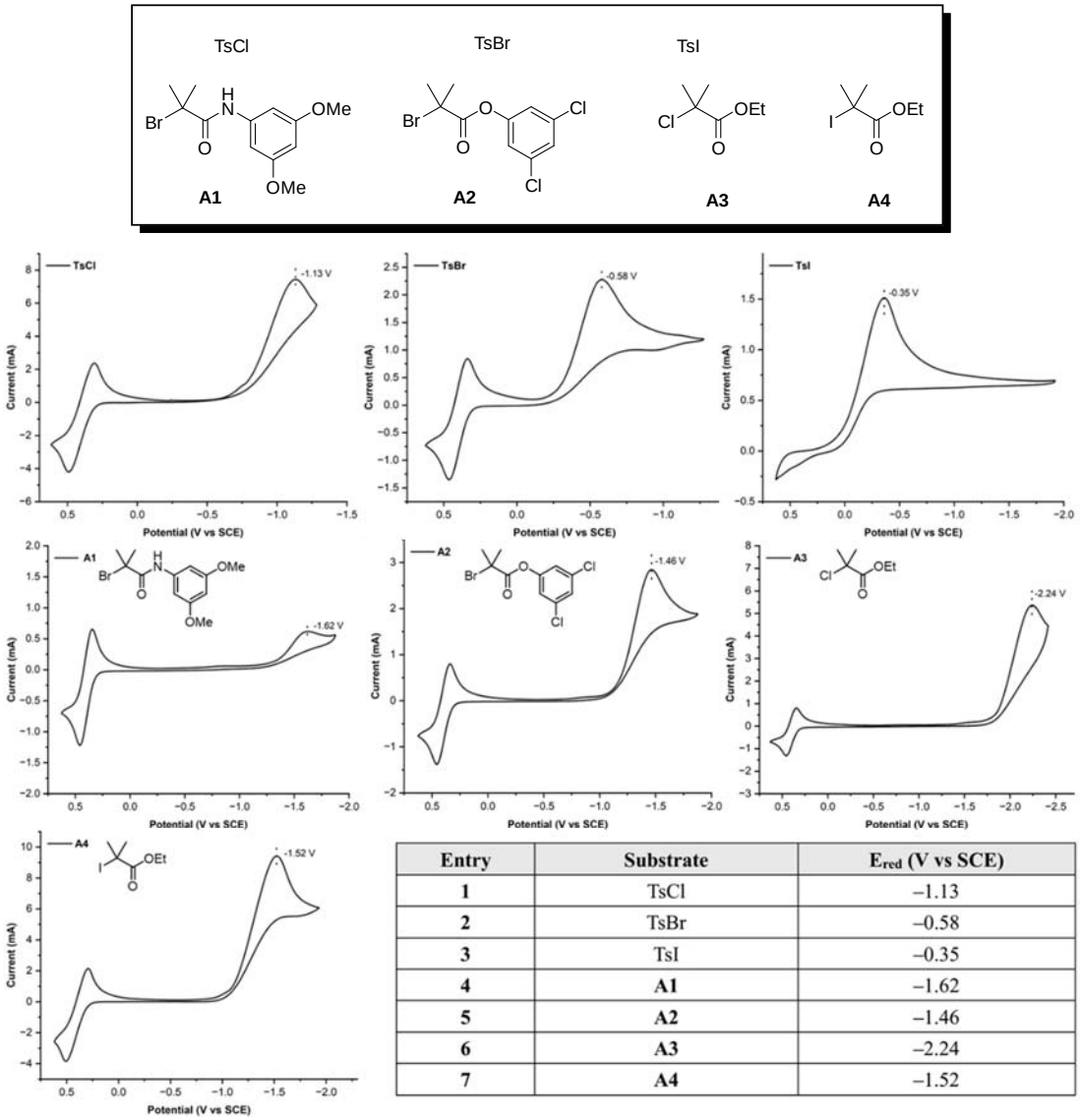
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.73 (m, 4H), 7.62 – 7.50 (m, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.38 (dd, J = 8.5, 1.8 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.03 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 144.7, 137.6, 134.1, 132.2, 131.5(9), 131.5(5), 129.6, 129.6, 128.9, 128.0, 127.9(4), 127.8(9), 127.8(7), 127.0, 125.2, 21.7.

HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{15}ClNaO_2S$ $[M + Na]^+$ 365.0373, found 365.0372.

Electrochemical analysis results of radical precursors

Cyclic voltammetry (CV) was performed using a CHI 650E potentiostat with a three-electrode cell configuration. The setup consisted of a glassy carbon working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode. The test solution was prepared by dissolving the radical precursor sample (2.0 mg) in 4.0 mL of a 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution in CH_3CN, which served as the supporting electrolyte. The measurements were conducted at a scan rate of 0.1 V s^{-1}. Ferrocene (E1/2 = +0.40 V vs. SCE)[19] was added at the end of the measurements as an internal standard, except for TsI, to calibrate the potential scale. All potential values are reported relative to the saturated calomel electrode (SCE).



Entry	Substrate	E_{red} (V vs SCE)
1	TsCl	–1.13
2	TsBr	–0.58
3	TsI	–0.35
4	A1	–1.62
5	A2	–1.46
6	A3	–2.24
7	A4	–1.52

Figure S7. Cyclic voltammetry and reduction potential values of radical precursors. Applicable precursors generally have reduction potentials higher than −1.6 V, while inapplicable precursors exhibit reduction potentials well below −2.0 V. Cyclic voltammetry measurements were performed by dissolving each sample (2.0 mg) in a 0.10 M solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_3CN (4.0 mL) and analyzing the solution at a scan rate of 0.1 V s^{-1}. All data, except for TsI,

were calibrated using ferrocene as an internal standard, with a redox potential of +0.40 V vs SCE (saturated calomel electrode).

Computational study

Computational Details

All of the calculations were performed using the Gaussian 16 program.[20] Conformational searches on the transition states and intermediates were extensively performed using Grimme's programs xTB 6.3 and CREST 2.10.2.[21] Structures were optimized at the (U)B3LYP level of density functional theory[22] with Grimme's D3(BJ) dispersion correction[23] in gas phase. For optimizations, Ahlrichs's Def2TZVP basis set was used for Cu,[24] while Pople's 6-31G(d) basis set was applied for all other atoms.[25] Frequency calculations have been performed to verify the optimized structures as local minima or transition states and to obtain Gibbs free energy at 298 K. To reduce error caused by the breakdown of the harmonic oscillator approximation, Truhlar's quasi-harmonic correction was used to compute molecular entropies by setting all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}.[26] Intrinsic reaction coordinate (IRC) calculations were carried out to make sure that every transition state links relevant intermediates.[27] The electronic energies were further refined by carrying out single-point energy calculations using M. Head-Gordon's long-range corrected hybrid density functional (U)ωB97X-D.[28] The Def2TZVP and 6-311+G(d,p) basis set was applied for Cu[24] and non-metal atoms,[25] respectively. The PCM solvation model with DCM as the solvent was employed to account for the solvation effect.[29] The three-dimensional (3D) structures were depicted using CYLview and VMD software.

Computational results

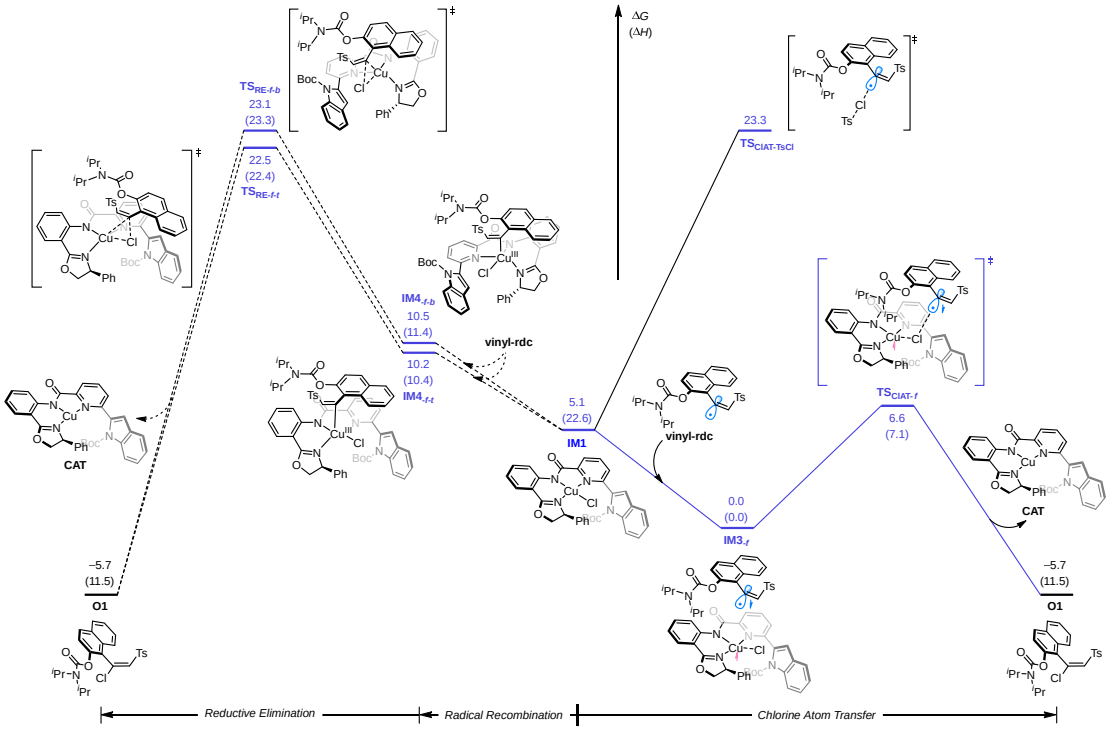


Figure S8. Energy profiles comparing the Cl atom transfer pathways and the reductive elimination pathway. The relative free energies and enthalpies (in parentheses) are provided in kcal/mol. For vinyl ligands occupying the Cu(II) complex on either the top or bottom side, the reductive elimination transition states are significantly less stable than the Cl atom transfer transition state (**TS$_{CIAT\text{-}f}$**). In addition, the Cl atom transfer involving TsCl proceeds through an energetically unfavorable transition state (**TS$_{CIAT\text{-}TsCl}$**).

Cartesian coordinates of computed species

CAT

E = -3473.56793286 G = -3473.059095

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8	-3.79492100	-2.24401300	-1.75205200
8	1.46065000	-0.19359500	2.46144800
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7	-0.30702800	-1.71742700	-1.15316600
7	-2.67736100	-0.40908500	-0.77960800
7	-0.98506000	1.75311900	0.32092700
6	-1.42962500	-1.10525400	2.63164700
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1	-2.23548800	-1.34215900	3.33494700
1	-1.87826600	-0.90667100	1.65431600
6	-0.47874700	-2.29884200	2.56020100
6	1.38372900	-1.02941400	1.58092600
6	2.09292700	-1.68914400	-0.77266000
6	0.87134400	-2.36967800	-1.22710500
6	-1.44466900	-2.32343200	-1.55643800
6	-2.79465500	-1.61735700	-1.36983700
6	-3.73416100	0.40716500	-0.44277500
6	-3.49183100	1.68673900	0.17879500
6	-2.17614300	2.25202100	0.48160700
6	0.03123900	2.70590200	0.79969700
1	0.47585400	2.29238300	1.71187800
6	0.20570200	-2.58608700	3.89625200
1	0.91118000	-3.41735800	3.79313100
1	-0.54966100	-2.86789100	4.63741000
1	0.74113400	-1.70687800	4.25846900
6	3.24054000	-1.52924800	-1.50019000
1	3.38469000	-1.89034000	-2.50924200
6	4.16398100	-0.74632100	-0.72768200
6	5.47058800	-0.29330100	-0.96177300
1	5.96580500	-0.51177100	-1.90344200
6	6.11896400	0.42349300	0.03615000
1	7.13290200	0.77764700	-0.12541900
6	5.47969900	0.68813400	1.26238000
1	6.01029600	1.24199700	2.03141700
6	4.17834300	0.26180800	1.51504500
1	3.68202600	0.47241100	2.45207100
6	3.52545400	-0.44191400	0.50016200
6	0.95161600	-3.65549800	-1.77187800
1	1.91186200	-4.15693400	-1.80806500
6	-0.21102900	-4.27088800	-2.22939800
1	-0.16927400	-5.26935000	-2.65477600
6	-1.42669900	-3.60371000	-2.10918800
1	-2.37131100	-4.03331400	-2.41819500
6	-5.08852100	0.04857100	-0.66968700
1	-5.27418500	-0.90516100	-1.14121600
6	-6.13749300	0.87621800	-0.30632700
1	-7.15734400	0.55217200	-0.49931500
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1	-0.65501700	4.37313100	2.10103800
1	-0.67579800	4.74963000	0.35473900
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29	-0.67529000	0.06878800	-0.47324400
6	1.12316300	2.90129000	-0.22662700
6	0.79952800	3.16298200	-1.56464700
6	2.46409500	2.78609500	0.13997700
6	1.80632200	3.30459000	-2.51703000
1	-0.24355000	3.23115600	-1.86162900
6	3.47545400	2.92203200	-0.81269100
1	2.71869100	2.55805200	1.16978900
6	3.14761600	3.18122700	-2.14246300
1	1.54503600	3.49919500	-3.55346200
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1	3.93191700	3.27744100	-2.88806900

IM1

E = -3933.81771771 G = -3933.30907

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8	-4.59390500	-1.43831900	-1.26213500
7	-3.28459400	-0.19890000	0.16930100
7	-0.03769700	-1.20316100	1.19308600
7	2.54663100	-1.26087400	0.46010100
7	2.10284400	1.17068900	-0.90632400

6	-2.60646800	-3.18635200	-2.67265000	1	5.86958100	1.01707300	-1.76530600
1	-3.56148200	-2.77450600	-3.00125400	6	2.87012800	3.17889600	-1.82553800
1	-2.40264900	-4.10119600	-3.24009000	1	2.82842700	3.24583600	-2.91629500
1	-1.81575900	-2.45918300	-2.87791700	1	3.10043100	4.15470100	-1.39698200
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6	-2.12183200	0.00853300	0.94484200	1	-1.14475800	-5.09457100	-1.25316800
6	-1.33495800	-1.09089200	1.52540800	1	-1.28302600	-4.30671500	0.33422100
6	0.74316200	-2.11753900	1.80236000	29	0.97390200	-0.28876900	-0.29619100
6	2.20683000	-2.16388700	1.42842900	17	-0.57729100	-0.04838400	-1.91093700
6	3.85366500	-1.14571600	-0.01709300	6	1.07442800	3.21677500	0.01566700
6	4.27146400	0.01320000	-0.74569000	6	1.52279700	2.88161000	1.29825800
6	3.38985400	1.13114000	-1.02758000	6	0.14812500	4.25380800	-0.13267500
6	1.60627600	2.51400700	-1.21972700	6	1.05188100	3.57496500	2.41454300
1	0.80557300	2.42338500	-1.95719400	1	2.23169000	2.06971300	1.42553000
6	-3.81288700	-4.40336800	-0.78774500	6	-0.30623900	4.96145500	0.97981500
1	-3.80479200	-4.59412100	0.29101700	1	-0.22669100	4.50174600	-1.12234900
1	-3.74426000	-5.36573700	-1.30635000	6	0.14022600	4.62061200	2.25833300
1	-4.75652600	-3.92563900	-1.05807800	1	1.40264600	3.30048700	3.40534800
6	-1.97803000	1.34019800	1.20383600	1	-1.01745400	5.77185000	0.84844000
1	-1.19397600	1.78052900	1.80415600	1	-0.22197900	5.16437500	3.12594800
6	-3.07071700	2.03298800	0.57219600				
6	-3.44378500	3.38275800	0.51507500				
1	-2.84699100	4.13213800	1.02234500				
6	-4.58099300	3.73261800	-0.20274800	**IM3$_{-f}$**			
1	-4.88420000	4.77436700	-0.25867500	E =	-5695.16800074	G = -5694.193921	
6	-5.34660400	2.75307000	-0.86007400	8	-4.21103000	-0.51267700	-2.27869100
1	-6.22941700	3.05167000	-1.41804400	8	-1.06243800	4.70999700	2.93758000
6	-5.00682300	1.40288800	-0.80878600	8	0.62182800	2.89459300	-3.04845700
1	-5.59270300	0.64614800	-1.31035500	8	-5.92362700	-1.81865200	-1.53156400
6	-3.86876900	1.05891500	-0.07754300	7	-3.85988000	-1.85376800	-0.51344600
6	-1.90051700	-1.94728700	2.48042000	7	-1.34482000	0.49007100	-1.33709400
1	-2.94952400	-1.83314700	2.72853000	7	-0.53518600	3.05248700	-1.00715700
6	-1.10913700	-2.91094300	3.09165200	7	-1.50268900	2.92477600	1.67555100
1	-1.53520700	-3.58002200	3.83334000	6	-6.13260700	1.00115300	-2.54510500
6	0.24260400	-2.99463500	2.75569300	1	-6.89644300	0.30331400	-2.19964200
1	0.92336300	-3.70670400	3.20534600	1	-6.59186600	1.70873900	-3.24417100
6	4.82552100	-2.15679200	0.17350000	1	-5.74242500	1.55521900	-1.68652400
1	4.54381700	-3.03867800	0.72566000	6	-4.99195400	0.27278300	-3.25519500
6	6.11695700	-2.02817800	-0.31770400	6	-4.78458300	-1.40436700	-1.47532500
1	6.82130500	-2.83896900	-0.15150800	6	-2.53578800	-1.39102300	-0.33814700
6	6.51921500	-0.88571900	-1.01613200	6	-1.76002500	-0.78442300	-1.43484700
1	7.53149100	-0.78914900	-1.39508600	6	-0.56571100	1.01777100	-2.30222700
6	5.59342200	0.12131600	-1.22206800	6	-0.09747200	2.44469100	-2.15223500

6	-0.12574200	4.33808600	-0.66084200	16	5.00728000	-2.71694200	-1.65588800
6	-0.33924000	4.85562200	0.65813200	8	1.04275500	-1.80926700	-0.22981500
6	-0.98682500	4.11076600	1.72204800	8	1.55998300	-2.33771900	1.93358400
6	-1.94370900	2.52733500	3.03597900	8	6.16850400	-2.64765500	-2.55867300
1	-2.94947500	2.11469900	2.95735300	8	4.60579300	-4.01081900	-1.06670300
6	-5.47767800	-0.65856900	-4.36464400	7	0.88129400	-3.95778600	0.45128800
1	-4.63065800	-1.18264900	-4.82069100	6	1.54637300	-0.52931500	-0.14434100
1	-5.97682900	-0.07199500	-5.14341900	6	3.73556600	1.66414300	-2.28564500
1	-6.18293200	-1.39392600	-3.97302800	1	3.99209100	0.98517100	-3.09239900
6	-2.07957800	-1.78202900	0.88590900	6	1.18567300	0.36236600	0.86652500
1	-1.09114900	-1.60007300	1.27289700	1	0.53519600	0.03760100	1.66482200
6	-3.13849500	-2.49945700	1.54778200	6	1.19551500	-2.69950100	0.82467300
6	-3.24221800	-3.12007200	2.80133900	6	2.90702600	1.20465900	-1.24413700
1	-2.40321200	-3.11719800	3.48854500	6	2.42845800	-0.16487700	-1.19086100
6	-4.43735600	-3.74064500	3.14561000	6	1.69073400	1.64878900	0.84727800
1	-4.53312100	-4.22455900	4.11319800	1	1.41123700	2.34217200	1.63042500
6	-5.52532500	-3.74844800	2.25548700	6	2.81654800	-1.10930000	-2.11512800
1	-6.44957000	-4.23843100	2.54735500	6	5.89203100	-0.34316500	-0.58824600
6	-5.44911100	-3.14556400	1.00164800	1	6.43789200	-0.21836400	-1.51693400
1	-6.28337100	-3.14714700	0.31515700	6	5.19214400	-1.52489900	-0.34456600
6	-4.24363600	-2.53029300	0.66059000	6	5.84086600	0.67341300	0.36111600
6	-1.40659000	-1.56836700	-2.54108900	1	6.35153000	1.61203000	0.16651600
1	-1.76136200	-2.59099900	-2.58774500	6	4.47366400	-1.71376800	0.83409400
6	-0.60638000	-1.02950000	-3.53899600	1	3.93480200	-2.63666900	1.00176100
1	-0.31416000	-1.63099300	-4.39436700	6	4.21825900	2.95865800	-2.28050300
6	-0.17439200	0.28951600	-3.41824200	1	4.85354800	3.30063500	-3.09208400
1	0.46219400	0.77573400	-4.14611600	6	2.55036700	2.09633500	-0.19185600
6	0.52138700	5.20523700	-1.57715800	6	4.41713100	-0.67999400	1.76272800
1	0.70154900	4.84420100	-2.57537100	1	3.79839100	-0.80288400	2.64575900
6	0.94365900	6.47449800	-1.21425700	6	3.88116400	3.84162700	-1.23413900
1	1.43375900	7.09355800	-1.96116200	1	4.25184700	4.86211700	-1.24515300
6	0.74891400	6.96261200	0.08137500	6	5.08271100	0.53094100	1.53170400
1	1.08219500	7.95617900	0.36338800	6	3.56635500	-2.06127600	-2.58332600
6	0.10329900	6.15283300	0.99702300	1	3.44782400	-2.59007000	-3.52765800
1	-0.07845400	6.50673100	2.00407200	6	0.45026100	-4.31745100	-0.91970900
6	-1.92750900	3.88322300	3.76074000	1	0.44754700	-3.38594500	-1.48019300
1	-2.91438700	4.35478500	3.78319900	6	1.03264600	-5.04485500	1.44839300
1	-1.50343600	3.84992800	4.76399600	1	0.75669200	-5.95128900	0.90515600
6	-3.95072500	1.26659200	-3.76803300	6	3.05703200	3.41867600	-0.21246500
1	-3.59347800	1.89569800	-2.94756600	1	2.76607500	4.10096600	0.58109300
1	-4.39492100	1.90842500	-4.53523200	6	-0.97824500	-4.87465600	-0.90948300
1	-3.09497400	0.74262300	-4.20446300	1	-1.04162400	-5.82659900	-0.37091000
29	-1.78599900	1.89333900	0.04731800	1	-1.30959100	-5.06252500	-1.93742100
17	-3.91646500	1.33672500	0.58080500	1	-1.66940500	-4.16958200	-0.43998500

6	0.05162100	-4.88883100	2.61459300
1	-0.97796800	-4.81735000	2.25118600
1	0.28458200	-3.99036400	3.19045000
1	0.12411400	-5.75685100	3.27925200
6	2.48814400	-5.20434800	1.90355800
1	2.59415000	-6.12866700	2.48232300
1	2.78932400	-4.36546800	2.53453600
1	3.16164900	-5.25274900	1.04215100
6	1.44867400	-5.26595400	-1.59201800
1	1.46285800	-6.25263300	-1.11540800
1	2.46124200	-4.85548500	-1.56331100
1	1.15732800	-5.41610200	-2.63802900
6	4.96367400	1.66505200	2.51777200
1	3.96802100	1.67563100	2.97368900
1	5.12444200	2.63085700	2.02960200
1	5.69905700	1.56995400	3.32726300
6	-0.99253300	1.48772700	3.59422100
6	-1.36781600	0.14049700	3.62685000
6	0.29232500	1.84952500	4.02121400
6	-0.46350600	-0.82847100	4.06596600
1	-2.35736800	-0.14805600	3.28424500
6	1.19360600	0.87991500	4.45916600
1	0.59721500	2.89277300	3.99627800
6	0.81918700	-0.46468400	4.47471900
1	-0.75008800	-1.87414800	4.07231100
1	2.18950600	1.17324300	4.77917900
1	1.52504800	-1.22777300	4.78524800

O1

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16	-1.10689600	2.35059900	9.25501400
8	2.53102600	3.20924400	9.30165300
8	4.49789000	4.32904100	9.45462300
8	-2.54069200	2.35578300	9.52806700
8	-0.21259600	1.49832600	10.03543400
7	3.49847200	3.43210200	11.32169300
6	2.33773700	3.62913300	8.01150900
6	-0.29969600	5.41717100	6.06160300
1	-0.97536700	5.73414400	6.85009100
6	3.22776100	3.24669200	6.98607300
1	4.12791000	2.70538400	7.24977100
6	3.60505700	3.71779700	10.00530900
6	0.87241400	4.69485600	6.40012200
6	1.18952800	4.33692400	7.74516700
6	2.93111800	3.56731000	5.69058500
1	3.60426000	3.27205100	4.89023000
6	0.32114100	4.74852200	8.87133000
6	0.26647800	1.27920300	7.14140100
1	0.96019200	0.91207000	7.88995100
6	-0.85731200	1.99794800	7.53539600
6	0.48830700	1.07381700	5.78694100
1	1.37634300	0.53525600	5.46843900
6	-1.77425300	2.47772900	6.60542400
1	-2.65463200	3.01846700	6.93703700
6	-0.59132600	5.70338400	4.75219300
1	-1.49309400	6.25694500	4.50867700
6	1.74934000	4.28287400	5.36051700
6	-1.53375600	2.26419400	5.25461100
1	-2.22931400	2.65815400	4.51922000
6	0.26970400	5.27834600	3.71577800
1	0.02551600	5.50827300	2.68307900
6	-0.39574000	1.57581600	4.82687100
6	-0.61338500	4.04791000	9.50945000
1	-1.17161800	4.46962700	10.34010300
6	2.32484000	2.74228900	11.89203000
1	1.73879900	2.37572500	11.05282100
6	4.51816500	3.97459500	12.23932700
1	4.18512400	3.66863000	13.23475700
6	1.41565000	4.58703600	4.01663400
1	2.08720500	4.26168200	3.22622000
6	1.44297400	3.71234600	12.67963700
1	1.94930800	4.09915900	13.57211900
1	0.53115800	3.20037800	13.00403400
1	1.15725400	4.56216300	12.05066100
6	4.55828700	5.50471300	12.22506800
1	4.91300100	5.87560100	11.26142900
1	5.23347200	5.86273400	13.00975500
1	3.56170000	5.91678100	12.41446800
6	5.89107400	3.34477100	11.99996500
1	5.82790000	2.25339400	12.06107200
1	6.59785700	3.69208600	12.76122200
1	6.27477000	3.62188900	11.01551700
6	2.73794100	1.52231300	12.71617100
1	3.37827400	0.85950600	12.12603100
1	1.84162300	0.96417800	13.00402700

1	3.27107900	1.79169300	13.63510500	6	-6.01258600	1.86937800	2.31688100
6	-0.13182100	1.36964700	3.35837600	1	-5.82178600	2.76384400	2.89142200
1	0.93993700	1.27259000	3.15998300	6	-5.23658500	1.55344400	1.19970100
1	-0.51133500	2.20991300	2.76966600	6	-2.71879900	3.05934200	-2.14598200
1	-0.62116400	0.45714700	2.99732500	1	-3.51372400	3.76096200	-1.92119700
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8	-0.80638800	-4.80267700	-0.77986600	6	2.31116500	-1.91696400	-3.03238800
8	0.87317300	0.24206300	-4.02861300	1	2.57377500	-0.97030100	-3.47530500
8	-4.10171900	3.99598100	2.07014600	6	3.13373300	-3.02087800	-3.20322500
7	-4.13891000	2.22537000	0.61853300	1	4.04938300	-2.91129300	-3.77802800
7	-1.68786700	0.94565600	-1.68910800	6	2.81405500	-4.25167700	-2.62404700
7	0.27137900	-0.90812100	-2.09395400	1	3.47008700	-5.10845000	-2.74126500
7	-1.34805500	-2.63283300	-0.64914500	6	1.63743700	-4.36721400	-1.89851500
6	-1.34466700	5.00720600	2.47339000	1	1.36136400	-5.31133100	-1.44512800
1	-2.25563400	5.10587800	3.06325900	6	-1.99365500	-4.77276500	0.05425500
1	-0.71928500	5.89328000	2.63064400	1	-1.68091800	-4.99552700	1.07871400
1	-0.77525300	4.13797400	2.81071400	1	-2.68075700	-5.53604500	-0.31156200
6	-1.65723600	4.88814700	0.98277300	6	-0.36907200	4.79645300	0.16769800
6	-3.54134900	3.34730500	1.20929600	1	0.29885500	4.03889300	0.57899800
6	-3.69913200	1.45859500	-0.48762800	1	0.15666700	5.75545100	0.21038600
6	-2.64707100	1.85189900	-1.43316000	1	-0.58080400	4.55991000	-0.87813400
6	-0.79614700	1.19214600	-2.66436500	29	-0.73225400	-0.67434500	-0.40793200
6	0.22326100	0.12896200	-2.98322900	17	-1.90272000	-0.33559100	1.47334200
6	1.10841200	-2.00212800	-2.29469300	16	2.06653900	2.02857400	1.99900700
6	0.77157900	-3.27298700	-1.73757500	8	3.17507400	0.24513400	-0.93310000
6	-0.48733100	-3.51136900	-1.03998300	8	5.34270700	0.62308400	-0.30040400
6	-2.51791900	-3.32291000	-0.10058700	8	1.29709800	2.95556700	2.84897700
1	-2.75950300	-2.87861100	0.86819900	8	3.15578900	2.55513500	1.15408300
6	-2.54155700	6.02519800	0.46782900	7	4.29535200	2.01688900	-1.79615200
1	-2.74507800	5.90019300	-0.60168500	6	3.08498000	-0.88907800	-0.17494000
1	-2.01766200	6.97702500	0.60340400	6	0.64006700	-2.48563500	2.19162200
1	-3.48686600	6.07061000	1.01072400	1	-0.12788100	-1.72759000	2.26750700
6	-4.49429100	0.35796800	-0.61681000	6	4.08758000	-1.87815200	-0.21470100
1	-4.39606500	-0.38713200	-1.39224200	1	4.96486600	-1.71015900	-0.82156500
6	-5.47145700	0.38429700	0.43456000	6	4.37411700	0.96395600	-0.96111600
6	-6.51909600	-0.47857700	0.78512100	6	1.76341200	-2.25599200	1.36477100
1	-6.70477300	-1.37003800	0.19632600	6	1.92628400	-1.04356900	0.59789300
6	-7.29681200	-0.16849500	1.89374100	6	3.92813300	-3.03646900	0.50218600
1	-8.11246300	-0.82575100	2.18232000	1	4.69041000	-3.80905700	0.45540900
6	-7.04101700	0.98971500	2.64914600	6	0.91562600	-0.02179800	0.53696200
1	-7.66241600	1.21222400	3.51194400	6	1.89758000	0.18006600	4.00937800

1	0.92278600	0.61440900	4.20416200	6	-4.98338400	-3.55990400	-0.54391700
6	2.71398800	0.71063200	3.00870900	6	-4.71402200	-2.66064300	-3.16551400
6	2.35246700	-0.91789900	4.73065800	1	-2.61747400	-2.44495600	-2.70676600
1	1.72188600	-1.34898700	5.50329000	6	-6.10266500	-3.48477800	-1.37228700
6	3.97228500	0.18117500	2.73043400	1	-5.09439000	-3.88963400	0.48654500
1	4.58099700	0.59822600	1.93582500	6	-5.97140200	-3.02946100	-2.68647600
6	0.51100400	-3.66589300	2.89704100	1	-4.60310300	-2.30089200	-4.18453700
1	-0.36152200	-3.81562300	3.52699800	1	-7.07840200	-3.77101500	-0.98932100
6	2.78088700	-3.25682200	1.30778800	1	-6.84402000	-2.96031900	-3.32936900
6	4.40482100	-0.92203600	3.46365400				
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6	1.50418200	-4.66623400	2.82201900	**IM4**$_{\text{f-t}}$			
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6	3.60213800	-1.49409100	4.45809200	8	4.41871800	0.13647100	-2.11232300
6	0.82831000	1.22462800	0.95927600	8	2.25592900	-4.07660500	0.09348700
1	-0.02990800	1.86946100	0.80781900	8	-0.48548200	0.07391300	-3.73393300
6	3.06202700	2.38226100	-2.52845700	8	4.97023800	-1.38915500	-0.51189900
1	2.34570200	1.59478800	-2.31969400	7	4.42401800	0.77353200	0.04227000
6	5.46301500	2.92771800	-1.88607900	7	1.90681400	1.22599100	-1.43447500
1	5.13773300	3.71616400	-2.56889100	7	0.15827200	-0.82257600	-1.67416900
6	2.62287100	-4.45676000	2.04417000	7	1.79160700	-1.90228400	0.34258800
1	3.40353000	-5.21051300	1.98114000	6	3.37031900	-1.91561200	-2.99491300
6	3.30702800	2.39001200	-4.03986700	1	3.70385000	-2.60512500	-2.21878100
1	3.99884900	3.18453800	-4.34194900	1	3.21335900	-2.48007800	-3.91989700
1	2.36023700	2.54362900	-4.56455000	1	2.41724700	-1.47841300	-2.69341100
1	3.71339100	1.42896200	-4.36881500	6	4.39508000	-0.81192700	-3.24750600
6	6.66972900	2.23147000	-2.52430900	6	4.61892600	-0.27721700	-0.86568100
1	6.40459500	1.81523500	-3.50215200	6	3.81229400	2.02261200	-0.21422100
1	7.02971600	1.42405800	-1.88323000	6	2.80571500	2.21139900	-1.26287700
1	7.48227000	2.95274300	-2.66655700	6	0.99040500	1.33644000	-2.40066900
6	5.79728600	3.58716900	-0.54360600	6	0.10572600	0.13932400	-2.65432600
1	6.55702600	4.36171000	-0.69953200	6	-0.16942500	-2.14481500	-1.96144100
1	6.18411300	2.85252300	0.16423100	6	0.55483600	-3.21147900	-1.35018100
1	4.90832700	4.04484200	-0.10317600	6	1.54841100	-2.99444800	-0.30481900
6	2.47737000	3.70009800	-2.00972400	6	2.67087400	-2.21792700	1.48499700
1	3.12174300	4.55590000	-2.24157200	1	3.47258200	-1.48434400	1.54036600
1	2.34219200	3.65122200	-0.92700200	6	5.80721900	-1.35327200	-3.46580400
1	1.50497000	3.87858000	-2.48061000	1	6.13111000	-1.94897500	-2.61071100
6	4.04604300	-2.73355400	5.19252100	1	6.51368700	-0.53010200	-3.61582600
1	5.13007200	-2.87007000	5.13056100	1	5.82105000	-1.98474700	-4.36067900
1	3.57118600	-3.62104100	4.75629300	6	4.12492800	2.88437900	0.79805700
1	3.76451000	-2.69598300	6.25034600	1	3.71594300	3.87914200	0.90929500
6	-3.71880100	-3.19756100	-1.02096000	6	4.92405500	2.17771200	1.76146500
6	-3.59173700	-2.74828000	-2.33894500	6	5.47798200	2.53643900	2.99789600

1	5.34084200	3.54016900	3.38948500	8	-5.31236400	-0.39320300	-0.88272500
6	6.19799000	1.58512800	3.71120500	8	-2.68086200	0.60171300	4.00527300
1	6.62730700	1.84457000	4.67439700	8	-4.05638100	-0.44626900	2.13053700
6	6.38065600	0.28804800	3.19924000	7	-4.48148200	-2.45415900	-0.30828500
1	6.95385100	-0.43565400	3.77151900	6	-2.79350400	0.52843600	-1.22204300
6	5.84055700	-0.09610700	1.97235300	6	-0.48182200	3.25863700	-0.08476300
1	5.98408100	-1.09070700	1.57329200	1	0.05506700	2.76288300	0.71614500
6	5.09631100	0.85693100	1.27505500	6	-3.45904300	1.17180900	-2.28458100
6	2.76926400	3.37563000	-2.03762700	1	-4.21561100	0.63099600	-2.83500800
1	3.51694400	4.14589800	-1.88218000	6	-4.38603100	-1.16657300	-0.69630900
6	1.78752800	3.50270200	-3.01960700	6	-1.47071500	2.54336500	-0.80282300
1	1.73459800	4.40101300	-3.62687900	6	-1.80589500	1.18457300	-0.48260400
6	0.89451700	2.45724500	-3.22856700	6	-3.15132200	2.47632600	-2.58987400
1	0.12887600	2.48133000	-3.99300100	1	-3.66405400	2.97260600	-3.40928600
6	-1.14185100	-2.48695700	-2.92776800	6	-1.10561200	0.47201900	0.55408800
1	-1.70847500	-1.69265300	-3.38519800	6	-2.74123200	3.22471300	2.44104900
6	-1.33501000	-3.80451300	-3.31848700	1	-1.97787900	3.09431500	3.20067100
1	-2.07925100	-4.02406500	-4.07922800	6	-3.44790100	2.11994900	1.96385900
6	-0.59470500	-4.84257000	-2.74428500	6	-3.03231400	4.48121300	1.92121200
1	-0.75074900	-5.87185400	-3.05119400	1	-2.48236300	5.34829600	2.27670600
6	0.32940600	-4.54015400	-1.75709800	6	-4.44463200	2.24880600	0.99821300
1	0.90476900	-5.32674200	-1.28423100	1	-4.97253800	1.37525800	0.63251500
6	3.21328800	-3.60557300	1.08389200	6	-0.19500300	4.56706400	-0.40925400
1	4.18782600	-3.53511700	0.59654300	1	0.56948900	5.10098700	0.14751700
1	3.23023300	-4.32963800	1.89838900	6	-2.17027100	3.19828600	-1.86157900
6	3.95455200	0.08243400	-4.40532200	6	-4.71609300	3.51682700	0.48950400
1	4.63645400	0.93134100	-4.51558200	1	-5.47827600	3.62709000	-0.27671800
1	2.94424200	0.46579300	-4.23835600	6	-0.88313800	5.21948900	-1.45730500
1	3.95742500	-0.49165000	-5.33709200	1	-0.64479700	6.25085700	-1.70186100
29	0.74266500	-0.18730200	0.07984200	6	-4.01231400	4.64405800	0.93146500
17	1.51967700	0.91359100	1.83141900	6	-1.44994800	0.09120600	1.77112300
6	1.88424500	-2.20908600	2.78134800	1	-0.82002400	-0.45514600	2.46393500
6	0.57717800	-2.70488000	2.83918500	6	-3.30726200	-3.32712200	-0.07992800
6	2.46765900	-1.68844400	3.93941900	1	-2.45943500	-2.81409500	-0.52713700
6	-0.14399600	-2.66329400	4.03315700	6	-5.82804500	-2.97721900	0.03936900
1	0.10233000	-3.09166400	1.94263100	1	-5.63595300	-3.98058700	0.42502400
6	1.75246700	-1.65505400	5.13564700	6	-1.85206800	4.54533900	-2.16844200
1	3.47023300	-1.27113100	3.89015000	1	-2.38853800	5.03571900	-2.97688900
6	0.44189900	-2.13455100	5.18437100	6	-3.46922800	-4.66916900	-0.80205600
1	-1.16721300	-3.02715700	4.05785500	1	-3.69110600	-4.51787200	-1.86187900
1	2.20952100	-1.23009100	6.02482300	1	-4.26133800	-5.28515400	-0.36329700
1	-0.12504500	-2.08393400	6.10905600	1	-2.53330600	-5.22942100	-0.73099300
16	-3.01746700	0.50146100	2.57584300	6	-6.70640600	-3.11389100	-1.20909800
8	-3.05622200	-0.77906500	-0.89375100	1	-7.66099400	-3.58272100	-0.94491500

1	-6.21573500	-3.73553200	-1.96560900
1	-6.90986000	-2.13069800	-1.63940600
6	-6.51455200	-2.19025600	1.16076500
1	-7.41683700	-2.72986000	1.47157800
1	-6.80030400	-1.19338100	0.82300800
1	-5.85176200	-2.07838600	2.02097600
6	-3.02675200	-3.51493600	1.41488600
1	-2.90187700	-2.54852500	1.90515600
1	-2.11620100	-4.11134900	1.54594600
1	-3.84661900	-4.04478700	1.91382300
6	-4.27250700	6.00252200	0.33174200
1	-4.24384500	6.78953600	1.09311800
1	-5.24693100	6.04159100	-0.16482100
1	-3.50566100	6.23930300	-0.41591300

vinyl-rdc

E = -1761.30851372 G = -1760.875203

16	-0.38622900	3.01806400	-0.23533100
8	1.24908000	-0.74352500	-0.55330700
8	2.51125000	-2.64816700	-0.37418800
8	-1.27104200	4.15832000	-0.52462500
8	0.99328600	3.25500300	0.23543900
7	3.44138900	-0.56176400	-0.08299700
6	0.01506700	-1.32969500	-0.62374000
6	-3.37094300	-0.13959400	-1.79758100
1	-3.10854900	0.79533500	-2.28257000
6	-0.32761500	-2.55877700	-0.04727600
1	0.44788400	-3.17080900	0.38938800
6	2.43347800	-1.43211900	-0.32893000
6	-2.34644600	-0.92635000	-1.23387300
6	-0.96180900	-0.48714300	-1.22481100
6	-1.65049300	-2.96218300	-0.04095700
1	-1.91870000	-3.91054500	0.41588400
6	-0.58119400	0.72896600	-1.73733000
6	-0.43328000	1.04751000	1.68624300
1	0.64464000	1.15315900	1.70835000
6	-1.20019100	1.90875500	0.90183300
6	-1.07363300	0.03691800	2.39540300
1	-0.48317000	-0.66102800	2.98283700
6	-2.58897000	1.80291500	0.85376800
1	-3.16132300	2.48593000	0.23587800
6	-4.69164900	-0.54068600	-1.72258900
1	-5.46984700	0.07929700	-2.15781500
6	-2.68201200	-2.16079600	-0.60675100
6	-3.21279600	0.78782400	1.57364200
1	-4.29059100	0.67170800	1.50952500
6	-5.03306400	-1.75130100	-1.08369900
1	-6.07311300	-2.05861500	-1.02605900
6	-2.46563500	-0.12327800	2.32974200
6	-0.29250600	1.99474900	-1.75156600
1	0.04789700	2.58586800	-2.60020000
6	3.24725900	0.90640600	-0.01003000
1	2.18765000	1.08478600	-0.15292100
6	4.80734500	-1.10308100	0.10918600
1	5.43033700	-0.21937300	0.26701300
6	-4.04374800	-2.54771100	-0.54384500
1	-4.29527200	-3.48737500	-0.05878500
6	3.98050000	1.62969400	-1.14240600
1	5.06985900	1.54122200	-1.05813600
1	3.72210400	2.69281800	-1.11216400
1	3.67500000	1.22799800	-2.11400000
6	5.32410000	-1.81450700	-1.14621400
1	4.73616800	-2.71072200	-1.35351400
1	6.37008400	-2.10700400	-1.00174800
1	5.27070200	-1.14965000	-2.01457900
6	4.90748300	-1.97254300	1.36762100
1	4.56690600	-1.41738400	2.24795700
1	5.94940100	-2.26910200	1.53180700
1	4.30001700	-2.87358900	1.26259500
6	3.61763100	1.45235900	1.37212700
1	3.09582800	0.89686600	2.15937700
1	3.31126000	2.50043800	1.43255900
1	4.69378700	1.39494700	1.57155100
6	-3.13720400	-1.26482500	3.04920600
1	-2.55586900	-2.18673500	2.94061800
1	-4.13929300	-1.44743500	2.65067800
1	-3.23250700	-1.05977800	4.12315800

$TS_{CIAT\text{-}f}$

E = -5695.15556948 G = -5694.177021

8	-4.22358300	-1.72200600	-1.38308700
8	-3.09440500	4.20555200	-0.59711800
8	-0.12879400	0.29072200	-4.40048100
8	-5.12170000	-0.57680800	0.37325100

7	-3.41268300	-2.08023200	0.68041700	1	1.68789600	4.45478200	-4.24750300
7	-1.39028200	-1.39887400	-1.53545100	6	0.14087600	5.19116000	-2.93460900
7	-0.78692300	1.10568200	-2.31029500	1	0.37601500	6.23924200	-3.08957300
7	-2.46471200	2.08887000	-0.23147000	6	-0.89141000	4.82299900	-2.08645400
6	-4.62535000	0.45944300	-2.46299500	1	-1.46989400	5.57860500	-1.56807600
1	-5.00776500	0.96577500	-1.57568200	6	-4.12664100	3.66809000	0.26765000
1	-5.07409400	0.92395500	-3.34750800	1	-5.03187900	3.54706800	-0.33537000
1	-3.54278300	0.60132100	-2.51423600	1	-4.30546400	4.38600900	1.06803900
6	-4.98053700	-1.02661100	-2.44860600	6	-4.47327000	-1.72120500	-3.71087100
6	-4.33091800	-1.37327000	-0.10356900	1	-4.65716300	-2.79858400	-3.65597400
6	-2.27438400	-2.79780800	0.24199000	1	-3.40061700	-1.55798300	-3.84138300
6	-1.66798600	-2.64034300	-1.08426700	1	-4.99455200	-1.32193900	-4.58635300
6	-0.87663100	-1.24577500	-2.76714800	29	-1.36539200	0.45693400	-0.51960200
6	-0.55324100	0.15179900	-3.24721500	17	-0.71011900	-0.15477700	1.53051400
6	-0.47627400	2.44250400	-2.53183000	6	-3.01977300	2.33381300	2.16816400
6	-1.19550000	3.46823100	-1.85125900	6	-2.20837100	3.37991800	2.61977100
6	-2.25188000	3.18414900	-0.88725500	6	-3.30515700	1.27164900	3.02509400
6	-3.55540500	2.31957300	0.75440900	6	-1.68010300	3.35409700	3.90874600
1	-4.28729000	1.51722100	0.65662700	1	-1.98474900	4.21314100	1.95944300
6	-6.47516800	-1.27393000	-2.24546900	6	-2.77717300	1.23948100	4.31516000
1	-6.83117700	-0.80101400	-1.32928900	1	-3.91814800	0.45362300	2.66892900
1	-6.67935100	-2.34854200	-2.19429900	6	-1.96016500	2.27891700	4.75819600
1	-7.02881500	-0.86107900	-3.09551100	1	-1.04993400	4.17015400	4.25145100
6	-1.78493900	-3.53102700	1.28319300	1	-2.99301100	0.39153800	4.95871500
1	-0.87808800	-4.11662800	1.24337700	1	-1.54073200	2.25602700	5.76005400
6	-2.59902300	-3.27291500	2.43931600	16	4.04512900	-0.73544700	2.93517200
6	-2.55100700	-3.72276400	3.76583600	8	1.93431100	1.20840100	-0.33912300
1	-1.76657900	-4.40209500	4.08633000	8	3.92695300	1.89643500	-1.22226100
6	-3.52405300	-3.28550900	4.65676400	8	4.22349700	-1.63964000	4.08390600
1	-3.49860700	-3.61960100	5.68972900	8	4.51930500	0.65989900	3.00954600
6	-4.55102700	-2.42254800	4.23351400	7	2.80960900	3.18452300	0.32162600
1	-5.31057400	-2.10757500	4.94305500	6	2.06796200	-0.05015000	-0.86939200
6	-4.62017000	-1.95820600	2.92098300	6	1.73335900	-3.58473700	0.36164600
1	-5.41250900	-1.29939700	2.59318600	1	1.50816400	-3.41469600	1.40927400
6	-3.61614200	-2.36942600	2.04339200	6	2.32979600	-0.26589100	-2.22754700
6	-1.37972800	-3.77194200	-1.85169000	1	2.45791000	0.58662500	-2.87810000
1	-1.60676900	-4.75214900	-1.44992900	6	2.98490500	2.11091500	-0.47360600
6	-0.84667200	-3.61300600	-3.12779700	6	1.95336200	-2.46759800	-0.47258700
1	-0.62788300	-4.48117000	-3.74117300	6	1.93177700	-1.11677500	0.03767600
6	-0.61216800	-2.32835000	-3.60449700	6	2.43039900	-1.55484700	-2.70632300
1	-0.20965600	-2.12395800	-4.58841600	1	2.62816300	-1.72246700	-3.76064900
6	0.55789200	2.84861000	-3.40452500	6	1.75984400	-0.84700700	1.39187500
1	1.09152700	2.08909600	-3.95487900	6	4.82567300	-2.88183100	1.40817500
6	0.86970300	4.18859400	-3.58413500	1	4.56864600	-3.48352200	2.27296200

6	4.73901400	-1.49227200	1.47907300	**$TS_{RE\text{-}f\text{-}b}$**			
6	5.22567000	-3.46858800	0.21022600	E =	-5695.12996997	G = -5694.155452	
1	5.27501500	-4.55098300	0.13467500	8	-2.34872800	3.57305600	0.72077200
6	5.06229900	-0.68578200	0.38837100	8	-0.00518500	-4.60490600	-1.34445400
1	4.98451700	0.39142300	0.45603800	8	0.77962600	0.75153600	-4.51629400
6	1.81594800	-4.86854700	-0.14110700	8	-4.18133000	3.84728500	2.04880600
1	1.64916700	-5.71832800	0.51477300	7	-4.08014300	2.12144800	0.54467400
6	2.24878600	-2.67665400	-1.85227900	7	-1.65231600	1.15356100	-1.96243400
6	5.44358600	-1.29003500	-0.80412600	7	0.43115300	-0.49911800	-2.56771300
1	5.64642400	-0.66336500	-1.66713300	7	-0.87920200	-2.55529400	-1.07353100
6	2.13257600	-5.08225300	-1.50040300	6	-1.46470300	4.97578500	2.55943000
1	2.20631200	-6.09513600	-1.88593600	1	-2.39034500	4.97839300	3.13501600
6	5.51848000	-2.68580300	-0.91378500	1	-0.91787800	5.90335400	2.76249700
6	2.25625500	-0.68554800	2.58461100	1	-0.83047800	4.14602800	2.88270700
1	1.68739600	-0.45610800	3.48167600	6	-1.74512400	4.89222800	1.05996100
6	1.66204600	3.33097000	1.25049300	6	-3.56453500	3.25867200	1.18389600
1	0.96189600	2.53592900	1.00157000	6	-3.59310000	1.44740700	-0.60294600
6	3.89398500	4.19398600	0.37365900	6	-2.63542100	1.98787700	-1.57490400
1	3.57118900	4.89979500	1.14177000	6	-0.84039800	1.50608800	-2.97687500
6	2.34017200	-4.00545900	-2.33666500	6	0.22812400	0.52913200	-3.42693500
1	2.57573200	-4.15922300	-3.38658800	6	1.38088300	-1.47704500	-2.83194000
6	0.95631100	4.67120900	1.02620900	6	1.21386000	-2.81916400	-2.37030600
1	0.65226000	4.78298200	-0.01679800	6	0.06577300	-3.26764600	-1.59012700
1	1.58848900	5.52373900	1.29809900	6	-1.81982700	-3.43959500	-0.38067100
1	0.06430700	4.71464000	1.65636400	1	-1.93937600	-3.08735500	0.64736800
6	4.00576500	4.95585500	-0.95125600	6	-2.67208200	6.00526900	0.56927800
1	4.74468300	5.76011000	-0.86028000	1	-2.85986000	5.90321600	-0.50507000
1	3.04186100	5.39671100	-1.22660100	1	-2.18880300	6.97318400	0.73741000
1	4.32029600	4.28161400	-1.75103300	1	-3.62328900	5.99639100	1.10359200
6	5.22852500	3.59739600	0.83892800	6	-4.25097100	0.25801000	-0.73431600
1	5.92907200	4.40803900	1.06996400	1	-4.09518700	-0.45082100	-1.53461500
1	5.66816300	2.97147400	0.06026400	6	-5.18294000	0.13485700	0.35071400
1	5.09075600	2.98848500	1.73781800	6	-6.09444500	-0.86597800	0.71524400
6	2.09453800	3.14059200	2.70760300	1	-6.18236500	-1.76369900	0.11343800
1	2.65734600	2.21312600	2.83216200	6	-6.86163300	-0.68200900	1.85875700
1	1.20466700	3.10073600	3.34484500	1	-7.57323600	-1.44590400	2.15955400
1	2.72415600	3.96860200	3.05532400	6	-6.73001000	0.48412800	2.63430000
6	5.90027700	-3.32633700	-2.22375200	1	-7.34337600	0.60616200	3.52249100
1	6.98653300	-3.29839300	-2.37852900	6	-5.83699700	1.49708500	2.28986100
1	5.43716100	-2.79762700	-3.06380400	1	-5.74313800	2.39782500	2.87910400
1	5.58185700	-4.37217800	-2.26203900	6	-5.07063400	1.30735000	1.13819500
				6	-2.80769100	3.24074800	-2.17896900
				1	-3.61528300	3.88529300	-1.85156700
				6	-1.96019800	3.61335800	-3.21565700

1	-2.08423100	4.57497500	-3.70527700	6	0.15423700	-3.68341100	3.28071000
6	-0.96945200	2.72657700	-3.63685700	1	-0.61247000	-3.80058100	4.04104200
1	-0.30316300	2.94036900	-4.46304800	6	2.18722800	-3.34631500	1.38655600
6	2.57846500	-1.18371200	-3.52676900	6	4.05800200	-1.16886600	3.63157300
1	2.71178500	-0.18333000	-3.90580800	1	4.94458800	-1.71263500	3.31792100
6	3.54718900	-2.14741300	-3.75945500	6	1.01045400	-4.76319900	2.97515900
1	4.45185800	-1.86978500	-4.29434700	1	0.88886500	-5.71659700	3.48103300
6	3.36735300	-3.46373700	-3.31855200	6	3.27955800	-1.66270800	4.68509000
1	4.12085900	-4.22230900	-3.50660200	6	0.59193900	1.33722900	1.43005900
6	2.20709200	-3.78341900	-2.63399500	1	-0.24031000	2.02693700	1.35577800
1	2.04917400	-4.79150100	-2.27181500	6	2.91992400	2.35184100	-2.28811900
6	-1.08343200	-4.80473100	-0.40227600	1	2.19313300	1.54623600	-2.23496800
1	-0.63873200	-5.05311500	0.56571500	6	5.32965300	2.69366500	-1.53349400
1	-1.69881000	-5.63102300	-0.76127400	1	5.09059900	3.53002500	-2.19366000
6	-0.44462800	4.88067500	0.26212900	6	2.01757400	-4.58666700	2.05068700
1	0.23415700	4.10912200	0.62938700	1	2.70841000	-5.39371600	1.82179200
1	0.06052400	5.84532200	0.37111700	6	3.29459800	2.55343800	-3.76054800
1	-0.63771400	4.70206000	-0.79879800	1	3.88947400	3.45988400	-3.91737900
29	-0.73515500	-0.48177300	-0.91270600	1	2.38120900	2.62884400	-4.35436200
17	-1.63272200	-0.38942500	1.17786000	1	3.86191600	1.69896000	-4.14112000
16	1.94984700	2.04242200	2.37874200	6	6.47998300	1.90604600	-2.16987700
8	2.73108100	0.31239500	-0.55752800	1	6.20088000	1.54490600	-3.16521400
8	4.95173500	0.39168600	0.00424900	1	6.74549700	1.04964500	-1.54640600
8	1.27786800	3.00345100	3.27352800	1	7.36034900	2.55036300	-2.27268400
8	3.02857100	2.50941500	1.49274800	6	5.69904200	3.28318000	-0.16805700
7	4.08036500	1.89163700	-1.49390300	1	6.52976900	3.98688300	-0.29477200
6	2.56185500	-0.87887800	0.08715900	1	6.00570800	2.50083100	0.52762600
6	0.28794300	-2.46994700	2.63539700	1	4.84953700	3.81182600	0.27045600
1	-0.35995800	-1.65083900	2.90644600	6	2.29329500	3.60455000	-1.67264000
6	3.46145000	-1.94141200	-0.13344400	1	2.97673500	4.46059200	-1.72220000
1	4.28038200	-1.79659700	-0.82124500	1	2.04684200	3.42623700	-0.62482000
6	4.02485700	0.85069800	-0.64552400	1	1.38057600	3.86825800	-2.21718900
6	1.27963000	-2.27241900	1.64459000	6	3.62170600	-2.97149000	5.34944300
6	1.44500100	-1.02560800	0.93249500	1	4.69078700	-3.19314700	5.27373100
6	3.26116500	-3.14825500	0.48021300	1	3.07668400	-3.79159700	4.86505600
1	3.93252700	-3.97629800	0.27335300	1	3.34402400	-2.97053400	6.40859000
6	0.52296000	0.07321800	1.03595500	6	-3.18019600	-3.45795000	-1.05262100
6	1.76343500	0.21769900	4.40990600	6	-3.36481100	-2.96614300	-2.34851400
1	0.87638800	0.76983200	4.70193900	6	-4.27199000	-4.00816100	-0.37177500
6	2.54351200	0.66346300	3.34069800	6	-4.62279500	-3.02330800	-2.95236200
6	2.14283200	-0.94057200	5.07873100	1	-2.52286600	-2.52696000	-2.87315000
1	1.53916900	-1.30375500	5.90599900	6	-5.52538000	-4.08018500	-0.97909600
6	3.70162300	-0.00626200	2.95083200	1	-4.14100800	-4.37670600	0.64329800
1	4.29008200	0.34831500	2.11201900	6	-5.70543300	-3.58267800	-2.27225400

1	-4.75447600	-2.63165700	-3.95711700	1	-5.60616900	-0.40320000	2.05413800
1	-6.36326300	-4.51346900	-0.43965000	6	-4.40337200	-1.93147900	1.11269100
1	-6.68296500	-3.62877700	-2.74346100	6	-2.03260000	-2.81165500	-2.92759600
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8	-4.32115700	-0.12500100	-1.91427900	1	0.12516700	-0.82727100	-4.65796200
8	-2.61540200	3.98745500	1.31796500	6	0.36723800	3.82049200	-2.45917300
8	0.45274300	1.37515000	-3.72660200	1	0.95547600	3.29456800	-3.19348700
8	-4.93171700	0.70991000	0.11783400	6	0.27229600	5.20373300	-2.49855900
7	-3.92453700	-1.34786100	-0.07338700	1	0.81451800	5.74525700	-3.26982600
7	-1.56888500	-0.76881900	-1.76520400	6	-0.49404300	5.90048100	-1.56079000
7	-0.37182200	1.65729700	-1.54107900	1	-0.56640800	6.98316000	-1.58865000
7	-1.91116200	1.90428100	0.89911800	6	-1.15412500	5.17952900	-0.58014100
6	-3.82252700	2.27861300	-2.18720300	1	-1.74985500	5.69568800	0.16226700
1	-4.18235700	2.61908200	-1.21591200	6	-3.38188800	3.15996800	2.22644700
1	-3.90580400	3.10515200	-2.90065600	1	-4.41516200	3.13531400	1.86848100
1	-2.76990100	2.00600900	-2.09683800	1	-3.33153900	3.61261400	3.21751100
6	-4.63101300	1.09044800	-2.70185600	6	-4.17418900	0.68747500	-4.10288300
6	-4.42948200	-0.14333000	-0.59181700	1	-4.69019800	-0.22085000	-4.42949500
6	-3.11292800	-2.29508600	-0.73869100	1	-3.09666200	0.50184800	-4.12028600
6	-2.22016400	-1.94262900	-1.84756900	1	-4.39953700	1.49138000	-4.81049000
6	-0.75764400	-0.39302600	-2.76223300	29	-0.83470500	0.43756200	0.01698600
6	-0.13130300	0.98831200	-2.70425200	17	-1.03644300	-1.26870200	1.46875900
6	-0.33096500	3.04606200	-1.49789100	6	-1.82045400	1.41523200	3.30756300
6	-1.09131000	3.77140900	-0.51855700	6	-0.58421800	2.04447900	3.48744000
6	-1.86440600	3.14730000	0.55258700	6	-2.21844100	0.42488500	4.20974100
6	-2.70680800	1.77280900	2.13195200	6	0.24854000	1.68111800	4.54630200
1	-3.45366000	0.99202700	1.98751300	1	-0.25526400	2.79600600	2.77642000
6	-6.13875200	1.33227600	-2.65143000	6	-1.38894100	0.06023500	5.27030300
1	-6.45972200	1.56803700	-1.63516400	1	-3.16229600	-0.09170300	4.05420200
1	-6.68143900	0.44788900	-3.00170400	6	-0.15028900	0.68239800	5.43829200
1	-6.39455800	2.17331800	-3.30481800	1	1.21529800	2.16241000	4.66287600
6	-3.11831600	-3.46085900	-0.02495000	1	-1.70029300	-0.72560700	5.95264100
1	-2.50622600	-4.32159600	-0.25483200	1	0.50729400	0.38375500	6.24911900
6	-3.91474000	-3.26295400	1.15553200	16	3.35066100	-0.79674900	2.37461000
6	-4.22603000	-4.07760200	2.25335400	8	2.50409500	0.96267400	-0.66346500
1	-3.84848800	-5.09478900	2.30576500	8	4.72503000	0.92569000	-1.22194100
6	-5.02093400	-3.55942800	3.26896600	8	3.29725900	-1.18556400	3.79397100
1	-5.26594100	-4.17530900	4.12924900	8	4.20321500	0.32668800	1.95181500
6	-5.51675200	-2.24504800	3.19551000	7	3.83891400	2.71305300	-0.08754900
1	-6.14216000	-1.86535300	3.99830600	6	2.29337800	-0.27018200	-1.21565600
6	-5.22307500	-1.41235200	2.11654900	6	0.61238600	-3.51654600	-0.29477300

1	0.22495800	-3.29687600	0.68940100	6	2.75589500	3.26205400	2.08770000
6	2.78130800	-0.59299300	-2.49773000	1	2.82207900	2.22429100	2.41444900
1	3.32283600	0.15722000	-3.05386700	1	1.86998900	3.72957500	2.53208400
6	3.79333400	1.51183400	-0.69269700	1	3.63598700	3.79337800	2.46807200
6	1.30513500	-2.50821600	-1.00617900	6	4.63097000	-5.64478900	-1.05093700
6	1.53336000	-1.18992100	-0.47151700	1	4.78821700	-6.55221300	-0.45838800
6	2.55990300	-1.84499100	-3.01397100	1	5.50979400	-5.49223700	-1.68507800
1	2.93361200	-2.09243500	-4.00362700	1	3.77156600	-5.82424300	-1.70839300
6	1.05191800	-0.75877300	0.81177000				
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6	3.63166900	-4.58388400	1.01280600	16	-0.59315900	-1.18062700	-2.18222100
1	3.27707200	-5.56638700	1.31202500	8	-0.68328000	2.51281400	-0.43214800
6	4.55073800	-2.05556100	0.24165500	8	0.47369500	3.19479800	1.41137500
1	4.89109300	-1.07047400	-0.05745800	8	-0.28458000	-2.59934500	-2.44483200
6	0.43605500	-4.77299300	-0.83789700	8	-0.20375800	-0.15109700	-3.16249600
1	-0.08925100	-5.53294300	-0.26609400	7	1.53796300	3.00376100	-0.62437200
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6	4.83055900	-3.17691600	-0.53558500	6	-2.43760600	-1.35203700	1.99107100
1	5.40638900	-3.05607500	-1.44875700	1	-1.52428700	-1.90435200	1.79704200
6	0.94342500	-5.08471700	-2.11725200	6	-2.79551600	2.67561000	0.68061300
1	0.79166900	-6.07523100	-2.53650100	1	-2.85771200	3.70602200	0.34903800
6	4.37049600	-4.44868000	-0.17135000	6	0.49399500	2.92740900	0.22688700
6	1.62662800	-0.46048800	1.96592200	6	-2.54066900	-0.02024000	1.53482800
1	1.09497900	-0.09430400	2.83654900	6	-1.49872200	0.60230800	0.75610200
6	2.66968300	3.35166300	0.56081500	6	-3.82216500	2.07420200	1.37939000
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1	4.95940500	4.27076600	0.63053900	6	-2.96004900	0.20710700	-2.07680900
6	1.64035500	-4.12910200	-2.82387400	1	-2.40327800	1.02094900	-2.52715700
1	2.04856500	-4.35358500	-3.80600600	6	-2.33450300	-1.01724400	-1.84545400
6	2.50316900	4.80138400	0.09615000	6	-4.28858200	0.36289100	-1.69335400
1	2.54510100	4.87099600	-0.99178900	1	-4.77904800	1.31979800	-1.84596800
1	3.26422100	5.46323700	0.52385700	6	-3.01539400	-2.08478200	-1.26072900
1	1.52475300	5.17075900	0.41432800	1	-2.50402000	-3.02659600	-1.09506200
6	5.68288800	3.83357600	-1.33097600	6	-3.47999900	-1.94001100	2.67879000
1	6.61153100	4.40161700	-1.20521300	1	-3.38679200	-2.96421100	3.02740200
1	4.95131000	4.47621300	-1.83172100	6	-3.72575000	0.72424300	1.81540000
1	5.88711900	2.97043400	-1.96832600	6	-4.34425800	-1.90985100	-0.88741500
6	6.18648700	2.54230300	0.81155800	1	-4.87814900	-2.72667900	-0.41073400
1	7.07500500	3.15565500	1.00161900	6	-4.66578700	-1.21757100	2.93669000
1	6.48409800	1.66019000	0.24318400	1	-5.47961200	-1.69086700	3.47804600
1	5.77446200	2.20744200	1.76568900	6	-4.99380100	-0.68400700	-1.08429900

6	0.19797700	-0.80252200	-0.60200100
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6	1.48213400	2.51160300	-2.01883000
1	0.52029500	2.01855500	-2.13043700
6	2.81535600	3.56153500	-0.11394500
1	3.47110600	3.58317200	-0.98821700
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6	2.55655600	1.45245400	-2.28557600
1	3.56859100	1.87319000	-2.29451300
1	2.36749700	0.98994900	-3.25844700
1	2.51505000	0.66704800	-1.52793200
6	3.45427400	2.65021300	0.93857000
1	2.83075400	2.59040600	1.83177700
1	4.43961900	3.03645900	1.22154500
1	3.58290500	1.63681700	0.55038700
6	2.65343900	5.00612600	0.37078500
1	2.21758900	5.63124700	-0.41622900
1	3.63433400	5.41754200	0.63308700
1	2.01076000	5.04994900	1.25201500
6	1.54727300	3.67461200	-3.01331700
1	0.73408500	4.38398000	-2.82857900
1	1.45196300	3.29702200	-4.03708200
1	2.49788500	4.21638100	-2.94320700
6	-6.42660200	-0.49862200	-0.65458500
1	-6.64928100	0.55593700	-0.46461600
1	-6.63791300	-1.06159500	0.25940700
1	-7.11997500	-0.84849900	-1.43025100
16	3.37703200	-1.26491800	2.51645100
8	3.18181800	-2.29549000	3.54725500
8	4.43765800	-0.25003800	2.61018200
6	4.07261500	-1.37129000	-0.14059800
1	4.64776300	-0.47366500	0.05544500
6	3.43765200	-2.03615100	0.90540600
6	3.94035400	-1.88038400	-1.43301400
1	4.42722900	-1.36845000	-2.25795400
6	2.67136100	-3.18355700	0.68807500
1	2.17204200	-3.66759200	1.52006700
6	2.54802900	-3.66863000	-0.60921300
1	1.93819500	-4.54743500	-0.79638700
6	3.16671200	-3.01949000	-1.69097600
6	2.94926800	-3.51583500	-3.09575800
1	3.59363100	-2.99502600	-3.80985500
1	1.90516400	-3.35053600	-3.38560000
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17	1.28425400	-0.23316700	2.04740100

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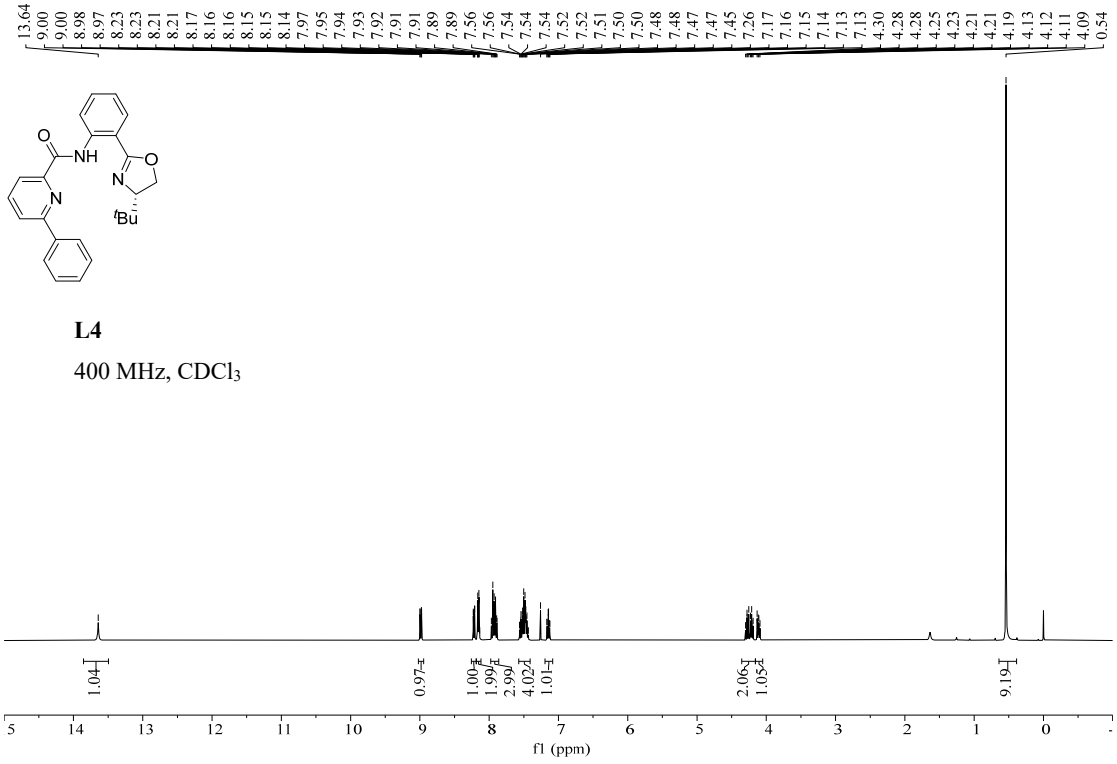
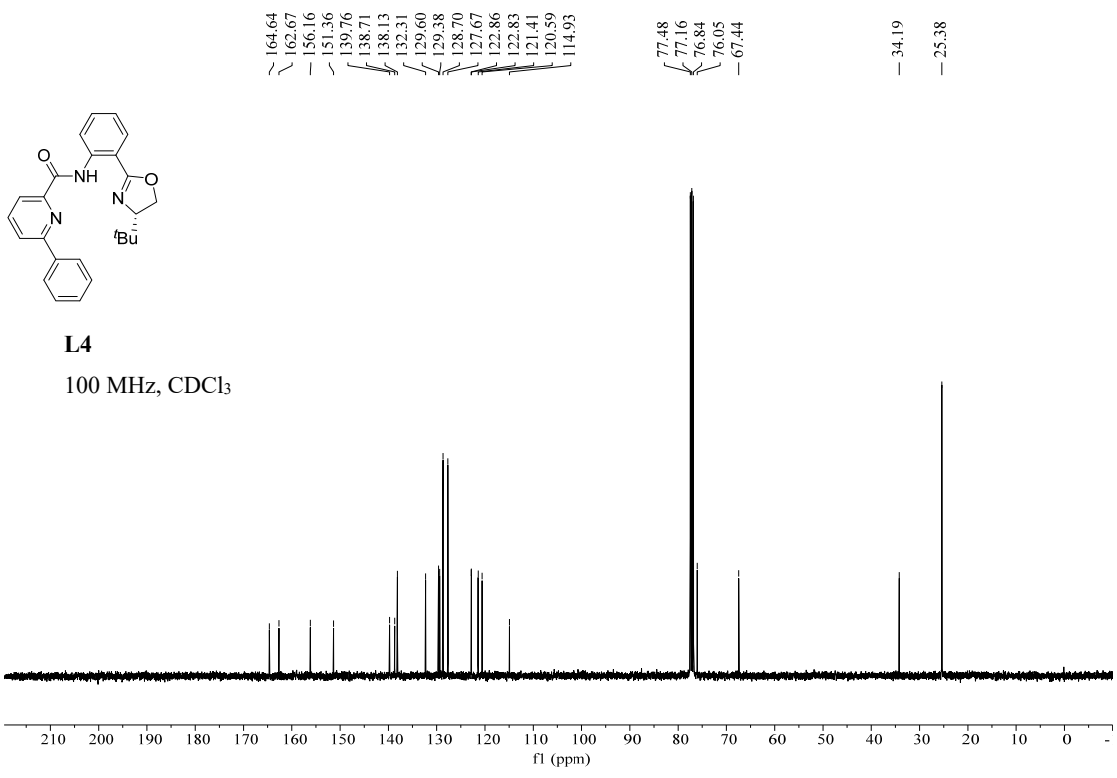
6	-0.77517200	1.22074500	-0.17532400
1	-0.22465400	2.15146700	-0.25153500
6	-0.10731000	0.00011700	-0.26773900
6	-2.15441300	1.20709200	0.00835300
1	-2.69142300	2.14867500	0.08048800
6	-0.77502600	-1.22058400	-0.17600000
1	-0.22439600	-2.15119900	-0.25267100
6	-2.15431500	-1.20720400	0.00768400
1	-2.69120100	-2.14889100	0.07928800
6	-2.86246100	-0.00014100	0.10127300
6	-4.36047400	-0.00010300	0.27072800
1	-4.70105700	0.88455700	0.81751500
1	-4.70222100	-0.88993900	0.80824800
1	-4.86098400	0.00543400	-0.70628100
17	2.33104500	-0.00055400	1.52299000

NMR spectra



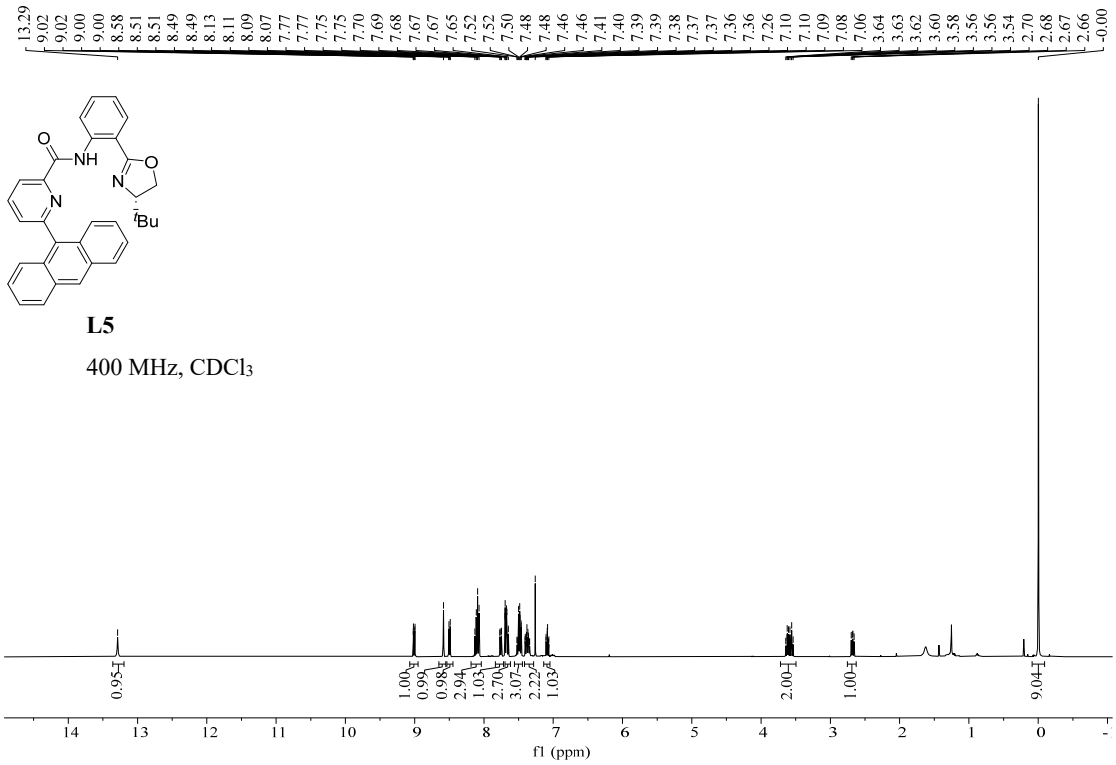
L4

400 MHz, $CDCl_3$



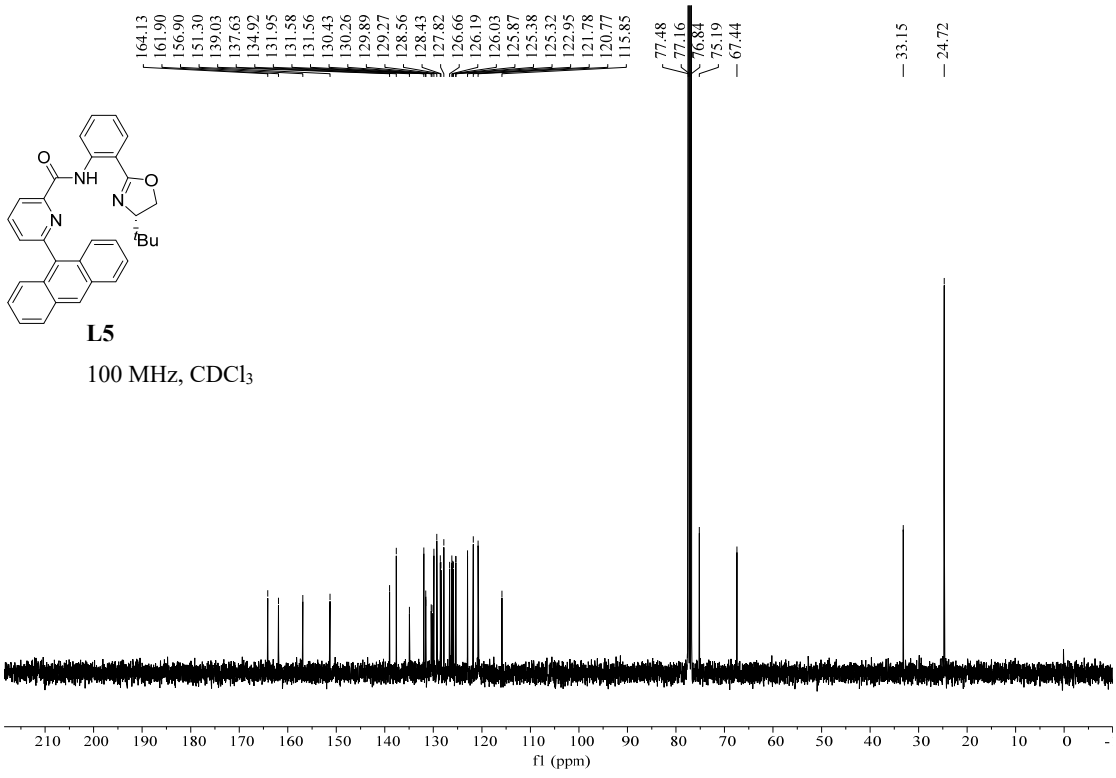
L4

100 MHz, $CDCl_3$



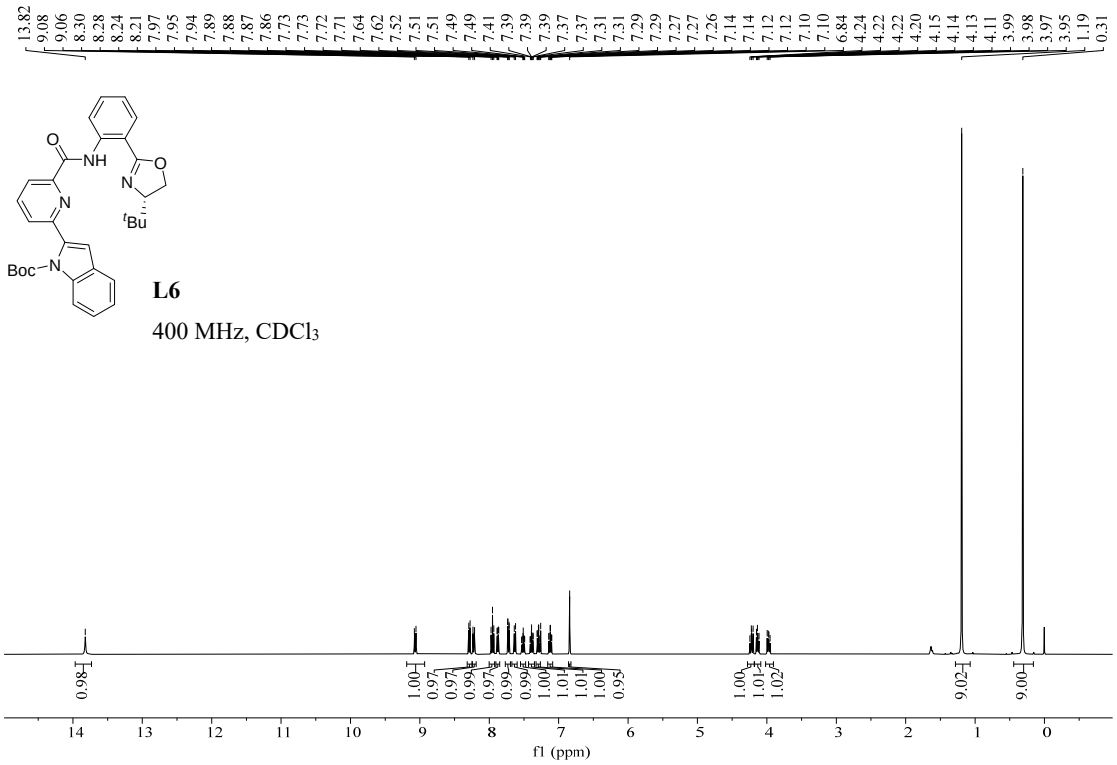
L5

400 MHz, $CDCl_3$



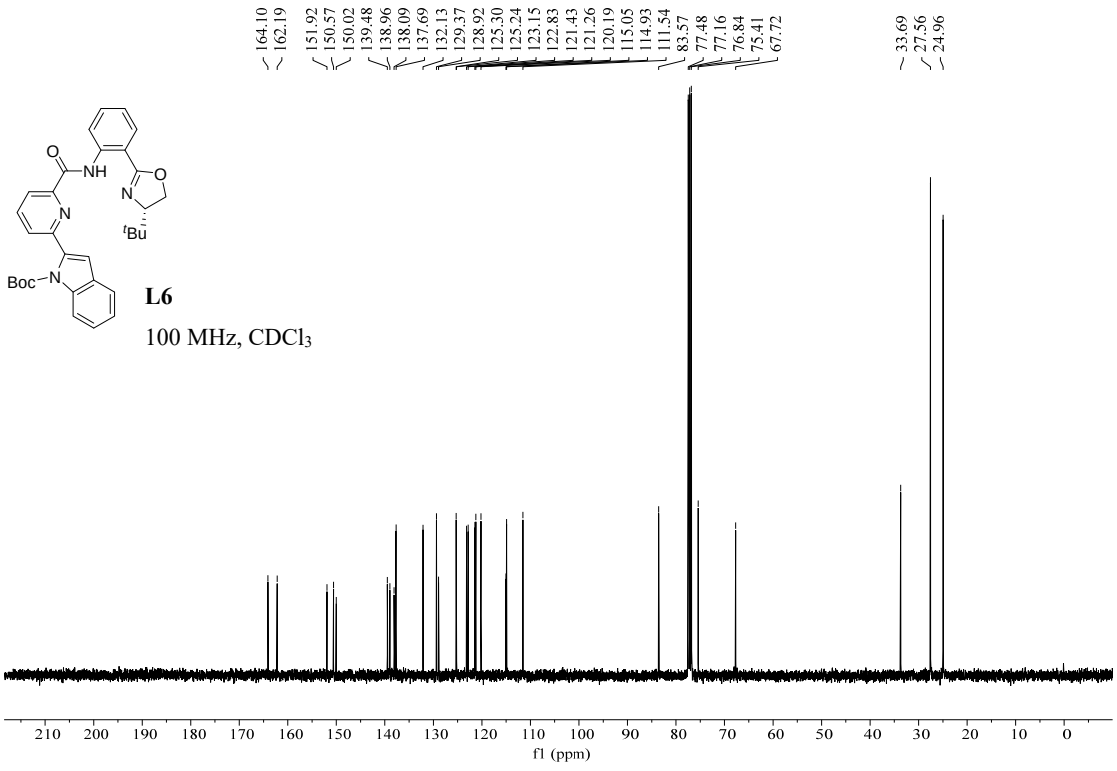
L5

100 MHz, $CDCl_3$



L6

400 MHz, $CDCl_3$



L6

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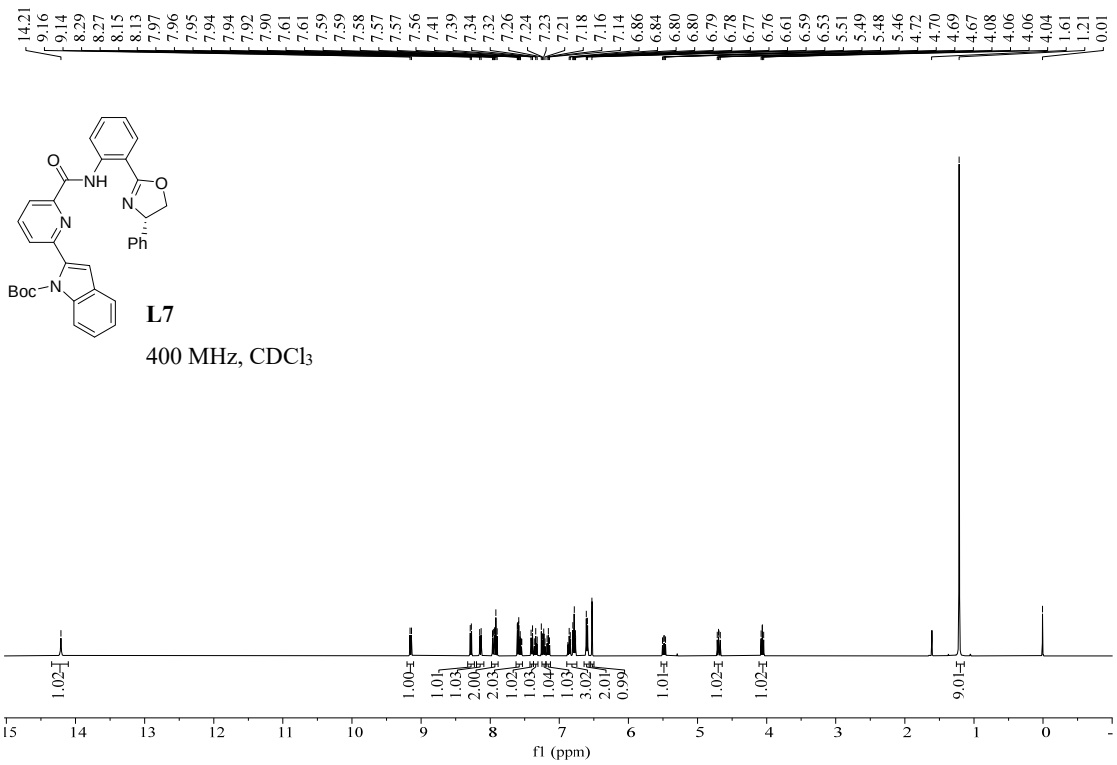
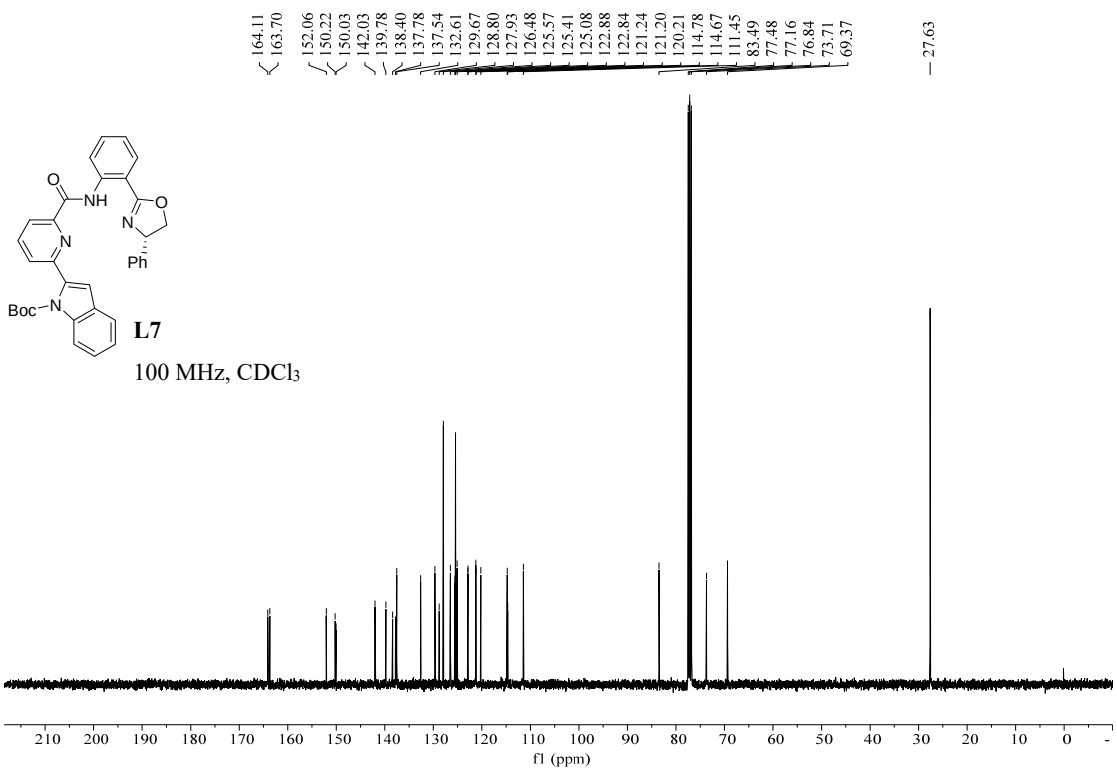


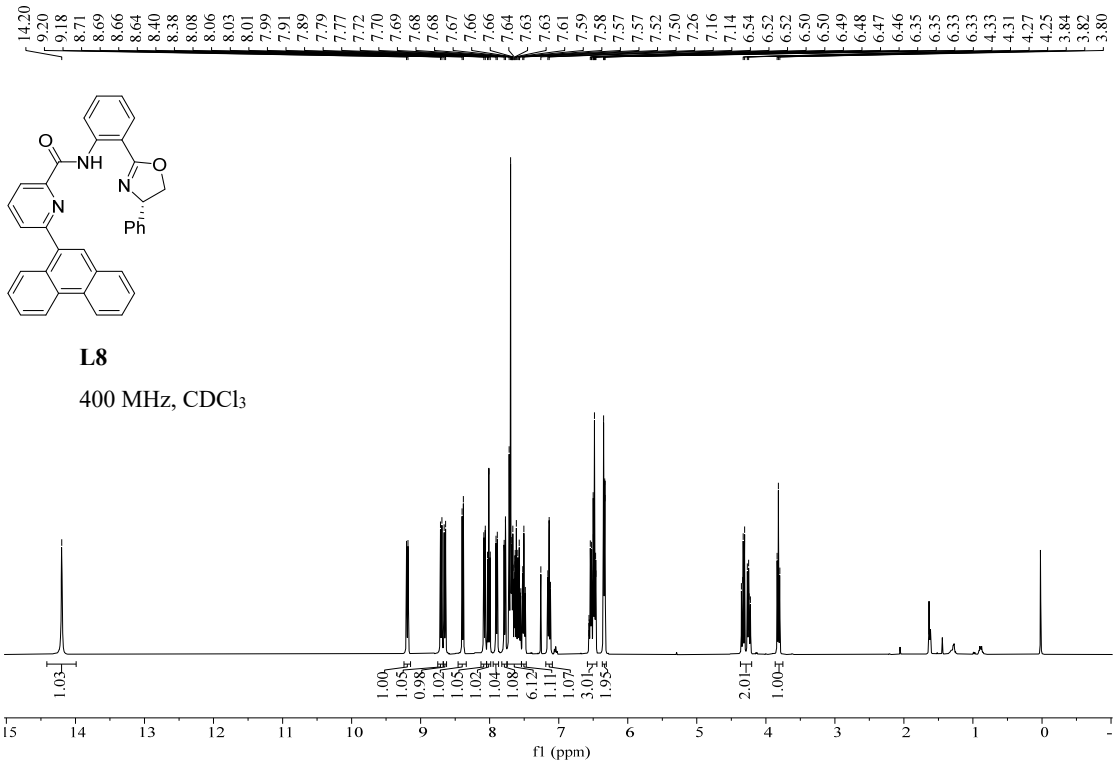
L7

400 MHz, $CDCl_3$



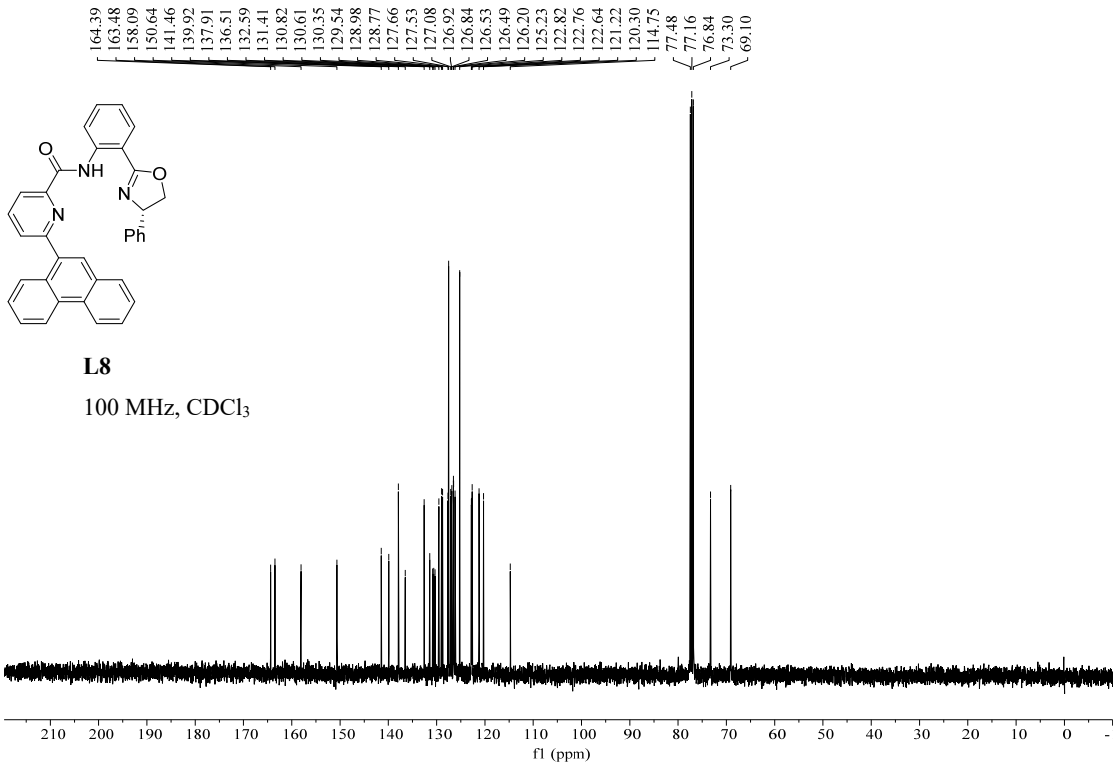
L7

100 MHz, $CDCl_3$



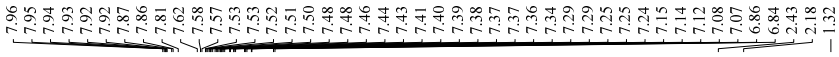
L8

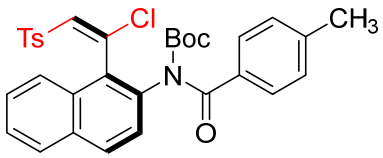
400 MHz, $CDCl_3$



L8

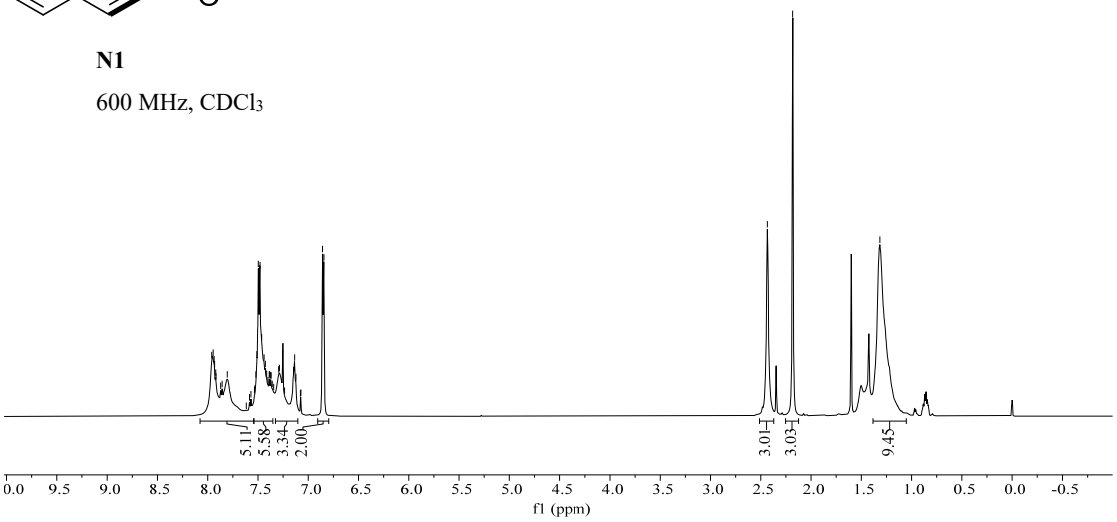
100 MHz, $CDCl_3$

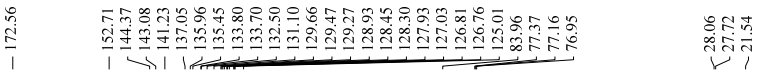


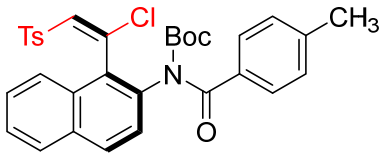


N1

600 MHz, $CDCl_3$

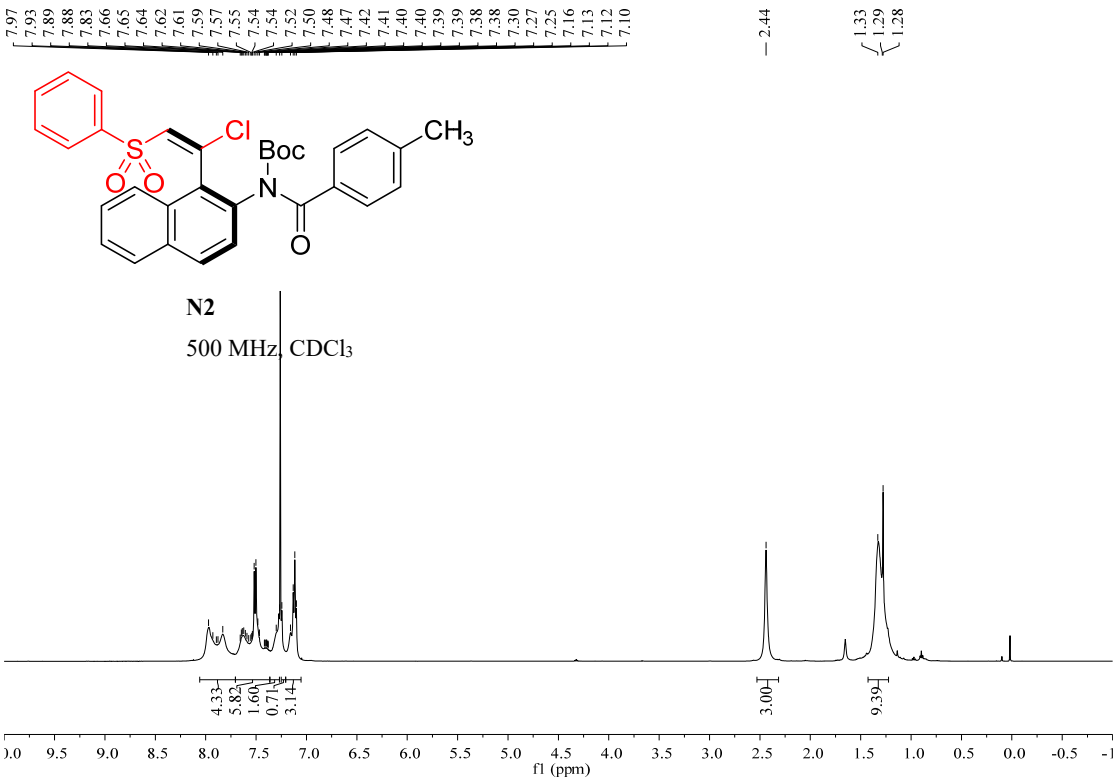






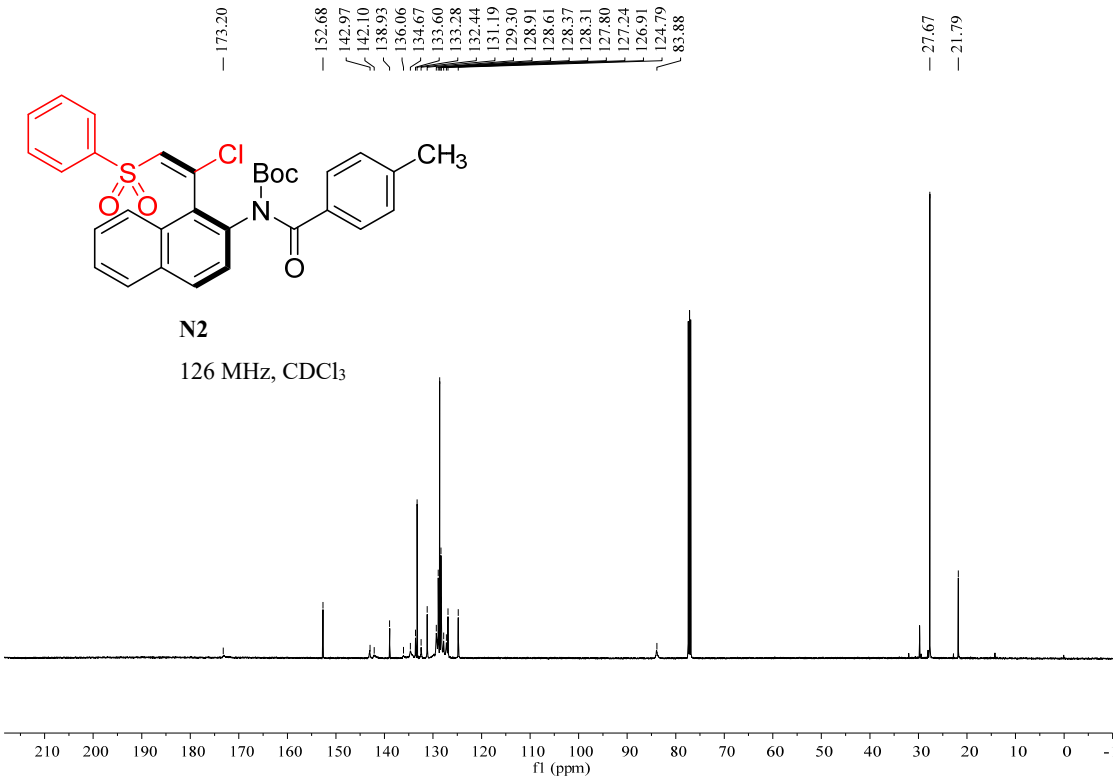
N1

150 MHz, $CDCl_3$



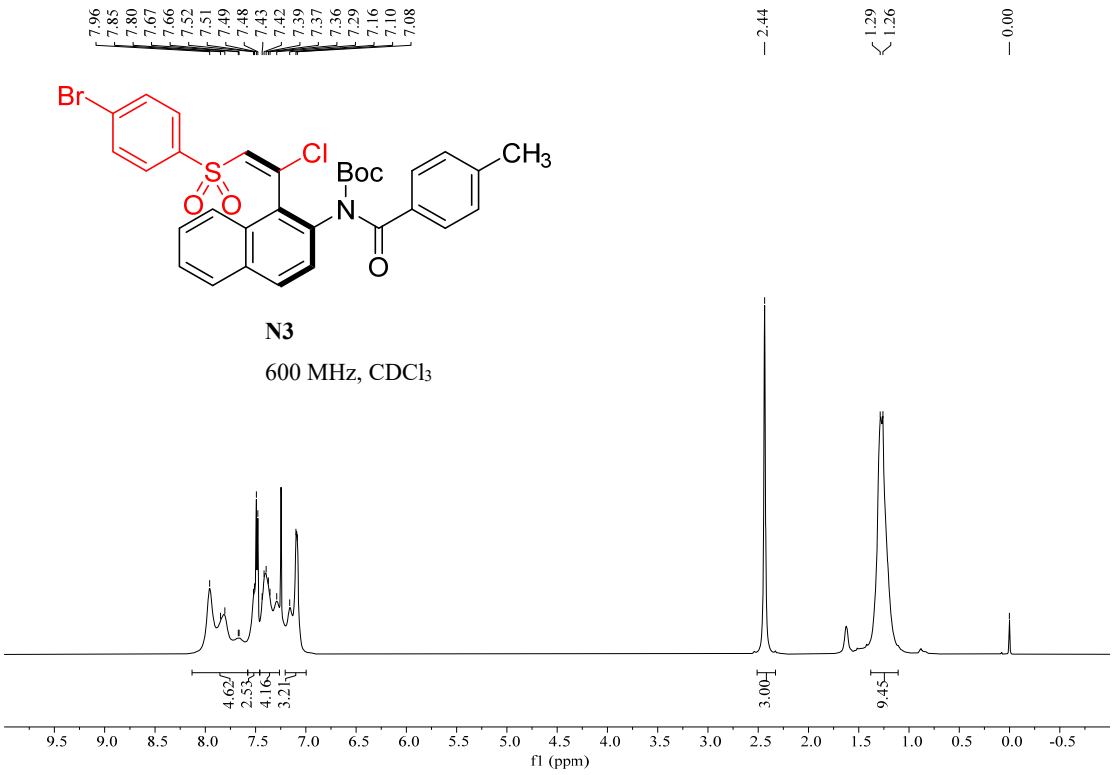
N2

500 MHz, $CDCl_3$



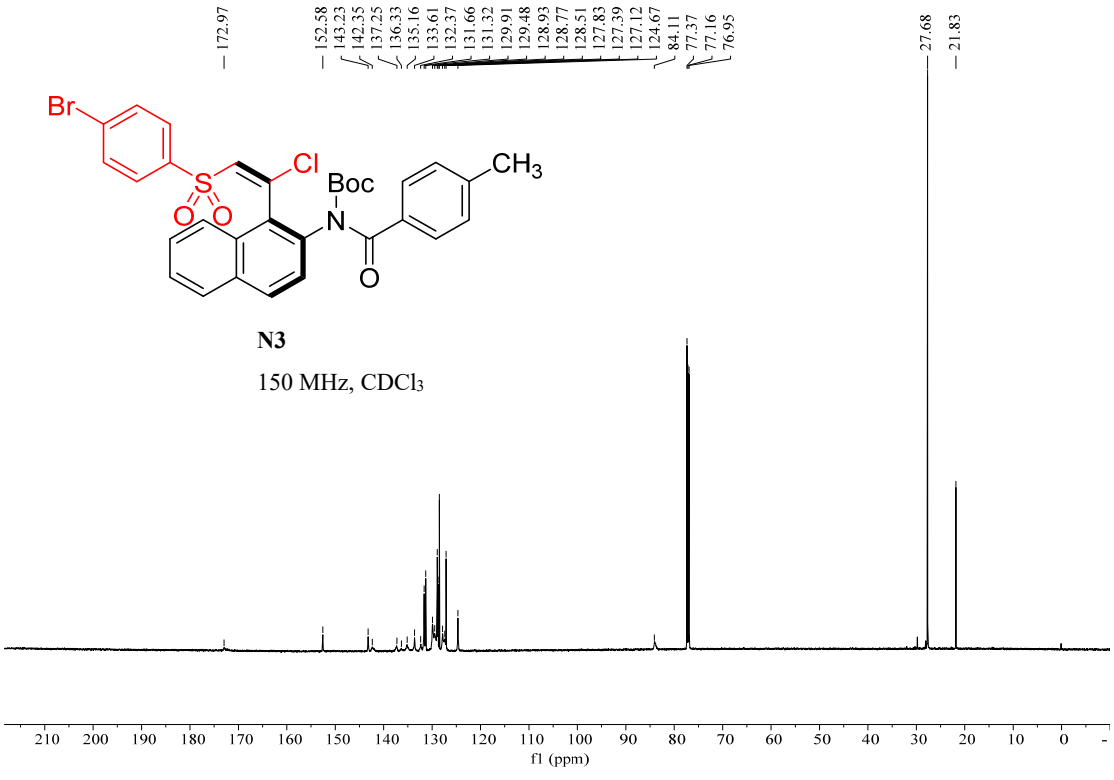
N2

126 MHz, $CDCl_3$



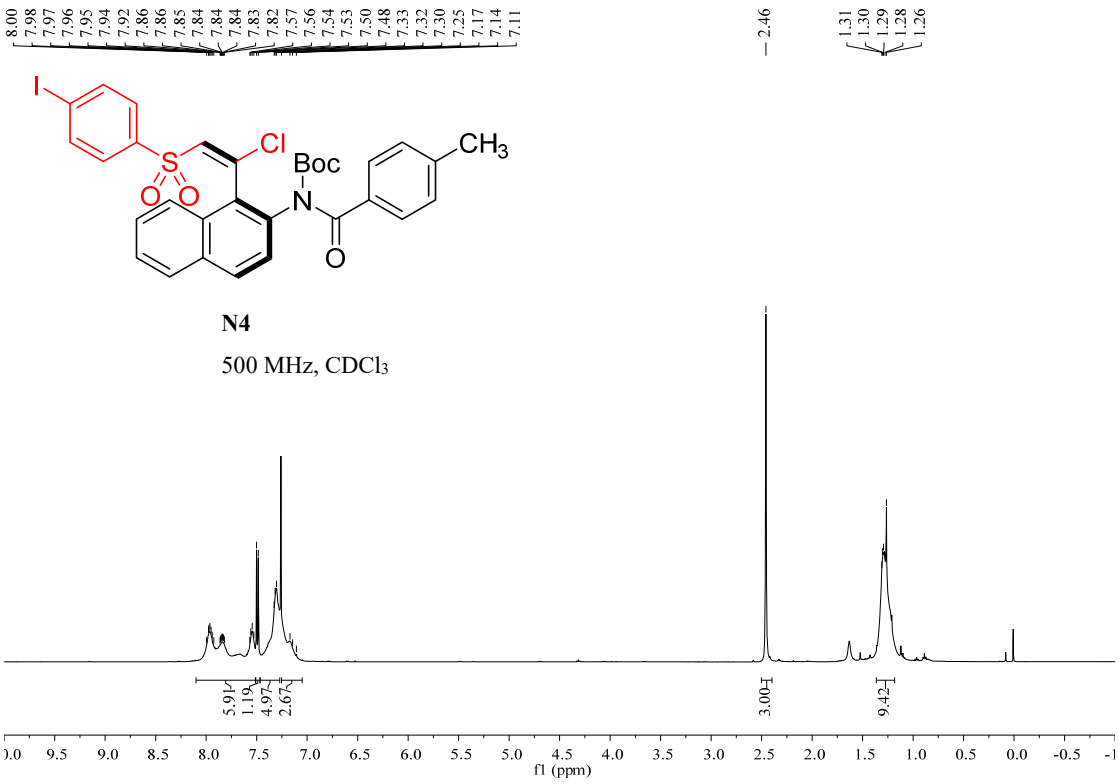
N3

600 MHz, $CDCl_3$



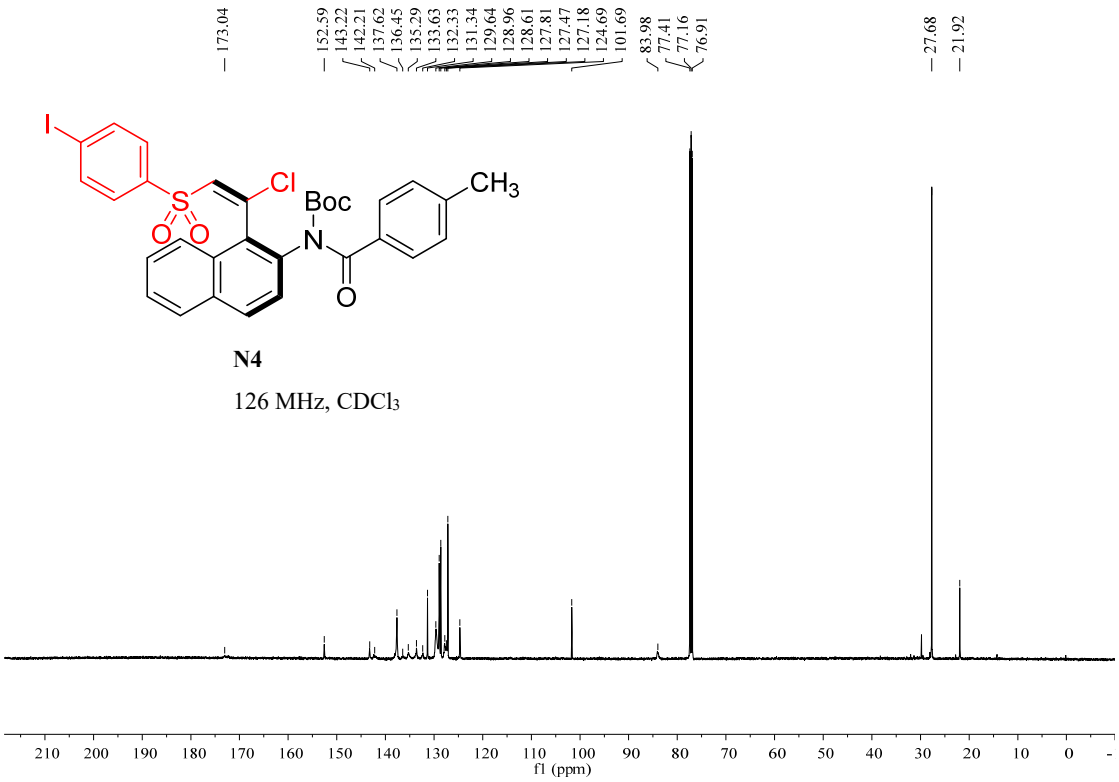
N3

150 MHz, $CDCl_3$



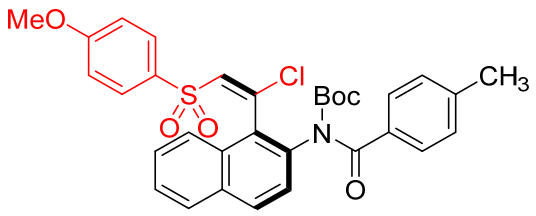
N4

500 MHz, $CDCl_3$



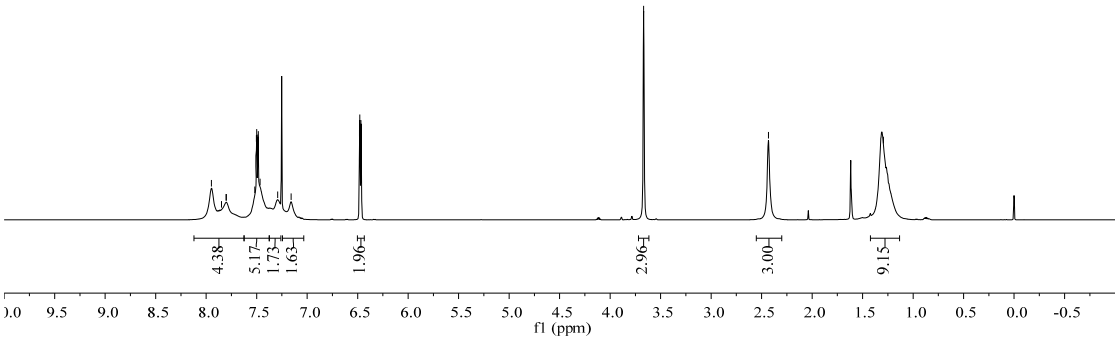
N4

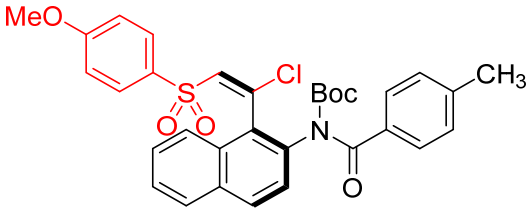
126 MHz, $CDCl_3$



N5

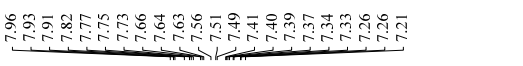
600 MHz, $CDCl_3$

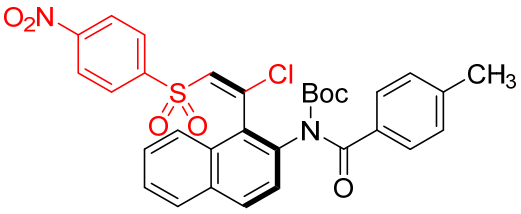




N5

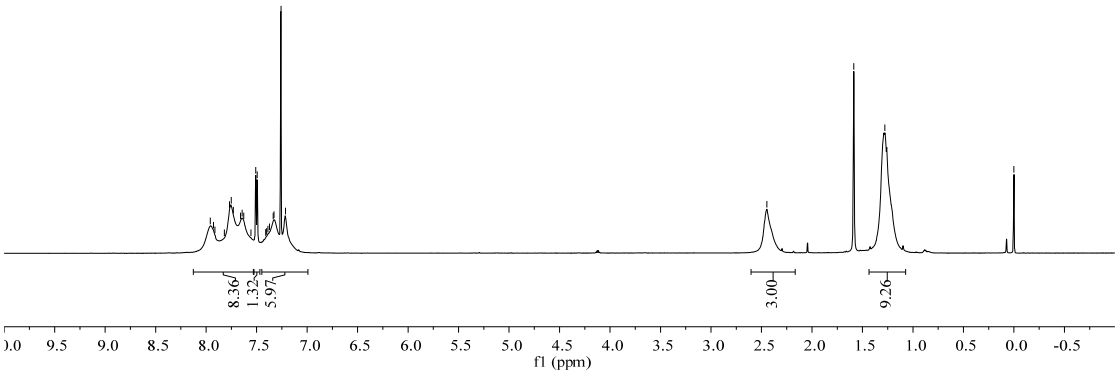
150 MHz, $CDCl_3$

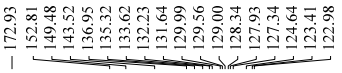


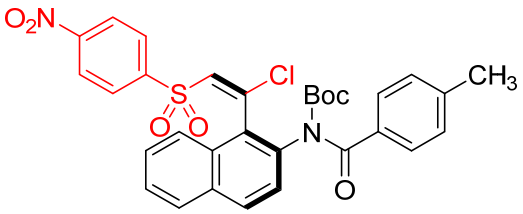


N6

600 MHz, $CDCl_3$

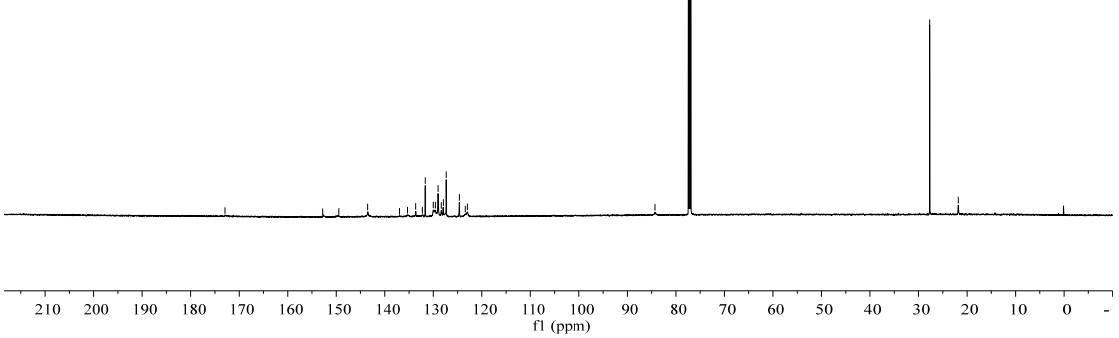


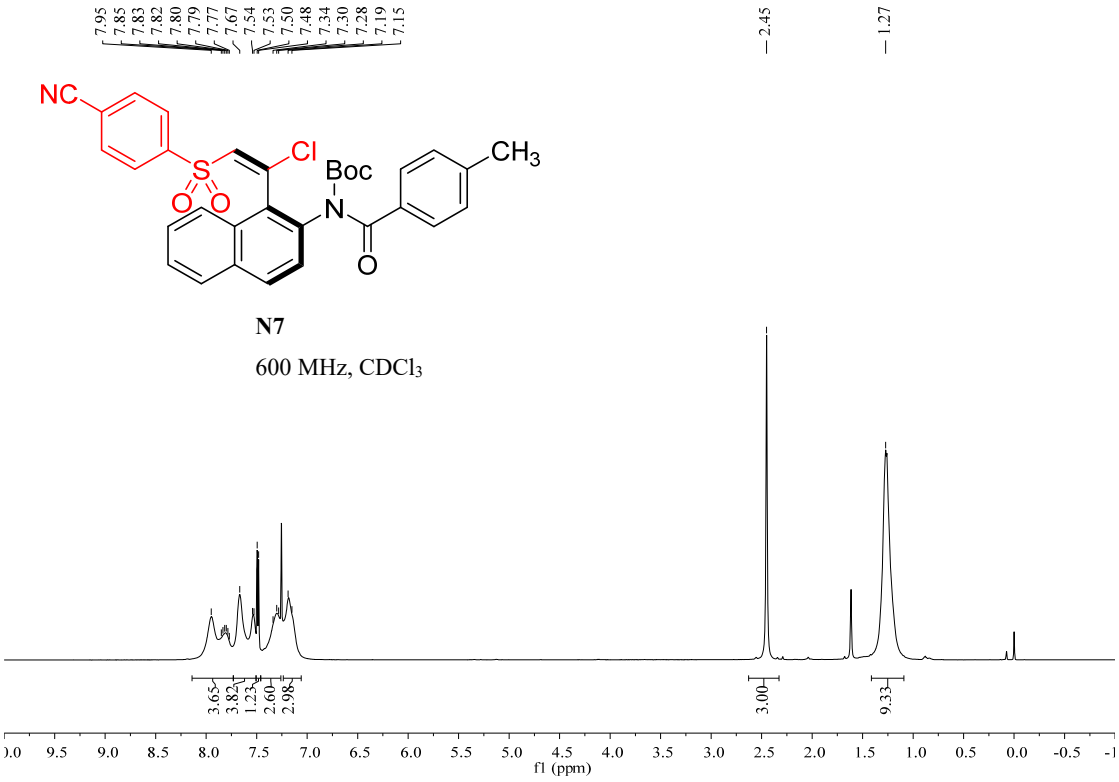




N6

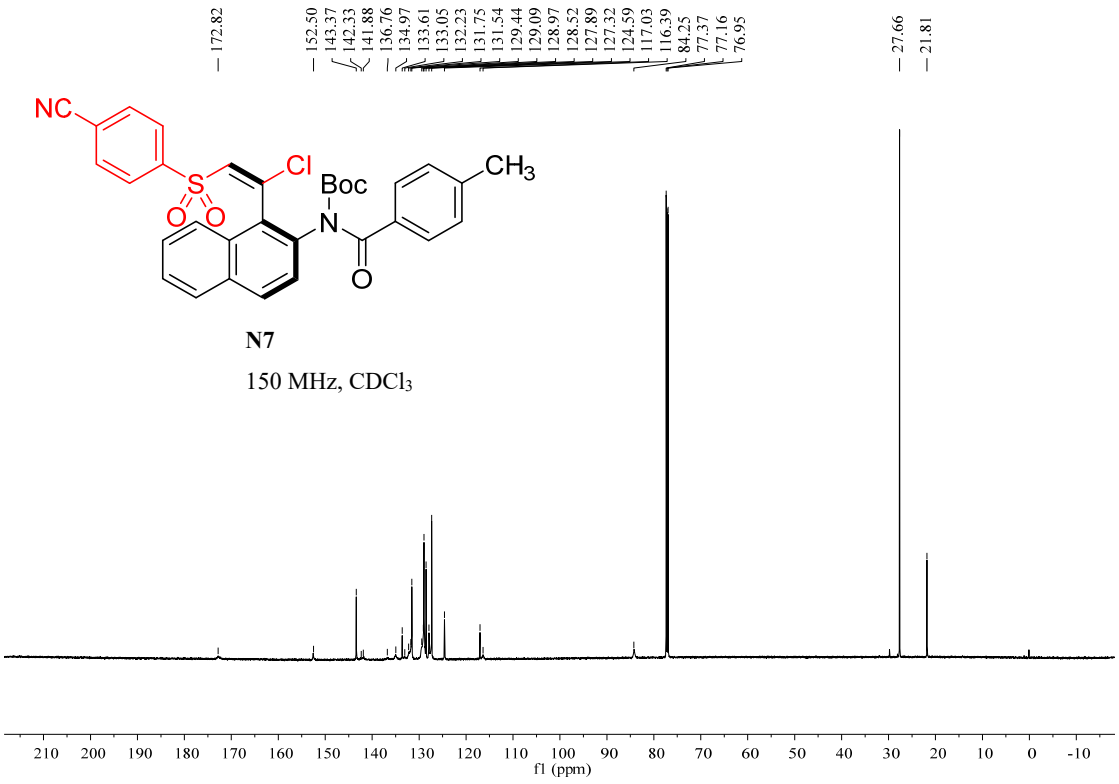
150 MHz, $CDCl_3$





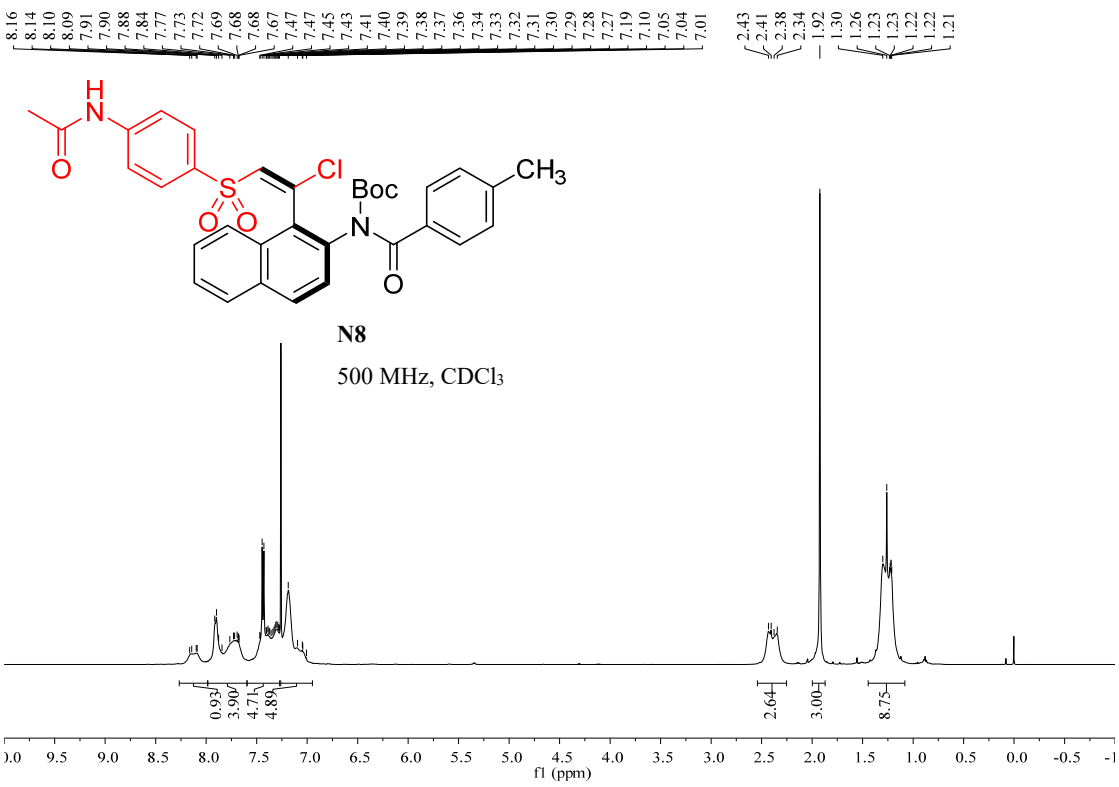
N7

600 MHz, $CDCl_3$



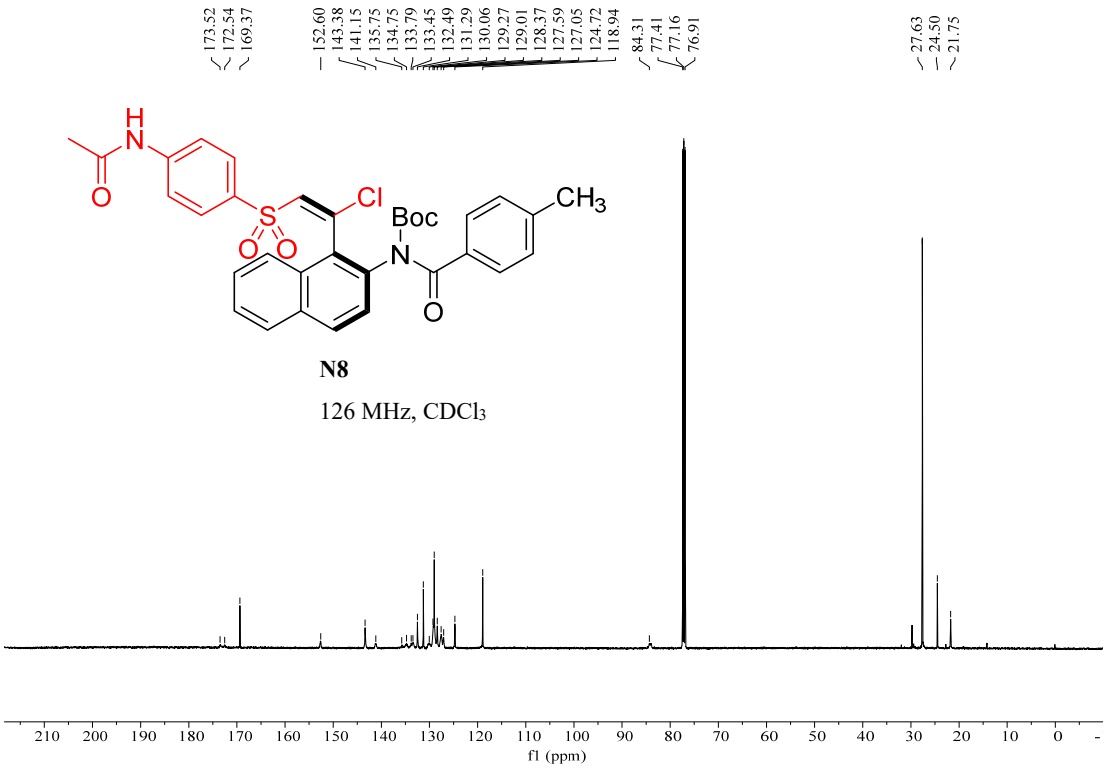
N7

150 MHz, $CDCl_3$



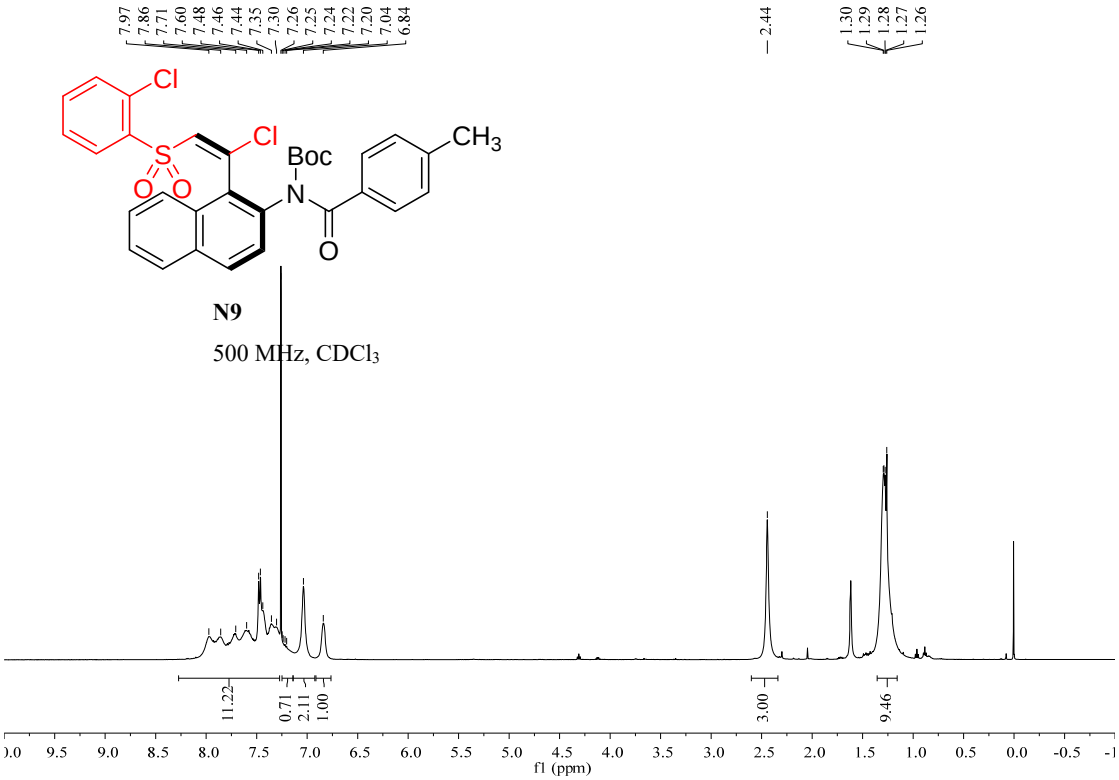
N8

500 MHz, $CDCl_3$



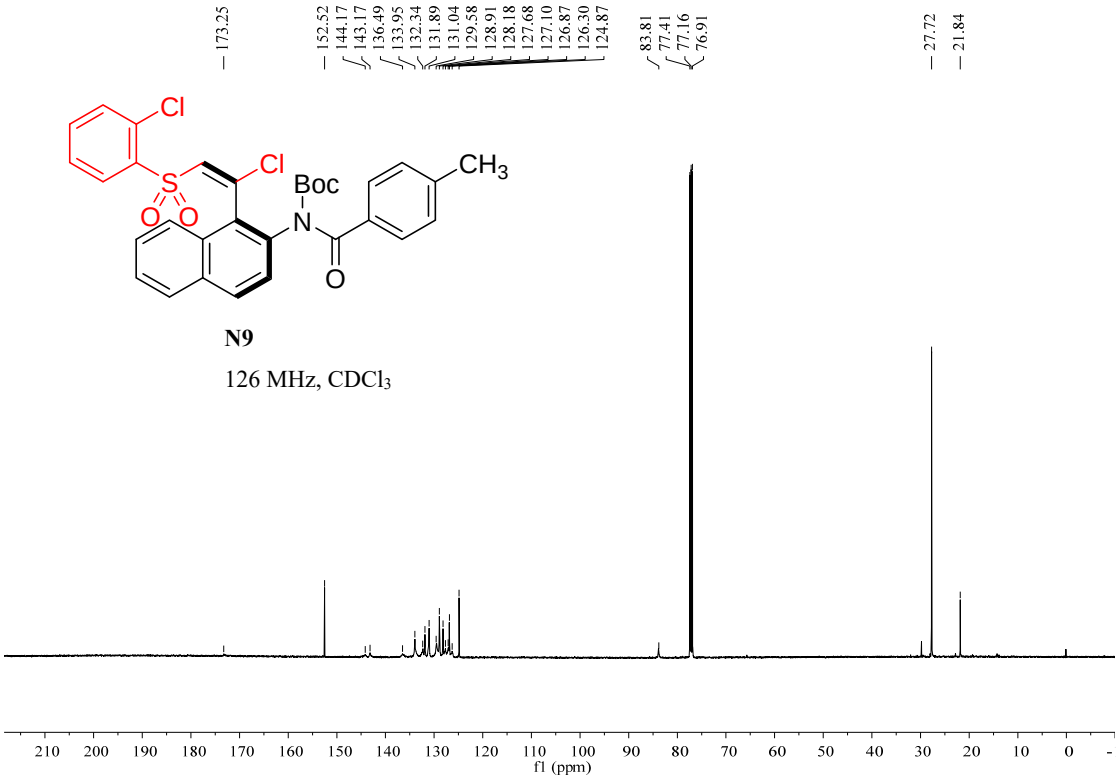
N8

126 MHz, $CDCl_3$



N9

500 MHz, $CDCl_3$



N9

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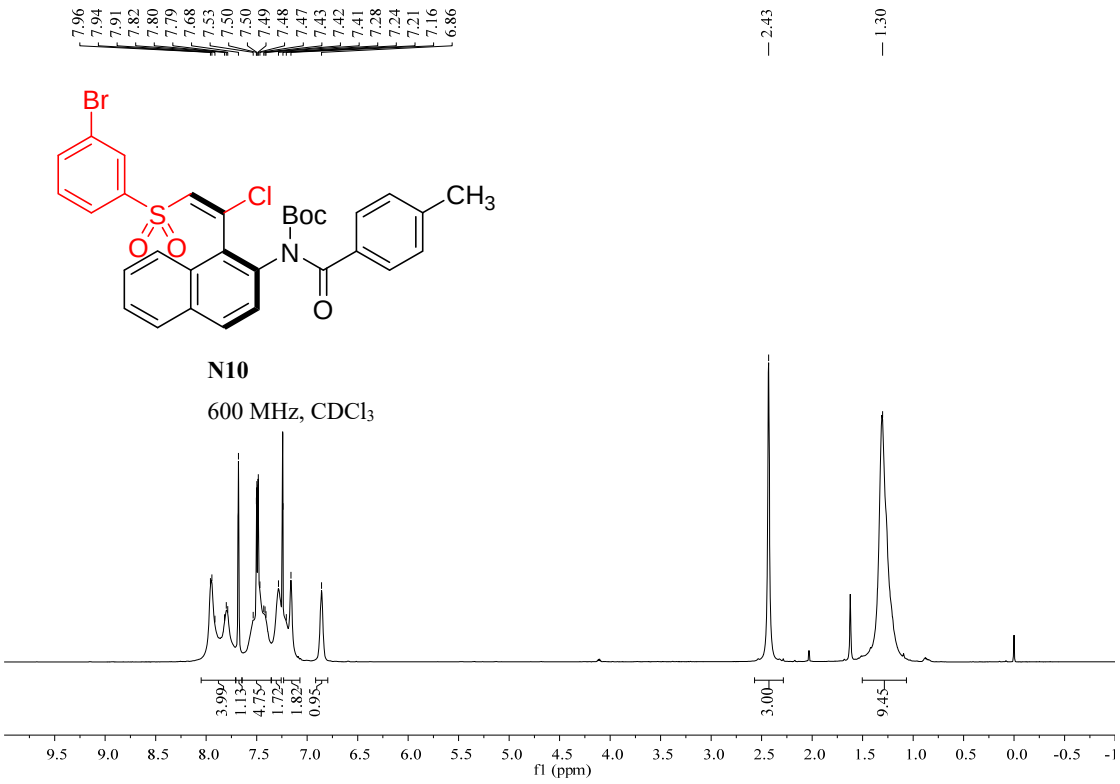
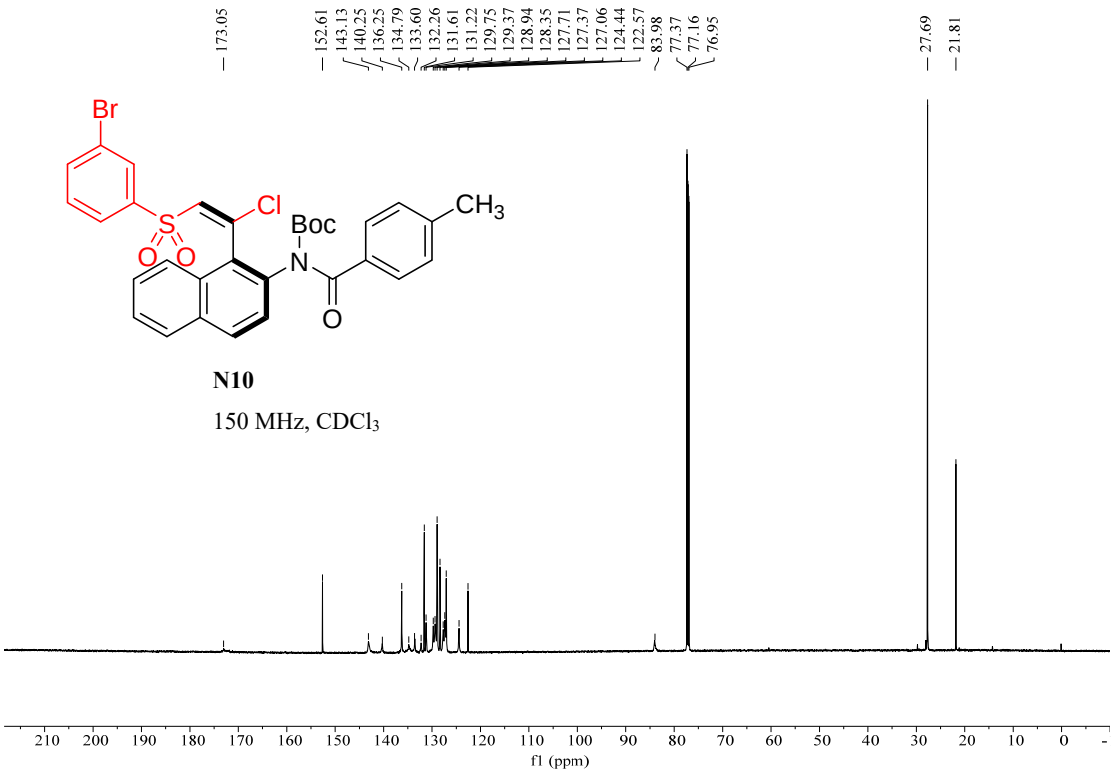


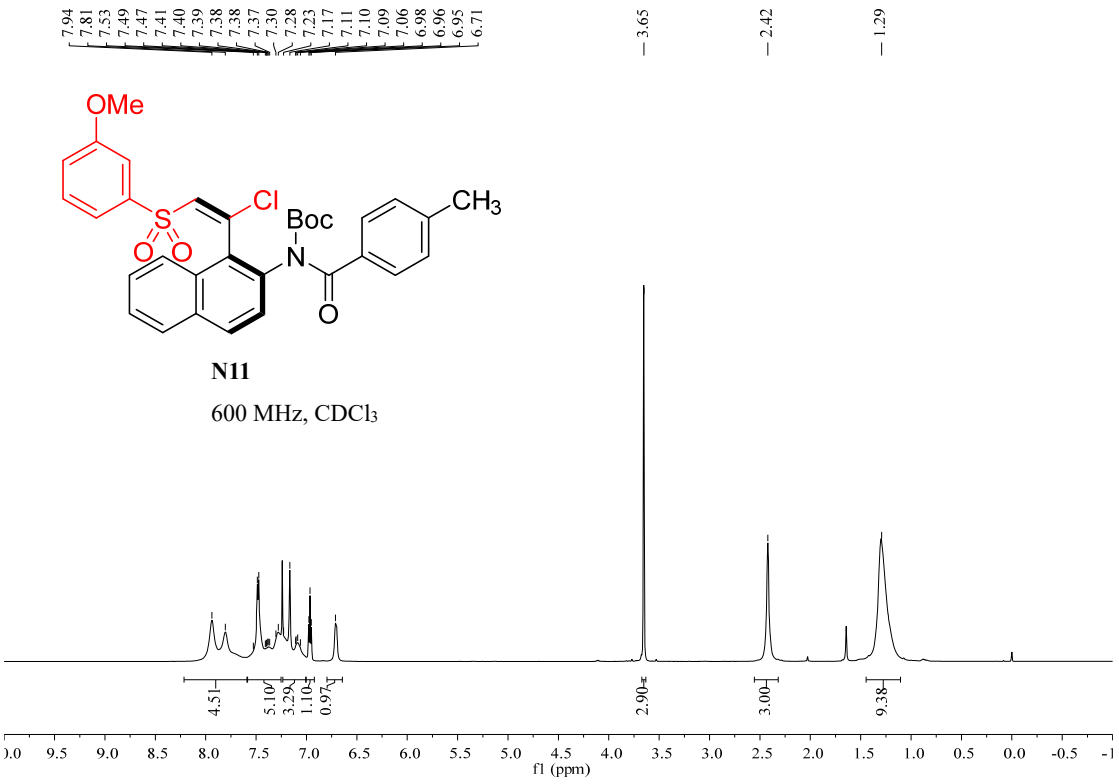
N10

600 MHz, $CDCl_3$



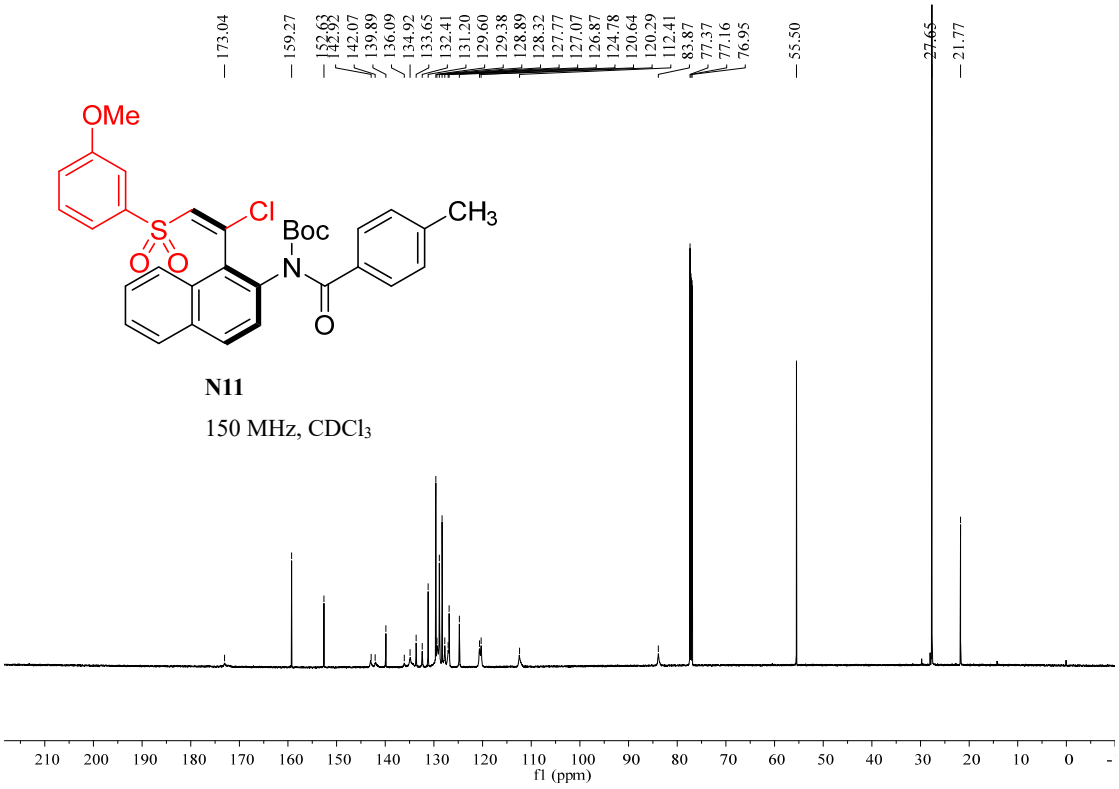
N10

150 MHz, $CDCl_3$



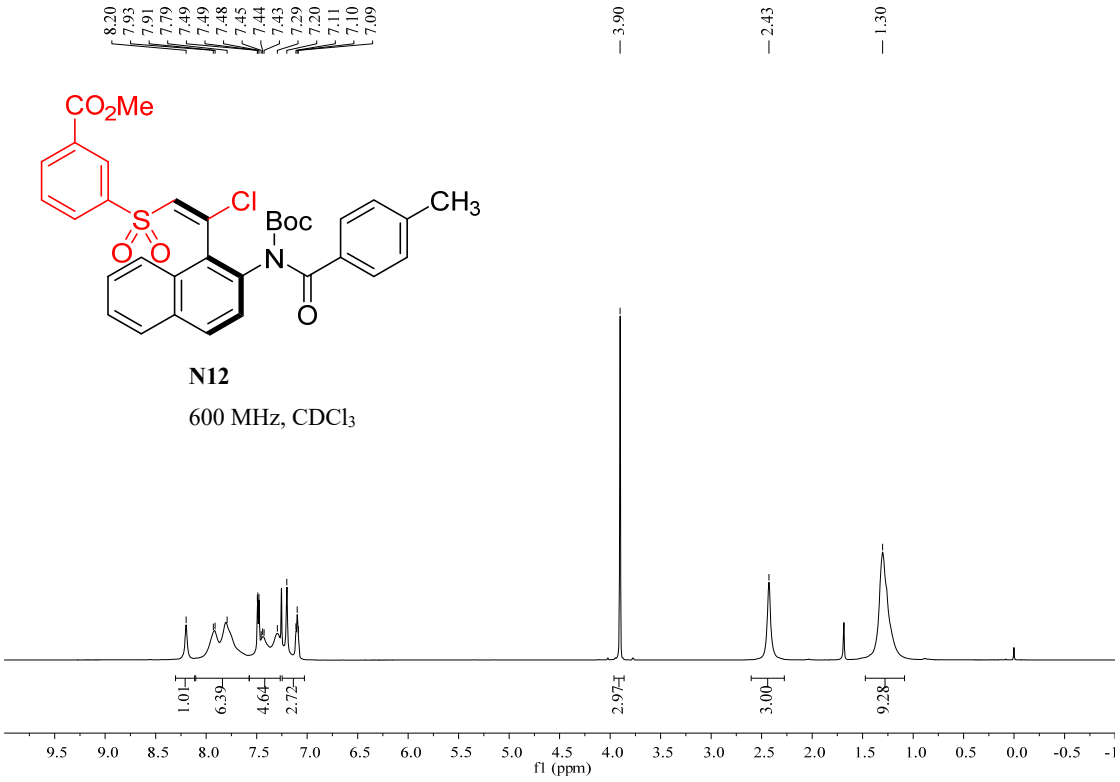
N11

600 MHz, $CDCl_3$



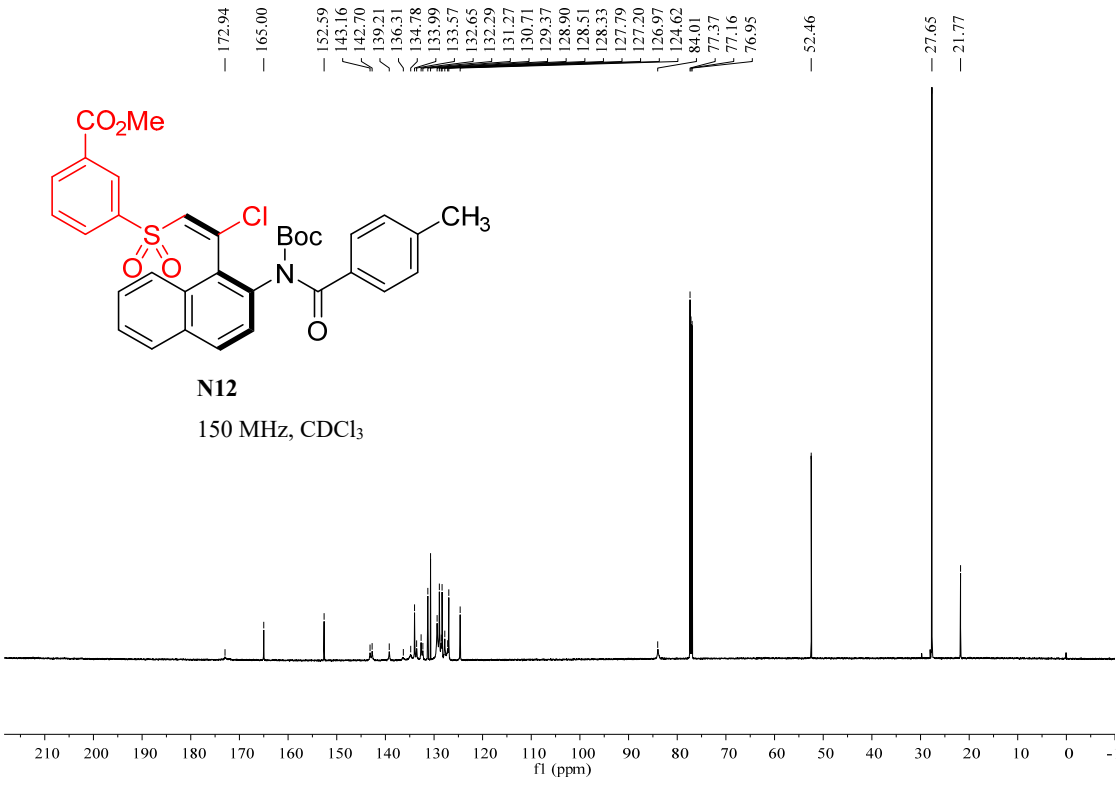
N11

150 MHz, $CDCl_3$



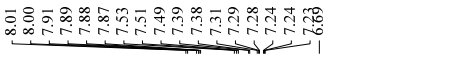
N12

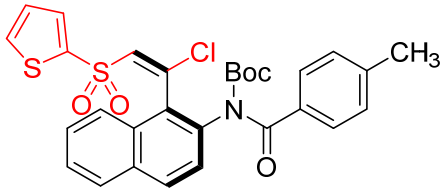
600 MHz, $CDCl_3$



N12

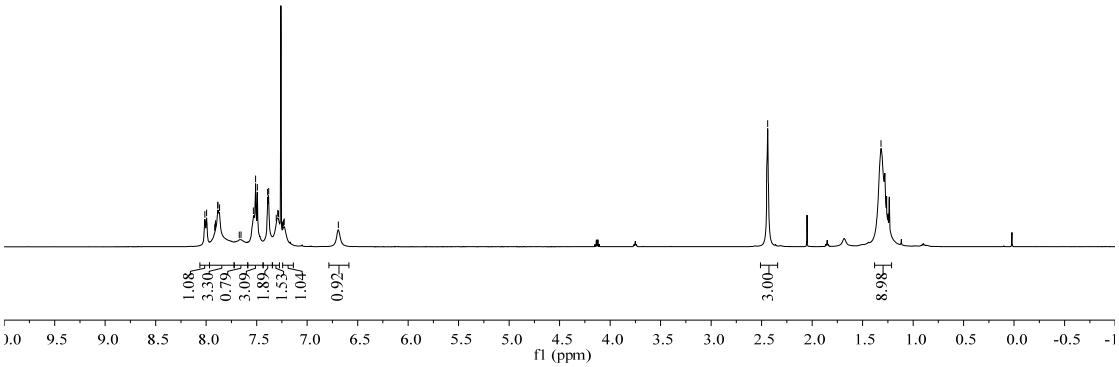
150 MHz, $CDCl_3$

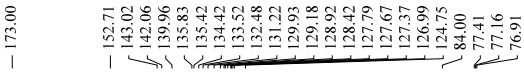


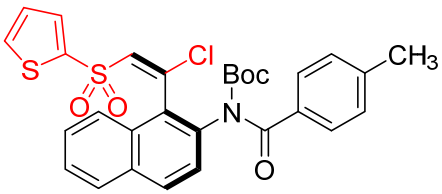


N13

500 MHz, $CDCl_3$

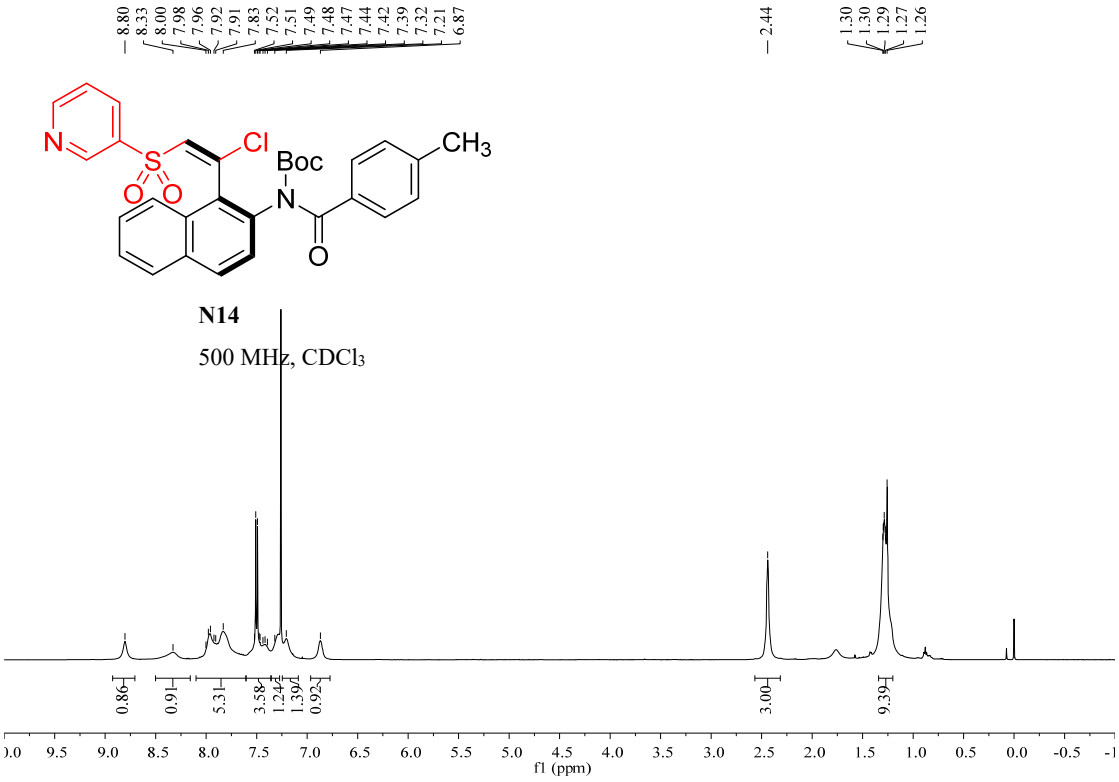






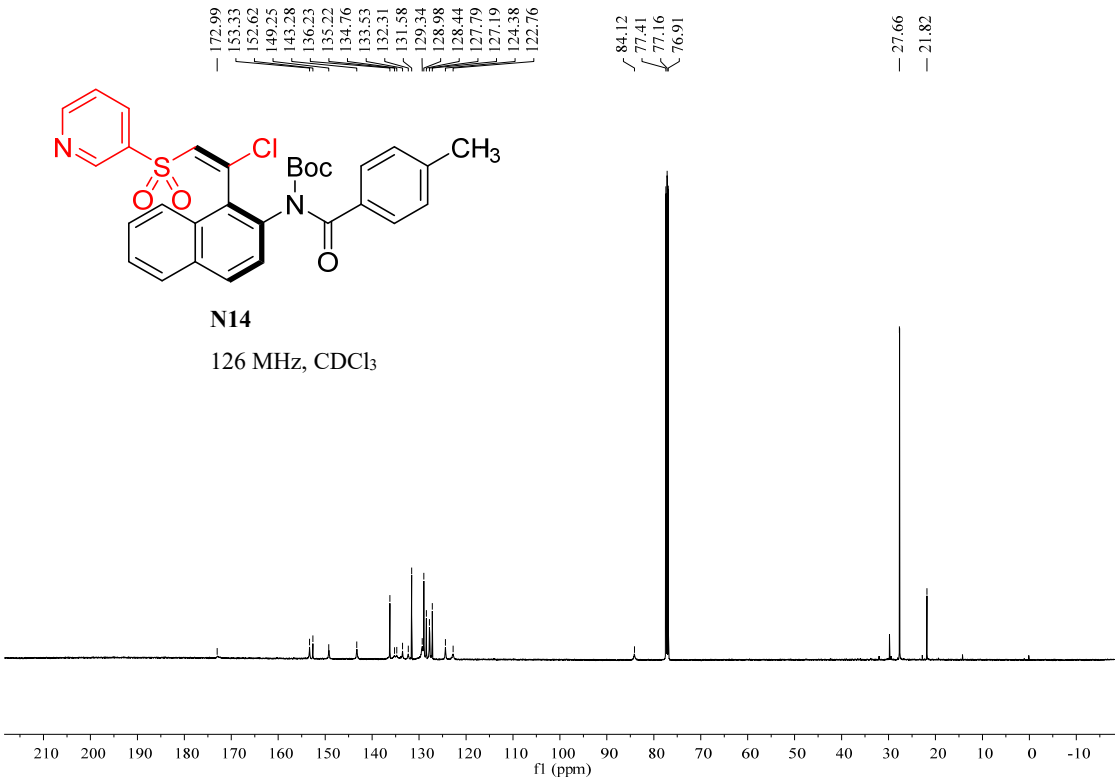
N13

126 MHz, $CDCl_3$



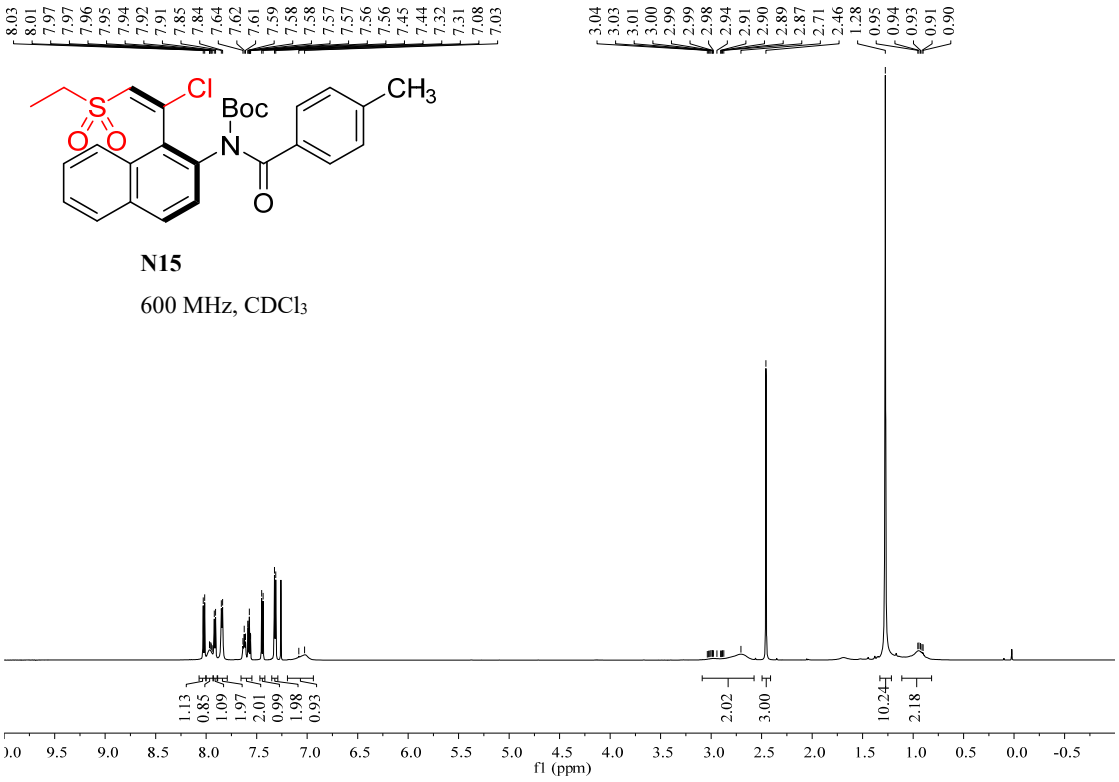
N14

500 MHz, $CDCl_3$



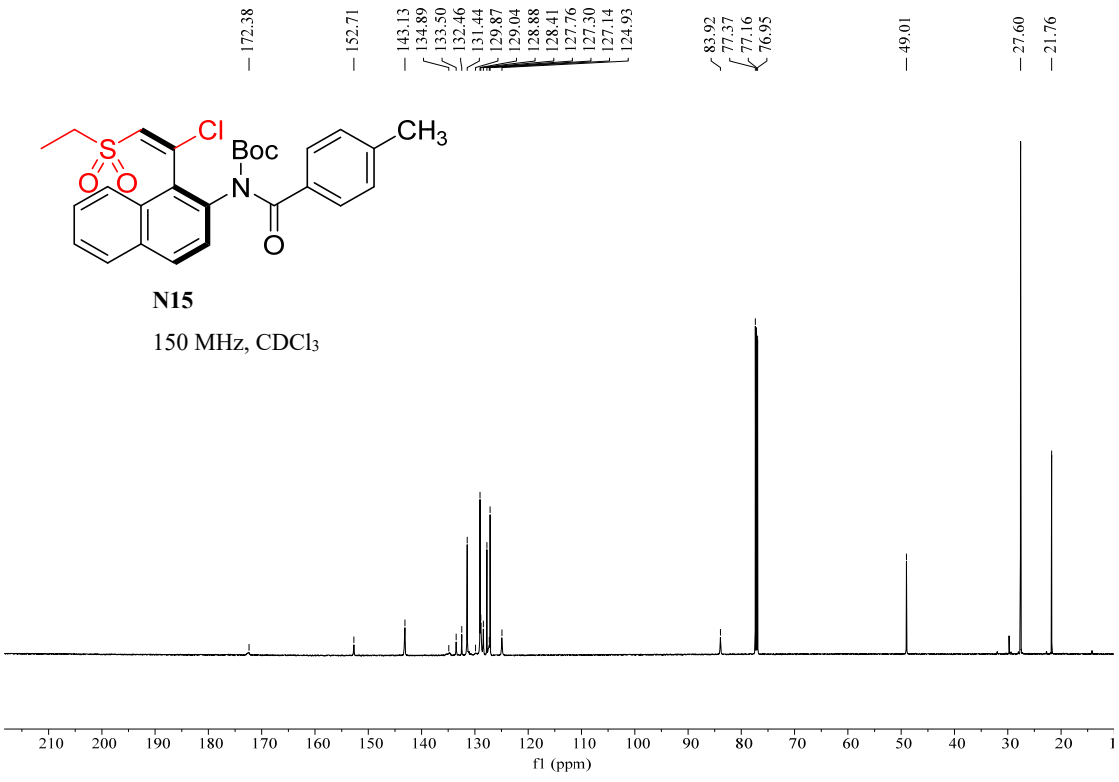
N14

126 MHz, $CDCl_3$



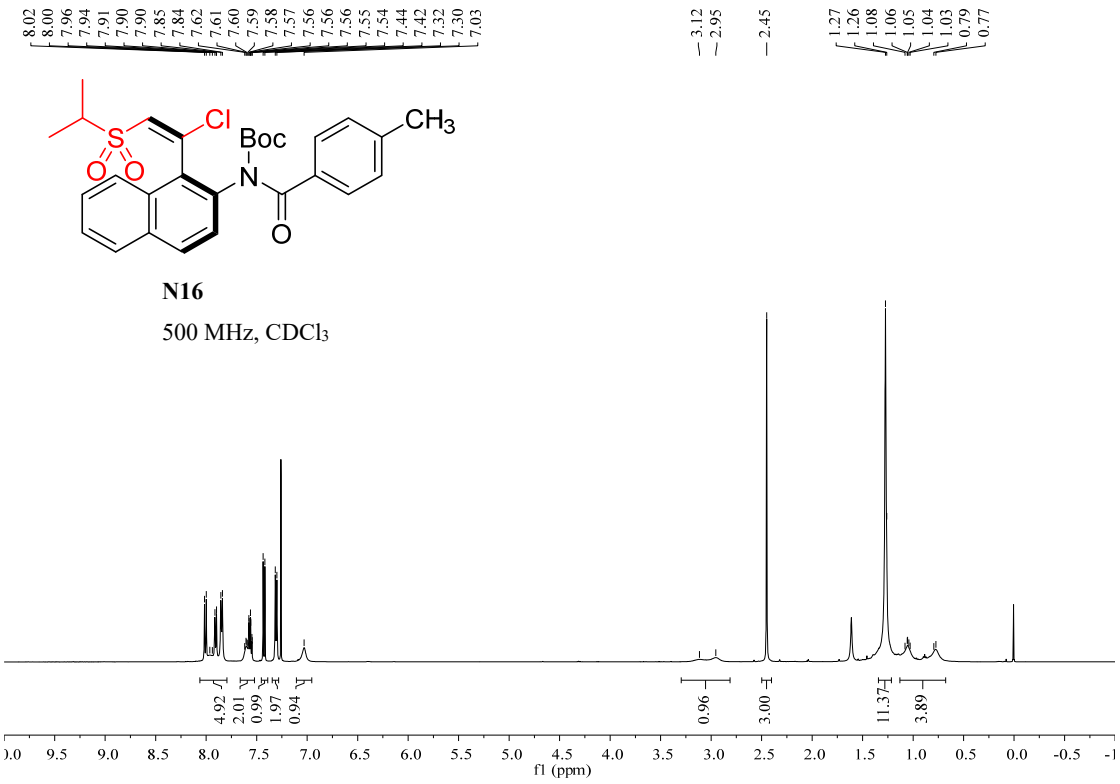
N15

600 MHz, $CDCl_3$



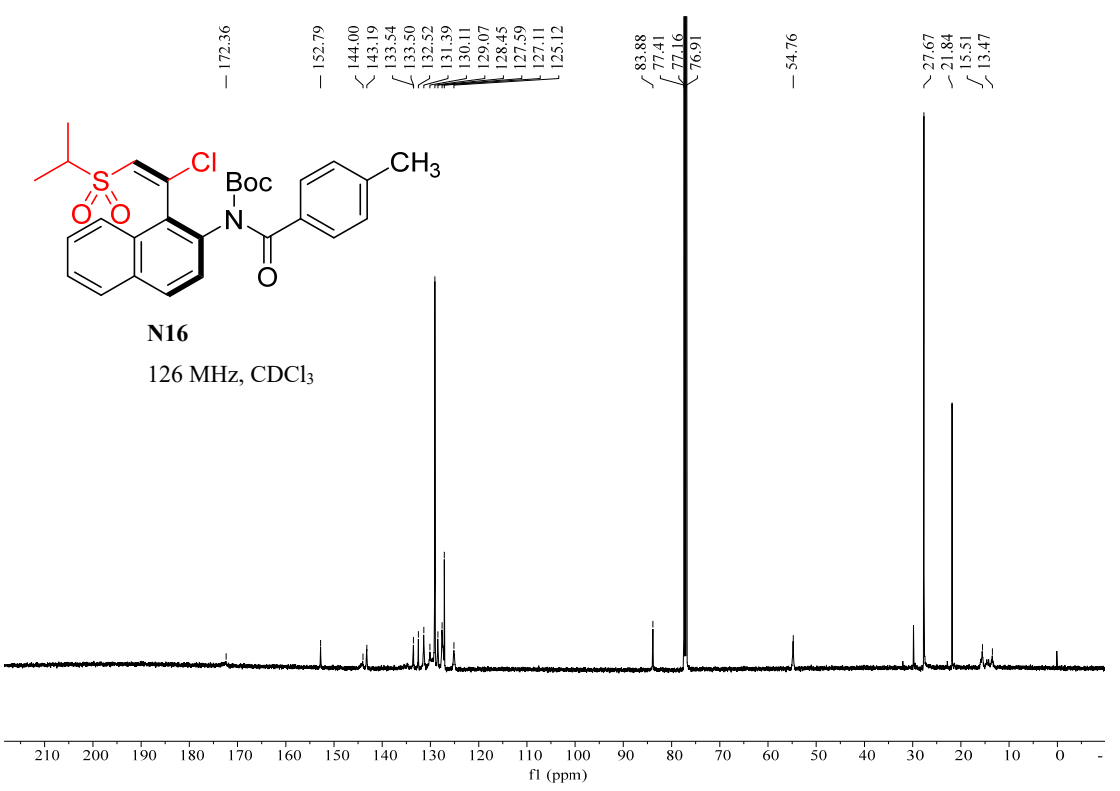
N15

150 MHz, $CDCl_3$



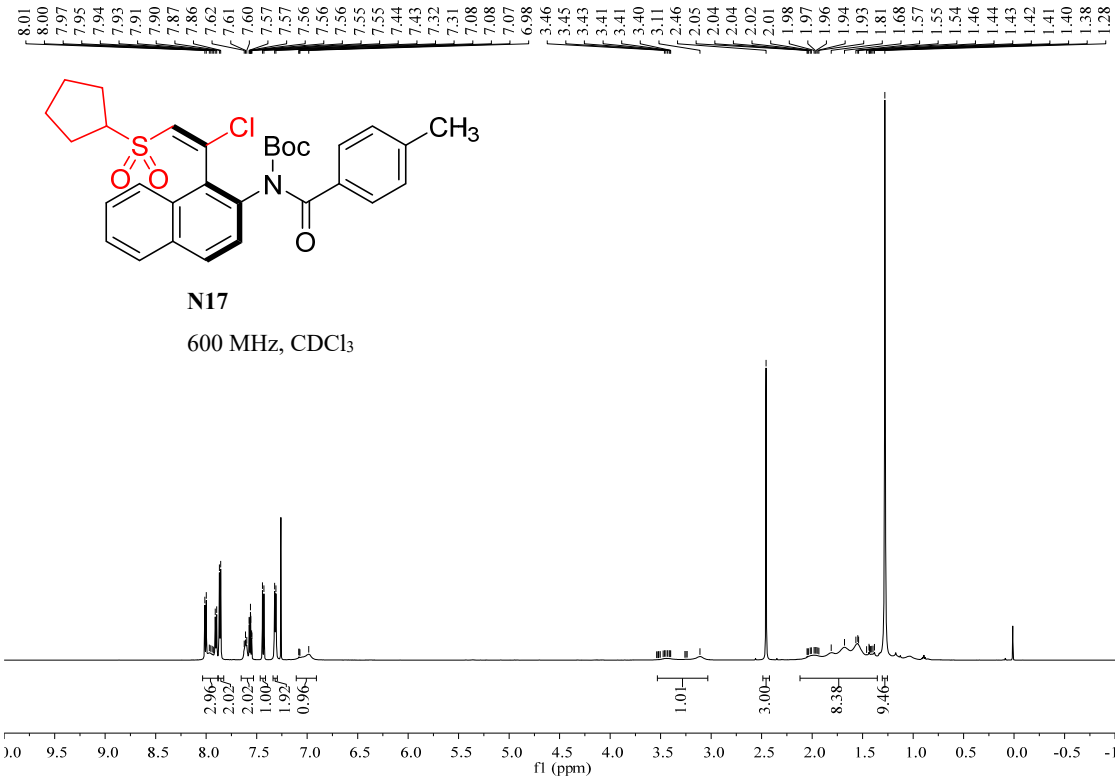
N16

500 MHz, $CDCl_3$



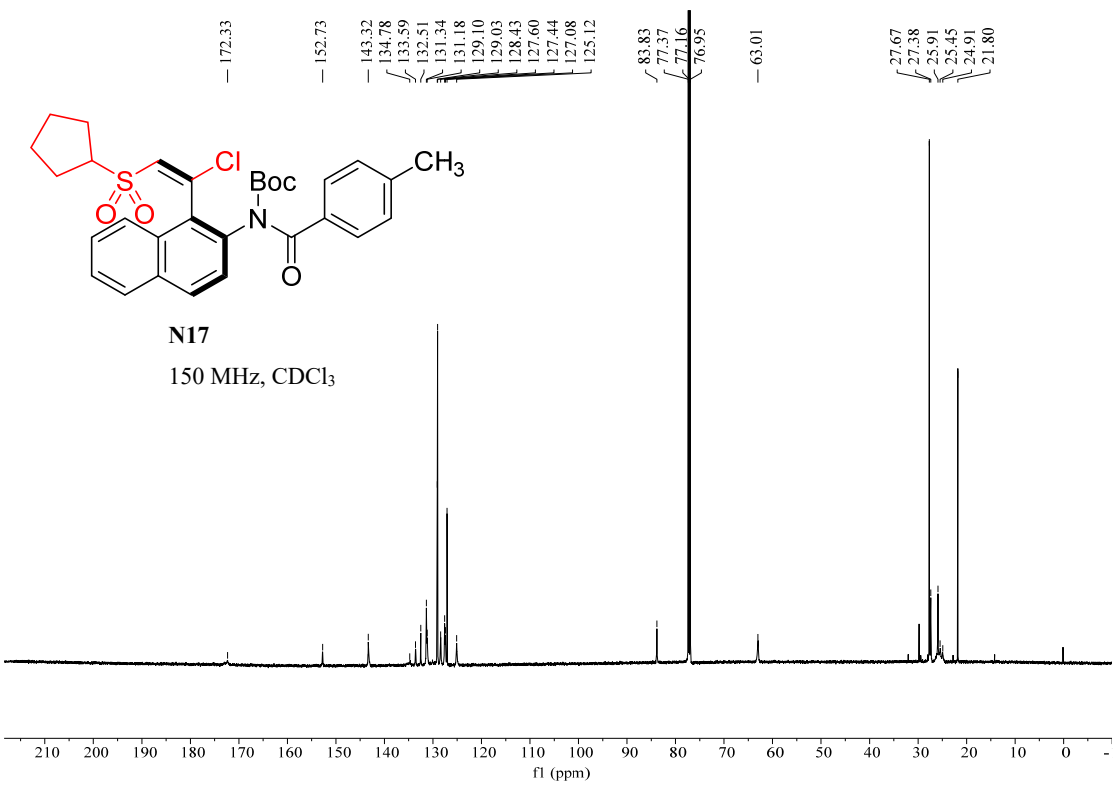
N16

126 MHz, $CDCl_3$



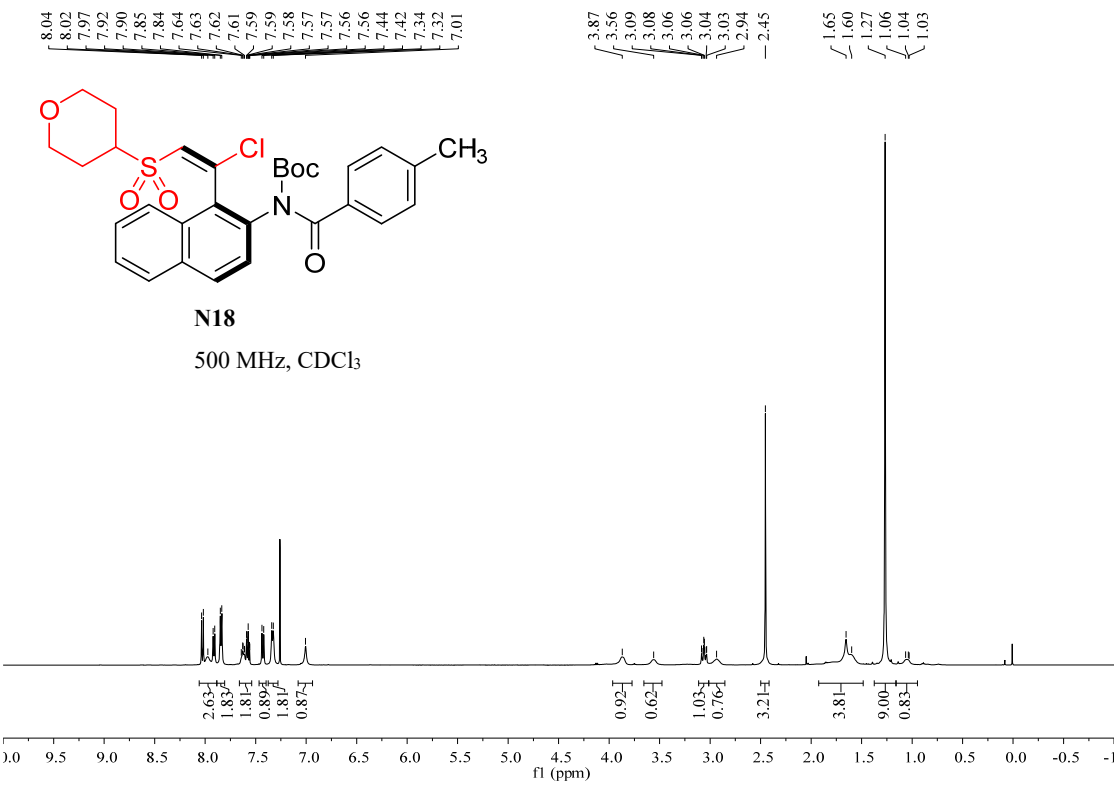
N17

600 MHz, $CDCl_3$



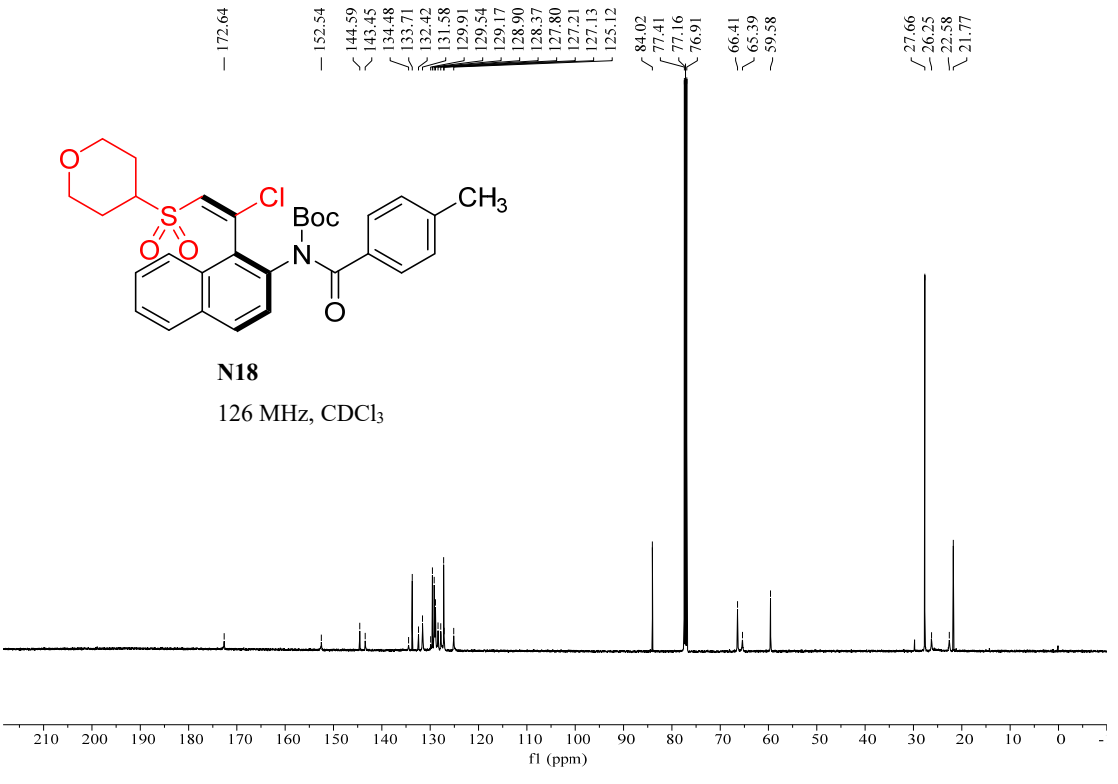
N17

150 MHz, $CDCl_3$



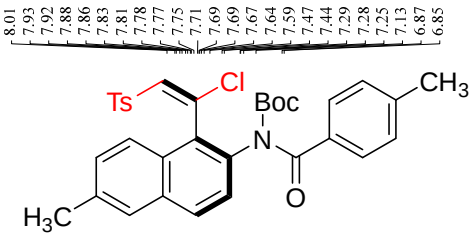
N18

500 MHz, $CDCl_3$



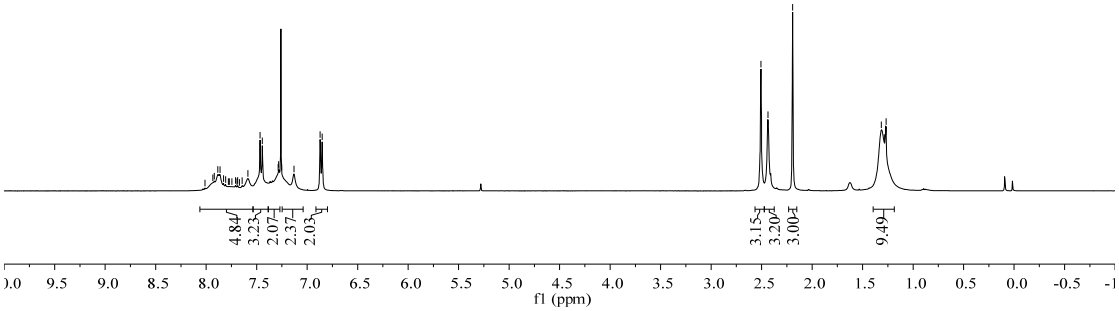
N18

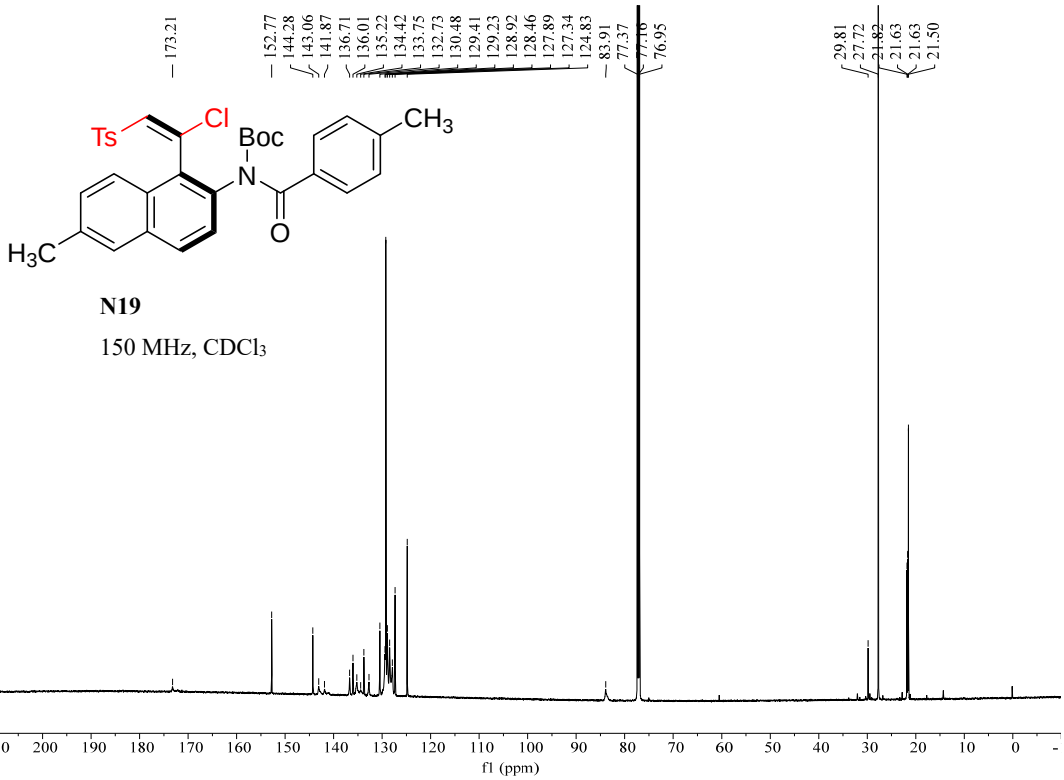
126 MHz, $CDCl_3$



N19

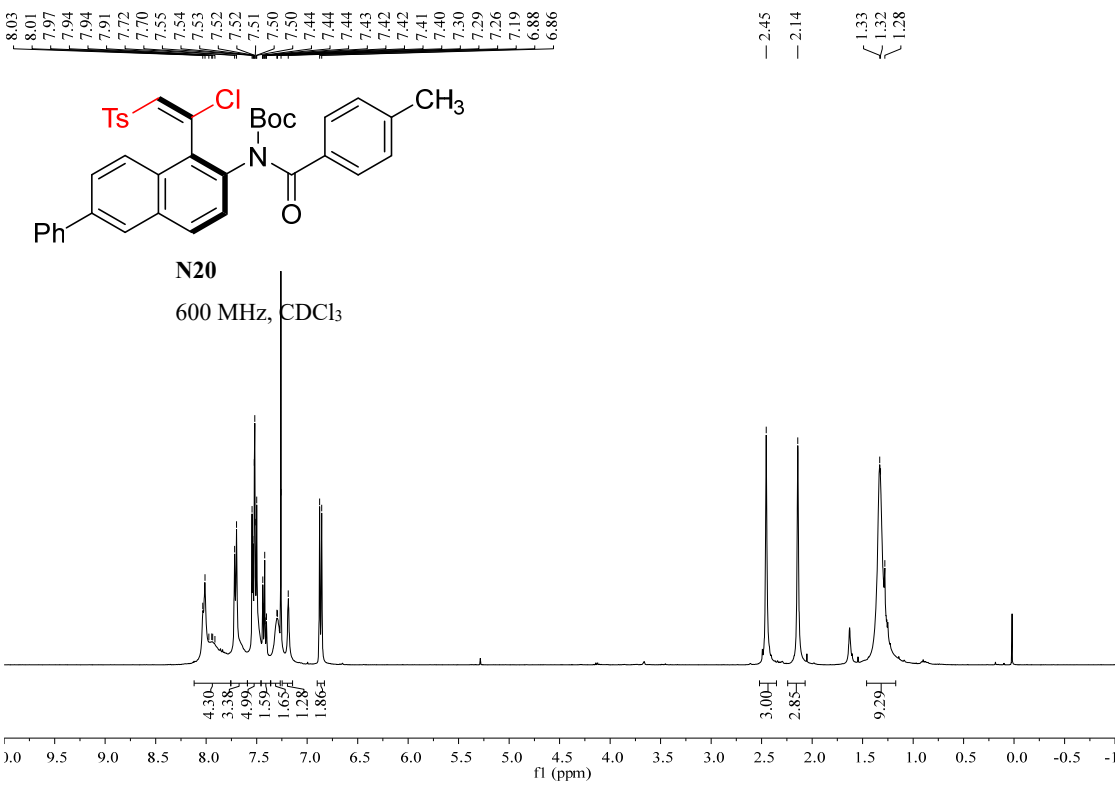
500 MHz, $CDCl_3$





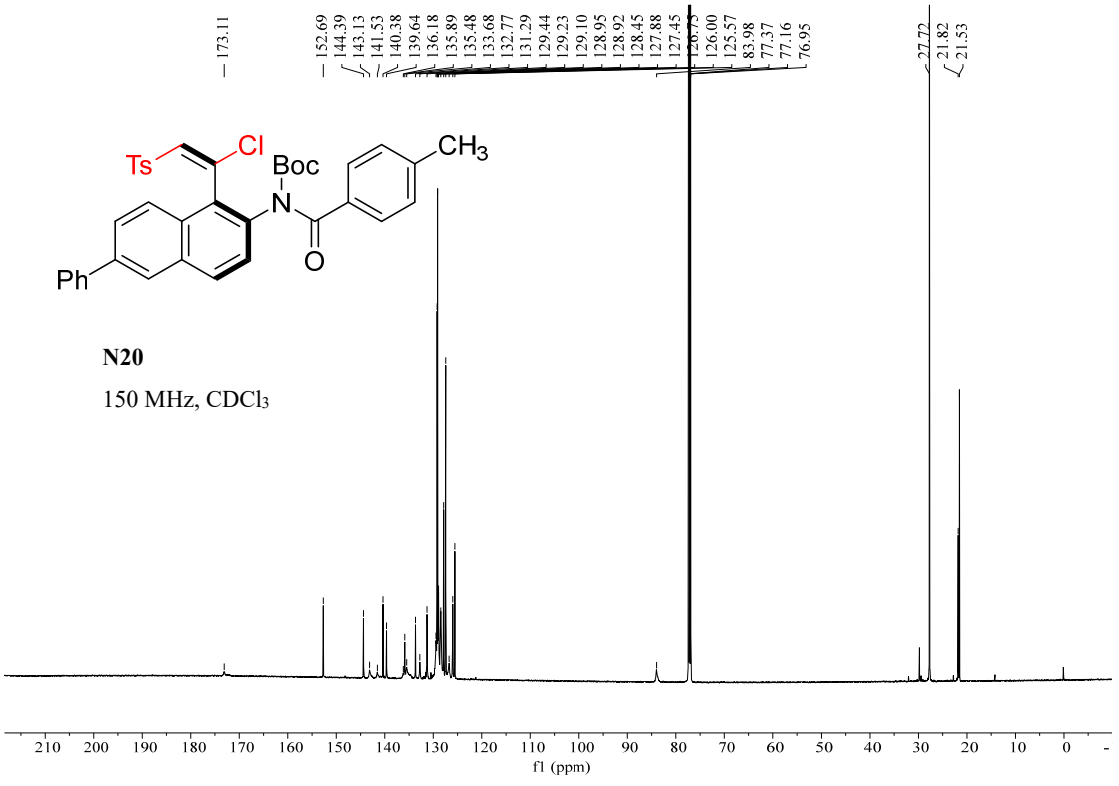
N19

150 MHz, $CDCl_3$



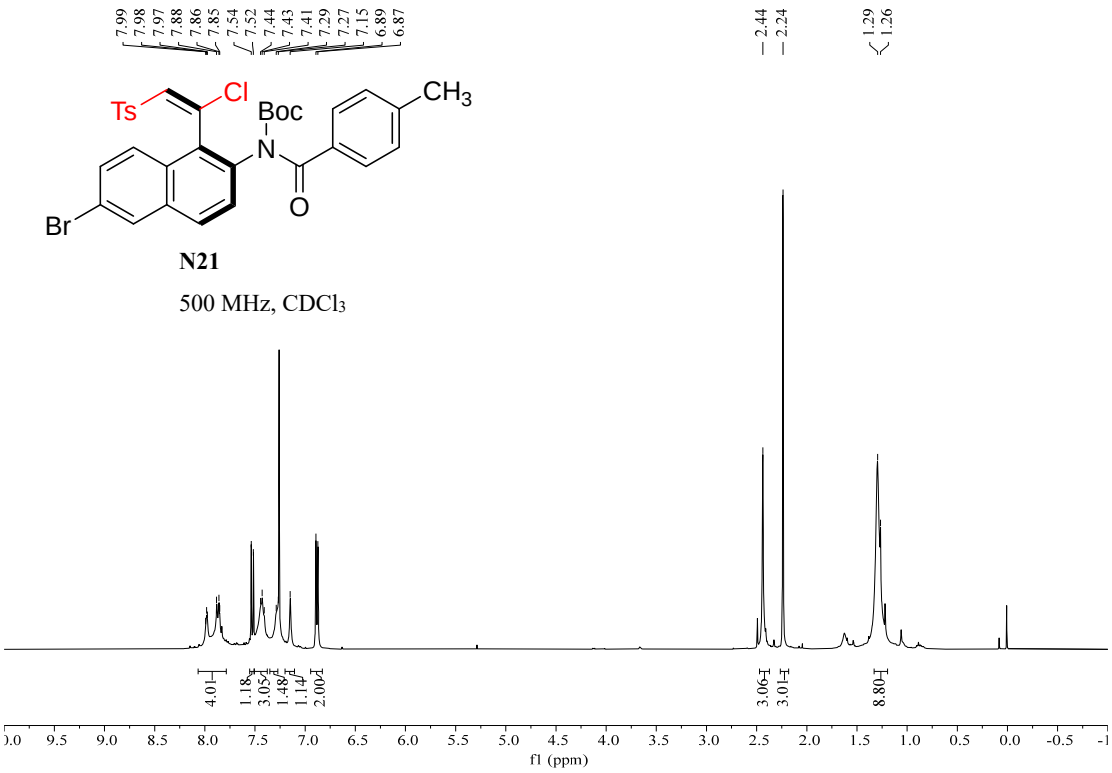
N20

600 MHz, $CDCl_3$



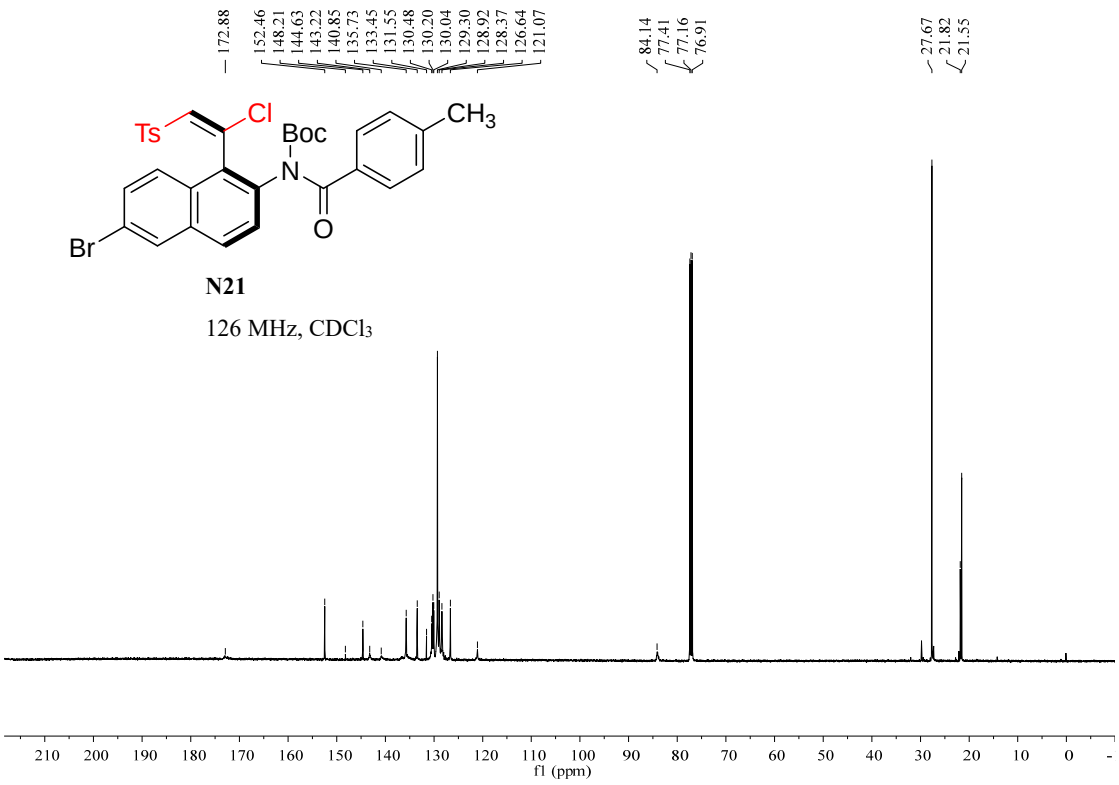
N20

150 MHz, $CDCl_3$



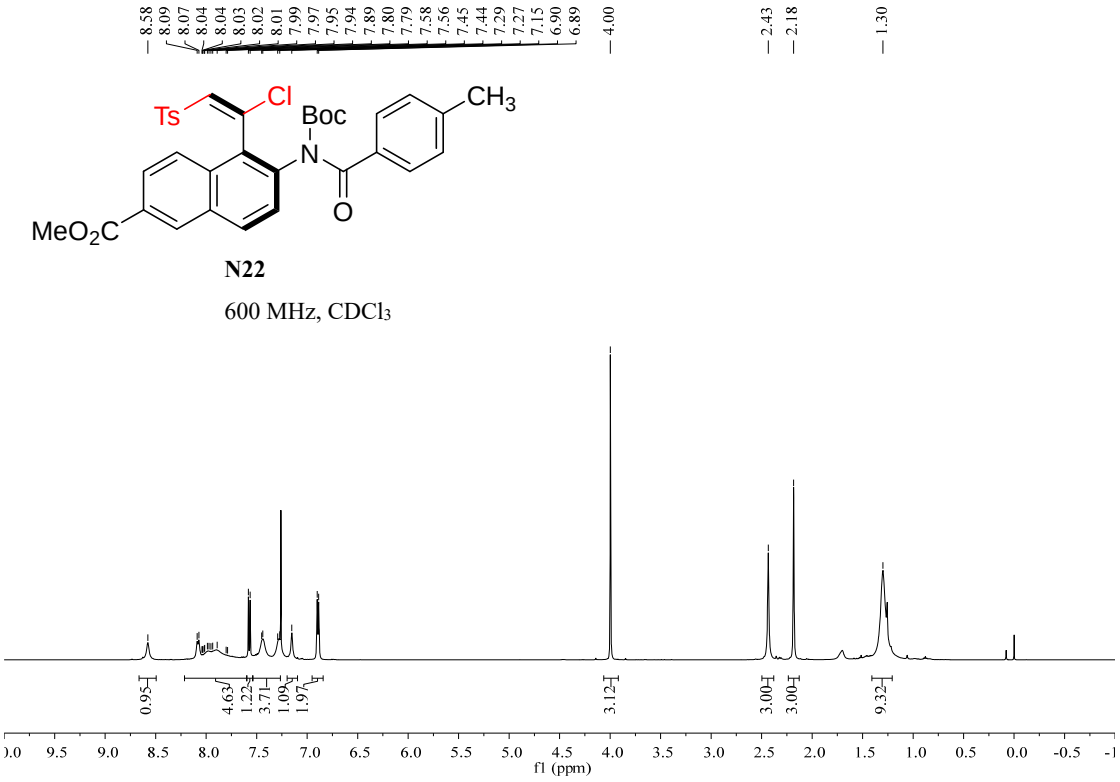
N21

500 MHz, $CDCl_3$



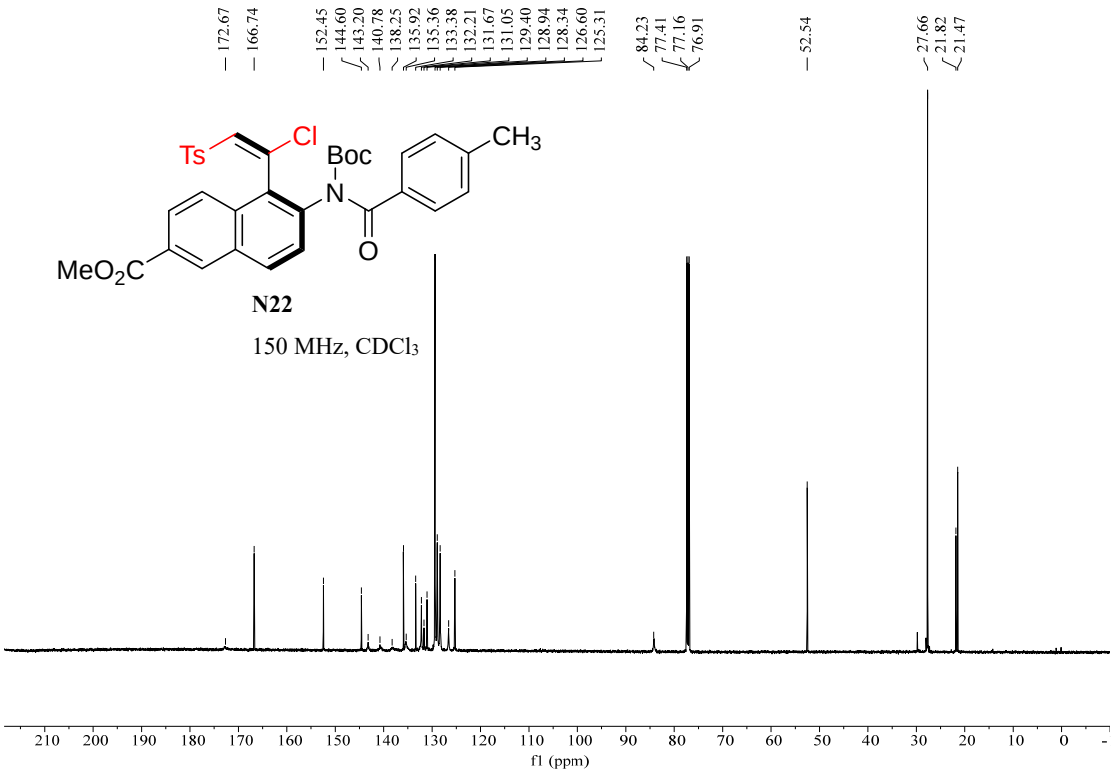
N21

126 MHz, $CDCl_3$



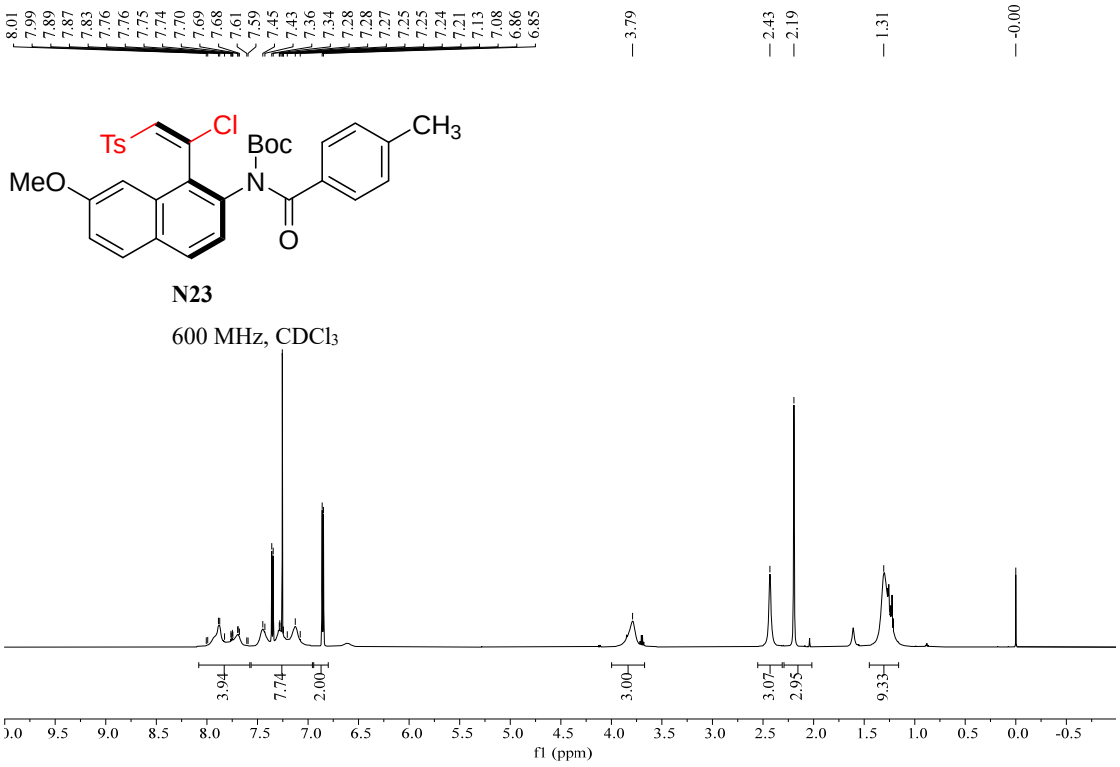
N22

600 MHz, $CDCl_3$



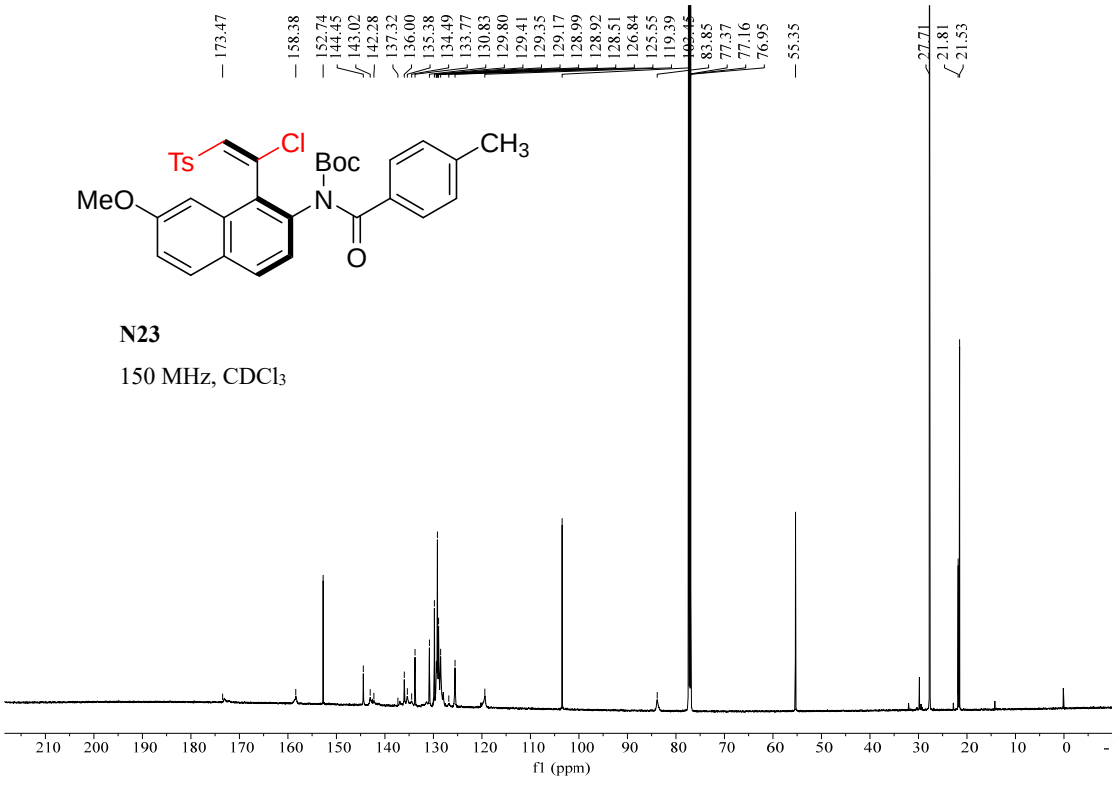
N22

150 MHz, $CDCl_3$



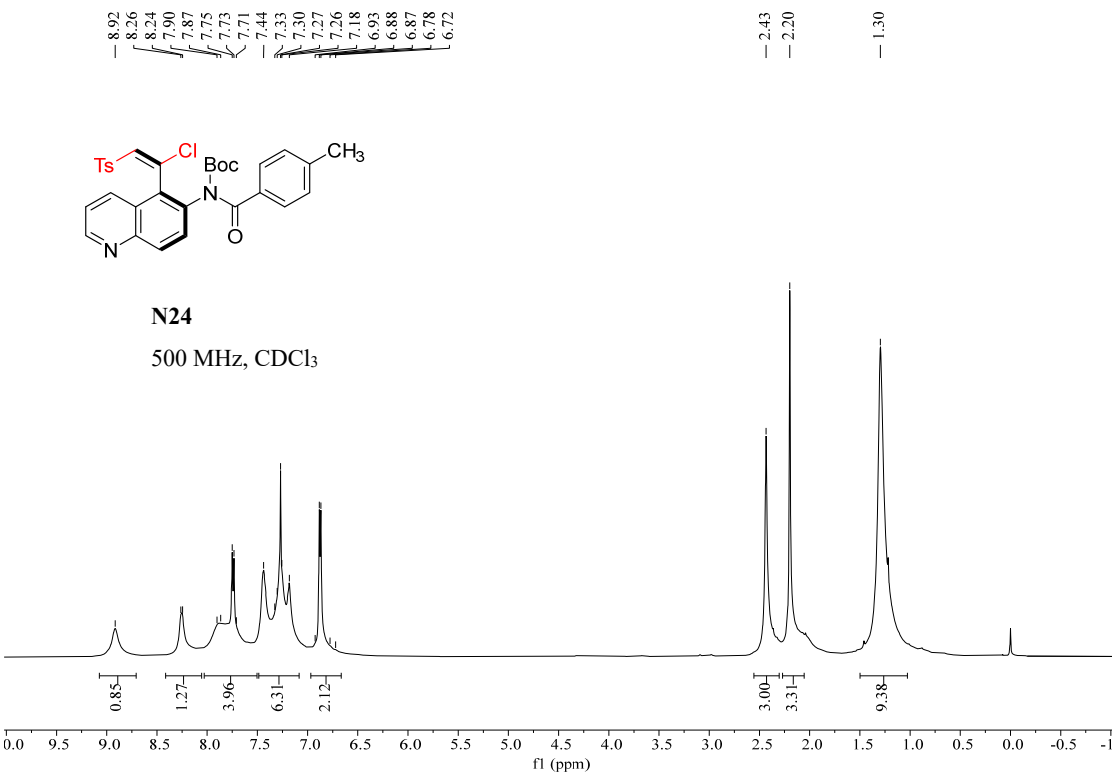
N23

600 MHz, $CDCl_3$



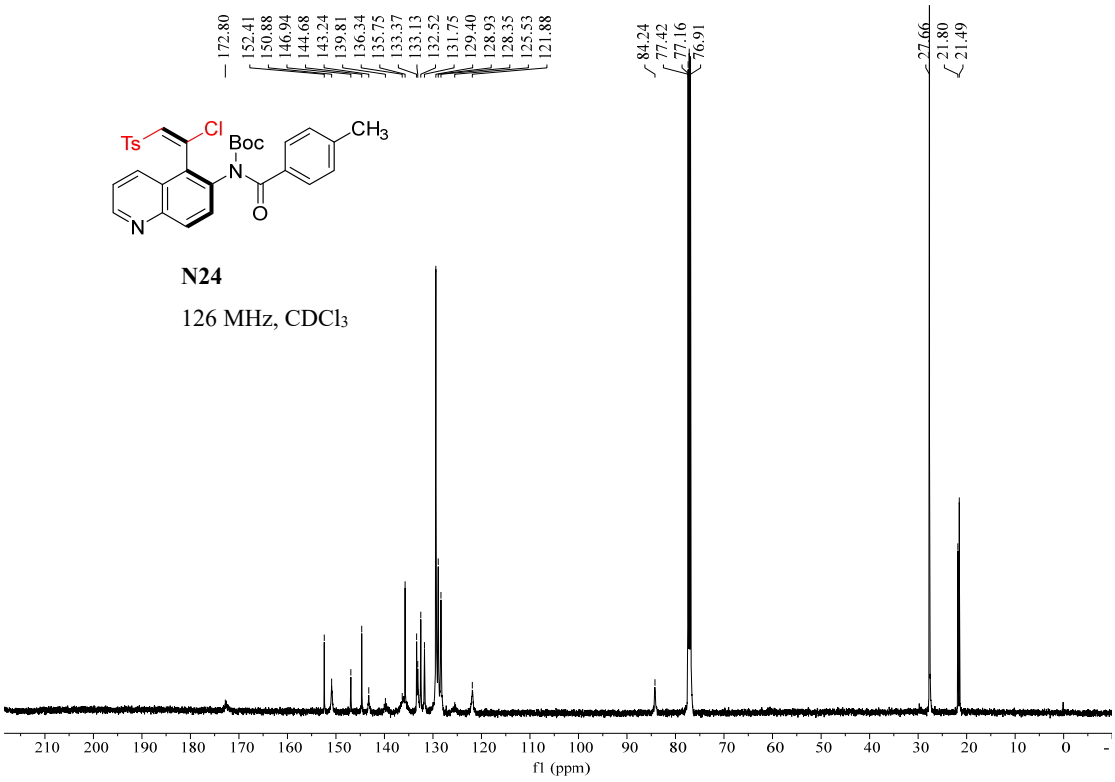
N23

150 MHz, $CDCl_3$



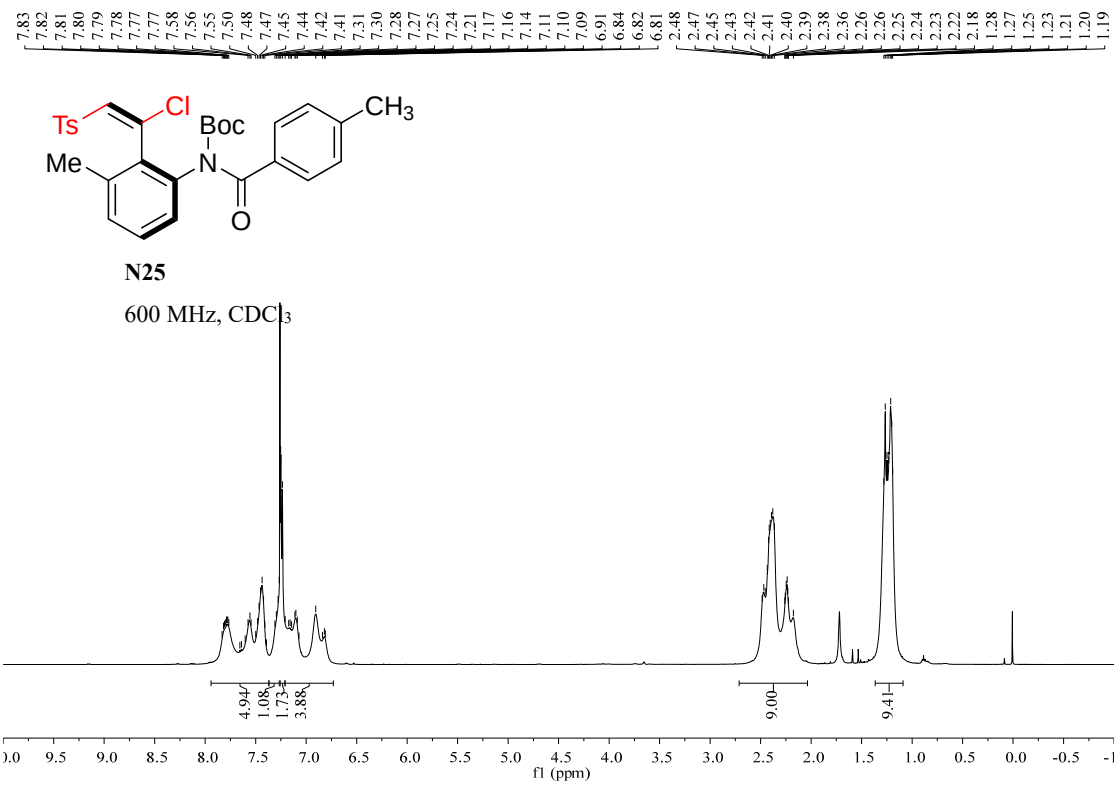
N24

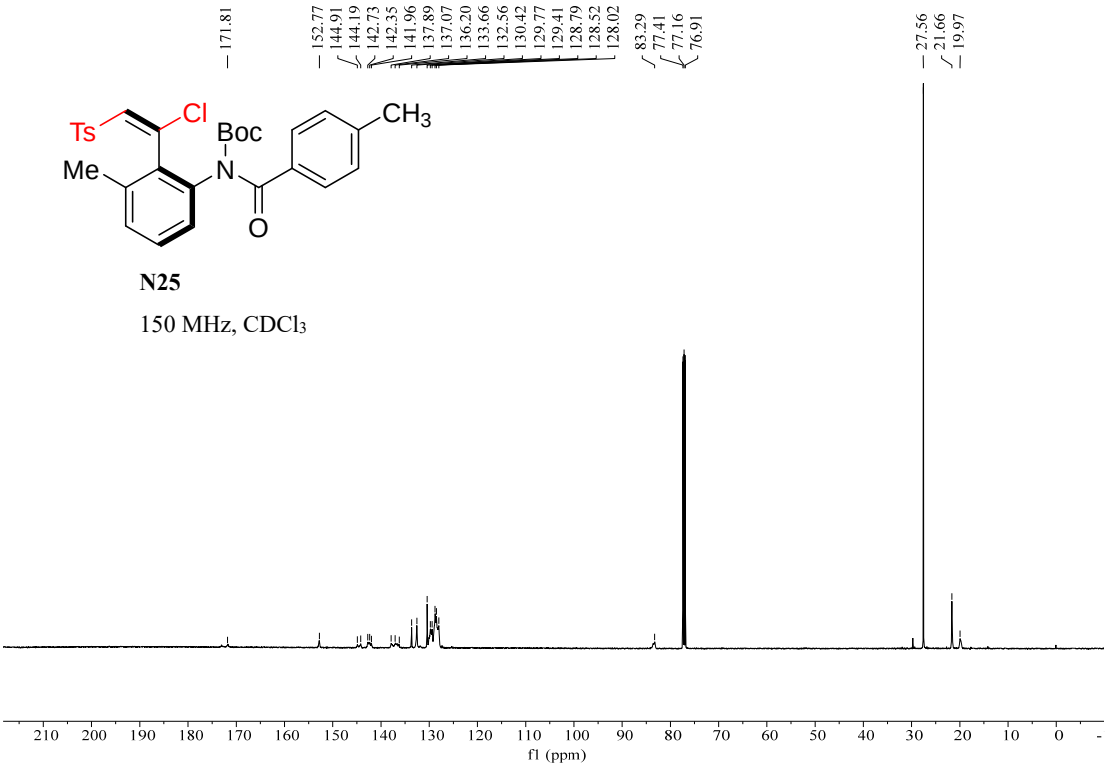
500 MHz, $CDCl_3$

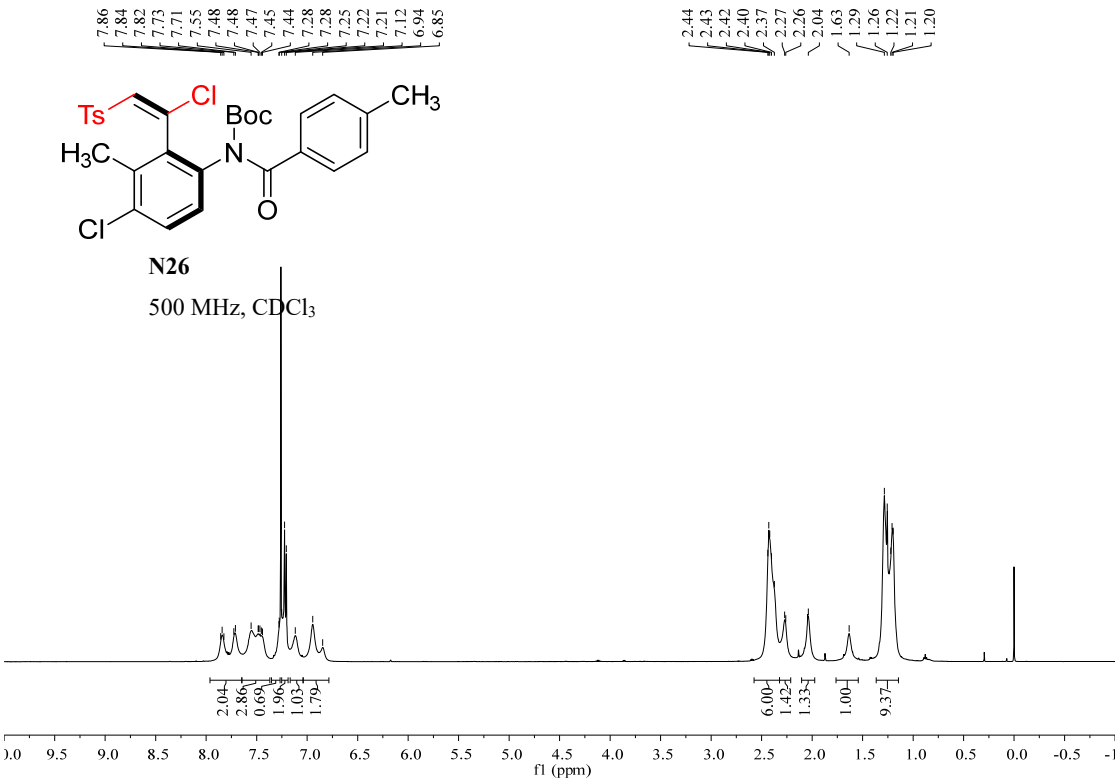


N24

126 MHz, $CDCl_3$

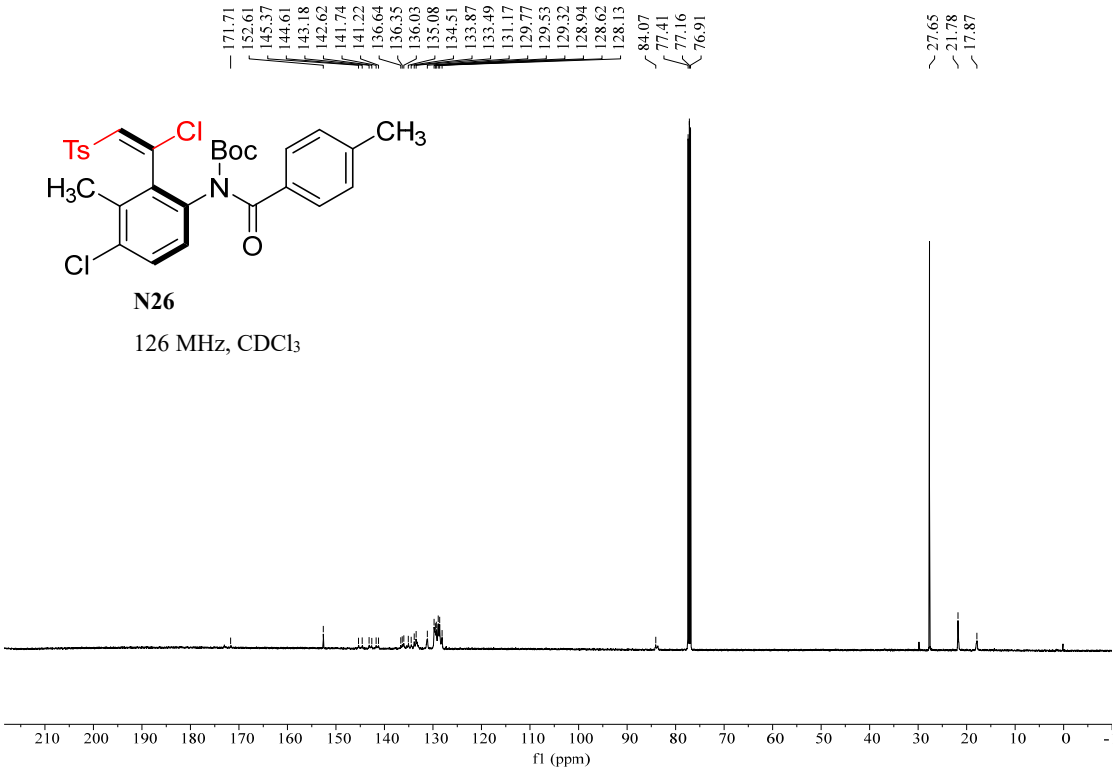

7.83
7.82
7.81
7.80
7.79
7.78
7.77
7.77
7.58
7.56
7.55
7.50
7.48
7.47
7.45
7.44
7.42
7.41
7.31
7.30
7.28
7.27
7.25
7.24
7.21
7.17
7.16
7.14
7.11
7.10
7.09
6.91
6.84
6.82
6.81
2.48
2.47
2.45
2.43
2.42
2.41
2.40
2.39
2.38
2.36
2.26
2.26
2.25
2.24
2.23
2.22
2.18
1.28
1.27
1.25
1.23
1.21
1.20
1.19
Ts
Cl
Boc
N
Me
CH3
O
N25
600 MHz, CDCl3
4.94
1.08
1.73
3.88
9.00
9.41
f1 (ppm)


171.81
152.77
144.91
144.19
142.73
142.35
141.96
137.89
137.07
136.20
133.66
132.56
130.42
129.77
129.41
128.79
128.52
128.02
83.29
77.41
77.16
76.91
27.56
21.66
19.97
Ts
Cl
Boc
N
Me
CH3
O
N25
150 MHz, CDCl3
f1 (ppm)



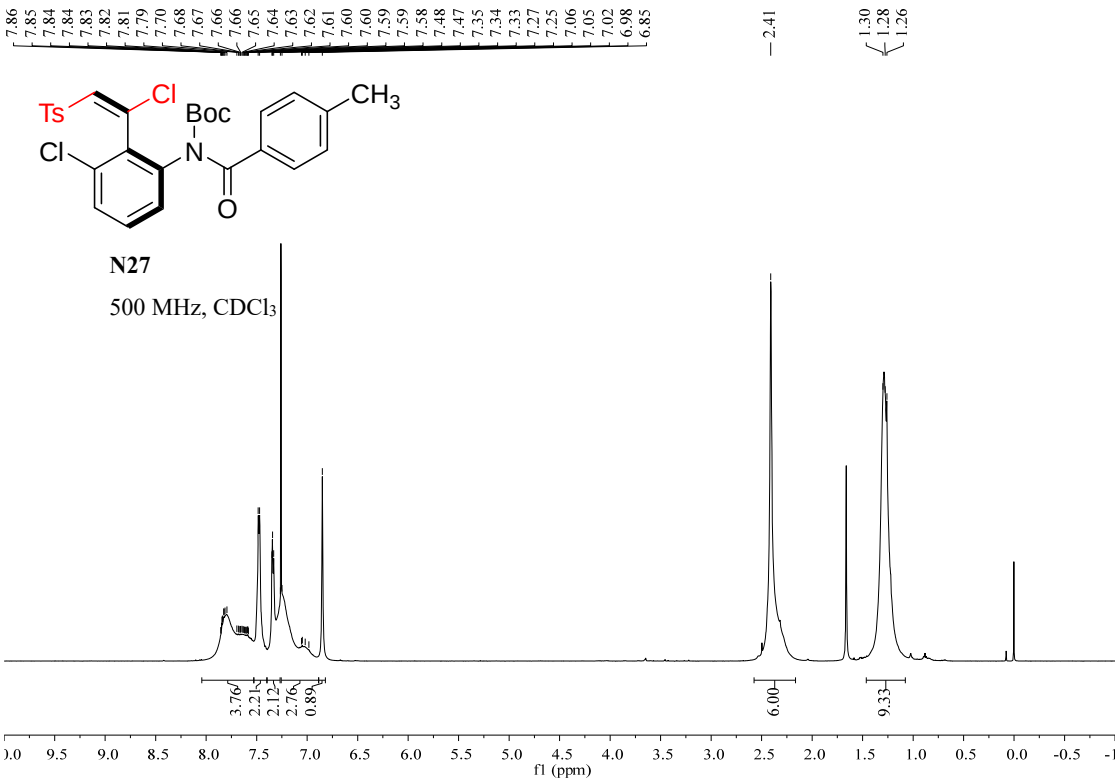
N26

500 MHz, $CDCl_3$



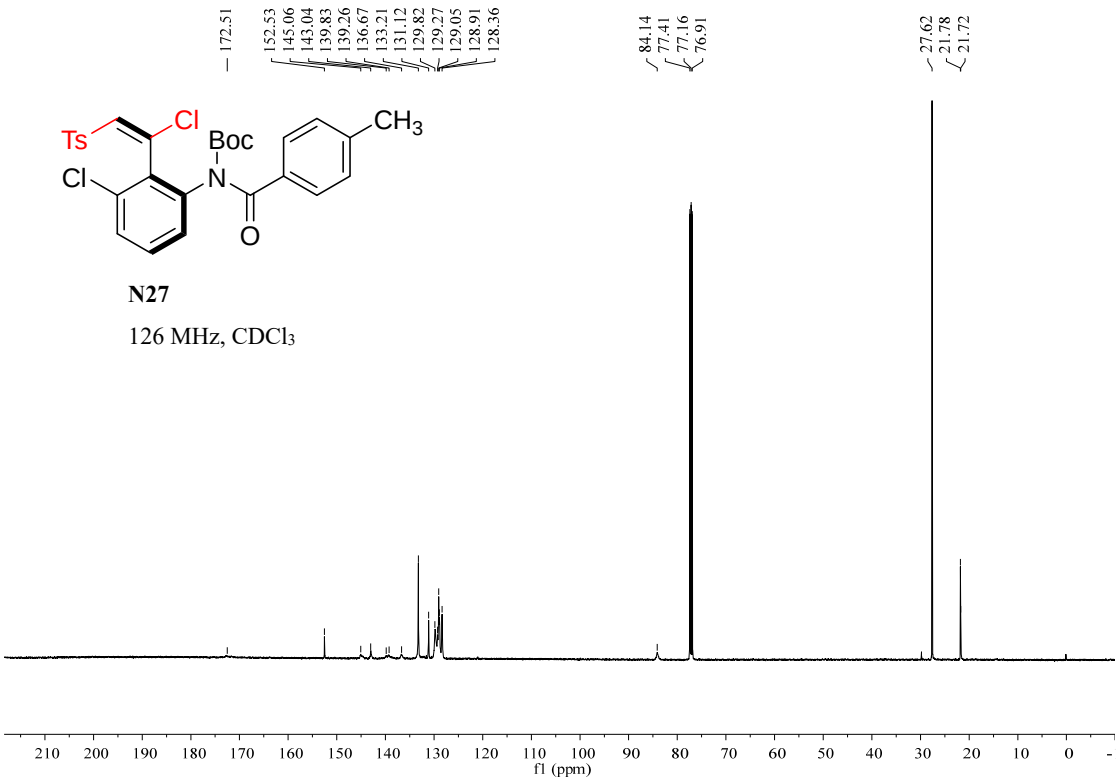
N26

126 MHz, $CDCl_3$



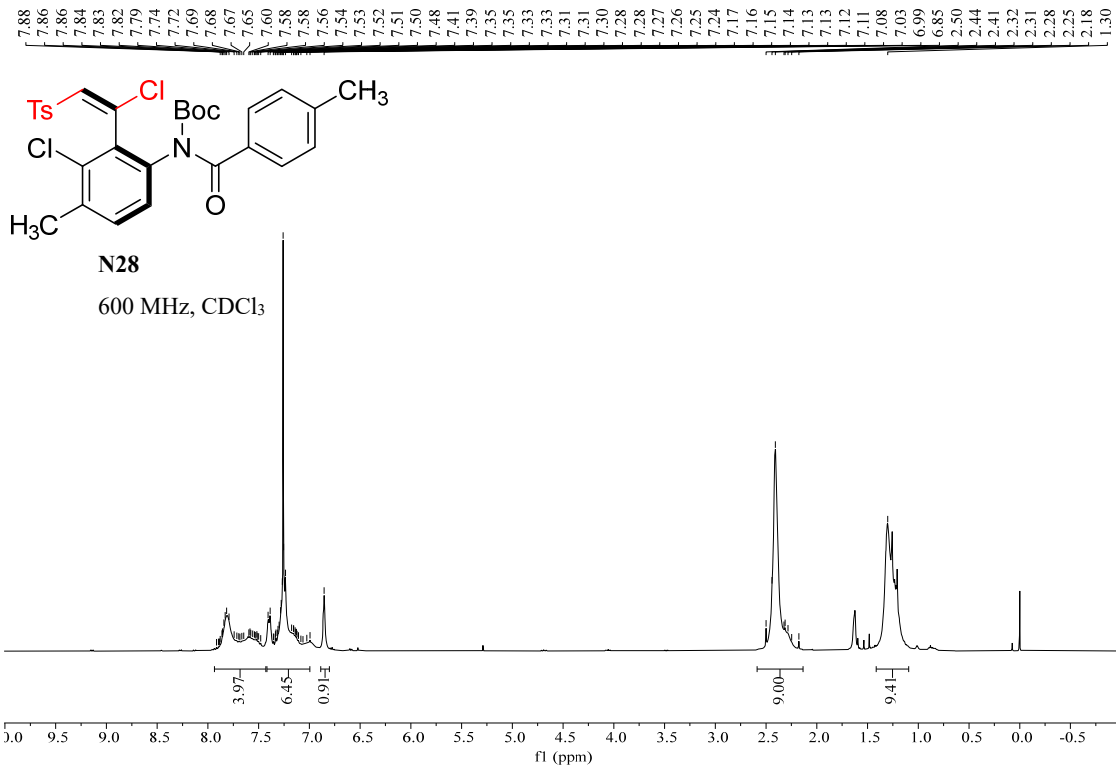
N27

500 MHz, $CDCl_3$



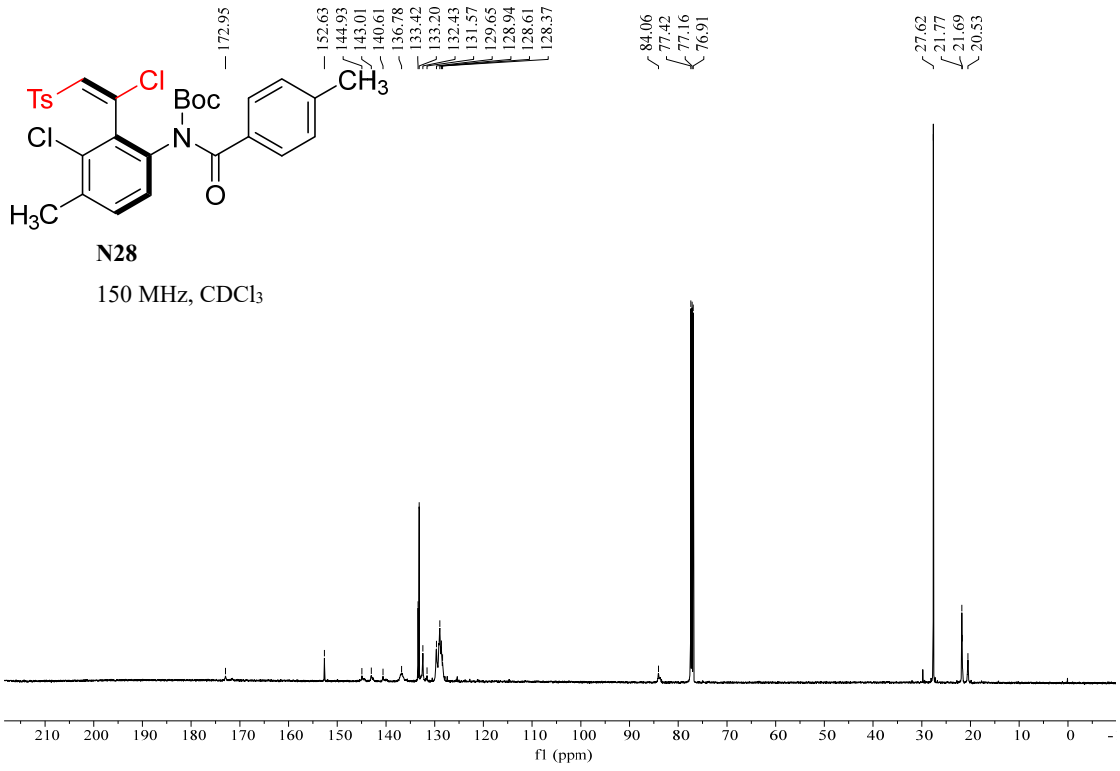
N27

126 MHz, $CDCl_3$



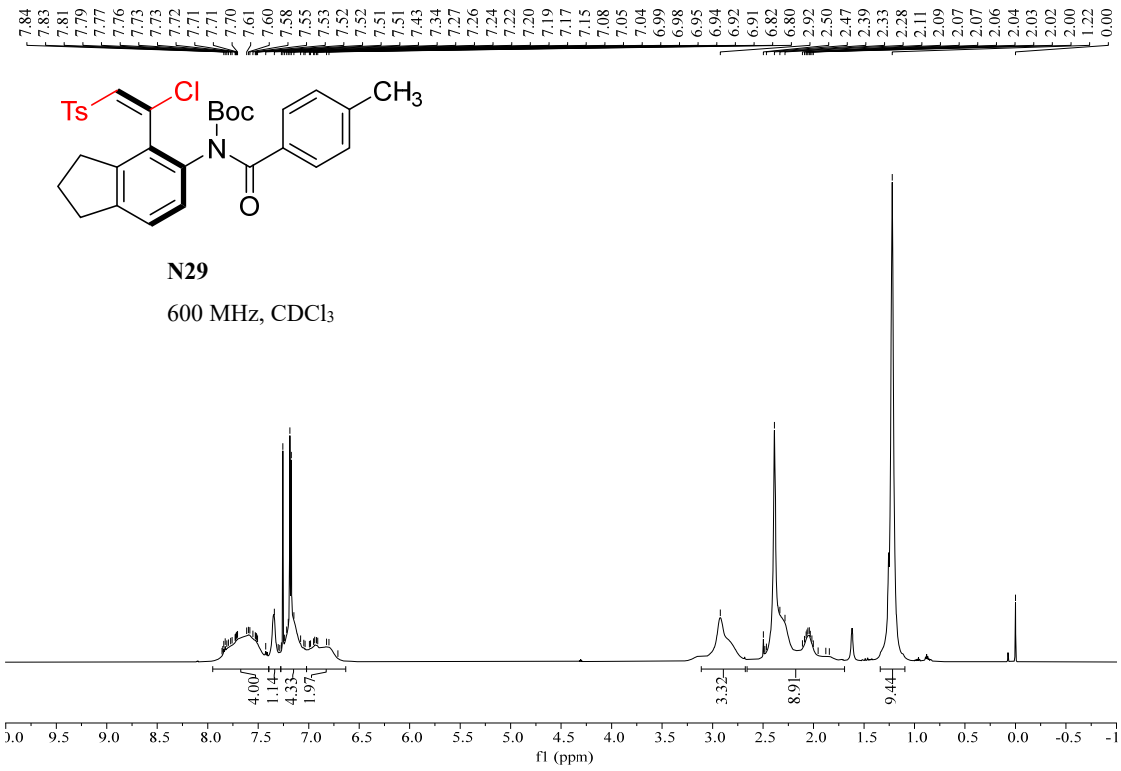
N28

600 MHz, $CDCl_3$



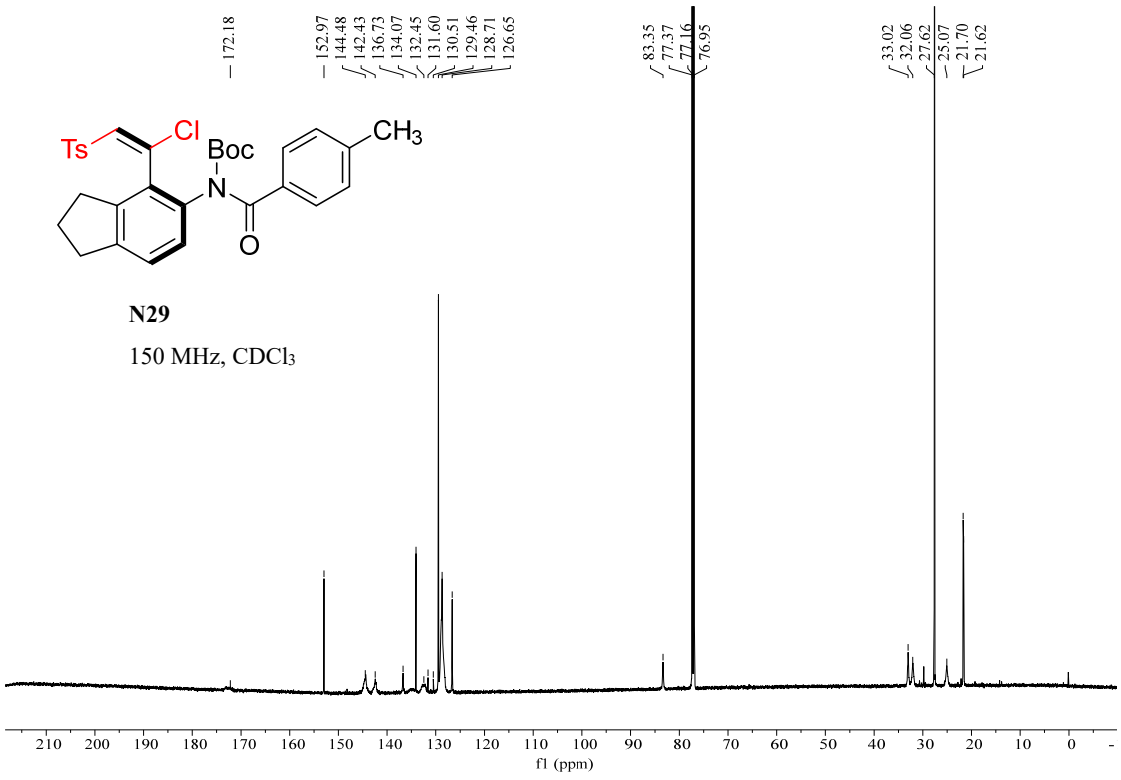
N28

150 MHz, $CDCl_3$



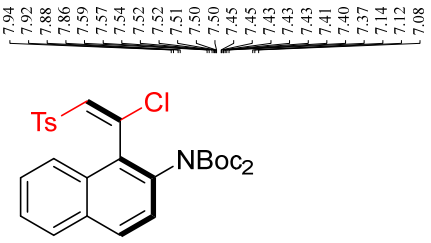
N29

600 MHz, $CDCl_3$



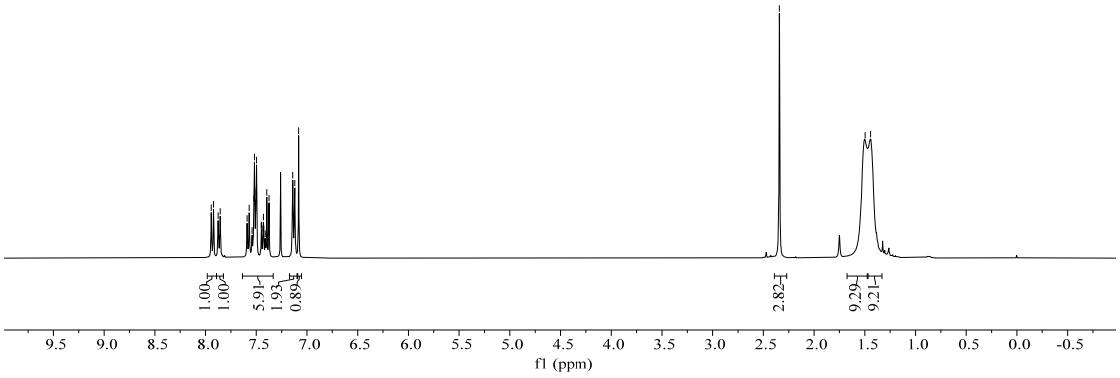
N29

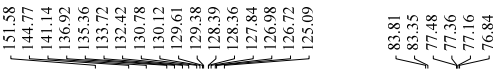
150 MHz, $CDCl_3$

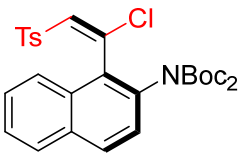


N30

400 MHz, $CDCl_3$

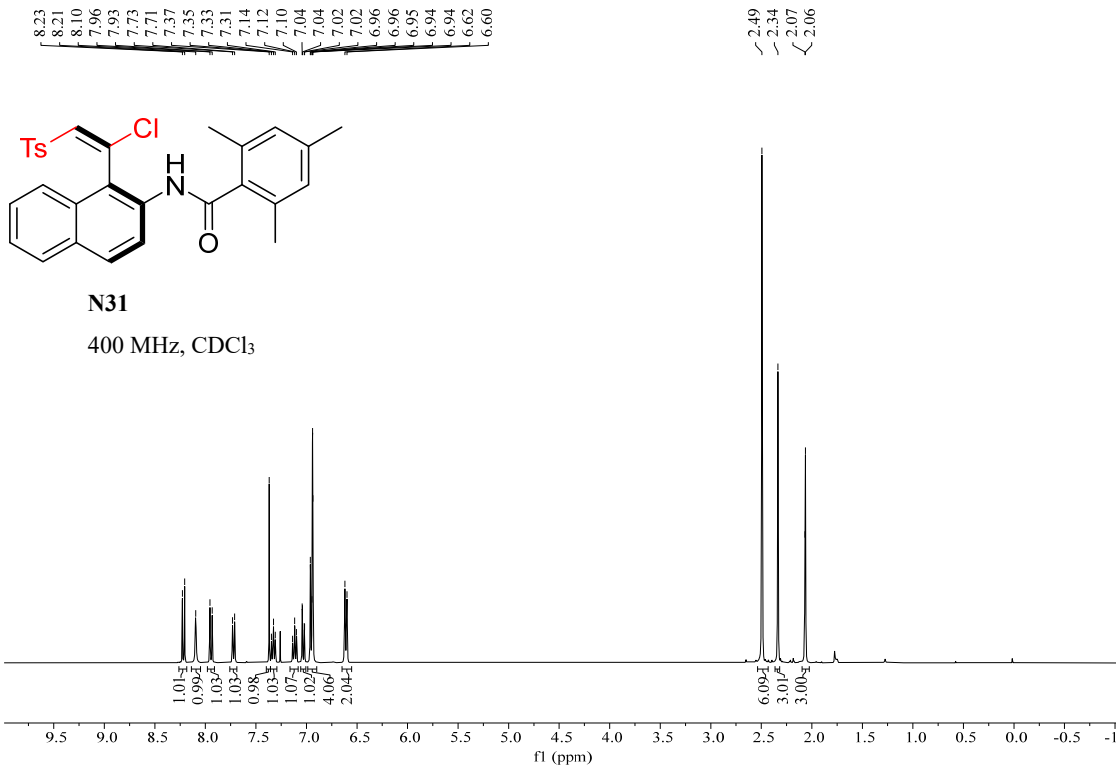






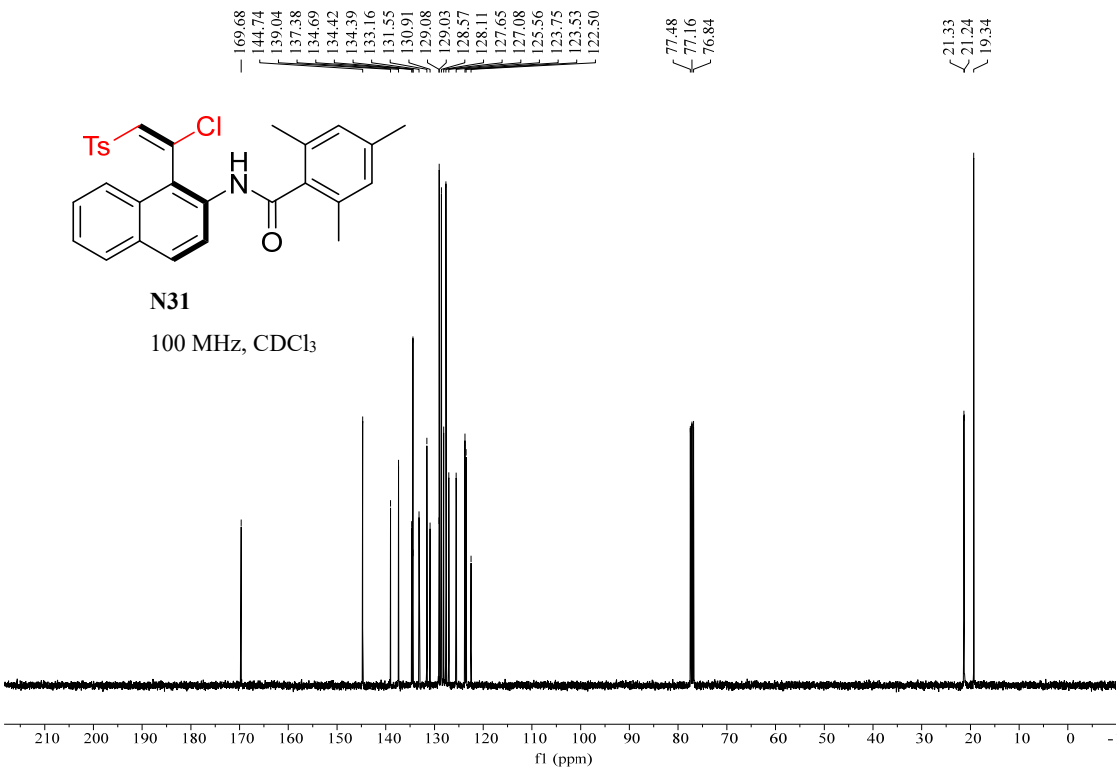
N30

100 MHz, $CDCl_3$



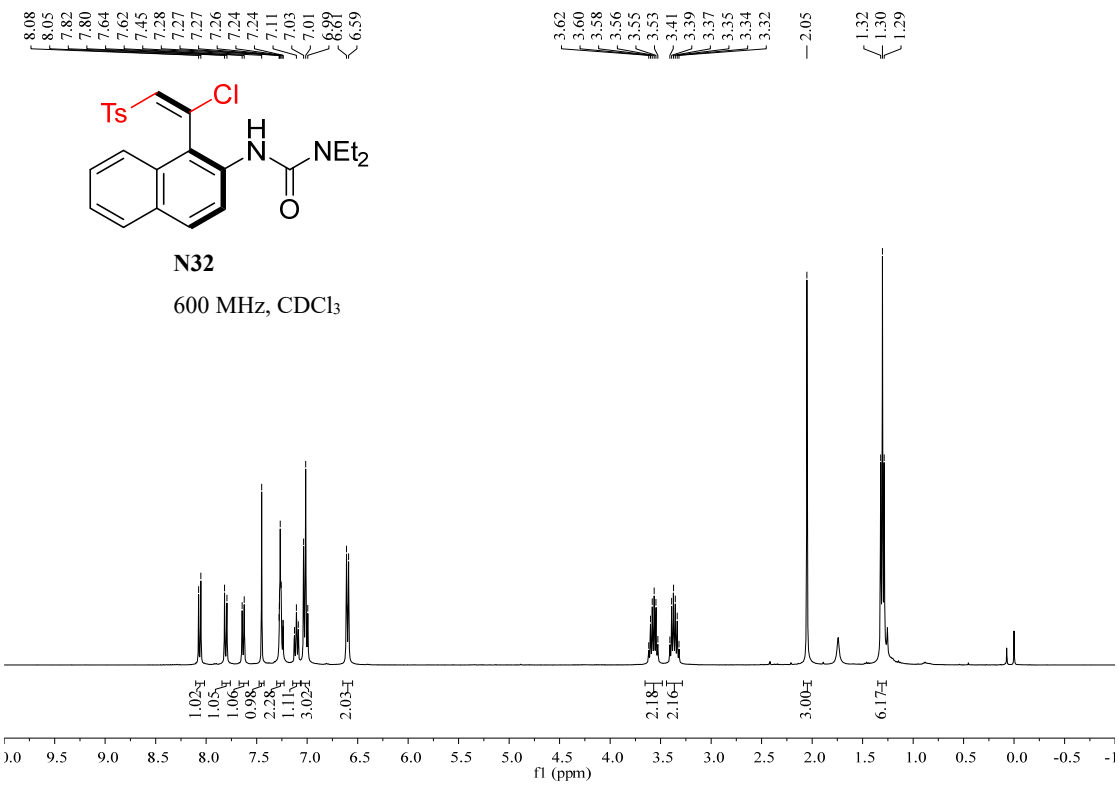
N31

400 MHz, $CDCl_3$



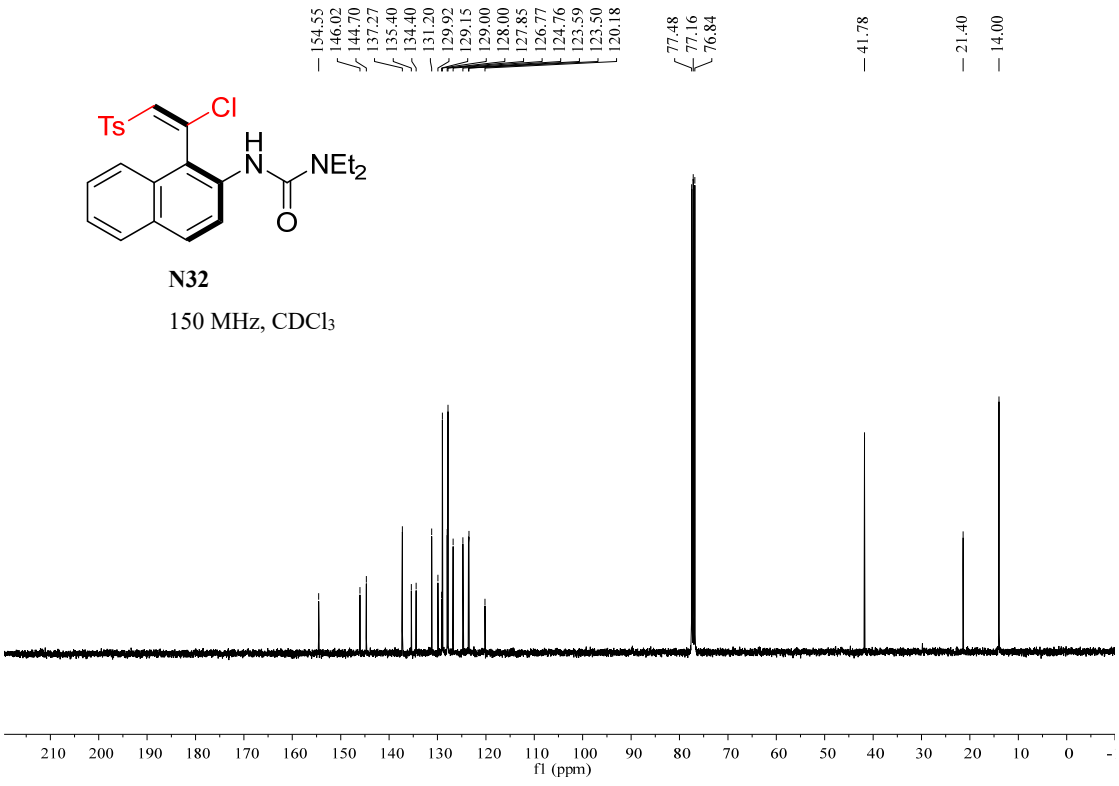
N31

100 MHz, $CDCl_3$



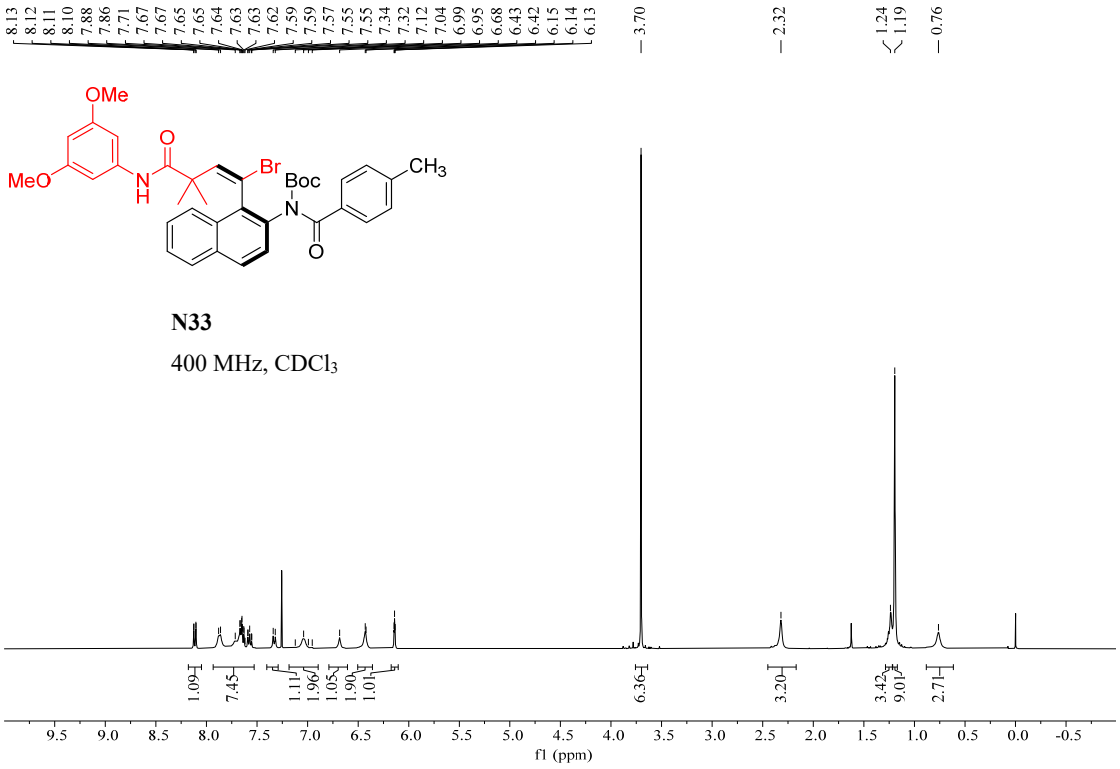
N32

600 MHz, $CDCl_3$



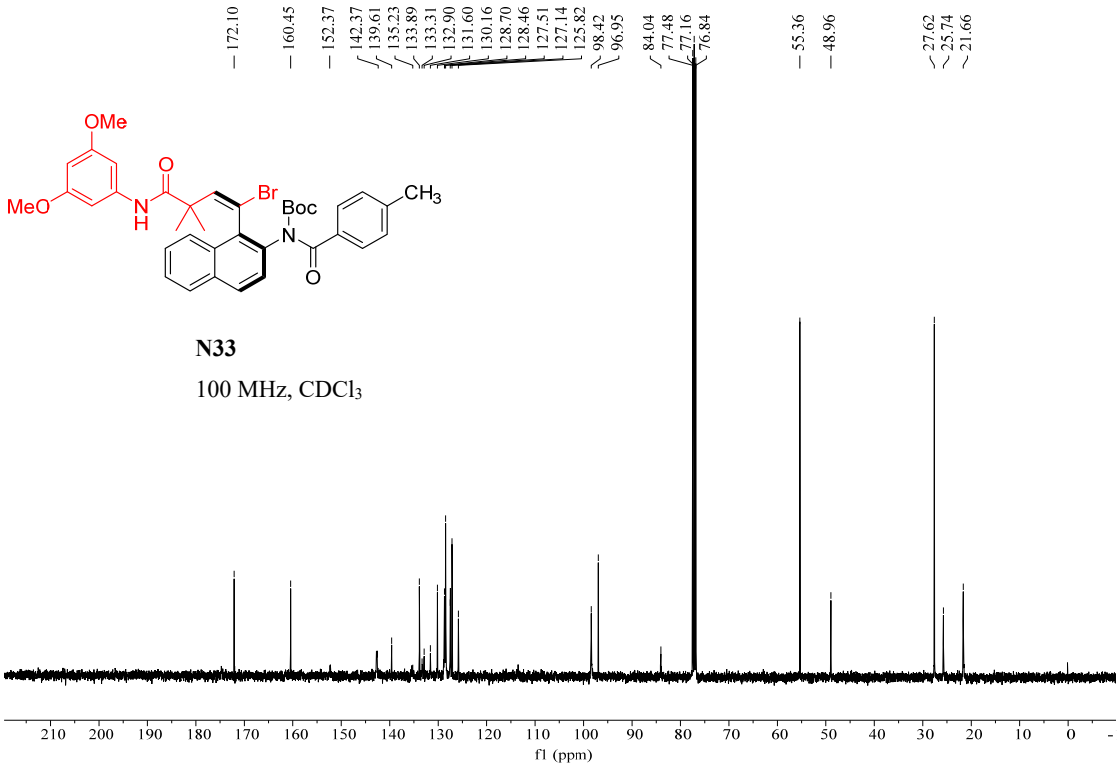
N32

150 MHz, $CDCl_3$



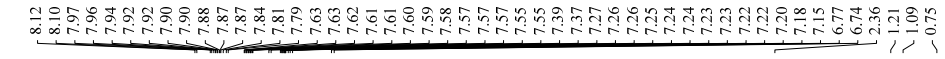
N33

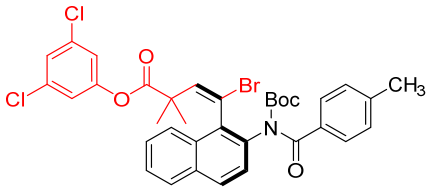
400 MHz, $CDCl_3$



N33

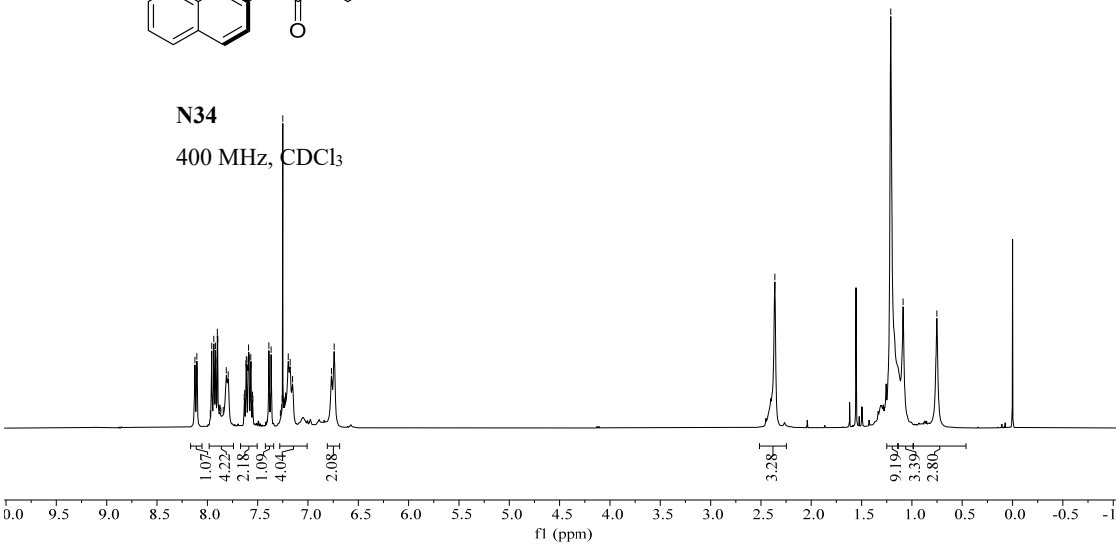
100 MHz, $CDCl_3$

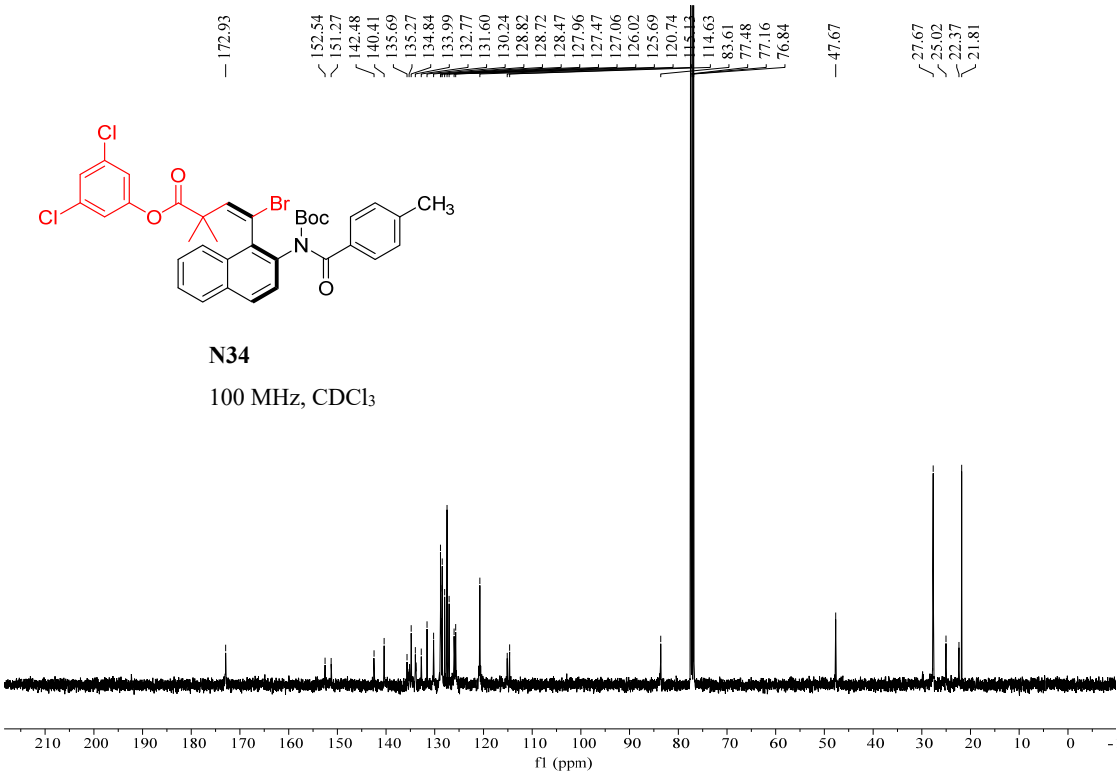




N34

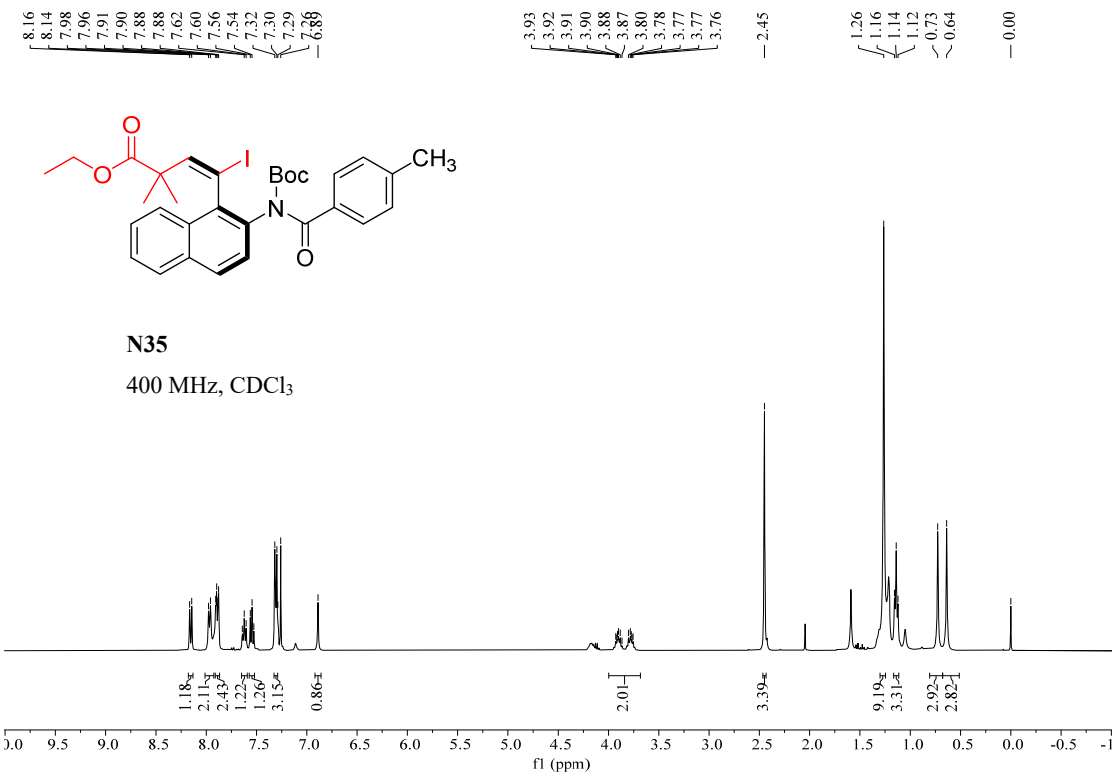
400 MHz, $CDCl_3$





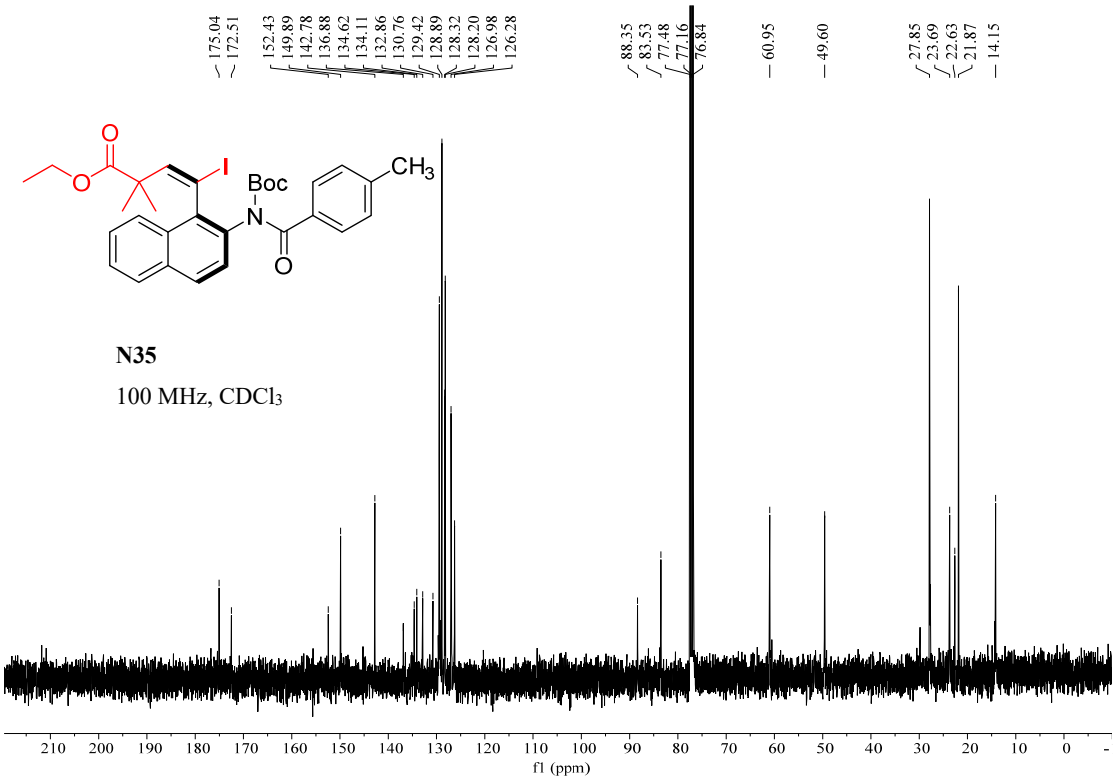
N34

100 MHz, $CDCl_3$



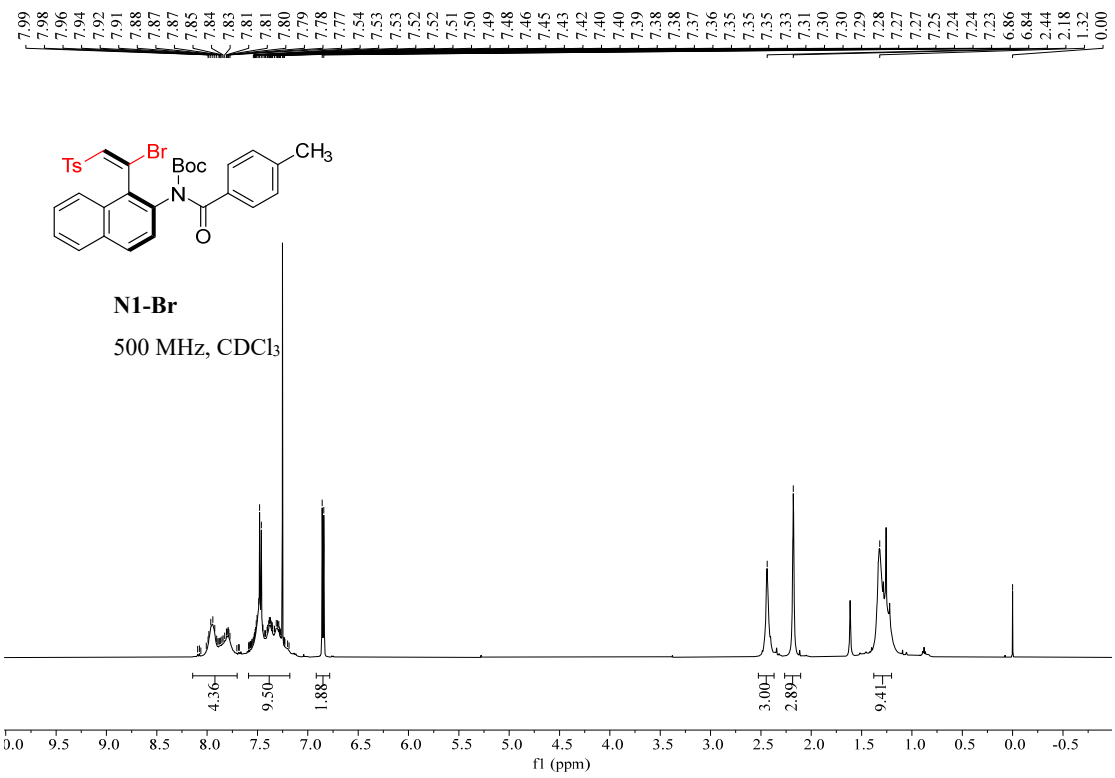
N35

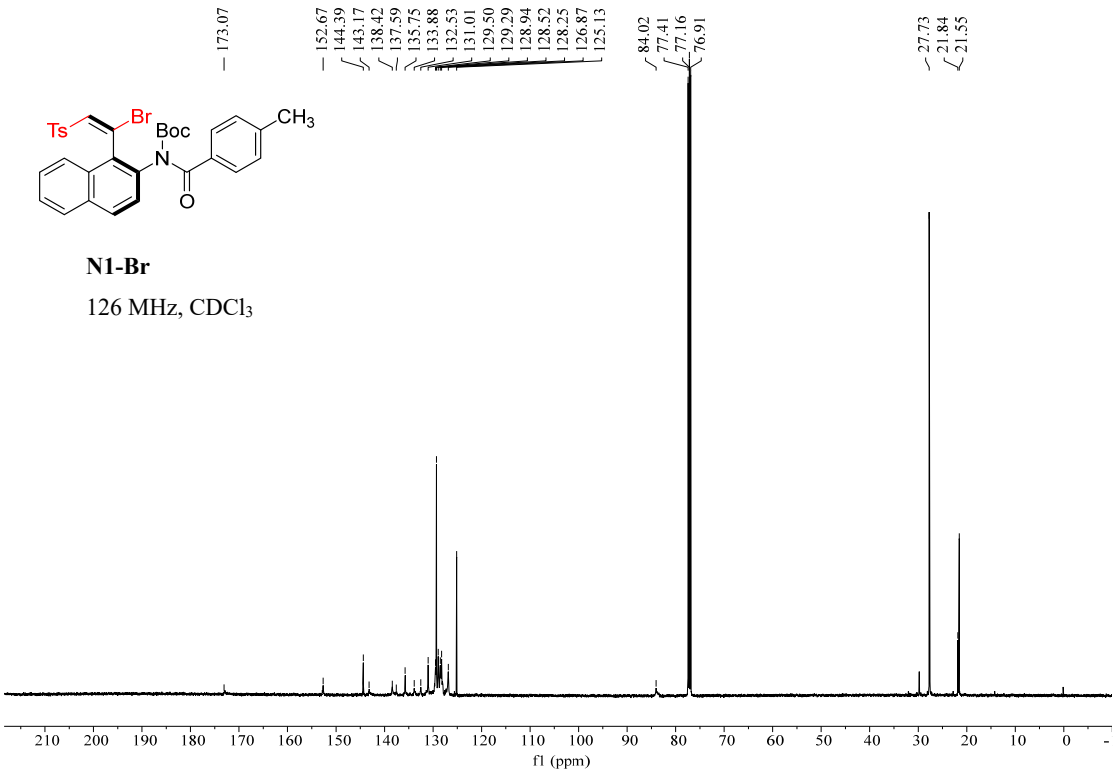
400 MHz, $CDCl_3$

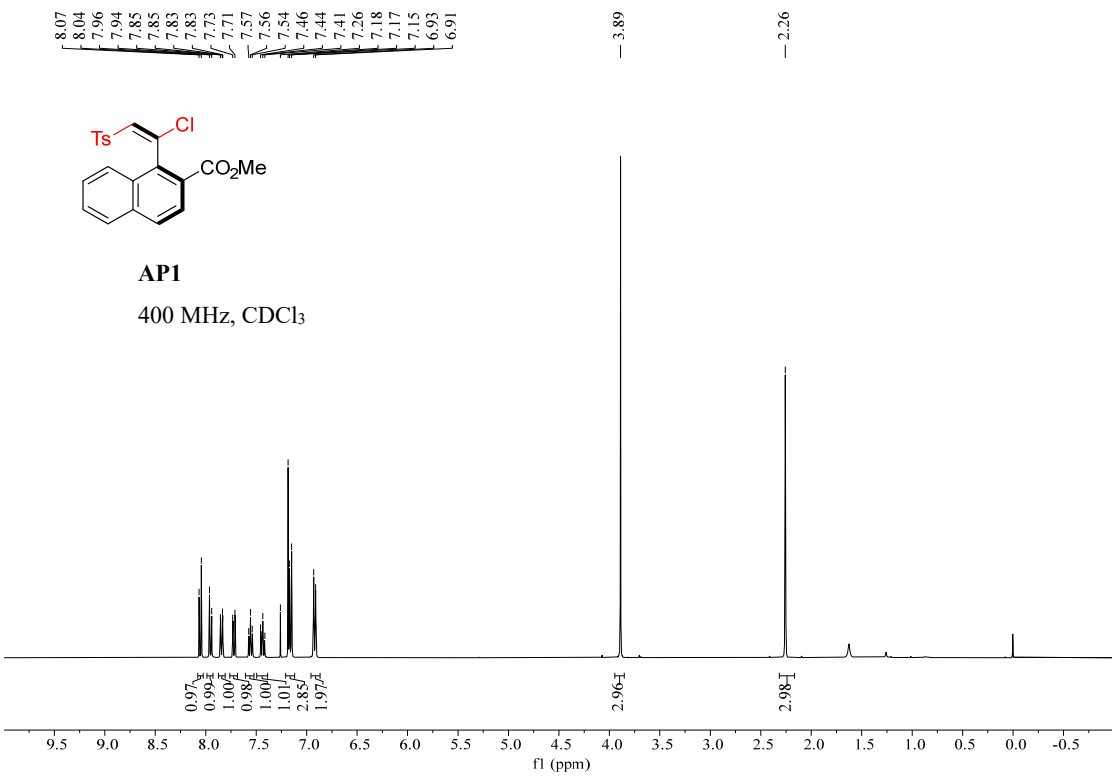


N35

100 MHz, $CDCl_3$

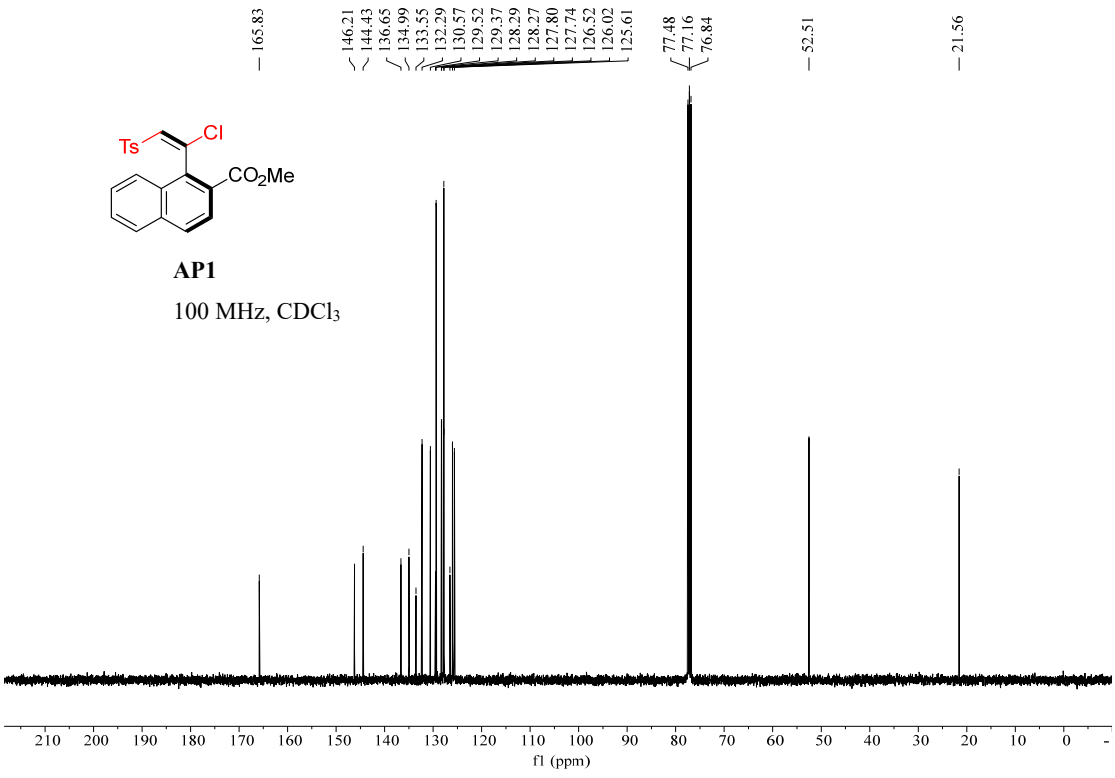

7.99 7.98 7.96 7.94 7.92 7.91 7.88 7.87 7.87 7.85 7.84 7.83 7.81 7.81 7.80 7.79 7.78 7.77 7.54 7.53 7.53 7.52 7.52 7.51 7.50 7.49 7.48 7.46 7.45 7.43 7.42 7.40 7.40 7.39 7.38 7.38 7.37 7.36 7.35 7.35 7.35 7.33 7.31 7.30 7.30 7.29 7.28 7.27 7.27 7.25 7.24 7.24 7.23 6.86 6.84 2.44 2.18 1.32 0.00
Ts
Br
Boc
N
O
CH3
N1-Br
500 MHz, CDCl3
4.36
9.50
1.88
3.00
2.89
9.41
f1 (ppm)


173.07
152.67 144.39 143.17 138.42 137.59 135.75 133.88 132.53 131.01 129.50 129.29 128.94 128.52 128.25 126.87 125.13
84.02 77.41 77.16 76.91
27.73 21.84 21.55
Ts
Br
Boc
N
O
CH3
N1-Br
126 MHz, CDCl3
f1 (ppm)



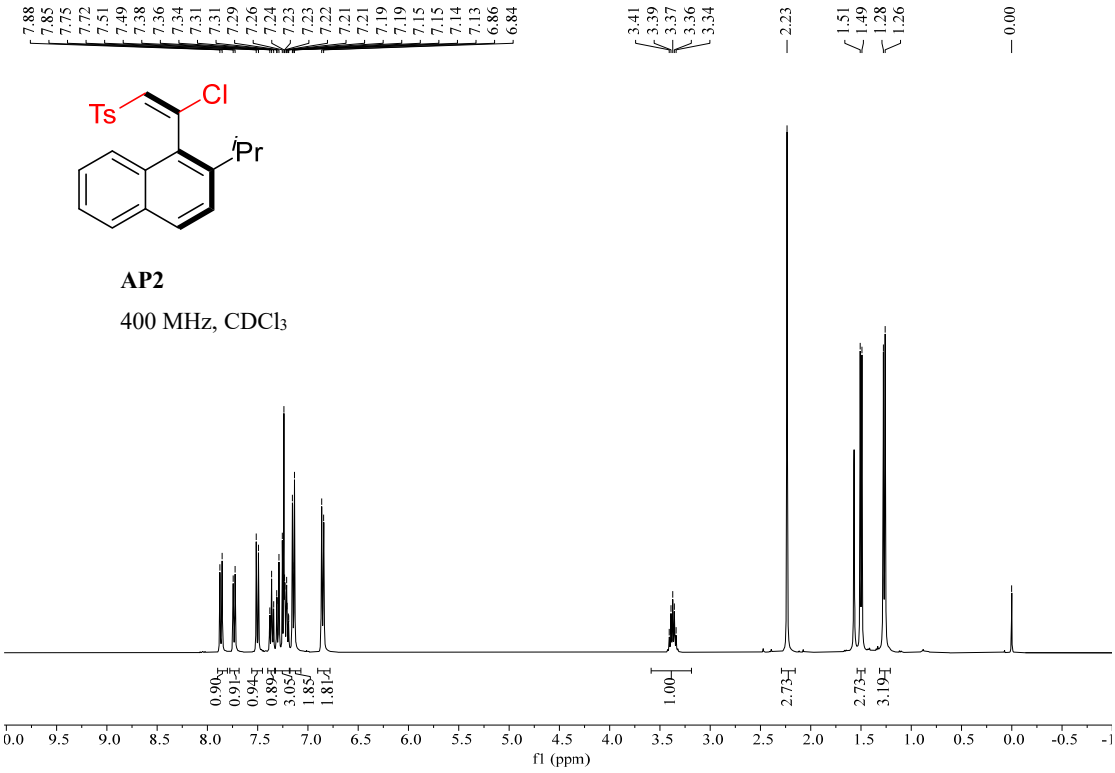
AP1

400 MHz, $CDCl_3$



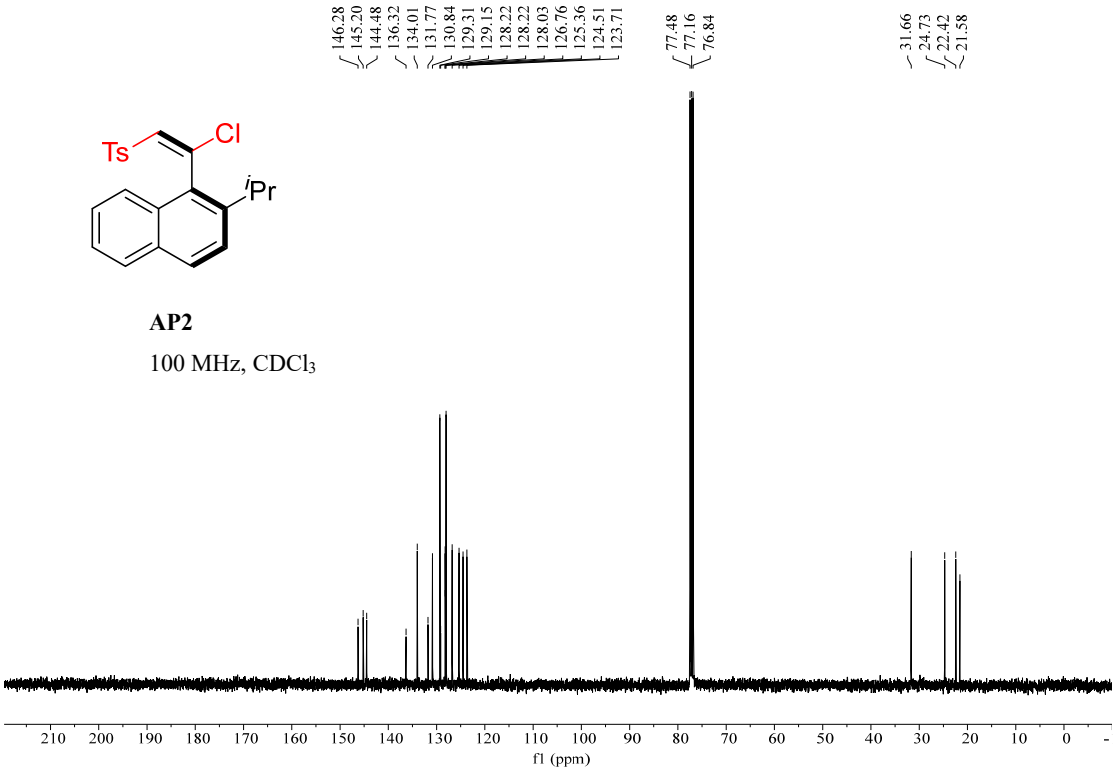
AP1

100 MHz, $CDCl_3$



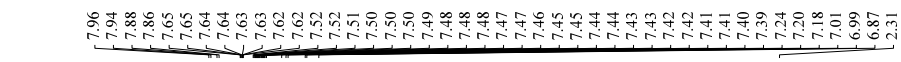
AP2

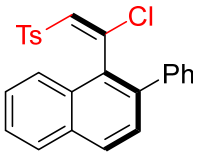
400 MHz, $CDCl_3$



AP2

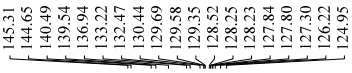
100 MHz, $CDCl_3$

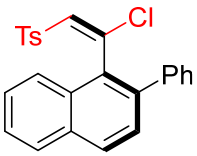




AP3

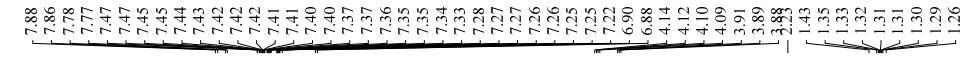
400 MHz, $CDCl_3$

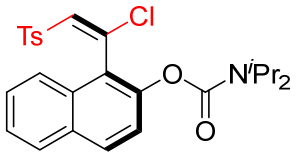




AP3

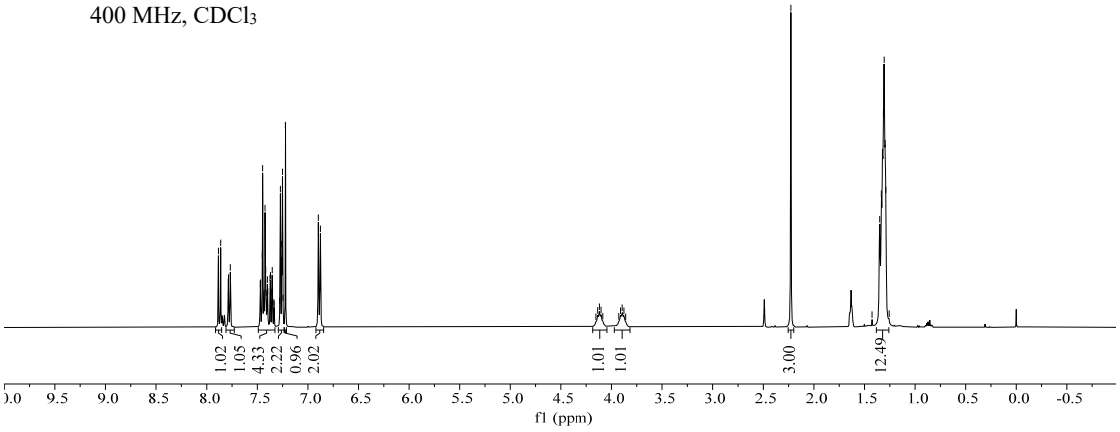
100 MHz, $CDCl_3$

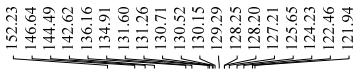


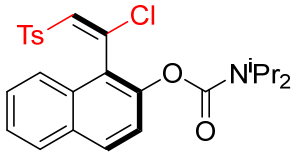


O1

400 MHz, $CDCl_3$

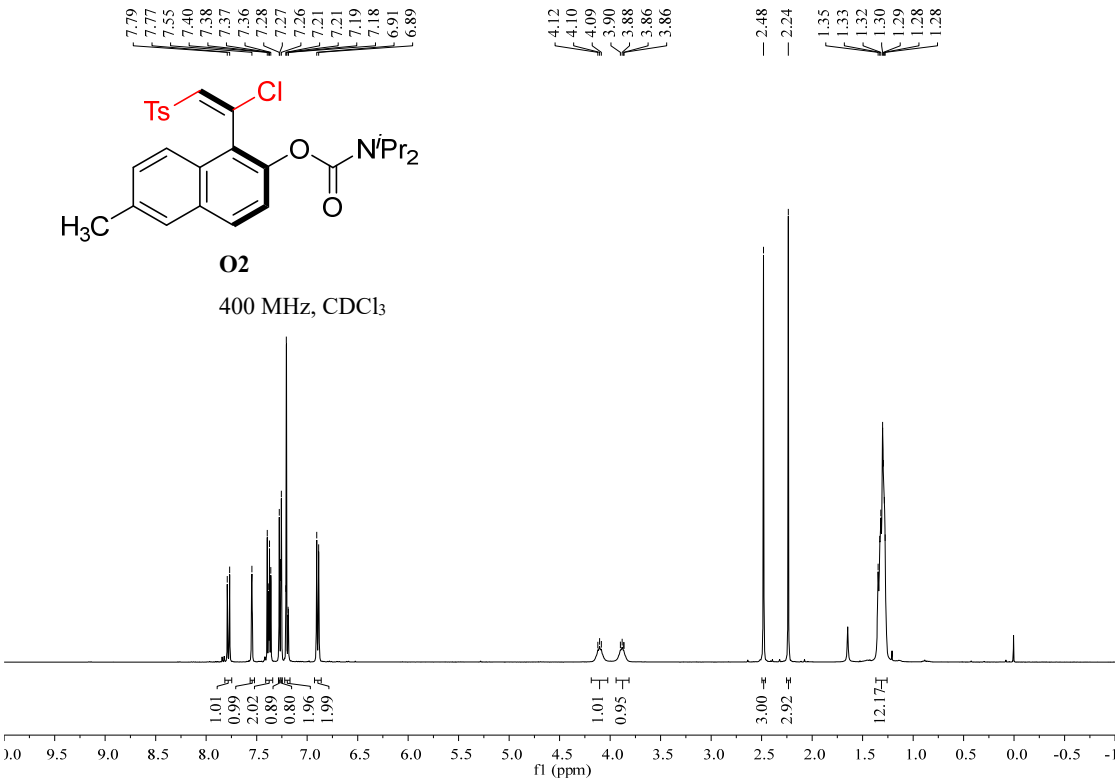






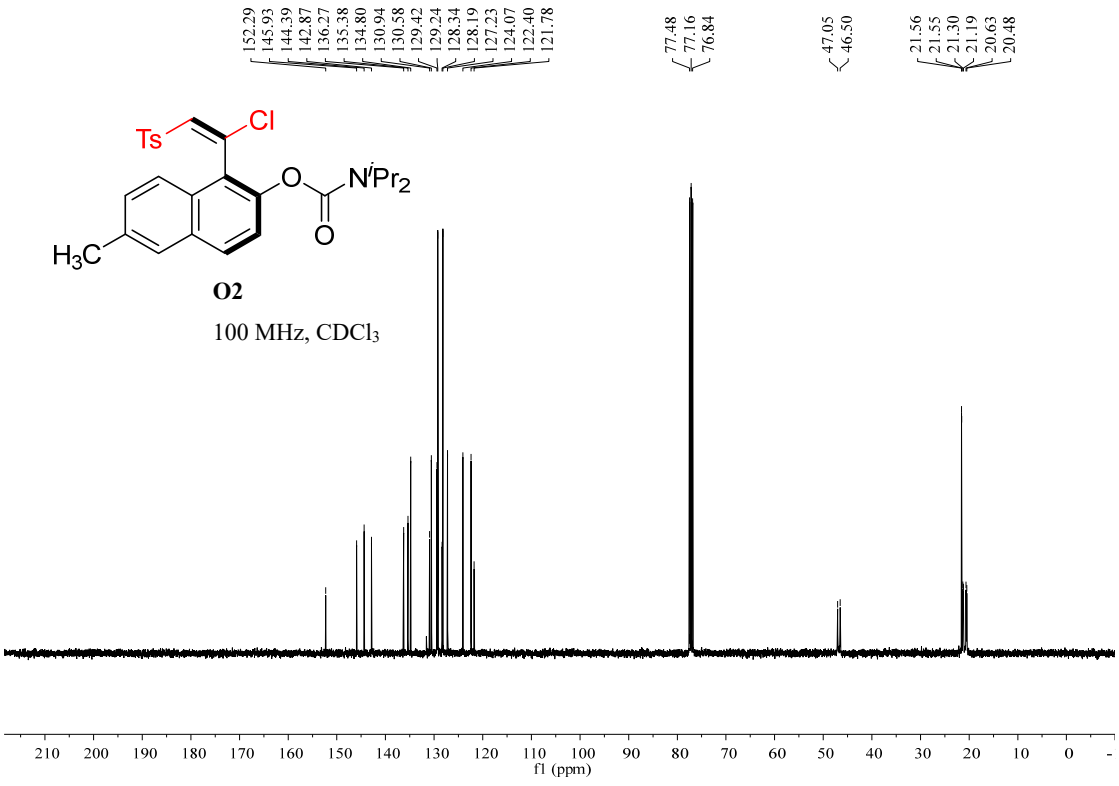
O1

100 MHz, $CDCl_3$



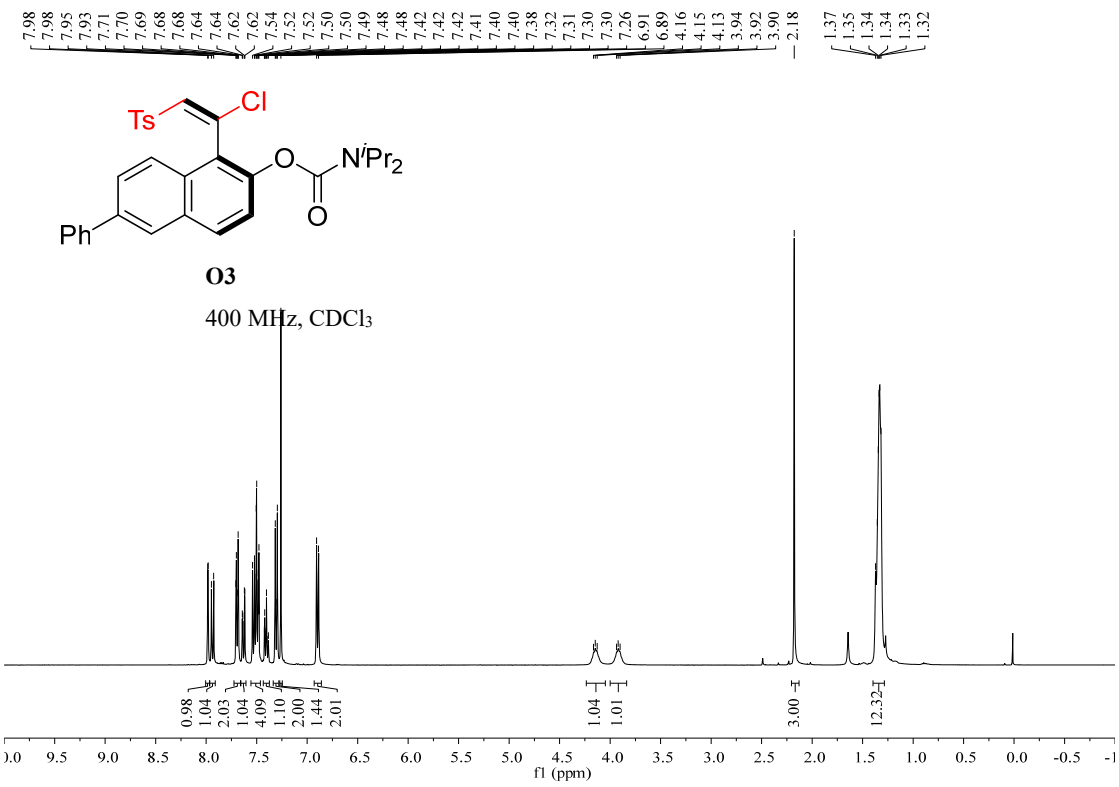
O2

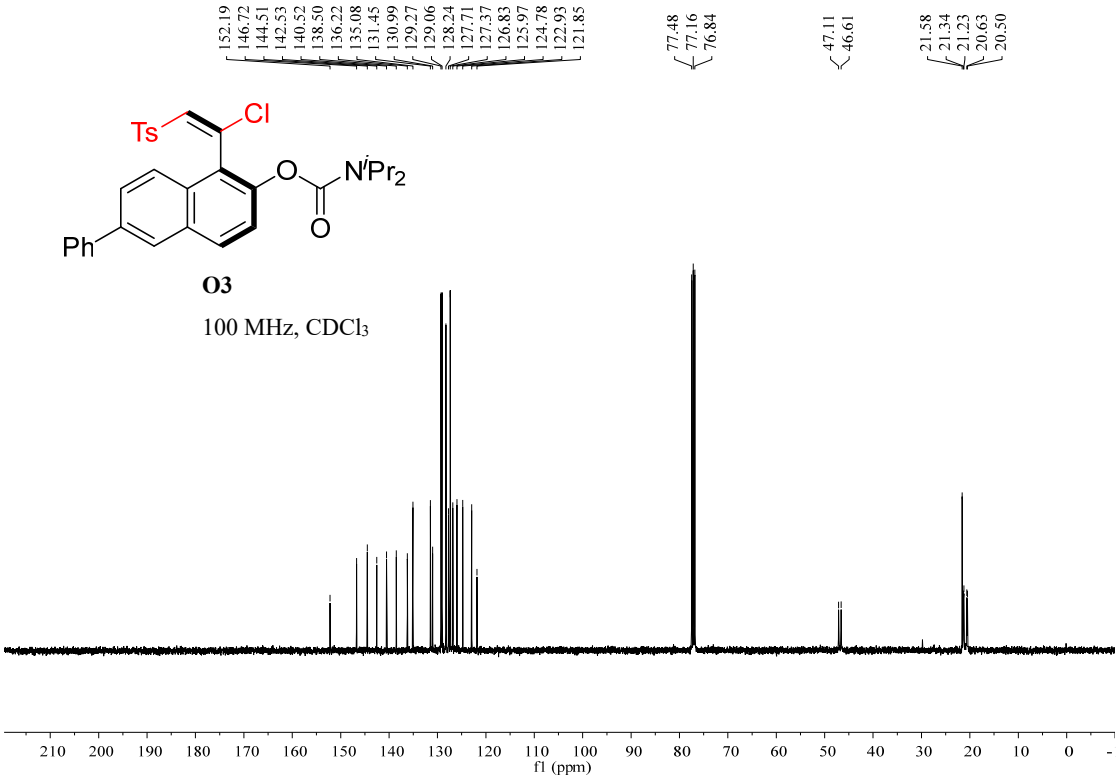
400 MHz, $CDCl_3$

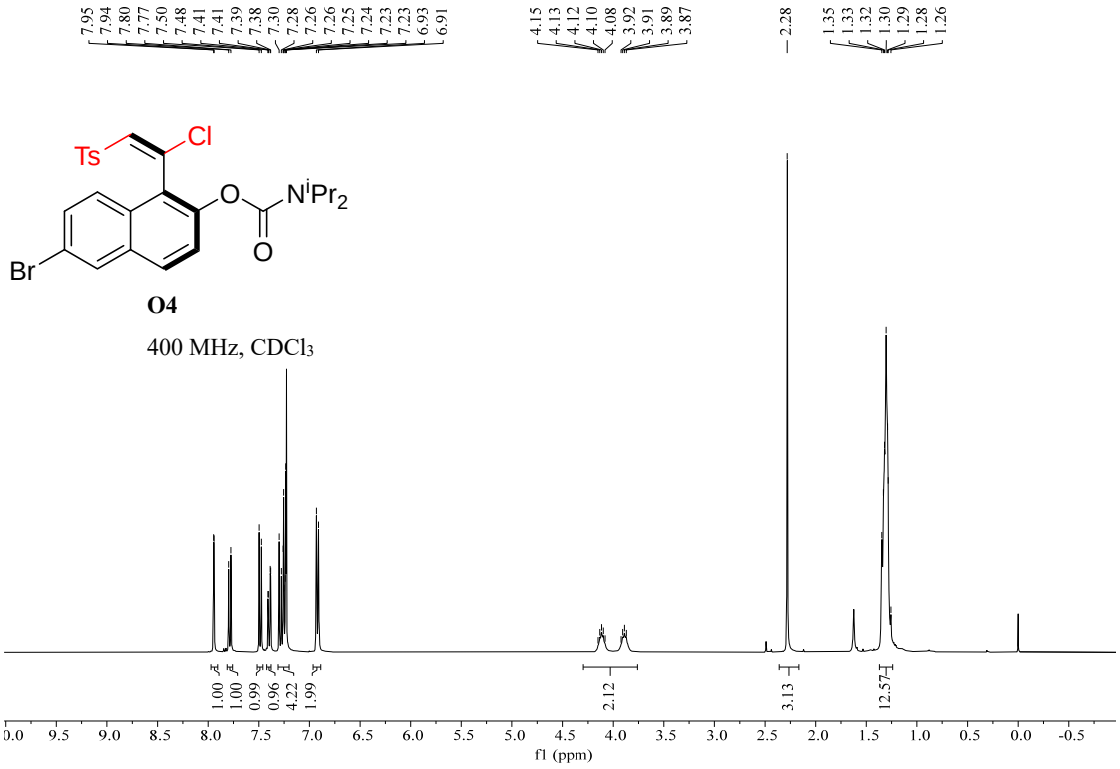


O2

100 MHz, $CDCl_3$

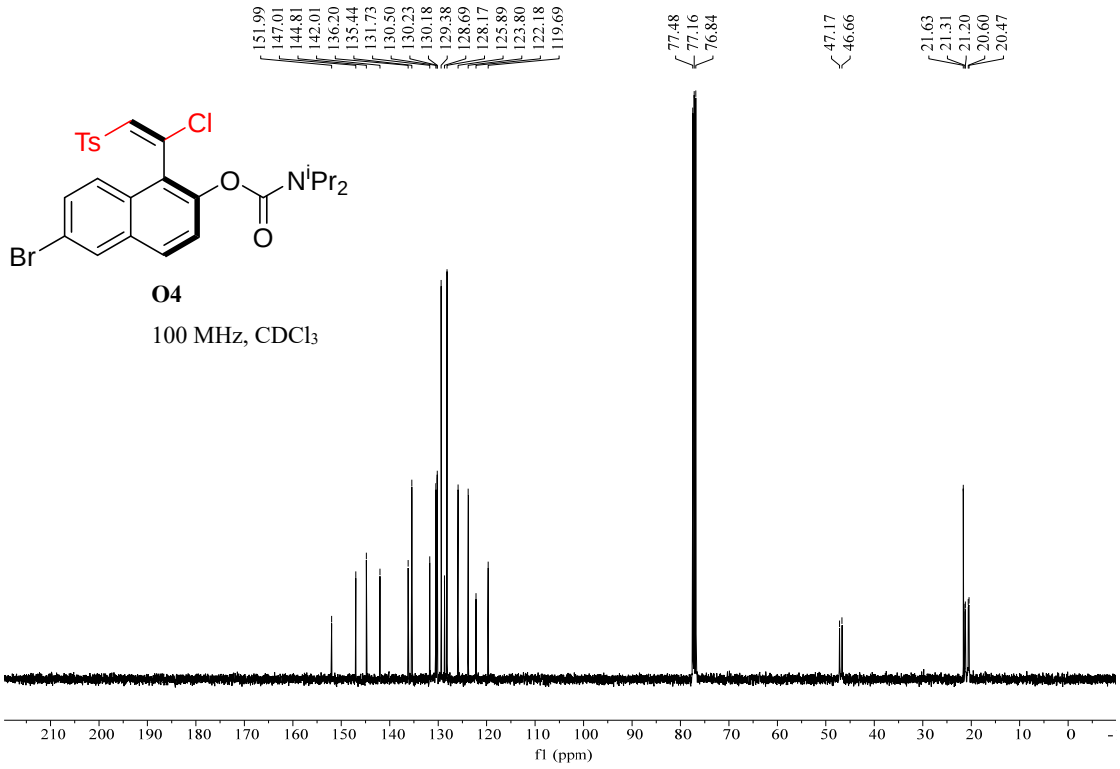

Ts
Cl
O
N^{i}Pr$_2$
O
Ph
O3
400 MHz, CDCl3
f1 (ppm)


Ts
Cl
O
N^{i}Pr$_2$
O
Ph
O3
100 MHz, CDCl3
f1 (ppm)



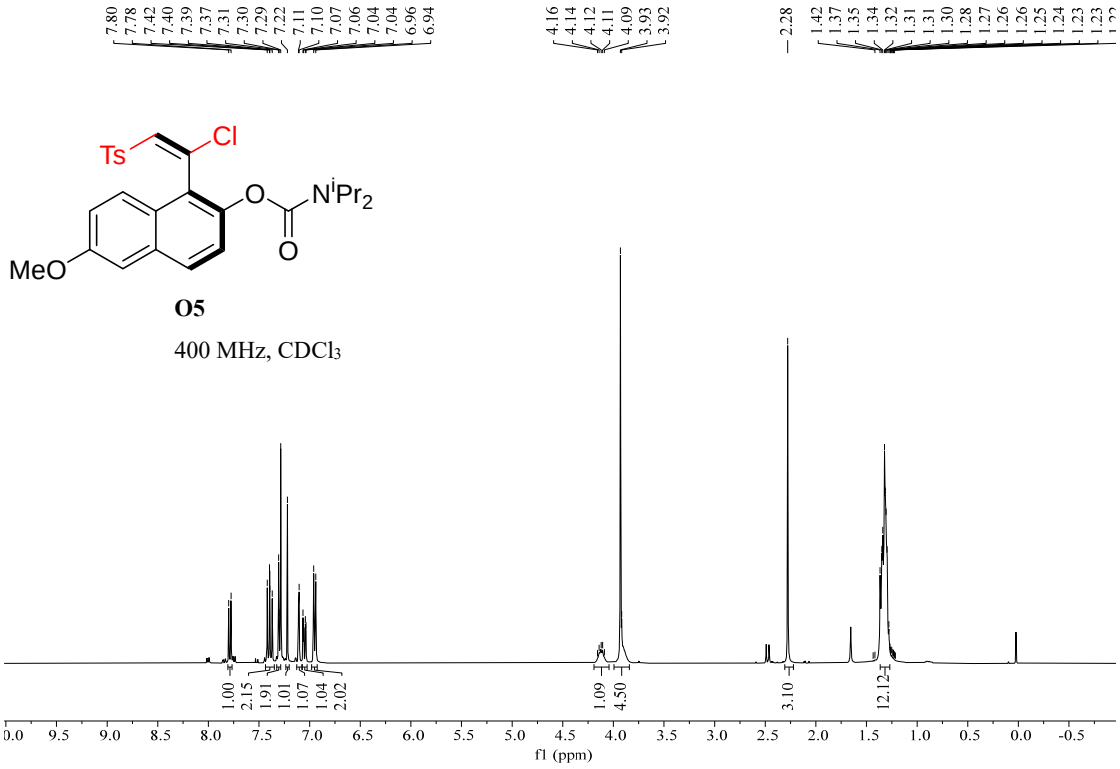
O4

400 MHz, $CDCl_3$



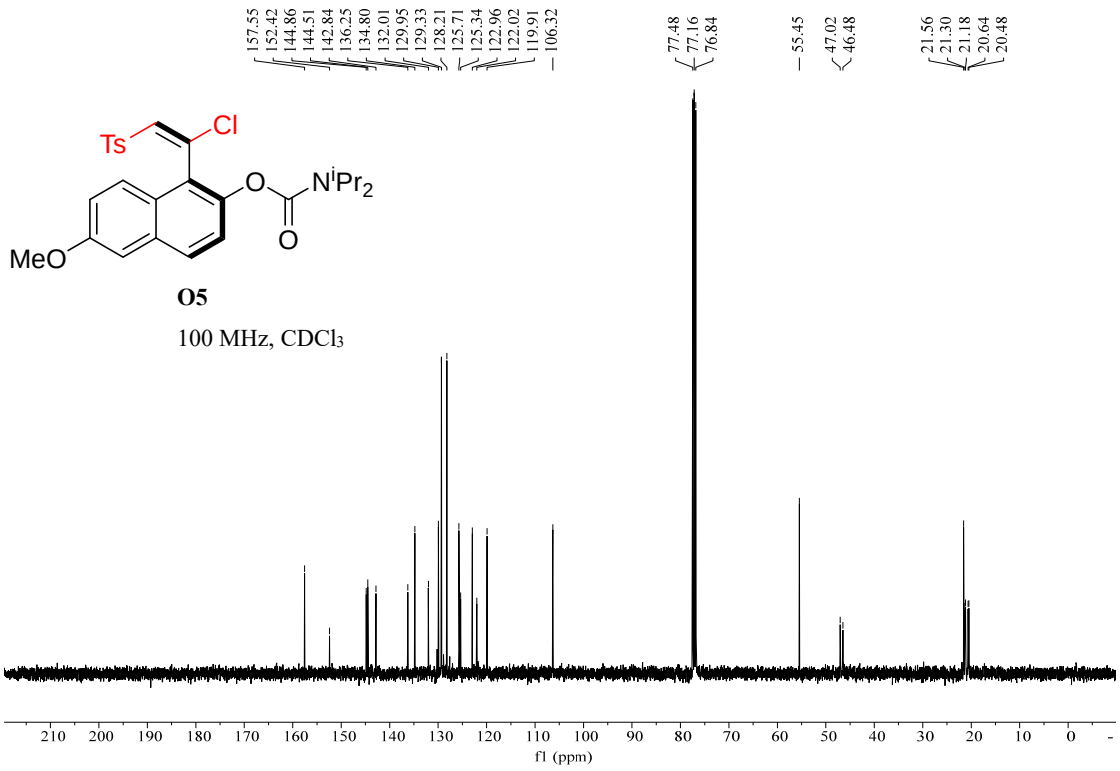
O4

100 MHz, $CDCl_3$



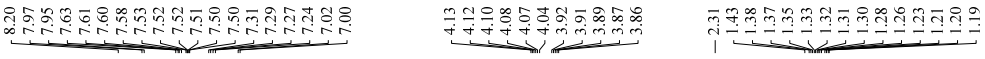
O5

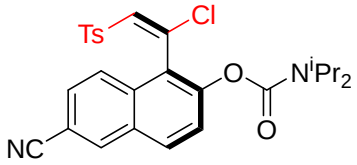
400 MHz, $CDCl_3$



O5

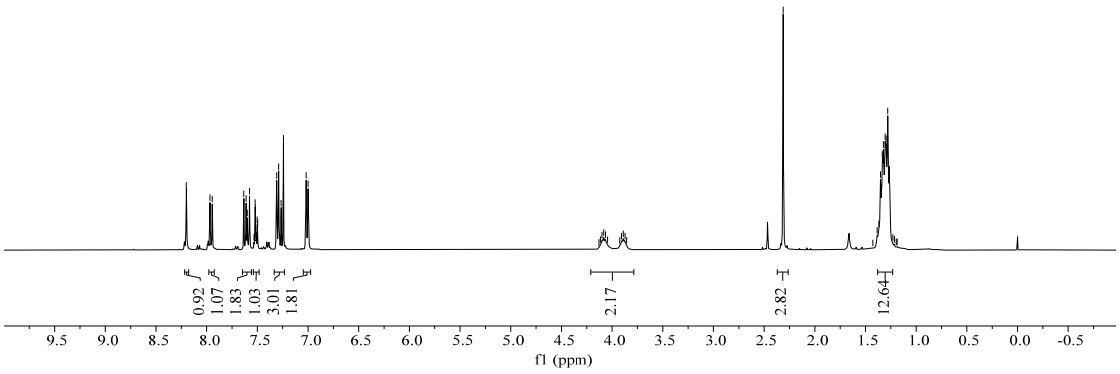
100 MHz, $CDCl_3$

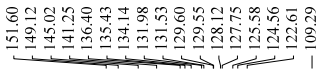


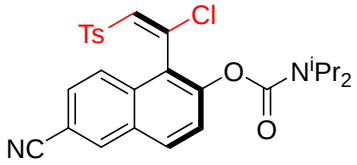


O6

400 MHz, $CDCl_3$

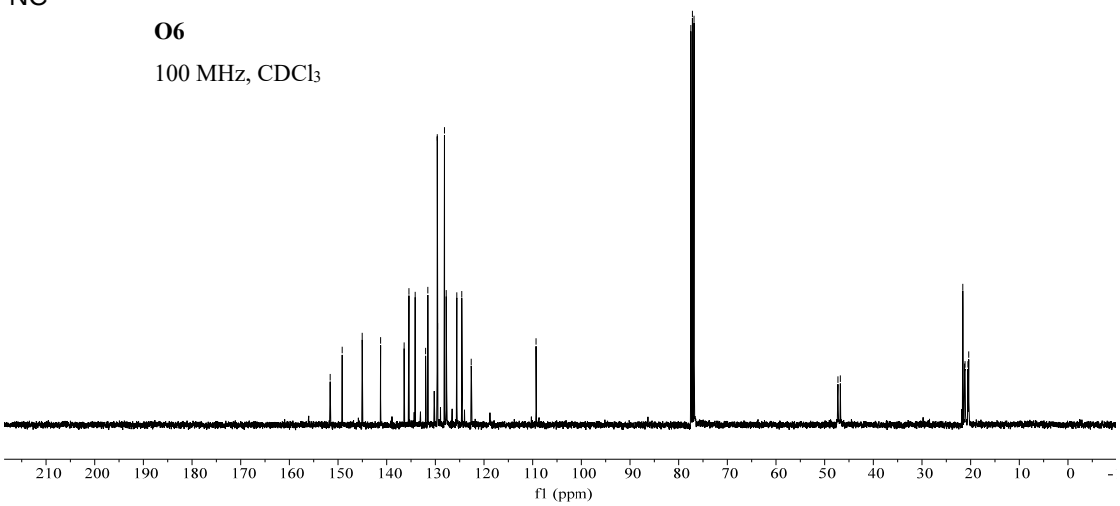


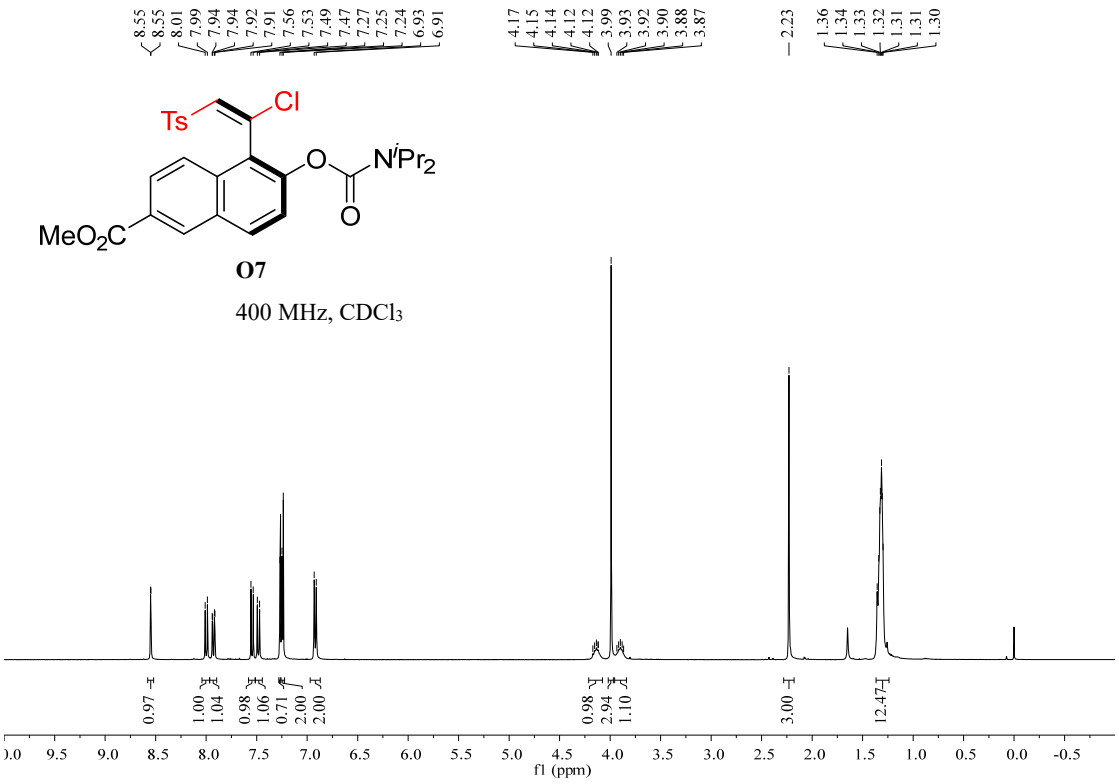




O6

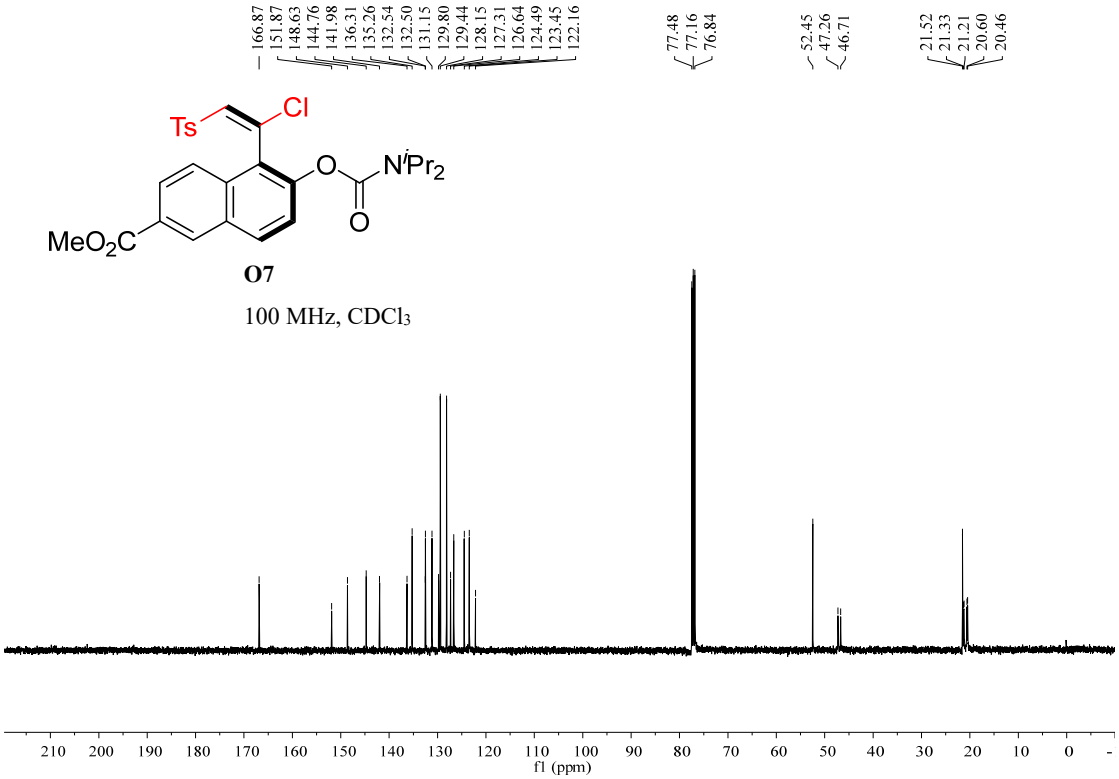
100 MHz, $CDCl_3$





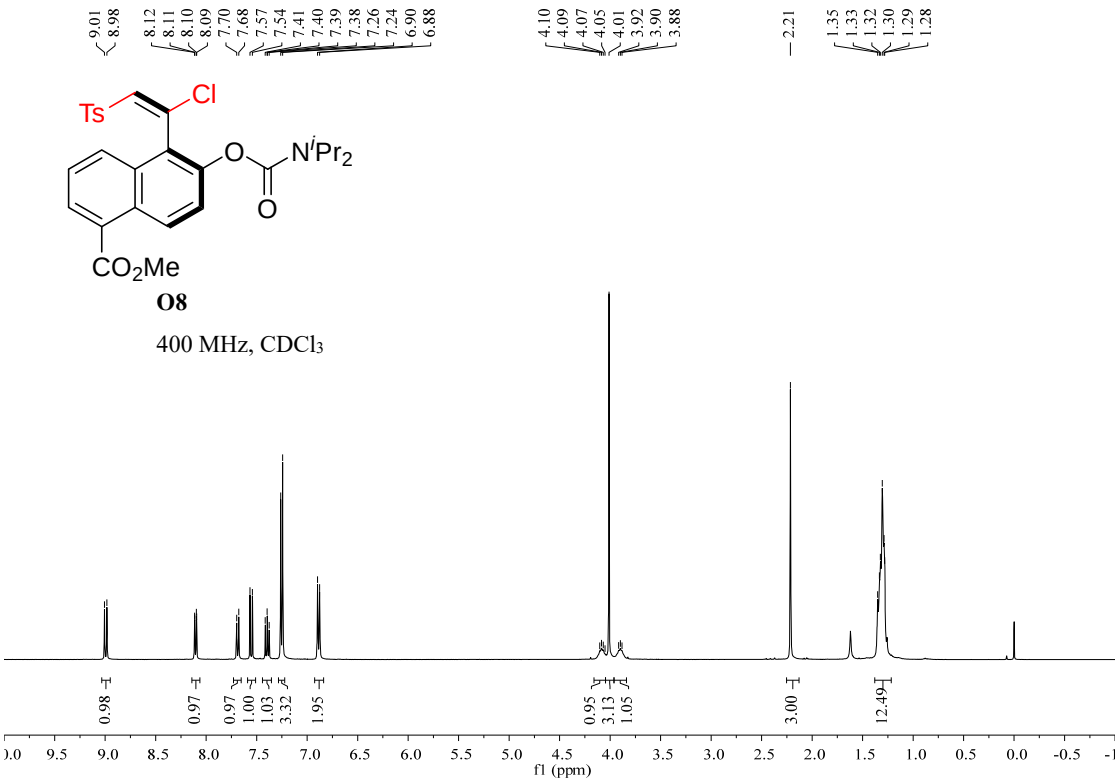
O7

400 MHz, $CDCl_3$



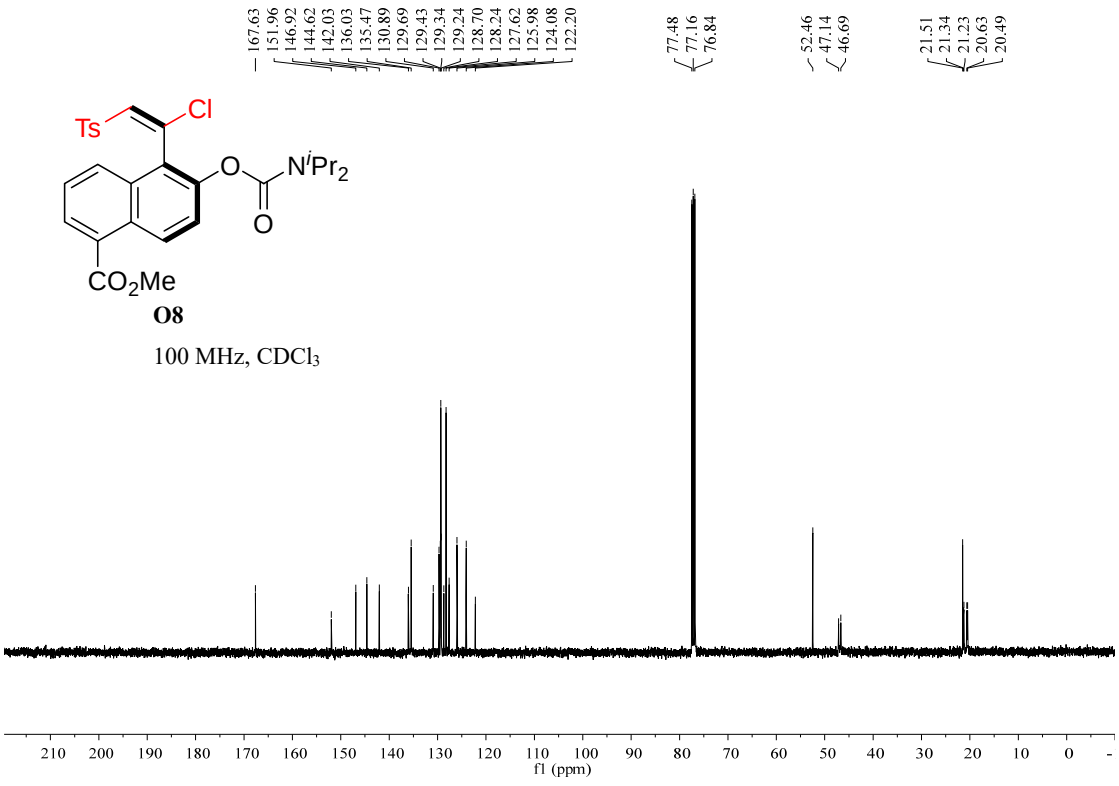
O7

100 MHz, $CDCl_3$



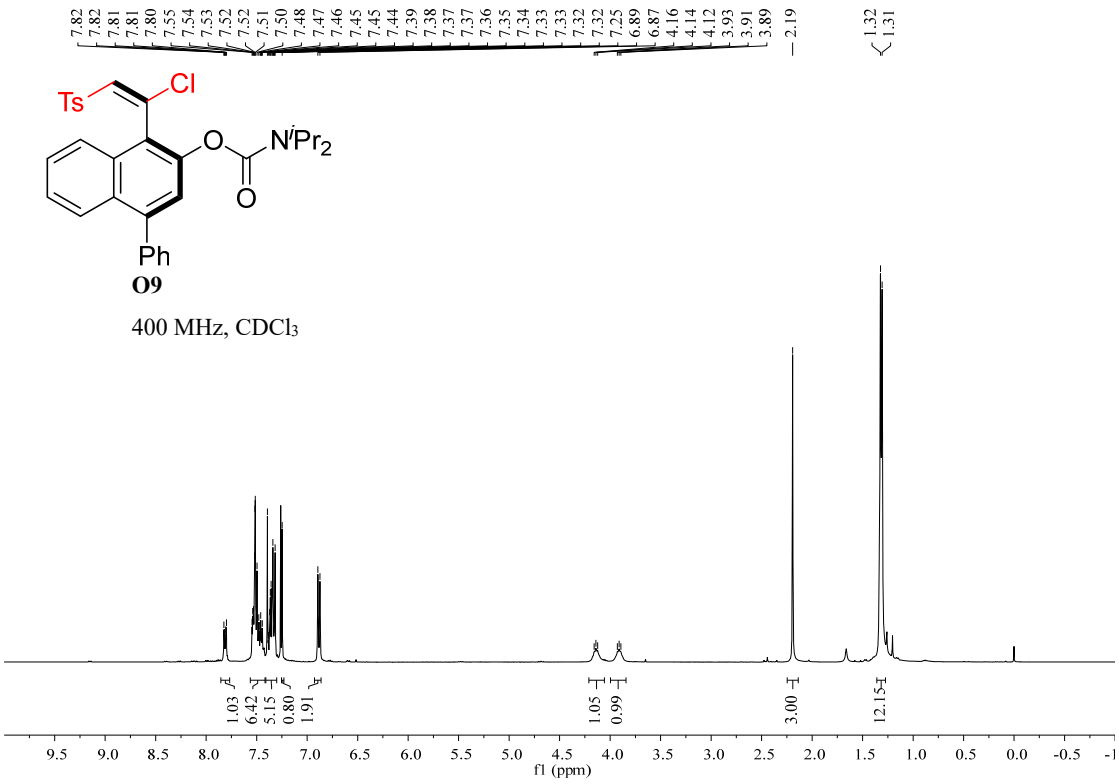
O8

400 MHz, $CDCl_3$



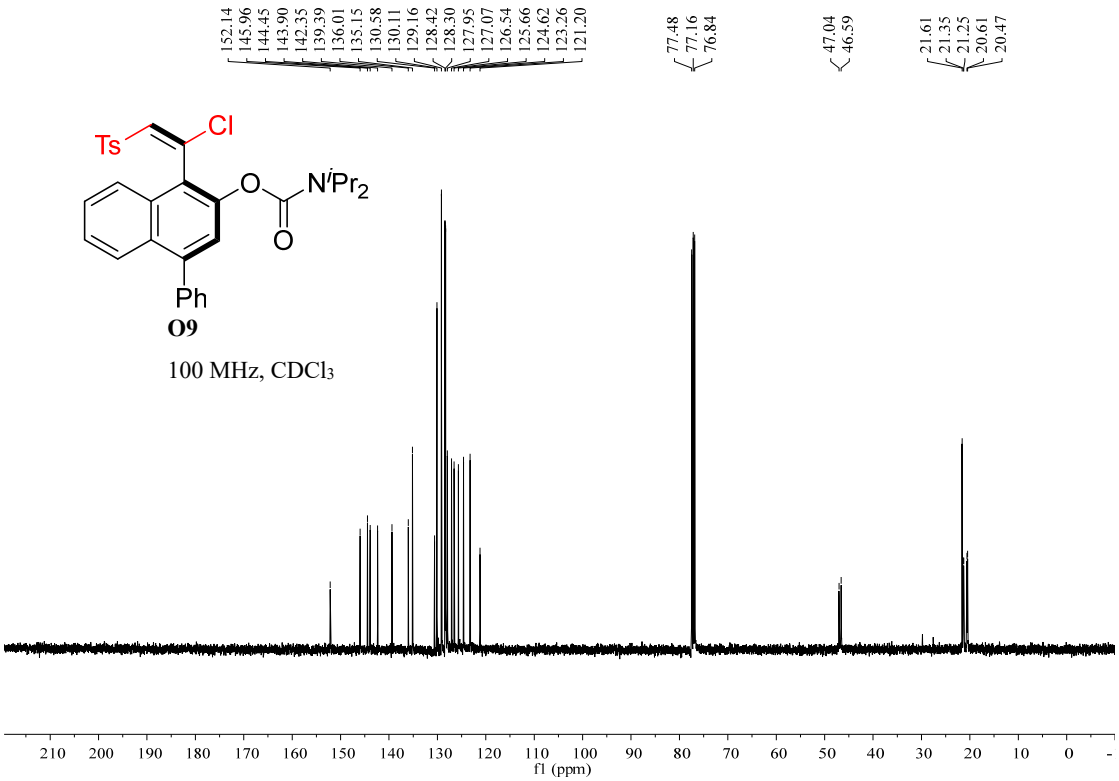
O8

100 MHz, $CDCl_3$



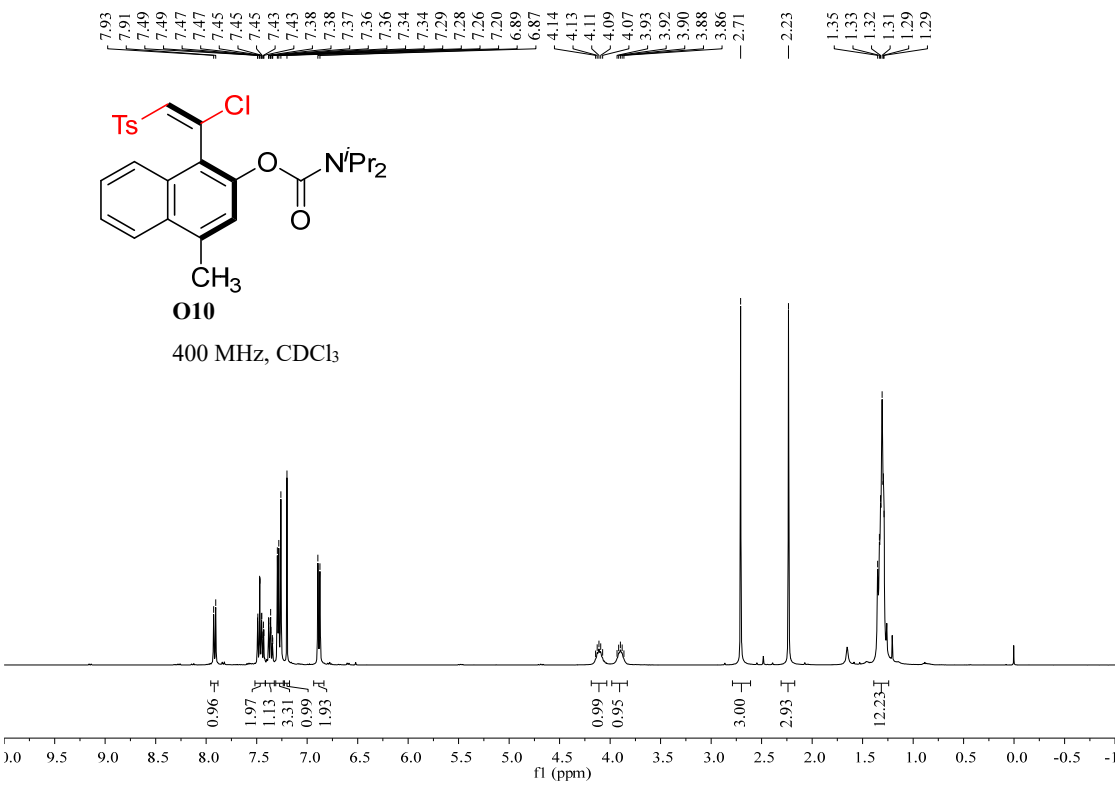
O9

400 MHz, $CDCl_3$



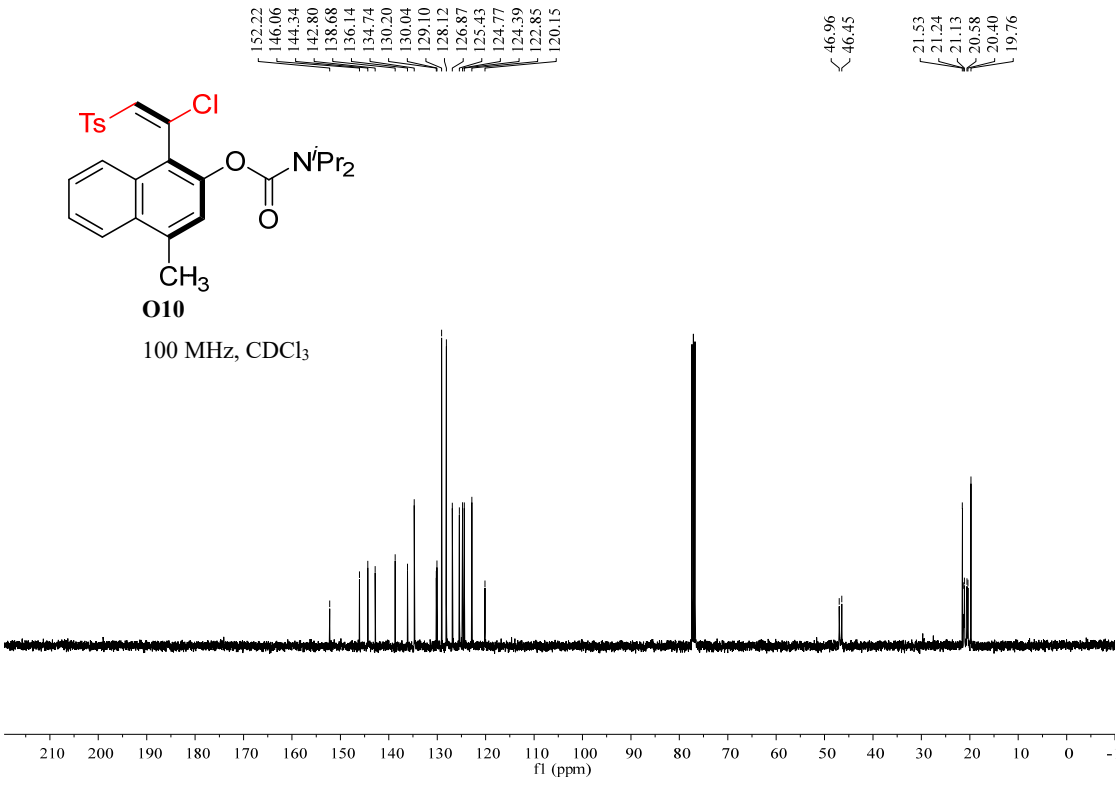
O9

100 MHz, $CDCl_3$



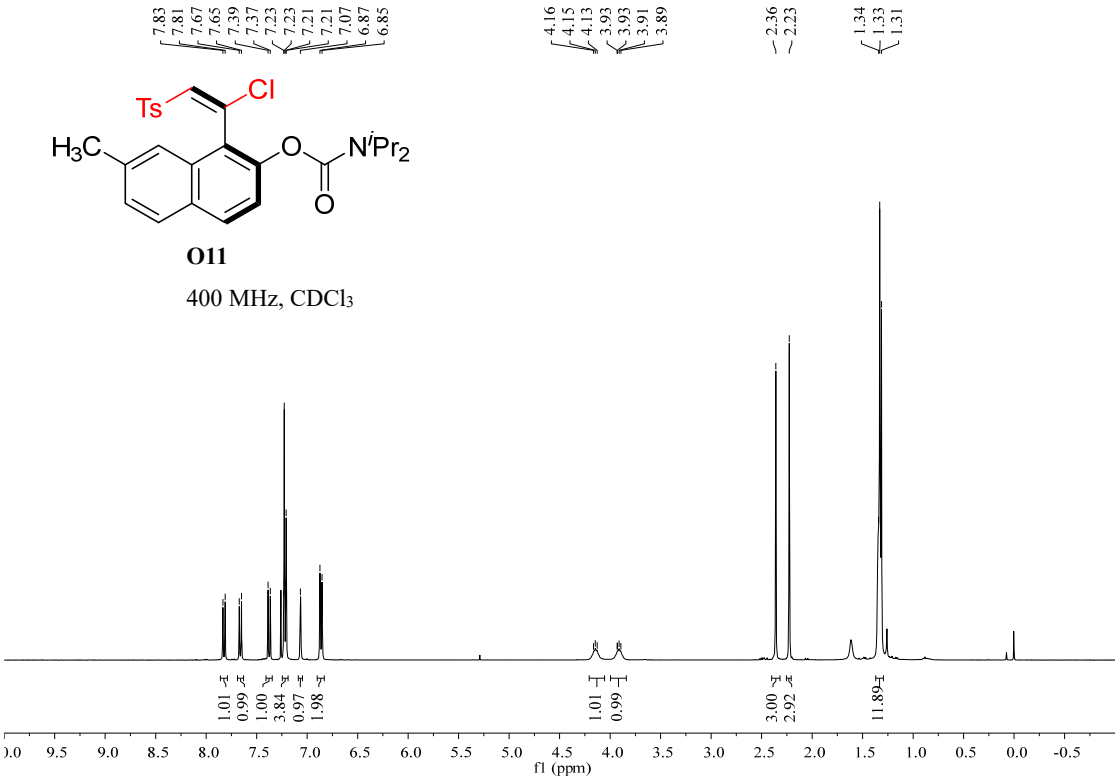
O10

400 MHz, $CDCl_3$



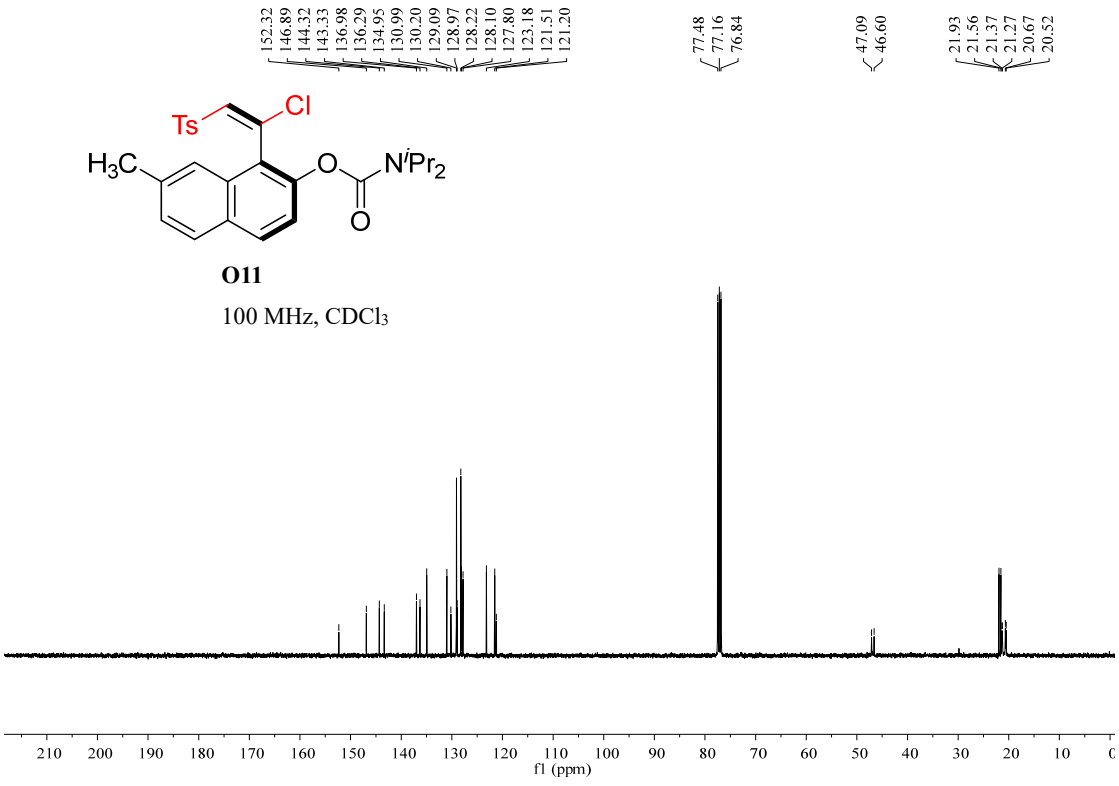
O10

100 MHz, $CDCl_3$



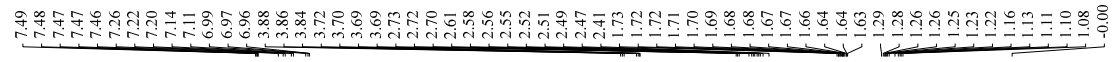
O11

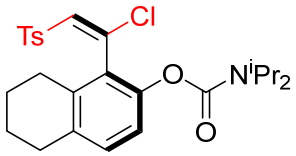
400 MHz, $CDCl_3$



O11

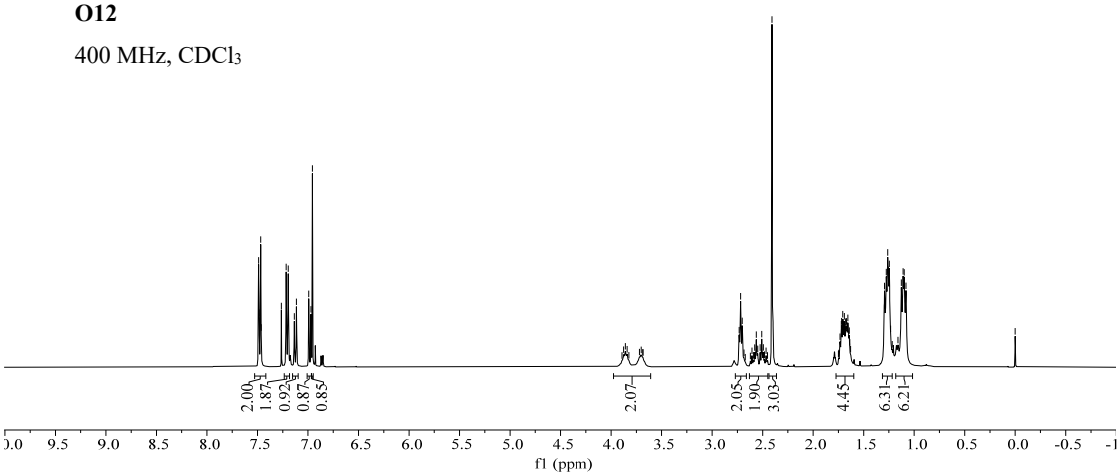
100 MHz, $CDCl_3$

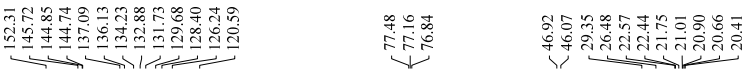


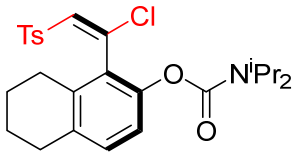


O12

400 MHz, $CDCl_3$

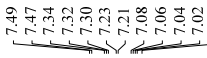


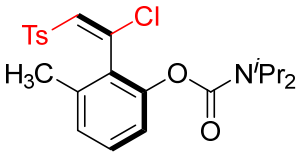




O12

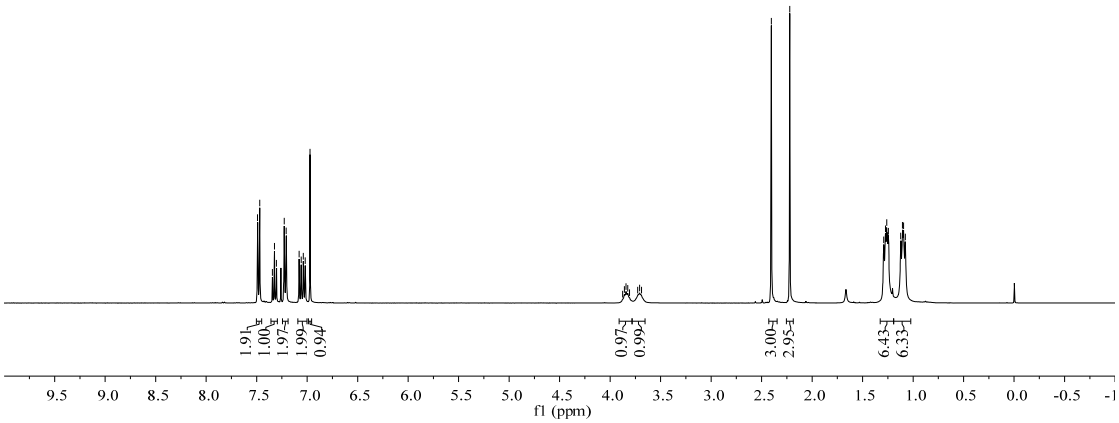
100 MHz, $CDCl_3$

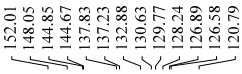


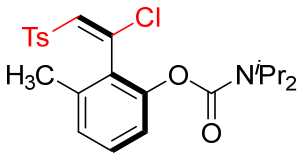


O13

400 MHz, $CDCl_3$

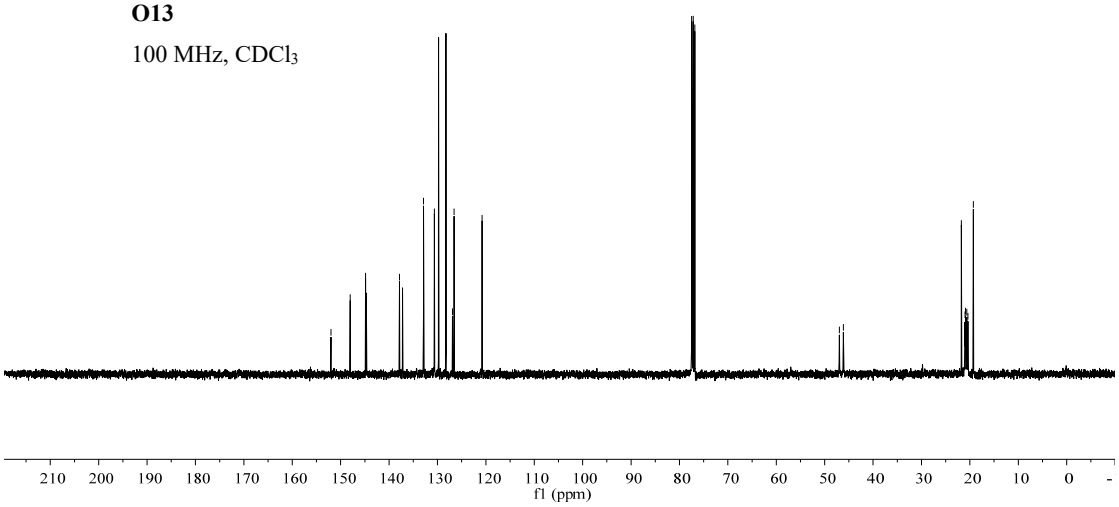


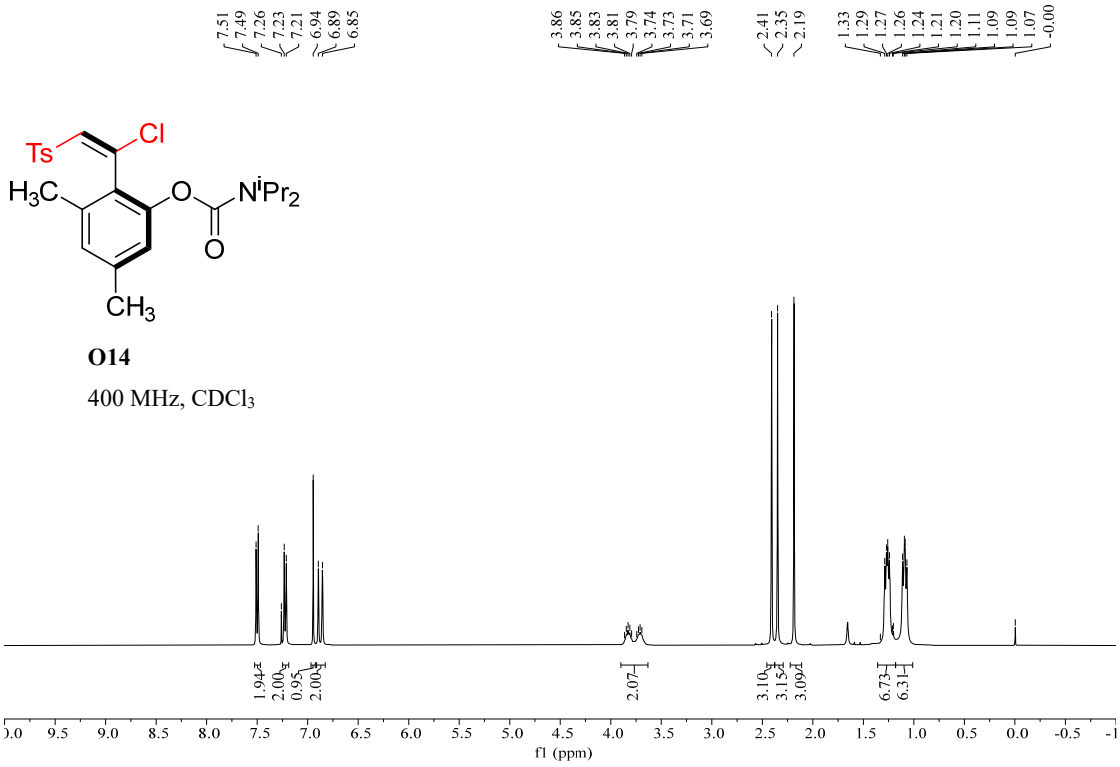




O13

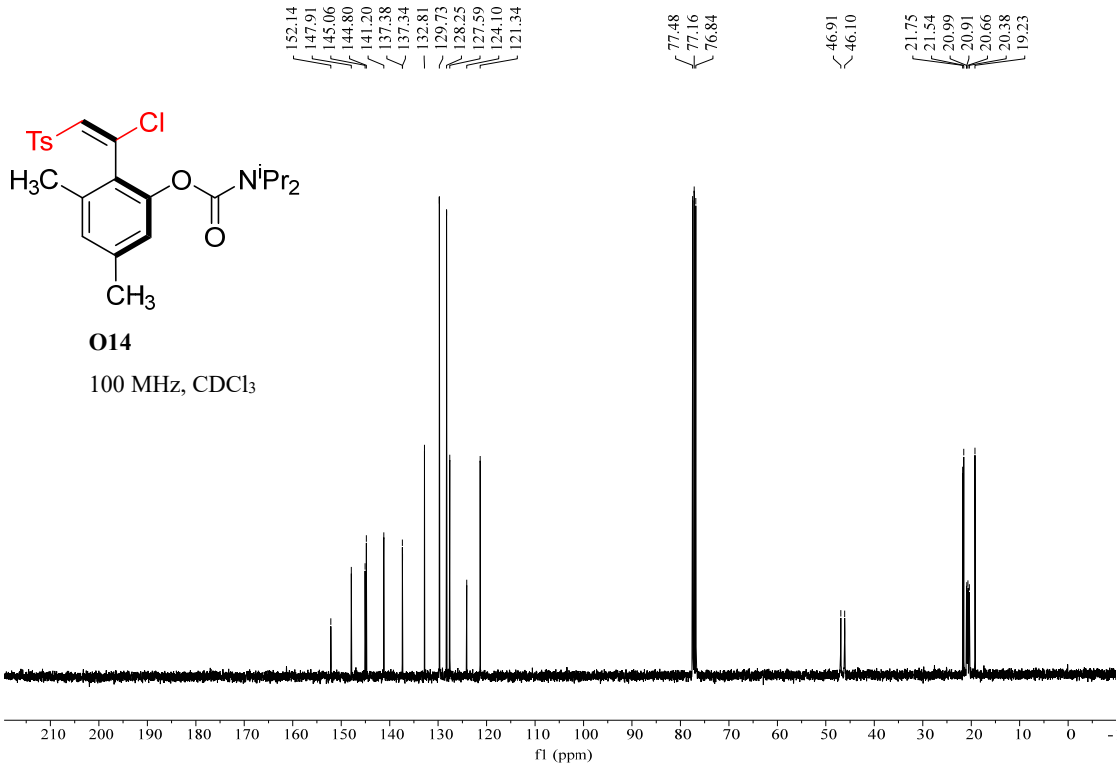
100 MHz, $CDCl_3$





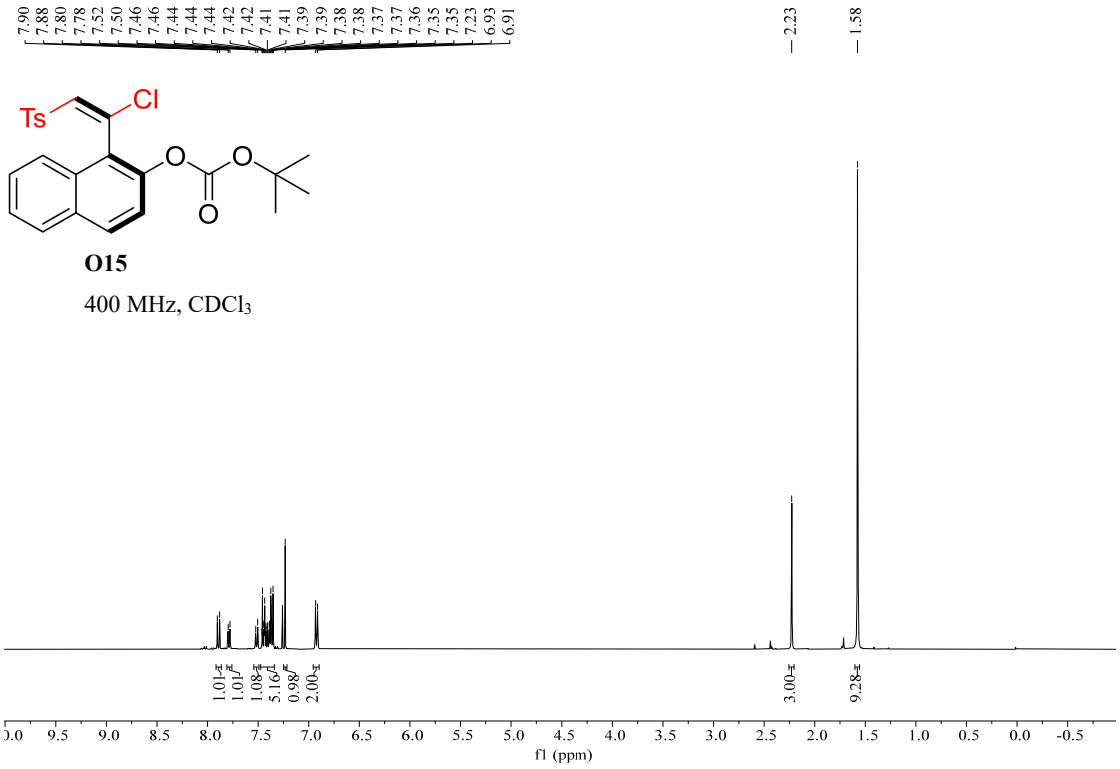
O14

400 MHz, $CDCl_3$



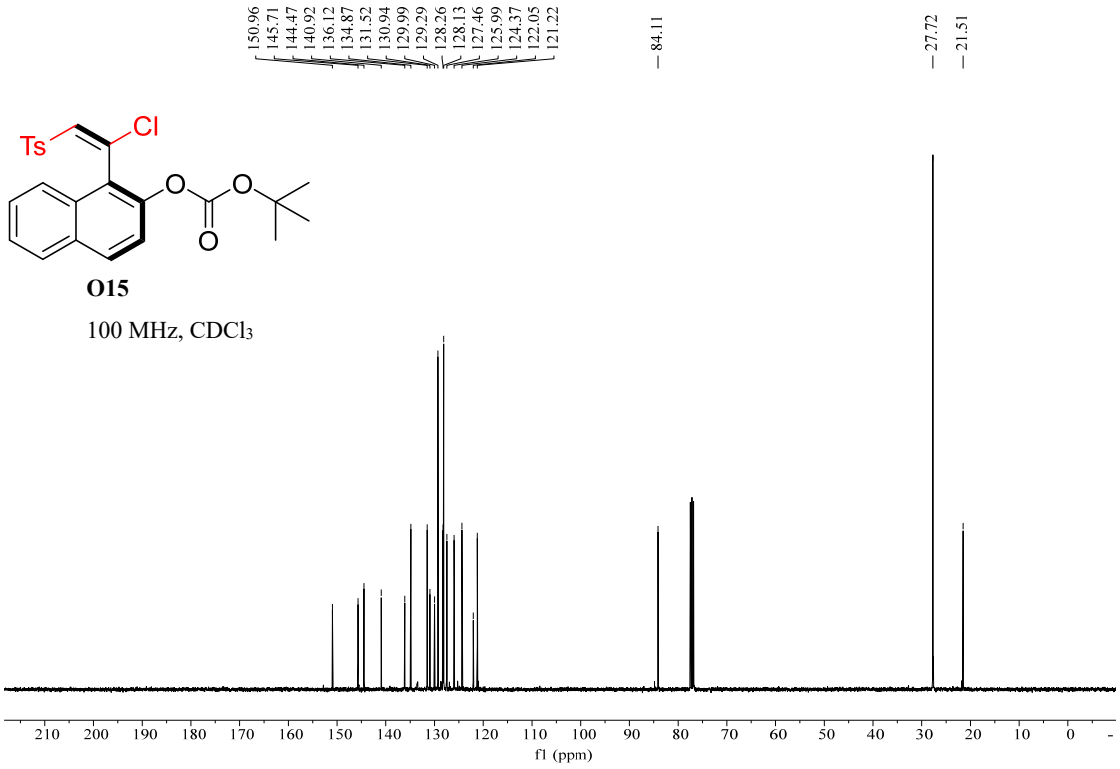
O14

100 MHz, $CDCl_3$



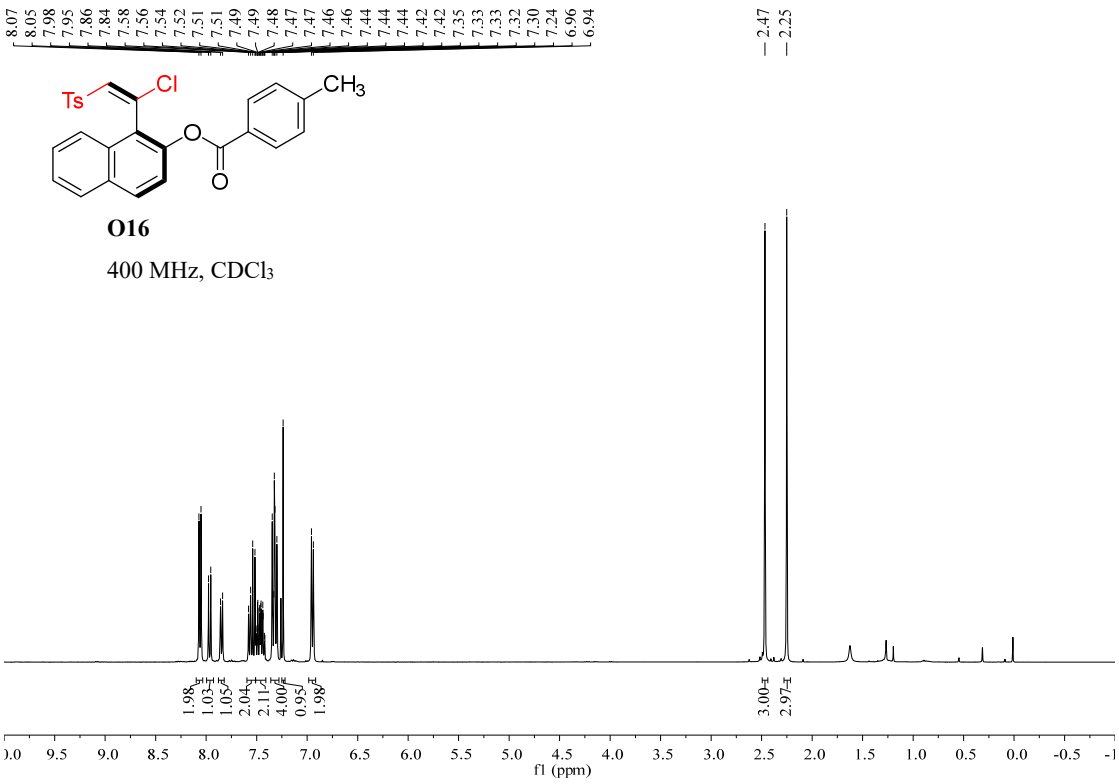
O15

400 MHz, $CDCl_3$



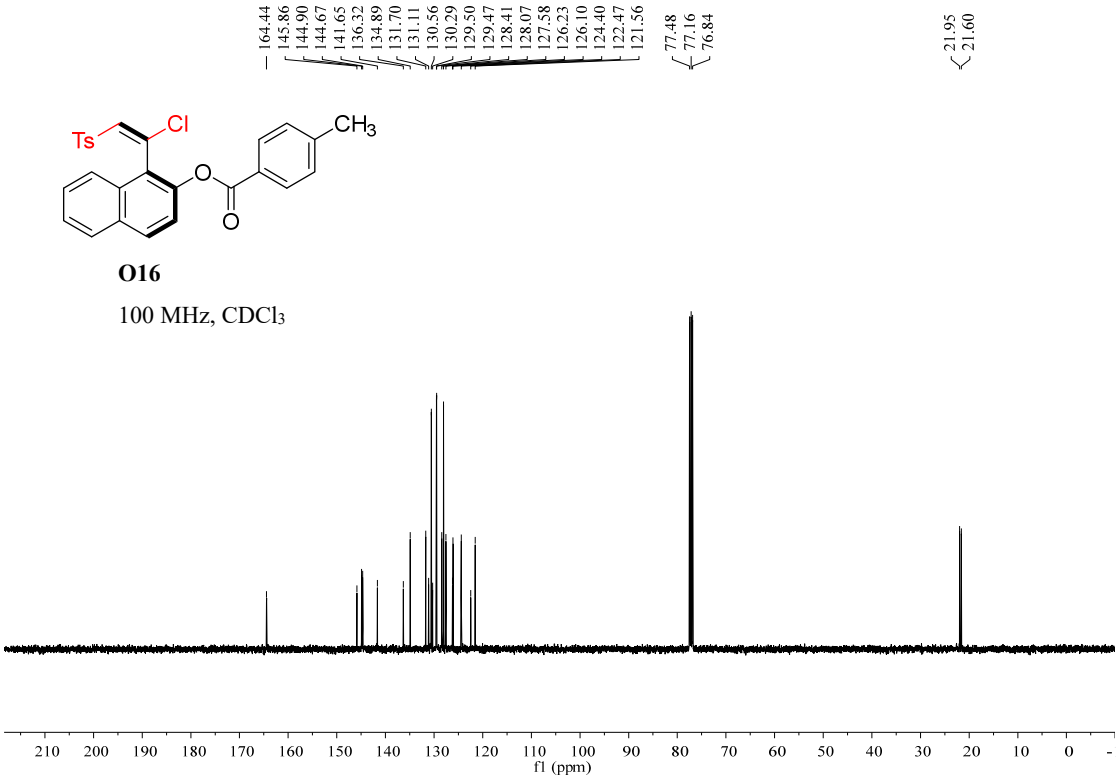
O15

100 MHz, $CDCl_3$



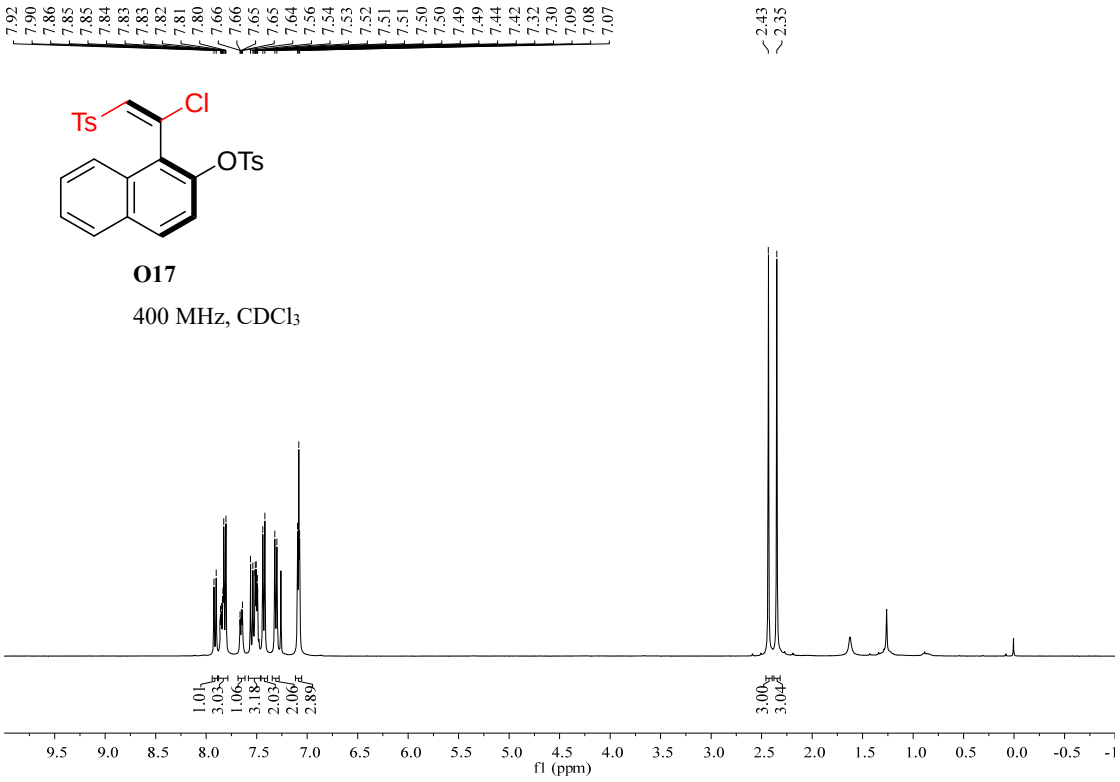
O16

400 MHz, $CDCl_3$



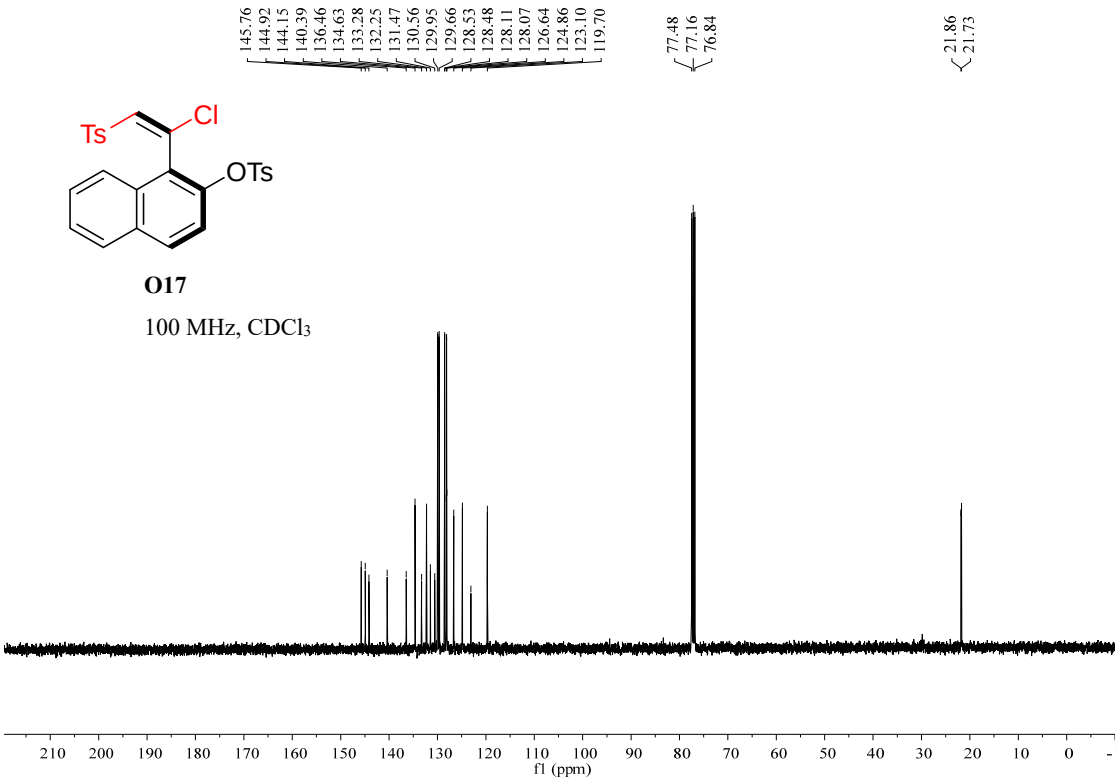
O16

100 MHz, $CDCl_3$



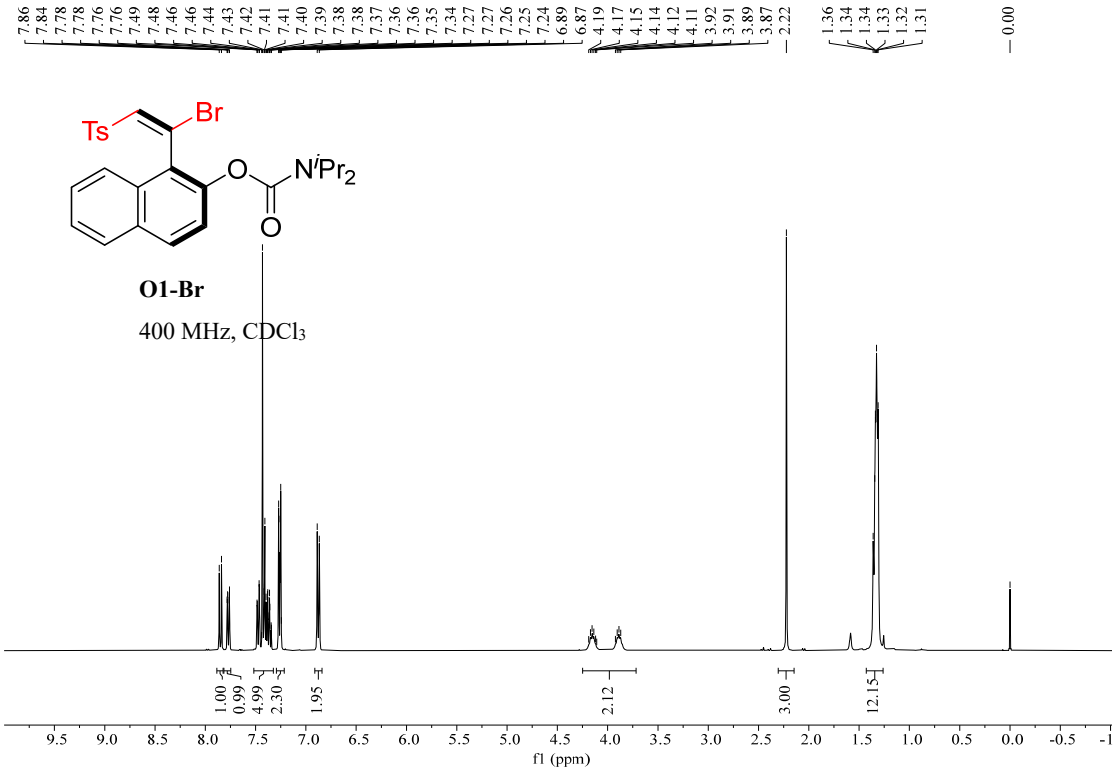
O17

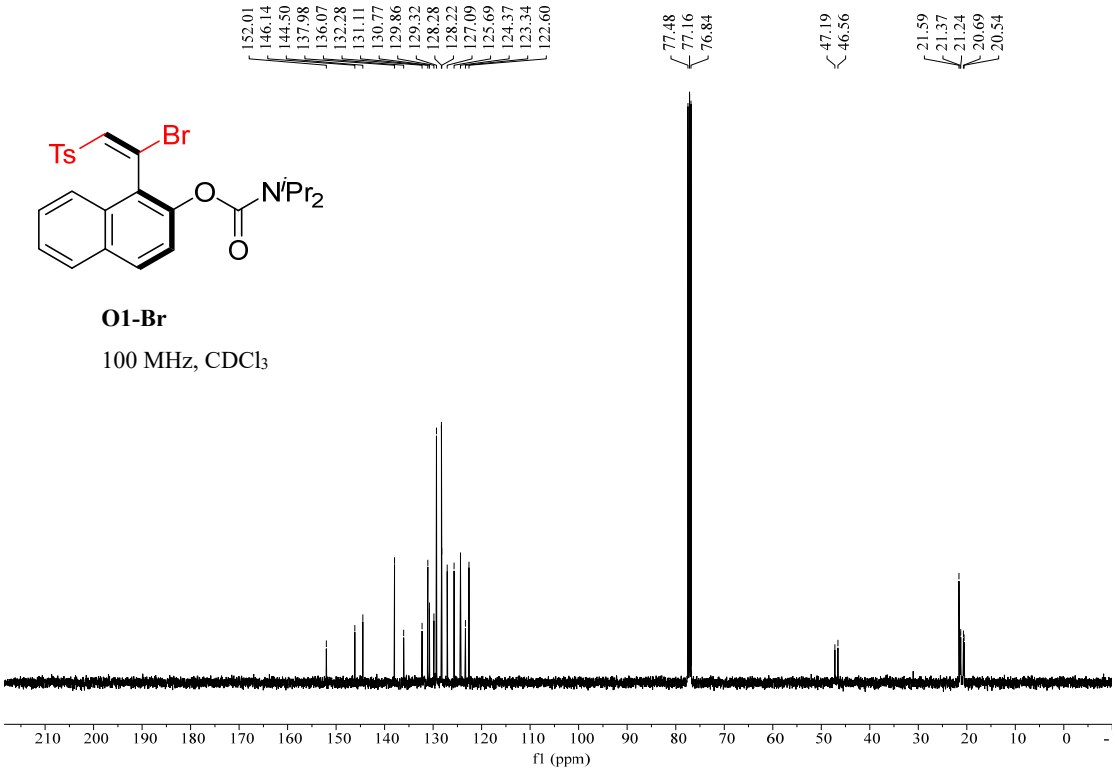
400 MHz, $CDCl_3$

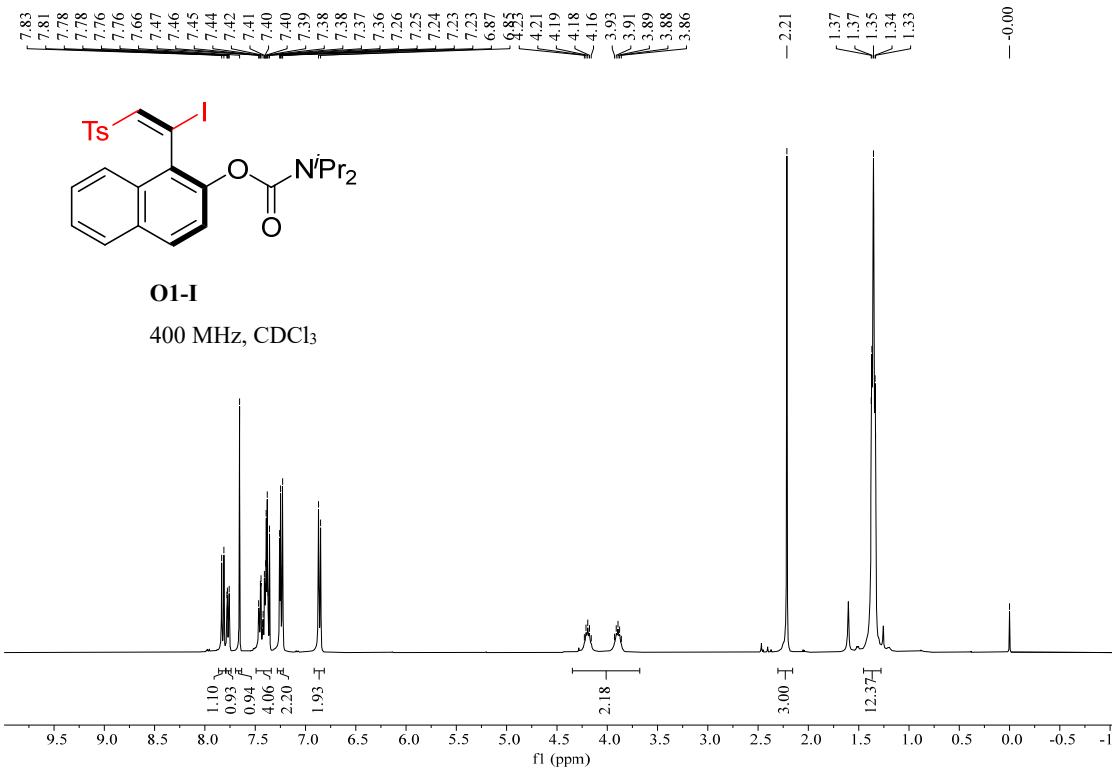


O17

100 MHz, $CDCl_3$

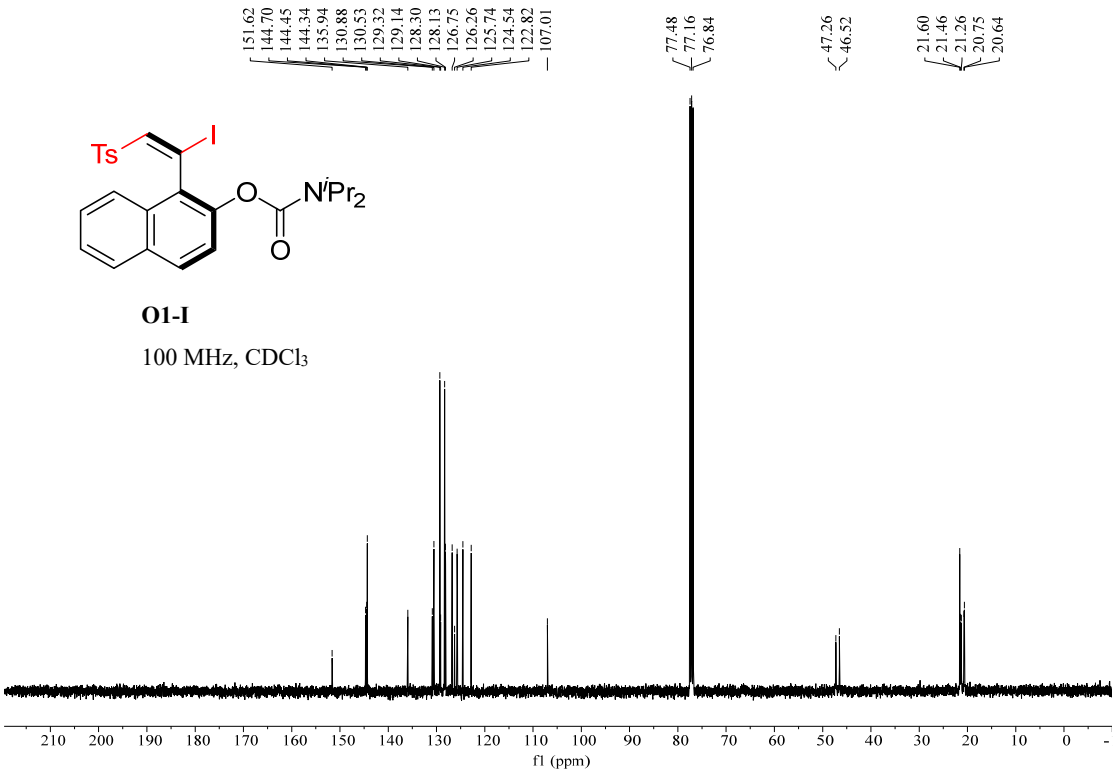

Ts
Br
O
N^{i}Pr$_2$
O
O1-Br
400 MHz, CDCl3
f1 (ppm)


Ts
Br
O
N^{i}Pr$_2$
O
O1-Br
100 MHz, CDCl3
f1 (ppm)



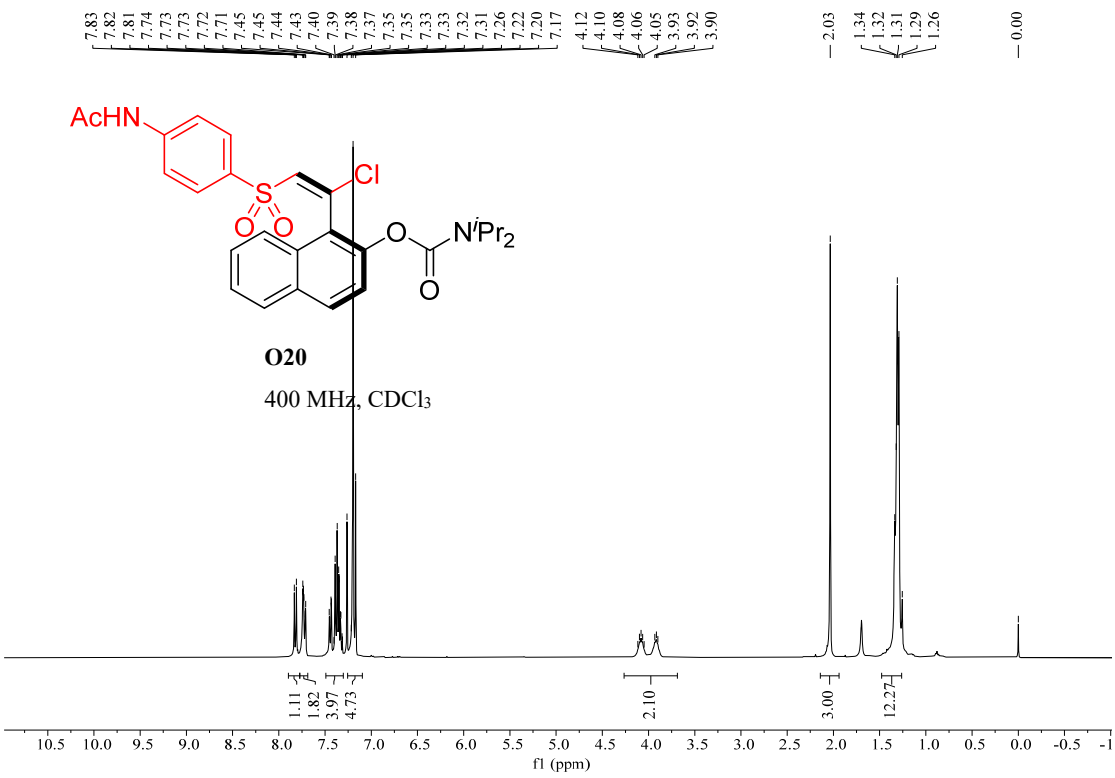
O1-I

400 MHz, $CDCl_3$



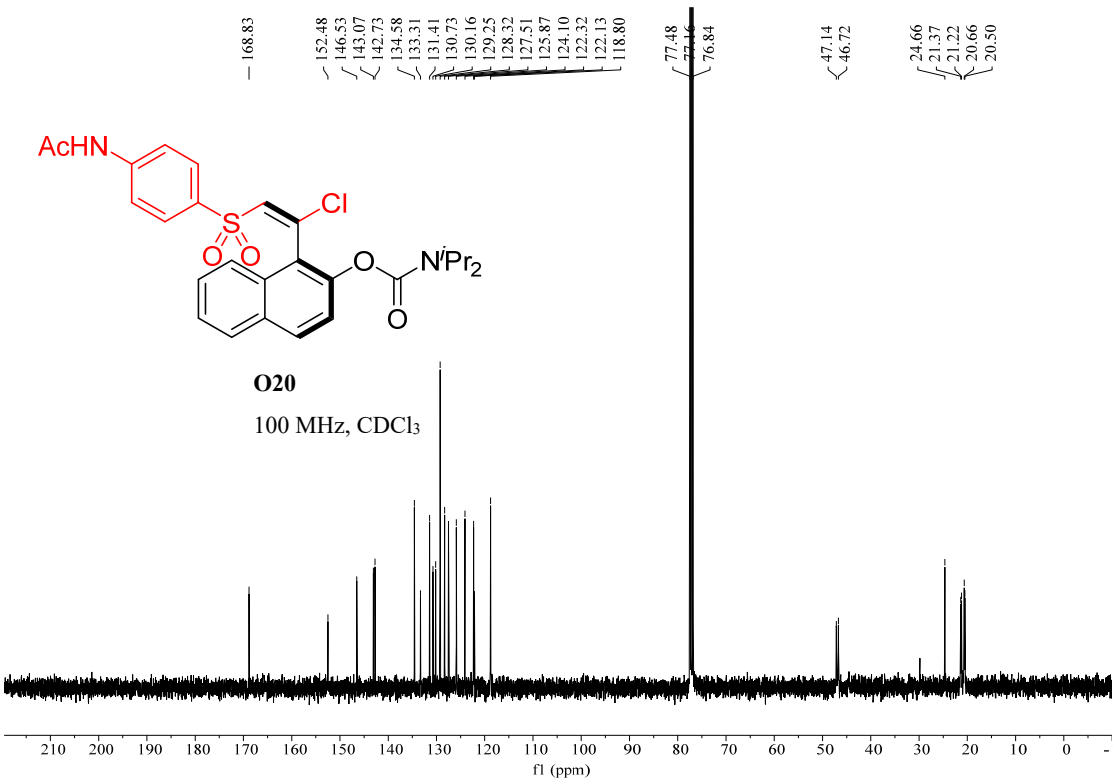
O1-I

100 MHz, $CDCl_3$



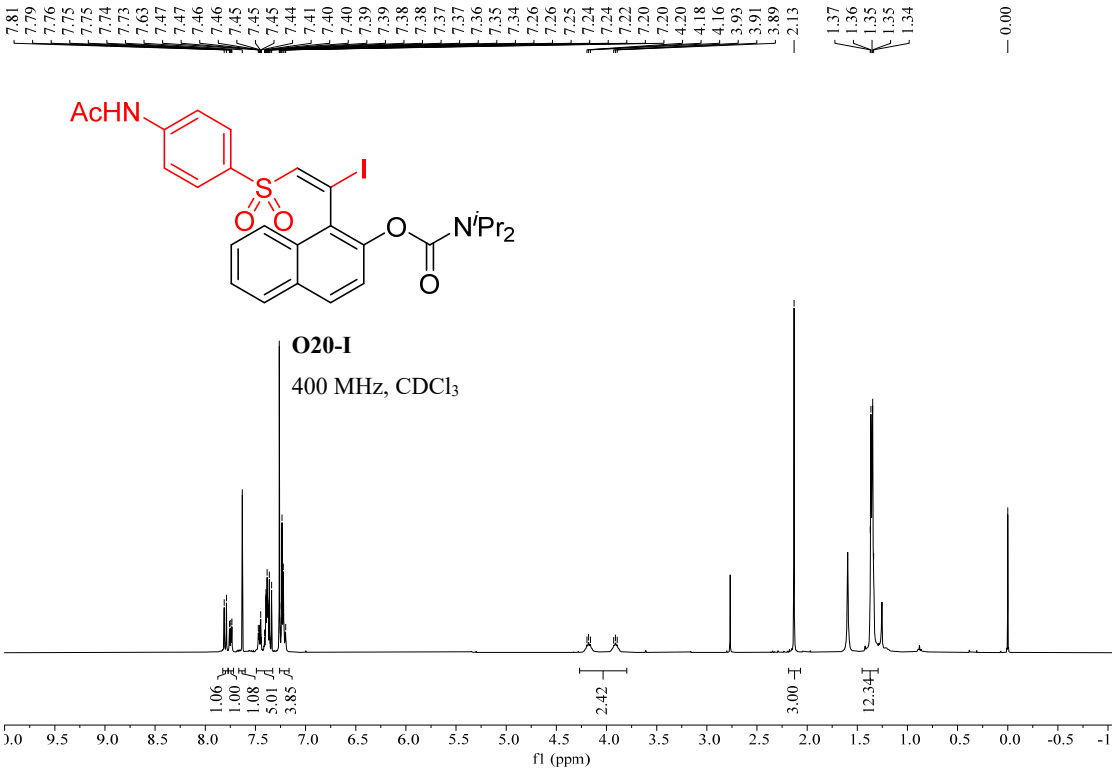
O20

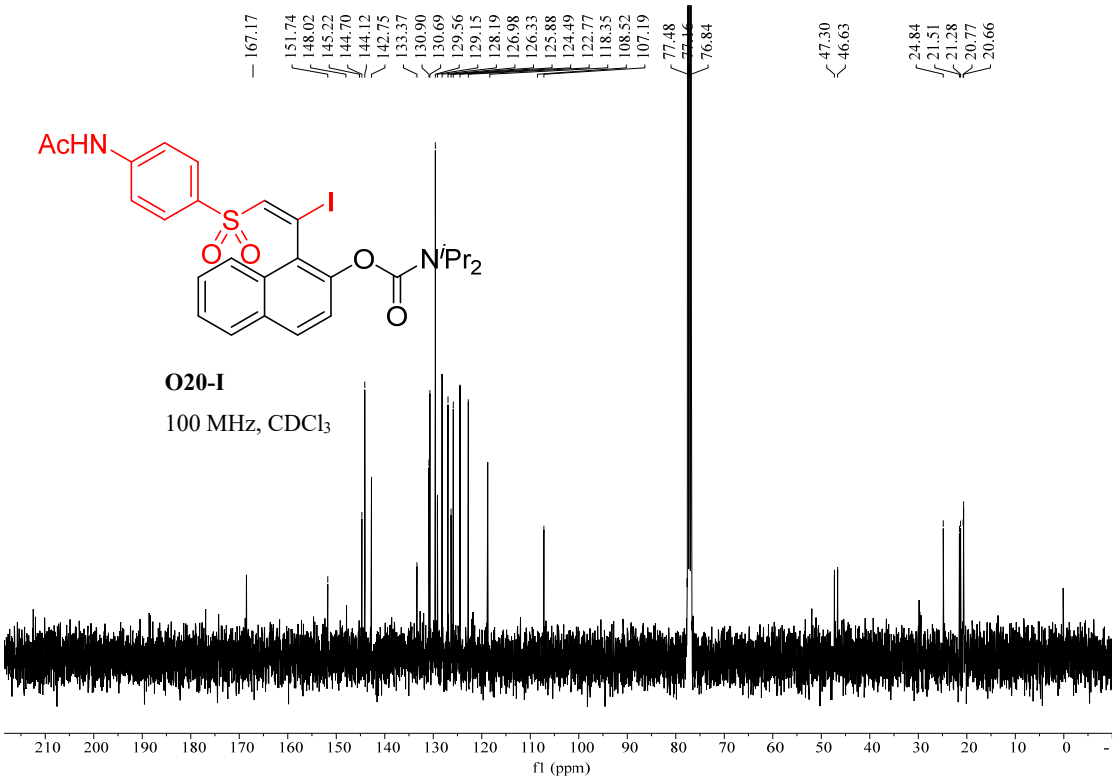
400 MHz, $CDCl_3$

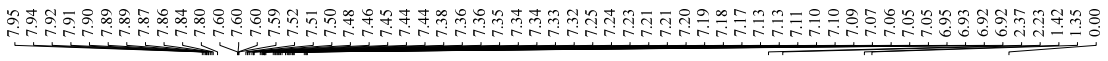


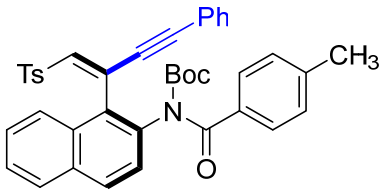
O20

100 MHz, $CDCl_3$


7.81 7.79 7.76 7.75 7.75 7.74 7.73 7.63 7.47 7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.34 7.26 7.26 7.25 7.24 7.24 7.22 7.20 7.20 4.20 4.18 4.16 3.93 3.91 3.89 2.13 1.37 1.36 1.35 1.35 1.34 0.00
AcHN
S
O
O
I
O
O
N^{i}Pr$_2$
O20-I
400 MHz, CDCl$_3$
1.06 1.00 1.08 5.01 3.85 2.42 3.00 12.34
f1 (ppm)

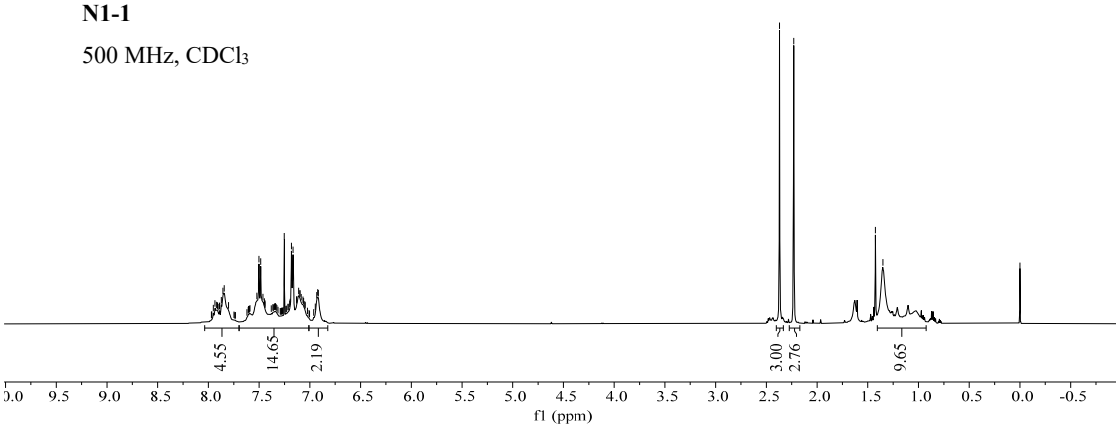

167.17 151.74 148.02 145.22 144.70 144.12 142.75 133.37 130.90 130.69 129.56 129.15 128.19 126.98 126.33 125.88 124.49 122.77 118.35 108.52 107.19 77.48 77.16 76.84 47.30 46.63 24.84 21.51 21.28 20.77 20.66
AcHN
S
O
O
I
O
O
N^{i}Pr$_2$
O20-I
100 MHz, CDCl$_3$
f1 (ppm)

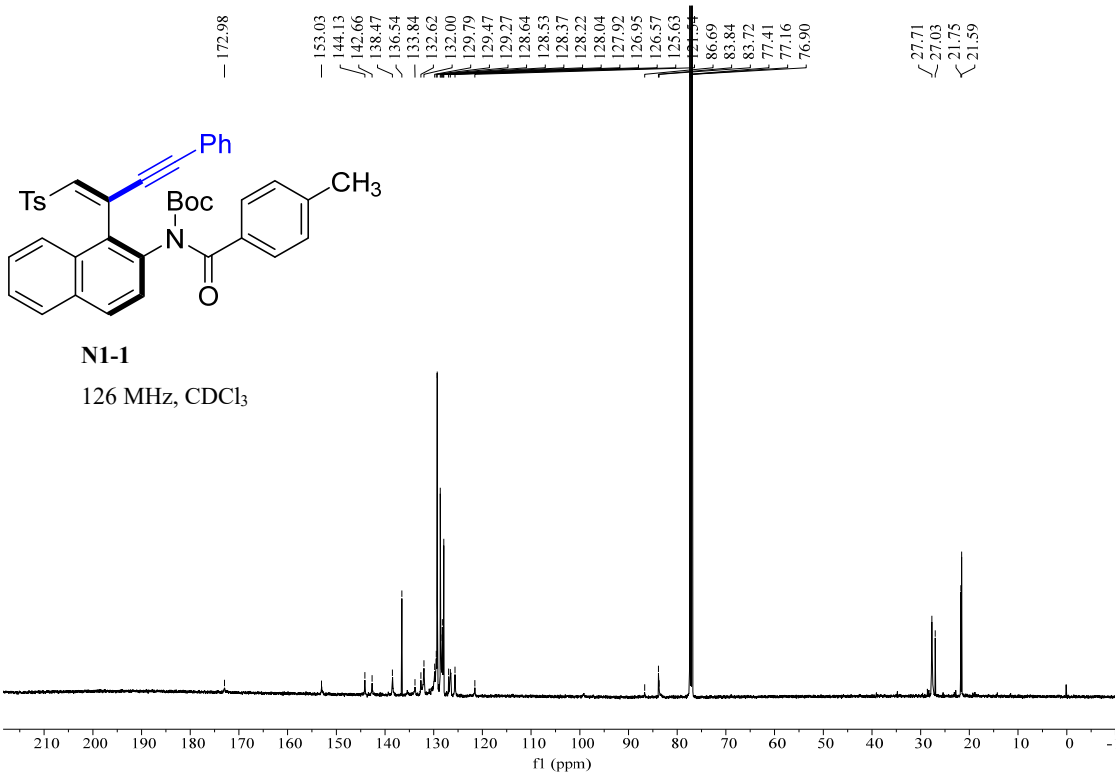




N1-1

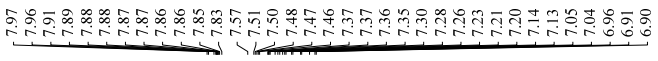
500 MHz, $CDCl_3$

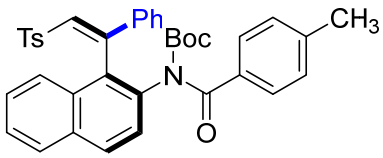




N1-1

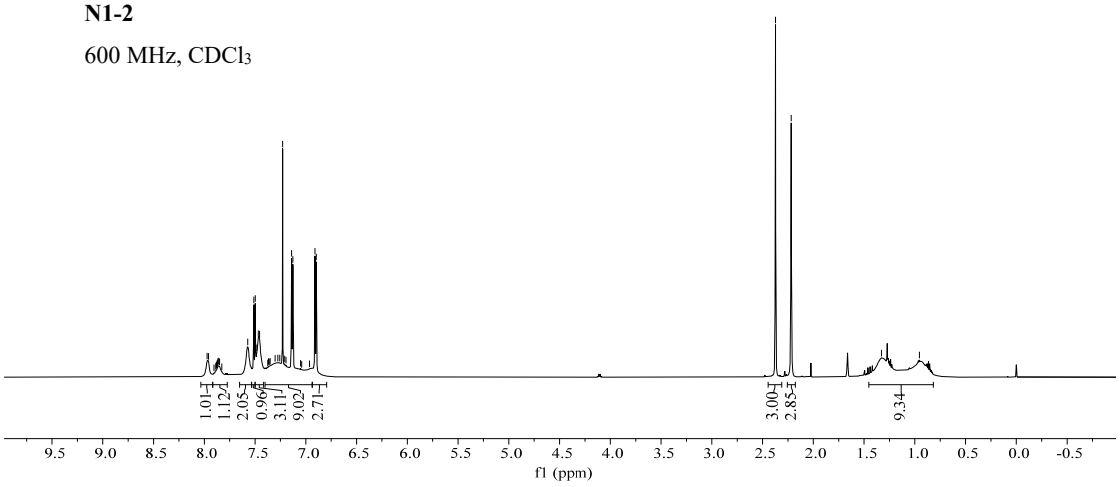
126 MHz, $CDCl_3$

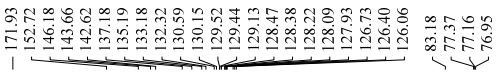


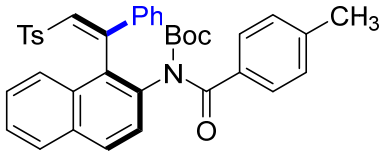


N1-2

600 MHz, $CDCl_3$

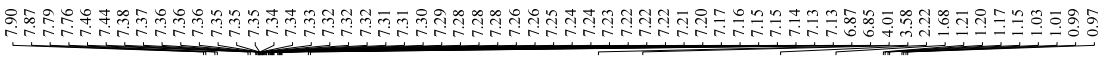


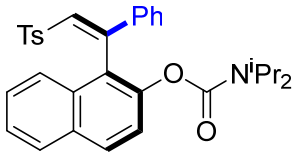




N1-2

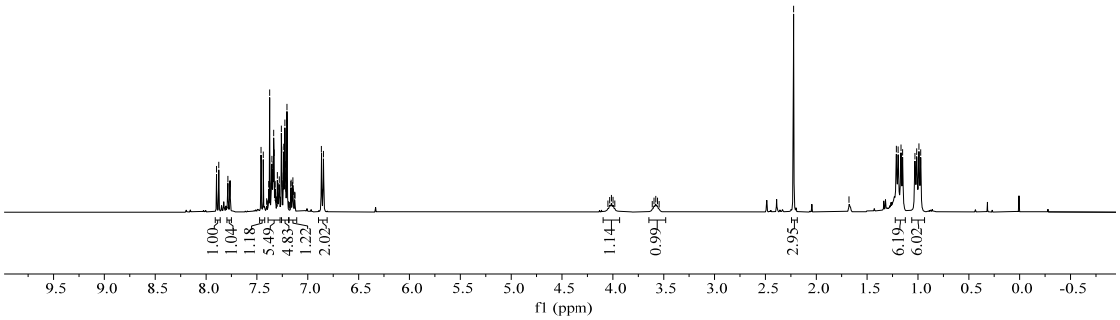
150 MHz, $CDCl_3$

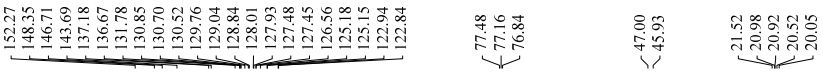


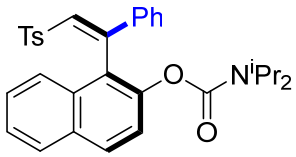


O1-1

400 MHz, $CDCl_3$

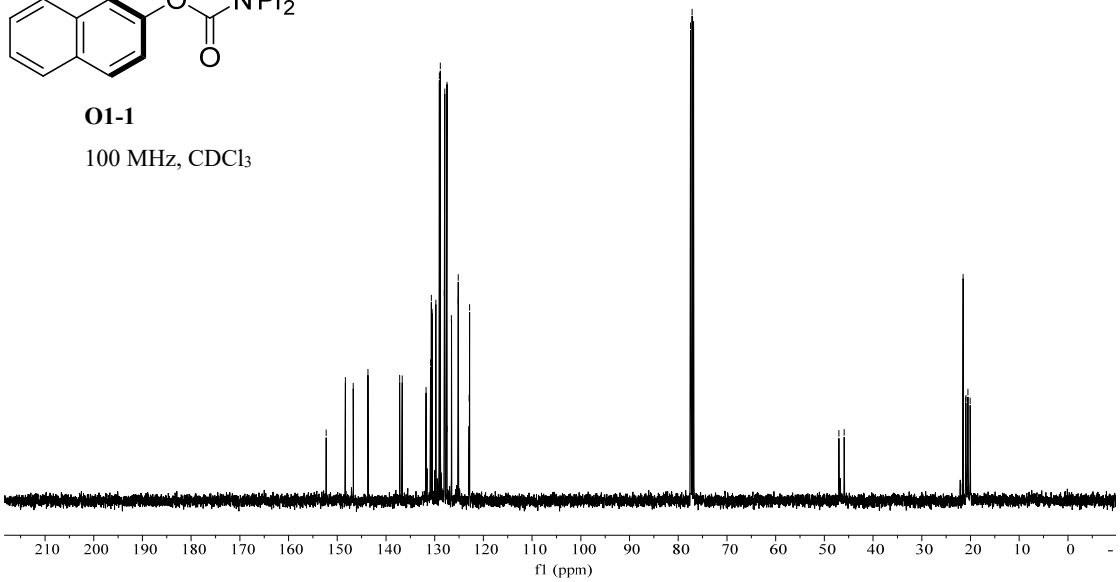


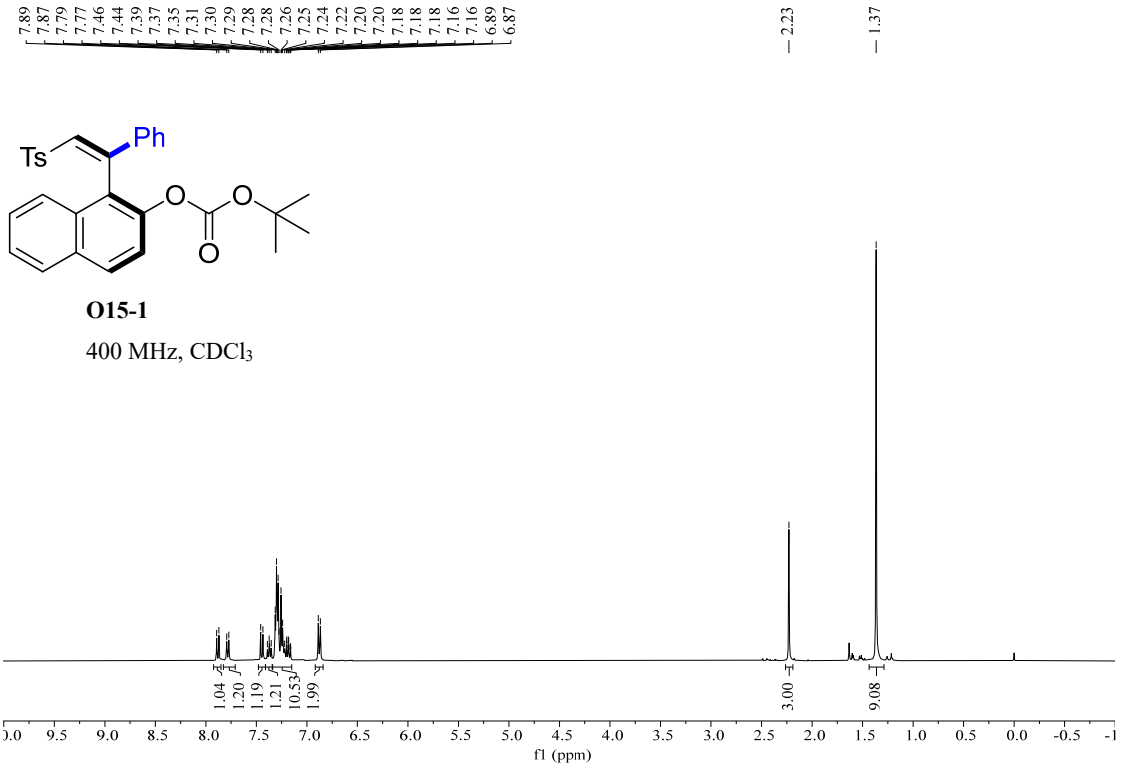




O1-1

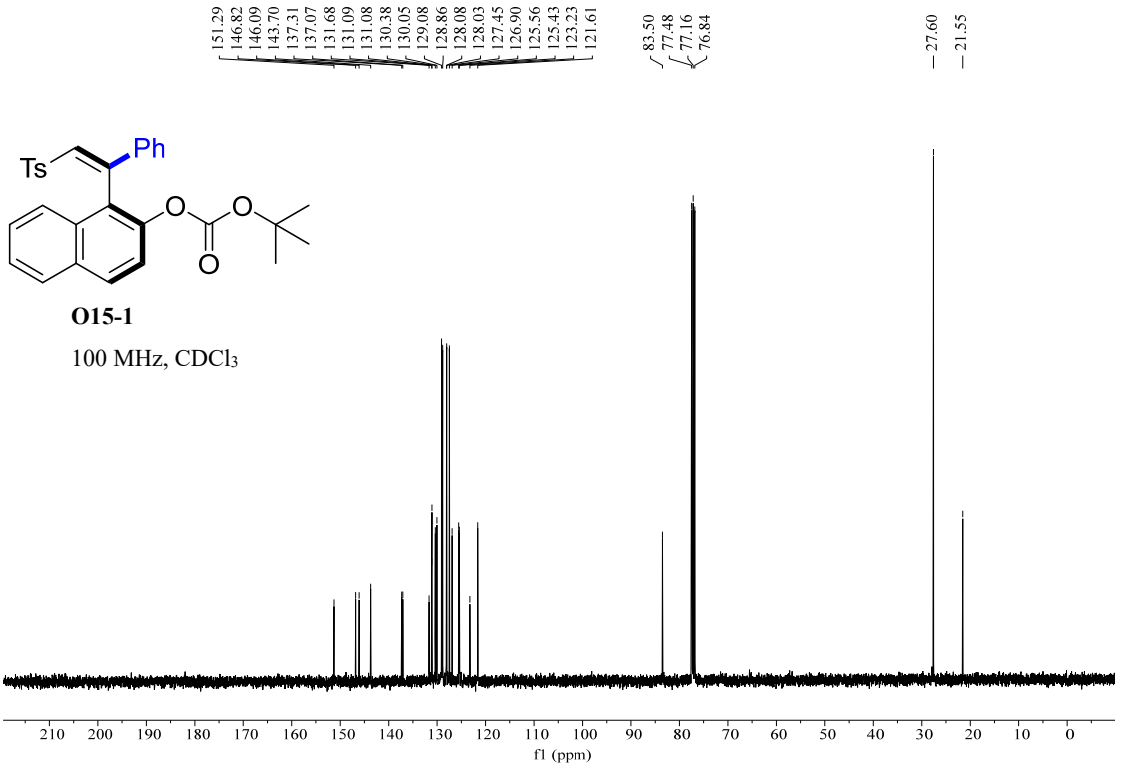
100 MHz, $CDCl_3$





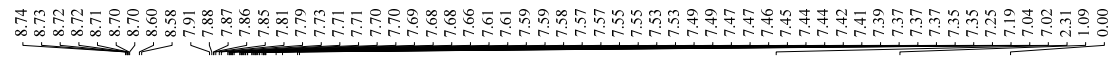
O15-1

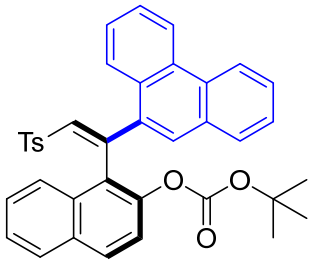
400 MHz, $CDCl_3$



O15-1

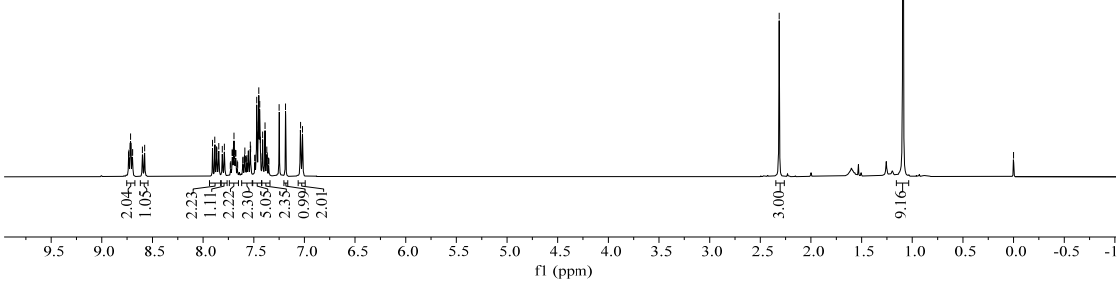
100 MHz, $CDCl_3$

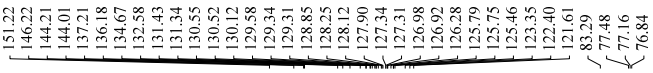


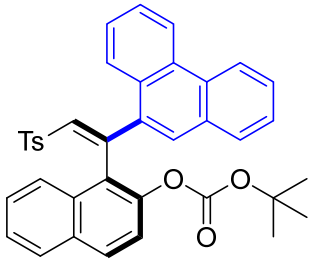


O15-2

400 MHz, $CDCl_3$

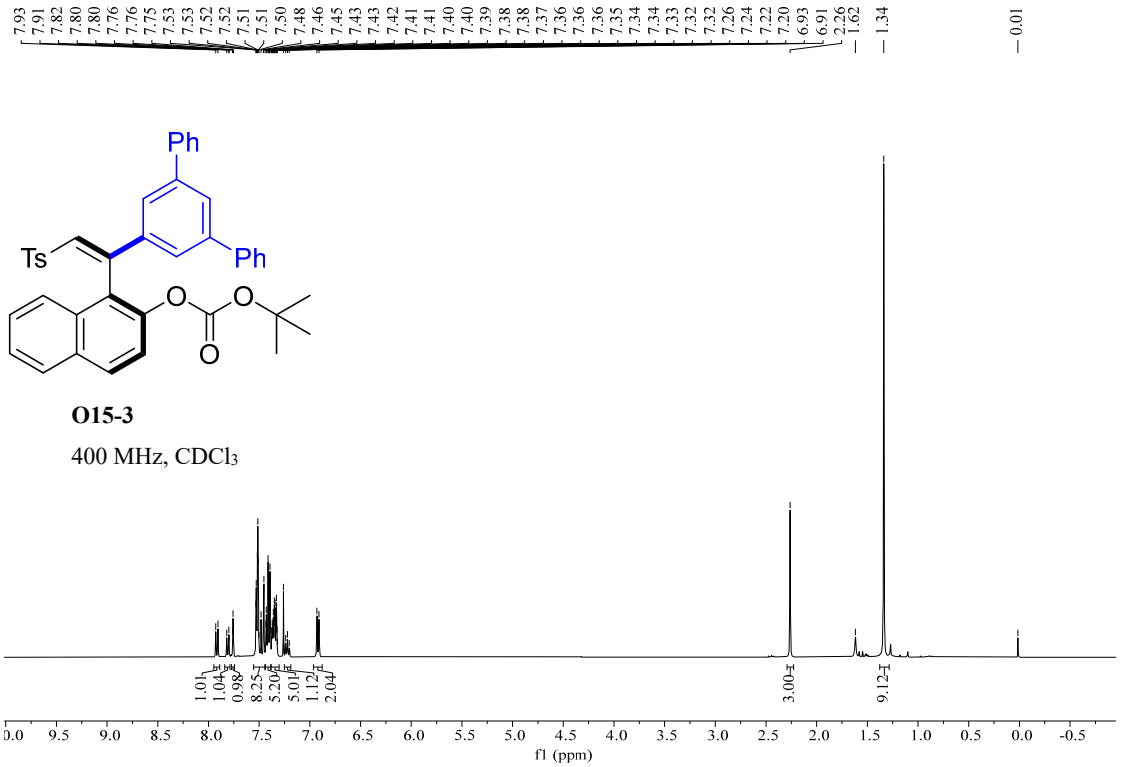


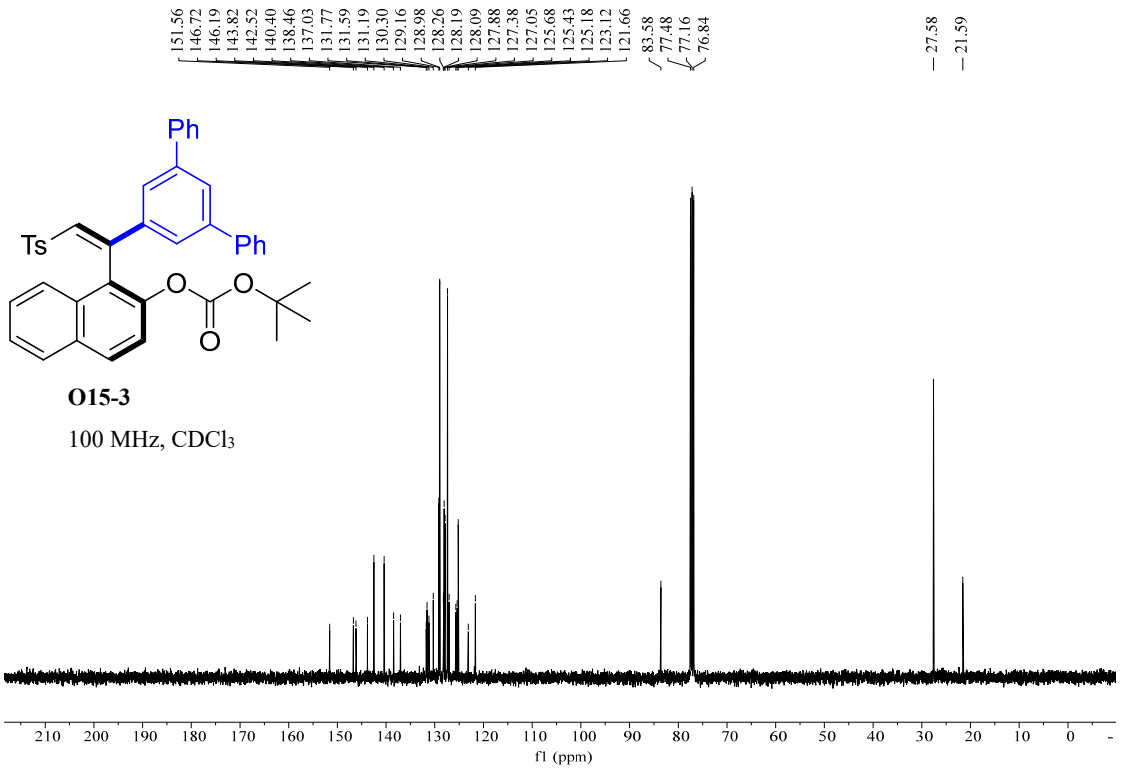


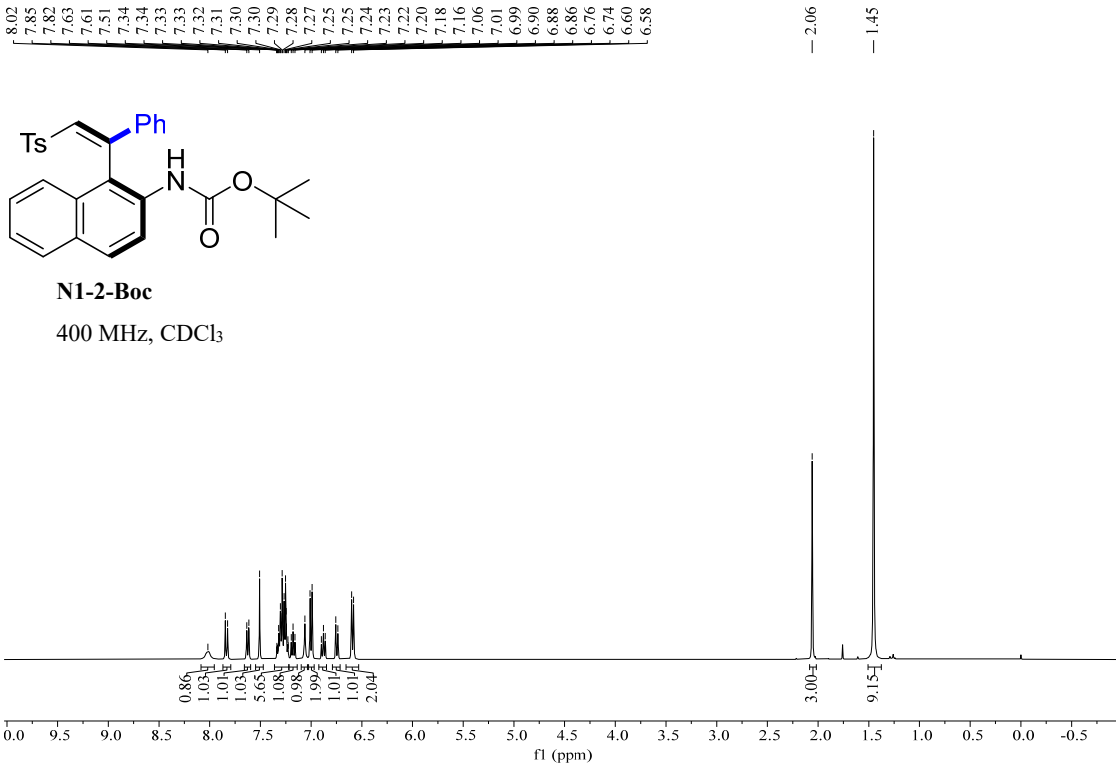


O15-2

100 MHz, $CDCl_3$

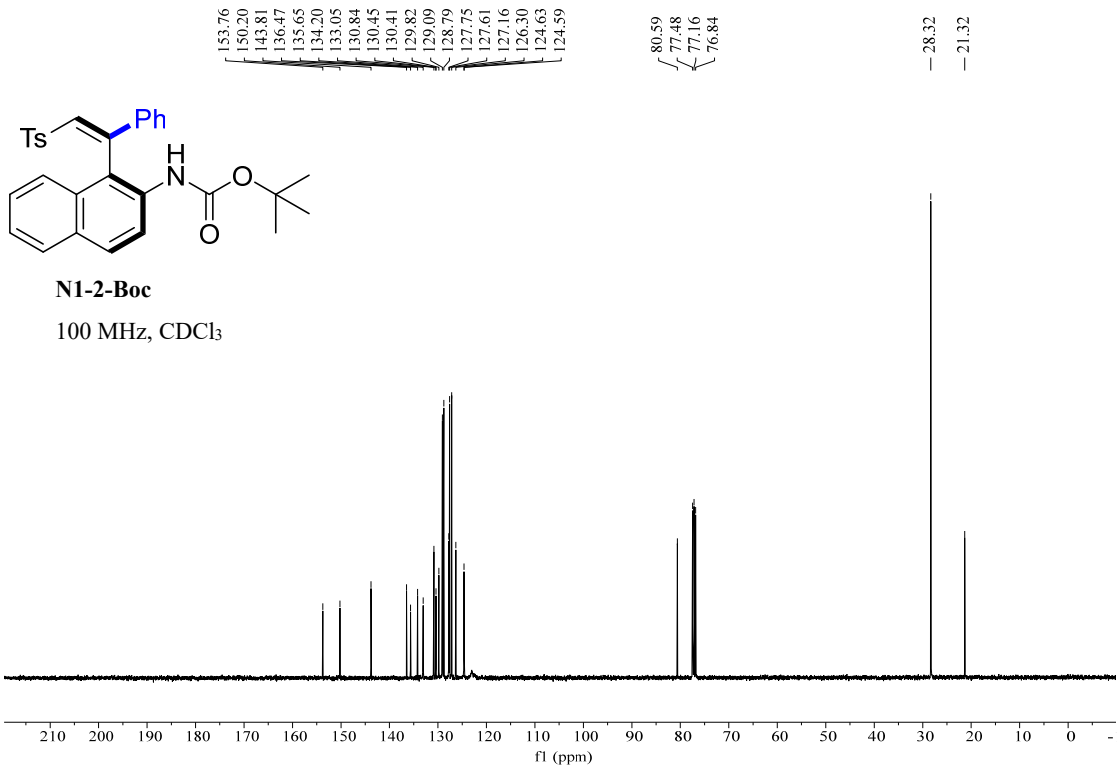

7.93
7.91
7.82
7.80
7.80
7.76
7.76
7.75
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.48
7.46
7.45
7.43
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.26
7.24
7.22
7.20
6.93
6.91
2.26
1.62
1.34
0.01
Ph
Ts
Ph
O
O
O
O15-3
400 MHz, CDCl3
1.01
1.04
0.98
8.25
5.20
5.01
1.12
2.04
3.00
9.12
f1 (ppm)


151.56
146.72
146.19
143.82
142.52
140.40
138.46
137.03
131.77
131.59
131.19
130.30
129.16
128.98
128.26
128.19
128.09
127.88
127.38
127.05
125.68
125.43
125.18
123.12
121.66
83.58
77.48
77.16
76.84
27.58
21.59
Ph
Ts
Ph
O
O
O
O15-3
100 MHz, CDCl3
f1 (ppm)



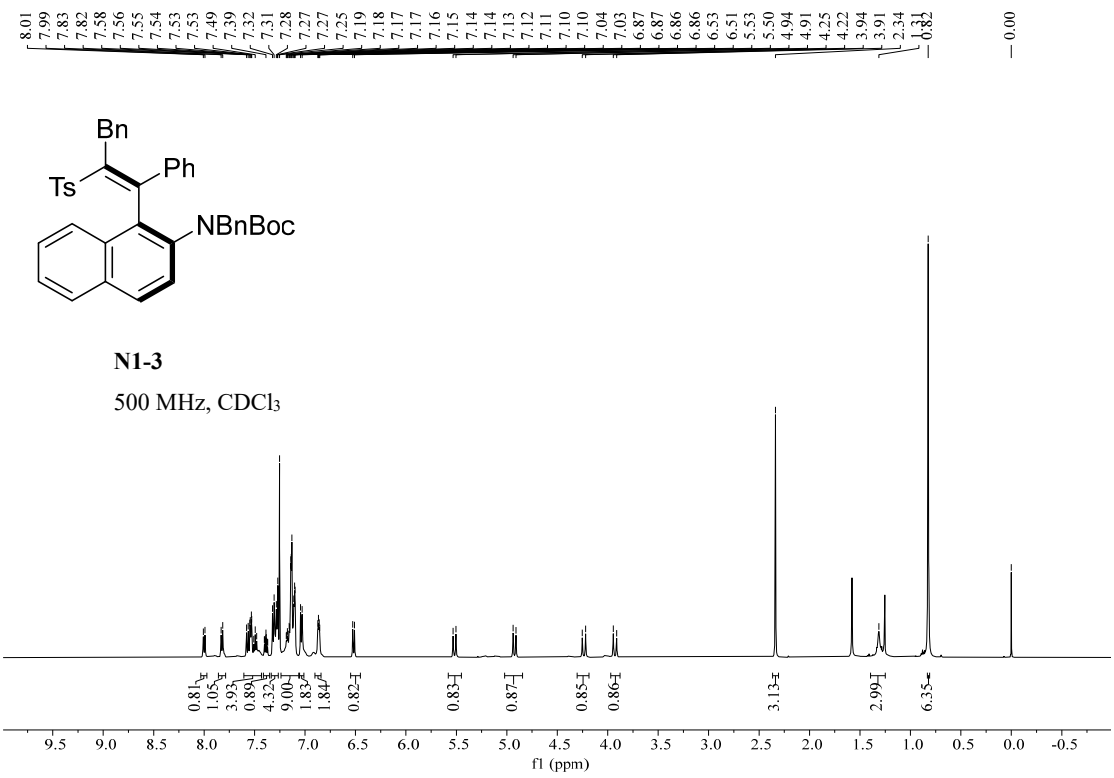
N1-2-Boc

400 MHz, $CDCl_3$



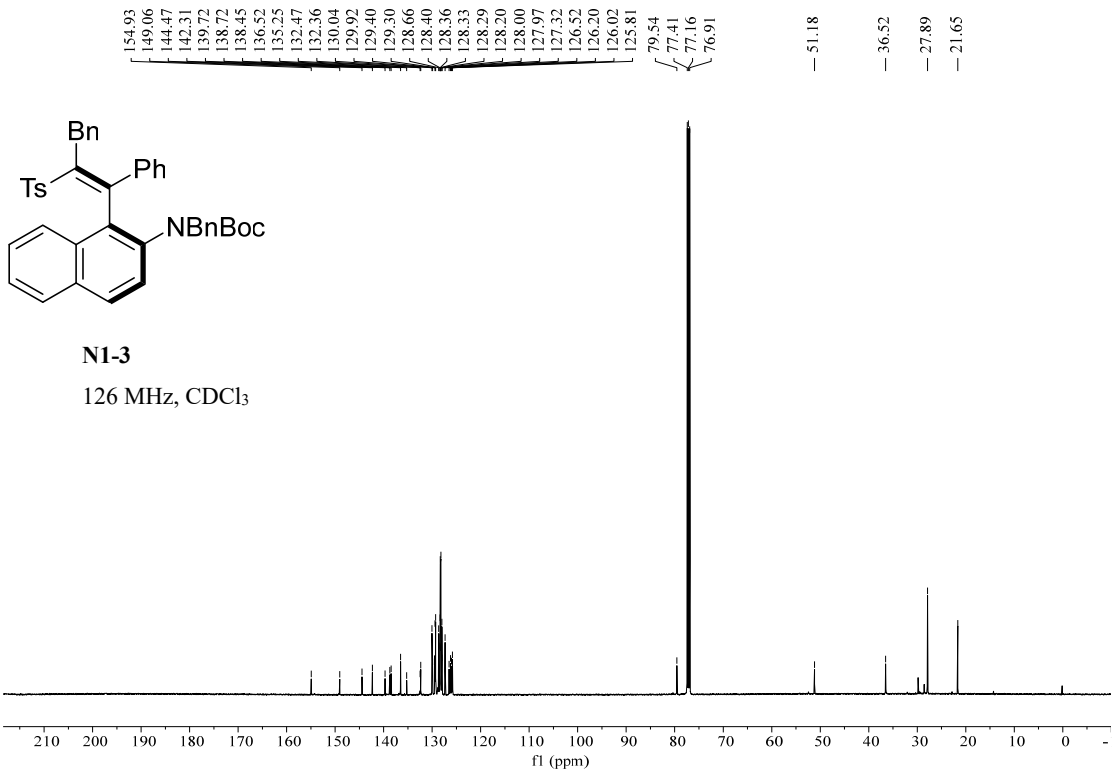
N1-2-Boc

100 MHz, $CDCl_3$



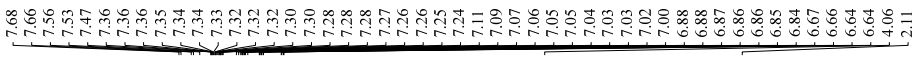
N1-3

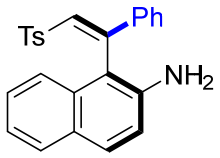
500 MHz, $CDCl_3$



N1-3

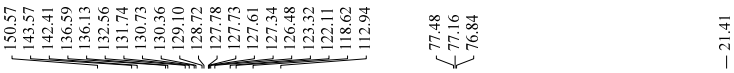
126 MHz, $CDCl_3$

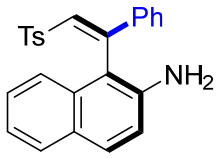




N1-4

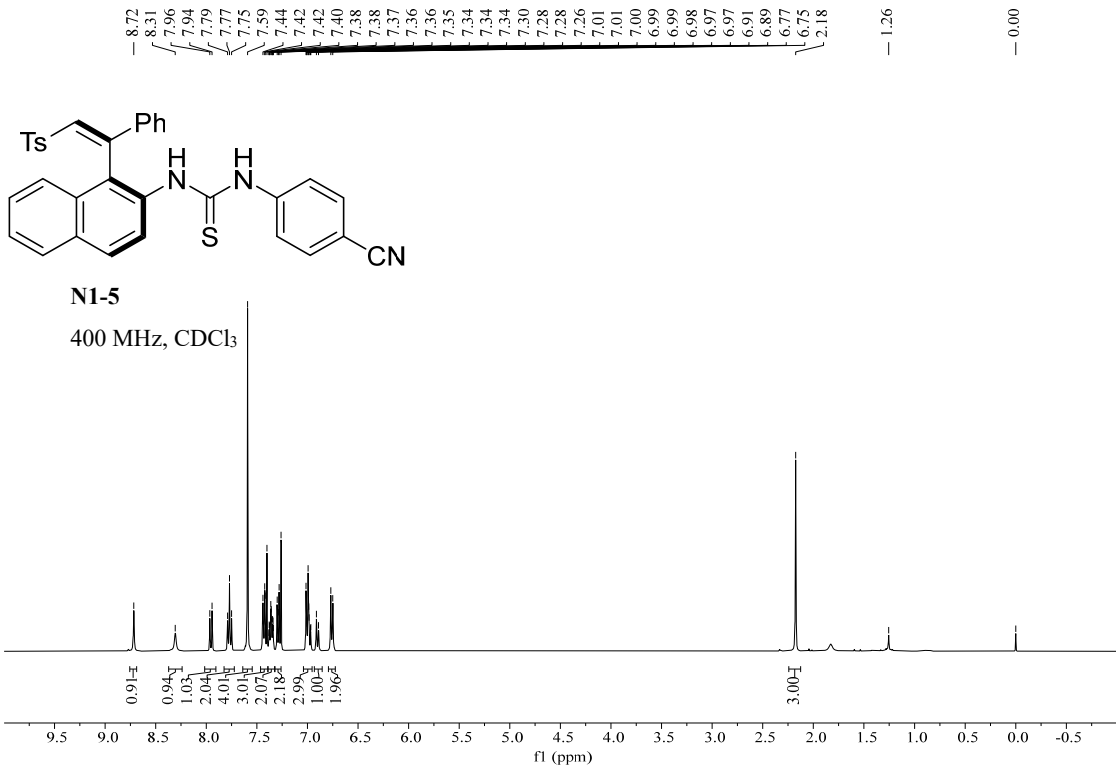
400 MHz, $CDCl_3$

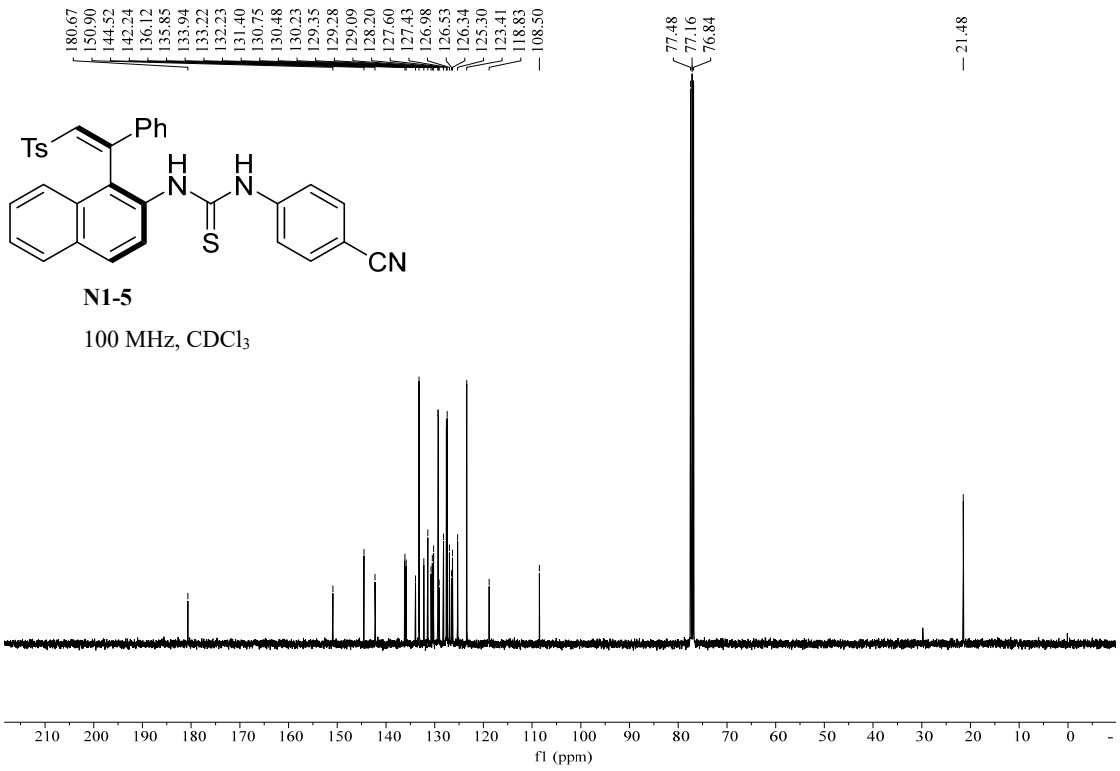


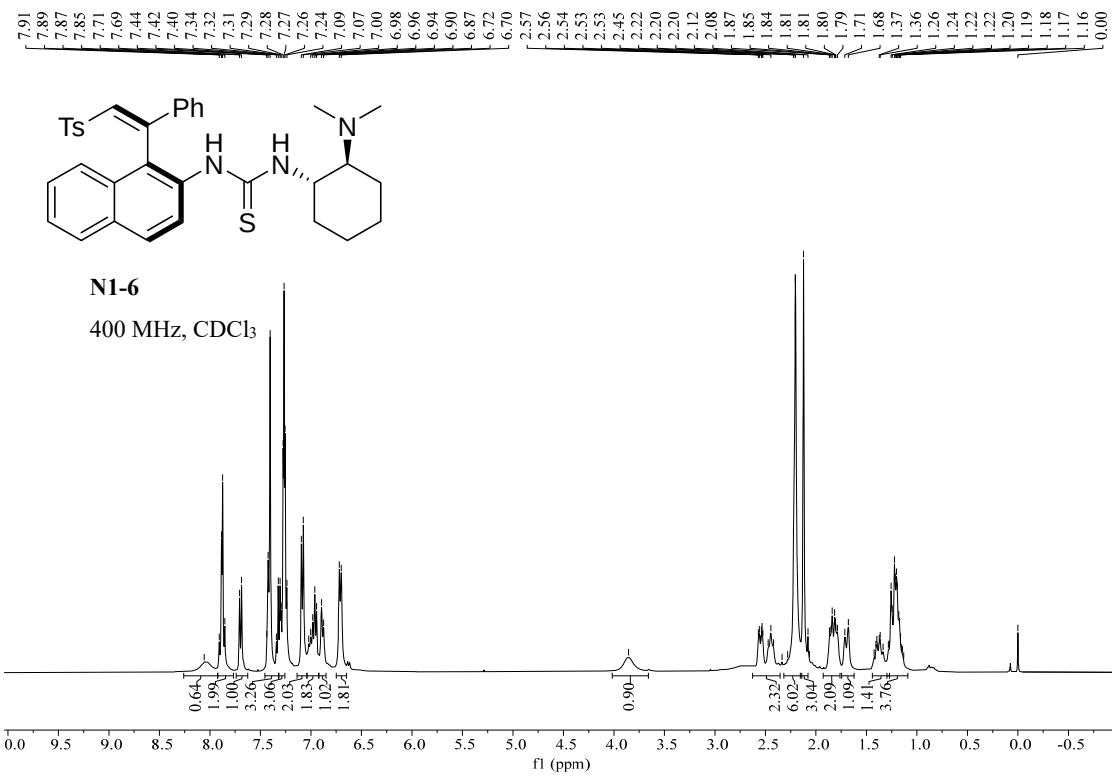


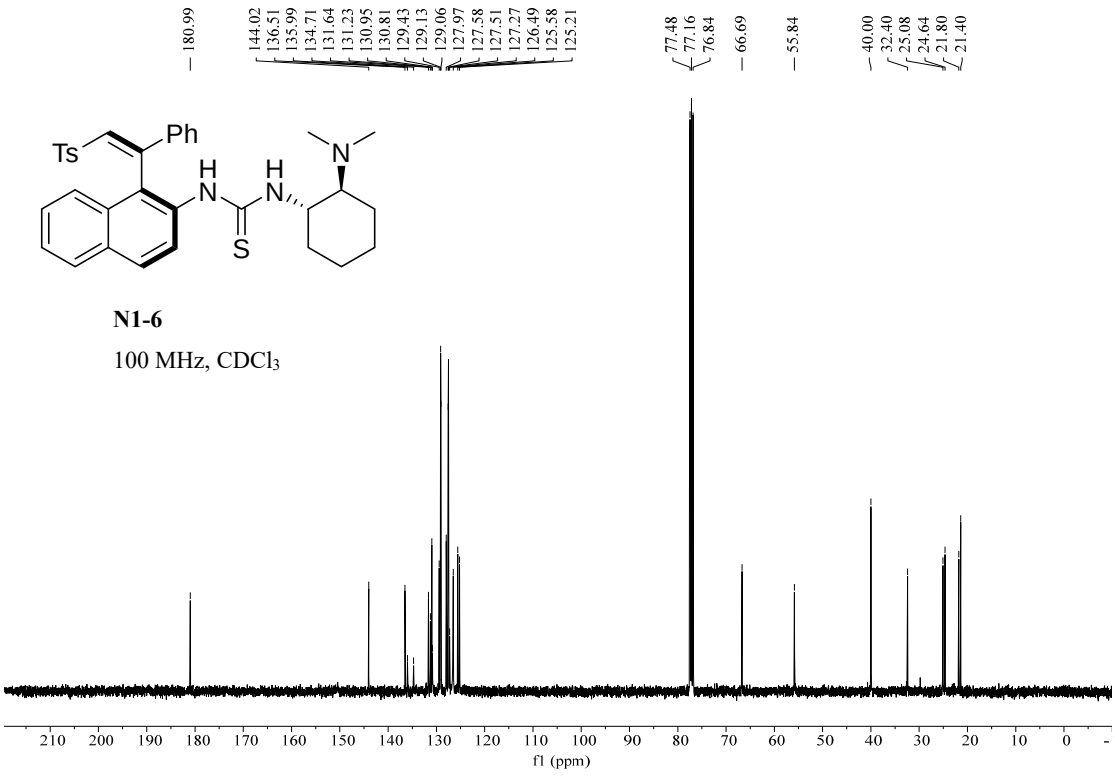
N1-4

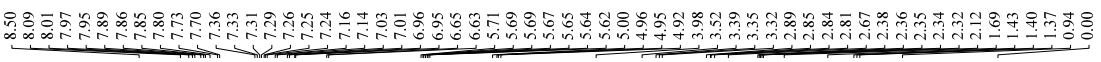
100 MHz, $CDCl_3$

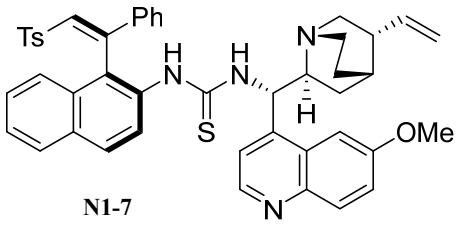

8.72
8.31
7.96
7.94
7.79
7.77
7.75
7.59
7.44
7.42
7.42
7.40
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.30
7.28
7.28
7.26
7.01
7.01
7.00
6.99
6.99
6.98
6.97
6.97
6.91
6.89
6.77
6.75
2.18
1.26
0.00
Ts
Ph
H
N
H
N
S
CN
N1-5
400 MHz, CDCl3
0.91
0.94
1.03
2.04
4.01
3.01
2.07
2.18
2.99
1.00
1.96
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


180.67
150.90
144.52
142.24
136.12
135.85
133.94
133.22
132.23
131.40
130.75
130.48
130.23
129.35
129.28
129.09
128.20
127.60
127.43
126.98
126.53
126.34
125.30
123.41
118.83
108.50
77.48
77.16
76.84
21.48
Ts
Ph
H
N
H
N
S
CN
N1-5
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)


Ts
Ph
H
N
H
N
N
S
N1-6
400 MHz, CDCl3
f1 (ppm)

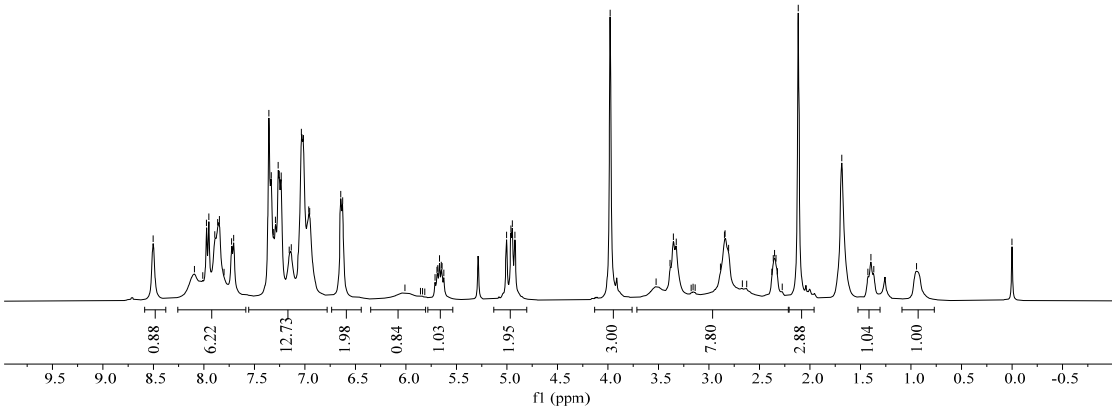

Ts
Ph
H
N
H
N
N
S
N1-6
100 MHz, CDCl3
f1 (ppm)

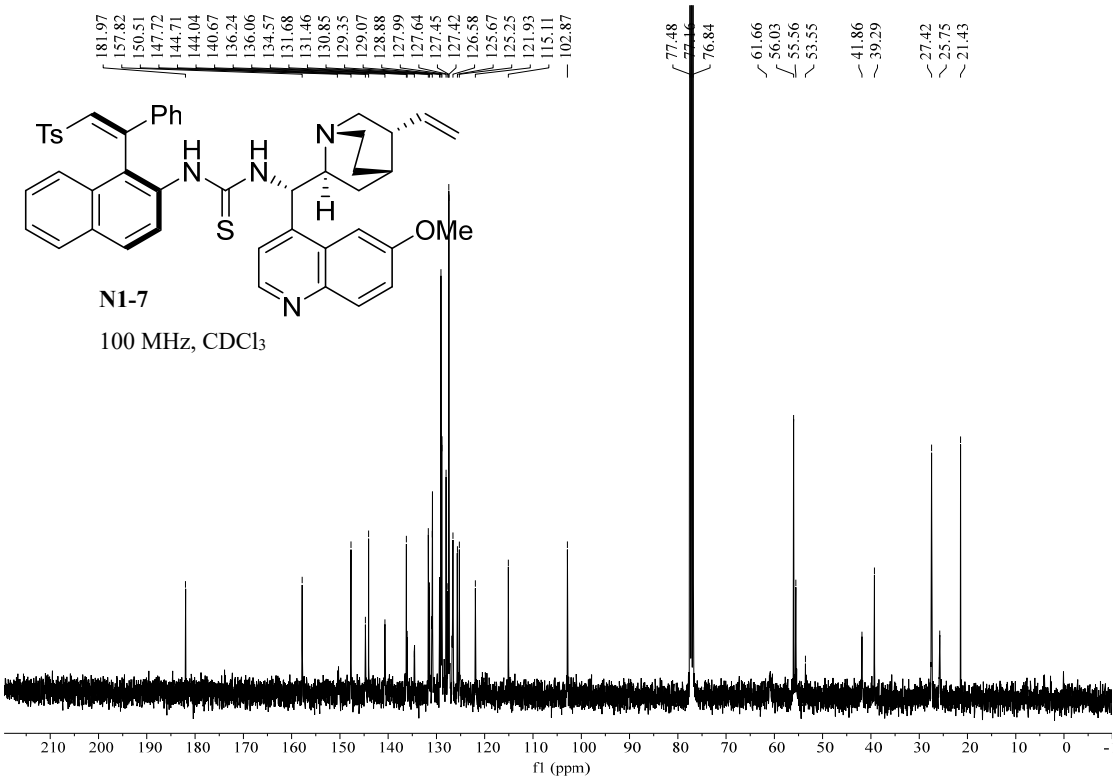




N1-7

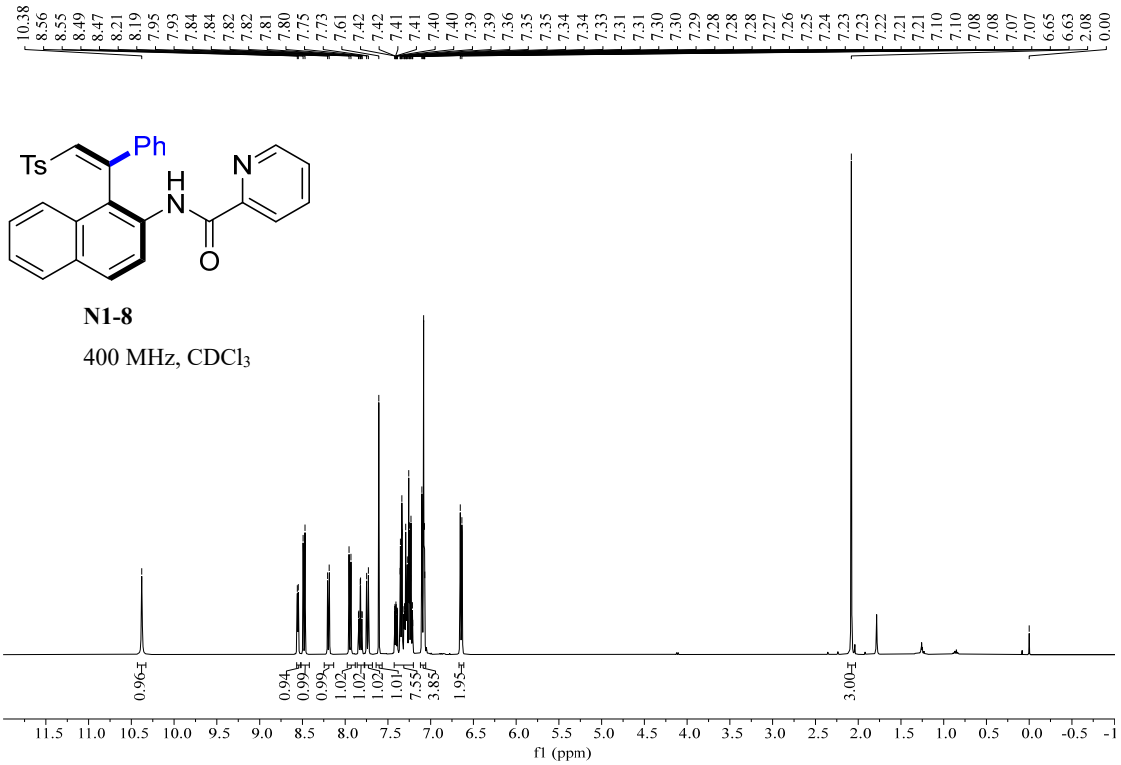
400 MHz, $CDCl_3$

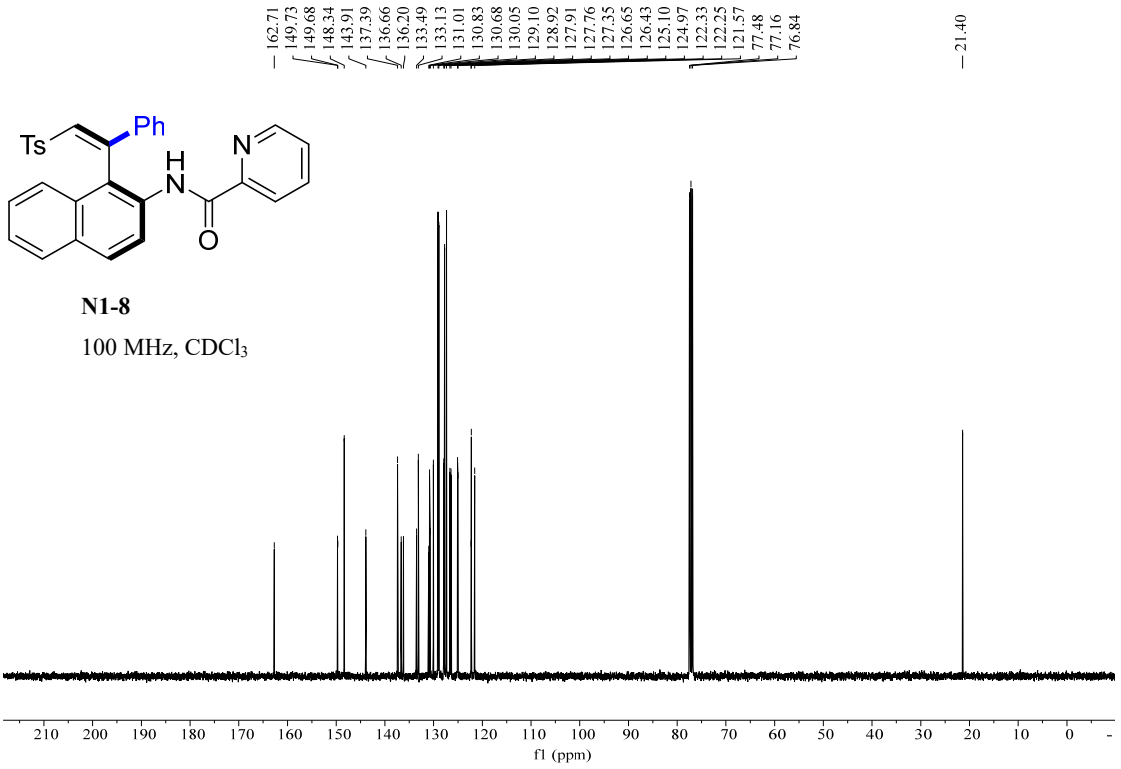


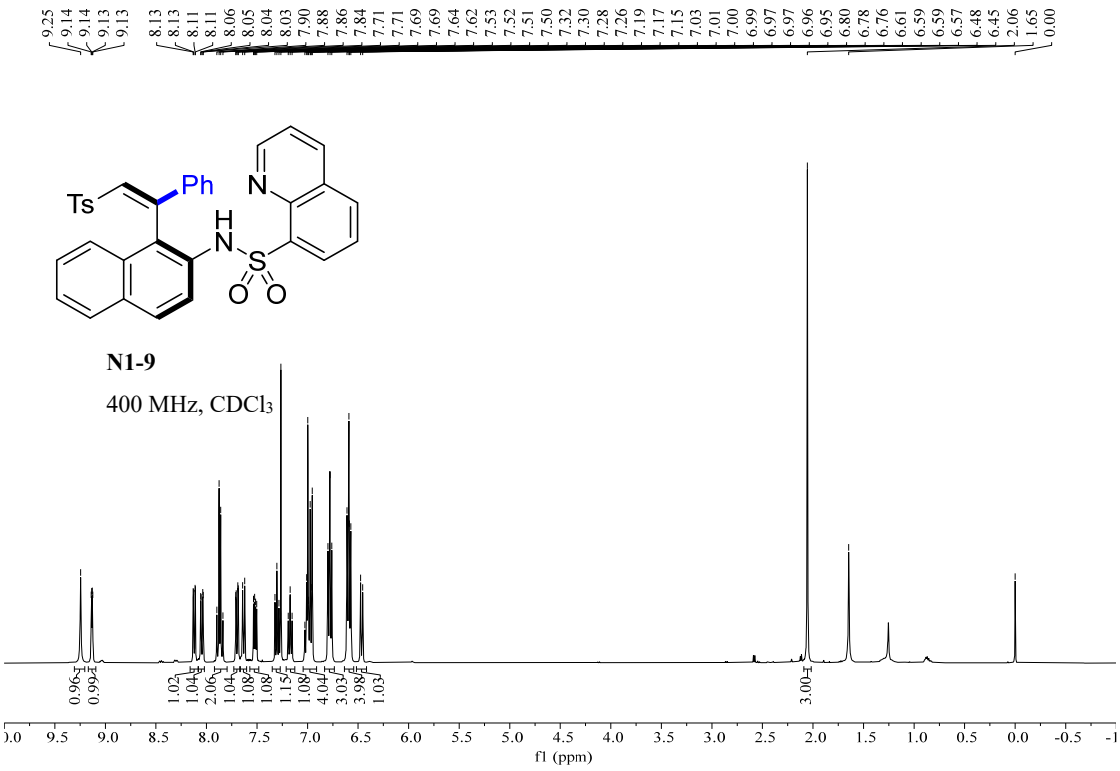


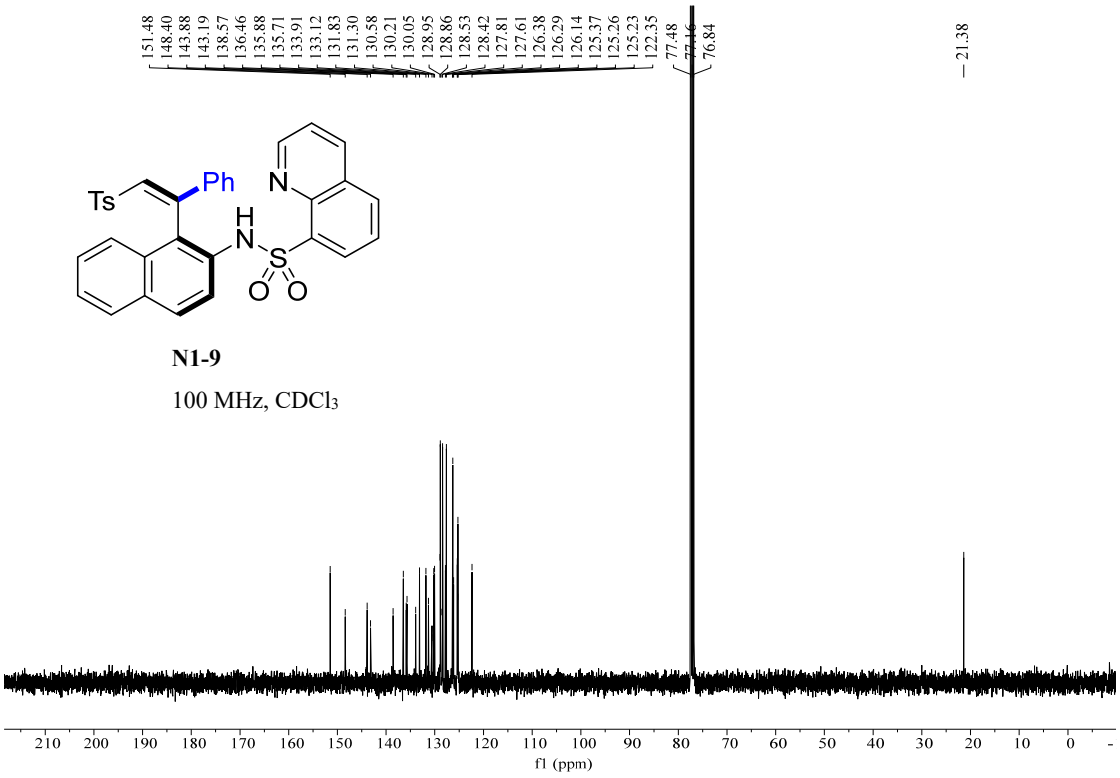
N1-7

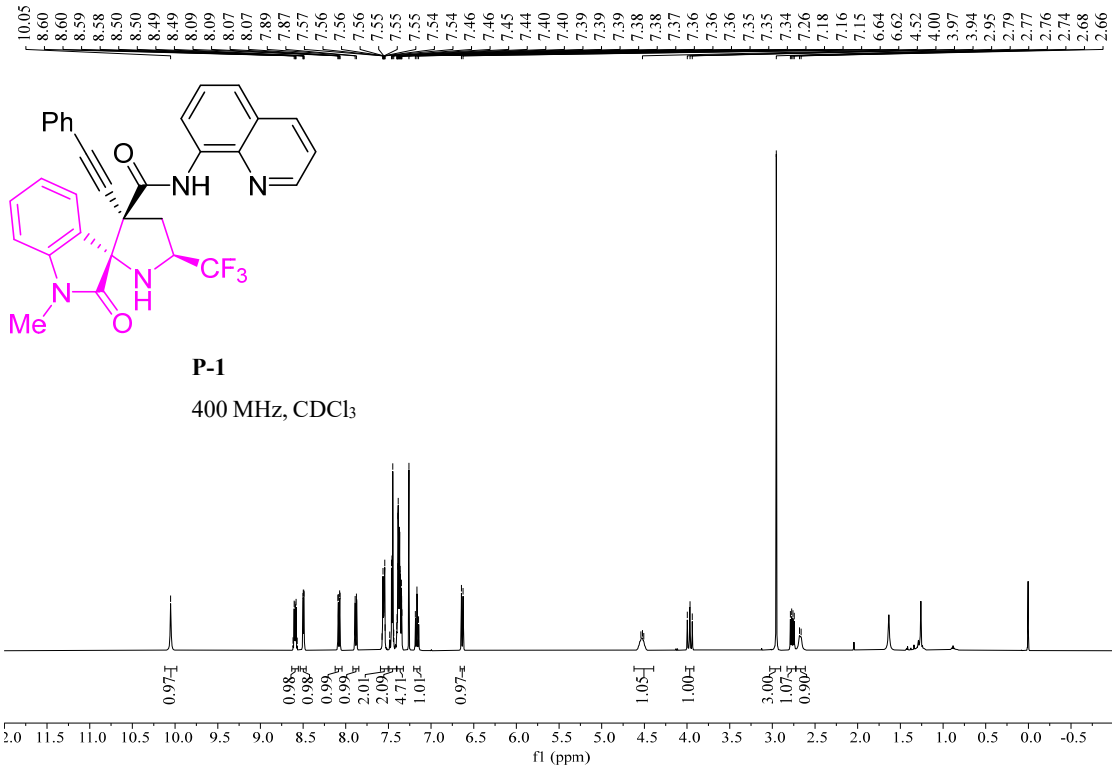
100 MHz, $CDCl_3$

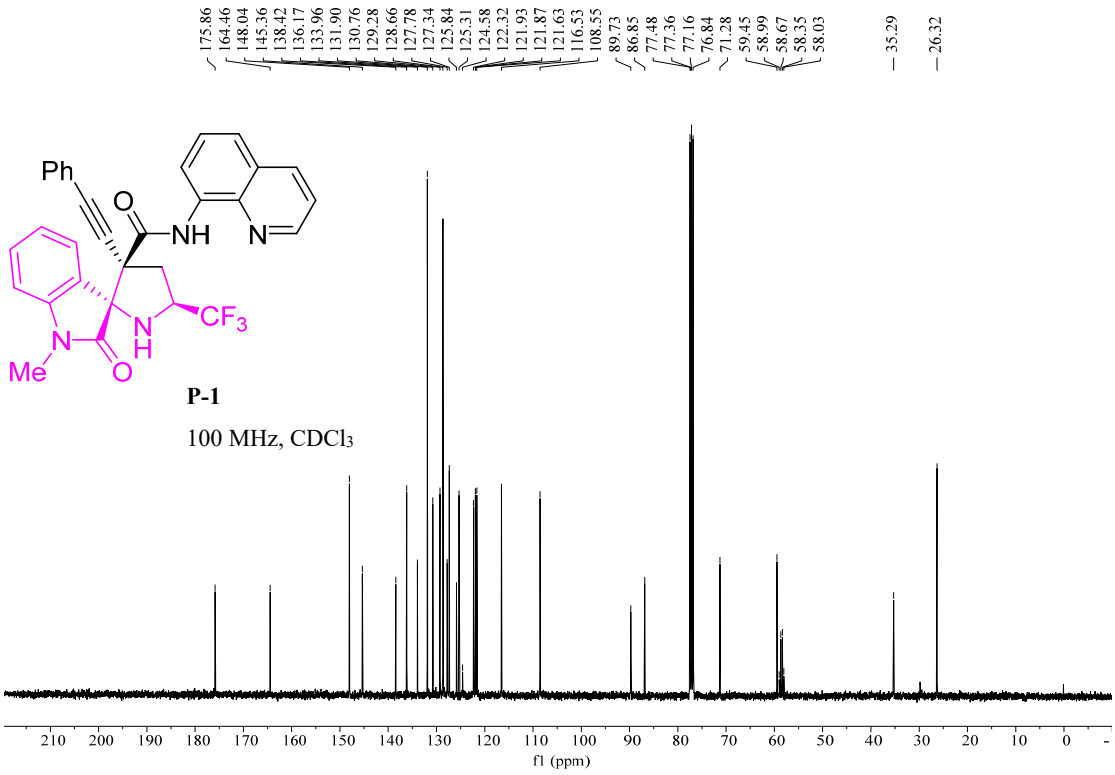

Ts
Ph
H
N
N
O
N1-8
400 MHz, CDCl3
f1 (ppm)

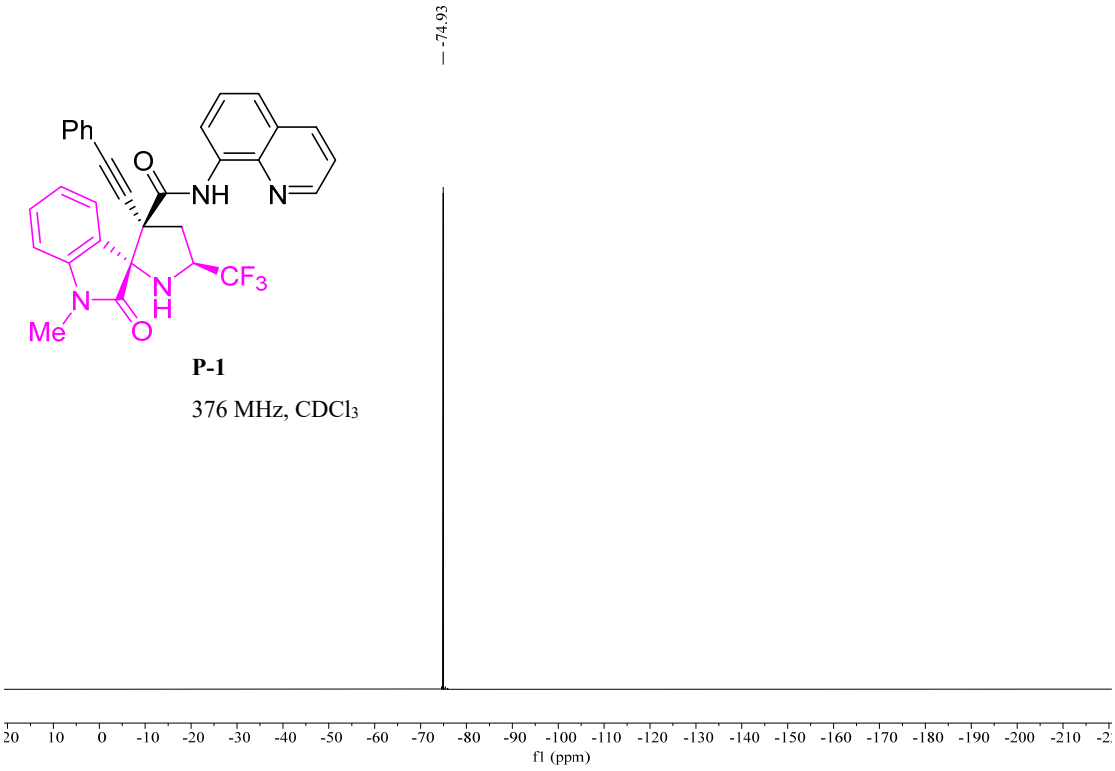

Ts
Ph
H
N
N
O
N1-8
100 MHz, CDCl3
f1 (ppm)


Ts
Ph
N
H
N
S
O
O
N1-9
400 MHz, CDCl3
f1 (ppm)


Ts
Ph
N
H
N
S
O
O
N1-9
100 MHz, CDCl3
f1 (ppm)

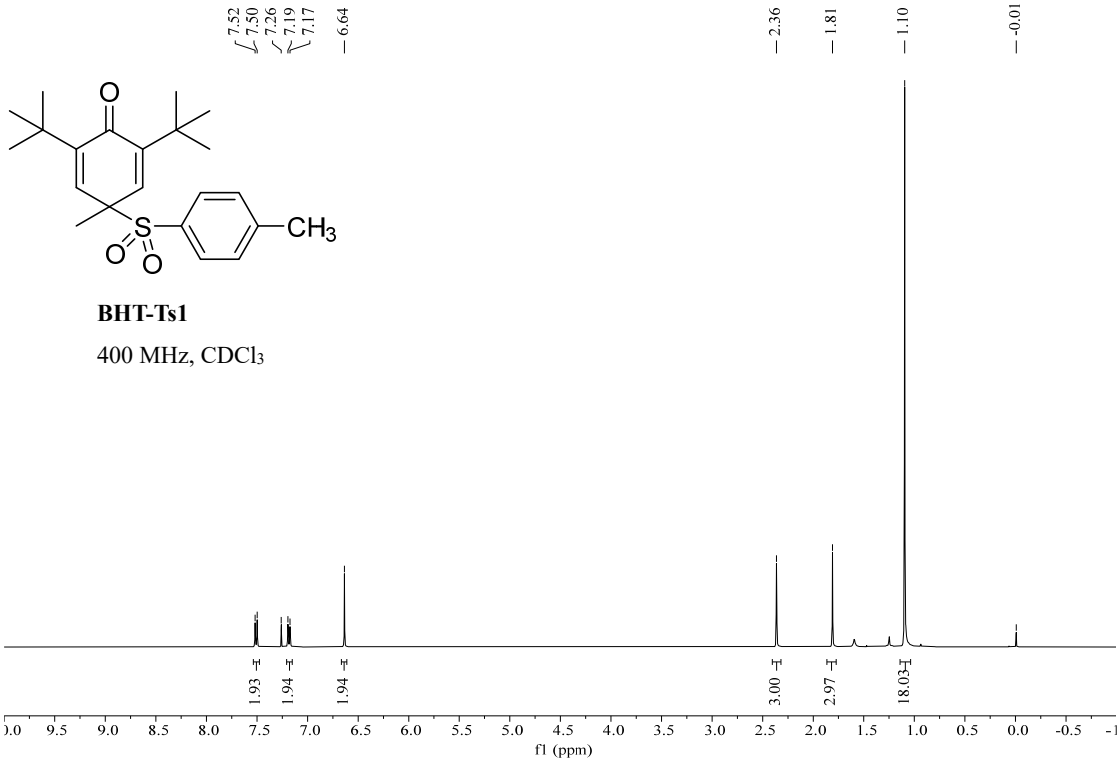

Ph
O
NH
N
CF3
N
H
N
Me
O
P-1
400 MHz, CDCl3
f1 (ppm)


Ph
O
NH
N
CF3
N
H
N
Me
O
P-1
100 MHz, CDCl3
f1 (ppm)



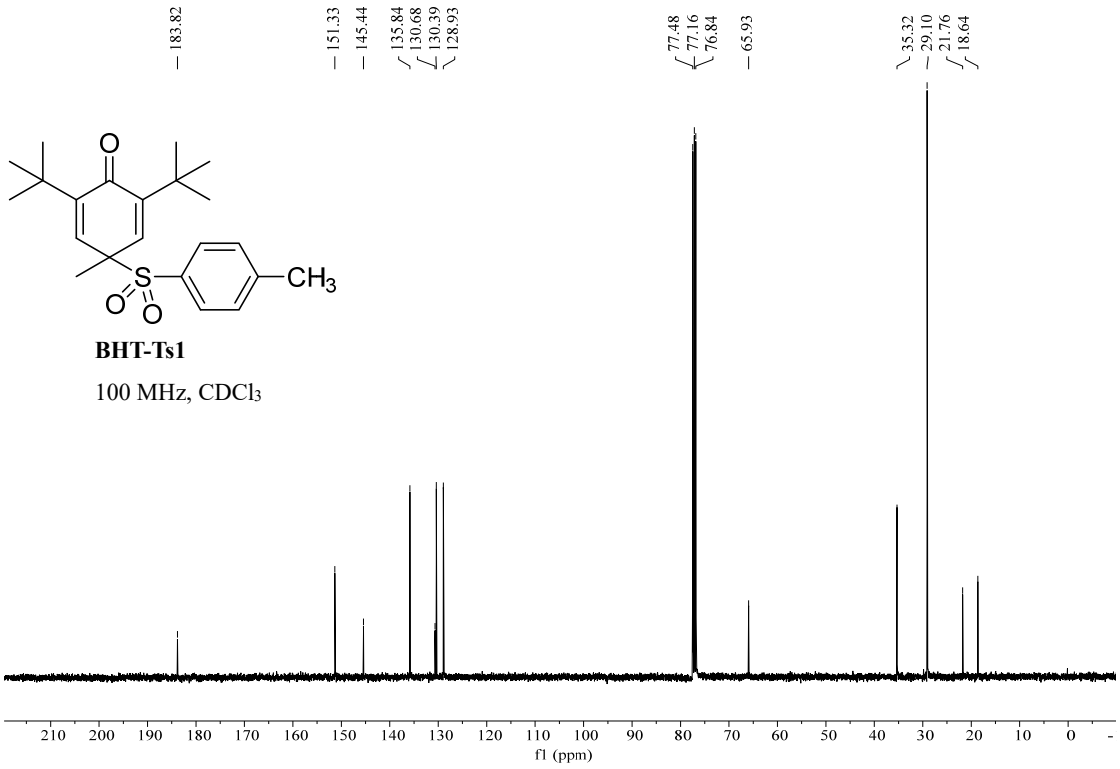
P-1

376 MHz, $CDCl_3$



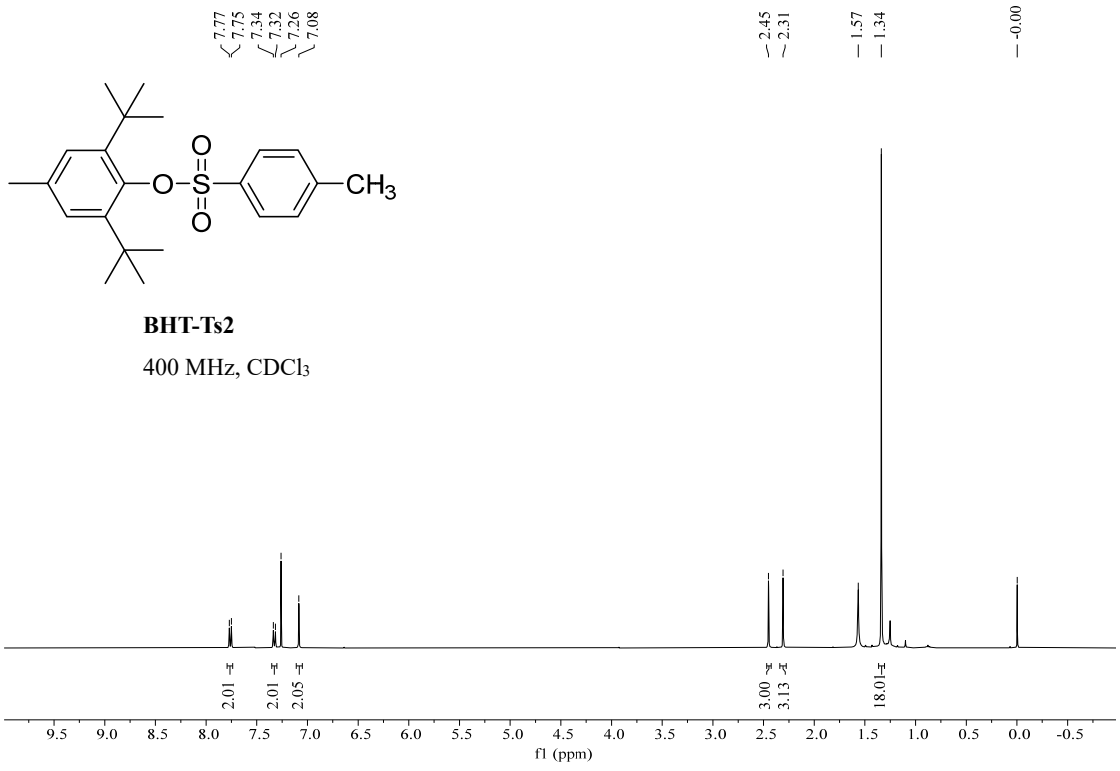
BHT-Ts1

400 MHz, $CDCl_3$



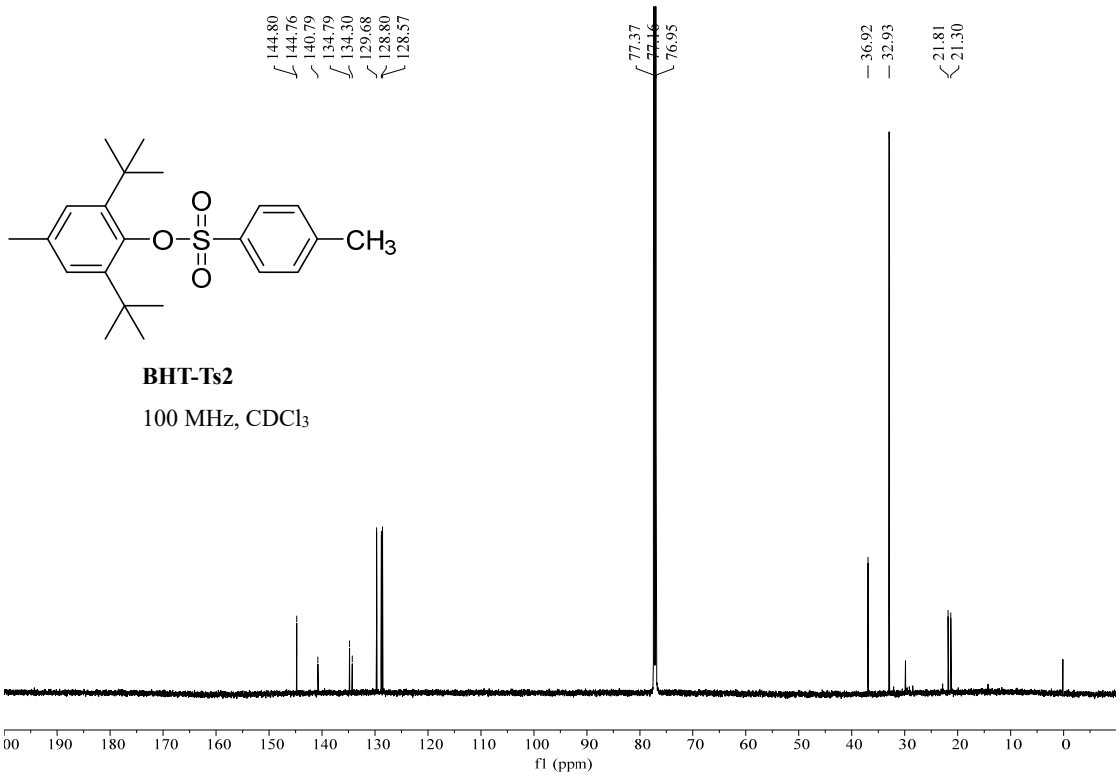
BHT-Ts1

100 MHz, $CDCl_3$



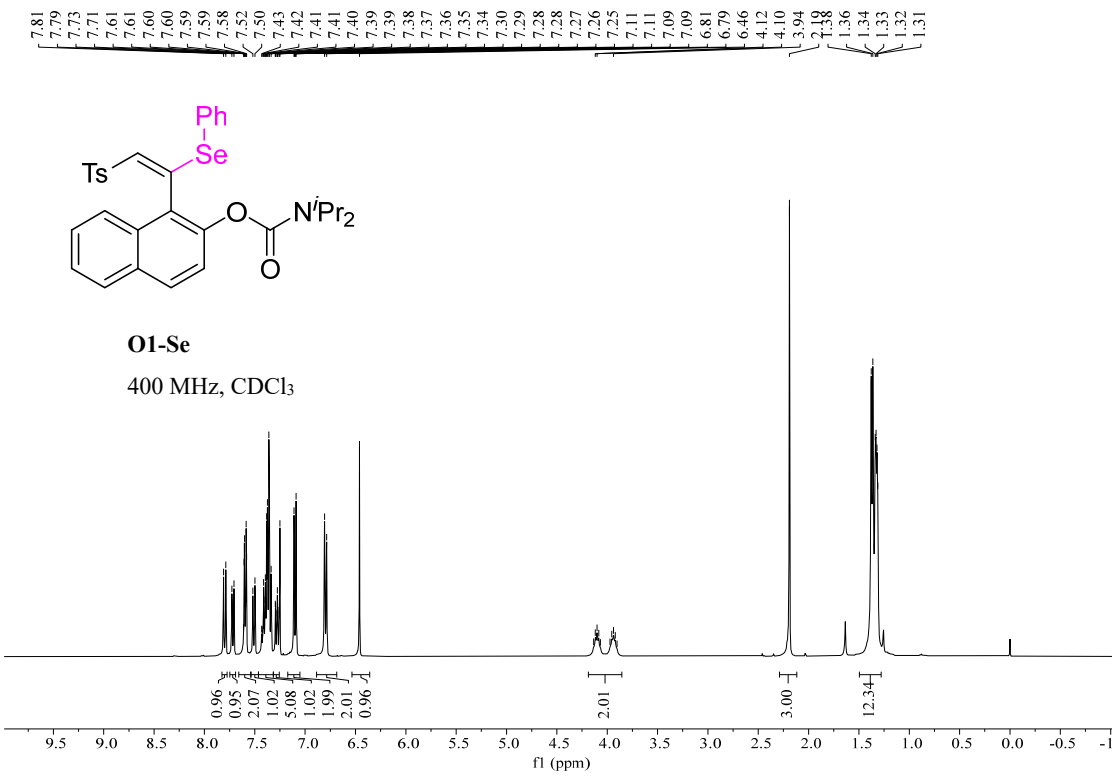
BHT-Ts2

400 MHz, $CDCl_3$



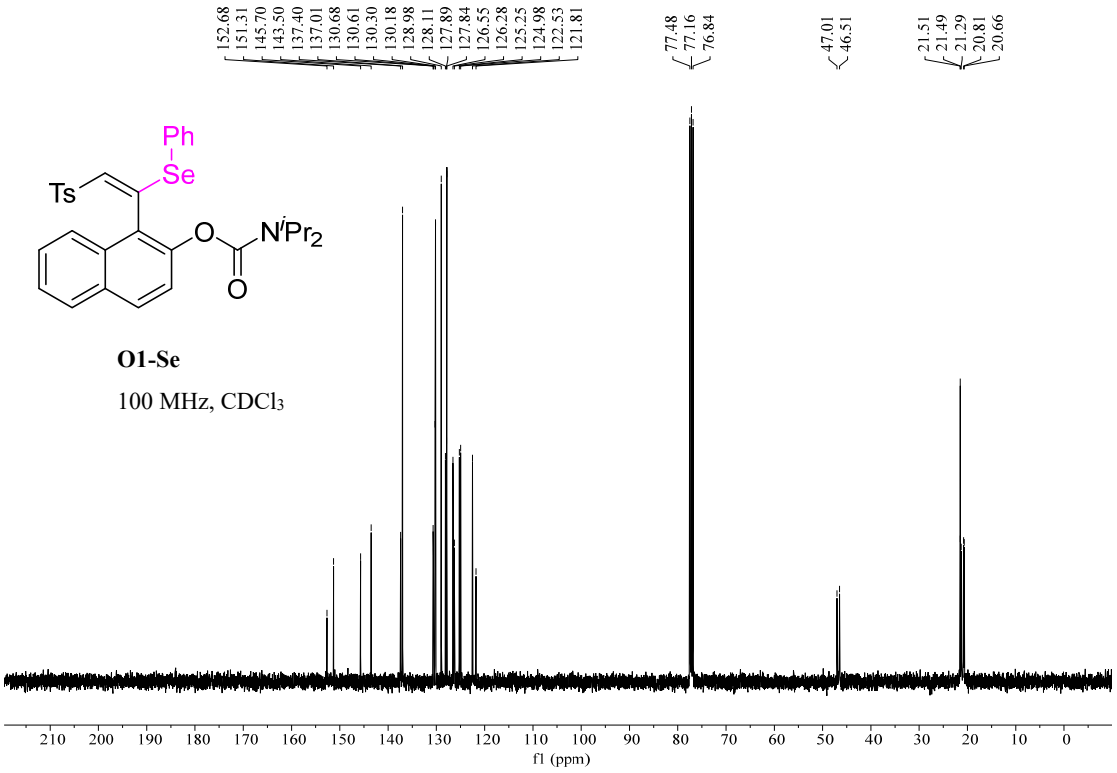
BHT-Ts2

100 MHz, $CDCl_3$



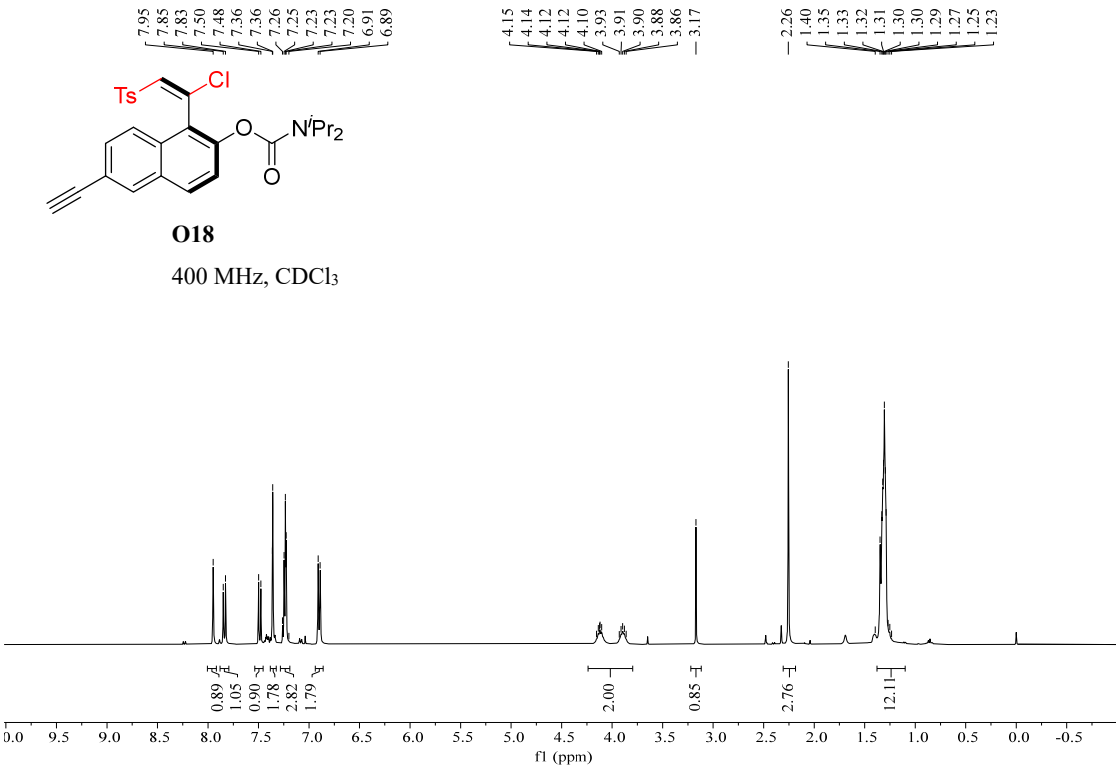
O1-Se

400 MHz, $CDCl_3$



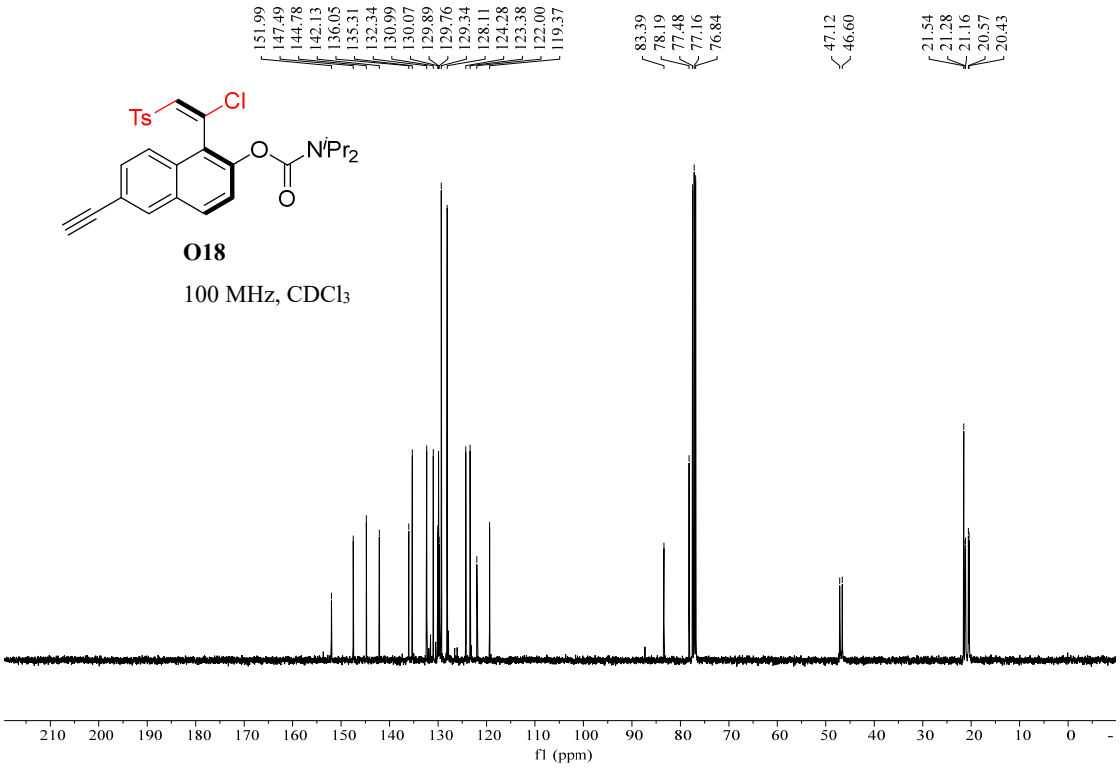
O1-Se

100 MHz, $CDCl_3$



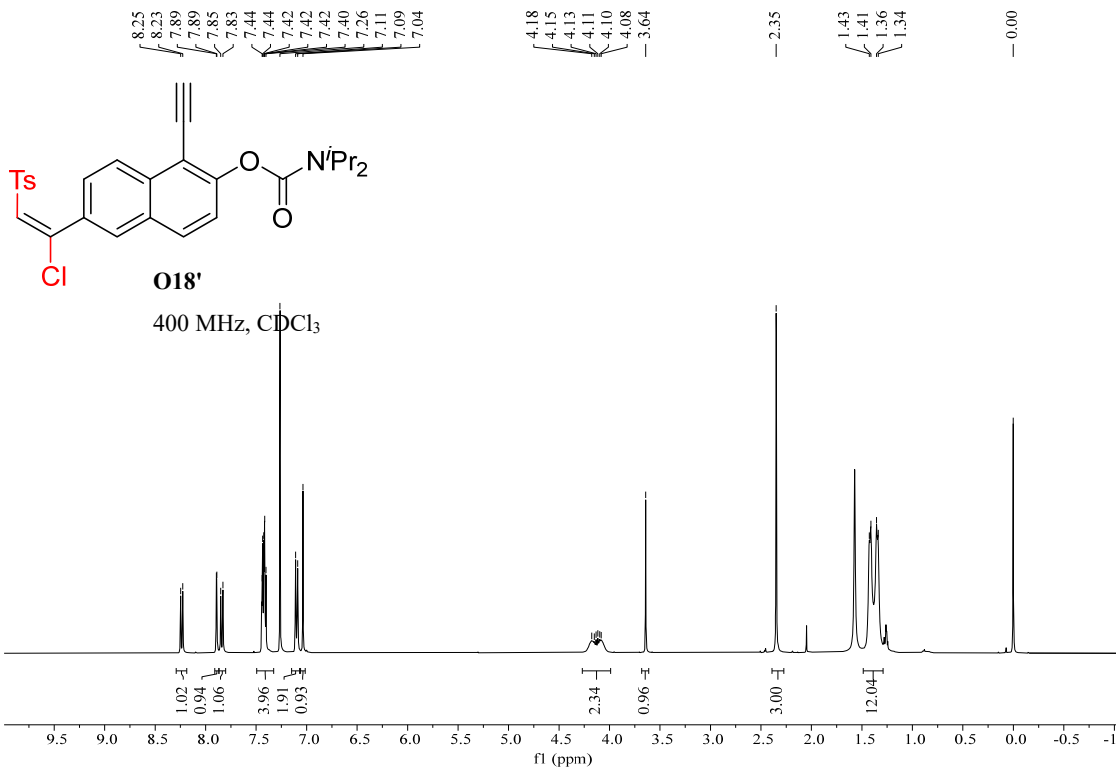
O18

400 MHz, $CDCl_3$



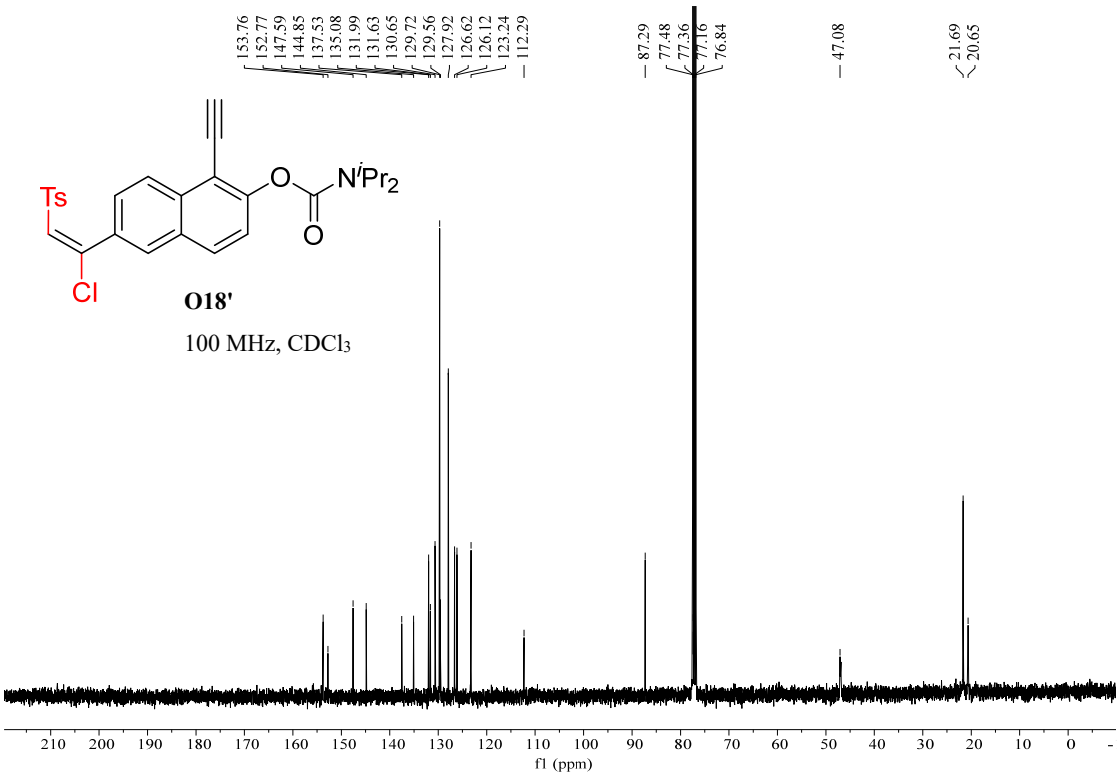
O18

100 MHz, $CDCl_3$



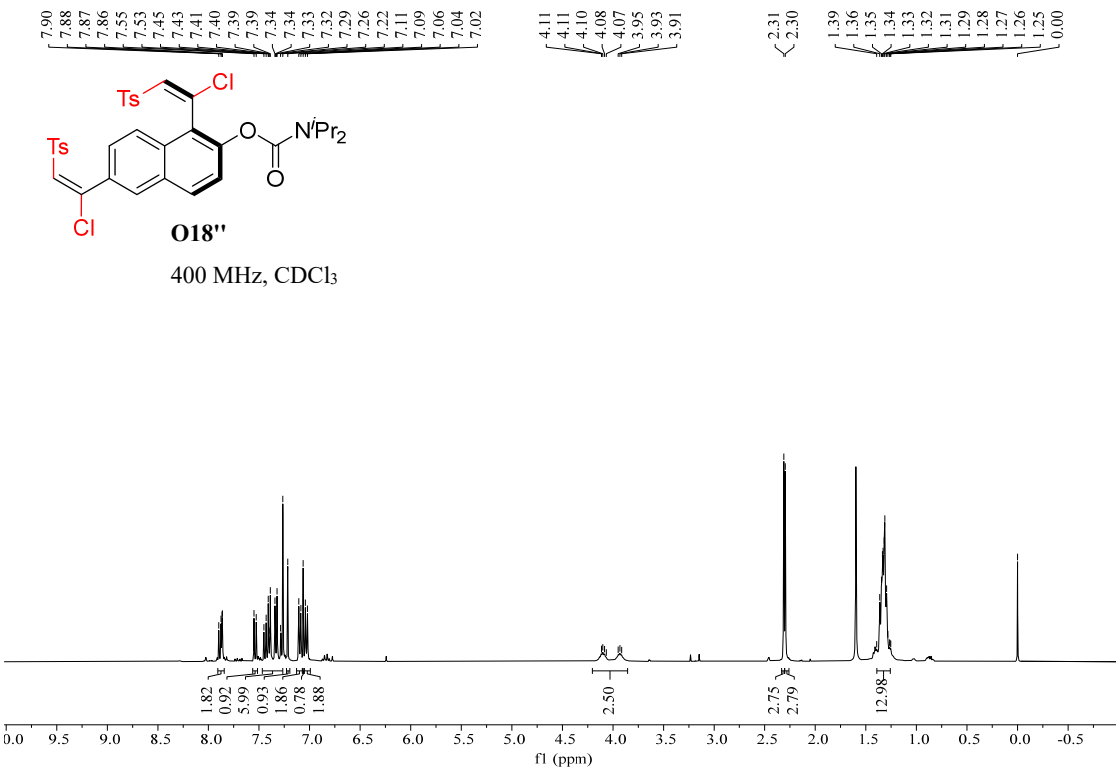
O18'

400 MHz, $CDCl_3$



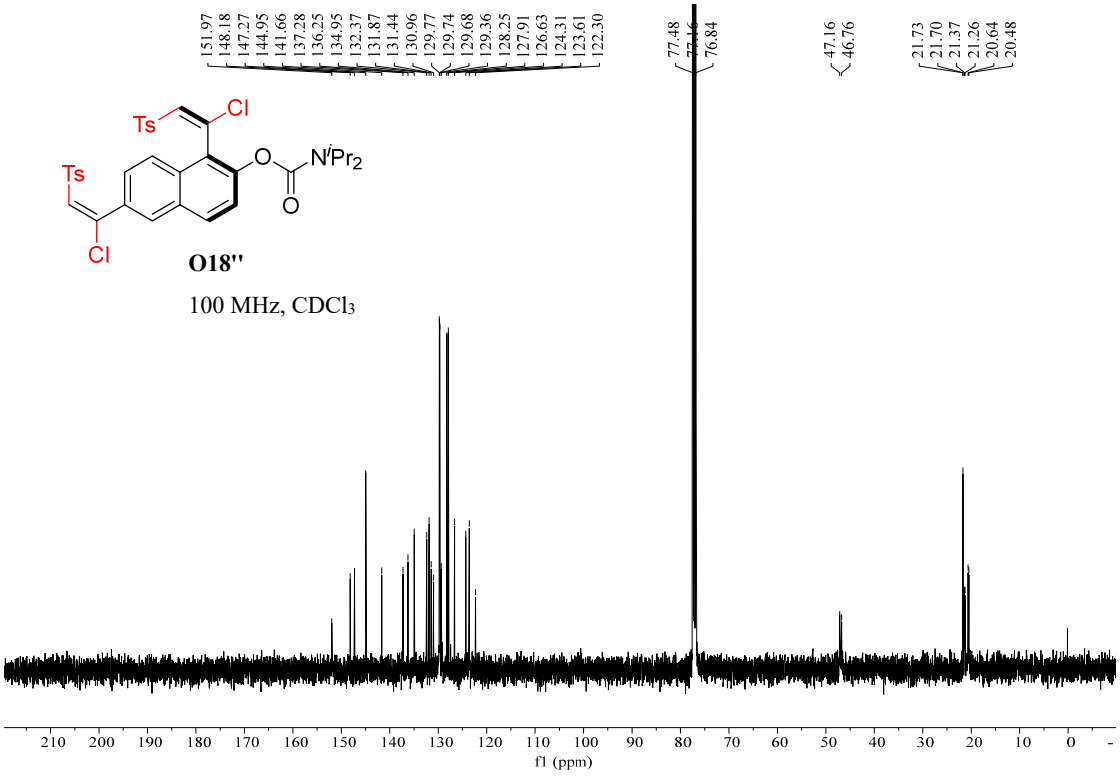
O18'

100 MHz, $CDCl_3$



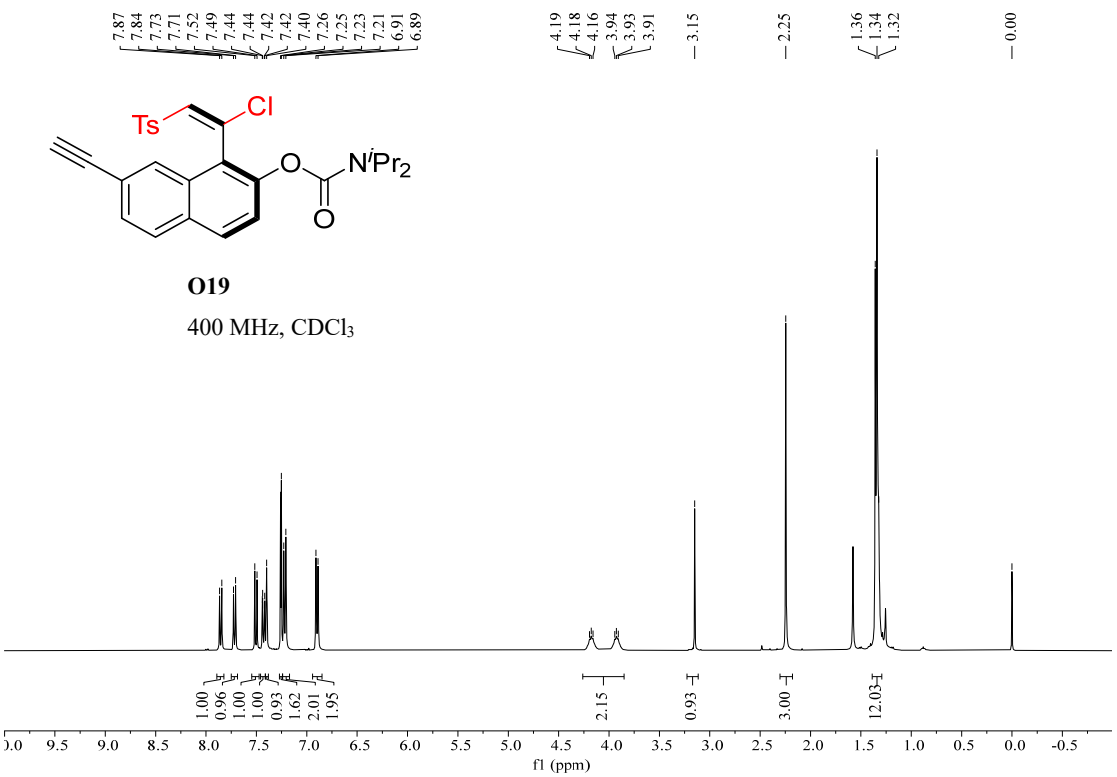
O18''

400 MHz, $CDCl_3$



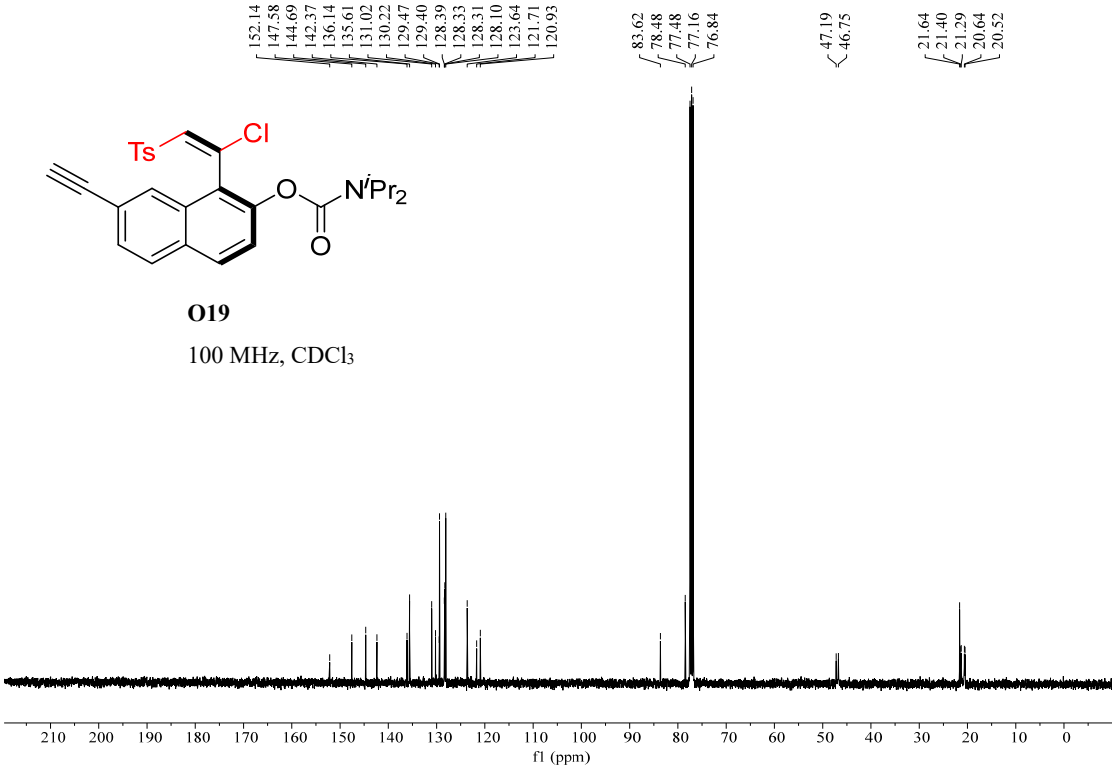
O18''

100 MHz, $CDCl_3$



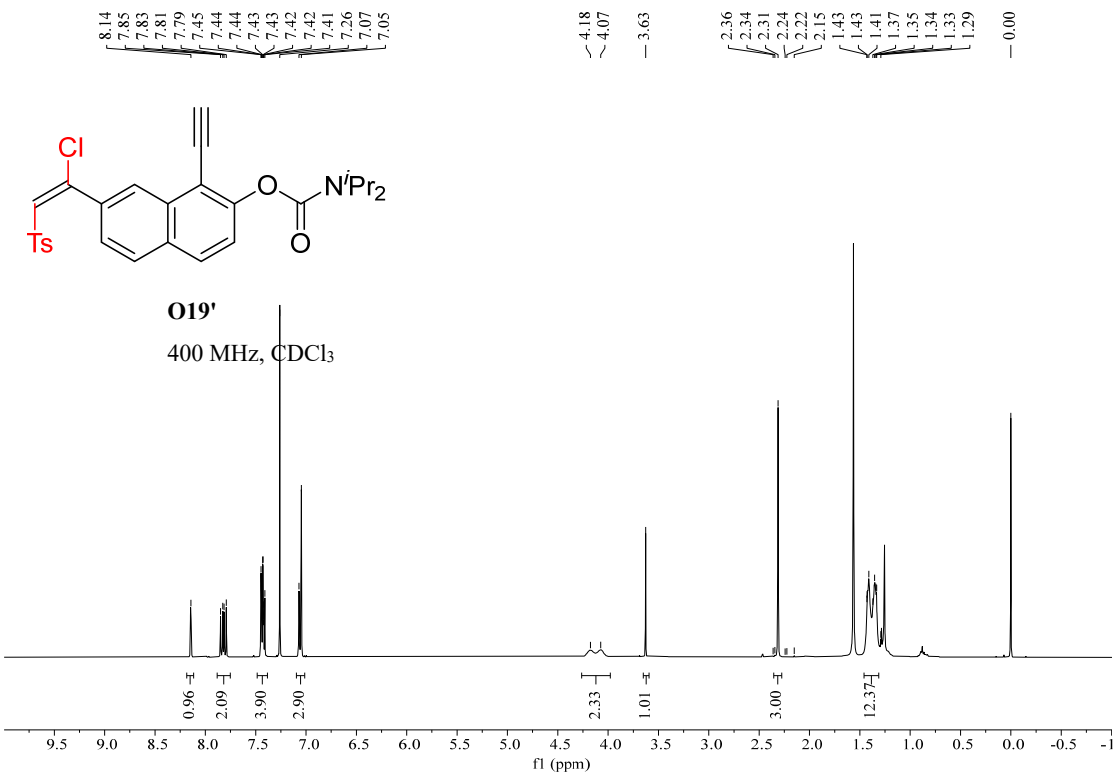
O19

400 MHz, $CDCl_3$



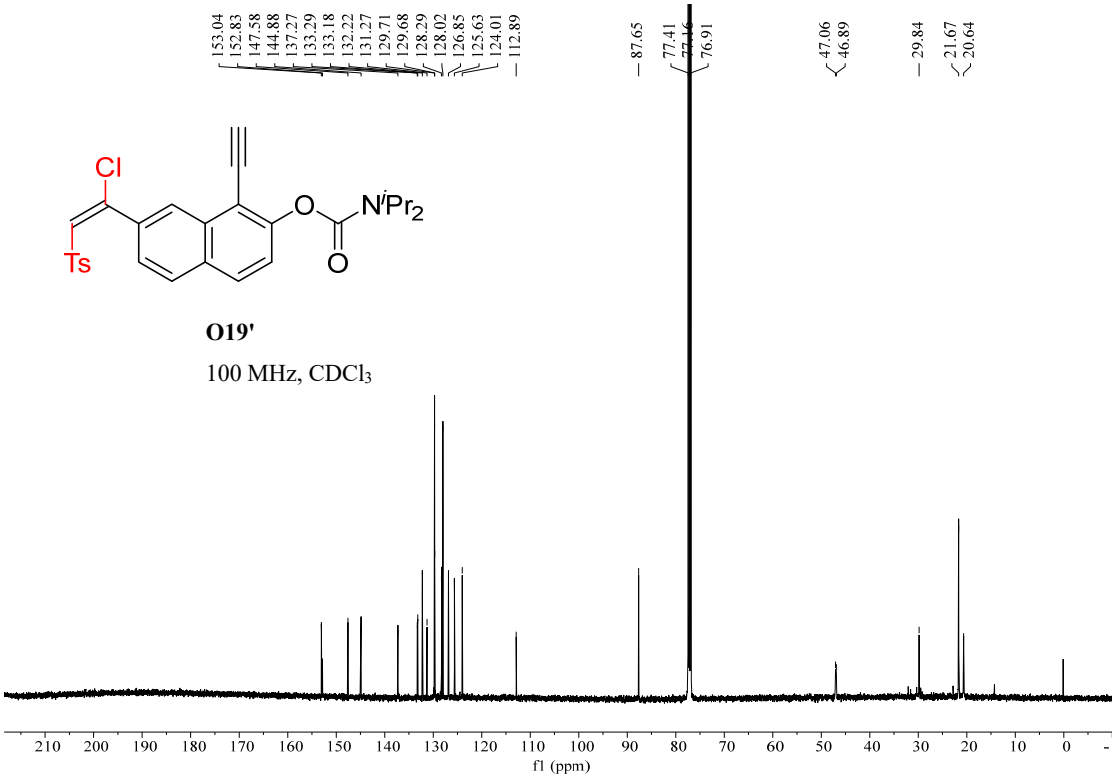
O19

100 MHz, $CDCl_3$



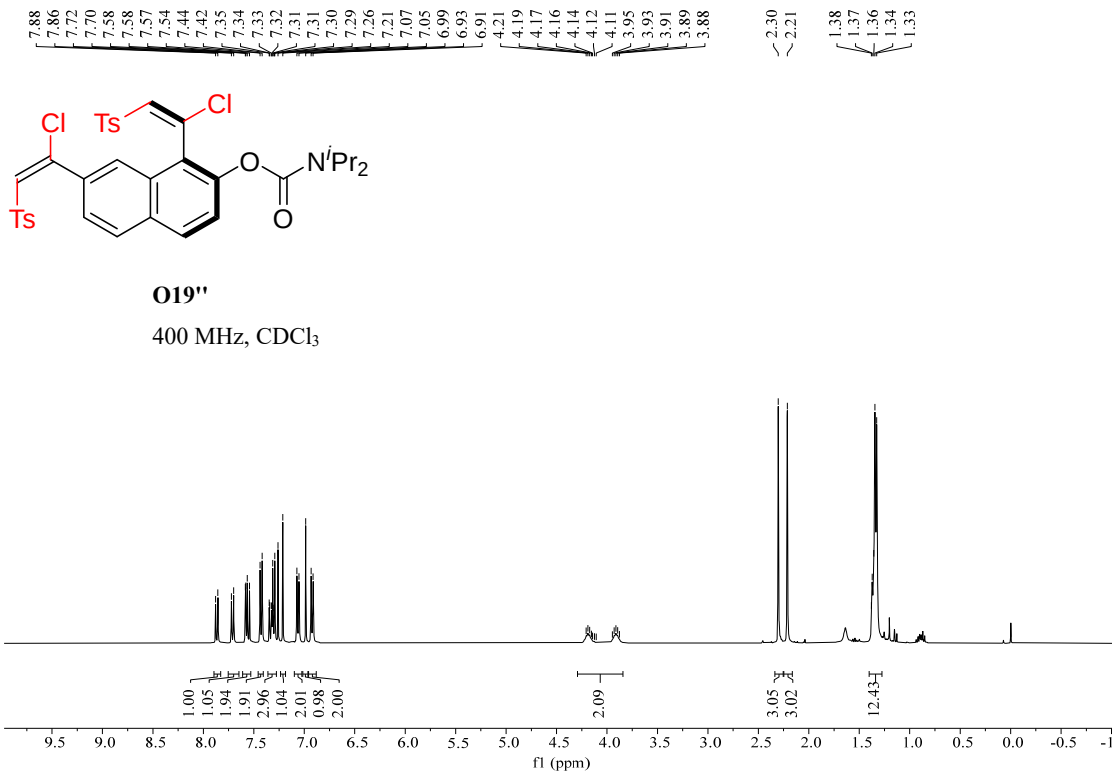
O19'

400 MHz, $CDCl_3$



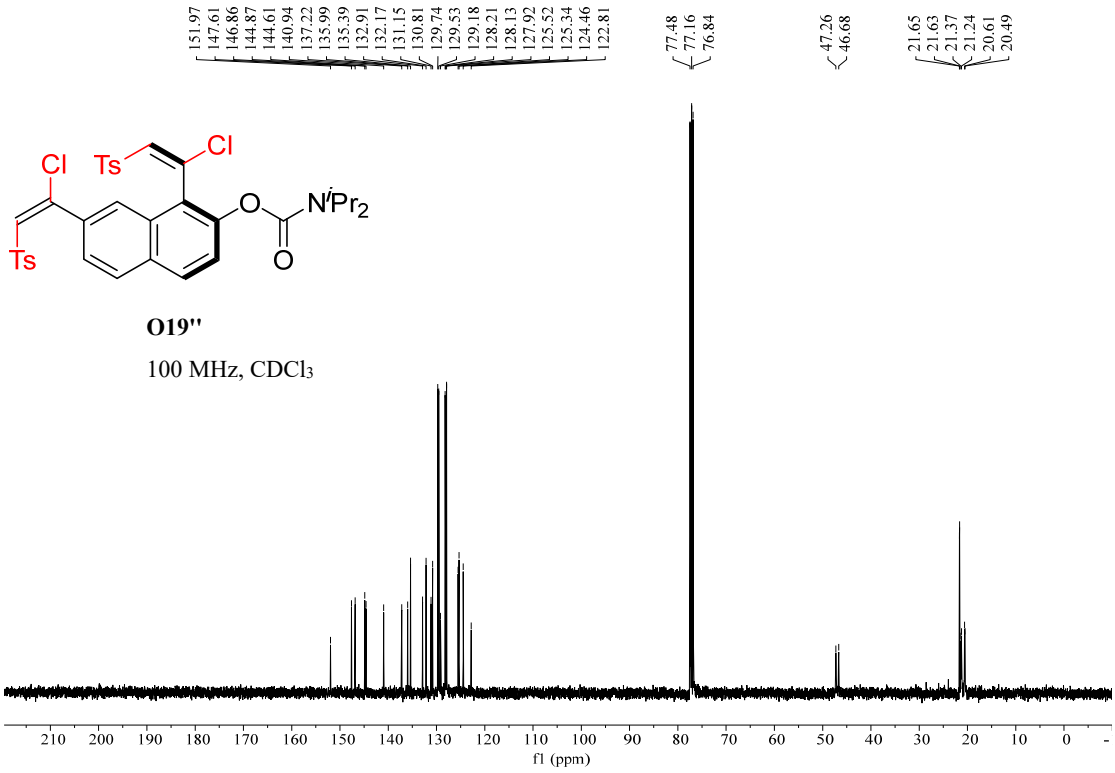
O19'

100 MHz, $CDCl_3$



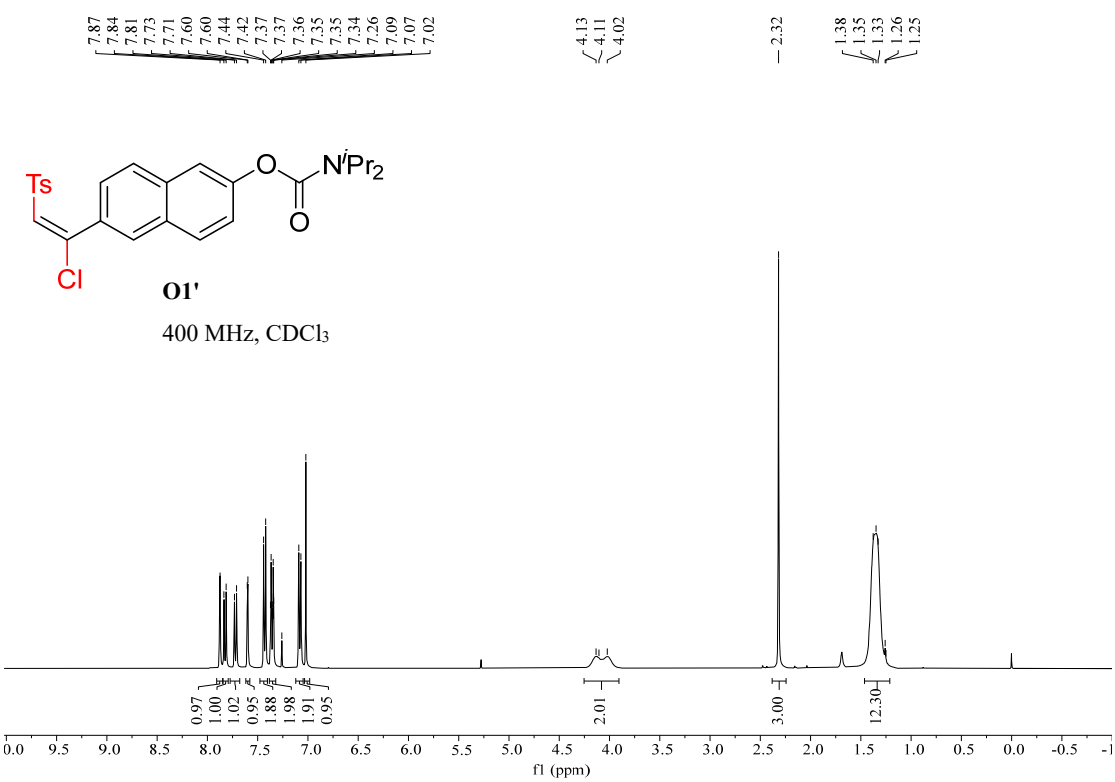
O19''

400 MHz, $CDCl_3$



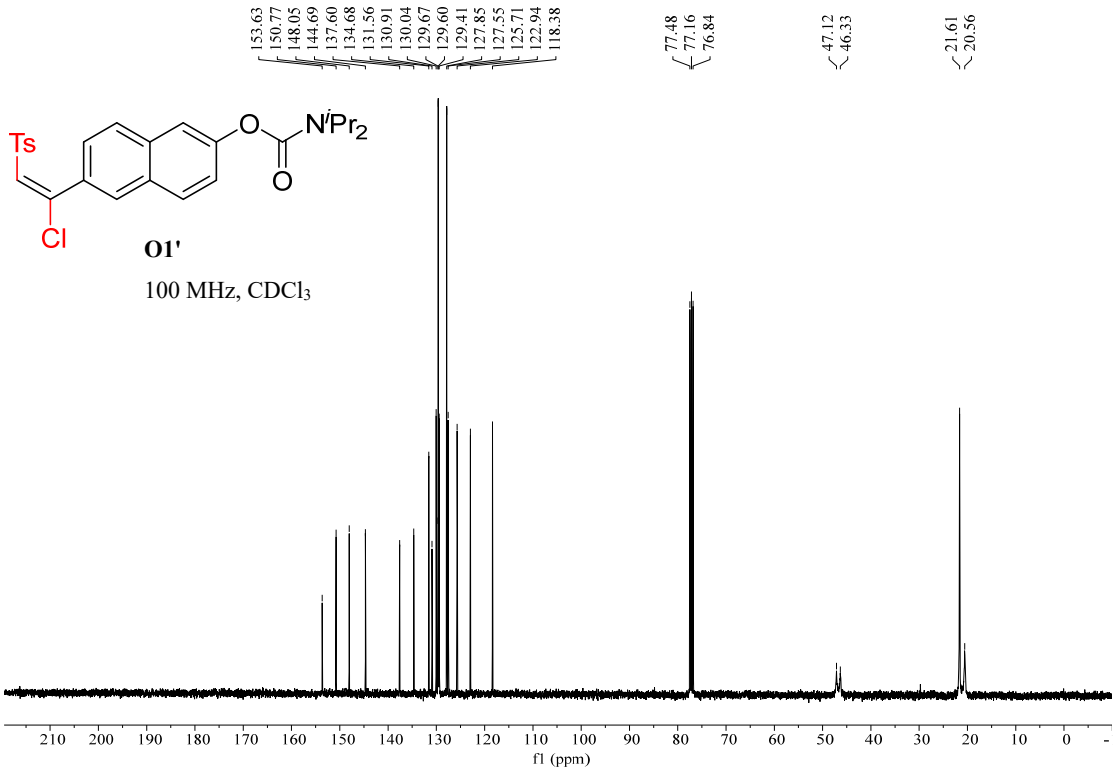
O19''

100 MHz, $CDCl_3$



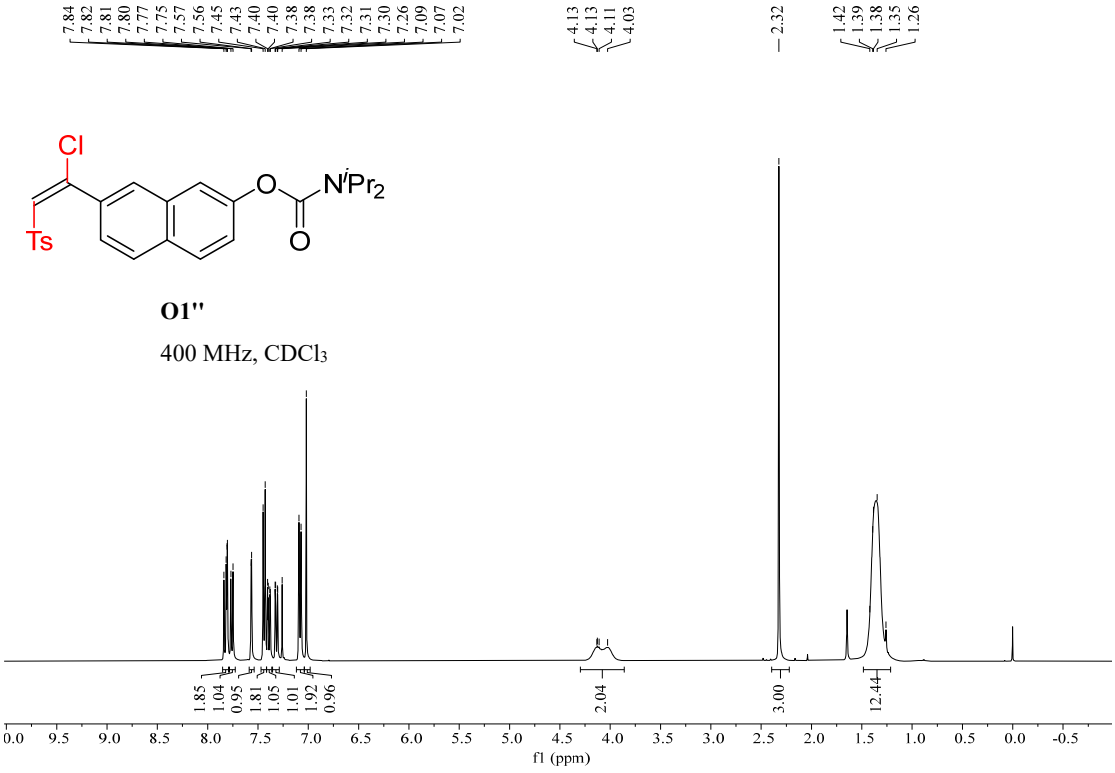
O1'

400 MHz, $CDCl_3$



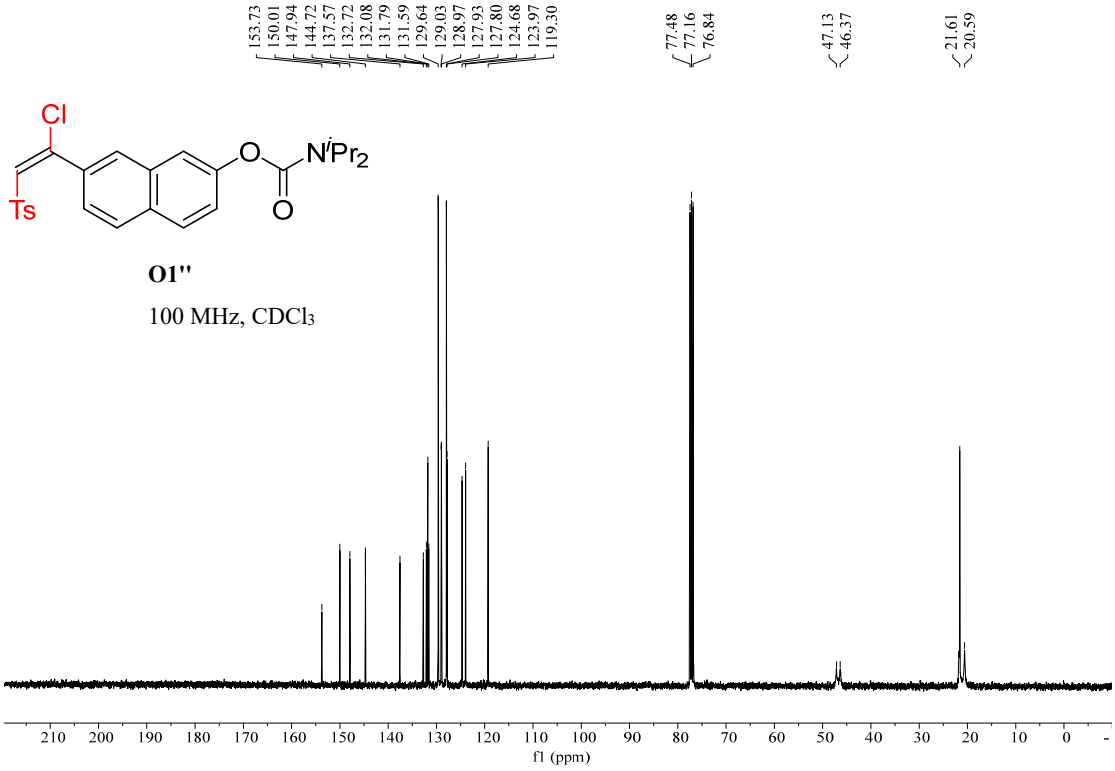
O1'

100 MHz, $CDCl_3$



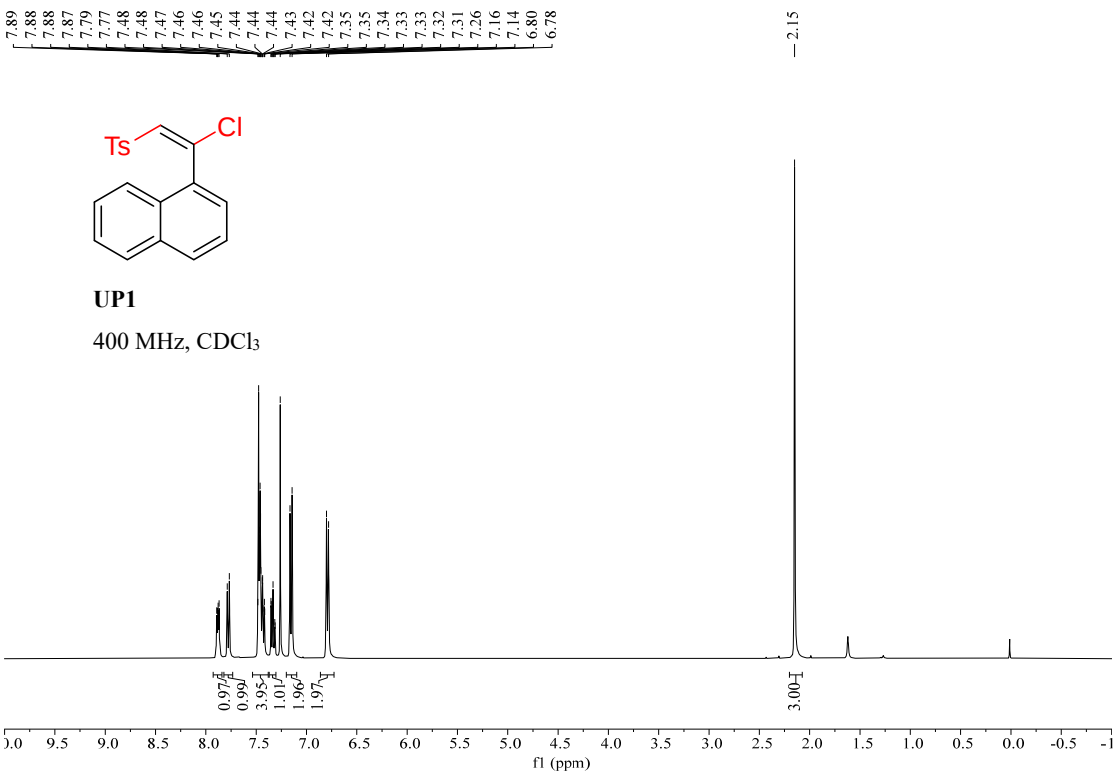
O1''

400 MHz, $CDCl_3$



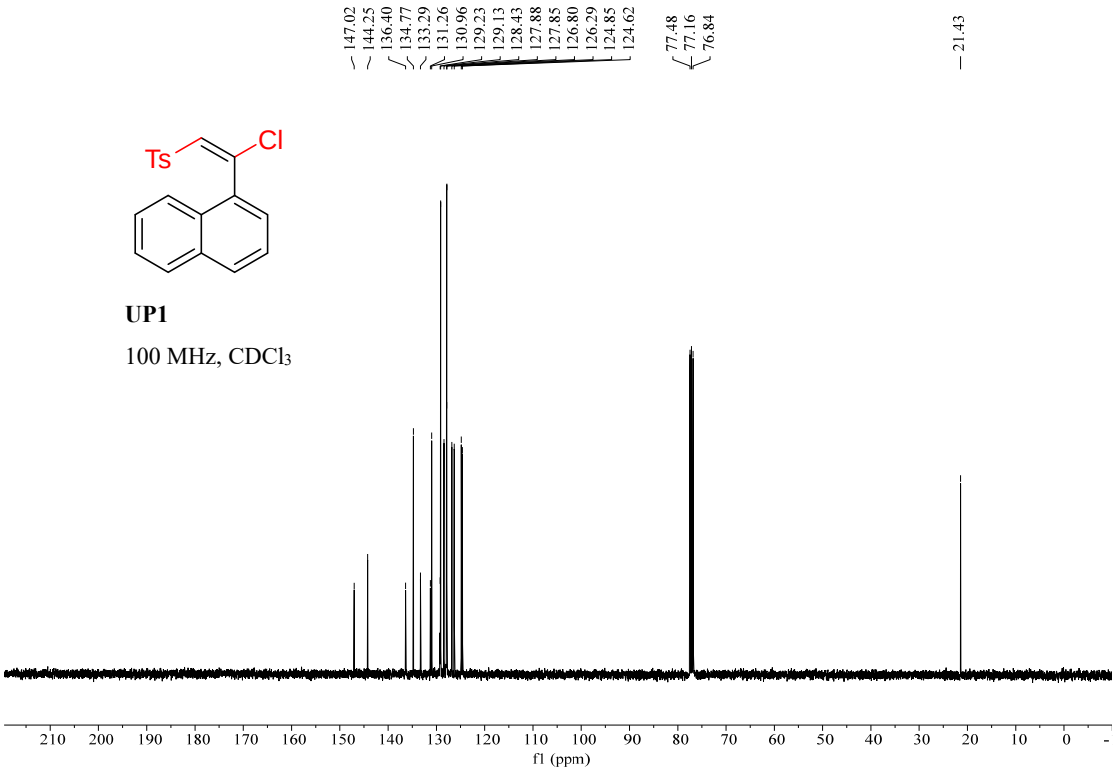
O1"

100 MHz, $CDCl_3$



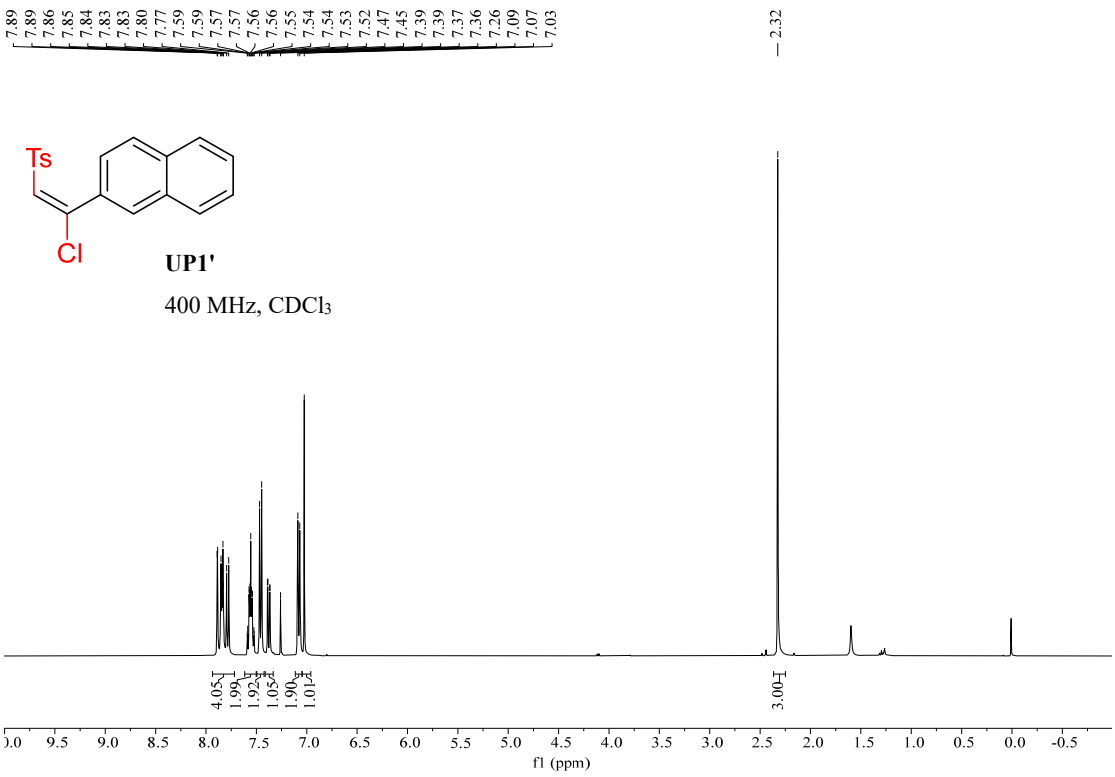
UP1

400 MHz, $CDCl_3$



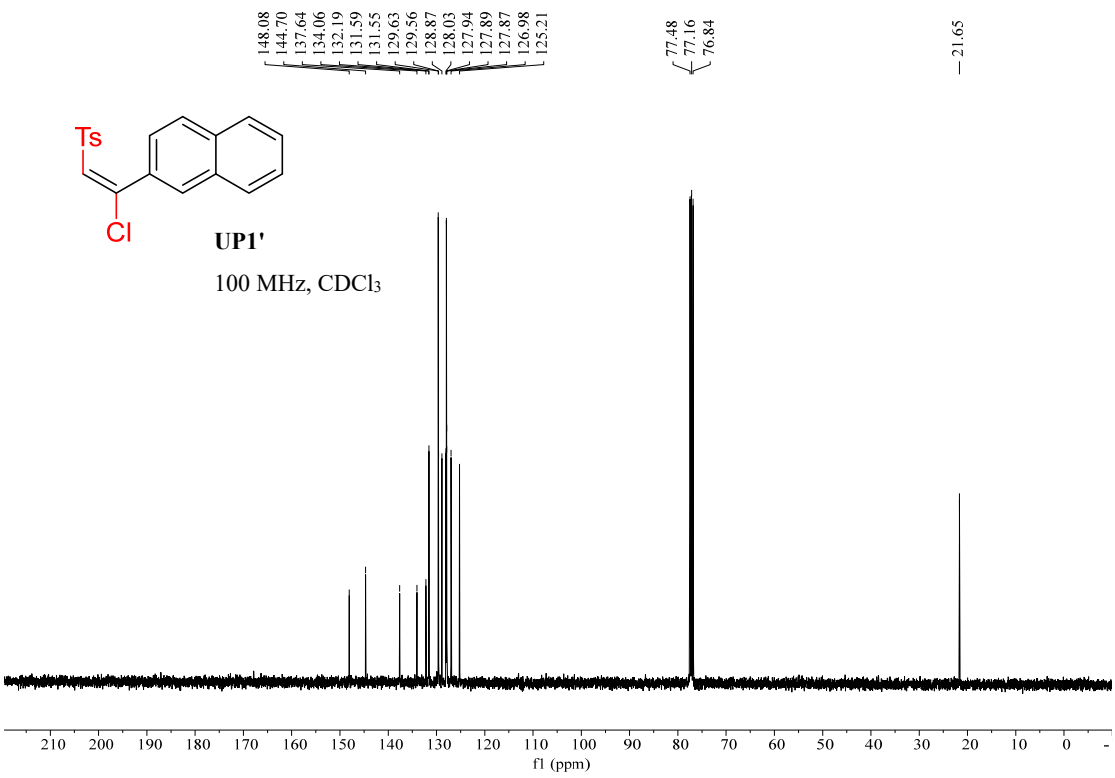
UP1

100 MHz, $CDCl_3$

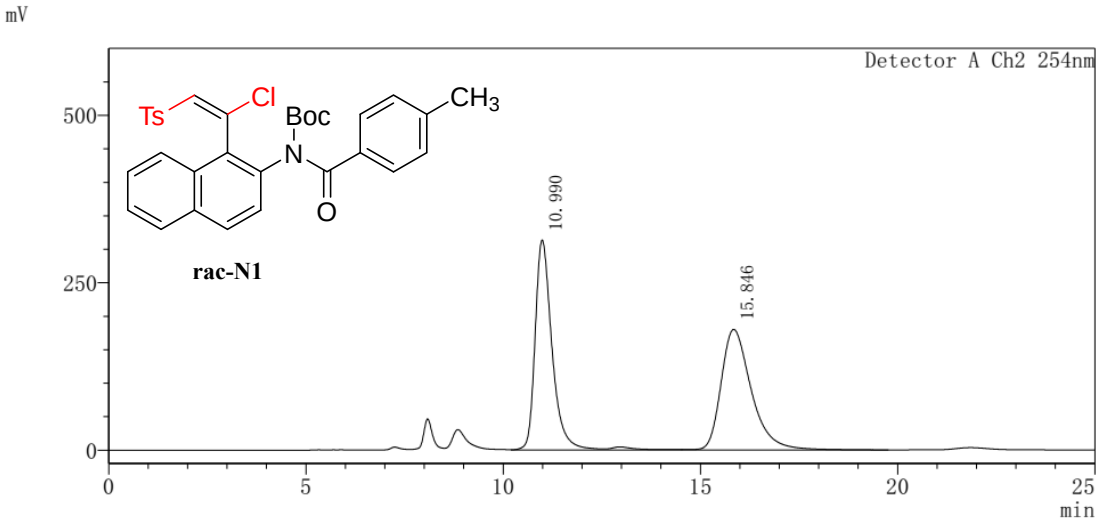


UP1'

400 MHz, $CDCl_3$


148.08
144.70
137.64
134.06
132.19
131.59
131.55
129.63
129.56
128.87
128.03
127.94
127.89
127.87
126.98
125.21
77.48
77.16
76.84
21.65
Ts
Cl
UP1'
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)

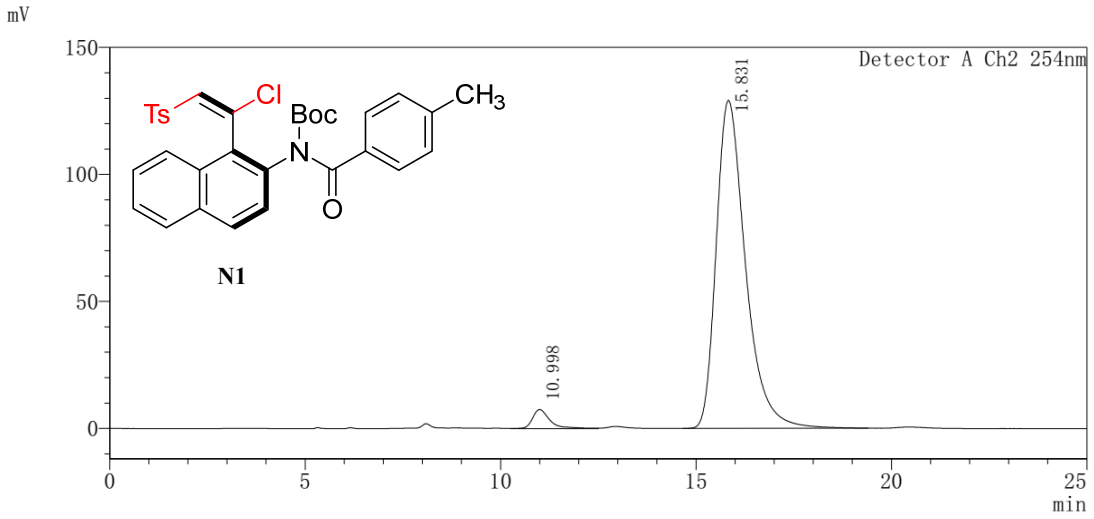
HPLC spectra



Peak Table

Detector A Ch2 254nm

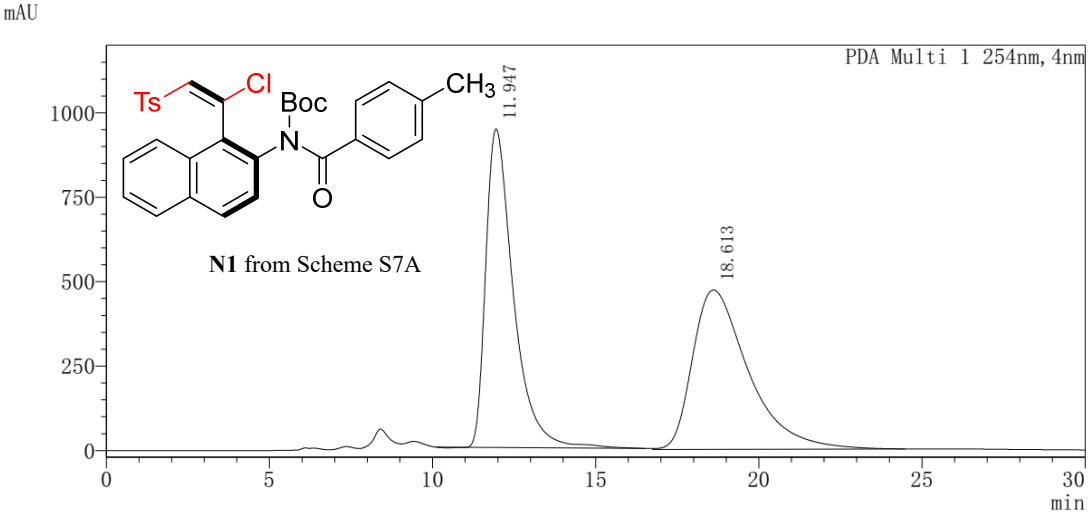
Peak#	Ret. Time	Area	Area%
1	10.990	9522509	49.740
2	15.846	9621930	50.260



Peak Table

Detector A Ch2 254nm

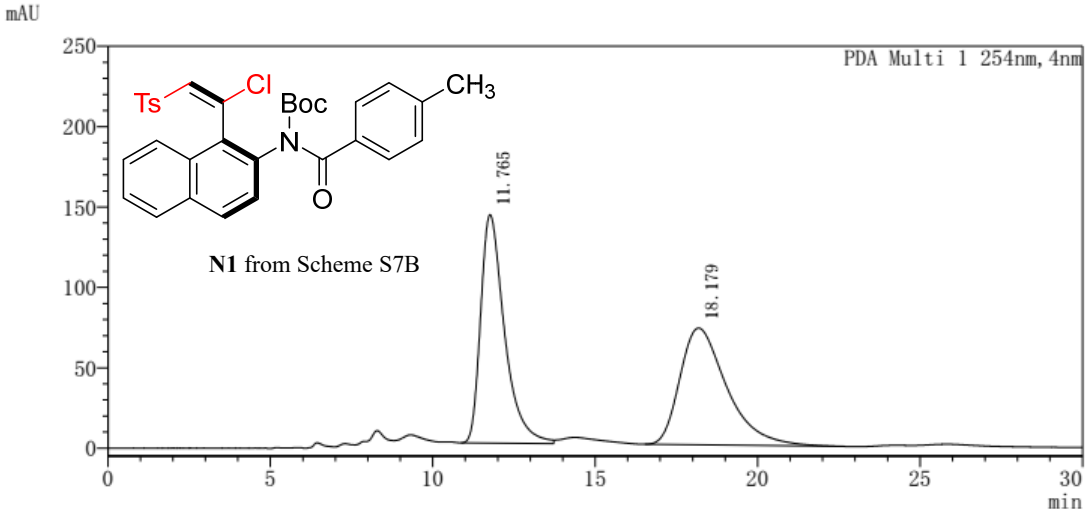
Peak#	Ret. Time	Area	Area%
1	10.998	231530	3.321
2	15.831	6739893	96.679



Peak Table

PDA Ch1 254nm

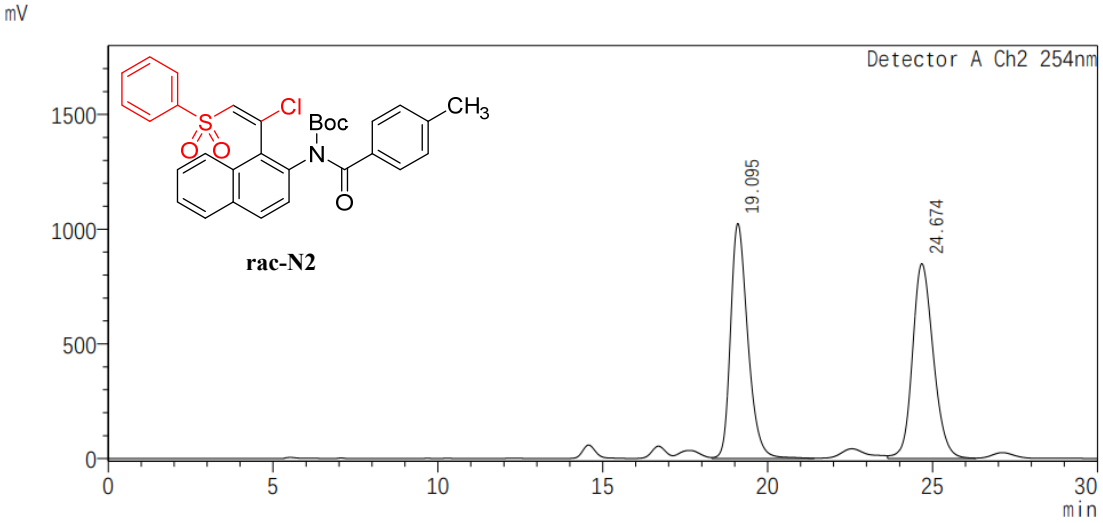
Peak#	Ret. Time	Area	Area%
1	11.947	55743398	49.718
2	18.613	56375876	50.282



Peak Table

PDA Ch1 254nm

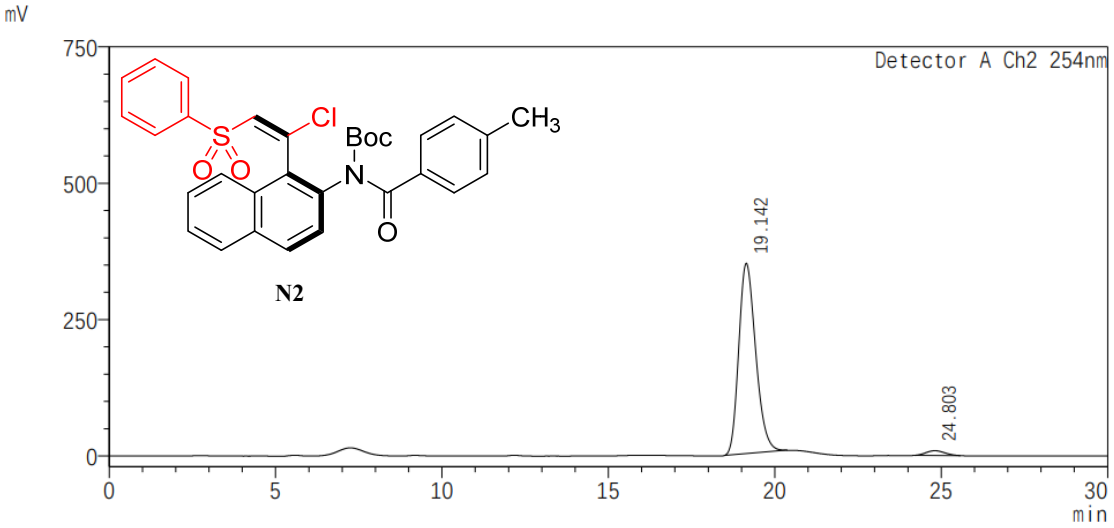
Peak#	Ret. Time	Area	Area%
1	11.765	7276367	49.894
2	18.179	7307268	50.106



Peak Table

Detector A Ch2 254nm

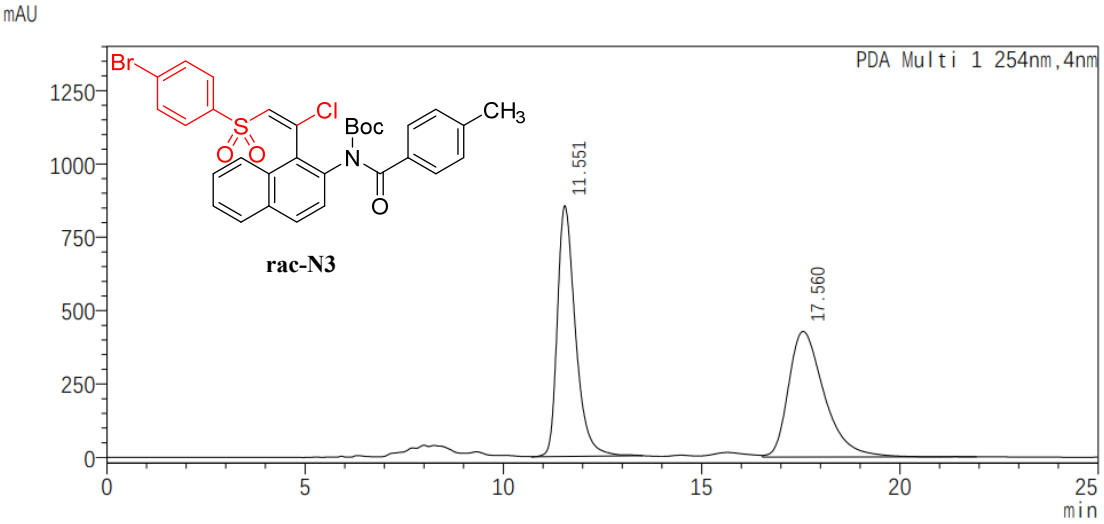
Peak#	Ret. Time	Area	Area%
1	19.095	37492144	49.951
2	24.674	37565899	50.049



Peak Table

Detector A Ch2 254nm

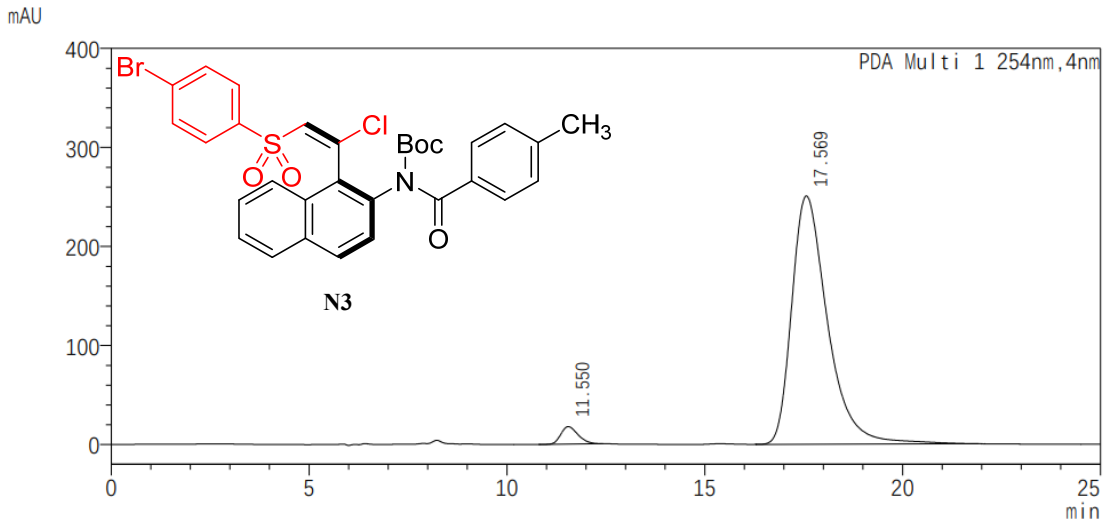
Peak#	Ret. Time	Area	Area%
1	19.142	12346703	97.338
2	24.803	337634	2.662



Peak Table

PDA Ch1 254nm

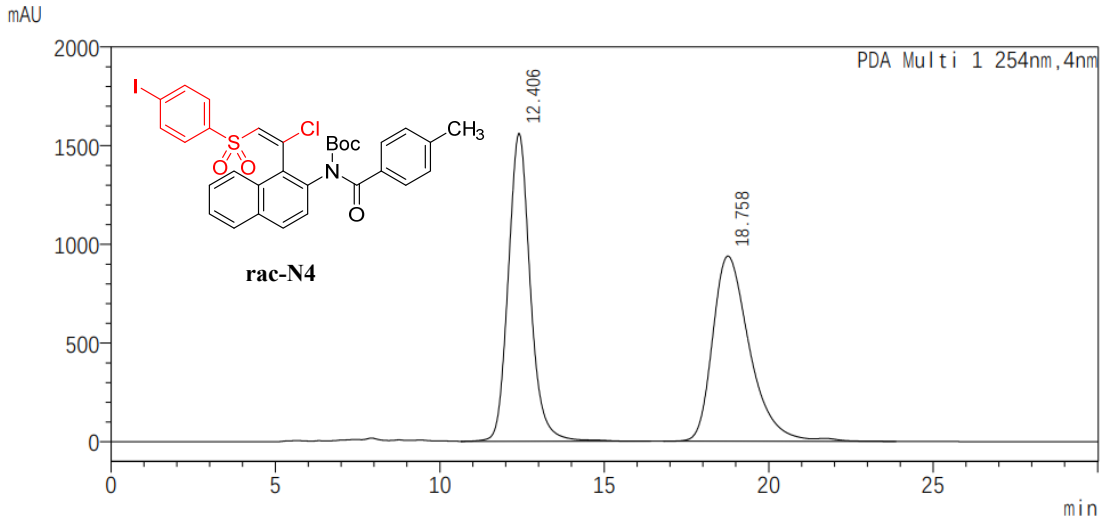
Peak#	Ret. Time	Area	Area%
1	11.551	27114267	50.197
2	17.560	26901814	49.803



Peak Table

PDA Ch1 254nm

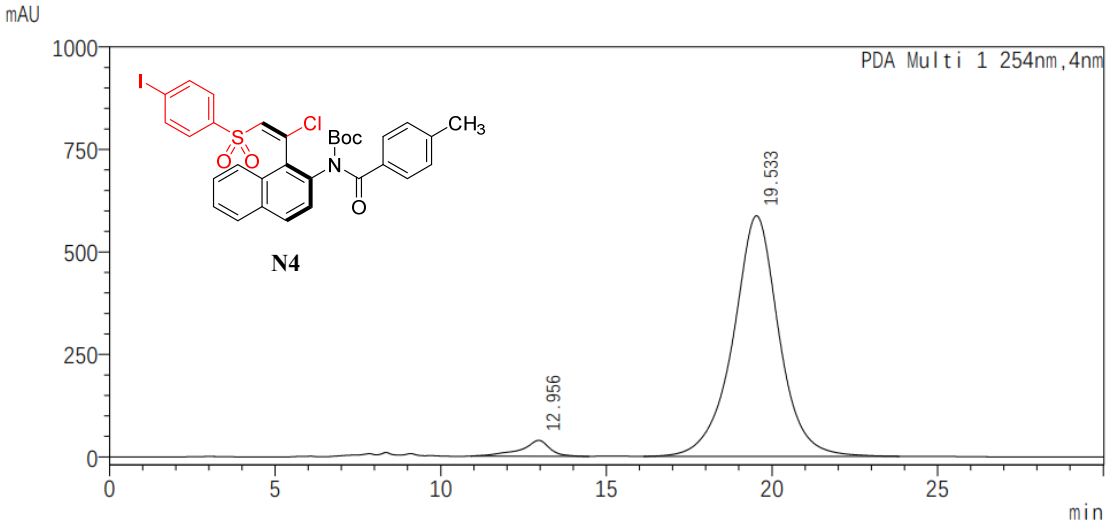
Peak#	Ret. Time	Area	Area%
1	11.550	537458	3.286
2	17.569	15818664	96.714



Peak Table

PDA Ch1 254nm

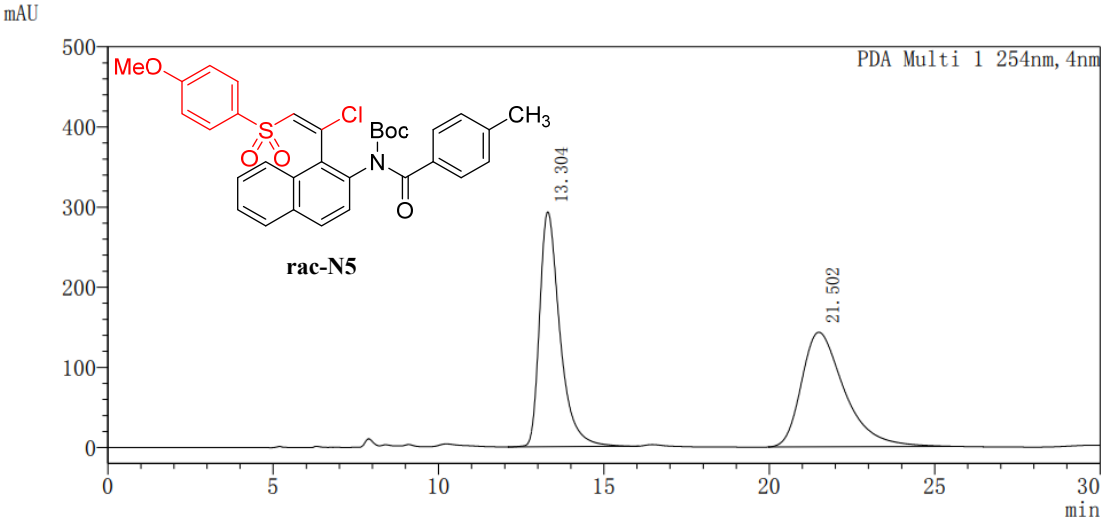
Peak#	Ret. Time	Area	Area%
1	12.406	72691974	49.670
2	18.758	73658660	50.330



Peak Table

PDA Ch1 254nm

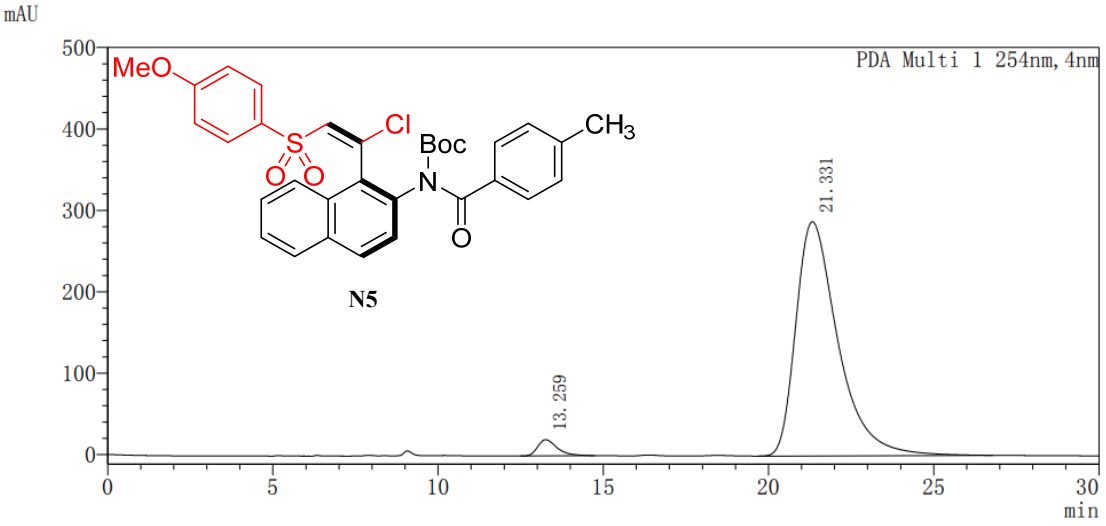
Peak#	Ret. Time	Area	Area%
1	12.956	2346011	3.977
2	19.533	56637486	96.023



Peak Table

PDA Ch1 254nm

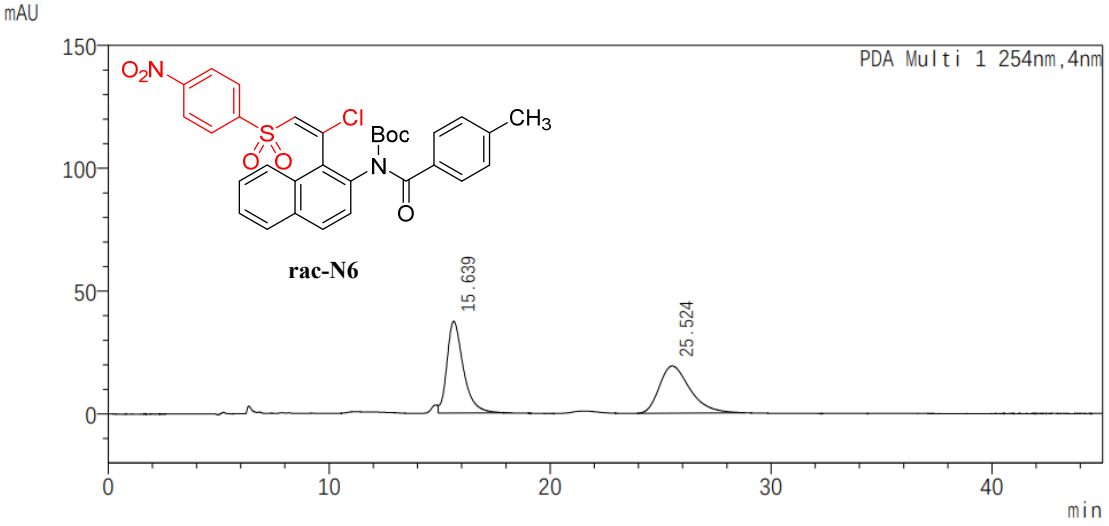
Peak#	Ret. Time	Area	Area%
1	13.304	12508667	49.265
2	21.502	12881893	50.735



Peak Table

PDA Ch1 254nm

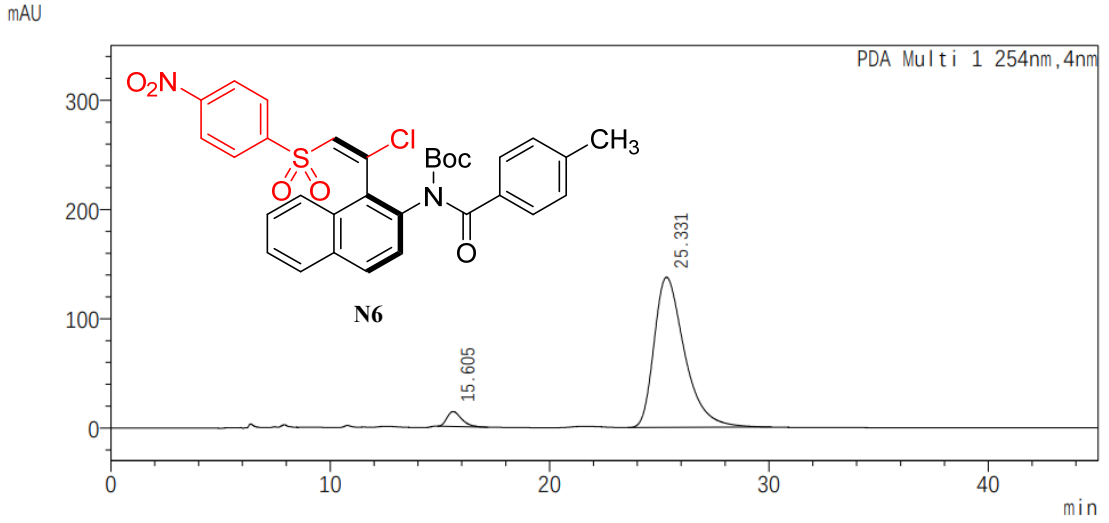
Peak#	Ret. Time	Area	Area%
1	13.259	813881	3.090
2	21.331	25525860	96.910



Peak Table

PDA Ch1 254nm

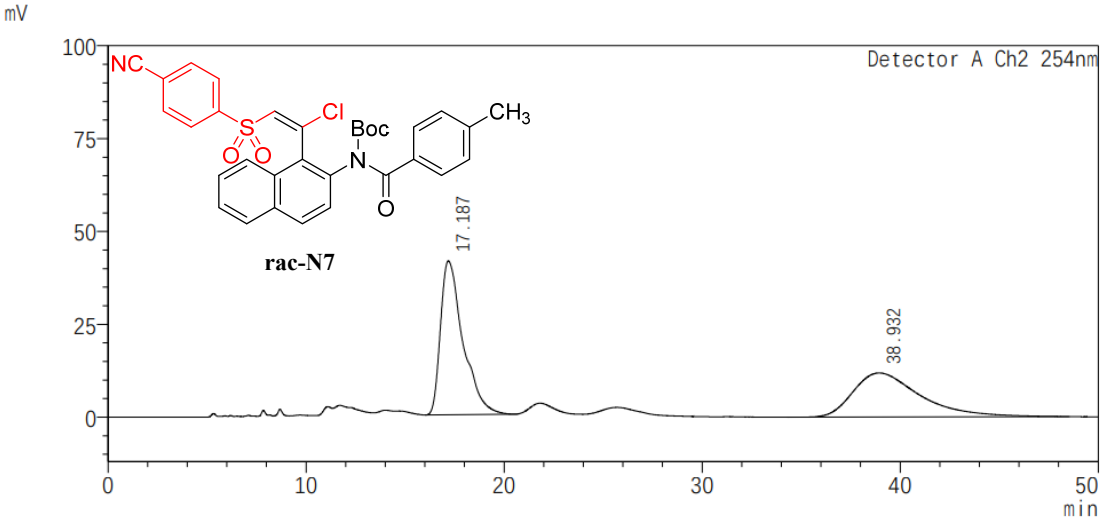
Peak#	Ret. Time	Area	Area%
1	15.639	1933405	51.123
2	25.524	1848452	48.877



Peak Table

PDA Ch1 254nm

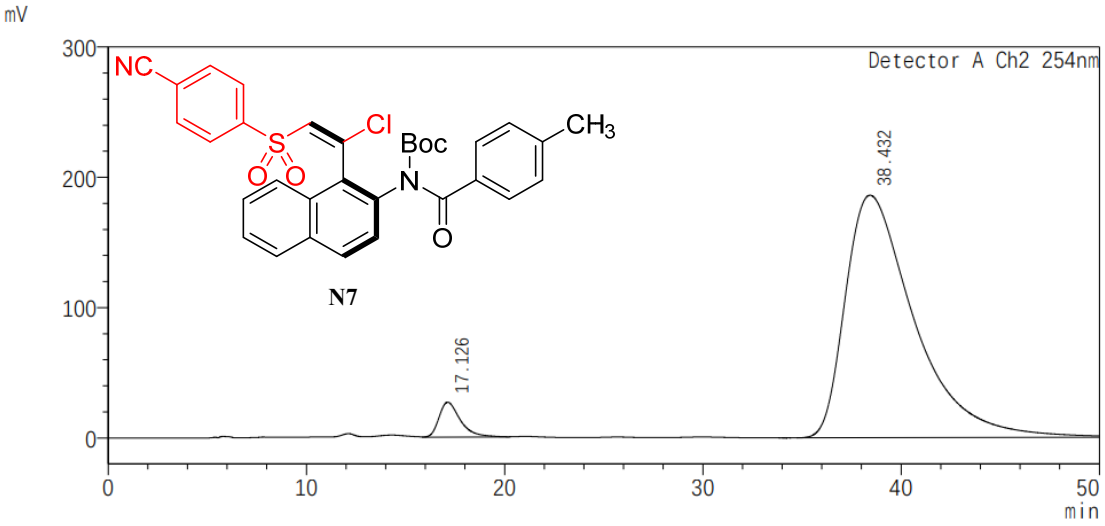
Peak#	Ret. Time	Area	Area%
1	15.605	636021	4.564
2	25.331	13299917	95.436



Peak Table

Detector A Ch2 254nm

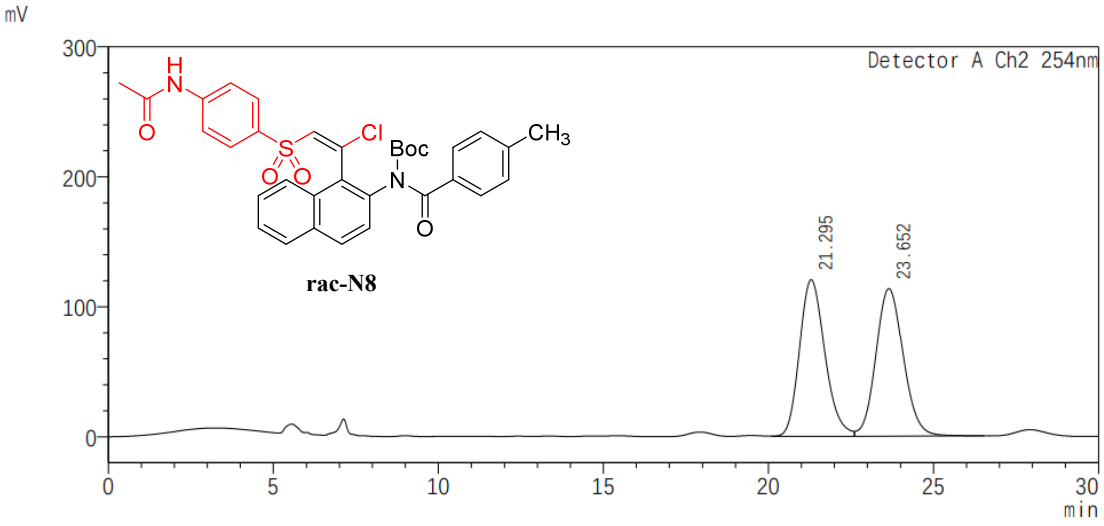
Peak#	Ret. Time	Area	Area%
1	17.187	3270238	53.958
2	38.932	2790450	46.042



Peak Table

Detector A Ch2 254nm

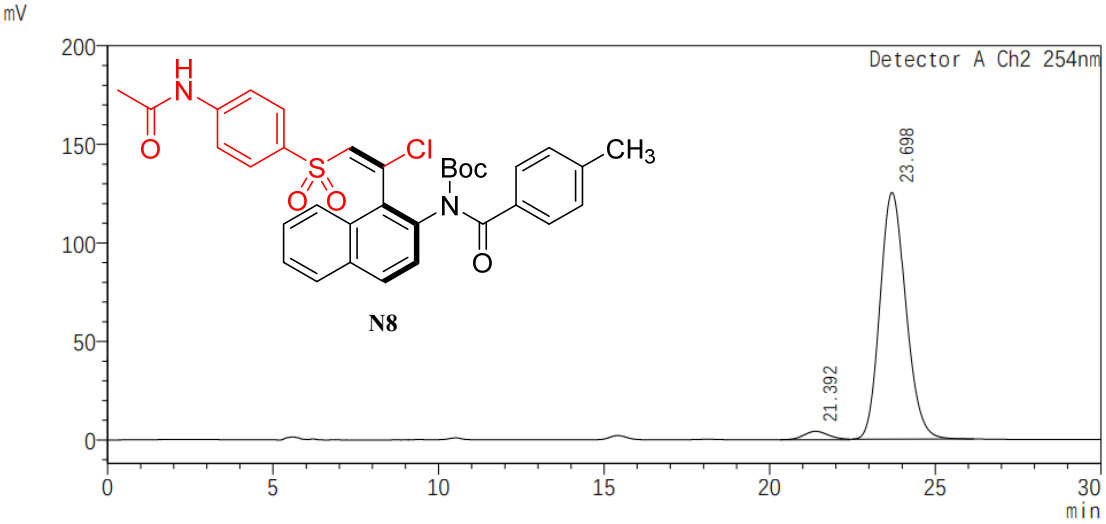
Peak#	Ret. Time	Area	Area%
1	17.126	1994510	4.238
2	38.432	45067244	95.762



Peak Table

Detector A Ch2 254nm

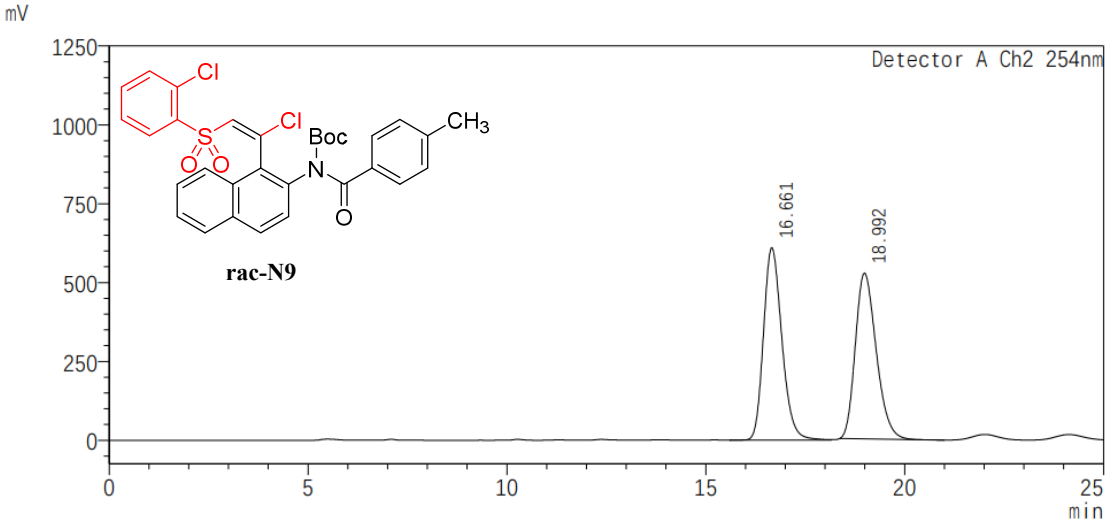
Peak#	Ret. Time	Area	Area%
1	21.295	6466330	49.654
2	23.652	6556497	50.346



Peak Table

Detector A Ch2 254nm

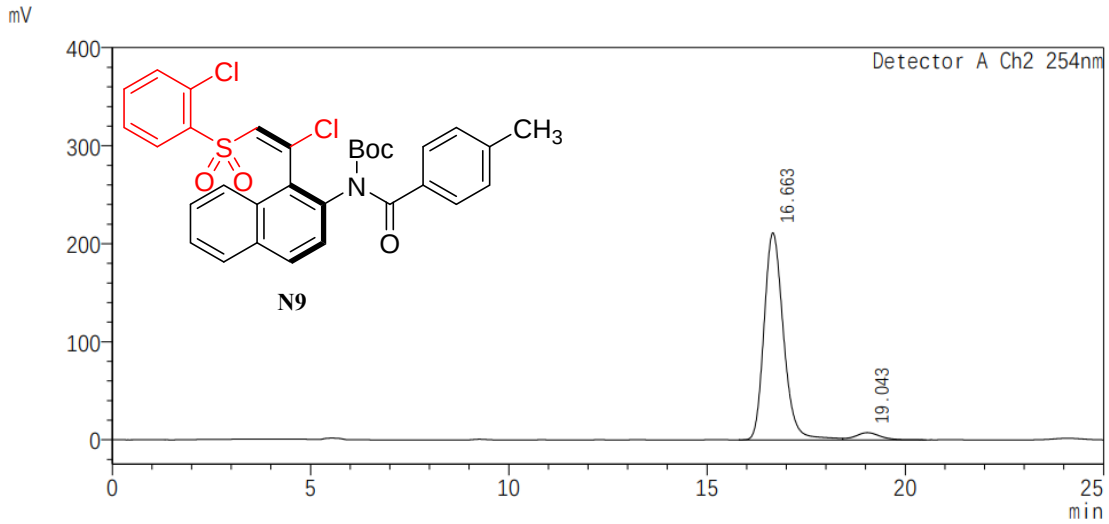
Peak#	Ret. Time	Area	Area%
1	21.392	224123	3.197
2	23.698	6785282	96.803



Peak Table

Detector A Ch2 254nm

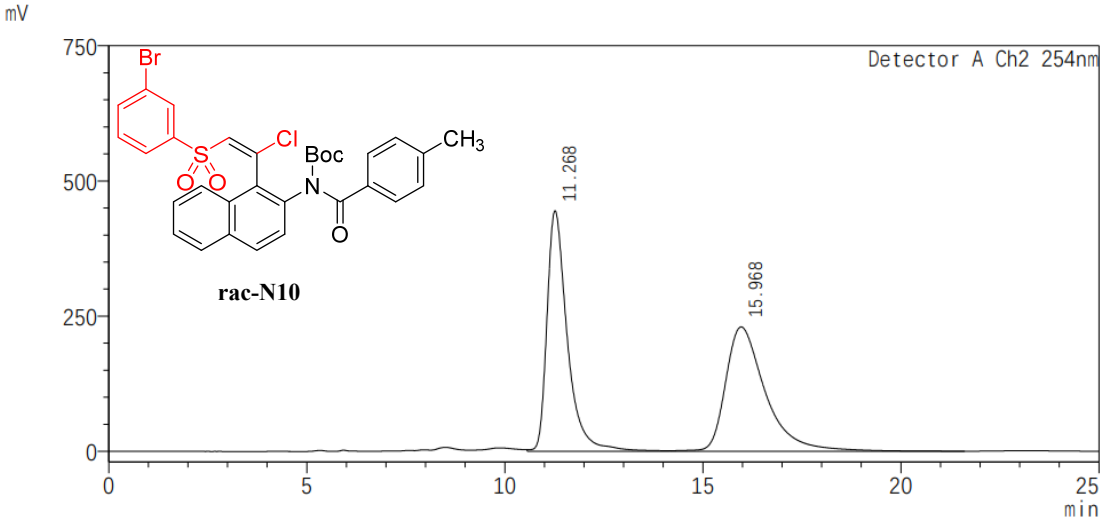
Peak#	Ret. Time	Area	Area%
1	16.661	19713279	50.663
2	18.992	19197693	49.337



Peak Table

Detector A Ch2 254nm

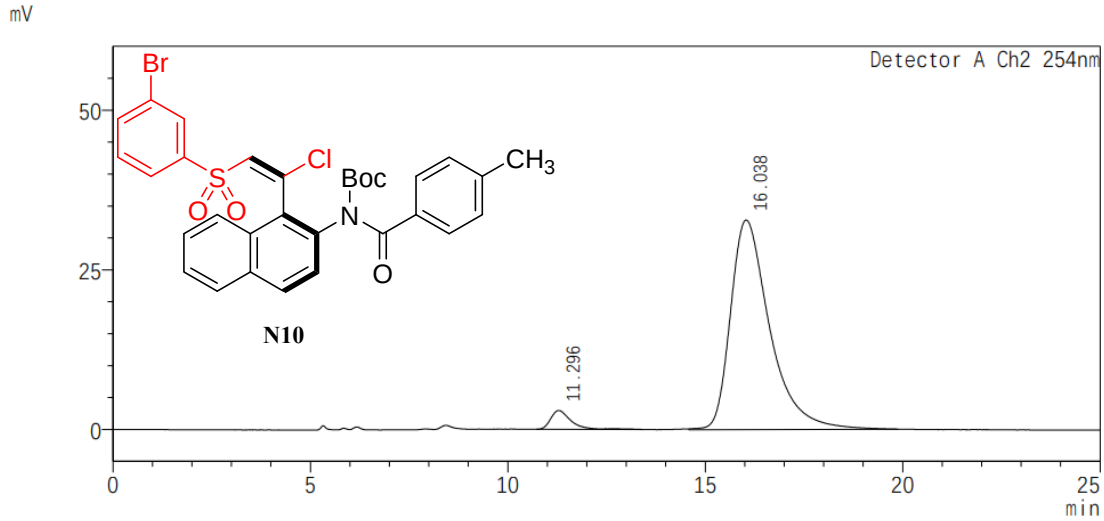
Peak#	Ret. Time	Area	Area%
1	16.663	7212399	95.778
2	19.043	317899	4.222



Peak Table

Detector A Ch2 254nm

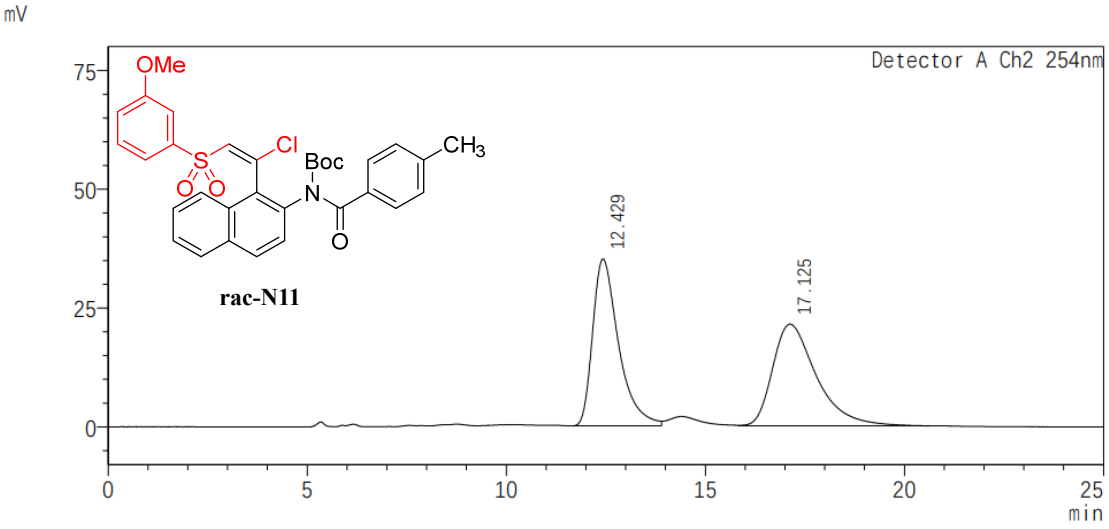
Peak#	Ret. Time	Area	Area%
1	11.268	15950296	49.724
2	15.968	16127090	50.276



Peak Table

Detector A Ch2 254nm

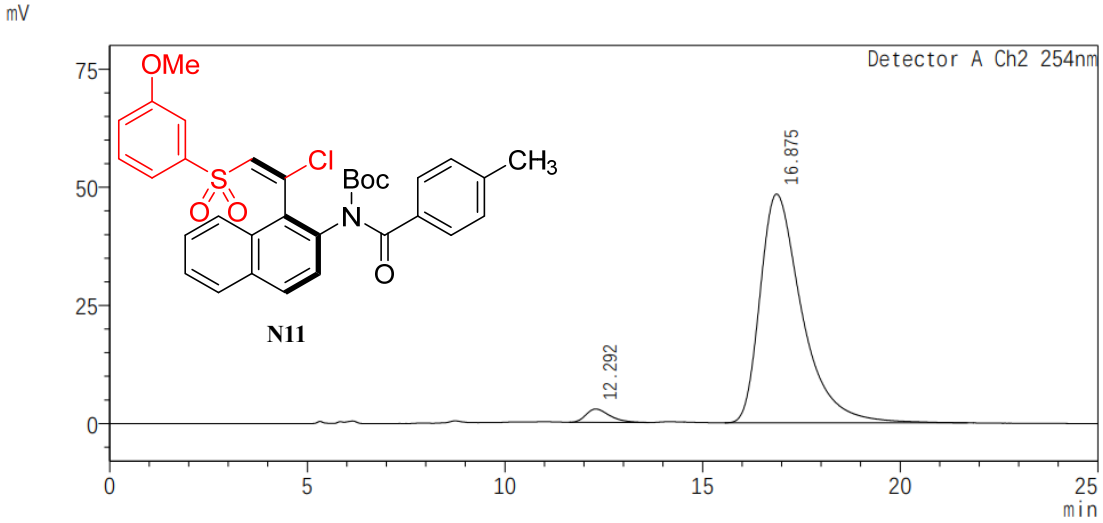
Peak#	Ret. Time	Area	Area%
1	11.296	105737	4.452
2	16.038	2269461	95.548



Peak Table

Detector A Ch2 254nm

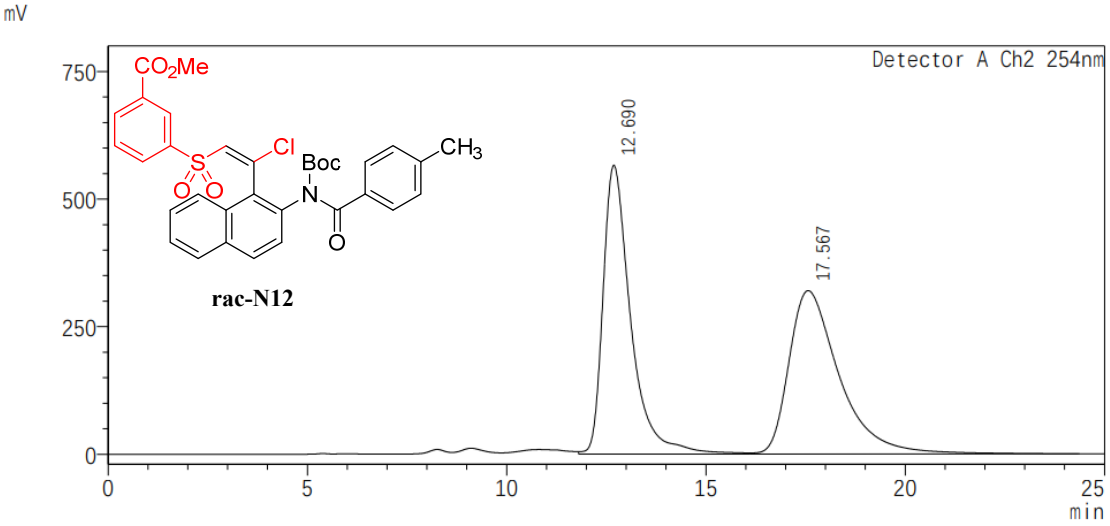
Peak#	Ret. Time	Area	Area%
1	12.429	1594038	49.358
2	17.125	1635526	50.642



Peak Table

Detector A Ch2 254nm

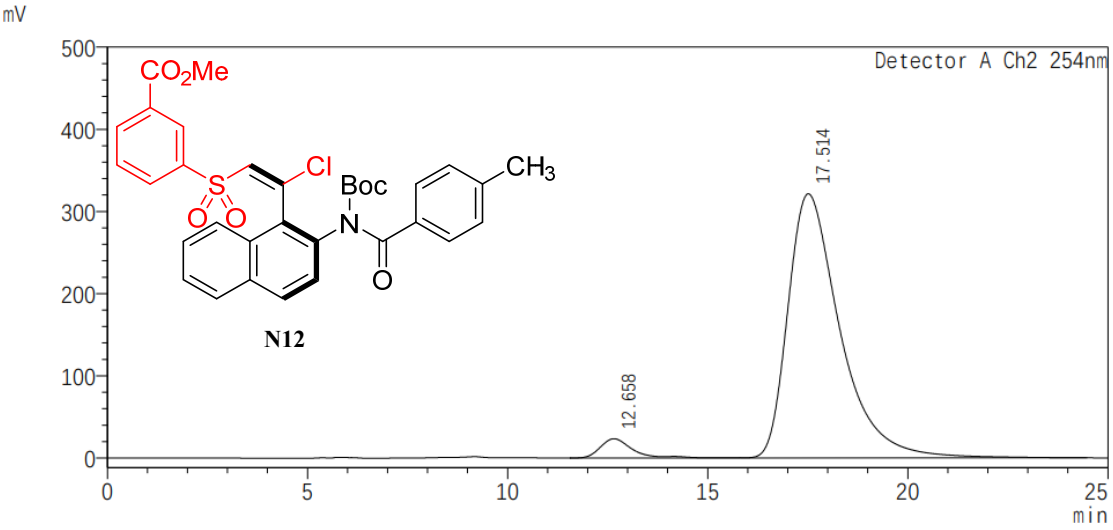
Peak#	Ret. Time	Area	Area%
1	12.292	117928	3.199
2	16.875	3568019	96.801



Peak Table

Detector A Ch2 254nm

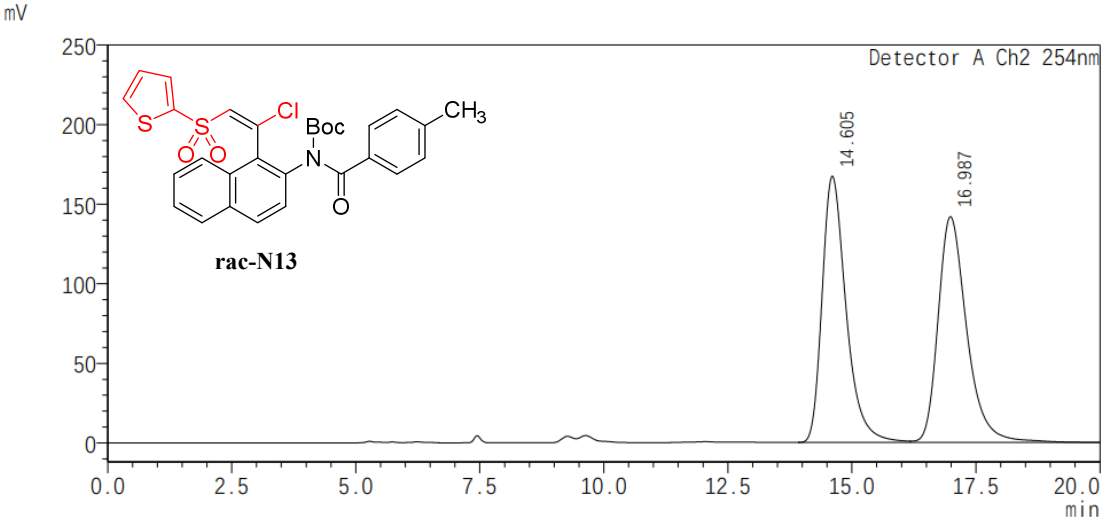
Peak#	Ret. Time	Area	Area%
1	12.690	27310636	49.309
2	17.567	28076264	50.691



Peak Table

Detector A Ch2 254nm

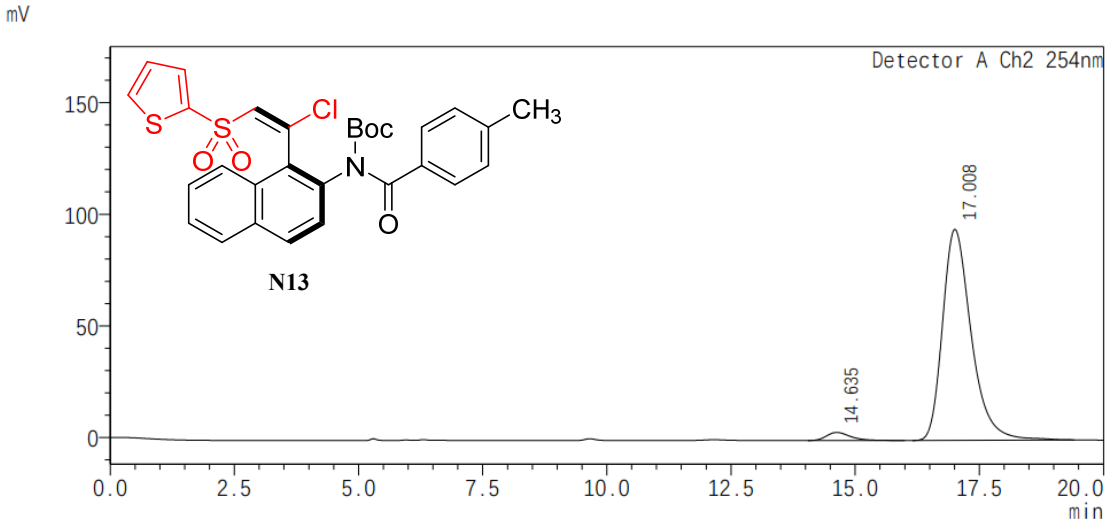
Peak#	Ret. Time	Area	Area%
1	12.658	1326123	4.359
2	17.514	29093405	95.641



Peak Table

Detector A Ch2 254nm

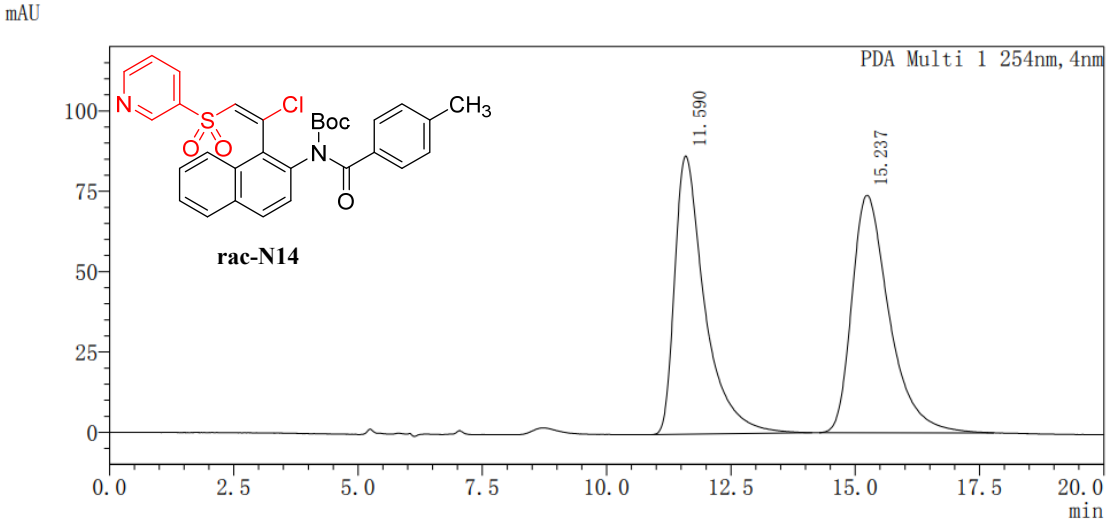
Peak#	Ret. Time	Area	Area%
1	14.605	5652637	49.617
2	16.987	5739907	50.383



Peak Table

Detector A Ch2 254nm

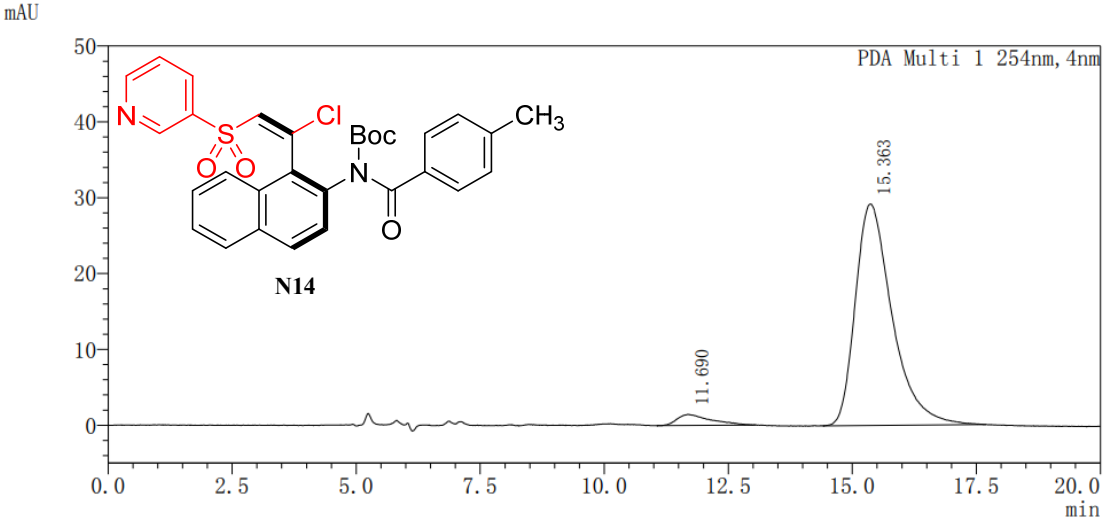
Peak#	Ret. Time	Area	Area%
1	14.635	123642	3.146
2	17.008	3806907	96.854



Peak Table

PDA Ch1 254nm

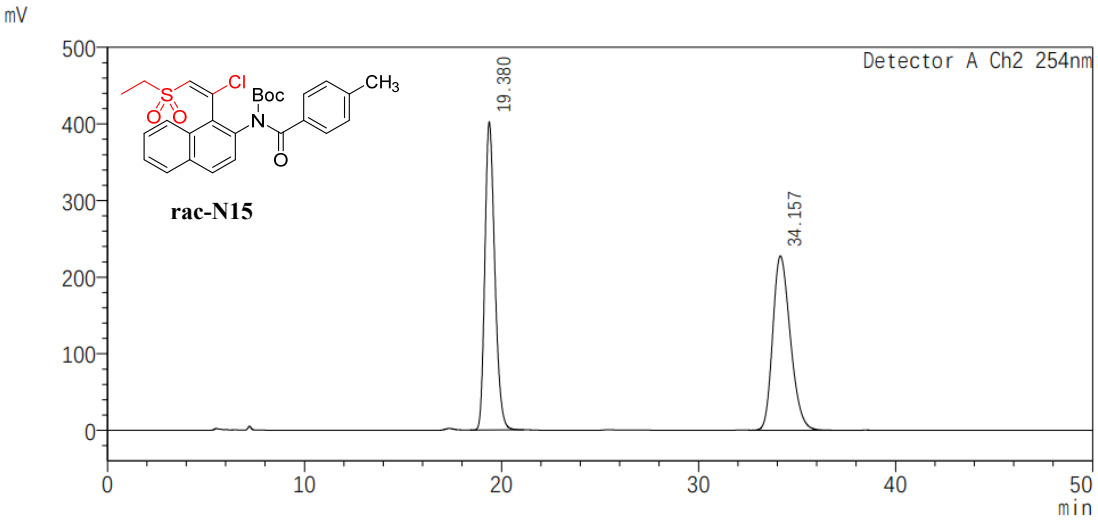
Peak#	Ret. Time	Area	Area%
1	11.590	3649550	48.589
2	15.237	3861520	51.411



Peak Table

PDA Ch1 254nm

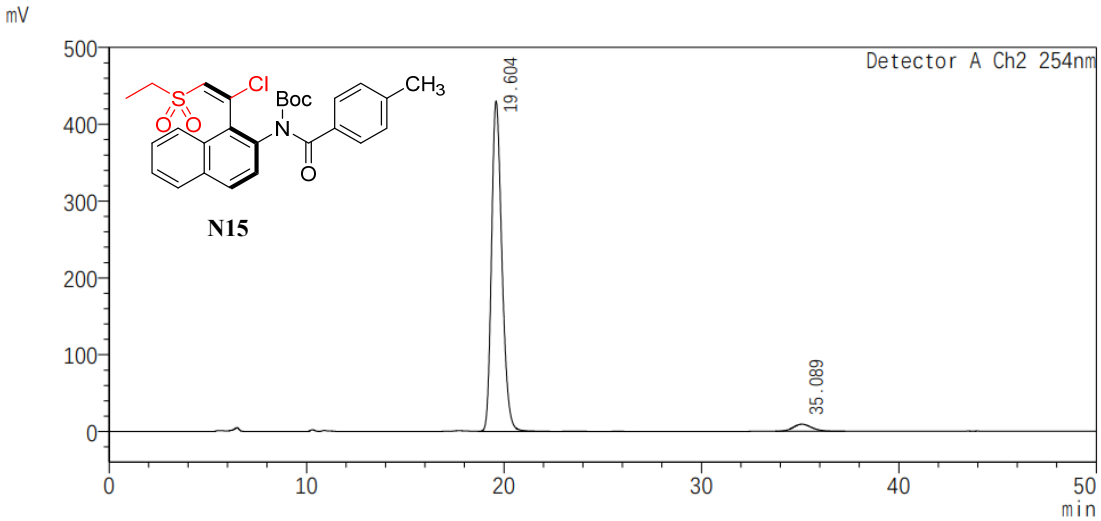
Peak#	Ret. Time	Area	Area%
1	11.690	66723	4.232
2	15.363	1510002	95.768



Peak Table

Detector A Ch2 254nm

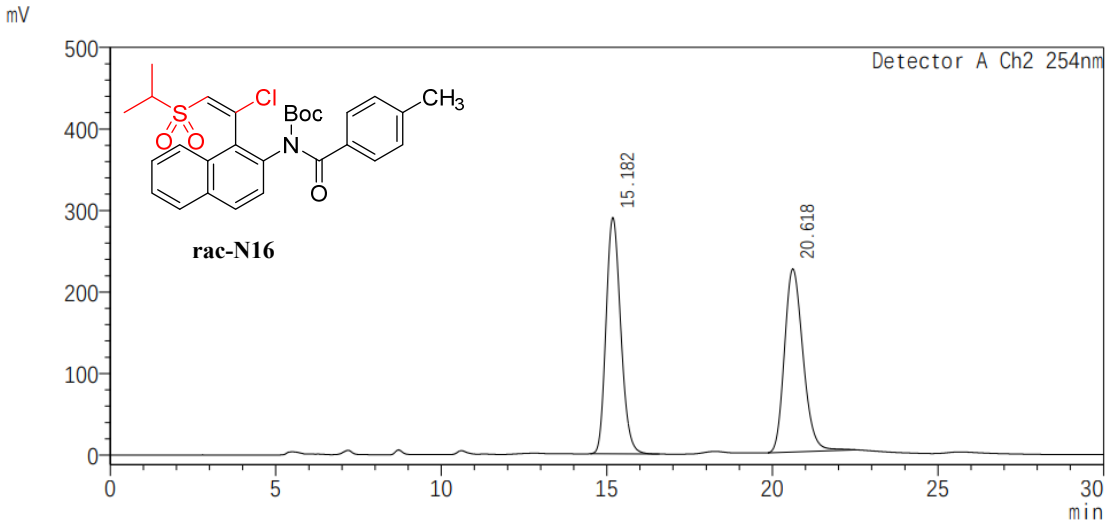
Peak#	Ret. Time	Area	Area%
1	19.380	14089517	49.898
2	34.157	14147306	50.102



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	19.604	15749206	96.301
2	35.089	604866	3.699

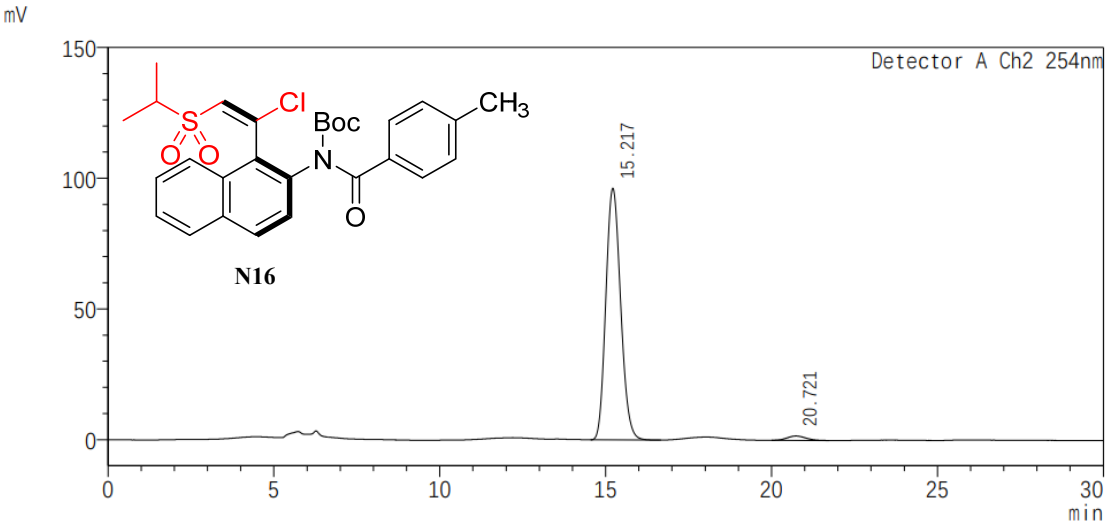


rac-N16

Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	15.182	8928467	50.459
2	20.618	8765859	49.541

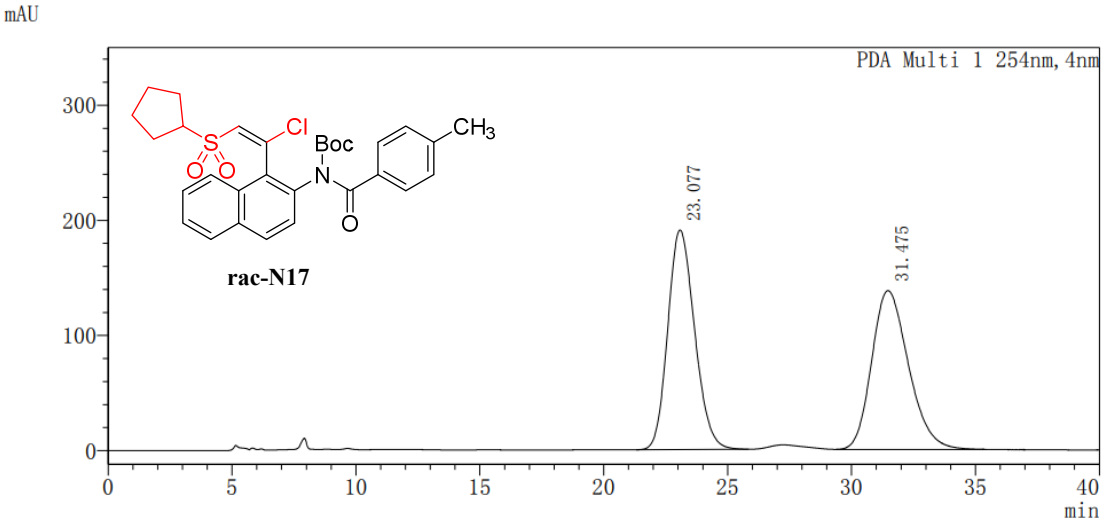


N16

Peak Table

Detector A Ch2 254nm

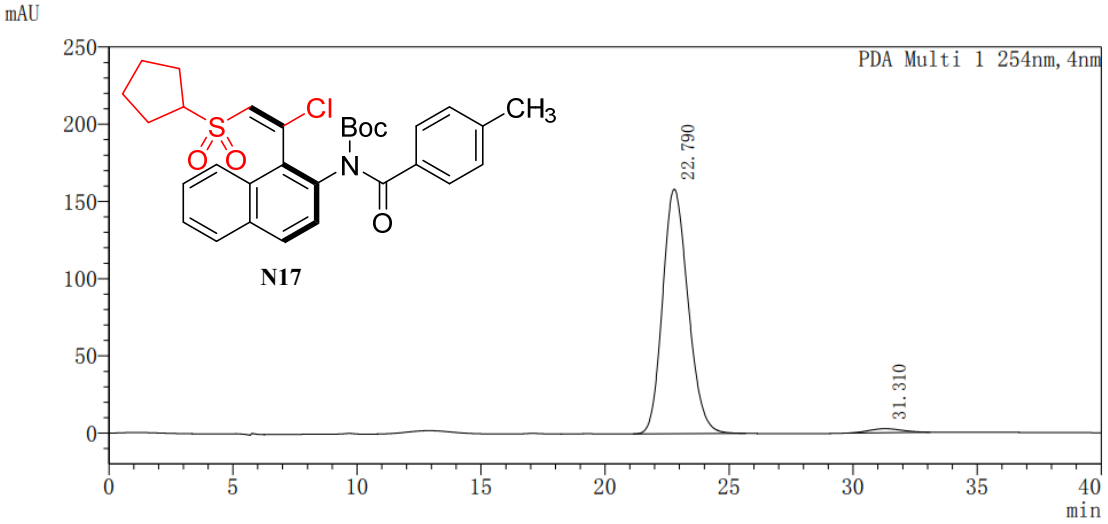
Peak#	Ret. Time	Area	Area%
1	15.217	2988097	97.808
2	20.721	66952	2.192



Peak Table

PDA Ch1 254nm

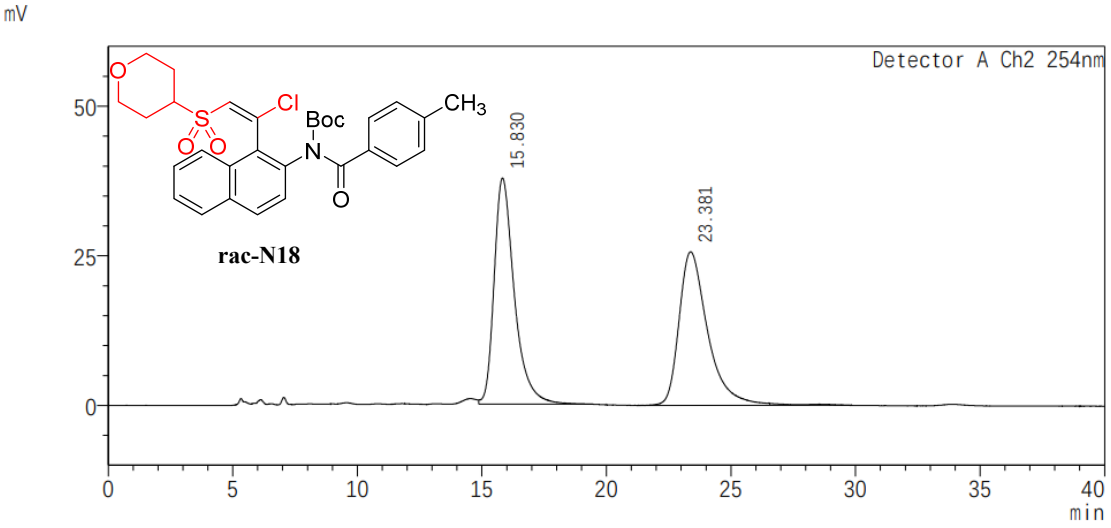
Peak#	Ret. Time	Area	Area%
1	23.077	14358138	50.202
2	31.475	14242371	49.798



Peak Table

PDA Ch1 254nm

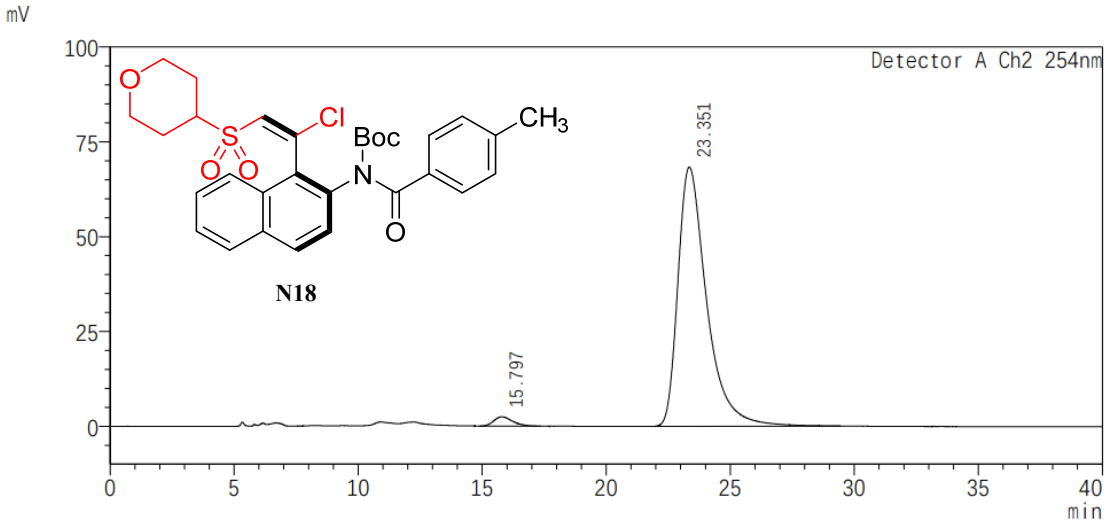
Peak#	Ret. Time	Area	Area%
1	22.790	11301828	97.877
2	31.310	245179	2.123



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	15.830	2137315	50.801
2	23.381	2069923	49.199

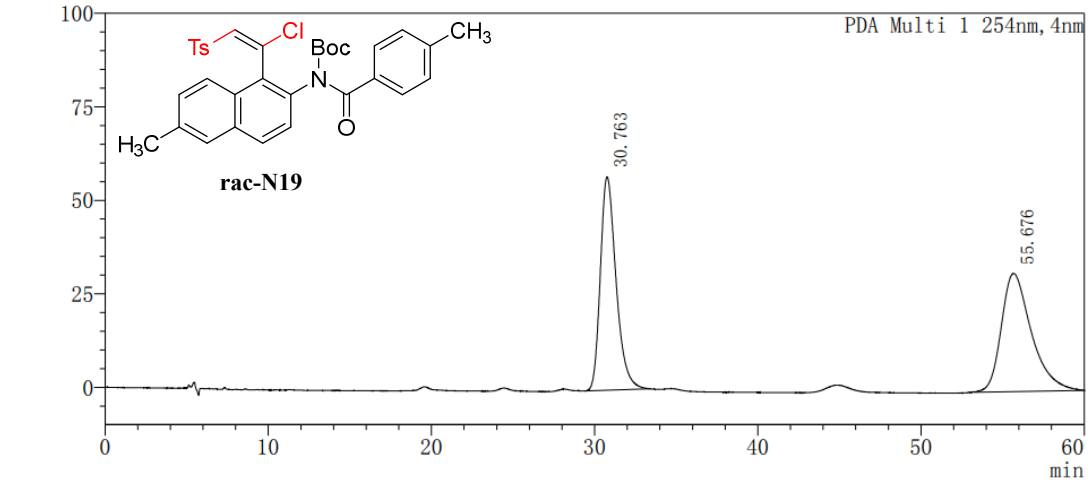


Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	15.797	129381	2.294
2	23.351	5509630	97.706

mAU

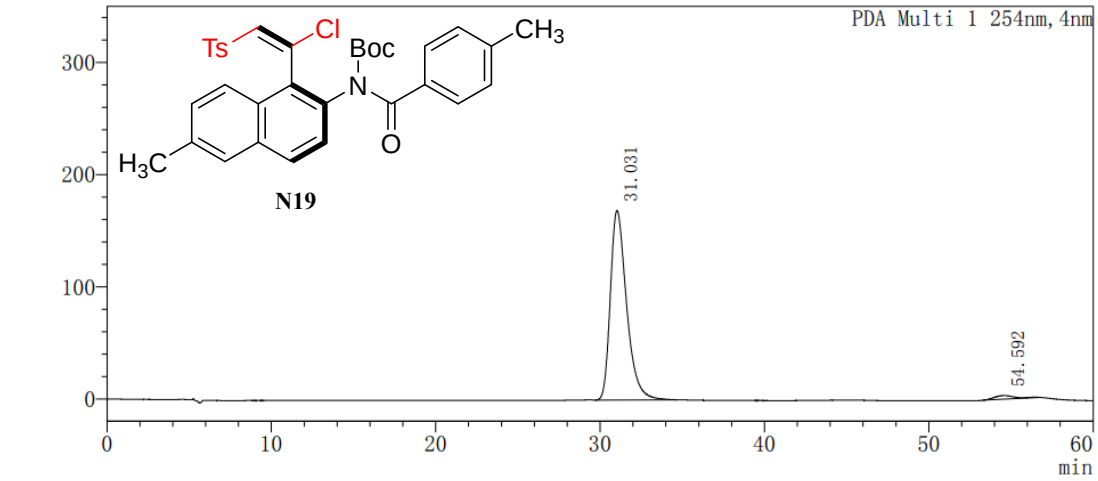


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	30.763	3821149	48.623
2	55.676	4037539	51.377

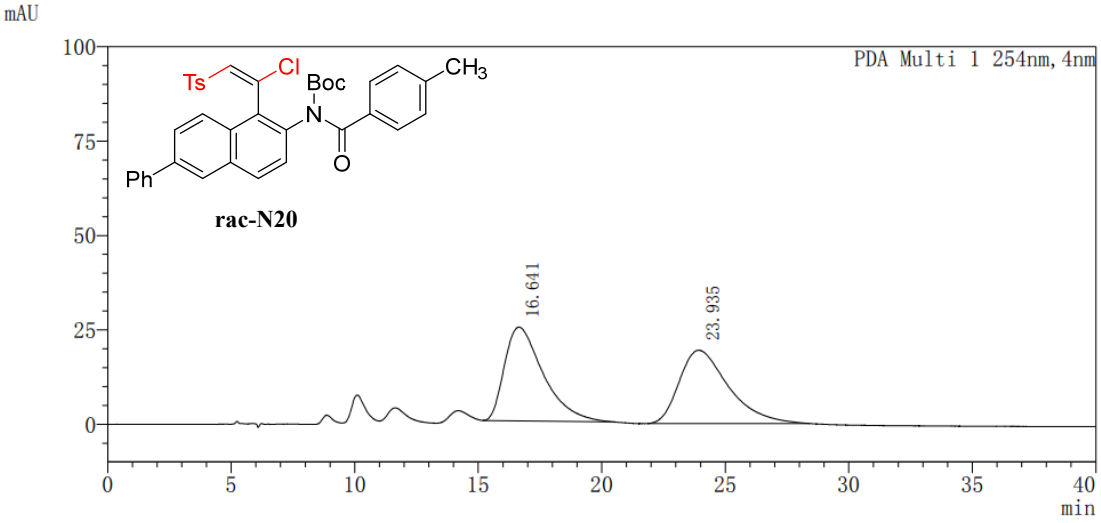
mAU



Peak Table

PDA Ch1 254nm

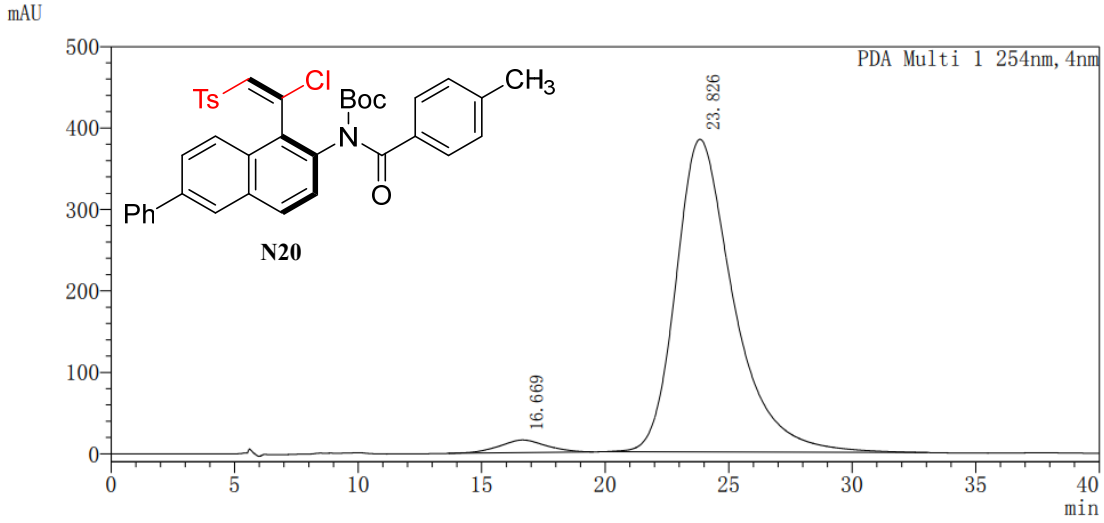
Peak#	Ret. Time	Area	Area%
1	31.031	11586921	97.587
2	54.592	286527	2.413



Peak Table

PDA Ch1 254nm

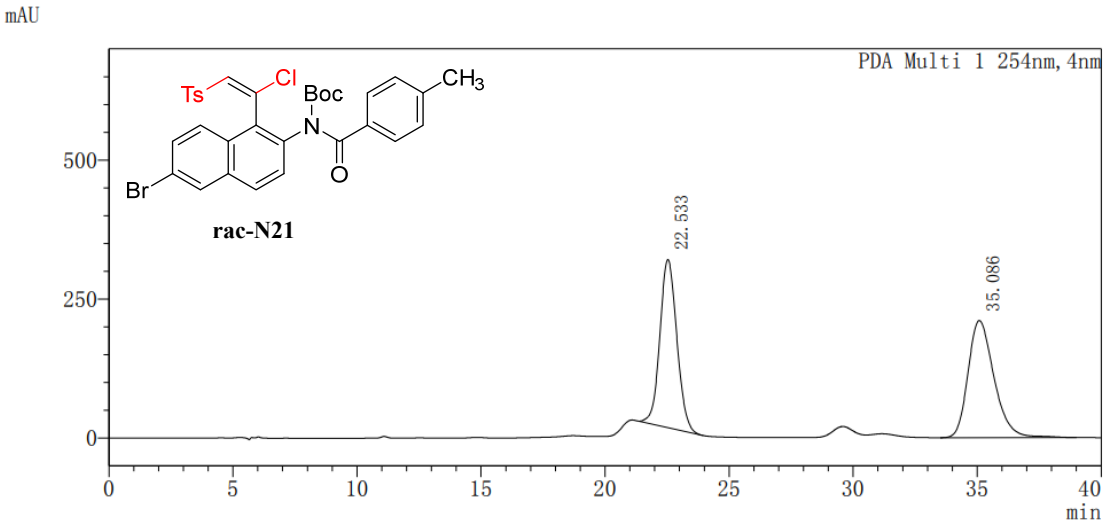
Peak#	Ret. Time	Area	Area%
1	16.641	2719322	50.248
2	23.935	2692509	49.752



Peak Table

PDA Ch1 254nm

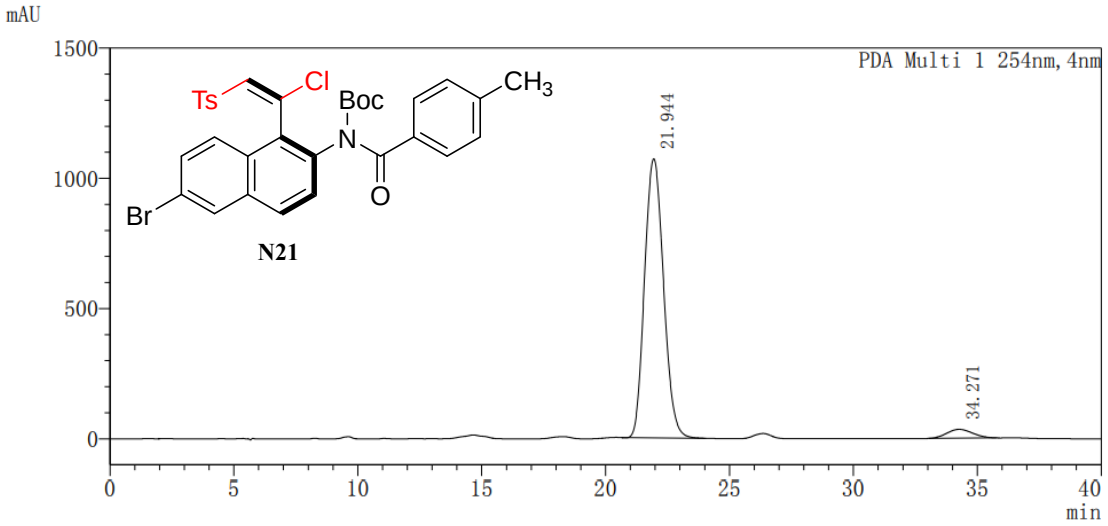
Peak#	Ret. Time	Area	Area%
1	16.669	2044922	3.169
2	23.826	62493406	96.831



Peak Table

PDA Ch1 254nm

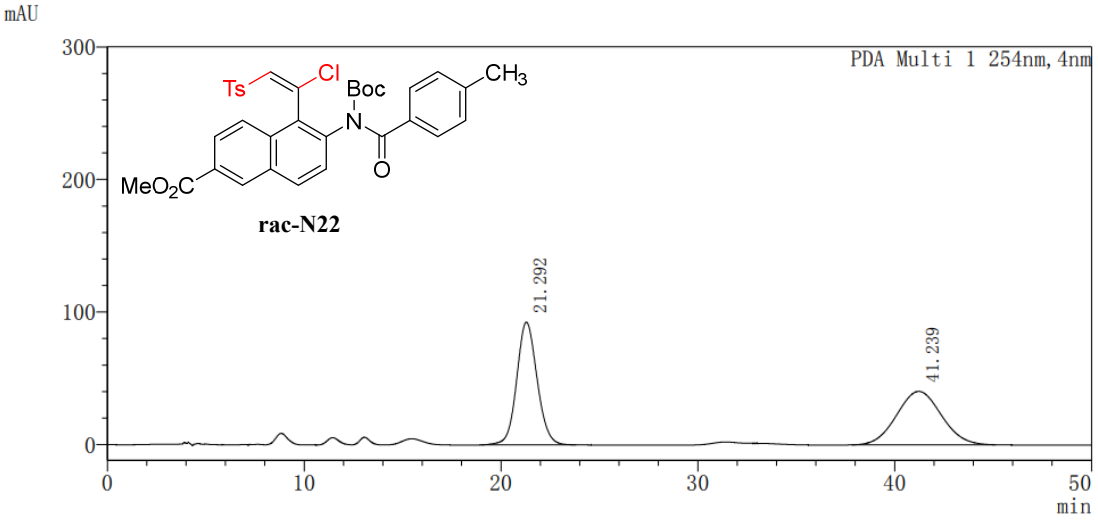
Peak#	Ret. Time	Area	Area%
1	22.533	14376948	48.387
2	35.086	15335765	51.613



Peak Table

PDA Ch1 254nm

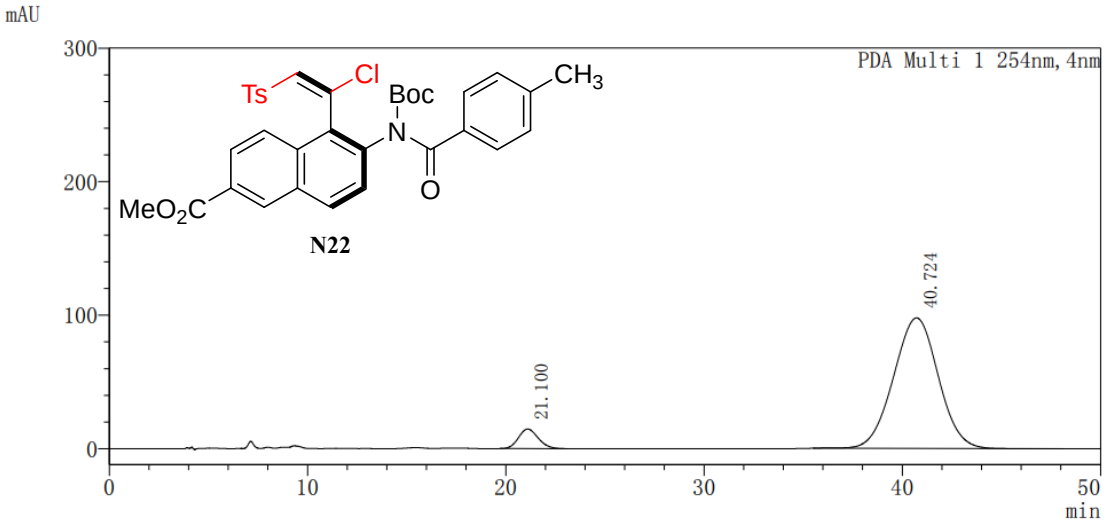
Peak#	Ret. Time	Area	Area%
1	21.944	57093244	95.882
2	34.271	2451865	4.118



Peak Table

PDA Ch1 254nm

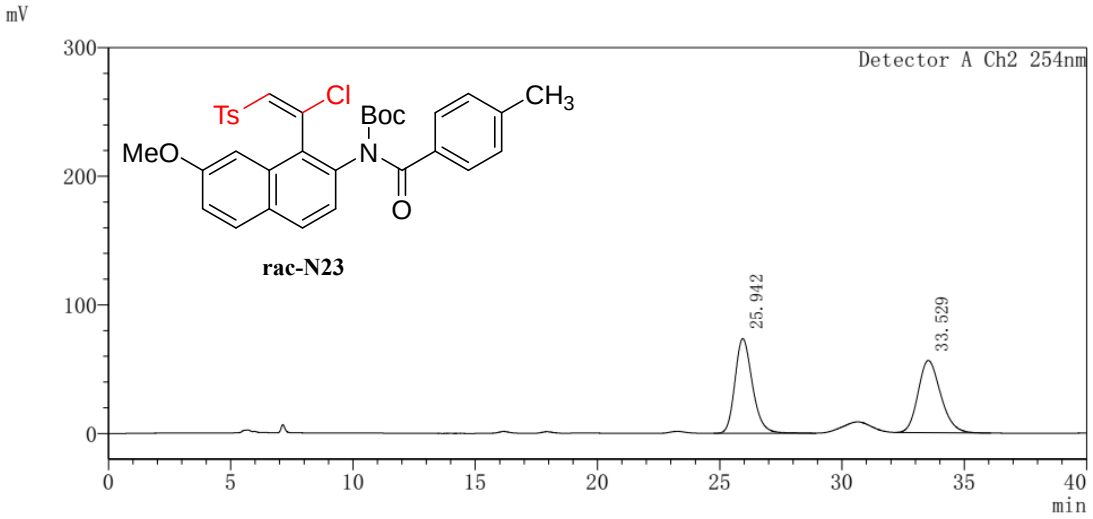
Peak#	Ret. Time	Area	Area%
1	21.292	6668482	51.142
2	41.239	6370620	48.858



Peak Table

PDA Ch1 254nm

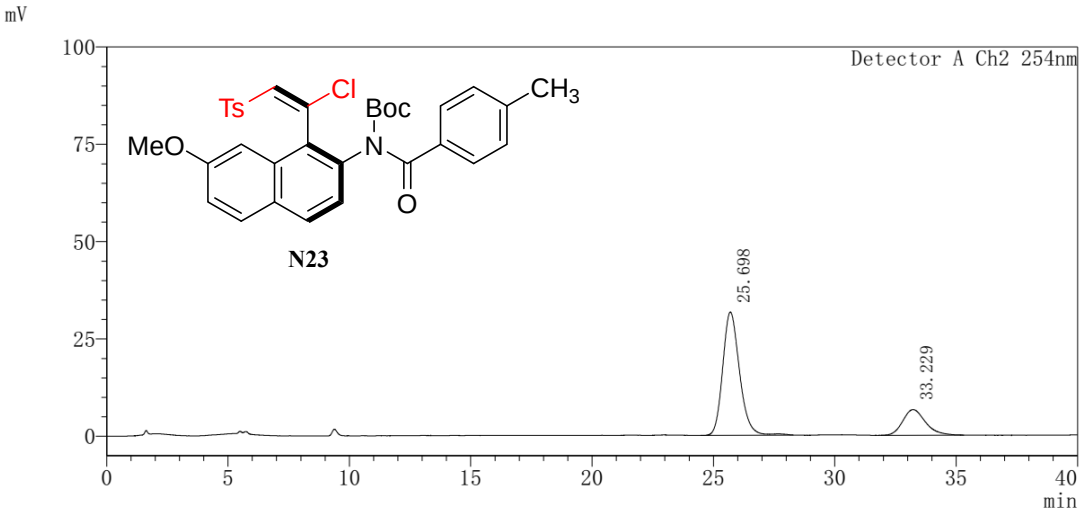
Peak#	Ret. Time	Area	Area%
1	21.100	1011838	6.185
2	40.724	15348753	93.815



Peak Table

Detector A Ch2 254nm

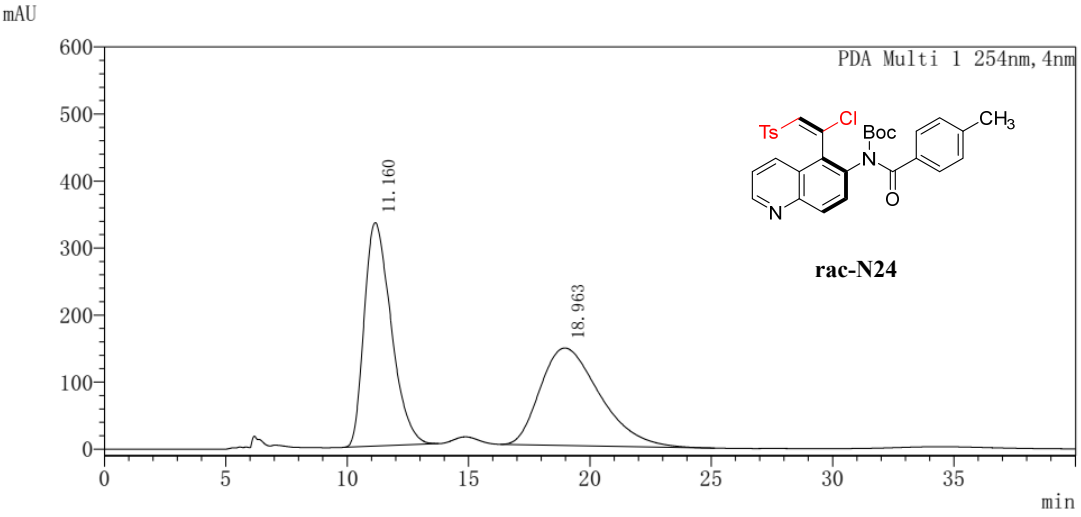
Peak#	Ret. Time	Area	Area%
1	25.942	3658980	50.339
2	33.529	3609673	49.661



Peak Table

Detector A Ch2 254nm

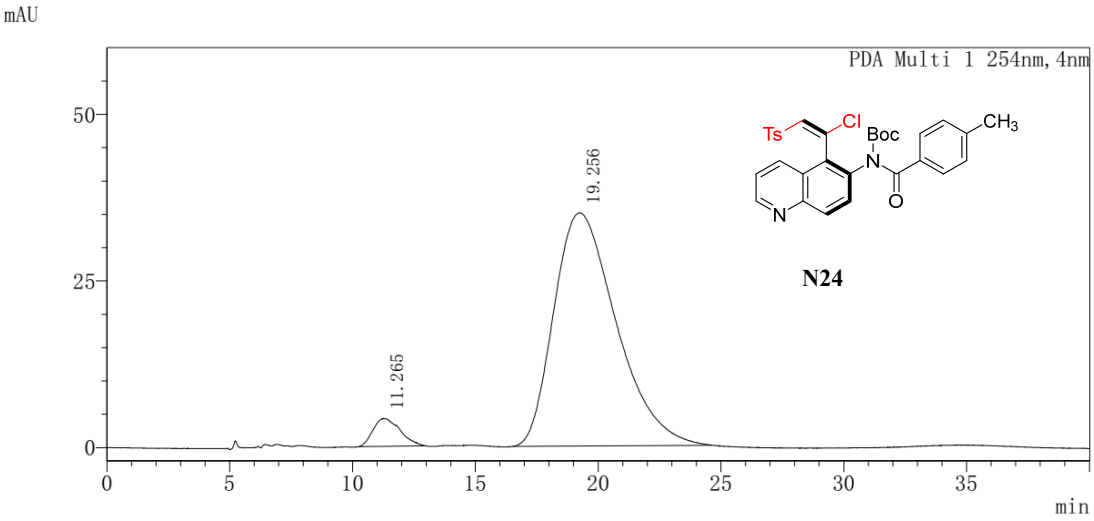
Peak#	Ret. Time	Area	Area%
1	25.698	1527085	78.041
2	33.229	429698	21.959



Peak Table

PDA Ch1 254nm

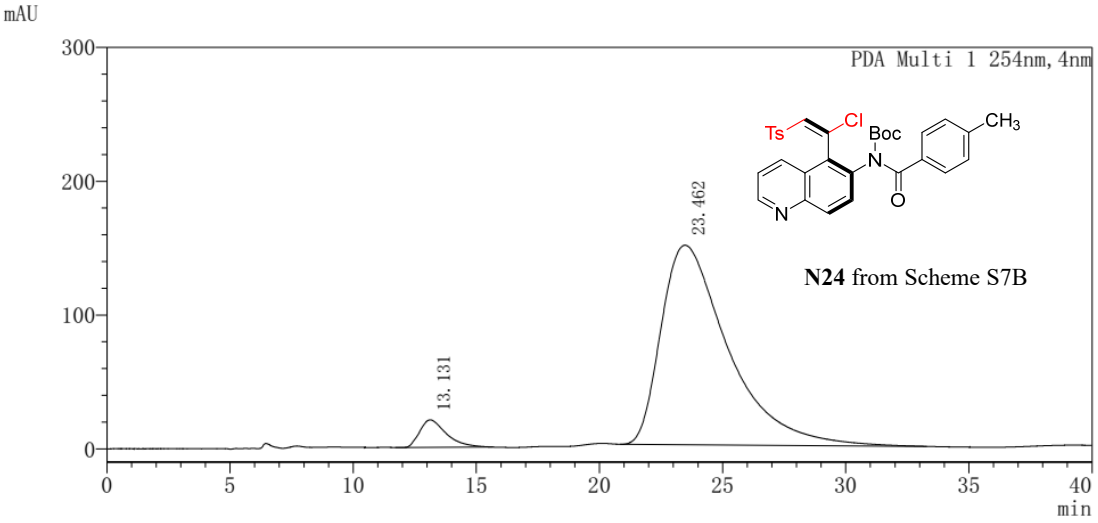
Peak#	Ret. Time	Area	Area%
1	11.160	25755165	50.925
2	18.963	24819779	49.075



Peak Table

PDA Ch1 254nm

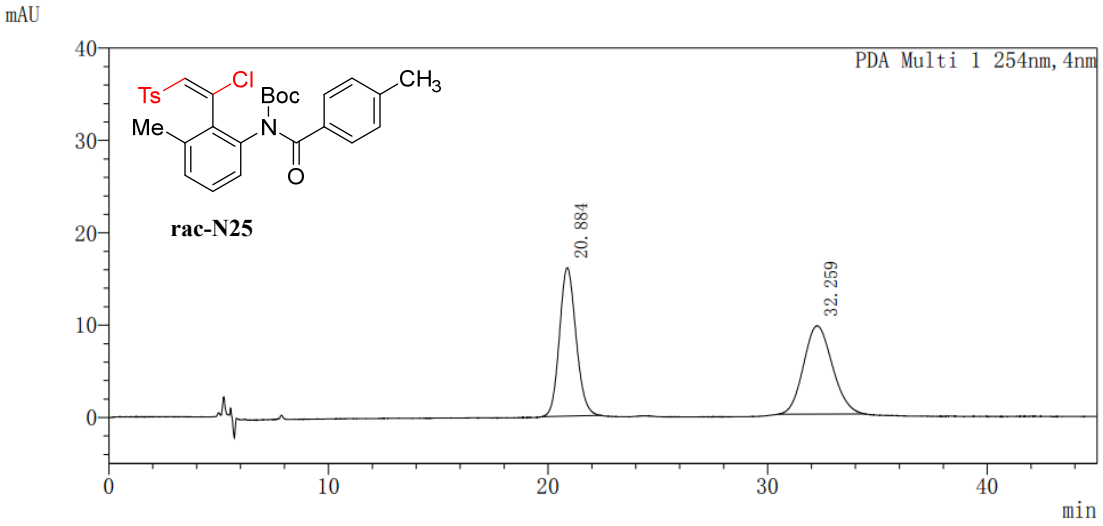
Peak#	Ret. Time	Area	Area%
1	11.265	319155	4.903
2	19.256	6190246	95.097



Peak Table

PDA Ch1 254nm

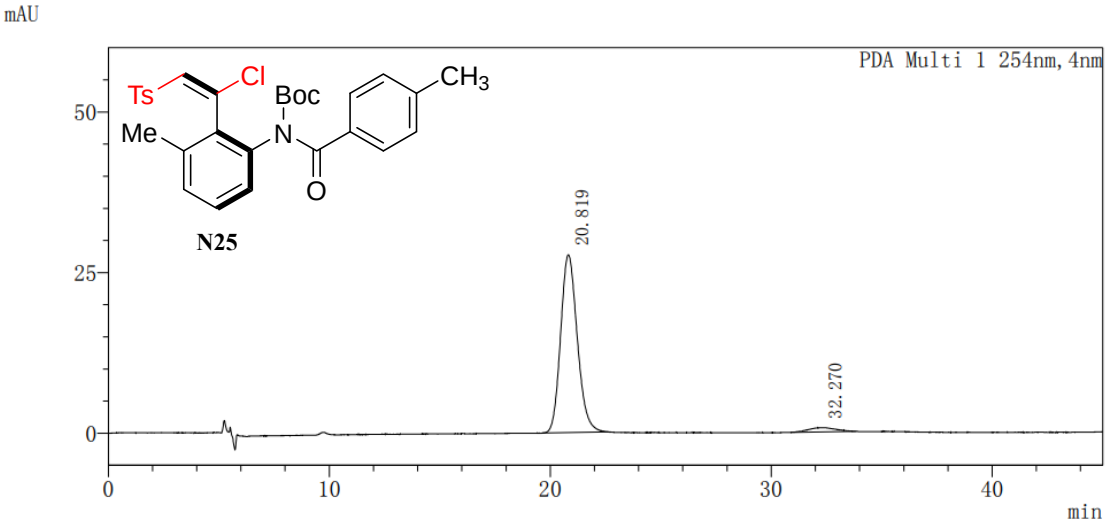
Peak#	Ret. Time	Area	Area%
1	13.131	1543793	5.161
2	23.462	28366007	94.839



Peak Table

PDA Ch1 254nm

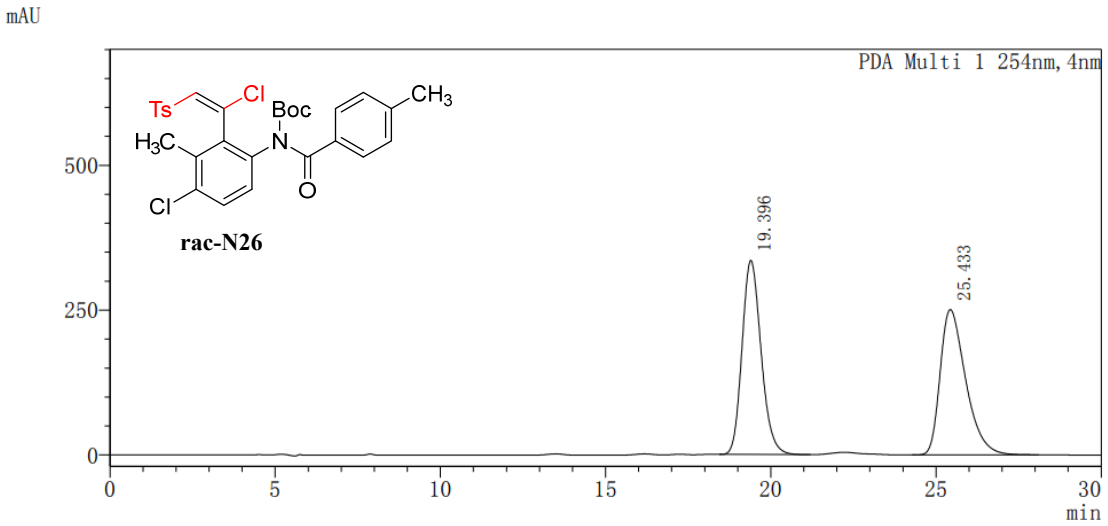
Peak#	Ret. Time	Area	Area%
1	20.884	843224	49.140
2	32.259	872743	50.860



Peak Table

PDA Ch1 254nm

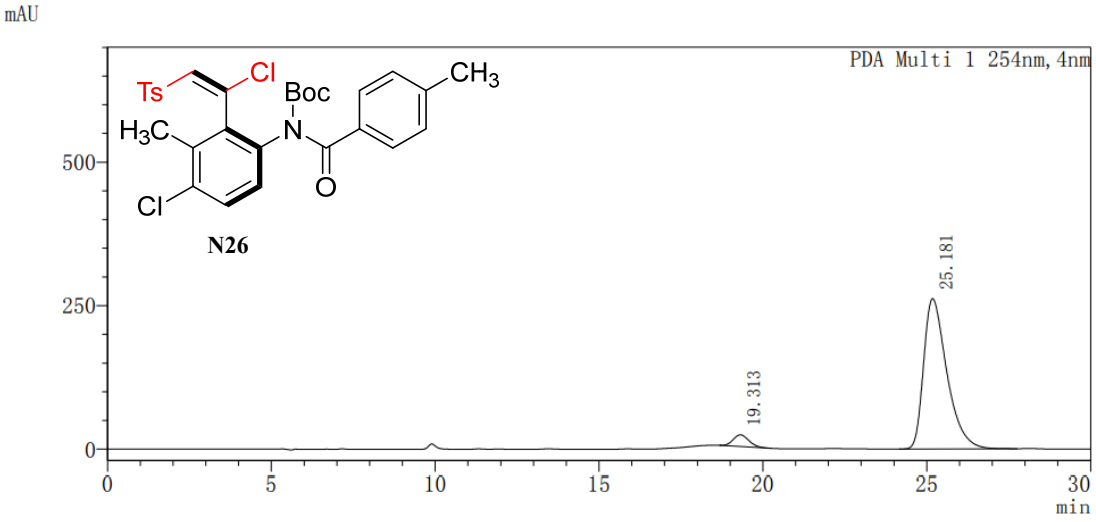
Peak#	Ret. Time	Area	Area%
1	20.819	1451899	96.219
2	32.270	57053	3.781



Peak Table

PDA Ch1 254nm

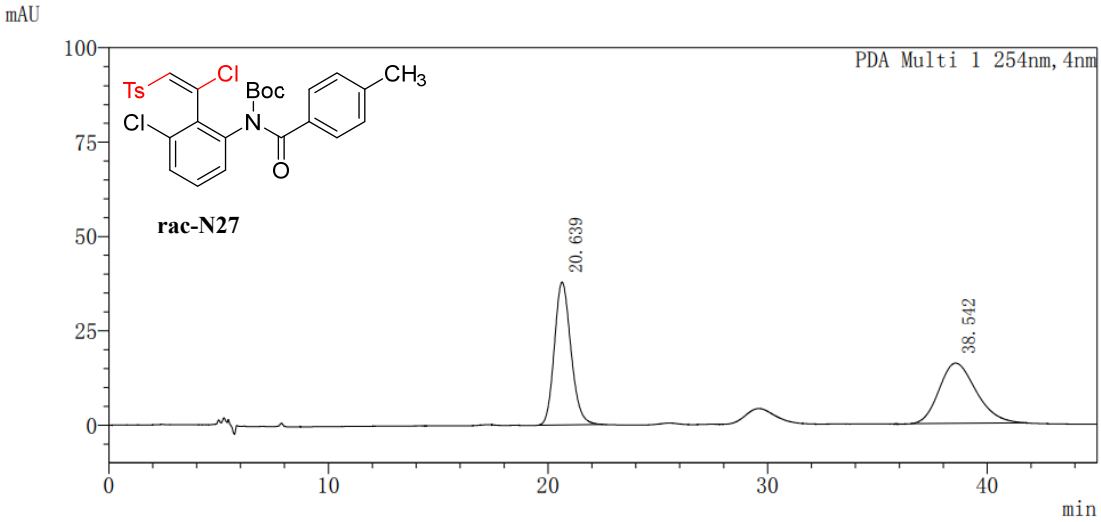
Peak#	Ret. Time	Area	Area%
1	19.396	13454534	49.931
2	25.433	13491706	50.069



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.313	684803	5.021
2	25.181	12953552	94.979

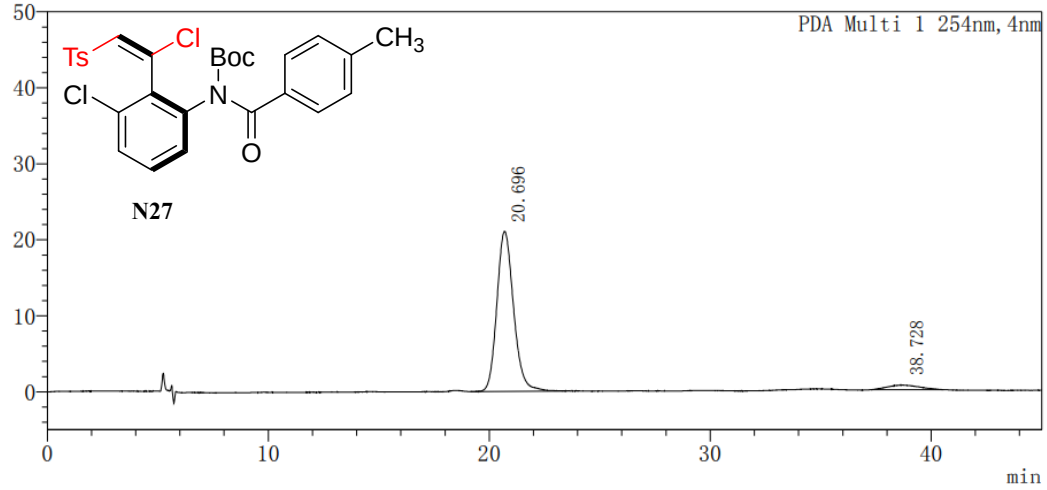


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.639	1986849	51.503
2	38.542	1870868	48.497

mAU

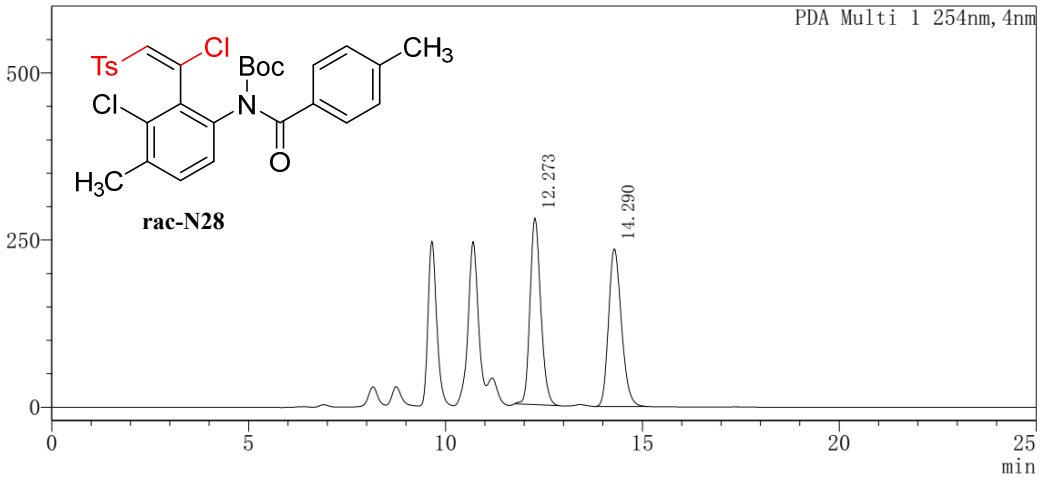


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.696	1108717	94.855
2	38.728	60138	5.145

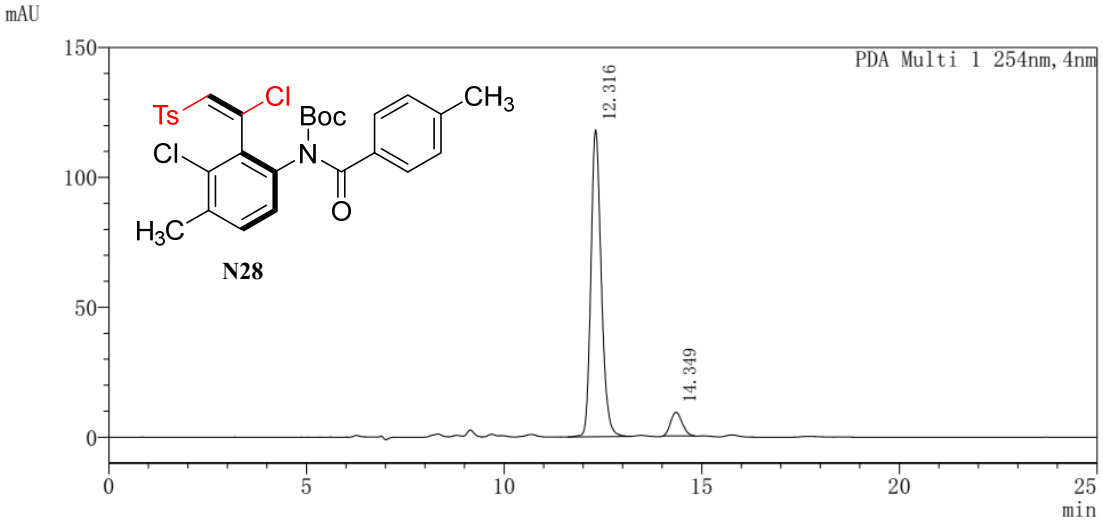
mAU



Peak Table

PDA Ch1 254nm

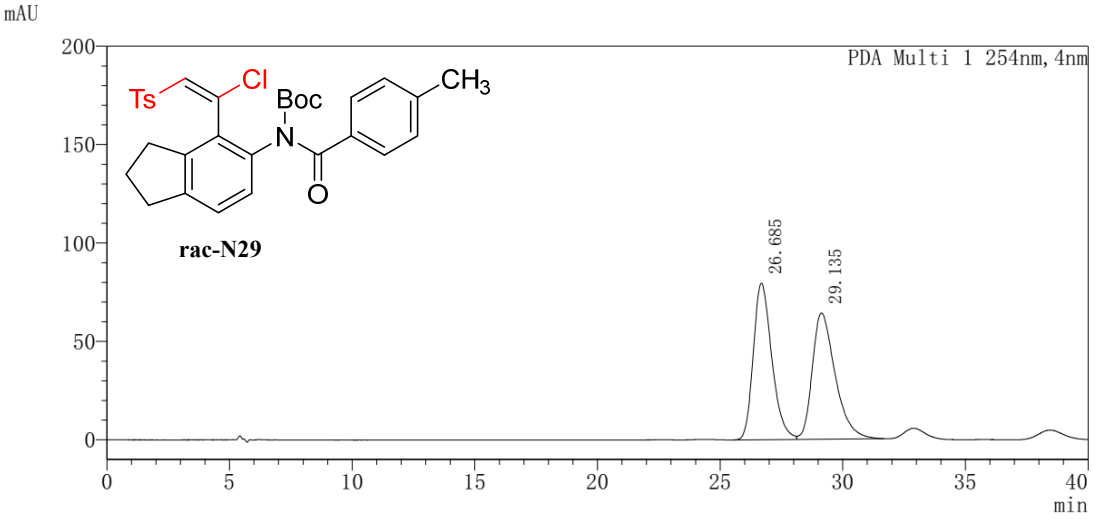
Peak#	Ret. Time	Area	Area%
1	12.273	5311974	49.753
2	14.290	5364670	50.247



Peak Table

PDA Ch1 254nm

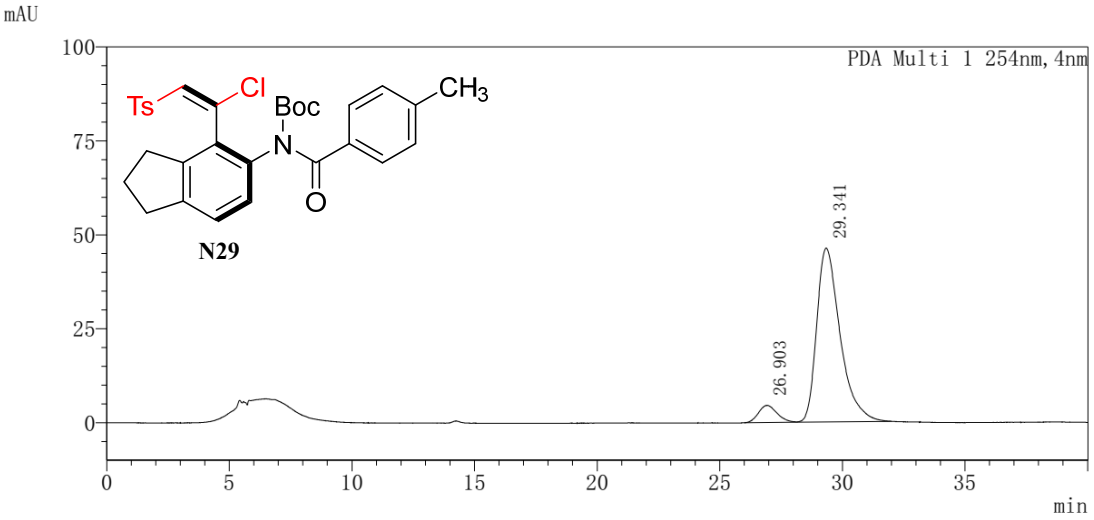
Peak#	Ret. Time	Area	Area%
1	12.316	2156002	92.084
2	14.349	185331	7.916



Peak Table

PDA Ch1 254nm

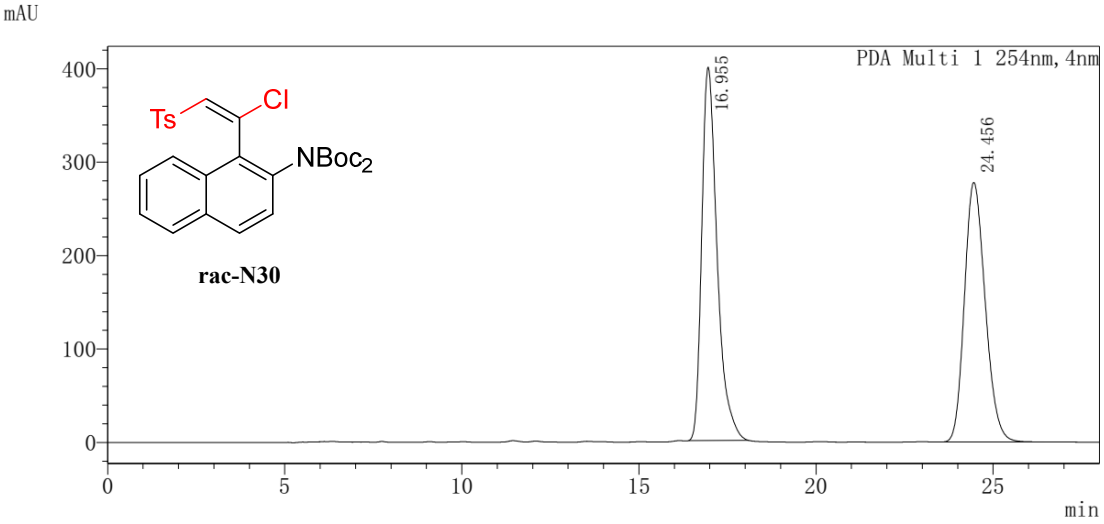
Peak#	Ret. Time	Area	Area%
1	26.685	4176575	50.032
2	29.135	4171221	49.968



Peak Table

PDA Ch1 254nm

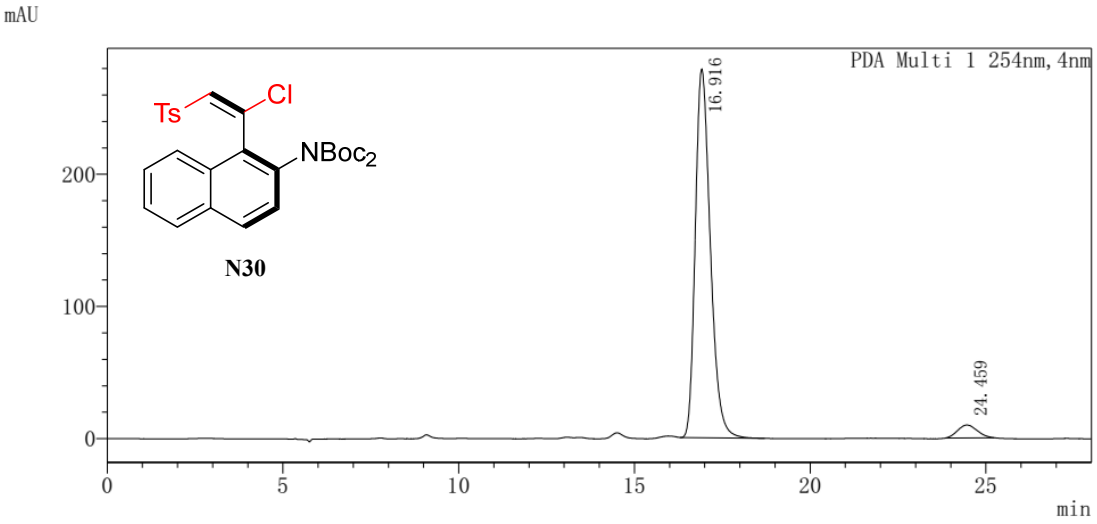
Peak#	Ret. Time	Area	Area%
1	26.903	239945	7.246
2	29.341	3071259	92.754



Peak Table

PDA Ch1 254nm

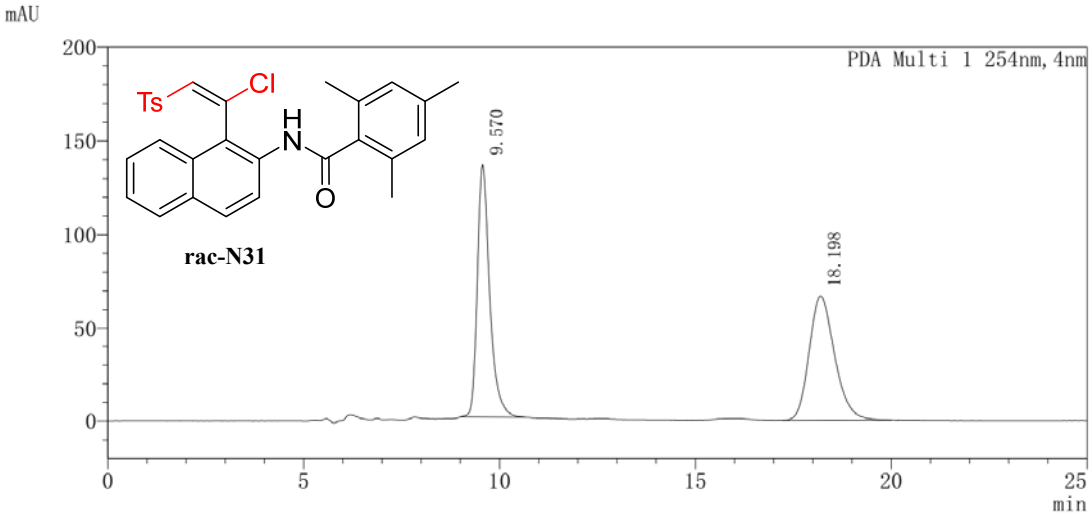
Peak#	Ret. Time	Area	Area%
1	16.955	12048111	51.559
2	24.456	11319578	48.441



Peak Table

PDA Ch1 254nm

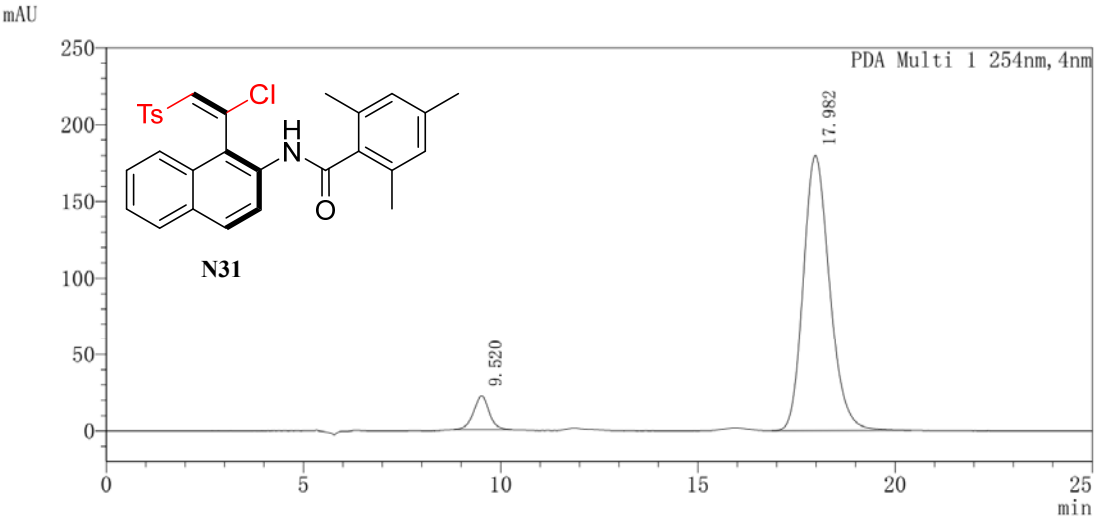
Peak#	Ret. Time	Area	Area%
1	16.916	8307989	95.637
2	24.459	379050	4.363



Peak Table

PDA Ch1 254nm

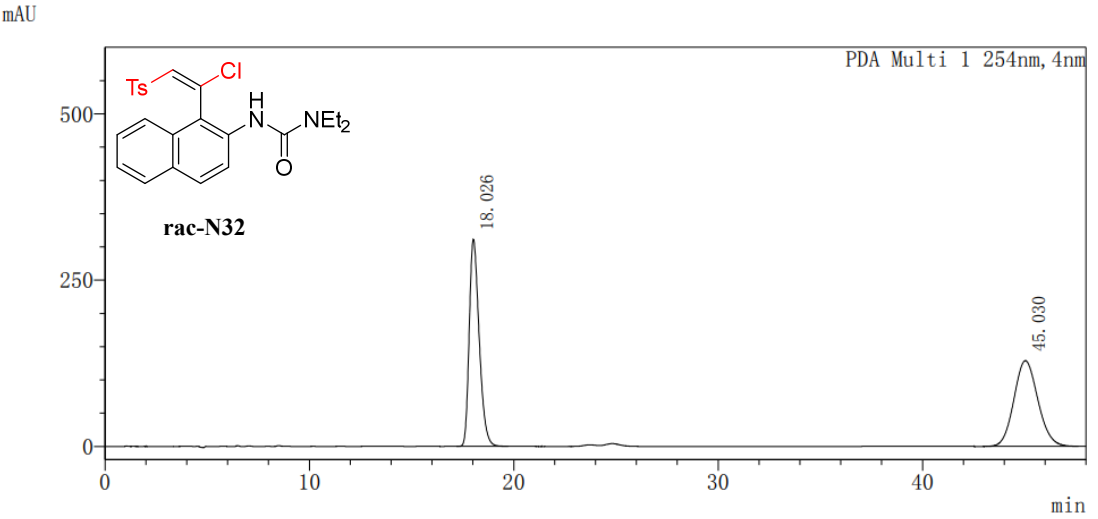
Peak#	Ret. Time	Area	Area%
1	9.570	2980207	49.589
2	18.198	3029559	50.411



Peak Table

PDA Ch1 254nm

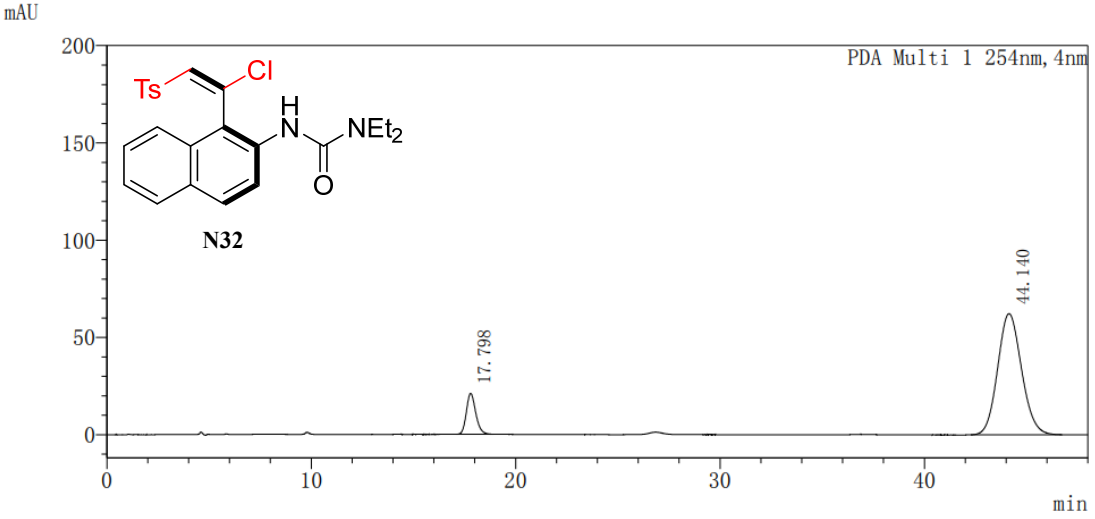
Peak#	Ret. Time	Area	Area%
1	9.520	620271	6.898
2	17.982	8371482	93.102



Peak Table

PDA Ch1 254nm

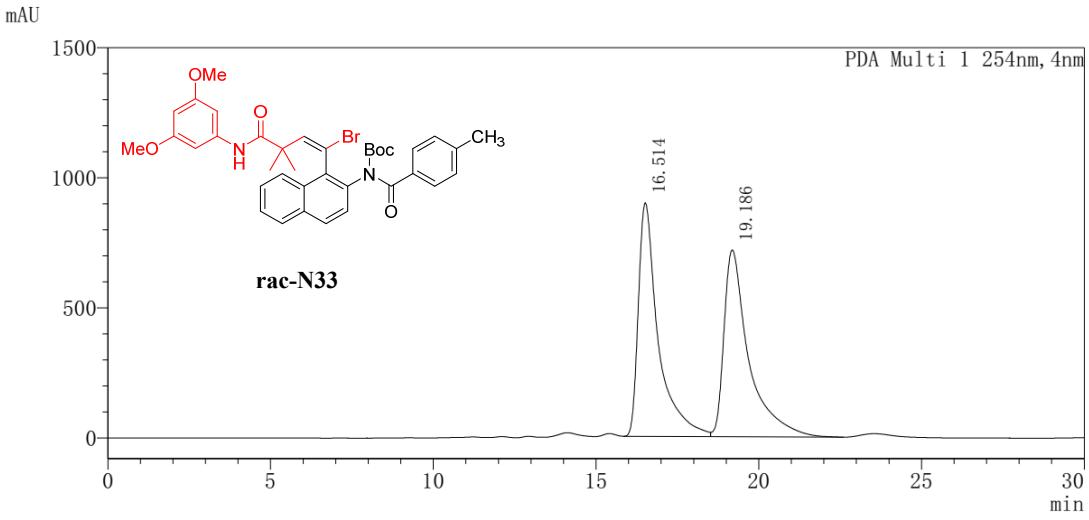
Peak#	Ret. Time	Area	Area%
1	18.026	10555741	50.144
2	45.030	10495055	49.856



Peak Table

PDA Ch1 254nm

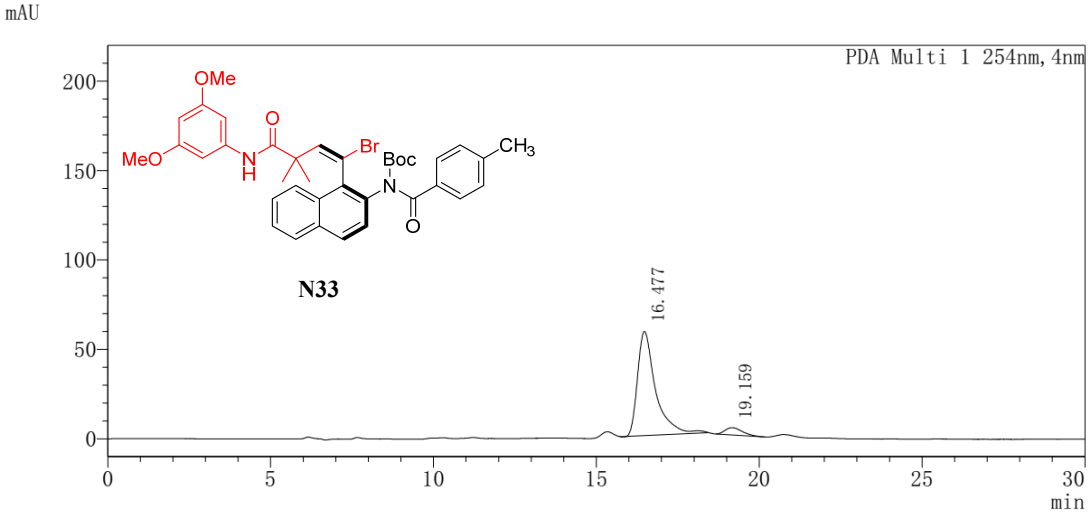
Peak#	Ret. Time	Area	Area%
1	17.798	669374	11.698
2	44.140	5052890	88.302



Peak Table

PDA Ch1 254nm

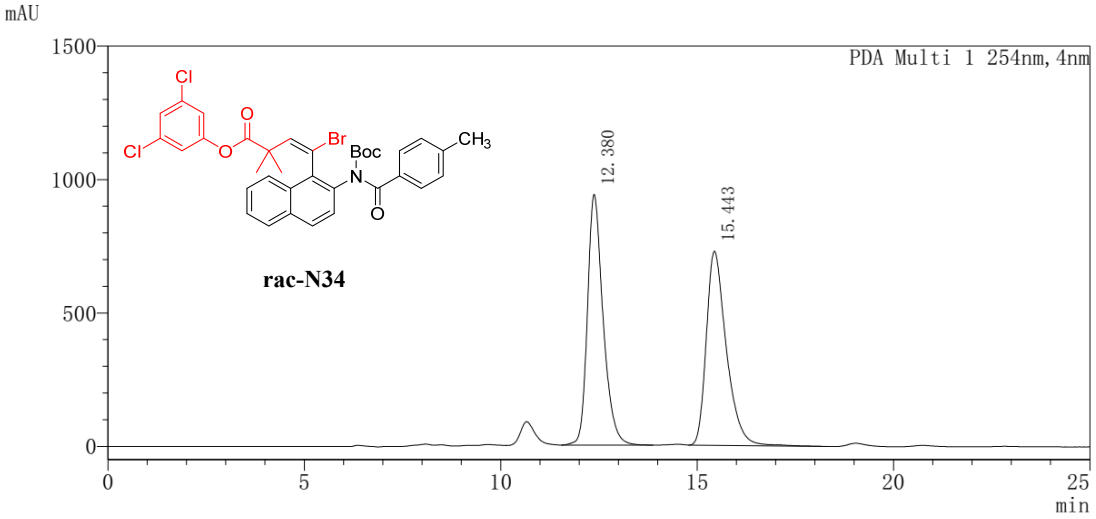
Peak#	Ret. Time	Area	Area%
1	16.514	38172517	50.010
2	19.186	38156642	49.990



Peak Table

PDA Ch1 254nm

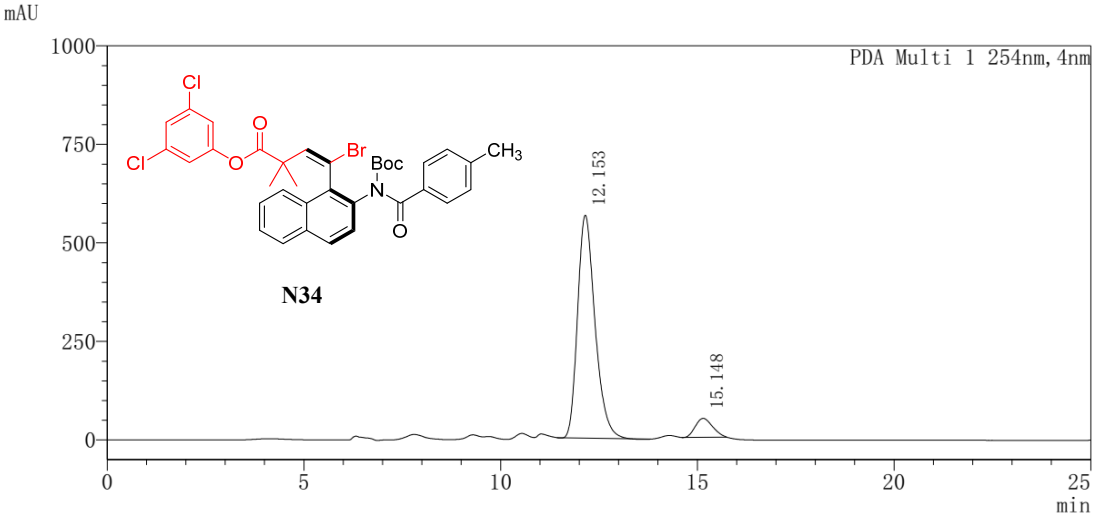
Peak#	Ret. Time	Area	Area%
1	16.477	2238994	93.723
2	19.159	149957	6.277



Peak Table

PDA Ch1 254nm

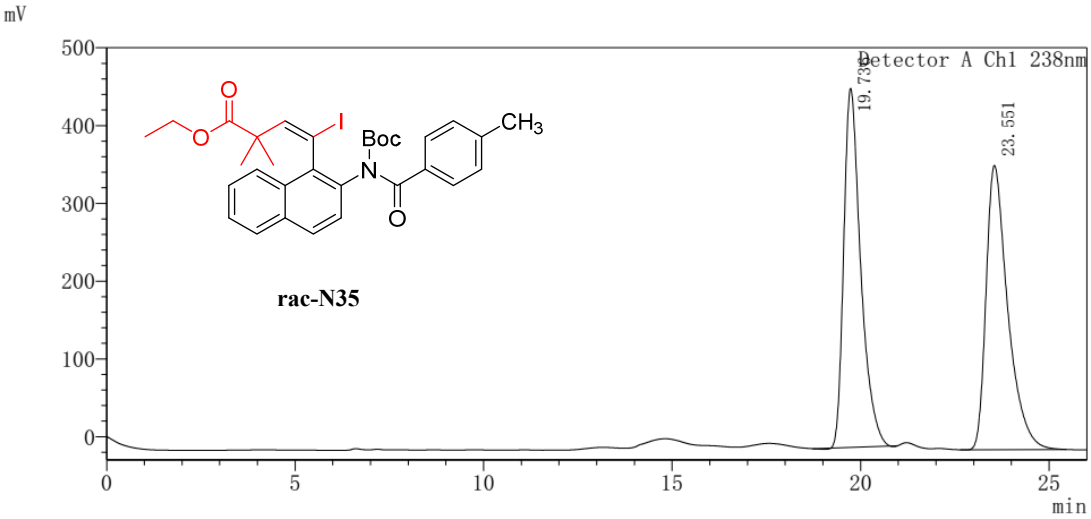
Peak#	Ret. Time	Area	Area%
1	12.380	26081177	50.219
2	15.443	25853515	49.781



Peak Table

PDA Ch1 254nm

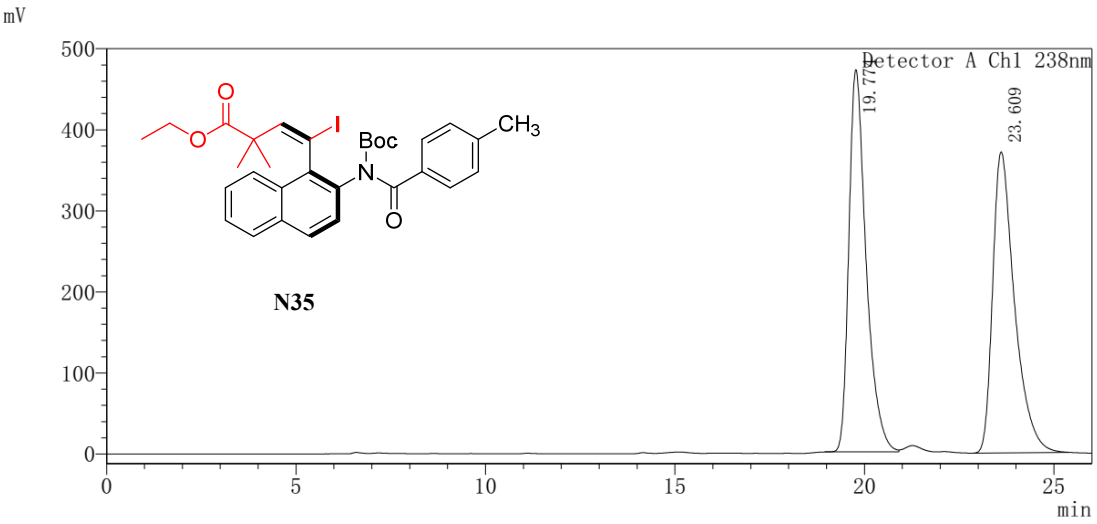
Peak#	Ret. Time	Area	Area%
1	12.153	17458902	92.246
2	15.148	1467621	7.754



Peak Table

Detector A Ch1 238nm

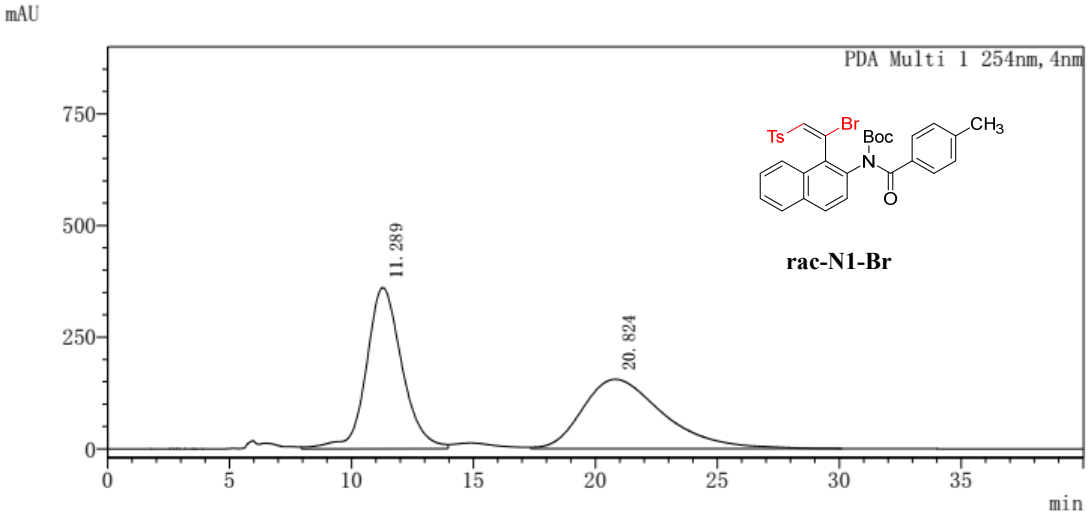
Peak#	Ret. Time	Area	Area%
1	19.736	14422152	49.605
2	23.551	14651551	50.395



Peak Table

Detector A Ch1 238nm

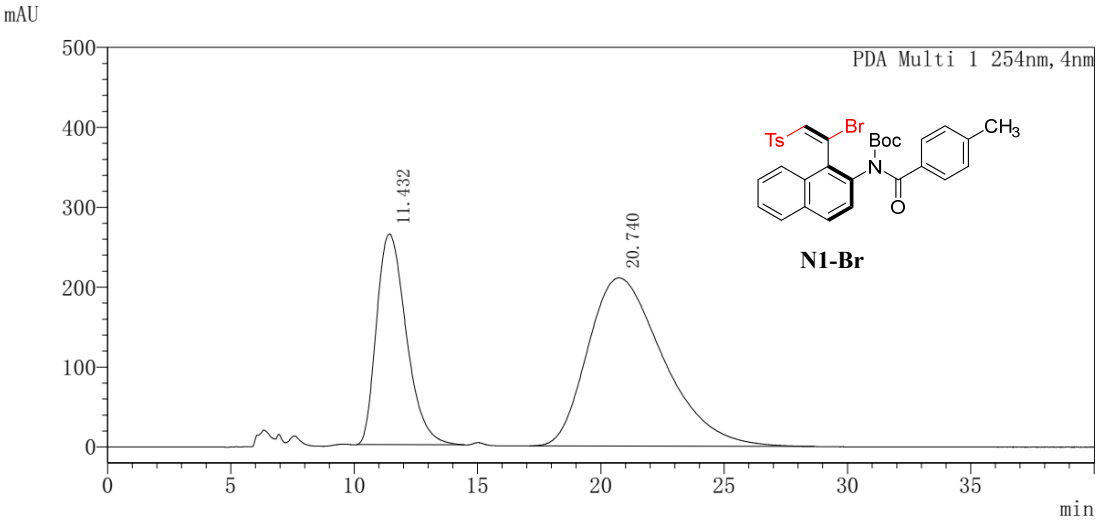
Peak#	Ret. Time	Area	Area%
1	19.774	14975259	50.148
2	23.609	14886680	49.852



Peak Table

PDA Ch1 254nm

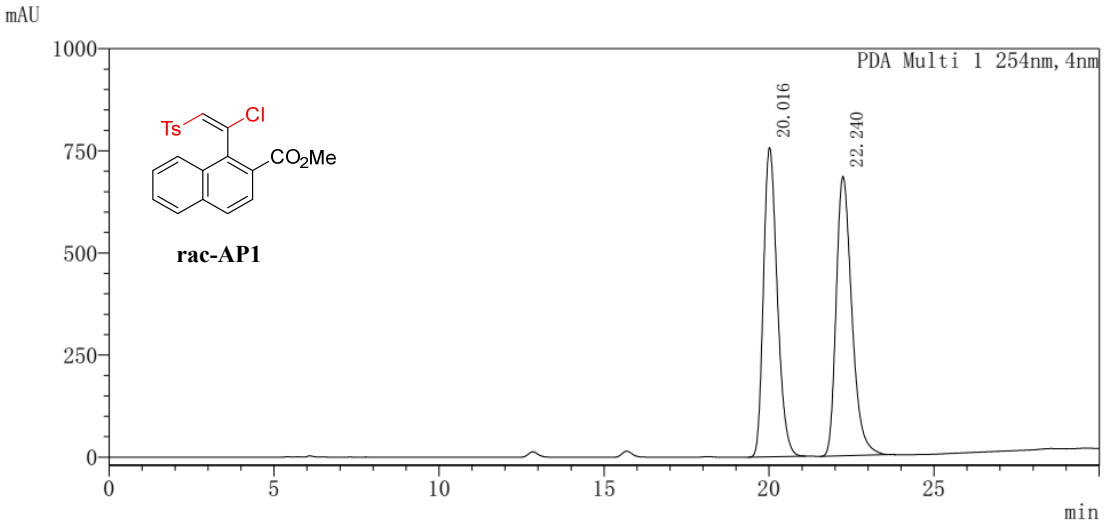
Peak#	Ret. Time	Area	Area%
1	11.289	36771572	50.685
2	20.824	35777589	49.315



Peak Table

PDA Ch1 254nm

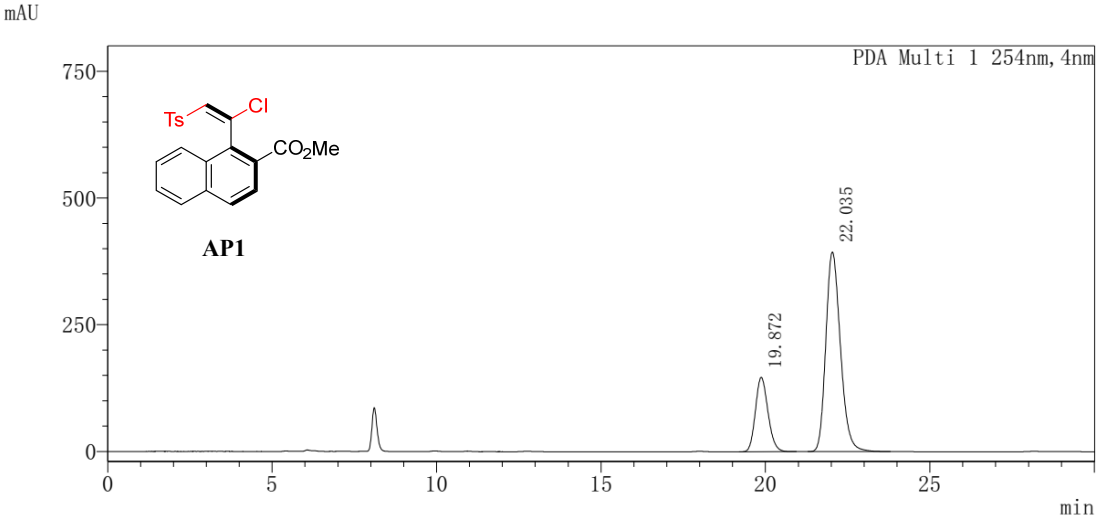
Peak#	Ret. Time	Area	Area%
1	11.432	22128607	33.030
2	20.740	44867091	66.970



Peak Table

PDA Ch1 254nm

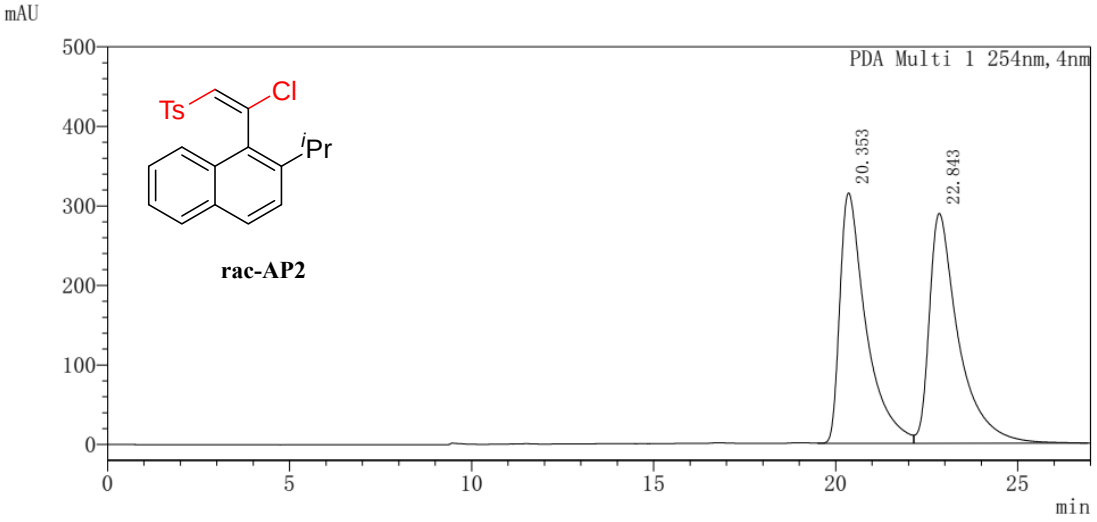
Peak#	Ret. Time	Area	Area%
1	20.016	21977848	49.293
2	22.240	22608061	50.707



Peak Table

PDA Ch1 254nm

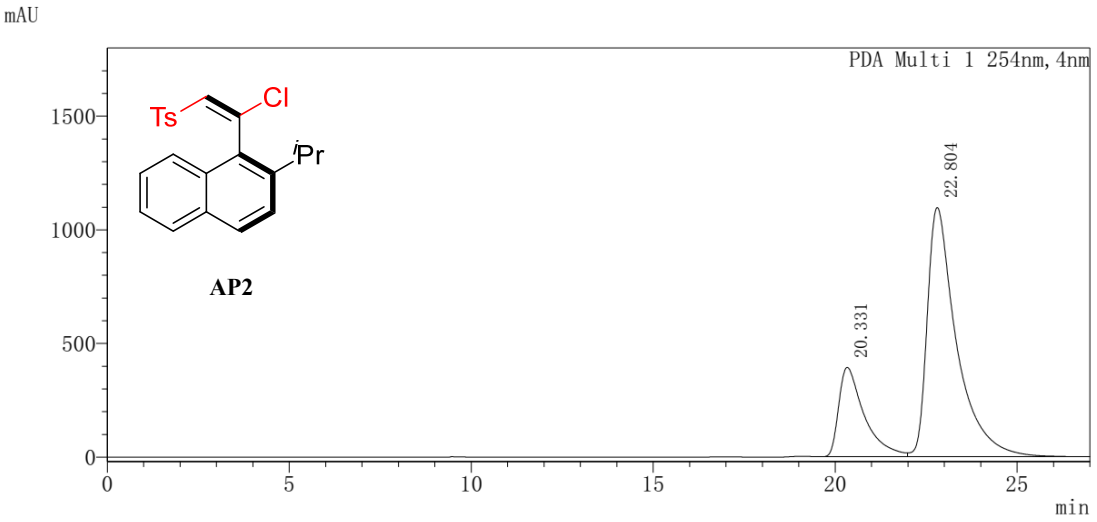
Peak#	Ret. Time	Area	Area%
1	19.872	3894153	24.280
2	22.035	12144364	75.720



Peak Table

PDA Ch1 254nm

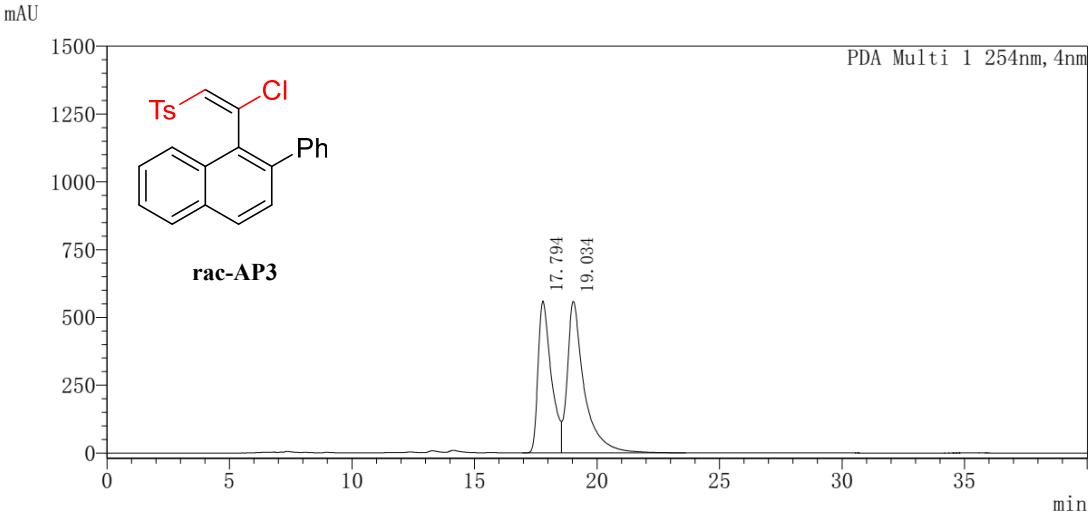
Peak#	Ret. Time	Area	Area%
1	20.353	15769163	49.365
2	22.843	16174622	50.635



Peak Table

PDA Ch1 254nm

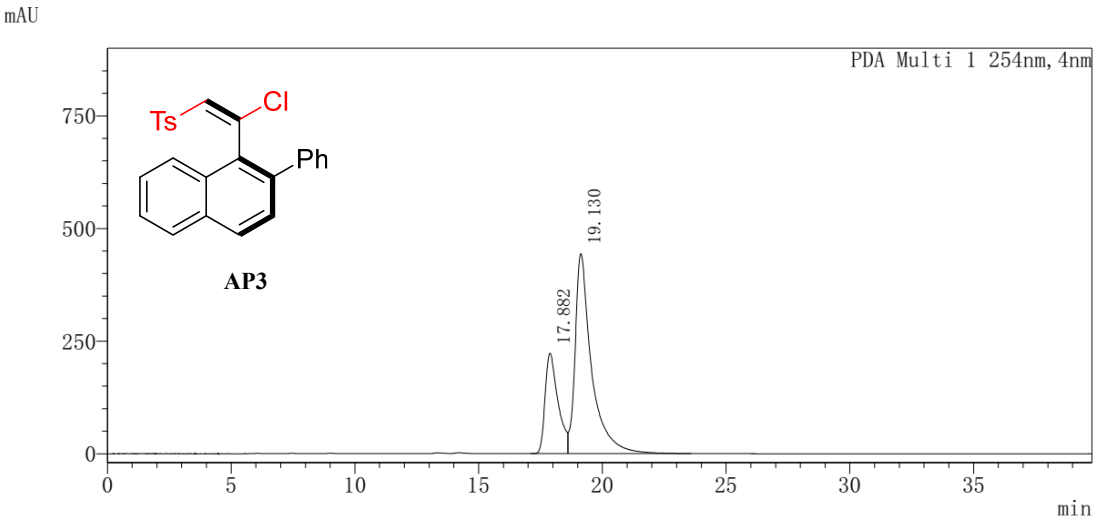
Peak#	Ret. Time	Area	Area%
1	20.331	19106640	23.758
2	22.804	61315924	76.242



Peak Table

PDA Ch1 254nm

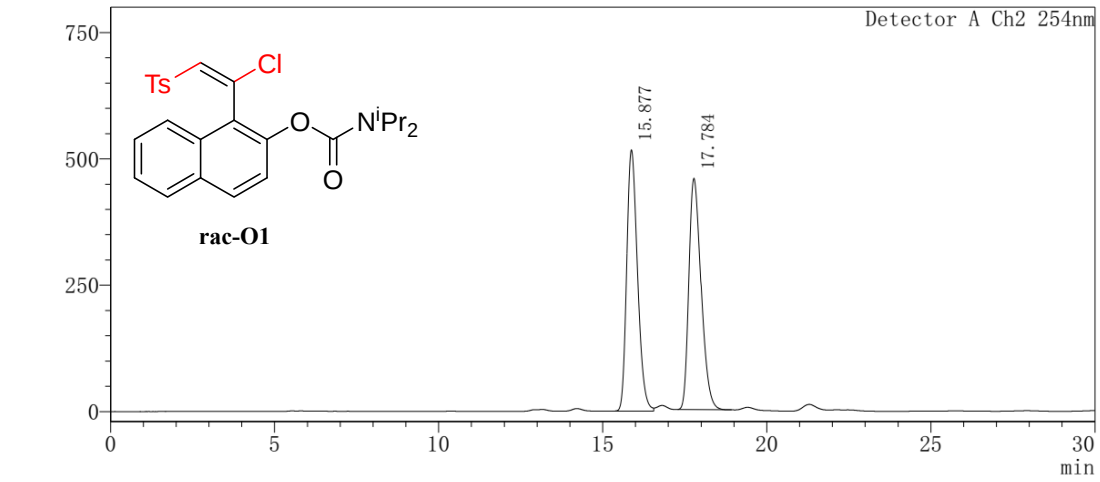
Peak#	Ret. Time	Area	Area%
1	17.794	20982132	43.857
2	19.034	26860114	56.143



Peak Table

PDA Ch1 254nm

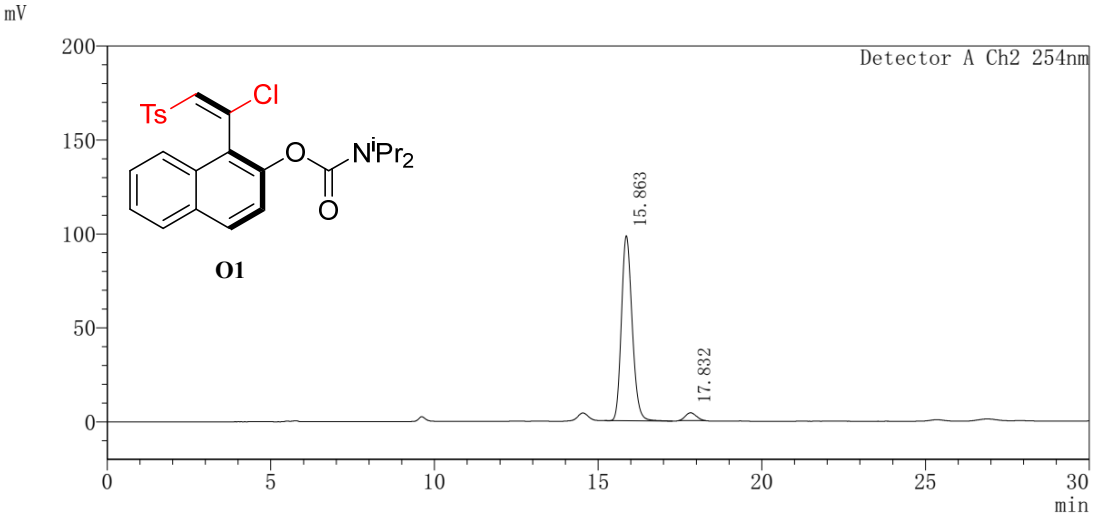
Peak#	Ret. Time	Area	Area%
1	17.882	8119032	28.375
2	19.130	20494514	71.625



Peak Table

Detector A Ch2 254nm

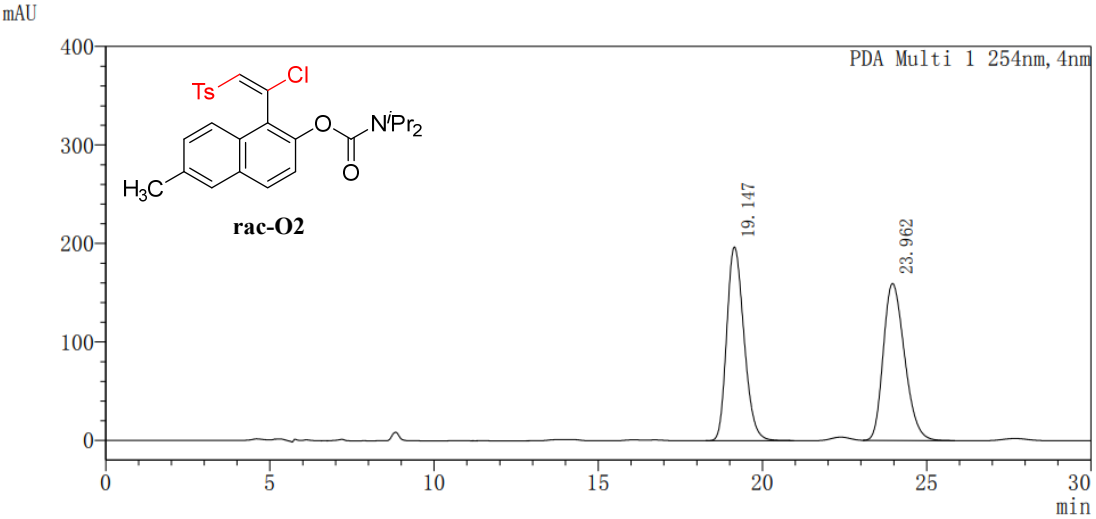
Peak#	Ret. Time	Area	Area%
1	15.877	11847772	50.181
2	17.784	11762511	49.819



Peak Table

Detector A Ch2 254nm

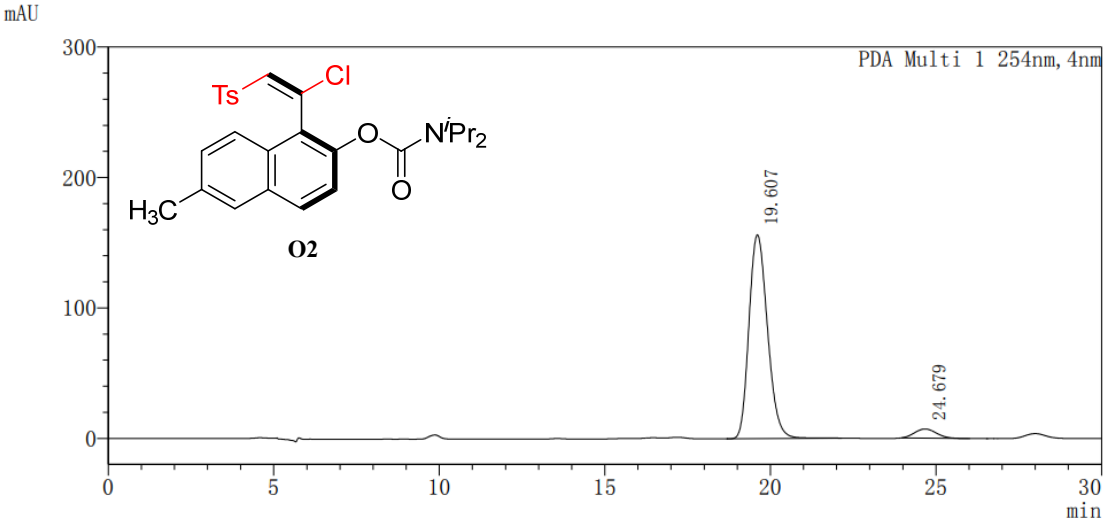
Peak#	Ret. Time	Area	Area%
1	15.863	2249314	95.933
2	17.832	95350	4.067



Peak Table

PDA Ch1 254nm

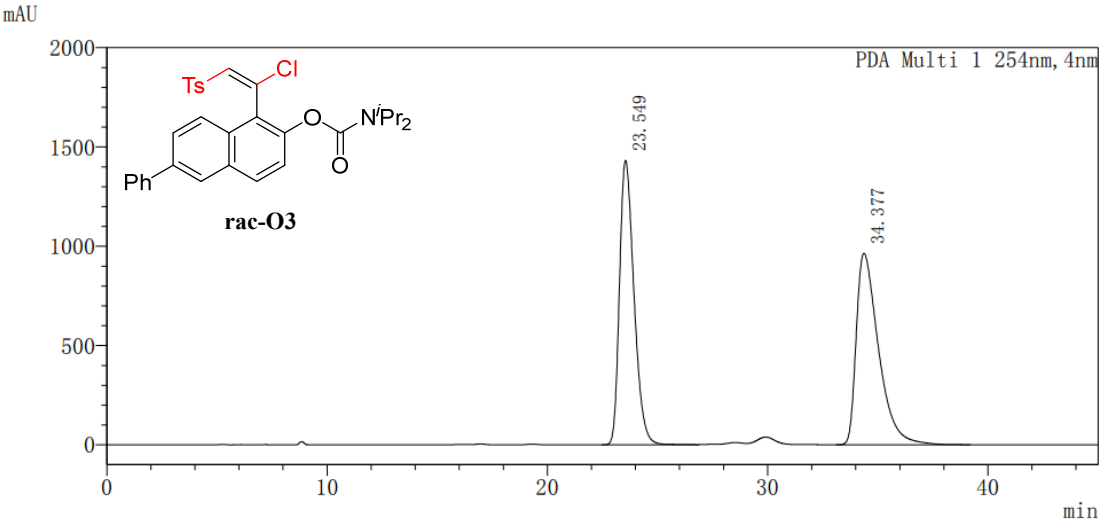
Peak#	Ret. Time	Area	Area%
1	19.147	7199570	50.042
2	23.962	7187429	49.958



Peak Table

PDA Ch1 254nm

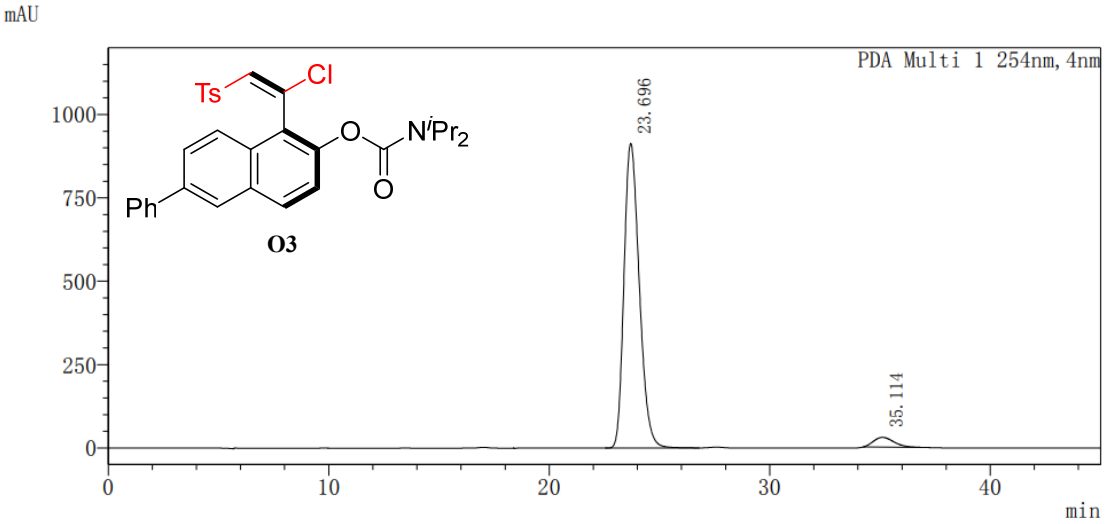
Peak#	Ret. Time	Area	Area%
1	19.607	6083875	95.015
2	24.679	319186	4.985



Peak Table

PDA Ch1 254nm

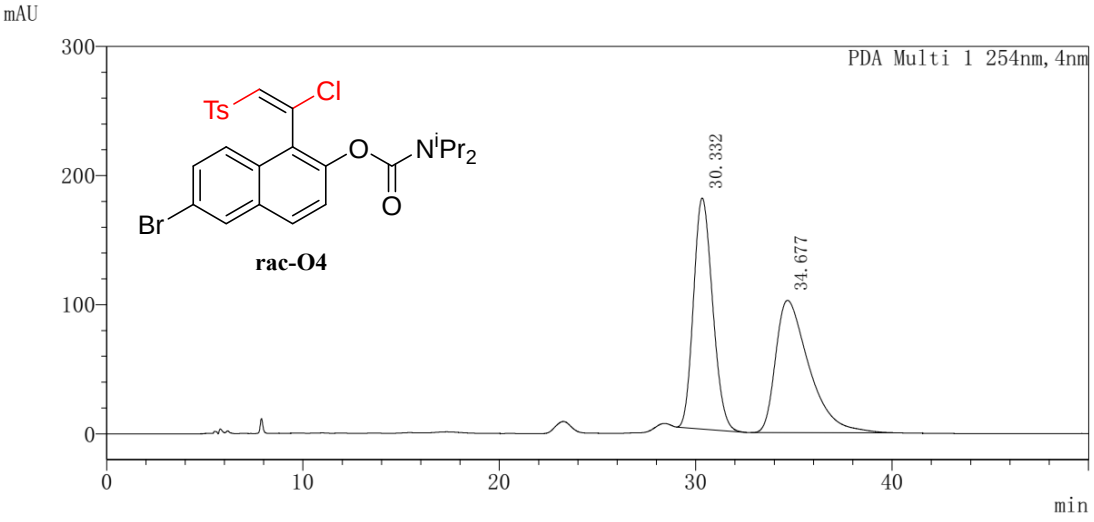
Peak#	Ret. Time	Area	Area%
1	23.549	65411591	49.160
2	34.377	67648251	50.840



Peak Table

PDA Ch1 254nm

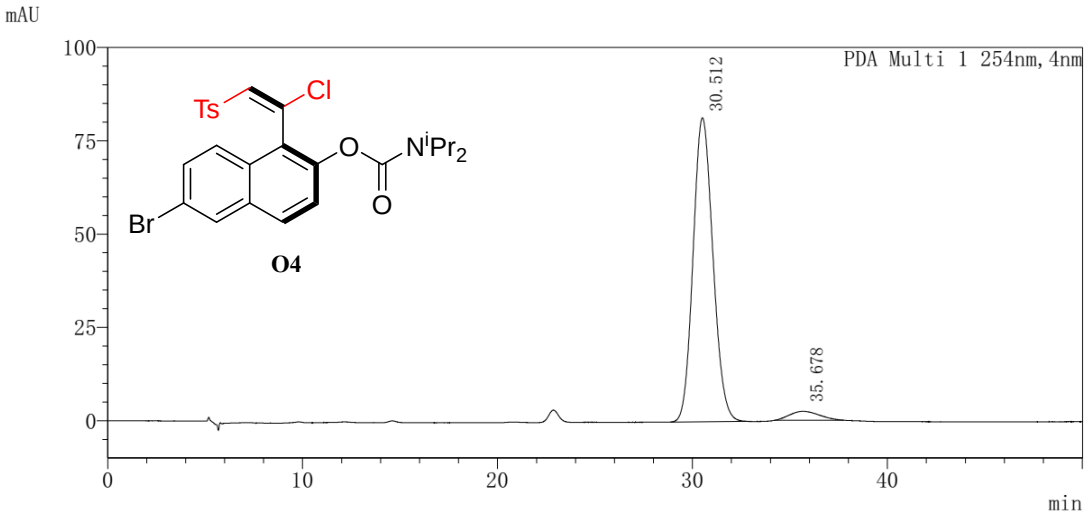
Peak#	Ret. Time	Area	Area%
1	23.696	44084033	95.880
2	35.114	1894451	4.120



Peak Table

PDA Ch1 254nm

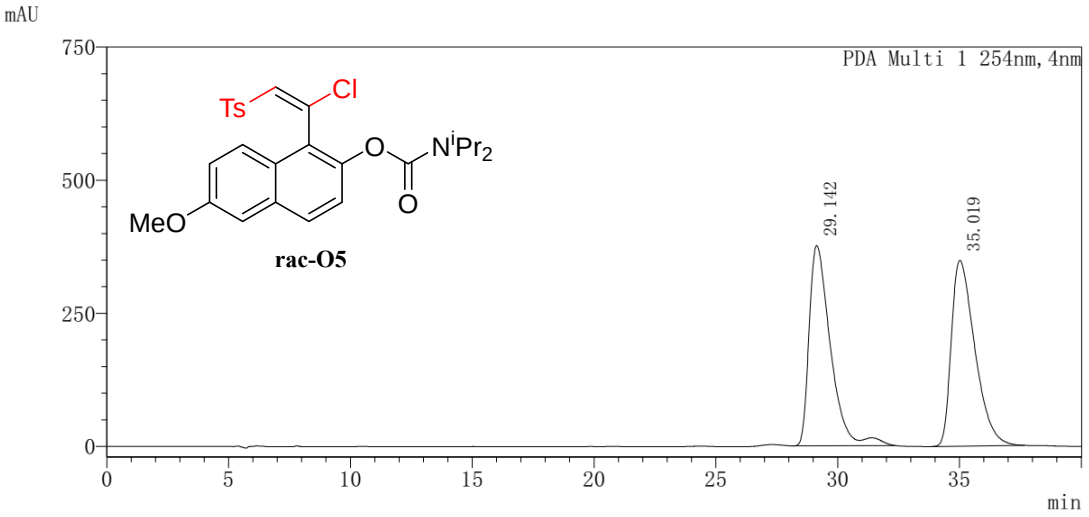
Peak#	Ret. Time	Area	Area%
1	30.332	12111343	49.897
2	34.677	12161489	50.103



Peak Table

PDA Ch1 254nm

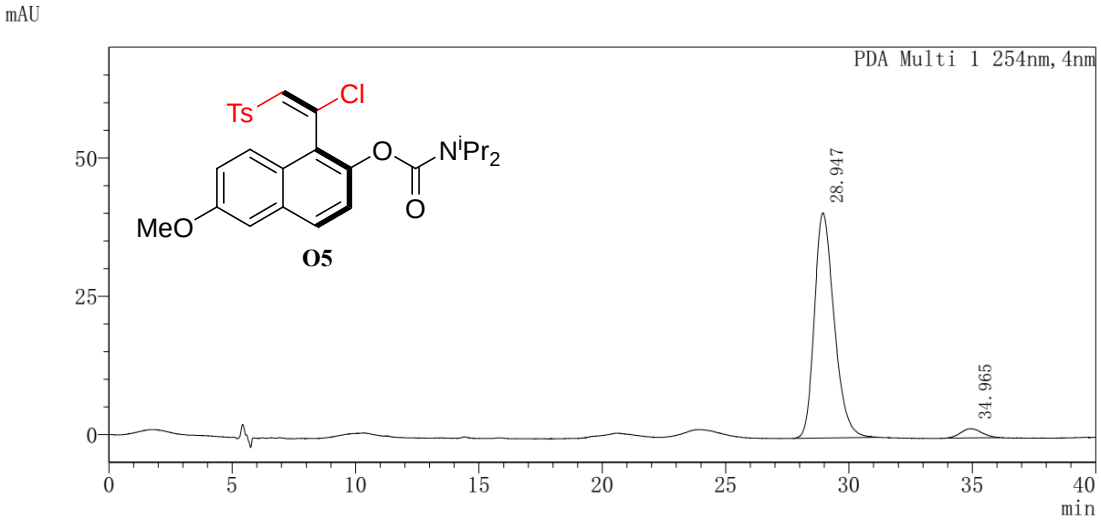
Peak#	Ret. Time	Area	Area%
1	30.512	5766098	95.732
2	35.678	257087	4.268



Peak Table

PDA Ch1 254nm

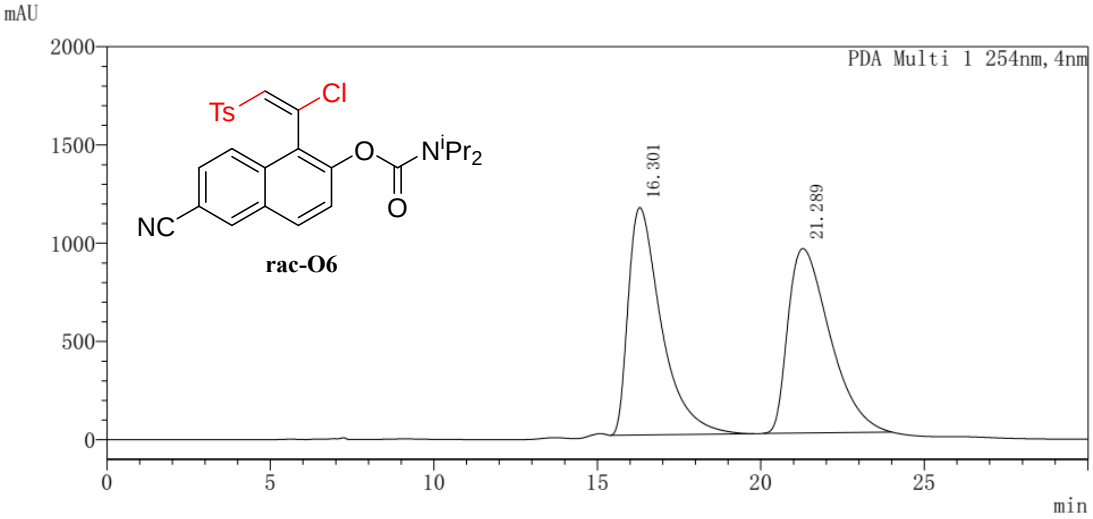
Peak#	Ret. Time	Area	Area%
1	29.142	22982516	49.478
2	35.019	23467904	50.522



Peak Table

PDA Ch1 254nm

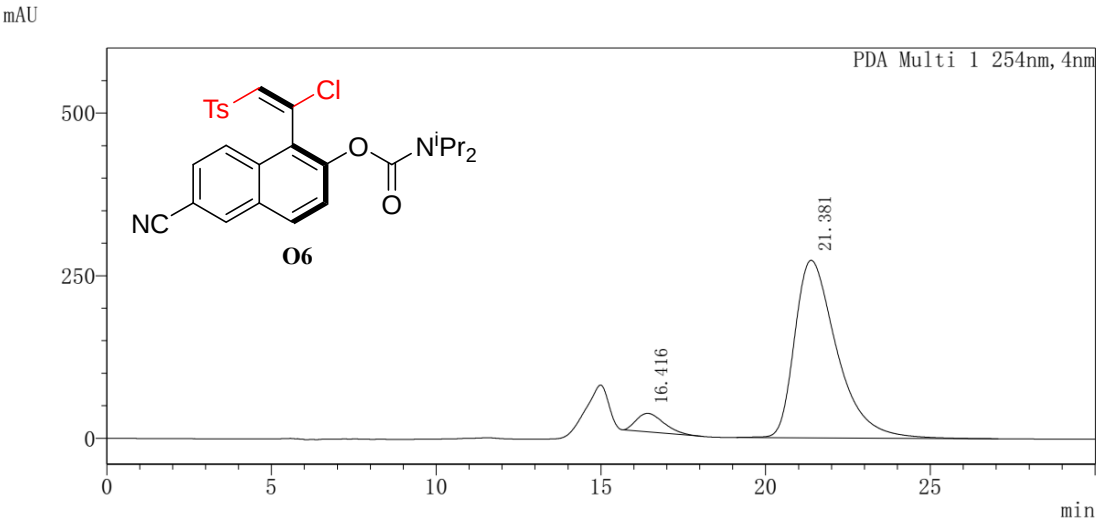
Peak#	Ret. Time	Area	Area%
1	28.947	2270340	95.825
2	34.965	98925	4.175



Peak Table

PDA Ch1 254nm

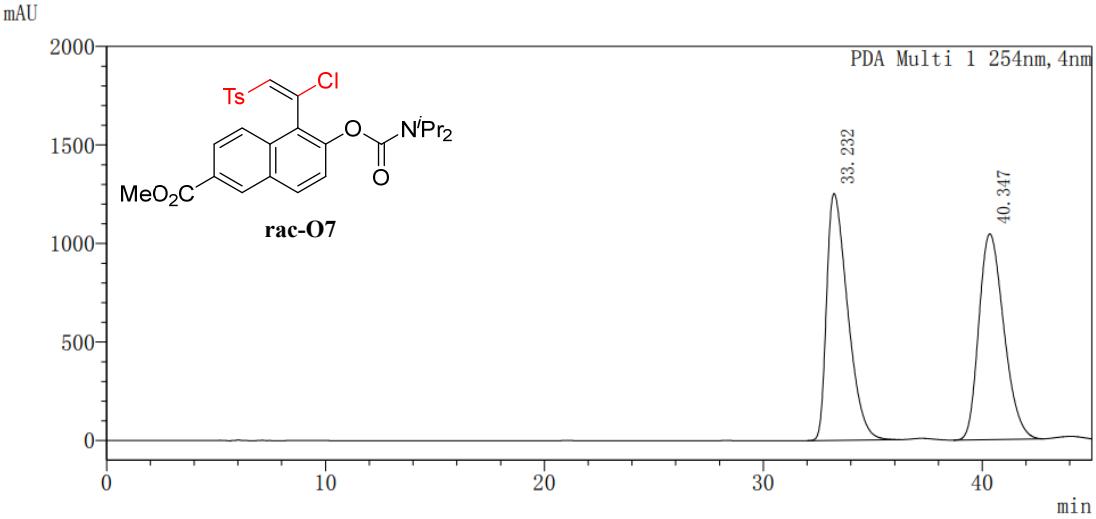
Peak#	Ret. Time	Area	Area%
1	16.301	81754074	49.384
2	21.289	83792300	50.616



Peak Table

PDA Ch1 254nm

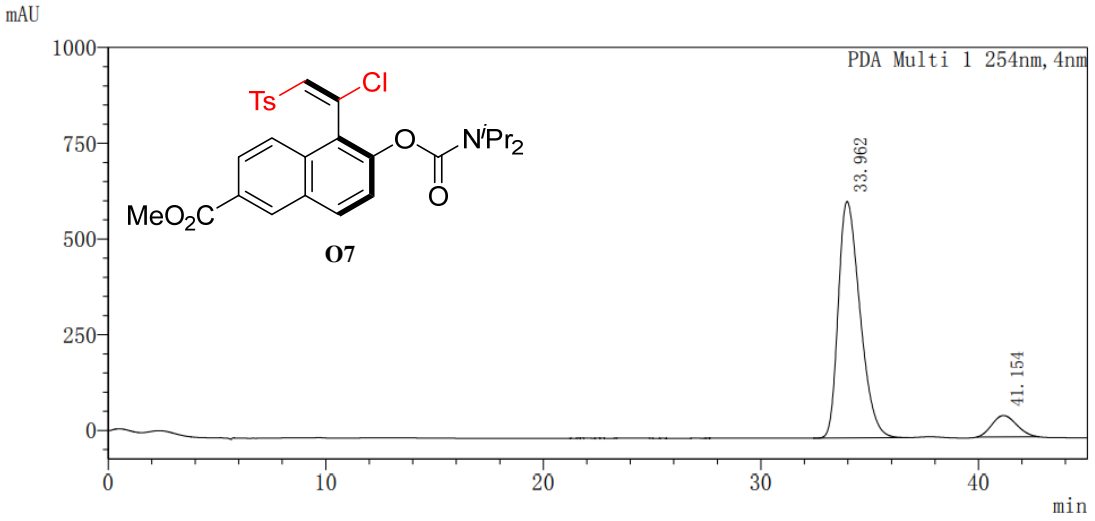
Peak#	Ret. Time	Area	Area%
1	16.416	1668466	6.429
2	21.381	24284307	93.571



Peak Table

PDA Ch1 254nm

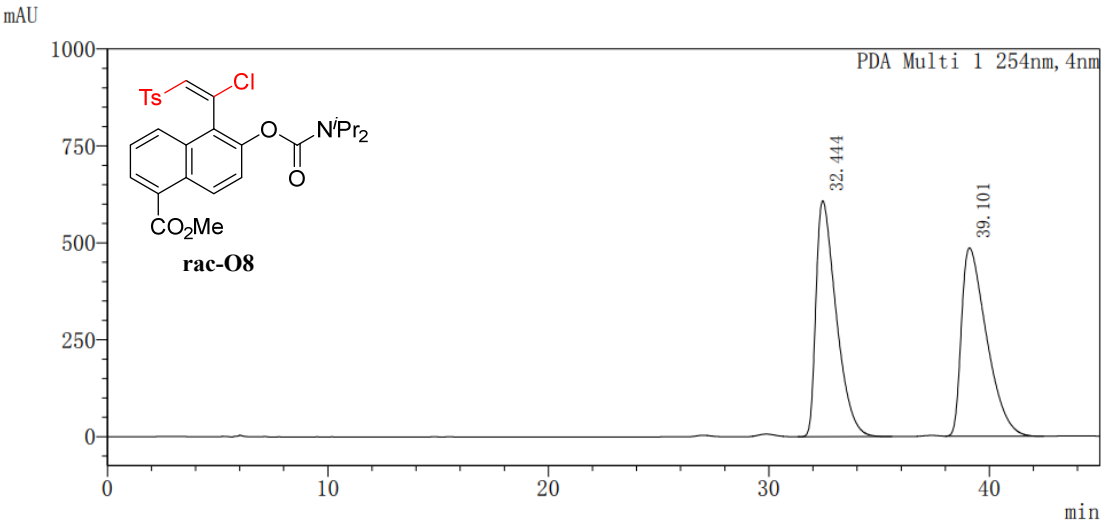
Peak#	Ret. Time	Area	Area%
1	33.232	83595351	50.140
2	40.347	83128628	49.860



Peak Table

PDA Ch1 254nm

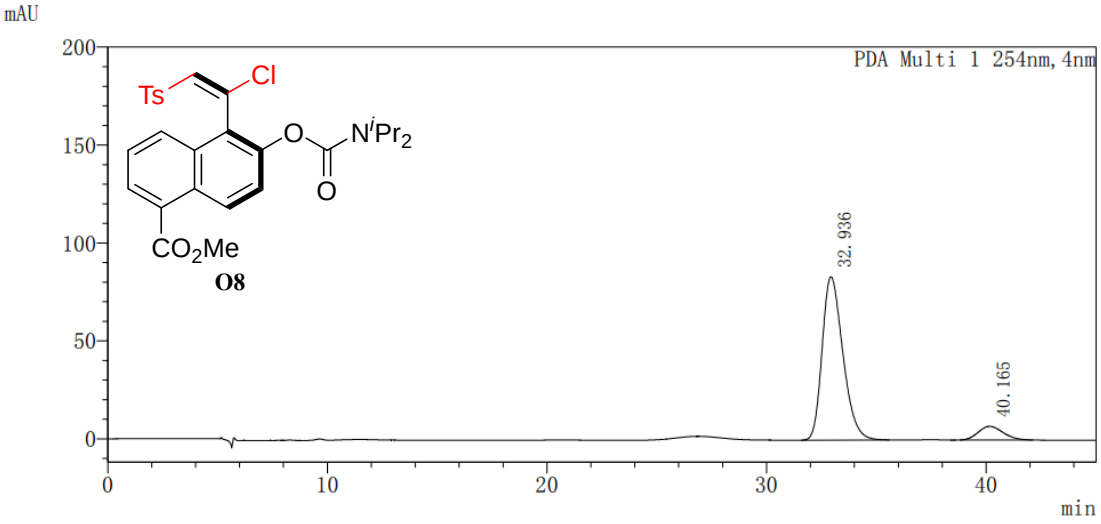
Peak#	Ret. Time	Area	Area%
1	33.962	42852148	90.722
2	41.154	4382594	9.278



Peak Table

PDA Ch1 254nm

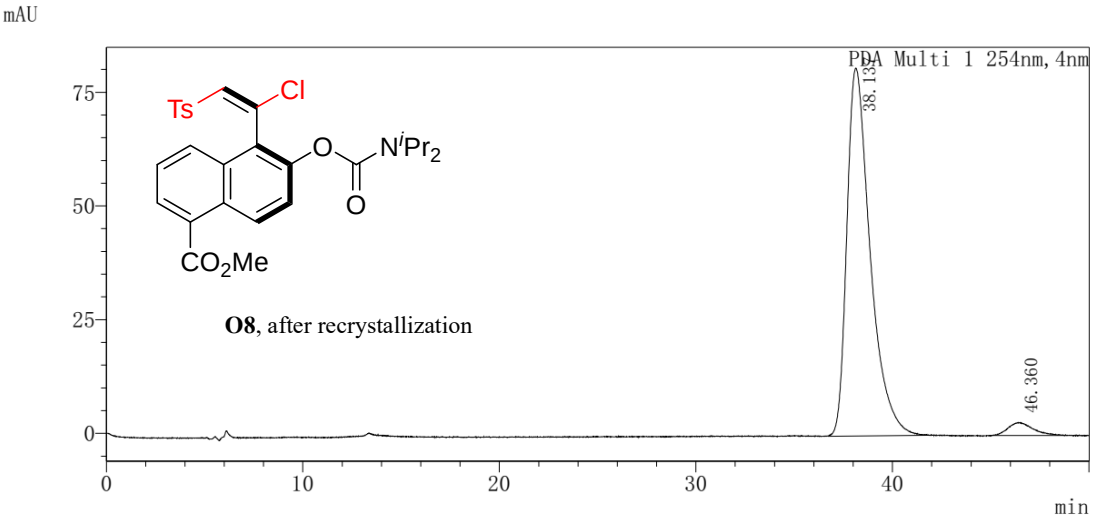
Peak#	Ret. Time	Area	Area%
1	32.444	38813929	50.136
2	39.101	38603113	49.864



Peak Table

PDA Ch1 254nm

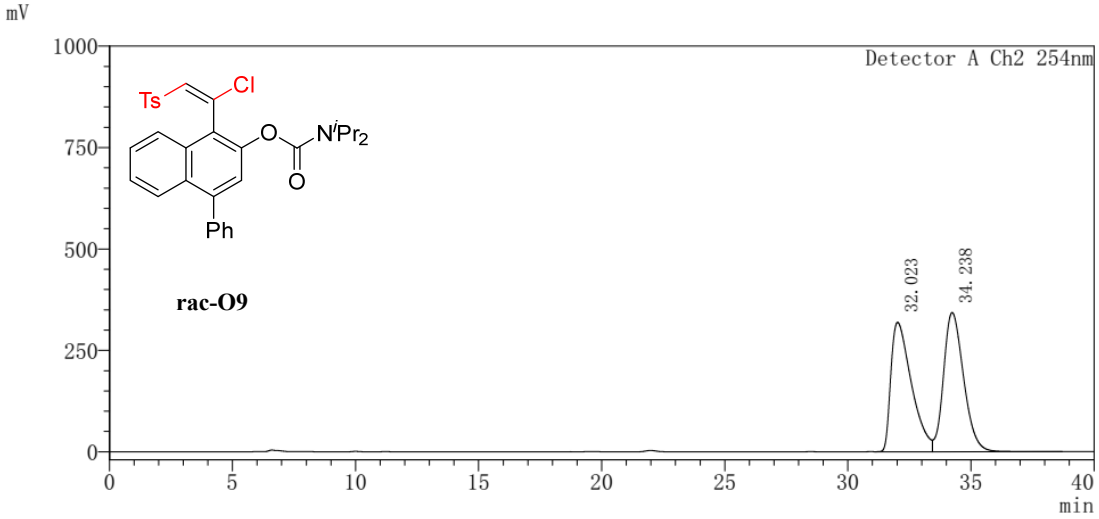
Peak#	Ret. Time	Area	Area%
1	32.936	5481958	90.923
2	40.165	547248	9.077



Peak Table

PDA Ch1 254nm

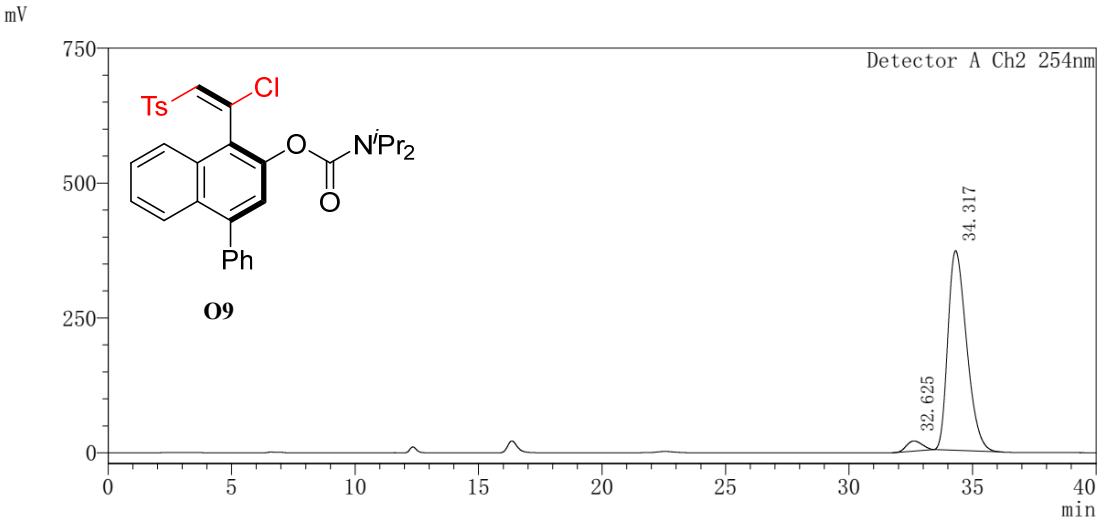
Peak#	Ret. Time	Area	Area%
1	38.137	6680785	96.312
2	46.360	255823	3.688



Peak Table

Detector A Ch2 254nm

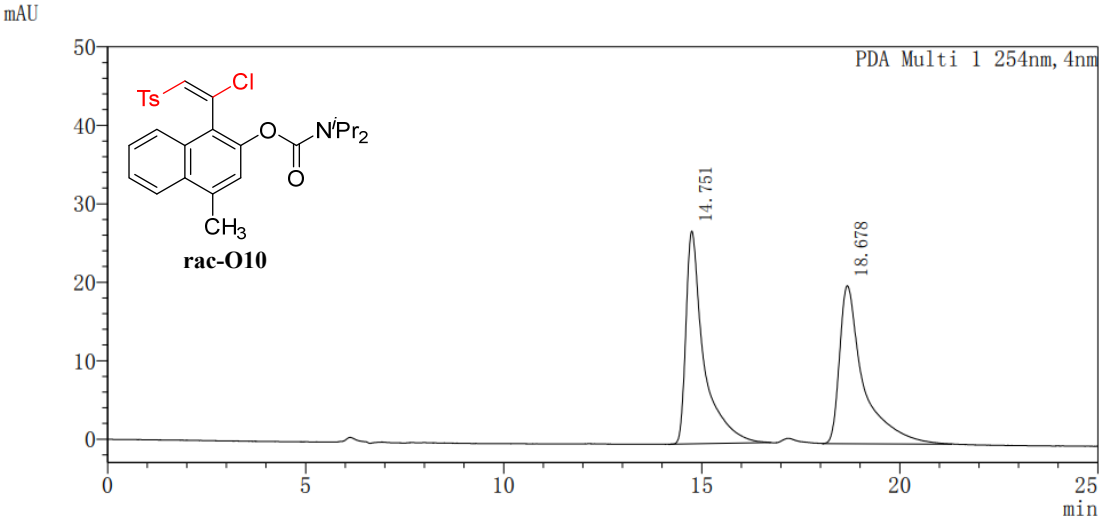
Peak#	Ret. Time	Area	Area%
1	32.023	18527915	48.720
2	34.238	19501720	51.280



Peak Table

Detector A Ch2 254nm

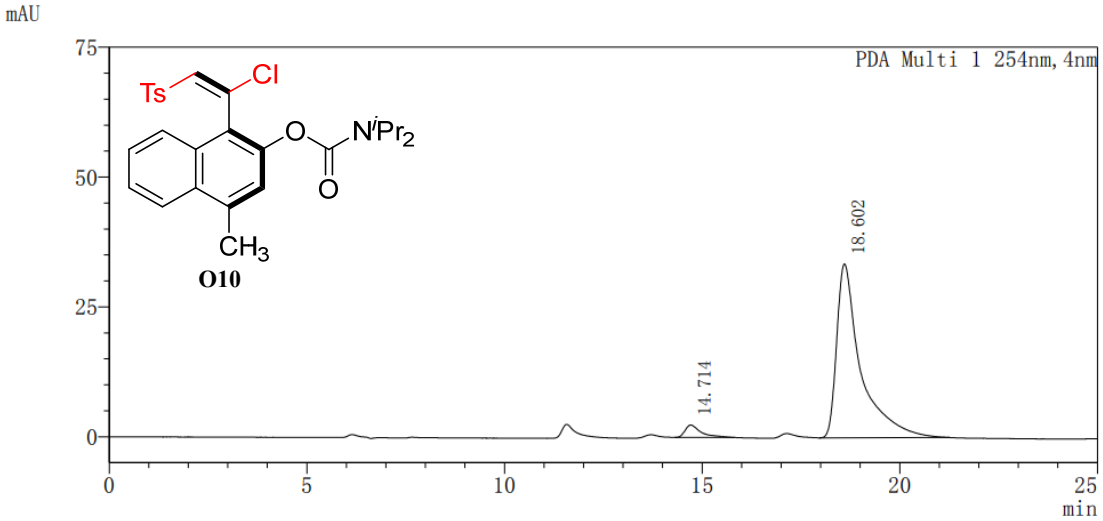
Peak#	Ret. Time	Area	Area%
1	32.625	821288	4.034
2	34.317	19538408	95.966



Peak Table

PDA Ch1 254nm

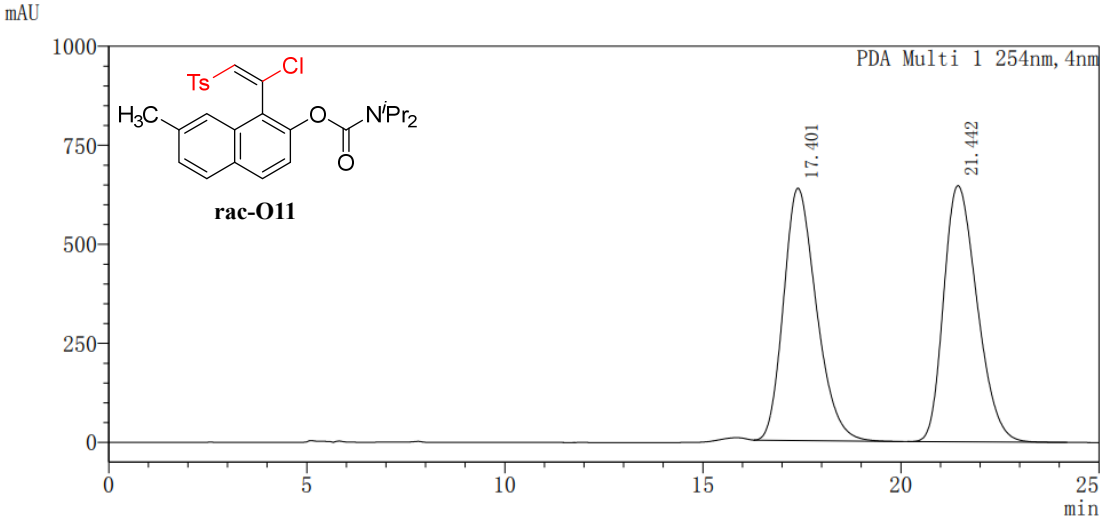
Peak#	Ret. Time	Area	Area%
1	14.751	850333	50.235
2	18.678	842377	49.765



Peak Table

PDA Ch1 254nm

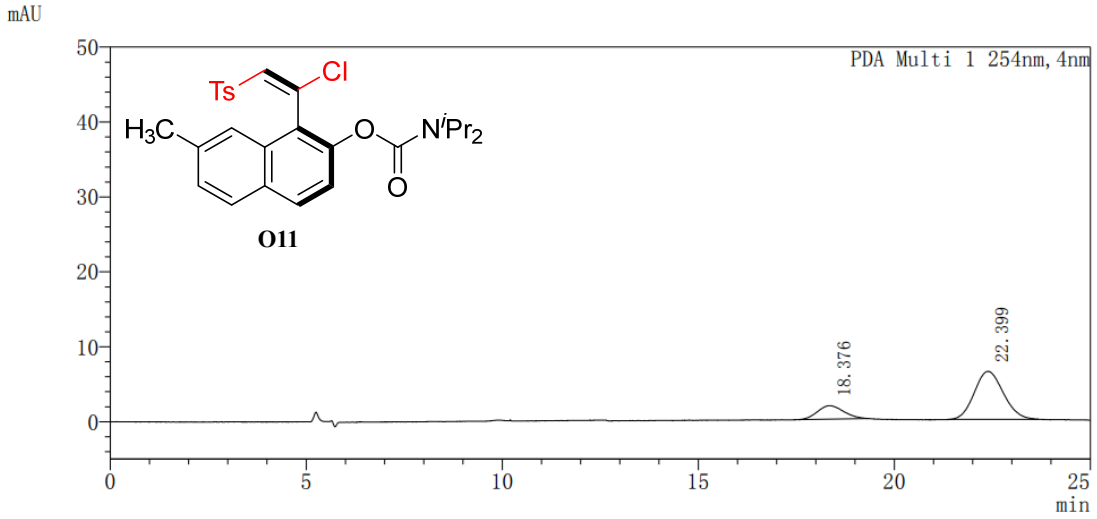
Peak#	Ret. Time	Area	Area%
1	14.714	67307	4.535
2	18.602	1416913	95.465



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.401	36860391	49.228
2	21.442	38017051	50.772

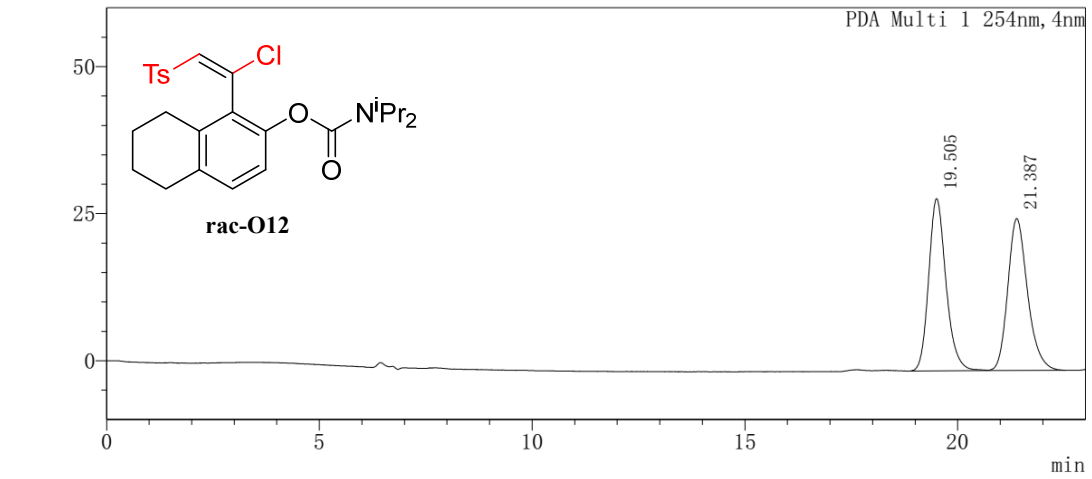


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.376	82694	20.059
2	22.399	329569	79.941

mAU

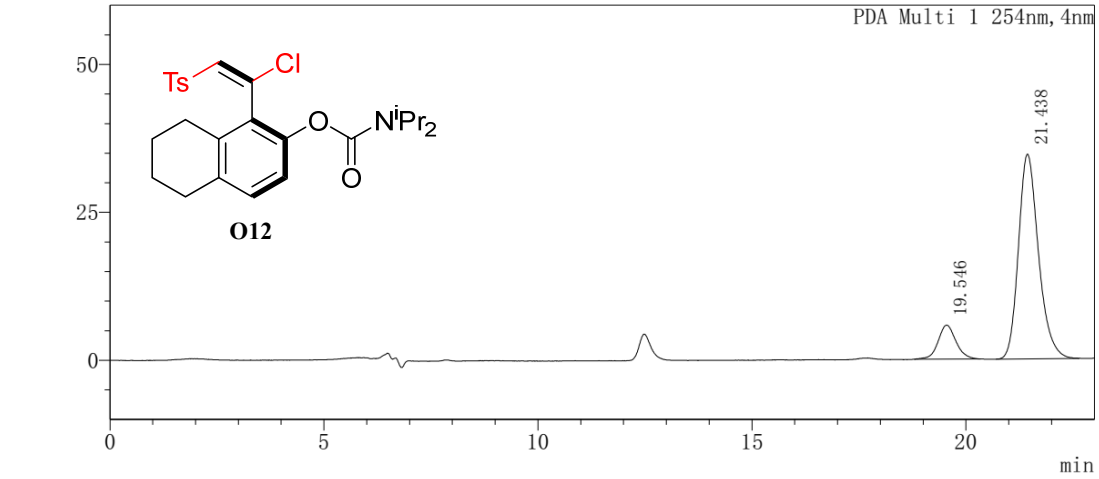


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.505	831567	49.890
2	21.387	835234	50.110

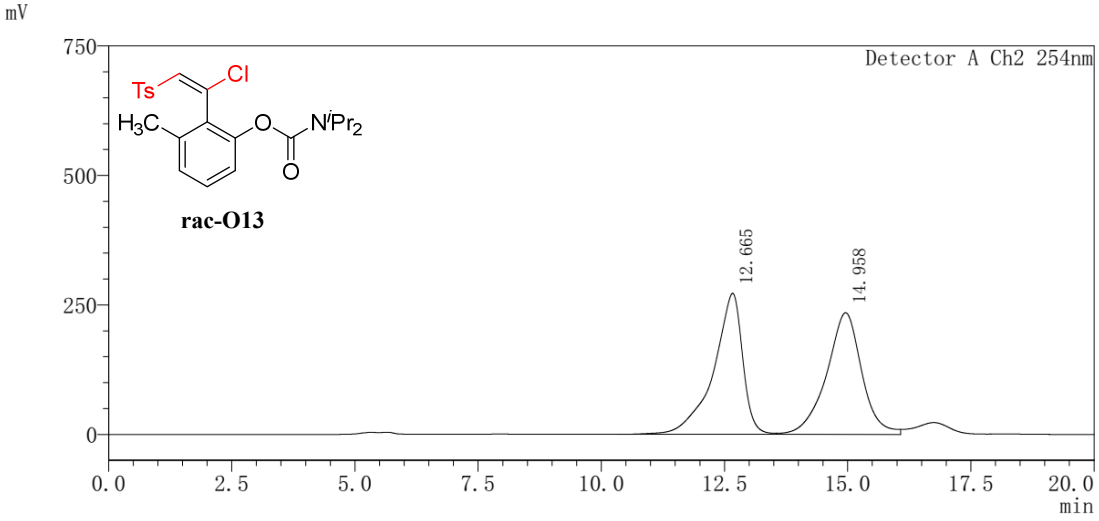
mAU



Peak Table

PDA Ch1 254nm

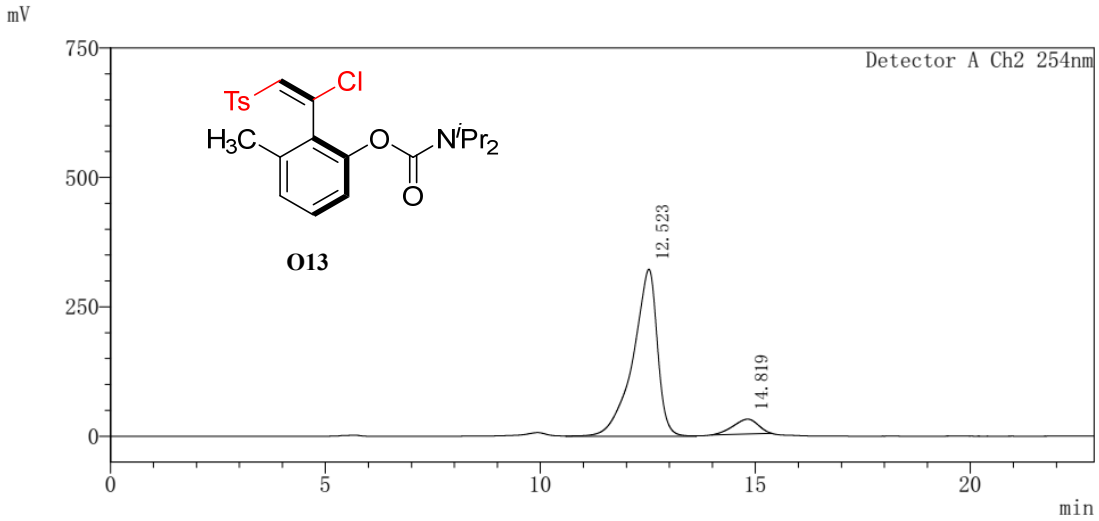
Peak#	Ret. Time	Area	Area%
1	19.546	167988	12.970
2	21.438	1127253	87.030



Peak Table

Detector A Ch2 254nm

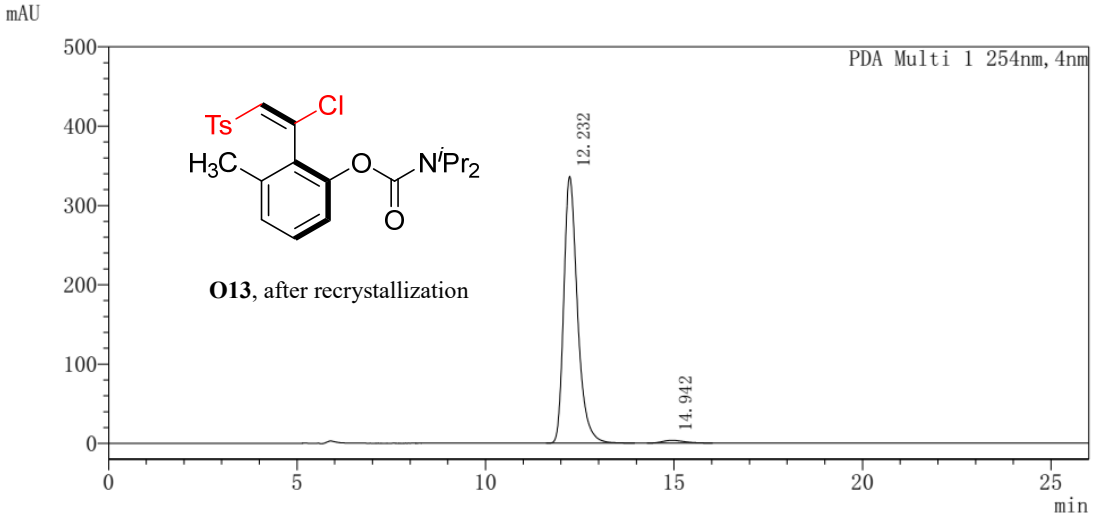
Peak#	Ret. Time	Area	Area%
1	12.665	11234058	49.048
2	14.958	11670093	50.952



Peak Table

Detector A Ch2 254nm

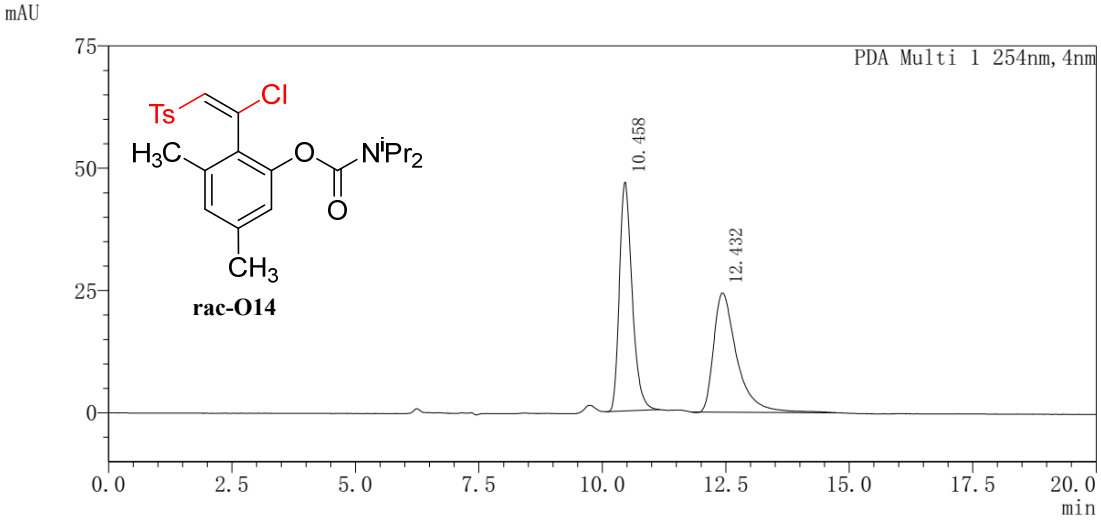
Peak#	Ret. Time	Area	Area%
1	12.523	12773014	91.678
2	14.819	1159481	8.322



Peak Table

PDA Ch1 254nm

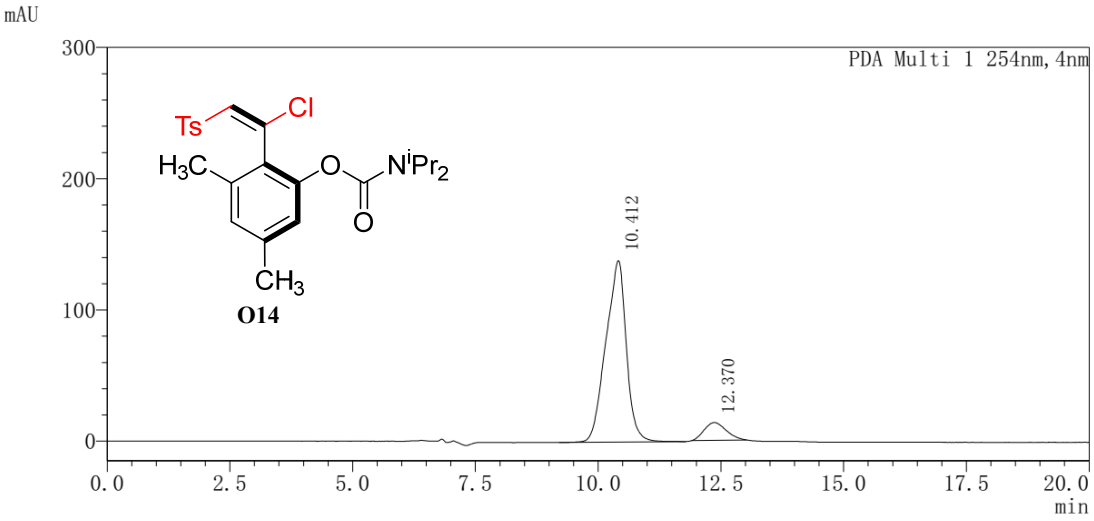
Peak#	Ret. Time	Area	Area%
1	12.232	8482517	98.351
2	14.942	142263	1.649



Peak Table

PDA Ch1 254nm

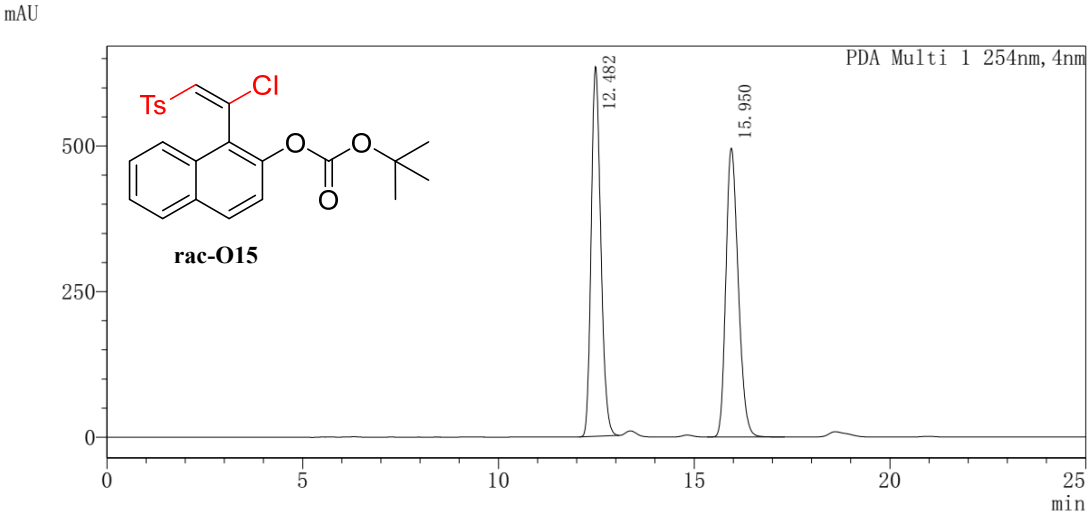
Peak#	Ret. Time	Area	Area%
1	10.458	837346	51.226
2	12.432	797254	48.774



Peak Table

PDA Ch1 254nm

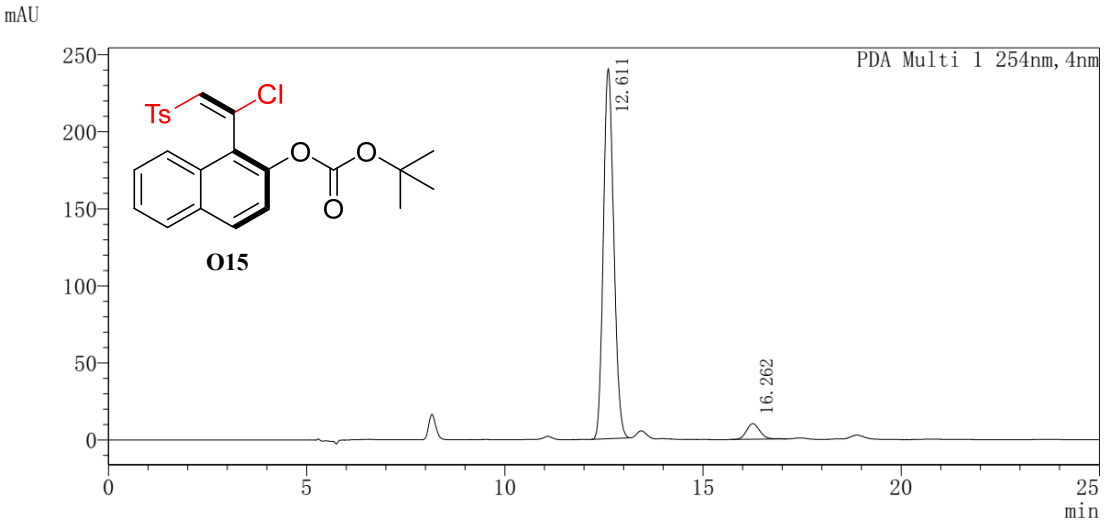
Peak#	Ret. Time	Area	Area%
1	10.412	4007763	90.410
2	12.370	425099	9.590



Peak Table

PDA Ch1 254nm

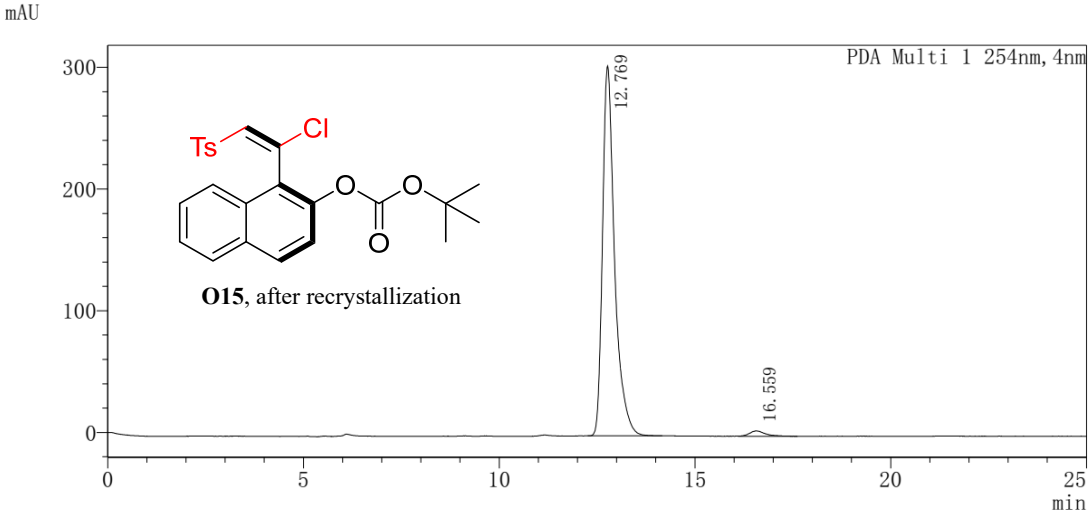
Peak#	Ret. Time	Area	Area%
1	12.482	10845357	49.878
2	15.950	10898425	50.122



Peak Table

PDA Ch1 254nm

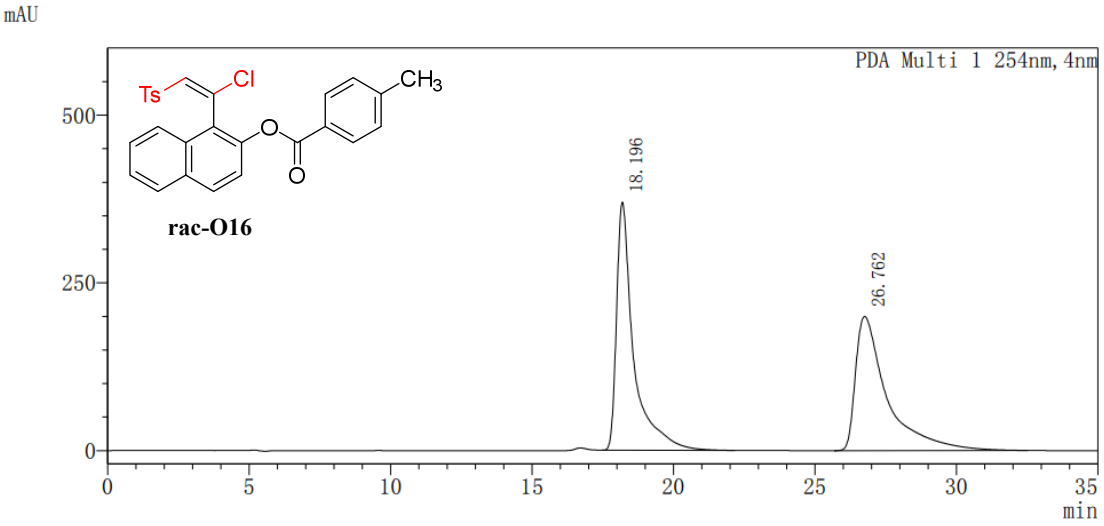
Peak#	Ret. Time	Area	Area%
1	12.611	4396173	94.799
2	16.262	241180	5.201



Peak Table

PDA Ch1 254nm

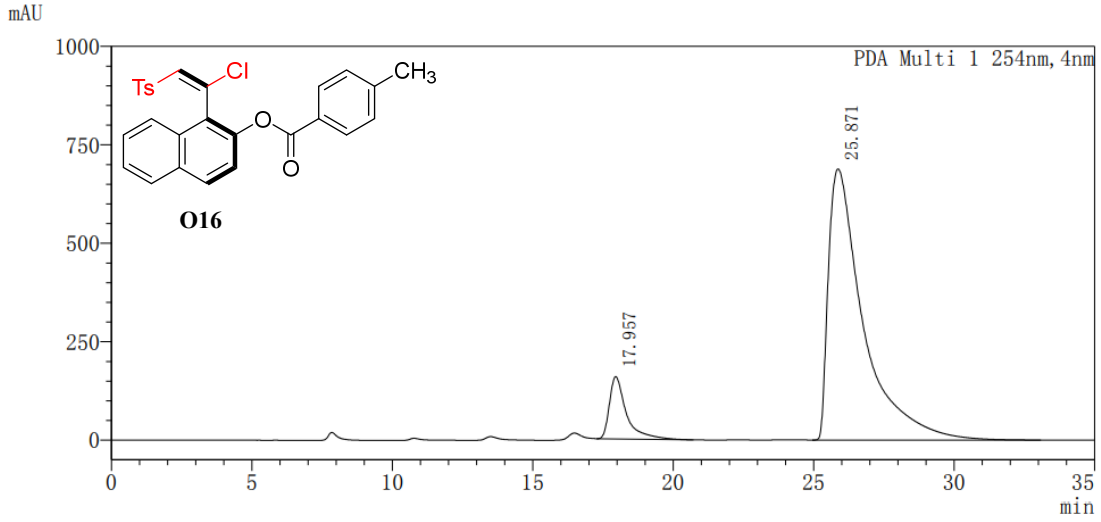
Peak#	Ret. Time	Area	Area%
1	12.769	6526687	98.152
2	16.559	122893	1.848



Peak Table

PDA Ch1 254nm

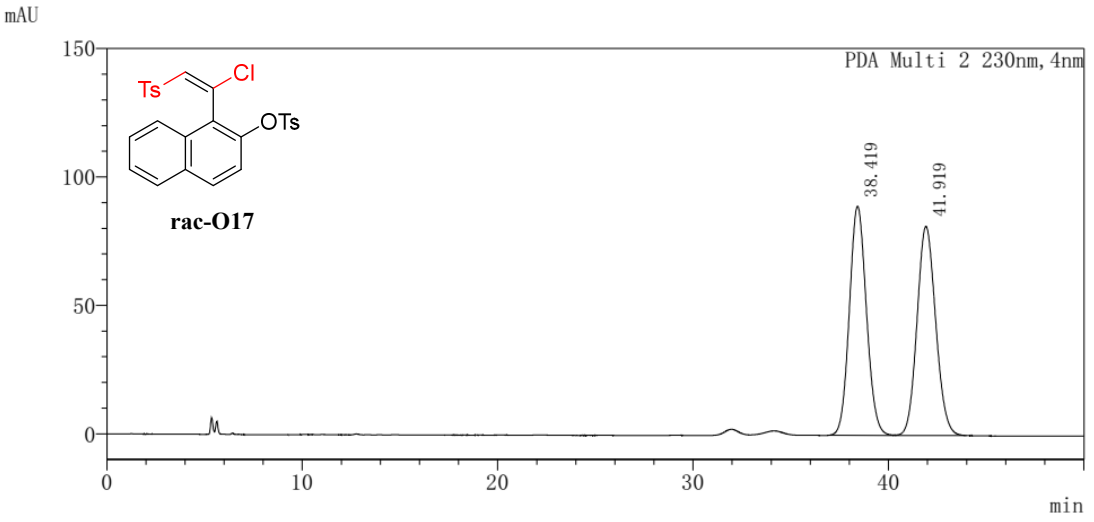
Peak#	Ret. Time	Area	Area%
1	18.196	15550968	50.057
2	26.762	15515408	49.943



Peak Table

PDA Ch1 254nm

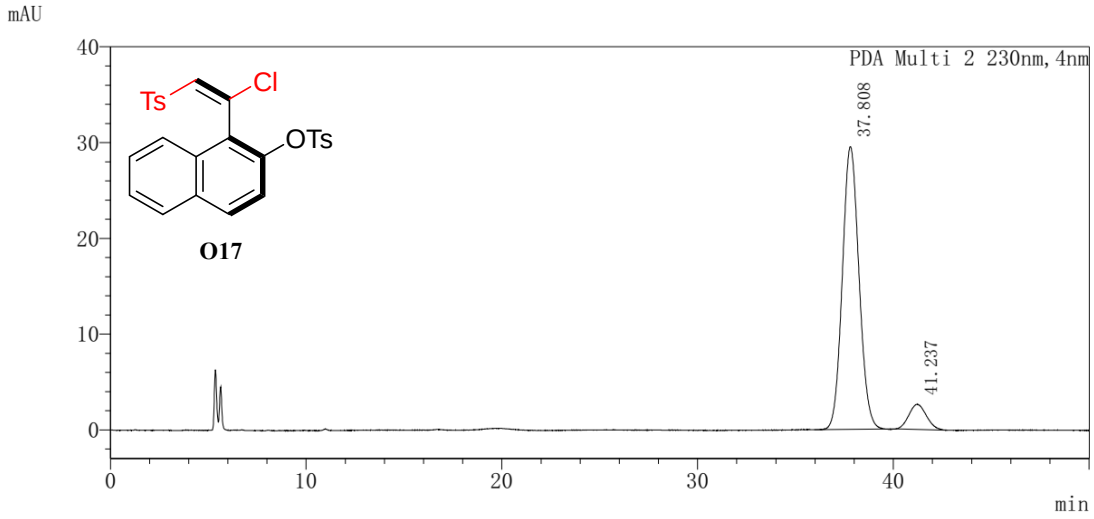
Peak#	Ret. Time	Area	Area%
1	17.957	6631937	10.027
2	25.871	59510825	89.973



Peak Table

PDA Ch2 230nm

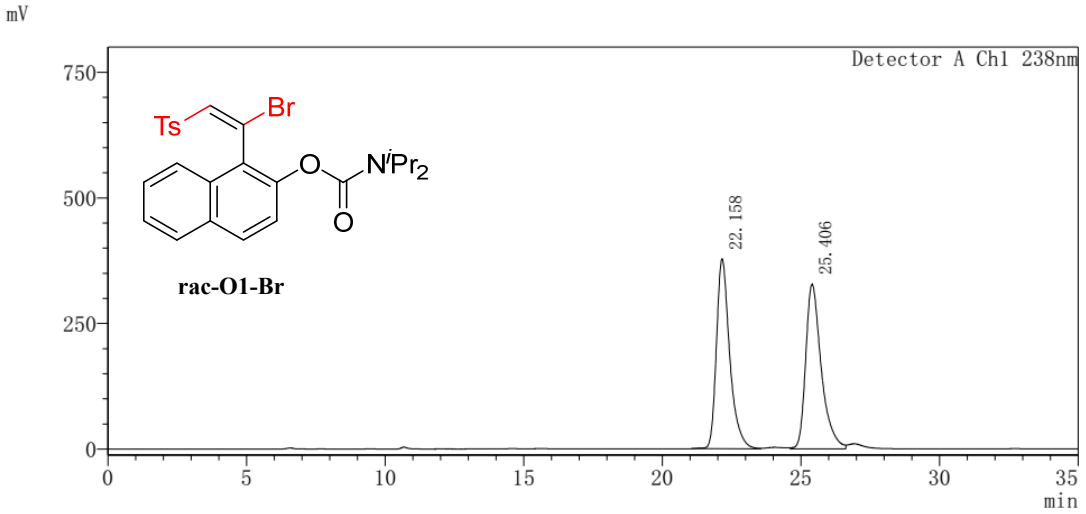
Peak#	Ret. Time	Area	Area%
1	38.419	5421610	50.062
2	41.919	5408177	49.938



Peak Table

PDA Ch2 230nm

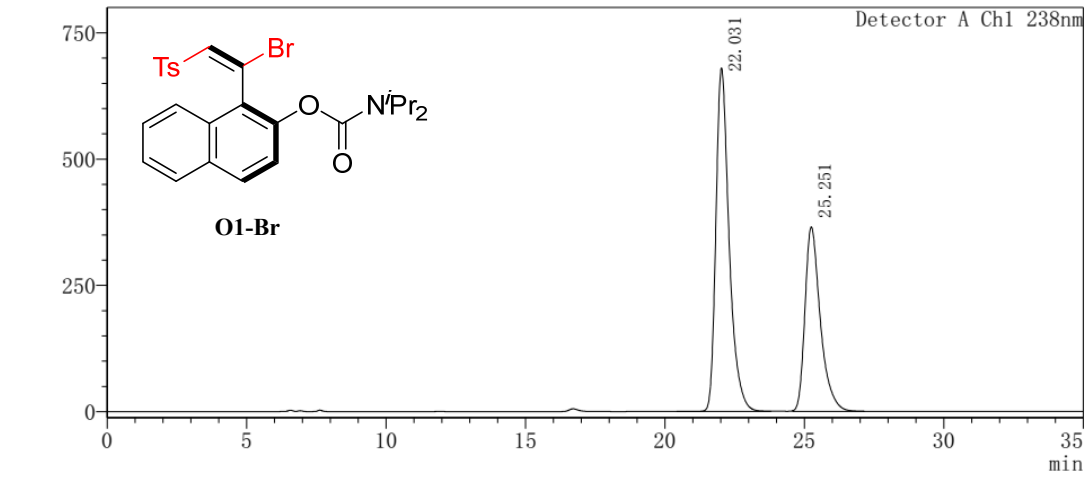
Peak#	Ret. Time	Area	Area%
1	37.808	1743411	91.518
2	41.237	161573	8.482



Peak Table

Detector A Ch1 238nm

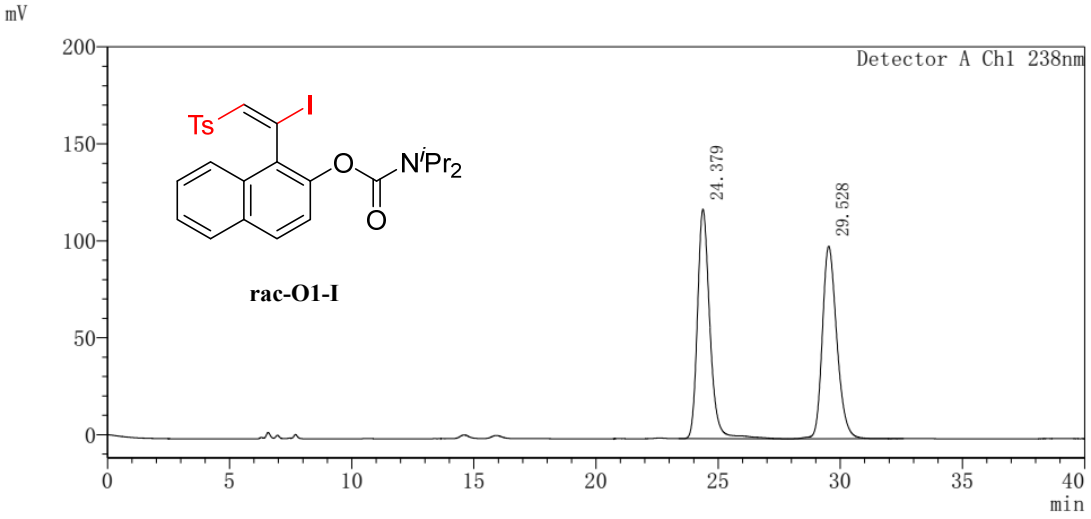
Peak#	Ret. Time	Area	Area%
1	22.158	12599876	49.642
2	25.406	12781788	50.358



Peak Table

Detector A Ch1 238nm

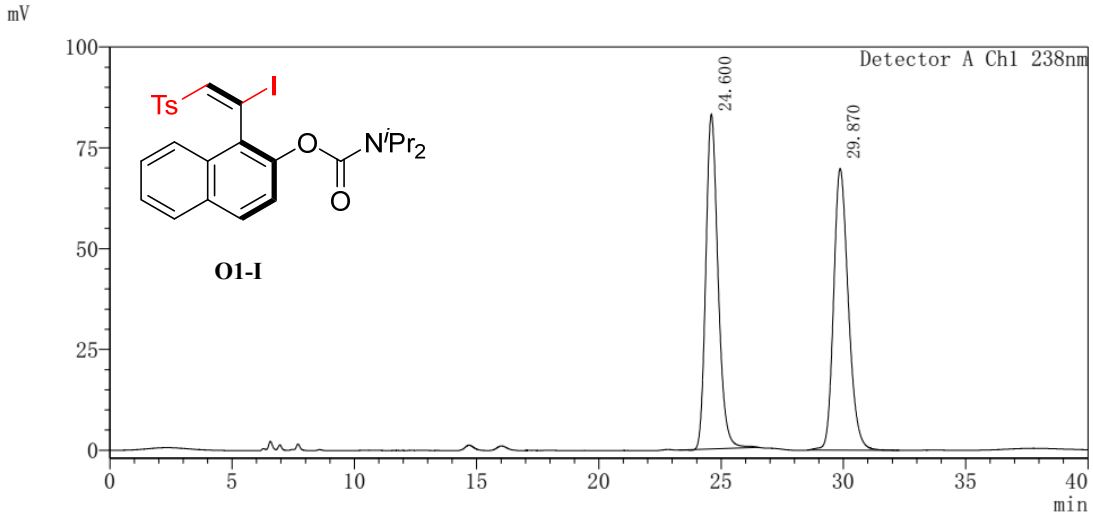
Peak#	Ret. Time	Area	Area%
1	22.031	22442658	61.476
2	25.251	14063577	38.524



Peak Table

Detector A Ch1 238nm

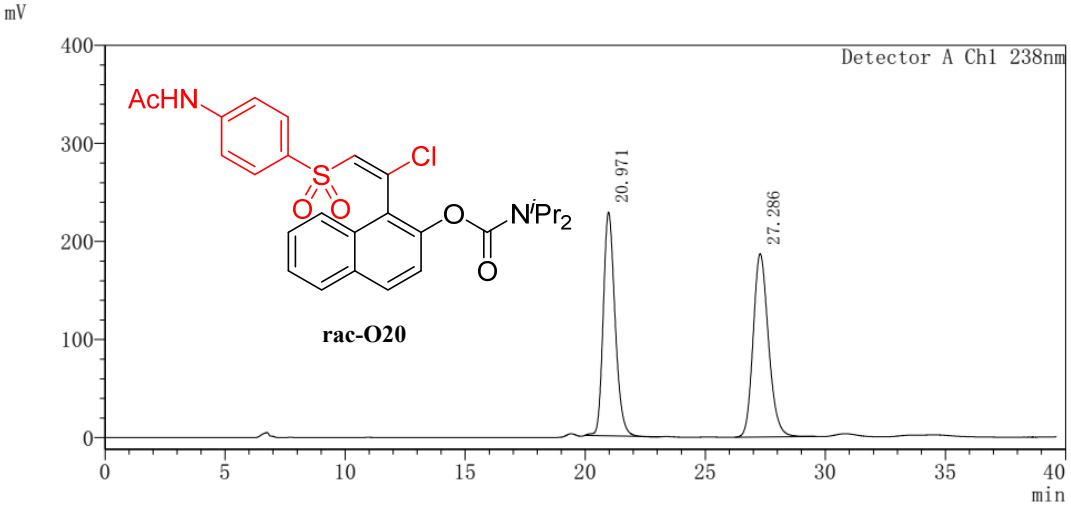
Peak#	Ret. Time	Area	Area%
1	24.379	4188387	50.569
2	29.528	4094139	49.431



Peak Table

Detector A Ch1 238nm

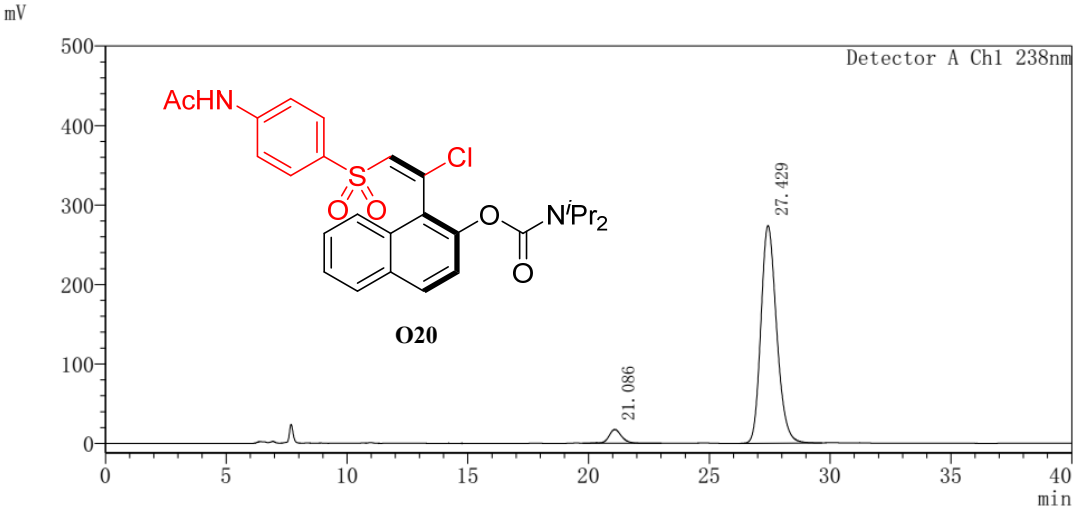
Peak#	Ret. Time	Area	Area%
1	24.600	2887924	49.694
2	29.870	2923433	50.306



Peak Table

Detector A Ch1 238nm

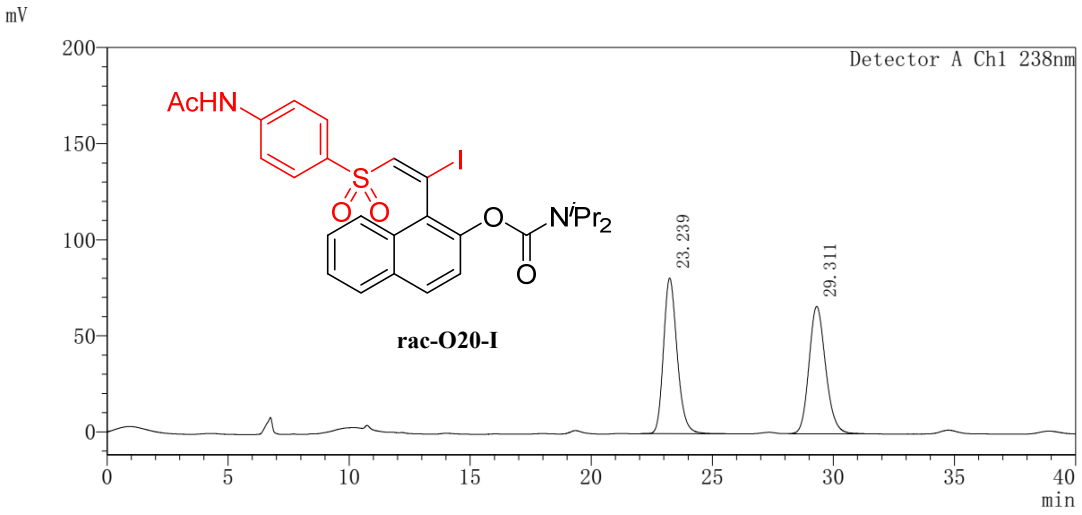
Peak#	Ret. Time	Area	Area%
1	20.971	7831236	48.510
2	27.286	8312343	51.490



Peak Table

Detector A Ch1 238nm

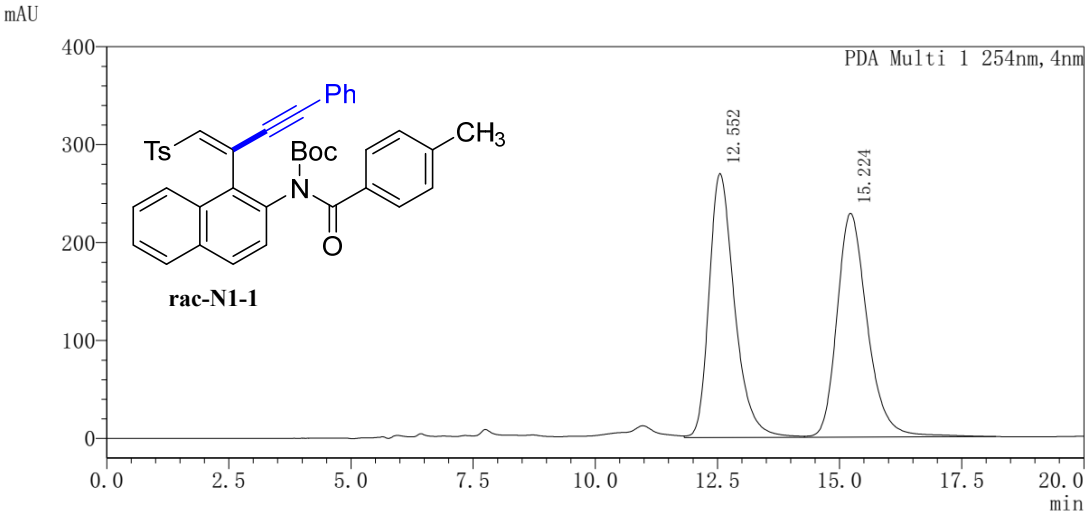
Peak#	Ret. Time	Area	Area%
1	21.086	624871	4.802
2	27.429	12387690	95.198



Peak Table

Detector A Ch1 238nm

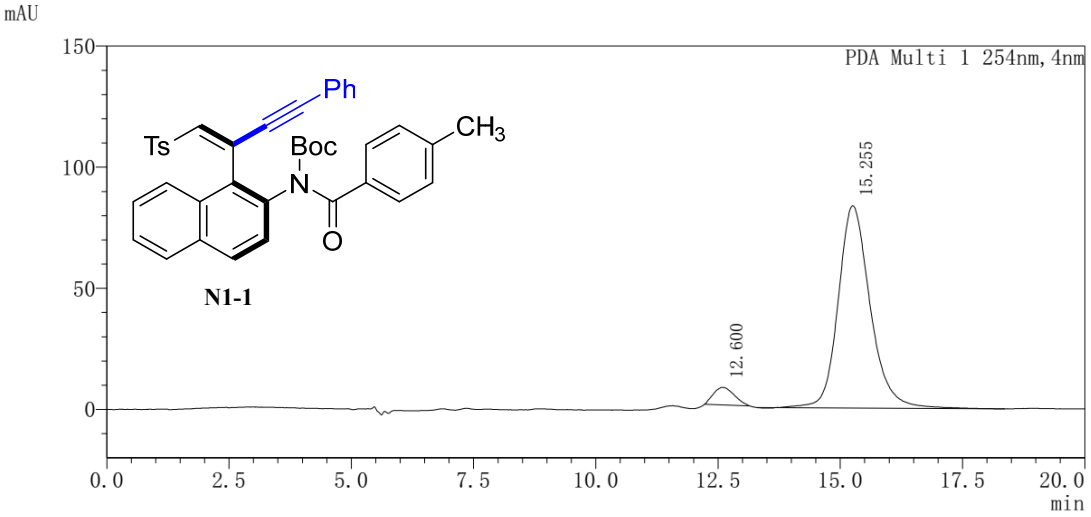
Peak#	Ret. Time	Area	Area%
1	23.239	3179821	49.953
2	29.311	3185741	50.047



Peak Table

PDA Ch1 254nm

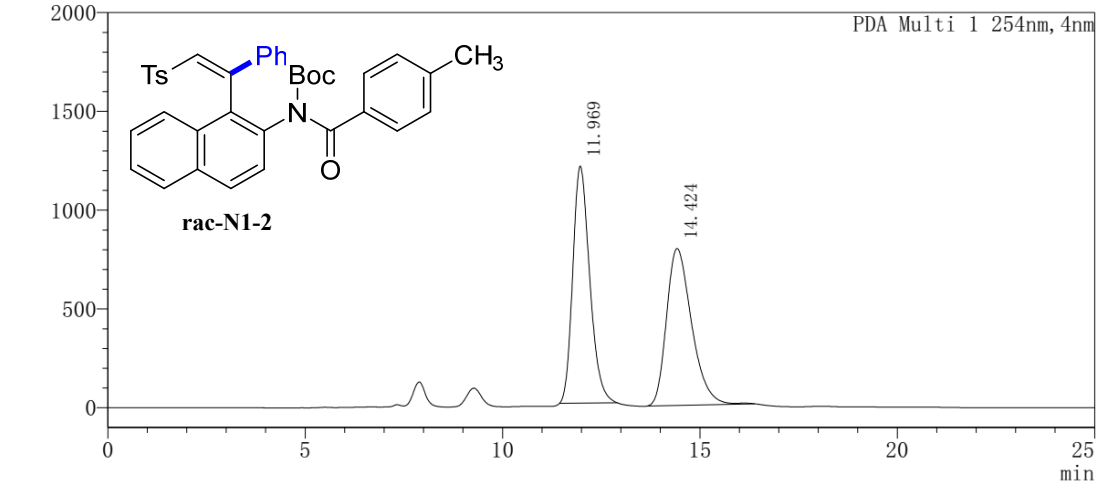
Peak#	Ret. Time	Area	Area%
1	12.552	9797278	49.736
2	15.224	9901370	50.264



Peak Table

PDA Ch1 254nm

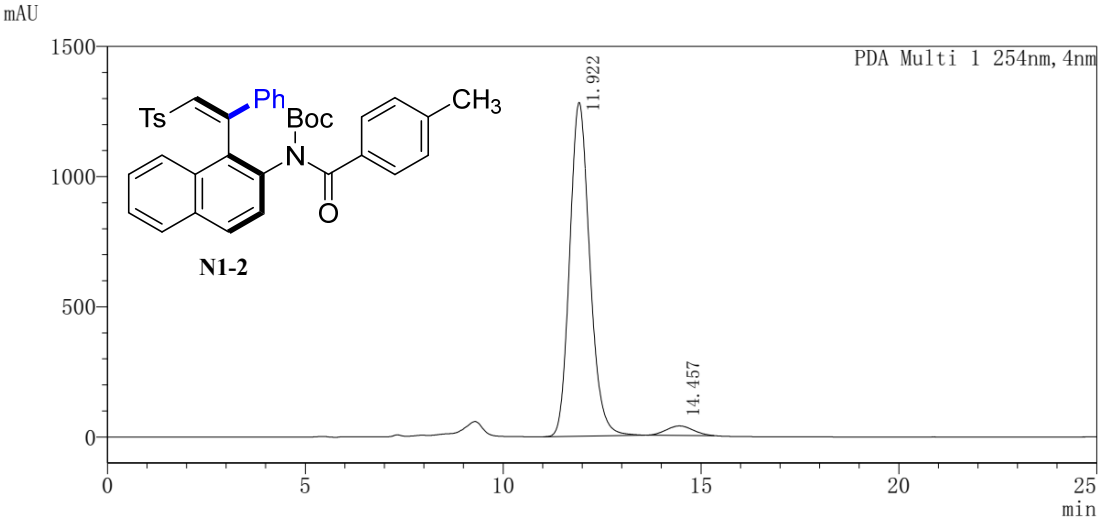
Peak#	Ret. Time	Area	Area%
1	12.600	211489	5.244
2	15.255	3821696	94.756



Peak Table

PDA Ch1 254nm

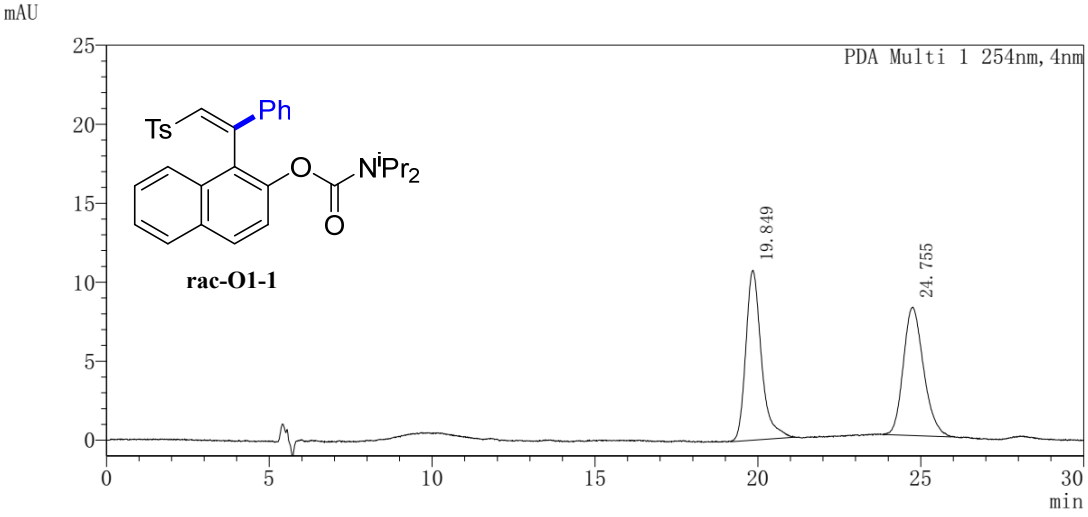
Peak#	Ret. Time	Area	Area%
1	11.969	35927055	50.570
2	14.424	35116584	49.430



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.922	45291749	96.354
2	14.457	1713893	3.646

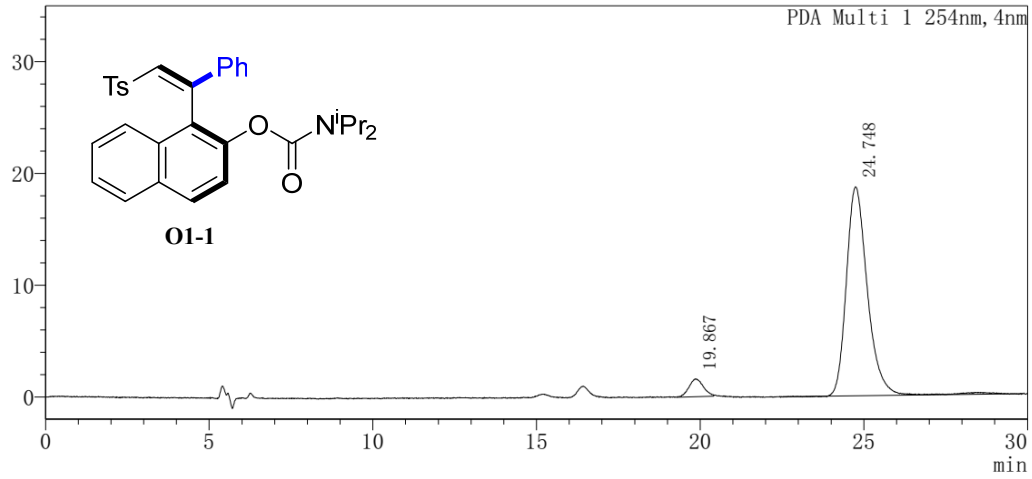


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.849	357699	50.414
2	24.755	351822	49.586

mAU

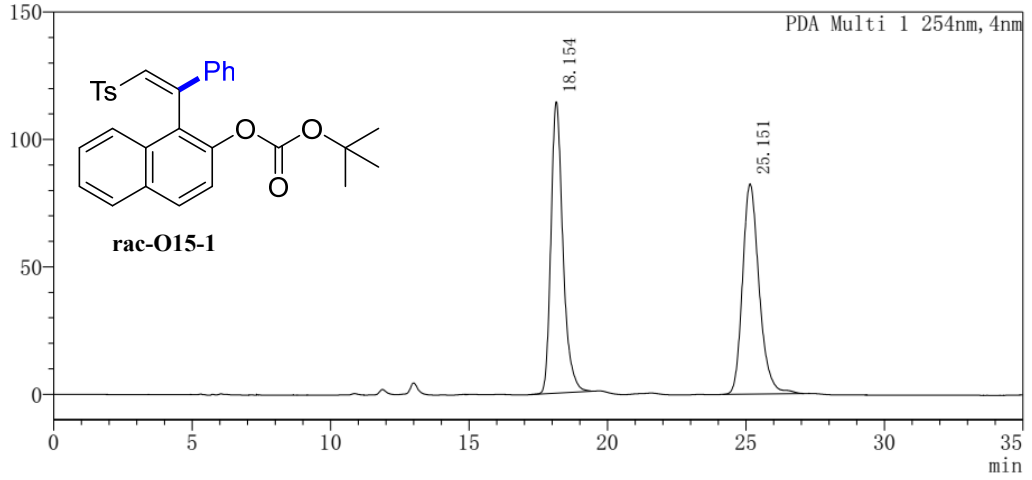


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.867	48208	5.405
2	24.748	843775	94.595

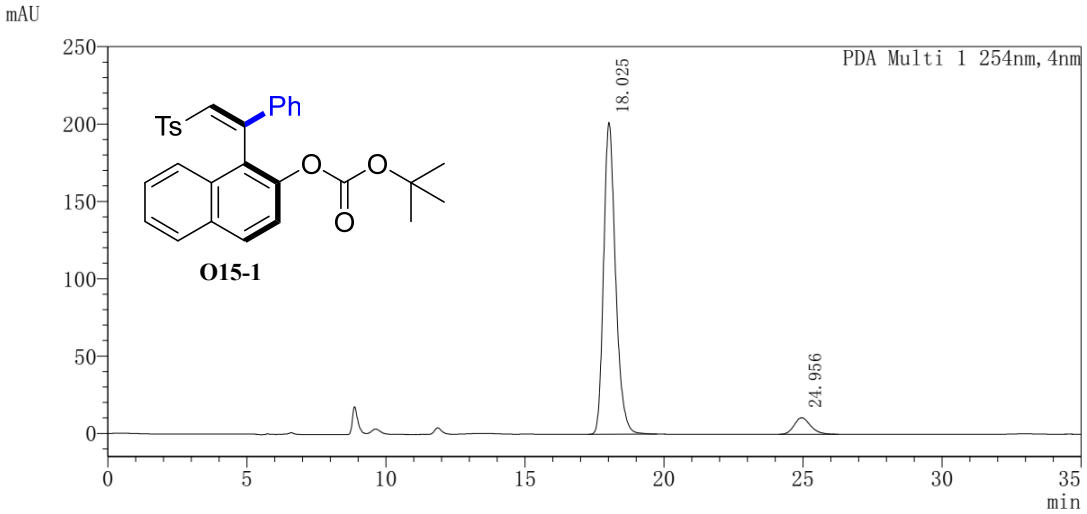
mAU



Peak Table

PDA Ch1 254nm

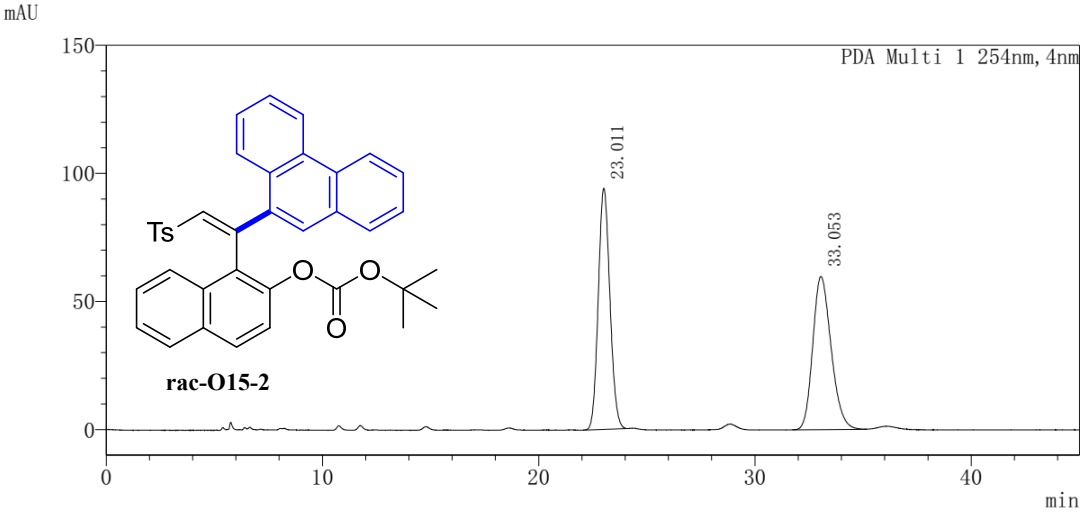
Peak#	Ret. Time	Area	Area%
1	18.154	3442773	49.986
2	25.151	3444736	50.014



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.025	6012278	93.185
2	24.956	439702	6.815

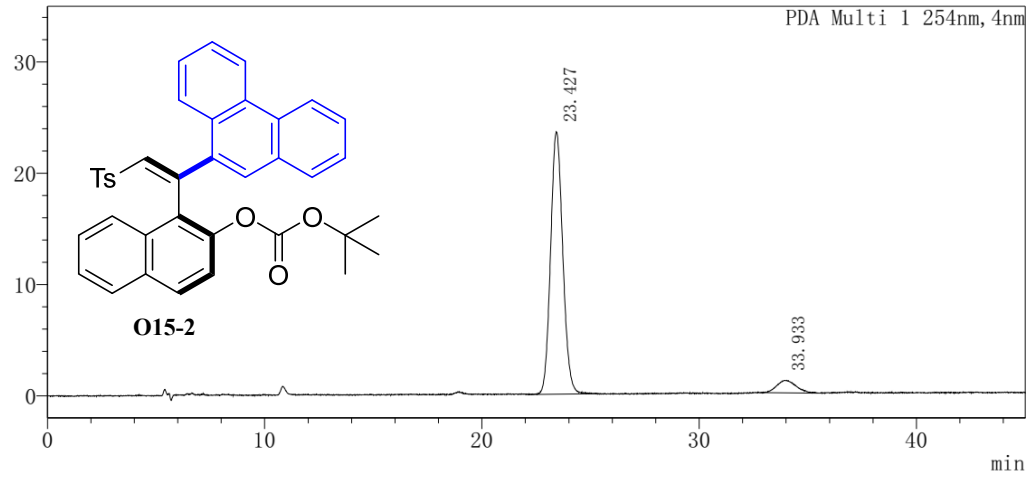


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.011	3522058	49.869
2	33.053	3540614	50.131

mAU

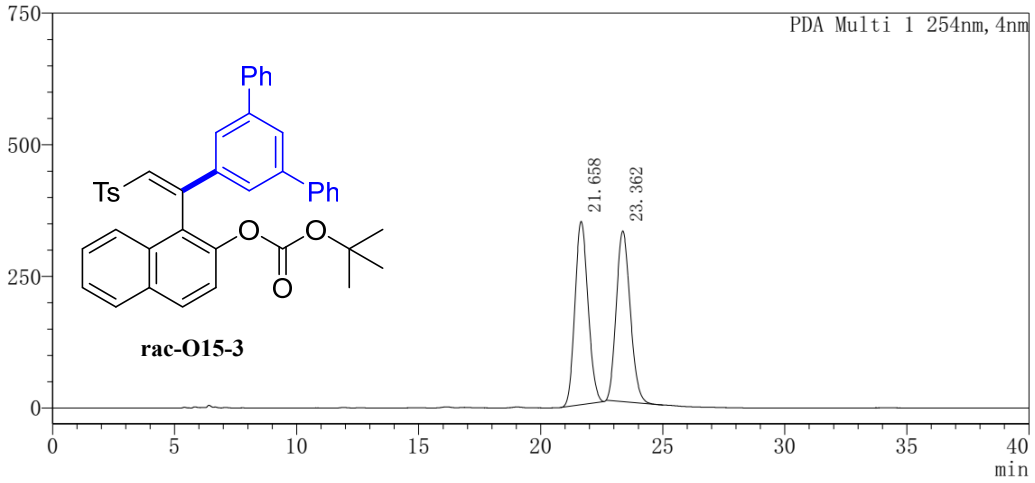


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.427	921260	92.948
2	33.933	69893	7.052

mAU

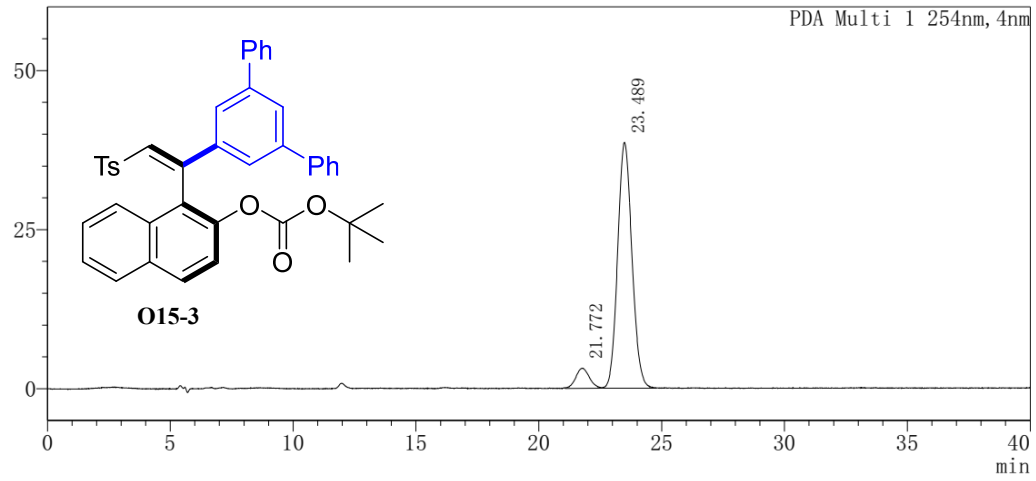


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.658	13018659	50.196
2	23.362	12916830	49.804

mAU

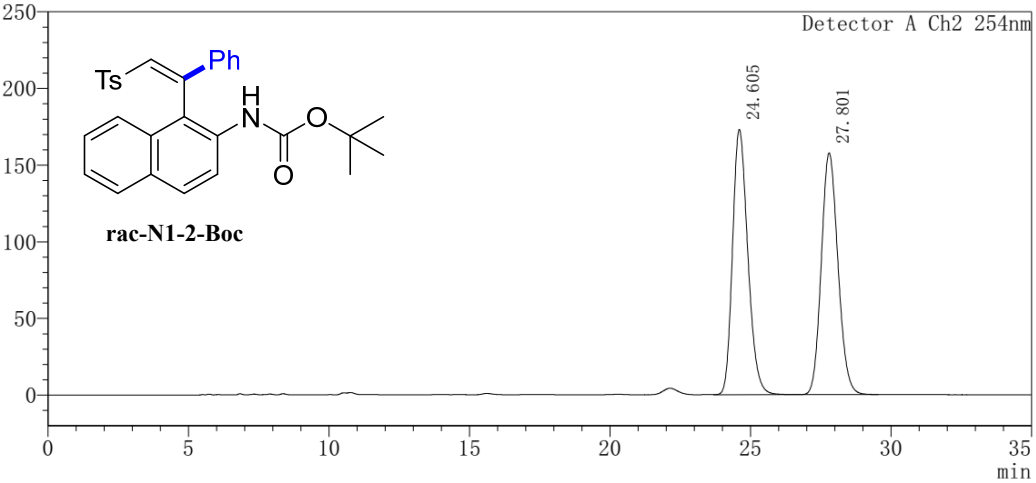


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.772	122060	7.236
2	23.489	1564744	92.764

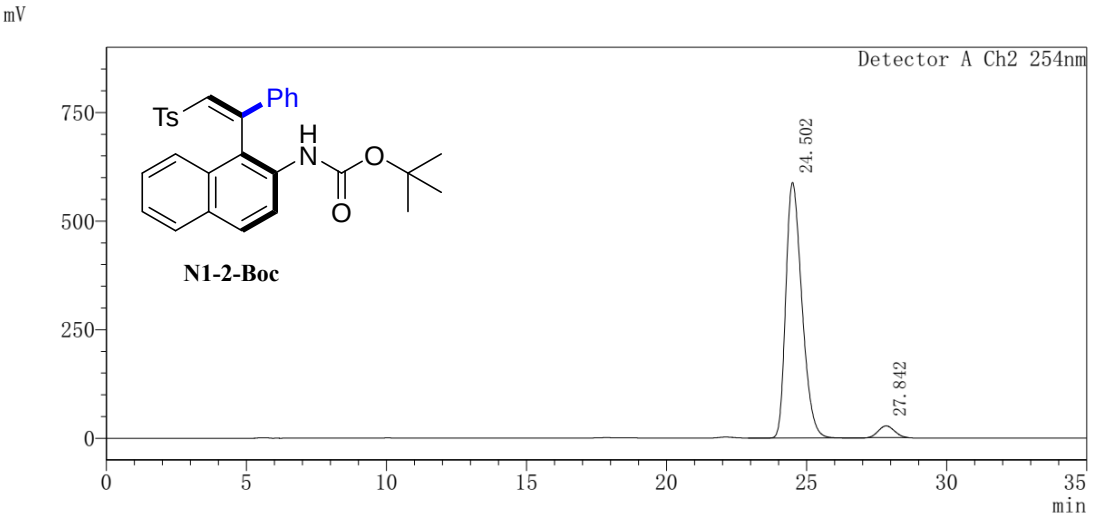
mV



Peak Table

Detector A Ch2 254nm

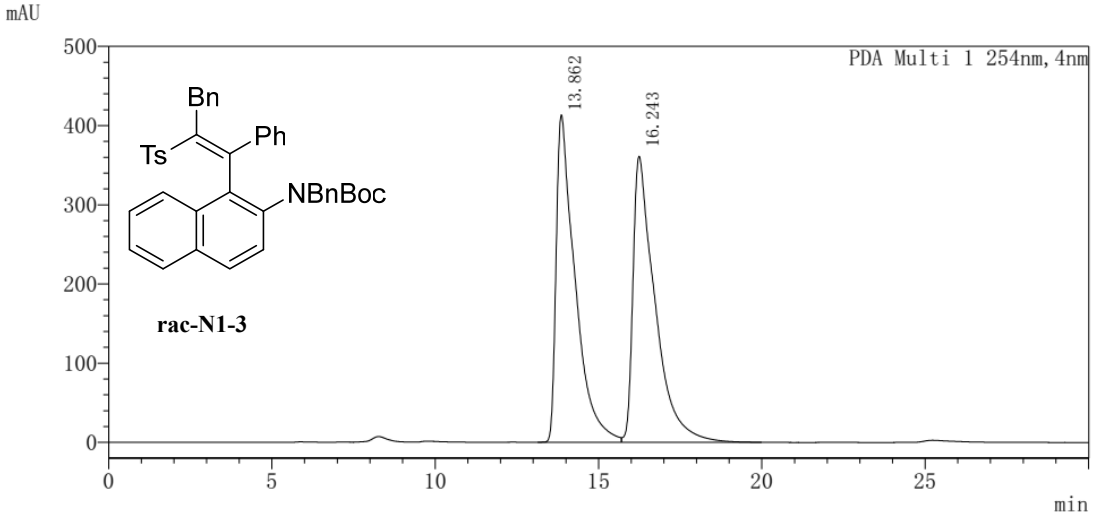
Peak#	Ret. Time	Area	Area%
1	24.605	6565729	50.232
2	27.801	6505093	49.768



Peak Table

Detector A Ch2 254nm

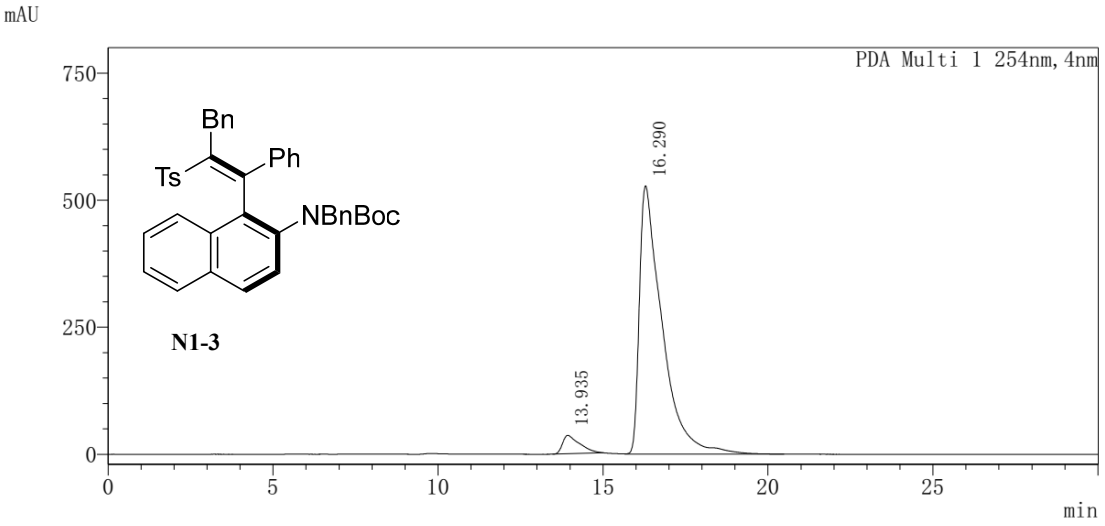
Peak#	Ret. Time	Area	Area%
1	24.502	23467804	95.621
2	27.842	1074745	4.379



Peak Table

PDA Ch1 254nm

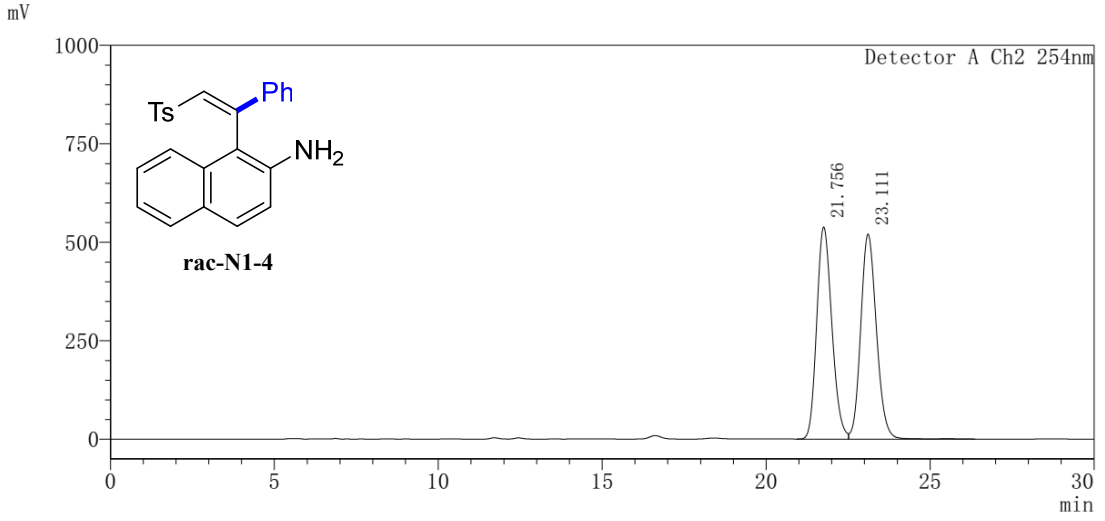
Peak#	Ret. Time	Area	Area%
1	13.862	16694408	49.599
2	16.243	16964318	50.401



Peak Table

PDA Ch1 254nm

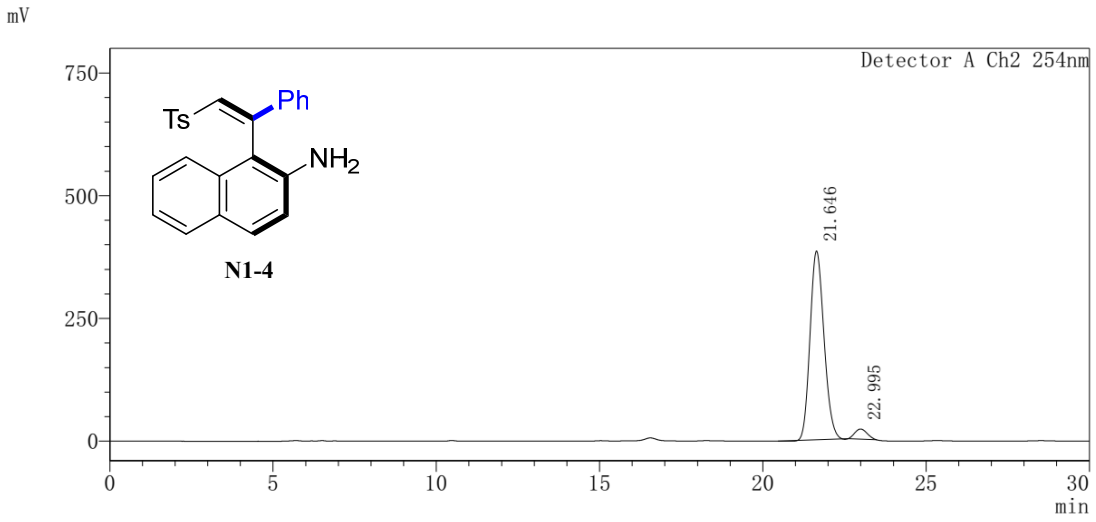
Peak#	Ret. Time	Area	Area%
1	13.935	1304368	4.899
2	16.290	25323438	95.101



Peak Table

Detector A Ch2 254nm

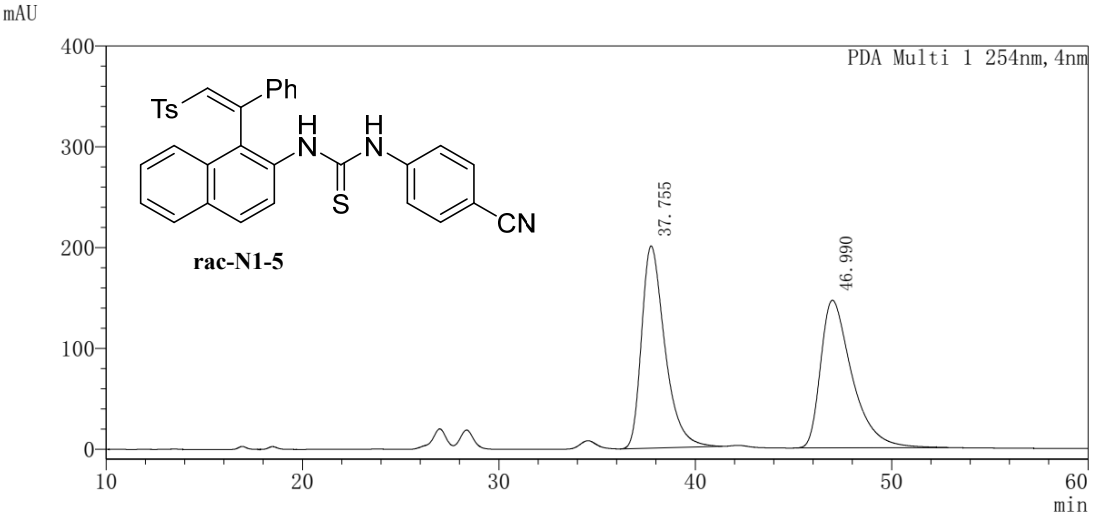
Peak#	Ret. Time	Area	Area%
1	21.756	17309440	49.906
2	23.111	17374767	50.094



Peak Table

Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	21.646	11430451	95.411
2	22.995	549721	4.589

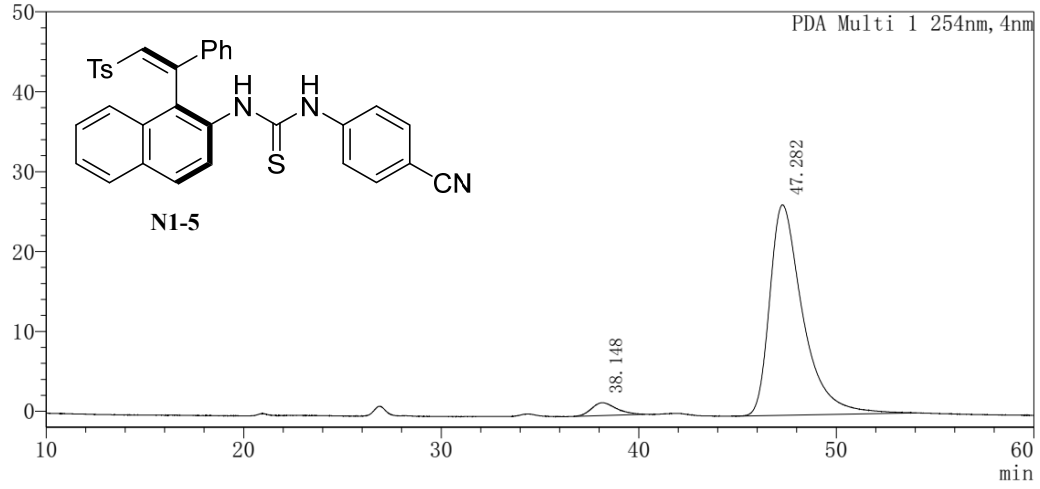


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	37.755	16571792	50.434
2	46.990	16286380	49.566

mAU

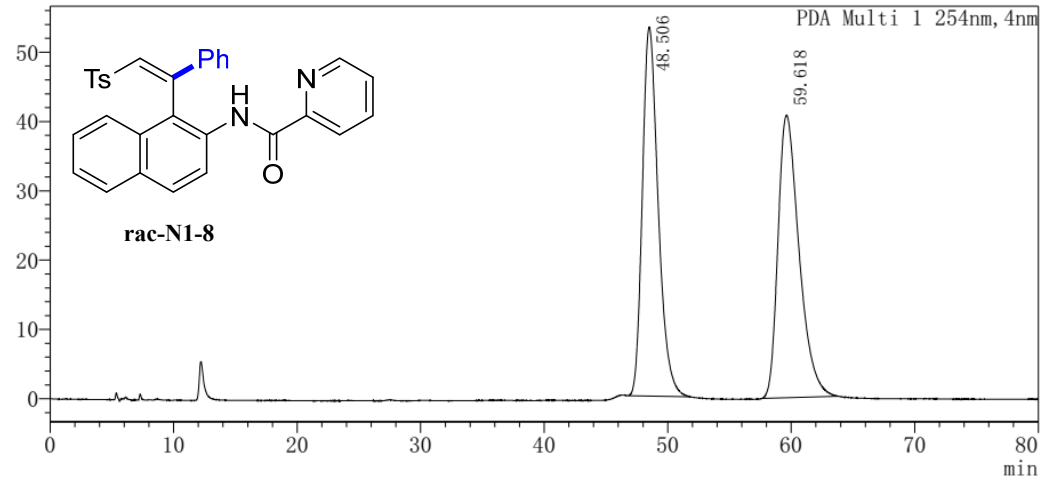


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	38.148	139854	4.359
2	47.282	3068569	95.641

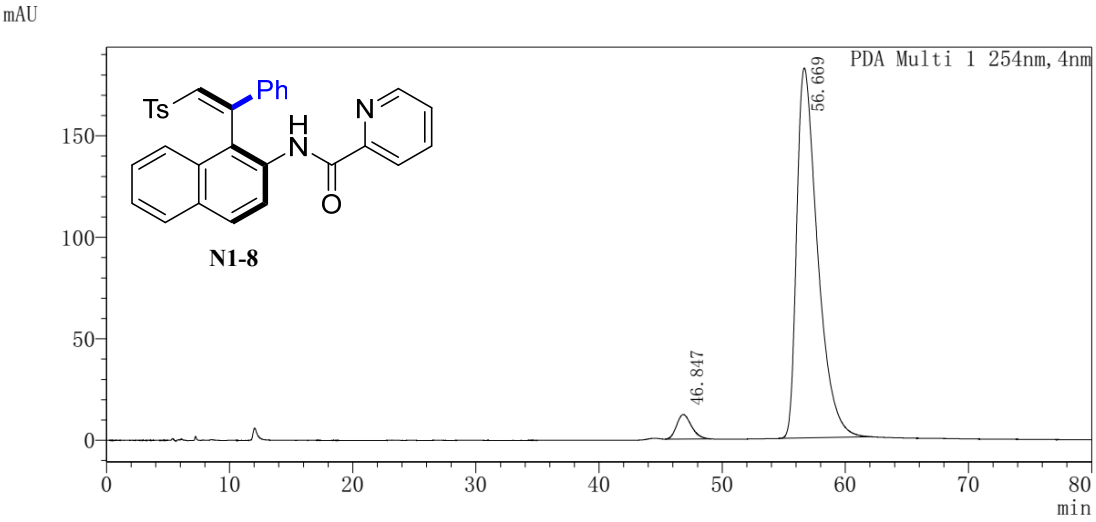
mAU



Peak Table

PDA Ch1 254nm

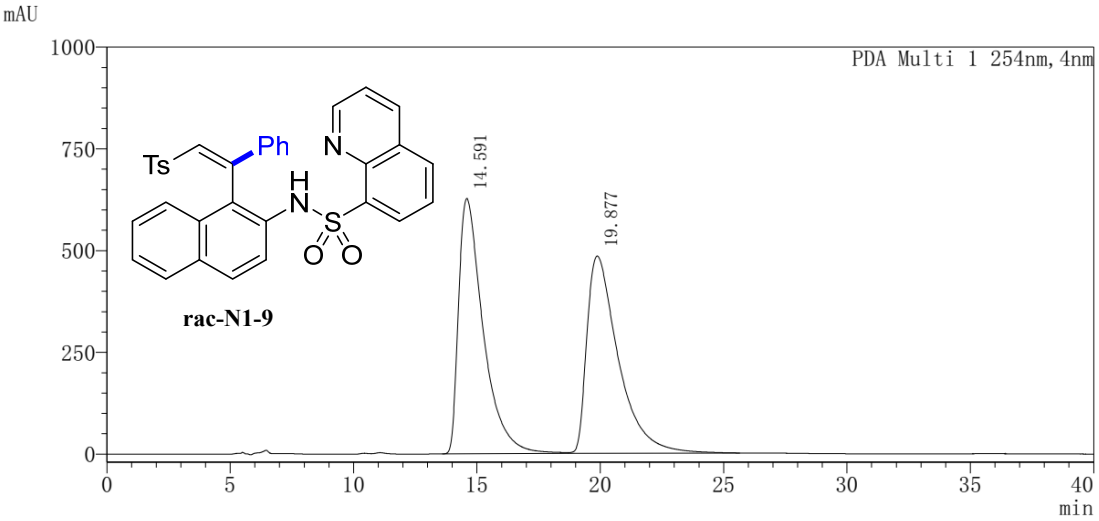
Peak#	Ret. Time	Area	Area%
1	48.506	4742642	49.526
2	59.618	4833371	50.474



Peak Table

PDA Ch1 254nm

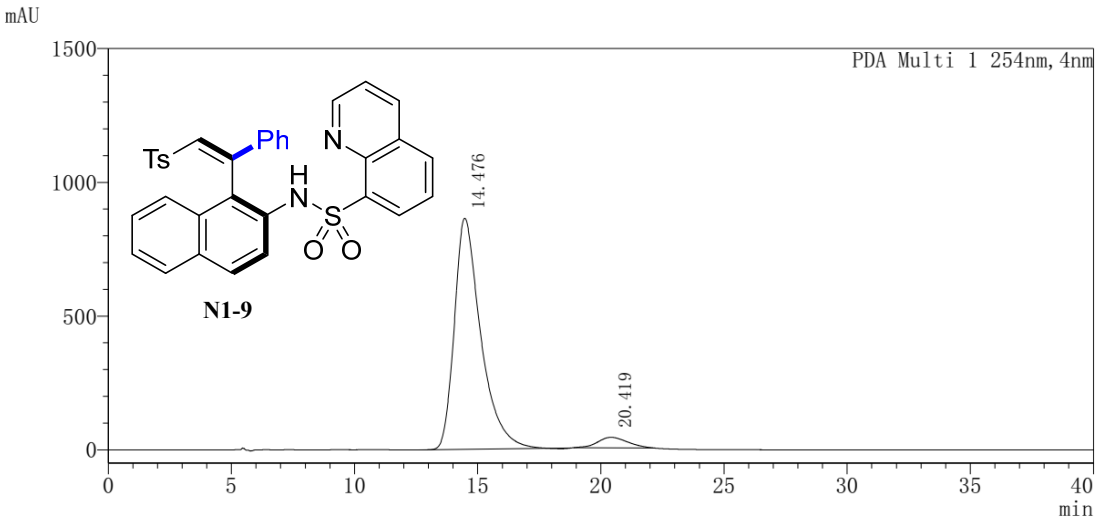
Peak#	Ret. Time	Area	Area%
1	46.847	1010478	4.497
2	56.669	21460277	95.503



Peak Table

PDA Ch1 254nm

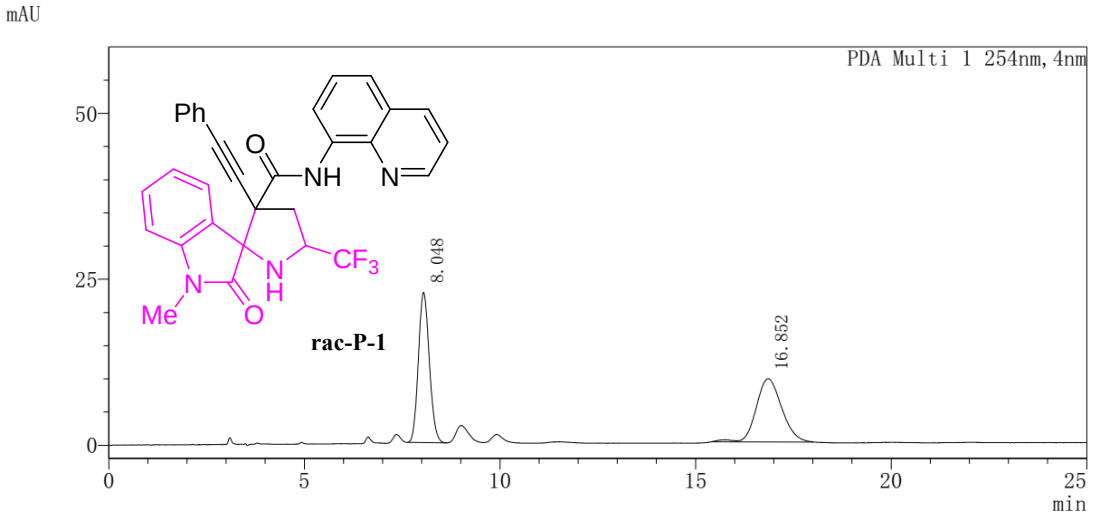
Peak#	Ret. Time	Area	Area%
1	14.591	43581821	50.283
2	19.877	43091716	49.717



Peak Table

PDA Ch1 254nm

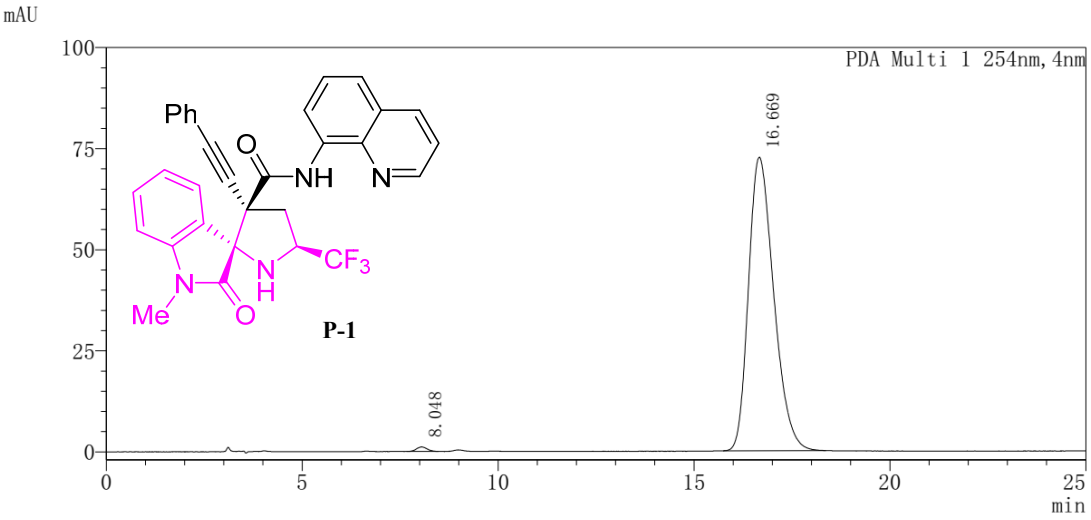
Peak#	Ret. Time	Area	Area%
1	14.476	64537152	95.026
2	20.419	3378219	4.974



Peak Table

PDA Ch1 254nm

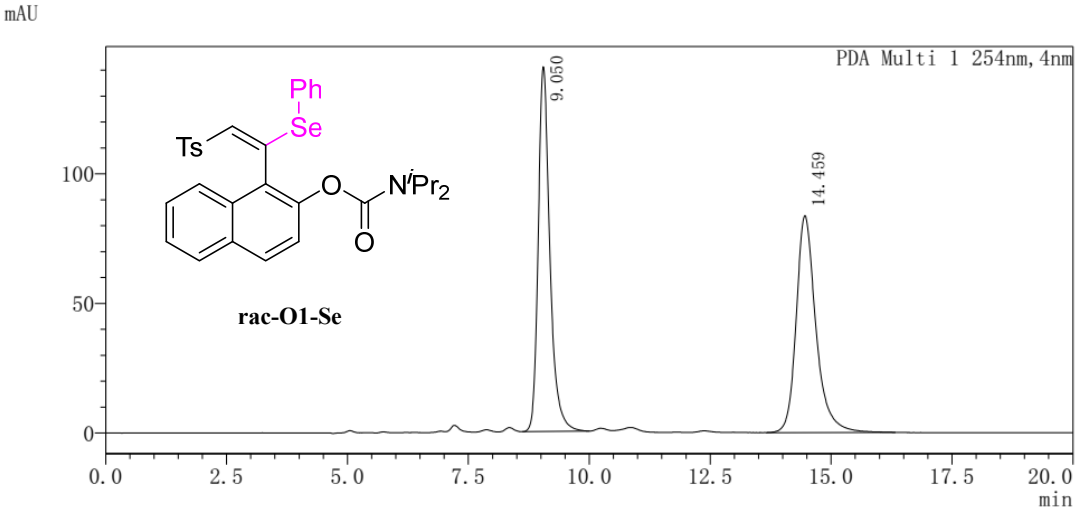
Peak#	Ret. Time	Area	Area%
1	8.048	442120	50.517
2	16.852	433073	49.483



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.048	21327	0.651
2	16.669	3253110	99.349

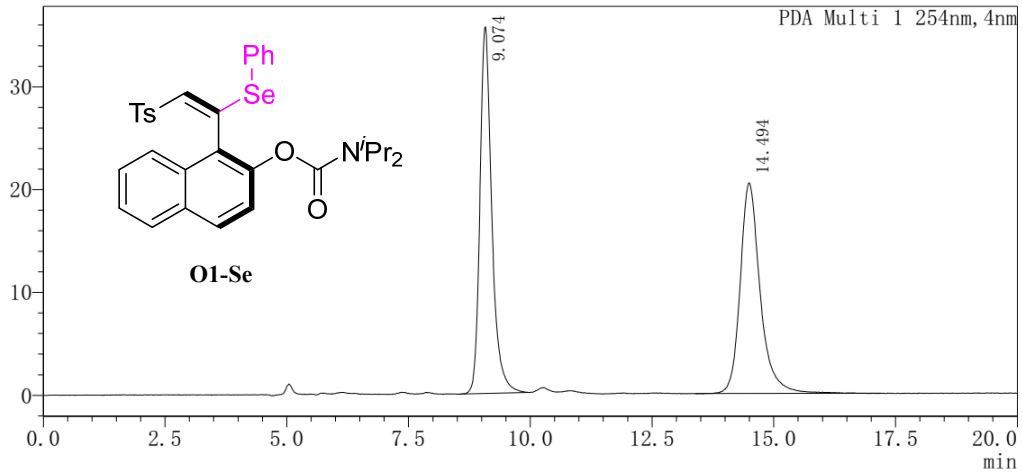


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.050	2361271	49.889
2	14.459	2371795	50.111

mAU

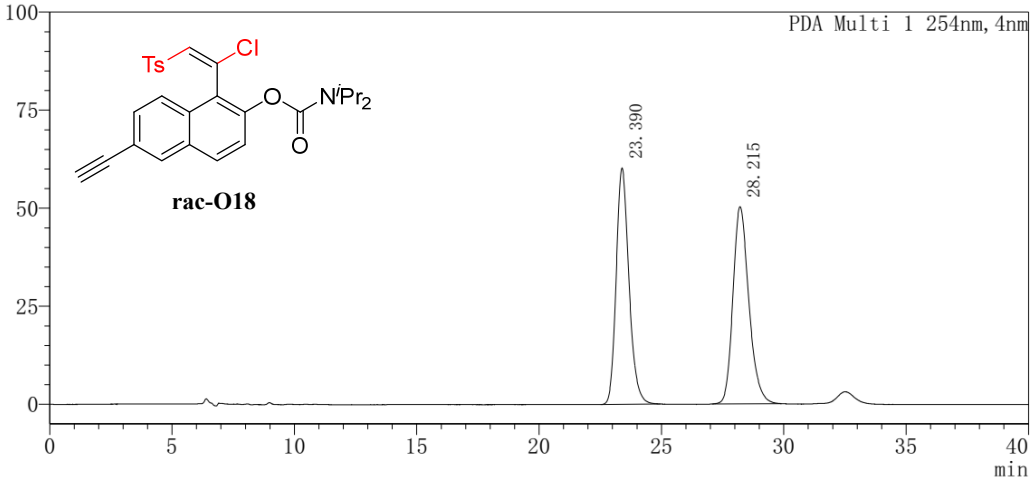


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.074	604129	50.836
2	14.494	584254	49.164

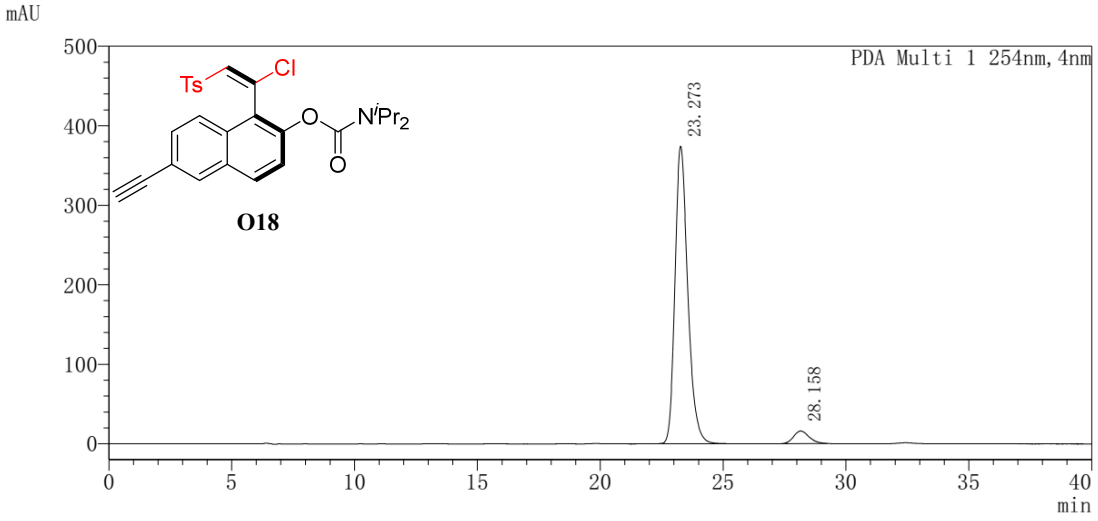
mAU



Peak Table

PDA Ch1 254nm

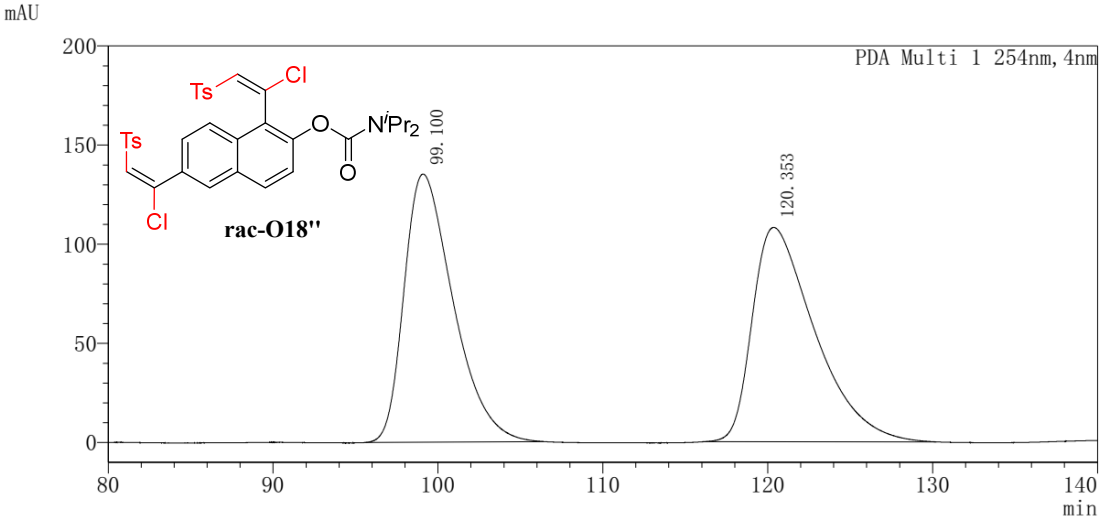
Peak#	Ret. Time	Area	Area%
1	23.390	2191582	49.042
2	28.215	2277210	50.958



Peak Table

PDA Ch1 254nm

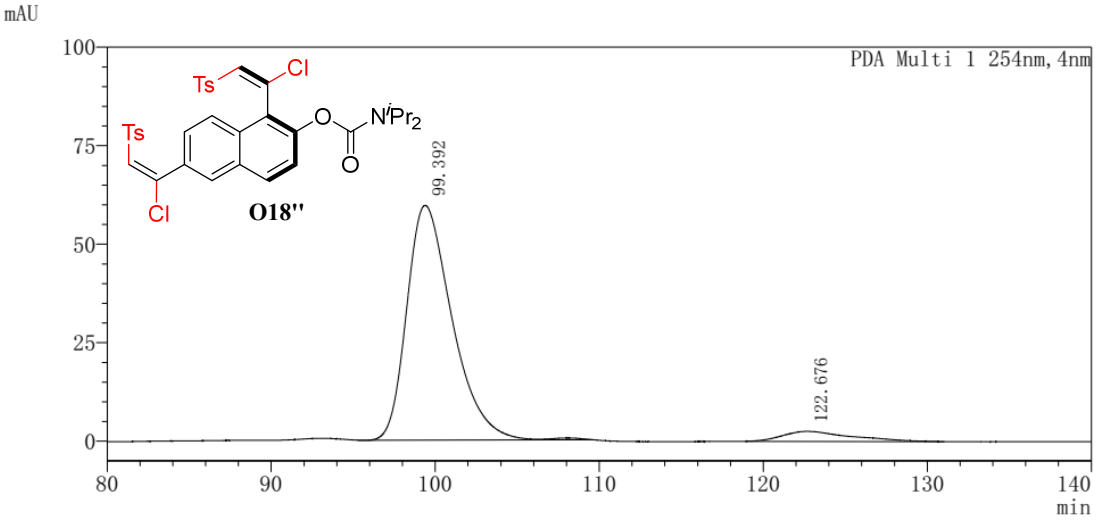
Peak#	Ret. Time	Area	Area%
1	23.273	13559561	95.121
2	28.158	695494	4.879



Peak Table

PDA Ch1 254nm

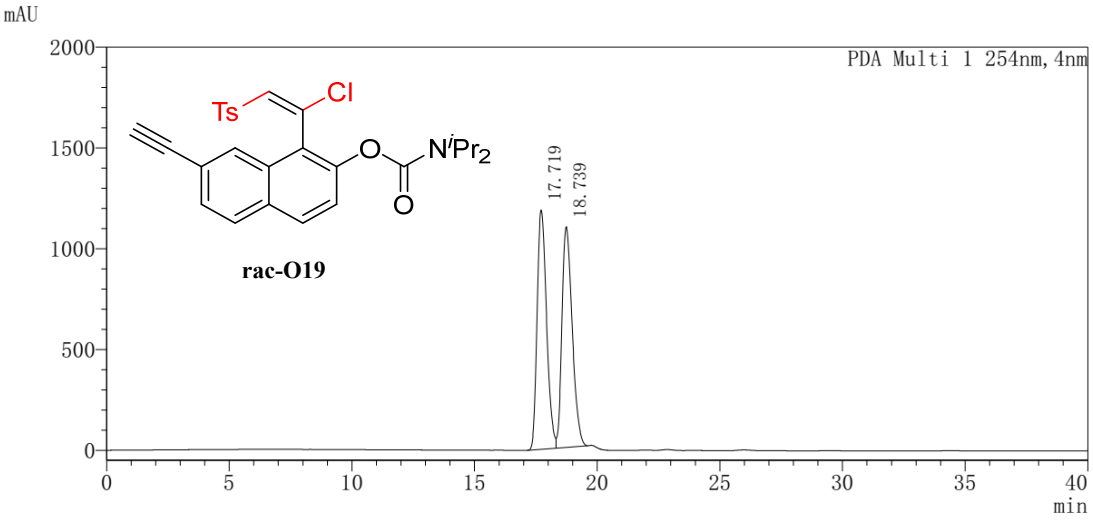
Peak#	Ret. Time	Area	Area%
1	99.100	28025954	49.516
2	120.353	28573491	50.484



Peak Table

PDA Ch1 254nm

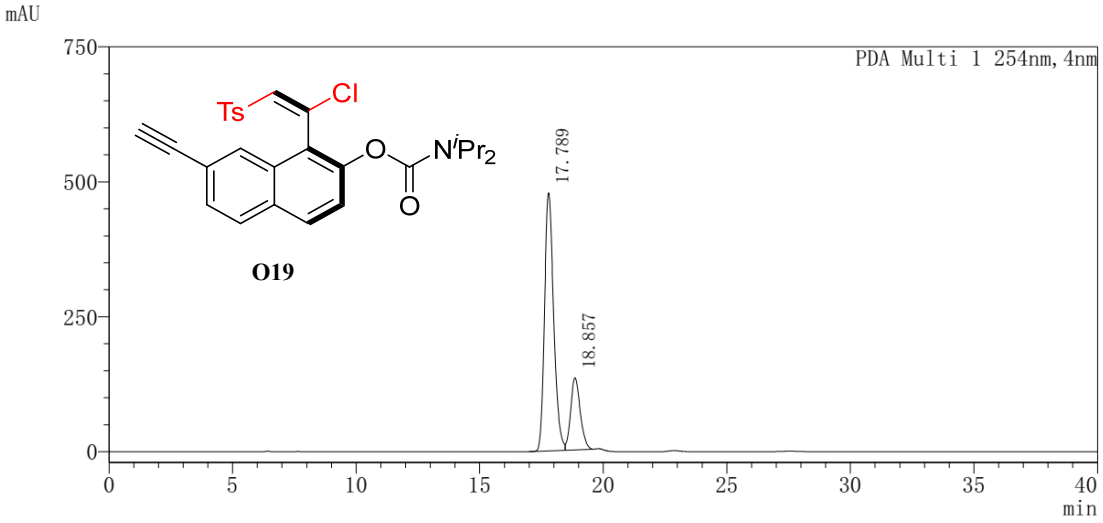
Peak#	Ret. Time	Area	Area%
1	99.392	11480185	93.918
2	122.676	743465	6.082



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.719	31875263	50.023
2	18.739	31845695	49.977

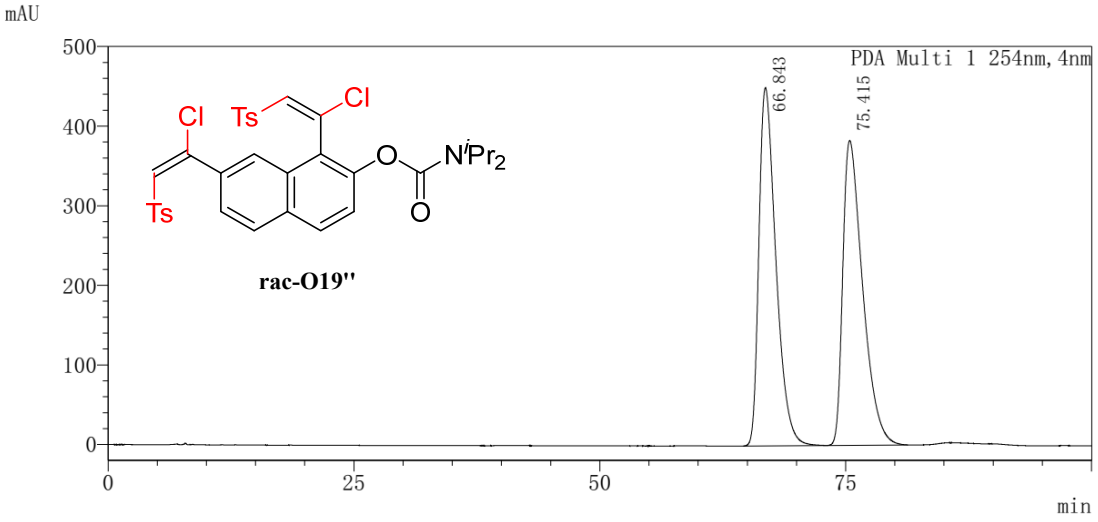


O19

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.789	12313424	77.339
2	18.857	3608000	22.661

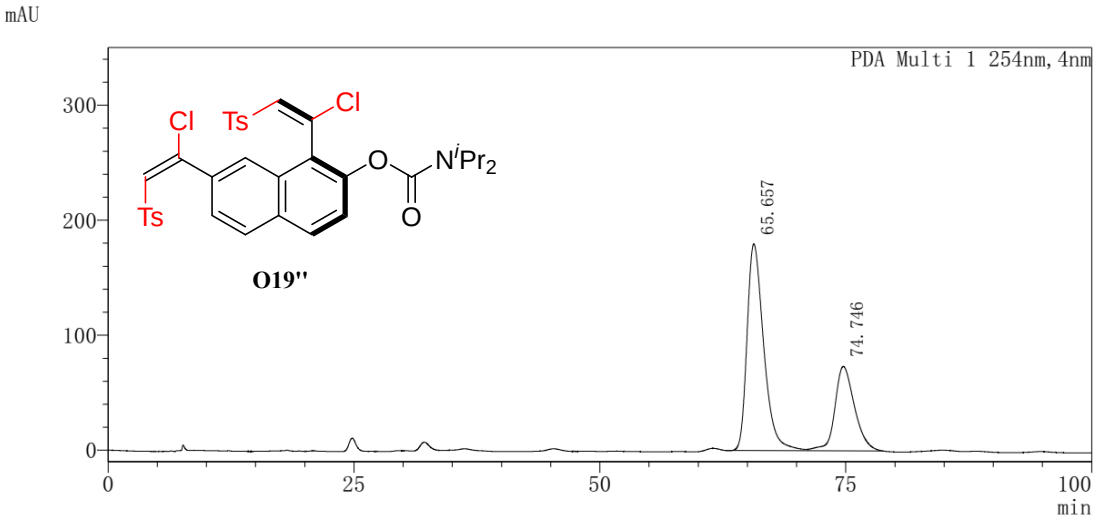


rac-O19''

Peak Table

PDA Ch1 254nm

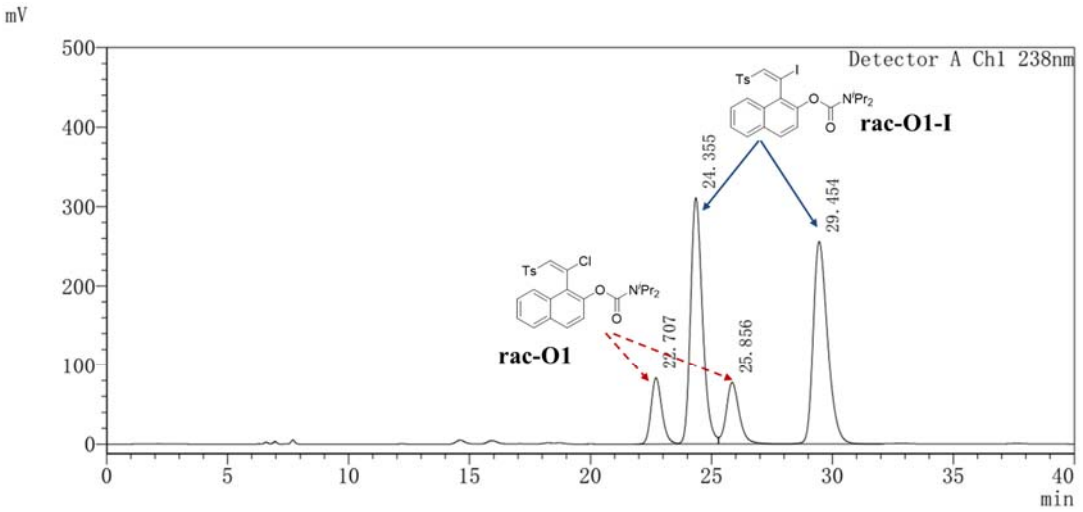
Peak#	Ret. Time	Area	Area%
1	66.843	54103501	50.140
2	75.415	53801673	49.860



Peak Table

PDA Ch1 254nm

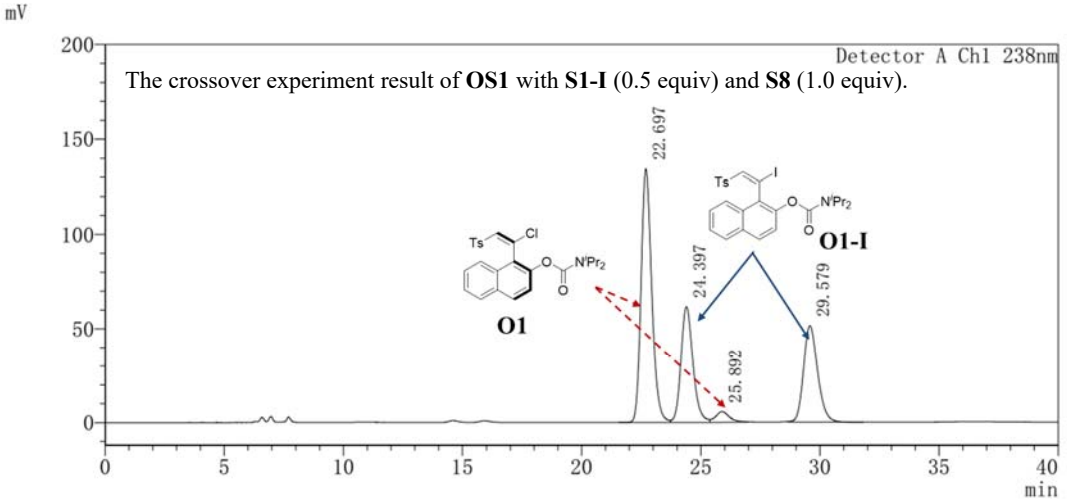
Peak#	Ret. Time	Area	Area%
1	65.657	21225196	67.446
2	74.746	10244496	32.554



Peak Table

Detector A Ch1 238nm

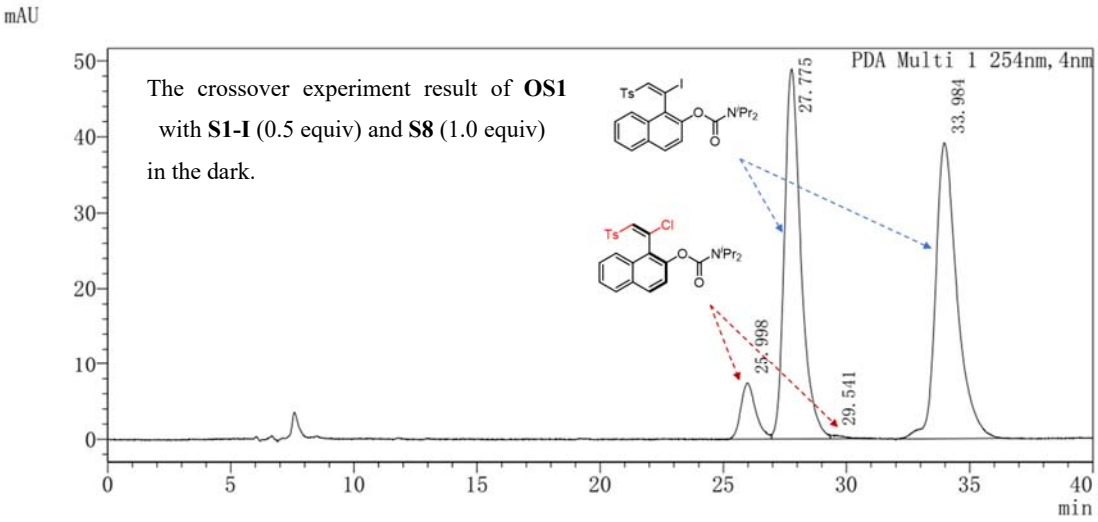
Peak#	Ret. Time	Area	Area%
1	22.707	2592347	9.690
2	24.355	10689409	39.957
3	25.856	2887846	10.795
4	29.454	10582547	39.558



Peak Table

Detector A Ch1 238nm

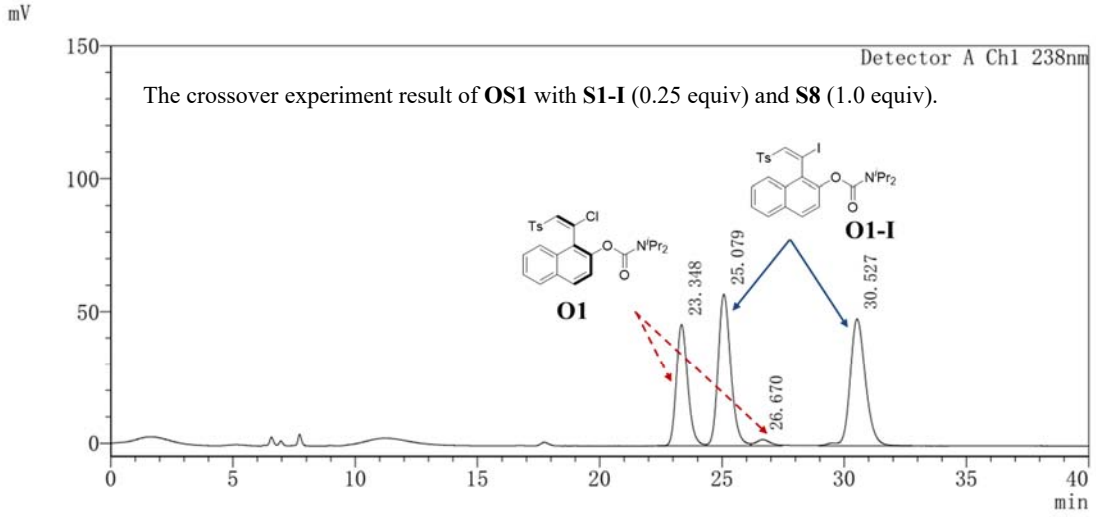
Peak#	Ret. Time	Area	Area%
1	22.697	4188971	48.161
2	24.397	2154471	24.770
3	25.892	231594	2.663
4	29.579	2122789	24.406



Peak Table

PDA Ch1 254nm

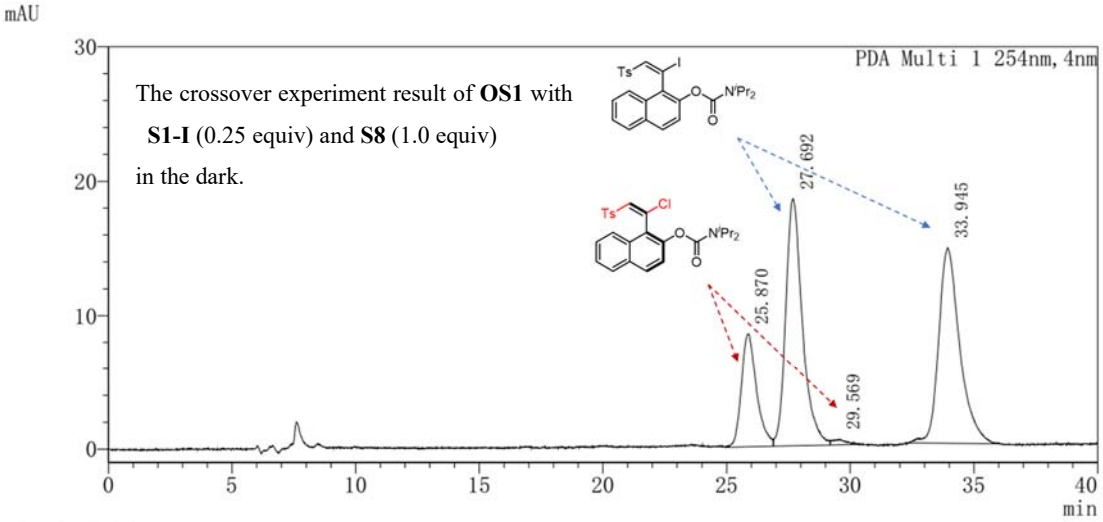
Peak#	Ret. Time	Area	Area%
1	25.998	311720	6.249
2	27.775	2285460	45.814
3	29.541	16774	0.336
4	33.984	2374632	47.601



Peak Table

Detector A Ch1 238nm

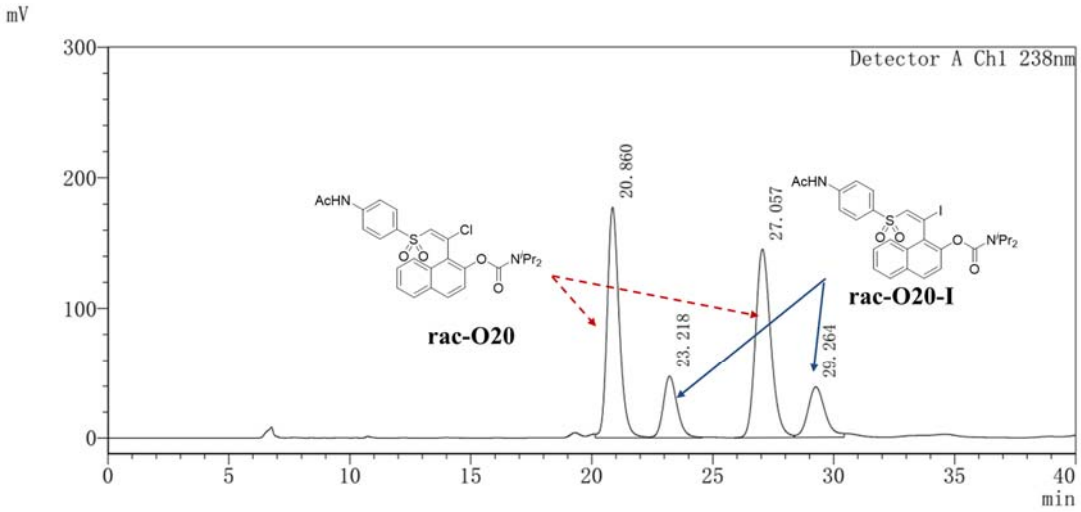
Peak#	Ret. Time	Area	Area%
1	23.348	1498092	25.885
2	25.079	2074051	35.836
3	26.670	97118	1.678
4	30.527	2118311	36.601



Peak Table

PDA Ch1 254nm

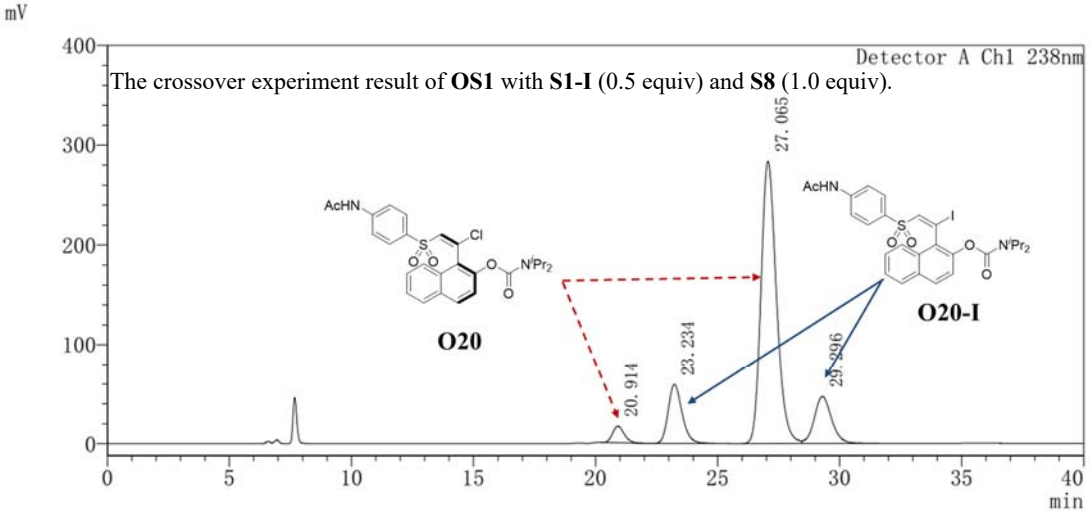
Peak#	Ret. Time	Area	Area%
1	25.870	361134	17.104
2	27.692	867139	41.069
3	29.569	15739	0.745
4	33.945	867428	41.082



Peak Table

Detector A Ch1 238nm

Peak#	Ret. Time	Area	Area%
1	20.860	6114433	37.481
2	23.218	1881580	11.534
3	27.057	6382619	39.125
4	29.264	1934845	11.860



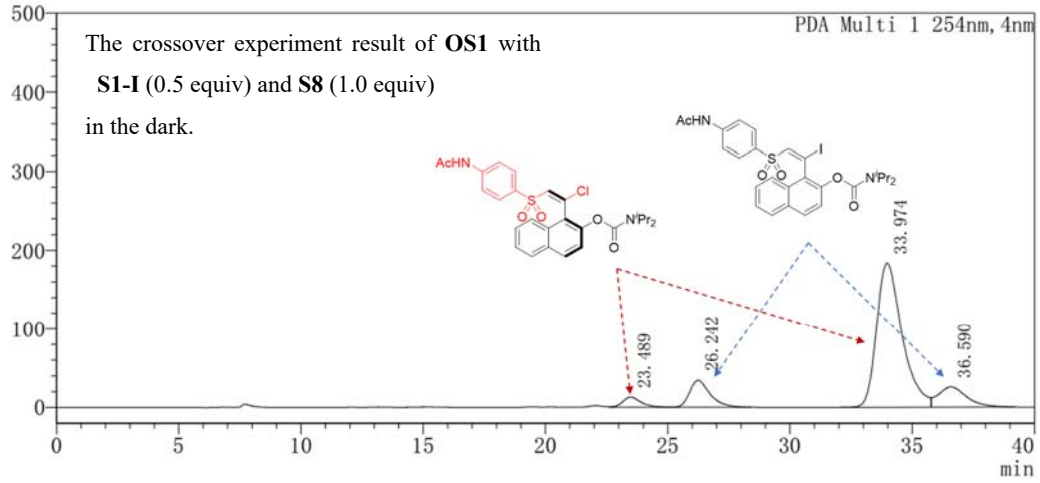
The crossover experiment result of **OS1** with **S1-I** (0.5 equiv) and **S8** (1.0 equiv).

Peak Table

Detector A Ch1 238nm

Peak#	Ret. Time	Area	Area%
1	20.914	555655	3.135
2	23.234	2341154	13.209
3	27.065	12503222	70.543
4	29.296	2324121	13.113

mAU

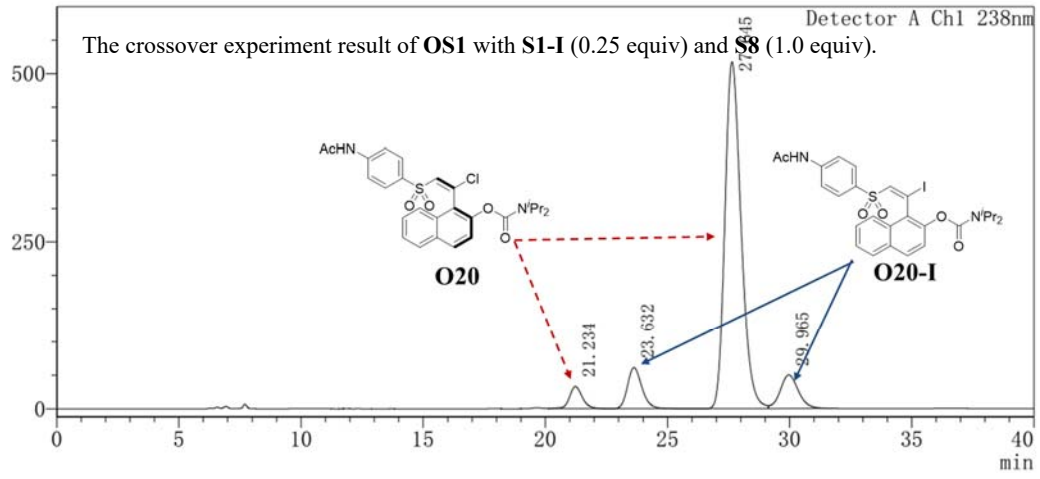


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.489	676917	3.743
2	26.242	1991950	11.013
3	33.974	13328040	73.688
4	36.590	2090189	11.556

mV

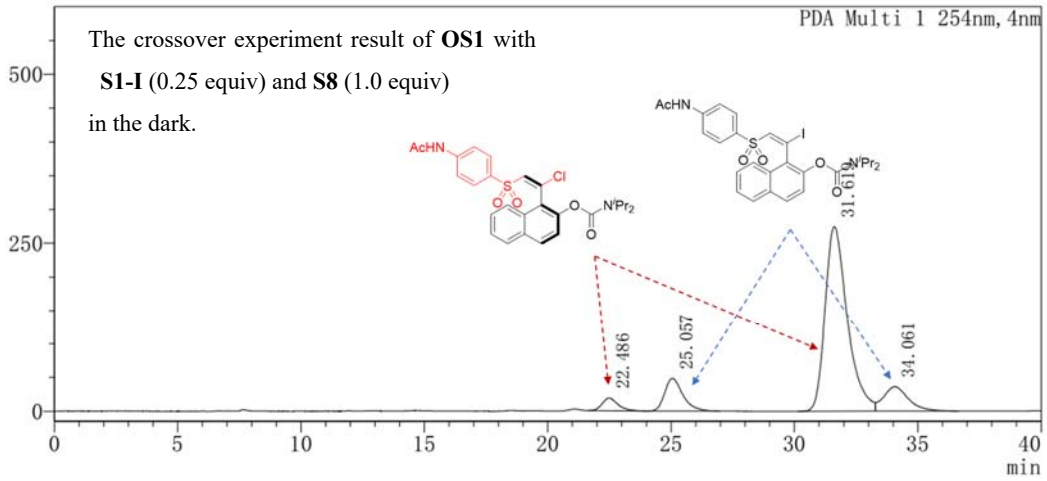


Peak Table

Detector A Ch1 238nm

Peak#	Ret. Time	Area	Area%
1	21.234	1196536	3.972
2	23.632	2499123	8.295
3	27.645	23854514	79.180
4	29.965	2576788	8.553

mAU



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.486	842433	3.635
2	25.057	2482203	10.711
3	31.619	17284844	74.585
4	34.061	2565129	11.069

References

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