Supporting Information

Enantioselective Au(I)-Catalyzed Dearomatization of 1-Naphthols with Allenamides through Tethered Counterion-Directed Catalysis

Yunliang Yu,[a,b] Zhenhao Zhang,[a,c] Arnaud Voituriez,[a] Nicolas Rabasso,[b] Gilles Frison,[c,d] Angela Marinetti,[a,*] Xavier Guinchard[a,*]

[a] Université Paris-Saclay, CNRS, Institut de Chimie des Substances Naturelles, UPR 2301, 91198, Gif-sur-Yvette, France.

[b] Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS UMR 8182, Université Paris-Saclay, Bâtiment 420, 91405 Orsay cedex, France.

[c] LCM, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, 91128 Palaiseau, France.

[d] Sorbonne Université, CNRS, Laboratoire de Chimie Théorique, 75005 Paris, France.

angela.marinetti@cnrs.fr

xavier.guinchard@cnrs.fr

Table of Contents:

I. General information:

Unless otherwise noted, all of the reactions were performed under argon atmosphere, the solvents were dried by standard methods, and the purifications were carried out under flash-chromatographic conditions on silica gel (Redi Sep prepacked column, 230-400 mesh) with use of a CombiFlash Companion. Reagent-grade chemicals were obtained from diverse commercial suppliers (Sigma-Aldrich, Acros Organics, TCI and Alfa-Aesar) and were used as received. ^{1}H NMR (300 and 500 MHz), ^{19}F (282 MHz) and ^{13}C (75 and 125 MHz) NMR spectra were recorded on Bruker Advance spectrometers. The chemical shifts (δ) are reported in part per million (ppm) and coupling values (*J*) are given in Hertz (Hz). Multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), bs (broad singlet) dd (doublet of doublet), dt (doublet of triplet), m (multiplet). Optical rotations were measured on Anton Paar MCP 300 polarimeter at 589 nm. $[\alpha]_D$ is expressed in deg.cm^3.g^{-1}.dm^{-1} and *c* is expressed in g/100 cm^3. High resolution mass spectra (HRMS) were recorded using a Micromass LCT Premier XE instrument (Waters) and were determined by electrospray ionization (ESI) with a TOF analyzer.

1-Naphthols[1] and allenamides[2] were synthesized by the reported methods. Catalyst **1** was prepared according to our previous study.[3]

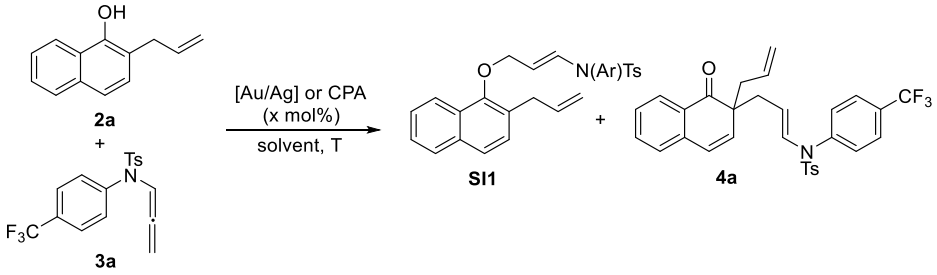
[1]a) Tsang, K. Y.; Brimble, M. A. *Tetrahedron* **2007**, *63*, 6015–6034; b) Zhou, D.; Yu, X.; Zhang, J.; Wang, W.; Xie, H. *Org. Lett.* **2018**, *20*, 174-177; c) Yang, B.; Zhai, X.; Feng, S.; Hu, D.; Deng, Y.; Shao, Z. *Org. Lett.* **2019**, *21*, 330-334.

[2] Suárez-Pantiga, S.; Hernández-Díaz, C.; Rubio, E.; González, J. M. *Angew. Chem., Int. Ed.,* **2012**, *51*, 11552-11555.

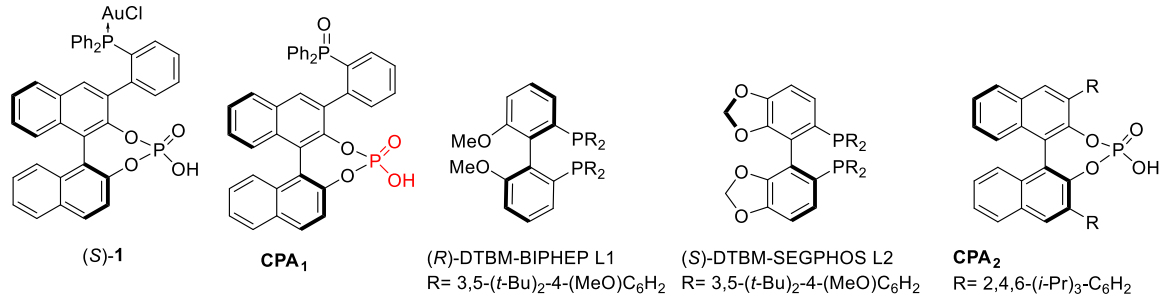
[3] Zhang, Z.; Smal, V.; Retailleau, P.; Voituriez, A.; Frison, G.; Marinetti, A.; Guinchard, X. *J. Am. Chem. Soc.* **2020**, *142*, 3797.

II. Optimization of the reaction

Table S1: Optimization of the reaction



entry	Au (mol%)	Ag (mol%)	CPA (mol%)	Solvent	T (°C)	SI1/4a/2a NMR ratio[a]	Isolated Yield 4a (%)[b]	ee 4a (%)[c]	Equiv. 3a
1	PPh_3AuCl (5)	AgTFA (5)	-	DCE	rt	0.15/1/1.8	12%	0%	1.5
2	$L1(AuCl)_2$ (5)	$AgNTf_2$ (10)	-	DCE	rt	0/0/1	NR	-	1.5
3	$L2(AuCl)_2$(5)	$AgNTf_2$ (10)	-	DCE	rt	0/0/1	NR	-	1.5
4	-	-	CPA_1	DCE	rt	ND	0	-	1.5
5	-	Ag_2CO_3	CPA_1	DCE	rt	ND	0	-	1.5
6	PPh_3AuMe (5)	-	(*S*)-TRIP (5)	DCE	rt	1.1/1/3.6	5%	55%	1.5
7	-	-	(*S*)-TRIP (5)	DCE	rt	0.05/1/1.1	38%	57%	1.5
8	-	-	(*S*)-**1** (5)	DCE	rt	0.6/1/1.3	19%	0%	1.5
9	-	Ag_2CO_3 (2.5)	-	DCE	rt	0/0/1	NR	-	1.5
10	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	rt	0.2/1/0.8	39%	84%	1.5
11	(*S*)-**1** (5)	Ag_2O (2.5)	-	DCE	rt	0.3/1/2.3	11%	83%	1.5
12	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	0	0.27/1/3.1	21%	86%	1.5
13	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	40	0.13/1/2	23%	74%	1.5
14[d]	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	rt	0.35/1/0.5	42%	81%	1.5
15[e]	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	rt	0.2/1/1	37%	84%	1.5
16[f]	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	rt	0.3/1/1.5	26%	85%	1.5
17	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	rt	0.2/1/0.4	60%	84%	3
18	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	0	0.2/1/0.4	68%	88%	3
19	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	-10	0.2/1/0.1	50%	89%	3
20	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCM	0	0.4/1/2.1	21%	88%	3
21	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	THF	0	0/0/1	NR	-	3
22	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	0	0.2/1/0.1	60%	88%	5
23	(*S*)-**1** (2)	Ag_2CO_3 (1)	-	DCE	0	0.2/1/0.1	58%	88%	3
24	(*S*)-**1** (0.5)	Ag_2CO_3 (0.25)	-	DCE	0	0.3/1/1.8	25%	83%	3
25[g]	(*S*)-**1** (5)	Ag_2CO_3 (2.5)	-	DCE	0	0.2/1/0.2	54%	88%	3

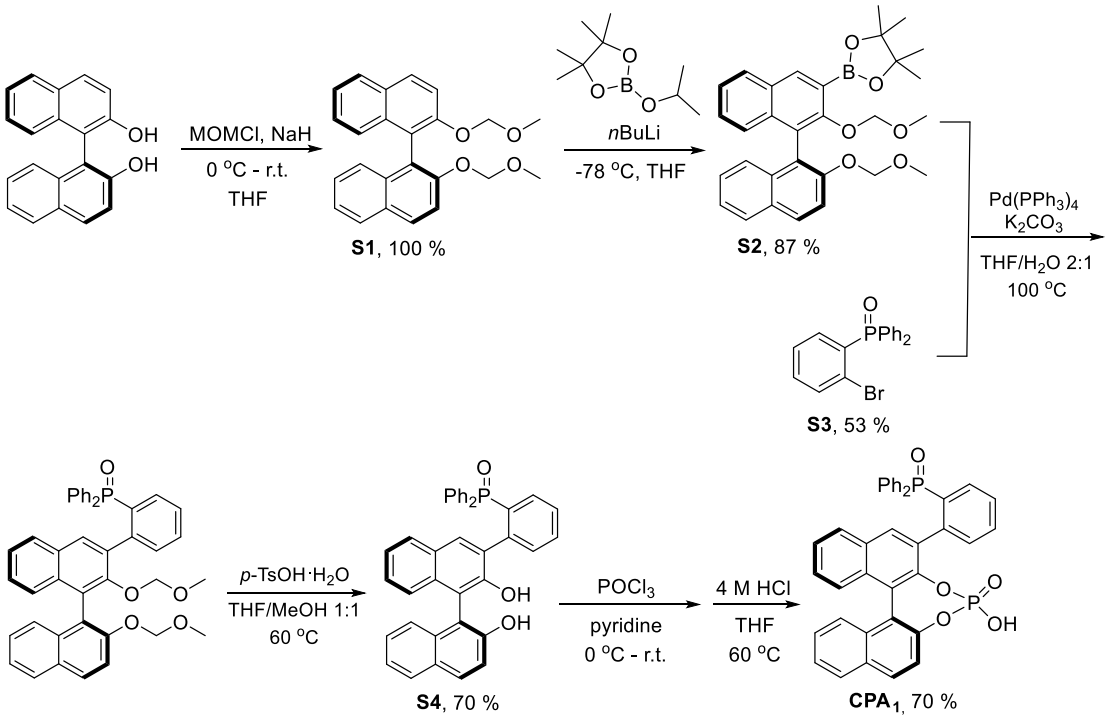


[a] Ratio measured by ^{1}H NMR. [b] Isolated yields. [c] Measured by chiral HPLC. [d] Performed in the presence of molecular sieves. [e] The allenamide was added in 5 portions over 5 h. [f] The allenamide was added as a solution in DCE with a syringe pump. [g] Reaction time of 24 h. NR: No reaction.

III. Experimental procedures

Synthesis of CPA_1

CPA_1 was prepared by adapting our previous synthesis of catalyst **1**.[3]



(*S*)-BINOL (5.13 g, 517.9 mmol, 1.0 equiv.) was dissolved in 30 mL of anhydrous THF and added dropwise to a suspension of NaH (60 % wt in grease, 2.15 g, 53.8 mmol, 3 equiv.) in 30 ml of anhydrous THF at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then MOMCl (4.1 mL, 53.8 mmol, 3 equiv.) was added dropwise at 0 °C. The reaction mixture was stirred for another 3 hours at room temperature. When the reaction was completed, it was quenched with saturated aqueous $NaHCO_3$ and extracted twice with CH_2Cl_2. Combined organic layers were then dried over $MgSO_4$

and evaporated. The crude product **S1** (6.7 g, 100 %) was used directly for further synthesis without purification.

To a solution of **S1** (6.7 g, 17.9 mmol, 1.0 equiv.) in 100 mL of anhydrous THF, *n*-BuLi (4.8 mL, 23 mmol, 1.4 equiv.) was added dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 4 hours, then isopropoxypinacolborate (17.5 mL, 25.1 mmol, 1.3 equiv.) was added to the flask and the resulting solution was allowed to warm to room temperature. It was stirred overnight at room temperature and then quenched with water and extracted with DCM. Combined organic layers were dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography on silica gel (pure heptane to heptane:DCM = 2:1) yielding the product as a white solid **S2** (7.79 g, 87 %).

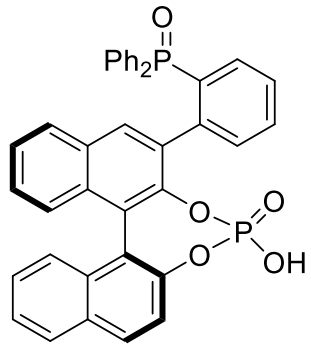
Diphenylphosphine oxide (4.04 g, 20 mmol, 1.0 equiv.) was dissolved in toluene (50 mL), and then $Pd_2(dba)_3$ (0.32 g, 0.35 mmol, 1.75 mol %), 1,3-bis(diphenylphosphino)propane (0.29 g, 0.7 mmol, 3.5 mol %), then bromoiodobenzene (2.83 mL, 22 mmol, 1.1 equiv.), and *i*Pr_2NEt (4.12 mL, 25 mmol, 1.25 equiv.) were added and the mixture stirred at 90 °C for 4 days. After cooling to room temperature, water was added and the solution was extracted with DCM. Organic layers were dried over $MgSO_4$, filtered and evaporated under vacuum. The crude product was purified by flash column chromatography (Hept: EA = 1:1 to EA), giving product as a pale yellow solid **S3** (3.78 g, 53 %).

(2-bromophenyl)diphenylphosphine oxide **S3** (3.78 g, 10.62 mmol, 1.1 equiv.) and $Pd(PPh_3)_4$ (0.56 g, 0.48 mmol, 5 mol %) were added to a flask, followed by anhydrous, degassed THF (100 mL) and H_2O (50 mL). The mixture was stirred at room temperature for 10 min. To this solution were added **S2** (4.82 g, 9.65 mmol, 1.0 equiv.) and K_2CO_3 (40 g, 28.95 mmol, 3 equiv.), and the solution was stirred at 100 °C for 24 h. After cooling to room temperature, water was added and the reaction mixture was extracted twice with DCM. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was dissolved in a mixture of THF/MeOH 1:1 (80 mL), then *p*-TsOH·H_2O was added to this solution and reaction mixture was stirred at 60 °C for overnight. After that, it was cooled down to room temperature and solvents were evaporated under reduced pressure. Water was added and the reaction mixture was extracted twice with DCM. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography (Hept:EtOAc = 80:20 to 60:40) giving the product as a brown solid **S4** (3.8 g, 70 %, over two steps).

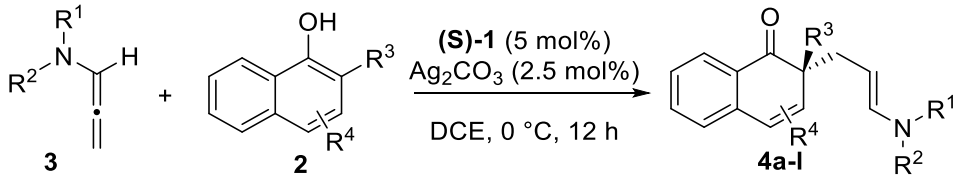
S4 (112 mg, 0.2 mmol, 1.0 equiv.) was dissolved in pyridine (4 mL) at 0 °C, and then $POCl_3$ (0.02 mL, 0.24 mmol, 1.2 equiv.) was added to the solution dropwise at 0 °C. The reaction was then stirred at room temperature for 60 h. The reaction mixture was poured into HCl (2 M), extracted with DCM, and dried over anhydrous $MgSO_4$. The crude product was afforded by removing solvent and was dissolved in THF (5 mL) at

room temperature, and then 4 M HCl (5 mL) was added to the solution. The reaction was then stirred at 60 °C overnight. The reaction mixture was extracted with DCM. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was afforded by removing solvent and was purified by a flash column chromatography (DCM:MeOH = 1:0 to 9:1) to afford the products **CPA_1** (yellow solid, 87 mg, 70%).

(4*R*,11c*S*)-2-(2-(diphenylphosphoryl)phenyl)-4-hydroxydinaphtho[2,1-d:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (CPA_1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.66 – 7.57 (m, 5H), 7.56 – 7.48 (m, 7H), 7.44 – 7.39 (m, 2H), 7.37 – 7.24 (m, 4H), 7.24 – 7.19 (m, 2H), 7.16 (dd, *J* = 14.0, 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (d, $J_{c\text{-}p}$ = 8.6 Hz), 145.3 (d, $J_{c\text{-}p}$ = 10.4 Hz), 142.5 (d, $J_{c\text{-}p}$ = 6.8 Hz), 134.0 (d, J = 13.5 Hz), 133.6 (d, $J_{c\text{-}p}$ = 9.5 Hz), 133.0, 133.0, 132.8, 132.4, 132.3, 132.3, 131.8 (d, $J_{c\text{-}p}$ = 10.4 Hz), 131.7, 131.3 (d, $J_{c\text{-}p}$ = 19.9 Hz), 130.4 (d, $J_{c\text{-}p}$ = 8.1 Hz), 129.8, 129.6, 129.5, 129.4, 129.1 (d, $J_{c\text{-}p}$ = 2.8 Hz), 129.0 (d, $J_{c\text{-}p}$ = 2.8 Hz), 128.8, 128.5, 128.1, 127.7 (d, $J_{c\text{-}p}$ = 12.6 Hz), 127.3, 126.9, 126.6, 126.3, 125.5, 125.3, 122.5, 121.6, 121.4; ^{31}P NMR ($CDCl_3$, 500 MHz) δ = 39.0, 1.2; $C_{38}H_{27}O_5P^+$ $[M + H]^+$: 625.1328, found: 625.1328; $[\alpha]_D$ = +196.6 (c 1.0, $CHCl_3$).

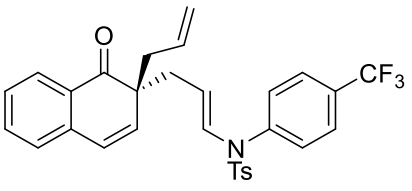


General procedures for gold-catalyzed dearomatization of 1-naphthols with *N*-allenyl amides.



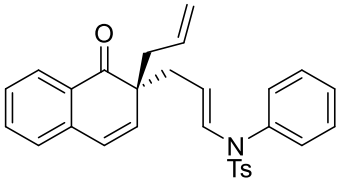
An oven-dried flask was charged with anhydrous solvent (1 mL), Au(I) catalyst (5 mol%) and Ag_2CO_3 (2.5 mol%). After stirring for 15 min, substrate **2** (0.05 mmol, 1 equiv) and **3** (0.15 mmol, 3 equiv) were added. Then, the reaction was kept stirring at 0 °C, and the reaction conversion was followed by TLC. After 12h, the solution was directly purified by preparative TLC (15% EtOAc/*n*-heptane) to afford compounds **4a-l**.

(*E*)-*N*-(3-(2-allyl-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-4-methyl-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (4a). Yellow oil, 18.3 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.20 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 14.0 Hz, 1H), 6.53 (d, *J* = 10.0 Hz, 1H), 6.45 (d, *J* = 8.5 Hz, 2H), 5.94 (d, *J* = 10.0 Hz,

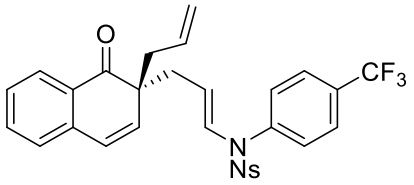


1H), 5.55 – 5.42 (m, 1H), 4.98 (d, *J* = 17.0 Hz, 1H), 4.89 (d, *J* = 10.5 Hz, 1H), 3.98 (ddd, *J* = 14.1, 8.5, 7.2 Hz, 1H), 2.70 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.54 (dd, *J* = 13.0, 8.5 Hz, 1H), 2.49 (s, 3H), 2.29 – 2.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.2, 144.0, 139.8, 138.4, 137.5, 135.3, 134.1, 132.9, 130.9, 130.5 (q, $^2J_{C\text{-}F}$ = 33 Hz), 130.1, 129.9, 129.7, 127.7, 127.4, 127.3, 126.4, 126.2 (q, $^3J_{C\text{-}F}$ = 3 Hz), 125.7, 123.5 (q, $^1J_{C\text{-}F}$ = 269 Hz), 118.1, 106.5, 54.1, 43.3, 40.8, 21.6; ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.7; HRMS calcd for $C_{30}H_{26}F_3NNaO_3S$ $[M + Na]^+$: 560.1483, found: 560.1478; $[\alpha]_D$ = +60.3 (*c* 0.63, $CHCl_3$); HPLC Analysis: 88% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 319 nm, retention times: 8.9 min (major) and 10.2 min (minor)].

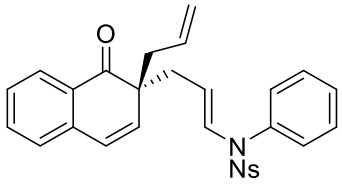
(*E*)-*N*-(3-(2-allyl-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (4b). Colorless oil, 15.7 mg, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.05 – 6.99 (m, 2H), 6.84 (d, *J* = 14.0 Hz, 1H), 6.52 (d, *J* = 10.0 Hz, 1H), 6.31 (d, *J* = 7.0 Hz, 2H), 5.93 (d, *J* = 10.0 Hz, 1H), 5.54 – 5.42 (m, 1H), 4.97 (d, *J* = 17.0 Hz, 1H), 4.88 (d, *J* = 10.5 Hz, 1H), 3.98 (ddd, *J* = 14.0, 8.4, 7.3 Hz, 1H), 2.70 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.48 (s, 3H), 2.27 – 2.15 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 143.5, 138.4, 137.5, 136.2, 135.8, 134.0, 133.1, 131.4, 129.7, 129.5, 129.1, 128.5, 127.6, 127.5, 127.3, 126.4, 125.6, 121.8, 118.0, 105.2, 54.1, 43.1, 40.9, 21.6; HRMS calcd for $C_{29}H_{27}NNaO_3S$ $[M + Na]^+$: 492,1609, found: 492.1614; $[\alpha]_D$ = +60.4 (*c* 1.11, $CHCl_3$); HPLC Analysis: 88% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 280 nm, retention times: 15.2 min (major) and 18.2 min (minor)].



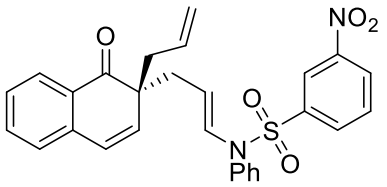
(*E*)-*N*-(3-(2-allyl-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-4-nitro-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (4c). Yellow oil, 15.4 mg, 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.0 Hz, 2H), 7.82 – 7.77 (m, 1H), 7.70 (d, *J* = 9.0 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 13.8 Hz, 1H), 6.55 (d, *J* = 9.6 Hz, 1H), 6.45 (d, *J* = 8.1 Hz, 2H), 5.95 (d, *J* = 9.9 Hz, 1H), 5.56 – 5.41 (m, 1H), 5.02 – 4.88 (m, 2H), 4.13 (ddd, *J* = 14.0, 9.2, 6.5 Hz, 1H), 2.71 – 2.56 (m, 2H), 2.29 – 2.14 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 160.3, 150.3, 143.5, 139.0, 138.2, 137.5, 134.5, 132.5, 130.0, 129.9, 128.6, 128.5, 127.8, 127.4, 126.6 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 126.3, 125.7, 124.3, 122.6 (q, $^1J_{C\text{-}F}$ = 289 Hz), 118.5, 108.9, 54.1, 43.6, 40.3; ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.8; HRMS calcd for $C_{29}H_{24}F_3N_2O_5S$ $[M + H]^+$: 569.1358, found: 569.1355; $[\alpha]_D$ = -4.2 (*c* 0.50, $CHCl_3$); HPLC Analysis: 88% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 352 nm, retention times: 11.0 min (major) and 14.9 min (minor)].



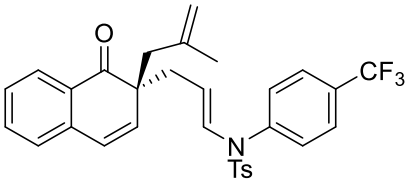
(*E*)-*N*-(3-(2-allyl-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-4-nitro-*N*-phenylbenzenesulfonamide (4d). Yellow oil, 11.0 mg, 44% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.83 (d, *J* = 13.5 Hz, 1H), 6.54 (d, *J* = 9.5 Hz, 1H), 6.28 (d, *J* = 7.5 Hz, 2H), 5.93 (d, *J* = 10.0 Hz, 1H), 5.53 – 5.43 (m, 1H), 4.98 (d, *J* = 17.0 Hz, 1H), 4.89 (d, *J* = 10.0 Hz, 1H), 4.17 – 4.07 (m, 1H), 2.62 (ddd, J = 22.4, 13.3, 8.3 Hz, 2H), 2.21 (ddd, J = 20.5, 13.4, 6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.1, 143. 9, 138.3, 137.5, 134.3, 132.7, 130.4, 129.5, 129.4, 129.3, 129.3, 128.6, 128.3, 127.7, 127.4, 126.3, 125.7, 124.1, 123.8, 118.3, 107.6, 43.5, 40.4, 29.7; HRMS calcd for $C_{28}H_{24}N_2NaO_5S$ $[M + Na]^+$: 523.1304, found: 523.1303; $[\alpha]_D$ = -6.0 (*c* 0.12, $CHCl_3$); HPLC Analysis: 92% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 343 nm, retention times: 18.2 min (major) and 30.2 min (minor)].



(*E*)-*N*-(3-(2-allyl-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-3-nitro-*N*-phenylbenzenesulfonamide (4e). Yellow oil, 13.0 mg, 52% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.0 Hz, 1H), 8.34 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.09 – 7.04 (m, 3H), 6.82 (d, *J* = 13.5 Hz, 1H), 6.52 (d, *J* = 9.5 Hz, 1H), 6.31 (d, *J* = 7.5 Hz, 2H), 5.94 (d, *J* = 9.5 Hz, 1H), 5.54 – 5.41 (m, 1H), 4.97 (d, *J* = 16.5 Hz, 1H), 4.89 (d, *J* = 10.0 Hz, 1H), 4.15 – 4.03 (m, 1H), 2.68 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.54 (dd, *J* = 13.5, 9.0 Hz, 1H), 2.27 – 2.17 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.3, 137.5, 134.7, 134.2, 132.9, 132.8, 132.7, 130.3, 129.7, 129.5, 129.2, 127.7, 127.4, 127.3, 127.2, 126.4, 126.3, 125.6, 122.6, 122.5, 122.3, 118.2, 107.3, 44.5, 43.3, 40.5; HRMS calcd for $C_{28}H_{24}N_2NaO_5S$ $[M + Na]^+$: 523.1304, found: 523.1305; $[\alpha]_D$ = +76.0 (*c* 0.53, $CHCl_3$); HPLC Analysis: 91% ee [©Chiralpak IC, 20 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 322 nm, retention times: 13.1 min (minor) and 17.6 min (major)].

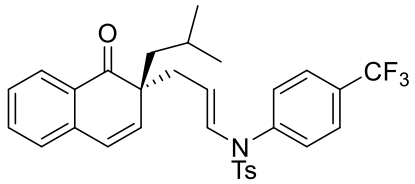


(*E*)-4-methyl-*N*-(3-(2-(2-methylallyl)-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (4f). Yellow oil, 12.6 mg, 46% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 14.0 Hz, 1H), 6.51 (d, *J* = 10.0 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 2H), 5.95 (d, *J* = 10.0 Hz, 1H), 4.58 (s, 1H), 4.50 (s, 1H), 3.97 – 3.85 (m, 1H), 2.94 (d, *J* = 14.0 Hz, 1H), 2.52 – 2.47 (m, 4H), 2.23 – 2.15 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 144.0, 142.1, 139.6, 138.3, 138.2, 135.4, 134.0, 131.0, 130.5 (q, $^2J_{C\text{-}F}$ = 33 Hz), 130.1, 129.9, 129.7, 127.6, 127.5, 127.4, 126.4, 126.2 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 125.2, 123.5 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 113.1, 105.7, 53.8, 47.0, 42.7, 23.7, 21.6; ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.7; HRMS calcd for $C_{31}H_{28}F_3NNaO_3S$ $[M + Na]^+$: 574.1640, found: 574.1635; $[\alpha]_D$ = +3.8 (*c* 0.60, $CHCl_3$); HPLC Analysis: 68% ee [©Chiralpak IC, 25 °C, 20%

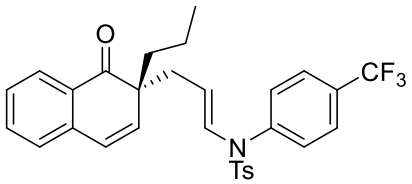


*i*PrOH/*n*-heptane, 1 mL/min, 294 nm, retention times: 8.4 min (major) and 9.3 min (minor)].

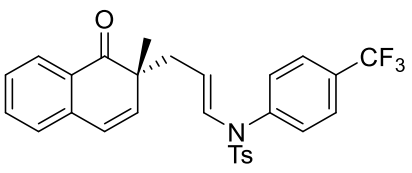
(R,E)-N-(3-(2-isobutyl-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-4-methyl-N-(4-(trifluoromethyl)phenyl)benzenesulfonamide (4g). Colorless oil, 31.0 mg, 56% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.75 (d, J = 14.0 Hz, 1H), 6.50 (d, J = 9.5 Hz, 1H), 6.31 (d, J = 8.5 Hz, 2H), 5.93 (d, J = 9.5 Hz, 1H), 3.86 (ddd, J = 14.1, 8.7, 7.0 Hz, 1H), 2.49 (s, 3H), 2.44 (dd, J = 12.9, 8.8 Hz, 1H), 2.12 – 2.05 (m, 2H), 1.45 (m, 2H), 0.79 (d, J = 6.5 Hz, 3H), 0.50 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 144.0, 139.6, 138.6, 138.3, 135.4, 133.9, 130.8, 130.4 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 130.1, 129.7, 129.7, 127.6, 127.5, 127.3, 126.4, 126.2 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 125.1, 122.3 (q, $^1J_{C\text{-}F}$ = 272.9 Hz), 105.9, 54.2, 48.5, 43.3, 26.5, 24.0, 23.5, 21.6. ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.8. HRMS calcd for $C_{31}H_{30}F_3NNaO_3S$ $[M + Na]^+$: 576.1791, found: 576.1787; $[\alpha]_D$ = +76.1 (*c* 1.0, $CHCl_3$); HPLC Analysis: 62% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 285 nm, retention times: 8.0 min (major) and 8.8 min (minor)].



(*E*)-4-methyl-*N*-(3-(1-oxo-2-propyl-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (4h). Yellow oil, 16.0 mg, 59% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 14.0 Hz, 1H), 6.54 (d, *J* = 10.0 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 2H), 5.91 (d, *J* = 10.0 Hz, 1H), 3.97 (ddd, *J* = 14.1, 8.6, 7.1 Hz, 1H), 2.55 – 2.48 (m, 4H), 2.15 (dd, *J* = 12.5, 6.5 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.44 – 1.37 (m, 1H), 1.17 – 1.07 (m, 1H), 1.00 – 0.93 (m, 1H), 0.77 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.0, 144.0, 138.5, 135.4, 134.1, 130.8, 130.3 (q, $^2J_{C\text{-}F}$ = 33.9 Hz), 130.1, 129.9, 129.7, 127.6, 127.4, 127.3, 127.2, 126.3, 126.2 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 122.7 (q, $^1J_{C\text{-}F}$ = 270 Hz), 125.6, 119.8, 106.8, 54.7, 42.0, 41.7, 21.6, 18.4, 14.4; ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.7; HRMS calcd for $C_{30}H_{28}F_3NNaO_3S$ $[M + Na]^+$: 562.1640, found: 562.1639; $[\alpha]_D$ = +27.0 (*c* 0.50, $CHCl_3$); HPLC Analysis: 77% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 343 nm, retention times: 9.2 min (major) and 10.3 min (minor)].

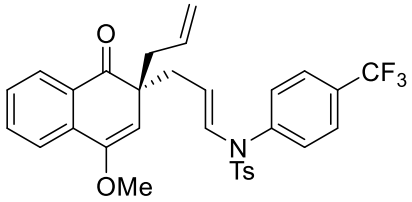


(*E*)-4-methyl-*N*-(3-(2-methyl-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (4i). Yellow oil, 18.0 mg, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 14.0 Hz, 1H), 6.52 – 6.41 (m, 3H), 5.90 (d, *J* = 9.5 Hz, 1H), 4.03 – 3.95 (m, 1H), 2.55

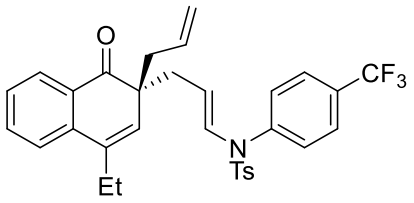


– 2.45 (m, 1H), 2.49 (s, 3H) 2.14 (dd, *J* = 13.0, 7.0 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.9, 144.0, 139.9, 139.1, 138.4, 134.1, 130.8, 130.1, 130.0 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 129.9, 129.7, 127.7, 127.4, 127.2, 127.2, 126.6, 124.2, 126.2 (q, $^3J_{C\text{-}F}$ = 4 Hz), 123.2 (q, $^1J_{C\text{-}F}$ = 268.5 Hz), 119.8, 107.2, 49.9, 41.8, 24.1, 21.6; ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.7; HRMS calcd for $C_{28}H_{24}F_3NNaO_3S$ $[M + Na]^+$: 534.1327, found: 534.1332; $[\alpha]_D$ = +27.4 (*c* 0.50, $CHCl_3$); HPLC Analysis: 81% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 295 nm, retention times: 9.7 min (major) and 12.0 min (minor)].

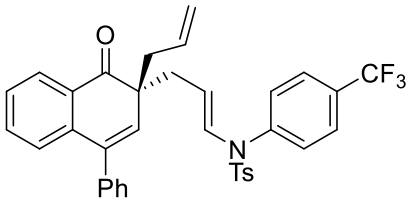
(*E*)-*N*-(3-(2-allyl-4-methoxy-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-4-methyl-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (4j). Colorless oil, 20.0 mg, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 1H), 7.70 – 7.65 (m, 1H), 7.61 – 7.56 (m, 1H), 7.43 – 7.37 (m, 2H), 7.31 – 7.25 (m, 5H), 6.80 (d, *J* = 13.8 Hz, 1H), 6.45 (d, *J* = 8.1 Hz, 2H), 5.61 – 5.45 (m, 1H), 5.06 – 4.85 (m, 3H), 4.04 – 3.93 (m, 1H), 3.72 (s, 3H), 2.73 – 2.51 (m, 2H), 2.47 (s, 3H), 2.29 – 2.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 149.6, 144.0, 135.4, 133.9, 133.2, 130.8, 130.1, 130.0 (q, $^2J_{C\text{-}F}$ = 33 Hz), 129.9, 129.7, 128.0, 127.7, 127.5, 127.3, 126.4, 126.2 (q, $^3J_{C\text{-}F}$ = 3 Hz), 122.4, 121.1 (q, $^1J_{C\text{-}F}$ = 271 Hz), 118.1, 107.2, 104.2, 54.9, 53.0, 44.4, 41.9, 21.6; ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.8; HRMS calcd for $C_{31}H_{28}F_3NNaO_4S$ $[M + Na]^+$: 590.1589, found: 590.1592; $[\alpha]_D$ = +7.2 (*c* 0.75, $CHCl_3$); HPLC Analysis: 83% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 351 nm, retention times: 9.2 min (major) and 10.9 min (minor)].



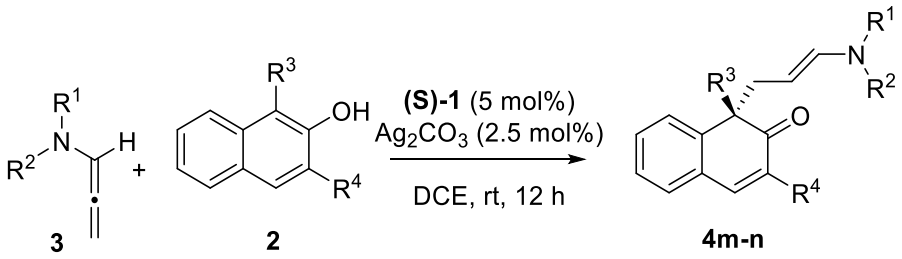
(*E*)-*N*-(3-(2-allyl-4-ethyl-1-oxo-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-4-methyl-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (4k). Colorless oil, 16.5 mg, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.19 (m, 3H), 6.79 (d, *J* = 14.0 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 2H), 5.69 (s, 1H), 5.53 – 5.40 (m, 1H), 4.96 (d, *J* = 17.0 Hz, 1H), 4.87 (d, *J* = 10.0 Hz, 1H), 3.99 – 3.88 (m, 1H), 2.67 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.55 – 2.47 (m, 4H), 2.42 (q, *J* = 15.0, 7.5 Hz, 2H), 2.27 – 2.14 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 144.0, 139.9, 138.6, 135.5, 135.4, 134.0, 133.1, 132.8, 130.7, 130.4 (q, $^2J_{C\text{-}F}$ = 36 Hz), 130.1, 129.9, 129.7, 127.4, 127.2, 126.8, 126.2 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 123.9, 123.5 (q, $^1J_{C\text{-}F}$ = 274.5 Hz), 118.0, 107.1, 53.3, 43.5, 41.0, 25.2, 21.6, 13.4; ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.8; HRMS calcd for $C_{32}H_{30}F_3NNaO_3S$ $[M + Na]^+$: 588.1796, found: 588.1795; $[\alpha]_D$ = +4.4 (*c* 0.75, $CHCl_3$); HPLC Analysis: 81% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 284 nm, retention times: 8.1 min (major) and 8.9 min (minor)].



(*E*)-*N*-(3-(2-allyl-1-oxo-4-phenyl-1,2-dihydronaphthalen-2-yl)prop-1-en-1-yl)-4-methyl-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (4l). Colorless oil, 7.2 mg, 23% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.36 (m, 6H), 7.33 – 7.26 (m, 3H), 7.25 – 7.19 (m, 2H), 7.04 (d, *J* = 7.2 Hz, 3H), 6.87 (d, *J* = 14.1 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 2H), 5.82 (s, 1H), 5.64 – 5.47 (m, 1H), 5.06 – 4.90 (m, 2H), 4.05 (ddd, *J* = 14.0, 9.3, 6.3 Hz, 1H), 2.77 (dd, *J* = 13.5, 7.2 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.48 (s, 3H), 2.33 – 2.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.1, 144.0, 139.9, 138.9, 138.6, 137.8, 136.5, 135.4, 134.9, 133.8, 132.9, 131.0, 130.5 (q, $^2J_{C\text{-}F}$ = 34.5 Hz), 130.3, 129.7, 128.9, 128.5, 127.7, 127.6, 127.4, 126.8, 126.6, 126.4 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 123.2 (q, $^1J_{C\text{-}F}$ = 277 Hz), 118.3, 106.7, 53.8, 43.4, 41.0, 21.6; ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.7; HRMS calcd for $C_{36}H_{30}F_3NNaO_3S$ [M + Na]$^+$: 636.1796, found: 636.1794; $[\alpha]_D$ = -6.7 (*c* 0.24, $CHCl_3$); HPLC Analysis: 36% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 247 nm, retention times: 8.0 min (major) and 8.6 min (minor)].

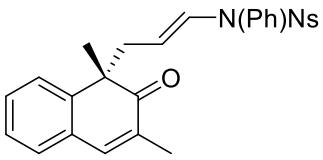


General procedures for gold-catalyzed dearomatization of 2-naphthols with *N*-allenyl amides.



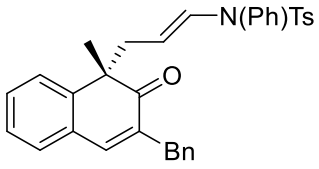
An oven-dried flask was charged with anhydrous solvent (1 ml), Au(I) catalyst (5 mol%) and $AgCO_3$ (2.5 mol%). After stirring for 15 min, substrate **2** (0.05 mmol, 1 equiv) and **3** (0.10 mmol, 2 equiv) were added. Then, the reaction was kept stirring at room temperature overnight, and the reaction conversion was verified by TLC. Then, the crude mixture was directly transferred into silica gel column chromatography (2.5% to 5% to 7.5% EtOAc/*n*-heptane), to afford compounds **4**.

(*E*)-*N*-(3-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)prop-1-en-1-yl)-4-nitro-*N*-phenylbenzenesulfonamide (4m). Colorless oil, 18.2 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.38 – 7.26 (m, 4H), 7.26 – 7.22 (m, 2H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.11 (s, 1H), 6.64 (d, *J* = 7.5 Hz, 2H), 6.56 (d, *J* = 14.0 Hz, 1H), 3.97 (ddd, J = 14.1, 8.4, 7.2 Hz, 1H), 2.72 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.40 (dd, *J* = 13.5, 9.0 Hz, 1H), 1.82 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.4, 150.0, 144.9, 144.1, 141.5, 135.6, 132.4, 130.2, 130.1, 129.6, 129.5, 129.2, 128.9, 128.5, 128.3, 126.7, 126.4, 124.1, 108.8, 51.6, 44.1, 26.2, 15.6; HRMS calcd for $C_{27}H_{24}N_2NaO_5S$ [M + Na]$^+$: 511.1304, found: 511.1306; $[\alpha]_D$ = -0.9 (*c* 0.57, $CHCl_3$); HPLC Analysis: 65% ee [©Chiralpak IC, 25

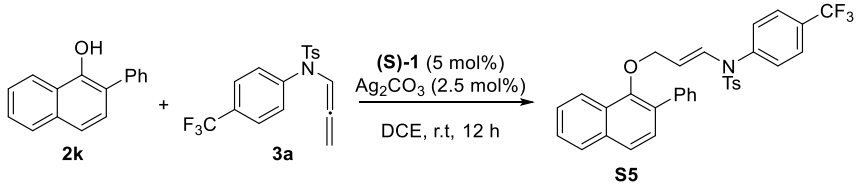


°C, 30% *i*PrOH/*n*-heptane, 1 mL/min, 279 nm, retention times: 21.1 min (minor) and 31.6 min (major)].

(*E*)-*N*-(3-(3-benzyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)prop-1-en-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (4n). White solid, 17.0 mg, 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.25 – 7.16 (m, 7H), 7.11 – 7.04 (m, 3H), 6.84 (s, 1H), 6.71 – 6.62 (m, 3H), 3.83 (dt, *J* = 14.1, 7.7 Hz, 1H), 3.62 (d, *J* = 16.0 Hz, 1H), 3.44 (d, *J* = 16.5 Hz, 1H), 2.66 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.40 (s, 3H), 2.36 (dd, *J* = 13.4, 8.1 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.9, 144.8, 143.6, 141.7, 138.9, 136.6, 135.8, 135.7, 131.3, 129.9, 129.5, 129.2, 129.1, 129.0, 128.8, 128.6, 128.5, 127.4, 126.6, 126.4, 126.3, 125.4, 121.8, 106.6, 51.9, 44.6, 35.1, 25.3, 21.5; HRMS calcd for $C_{34}H_{31}NNaO_3S$ $[M + Na]^+$: 556.1922, found: 556.1918; $[\alpha]_D$ = -20.0 (*c* 0.34, $CHCl_3$); HPLC Analysis: 59% ee [©Chiralpak IC, 25 °C, 30% *i*PrOH/*n*-heptane, 1 mL/min, 292 nm, retention times: 18.7 min (minor) and 21.0 min (major)].

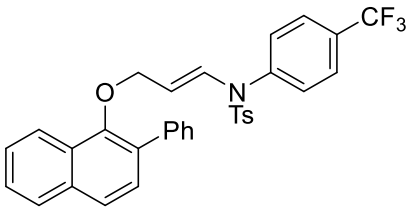


Reaction with phenyl naphthol



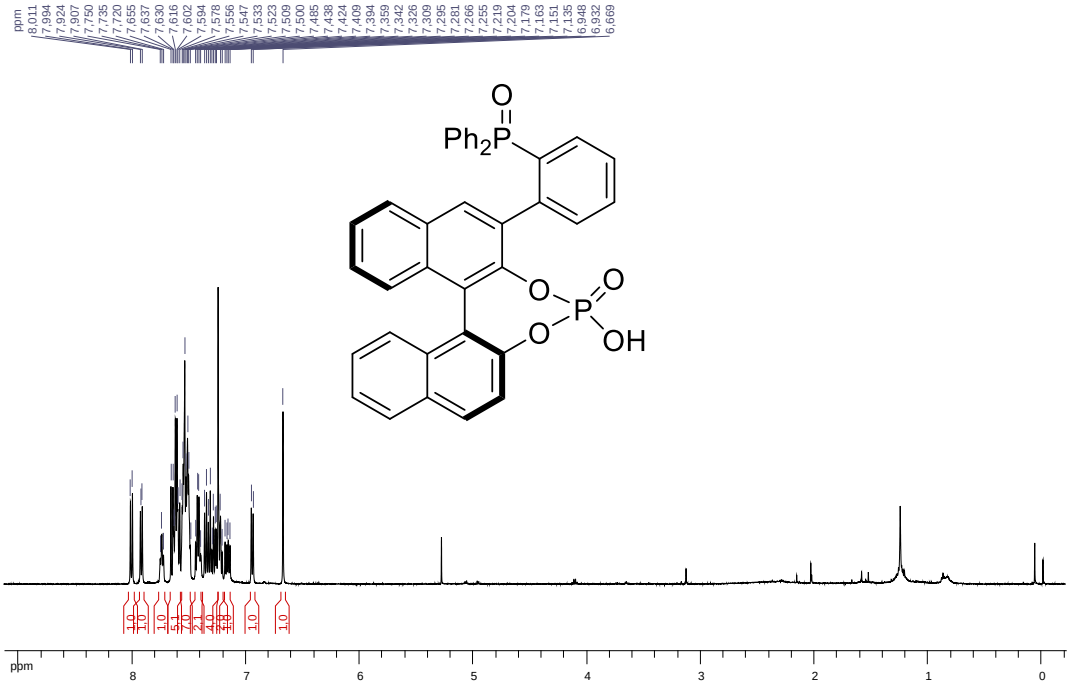
An oven-dried flask was charged with anhydrous solvent (1 mL), Au(I) catalyst (5 mol%) and Ag_2CO_3 (2.5 mol%). After stirring for 15 min, substrate **2k** (0.15 mmol, 1 equiv) and **3a** (0.45 mmol, 3 equiv) were added. Then, the reaction was kept stirring at r.t, and the reaction conversion was followed by TLC. After 12h, the solution was directly purified by preparative TLC (15% EtOAc/*n*-heptane) to afford compounds **S5**.

4-methyl-*N*-(3-((2-phenylnaphthalen-1-yl)oxy)prop-1-en-1-yl)-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (S5). Colorless oil, 72.5 mg, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.49 – 7.38 (m, 8H), 7.35 – 7.31 (m, 3H), 7.25 (m, 1H), 6.85 (d, *J* = 14.0 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 4.28 (dt, *J* = 14.4, 7.3 Hz, 1H), 4.09 (d, *J* = 7.5 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 144.3, 139.3, 138.8, 135.2, 134.0, 132.9, 130.9 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 130.5, 130.1, 129.8, 129.3, 128.4, 128.4, 127.6, 127.3, 127.2, 126.5 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 126.1, 126.0, 123.9, 123.6 (q, $^1J_{C\text{-}F}$ = 270.5 Hz), 122.9, 106.7, 71.7, 21.6. ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.7. HRMS calcd for $C_{33}H_{26}F_3NNaO_3S$ $[M + Na]^+$: 596.1478, found: 596.1475.

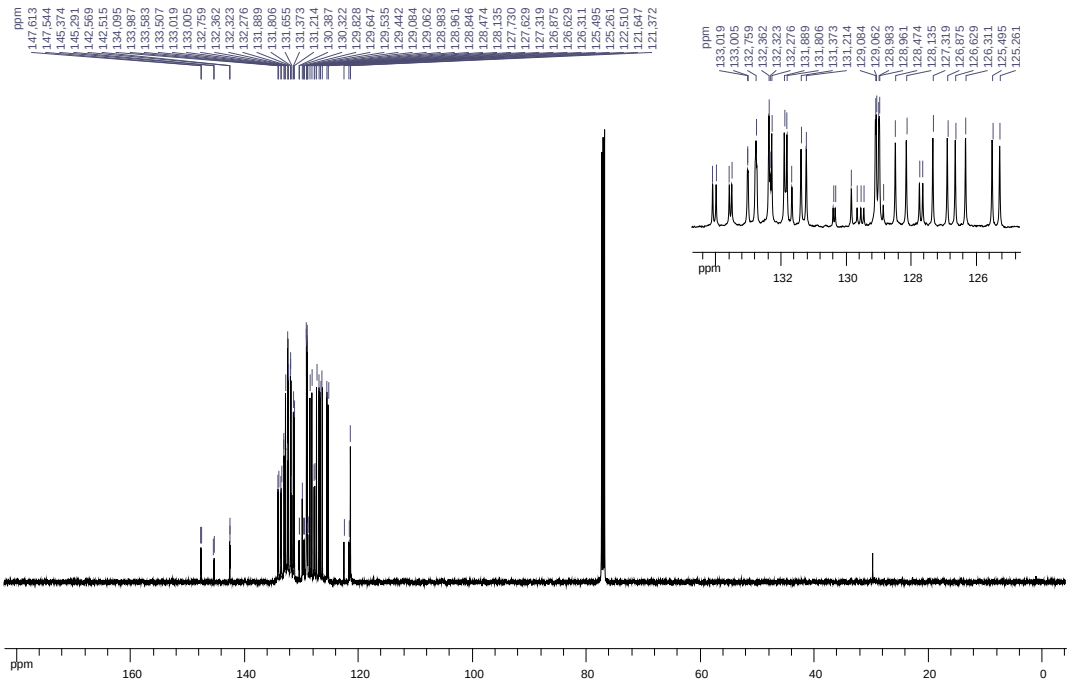


IV. NMR Spectra (^{1}H and ^{13}C NMR)

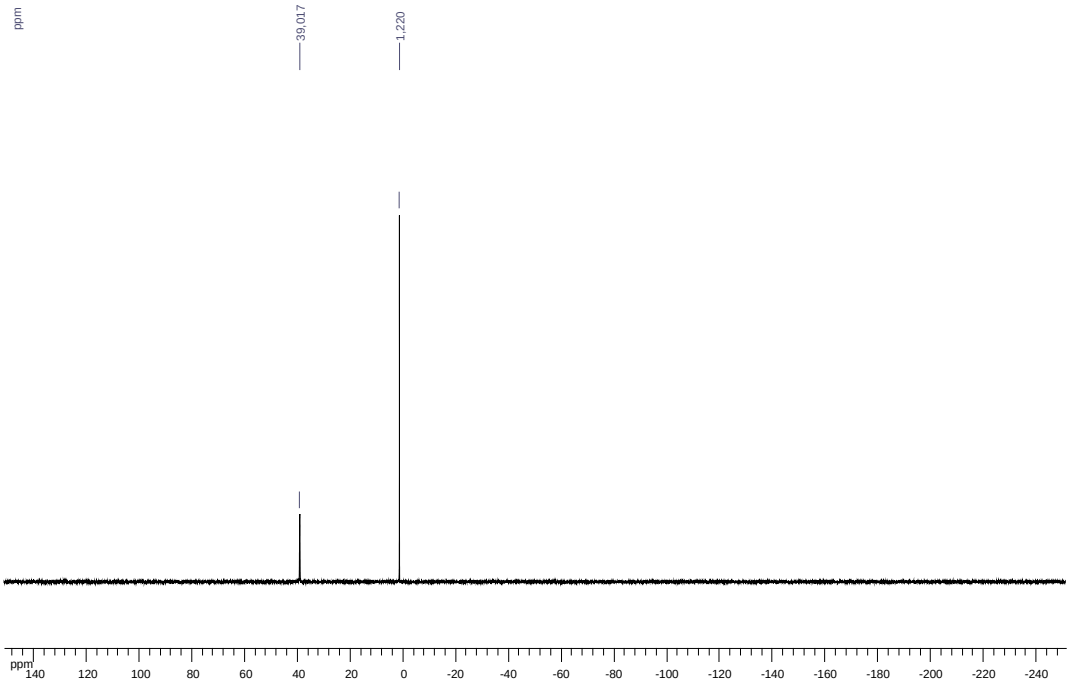
^{1}H NMR ($CDCl_3$, 500 MHz) (**CPA_1**)



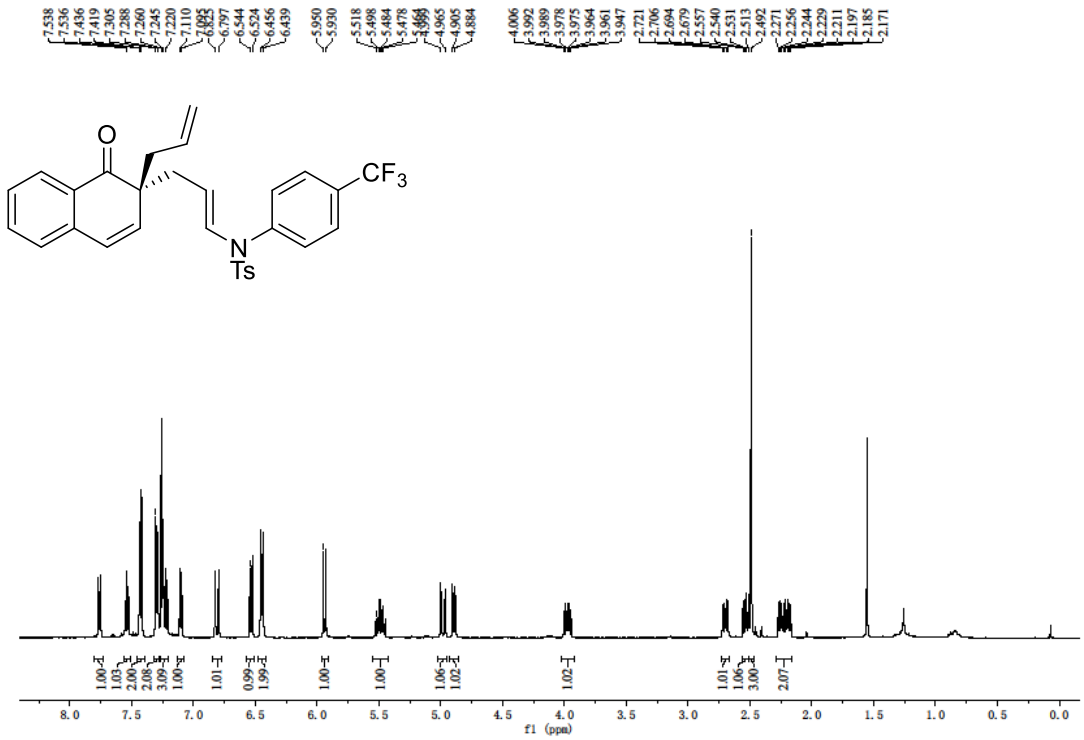
^{13}C NMR ($CDCl_3$, 125 MHz)



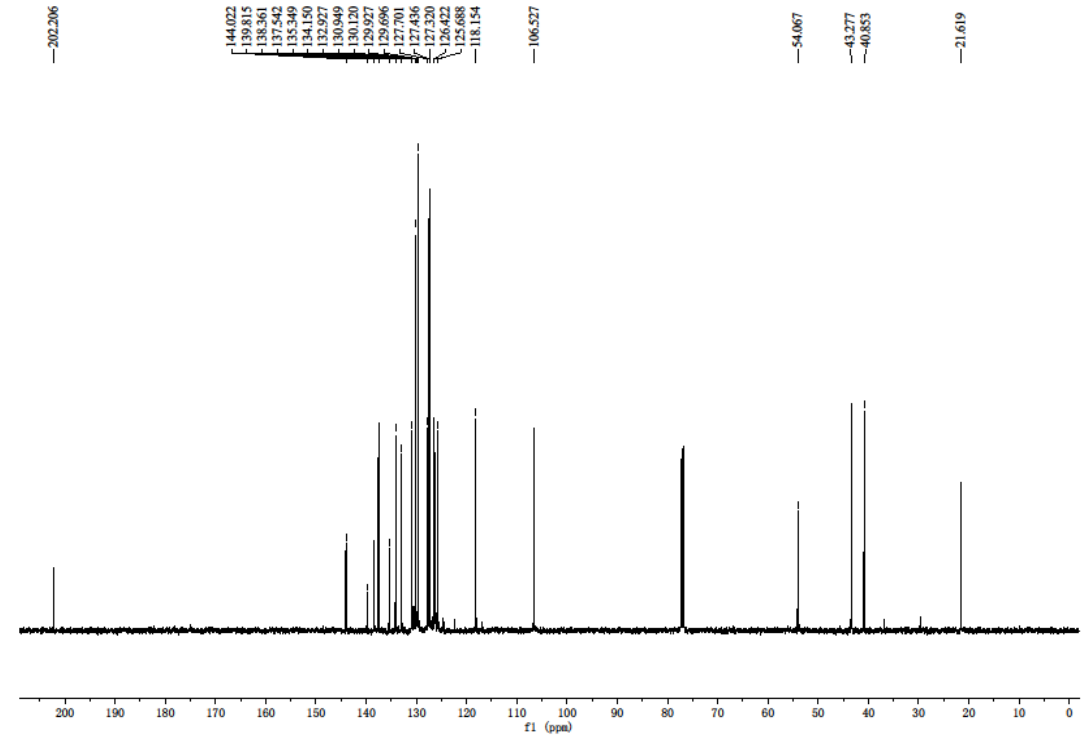
^{31}P NMR ($CDCl_3$, 500 MHz)



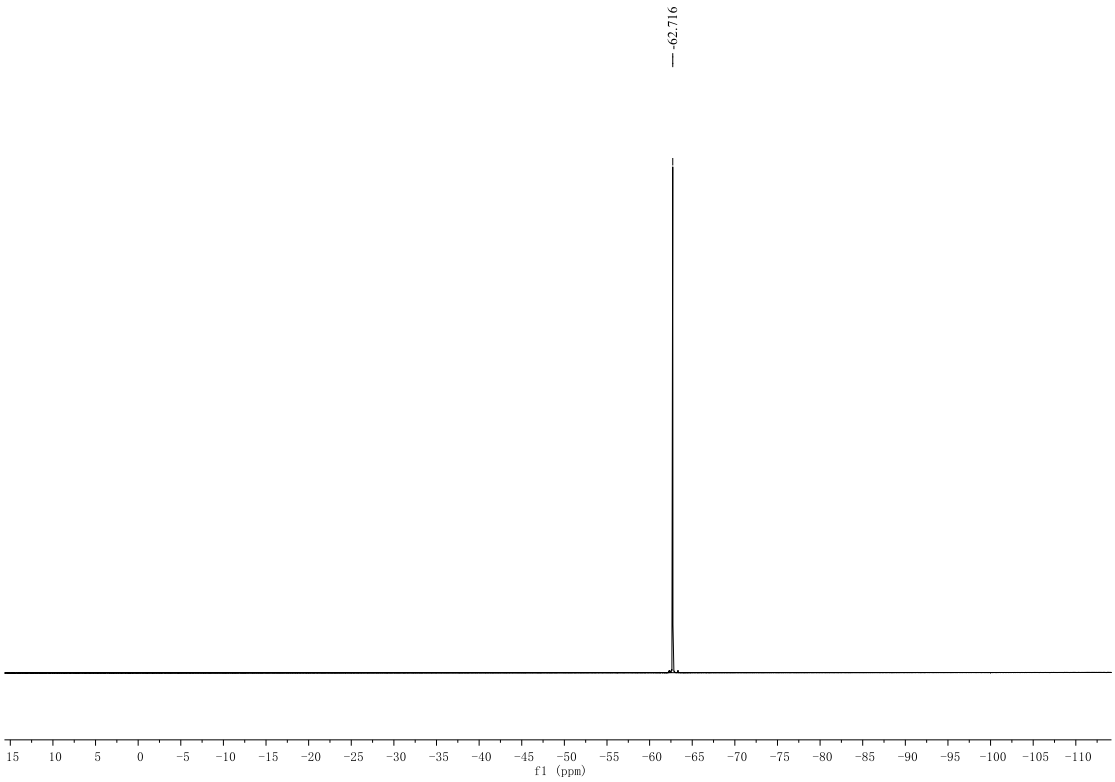
^{1}H NMR ($CDCl_3$, 500 MHz) (**4a**)



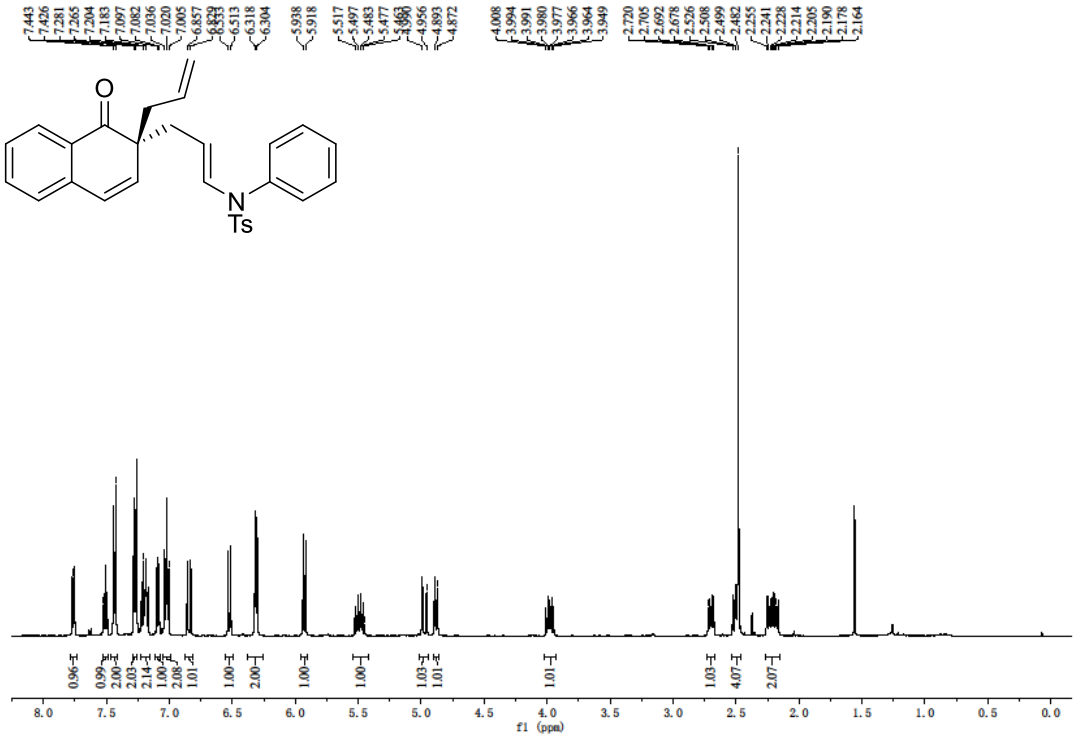
^{13}C NMR ($CDCl_3$, 125 MHz)



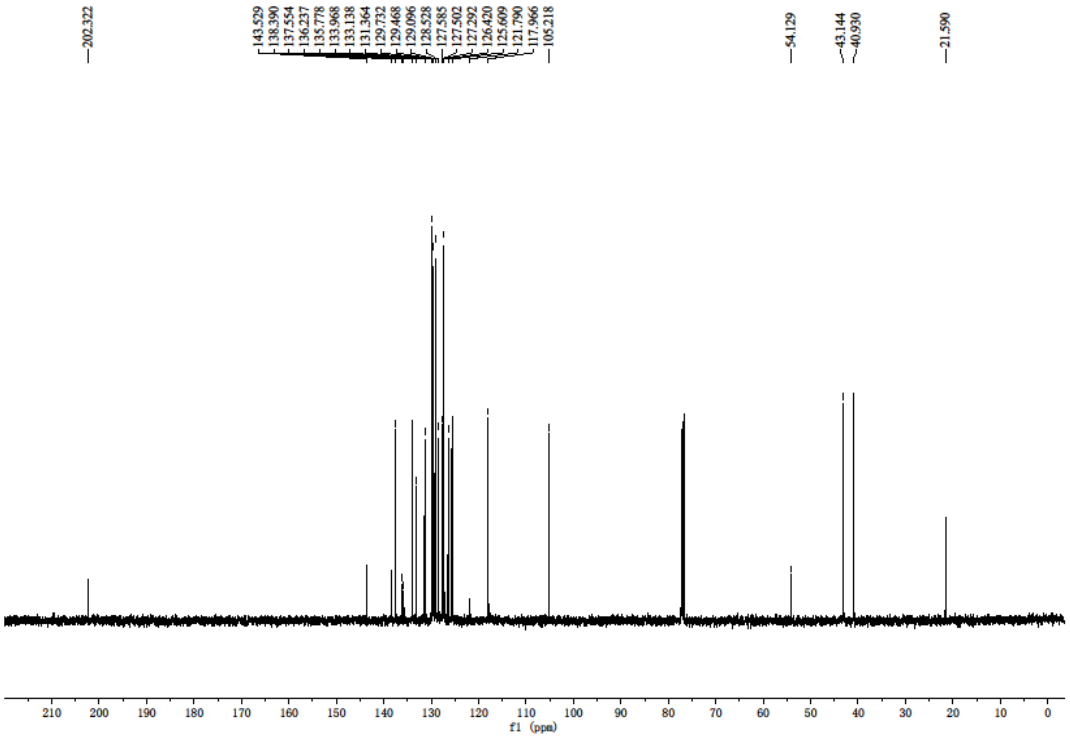
^{19}F NMR ($CDCl_3$, 300 MHz)



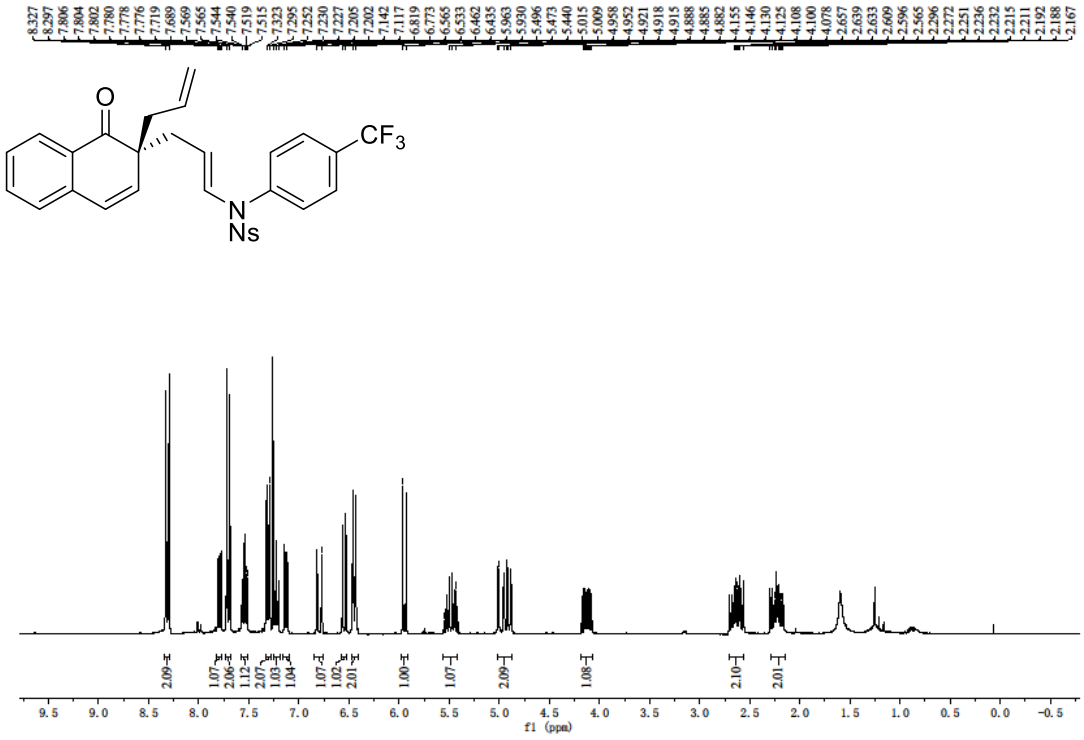
^{1}H NMR ($CDCl_3$, 500 MHz) (**4b**)



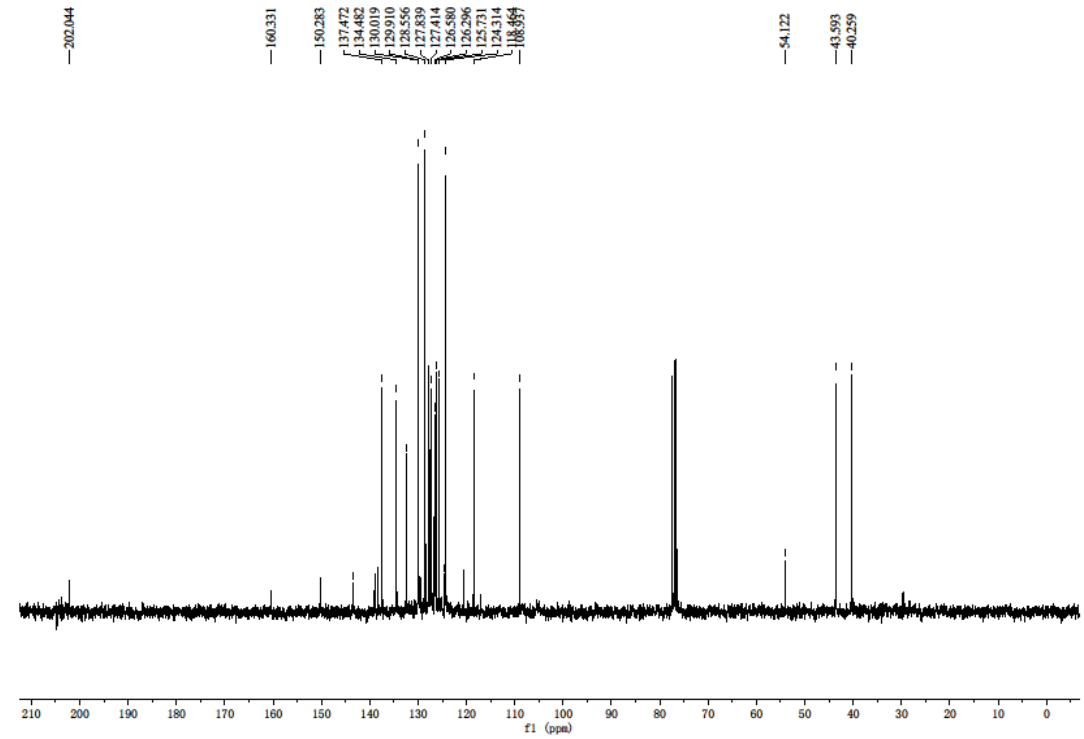
^{13}C NMR ($CDCl_3$, 125 MHz)



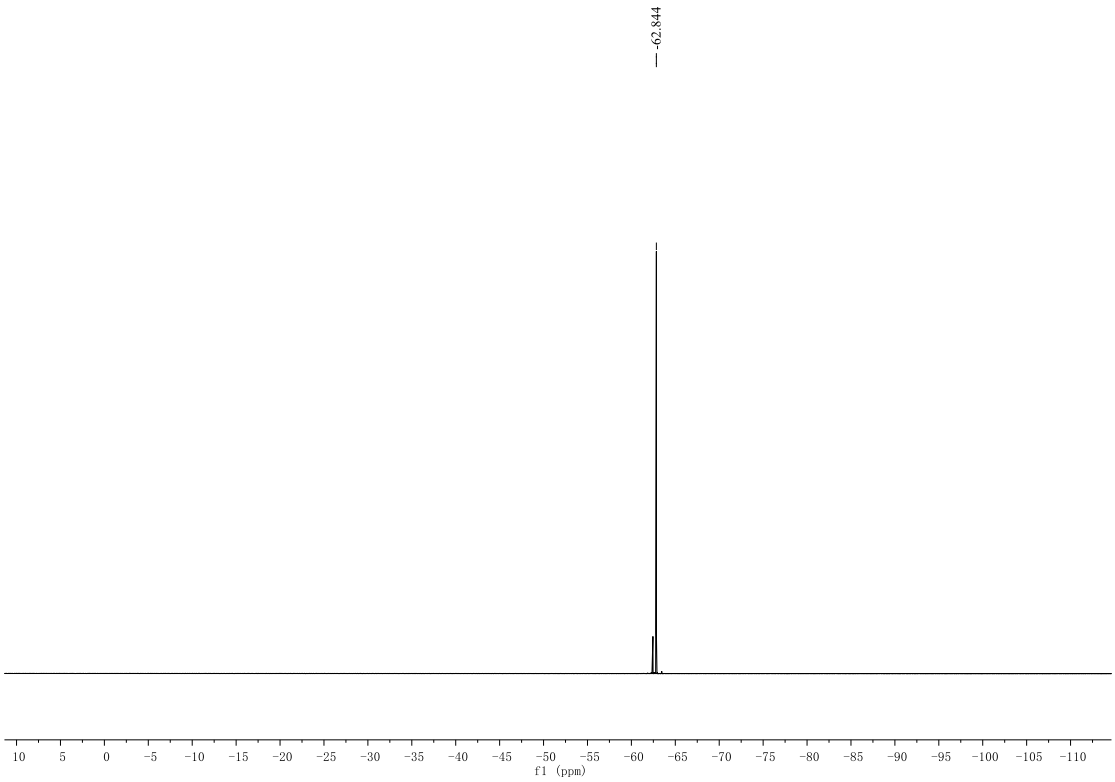
^{1}H NMR ($CDCl_3$, 300 MHz) (**4c**)



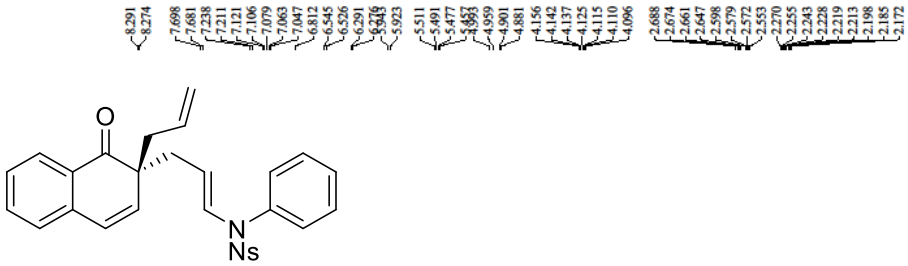
^{13}C NMR ($CDCl_3$, 75 MHz)

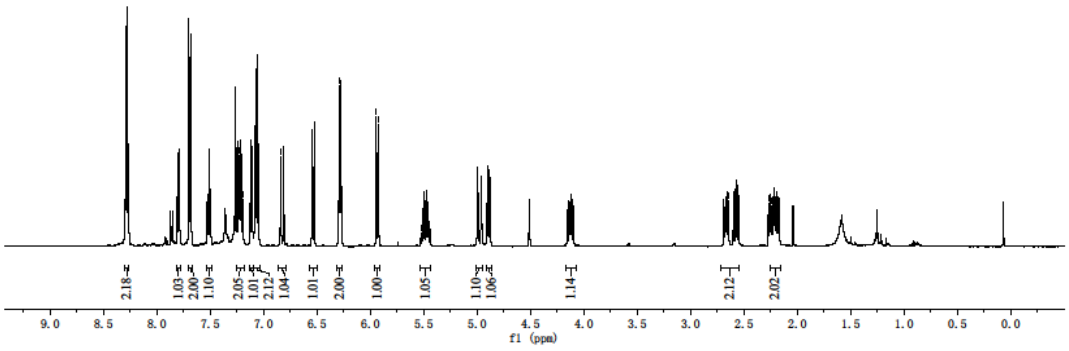


^{19}F NMR ($CDCl_3$, 300 MHz)

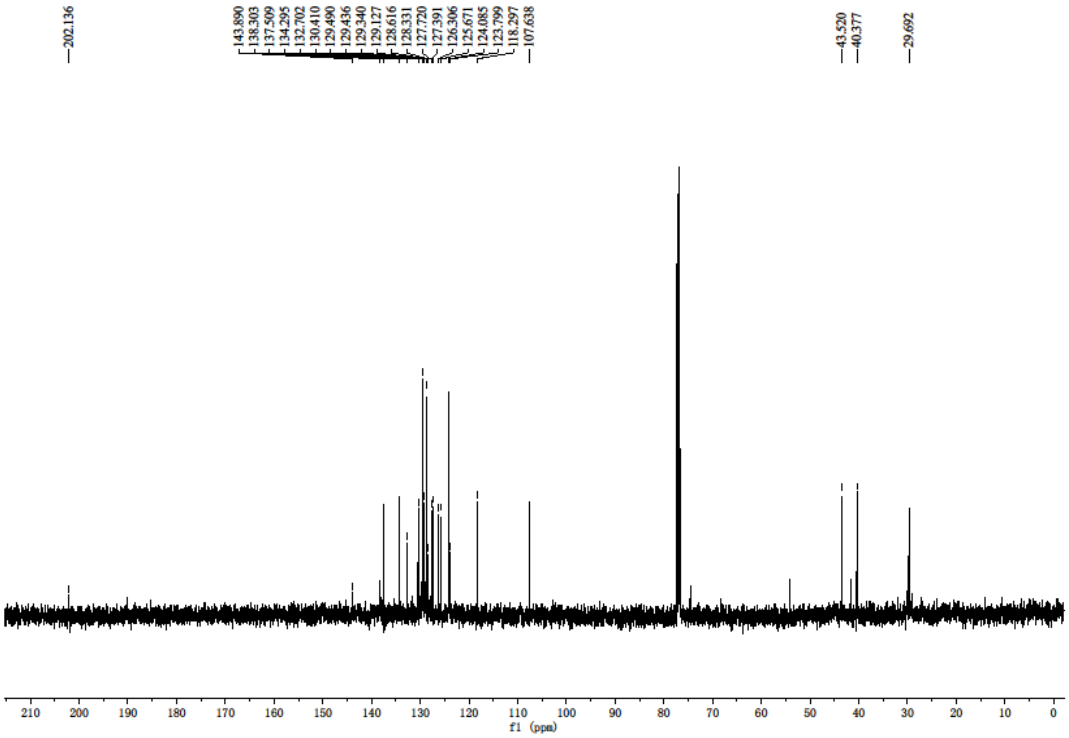


^{1}H NMR ($CDCl_3$, 500 MHz) (**4d**)

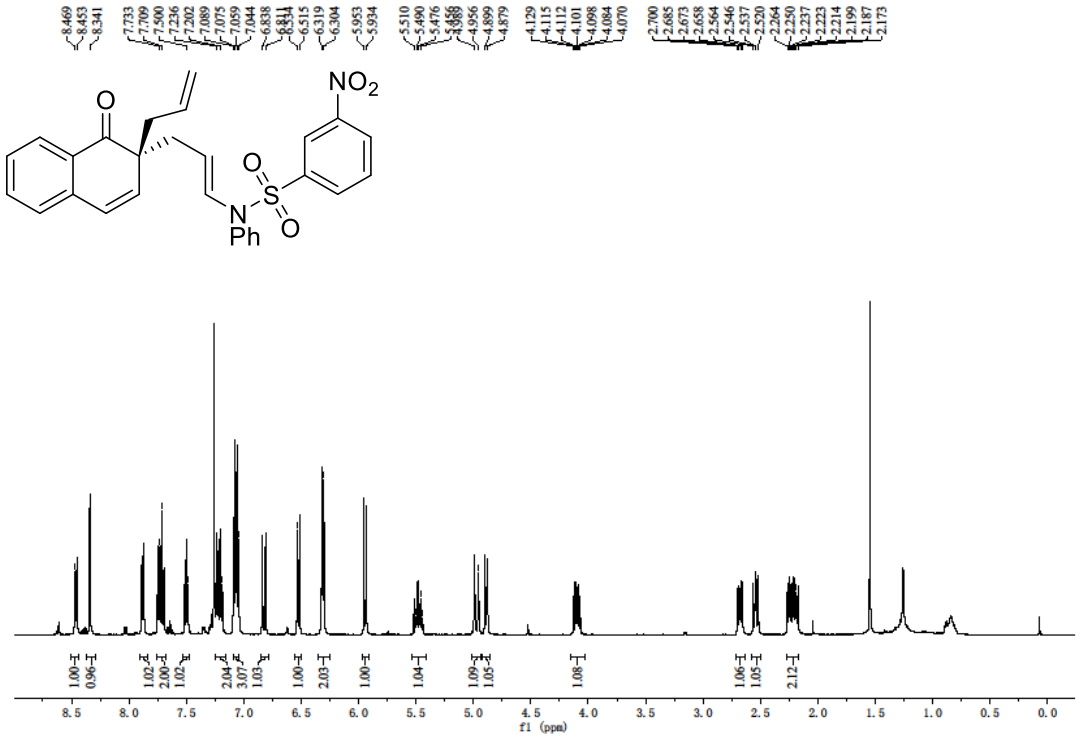




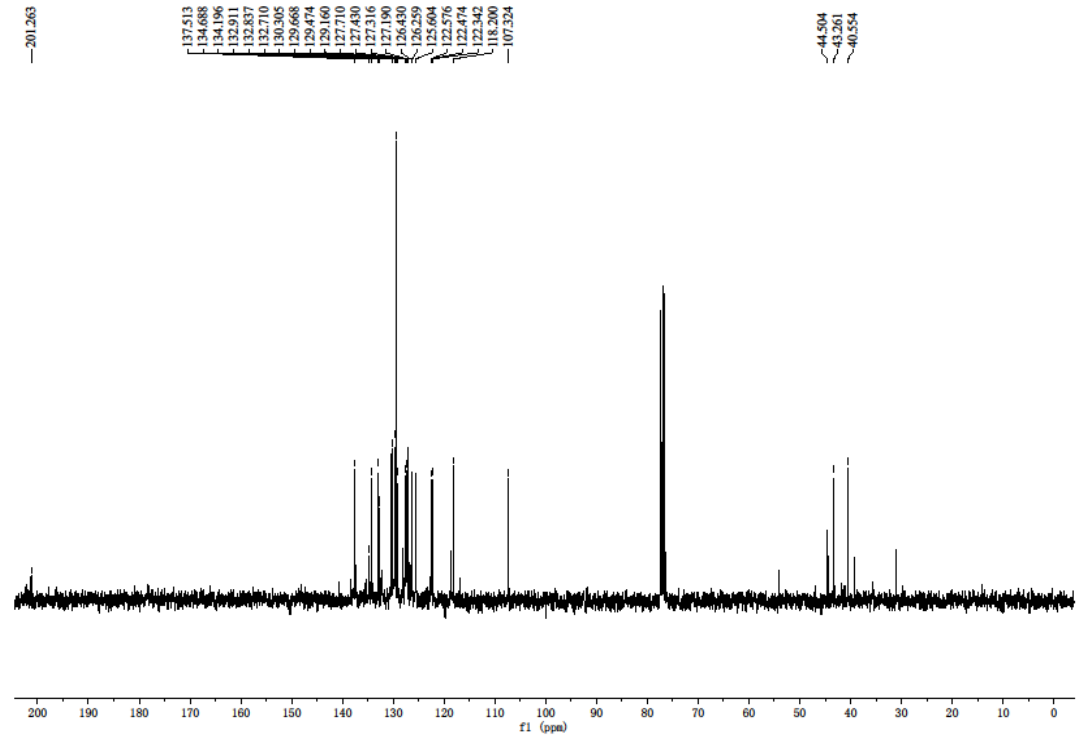
^{13}C NMR ($CDCl_3$, 125 MHz)



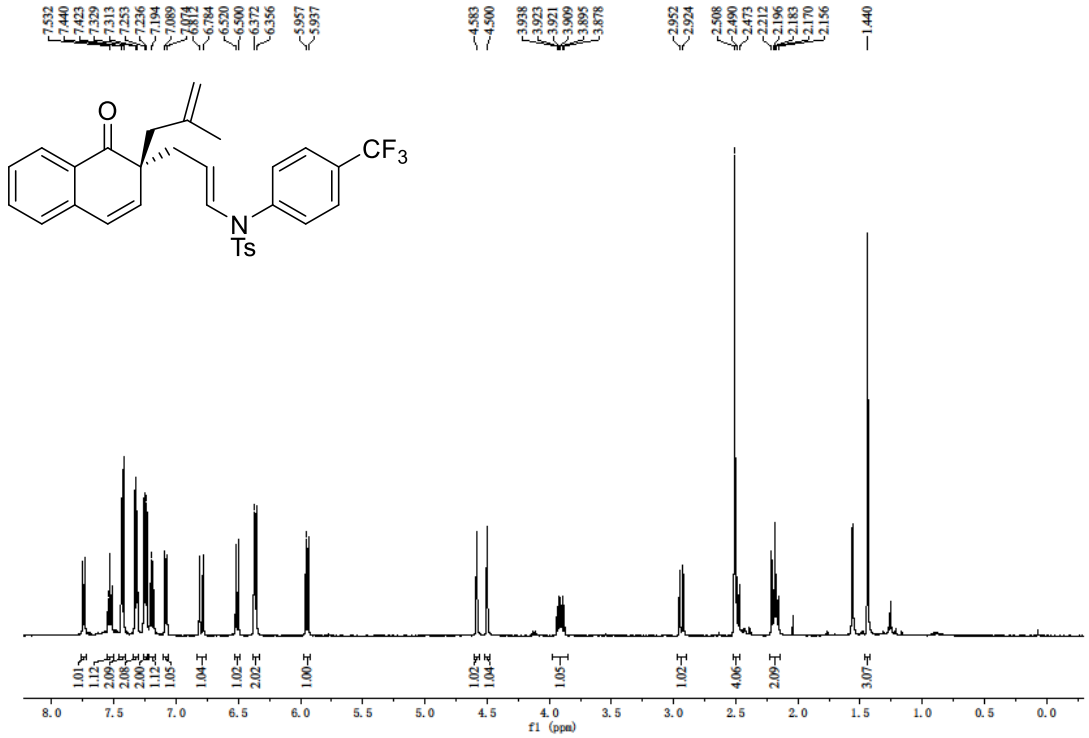
^{1}H NMR ($CDCl_3$, 500 MHz) (**4e**)



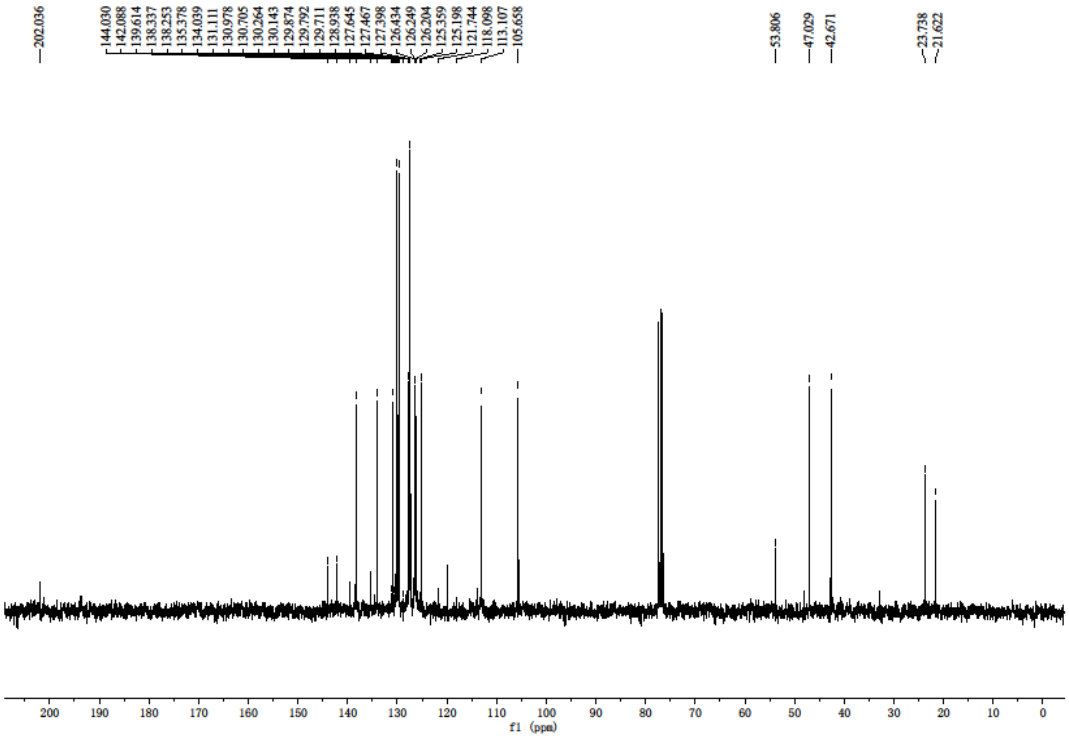
^{13}C NMR ($CDCl_3$, 75 MHz)



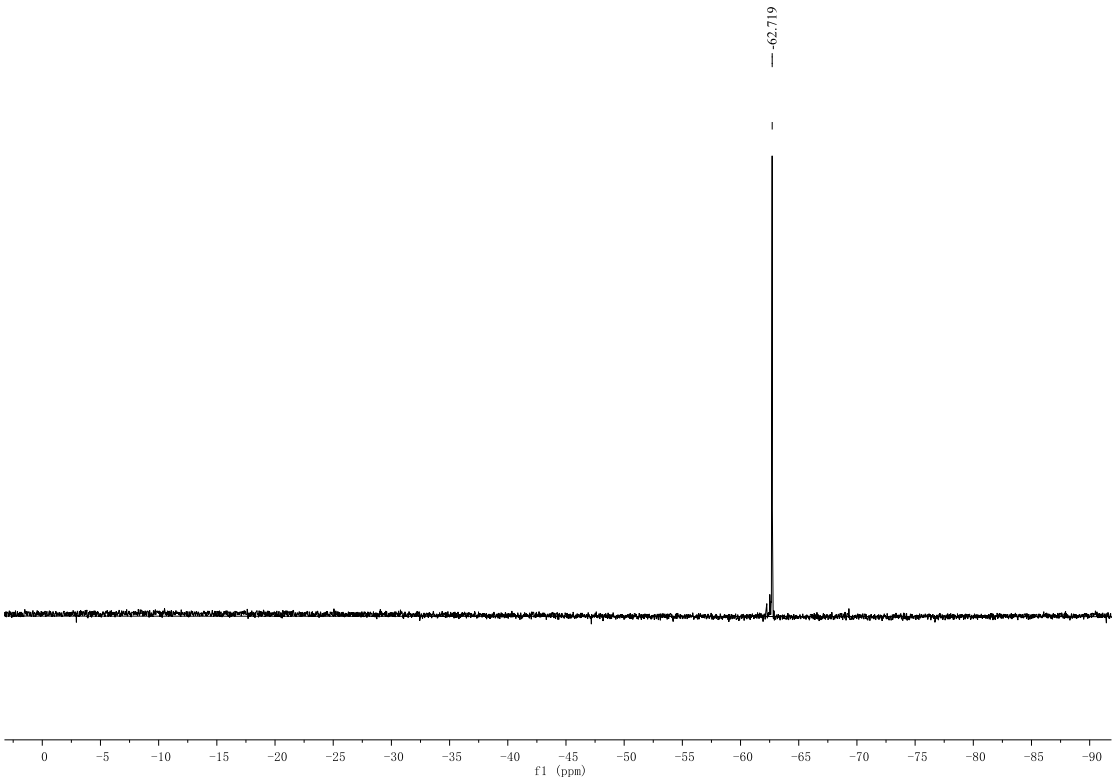
^{1}H NMR ($CDCl_3$, 500 MHz) (**4f**)



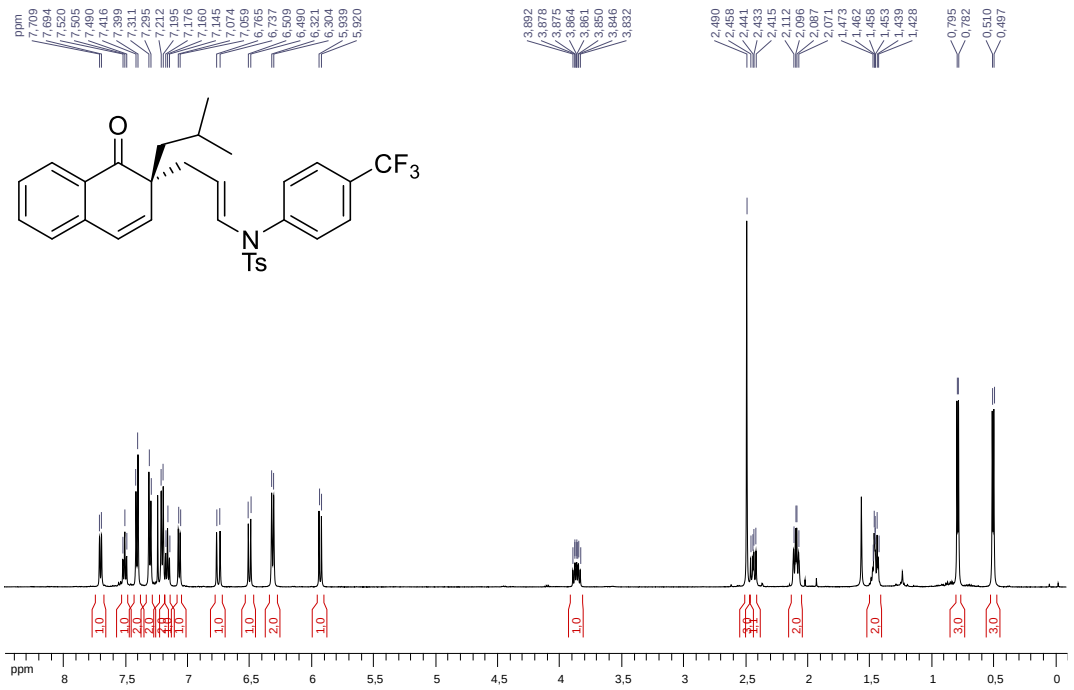
^{13}C NMR ($CDCl_3$, 75 MHz)



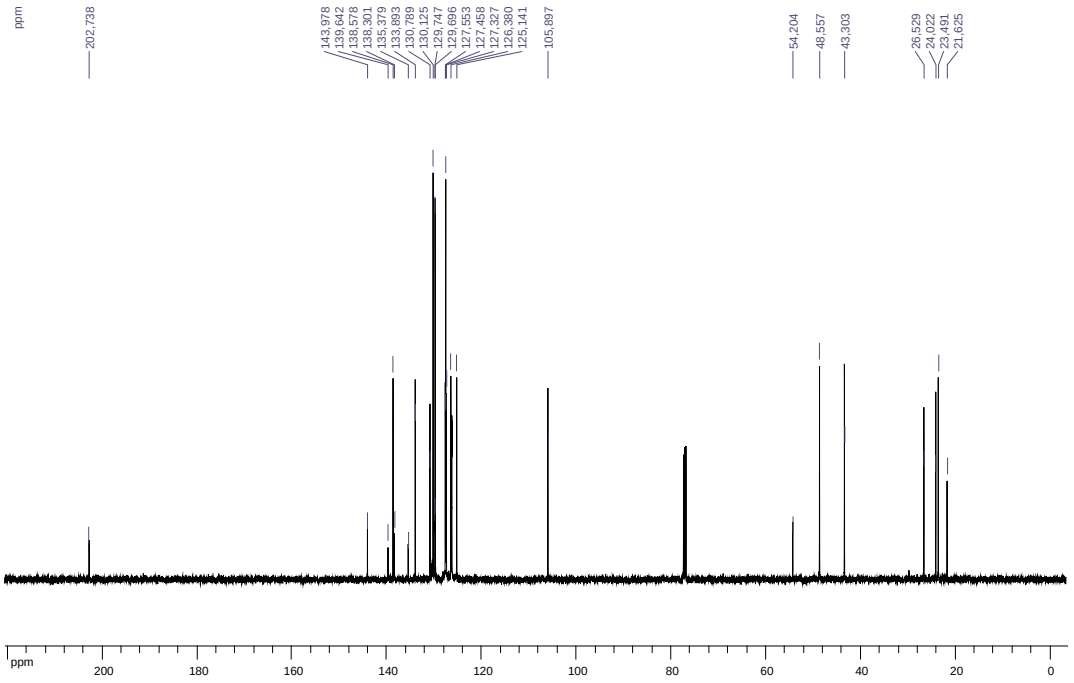
^{19}F NMR ($CDCl_3$, 300 MHz)



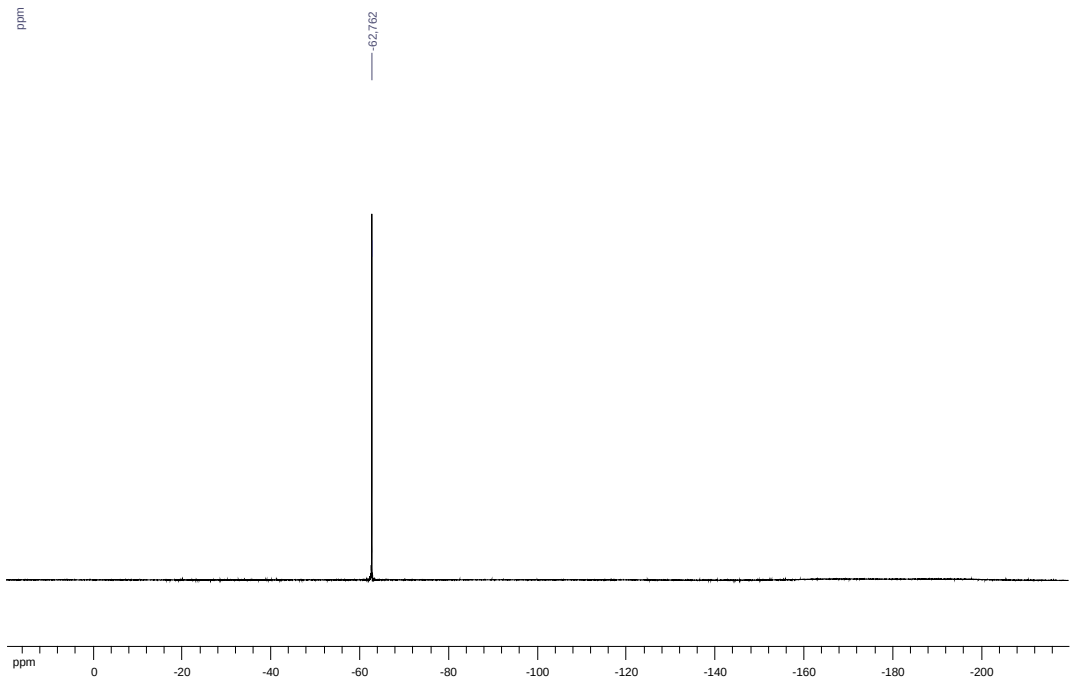
^{1}H NMR ($CDCl_3$, 500 MHz) (**4g**)



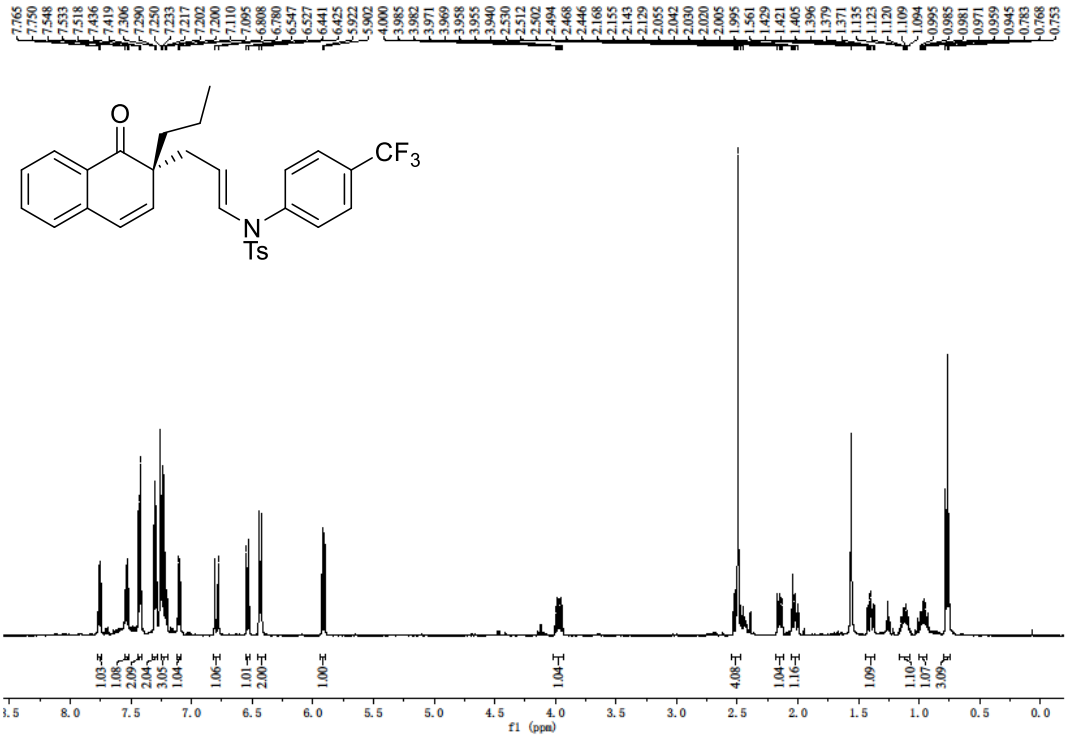
^{13}C NMR ($CDCl_3$, 125 MHz)



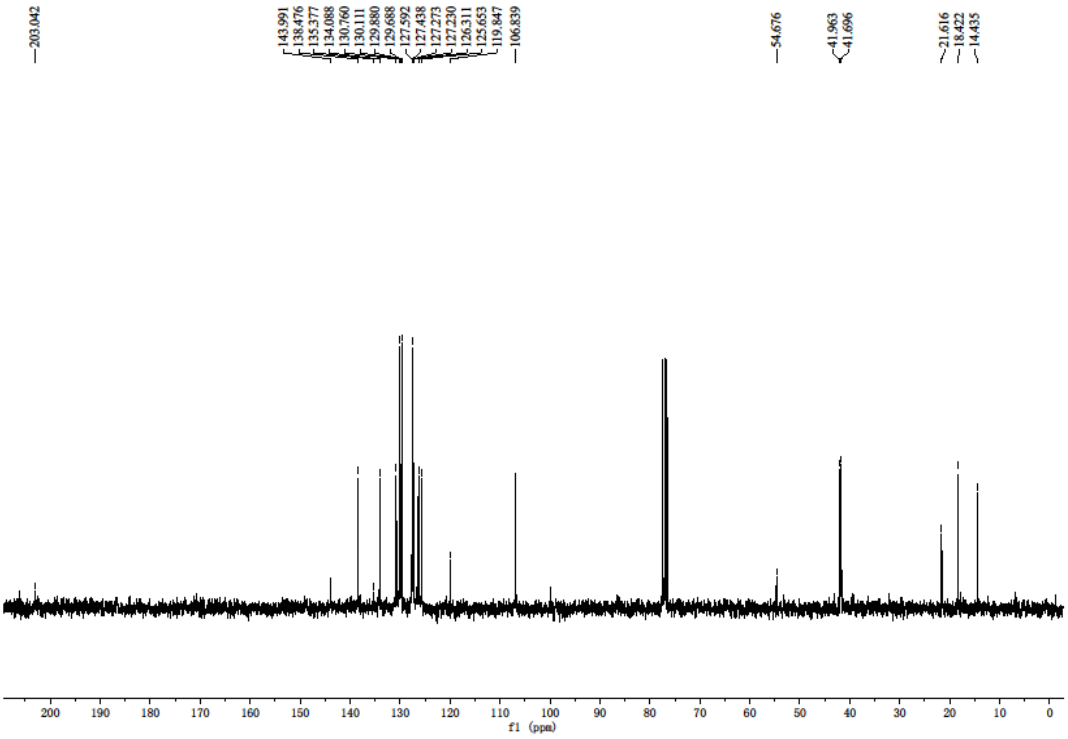
^{19}F NMR ($CDCl_3$, 300 MHz)



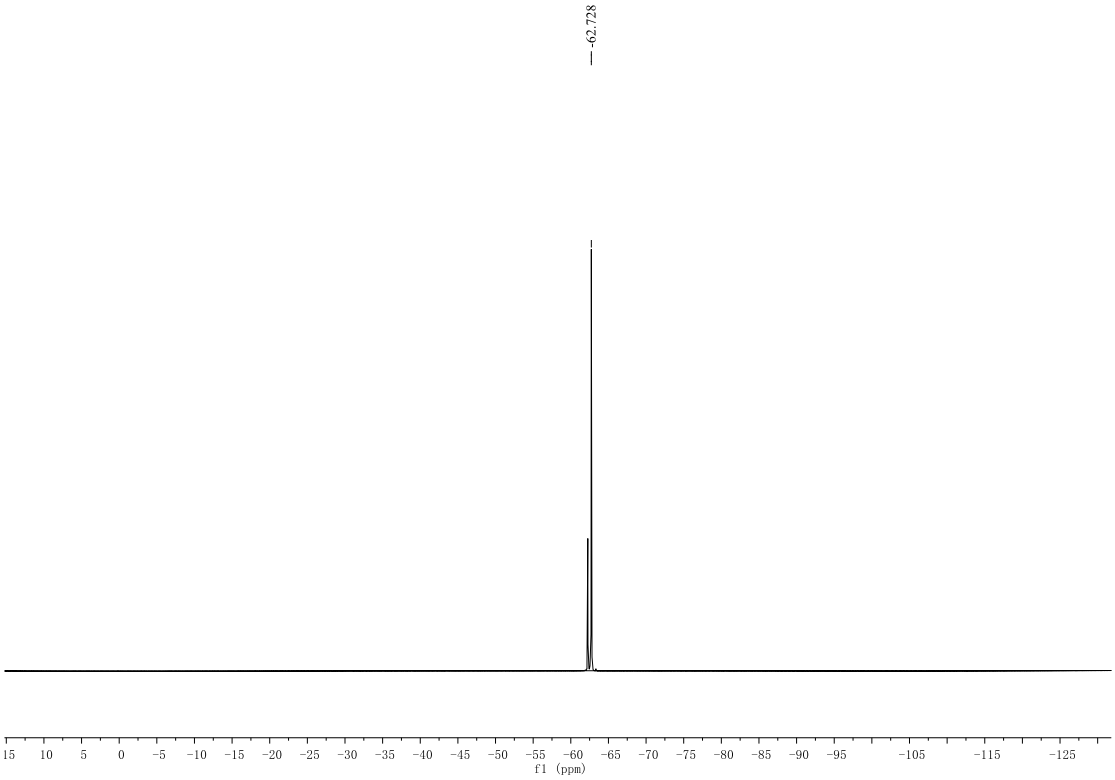
^{1}H NMR ($CDCl_3$, 500 MHz) (**4h**)



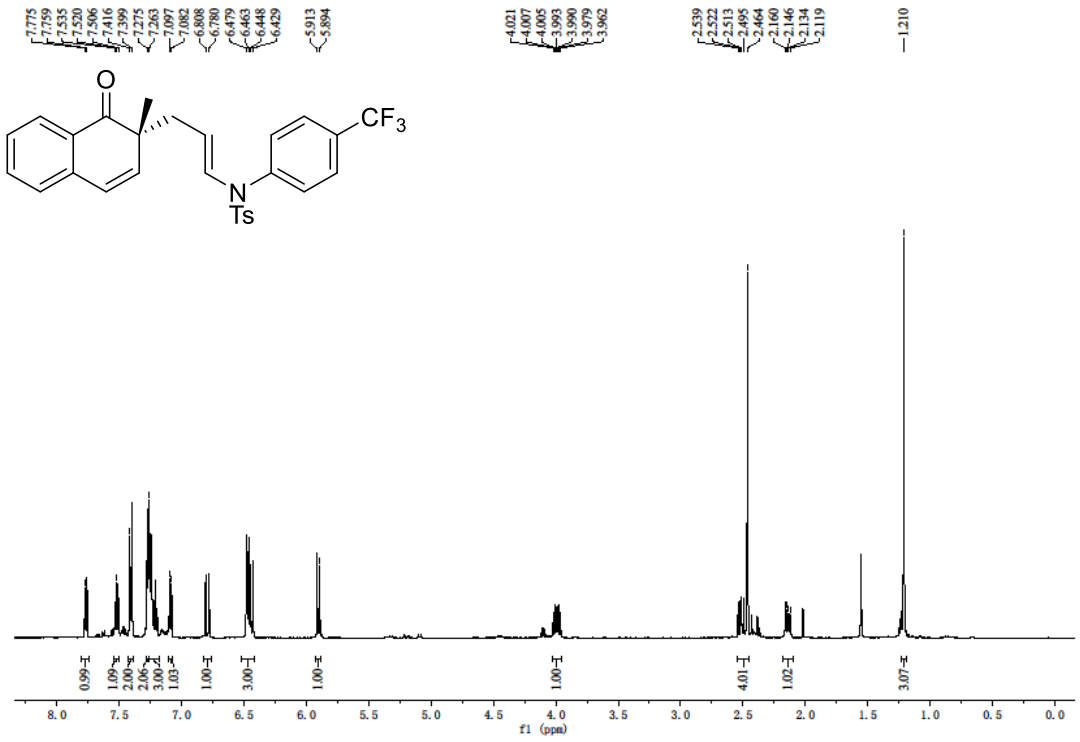
^{13}C NMR ($CDCl_3$, 75 MHz)



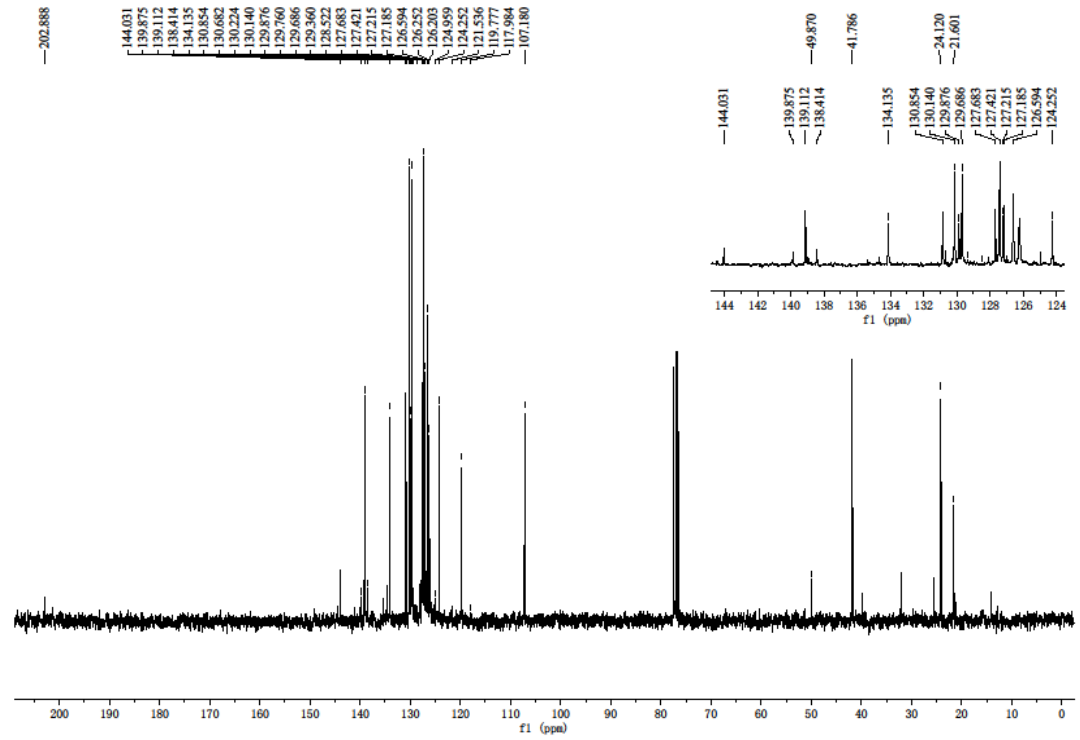
^{19}F NMR ($CDCl_3$, 300 MHz)



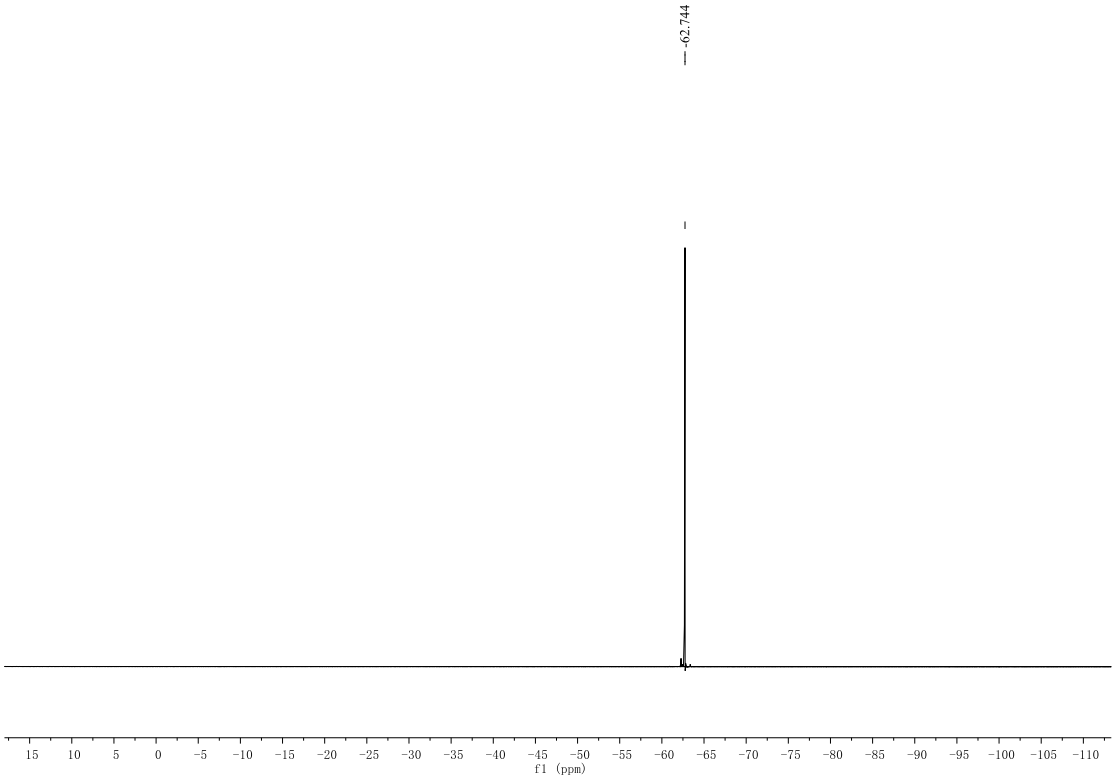
^{1}H NMR ($CDCl_3$, 500 MHz) (**4i**)



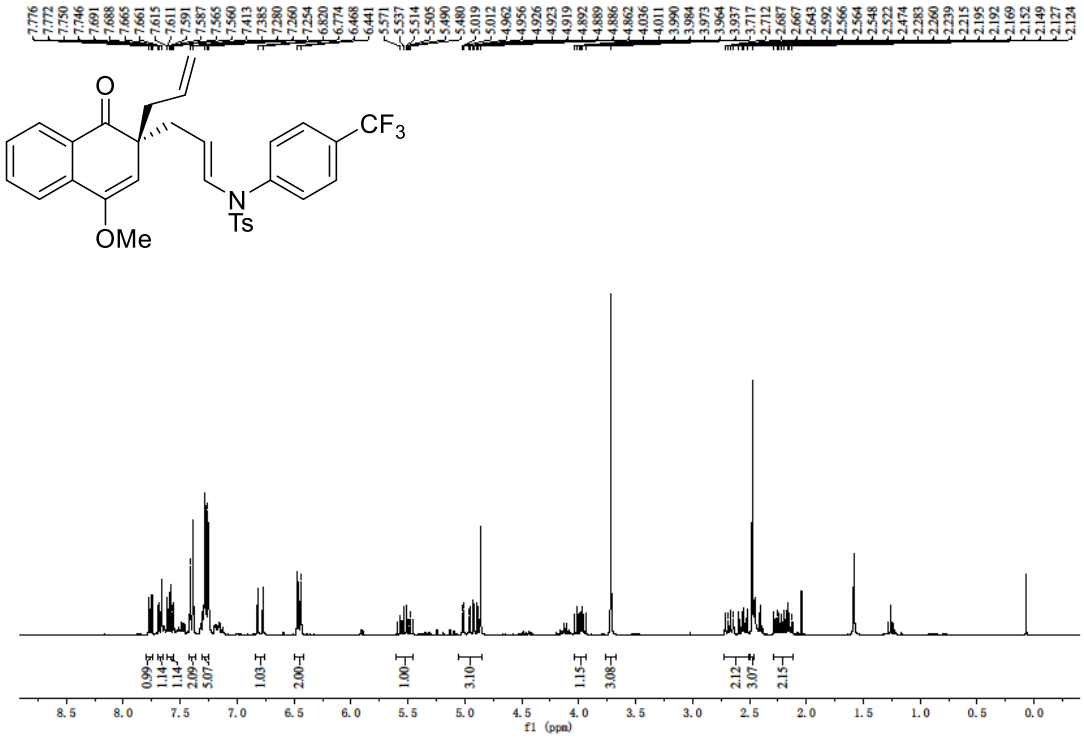
^{13}C NMR ($CDCl_3$, 75 MHz)



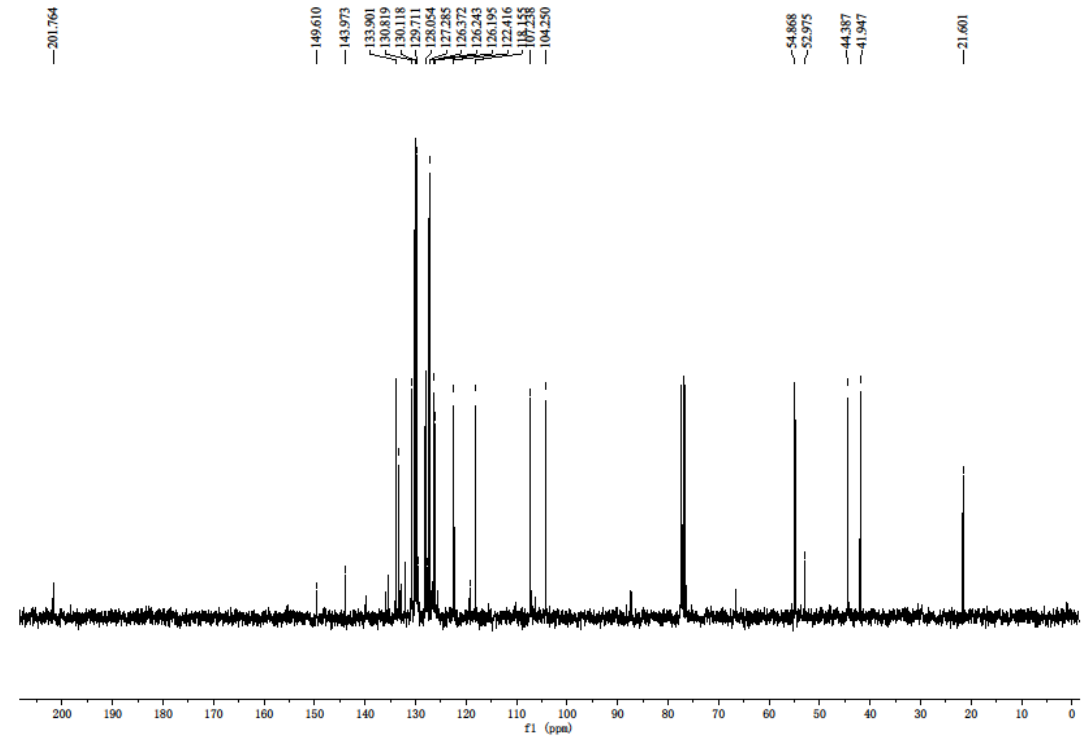
^{19}F NMR ($CDCl_3$, 300 MHz)



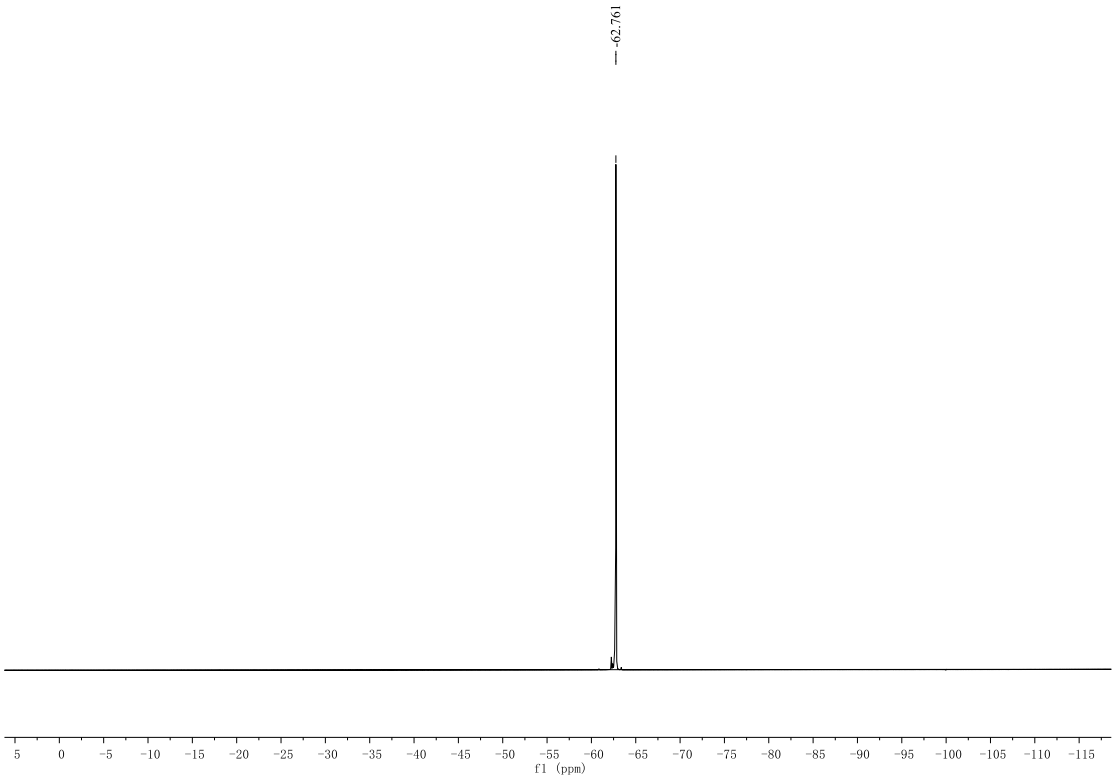
^{1}H NMR ($CDCl_3$, 300 MHz) (**4j**)



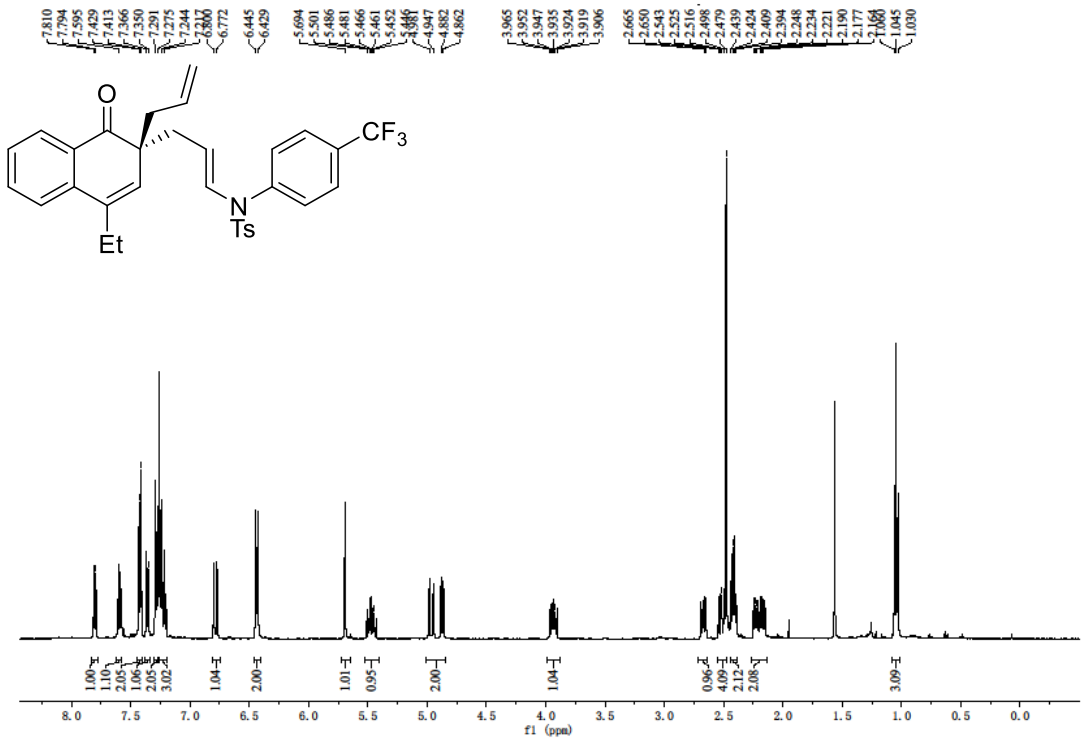
^{13}C NMR ($CDCl_3$, 75 MHz)



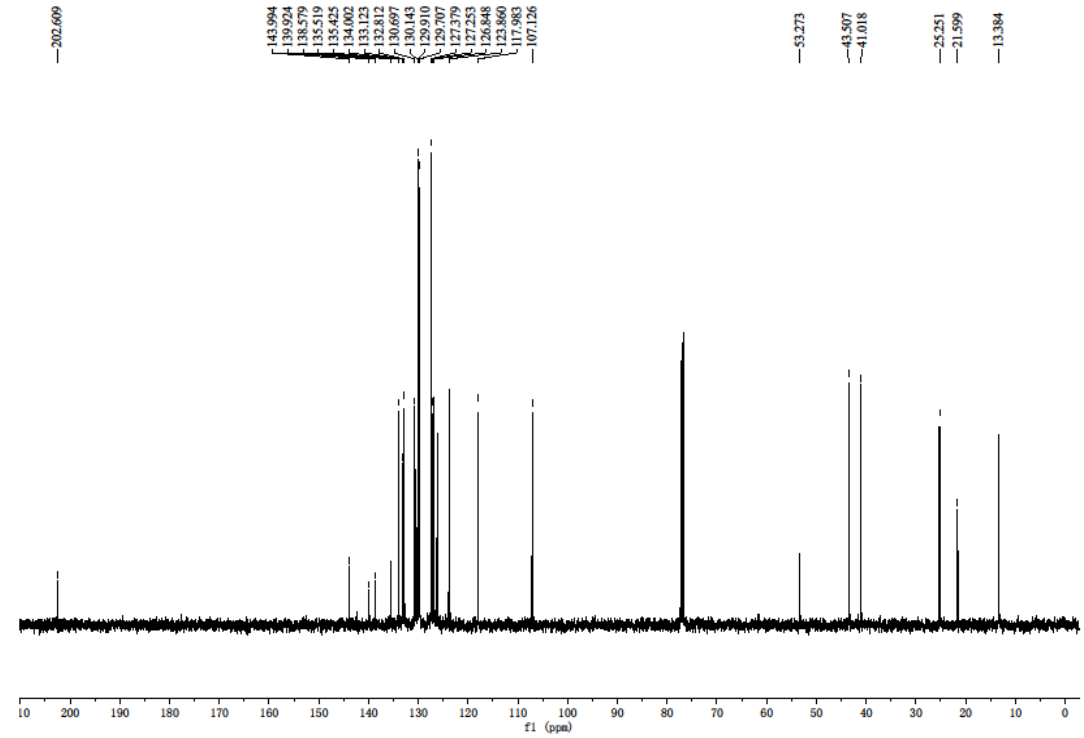
^{19}F NMR ($CDCl_3$, 300 MHz)



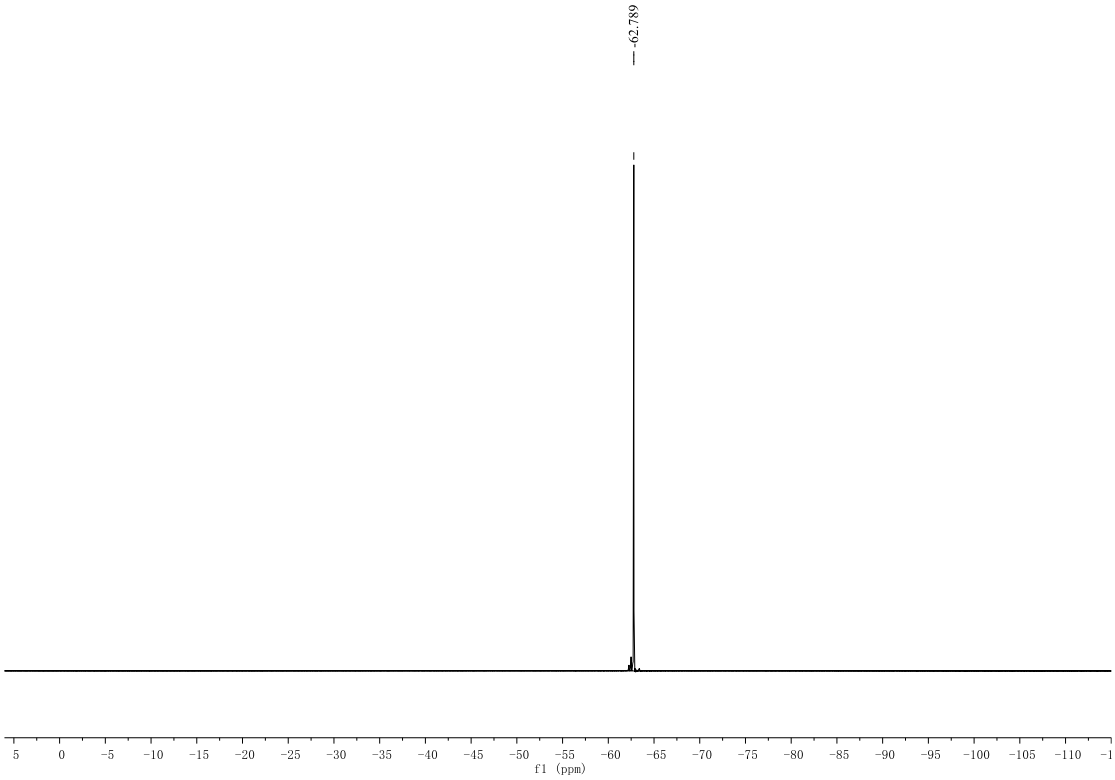
^{1}H NMR ($CDCl_3$, 500 MHz) (**4k**)



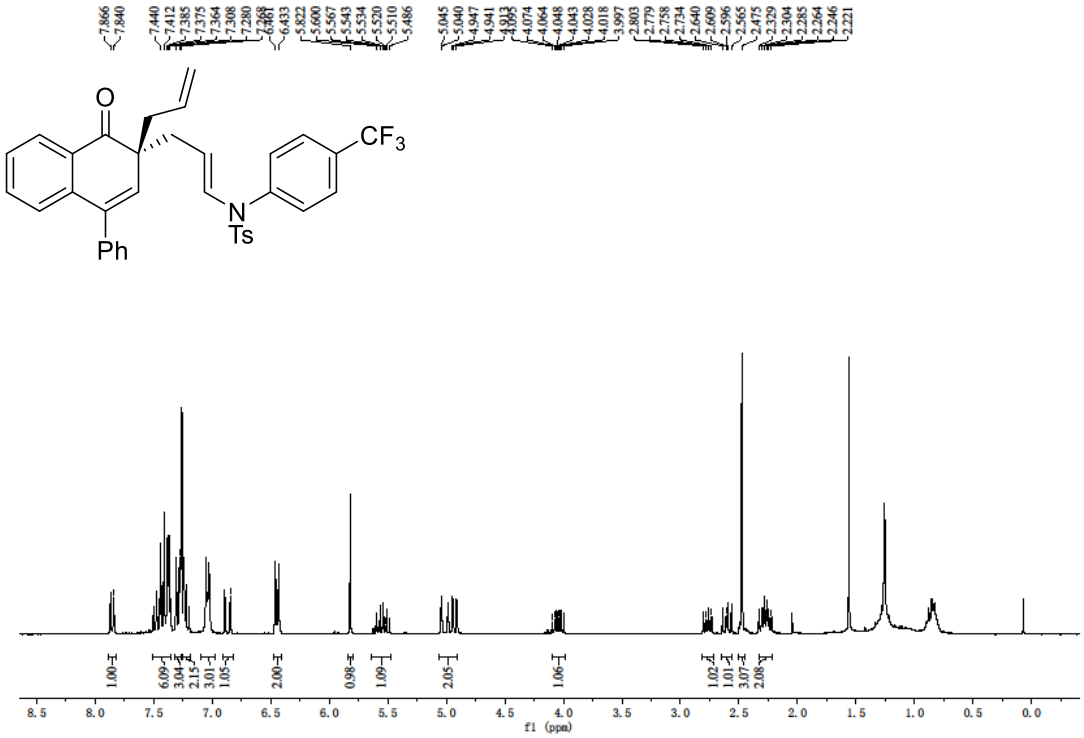
^{13}C NMR ($CDCl_3$, 125 MHz)



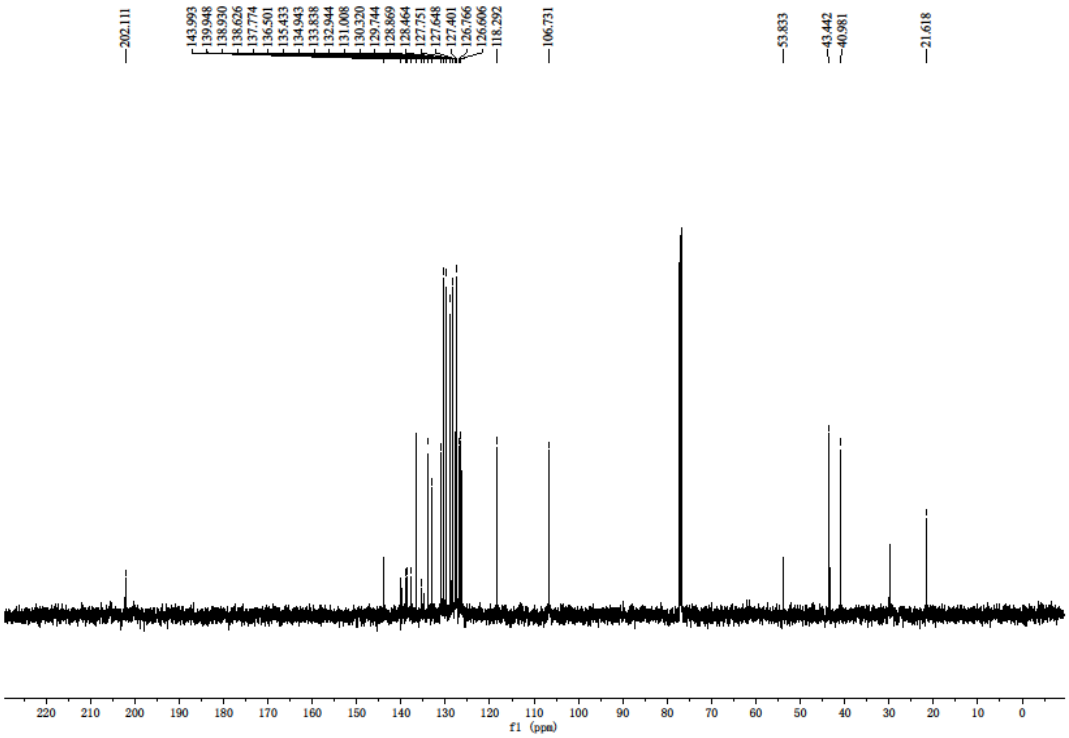
^{19}F NMR ($CDCl_3$, 300 MHz)



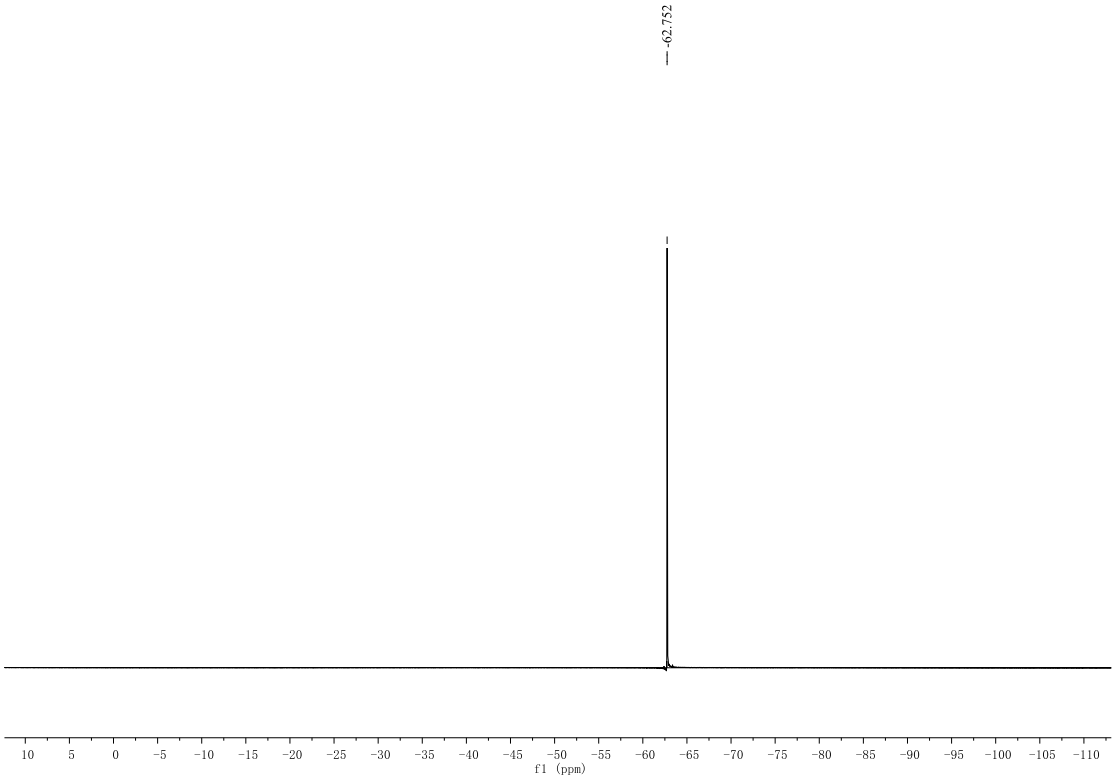
^{1}H NMR ($CDCl_3$, 300 MHz) (4l)



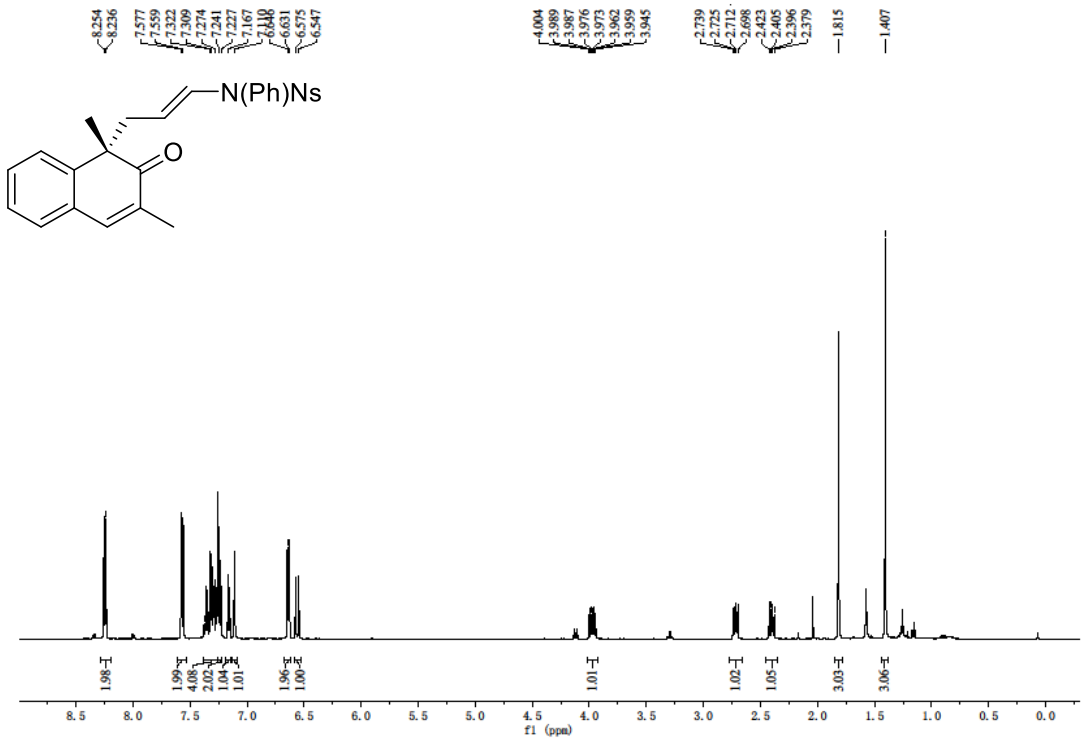
^{13}C NMR ($CDCl_3$, 125 MHz)



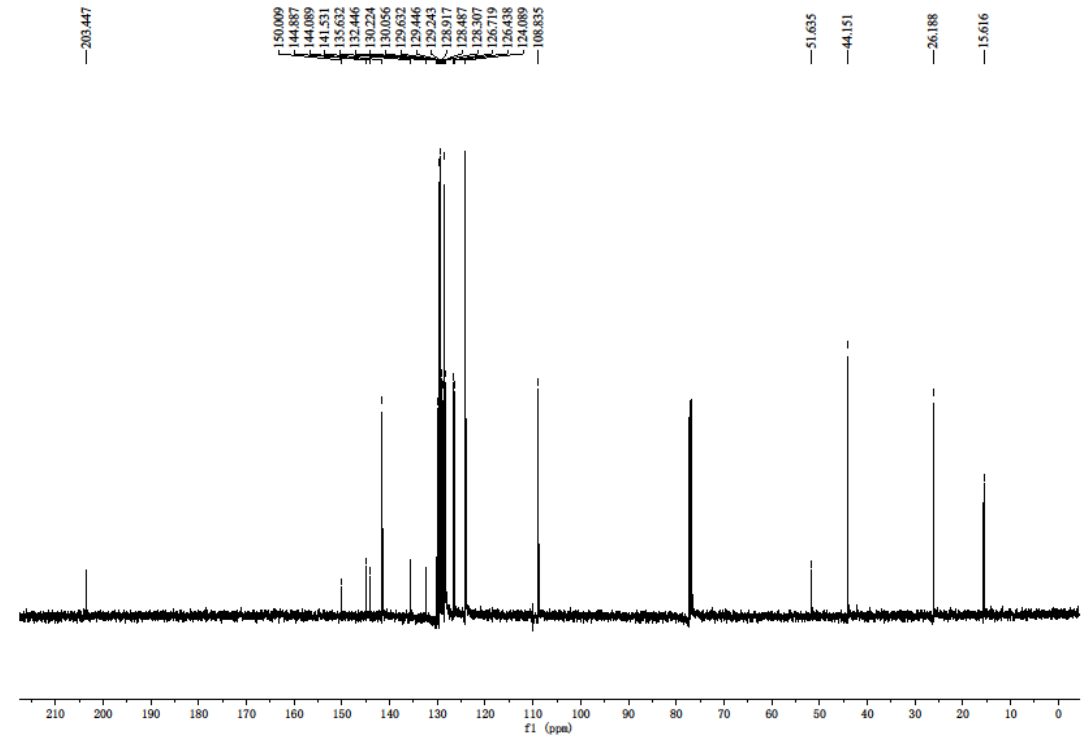
^{19}F NMR ($CDCl_3$, 300 MHz)



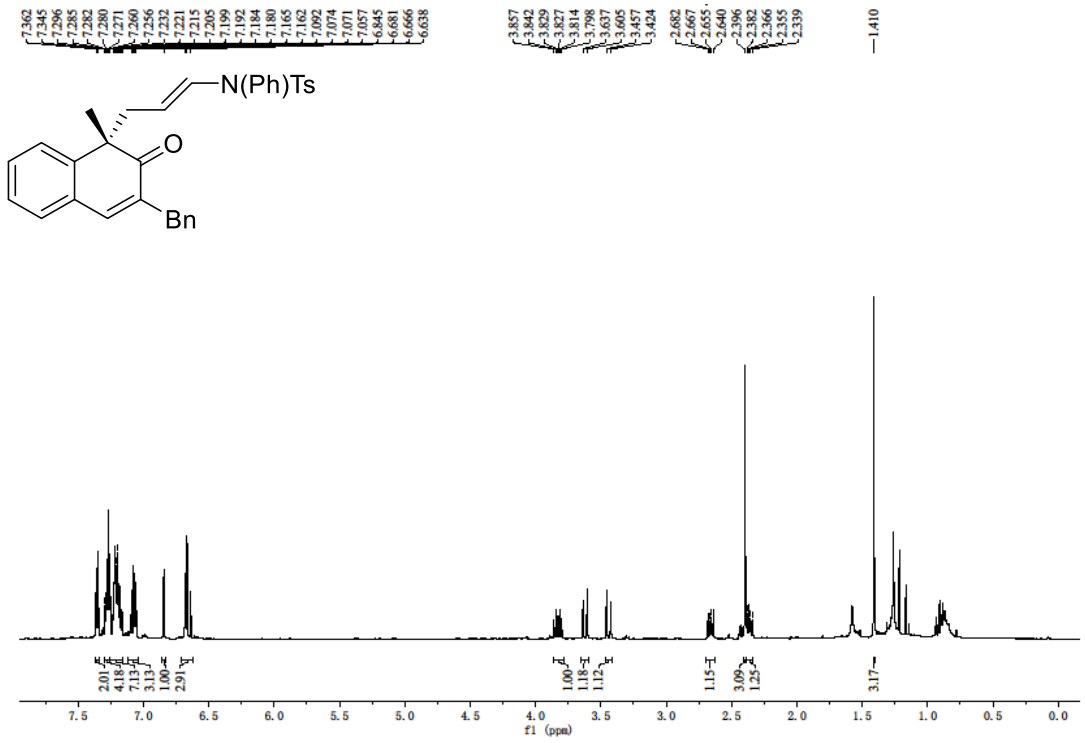
^{1}H NMR ($CDCl_3$, 500 MHz) (**4m**)



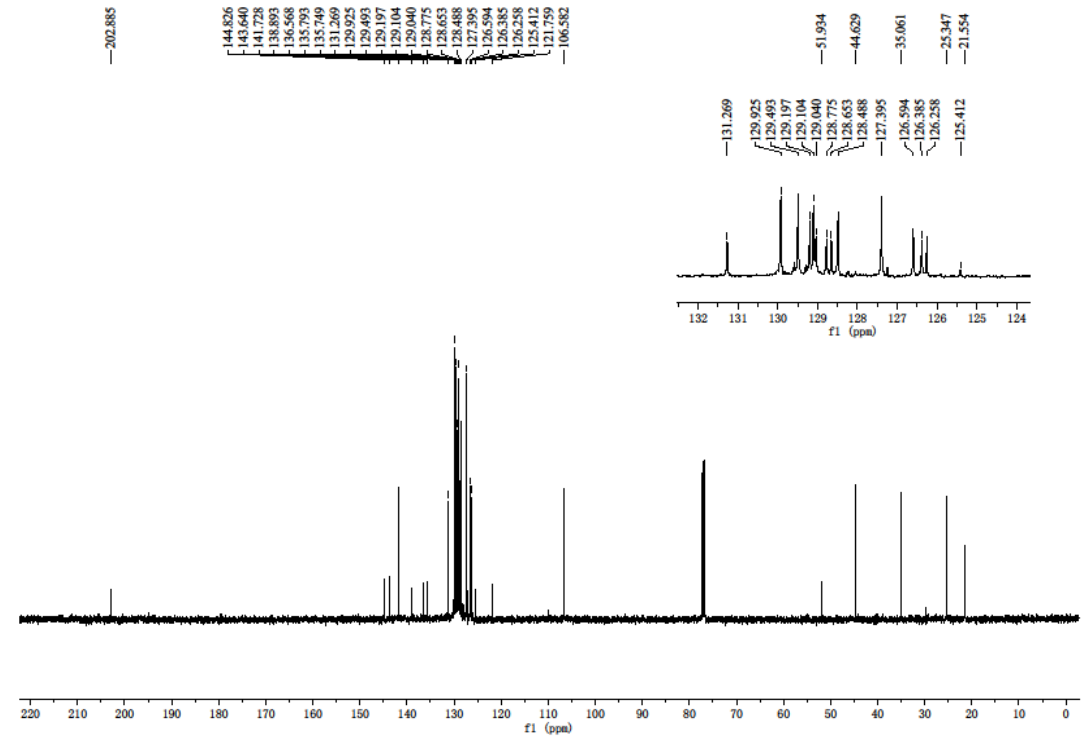
^{13}C NMR ($CDCl_3$, 125 MHz)



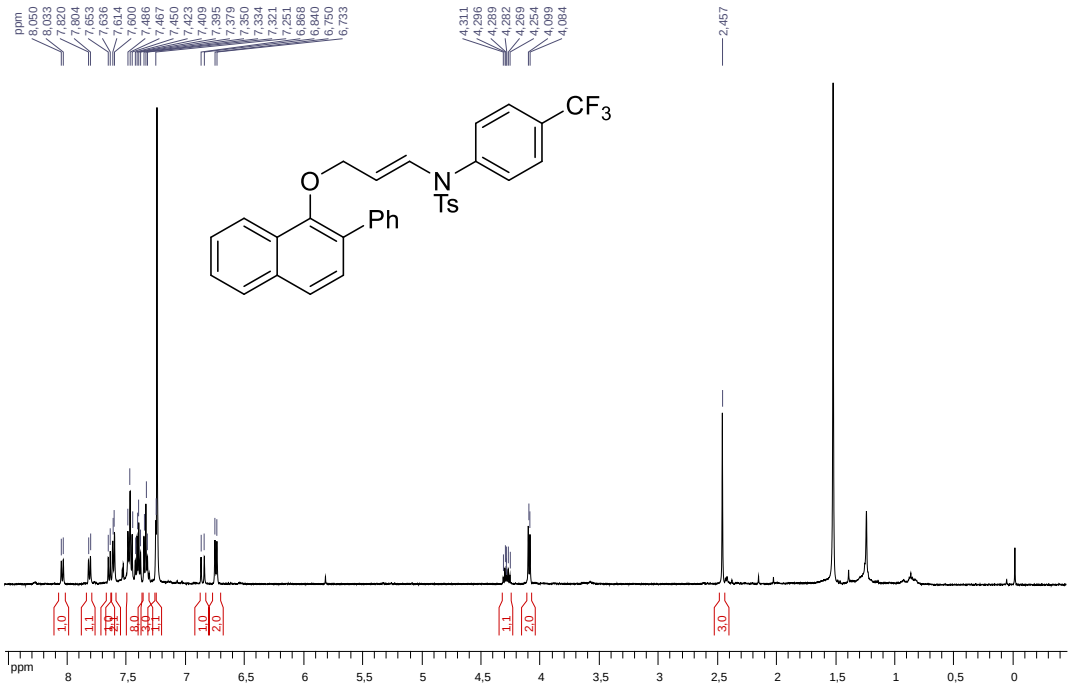
^{1}H NMR ($CDCl_3$, 500 MHz) (**4n**)



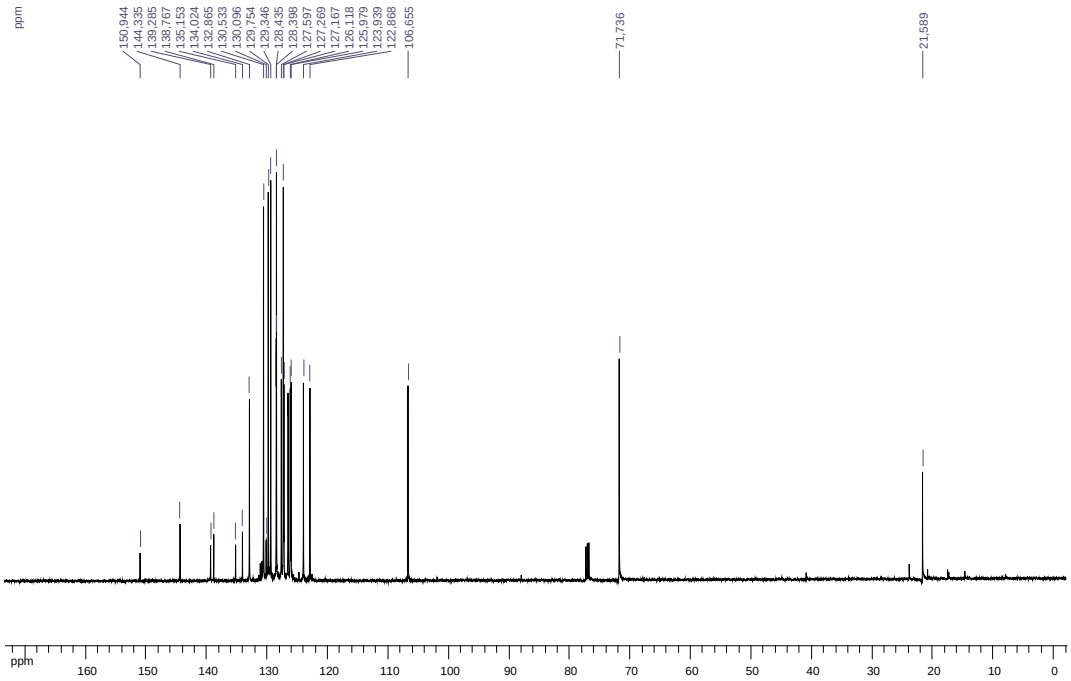
^{13}C NMR ($CDCl_3$, 125 MHz)



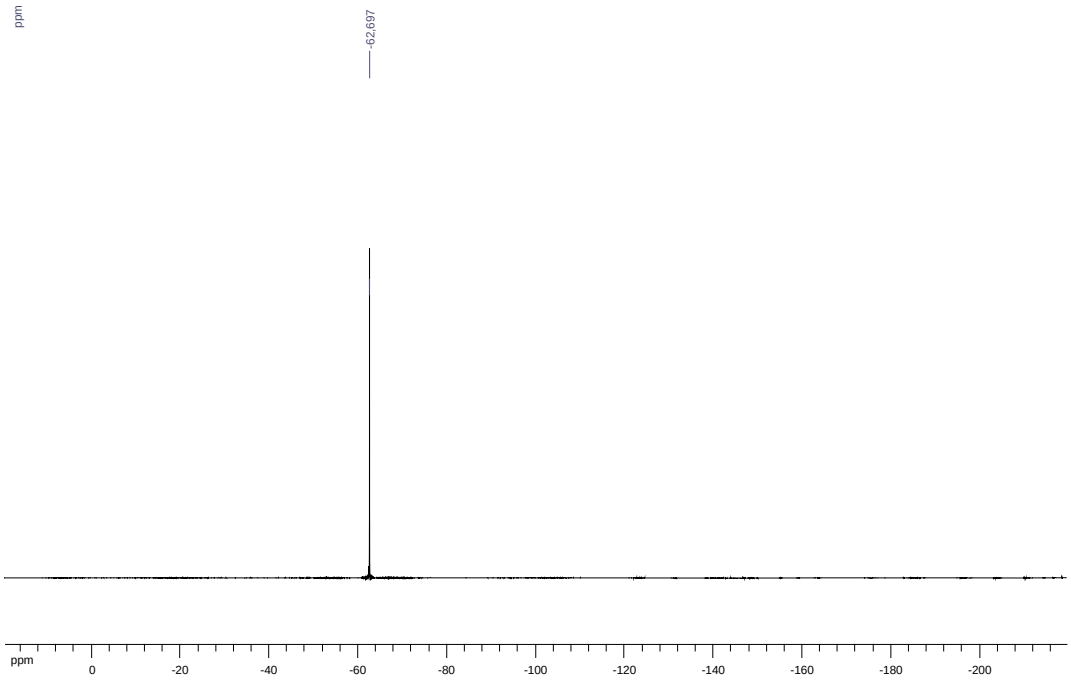
^{1}H NMR ($CDCl_3$, 500 MHz) (**S5**)



^{13}C NMR ($CDCl_3$, 125 MHz)



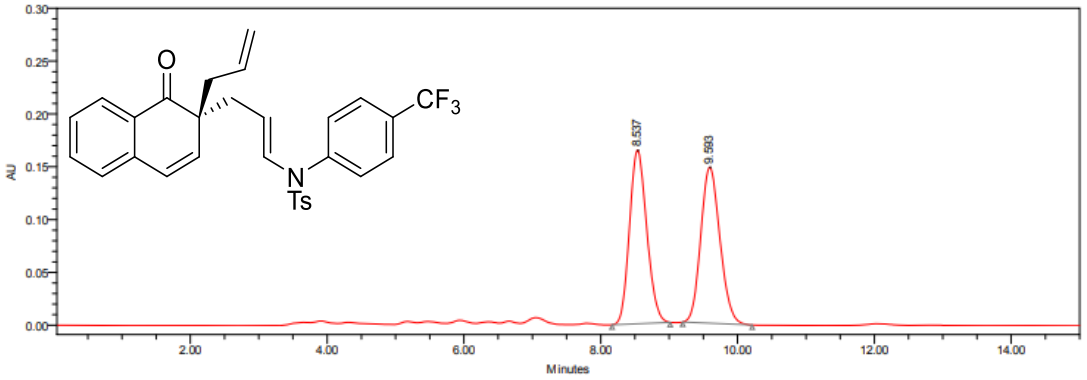
^{19}F NMR ($CDCl_3$, 300 MHz)



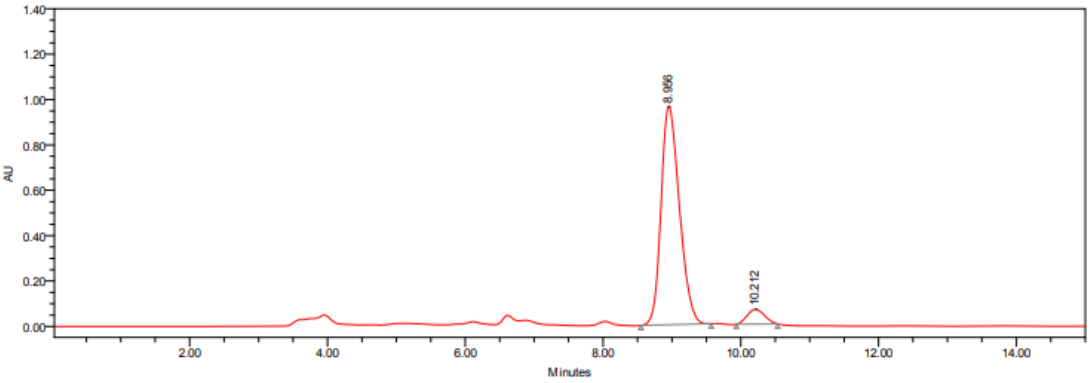
V. HPLC Data:

Compound **4a**.

HPLC Analysis: 88% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 319 nm, retention times: 8.9 min (major) and 10.2 min (minor)].



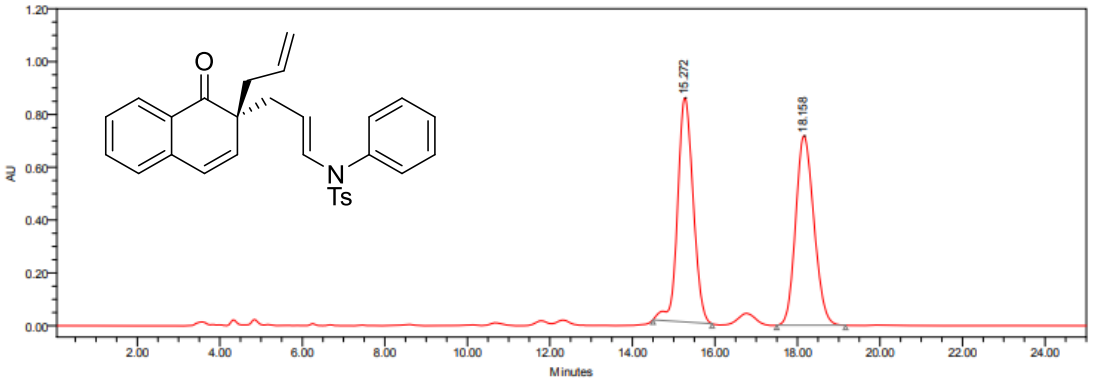
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.537	2881238	50.02
2	PDA 200.0 to 400.0 nm at 2.4 nm	9.593	2878680	49.98



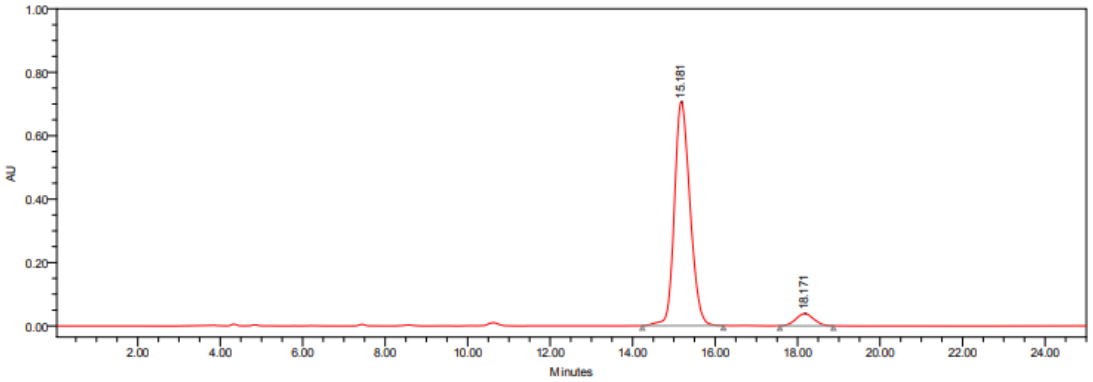
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.956	17786104	93.97
2	PDA 200.0 to 400.0 nm at 2.4 nm	10.212	1140416	6.03

Compound **4b**

HPLC Analysis: 88% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 280 nm, retention times: 15.2 min (major) and 18.2 min (minor)].



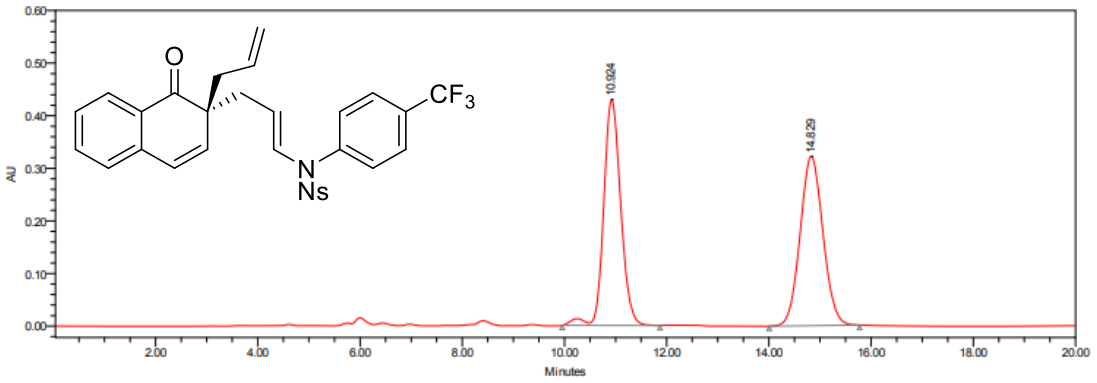
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	15.272	22159195	50.07
2	PDA 200.0 to 400.0 nm at 2.4 nm	18.158	22098167	49.93



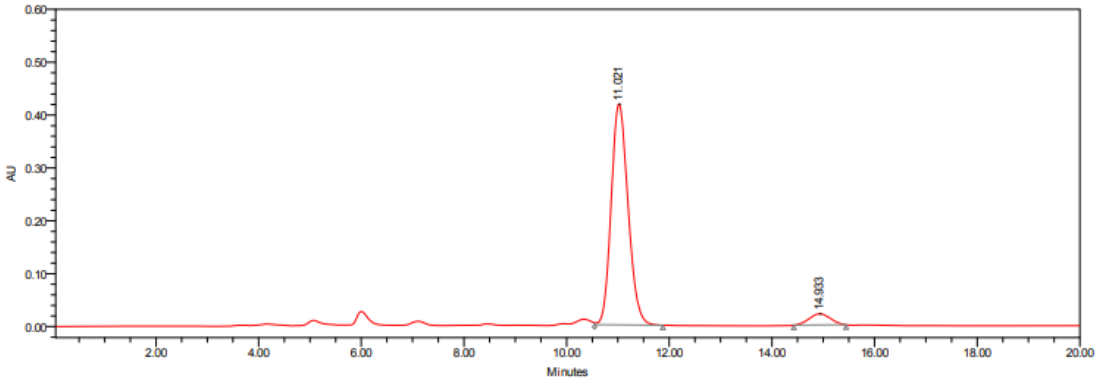
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	15.181	18502088	94.09
2	PDA 200.0 to 400.0 nm at 2.4 nm	18.171	1161885	5.91

Compound **4c**.

HPLC Analysis: 88% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 352 nm, retention times: 11.0 min (major) and 14.9 min (minor)].



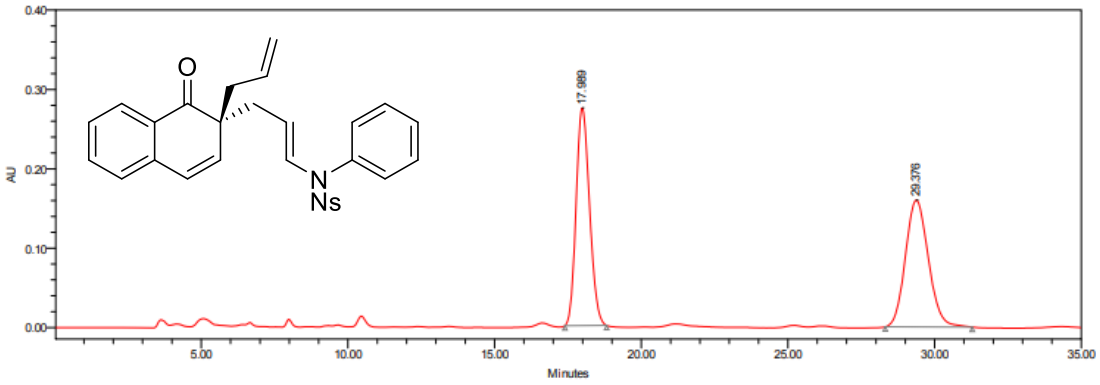
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	10.924	9950359	49.92
2	PDA 200.0 to 400.0 nm at 2.4 nm	14.829	9983914	50.08



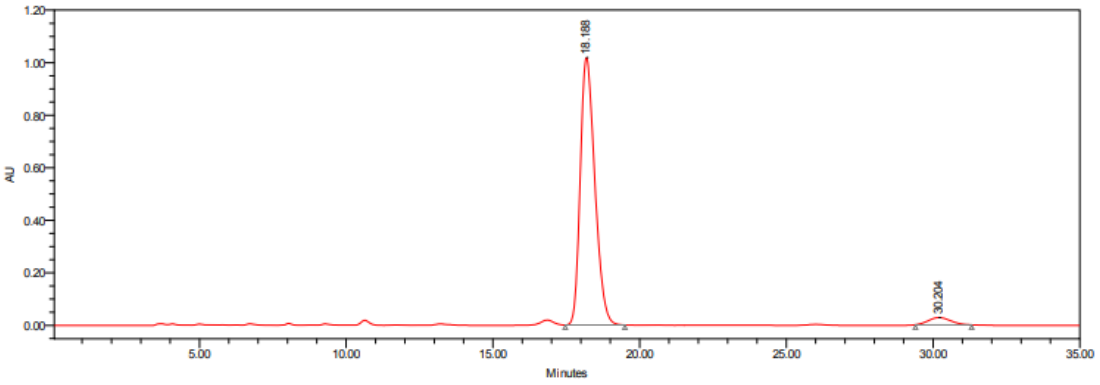
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	11.021	9518944	94.00
2	PDA 200.0 to 400.0 nm at 2.4 nm	14.933	607613	6.00

Compound **4d**.

HPLC Analysis: 92% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 343 nm, retention times: 18.2 min (major) and 30.2 min (minor)].



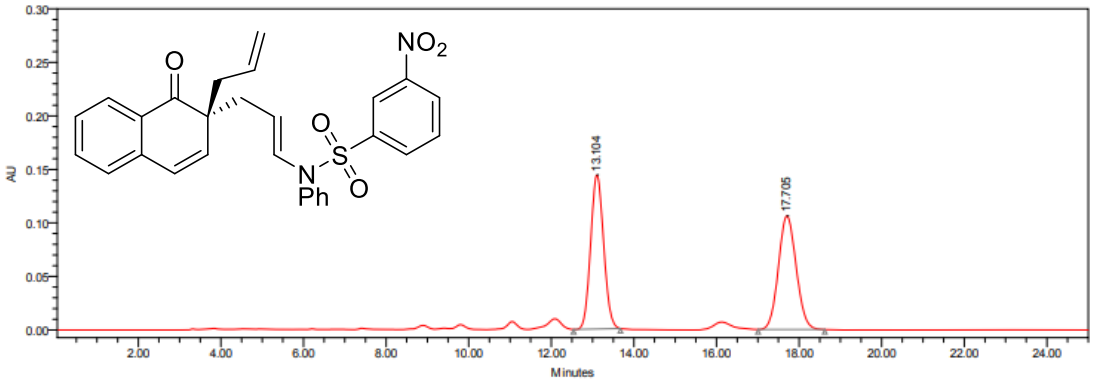
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	17.989	8700182	50.06
2	PDA 200.0 to 400.0 nm at 2.4 nm	29.376	8679454	49.94



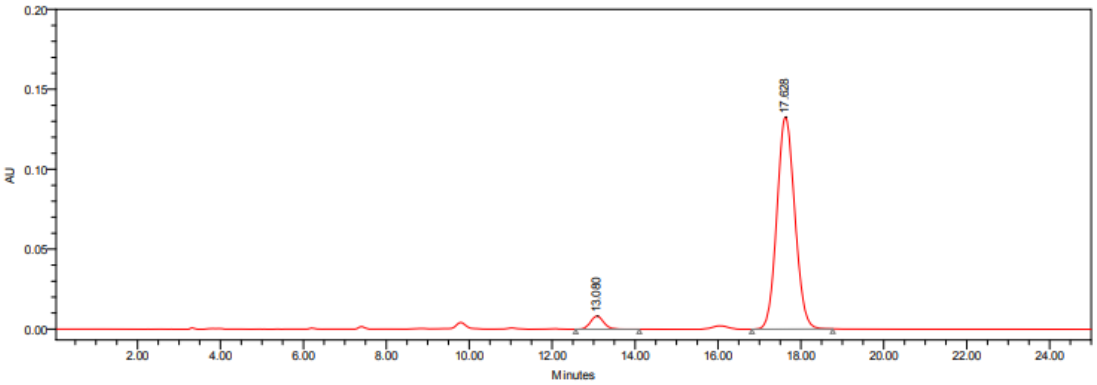
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	18.188	35106640	96.06
2	PDA 200.0 to 400.0 nm at 2.4 nm	30.204	1438627	3.94

Compound **4e**.

HPLC Analysis: 91% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 322 nm, retention times: 13.1 min (minor) and 17.6 min (major)].



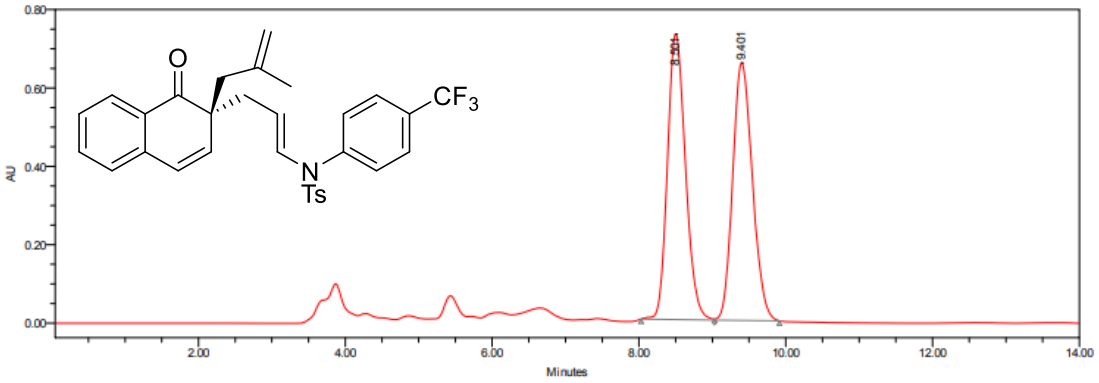
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	13.104	3154276	49.80
2	PDA 200.0 to 400.0 nm at 2.4 nm	17.705	3180202	50.20



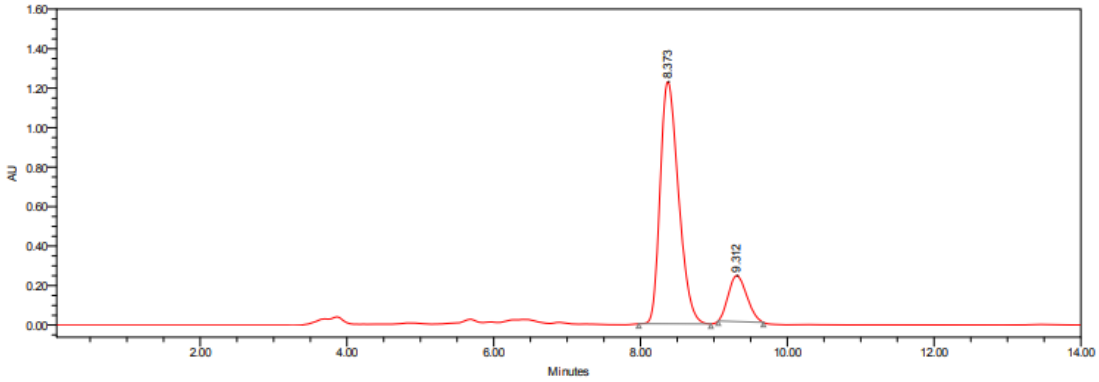
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	13.080	183986	4.42
2	PDA 200.0 to 400.0 nm at 2.4 nm	17.628	3976470	95.58

Compound **4f**.

HPLC Analysis: 68% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 294 nm, retention times: 8.4 min (major) and 9.3 min (minor)].



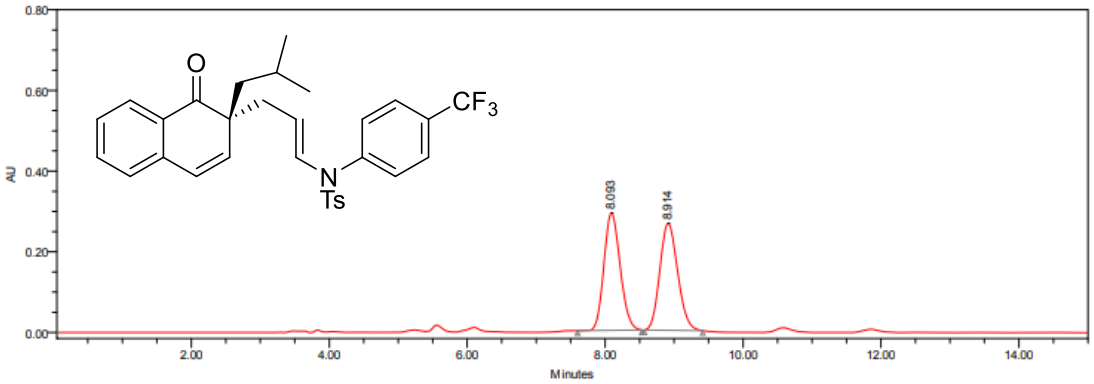
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.501	12410516	50.38
2	PDA 200.0 to 400.0 nm at 2.4 nm	9.401	12222505	49.62



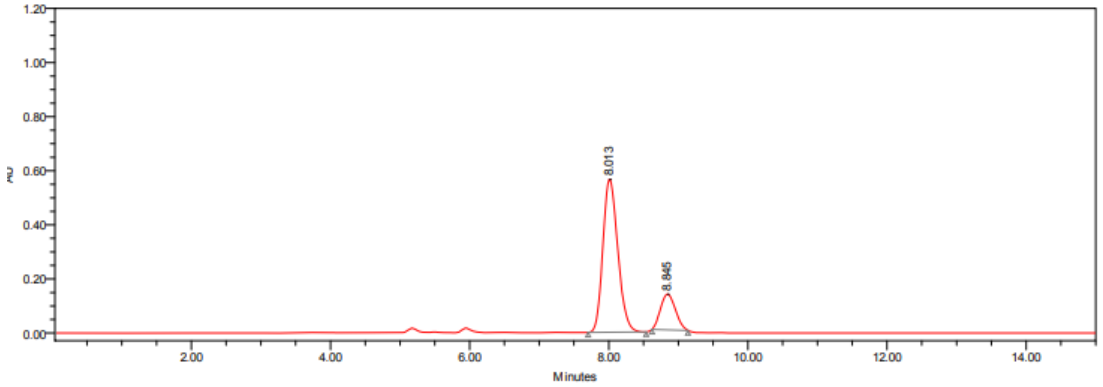
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.373	21355628	84.06
2	PDA 200.0 to 400.0 nm at 2.4 nm	9.312	4048294	15.94

Compound **4g**.

HPLC Analysis: 62% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 285 nm, retention times: 8.0 min (major) and 8.8 min (minor)].



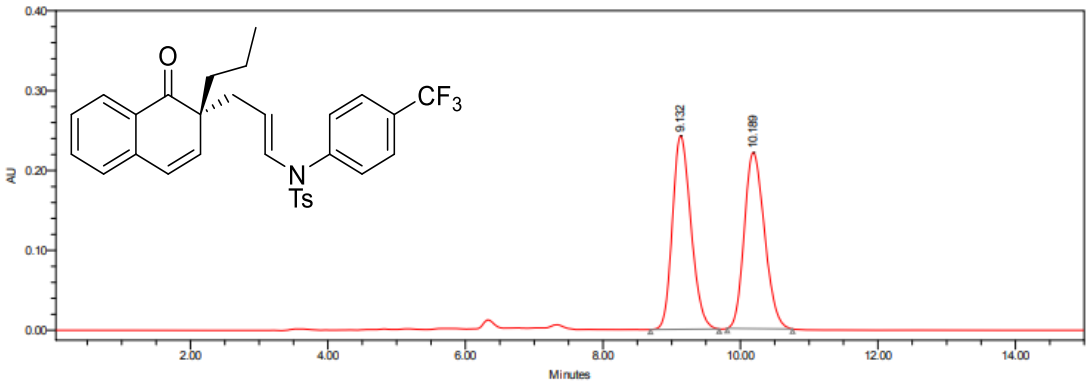
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.093	4774708	50.01
2	PDA 200.0 to 400.0 nm at 2.4 nm	8.914	4773493	49.99



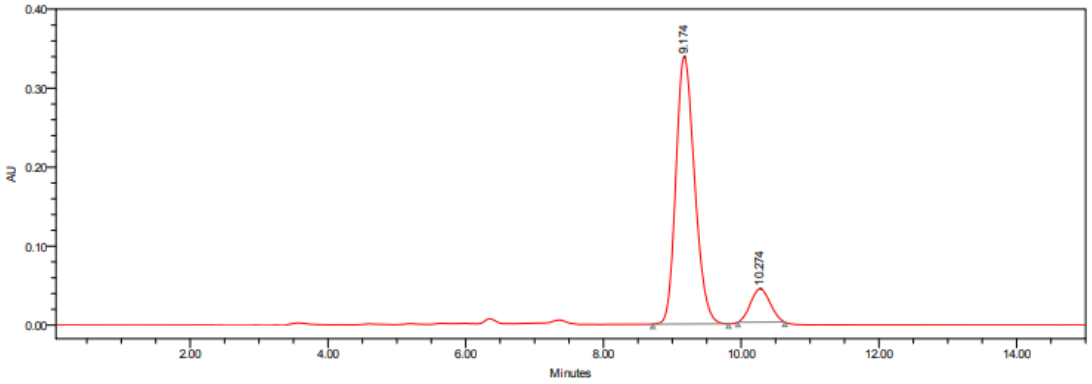
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.013	8423237	81.09
2	PDA 200.0 to 400.0 nm at 2.4 nm	8.845	1963804	18.91

Compound **4h**.

HPLC Analysis: 77% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 343 nm, retention times: 9.2 min (major) and 10.3 min (minor)].



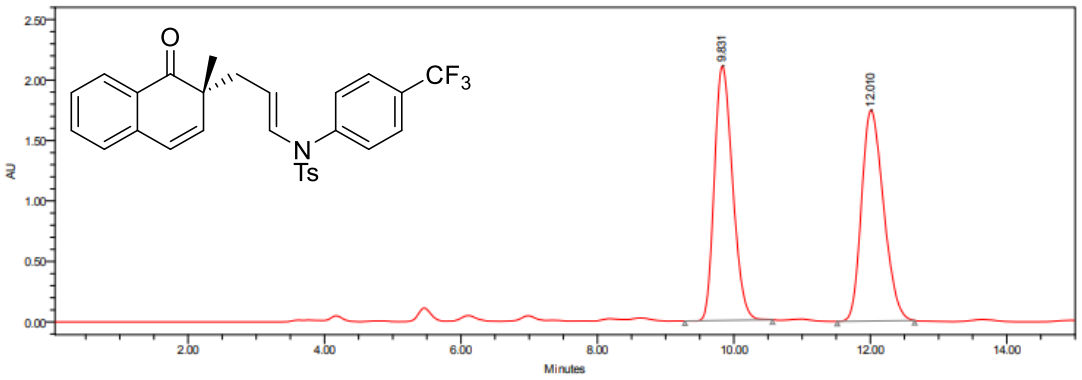
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	9.132	4543180	50.19
2	PDA 200.0 to 400.0 nm at 2.4 nm	10.189	4508845	49.81



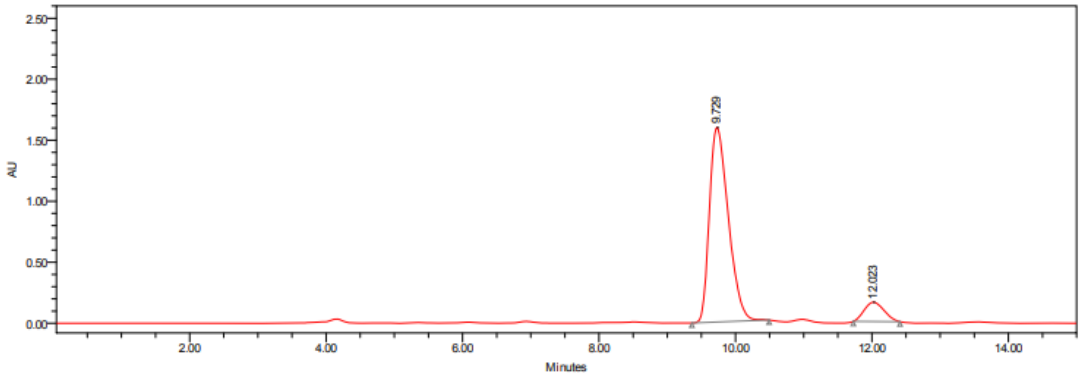
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	9.174	6388300	88.54
2	PDA 200.0 to 400.0 nm at 2.4 nm	10.274	826645	11.46

Compound **4i**.

HPLC Analysis: 81% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 295 nm, retention times: 9.7 min (major) and 12.0 min (minor)].



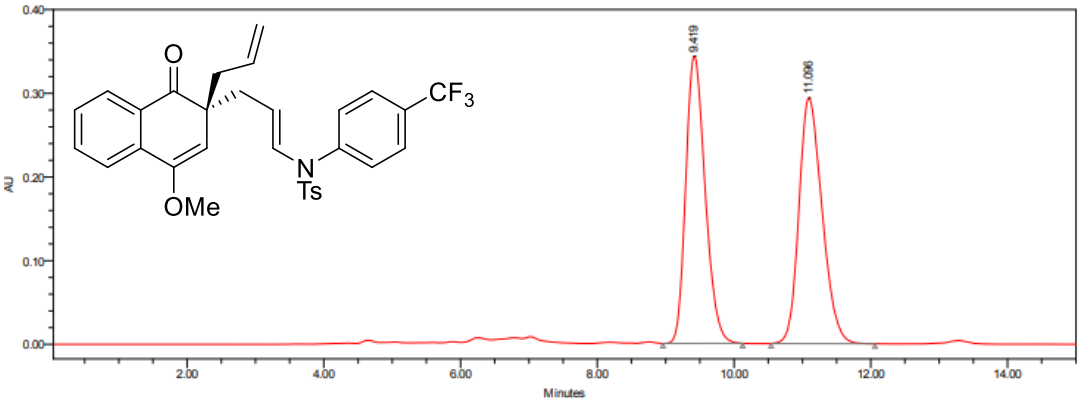
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	9.831	39011455	49.92
2	PDA 200.0 to 400.0 nm at 2.4 nm	12.010	39143120	50.08



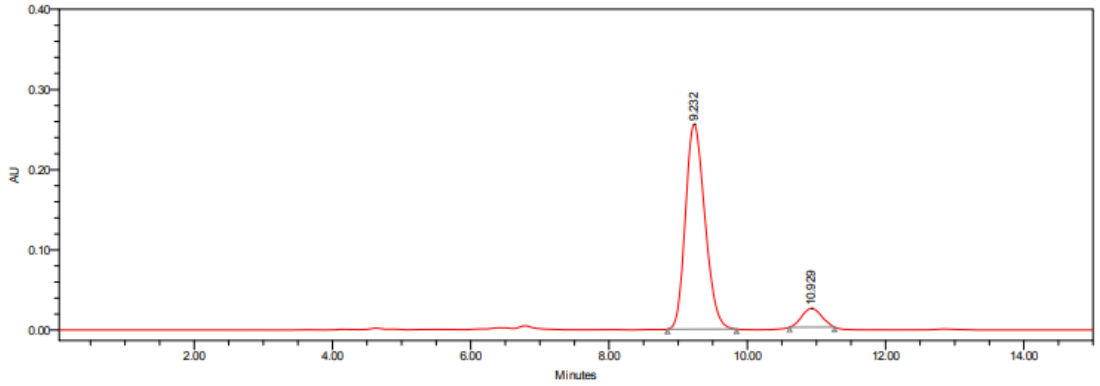
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	9.729	30619086	90.56
2	PDA 200.0 to 400.0 nm at 2.4 nm	12.023	3192999	9.44

Compound **4j**.

HPLC Analysis: 83% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 351 nm, retention times: 9.2 min (major) and 10.9 min (minor)].



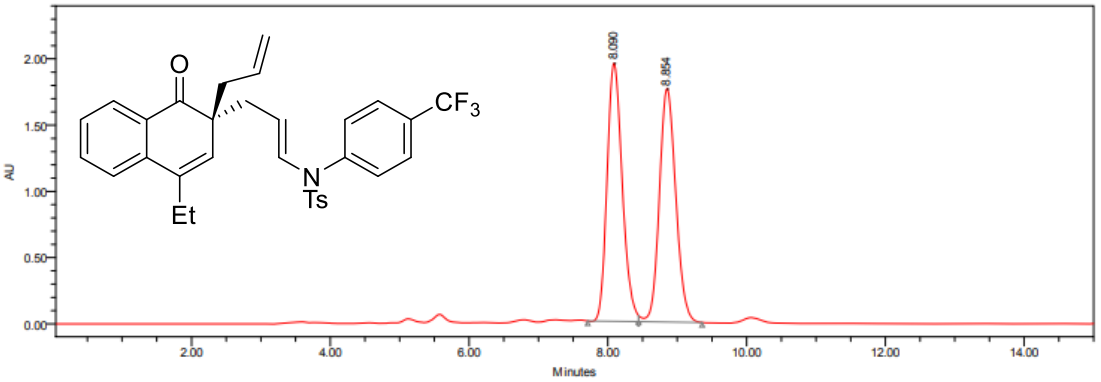
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	9.419	6761186	49.42
2	PDA 200.0 to 400.0 nm at 2.4 nm	11.096	6918918	50.58



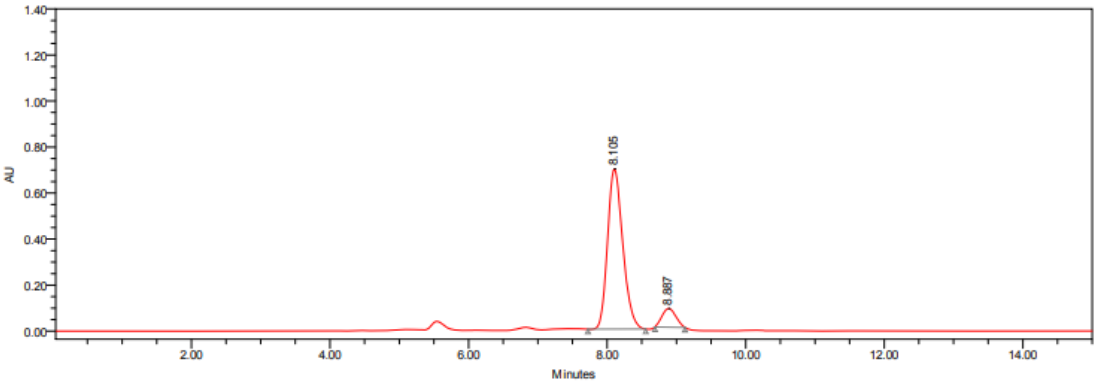
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	9.232	5000738	91.51
2	PDA 200.0 to 400.0 nm at 2.4 nm	10.929	464042	8.49

Compound **4k**.

HPLC Analysis: 81% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 284 nm, retention times: 8.1 min (major) and 8.9 min (minor)].



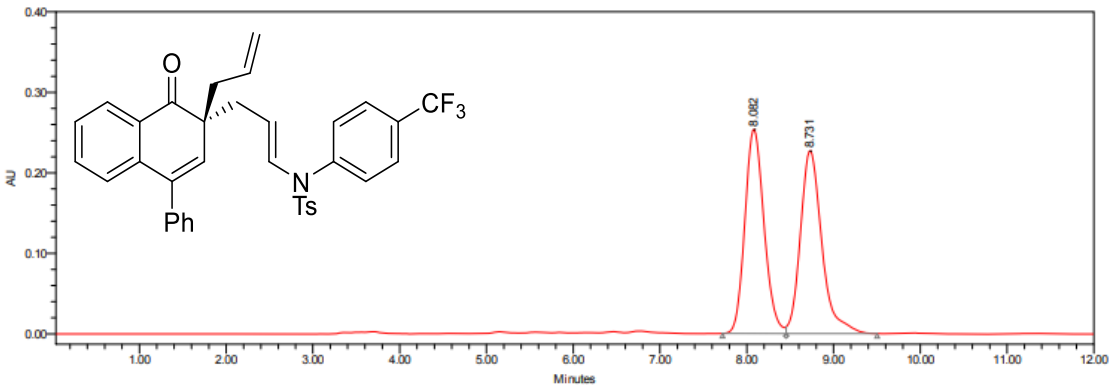
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.090	29569486	50.49
2	PDA 200.0 to 400.0 nm at 2.4 nm	8.854	28993902	49.51



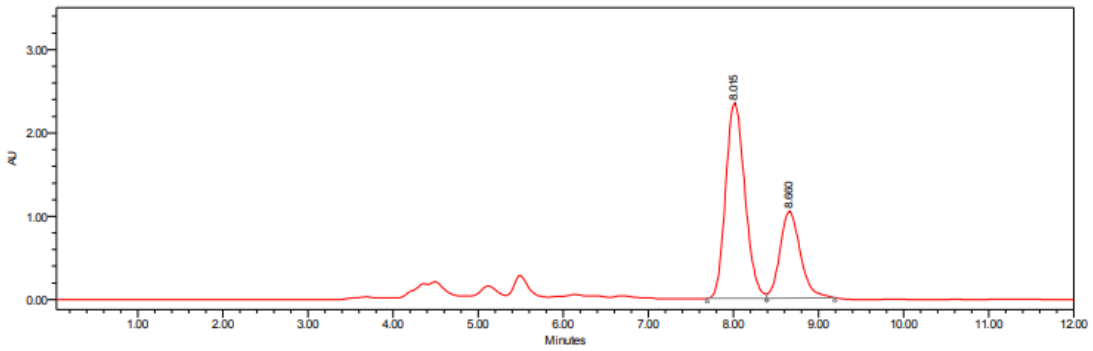
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.105	10602340	90.50
2	PDA 200.0 to 400.0 nm at 2.4 nm	8.887	1112941	9.50

Compound **4l**

HPLC Analysis: 36% ee [©Chiralpak IC, 25 °C, 20% *i*PrOH/*n*-heptane, 1 mL/min, 247 nm, retention times: 8.0 min (major) and 8.6 min (minor)].



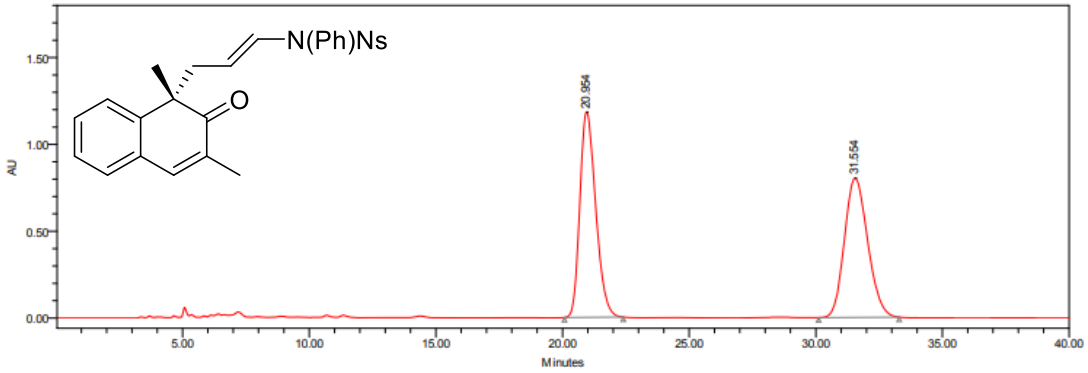
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.082	3895447	49.94
2	PDA 200.0 to 400.0 nm at 2.4 nm	8.731	3904951	50.06



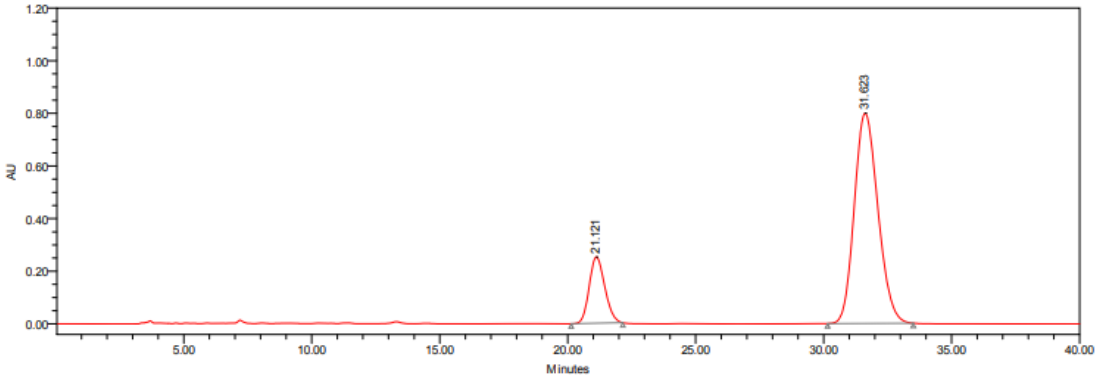
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	8.015	36842053	68.06
2	PDA 200.0 to 400.0 nm at 2.4 nm	8.660	17285947	31.94

Compound **4m**.

HPLC Analysis: 65% ee [©Chiralpak IC, 25 °C, 30% *i*PrOH/*n*-heptane, 1 mL/min, 279 nm, retention times: 21.1 min (minor) and 31.6 min (major)].



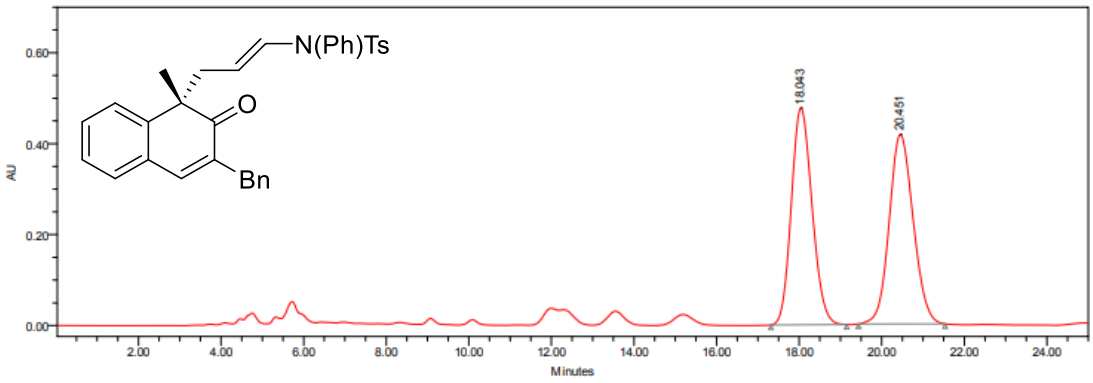
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	20.954	51472245	50.10
2	PDA 200.0 to 400.0 nm at 2.4 nm	31.554	51266384	49.90



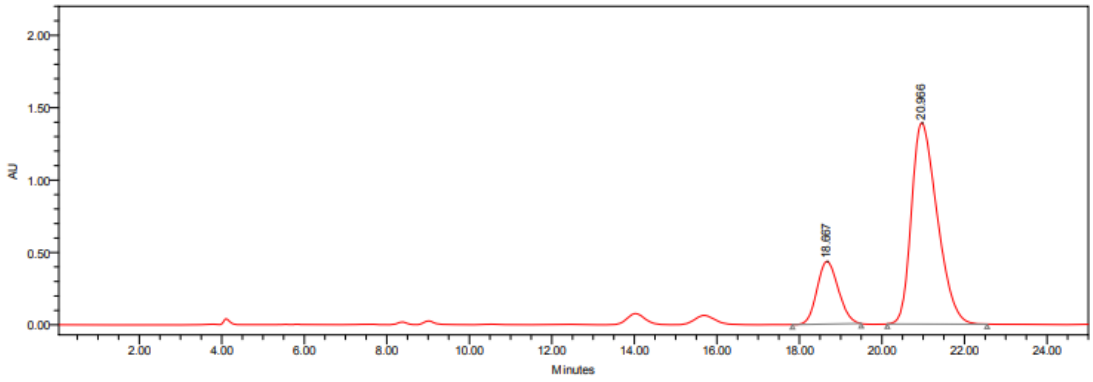
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	21.121	10669578	17.24
2	PDA 200.0 to 400.0 nm at 2.4 nm	31.623	51212967	82.76

Compound **4n**.

HPLC Analysis: 59% ee [©Chiralpak IC, 25 °C, 30% *i*PrOH/*n*-heptane, 1 mL/min, 292 nm, retention times: 18.7 min (minor) and 21.0 min (major)].



	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	18.043	16669813	49.74
2	PDA 200.0 to 400.0 nm at 2.4 nm	20.451	16847382	50.26



	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	18.667	15513901	20.46
2	PDA 200.0 to 400.0 nm at 2.4 nm	20.966	60293222	79.54

VI. DFT Calculations

The level of calculation used in this work is the same as the one used in our previous study,[3] in which it showed its relevance. Only the solvent used has changed (DCE instead of toluene), to consider the experimental conditions.

Calculations were carried out with the Gaussian09 package[4] and all structures were fully optimized without any symmetry constraints at the DFT level by means of the M06 functional.[5] The def2-SVP basis set[6] was applied for all atoms and solvent effects are accounted for by continuum solvation method (integral equation formalism version of the polarizable continuum model (IEFPCM) for DCE). Each stationary point has been characterized with frequency analysis and shows the correct number of negative eigenvalues (zero for a local minimum and one for a transition state). All transition states were verified by stepping along the reaction coordinate (intrinsic reaction coordinate calculations) and confirming that they transformed into the corresponding reactants/products. Final energy calculations at the M06 level associated with the def2-TZVPP basis set, including solvation effect, have been achieved on the IEFPCM(DCE)-M06/def2-SVP geometries. To get accurate geometries and energies, the SCF convergence criterion was systematically tightened to 10^{-8} au, and the force minimizations were carried out until the rms force became smaller that (at least) 1 x 10^{-5} au ("tight" optimization keyword in Gaussian 09). The "UltraFine" grid (99 radial shells and 590 angular points per shell) was used throughout the calculations, as recommended when using Gaussian 09. The Gibbs free energies presented in this article are IEFPCM(DCE)-M06/def2-TZVPP//IEFPCM(DCE)-M06/def2-SVP electronic energies (which include solvation-energy

---

[4] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, Gaussian 09, Revision D.01, **2013**.

[5] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215-241.

[6] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

corrections from the IEFPCM method) modified with thermal and entropy corrections from IEFPCM(DCE)-M06/def2-SVP calculations. Due to the well-known errors associated with entropy calculations, we apply a scaling factor of 0.5 to the entropic contributions as recommended in the literature.[7] Therefore, the calculated ΔG values reported in this study include the ZPE, enthalpic temperature correction, solvation energy, and half the entropy. Note that application of this scheme only slightly modifies the activation barriers and the general profile, but changes the interaction between 2 molecules or the formation of two separate molecules from a single one.

The effect of solvent change from toluene to DCE was estimated on catalyst **6** and is negligible (Figure S1).

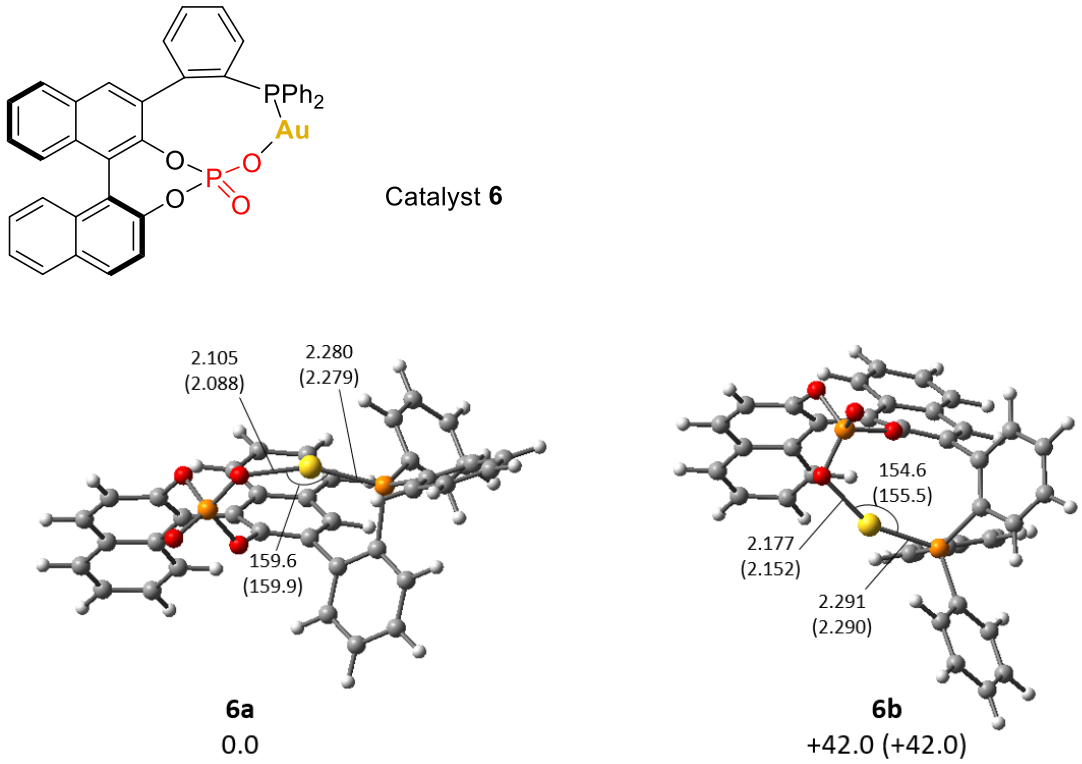


Figure S1. DFT calculated structures of catalyst **6** at the IEFPCM(DCE)-M06/def2-TZVPP//IEFPCM(DCE)-M06/def2-SVP level (values in parentheses: solvent = toluene[1]). Relative Gibbs free energy in kJ mol^{-1}.

[7] (a) Cooper, J.; Ziegler, T. A *Inorg. Chem.* **2002**, *41*, 6614-6622. (b) Lau, J. K. C.; Deudel, D. V. *J. Chem. Theory Comput.* **2006**, *2*, 103-106. (c) Li, H.; Lu, G.; Jiang, J.; Huang, F.; Wang, Z. X. *Organometallics* **2011**, *30*, 2349-2363. (d) Hua, J.; Krizner, H. E.; De Haan, D. O. *J. Phys. Chem. A* **2011**, *115*, 1667-1675.

In order to determine the most stable conformation of intermediate **7**, a thorough exploration of the different conformers and isomers of the latter was performed. For each isomer (η^2-coordinated, σ-coordinated or with a covalent bond), possible conformers were searched by rotating around the N-S(Ts), N-C, NC-CC and Au-C bonds (Figure S2). Consequently, many conformers have been obtained for each isomer, the most stable being **7a**.

The two lowest energy reaction paths leading to the formation of the two enantiomers of **4** are shown in Figure S3. Other conformations for the (*R*) and (*S*) transition states were searched for but were found in all cases to be higher in energy (Figure S4).

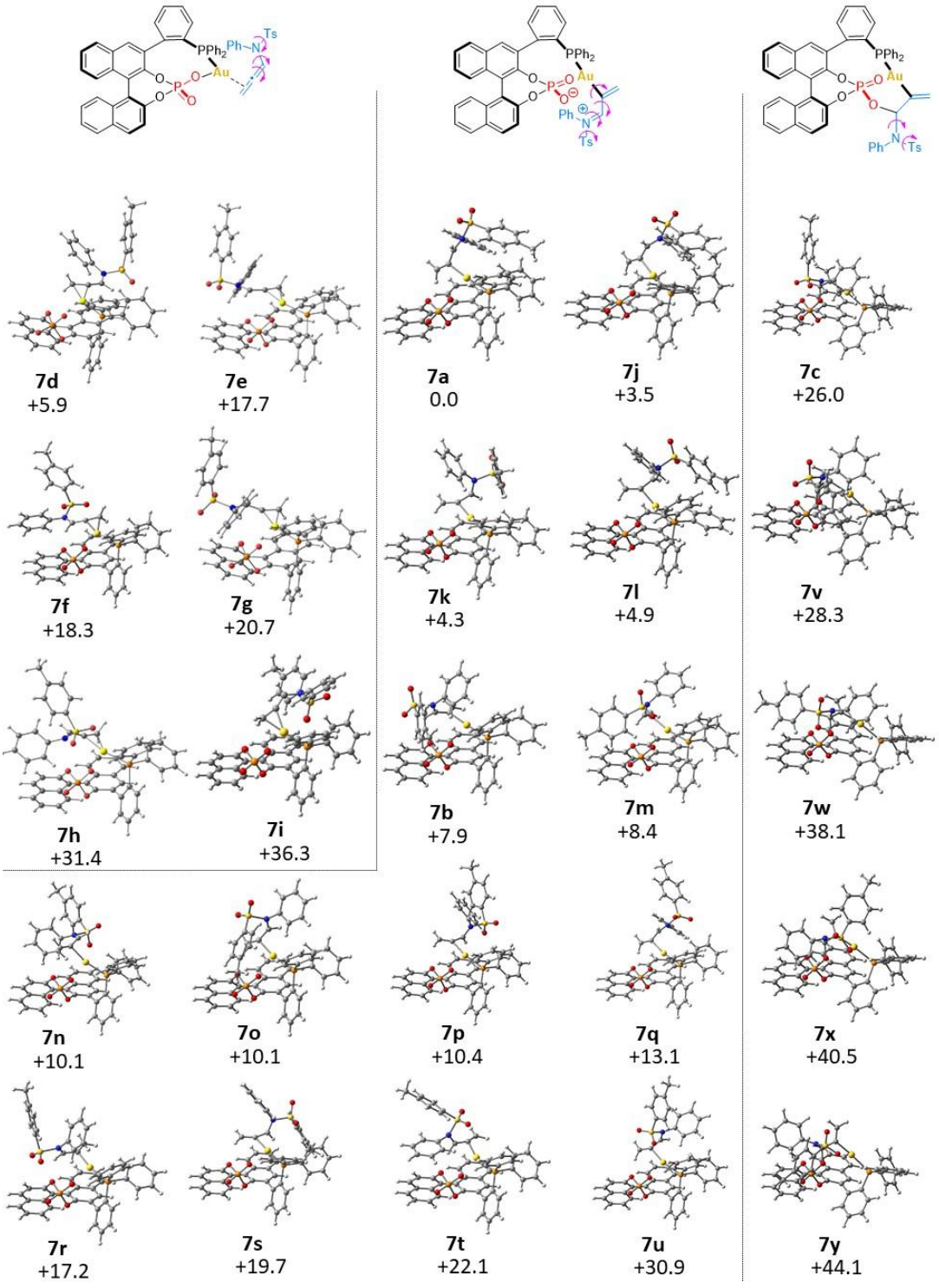


Figure S2. DFT calculated structures of intermediate ***i***. Relative Gibbs free energy in kJ mol^{-1}.

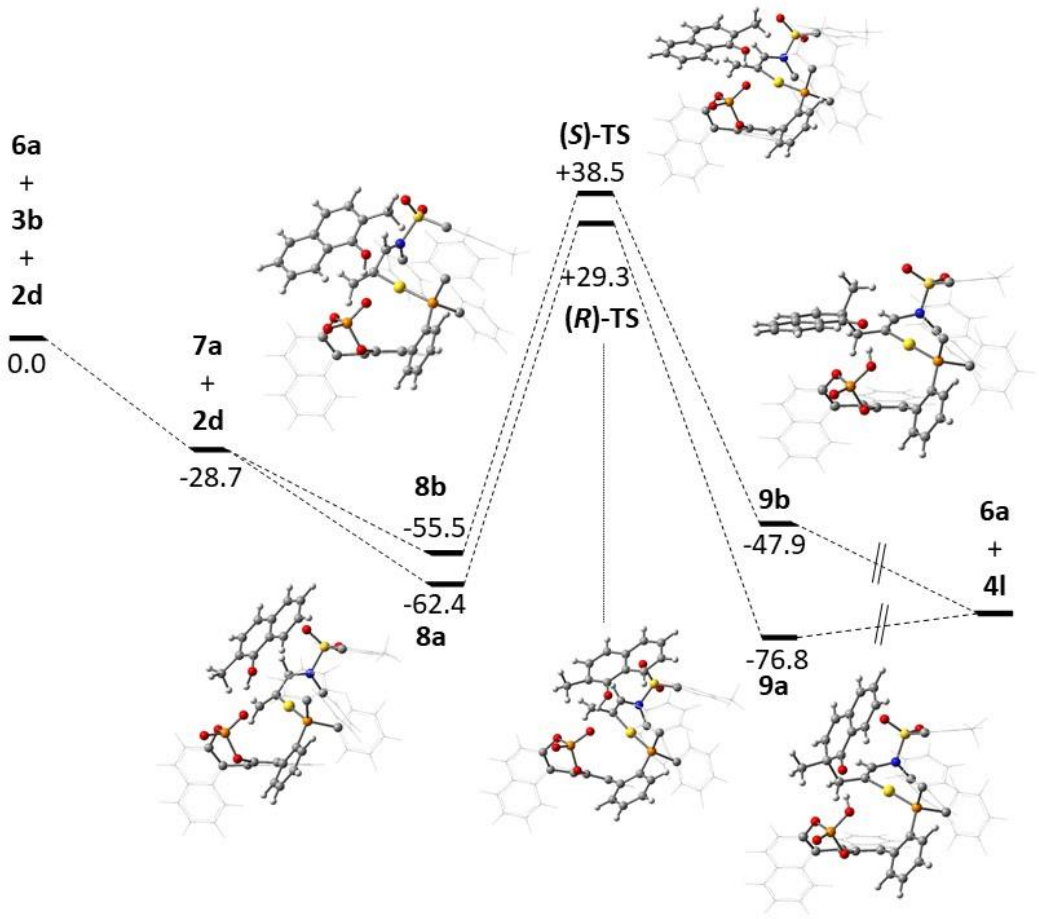


Figure S3. Computed mechanistic patterns. Relative Gibbs free energy in kJ mol^{-1}.

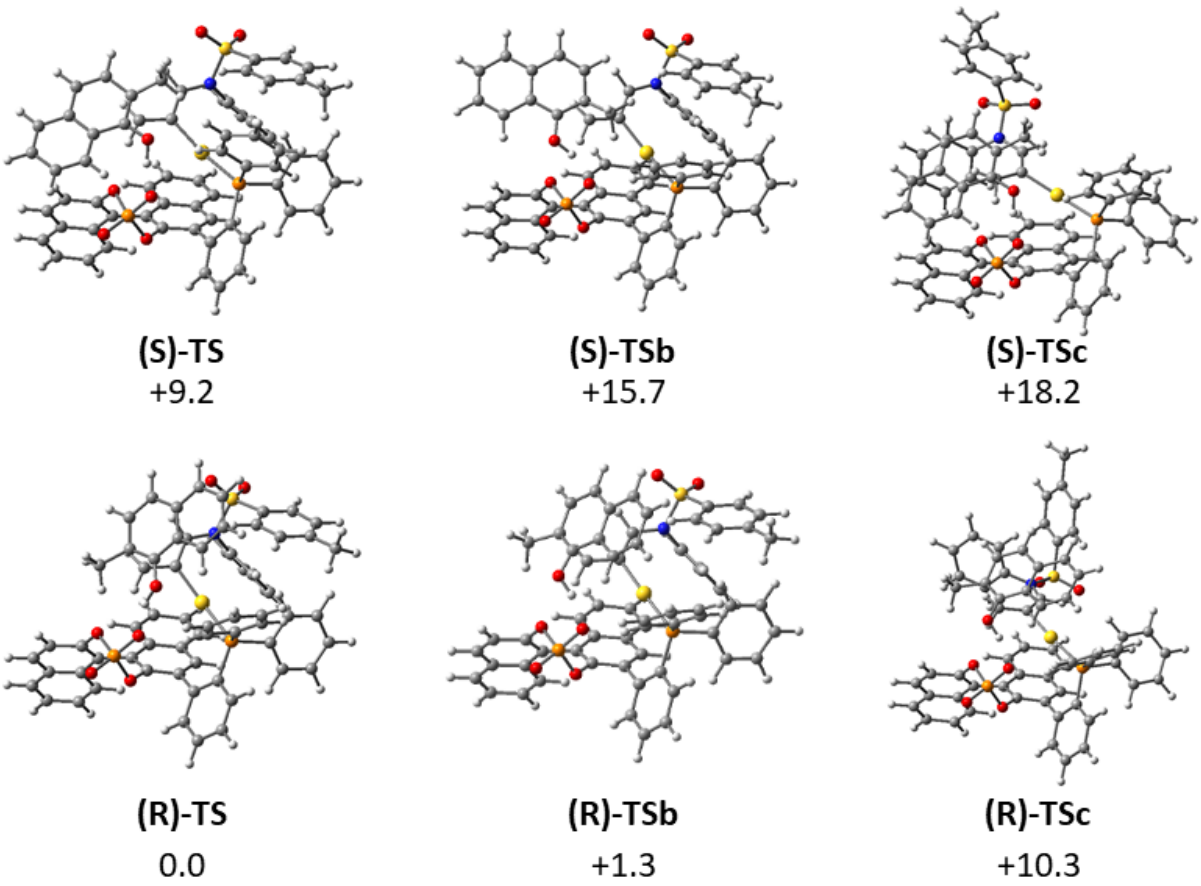


Figure S4. DFT calculated structures of (*R*) and (*S*) transition states. Relative Gibbs free energy in kJ mol^{-1}.

Table S1. Absolute electronic energies and thermal corrections for all molecules.

	E (IEFPCM(DCE)-M06/def2-SVP)	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	E (IEFPCM(DCE)-M06/def2-TZVPP)[a]
3b	-1220,674680	0,290219	0,220258	-1221,772136
2d	-499,704914	0,189288	0,143822	-500,250582
4l	-1720,432048	0,484046	0,393908	-1722,066878
6a	-2579,885739	0,563488	0,457764	-2582,076408
6b	-2579,870406	0,563083	0,458530	-2582,060574
7a	-3800,592858	0,856540	0,707619	-3803,875686
7b	-3800,598234	0,856934	0,708657	-3803,873403
7c	-3800,589327	0,857926	0,706645	-3803,866002
7d	-3800,590694	0,855879	0,704411	-3803,871489
7e	-3800,587543	0,856147	0,705271	-3803,867589
7f	-3800,586776	0,856013	0,703193	-3803,866248
7g	-3800,588399	0,855823	0,706055	-3803,866645
7h	-3800,585109	0,855830	0,705788	-3803,862455

7i	-3800,579658	0,855367	0,705011	-3803,858262
7j	-3800,592690	0,856569	0,709615	-3803,875348
7k	-3800,591808	0,856029	0,703634	-3803,871792
7l	-3800,591484	0,856150	0,705911	-3803,872781
7m	-3800,594555	0,856440	0,707084	-3803,872179
7n	-3800,591175	0,856132	0,705591	-3803,870630
7o	-3800,593762	0,856188	0,708081	-3803,871903
7p	-3800,591817	0,856268	0,704338	-3803,869965
7q	-3800,587823	0,856415	0,703053	-3803,868362
7r	-3800,592003	0,856466	0,705131	-3803,867836
7s	-3800,586179	0,856077	0,704701	-3803,866505
7t	-3800,585594	0,856076	0,702544	-3803,864516
7u	-3800,581111	0,855910	0,702849	-3803,861232
7v	-3800,593565	0,857989	0,712120	-3803,867882
7w	-3800,587369	0,858187	0,709744	-3803,863070
7x	-3800,585465	0,857417	0,706732	-3803,860237
7y	-3800,585806	0,857479	0,707845	-3803,859487
8a	-4300,332401	1,047112	0,875579	-4304,151826
8b	-4300,332254	1,048245	0,879040	-4304,151488
(R)-TS	-4300,302724	1,046539	0,881098	-4304,119376
(S)-TS	-4300,299674	1,045840	0,881643	-4304,115801
9a	-4300,345579	1,048291	0,881992	-4304,161098
9b	-4300,336079	1,048806	0,883749	-4304,151210
(R)-TSb	-4300,301940	1,046246	0,882527	-4304,119458
(S)-TSb	-4300,293136	1,046725	0,879326	-4304,112614
(R)-TSc	-4300,297043	1,046356	0,875143	-4304,112391
(S)-TSc	-4300,291591	1,046166	0,874650	-4304,109046

[a] Energies computed at the IEFPCM(DCE)-M06/def2-SVP geometries.

References

(1) Zhang, Z.; Smal, V.; Retailleau, P.; Voituriez, A.; Frison, G.; Marinetti, A.; Guinchard, X. *J. Am. Chem. Soc.* **2020**, *142*, 3797-3805.

(2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.;

Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, Gaussian 09, Revision D.01, **2013**.

(3) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215-241.

(4) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

(5) Cooper, J.; Ziegler, T. A *Inorg. Chem.* **2002**, *41*, 6614-6622.

(6) Lau, J. K. C.; Deudel, D. V. *J. Chem. Theory Comput.* **2006**, *2*, 103-106.

(7) Li, H.; Lu, G.; Jiang, J.; Huang, F.; Wang, Z. X. *Organometallics* **2011**, *30*, 2349-2363.

(8) Hua, J.; Krizner, H. E.; De Haan, D. O. *J. Phys. Chem. A* **2011**, *115*, 1667-1675.