Supporting Information

Palladium-Catalyzed Intramolecular Enantioselective C(sp^3)-H Insertion of Donor/Donor Carbenes

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1. General information

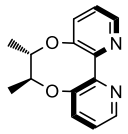
Unless stated otherwise, all reactions were conducted in Schlenk tube under an inert atmosphere of dry N_2. All reactions that required heating were proceeded in oil bath. Commercially obtained reagents were used without purification. Reaction starting materials and ligands were prepared as depicted in the literature. ^{1}H, ^{13}C, ^{19}F NMR pectra were recorded on a Bruker AVANCE 400 (400 MHz for ^{1}H; 101 MHz for ^{13}C; 376 MHz for ^{19}F) or Bruker AVANCE 500 (500 MHz for ^{1}H; 126 MHz for ^{13}C; 471 MHz for ^{19}F). ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and δ 77.16. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (HRMS) were obtained using ESI mass spectrometer. Melting points were determined using a hot stage apparatus. Diastereotopic ratios was determined by ^{1}H NMR. Enantiomeric ratios were determined by HPLC, using a chiralcel OD-H or INA and INC column with hexane and *i*-PrOH as solvents.

2. The synthesis of ligands and optimization of reaction conditions

2.1 The synthesis of ligands Cn-ACBP L5-L7

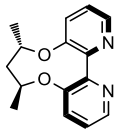
The synthesis of ligands **L5-L7** were prepared according to the literature previously reported by Zhou and coworkers.[1]

(*Ra*,*S*,*S*)-C2-ACBP (L5)



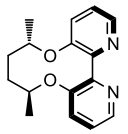
Known compound.[1] 25% yield, white solid, m.p. = 193.8-195.7 °C, $[\alpha]_D^{21}$ = -122 (c 0.60, CH_2Cl_2), R_f = 0.10 (ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.1 Hz, 2H), 7.46 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.34 (dd, *J* = 8.1, 4.6 Hz, 2H), 3.98 – 3.92 (m, 2H), 1.42 (d, *J* = 5.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.3, 149.5, 146.1, 130.1, 124.9, 85.2, 19.0.

(*Ra*,*S*,*S*)-C3-ACBP (L6)



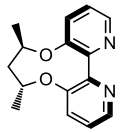
Known compound.[1] 51% yield, white solid, m.p. = 204.7-204.9 °C, $[\alpha]_D^{21}$ = -392 (c 0.72, CH_2Cl_2), R_f = 0.10 (ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.1 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.25 (m, 2H), 4.68 – 4.58 (m, 2H), 1.98 – 1.93 (m, 2H), 1.43 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.1, 149.5, 144.4, 124.9, 123.9, 75.7, 41.8, 22.7.

(*Ra*,*S*,*S*)-C4-ACBP (L7)



Known compound.[1] 17% yield, white solid, m.p. = 205.2-205.3 °C, $[\alpha]_D^{21}$ = -306 (c 0.48, CH_2Cl_2), R_f = 0.10 (ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 3.2 Hz, 2H), 7.32 – 7.27 (m, 4H), 4.38 – 4.31 (m, 2H), 1.90 – 1.83 (m, 2H), 1.80 – 1.72 (m, 2H), 1.42 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.2, 146.6, 142.3, 123.9, 120.6, 80.6, 36.3, 22.5.

(*Sa*,*R*,*R*)-C3-ACBP (L6)

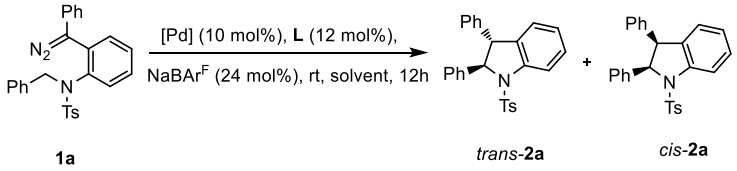


(*Sa*,*R*,*R*)-C3-ACBP **L6** was synthesized identically to (*Ra*,*S*,*S*)-C3-ACBP **L6**.

Known compound.[1] 56% yield, white solid, m.p. = 203.8-204.2 °C, $[\alpha]_D^{21}$ = 368 (c 0.64, CH_2Cl_2), R_f = 0.10 (ethyl acetate). **^{1}H NMR** (500 MHz, $CDCl_3$-*d*) δ 8.46 (d, *J* = 3.9 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.26 (m, 2H), 4.66 – 4.59 (m, 2H), 1.98 – 1.92 (m, 2H), 1.42 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.0, 149.4, 144.3, 124.8, 123.8, 75.6, 41.7, 22.6.

2.2 Condition optimization of enantioselective C(sp^3)-H insertion reaction

Table S2-1. The screening for the enantioselective C(sp^3)-H insertion reaction of **1a**[a]

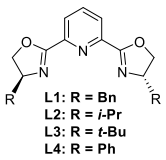


1a *trans*-**2a** *cis*-**2a**

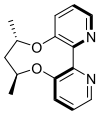
entry	cat.	ligand	solvent	*trans*:*cis*	yield	*ee* [*trans*]	*ee* [*cis*]
1	$Pd(PhCN)_2Cl_2$	**L1**	toluene	1:15.7	66%	-2%	10%
2	$Pd(PhCN)_2Cl_2$	**L2**	toluene	1:7.3	44%	1%	-2%
3	$Pd(PhCN)_2Cl_2$	**L3**	toluene	1:7.3	58%	15%	-4%
4	$Pd(PhCN)_2Cl_2$	**L4**	toluene	1:9.0	67%	3%	-11%
5	$Pd(PhCN)_2Cl_2$	**L5**	toluene	1:5.7	54%	28%	0
6	$Pd(PhCN)_2Cl_2$	**L6**	toluene	1.2:1	66%	93%	-8%
7	$Pd(PhCN)_2Cl_2$	**L7**	toluene	1:3.8	41%	63%	-7%
8	$Pd(PhCN)_2Cl_2$	**L8**	toluene	1:9.0	66%	8%	-2%
9	$Pd(PhCN)_2Cl_2$	**L9**	toluene	1:15.7	47%	8%	-17%
10	$Pd(PhCN)_2Cl_2$	**L10**	toluene	1:13.3	30%	35%	23%
11	$Pd(PhCN)_2Cl_2$	**L11**	toluene	1:8.1	41%	5%	2%
12	$Pd(PhCN)_2Cl_2$	**L12**	toluene	1:8.1	53%	9%	-1%
13	$Pd(PhCN)_2Cl_2$	**L13**	toluene	1:3.5	16%	58%	-6%
14	$Pd(PhCN)_2Cl_2$	**L14**	toluene	1:5.3	61%	71%	-44%
15	$Pd(PhCN)_2Cl_2$	**L15**	toluene	1:13.3	14%	10%	35%
16	$Pd(PhCN)_2Cl_2$	**L16**	toluene	1:9.0	21%	-49%	-4%
17	$Pd(PhCN)_2Cl_2$	**L17**	toluene	1:7.3	32%	-31%	-12%
18	$Pd(PhCN)_2Cl_2$	**L18**	toluene	1:11.5	44%	3%	-4%
19	$Pd(PhCN)_2Cl_2$	**L19**	toluene	1:11.5	8%	34%	-13%
20	$Pd(PhCN)_2Cl_2$	**L20**	toluene	1:10.1	50%	-24	10%
21	$Pd(PhCN)_2Cl_2$	**L21**	toluene	-	trace	-	-
22	$Pd(PhCN)_2Cl_2$	**L22**	toluene	1:10.1	9%	3%	-3%
23	$Pd(PhCN)_2Cl_2$	**L23**	toluene	1:3.2	47%	7%	-13%
24	$Pd(PhCN)_2Cl_2$	**L24**	toluene	1:8.1	16%	7%	-10%
25	$Pd(PhCN)_2Cl_2$	**L25**	toluene	1:11.5	15%	-6%	-4%
26	$Pd(PhCN)_2Cl_2$	**L6**	DCE	1.7:1	71%	88%	-2%
27	$Pd(PhCN)_2Cl_2$	**L6**	DCM	1:1.2	59%	82%	-5%
28	$Pd(PhCN)_2Cl_2$	**L6**	$CHCl_3$	1:11.5	69%	5%	20%
29	$Pd(PhCN)_2Cl_2$	**L6**	$PhCF_3$	1.6:1	63%	93%	-9%
30	$Pd(PhCN)_2Cl_2$	**L6**	PhF	1:6.1	35%	20%	-3%
31	$Pd(PhCN)_2Cl_2$	**L6**	mesitylene	1:5.3	66%	67%	-19%
32	$Pd(PhCN)_2Cl_2$	**L6**	PhCl	1:1.2	14%	88%	-3%
33	$Pd(PPh_3)_4$	**L6**	$PhCF_3$	1:8.1	41%	16%	48%
34	$Pd_2(dba)_3$	**L6**	$PhCF_3$	1:10.1	84%	-13%	-2%

35	$Pd(cod)Cl_2$	**L6**	$PhCF_3$	1:2.3	49%	79%	-44%
36	$Pd(PPh_3)_2Cl_2$	**L6**	$PhCF_3$	1:2.7	17%	6%	42%
37	$PdCl_2$	**L6**	$PhCF_3$	1.7:1	46%	85%	-10%
38	$[Pd(allyl)Cl]_2$	**L6**	$PhCF_3$	1:4.0	58%	32%	-2%
39	$PdBr_2$	**L6**	$PhCF_3$	1:2.2	57%	0	2%
40	$Pd(CH_3CN)_2Cl_2$	**L6**	$PhCF_3$	5.2:1	73%	94%	-21%
41	$Pd(CH_3CN)_2Cl_2$	**L1**	$PhCF_3$	1:3.0	69%	-12%	8%
42	$Pd(CH_3CN)_2Cl_2$	**L2**	$PhCF_3$	1:2.4	62%	-7%	6%
43	$Pd(CH_3CN)_2Cl_2$	**L3**	$PhCF_3$	1:6.7	58%	4%	-3%
44	$Pd(CH_3CN)_2Cl_2$	**L4**	$PhCF_3$	1:8.1	76%	5%	20%
45	$Pd(CH_3CN)_2Cl_2$	**L5**	$PhCF_3$	7.3:1	65%	95%	-12%
46	$Pd(CH_3CN)_2Cl_2$	**L7**	$PhCF_3$	2.8:1	57%	91%	-19%
47[b]	$Pd(CH_3CN)_2Cl_2$	**L6**	$PhCF_3$	1:2.1	19%	4%	-2%

[a]**1a** was prepared in situ through the oxidization of hydrazone **S1a'** by MnO_2 (8.0 eq) and filtered followed by concentration; **1a** (0.1 mmol), [**1a**] = 0.033 M, rt; The yield was isolated yield; The *ee* values of **2a** were determined by HPLC using chiral stationary phase; The ratio of *cis*/*trans* was determined by ^1H NMR spectrum of the crude reaction mixture. [b] The reaction was conducted for four days without $NaBAr^F$.



L5



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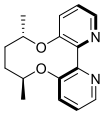

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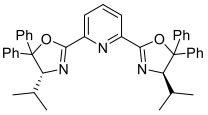

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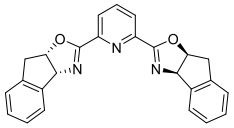

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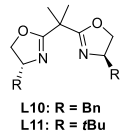

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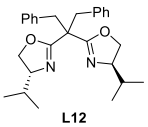

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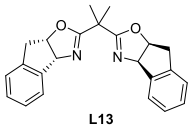

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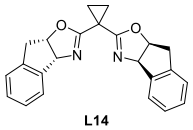

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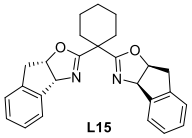

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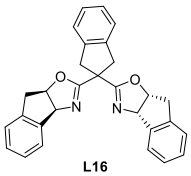

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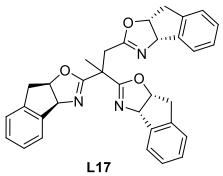

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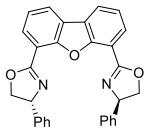

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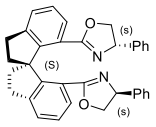

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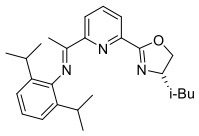

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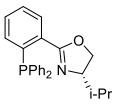

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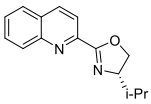

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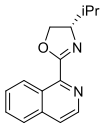

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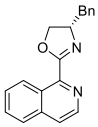

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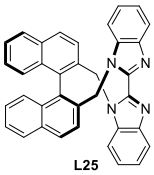
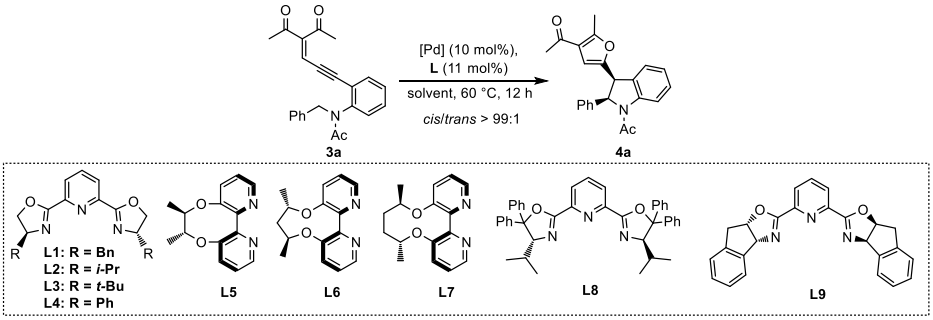


Table S2-2. The screening for the enantioselective C(sp^3)-H insertion reaction of enynone **3a**[a]



entry	cat. (mol %)	add. (0.22 eq)	ligand	solvent	yield	*ee*
1	**$Pd(PhCN)_2Cl_2$**	**$NaBAr^F$**	**L1**	**toluene**	**82%**	**89%**
2	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L2**	toluene	86%	24%
3	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L3**	toluene	90%	0
4	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L4**	toluene	89%	39%
5	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L5**	toluene	47%	10%
6	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L6**	toluene	37%	3%
7	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L7**	toluene	51%	4%
8	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L8**	toluene	90%	0
9	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L9**	toluene	72%	7%
10	$Pd(dba)_2$	$NaBAr^F$	**L1**	toluene	0	-
11	$Pd(PPh_3)_4$	$NaBAr^F$	**L1**	toluene	20%	0
12	$PdCl_2$	$NaBAr^F$	**L1**	toluene	90%	10%
13	$PdCl_2(cod)$	$NaBAr^F$	**L1**	toluene	84%	66%
14	$Pd(CH_3CN)_2Cl_2$	$NaBAr^F$	**L1**	toluene	87%	30%
15	$Pd(PhCN)_2Cl_2$	-	**L1**	toluene	85%	7%
16	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L1**	DCE	76%	20%
17	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L1**	$CHCl_3$	44%	55%
18	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L1**	DCM	76%	11%
19	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L1**	THF	83%	53%
20	$Pd(PhCN)_2Cl_2$	$NaBAr^F$	**L1**	$PhCF_3$	61%	20%
21	$Pd(CH_3CN)_2Cl_2$	$NaBAr^F$	**L1**	$PhCF_3$	63%	8%
22	$Pd(CH_3CN)_2Cl_2$	$NaBAr^F$	**L2**	$PhCF_3$	79%	5%
23	$Pd(CH_3CN)_2Cl_2$	$NaBAr^F$	**L3**	$PhCF_3$	73%	1%
24	$Pd(CH_3CN)_2Cl_2$	$NaBAr^F$	**L4**	$PhCF_3$	69%	14%
25	$Pd(CH_3CN)_2Cl_2$	$NaBAr^F$	**L5**	$PhCF_3$	43%	3%
26	$Pd(CH_3CN)_2Cl_2$	$NaBAr^F$	**L6**	$PhCF_3$	43%	5%
27	$Pd(CH_3CN)_2Cl_2$	$NaBAr^F$	**L7**	$PhCF_3$	42%	3%

[a] **3a** (0.1 mmol), [**3a**] = 0.2 M, 60℃; The yield was isolated yield; The *ee* values of **4a** were determined by HPLC using chiral stationary phase; The ratio of *cis*/*trans* was determined by ^{1}H NMR spectrum of the crude reaction mixture.

3. General procedure for preparation of hydrazones and diazo compounds

Typical procedure for formation of 2-aminobenzophenones (precursor of S1w'&S1x')[2]

A Schlenk tube was charged with 2-aminobenzonitrile (1.0 equiv.), arylboronic acids (2.0 equiv.), $Pd(TFA)_2$ (5 mol%), 5,5'-dimethyl-2,2'-dipyridyl (7.5 mol%), MsOH (10.0 equiv.) THF: H_2O=2:1 (0.5 M) at room temperature. The reaction mixture was stirred vigorously at 80 °C for 24-36 h. The mixture was poured into ethyl acetate, which was washed with saturated $NaHCO_3$ and then brine. After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The residue was purified by flash column chromatography to yield the desired products.

Typical procedure for acetylation of 2-aminobenzophenones (precursor of S1aa')

To a solution of 2-aminobenzophenones (1.0 equiv.) and Et_3N (2.2 equiv.) in DCM (0.5 M) at 0°C under nitrogen was added Ac_2O (1.2 equiv.) dropwise. The resulting mixture was allowed to warm up to room temperature and stirred until the reaction was completed by TLC. Water was added and the organic phase was separated. Aqueous phase was extracted with DCM twice. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography to yield the desired acetylated 2-aminobenzophenones.

Typical procedure for sulfonylation of 2-aminobenzophenones or 2-aminoacetophenone

To a solution of 2-aminobenzophenones or 2-aminoacetophenone (1.0 equiv.) in DCM (0.5M) at 0 °C was added pyridine (1.5 equiv.) and tosyl chloride or methanesulfonyl chloride (1.5 equiv.). The reaction was allowed to come to room temperature while stirring overnight. Water was added to the reaction and the layers were separated. The organic layer was washed with water and brine, then dried over Na_2SO_4, filtered and concentrated *in vacuo*, and purified by flash column chromatography to yield the desired sulfonylated products.

Typical procedure for benzylation or alkylation of amides

To a flame-dried flask was added the sulfonylated or acetylated 2-aminobenzophenones (1.0 equiv.), anhydrous K_2CO_3 or Cs_2CO_3 (2.5 equiv.) and anhydrous acetonitrile (0.5 M). The desired benzyl bromide or alkyl bromide (1.5 equiv) was added dropwise and the reaction was heated to ranging 60°C from 80°C overnight. The K_2CO_3 or Cs_2CO_3 was removed by filtraltion and washed with ethyl acetate twice. Then the acetonitrile in filtrate was removed *in vacuo*. The residue was dissolved in ethyl acetate and washed with H_2O and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*, and purified by flash column chromatography to yield the desired benzylated or alkylated amides **S1a-S1y, S1aa-S1ab**.

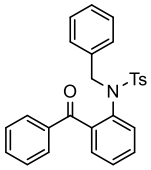
Typical procedure for dibenzylation of 2-aminobenzophenones

To a flame-dried flask was added the 2-aminobenzophenone (1.0 equiv.), anhydrous K_2CO_3 (5.0 equiv.) and anhydrous acetonitrile (0.5 M). Benzyl bromide (3.0 equiv) was added dropwise and the reaction was heated to 80°C overnight. The K_2CO_3 was removed by filtraltion and washed with ethyl acetate twice. Then the solvent in filtrate was removed *in vacuo* and the residue was purified by flash column chromatography to yield the desired dibenzylated amine **S1ac** as bright yellow oil.

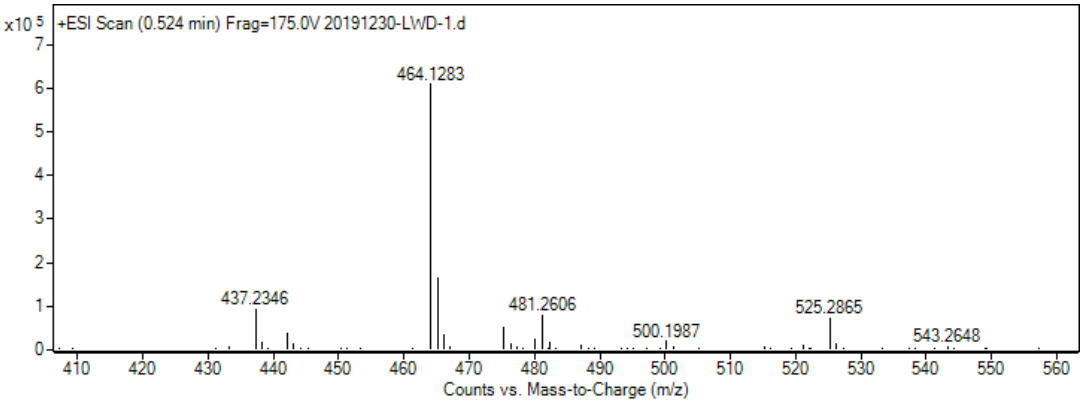
Typical procedure for formation of hydrazones[3]

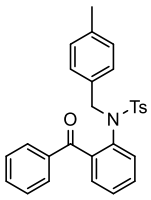
To a flame-dried flask was added anhydrous 1-butanol or ethanol (0.5 M) along with the desired

both amidated and benzylated or alkylated **S1a-S1y, S1aa-S1ab** as well as dibenzylated **S1ac**. (1.0 equiv.). Glacial acetic acid (0.5 to 2.0 equiv.) was added followed by hydrazine hydrate (5.0 to 10.0 equiv.), and the reaction was heated to 100-120℃ reflux for 18-120 h upon completion by TLC. The residue was dissolved in ethyl acetate and washed with H_2O and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*, and purified by flash column chromatography to yield the desired hydrazones **S1a'-S1y'**. Most notably, if ethanol was used, removing *in vacuo* was required first. ***Note:*** *Hydrazones were often isolated as a mixture of E/Z isomers or were used without further purification. Therefore, ^1H NMR and ^{13}C NMR peaks have been reported only for major isomer of hydrazones (slightly larger R_f value, major isomer). However, due to obataining an inseparable mixture of two isomers, NMR spectrogram of **S1aa** were characterized in the form of mixed spectrum.*

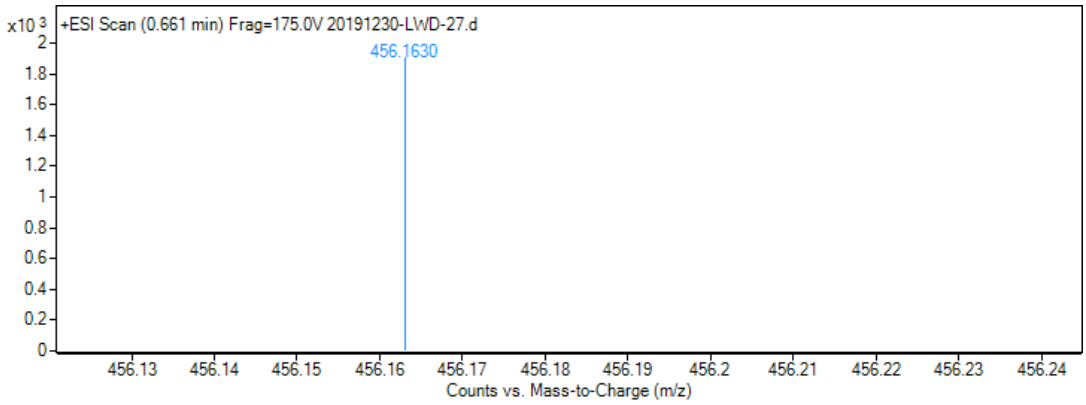


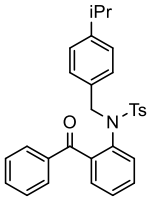
Compound S1a: 99% yield, white solid, m.p. = 105.4-107.0 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.23 (m, 5H), 7.22 – 7.18 (m, 3H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.94 – 6.90 (m, 1H), 4.96 (s, 2H), 2.21 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.1, 143.3, 139.6, 137.0, 136.9, 136.8, 136.1, 133.0, 133.0, 130.7, 130.6, 130.2, 129.9, 129.3, 128.3, 128.1, 127.9, 127.8, 127.4, 56.8, 21.5. **IR** (KBr, cm^{-1}) 3062, 3031, 1668, 1597, 1489, 1448, 1343, 1289, 1264, 1215, 1160, 1092, 1055, 932, 860, 814, 733, 703, 657, 562. **HRMS** (ESI) Calcd for $C_{27}H_{23}NNaO_3S$ $(M+Na)^+$ 464.1291, found 464.1283.



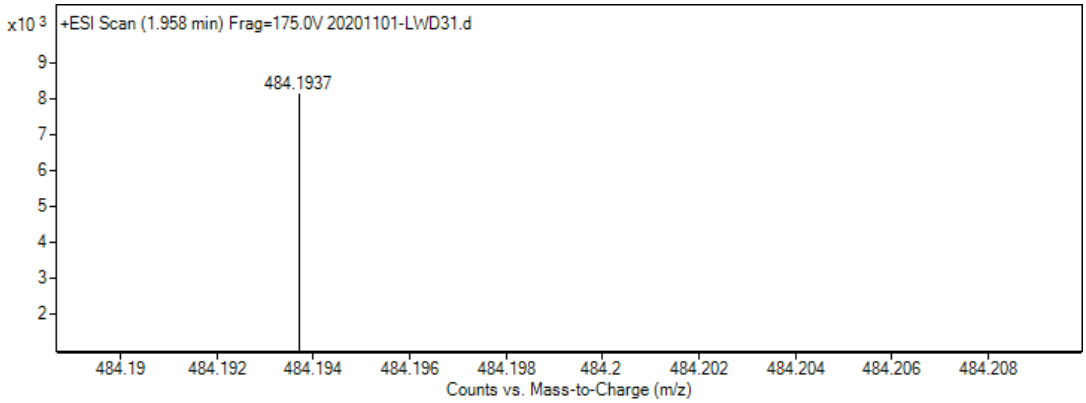


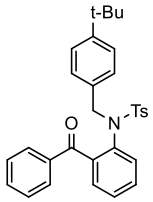
Compound S1b: 90% yield, white solid, m.p. = 148.1-149.5 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.24 (m, 3H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.03 – 6.91 (m, 5H), 4.90 (s, 2H), 2.26 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 143.2, 139.7, 137.5, 137.1, 137.0, 136.9, 133.00, 132.96, 132.9, 130.7, 130.7, 130.2, 129.8, 129.3, 129.0, 128.0, 127.9, 127.4, 56.6, 21.5, 21.3. **IR** (KBr, cm^{-1}) 3059, 3029, 2923, 1669, 1596, 1487, 1447, 1344, 1290, 1264, 1160, 1092, 1057, 932, 863, 814, 765, 704, 657, 576, 547. **HRMS** (ESI) Calcd for $C_{28}H_{26}NO_3S$ $(M+H)^+$ 456.1628, found 456.1630.



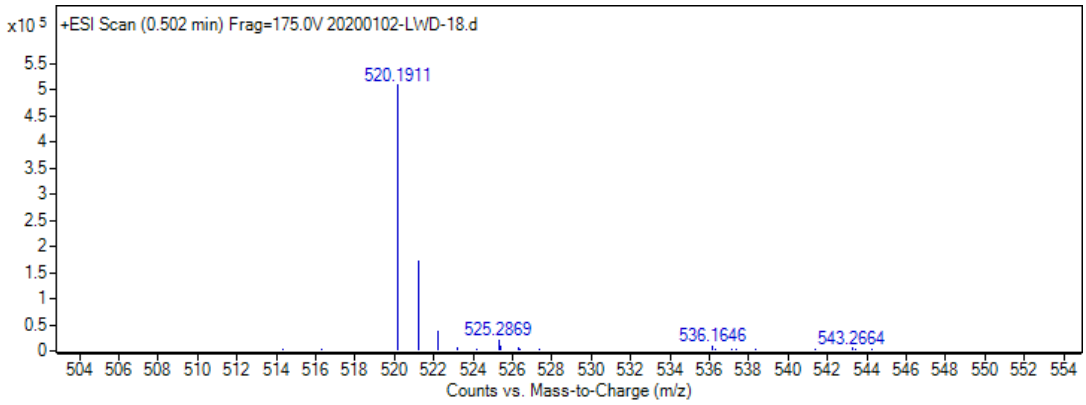


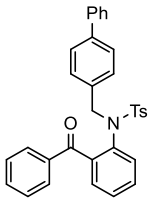
Compound S1c: 97% yield, white solid, m.p. = 107.5-108.5 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.24 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.99 – 6.91 (m, 3H), 4.92 (s, 2H), 2.83 (hept, *J* = 6.8 Hz, 1H), 2.20 (s, 3H), 1.19 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.1, 148.4, 143.1, 139.6, 137.3, 137.0, 136.9, 133.5, 133.0, 132.9, 130.7, 130.6, 130.2, 129.8, 129.3, 128.0, 127.9, 127.4, 126.3, 56.7, 33.8, 24.0, 21.5. **IR** (KBr, cm^{-1}) 3060, 2961, 2871, 1669, 1597, 1487, 1447, 1344, 1289, 1264, 1160, 1092, 1058, 932, 864, 815, 765, 733, 705, 657, 575, 548. **HRMS** (ESI) Calcd for $C_{30}H_{30}NO_3S$ $(M+H)^+$ 484.1941, found 484.1937.



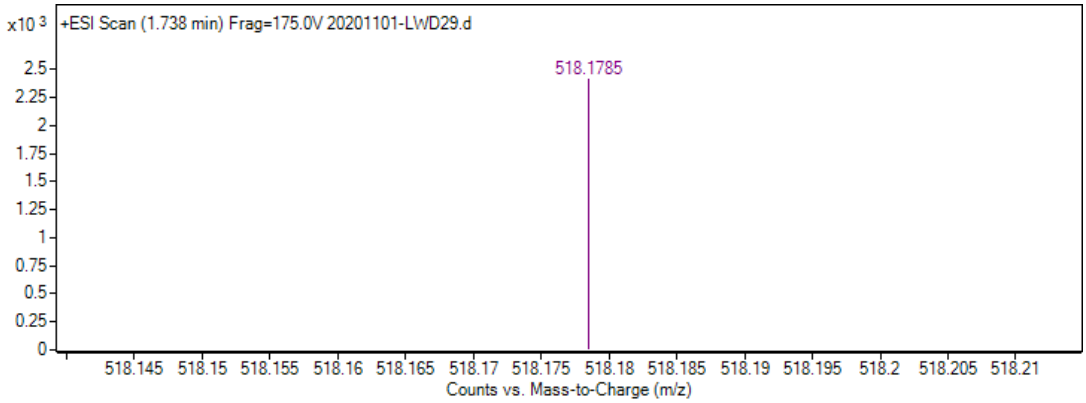


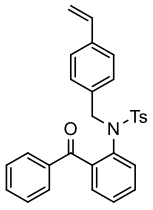
Compound S1d: 99% yield, white solid, m.p. = 125.4-127.4 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.30 – 7.17 (m, 4H), 7.06 – 7.01 (m, 1H), 6.99 (d, *J* = 7.9 Hz, 2H), 4.97 (s, 2H), 2.24 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.1, 150.7, 143.1, 139.5, 137.3, 137.0, 136.9, 133.1, 133.0, 132.9, 130.7, 130.6, 130.2, 129.4, 129.2, 128.1, 127.9, 127.4, 125.2, 56.6, 34.5, 31.4, 21.5. **IR** (KBr, cm^{-1}) 3062, 2961, 2868, 1669, 1596, 1485, 1446, 1402, 1344, 1289, 1264, 1160, 1092, 1060, 931, 863, 812, 704, 652, 573, 548. **HRMS** (ESI) Calcd for $C_{31}H_{31}NNaO_3S$ $(M+Na)^+$ 520.1917, found 520.1911.



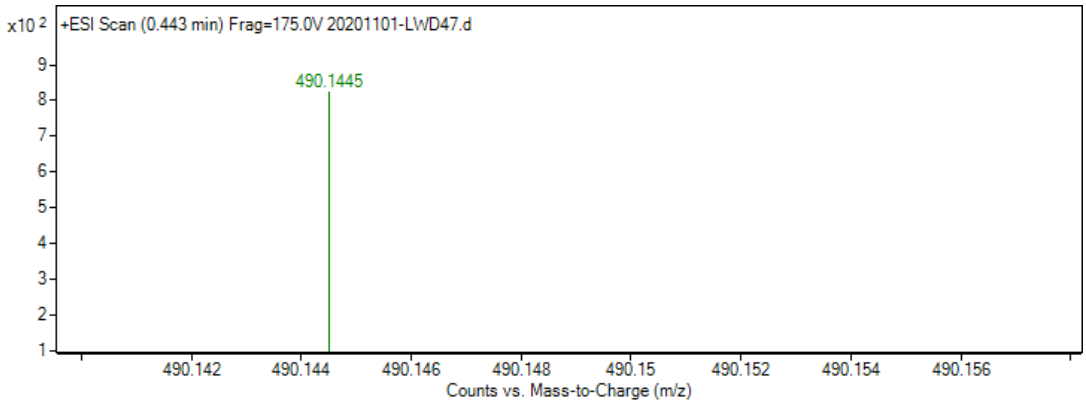


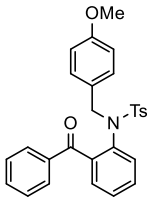
Compund S1e: 99% yield, white solid, m.p. = 146.9-148.7 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.3 Hz, 2H), 7.55 – 7.50 (m, 3H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.38 (m, 4H), 7.37 – 7.26 (m, 8H), 7.05 – 7.00 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.99 (s, 2H), 2.21 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.1, 143.3, 140.7, 140.6, 139.6, 137.2, 137.0, 136.8, 135.2, 133.0, 130.8, 130.6, 130.3, 130.2, 129.4, 128.8, 128.1, 127.9, 127.5, 127.4, 127.1, 127.0, 56.6, 21.5. **IR** (KBr, cm^{-1}) 3060, 3031, 2924, 1669, 1597, 1487, 1447, 1408, 1345, 1290, 1265, 1160, 1092, 1058, 932, 864, 762, 735, 702, 657, 568, 546. **HRMS** (ESI) Calcd for $C_{33}H_{28}NO_3S$ $(M+H)^+$ 518.1785, found 518.1785.



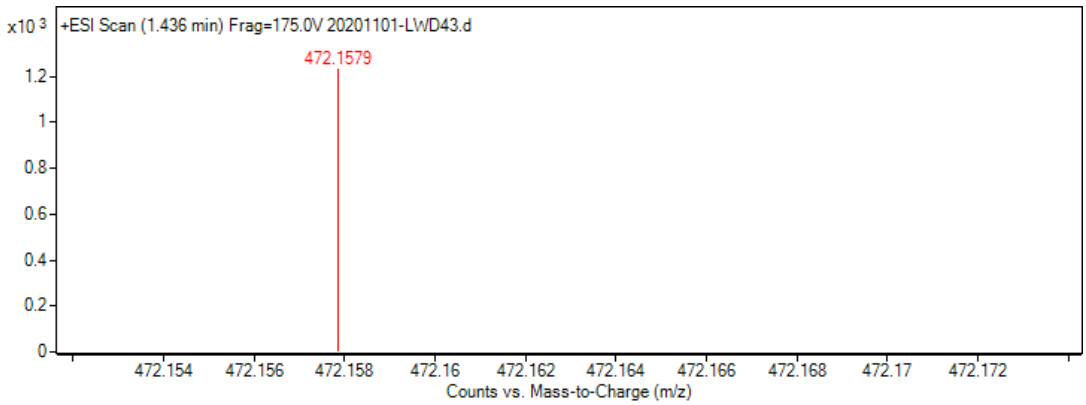


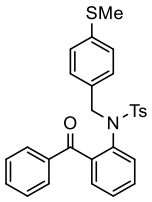
Compound S1f: 66% yield, white solid, m.p. = 118.3-120.3 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.15 (m, 5H), 7.01 – 6.92 (m, 3H), 6.63 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.68 (d, *J* = 17.6 Hz, 1H), 5.20 (d, *J* = 10.9 Hz, 1H), 4.93 (s, 2H), 2.21 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 143.3, 139.6, 137.1, 137.0, 136.9, 136.7, 136.6, 135.7, 132.9, 132.9, 130.7, 130.6, 130.2, 130.0, 129.3, 128.1, 127.9, 127.5, 126.2, 114.0, 56.5, 21.5. **IR** (KBr, cm^{-1}) 3060, 1669, 1596, 1487, 1447, 1344, 1289, 1264, 1216, 1160, 1092, 1058, 931, 863, 816, 735, 704, 657, 575, 547. **HRMS** (ESI) Calcd for $C_{39}H_{25}NNaO_3S$ $(M+Na)^+$ 490.1447, found 490.1445.



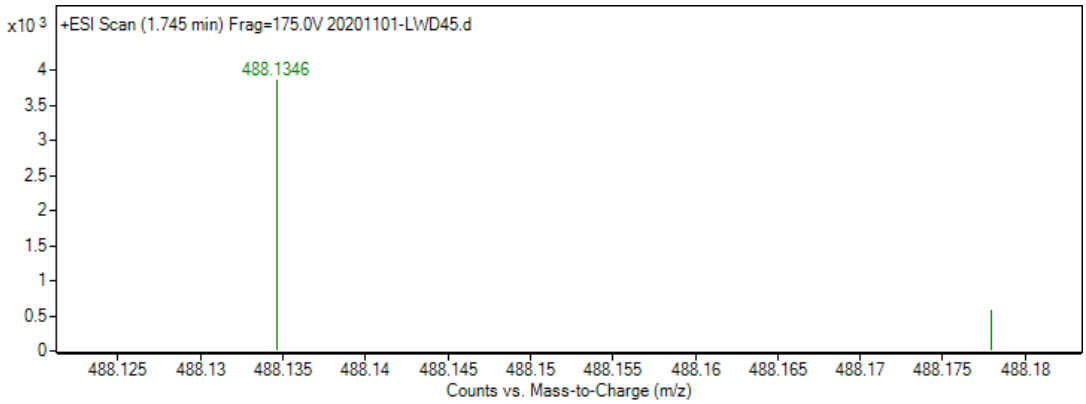


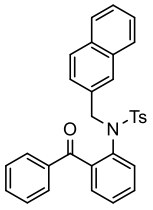
Compound S1g: 99% yield, white solid, m.p. = 110.2-112.4 °C, R_f = 0.2 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.94 – 6.89 (m, 1H), 6.71 (d, *J* = 8.6 Hz, 2H), 4.88 (s, 2H), 3.73 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.1, 159.3, 143.2, 139.7, 136.97, 136.96, 136.9, 133.0, 132.9, 131.2, 130.6, 130.1, 129.3, 128.2, 128.1, 127.9, 127.4, 113.6, 56.3, 55.2, 21.5. **IR** (KBr, cm^{-1}) 3061, 2956, 2837, 1669, 1596, 1514, 1447, 1343, 1288, 1250, 1159, 1092, 1034, 932, 864, 816, 762, 735, 704, 657, 576, 548. **HRMS** (ESI) Calcd for $C_{28}H_{26}NO_4S$ $(M+H)^+$ 472.1577, found 472.1579.



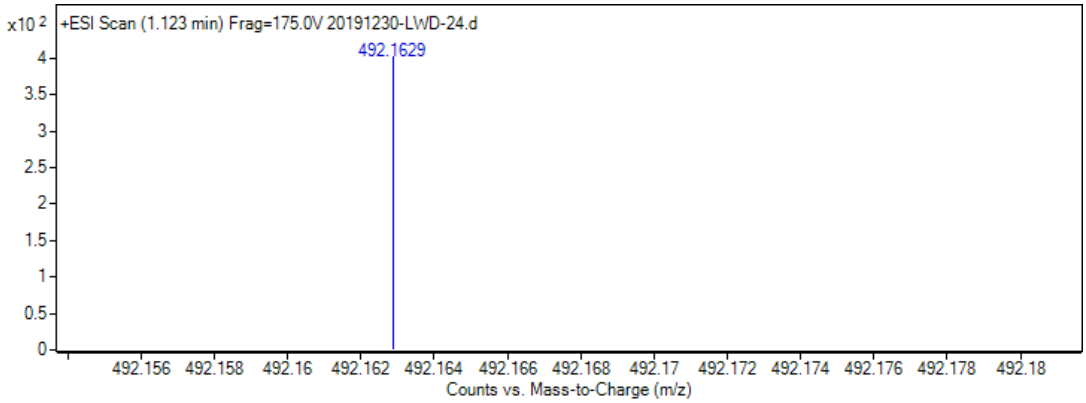


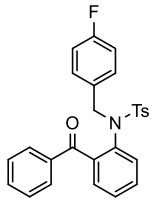
Compound S1h: 99% yield, white solid, m.p. = 109.8-111.9 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$)) δ 7.58 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 7.01 – 6.91 (m, 3H), 4.89 (s, 2H), 2.41 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 143.3, 139.6, 138.1, 137.0, 136.9, 136.7, 133.0, 132.9, 132.8, 130.7, 130.6, 130.3, 130.2, 129.3, 128.0, 127.9, 127.5, 126.2, 56.4, 21.5, 15.6. **IR** (KBr, cm^{-1}) 3060, 2921, 1668, 1597, 1490, 1445, 1344, 1289, 1264, 1160, 1092, 1055, 932, 863, 812, 767, 735, 704, 657, 572, 546. **HRMS** (ESI) Calcd for $C_{28}H_{26}NO_3S_2$ $(M+H)^+$ 488.1349, found 488.1346.



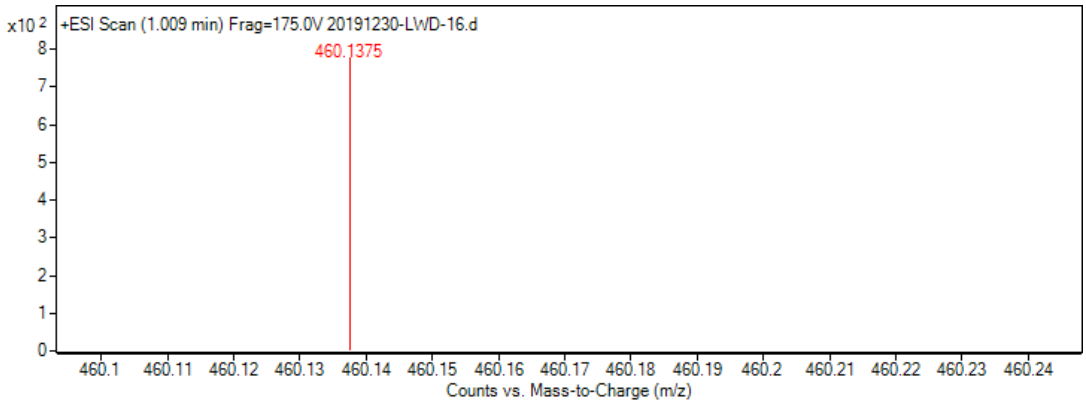


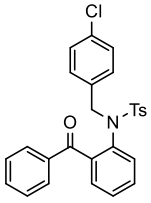
Compound S1i: 99% yield, white solid, m.p. = 132.2-133.4 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 1H), 7.71 – 7.63 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 3H), 7.54 – 7.44 (m, 4H), 7.44 – 7.37 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.17 (m, 3H), 7.02 – 6.91 (m, 3H), 5.11 (s, 2H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.1, 143.3, 139.6, 137.1, 136.9, 136.8, 133.6, 133.2, 132.98, 132.95, 132.9, 130.8, 130.6, 130.2, 129.4, 128.9, 128.1, 128.00, 127.96, 127.96, 127.7, 127.5, 127.5, 126.04, 126.01, 57.0, 21.5. **IR** (KBr, cm^{-1}) 3059, 1668, 1597, 1487, 1447, 1400, 1344, 1289, 1264, 1160, 1092, 1066, 933, 896, 859, 817, 759, 734, 705, 660, 575, 547, 476. **HRMS** (ESI) Calcd for $C_{31}H_{26}NO_3S$ $(M+H)^+$ 492.1628, found 492.1629.



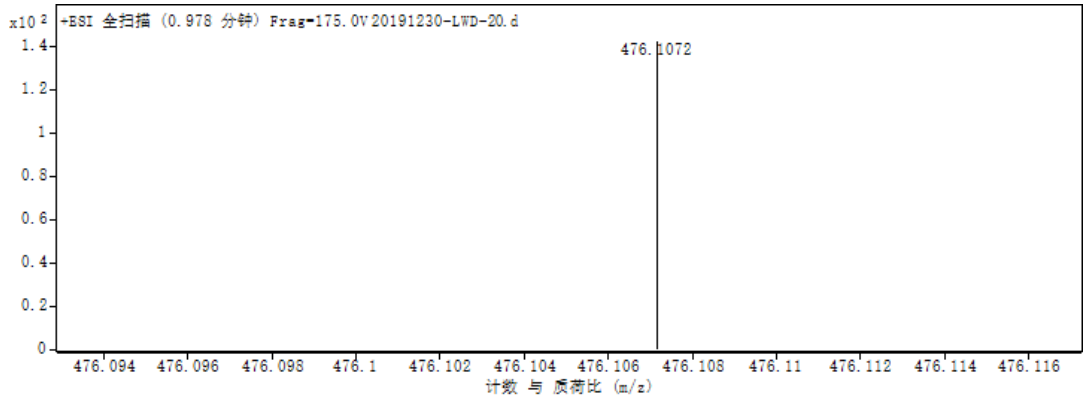


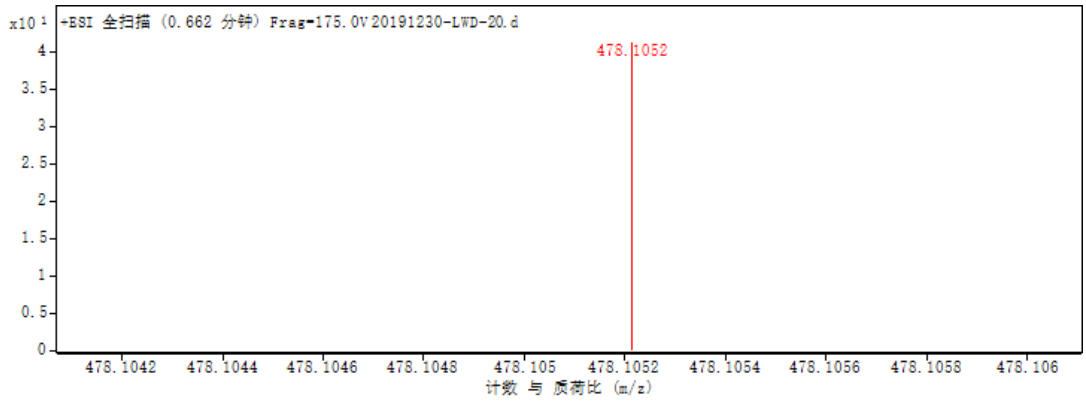
Compound S1j: 65% yield, white solid, m.p. = 117.7-118.7 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.20 (m, 5H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.94 – 6.83 (m, 3H), 4.92 (s, 2H), 2.21 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.39. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 162.4 (d, *J* = 246.1 Hz), 143.4, 139.6, 136.8, 136.5, 133.0, 132.8, 131.9 (d, *J* = 3.2 Hz), 131.6 (d, *J* = 8.2 Hz), 130.7, 130.6, 130.2, 129.4, 128.1, 127.8, 127.5, 115.2 (d, *J* = 21.3 Hz), 56.0, 21.5. **IR** (KBr, cm^{-1}) 3065, 1669, 1599, 1510, 1446, 1345, 1289, 1264, 1223, 1160, 1093, 1058, 932, 860, 764, 735, 704, 657, 575, 547. **HRMS** (ESI) Calcd for $C_{27}H_{23}FNO_3S$ $(M+H)^+$ 460.1377, found 460.1375.

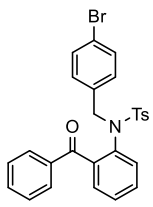




Compound S1k: 97% yield, white solid, m.p. = 133.2-133.4 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.53 (m, 3H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.26 – 7.15 (m, 4H), 7.05 – 6.94 (m, 3H), 4.95 (s, 2H), 2.24 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 143.5, 139.6, 136.9, 136.8, 136.5, 134.7, 133.8, 133.1, 132.7, 131.2, 130.8, 130.6, 130.3, 129.4, 128.5, 128.1, 127.9, 127.6, 56.1, 21.5. **IR** (KBr, cm^{-1}) 3062, 2924, 1669, 1596, 1490, 1446, 1409, 1347, 1290, 1265, 1161, 1091, 1060, 932, 863, 813, 704, 657, 572, 546. **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_3S$ $(M+H)^+$ 476.1082, found 476.1072; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_3S$ $(M+H)^+$ 478.1053, found 478.1052.

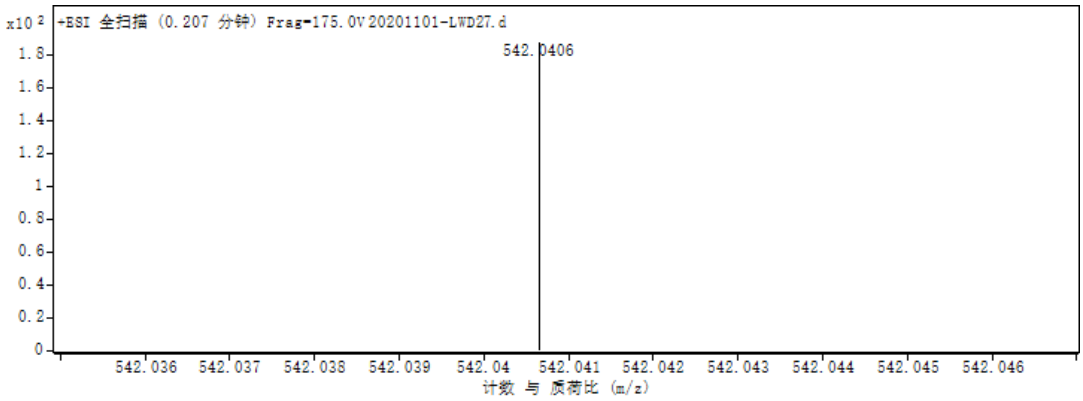


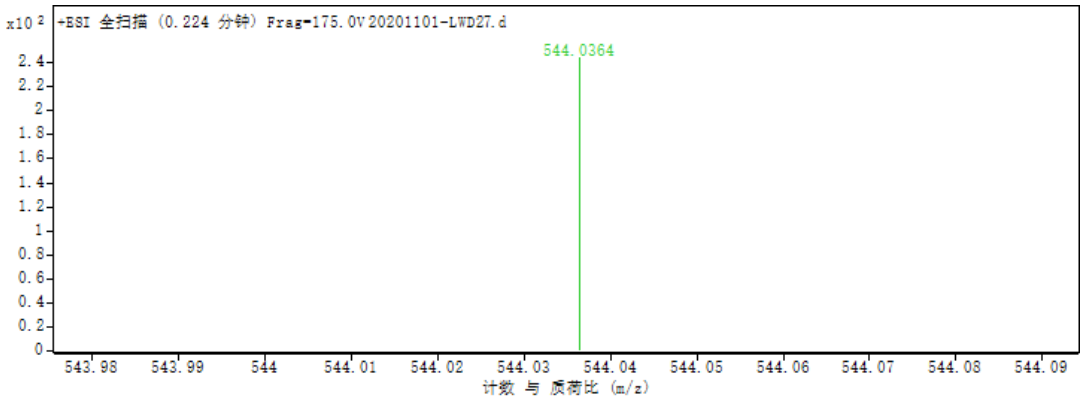


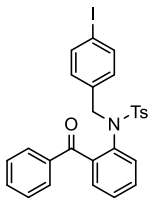


Compound S1l: 80% yield, white solid, m.p. = 138.7-140.1 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.01 – 6.91 (m, 3H), 4.89 (s, 2H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.8, 143.4, 139.5, 136.8, 136.7, 136.3, 135.1, 133.0,

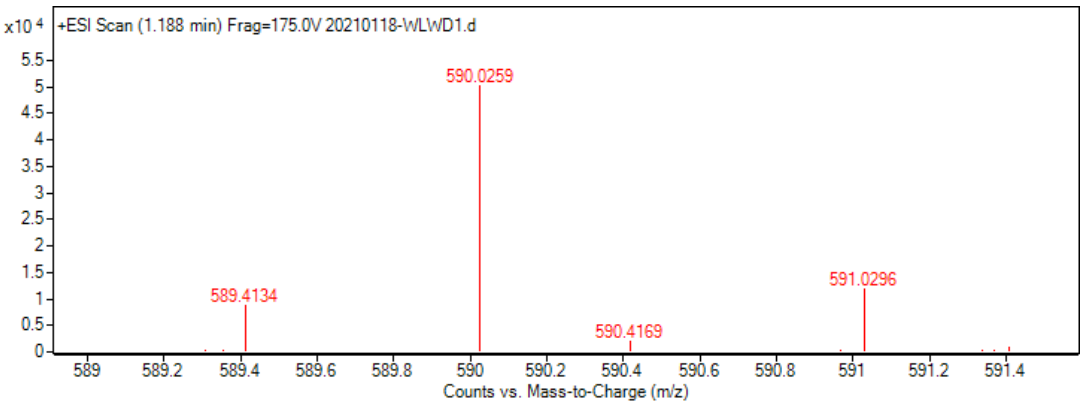
132.5, 131.5, 131.4, 130.8, 130.5, 130.2, 129.3, 128.0, 127.8, 127.5, 121.9, 56.0, 21.5. **IR** (KBr, cm^{-1}) 3063, 1668, 1596, 1487, 1446, 1403, 1346, 1289, 1263, 1160, 1091, 1068, 1011, 931, 862, 813, 765, 735, 703, 657, 637, 570, 545. **HRMS** (ESI) Calcd for $C_{27}H_{22}BrNNaO_3S$ $(M+Na)^+$ 542.0396, found 542.0406; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{22}BrNNaO_3S$ $(M+Na)^+$ 544.0376, found 544.0364.

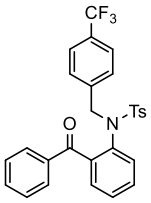




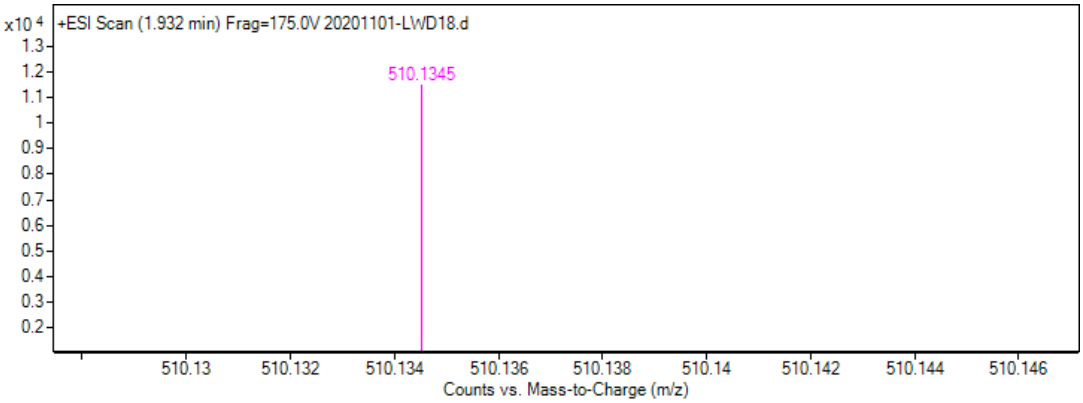


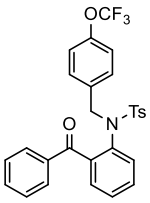
Compound S1m: 59% yield, white solid, m.p. = 130.3-133.4 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.03 – 6.92 (m, 5H), 4.87 (s, 2H), 2.21 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.9, 143.4, 139.5, 137.4, 136.9, 136.8, 136.4, 135.8, 133.0, 132.5, 131.7, 130.8, 130.6, 130.3, 129.4, 128.1, 127.9 127.6, 93.8, 56.2, 21.5. **IR** (KBr, cm^{-1}) 3060, 2924, 1669, 1596, 1485, 1448, 1346, 1289, 1264, 1161, 1091, 1061, 1008, 932, 863, 814, 735, 704, 657, 569, 546. **HRMS** (ESI) Calcd for $C_{27}H_{23}INNaO_3S$ $(M+Na)^+$ 590.0257, found 590.0259.



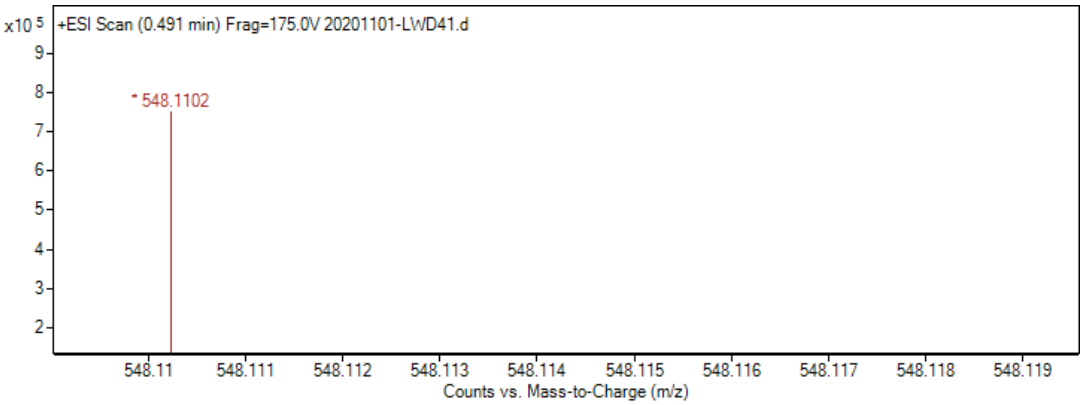


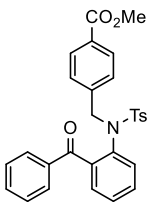
Compound S1n: 91% yield, white solid, m.p. = 149.2-151.5 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.40 (m, 6H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.01 – 6.94 (m, 3H), 5.01 (s, 2H), 2.21 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.46. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.0, 143.6, 140.3, 139.5, 137.1, 136.8, 136.3, 133.1, 132.6, 131.0, 130.6, 130.4, 130.00, 129.99 (q, *J* = 32.3 Hz), 129.4, 128.1, 127.9, 127.7, 125.3 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 272.2 Hz), 56.4, 21.5. **IR** (KBr, cm^{-1}) 3127, 1669, 1597, 1487, 1446, 1401, 1325, 1289, 1162, 1120, 1067, 1019, 932, 862, 815, 704, 657, 638, 570, 545. **HRMS** (ESI) Calcd for $C_{28}H_{23}F_3NO_3S$ $(M+H)^+$ 510.1345, found 510.1345.





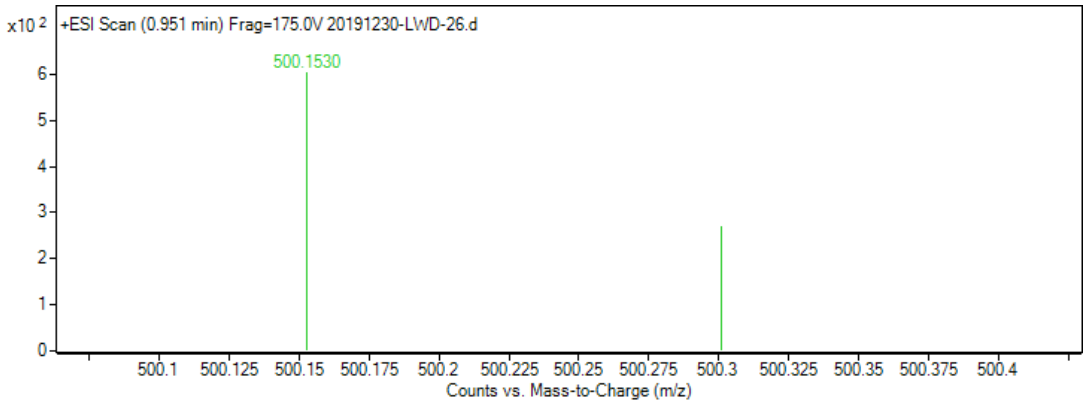
Compound S1o: 95% yield, white solid, m.p. = 110.1-112.9 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.26 (m, 5H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.99 – 6.92 (m, 3H), 4.96 (s, 2H), 2.19 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -57.76. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.0, 148.8(d, *J* = 1.4 Hz), 143.5, 139.5, 137.0, 136.8, 136.5, 135.0, 133.1, 132.6, 131.2, 130.8, 130.6, 130.3, 129.4, 128.1, 127.8, 127.6, 120.6, 120.5 (q, *J* = 257.0 Hz), 56.1, 21.42. **IR** (KBr, cm^{-1}) 3063, 1670, 1597, 1509, 1447, 1347, 1261, 1222, 1162, 1092, 1061, 931, 862, 815, 764, 735, 704, 657, 571, 546. **HRMS** (ESI) Calcd for $C_{28}H_{22}F_3NNaO_4S$ $(M+Na)^+$ 548.1114, found 548.1102.

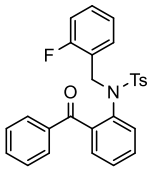




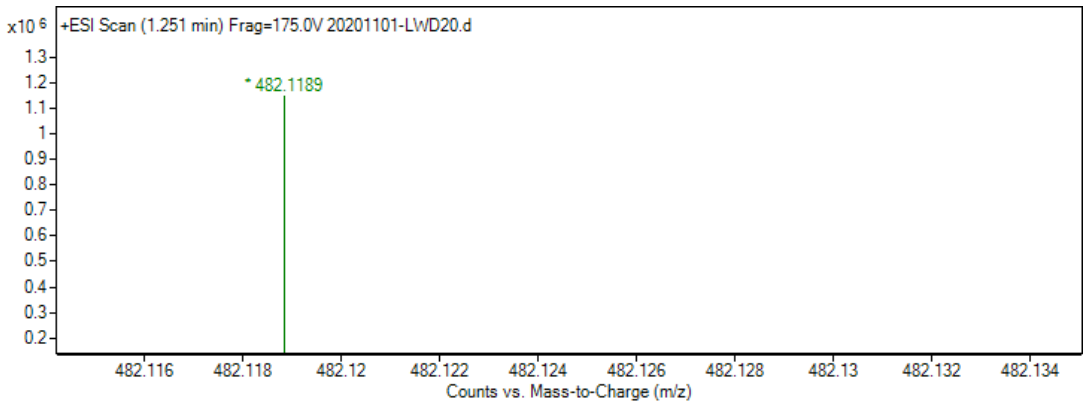
Compound S1p: 99% yield, white solid, m.p. = 133.1-135.1 °C, R_f = 0.2 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.31 (m, 4H), 7.32 – 7.27 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.95 – 6.90 (m, 1H), 5.01 (s, 2H), 3.89 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 167.0, 143.5, 141.4,

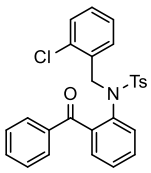
139.5, 136.9, 136.8, 136.5, 133.1, 132.8, 130.9, 130.7, 130.4, 129.8, 129.7, 129.6, 129.4, 128.1, 127.9, 127.6, 56.5, 52.2, 21.5. **IR** (KBr, cm^{-1}) 3064, 2952, 1721, 1669, 1597, 1441, 1347, 1283, 1161, 1110, 932, 865, 760, 705, 657, 571, 546. **HRMS** (ESI) Calcd for $C_{29}H_{26}NO_5S$ $(M+H)^+$ 500.1526, found 500.1530.



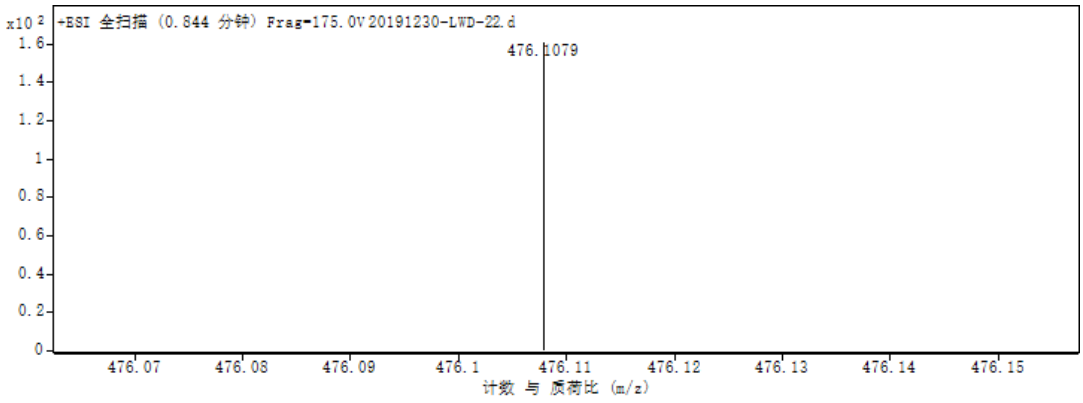


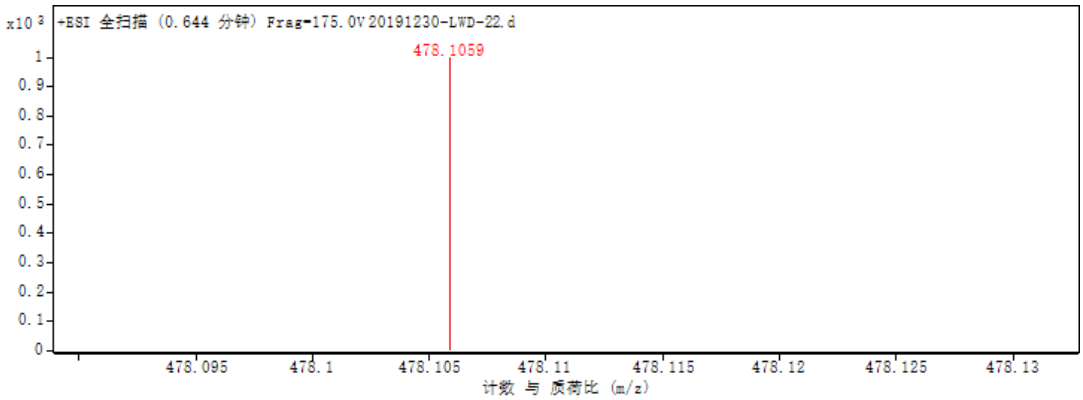
Compound S1q: 87% yield, white solid, m.p. = 122.8-126.5 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.20 – 7.12 (m, 1H), 7.04 – 6.93 (m, 4H), 6.85 (t, *J* = 9.0 Hz, 1H), 5.03 (s, 2H), 2.21 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.62. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.9, 161.14 (d, *J* = 247.7 Hz), 143.3, 139.7, 137.1, 137.0, 136.3, 132.8, 132.4 (d, *J* = 3.6 Hz), 131.9, 130.7, 130.6, 130.2, 129.73 (d, *J* = 8.2 Hz), 129.3, 128.0, 127.8, 127.5, 124.0 (d, *J* = 3.7 Hz), 123.1 (d, *J* = 14.4 Hz), 115.0 (d, *J* = 21.8 Hz), 49.6, 21.4. **IR** (KBr, cm^{-1}) 3063, 1669, 1597, 1493, 1450, 1346, 1289, 1265, 1230, 1160, 1111, 1091, 1060, 933, 865, 814, 762, 736, 704, 657, 639, 611, 570, 547. **HRMS** (ESI) Calcd for $C_{27}H_{22}FNNaO_3S$ $(M+Na)^+$ 482.1196 found 482.1189.

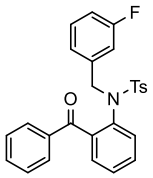




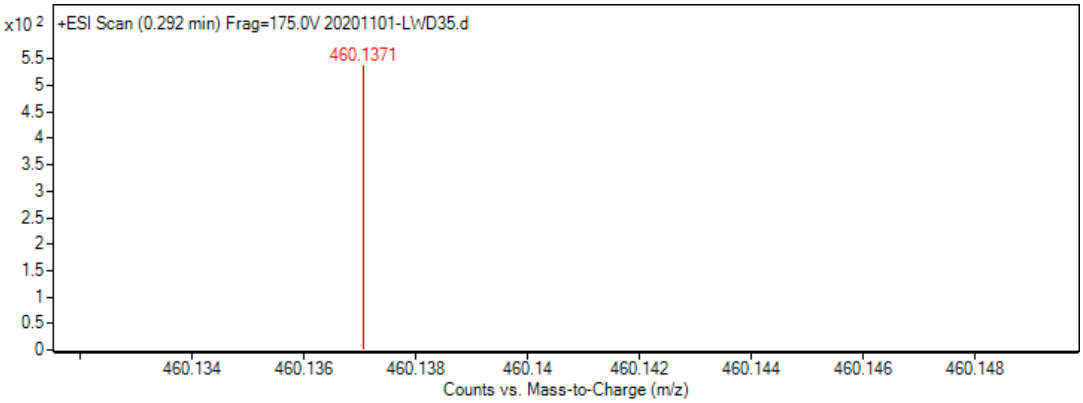
Compound S1r: 82% yield, white solid, m.p. = 159.3-165.0 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.22 – 7.11 (m, 3H), 7.05 – 6.98 (m, 3H), 5.16 (s, 2H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.9, 143.5, 139.6, 137.2, 137.0, 136.2, 134.5, 133.8, 132.9, 132.3, 132.2, 131.0, 130.7, 130.5, 129.4, 129.3, 129.2, 128.1, 128.0, 127.5, 127.1, 127.0, 53.5, 21.6. **IR** (KBr, cm^{-1}) 3062, 1668, 1594, 1483, 1444, 1345, 1291, 1260, 1160, 1093, 1039, 931, 857, 813, 756, 702, 655, 610, 566. **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_3S$ $(M+H)^+$ 476.1082, found 476.1079; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_3S$ $(M+H)^+$ 478.1053, found 478.1059.

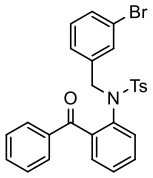




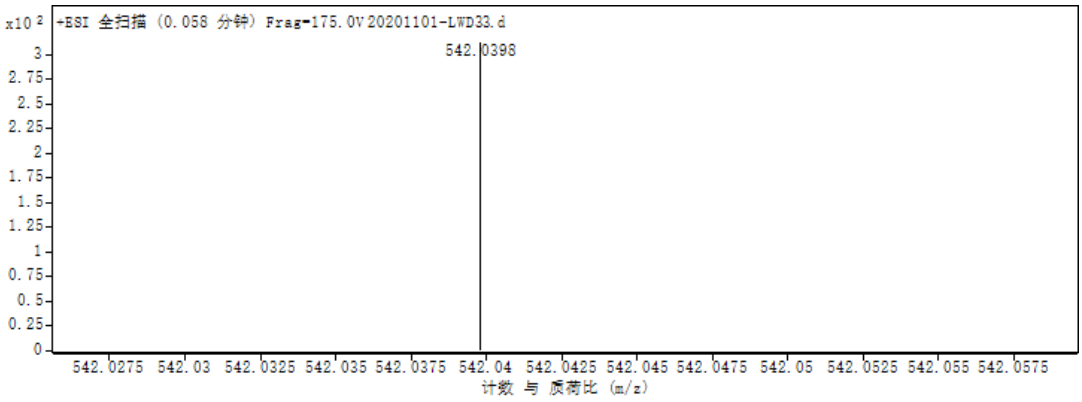


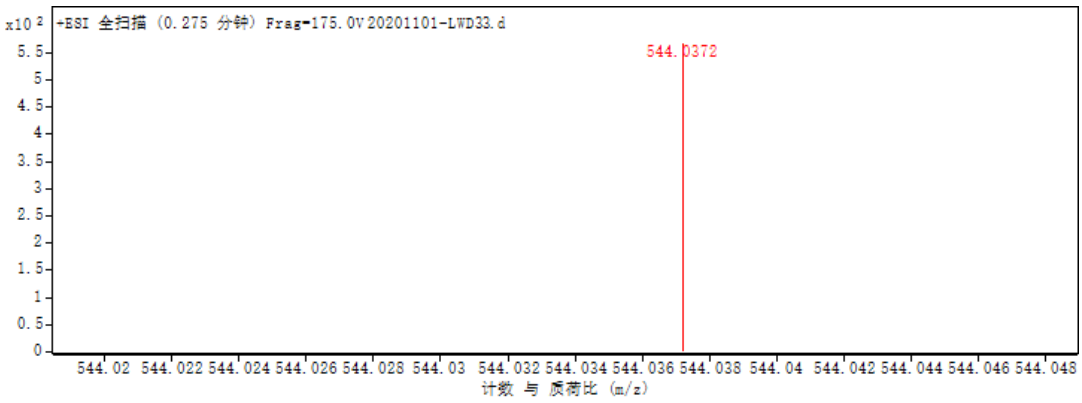
Compound S1s: 90% yield, white solid, m.p. = 113.0-114.6 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.21 – 7.14 (m, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.02 – 6.94 (m, 4H), 6.89 (td, *J* = 8.5, 2.3 Hz, 1H), 4.95 (s, 2H), 2.20 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.10. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.0, 162.7 (d, *J* = 245.9 Hz), 143.5, 139.5, 138.8 (d, *J* = 7.2 Hz), 136.9 (d, *J* = 10.9 Hz), 136.6, 133.1, 132.9, 130.9, 130.7, 130.3, 129.9, 129.8, 129.4, 128.1, 127.9, 127.6, 125.4 (d, *J* = 2.8 Hz), 116.6 (d, *J* = 21.2 Hz), 114.8 (d, *J* = 21.1 Hz), 56.4, 21.5. **IR** (KBr, cm^{-1}) 3063, 1669, 1595, 1487, 1448, 1347, 1289, 1261, 1161, 1092, 1057, 933, 875, 767, 737, 706, 658, 566. **HRMS** (ESI) Calcd for $C_{27}H_{23}FNO_3S$ $(M+H)^+$ 460.1377, found 460.1371.

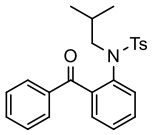




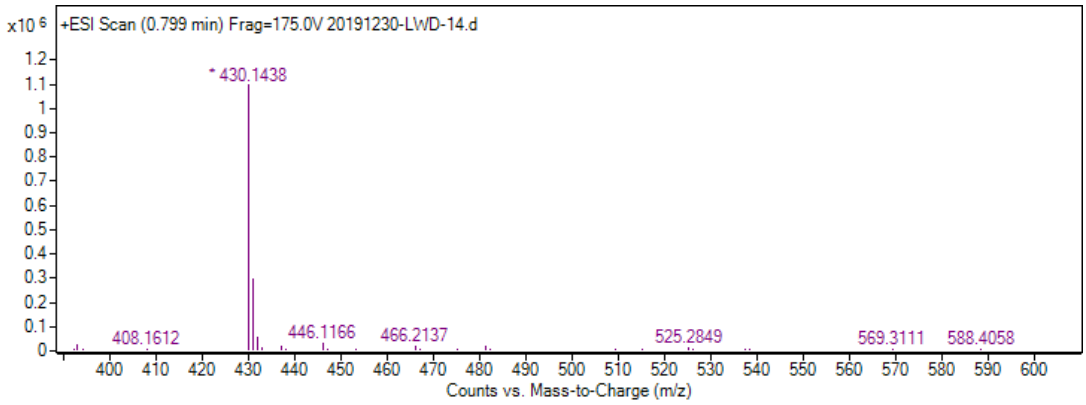
Compound S1t: 99% yield, white solid, m.p. = 105.4-107.3 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.27 (m, 5H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 8.1 Hz, 1H), 7.01 – 6.92 (m, 3H), 4.91 (s, 2H), 2.21 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 143.5, 139.6, 138.5, 136.9, 136.8, 136.6, 133.1, 132.8, 132.6, 130.9, 130.8, 130.6, 130.3, 129.9, 129.4, 128.4, 128.1, 127.8, 127.7, 122.3, 56.3, 21.5. **IR** (KBr, cm^{-1}) 3061, 2924, 1669, 1596, 1574, 1482, 1448, 1346, 1290, 1264, 1211, 1161, 1094, 1067, 933, 845, 813, 788, 766, 735, 705, 660, 639, 564. **HRMS** (ESI) Calcd for $C_{27}H_{22}BrNNaO_3S$ $(M+Na)^+$ 542.0396, found 542.0398; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{22}BrNNaO_3S$ $(M+Na)^+$ 544.0376, found 544.0372.

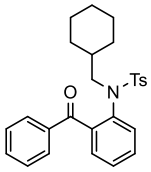




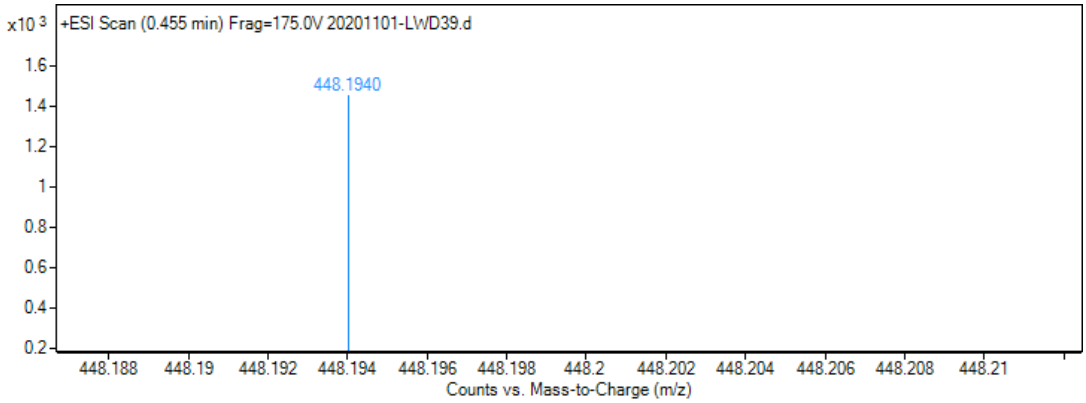


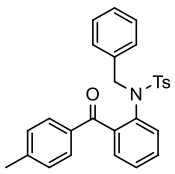
Compound S1u: 97% yield, white solid, m.p. = 111.4-112.5 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.48 – 7.37 (m, 5H), 7.38 – 7.30 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 2H), 3.45 (d, *J* = 34.3 Hz, 2H), 2.29 (s, 3H), 1.82 (hept, *J* = 6.8 Hz, 1H), 0.90 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.00, 143.3, 140.1, 138.1, 137.1, 135.9, 133.0, 130.8, 130.8, 130.3, 130.2, 129.3, 128.1, 128.0, 127.1, 60.0, 27.2, 21.6, 20.6. **IR** (KBr, cm^{-1}) 3061, 2958, 2871, 1672, 1596, 1487, 1447, 1346, 1289, 1262, 1159, 1090, 1061, 926, 850, 815, 771, 735, 705, 657, 638, 575, 548. **HRMS** (ESI) Calcd for $C_{24}H_{25}NNaO_3S$ $(M+Na)^+$ 430.1447, found 430.1438.



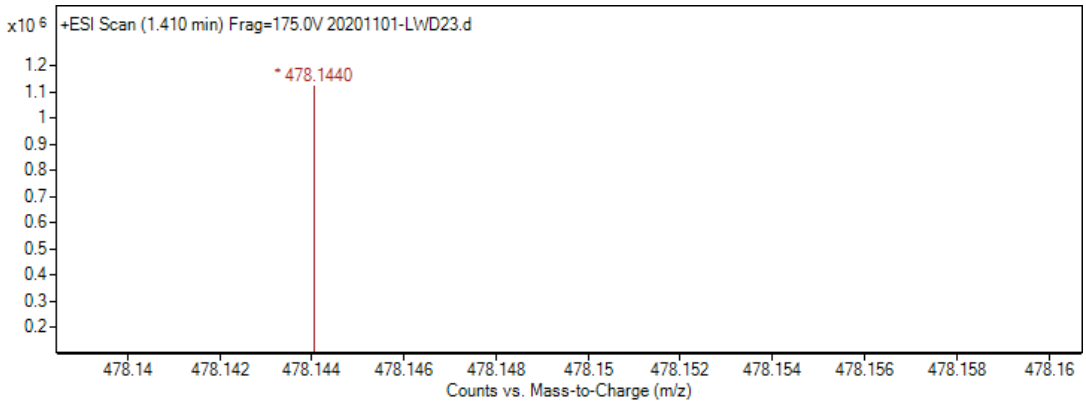


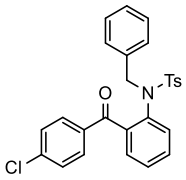
Compound S1v: 96% yield, white solid, m.p. = 105.5-106.8 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.31 (m, 7H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.46 (s, 2H), 2.29 (s, 3H), 1.85 – 1.40 (m, 6H), 1.21 – 1.05 (m, 3H), 0.92 – 0.77 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 143.27, 140.1, 138.3, 137.2, 136.1, 133.0, 130.8, 130.6, 130.2, 129.3, 128.1, 128.1, 127.1, 59.1, 36.2, 31.2, 26.5, 25.8, 21.6. **IR** (KBr, cm^{-1}) 3062, 2924, 2851, 1672, 1597, 1487, 1447, 1347, 1290, 1263, 1162, 1092, 1042, 932, 879, 821, 770, 734, 705, 657, 637, 579. **HRMS** (ESI) Calcd for $C_{27}H_{30}NO_3S$ $(M+H)^+$ 448.1941, found 448.1940.



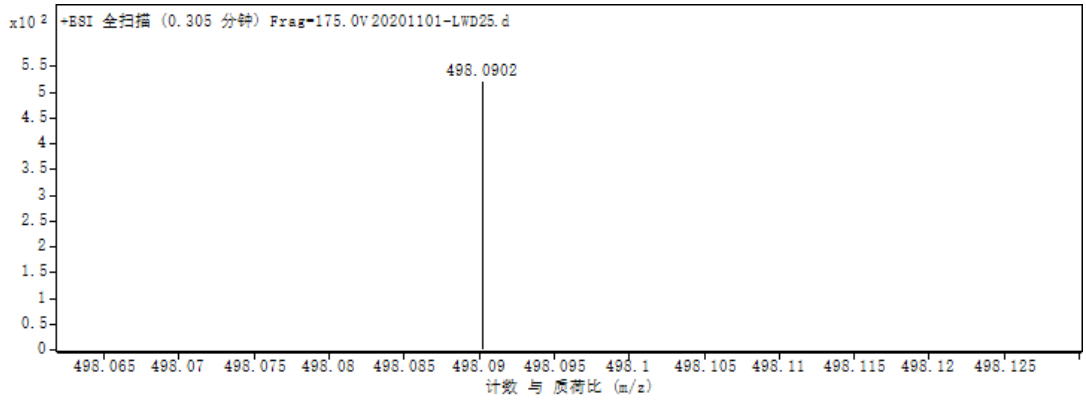


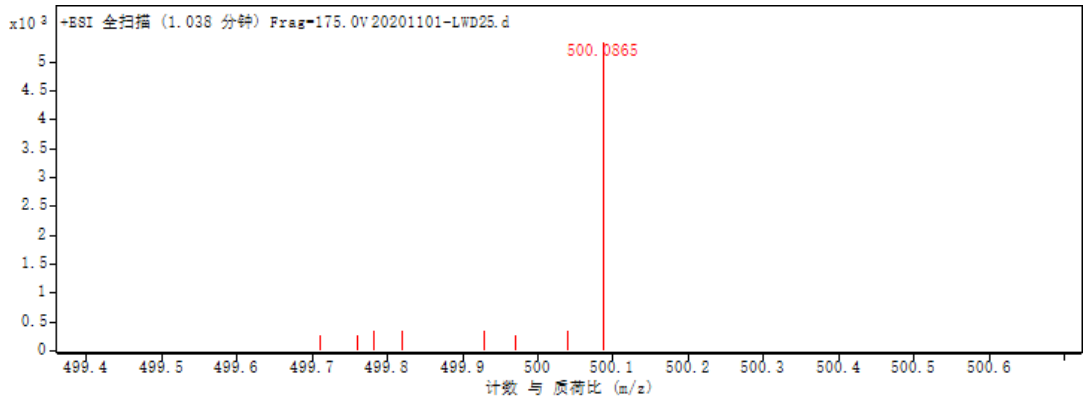
Compound S1w: 84% yield, white solid, m.p. = 117.5-119.1 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.33 – 7.13 (m, 10H), 7.01 – 6.88 (m, 3H), 4.97 (s, 2H), 2.41 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.8, 143.9, 143.2, 139.9, 136.9, 136.8, 136.2, 134.4, 133.2, 130.8, 130.5, 130.1, 129.9, 129.3, 128.8, 128.3, 127.9, 127.8, 127.4, 56.9, 21.8, 21.5. **IR** (KBr, cm^{-1}) 3031, 2923, 1664, 1603, 1488, 1448, 1342, 1291, 1265, 1214, 1159, 1092, 1055, 931, 861, 814, 776, 726, 698, 656, 607, 561. **HRMS** (ESI) Calcd for $C_{28}H_{25}NNaO_3S$ $(M+Na)^+$ 478.1447, found 478.1440.

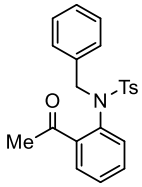




Compound S1x: 78% yield, white solid, m.p. = 149.9-151.7 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.25 (m, 4H), 7.27 – 7.16 (m, 6H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.95 – 6.86 (m, 1H), 4.94 (s, 2H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.8, 143.5, 139.5, 139.4, 137.0, 136.6, 135.9, 135.3, 132.6, 132.0, 130.9, 129.9, 129.8, 129.4, 128.4, 128.3, 127.9, 127.5, 56.8, 21.5. **IR** (KBr, cm^{-1}) 3064, 1671, 1590, 1486, 1448, 1400, 1344, 1290, 1263, 1215, 1160, 1091, 1056, 1020, 930, 860, 815, 777, 736, 656, 562. **HRMS** (ESI) Calcd for $C_{27}H_{22}ClNNaO_3S$ $(M+Na)^+$ 498.0901, found 498.0902; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{22}ClNNaO_3S$ $(M+Na)^+$ 500.0872, found 500.0865.

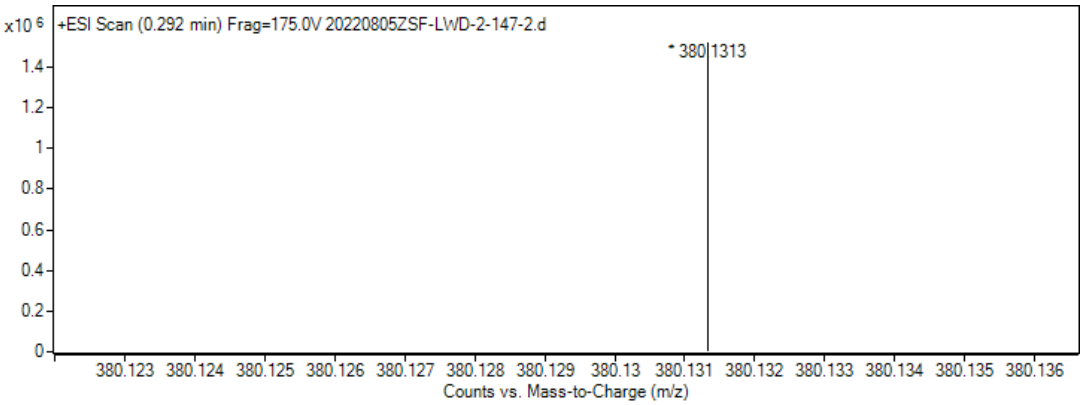


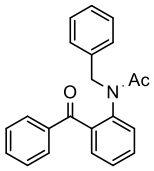




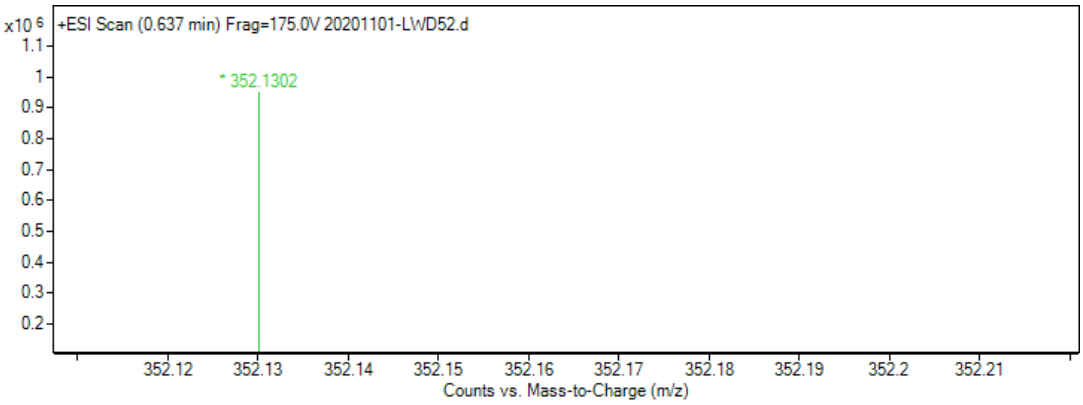
Compound S1y: Yield: 94%, white solid, m.p. = 118.4-119.7 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.16 (m, 5H), 6.74 (d, *J* = 7.7 Hz, 1H), 4.80 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 143.8, 141.4, 136.3, 135.5, 135.2, 131.2, 129.9, 129.53, 129.45, 129.4,

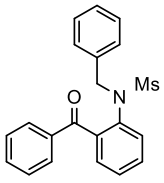
128.4, 128.3, 128.1, 128.0, 55.7, 29.9, 21.6. **IR** (KBr, cm^{-1}) 3065, 3032, 1691, 1596, 1488, 1447, 1348, 1285, 1243, 1162, 1090, 1042, 859, 816, 784, 739, 702, 655, 601, 562. **HRMS** (ESI) Calcd for $C_{22}H_{22}NO_3S$ $(M+H)^+$ 380.1315, found 380.1313.



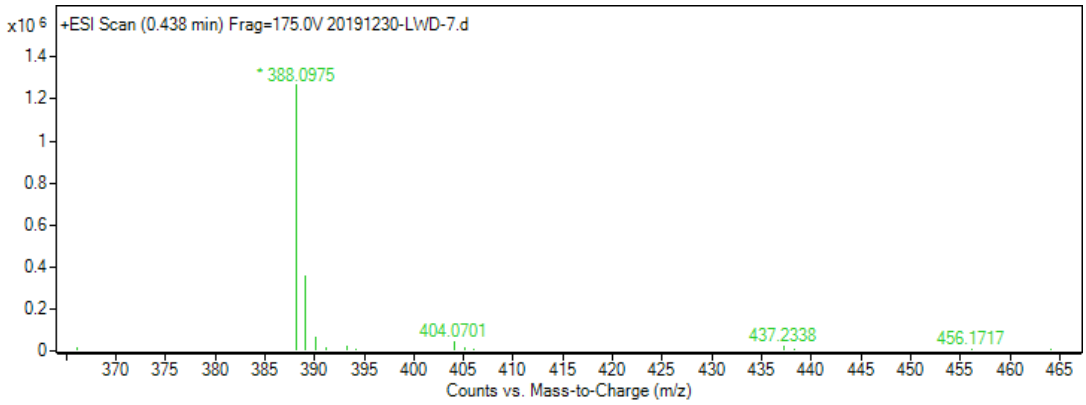


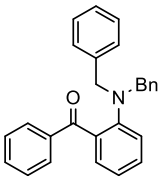
Compound S1aa: 88% yield, white solid, m.p. = 61.1-63.6 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.37 (m, 5H), 7.17 – 7.04 (m, 5H), 6.94 – 6.91 (m, 1H), 5.26 (d, *J* = 14.5 Hz, 2H), 4.17 (d, *J* = 14.4 Hz, 2H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.8, 170.7, 140.9, 137.0, 136.9, 136.5, 133.4, 131.4, 130.9, 130.0, 129.9, 129.0, 128.4, 128.1, 127.5, 127.3, 52.7, 22.9. **IR** (KBr, cm^{-1}) 3062, 3030, 2928, 1664, 1596, 1487, 1448, 1339, 1357, 1314, 1287, 1214, 1072, 932, 762, 733, 705, 637. **HRMS** (ESI) Calcd for $C_{22}H_{19}NNaO_2$ $(M+Na)^+$ 352.1308, found 352.1302.



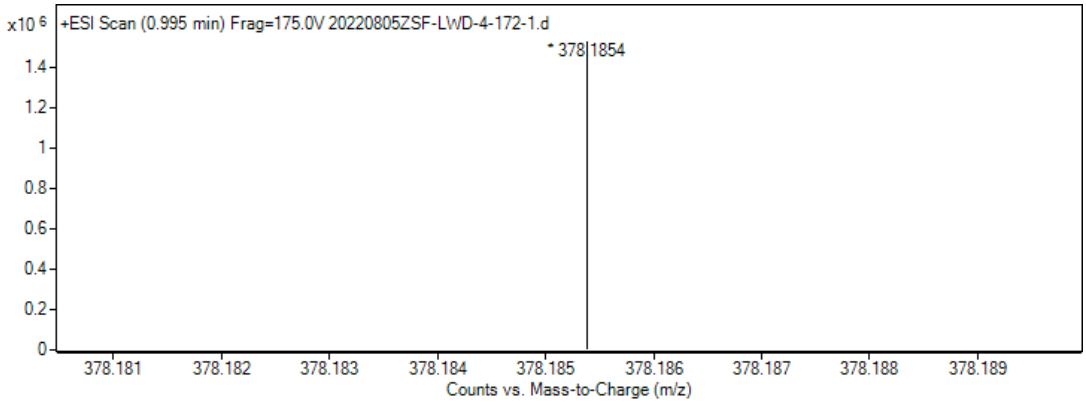


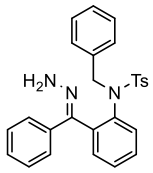
Compound S1ab: 99% yield, white solid, m.p. = 85.3-86.4 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.29 (m, 3H), 7.26 – 7.18 (m, 6H), 4.73 (s, 2H), 2.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.9, 138.6, 137.5, 137.0, 135.9, 133.6, 133.1, 131.0, 130.5, 130.0, 129.4, 128.54, 128.47, 128.0, 127.5, 55.9, 40.5. **IR** (KBr, cm^{-1}) 3062, 3031, 2933, 1667, 1595, 1488, 148, 1337, 1289, 1264, 1151, 1063, 960, 932, 861, 778, 703, 638, 540, 518. **HRMS** (ESI) Calcd for $C_{21}H_{19}NNaO_3S$ $(M+Na)^+$ 388.0978, found 388.0975.



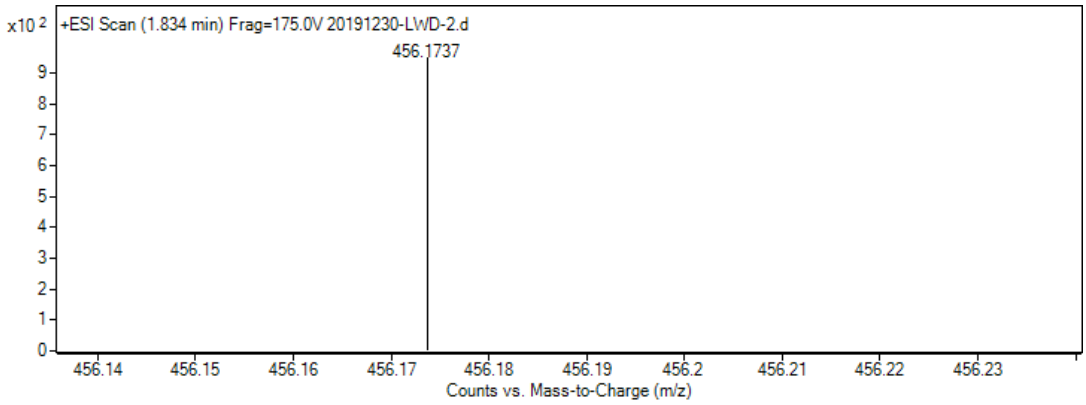


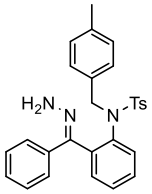
Compound 1ac: 96% yield, bright yellow oil, R_f = 0.6 (petroleum ether: ethyl acetate = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.30 (m, 2H), 7.17 – 7.10 (m, 6H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.85 – 6.79 (m, 4H), 4.01 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.2, 150.0, 138.4, 137.2, 134.5, 132.9, 130.8, 129.8, 129.7, 128.8, 128.5, 128.1, 127.1, 122.2, 121.7, 56.6. **IR** (KBr, cm^{-1}) 3061, 3028, 1662, 1595, 1489, 1448, 1315, 1289, 1260, 926, 742, 700, 641. **HRMS** (ESI) Calcd for $C_{27}H_{24}NO$ $(M+H)^+$ 378.1852, found 378.1854.



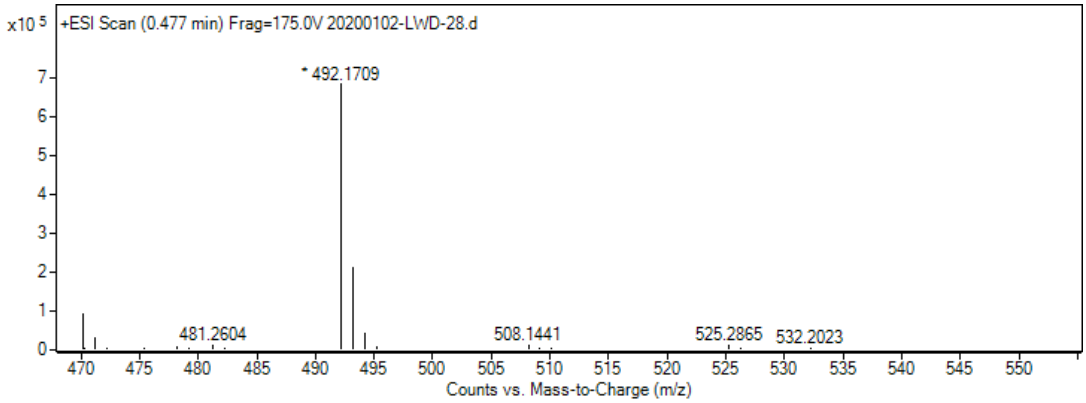


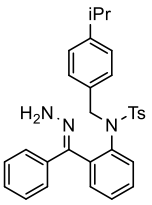
Compound S1a': 46% yield, yellowish white solid, m.p. = 139.7-141.2 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 5H), 7.39 (d, *J* = 6.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.22 (m, 3H), 7.18 – 7.03 (m, 4H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.71 (d, *J* = 6.5 Hz, 2H), 5.52 (s, 2H), 4.37 (d, *J* = 14.8 Hz, 1H), 3.99 (d, *J* = 14.5 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1, 143.6, 138.6, 138.5, 136.9, 134.9, 134.8, 131.8, 131.3, 129.7, 129.6, 129.4, 129.2, 128.4, 128.2, 128.0, 127.7, 126.3, 54.9, 21.6. **IR** (KBr, cm^{-1}) 3408, 3299, 3061, 3032, 2925, 1596, 1494, 1447, 1331, 1268, 1213, 1159, 1090, 1033, 858, 816, 771, 736, 698, 658, 609, 566. **HRMS** (ESI) Calcd for $C_{27}H_{26}N_3O_2S$ $(M+H)^+$ 456.1740, found 456.1737.



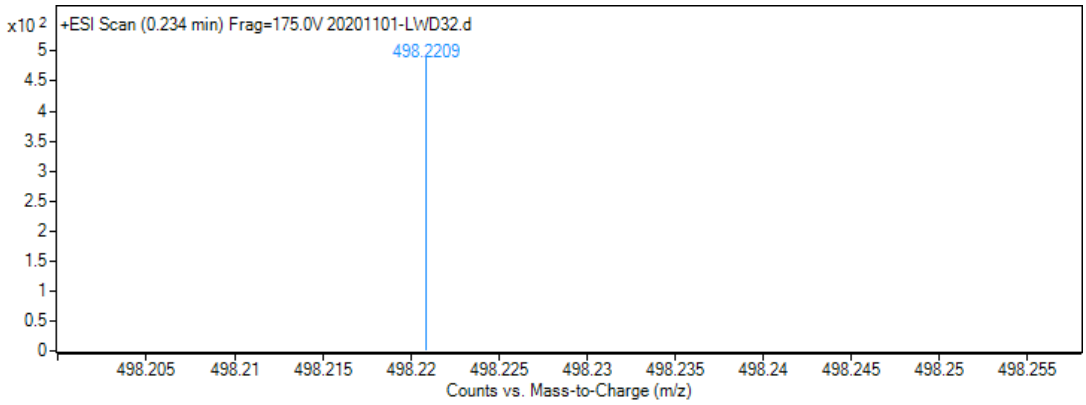


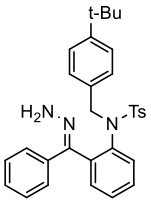
Compound S1b': 74% yield, yellowish white solid, m.p. = 121.0-124.1 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.31 (m, 7H), 7.26 (d, *J* = 6.0 Hz, 3H), 7.20 – 7.08 (m, 3H), 6.78 (d, *J* = 7.5 Hz, 2H), 6.56 (s, 2H), 5.59 (s, 2H), 4.31 (d, *J* = 14.6 Hz, 1H), 3.97 (d, *J* = 14.0 Hz, 1H), 2.38 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2, 143.6, 138.6, 138.5, 137.4, 136.9, 135.0, 131.8, 131.7, 131.3, 129.7, 129.6, 129.4, 129.2, 128.7, 128.4, 128.3, 128.1, 126.3, 54.8, 21.6, 21.1. **IR** (KBr, cm^{-1}) 3409, 3299, 3057, 2923, 1594, 1488, 1444, 1330, 1266, 1157, 1089, 1042, 861, 813, 737, 696, 657, 572, 547. **HRMS** (ESI) Calcd for $C_{28}H_{27}N_3NaO_2S$ $(M+Na)^+$ 492.1716, found 492.1709.



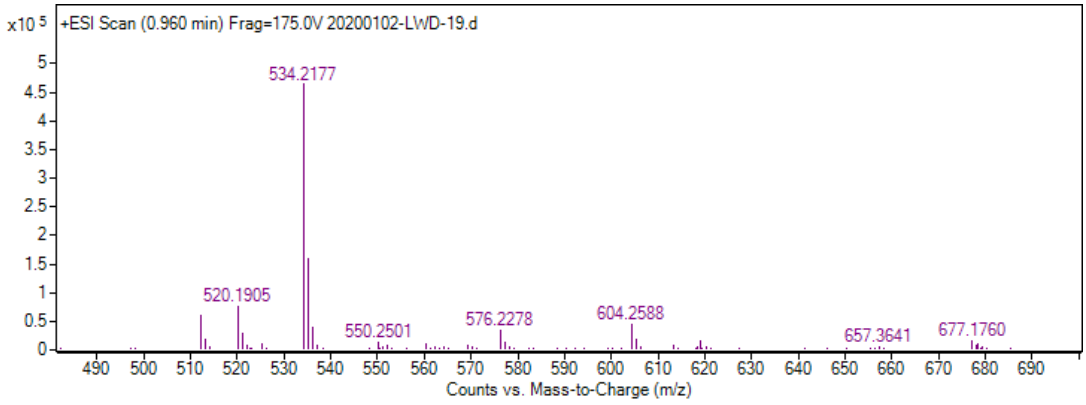


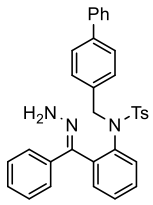
Compound S1c': 29% yield, yellowish white foam, m.p. = 65.9-69.9 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ7.55 – 7.36 (m, 7H), 7.36 – 7.19 (m, 4H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 7.7 Hz, 2H), 6.59 (s, 2H), 5.28 (s, 2H), 4.30 (d, *J* = 14.4 Hz, 1H), 4.04 (d, *J* = 13.5 Hz, 1H), 2.75 (hept, *J* = 6.8 Hz, 1H), 2.36 (s, 3H), 1.15 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.4, 147.4, 143.4, 139.1, 138.6, 137.2, 134.9, 132.1, 131.6, 131.4, 129.9, 129.8, 129.29, 129.26, 128.43, 128.40, 128.3, 126.4, 126.1, 55.2, 33.8, 24.04, 24.00, 21.6. **IR** (KBr, cm^{-1}) 3410, 3300, 3059, 2961, 2927, 1596, 1488, 1444, 1329, 1157, 1090, 1058, 863, 840, 815, 769, 736, 694, 657, 572, 547. **HRMS** (ESI) Calcd for $C_{30}H_{32}N_3O_2S$ $(M+H)^+$ 498.2210, found 498.2209.



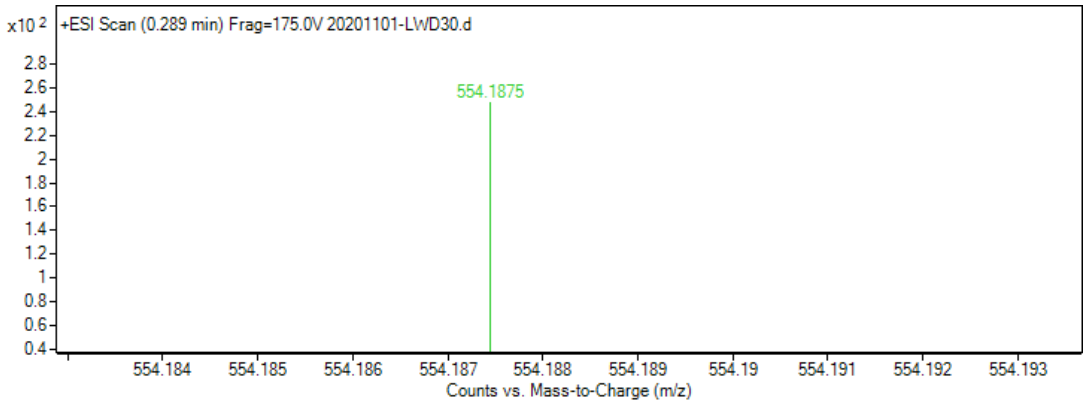


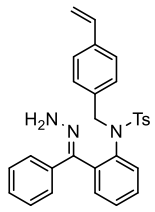
Compound S1d': 82% yield, yellowish white foam, m.p. = 63.6-66.5 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 3H), 7.44 – 7.37 (m, 4H), 7.33 – 7.24 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.59 (s, 2H), 5.56 (s, 2H), 4.30 (d, *J* = 14.2 Hz, 1H), 4.07 (d, *J* = 12.9 Hz, 1H), 2.34 (s, 3H), 1.21 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.6, 147.3, 143.3, 139.3, 138.6, 137.2, 134.9, 131.7, 131.5, 131.3, 129.9, 129.5, 129.3, 129.2, 128.42, 128.35, 128.3, 126.4, 124.9, 55.2, 34.5, 31.4, 21.6. **IR** (KBr, cm^{-1}) 3408, 3229, 3059, 2962, 2869, 1596, 1488, 1445, 1130, 1267, 1158, 1090, 1024, 863, 813, 768, 737, 698, 657, 572, 549. **HRMS** (ESI) Calcd for $C_{31}H_{33}N_3NaO_2S$ $(M+Na)^+$ 534.2185, found 534.2177.



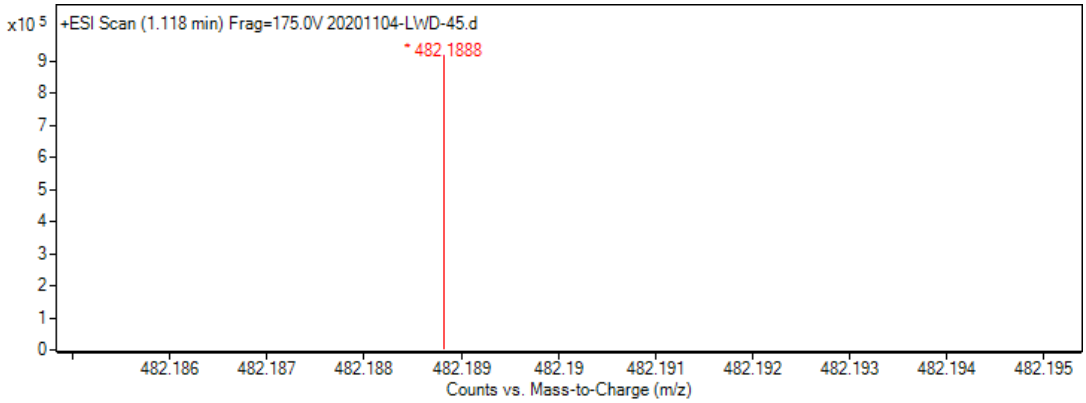


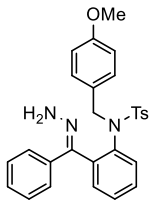
Compound S1e': 58% yield, yellowish white foam, m.p. = 92.1-98.4 °C, R_f = 0.2 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.37 (m, 11H), 7.35 – 7.25 (m, 5H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.72 (s, 2H), 5.54 (s, 2H), 4.36 (d, *J* = 14.6 Hz, 1H), 4.15 (d, *J* = 14.3 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.3, 143.6, 140.7, 140.6, 139.1, 138.6, 137.0, 135.0, 133.8, 131.54, 131.45, 130.1, 130.0, 129.39, 129.36, 128.9, 128.5, 128.5, 128.3, 127.5, 127.0, 126.7, 126.4, 55.2, 21.6. **IR** (KBr, cm^{-1}) 3407, 3298, 3058, 1596, 1487, 1444, 1406, 1329, 1265, 1157, 1089, 1043, 843, 815, 765, 737, 698, 658, 569, 545. **HRMS** (ESI) Calcd for $C_{33}H_{29}N_3NaO_2S$ $(M+Na)^+$ 554.1872, found 554.1875.



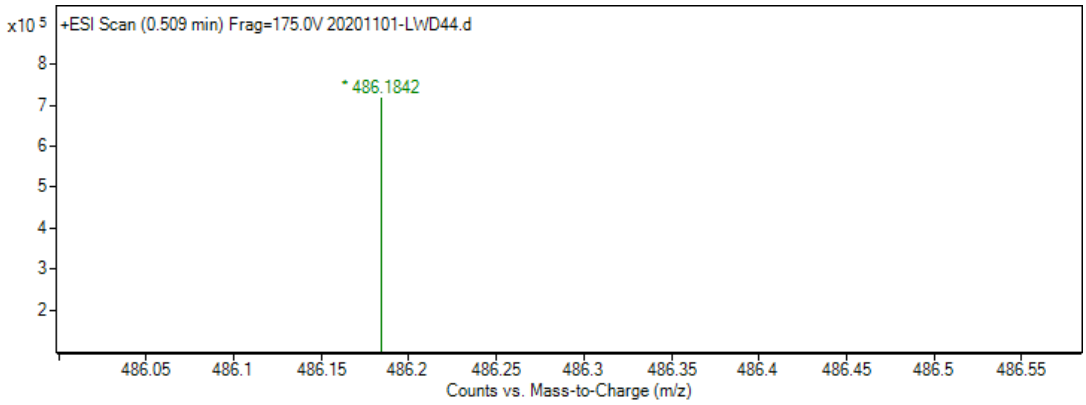


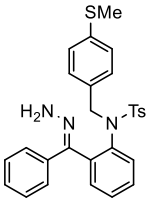
Compound S1f': 71% yield, yellowish white foam, m.p. = 182.4-218.9 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.57 – 7.33 (m, 8H), 7.29 – 7.25 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.70 – 6.49 (m, 3H), 5.63 (d, *J* = 17.6 Hz, 1H), 5.39 (s, 2H), 5.18 (d, *J* = 10.9 Hz, 1H), 4.32 (d, *J* = 14.6 Hz, 1H), 4.04 (d, *J* = 14.2 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2, 143.7, 138.7, 138.6, 137.0, 136.8, 136.4, 135.0, 134.3, 131.6, 131.4, 129.83, 129.79, 129.4, 129.3, 128.41, 128.39, 128.2, 126.3, 125.8, 114.0, 54.9, 21.6. **IR** (KBr, cm^{-1}) 3408, 3300, 3058, 2924, 1627, 1596, 1512, 1488, 1444, 1407, 1330, 1268, 1214, 1158, 1089, 1043, 993, 911, 847, 817, 770, 736, 695, 659, 573, 546. **HRMS** (ESI) Calcd for $C_{29}H_{28}N_3O_2S$ $(M+H)^+$ 482.1897, found 482.1888.



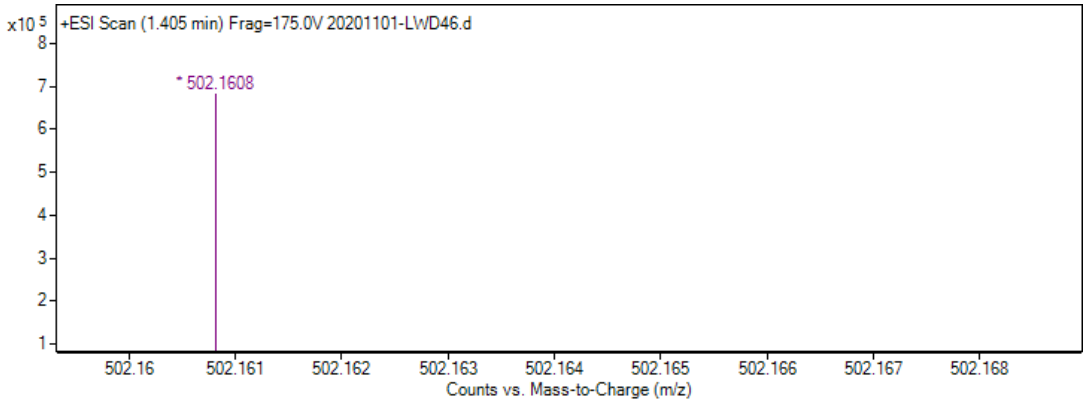


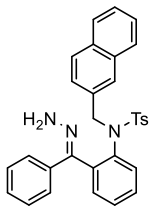
Compound S1g': 36% yield, yellowish white foam, m.p. = 57.7-74.9 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 3H), 7.45 – 7.39 (m, 3H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.12 (s, 1H), 6.59 (s, 2H), 6.50 (d, *J* = 8.3 Hz, 2H), 5.59 (s, 2H), 4.27 (d, *J* = 14.6 Hz, 1H), 3.94 (d, *J* = 11.8 Hz, 1H), 3.70 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.2, 147.4, 143.6, 138.7, 138.5, 137.0, 135.1, 131.9, 131.4, 131.0, 129.8, 129.4, 129.3, 128.5, 128.4, 128.3, 126.8, 126.4, 113.4, 55.2, 54.5, 21.6. **IR** (KBr, cm^{-1}) 3406, 3300, 3061, 2934, 1609, 1513, 1488, 1444, 1328, 1248, 1157, 1113, 1089, 1034, 949, 861, 840, 816, 771, 735, 693, 657, 573, 548. **HRMS** (ESI) Calcd for $C_{28}H_{28}N_3O_3S$ $(M+H)^+$ 486.1846, found 486.1842.



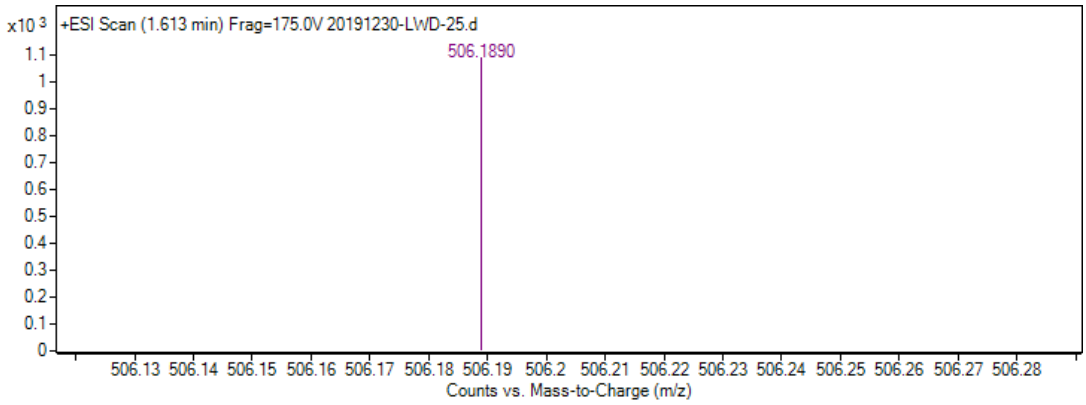


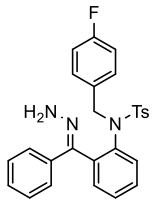
Compound S1h': 79% yield, yellowish white foam, m.p. = 60.1-66.3 °C, R_f = 0.15 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.33 (m, 7H), 7.31 – 7.22 (m, 3H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 6.63 – 6.50 (m, 2H), 5.10 (s, 2H), 4.27 (d, *J* = 14.6 Hz, 1H), 4.03 (d, *J* = 14.5 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2, 143.6, 138.7, 138.5, 138.1, 136.7, 134.9, 131.5, 131.3, 130.0, 129.8, 129.4, 129.3, 128.4, 128.2, 126.2, 125.8, 54.8, 21.6, 15.6. **IR** (KBr, cm^{-1}) 3408, 3300, 3058, 2924, 1627, 1596, 1512, 1488, 1444, 1407, 1330, 1268, 1214, 1158, 1089, 1043, 993, 949, 911, 847, 817, 770, 736, 695, 659, 573, 546. **HRMS** (ESI) Calcd for $C_{28}H_{28}N_3O_2S_2$ $(M+H)^+$ 502.1618, found 502.1608.



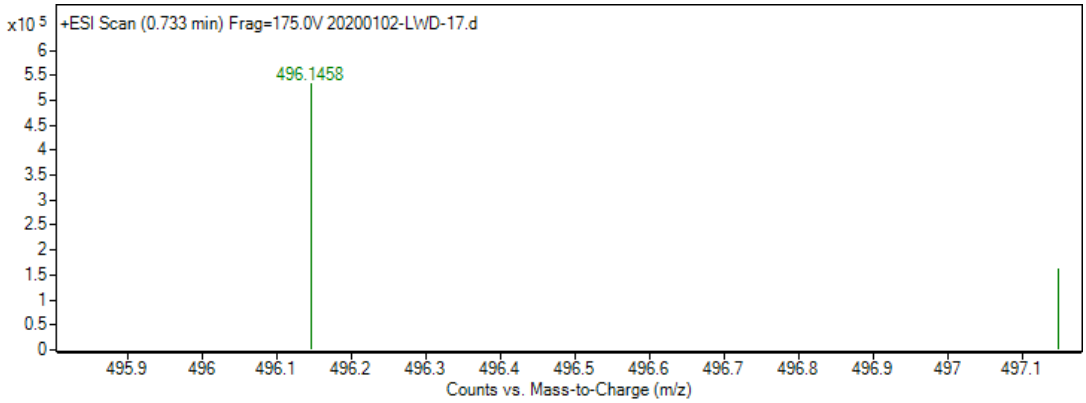


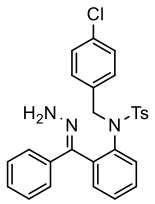
Compound S1i': 70% yield, yellowish white foam, m.p. = 77.0-86.9 °C, R_f = 0.2 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 1H), 7.53 – 7.35 (m, 12H), 7.32 – 7.20 (m, 3H), 7.03 – 6.95 (m, 3H), 6.81 – 6.69 (m, 1H), 5.21 (s, 2H), 4.49 (d, *J* = 14.5 Hz, 1H), 4.30 (d, *J* = 14.6 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.4, 143.7, 139.2, 138.6, 137.0, 135.0, 132.9, 132.1, 131.5, 131.4, 130.1, 129.4, 129.3, 129.0, 128.5, 128.4, 127.9, 127.7, 127.5, 127.2, 126.4, 126.1, 125.9, 55.7, 21.5. **IR** (KBr, cm^{-1}) 3408, 3300, 3056, 2923, 1596, 1488, 1444, 1328, 1269, 1157, 1089, 1043, 951, 896, 859, 816, 756, 696, 661, 572, 547, 478. **HRMS** (ESI) Calcd for $C_{31}H_{28}N_3O_2S$ $(M+H)^+$ 506.1897, found 506.1890.



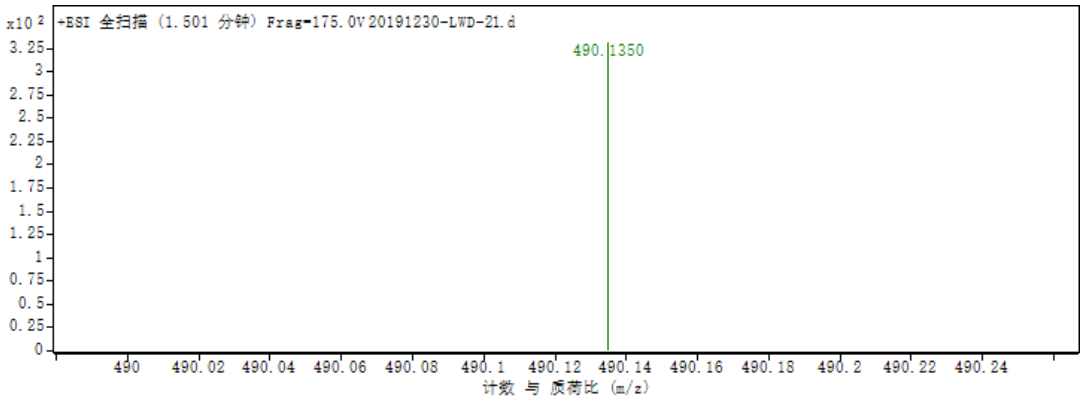


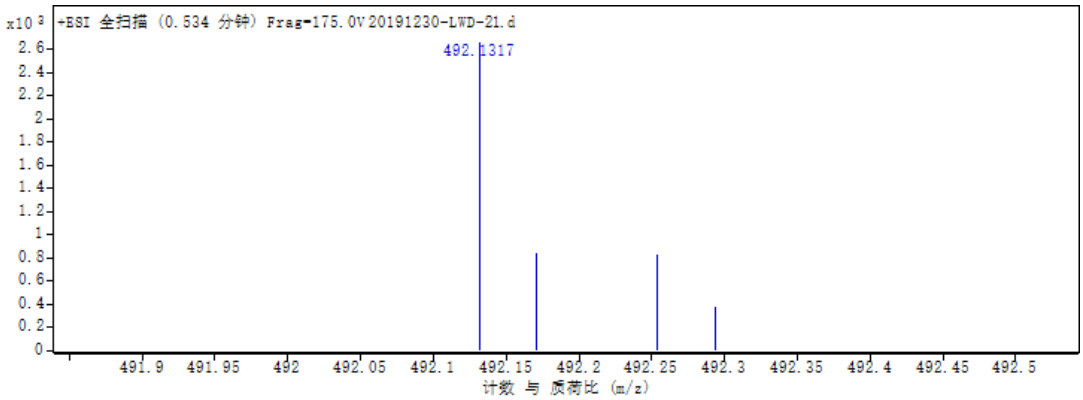
Compound S1j': 68% yield, yellowish white solid, m.p. = 145.5-147.5 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 3H), 7.44 – 7.33 (m, 4H), 7.29 – 7.26 (m, 3H), 7.18 – 7.11 (m, 3H), 6.78 – 6.48 (m, 4H), 5.63 (s, 2H), 4.28 (d, *J* = 14.7 Hz, 1H), 4.05 (d, *J* = 14.6 Hz, 1H), 2.39 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.48. **^{13}C NMR** (126 MHz, $CDCl_3$) δ162.4 (d, *J* = 246.6 Hz), 147.2, 143.8, 138.71, 138.65, 136.8, 135.0, 131.6, 131.5, 131.3 (d, *J* = 8.2 Hz), 130.6 (d, *J* = 2.7 Hz), 129.9, 129.5, 129.4, 128.5, 128.3, 126.3, 114.9 (d, *J* = 21.3 Hz), 54.5, 21.6. **IR** (KBr, cm^{-1}) 3408, 3299, 3062, 2925, 1600, 1510, 1489, 1443, 1328, 1222, 1157, 1089, 1037, 842, 768, 735, 692, 655, 570, 547. **HRMS** (ESI) Calcd for $C_{27}H_{24}FN_3NaO_2S$ $(M+Na)^+$ 496.1495, found 496.1458.

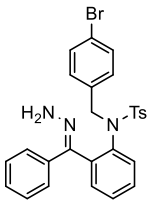




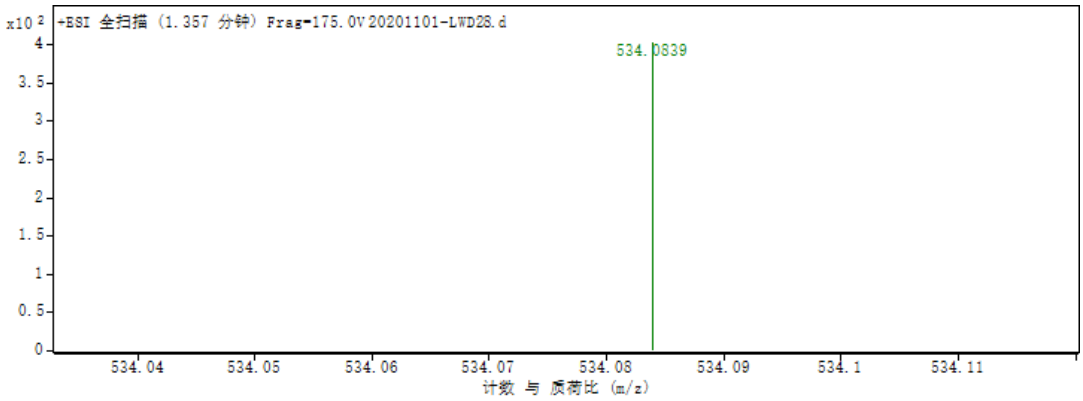
Compound S1k': 75% yield, yellowish white solid, m.p. = 120.0-121.1 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.34 (m, 7H), 7.28 – 7.17 (m, 4H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.67 – 6.48 (m, 2H), 5.65 (s, 2H), 4.24 (d, *J* = 14.7 Hz, 1H), 4.11 (d, *J* = 14.9 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 143.8, 138.8, 138.5, 136.4, 134.8, 133.5, 133.1, 131.4, 131.1, 130.8, 129.9, 129.4, 128.4, 128.2, 128.0, 126.1, 54.7, 21.6. **IR** (KBr, cm^{-1}) 3408, 3300, 3060, 2924, 1597, 1493, 1444, 1408, 1329, 1267, 1158, 1090, 1039, 1016, 948, 862, 813, 768, 737, 695, 658, 571, 547. **HRMS** (ESI) Calcd for $C_{27}H_{25}ClN_3O_2S$ $(M+H)^+$ 490.1351, found 490.1350; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{25}ClN_3O_2S$ $(M+H)^+$ 492.1322, found 492.1317.

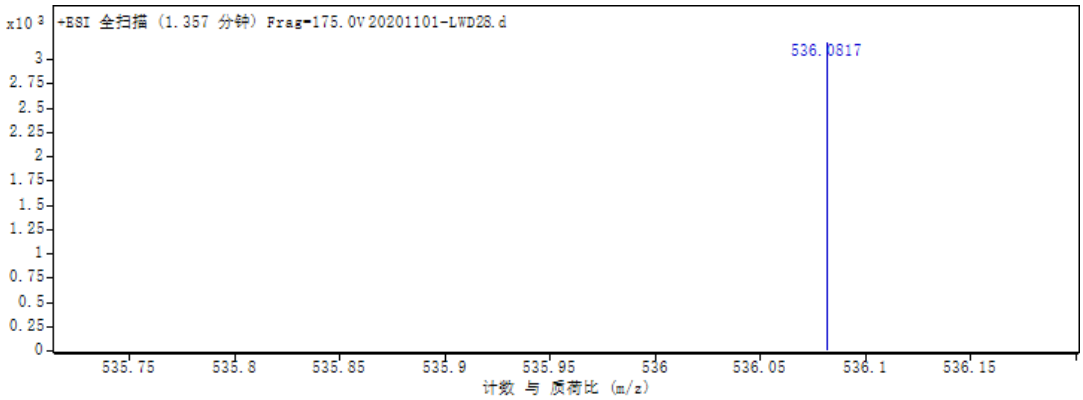


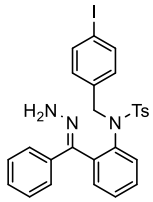




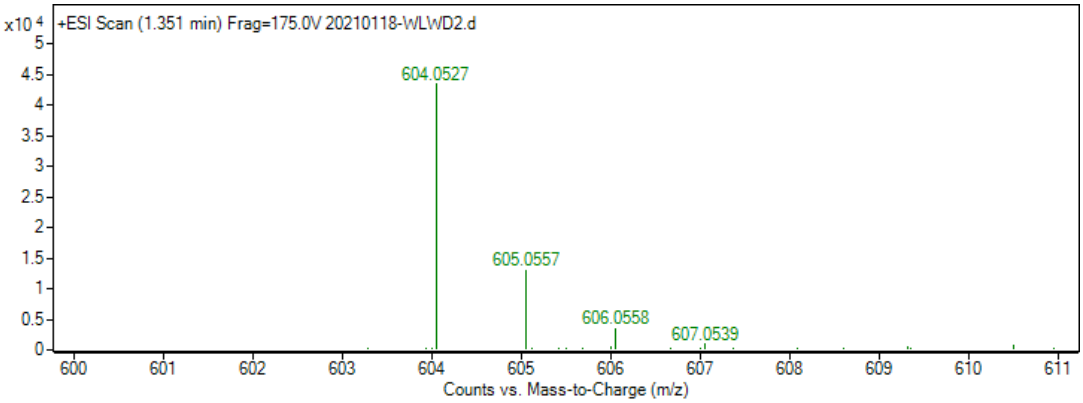
Compound S1l': 41% yield, yellowish white solid, m.p. = 117.0-119.4 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.35 (m, 6H), 7.26 – 7.20 (m, 4H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.49 (s, 2H), 4.23 (d, *J* = 14.6 Hz, 1H), 4.12 (d, *J* = 14.4 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.1, 143.9, 139.0, 138.5, 136.5, 134.8, 133.7, 131.5, 131.2, 131.0, 130.0, 129.4, 128.4, 128.3, 126.1, 121.9, 54.9, 21.7. **IR** (KBr, cm^{-1}) 3403, 3300, 3059, 2923, 1593, 1487, 1443, 1406, 1329, 1158, 1089, 1068, 1042, 1011, 862, 811, 768, 737, 692, 657, 570, 546. **HRMS** (ESI) Calcd for $C_{27}H_{25}BrN_3O_2S$ $(M+H)^+$ 534.0846, found 534.0839; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{25}BrN_3O_2S$ $(M+H)^+$ 536.0825, found 534.0817.

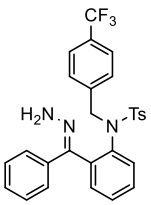




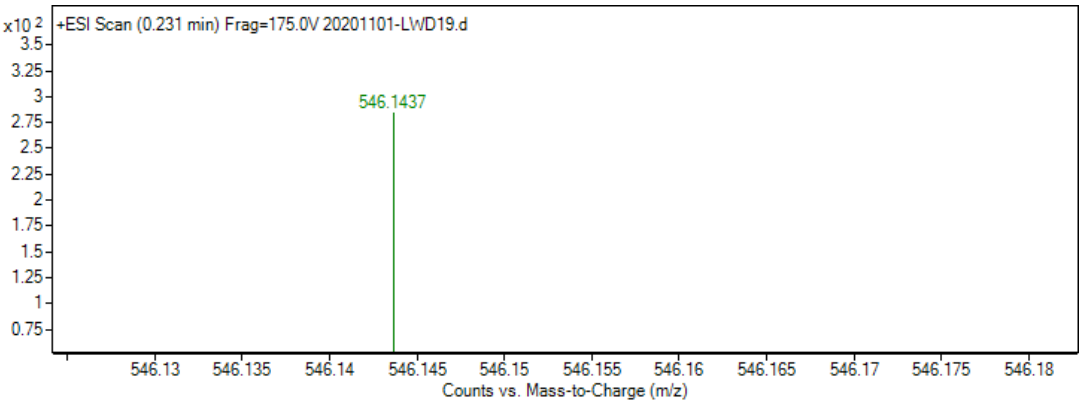


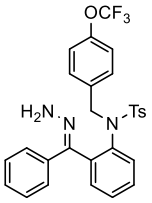
Compound S1m': 37% yield, yellowish white foam, m.p. = 66.6-72.5 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.36 (m, 6H), 7.27 – 7.25 (m, 4H), 7.22 (d, *J* = 8.1 Hz, 4H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.34 (s, 2H), 5.54 (s, 2H), 4.21 (d, *J* = 14.6 Hz, 1H), 4.13 (d, *J* = 14.6 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.1, 143.9, 139.1, 138.5, 137.0, 136.6, 134.8, 134.3, 131.5, 131.4, 131.1, 130.1, 129.4, 128.5, 128.4, 128.3, 126.2, 93.8, 55.1, 21.7. **IR** (KBr, cm^{-1}) 3406, 3299, 3059, 2923, 1593, 1486, 1444, 1403, 1329, 1159, 1089, 1060, 1007, 948, 861, 812, 768, 736, 695, 658, 570, 546. **HRMS** (ESI) Calcd for $C_{27}H_{25}IN_3O_2S$ $(M+Na)^+$ 604.0526, found 604.0527.



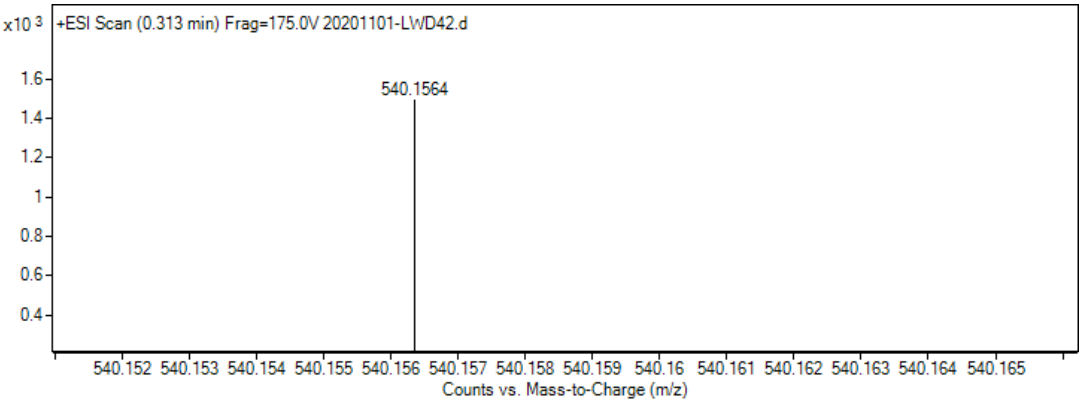


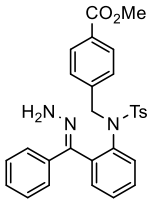
Compound S1n': 28% yield, yellowish white foam, m.p. = 84.3-89.0 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (td, *J* = 7.4, 1.0 Hz, 1H), 7.49 – 7.35 (m, 6H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.23 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.77 – 6.67 (m, 2H), 5.26 (s, 2H), 4.32 (s, 2H), 2.35 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.7. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.2, 144.0, 139.5, 138.7, 138.5, 136.4, 134.7, 131.5, 130.9, 130.2, 129.70, 129.69 (q, *J* = 34.0 Hz), 129.6, 129.4, 128.5, 128.5, 126.1, 124.8 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 272.1 Hz), 55.4, 21.5. **IR** (KBr, cm^{-1}) 3409, 3301, 3063, 2924, 1595, 1489, 1443, 1421, 1325, 1160, 1122, 1066, 1020, 843, 815, 769, 737, 693, 657, 569, 545. **HRMS** (ESI) Calcd for $C_{28}H_{24}F_3N_3NaO_2S$ $(M+Na)^+$ 546.1433, found 546.1437.



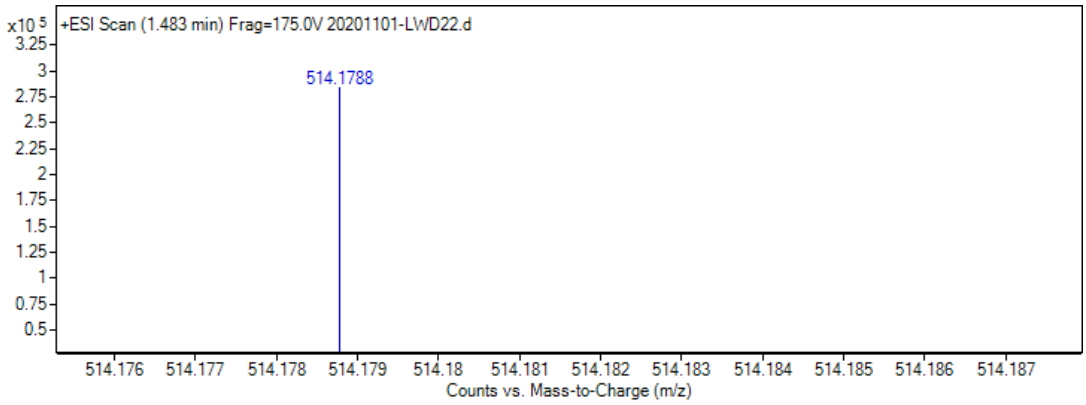


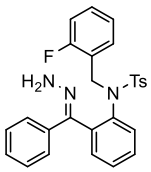
Compound S1o': 47% yield, yellowish white foam, m.p. = 84.3-89.0 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.38 (m, 6H), 7.30 – 7.25 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 8.1 Hz, 2H), 6.66 (s, 2H), 5.58 (s, 2H), 4.28 (d, *J* = 14.6 Hz, 1H), 4.20 (d, *J* = 14.6 Hz, 1H), 2.36 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -57.84. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.7, 147.2, 143.9, 139.3, 138.6, 136.7, 134.8, 133.5, 131.5, 131.2, 131.0, 130.1, 129.5, 129.4, 128.5, 128.4, 126.2, 120.32, 120.32(q, *J* = 257.2 Hz), 54.9, 21.5. **IR** (KBr, cm^{-1}) 3408, 3300, 3062, 2926, 1596, 1508, 1444, 1330, 1262, 1222, 1159, 1090, 1040, 859, 816, 770, 735, 694, 657, 571, 547. **HRMS** (ESI) Calcd for $C_{28}H_{25}F_3N_3O_3S$ $(M+H)^+$ 540.1563, found 540.1564.



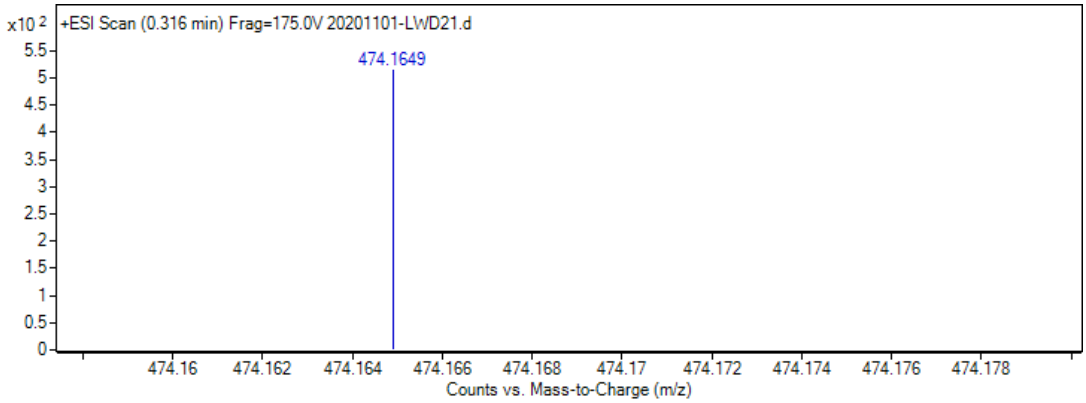


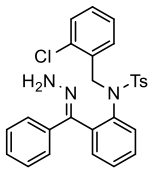
Compound S1p': 15% yield, yellowish white foam, m.p. = 70.3-85.1 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.44 (m, 3H), 7.43 – 7.35 (m, 4H), 7.26 – 7.24 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.77 – 6.68 (m, 2H), 5.44 (s, 2H), 4.37 (d, *J* = 15.0 Hz, 1H), 4.17 (d, *J* = 14.9 Hz, 1H), 3.87 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.8, 147.1, 144.0, 140.0, 138.9, 138.6, 136.5, 134.9, 131.5, 131.4, 130.0, 129.51, 129.48, 129.44, 129.39, 129.3, 128.5, 128.4, 126.3, 54.9, 52.2, 21.6. **IR** (KBr, cm^{-1}) 3407, 3300, 3060, 2951, 1720, 1603, 1488, 1441, 1331, 1282, 1159, 1111, 1046, 964, 861, 813, 771, 735, 698, 658, 572, 546. **HRMS** (ESI) Calcd for $C_{29}H_{28}N_3O_4S$ $(M+H)^+$ 514.1795, found 514.1788.



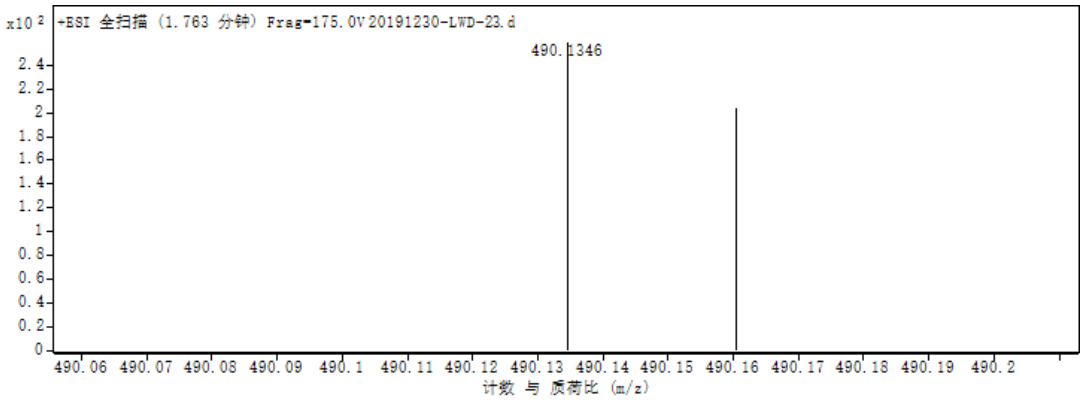


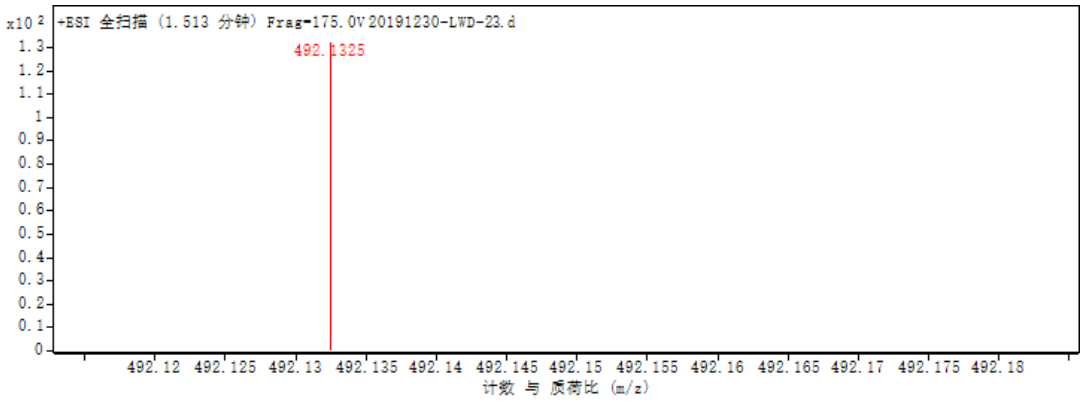
Compound S1q': 96% yield, yellowish white solid, m.p. = 121.2-127.3 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 3H), 7.45 – 7.33 (m, 4H), 7.27 – 7.21 (m, 3H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.3 Hz, 2H), 6.85 – 6.70 (m, 3H), 5.61 (s, 2H), 4.31 (d, *J* = 15.1 Hz, 1H), 4.16 (d, *J* = 15.1 Hz, 1H), 2.39 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.56. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0 (d, *J* = 247.8 Hz), 147.2, 143.9, 138.7 (d, *J* = 12.7 Hz), 136.1, 135.1, 132.2 (d, *J* = 3.7 Hz), 131.6, 131.2, 129.8, 129.8, 129.7, 129.4, 129.4, 128.5, 128.3, 128.2, 126.3, 123.9 (d, *J* = 3.6 Hz), 122.1 (d, *J* = 14.3 Hz), 115.1 (d, *J* = 22.0 Hz), 48.4, 21.7. **IR** (KBr, cm^{-1}) 3408, 3301, 3060, 1591, 1491, 1448, 1333, 1270, 1228, 1159, 1089, 1036, 946, 861, 816, 763, 738, 694, 656, 570, 548. **HRMS** (ESI) Calcd for $C_{27}H_{25}FN_3O_2S$ $(M+H)^+$ 474.1646, found 474.1649.

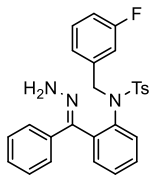




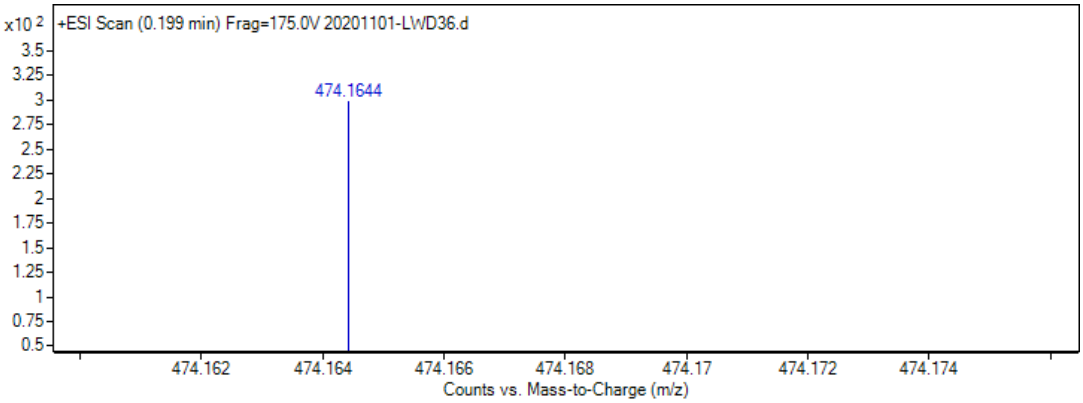
Compound S1r': 79% yield, yellowish white solid, m.p. = 127.0-129.2 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 4H), 7.38 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.33 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.12 (m, 5H), 7.03 (d, *J* = 7.3 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.87 – 6.77 (m, 2H), 5.43 (s, 2H), 4.53 (d, *J* = 15.4 Hz, 1H), 4.43 (d, *J* = 15.5 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.1, 144.0, 140.0, 138.6, 135.6, 134.9, 133.5, 132.7, 131.8, 131.5, 130.3, 129.9, 129.4, 129.3, 129.1, 128.8, 128.7, 128.2, 128.0, 126.4, 126.2, 53.1, 21.6. **IR** (KBr, cm^{-1}) 3409, 3302, 3061, 2925, 1596, 1486, 1444, 1335, 1269, 1209, 1161, 1090, 1038, 947, 851, 817, 740, 697, 657, 570, 547. **HRMS** (ESI) Calcd for $C_{27}H_{25}ClN_3O_2S$ $(M+H)^+$ 490.1351, found 490.1346; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{25}ClN_3O_2S$ $(M+H)^+$ 492.1322, found 492.1325.

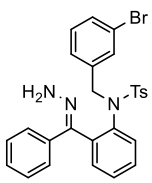






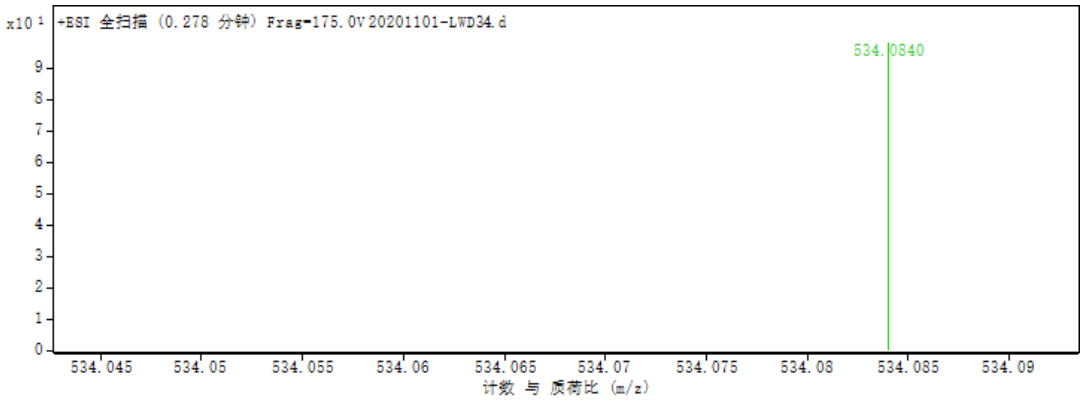
Compound S1s': 49% yield, yellowish white foam, m.p. = 63.9-65.4 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 – 7.36 (m, 7H), 7.32 – 7.25 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.00 – 6.92 (m, 1H), 6.75 (td, *J* = 8.4, 2.0 Hz, 1H), 6.55 (d, *J* = 6.8 Hz, 1H), 6.34 – 6.24 (m, 1H), 5.49 (s, 2H), 4.32 (d, *J* = 14.9 Hz, 1H), 4.07 (d, *J* = 14.8 Hz, 1H), 2.39 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.29. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.9 Hz), 147.2, 143.9, 138.8, 138.5, 137.4 (d, *J* = 7.0 Hz), 136.7, 134.9, 131.6, 131.4, 130.0, 129.48, 129.47, 129.4, 128.5, 128.4, 126.3, 125.2 (d, *J* = 2.7 Hz), 116.4 (d, *J* = 21.9 Hz), 114.7 (d, *J* = 21.2 Hz), 54.7, 21.6. **IR** (KBr, cm^{-1}) 3408, 3300, 3062, 2925, 1616, 1593, 1488, 1447, 1331, 1256, 1208, 1159, 1090, 1043, 927, 879, 815, 769, 738, 692, 658, 570, 548. **HRMS** (ESI) Calcd for $C_{27}H_{25}FN_3O_2S$ $(M+H)^+$ 474.1646, found 476.1644.

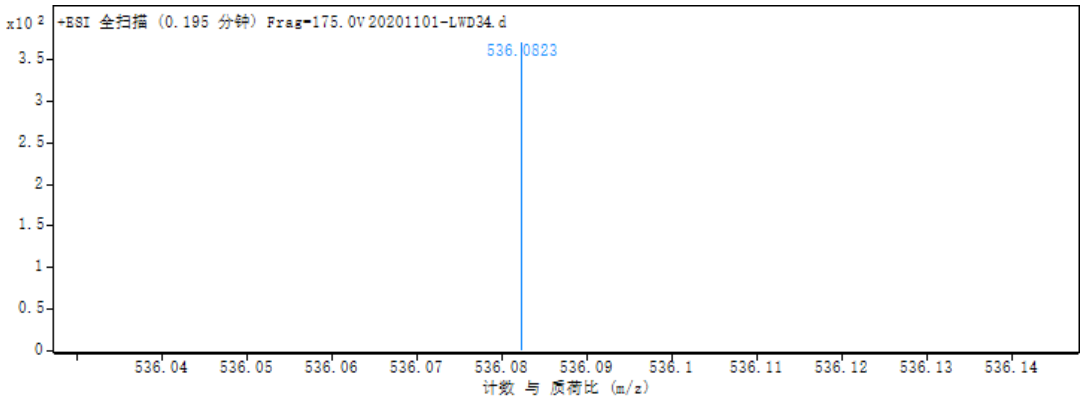


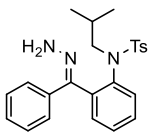


Compound S1t': 50% yield, yellowish white foam, m.p. = 56.8-71.1 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.39 (m, 6H), 7.34 – 7.25 (m, 4H), 7.17 – 7.09 (m, 3H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 5.8 Hz, 1H), 6.50 (s, 1H), 5.51 (s, 2H), 4.27 (d, *J* = 14.7 Hz, 1H), 4.10

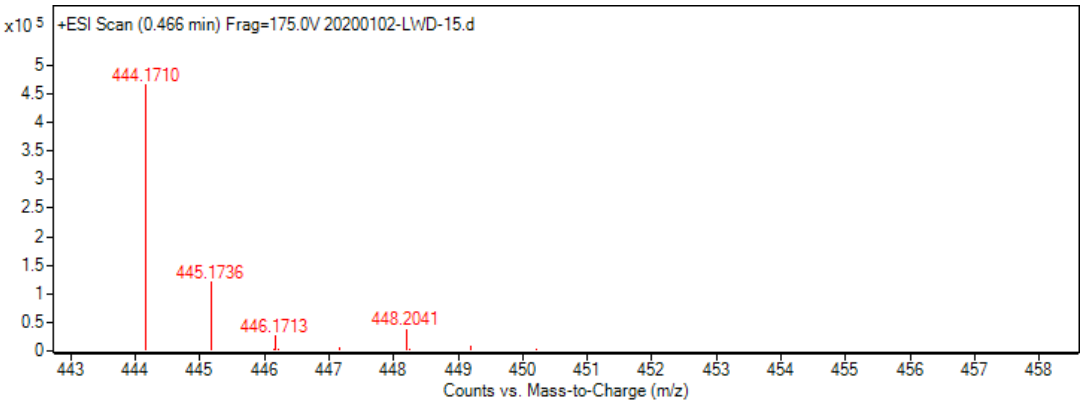
(d, *J* = 14.6 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.2, 144.0, 139.2, 138.5, 136.9, 136.8, 134.8, 132.5, 131.4, 131.3, 130.8, 130.1, 129.5, 129.5, 128.6, 128.5, 128.3, 128.2, 126.2, 122.2, 55.0, 21.7. **IR** (KBr, cm^{-1}) 3407, 3299, 3060, 2923, 1597, 1571, 1485, 1444, 1330, 1266, 1207, 1158, 1090, 1067, 1041, 889, 845, 815, 768, 736, 695, 660, 568. **HRMS** (ESI) Calcd for $C_{27}H_{25}BrN_3O_2S$ $(M+H)^+$ 534.0846, found 534.0840. isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{25}BrN_3O_2S$ $(M+H)^+$ 536.0825, found 536.0823.

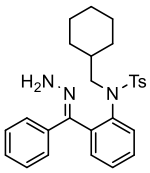




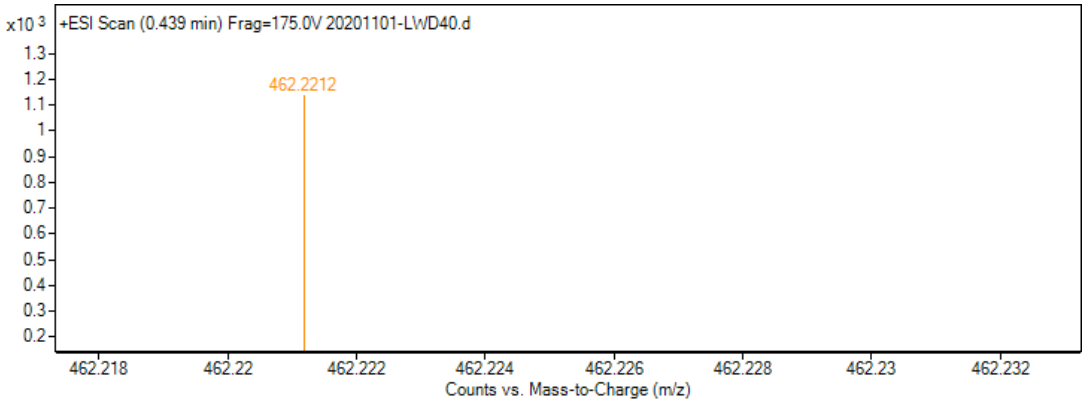


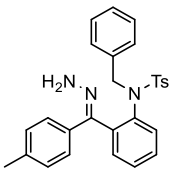
Compound S1u': 27% yield, yellowish white solid, m.p. = 106.2-107.8 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.54 – 7.36 (m, 6H), 7.28 – 7.21 (m, 5H), 5.68 (s, 2H), 3.02 – 2.88 (m, 2H), 2.42 (s, 3H), 1.24 (s, 1H), 0.46 (s, 3H), 0.20 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.6, 143.8, 138.8, 138.7, 136.6, 131.9, 130.3, 129.9, 129.6, 129.1, 128.4, 128.2, 128.1, 126.2, 58.4, 26.6, 21.7, 20.1, 19.7. **IR** (KBr, cm^{-1}) 3412, 3303, 3059, 2961, 2872, 1594, 1488, 1444, 1338, 1267, 1221, 1155, 1089, 1064, 1040, 961, 855, 817, 768, 739, 698, 659, 577, 546. **HRMS** (ESI) Calcd for $C_{24}H_{27}N_3NaO_2S$ $(M+Na)^+$ 444.1716, found 444.1710.



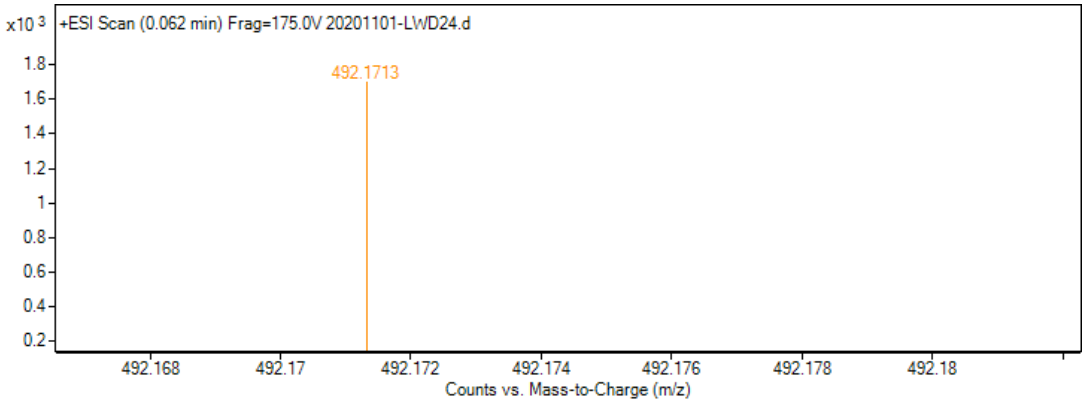


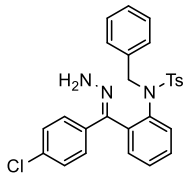
Compound S1v': 66% yield, yellowish white solid, m.p. = 135.2-136.5 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.54 – 7.34 (m, 6H), 7.28 – 7.22 (m, 5H), 5.23 (s, 2H), 3.02 – 2.91 (m, 2H), 2.42 (s, 3H), 1.47 – 1.22 (m, 5H), 1.06 – 0.77 (m, 4H), 0.64 (s, 1H), 0.36 (q, *J* = 10.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.6, 143.8, 139.0, 138.8, 136.6, 131.8, 131.8, 130.5, 129.9, 129.5, 129.0, 128.4, 128.3, 128.1, 126.2, 57.5, 35.4, 30.9, 30.6, 26.2, 25.6, 25.4, 21.7, 21.6. **IR** (KBr, cm^{-1}) 3413, 3303, 3059, 2926, 2851, 1597, 1487, 1445, 1338, 1266, 1210, 1159, 1090, 1060, 1035, 973, 923, 895, 821, 769, 737, 697, 658, 581, 547. **HRMS** (ESI) Calcd for $C_{27}H_{32}N_3O_2S$ $(M+H)^+$ 462.2210, found 462.2212.



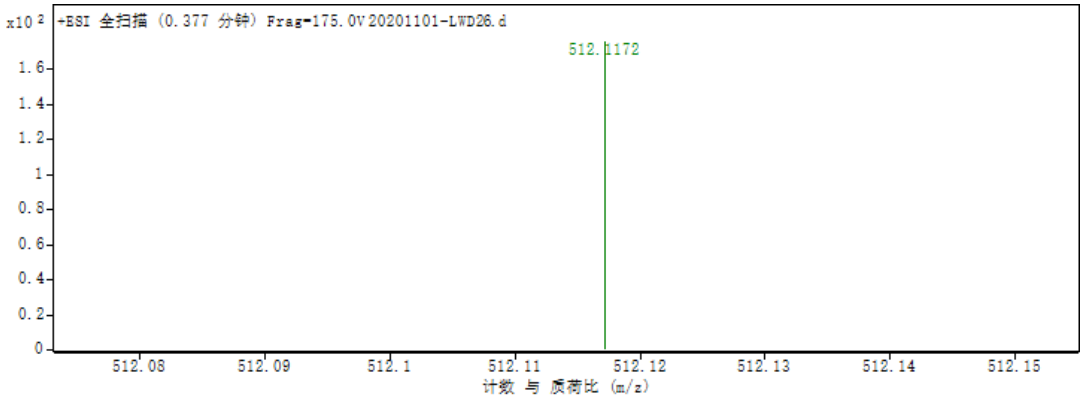


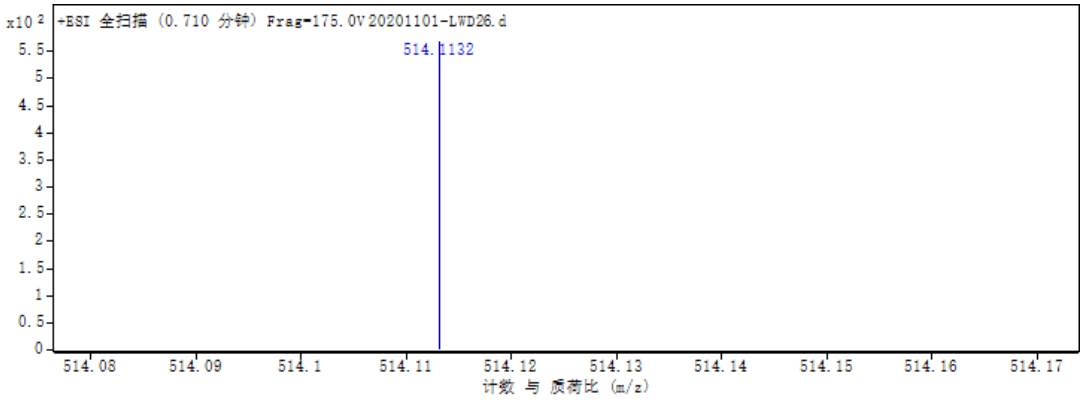
Compound S1w': 85% yield, yellowish white foam, m.p. = 72.9-83.0 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 3H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.12 – 7.06 (m, 4H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.76 – 6.69 (m, 2H), 5.47 (s, 2H), 4.36 (d, *J* = 14.8 Hz, 1H), 4.00 (d, *J* = 14.5 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.6, 143.7, 138.5, 138.3, 137.0, 135.9, 135.2, 135.0, 131.9, 131.4, 129.8, 129.7, 129.5, 129.3, 129.2, 128.5, 128.1, 127.7, 126.4, 55.0, 21.7, 21.4. **IR** (KBr, cm^{-1}) 3406, 3297, 3062, 3031, 2923, 1600, 1489, 1448, 1333, 1266, 1158, 1090, 1043, 858, 819, 732, 700, 657, 607, 563, 545. **HRMS** (ESI) Calcd for $C_{28}H_{27}N_3NaO_2S$ $(M+Na)^+$ 492.1716, found 492.1713. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.44 (m, 3H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.38 – 7.29 (m, 4H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.12 – 7.06 (m, 4H), 7.00 (t, *J* = 7.5 Hz, 2H), , 5.47 (s, 1H), 4.36 (d, *J* = 14.8 Hz, 1H), 4.00 (d, *J* = 14.5 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H).

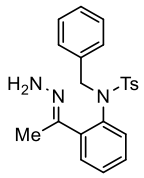




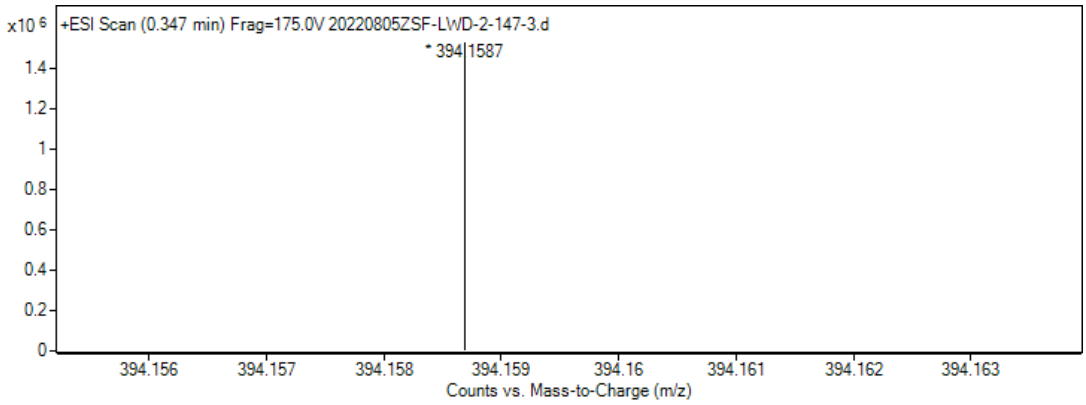
Compound S1x': 24% yield, yellowish white solid, m.p. = 132.8-134.0 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.43 (m, 3H), 7.41 – 7.32 (m, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.08 (m, 6H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.72 (s, 2H), 5.52 (s, 2H), 4.35 (d, *J* = 14.7 Hz, 1H), 4.16 (d, *J* = 14.5 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.9, 143.9, 138.8, 137.2, 136.4, 134.8, 134.6, 133.9, 131.4, 131.3, 129.9, 129.5, 129.4, 129.4, 128.4, 128.1, 127.8, 127.4, 55.2, 21.6. **IR** (KBr, cm^{-1}) 3409, 3301, 3062, 1597, 1489, 1446, 1333, 1159, 1091, 1037, 950, 836, 742, 675, 610, 566. **HRMS** (ESI) Calcd for $C_{27}H_{24}ClN_3NaO_2S$ $(M+Na)^+$ 512.1170, found 512.1172; isotopic peak : **HRMS** (ESI) Calcd for $C_{27}H_{24}ClN_3NaO_2S$ $(M+Na)^+$ 514.1141, found 514.1132.

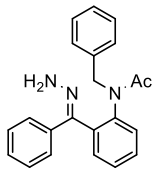




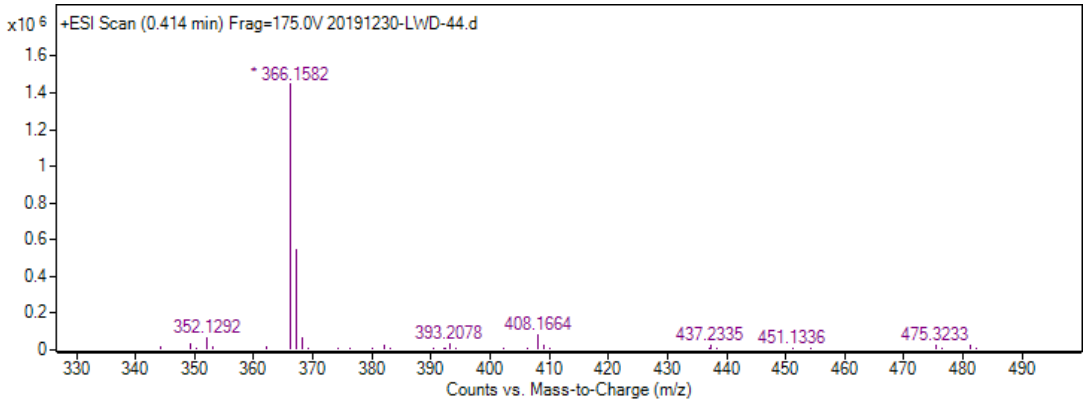


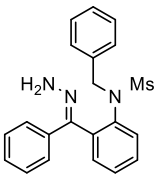
Compound S1y': Yield: 90%, white solid, m.p. = 85.8-88.1 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.13 (m, 6H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.85 (s, 2H), 2.39 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 143.4, 141.4, 136.7, 136.5, 135.6, 130.3, 130.03, 130.00, 129.4, 128.6, 128.3, 128.21, 128.18, 127.9, 56.1, 21.5, 18.8. **IR** (KBr, cm^{-1}) 3397, 3063, 3032, 1597, 1491, 1445, 1343, 1215, 1091, 1044, 862, 817, 701, 607, 560. **HRMS** (ESI) Calcd for $C_{22}H_{24}N_3OS$ $(M+H)^+$ 394.1584, found 394.1587.



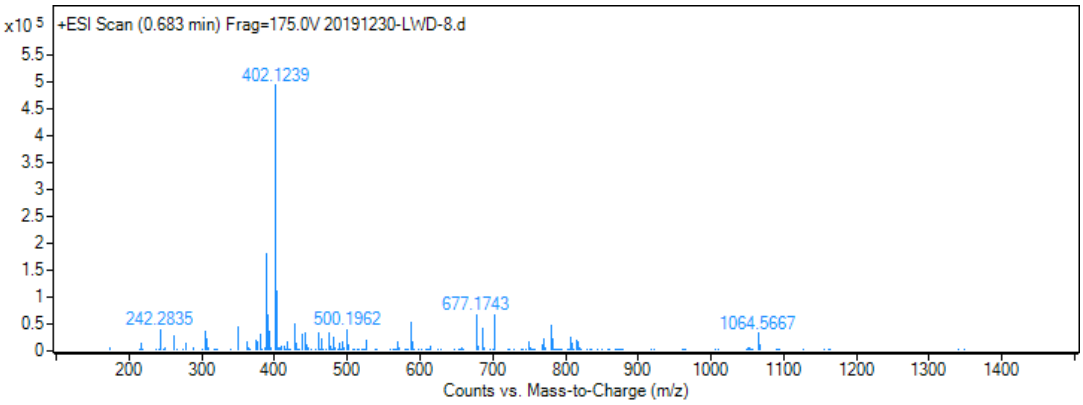


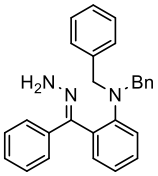
Compound S1aa': 62% yield, yellowish white foam (contains an inseparable *Z*/*E* mixture), m.p. = 52.0-54.2 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 – 7.26 (m, 14H), 7.23 – 7.09 (m, 7H), 7.01 (d, *J* = 5.8 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 5.62 and 5.52 (s, 2H), 5.58 and 5.22 (d, *J* = 14.6 Hz, 1H), ,3.98 and 3.22 (d, *J* = 14.5 Hz, 1H), 1.98 and 1.46 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.7 and 169.7, 147.6 and 146.0, 141.4 and 141.1, 138.3 and 137.7, 132.5 and 131.8, 132.1 and 132.0, 130.8 and 130.3, 130.1 and 130.0, 128.95, 128.89, 128.82, 128.77, 128.7, 128.5, 128.4, 128.2, 127.6 and 127.2, 126.7, 126.33 and 126.28, 126.1, 51.0 and 50.6, 22.5 and 22.1.**IR** (KBr, cm^{-1}) 3306, 3059, 3029, 2927, 1698, 1664, 1602, 1579, 1489, 1447, 1372, 1292, 1266, 1166, 1070, 1022, 953, 736, 699, 654, 536. **HRMS** (ESI) Calcd for $C_{22}H_{21}N_3NaO$ $(M+Na)^+$ 366.1577, found 366.1582.



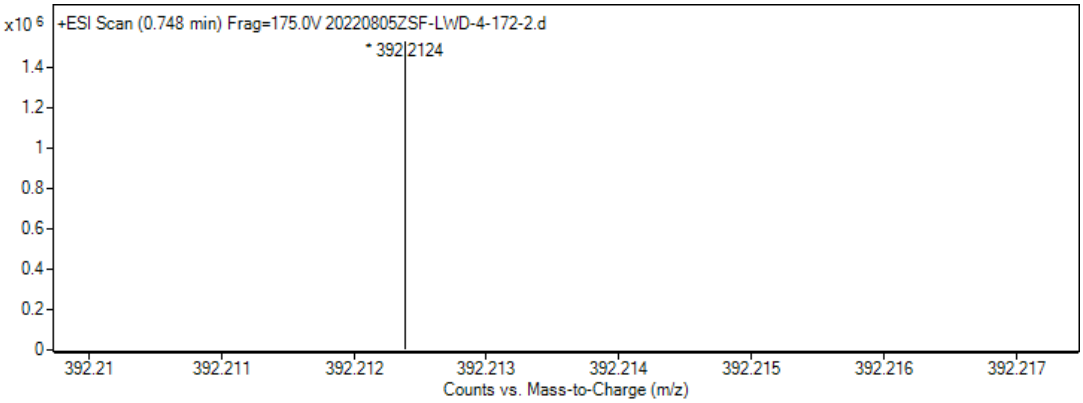


Compound S1ab': 50% yield, yellowish white solid, m.p. = 123.6-125.4 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.8 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.39 – 7.29 (m, 5H), 7.22 – 7.15 (m, 4H), 7.07 (s, 2H), 5.58 (s, 2H), 4.43 (d, *J* = 14.3 Hz, 1H), 4.23 (s, 1H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.8, 138.9, 138.4, 135.3, 133.6, 132.9, 130.6, 129.9, 129.2, 128.6, 128.5, 128.4, 128.1, 126.1, 54.9, 41.5. **IR** (KBr, cm^{-1}) 3408, 3298, 3061, 3030, 2931, 1589, 1489, 1445, 1330, 1213, 1148, 1061, 964, 864, 775, 735, 699, 654, 608, 541, 521, 497. **HRMS** (ESI) Calcd for $C_{21}H_{21}N_3NaO_2S$ $(M+Na)^+$ 402.1246, found 402.1239.

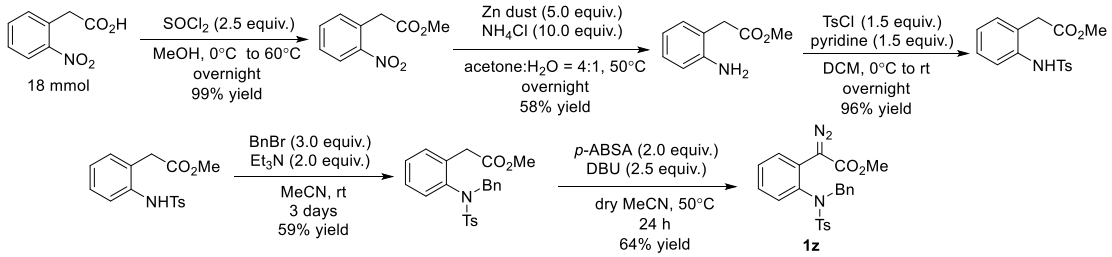




Compound 1ac': Yield: 90%, yellowish oil, R_f = 0.4 (petroleum ether:ethyl acetate = 30:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.36 – 7.26 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.17 – 7.08 (m, 7H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.89 – 6.84 (m, 4H), 5.54 (s, 2H), 4.03 (d, *J* = 14.4 Hz, 2H), 3.95 (d, *J* = 14.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.8, 149.6, 138.8, 137.7, 130.8, 129.8, 128.9, 128.3, 128.13, 128.08, 127.1, 127.0, 126.4, 122.7, 122.4, 55.9. **IR** (KBr, cm^{-1}) 3409, 3059, 3027, 1591, 1489, 1446, 1367, 1330, 1207, 1074, 954, 767, 741, 697, 656. **HRMS** (ESI) Calcd for $C_{27}H_{26}N_3$ $(M+H)^+$ 392.2121, found 392.2124.



The procedure for formation of diazo compound 1z



The procedures were slightly modified according to *Ref* 4.

2-nitrophenylacetic acid (3.3 g, 18 mmol) was dissolved in methanol (30 mL) and the solution was cooled down to 0 °C before addition of thionyl dichloride (3.4 mL, 45 mmol) dropwise. The reaction was stirred overnight at 60 °C and checked by TLC. The solvent was evaporated in vacuo and the residual oil washed with a saturated solution of $NaHCO_3$ and extracted with EtOAc. Subsequently, the combined organic fractions were washed with water and brine, dried over $NaSO_4$ and concentrated *in vacuo* to afford methyl 2-(2-nitrophenyl)acetate (3.6g, 99% yield) as yellow solid without purification.

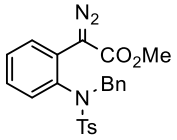
To methyl 2-(2-nitrophenyl)acetate from the previous reaction (3.6 g, 18 mmol) in 4:1 acetone/water (60 mL) was added zinc dust (6.0 g, 90 mmol) and NH_4Cl (10.0 g, 180 mmol), and stirred 12 hours at

50 °C. The solution was then concentrated and diluted with ethyl acetate. The organic layer was washed with water and brine, then dried over Na_2SO_4, filtered and concentrated *in vacuo*, and purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 5:1) to afford methyl 2-(2-aminophenyl)acetate (1.8 g, 58%) as red oil.

To a solution of methyl 2-(2-aminophenyl)acetate (1.8 g, 11 mmol) in DCM (30 mL) at 0 °C was added pyridine (1.3 mL,16.5 mmol) and tosyl chloride (3.1 g, 16.5 mmol). The reaction was allowed to come to room temperature while stirring overnight. Water was added to the reaction and the layers were separated. The organic layer was washed with water and brine, then dried over Na_2SO_4, filtered and concentrated *in vacuo*, and purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 5:1) to afford methyl 2-(2-((4-methylphenyl)sulfonamido)phenyl)acetate as white solid (3.3g, 96%).

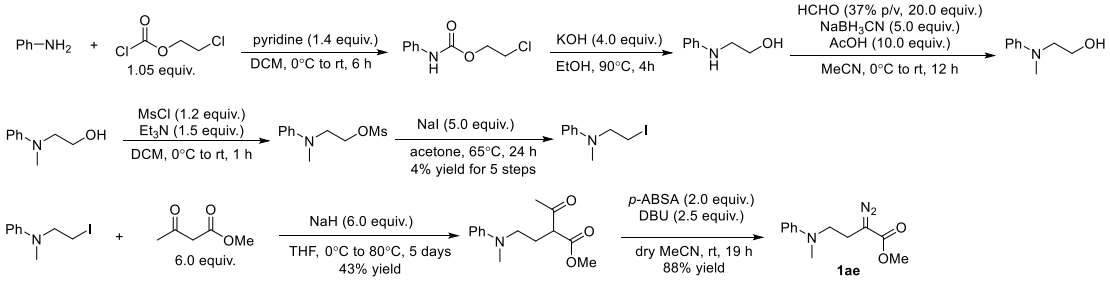
A solution of above material (3.3 g, 10.3 mmol) was dissolved in acetonitrile (30 mL). After the addition of triethylamine (3.0 mL, 20.6 mmol), the reaction mixture was cooled down to 0 °C. Next, benzyl bromide (3.6 mL, 15.5 mmol) was added dropwise and the reaction mixture was stirred at room temperature for 3 days until no starting material was detected anymore. Subsequently, the solvent was evaporated in vacuo and the residual oil was dissolved in DCM, and washed with water and brine. After drying over Na_2SO_4, the mixture was concentrated in vacuo and purified *via* column chromatography (silica gel, petroleum ether/AcOEt = 5:1) to afford methyl 2-(2-((*N*-benzyl-4-methylphenyl)sulfonamido)phenyl)acetate (2.5g, 59%) as white solid.

A solution containing the ester above (2.5 g, 6.1 mmol) and *p*-ABSA (2.93g, 12.2 mmol) in MeCN (30 mL) was cooled to 0 °C. DBU (2.3 g, 15.3 mmol) was added dropwise. The reaction stirred for 24 h at 50 °C monitored by TLC. Then, the reaction mixture was cooled down to 0 °C and saturated NH_4Cl solution was added to quench the reaction. The mixture was extracted with DCM, washed with brine and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the crude reaction mixture was purified via flash column chromatography (silica gel, petroleum ether/AcOEt = 5:1) to afford methyl 2-(2-((*N*-benzyl-4-methylphenyl)sulfonamido)phenyl)-2-diazoacetate **1z** (1.70 g, 64%) as bright yellow solid.

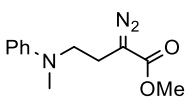


Compound 1z: known compound.[4] Yield: 64%, bright yellow solid, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.23 – 7.12 (m, 3H), 7.12 – 7.06 (m, 3H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.05 (s, 1H), 4.10 (s, 1H), 3.62 (s, 3H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 144.1, 137.0, 135.8, 134.5, 131.3, 129.8, 129.5, 128.7, 128.4, 128.2, 128.0, 127.7, 60.6, 56.9, 51.8, 21.7.

The procedure for formation of diazo compound 1ad



The procedures referred to *Ref* 5.

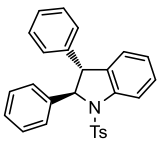


Compound **1ad**: known compound.[5] 88% yield, yellow oil, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.18 (m, 2H), 6.75 – 6.67 (m, 3H), 3.76 (s, 3H), 3.52 (t, *J* = 6.9 Hz, 2H), 2.93 (s, 3H), 2.53 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 148.7, 129.3, 116.8, 112.2, 52.0, 50.8, 38.3, 21.7.

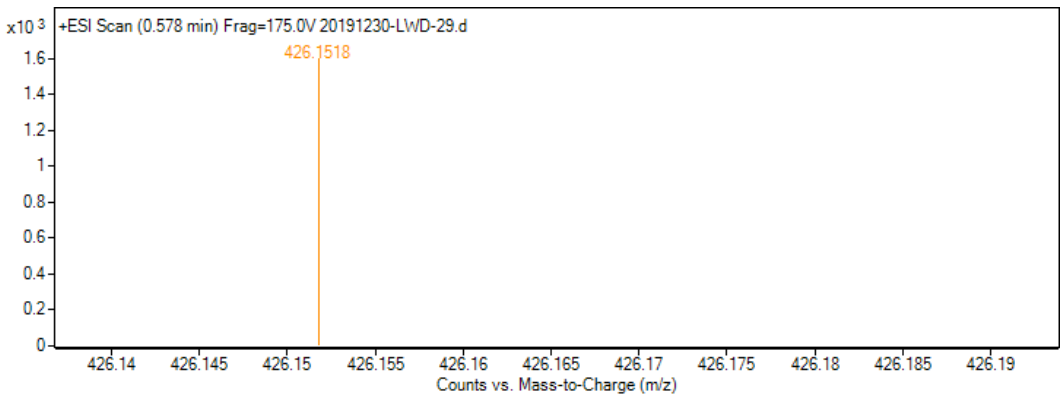
4. General procedure for Pd(II)-catalyzed C-H insertion of diazo compounds and synthetic applications

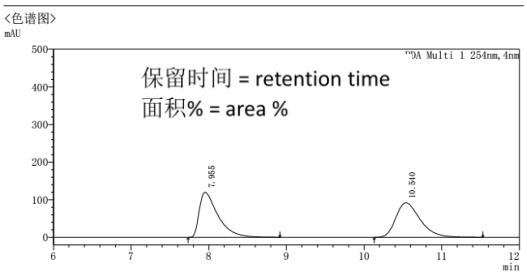
4.1 General procedure for enantioselective Pd(II)-catalyzed C-H insertion of diazo compounds (0.1 mmol)

In a flame-dried scintillation vial, the desired hydrazones **S1a'-S1y'**, **S1aa'-S1ac'** (0.1 mmol, 1.0 equiv.) were dissolved in anhydrous benzotrifluoride (0.033 M). The scintillation vial was wrapped in foil, and MnO_2 (8.0 equiv.) was added. The oxidation was allowed to stir until full conversion of the starting material was observed by TLC, then the MnO_2 was removed by filtering through celite into a new flame-dried flask using dry ethyl acetate quickly. Next the solvent was removed *in vacuo* at room temperature. The crude magenta diazo compounds **1a-1y**, **1aa-1ac** were used for next step without purification and were diluted to 0.033 M with anhydrous benzotrifluoride. By the way, pure diazo compounds **1z** and **1ad** were not generated in suit through this method. In the meantime, under nitrogen atmosphere, $Pd(CH_3CN)_2Cl_2$ (10 mol%), chiral ligand **L5** or **L6** (12 mol%) and $NaBAr^F$ (24 mol%) were added in dry benzotrifluoride (6.7×10^{-3} M). The chiral catalysts mixture was stirred to bright yellow at room temperature for 2 h. Then the magenta solution of diazo compounds **1a-1ad** was added dropwise into the catalyst system for 10 min. The insertion reaction was stirred at room temperature within 12 h until completion monitored by TLC. The crude reaction mixture was filtered over Celite, concentrated *in vacuo*, and purified by column chromatography to yield the desired insertion products **2a-2ad.**



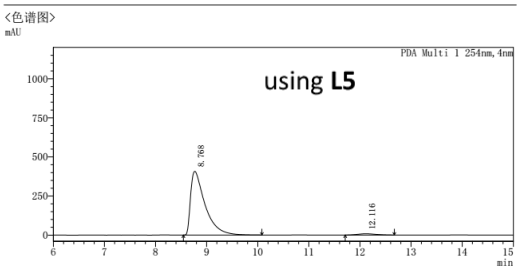
Compound *trans*-2a: 47.1 mg of **S1a'** yields 28.6 mg of **2a** (65%, 12 h, *trans*/*cis* = 7.3:1, using **L5**); 46.1 mg of **S1a'** yields 31.4 mg of **2a** (73%, 12 h, *trans*/*cis* = 5.2:1, using **L6**), white solid, m.p. = 133.4-135.3 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.31 (m, 5H), 7.33 – 7.25 (m, 1H), 7.17 – 7.09 (m, 3H), 7.07 – 7.00 (m, 3H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 7.5 Hz, 2H), 5.02 (d, *J* = 4.0 Hz, 1H), 4.23 (d, *J* = 3.9 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.1, 143.6, 143.2, 142.5, 134.7, 133.1, 129.7, 129.0, 128.81, 128.76, 127.9, 127.6, 126.9, 126.3, 125.9, 124.7, 115.7, 74.4, 57.4, 21.7. **IR** (KBr, cm^{-1}) 3063, 3030, 2922, 1598, 1456, 1400, 1359, 1169, 1090, 1025, 957, 812, 733, 699, 665, 575, 542. **HRMS** (ESI) Calcd for $C_{27}H_{24}NO_2S$ $(M+H)^+$ 426.1522, found 426.1518. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.8 min, minor: 12.1 min. 95% ee. $[\alpha]_D^{21}$ = -127° (*c* 0.75, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 7.8 min, minor: 10.5 min. 94% ee. $[\alpha]_D^{21}$ = -125° (*c* 0.46, CH_2Cl_2).





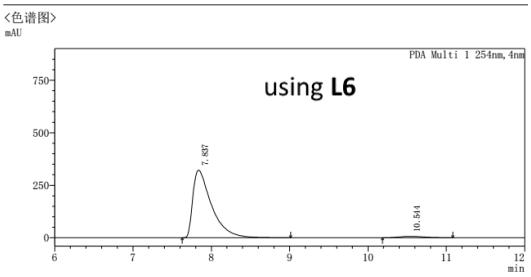
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.955	2014354	119875		50.070	56.662
2	10.540	2008709	91687		49.930	43.338
总计		4023063	211561		100.000	100.000



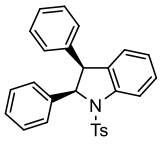
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.768	8038544	407756		97.533	98.070
2	12.116	203357	8025		2.467	1.930
总计		8241901	415780		100.000	100.000

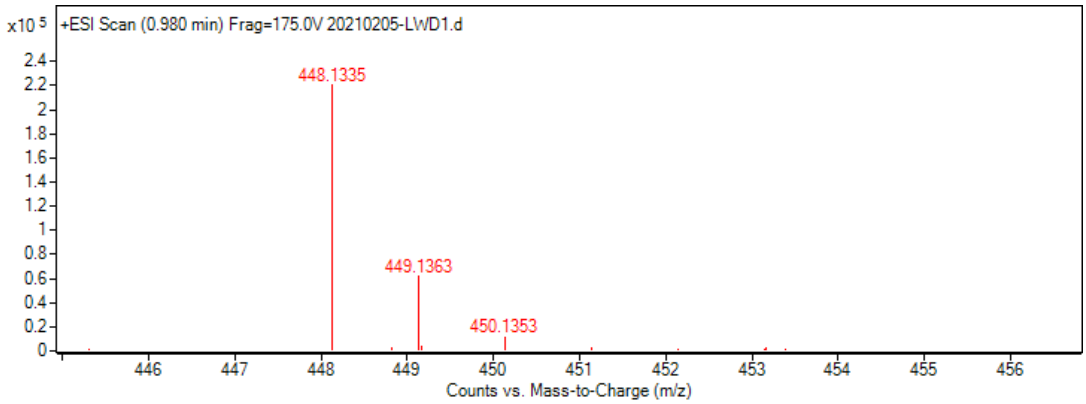


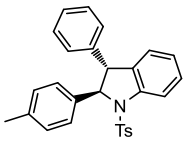
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.837	5344901	321694		97.239	97.878
2	10.544	151777	6975		2.761	2.122
总计		5496677	328669		100.000	100.000

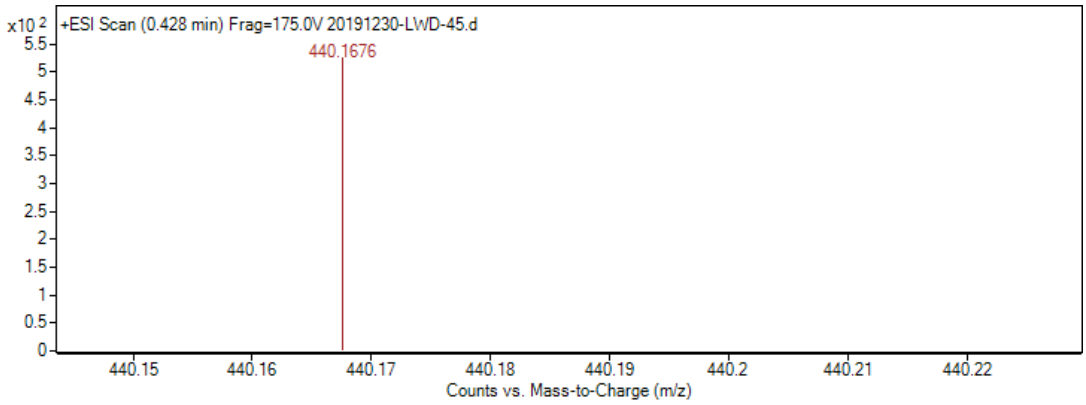


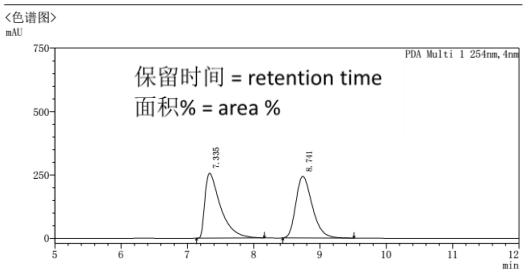
Compound *cis*-2a: white solid, m.p. = 163.6-166.0 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.08 – 6.88 (m, 7H), 6.83 (d, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 7.3 Hz, 2H), 6.64 (d, *J* = 7.2 Hz, 2H), 5.57 (d, *J* = 9.5 Hz, 1H), 4.68 (d, *J* = 9.5 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 143.3, 137.5, 136.7, 136.0, 134.4, 129.9, 129.7, 128.5, 127.9, 127.7, 127.4, 127.2, 127.1, 126.0, 124.8, 115.9, 71.0, 54.0, 21.7. **IR** (KBr, cm^{-1}) 3058, 2986, 1598, 1494, 1456, 1356, 1266, 1166, 1096, 1027, 950, 895, 813, 776, 736, 702, 661, 576, 542. **HRMS** (ESI) Calcd for $C_{27}H_{23}NNaO_2S$ $(M+Na)^+$ 448.1342, found 448.1335.





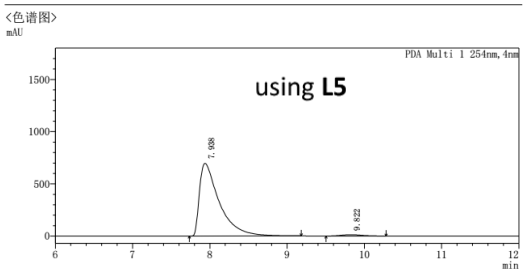
Compound *trans*-2b: 47.6 mg of **S1b'** yields 28.1 mg of **2b** (63%, 4 h, *trans*/*cis* = 4.9:1, using **L5**); 46.9 mg of **S1b'** yields 24.6 mg of **2b** (56%, 4 h, *trans*/*cis* = 2.4:1, using **L6**), white solid, m.p. = 162.8-163.9 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.09 (m, 5H), 7.06 – 6.99 (m, 3H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 7.5 Hz, 2H), 4.97 (d, *J* = 4.0 Hz, 1H), 4.21 (d, *J* = 3.9 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0, 143.6, 142.5, 140.3, 137.5, 134.7, 133.2, 129.7, 129.6, 128.8, 128.7, 127.6, 126.8, 126.3, 125.9, 124.6, 115.7, 74.3, 57.4, 21.7, 21.3. **IR** (KBr, cm^{-1}) 3028, 2921, 1597, 1457, 1358, 1260, 1166, 1090, 1022, 957, 808, 735, 700, 665, 573, 542. **HRMS** (ESI) Calcd for $C_{28}H_{26}NO_2S$ $(M+H)^+$ 440.1679, found 440.1676. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 7.9 min, minor: 9.8 min. 96% ee. $[\alpha]_D^{21}$ = -158° (*c* 0.68, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 7.2 min, minor: 8.7 min. 92% ee. $[\alpha]_D^{21}$ = -138° (*c* 0.57, CH_2Cl_2).





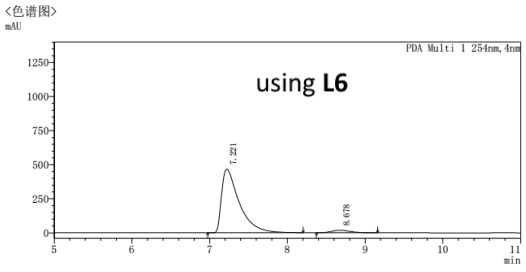
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.335	4199083	255735		50.042	51.307
2	8.741	4192025	242707		49.958	48.693
总计		8391109	498443		100.000	100.000



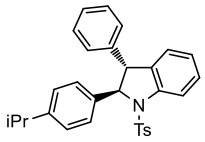
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.938	12465528	696950		98.082	98.185
2	9.822	243780	12881		1.918	1.815
总计		12709308	709831		100.000	100.000

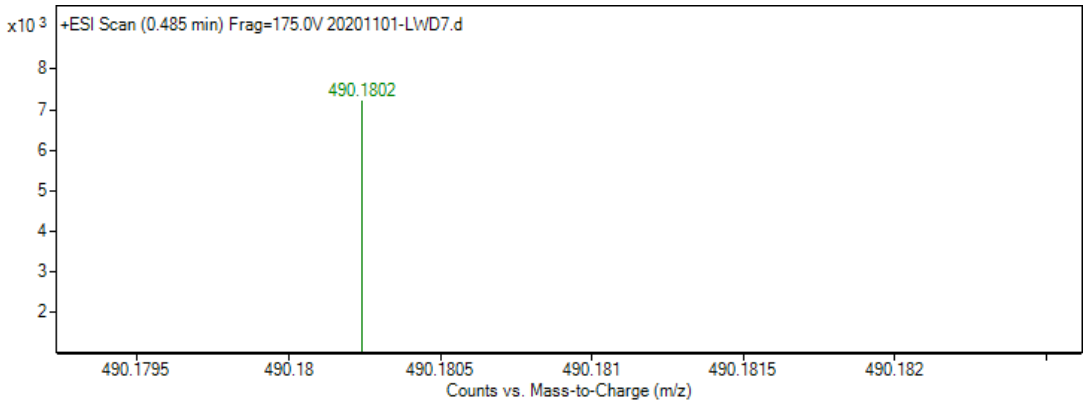


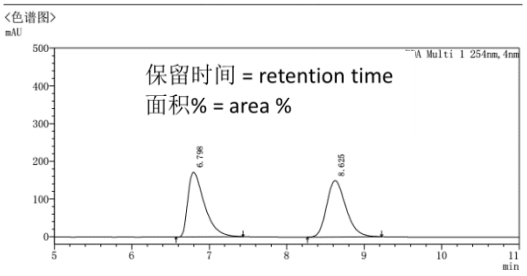
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.221	7383257	467091		96.062	96.308
2	8.678	302674	17907		3.938	3.692
总计		7685931	484999		100.000	100.000



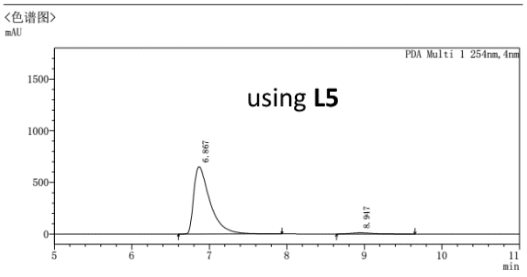
Compound *trans*-2c: 51.1 mg of **S1c'** yields 25.0 mg of **2c** (52%, 11 h, *trans*/*cis* = 3.0:1, using **L5**); 49.7 mg of **S1c'** yields 31.8 mg of **2c** (68%, 11h, *trans*/*cis* = 3.5:1, using **L6**), white solid, m.p. = 176.2-177.4 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.19 – 7.08 (m, 5H), 7.06 – 6.99 (m, 3H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 7.5 Hz, 2H), 5.03 (d, *J* = 3.6 Hz, 1H), 4.24 (d, *J* = 3.3 Hz, 1H), 2.89 (hept, *J* = 7.0 Hz, 1H), 2.38 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.4, 143.9, 143.7, 142.5, 140.5, 135.0, 133.3, 129.7, 128.75, 128.73, 127.5, 127.0, 126.8, 126.4, 125.8, 124.6, 115.6, 74.2, 57.2, 33.9, 24.13, 24.11, 21.6. **IR** (KBr, cm^{-1}) 3027, 2961, 2926, 1598, 1458, 1401, 1458, 1359, 1261, 1169, 1106, 1022, 959, 813, 753, 700, 667, 575, 544. **HRMS** (ESI) Calcd for $C_{30}H_{29}NNaO_2S$ $(M+Na)^+$ 490.1811, found 490.1802. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.9 min, minor: 8.9 min. 96% ee. $[\alpha]_D^{21}$ = -132° (*c* 0.42, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.8 min, minor: 8.6 min. 96% ee. $[\alpha]_D^{21}$ = -139° (*c* 0.45, CH_2Cl_2).





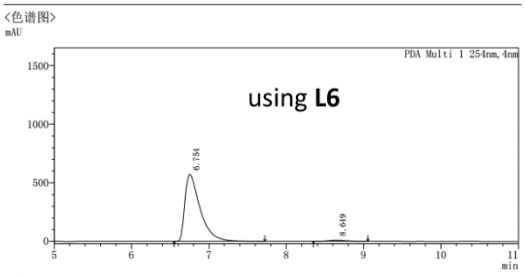
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.798	2554170	171376		49.813	53.465
2	8.625	2573306	149165		50.187	46.535
总计		5127476	320541		100.000	100.000



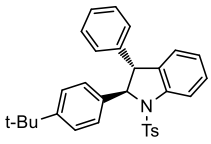
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.867	9477803	651453		97.870	98.342
2	8.947	206265	10982		2.130	1.658
总计		9684069	662435		100.000	100.000

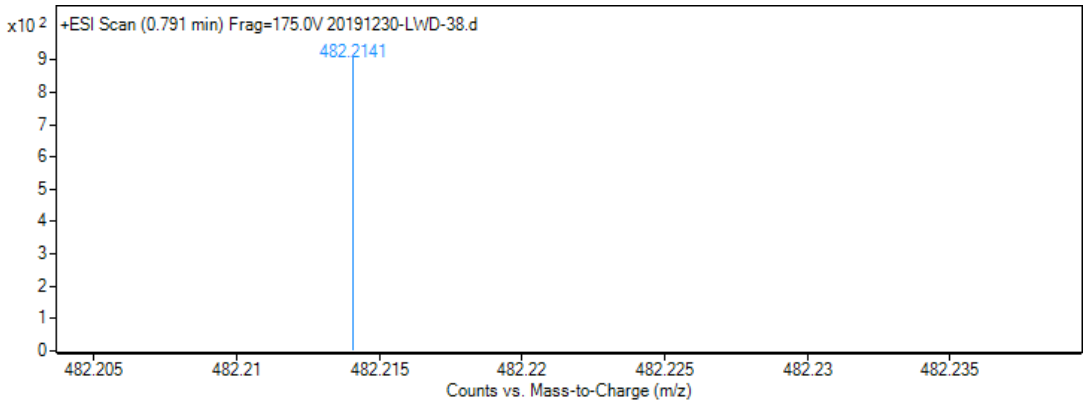


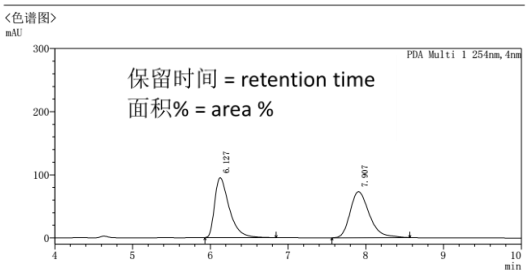
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.754	7846667	571492		98.011	98.325
2	8.649	159218	9736		1.989	1.675
总计		8005884	581228		100.000	100.000



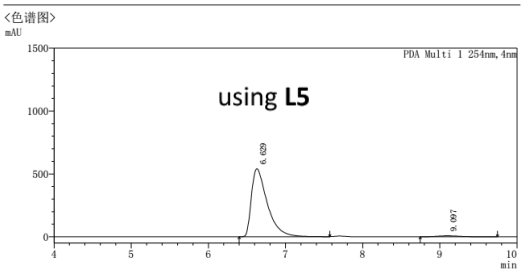
Compound *trans*-2d: 52.3 mg of **S1d'** yields 27.3 mg of **2d** (55%, 6 h, *trans*/*cis* = 3.2:1, using **L5**); 53.8 mg of **S1d'** yields 41.0 mg of **2d** (81%, 6 h, *trans*/*cis* = 4.0:1, using **L6**), white solid, m.p. = 151.9-153.8 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.27 – 7.24 (m, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.06 – 7.01 (m, 3H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 7.5 Hz, 2H), 5.04 (d, *J* = 3.4 Hz, 1H), 4.25 (d, *J* = 3.1 Hz, 1H), 2.37 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.6, 143.9, 143.8, 142.5, 140.1, 135.0, 133.3, 129.7, 128.75, 128.73, 127.5, 126.8, 126.4, 125.8, 125.5, 124.6, 115.6, 74.1, 57.2, 34.7, 31.5, 21.6. **IR** (KBr, cm^{-1}) 3030, 2962, 2869, 1598, 1494, 1477, 1460, 1360, 1265, 1170, 1108, 1023, 961, 814, 737, 703, 668, 576, 546. **HRMS** (ESI) Calcd for $C_{31}H_{32}NO_2S$ $(M+H)^+$ 482.2148, found 482.2141. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.6 min, minor: 9.1 min. 96% ee. $[\alpha]_D^{21}$ = -107° (*c* 0.69, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.0 min, minor: 7.9 min. 97% ee. $[\alpha]_D^{21}$ = -109° (*c* 0.28, CH_2Cl_2).





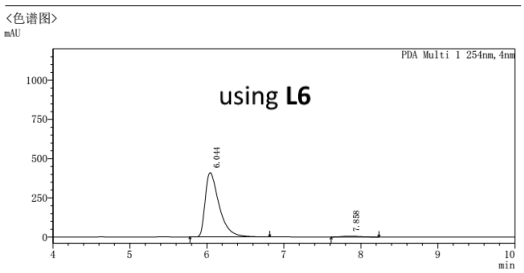
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.127	1239183	94797		49.630	56.478
2	7.907	1257656	73050		50.370	43.522
总计		2496839	167847		100.000	100.000



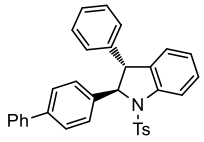
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.629	7759262	539464		97.955	98.553
2	9.097	162023	7920		2.045	1.447
总计		7921285	547384		100.000	100.000

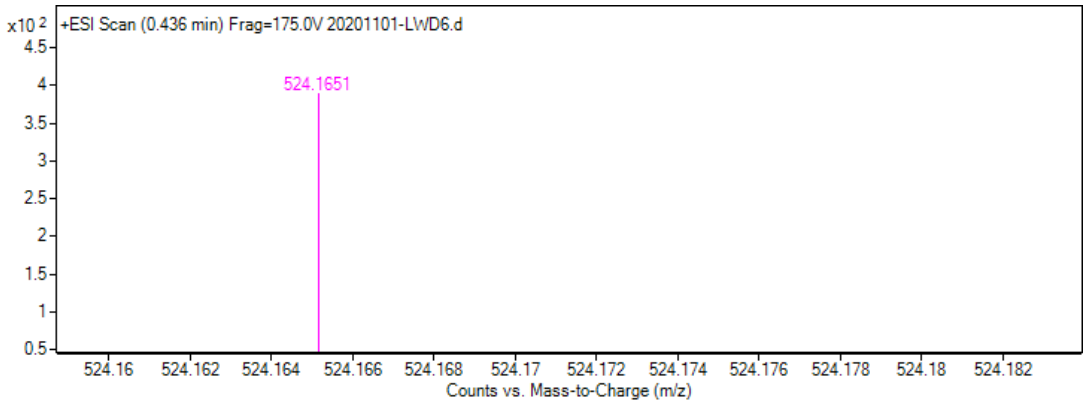


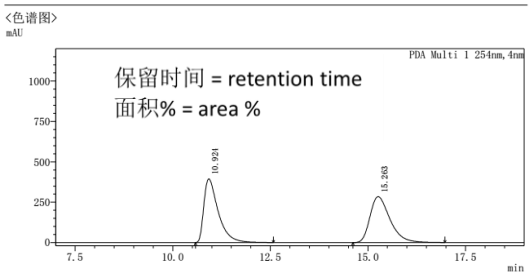
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.044	5166941	409314		98.400	98.719
2	7.858	84014	5312		1.600	1.281
总计		5250955	414626		100.000	100.000



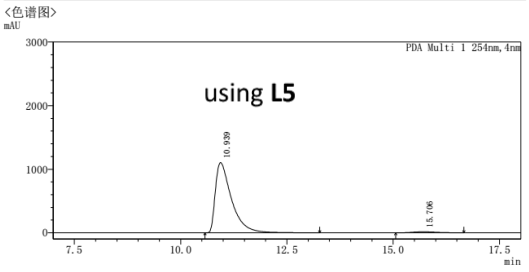
Compound *trans*-2e: 54.9 mg of **S1e'** yields 28.2 mg of **2e** (54%, 11 h , *trans*/*cis* = 3.3:1, using **L5**); 52.7 mg of **S1e'** yields 45.3 mg of **2e** (91%, 11 h, *trans*/*cis* = 4.0:1, using **L6**), white solid, m.p. = 147.7-149.1 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.52 (m, 6H), 7.45 – 7.38 (m, 4H), 7.37 – 7.32 (m, 2H), 7.18 – 7.10 (m, 3H), 7.08 – 7.01 (m, 3H), 6.90 (d, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 7.6 Hz, 2H), 5.07 (d, *J* = 3.9 Hz, 1H), 4.27 (d, *J* = 3.8 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.1, 143.5, 142.4, 142.2, 141.0, 140.8, 134.7, 133.1, 129.7, 128.89, 128.85, 128.8, 127.7, 127.6, 127.4, 127.3, 126.9, 126.4, 124.7, 115.7, 74.2, 57.4, 21.7. **IR** (KBr, cm^{-1}) 3030, 2923, 1598, 1484, 1460, 1405, 1359, 1261, 1169, 1108, 1028, 960, 839, 813, 760, 732, 700, 667, 575, 544. **HRMS** (ESI) Calcd for $C_{33}H_{27}NNaO_2S$ $(M+Na)^+$ 524.1654, found 424.1651. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 10.9 min, minor: 15.7 min. 96% ee. $[\alpha]_D^{21}$ = -180° (*c* 0.53, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 10.8 min, minor: 15.4 min. 97% ee. $[\alpha]_D^{21}$ = -179° (*c* 0.42, CH_2Cl_2).





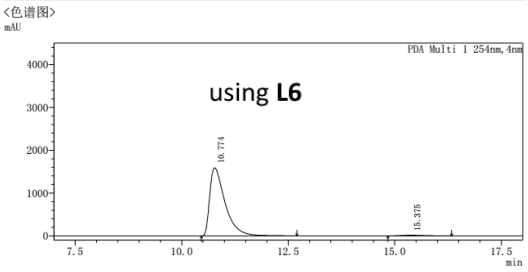
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.924	10149906	394256		50.005	58.107
2	15.263	10147876	284243		49.995	41.893
总计		20297781	678499		100.000	100.000



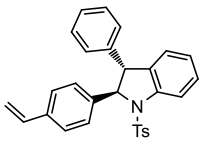
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.939	29283369	1103539		97.899	98.521
2	15.706	628596	16564		2.101	1.479
总计		29911965	1120103		100.000	100.000

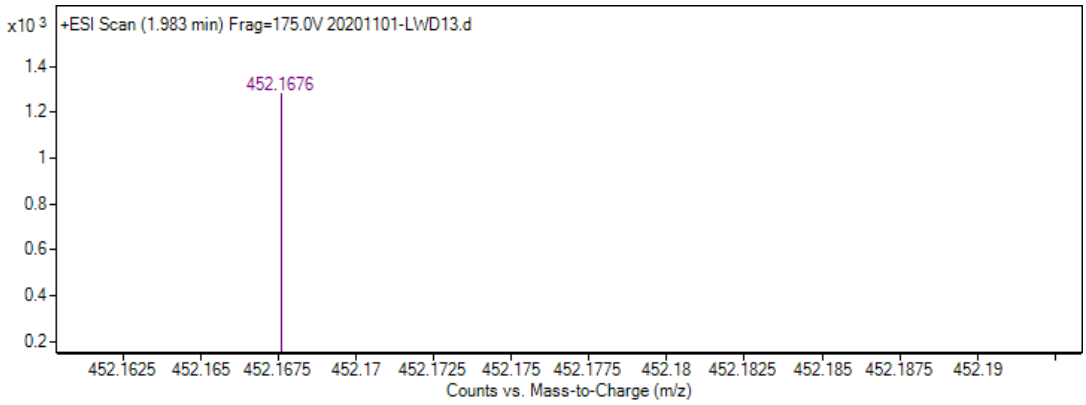


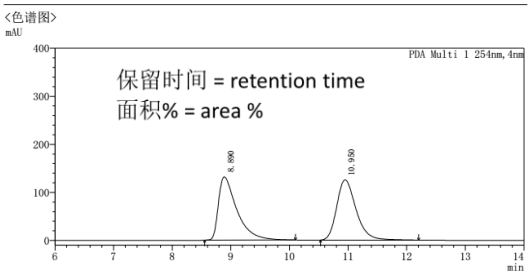
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.774	39775497	1587747		98.533	98.947
2	15.375	592070	16896		1.467	1.053
总计		40367567	1604643		100.000	100.000



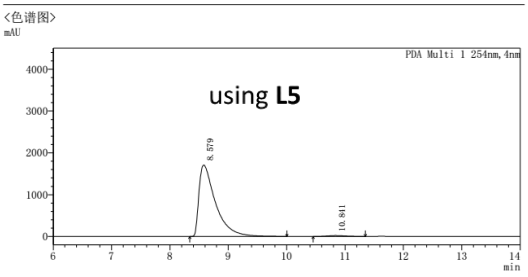
Compound *trans*-2f: 49.0 mg of **S1f'** yields 19.1 mg of **2f** (42%, 12 h, *trans*/*cis* = 2.8:1, using **L5**); 52.3 mg of **S1f'** yields 28.9 mg of **2f** (59%, 12 h, *trans*/*cis* = 3.8:1, using **L6**), white solid, m.p. = 148.4-150.9 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.09 (m, 3H), 7.07 – 7.00 (m, 3H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.43 (d, *J* = 7.4 Hz, 2H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.23 (d, *J* = 10.9 Hz, 1H), 4.99 (d, *J* = 4.2 Hz, 1H), 4.21 (d, *J* = 4.0 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.1, 143.5, 142.7, 142.4, 137.3, 136.6, 134.6, 133.1, 129.7, 128.83, 128.77, 127.6, 126.9, 126.8, 126.3, 126.1, 124.7, 115.7, 114.1, 74.2, 57.4, 21.7. **IR** (KBr, cm^{-1}) 3029, 1598, 1482, 1358, 1264, 1167, 1098, 1023, 911, 813, 748, 701, 666, 575, 543. **HRMS** (ESI) Calcd for $C_{29}H_{26}NO_2S$ $(M+H)^+$ 452.1679, found 452.1676. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.6 min, minor: 10.8 min. 97% ee. $[\alpha]_D^{21}$ = -173° (*c* 0.53, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.7 min, minor: 11.0 min. 97% ee. $[\alpha]_D^{21}$ = -156° (*c* 0.74, CH_2Cl_2).





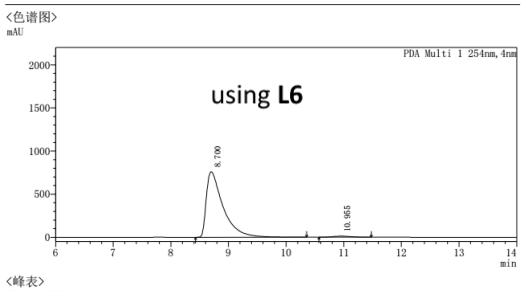
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.890	2879869	131589		49.937	51.184
2	10.950	2887147	125499		50.063	48.816
总计		5767016	257088		100.000	100.000



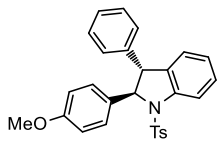
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.579	33791943	1707696		98.643	98.718
2	10.841	464893	22176		1.357	1.282
总计		34256836	1729872		100.000	100.000

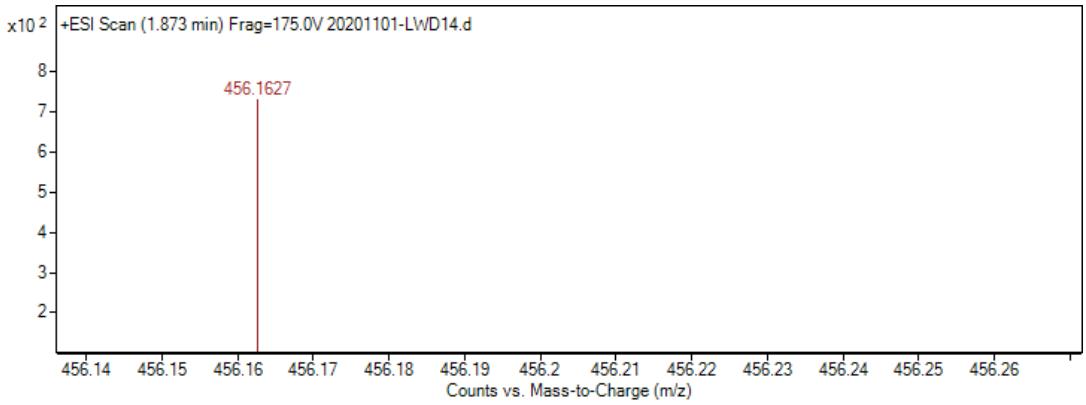


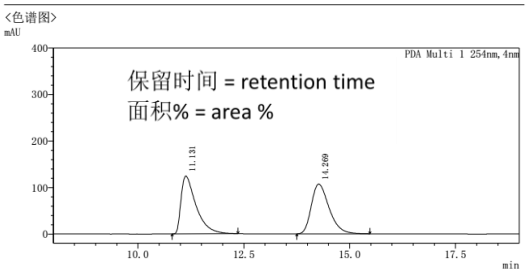
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.700	15397952	759824		98.319	98.420
2	10.955	263312	12200		1.681	1.580
总计		15661264	772025		100.000	100.000



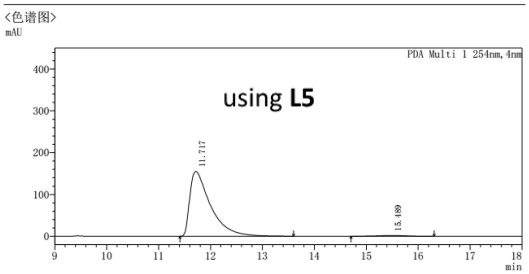
Compound *trans*-2g: 49.4 mg of **S1g'** yields 29.6 mg of **2g** (64%, 11 h, *trans*/*cis* =1.0:1, 14.8 mg *trans* product, using **L5**); 50.9 mg of **S1g'** yields 34.9 mg of **2g** (73%, 11 h, *trans*/*cis* = 1.7:1, 22.0 mg *trans* product, using **L6**), white solid, m.p. = 135.0-137.1 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.24 (m, 2H), 7.15 – 7.09 (m, 3H), 7.06 – 6.99 (m, 3H), 6.91 – 6.83 (m, 3H), 6.43 (d, *J* = 7.4 Hz, 2H), 4.96 (d, *J* = 4.0 Hz, 1H), 4.21 (d, *J* = 3.9 Hz, 1H), 3.80 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.3, 144.0, 143.6, 142.4, 135.5, 134.7, 133.2, 129.7, 128.8, 128.7, 127.5, 127.2, 126.8, 126.3, 124.6, 115.6, 114.3, 74.0, 57.4, 55.4, 21.7. **IR** (KBr, cm^{-1}) 3031, 2933, 2837, 1605, 1513, 1459, 1358, 1300, 1249, 1170, 1101, 1033, 957, 817, 743, 702, 667, 575, 547. **HRMS** (ESI) Calcd for $C_{28}H_{26}NO_3S$ $(M+H)^+$ 456.1628, found 456.1627. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 11.7 min, minor: 15.5 min. 96% ee. $[\alpha]_D^{21}$ = -180° (*c* 0.63, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 11.6 min, minor: 15.5 min. 98% ee. $[\alpha]_D^{21}$ = -170° (*c* 0.37, CH_2Cl_2).





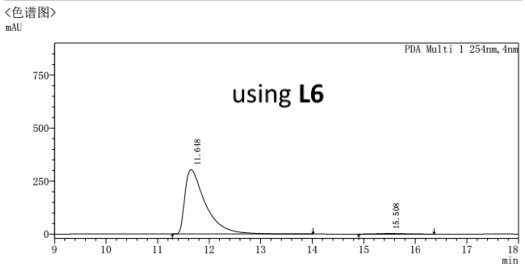
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.131	3081280	124291		49.568	53.711
2	14.269	3135021	107117		50.432	46.289
总计		6216302	231407		100.000	100.000



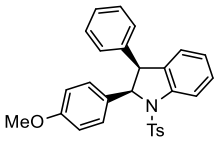
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.717	4322691	154940		98.053	98.560
2	15.489	85821	2264		1.947	1.440
总计		4408512	157204		100.000	100.000

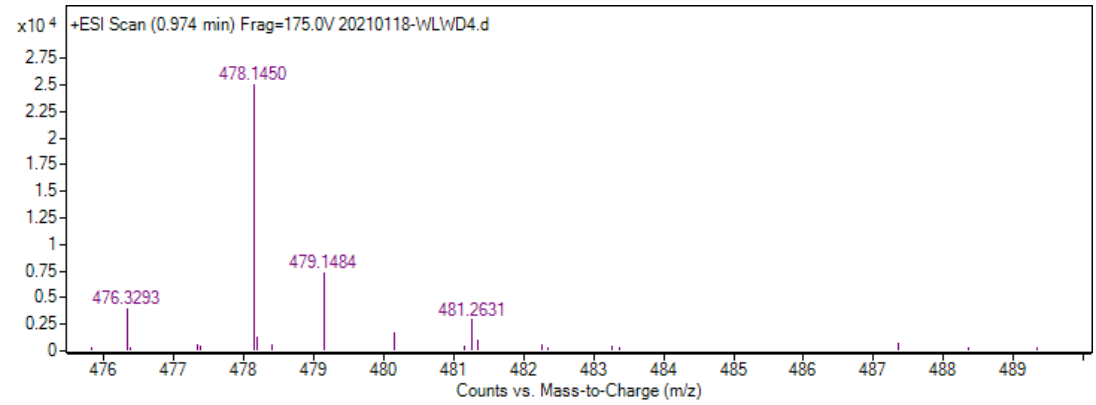


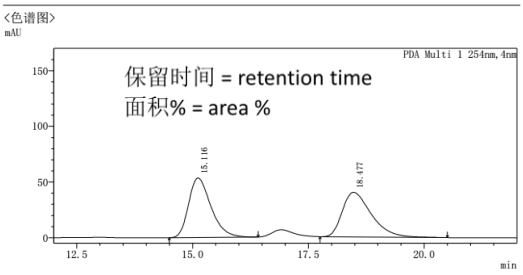
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.648	8398753	303441		98.859	99.072
2	15.508	96966	2841		1.141	0.928
总计		8495720	306282		100.000	100.000



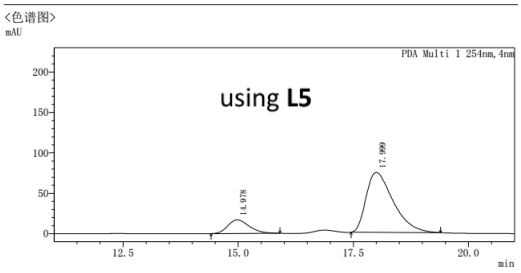
Compound *cis*-2g: 49.4 mg of **S1g'** yields 29.6 mg of **2g** (64%, 11 h, *trans*/*cis* = 1.0:1.0, 14.8 mg *cis* product, using **L5**); 50.9 mg of **S1g'** yield 34.9 mg of **2g** (73%, 11 h, *trans*/*cis* = 1.7:1, 12.9 mg *cis* product, using **L6**), white solid, m.p. 209.7-211.9 °C, R_f = 0.2 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 – 6.97 (m, 4H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.70 – 6.63 (m, 4H), 6.47 (d, *J* = 8.6 Hz, 2H), 5.53 (d, *J* = 9.5 Hz, 1H), 4.64 (d, *J* = 9.4 Hz, 1H), 3.64 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.7, 144.0, 143.3, 136.8, 136.1, 134.4, 129.9, 129.8, 129.7, 128.5, 128.4, 127.9, 127.2, 127.1, 126.0, 124.7, 115.9, 113.1, 70.6, 55.2, 54.0, 21.7. **IR** (KBr, cm^{-1}) 3034, 2836, 1605, 1512, 1461, 1355, 1298, 1248, 1168, 1097, 1032, 951, 818, 739, 702, 673, 576, 546. **HRMS** (ESI) Calcd for $C_{28}H_{25}NNaO_3S$ $(M+Na)^+$ 478.1447, found 478.1450. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 18.0 min, minor: 15.0 min. 70% ee. $[\alpha]_D^{21}$ = -52° (*c* 0.37, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 18.2 min, minor: 15.1 min. 66% ee. $[\alpha]_D^{21}$ = -45° (*c* 0.35, CH_2Cl_2).





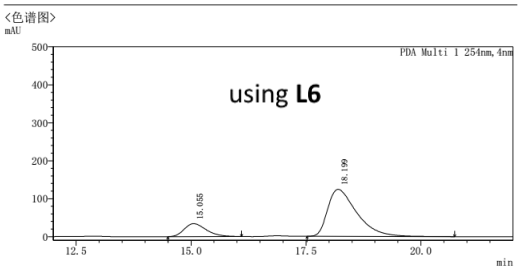
峰表
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	15.116	1795983	53405		50.644	57.131
2	18.477	1750278	40074		49.356	42.869
总计		3546261	93479		100.000	100.000



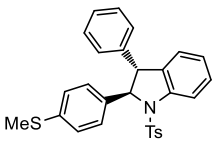
峰表
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	14.978	547668	16924		15.264	18.579
2	17.999	3040192	74166		84.736	81.421
总计		3587859	91090		100.000	100.000

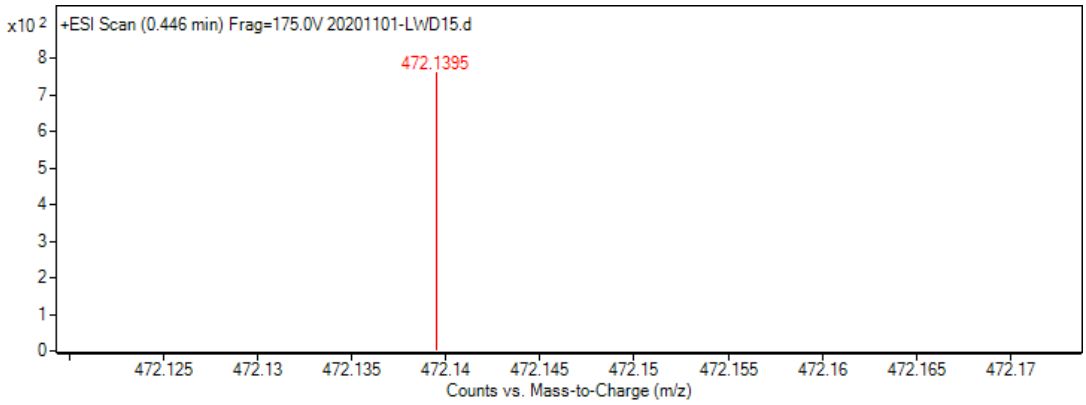


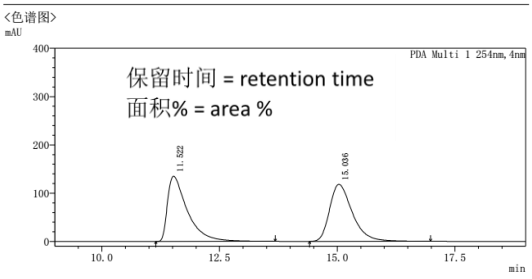
峰表
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	15.055	1145418	34157		17.370	21.636
2	18.199	5448866	123712		82.630	78.364
总计		6594284	157869		100.000	100.000



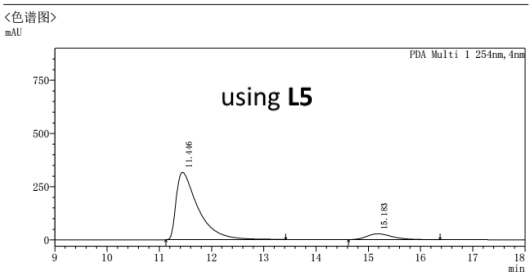
Compound *trans*-2h: 50.0 mg of **S1h'** yields 26.9 mg of **2h** (57%, 12 h, *cis*/*trans* = 1.3:1, 11.8 mg *trans* product, using **L5**); 61.1 mg of **S1h'** yields 36.1 mg of **2h** (63%, 12 h, *trans*/*cis* = 1.7:1, 22.7 mg *trans* product, using **L6**), white solid, m.p. = 136.3-138.8 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.17 – 7.09 (m, 3H), 7.07 – 7.00 (m, 3H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 7.5 Hz, 2H), 4.96 (d, *J* = 4.1 Hz, 1H), 4.19 (d, *J* = 3.9 Hz, 1H), 2.47 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 143.4, 142.4, 140.1, 138.0, 134.6, 133.0, 129.7, 128.82, 128.76, 127.5, 127.2, 126.9, 126.5, 126.3, 124.7, 115.6, 74.1, 57.4, 21.7, 16.1. **IR** (KBr, cm^{-1}) 3026, 1595, 1486, 1356, 1264, 1165, 1095, 1021, 958, 809, 755, 702, 664, 572, 540. **HRMS** (ESI) Calcd for $C_{28}H_{26}NO_2S_2$ $(M+H)^+$ 472.1400, found 472.1395. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 11.4 min, minor: 15.2 min. 82% ee. $[\alpha]_D^{21}$ = -80° (*c* 0.43, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 11.3 min, minor: 15.0 min. 96% ee. $[\alpha]_D^{21}$ = -112° (*c* 0.51, CH_2Cl_2).





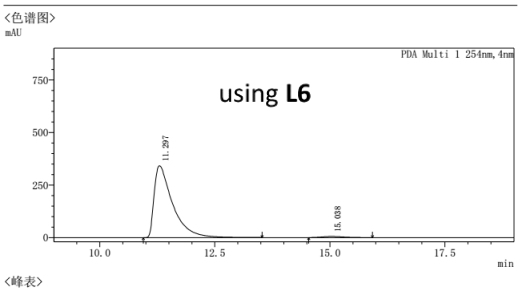
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.522	3981490	135240		50.071	53.384
2	15.036	3970144	118095		49.929	46.616
总计		7951634	253335		100.000	100.000



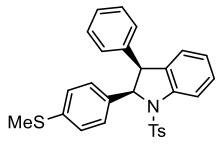
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.446	9220884	316439		90.707	92.022
2	15.183	944643	27432		9.293	7.978
总计		10165527	343871		100.000	100.000

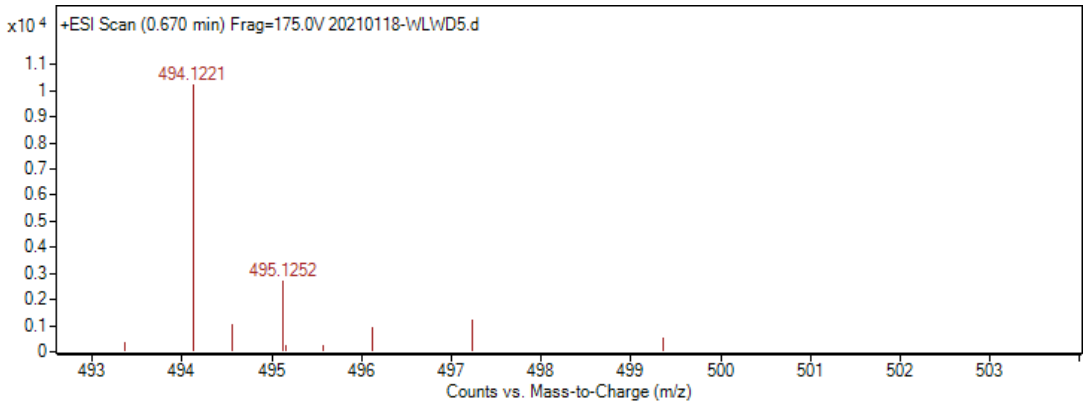


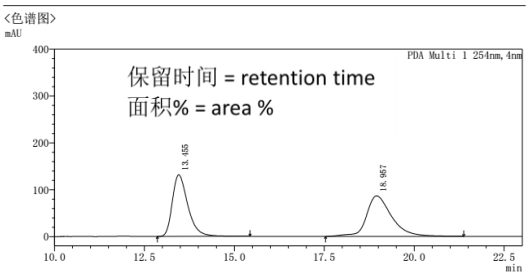
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.297	9572892	341810		98.150	98.422
2	15.038	180418	5479		1.850	1.578
总计		9753310	347289		100.000	100.000



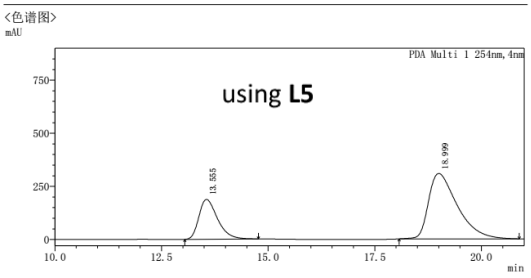
Compound *cis*-2h: 50.0 mg of **S1h'** yields 26.9 mg (57%, 12 h, *cis*/*trans* = 1.3:1, 15.1 mg *cis* product, using **L5**); 61.1 mg of **S1h'** yields 36.1 mg of **2h** (63%, 12 h, *trans*/*cis* = 1.7:1, 13.4 mg *cis* product, using **L6**), white solid, m.p. = 204.9-206.2 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.08 – 6.97 (m, 4H), 6.87 – 6.80 (m, 3H), 6.70 – 6.63 (m, 4H), 5.52 (d, *J* = 9.5 Hz, 1H), 4.66 (d, *J* = 9.5 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.1, 143.2, 137.2, 136.6, 136.0, 134.6, 134.3, 129.9, 129.8, 128.6, 128.0, 127.8, 127.24, 127.20, 126.1, 126.0, 124.8, 115.9, 70.6, 53.9, 21.7, 16.1. **IR** (KBr, cm^{-1}) 3032, 2922, 1597, 1464, 1353, 1300, 1220, 1164, 1095, 1021, 952, 813, 735, 700, 664, 577, 543. **HRMS** (ESI) Calcd for $C_{28}H_{25}NNaO_2S_2$ $(M+Na)^+$ 494.1219, found 494.1221. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 19.0 min, minor: 13.6 min. 54% ee. $[\alpha]_D^{21}$ = -19° (*c* 0.42, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 19.0 min, minor: 13.5 min. 42% ee. $[\alpha]_D^{21}$ = -10° (*c* 0.39, CH_2Cl_2). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.08 – 6.97 (m, 4H), 6.87 – 6.80 (m, 3H), , 5.52 (d, *J* = 9.5 Hz, 1H), 4.66 (d, *J* = 9.5 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H).





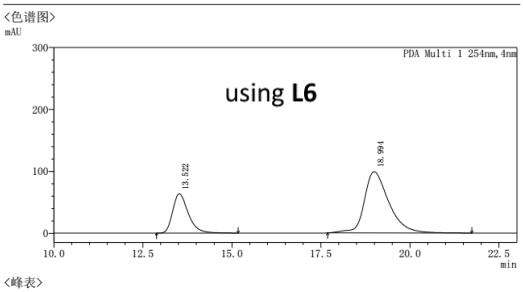
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.455	3971261	131816		48.659	60.417
2	18.957	4190159	86360		51.341	39.583
总计		8161420	218176		100.000	100.000



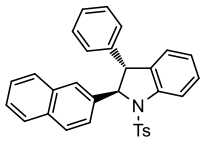
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.555	5688881	187520		28.193	37.842
2	18.999	14489268	308015		71.807	62.158
总计		20178149	495535		100.000	100.000

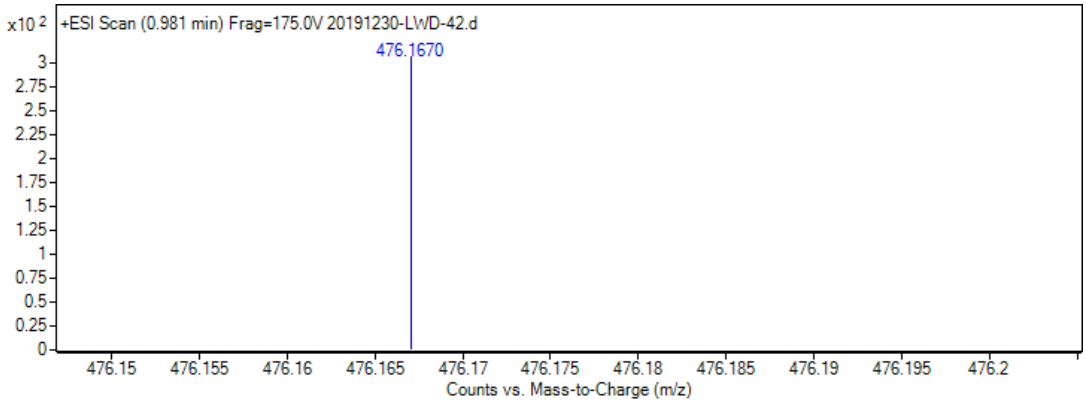


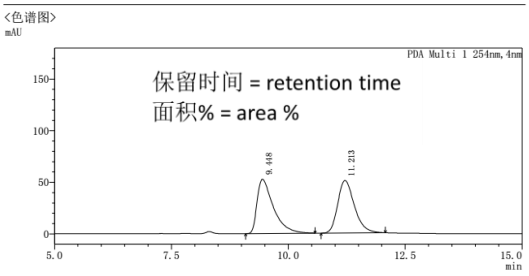
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.522	1943039	63527		28.985	39.086
2	18.994	4760666	99005		71.015	60.914
总计		6703704	162532		100.000	100.000



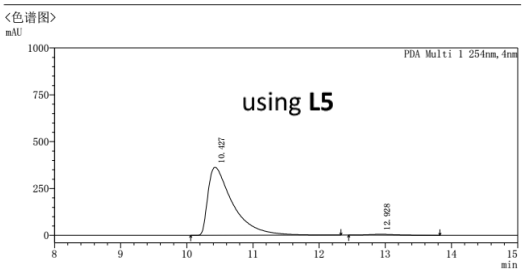
Compound *trans*-2i: 51.4 mg of **S1i'** yields 28.5 mg of **2i** (59%, 3 h, *trans*/*cis* = 2.3:1, using **L5**); 50.6 mg of **S1i'** yields 21.4 mg of **2i** (45%, 3 h, *trans*/*cis* = 4.0:1, using **L6**), white solid, m.p. = 189.0-190.9 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.75 (m, 4H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.42 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.09 – 7.02 (m, 3H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.46 (d, *J* = 7.4 Hz, 2H), 5.17 (d, *J* = 4.2 Hz, 1H), 4.29 (d, *J* = 4.2 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.1, 143.5, 142.6, 140.3, 134.7, 133.5, 133.18, 133.17, 129.7, 129.1, 128.9, 128.8, 128.3, 127.8, 127.64, 127.60, 127.0, 126.37, 126.35, 126.1, 124.9, 124.7, 123.9, 115.7, 74.6, 57.4, 21.7. **IR** (KBr, cm^{-1}) 3058, 2923, 1598, 1493, 1447, 1460, 1359, 1264, 1170, 1107, 1090, 1026, 956, 815, 737, 701, 666, 574, 544, 476. **HRMS** (ESI) Calcd for $C_{31}H_{26}NO_2S$ $(M+H)^+$ 476.1679, found 476.1670. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 10.4 min, minor: 12.9 min. 97% ee. $[\alpha]_D^{21}$ = -86° (*c* 0.50, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 9.2 min, minor: 11.3 min. 98% ee. $[\alpha]_D^{21}$ = -83° (*c* 0.26, CH_2Cl_2).





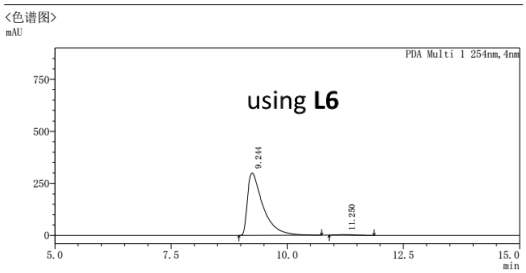
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.448	1277780	52570		50.284	50.756
2	11.213	1263357	51004		49.716	49.244
总计		2541137	103574		100.000	100.000



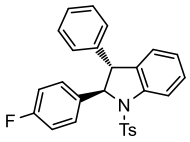
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.427	9496137	363164		98.597	98.692
2	12.928	135107	4812		1.403	1.308
总计		9631244	367976		100.000	100.000

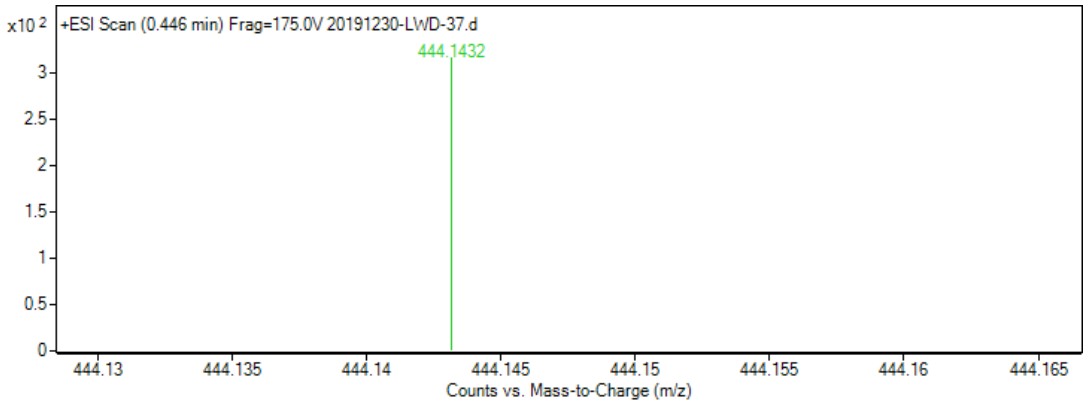


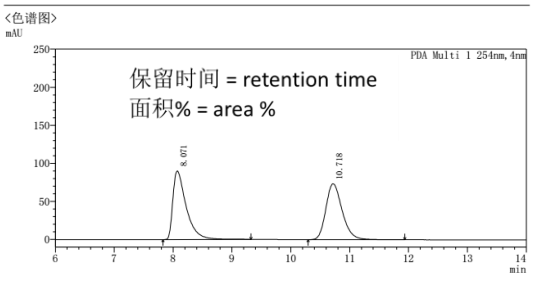
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.244	6962038	299613		99.068	99.062
2	11.250	65493	2837		0.932	0.938
总计		7027531	302450		100.000	100.000



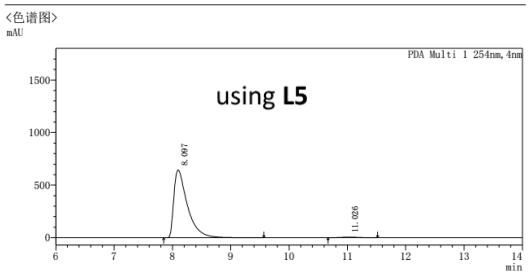
Compound *trans*-2j: 48.7 mg of **S1j'** yields 29.6 mg of **2j** (65%, 11 h, *trans*/*cis* = 5.3:1, using **L5**); 48.0 mg of **S1j'** yields 24.7 mg of **2j** (55%, 11 h, *trans*/*cis* = 5.3:1, using **L6**), white solid, m.p. = 129.5-130.6 °C, R_f = 0.6 (petroleum ether:ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.15 – 7.10 (m, 3H), 7.07 – 6.97 (m, 5H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 2H), 4.98 (d, *J* = 4.1 Hz, 1H), 4.18 (d, *J* = 4.0 Hz, 1H), 2.39 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.8. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245.8 Hz), 144.2, 143.3, 142.3, 139.1(d, *J* = 2.9 Hz), 134.5, 132.9, 129.8, 128.9, 128.8, 127.7 (d, *J* = 8.1 Hz), 127.55, 127.52, 127.0, 126.3, 124.8, 115.9, 115.7 (d, *J* = 2.5 Hz), 73.8, 57.4, 21.6. **IR** (KBr, cm^{-1}) 3032, 2922, 1600, 1509, 1458, 1359, 1226, 1170, 1096, 1023, 957, 817, 736, 701, 667, 574, 543. **HRMS** (ESI) Calcd for $C_{27}H_{23}FNO_2S$ $(M+H)^+$ 444.1428, found 444.1432. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.1 min, minor: 11.0 min. 98% ee. $[\alpha]_D^{21}$ = -145° (*c* 0.76, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.0 min, minor: 10.7 min. 97% ee. $[\alpha]_D^{21}$ = -101° (*c* 0.41, CH_2Cl_2).





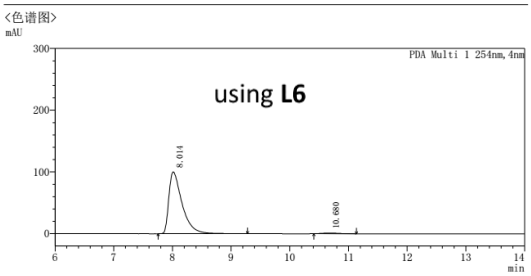
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.071	1424977	90069		50.166	55.051
2	10.718	1415533	73543		49.834	44.949
总计		2840510	163612		100.000	100.000



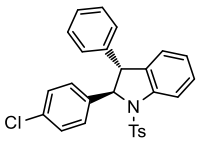
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.097	10468924	645055		98.831	99.070
2	11.026	123808	6052		1.169	0.930
总计		10592732	651107		100.000	100.000

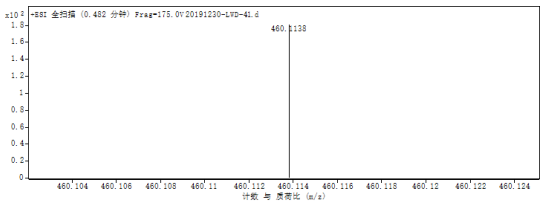


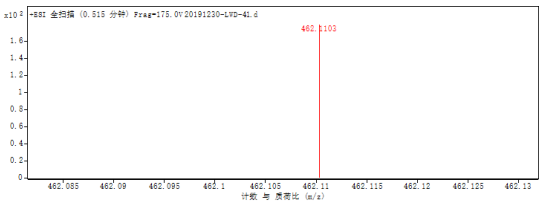
〈峰表〉
PDA Ch1 254nm

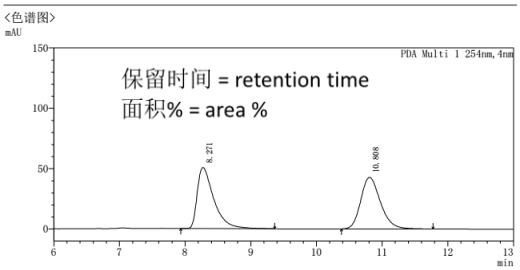
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.014	1575393	100196		98.608	98.809
2	10.680	22233	1207		1.392	1.191
总计		1597626	101404		100.000	100.000



Compound *trans*-2k: 51.0 mg of **S1k'** yields 27.5 mg of **2k** (57%, 12 h, *trans*/*cis* = 4.6:1, using **L5**); 48.9 mg of **S1k'** yields 23.9 mg of **2k** (52%, 12 h, *trans*/*cis* = 1.8:1, using **L6**), white solid, m.p. = 145.6-147.6 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.26 (m, 5H), 7.19 – 7.10 (m, 3H), 7.09 – 6.99 (m, 3H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 2H), 4.95 (d, *J* = 4.2 Hz, 1H), 4.16 (d, *J* = 4.0 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 143.2, 142.3, 141.7, 134.4, 133.6, 132.8, 129.8, 129.1, 128.9, 128.8, 127.6, 127.5, 127.4, 127.1, 126.3, 124.9, 115.7, 73.8, 57.4, 21.7. **IR** (KBr, cm^{-1}) 3029, 1597, 1486, 1458, 1359, 1263, 1168, 1090, 1016, 956, 812, 751, 703, 665, 574, 542. **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_2S$ $(M+H)^+$ 460.1133, found 460.1138; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_2S$ $(M+H)^+$ 462.1104, found 462.1103. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.1 min, minor: 10.8 min. 96% ee. $[\alpha]_D^{21}$ = -135° (*c* 0.64, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.2 min, minor: 10.9 min. 92% ee. $[\alpha]_D^{21}$ = -154° (*c* 0.68, CH_2Cl_2).

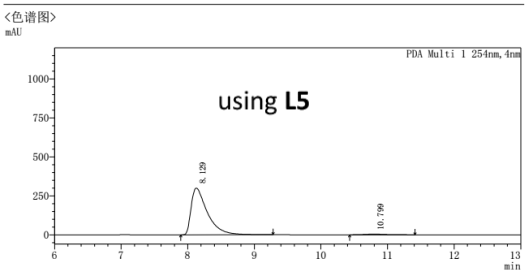






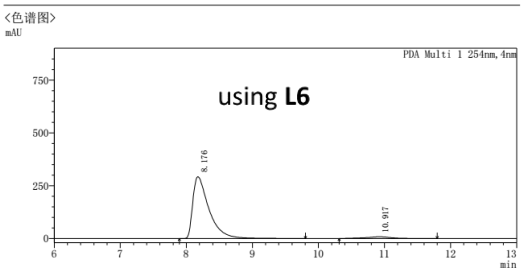
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.271	890614	50618		49.959	54.227
2	10.808	892063	42726		50.041	45.773
总计		1782678	93344		100.000	100.000



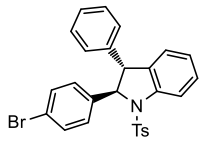
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.129	5073003	300125		98.276	98.628
2	10.799	88975	4175		1.724	1.372
总计		5161977	304300		100.000	100.000

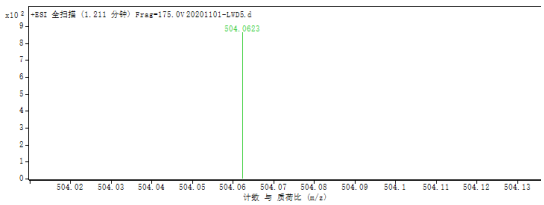


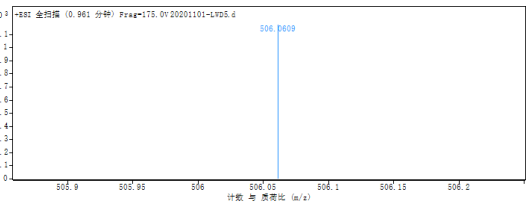
〈峰表〉
PDA Ch1 254nm

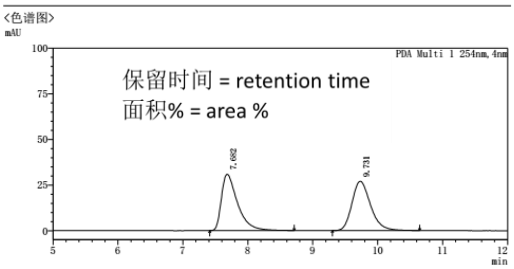
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.176	4959265	292021		95.776	97.288
2	10.917	218745	8141		4.224	2.712
总计		5178010	300162		100.000	100.000



Compound *trans*-2l: 54.0 mg of **S1l'** yields 30.6 mg of **2l** (60%, 11 h, *trans*/*cis* =4.3:1, using **L5**); 52.1 mg of **S1l'** yields 24.1 mg **2l** (49%, 11 h, *trans*/*cis* = 3.5:1, using **L6**), white solid, m.p. = 169.6-172.2 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.11 (m, 3H), 7.08 – 7.00 (m, 3H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 7.5 Hz, 2H), 4.93 (d, *J* = 4.3 Hz, 1H), 4.16 (d, *J* = 4.2 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 143.2, 142.3, 142.2, 132.8, 132.1, 129.8, 128.9, 128.8, 127.7, 127.6, 127.5, 127.1, 126.3, 124.9, 121.8, 115.7, 73.8, 57.3, 21.7. **IR** (KBr, cm^{-1}) 3029, 2921, 1597, 1484, 1458, 1359, 1261, 1167, 1106, 1010, 957, 811, 754, 702, 665, 575, 542. **HRMS** (ESI) Calcd for $C_{27}H_{23}BrNO_2S$ $(M+H)^+$ 504.0628, found 504.0623; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{23}BrNO_2S$ $(M+H)^+$ 506.0607, found 506.0609. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.3 min, minor: 11.0 min. 97% ee. $[\alpha]_D^{21}$ = -140° (*c* 0.48, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 7.6 min, minor: 9.8 min. 97% ee. $[\alpha]_D^{21}$ = -119° (*c* 0.51, CH_2Cl_2).



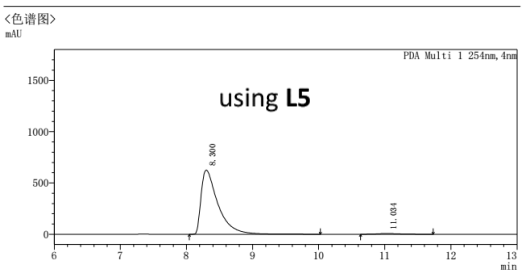




〈峰表〉

PDA Ch1 254nm

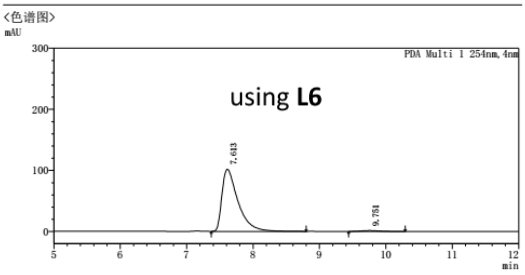
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.682	534860	30910		49.810	53.314
2	9.731	538940	27067		50.190	46.686
总计		1073800	57977		100.000	100.000



〈峰表〉

PDA Ch1 254nm

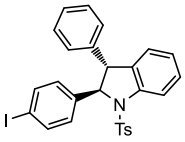
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.300	11089083	626287		98.648	98.928
2	11.034	151935	6790		1.352	1.072
总计		11241018	633077		100.000	100.000



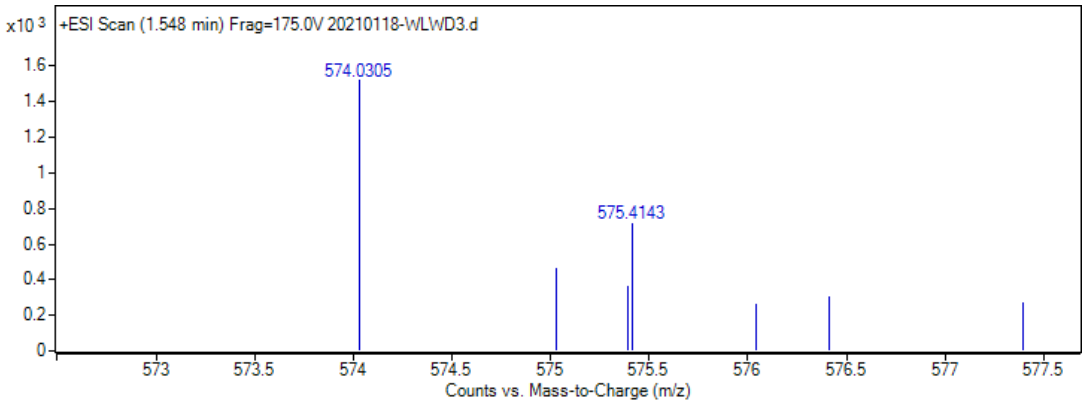
〈峰表〉

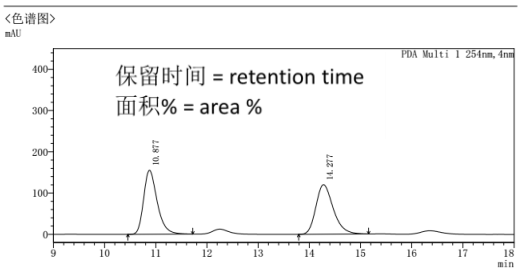
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.613	1709126	101633		98.429	98.629
2	9.751	27275	1413		1.571	1.371
总计		1736400	103046		100.000	100.000



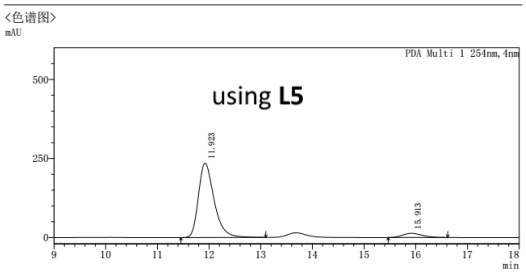
Compound *trans*-2m: 53.5 mg of **S1m'** yields 21.2 mg of **2m** (42%, 12 h, *trans*/*cis* = 4.3:1, using **L5**); 55.5 mg of **S1m'** yields 24.8 mg of **2m** (47%, 12 h, *trans*/*cis* = 3.2:1, using **L6**), white solid, m.p. = 186.9-191.0 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.16 – 7.12 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.06 – 7.01 (m, 3H), 6.86 (d, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 2H), 4.92 (d, *J* = 4.1 Hz, 1H), 4.16 (d, *J* = 3.9 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 143.2, 142.9, 142.3, 138.0, 134.4, 132.8, 129.8, 128.9, 128.8, 128.0, 127.6, 127.5, 127.1, 126.3, 124.9, 115.7, 93.4, 73.9, 57.3, 21.7. **IR** (KBr, cm^{-1}) 3031, 1596, 1482, 1359, 1167, 1098, 1006, 957, 811, 733, 703, 666, 576, 545. **HRMS** (ESI) Calcd for $C_{27}H_{22}INNaO_2S$ $(M+Na)^+$ 574.0308, found 574.0305. **HPLC** (using **L5**): INA column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 11.9 min, minor: 15.9 min. 86% ee. $[\alpha]_D^{21}$ = -96° (*c* 0.34, CH_2Cl_2); **HPLC** (using **L6**): INA column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 11.6 min, minor: 15.3 min. 96% ee. $[\alpha]_D^{21}$ = -126° (*c* 0.40, CH_2Cl_2).





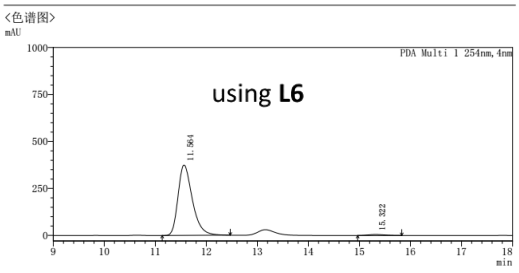
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.877	2860969	155085		50.243	56.383
2	14.277	2833351	119971		49.757	43.617
总计		5694320	275056		100.000	100.000



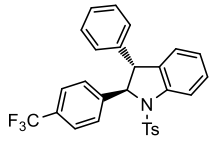
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.923	4959966	235125		93.351	94.638
2	15.913	353301	13321		6.649	5.362
总计		5313267	248446		100.000	100.000

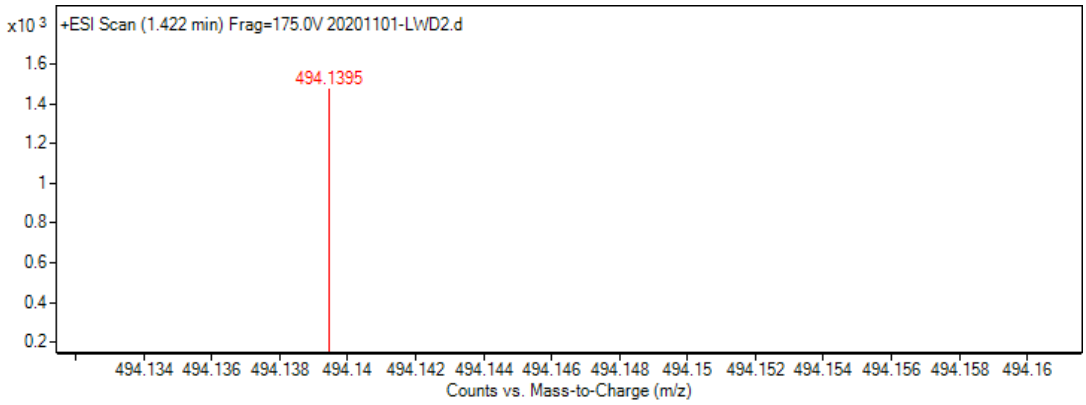


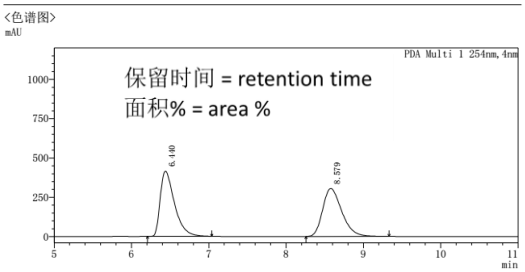
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.564	7314512	374636		98.396	98.661
2	15.322	119213	5086		1.604	1.339
总计		7433725	379723		100.000	100.000



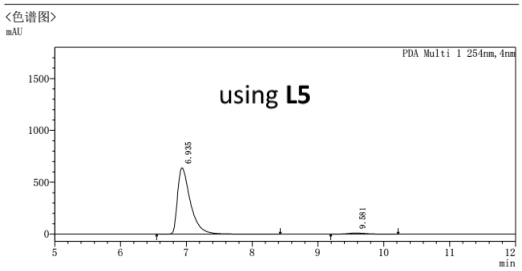
Compound *trans*-2n: 53.1 mg of **S1n'** yields 27.0 mg of **2n** (54%, 11 h, *trans*/*cis* = 2.8:1, using **L5**); 52.2 mg of **S1n'** yields 24.1 mg of **2n** (49%, 11 h, *trans*/*cis* = 1.9:1, using **L6**), white solid, m.p. = 160.9-162.5 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.54 (m, 4H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.09 – 7.02 (m, 3H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.41 (d, *J* = 7.4 Hz, 2H), 5.03 (d, *J* = 4.3 Hz, 1H), 4.17 (d, *J* = 4.2 Hz, 1H), 2.41 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.5. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.0, 144.4, 143.0, 142.3, 134.3, 132.7, 130.1 (q, *J* = 32.4 Hz), 129.8, 129.0, 128.9, 127.6, 127.5, 126.33, 126.31, 126.0 (q, *J* = 3.5 Hz), 125.0, 124.2 (q, *J* = 272.16 Hz), 115.7, 73.9, 57.3, 21.7. **IR** (KBr, cm^{-1}) 3032, 2922, 1620, 1598, 1494, 1478, 1461, 1419, 1361, 1325, 1263, 1167, 1121, 1068, 1017, 950, 840, 814, 739, 701, 667, 576, 544. **HRMS** (ESI) Calcd for $C_{28}H_{23}F_3NO_2S$ $(M+H)^+$ 494.1396, found 494.1395. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.9 min, minor: 9.6 min. 96% ee. $[\alpha]_D^{21}$ = -116° (*c* 0.61, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.4 min, minor: 8.6 min. 96% ee. $[\alpha]_D^{21}$ = -116° (*c* 0.36, CH_2Cl_2).





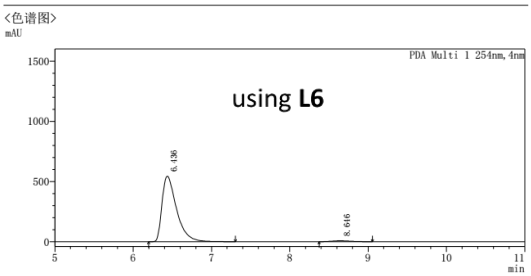
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.440	5318408	414038		50.284	57.571
2	8.579	5258352	305135		49.716	42.429
总计		10576760	719173		100.000	100.000



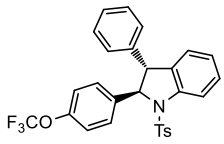
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.935	8655917	639257		97.733	98.378
2	9.581	200821	10541		2.267	1.622
总计		8856738	649798		100.000	100.000

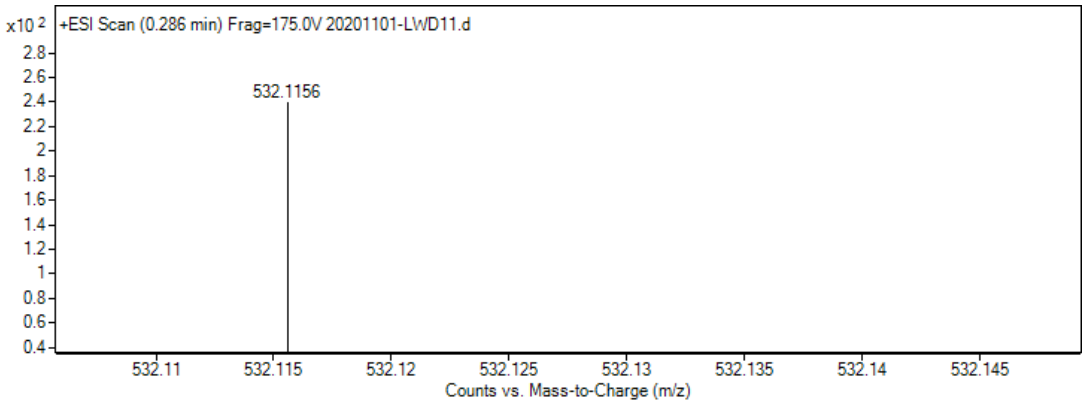


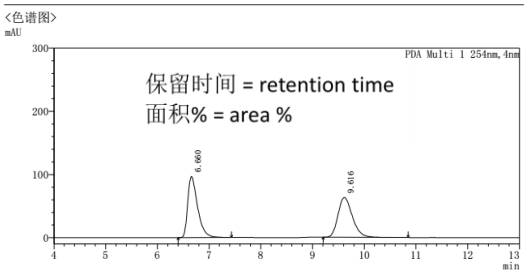
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.436	7030334	543586		98.108	98.557
2	8.646	135544	7956		1.892	1.443
总计		7165879	551542		100.000	100.000



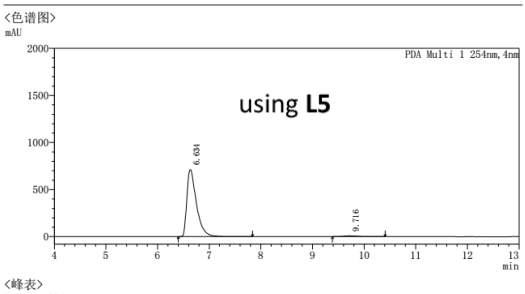
Compound *trans*-2o: 53.4 mg of **S1o'** yields 36.8 mg of **2o** (73%, 10 h, *trans*/*cis* = 4.6:1, using **L5**); 56.3 mg of **S1o'** yields 34.0 mg of **2o** (64%, 10 h, *trans*/*cis* = 4.3:1, using **L6**), white solid, m.p. = 118.1-120.7 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.20 – 7.10 (m, 5H), 7.09 – 7.01 (m, 3H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 7.7 Hz, 2H), 5.02 (d, *J* = 4.0 Hz, 1H), 4.19 (d, *J* = 3.9 Hz, 1H), 2.40 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -57.8. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.8, 144.3, 143.2, 142.2, 141.9, 134.5, 132.8, 129.8, 129.0, 128.9, 127.55, 127.52, 127.4, 127.1, 126.4, 124.9, 121.5, 120.6 (q, *J* = 258.3 Hz), 115.7, 73.6, 57.3, 21.6. **IR** (KBr, cm^{-1}) 2968, 1596, 1505, 1361, 1261, 1222, 1167, 1167, 1101, 1022, 957, 811, 752, 702, 667, 575, 543. **HRMS** (ESI) Calcd for $C_{28}H_{22}F_3NNaO_3S$ $(M+Na)^+$ 532.1164, found 532.1156. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.6 min, minor: 9.7 min. 97% ee. $[\alpha]_D^{21}$ = -77° (*c* 0.62, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.6 min, minor: 9.6 min. 98% ee. $[\alpha]_D^{21}$ = -72° (*c* 0.58, CH_2Cl_2).





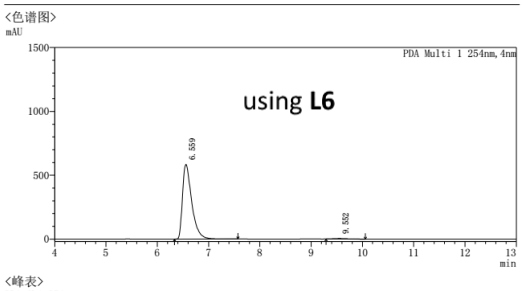
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.660	1284867	96594		51.339	60.520
2	9.616	1217827	63012		48.661	39.480
总计		2502694	159606		100.000	100.000



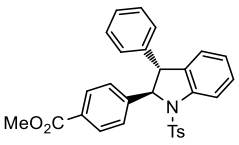
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.634	9185237	712475		98.357	98.896
2	9.716	153390	7957		1.643	1.104
总计		9338627	720432		100.000	100.000

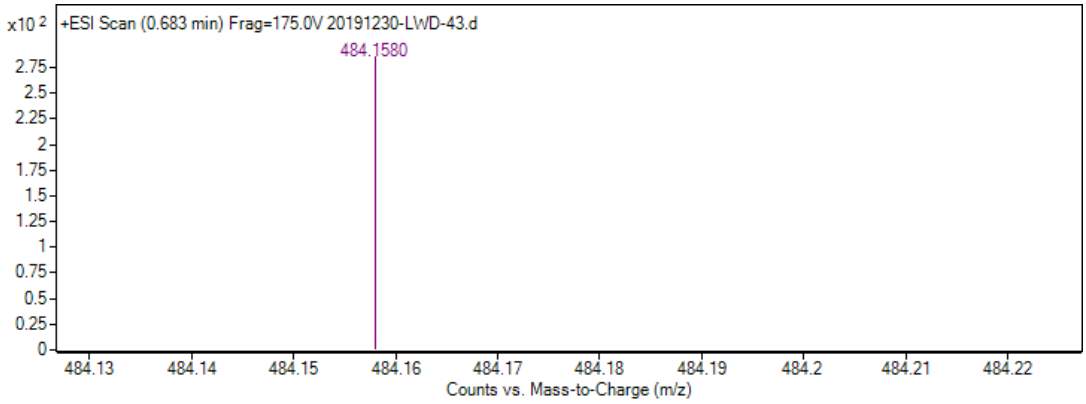


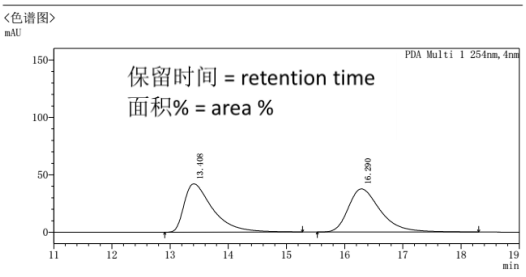
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.559	7325628	585589		99.006	99.307
2	9.552	73542	4086		0.994	0.693
总计		7399170	589676		100.000	100.000



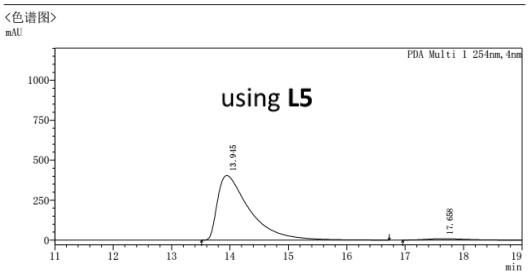
Compound *trans*-2p: 55.0 mg of **S1p'** yields 22.0 mg of **2p** (42%, 4 h, *trans*/*cis* = 4.6:1, using **L5**); 51.3 mg of **S1p'** yields 23.7 mg of **2p** (49%, 4 h, *trans*/*cis* = 3.5:1, using **L6**), white solid, m.p. = 148.6-149.9 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.17 – 7.11 (m, 3H), 7.08 – 7.01 (m, 3H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.41 (d, *J* = 7.5 Hz, 2H), 5.03 (d, *J* = 4.4 Hz, 1H), 4.17 (d, *J* = 4.2 Hz, 1H), 3.91 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 148.1, 144.4, 143.1, 142.3, 134.3, 132.8, 130.4, 129.8, 129.7, 129.0, 128.8, 127.61, 127.57, 127.1, 126.3, 125.9, 124.9, 115.7, 74.1, 57.3, 52.2, 21.6. **IR** (KBr, cm^{-1}) 3059, 2952, 1721, 1604, 1458, 1437, 1359, 1279, 1169, 1109, 1021, 958, 811, 737, 702, 666, 575, 543. **HRMS** (ESI) Calcd for $C_{29}H_{26}NO_4S$ $(M+H)^+$ 484.1577, found 484.1580. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 13.9 min, minor: 17.7 min. 95% ee. $[\alpha]_D^{21}$ = -113° (*c* 1.08, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 13.2 min, minor: 16.3 min. 94% ee. $[\alpha]_D^{21}$ = -86° (*c* 0.35, CH_2Cl_2).





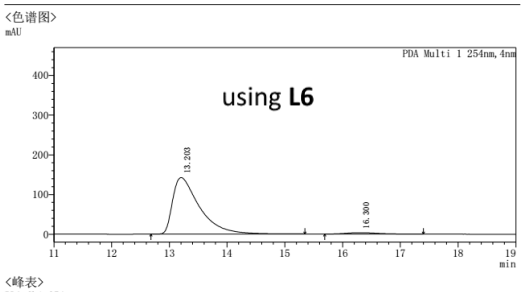
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.408	1439521	42174		49.897	52.881
2	16.290	1445452	37578		50.103	47.119
总计		2884973	79752		100.000	100.000



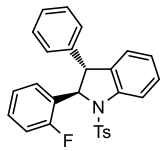
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.945	15459906	403834		97.444	97.959
2	17.658	405531	8414		2.556	2.041
总计		15865436	412248		100.000	100.000

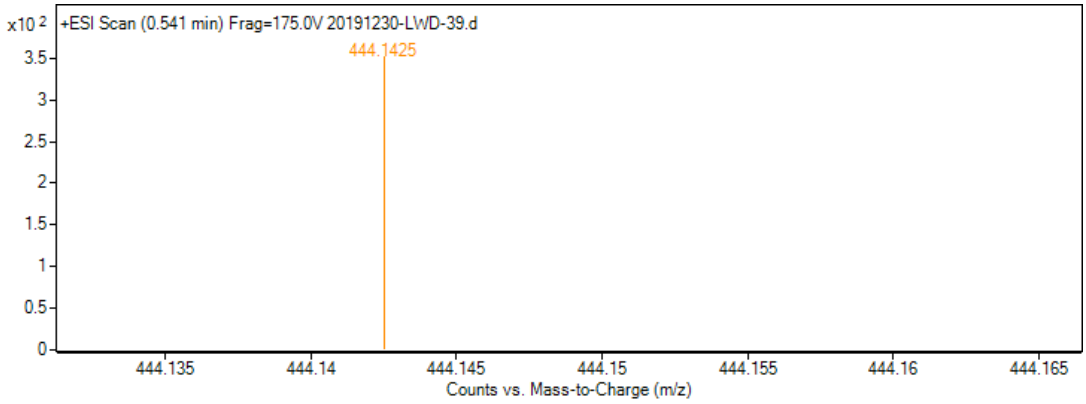


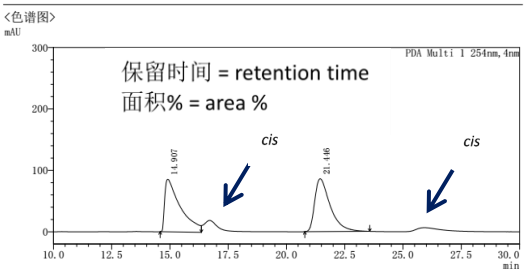
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.203	4600868	142310		97.162	97.533
2	16.300	134386	3600		2.838	2.467
总计		4735254	145909		100.000	100.000



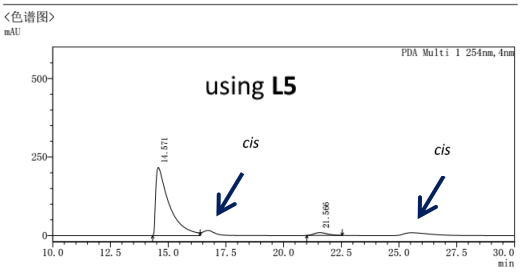
Compound *trans*-2q: 48.2 mg of **S1q'** yields 28.5 mg of **2q** (63%, 12 h, *trans*/*cis* = 7.3:1, using **L5**); 47.3 mg of **1q** yields 27.5 mg of **S2q'** (62%, 12 h, *trans*/*cis* = 5.3:1, using **L6**), white solid, m.p. = 168.8-170.6 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.15 – 7.02 (m, 6H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 2H), 5.34 (d, *J* = 3.4 Hz, 1H), 4.21 (d, *J* = 3.0 Hz, 1H), 2.38 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -117.2. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8 (d, *J* = 246.4 Hz), 144.2, 143.2, 142.2, 134.7, 133.0, 130.2 (d, *J* = 13.1 Hz), 129.8, 129.4 (d, *J* = 8.1 Hz), 128.9, 128.5, 127.9 (d, *J* = 3.9 Hz), 127.6, 127.5, 126.8, 126.5, 124.8, 124.7 (d, *J* = 3.5 Hz),115.68, 115.68 (d, *J* = 21.1 Hz), 68.6, 56.4, 21.7. **IR** (KBr, cm^{-1}) 3064, 2924, 1595, 1486, 1457, 1360, 1261, 1228, 1168, 1098, 1028, 959, 812, 758, 733, 700, 666, 574, 546. **HRMS** (ESI) Calcd for $C_{27}H_{23}FNO_2S$ $(M+H)^+$ 444.1428, found 444.1425. **HPLC** (using **L5**): OD-H column, 97.5:2.5 hexane: isopropanol, 0.70 mL/min, t_R = major: 14.6 min, minor: 21.6 min. 92% ee; **HPLC** (using **L6**): OD-H column, 97.5:2.5 hexane: isopropanol, 0.70 mL/min, t_R = major: 15.5 min, minor: 22.2 min. 94% ee. (The specific rotation did not measure due to a pair of an inseparable diastereoisomers.)





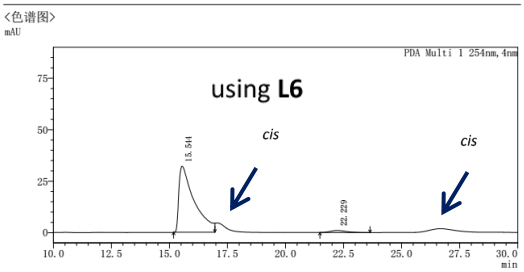
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	14.907	3996607	85556		50.147	49.841
2	21.446	3973102	86100		49.853	50.159
总计		7969709	171656		100.000	100.000



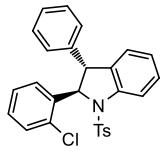
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	14.571	8945613	217081		96.021	95.997
2	21.566	370730	9053		3.979	4.003
总计		9316344	226134		100.000	100.000

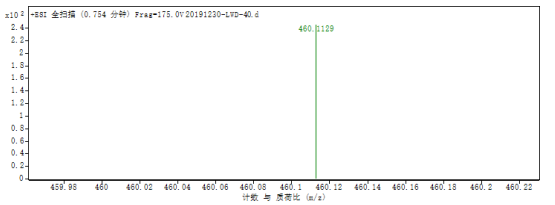


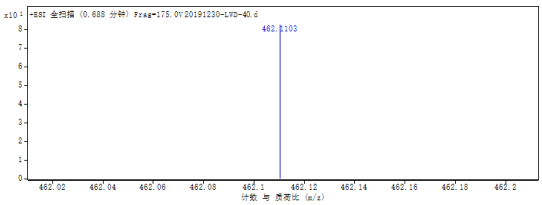
<峰表>
PDA Ch1 254nm

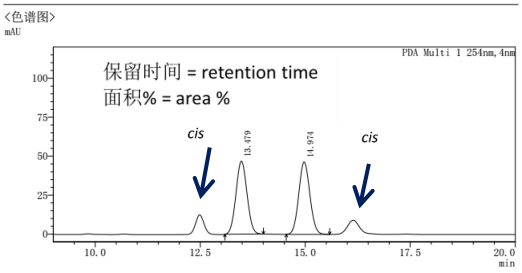
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	15.544	1473896	32074		96.958	97.060
2	22.229	46238	971		3.042	2.940
总计		1520135	33046		100.000	100.000



Compound *trans*-2r: 48.6 mg of **S1r'** yields 27.6 mg of **2r** (61%, 7 h, *trans*/*cis* = 4.3:1, using **L5**); 48.8 mg of **S1r'** yields 24.3 mg of **2r** (53%, 7 h, *trans*/*cis* = 2.8:1, using **L6**), white solid, m.p. = 155.6-159.5 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.45 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.25 – 7.17 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 7.5 Hz, 2H), 5.51 (d, *J* = 3.5 Hz, 1H), 4.13 (d, *J* = 3.5 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 143.2, 142.2, 140.7, 134.7, 133.2, 131.8, 129.9, 129.8, 128.9, 128.4, 127.8, 127.7, 127.6, 126.9, 126.4, 124.8, 115.2, 70.6, 56.7, 21.7. **IR** (KBr, cm^{-1}) 3031, 1598, 1455, 1354, 1247, 1166, 1098, 1025, 961, 811, 738, 702, 667, 579, 548. **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_2S$ $(M+H)^+$ 460.1133, found 460.1129. isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_2S$ $(M+H)^+$ 462.1104, found 460.1103. **HPLC** (using **L5**): INC column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 14.6 min, minor: 13.2 min. 89% ee. **HPLC** (using **L6**): INC column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 15.0 min, minor: 13.5 min. 88% ee. (The specific rotation did not measure due to a pair of an inseparable diastereoisomers.)

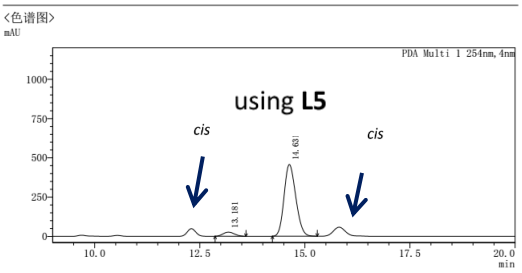






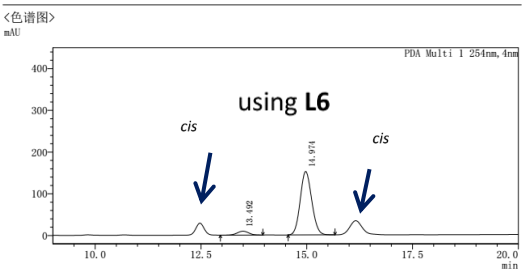
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.479	856653	46867		49.856	50.179
2	14.974	861598	46533		50.144	49.821
总计		1718251	93401		100.000	100.000



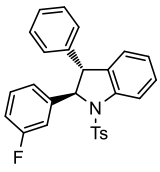
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.181	498396	26257		5.336	5.436
2	14.631	8841811	456727		94.664	94.564
总计		9340207	482984		100.000	100.000

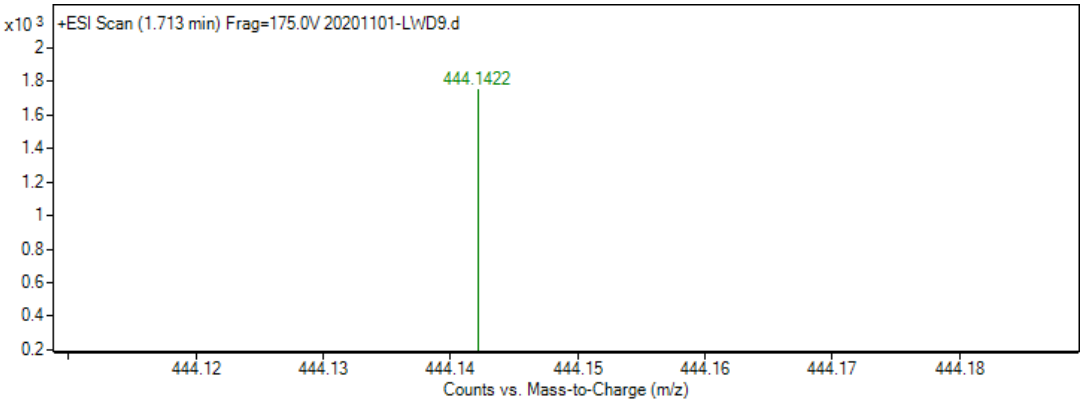


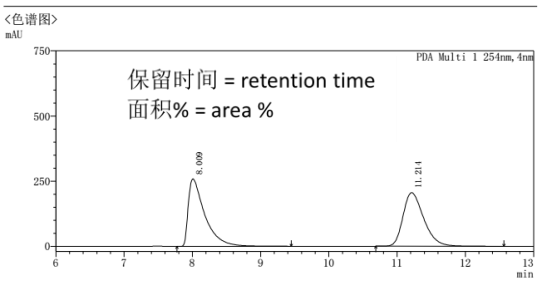
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.492	173285	9281		5.673	5.750
2	14.974	2881309	152110		94.327	94.250
总计		3054594	161391		100.000	100.000



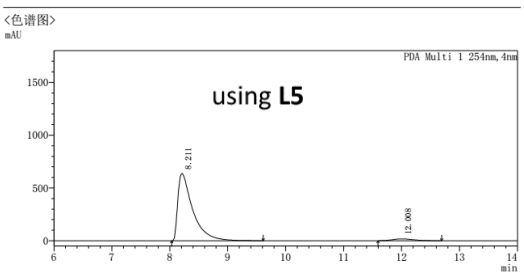
Compound *trans*-2s: 50.4 mg of **S1s'** yields 21.9 mg of **2s** (46%, 11 h, *trans*/*cis* = 4.9:1, using **L5**); 48.1 mg of **S1s'** yields 25.2 mg of **2s** (56%, 11 h, *trans*/*cis* = 4.0:1, using **L6**), white solid, m.p. = 121.4-122.5 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.27 (m, 2H), 7.18 – 7.11 (m, 4H), 7.08 – 7.01 (m, 4H), 6.98 (t, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 2H), 4.98 (d, *J* = 4.0 Hz, 1H), 4.19 (d, *J* = 3.9 Hz, 1H), 2.40 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.2. **^{13}C NMR** (126 MHz, $CDCl_3$) δ163.2 (d, *J* = 246.6 Hz), 145.7 (d, *J* = 6.6 Hz), 144.3, 143.2, 142.3, 134.4, 132.8, 130.6 (d, *J* = 8.2 Hz), 129.8, 129.0, 128.8, 127.6, 127.5, 127.1, 126.3, 124.9, 121.5 (d, *J* = 2.6 Hz), 115.8, 114.8 (d, *J* = 21.2 Hz), 113.0 (d, *J* = 22.5 Hz), 73.8, 57.3, 21.7. **IR** (KBr, cm^{-1}) 3063, 3031, 2924, 1595, 1484, 1455, 1359, 1264, 1168, 1098, 1027, 959, 879, 811, 789, 737, 698, 665, 577, 543. **HRMS** (ESI) Calcd for $C_{27}H_{23}FNO_2S$ $(M+H)^+$ 444.1428, found 444.1422. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.2 min, minor: 12.0 min. 93% ee. $[\alpha]_D^{21}$ = -134° (*c* 0.69, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 7.9 min, minor: 11.2 min. 95% ee. $[\alpha]_D^{21}$ = -155° (*c* 0.59, CH_2Cl_2).





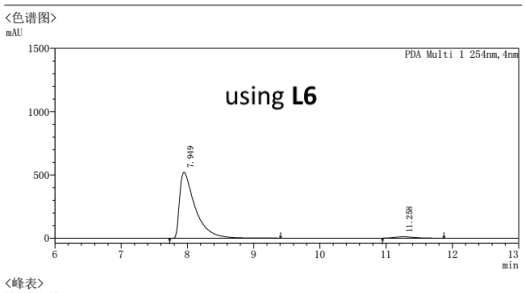
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.009	4356060	258898		50.064	55.765
2	11.214	4344942	205368		49.936	44.235
总计		8701002	464266		100.000	100.000



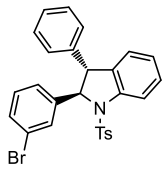
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.211	11422361	637482		96.374	97.374
2	12.008	429757	17194		3.626	2.626
总计		11852118	654676		100.000	100.000

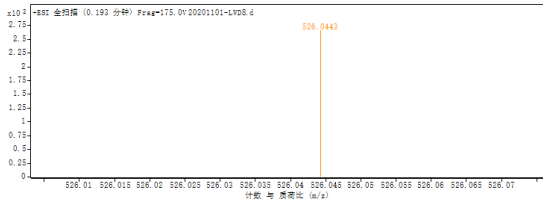


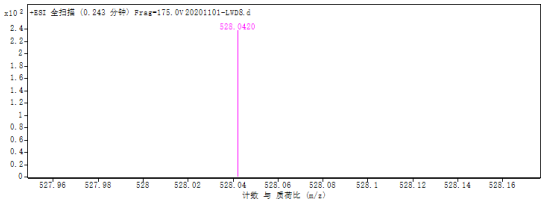
<峰表>
PDA Ch1 254nm

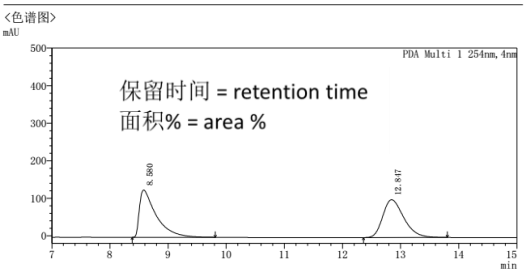
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.949	8531447	521595		97.399	97.931
2	11.258	227813	11021		2.601	2.069
总计		8759260	532616		100.000	100.000



Compound *trans*-2t: 53.2 mg of **S1t'** yields 20.4 mg of **2t** (40%, 10 h, *trans*/*cis* = 4.0:1, using **L5**); 50.5 mg of **S1t'** yields 20.0 mg of **2t** (42%, 10 h, *trans*/*cis* = 2.8:1, using **L6**), white solid, m.p. = 168.9-175.5 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.44 (s, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.17 – 7.11 (m, 3H), 7.08 – 7.00 (m, 3H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.41 (d, *J* = 7.5 Hz, 2H), 4.95 (d, *J* = 4.2 Hz, 1H), 4.18 (d, *J* = 4.1 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.4, 144.3, 143.2, 142.3, 134.4, 132.8, 131.0, 130.6, 129.8, 129.0, 128.9, 127.6, 127.5, 127.1, 126.3, 124.9, 124.7, 123.0, 115.7, 73.7, 57.3, 21.7. **IR** (KBr, cm^{-1}) 3063, 2923, 1597, 1572, 1475, 1428, 1401, 1359, 1260, 1167, 1094, 1027, 955, 811, 787, 735, 699, 666, 575, 543. **HRMS** (ESI) Calcd for $C_{27}H_{22}BrNNaO_2S$ $(M+Na)^+$ 526.0447, found 526.0443; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{22}BrNNaO_2S$ $(M+Na)^+$ 528.0427, found 528.0420. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.7 min, minor: 13.5 min. 94% ee. $[\alpha]_D^{21}$ = -158° (*c* 0.48, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.6 min, minor: 13.0 min. 98% ee. $[\alpha]_D^{21}$ = -162° (*c* 0.46, CH_2Cl_2).

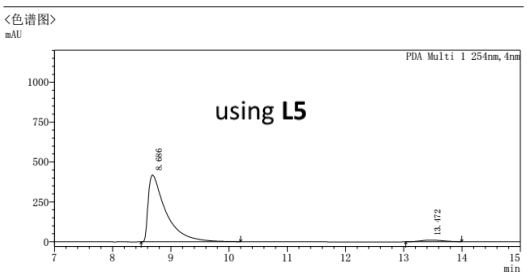






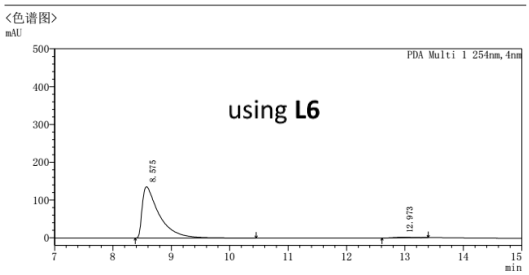
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.580	2528456	125688		49.896	55.522
2	12.847	2539032	100686		50.104	44.478
总计		5067489	226373		100.000	100.000



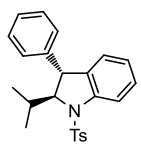
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.686	8868095	418698		96.859	97.500
2	13.472	287540	10737		3.141	2.500
总计		9155635	429435		100.000	100.000

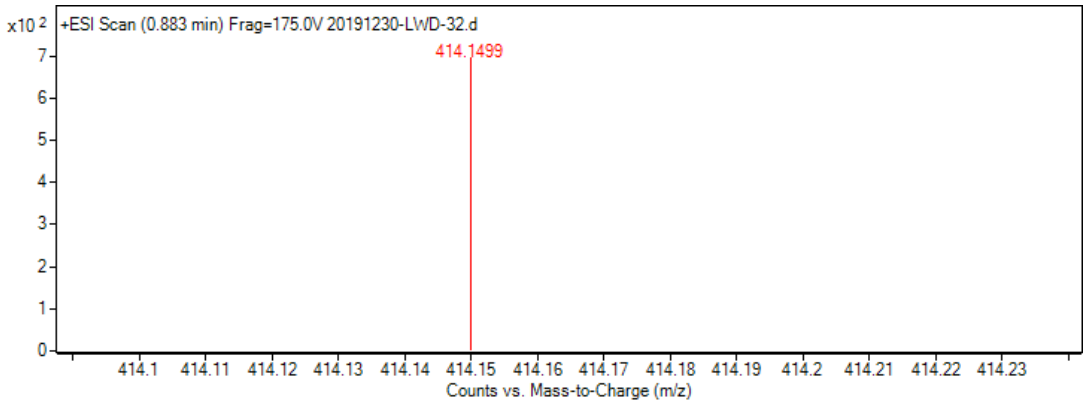


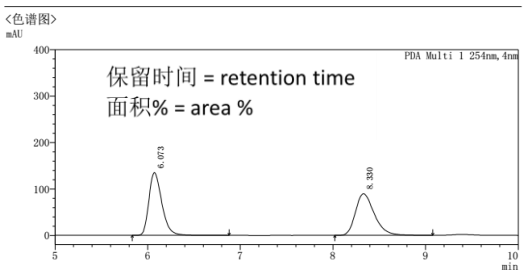
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.575	2741204	135492		98.753	98.730
2	12.973	34603	1743		1.247	1.270
总计		2775807	137236		100.000	100.000



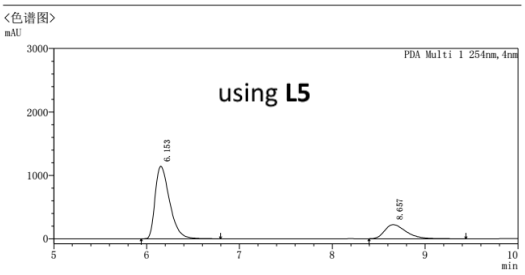
Compound *trans*-2u: 41.2 mg of **S1u'** yields 21.6 mg **2u** (56%, 11 h, *trans*/*cis* = 12.0:1 dr, using **L5**); 42.1 mg of **S1u'** yields 20.3 mg of **2u** (52%, 11 h, *trans*/*cis* = 15.7:1, using **L6**), white solid, m.p. = 157.8-161.4 °C, R_f = 0.8 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.05 – 6.97 (m, 4H), 6.94 – 6.86 (m, 3H), 6.23 (d, *J* = 7.7 Hz, 2H), 4.07 (d, *J* = 2.2 Hz, 1H), 4.01 – 3.93 (m, 1H), 2.45 (dh, *J* = 12.5, 6.1 Hz, 1H), 2.35 (s, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.5, 143.8, 142.6, 134.9, 134.7, 129.7, 128.5, 128.4, 127.5, 126.09, 126.07, 124.6, 116.3, 76.5, 47.5, 34.1, 21.6, 18.6, 15.8. **IR** (KBr, cm^{-1}) 3030, 2961, 2873, 1598, 1459, 1356, 1301, 1168, 1093, 1027, 958, 812, 734, 700, 667, 577, 542. **HRMS** (ESI) Calcd for $C_{24}H_{25}NNaO_2S$ $(M+Na)^+$ 414.1498, found 414.1499. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.2 min, minor: 8.7 min. 56% ee. $[\alpha]_D^{21}$ = -177° (*c* 0.56, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 6.0 min, minor: 8.3 min. 60% ee. $[\alpha]_D^{21}$ = -187° (*c* 0.06, CH_2Cl_2).





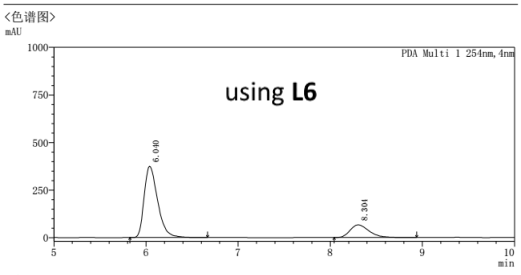
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.073	1319192	135175		50.996	60.129
2	8.330	1267658	89635		49.004	39.871
总计		2586850	224810		100.000	100.000



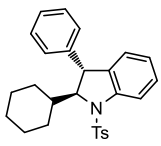
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.153	12374050	1147074		77.641	83.761
2	8.657	3563566	222383		22.359	16.239
总计		15937617	1369457		100.000	100.000

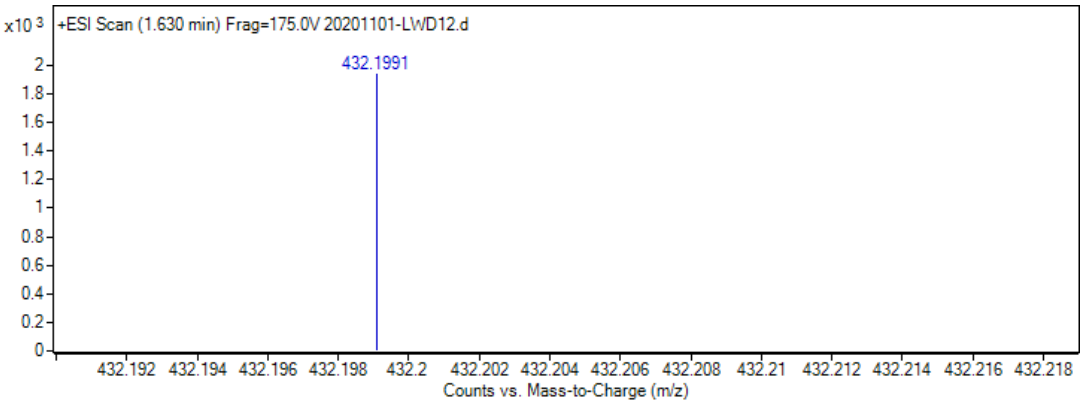


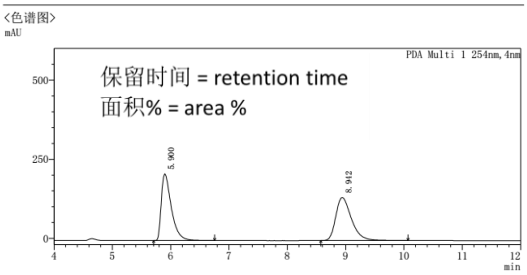
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.040	3820278	374385		79.988	84.902
2	8.304	955761	66575		20.012	15.098
总计		4776039	440960		100.000	100.000



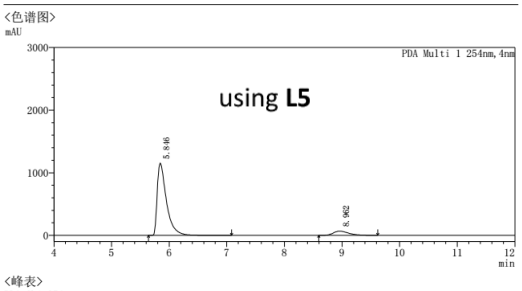
Compound *trans*-2v: 47.2 mg of **S1v'** yields 29.9 mg of **2v** (68%, 12 h, *trans*/*cis* = 19.0:1 dr, using **L5**); 48.0 mg of **S1v'** yields 29.2 mg of **2v** (65%, 12 h, *trans*/*cis* = 24.0:1, using **L6**), white solid, m.p. = 114.8-118.9 °C, R_f = 0.7 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.94 – 6.86 (m, 3H), 6.24 (d, *J* = 7.5 Hz, 2H), 4.13 (d, *J* = 0.4 Hz, 1H), 3.96 (dd, *J* = 4.3, 2.8 Hz, 1H), 2.34 (s, 3H), 2.08 – 2.00 (m, 1H), 1.84 – 1.67 (m, 5H), 1.39 – 1.22 (m, 3H), 1.21 – 1.12 (m, 1H), 0.98 (qd, *J* = 12.3, 3.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4, 143.7, 142.6, 134.9, 134.6, 129.6, 128.5, 128.4, 127.4, 126.2, 126.0, 124.6, 116.5, 76.4, 48.3, 44.4, 29.1, 26.7, 26.6, 26.3, 26.1, 21.6. **IR** (KBr, cm^{-1}) 3031, 2928, 2853, 1598, 1455, 1354, 1247, 1166, 1098, 1025, 961, 811, 738, 702, 667, 580, 548. **HRMS** (ESI) Calcd for $C_{27}H_{30}NO_2S$ $(M+H)^+$ 432.1992, found 432.1991. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 5.8 min, minor: 9.0 min. 82% ee. $[\alpha]_D^{21}$ = -158° (*c* 0.73, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 5.9 min, minor: 9.0 min. 86% ee. $[\alpha]_D^{21}$ = -168° (*c* 0.99, CH_2Cl_2).





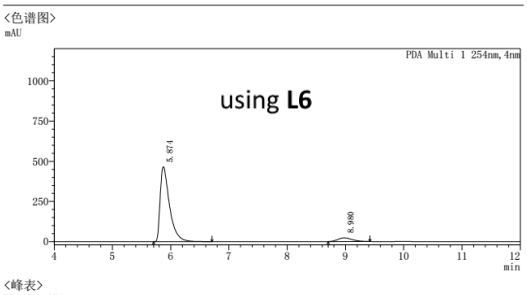
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	5.900	2519799	210673		49.966	60.757
2	8.942	2523187	136076		50.034	39.243
总计		5042986	346749		100.000	100.000



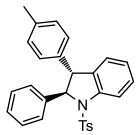
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	5.846	12808200	1152618		91.150	94.495
2	8.962	1243589	67155		8.850	5.505
总计		14051790	1219772		100.000	100.000

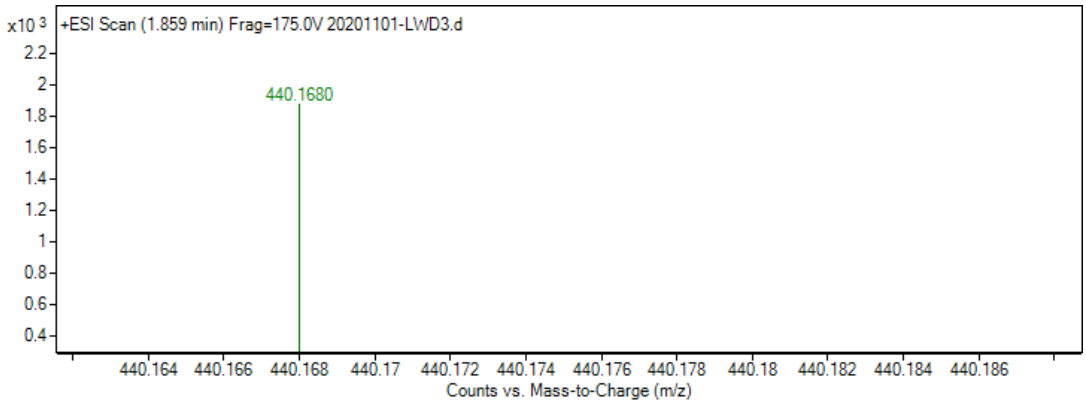


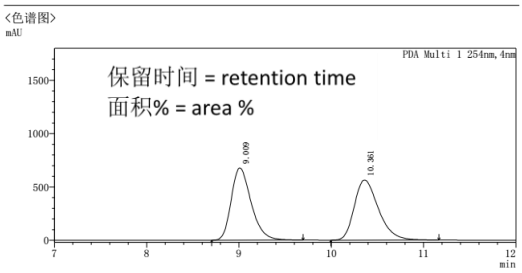
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	5.874	5188943	465633		92.872	95.358
2	8.980	398235	22667		7.128	4.642
总计		5587178	488300		100.000	100.000



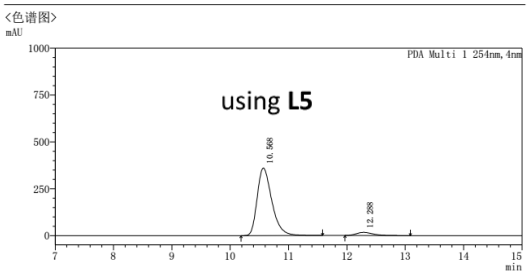
Compound *trans*-2w: 48.3 mg of **S1w'** yields 27.3 mg of **2w** (60%, 8 h, *trans*/*cis* = 6.1:1, using **L5**); 47.3 mg of **S1w'** yields 22.1 mg of **2w** (50%, 8 h, *trans*/*cis* = 3.8:1, using **L6**), white solid, m.p. = 139.7-140.4 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.29 (m, 5H), 7.30 – 7.25 (m, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.89 – 6.81 (m, 3H), 6.33 (d, *J* = 8.0 Hz, 2H), 5.00 (d, *J* = 4.2 Hz, 1H), 4.19 (d, *J* = 4.0 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0, 143.3, 142.4, 140.6, 136.5, 134.8, 133.3, 129.7, 129.4, 128.9, 128.7, 127.8, 127.6, 127.4, 126.3, 125.9, 124.6, 115.6, 74.5, 57.0, 21.6, 21.1. **IR** (KBr, cm^{-1}) 3030, 2922, 1597, 1512, 1477, 1457, 1359, 1261, 1167, 1107, 1025, 959, 808, 751, 701, 664, 572, 542. **HRMS** (ESI) Calcd for $C_{28}H_{26}NO_2S$ $(M+H)^+$ 440.1679, found 440.1680. **HPLC** (using **L5**): INA column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 10.6 min, minor: 12.3 min. 90% ee. $[\alpha]_D^{21}$ = -157° (*c* 0.45, CH_2Cl_2); **HPLC** (using **L6**): INA column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 9.0 min, minor: 10.3 min. 90% ee. $[\alpha]_D^{21}$ = -180° (*c* 0.41, CH_2Cl_2).





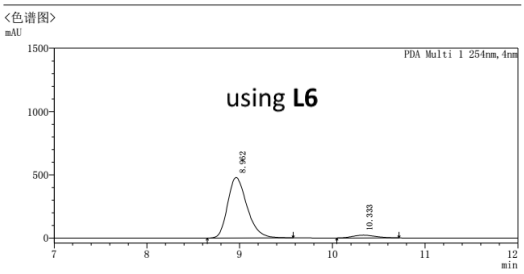
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.009	10177940	676084		49.796	54.542
2	10.361	10261177	563473		50.204	45.458
总计		20439117	1239557		100.000	100.000



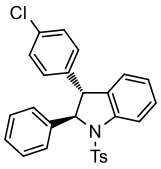
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.568	6297001	360900		94.974	95.583
2	12.288	333252	16677		5.026	4.417
总计		6630253	377577		100.000	100.000

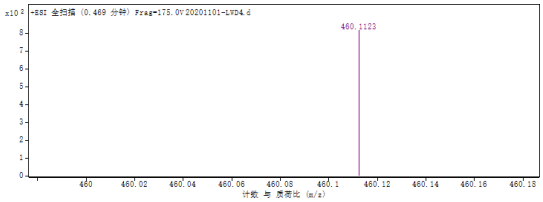


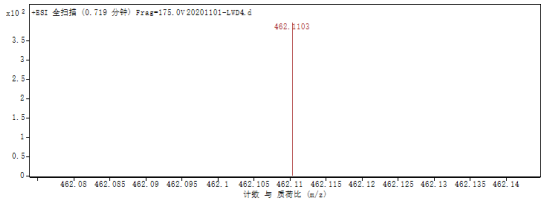
<峰表>
PDA Ch1 254nm

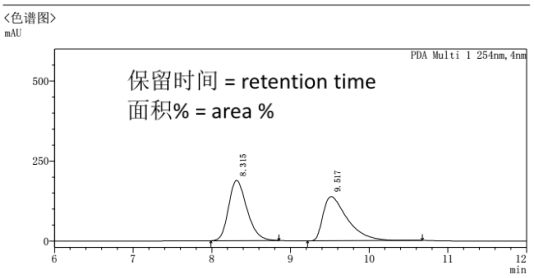
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.962	6966913	477500		94.813	95.531
2	10.333	381144	22336		5.187	4.469
总计		7348057	499836		100.000	100.000



Compound *trans*-2x: 50.8 mg of **S1x'** yields 22.9 mg of **2x** (48%, 12 h, *trans*/*cis* = 1.5:1, using **L5**); 49.0 mg of **S1x'** yields 24.8 mg of **2x** (54%, 12 h, *trans*/*cis* = 2.4:1, using **L6**), white solid, m.p. = 139.6-143.4 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.29 (m, 6H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 8.3 Hz, 2H), 4.96 (d, *J* = 3.8 Hz, 1H), 4.21 (d, *J* = 3.6 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 142.8, 142.5, 142.0, 134.7, 132.8, 132.5, 129.7, 129.1, 129.0, 128.9, 128.8, 128.0, 127.5, 126.3, 125.9, 124.9, 116.0, 74.3, 56.5, 21.7. **IR** (KBr, cm^{-1}) 3029, 1597, 1485, 1457, 1358, 1260, 1166, 1091, 1020, 960, 810, 752, 701, 665, 566, 544. **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_2S$ $(M+H)^+$ 460.1133, found 460.1123; isotopic peak: **HRMS** (ESI) Calcd for $C_{27}H_{23}ClNO_2S$ $(M+H)^+$ 462.1104, found 462.1103. **HPLC** (using **L5**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 10.9 min, minor: 9.4 min. 82% ee. $[\alpha]_D^{21}$ = -144° (*c* 0.24, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 9.5 min, minor: 8.4 min. 89% ee. $[\alpha]_D^{21}$ = -125° (*c* 0.34, CH_2Cl_2).

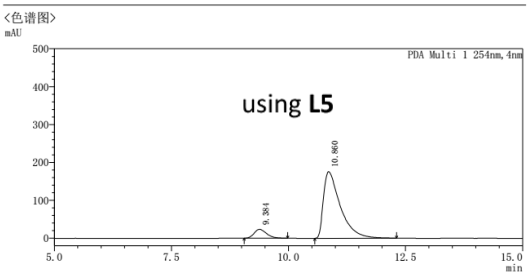






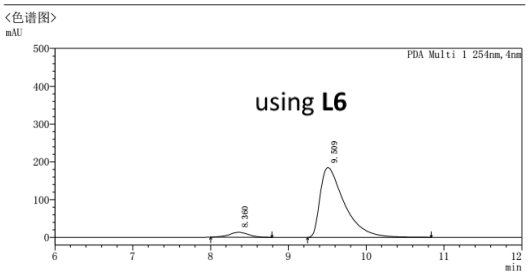
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.315	3056411	187973		50.777	57.636
2	9.517	2962918	138162		49.223	42.364
总计		6019328	326135		100.000	100.000



<峰表>
PDA Ch1 254nm

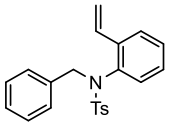
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.384	434522	23414		8.975	11.766
2	10.860	4406746	175577		91.025	88.234
总计		4841268	198991		100.000	100.000



<峰表>
PDA Ch1 254nm

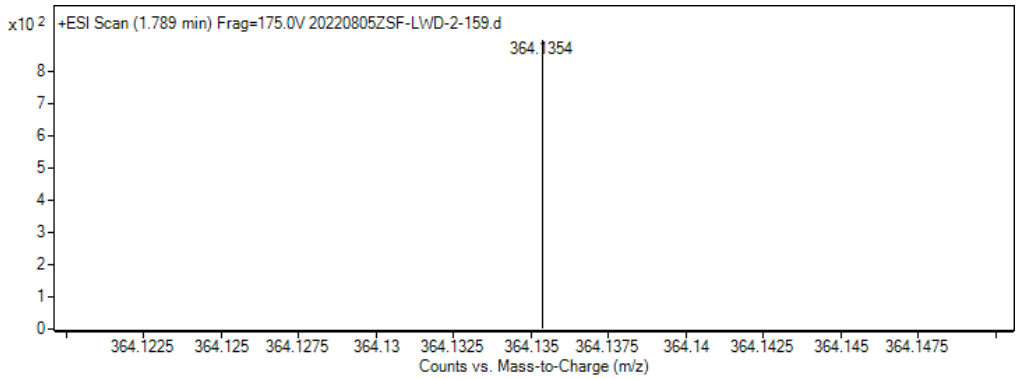
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.360	229020	13098		5.402	6.630
2	9.509	4010189	184460		94.598	93.370
总计		4239209	197558		100.000	100.000

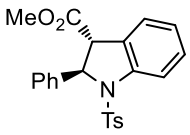
The alkyl-containing diazo **1y** could not be prepared because of the alkyl-containing diazo compound was unstable at ambient temperature and quickly delivered to the olefin one by [1,2]-H shift. In addition, using one-pot method (The desired hydrazone and catalyst were mixed first at 0°C, then MnO_2 was added into the catalyst system slowly.) also failed.



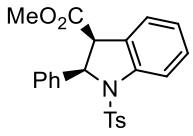
Compound 2y: white solid, m.p. = 131.3-132.1 °C, R_f = 0.8 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.04 (m, 7H), 6.76 (dd, *J* = 17.6, 11.0 Hz,

1H), 6.66 (d, *J* = 7.9 Hz, 1H), 5.54 (d, *J* = 17.6 Hz, 1H), 5.11 (d, *J* = 11.0 Hz, 1H), 4.87 (d, *J* = 7.5 Hz, 1H), 4.42 (d, *J* = 9.5 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 138.7, 136.5, 136.2, 135.4, 132.6, 129.6, 129.4, 129.2, 128.5, 128.2, 127.9, 127.8, 126.0, 115.4, 55.9, 21.6. **IR** (KBr, cm^{-1}) 3063, 3030, 1629, 1482, 1451, 1345, 1186, 1090, 1051, 861, 814, 774, 705, 655, 560. **HRMS** (ESI) Calcd for $C_{22}H_{22}NO_2S$ $(M+H)^+$ 364.1366, found 364.1354.

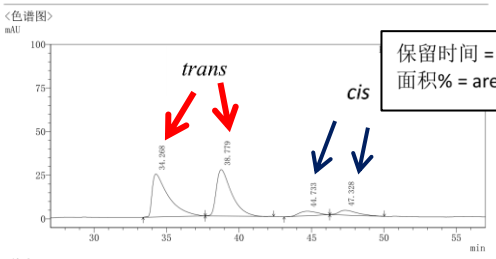




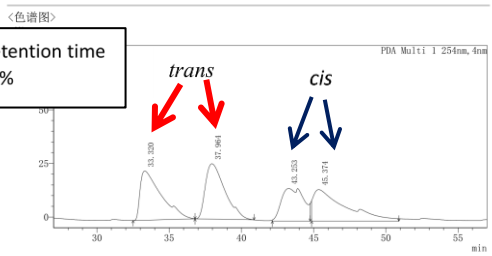
Compound *trans*-2z: known compound.[4] 43.8 mg of **1z** yields 9.4 mg of **2z** (23%, 24 h, *trans*/*cis* = 1.4:1, using **L6**), white solid, R_f = 0.4 (petroleum ether: ethyl acetate = 8:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.25 (m, 7H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.77 (d, *J* = 3.6 Hz, 1H), 3.91 (d, *J* = 3.6 Hz, 1H), 3.54 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.6, 144.0, 142.2, 141.9, 134.8, 129.5, 129.4, 128.9, 127.9, 127.6, 127.4, 126.3, 125.8, 124.3, 115.7, 67.0, 55.7, 52.6, 21.5. **HPLC** (using **L6**): OD-H column, 99:1 hexane: isopropanol, 1.00 mL/min, t_R = major: 38.0 min, minor: 33.3 min. 2% ee.



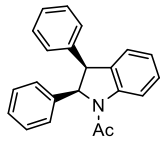
Compound *cis*-2z: known compound.[4] 43.8 mg of **1z** yields 9.4 mg of **2z** (23%, 24 h, *trans*/*cis* = 1.4:1, using **L6**), white solid, R_f = 0.4 (petroleum ether: ethyl acetate = 8:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.28 (m, 1H), 7.24 – 7.12 (m, 9H), 5.59 (d, *J* = 10.1 Hz, 1H), 4.37 (d, *J* = 10.1 Hz, 1H), 3.22 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 144.1, 142.7, 137.4, 135.3, 129.0, 128.2, 127.11, 127.06, 126.9, 124.8, 116.1, 67.2, 52.7, 51.7, 21.6. (Only the peak of the *cis*-product is marked in the ^{13}C NMR spectrum.) **HPLC** (using **L6**): OD-H column, 99:1 hexane: isopropanol, 1.00 mL/min, t_R = major: 45.4 min, minor: 43.3 min. 16% ee.



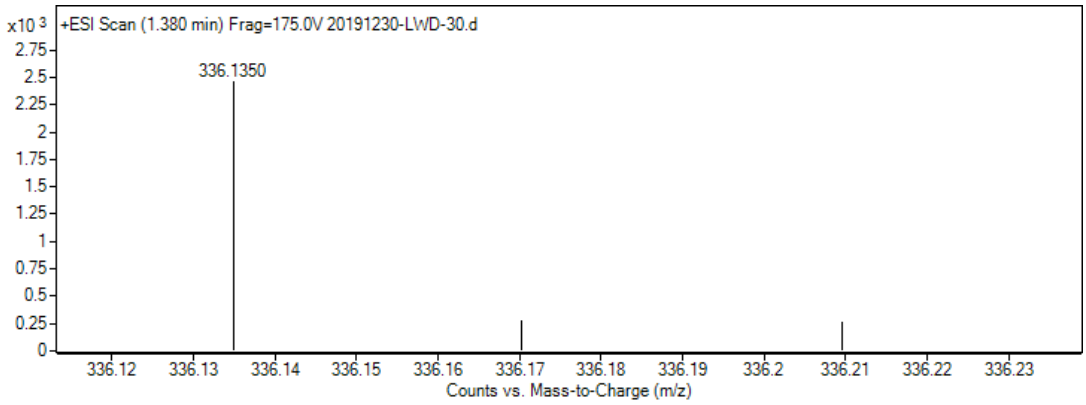
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	34.268	1927803	24637		44.426	43.538
2	38.779	1936145	26531		44.619	46.886
3	44.733	220828	2579		5.089	4.557
4	47.328	254555	2840		5.866	5.019
总计		4339332	56586		100.000	100.000

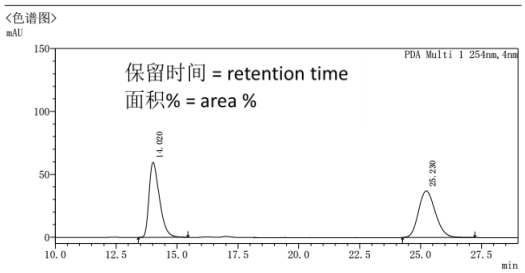


峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	33.320	2317004	22942		26.676	29.154
2	37.964	2424296	25786		27.911	32.769
3	43.253	1653788	15248		19.040	19.377
4	45.374	2290624	14715		26.372	18.700
总计		8685711	78691		100.000	100.000



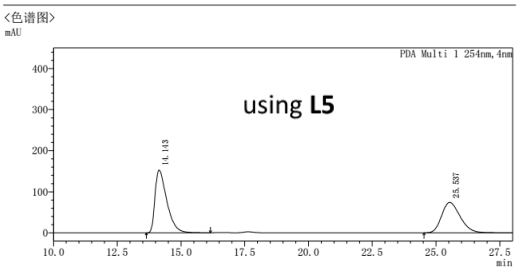
Compound *cis*-2aa: 34.0 mg of **S1aa'** yields 7.8 mg of **2aa** (25%, 12 h, *cis*/*trans* > 99:1 dr, using **L5**); 34.0 mg of **S1aa'** yields 16.6 mg of **2aa** (54%, 12 h, *cis*/*trans* > 99:1 dr, using **L6**), white solid, m.p. = 171.0-172.2 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.10 – 6.91 (m, 8H), 6.79 (d, *J* = 7.2 Hz, 2H), 6.69 (s, 2H), 5.55 (d, *J* = 9.4 Hz, 1H), 5.19 (d, *J* = 9.3 Hz, 1H), 2.04 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 144.4, 137.8, 136.8, 132.7, 130.0, 128.4, 128.2, 127.9, 127.6, 127.1, 126.8, 125.4, 124.3, 116.8, 70.0, 53.9, 24.3. **IR** (KBr, cm^{-1}) 3032, 2920, 1663, 1597, 1477, 1457, 1394, 1351, 1265, 1127, 1028, 925, 852, 781, 732, 700, 655, 611, 562. **HRMS** (ESI) Calcd for $C_{22}H_{19}NNaO$ $(M+Na)^+$ 336.1359, found 336.1350. **HPLC** (using **L5**): OD-h column, 95:5 hexane: isopropanol, 1.00 mL/min, t_R = major: 14.1 min, minor: 25.5 min. 14% ee. $[\alpha]_D^{21}$ = -5° (*c* 0.28, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 95:5 hexane: isopropanol, 1.00 mL/min, t_R = major: 14.0 min, minor: 25.3 min. 10% ee. $[\alpha]_D^{21}$ = -3° (*c* 0.38, CH_2Cl_2).





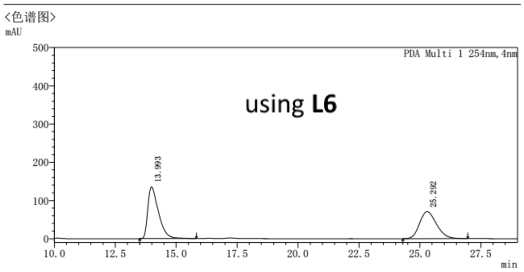
峰表
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	14.020	1775349	59810		49.887	61.753
2	25.230	1783358	37044		50.113	38.247
总计		3558707	96854		100.000	100.000



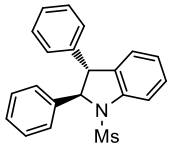
峰表
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	14.143	4908712	152546		56.599	67.350
2	25.537	3764148	73950		43.401	32.650
总计		8672861	226496		100.000	100.000

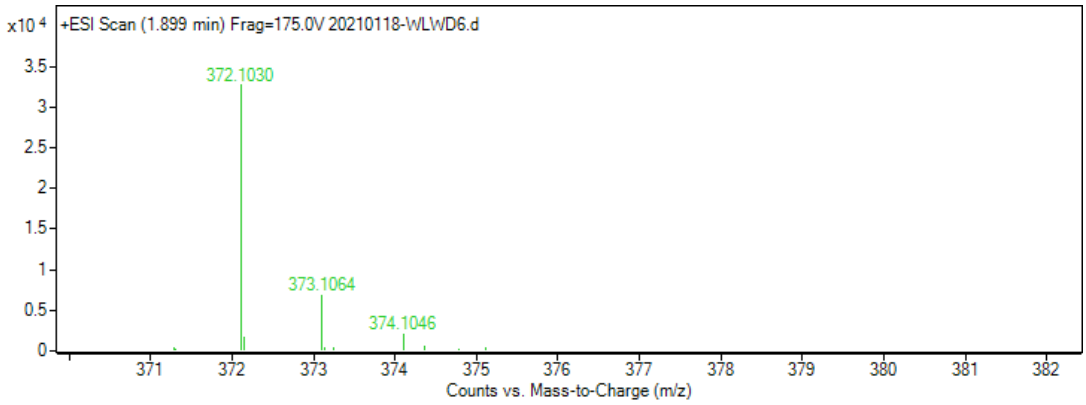


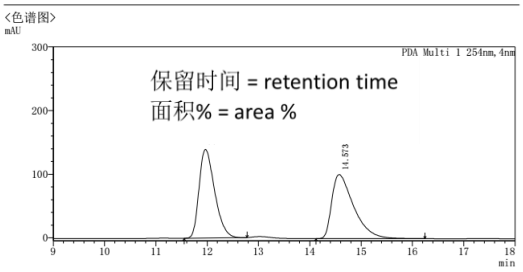
峰表
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.993	4128038	135346		54.801	65.717
2	25.292	3404699	70608		45.199	34.283
总计		7532738	205953		100.000	100.000



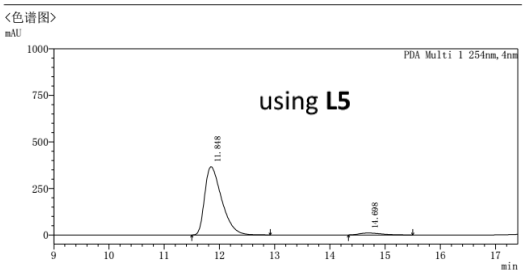
Compound *trans*-2ab: 39.3 mg of **S1ab'** yields 25.4 mg of **2ab** (70%, 12 h, *trans*/*cis* = 5.7:1, using **L5**); 39.6 mg of **S1ab'** yields 26.6 mg of **2ab** (73%, 12 h, *trans*/*cis* = 4.3:1, using **L6**), white solid, m.p. = 95.4-96.6 °C, R_f = 0.3 (petroleum ether:ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.26 (m, 9H), 7.14 – 7.06 (m, 4H), 5.18 (d, *J* = 3.9 Hz, 1H), 4.43 (d, *J* = 3.8 Hz, 1H), 2.69 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 142.4, 142.2, 132.8, 129.2, 129.1, 128.3, 127.63, 127.61, 126.6, 126.2, 124.3, 114.1, 74.7, 56.9, 37.9. **IR** (KBr, cm^{-1}) 3056, 2986, 1599, 1495, 1479, 1460, 1422, 1352, 1265, 1160, 1109, 1028, 970, 897, 738, 703, 544, 515. **HRMS** (ESI) Calcd for $C_{21}H_{19}NNaO_2S$ $(M+Na)^+$ 372.1028, found 372.1030. **HPLC** (using **L5**): OD-H column, 90:10 hexane:isopropanol, 0.80 mL/min, t_R = major: 11.8 min, minor: 14.7 min. 96.5:3.5 er. $[\alpha]_D^{21}$ = -185° (*c* 0.50, CH_2Cl_2); **HPLC** (using **L6**): OD-H column, 90:10 hexane:isopropanol, 0.80 mL/min, t_R = major: 11.9 min, minor: 14.8 min. 96.5:3.5 er. $[\alpha]_D^{21}$ = -200° (*c* 0.63, CH_2Cl_2).





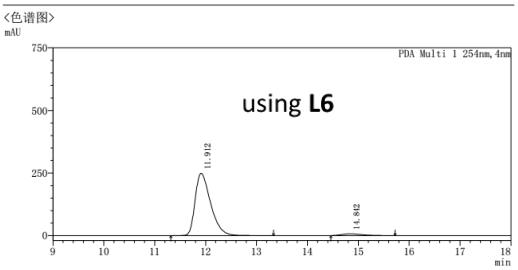
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.966	2937276	139392		49.610	58.072
2	14.573	2983470	100639		50.390	41.928
总计		5920746	240031		100.000	100.000



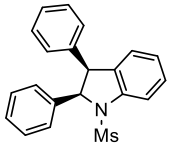
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.848	7875431	366699		96.457	97.194
2	14.698	289239	10586		3.543	2.806
总计		8164670	377285		100.000	100.000

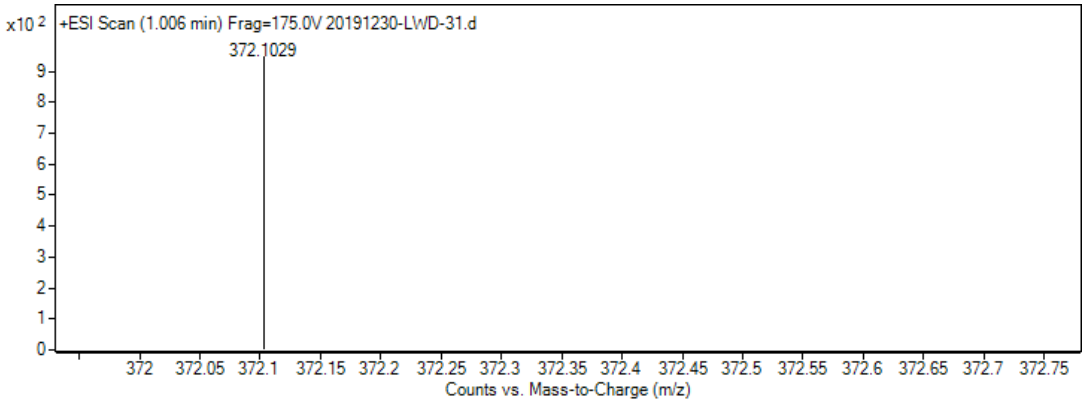


<峰表>
PDA Ch1 254nm

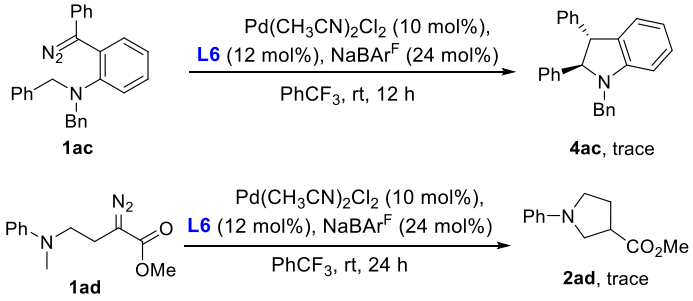
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.912	5274120	248746		96.477	97.267
2	14.842	192610	6990		3.523	2.733
总计		5466730	255735		100.000	100.000



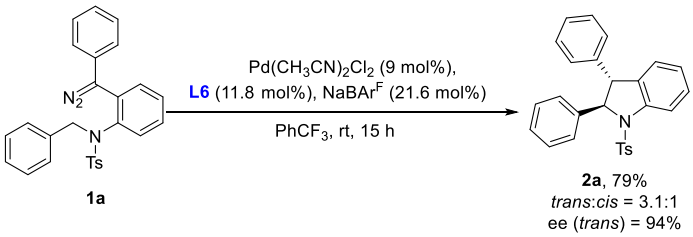
Compound *cis*-2ab: white solid, m.p. = 152.8-153.5 °C, R_f = 0.2 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.13 – 6.96 (m, 8H), 6.87 – 6.79 (m, 4H), 5.68 (d, *J* = 9.7 Hz, 1H), 5.25 (d, *J* = 9.6 Hz, 1H), 2.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 137.1, 136.3, 133.0, 129.8, 128.6, 127.93, 127.85, 127.6, 127.2, 127.1, 126.3, 124.0, 113.6, 71.0, 53.9, 38.9. **IR** (KBr, cm^{-1}) 3031, 2927, 1598, 1476, 1456, 1347, 1157, 963, 780, 738, 700, 546, 512. **HRMS** (ESI) Calcd for $C_{21}H_{19}NNaO_2S$ $(M+Na)^+$ 372.1028, found 372.1029.



The diazo compound **3ac** and **3ad** were conducted in standard condition. However, only trace of C(sp^3)-H insertion products was observed.



4.2 Gram scale experiment (3 mmol) for diazo compound 1a

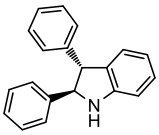


In a flame-dried 100 mL flask, the desired hydrazones **S1a'** (3 mmol, 1.40 g) were dissolved in 20 mL anhydrous benzotrifluoride (0.15 M). The flask was wrapped in foil, and MnO_2 (24.0 mmol, 1.96 g) was added. The oxidation was allowed to stir for 10 min until full conversion of the starting material was observed by TLC and dry Na_2SO_4 (1.0 g) was added to stir for 1 min to remove H_2O generated in suit. Then MnO_2 and Na_2SO_4 was removed by filtering through alumina (neutral) into a new flame-dried flask using dry ethyl acetate (30 mL) quickly. Next the solvent was removed *in vacuo* at room temperature. The crude magenta diazo compounds **1a** were used for next step without purification and were diluted to 0.15 M with anhydrous benzotrifluoride (20 mL). In the meantime, under nitrogen atmosphere, $Pd(CH_3CN)_2Cl_2$ (9 mol%, 69.1 mg), chiral ligand **L6** (10.8 mol%, 82.0 mg) and $NaBAr^F$ (21.6 mol%, 575 mg) were added in dry benzotrifluoride (15 mL, 1.8×10^{-2} M). The chiral catalysts mixture was stirred

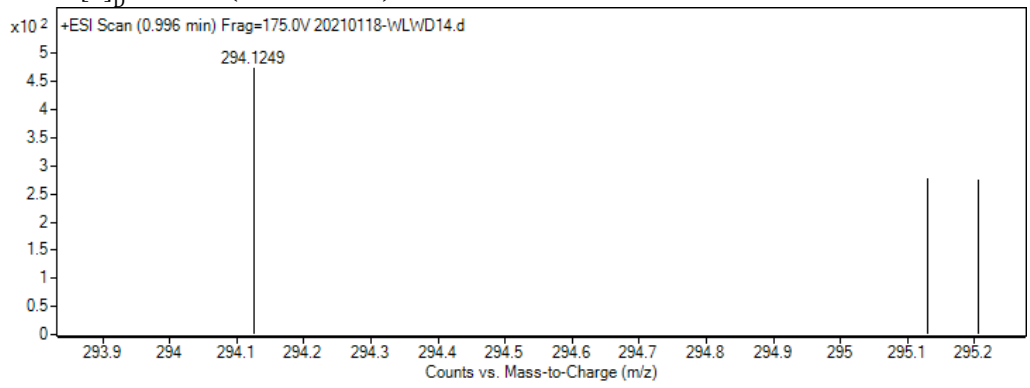
to bright yellow at room temperature for 2 h and the grey aggregation was removed through cotton. The bright yellow solution was transferred into a new flame-dry flask and the magenta solution of diazo compounds **1a** was added dropwise into the catalyst system with syringe pump for 2 hours (10 mL/h) under nitrogen atmosphere. The insertion reaction was stirred at room temperature overnight (for another 13 h). The crude reaction mixture was filtered over Celite, concentrated *in vacuo*, and purified by column chromatography (PE: DCM = 3:1) to yield the insertion product **2a** (1.03 g, 79%, *trans*:*cis* = 3.1:1, 94% ee for *trans*-**2a**).

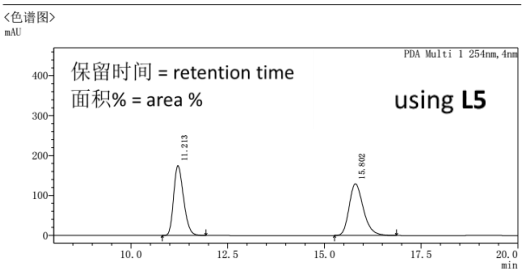
4.3 Procedure for the removal of tosyl in *trans*-2a[6]

The C-H inserion of **1a** was conducted repeatedly and could be expanded to 0.26 mmol scale (111 mg of **S1a'**, 0.26 mmol), thus delivering **2a** (63.4 mg) with 61% yield, 5.5:1 *trans*/*cis* ratio and 94% ee. Then a mixture of *trans*-**2a** (53.5 mg, 0.13mmol, 1.0 equiv.) and Mg powder (43.4 mg, 1.82 mmol, 14.0 equiv.) in dry MeOH (5.0 mL) was sonicated under N_2 atmosphere, then the mixture was stirred at 50℃ for 2h until completion, quenched with saturated NH_4Cl, and the aqueous layer was extracted with DCM. The combined organic layers were dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and purified by flash column chromatography to yield the product *trans*-**2a'**.



Compound *trans*-2a': 53.5 mg of *trans*-**2a'** yields 24.2 mg of *trans*-**2a'** (71%, 2 h, *trans*/*cis* > 99:1), yellow oil, R_f = 0.8 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 8H), 7.18 – 7.09 (m, 3H), 6.84 (d, *J* = 7.3 Hz, 1H), 6.78 – 6.70 (m, 2H), 4.82 (d, *J* = 9.5 Hz, 1H), 4.29 (d, *J* = 9.5 Hz, 1H), 4.17 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.9, 143.0, 142.3, 131.4, 129.0, 128.63, 128.55, 128.2, 127.7, 127.0, 126.8, 125.2, 119.3, 109.2, 73.8, 58.9. **IR** (KBr, cm^{-1}) 3363, 3030, 2918, 2851, 1603, 1486, 1460, 1359, 1262, 1033, 742, 700, 616**. HRMS** (ESI) Calcd for $C_{20}H_{17}NNa$ $(M+Na)^+$ 294.1253, found 294.1249. **HPLC**: OD-H column, 95:5 hexane: isopropanol, 1.00 mL/min, t_R = major: 15.7 min, minor: 11.2 min. 94% ee. $[\alpha]_D^{21}$ = -49° (*c* 7.7, CH_2Cl_2).





<峰表>
PDA Ch1 254nm

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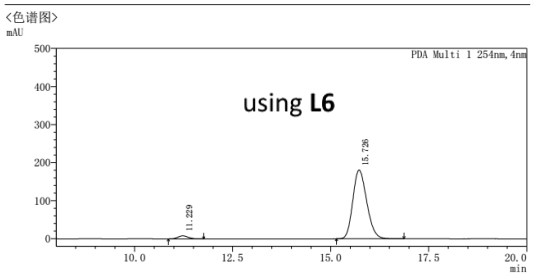
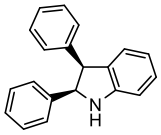
2	15.802	3327673	129626		51.492	42.520
总计		6462550	304859		100.000	100.000



<峰表>
PDA Ch1 254nm

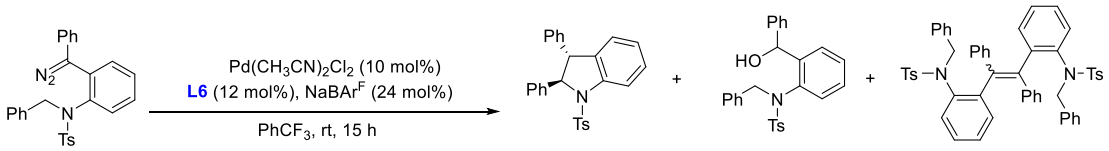
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.229	140690	7839		3.056	4.157
2	15.726	4462490	180738		96.944	95.843
总计		4603180	188577		100.000	100.000



Compound *cis*-2a': known compound[3], yellow oil (The procedure of the removal of tosyl in *cis*-**2a** was the same as that of *trans*-**2a**), R_f = 0.7 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.6 Hz, 1H), 7.06 – 6.96 (m, 9H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.75 – 6.69 (m, 2H), 5.24 (d, *J* = 9.0 Hz, 1H), 4.73 (d, *J* = 9.0 Hz, 1H), 4.20 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.7, 140.1, 139.3, 131.3, 129.4, 128.1, 127.7, 127.6, 127.3, 126.9, 126.2, 125.9, 119.3, 109.1, 69.0, 54.2.

4.4 Side product in the Pd(II)-catalyzed C-H insertion of diazo compound

The major side product in the Pd(II)-catalyzed C-H insertion of diazo compound is O-H insertion product. Because of the high activity of donor-type diazo compounds, the attack by H_2O to deliver O-H insertion easily happens in the catalytic system. Taking diazo compound **1a** in scale-up experiment for example, in addition to C-H insertion product **2a** (79% yield, *trans*: *cis* = 3.1:1), side product **7** (12% yield) and trace of carbene dimer were also obtained.

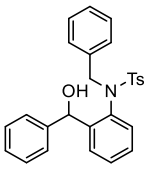


1a, 3.0 mmol

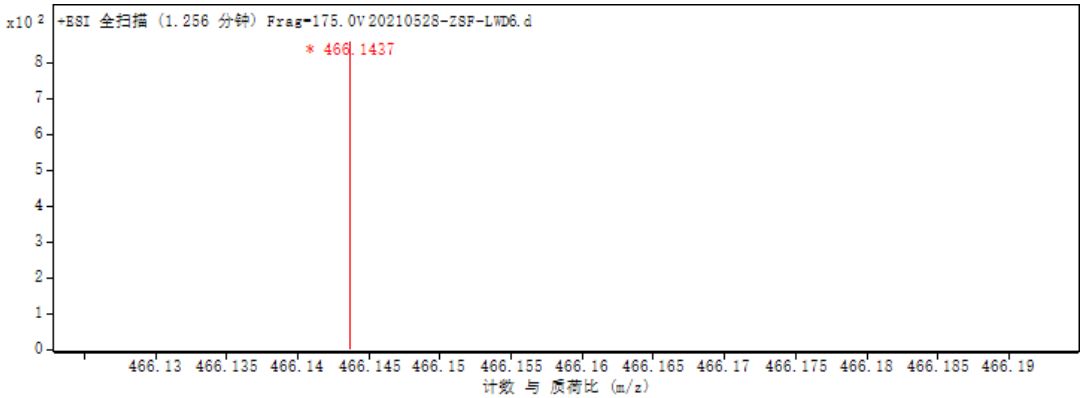
2a, 79%
trans:*cis* = 3.1:1, 94% ee
C-H insertion product

7, 12%
side product

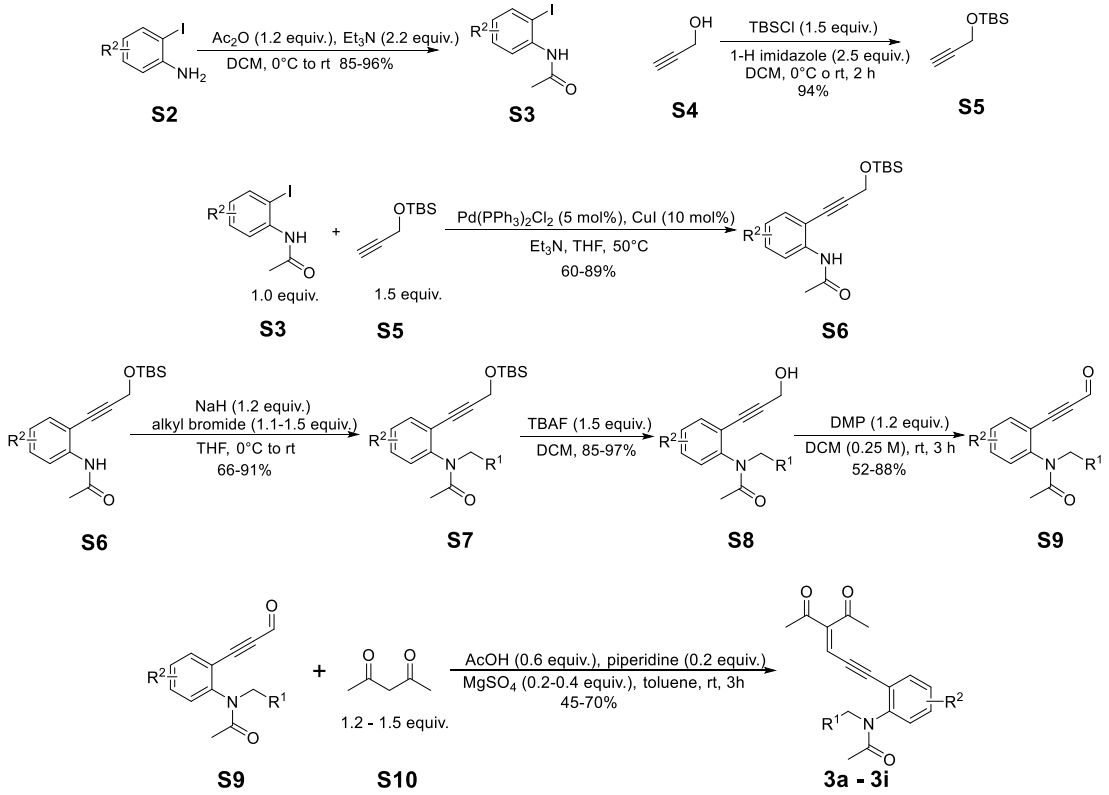
trace
carbene dimer



Compound 7: white solid, m.p. = 152.1-153.0 °C, R_f = 0.4 (petroleum ether:ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.22 – 7.17 (m, 4H), 7.14 – 7.05 (m, 5H), 6.94 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 6.48 (d, *J* = 6.6 Hz, 2H), 6.07 (s, 1H), 5.28 (d, *J* = 13.1 Hz, 1H), 4.12 (d, *J* = 13.1 Hz, 1H), 4.10 – 4.07 (m, 1H), 2.47 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.4, 144.4, 142.6, 136.9, 134.8, 134.3, 130.8, 130.0, 129.8, 129.3, 128.9, 128.34, 128.28, 128.1, 127.5, 126.5, 126.3, 126.2, 68.5, 56.3, 21.7. **IR** (KBr, cm^{-1}) 3515, 3063, 3032, 1598, 1490, 1451, 1338, 1158, 1091, 1049, 873, 844, 816, 740, 715, 661, 561. **HRMS** (ESI) Calcd for $C_{27}H_{25}NNaO_3S$ $(M+Na)^+$ 466.1447, found 466.1437.



5. General procedure for preparation of enynones



Typical procedure for preparation of S3

To a solution of 2-iodoaniline and Et_3N (2.2 equiv.) in DCM (0.5 M) at 0℃ under nitrogen was added Ac_2O (1.2 equiv.) dropwise. The resulting mixture was allowed to warmed up to room temperature and stirred until the reaction was completed by TLC. Water was added and the organic phase was separated. Aqueous phase was extracted with DCM twice. The combined organic phase was washed with $NaHCO_3$ and NH_4Cl, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (silica gel, petroleum ether/AcOEt = 5:1) gave **S3** with 85-96% yield.

Typical procedure for preparation of S5

To a solution of 2-propynol **S4** (300 mmol) in CH_2Cl_2 (150 mL) was added *tert*-butyldimethylsilyl chloride (450 mmol) and 1-H imidazole (750 mmol) at 0ºC. After about 2 h, the reaction was monitored by TLC until totally completed. The reaction mixture was washed with water, dried over $MgSO_4$, and was concentrated in vacuo. The crude product was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 20:1) to afford **S5** as colorless oil (94% yield).

Typical procedure for preparation of S6

Under nitrogen atmosphere, a mixture of **S3** (10 mmol, 1.0 equiv.), CuI (10 mol%), $Pd(PPh_3)_2Cl_2$ (5 mol%) were added to a schlenk tube, Et_3N (20 mL) and THF (20 mL) as co-solvent was added to the reaction mixture, then **S5** (15 mmol, 1.5 equiv.) was added slowly. The reaction was stirred for 12 h at 50 ºC. The mixture was diluted with H_2O, and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **S6** (60-89%).

Typical procedure for preparation of S7

To a stirred suspension of NaH (3.6 mmol) in 3 ml of dry THF at 0 °C the **S6** (3.0 mmol, 1.0 equiv.) dissolved in 4 mL of THF was added dropwise within 5 min. The reaction mixture was stirred until the solution became clear, and the solution of alkyl bromide (1.1-1.5 equiv.) in 3 mL of THF was added dropwise within 5 min. The solution was warmed up to room temperature and monitored by TLC. After **S6** was completely consumed, the reaction mixture was quenched with water (15 mL). The resulting solution was extracted with ethyl acetate (3×10 mL). Combined organic layers were washed with brine (1×20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (silica gel, petroleum ether/AcOEt = 5:1) gave **S7** (66-91%).

Typical procedure for preparation of S8

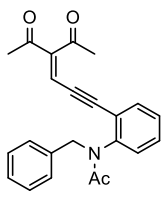
To a solution of **S7** in DCM tetrabutylammonium fluoride (TBAF, 1.5 equiv.) was added slowly, the reaction was monitored by TLC. After totally completed, the reaction mixture was quenched with water. The resulting solution was extracted with DCM. Combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (silica gel, petroleum ether/AcOEt = 2:1) gave **S8** as yellow oil (85-97%).

Typical procedure for preparation of S9

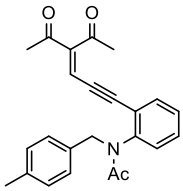
To a solution of **S8** in DCM (0.25 M) Dess-Martin regent (1.5 equiv.) was added with portions. The reaction was monitored by TLC, after totally completed, the reaction mixture was added saturated $NaHCO_3$ aqueous solution and saturated $Na_2S_2O_3$ aqueous solution to quench the reaction. The resulting solution was extracted with DCM. Combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (silica gel, petroleum ether/AcOEt = 3:1) gave **S9** as yellow oil (52-88%).

Typical procedure for preparation of enynones 3a-3i[7]

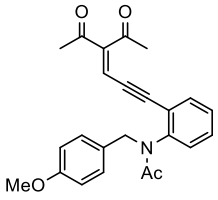
S9 (1.0 equiv.), AcOH (0.6 equiv.), piperidine (0.2 equiv.) and $MgSO_4$ (0.2 - 0.5 equiv.) were added to a solution of **S10** (1.2-1.5 equiv.) in toluene at room temperature. The reaction was stirred at room temperature and monitored by TLC. The reaction mixture was extracted with ethyl acetate and water. Combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 2:1) to yield **3a-3i** (45-70%).



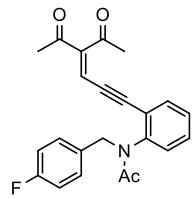
Compound 3a: known compound.[7] 61% yield, yellow oil, R_f = 0.2 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 1H), 7.36 – 7.29 (m, 2H), 7.26 – 7.21 (m, 3H), 7.21 – 7.17 (m, 2H), 6.90 – 6.81 (m, 1H), 6.80 (s, 1H), 5.38 (d, *J* = 14.2 Hz, 1H), 4.34 (d, *J* = 14.2 Hz, 1H), 2.49 (s, 3H), 2.38 (s, 3H), 1.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.8, 195.7, 170.1, 150.5, 144.2, 137.2, 134.2, 131.2, 129.9, 129.4, 128.5, 128.4, 127.7, 121.8, 121.2, 101.9, 89.3, 52.3, 31.1, 27.2, 22.6.



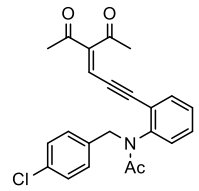
Compound 3b: known compound.[5] 55% yield, yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.36 – 7.31 (m, 2H), 7.09 – 7.01 (m, 4H), 6.89 – 6.84 (m, 1H), 6.83 – 6.79 (m, 1H), 5.31 (d, *J* = 14.2 Hz, 1H), 4.32 (d, *J* = 14.2 Hz, 1H), 2.49 (s, 3H), 2.37 (s, 3H), 2.28 (s, 3H), 1.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.6, 195.5, 169.8, 150.1, 144.0, 137.0, 133.95, 133.93 131.1, 129.8, 129.2, 128.9, 128.3, 121.5, 121.1, 101.9, 89.0, 51.8, 30.9, 27.0, 22.4, 21.1.



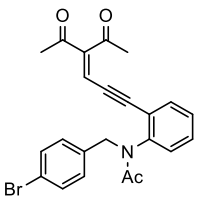
Compound 3c: known compound.[7] 46% yield, yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 1H), 7.19 – 7.12 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.74 – 6.67 (m, 1H), 6.64 (s, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.05 (d, *J* = 14.2 Hz, 1H), 4.20 (d, *J* = 14.2 Hz, 1H), 3.54 (s, 3H), 2.30 (s, 3H), 2.18 (s, 3H), 1.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.3, 195.2, 169.3, 158.6, 149.8, 143.5, 133.6, 130.8, 130.2, 129.4, 128.8, 128.0, 121.2, 120.7, 113.2, 101.5, 88.6, 54.7, 51.1, 30.5, 26.6, 22.0.



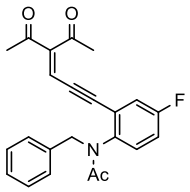
Compound 3d: known compound.[7] 56% yield, yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 5.5, 3.7 Hz, 1H), 7.35 (dd, *J* = 5.6, 3.6 Hz, 2H), 7.18 – 7.12 (m, 2H), 6.92 (t, *J* = 8.6 Hz, 2H), 6.85 (dd, *J* = 5.4, 3.6 Hz, 1H), 6.78 (s, 1H), 5.29 (d, *J* = 14.2 Hz, 1H), 4.36 (d, *J* = 14.3 Hz, 1H), 2.49 (s, 3H), 2.38 (s, 3H), 1.84 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -114.74. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.8, 195.6, 170.1, 162.3 (d, *J* = 245.9 Hz), 150.5, 144.0, 134.3, 133.00 (d, *J* = 3.3 Hz), 131.3 (d, *J* = 6.1 Hz), 131.1, 129.8, 128.6, 121.7, 121.0, 115.26 (d, *J* = 21.3 Hz), 101.7, 89.2, 51.5, 31.0, 27.1, 22.5.



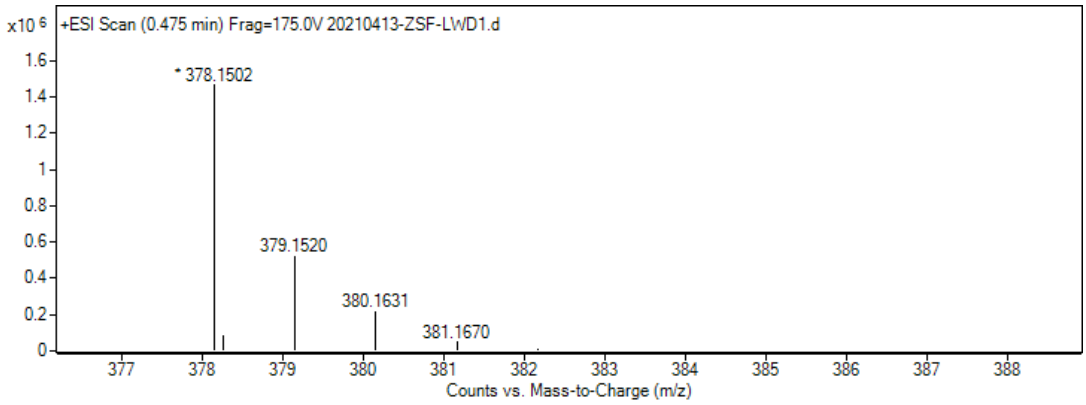
Compound 3e: known compound.[7] 55% yield, yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.12 – 7.04 (m, 2H), 6.94 – 6.86 (m, 4H), 6.69 (d, *J* = 7.4 Hz, 1H), 6.55 (s, 1H), 4.92 (d, *J* = 14.4 Hz, 1H), 4.19 (d, *J* = 14.4 Hz, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.0, 195.0, 169.2, 149.9, 143.1, 135.2, 133.5, 132.5, 130.8, 130.1, 129.0, 128.0, 127.8, 120.9, 120.1, 100.8, 88.5, 50.9, 30.2, 26.2, 21.7.

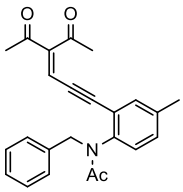


Compound 3f: known compound.[7] 45% yield, yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 1H), 7.19 – 7.09 (m, 4H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 7.1 Hz, 1H), 6.58 (s, 1H), 4.93 (d, *J* = 14.3 Hz, 1H), 4.25 (d, *J* = 14.3 Hz, 1H), 2.25 (s, 3H), 2.16 (s, 3H), 1.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.3, 195.2, 169.5, 149.9, 143.3, 135.8, 133.7, 130.95, 130.90, 130.7, 129.1, 128.1, 121.09, 121.05, 120.4, 101.0, 88.7, 51.2, 30.4, 26.5, 21.9.

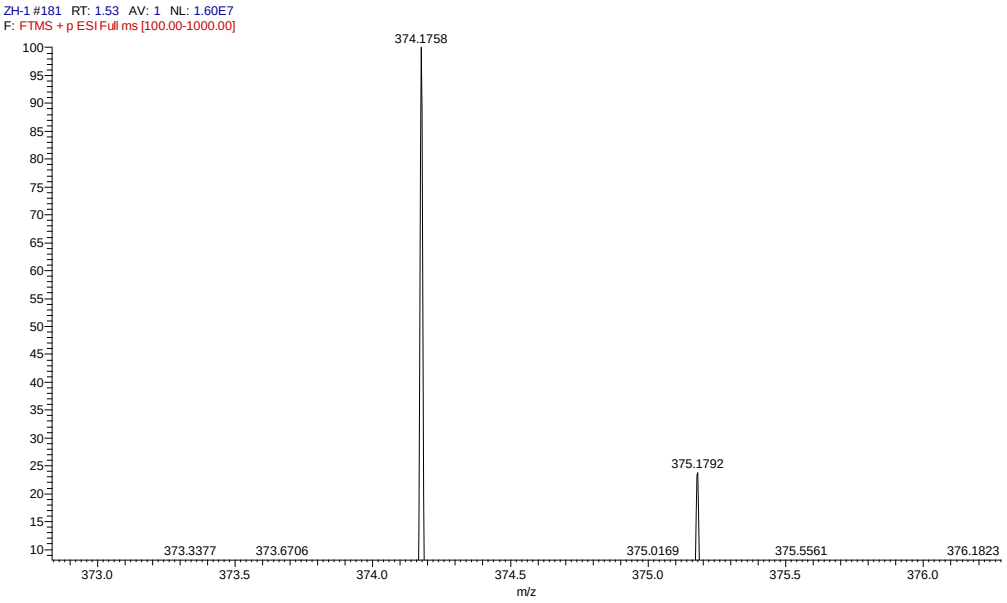


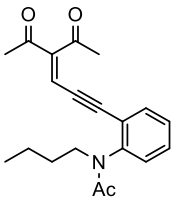
Compound 3g: 50% yield, yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 4H), 7.13 – 7.07 (m, 2H), 6.97 – 6.88 (m, 1H), 6.74 (dd, *J* = 8.6, 5.3 Hz, 1H), 6.71 (s, 1H), 5.30 (d, *J* = 14.2 Hz, 1H), 4.23 (d, *J* = 14.2 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 1.78 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.8. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.4, 195.4, 169.9, 161.2 (d, *J* = 250.4 Hz), 150.9, 140.1 (d, *J* = 3.5 Hz), 136.7, 131.4 (d, *J* = 9.1 Hz), 129.2, 128.3, 127.6, 123.3 (d, *J* = 10.1 Hz), 120.26 (d, *J* = 24.2 Hz), 120.26, 120.1, 118.2 (d, *J* = 22.4 Hz), 99.8, 89.6, 52.0, 30.8, 26.9, 22.3. **IR** (KBr, cm^{-1}) 3608, 3325, 3062, 2919, 1676, 1597, 1565, 1487, 1460, 1393, 1365, 1308, 1231, 1158, 1059, 1028, 952, 856, 801, 755, 701, 674, 632, 610, 555, 486, 433. **HRMS** (ESI) Calcd for $C_{23}H_{21}FNO_3$ $(M+H)^+$ 378.1500, found 378.1502.





Compound 3h: 55% yield, yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.27 – 7.16 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.80 (s, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 5.35 (d, *J* = 14.2 Hz, 1H), 4.34 (d, *J* = 14.2 Hz, 1H), 2.49 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H), 1.84 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.7, 195.5, 170.1, 150.1, 141.6, 138.5, 137.1, 134.3, 132.0, 129.4, 129.2, 128.2, 127.4, 121.2, 121.1, 102.2, 88.7, 52.1, 30.9, 27.0, 22.4, 20.8. **IR** (KBr, cm^{-1}) 3609, 3306, 3030, 2924, 2353, 2192, 1786, 1766, 1711, 1664, 1585, 1535, 1517, 1497, 1392, 1375, 1292, 1246, 1171, 1070, 1022, 969, 887, 831, 745, 703, 628, 584, 536, 508, 441. **HRMS** (ESI) Calcd for $C_{24}H_{24}NO_3$ $(M+H)^+$ 374.1751, found 374.1758.



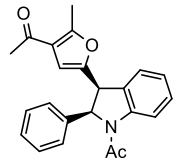


Compound 3i: known compound.[7] 70% yield, yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 4.02 – 3.90 (m, 1H), 3.51 – 3.35 (m, 1H), 2.51 (s, 3H), 2.38 (s, 3H), 1.81 (s, 3H), 1.56 – 1.44 (m, 2H), 1.38 – 1.29 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 200.8, 195.6, 169.9, 150.4, 144.6, 134.2, 131.3, 129.4, 128.2, 121.7, 121.0, 101.9, 89.1, 48.5, 30.9, 29.8, 27.0, 22.5, 20.1, 13.8.

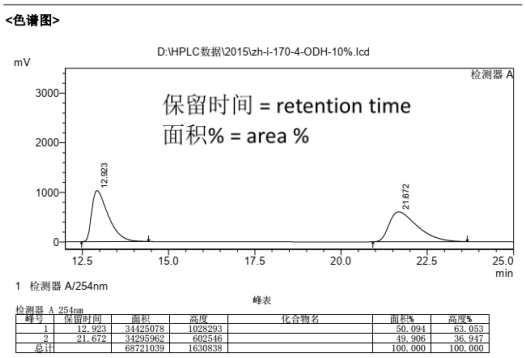
6. General procedure for Pd(II)-catalyzed C-H insertion of enynones

General procedure for enantioselective Pd(II)-catalyzed C-H insertion of enynones

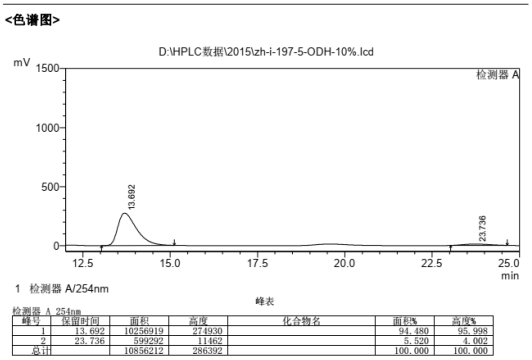
Under nitrogen atmosphere, to a solution of enynone **3a-3i** (0.2 mmol) in dry toluene (0.2 M), $[Pd(PhCN)_2Cl_2]$ (10 mol%), Pybox ligand **L1** (11 mol%) and $NaBAr^F$ (22 mol%) were added. The reaction mixture was then heated to a temperature of 60 ºC and stirred for 12 h. After the reaction was completed, the reaction mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The crude C-H insertion product was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 3:1) to yield **4a**-**4i**.



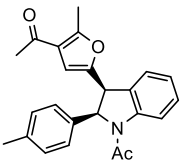
Compound 4a: known compound.[7] 72.0 mg of **3a** yields 59.8 mg of **4a** (83%, 12 h, >99:1 dr), yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.16 – 7.08 (m, 5H), 6.89 (dd, *J* = 6.5, 3.0 Hz, 2H), 5.96 (s, 1H), 5.59 (d, *J* = 9.3 Hz, 1H), 5.22 (d, *J* = 9.5 Hz, 1H), 2.34 (s, 3H), 2.16 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.0, 169.5, 157.9, 149.0, 143.9, 138.0, 129.0, 128.4, 128.0, 126.3, 125.2, 124.4, 121.7, 117.0, 109.8, 68.2, 47.0, 29.0, 24.3, 14.0. **HPLC**: OD-H column, 90:10 hexane: isopropanol, 1.00 mL/min, t_R = major: 13.7 min, minor: 23.7 min. 89% ee. $[\alpha]_D^{23}$ = -38° (*c* 0.10, CH_2Cl_2).



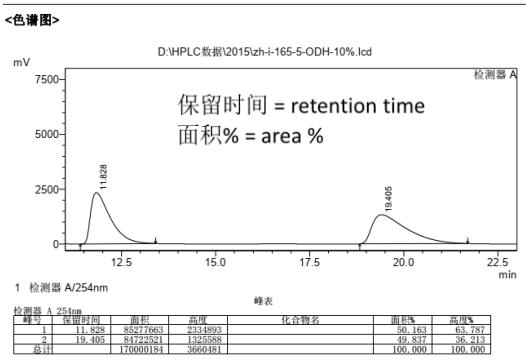
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	12.923	34425078	1028293		50.094	63.053
2	21.672	34295962	602546		49.906	36.947
总计		68721039	1630838		100.000	100.000



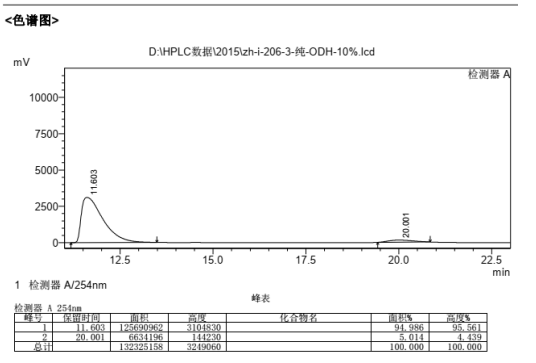
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.692	10256919	274930		94.480	95.998
2	23.736	599202	11462		5.520	4.002
总计		10856212	286392		100.000	100.000



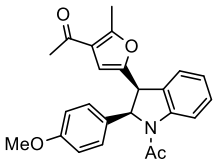
Compound 4b: known compound.[7] 74.7 mg of **3b** yields 63.5 mg of **4b** (85%, 12 h, >99:1 dr), yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.1 Hz, 1H), 7.42 – 7.32 (m, 1H), 7.10 (d, *J* = 3.9 Hz, 2H), 6.90 (d, *J* = 7.5 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 2H), 5.96 (s, 1H), 5.56 (d, *J* = 9.0 Hz, 1H), 5.19 (d, *J* = 9.2 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.2, 169.5, 157.9, 149.1, 143.9, 137.7, 135.0, 129.4, 129.0, 128.9, 126.2, 125.2, 124.4, 121.7, 117.0, 109.7, 68.1, 47.1, 29.0, 24.3, 21.0, 14.1. **HPLC**: OD-H column, 90:10 hexane: isopropanol, 1.00 mL/min, t_R = major: 11.6 min, minor: 20.0 min. 90% ee. $[\alpha]_D^{23}$ = -89° (*c* 0.17, CH_2Cl_2).



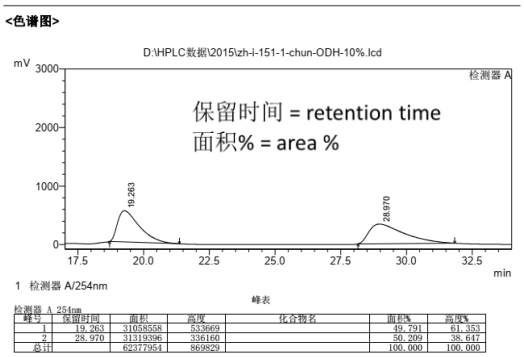
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.828	85277663	2334893		50.163	63.787
2	19.405	84722521	1325588		49.837	36.213
总计		170000184	3660481		100.000	100.000



峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.603	125690962	3104830		94.986	95.561
2	20.001	6634196	144230		5.014	4.439
总计		132325158	3249060		100.000	100.000

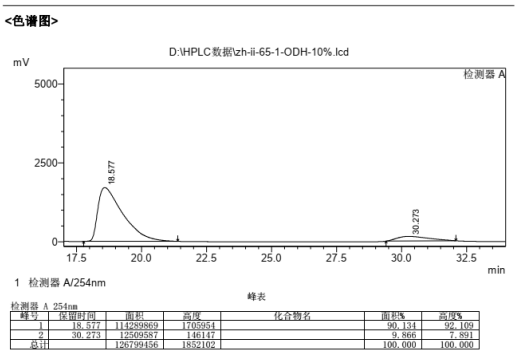


Compound 4c: known compound.[7] 77.9 mg of **3c** yields 65.4 mg of **4c** (84%, 12 h, >99:1 dr), yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.3 Hz, 2H), 5.98 (s, 1H), 5.52 (d, *J* = 9.1 Hz, 1H), 5.14 (d, *J* = 9.2 Hz, 1H), 3.64 (s, 3H), 2.33 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.0, 169.4, 159.2, 157.8, 149.1, 143.8, 130.0, 129.3, 128.8, 127.4, 125.1, 124.3, 121.7, 116.9, 113.6, 109.6, 67.7, 55.2, 46.9, 29.0, 24.2, 14.0. **HPLC**: OD-H column, 90:10 hexane: isopropanol, 1.00 mL/min, t_R = major: 18.6 min, minor: 30.3 min. 80% ee. $[\alpha]_D^{23}$ = -71° (*c* 0.12, CH_2Cl_2).



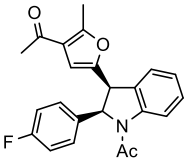
峰表

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	19.263	31058558	533669		49.791	61.353
2	28.970	31319396	336160		50.209	38.647
总计		62377954	869829		100.000	100.000

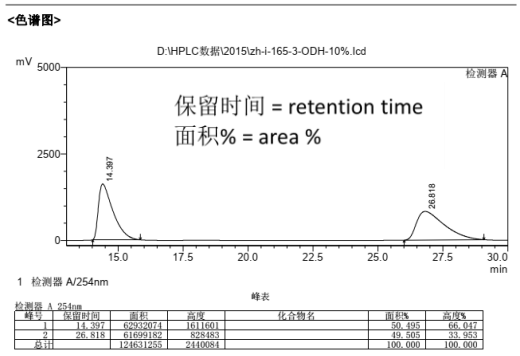


峰表

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	18.577	114289869	1705954		90.134	92.109
2	30.273	12509587	146147		9.866	7.891
总计		126799456	1852102		100.000	100.000

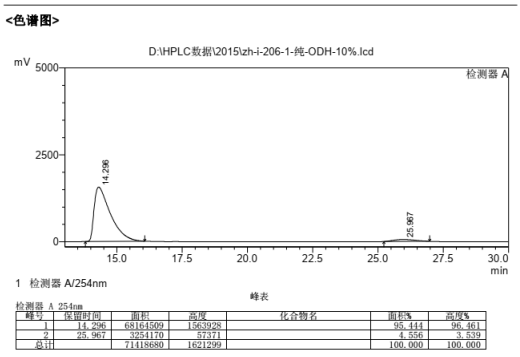


Compound 4d: known compound.[7] 75.5 mg of **3d** yields 60.4 mg of **4d** (80%, 12 h, >99:1 dr), yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 6.9 Hz, 1H), 7.37 (dt, *J* = 8.1, 4.5 Hz, 1H), 7.12 (d, *J* = 3.9 Hz, 2H), 6.96 – 6.74 (m, 4H), 6.05 (s, 1H), 5.59 (d, *J* = 9.0 Hz, 1H), 5.21 (d, *J* = 9.2 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 2.04 (s, 3H). **^{19}F NMR** (376 MHz, CDCl3) *δ* -113.76. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.9, 169.3, 162.3 (d, *J* = 247.9 Hz), 158.0, 148.8, 143.6, 133.9 (d, *J* = 2.0 Hz), 129.0, 128.9, 127.9 (d, *J* = 8.1 Hz), 125.2, 124.6, 121.8, 117.0, 115.3 (d, *J* = 21.9 Hz), 109.8, 67.5, 46.9, 29.0, 24.2, 14.1. **HPLC**: OD-H column, 90:10 hexane: isopropanol, 1.00 mL/min, t_R = major: 14.3 min, minor: 26.0 min. 91% ee. $[\alpha]_D^{23}$ = -88° (*c* 0.11, CH_2Cl_2). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 6.9 Hz, 1H), 7.37 (dt, *J* = 8.1, 4.5 Hz, 2H), 7.12 (d, *J* = 3.9 Hz, 2H), , 6.05 (s, 1H), 5.59 (d, *J* = 9.0 Hz, 1H), 5.21 (d, *J* = 9.2 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 2.04 (s, 3H).



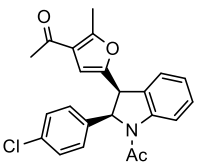
峰表

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	14.397	62932074	1611601		50.495	66.047
2	26.818	61699182	828483		49.505	33.953
总计		124631255	2440084		100.000	100.000



峰表

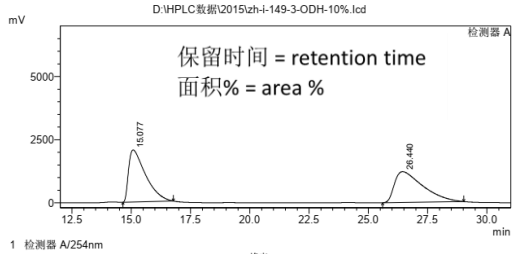
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	14.296	68164509	1563928		95.444	96.461
2	25.967	3254170	57371		4.556	3.539
总计		71418680	1621299		100.000	100.000



Compound 4e: known compound.[7] 78.8 mg of **3e** yields 59.9 mg of **4e** (76%, 12 h, >99:1 dr), yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.14 – 7.04 (m, 4H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.04 (s, 1H), 5.55 (d, *J* = 8.7 Hz, 1H), 5.19 (d, *J* = 9.1 Hz, 1H), 2.33 (s, 3H), 2.19 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.9, 169.2, 158.0, 148.6, 143.6, 136.7, 133.8, 129.0, 128.5, 127.6, 125.2, 124.6, 121.8, 117.0, 109.9,

67.5, 46.9, 29.0, 24.2, 14.0. **HPLC**: OD-H column, 90:10 hexane: isopropanol, 1.00 mL/min, t_R = major: 15.5 min, minor: 27.8 min. 94% ee. $[\alpha]_D^{23}$ = -41° (*c* 0.13, CH_2Cl_2).

<色谱图>

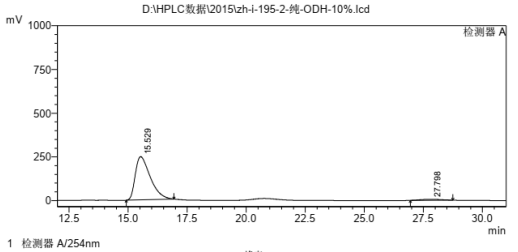


峰表

检测器 A 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	15.077	102884740	2061893		50.329	62.858
2	26.440	101538530	1218369		49.671	37.142
总计		204423270	3280262		100.000	100.000

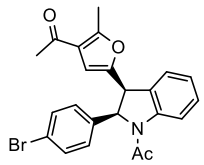
<色谱图>



峰表

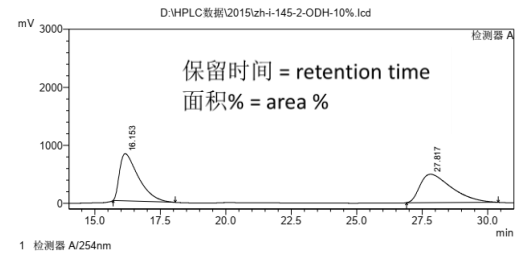
检测器 A 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	15.529	10916262	247138		96.943	97.743
2	27.798	344280	5708		3.057	2.257
总计		11260543	252846		100.000	100.000



Compound 4f: known compound.[7] 87.6 mg of **3f** yields 72.4 mg of **4f** (83%, 12 h, >99:1 dr), yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.8 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.14 – 7.06 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.04 (s, 1H), 5.54 (d, *J* = 9.0 Hz, 1H), 5.20 (d, *J* = 9.0 Hz, 1H), 2.34 (s, 3H), 2.20 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.9, 169.2, 158.1, 148.5, 143.5, 137.2, 131.5, 129.0, 128.8, 128.0, 125.2, 124.6, 121.9, 121.8, 117.0, 110.0, 67.6, 46.9, 29.0, 24.2, 14.0. **HPLC**: OD-H column, 90:10 hexane: isopropanol, 1.00 mL/min, t_R = major: 15.6 min, minor: 28.4 min. 95% ee. $[\alpha]_D^{23}$ = -46° (*c* 0.14, CH_2Cl_2).

<色谱图>

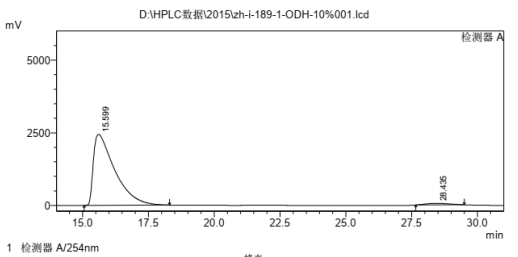


峰表

检测器 A 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	16.153	40888460	812021		49.782	62.394
2	27.817	41245883	489410		50.218	37.606
总计		82134343	1301431		100.000	100.000

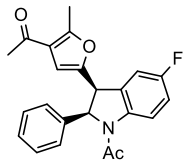
<色谱图>



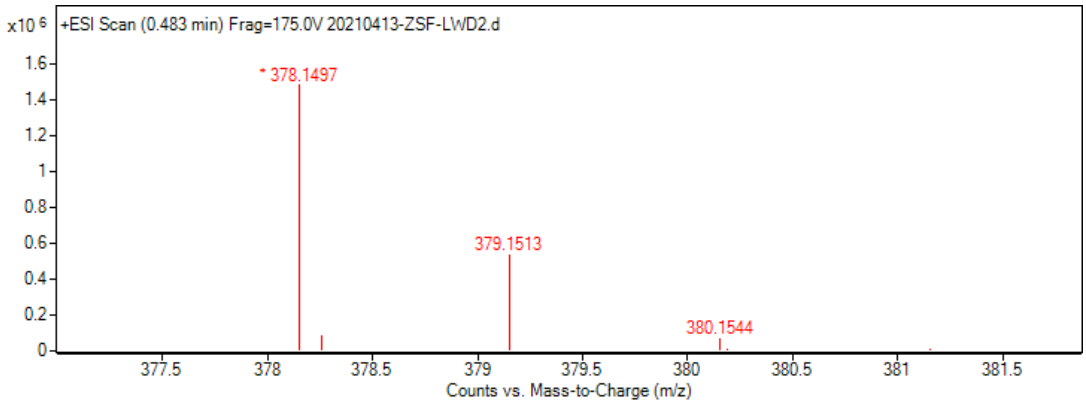
峰表

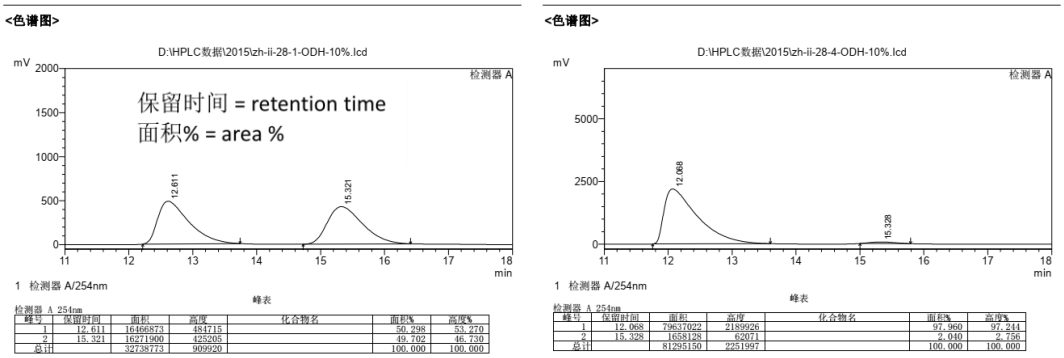
检测器 A 254nm

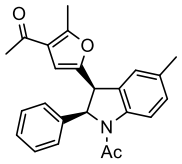
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	15.599	137775380	2441070		97.512	97.751
2	28.435	3515337	56159		2.488	2.249
总计		141290717	2497229		100.000	100.000



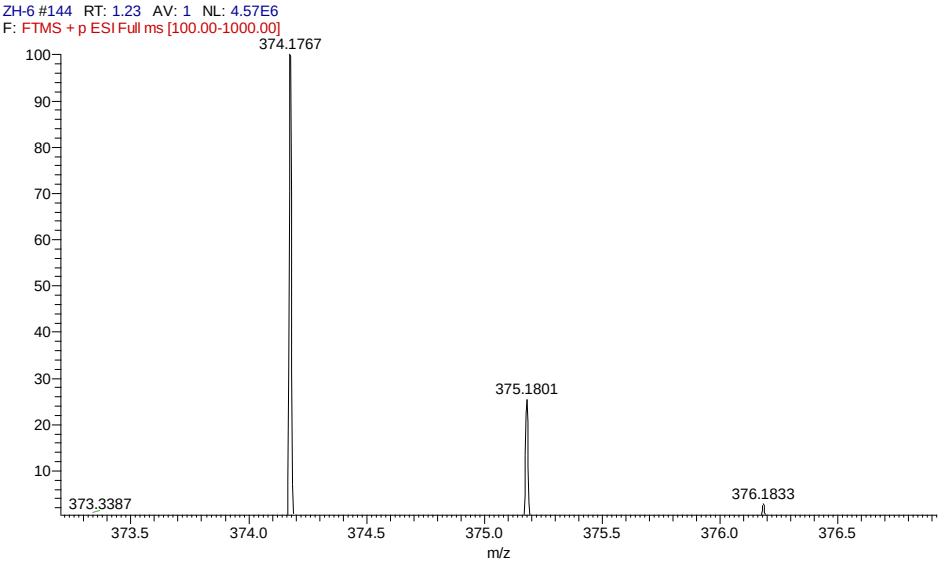
Compound 4g: 94.4 mg of **3g** yields 59.2 mg of **4g** (63%, 12 h, >99:1 dr), yellow oil, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 7.7, 4.4 Hz, 1H), 7.19 – 7.09 (m, 3H), 7.04 (td, *J* = 8.9, 2.5 Hz, 1H), 6.95 – 6.84 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.99 (s, 1H), 5.61 (d, *J* = 9.5 Hz, 1H), 5.22 (d, *J* = 9.5 Hz, 1H), 2.34 (s, 3H), 2.18 (s, 3H), 2.03 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -117.87. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.9, 169.2, 159.8 (d, *J* = 243.3 Hz), 158.1, 148.1, 140.0, 137.7, 131.4 (d, *J* = 8.3 Hz), 128.5, 128.2, 126.2, 121.8, 117.9 (d, *J* = 8.3 Hz), 115.3 (d, *J* = 22.7 Hz), 112.5 (d, *J* = 24.4 Hz), 110.0, 68.5, 46.9, 29.0, 24.0, 14.0. **IR** (KBr, cm^{-1}) 3743, 3609, 3307, 3032, 2923, 2853, 2353, 1726, 1667, 1608, 1566, 1481, 1453, 1392, 1354, 1316, 1256, 1229, 1173, 1128, 1078, 1057, 1030, 948, 874, 822, 804, 755, 706, 675, 631, 608, 546, 517, 485. **HRMS** (ESI) Calcd for $C_{23}H_{21}FNO_3$ $(M+H)^+$ 378.1500, found 378.1497. **HPLC**: OD-H column, 90:10 hexane: isopropanol, 1.00 mL/min, t_R = major: 12.1min, minor: 15.3 min. 96% ee. $[\alpha]_D^{23}$ = -44° (*c* 0.13, CH_2Cl_2).







Compound 4h: 74.7 mg of **3h** yields 63.5 mg of **4h** (85%, 12 h, >99:1 dr), yellow solid, m. p. = 118-119 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.13 – 7.06 (m, 3H), 6.93 – 6.85 (m, 3H), 5.96 (s, 1H), 5.57 (d, *J* = 9.2 Hz, 1H), 5.18 (d, *J* = 9.3 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.17 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.1, 169.2, 157.9, 149.1, 141.7, 138.2, 134.2, 129.5, 129.3, 128.4, 128.0, 126.3, 125.7, 121.8, 116.7, 109.8, 68.4, 47.0, 29.0, 24.2, 21.2, 14.1. **IR** (KBr, cm^{-1}) 3855, 3746, 3493, 3030, 2921, 2852, 2352, 2319, 1727, 1664, 1566, 1486, 1451, 1429, 1391, 1350, 1304, 1270, 1228, 1182, 1058, 1030, 955, 821, 756, 706, 676, 633, 606, 538, 519. **HRMS** (ESI) Calcd for $C_{24}H_{24}NO_3$ $(M+H)^+$ 374.1751, found 374.1767. **HPLC**: OD-H column, 90:10 hexane: isopropanol, 1.00 mL/min, t_R = major: 13.5 min, minor: 16.9 min. 92% ee. $[\alpha]_D^{23}$ = -46° (*c* 0.04, CH_2Cl_2).



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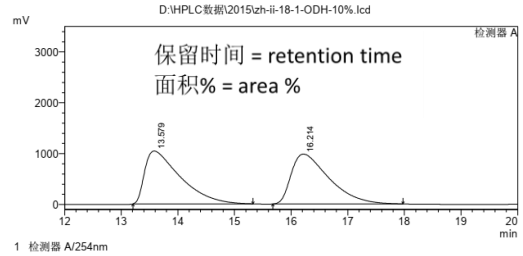
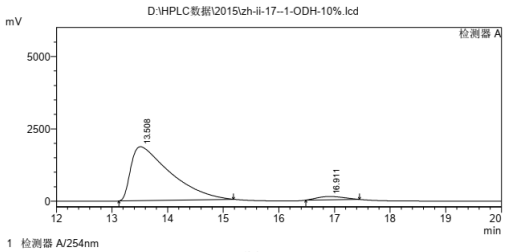


峰表

检测器 A 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.579	45535380	1038872		49.885	51.419
2	16.214	45746013	981519		50.115	48.581
总计		91281393	2020391		100.000	100.000

<色谱图>

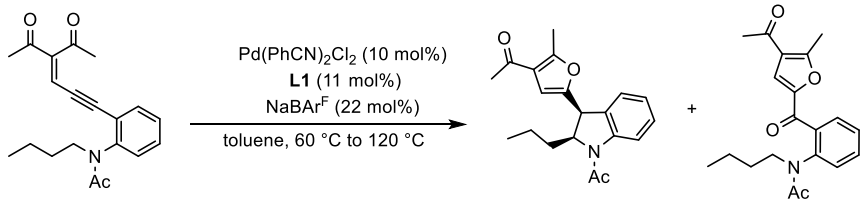


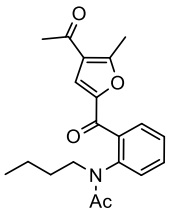
峰表

检测器 A 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.508	91367184	1861186		95.962	94.178
2	16.911	3844860	115055		4.038	5.822
总计		95212044	1976241		100.000	100.000

The alkyl substituted enynone **3i** was tested in the optimal condition. Substrate **3i** basically remained in this system and there was no desired C-H insertion product **4i** even at 120 °C, only trace of **4j**.





Compound 4j: yellow oil, R_f = 0.2 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.53 – 7.48 (m, 1H), 7.30 – 7.26 (m, 2H), 4.06 – 3.94 (m, 1H), 3.06 – 2.96 (m, 1H), 2.70 (s, 3H), 2.44 (s, 3H), 1.87 (s, 3H), 1.52 – 1.38 (m, 2H), 1.25 – 1.17 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.9, 181.5, 170.5, 163.8, 149.6, 141.6, 136.0, 132.1, 130.9, 129.7, 127.9, 123.6, 120.8, 49.4, 29.8, 29.7, 29.0, 23.0, 20.1, 15.0, 13.8. **IR** (KBr, cm^{-1}) 3608, 3325, 3062, 2919, 1676, 1597, 1565, 1487, 1460, 1393, 1365, 1308, 1231, 1158, 1059, 1028, 952, 856, 801, 755, 701, 674, 632, 610, 555, 486, 433. **HRMS** (ESI) Calcd for $C_{20}H_{23}NNaO_4^+$ $(M+Na)^+$ 364.1519, found 364.1522.

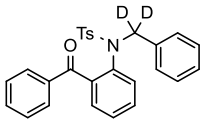
7. Deuteration experiment

7.1 Preparation of the dideutierium-labled d_2-S1a'

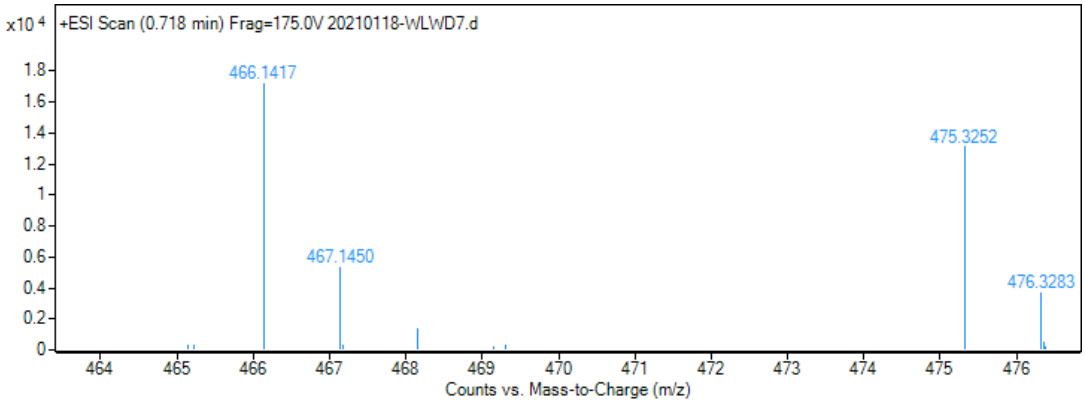
Step 1: Under a N_2 atmosphere, to a stirring suspension of $LiAlD_4$ (3.2 mmol) in dry THF (10 mL) was added dropwise a THF solution (5 mL) of benzoyl chloride (5.1 mmol) at 0℃. The solution was then refluxed to 80℃ for 2 h until the reaction was completely transformed. The mixture was carefully quenched by dropwise addition of H_2O at 0 ℃. The resulting mixture was acidified with 1 M HCl (30 mL), extracted with Et_2O (3× 20 mL), washed with 10% acqueous K_2CO_3 (30 mL) and saturated brine. Organic layer was dried over anhydrous Na_2SO_4, filtered and evapoured under reduced pressure. The crude mixture **S12** was directly used for next step.

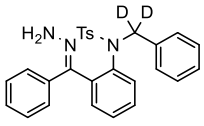
Step 2: To a round bottom flask containing crude alcohol **S12** and dry DCM, PBr_3 (6.8 mmol) was added dropwise at 0 ℃. The reaction mixture was warmed up to rt and stirred overnight. Upon completion, the reaction mixture was carefully quenched by $NaHCO_3$ at 0 ℃. The resulting mixture was extracted with DCM (3× 20 mL) and washed with saturated brine. Organic layer was dried over anhydrous Na_2SO_4, filtered and evapoured under reduced pressure very carefully. The crude mixture was purified by column chromatography (in petroleum ether) to afforded 607 mg (69%) of (bromomethyl-d_2)benzene **S13** as colorless liquid.

Step 3: The dideutierium-labled d_2-**S1a'** was afforded as yellowish white solid (798 mg, 91%) according to the typical procedure for formation of hydrazones in **Chapter 3.**



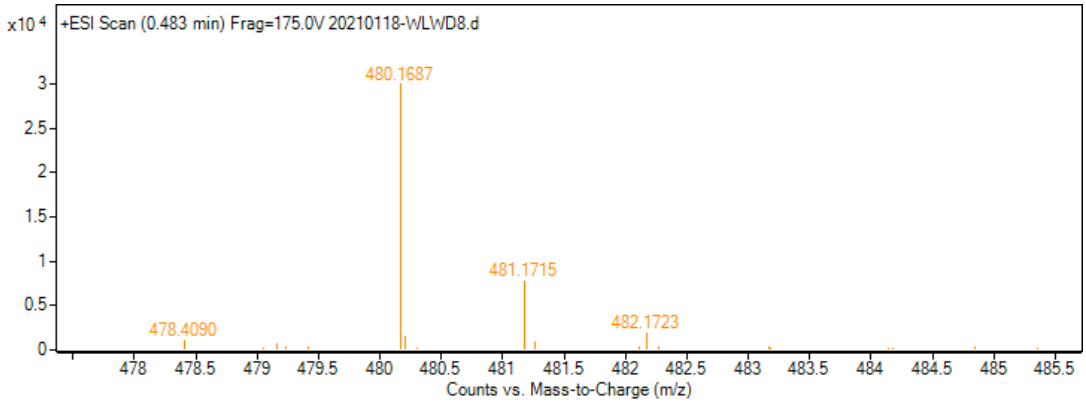
Compound d_2-S1a: 67% yield, white solid, m.p. = 105.1-106.7 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.30 – 7.24 (m, 5H), 7.22 – 7.17 (m, 3H), 6.96 (d, J = 8.0 Hz, 2H), 6.94 – 6.90 (m, 1H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.1, 143.2, 139.6, 136.9, 136.8, 136.0, 133.1, 133.0, 130.67, 130.65, 130.2, 129.9, 129.3, 128.3, 128.0, 127.8, 127.4, 21.5. **IR** (KBr, cm^{-1}) 3061, 3030, 1669, 1596, 1488, 1447, 1345, 1287, 1265, 1162, 1101, 929, 809, 734, 702, 648, 603, 550. **HRMS** (ESI) Calcd for $C_{27}H_{21}D_2NNaO_3S$ $(M+Na)^+$ 466.1416, found 466.1417.



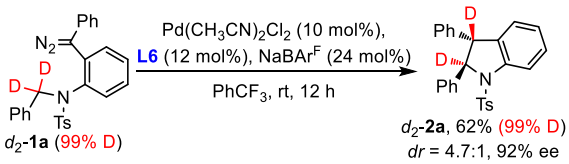


Compound d_2-S1a': 91% yield, yellowish white solid, m.p. = 135.6-136.9 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 5H), 7.40 (d, J = 7.0 Hz, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.31 – 7.25 (m,

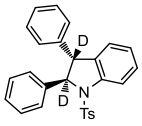
3H), 7.19 – 7.05 (m, 4H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.76 – 6.66 (m, 2H), 5.55 (s, 2H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.2, 143.6, 138.6, 138.5, 136.9, 135.0, 134.8, 131.9, 131.4, 129.7, 129.6, 129.4, 129.3, 128.40, 128.39, 128.3, 128.1, 127.8, 126.4, 21.6. **IR** (KBr, cm^{-1}) 3408, 3299, 3060, 1594, 1489, 1445, 1331, 1269, 1234, 1161, 1094, 1028, 854, 810, 766, 735, 695, 656, 604, 562. **HRMS** (ESI) Calcd for $C_{27}H_{23}D_2N_3NaO_2S$ $(M+Na)^+$ 480.1685, found 480.1687.



7.2 Deuteration Experiment

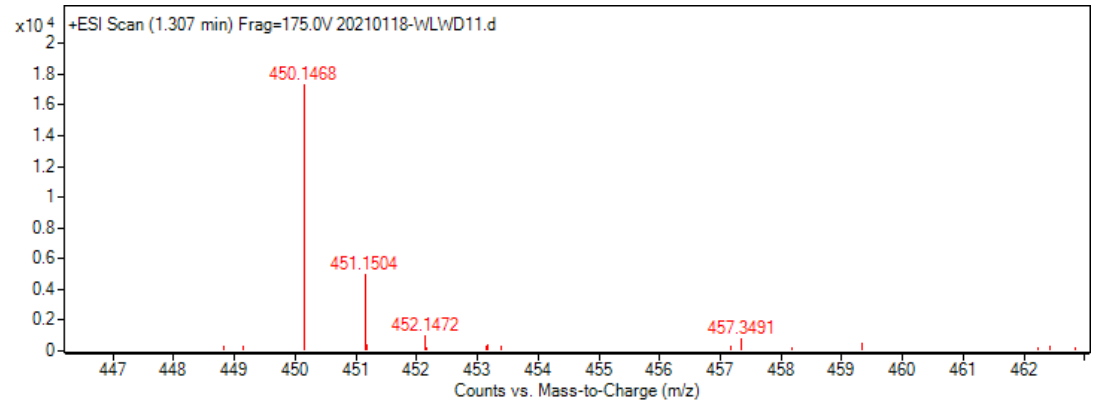


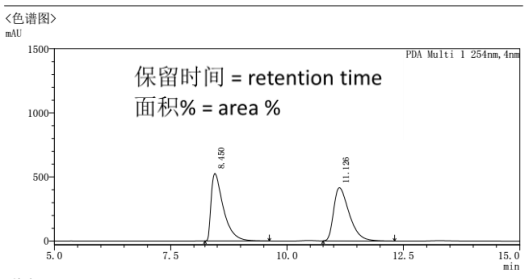
In a flame-dried scintillation vial, the substrate *d*$_2$-S**1a'** (0.1 mmol) was dissolved in anhydrous benzotrifluoride (0.033 M). The scintillation vial was wrapped in foil, and MnO_2 (0.8 equiv.) was added. The oxidation was allowed to stir until full conversion of the starting material was observed by TLC, then the MnO_2 was removed by filtering through celite into a new flame-dried flask using dry ethyl acetate quickly. Next the solvent was removed *in vacuo* at room temperature. The crude magenta diazo compound *d*$_2$-**1a** was used for next step without purification and was diluted to 0.033 M with anhydrous benzotrifluoride. In the meantime, under nitrogen atmosphere, $Pd(CH_3CN)_2Cl_2$ (10 mol%), chiral ligand **L6** (12 mol%) and $NaBAr^F$ (24 mol%) were added in dry benzotrifluoride (6.7×10^{-3} M). The chiral catalysts mixture was stirred at room temperature for 2 h. Then the magenta solution of diazo compounds *d*$_2$-**1a** was added dropwise into the catalyst system for 10 min. The insertion reaction was stirred at room temperature for 12 h. The crude reaction mixture was filtered over Celite, concentrated *in vacuo*, and purified by column chromatography (silica gel, petroleum ether/AcOEt = 30:1) to yield the desired insertion product *d*$_2$-**2a**. The *dr* value (*trans*/*cis*) was determined by ^{1}H NMR using crude mixture. The value of D-incorporation (*cis* &*trans* product) was calculated through ^{1}H NMR.



Compound *d*$_2$-2a (*trans*): 48.4 mg of *d*$_2$-**1a** yields 27.8 mg of *d*$_2$-**2a** (62%, 12 h, *trans*:*cis* = 4.7:1, 22.9 mg *trans* product, using **L6**), white solid, m.p. = 133.1-135.8 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.39 – 7.26 (m, 6H), 7.17 – 7.08 (m, 3H), 7.07 – 6.99 (m, 3H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 143.5, 143.1, 142.5, 134.7, 133.1, 129.7, 129.0, 128.8, 128.7, 127.9, 127.6, 127.5, 126.9, 126.3, 125.9, 124.7, 115.7, 21.7. **IR** (KBr, cm^{-1}) 3028, 2923, 1597, 1545, 1358, 1261, 1166, 1120, 1089, 974, 939, 812, 754, 700, 663, 575, 541. **HRMS** (ESI) Calcd for $C_{27}H_{21}D_2NNaO_2S$ $(M+Na)^+$ 450.1467, found

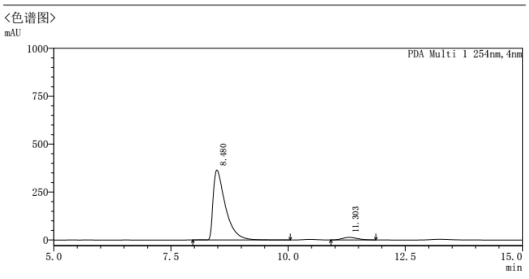
450.1468. **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 8.5 min, minor: 11.3 min. 92% ee. $[\alpha]_D^{21}$ = -164° (*c* 0.55, CH_2Cl_2).





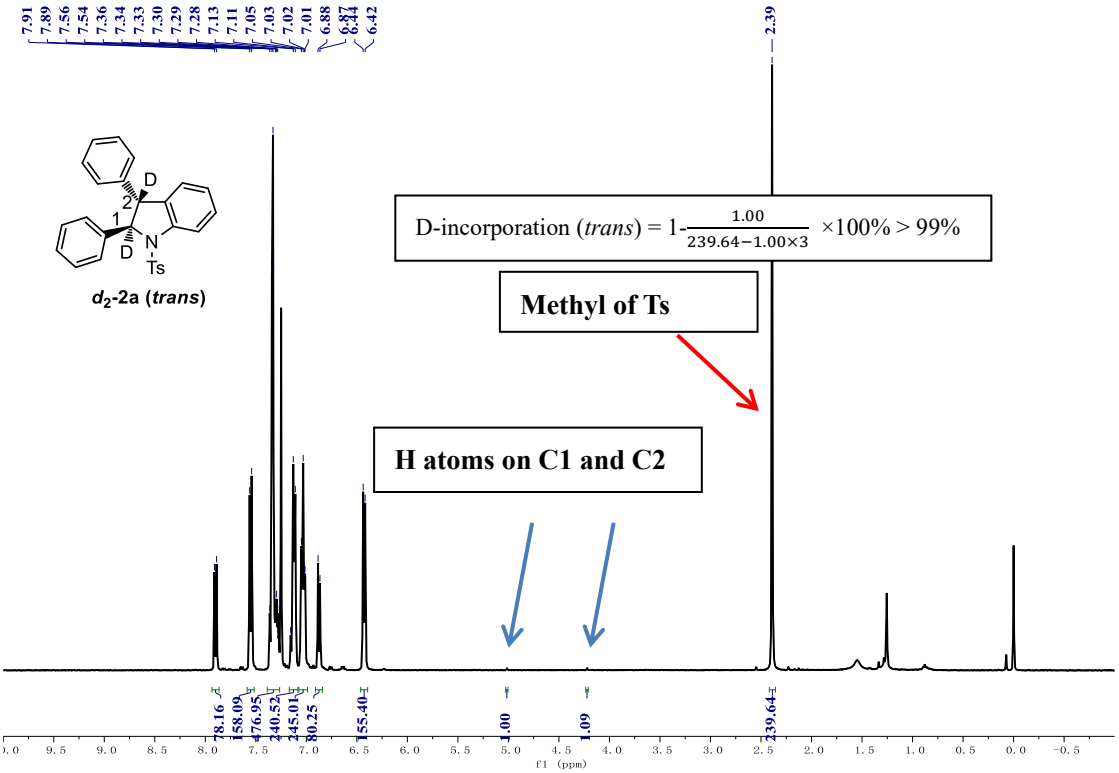
〈峰表〉
PDA Ch1 254nm

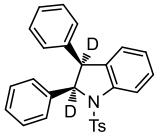
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.450	9677320	526842		50.069	55.894
2	11.126	9650685	415733		49.931	44.106
总计		19328005	942575		100.000	100.000



〈峰表〉
PDA Ch1 254nm

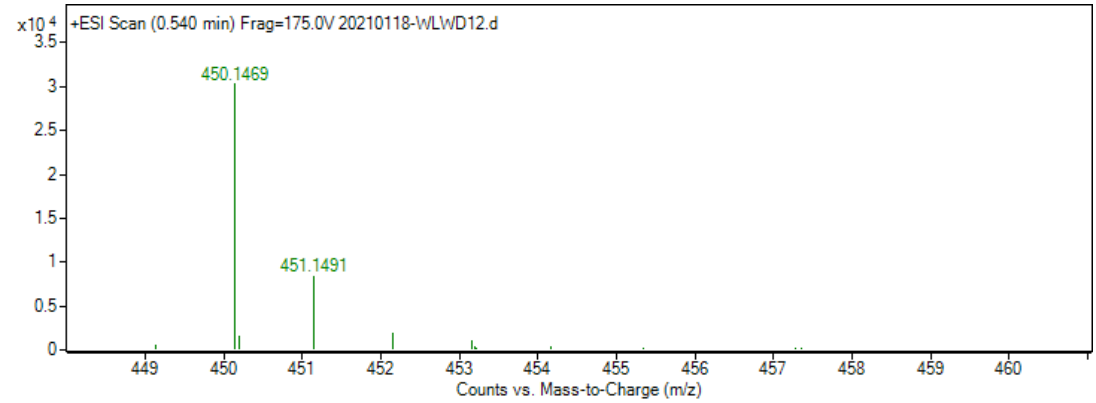
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.480	6670011	364858		95.622	96.416
2	11.303	305376	13564		4.378	3.584
总计		6975387	378422		100.000	100.000

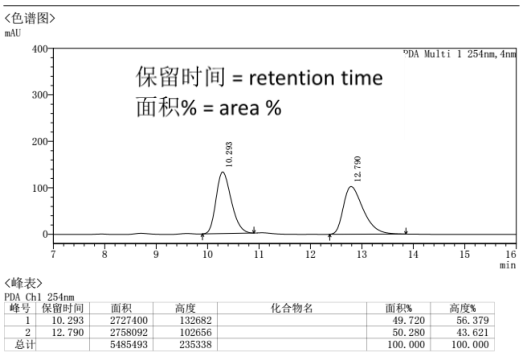




Compound *d*$_2$-2a (*cis*): 48.4 mg of ***d*$_2$-1a** yields 27.8 mg of ***d*$_2$-2a** (62%, 12 h, *trans*:*cis* = 4.7:1, 4.9 mg of *cis* product, using **L6**), white solid, m.p. = 151.7-153.1 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H),

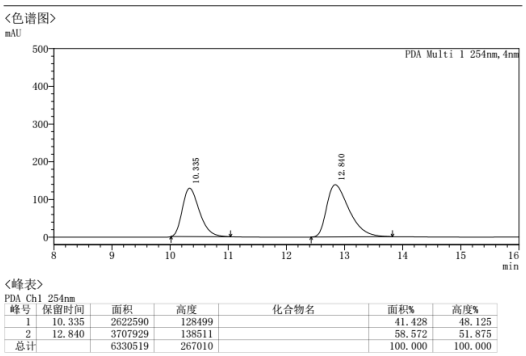
7.08 – 7.01 (m, 2H), 7.01 – 6.96 (m, 3H), 6.93 (t, *J* = 7.4 Hz, 2H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 7.3 Hz, 2H), 6.64 (d, *J* = 7.1 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0, 143.4, 137.5, 136.7, 136.1, 134.4, 129.9, 129.8, 128.6, 127.9, 127.7, 127.4, 127.3, 127.2, 127.1, 126.1, 124.8, 115.9, 21.7. **IR** (KBr, cm^{-1}) 3028, 2921, 1596, 1453, 1353, 1266, 1164, 1035, 930, 811, 753, 701, 657, 575, 546. **HRMS** (ESI) Calcd for $C_{27}H_{21}D_2NNaO_2S$ $(M+Na)^+$ 450.1467, found 450.1469. **HPLC** (using **L6**): OD-H column, 90:10 hexane: isopropanol, 0.80 mL/min, t_R = major: 12.8 min, minor: 10.3 min. 17% ee. $[\alpha]_D^{21}$ = -3° (*c* 0.99, CH_2Cl_2).





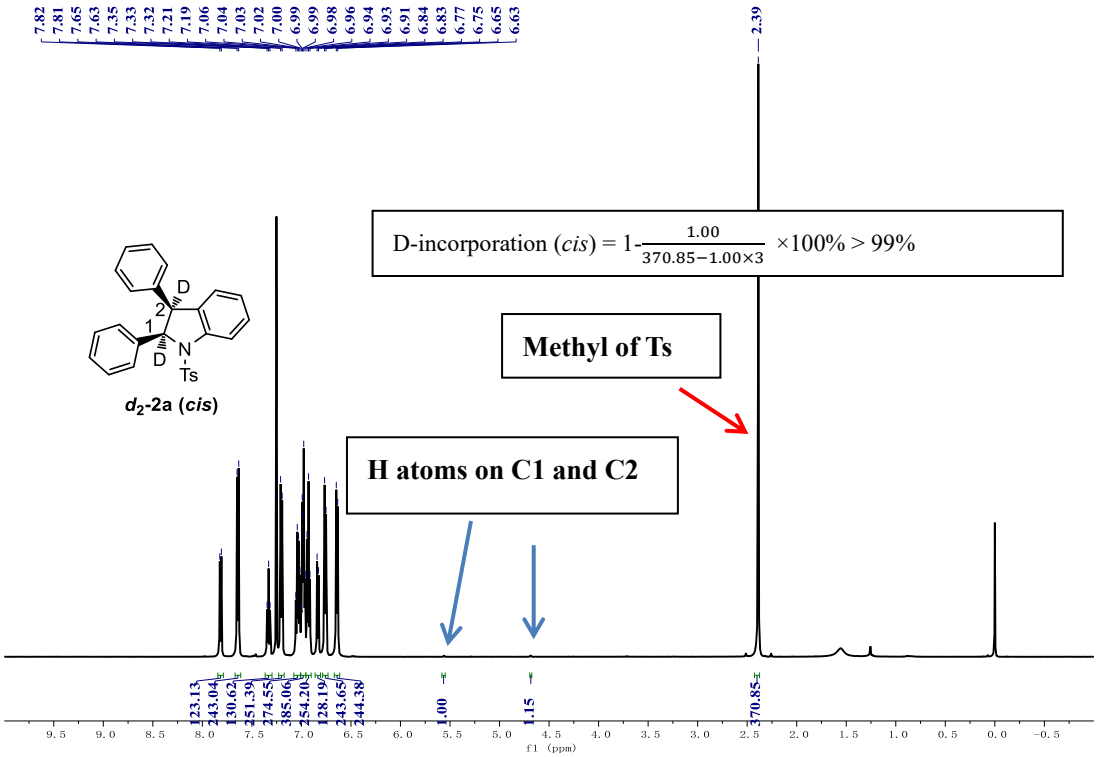
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.293	2727400	132682		49.720	56.379
2	12.790	2758092	102656		50.280	43.621
总计		5485493	235338		100.000	100.000



〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.335	2622590	128499		41.428	48.125
2	12.840	3707929	138511		58.572	51.875
总计		6330519	267010		100.000	100.000

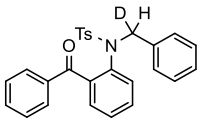


7.3 Preparation of the monodeutierium-labled *d*-1a

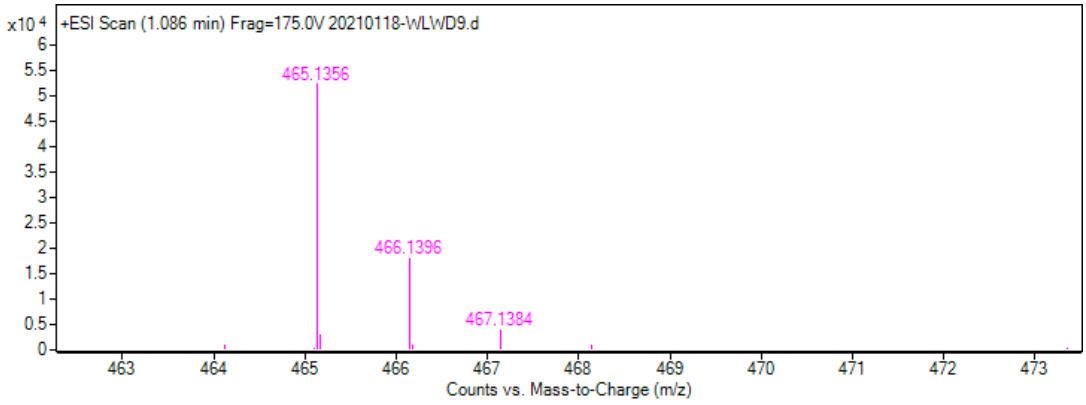
Step 1: Under a N_2 atmosphere, to a stirring suspension of $LiAlD_4$ (3.3 mmol) in dry THF (10 mL) was added dropwise a THF solution (10 mL) of benzaldehyde **S14** (6.8 mmol) at 0℃. The resulting mixture was then warmed to room temperature and stirred for 2 h. The reaction was diluted with Et_2O (10 mL), carefully quenched by dropwise addition of aqueous 2.0 M NaOH (30 mL) at 0 ℃, filtered through a pad of silica and extracted with Et_2O (3× 20 mL). The combined organic solution was dried over anhydrous Na_2SO_4, filtered and evapoured under reduced pressure. The crude mixture **S15** was directly used for next step.

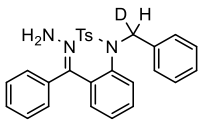
Step 2: To a round bottom flask containing crude alcohol and dry DCM, PBr_3 (7.6 mmol) was added dropwise at 0 ℃. The reaction mixture was warmed up to room temperature and stirred overnight. Upon completion, the reaction mixture was carefully quenched by $NaHCO_3$ at 0 ℃. The resulting mixture was extracted with DCM (3× 20 mL) and washed with saturated brine. Organic layer was dried over anhydrous Na_2SO_4, filtered and evapoured under reduced pressure very carefully. The crude mixture was purified by column chromatography (in petroleum ether) to afforded (bromomethyl-*d*)benzene **S16** (902 mg, 77%) as colorless liquid.

Step 3: The monodeutierium-labled *d*-**S1a'** was afforded as yellowish white solid (1183 mg, 81%) according to the typical procedure for formation of hydrazones in **Chapter 3.**



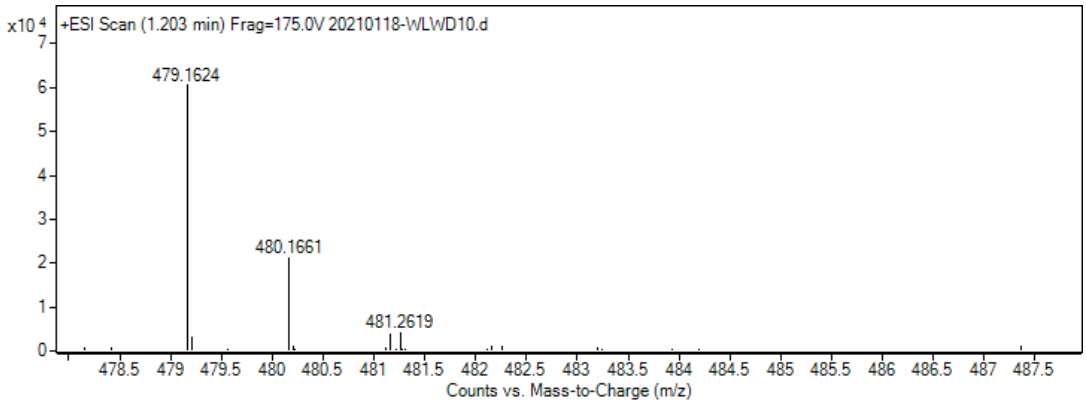
Compound *d*-S1a: Yield: 90%, white solid, m.p. = 102.8-104.9 °C, R_f = 0.5 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.24 (m, 5H), 7.23 – 7.18 (m, 3H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.95 – 6.90 (m, 1H), 4.95 (s, 1H), 2.20 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.1, 143.2, 139.6, 137.0, 136.9, 136.8, 136.1, 133.1, 133.0, 130.68, 130.67, 130.2, 129.9, 129.3, 128.3, 128.1, 127.87, 127.86, 127.5, 56.7, 56.6, 56.4, 21.5. **IR** (KBr, cm^{-1}) 3062, 3032, 1669, 1296, 1488, 1448, 1346, 1265, 1161, 1098, 932, 818, 735, 703, 650, 552. **HRMS** (ESI) Calcd for $C_{27}H_{22}DNNaO_3S$ $(M+Na)^+$ 465.1353, found 465.1356.



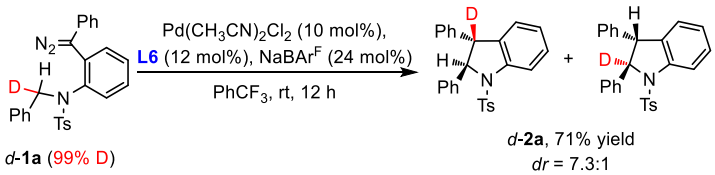


Compound *d*-S1a': Yield: 81%, yellowish white solid, m.p. = 135.3-136.5 °C, R_f = 0.3 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.37 (m, 6H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.18 – 7.05 (m, 4H), 7.00 (t, *J* = 7.4 Hz, 2H), 6.71 (d, *J* = 6.2 Hz, 2H), 5.51 (s, 2H), 4.35 (s, 0.5H), 3.97

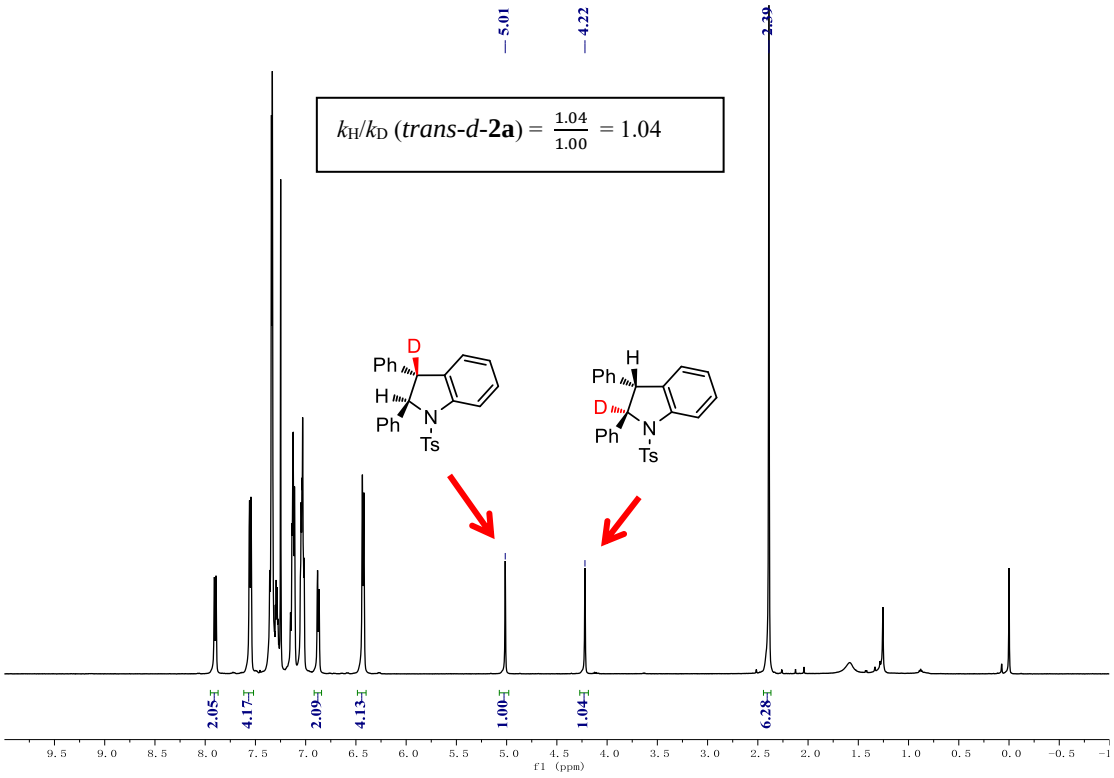
(s, 0.5H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1, 143.6, 138.6, 136.9, 134.9, 134.8, 131.9, 131.4, 129.7, 129.6, 129.4, 129.2, 128.4, 128.2, 128.0, 127.7, 126.4, 54.9, 54.7, 54.4, 21.6. **IR** (KBr, cm^{-1}) 3408, 3300, 3060, 1594, 1489, 1446, 1333, 1269, 1159, 1092, 948, 907, 818, 767, 737, 696, 656, 564. **HRMS** (ESI) Calcd for $C_{27}H_{24}DN_3NaO_2S$ $(M+Na)^+$ 479.1622, found 479.1624.

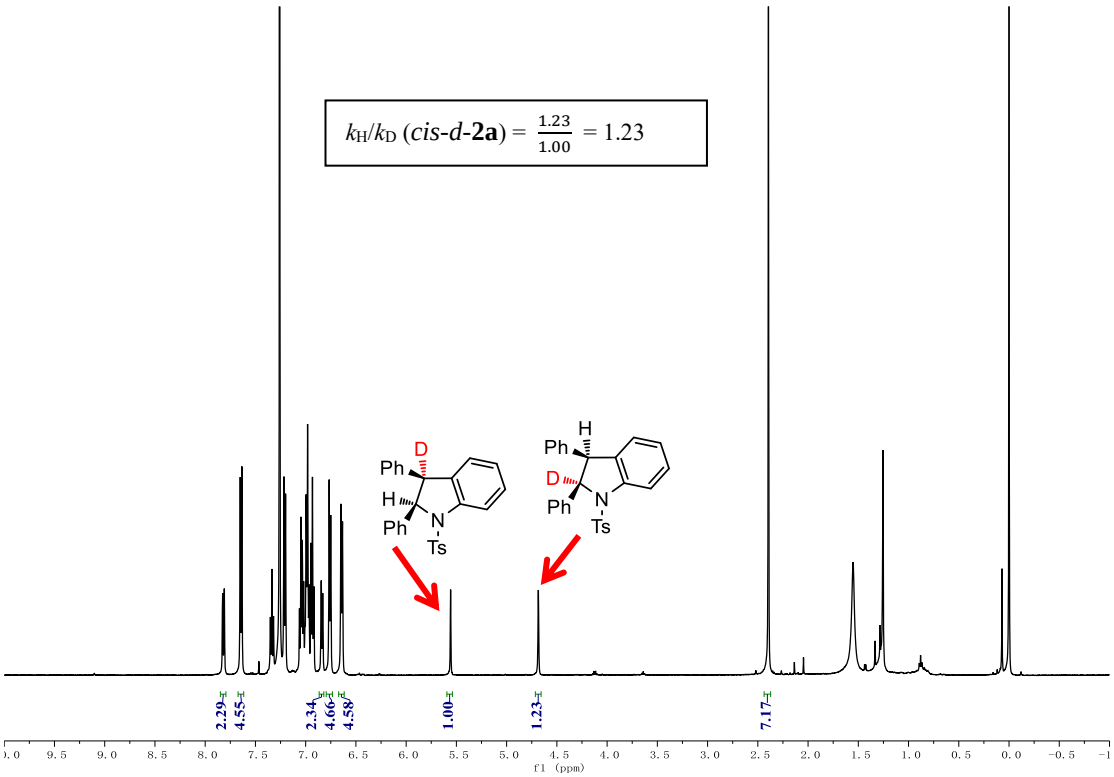


7.4 Kinetic Isotope Effect (KIE) Experiment



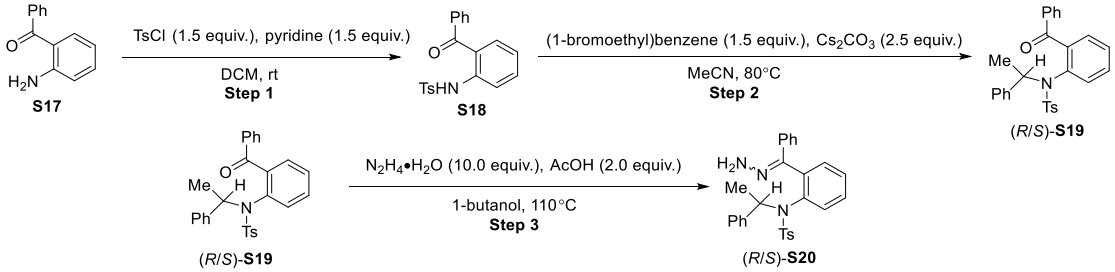
In a flame-dried scintillation vial, the substrate ***d*-S1a'** (0.1 mmol) was dissolved in anhydrous benzotrifluoride (0.033 M). The scintillation vial was wrapped in foil, and MnO_2 (0.8 equiv.) was added. The oxidation was allowed to stir until full conversion of the starting material was observed by TLC, then the MnO_2 was removed by filtering through celite into a new flame-dried flask using dry ethyl acetate quickly. Next the solvent was removed *in vacuo* at room temperature. The crude magenta diazo compound ***d*-1a** was used for next step without purification. Then diazo compound ***d*-1a** was diluted to 0.033 M. In the meantime, under nitrogen atmosphere, $Pd(CH_3CN)_2Cl_2$ (10 mol%), chiral ligand **L6** (12 mol%) and $NaBAr^F$ (24 mol%) were added in dry benzotrifluoride (6.7×10^{-3} M). The chiral catalysts mixture was stirred at room temperature for 2 h. Then the magenta solution of diazo compounds ***d*-1a** was added dropwise into the catalyst system for 10 min. The insertion reaction was stirred at room temperature for 12 h. The crude reaction mixture was filtered over Celite, concentrated *in vacuo*, and purified by column chromatography (silica gel, petroleum ether/AcOEt = 30:1) to yield the desired insertion product. The *dr* value (*trans*/*cis*) was determined by ^{1}H NMR using crude mixture. KIE value (k_H/k_D (*trans*-*d*-**2a**) = 1.0:1; k_H/k_D (*cis*-*d*-**2a**) = 1.2:1) was determined by the ratio of desired products by ^{1}H NMR analysis.


5.01
4.22
2.39
k_H/k_D (*trans-d*-**2a**) = $\frac{1.04}{1.00}$ = 1.04
D
Ph
H
Ph
N
Ts
H
Ph
D
Ph
N
Ts
2.05
4.17
2.09
4.13
1.00
1.04
6.28
f1 (ppm)


k_H/k_D (*cis-d*-**2a**) = $\frac{1.23}{1.00}$ = 1.23
D
Ph
H
Ph
N
Ts
H
Ph
D
Ph
N
Ts
2.29
4.55
2.34
4.66
4.58
1.00
1.23
7.17
f1 (ppm)

8. Mechanistic Studies

8.1 Preparation of substrate (*R*/*S*)-S20 for control experiments

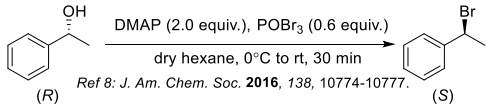


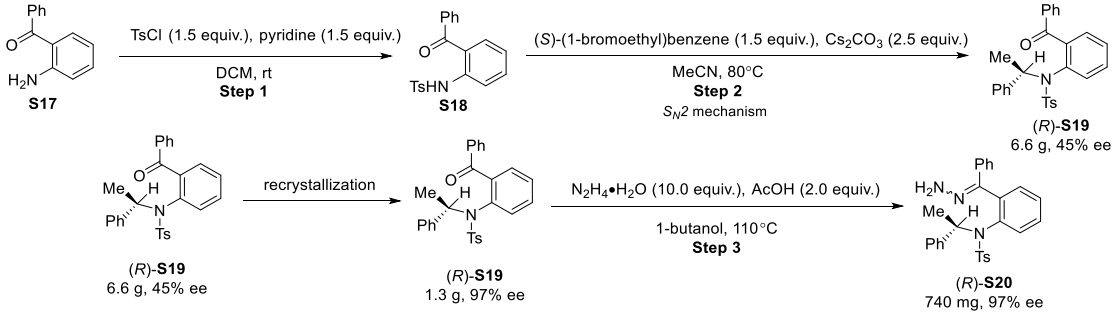
Step 1: To a solution of 2-aminobenzophenone **S17** (3.8 mmol, 1.0 equiv.) in DCM (0.3 M) at 0 °C was added pyridine (5.7 mmol, 1.5 equiv.) and tosyl chloride (5.7 mmol, 1.5 equiv.). The reaction was allowed to come to room temperature while stirring overnight. Water was added to the reaction and the layers were separated. The organic layer was washed with water and brine, then dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*, and purified by column chromatography (silica gel, petroleum ether/AcOEt = 5:1) to yield the desired products.

Step 2: To a flame-dried flask was added the sulfonylated 2-aminobenzophenone **S18** (3.5 mmol, 1.0 equiv.), anhydrous Cs_2CO_3 (8.7 mmol, 2.5 equiv.) and anhydrous acetonitrile (0.3 M). (1-Bromoethyl)benzene (5.2 mmol, 1.5 equiv.) was added dropwise and the reaction was heated to 80°C overnight. The Cs_2CO_3 was removed by filtraltion and washed with ethyl acetate twice. Then the acetonitrile in filtrate was removed *in vacuo*. The residue was dissolved in ethyl acetate and washed with H_2O and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*, and purified by column chromatography (silica gel, petroleum ether/AcOEt = 5:1) to yield (*R*/*S*)-**S19** (1600 mg, 99%).

Step 3: To a flame-dried flask was added anhydrous 1-butanol (0.5 M) along with (*R*/*S*)-**S19** (2.9 mmol, 1.0 equiv.). Glacial acetic acid (5.7 mmol, 2.0 equiv.) was added followed by anhydrous hydrazine (29 mmol, 10.0 equiv.), and the reaction was heated to 110°C reflux for 40 h upon completion by TLC. The residue was dissolved in ethyl acetate and washed with H_2O and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*, and purified by column chromatography (silica gel, petroleum ether/AcOEt = 5:1) to yield the desired hydrazone (*R*/*S*)-**S20** (471 mg, 27%).

8.2 Preparation of substrate (*R*)-S20 for control experiments



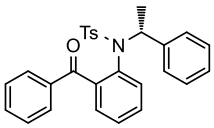


The synthesis of (*S*)-(1-bromoethyl)benzene[6]: To a solution of (*R*)-1-phenylethan-1-ol (50 mmol, 1.0 equiv.) in dry hexane (100 mL) was added DMAP (100 mmol, 2.0 equiv.) and the mixture was cooled to

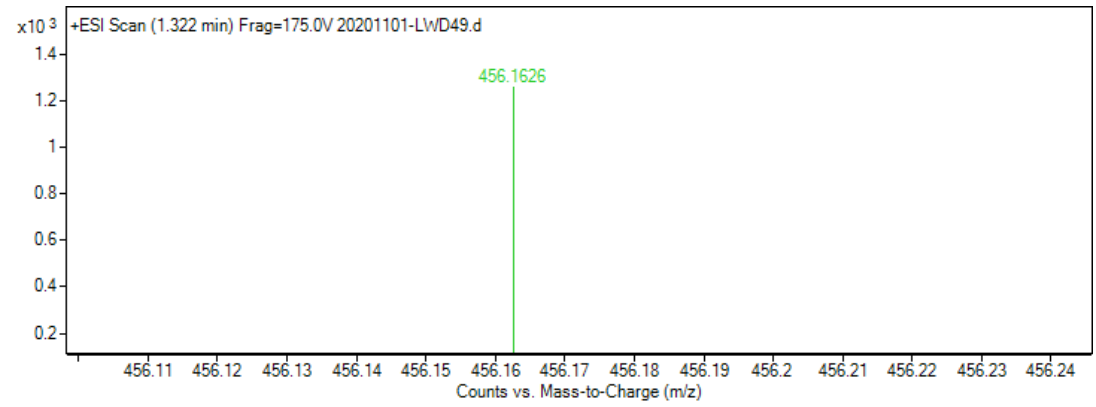
0 ºC. To the mixture was added $POBr_3$ (30 mmol, 0.6 equiv.) slowly. The mixture was stirred at 0 ºC for 30 min, then filtered and the solid was washed with hexane (50 mL). The combined filtrate was washed with water (100 mL) and saturated aqueous solution Na_2CO_3 (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford the target product as colourless oil, which was used for next step without further purification.

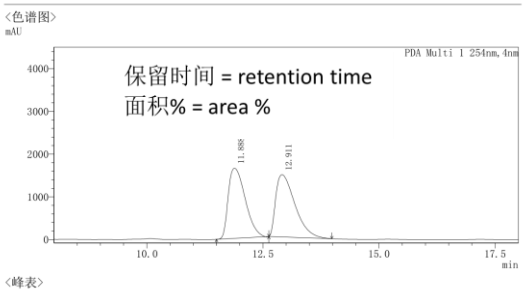
The synthesis of (*R*)-S20

The (*R*)-**S19** (6.6 g, 60% yield for two steps, 45% ee) was afforded according to **Step 1** and **2** above using (*S*)-(1-bromoethyl)benzene as chiron. (*R*)-**S19** with low ee value was required to recrystallize in DCM/i-PrOH system for three times and the optically pure (*R*)-**S19** (1.3 g, 97% ee) was obtained. The target product (*R*)-**S20** (740 mg, 55%, 97% ee) was afforded according to **Step 3** and the ee value was supposed to be consistent.



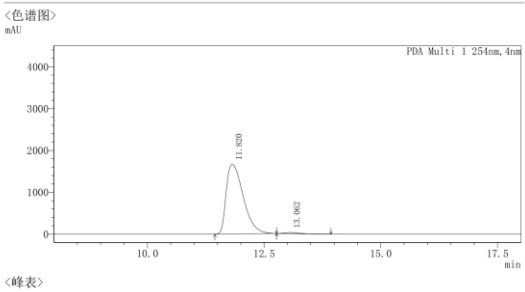
Compound (*R*)-S19: 60% yield, white solid, m.p. = 128.2-129.2 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 1H), 7.64 – 7.27 (m, 8H), 7.21 – 7.07 (m, 5H), 7.00 and 6.73 (d, *J* = 7.2 Hz, 4H), 5.37 and 5.04 (m, 1H), 2.32 and 2.29 (s, 1H), 1.54 and 1.44 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.8 and 194.4, 143.1 and 142.8, 141.9 and 140.4 141.0 and 140.1, 137.9 and 137.5, 137.6 and 137.0, 136.9 and 135.9, 133.8, 133.0 and 132.9, 131.0 and 130.7, 130.5 and 130.22, 130.16, 129.2 and 129.0, 128.7 and 128.5, 128.4 and 128.2, 128.1 and 128.0, 127.8, 127.7 and 127.6, 61.9 and 61.2, 21.60 and 19.9, 21.55. **IR** (KBr, cm^{-1}) 3062, 3031, 2981, 2993, 1670, 1596, 1486, 1448, 1343, 1287, 1263, 1160, 1085, 1021, 940, 907, 812, 768, 733, 703, 660, 639, 572, 550. **HRMS** (ESI) Calcd for $C_{28}H_{26}NO_3S$ $(M+H)^+$ 456.1628, found 456.1626. **HPLC**: INA column, 90:10 hexane: isopropanol, 1.00 mL/min, t_R = major: 11.8 min, minor: 13.1 min. 97% ee. $[\alpha]_D^{21}$ = 104 (*c* 0.61, CH_2Cl_2)).





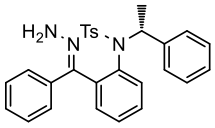
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.888	41713732	1641694		49.829	52.952
2	12.911	42000269	1458623		50.171	47.048
总计		83714000	3100317		100.000	100.000

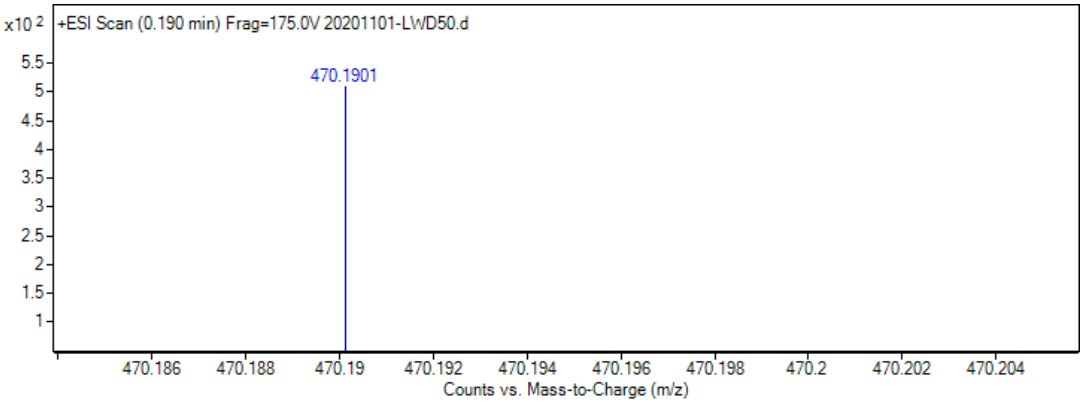


〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.820	42217366	1663060		98.284	98.192
2	13.062	736927	30627		1.716	1.808
总计		42954293	1693688		100.000	100.000



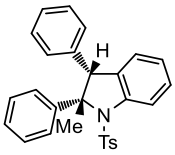
Compound (*R*)-S20: 55% yield, yellow foam, m.p. = 57.4-72.4 °C, R_f = 0.4 (petroleum ether: ethyl acetate = 5:1), 97% ee. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 and 7.56 (d, *J* = 7.2 Hz, 2H), 7.49 and 7.36 (t, *J* = 7.6 Hz, 2H), 7.41 and 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.00 (m, 10H), 6.96 and 6.86(d, *J* = 8.1 Hz, 2H), 6.79 and 6.59 (s, 1H), 5.57 (s, 2H), 5.28 and 5.06 (q, *J* = 7.0 Hz, 1H), 2.40 and 2.33 (s, 3H), 1.40 and 1.30 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.6 and 146.5, 142.8 and 142.4, 142.2, 142.0 and 140.9, 139.5 and 139.0, 136.3 and 135.8, 133.9 and 133.4, 133.2 and 132.8, 132.1 and 131.7, 129.6 and 129.2, 129.1 and 128.9, 128.82 and 128.72, 128.79 and 128.54, 128.34 and 128.09, 128.26 and 128.19, 128.0 and 127.4, 127.74 and 127.52, 127.68 and 127.28, 127.6, 61.6 and 61.4, 22.6 and 21.6, 21.5 and 20.1. **IR** (KBr, cm^{-1}) 3408, 3301, 3061, 2980, 2934, 1594, 1494, 1446, 1324, 1157, 1088, 907, 815, 757, 697, 660, 577, 552. **HRMS** (ESI) Calcd for $C_{28}H_{28}N_3O_2S$ $(M+H)^+$ 470.1897, found 470.1901.



8.3 C(*sp*^{3})-H insertion of 5a for control experiments

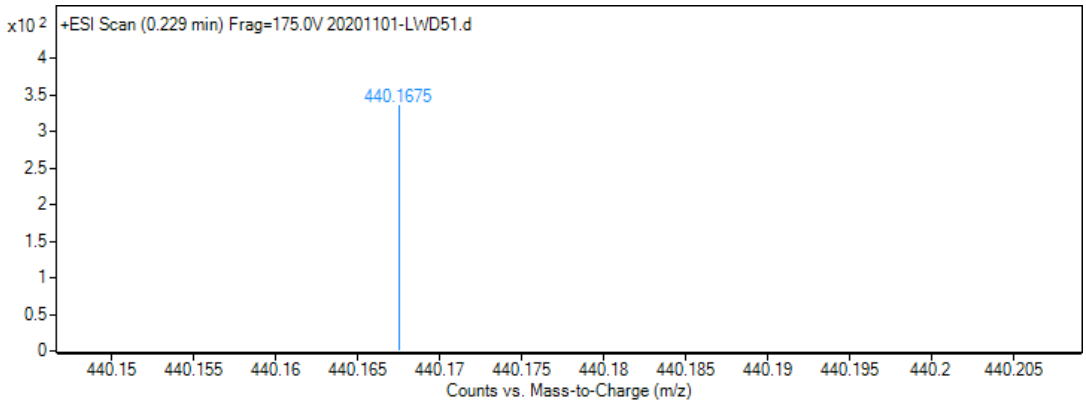
In a flame-dried scintillation vial, the hydrazone (*R*)-**S20** (0.08 mmol, 1.0 equiv.) was dissolved in anhydrous benzotrifluoride (0.04 M). The scintillation vial was wrapped in foil, and MnO_2 (0.64 mmol, 8.0 equiv.) was added. The oxidation was allowed to stir until full conversion of the starting material was observed by TLC, then the MnO_2 was removed by filtering through celite into a new flame-dried flask using dry ethyl acetate quickly. Next the solvent was removed *in vacuo* at room temperature. The crude magenta diazo compound (*R*)-**5a** was used for next step without purification and was diluted to 0.025 M. In the meantime, under nitrogen atmosphere, $Pd(CH_3CN)_2Cl_2$ (10 mol%), chiral ligand **L6** (12 mol%) and $NaBAr^F$ (24 mol%) were added in dry benzotrifluoride (4.0×10^{-3} M), The chiral catalysts mixture was stirred at room temperature for 2 h. Then the magenta solution of diazo compound (*R*)-**5a** was added dropwise into the catalyst system for 10 min. The insertion reaction was stirred at room temperature for 10 h. The crude reaction mixture was filtered over Celite, concentrated *in vacuo*, and purified by column chromatography (silica gel, petroleum ether/AcOEt = 30:1) to yield the desired insertion product **6a**.

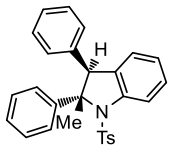
The procedures of other control experiments were analogous to that of the procedure above.



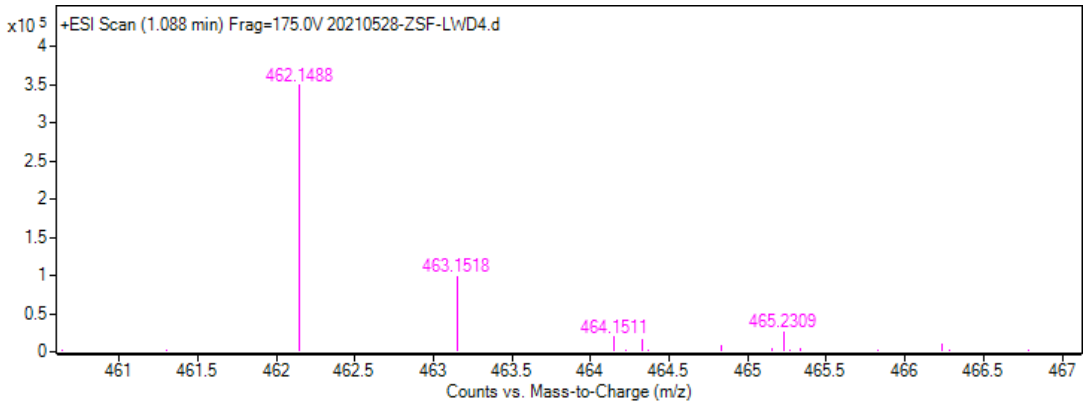
Compound 6a (*cis*): 68% yield, (catalyzed by $Pd(CH_3CN)_2Cl_2$ + *rac*-**L6** with 96% ee hydrazone (*R*)-**5a**), white solid, m.p. = 212.4-213.7 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.05 – 6.98 (m, 3H), 6.98 – 6.92 (m, 3H), 6.84 (d, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 5.9 Hz, 2H), 4.60 (s, 1H), 2.40 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.9, 143.6, 141.3, 139.2, 136.3, 131.4, 130.2, 129.7, 128.6, 127.8, 127.6, 127.4, 127.0, 126.9, 126.4, 125.7, 123.0, 112.9, 78.7, 63.0, 27.0, 21.7. **IR** (KBr, cm^{-1}) 3025, 1596, 1455, 1342, 1234, 1160, 1123, 1084, 997, 811, 778, 727, 695, 655, 575. **HRMS** (ESI) Calcd for $C_{28}H_{26}NO_2S$ $(M+H)^+$ 440.1679, found 440.1675. **HPLC**: OD-H column, 95:5 hexane:

isopropanol, 0.50 mL/min, t_R = major: 20.9 min, minor: 28.4 min. 96% ee. $[\alpha]_D^{21}$ = 109 (*c* 0.63, CH_2Cl_2). (More details see Figure **S8-1b** and Figure **S8-2b**) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.10 (t, *J* = 7.3 Hz, 1H), , 6.84 (d, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 5.9 Hz, 2H), 4.60 (s, 1H), 2.40 (s, 3H), 2.26 (s, 3H).



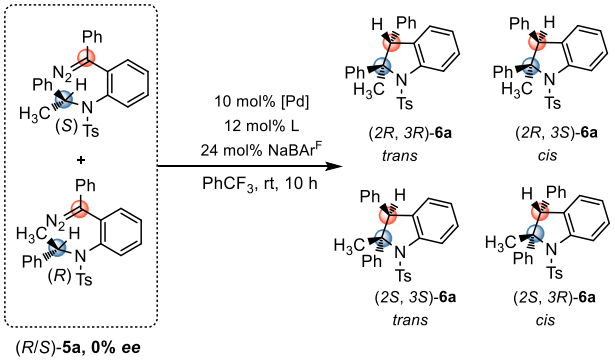


Compound 6a (*trans*): white solid (separated from a pair of diastereoisomers in the catalytic system of $Pd(CH_3CN)_2Cl_2$ with racemic hydrazone (*R*/*S*)-**5a,** *cis*:*trans* = 63:37), m.p. = 97.2-97.5 °C, R_f = 0.6 (petroleum ether: ethyl acetate = 12:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.26 (m, 4H), 7.23 – 7.18 (m, 3H), 7.14 (t, *J* = 7.3 Hz, 2H), 7.02 – 6.92 (m, 2H), 6.73 (d, *J* = 7.3 Hz, 2H), 4.65 (s, 1H), 2.40 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.6, 143.7, 142.7, 138.7, 138.5, 131.4, 129.6, 129.5, 128.6, 128.4, 128.3, 127.6, 127.3, 127.2, 126.1, 126.0, 123.4, 114.2, 77.9, 63.3, 22.9, 21.6. **IR** (KBr, cm^{-1}) 3129, 1610, 1461, 1401, 1350, 1239, 1162, 1084, 991, 808, 749, 696, 650, 571. **HRMS** (ESI) Calcd for $C_{28}H_{25}NNaO_2S$ $(M+Na)^+$ 462.1498, found 462.1488.



8.4 Intramolecular C(sp^3)-H insertion of (*R*/*S*)-5a monitored by HPLC

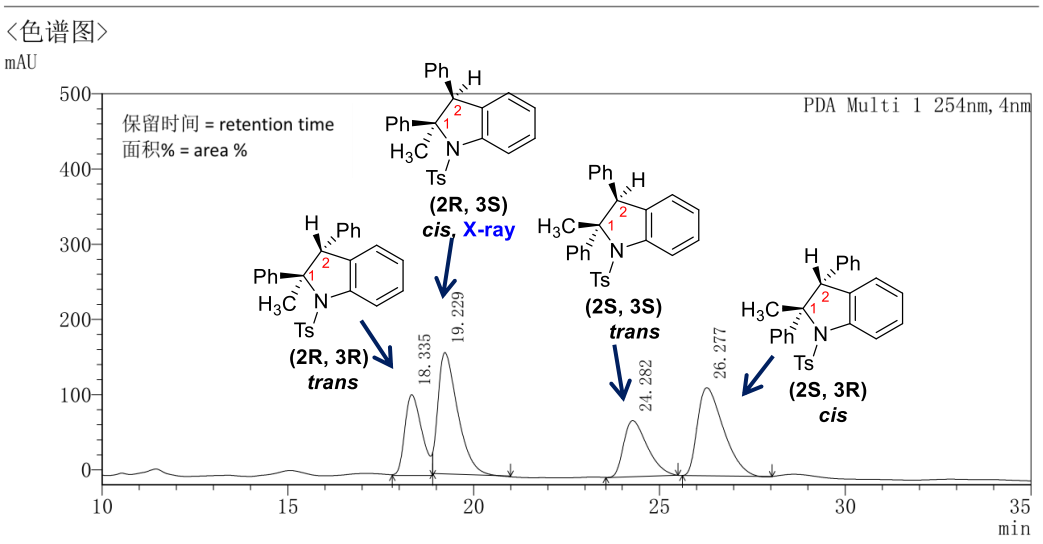
Table S8-1. Intramolecular C(sp^3)-H insertion of (*R*/*S*)-**5a** monitored by HPLC



entry	SM	cat. (mol %)	ligand	yield (%)	*cis*:*trans*	ee_{cis} (%)	ee_{trans} (%)
S8-1a	(*R*/*S*)-**5a**	$Pd(CH_3CN)_2Cl_2$	/	65	63:37	0	0
S8-1b	(*R*/*S*)-**5a**	$Pd(CH_3CN)_2Cl_2$	*rac*-**L6**	49	92:8	0	0

Reaction conditions: (*R*/*S*)-**5a** (0.08 mmol, 0.025M), [Pd] (10 mol%), **L** (12 mol%) and $NaBAr^F$ (24 mol%), $PhCF_3$, rt, under N_2; The ratio of *cis*/*trans* was determined by ^1H NMR spectrum of the crude reaction mixture. The *ee* value was determined by HPLC.

Cis and *trans* insertion products were shown in HPLC figure. The absolute configuration of the peak 2 (from left to right) in HPLC was determined by single crystal X-ray diffraction, which showed a *cis*-(*2R*, *3S*) configuration. According to the racemic standard for **6a** (Figure S8-1a and S8-1b), peak 2 and peak 4 were a pair of enantiomers and thus peak 4 showed a *cis*-(*2S*, *3R*) configuration. And we could also deduce that peak 1 and peak 3 were another pair of enantiomers, which showed a *trans* configuration. In addition, in Figure S8-2a, enantiomerically enriched (*R*)-5a (97% ee) delivered peak 3 and peak 4 (*2S*, *3R*) with 79:21 *cis*/*trans* ratio (consistent with the 78:22 *cis*/*trans* ratio determined by ^1H NMR) and 98% ee. It meant that the configuration at the insertion site (C1) basically retained. Based on above information, we could deduce that peak 3 showed a *trans*-(*2S*, *3S*) configuration and further deduce that peak 1 showed a *trans*-(*2R*, *3R*) configuration. Collectively, from left to right in HPLC figures, the attribution of each peak was shown below: peak 1 = *trans*-(*2R*, *3R*); peak 2 = *cis*-(*2R*, *3S*); peak 3 = *trans*-(*2S*, *3S*); peak 4 = *cis*-(*2S*, *3R*).

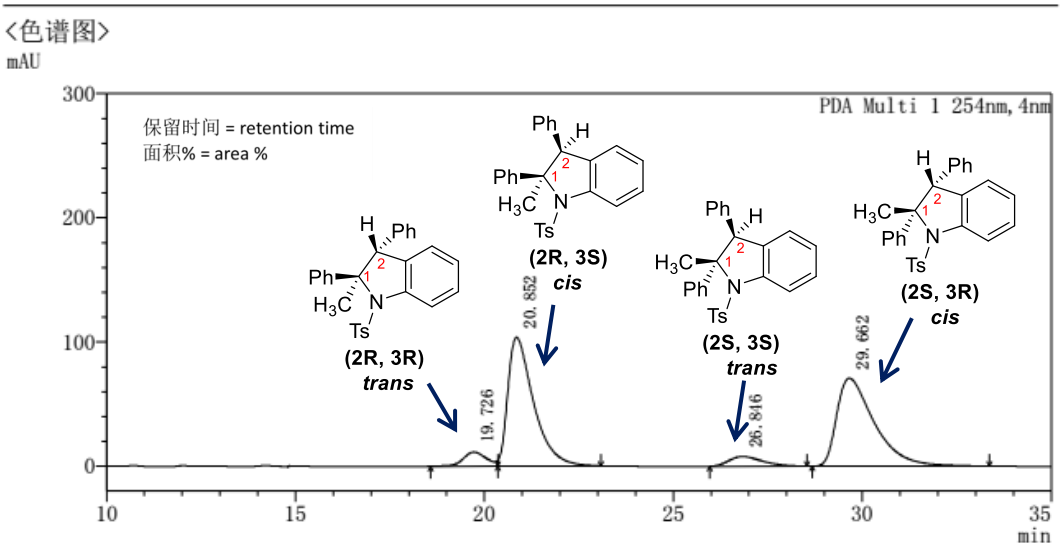


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	18.335	3463814	107372		18.810	23.327
2	19.229	5924221	161199		32.171	35.021
3	24.282	3311352	74562		17.982	16.199
4	26.277	5715472	117164		31.037	25.454
总计		18414859	460298		100.000	100.000

Figure S8-1a Intramolecular C(sp^3)-H insertion of (*R*/*S*)-**5a** catalyzed by $Pd(CH_3CN)_2Cl_2$



〈峰表〉

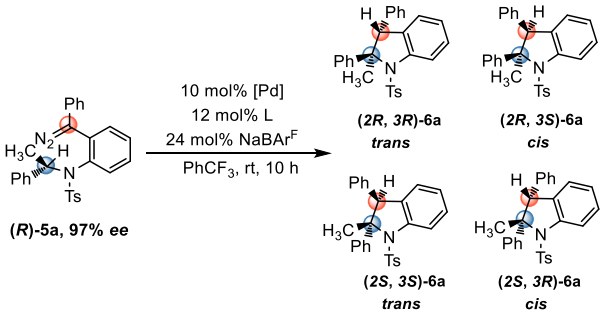
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	19. 726	501751	11418		4. 632	5. 877
2	20. 852	4919825	103956		45. 417	53. 511
3	26. 846	506876	8019		4. 679	4. 128
4	29. 662	4904000	70877		45. 271	36. 484
总计		10832451	194270		100. 000	100. 000

Figure S8-1b Intramolecular C(sp^3)-H insertion of (*R*/*S*)-**5a** catalyzed by $Pd(CH_3CN)_2Cl_2$ + *rac*-**L6**

8.5 Intramolecular C(sp^3)-H insertion of (*R*)-5a monitored by HPLC

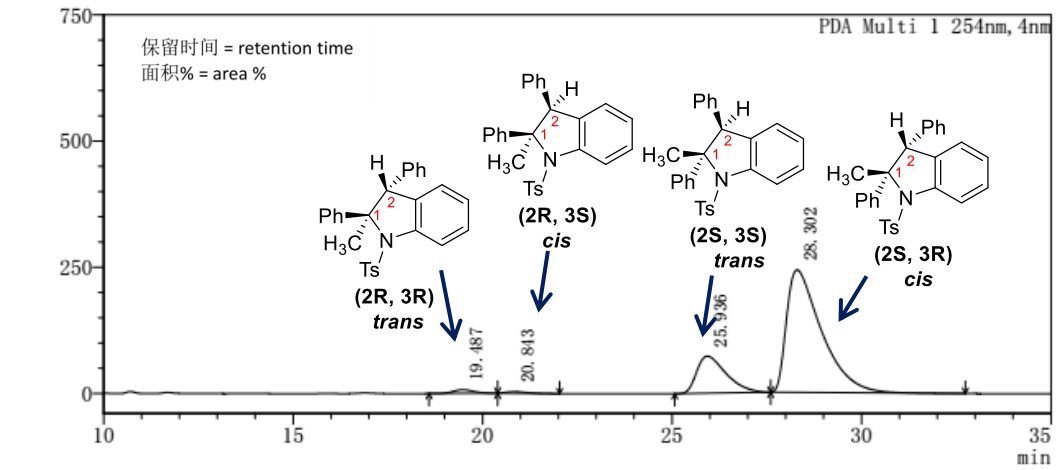
Table S8-2. Intramolecular C(sp^3)-H insertion of (*R*)-**5a** monitored by HPLC



entry	SM	cat. (mol %)	chiral ligand	yield (%)	*cis*:*trans*	ee_{cis} (%)	ee_{trans} (%)
S8-2a	(*R*)-**5a**	$Pd(CH_3CN)_2Cl_2$	/	55	78:22	98	88
S8-2b	(*R*)-**5a**	$Pd(CH_3CN)_2Cl_2$	*rac*-**L6**	68	94:6	96	97
S8-2c	(*R*)-**5a**	$Pd(CH_3CN)_2Cl_2$	(S_a, *R*, *R*)-**L6**	63	95:5	97	95
S8-2d	(*R*)-**5a**	$Pd(CH_3CN)_2Cl_2$	(R_a, *S*, *S*)-**L6**	36	93:7	92	95
S8-2e	(*R*)-**5a**	$Pd(CH_3CN)_2Cl_2$	(R_a, *S*, *S*)-**L6**	19	68:32	87	98

Reaction conditions: **S8-2a-2d**: (*R*)-**5a** (0.08 mmol, 0.025M), [Pd] (10 mol%), **L** (12 mol%) and $NaBAr^F$ (24 mol%), $PhCF_3$, rt, under N_2; **S8-2e**: -10°C. The ratio of *cis*/*trans* was determined by ^1H NMR spectrum of the crude reaction mixture. The *ee* value was determined by HPLC.

<色谱图>



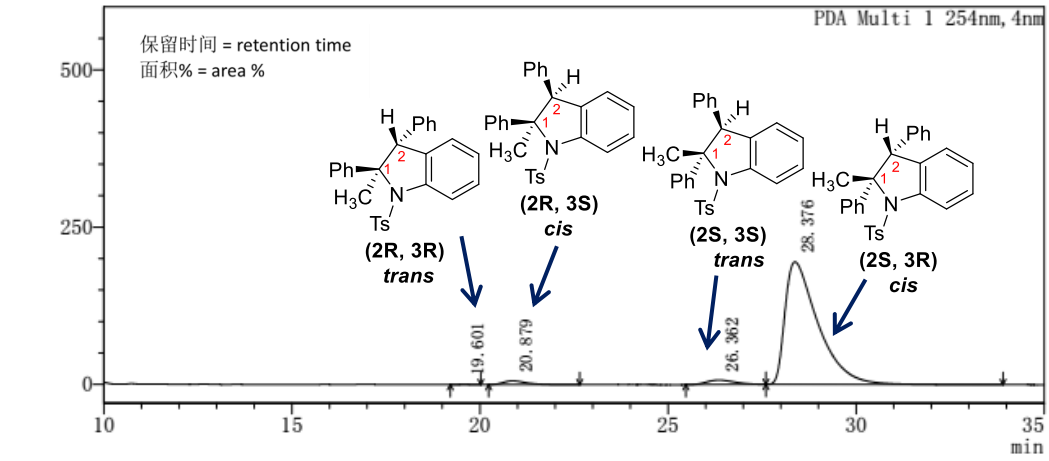
<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	19.487	259681	7100		1.301	2.174
2	20.843	114806	3137		0.575	0.960
3	25.936	3961401	73469		19.843	22.493
4	28.302	15627979	242921		78.281	74.373
总计		19963867	326626		100.000	100.000

Figure S8-2a Intramolecular C(sp^3)-H insertion of (*R*)-**5a** catalyzed by $Pd(CH_3CN)_2Cl_2$

<色谱图>

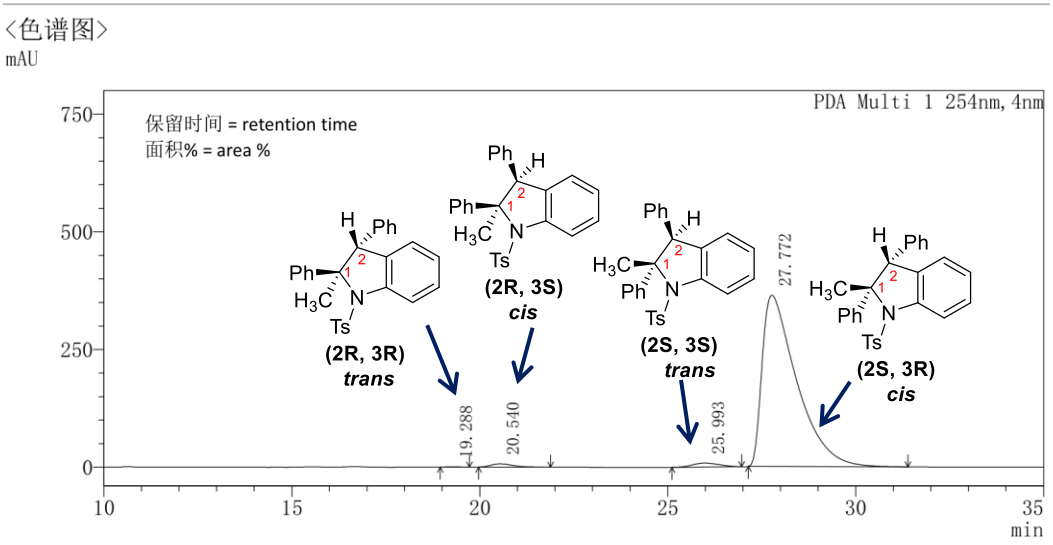


<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	19.601	6007	238		0.048	0.115
2	20.879	247887	5884		1.973	2.828
3	26.362	369707	7102		2.943	3.414
4	28.376	11939652	194801		95.036	93.643
总计		12563253	208026		100.000	100.000

Figure S8-2b Intramolecular C(sp^3)-H insertion of (*R*)-**5a** catalyzed by $Pd(CH_3CN)_2Cl_2$ + *rac*-**L6**

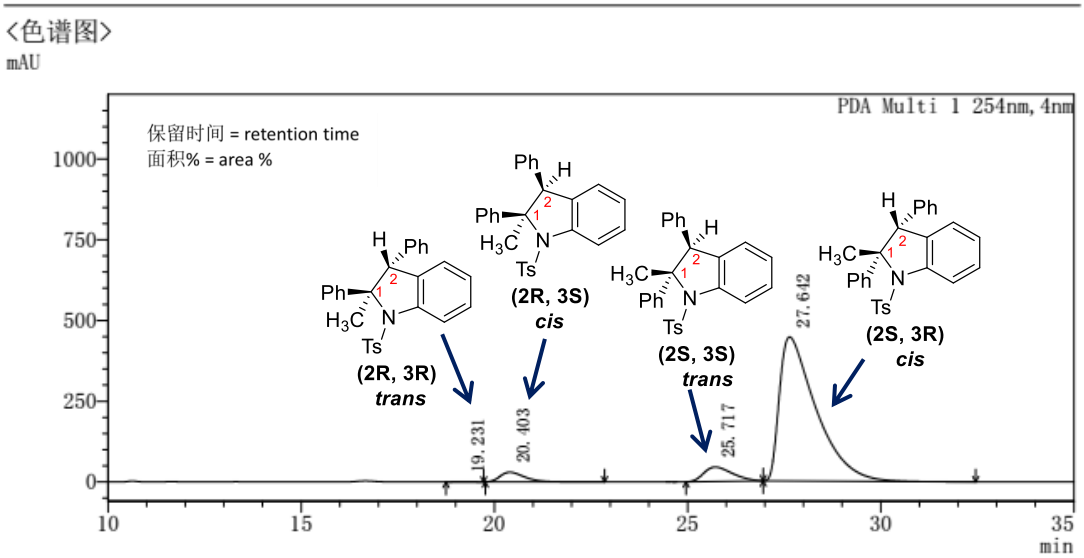


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	19.288	11522	438		0.048	0.115
2	20.540	290597	6947		1.210	1.830
3	25.993	422220	8453		1.759	2.227
4	27.772	23283324	363801		96.983	95.828
总计		24007663	379639		100.000	100.000

Figure S8-2c Intramolecular C(sp^3)-H insertion of (*R*)-**5a** catalyzed by $Pd(CH_3CN)_2Cl_2$ +(S_a, *R*, *R*)-**L6**

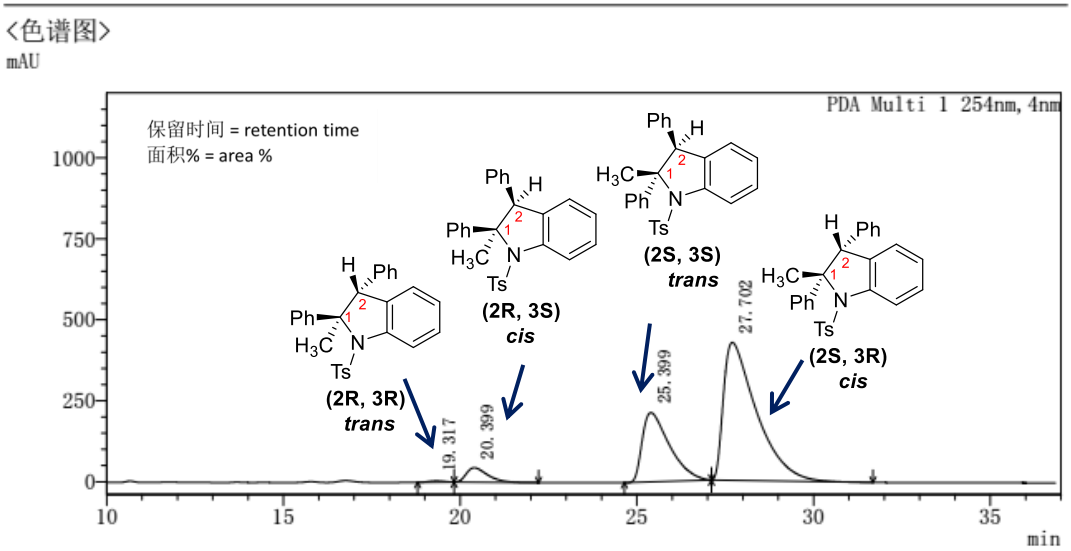


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	19.231	61945	1427		0.187	0.273
2	20.403	1315481	29791		3.967	5.707
3	25.717	2303386	44637		6.946	8.551
4	27.642	29479049	446131		88.900	85.468
总计		33159861	521986		100.000	100.000

Figure S8-2d Intramolecular C(sp^3)-H insertion of (*R*)-**5a** catalyzed by $Pd(CH_3CN)_2Cl_2$ + (R_a, *S*, *S*)-**L6** at room temperature



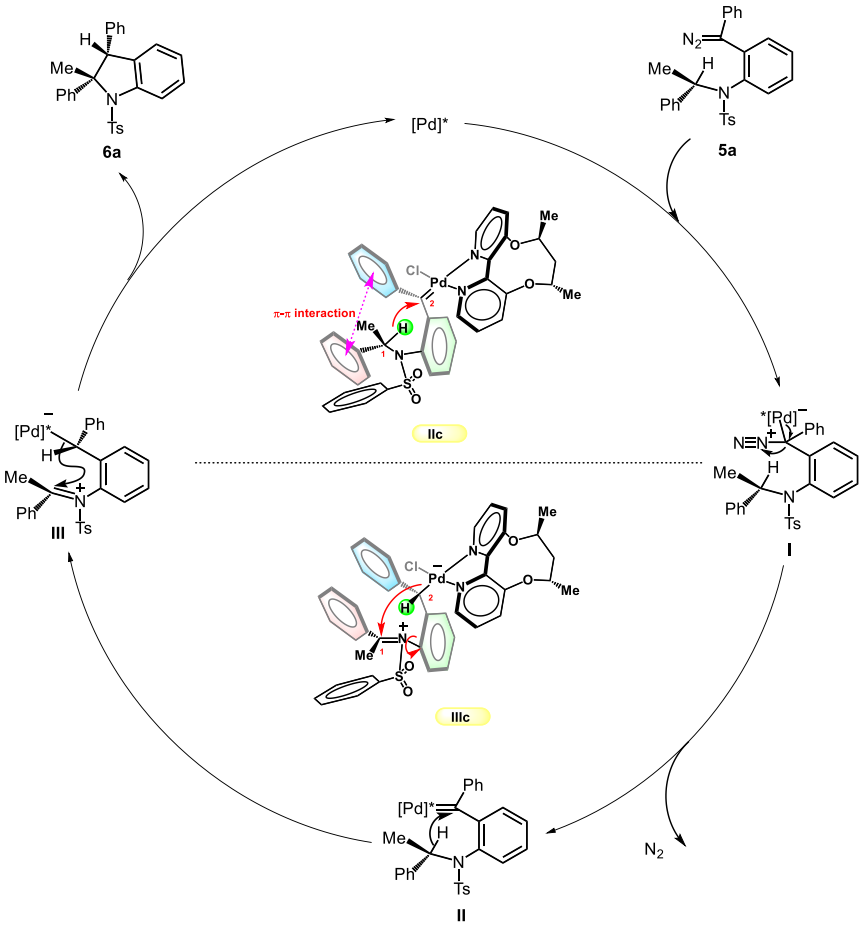
〈峰表〉

PDA Ch1 254nm

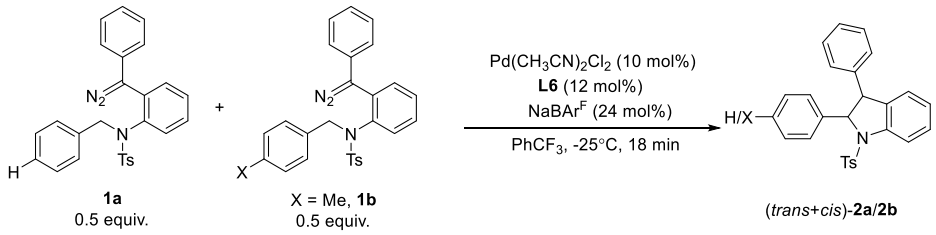
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	19.317	120575	3967		0.293	0.577
2	20.399	1853005	44437		4.500	6.459
3	25.399	11460350	213945		27.833	31.096
4	27.702	27741448	425668		67.374	61.869
总计		41175377	688017		100.000	100.000

Figure S8-2e Intramolecular C(sp^3)-H insertion of (*R*)-**5a** catalyzed by $Pd(CH_3CN)_2Cl_2$ + (R_a, *S*, *S*)-**L6** at -10°C

Based on the plausible reaction mechanism of prochiral substrate **2a** in Scheme 6 of main text, the possible working mode of chirality transfer of substrate **5a** is depicted following. When forming the chiral palladium carbene, an initial hydride shift from C1 to C2 to form short-lived and compact zwitterionic intermediate occurs with stereochemical selectivity, which is dominated by substrate and palladium catalyst and thus diastereoselectivity is governed in this process. Although the pyridine rings of axially chiral 2,2'-bipyridine ligand **L6** could influence diastereoselectivity to some extent, the π-π interaction between two phenyls on C1 and C2 is still favorable. Therefore, *cis*-indoline affords with higher proportion. Subsequently, a fast ring-closure follows, accounting for the stereochemical fidelity of C1. However, if there is a mismatch in stereochemical preference between the substrate and chiral palladium catalyst of zwitterionic intermediate, the rate of ring-closure would be inhibited. In order to reduce the steric repulsion or structure strain in the chiral cavity between substrate and catalyst, a trivial rotation around the C_{aryl}–N bond of zwitterionic intermediate to expose a favorable face might happen, which causes the chirality erosion of C1.


6a
[Pd]*
5a
π–π interaction
IIc
I
III
IIIc
II
N2

9. Hammett analysis



The general experiment procedure: In a flame-dried scintillation vial, the hydrazone S**1a'** (0.05 mmol, 0.5 equiv.) and S**1b'** (0.05 mmol, 0.5 equiv.) was dissolved in anhydrous benzotrifluoride (0.033 M). The scintillation vial was wrapped in foil, and MnO_2 (0.8 mmol, 8.0 equiv.) was added. The oxidation was allowed to stir until full conversion of the starting material was observed by TLC, then the MnO_2 was removed by filtering through celite into a new flame-dried flask quickly. The crude magenta diazo compound mixture containing **1a** and **1b** was used for next step without purification and then diluted to 0.033 M. In the meantime, under nitrogen atmosphere, $Pd(CH_3CN)_2Cl_2$ (10 mol%), chiral ligand **L6** (12 mol%) and $NaBAr^F$ (24 mol%) were added in dry benzotrifluoride (6.7×10^{-3} M). The chiral catalysts mixture was stirred at room temperature for 1 h and swifted to -25℃ (Due to a rapid transformation of diazo compound at room temperature, we changed the system at -25℃ to retard C-H insertion process). Then the magenta solution was added dropwise into the catalyst system for 9 min. The insertion reaction was stirred for another 9 min. The crude reaction mixture was filtered over Celite quickly to remove catalysis and concentrated *in vacuo*. The ratio of **2b**/**2a** was determined by ^{1}H NMR. Similar procedures were used to determine ratios of **2d**/**2a**, **2e**/**2a**, **2f**/**2a**, **2g**/**2a**, **2j**/**2a**, **2k**/**2a**, **2l**/**2a**, **2n**/**2a** and **2o**/**2a**. (The Hammett substituent constants were selected from the literature of *Chem. Rev.* **1991**, 91, 165–195.)[9]

Table S9-1. Hammett analysis through competition experiments with *p*-substitute benzyl substrate

entry	substrate	X	σ	conv.	K_X/K_H	$lg(K_x/K_H)$
1	**1g**	OMe	-0.27	8%	1.02	0.0086
2	**1d**	t-Bu	-0.20	13%	1.08	0.0334
3	**1b**	CH_3	-0.17	8%	1.03	0.0128
4	**1f**	vinyl	-0.04	11%	1.09	0.0374
5	**1e**	Ph	-0.01	9%	0.95	-0.0211
6	**1j**	F	0.06	9%	0.93	-0.0135
7	**1k**	Cl	0.23	8%	0.92	-0.0362
8	**1l**	Br	0.232	6%	0.81	-0.0915
9	**1n**	OCF_3	0.35	10%	0.70	-0.1549
10	**1o**	CF_3	0.54	9%	0.62	-0.2076

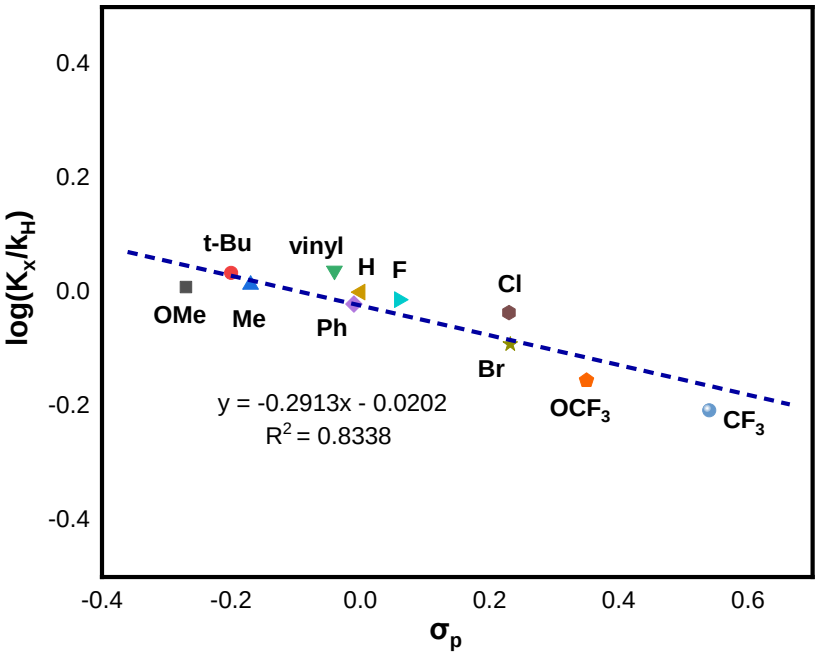


Figure S9-1 Hammett plot vervus σ_p

10. X-Ray diffraction analysis

10.1 Crystal data and structure refinement for *trans*-2a

Single crystal of *trans*-**2a** was grown from slow evaporation of PE/DCM solvent. A suitable crystal was selected and measured on a Agilent SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 100(10) K during data collection.

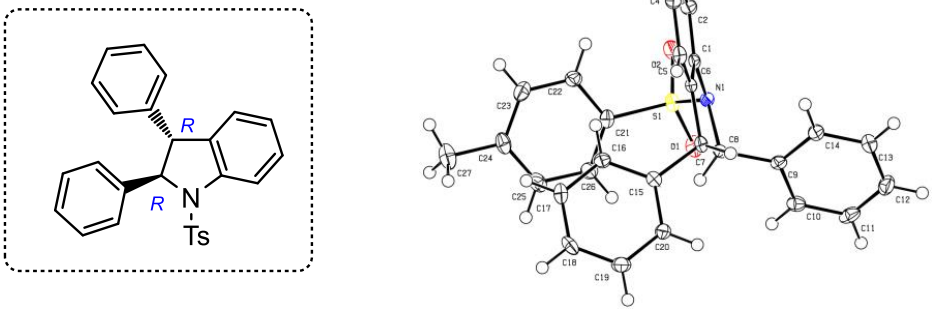


Figure S10-1 Ellipsoid plot of the crystal structure of *trans*-**2a** (Prob = 50, Temp = 100 K)

Table S10-1. Crystal data and structure refinement for *trans*-2**a**

CCDC	2142261
Identification code	*trans*-**2a** (LWD-II-78-1)
Empirical formula	$C_{27}H_{23}NO_2S$
Formula weight	425.52
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.4589(6)
b/Å	9.3504(5)
c/Å	12.9480(8)
α/°	90
β/°	110.298(7)
γ/°	90
Volume/Å^3	1074.06(12)
Z	2
ρ_{calc}g/cm^3	1.316
μ/mm^{-1}	0.175
F(000)	448.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.592 to 49.998
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -15 ≤ l ≤ 14
Reflections collected	4686
Independent reflections	3047 [R_{int} = 0.0233, R_{sigma} = 0.0416]
Data/restraints/parameters	3047/1/281

Goodness-of-fit on F^2	1.123
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0785
Final R indexes [all data]	R_1 = 0.0358, wR_2 = 0.0798
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.37
Flack parameter	-0.01(5)

10.2 Crystal data and structure refinement for 4h

Single crystal of **4h** was grown from slow evaporation of PE/EA solvent. A suitable crystal was selected and measured on a Agilent SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 150 K during data collection.

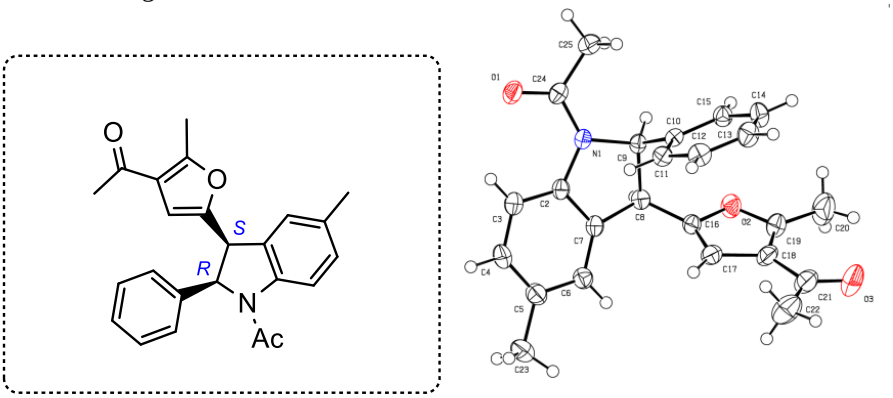


Figure S10-2 Ellipsoid plot of the crystal structure of **4h** (Prob = 50, Temp = 150 K)

Table S10-2. Crystal data and structure refinement for **4h**

CCDC	1908561
Identification code	**4h** (ZH-53-1)
Empirical formula	$C_{24}H_{23}NO_3$
Formula weight	373.43
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.94940(10)
b/Å	10.28380(10)
c/Å	24.4594(3)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1999.56(4)
Z	4
$\rho_{calc}g/cm^3$	1.240
μ/mm^{-1}	0.652
F(000)	792.0
Crystal size/mm^3	0.16 × 0.14 × 0.12

Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.228 to 148.368
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 12, -30 ≤ l ≤ 30
Reflections collected	18997
Independent reflections	3985 [R_{int} = 0.0323, R_{sigma} = 0.0204]
Data/restraints/parameters	3985/0/257
Goodness-of-fit on F^2	0.986
Final R indexes [I>=2σ (I)]	R_1 = 0.0349, wR_2 = 0.0923
Final R indexes [all data]	R_1 = 0.0369, wR_2 = 0.0935
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.20
Flack/Hooft parameter	0.02(7)/0.03(6)

10.3 Crystal data and structure refinement for the (*2R*, *3S*)-6a

Experimental Procedure

Single crystal of (*2R*, *3S*)-**6a** was grown from slow evaporation of PE/DCM solvent. A suitable crystal was selected and measured on a Agilent SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 150(10) K during data collection.

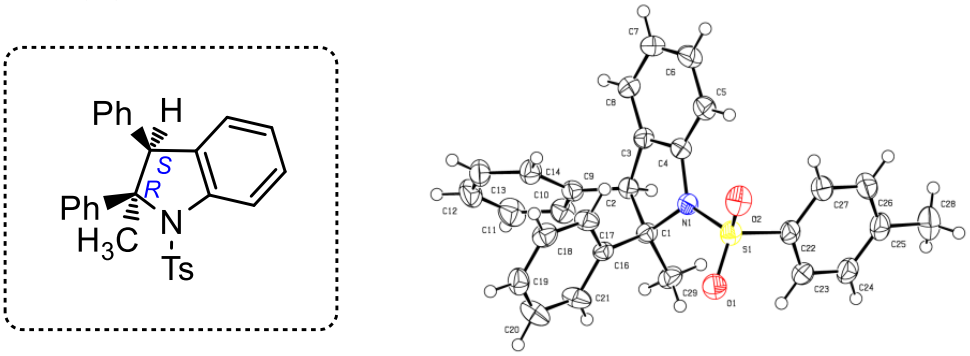


Figure S10-3 Ellipsoid plot of the crystal structure of (*2R*, *3S*)-**6a** (Prob = 50, Temp = 150 K)

Table S10-3 Crystal data and structure refinement for (*2R*, *3S*)-**6a**

CCDC	2142262
Identification code	(*2R*, *3S*)-**6a** (LWD-III-17-3)
Empirical formula	$C_{28}H_{25}NO_2S$
Formula weight	439.55
Temperature/K	150.00(10)
Crystal system	trigonal
Space group	$P3_1$
a/Å	10.2503(2)
b/Å	10.2503(2)
c/Å	18.6428(4)
α/°	90
β/°	90
γ/°	120

Volume/Å^3	1696.35(8)
Z	3
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	1.465
F(000)	696.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.964 to 148.012
Index ranges	-12 ≤ h ≤ 11, -9 ≤ k ≤ 12, -22 ≤ l ≤ 21
Reflections collected	10380
Independent reflections	4315 [R_{int} = 0.0271, R_{sigma} = 0.0294]
Data/restraints/parameters	4315/1/292
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0299, wR_2 = 0.0819
Final R indexes [all data]	R_1 = 0.0303, wR_2 = 0.0828
Largest diff. peak/hole / e Å^{-3}	0.19/-0.21
Flack/Hooft parameter	0.006(8)/-0.004(7)

11. References

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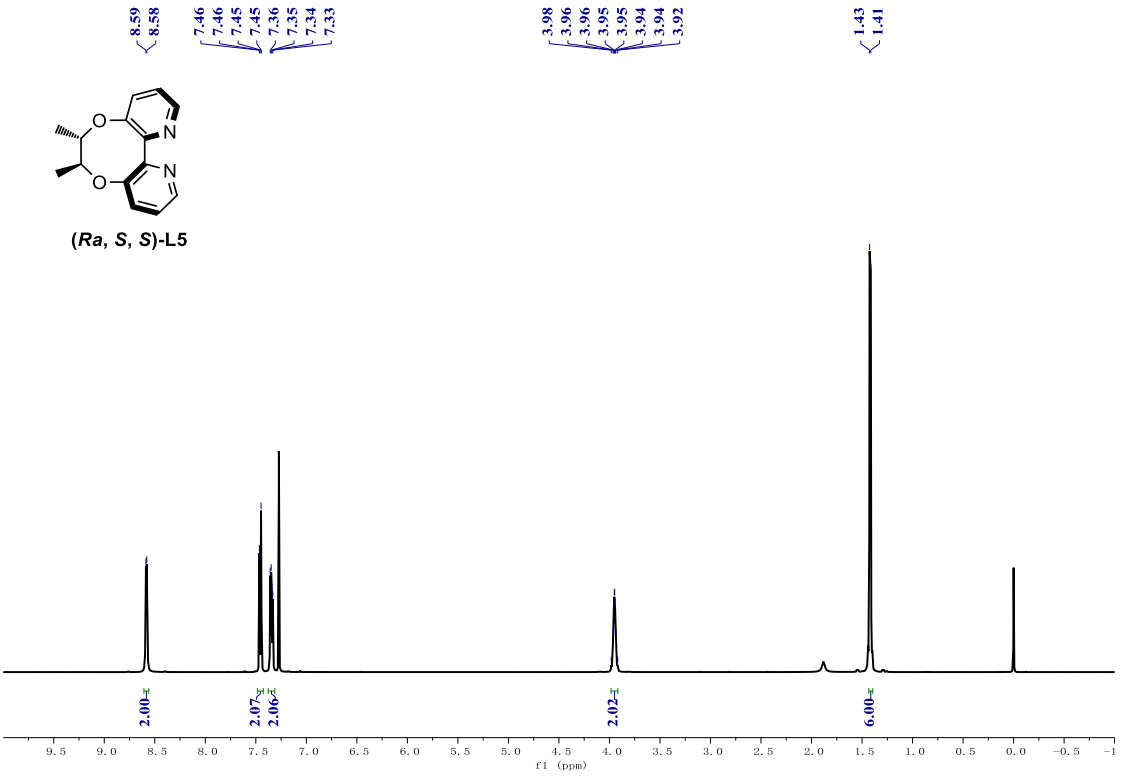
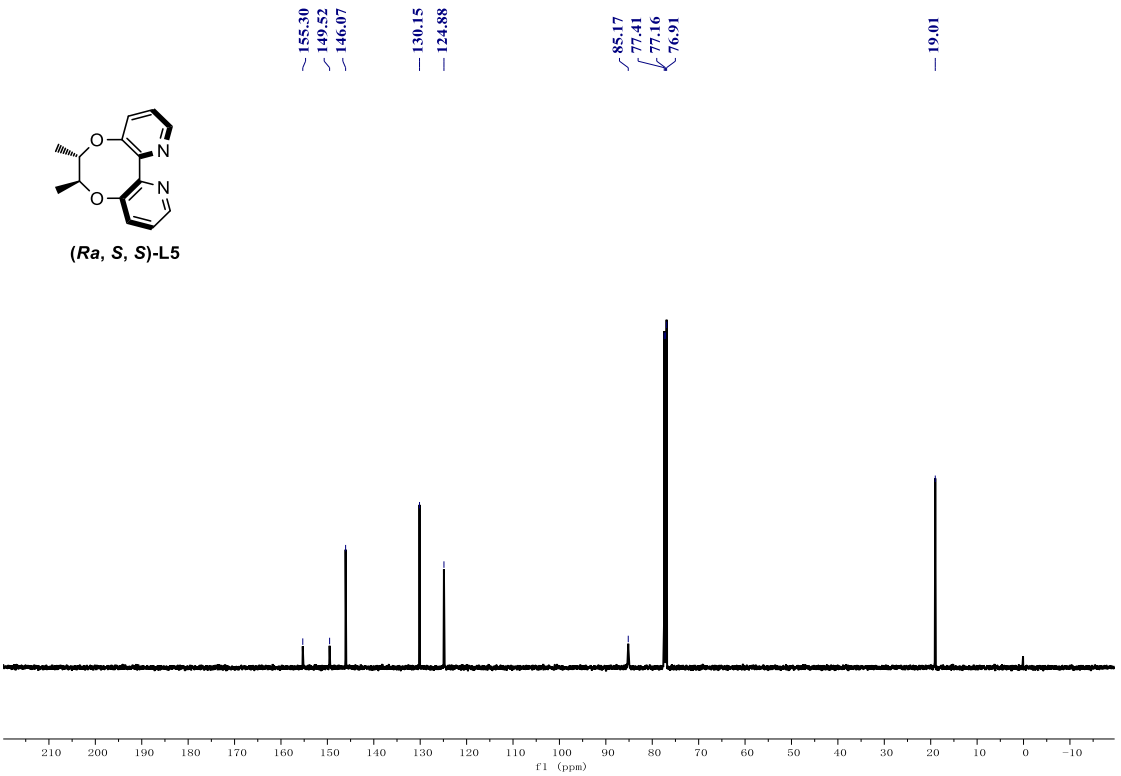
12. Spectrum of NMR



(*Ra*, *S*, *S*)-L5



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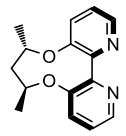

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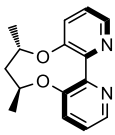

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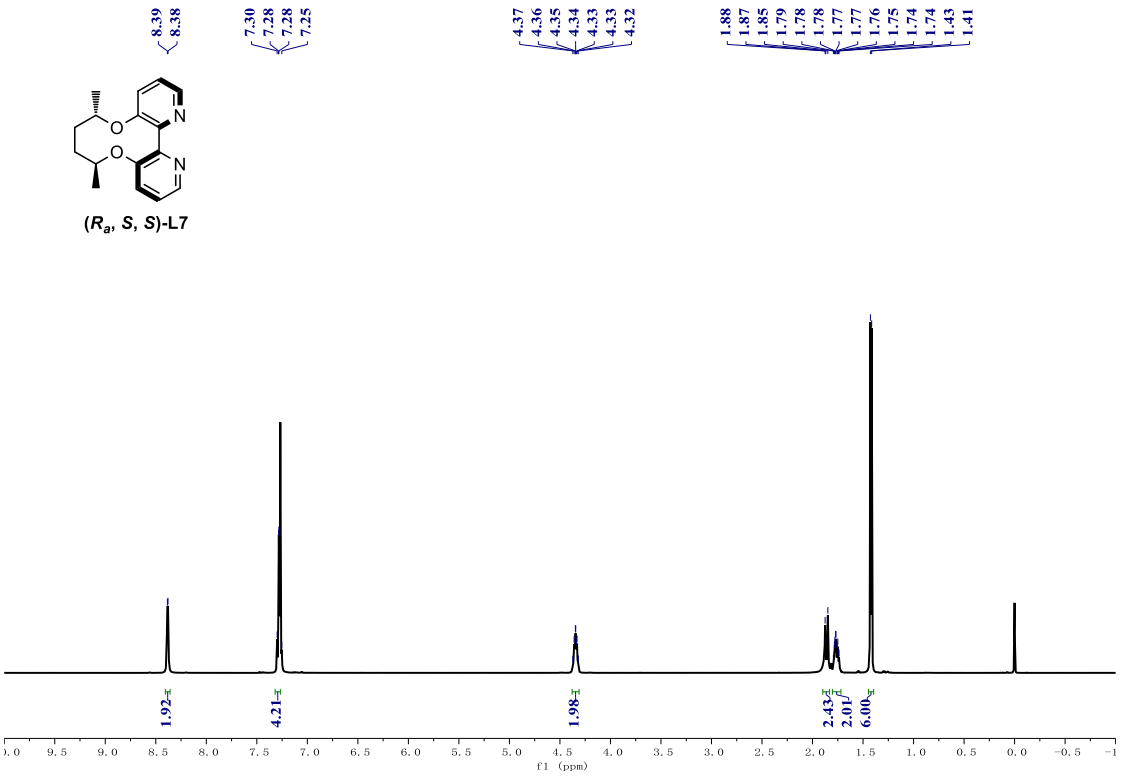
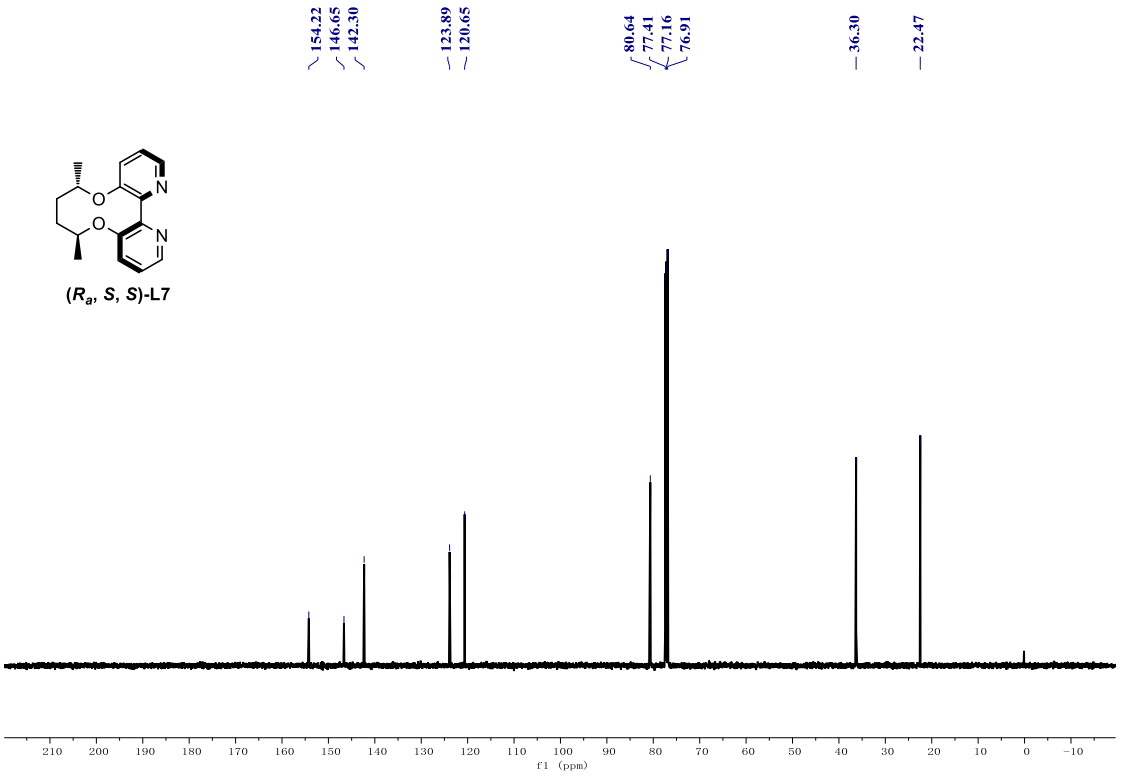


(R_a, *S*, *S*)-L7



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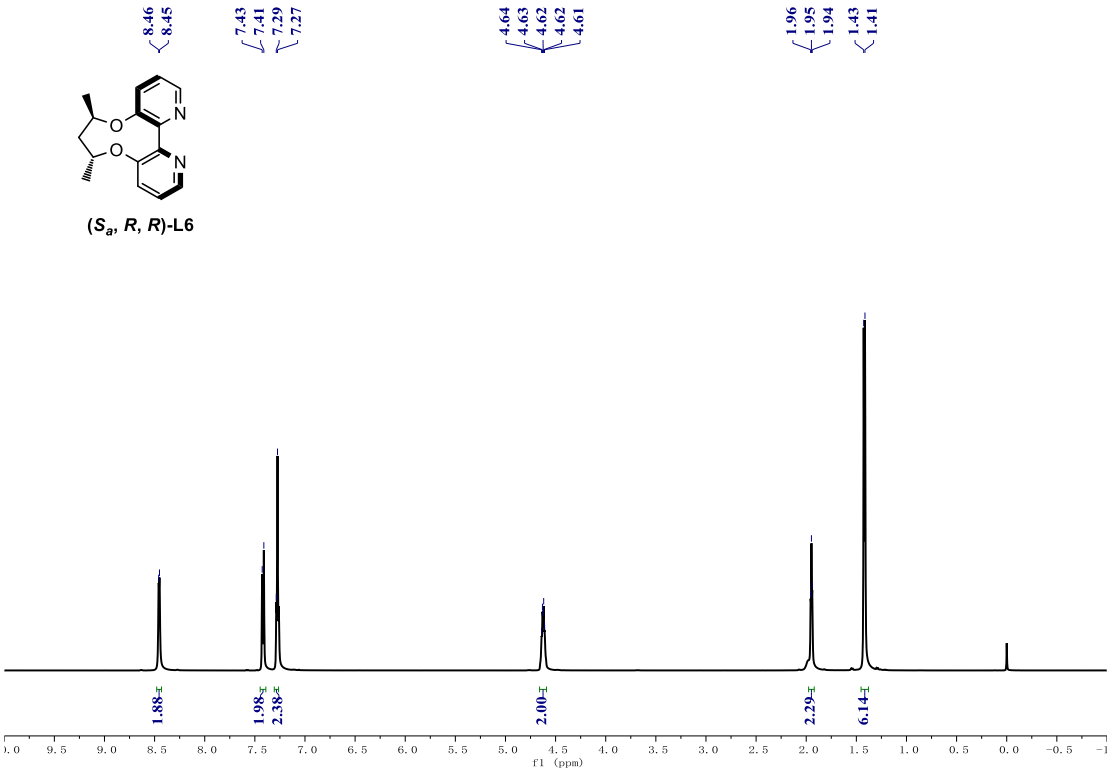

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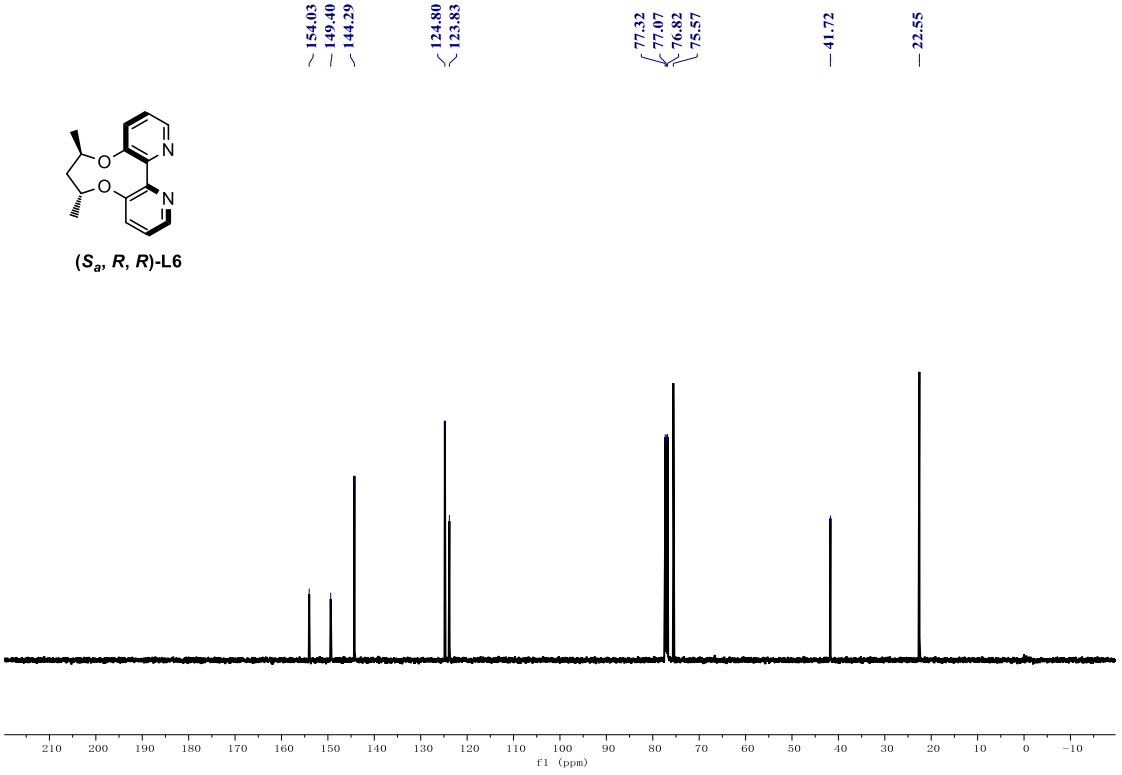

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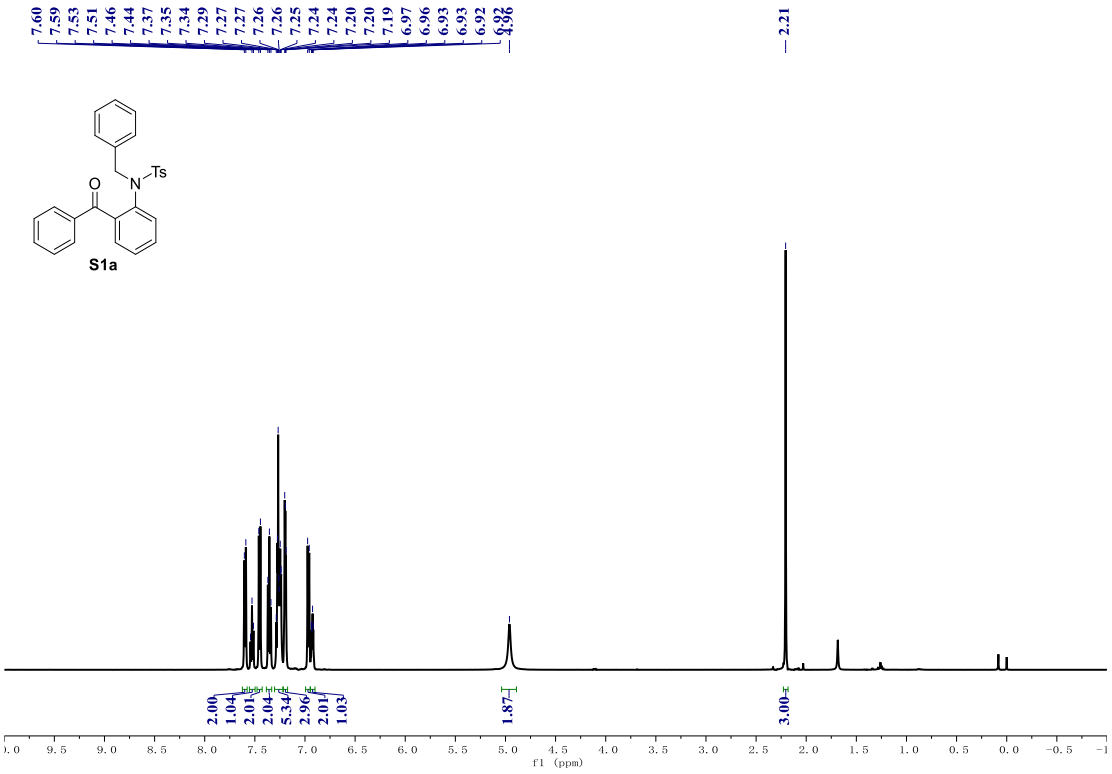
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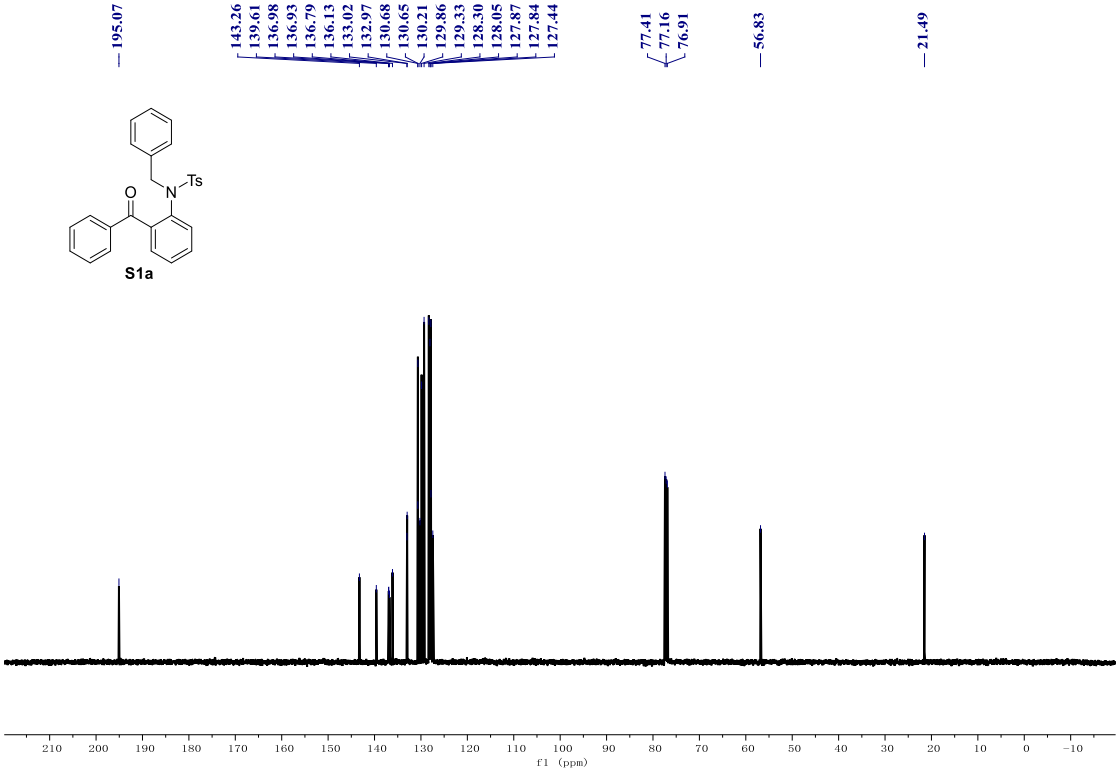
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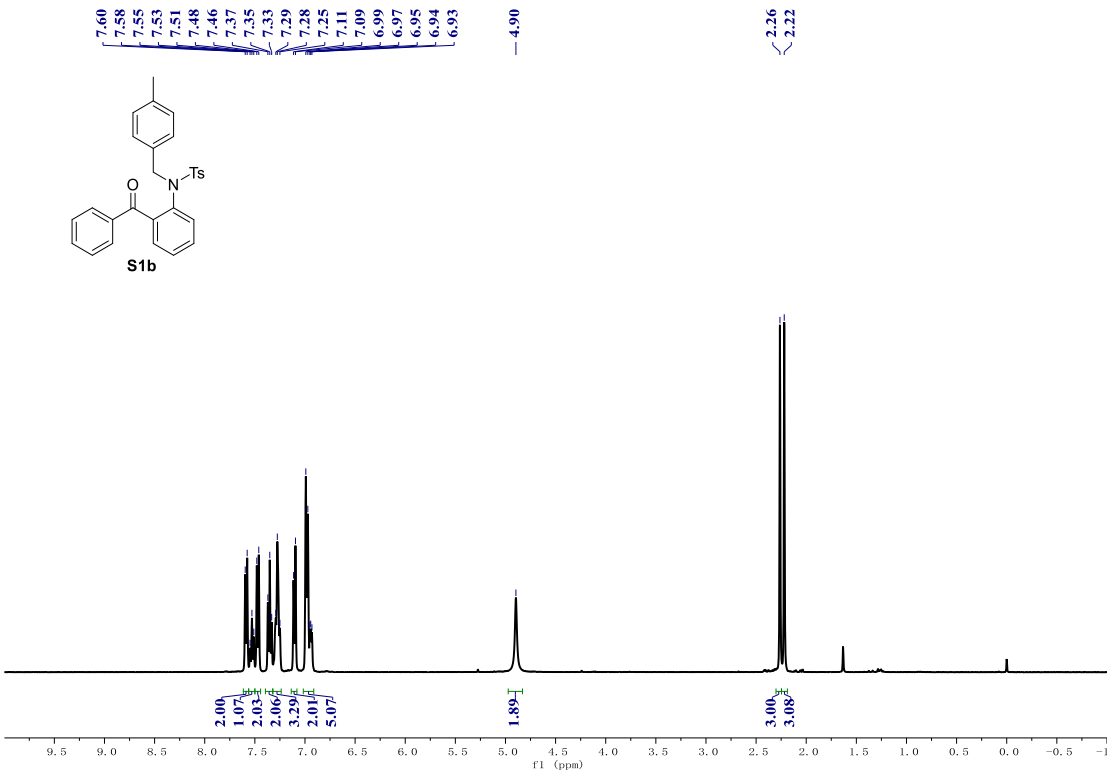
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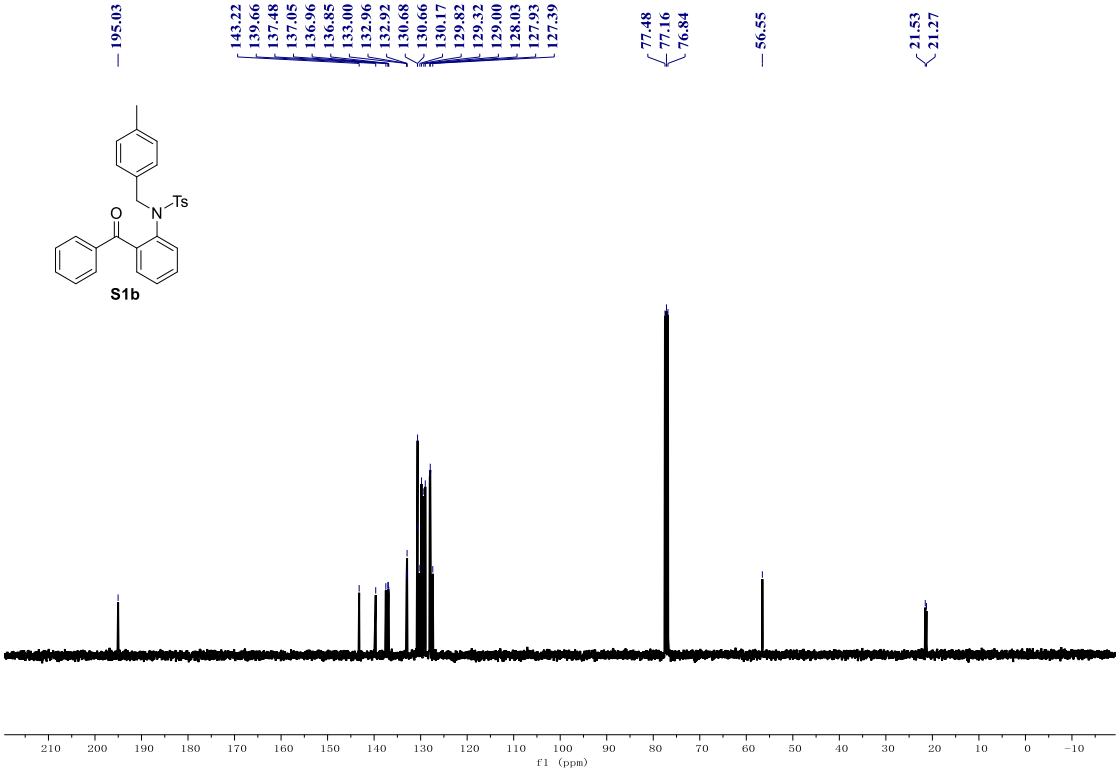
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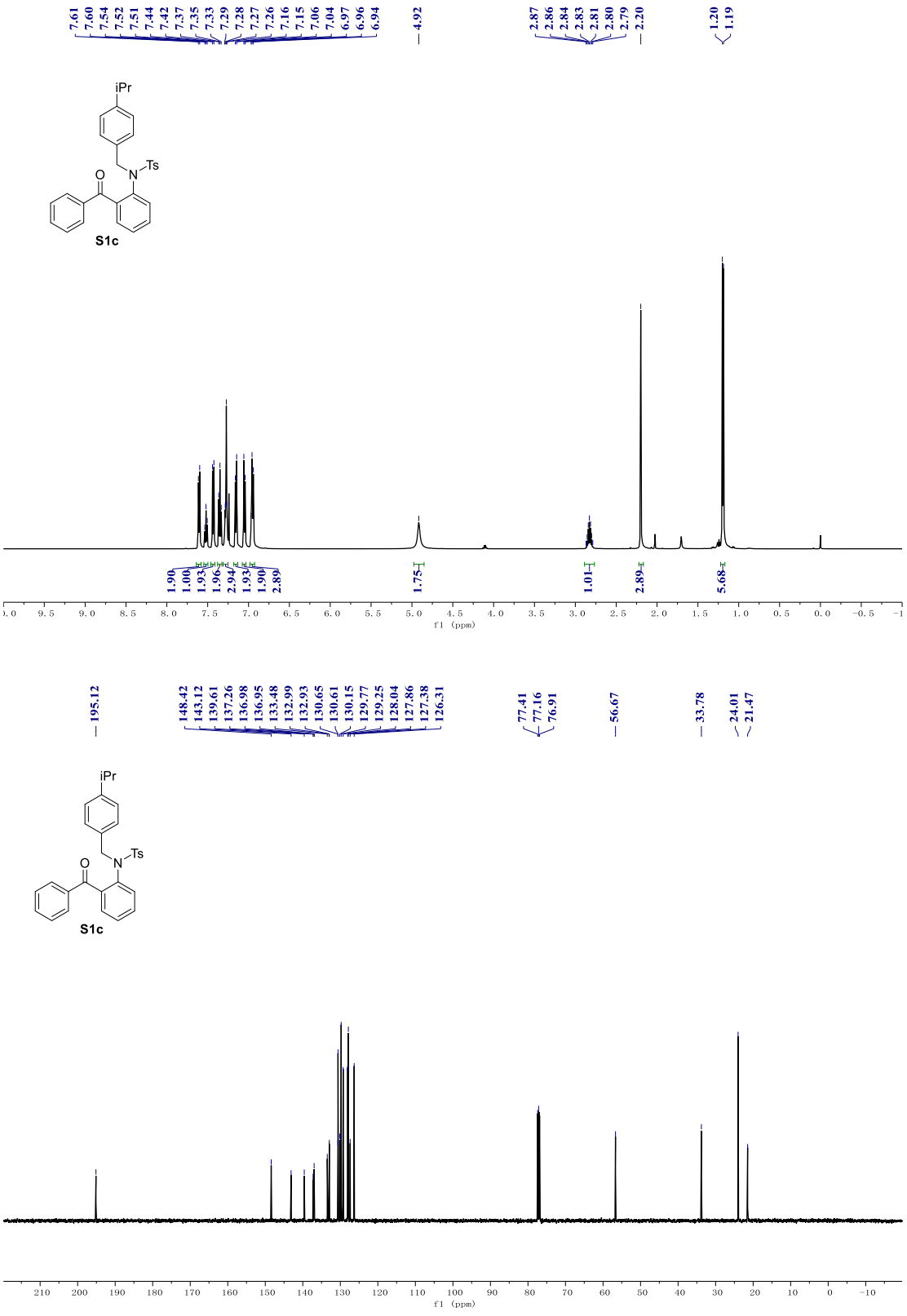
S1b
f1 (ppm)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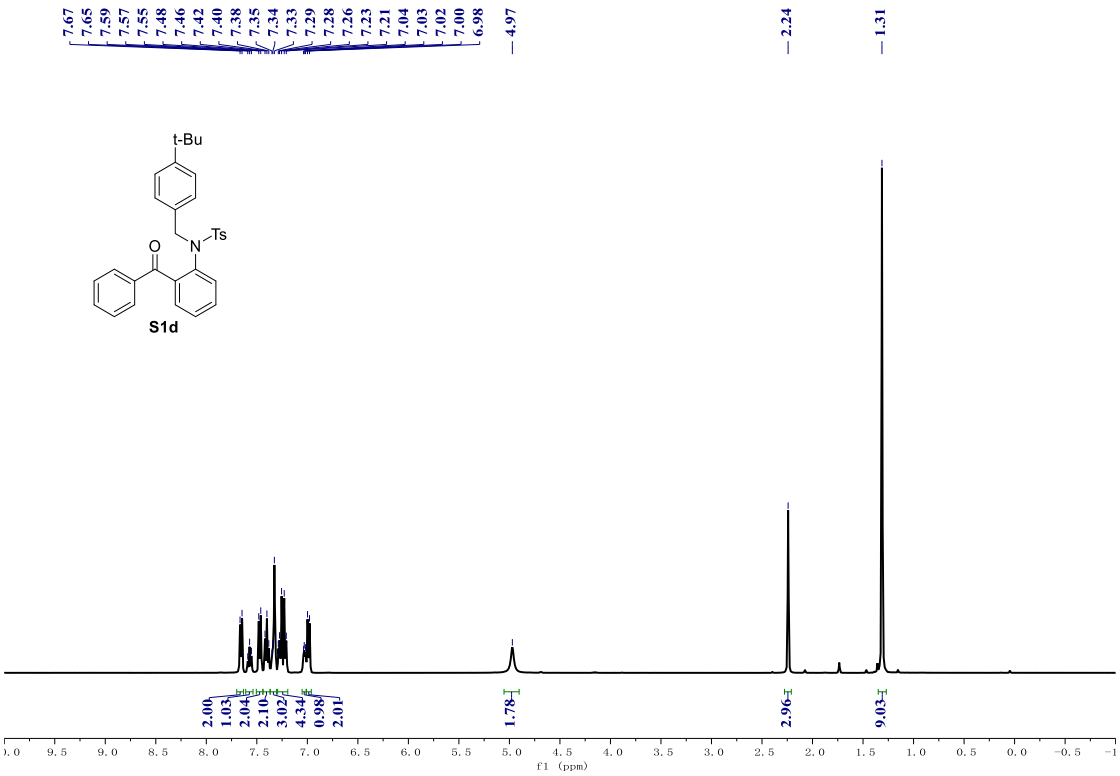
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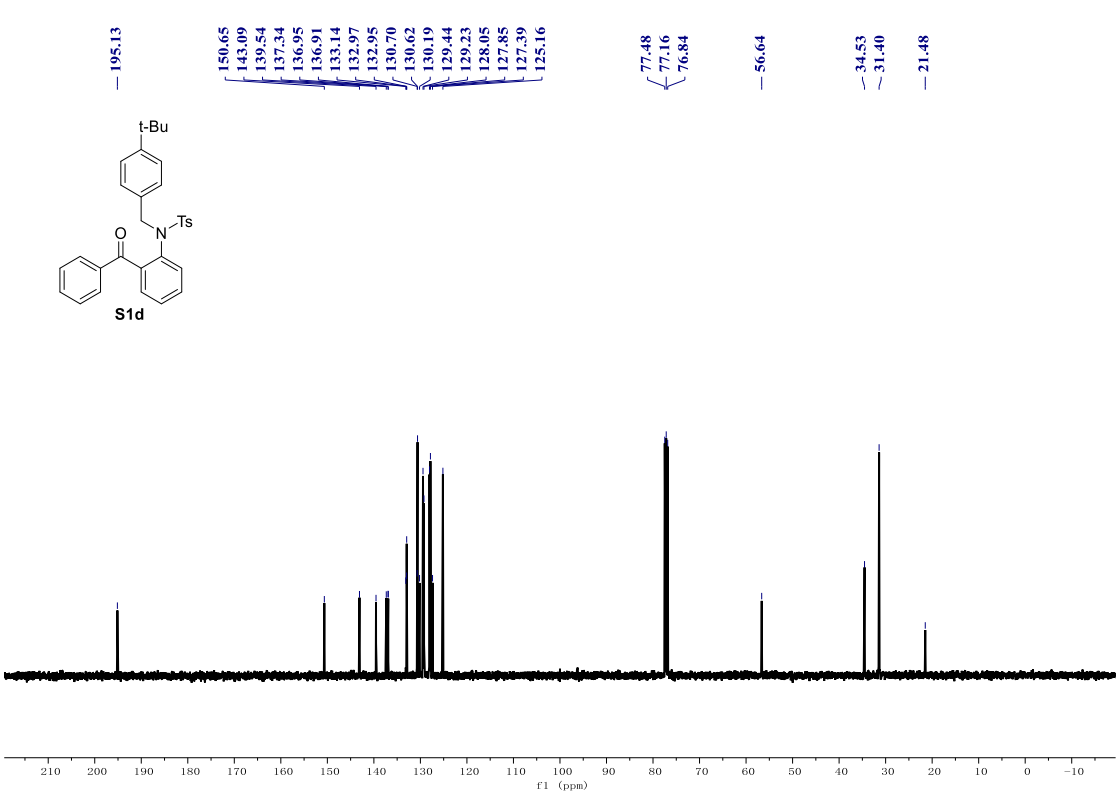
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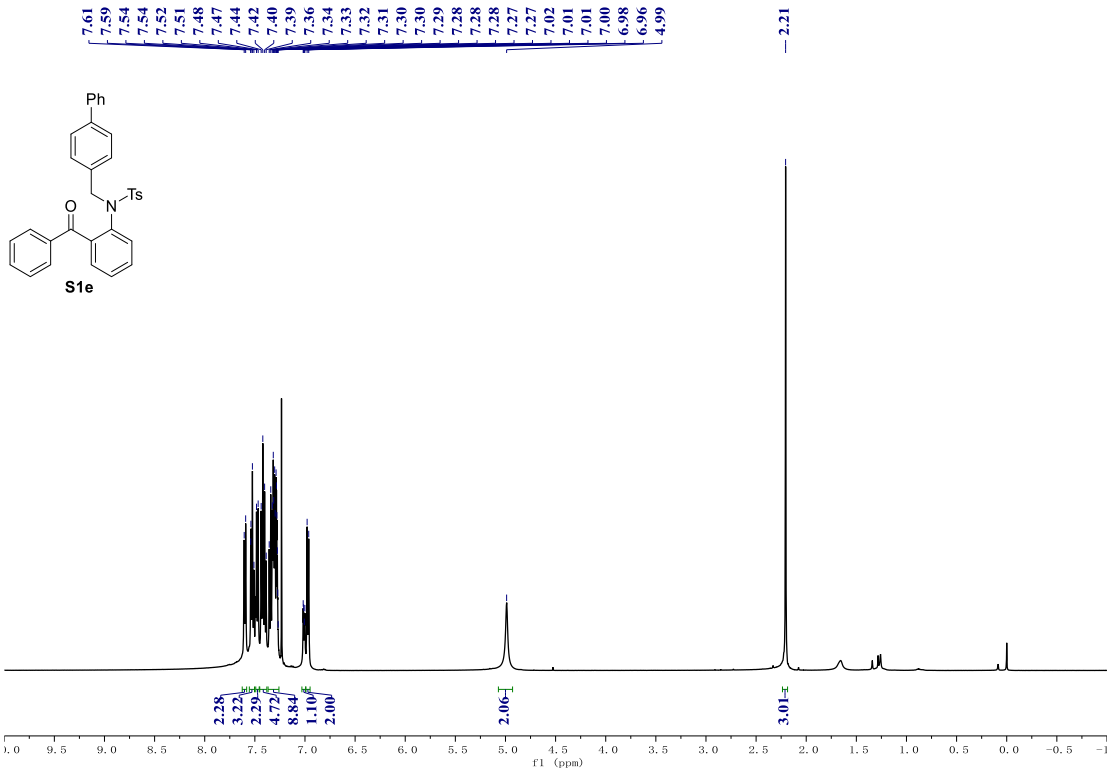
S1d
f1 (ppm)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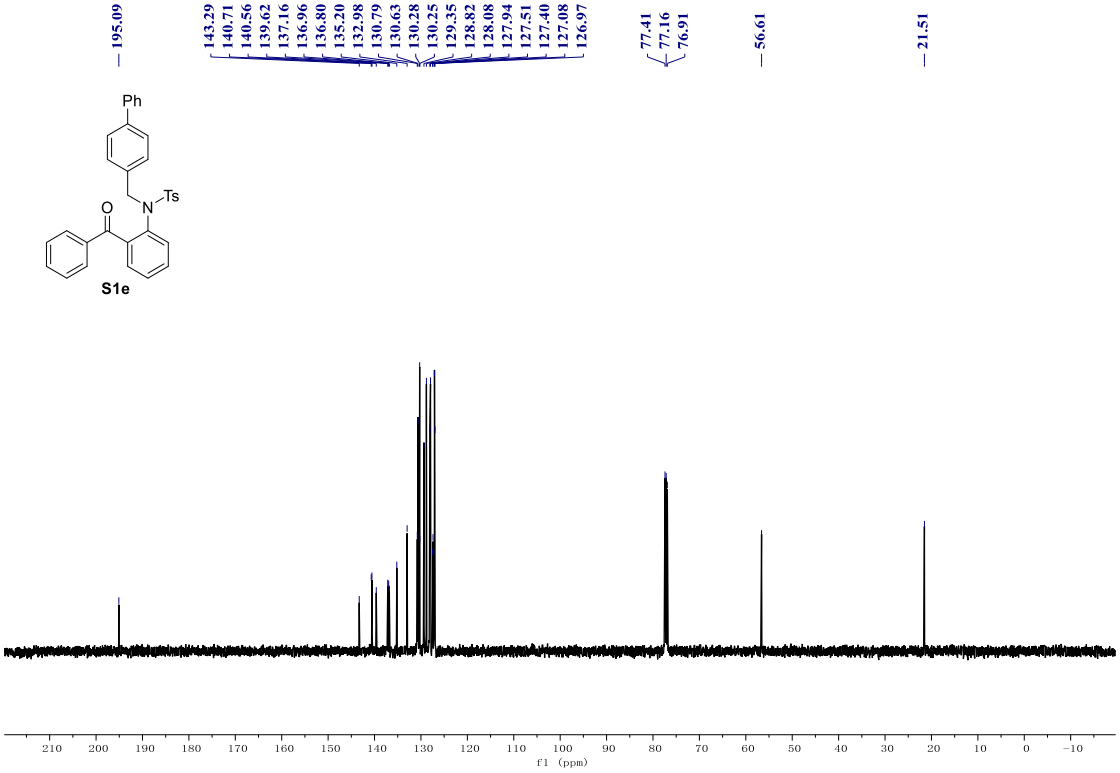
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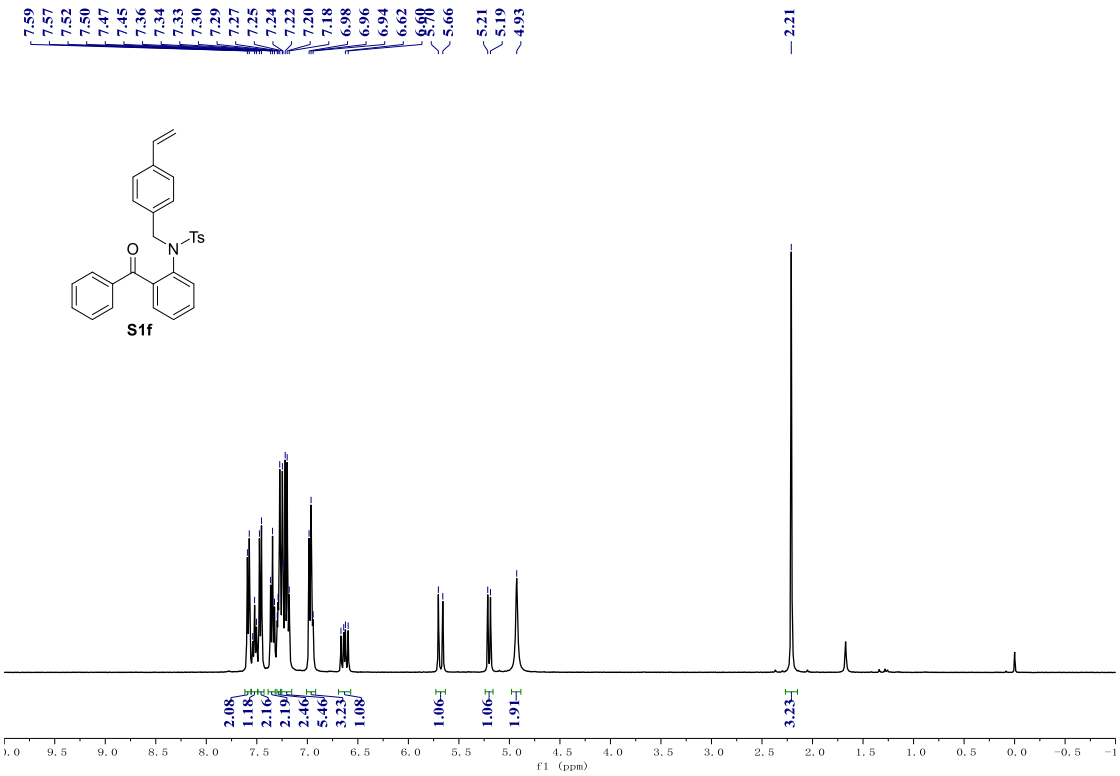
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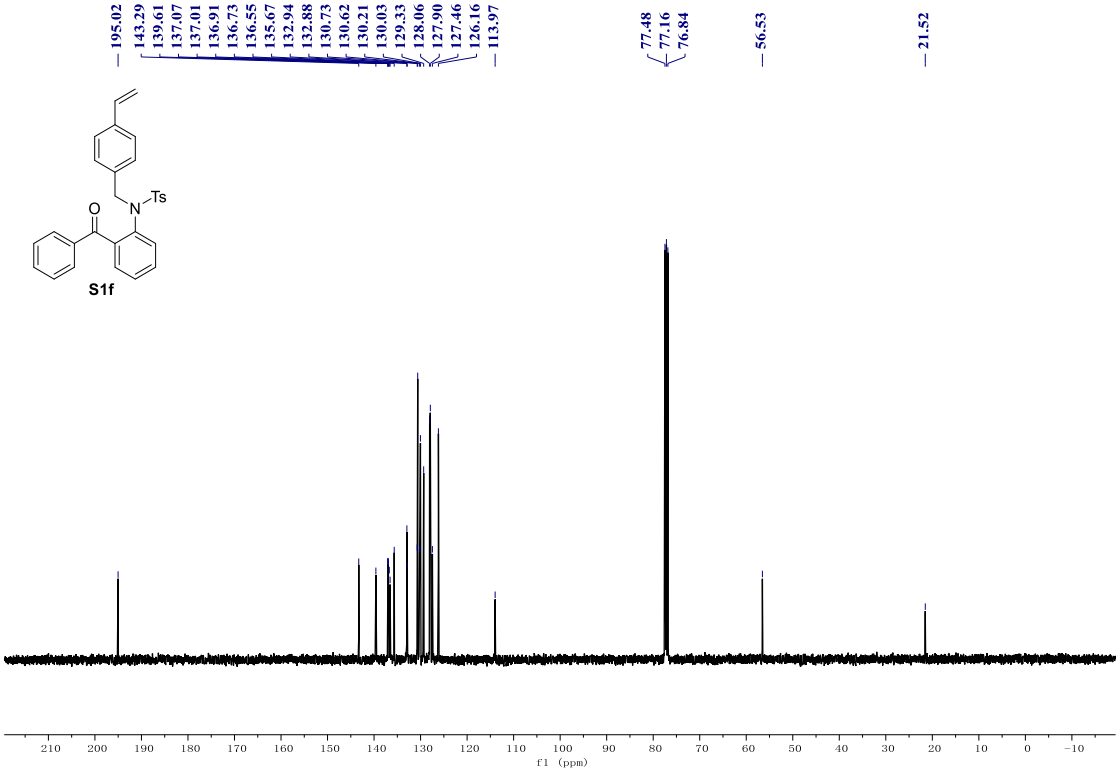
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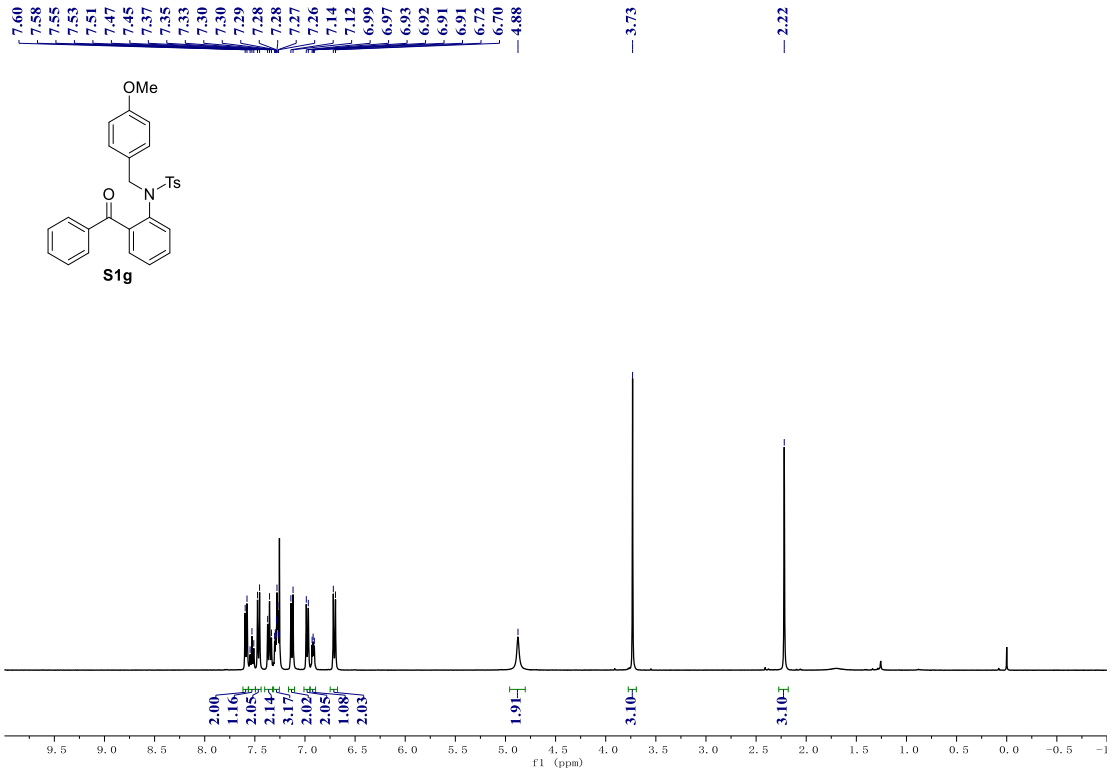
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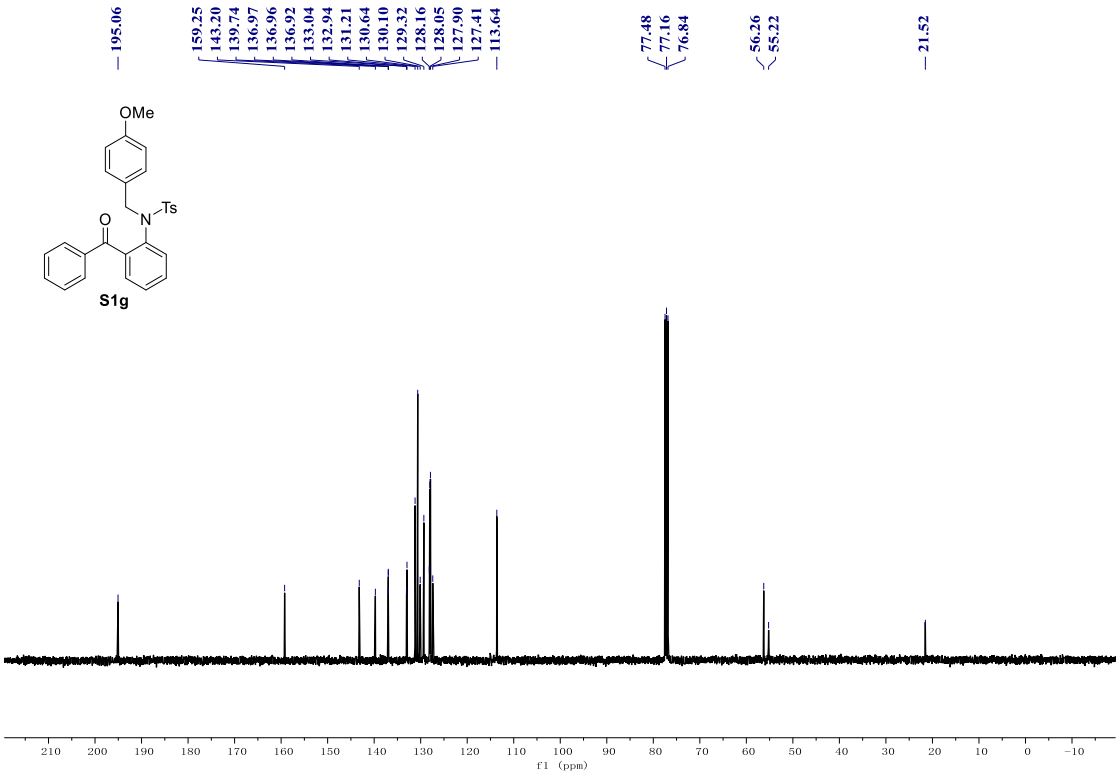
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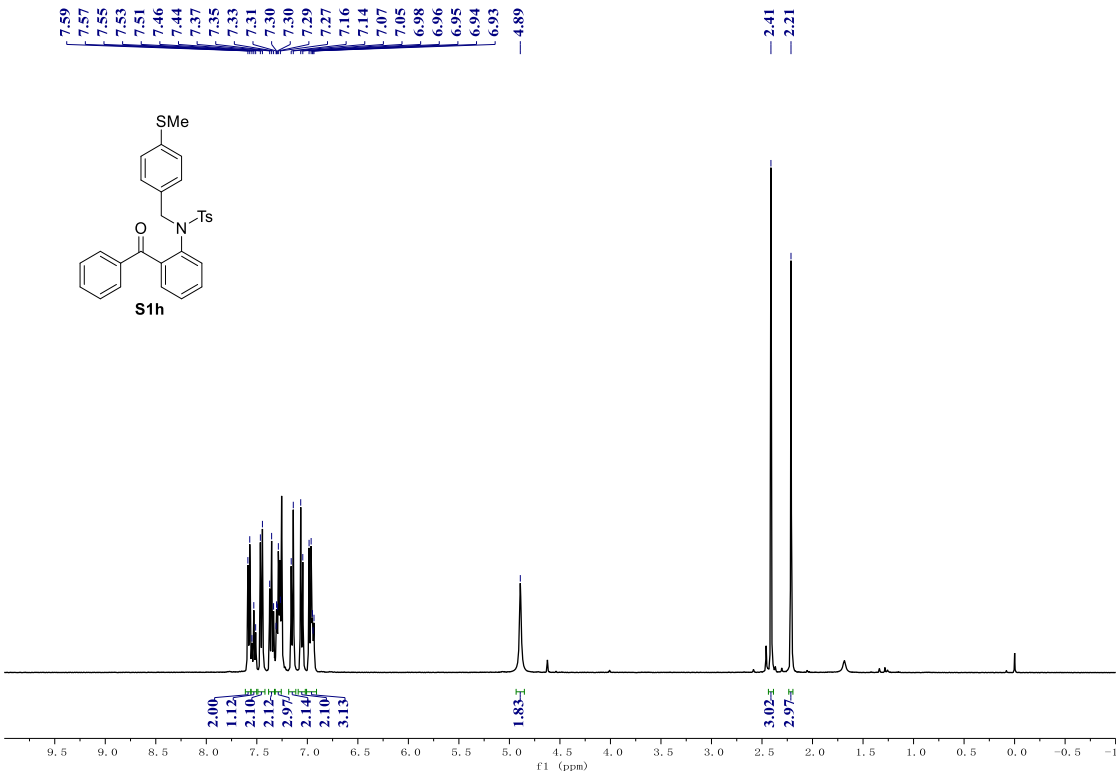
O
S1g
f1 (ppm)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2.21
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Ts
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S1h
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1.12
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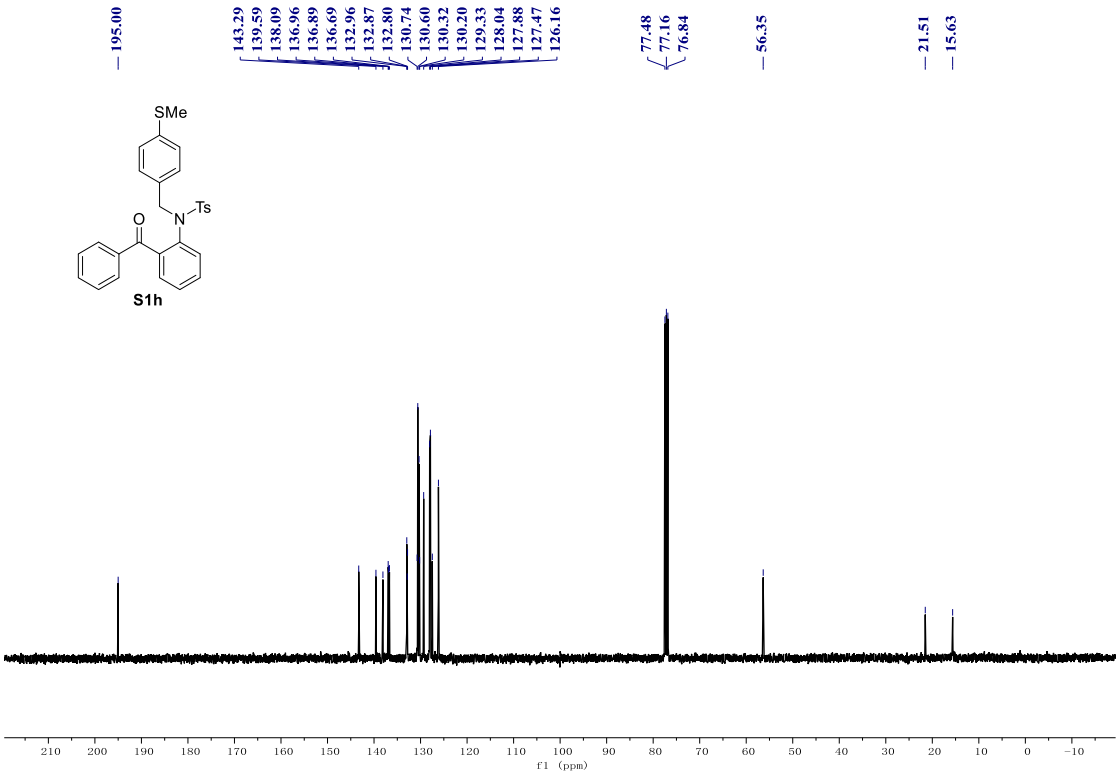
2.97
2.14
2.10
3.13
1.83
3.02
2.97
f1 (ppm)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127.47
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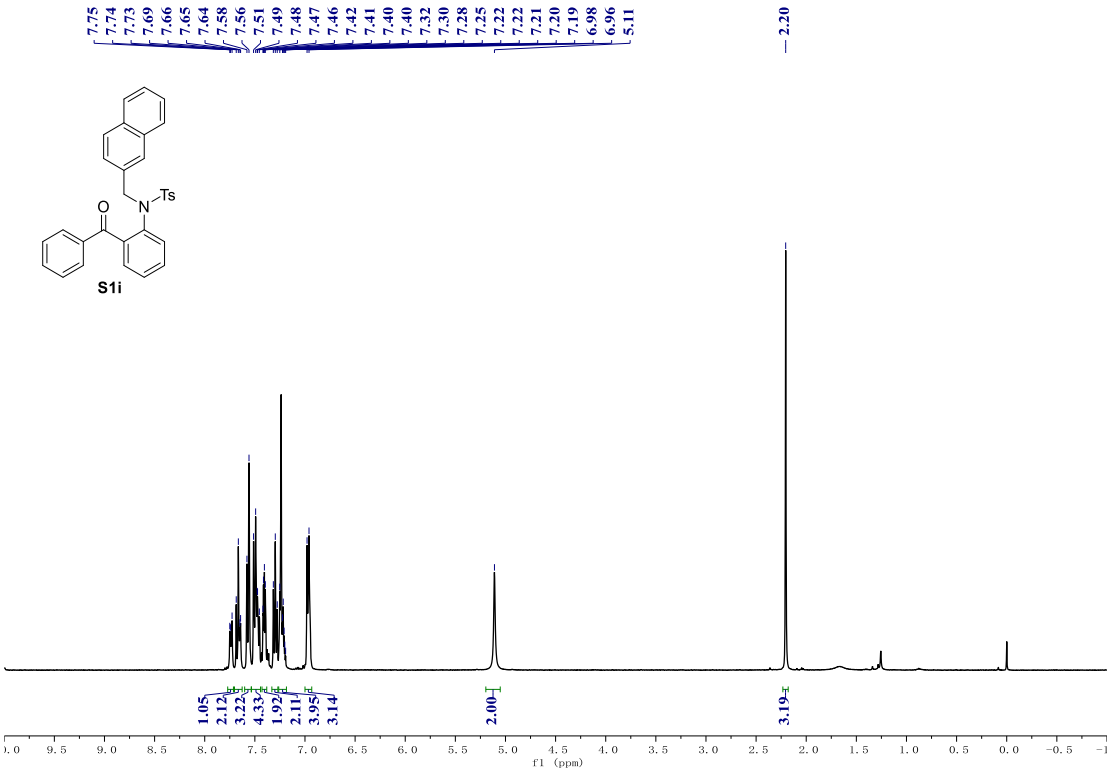
SMe
Ts
N
O
S1h
f1 (ppm)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7.22
7.22
7.21
7.20
7.19
6.98
6.96
5.11
2.20
Ts
N
O
S1i
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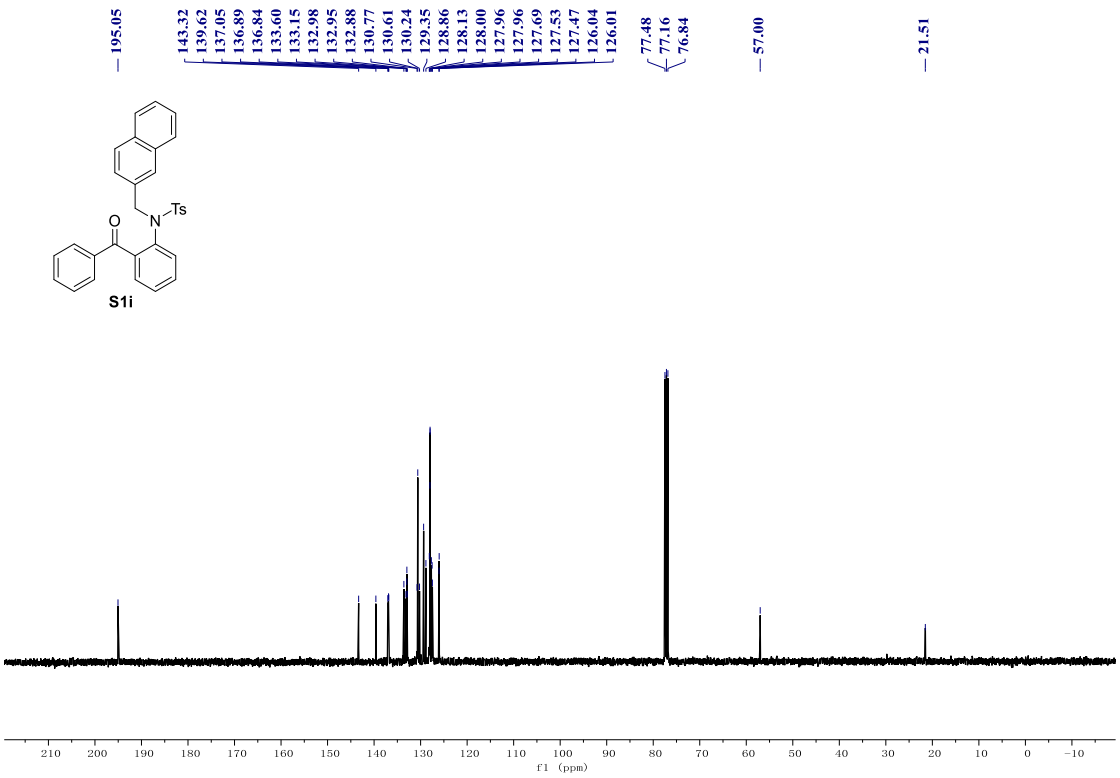
3.14
2.00
3.19
f1 (ppm)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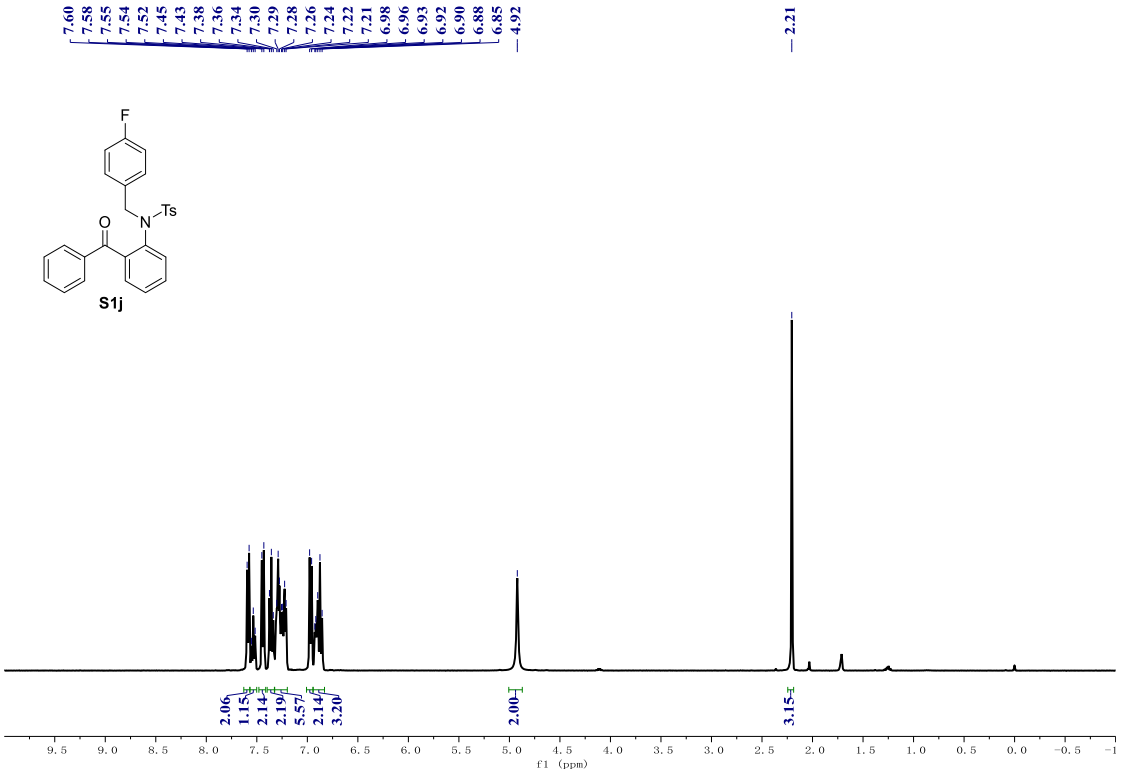
Ts
N
O
S1i
f1 (ppm)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7.21
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6.96
6.93
6.92
6.90
6.88
6.85
4.92
2.21
F
Ts
N
O
S1j
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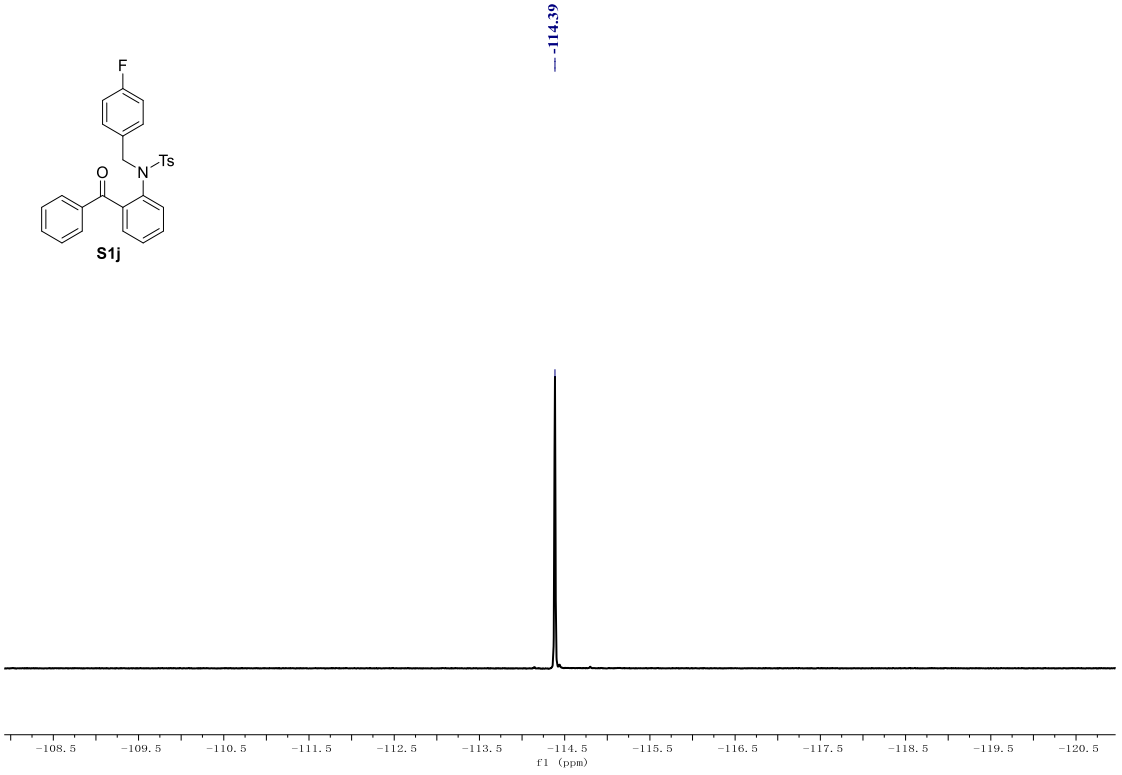
2.14
2.19
5.57
2.14
3.20
2.00
3.15
f1 (ppm)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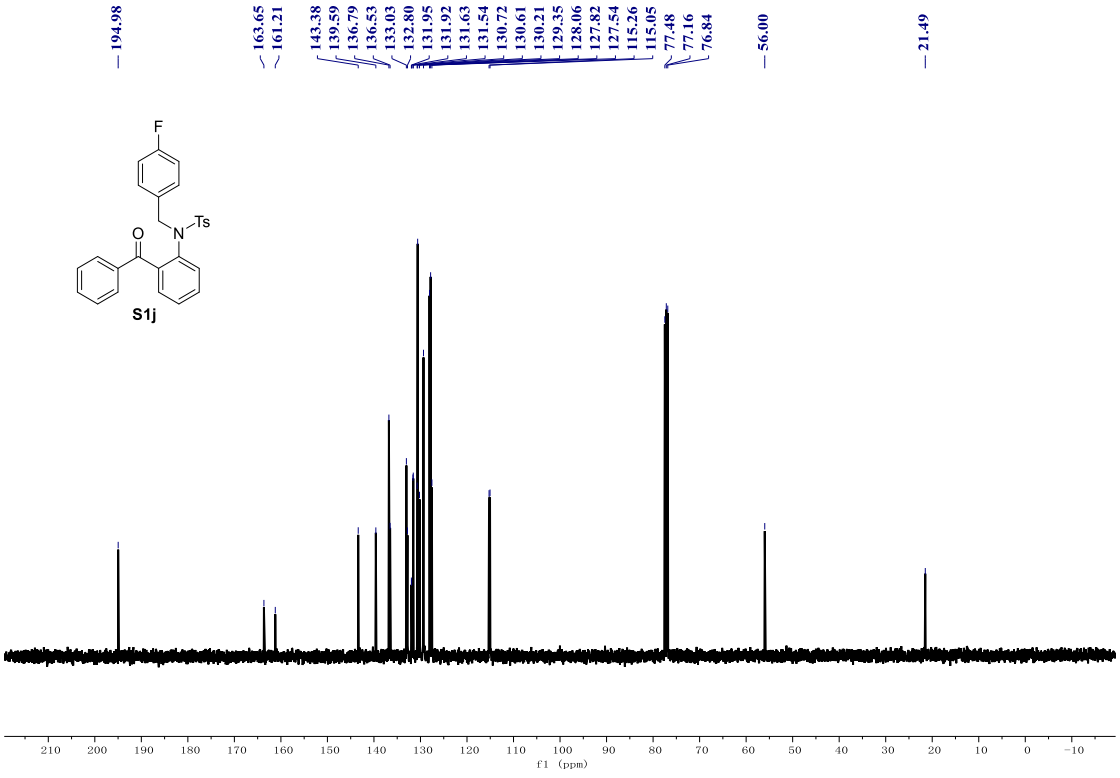
S1j
f1 (ppm)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115.05
77.48
77.16
76.84
56.00
21.49
F
Ts
N
O
S1j
210
200
190
180
170
160
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140
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100
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80
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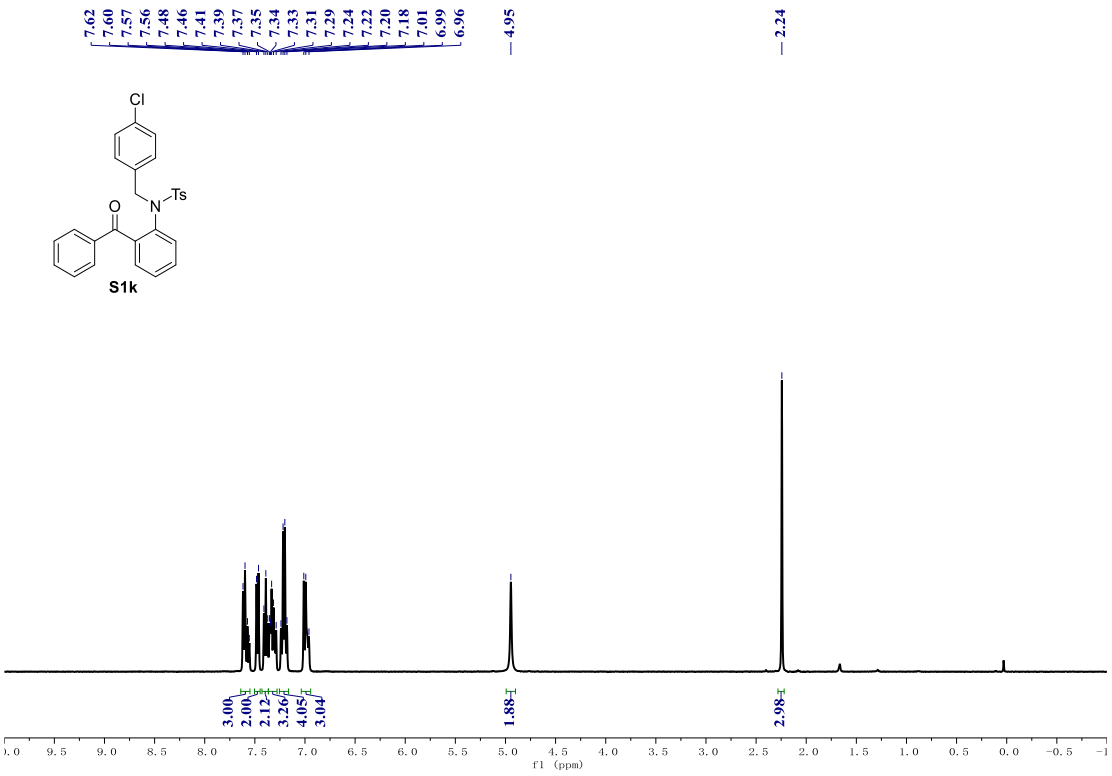
f1 (ppm)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7.29
7.24
7.22
7.20
7.18
7.01
6.99
6.96
4.95
2.24
Cl
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4.05
3.04
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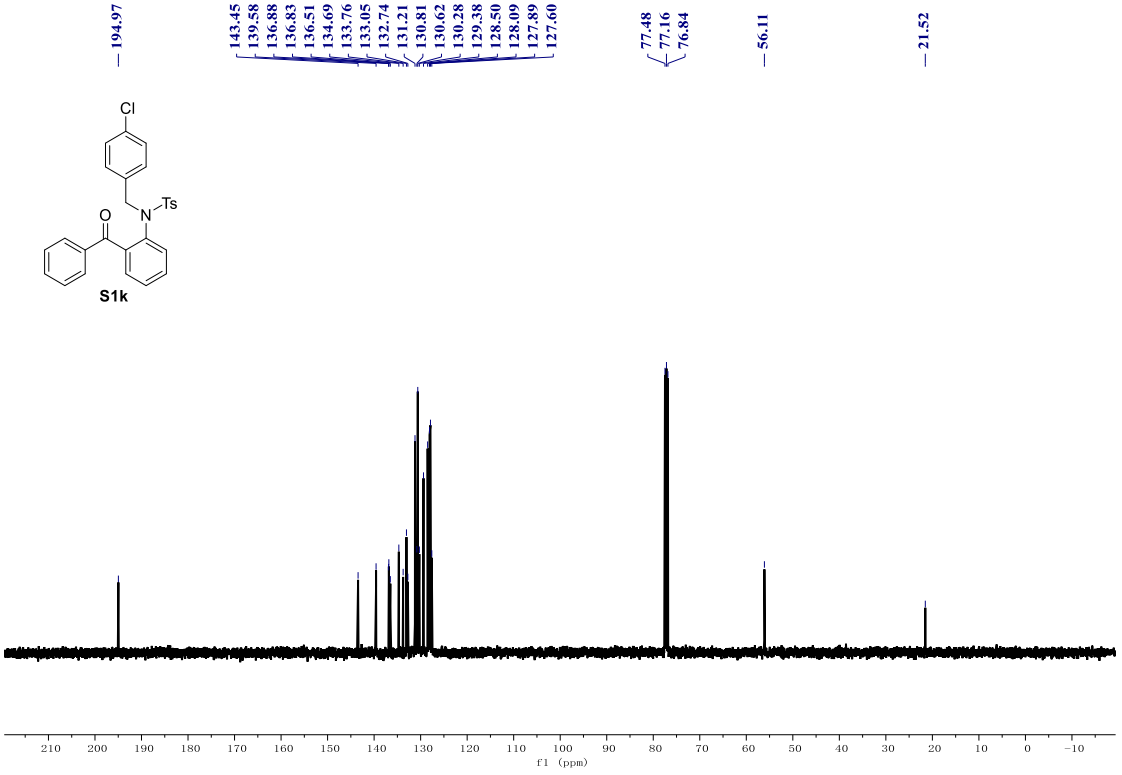
2.98
f1 (ppm)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129.38
128.50
128.09
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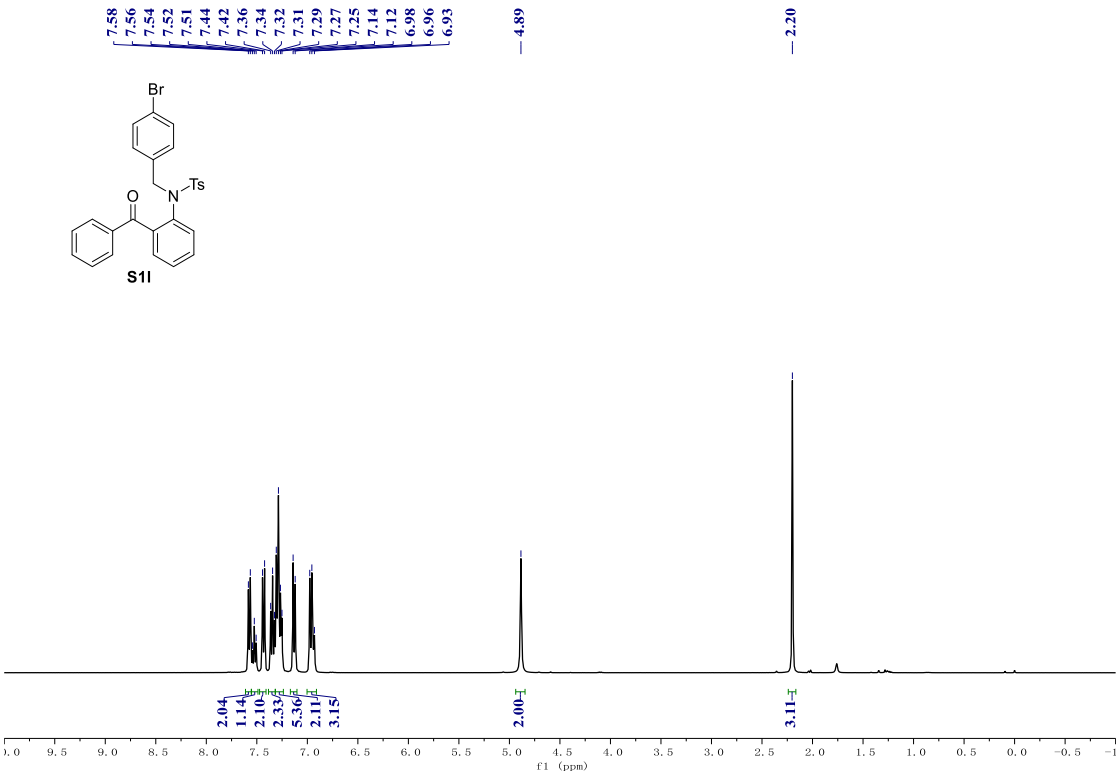
77.16
76.84
56.11
21.52
Cl
Ts
N
O
S1k
f1 (ppm)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7.14
7.12
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6.96
6.93
4.89
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Br
Ts
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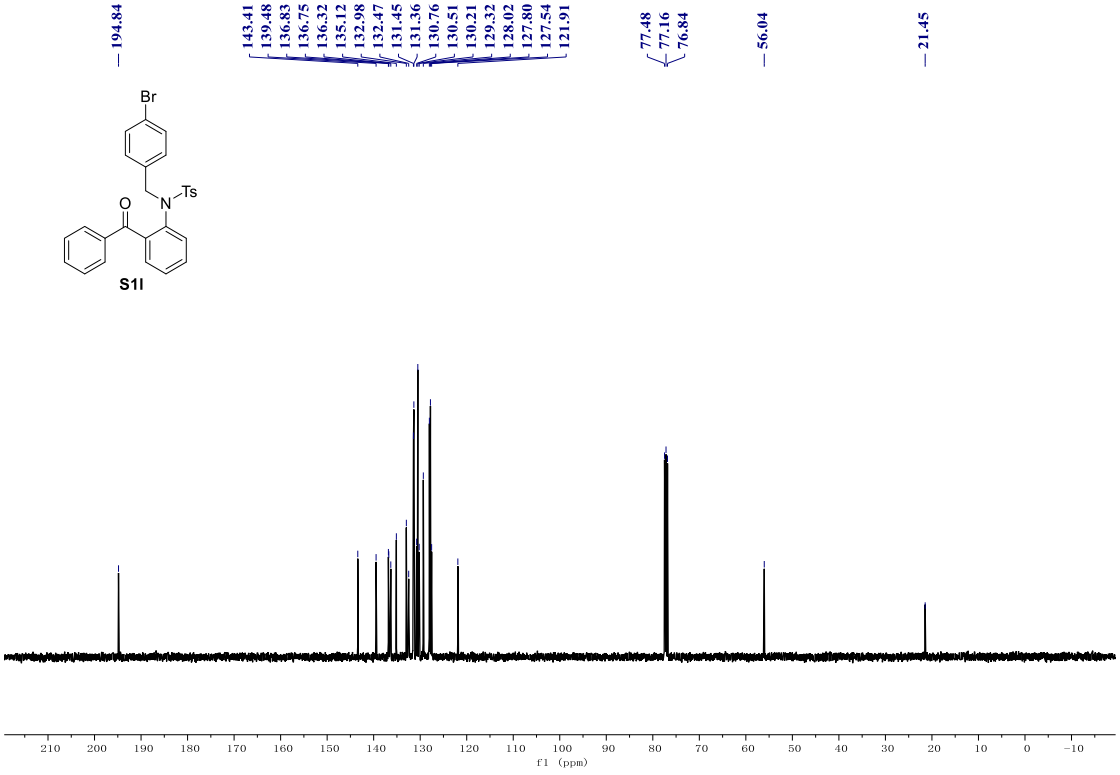
5.36
2.11
3.15
2.00
3.11
f1 (ppm)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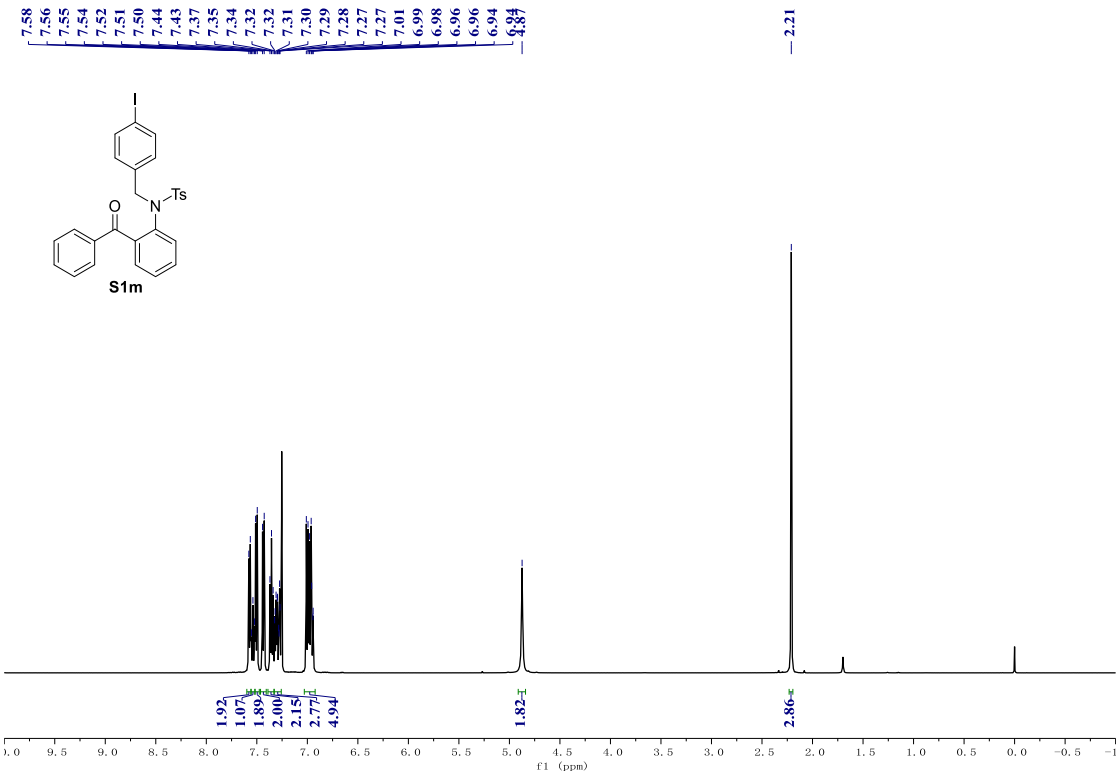
56.04
21.45
Br
Ts
N
O
S1l
f1 (ppm)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7.27
7.01
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6.98
6.96
6.96
6.94
6.94
4.87
2.21
I
O
N
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4.94
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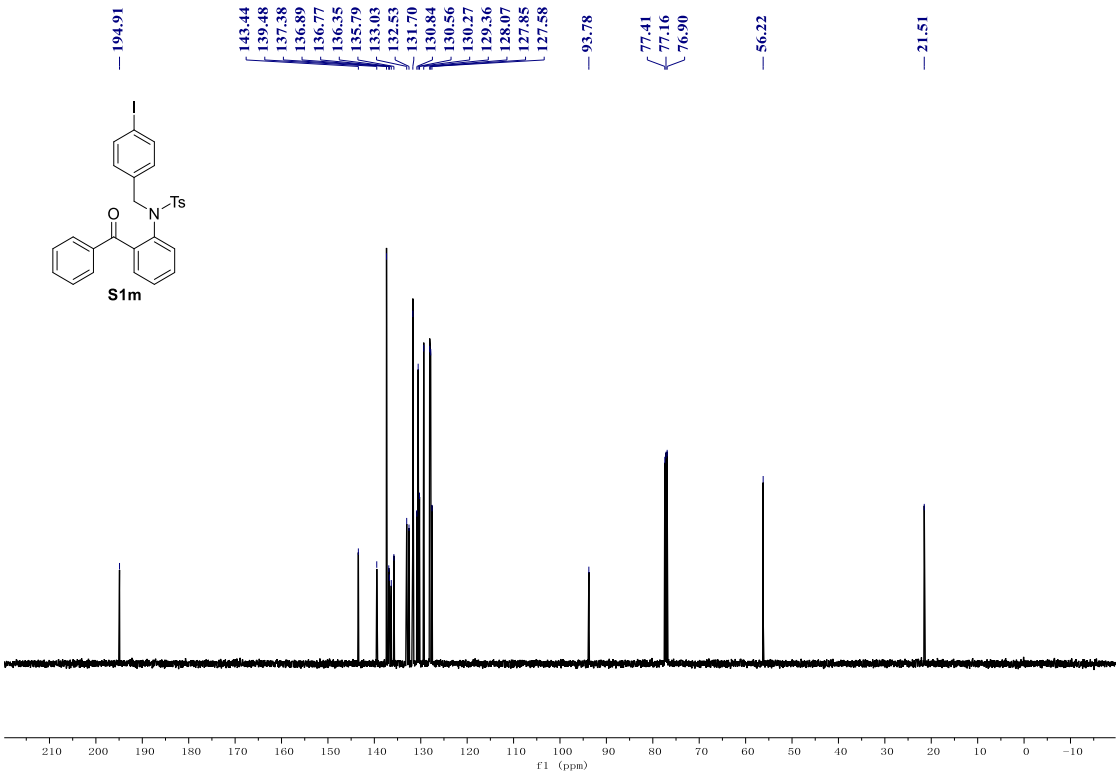
2.86
f1 (ppm)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129.36
128.07
127.85
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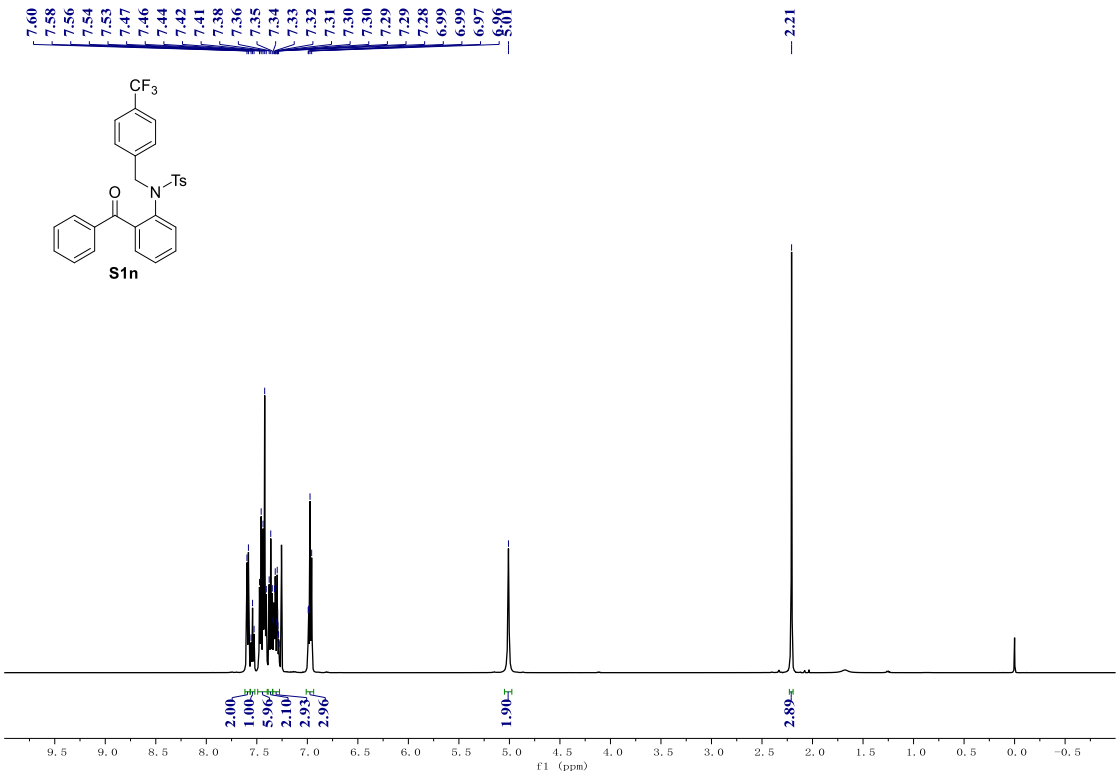
77.16
76.90
56.22
21.51
I
O
N
Ts
S1m
f1 (ppm)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7.30
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7.28
6.99
6.99
6.97
6.96
5.01
2.21
CF3
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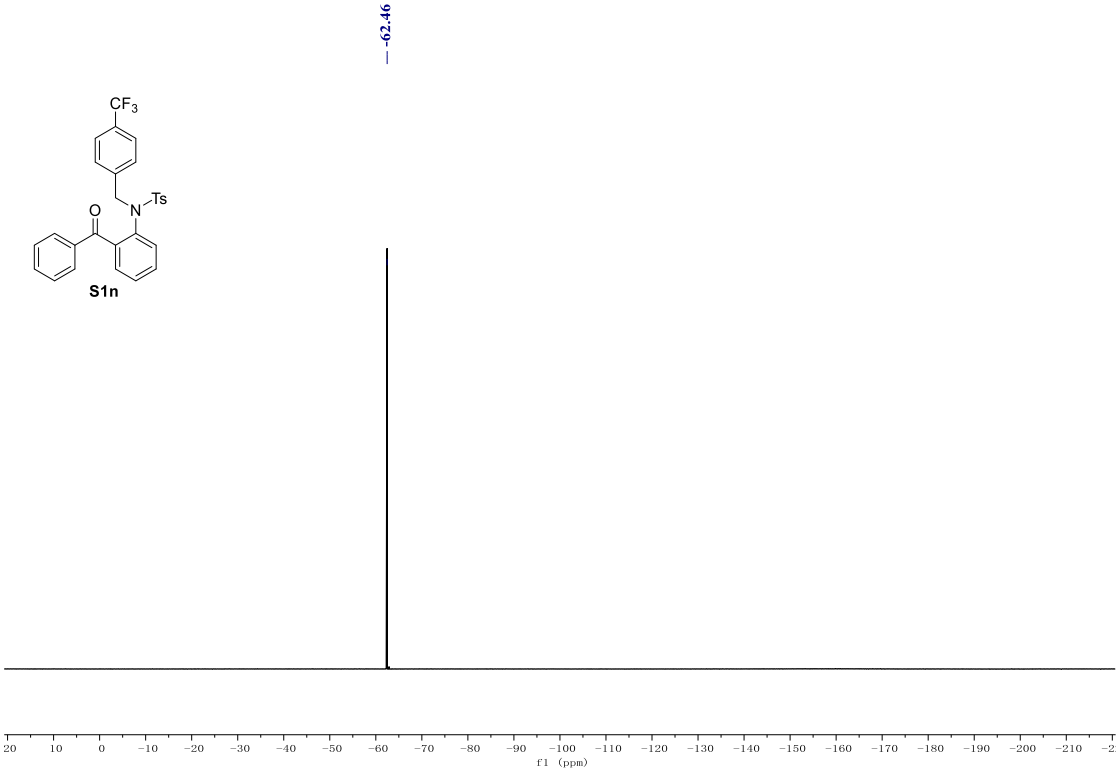
2.96
1.90
2.89
f1 (ppm)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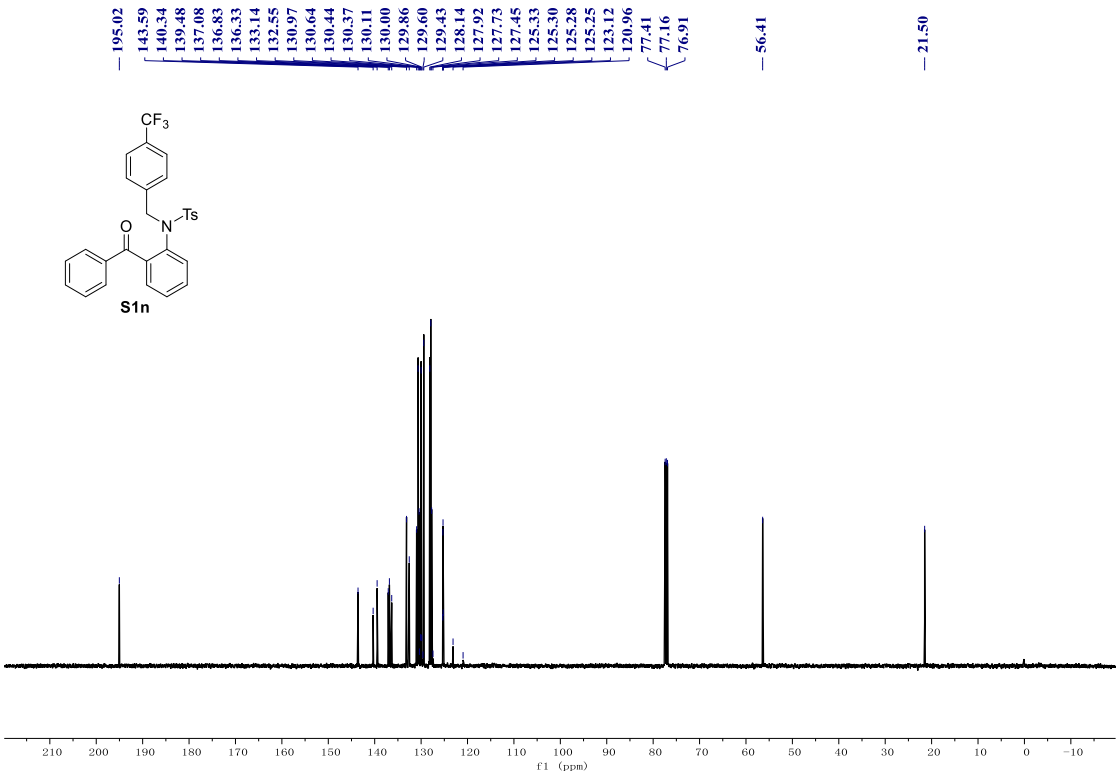
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76.91
56.41
21.50
CF3
O
N
Ts
S1n
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200
190
180
170
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100
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40
30
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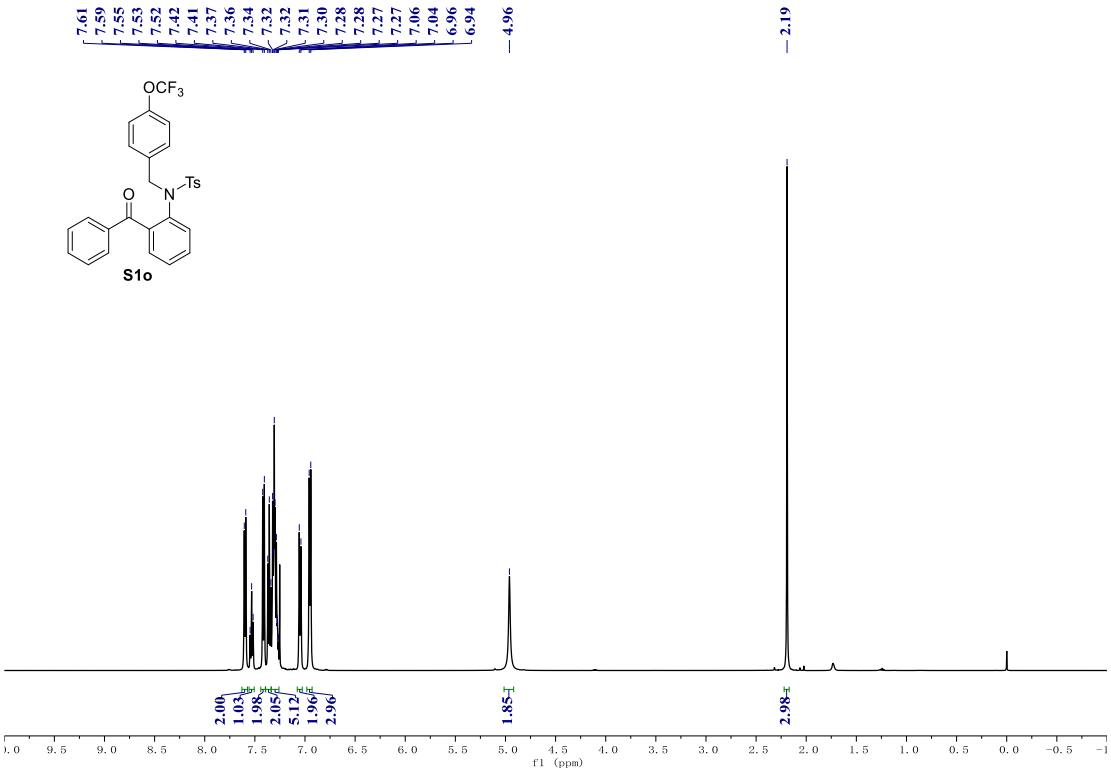
−10
f1 (ppm)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7.27
7.06
7.04
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6.94
4.96
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OCF3
N
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2.05
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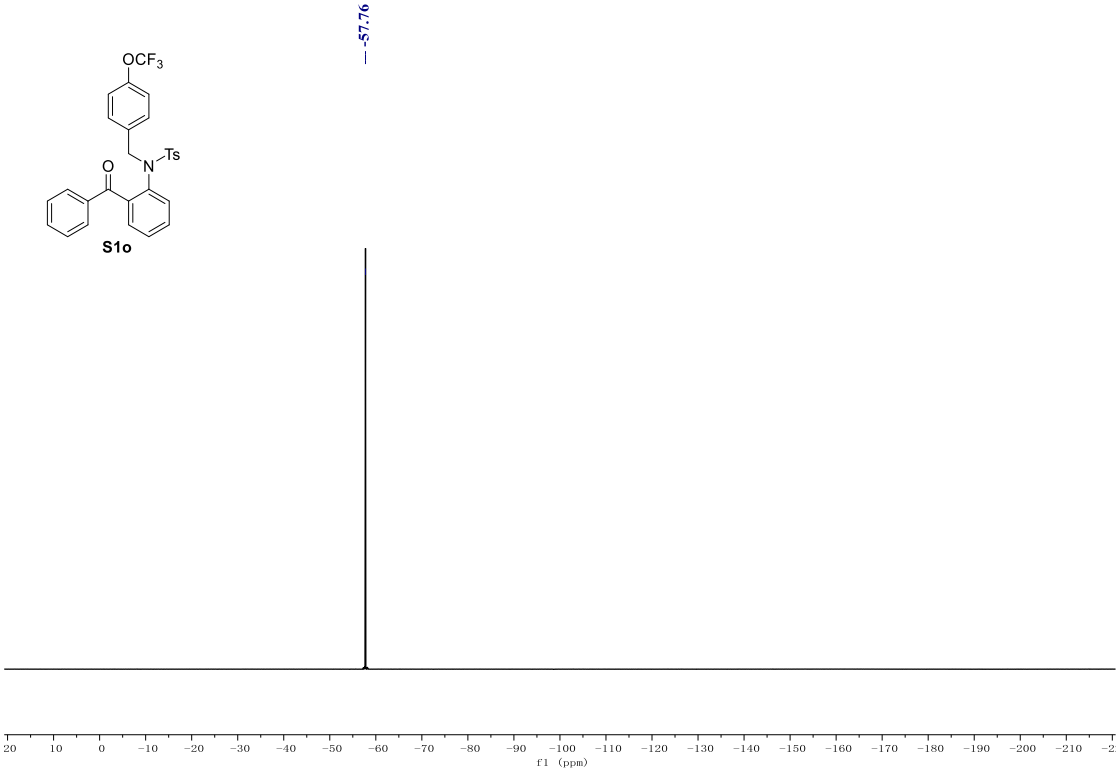
2.96
1.85
2.98
f1 (ppm)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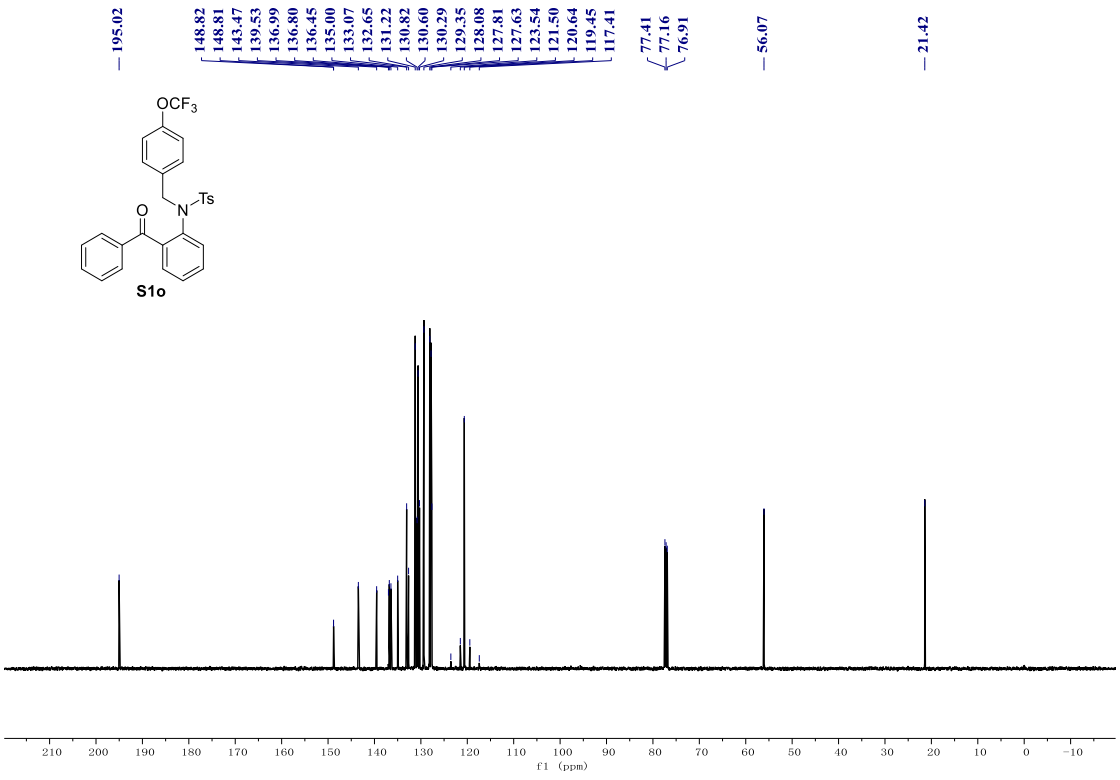
S1o
f1 (ppm)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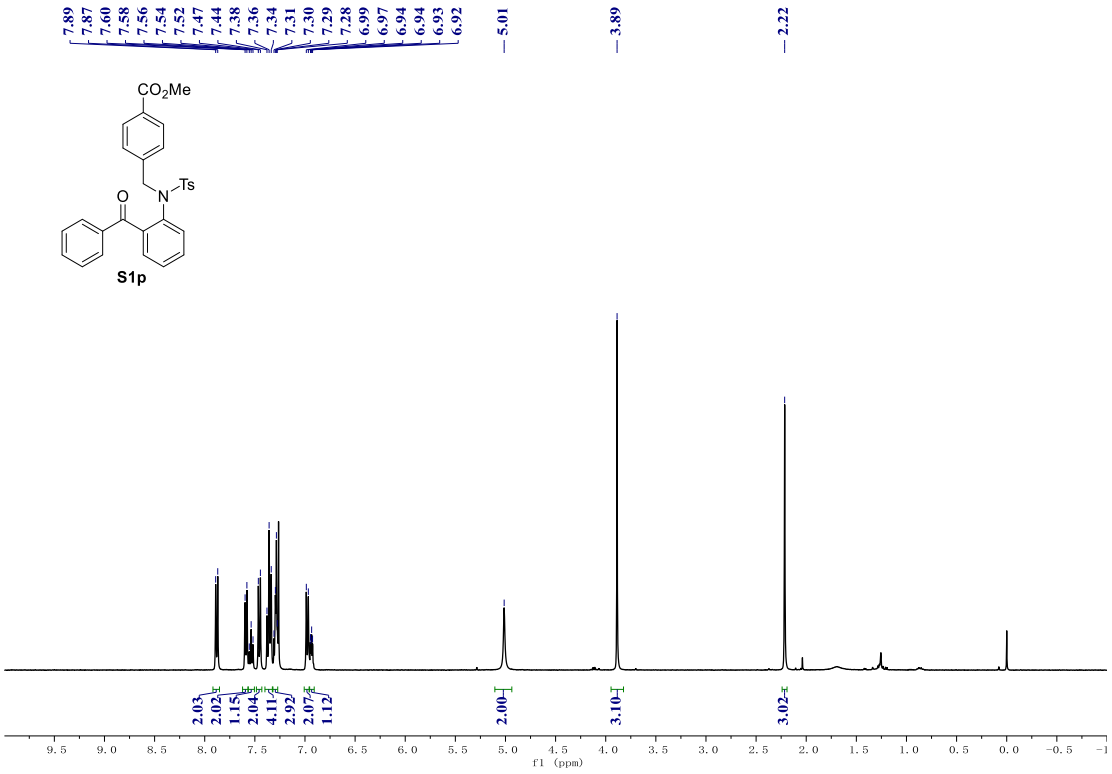
OCF3
N
Ts
O
S1o
f1 (ppm)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6.97
6.94
6.94
6.93
6.92
5.01
3.89
2.22
CO2Me
N
Ts
O
S1p
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2.02
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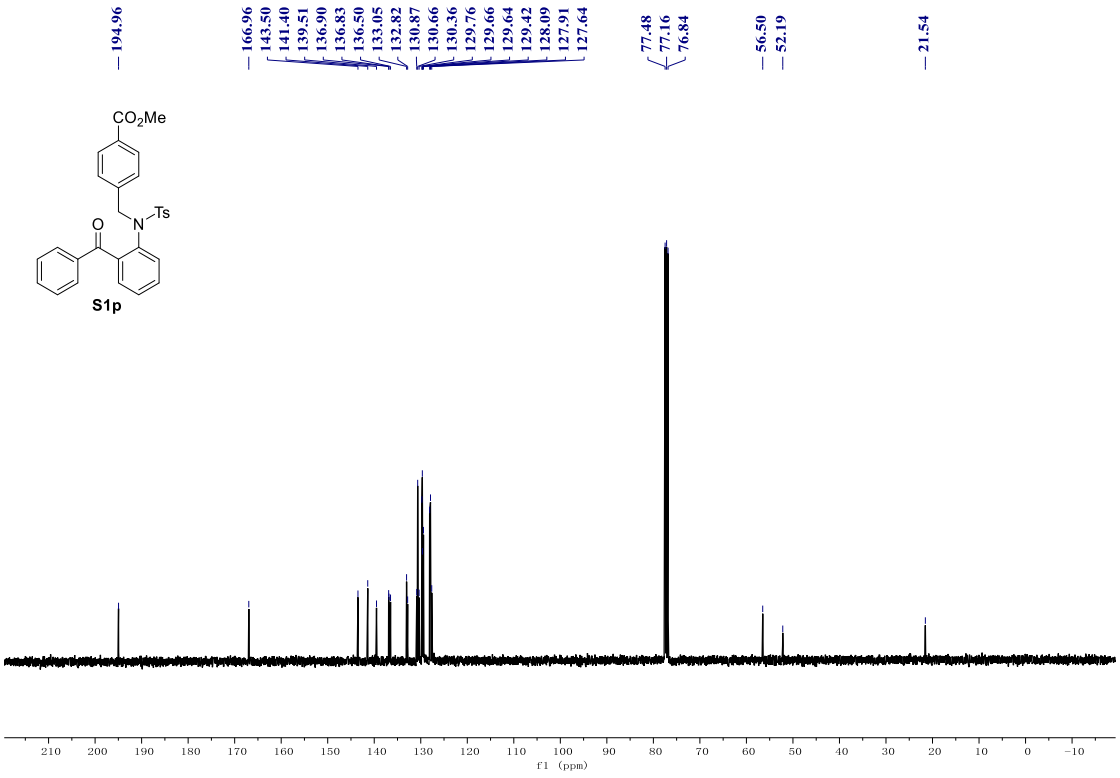
2.04
4.11
2.92
2.07
1.12
2.00
3.10
3.02
f1 (ppm)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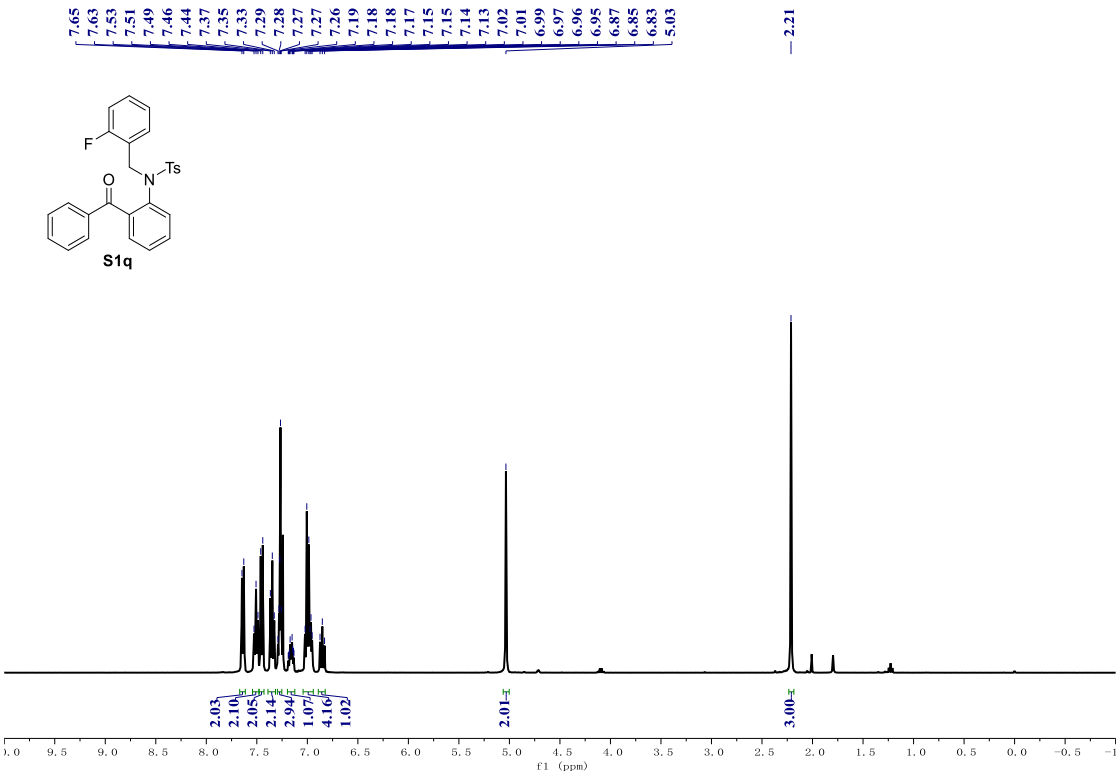
52.19
21.54
CO2Me
N
Ts
O
S1p
f1 (ppm)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6.97
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6.85
6.83
5.03
2.21
F
O
N
Ts
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2.94
1.07
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1.02
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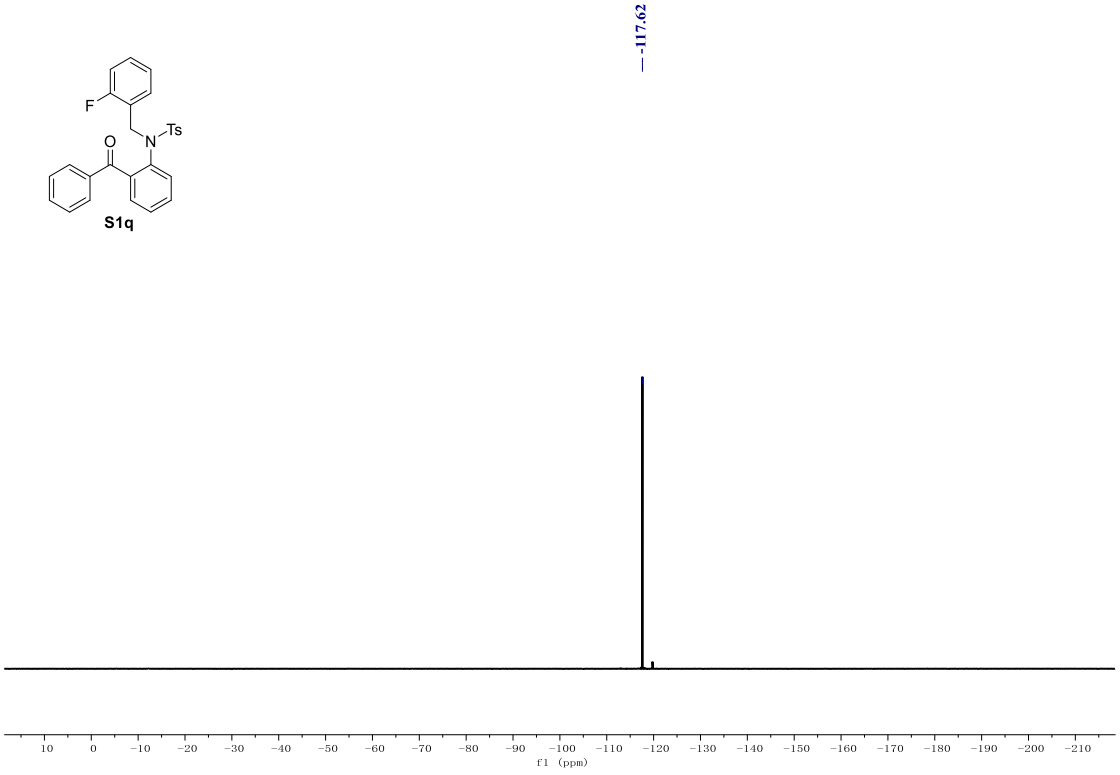
3.00
f1 (ppm)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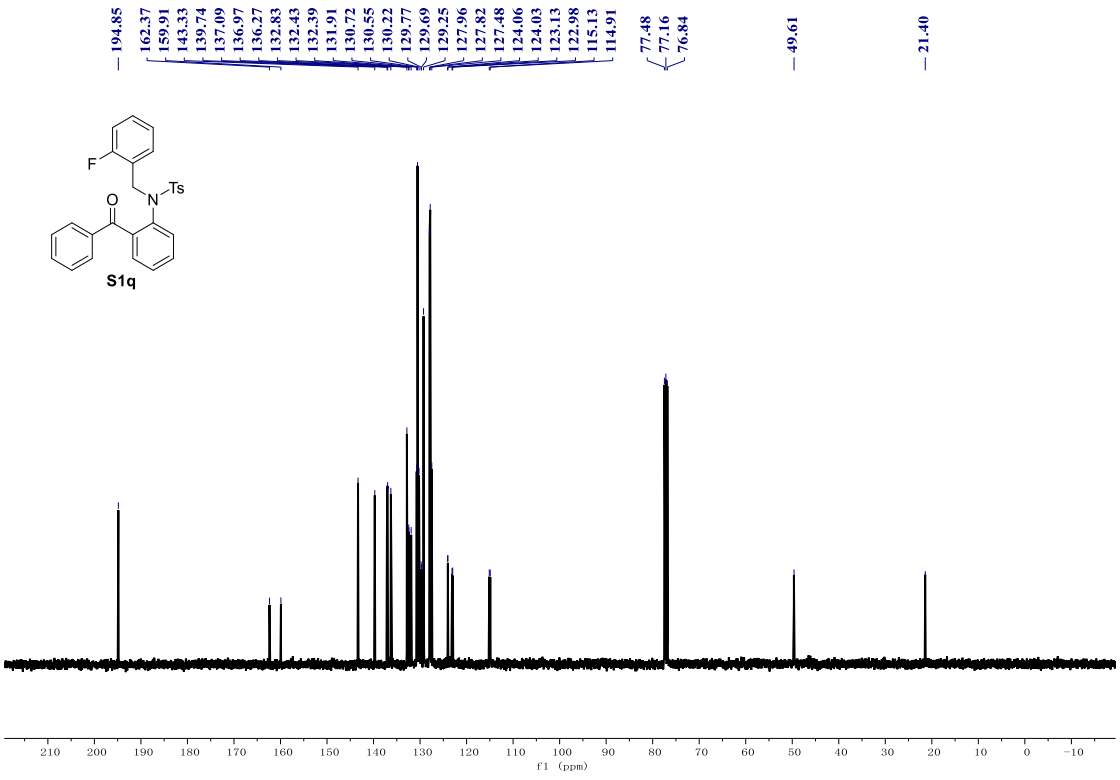
f1 (ppm)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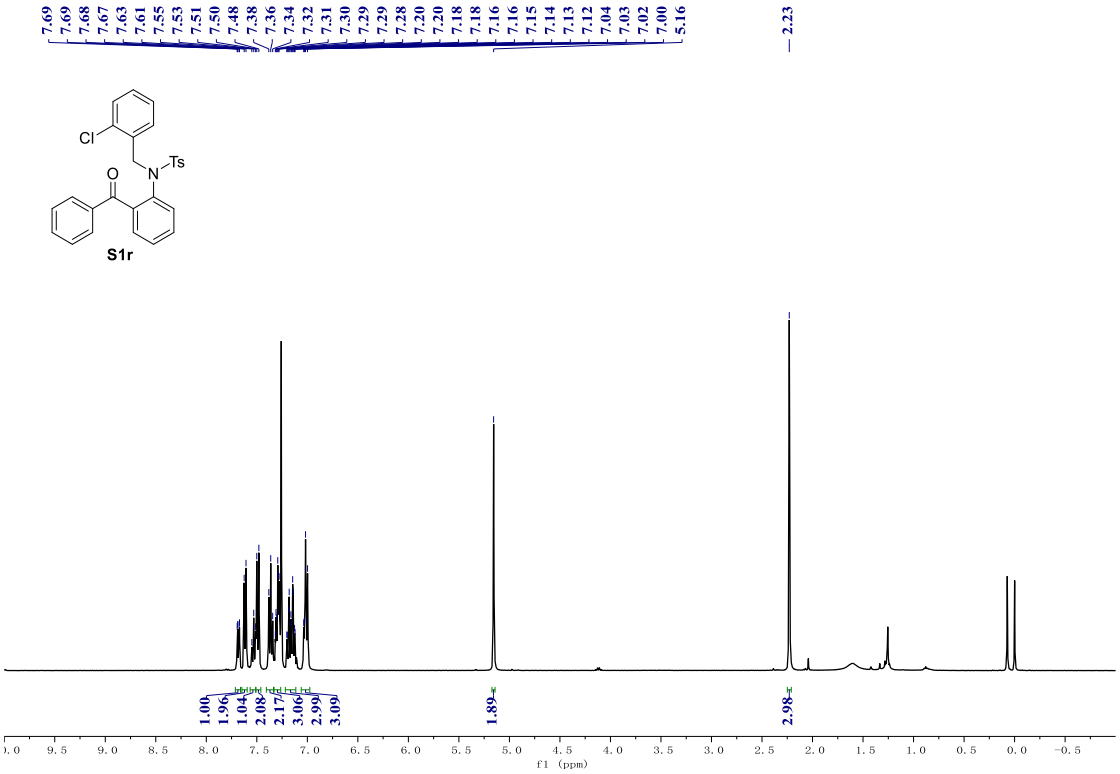
F
O
N
Ts
S1q
f1 (ppm)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7.16
7.15
7.14
7.13
7.12
7.04
7.03
7.02
7.00
5.16
2.23
Cl
N
Ts
O
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1.04
2.08
2.17
3.06
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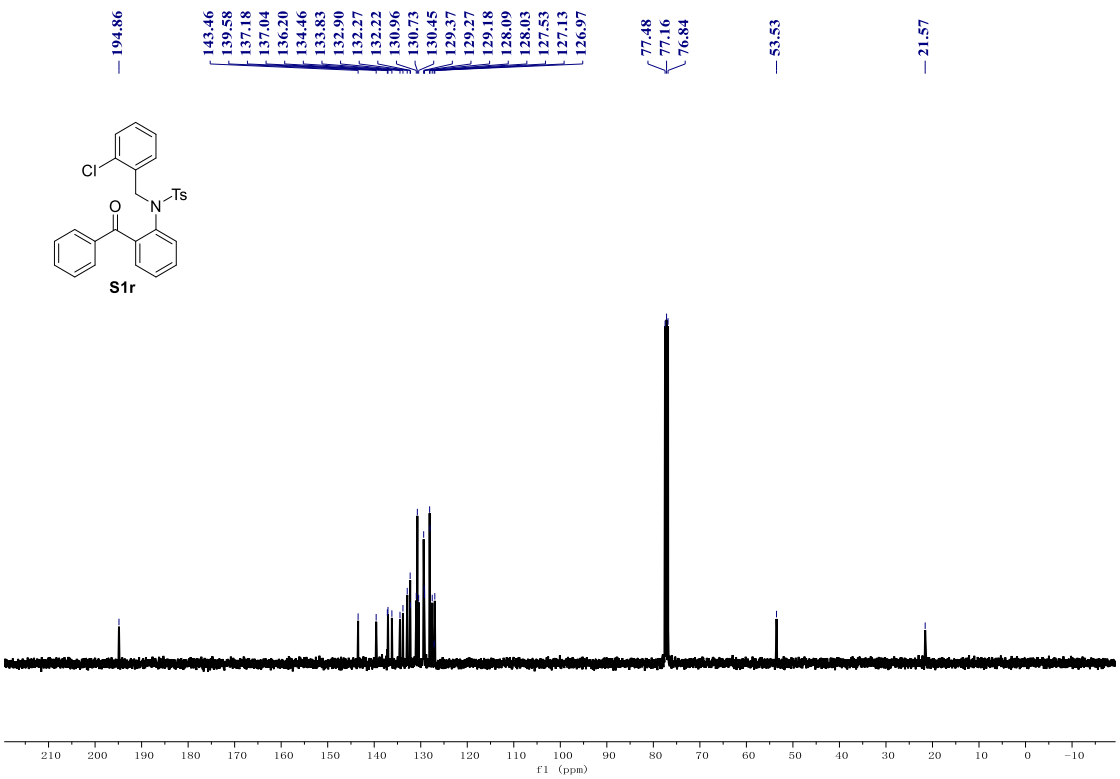
3.09
1.89
2.98
f1 (ppm)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128.09
128.03
127.53
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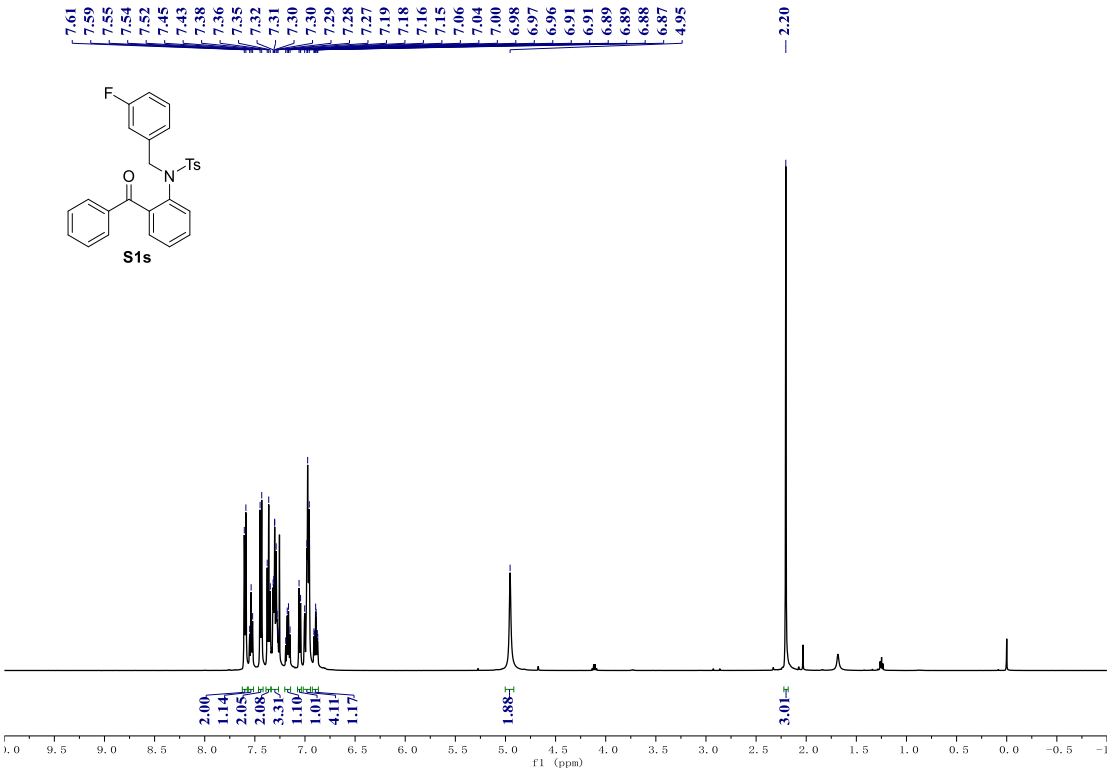
77.16
76.84
53.53
21.57
Cl
N
Ts
O
S1r
f1 (ppm)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6.89
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6.87
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2.20
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Ts
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O
S1s
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1.01
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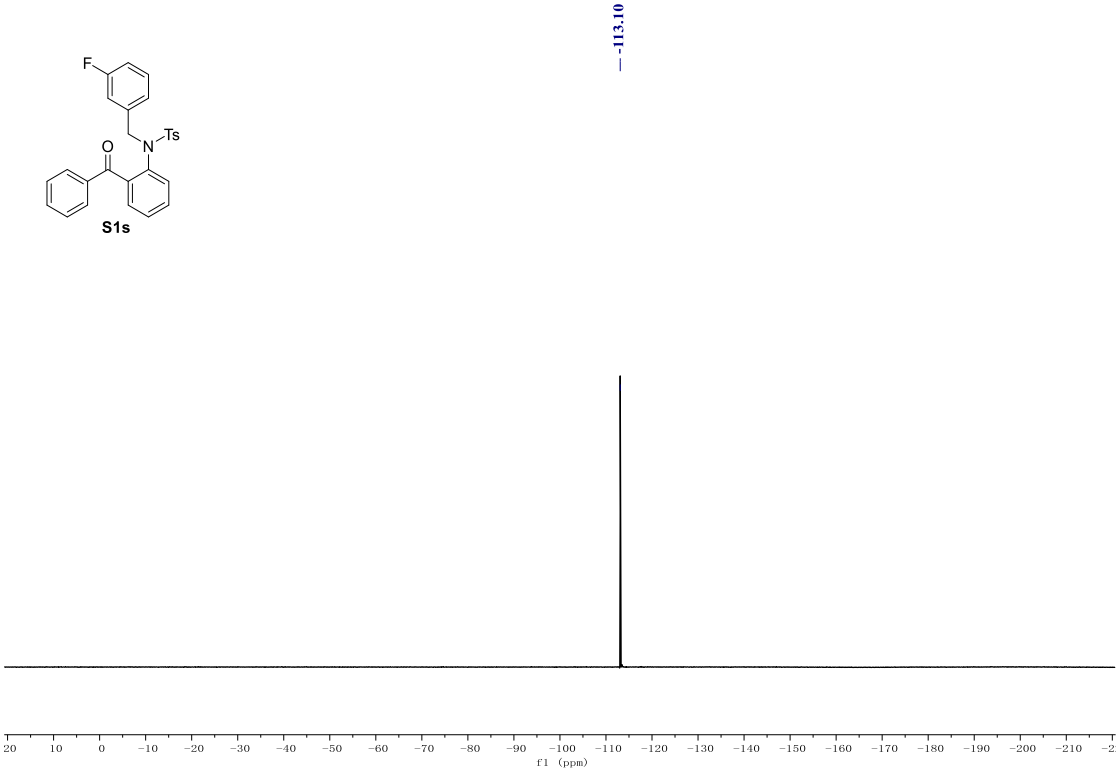
3.01
f1 (ppm)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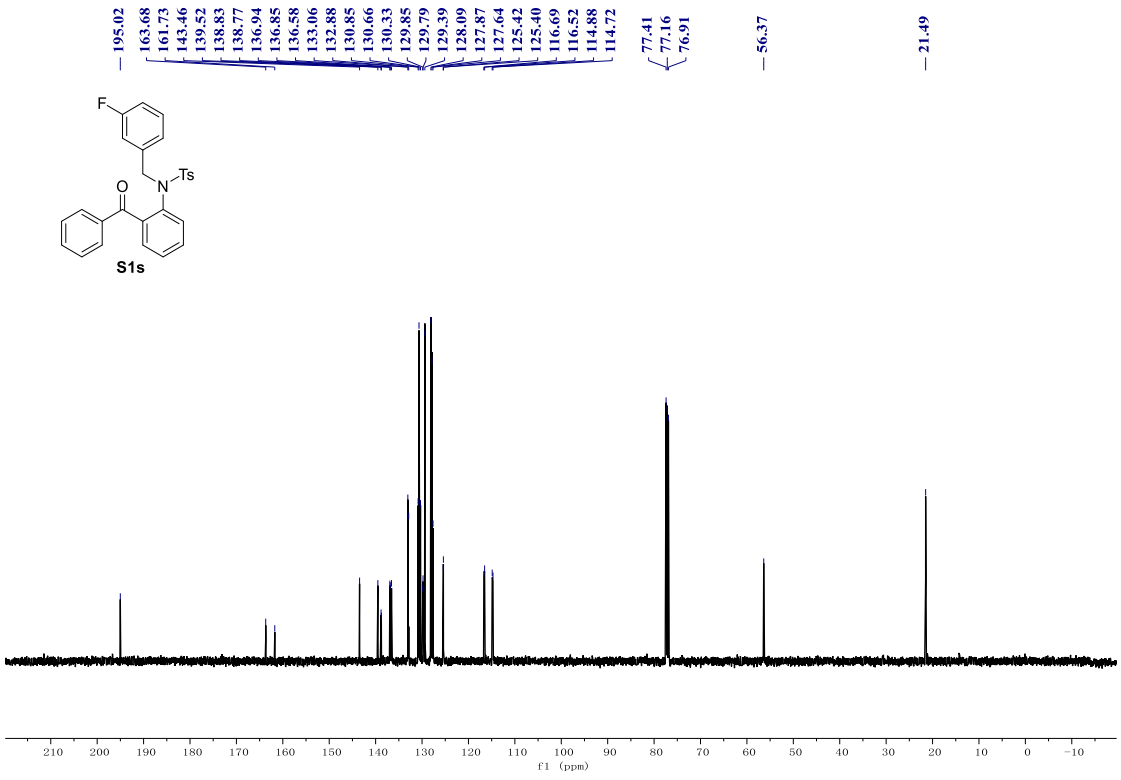
S1s
f1 (ppm)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125.40
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114.72
77.41
77.16
76.91
56.37
21.49
F
O
N
Ts
S1s
210
200
190
180
170
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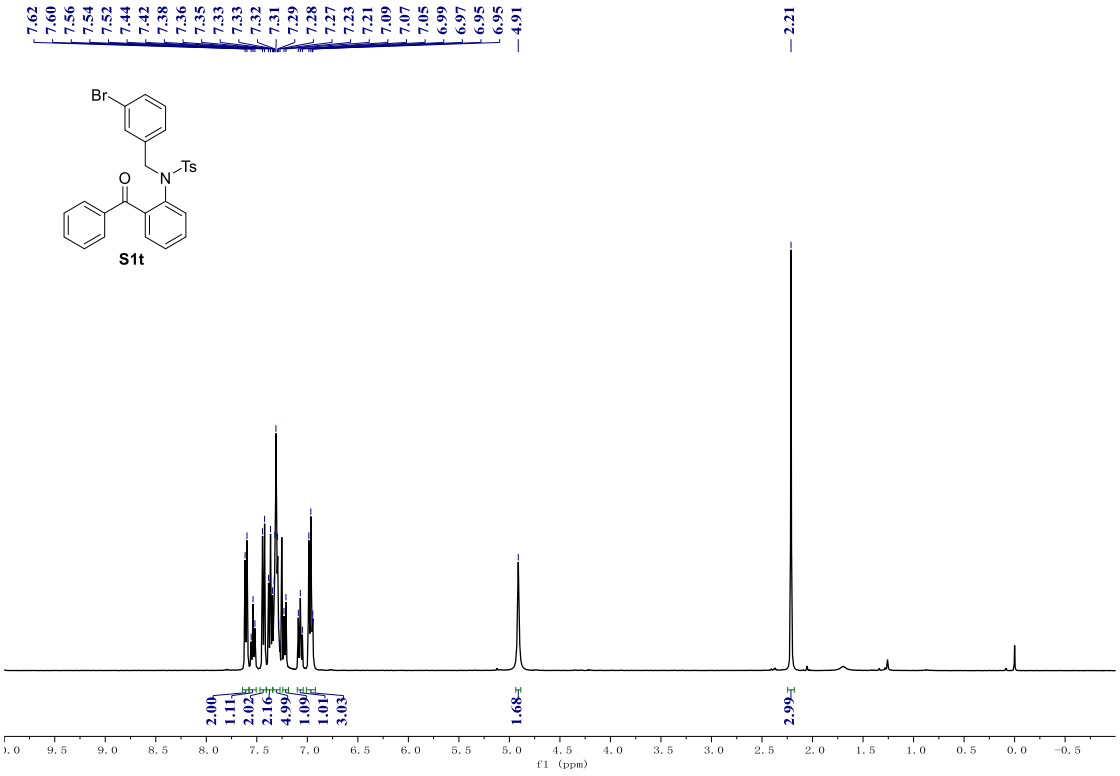
f1 (ppm)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7.07
7.05
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6.97
6.95
6.95
4.91
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Ts
N
O
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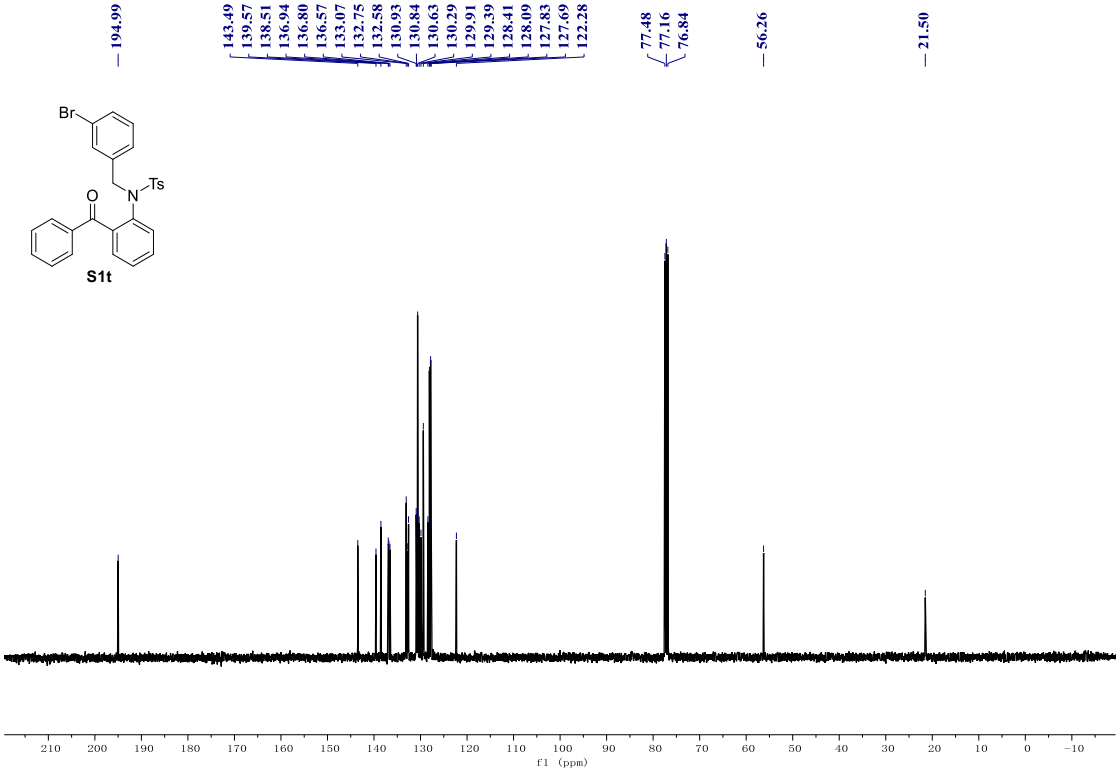
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128.09
127.83
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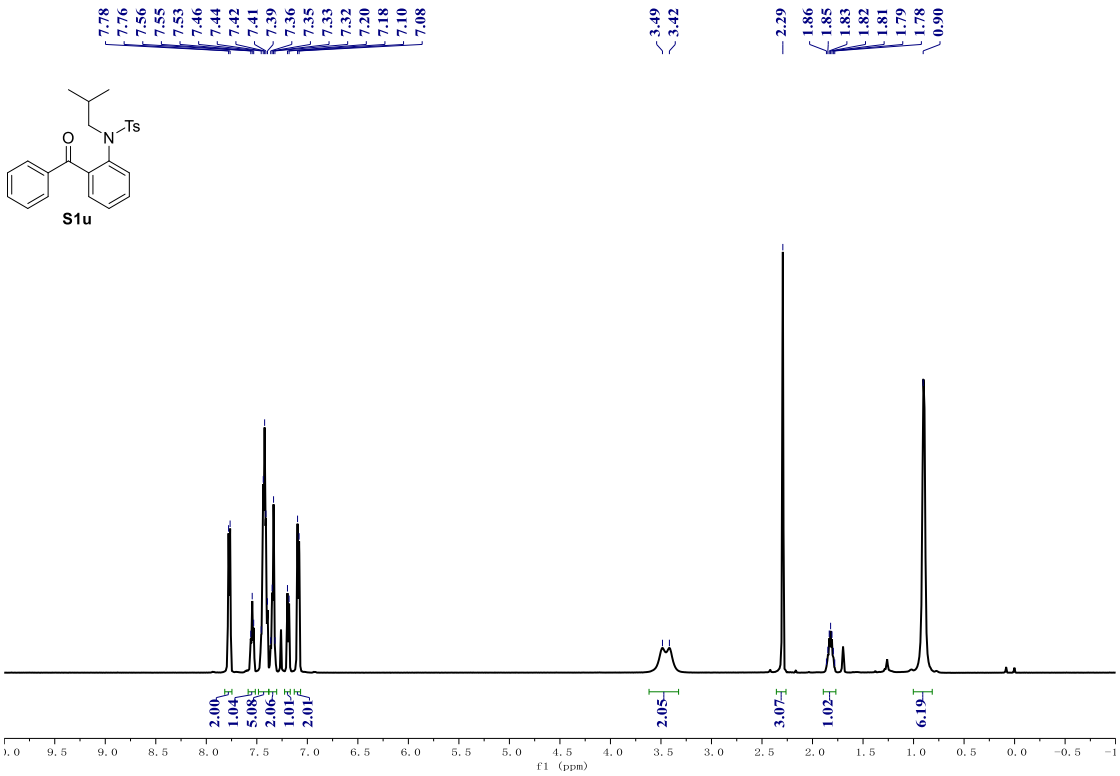
Br
Ts
N
O
S1t
f1 (ppm)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7.20
7.18
7.10
7.08
3.49
3.42
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1.85
1.83
1.82
1.81
1.79
1.78
0.90
O
N
Ts
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1.01
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3.07
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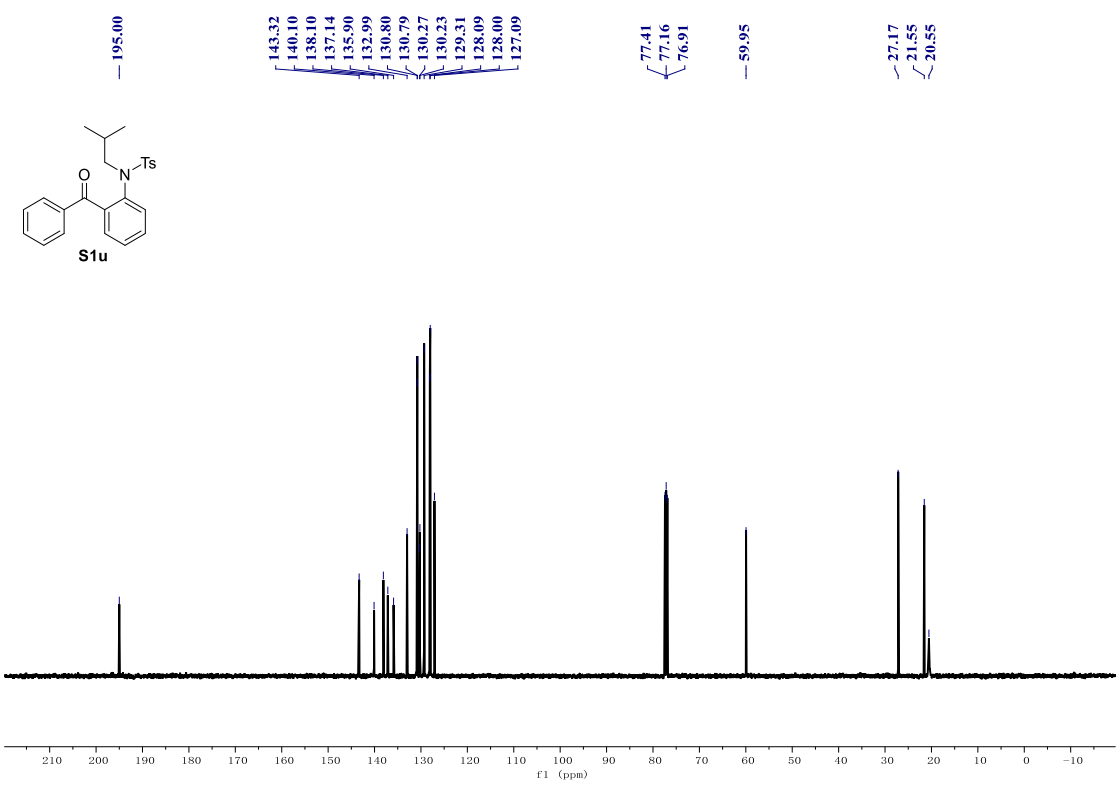
f1 (ppm)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128.00
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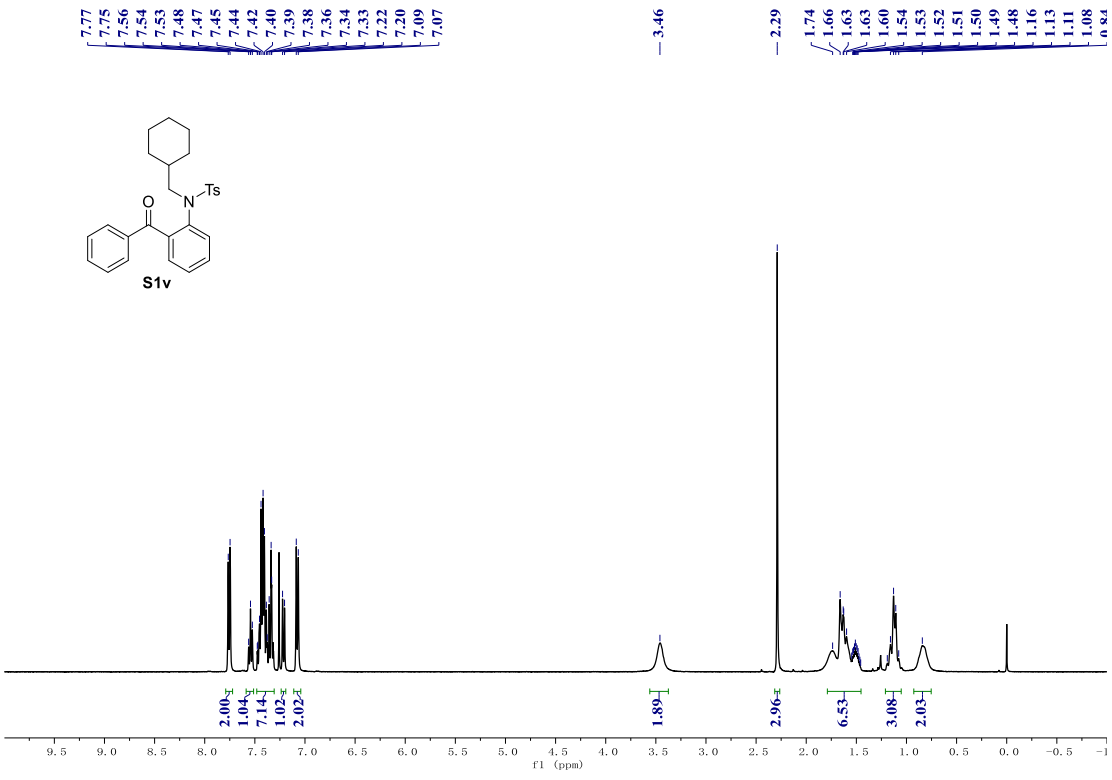
20.55
O
N
Ts
S1u
f1 (ppm)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7.33
7.22
7.20
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7.07
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1.66
1.63
1.63
1.60
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1.53
1.52
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1.49
1.48
1.16
1.13
1.11
1.08
O
N
Ts
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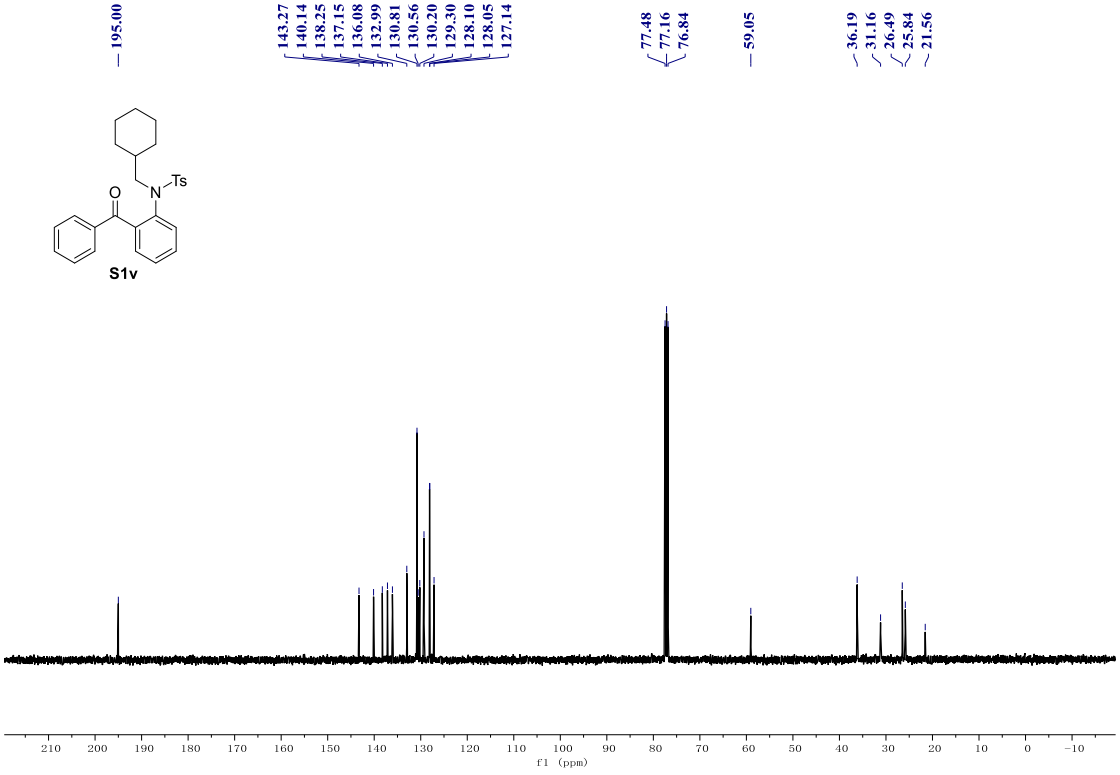
2.03
f1 (ppm)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127.14
77.48
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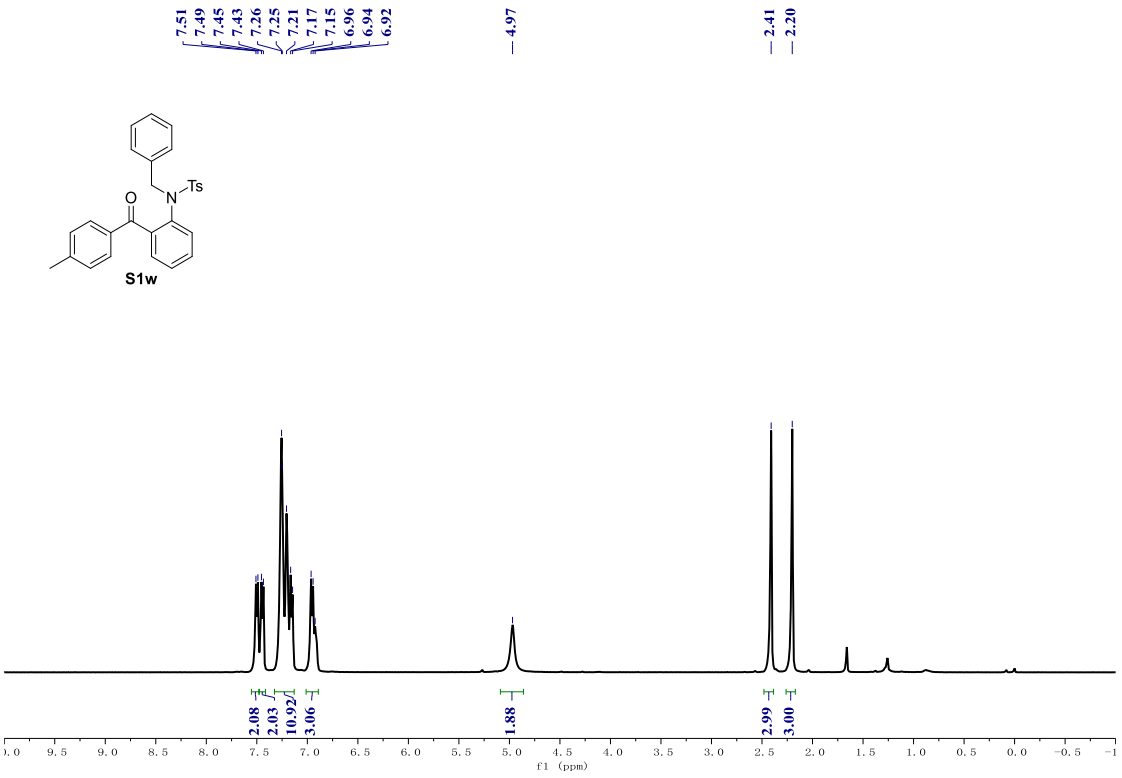
O
N
Ts
S1v
f1 (ppm)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6.94
6.92
4.97
2.41
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2.03
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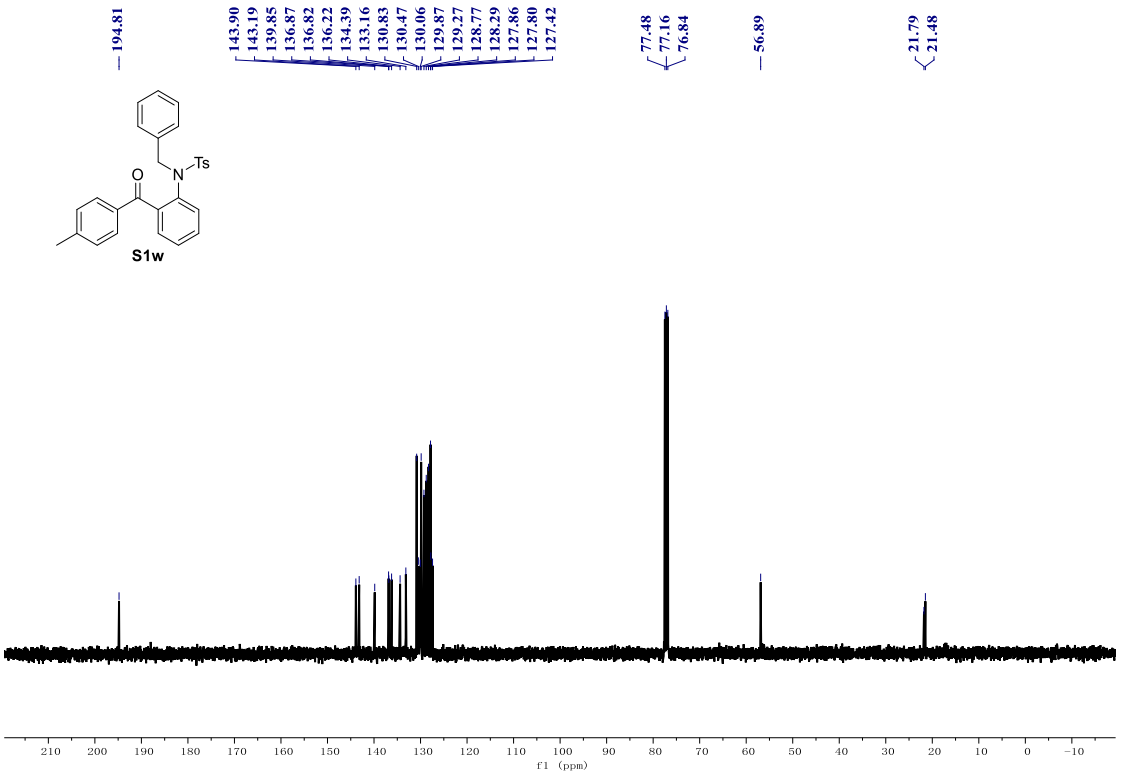
1.88
2.99
3.00
f1 (ppm)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128.77
128.29
127.86
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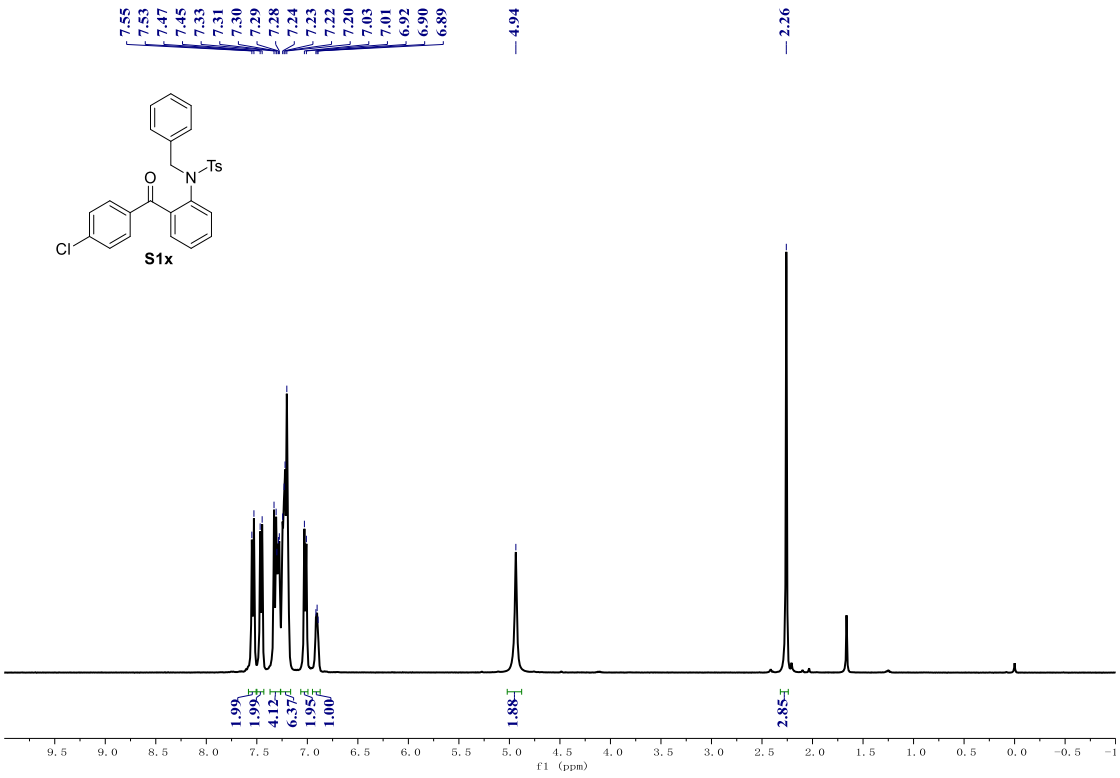
21.48
Ts
N
O
S1w
f1 (ppm)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7.03
7.01
6.92
6.90
6.89
4.94
2.26
O
N
Ts
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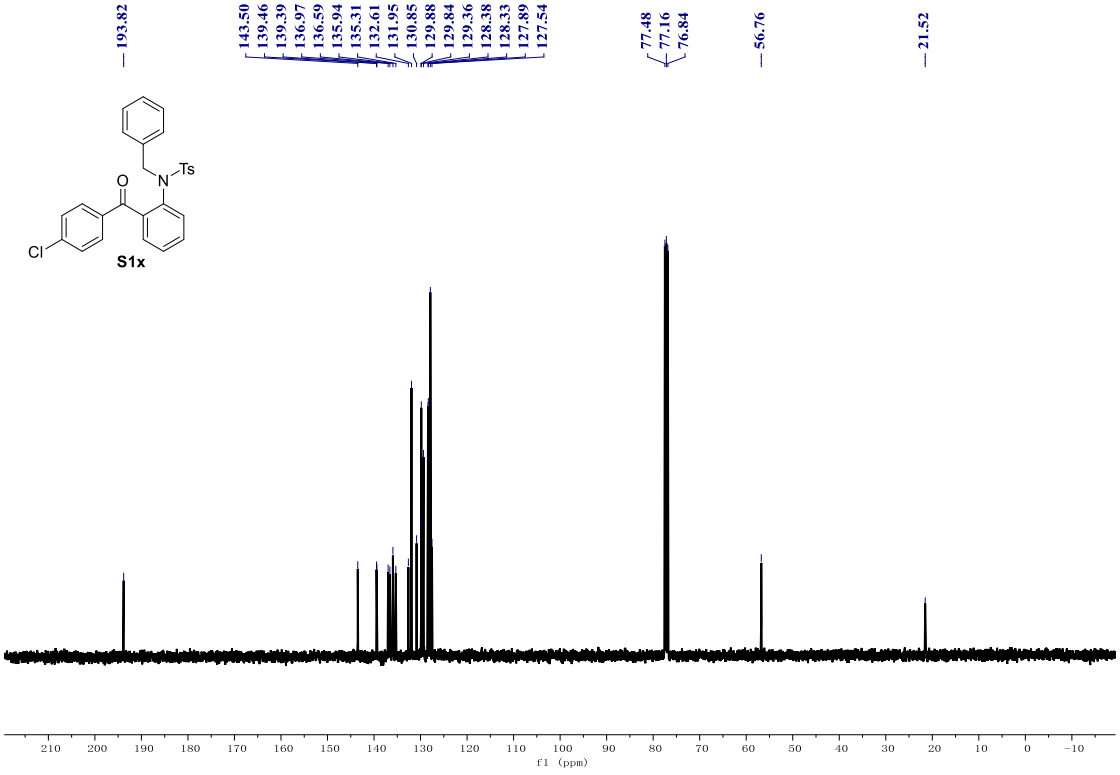
1.00
1.88
2.85
f1 (ppm)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129.36
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128.33
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77.16
76.84
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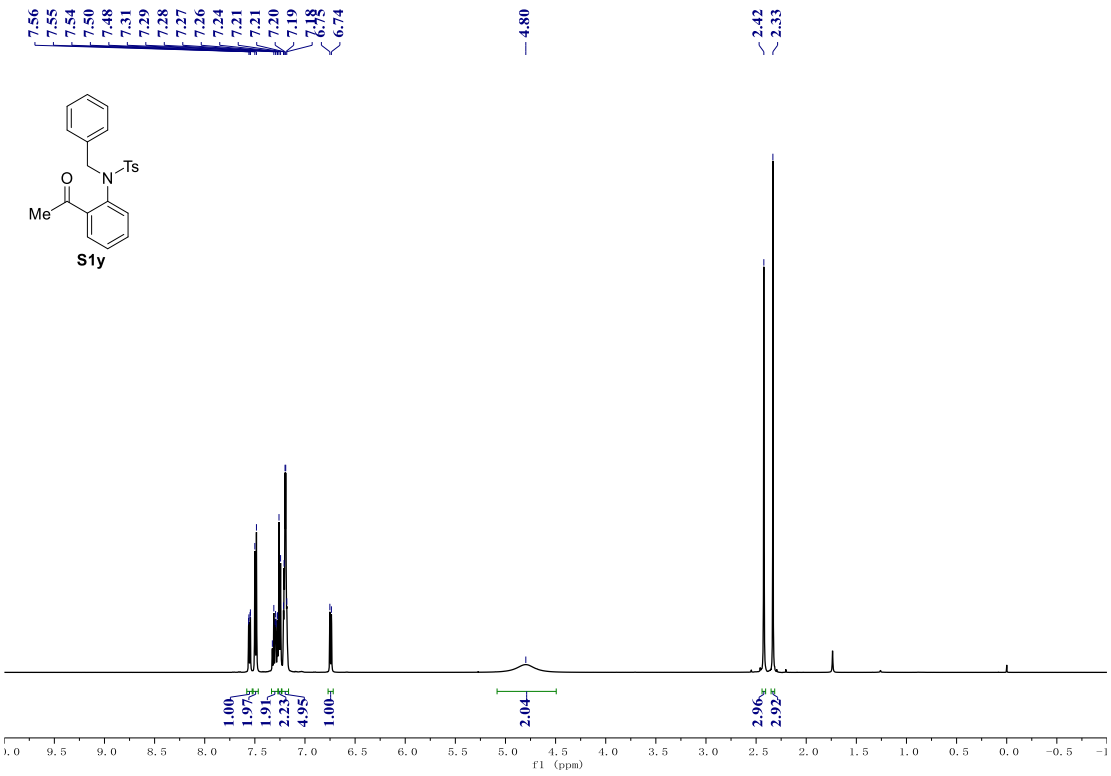
O
N
Ts
Cl
S1x
f1 (ppm)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7.19
7.18
6.75
6.74
4.80
2.42
2.33
Ts
N
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S1y
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2.04
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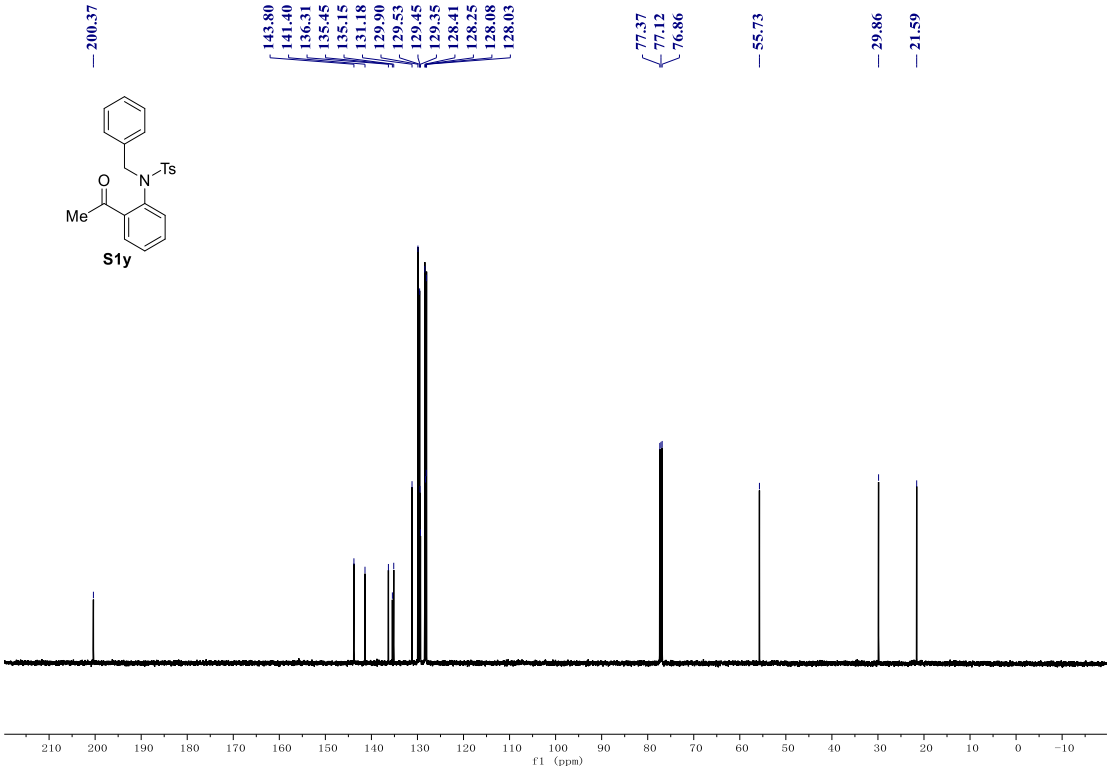
2.92
f1 (ppm)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128.08
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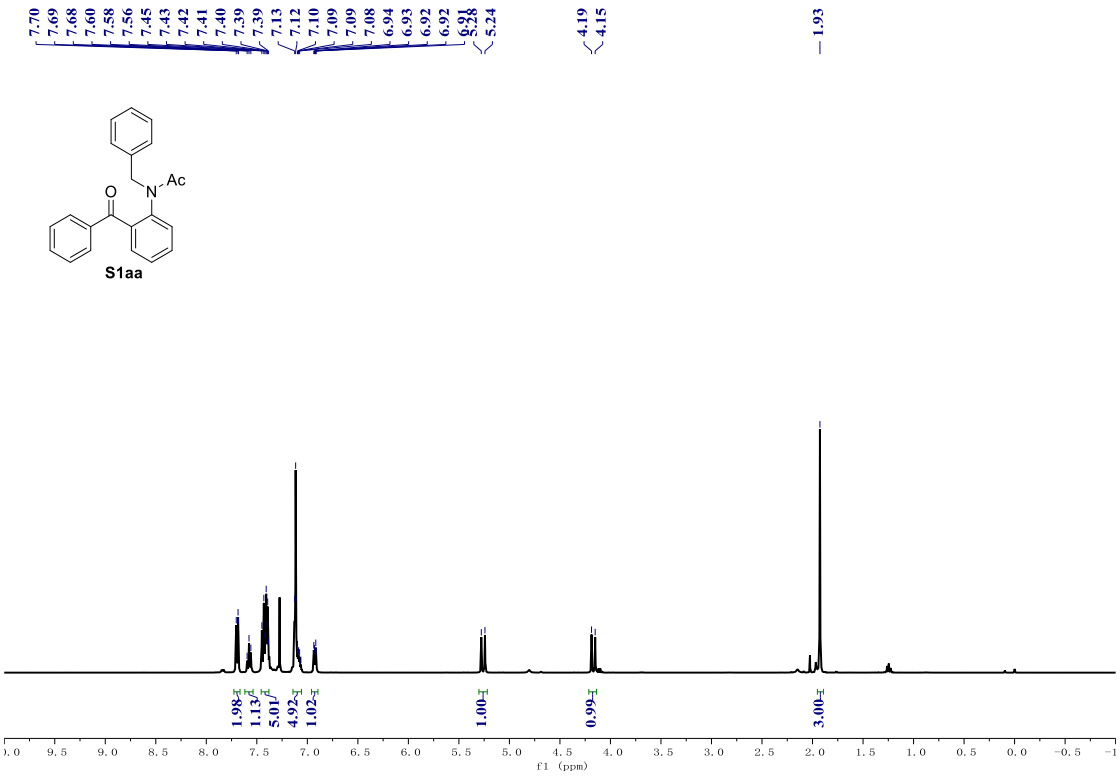
Ts
N
O
Me
S1y
f1 (ppm)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7.12
7.10
7.09
7.09
7.08
6.94
6.93
6.92
6.92
6.91
5.28
5.24
4.19
4.15
1.93
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O
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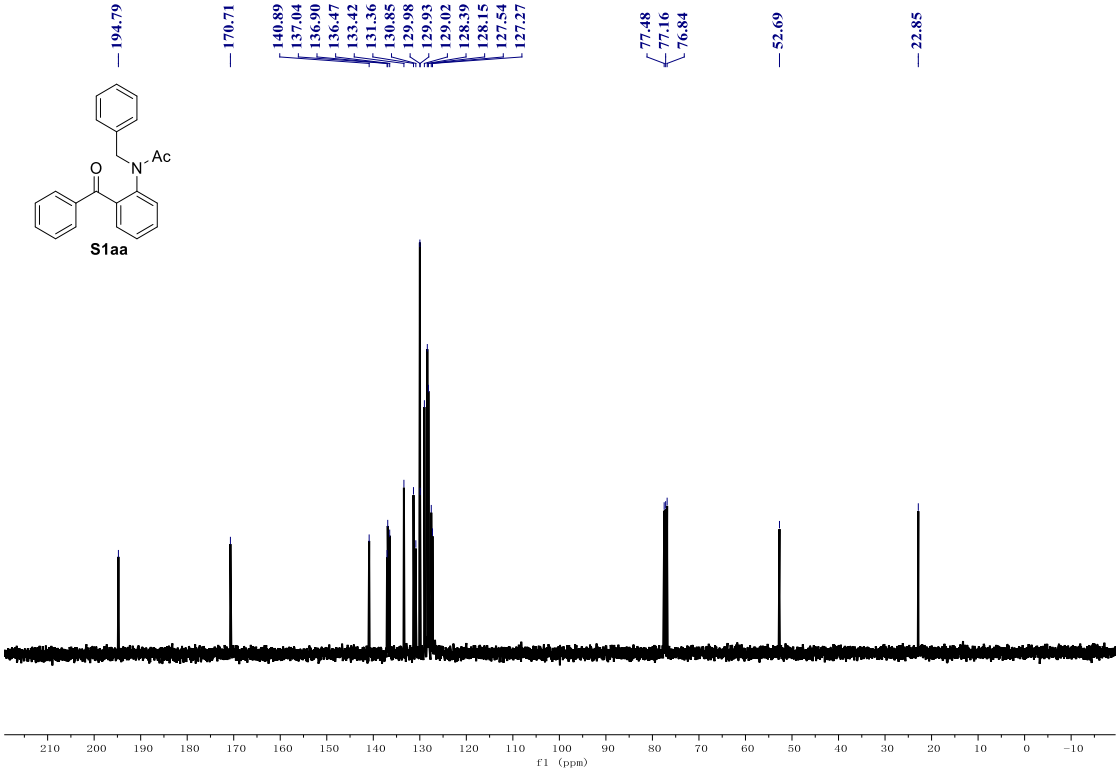
5.01
4.92
1.02
1.00
0.99
3.00
f1 (ppm)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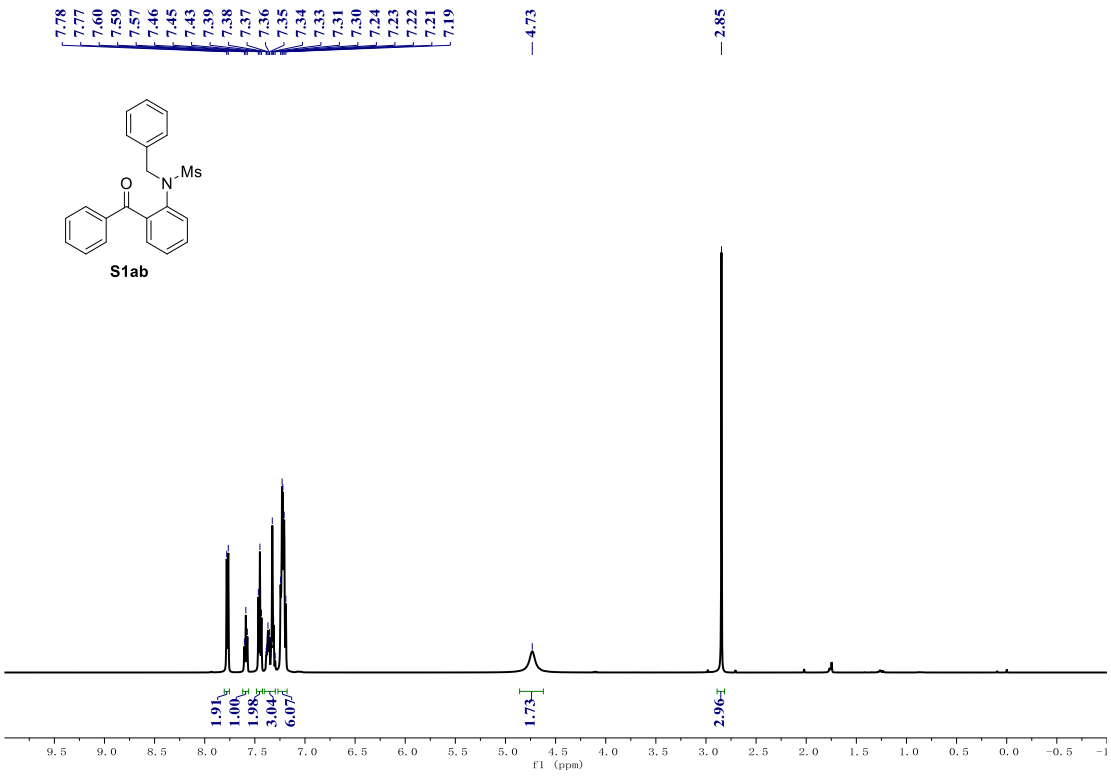
76.84
52.69
22.85
Ac
O
N
S1aa
f1 (ppm)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7.33
7.31
7.30
7.24
7.23
7.22
7.21
7.19
4.73
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O
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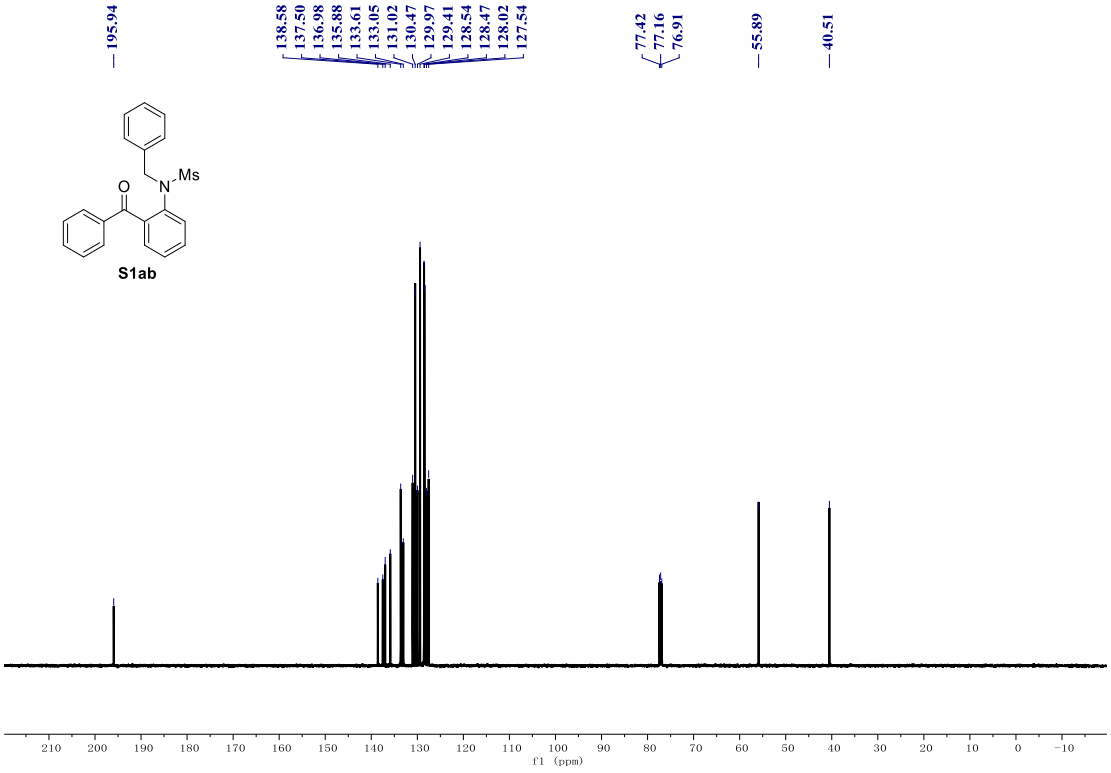
6.07
1.73
2.96
f1 (ppm)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55.89
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Ms
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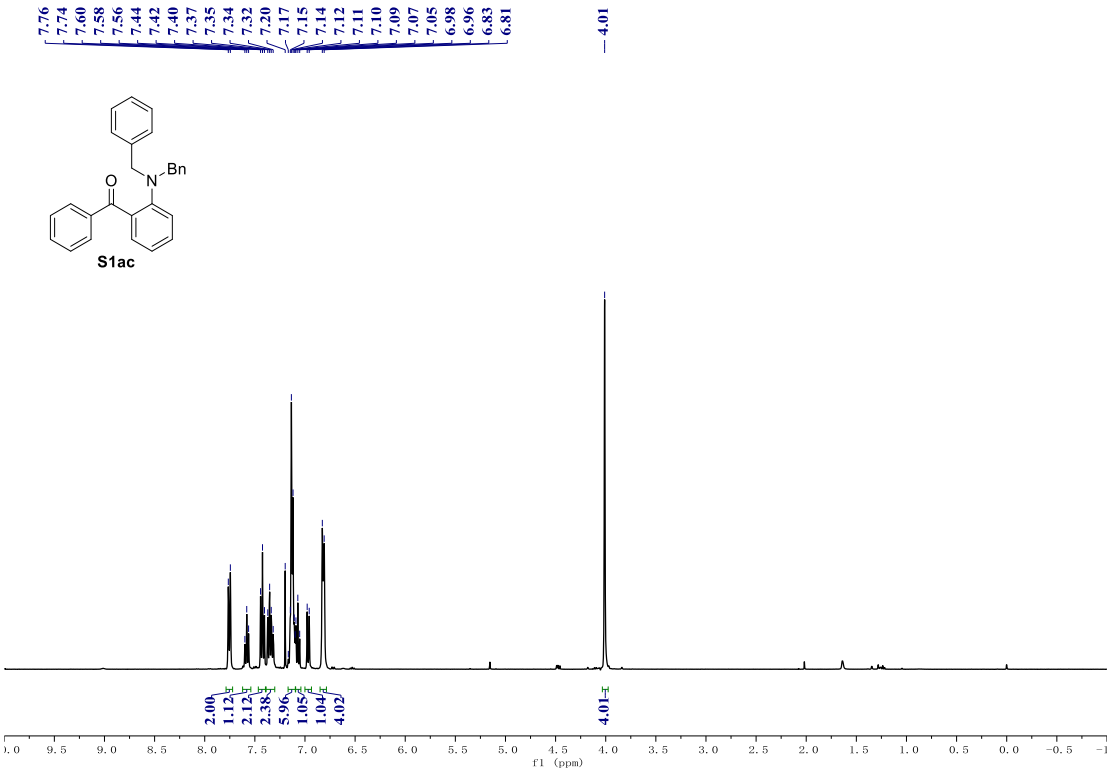
O
S1ab
f1 (ppm)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7.14
7.12
7.11
7.10
7.09
7.07
7.05
6.98
6.96
6.83
6.81
4.01
Bn
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O
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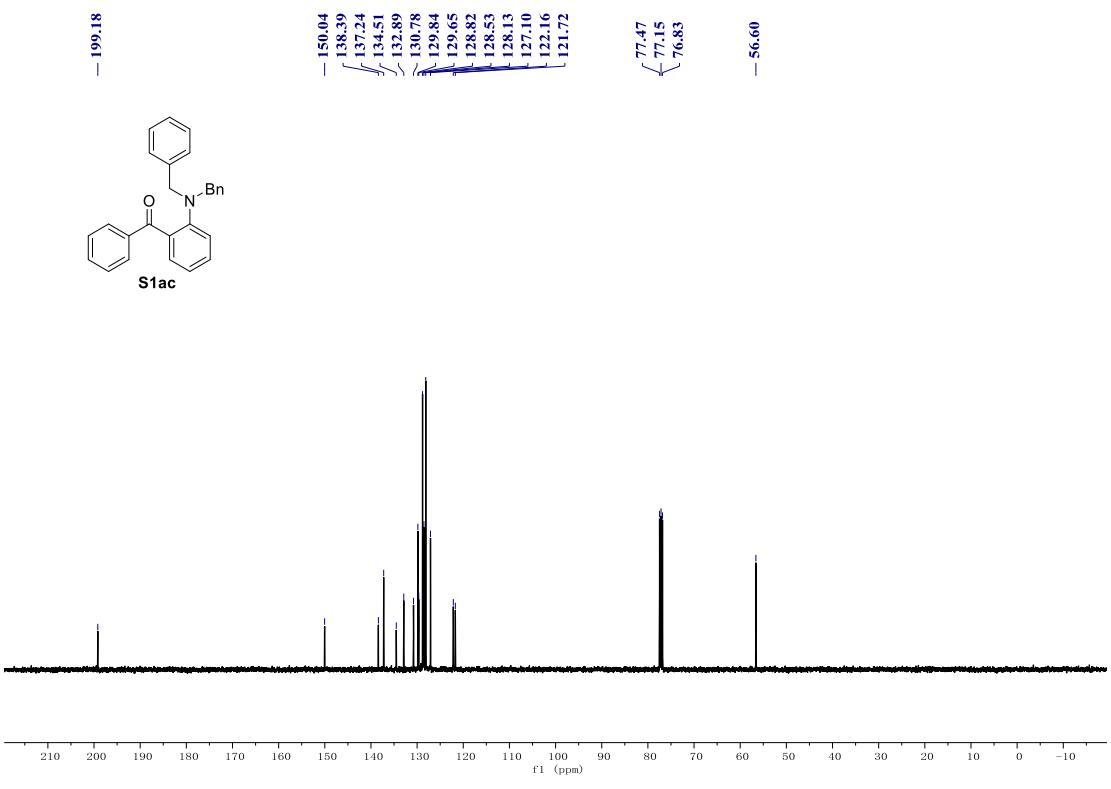
1.04
4.02
4.01
f1 (ppm)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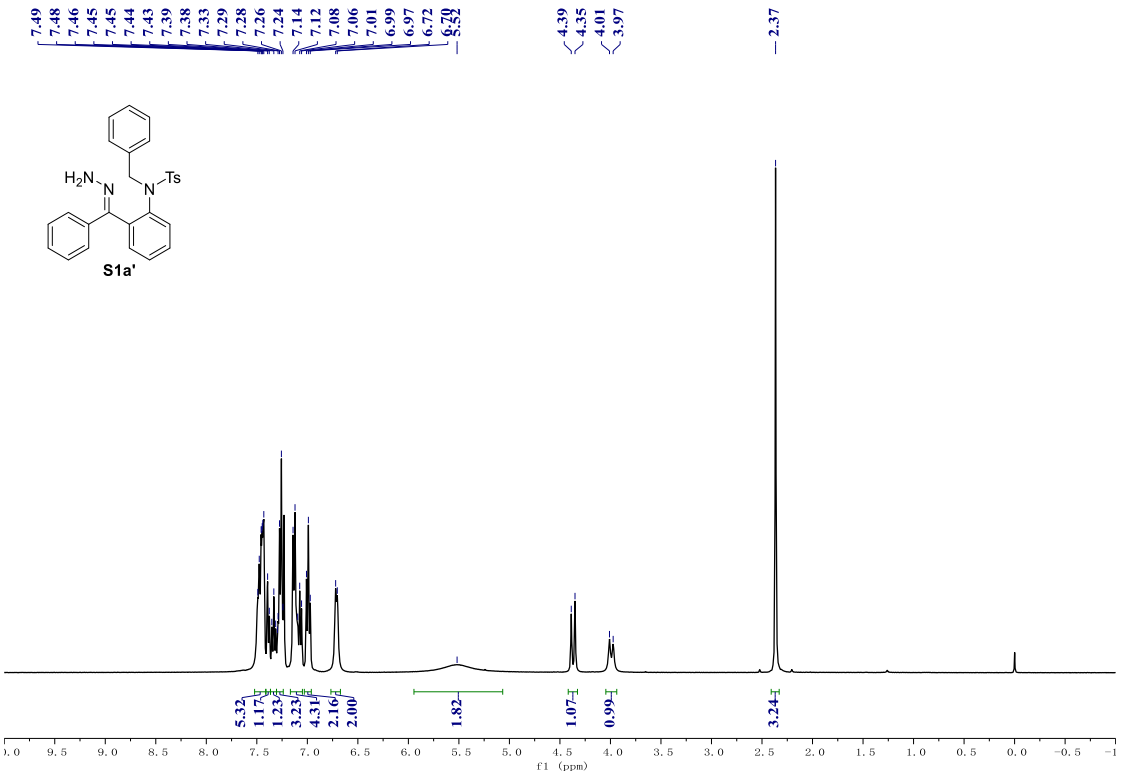
77.15
76.83
56.60
Bn
N
O
S1ac
f1 (ppm)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7.08
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7.01
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6.97
6.72
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4.39
4.35
4.01
3.97
2.37
H2N
N
N
Ts
S1a'
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1.07
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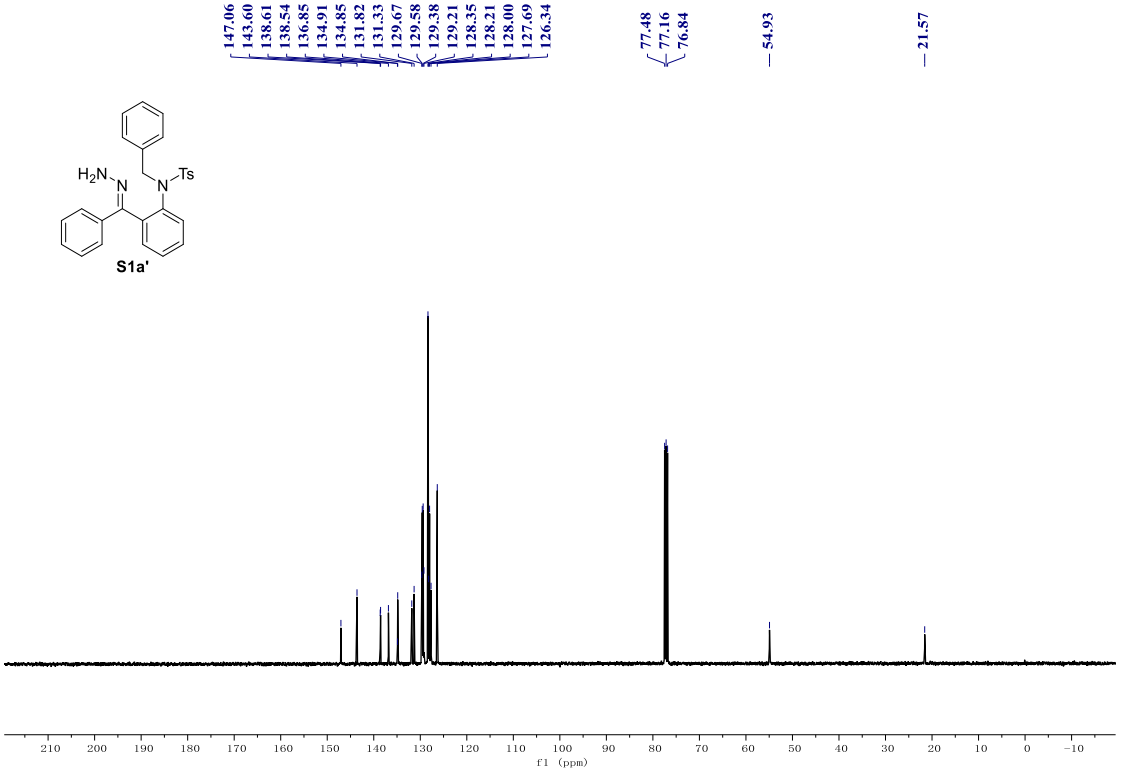
3.24
f1 (ppm)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128.00
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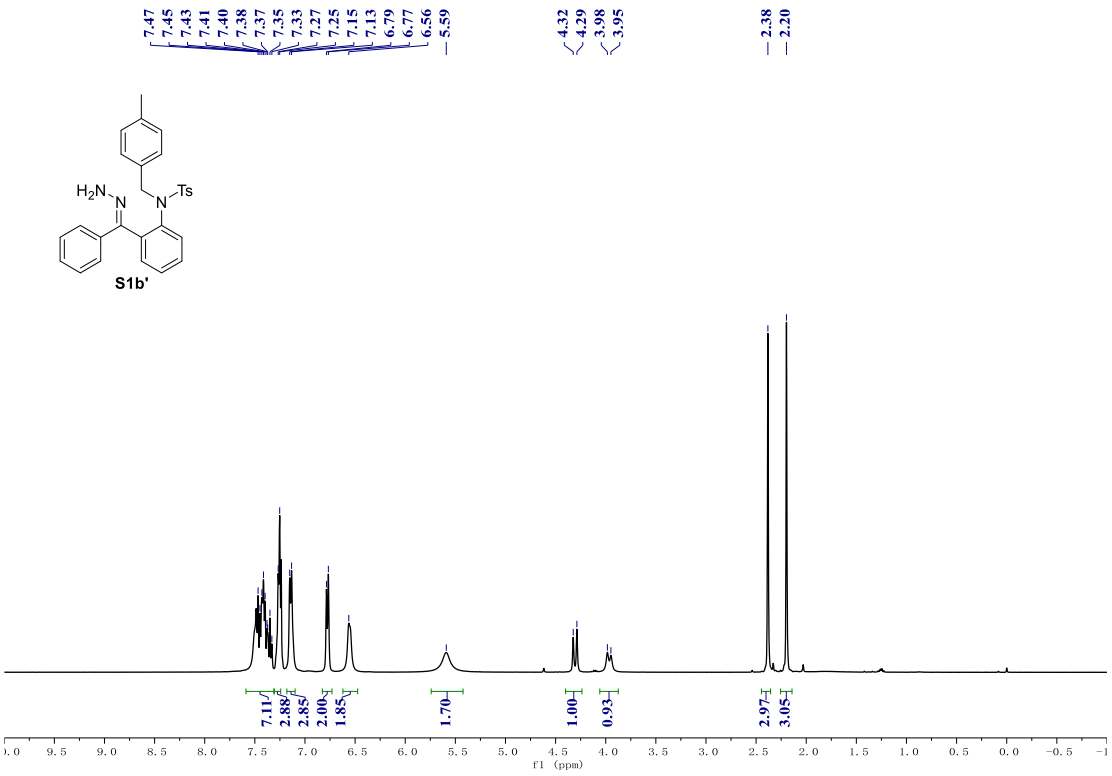
76.84
54.93
21.57
H2N
N
N
Ts
S1a'
f1 (ppm)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6.77
6.56
5.59
4.32
4.29
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3.95
2.38
2.20
H2N
N
N
Ts
S1b'
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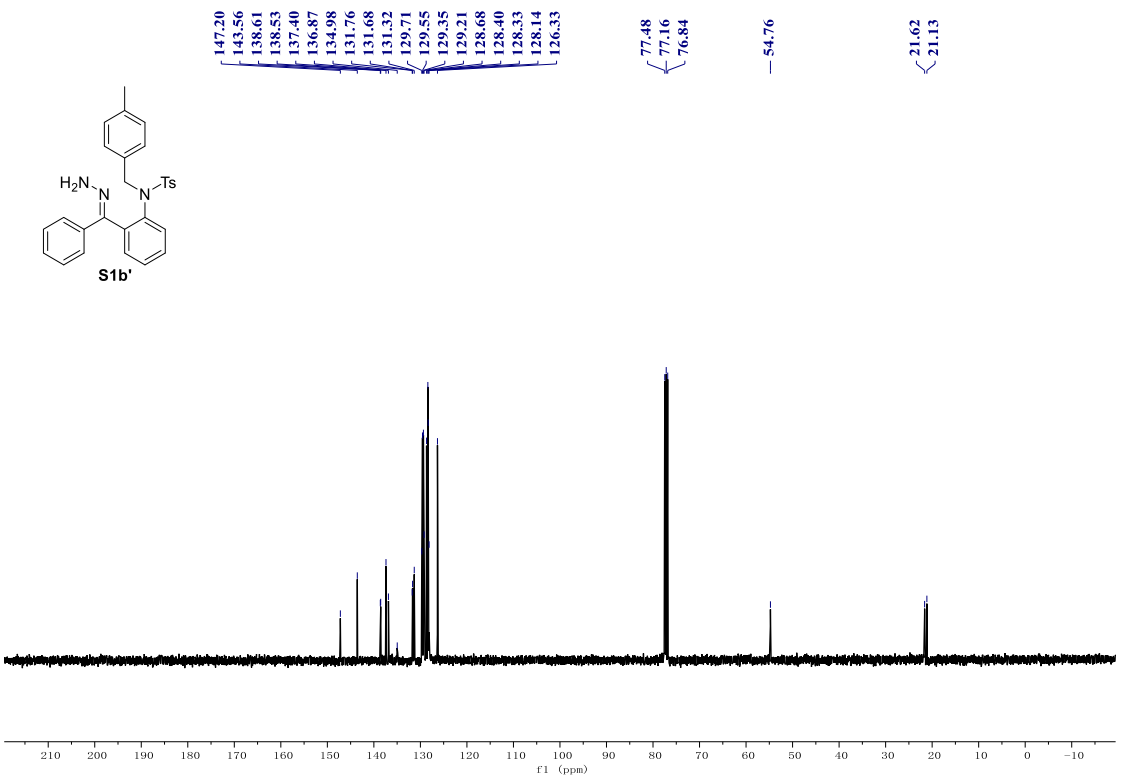
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128.14
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N
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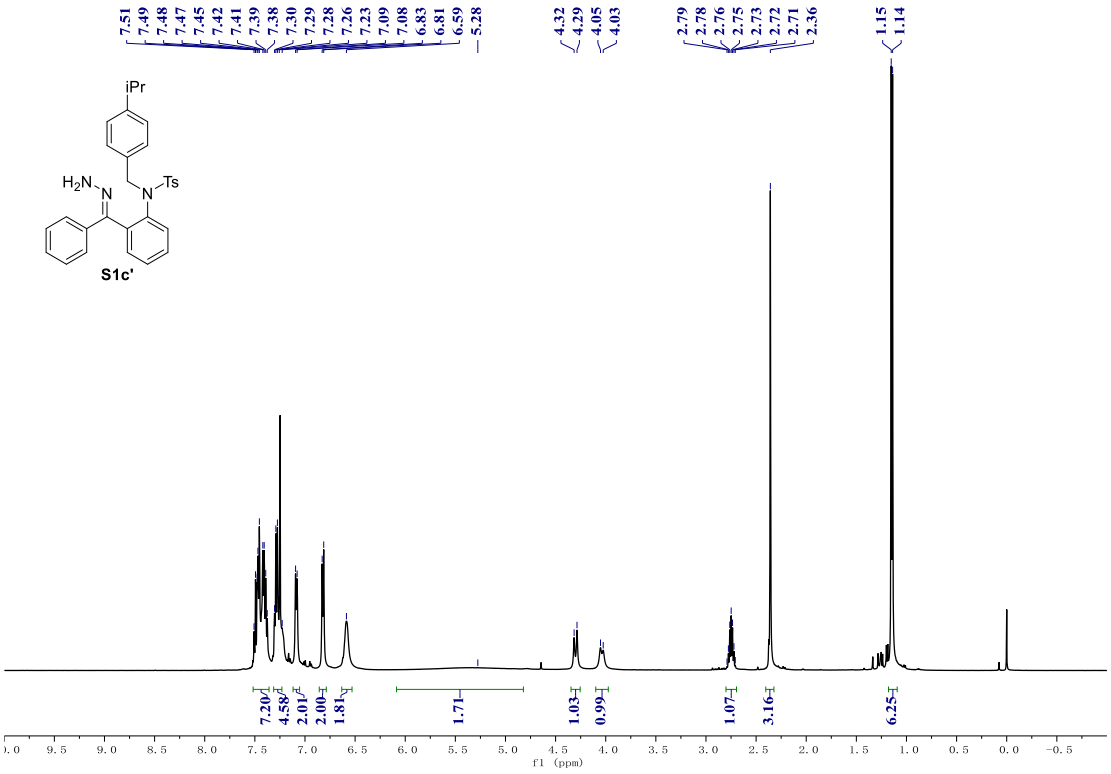
Ts
S1b'
f1 (ppm)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7.26
7.23
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7.08
6.83
6.81
6.59
5.28
4.32
4.29
4.05
4.03
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2.78
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2.72
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2.36
1.15
1.14
iPr
H2N
N
N
Ts
S1c'
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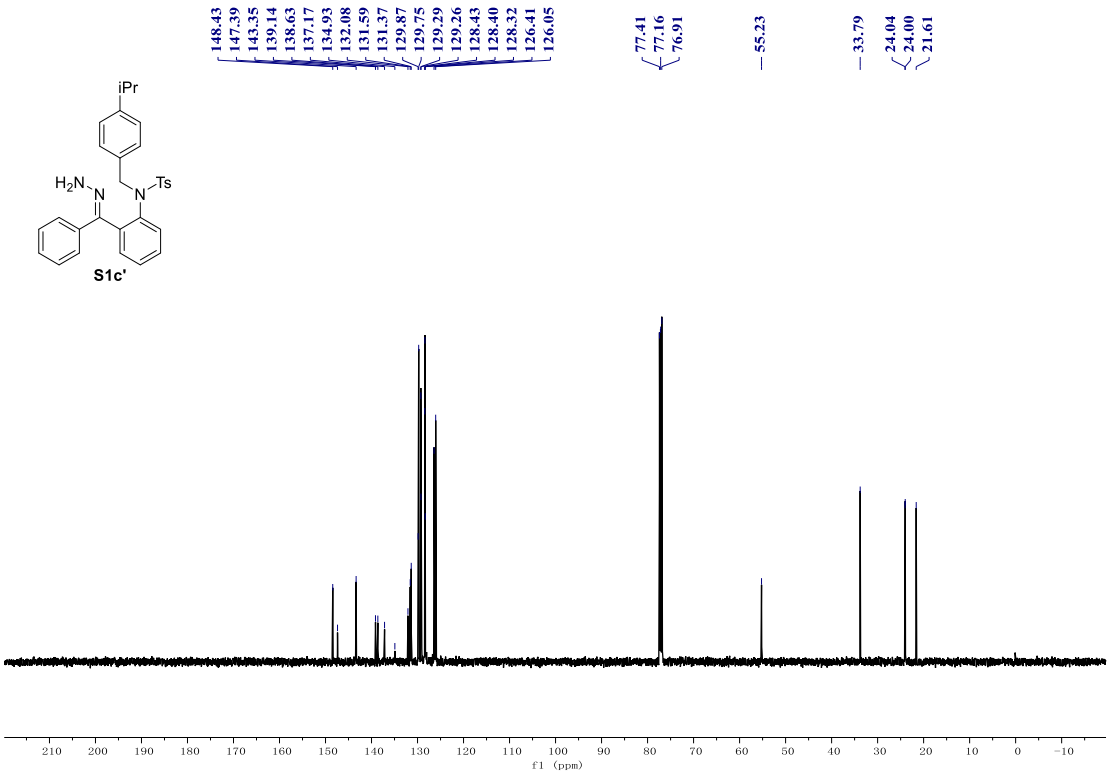
f1 (ppm)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126.05
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77.16
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24.00
21.61
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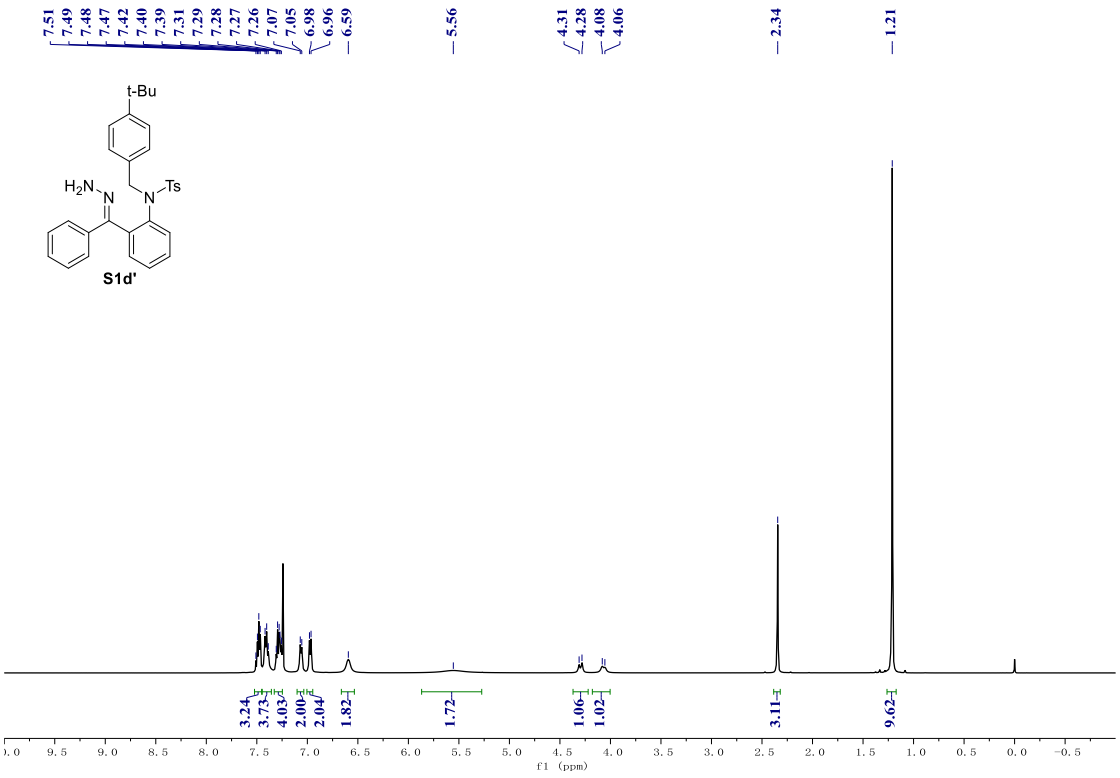
H2N
N
N
Ts
S1c'
f1 (ppm)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7.07
7.05
6.98
6.96
6.59
5.56
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4.28
4.08
4.06
2.34
1.21
t-Bu
H2N
N
N
Ts
S1d'
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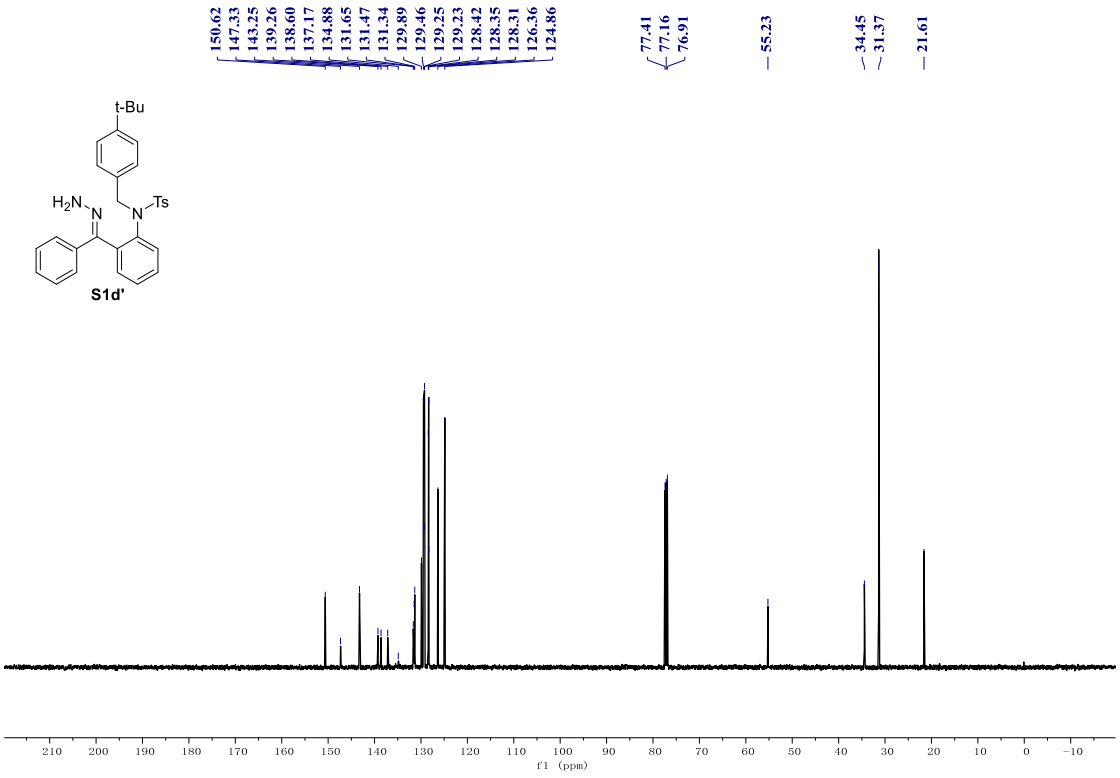
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77.41
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31.37
21.61
t-Bu
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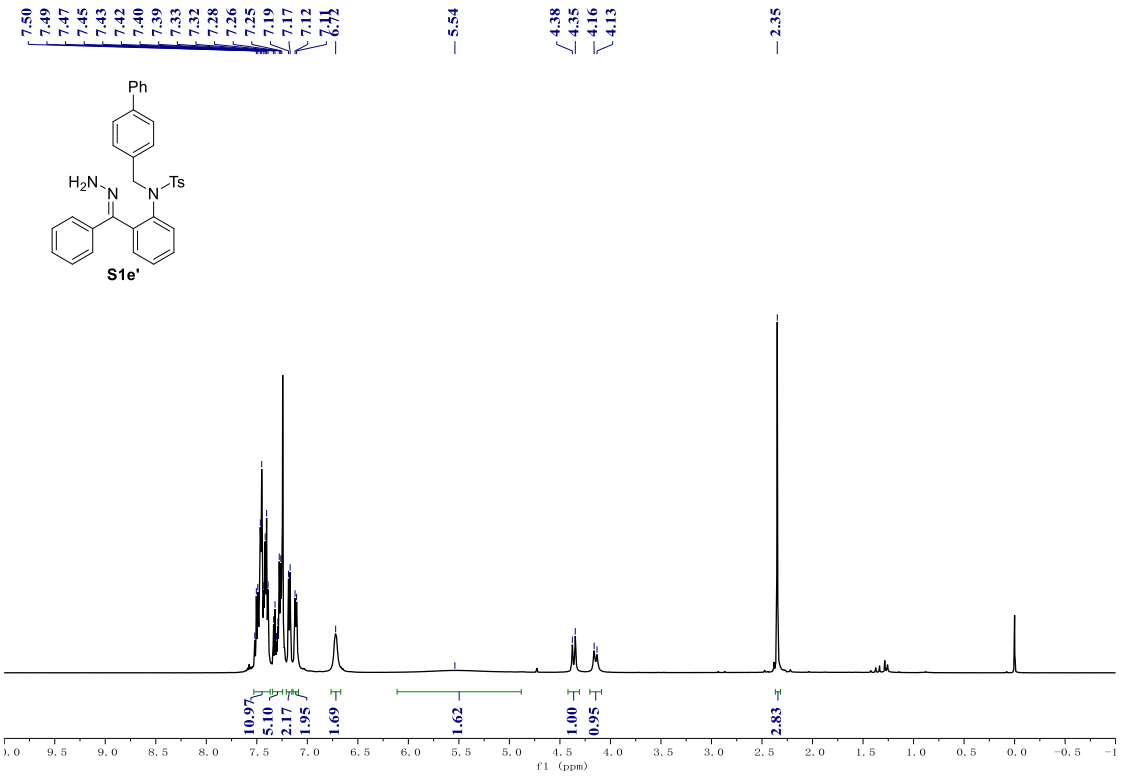
N
N
Ts
S1d'
f1 (ppm)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7.25
7.19
7.17
7.12
7.11
6.12
5.54
4.38
4.35
4.16
4.13
2.35
Ph
H2N
N
N
Ts
S1e'
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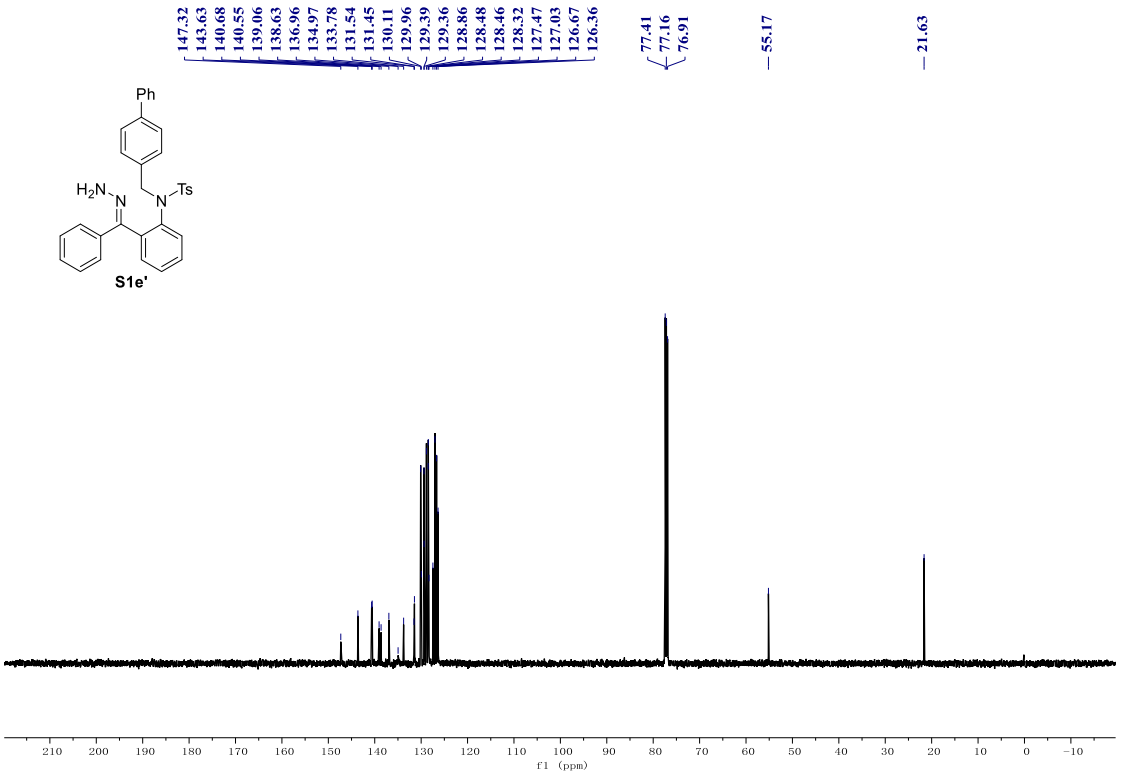
1.00
0.95
2.83
f1 (ppm)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128.32
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126.67
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76.91
55.17
21.63
Ph
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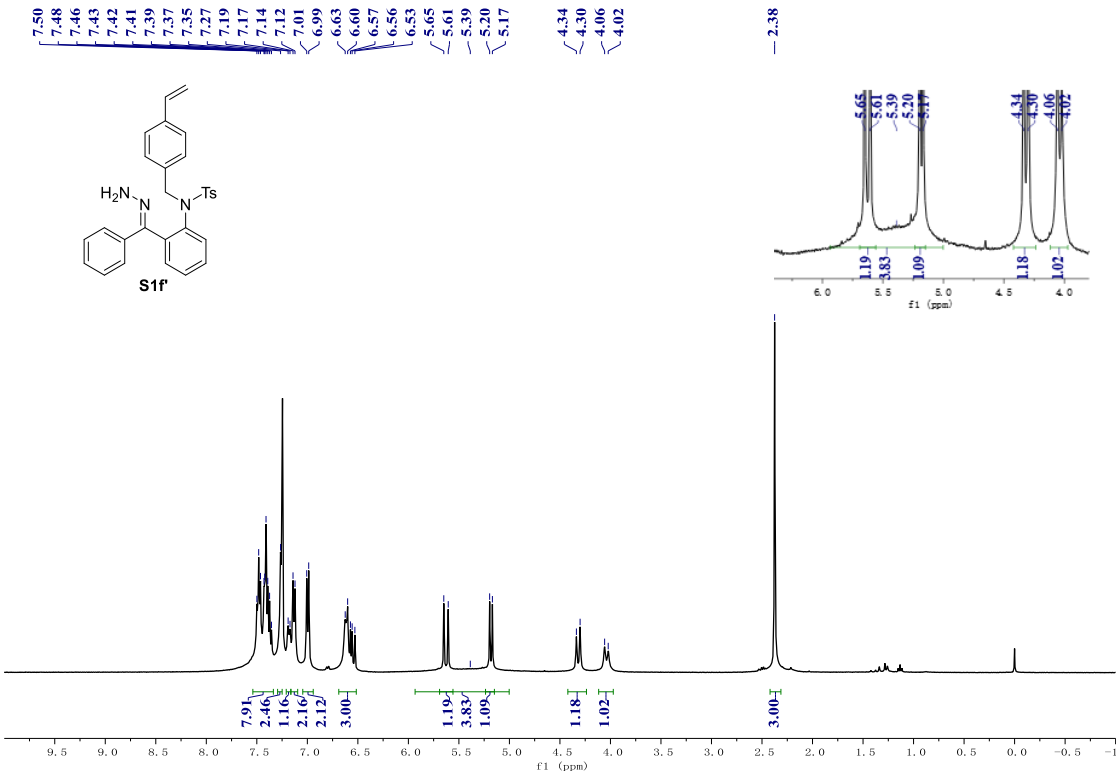
N
N
Ts
S1e'
f1 (ppm)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7.01
6.99
6.63
6.60
6.57
6.56
6.53
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5.61
5.39
5.20
5.17
4.34
4.30
4.06
4.02
2.38
H2N
N
N
Ts
S1f'
7.91
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3.83
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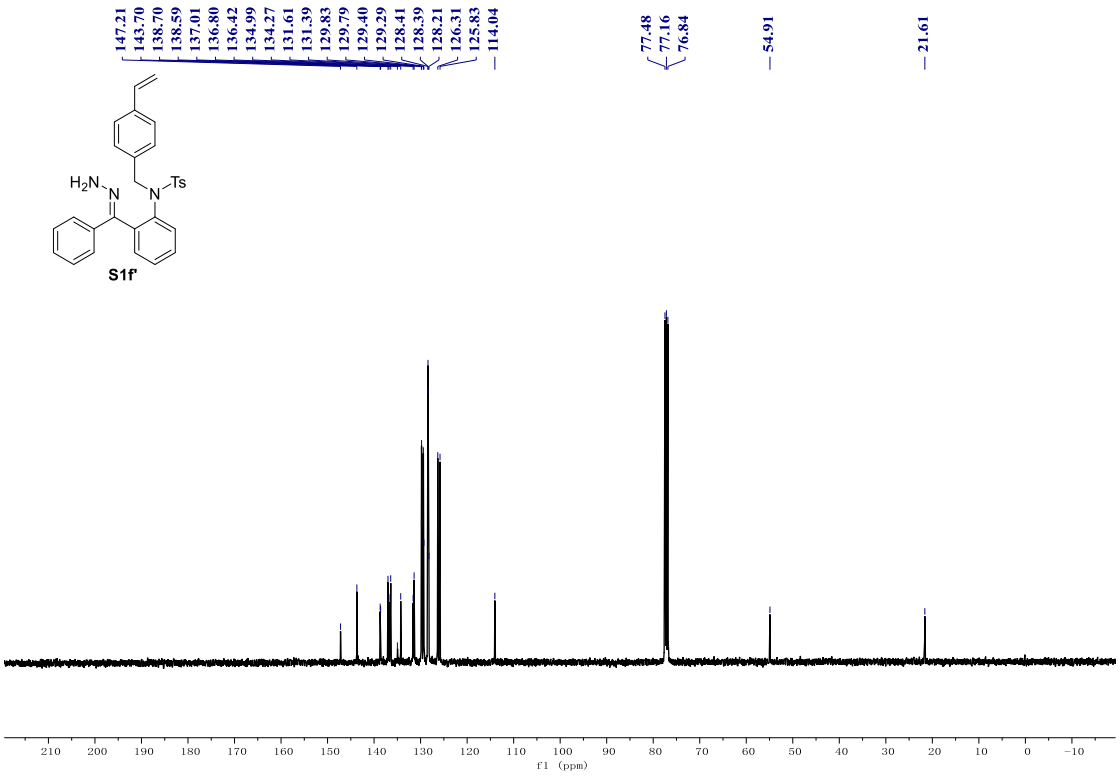
3.00
f1 (ppm)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129.29
128.41
128.39
128.21
126.31
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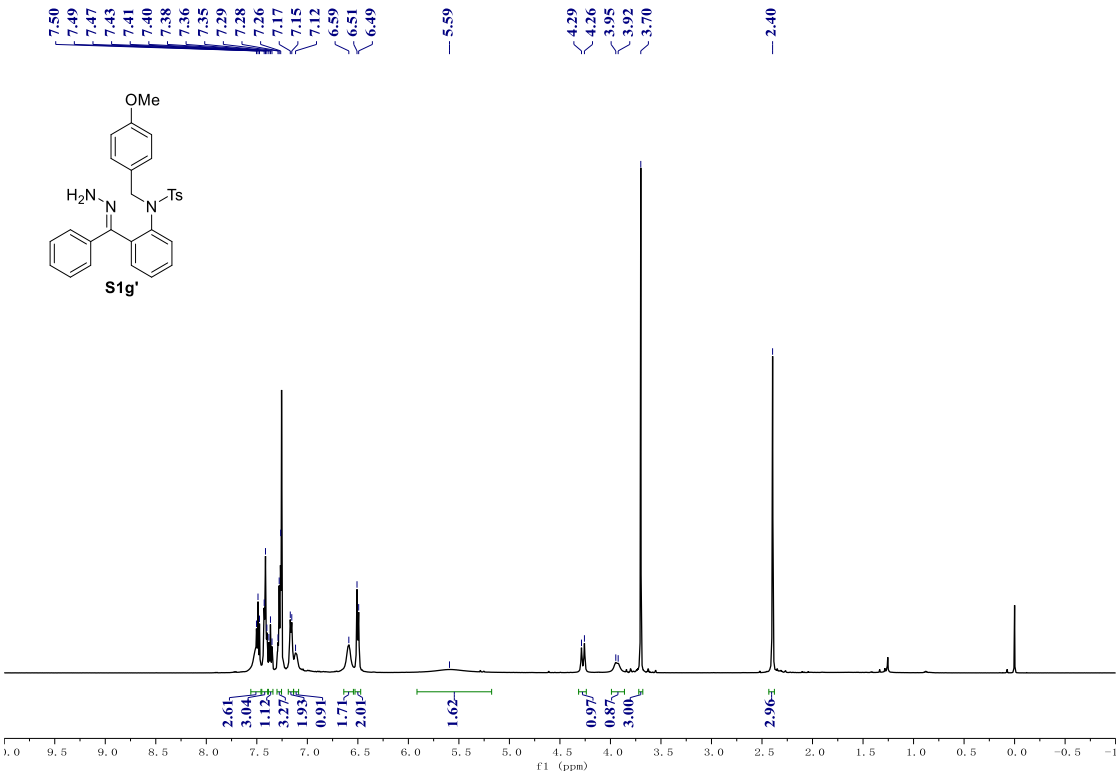
77.16
76.84
54.91
21.61
H2N
N
N
Ts
S1f'
f1 (ppm)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7.12
6.59
6.51
6.49
5.59
4.29
4.26
3.95
3.92
3.70
2.40
OMe
H2N
N
N
Ts
S1g'
2.61
3.04
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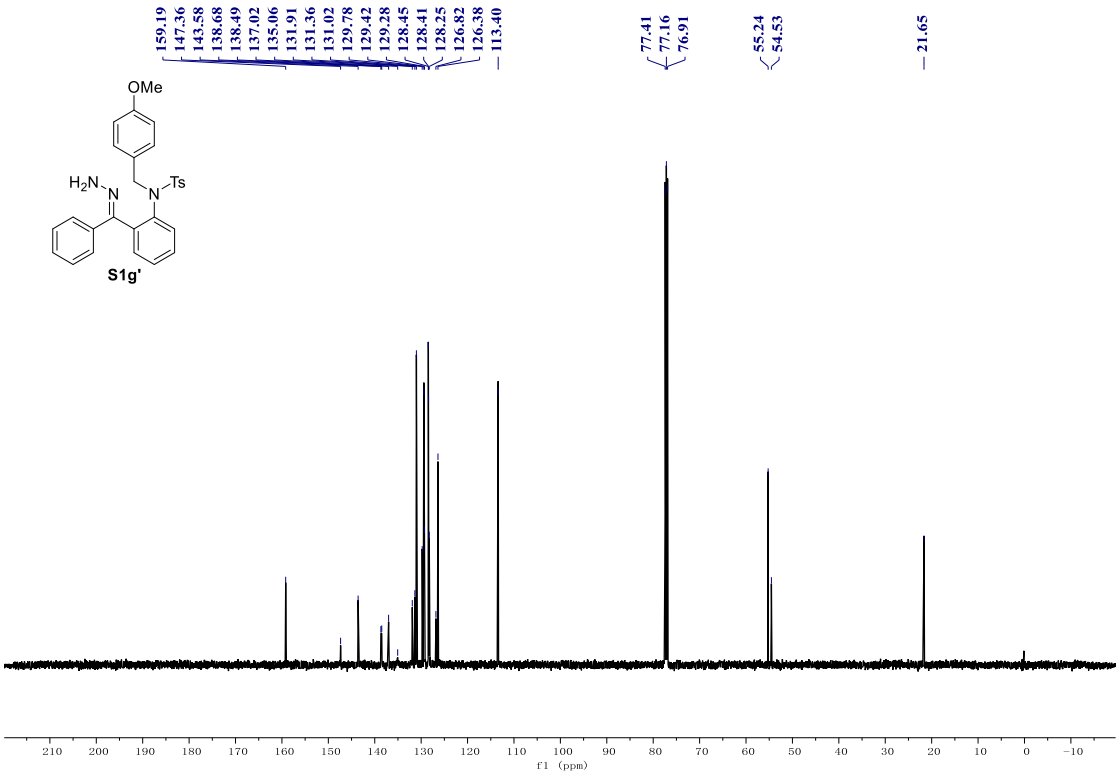
3.00
2.96
f1 (ppm)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128.41
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126.38
113.40
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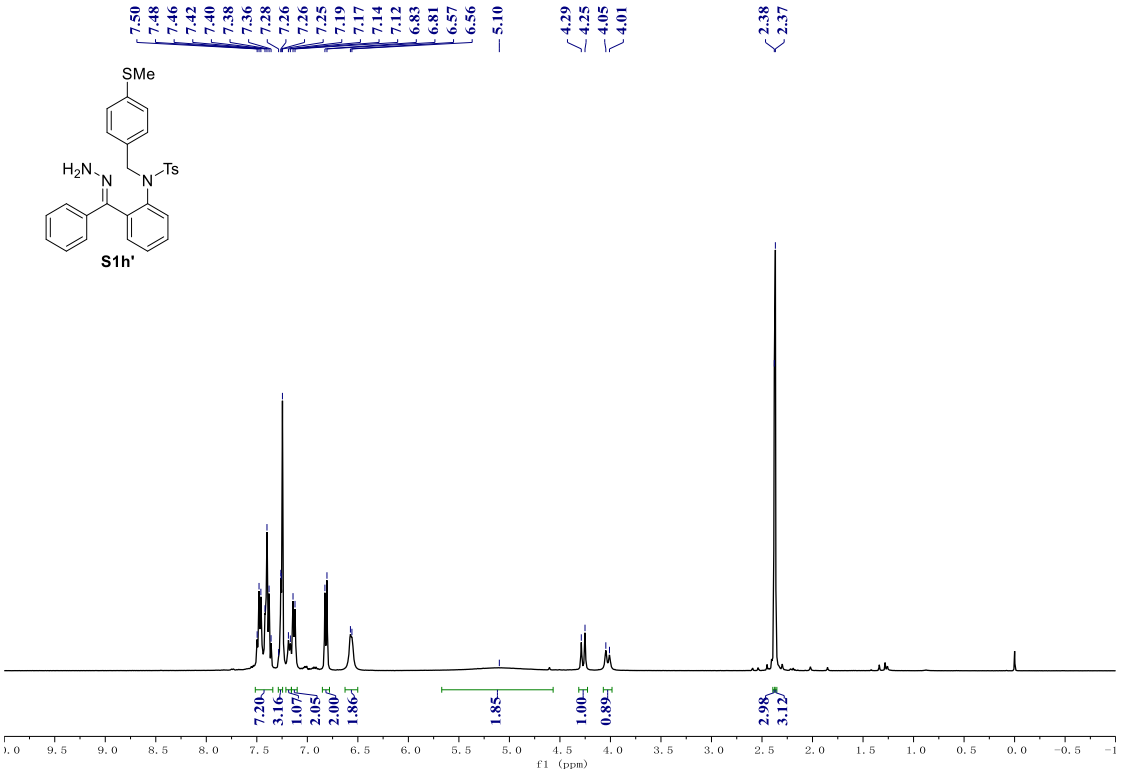
21.65
OMe
H2N
N
N
Ts
S1g'
f1 (ppm)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7.17
7.14
7.12
6.83
6.81
6.57
6.56
5.10
4.29
4.25
4.05
4.01
2.38
2.37
SMe
H2N
N
N
Ts
S1h'
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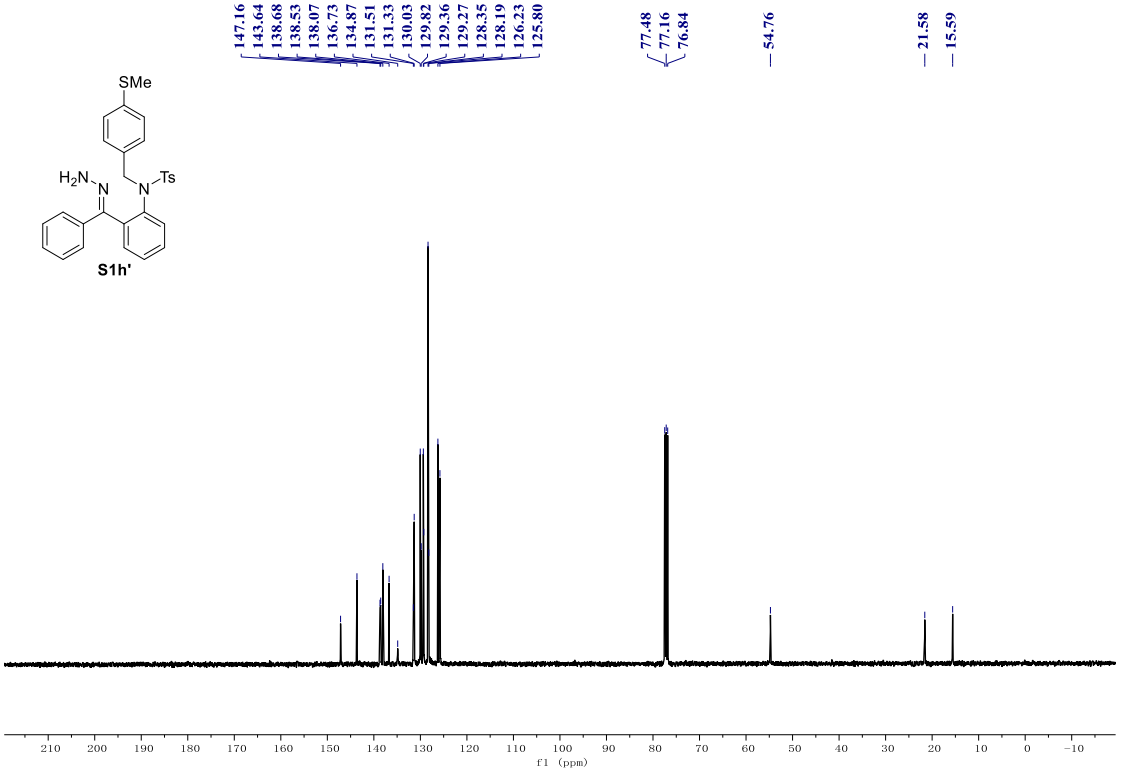
2.05
2.00
1.86
1.85
1.00
0.89
2.98
3.12
f1 (ppm)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129.27
128.35
128.19
126.23
125.80
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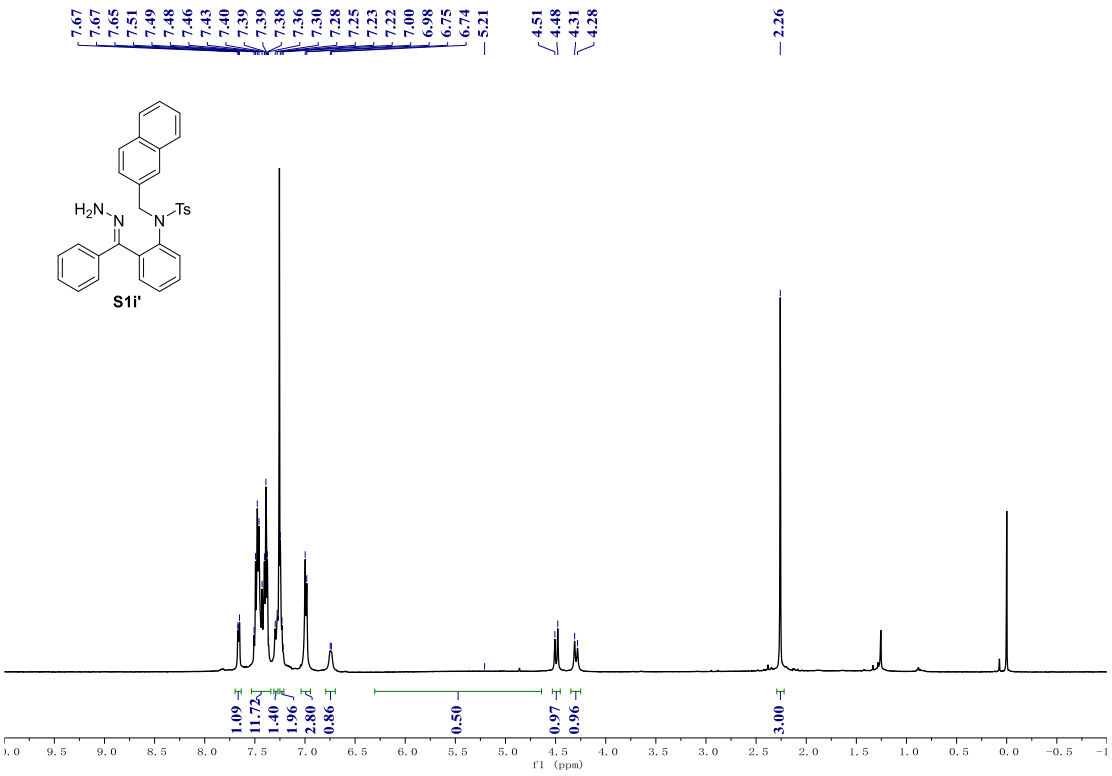
77.16
76.84
54.76
21.58
15.59
SMe
H2N
N
N
Ts
S1h'
f1 (ppm)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7.28
7.25
7.23
7.22
7.00
6.98
6.75
6.74
5.21
4.51
4.48
4.31
4.28
2.26
H2N
N
N
Ts
S1i'
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1.40
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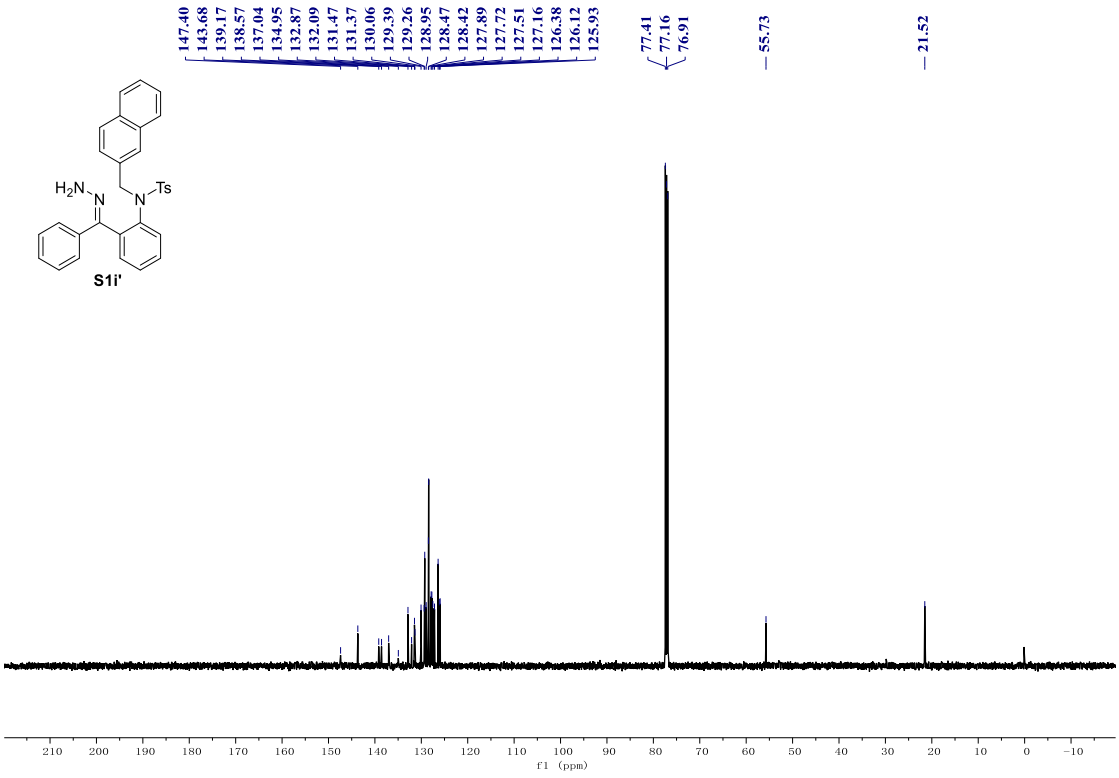
2.80
0.86
0.50
0.97
0.96
3.00
f1 (ppm)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128.47
128.42
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127.51
127.16
126.38
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76.91
55.73
21.52
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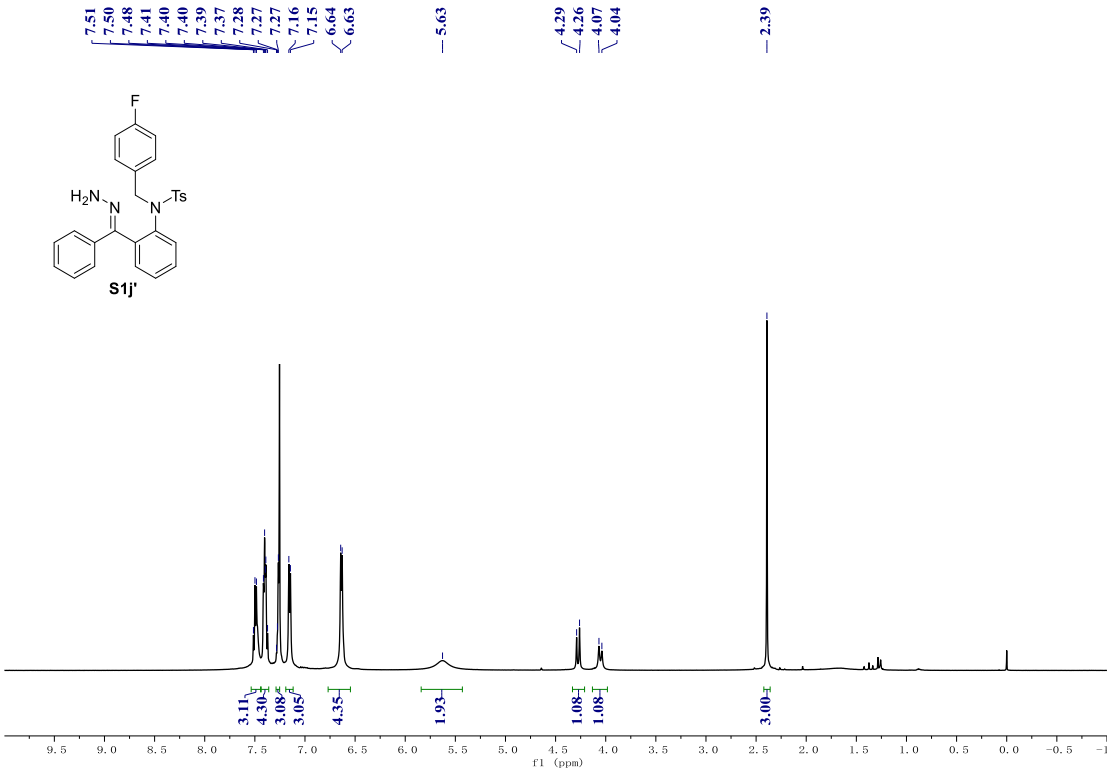
N
N
Ts
S1i'
f1 (ppm)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6.63
5.63
4.29
4.26
4.07
4.04
2.39
F
H2N
N
N
Ts
S1j'
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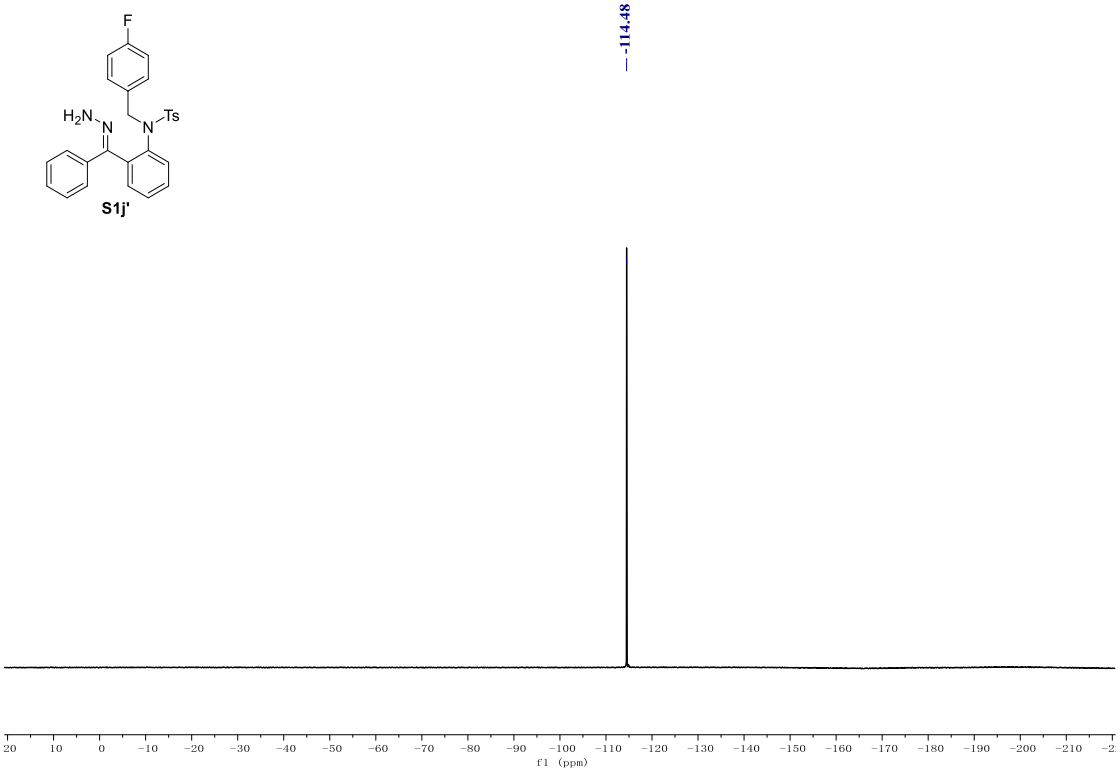
4.30
3.08
3.05
4.35
1.93
1.08
1.08
3.00
f1 (ppm)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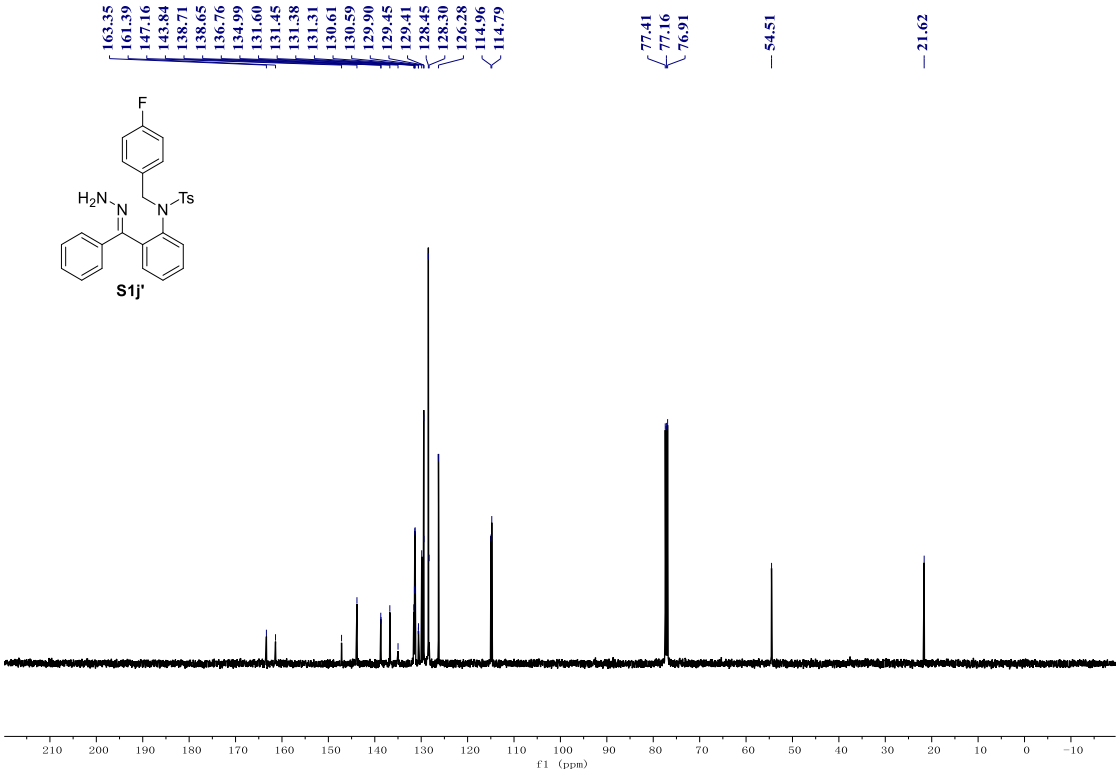
N
N
Ts
S1j'
f1 (ppm)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129.41
128.45
128.30
126.28
114.96
114.79
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77.16
76.91
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21.62
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N
N
Ts
S1j'
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200
190
180
170
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30
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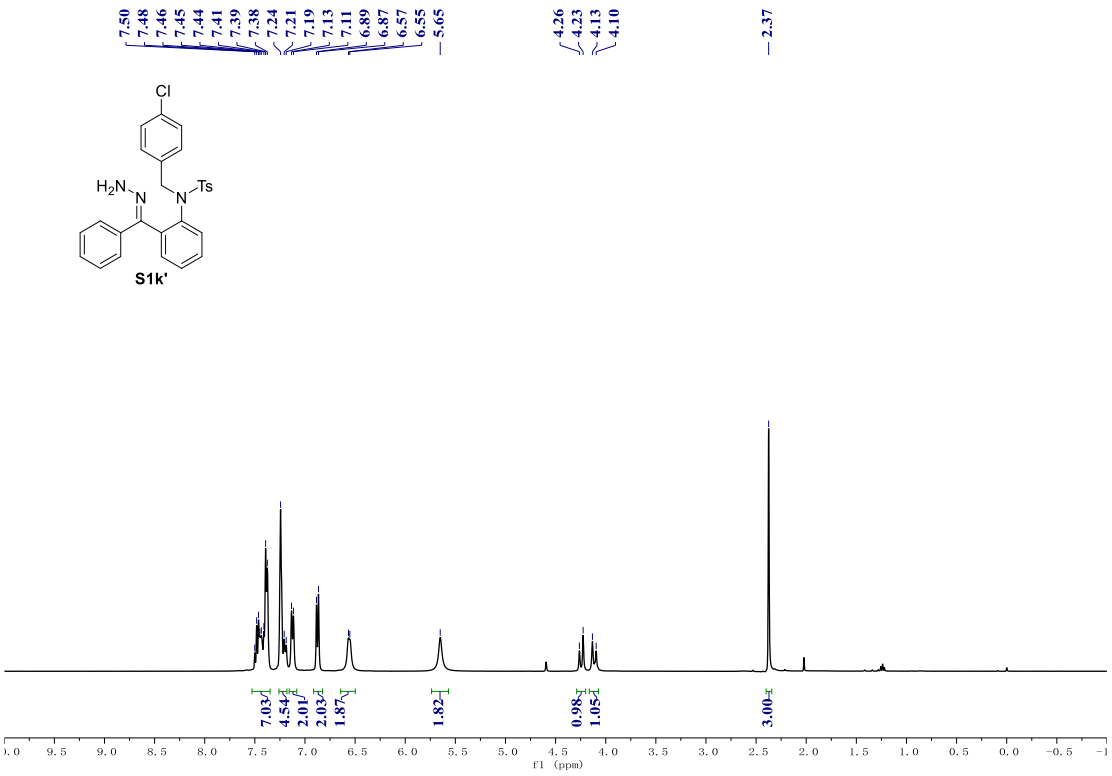
f1 (ppm)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7.11
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6.87
6.57
6.55
5.65
4.26
4.23
4.13
4.10
2.37
Cl
H2N
N
N
Ts
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2.03
1.87
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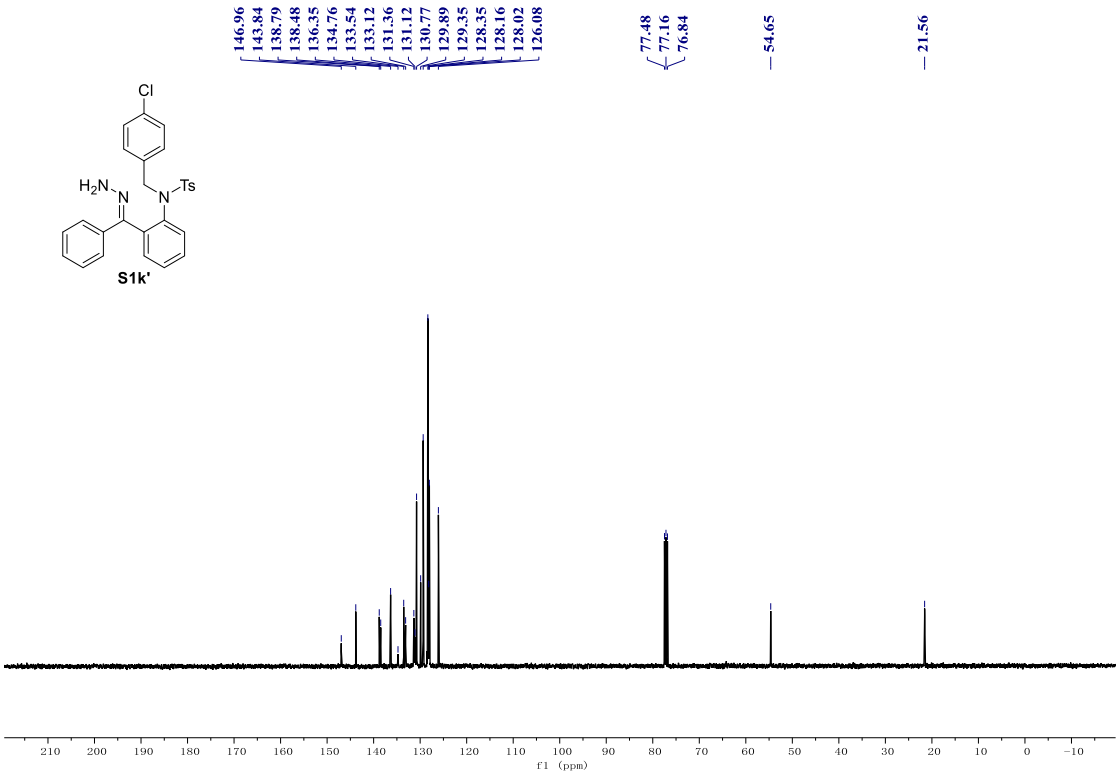
0.98
1.05
3.00
f1 (ppm)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129.35
128.35
128.16
128.02
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76.84
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Cl
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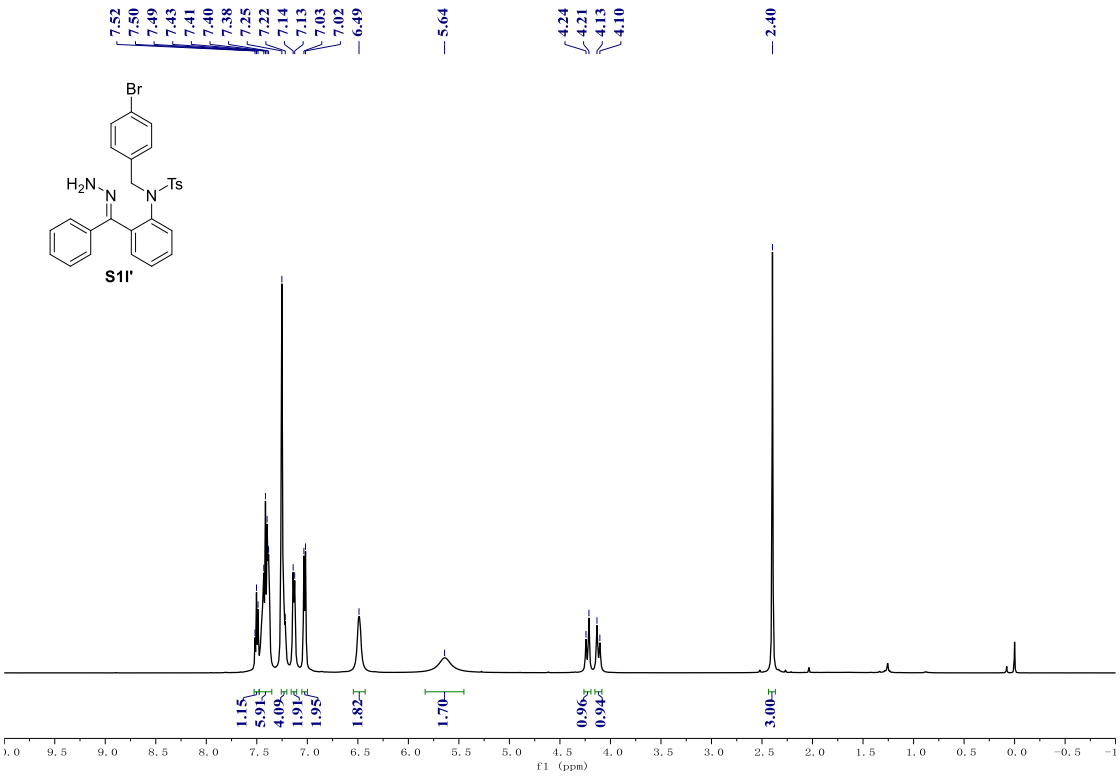
N
N
Ts
S1k'
f1 (ppm)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7.03
7.02
6.49
5.64
4.24
4.21
4.13
4.10
2.40
Br
H2N
N
N
Ts
S1l'
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4.09
1.91
1.95
1.82
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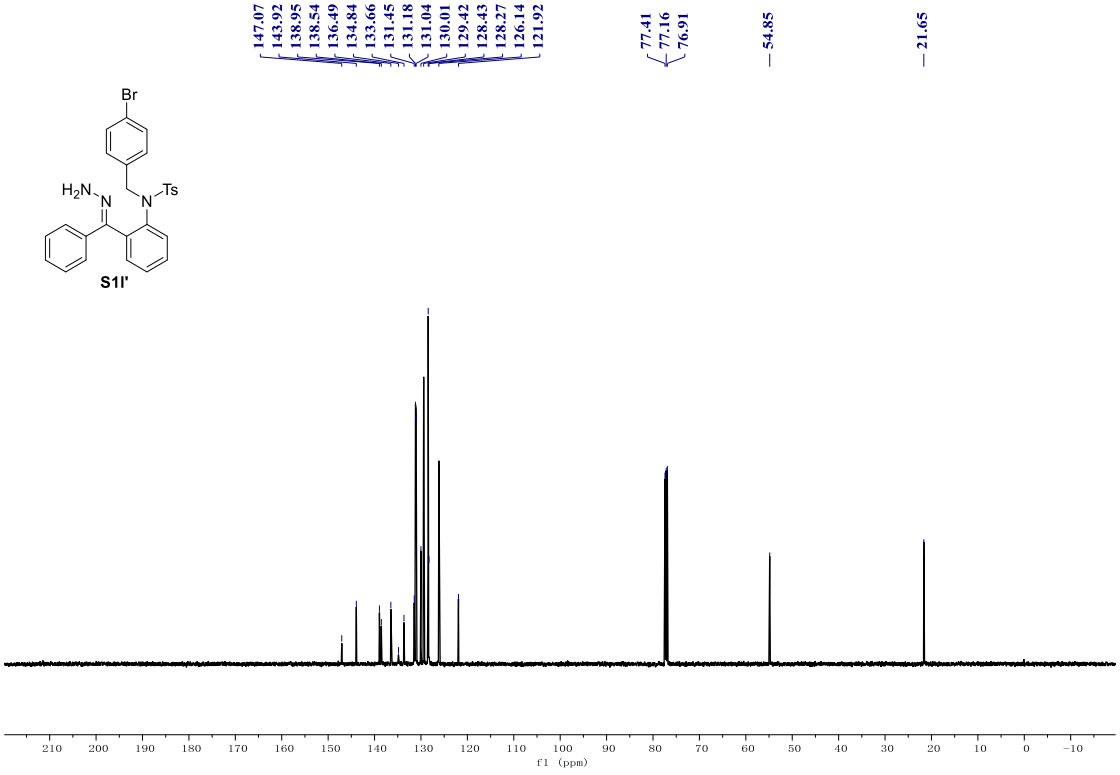
0.96
0.94
3.00
f1 (ppm)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128.27
126.14
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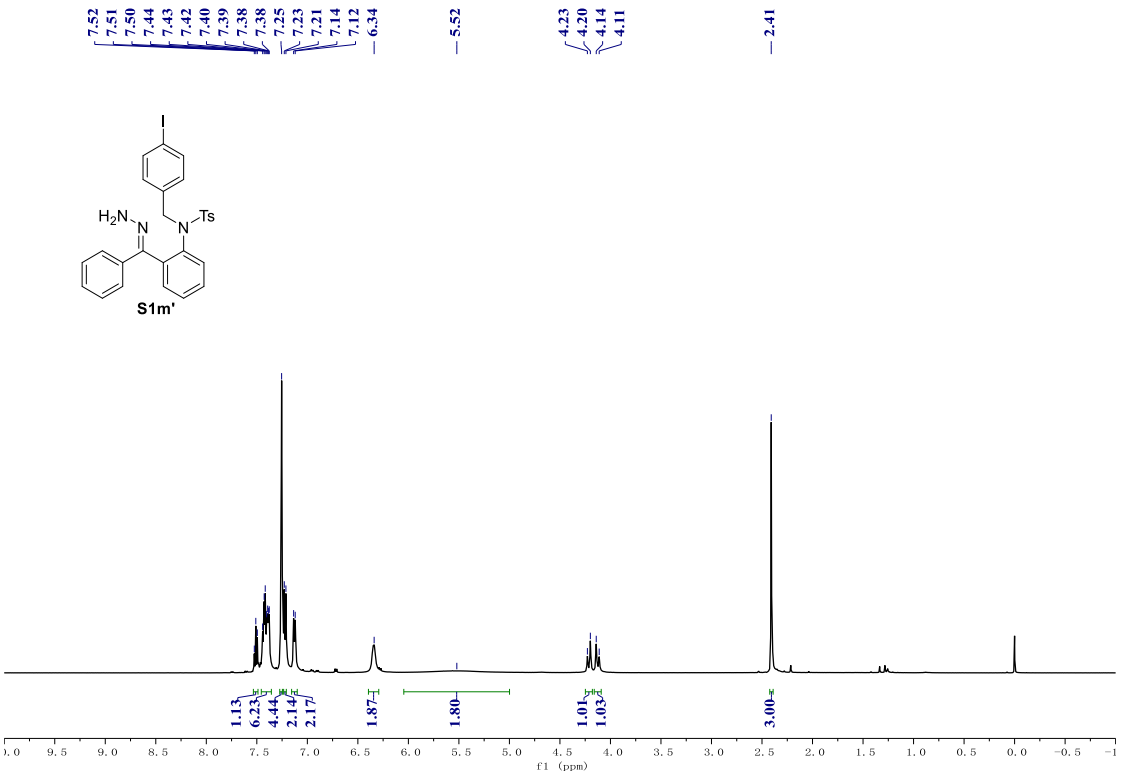
76.91
54.85
21.65
Br
H2N
N
N
Ts
S1l'
f1 (ppm)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7.23
7.21
7.14
7.12
6.34
5.52
4.23
4.20
4.14
4.11
2.41
I
H2N
N
N
Ts
S1m'
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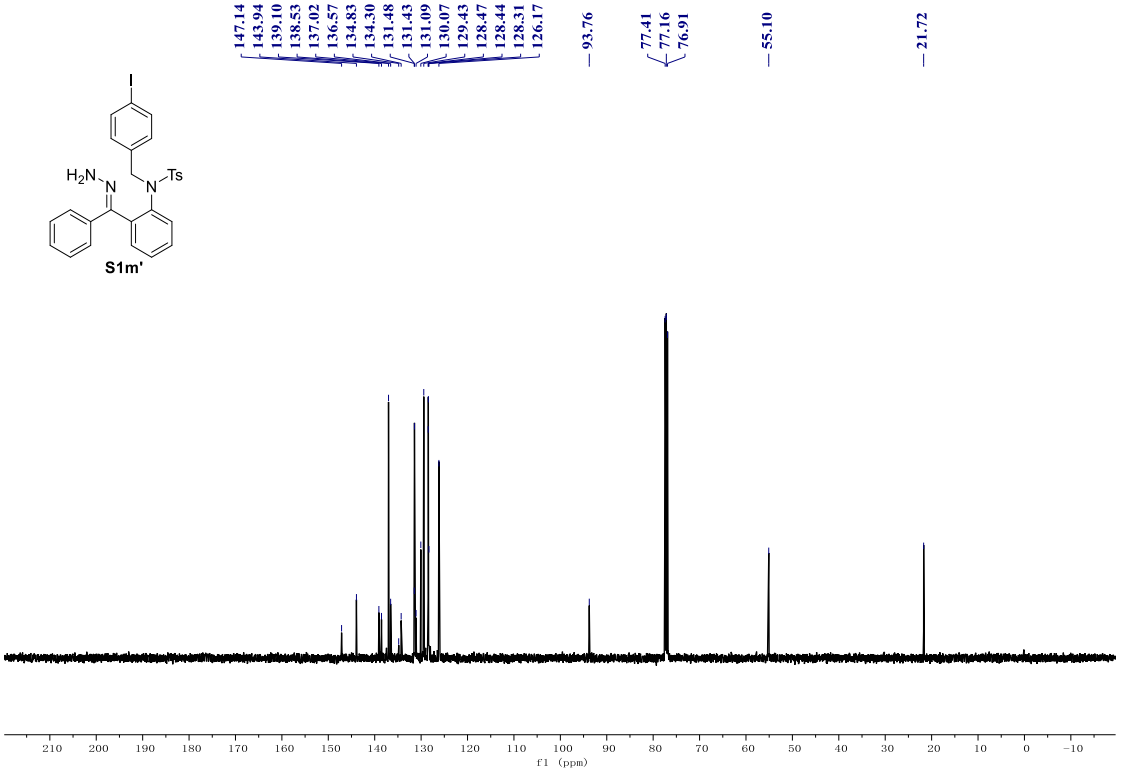
1.01
1.03
3.00
f1 (ppm)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128.44
128.31
126.17
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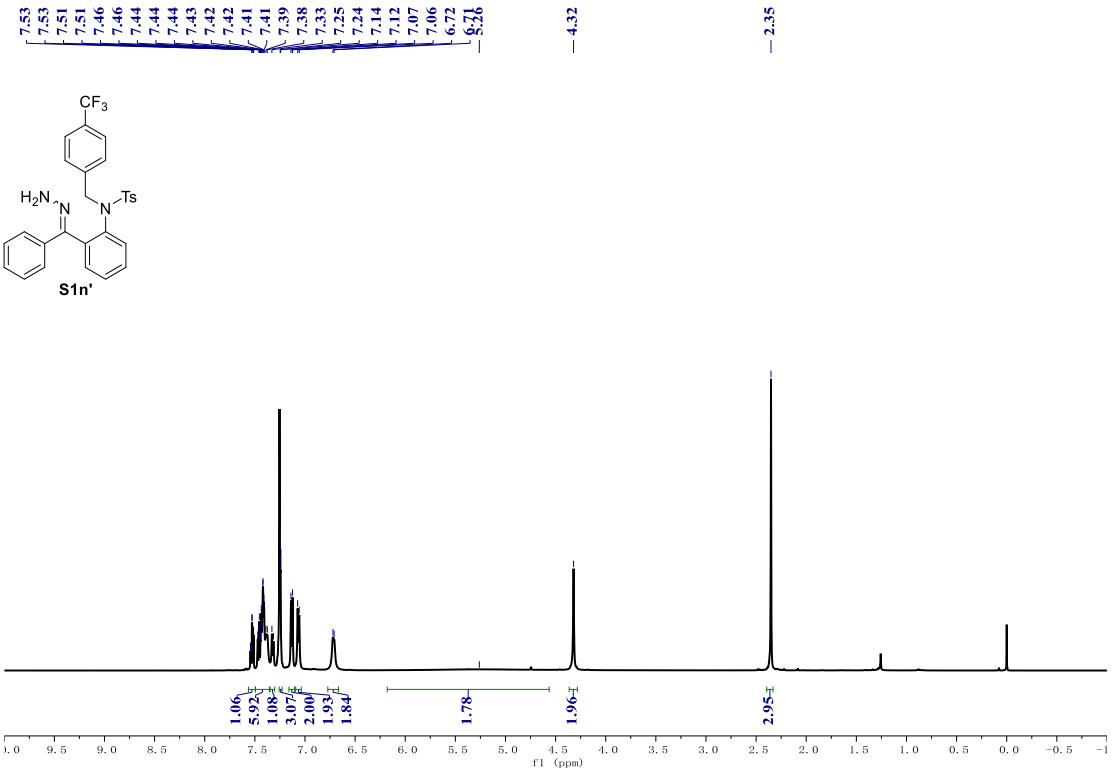
76.91
55.10
21.72
I
H2N
N
N
Ts
S1m'
f1 (ppm)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7.41
7.39
7.38
7.33
7.25
7.24
7.14
7.12
7.07
7.06
6.72
6.71
5.26
4.32
2.35
CF3
H2N
N
N
Ts
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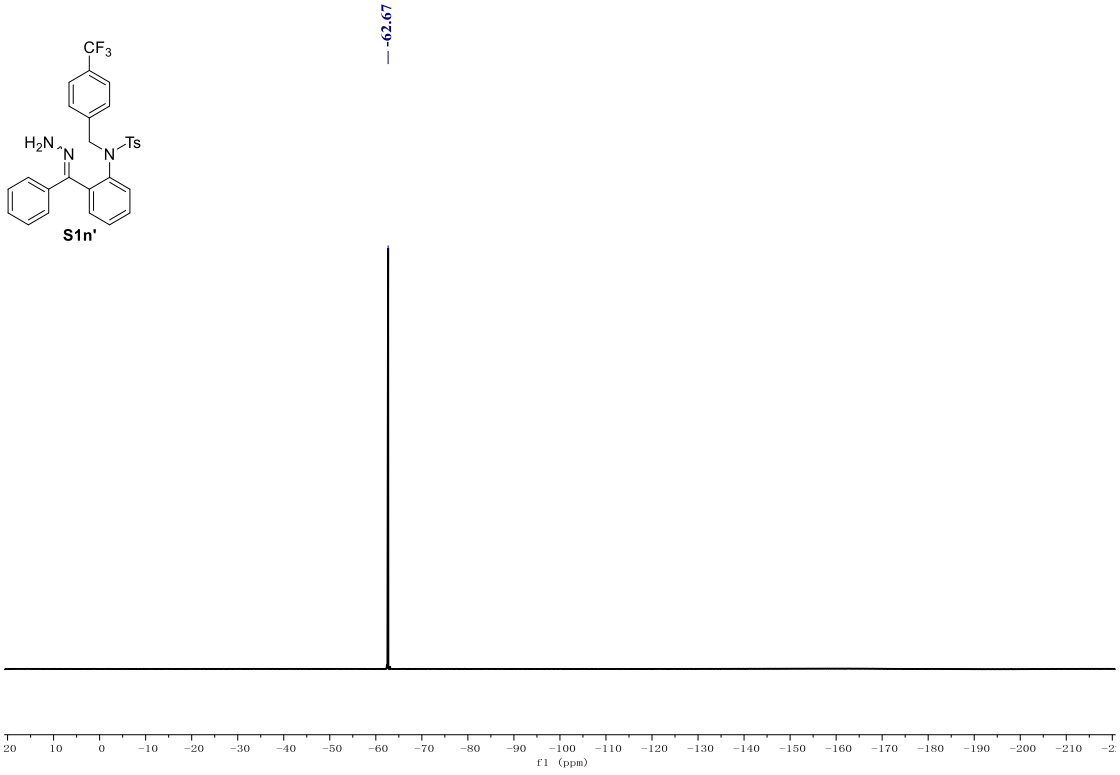
1.08
3.07
2.00
1.93
1.84
1.78
1.96
2.95
f1 (ppm)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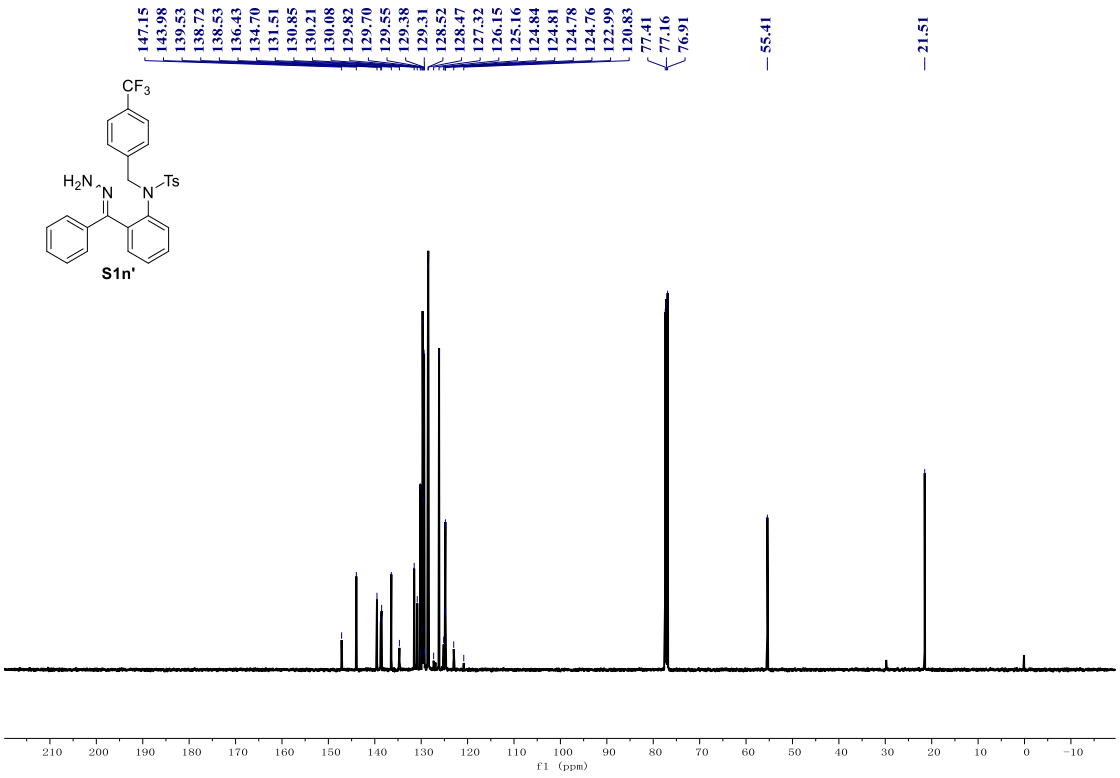
f1 (ppm)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124.81
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124.76
122.99
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77.41
77.16
76.91
55.41
21.51
CF3
H2N
N
N
Ts
S1n'
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200
190
180
170
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120
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100
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80
70
60
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40
30
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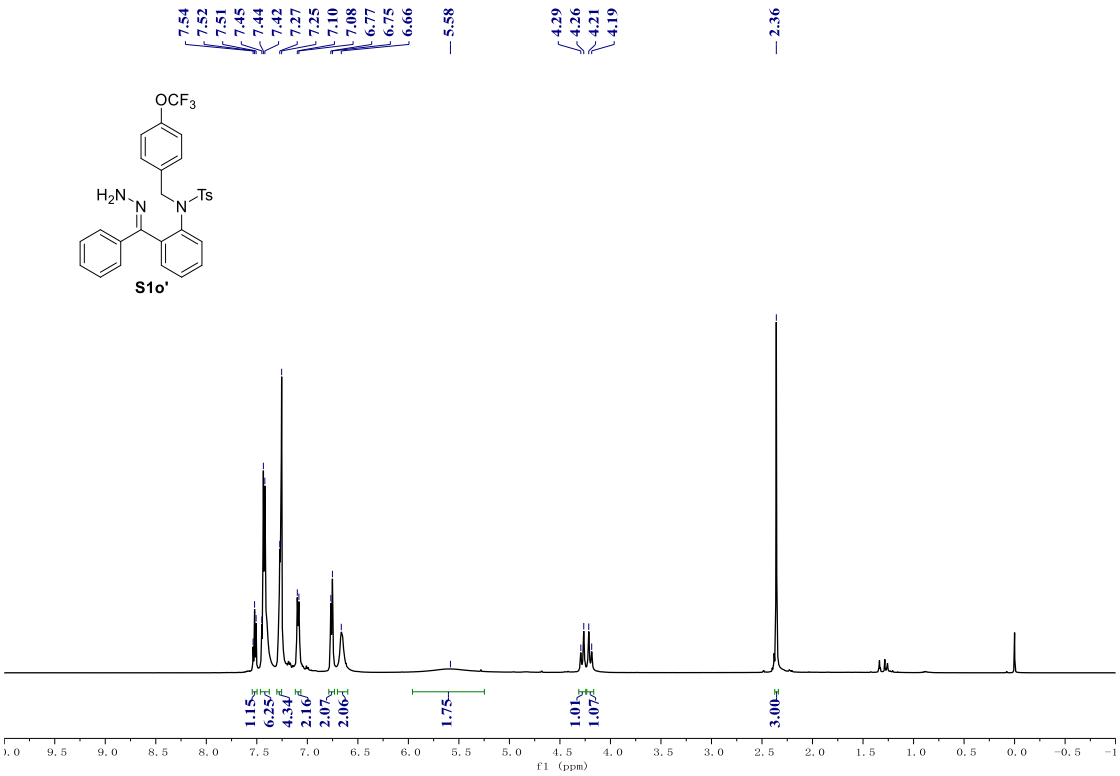
f1 (ppm)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6.75
6.66
5.58
4.29
4.26
4.21
4.19
2.36
OCF3
H2N
N
N
Ts
S1o'
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4.34
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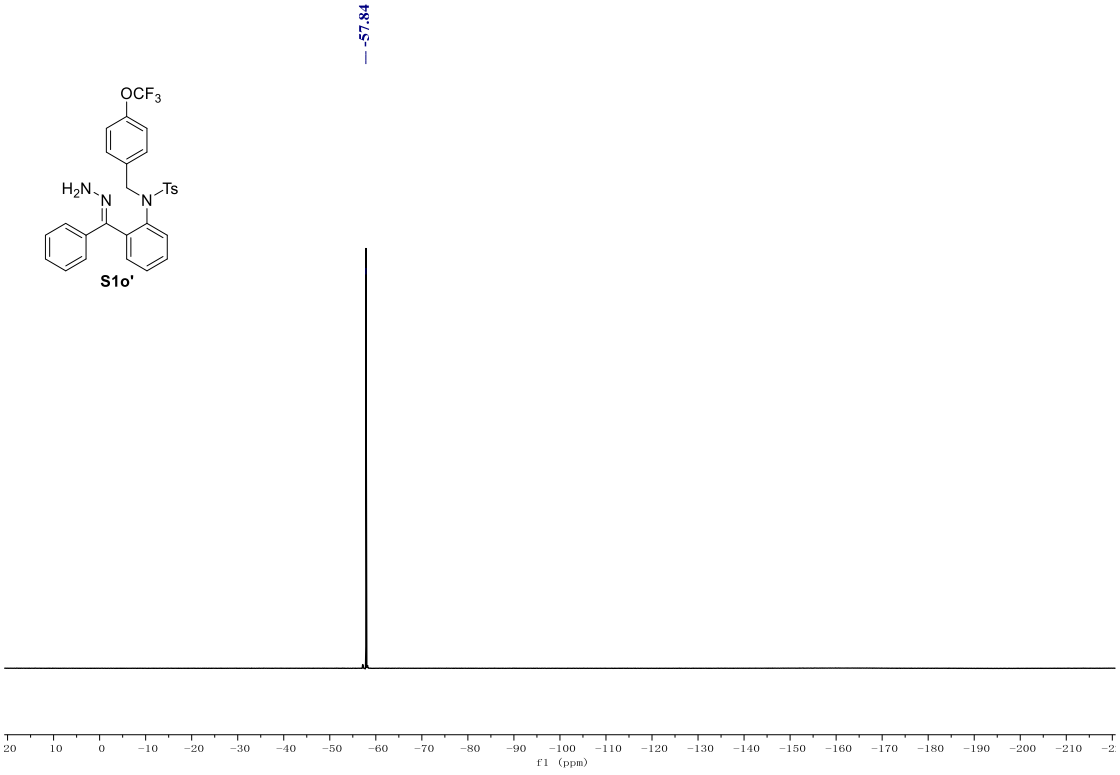
2.07
2.06
1.75
1.01
1.07
3.00
f1 (ppm)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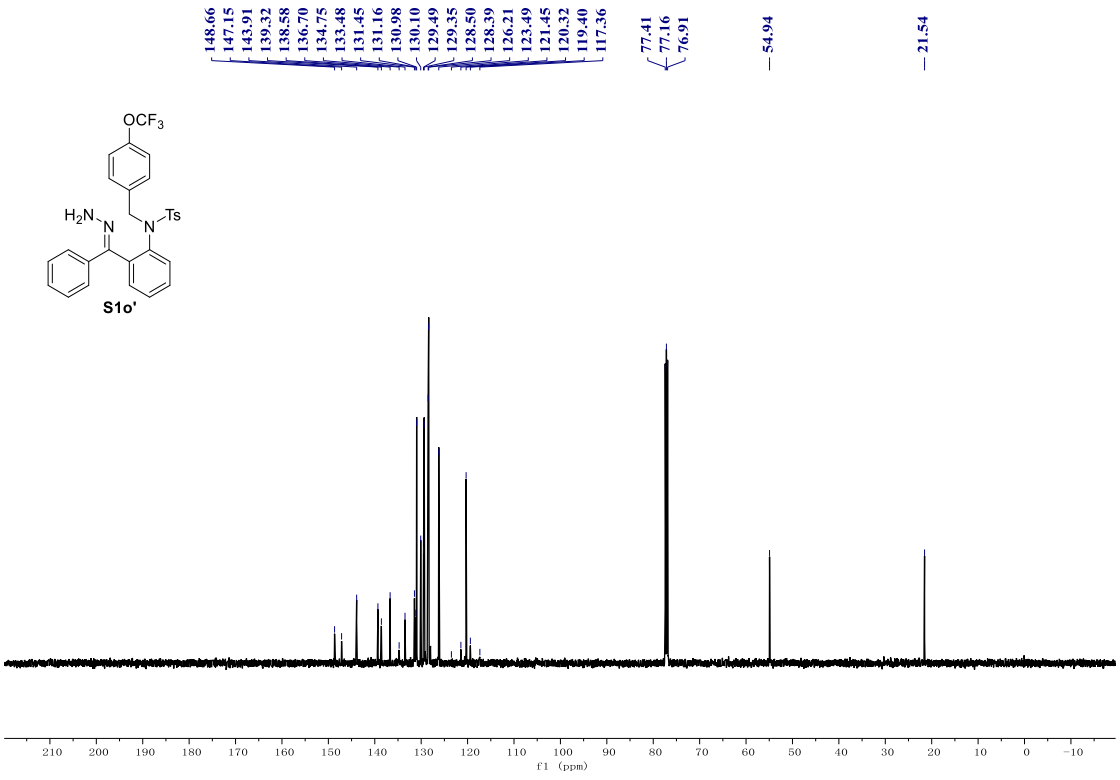
H2N
N
N
Ts
S1o'
f1 (ppm)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126.21
123.49
121.45
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119.40
117.36
77.41
77.16
76.91
54.94
21.54
OCF3
H2N
N
N
Ts
S1o'
210
200
190
180
170
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100
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60
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40
30
20
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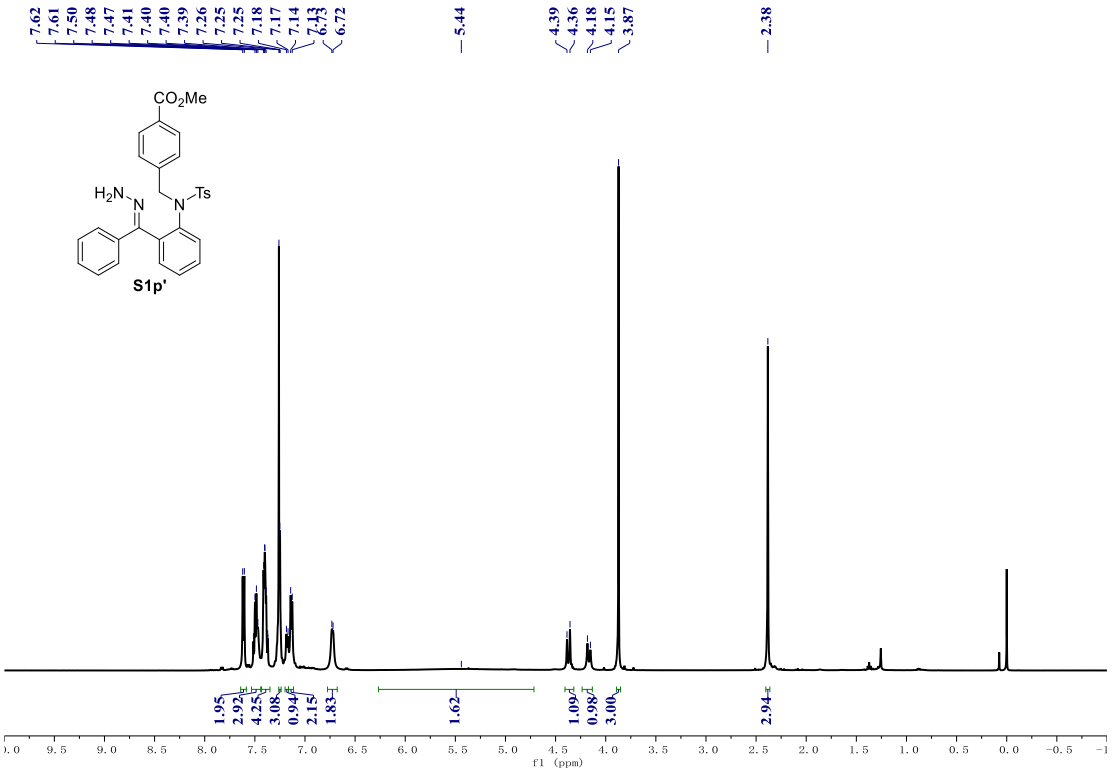
0
−10
f1 (ppm)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7.18
7.17
7.14
6.72
5.44
4.39
4.36
4.18
4.15
3.87
2.38
CO2Me
H2N
N
N
Ts
S1p'
1.95
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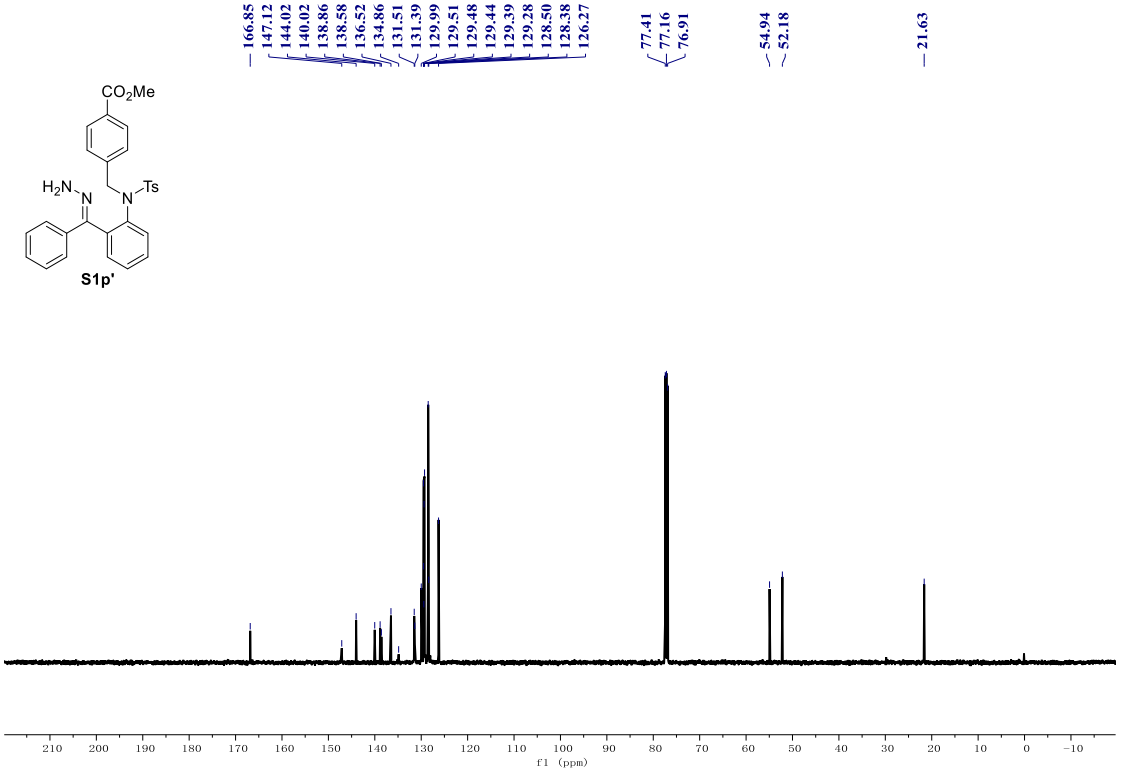
2.15
1.83
1.62
1.09
0.98
3.00
2.94
f1 (ppm)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54.94
52.18
21.63
CO2Me
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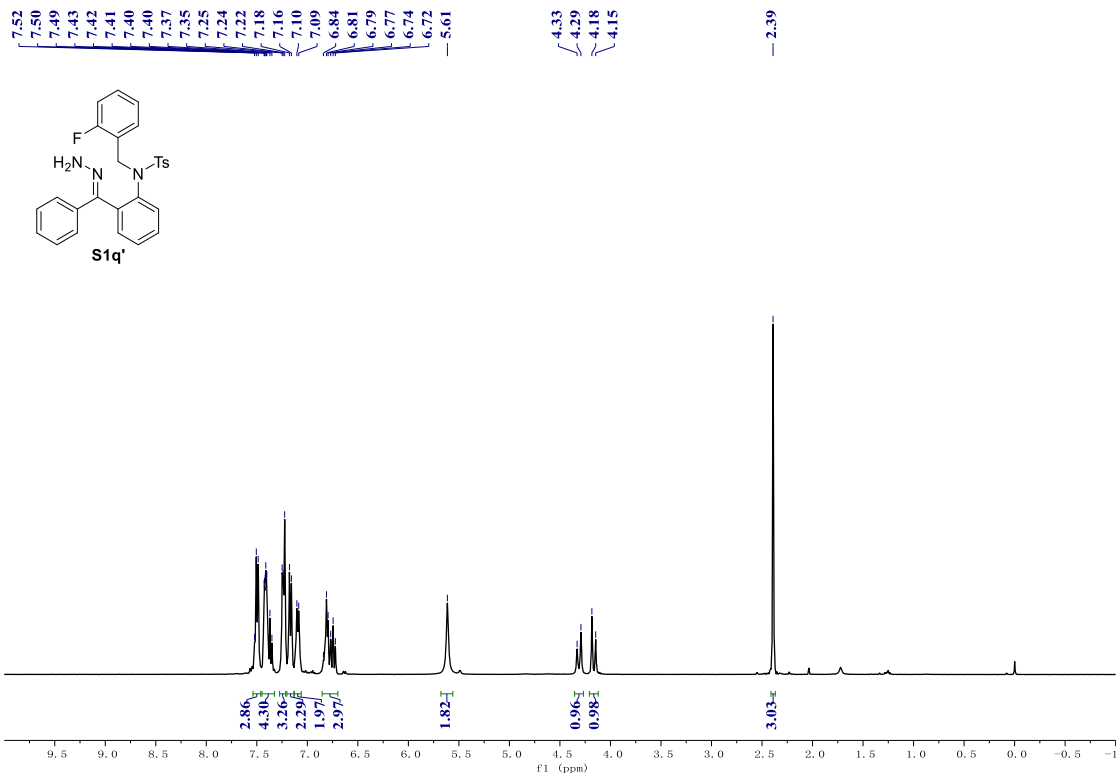
Ts
S1p'
f1 (ppm)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7.16
7.10
7.09
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6.81
6.79
6.77
6.74
6.72
5.61
4.33
4.29
4.18
4.15
2.39
F
H2N
N
N
Ts
S1q'
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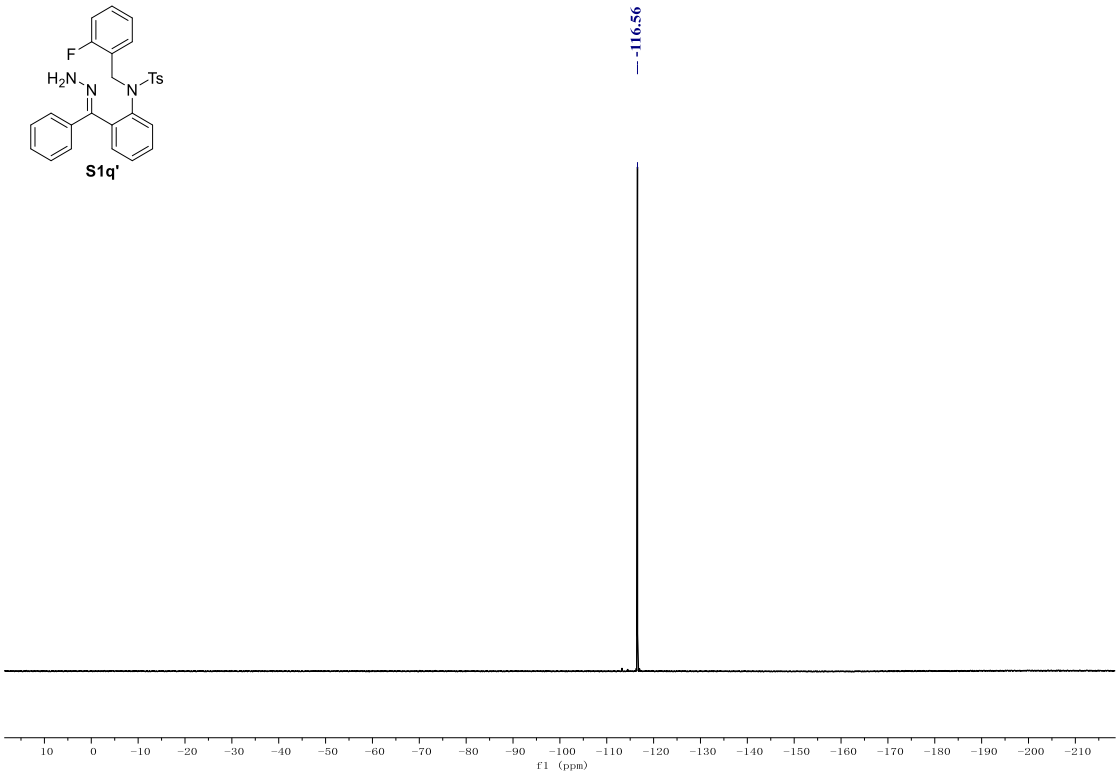
f1 (ppm)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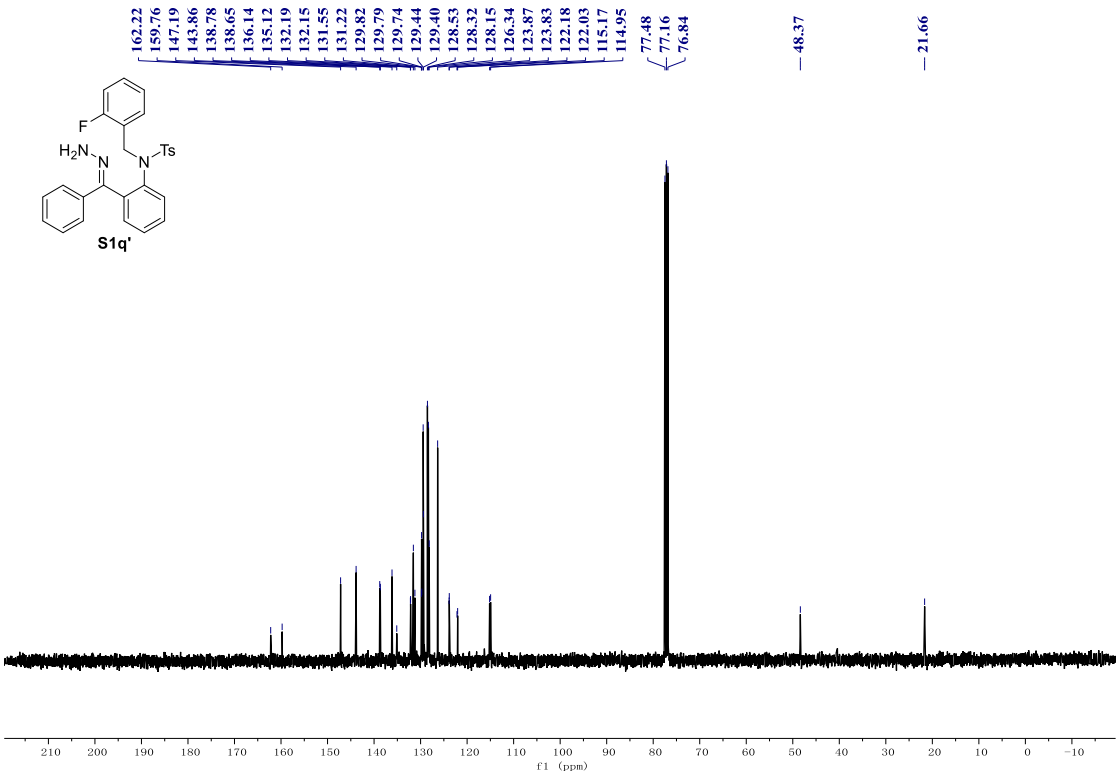
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128.15
126.34
123.87
123.83
122.18
122.03
115.17
114.95
77.48
77.16
76.84
48.37
21.66
F
H2N
N
N
Ts
S1q'
210
200
190
180
170
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100
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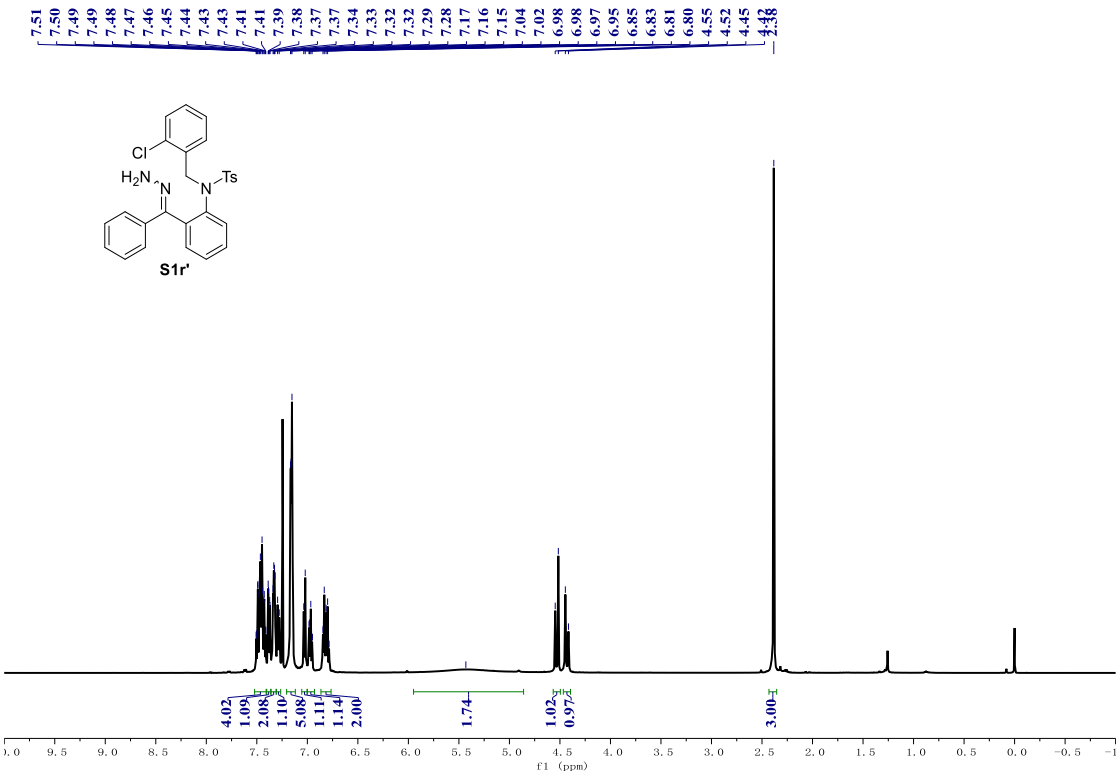
f1 (ppm)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7.15
7.04
7.02
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6.98
6.97
6.95
6.85
6.83
6.81
6.80
4.55
4.52
4.45
2.38
Cl
H2N
N
N
Ts
S1r'
4.02
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1.02
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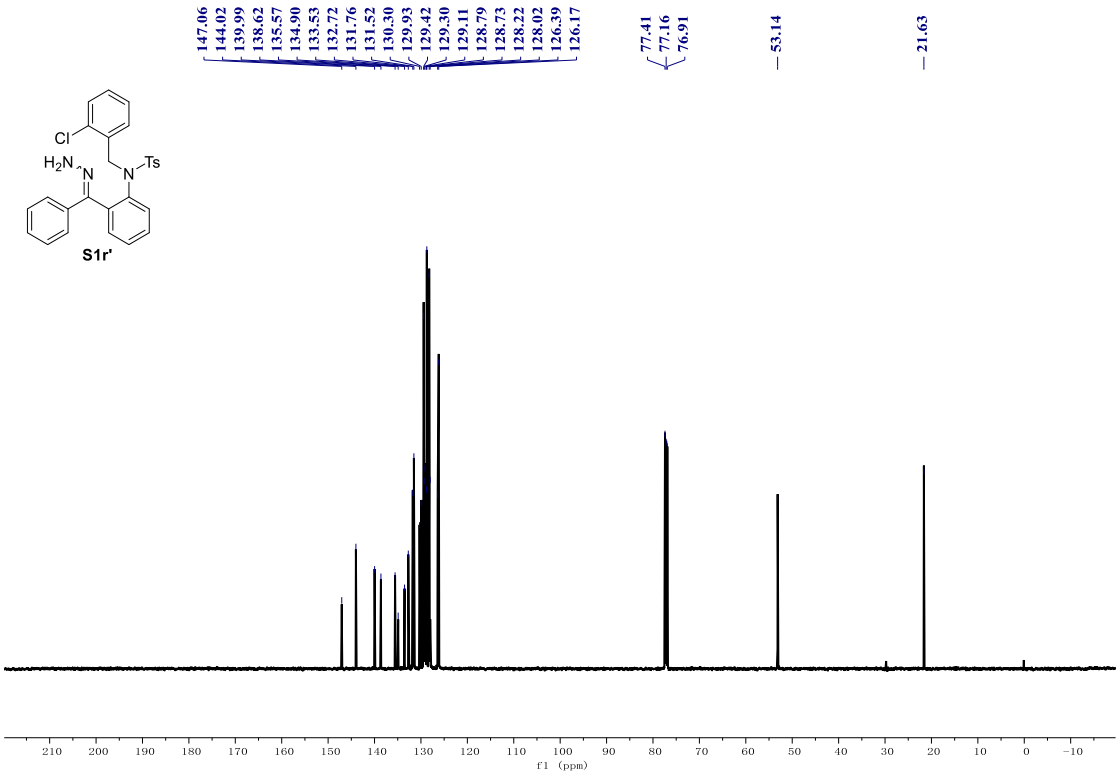
f1 (ppm)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128.22
128.02
126.39
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76.91
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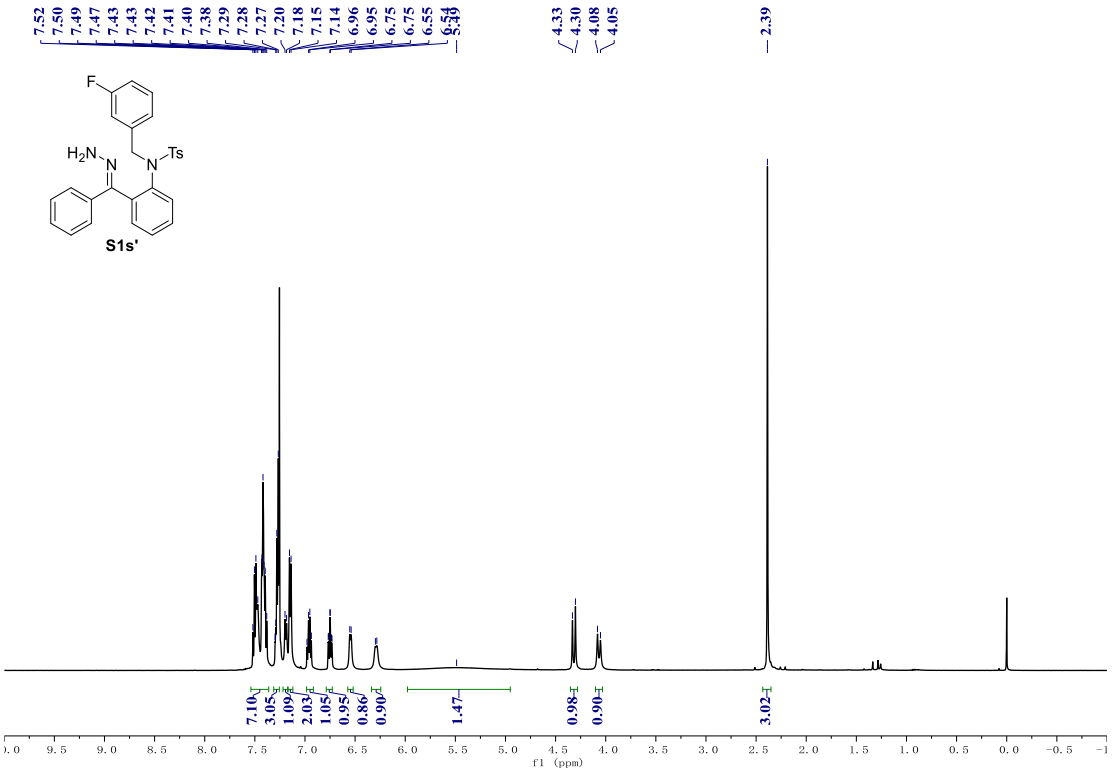
Cl
H2N
N
N
Ts
S1r'
f1 (ppm)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7.15
7.14
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6.75
6.75
6.55
6.54
5.40
4.33
4.30
4.08
4.05
2.39
F
H2N
N
N
Ts
S1s'
7.10
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1.05
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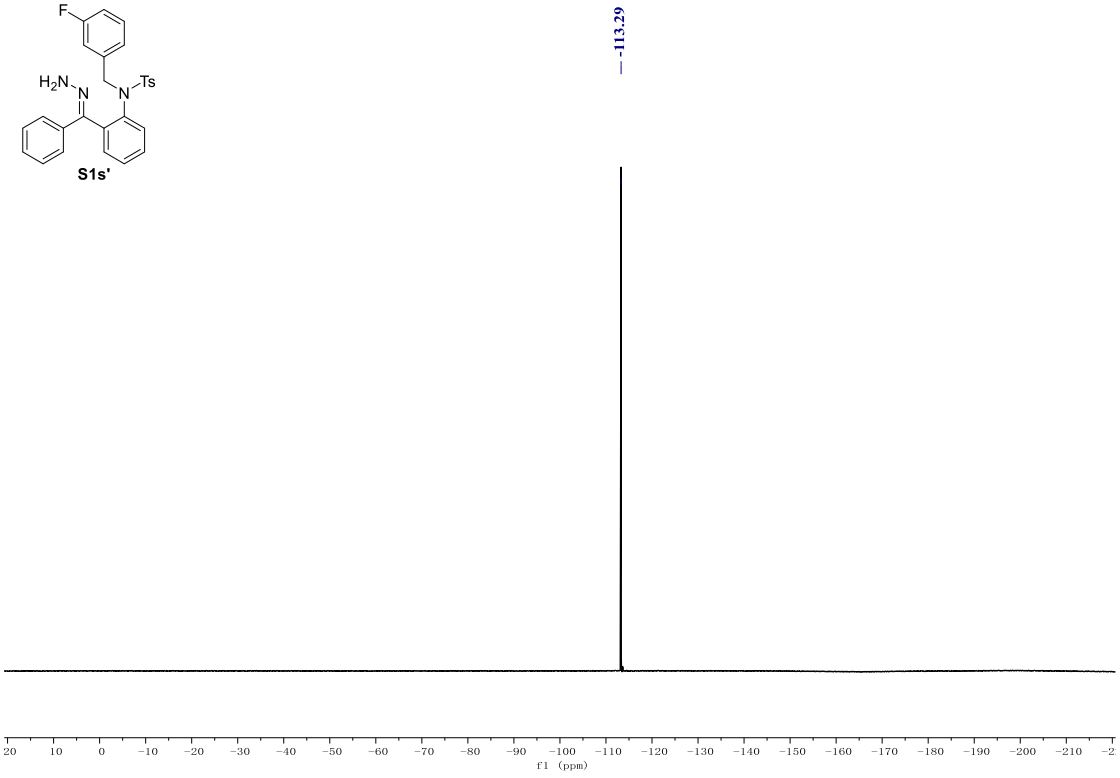
1.47
0.98
0.90
3.02
f1 (ppm)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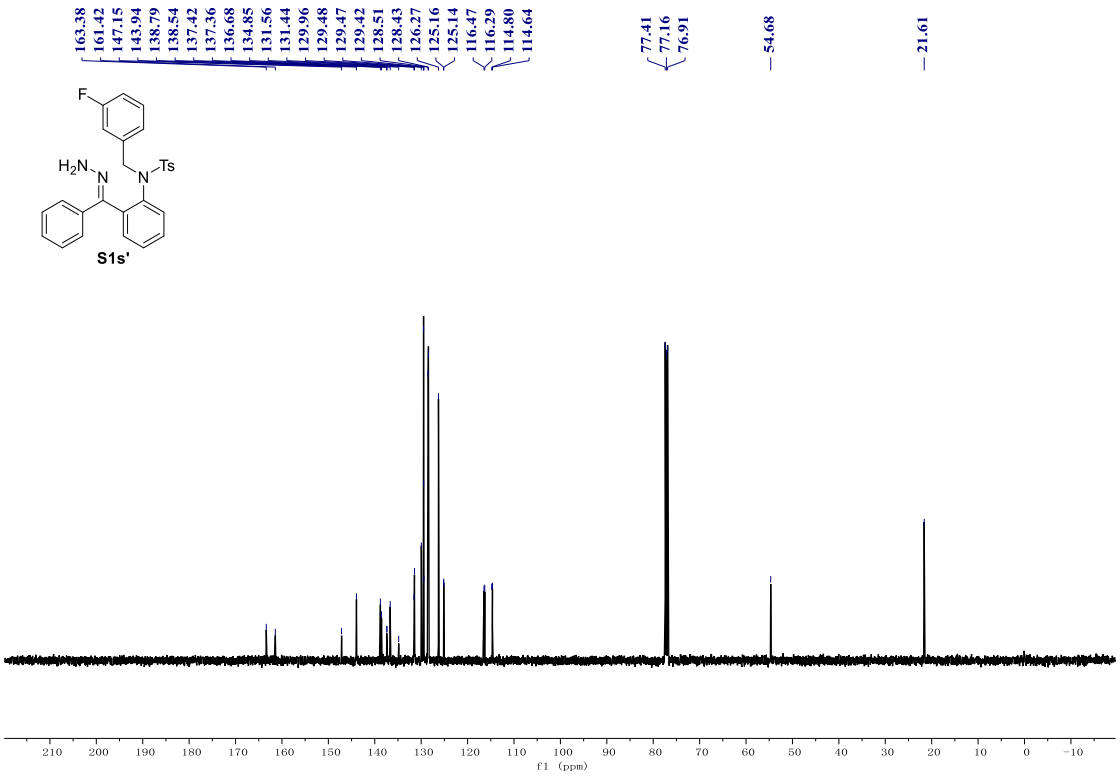
N
N
Ts
S1s'
f1 (ppm)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128.43
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125.14
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116.29
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114.64
77.41
77.16
76.91
54.68
21.61
F
H2N
N
N
Ts
S1s'
210
200
190
180
170
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100
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80
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30
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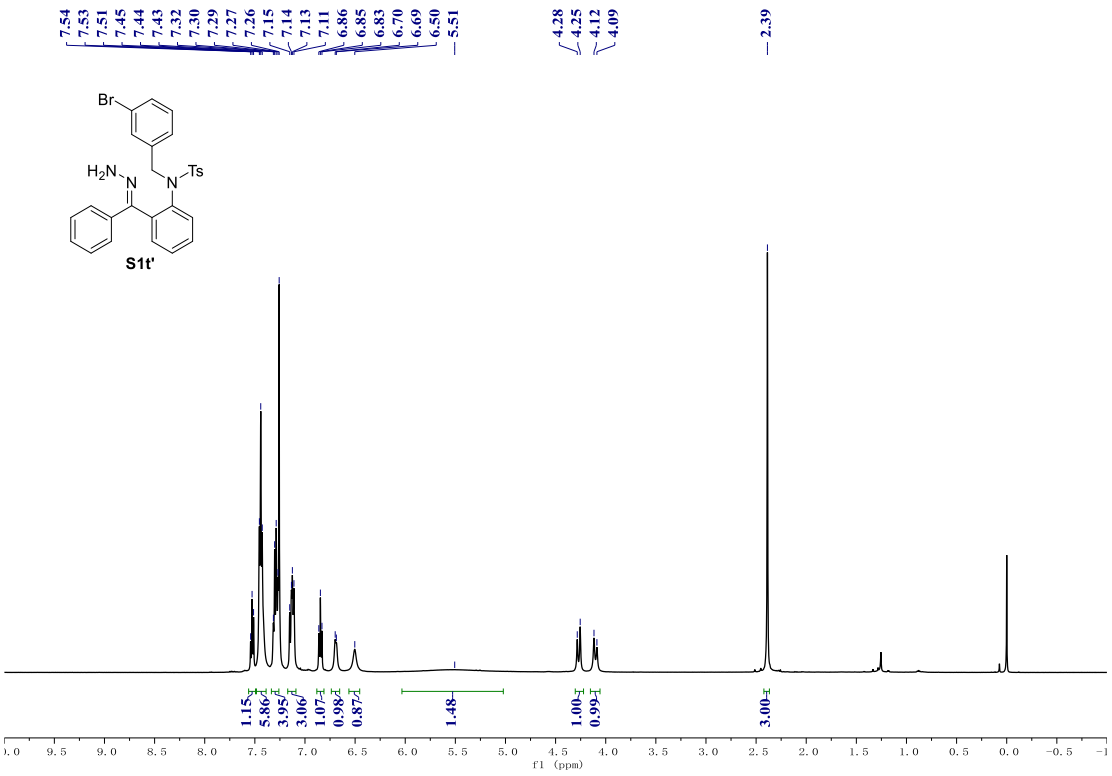
-10
f1 (ppm)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7.13
7.11
6.86
6.85
6.83
6.70
6.69
6.50
5.51
4.28
4.25
4.12
4.09
2.39
Br
H2N
N
N
Ts
S1t'
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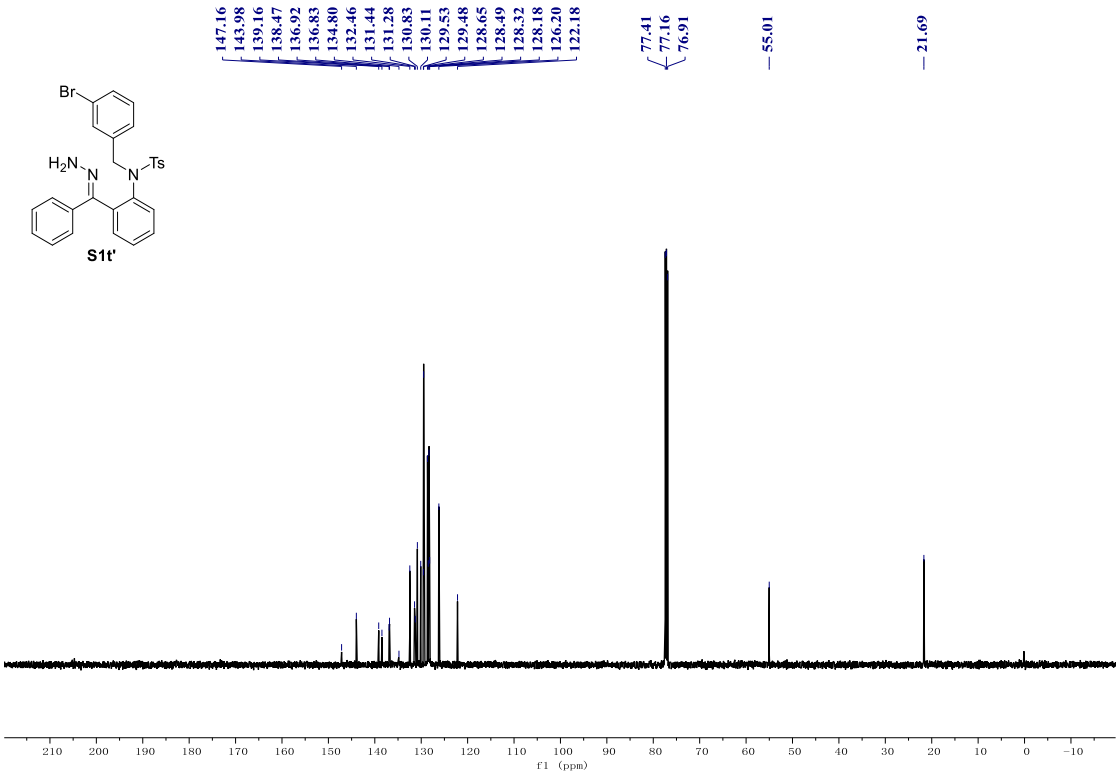
3.06
1.07
0.98
0.87
1.48
1.00
0.99
3.00
f1 (ppm)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128.65
128.49
128.32
128.18
126.20
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77.16
76.91
55.01
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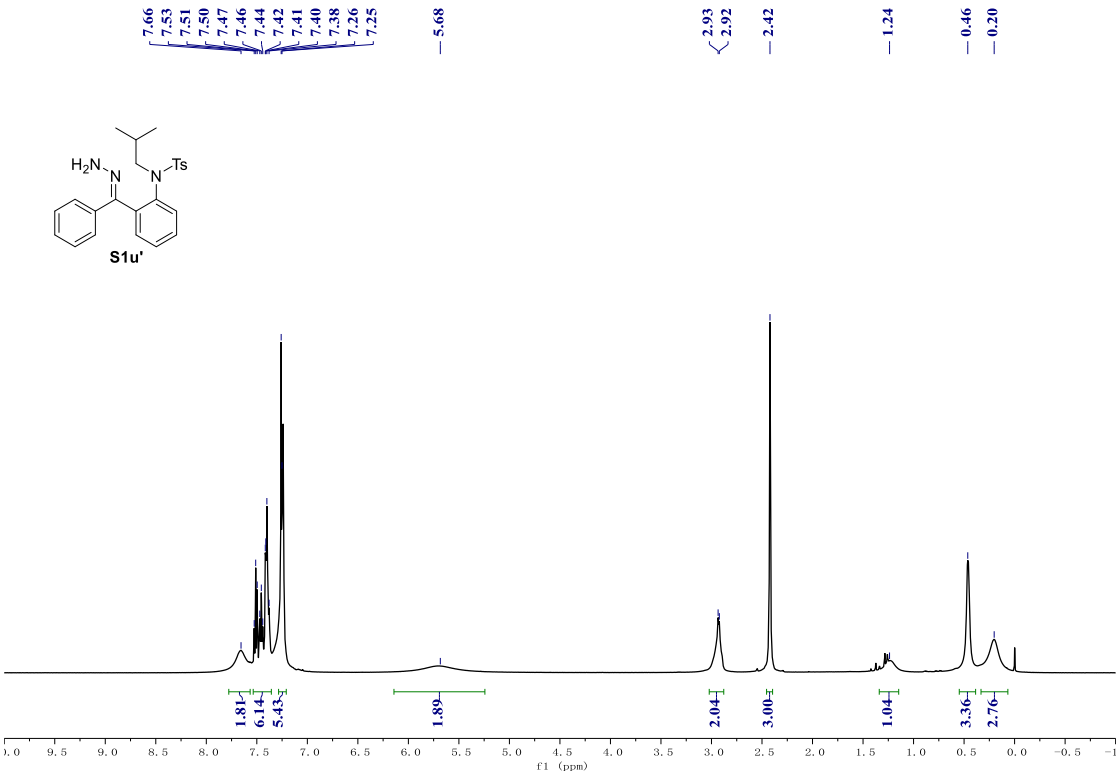
Br
H2N
N
N
Ts
S1t'
f1 (ppm)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7.26
7.25
5.68
2.93
2.92
2.42
1.24
0.46
0.20
S1u'
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5.43
1.89
2.04
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1.04
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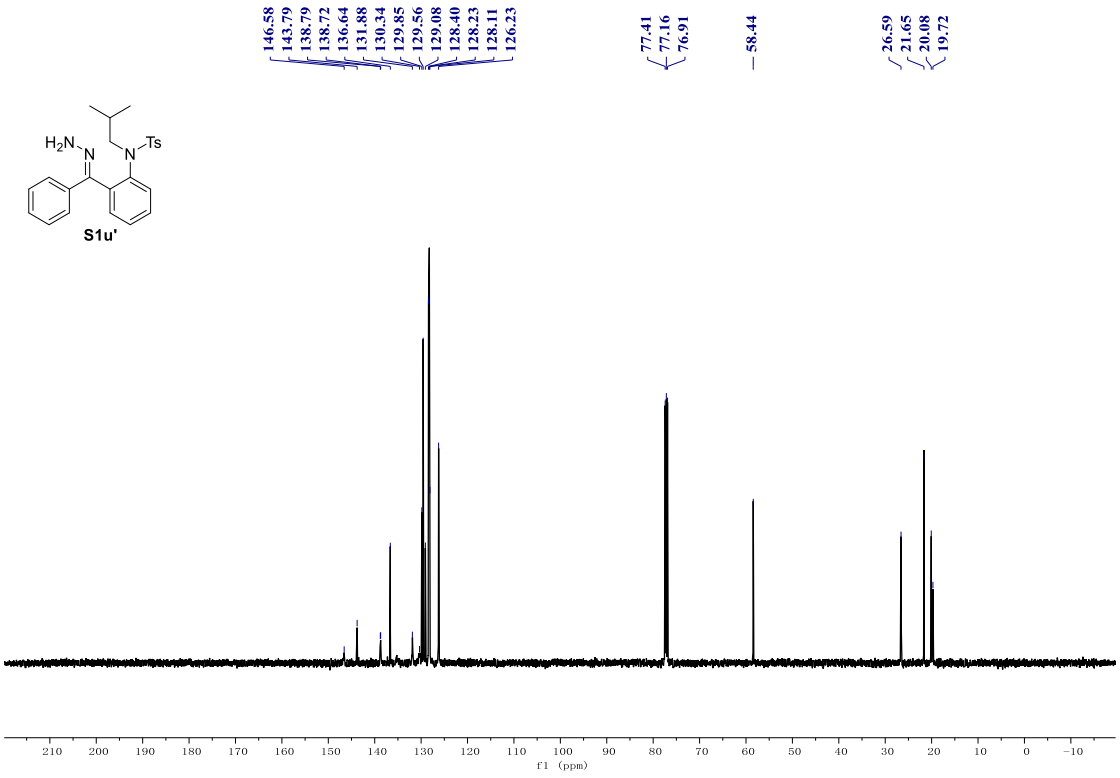
2.76
f1 (ppm)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58.44
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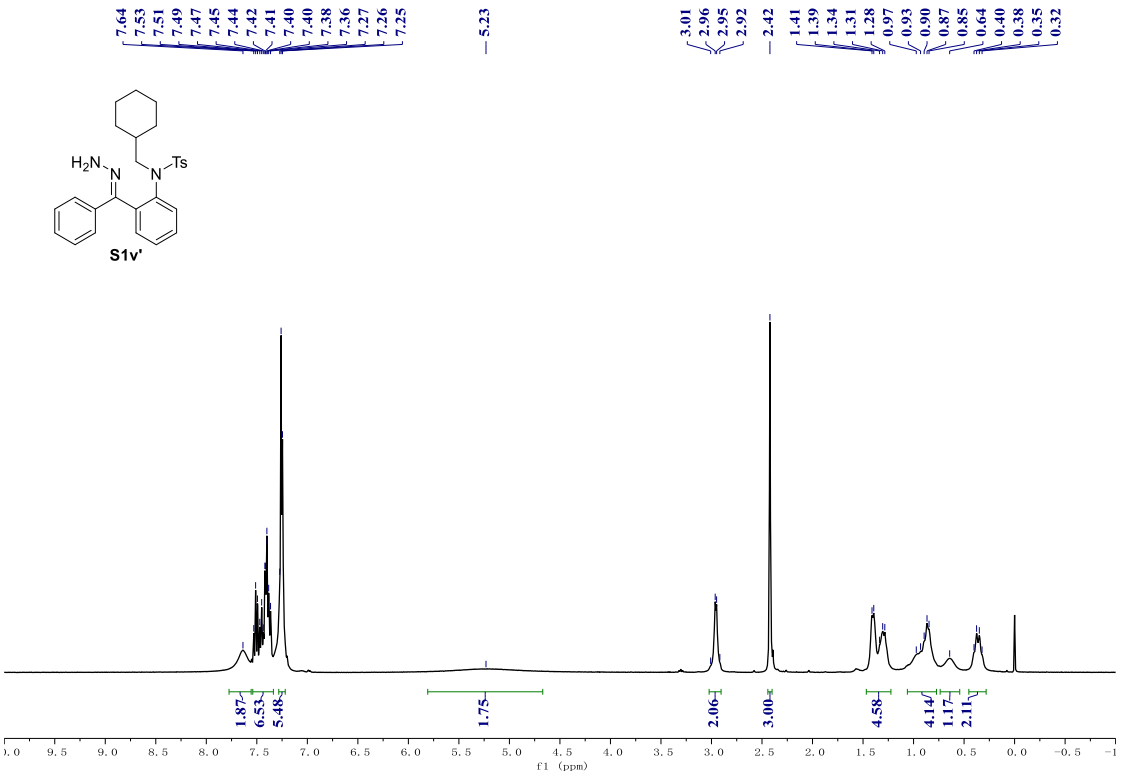
20.08
19.72
S1u'
f1 (ppm)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7.25
5.23
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2.95
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1.31
1.28
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0.93
0.90
0.87
0.85
0.64
0.40
0.38
0.35
0.32
H2N
N
N
Ts
S1v'
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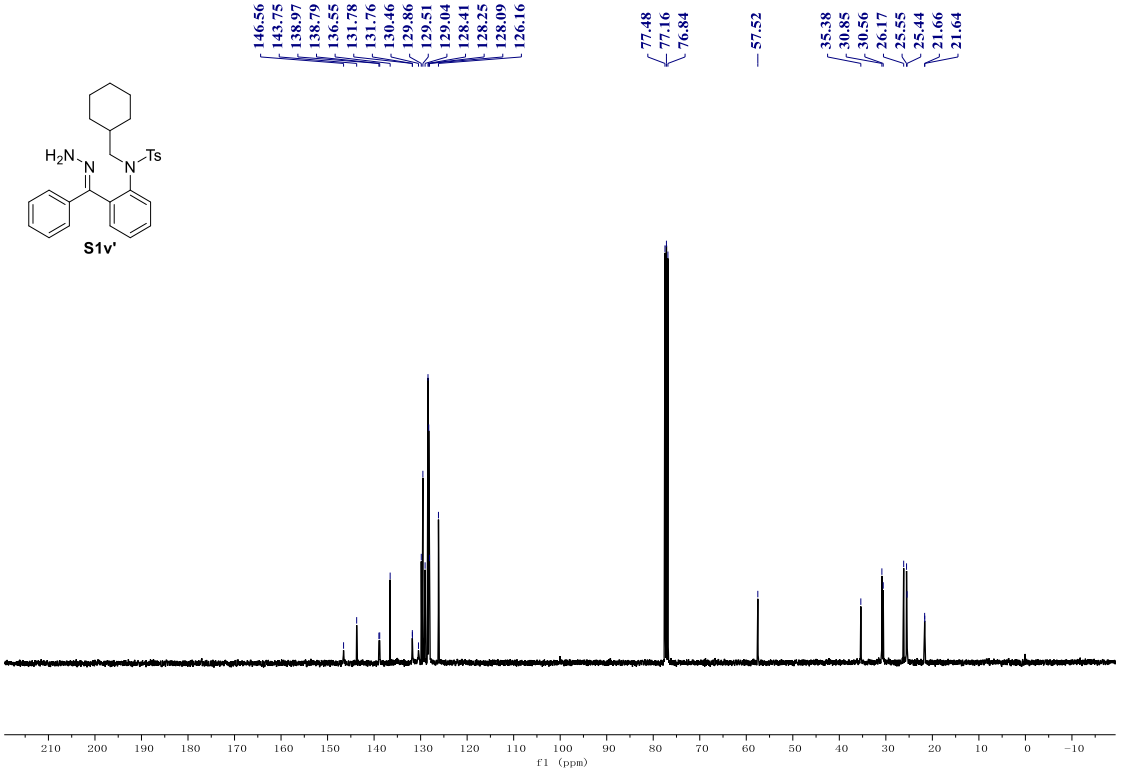
f1 (ppm)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76.84
57.52
35.38
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N
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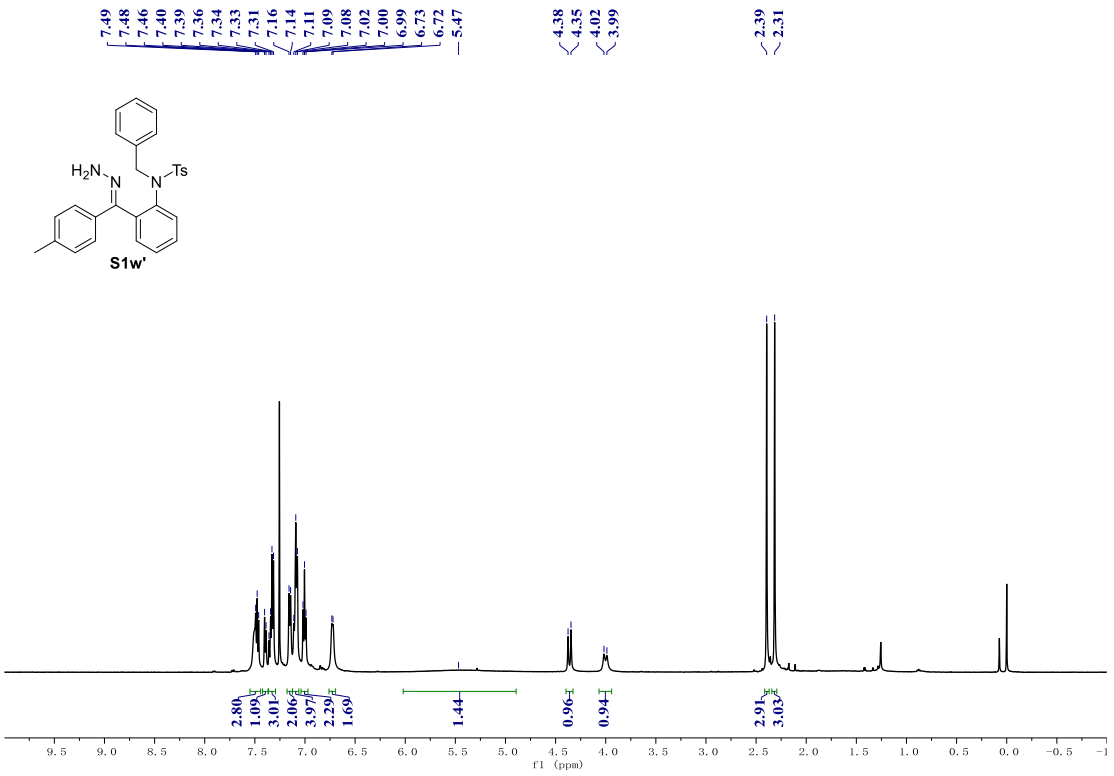
Ts
S1v'
f1 (ppm)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7.02
7.00
6.99
6.73
6.72
5.47
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4.35
4.02
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2.31
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N
N
Ts
S1w'
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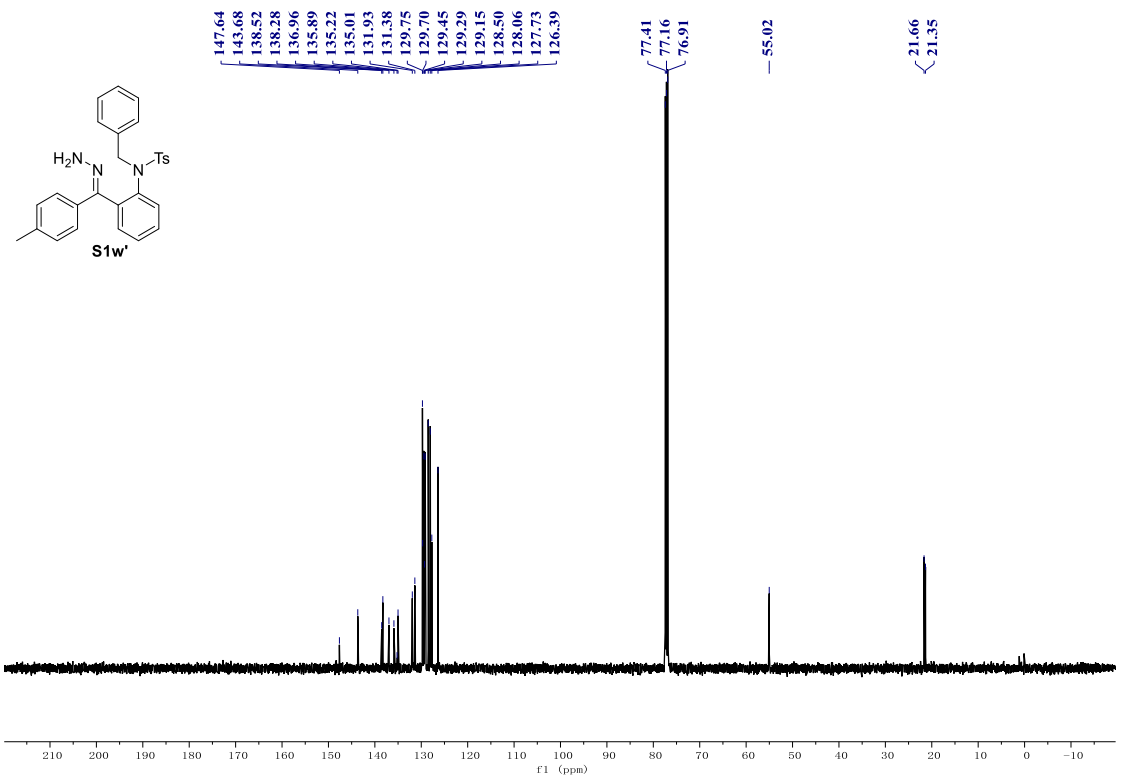
f1 (ppm)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127.73
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N
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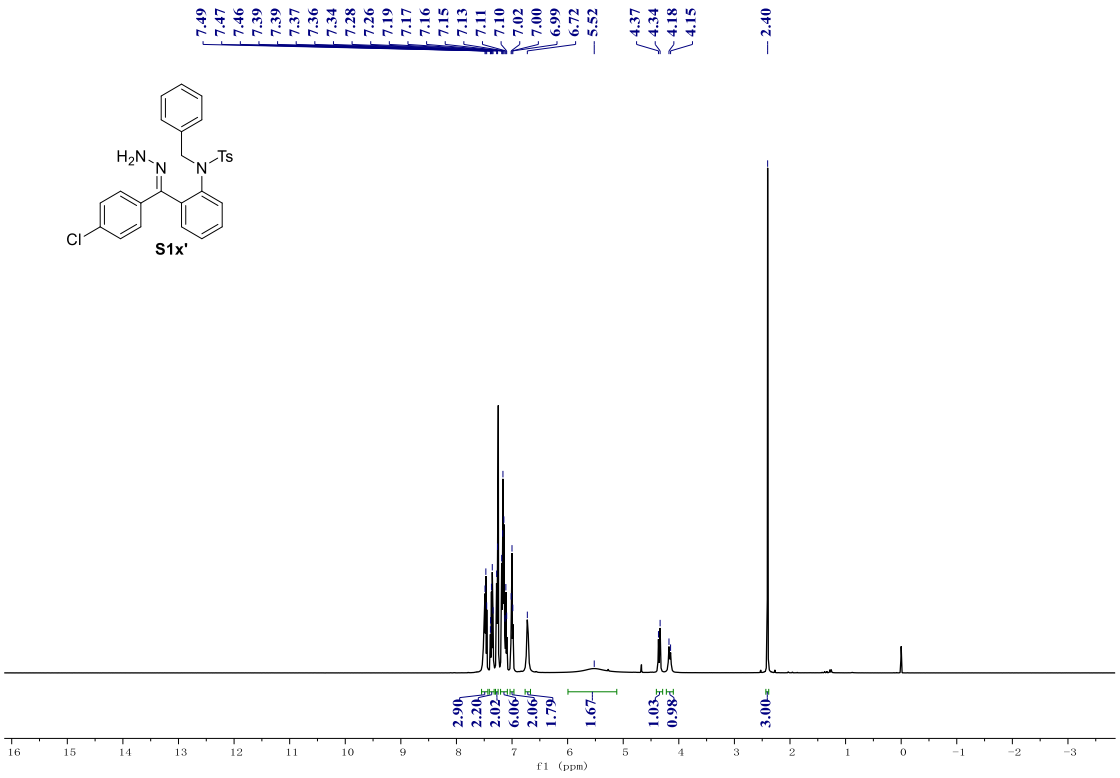
Ts
S1w'
f1 (ppm)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4.18
4.15
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N
N
Ts
Cl
S1x'
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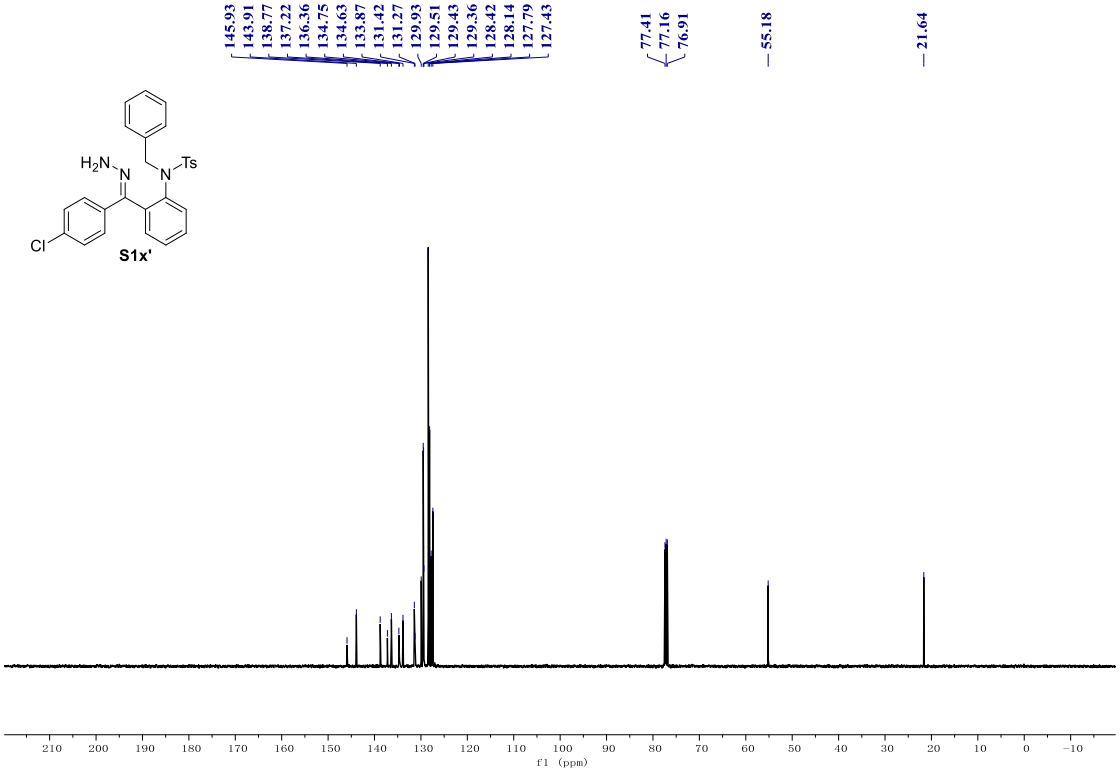
f1 (ppm)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128.14
127.79
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76.91
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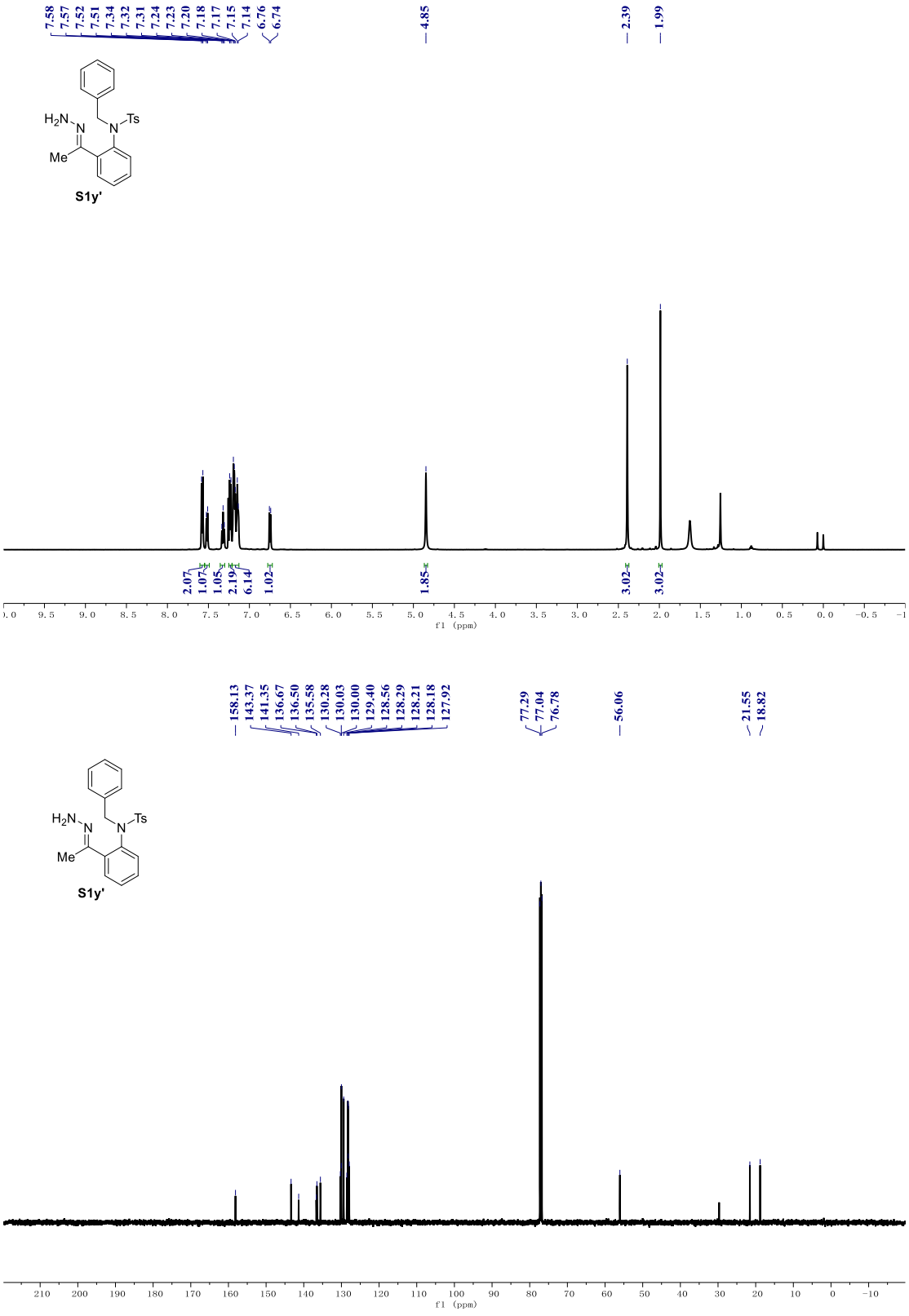
N
N
Ts
Cl
S1x'
f1 (ppm)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6.74
4.85
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H2N
N
N
Ts
Me
S1y'
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1.07
1.05
2.19
6.14
1.02
1.85
3.02
3.02
f1 (ppm)
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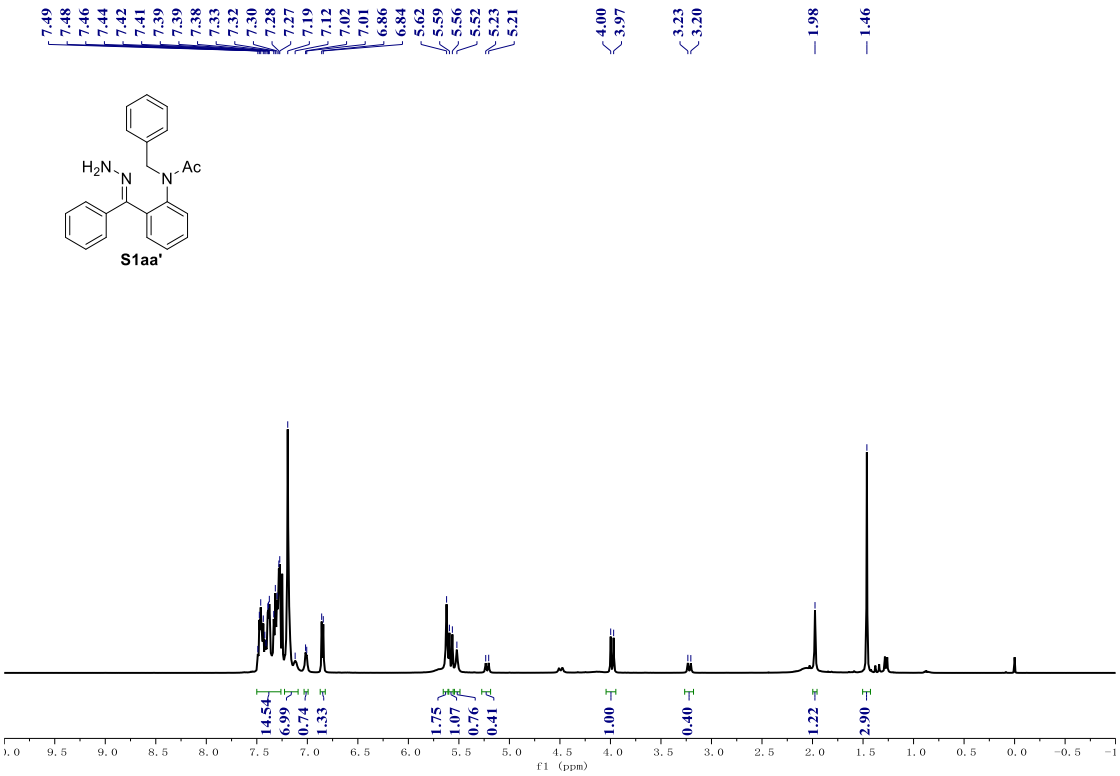
Me
S1y'
f1 (ppm)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5.56
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5.23
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3.20
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1.46
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Ac
S1aa'
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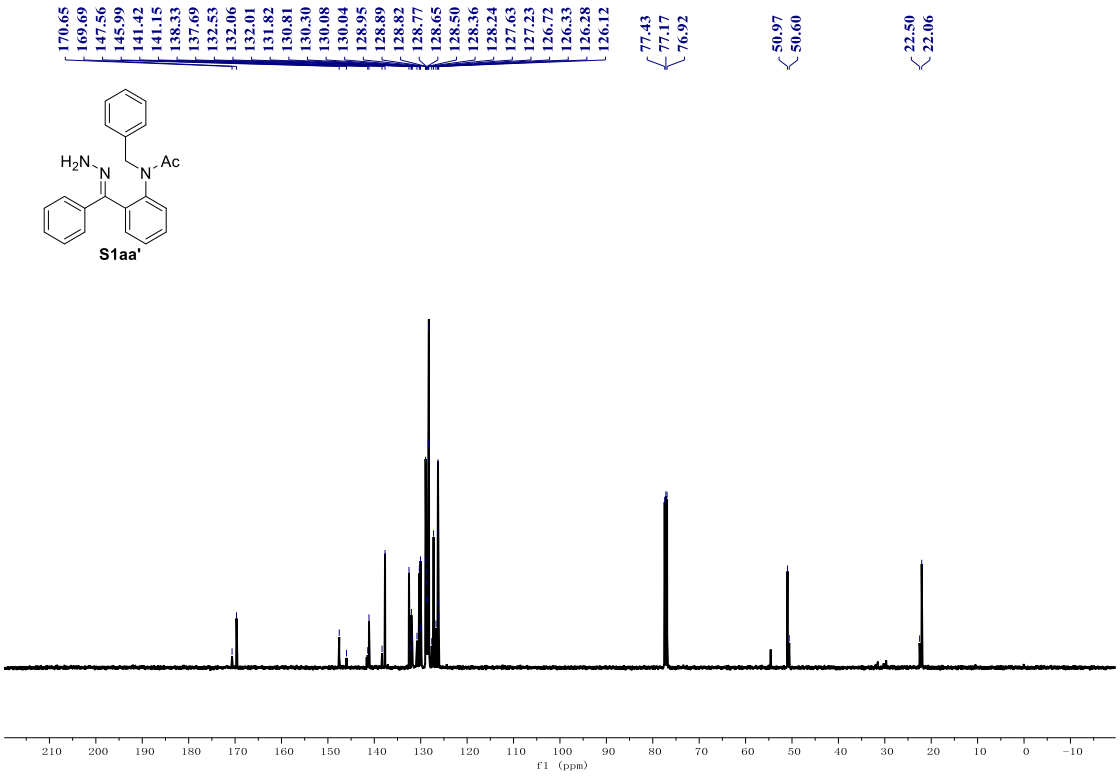
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126.12
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N
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Ac
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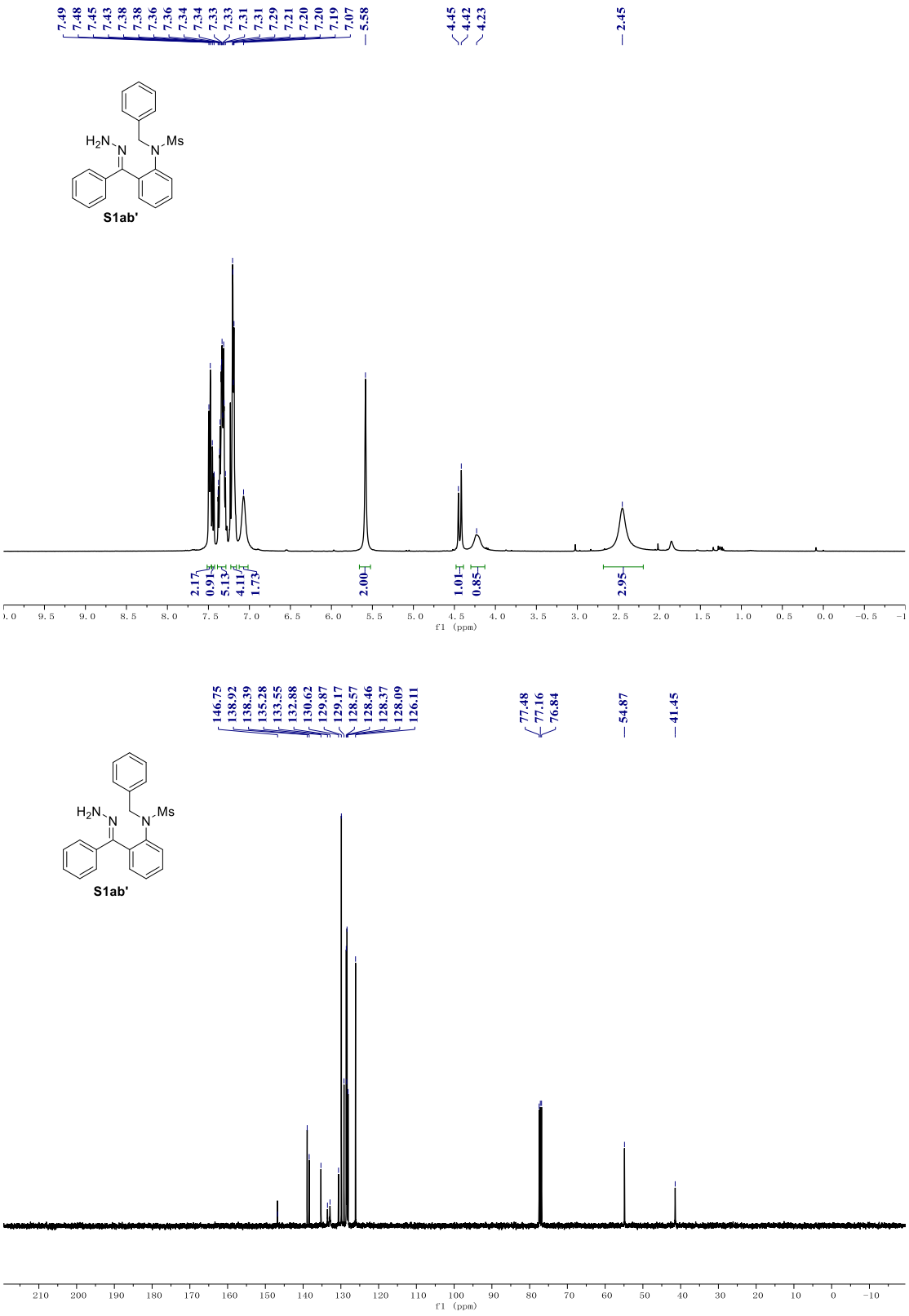
f1 (ppm)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7.29
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7.20
7.19
7.07
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4.42
4.23
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H2N
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N
Ms
S1ab'
2.17
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4.11
1.73
2.00
1.01
0.85
2.95
f1 (ppm)
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138.92
138.39
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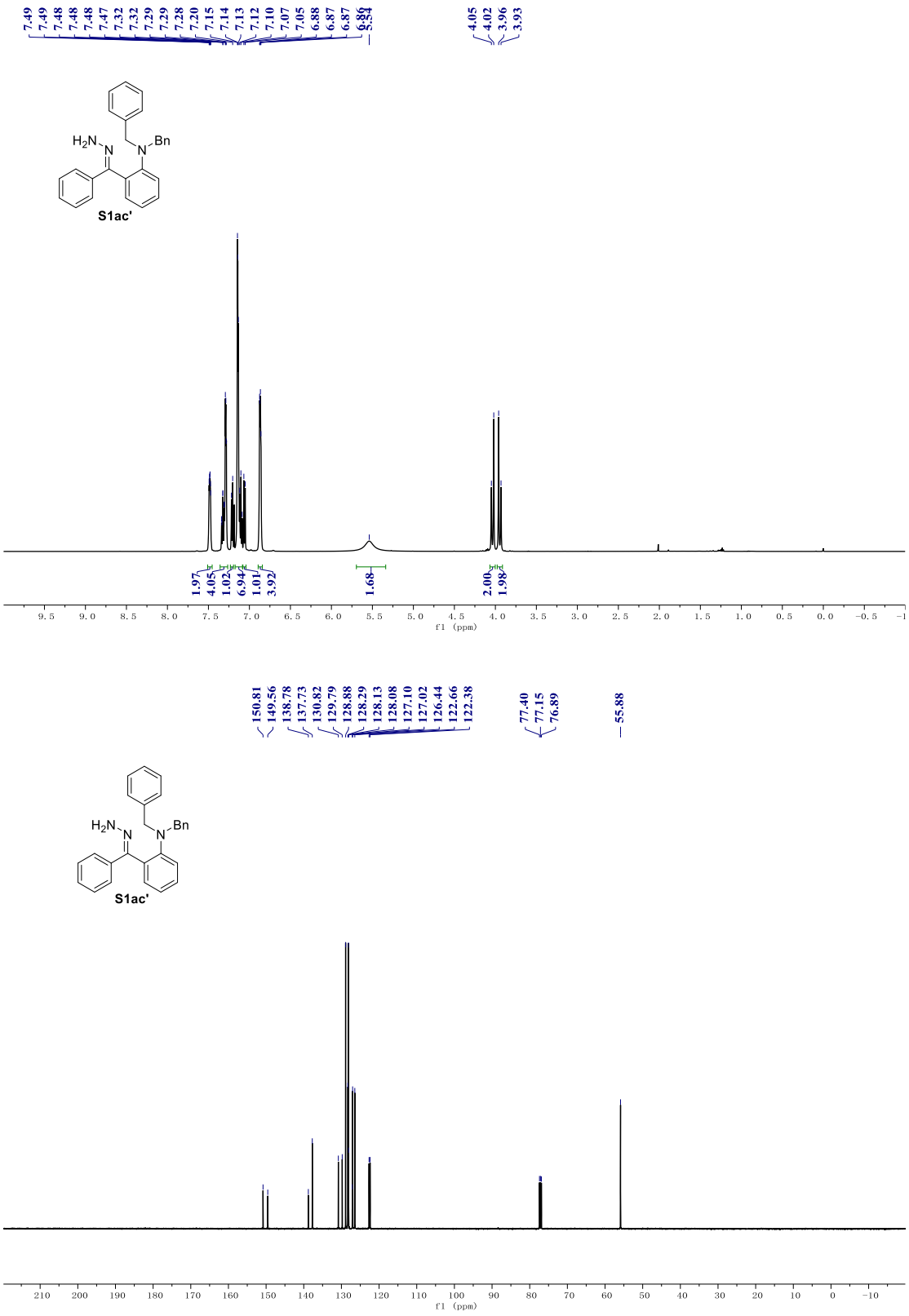
N
N
Ms
S1ab'
f1 (ppm)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Bn
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1.02
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1.01
3.92
1.68
2.00
1.98
f1 (ppm)
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149.56
138.78
137.73
130.82
129.79
128.88
128.29
128.13
128.08
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127.02
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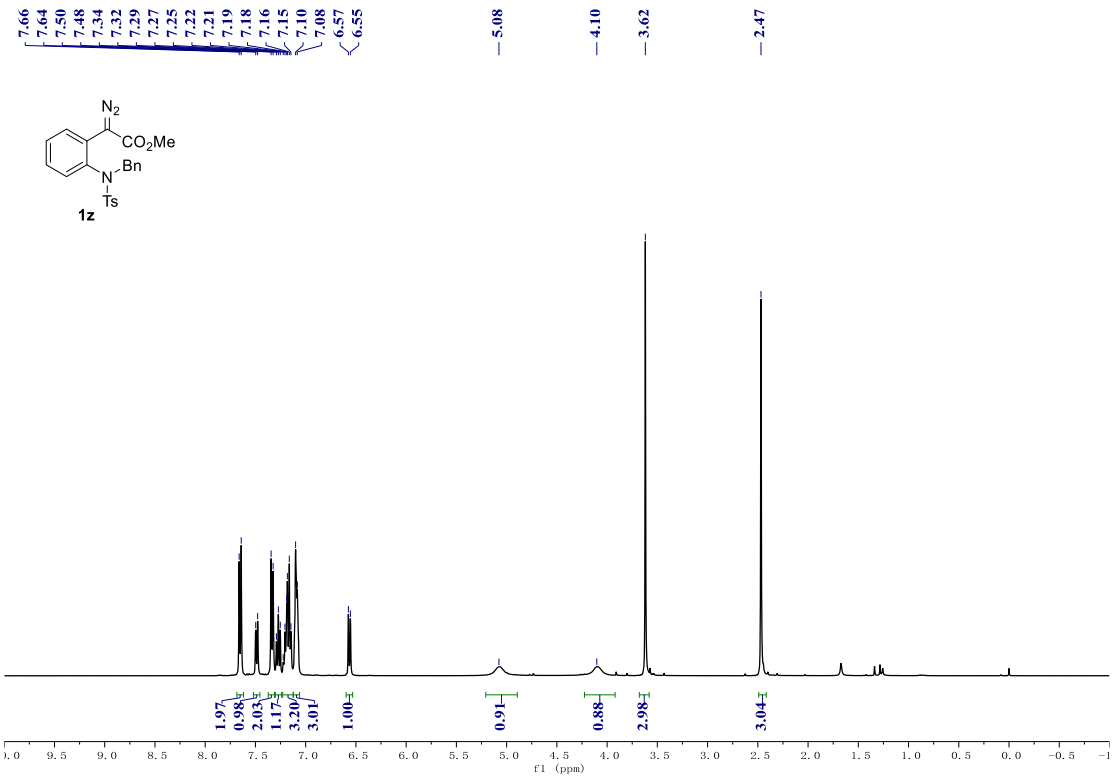
Bn
S1ac'
f1 (ppm)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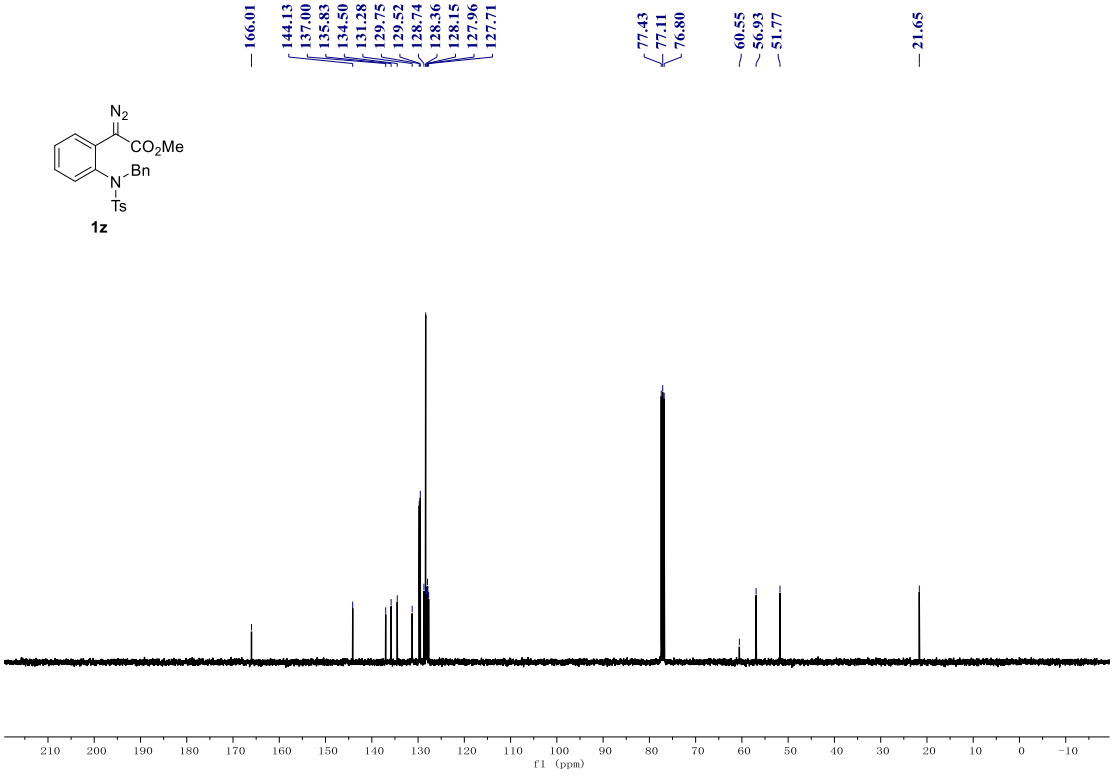
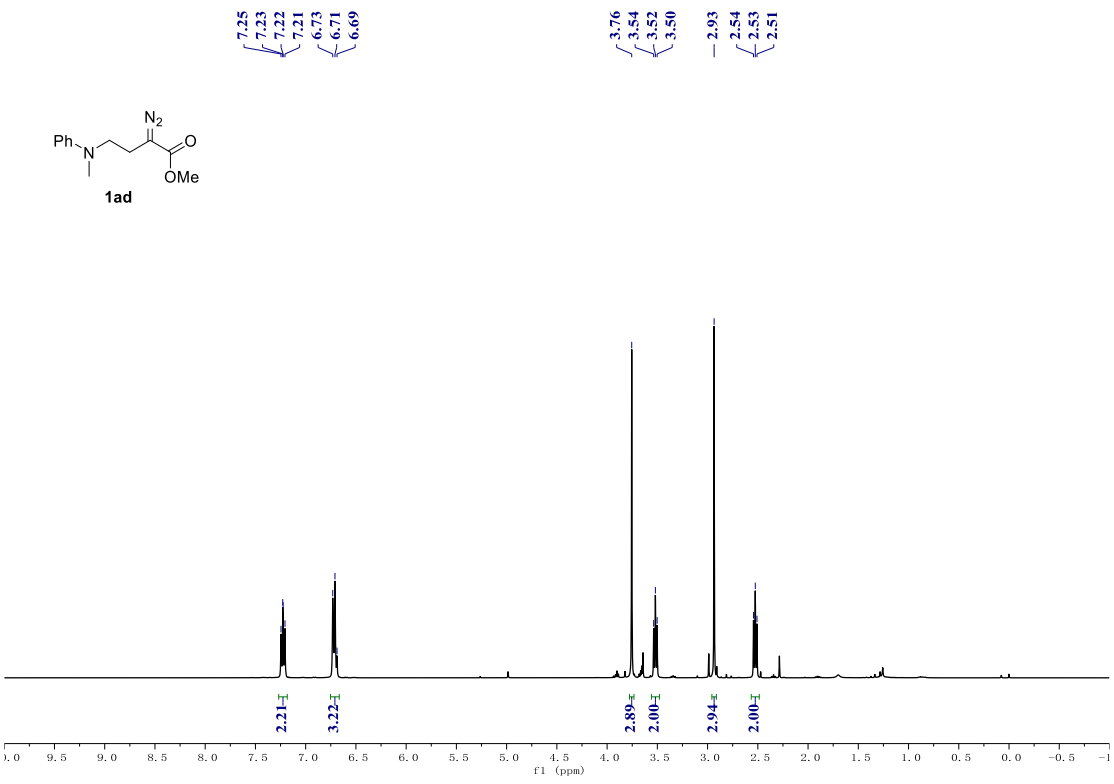
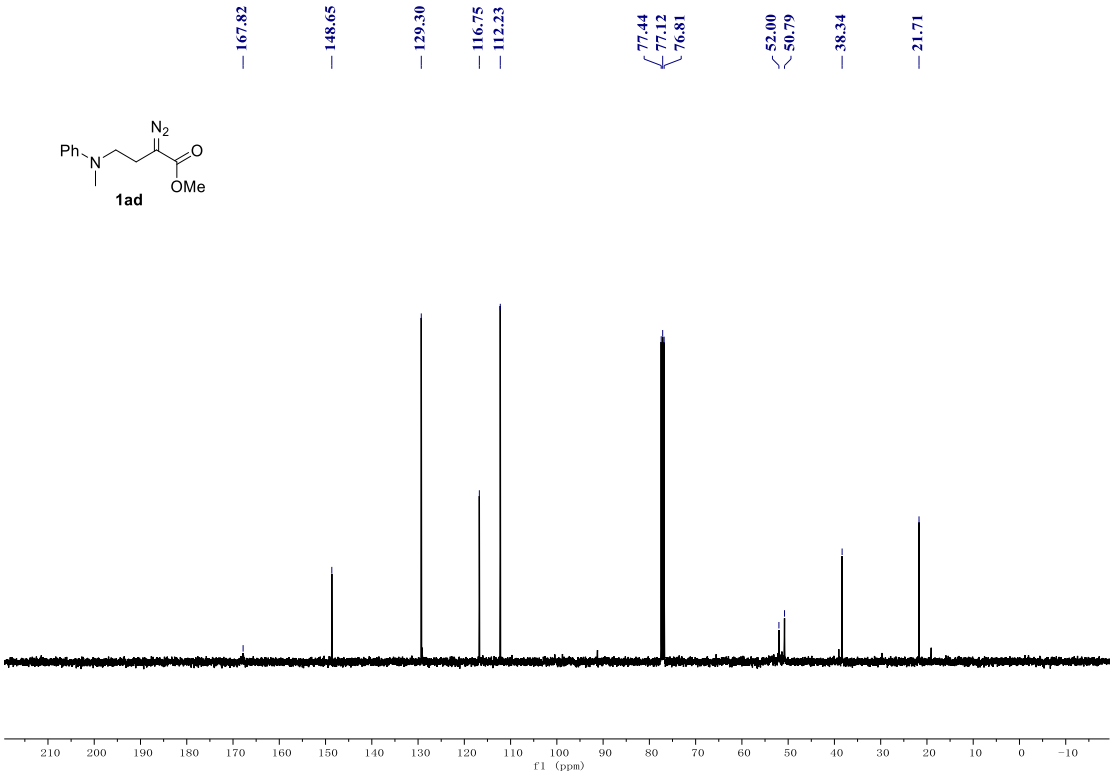
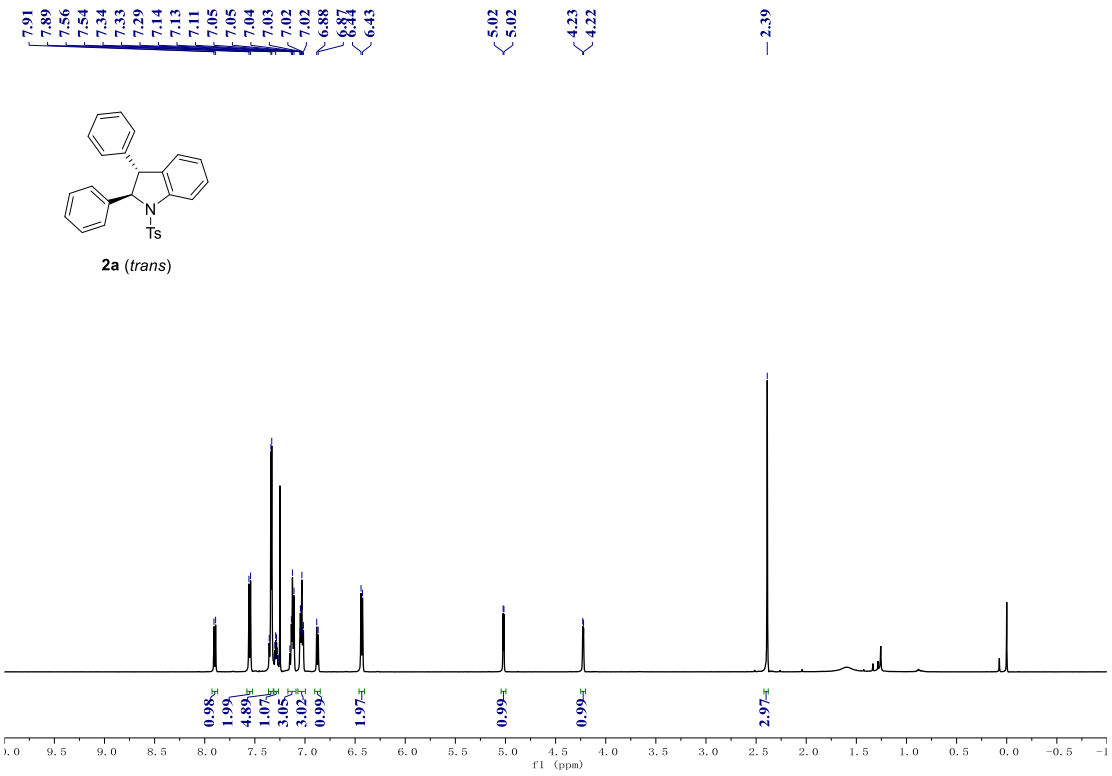
7.15
7.10
7.08
6.57
6.55
5.08
4.10
3.62
2.47
N2
CO2Me
Bn
N
Ts
1z
1.97
0.98
2.03
1.17
3.20
3.01
1.00
0.91
0.88
2.98
3.04
f1 (ppm)

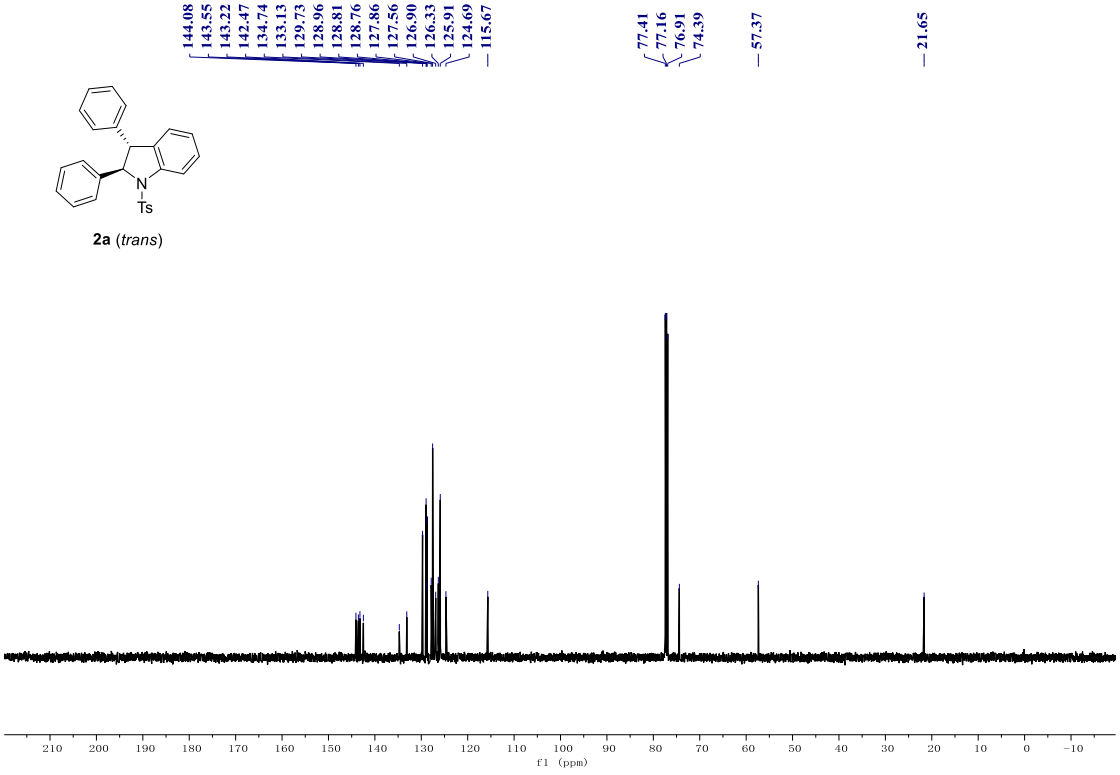

166.01
144.13
137.00
135.83
134.50
131.28
129.75
129.52
128.74
128.36
128.15
127.96
127.71
77.43
77.11
76.80
60.55
56.93
51.77
21.65
N2
CO2Me
Bn
N
Ts
1z
f1 (ppm)


7.25
7.23
7.22
7.21
6.73
6.71
6.69
3.76
3.54
3.52
3.50
2.93
2.54
2.53
2.51
Ph
N
N2
O
OMe
1ad
2.21
3.22
2.89
2.00
2.94
2.00
f1 (ppm)

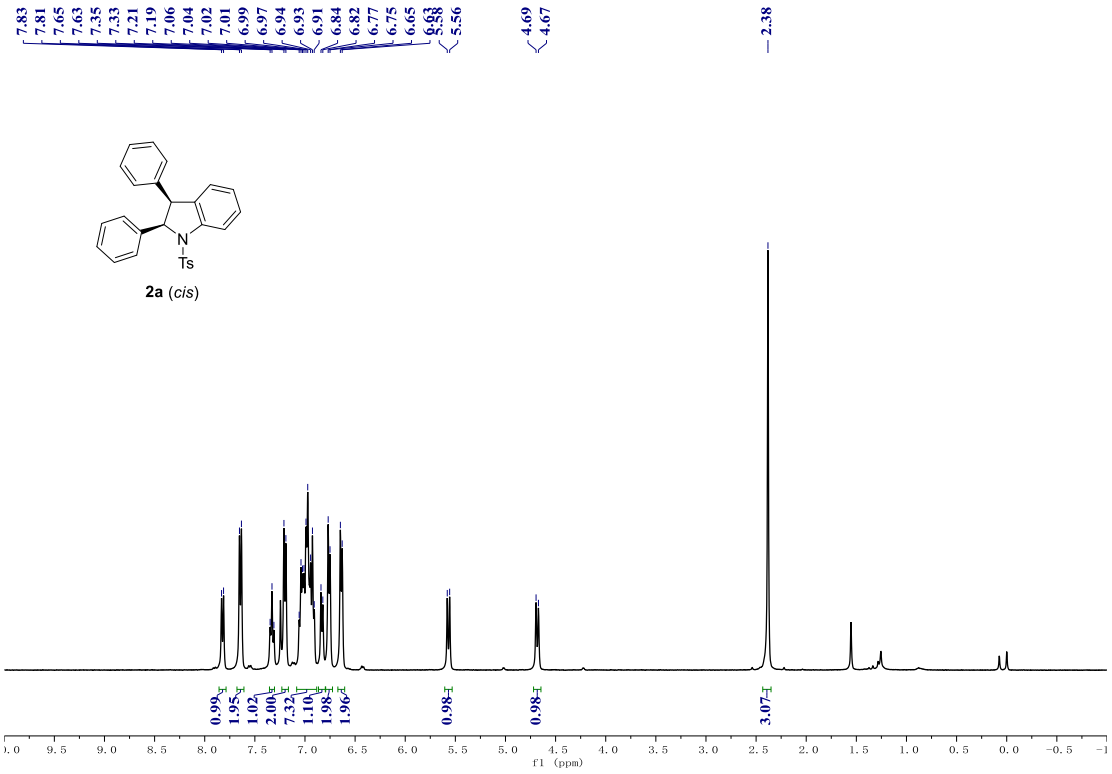

167.82
148.65
129.30
116.75
112.23
77.44
77.12
76.81
52.00
50.79
38.34
21.71
Ph
N
N2
O
OMe
1ad
f1 (ppm)



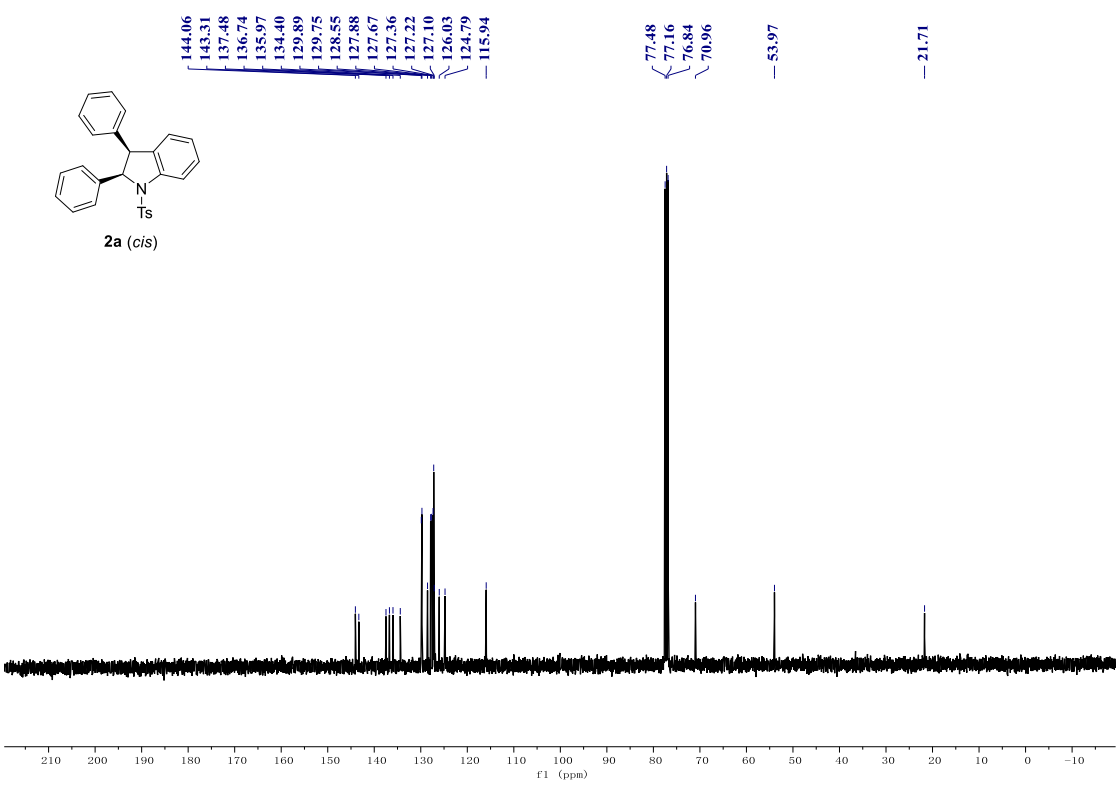
2a (*trans*)



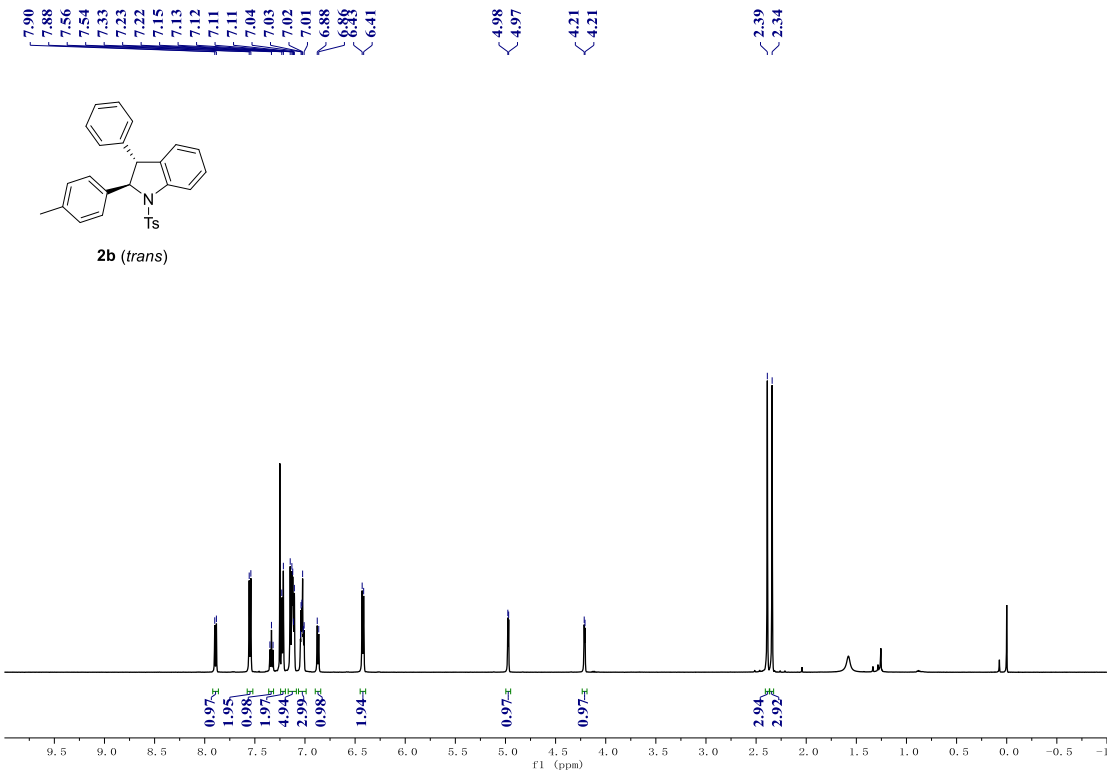
2a (*trans*)


7.83
7.81
7.65
7.63
7.35
7.33
7.21
7.19
7.06
7.04
7.02
7.01
6.99
6.97
6.94
6.93
6.91
6.84
6.82
6.77
6.75
6.65
6.63
5.58
5.56
4.69
4.67
2.38
0.99
1.95
1.02
2.00
7.32
1.10
1.98
1.96
0.98
0.98
3.07
f1 (ppm)

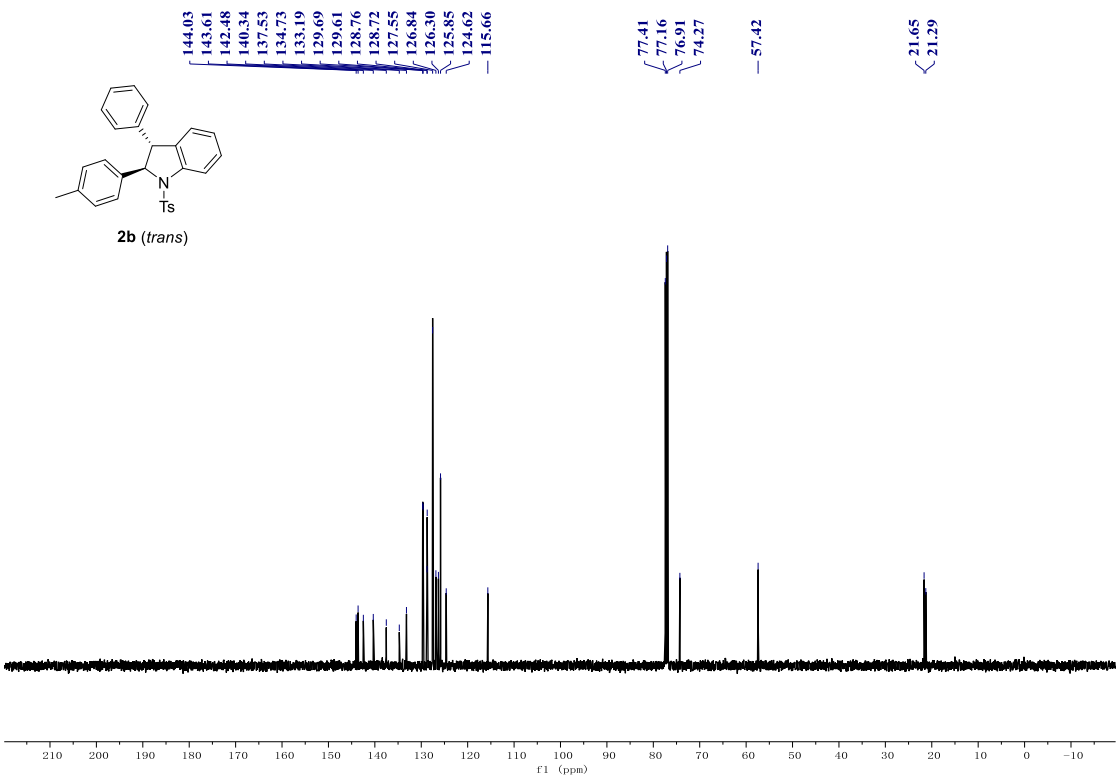
2a (*cis*)


144.06
143.31
137.48
136.74
135.97
134.40
129.89
129.75
128.55
127.88
127.67
127.36
127.22
127.10
126.03
124.79
115.94
77.48
77.16
76.84
70.96
53.97
21.71
f1 (ppm)

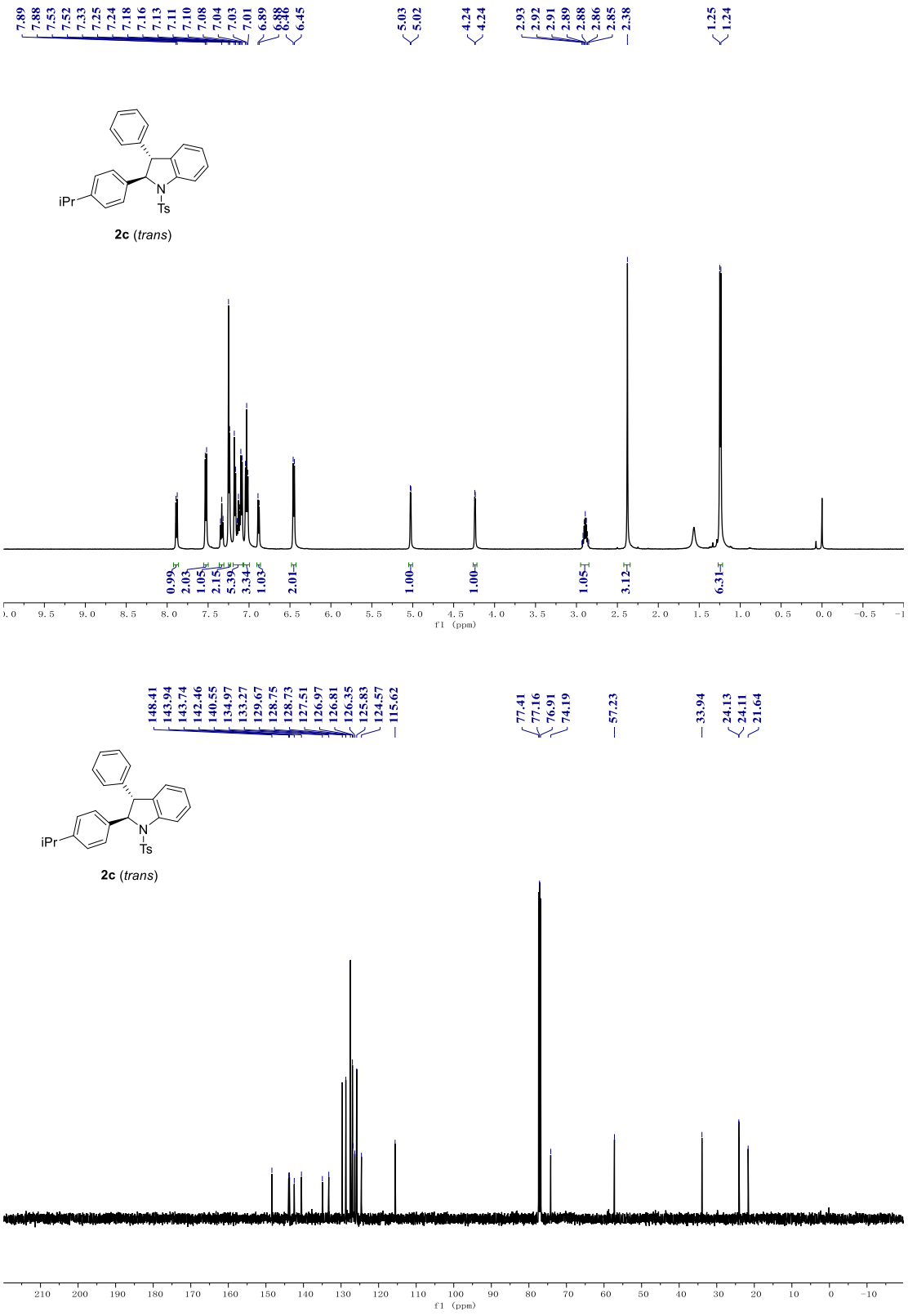
2a (*cis*)

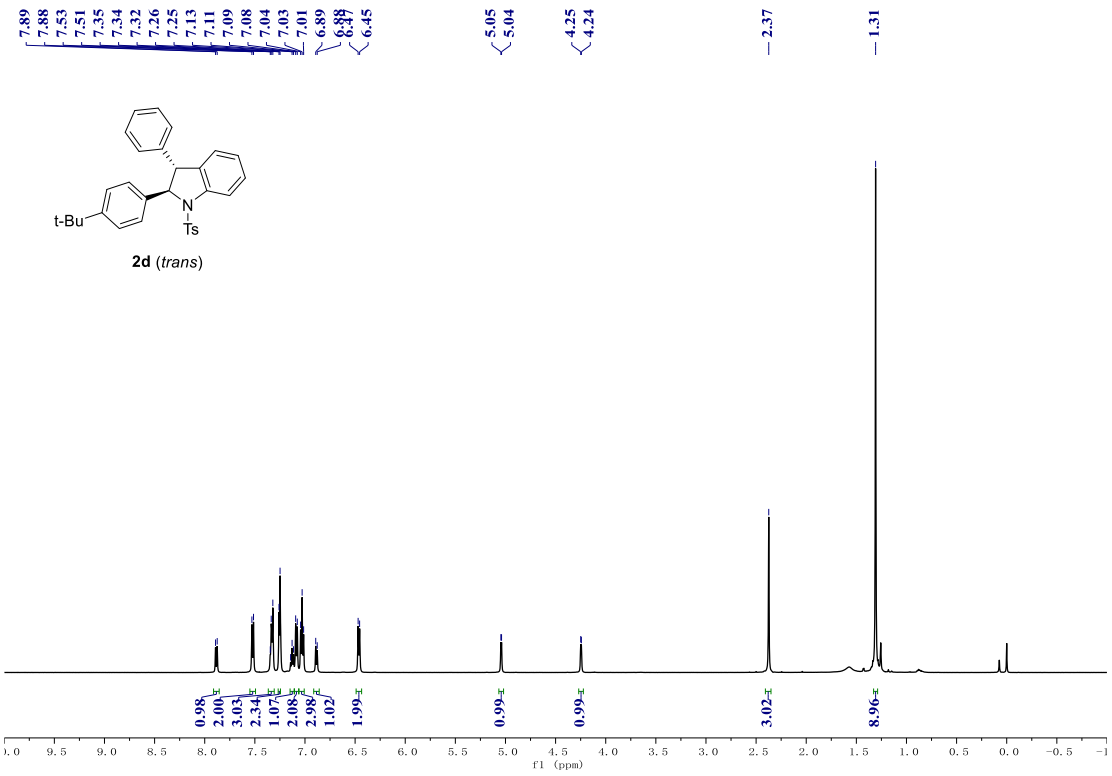


2b (*trans*)

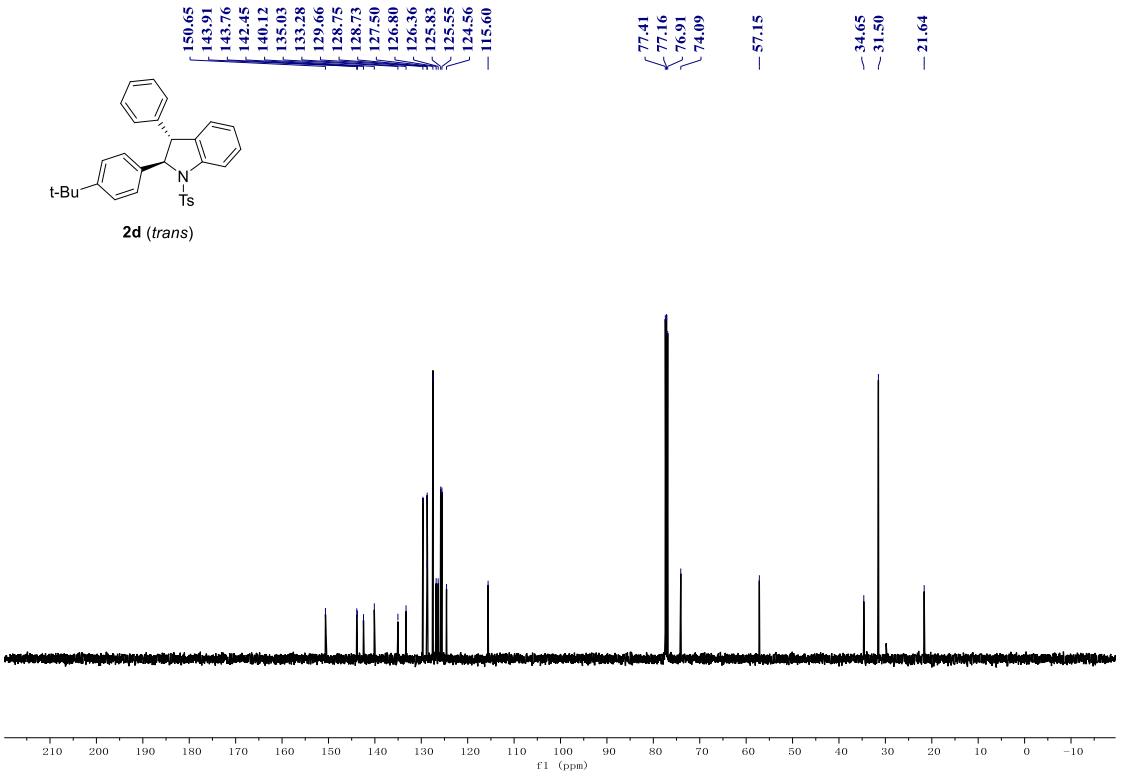


2b (*trans*)

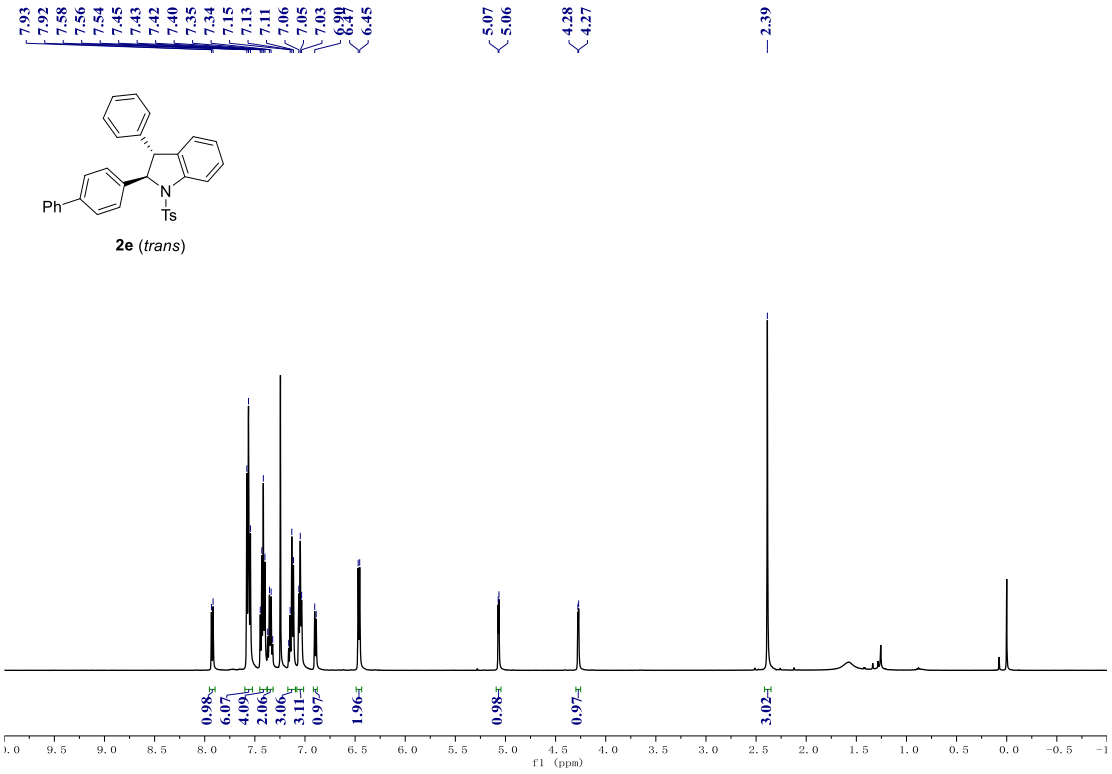

7.89
7.88
7.53
7.52
7.33
7.25
7.24
7.18
7.16
7.13
7.11
7.10
7.08
7.04
7.03
7.01
6.89
6.88
6.45
5.03
5.02
4.24
4.24
2.93
2.92
2.91
2.89
2.88
2.86
2.85
2.38
1.25
1.24
iPr
N
Ts
2c (trans)
0.99
2.03
1.05
2.15
5.39
3.34
1.03
2.01
1.00
1.00
1.05
3.12
6.31
f1 (ppm)
148.41
143.94
143.74
142.46
140.55
134.97
133.27
129.67
128.75
128.73
127.51
126.97
126.81
126.35
125.83
124.57
115.62
77.41
77.16
76.91
74.19
57.23
33.94
24.13
24.11
21.64
iPr
N
Ts
2c (trans)
f1 (ppm)



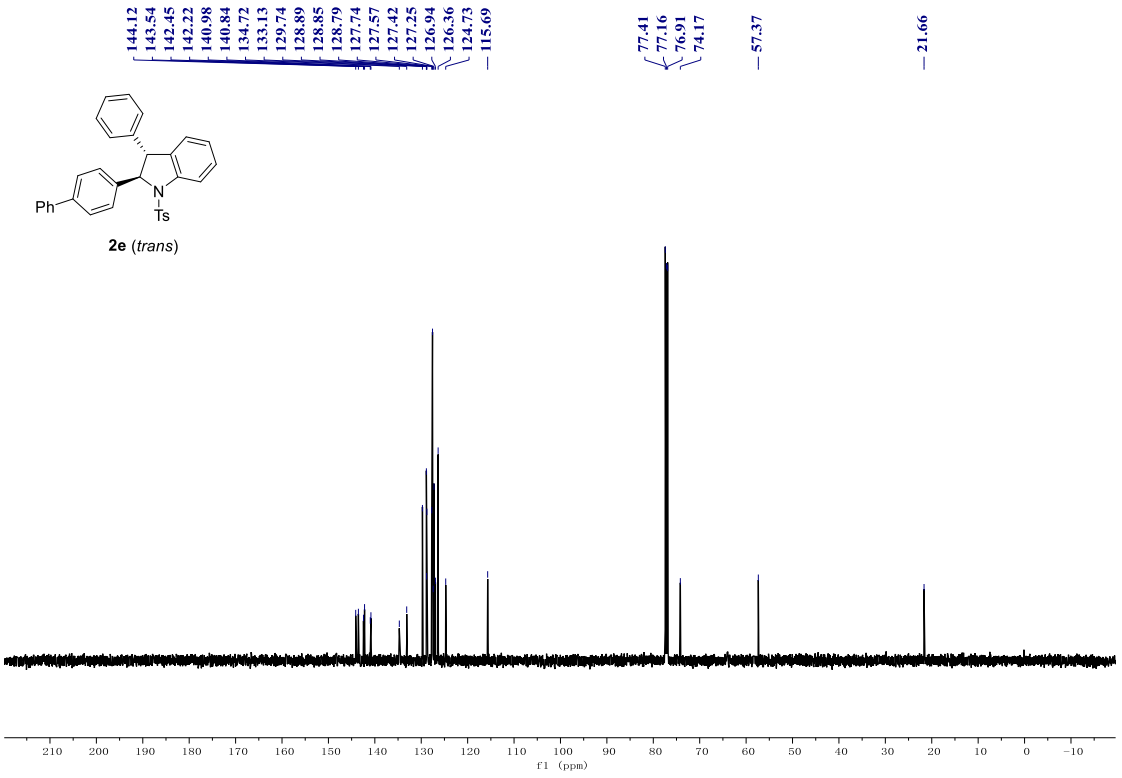
2d (*trans*)



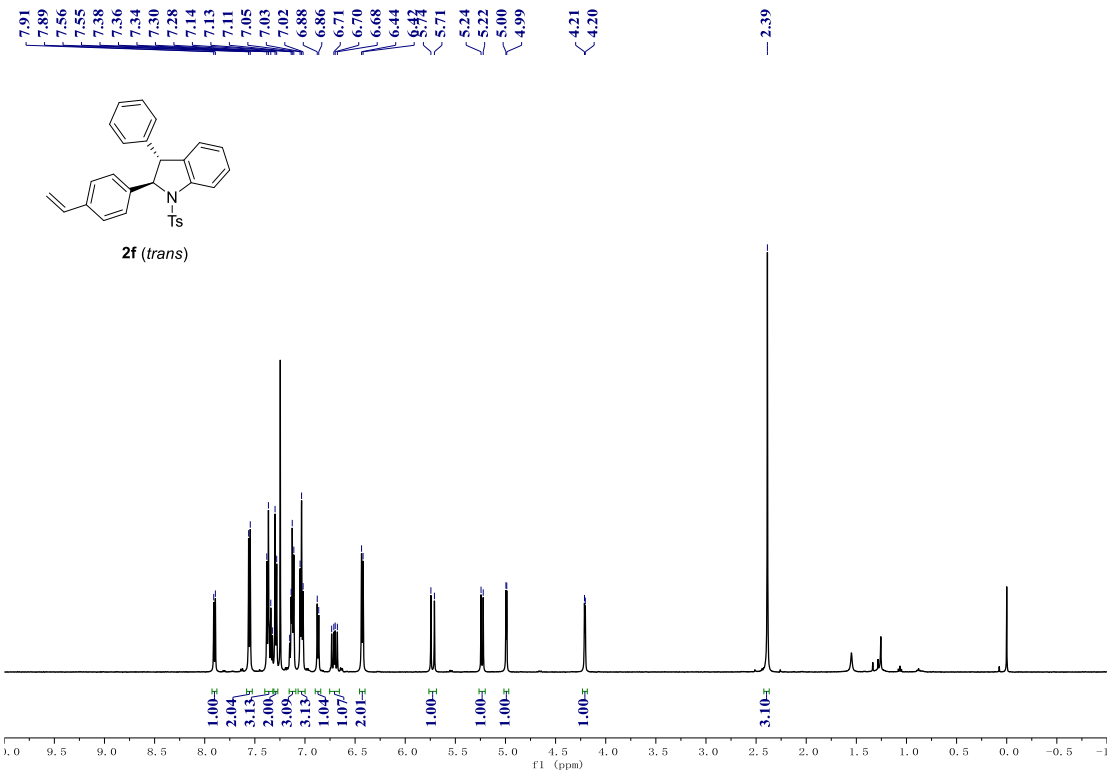
2d (*trans*)



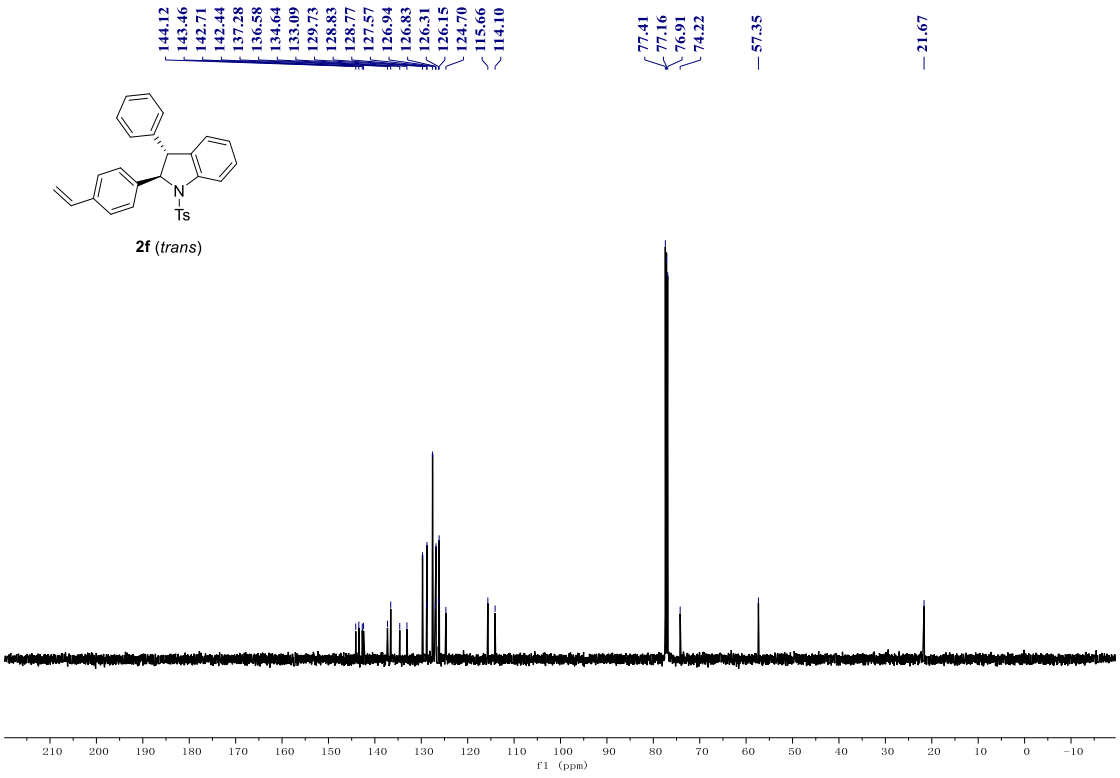
2e (*trans*)



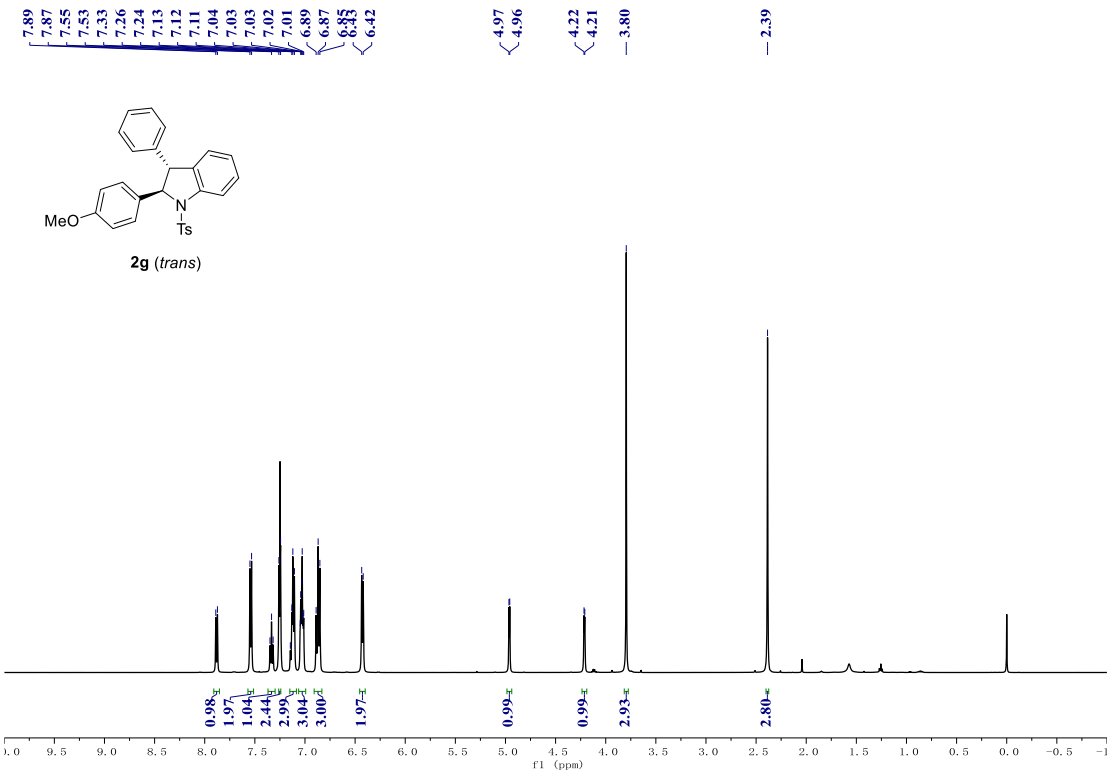
2e (*trans*)



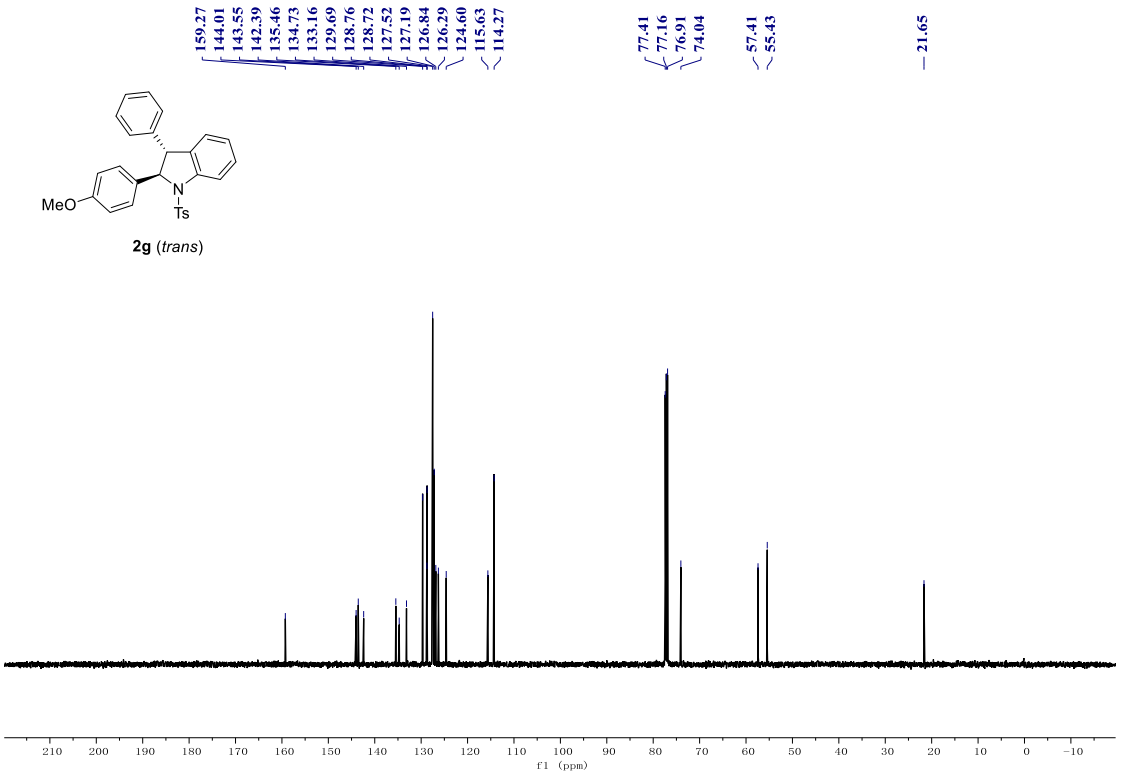
2f (*trans*)



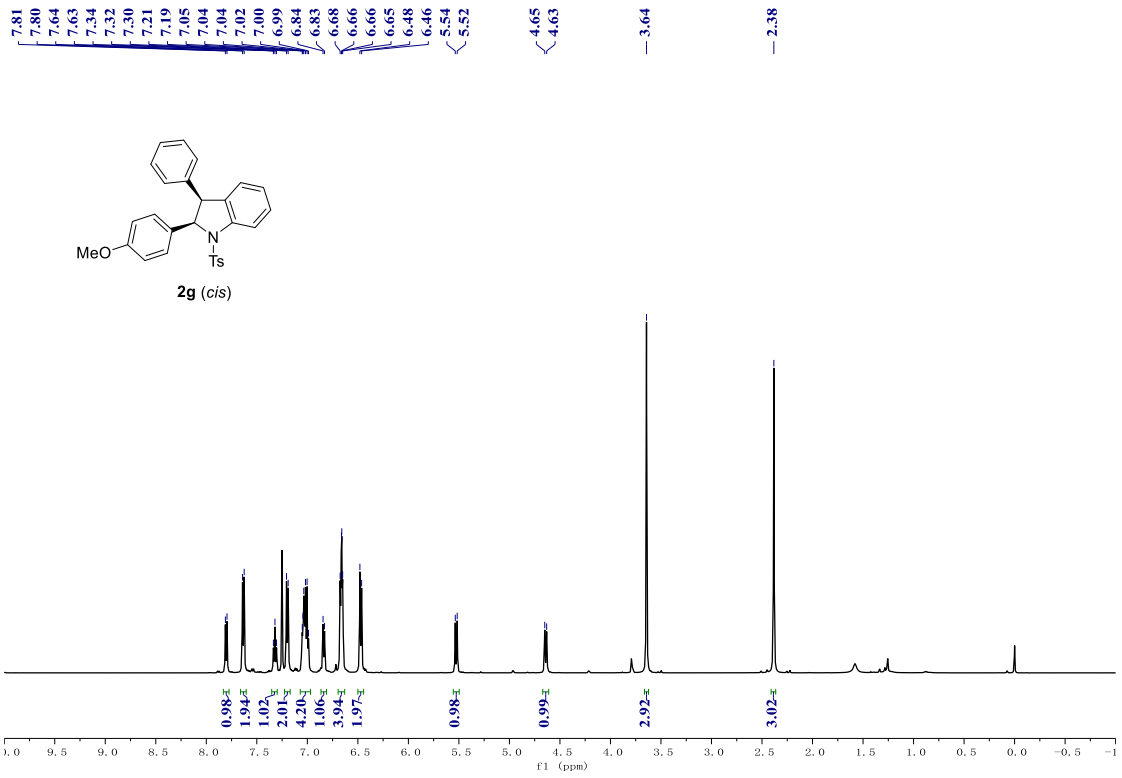
2f (*trans*)



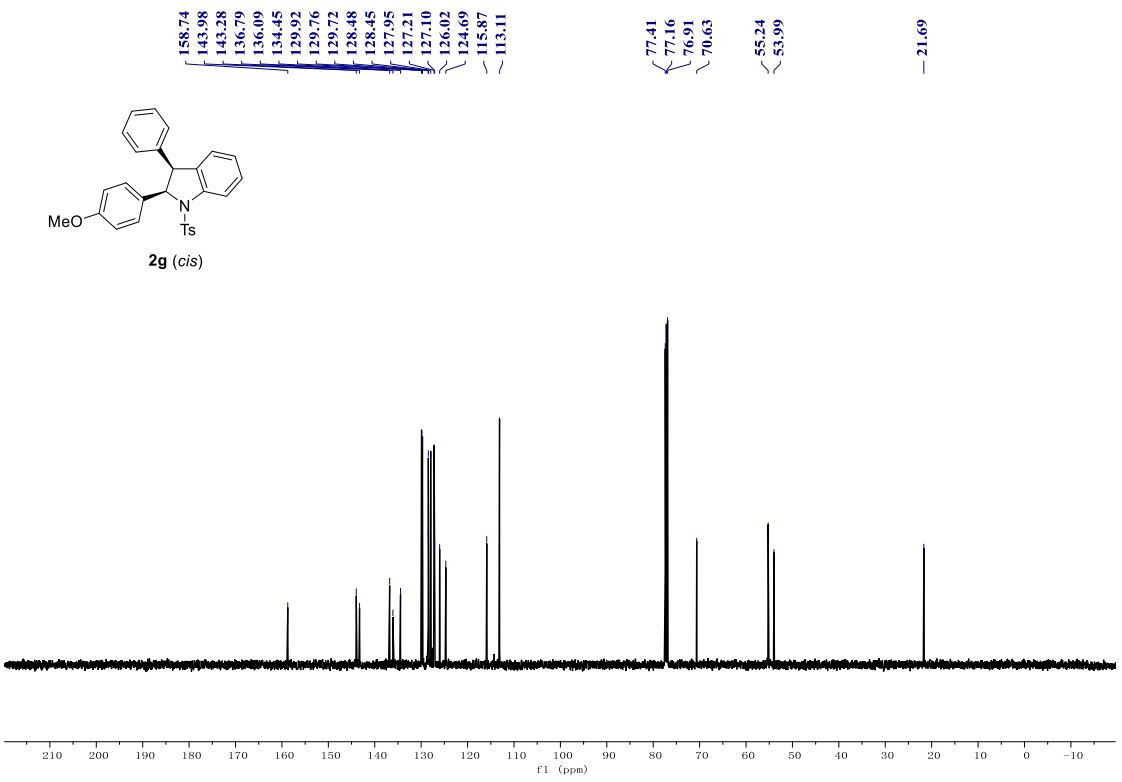
2g (*trans*)



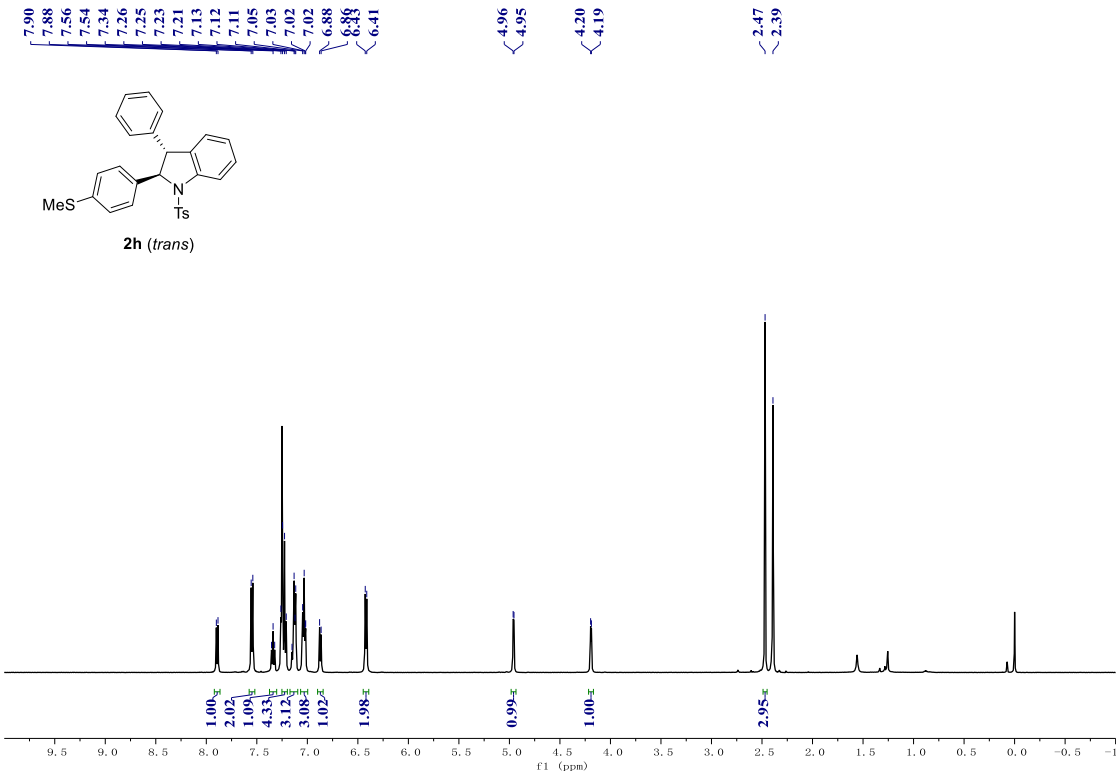
2g (*trans*)


7.81
7.80
7.64
7.63
7.34
7.32
7.30
7.21
7.19
7.05
7.04
7.04
7.02
7.00
6.99
6.84
6.83
6.68
6.66
6.66
6.65
6.48
6.46
5.54
5.52
4.65
4.63
3.64
2.38
MeO
N
Ts
0.98
1.94
1.02
2.01
4.20
1.06
3.94
1.97
0.98
0.99
2.92
3.02
f1 (ppm)

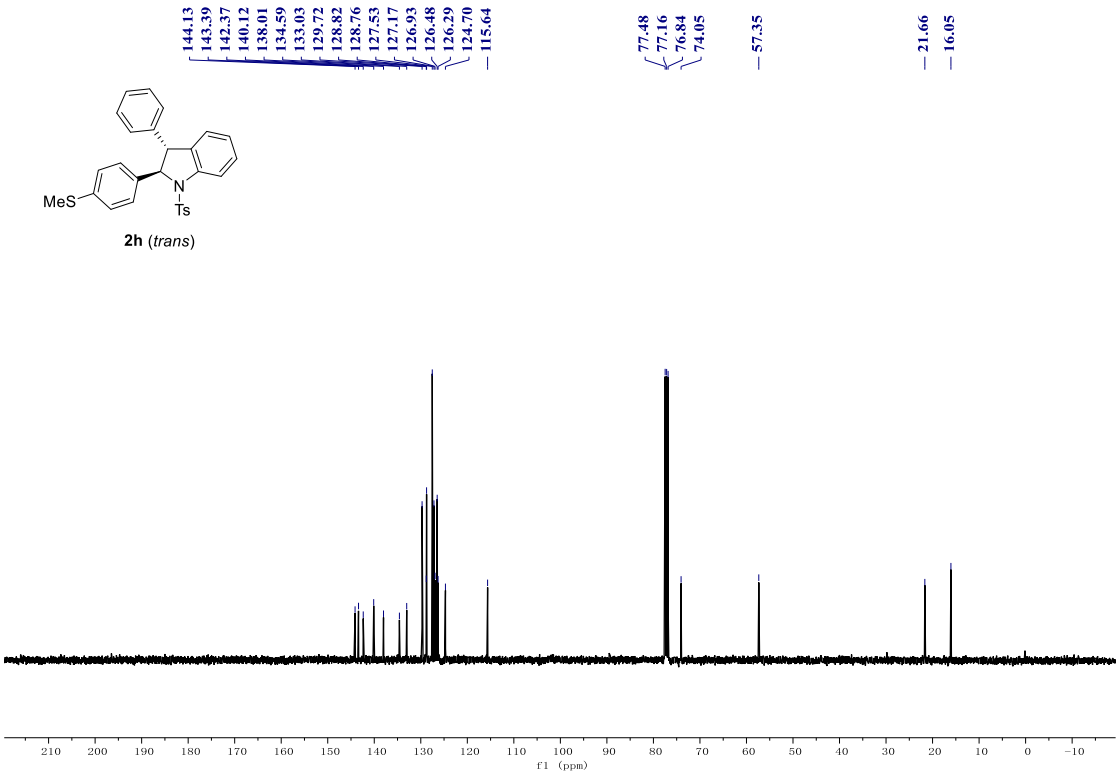
2g (*cis*)


158.74
143.98
143.28
136.79
136.09
134.45
129.92
129.76
129.72
128.48
128.45
127.95
127.21
127.10
126.02
124.69
115.87
113.11
77.41
77.16
76.91
70.63
55.24
53.99
21.69
MeO
N
Ts
f1 (ppm)

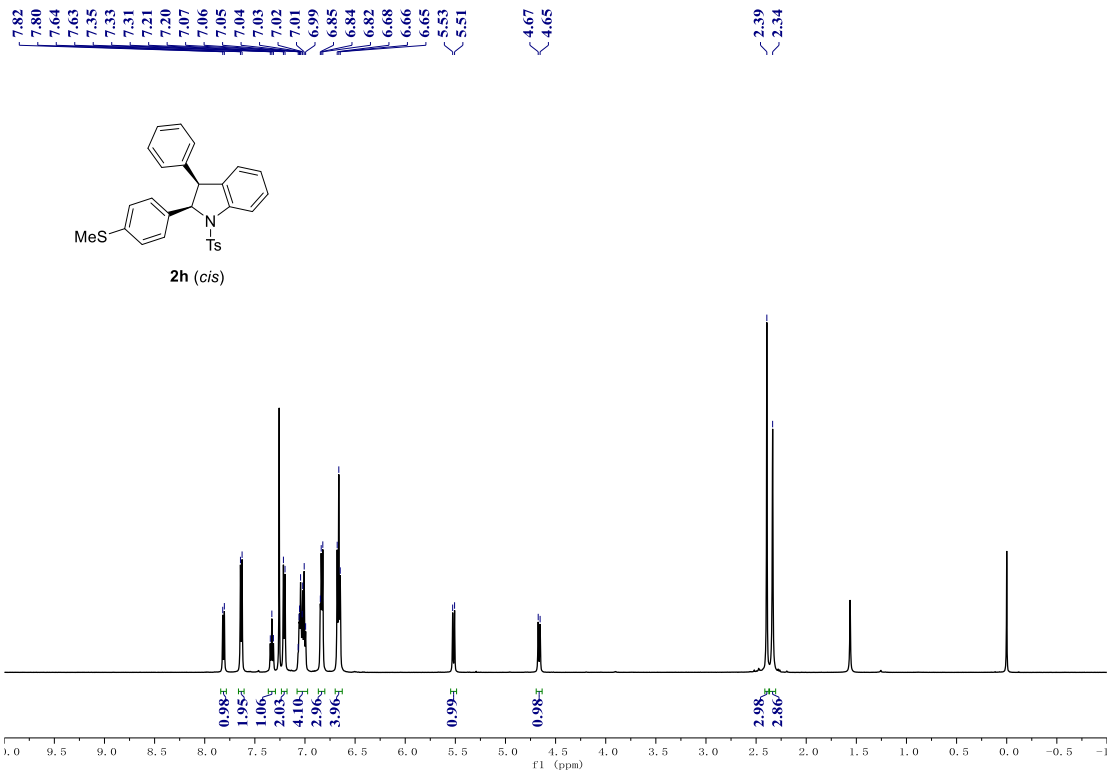
2g (*cis*)



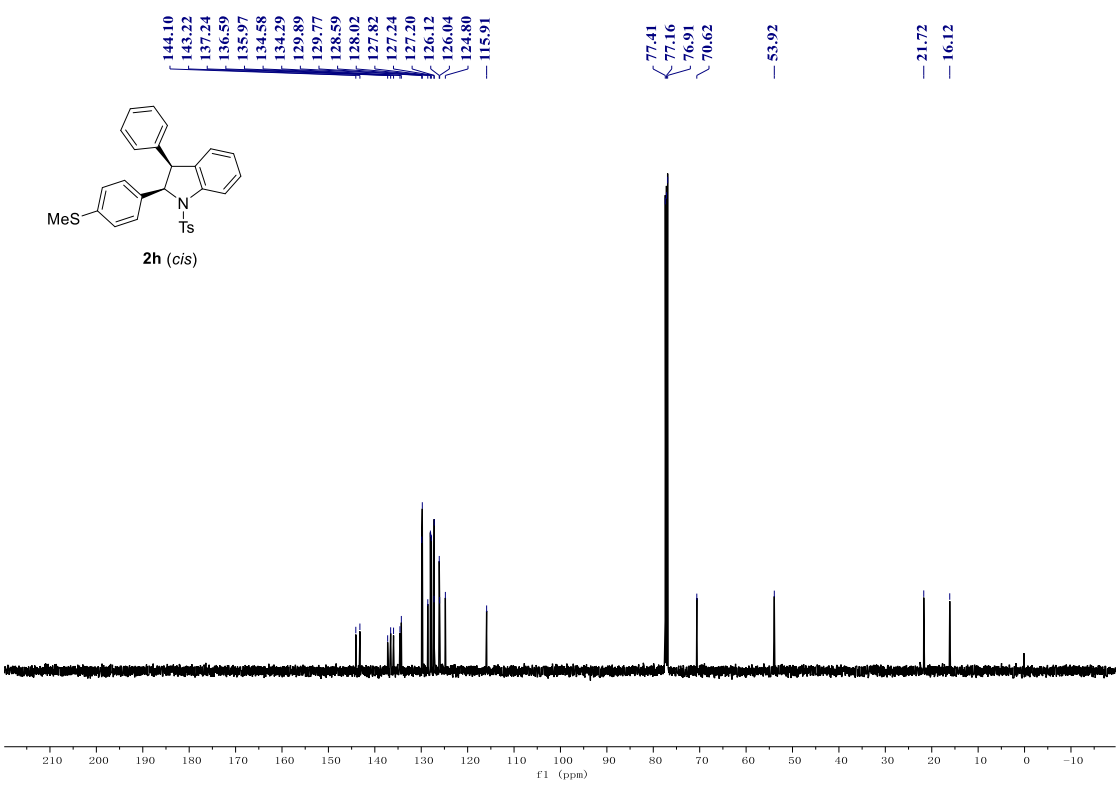
2h (*trans*)



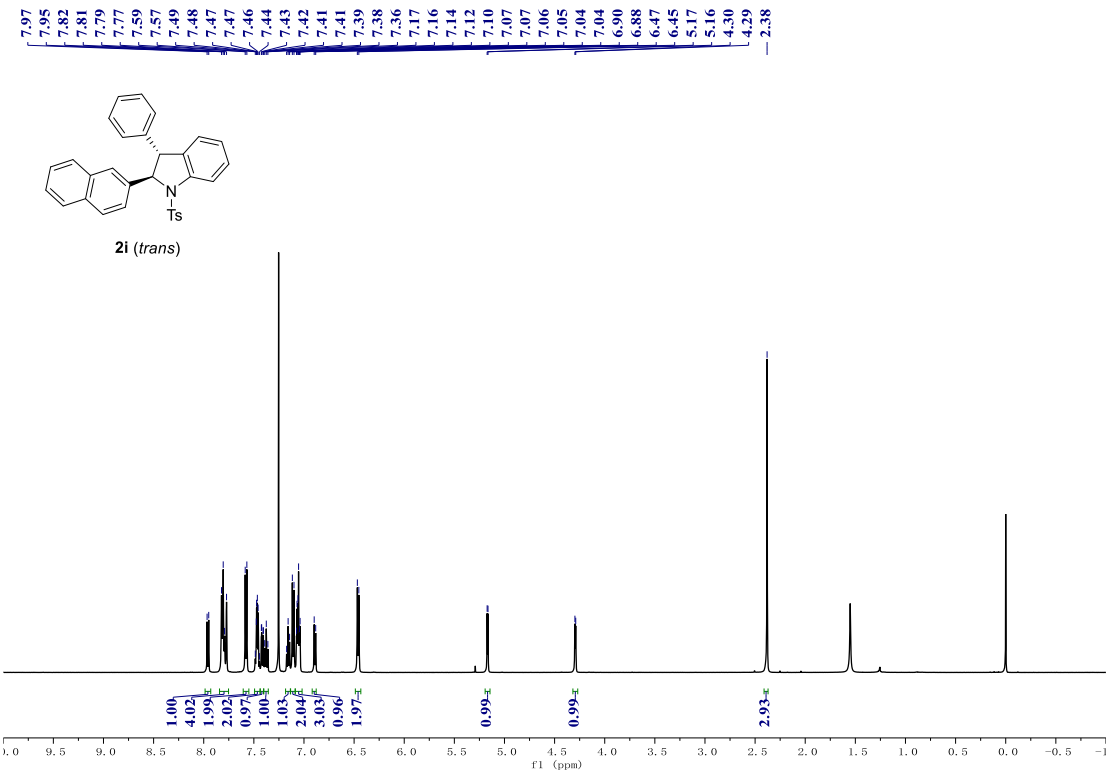
2h (*trans*)


7.82
7.80
7.64
7.63
7.35
7.33
7.31
7.21
7.20
7.07
7.06
7.05
7.04
7.03
7.02
7.01
6.99
6.85
6.84
6.82
6.68
6.66
6.65
5.53
5.51
4.67
4.65
2.39
2.34
MeS
N
Ts
0.98
1.95
1.06
2.03
4.10
2.96
3.96
0.99
0.98
2.98
2.86
f1 (ppm)

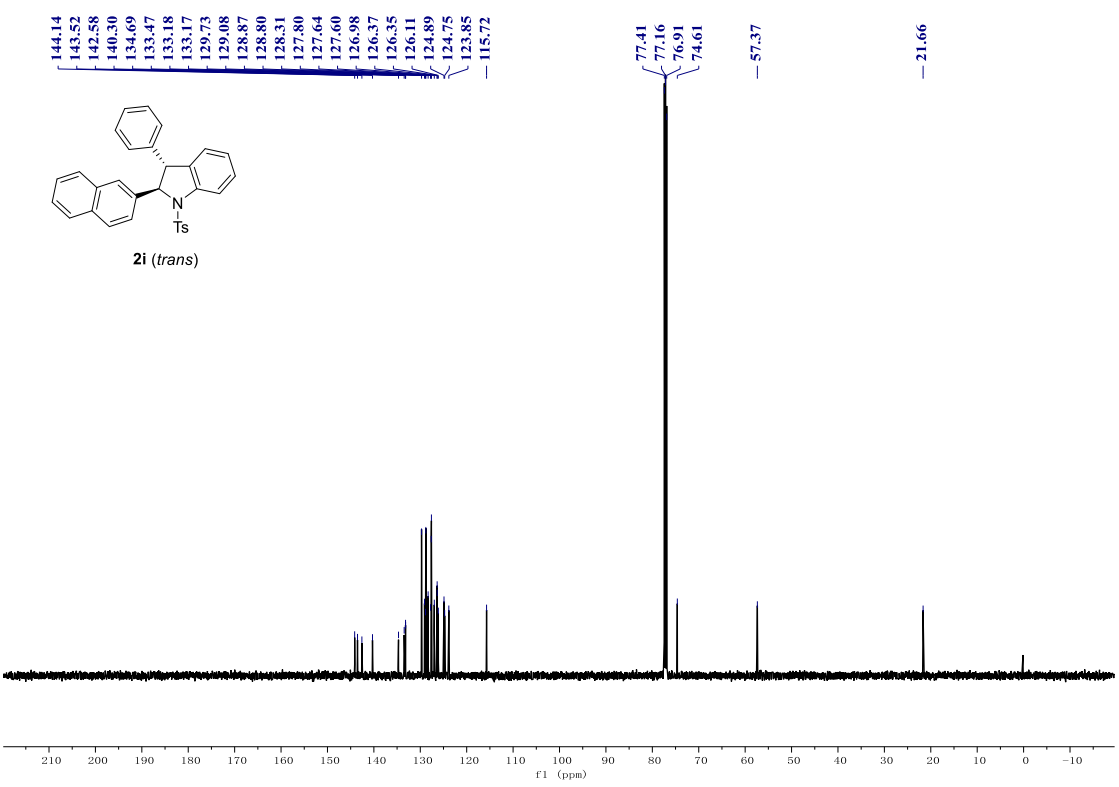
2h (*cis*)


144.10
143.22
137.24
136.59
135.97
134.58
134.29
129.89
129.77
128.59
128.02
127.82
127.24
127.20
126.12
126.04
124.80
115.91
77.41
77.16
76.91
70.62
53.92
21.72
16.12
MeS
N
Ts
f1 (ppm)

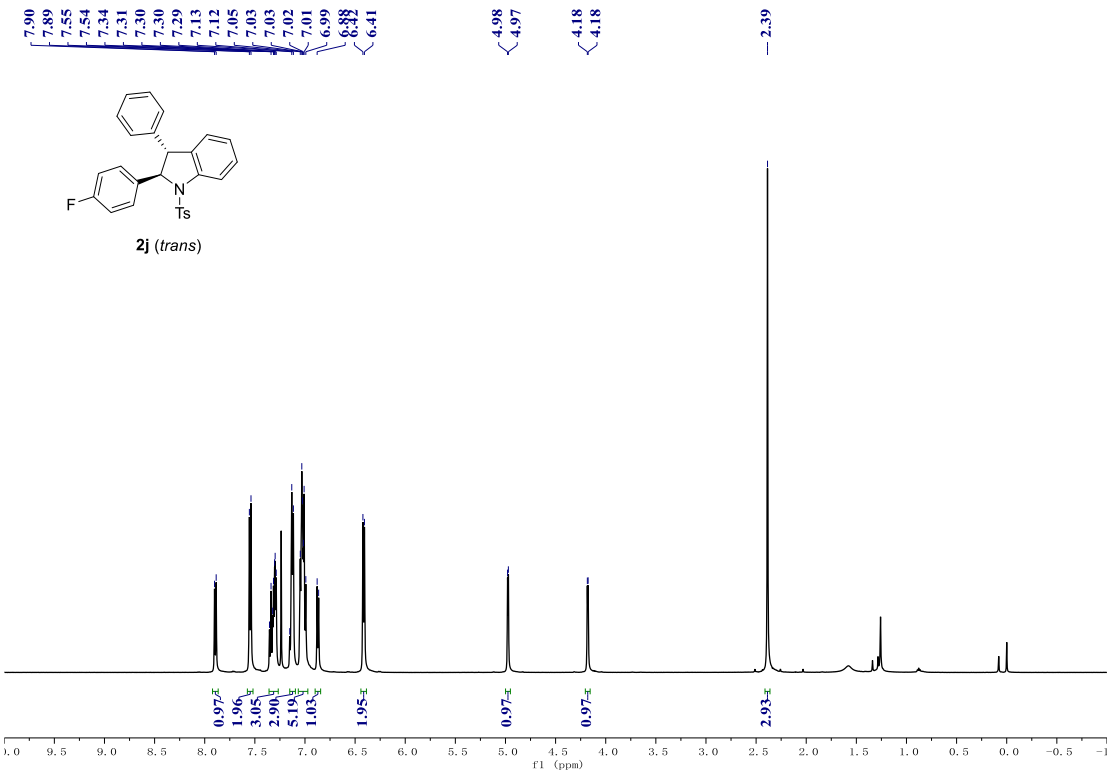
2h (*cis*)



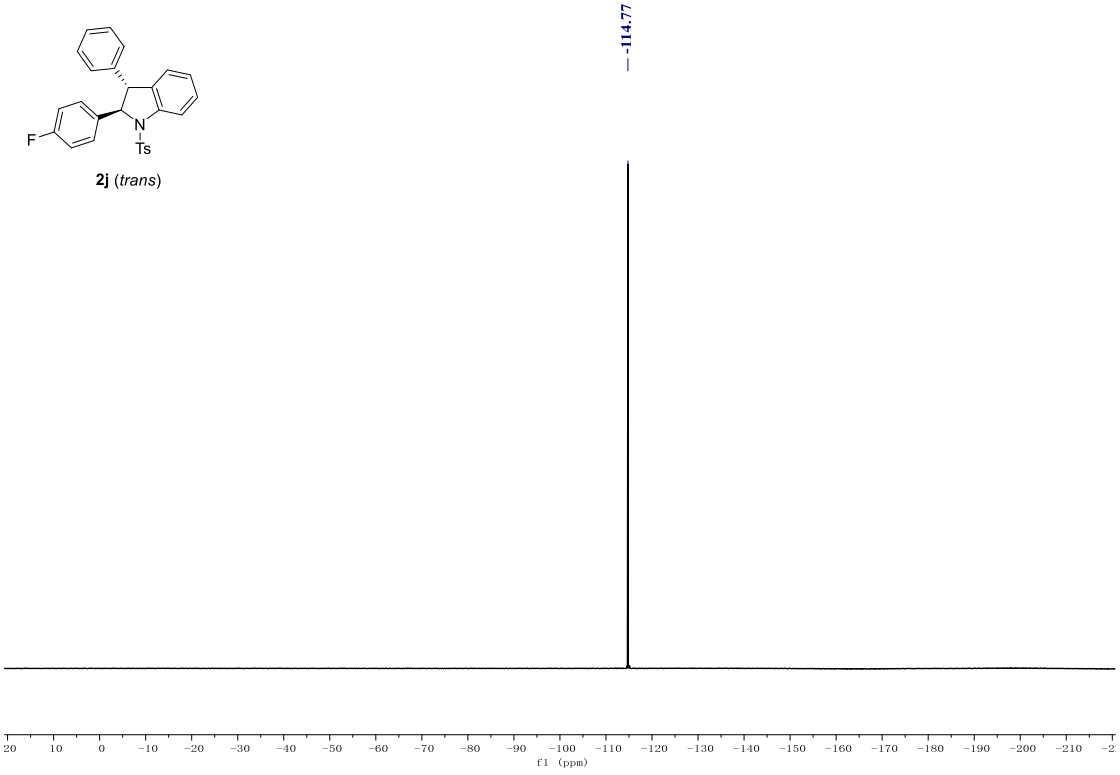
2i (*trans*)



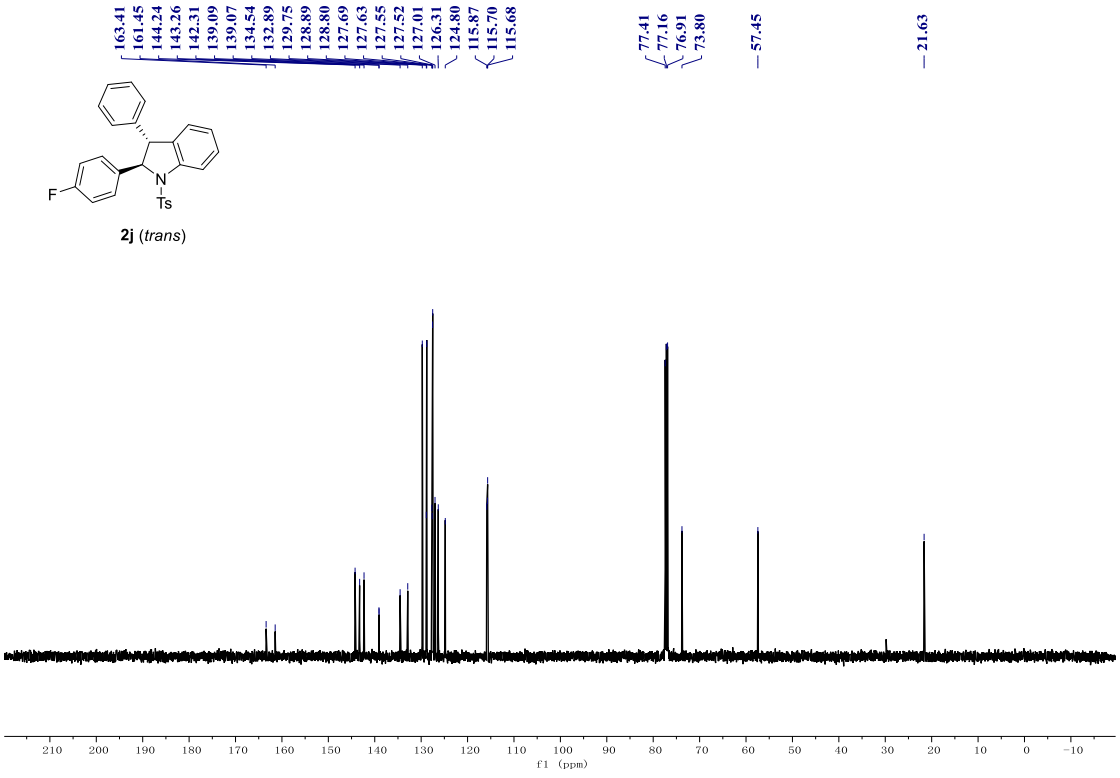
2i (*trans*)



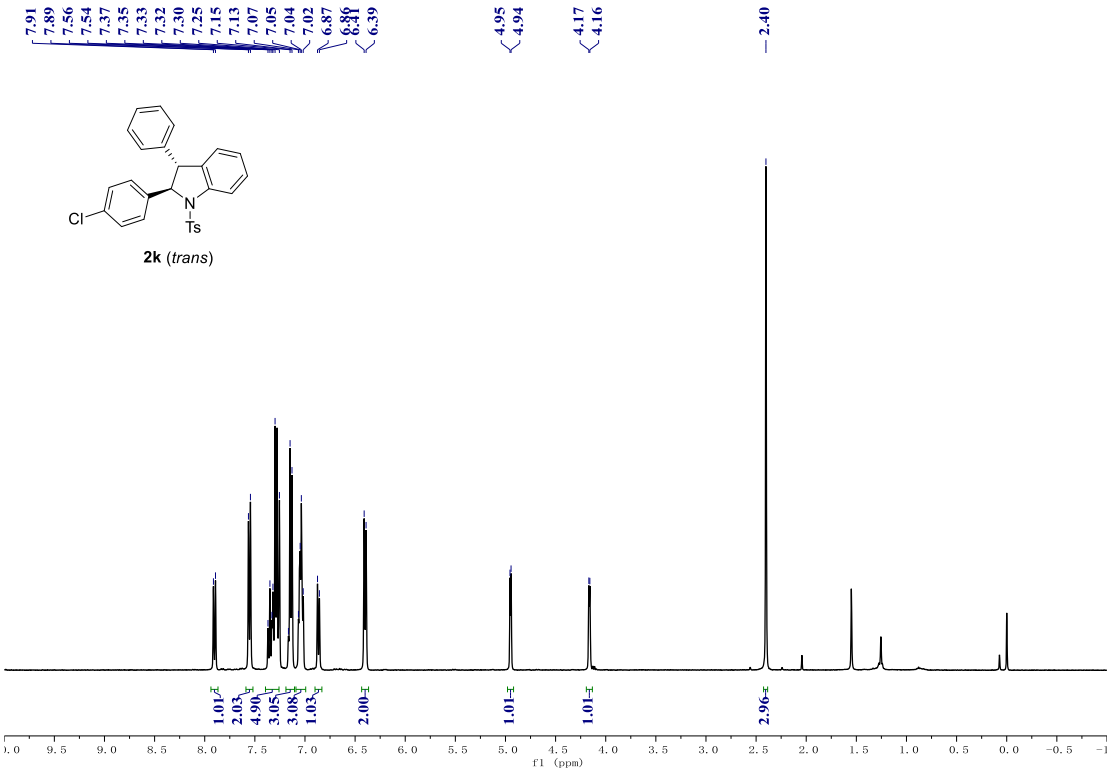
2j (*trans*)



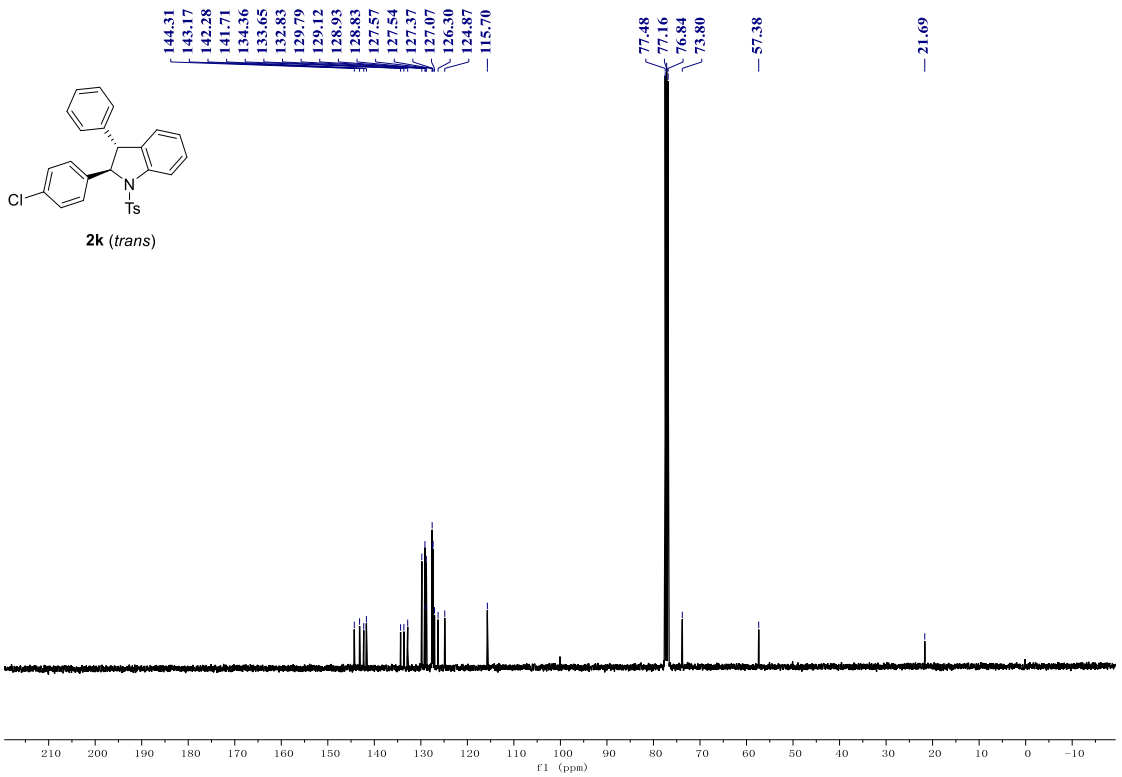
2j (*trans*)


163.41
161.45
144.24
143.26
142.31
139.09
139.07
134.54
132.89
129.75
128.89
128.80
127.69
127.63
127.55
127.52
127.01
126.31
124.80
115.87
115.70
115.68
77.41
77.16
76.91
73.80
57.45
21.63
F
N
Ts
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

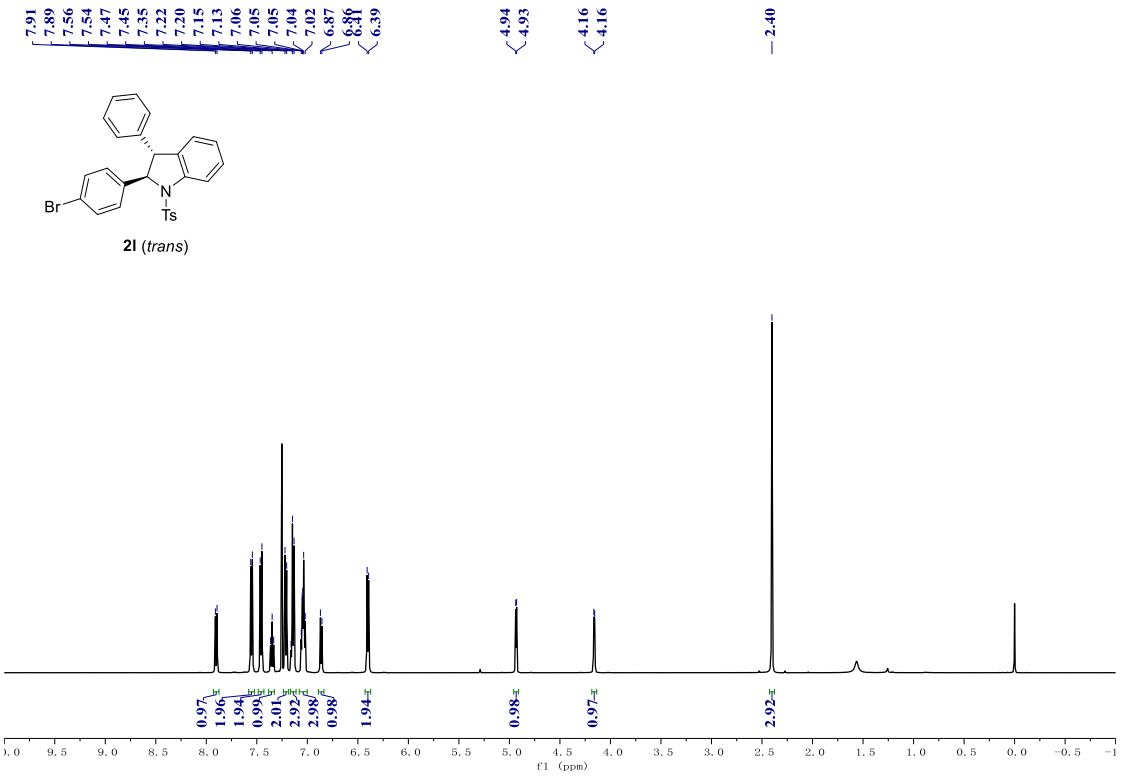
2j (*trans*)



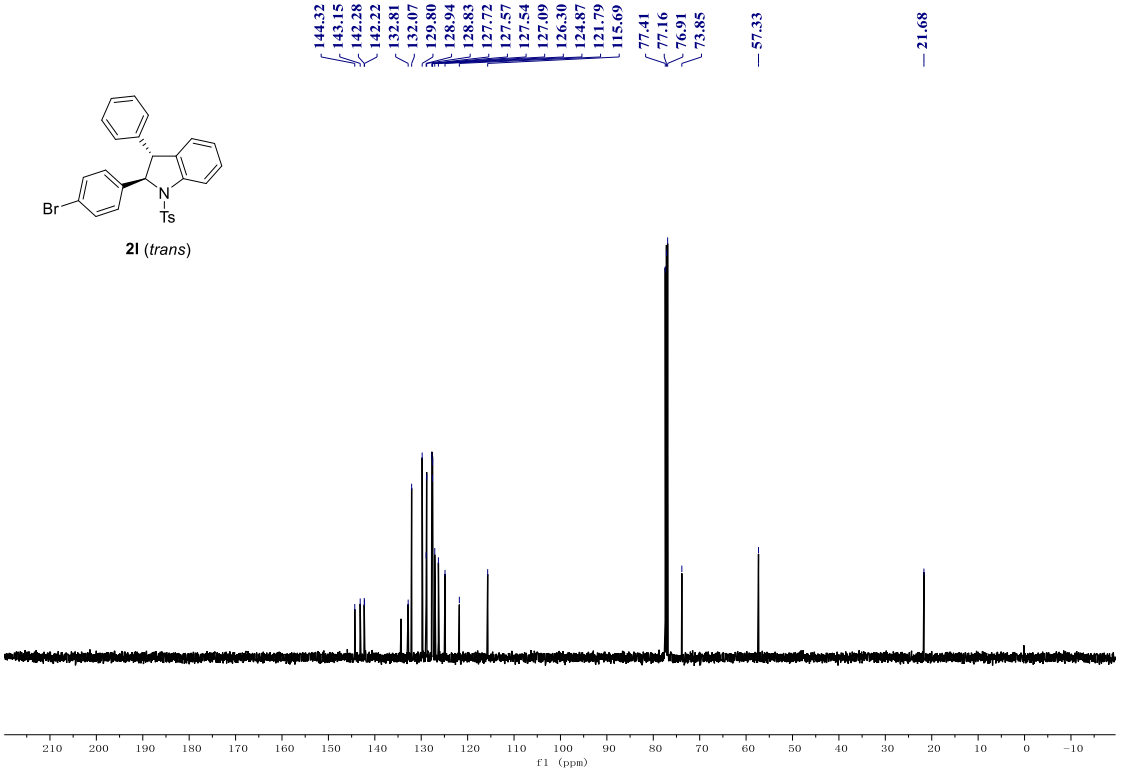
2k (*trans*)



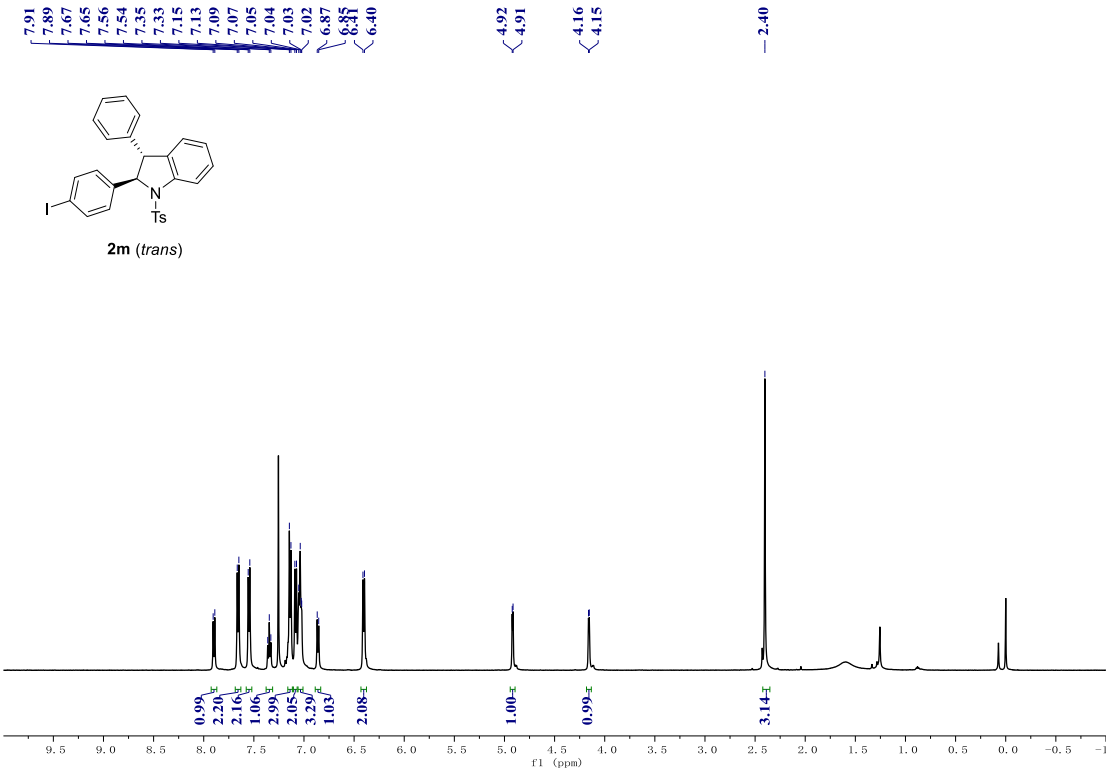
2k (*trans*)



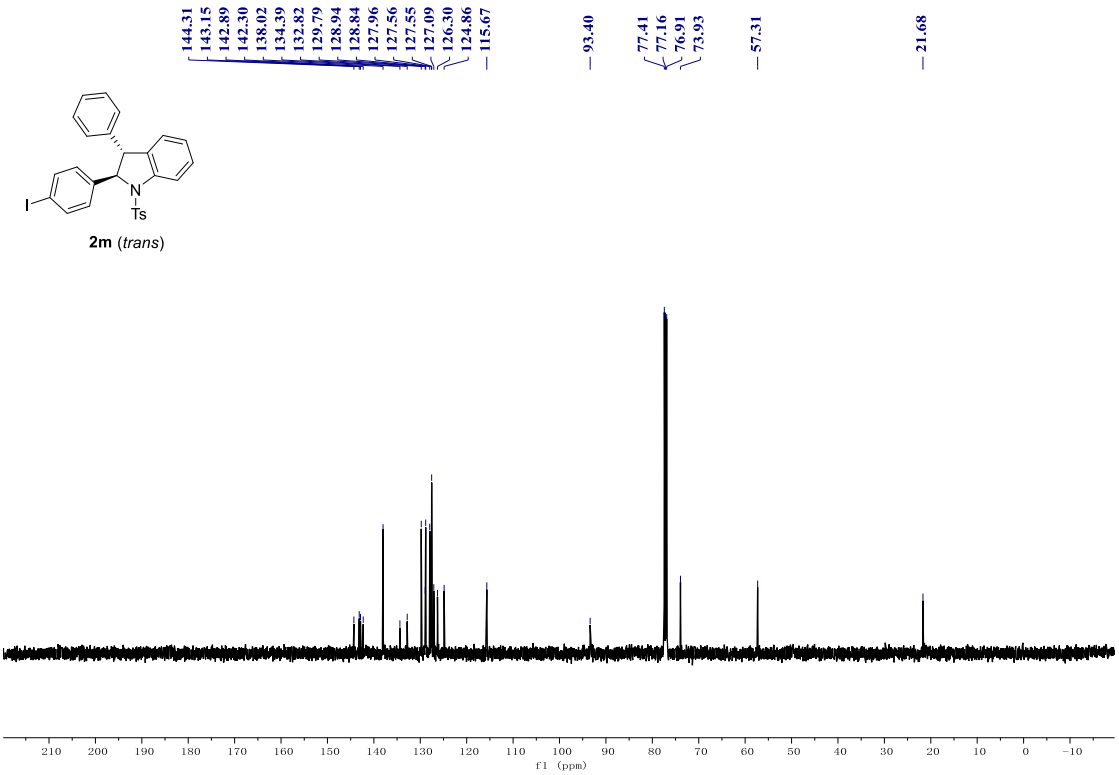
2l (*trans*)



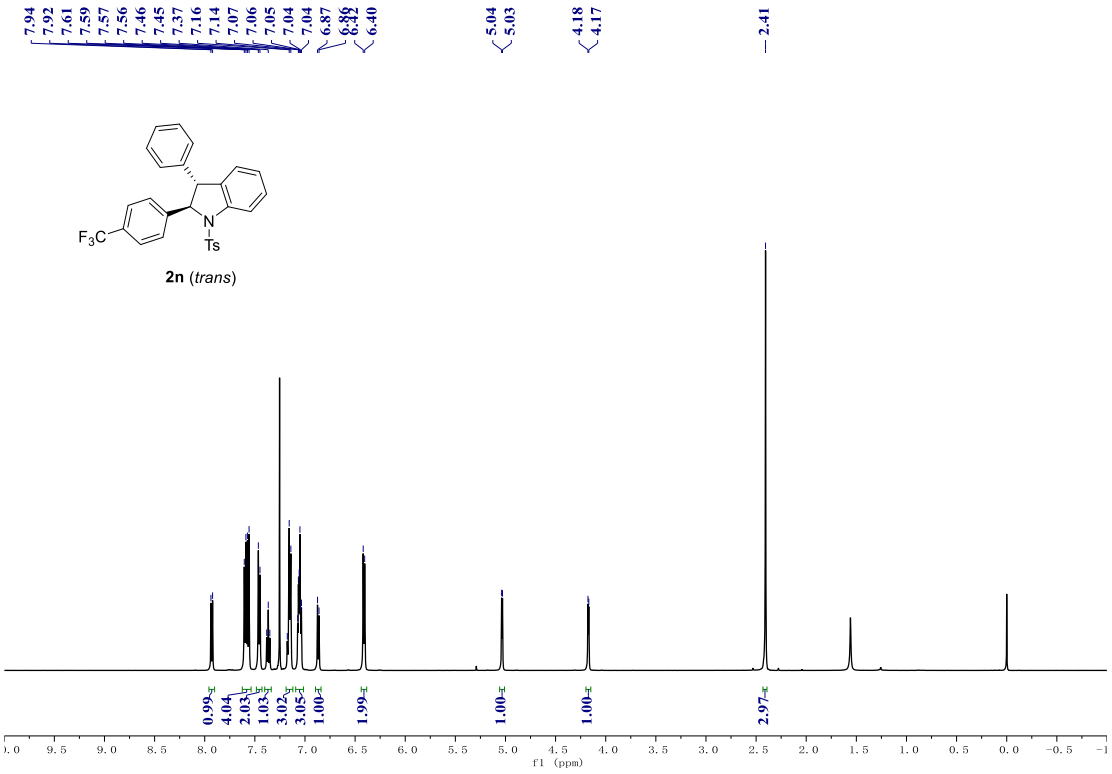
2l (*trans*)



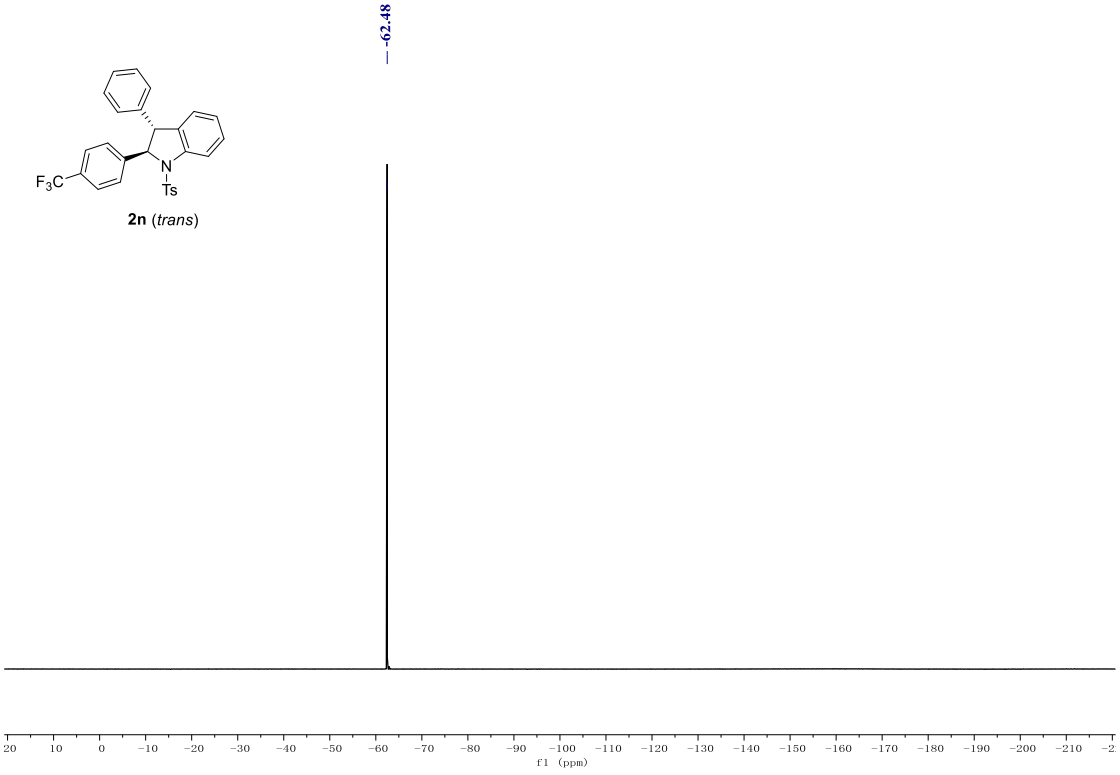
2m (*trans*)



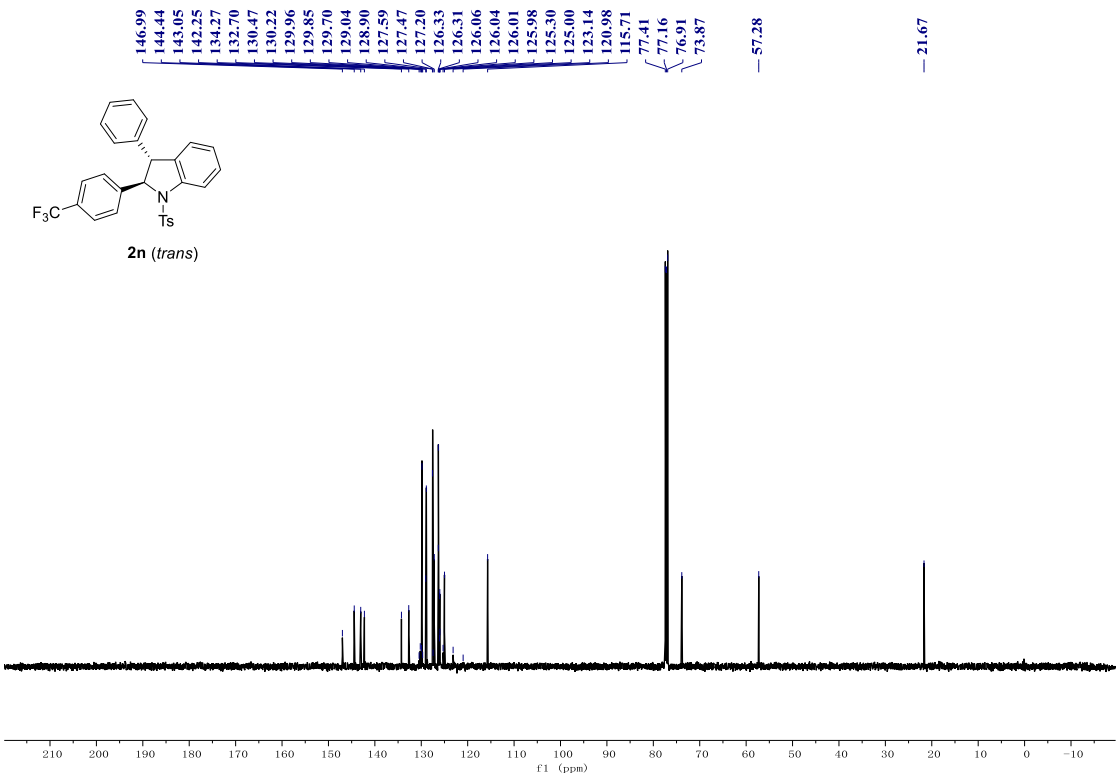
2m (*trans*)

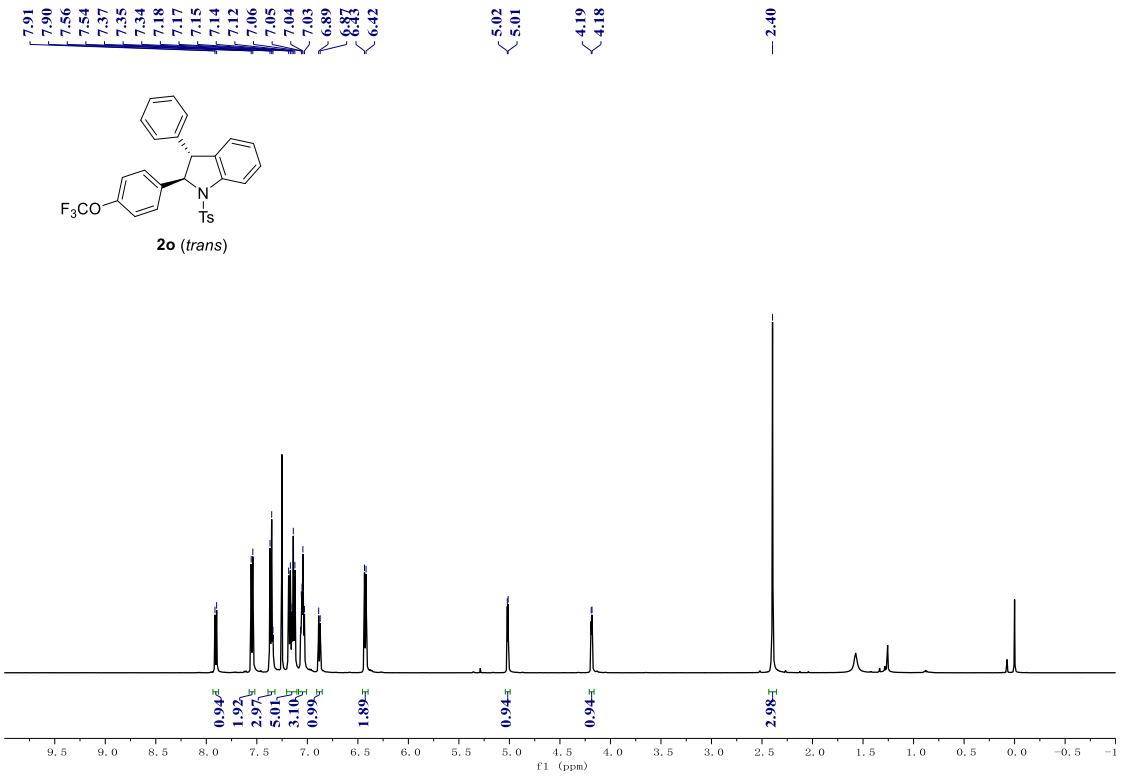


2n (*trans*)

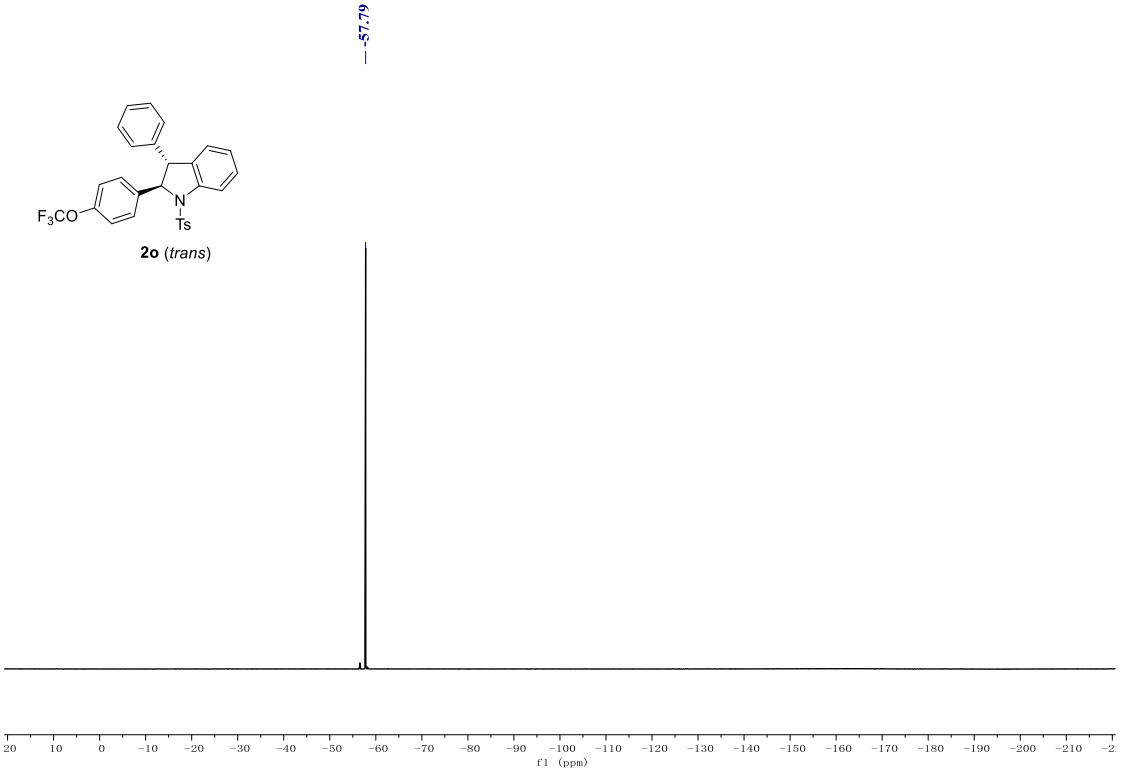


2n (*trans*)

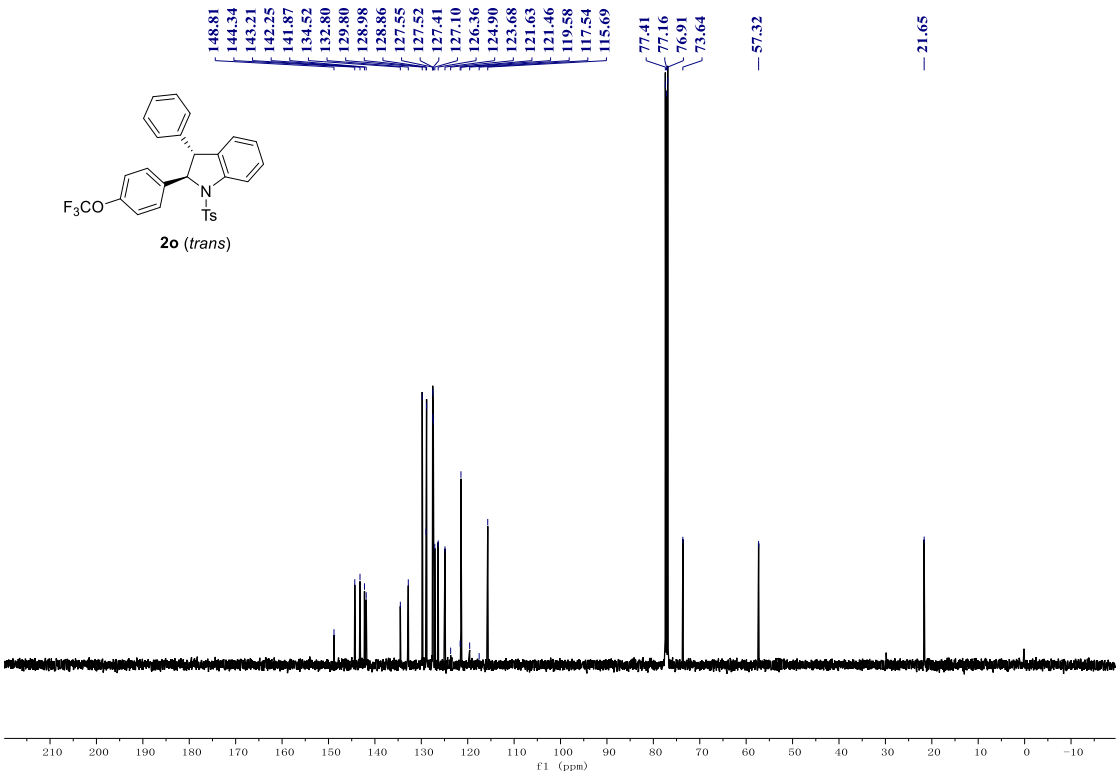

146.99
144.44
143.05
142.25
134.27
132.70
130.47
130.22
129.96
129.85
129.70
129.04
128.90
127.59
127.47
127.20
126.33
126.31
126.06
126.04
126.01
125.98
125.30
125.00
123.14
120.98
115.71
77.41
77.16
76.91
73.87
57.28
21.67
F3C
N
Ts
2n (trans)
f1 (ppm)

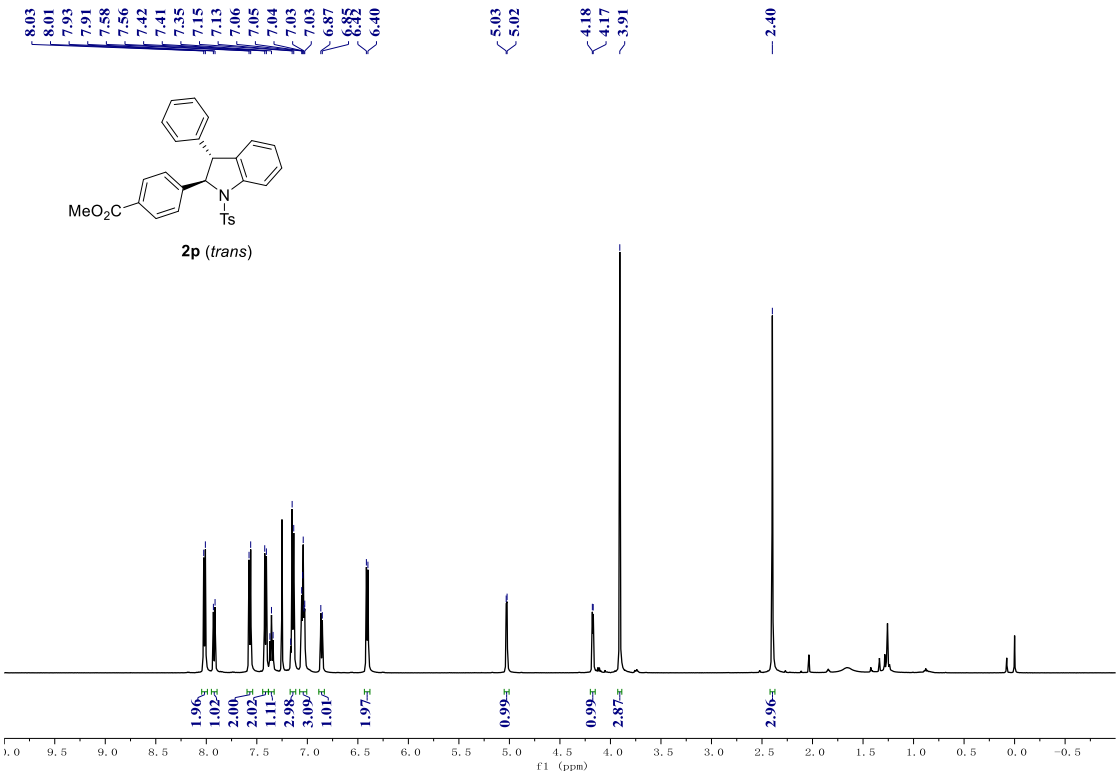


2o (*trans*)

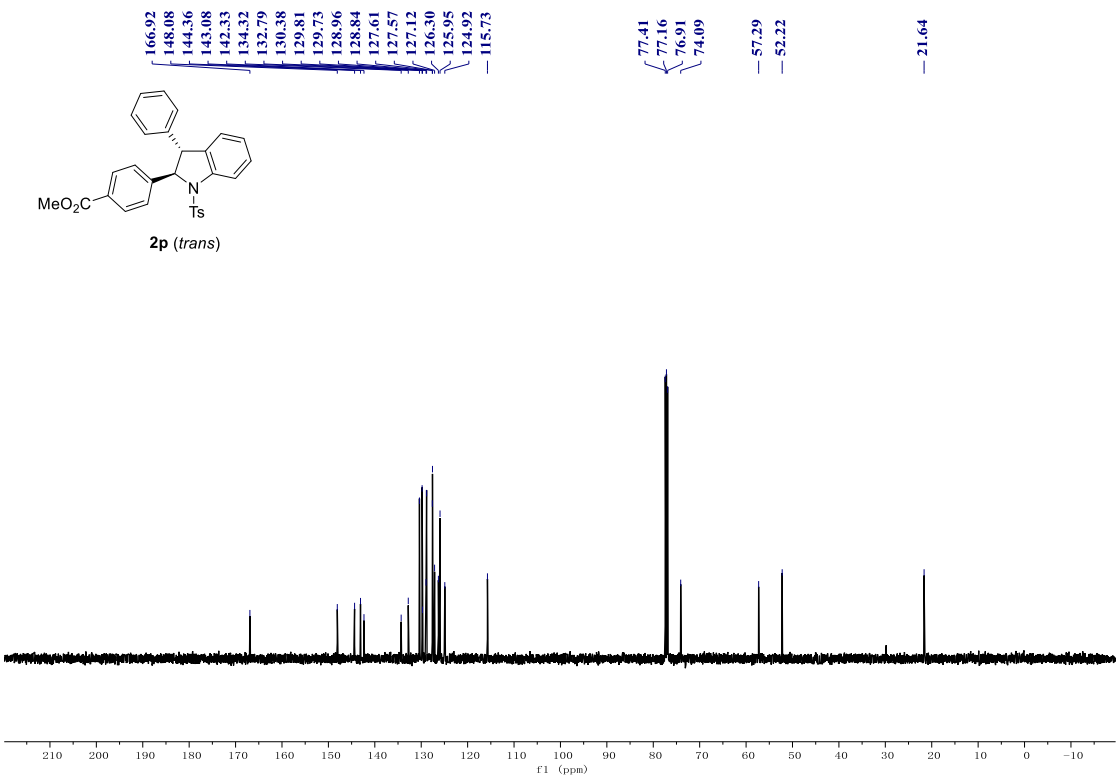


2o (*trans*)

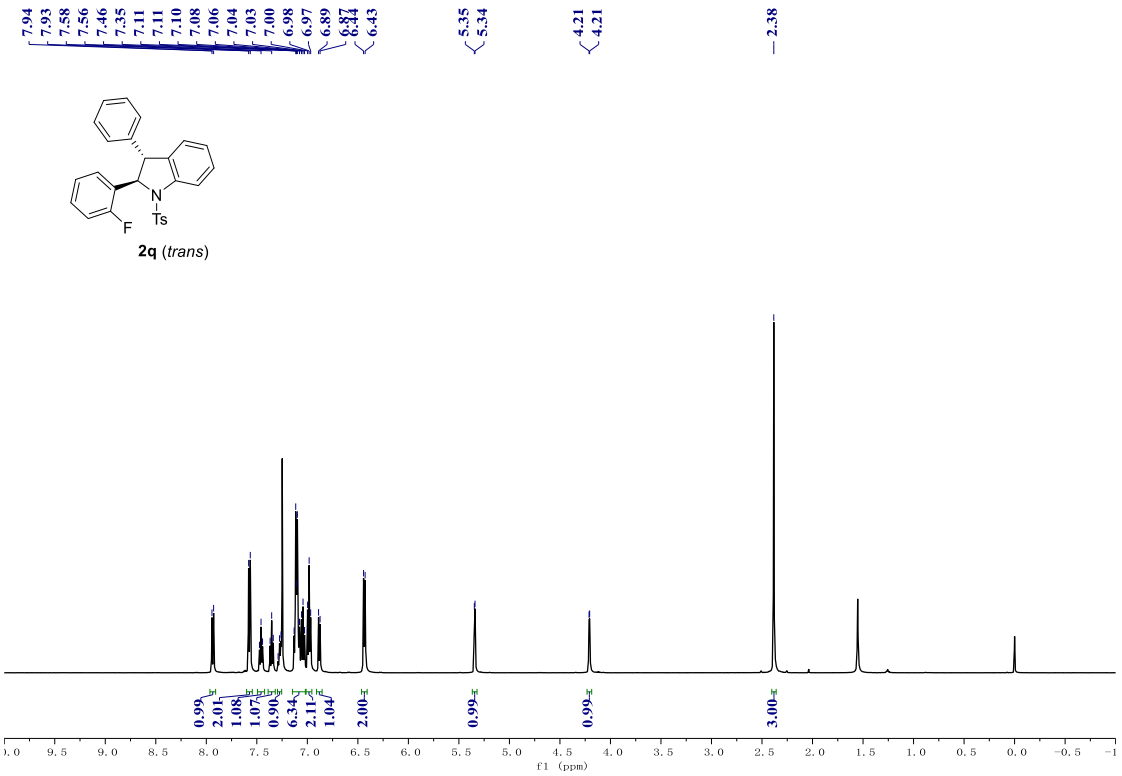

148.81
144.34
143.21
142.25
141.87
134.52
132.80
129.80
128.98
128.86
127.55
127.52
127.41
127.10
126.36
124.90
123.68
121.63
121.46
119.58
117.54
115.69
77.41
77.16
76.91
73.64
57.32
21.65
F3CO
N
Ts
2o (trans)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



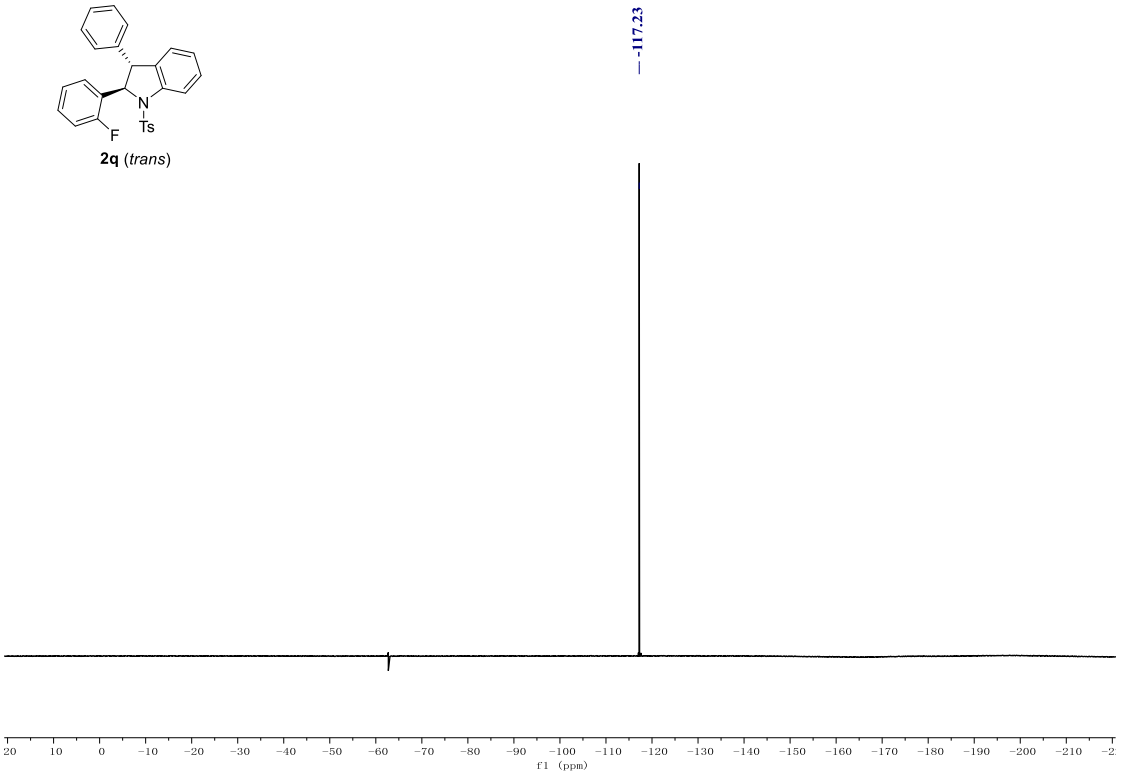
2p (*trans*)



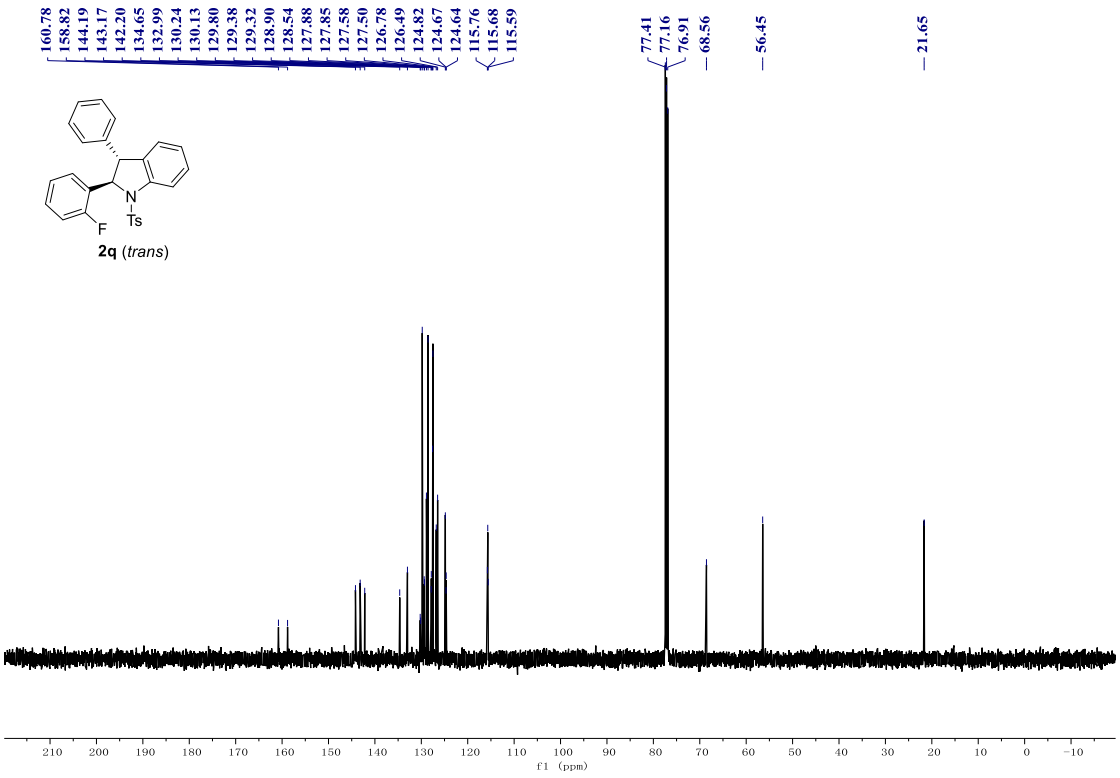
2p (*trans*)

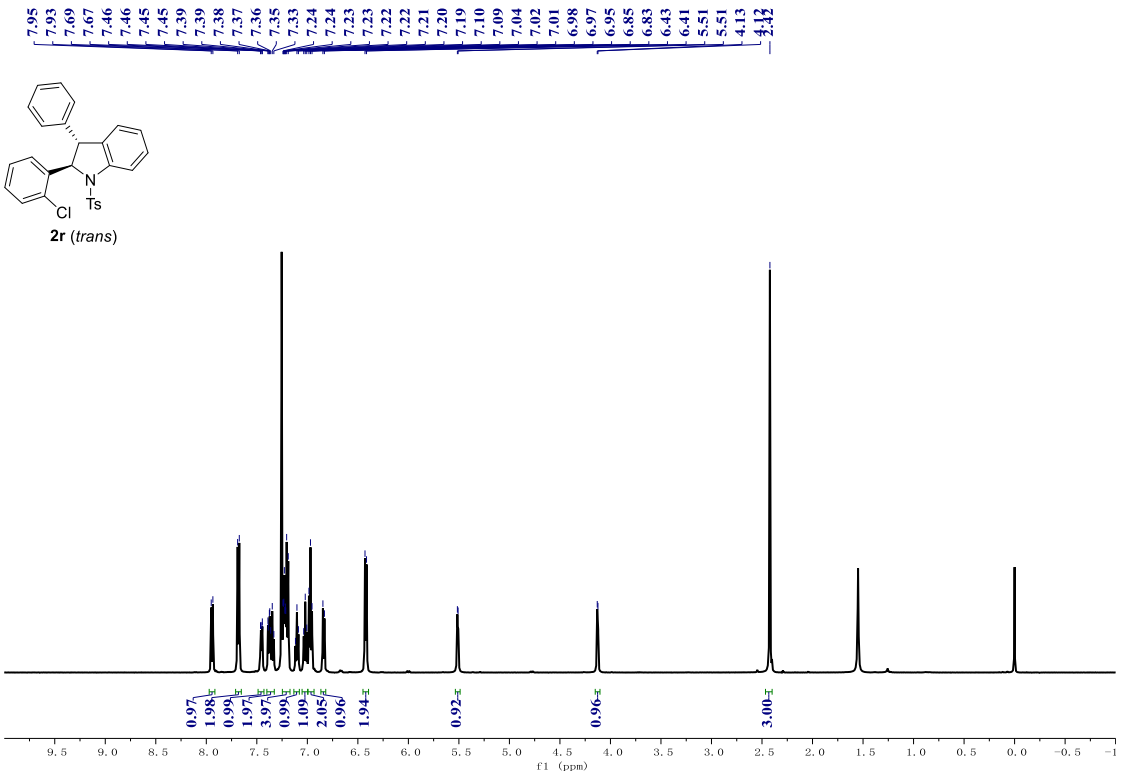


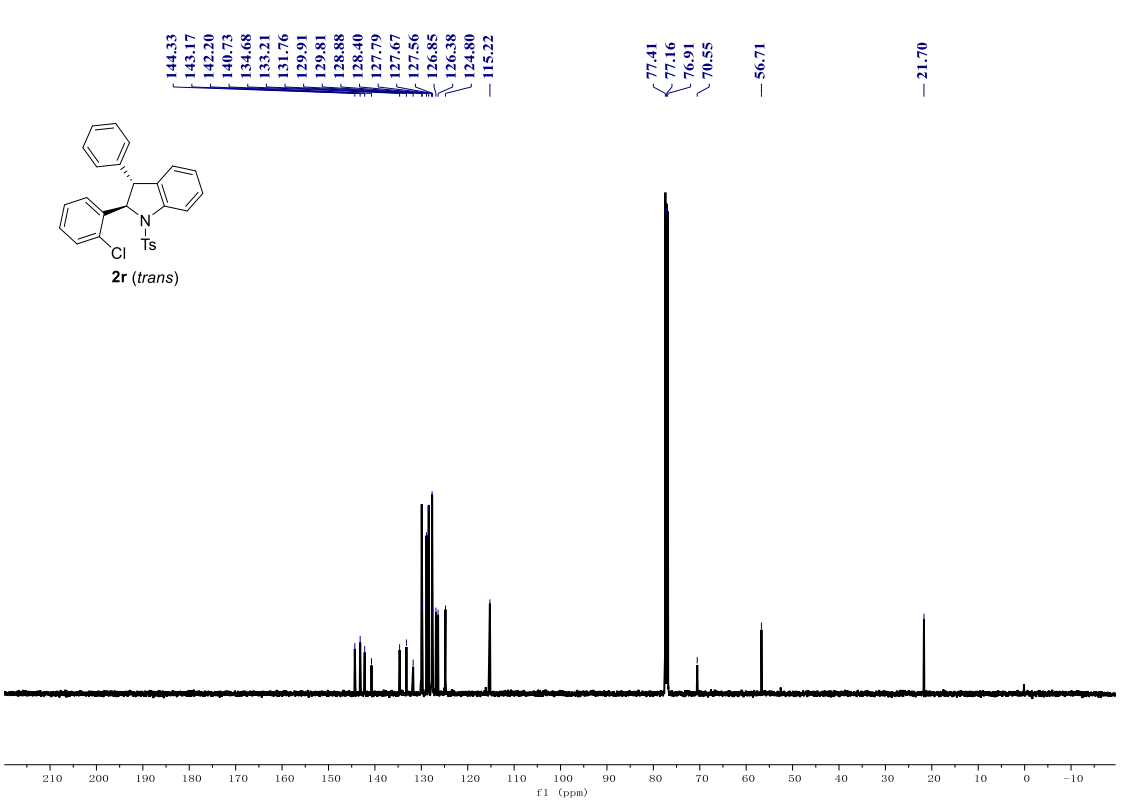
2q (*trans*)

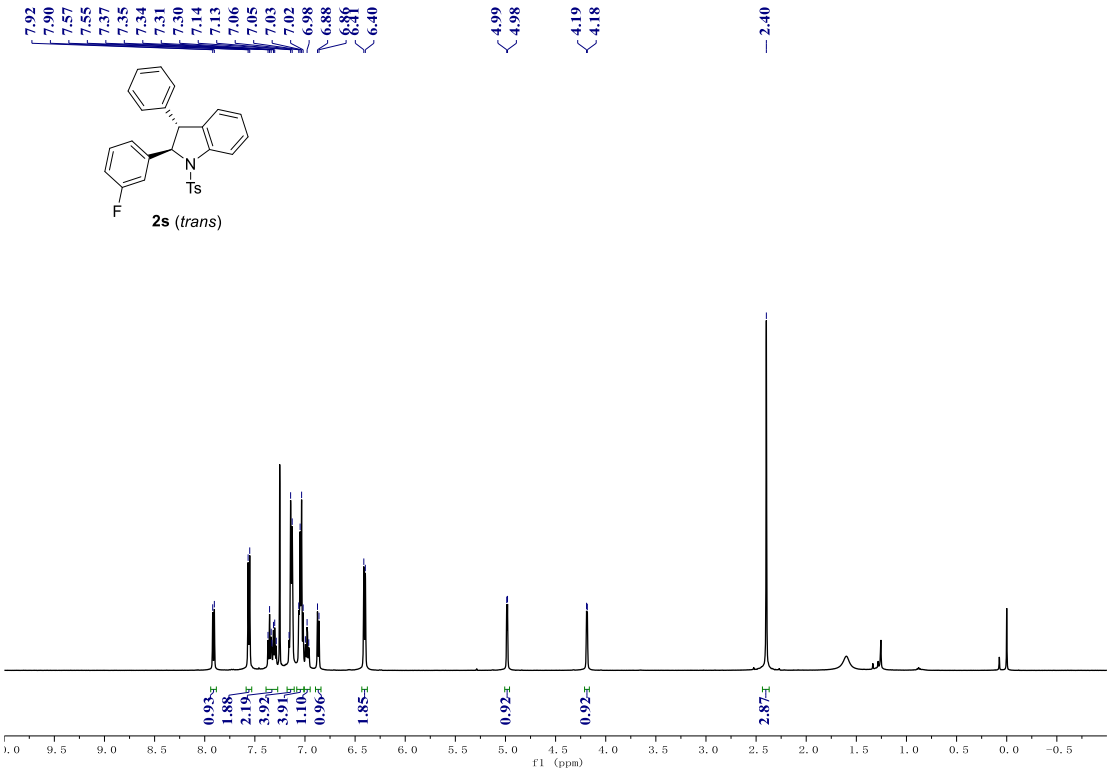


2q (*trans*)

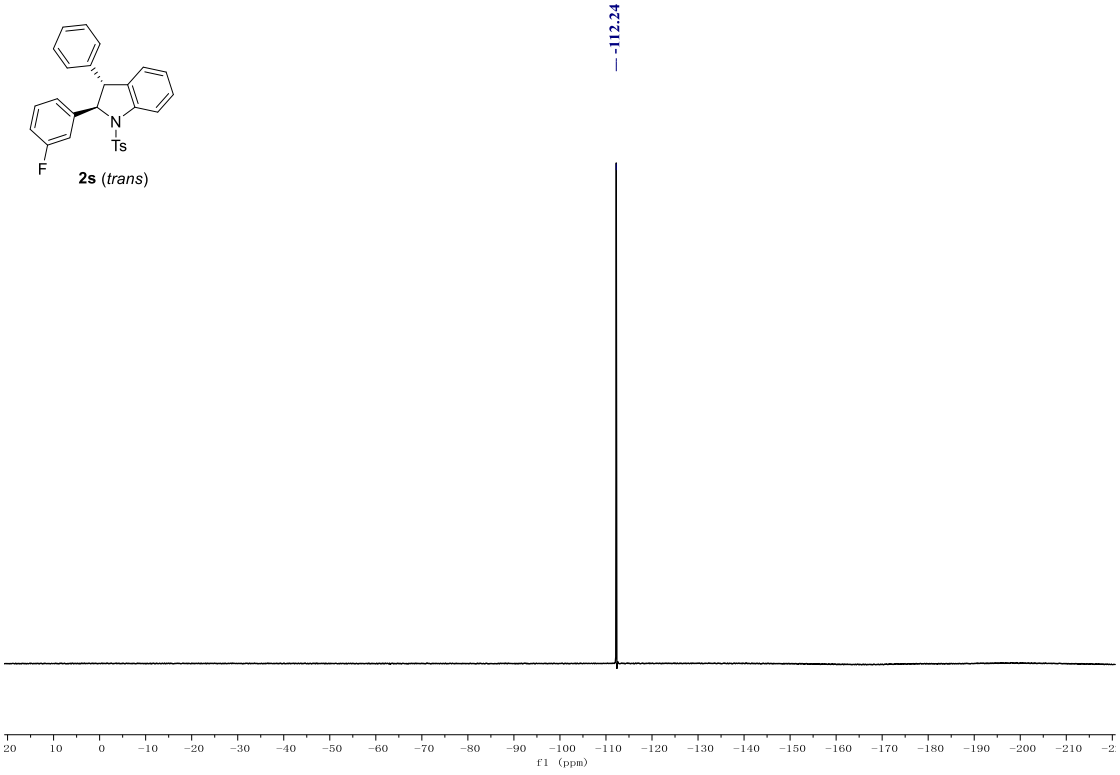

160.78
158.82
144.19
143.17
142.20
134.65
132.99
130.24
130.13
129.80
129.38
129.32
128.90
128.54
127.88
127.85
127.58
127.50
126.78
126.49
124.82
124.67
124.64
115.76
115.68
115.59
77.41
77.16
76.91
68.56
56.45
21.65
N
Ts
F
2q (trans)
f1 (ppm)

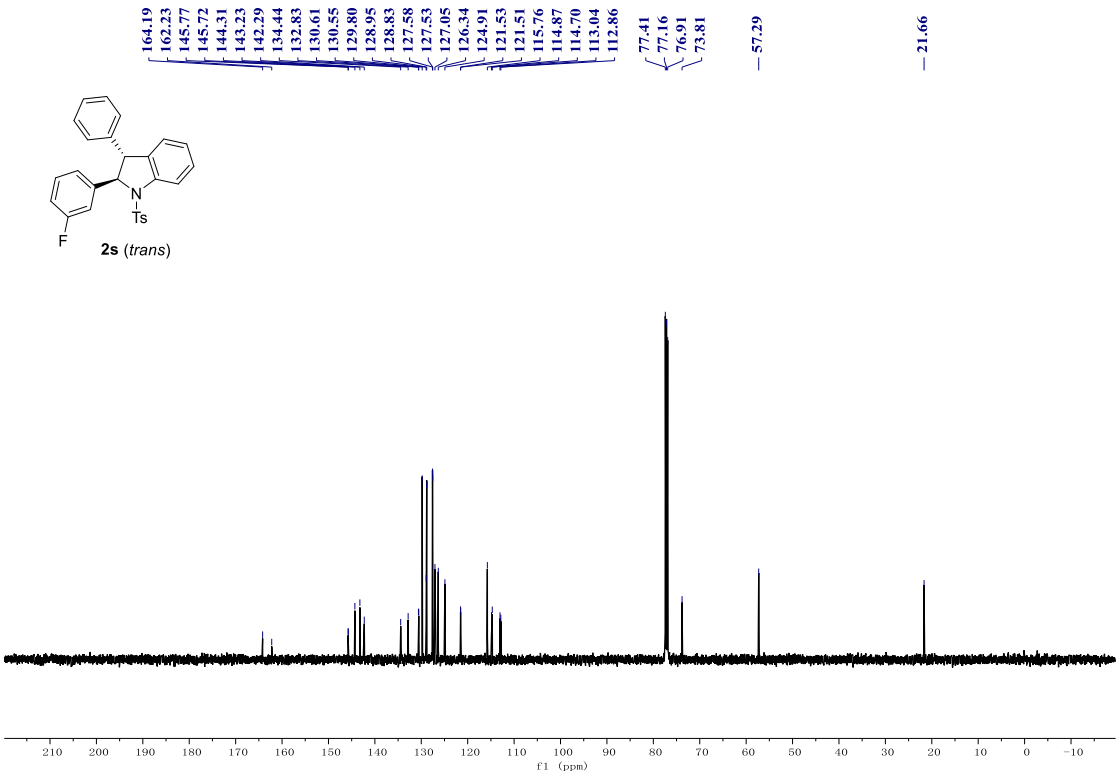

7.95
7.93
7.69
7.67
7.46
7.46
7.45
7.45
7.39
7.39
7.38
7.37
7.36
7.35
7.33
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.19
7.10
7.09
7.04
7.02
7.01
6.98
6.97
6.95
6.85
6.83
6.43
6.41
5.51
5.51
4.13
4.12
2.42
N
Ts
Cl
2r (trans)
0.97
1.98
0.99
1.97
3.97
0.99
1.09
2.05
0.96
1.94
0.92
0.96
3.00
f1 (ppm)

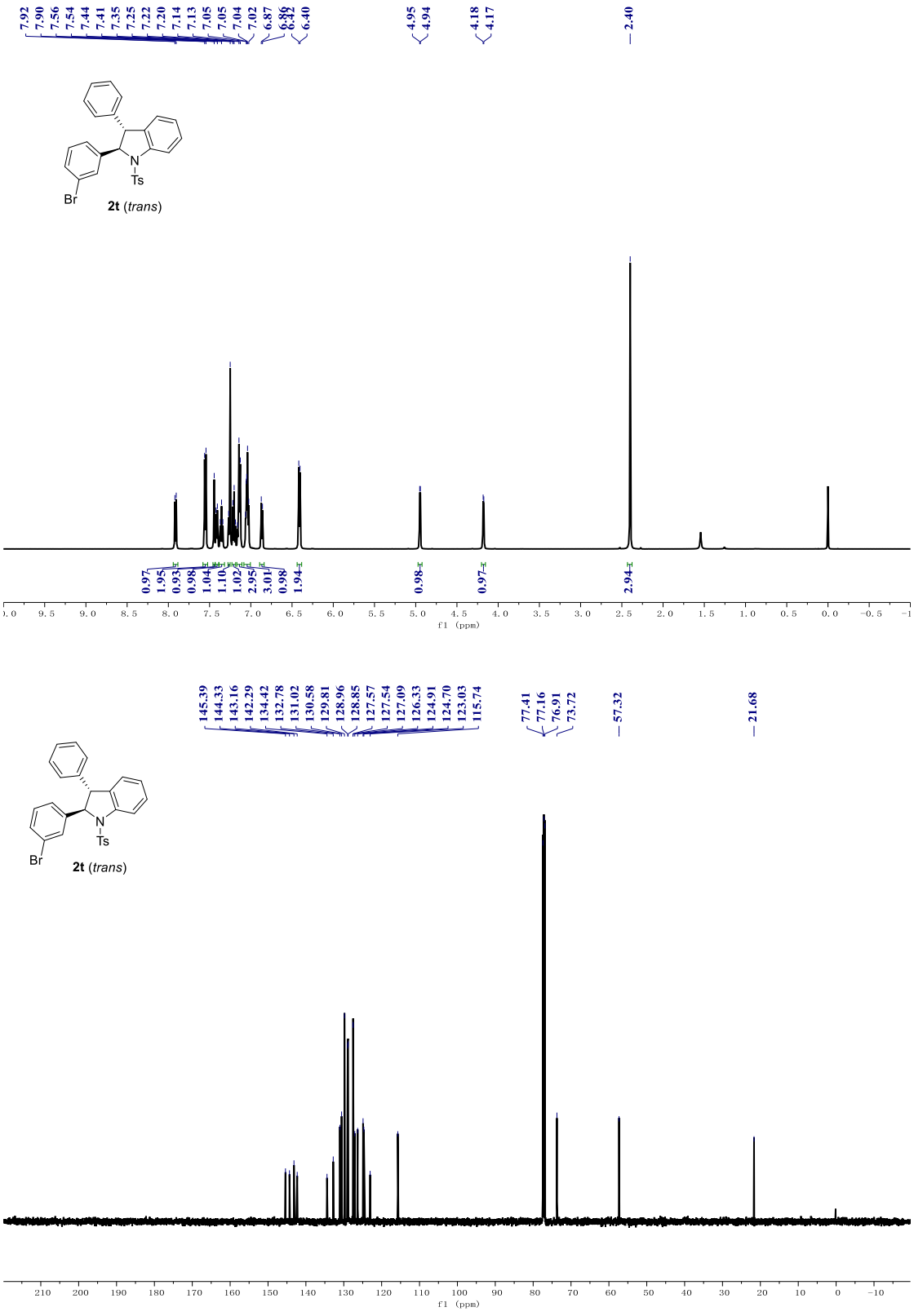

144.33
143.17
142.20
140.73
134.68
133.21
131.76
129.91
129.81
128.88
128.40
127.79
127.67
127.56
126.85
126.38
124.80
115.22
77.41
77.16
76.91
70.55
56.71
21.70
N
Ts
Cl
2r (trans)
f1 (ppm)

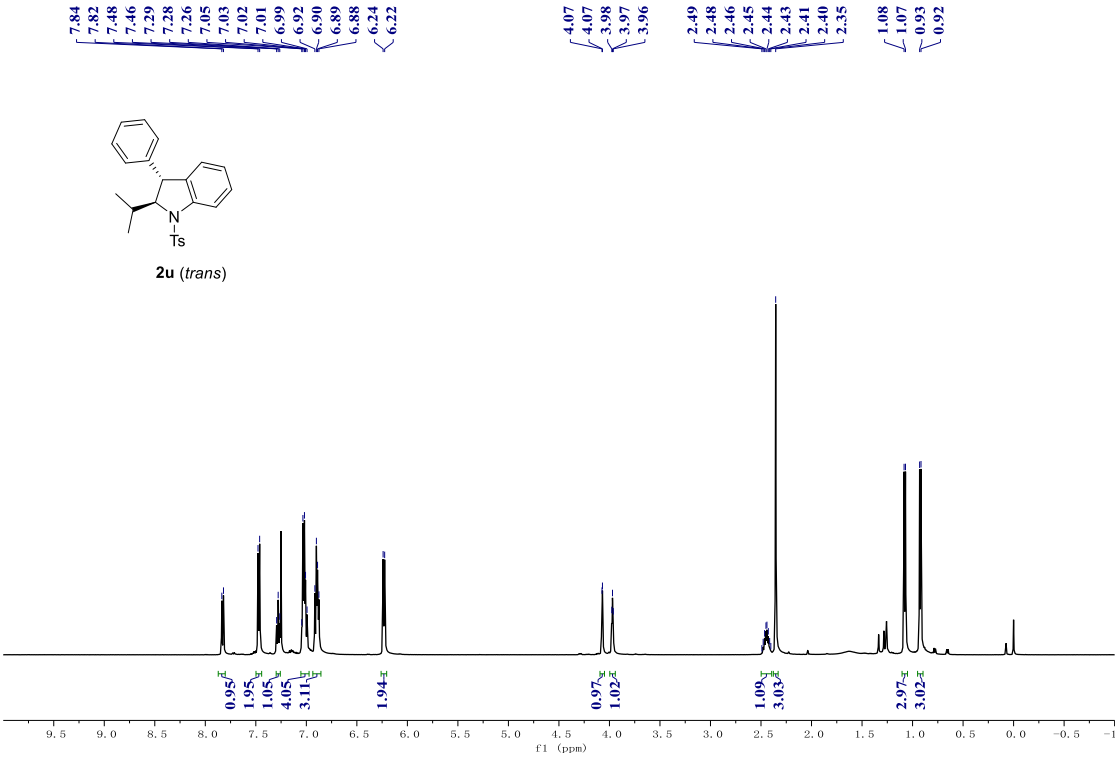

7.92
7.90
7.57
7.55
7.37
7.35
7.34
7.31
7.30
7.14
7.13
7.06
7.05
7.03
7.02
6.98
6.88
6.86
6.41
6.40
4.99
4.98
4.19
4.18
2.40
N
Ts
F
0.93
1.88
2.19
3.92
3.91
1.10
0.96
1.85
0.92
0.92
2.87
f1 (ppm)

2s (*trans*)

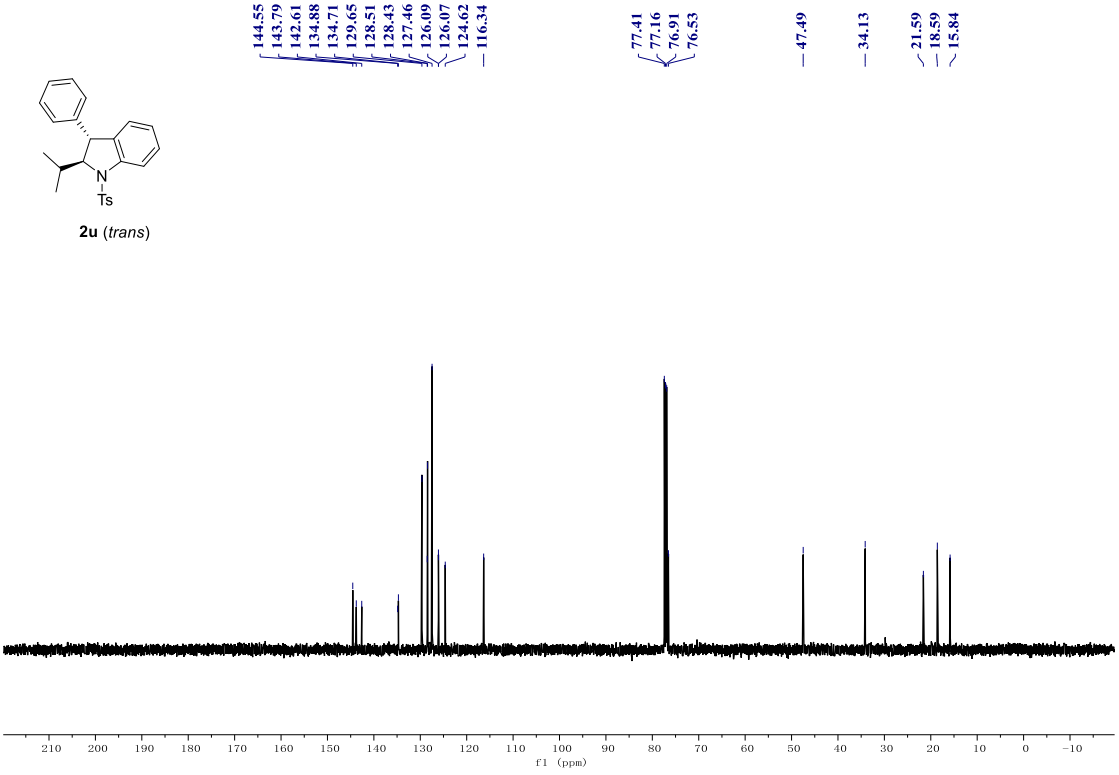

-112.24
f1 (ppm)


164.19
162.23
145.77
145.72
144.31
143.23
142.29
134.44
132.83
130.61
130.55
129.80
128.95
128.83
127.58
127.53
127.05
126.34
124.91
121.53
121.51
115.76
114.87
114.70
113.04
112.86
77.41
77.16
76.91
73.81
57.29
21.66
N
Ts
F
2s (trans)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

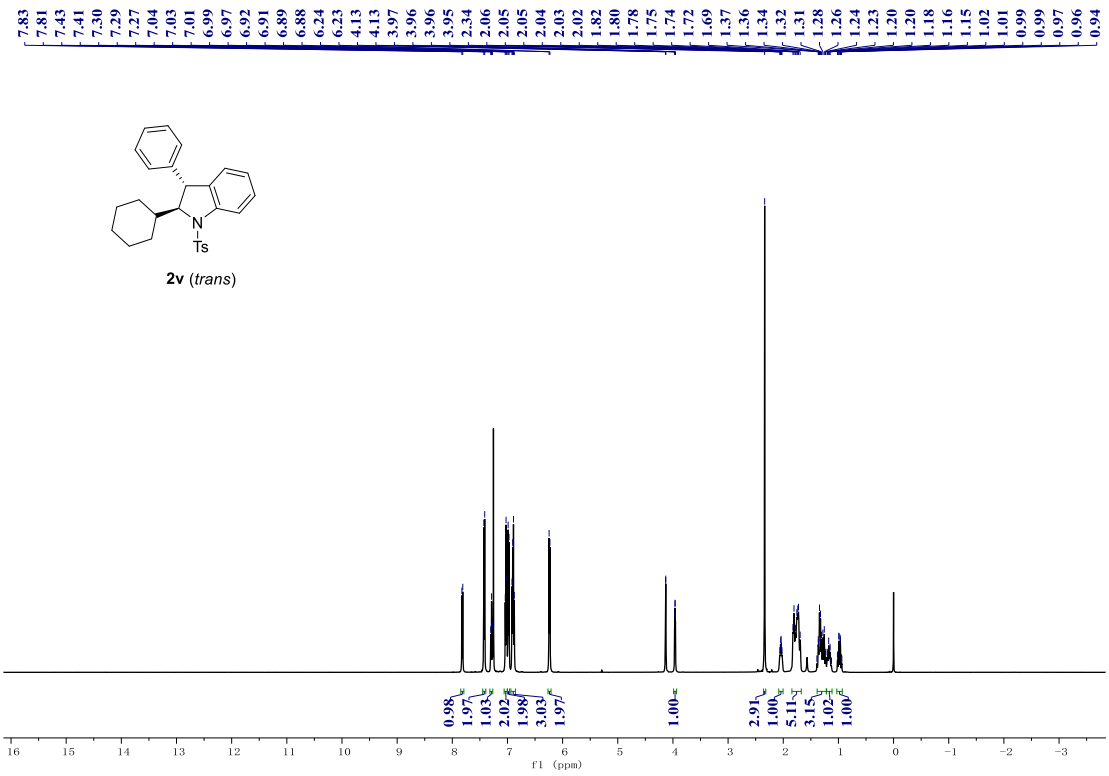

7.92
7.90
7.56
7.54
7.44
7.41
7.35
7.25
7.22
7.20
7.14
7.13
7.05
7.05
7.04
7.02
6.87
6.86
6.42
6.40
4.95
4.94
4.18
4.17
2.40
N
Ts
Br
2t (trans)
0.97
1.95
0.93
0.98
1.04
1.10
1.02
2.95
3.01
0.98
1.94
0.98
0.97
2.94
f1 (ppm)
145.39
144.33
143.16
142.29
134.42
132.78
131.02
130.58
129.81
128.96
128.85
127.57
127.54
127.09
126.33
124.91
124.70
123.03
115.74
77.41
77.16
76.91
73.72
57.32
21.68
N
Ts
Br
2t (trans)
f1 (ppm)

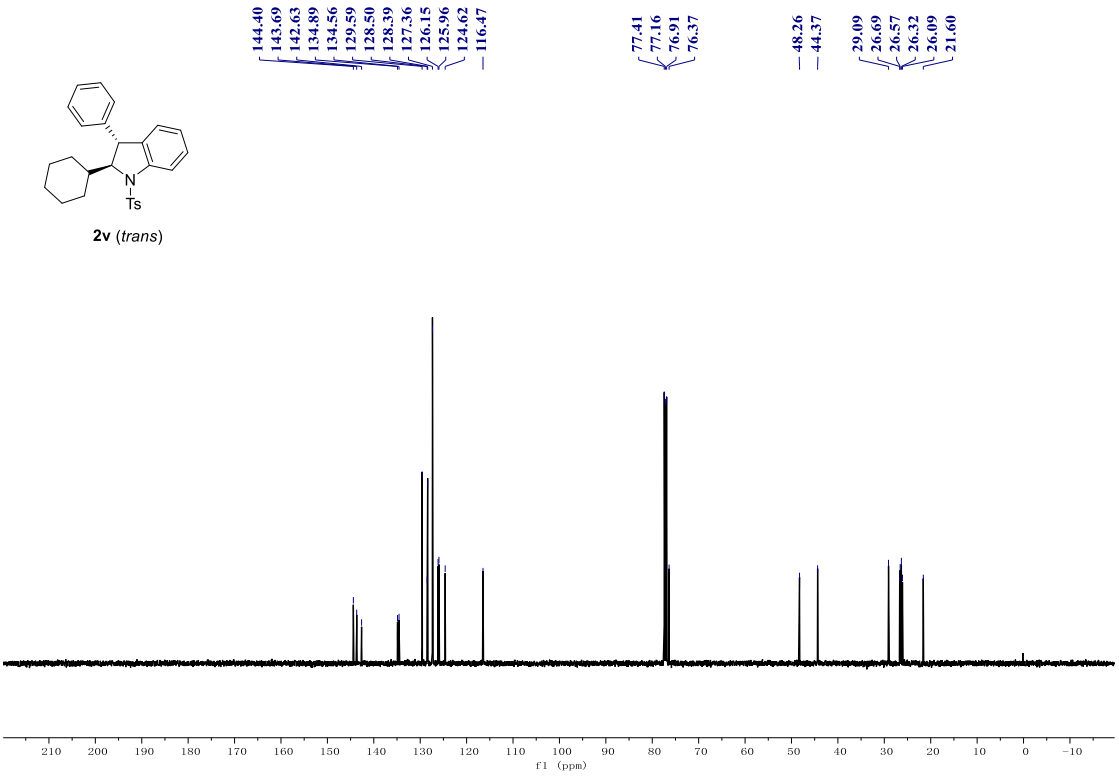


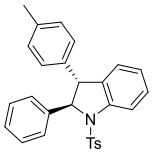
2u (*trans*)



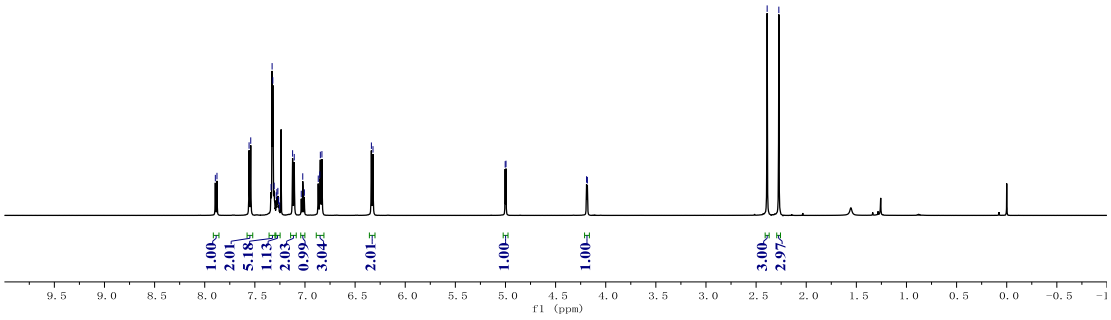
2u (*trans*)

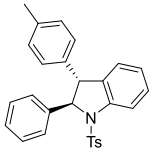

7.83 7.81 7.43 7.41 7.30 7.29 7.27 7.04 7.03 7.01 6.99 6.97 6.92 6.91 6.89 6.88 6.24 6.23 4.13 4.13 3.97 3.96 3.96 3.95 2.34 2.06 2.05 2.05 2.04 2.03 2.02 1.82 1.80 1.78 1.75 1.74 1.72 1.69 1.37 1.36 1.34 1.32 1.31 1.28 1.26 1.24 1.23 1.20 1.20 1.18 1.16 1.15 1.02 1.01 0.99 0.99 0.97 0.96 0.94
N
Ts
2v (trans)
0.98 1.97 1.03 2.02 1.98 3.03 1.97 1.00 2.91 1.00 5.11 3.15 1.02 1.00
f1 (ppm)


144.40 143.69 142.63 134.89 134.56 129.59 128.50 128.39 127.36 126.15 125.96 124.62 116.47
77.41 77.16 76.91 76.37
48.26 44.37
29.09 26.69 26.57 26.32 26.09 21.60
N
Ts
2v (trans)
f1 (ppm)

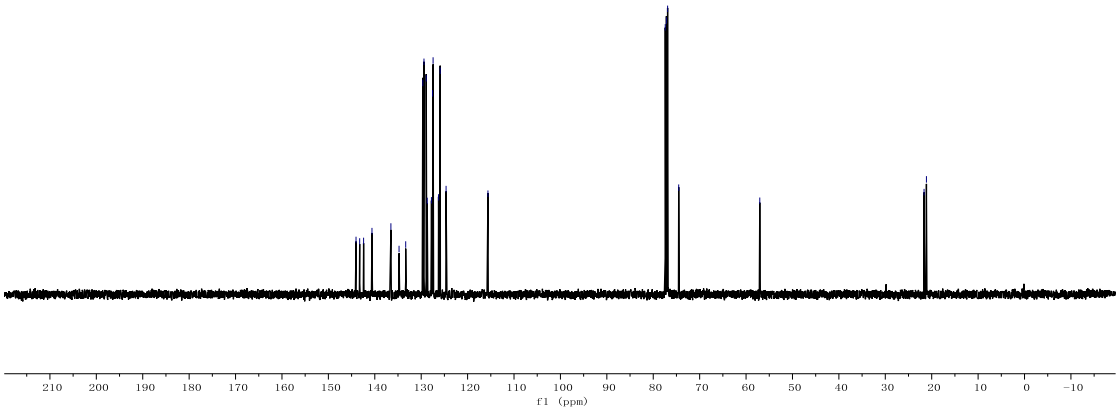


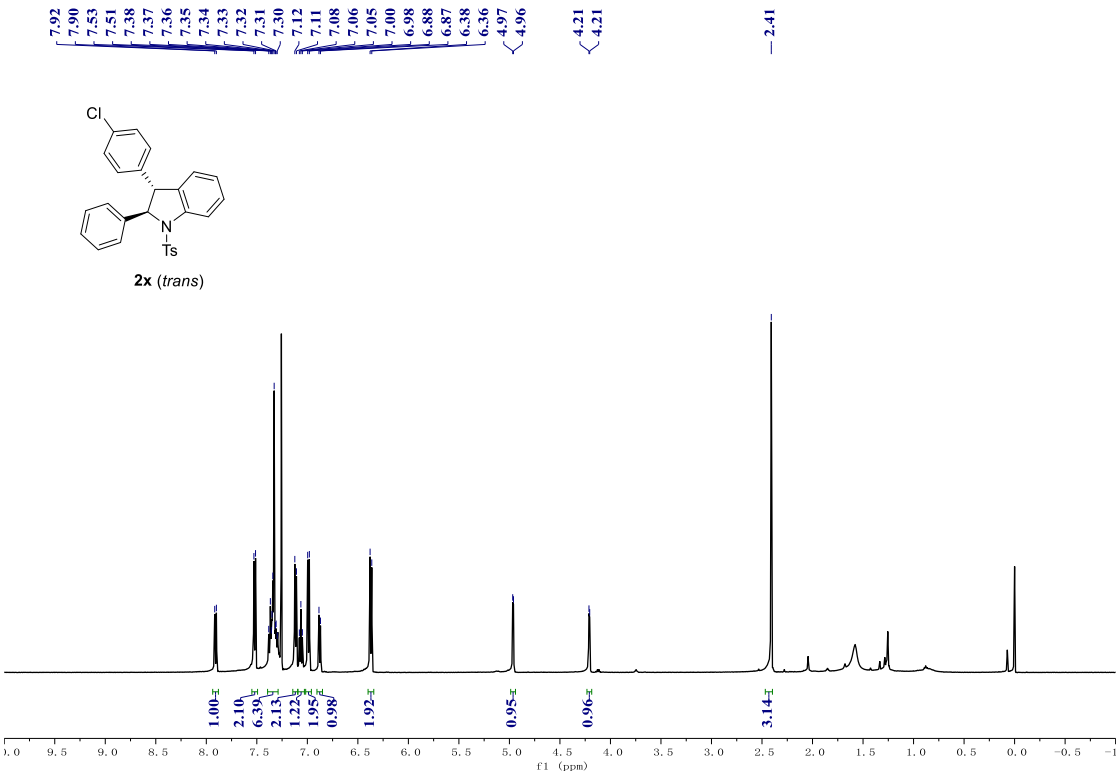
2w (*trans*)



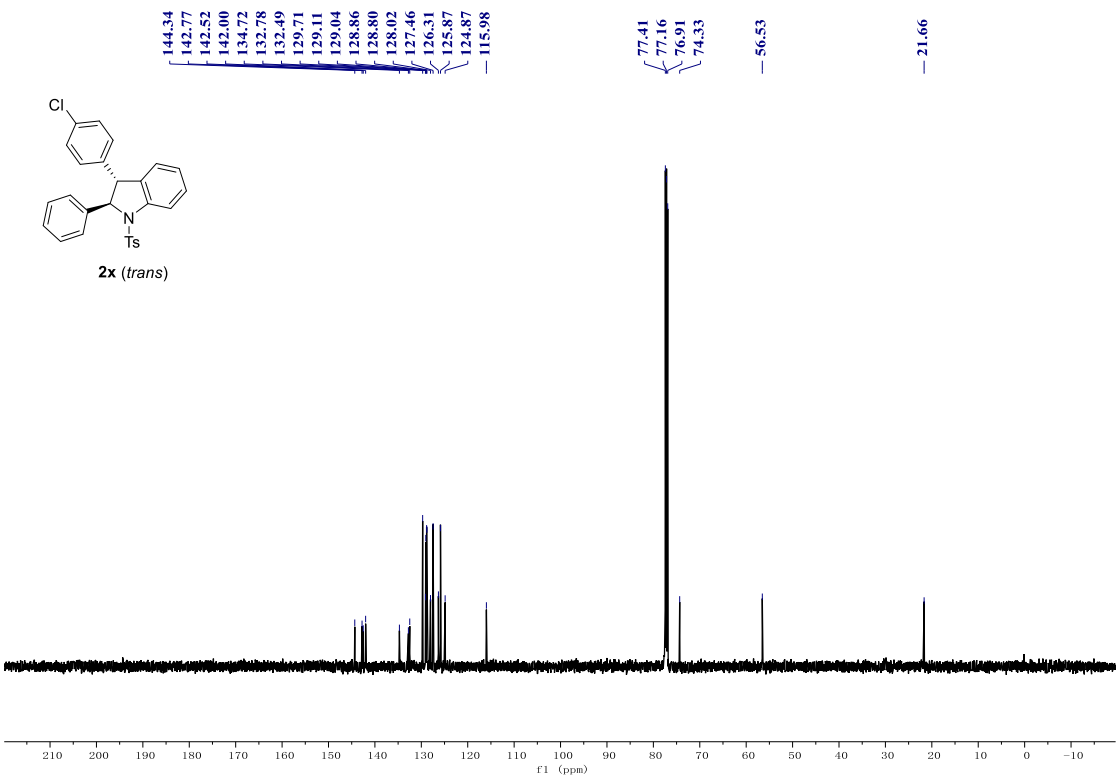


2w (*trans*)

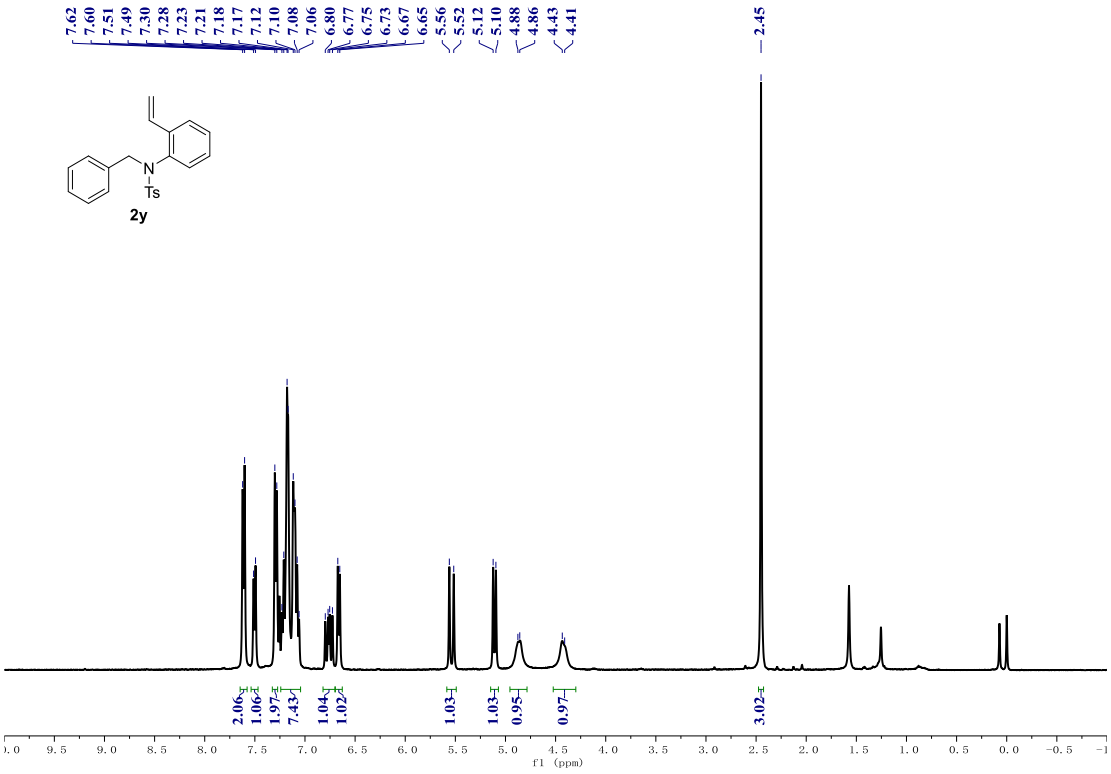


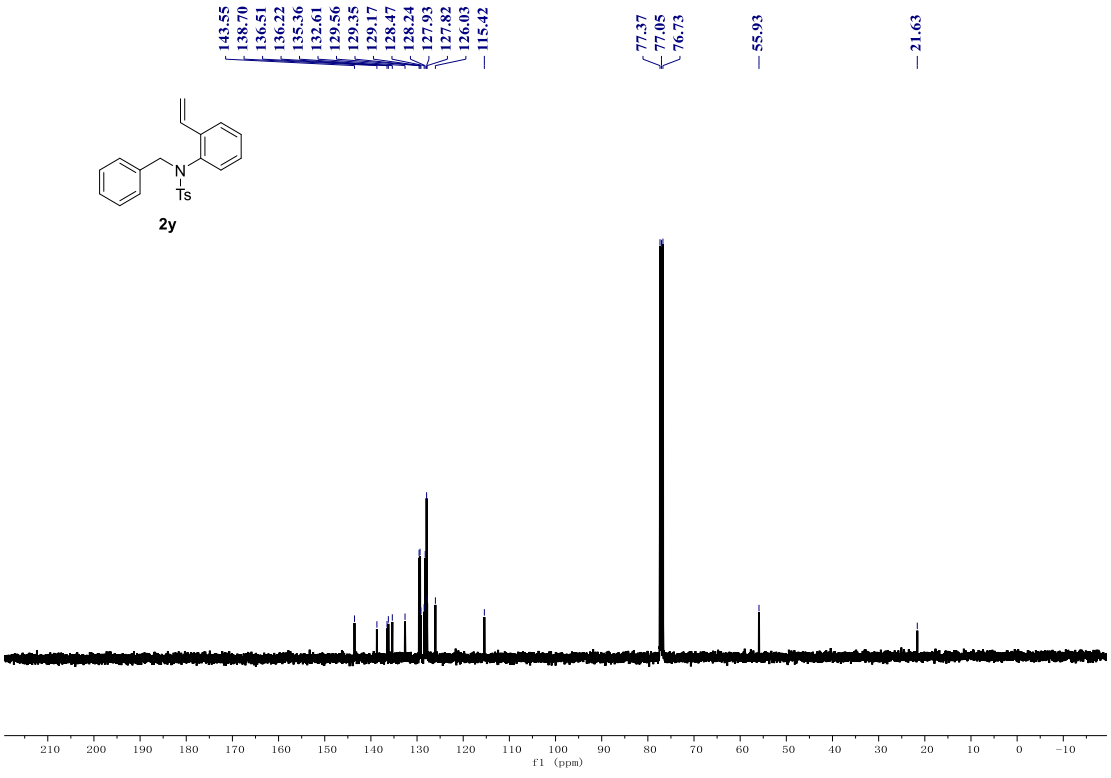


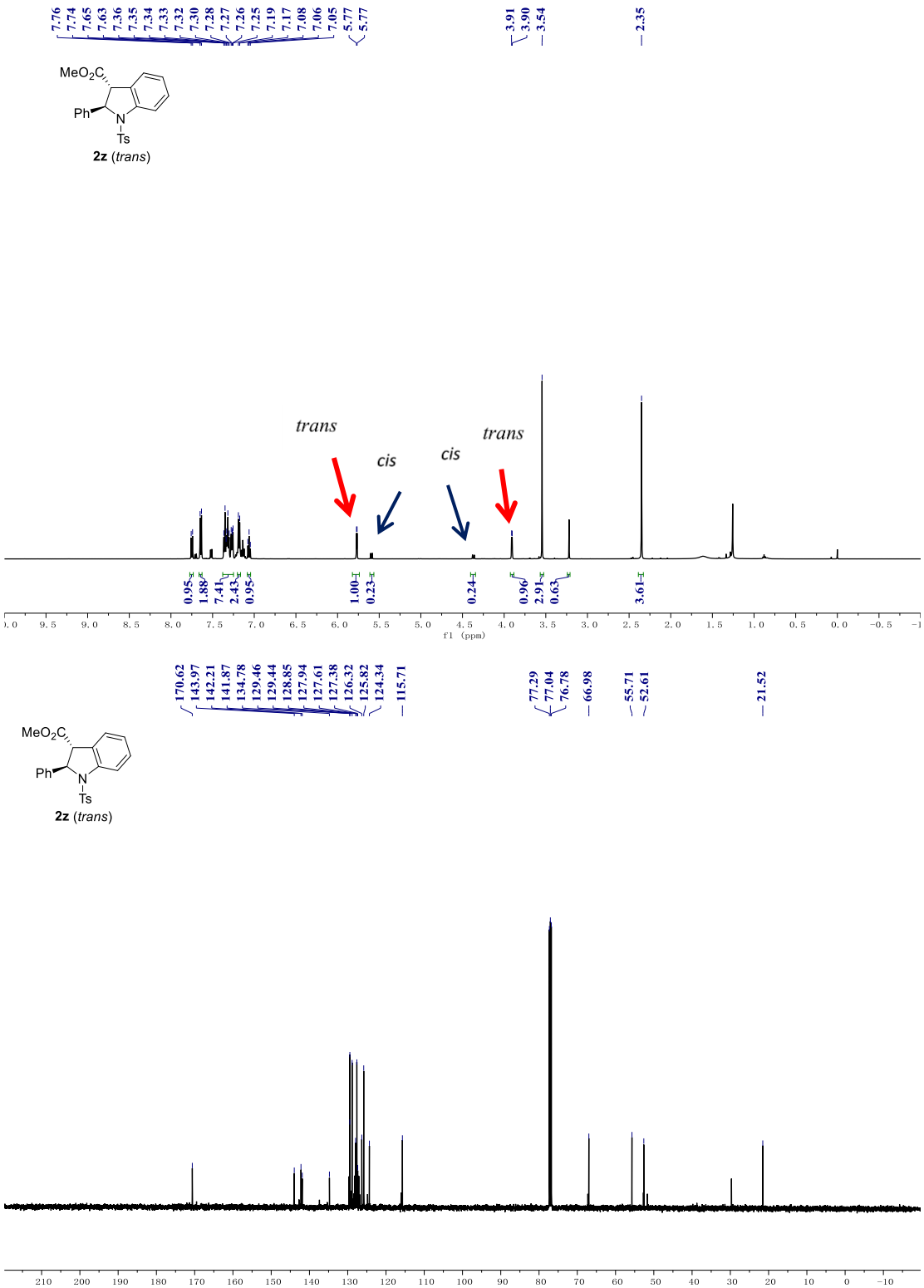
2x (*trans*)

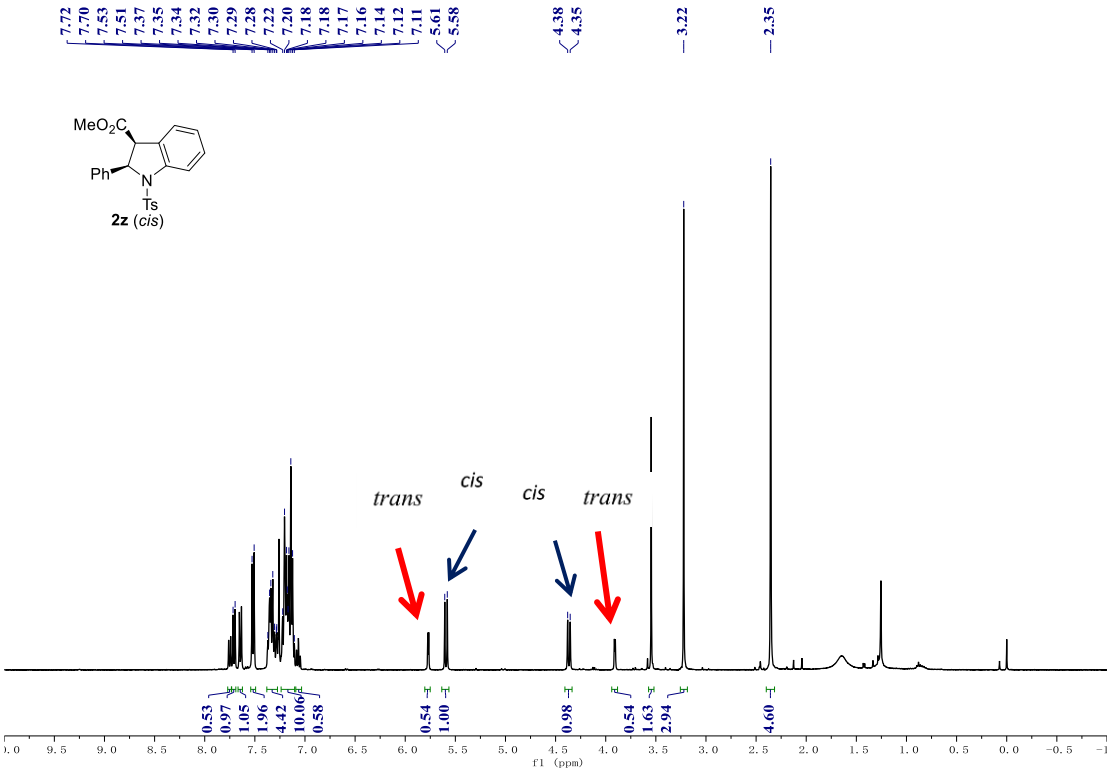


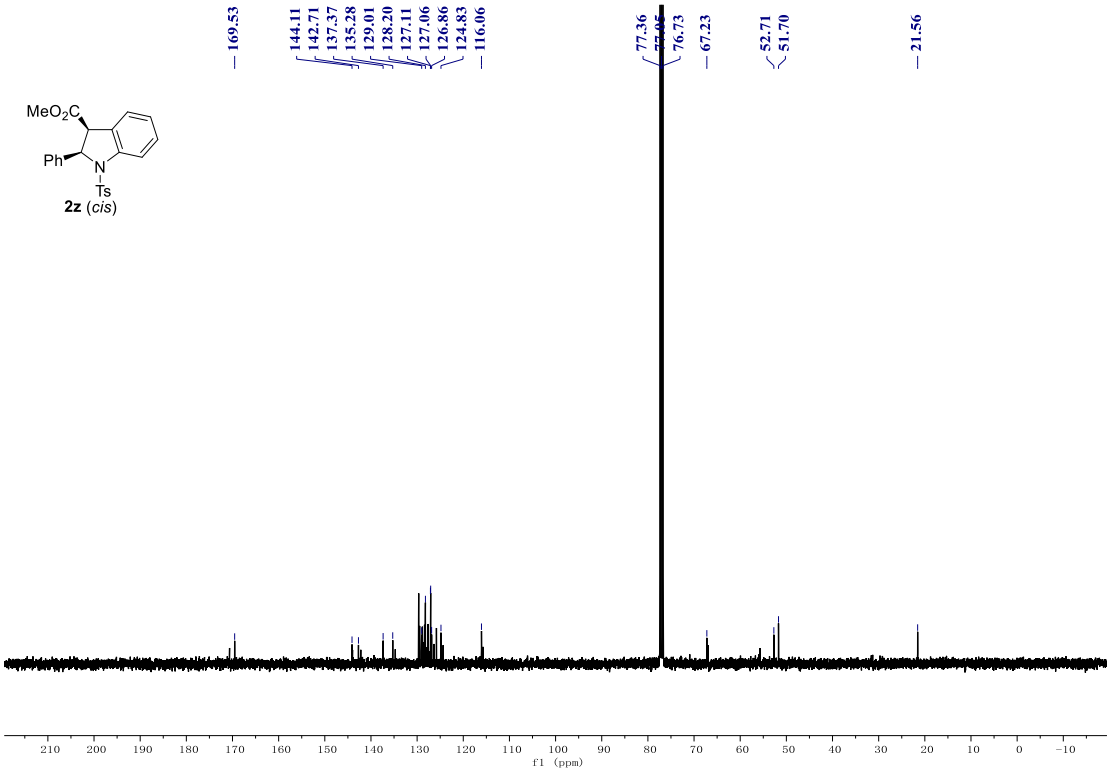
2x (*trans*)

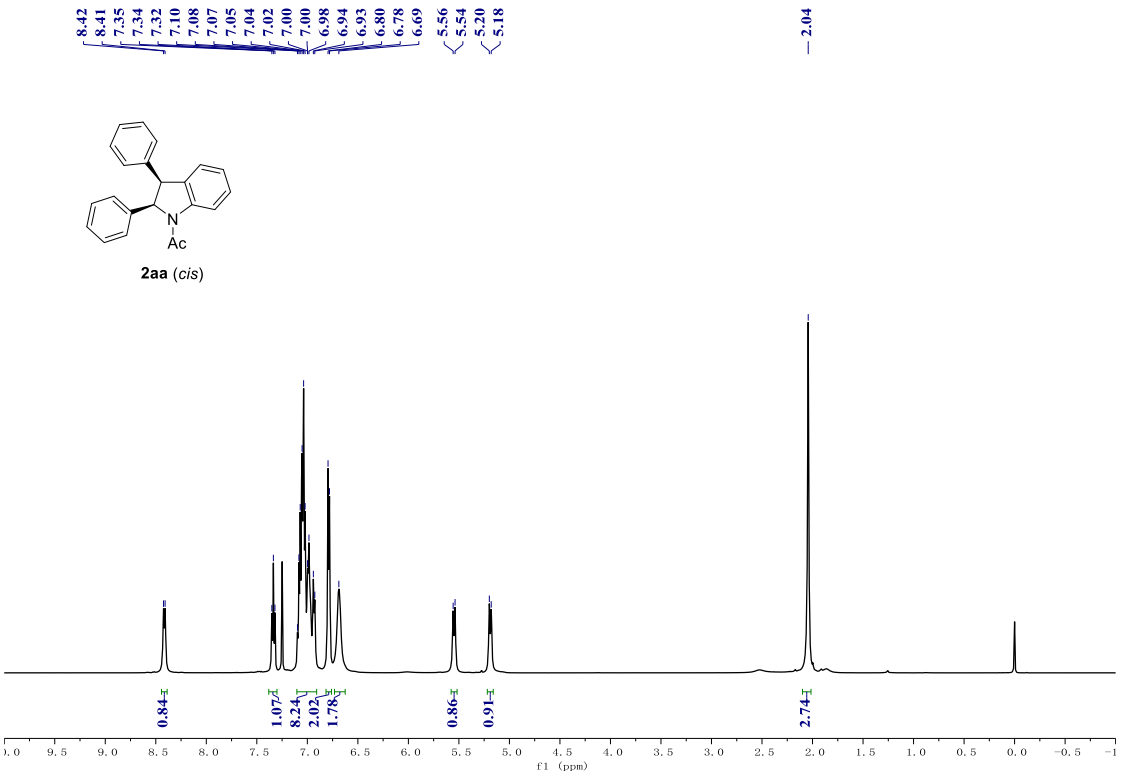

7.62
7.60
7.51
7.49
7.30
7.28
7.23
7.21
7.18
7.17
7.12
7.10
7.08
7.06
6.80
6.77
6.75
6.73
6.67
6.65
5.56
5.52
5.12
5.10
4.88
4.86
4.43
4.41
2.45
N
Ts
2y
2.06
1.06
1.97
7.43
1.04
1.02
1.03
1.03
0.95
0.97
3.02
f1 (ppm)


143.55
138.70
136.51
136.22
135.36
132.61
129.56
129.35
129.17
128.47
128.24
127.93
127.82
126.03
115.42
77.37
77.05
76.73
55.93
21.63
N
Ts
2y
f1 (ppm)

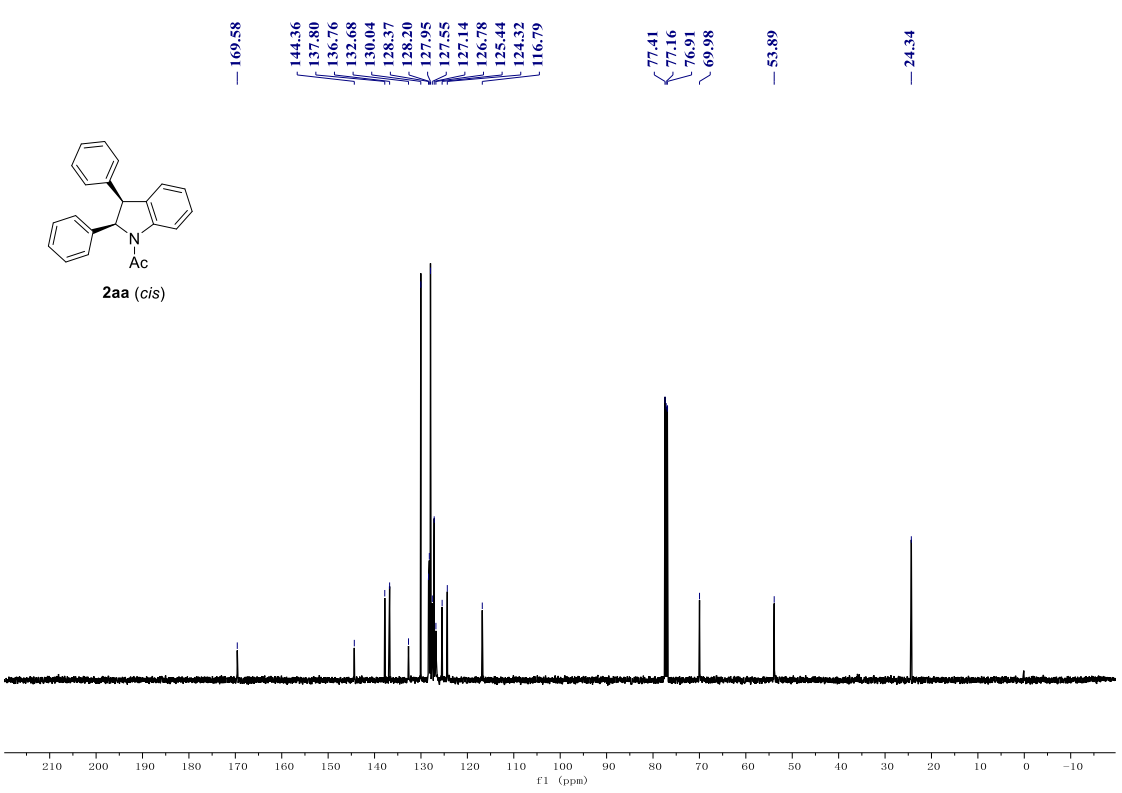

7.76
7.74
7.65
7.63
7.36
7.35
7.34
7.33
7.32
7.30
7.28
7.27
7.26
7.25
7.19
7.17
7.08
7.06
7.05
5.77
5.77
3.91
3.90
3.54
2.35
MeO2C
Ph
N
Ts
2z (trans)
trans
cis
cis
trans
0.95
1.88
7.41
2.43
0.95
1.00
0.23
0.24
0.96
2.91
0.63
3.61
f1 (ppm)
170.62
143.97
142.21
141.87
134.78
129.46
129.44
128.85
127.94
127.61
127.38
126.32
125.82
124.34
115.71
77.29
77.04
76.78
66.98
55.71
52.61
21.52
MeO2C
Ph
N
Ts
2z (trans)
f1 (ppm)


7.72
7.70
7.53
7.51
7.37
7.35
7.34
7.32
7.30
7.29
7.28
7.22
7.20
7.18
7.18
7.17
7.16
7.14
7.12
7.11
5.61
5.58
4.38
4.35
3.22
2.35
MeO2C
Ph
N
Ts
2z (cis)
trans
cis
cis
trans
0.53
0.97
1.05
1.96
4.42
10.06
0.58
0.54
1.00
0.98
0.54
1.63
2.94
4.60
f1 (ppm)

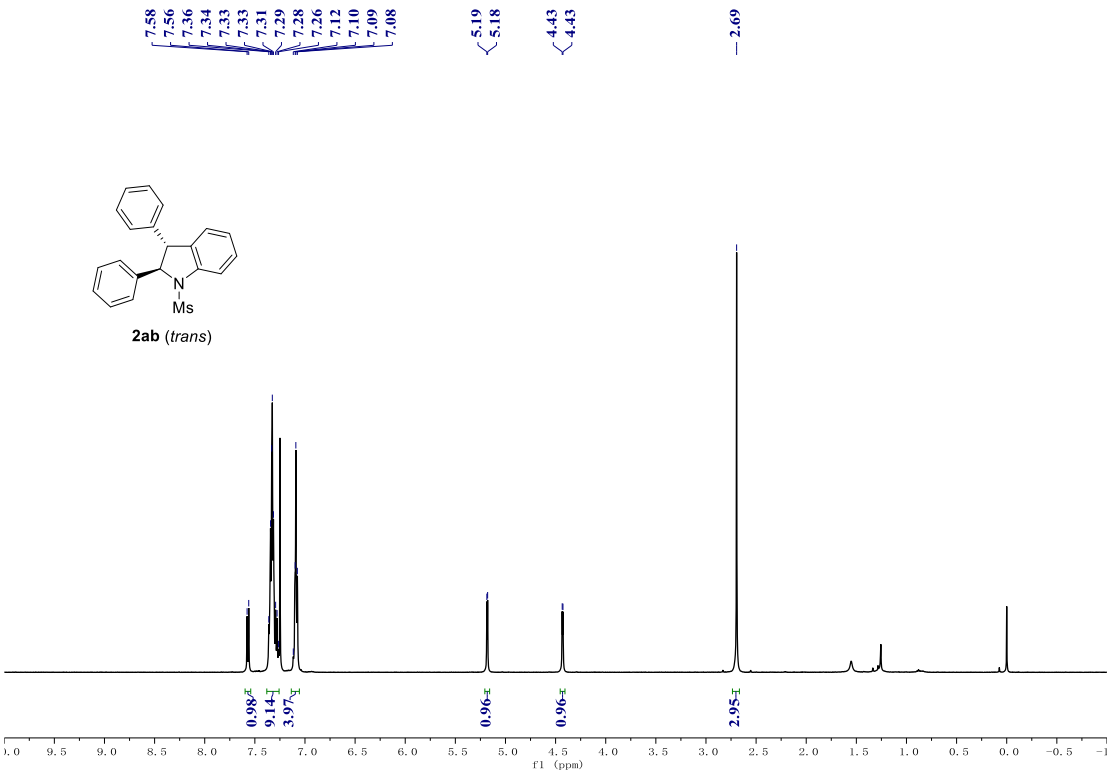

169.53
144.11
142.71
137.37
135.28
129.01
128.20
127.11
127.06
126.86
124.83
116.06
77.36
77.05
76.73
67.23
52.71
51.70
21.56
MeO2C
Ph
N
Ts
2z (cis)
f1 (ppm)



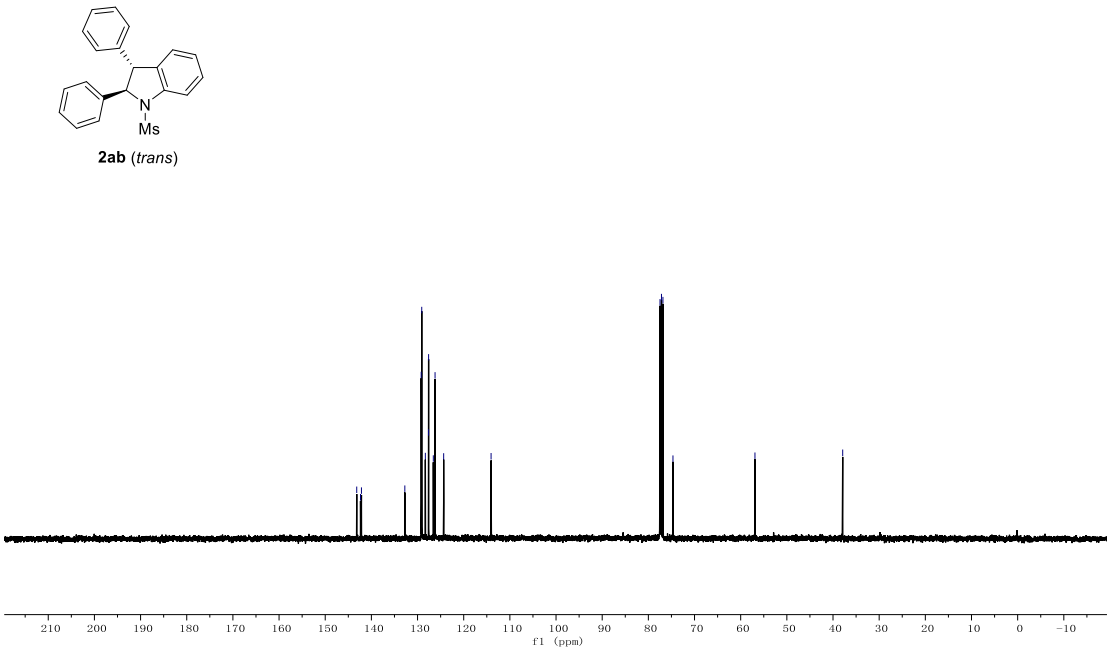
2aa (*cis*)



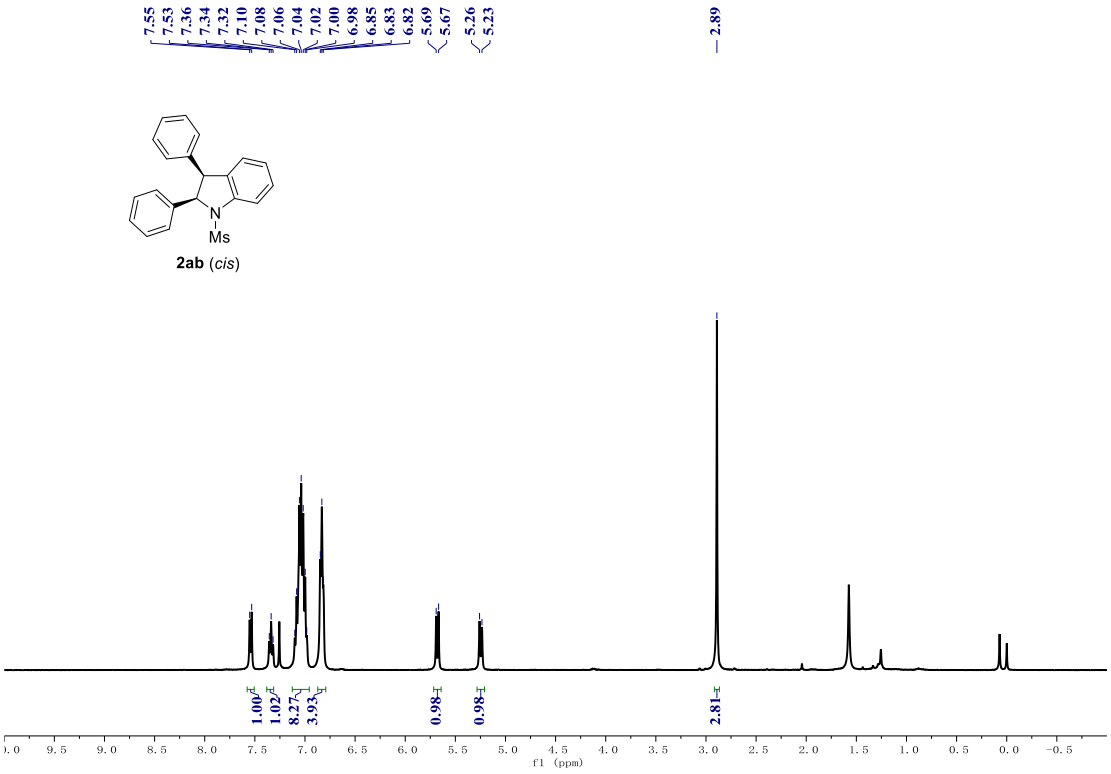
2aa (*cis*)



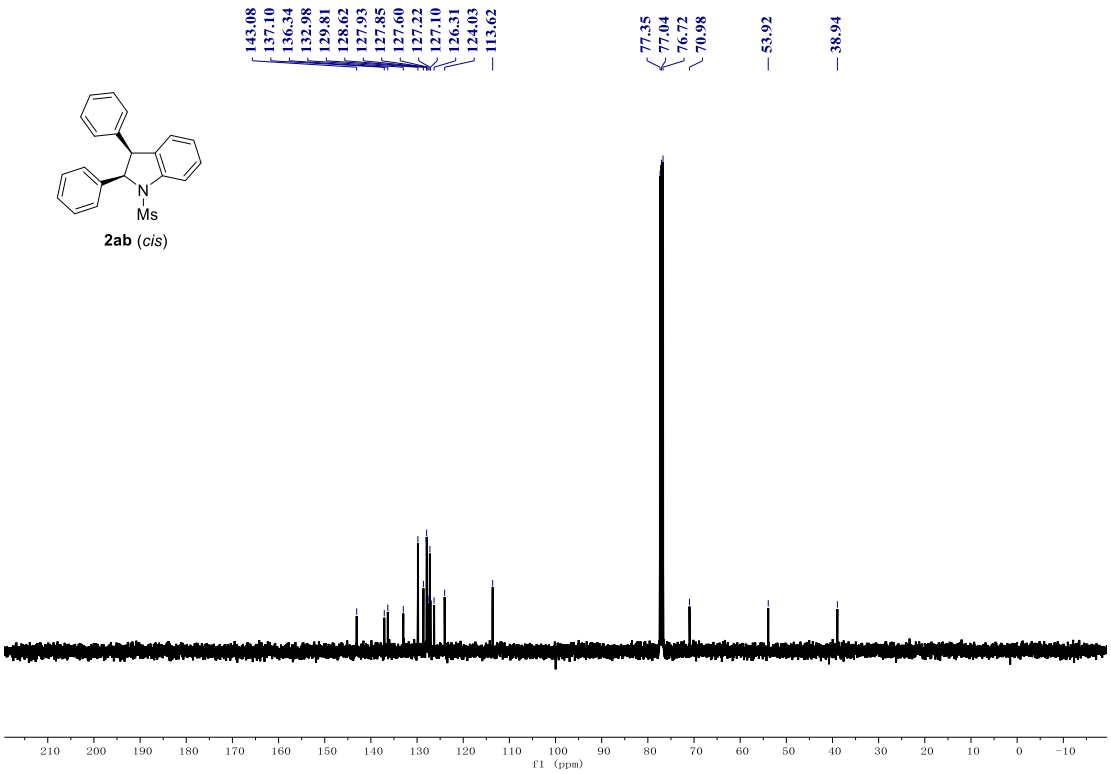
2ab (*trans*)



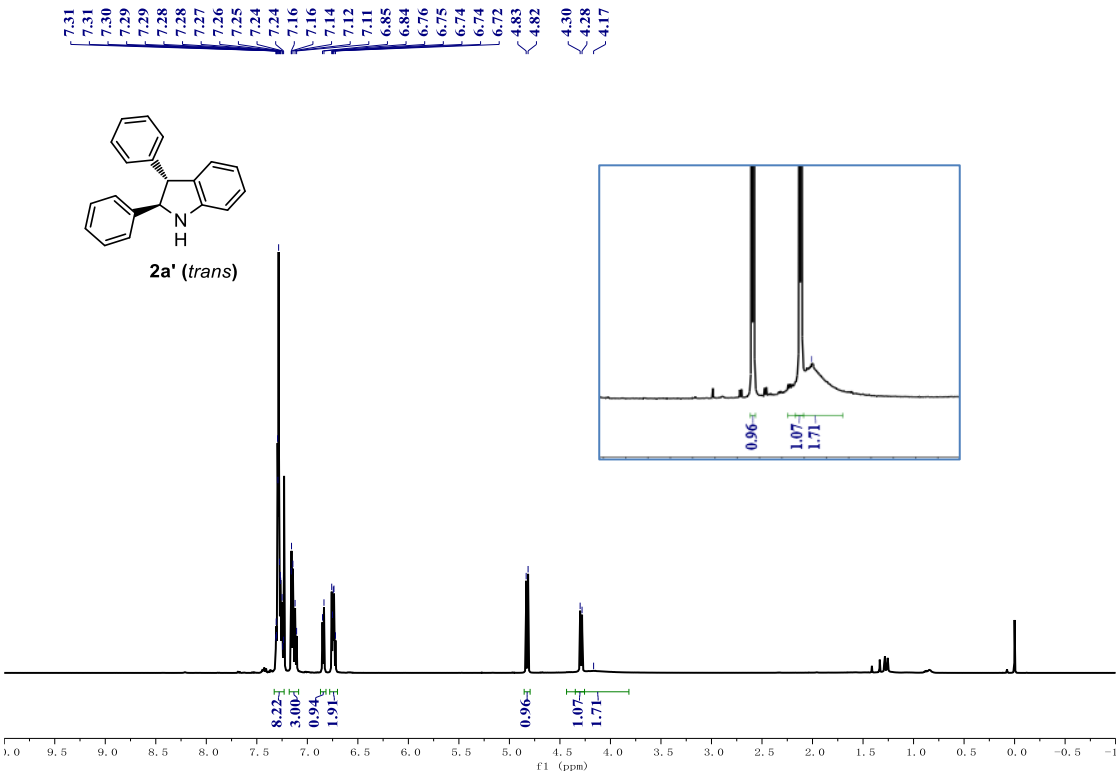
2ab (*trans*)

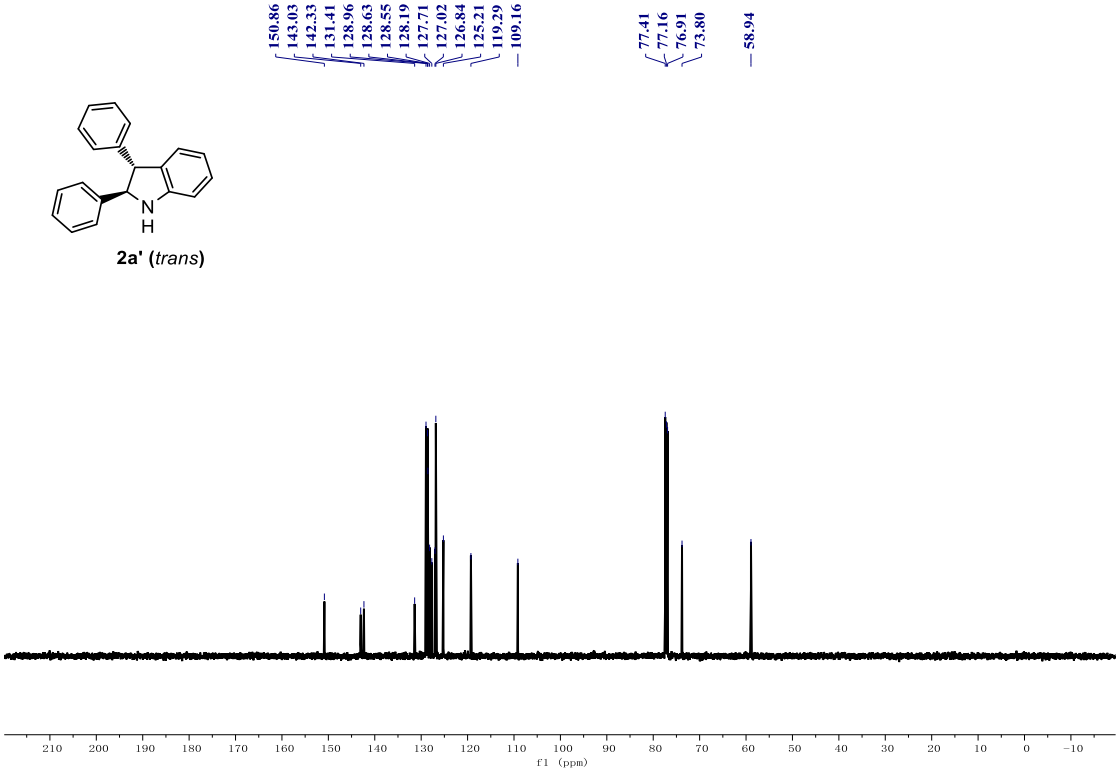


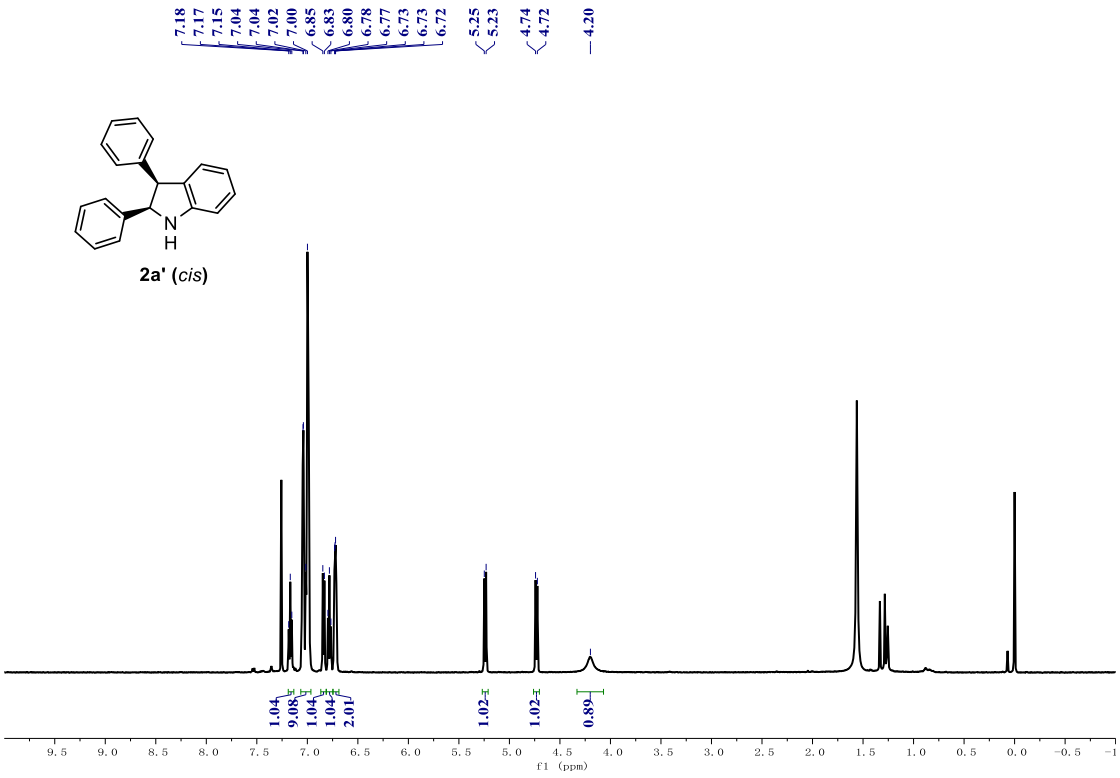
2ab (*cis*)



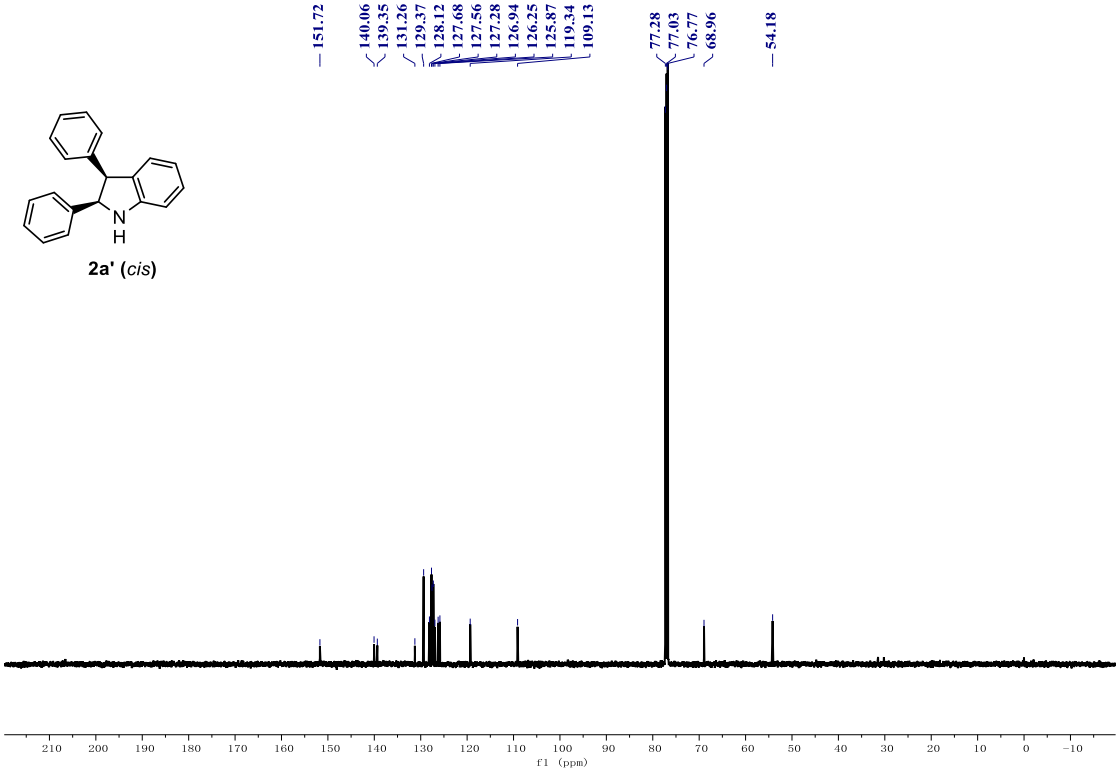
2ab (*cis*)


7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.24
7.24
7.16
7.16
7.14
7.12
7.11
6.85
6.84
6.76
6.75
6.74
6.74
6.72
4.83
4.82
4.30
4.28
4.17
N
H
2a' (trans)
0.96
1.07
1.71
8.22
3.00
0.94
1.91
0.96
1.07
1.71
f1 (ppm)

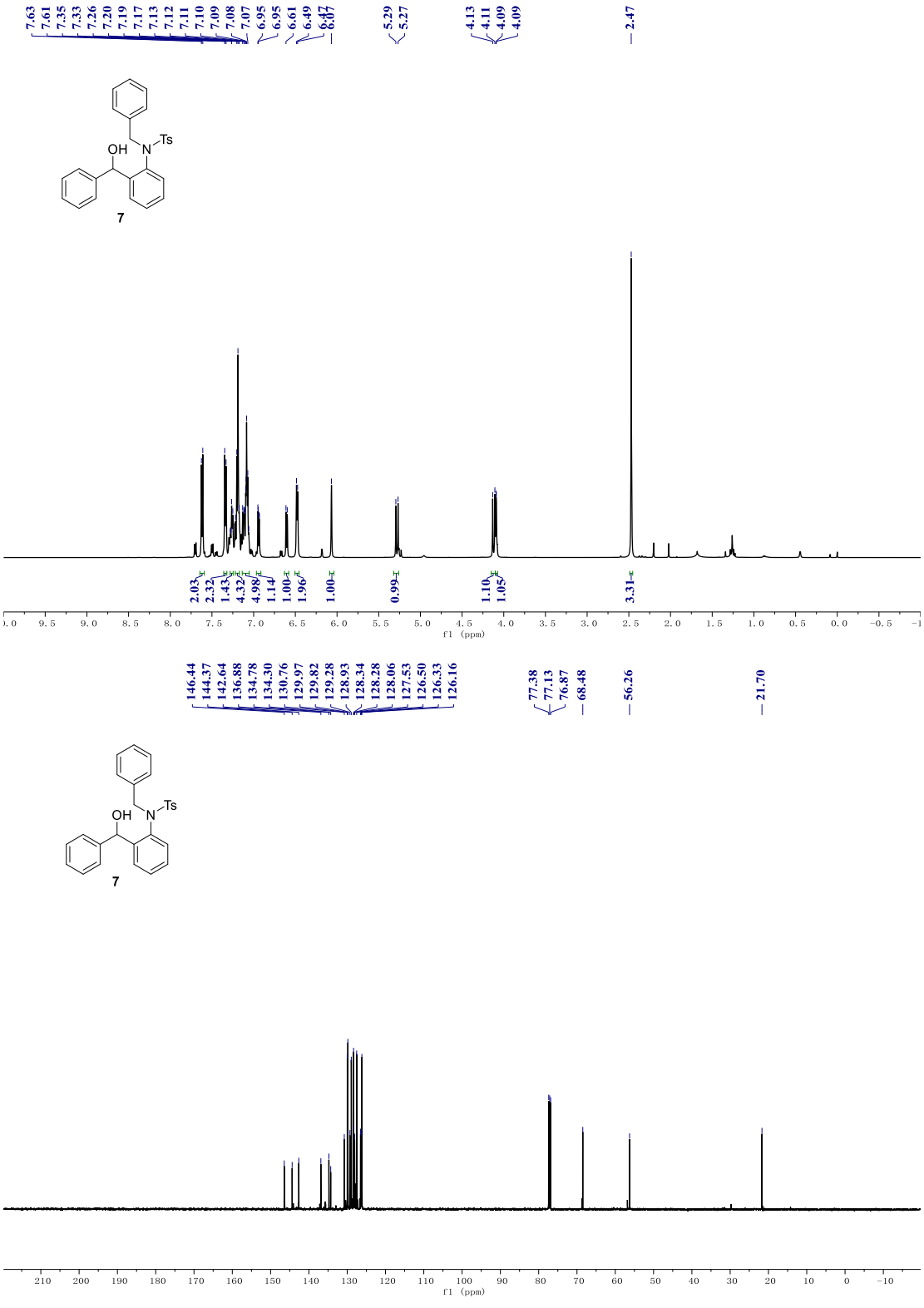

150.86
143.03
142.33
131.41
128.96
128.63
128.55
128.19
127.71
127.02
126.84
125.21
119.29
109.16
77.41
77.16
76.91
73.80
58.94
N
H
2a' (trans)
f1 (ppm)

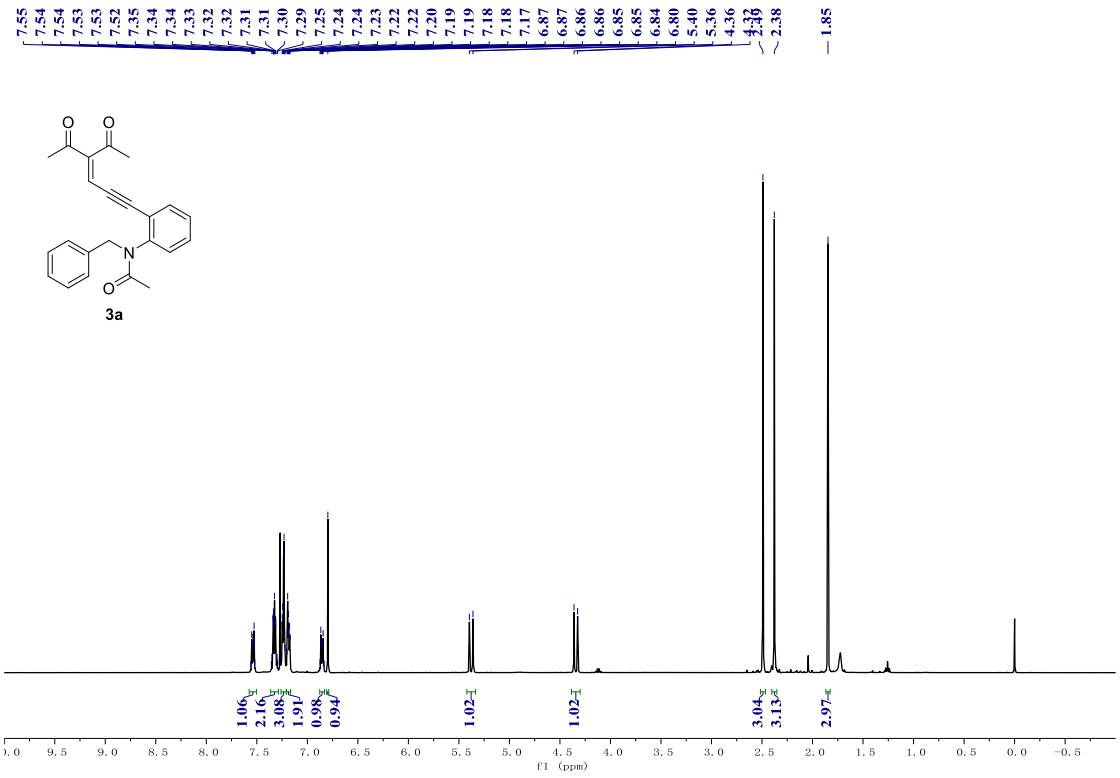

7.18
7.17
7.15
7.04
7.04
7.02
7.00
6.85
6.83
6.80
6.78
6.77
6.73
6.73
6.72
5.25
5.23
4.74
4.72
4.20
1.04
9.08
1.04
1.04
2.01
1.02
1.02
0.89
f1 (ppm)

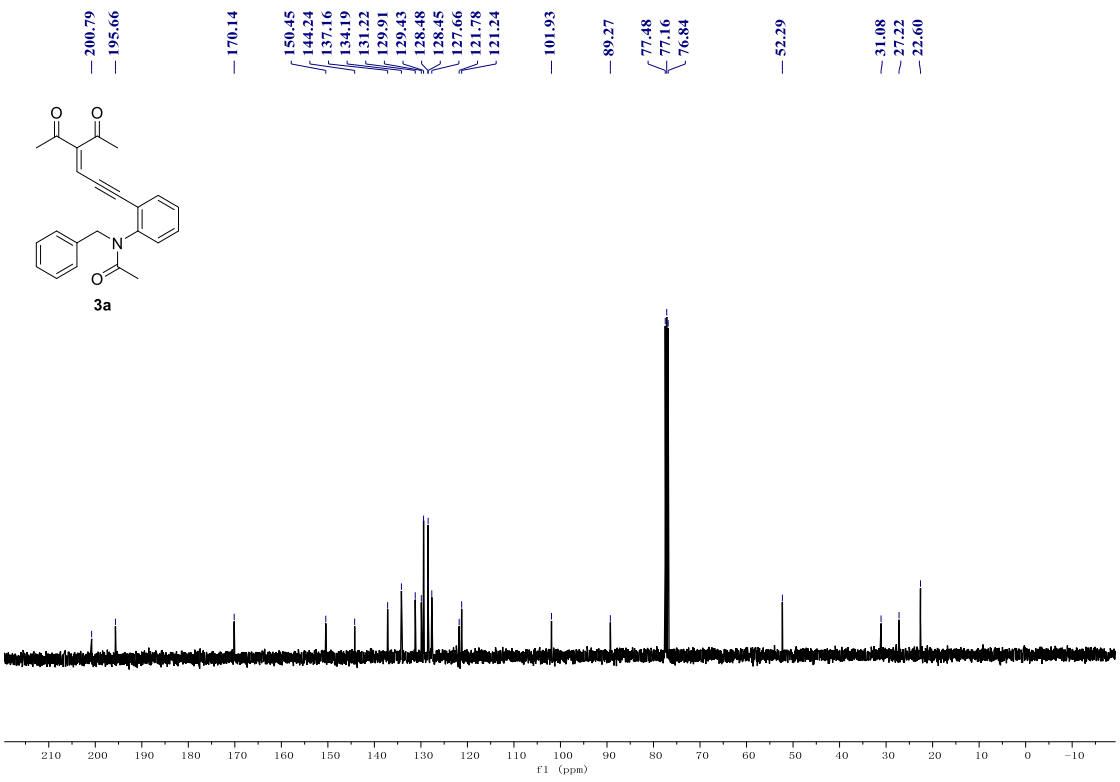
2a' (*cis*)

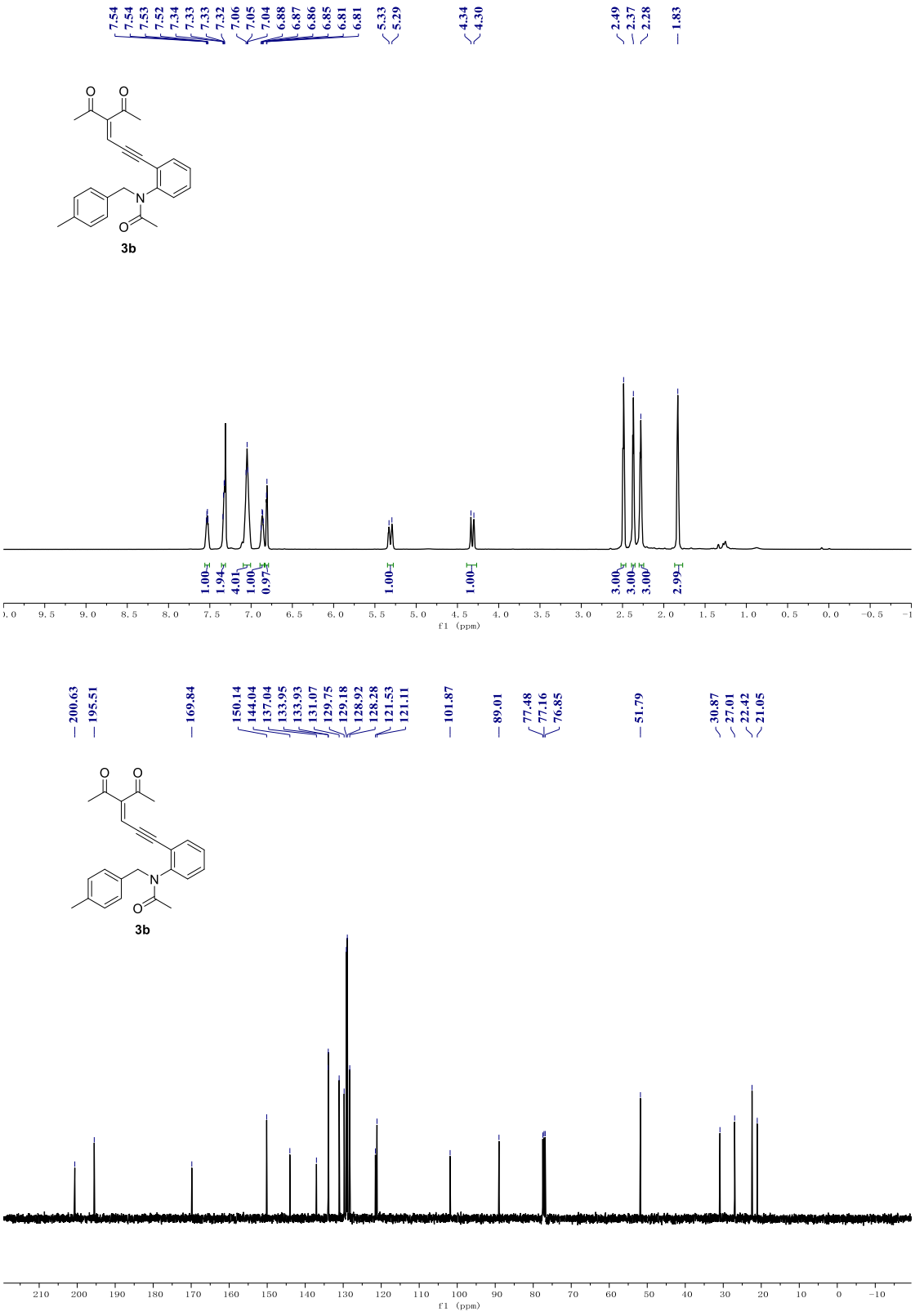

151.72
140.06
139.35
131.26
129.37
128.12
127.68
127.56
127.28
126.94
126.25
125.87
119.34
109.13
77.28
77.03
76.77
68.96
54.18
f1 (ppm)

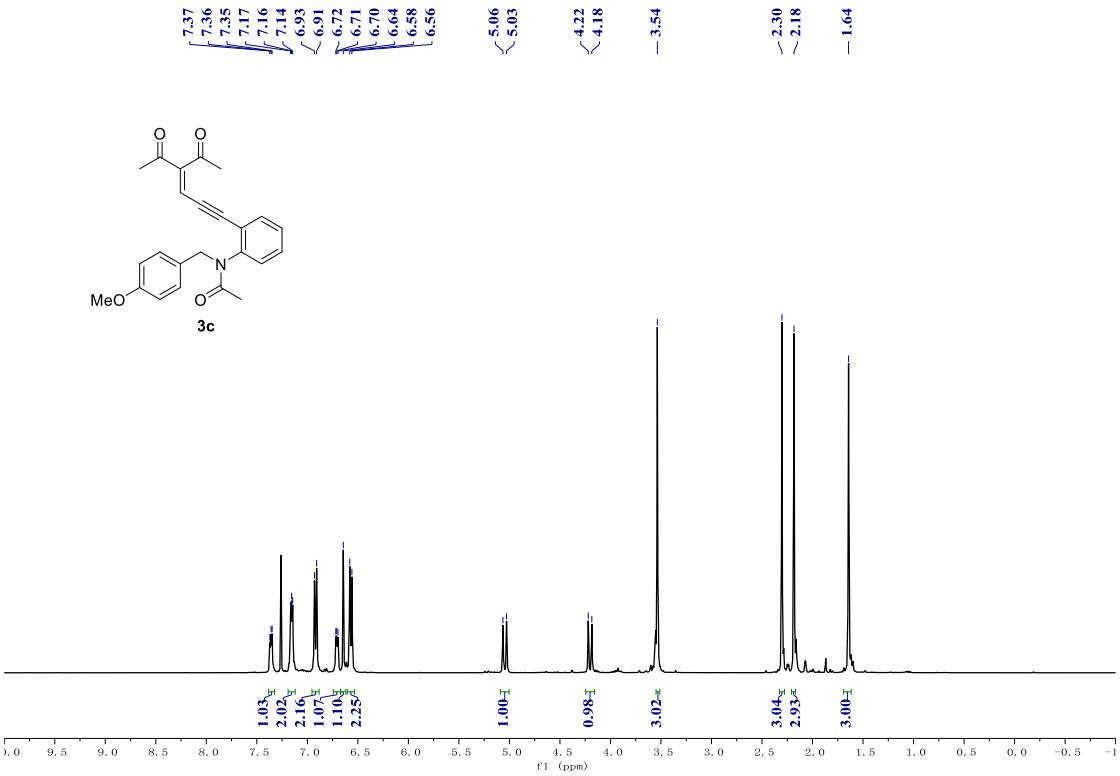
2a' (*cis*)

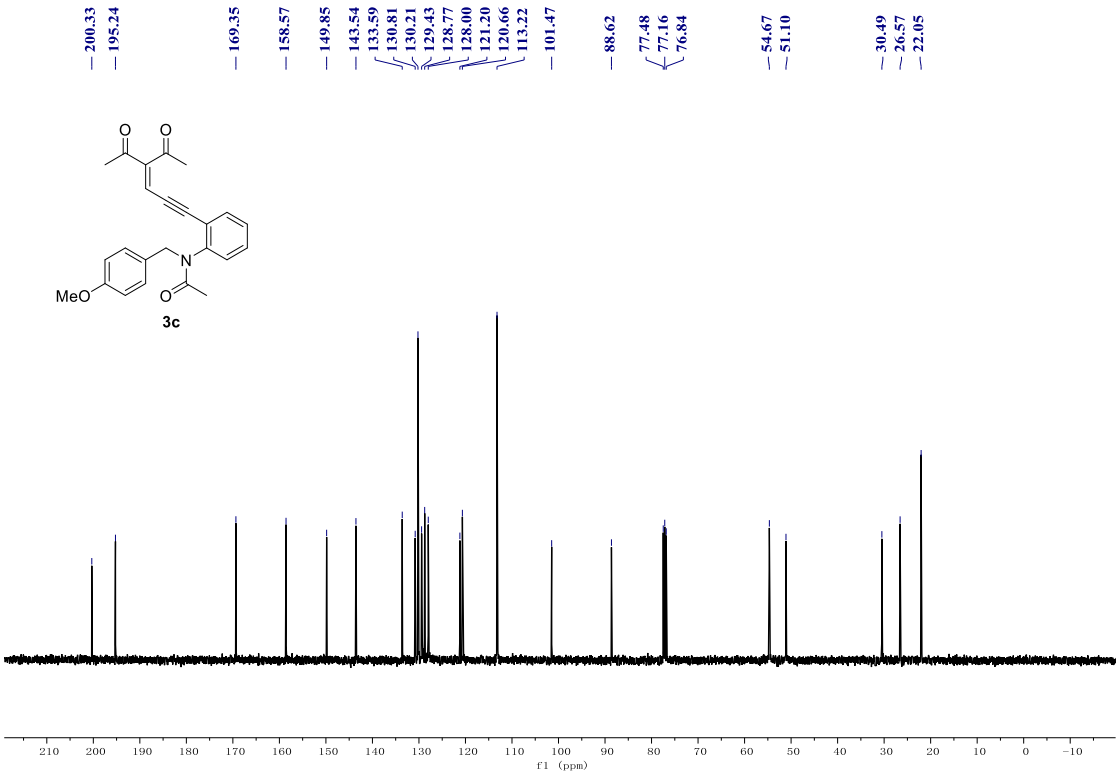

7.63
7.61
7.35
7.33
7.26
7.20
7.19
7.17
7.13
7.12
7.11
7.10
7.09
7.08
7.07
6.95
6.95
6.61
6.49
6.47
6.07
5.29
5.27
4.13
4.11
4.09
4.09
2.47
OH
N
Ts
7
2.03
2.32
1.43
4.32
4.98
1.14
1.00
1.96
1.00
0.99
1.10
1.05
3.31
f1 (ppm)
146.44
144.37
142.64
136.88
134.78
134.30
130.76
129.97
129.82
129.28
128.93
128.34
128.28
128.06
127.53
126.50
126.33
126.16
77.38
77.13
76.87
68.48
56.26
21.70
OH
N
Ts
7
f1 (ppm)

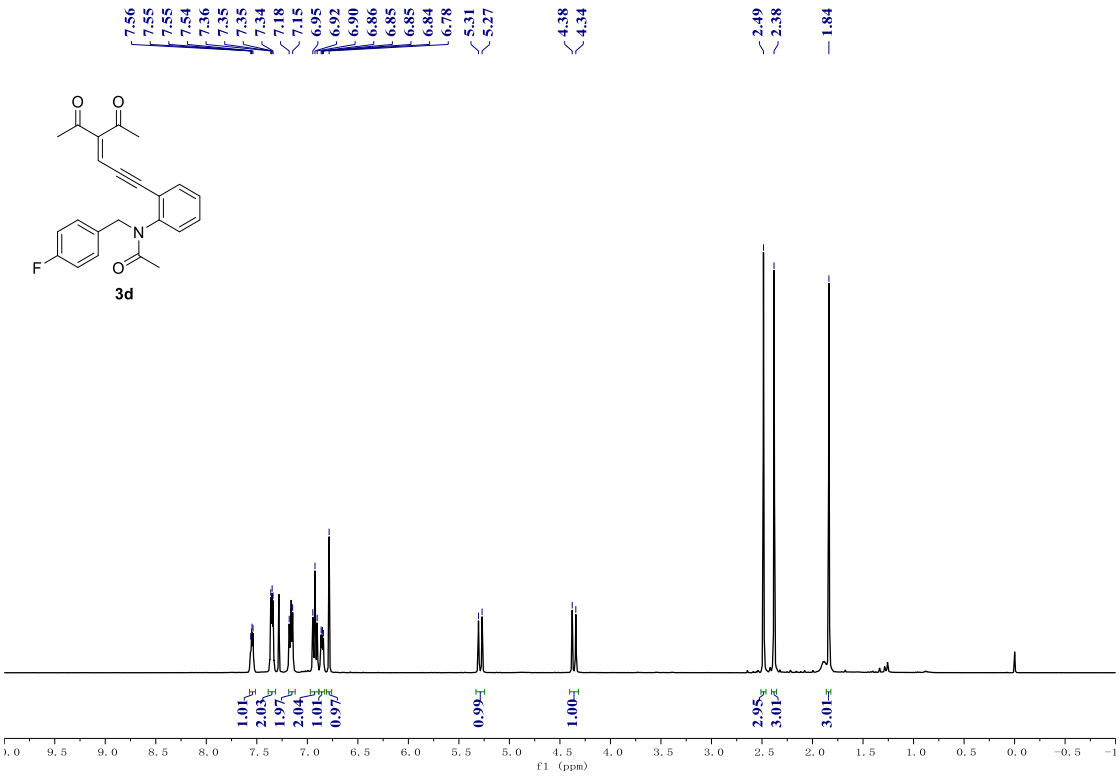

7.55 7.54 7.54 7.53 7.53 7.52 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.25 7.24 7.24 7.23 7.22 7.22 7.20 7.19 7.19 7.18 7.18 7.17 6.87 6.87 6.86 6.86 6.85 6.85 6.84 6.80 5.40 5.36 4.36 2.49 2.38 1.85
O
O
N
O
3a
1.06 2.16 3.08 1.91 0.98 0.94 1.02 1.02 3.04 3.13 2.97
f1 (ppm)


200.79 195.66 170.14 150.45 144.24 137.16 134.19 131.22 129.91 129.43 128.48 128.45 127.66 121.78 121.24 101.93 89.27 77.48 77.16 76.84 52.29 31.08 27.22 22.60
O
O
N
O
3a
f1 (ppm)

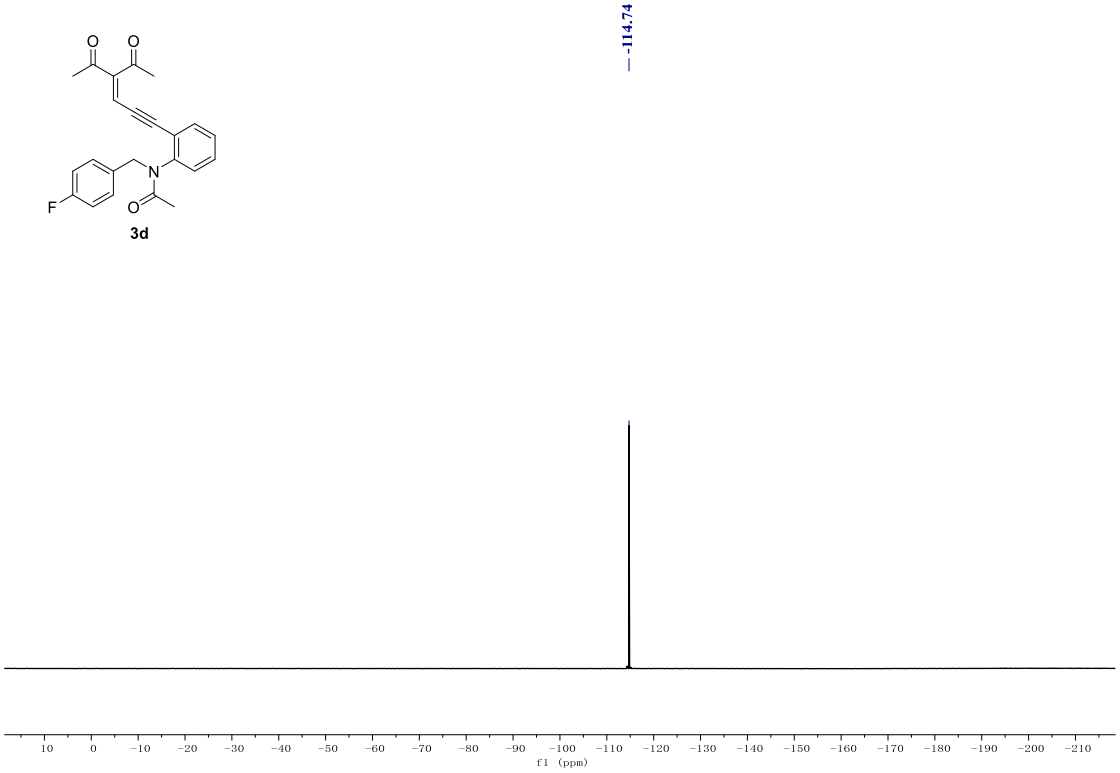

7.54
7.54
7.53
7.52
7.34
7.33
7.33
7.32
7.06
7.05
7.04
6.88
6.87
6.86
6.85
6.81
6.81
5.33
5.29
4.34
4.30
2.49
2.37
2.28
1.83
3b
1.00
1.94
4.01
1.00
0.97
1.00
1.00
3.00
3.00
3.00
2.99
f1 (ppm)
200.63
195.51
169.84
150.14
144.04
137.04
133.95
133.93
131.07
129.75
129.18
128.92
128.28
121.53
121.11
101.87
89.01
77.48
77.16
76.85
51.79
30.87
27.01
22.42
21.05
3b
f1 (ppm)


7.37
7.36
7.35
7.17
7.16
7.14
6.93
6.91
6.72
6.71
6.70
6.64
6.58
6.56
5.06
5.03
4.22
4.18
3.54
2.30
2.18
1.64
MeO
N
O
3c
1.03
2.02
2.16
1.07
1.10
2.25
1.00
0.98
3.02
3.04
2.93
3.00
f1 (ppm)

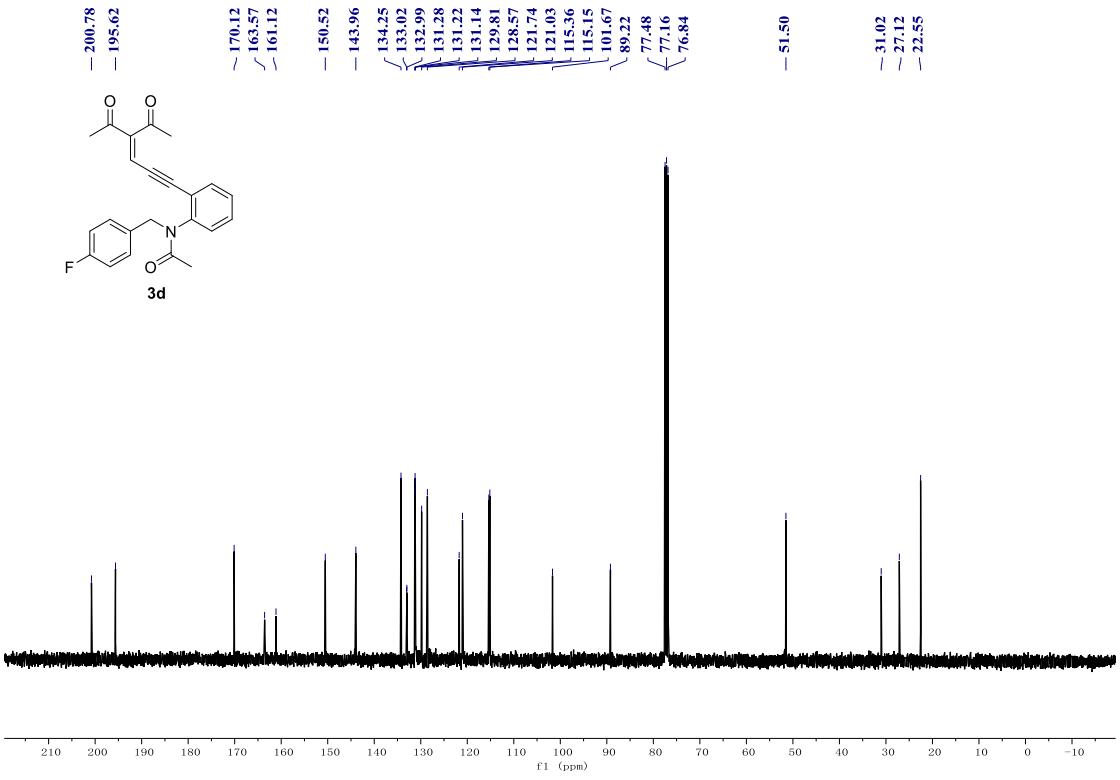

200.33
195.24
169.35
158.57
149.85
143.54
133.59
130.81
130.21
129.43
128.77
128.00
121.20
120.66
113.22
101.47
88.62
77.48
77.16
76.84
54.67
51.10
30.49
26.57
22.05
MeO
N
O
3c
f1 (ppm)


7.56
7.55
7.55
7.54
7.36
7.35
7.35
7.34
7.18
7.15
6.95
6.92
6.90
6.86
6.85
6.84
6.78
5.31
5.27
4.38
4.34
2.49
2.38
1.84
1.01
2.03
1.97
2.04
1.01
0.97
0.99
1.00
2.95
3.01
3.01
f1 (ppm)

3d


-114.74
f1 (ppm)

3d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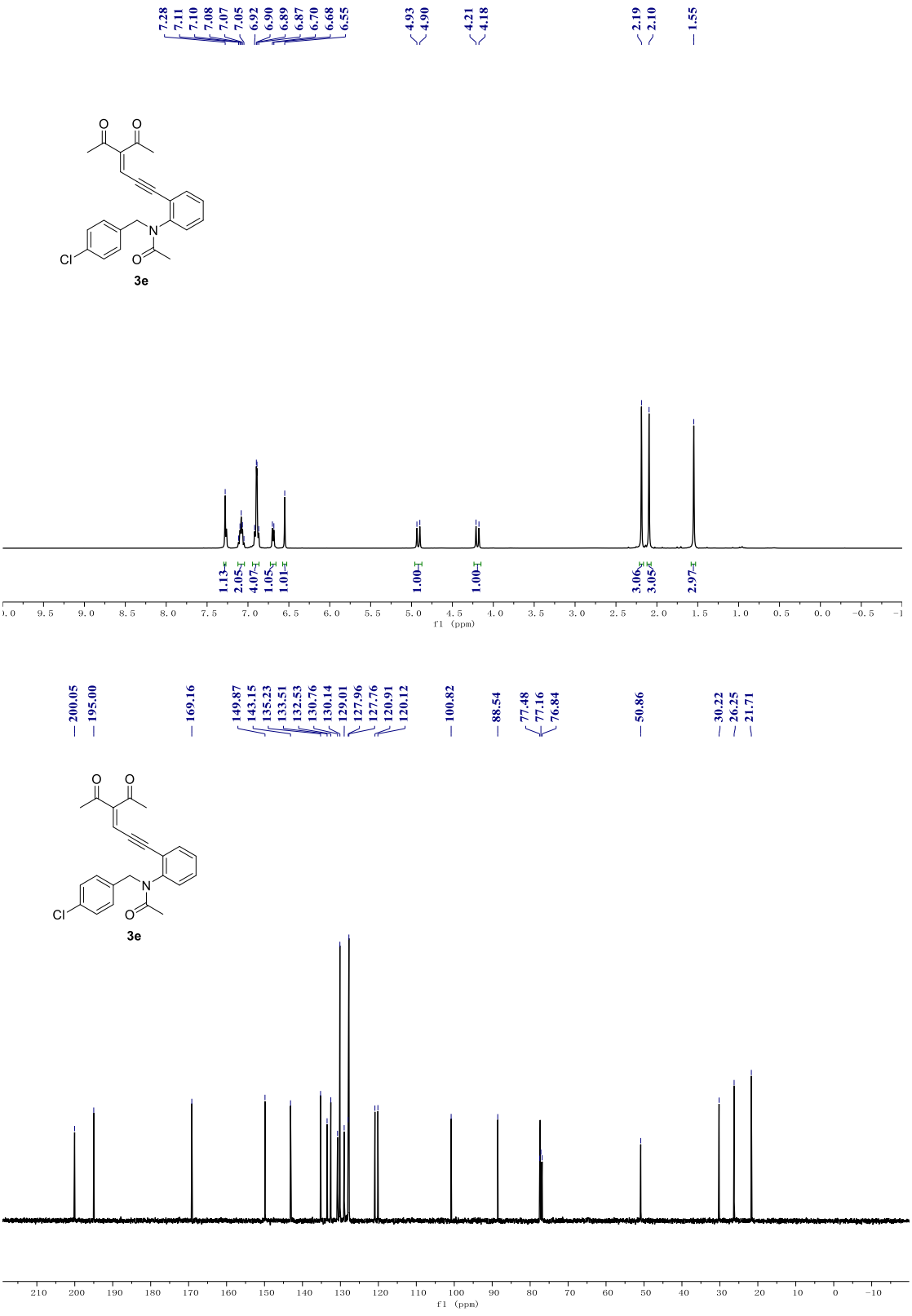
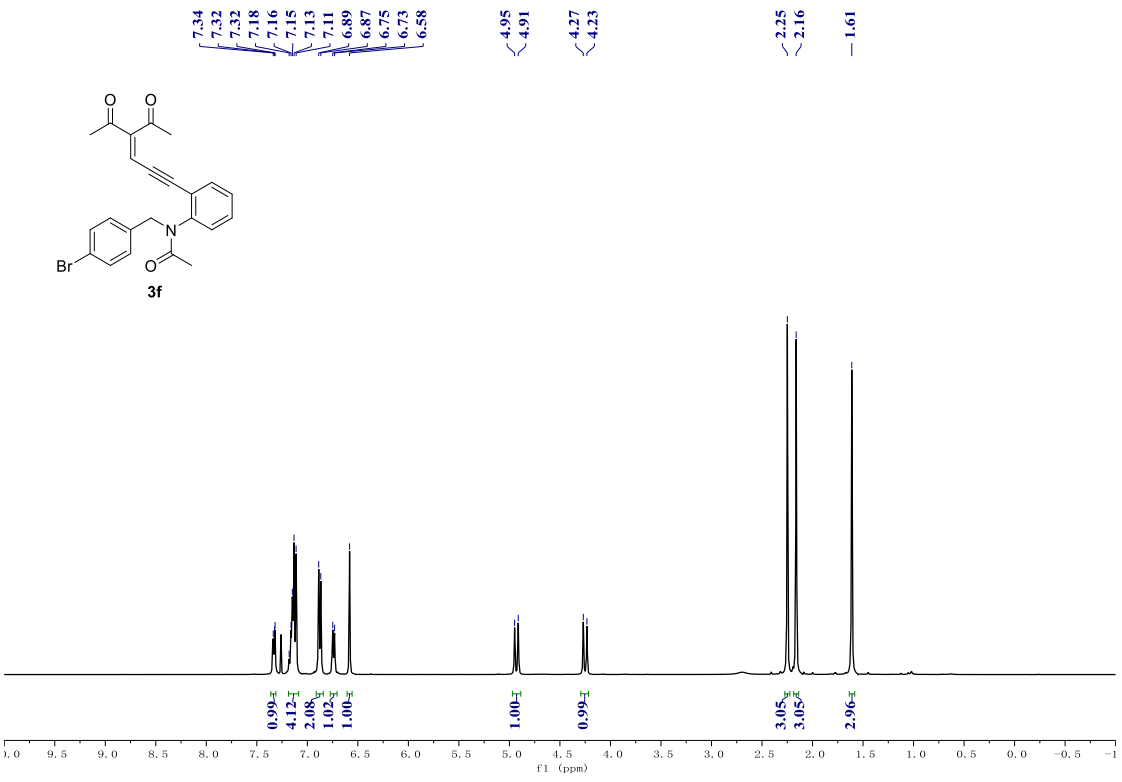
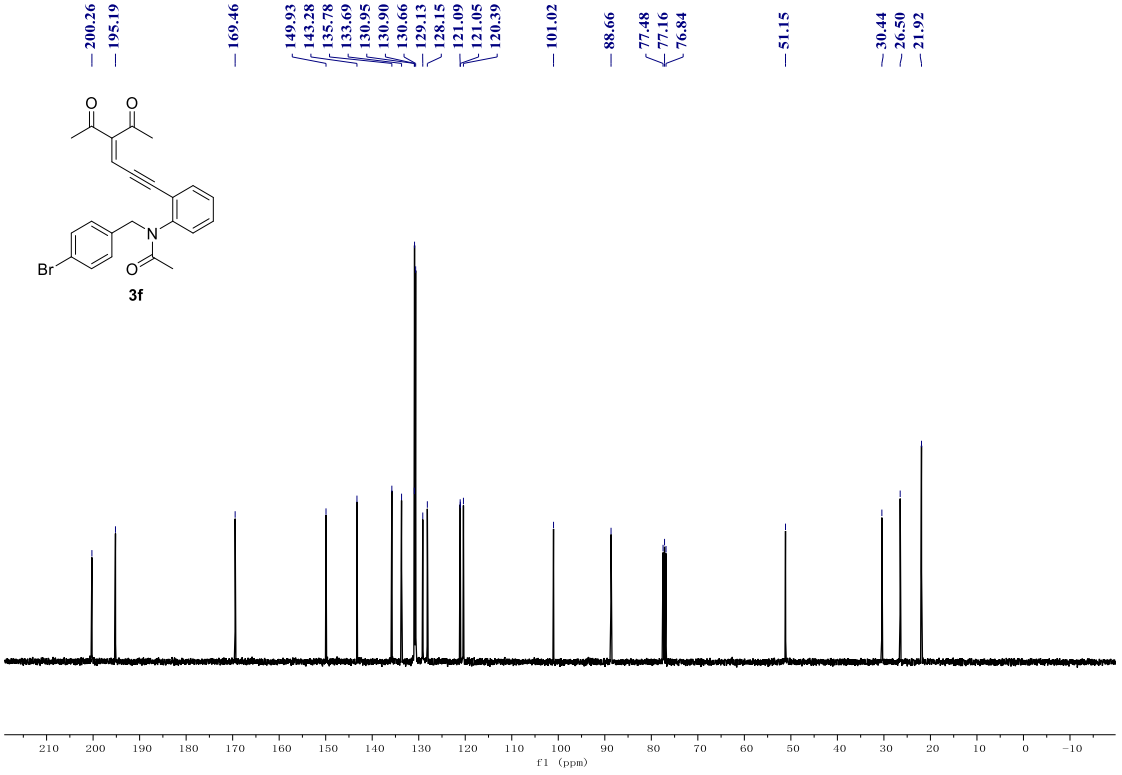
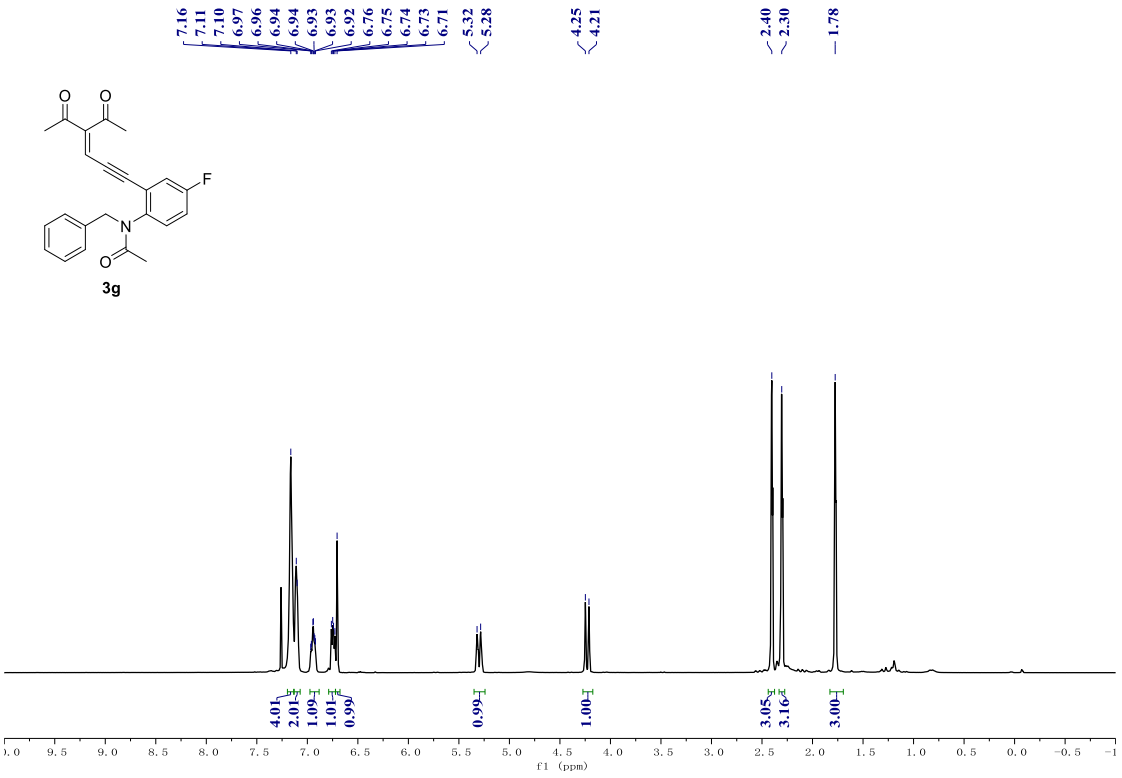
195.62
170.12
163.57
161.12
150.52
143.96
134.25
133.02
132.99
131.28
131.22
131.14
129.81
128.57
121.74
121.03
115.36
115.15
101.67
89.22
77.48
77.16
76.84
51.50
31.02
27.12
22.55
O
O
N
O
F
3d
f1 (ppm)

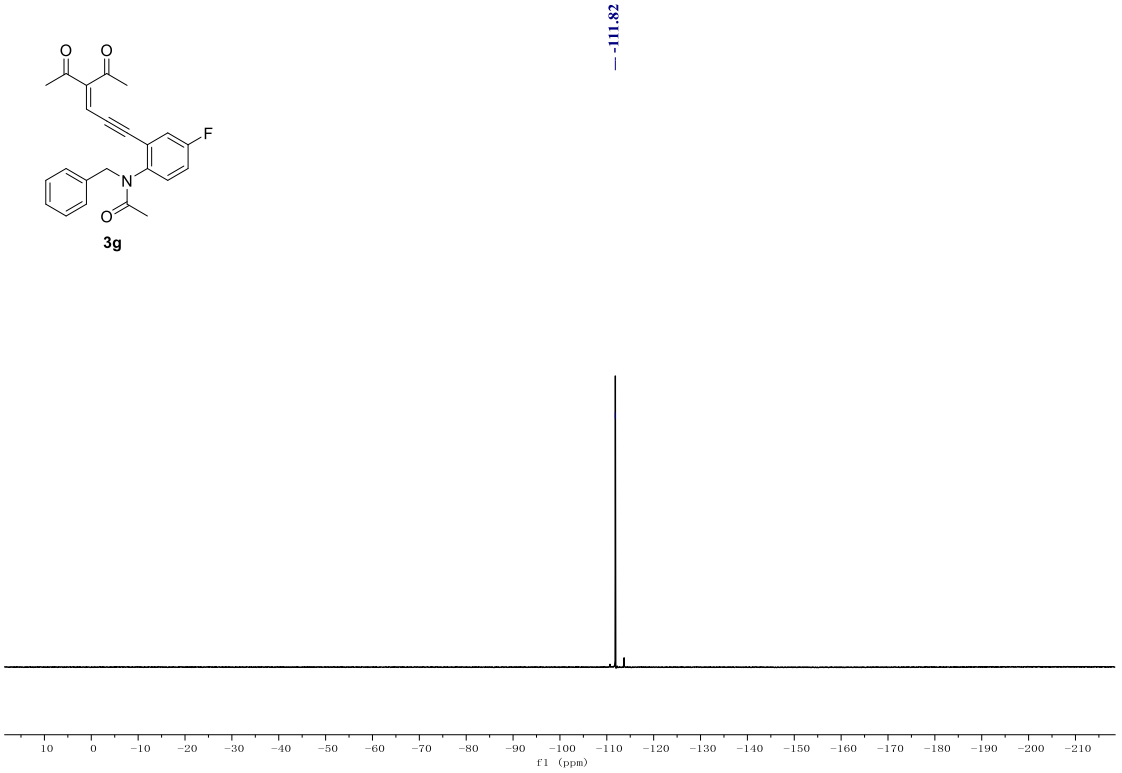

7.28
7.11
7.10
7.08
7.07
7.05
6.92
6.90
6.89
6.87
6.70
6.68
6.55
4.93
4.90
4.21
4.18
2.19
2.10
1.55
3e
1.13
2.05
4.07
1.05
1.01
1.00
1.00
3.06
3.05
2.97
f1 (ppm)
200.05
195.00
169.16
149.87
143.15
135.23
133.51
132.53
130.76
130.14
129.01
127.96
127.76
120.91
120.12
100.82
88.54
77.48
77.16
76.84
50.86
30.22
26.25
21.71
3e
f1 (ppm)


7.34
7.32
7.32
7.18
7.16
7.15
7.13
7.11
6.89
6.87
6.75
6.73
6.58
4.95
4.91
4.27
4.23
2.25
2.16
1.61
Br
N
O
O
O
3f
0.99
4.12
2.08
1.02
1.00
1.00
0.99
3.05
3.05
2.96
f1 (ppm)

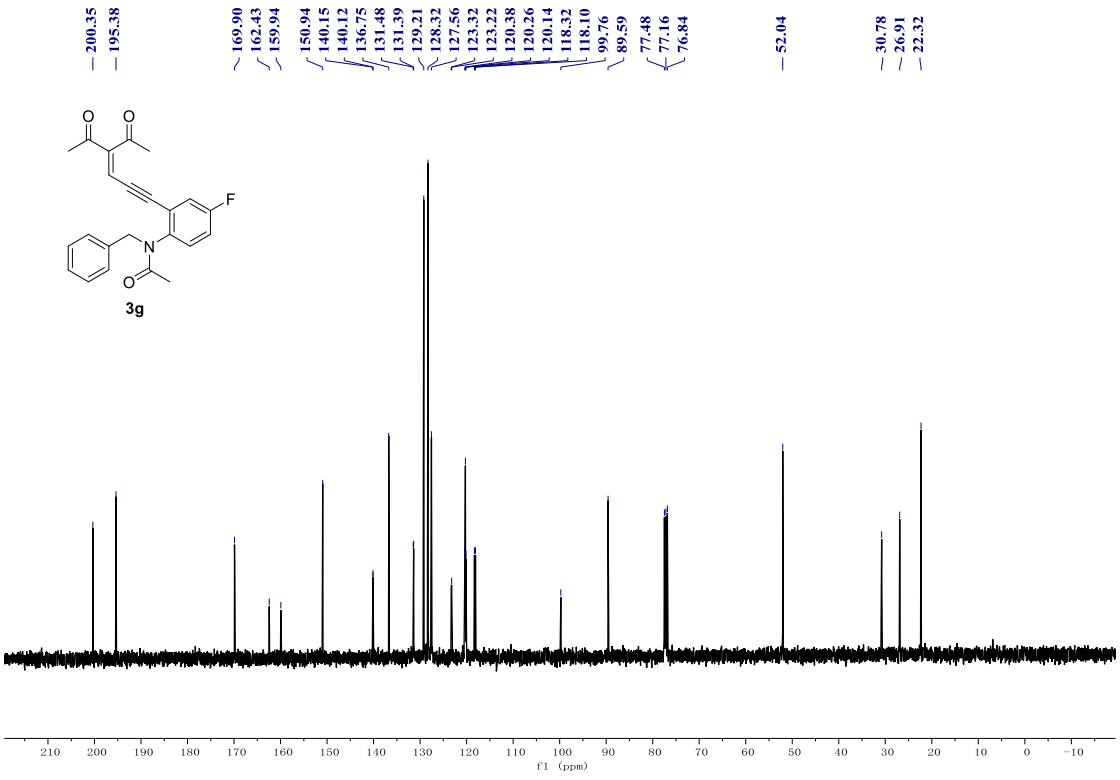

200.26
195.19
169.46
149.93
143.28
135.78
133.69
130.95
130.90
130.66
129.13
128.15
121.09
121.05
120.39
101.02
88.66
77.48
77.16
76.84
51.15
30.44
26.50
21.92
Br
N
O
O
O
3f
f1 (ppm)

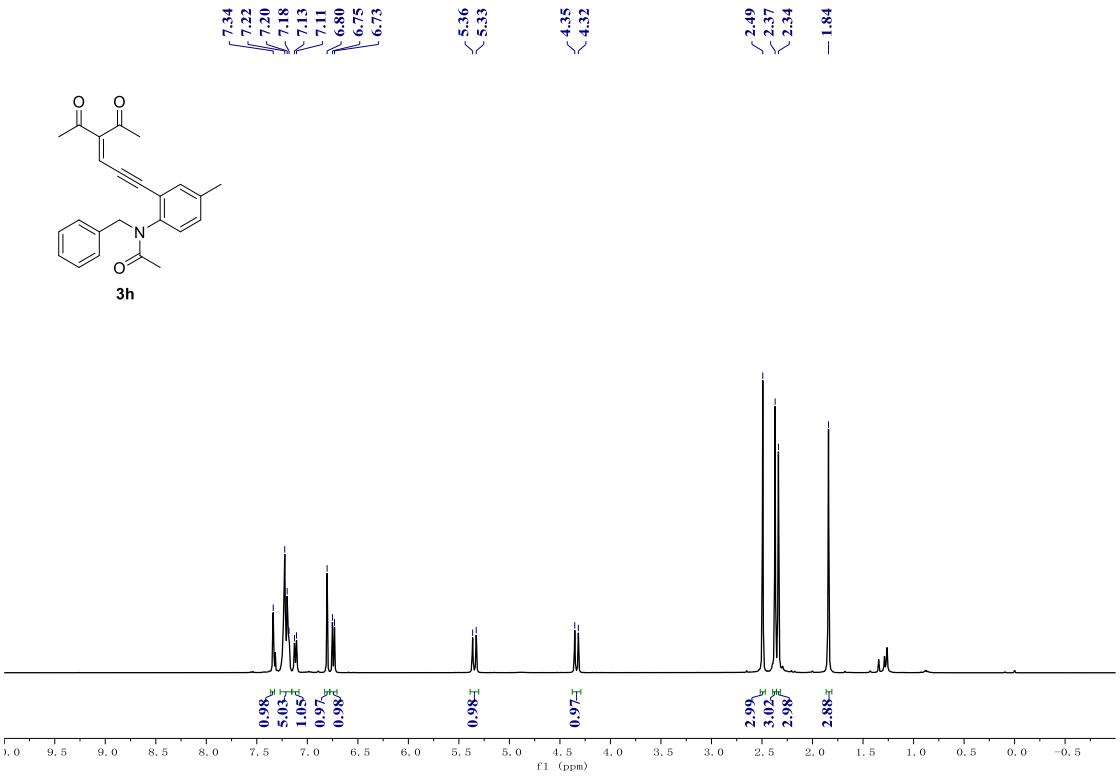

7.16
7.11
7.10
6.97
6.96
6.94
6.94
6.93
6.93
6.92
6.76
6.75
6.74
6.73
6.71
5.32
5.28
4.25
4.21
2.40
2.30
1.78
O
O
F
N
O
4.01
2.01
1.09
1.01
0.99
0.99
1.00
3.05
3.16
3.00
f1 (ppm)

3g


-111.82
O
O
F
N
O
f1 (ppm)

3g


200.35
195.38
169.90
162.43
159.94
150.94
140.15
140.12
136.75
131.48
131.39
129.21
128.32
127.56
123.32
123.22
120.38
120.26
120.14
118.32
118.10
99.76
89.59
77.48
77.16
76.84
52.04
30.78
26.91
22.32
O
O
F
N
O
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.34
7.22
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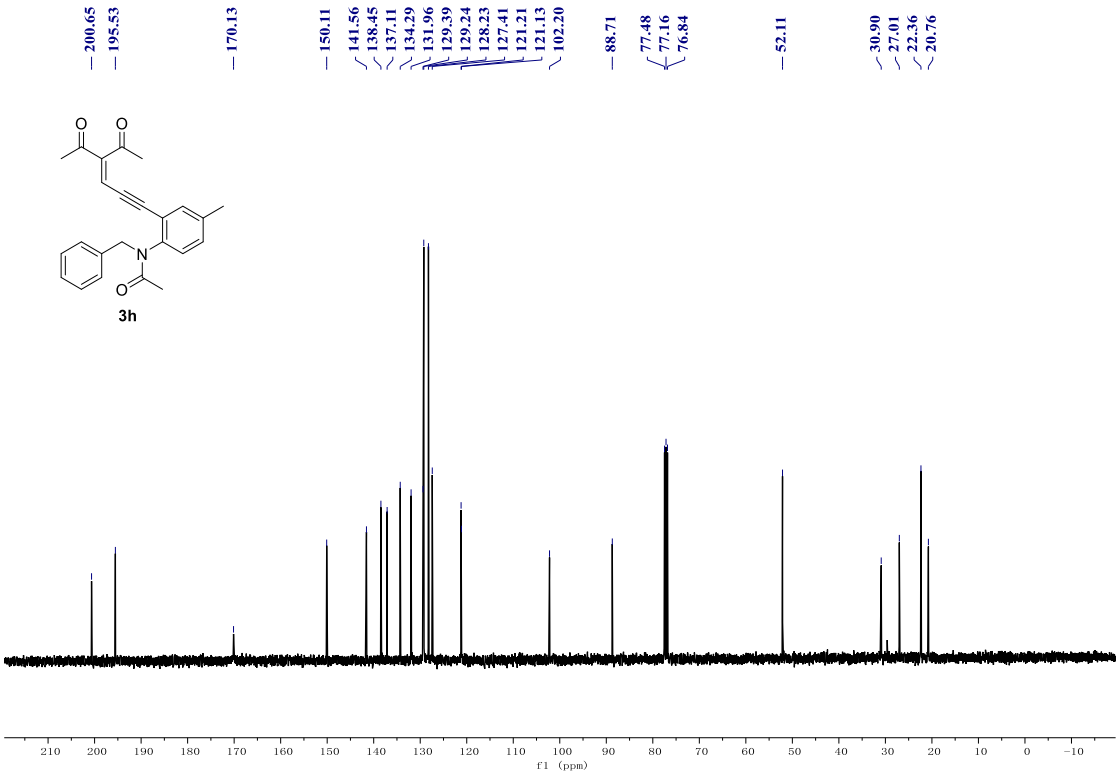
7.18
7.13
7.11
6.80
6.75
6.73
5.36
5.33
4.35
4.32
2.49
2.37
2.34
1.84
3h
0.98
5.03
1.05
0.97
0.98
0.98
0.97
2.99
3.02
2.98
2.88
f1 (ppm)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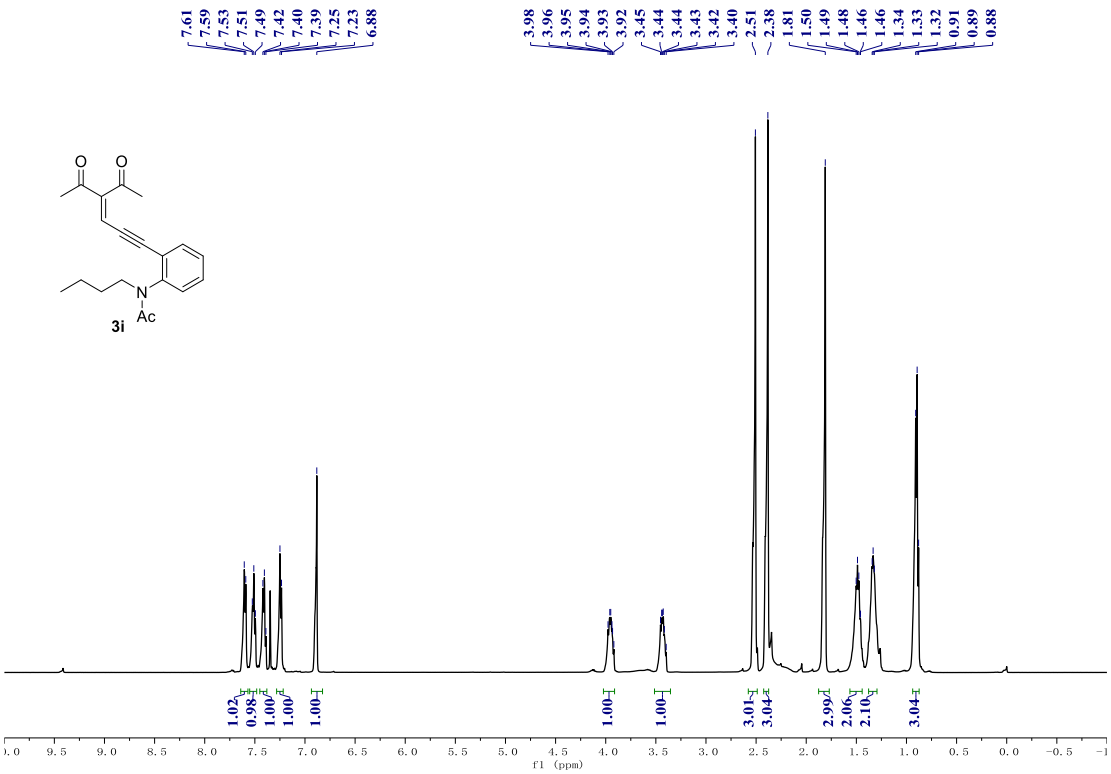
141.56
138.45
137.11
134.29
131.96
129.39
129.24
128.23
127.41
121.21
121.13
102.20
88.71
77.48
77.16
76.84
52.11
30.90
27.01
22.36
20.76
3h
f1 (ppm)


7.61
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7.53
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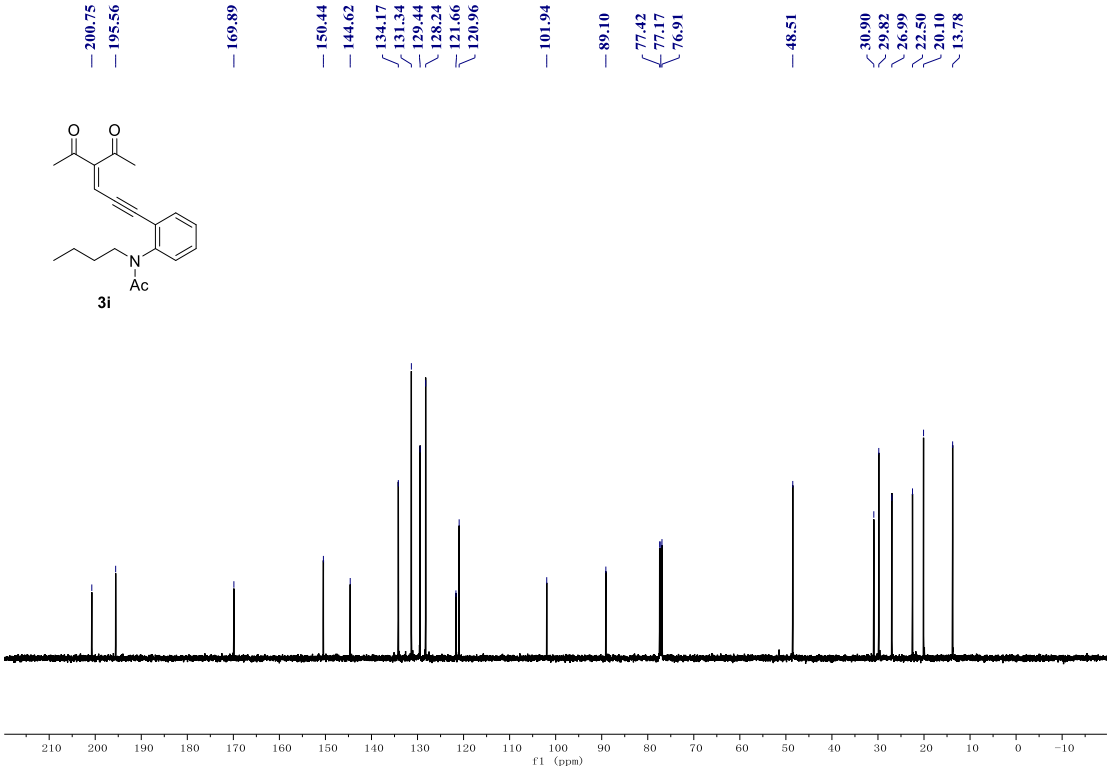
7.42
7.40
7.39
7.25
7.23
6.88
3.98
3.96
3.95
3.94
3.93
3.92
3.45
3.44
3.44
3.43
3.42
3.40
2.51
2.38
1.81
1.50
1.49
1.48
1.46
1.46
1.34
1.33
1.32
0.91
0.89
0.88
O
O
N
Ac
3i
1.02
0.98
1.00
1.00
1.00
1.00
1.00
3.01
3.04
2.99
2.06
2.10
3.04
f1 (ppm)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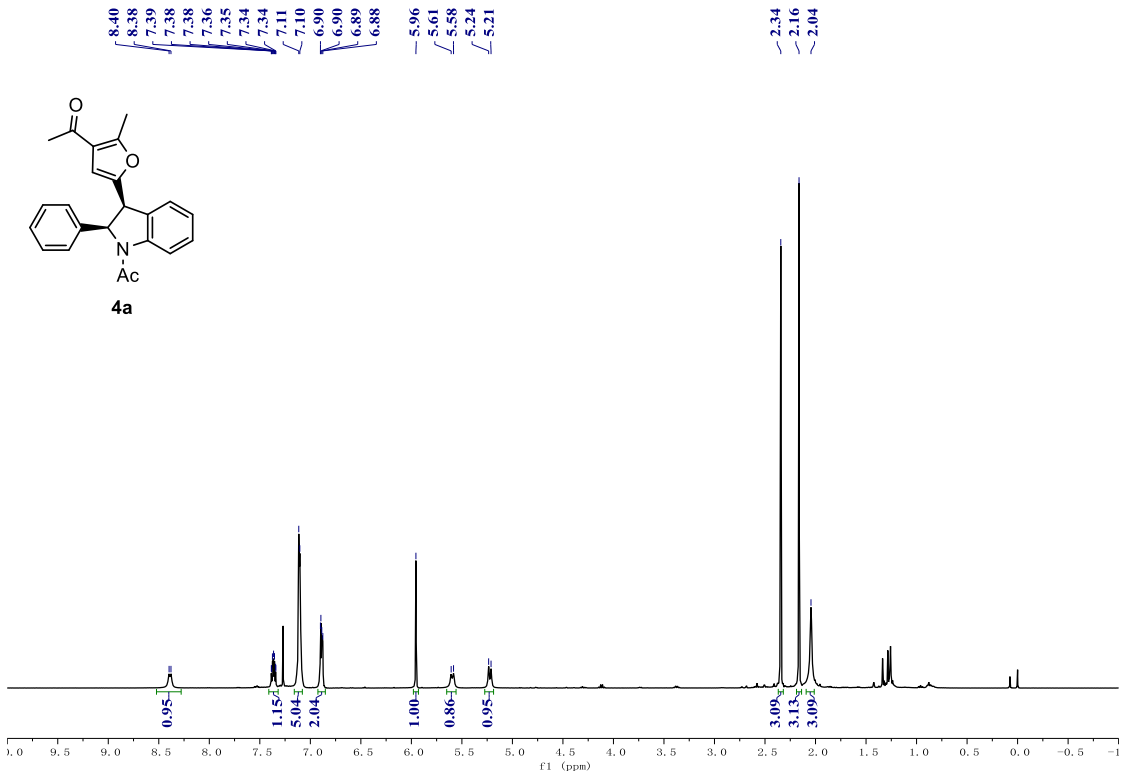
144.62
134.17
131.34
129.44
128.24
121.66
120.96
101.94
89.10
77.42
77.17
76.91
48.51
30.90
29.82
26.99
22.50
20.10
13.78
O
O
N
Ac
3i
f1 (ppm)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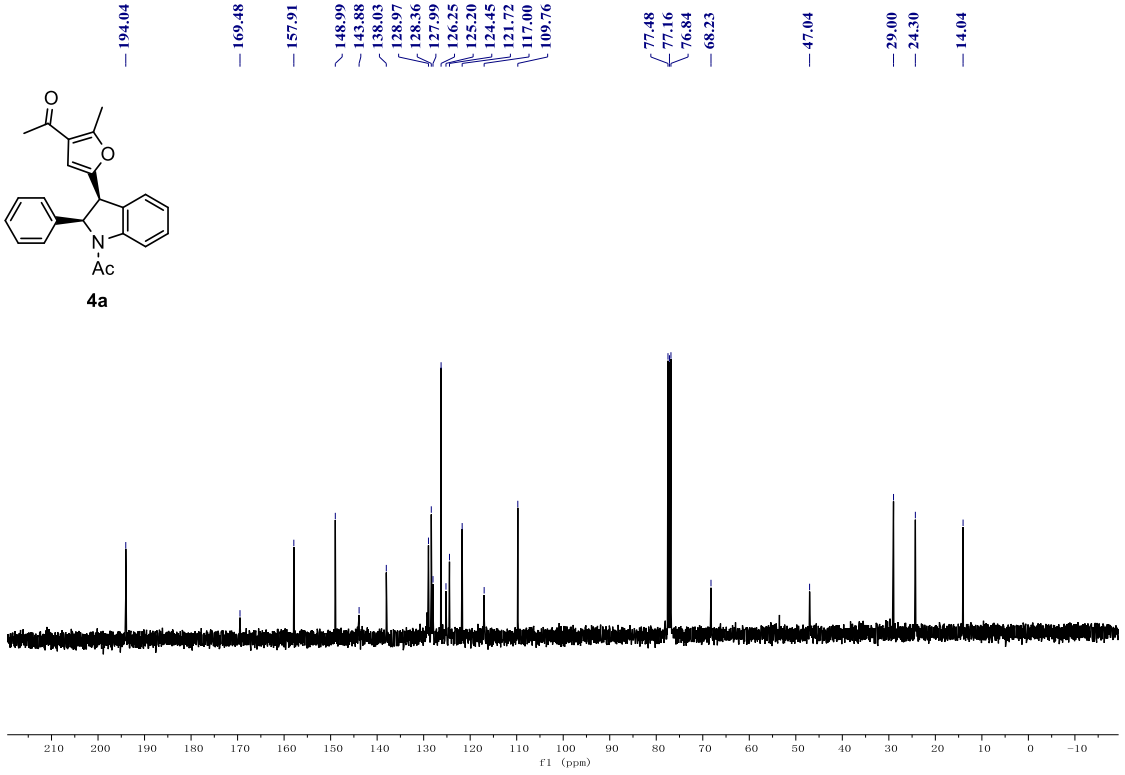
7.39
7.38
7.38
7.36
7.35
7.34
7.34
7.11
7.10
6.90
6.90
6.89
6.88
5.96
5.61
5.58
5.24
5.21
2.34
2.16
2.04
O
O
N
Ac
4a
0.95
1.15
5.04
2.04
1.00
0.86
0.95
3.09
3.13
3.09
f1 (ppm)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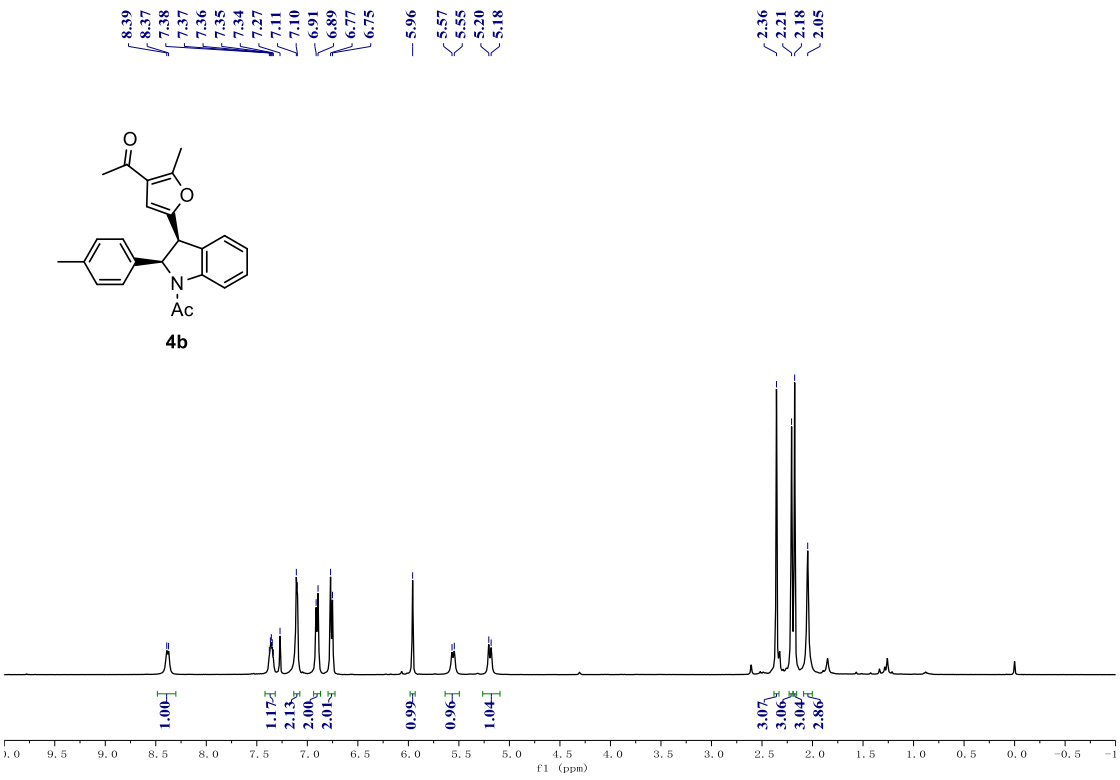
157.91
148.99
143.88
138.03
128.97
128.36
127.99
126.25
125.20
124.45
121.72
117.00
109.76
77.48
77.16
76.84
68.23
47.04
29.00
24.30
14.04
O
O
N
Ac
4a
f1 (ppm)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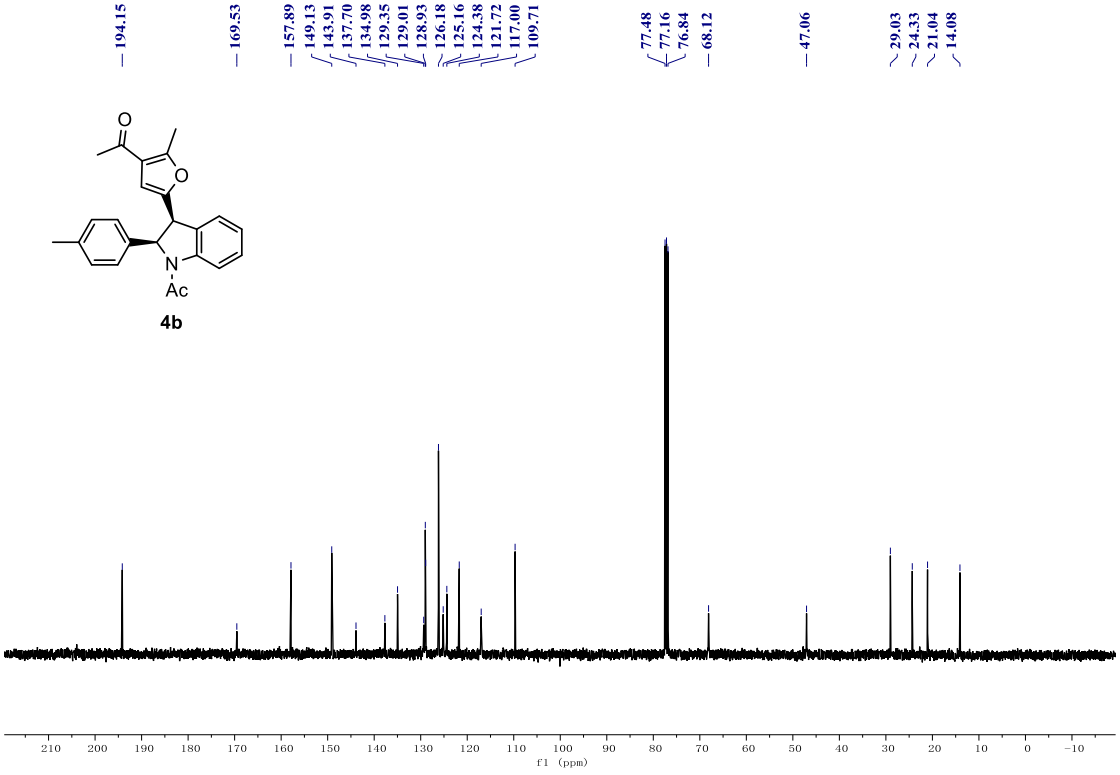
8.37
7.38
7.37
7.36
7.35
7.34
7.27
7.11
7.10
6.91
6.89
6.77
6.75
5.96
5.57
5.55
5.20
5.18
2.36
2.21
2.18
2.05
O
O
N
Ac
4b
1.00
1.17
2.13
2.00
2.01
0.99
0.96
1.04
3.07
3.06
3.04
2.86
f1 (ppm)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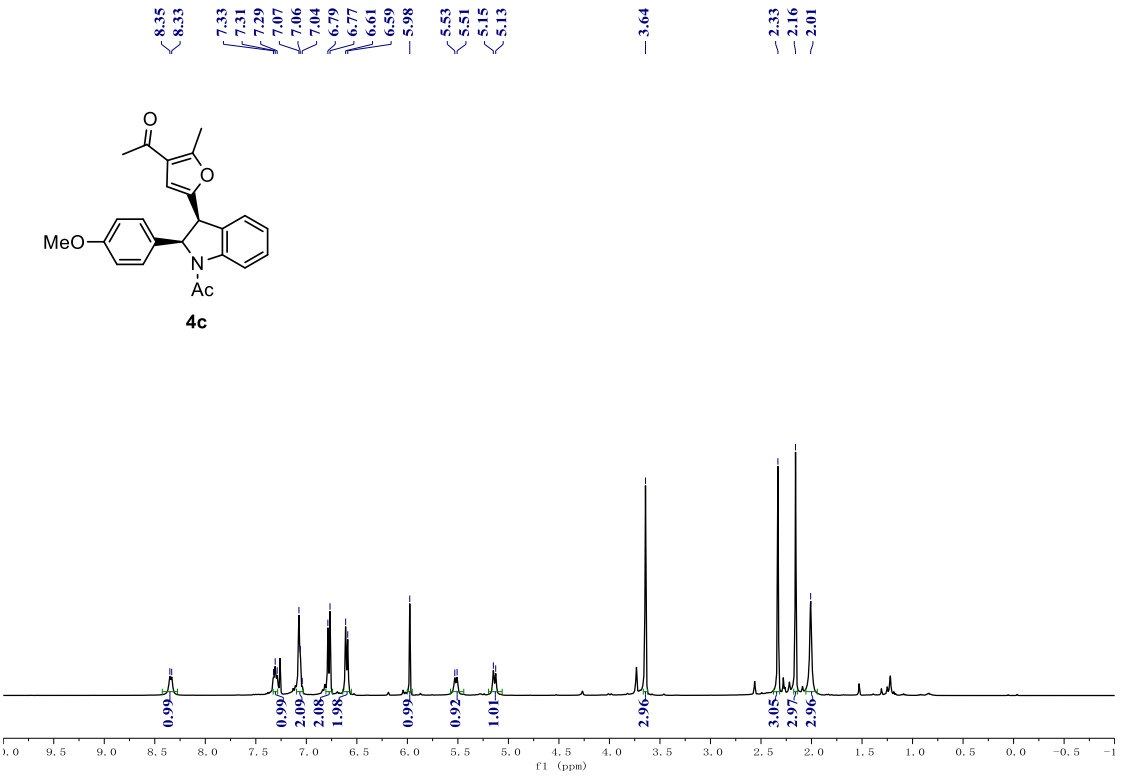
137.70
134.98
129.35
129.01
128.93
126.18
125.16
124.38
121.72
117.00
109.71
77.48
77.16
76.84
68.12
47.06
29.03
24.33
21.04
14.08
O
O
N
Ac
4b
f1 (ppm)


8.35
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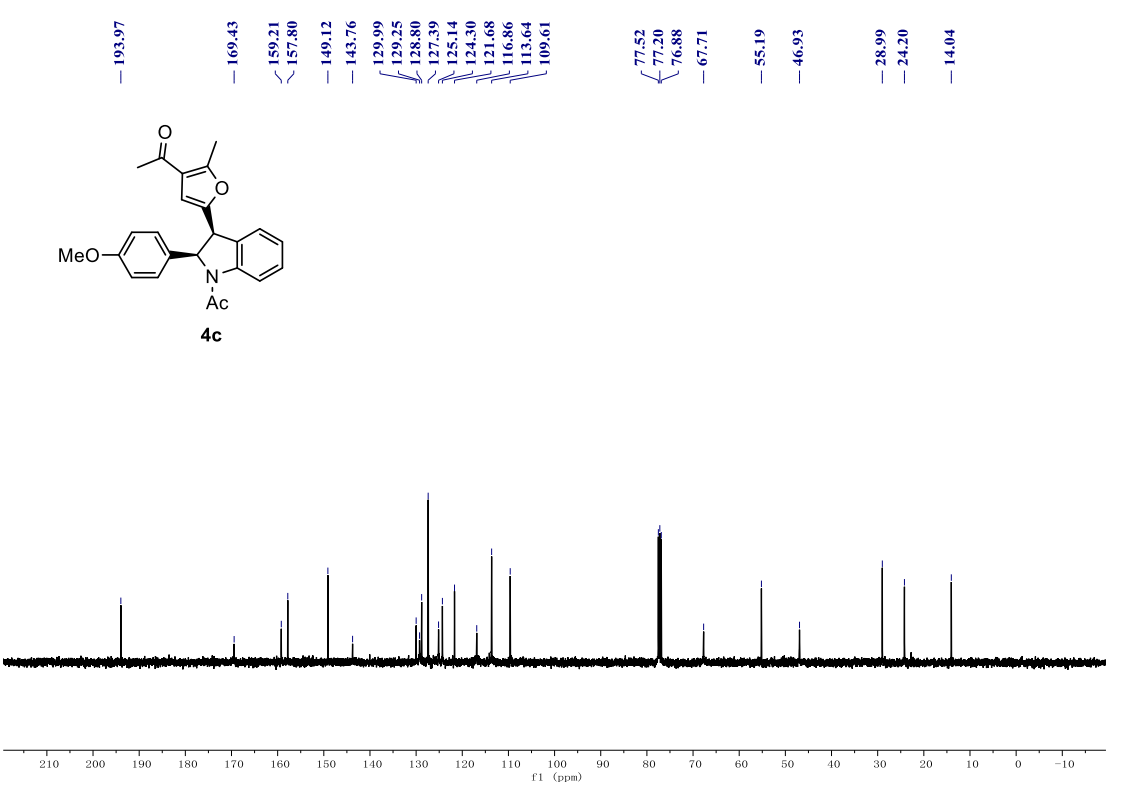
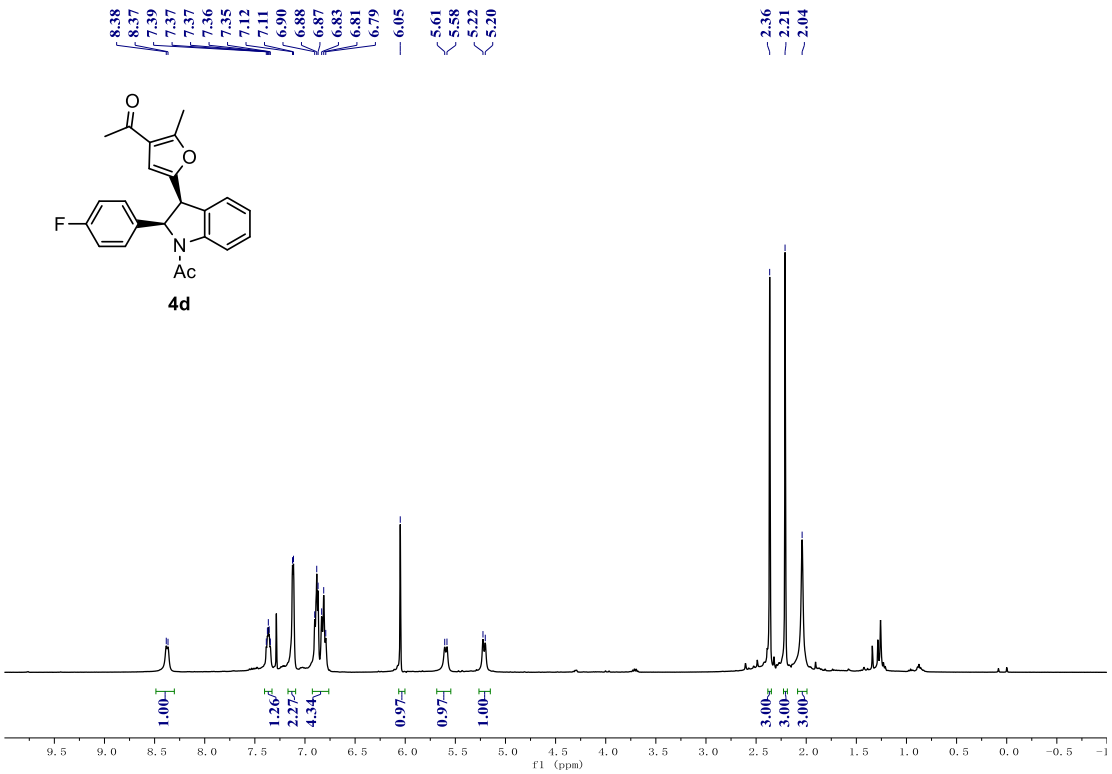
7.31
7.29
7.07
7.06
7.04
6.79
6.77
6.61
6.59
5.98
5.53
5.51
5.15
5.13
3.64
2.33
2.16
2.01
O
O
MeO
N
Ac
0.99
0.99
2.09
2.08
1.98
0.99
0.92
1.01
2.96
3.05
2.97
2.96
f1 (ppm)

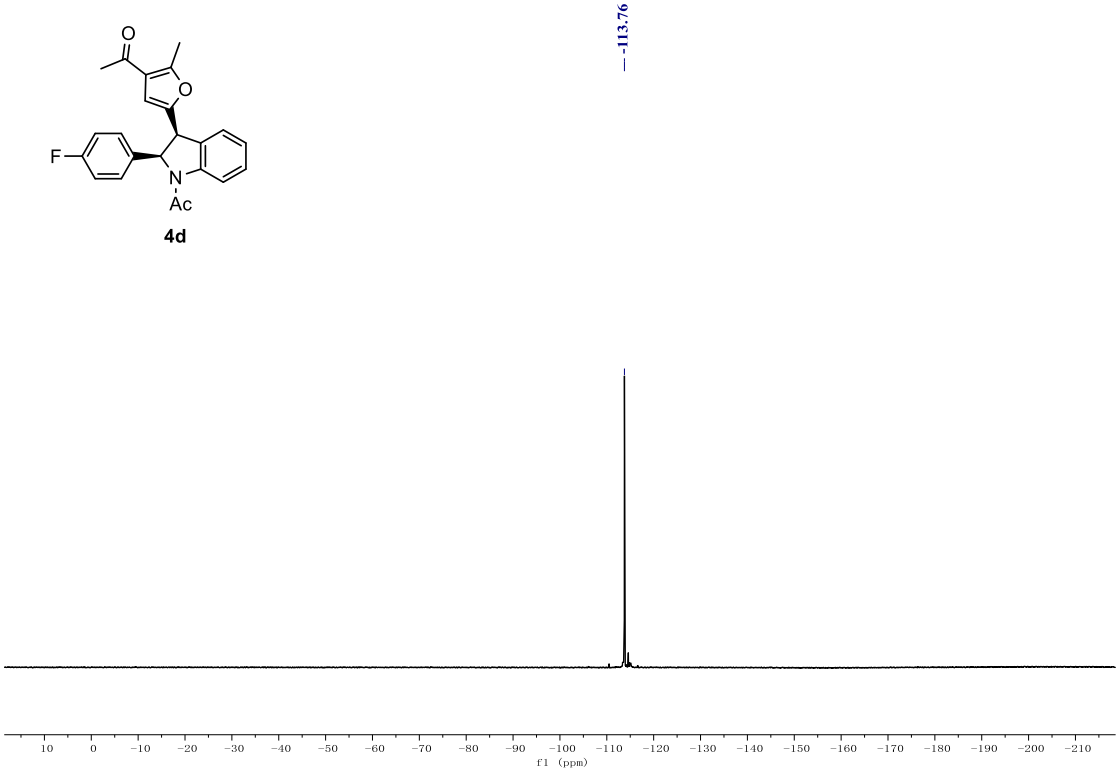
4c


193.97
169.43
159.21
157.80
149.12
143.76
129.99
129.25
128.80
127.39
125.14
124.30
121.68
116.86
113.64
109.61
77.52
77.20
76.88
67.71
55.19
46.93
28.99
24.20
14.04
O
O
MeO
N
Ac
f1 (ppm)

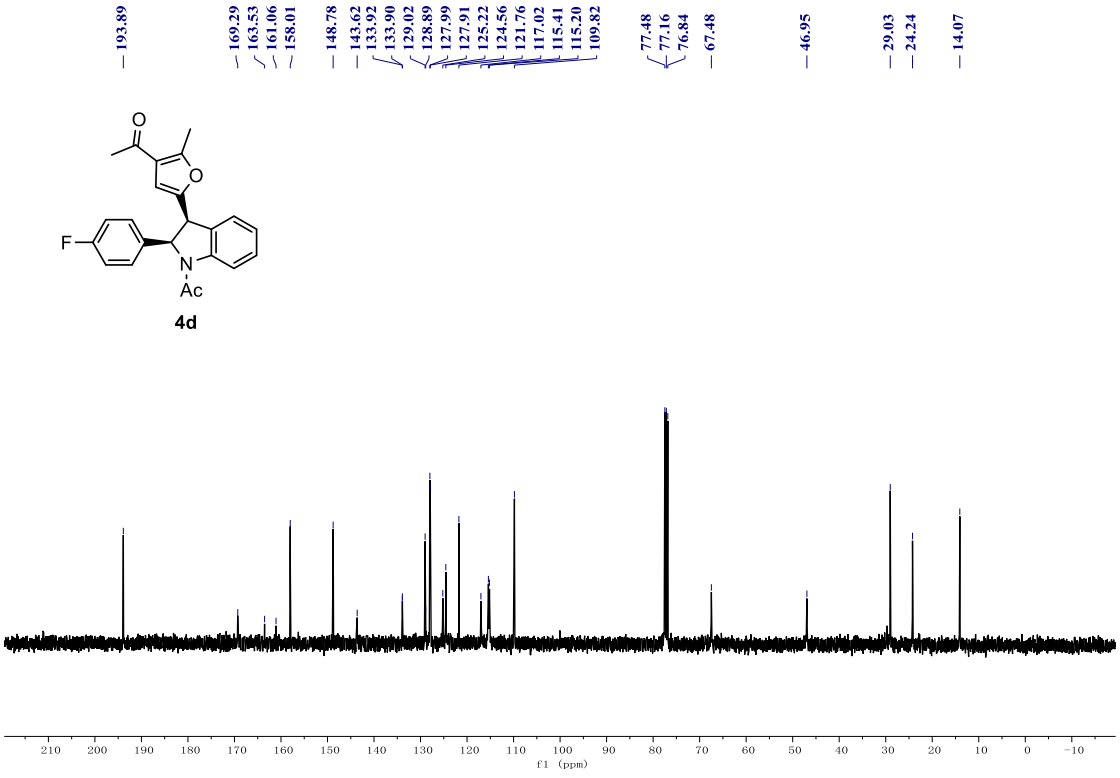
4c

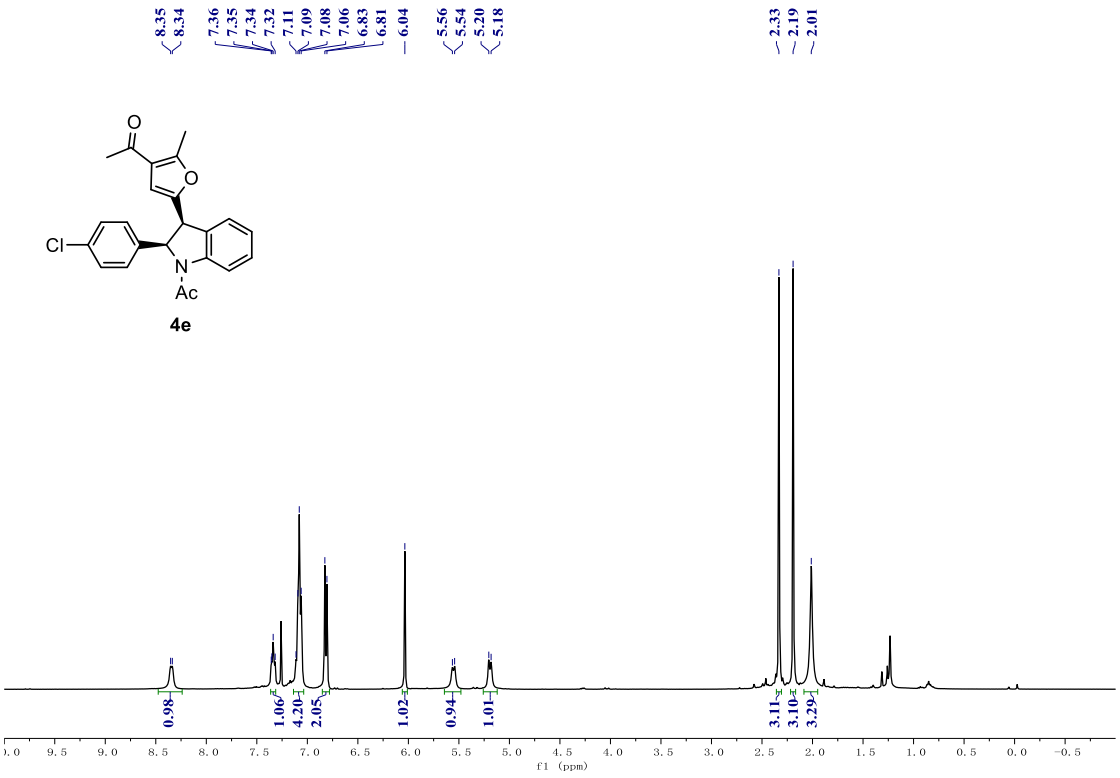

8.38
8.37
7.39
7.37
7.37
7.36
7.35
7.12
7.11
6.90
6.88
6.87
6.83
6.81
6.79
6.05
5.61
5.58
5.22
5.20
2.36
2.21
2.04
O
O
F
N
Ac
1.00
1.26
2.27
4.34
0.97
0.97
1.00
3.00
3.00
3.00
f1 (ppm)

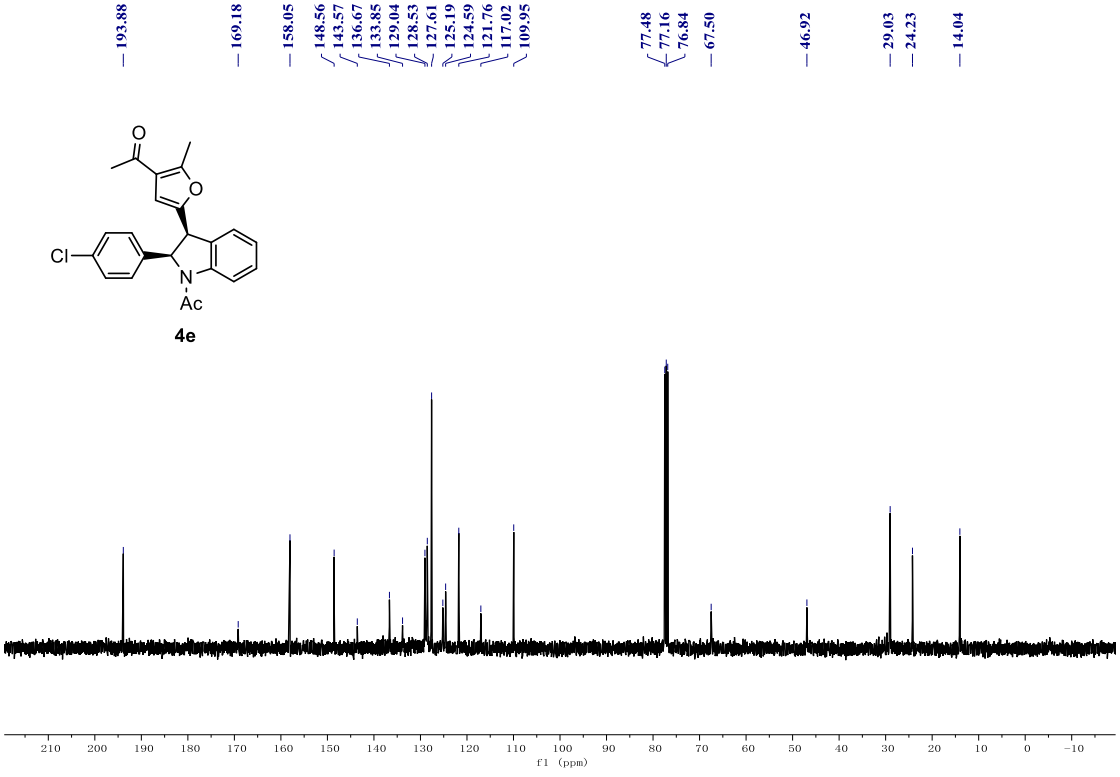
4d

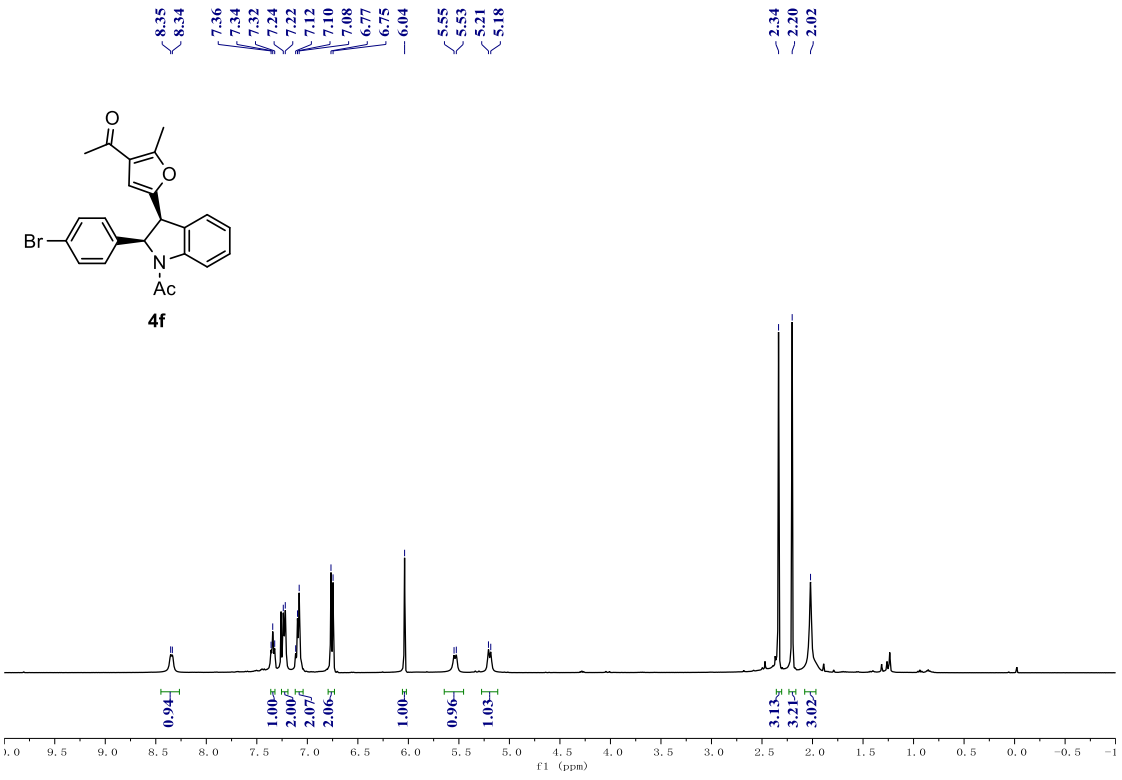

-113.76
O
O
F
N
Ac
f1 (ppm)

4d

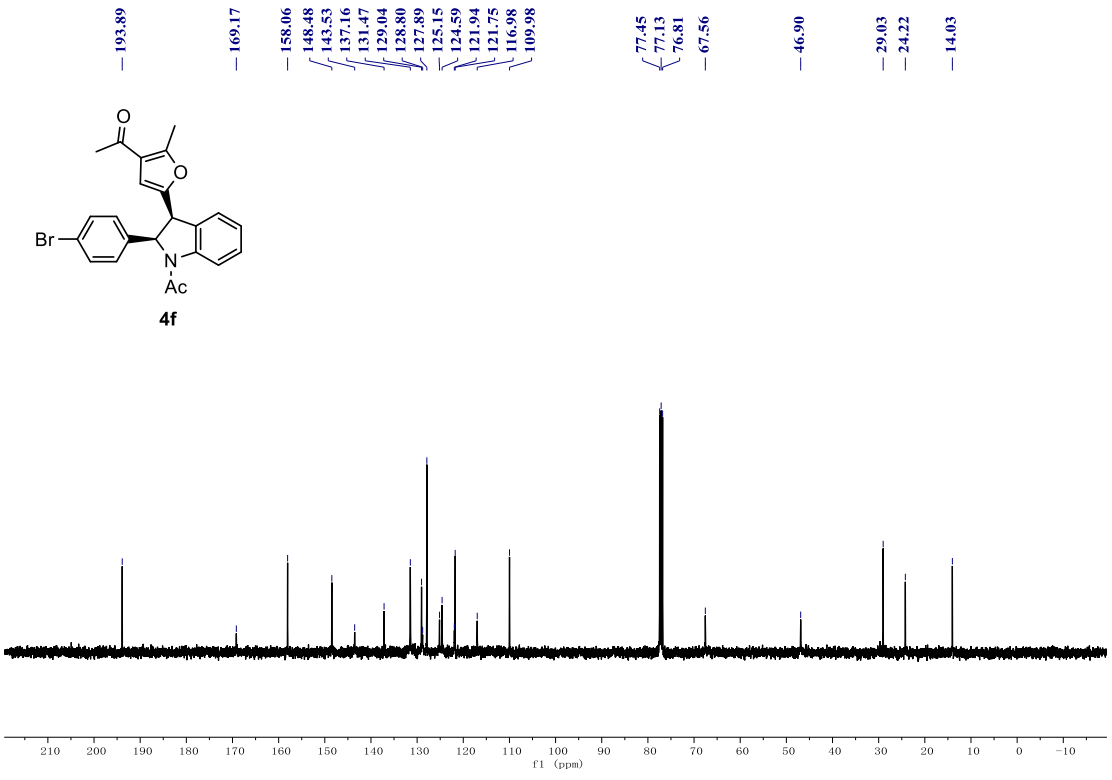

193.89
169.29
163.53
161.06
158.01
148.78
143.62
133.92
133.90
129.02
128.89
127.99
127.91
125.22
124.56
121.76
117.02
115.41
115.20
109.82
77.48
77.16
76.84
67.48
46.95
29.03
24.24
14.07
O
O
F
N
Ac
4d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.35
8.34
7.36
7.35
7.34
7.32
7.11
7.09
7.08
7.06
6.83
6.81
6.04
5.56
5.54
5.20
5.18
2.33
2.19
2.01
O
O
Cl
N
Ac
4e
0.98
1.06
4.20
2.05
1.02
0.94
1.01
3.11
3.10
3.29
f1 (ppm)

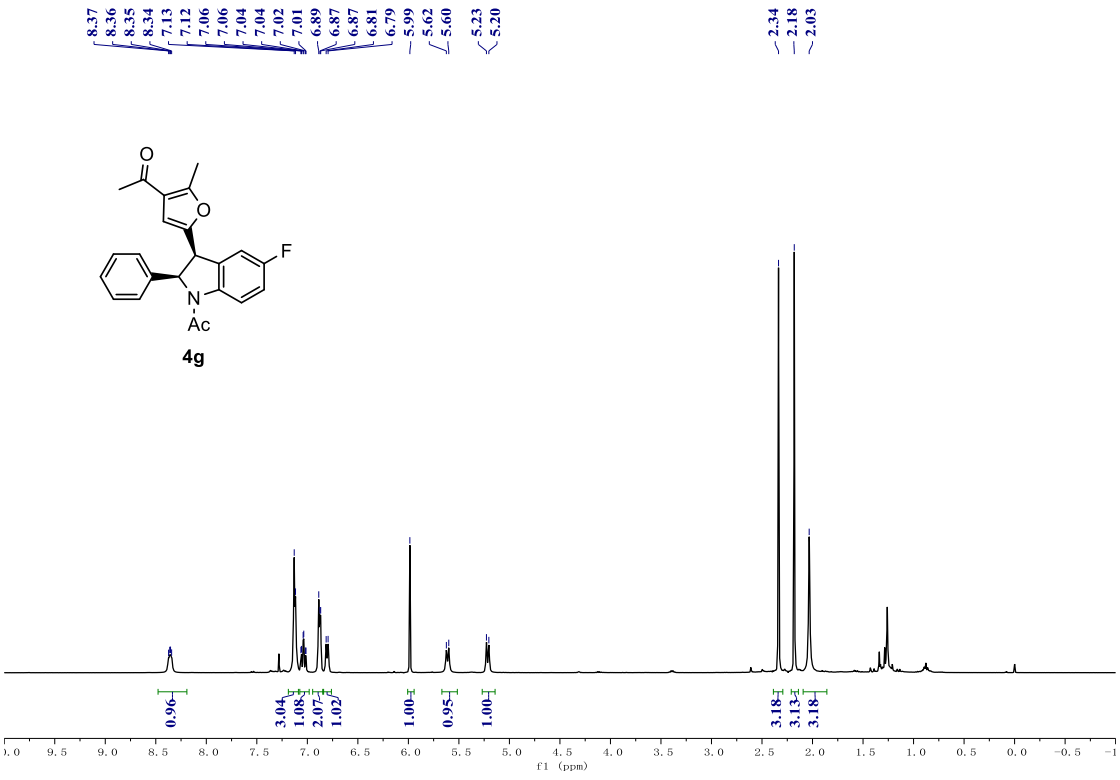

193.88
169.18
158.05
148.56
143.57
136.67
133.85
129.04
128.53
127.61
125.19
124.59
121.76
117.02
109.95
77.48
77.16
76.84
67.50
46.92
29.03
24.23
14.04
O
O
Cl
N
Ac
4e
f1 (ppm)


8.35
8.34
7.36
7.34
7.32
7.24
7.22
7.12
7.10
7.08
6.77
6.75
6.04
5.55
5.53
5.21
5.18
2.34
2.20
2.02
O
O
Br
N
Ac
0.94
1.00
2.00
2.07
2.06
1.00
0.96
1.03
3.13
3.21
3.02
f1 (ppm)

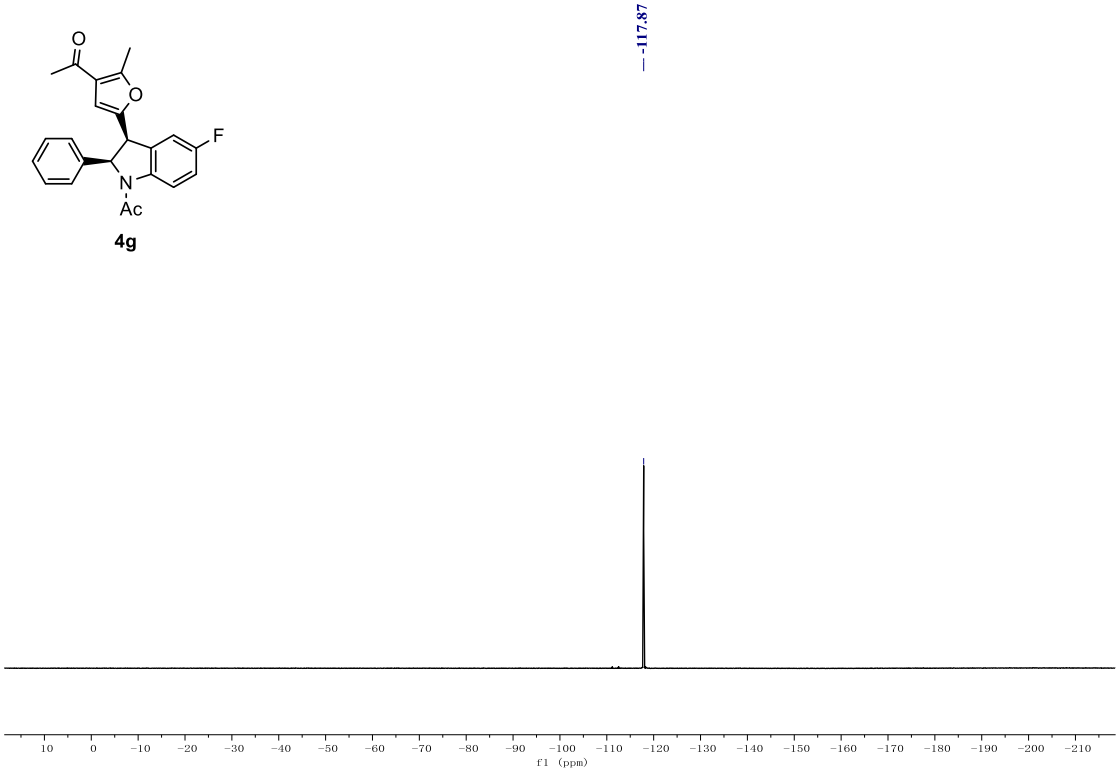
4f

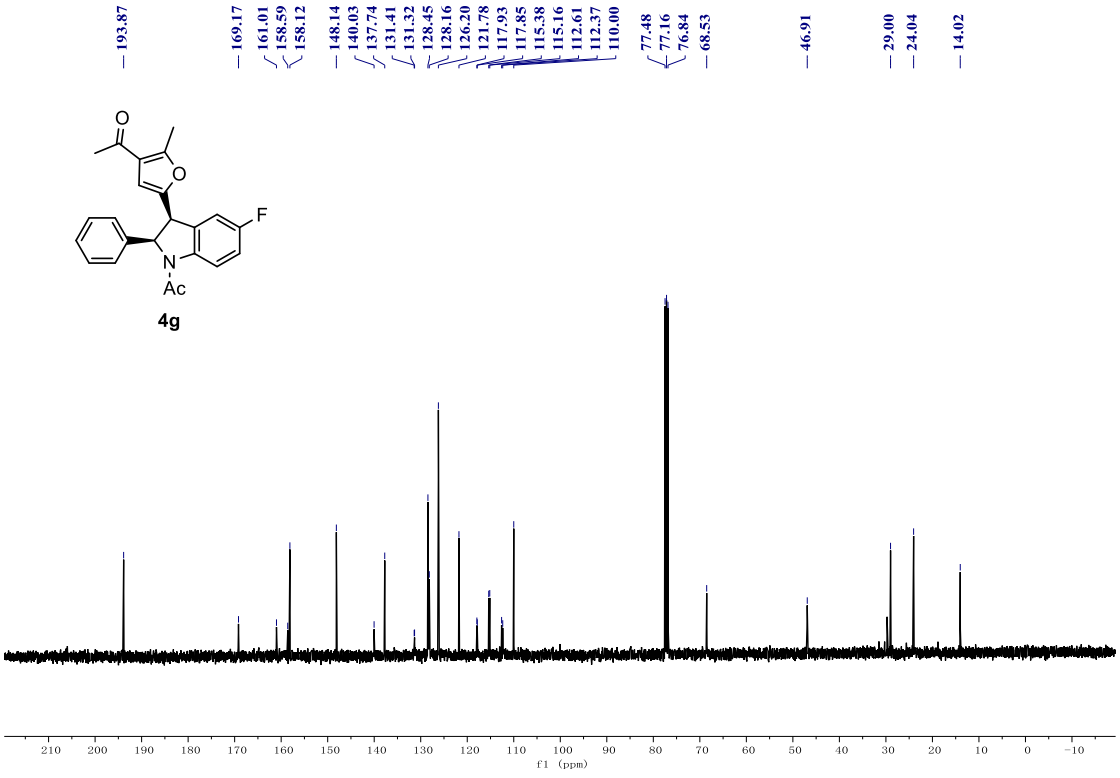

193.89
169.17
158.06
148.48
143.53
137.16
131.47
129.04
128.80
127.89
125.15
124.59
121.94
121.75
116.98
109.98
77.45
77.13
76.81
67.56
46.90
29.03
24.22
14.03
O
O
Br
N
Ac
f1 (ppm)

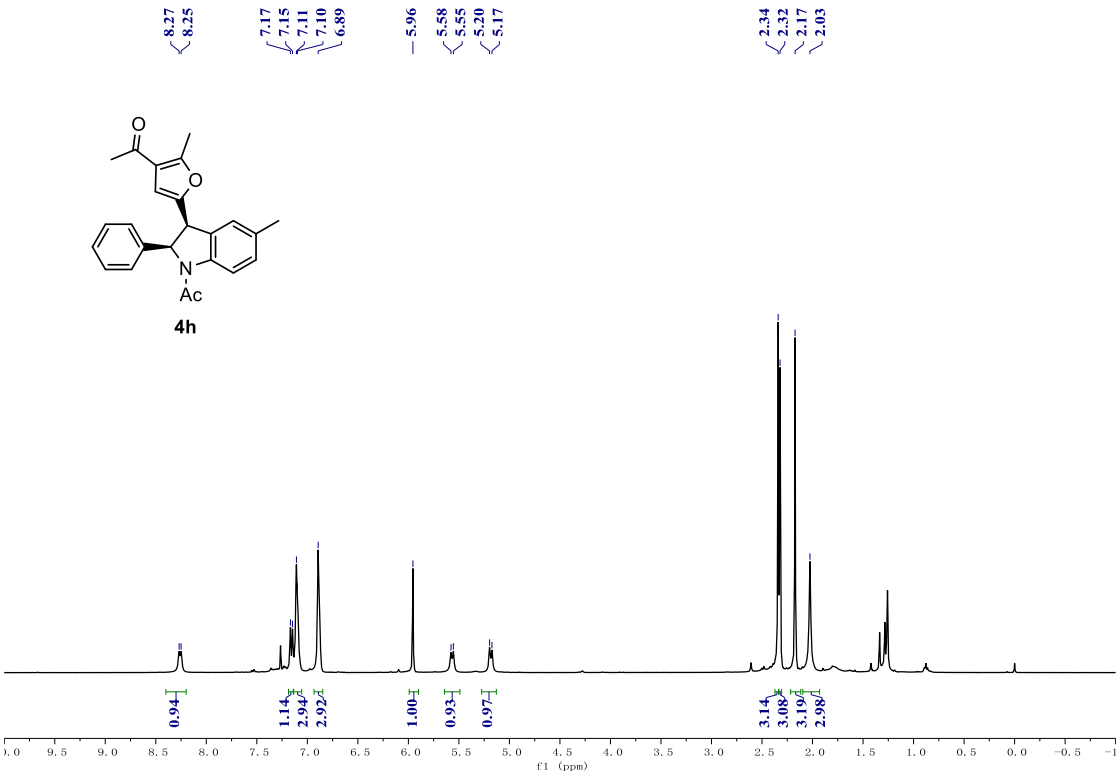
4f


8.37
8.36
8.35
8.34
7.13
7.12
7.06
7.06
7.04
7.04
7.02
7.01
6.89
6.87
6.87
6.81
6.79
5.99
5.62
5.60
5.23
5.20
2.34
2.18
2.03
O
O
F
N
Ac
0.96
3.04
1.08
2.07
1.02
1.00
0.95
1.00
3.18
3.13
3.18
f1 (ppm)

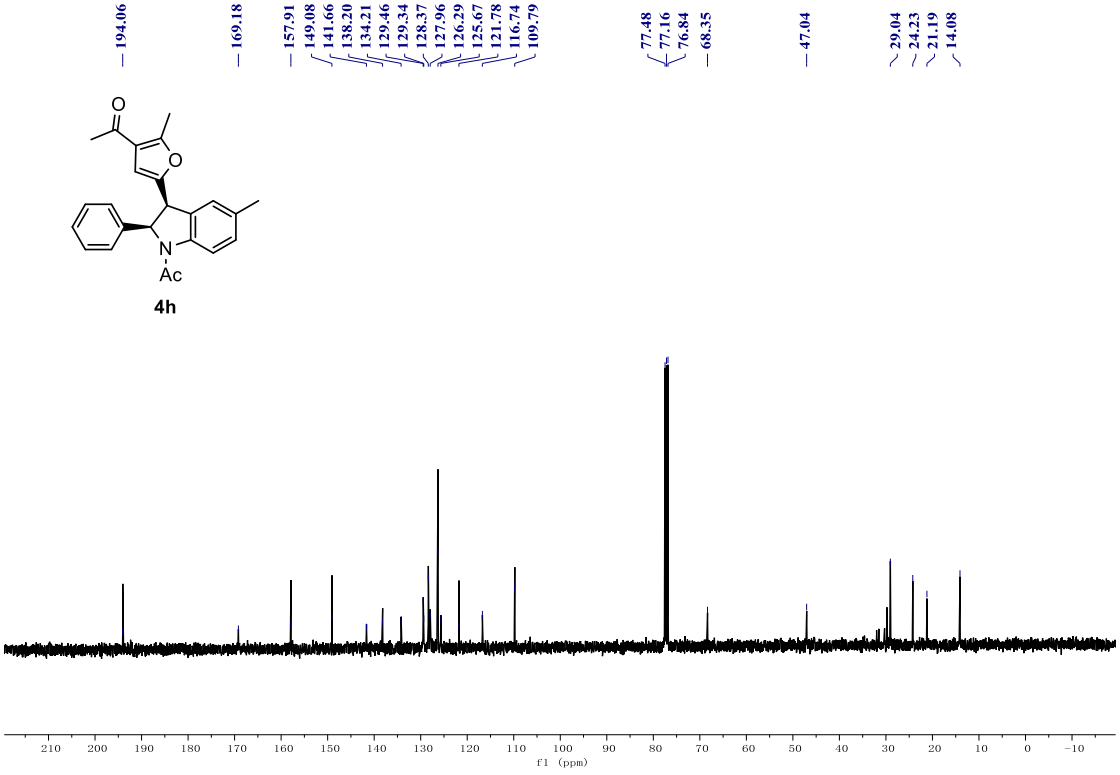
4g


-117.87
f1 (ppm)

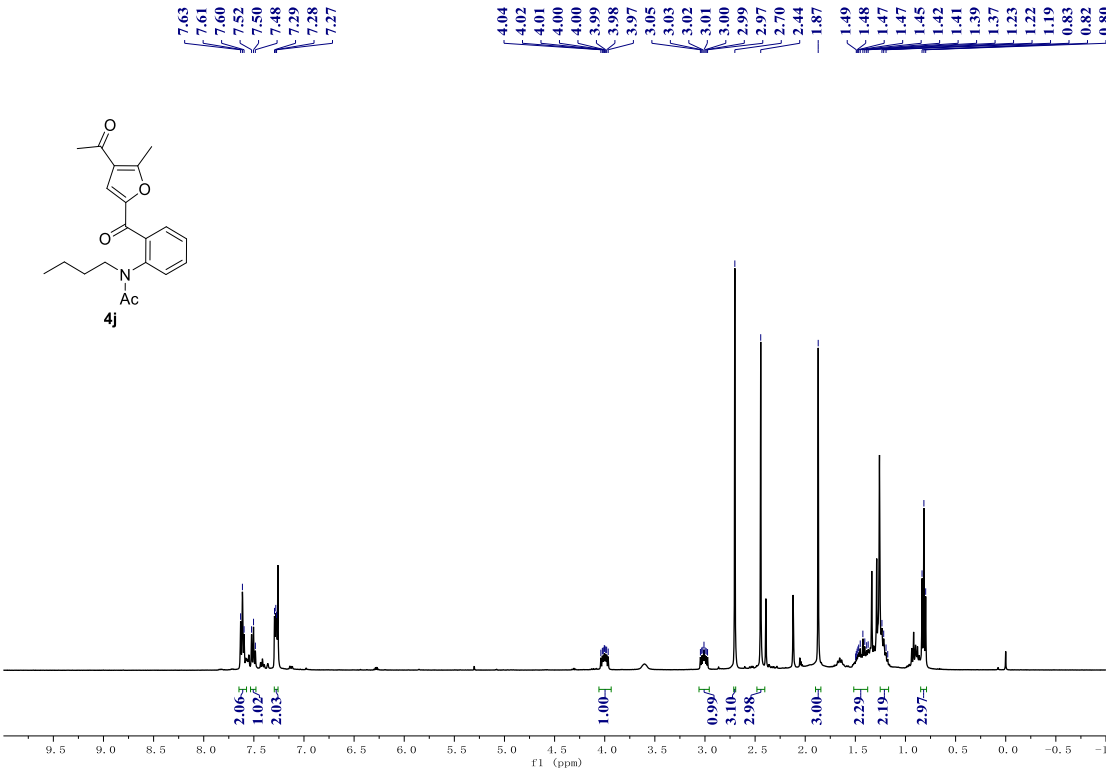

193.87
169.17
161.01
158.59
158.12
148.14
140.03
137.74
131.41
131.32
128.45
128.16
126.20
121.78
117.93
117.85
115.38
115.16
112.61
112.37
110.00
77.48
77.16
76.84
68.53
46.91
29.00
24.04
14.02
O
O
F
N
Ac
4g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

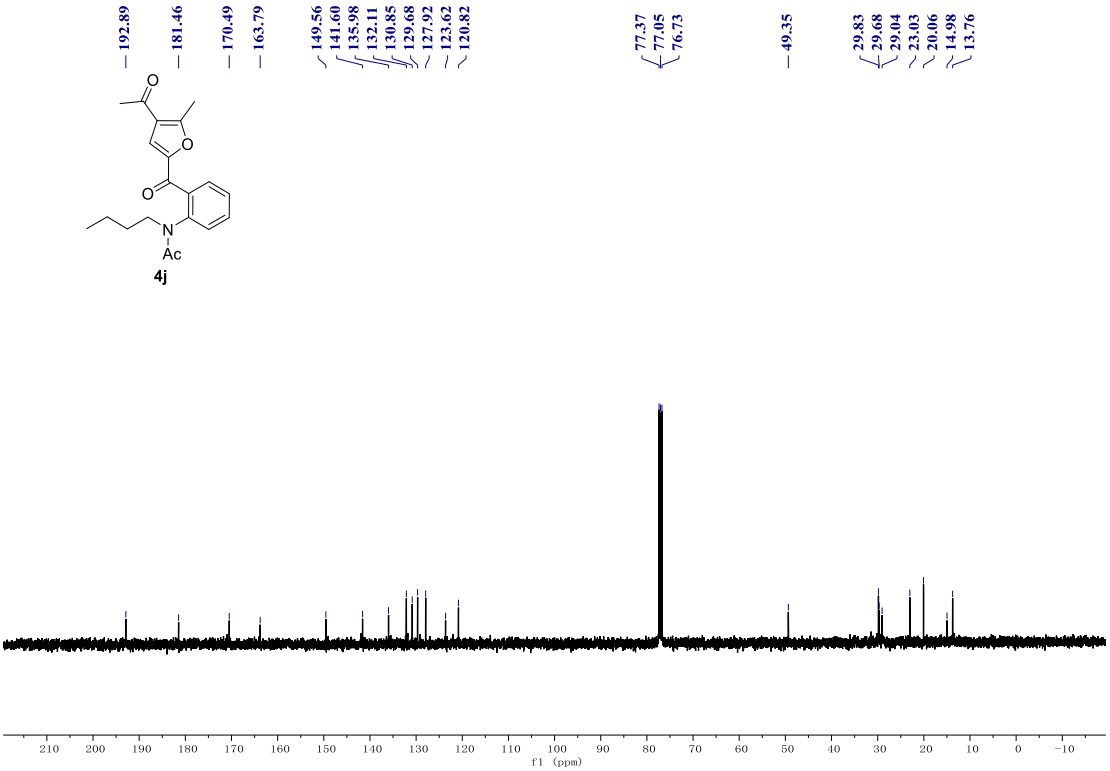

8.27
8.25
7.17
7.15
7.11
7.10
6.89
5.96
5.58
5.55
5.20
5.17
2.34
2.32
2.17
2.03
O
O
N
Ac
0.94
1.14
2.94
2.92
1.00
0.93
0.97
3.14
3.08
3.19
2.98
f1 (ppm)

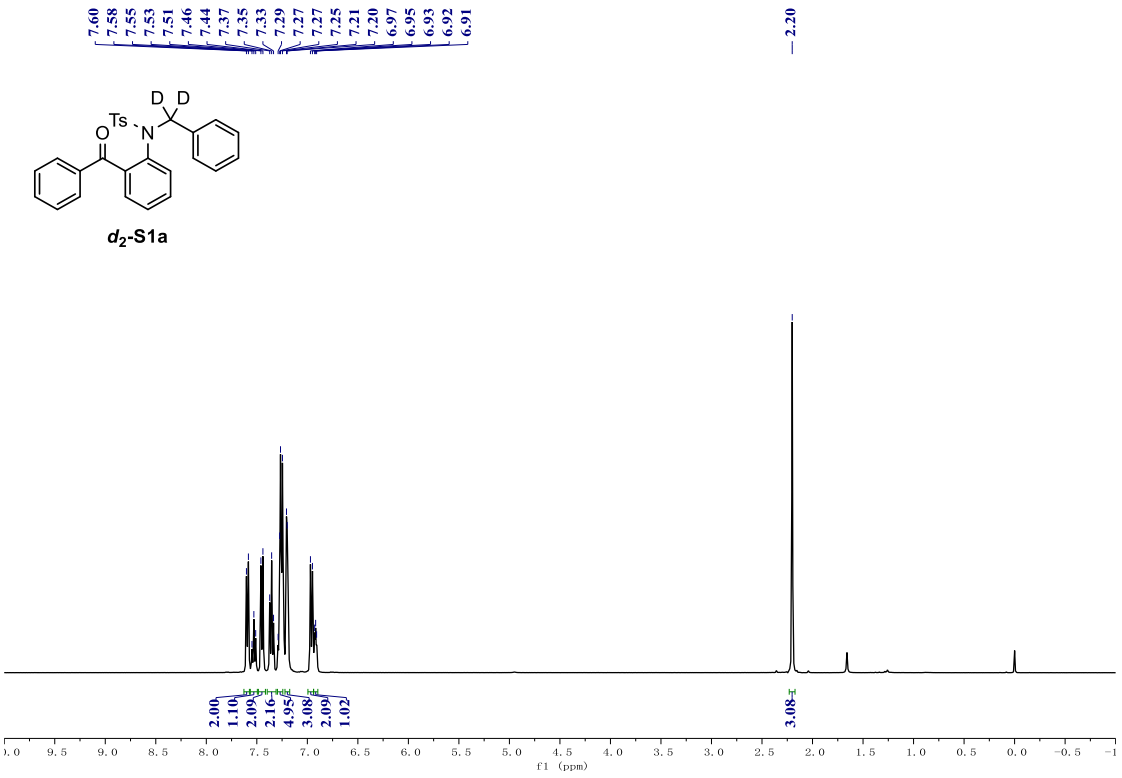
4h


194.06
169.18
157.91
149.08
141.66
138.20
134.21
129.46
129.34
128.37
127.96
126.29
125.67
121.78
116.74
109.79
77.48
77.16
76.84
68.35
47.04
29.04
24.23
21.19
14.08
O
O
N
Ac
f1 (ppm)

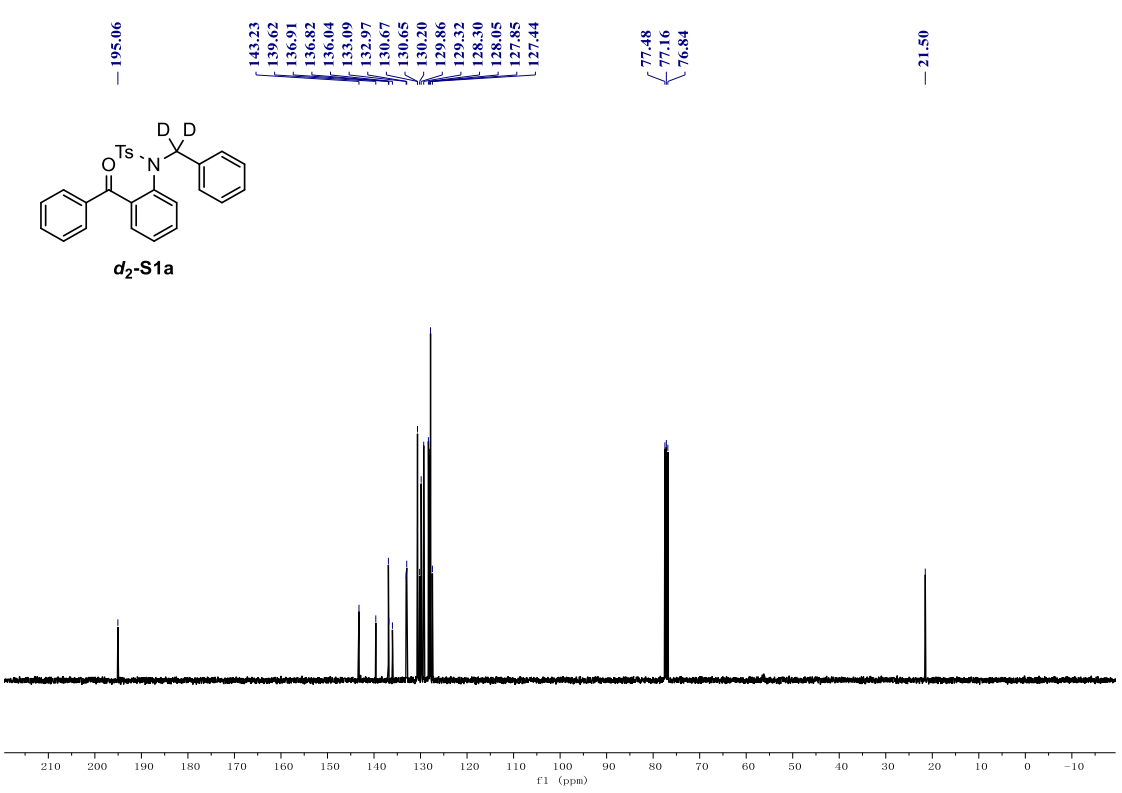
4h


7.63
7.61
7.60
7.52
7.50
7.48
7.29
7.28
7.27
4.04
4.02
4.01
4.00
4.00
3.99
3.98
3.97
3.05
3.03
3.02
3.01
3.00
2.99
2.97
2.70
2.44
1.87
1.49
1.48
1.47
1.47
1.45
1.42
1.41
1.39
1.37
1.23
1.22
1.19
0.83
0.82
O
O
O
N
Ac
4j
2.06
1.02
2.03
1.00
0.99
3.10
2.98
3.00
2.29
2.19
2.97
f1 (ppm)

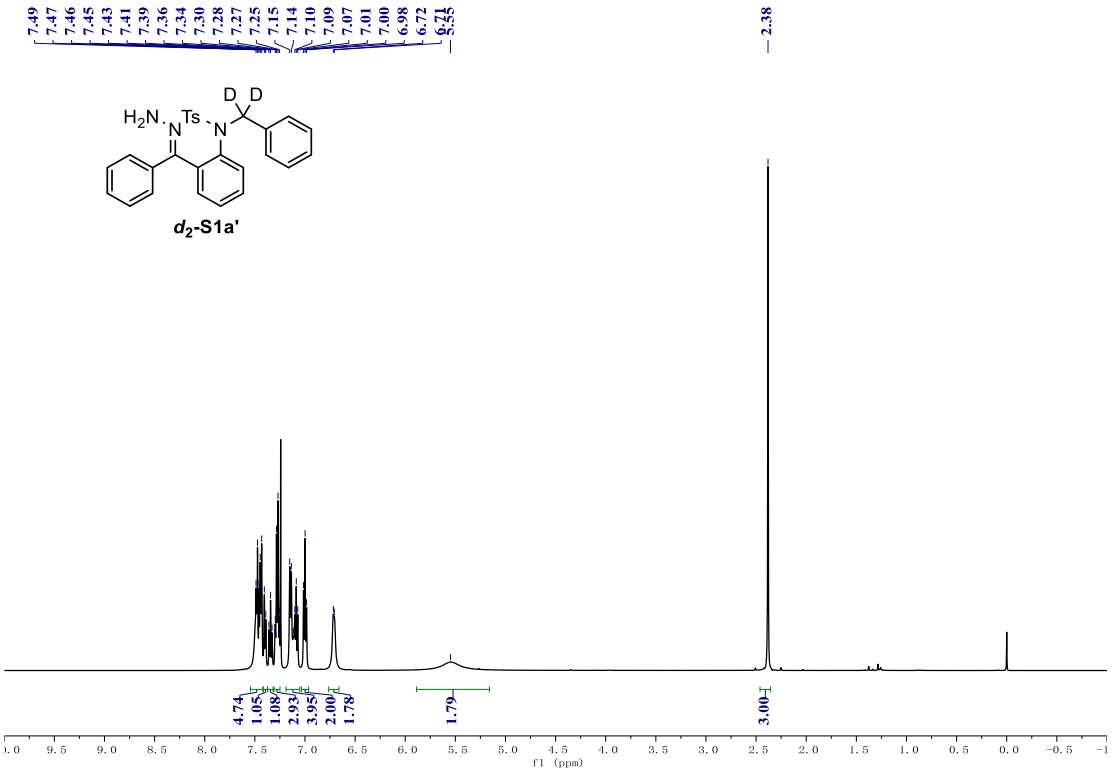

192.89
181.46
170.49
163.79
149.56
141.60
135.98
132.11
130.85
129.68
127.92
123.62
120.82
77.37
77.05
76.73
49.35
29.83
29.68
29.04
23.03
20.06
14.98
13.76
O
O
O
N
Ac
4j
f1 (ppm)

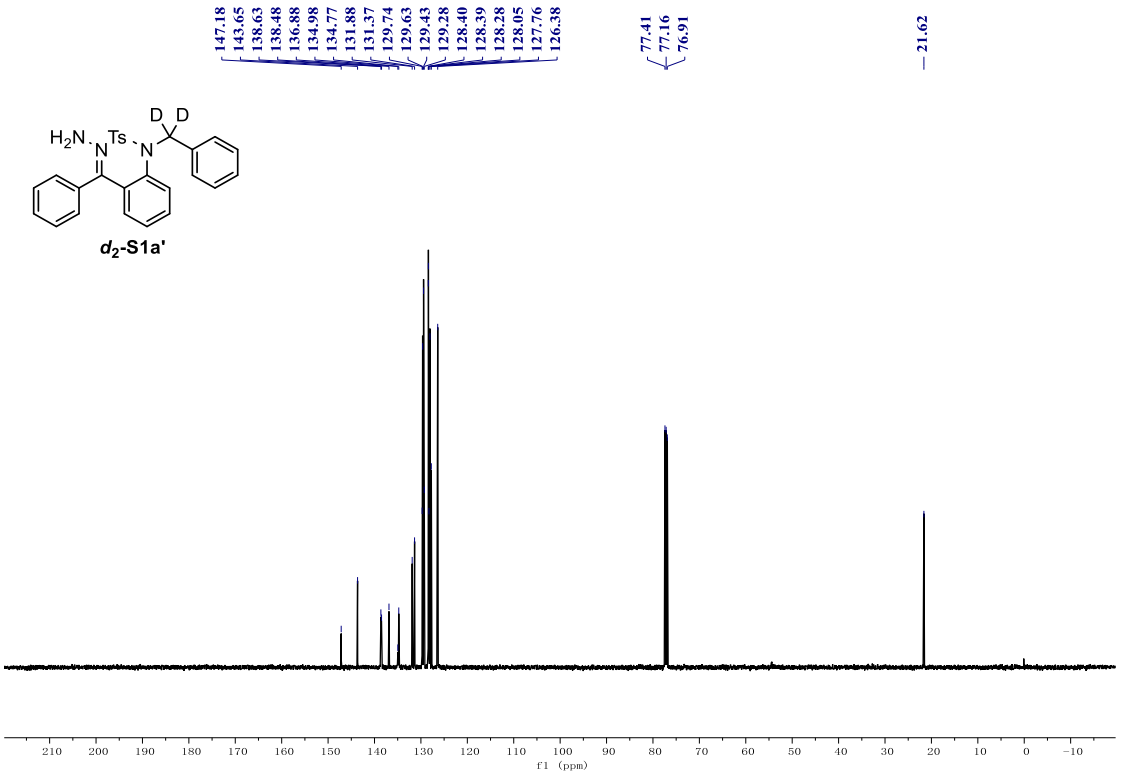

7.60
7.58
7.55
7.53
7.51
7.46
7.44
7.37
7.35
7.33
7.29
7.27
7.27
7.25
7.21
7.20
6.97
6.95
6.93
6.92
6.91
2.20
D D
Ts
O
N
2.00
1.10
2.09
2.16
4.95
3.08
2.09
1.02
3.08
f1 (ppm)

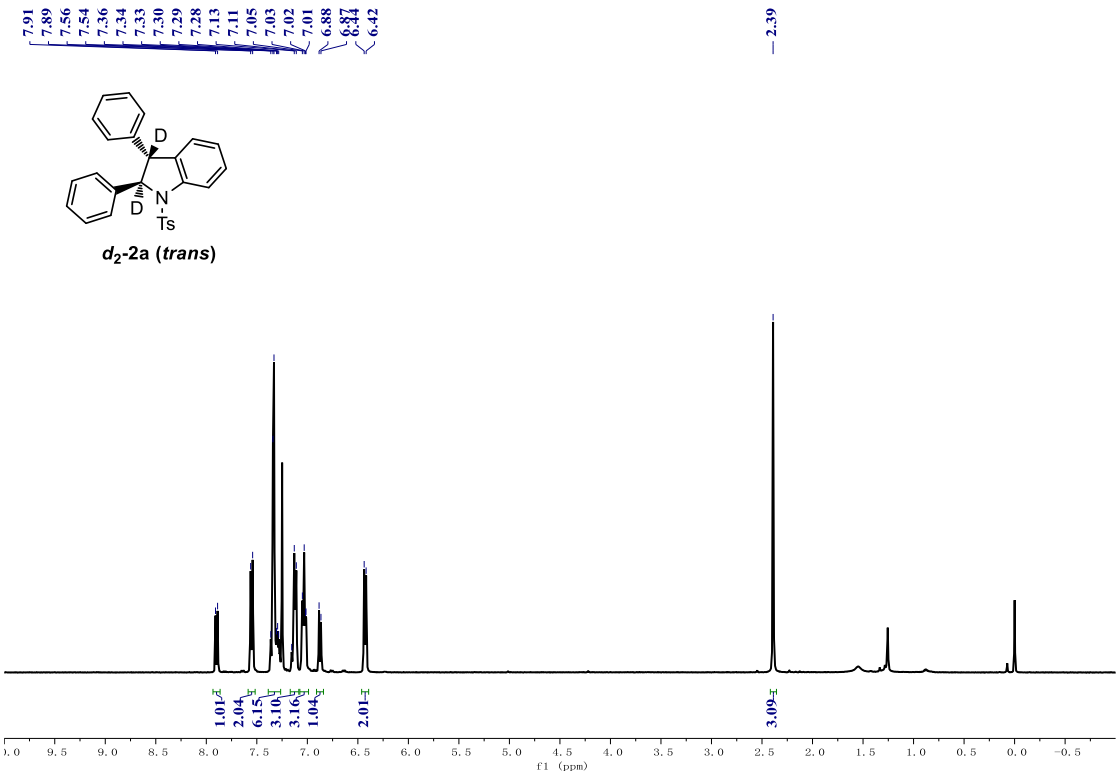
d_2-S1a


195.06
143.23
139.62
136.91
136.82
136.04
133.09
132.97
130.67
130.65
130.20
129.86
129.32
128.30
128.05
127.85
127.44
77.48
77.16
76.84
21.50
D D
Ts
O
N
f1 (ppm)

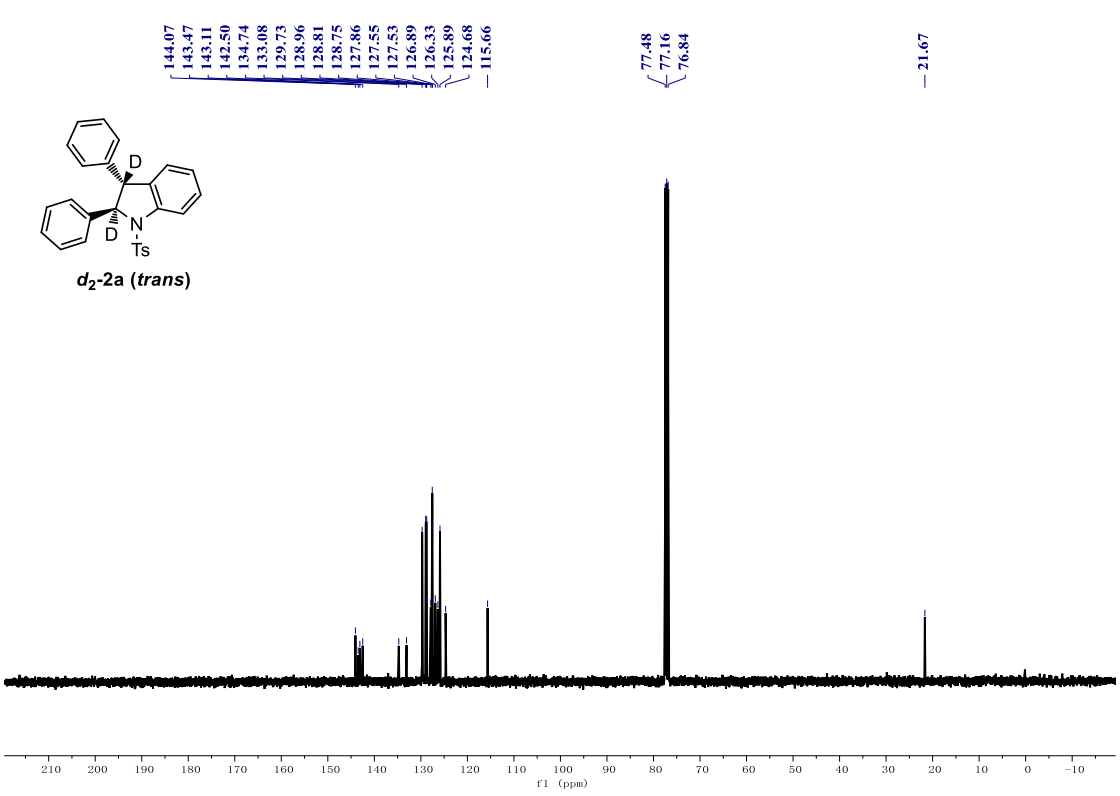
d_2-S1a


7.49
7.47
7.46
7.45
7.43
7.41
7.39
7.36
7.34
7.30
7.28
7.27
7.25
7.15
7.14
7.10
7.09
7.07
7.01
7.00
6.98
6.72
6.71
5.55
2.38
D D
H2N
Ts
N
N
d2-S1a'
4.74
1.05
1.08
2.93
3.95
2.00
1.78
1.79
3.00
f1 (ppm)

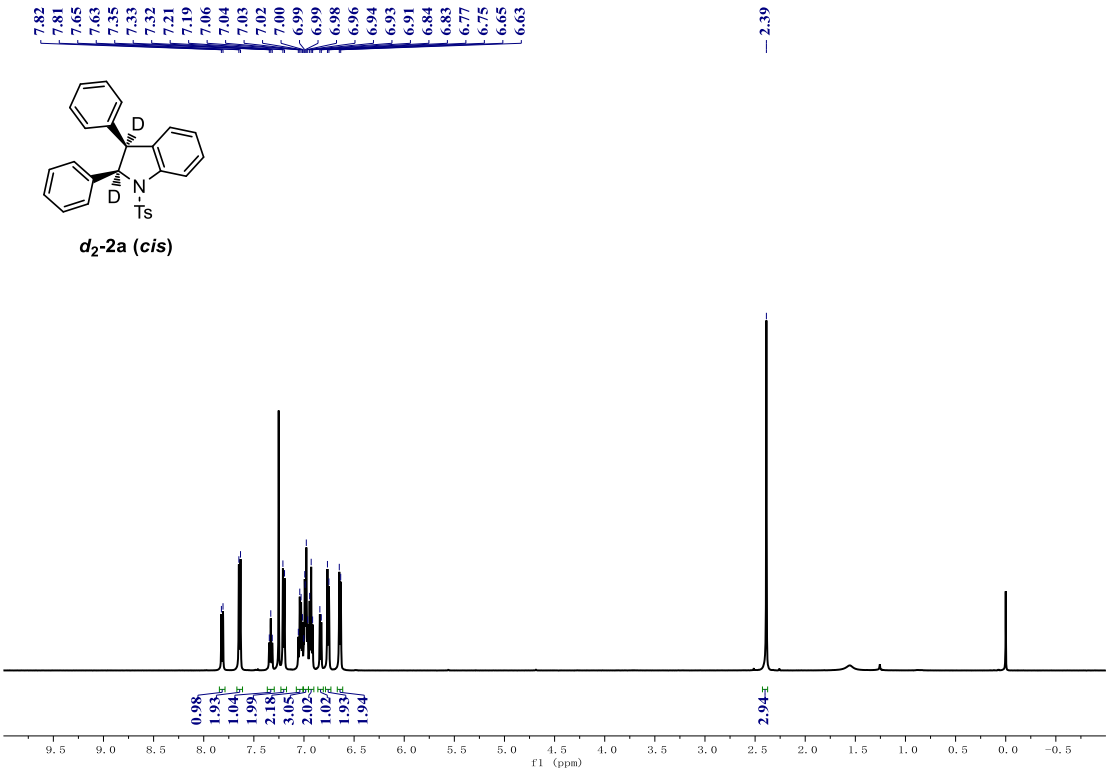

147.18
143.65
138.63
138.48
136.88
134.98
134.77
131.88
131.37
129.74
129.63
129.43
129.28
128.40
128.39
128.28
128.05
127.76
126.38
77.41
77.16
76.91
21.62
D D
H2N
Ts
N
N
d2-S1a'
f1 (ppm)



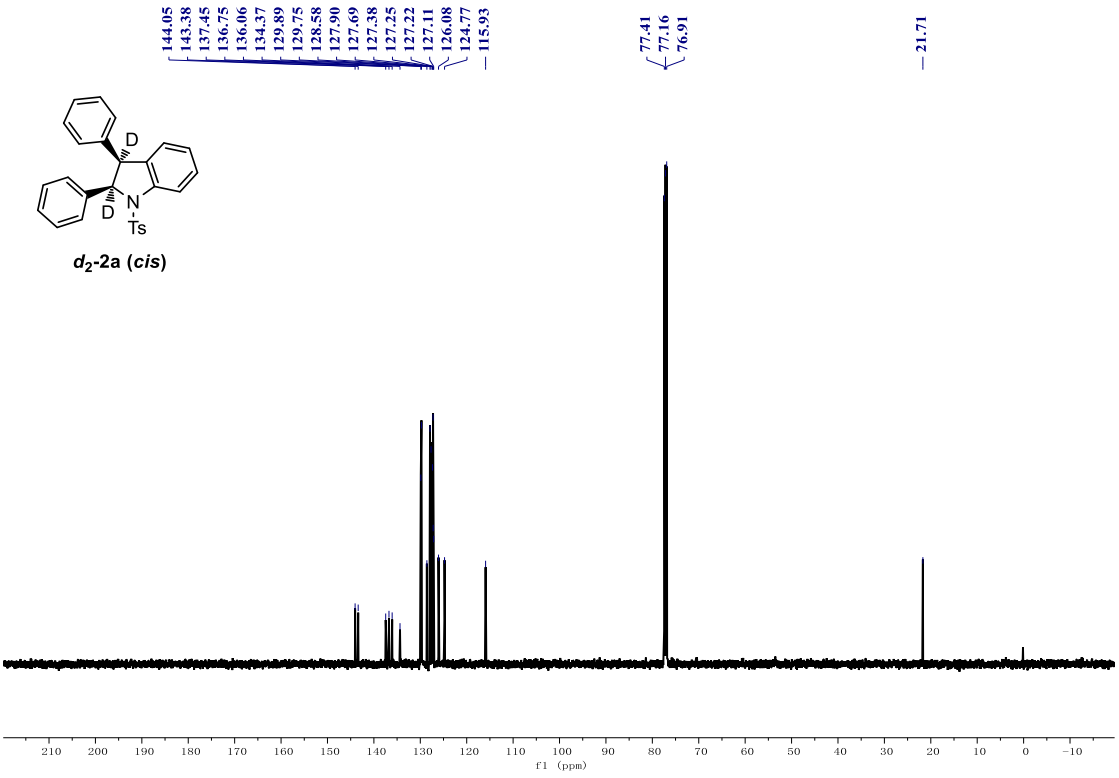
d_2-2a (*trans*)



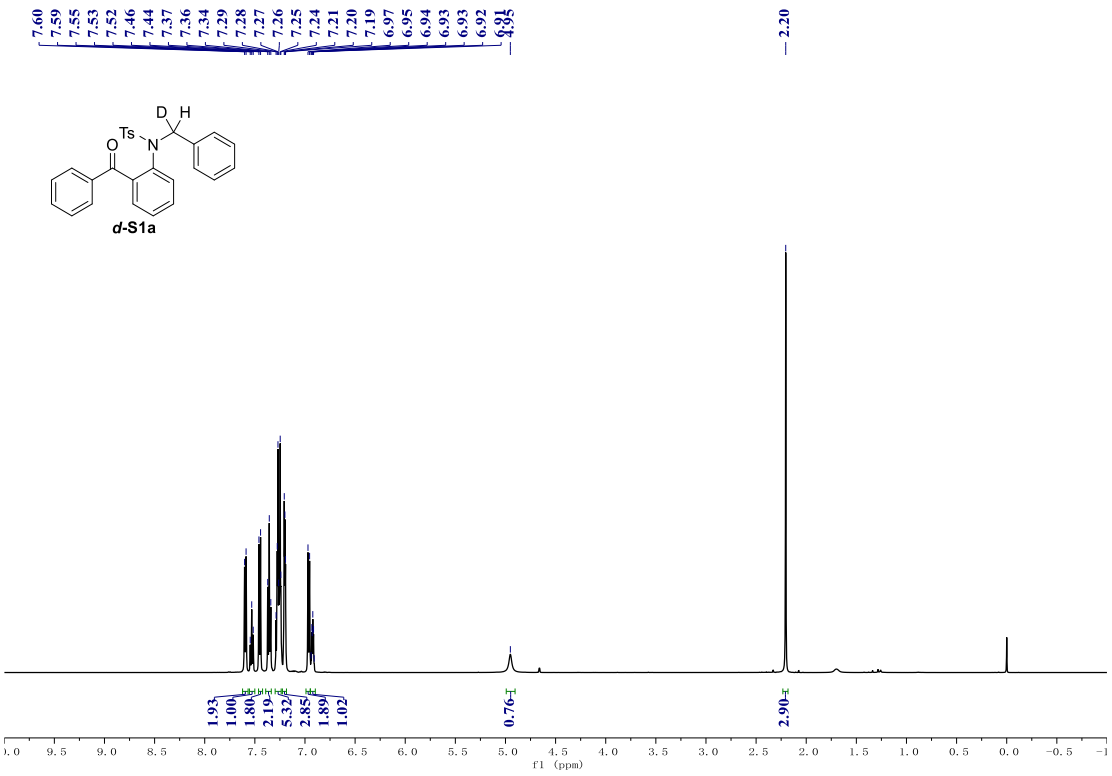
d_2-2a (*trans*)

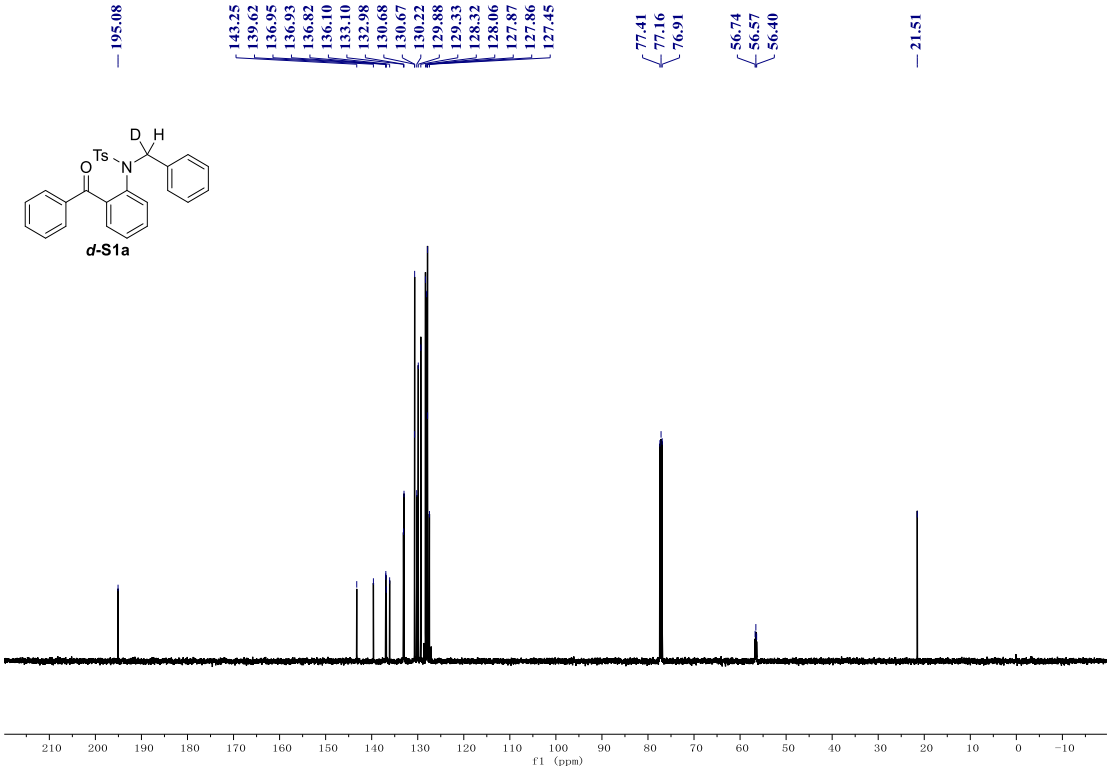


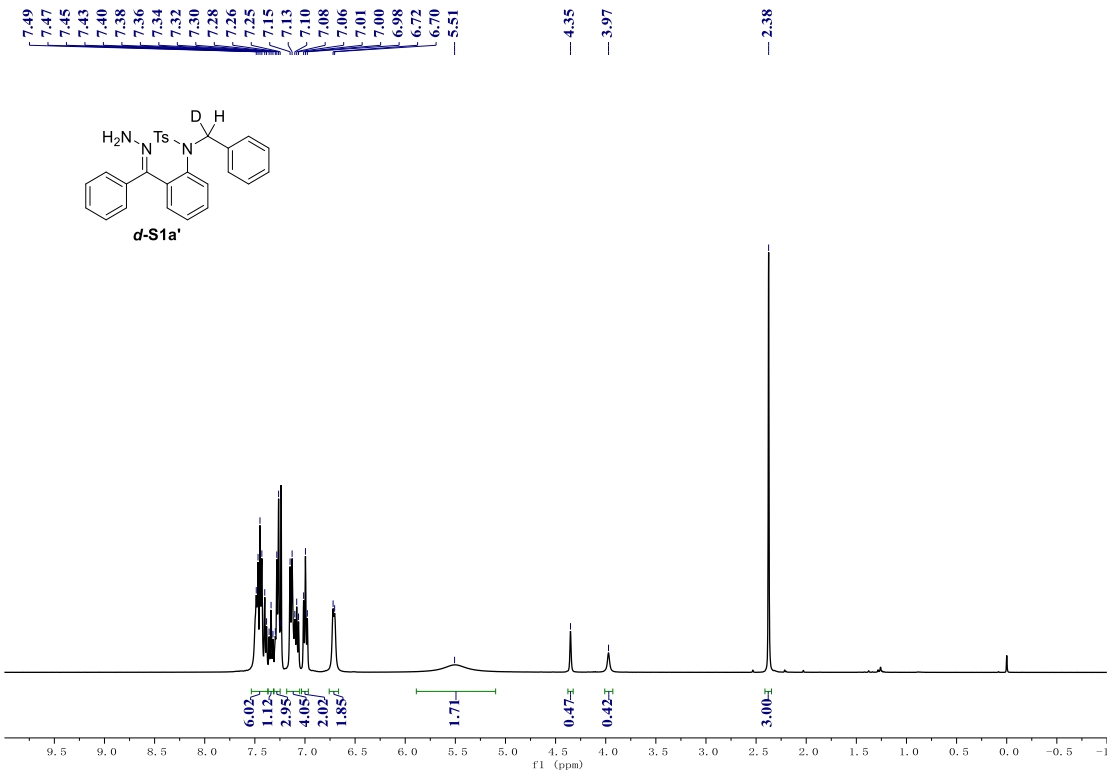
d_2-2a (*cis*)

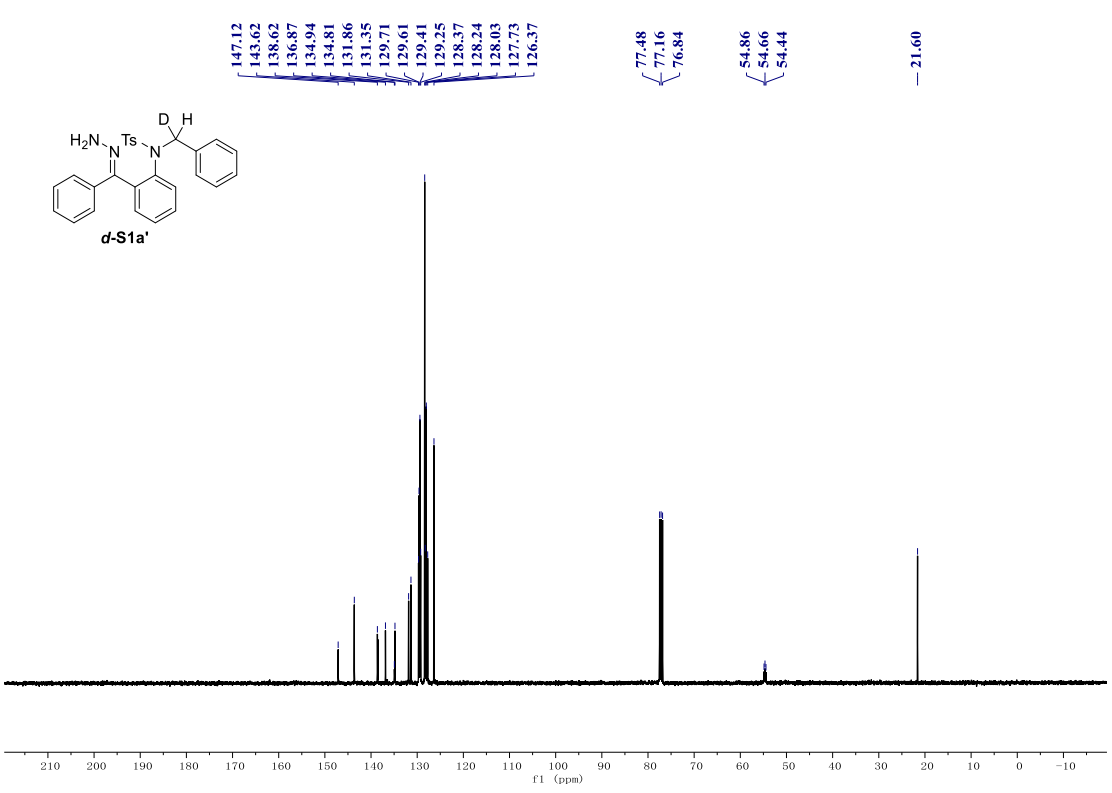


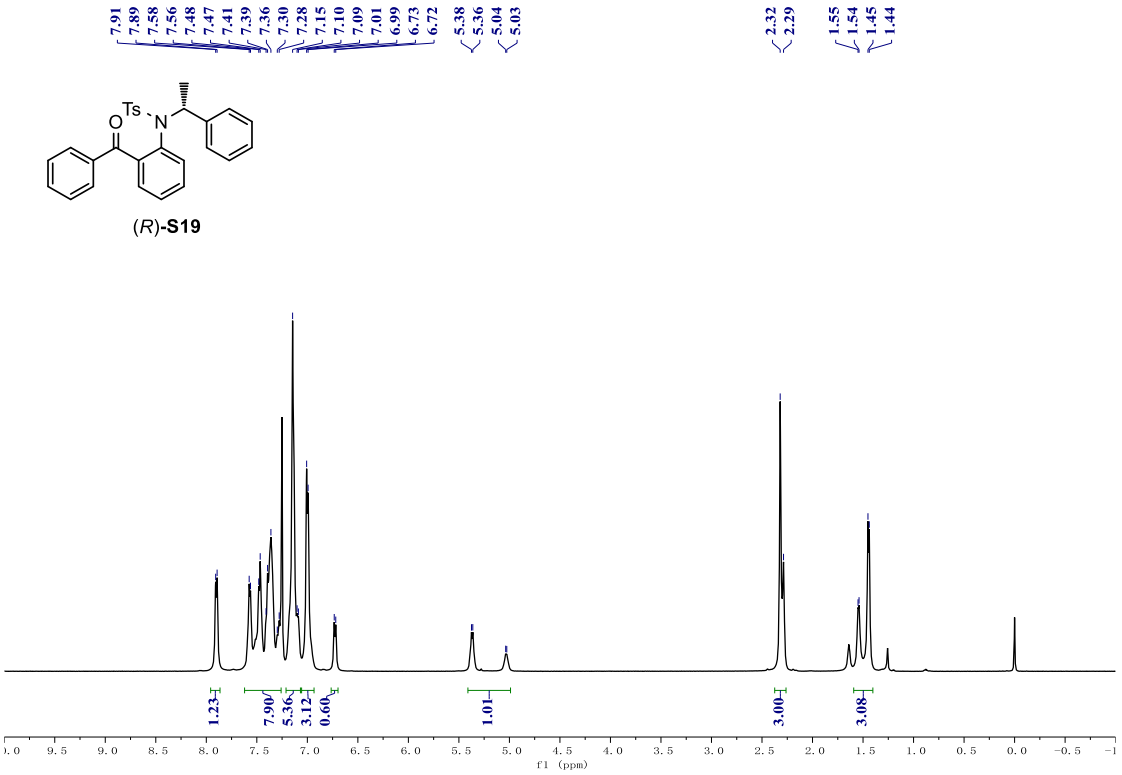
d_2-2a (*cis*)


7.60
7.59
7.55
7.53
7.52
7.46
7.44
7.37
7.36
7.34
7.29
7.28
7.27
7.26
7.25
7.24
7.21
7.20
7.19
6.97
6.95
6.94
6.93
6.93
6.92
6.91
4.95
2.20
D
H
Ts
O
N
d-S1a
1.93
1.00
1.80
2.19
5.32
2.85
1.89
1.02
0.76
2.90
f1 (ppm)

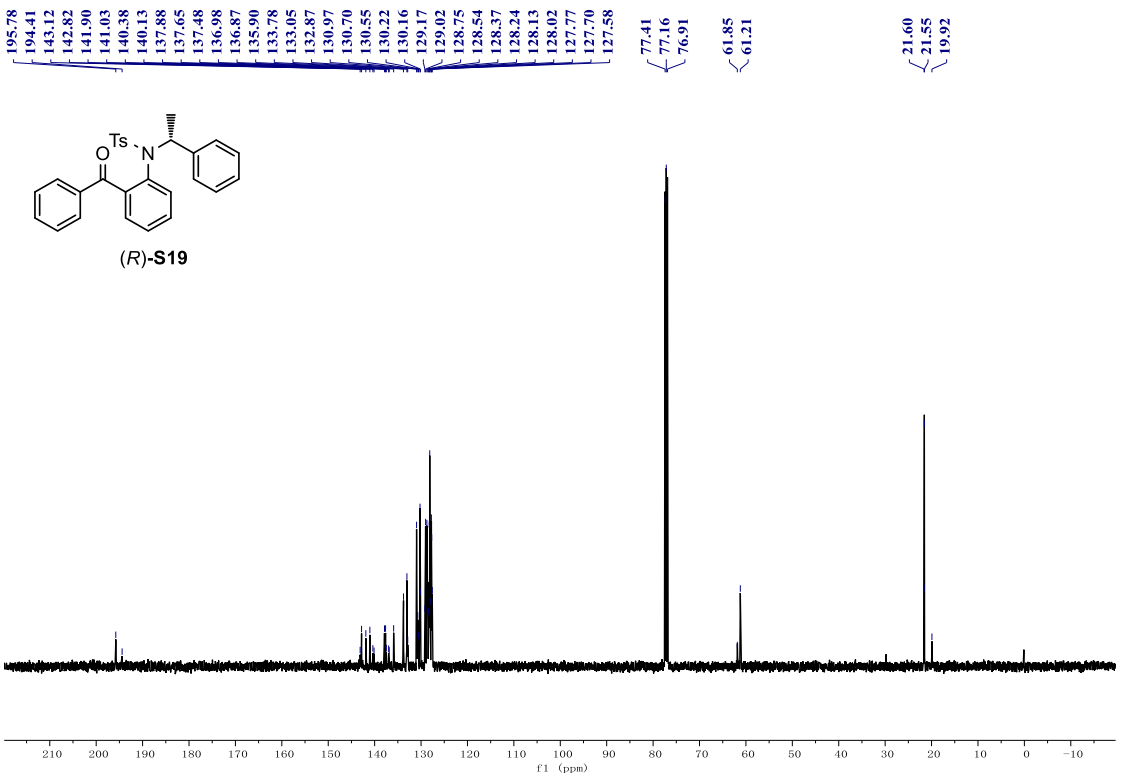

195.08
143.25
139.62
136.95
136.93
136.82
136.10
133.10
132.98
130.68
130.67
130.22
129.88
129.33
128.32
128.06
127.87
127.86
127.45
77.41
77.16
76.91
56.74
56.57
56.40
21.51
D
H
Ts
O
N
d-S1a
f1 (ppm)


7.49
7.47
7.45
7.43
7.40
7.38
7.36
7.34
7.32
7.30
7.28
7.26
7.25
7.15
7.13
7.10
7.08
7.06
7.01
7.00
6.98
6.72
6.70
5.51
4.35
3.97
2.38
D H
H2N
Ts
N
N
d-S1a'
6.02
1.12
2.95
4.05
2.02
1.85
1.71
0.47
0.42
3.00
f1 (ppm)

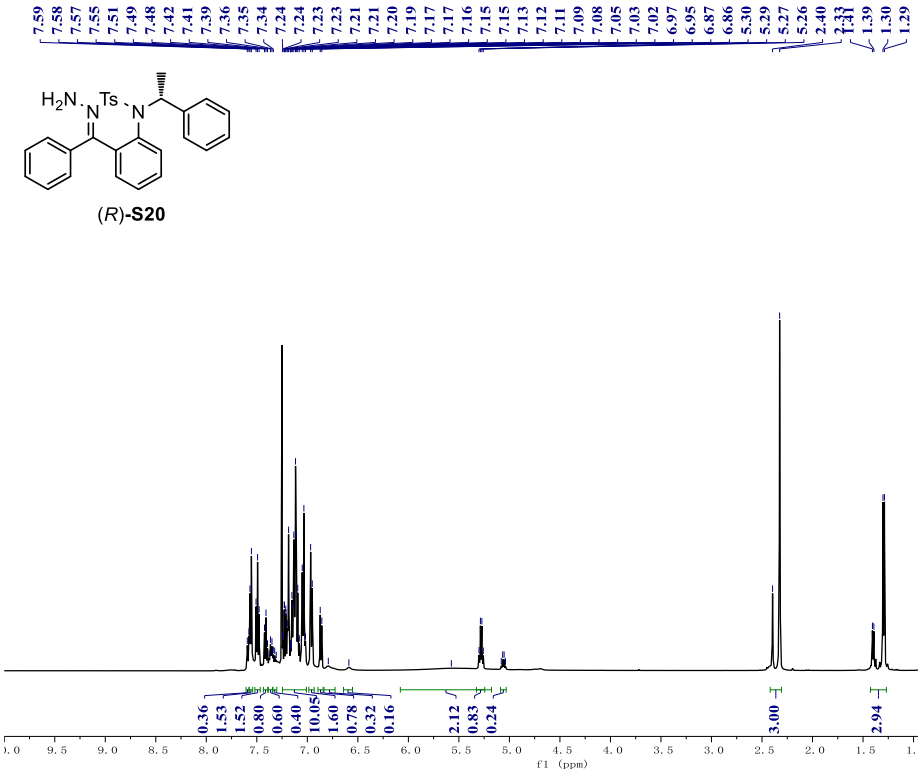

147.12
143.62
138.62
136.87
134.94
134.81
131.86
131.35
129.71
129.61
129.41
129.25
128.37
128.24
128.03
127.73
126.37
77.48
77.16
76.84
54.86
54.66
54.44
21.60
D H
H2N
Ts
N
N
d-S1a'
f1 (ppm)

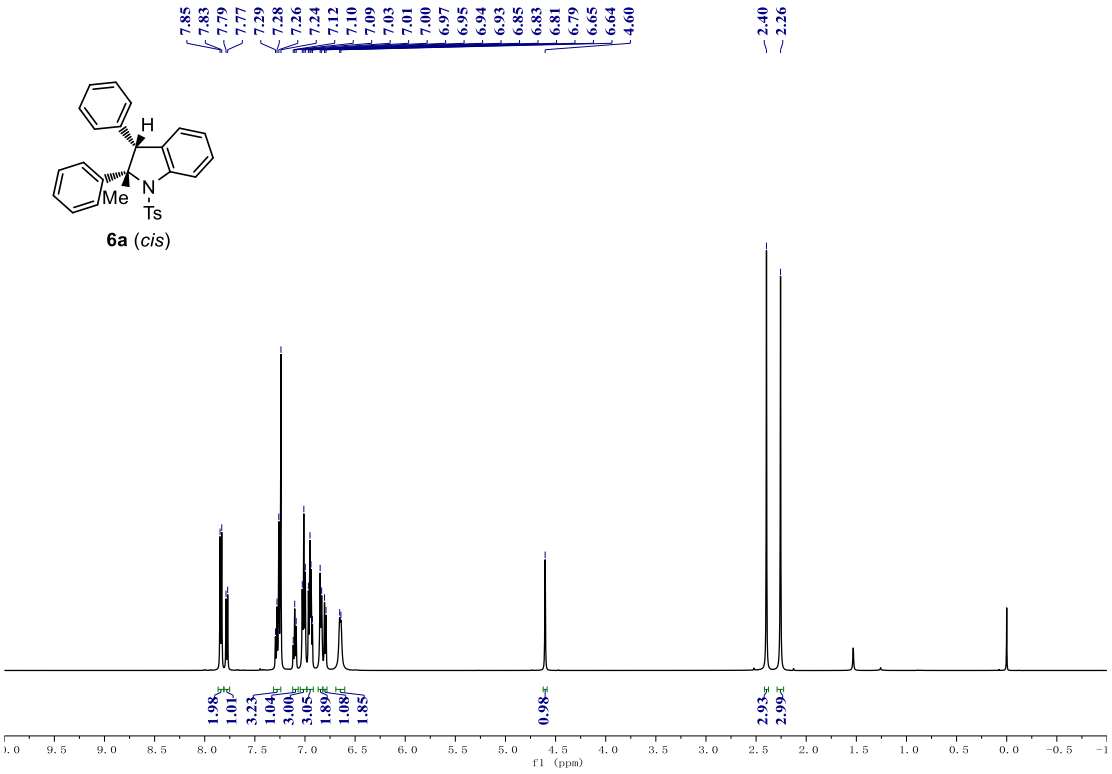

7.91
7.89
7.58
7.56
7.48
7.47
7.41
7.39
7.36
7.30
7.28
7.15
7.10
7.09
7.01
6.99
6.73
6.72
5.38
5.36
5.04
5.03
2.32
2.29
1.55
1.54
1.45
1.44
Ts
O
N
1.23
7.90
5.36
3.12
0.60
1.01
3.00
3.08
f1 (ppm)

(*R*)-**S19**

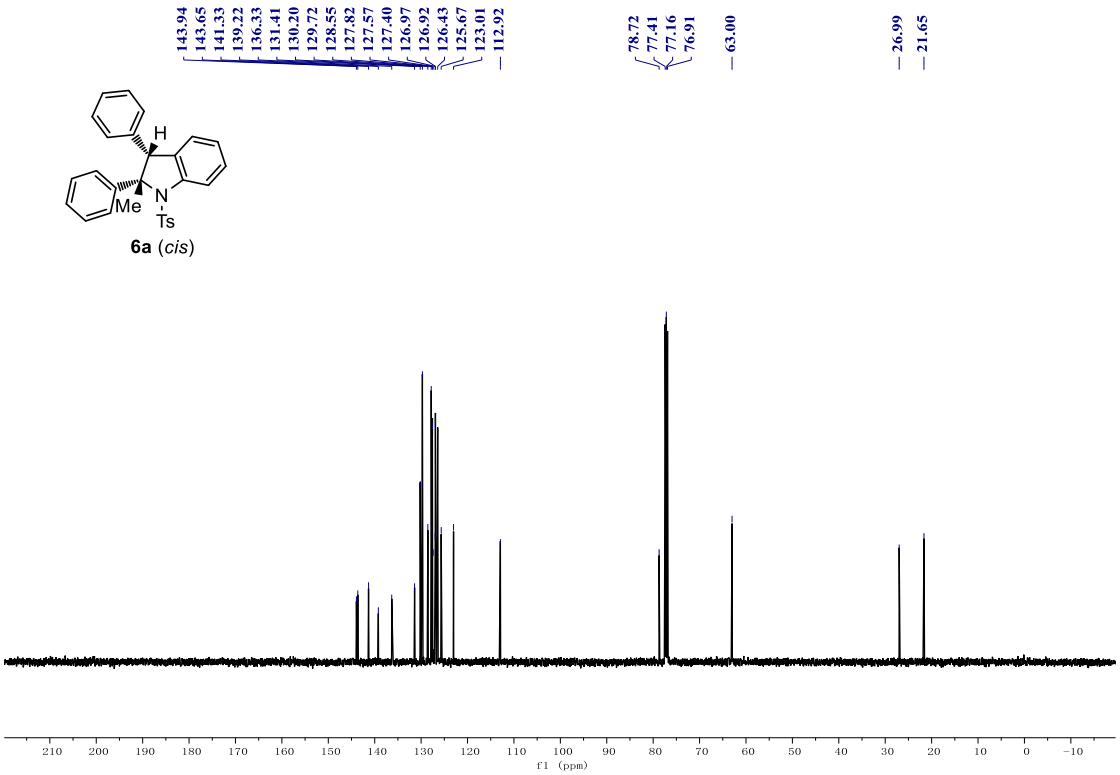

195.78
194.41
143.12
142.82
141.90
141.03
140.38
140.13
137.88
137.65
137.48
136.98
136.87
135.90
133.78
133.05
132.87
130.97
130.70
130.55
130.22
130.16
129.17
129.02
128.75
128.54
128.37
128.24
128.13
128.02
127.77
127.70
127.58
77.41
77.16
76.91
61.85
61.21
21.60
21.55
19.92
Ts
O
N
f1 (ppm)

(*R*)-**S19**

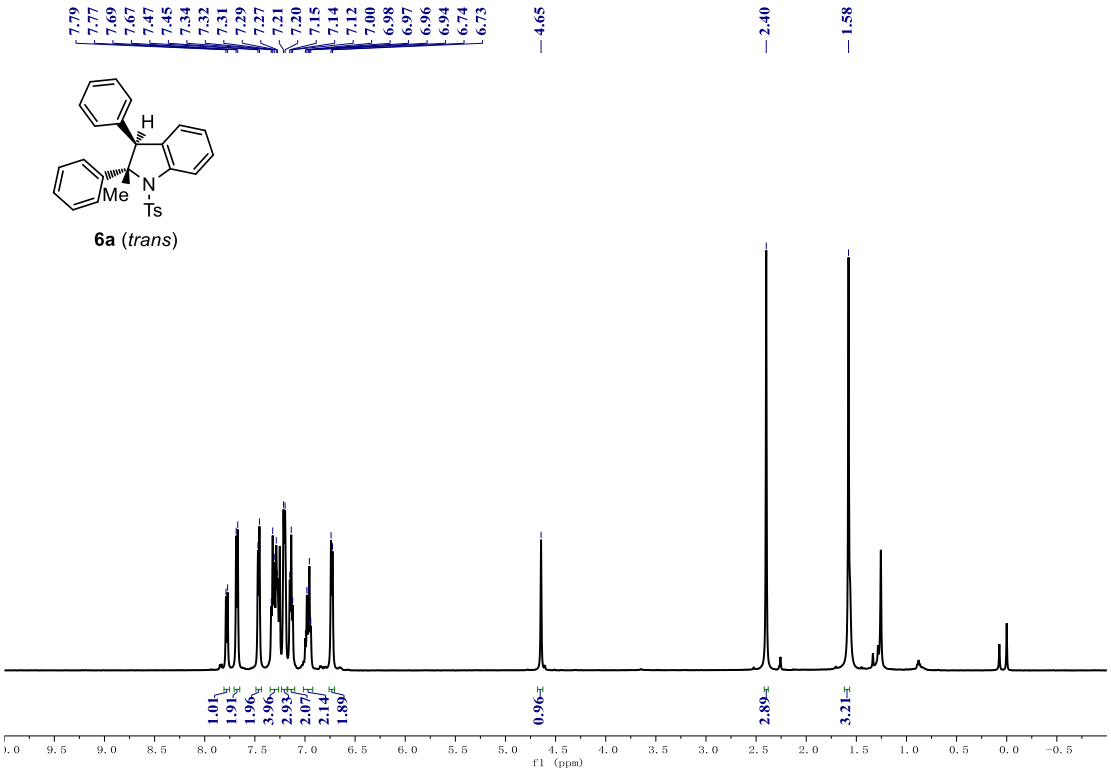

7.59 7.58 7.57 7.55 7.51 7.49 7.48 7.42 7.41 7.39 7.36 7.35 7.34 7.24 7.24 7.23 7.23 7.21 7.21 7.20 7.19 7.17 7.17 7.16 7.15 7.15 7.13 7.12 7.11 7.09 7.08 7.05 7.03 7.02 6.97 6.95 6.87 6.86 5.30 5.29 5.27 5.26 2.40 2.33 1.41 1.39 1.30 1.29
H2N Ts N N
(R)-S20
0.36 1.53 1.52 0.80 0.60 0.40 10.05 1.60 0.78 0.32 0.16 2.12 0.83 0.24 3.00 2.94
f1 (ppm)
147.64 142.84 142.45 142.17 141.98 140.91 139.48 138.97 135.82 133.92 133.36 133.17 132.82 132.09 131.70 129.59 129.21 129.06 128.91 128.82 128.79 128.72 128.54 128.34 128.26 128.19 128.09 127.96 127.74 127.68 127.64 127.52 127.38 77.41 77.16 76.91 61.64 61.43 22.64 21.62 21.51 20.13
H2N Ts N N
(R)-S20
f1 (ppm)


7.85
7.83
7.79
7.77
7.29
7.28
7.26
7.24
7.12
7.10
7.09
7.03
7.01
7.00
6.97
6.95
6.94
6.93
6.85
6.83
6.81
6.79
6.65
6.64
4.60
2.40
2.26
H
Me
N
Ts
1.98
1.01
3.23
1.04
3.00
3.05
1.89
1.08
1.85
0.98
2.93
2.99
f1 (ppm)

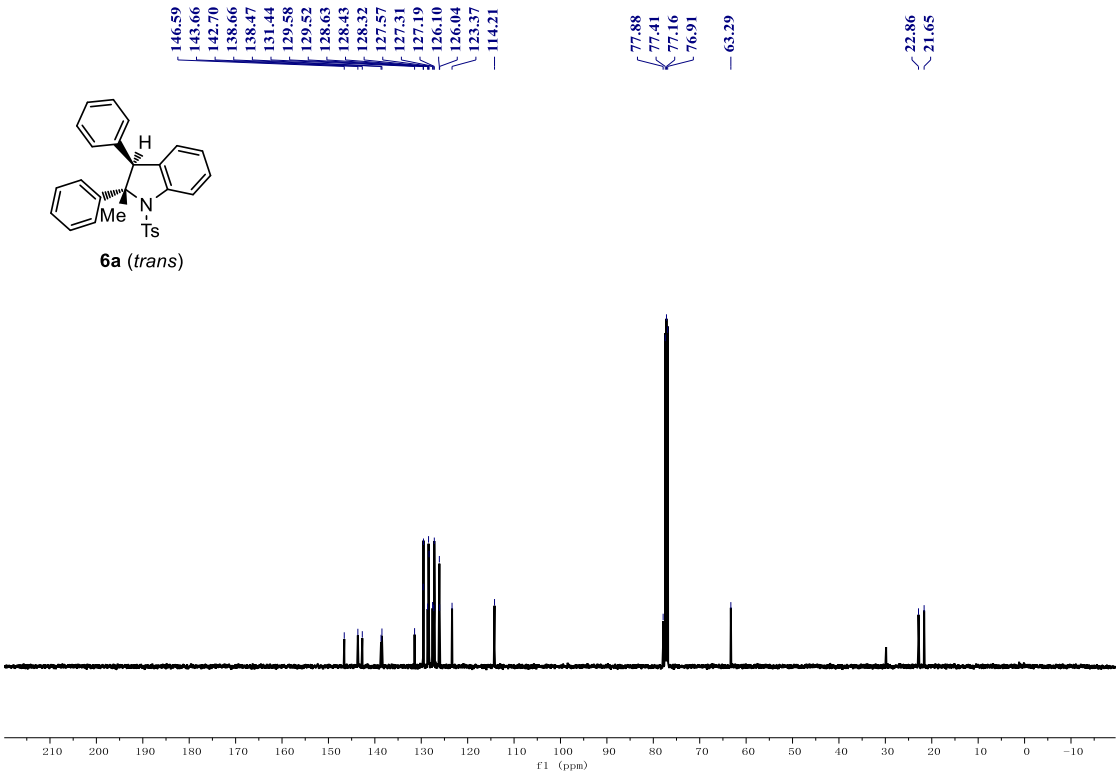
6a (*cis*)


143.94
143.65
141.33
139.22
136.33
131.41
130.20
129.72
128.55
127.82
127.57
127.40
126.97
126.92
126.43
125.67
123.01
112.92
78.72
77.41
77.16
76.91
63.00
26.99
21.65
H
Me
N
Ts
f1 (ppm)

6a (*cis*)



6a (*trans*)



6a (*trans*)