Supporting Information

Palladium/norbornene/copper-catalysed intermolecular thioesterification from ketones: modular access towards tetrasubstituted vinyl sulfides

Guopeng Du, Yu Zhao, Pingliang Zhu, Shaowen Ling, Baolong Xu, Hui Liu, Xinjin Li and Feng-Gang Sun*

School of Chemistry and Chemical Engineering, Shandong University of Technology, 266 West Xincun Road, Zibo 255049

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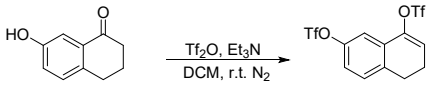
1. General Information

DCM, DMF, DMSO, toluene and CH_3CN solvents were dried from CaH_2 and purified by distillation before being used. Purifications of reactions products were carried out by column chromatography on silica gel (200-300 mesh) using a mixture of petroleum ether (60-90°C), dichloromethane and ethyl acetate as eluent. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) were measured on a Brucker Avance 400 MHz spectrometer. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal ($CDCl_3$ δ = 7.26 for ^1H NMR and δ = 77.0 for ^{13}C NMR). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). Electrospray mass spectra were obtained using Bruker micrOTOF-Q II 10410 Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

2. Preparation and Characterization Data of Alkenyl Triflates

General Procedure 1

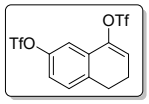


1s, 80%

A mixture of ketone (1.0 equiv, 20 mmol), Et_3N (3.0 equiv, 60 mmol) in anhydrous DCM (15 mL) dropwise for 10 minutes at room temperature into a mixture of Tf_2O (4.0 equiv, 80 mmol) in anhydrous DCM (15 mL) under N_2, the mixture was stirred at room temperature for 24 h. The mixture solution was diluted with DCM and washed with aqueous solution of $NaHCO_3$, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford the product **1s** (6816.0 mg, 80% yield).

Synthesis methods for other alkenyl triflates (**1t-1A**) have been reported.[1,2]

3,4-dihydronaphthalene-1,7-diyl bis(trifluoromethanesulfonate) (1s)



Compound **1s** was prepared from 7-hydroxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate and Tf_2O according to general procedure 1. The resultant residue was purified by column chromatography on silica gel (PE) to afford **1s** as colorless oil (6816.0 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.0 Hz, 1H), 7.24 - 7.15 (m, 2H), 6.18 (t, *J* = 6.0 Hz, 1H), 2.91 (t, *J* = 10.0 Hz, 2H), 2.56 (q, *J* = 8.0 Hz, 2H);

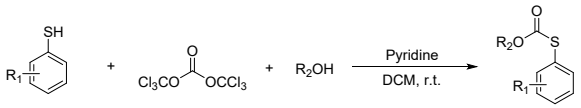
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 144.4, 136.4, 130.7, 129.5, 123.5 (q, *J* = 318.7 Hz), 123.3 (q, *J* = 318.7 Hz), 121.7, 120.4, 114.3, 26.1, 22.1;

^{19}F NMR (376 MHz, $CDCl_3$): δ -72.79 (s, 3F), -72.63 (s, 3F);

HRMS (ESI) calcd for $C_{12}H_9F_6O_6S_2$ $[M+H]^+$ 426.9739, found 426.9736.

3. Preparation and Characterization Data of Thiocarbonate

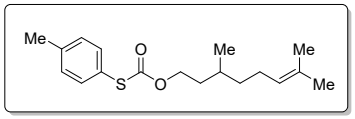
General Procedure 2



A stirred solution of thiophenol (5.0 mmol), alcohol (5.0 mmol), and pyridine (20.0 mmol) in dry CH_2Cl_2 (25 mL) at room temperature, triphosgene (5.0 mmol) was added to the solution stirring at room temperature for 4 h. After completion of the reaction, the mixture was washed two times with aqueous HCl (1 M), the combine organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford corresponding thiocarbonate (**2j**-**2l)**.

Synthesis methods for other thiocarbonates **(2a**-**2i, 2m**-**2u)** have been reported.[3,4]

***O*-(3,7-dimethyloct-6-en-1-yl) *S*-(*p*-tolyl) carbonothioate (2j)**



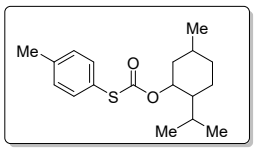
Compound **2j** was prepared from 4-methylbenzenethiol and 3,7-dimethyloct-6-en-1-ol according to general procedure 2. The resultant residue was purified by column chromatography on silica gel (PE) to afford **2j** as colorless oil (1378.2 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 - 7.16 (m, 5H), 5.08 (t, *J* = 8.0 Hz, 1H), 4.25 (t, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.06 – 1.90 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.55 – 1.25 (m, 4H), 1.20 – 1.12 (m, 1H), 0.90 (d, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 135.1, 134.8, 131.3, 129.9, 124.4, 123.6, 66.4, 36.8, 35.3, 29.2, 25.7, 25.3, 21.2, 19.3, 17.6;

HRMS (ESI) calcd for $C_{18}H_{27}O_2S$ $[M+H]^+$ 307.1726, found 307.1725.

***O*-(2-isopropyl-5-methylcyclohexyl) *S*-(*p*-tolyl) carbonothioate (2k)**



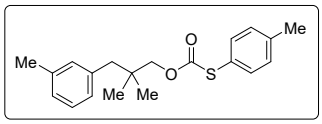
Compound **2k** was prepared from 4-methylbenzenethiol and 2-isopropyl-5-methylcyclohexan-1-ol according to general procedure 2. The resultant residue was purified by column chromatography on silica gel (PE) to afford **2k** as colorless oil (1254.8 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.82 – 4.70 (m, 1H), 2.36 (s, 3H), 2.14 – 2.04 (m, 1H), 1.99 – 1.85 (m, 1H), 1.70 – 1.60 (m, 2H), 1.50 – 1.35 (m, 2H), 1.07 (q, *J* = 12.0 Hz, 2H), 0.94 – 0.84 (m, 7H), 0.78 (d, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 139.6, 134.8, 129.8, 124.5, 78.7, 47.0, 40.8, 34.0, 31.4, 26.2, 23.4, 21.9, 21.3, 20.6, 16.3;

HRMS (ESI) calcd for $C_{18}H_{27}O_2S$ $[M+H]^+$ 307.1726, found 307.1723.

***O*-(2,2-dimethyl-3-(*m*-tolyl)propyl) *S*-(*p*-tolyl) carbonothioate (2l)**



Compound **2l** was prepared from 4-methylbenzenethiol and 2,2-dimethyl-3-(*m*-tolyl)propan-1-ol according to general procedure 2. The resultant residue was purified by column chromatography on silica gel (PE) to afford **2l** as colorless oil (1394.6 mg, 85% yield).

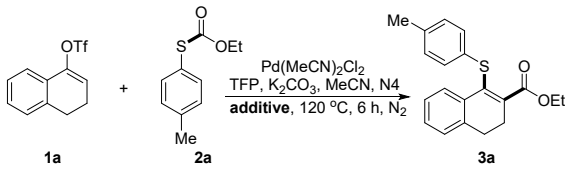
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 12.0 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 4.0 Hz, 1H), 6.87 (s, 1H), 3.88 (s, 2H), 2.46 (s, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 0.88 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 140.4, 139.9, 137.3, 135.0, 131.2, 129.9, 127.7, 126.8, 124.3, 123.6, 74.7, 44.5, 35.2, 24.1, 21.4, 21.3;

HRMS (ESI) calcd for $C_{20}H_{25}O_2S$ $[M+H]^+$ 329.1570, found 329.1573.

4. Optimization of Reaction Conditions

Table 1. Screening of Additive[a]



1a + **2a** → **3a**

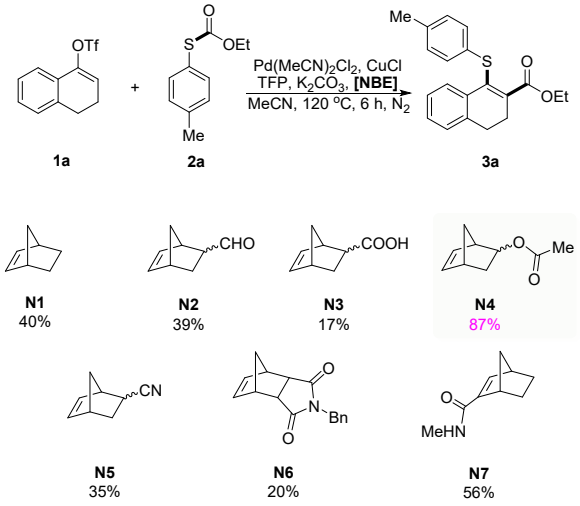
Entry	additive (20 mol%)	Yield(%)
1	-	42
2	CuCl	68
3	CuI	64
4	CuTC	52
5	Cu_2O	54
6	$MgCl_2$	35
7	$ZnCl_2$	40
8	$FeCl_2$	27
9	$CoCl_2$	25
10	$CuCl_2$	35

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), $Pd(MeCN)_2Cl_2$ (0.02 mmol, 10 mol%), TFP (0.05 mmol, 25 mol%), N4 (0.6 mmol, 3.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), additive (0.04 mmol, 20 mol%), MeCN (2.0 mL), 120 °C, 6 h, N_2. Isolated yields.

Entry	The usage of CuCl	Yield(%)
1	0.04 mmol (20 mol%)	68
2	0.08 mmol (40 mol%)	73
3	0.12 mmol (60 mol%)	87
4	0.16 mmol (80 mol%)	70
5	0.20 mmol (100 mol%)	64

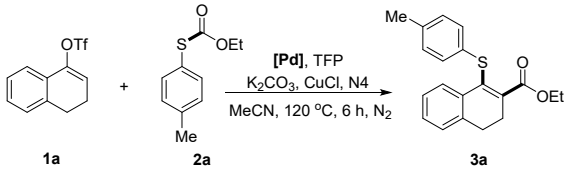
[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), $Pd(MeCN)_2Cl_2$ (0.02 mmol, 10 mol%), TFP (0.05 mmol, 25 mol%), N4 (0.6 mmol, 3.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), additive, MeCN (2.0 mL), 120 °C, 6 h, N_2. Isolated yields.

Table 2. Screening of [NBE][a]



[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), $Pd(MeCN)_2Cl_2$ (0.02 mmol, 10 mol%), TFP (0.05 mmol, 25 mol%), [NBE] (0.6 mmol, 3.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), CuCl (0.12 mmol, 60 mol%), MeCN (2.0 mL), 120 °C, 6 h, N_2. Isolated yields.

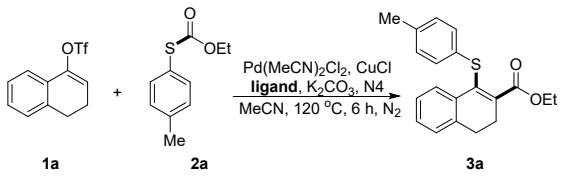
Table 3. Screening of [Pd][a]



Entry	[Pd]	Yield(%)
1	$Pd(OAc)_2$	20
2	$Pd(TFA)_2$	75
3	$PdBr_2$	66
4	$PdCl_2$	78
5	$Pd(MeCN)_2Cl_2$	87
6	$PdCl_2$(dppf)	26
7	$Pd(PCy_3)_2Cl_2$	14
8	$Pd(PPh_3)_2Cl_2$	15
9[b]	$Pd_2(dba)_3$	19

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), [Pd] (0.02 mmol, 10 mol%), TFP (0.05 mmol, 25 mol%), N4 (0.6 mmol, 3.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), CuCl (0.12 mmol, 60 mol%), MeCN (2.0 mL), 120 °C, 6 h, N_2. Isolated yields. [b] 5 mol % [Pd] was used.

Table 4. Screening of Ligand[a]



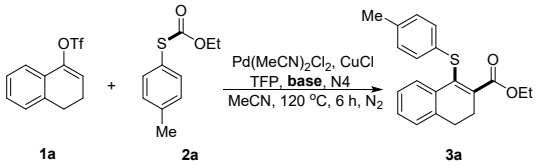
1a **2a** **3a**

Entry	Monophosphine ligand	Yield(%)
1	TFP	87
2	PPh_3	25
3	PCy_3	5
4	(*p*-Cl-Ph)$_3$P	46
5	(*p*-F-Ph)$_3$P	40
6	(*p*-OMe-Ph)$_3$P	30
7	(2,4-Me-Ph)$_3$P	11
8	RuPhos	12

Entry	Bisphosphine ligand	Yield(%)
1	dppm	5
2	dppe	38
3	dppp	40
4	dppb	40
5	dppf	20
6	XantPhos	5
7	DavePhos	6

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), $Pd(MeCN)_2Cl_2$ (0.02 mmol, 10 mol%), ligand (monophosphine ligand**,** 0.05 mmol, 25 mol%. bisphosphine ligand**,** 0.026 mmol, 13 mol%), N4 (0.6 mmol, 3.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), CuCl (0.12 mmol, 60 mol%), MeCN (2.0 mL), 120 ℃, 6 h, N_2. Isolated yields.

Table 5. Screening of Base[a]

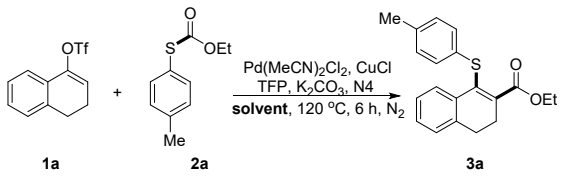


1a **2a** **3a**

Entry	base	Yield(%)
1	K_2CO_3	87
2	Cs_2CO_3	10
3	K_3PO_4	18
4	Na_2CO_3	5
5	Ag_2CO_3	8
6	KOAc	7
7	NaOAc	5

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), $Pd(MeCN)_2Cl_2$ (0.02 mmol, 10 mol%), TFP (0.05 mmol, 25 mol%), N4 (0.6 mmol, 3.0 equiv), base (0.4 mmol, 2.0 equiv), CuCl (0.12 mmol, 60 mol%), MeCN (2.0 mL), 120 ℃, 6 h, N_2. Isolated yields.

Table 6. Screening of Solvent[a]

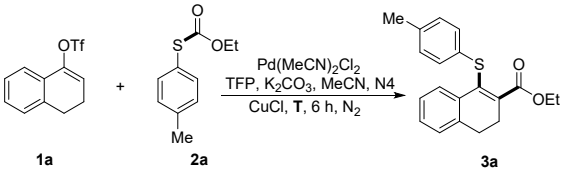


1a 2a 3a

Entry	solvent	Yield(%)
1	toluene	15
2	dioxane	37
3	MeCN	87
4	DMF	56
5	DMSO	45

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), $Pd(MeCN)_2Cl_2$ (0.02 mmol, 10 mol%), TFP (0.05 mmol, 25 mol%), N4 (0.6 mmol, 3.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), CuCl (0.12 mmol, 60 mol%), solvent (2.0 mL), 120 °C, 6 h, N_2. Isolated yields.

Table 7. Screening of Temperature[a]



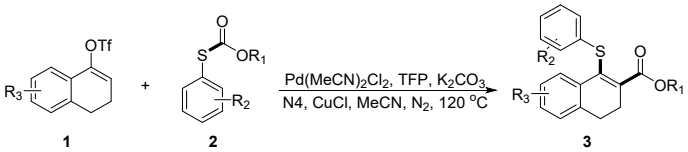
1a 2a 3a

Entry	T (°C)	Yield(%)
1	100 °C	20
2	110 °C	41
3	120 °C	87
4	130 °C	62

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), $Pd(MeCN)_2Cl_2$ (0.02 mmol, 10 mol%), TFP (0.05 mmol, 25 mol%), N4 (0.6 mmol, 3.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), CuCl (0.12 mmol, 60 mol%), MeCN (2.0 mL), T, 6 h, N_2. Isolated yields.

5. Synthesis and Characterization of Compound 3

General Procedure 3

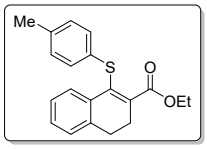


1 2 3

A Schlenk-tube equipped with a magnetic stir bar was charged with $Pd(MeCN)_2Cl_2$ (10 mol%, 0.02 mmol), TFP (25 mol%, 0.05 mmol), K_2CO_3 (2.0 equiv, 0.4 mmol), CuCl (60 mol%, 0.12 mmol) and then evacuated and backfilled with N_2 for 3 times. Afterwards, alkenyl triflates **1** (1.0 equiv, 0.2 mmol), thiocarbonate **2** (1.5 equiv, 0.3 mmol), N4 (3.0 equiv, 0.6 mmol) and MeCN (2 mL) were added

consecutively under N_2 atmosphere. The tight tube was stirred and heated at 120 °C in the oil bath for 6 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the product **3**.

ethyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3a)



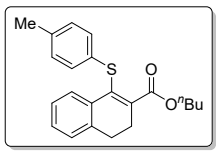
Compound **3a** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3a** as colorless oil (56.4 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.09 – 7.03 (m, 4H), 7.02 – 6.96 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 4.21 (q, *J* = 6.7 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.62 (t, *J* = 6.0 Hz, 2H), 2.15 (s, 3H), 1.23 (t, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 138.4, 136.7, 135.7, 133.5, 132.5, 132.4, 129.6, 128.6, 128.4, 127.4, 127.2, 126.6, 61.1, 27.6, 26.4, 20.9, 14.1;

HRMS (ESI) calcd for $C_{20}H_{21}O_2S$ $[M+H]^+$ 325.1257, found 325.1256.

butyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3b)



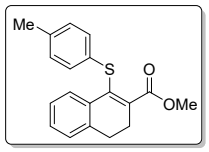
Compound **3b** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-butyl *S*-(*p*-tolyl) carbonothioate **2b** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3b** as colorless oil (54.2 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.10 (m, 4H), 7.09 – 7.04 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.22 (t, *J* = 6.0 Hz, 2H), 2.90 (t, *J* = 6.0 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.22 (s, 3H), 1.70 – 1.60 (m, 2H), 1.44 – 1.35 (m, 2H), 0.90 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 138.5, 136.7, 135.7, 133.3, 132.5, 132.4, 129.6, 128.5, 128.4, 127.4, 127.2, 126.6, 65.1, 30.5, 27.6, 26.5, 20.9, 19.2, 13.7;

HRMS (ESI) calcd for $C_{22}H_{25}O_2S$ $[M+H]^+$ 353.1570, found 353.1573.

methyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3c)



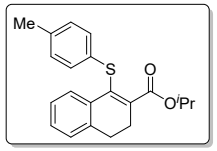
Compound **3c** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-methyl *S*-(*p*-tolyl) carbonothioate **2c** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3c** as colorless oil (52.7 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.09 (m, 4H), 7.08 - 7.03 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 2.88 (t, *J* = 8.0 Hz, 2H), 2.69 (t, *J* = 6.0 Hz, 2H), 2.22 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 137.6, 136.8, 135.8, 134.3, 132.4, 132.2, 129.6, 128.7, 128.5, 127.5, 127.2, 126.6, 52.0, 27.6, 26.4, 20.9;

HRMS (ESI) calcd for $C_{19}H_{19}O_2S$ $[M+H]^+$ 311.1100, found 311.1101.

isopropyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3d)



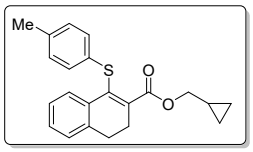
Compound **3d** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-isopropyl *S*-(*p*-tolyl) carbonothioate **2d** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3d** as yellow oil (47.3 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.10 – 6.98 (m, 5H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.14 – 5.03 (m, 1H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.15 (s, 3H), 1.22 (d, *J* = 4.0 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 139.2, 136.2, 135.6, 132.6, 132.4, 129.6, 128.5, 128.3, 127.2, 126.6, 68.9, 27.6, 26.4, 21.8, 20.9;

HRMS (ESI) calcd for $C_{21}H_{23}O_2S$ $[M+H]^+$ 339.1413, found 339.1417.

cyclopropylmethyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3e)



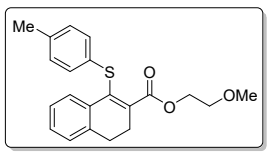
Compound **3e** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-(cyclopropylmethyl) *S*-(*p*-tolyl) carbonothioate **2e** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3e** as colorless oil (45.5 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.10 – 7.04 (m, 4H), 7.02 – 6.95 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.98 (d, *J* = 8.0 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.15 (s, 3H), 1.14 – 1.04 (m, 1H), 0.47 (q, *J* = 5.3 Hz, 2H), 0.22 (q, *J* = 5.3 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 138.5, 136.7, 135.7, 133.3, 132.5, 132.4, 129.6, 128.7, 128.4, 127.4, 127.2, 126.6, 70.0, 27.6, 26.5, 20.9, 9.7, 3.4;

HRMS (ESI) calcd for $C_{22}H_{23}O_2S$ $[M+H]^+$ 351.1413, found 351.1415.

2-methoxyethyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3f)



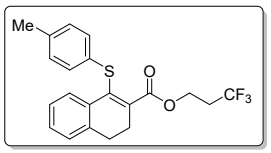
Compound **3f** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-(2-methoxyethyl) *S*-(*p*-tolyl) carbonothioate **2f** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3f** as colorless oil (56.5 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.10 (m, 4H), 7.09 - 7.03 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.37 (t, *J* = 4.0 Hz, 2H), 3.62 (t, *J* = 4.0 Hz, 2H), 3.34 (s, 3H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.22 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 137.9, 136.8, 135.7, 134.1, 132.4, 132.3, 129.6, 128.7, 128.5, 127.5, 127.2, 126.6, 70.3, 64.0, 58.9, 27.6, 26.4, 20.9;

HRMS (ESI) calcd for $C_{21}H_{23}O_3S$ $[M+H]^+$ 355.1362, found 355.1358.

3,3,3-trifluoropropyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3g)



Compound **3g** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *S*-(*p*-tolyl) *O*-(3,3,3-trifluoropropyl) carbonothioate **2g** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 3 : 1) to afford **3g** as yellow oil (54.9 mg, 70% yield).

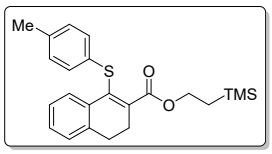
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.09 – 6.98 (m, 5H), 6.90 (d, *J* = 8.0 Hz, 2H), 4.35 (t, *J* = 6.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.48 – 2.38 (m, 2H), 2.16 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 136.9, 136.6, 136.0, 135.5, 132.3, 132.1, 130.3 (q, *J* = 290.6 Hz), 129.7, 128.7, 126.7, 127.7, 127.3, 126.7, 57.7 (q, *J* = 3.0 Hz), 33.7 (q, *J* = 29.0 Hz), 27.6, 26.2, 20.9;

^{19}F NMR (376 MHz, $CDCl_3$): δ -64.91 (t, *J* = 9.4 Hz, 3F);

HRMS (ESI) calcd for $C_{21}H_{20}F_3O_2S$ $[M+H]^+$ 393.1131, found 393.1132.

2-(trimethylsilyl)ethyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3h)



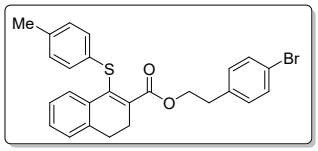
Compound **3h** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *S*-(*p*-tolyl) *O*-(2-(trimethylsilyl)ethyl) carbonothioate **2h** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3h** as colorless oil (27.0 mg, 34% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.11 (m, 4H), 7.10 - 7.06 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.30 (t, *J* = 8.0 Hz, 2H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.23 (s, 3H), 1.05 (t, *J* = 8.0 Hz, 2H), 0.04 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 138.4, 136.8, 135.7, 135.1, 133.4, 132.6, 132.4, 129.6, 128.7, 128.3, 127.4, 126.6, 63.5, 27.7, 26.4, 20.9, 17.3, -1.5;

HRMS (ESI) calcd for $C_{23}H_{29}O_2SSi$ $[M+H]^+$ 397.1652, found 397.1650.

4-bromophenethyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3i)



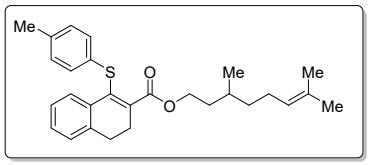
Compound **3i** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-(4-bromophenethyl) *S*-(*p*-tolyl) carbonothioate **2i** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3i** as colorless oil (75.5 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.28 - 7.23 (m, 2H), 7.03 – 6.96 (m, 6H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.33 (t, *J* = 6.0 Hz, 2H), 2.88 – 2.79 (m, 4H), 2.54 (t, *J* = 8.0 Hz, 2H), 2.14 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 137.8, 136.8, 136.7, 135.7, 133.8, 132.3, 131.6, 131.4, 130.6, 130.6, 129.6, 128.5, 127.5, 127.2, 126.6, 120.3, 65.0, 34.3, 27.6, 26.4, 20.9;

HRMS (ESI) calcd for $C_{26}H_{24}BrO_2S$ $[M+H]^+$ 479.0675, found 479.0677.

3,7-dimethyloct-6-en-1-yl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3j)



Compound **3j** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-(3,7-dimethyloct-6-en-1-yl) *S*-(*p*-tolyl) carbonothioate **2j** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3j** as colorless oil (62.5 mg, 72% yield).

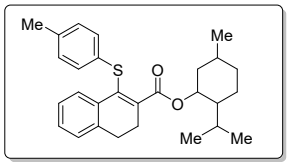
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.04 (m, 5H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.07 (t, *J* = 8.0 Hz, 1H), 4.25 (t, *J* = 8.0 Hz, 2H), 2.90 (t, *J* = 6.0 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.22 (s, 3H), 1.94 (q, *J* = 8.0 Hz, 2H), 1.68 (s, 3H), 1.62 – 1.54 (m, 5H), 1.51 – 1.13 (m, 1H), 1.34 (q, *J* = 8.0 Hz, 2H), 0.89 (d, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 138.5, 136.7, 135.7, 133.2, 132.5, 132.4, 131.2, 129.6, 128.5, 128.4, 127.4, 127.3, 126.6, 124.6, 63.7, 36.9, 35.3, 29.4, 27.6, 26.5, 25.7,

25.4, 20.9, 19.3, 17.6;

HRMS (ESI) calcd for $C_{28}H_{35}O_2S$ $[M+H]^+$ 435.2352, found 435.2355.

2-isopropyl-5-methylcyclohexyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3k)



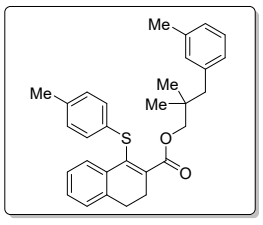
Compound **3k** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-(2-isopropyl-5-methylcyclohexyl) *S*-(*p*-tolyl) carbonothioate **2k** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3k** as colorless oil (66.0 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.05 (m, 5H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.87 – 4.78 (m, 1H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.22 (s, 3H), 2.13 – 2.05 (m, 1H), 1.96 – 1.90 (m, 1H), 1.71 – 1.63 (m, 2H), 1.52 – 1.47 (m, 1H), 1.43 – 1.36 (m, 2H), 1.10 – 1.01 (m, 2H), 0.90 (d, *J* = 8.0 Hz, 3H), 0.81 (d, *J* = 4.0 Hz, 3H), 0.75 (d, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 139.9, 136.4, 135.5, 132.5, 132.5, 131.3, 129.5, 128.3, 128.2, 127.3, 127.1, 126.7, 75.3, 46.9, 40.6, 34.2, 31.4, 27.6, 26.6, 26.0, 23.2, 22.0, 20.9, 20.7, 16.1;

HRMS (ESI) calcd for $C_{28}H_{35}O_2S$ $[M+H]^+$ 435.2352, found 435.2350.

2,2-dimethyl-3-(*m*-tolyl)propyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3l)



Compound **3l** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-(2,2-dimethyl-3-(*m*-tolyl)propyl) *S*-(*p*-tolyl) carbonothioate **2l** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3l** as colorless oil (73.9 mg, 81% yield).

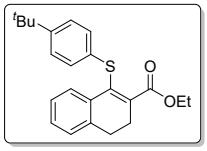
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.11 (m, 6H), 7.02 –

6.92 (m, 5H), 3.93 (s, 1H), 3.85 (s, 1H), 2.92 (t, *J* = 8.0 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 2.20 (s, 2H), 0.96 (s, 3H), 0.92 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 138.6, 138.0, 137.3, 136.7, 135.6, 133.2, 132.4, 131.3, 129.6, 128.4, 127.7, 127.6, 127.5, 127.5, 127.3, 126.8, 126.7, 126.6, 75.0, 44.8, 35.1, 27.7, 26.7, 24.3, 24.1, 21.4, 20.9;

HRMS (ESI) calcd for $C_{30}H_{33}O_2S$ $[M+H]^+$ 457.2196, found 457.2204.

ethyl 1-((4-(*tert*-butyl)phenyl)thio)-3,4-dihydronaphthalene-2-carboxylate (3m)



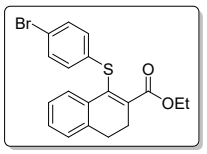
Compound **3m** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *S*-(4-(*tert*-butyl)phenyl) *O*-ethyl carbonothioate **2m** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3m** as colorless oil (62.9 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.13 (m, 4H), 7.11 - 7.06 (m, 1H), 4.26 (q, *J* = 6.7 Hz, 2H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.28 (t, *J* = 8.0 Hz, 3H), 1.23 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 148.9, 138.8, 136.6, 132.8, 132.7, 132.4, 128.4, 128.0, 127.3, 127.3, 126.7, 125.9, 61.1, 34.3, 31.2, 27.6, 26.5, 14.1;

HRMS (ESI) calcd for $C_{23}H_{27}O_2S$ $[M+H]^+$ 367.1726, found 367.1729.

ethyl 1-((4-bromophenyl)thio)-3,4-dihydronaphthalene-2-carboxylate (3n)



Compound **3n** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *S*-(4-bromophenyl) *O*-ethyl carbonothioate **2n** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 3 : 1) to afford **3n** as colorless oil (64.4 mg, 83% yield).

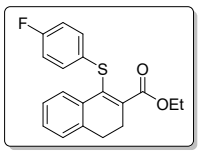
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 - 7.04 (m, 2H), 7.03 – 6.97 (m, 3H), 4.20 (q, *J* = 8.0 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H),

2.63 (t, *J* = 8.0 Hz, 2H), 1.22 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 139.6, 136.7, 135.4, 132.2, 132.1, 131.8, 129.7, 128.7, 127.4, 127.2, 126.8, 119.6, 61.2, 27.5, 26.5, 14.1;

HRMS (ESI) calcd for $C_{19}H_{18}BrO_2S$ $[M+H]^+$ 389.0205, found 389.0200.

ethyl 1-((4-fluorophenyl)thio)-3,4-dihydronaphthalene-2-carboxylate (3o)



Compound **3o** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-ethyl *S*-(4-fluorophenyl) carbonothioate **2o** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 2 : 1) to afford **3o** as colorless oil (50.5 mg, 77% yield).

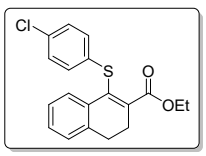
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.12 (m, 4H), 7.10 - 7.05 (m, 1H), 6.87 (t, *J* = 8.0 Hz, 2H), 4.29 (q, *J* = 6.7 Hz, 2H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.31 (t, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 162.6 (d, *J* = 245.0 Hz), 138.6, 136.8, 133.4, 132.1, 131.0 (d, *J* = 3.0 Hz), 130.5 (d, *J* = 8.0 Hz), 128.6, 127.4, 127.3, 126.6, 116.0 (d, *J* = 22.0 Hz), 61.2, 27.6, 26.4, 14.1;

^{19}F NMR (376 MHz, $CDCl_3$): δ -116.05 (s, 1F);

HRMS (ESI) calcd for $C_{19}H_{18}FO_2S$ $[M+H]^+$ 329.1006, found 329.1005.

ethyl 1-((4-chlorophenyl)thio)-3,4-dihydronaphthalene-2-carboxylate (3p)



Compound **3p** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *S*-(4-chlorophenyl) *O*-ethyl carbonothioate **2p** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 3 : 1) to afford **3p** as colorless oil (55.7 mg, 81% yield).

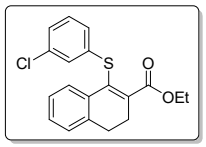
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.18 – 7.06 (m, 7H), 4.27 (q, *J* = 6.7 Hz, 2H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.70 (t, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 8.0 Hz,

3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 139.4, 136.7, 134.7, 132.4, 132.0, 131.6, 129.5, 128.9, 128.6, 127.4, 127.1, 126.7, 61.2, 27.5, 26.4, 14.1;

HRMS (ESI) calcd for $C_{19}H_{18}ClO_2S$ $[M+H]^+$ 345.0711, found 345.0714.

ethyl 1-((3-chlorophenyl)thio)-3,4-dihydronaphthalene-2-carboxylate (3q)



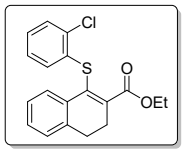
Compound **3q** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *S*-(3-chlorophenyl) *O*-ethyl carbonothioate **2q** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 3 : 1) to afford **3q** as colorless oil (57.8 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 7.19 – 7.01 (m, 6H), 4.27 (q, *J* = 8.0 Hz, 2H), 2.92 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 140.3, 136.6, 135.6, 132.2, 131.9, 131.8, 129.4, 128.9, 128.8, 127.4, 127.0, 126.9, 126.4, 61.2, 27.5, 26.6, 14.0;

HRMS (ESI) calcd for $C_{19}H_{18}ClO_2S$ $[M+H]^+$ 345.0711, found 345.0711.

ethyl 1-((2-chlorophenyl)thio)-3,4-dihydronaphthalene-2-carboxylate (3r)



Compound **3r** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *S*-(2-chlorophenyl) *O*-ethyl carbonothioate **2r** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 3 : 1) to afford **3r** as colorless oil (52.3 mg, 76% yield).

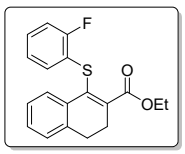
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 4.0 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.02 – 6.97 (m, 3H), 4.26 (q, *J* = 8.0 Hz, 2H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.74 (t, *J* = 6.0 Hz, 2H), 1.26 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 140.3, 136.6, 135.6, 132.2, 131.9, 131.8, 129.4,

128.9, 128.8, 127.4, 127.0, 126.9, 126.4, 61.2, 27.5, 26.6, 14.0;

HRMS (ESI) calcd for $C_{19}H_{18}ClO_2S$ $[M+H]^+$ 345.0711, found 345.0714.

ethyl 1-((2-fluorophenyl)thio)-3,4-dihydronaphthalene-2-carboxylate (3s)



Compound **3s** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-ethyl *S*-(2-fluorophenyl) carbonothioate **2s** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 2 : 1) to afford **3s** as colorless oil (47.3 mg, 72% yield).

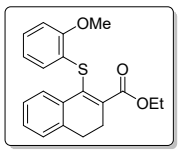
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 12.0 Hz, 1H), 7.09 – 6.97 (m, 5H), 6.92 – 6.81 (m, 2H), 4.21 (q, *J* = 8.0 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 1.23 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 161.2 (d, *J* = 244.0 Hz), 138.6, 136.8, 133.0, 132.9, 132.3, 130.7 (d, *J* = 2.0 Hz), 128.6, 127.7 (d, *J* = 8.0 Hz), 127.3, 127.1, 126.6, 124.4 (d, *J* = 4.0 Hz), 123.4 (d, *J* = 7.0 Hz), 115.5 (d, *J* = 22.0 Hz), 61.2, 27.6, 26.4, 14.1;

^{19}F NMR (376 MHz, $CDCl_3$): δ -111.28 (s, 1F);

HRMS (ESI) calcd for $C_{19}H_{18}FO_2S$ $[M+H]^+$ 329.1006, found 329.1003.

ethyl 1-((2-methoxyphenyl)thio)-3,4-dihydronaphthalene-2-carboxylate (3t)



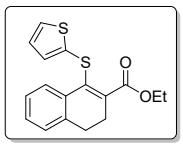
Compound **3t** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-ethyl *S*-(2-methoxyphenyl) carbonothioate **2t** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 2 : 1) to afford **3t** as colorless oil (48.3 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.01 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.81 – 6.68 (m, 2H), 4.25 (q, *J* = 6.7 Hz, 2H), 3.85 (s, 3H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.70 (t, *J* = 8.0 Hz, 2H), 1.26 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 156.1, 138.5, 136.6, 133.2, 132.6, 128.9, 128.4, 127.1, 127.1, 126.7, 126.5, 124.5, 121.0, 110.4, 61.0, 55.7, 27.7, 26.5, 14.0;

HRMS (ESI) calcd for $C_{20}H_{21}O_3S$ $[M+H]^+$ 341.1206, found 341.1207.

ethyl 1-(thiophen-2-ylthio)-3,4-dihydronaphthalene-2-carboxylate (3u)



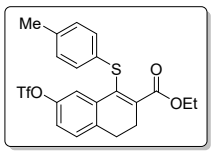
Compound **3u** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1a** and *O*-ethyl *S*-(thiophen-2-yl) carbonothioate **2u** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 3 : 1) to afford **3u** as yellow oil (51.2 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (t, *J* = 4.0 Hz, 1H), 7.12 – 7.00 (m, 5H), 6.76 (t, *J* = 4.0 Hz, 1H), 4.27 (q, *J* = 8.0 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.56 (t, *J* = 8.0 Hz, 2H), 1.31 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 137.0, 136.7, 135.7, 134.1, 132.3, 131.9, 128.5, 128.5, 127.3, 127.2, 127.1, 126.4, 61.2, 27.5, 26.4, 14.2;

HRMS (ESI) calcd for $C_{17}H_{17}O_2S_2$ $[M+H]^+$ 317.0664, found 317.0666.

ethyl 1-(*p*-tolylthio)-7-(((trifluoromethyl)sulfonyl)oxy)-3,4-dihydronaphthalene-2-carboxylate (3v)



Compound **3v** was prepared from 3,4-dihydronaphthalene-1,7-diyl bis(trifluoromethanesulfonate) **1v** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 3 : 1) to afford **3v** as yellow oil (76.5 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.13 – 7.04 (m, 3H), 7.00 – 6.89 (m, 3H), 4.23 (q, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.63 (t, *J* = 8.0 Hz, 2H), 2.16 (s, 3H), 1.25 (t, *J* = 8.0 Hz, 3H);

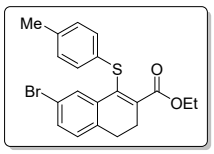
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 148.4, 140.3, 136.8, 136.6, 135.1, 132.0, 130.8,

129.8, 129.2, 128.8, 123.3 (q, J = 302.0 Hz), 120.8, 120.0, 61.4, 27.0, 26.2, 20.9, 14.1;

^{19}F NMR (376 MHz, $CDCl_3$): δ -72.91 (s, 3F);

HRMS (ESI) calcd for $C_{21}H_{20}F_3O_5S_2$ $[M+H]^+$ 473.0699, found 473.0697.

ethyl 7-bromo-1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3w)



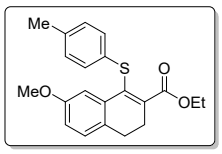
Compound **3w** was prepared from 7-bromo-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1w** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 3 : 1) to afford **3w** as yellow oil (68.4 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.02 – 6.96 (m, 3H), 4.28 (q, J = 6.7 Hz, 2H), 2.82 (t, J = 8.0 Hz, 2H), 2.67 (t, J = 8.0 Hz, 2H), 2.24 (s, 3H), 1.31 (t, J = 6.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 139.5, 136.3, 135.5, 134.6, 132.5, 131.5, 131.1, 130.2, 129.7, 129.1, 128.8, 120.3, 61.3, 27.1, 26.3, 21.0, 14.1;

HRMS (ESI) calcd for $C_{20}H_{20}BrO_2S$ $[M+H]^+$ 403.0362, found 403.0359.

ethyl 7-methoxy-1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3x)



Compound **3x** was prepared from 7-methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1x** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 2 : 1) to afford **3x** as colorless oil (51.7 mg, 73% yield).

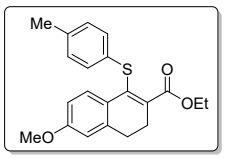
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 1H), 7.12 – 7.05 (m, 2H), 6.97 – 6.88 (m, 3H), 6.61 (d, J = 8.0 Hz, 1H), 4.21 (q, J = 8.0 Hz, 2H), 3.55 (s, 3H), 2.75 (t, J = 6.0 Hz, 2H), 2.60 (t, J = 6.0 Hz, 2H), 2.16 (s, 3H), 1.24 (t, J = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 158.2, 138.6, 135.9, 133.7, 133.5, 132.3, 129.6,

128.9, 128.0, 114.4, 112.8, 61.2, 55.2, 26.8, 26.7, 21.0, 14.1;

HRMS (ESI) calcd for $C_{21}H_{23}O_3S$ $[M+H]^+$ 355.1362, found 355.1364.

ethyl 6-methoxy-1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3y)



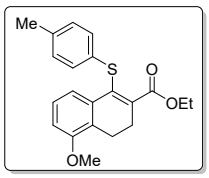
Compound **3y** was prepared from 6-methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1y** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 2 : 1) to afford **3y** as colorless oil (54.7 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.59 (s, 1H), 6.51 (d, *J* = 12.0 Hz, 1H), 4.19 (q, *J* = 6.7 Hz, 2H), 3.68 (s, 3H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.16 (s, 3H), 1.23 (t, *J* = 6.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 159.6, 138.8, 135.6, 135.3, 134.0, 132.7, 129.6, 129.2, 128.6, 125.6, 113.3, 111.3, 61.0, 55.2, 28.2, 26.4, 20.9, 14.2;

HRMS (ESI) calcd for $C_{21}H_{23}O_3S$ $[M+H]^+$ 355.1362, found 355.1361.

ethyl 5-methoxy-1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (3z)



Compound **3z** was prepared from 5-methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **1z** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 2 : 1) to afford **3z** as colorless oil (53.2 mg, 75% yield).

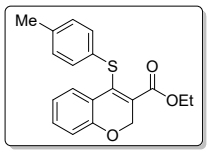
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 12.0 Hz, 1H), 4.27 (q, *J* = 8.0 Hz, 2H), 3.82 (s, 3H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.22 (s, 3H), 1.30 (t, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 155.6, 139.0, 135.6, 133.6, 132.8, 132.6, 129.6,

128.4, 126.5, 124.8, 120.1, 110.9, 61.1, 55.6, 26.0, 20.9, 19.5, 14.1;

HRMS (ESI) calcd for $C_{21}H_{23}O_3S$ $[M+H]^+$ 355.1362, found 355.1366.

ethyl 4-(*p*-tolylthio)-2*H*-chromene-3-carboxylate (3A)



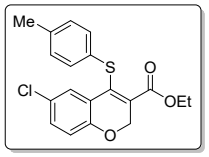
Compound **3A** was prepared from 2*H*-chromen-4-yl trifluoromethanesulfonate **1A** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 2 : 1) to afford **3A** as colorless oil (45.1 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 12.0 Hz, 1H), 7.09 – 6.99 (m, 3H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.68 (t, *J* = 8.0 Hz, 1H), 4.86 (s, 2H), 4.21 (q, *J* = 6.7 Hz, 2H), 2.16 (s, 3H), 1.26 (t, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 155.8, 138.0, 136.3, 131.7, 130.9, 129.7, 129.5, 128.8, 127.7, 122.0, 121.6, 116.3, 66.2, 61.2, 21.0, 14.2;

HRMS (ESI) calcd for $C_{19}H_{19}O_3S$ $[M+H]^+$ 327.1049, found 327.1051.

ethyl 6-chloro-4-(*p*-tolylthio)-2*H*-chromene-3-carboxylate (3B)



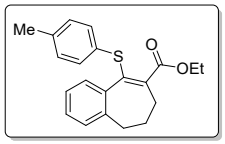
Compound **3B** was prepared from 6-chloro-2*H*-chromen-4-yl trifluoromethanesulfonate **1B** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 2 : 1) to afford **3B** as colorless oil (53.3 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 12.0 Hz, 1H), 4.92 (s, 2H), 4.28 (q, *J* = 6.7 Hz, 2H), 2.25 (s, 3H), 1.32 (t, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 154.2, 136.9, 136.7, 130.9, 130.5, 129.8, 129.8, 128.6, 128.3, 126.7, 123.4, 117.7, 66.4, 61.4, 21.0, 14.1;

HRMS (ESI) calcd for $C_{19}H_{18}ClO_3S$ $[M+H]^+$ 361.0660, found 361.0662.

ethyl 9-(*p*-tolylthio)-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (3C)



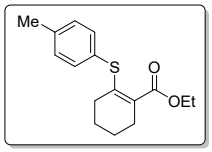
Compound **3C** was prepared from 6,7-dihydro-5*H*-benzo[7]annulen-9-yl trifluoromethanesulfonate **1C** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3C** as colorless oil (55.5 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, *J* = 10.0 Hz, 1H), 6.99 – 6.91 (m, 4H), 6.87 (t, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 4.25 (q, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 6.0 Hz, 2H), 2.17 – 2.06 (m, 7H), 1.30 (t, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 146.3, 140.9, 137.4, 136.9, 132.3, 131.0, 129.7, 129.3, 129.1, 128.0, 127.9, 125.7, 60.8, 34.7, 31.7, 27.8, 21.0, 14.3;

HRMS (ESI) calcd for $C_{21}H_{23}O_2S$ $[M+H]^+$ 339.1413, found 339.1417.

ethyl 2-(*p*-tolylthio)cyclohex-1-ene-1-carboxylate (3D)



Compound **3D** was prepared from cyclohex-1-en-1-yl trifluoromethanesulfonate **1D** and *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** according to general procedure 3. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 4 : 1) to afford **3D** as colorless oil (27.7 mg, 50% yield).

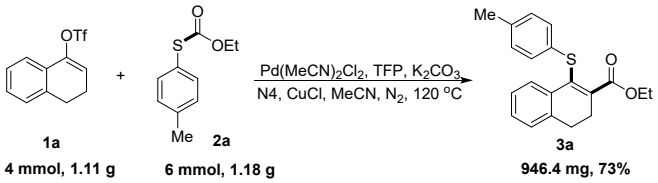
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.18 (q, *J* = 8.0 Hz, 2H), 2.46 – 2.20 (m, 7H), 1.96 – 1.85 (m, 2H), 1.52 – 1.44 (m, 2H), 1.25 (t, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 148.9, 138.8, 135.6, 129.6, 128.5, 122.4, 60.3, 31.7, 27.2, 23.0, 21.8, 21.2, 14.3;

HRMS (ESI) calcd for $C_{16}H_{21}O_2S$ $[M+H]^+$ 277.1257, found 277.1258.

6. Scale-up Reaction

General Procedure 4

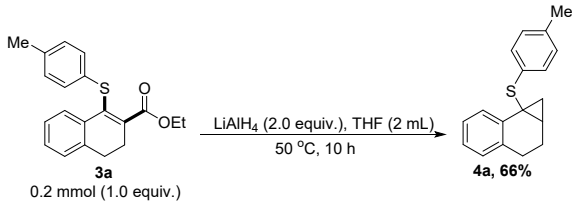


A Schlenk-tube equipped with a magnetic stir bar was charged with $Pd(MeCN)_2Cl_2$ (103.8 mg, 10 mol%, 0.4 mmol), TFP (232.0 mg, 25 mol%, 1.0 mmol), K_2CO_3 (1105.7 mg, 2.0 equiv, 8.0 mmol), CuCl (237.6 mg, 60 mol%, 2.4 mmol) and then evacuated and backfilled with N_2 for 3 times. Afterwards, alkenyl triflates **1** (1112.8 mg, 1.0 equiv, 4.0 mmol), thiocarbonate **2** (1176.3 mg, 1.5 equiv, 6.0 mmol), N4 (1826.3 mg, 3.0 equiv, 12.0 mmol) and MeCN (40 mL) were added consecutively under N_2 atmosphere. The tight tube was stirred and heated at 120 °C in the oil bath for 6 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the product **3a** (946.4 mg, 73% yield).

7. Synthetic Transformation

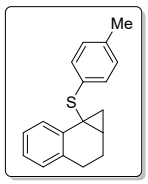
Preparation and Characterization Data of 4a

General Procedure 5



A stirred solution of **3a** (0.2 mmol), $LiAlH_4$ (0.4 mmol) in THF (2 mL) at 50 °C for 10 h. After filtering and evaporating the solvent, the crude product was purified by column chromatography on silica gel to afford the product **4a** (35.3 mg, 66% yield).

(1, 1a, 2, 3-tetrahydro-7b*H*-cyclopropa[a]naphthalen-7b-yl)(*p*-tolyl)sulfane (4a)



Compound **4a** was prepared from ethyl 1-(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate **3a** and $LiAlH_4$ according to general procedure 5. The resultant residue was purified by column chromatography on silica gel (PE) to afford **4a** as colorless oil (35.3 mg,

66% yield).

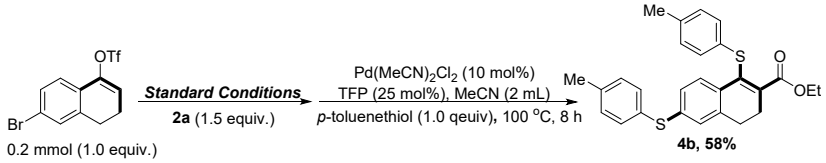
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.20 – 6.95 (m, 7H), 2.72 (t, *J* = 8.0 Hz, 1H), 2.56 (t, *J* = 16.0 Hz, 1H), 2.31 – 2.15 (m, 4H), 2.09 – 1.92 (m, 2H), 1.50 (t, *J* = 4.0 Hz, 1H), 1.42 (t, *J* = 8.0 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 134.4, 134.3, 133.5, 129.4, 128.6, 128.2, 126.5, 125.6, 28.3, 26.3, 26.3, 20.8, 19.7, 19.4;

HRMS (ESI) calcd for $C_{18}H_{19}S$ $[M+H]^+$ 267.1202, found 267.1200.

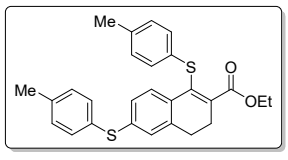
Preparation and Characterization Data of 4b

General Procedure 6



A Schlenk-tube equipped with a magnetic stir bar was charged with $Pd(MeCN)_2Cl_2$ (10 mol%, 0.02 mmol), TFP (25 mol%, 0.05 mmol), K_2CO_3 (2.0 equiv, 0.4 mmol), CuCl (60 mol%, 0.12 mmol) and then evacuated and backfilled with N_2 for 3 times. Afterwards, alkenyl triflates (1.0 equiv, 0.2 mmol), thiocarbonate **2a** (1.5 equiv, 0.3 mmol), N4 (3.0 equiv, 0.6 mmol) and MeCN (2 mL) were added consecutively under N_2 atmosphere. The tight tube was stirred and heated at 120 °C in the oil bath for 6 h. After the reaction was completed, the system was cooled to room temperature and *p*-toluenethiol (1.0 equiv, 0.2 mmol) was added to the system under N_2 atmosphere and stirred for 8 h at 100 °C. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the product **4b** (53.1 mg, 58% yield).

ethyl 1,6-bis(*p*-tolylthio)-3,4-dihydronaphthalene-2-carboxylate (4b)



Compound **4b** was prepared from 6-bromo-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate, *O*-ethyl *S*-(*p*-tolyl) carbonothioate **2a** and *p*-toluenethiol according to

general procedure 6. The resultant residue was purified by column chromatography on silica gel (PE/DCM = 3 : 1) to afford **4b** as colorless oil (53.1 mg, 58% yield).

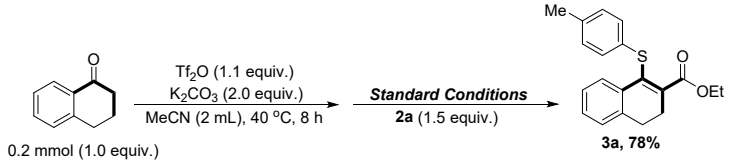
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.11 – 6.96 (m, 4H), 6.92 – 6.87 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.19 (q, *J* = 8.0 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.59 (t, *J* = 6.0 Hz, 2H), 2.28 (s, 3H), 2.17 (s, 3H), 1.22 (t, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 138.4, 137.7, 137.5, 135.8, 133.3, 133.2, 132.3, 132.1, 132.1, 130.2, 129.8, 129.6, 128.7, 128.0, 127.0, 126.5, 61.1, 27.7, 26.4, 21.2, 21.0, 14.1;

HRMS (ESI) calcd for $C_{27}H_{27}O_2S_2$ $[M+H]^+$ 447.1447, found 447.1449.

8. One-Pot Triflation/Thioesterification from Ketone

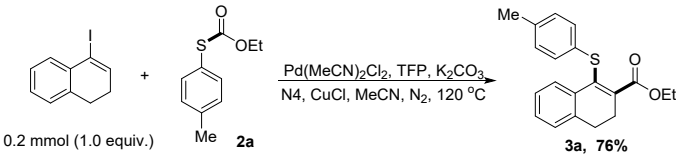
General Procedure 7



A Schlenk-tube equipped with a magnetic stir bar was charged with K_2CO_3 (2.0 equiv, 0.4 mmol) and then evacuated and backfilled with N_2 for 3 times. Afterwards, 3,4-dihydronaphthalen-1(2*H*)-one (1.0 equiv, 0.2 mmol), Tf_2O (1.1 equiv, 0.22 mmol) and MeCN (2 mL) were added consecutively under N_2 atmosphere. The tight tube was stirred and heated at 40 °C in the oil bath for 8 h. After the reaction was completed, the system was cooled to room temperature and $Pd(MeCN)_2Cl_2$ (10 mol%, 0.02 mmol), TFP (25 mol%, 0.05 mmol), CuCl (60 mol%, 0.12 mmol), thiocarbonate **2** (1.5 equiv, 0.3 mmol) and N4 (3.0 equiv, 0.6 mmol) was added to the system under N_2 atmosphere and stirred for 6 h at 120 °C. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the product **3a** (50.6 mg, 78% yield).

9. Thioesterification of Alkenes by Alkenyl Iodides

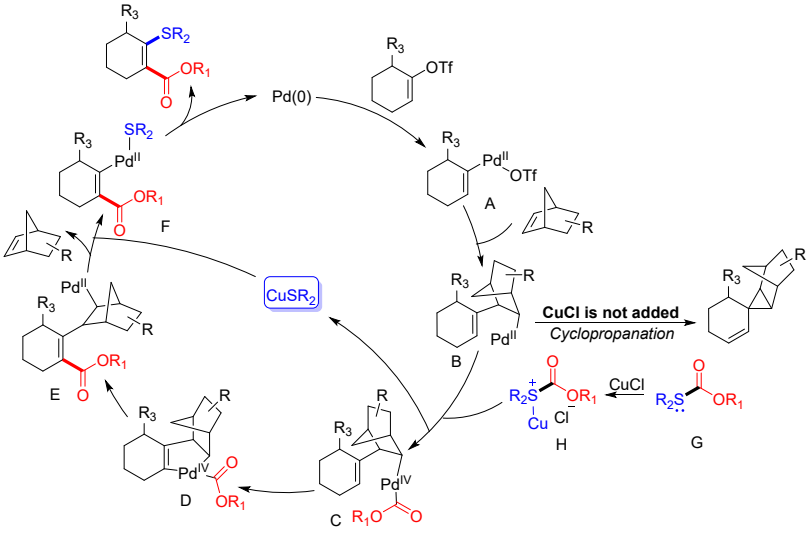
General Procedure 8



A Schlenk-tube equipped with a magnetic stir bar was charged with $Pd(MeCN)_2Cl_2$ (10 mol%, 0.02 mmol), TFP (25 mol%, 0.05 mmol), K_2CO_3 (2.0 equiv, 0.4 mmol), CuCl (60 mol%, 0.12 mmol) and then evacuated and backfilled with N_2 for 3 times. Afterwards, 4-iodo-1,2-dihydronaphthalene (1.0 equiv, 0.2 mmol), thiocarbonate **2a** (1.5 equiv, 0.3 mmol), N4 (3.0 equiv, 0.6 mmol) and MeCN (2 mL) were added consecutively under N_2 atmosphere. The tight tube was stirred and heated at 120 °C in the oil bath for 6 h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the product **3a** (49.3 mg, 76% yield).

10.Investigation of Reaction Mechanism

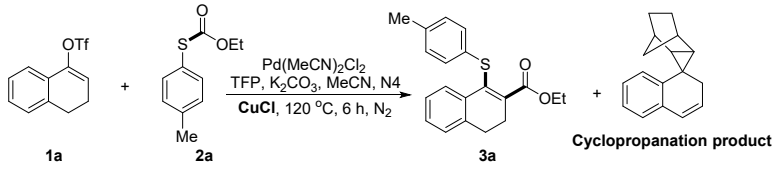
Proposed Reaction Mechanism

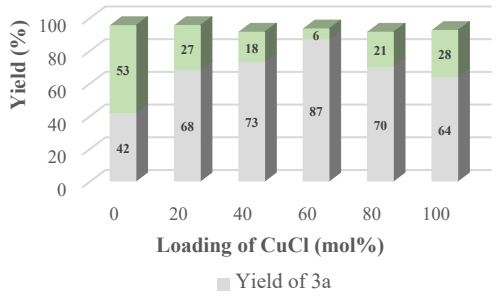


According to previous literature,[5-7] a possible mechanism is proposed. Firstly, the vinyl-Pd(II) intermediate A is formed by oxidative addition of alkenyl triflates to the Pd(0) complex, then it undergoes the insertion of norbornene to obtain intermediate B. The thiocarbonate G then forms sulfonium salt H with the CuCl and activates the C(O)-

S bond. Sulfonium salt G undergoes oxidative addition with intermediate B to form the intermediate C. Subsequent *ortho*-C−H activation generate a five-membered palladacycle D (ANP). The intermediate E of alkoxycarbonylation of olefin was obtained by reduction elimination. Intermediate E undergoes the extrusion of norbornene and transmetallization with $CuSR_2$ to give intermediate F. Finally, The product of olefin thioesterification was obtained by reduction elimination. When CuCl is not added, the intermediate B is easy to form cyclopropanated products.

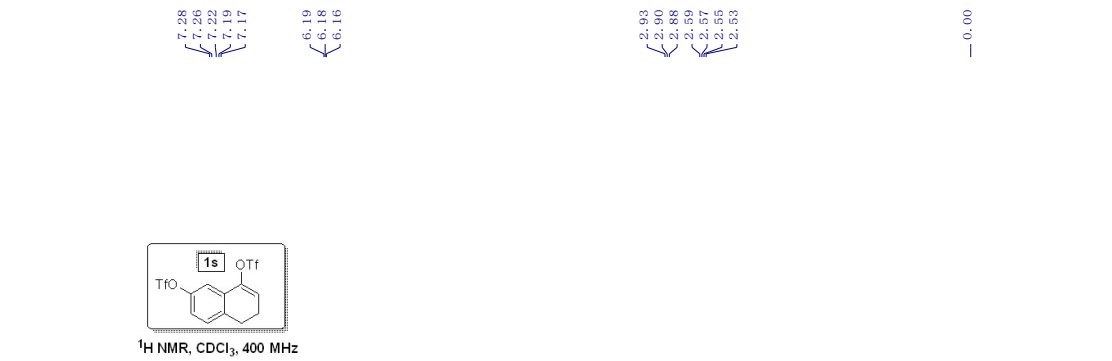
Control Experiment of CuCl

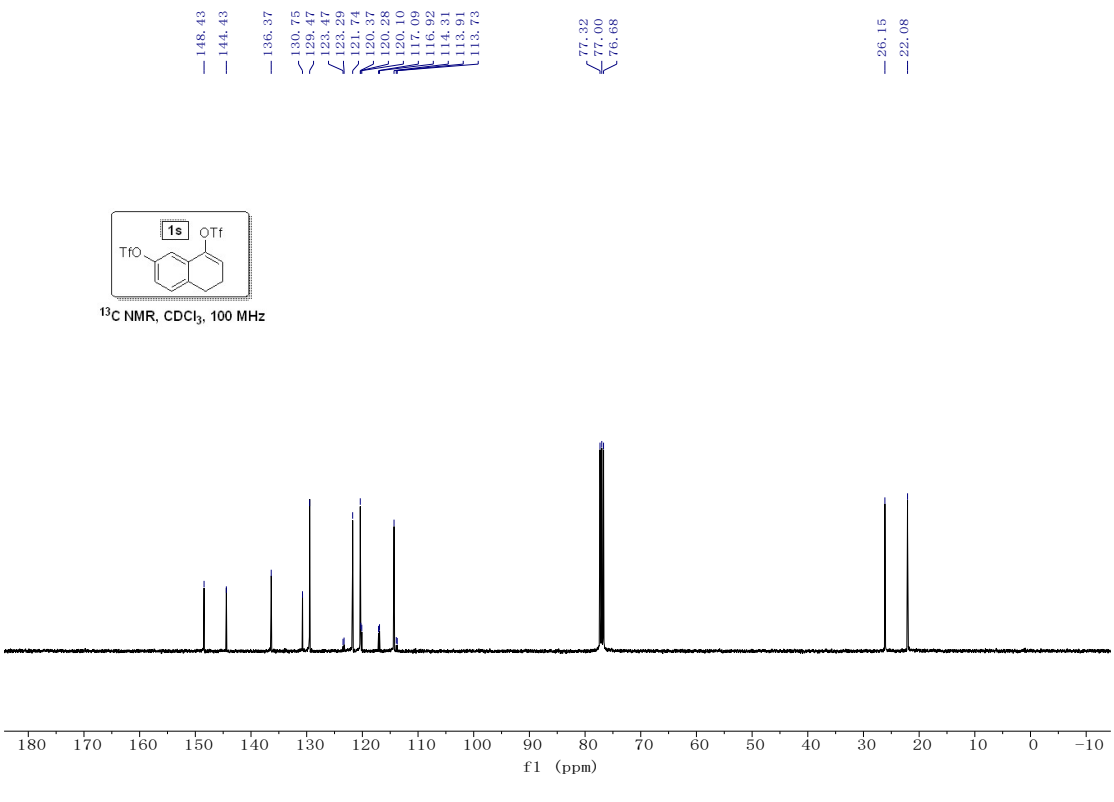


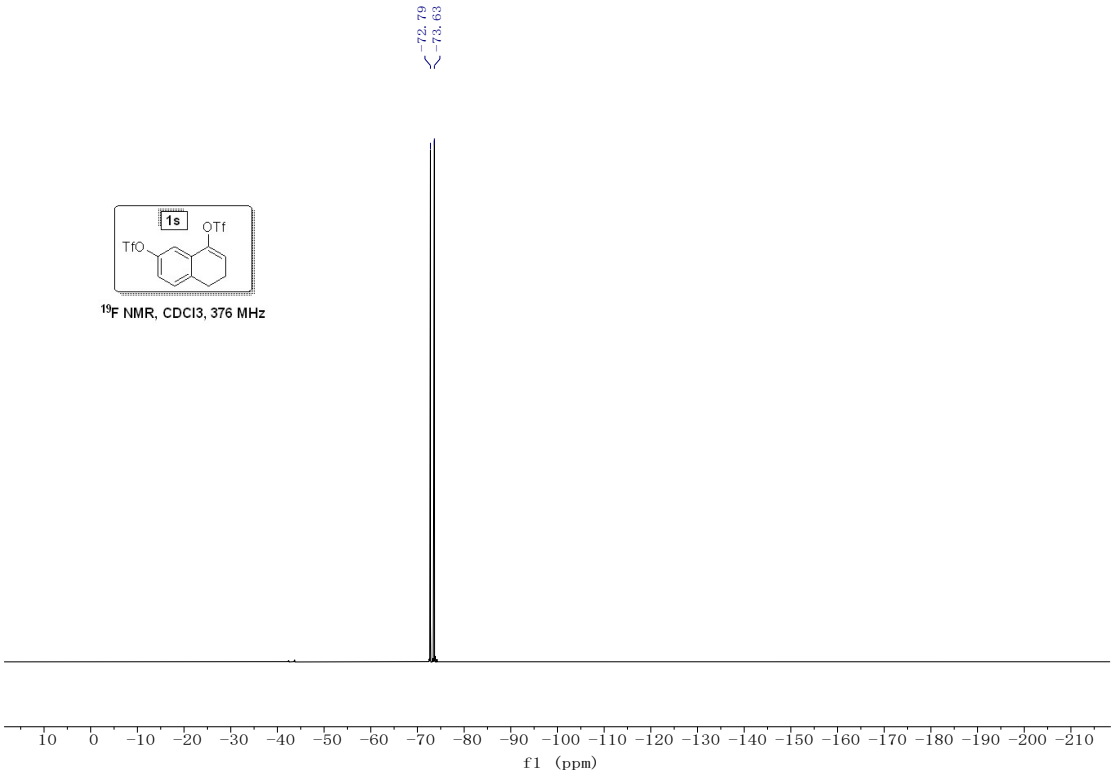


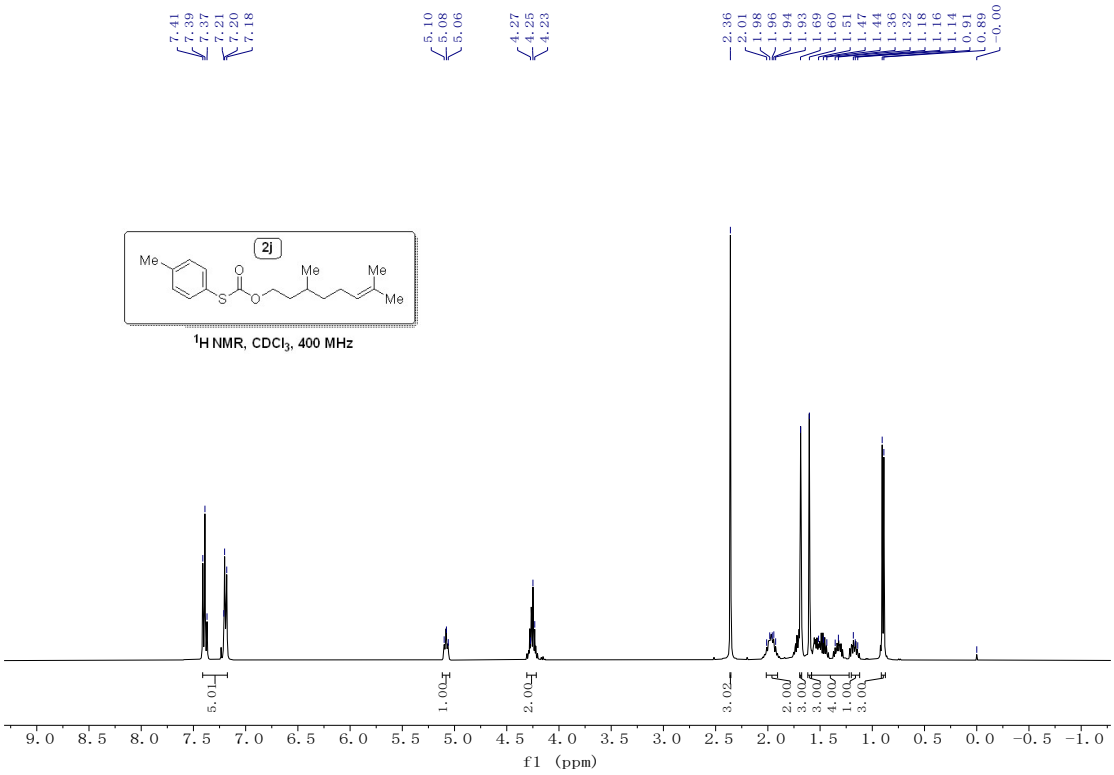
Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), $Pd(MeCN)_2Cl_2$ (0.02 mmol, 10 mol%), TFP (0.05 mmol, 25 mol%), N4 (0.6 mmol, 3.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv), CuCl, MeCN (2.0 mL), 120 °C, 6 h, N_2. Isolated yields.

11.Copies of ^{1}H, ^{13}C, and ^{19}F NMR Spectra






-72.79
-73.63
1s
OTf
TfO
19F NMR, CDCl3, 376 MHz
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)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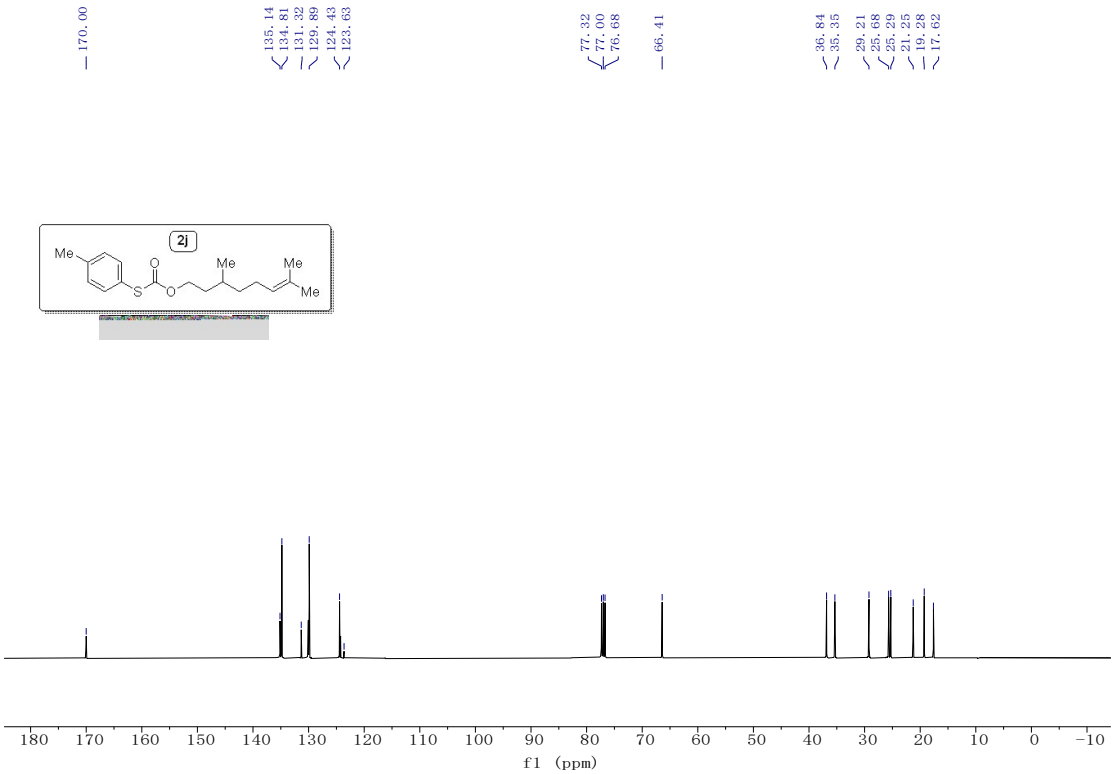
7.37
7.21
7.20
7.18
5.10
5.08
5.06
4.27
4.25
4.23
2.36
2.01
1.98
1.96
1.94
1.93
1.69
1.60
1.51
1.47
1.44
1.36
1.32
1.18
1.16
1.14
0.91
0.89
-0.00
2j
Me
Me
Me
Me
O
S
O
1H NMR, CDCl3, 400 MHz
5.01
1.00
2.00
3.02
2.00
3.00
4.00
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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129.89
124.43
123.63
77.32
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76.68
66.41
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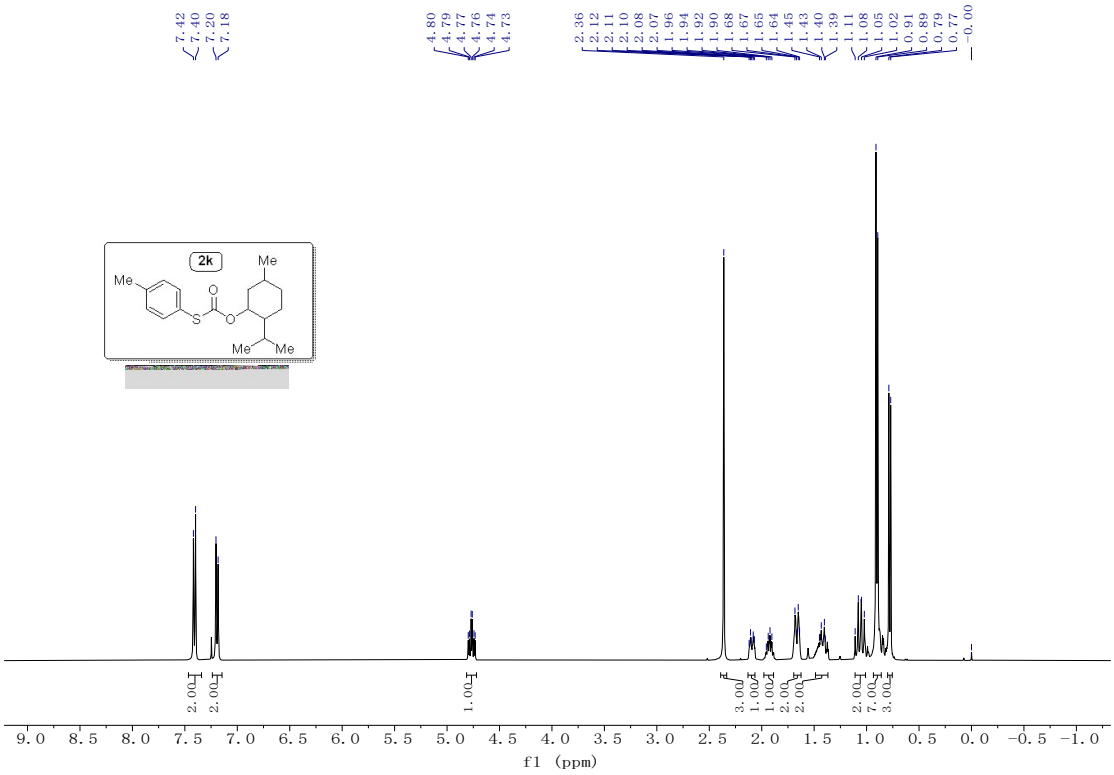
35.35
29.21
25.68
25.29
21.25
19.28
17.62
2j
Me
Me
Me
Me
f1 (ppm)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4.76
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4.73
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2.11
2.10
2.08
2.07
1.96
1.94
1.92
1.90
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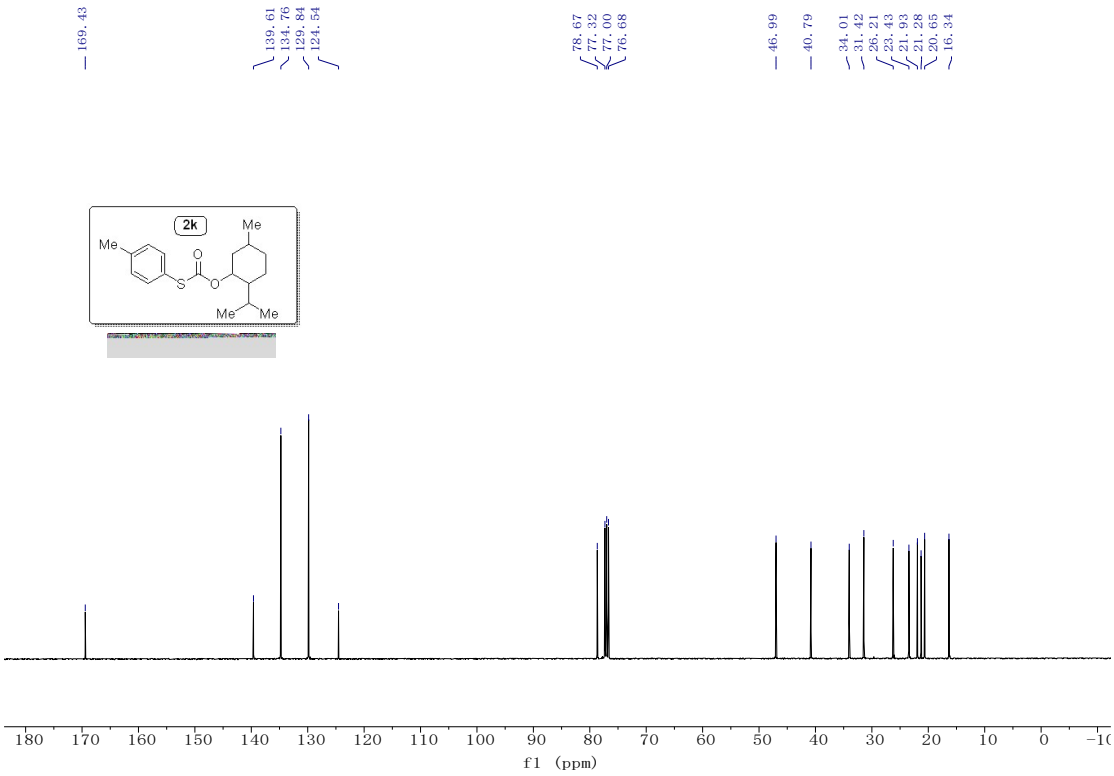
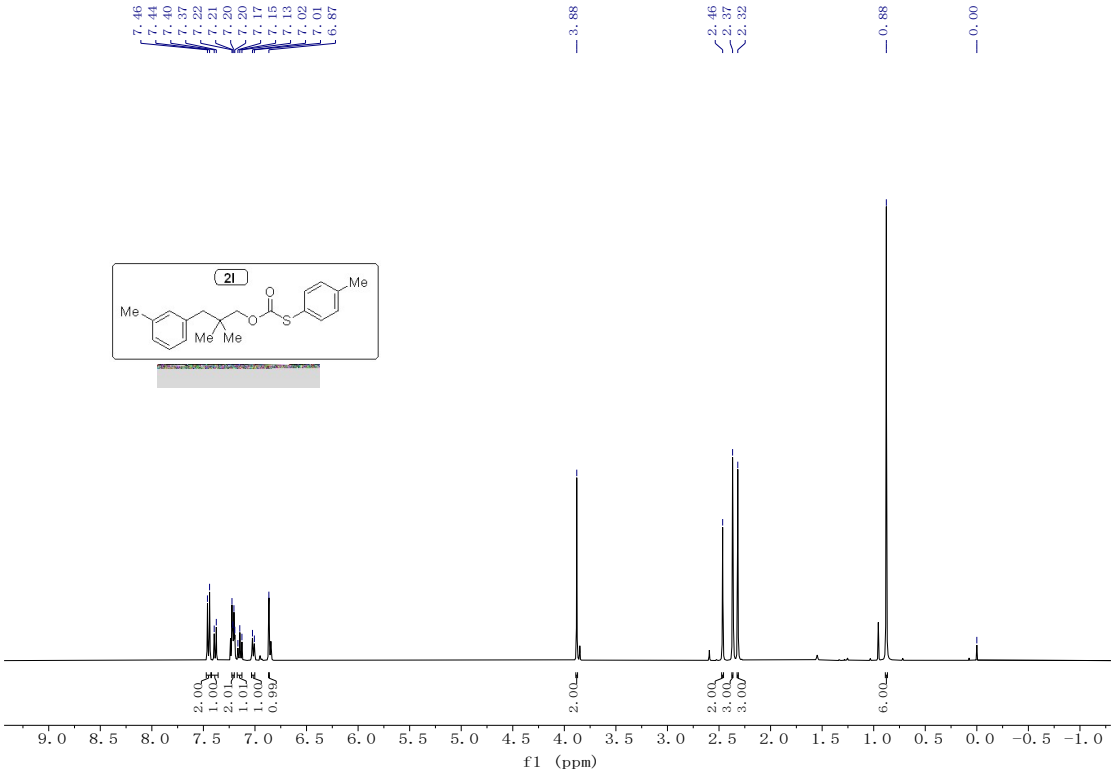
1.67
1.65
1.64
1.45
1.43
1.40
1.39
1.11
1.08
1.05
1.02
0.91
0.89
0.79
0.77
0.00
2k
Me
Me
Me
Me
2.00
2.00
1.00
3.00
1.00
2.00
2.00
2.00
7.00
3.00
f1 (ppm)


169.43
139.61
134.76
129.84
124.54
78.67
77.32
77.00
76.68
46.99
40.79
34.01
31.42
26.21
23.43
21.93
21.28
20.65
16.34
2k
Me
Me
Me
Me
Me
f1 (ppm)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7.44
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7.22
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7.20
7.20
7.17
7.15
7.13
7.02
7.01
6.87
3.88
2.46
2.37
2.32
0.88
0.00
2l
Me
Me
Me
Me
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1.00
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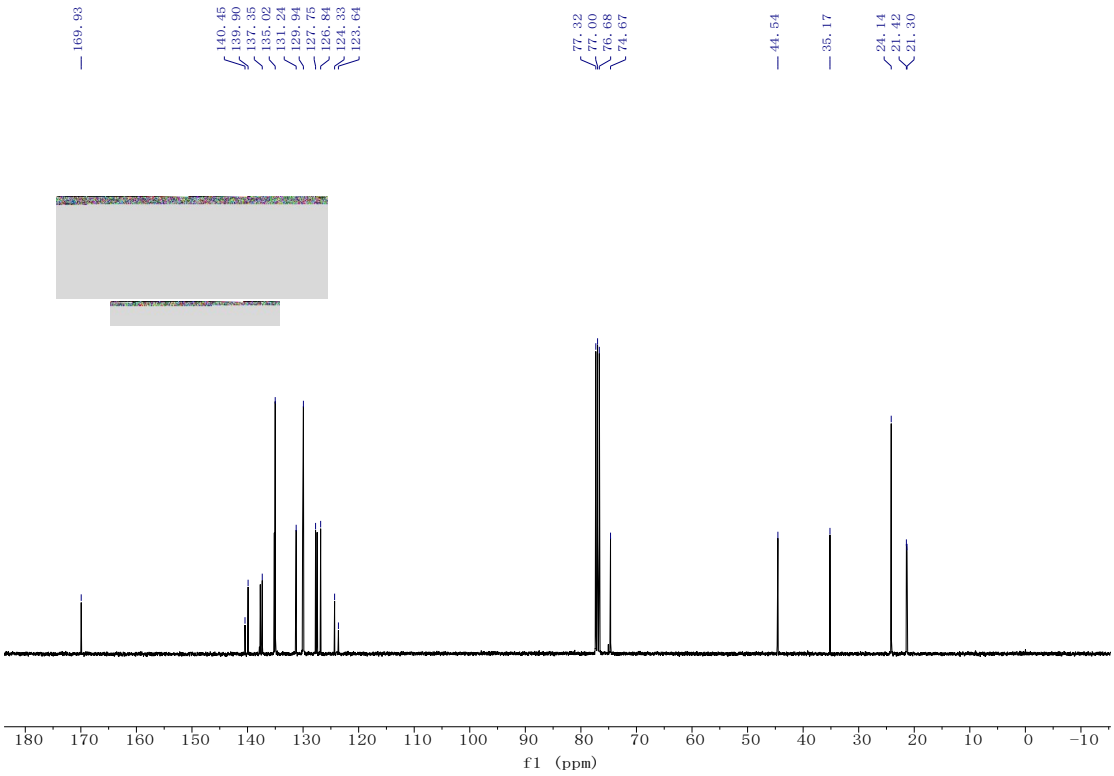
1.01
1.00
0.99
2.00
2.00
3.00
3.00
6.00
f1 (ppm)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137.35
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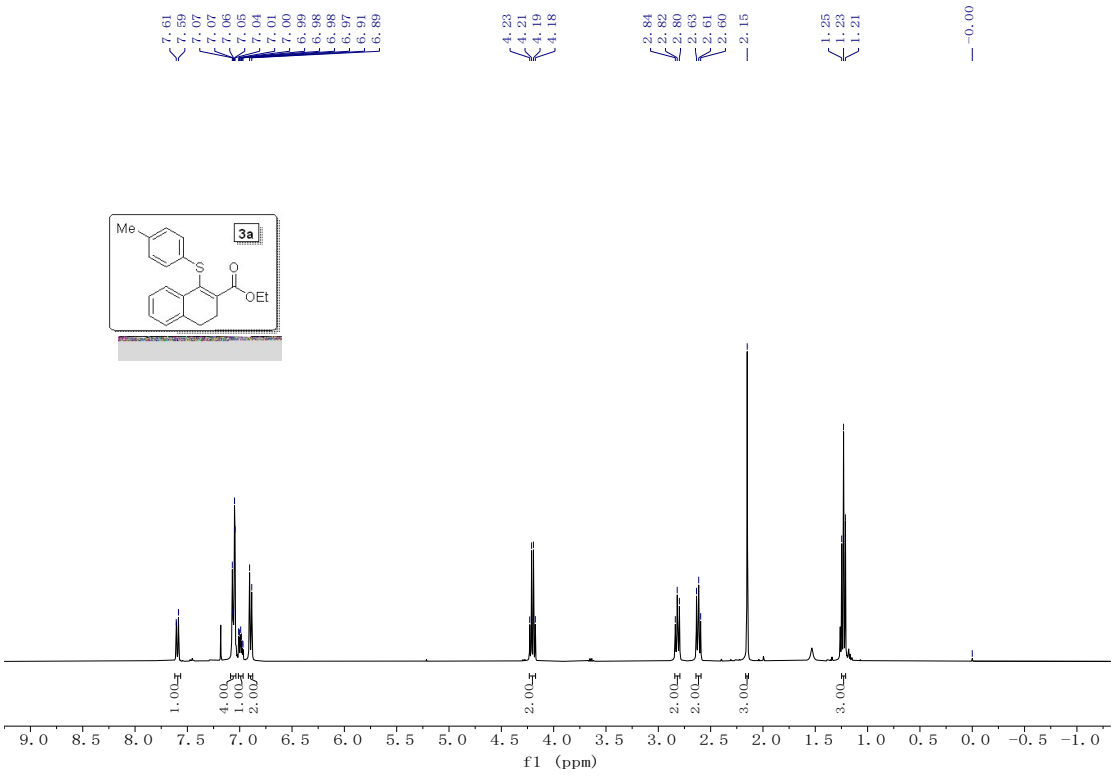
131.24
129.94
127.75
126.84
124.33
123.64
77.32
77.00
76.68
74.67
44.54
35.17
24.14
21.42
21.30
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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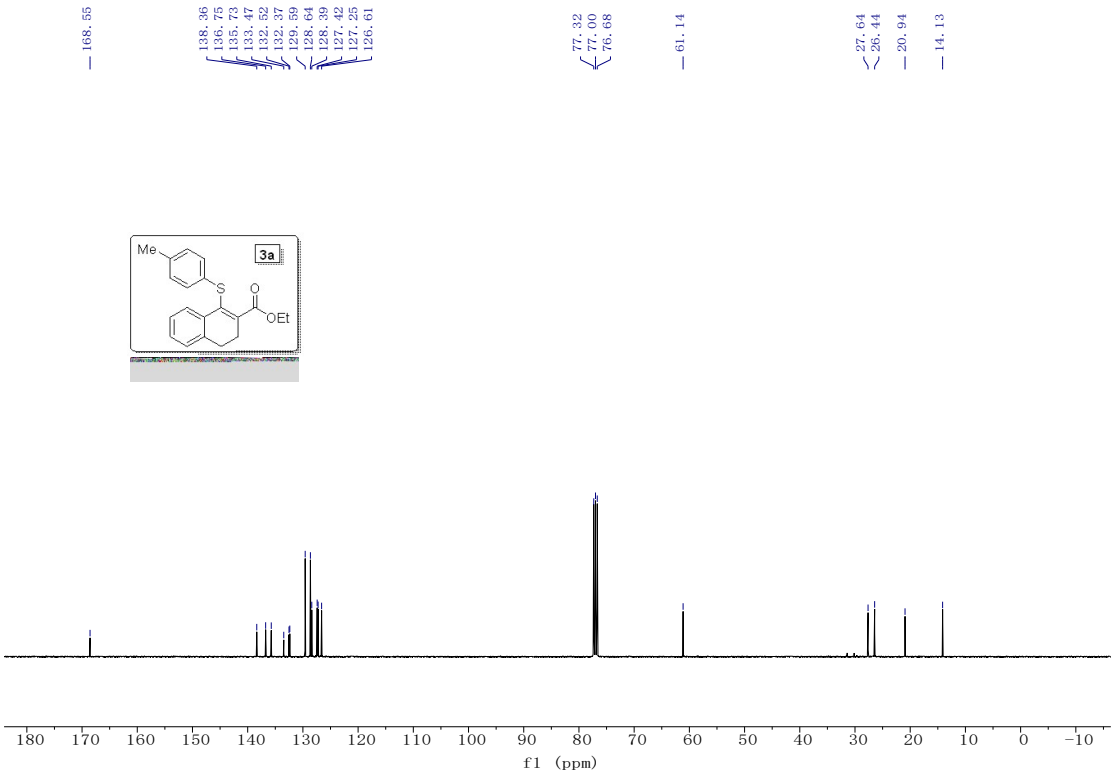
7.06
7.05
7.04
7.01
7.00
6.99
6.98
6.98
6.97
6.91
6.89
4.23
4.21
4.19
4.18
2.84
2.82
2.80
2.63
2.61
2.60
2.15
1.25
1.23
1.21
-0.00
Me
S
O
OEt
3a
1.00
4.00
1.00
2.00
2.00
2.00
2.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


168.55
138.36
136.75
135.73
133.47
132.52
132.37
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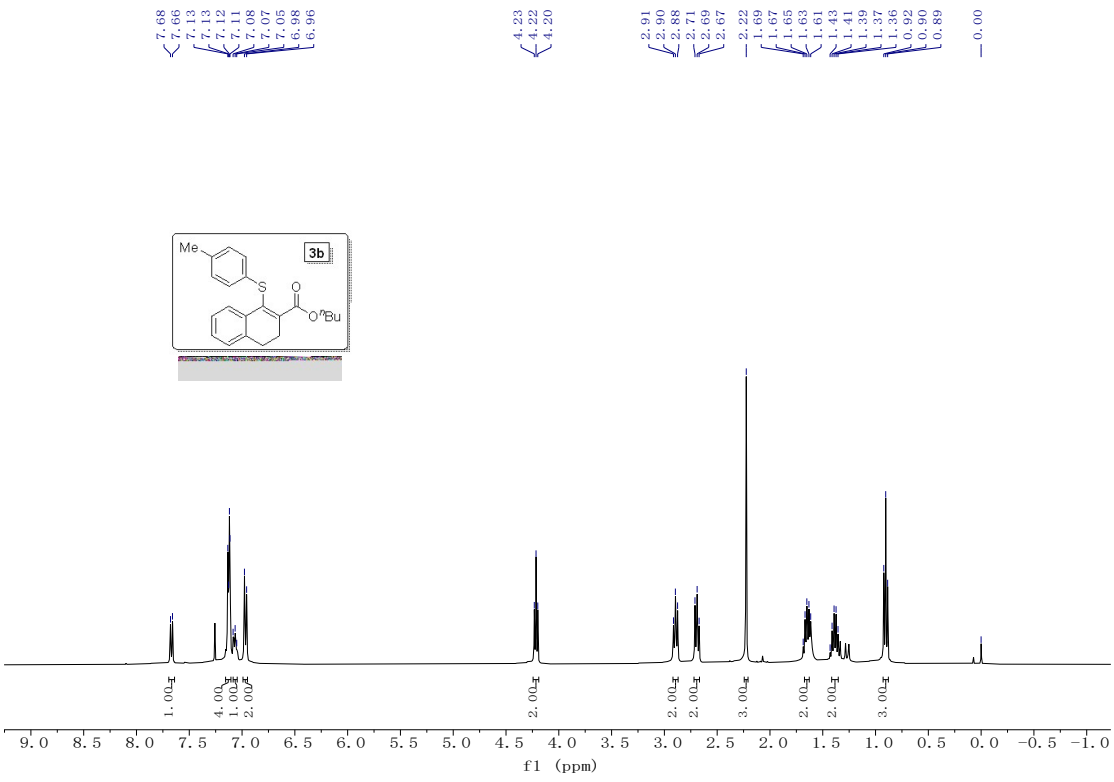
128.64
128.39
127.42
127.25
126.61
77.32
77.00
76.68
61.14
27.64
26.44
20.94
14.13
Me
3a
S
O
OEt
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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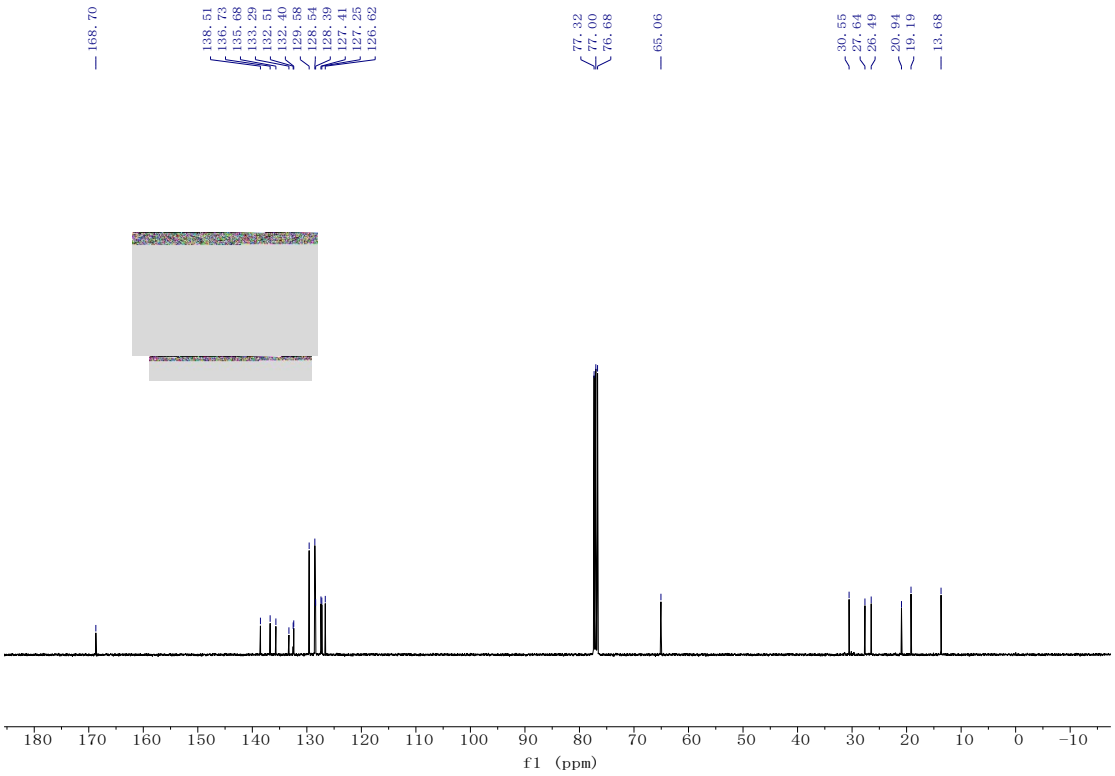
7.11
7.08
7.07
7.05
6.98
6.96
4.23
4.22
4.20
2.91
2.90
2.88
2.71
2.69
2.67
2.22
1.69
1.67
1.65
1.63
1.61
1.43
1.41
1.39
1.37
1.36
0.92
0.90
0.89
0.00
Me
3b
S
O
O
tBu
1.00
4.00
1.00
2.00
2.00
2.00
2.00
3.00
2.00
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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128.39
127.41
127.25
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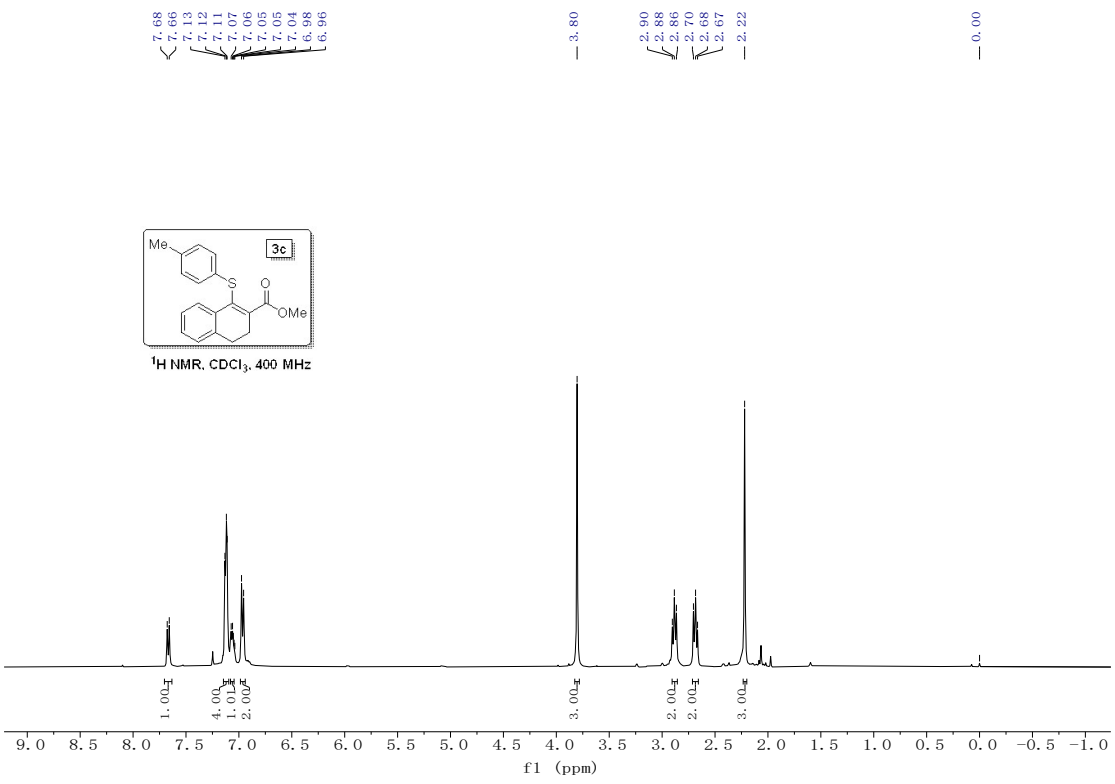
30.55
27.64
26.49
20.94
19.19
13.68
f1 (ppm)


7.68
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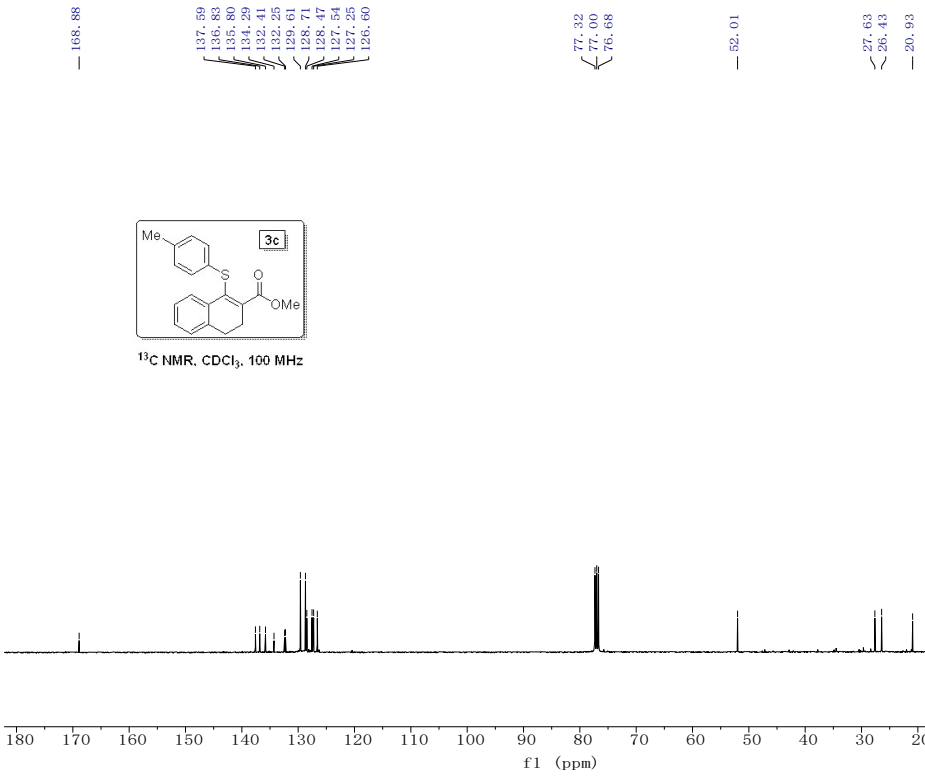
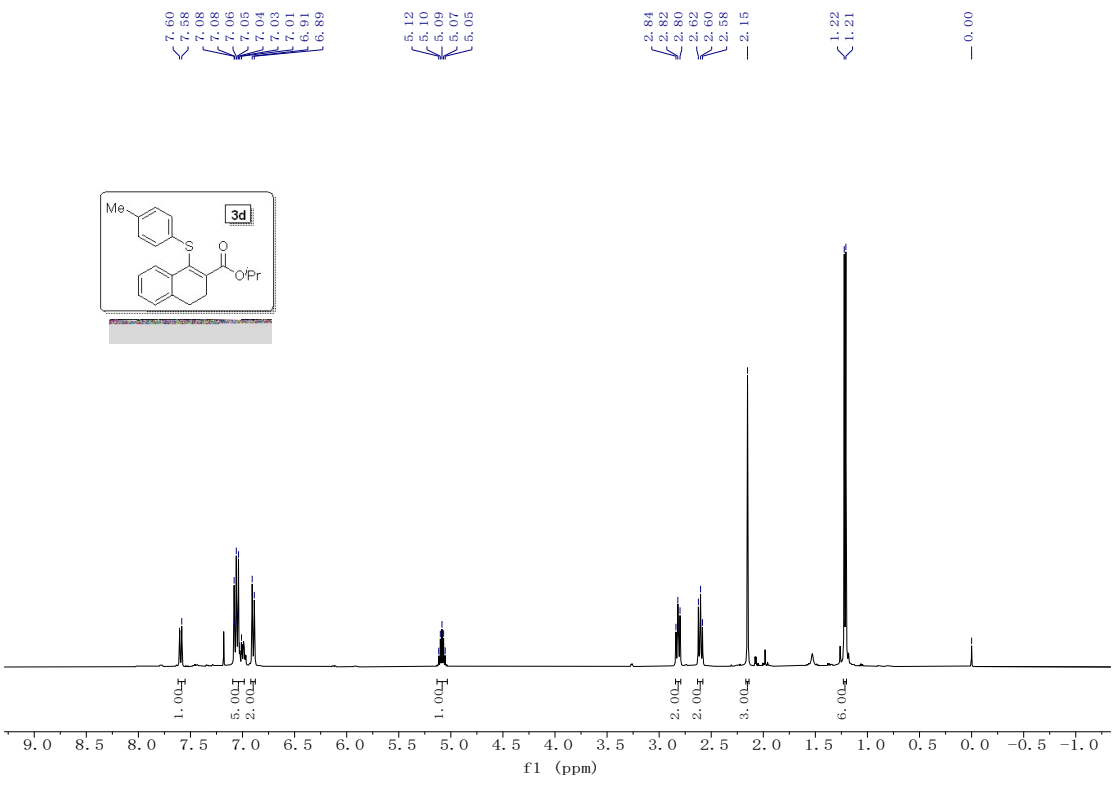
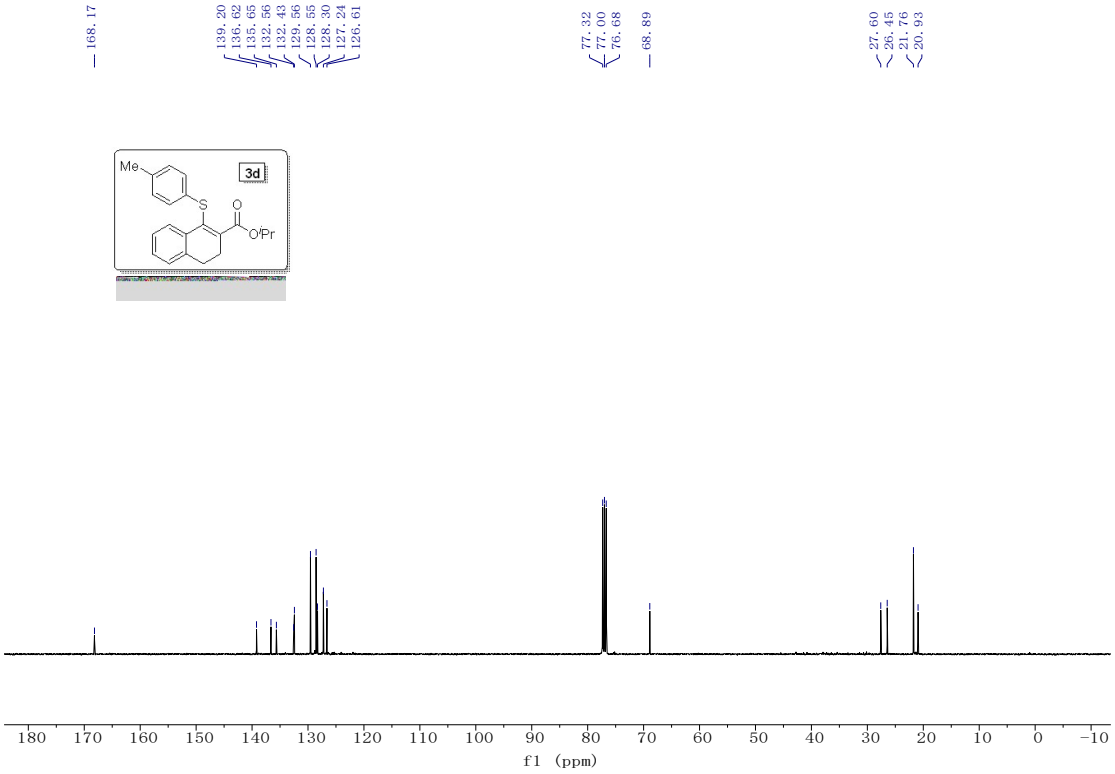
7.07
7.06
7.05
7.05
7.04
6.98
6.96
3.80
2.90
2.88
2.86
2.70
2.68
2.67
2.22
0.00
Me
S
O
OMe
3c
1H NMR, CDCl3, 400 MHz
1.00
4.00
1.01
2.00
3.00
2.00
2.00
3.00
f1 (ppm)



^{13}C NMR, $CDCl_3$, 100 MHz

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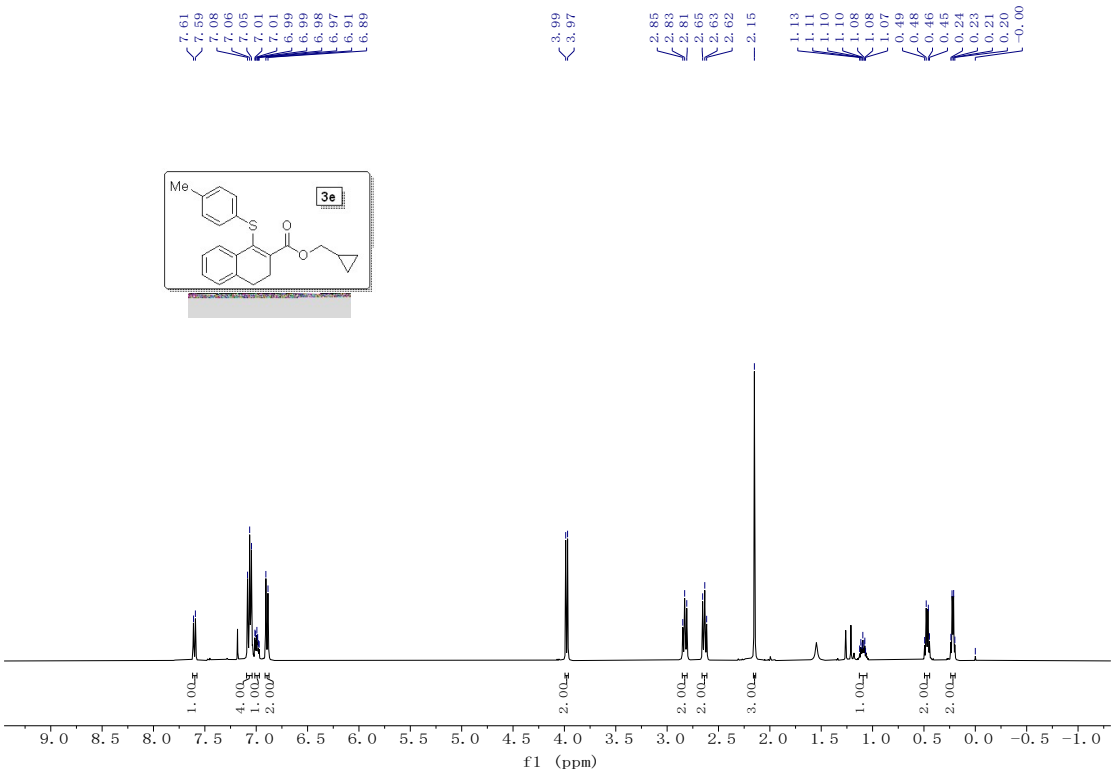
139.20
136.62
135.65
132.56
132.43
129.56
128.55
128.30
127.24
126.61
77.32
77.00
76.68
68.89
27.60
26.45
21.76
20.93
Me
S
O
O/Pr
3d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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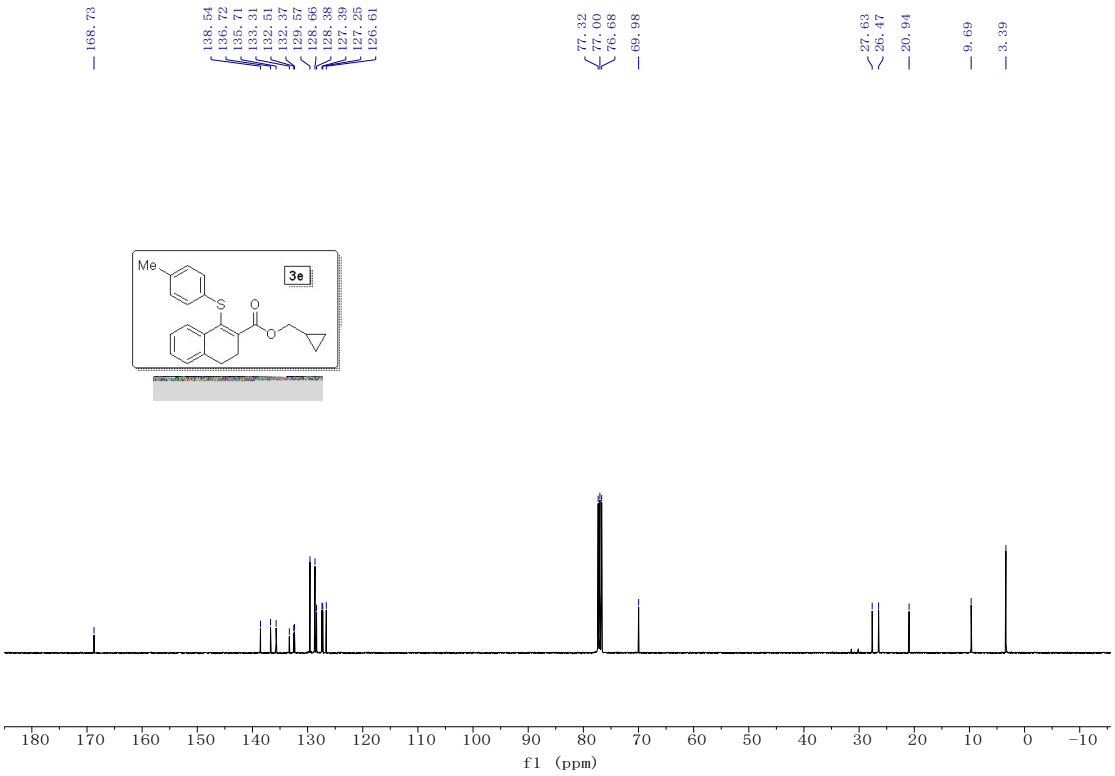
7.06
7.05
7.01
7.01
6.99
6.99
6.98
6.97
6.91
6.89
3.99
3.97
2.85
2.83
2.81
2.65
2.63
2.62
2.15
1.13
1.11
1.10
1.10
1.08
1.08
1.07
0.49
0.48
0.46
0.45
0.24
0.23
0.21
0.20
−0.00
Me
S
O
O
3e
1.00
4.00
1.00
2.00
2.00
2.00
2.00
3.00
1.00
2.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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136.72
135.71
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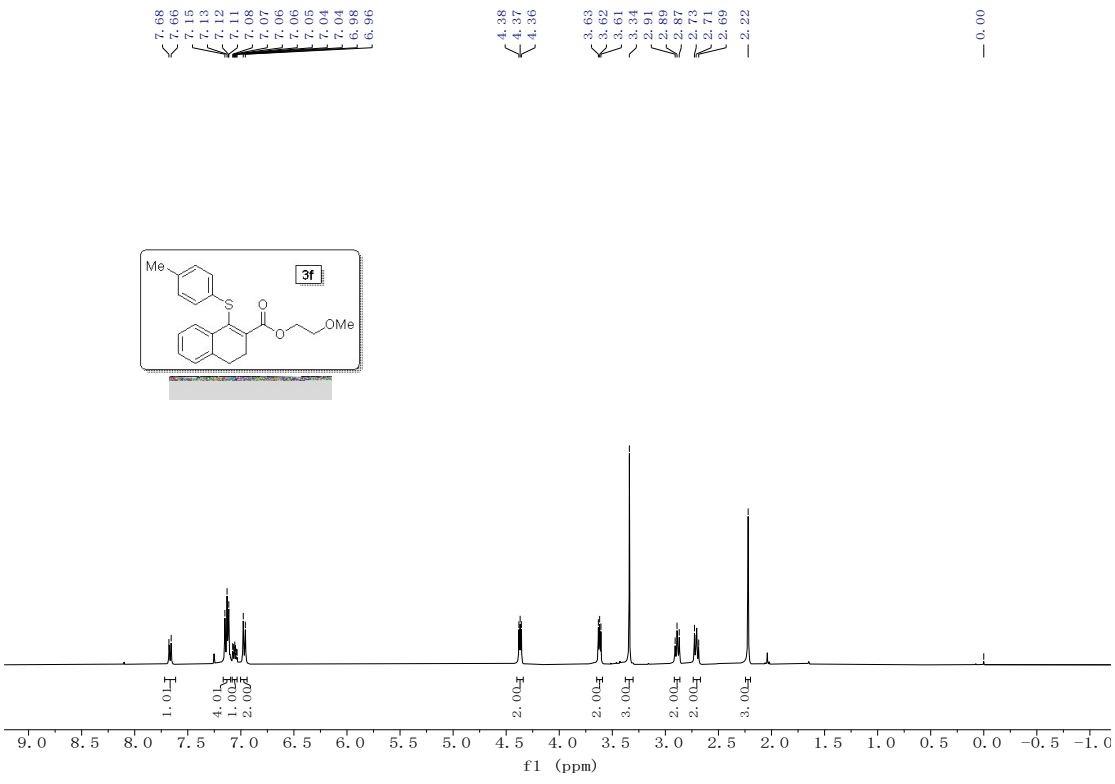
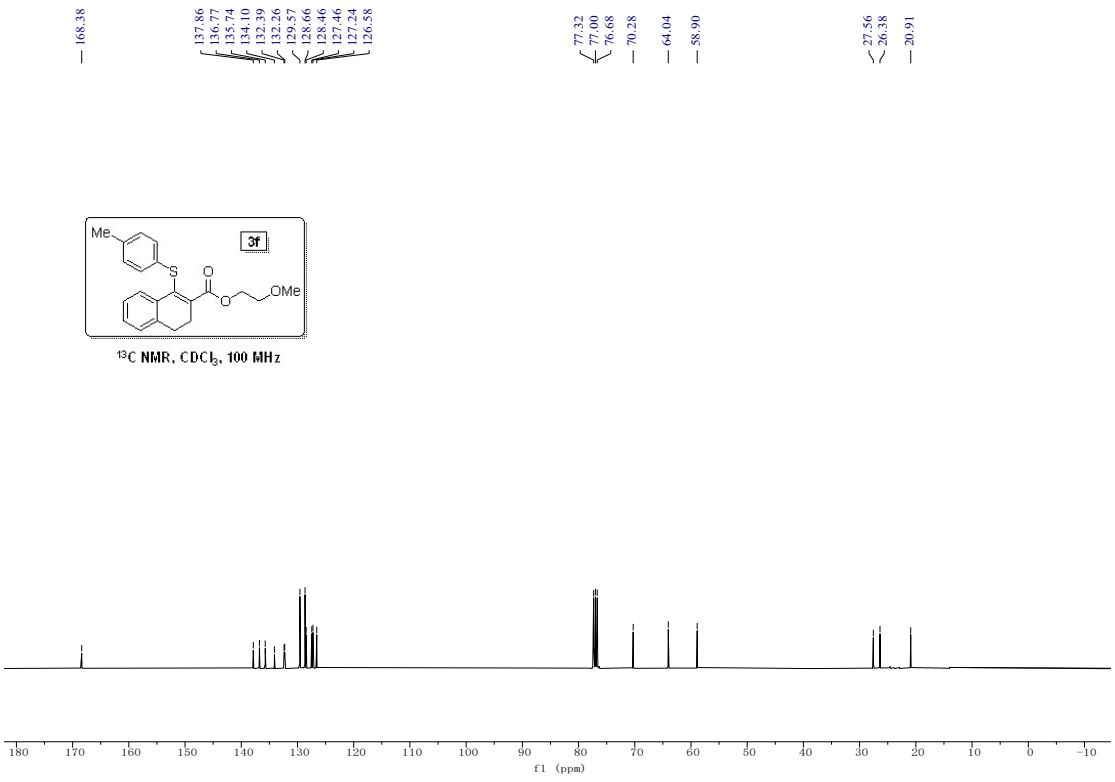
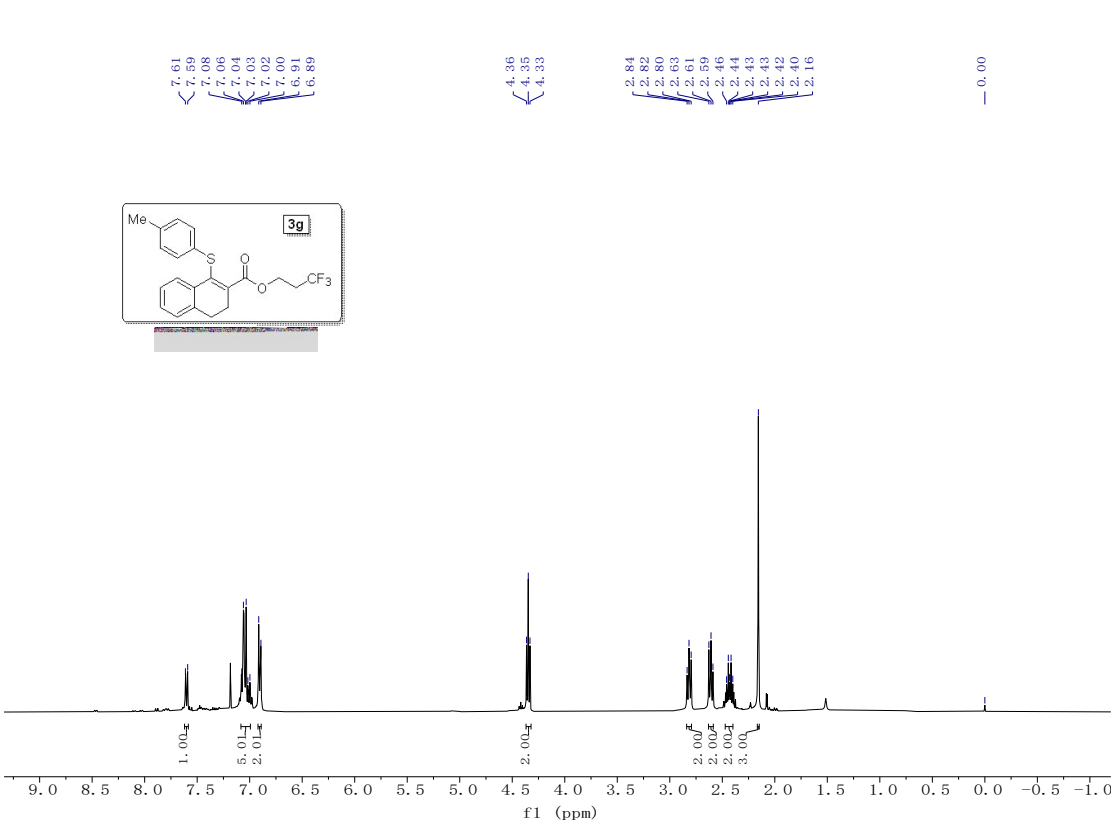
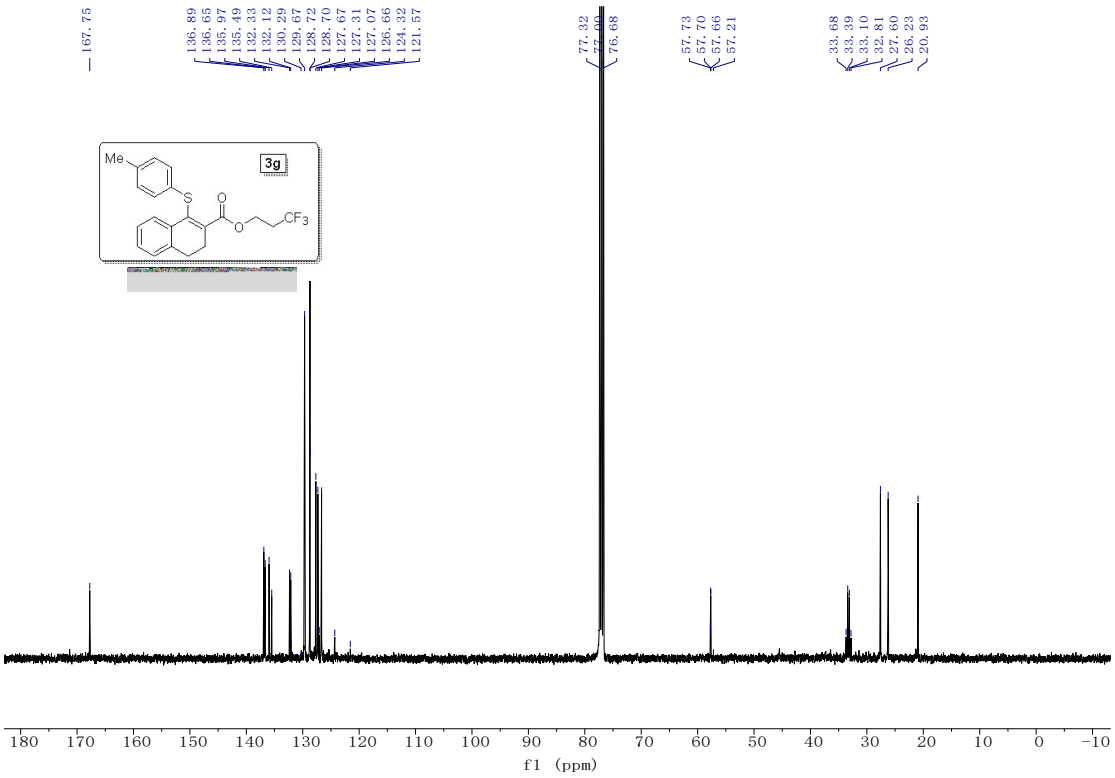
129.57
128.66
128.38
127.39
127.25
126.61
77.32
77.00
76.68
69.98
27.63
26.47
20.94
9.69
3.39
Me
S
O
O
3e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

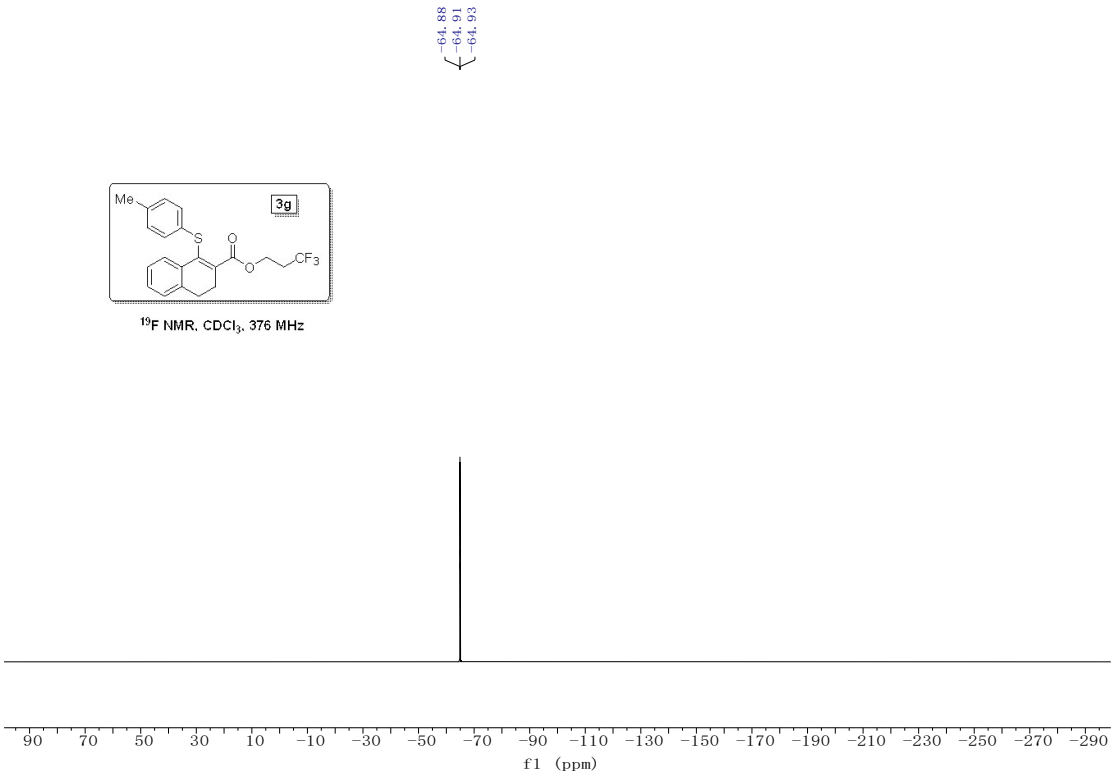

7.68
7.66
7.15
7.13
7.12
7.11
7.08
7.07
7.06
7.06
7.05
7.04
7.04
6.98
6.96
4.38
4.37
4.36
3.63
3.62
3.61
3.34
2.91
2.89
2.87
2.73
2.71
2.69
2.22
0.00
Me
S
O
O
OMe
3f
1.01
4.01
1.00
2.00
2.00
2.00
3.00
2.00
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)



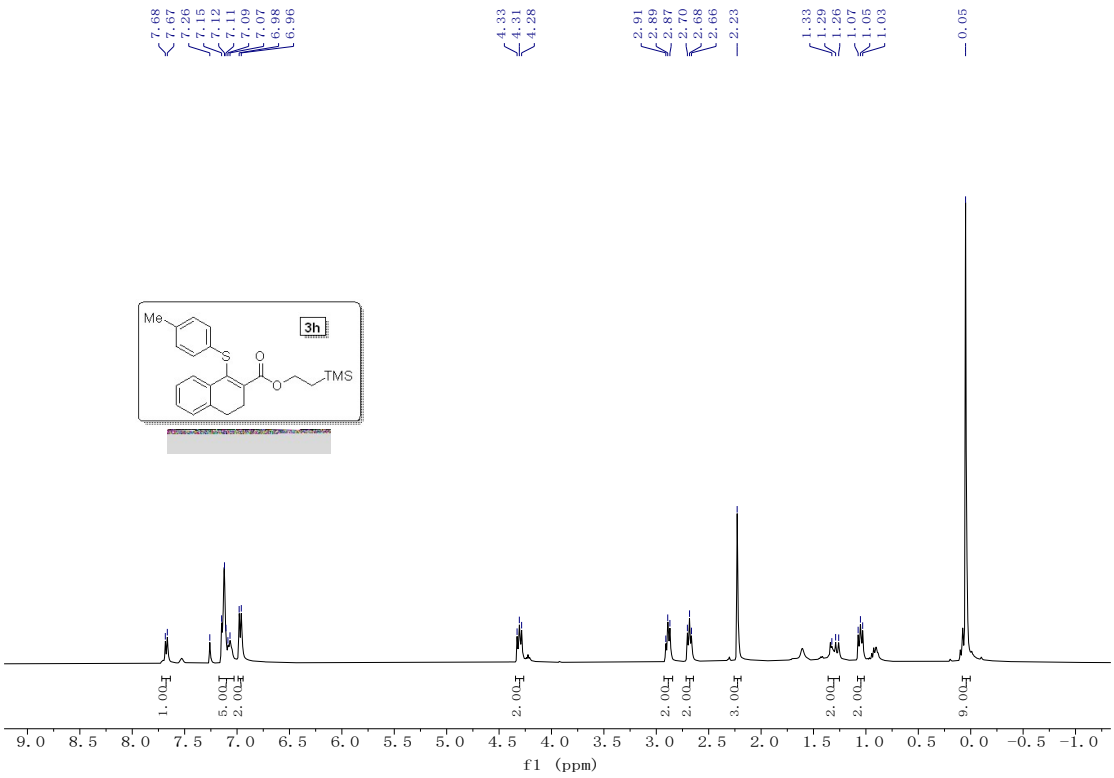
^{13}C NMR, $CDCl_3$, 100 MHz

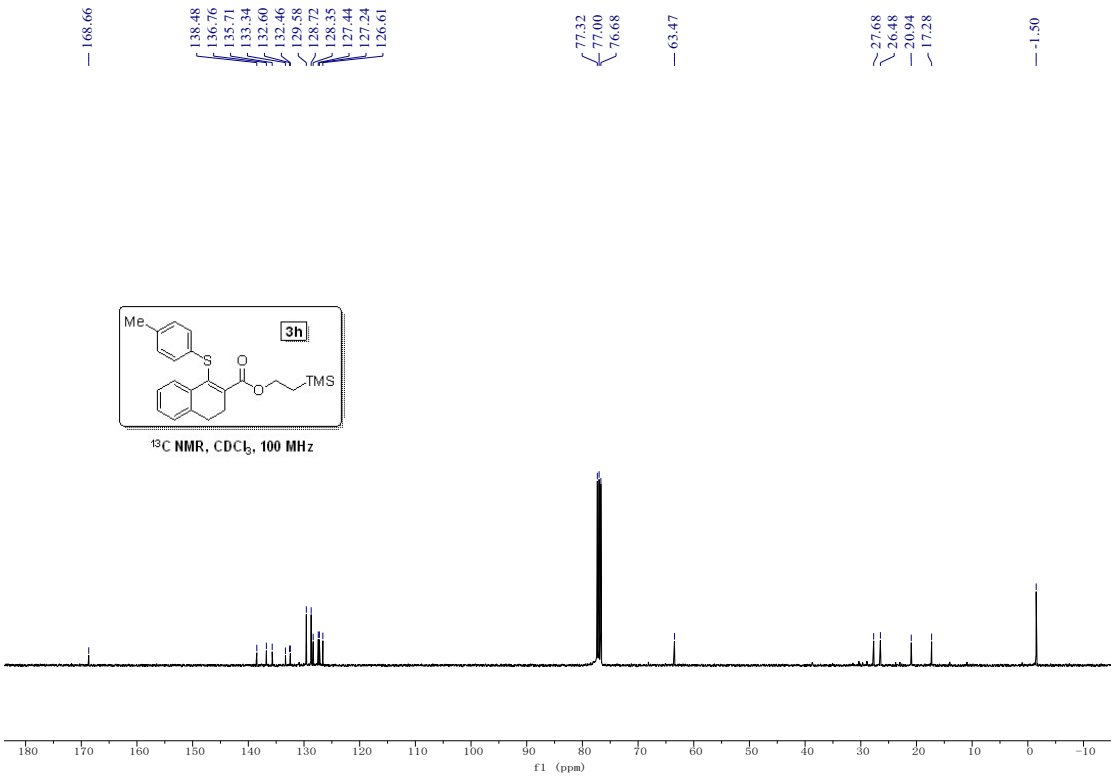




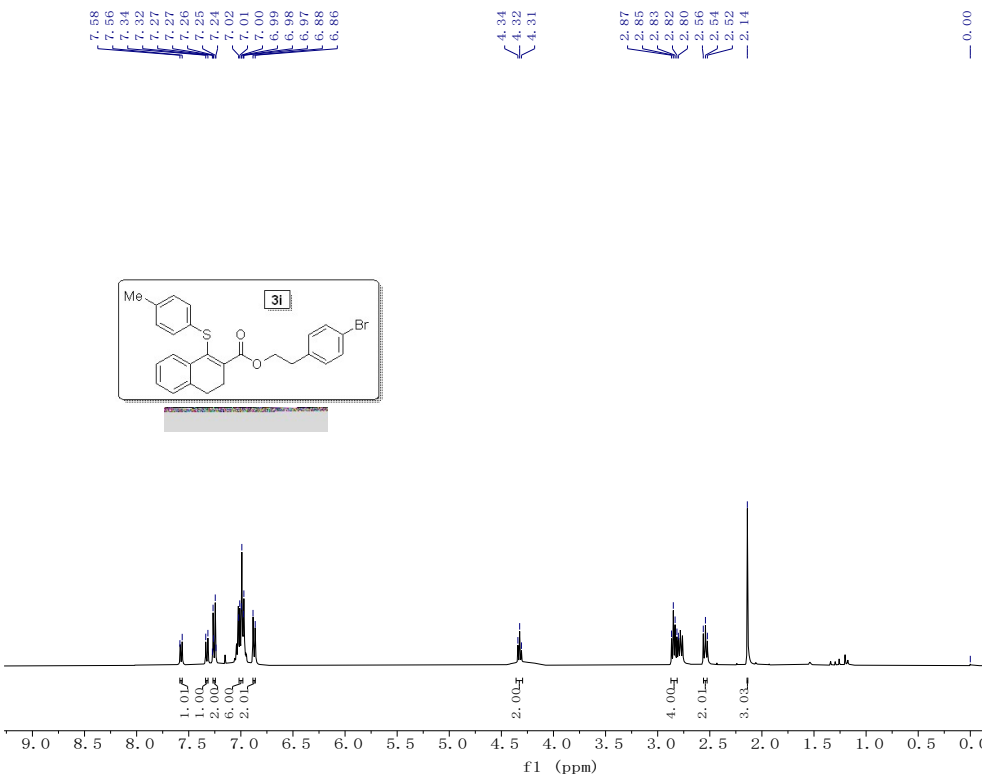


^{19}F NMR, $CDCl_3$, 376 MHz





^{13}C NMR, $CDCl_3$, 100 MHz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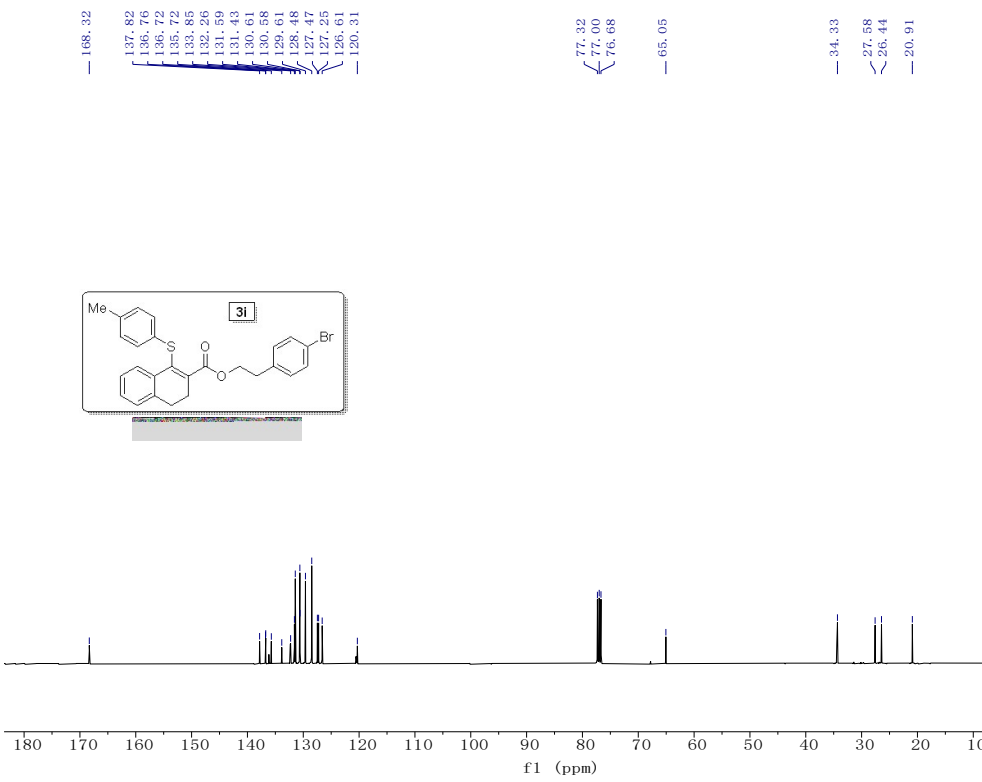
7.56
7.34
7.32
7.27
7.27
7.26
7.25
7.24
7.02
7.01
7.00
6.99
6.98
6.97
6.88
6.86
4.34
4.32
4.31
2.87
2.85
2.83
2.82
2.80
2.56
2.54
2.52
2.14
0.00
Me
S
O
O
Br
3i
1.01
1.00
2.00
6.00
2.01
2.00
4.00
2.01
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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135.72
133.85
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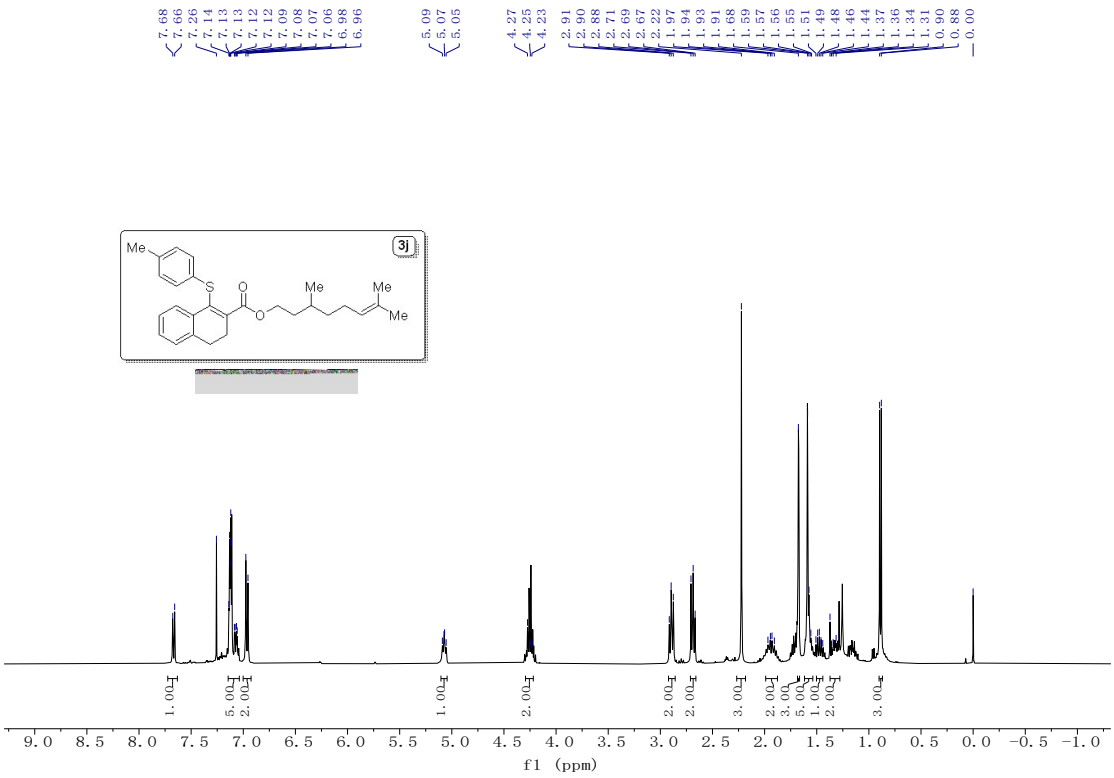
131.59
131.43
130.61
130.58
129.61
128.48
127.47
127.25
126.61
120.31
77.32
77.00
76.68
65.05
34.33
27.58
26.44
20.91
Me
S
O
O
Br
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.66
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7.12
7.12
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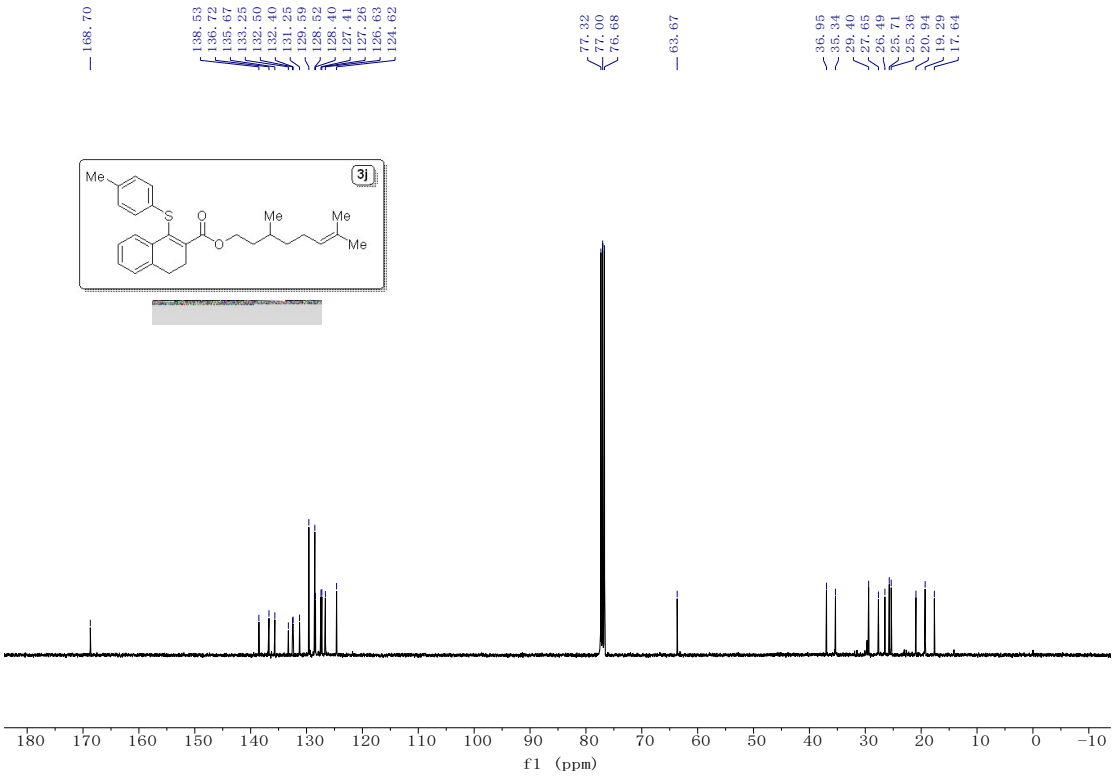
7.07
7.06
6.98
6.96
5.09
5.07
5.05
4.27
4.25
4.23
2.91
2.90
2.88
2.71
2.69
2.67
2.22
1.97
1.94
1.93
1.91
1.68
1.59
1.57
1.56
1.55
1.51
1.49
1.48
1.46
1.44
1.37
1.36
1.34
1.31
0.90
0.88
0.00
3j
Me
S
O
O
Me
Me
Me
1.00
5.00
2.00
1.00
2.00
2.00
2.00
3.00
2.00
3.00
5.00
1.00
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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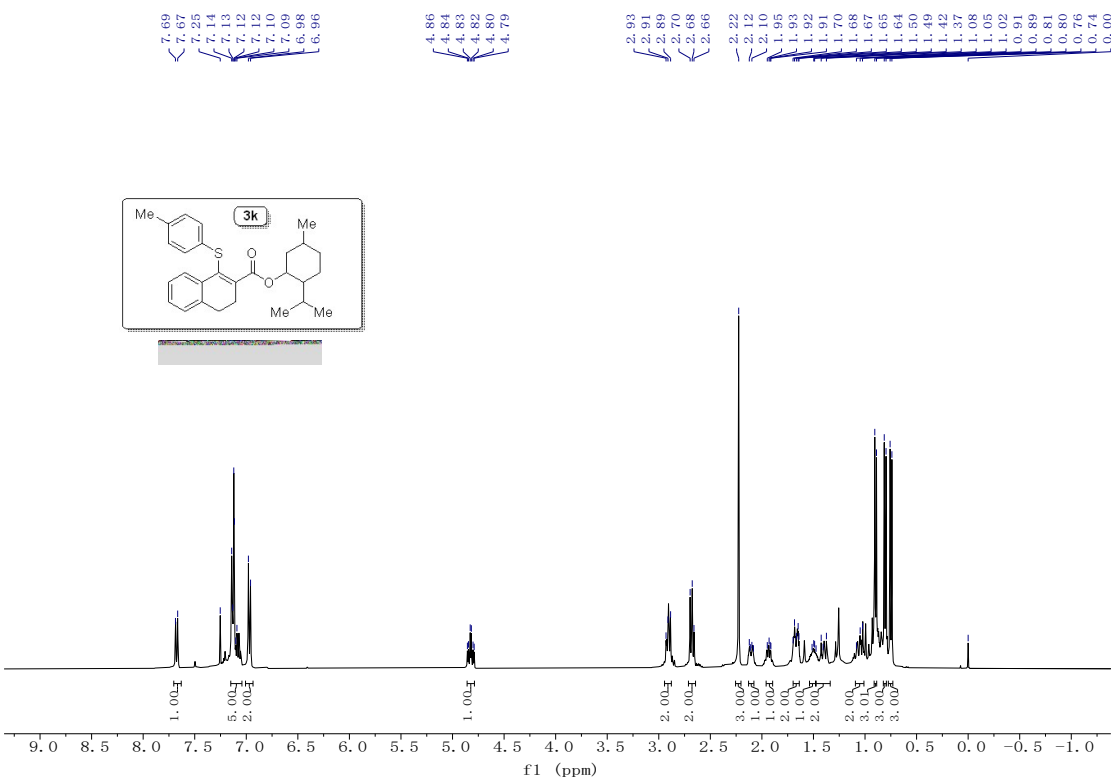
135.67
133.25
132.50
132.40
131.25
129.59
128.52
128.40
127.41
127.26
126.63
124.62
77.32
77.00
76.68
63.67
36.95
35.34
29.40
27.65
26.49
25.71
25.36
20.94
19.29
17.64
3j
Me
S
O
O
Me
Me
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.10
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4.83
4.82
4.80
4.79
2.93
2.91
2.89
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2.68
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2.22
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1.92
1.91
1.70
1.68
1.67
1.65
1.64
1.50
1.49
1.42
1.37
1.08
1.05
1.02
0.91
0.89
0.81
0.80
0.76
0.74
0.00
3k
Me
S
O
O
Me
Me
Me
1.00
5.00
2.00
1.00
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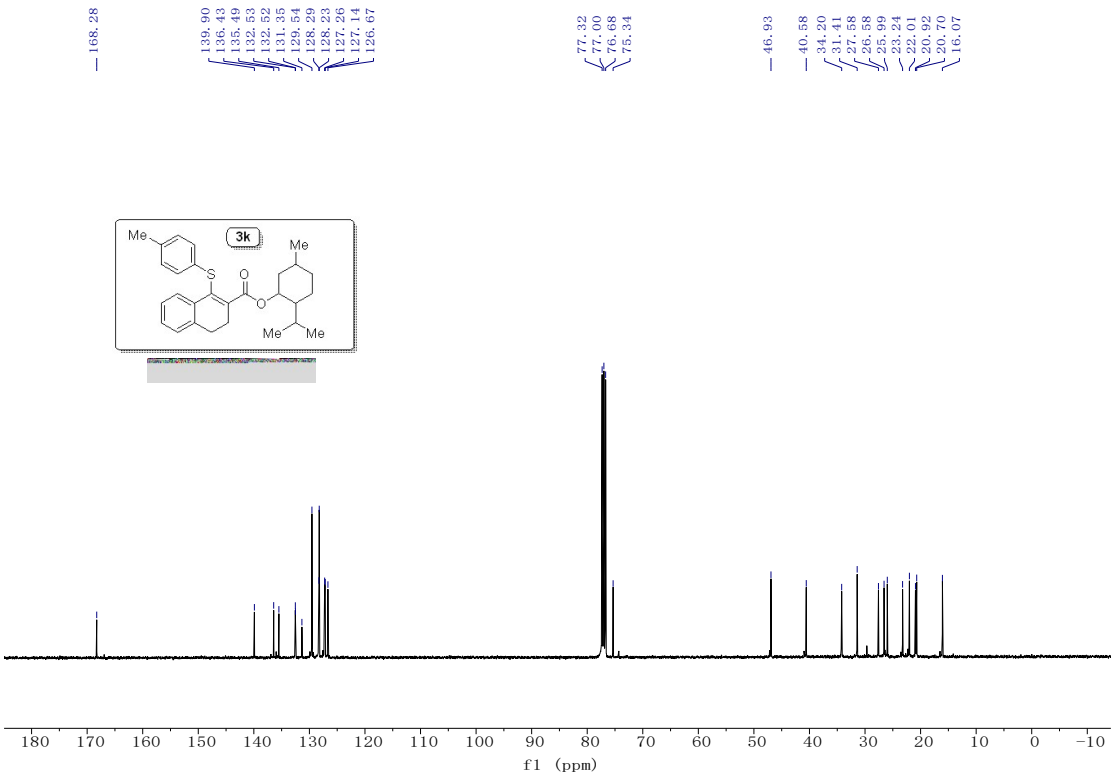
2.00
3.01
3.00
3.00
f1 (ppm)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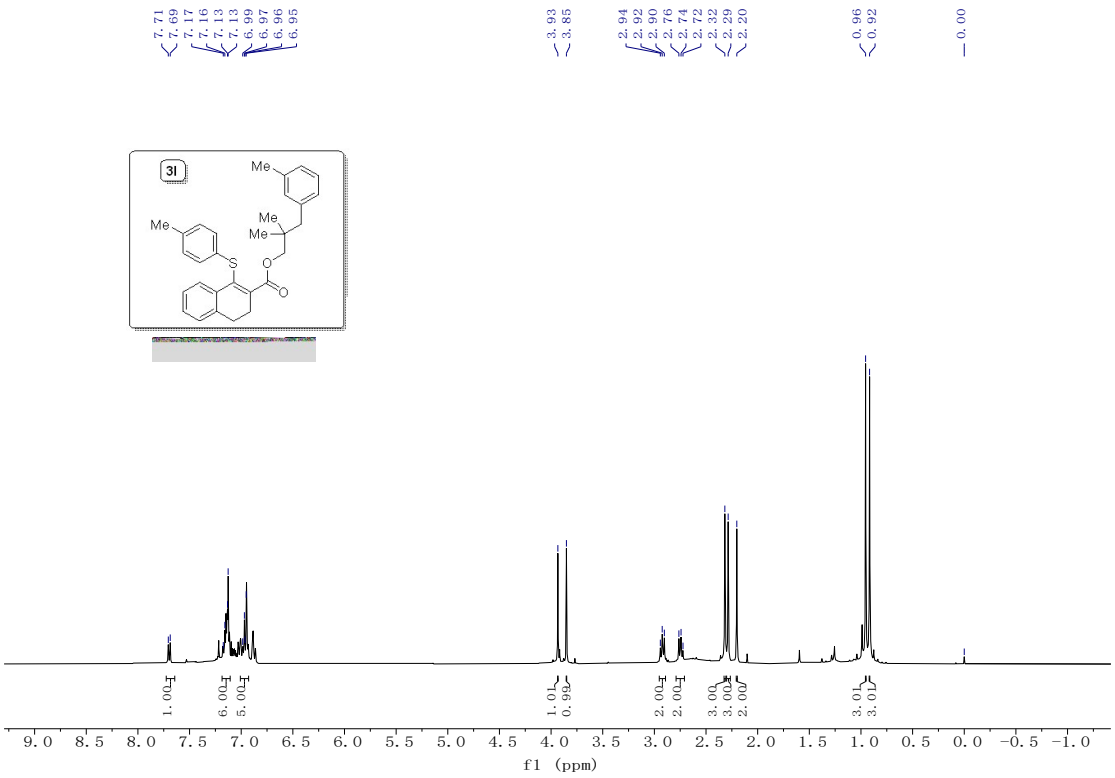
132.52
131.35
129.54
128.29
128.23
127.26
127.14
126.67
77.32
77.00
76.68
75.34
46.93
40.58
34.20
31.41
27.58
26.58
25.99
23.24
22.01
20.92
20.70
16.07
3k
Me
S
O
O
Me
Me
Me
f1 (ppm)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6.96
6.95
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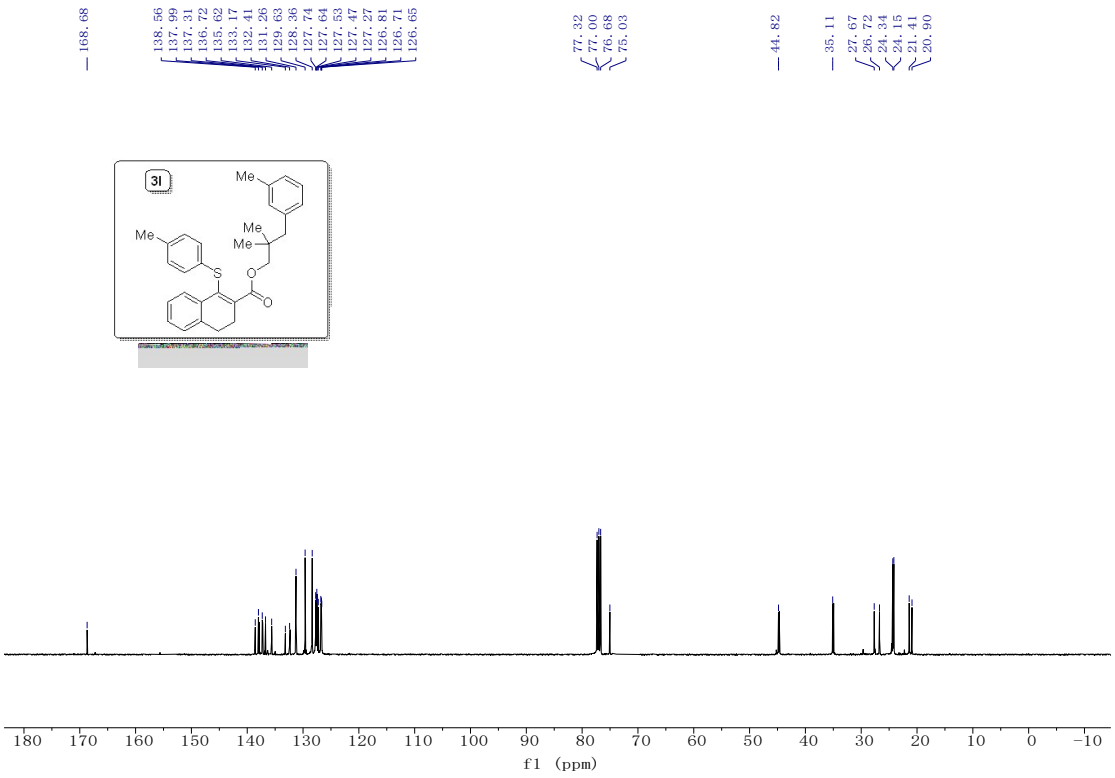
3.85
2.94
2.92
2.90
2.76
2.74
2.72
2.32
2.29
2.20
0.96
0.92
0.00
3l
Me
Me
Me
Me
S
O
O
1.00
6.00
5.00
1.01
0.99
2.00
2.00
3.00
3.00
2.00
3.01
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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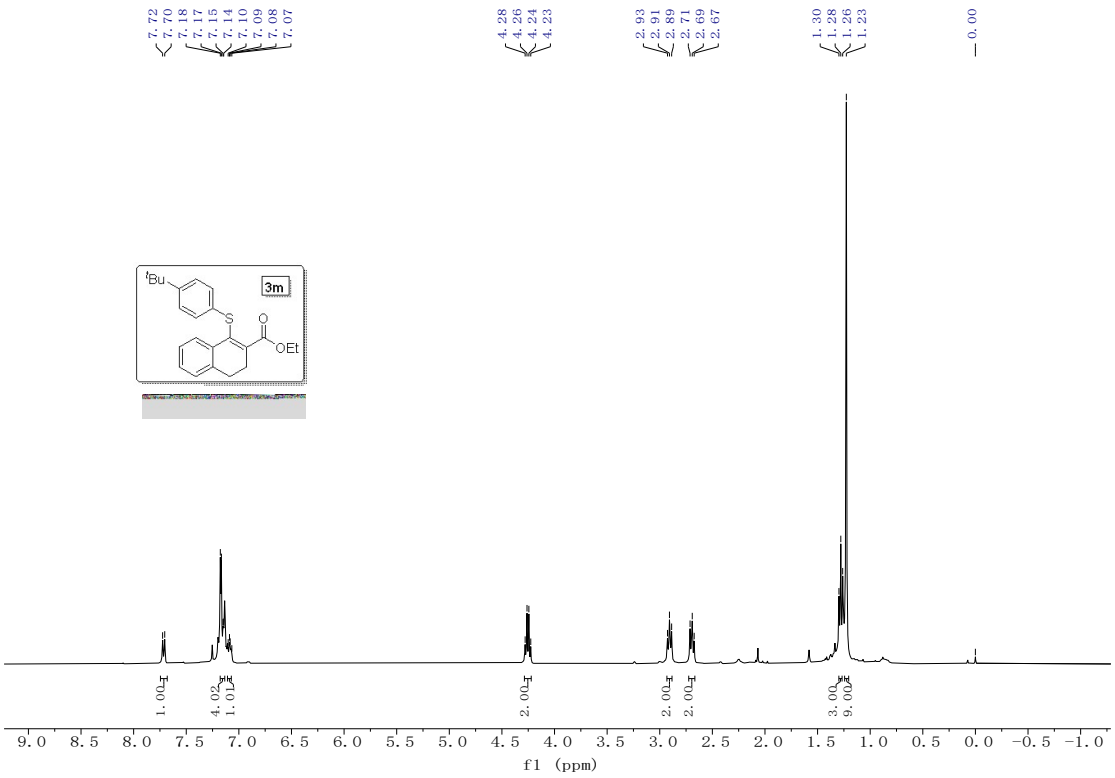
127.53
127.47
127.27
126.81
126.71
126.65
77.32
77.00
76.68
75.03
44.82
35.11
27.67
26.72
24.34
24.15
21.41
20.90
3l
Me
Me
Me
Me
S
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.70
7.18
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7.14
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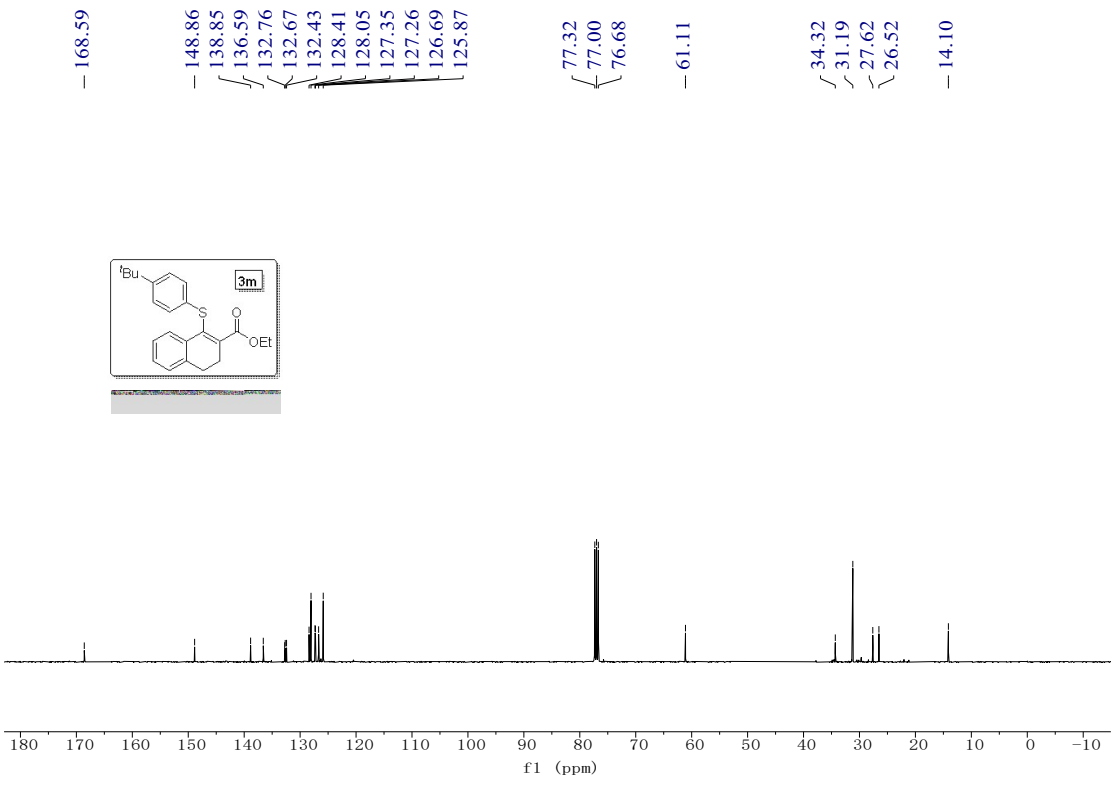
7.09
7.08
7.07
4.28
4.26
4.24
4.23
2.93
2.91
2.89
2.71
2.69
2.67
1.30
1.28
1.26
1.23
0.00
tBu
3m
S
O
OEt
1.00
4.02
1.01
2.00
2.00
2.00
3.00
9.00
f1 (ppm)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127.26
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125.87
77.32
77.00
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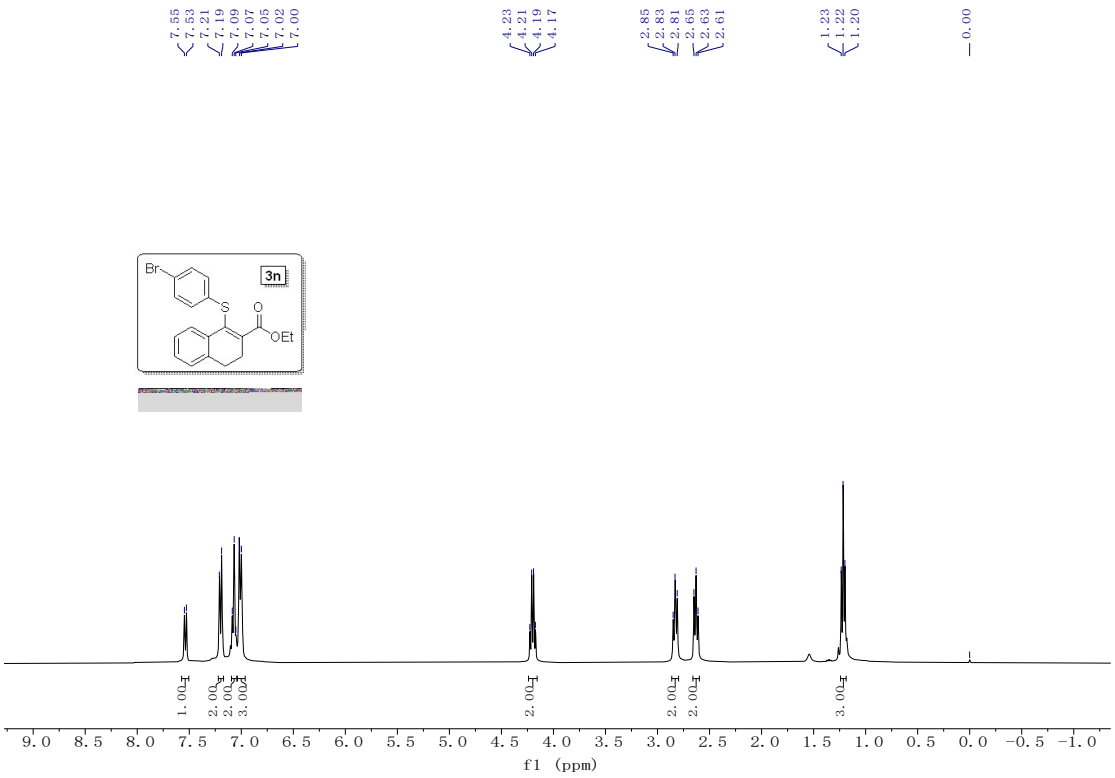
61.11
34.32
31.19
27.62
26.52
14.10
tBu
3m
S
O
OEt
f1 (ppm)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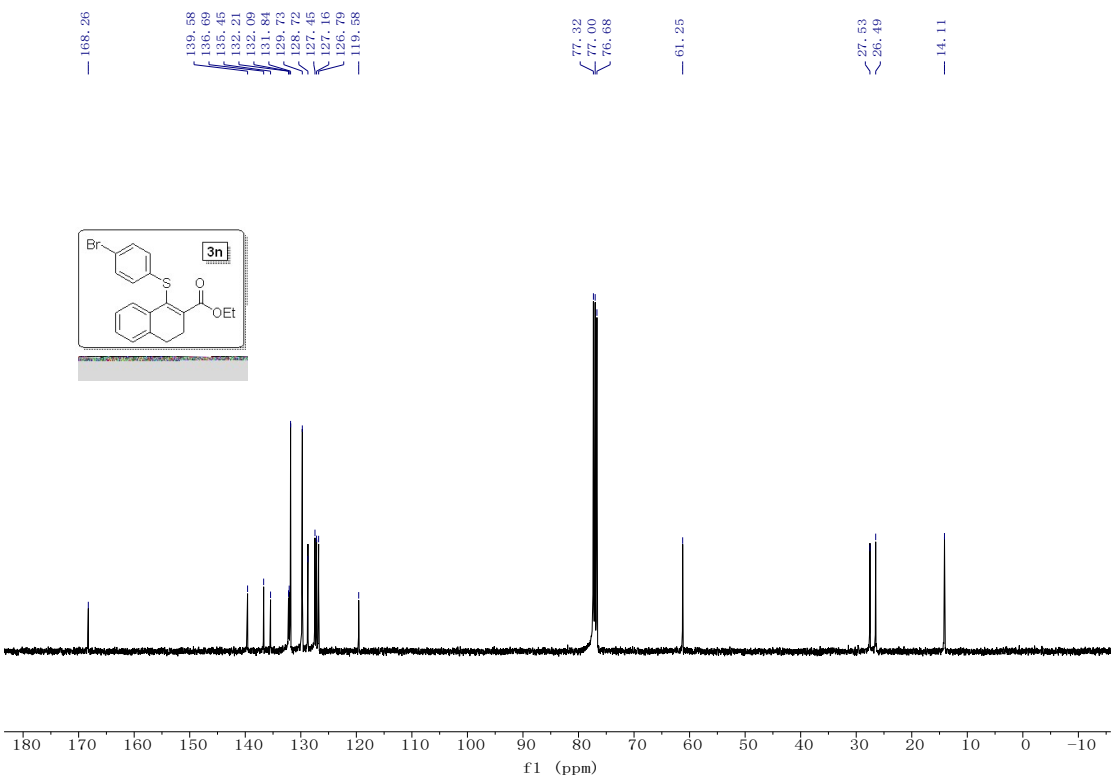
7.09
7.07
7.05
7.02
7.00
4.23
4.21
4.19
4.17
2.85
2.83
2.81
2.65
2.63
2.61
1.23
1.22
1.20
0.00
Br
S
O
OEt
3n
1.00
2.00
2.00
3.00
2.00
2.00
2.00
3.00
f1 (ppm)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119.58
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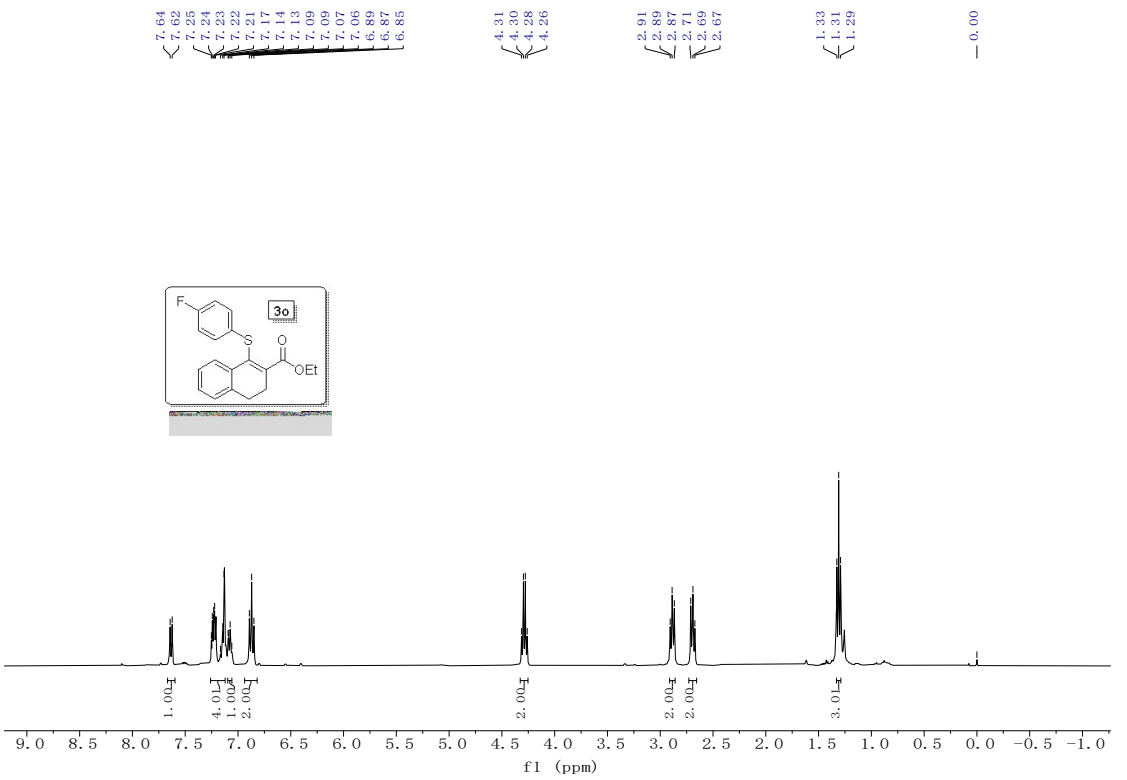
77.00
76.68
61.25
27.53
26.49
14.11
Br
S
O
OEt
3n
f1 (ppm)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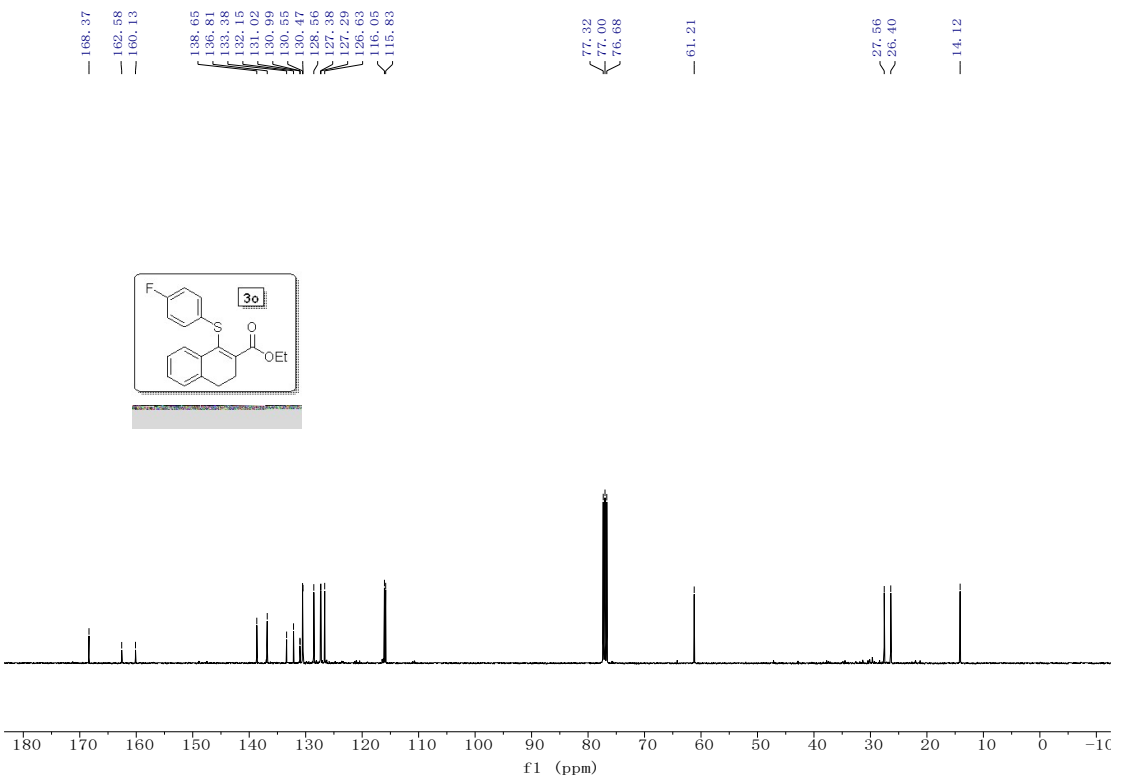
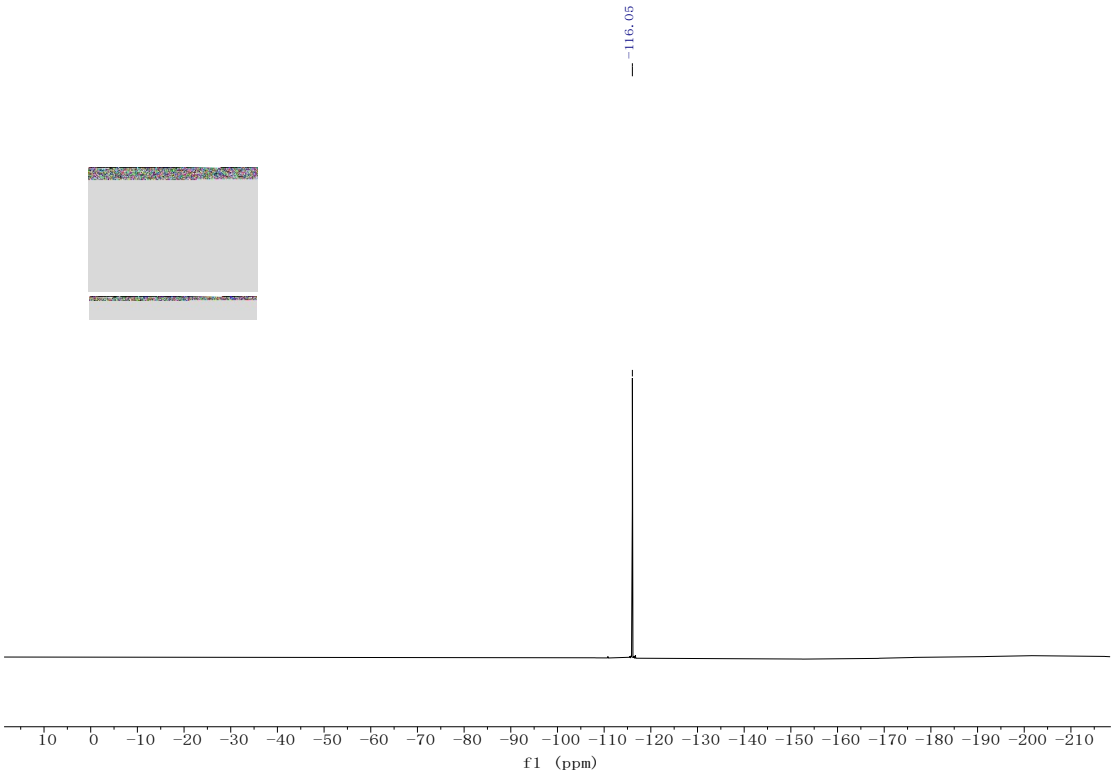
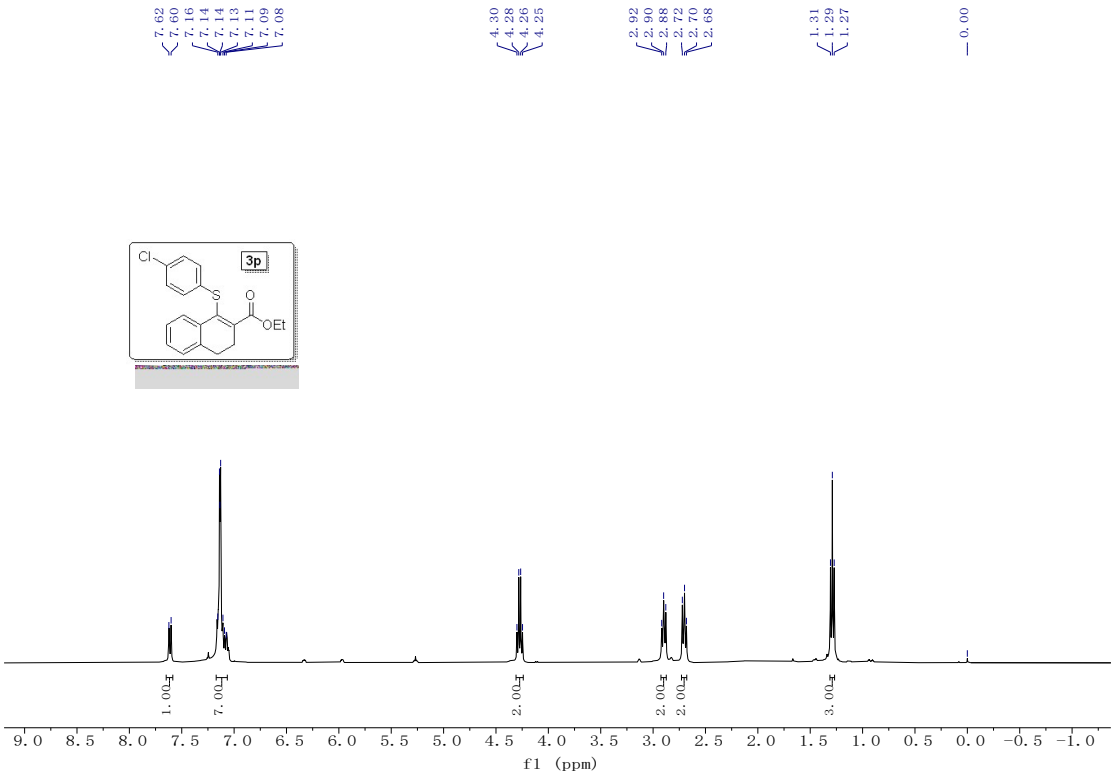
4.30
4.28
4.26
2.91
2.89
2.87
2.71
2.69
2.67
1.33
1.31
1.29
0.00
3o
F
S
O
OEt
1.00
4.01
1.00
2.00
2.00
2.00
2.00
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


168.37
162.58
160.13
138.65
136.81
133.38
132.15
131.02
130.99
130.55
130.47
128.56
127.38
127.29
126.63
116.05
115.83
77.32
77.00
76.68
61.21
27.56
26.40
14.12
3o
F
S
O
OEt
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-116.05
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.13
7.11
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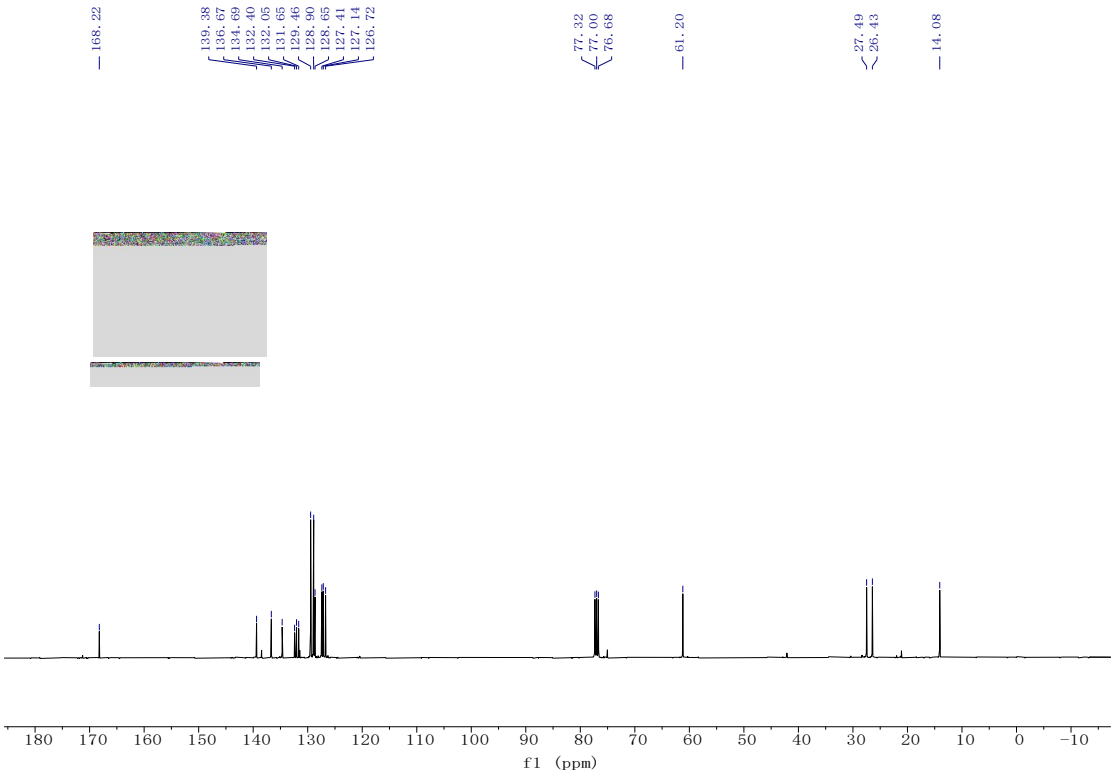
7.08
4.30
4.28
4.26
4.25
2.92
2.90
2.88
2.72
2.70
2.68
1.31
1.29
1.27
0.00
3p
Cl
S
O
OEt
1.00
7.00
2.00
2.00
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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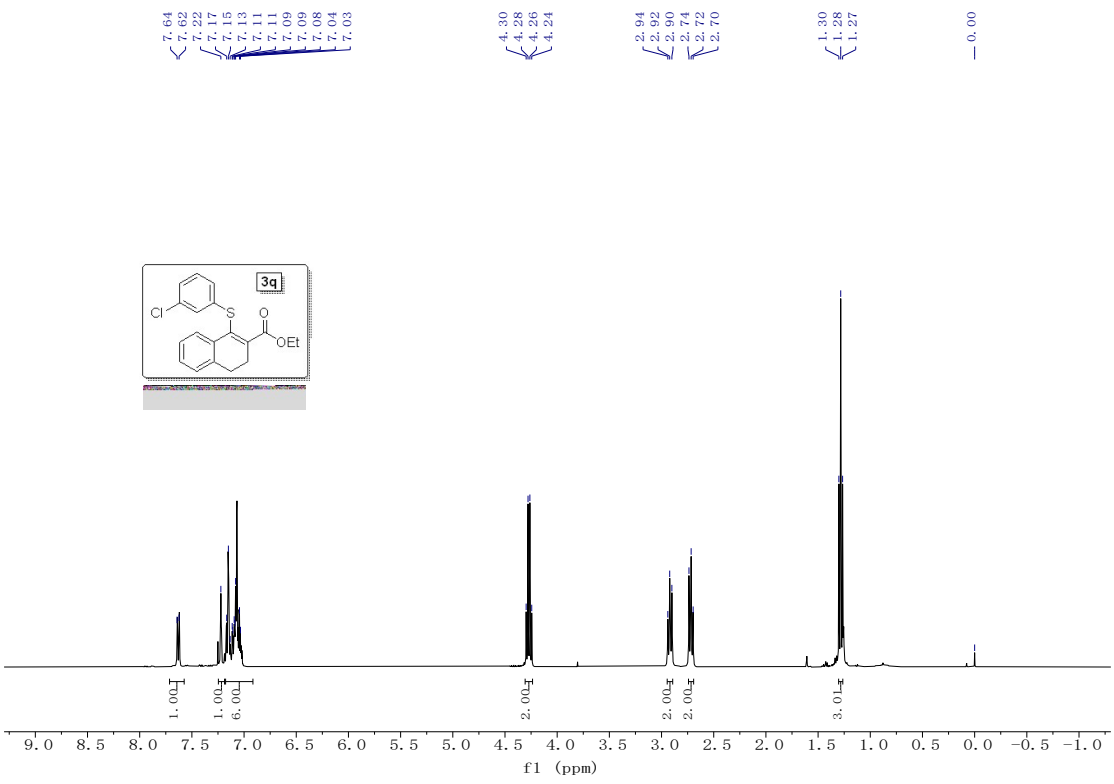
139.38
136.67
134.69
132.40
132.05
131.65
129.46
128.90
128.65
127.41
127.14
126.72
77.32
77.00
76.68
61.20
27.49
26.43
14.08
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.22
7.17
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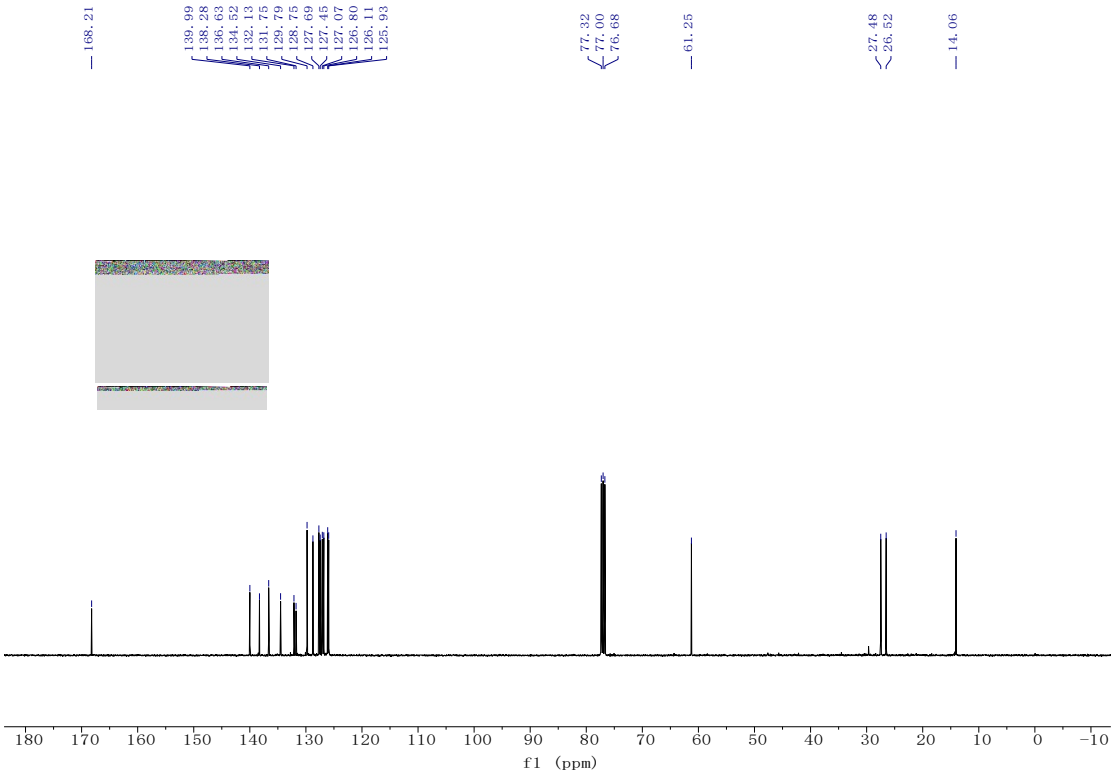
7.13
7.11
7.11
7.09
7.09
7.08
7.04
7.03
4.30
4.28
4.26
4.24
2.94
2.92
2.90
2.74
2.72
2.70
1.30
1.28
1.27
0.00
3q
Cl
S
O
OEt
1.00
1.00
6.00
2.00
2.00
2.00
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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139.99
138.28
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132.13
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129.79
128.75
127.69
127.45
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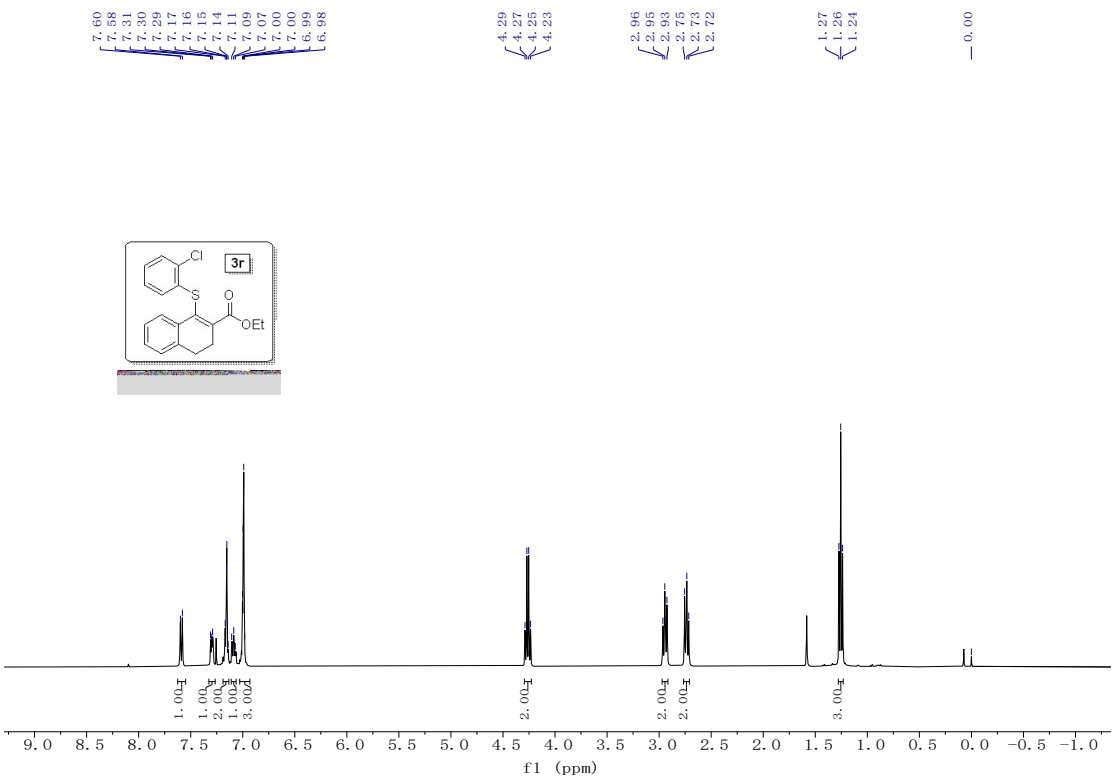
61.25
27.48
26.52
14.06
f1 (ppm)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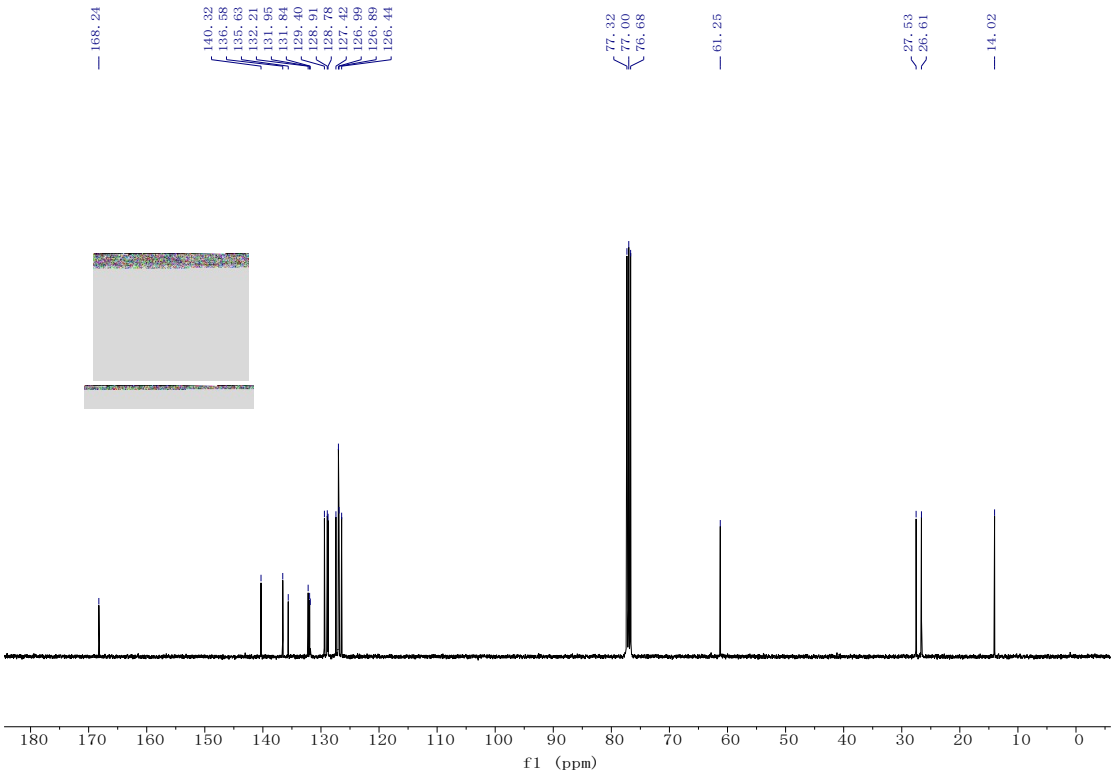
7.17
7.16
7.15
7.14
7.11
7.09
7.07
7.00
7.00
6.99
6.98
4.29
4.27
4.25
4.23
2.96
2.95
2.93
2.75
2.73
2.72
1.27
1.26
1.24
0.00
3r
Cl
S
O
OEt
1.00
1.00
2.00
1.00
3.00
2.00
2.00
2.00
3.00
f1 (ppm)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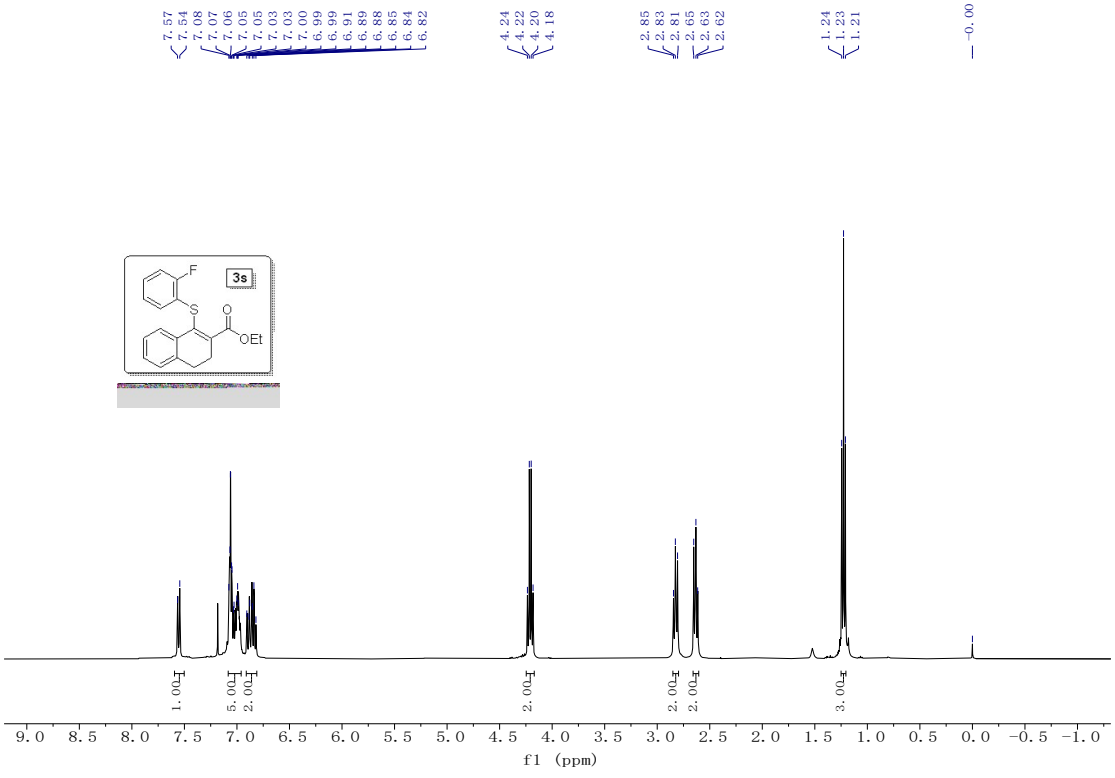
136.58
135.63
132.21
131.95
131.84
129.40
128.91
128.78
127.42
126.99
126.89
126.44
77.32
77.00
76.68
61.25
27.53
26.61
14.02
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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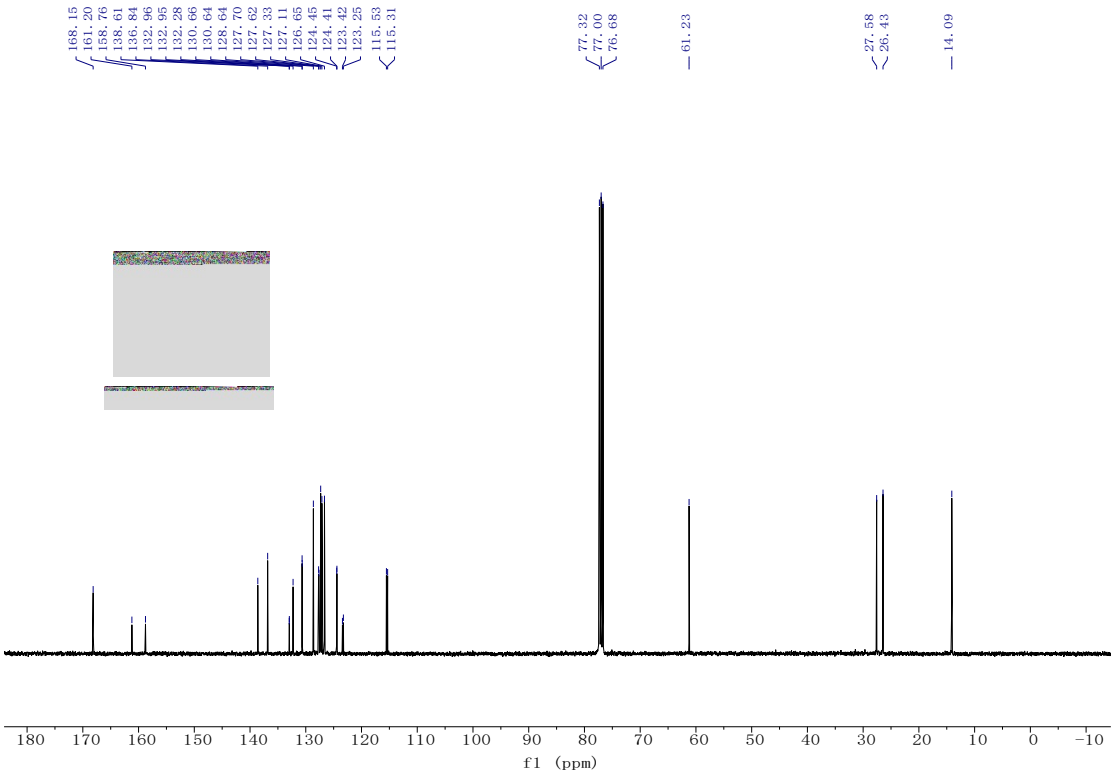
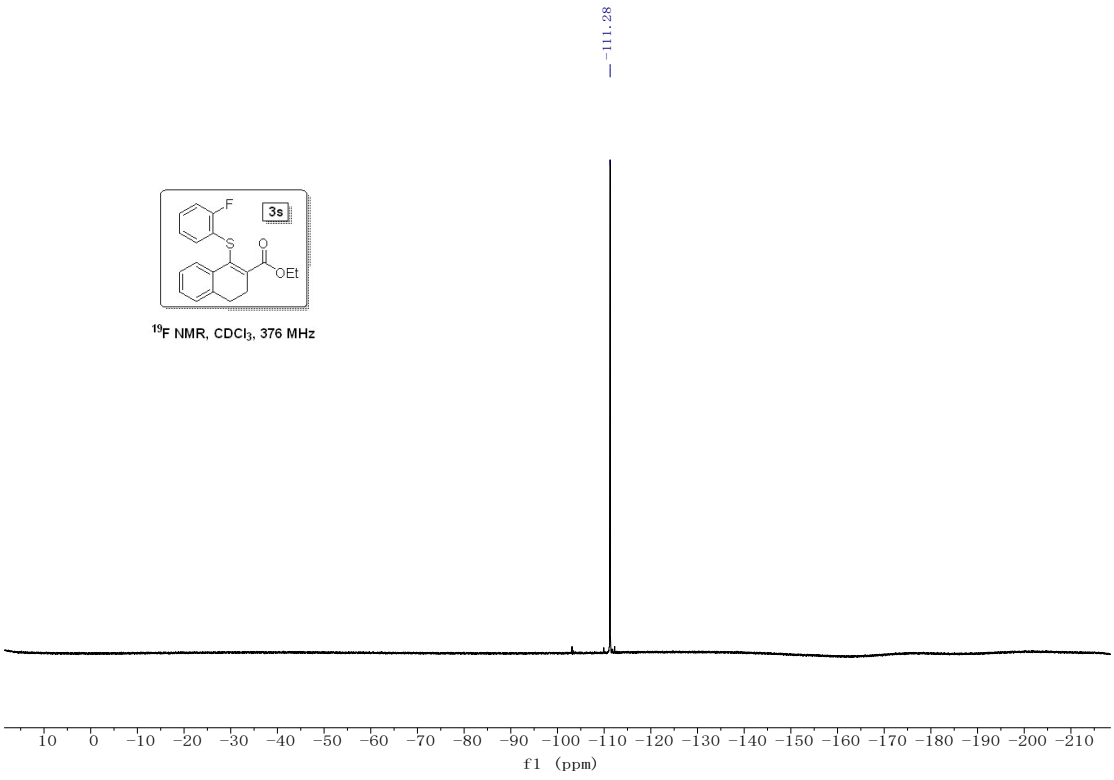
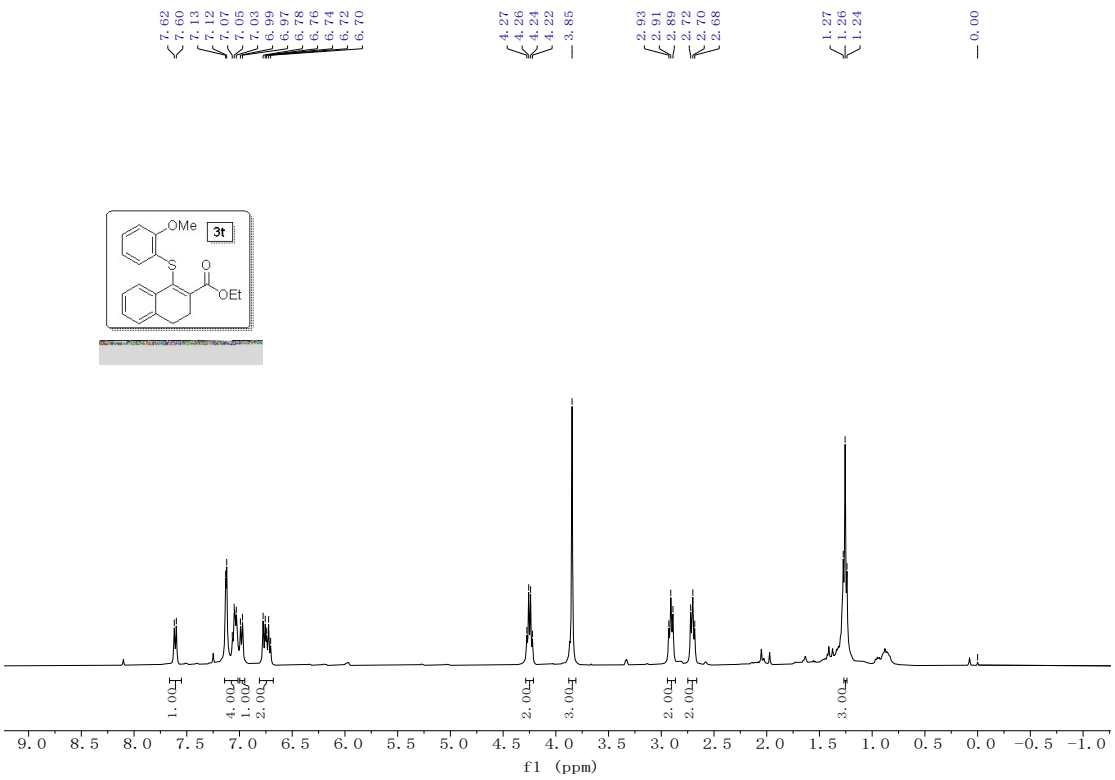
7.05
7.03
7.03
7.00
6.99
6.99
6.91
6.89
6.88
6.85
6.84
6.82
4.24
4.22
4.20
4.18
2.85
2.83
2.81
2.65
2.63
2.62
1.24
1.23
1.21
-0.00
F
S
O
OEt
3s
1.00
5.00
2.00
2.00
2.00
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)





^{19}F NMR, $CDCl_3$, 376 MHz


7.62
7.60
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7.12
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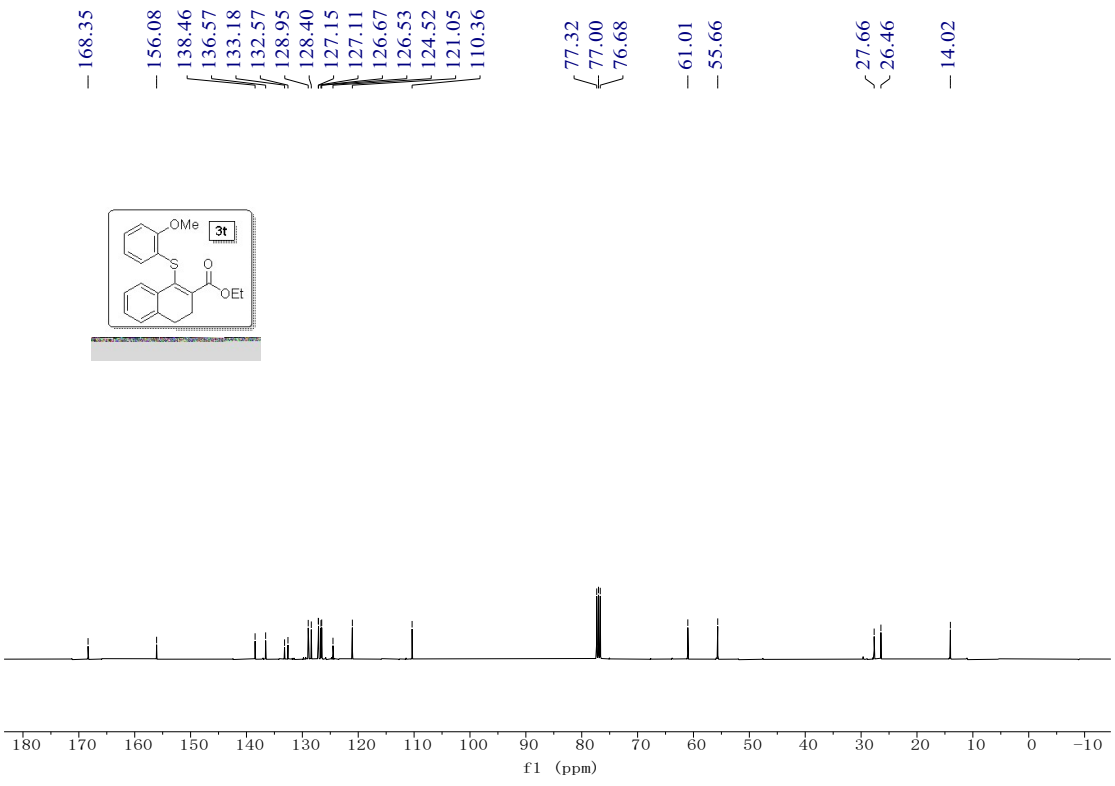
7.05
7.03
6.99
6.97
6.78
6.76
6.74
6.72
6.70
4.27
4.26
4.24
4.22
3.85
2.93
2.91
2.89
2.72
2.70
2.68
1.27
1.26
1.24
0.00
OMe
3t
S
O
OEt
1.00
4.00
1.00
2.00
2.00
3.00
2.00
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


168.35
156.08
138.46
136.57
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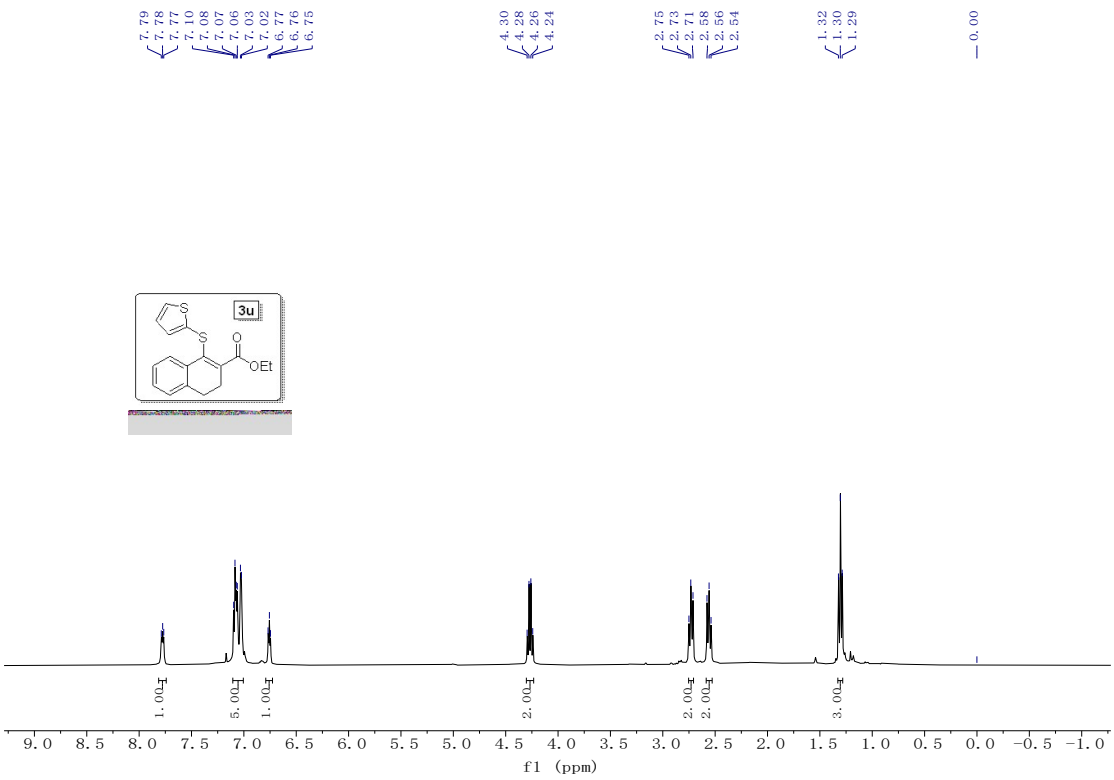
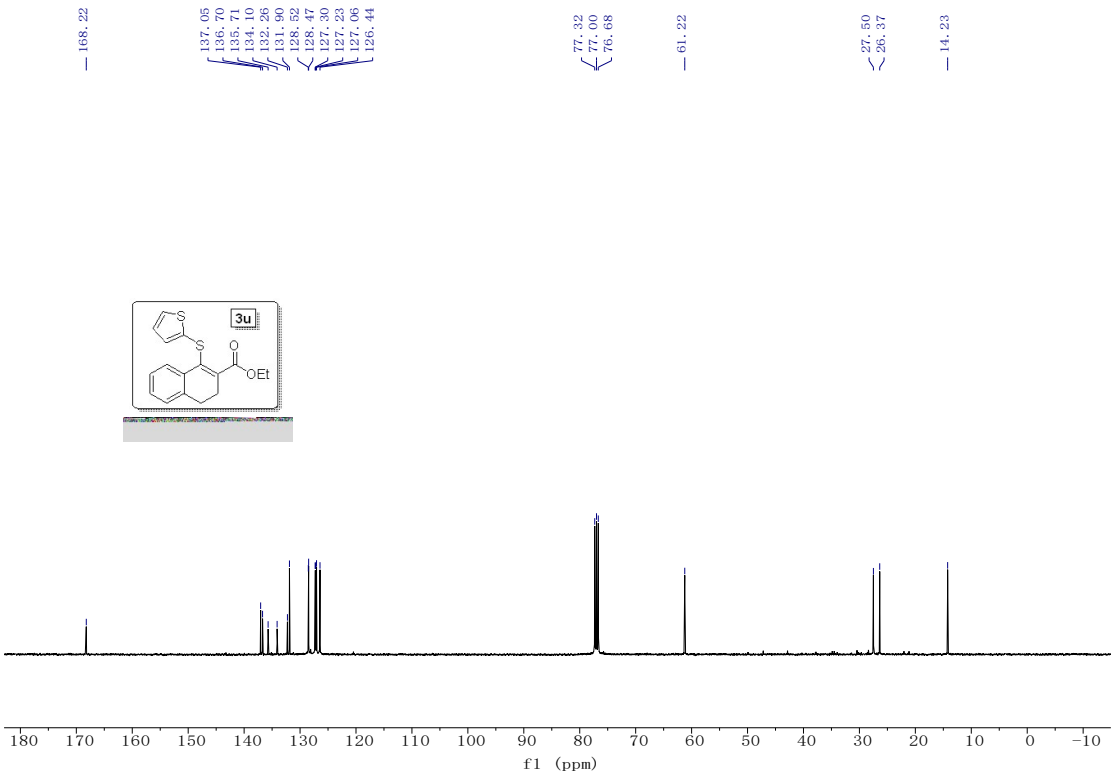
132.57
128.95
128.40
127.15
127.11
126.67
126.53
124.52
121.05
110.36
77.32
77.00
76.68
61.01
55.66
27.66
26.46
14.02
OMe
3t
S
O
OEt
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.79
7.78
7.77
7.10
7.08
7.07
7.06
7.03
7.02
6.77
6.76
6.75
4.30
4.28
4.26
4.24
2.75
2.73
2.71
2.58
2.56
2.54
1.32
1.30
1.29
0.00
3u
OEt
1.00
5.00
1.00
2.00
2.00
2.00
3.00
f1 (ppm)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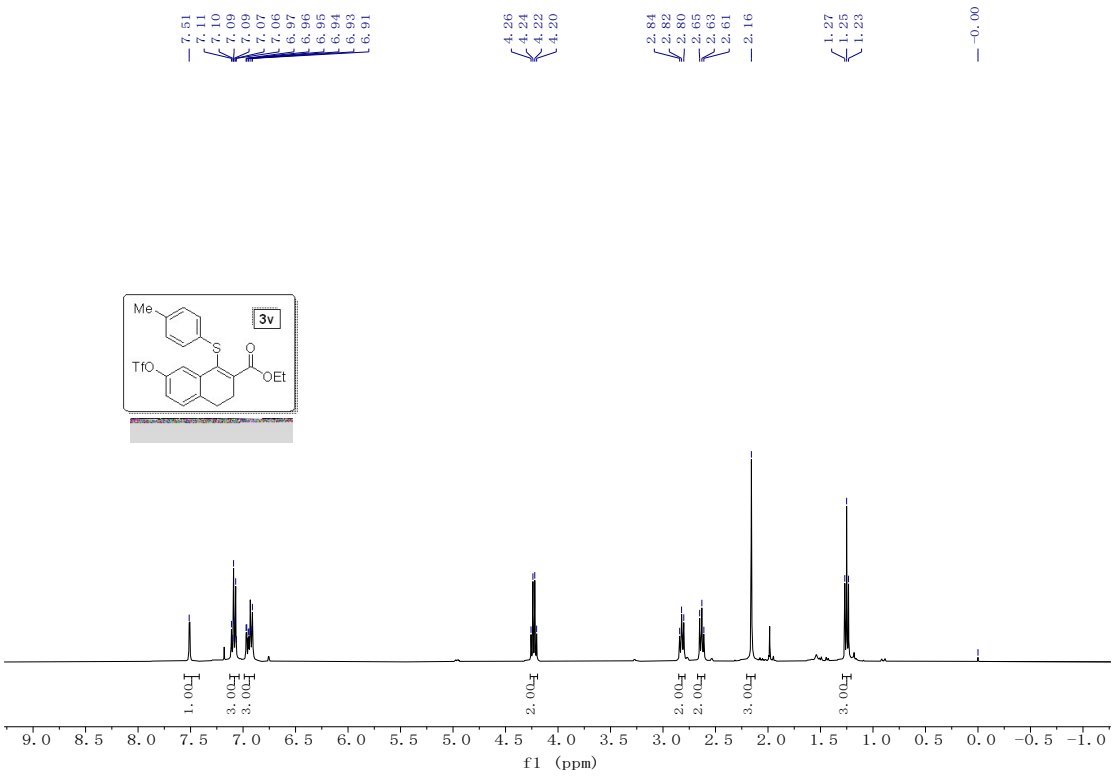
137.05
136.70
135.71
134.10
132.26
131.90
128.52
128.47
127.30
127.23
127.06
126.44
77.32
77.00
76.68
61.22
27.50
26.37
14.23
3u
OEt
f1 (ppm)


7.51
7.11
7.10
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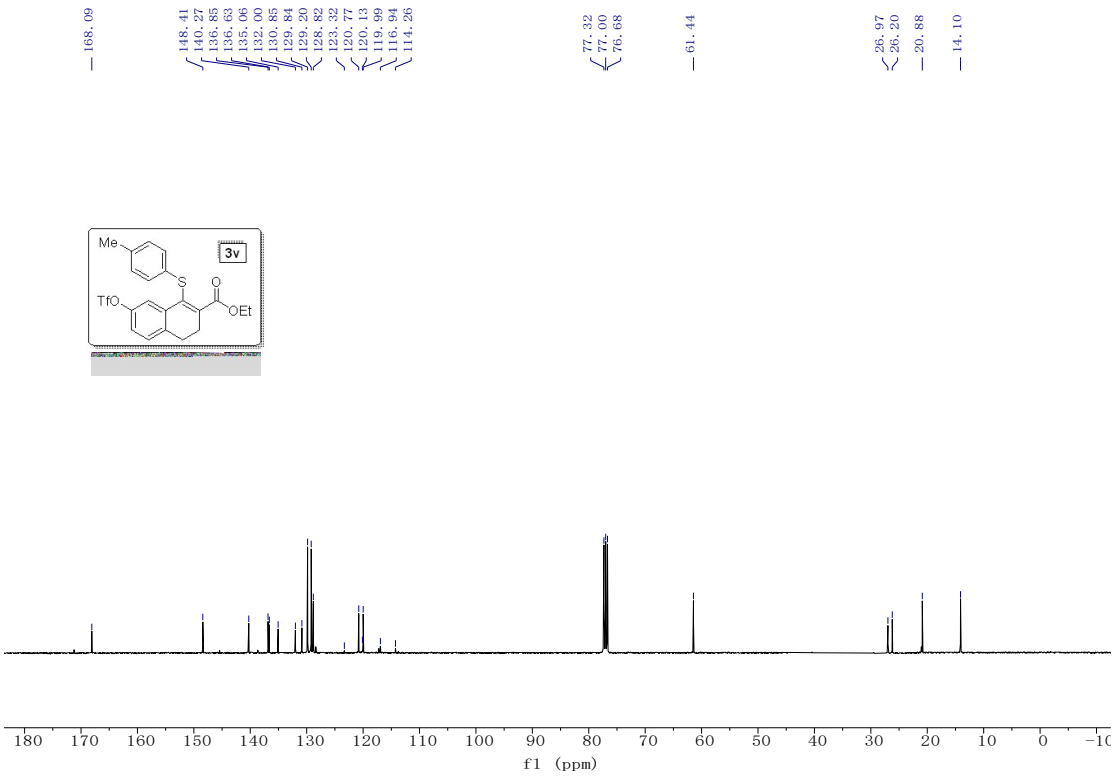
7.09
7.07
7.06
6.97
6.96
6.95
6.94
6.93
6.91
4.26
4.24
4.22
4.20
2.84
2.82
2.80
2.65
2.63
2.61
2.16
1.27
1.25
1.23
0.00
Me
3v
S
O
TfO
OEt
1.00
3.00
3.00
2.00
2.00
2.00
3.00
3.00
f1 (ppm)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148.41
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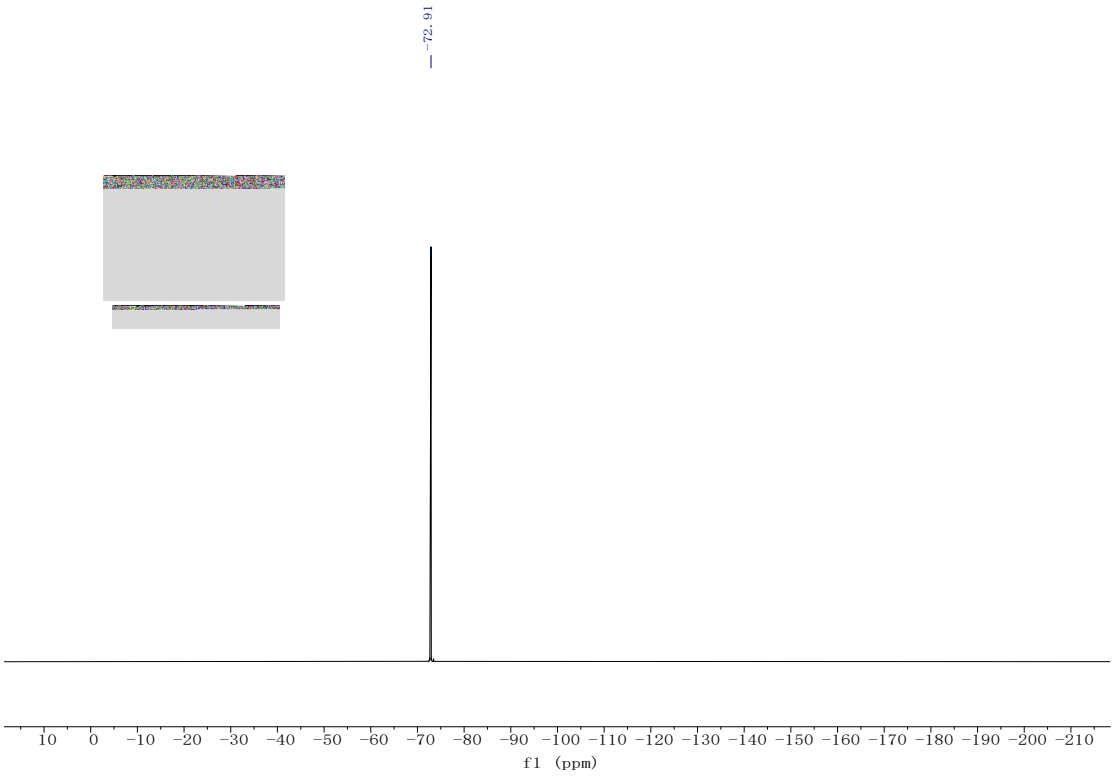
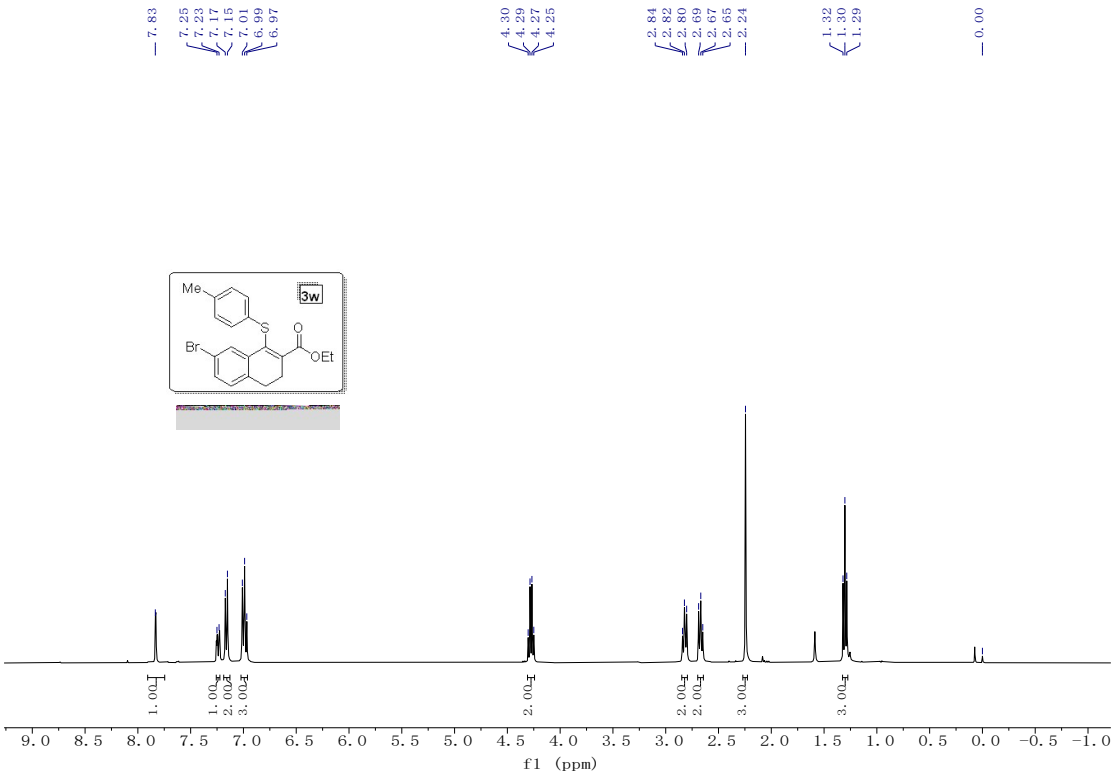
136.85
136.63
135.06
132.00
130.85
129.84
129.20
128.82
123.32
120.77
120.13
119.99
116.94
114.26
77.32
77.00
76.68
61.44
26.97
26.20
20.88
14.10
Me
3v
S
O
TfO
OEt
f1 (ppm)


-72.91
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.83
7.25
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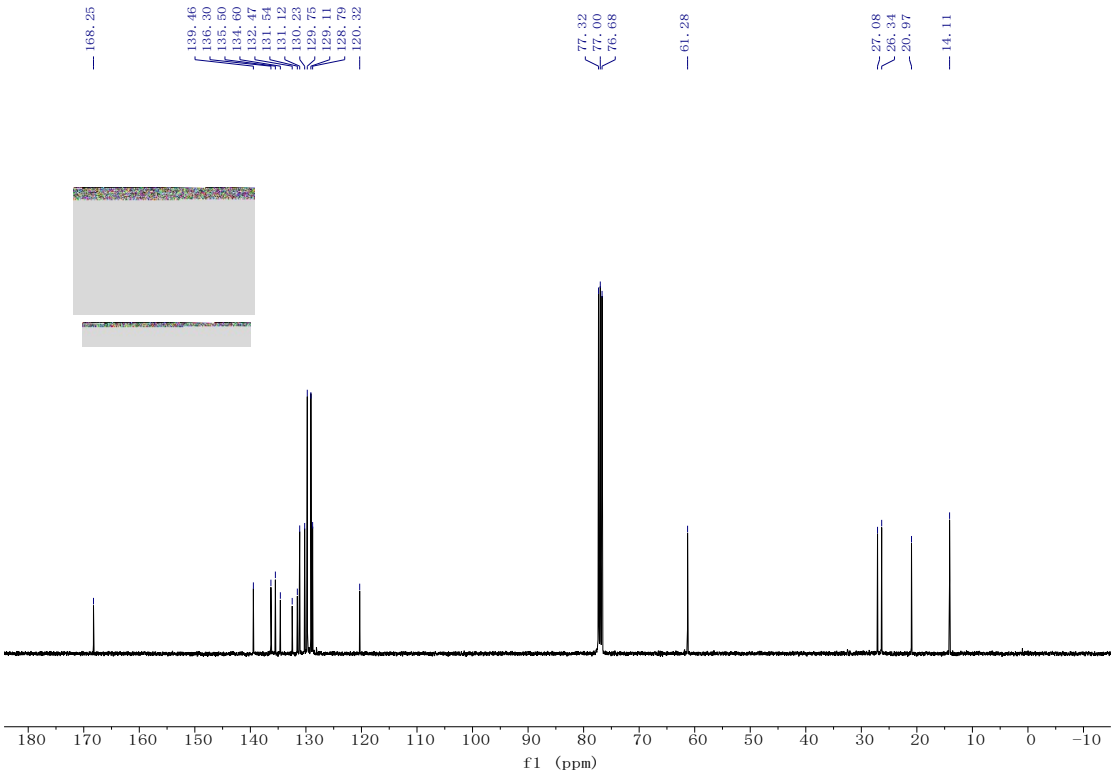
7.15
7.01
6.99
6.97
4.30
4.29
4.27
4.25
2.84
2.82
2.80
2.69
2.67
2.65
2.24
1.32
1.30
1.29
0.00
Me
3w
S
O
Br
OEt
1.00
1.00
2.00
3.00
2.00
2.00
2.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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139.46
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132.47
131.54
131.12
130.23
129.75
129.11
128.79
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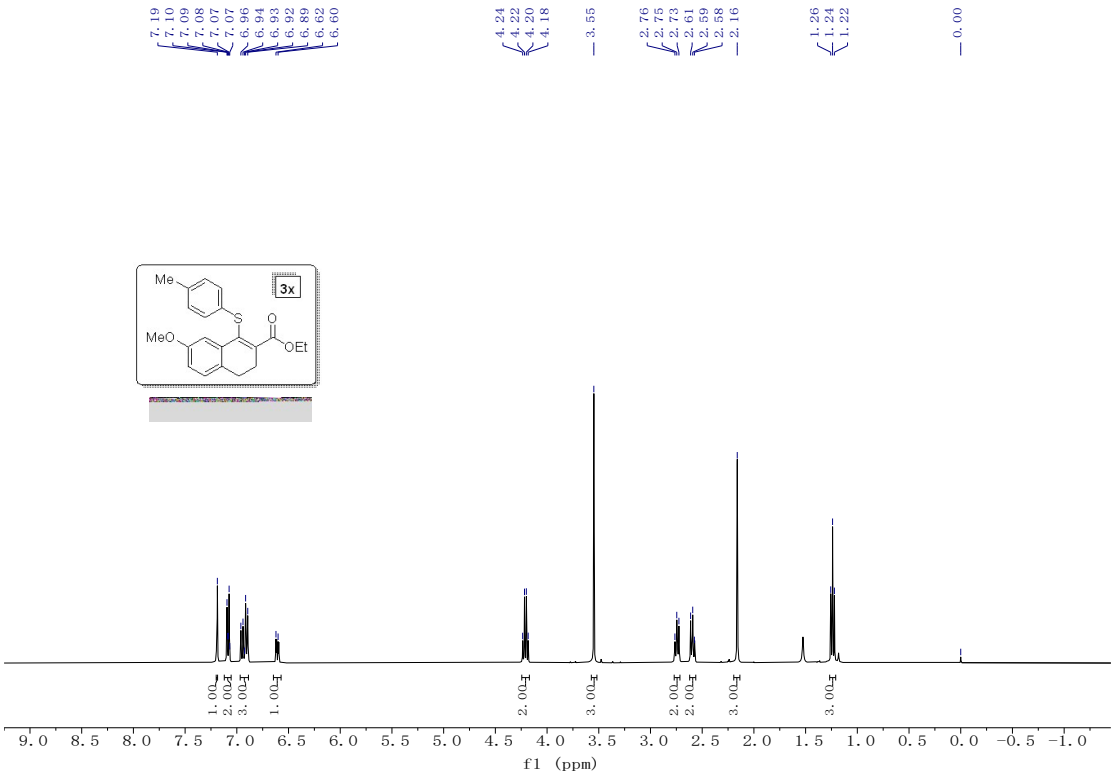
77.32
77.00
76.68
61.28
27.08
26.34
20.97
14.11
f1 (ppm)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7.07
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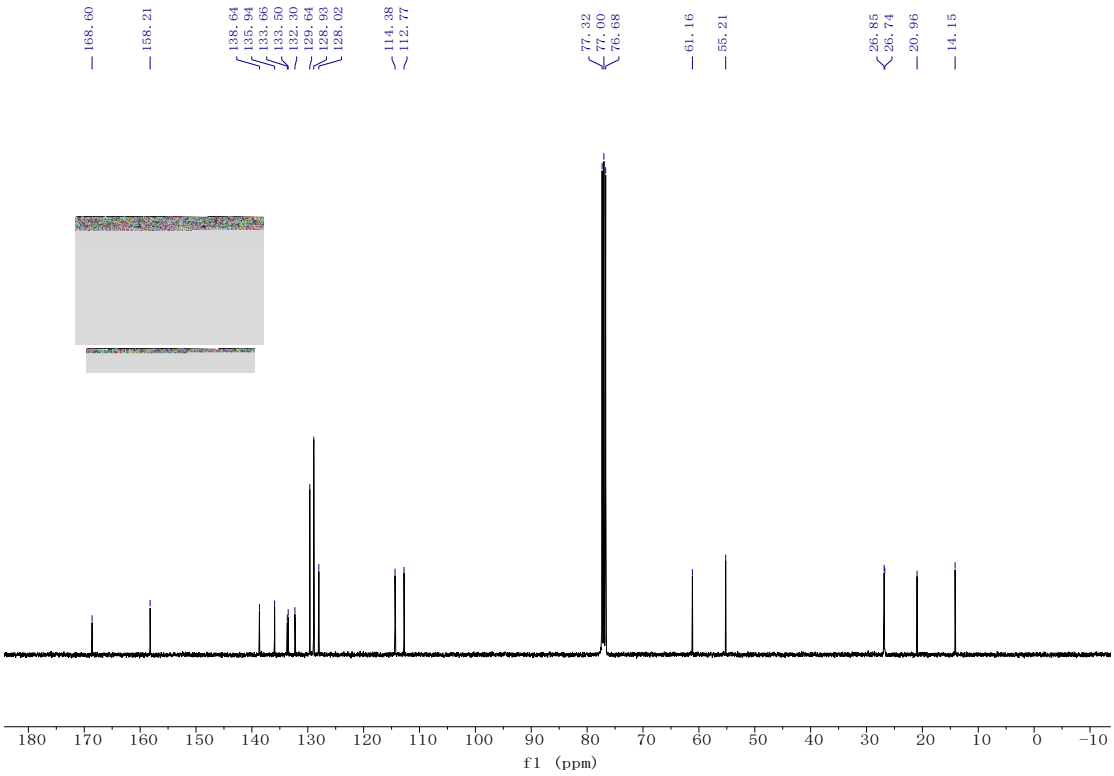
6.94
6.93
6.92
6.89
6.62
6.60
4.24
4.22
4.20
4.18
3.55
2.76
2.75
2.73
2.61
2.59
2.58
2.16
1.26
1.24
1.22
0.00
Me
3x
MeO
S
O
OEt
1.00
2.00
3.00
1.00
2.00
3.00
2.00
2.00
3.00
3.00
f1 (ppm)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129.64
128.93
128.02
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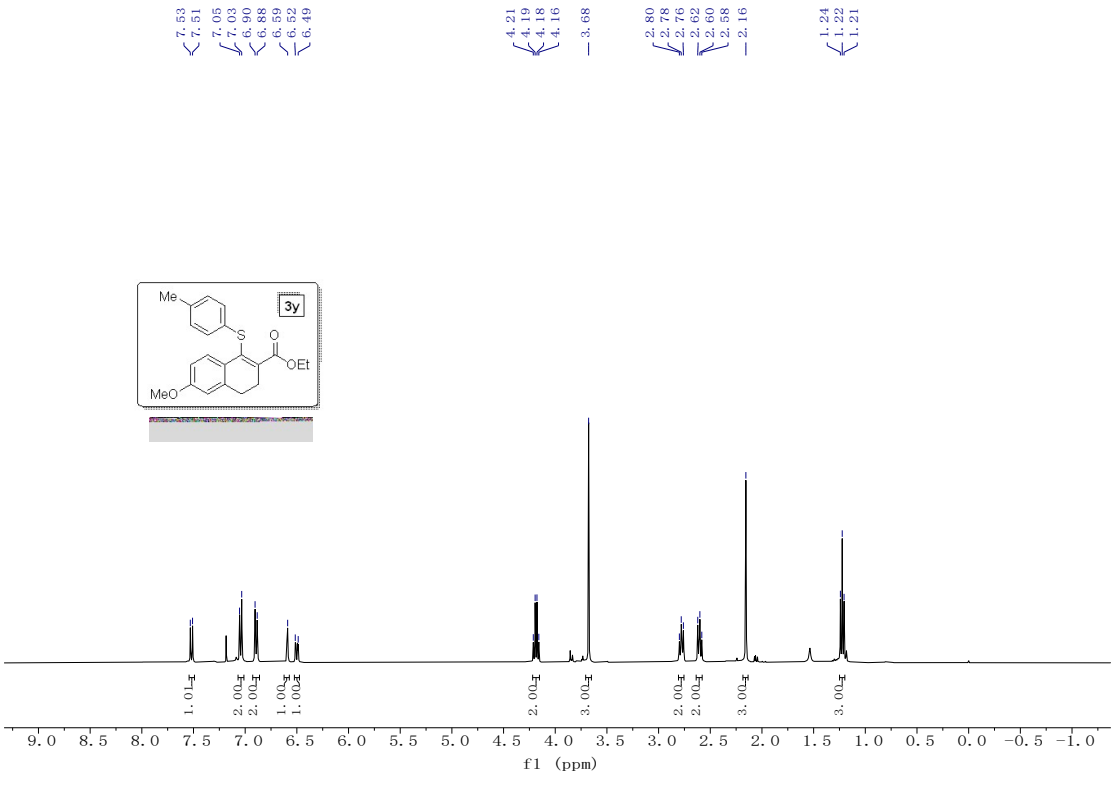
77.00
76.68
61.16
55.21
26.85
26.74
20.96
14.15
f1 (ppm)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6.88
6.59
6.52
6.49
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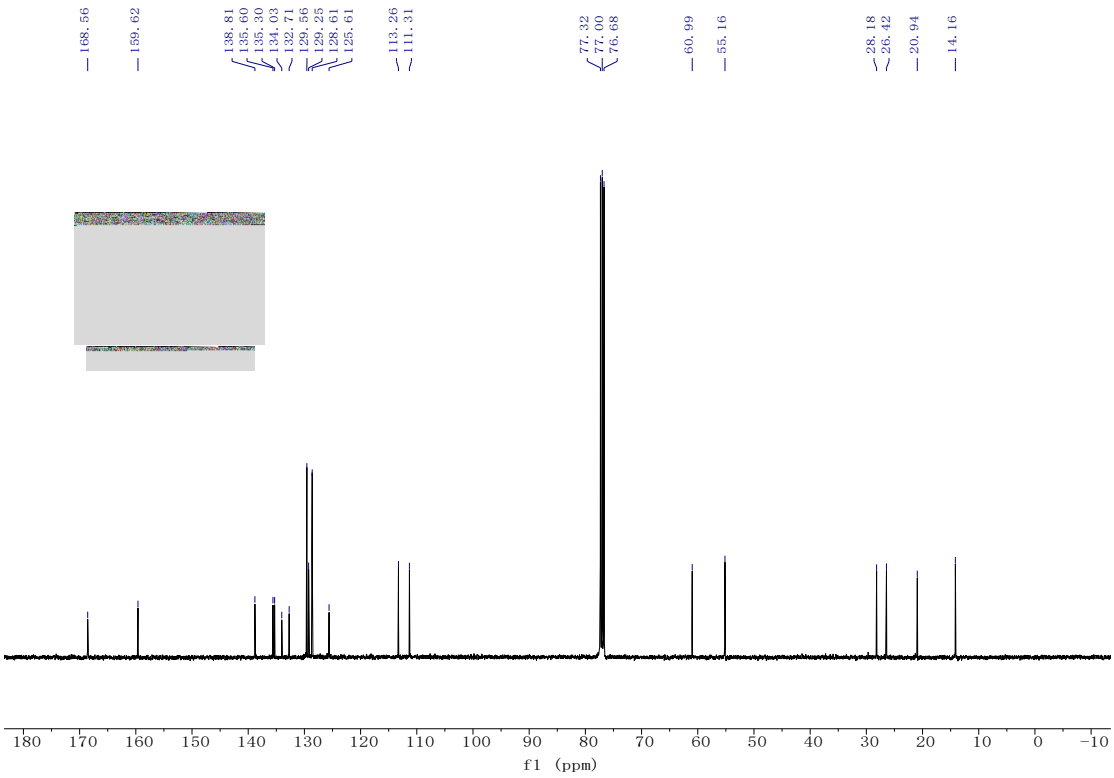
4.19
4.18
4.16
3.68
2.80
2.78
2.76
2.62
2.60
2.58
2.16
1.24
1.22
1.21
3y
Me
S
O
OEt
MeO
1.01
2.00
2.00
1.00
1.00
2.00
3.00
2.00
2.00
3.00
3.00
f1 (ppm)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128.61
125.61
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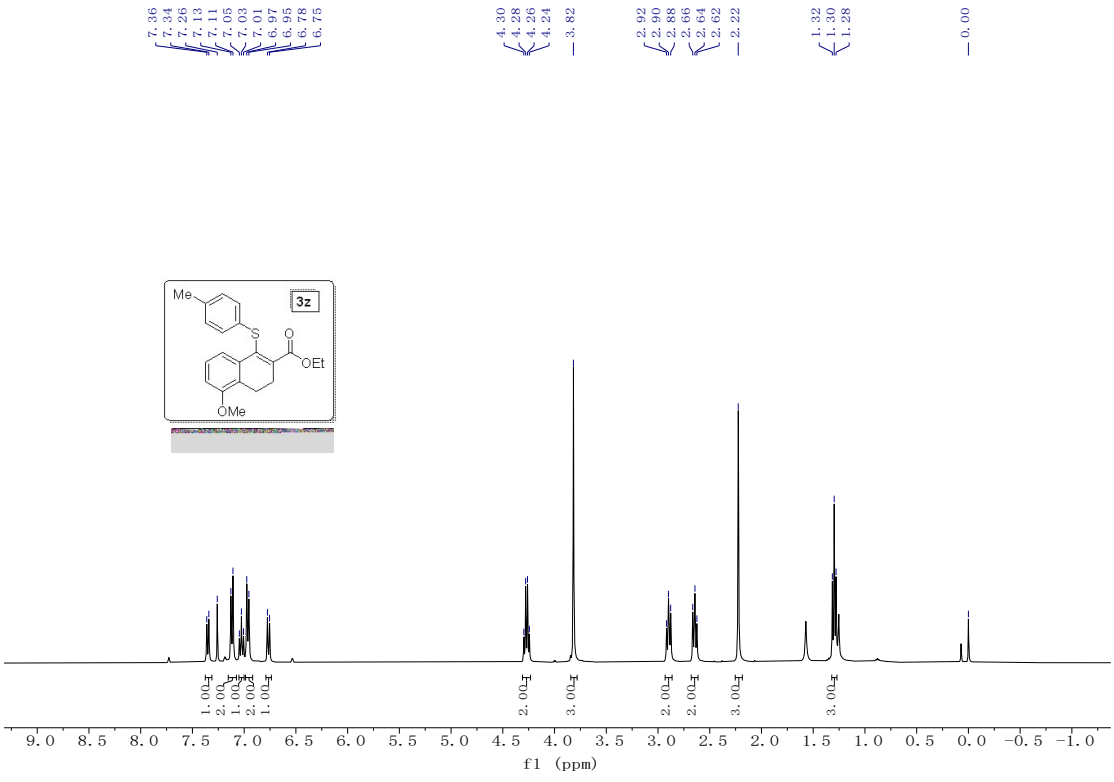
76.68
60.99
55.16
28.18
26.42
20.94
14.16
f1 (ppm)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7.03
7.01
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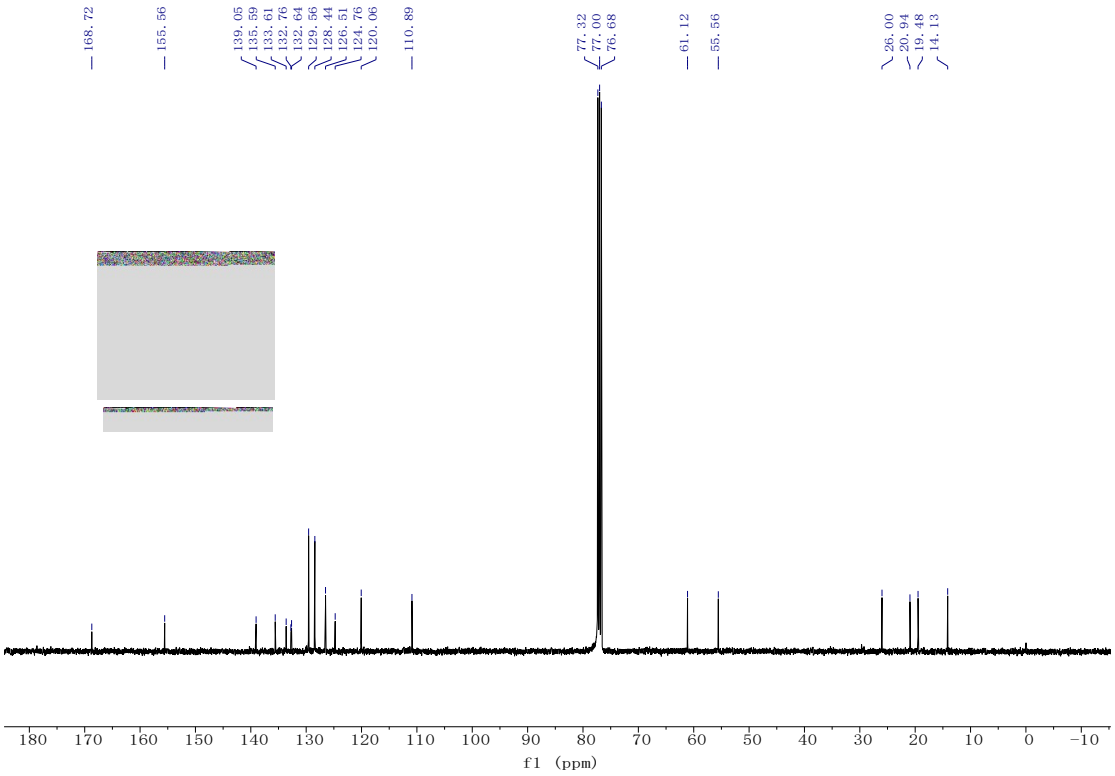
6.95
6.78
6.75
4.30
4.28
4.26
4.24
3.82
2.92
2.90
2.88
2.66
2.64
2.62
2.22
1.32
1.30
1.28
0.00
3z
Me
S
O
OEt
OMe
1.00
2.00
1.00
2.00
1.00
2.00
3.00
2.00
2.00
3.00
3.00
f1 (ppm)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129.56
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126.51
124.76
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77.00
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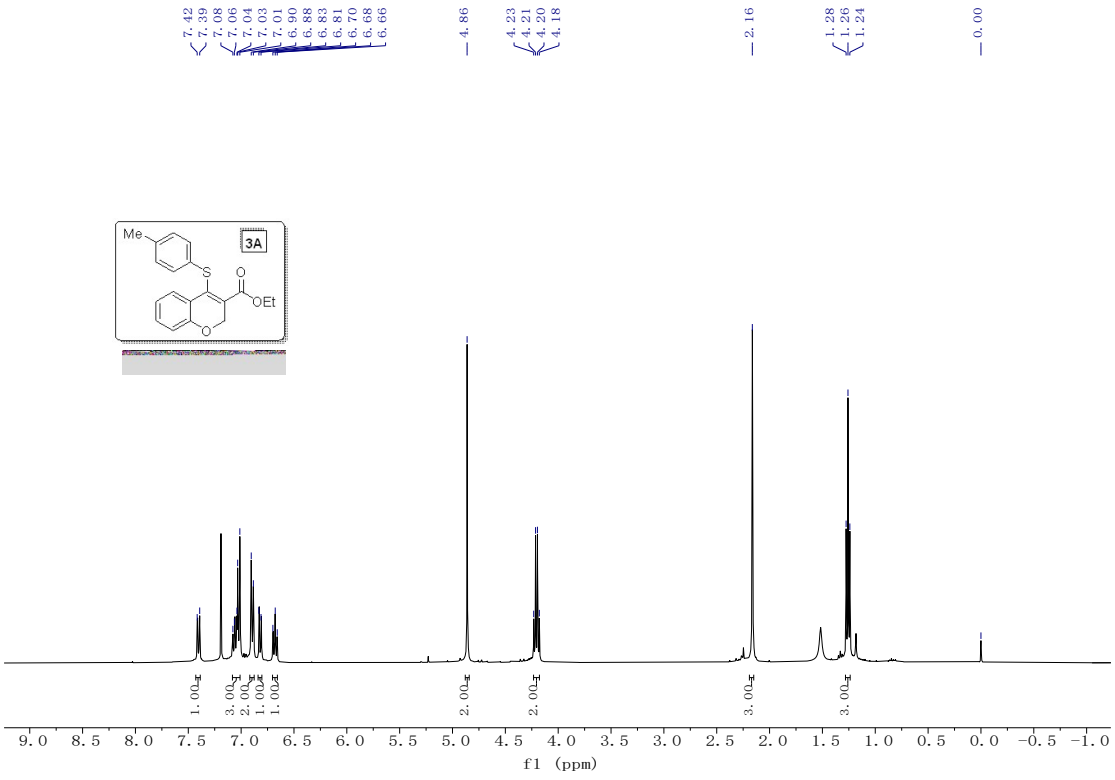
55.56
26.00
20.94
19.48
14.13
f1 (ppm)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6.81
6.70
6.68
6.66
4.86
4.23
4.21
4.20
4.18
2.16
1.28
1.26
1.24
0.00
Me
3A
S
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OEt
O
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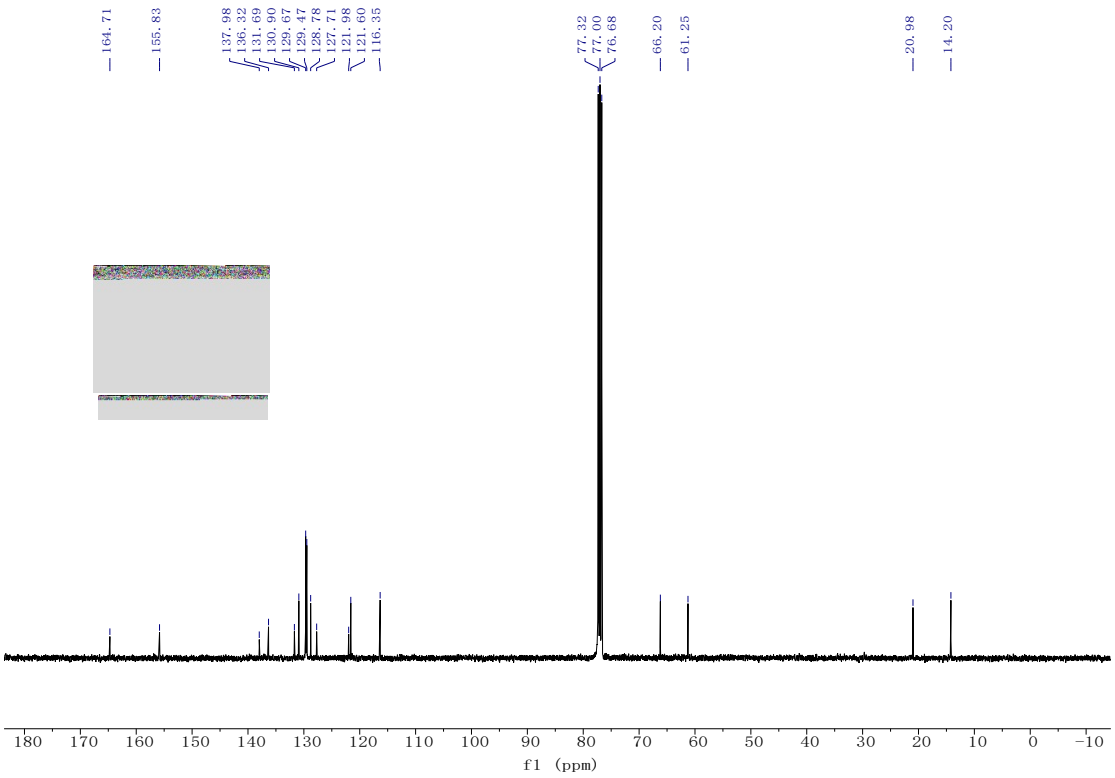
2.00
1.00
1.00
2.00
2.00
3.00
3.00
f1 (ppm)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116.35
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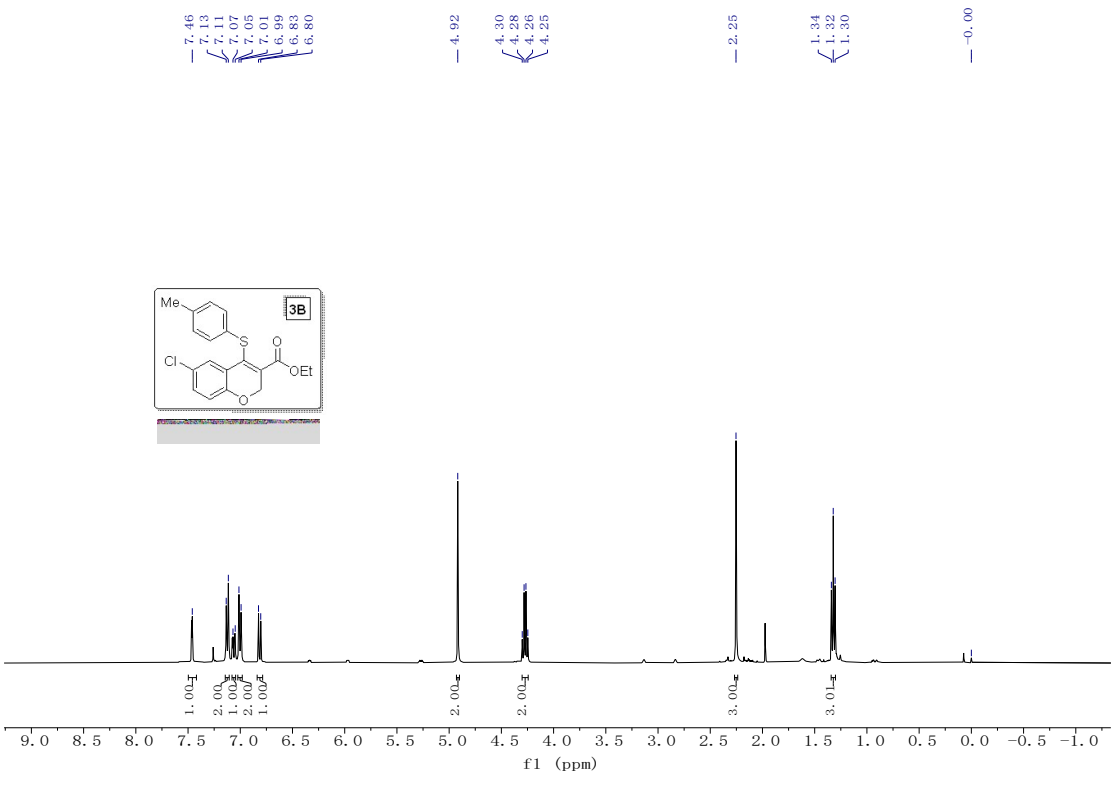
77.00
76.68
66.20
61.25
20.98
14.20
f1 (ppm)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4.28
4.26
4.25
2.25
1.34
1.32
1.30
-0.00
Me
3B
S
O
Cl
OEt
O
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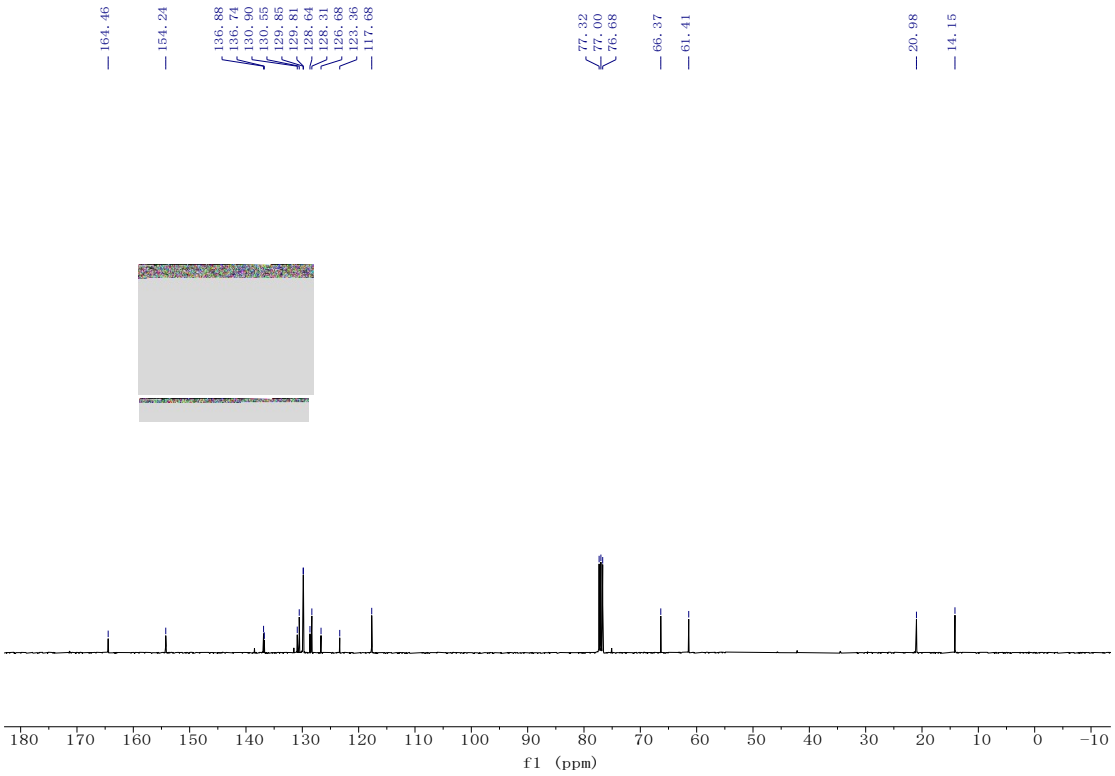
2.00
1.00
2.00
1.00
2.00
2.00
3.00
3.01
f1 (ppm)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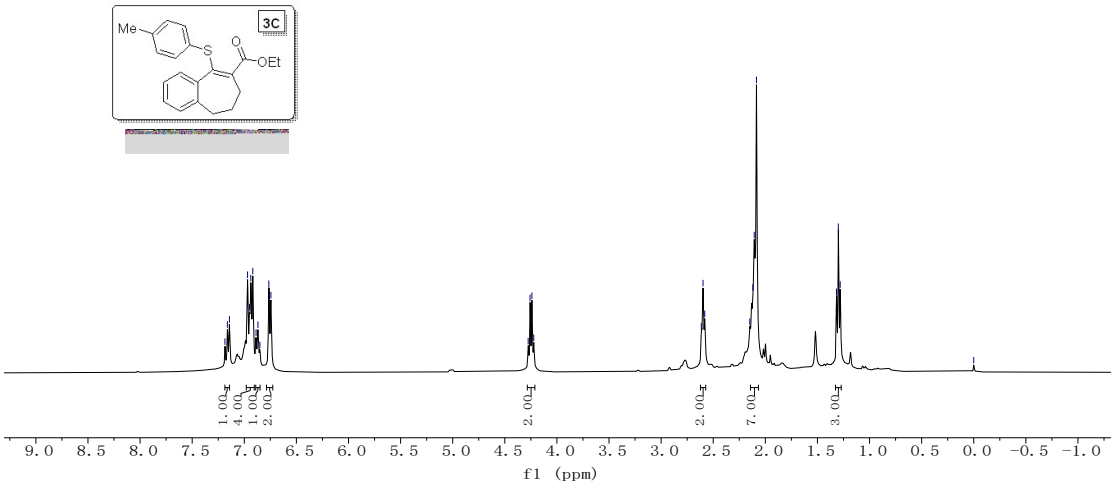
14.15
f1 (ppm)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4.24
4.22
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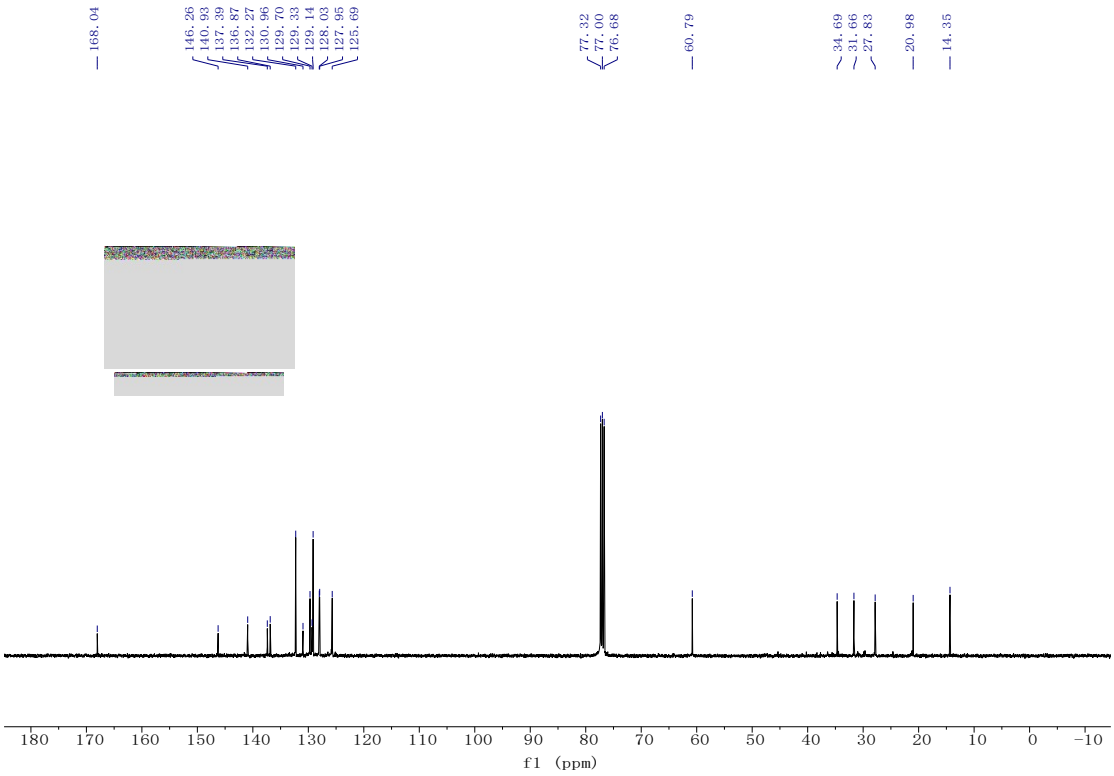
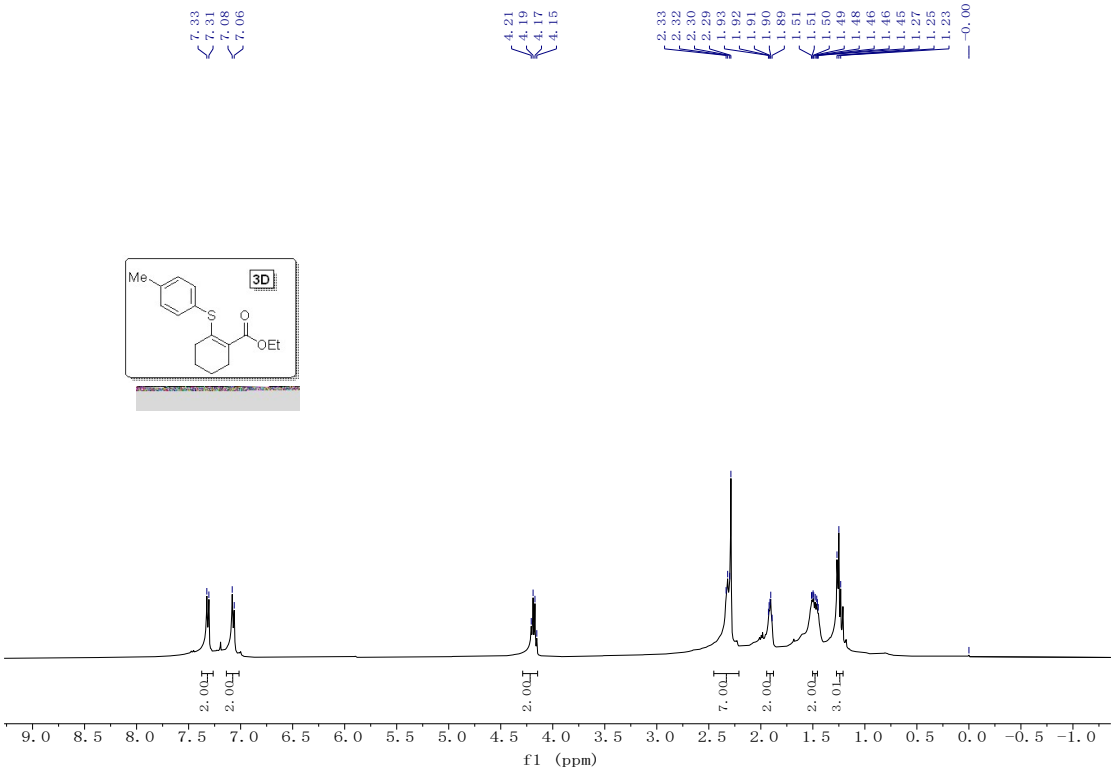
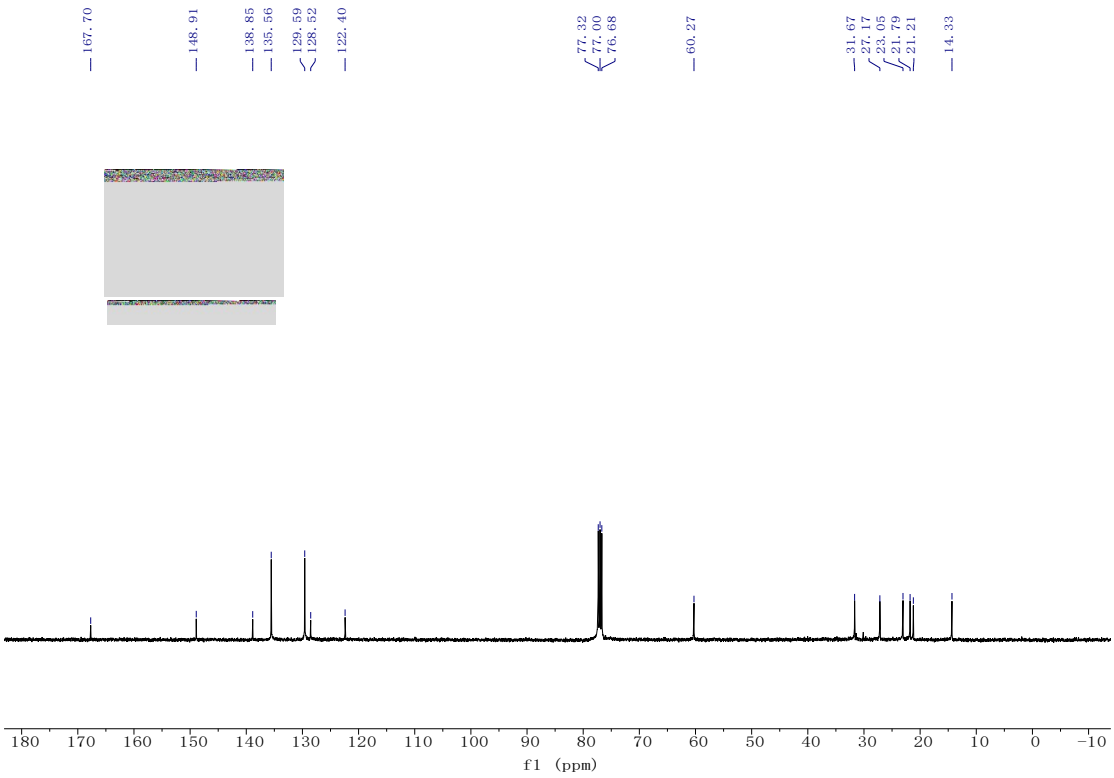
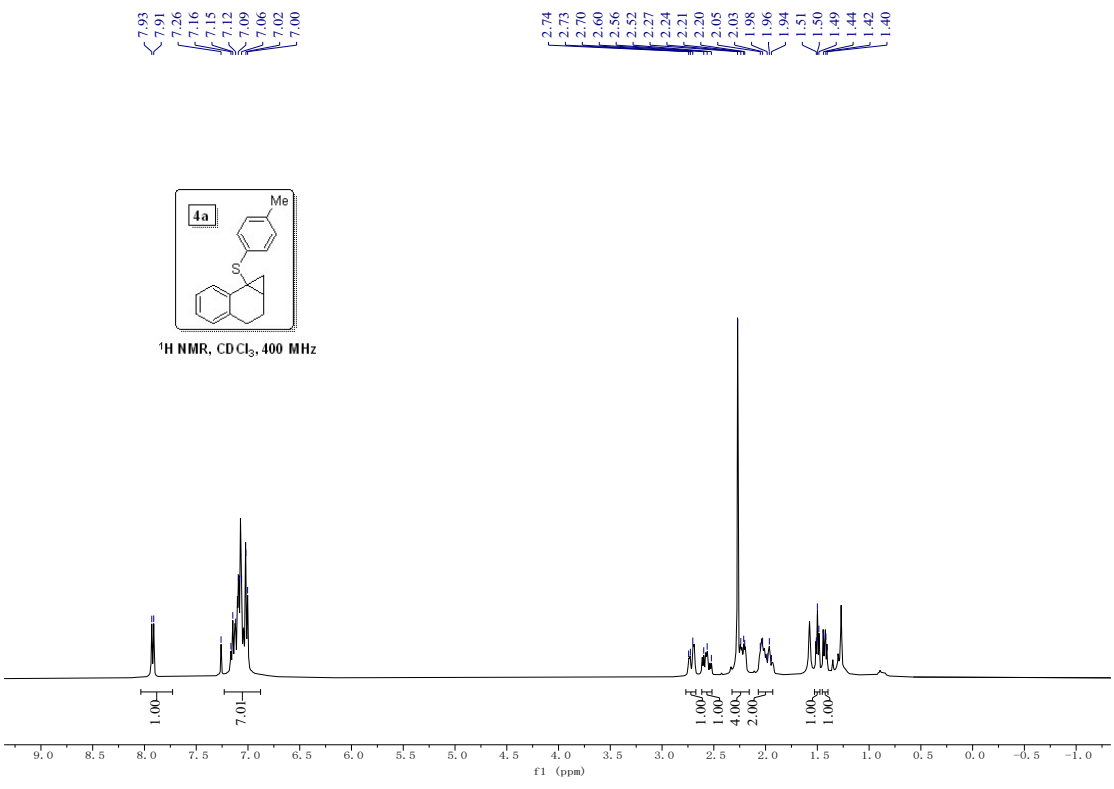
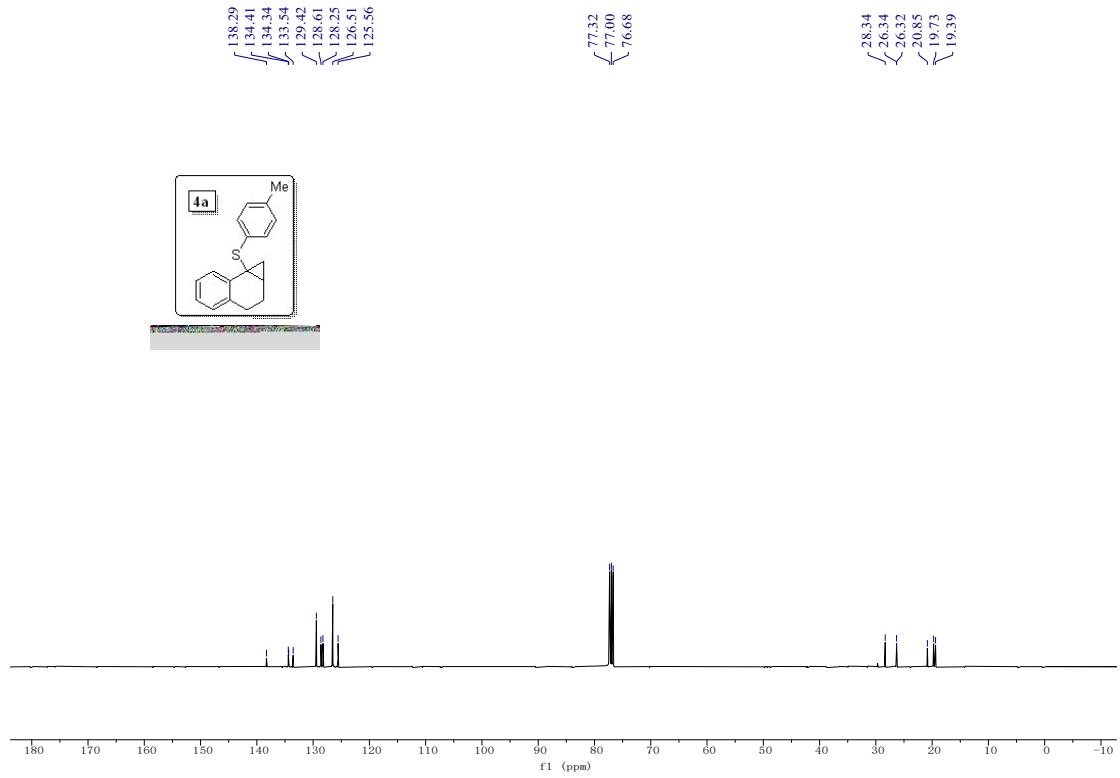
2.60
2.58
2.15
2.12
2.11
2.09
1.32
1.30
1.28
0.00
Me
S
O
OEt
3C
1.00
4.00
1.00
2.00
2.00
2.00
7.00
3.00
f1 (ppm)

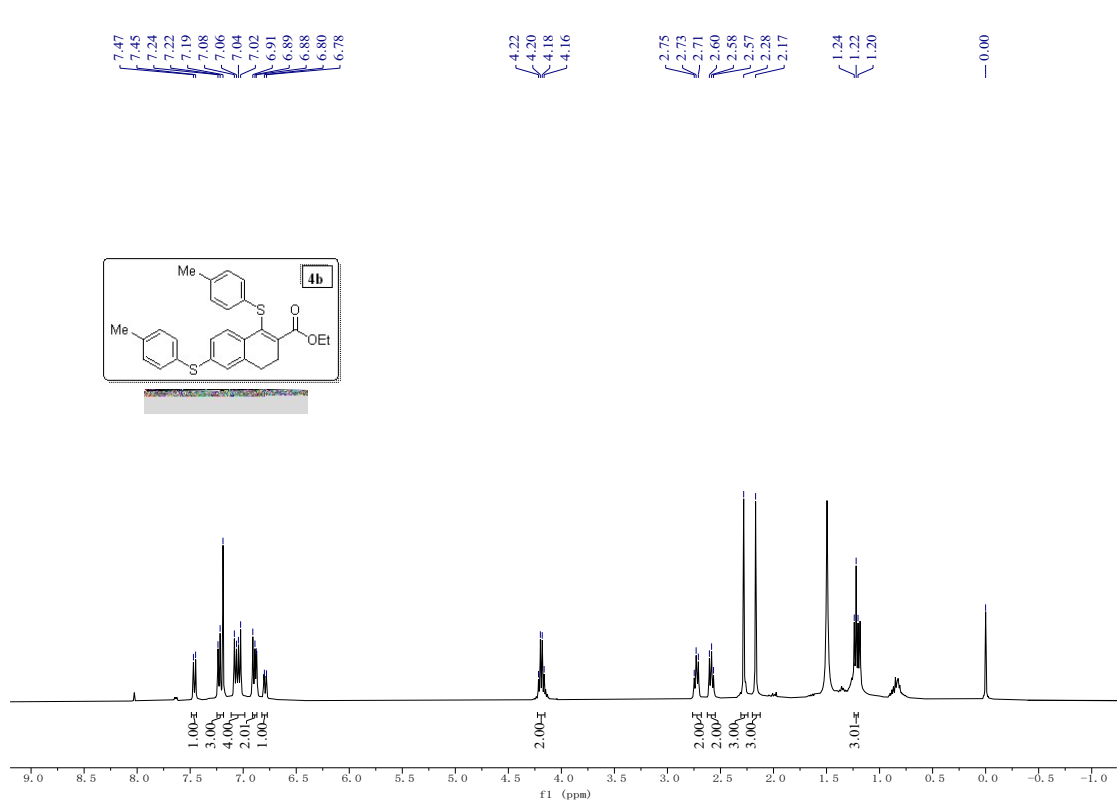

168.04
146.26
140.93
137.39
136.87
132.27
130.96
129.70
129.33
129.14
128.03
127.95
125.69
77.32
77.00
76.68
60.79
34.69
31.66
27.83
20.98
14.35
f1 (ppm)

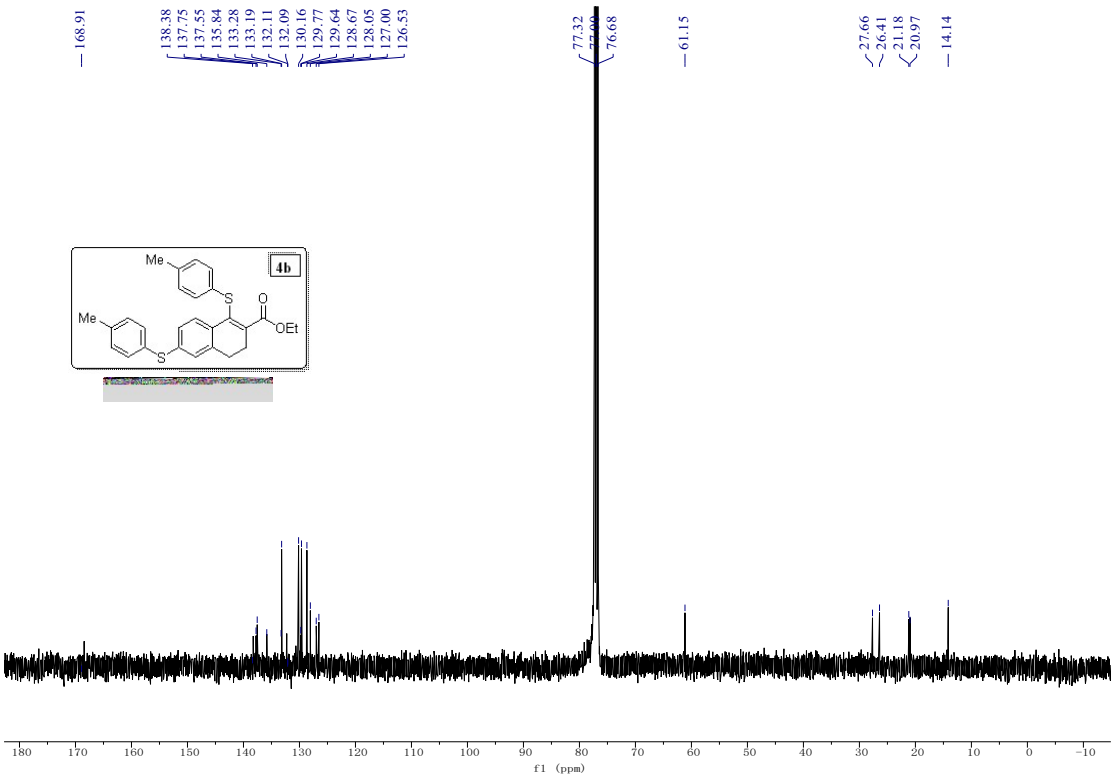

7.33
7.31
7.08
7.06
4.21
4.19
4.17
4.15
2.33
2.32
2.30
2.29
1.93
1.92
1.91
1.90
1.89
1.51
1.51
1.50
1.49
1.48
1.46
1.46
1.45
1.27
1.25
1.23
0.00
Me
3D
S
O
OEt
2.00
2.00
2.00
7.00
2.00
2.00
3.01
f1 (ppm)


167.70
148.91
138.85
135.56
129.59
128.52
122.40
77.32
77.00
76.68
60.27
31.67
27.17
23.05
21.79
21.21
14.33
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.93
7.91
7.26
7.16
7.15
7.12
7.09
7.06
7.02
7.00
2.74
2.73
2.70
2.60
2.56
2.52
2.27
2.24
2.21
2.20
2.05
2.03
1.98
1.96
1.94
1.51
1.50
1.49
1.44
1.42
1.40
4a
Me
S
1H NMR, CDCl3, 400 MHz
1.00
7.01
1.00
1.00
4.00
2.00
1.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


138.29
134.41
134.34
133.54
129.42
128.61
128.25
126.51
125.56
77.32
77.00
76.68
28.34
26.34
26.32
20.85
19.73
19.39
4a
Me
S
f1 (ppm)


7.47
7.45
7.24
7.22
7.19
7.08
7.06
7.04
7.02
6.91
6.89
6.88
6.80
6.78
4.22
4.20
4.18
4.16
2.75
2.73
2.71
2.60
2.58
2.57
2.28
2.17
1.24
1.22
1.20
0.00
4b
Me
Me
S
S
O
OEt
1.00
3.00
4.00
2.01
1.00
2.00
2.00
2.00
3.00
3.00
3.01
f1 (ppm)



12.References

[1] R. Oechsner, I. Lindenmaier and I. Fleischer, Nickel Catalyzed Cross-Coupling of Aryl and Alkenyl Triflates with Alkyl Thiols. *Org. Lett.*, 2023, **25**, 1655-1660.

[2] X. Wu, J. Li, S. Xia, C. Zhu and J. Xie, Nickel-catalyzed Thioester Transfer Reaction with sp^2-Hybridized Electrophiles. *J. Org. Chem*., 2022, **87**, 10003-10017.

[3] G. Du, P. Zhu, J. Wang, X. Li, D.-P. Zhang, C.-Z. Wang and F.-G. Sun, Modular Synthesis of ortho-Thiolated Aryl Esters Enabled with Thiocarbonate through Catellani Strategy. *Eur. J. Org. Chem*., 2023, **26**, e202201382.

[4] M. Soleiman-Beigi and B. Movassagh, Convenient Route to Thiocarbonates from Alcohols, Thiols, and Triphosgene. *Synth. Commun.*, 2010, **40**, 3467-3471.

[5] J. Wang, Z. Dong, C. Yang and G. Dong, Modular and Regioselective Synthesis of All-Carbon Tetrasubstituted Olefins Enabled by an Alkenyl Catellani Reaction. *Nat. Chem*., 2019, **11**, 1106-1112.

[6] W. Lambert, Y. Fang, S. Mahapatra, Z. Huang, C. am Ende and J. Fox, Installation

of Minimal Tetrazines through Silver-Mediated Liebeskind-Srogl Coupling with Arylboronic Acids, *J. Am. Chem. Soc*., 2019, **141**, 17068-17074.

[7] P. Ghosh, B. Ganguly, E. Perl and S. Das, A Synthesis of Biaryl Ketones via the C-S Bond Cleavage of Thiol Ester by a Cu/Ag Salt, *Tetrahedron Lett*., 2017, **58**, 2751-2756.