Metal-Free Allylic C-H Nitrogenation, Oxygenation, and Carbonation of Alkenes by Thianthrenation

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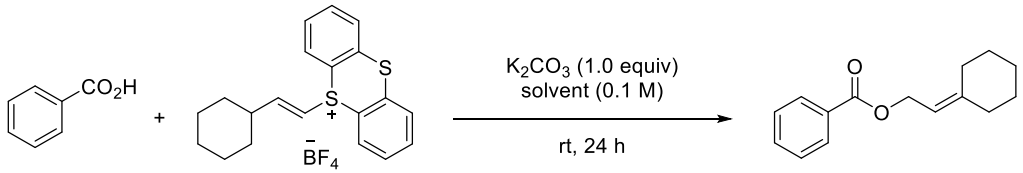
General Information

Unless otherwise noted, all reactions of substrates preparation were conducted in flame-dried glassware under a nitrogen atmosphere using anhydrous solvent were re-distilled according to *Purification of Laboratory Chemicals* (Fifth Edition). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Jiangyou TLC silica gel plates HSG F_{254} and visualized using UV light, anisaldehyde or potassium permanganate. Flash column chromatography was performed over silica gel (300-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise noted, on a Bruker AVANCE 600 MHz or a Bruker AVANCE 400 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.26 ppm). Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Herts (Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift in ppm from the central peak of $CDCl_3$ (77.16 ppm). MS experiments were performed on a Thermo Scientific Q Exactive.

Optimization of Reaction Conditions

Table S1. Investigation of solvent effect



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

entry	solvent	conversion	yield of **3a**[a]
1	DCM	>97%	92% (91%)
2	DCE	>95%	88%
3	CH_3CN	>95%	82%
4	DMSO	90%	34%
5	DMF	76%	27%
6	THF	93%	47%
7	acetone	>90%	69%
8	toluene	>95%	81%

[a] The reaction was conducted using **1a** (14.7 mg, 0.12 mmol), **2a** (41.2 mg, 0.1 mmol), and K_2CO_3 (13.8 mg, 0.10 mmol) in indicated solvent (1.0 mL) at room temperature for 24 h. Yield was determined by ^1H NMR of the crude mixture using mesitylene as internal standard. Isolated yield after flash chromatography is shown in the parentheses.

Table S2. Investigation of base effect

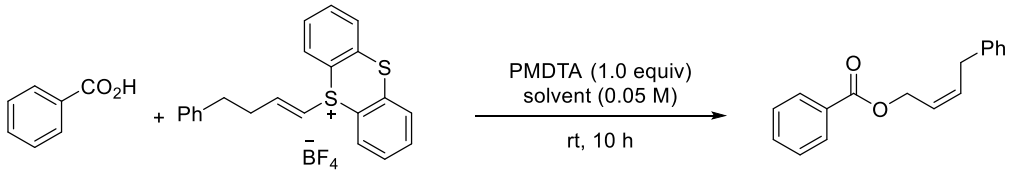
1a **2a** **3a**

entry	base	conversion	yield of **3a**[a]
1	K_2CO_3	>97%	92% (91%)
2	Cs_2CO_3	>97%	85% (80%)
3	Na_2CO_3	46%	10%
4	Li_2CO_3	5%	N.D.
5	K_3PO_4	>90%	72%

6	Na_3PO_4	50%	25%
7	K_2HPO_4	>90%	63%
8[b]	$PhCO_2K$	73%	56%

[a] The reaction was conducted using **1a** (14.7 mg, 0.12 mmol), **2a** (41.2 mg, 0.1 mmol), and base (0.10 mmol) in DCM (1.0 mL) at room temperature for 24 h. [b] The reaction was conducted using $PhCO_2K$ (16.0 mg, 0.10 mmol), **2a** (41.2 mg, 0.1 mmol) and H_2O (0.1 mg, 0.006 mmol) in DCM (1.0 mL) at room temperature for 24 h. Yield was determined by ^1H NMR of the crude mixture using mesitylene as internal standard. Isolated yield after flash chromatography is shown in the parentheses. N.D. = not detected.

Table S3. Investigation of solvent effect on Z/E selectivity

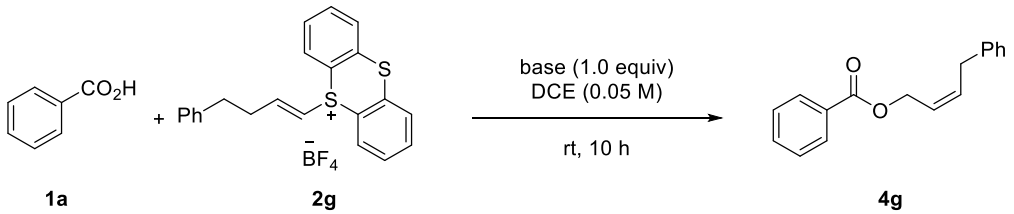


1a **2g** **4g**

entry	solvent	conversion	yield of **4g**[a]	Z/E of **4g**[a]
1	DCM	>97%	50%	6.7:1
2	DCE	>97%	63% (56%)	8.0:1
3	chlorobenzene	>97%	24%	8.4:1
4	CCl_4	>97%	49%	6.5:1
5	$PhCF_3$	>95%	36%	9.0:1
6	DCM/DCE = 1:1	>97%	45%	7.8:1
7	CCl_4/DCE = 1:1	>97%	19%	11.7:1
8	$PhCF_3$/DCE = 1:1	>97%	27%	8.0:1
9	DCM/DCE = 1:4	>97%	50%	7.6:1
10	DCM/DCE = 4:1	>97%	49%	6.5:1

[a] The reaction was conducted using **1a** (12.2 mg, 0.10 mmol), **2g** (20.6 mg, 0.05 mmol), and PMDTA (8.7 mg, 0.05 mmol) in indicated solvent (1.0 mL) at room temperature for 10 h. Yield was determined by ^1H NMR of the crude mixture using mesitylene as internal standard. Isolated yield after flash chromatography is shown in the parentheses.

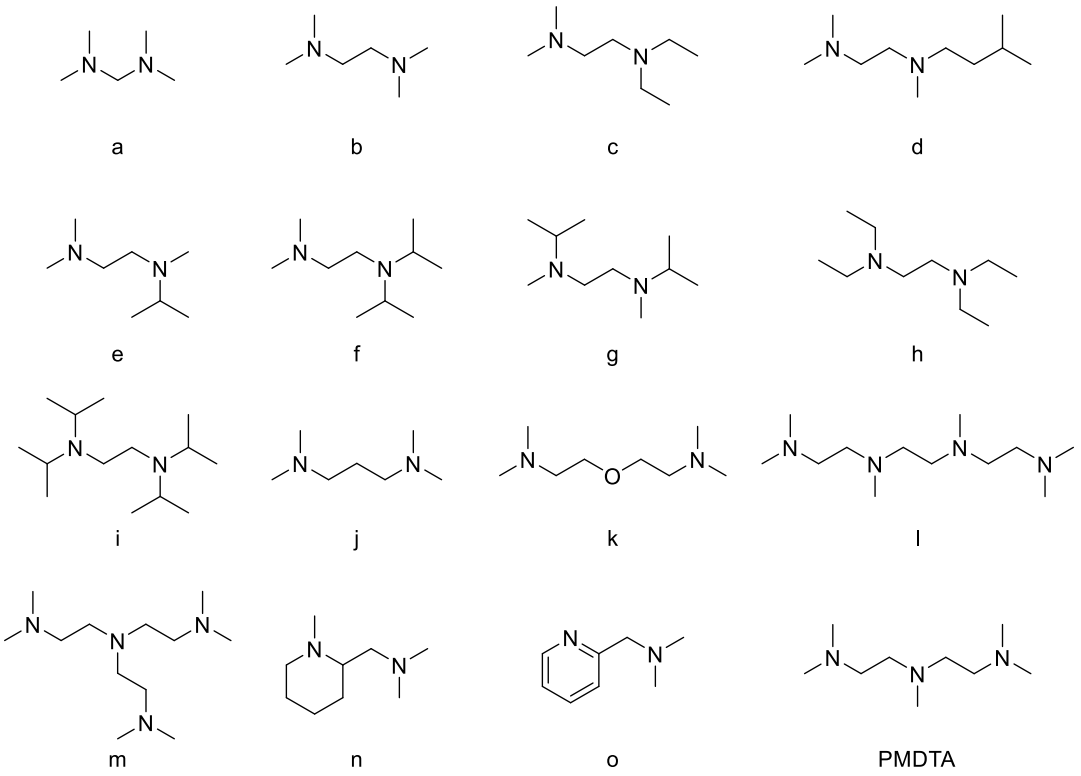
Table S4. Investigation of base effect on Z/E selectivity



1a **2g** **4g**

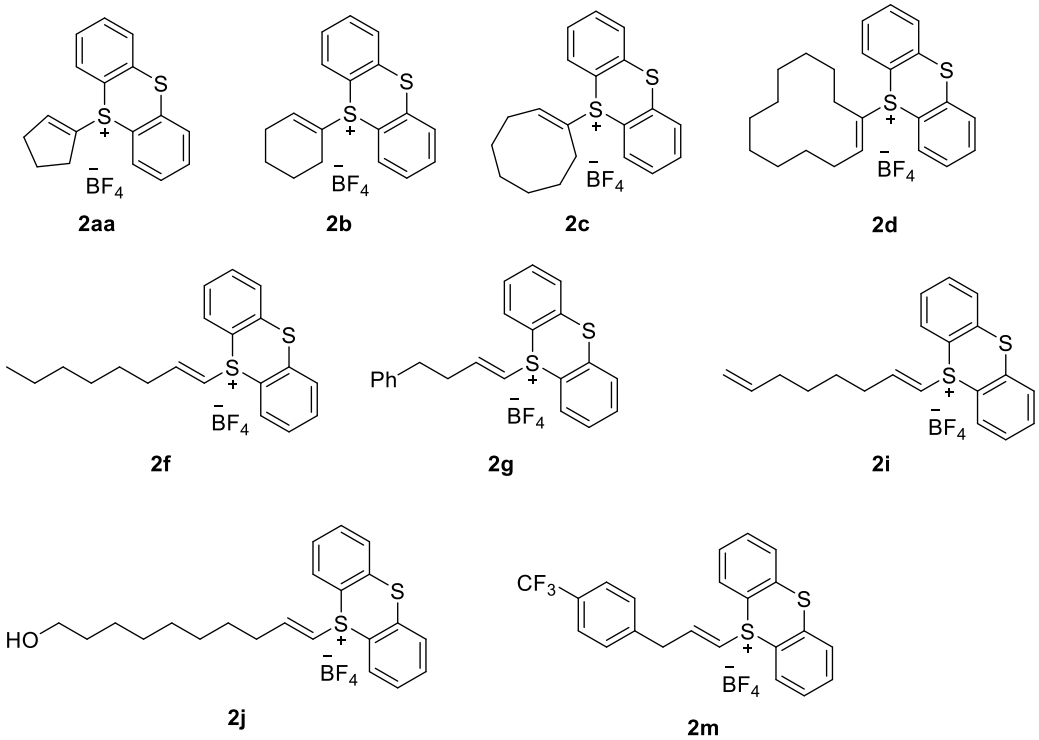
entry	base	conversion	yield of **4g**[a]	Z/E of **4g**[a]
1	a	>97%	39%	4.2:1
2	b	>97%	25%	7.3:1
3	c	>97%	38%	6.5:1
4	d	>95%	36%	8.1:1
5	e	>97%	43%	6.2:1
6	f	>97%	49%	5.1:1
7	g	>97%	82%	4.3:1
8	h	>97%	68%	4.0:1
9	i	>97%	89%	3.5:1
10	j	>97%	27%	8.0:1
11	k	>97%	45%	7.2:1
12	l	>97%	59%	6.8:1
13	m	>97%	50%	7.3:1
14	n	>97%	56%	5.5:1
15	o	>97%	19%	5.3:1
16	PMDTA	>97%	63% (56%)	8.0:1
17[b]	PMDTA (75 mol%)	>97%	68%	6.7:1
18[b]	PMDTA (1.25 equiv)	>97%	40%	10.4:1

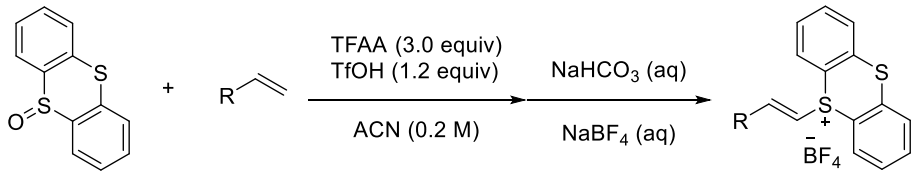
[a] The reaction was conducted using **1a** (12.2 mg, 0.10 mmol), **2g** (20.6 mg, 0.05 mmol), and base (0.05 mmol) in DCE (1.0 mL) at room temperature for 10 h. [b] The reaction was conducted using **1a** (12.2 mg, 0.10 mmol, 2.0 equiv), **2g** (20.6 mg, 0.05 mmol, 1.0 equiv) and PMDTA (x equiv) in DCE (1.0 mL) at room temperature for 10 h. Yield was determined by ^{1}H NMR of the crude mixture using mesitylene as internal standard. Isolated yield after flash chromatography is shown in the parentheses.



Substrate Synthesis and Characterization

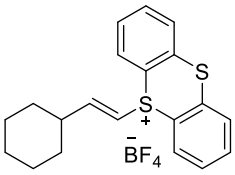
Alkenyl thianthren-5-ium tetrafluoroborate were synthesized following reported procedure[1-2].





Under nitrogen atmosphere, a 50 mL Schlenk vial equipped with a magnetic stir bar was charged with alkene (2.0 mmol, 1.00 equiv), thianthrene 5-oxide (464 mg, 2.0 mmol, 1.0 equiv), and MeCN (10 mL, c = 0.20 M). After cooling to 0°C, trifluoroacetic anhydride (1260 mg, 6.0 mmol, 3.0 equiv) was added dropwise within 2 minutes, followed by dropwise addition of TfOH (360 mg, 2.4 mmol, 1.2 equiv.) within 2 minutes. After stirring the lilac mixture at 0 °C for 1h followed by stirring for 1h at room temperature, the resulting mixture was concentrated under reduced pressure, and subsequently diluted with CH_2Cl_2 (30 mL). The saturated aqueous $NaHCO_3$ solution (stir 10 minute, 3x30 mL) pour into CH_2Cl_2 solution, and the layers were separated with separatory funnel. Then, aqueous $NaBF_4$ solution (5x30 mL, 5 % w/w, stir 10 minute) pour into CH_2Cl_2 solution, and the layers were separated with separatory funnel. The CH_2Cl_2 layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with MeOH/DCM = 0-10% to afford the alkenyl thianthrenium salt.

(*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate (2a)

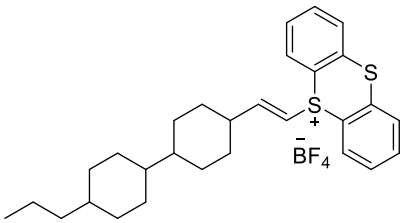


2a

Under nitrogen atmosphere, vinylcyclohexane (220 mg, 2.0 mmol, 1.00 equiv), thianthrene 5-oxide (464 mg, 2.0 mmol, 1.0 equiv), trifluoroacetic anhydride (1260 mg, 6.0 mmol, 3.0 equiv), HOTf (360 mg, 2.4 mmol, 1.2 equiv.) and MeCN (10 mL, c = 0.20 M). after chromatography on silica gel eluting with MeOH/DCM = 0-10% to afford the (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (535 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dt, *J* = 7.8, 1.5 Hz, 2H), 7.81 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.70 (dtd, *J* = 21.9, 7.6, 1.5 Hz, 4H), 7.20 (dd, *J* = 15.0, 6.9 Hz, 1H), 6.49 (dd, *J* = 14.9, 1.4 Hz, 1H), 2.27 – 2.15 (m, 1H), 1.75 – 1.66 (m, 4H), 1.62 (d, *J* = 4.4 Hz, 2H), 1.15 (dddd, *J* = 27.0, 23.8, 20.2, 12.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.36, 135.65, 134.46, 134.01, 130.47, 130.17, 120.87, 107.80, 42.15, 30.93, 25.56, 25.43; ^{19}F NMR (376 MHz, $CDCl_3$) δ -150.62 (bs), -150.67 (bs). HRMS-ESI (m/z) $[M+BF_4]^+$ calc'd for $C_{20}H_{21}S_2^+$, 325.1079, found 325.1080.

(*E*)-5-(2-(4'-propyl-[1,1'-bi(cyclohexan)]-4-yl)vinyl)-5*H*-thianthren-5-ium tetra-

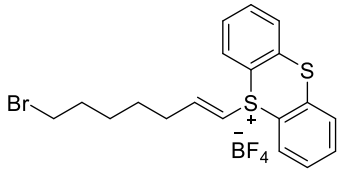
fluoroborate (2e)



2e

Under nitrogen atmosphere, 4-propyl-4'-vinyl-1,1'-bi(cyclohexane) (469 mg, 2.0 mmol, 1.00 equiv), thianthrene 5-oxide (464 mg, 2.0 mmol, 1.0 equiv), trifluoroacetic anhydride (1260 mg, 6.0 mmol, 3.0 equiv), HOTf (360 mg, 2.4 mmol, 1.2 equiv.) and MeCN (10 mL, c = 0.20 M). after chromatography on silica gel eluting with MeOH/DCM = 0-10% to afford the (*E*)-5-(2-(4'-propyl-[1,1'-bi(cyclohexan)]-4-yl)vinyl)-5*H*-thianthren-5-ium tetra-fluoroborate **2e** (497 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.81 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.69 (dtd, *J* = 20.8, 7.5, 1.5 Hz, 4H), 7.18 (ddd, *J* = 14.8, 6.9, 1.7 Hz, 1H), 6.48 (dd, *J* = 14.8, 1.3 Hz, 1H), 2.16 – 2.05 (m, 1H), 1.72 (t, *J* = 12.5 Hz, 8H), 1.66 – 1.59 (m, 2H), 1.33 – 1.21 (m, 2H), 1.10 (qt, *J* = 7.1, 3.9 Hz, 4H), 0.99 – 0.73 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.57, 135.59, 134.35, 134.19, 130.51, 130.05, 121.03, 107.58, 43.22, 42.52, 42.46, 39.86, 37.65, 33.57, 31.19, 30.05, 29.13, 20.13, 14.52; ^{19}F NMR (377 MHz, $CDCl_3$) δ -150.38 (bs), -150.44 (bs). HRMS-ESI (m/z) $[M+BF_4]^+$ calc'd for $C_{29}H_{37}S_2^+$, 449.2331, found 449.2334.

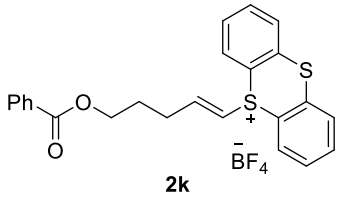
(*E*)-5-(7-bromohept-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate (2h)



2h

Under nitrogen atmosphere, 7-bromo-1-heptene (354 mg, 2.0 mmol, 1.00 equiv), thianthrene 5-oxide (464 mg, 2.0 mmol, 1.0 equiv), trifluoroacetic anhydride (1260 mg, 6.0 mmol, 3.0 equiv), HOTf (360 mg, 2.4 mmol, 1.2 equiv.) and MeCN (10 mL, c = 0.20 M). after chromatography on silica gel eluting with MeOH/DCM = 0-10% to afford the (*E*)-5-(7-bromohept-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2h** (454 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.83 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.74 (td, *J* = 7.6, 1.2 Hz, 2H), 7.67 (td, *J* = 7.6, 1.4 Hz, 2H), 7.25 (q, *J* = 6.9 Hz, 1H), 6.57 (dt, *J* = 14.8, 1.5 Hz, 1H), 3.34 (t, *J* = 6.6 Hz, 2H), 2.38 – 2.22 (m, 2H), 1.82 – 1.72 (m, 2H), 1.51 – 1.42 (m, 2H), 1.37 (qd, *J* = 7.4, 7.0, 3.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.80, 135.63, 134.48, 134.04, 130.49, 130.15, 120.73, 109.66, 33.87, 33.21, 32.15, 27.39, 26.36; ^{19}F NMR (377 MHz, $CDCl_3$) δ -150.54 (bs), -150.60 (bs). HRMS-ESI (m/z) $[M+BF_4]^+$ calc'd for $C_{19}H_{20}BrS_2^+$, 391.0184, found 391.0184.

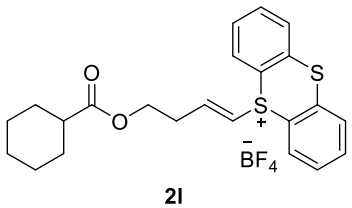
(*E*)-5-(5-(benzoyloxy)pent-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate (2k)



2k

Under nitrogen atmosphere, pent-4-en-1-yl benzoate (380 mg, 2.0 mmol, 1.00 equiv), thianthrene 5-oxide (464 mg, 2.0 mmol, 1.0 equiv), trifluoroacetic anhydride (1260 mg, 6.0 mmol, 3.0 equiv), HOTf (360 mg, 2.4 mmol, 1.2 equiv.) and MeCN (10 mL, c = 0.20 M). after chromatography on silica gel eluting with MeOH/DCM = 0-10% to afford the (*E*)-5-(5-(benzoyloxy)pent-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2k** (509 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 7.9, 1.4 Hz, 2H), 8.00 – 7.93 (m, 2H), 7.80 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.71 (td, *J* = 7.7, 1.4 Hz, 2H), 7.64 (td, *J* = 7.7, 1.5 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.38 (dd, *J* = 14.5, 7.2 Hz, 1H), 6.62 (dt, *J* = 14.7, 1.5 Hz, 1H), 4.24 (t, *J* = 6.2 Hz, 2H), 2.51 – 2.37 (m, 2H), 1.95 (dt, *J* = 8.1, 6.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.50, 156.05, 135.59, 134.43, 134.12, 133.28, 130.51, 130.08, 129.72, 128.62, 120.72, 110.17, 63.65, 30.29, 26.56; ^{19}F NMR (377 MHz, $CDCl_3$) δ -150.40 (bs), -150.45 (bs). HRMS-ESI (m/z) $[M+BF_4]^+$ calc'd for $C_{24}H_{21}O_2S_2^+$, 405.0977, found 405.0978.

(*E*)-5-(4-((cyclohexanecarbonyl)oxy)but-1-en-1-yl)-5*H*-thianthren-5-ium tetra-fluoroborate (2l)



2l

Under nitrogen atmosphere, but-3-en-1-yl cyclohexanecarboxylate (365 mg, 2.0 mmol, 1.00 equiv), thianthrene 5-oxide (464 mg, 2.0 mmol, 1.0 equiv), trifluoroacetic anhydride (1260 mg, 6.0 mmol, 3.0 equiv), HOTf (360 mg, 2.4 mmol, 1.2 equiv.) and MeCN (10 mL, c = 0.20 M). after chromatography on silica gel eluting with MeOH/DCM = 0-10% to afford the (*E*)-5-(4-((cyclohexane-carbonyl)oxy)but-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2l** (539 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.83 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.75 (td, *J* = 7.7, 1.4 Hz, 2H), 7.71 – 7.63 (m, 2H), 7.24 – 7.14 (m, 1H), 6.65 (dt, *J* = 14.8, 1.5 Hz, 1H), 4.12 (t, *J* = 6.1 Hz, 2H), 2.60 (pd, *J* = 5.8, 1.5 Hz, 2H), 2.11 (tdd, *J* = 10.3, 7.1, 4.1 Hz, 1H), 1.73 – 1.51 (m, 5H), 1.16 (tdd, *J* = 11.1, 8.0, 3.1 Hz, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.66, 152.33, 135.65, 134.61, 134.05, 130.48, 130.13, 120.21, 111.55, 60.68, 43.01, 32.56, 28.88, 25.70, 25.42; ^{19}F

NMR (377 MHz, $CDCl_3$) δ -150.46 (bs), -150.52 (bs). HRMS-ESI (m/z) $[M+BF_4]^+$ calc'd for $C_{23}H_{25}O_2S_2^+$, 397.1290, found 397.1292.

General Procedure for the Allylic C-H Functionalizations

Standard Procedure A:

Acid or amine (0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv), and thianthrene (0.20 mmol, 1.0 equiv) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), 2.0 mL DCM was added, the vial was sealed and at room temperature with stirring until TLC indicated the complete consumption of thianthrene (typically 24 h). The reaction mixture was evaporated and purified directly by column chromatography to afford the product.

Standard Procedure B:

Nucleophile (0.40 mmol, 2.0 equiv), H_2O (0.2 mg, 0.2 μL, 0.011 mmol, 0.056 equiv) and thianthrene (0.20 mmol, 1.0 equiv) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), 2.0 mL DCM was added, the vial was sealed and at room temperature with stirring until TLC indicated the complete consumption of thianthrene (typically 24 h). The reaction mixture was evaporated and purified directly by column chromatography to afford the product.

Standard Procedure C:

Nucleophile (0.60 mmol, 3.0 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv), and thianthrene (0.20 mmol, 1.0 equiv) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), 2.0 mL DCM was added, the vial was sealed and at room temperature with stirring until TLC indicated the complete consumption of thianthrene (typically 24 h). The reaction mixture was evaporated and purified directly by column chromatography to afford the product.

Standard Procedure D:

Nucleophile (0.24 mmol, 1.2 equiv), KOH (11.2 mg, 0.20 mmol, 1.0 equiv) and thianthrene (0.20 mmol, 1.0 equiv) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), 2.0 mL DCM was added, the vial was sealed and at room temperature with stirring until TLC indicated the complete consumption of thianthrene (typically 24 h). The reaction mixture was evaporated and purified directly by column chromatography to afford the product.

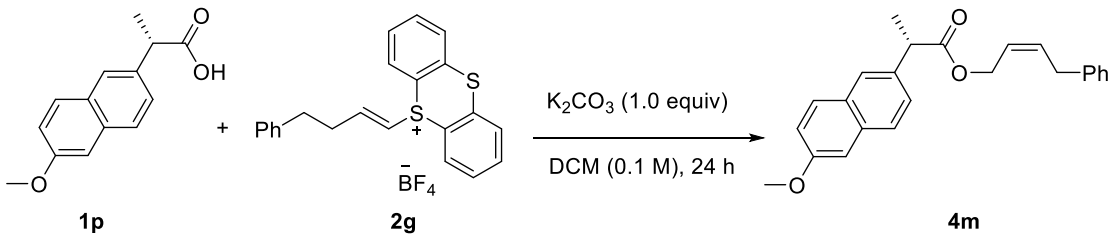
Standard Procedure E:

Acid (0.20 mmol, 2.0 equiv), PMDTA (17.3 mg, 0.10 mmol, 1.0 equiv), and thianthrene (0.10 mmol, 1.0 equiv) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), 2.0 mL DCE was added, the vial was sealed and at room temperature with stirring until TLC indicated the complete consumption of thianthrene (typically 10 h). The reaction mixture was evaporated and purified directly by column chromatography to afford the product.

Standard Procedure F:

Amine (0.40 mmol, 2.0 equiv), H_2O (0.2 mg, 0.011 mmol, 0.056 equiv) and thianthrene (0.20 mmol, 1.0 equiv) were placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), 2.0 mL DCM was added, the vial was sealed and at room temperature with stirring until TLC indicated the complete consumption of thianthrene (typically 24 h). The reaction mixture was evaporated and purified directly by column chromatography to afford the product.

Gram-Scale Synthesis

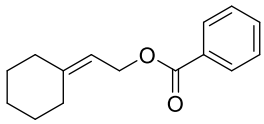


1p **2g** **4m**

Naproxen **1p** (1105 mg, 4.8 mmol, 1.2 equiv), K_2CO_3 (553.0 mg, 4.0 mmol, 1.0 equiv), and (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (1737 mg, 4.0 mmol, 1.0 equiv) were placed in 200 mL Schlenk flask equipped with a magnetic stirring bar. After backfilled with nitrogen (this process was repeated three times), 40 mL DCM was added, the flask was sealed at room temperature with stirring for 24 h. The reaction mixture was filtrated and washed with DCM (3 x 20 mL). The organic phase was purified directly by column chromatography to afford the product **4m** (1.19 g, 83% yield, *Z*/*E* = 3.4:1).

Characterization of Allylic C-H Functionalization Products

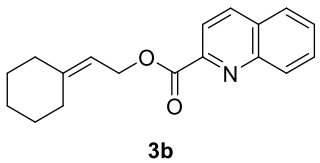
2-cyclohexylideneethyl benzoate (3a)



3a

Following the Standard Procedure A, the reaction of benzoic acid (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE =0-5% as colorless oil **3a** (41.9 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.59 – 7.50 (m, 1H), 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 5.42 (tt, *J* = 7.2, 1.3 Hz, 1H), 4.84 (d, *J* = 7.2 Hz, 2H), 2.32 – 2.24 (m, 2H), 2.20 – 2.12 (m, 2H), 1.58 (p, *J* = 2.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.81, 147.21, 132.88, 130.73, 129.72, 128.41, 115.36, 61.28, 37.14, 29.27, 28.50, 27.93, 26.75; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{15}H_{19}O_2^+$, 231.1380, found 231.1378.

2-cyclohexylideneethyl quinoline-2-carboxylate (3b)

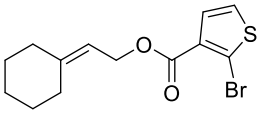


3b

Following the Standard Procedure A, the reaction of quinoline-2-carboxylic acid (41.6 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3b** (44.3 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (ddd, *J* = 15.7, 8.5, 3.0 Hz, 2H), 8.17 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.86 (dd, *J* = 8.4, 2.9 Hz, 1H), 7.82 – 7.74 (m, 1H), 7.63 (td, *J* = 8.2, 7.7, 2.7 Hz, 1H), 5.50 (t, *J* = 7.4 Hz,

1H), 5.01 (d, *J* = 7.2 Hz, 2H), 2.29 (d, *J* = 5.6 Hz, 2H), 2.14 (d, *J* = 5.5 Hz, 2H), 1.62 – 1.52 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.44, 148.41, 147.63, 147.41, 137.38, 130.84, 130.31, 129.39, 128.63, 127.60, 121.18, 115.14, 62.55, 37.17, 29.30, 28.40, 27.84, 26.72; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{18}H_{20}NO_2^+$, 282.1489, found 282.1485.

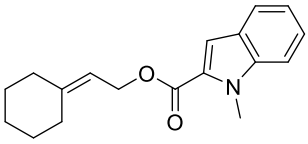
2-cyclohexylideneethyl 2-bromothiophene-3-carboxylate (3c)



3c

Following the Standard Procedure A, the reaction of 2-bromothiophene-3-carboxylic acid (49.7 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3c** (50.5 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 5.8 Hz, 1H), 7.20 (d, *J* = 5.8 Hz, 1H), 5.39 (tt, *J* = 7.2, 1.3 Hz, 1H), 4.79 (d, *J* = 7.2 Hz, 2H), 2.29 – 2.21 (m, 2H), 2.13 (d, *J* = 5.4 Hz, 2H), 1.57 (q, *J* = 2.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.11, 147.45, 131.44, 129.56, 125.82, 119.79, 115.10, 61.19, 37.12, 29.26, 28.47, 27.88, 26.73; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{13}H_{16}BrO_2S^+$, 315.0049, found 315.0042.

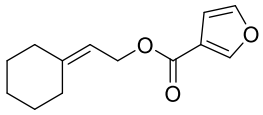
2-cyclohexylideneethyl 1-methyl-1*H*-indole-2-carboxylate (3d)



3d

Following the Standard Procedure A, the reaction of 1-methyl-1*H*-indole-2-carboxylic acid (42.0 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3d** (44.0 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dq, *J* = 7.9, 1.1 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.15 (ddt, *J* = 7.9, 6.6, 1.4 Hz, 1H), 5.44 (ddq, *J* = 8.4, 7.0, 1.3 Hz, 1H), 4.84 (dd, *J* = 7.2, 1.5 Hz, 2H), 4.09 (s, 3H), 2.33 – 2.27 (m, 2H), 2.17 (d, *J* = 5.4 Hz, 2H), 1.60 (dt, *J* = 4.3, 2.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.43, 147.30, 139.76, 128.23, 126.04, 124.99, 122.66, 120.59, 115.34, 110.34, 110.30, 60.81, 37.16, 31.75, 29.30, 28.51, 27.94, 26.76; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{18}H_{22}NO_2^+$, 284.1646, found 284.1646.

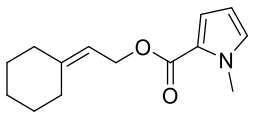
2-cyclohexylideneethyl furan-3-carboxylate (3e)



3e

Following the Standard Procedure A, the reaction of furan-3-carboxylic acid (26.9 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3e** (31.6 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 1.5 Hz, 1H), 7.43 – 7.39 (m, 1H), 6.74 (d, *J* = 1.8 Hz, 1H), 5.35 (t, *J* = 7.2 Hz, 1H), 4.76 (d, *J* = 7.2 Hz, 2H), 2.24 (d, *J* = 5.8 Hz, 2H), 2.13 (d, *J* = 5.4 Hz, 2H), 1.61 – 1.52 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.33, 147.76, 147.14, 143.72, 119.75, 115.28, 110.01, 60.80, 37.13, 29.24, 28.48, 27.90, 26.74; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{13}H_{17}O_3^+$, 221.1173, found 221.1169.

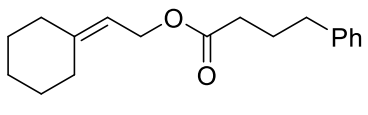
2-cyclohexylideneethyl 1-methyl-1*H*-pyrrole-2-carboxylate (3f)



3f

Following the Standard Procedure A, the reaction of 1-methyl-1*H*-pyrrole-2-carboxylic acid (30.0 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3f** (38.6 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 4.0, 1.8 Hz, 1H), 6.76 (t, *J* = 2.2 Hz, 1H), 6.10 (dd, *J* = 3.9, 2.5 Hz, 1H), 5.38 (ddq, *J* = 7.1, 5.9, 1.2 Hz, 1H), 4.73 (d, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 2.28 – 2.22 (m, 2H), 2.13 (d, *J* = 5.6 Hz, 2H), 1.56 (tt, *J* = 4.9, 2.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.52, 146.65, 129.42, 122.87, 117.87, 115.74, 107.86, 60.09, 37.11, 36.95, 29.24, 28.49, 27.90, 26.77; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{14}H_{20}NO_2^+$, 234.1489, found 234.1485.

2-cyclohexylideneethyl 4-phenylbutanoate (3g)

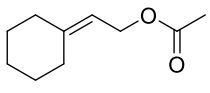


3g

Following the Standard Procedure A, the reaction of 4-phenylbutanoic acid (39.4 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3g** (44.3 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.6, 6.6 Hz,

2H), 7.20 (td, *J* = 6.6, 1.7 Hz, 3H), 5.30 (t, *J* = 7.3 Hz, 1H), 4.60 (d, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.21 (t, *J* = 5.5 Hz, 2H), 2.13 (d, *J* = 5.4 Hz, 2H), 1.97 (p, *J* = 7.5 Hz, 2H), 1.57 (dq, *J* = 7.3, 4.9, 3.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.61, 146.99, 141.57, 128.61, 128.47, 126.05, 115.33, 60.61, 37.10, 35.25, 33.82, 29.12, 28.43, 27.84, 26.70; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{18}H_{25}O_2^+$, 273.1850, found 273.1852.

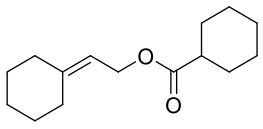
2-cyclohexylideneethyl acetate (3h)



3h

Following the Standard Procedure A, the reaction of acetic acid (14.4 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3h** (21.6 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (tt, *J* = 7.3, 1.2 Hz, 1H), 4.58 (d, *J* = 7.3 Hz, 2H), 2.22 – 2.17 (m, 2H), 2.11 (d, *J* = 5.6 Hz, 2H), 2.05 (s, 3H), 1.56 (tt, *J* = 6.9, 4.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.29, 147.07, 115.26, 60.81, 37.14, 29.14, 28.46, 27.86, 26.74, 21.25; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{10}H_{17}O_2^+$, 169.1224, found 169.1225.

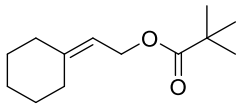
2-cyclohexylideneethyl cyclohexanecarboxylate (3i)



3i

Following the Standard Procedure A, the reaction of cyclohexanecarboxylic acid (30.8 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3i** (41.7 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (tt, *J* = 7.1, 1.3 Hz, 1H), 4.55 (d, *J* = 7.2 Hz, 2H), 2.27 (tt, *J* = 11.3, 3.6 Hz, 1H), 2.18 (t, *J* = 5.5 Hz, 2H), 2.11 (d, *J* = 5.5 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.73 (dq, *J* = 9.9, 3.7 Hz, 3H), 1.54 (h, *J* = 4.5, 4.0 Hz, 6H), 1.47 – 1.37 (m, 2H), 1.31 – 1.21 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.28, 146.78, 115.51, 60.43, 43.39, 37.09, 29.17, 29.15, 28.47, 27.87, 26.73, 25.90, 25.59; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{15}H_{25}O_2^+$, 237.1850, found 237.1847.

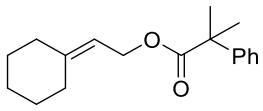
2-cyclohexylideneethyl pivalate (3j)



3j

Following the Standard Procedure A, the reaction of pivalic acid (24.5 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3j** (27.4 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (tt, *J* = 7.1, 1.2 Hz, 1H), 4.55 (d, *J* = 7.1 Hz, 2H), 2.23 – 2.15 (m, 2H), 2.10 (d, *J* = 5.2 Hz, 2H), 1.55 (q, *J* = 3.0, 2.6 Hz, 6H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.72, 146.62, 115.61, 60.69, 38.84, 37.07, 29.23, 28.55, 27.93, 27.35, 26.76; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{13}H_{23}O_2^+$, 211.1693, found 211.1689.

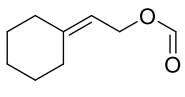
2-cyclohexylideneethyl 2-methyl-2-phenylpropanoate (3k)



3k

Following the Standard Procedure A, the reaction of 2-methyl-2-phenylpropanoic acid (39.4 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3k** (48.5 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.23 (ddt, *J* = 8.4, 6.0, 2.0 Hz, 1H), 5.22 (tt, *J* = 7.1, 1.3 Hz, 1H), 4.57 (d, *J* = 7.1 Hz, 2H), 2.16 – 2.10 (m, 2H), 2.08 (d, *J* = 5.4 Hz, 2H), 1.58 (s, 6H), 1.53 (p, *J* = 3.3, 2.9 Hz, 4H), 1.50 – 1.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.81, 147.06, 145.02, 128.41, 126.66, 125.79, 115.27, 61.11, 46.69, 37.02, 29.18, 28.51, 27.85, 26.71; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{18}H_{25}O_2^+$, 273.1850, found 273.1844.

2-cyclohexylideneethyl formate (3l)

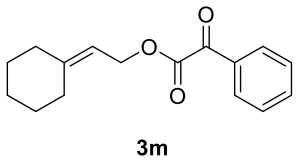


3l

Following the Standard Procedure A, the reaction of formic acid (11.0 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3l** (22.8 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 5.31 (tt, *J* = 7.4, 1.3 Hz, 1H), 4.68 (d, *J* = 7.4 Hz, 2H), 2.21 (t, *J* = 5.5 Hz, 2H), 2.16 – 2.09 (m, 2H), 1.56 (h, *J* = 4.2 Hz, 6H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 161.26, 147.99, 114.64, 60.17, 37.12, 29.15, 28.44, 27.84, 26.69; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_9H_{15}O_2^+$, 155.1067, found 155.1066.

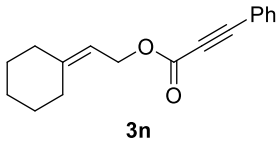
2-cyclohexylideneethyl 2-oxo-2-phenylacetate (3m)



3m

Following the Standard Procedure A, the reaction of 2-oxo-2-phenylacetic acid (36.0 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3m** (40.0 mg, 77% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.65 (td, *J* = 7.4, 1.4 Hz, 1H), 7.51 (td, *J* = 7.7, 1.3 Hz, 2H), 5.42 (tt, *J* = 7.5, 1.3 Hz, 1H), 4.90 (d, *J* = 7.5 Hz, 2H), 2.27 (d, *J* = 5.6 Hz, 2H), 2.16 (t, *J* = 5.4 Hz, 2H), 1.57 (h, *J* = 4.2, 3.2 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.63, 164.05, 149.17, 134.97, 132.71, 130.18, 128.99, 114.07, 62.40, 37.16, 29.28, 28.45, 27.87, 26.66; HRMS-ESI (m/z) $[M+Na]^+$ calc'd for $C_{16}H_{18}O_3Na^+$, 281.1149, found 281.1147.

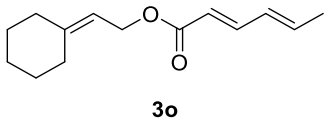
2-cyclohexylideneethyl 3-phenylpropiolate (3n)



3n

Following the Standard Procedure A, the reaction of 3-phenylpropiolic acid (35.1 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3n** (43.7 mg, 86% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.44 (td, *J* = 7.3, 1.4 Hz, 1H), 7.36 (dd, *J* = 8.4, 7.1 Hz, 2H), 5.36 (t, *J* = 7.5 Hz, 1H), 4.75 (d, *J* = 7.4 Hz, 2H), 2.24 (d, *J* = 5.6 Hz, 2H), 2.15 (t, *J* = 5.5 Hz, 2H), 1.57 (dq, *J* = 7.1, 3.9, 3.2 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.29, 148.35, 133.12, 130.69, 128.68, 119.86, 114.40, 86.22, 80.87, 62.30, 37.17, 29.21, 28.40, 27.83, 26.70; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{17}H_{19}O_2^+$, 255.1380, found 255.1375.

2-cyclohexylideneethyl (*2E*,*4E*)-hexa-2,4-dienoate (3o)

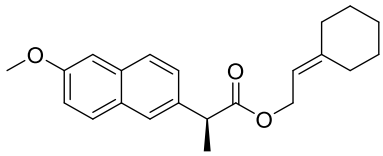


3o

Following the Standard Procedure A, the reaction of sorbic acid (26.9 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg,

0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3o** (39.8 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 15.3, 9.8 Hz, 1H), 6.26 – 6.05 (m, 2H), 5.77 (d, *J* = 15.4 Hz, 1H), 5.31 (tt, *J* = 7.3, 1.3 Hz, 1H), 4.64 (d, *J* = 7.2 Hz, 2H), 2.21 (d, *J* = 6.0 Hz, 2H), 2.11 (d, *J* = 5.5 Hz, 2H), 1.84 (d, *J* = 5.9 Hz, 3H), 1.55 (tt, *J* = 6.8, 4.7, 4.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.48, 146.82, 145.05, 139.30, 129.95, 119.18, 115.48, 60.57, 37.12, 29.16, 28.44, 27.84, 26.73, 18.75; HRMS-ESI (m/z) $[M+Na]^+$ calc'd for $C_{14}H_{20}O_2Na^+$, 243.1356, found 243.1354.

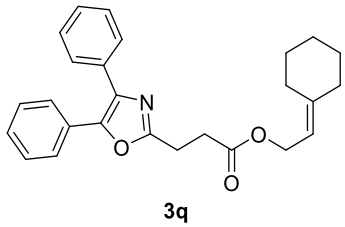
2-cyclohexylideneethyl naproxen ester (3p)



3p

Following the Standard Procedure A, the reaction of naproxen (27.6 mg, 0.12 mmol, 1.2 equiv), K_2CO_3 (13.8 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (41.2 mg, 0.10 mmol, 1.0 equiv) and DCM 1.0 mL for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3p** (28.5 mg, 84% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.41 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 5.30 – 5.19 (m, 1H), 4.62 (dd, *J* = 12.3, 7.2 Hz, 1H), 4.55 (dd, *J* = 12.3, 7.2 Hz, 1H), 3.91 (t, *J* = 1.4 Hz, 3H), 3.85 (q, *J* = 7.2 Hz, 1H), 2.13 (t, *J* = 6.1 Hz, 2H), 2.06 (d, *J* = 5.5 Hz, 2H), 1.57 (d, *J* = 7.1 Hz, 3H), 1.51 (qd, *J* = 6.0, 3.9, 2.8 Hz, 4H), 1.47 – 1.42 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.82, 157.70, 147.14, 136.01, 133.78, 129.39, 129.07, 127.19, 126.44, 126.05, 119.01, 115.22, 105.71, 61.12, 55.44, 45.64, 37.05, 29.16, 28.45, 27.81, 26.70, 18.82; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{22}H_{27}O_3^+$, 339.1955, found 339.1955.

2-cyclohexylideneethyl oxaprozin ester (3q)

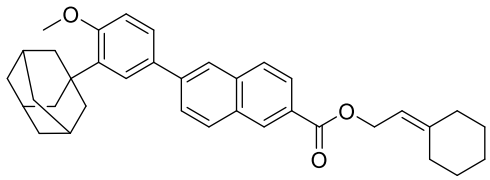


3q

Following the Standard Procedure A, the reaction of oxaprozin (35.2 mg, 0.12 mmol, 1.2 equiv), K_2CO_3 (13.8 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (41.2 mg, 0.10 mmol, 1.0 equiv) and DCM 1.0 mL for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3q** (28.7 mg, 71%

yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.59 – 7.54 (m, 2H), 7.40 – 7.29 (m, 6H), 5.29 (tt, *J* = 7.2, 1.2 Hz, 1H), 4.65 (d, *J* = 7.3 Hz, 2H), 3.20 (dd, *J* = 8.2, 6.8 Hz, 2H), 2.91 (dd, *J* = 8.2, 6.8 Hz, 2H), 2.19 (t, *J* = 5.4 Hz, 2H), 2.09 (d, *J* = 5.3 Hz, 2H), 1.58 – 1.49 (m, *J* = 3.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.12, 162.01, 147.30, 145.53, 135.11, 132.45, 129.06, 128.76, 128.67, 128.59, 128.20, 128.03, 126.60, 115.10, 61.12, 37.08, 31.36, 29.16, 28.44, 27.85, 26.70, 23.71; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{26}H_{28}NO_3^+$, 402.2064, found 402.2061.

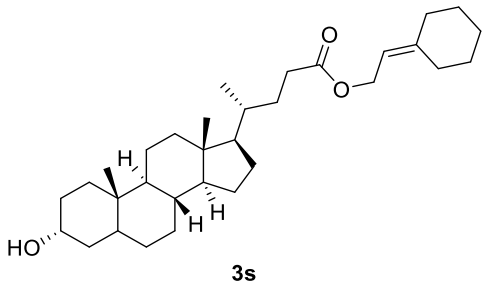
2-cyclohexylideneethyl adapalene ester (3r)



3r

Following the Standard Procedure A, the reaction of adapalene (49.5 mg, 0.12 mmol, 1.2 equiv), K_2CO_3 (13.8 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (41.2 mg, 0.10 mmol, 1.0 equiv) and DCM 1.0 mL for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless solid **3r** (34.8 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.6 Hz, 1H), 8.09 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.05 – 7.96 (m, 2H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.79 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 5.53 – 5.45 (m, 1H), 4.92 (d, *J* = 7.2 Hz, 2H), 3.91 (s, 3H), 2.31 (d, *J* = 5.7 Hz, 2H), 2.20 (d, *J* = 2.9 Hz, 8H), 2.15 – 2.09 (m, 3H), 1.82 (d, *J* = 3.0 Hz, 6H), 1.65 – 1.58 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.02, 159.02, 147.15, 141.39, 139.10, 136.03, 132.72, 131.38, 130.88, 129.81, 128.25, 127.46, 126.52, 126.09, 125.84, 125.80, 124.84, 115.48, 112.23, 61.42, 55.29, 40.75, 37.34, 37.27, 37.19, 29.32, 29.25, 28.51, 27.95, 26.78; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{36}H_{41}O_3^+$, 521.3050, found 521.3054.

2-cyclohexylideneethyl lithocholic ester (3s)

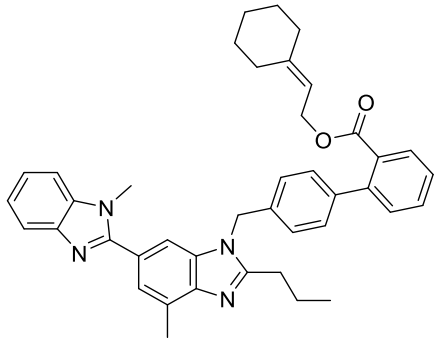


3s

Following the Standard Procedure A, the reaction of lithocholic acid (45.2 mg, 0.12 mmol, 1.2 equiv), K_2CO_3 (13.8 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (41.2 mg, 0.10 mmol, 1.0 equiv) and DCM 1.0 mL for 24

h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3s** (34.4 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (t, *J* = 7.3 Hz, 1H), 4.57 (d, *J* = 7.3 Hz, 2H), 3.61 (tq, *J* = 9.7, 4.7 Hz, 1H), 2.34 (ddd, *J* = 15.2, 9.9, 5.2 Hz, 1H), 2.26 – 2.14 (m, 3H), 2.11 (d, *J* = 5.2 Hz, 2H), 1.95 (dt, *J* = 12.4, 3.0 Hz, 1H), 1.90 – 1.71 (m, 4H), 1.72 – 1.60 (m, 4H), 1.55 (tt, *J* = 8.4, 6.0, 5.0 Hz, 7H), 1.37 (dtd, *J* = 17.4, 10.6, 8.6, 3.7 Hz, 6H), 1.25 (dddd, *J* = 14.2, 10.1, 8.3, 3.9 Hz, 4H), 1.17 – 0.94 (m, 6H), 0.93 – 0.88 (m, 6H), 0.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.51, 146.92, 115.43, 72.01, 60.59, 56.64, 56.13, 42.88, 42.25, 40.58, 40.31, 37.13, 36.60, 35.99, 35.49, 34.72, 31.52, 31.17, 31.06, 30.69, 29.16, 28.47, 28.33, 27.87, 27.34, 26.75, 26.56, 24.35, 23.52, 20.97, 18.42; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{32}H_{53}O_3^+$, 485.3990, found 485.4001.

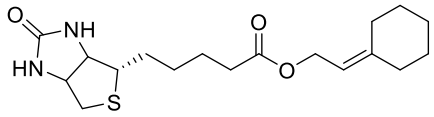
2-cyclohexylideneethyl telmisartan ester (3t)



3t

Following the Standard Procedure A, the reaction of telmisartan (61.8 mg, 0.12 mmol, 1.2 equiv), K_2CO_3 (13.8 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (41.2 mg, 0.10 mmol, 1.0 equiv) and DCM 1.0 mL for 24 h afforded product after flash chromatography MeOH: DCM =0-5% as colorless solid **3t** (43.1 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (ddd, *J* = 9.4, 6.7, 2.0 Hz, 2H), 7.46 (d, *J* = 1.5 Hz, 1H), 7.40 (td, *J* = 7.6, 1.5 Hz, 1H), 7.37 (t, *J* = 1.2 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 5H), 7.03 (d, *J* = 8.1 Hz, 2H), 5.38 (d, *J* = 4.1 Hz, 2H), 4.98 (tt, *J* = 7.2, 1.2 Hz, 1H), 4.48 (d, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 2.92 – 2.84 (m, 2H), 2.70 (s, 3H), 2.01 (t, *J* = 6.0 Hz, 2H), 1.92 (d, *J* = 5.7 Hz, 2H), 1.87 – 1.76 (m, 2H), 1.46 – 1.33 (m, 6H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.31, 156.70, 154.52, 147.14, 143.28, 141.68, 141.27, 136.52, 135.12, 134.73, 131.28, 131.20, 130.80, 129.91, 129.65, 129.31, 127.46, 126.06, 123.99, 123.43, 122.87, 122.73, 119.44, 114.87, 109.72, 109.33, 61.21, 47.30, 37.06, 32.02, 29.94, 29.08, 28.43, 27.82, 26.64, 22.01, 17.05, 14.22; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{41}H_{43}N_4O_2^+$, 623.3381, found 623.3390.

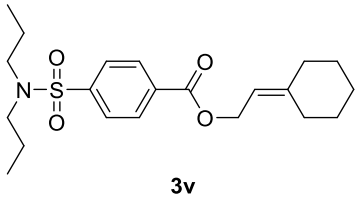
2-cyclohexylideneethyl *D*-biotin ester (3u)



3u

Following the Standard Procedure A, the reaction of *D*-biotin (29.3 mg, 0.12 mmol, 1.2 equiv), K_2CO_3 (13.8 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (41.2 mg, 0.10 mmol, 1.0 equiv) and DCM 1.0 mL for 24 h afforded product after flash chromatography MeOH: DCM =0-5% as colorless oil **3u** (26.9 mg, 76% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.00 (bs, 2H), 5.26 (t, *J* = 7.4 Hz, 1H), 4.56 (d, *J* = 7.3 Hz, 2H), 4.50 (dd, *J* = 7.7, 5.1 Hz, 1H), 4.30 (dd, *J* = 7.9, 4.6 Hz, 1H), 3.14 (dt, *J* = 11.4, 5.7 Hz, 1H), 2.89 (dd, *J* = 12.9, 4.9 Hz, 1H), 2.74 (d, *J* = 12.8 Hz, 1H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.18 (t, *J* = 5.6 Hz, 2H), 2.10 (d, *J* = 5.3 Hz, 2H), 1.68 (dhept, *J* = 27.8, 6.7 Hz, 4H), 1.54 (h, *J* = 6.3, 5.1 Hz, 6H), 1.43 (dp, *J* = 20.9, 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.86, 163.85, 147.06, 115.26, 62.13, 60.70, 60.34, 55.58, 40.64, 37.10, 34.11, 29.14, 28.47, 28.44, 28.34, 27.84, 26.70, 24.93; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{18}H_{29}N_2O_3S^+$, 353.1893, found 353.1902.

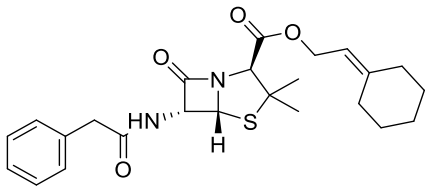
2-cyclohexylideneethyl probenecid ester (3v)



3v

Following the Standard Procedure A, the reaction of probenecid (34.2 mg, 0.12 mmol, 1.2 equiv), K_2CO_3 (13.8 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (41.2 mg, 0.10 mmol, 1.0 equiv) and DCM 1.0 mL for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **3v** (37.6 mg, 95% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 – 8.13 (m, 2H), 7.85 (dd, *J* = 8.5, 1.7 Hz, 2H), 5.40 (t, *J* = 7.3 Hz, 1H), 4.85 (d, *J* = 7.3 Hz, 2H), 3.08 (dd, *J* = 8.8, 6.7 Hz, 4H), 2.26 (d, *J* = 4.9 Hz, 2H), 2.19 – 2.10 (m, 2H), 1.63 – 1.49 (m, 10H), 0.86 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.43, 147.89, 144.19, 134.02, 130.33, 127.06, 114.83, 61.87, 50.03, 37.14, 29.27, 28.46, 27.92, 26.69, 22.04, 11.27; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{21}H_{32}NO_4S^+$, 394.2047, found 394.2057.

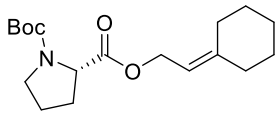
2-cyclohexylideneethyl neotame ester (3w)



3w

Following the Standard Procedure B, the reaction of benzylpenicillin potassium (149.0 mg, 0.40 mmol, 2.0 equiv), H_2O (0.2 mg, 0.2 μL, 0.0011 mmol, 0.056 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography MeOH: DCM =0-5% as colorless oil **3w** (81.2 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 3H), 7.22 – 7.19 (m, 2H), 6.03 (dt, *J* = 6.8, 3.4 Hz, 1H), 5.57 (dd, *J* = 9.0, 4.2 Hz, 1H), 5.43 (d, *J* = 4.2 Hz, 1H), 5.25 – 5.17 (m, 1H), 4.58 (dd, *J* = 7.5, 2.3 Hz, 2H), 4.28 (s, 1H), 3.57 (s, 2H), 2.13 (t, *J* = 5.5 Hz, 3H), 2.05 (d, *J* = 5.7 Hz, 3H), 1.48 (q, *J* = 4.0 Hz, 6H), 1.36 (d, *J* = 3.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.53, 170.48, 167.64, 148.73, 133.95, 129.71, 129.27, 127.78, 114.19, 70.45, 68.20, 64.71, 61.77, 58.90, 43.55, 37.10, 32.16, 29.18, 28.43, 27.84, 26.91, 26.64; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{24}H_{31}N_2O_4S^+$, 443.1999, found 443.2011.

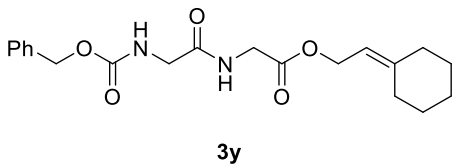
1-(*tert*-butyl) 2-(2-cyclohexylideneethyl) (*S*)-pyrrolidine-1,2-dicarboxylate (3x)



3x

Following the Standard Procedure A, the reaction of (51.7 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-20% as colorless oil **3x** (55.6 mg, 86% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (t, *J* = 7.3 Hz, 1H), 4.74 – 4.50 (m, 2H), 4.35 – 4.15 (m, 1H), 3.64 – 3.30 (m, 2H), 2.25 – 2.14 (m, 3H), 2.12 – 2.05 (m, 2H), 2.00 – 1.89 (m, 2H), 1.88 – 1.77 (m, 2H), 1.58 – 1.50 (m, 6H), 1.47 – 1.38 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.38, 154.00, 147.21, 115.13, 79.92, 61.15, 59.35, 46.44, 37.09, 31.02, 29.15, 28.56, 28.43, 27.82, 26.68, 23.74; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{18}H_{30}NO_4^+$, 324.2169, found 324.2173.

2-cyclohexylideneethyl ((benzyloxy)carbonyl)glycylglycinate (3y)

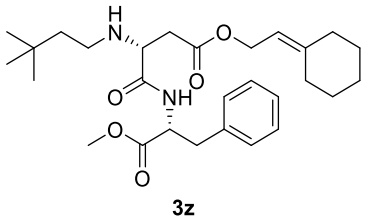


3y

Following the Standard Procedure A, the reaction of (69.3 mg, 0.24 mmol, 1.2 equiv) , K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetra-

fluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-20% as colorless oil **3y** (59.4 mg, 79% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 5H), 6.59 (br, 1H), 5.52 (br, 1H), 5.27 (t, *J* = 7.4 Hz, 1H), 5.13 (d, *J* = 2.1 Hz, 2H), 4.66 (dd, *J* = 7.4, 2.0 Hz, 2H), 4.03 (t, *J* = 3.9 Hz, 2H), 3.92 (d, *J* = 5.4 Hz, 2H), 2.19 (t, *J* = 5.4 Hz, 2H), 2.11 (d, *J* = 5.2 Hz, 2H), 1.62 – 1.51 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.86, 169.37, 156.77, 148.06, 136.22, 128.67, 128.36, 128.22, 114.49, 67.35, 61.84, 44.49, 41.40, 37.08, 29.13, 28.37, 27.82, 26.63; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{20}H_{27}N_2O_5^+$, 375.1914, found 375.1924.

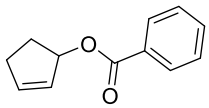
2-cyclohexylideneethyl neotame ester (3z)



3z

Following the Standard Procedure A, the reaction of neotame (90.8 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography MeOH: DCM =0-10% as colorless oil **3z** (82.0 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.21 (m, 3H), 7.18 – 7.11 (m, 2H), 5.27 (tt, *J* = 7.2, 1.3 Hz, 1H), 4.85 (dt, *J* = 8.6, 6.1 Hz, 1H), 4.65 – 4.50 (m, 2H), 3.71 (s, 3H), 3.43 (dd, *J* = 8.7, 3.8 Hz, 1H), 3.20 – 3.04 (m, 2H), 2.74 (dd, *J* = 16.5, 3.8 Hz, 1H), 2.53 (dddd, *J* = 17.0, 15.5, 12.5, 7.7 Hz, 3H), 2.23 – 2.15 (m, 3H), 2.13 (d, *J* = 5.5 Hz, 2H), 1.55 (hept, *J* = 4.5, 4.0 Hz, 6H), 1.37 – 1.29 (m, 2H), 0.86 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.60, 171.84, 171.70, 147.45, 136.08, 129.37, 128.65, 127.19, 114.91, 61.13, 59.40, 52.83, 52.33, 44.61, 44.13, 38.11, 37.08, 36.59, 29.87, 29.64, 29.14, 28.42, 27.84, 26.67; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{28}H_{43}N_2O_5^+$, 487.3166, found 487.3179.

cyclopent-2-en-1-yl benzoate (4a)

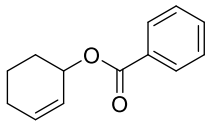


4a

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and 5-(cyclopent-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2aa** (74.0 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4a** (21.0 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.9 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* =

8.4, 7.0 Hz, 2H), 6.16 (dt, *J* = 4.5, 2.2 Hz, 1H), 5.95 (dt, *J* = 4.6, 1.7 Hz, 2H), 2.68 – 2.53 (m, 1H), 2.46 – 2.30 (m, 2H), 2.06 – 1.92 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 137.83, 132.88, 130.82, 129.70, 129.50, 128.40, 81.27, 31.31, 30.03; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{12}H_{13}O_2^+$, 189.0910, found 189.0911.

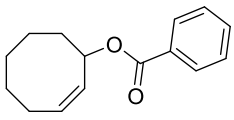
cyclohex-2-en-1-yl benzoate (4b)



4b

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and 5-(cyclohex-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2b** (76.8 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4b** (28.1 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.58 – 7.51 (m, 1H), 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 6.01 (dtd, *J* = 10.0, 3.7, 1.2 Hz, 1H), 5.84 (ddt, *J* = 10.1, 4.1, 2.2 Hz, 1H), 5.51 (tdq, *J* = 5.3, 3.4, 1.6 Hz, 1H), 2.19 – 2.04 (m, 2H), 1.98 (dddd, *J* = 13.3, 9.8, 5.1, 3.4 Hz, 1H), 1.94 – 1.79 (m, 2H), 1.71 (dddd, *J* = 13.8, 11.5, 5.9, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.36, 132.98, 132.87, 130.93, 129.72, 128.39, 125.87, 68.73, 28.56, 25.10, 19.09; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{13}H_{15}O_2^+$, 203.1067, found 203.1064.

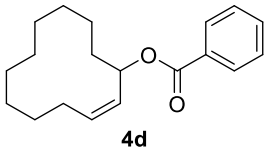
(*Z*)-cyclooct-2-en-1-yl benzoate (4c)



4c

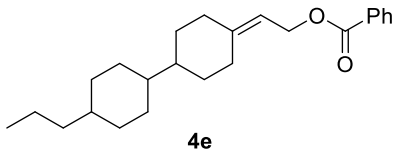
Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(cyclooct-1-en-1-yl)-5*H*-thianthren-5-ium tetra-fluoroborate **2c** (82.5 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4c** (33.9 mg, 74% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.91 (dt, *J* = 11.6, 5.8 Hz, 1H), 5.72 (tdd, *J* = 8.9, 7.0, 1.6 Hz, 1H), 5.62 (dd, *J* = 10.9, 6.9 Hz, 1H), 2.35 (tdd, *J* = 13.2, 9.1, 4.0 Hz, 1H), 2.22 – 2.13 (m, 1H), 2.06 (td, *J* = 8.4, 4.1 Hz, 1H), 1.77 – 1.54 (m, 7H), 1.44 (dddd, *J* = 13.1, 9.8, 6.7, 3.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.11, 132.88, 130.91, 130.81, 129.99, 129.69, 128.40, 73.12, 35.27, 28.96, 26.55, 26.03, 23.54; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{15}H_{19}O_2^+$, 231.1380, found 231.1389.

(*Z*)-cyclododec-2-en-1-yl benzoate (4d)


4d

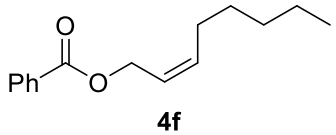
Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(cyclododec-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2d** (93.7 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4d** (33.0 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.57 – 7.50 (m, 1H), 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 5.79 (ddd, *J* = 14.9, 9.4, 5.4 Hz, 1H), 5.58 – 5.41 (m, 2H), 2.24 (ddp, *J* = 10.5, 5.2, 1.7 Hz, 1H), 2.12 – 1.98 (m, 1H), 1.90 (tt, *J* = 9.1, 3.9 Hz, 1H), 1.72 (tdd, *J* = 9.4, 6.7, 4.8 Hz, 1H), 1.65 – 1.52 (m, 2H), 1.48 – 1.21 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.89, 135.13, 132.82, 131.06, 129.68, 129.35, 128.39, 76.56, 32.28, 31.78, 25.96, 25.65, 25.09, 24.98, 24.70, 24.45, 22.39; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{19}H_{27}O_2^+$, 287.2006, found 287.2001.

2-(4'-propyl-[1,1'-bi(cyclohexan)]-4-ylidene)ethyl benzoate (4e)


4e

Following the Standard Procedure A, the reaction of benzoic acid **1a** (14.6 mg, 0.12 mmol, 1.2 equiv), K_2CO_3 (13.8 mg, 0.10 mmol, 1.0 equiv) and (*E*)-5-(2-(4'-propyl-[1,1'-bi(cyclohexan)]-4-yl)vinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2e** (53.6 mg, 0.10 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless solid **4e** (28.5 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H), 7.58 – 7.51 (m, 1H), 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 5.46 – 5.38 (m, 1H), 4.83 (d, *J* = 7.2 Hz, 2H), 2.81 – 2.70 (m, 1H), 2.27 (dq, *J* = 13.4, 3.2, 2.7 Hz, 1H), 2.13 – 2.01 (m, 1H), 1.82 (td, *J* = 13.9, 12.7, 3.6 Hz, 3H), 1.77 – 1.66 (m, 4H), 1.29 (dtdd, *J* = 14.6, 11.2, 5.3, 2.2 Hz, 3H), 1.19 – 1.01 (m, 5H), 0.95 (td, *J* = 12.0, 11.4, 2.9 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.83, 147.25, 132.88, 130.73, 129.73, 128.41, 115.13, 61.41, 43.44, 42.99, 39.93, 37.71, 36.77, 33.69, 31.60, 31.07, 30.31, 30.27, 28.84, 20.18, 14.57; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{24}H_{35}O_2^+$, 355.2632, found 355.2628.

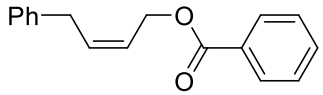
(*Z*)-oct-2-en-1-yl benzoate (4f)


4f

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(oct-1-en-1-yl)-

5*H*-thianthren-5-ium tetrafluoroborate **2f** (82.9 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4f** (41.0 mg, 88% yield, Z/*E* = 2.5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.43 (dd, *J* = 8.4, 7.1 Hz, 2H), 5.94 – 5.60 (m, 2H), 4.94 – 4.73 (m, 2H), 2.23 – 2.03 (m, 2H), 1.46 – 1.37 (m, 2H), 1.30 (td, *J* = 6.4, 5.7, 3.0 Hz, 4H), 0.89 (td, *J* = 6.9, 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.70, 135.88, 132.99, 130.49, 129.73, 128.44, 123.41, 61.01, 31.54, 29.26, 27.74, 22.66, 14.17; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{15}H_{21}O_2^+$, 233.1536, found 233.1541.

(*Z*)-4-phenylbut-2-en-1-yl benzoate (4g)

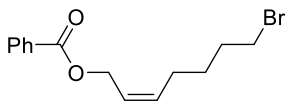


4g

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (86.8 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4g** (46.7 mg, 92% yield, Z/*E* = 3.1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 2H), 7.59 – 7.55 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.23 – 7.21 (m, 3H), 5.93 – 5.87 (m, 1H), 5.85 – 5.79 (m, 1H), 5.00 (d, *J* = 6.8 Hz, 2H), 3.56 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.67, 139.96, 134.63, 133.83, 133.09, 129.78, 128.71, 128.55, 128.50, 126.34, 124.43, 60.82, 34.02; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{17}H_{17}O_2^+$, 253.1223, found 253.1229.

Following the Standard Procedure E, the reaction of benzoic acid **1a** (24.4 mg, 0.20 mmol, 2.0 equiv), PMTDA (17.3 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (43.4 mg, 0.10 mmol, 1.0 equiv) and DCE 2.0 mL for 10 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4g** (14.1 mg, 56% yield, Z/*E* = 8.0:1).

(*Z*)-7-bromohept-2-en-1-yl benzoate (4h)



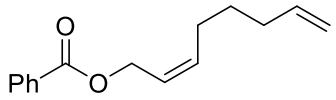
4h

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(7-bromohept-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2h** (95.8 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4h** (56.4 mg, 95% yield, Z/*E* = 2.7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 2H), 7.60 – 7.51 (m,

1H), 7.44 (dd, *J* = 8.3, 7.0 Hz, 2H), 5.75 – 5.64 (m, 2H), 4.87 (d, *J* = 5.7 Hz, 2H), 3.42 (t, *J* = 6.7 Hz, 2H), 2.27 – 2.19 (m, 2H), 1.90 (dt, *J* = 15.1, 6.7 Hz, 2H), 1.63 – 1.52 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.67, 134.81, 133.08, 130.40, 129.75, 128.49, 124.27, 60.82, 33.68, 32.34, 28.05, 26.88; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{14}H_{18}BrO_2^+$, 297.0485, found 297.0482.

Following the Standard Procedure E, the reaction of benzoic acid **1a** (24.4 mg, 0.20 mmol, 2.0 equiv), PMTDA (17.3 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(7-bromohept-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2h** (47.9 mg, 0.10 mmol, 1.0 equiv) and DCE 2.0 mL for 10 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4h** (14.4 mg, 48% yield, Z/*E* = 5.6:1).

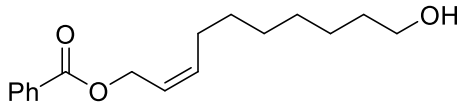
(*Z*)-octa-2,7-dien-1-yl benzoate (4i)



4i

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(octa-1,7-dien-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2i** (82.5 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4i** (33.7 mg, 73% yield, *Z*/*E* = 2.4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 8.4, 1.9 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.89 – 5.65 (m, 3H), 5.02 (ddq, *J* = 17.1, 3.8, 1.8 Hz, 1H), 4.96 (dp, *J* = 10.3, 1.7 Hz, 1H), 4.90 – 4.75 (m, 2H), 2.23 – 2.04 (m, 4H), 1.55 – 1.47 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.69, 138.55, 135.29, 133.01, 132.99, 129.74, 128.46, 123.85, 114.95, 61.01, 33.33, 28.74, 27.16; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{15}H_{19}O_2^+$, 231.1380, found 231.1382.

(*Z*)-10-hydroxydec-2-en-1-yl benzoate (4j)

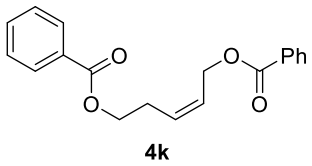


4j

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(10-hydroxydec-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2j** (91.7 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4j** (39.2 mg, 71% yield, Z/*E* = 2.6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.92 – 5.60 (m, 2H), 4.89-4.73 (m, 2H), 3.63 (td, *J* = 6.6, 2.5 Hz, 2H), 2.22-2.02 (m, 2H), 1.55 (qd, *J* = 8.1, 6.6, 2.3 Hz,

2H), 1.45 – 1.28 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 135.74, 133.02, 130.44, 129.73, 128.45, 123.49, 63.12, 61.00, 32.84, 29.44, 29.33, 29.23, 27.70, 25.78; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{17}H_{25}O_3^+$, 277.1798, found 277.1803.

(*Z*)-pent-2-ene-1,5-diyl dibenzoate (4k)

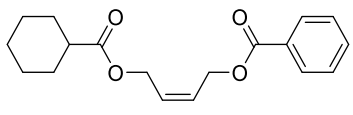


4k

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(5-(benzoyloxy)pent-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2k** (98.5 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4k** (50.9 mg, 82% yield, Z/*E* = 2.0:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dq, *J* = 7.0, 1.6 Hz, 4H), 7.59 – 7.50 (m, 2H), 7.46 – 7.37 (m, 4H), 5.88 – 5.75 (m, 2H), 4.93 (d, *J* = 6.0 Hz, 2H), 4.40 (t, *J* = 6.6 Hz, 2H), 2.69 (q, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.69, 166.60, 133.09, 133.08, 130.46, 130.29, 129.75, 129.70, 128.49, 126.50, 63.99, 60.76, 27.48; HRMS-ESI (m/z) $[M+Na]^+$ calc'd for $C_{19}H_{18}NaO_4^+$, 333.1097, found 333.1094.

Following the Standard Procedure E, the reaction of benzoic acid **1a** (24.4 mg, 0.20 mmol, 2.0 equiv), PMTDA (17.3 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(5-(benzoyloxy)pent-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2k** (49.2 mg, 0.10 mmol, 1.0 equiv) and DCE 2.0 mL for 10 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4k** (14.7 mg, 47% yield, Z/*E* = 5.0:1).

(*Z*)-4-((cyclohexanecarbonyl)oxy)but-2-en-1-yl benzoate (4l)

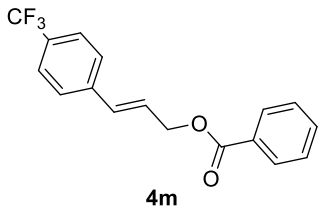


4l

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(4-((cyclohexanecarbonyl)oxy)but-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2l** (96.9 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4l** (44.9 mg, 74% yield, Z/*E* = 2.4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (tt, *J* = 6.5, 1.4 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.43 (td, *J* = 7.8, 3.0 Hz, 2H), 5.93 – 5.76 (m, 2H), 4.88 (dd, *J* = 40.4, 5.3 Hz, 2H), 4.78 – 4.55 (m, 2H), 2.31 (tdt, *J* = 11.5, 7.6, 3.7 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.80 – 1.69 (m, 3H), 1.44 (qd, *J* = 11.5, 3.8 Hz, 2H), 1.34 – 1.19 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.89, 166.40, 133.16, 130.13, 129.75, 128.67, 128.49, 128.14, 64.51, 60.67, 43.24, 29.10, 25.85,

25.55, 25.54; HRMS-ESI (m/z) $[M+Na]^+$ calc'd for $C_{18}H_{22}NaO_4^+$, 325.1410, found 325.1416.

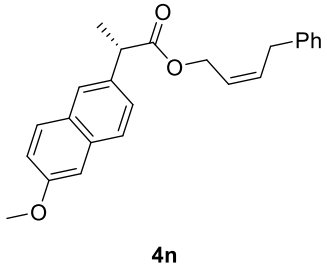
(*E*)-3-(4-(trifluoromethyl)phenyl)allyl benzoate (4m)



4m

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2m** (97.7 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4m** (43.5 mg, 71% yield, Z/E = 1:7.9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.04 (m, 2H), 7.68 – 7.55 (m, 3H), 7.53 – 7.39 (m, 4H), 6.81 – 6.73 (m, 1H), 6.50 (dt, *J* = 16.0, 6.1 Hz, 1H), 5.10 – 4.98 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.42, 139.83, 133.27, 132.51, 130.13, 129.81, 129.09, 128.57, 126.92, 126.24, 125.71 (q, *J* = 3.8 Hz), 124.24 (q, *J* = 273.0 Hz), 65.15; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.54 (s, 3F); HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{17}H_{14}F_3O_2^+$, 307.0940, found 307.0943.

(*Z*)-4-phenylbut-2-en-1-yl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (4n)



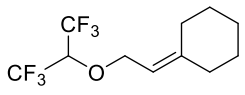
4n

Following the Standard Procedure A, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (86.8 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4n** (60.9 mg, 84% yield, Z/E = 3.8:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 3H), 7.42 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.24 (ddd, *J* = 7.9, 6.5, 1.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.15 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.13 – 7.09 (m, 3H), 5.77 (dtt, *J* = 10.4, 7.6, 1.3 Hz, 1H), 5.66 – 5.59 (m, 1H), 4.81 – 4.69 (m, 2H), 3.92 (s, 3H), 3.88 (q, *J* = 7.2 Hz, 1H), 3.41 (d, *J* = 7.6 Hz, 2H), 1.60 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.70, 157.78, 139.94, 135.81, 133.84, 133.74, 129.43, 129.08, 128.63, 128.49, 127.30, 126.37, 126.26, 126.11, 124.28, 119.11, 105.74, 60.66, 55.46, 45.60, 33.90, 18.73; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{24}H_{25}O_3^+$, 361.1799, found 361.1796.

Following the Standard Procedure E, the reaction of benzoic acid **1p** (24.4 mg, 0.20 mmol, 2.0 equiv), PMTDA (17.3 mg, 0.10 mmol, 1.0 equiv), (*E*)-5-(4-phenylbut-1-en-

1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (43.4 mg, 0.10 mmol, 1.0 equiv) and DCE 2.0 mL for 10 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **4n** (17.1 mg, 47% yield, Z/E = 9.0:1).

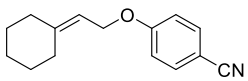
(2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)ethylidene)cyclohexane (5a)



5a

Following the Standard Procedure C, the reaction of 1,1,1,3,3,3-hexafluoro-2-propanol (100.8 mg, 0.60 mmol, 3.0 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 48 h afforded product after flash chromatography hexane as colorless oil **5a** (24.7 mg, 45% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.28 (t, *J* = 7.6 Hz, 1H), 4.36 (d, *J* = 7.5 Hz, 2H), 4.10 (p, *J* = 6.3 Hz, 1H), 2.18 (q, *J* = 6.3, 5.8 Hz, 4H), 1.59 (p, *J* = 3.0, 2.5 Hz, 4H), 1.57 – 1.52 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.13, 121.85 (m), 114.64, 73.36 (hept, *J* = 32.1 Hz), 69.21, 37.33, 29.05, 28.58, 28.01, 26.67; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{11}H_{15}F_6O^+$, 277.1002, found 277.1004.

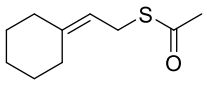
4-(2-cyclohexylideneethoxy)benzonitrile (5b)



5b

Following the Standard Procedure A, the reaction of 4-cyanophenol (28.6 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography hexane as colorless oil **5b** (30.2 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.42 – 5.35 (m, 1H), 4.58 (d, *J* = 6.8 Hz, 2H), 2.24 (d, *J* = 5.9 Hz, 2H), 2.16 (d, *J* = 5.3 Hz, 2H), 1.58 (q, *J* = 3.1, 2.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.33, 147.18, 134.02, 119.43, 115.58, 115.29, 103.82, 64.59, 37.11, 29.37, 28.40, 27.78, 26.64; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{15}H_{18}NO^+$, 228.1383, found 228.1389.

***S*-(2-cyclohexylideneethyl) ethanethioate (5c)**

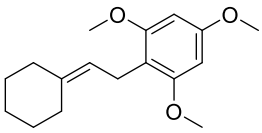


5c

Following the Standard Procedure B, the reaction of potassium thioacetate (45.7 mg, 0.40 mmol, 2.0 equiv), H_2O (0.2 mg, 0.011 mmol, 0.0056 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-5% as colorless oil **5c** (35.8 mg, 97% yield). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 5.09 (tt, *J* = 8.1, 1.3 Hz, 1H), 3.47 (d, *J* = 7.9 Hz, 2H), 2.25 (s, 3H), 2.10 (t, *J* = 5.3 Hz, 2H), 2.00 (t, *J* = 5.2 Hz, 2H), 1.51 – 1.42 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.17, 144.73, 115.24, 37.05, 30.56, 28.90, 28.53, 27.84, 26.82, 26.74; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{10}H_{17}OS^+$, 185.0995, found 185.1001.

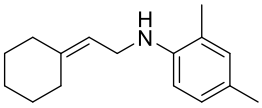
2-(2-cyclohexylideneethyl)-1,3,5-trimethoxybenzene (5d)



5d

Following the Standard Procedure C, the reaction of 1,3,5-trimethoxybenzene (100.9 mg, 0.60 mmol, 3.0 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 48 h afforded product after flash chromatography hexane as colorless oil **5d** (34.4 mg, 62% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 2H), 5.10 (tt, *J* = 7.2, 1.2 Hz, 1H), 3.80 (d, *J* = 1.3 Hz, 9H), 3.27 (d, *J* = 7.3 Hz, 2H), 2.33 (t, *J* = 5.2 Hz, 2H), 2.02 (t, *J* = 5.8 Hz, 2H), 1.54 (dq, *J* = 6.2, 3.5 Hz, 4H), 1.51 – 1.44 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.30, 158.76, 138.71, 120.05, 111.21, 90.86, 55.87, 55.46, 37.32, 28.85, 28.71, 28.00, 27.22, 21.03; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{17}H_{25}O_3^+$, 277.1798, found 277.1796.

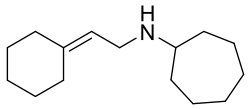
***N*-(2-cyclohexylideneethyl)-2,4-dimethylaniline (6a)**



6a

Following the Standard Procedure A, the reaction of 2,4-dimethyl aniline (29.1 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-50% as colorless oil **6a** (25.1 mg, 55% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.34 (t, *J* = 6.8 Hz, 1H), 3.72 (d, *J* = 6.8 Hz, 2H), 2.24 (s, 3H), 2.21 (d, *J* = 5.1 Hz, 2H), 2.16 – 2.10 (m, 5H), 1.58 (d, *J* = 5.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.11, 143.91, 131.03, 127.42, 126.29, 122.41, 118.58, 110.45, 41.66, 37.13, 29.15, 28.62, 28.02, 26.88, 20.48, 17.61; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{16}H_{24}N^+$, 230.1904, found 230.1904.

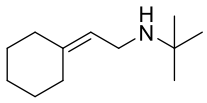
***N*-(2-cyclohexylideneethyl)cycloheptanamine (6b)**



6b

Following the Standard Procedure A, the reaction of cycloheptylamine (27.2 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-50% (0.5 mL Et_3N per 100 mL eluent) as colorless oil **6b** (24.4 mg, 55% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.19 (t, *J* = 7.0 Hz, 1H), 3.19 (d, *J* = 7.0 Hz, 2H), 2.65 (dp, *J* = 8.0, 4.1 Hz, 1H), 2.14 (t, *J* = 5.9 Hz, 2H), 2.08 (t, *J* = 5.6 Hz, 2H), 1.85–1.79 (m, 2H), 1.68–1.62 (m, 2H), 1.58–1.48 (m, 10H), 1.44 – 1.35 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.38, 119.86, 58.55, 43.98, 37.25, 34.93, 29.03, 28.64, 28.44, 28.02, 26.96, 24.62; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{15}H_{28}N^+$, 222.2217, found 222.2216.

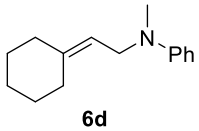
***N*-(2-cyclohexylideneethyl)-2-methylpropan-2-amine (6c)**



6c

Following the Standard Procedure A, the reaction of *tert*-butylamine (17.6 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-50% (0.5 mL Et_3N per 100 mL eluent) as colorless oil **6c** (21.6 mg, 60% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.30 – 5.18 (m, 1H), 3.16 (d, *J* = 6.9 Hz, 2H), 2.14 (t, *J* = 5.8 Hz, 2H), 2.07 (t, *J* = 5.6 Hz, 2H), 1.52 (pd, *J* = 7.0, 6.3, 3.0 Hz, 6H), 1.12 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ142.07, 120.22, 50.72, 39.43, 37.22, 29.09, 28.95, 28.53, 27.97, 26.96; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{12}H_{24}N^+$, 182.1903, found 182.1902.

***N*-(2-cyclohexylideneethyl)-*N*-methylaniline (6d)**

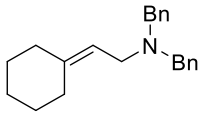


6d

Following the Standard Procedure A, the reaction of *N*-methylaniline (25.7 mg, 0.24 mmol,1.2 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-50% as colorless oil **6d** (30.3 mg, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.8 Hz, 2H), 6.84 – 6.75 (m, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 5.17 (t, *J* = 6.9 Hz, 1H), 3.91 (d, *J* = 6.7 Hz, 2H), 2.90 (s, 3H), 2.23 (t, *J* = 5.6 Hz, 2H), 2.09 (t, *J* = 5.8 Hz, 2H), 1.59 – 1.52 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.83, 143.11, 129.23, 117.14, 116.72, 113.28, 49.80, 38.01, 37.21, 29.03, 28.69,

27.93, 26.91; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{15}H_{22}N^+$, 216.1747, found 216.1752.

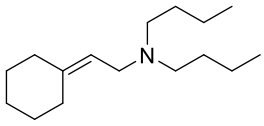
_N_,_N_-dibenzyl-2-cyclohexylideneethan-1-amine (6e)



6e

Following the Standard Procedure A, the reaction of dibenzylamine (47.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-50% (0.5 mL Et_3N per 100 mL eluent) as colorless oil **6e** (43.4 mg, 71% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.5 Hz, 4H), 7.31 (t, *J* = 7.4 Hz, 4H), 7.23 (t, *J* = 7.2 Hz, 2H), 5.27 (t, *J* = 7.0 Hz, 1H), 3.57 (s, 4H), 3.03 (d, *J* = 6.9 Hz, 2H), 2.10 (dt, *J* = 12.0, 5.5 Hz, 4H), 1.61 – 1.44 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.29, 140.18, 128.97, 128.25, 126.84, 118.63, 57.97, 50.22, 37.46, 29.11, 28.81, 27.87, 26.97; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{22}H_{28}N^+$, 306.2216, found 306.2222.

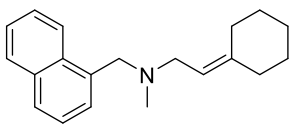
***N*-butyl-*N*-(2-cyclohexylideneethyl)butan-1-amine (6f)**



6f

Following the Standard Procedure A, the reaction of dibutylamine (31.0 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-50% (0.5 mL Et_3N per 100 mL eluent) as colorless oil **6f** (26.2 mg, 55% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 5.17 (t, *J* = 7.1 Hz, 1H), 3.04 (d, *J* = 7.1 Hz, 2H), 2.43 – 2.35 (m, 4H), 2.14 (t, *J* = 6.1 Hz, 2H), 2.09 (t, *J* = 5.6 Hz, 2H), 1.56 – 1.46 (m, 6H), 1.42 (tt, *J* = 8.0, 6.2 Hz, 4H), 1.28 (h, *J* = 7.4 Hz, 4H), 0.90 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.55, 118.49, 53.59, 50.61, 37.50, 29.25, 29.05, 28.78, 27.87, 27.01, 20.99, 14.27; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{16}H_{32}N^+$, 238.2530, found 238.2530.

2-cyclohexylidene-*N*-methyl-*N*-(naphthalen-1-ylmethyl)ethan-1-amine (6g)

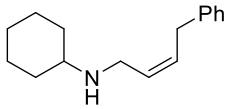


6g

Following the Standard Procedure A, the reaction of 1-methyl-aminomethyl naphthalene (41.1 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a**

(82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-50% (0.5 mL Et_3N per 100 mL eluent) as colorless oil **6g** (35.8mg, 64% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.51 (ddd, *J* = 8.4, 6.7, 1.4 Hz, 1H), 7.47 (td, *J* = 7.4, 6.7, 1.3 Hz, 1H), 7.41 (dt, *J* = 14.8, 7.0 Hz, 2H), 5.36 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 2H), 3.09 (d, *J* = 7.2 Hz, 2H), 2.22 – 2.18 (m, 5H), 2.17 – 2.13 (m, 2H), 1.58 – 1.54 (m, 4H), 1.54 – 1.49 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.81, 135.28, 134.01, 132.68, 128.52, 127.96, 127.62, 125.98, 125.65, 125.21, 124.84, 118.37, 59.94, 54.78, 42.51, 37.51, 29.10, 28.79, 27.85, 26.99; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{20}H_{26}N^+$, 280.2060, found 280.2059.

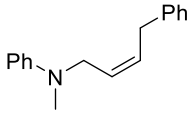
(*Z*)-*N*-(4-phenylbut-2-en-1-yl)cyclohexanamine (6h)



6h

Following the Standard Procedure A, the reaction of cyclohexylamine (23.8 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (86.8 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-20% as colorless oil **6h** (21.7 mg, 47% yield, Z/*E* = 4.9:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (td, *J* = 7.6, 1.8 Hz, 2H), 7.22 – 7.16 (m, 3H), 5.74 – 5.69 (m, 1H), 5.68 – 5.62 (m, 1H), 3.47 – 3.42 (m, 4H), 2.54 (tt, *J* = 10.5, 3.6 Hz, 1H), 1.96 – 1.88 (m, 2H), 1.74 (dt, *J* = 12.9, 3.7 Hz, 2H), 1.65 – 1.59 (m, 1H), 1.25 (qt, *J* = 12.3, 2.9 Hz, 2H), 1.15 (tdd, *J* = 15.2, 12.1, 6.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.62, 130.74, 128.64, 128.56, 128.43, 126.18, 56.44, 43.23, 33.80, 33.20, 26.13, 25.13; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{16}H_{24}N^+$, 230.1904, found 230.1901.

(*Z*)-*N*-methyl-*N*-(4-phenylbut-2-en-1-yl)aniline (6i)

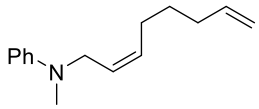


6i

Following the Standard Procedure A, the reaction of *N*-methylaniline (25.7 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (86.8 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-20% as colorless oil **6i** (35.7mg, 75% yield, Z/E = 3.0 :1).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.21 (m, 5H), 6.78 (d, *J* = 8.3 Hz, 2H), 6.76 – 6.73 (m, 1H), 5.78 (dddd, *J* = 12.5, 7.6, Hz, 1H), 5.59 (dddd, *J* = 12.4, 6.4, Hz, 1H), 4.07 (d, *J* = 6.4 Hz, 2H), 3.52 (d, *J* = 7.6 Hz, 2H), 2.94

(s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.72, 140.50, 130.85, 129.27, 128.68, 128.46, 127.22, 126.24, 116.93, 113.25, 49.87, 38.26, 33.79; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{17}H_{20}N^+$, 238.1591, found 238.1590.

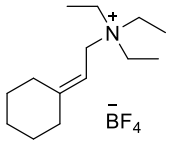
(*Z*)-*N*-methyl-*N*-(octa-2,7-dien-1-yl)aniline (6j)



6j

Following the Standard Procedure A, the reaction of *N*-methylaniline (25.7 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(octa-1,7-dien-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2i** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-20% as colorless oil **6j** (32.2 mg, 75% yield, Z/E = 1.9 :1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 6.80 – 6.68 (m, 3H), 5.91 – 5.74 (m, 1H), 5.58 (dtq, *J* = 12.3, 7.3, 1.6 Hz, 1H), 5.46 (ddddt, *J* = 14.2, 9.4, 6.2, 3.2, 1.4 Hz, 1H), 5.09 – 4.92 (m, 2H), 3.95 (d, *J* = 6.3 Hz, 2H), 2.91 (s, 3H), 2.24 – 2.00 (m, 4H), 1.49 (dpd, *J* = 22.4, 7.5, 1.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.64, 138.58, 132.36, 129.13, 126.18, 116.78, 114.77, 113.17, 49.81, 38.07, 33.33, 28.80, 26.94; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{15}H_{22}N^+$, 216.1747, found 216.1747.

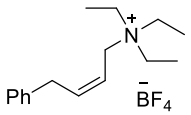
2-cyclohexylidene-*N*,*N*,*N*-triethylethan-1-aminium tetrafluoroborate (6k)



6k

Following the Standard Procedure E, the reaction of triethylamine (40.5 mg, 0.40 mmol, 2.0 equiv), H_2O (0.2 mg, 0.011 mmol, 0.056 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography MeOH: DCM =0-10% as colorless oil **6k** (45.4 mg, 76% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.14 (t, *J* = 7.8 Hz, 1H), 3.78 (d, *J* = 7.8 Hz, 2H), 3.26 (q, *J* = 7.2 Hz, 6H), 2.23 (dd, *J* = 12.9, 7.2 Hz, 4H), 1.58 (ddt, *J* = 10.4, 7.2, 3.2 Hz, 6H), 1.33 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.31, 106.43, 54.58, 52.54, 37.88, 29.65, 28.38, 27.82, 26.36, 7.70; ^{19}F NMR (377 MHz, $CDCl_3$) δ -152.43 (bs), -152.44 (bs), -152.48 (bs), -152.49 (bs); HRMS-ESI (m/z) $[M-BF_4]^+$ calc'd for $C_{14}H_{28}N^+$, 210.2217, found 210.2216.

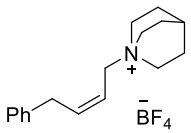
(*Z*)-*N*,*N*,*N*-triethyl-4-phenylbut-2-en-1-aminium tetrafluoroborate (6l)



6l

Following the Standard Procedure E, the reaction of triethylamine (40.5 mg, 0.40 mmol, 2.0 equiv), H_2O (0.2 mg, 0.011 mmol, 0.056 equiv) and (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (86.8 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography MeOH: DCM =0-10% as colorless solid **6l** (46.2 mg, 72% yield, *Z*/*E* = 4.4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.19 – 7.13 (m, 2H), 6.25 (dtd, *J* = 9.2, 7.7, 1.3 Hz, 1H), 5.64 – 5.54 (m, 1H), 3.96 (d, *J* = 7.5 Hz, 2H), 3.54 (d, *J* = 7.6, 2H), 3.31 (q, *J* = 7.3 Hz, 6H), 1.33 (t, *J* = 7.4 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.18, 138.58, 128.93, 128.47, 126.75, 115.16, 54.19, 53.05, 33.86, 7.67; ^{19}F NMR (377 MHz, $CDCl_3$) δ -152.43 (bs), -152.44 (bs), -152.48 (bs), -152.49 (bs). HRMS-ESI (m/z) $[M\text{-}BF_4]^+$ calc'd for $C_{16}H_{26}N^+$, 232.2060, found 232.2058.

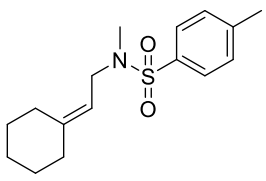
(*Z*)-1-(4-phenylbut-2-en-1-yl)quinuclidin-1-ium tetrafluoroborate (6m)



6m

Following the Standard Procedure E, the reaction of quinuclidine (44.5 mg, 0.40 mmol, 2.0 equiv), H_2O (0.2 mg, 0.011 mmol, 0.056 equiv) and (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (86.8 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography MeOH: DCM =0-10% as colorless solid **6m** (46.4 mg, 70% yield, Z/E = 4.4:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.18 (t, *J* = 5.7 Hz, 3H), 6.21 (dt, *J* = 14.6, 7.6 Hz, 1H), 5.63– 5.55 (m, 1H), 3.90 (t, *J* = 7.6 Hz, 2H), 3.51 (d, *J* = 7.3 Hz, 2H), 3.43 (dd, *J* = 9.7, 6.1 Hz, 6H), 2.11 (dd, *J* = 7.2, 3.7 Hz, 1H), 1.95 (dt, *J* = 10.4, 4.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ142.07, 138.85, 128.85, 128.55, 126.59, 115.50, 60.21, 54.35, 33.59, 23.91, 19.63; ^{19}F NMR (377 MHz, $CDCl_3$) δ -151.05 (bs), -151.10 (bs). HRMS-ESI (m/z) $[M\text{-}BF_4]^+$ calc'd for $C_{17}H_{24}N^+$, 242.1904, found 242.1901.

***N*-(2-cyclohexylideneethyl)-*N*,4-dimethylbenzenesulfonamide (6n)**

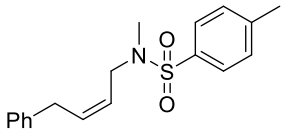


6n

Following the Standard Procedure D, the reaction of *N*-methyl-*p*-toluenesulfonamide (44.5 mg, 0.24 mmol, 1.2 equiv), KOH (11.2 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(2-cyclohexylvinyl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-10% as

colorless oil **6n** (42.9 mg, 73% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.04 (t, *J* = 7.5 Hz, 1H), 3.60 (d, *J* = 7.5 Hz, 2H), 2.63 (s, 3H), 2.43 (s, 3H), 2.07 (q, *J* = 6.5, 6.0 Hz, 4H), 1.57 – 1.49 (m, 4H), 1.46 (t, *J* = 5.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.96, 143.31, 134.67, 134.64, 129.72, 127.69, 115.15, 46.88, 37.23, 34.00, 28.75, 28.56, 27.80, 26.73, 21.64; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{16}H_{24}NO_2S^+$, 294.1523, found 294.1523.

(*Z*)-*N*,4-dimethyl-*N*-(4-phenylbut-2-en-1-yl)benzenesulfonamide (6o)

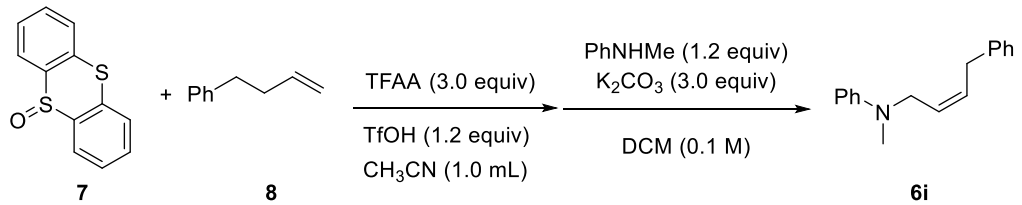


6o

Following the Standard Procedure D, the reaction of *N*-methyl-*p*-toluenesulfonamide (44.5 mg, 0.24 mmol, 1.2 equiv), KOH (11.2 mg, 0.20 mmol, 1.0 equiv) and (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2g** (86.8 mg, 0.20 mmol, 1.0 equiv) for 24 h afforded product after flash chromatography EA: PE = 0-10% as colorless solid **6o** (47.2 mg, 75% yield, *Z*/*E* =3.1:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.1 Hz, 2H), 5.83 – 5.77 (m, 1H), 5.51 – 5.44 (m, 1H), 3.77 (d, *J* = 5.5 Hz, 2H), 3.37 (d, *J* = 5.9 Hz, 2H), 2.69 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.54, 139.91, 134.47, 133.34, 129.83, 128.69, 128.36, 127.67, 126.34, 124.65, 46.89, 34.41, 33.48, 21.65; HRMS-ESI (m/z) $[M+H]^+$ calc'd for $C_{18}H_{22}NO_2S^+$, 316.1366, found 316.1368.

Mechanistic Study

One-Pot Experiments

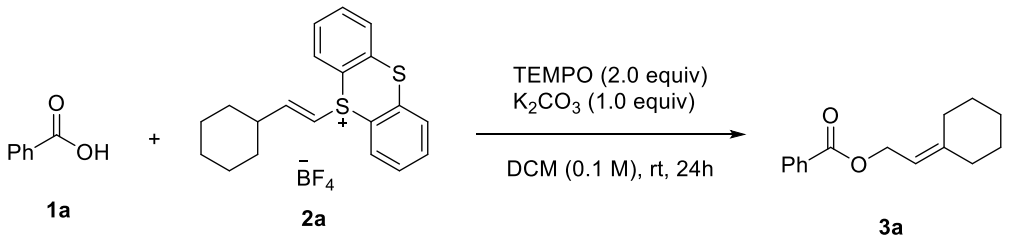


7 **8** **6i**

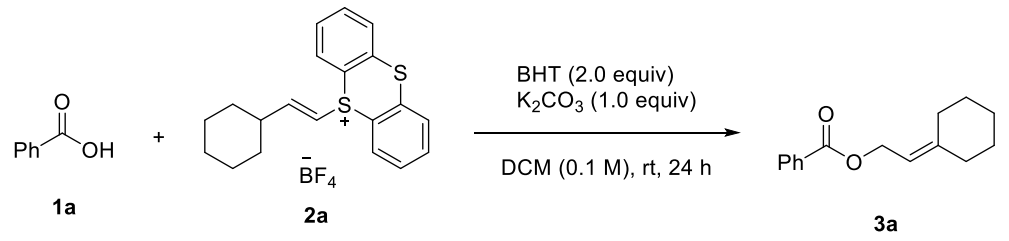
Under the nitrogen atmosphere, thianthrene 5-oxide **7** (69.7 mg, 0.3 mmol, 1.5 equiv), 4-Phenyl-1-butene **8** (26.4 mg, 0.2 mmol, 1.0 equiv) and CH_3CN (1.0 mL), 0 ºC add Trifluoroacetic anhydride (63.0 mg, 0.6 mmol, 3.0 equiv) and trifluoromethanesulfonic

(36.0 mg, 0.24 mmol, 1.2 equiv), stir 1h under 0 °C, then r.t. stir 1h. After evaporated the solvent, add K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv), N-Methylaniline (25.7 mg, 0.24 mmol, 1.2 equiv) and DCM (2.0 mL), stir 24 h under room temperature. Afforded product after flash chromatography EA: PE = 0-10% as colorless oil **6i** (30.1 mg, 63% yield, Z/E = 2.0 :1).

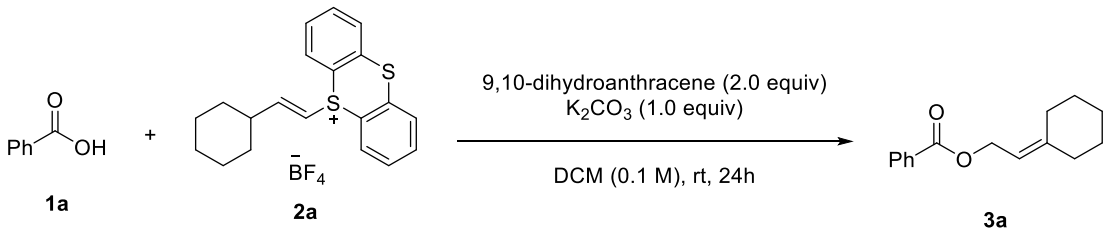
Radical Trap Experiments



Following the Standard Procedure, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv), (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) and TEMPO (61.0 mg, 0.40 mmol, 2.0 equiv) in DCM (2.0 mL) for 24 h. The conversion of **2a** >97%, and the yield of **3a** 76% yield. Yield was determined by ^{1}H NMR of the crude mixture using mesitylene (12.0 mg, 0.10 mmol, 0.5 equiv) as internal standard.

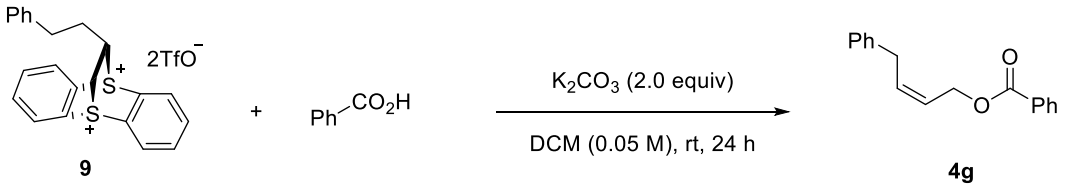


Following the Standard Procedure, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv), (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) and 2,6-Di-tert-butyl-4-methylphenol (88.1 mg, 0.40 mmol, 2.0 equiv) in DCM (2.0 mL) for 24 h. The conversion of **2a** >97%, and the yield of **3a** 88% yield. Yield was determined by ^{1}H NMR of the crude mixture using mesitylene (12.0 mg, 0.10 mmol, 0.5 equiv) as internal standard.

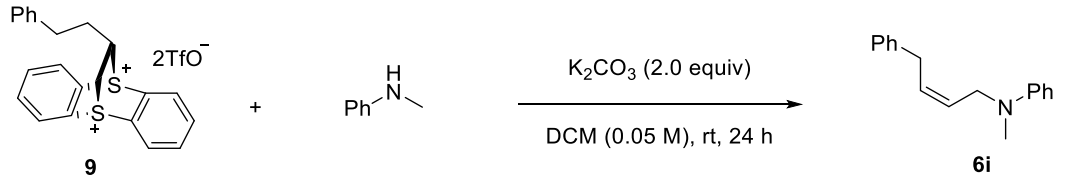


Following the Standard Procedure, the reaction of benzoic acid **1a** (29.3 mg, 0.24 mmol, 1.2 equiv), K_2CO_3 (27.6 mg, 0.20 mmol, 1.0 equiv), (*E*)-5-(4-phenylbut-1-en-1-yl)-5*H*-thianthren-5-ium tetrafluoroborate **2a** (82.4 mg, 0.20 mmol, 1.0 equiv) and 9,10-dihydroanthracene (72.1 mg, 0.40 mmol, 2.0 equiv) in DCM (2.0 mL) for 24 h. The conversion of **2a** >97%, and the yield of **3a** 86% yield. Yield was determined by ^{1}H NMR of the crude mixture using mesitylene (12.0 mg, 0.10 mmol, 0.5 equiv) as internal standard.

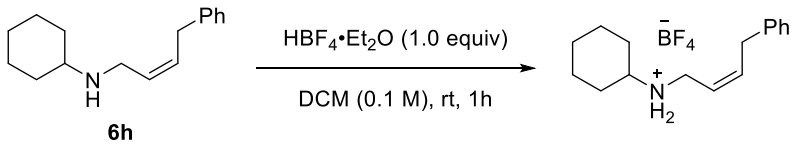
Assignment of Reaction Intermediate



Under the nitrogen atmosphere, 11-phenethyl-5,10-ethanothianthrene-5,10-diium di-trifluoromethanesulfonate (64.7 mg, 0.1 mmol, 1.0 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv) and benzoic acid (14.7 mg, 0.12 mmol, 1.2 equiv), add DCM (2.0 mL) rt stir 24 h. The reaction mixture was purified directly by column chromatography to afford the product **4g** (18.2 mg, 72% yield, *Z*/*E* = 3.6:1).



Under the nitrogen atmosphere, 11-phenethyl-5,10-ethanothianthrene-5,10-diium di-trifluoromethanesulfonate (64.7 mg, 0.1 mmol, 1.0 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv) and *N*-methylaniline (12.9 mg, 0.12 mmol, 1.2 equiv), add DCM (2.0 mL) rt stir 24 h. The reaction mixture was purified directly by column chromatography to afford the product **6i** (16.9 mg, 71% yield, *Z*/*E* = 3.2:1).



6h

N-(4-phenylbut-2-en-1-yl)cyclohexanamine **6h** (Z/E = 4.9:1, 22.9 mg, 0.10 mmol, 1.0 equiv) was placed in 10 mL Schlenk tube equipped with a magnetic stir bar. After back-filled with nitrogen (this process was repeated three times), 1.0 mL DCM and $HBF_4 \cdot Et_2O$ (16.2 mg, 0.10 mmol, 1.0 equiv) was added, the vial was sealed and at room temperature with stirring 1h. The reaction mixture was washed with Et_2O (5x5 mL) to afford the product (27.2 mg, 86% yield, *Z*/*E* = 5.4:1). ^{1}H NMR (600 MHz, $CDCl_3$) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.16 – 7.13 (m, 2H), 6.75 (s, 2H), 6.11 – 5.99 (m, 1H), 5.75 – 5.63 (m, 1H), 3.84 (q, *J* = 6.1 Hz, 2H), 3.46 (d, *J* = 8.2 Hz, 2H), 3.05 (tt, *J* = 12.2, 4.2 Hz, 1H), 2.06 (dd, *J* = 13.0, 3.9 Hz, 2H), 1.83 (dd, *J* = 13.3, 3.3 Hz, 2H), 1.64 (dd, *J* = 10.7, 4.1 Hz, 1H), 1.44 (qd, *J* = 12.1, 3.7 Hz, 2H), 1.27 – 1.15 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.97, 137.74, 128.89, 128.39, 126.66, 119.09, 57.00, 42.00, 33.63, 29.15, 24.71, 24.42.; ^{19}F NMR (376 MHz, $CDCl_3$) δ -147.83 (bs), -147.89 (bs). HRMS-ESI (m/z) $[M\text{-}BF_4]^+$ calc'd for $C_{16}H_{24}N^+$, 230.1903, found 230.1900.

Crystallographic Data

X-ray diffraction of 4n (CCDC 2110292)

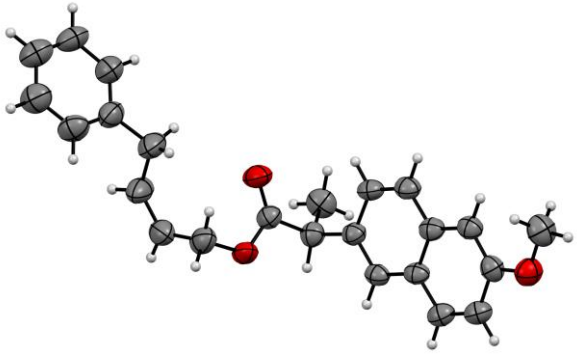


Table S5. Crystal data and structure refinement for cxy3383_0m_4 (4n).

Identification code	cxy3383_0m_4
Empirical formula	$C_{24}H_{24}O_3$
Formula weight	360.43
Temperature/K	150.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.0869(3)
b/Å	17.6346(9)
c/Å	17.8806(9)
α/°	90
β/°	92.230(3)
γ/°	90
Volume/Å^3	1917.85(17)
Z	4
ρ_{calc}g/cm^3	1.248
μ/mm^{-1}	0.643
F(000)	768.0
Crystal size/mm^3	0.32 × 0.26 × 0.25
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.946 to 136.664
Index ranges	? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ?
Reflections collected	7046
Independent reflections	7046 [R_{int} = 0.0868, R_{sigma} = 0.0677]
Data/restraints/parameters	7046/39/530

Goodness-of-fit on F^2	1.103
Final R indexes [I>=2σ (I)]	R_1 = 0.0680, wR_2 = 0.1896
Final R indexes [all data]	R_1 = 0.0778, wR_2 = 0.2070
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.28
Flack parameter	-0.11(16)

X-ray diffraction of the HBF_4 salt of 6k (CCDC 2107074)

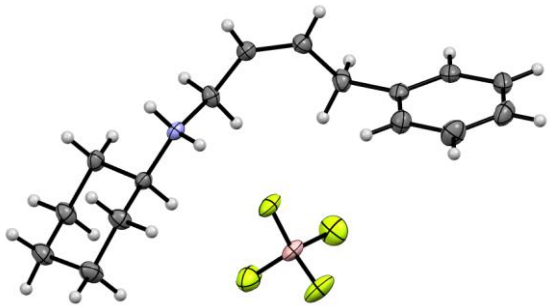


Table S6. Crystal data and structure refinement for cxy3292 (HBF_4 salt of 6k).

Identification code	cxy3292
Empirical formula	$C_{16}H_{24}BF_4N$
Formula weight	317.17
Temperature/K	100
Crystal system	orthorhombic
Space group	Iba2
a/Å	26.2135(15)
b/Å	48.489(3)
c/Å	7.7284(5)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	9823.3(10)
Z	24
ρ_{calc}g/cm^3	1.287
μ/mm^{-1}	0.894
F(000)	4032.0
Crystal size/mm^3	0.24 × 0.22 × 0.15
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.424 to 138.388
Index ranges	-31 ≤ h ≤ 26, -58 ≤ k ≤ 58, -9 ≤ l ≤ 9
Reflections collected	42810

Independent reflections	8964 [R_{int} = 0.0749, R_{sigma} = 0.0566]
Data/restraints/parameters	8964/208/615
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0580, wR_2 = 0.1544
Final R indexes [all data]	R_1 = 0.0622, wR_2 = 0.1580
Largest diff. peak/hole / e $Å^{-3}$	0.46/-0.23
Flack parameter	0.59(15)

X-ray diffraction of the HBF_4 salt of 7 (CCDC 2110458)

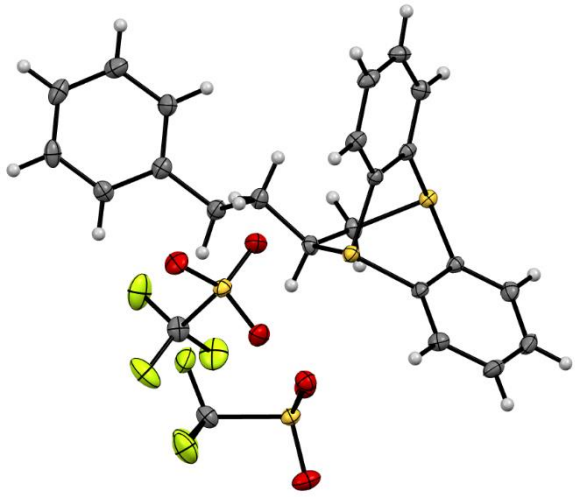


Table S7. Crystal data and structure refinement for cxy3323_0m (7)

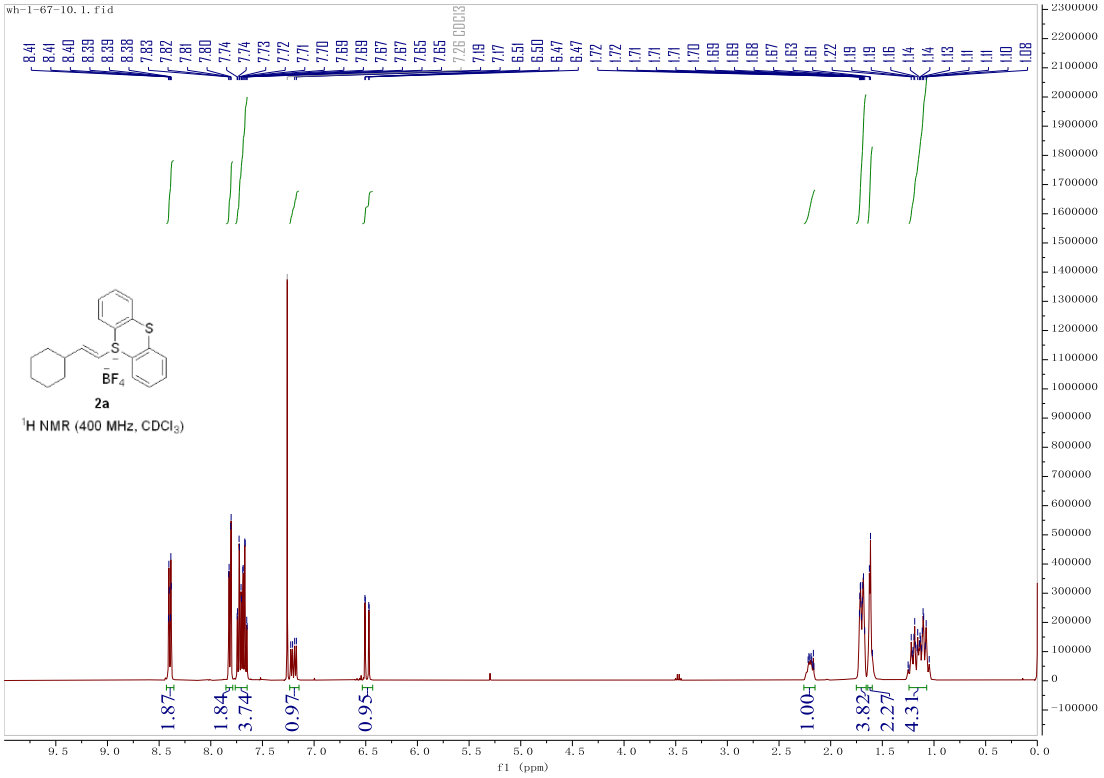
Identification code	cxy3323_0m
Empirical formula	$C_{24}H_{20}O_6F_6S_4$
Formula weight	646.64
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.1824(10)
b/Å	17.1893(15)
c/Å	16.2826(15)
α/°	90
β/°	99.542(4)
γ/°	90
Volume/$Å^3$	2534.5(4)
Z	4
$\rho_{calc}g/cm^3$	1.695
μ/mm^{-1}	4.240
F(000)	1320.0

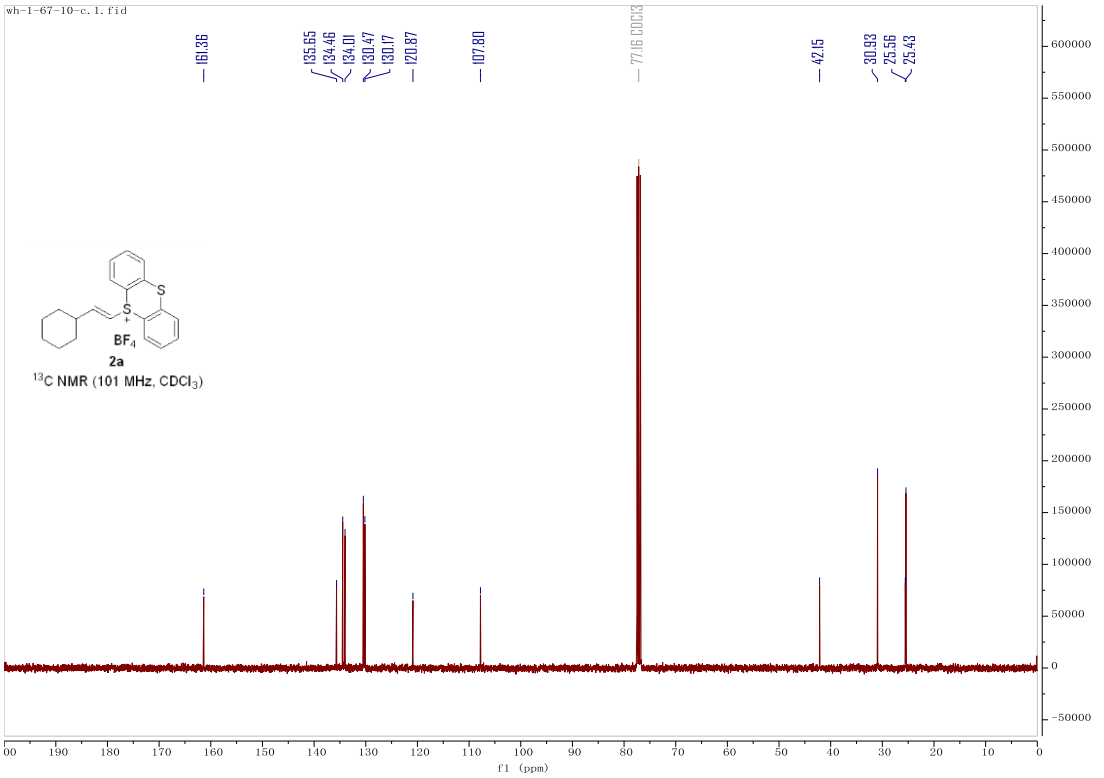
Crystal size/mm^3	0.25 × 0.22 × 0.18
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.534 to 136.892
Index ranges	-11 ≤ h ≤ 9, -18 ≤ k ≤ 20, -19 ≤ l ≤ 19
Reflections collected	23136
Independent reflections	4623 [R_{int} = 0.0543, R_{sigma} = 0.0342]
Data/restraints/parameters	4623/0/361
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0356, wR_2 = 0.0933
Final R indexes [all data]	R_1 = 0.0373, wR_2 = 0.0947
Largest diff. peak/hole / e Å^{-3}	0.91/-0.34

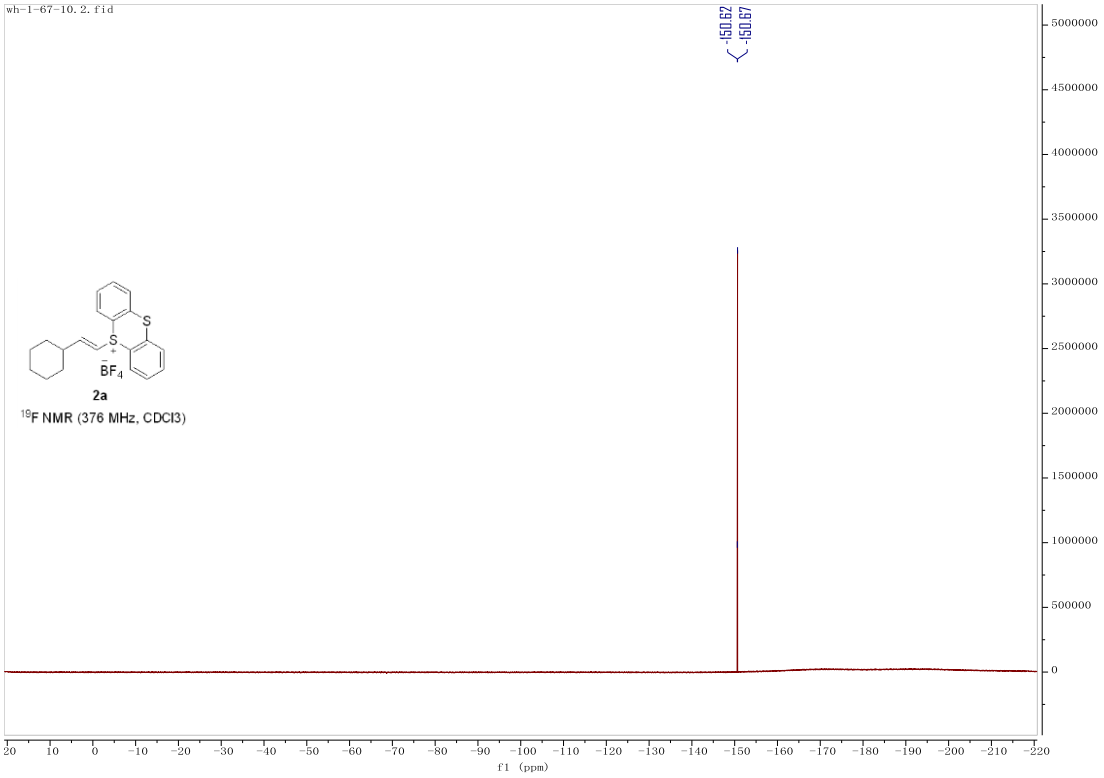
References

1. Qian, D. Q.; Shine, H. J.; Guzman-Jimenez, I. Y.; Thurston, J. H.; Whitmire, K. H., Mono- and Bisadducts from the Addition of Thianthrene Cation Radical Salts to Cycloalkenes and Alkenes. *J. Org. Chem.* **2002,** *67*, 4030-4039.
2. Chen, J.; Li, J.; Plutschack, M. B.; Berger, F.; Ritter, T., Regio- and Stereoselective Thianthrenation of Olefins To Access Versatile Alkenyl Electrophiles. *Angew. Chem. Int. Ed.* **2020,** *59*, 5616-5620.

Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra of New Compounds



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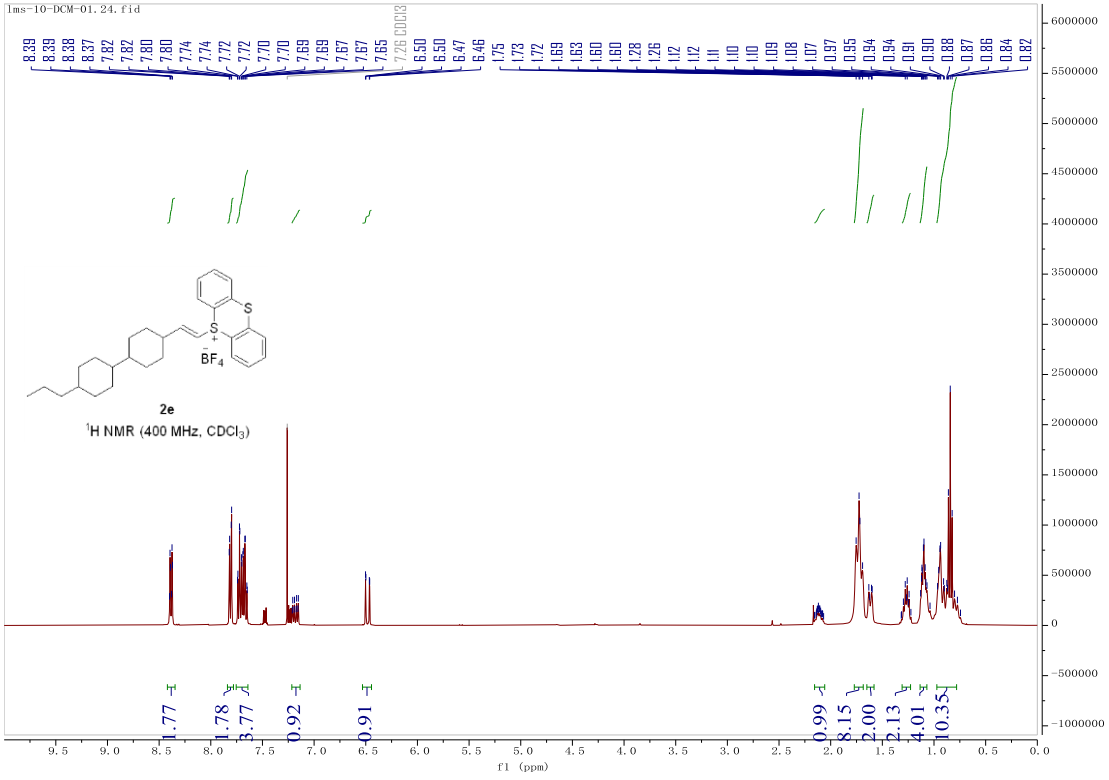
BF4
2a
19F NMR (376 MHz, CDCl3)
f1 (ppm)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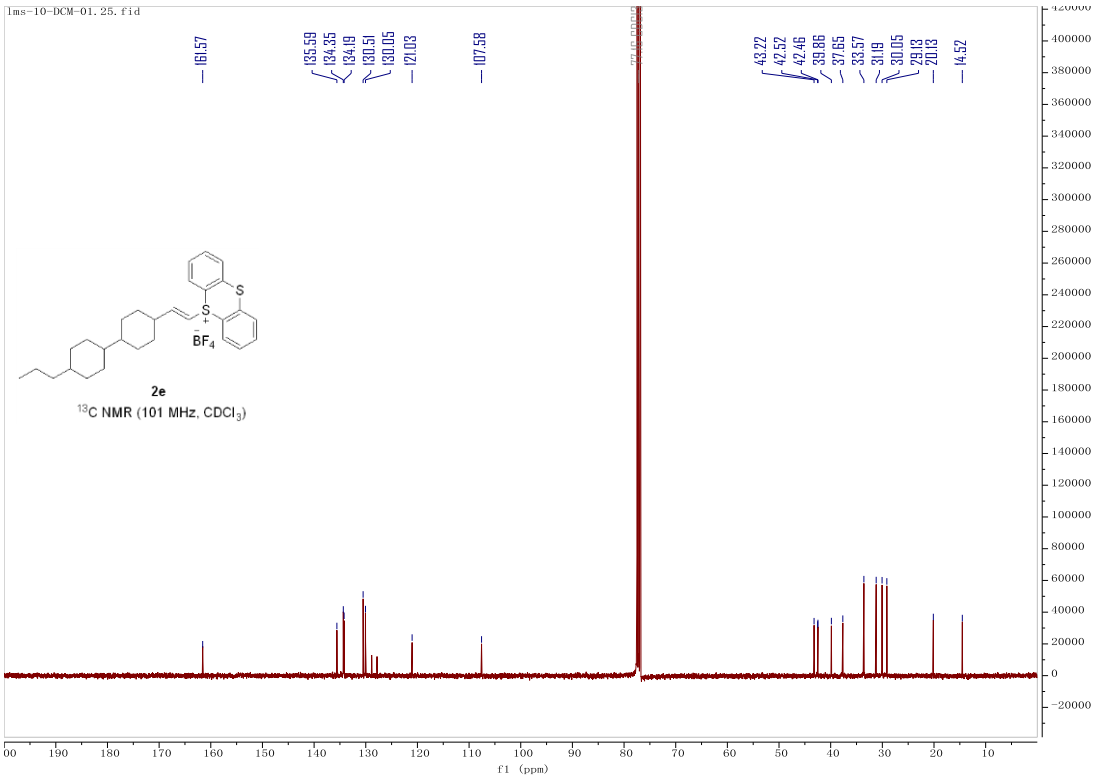
7.26 CDCl3
BF4
2e
1H NMR (400 MHz, CDCl3)
1.77
1.78
3.77
0.92
0.91
0.99
8.15
2.00
2.13
4.01
10.35
f1 (ppm)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134.35
134.19
130.51
130.05
121.03
107.58
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42.52
42.46
39.86
37.65
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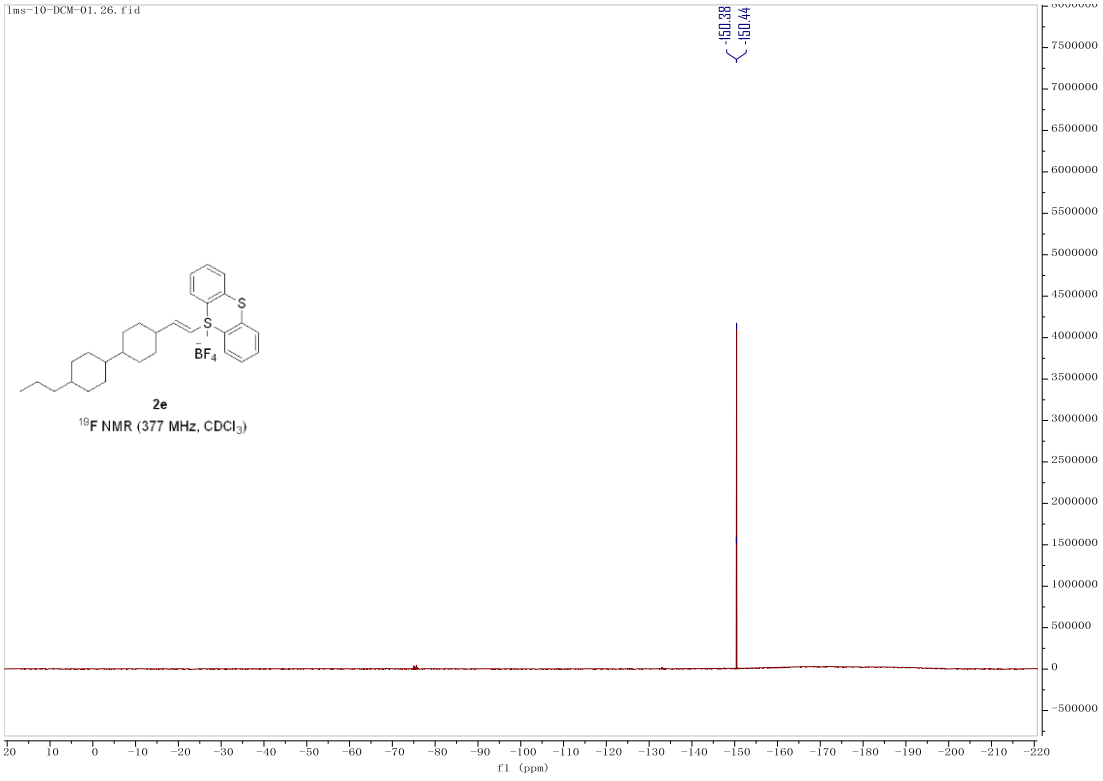
20.13
14.52
BF4
2e
13C NMR (101 MHz, CDCl3)
f1 (ppm)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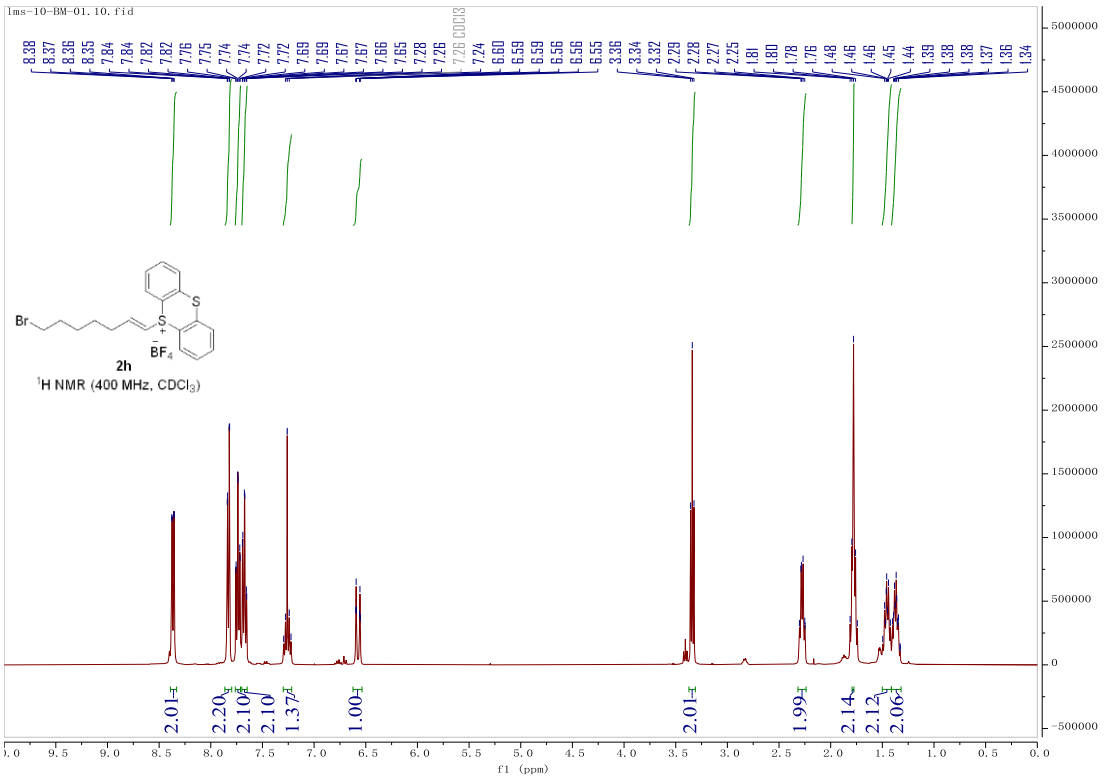
BF4
2e
19F NMR (377 MHz, CDCl3)
f1 (ppm)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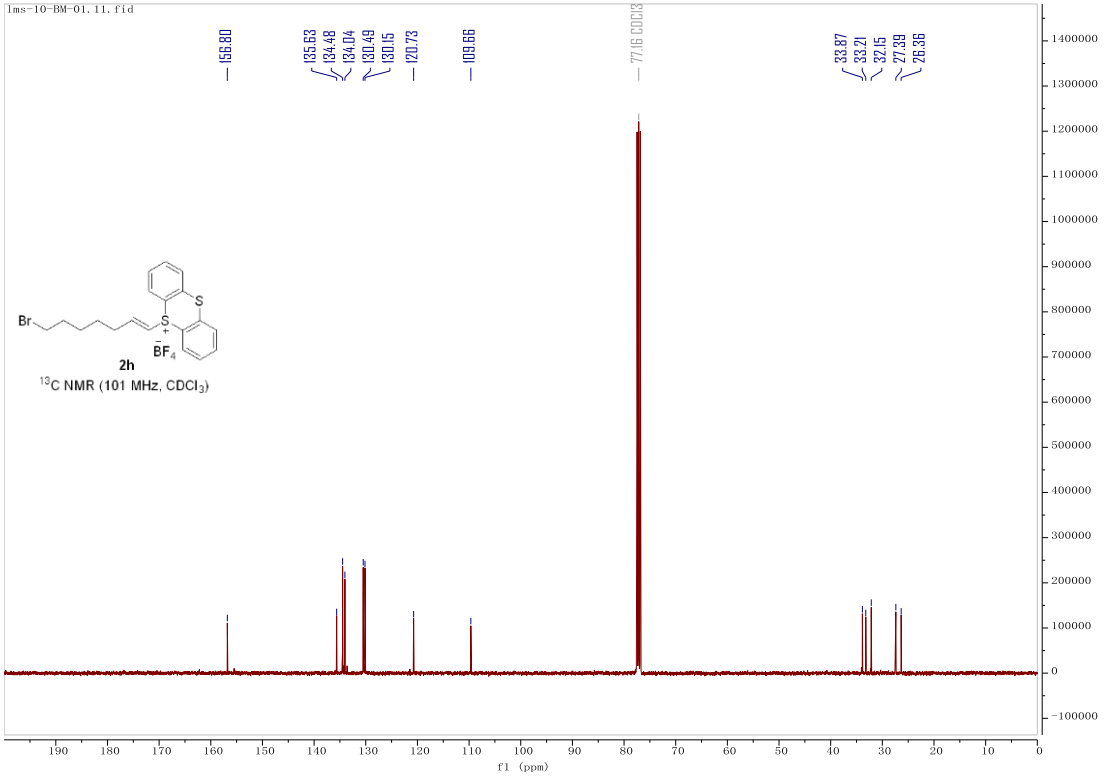
f1 (ppm)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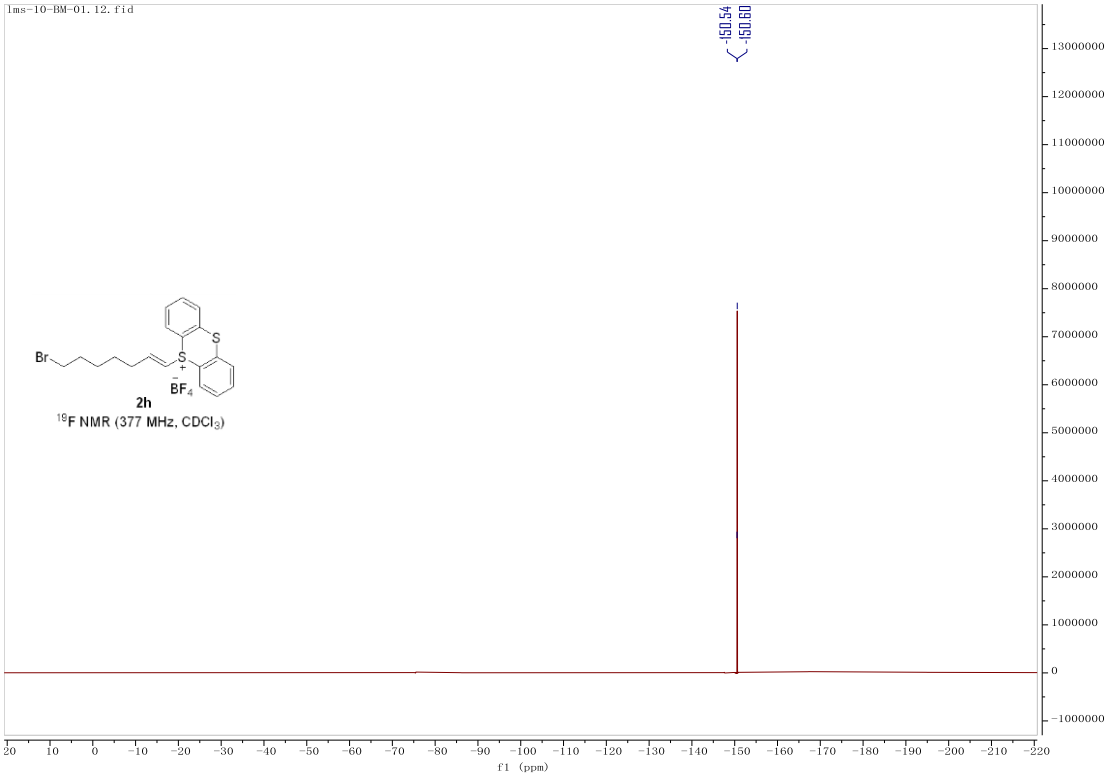
f1 (ppm)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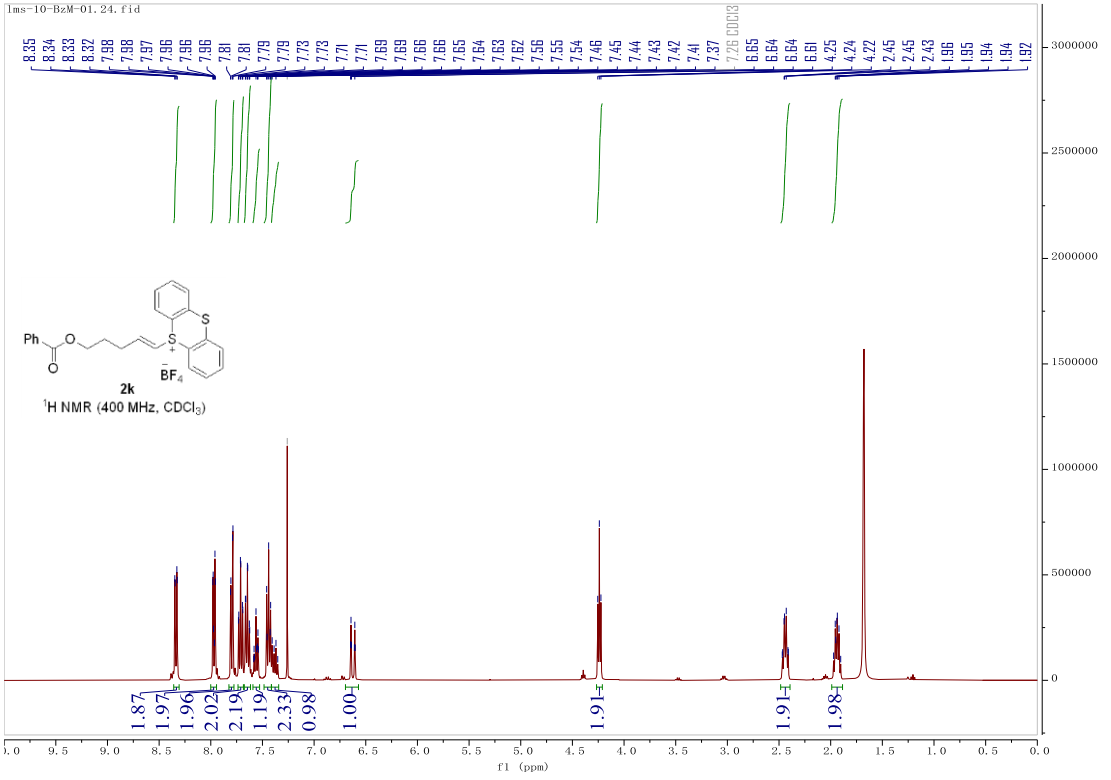
S
S
+
BF4
2h
19F NMR (377 MHz, CDCl3)
f1 (ppm)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Ph
O
O
S
S
+
BF4
2k
1H NMR (400 MHz, CDCl3)
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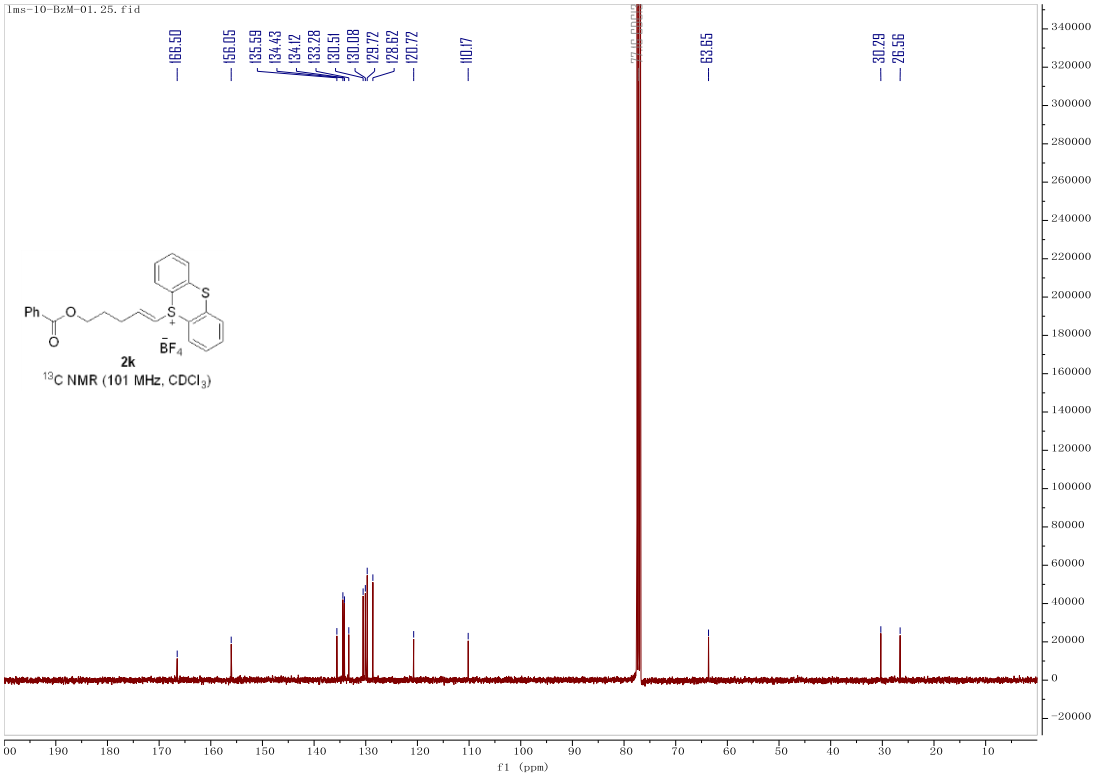
1.97
1.96
2.02
2.19
1.19
2.33
0.98
1.00
1.91
1.91
1.98
f1 (ppm)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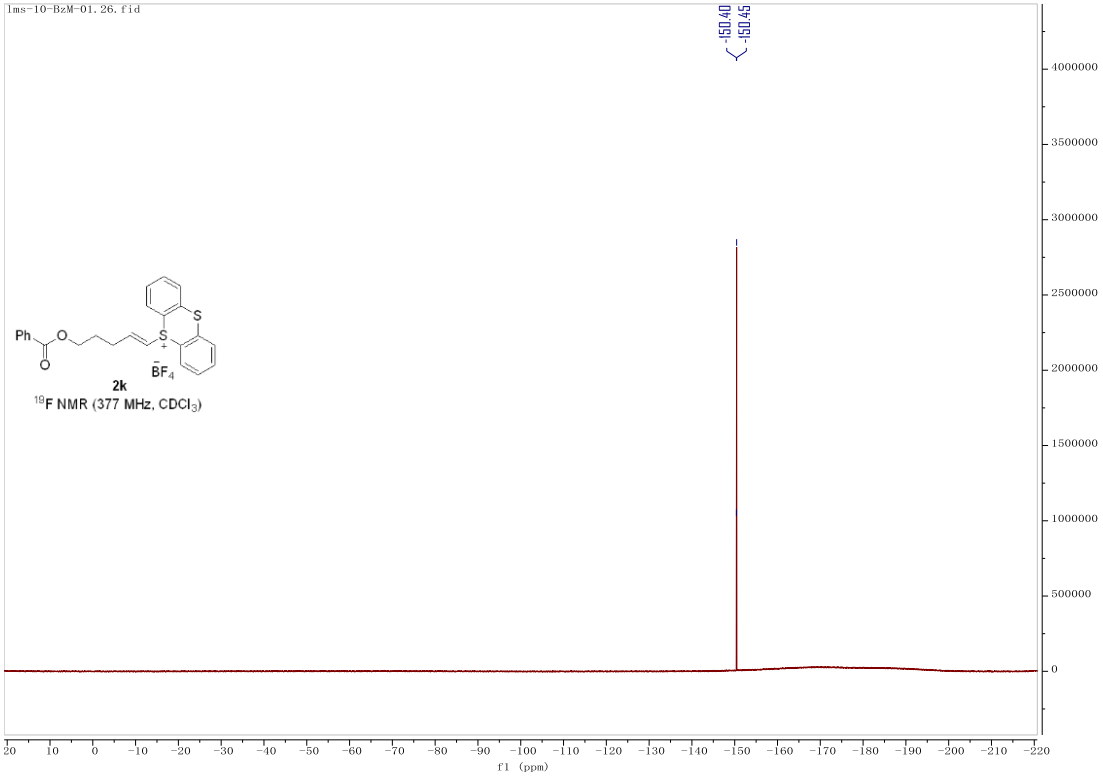
129.72
128.62
120.72
110.17
63.65
30.29
26.56
Ph
O
O
S
S
BF4
2k
13C NMR (101 MHz, CDCl3)
f1 (ppm)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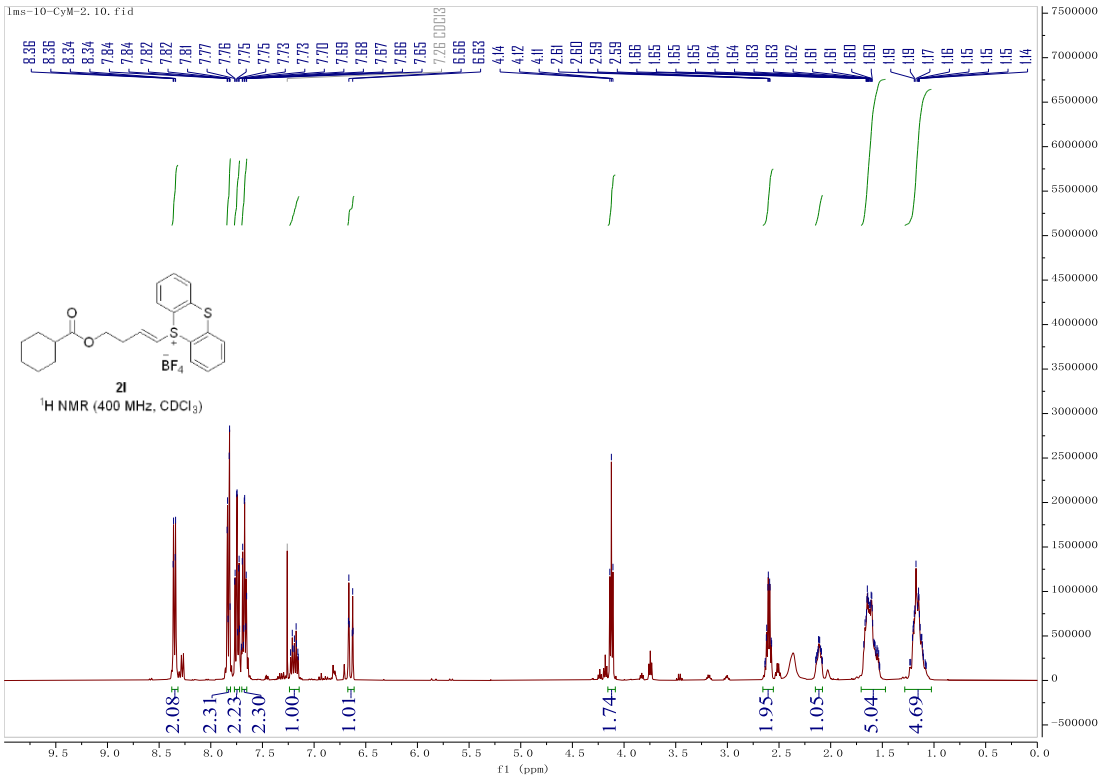
S
BF4
2k
19F NMR (377 MHz, CDCl3)
f1 (ppm)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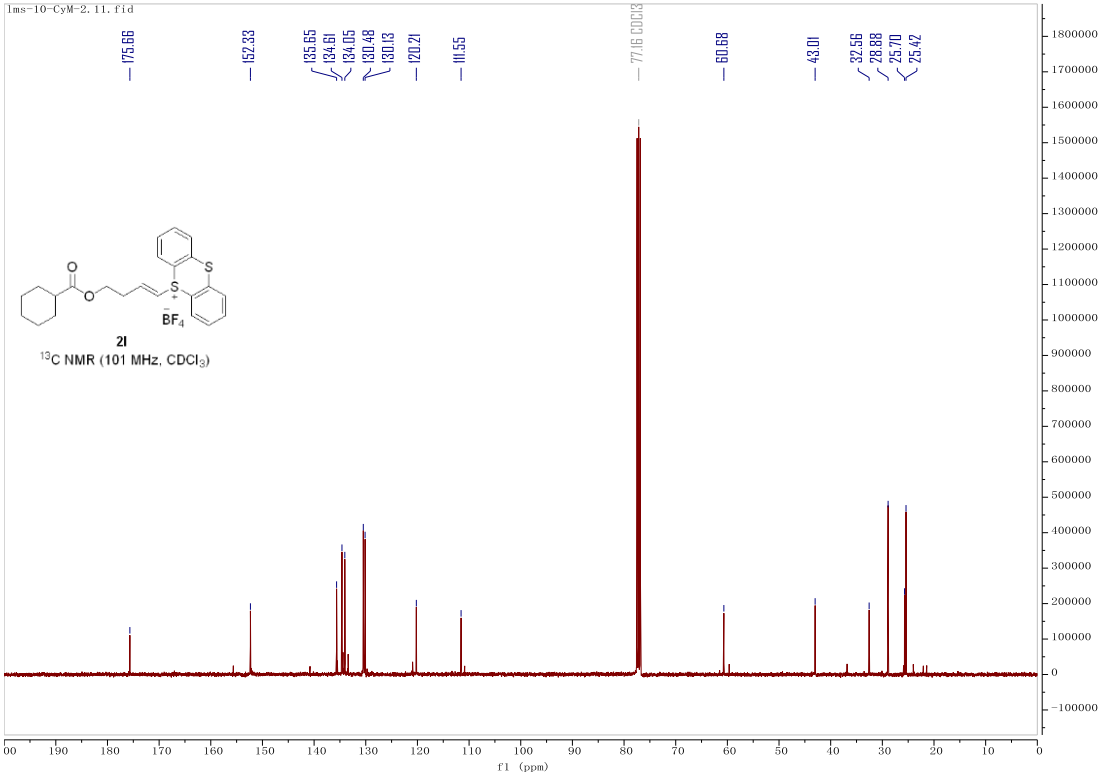
2I
1H NMR (400 MHz, CDCl3)
f1 (ppm)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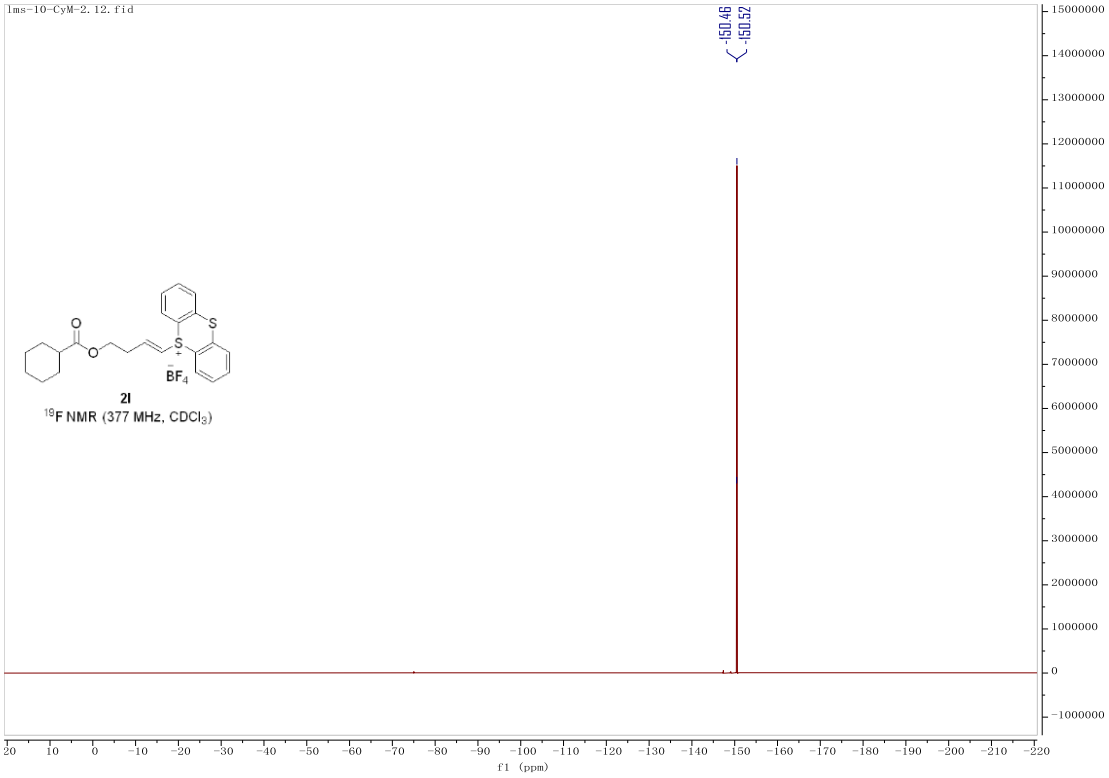
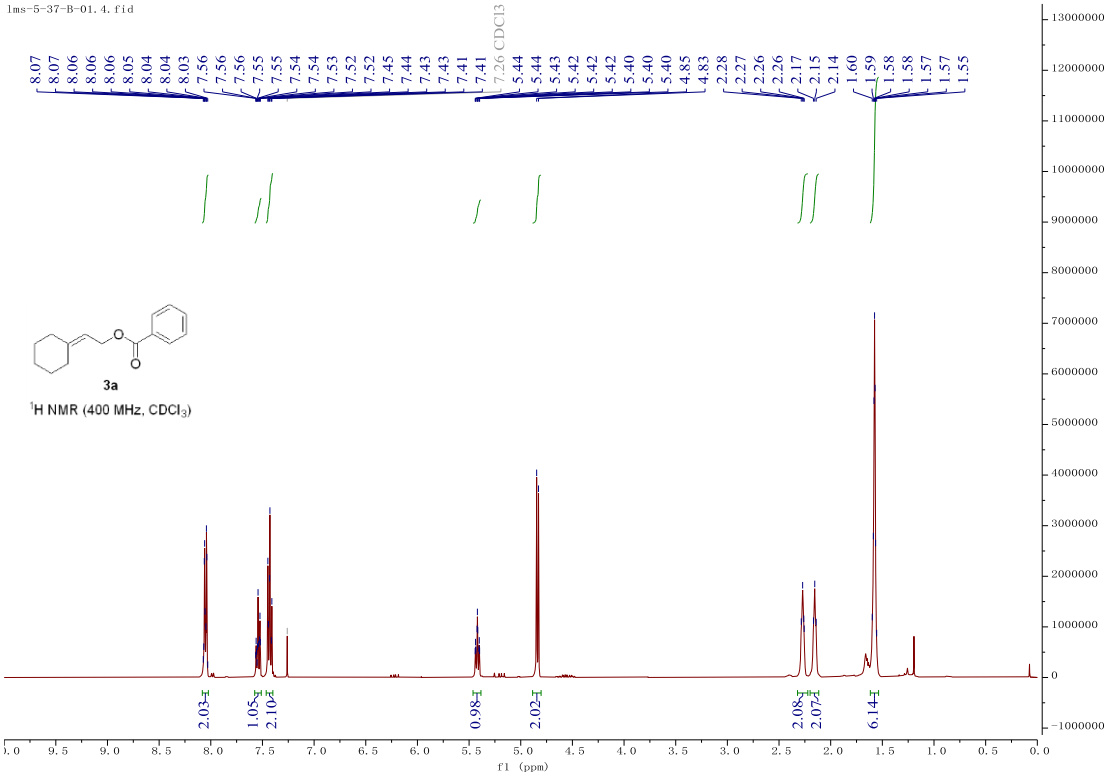
13C NMR (101 MHz, CDCl3)
f1 (ppm)



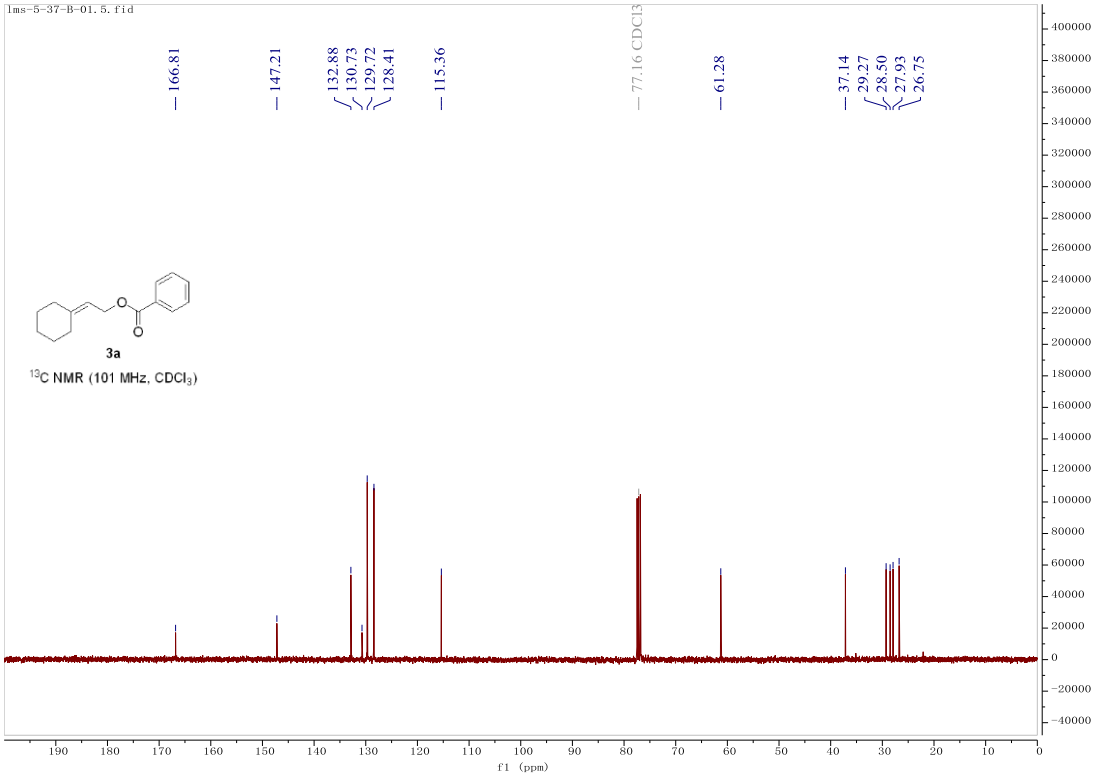
2l

^{19}F NMR (377 MHz, $CDCl_3$)



3a

^{1}H NMR (400 MHz, $CDCl_3$)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130.73
129.72
128.41
115.36
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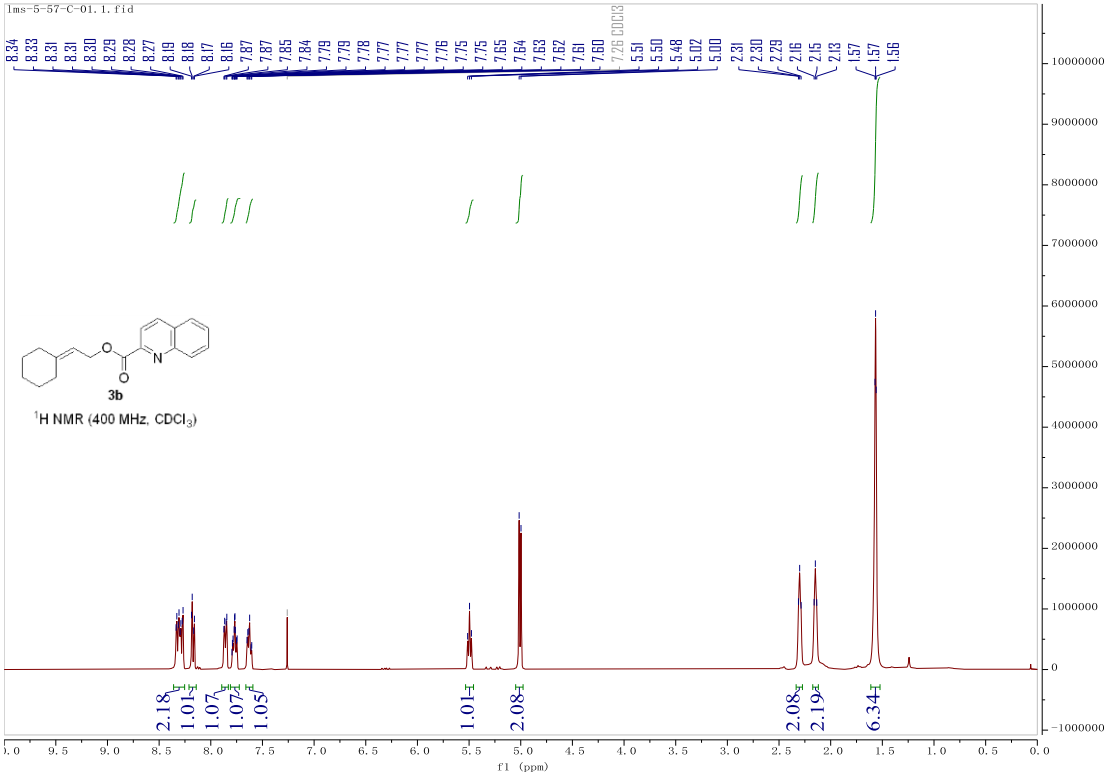
37.14
29.27
28.50
27.93
26.75
3a
13C NMR (101 MHz, CDCl3)
f1 (ppm)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1H NMR (400 MHz, CDCl3)
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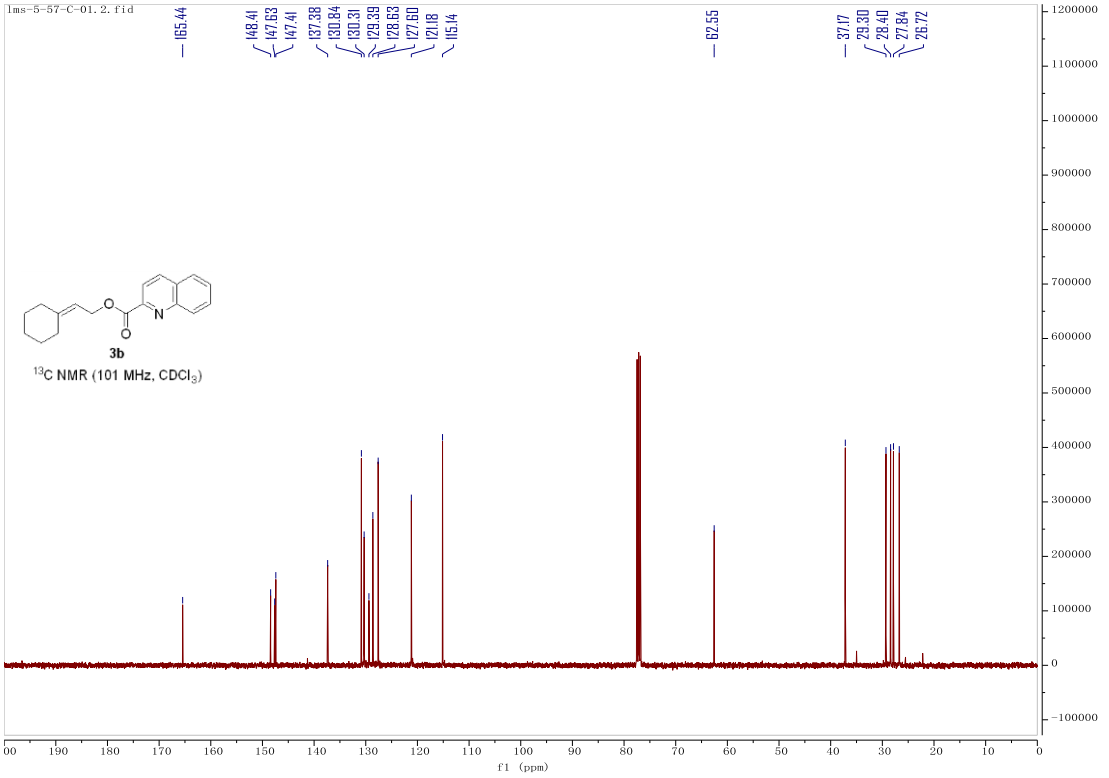
1.01
2.08
2.08
2.19
6.34
f1 (ppm)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127.60
121.18
115.14
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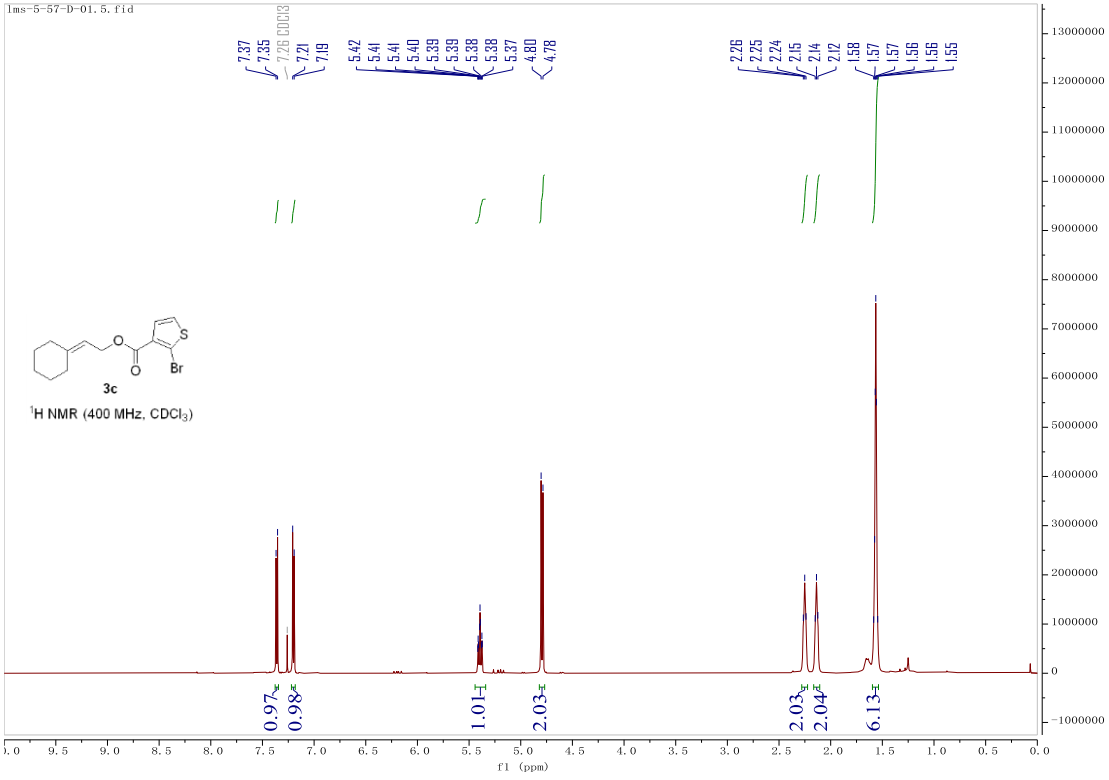
37.17
29.30
28.40
27.84
26.72
3b
13C NMR (101 MHz, CDCl3)
f1 (ppm)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5.39
5.39
5.38
5.38
5.37
4.80
4.78
2.26
2.25
2.24
2.15
2.14
2.12
1.58
1.57
1.57
1.56
1.56
1.55
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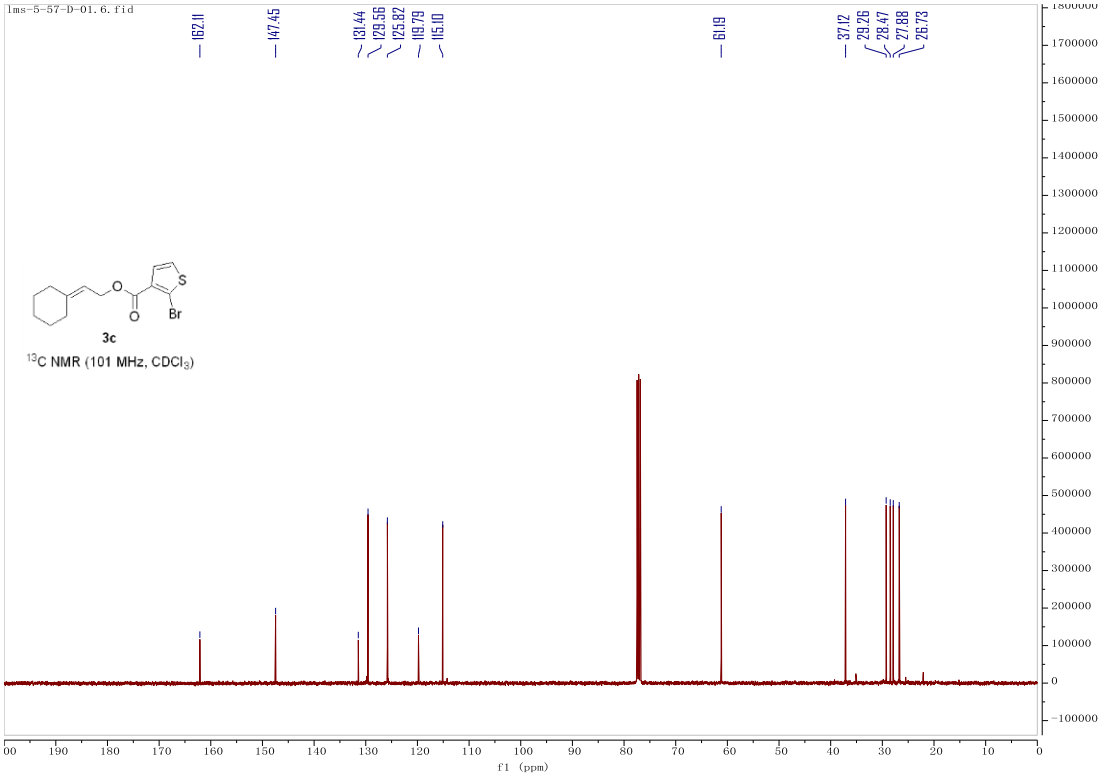
0.98
1.01
2.03
2.03
2.04
6.13
3c
1H NMR (400 MHz, CDCl3)
f1 (ppm)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119.79
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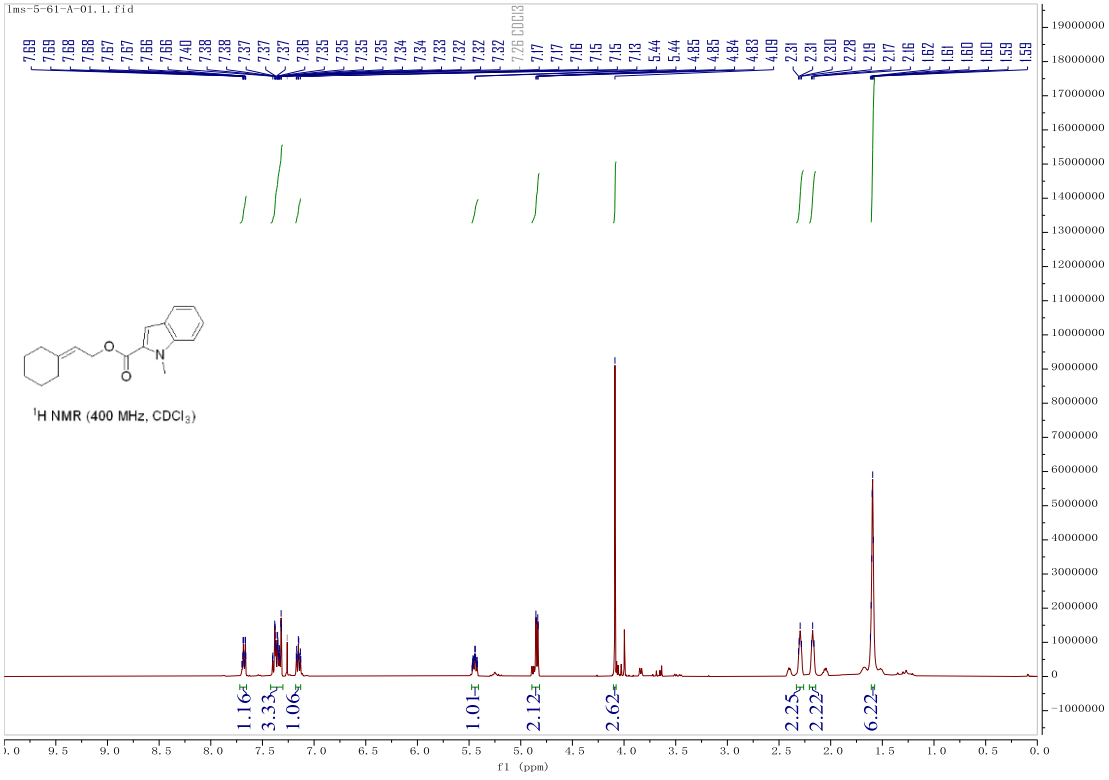
29.26
28.47
27.88
26.73
S
O
O
Br
3c
13C NMR (101 MHz, CDCl3)
f1 (ppm)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O
O
N
1H NMR (400 MHz, CDCl3)
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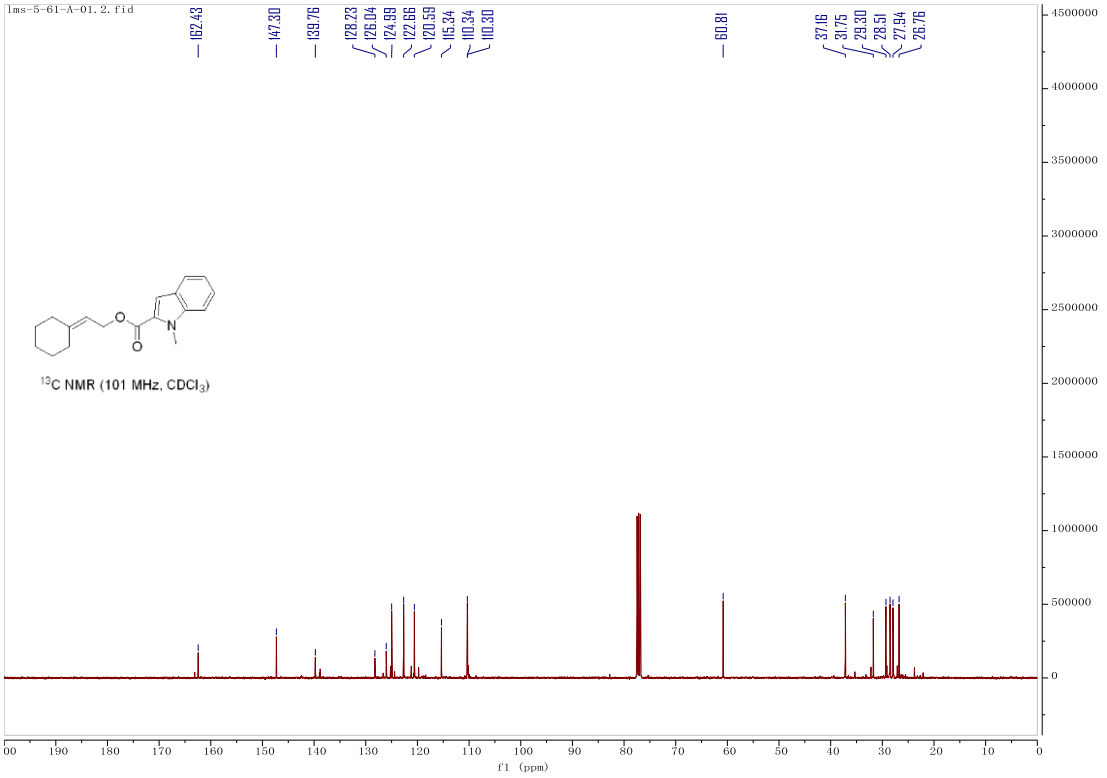
2.62
2.25
2.22
6.22
f1 (ppm)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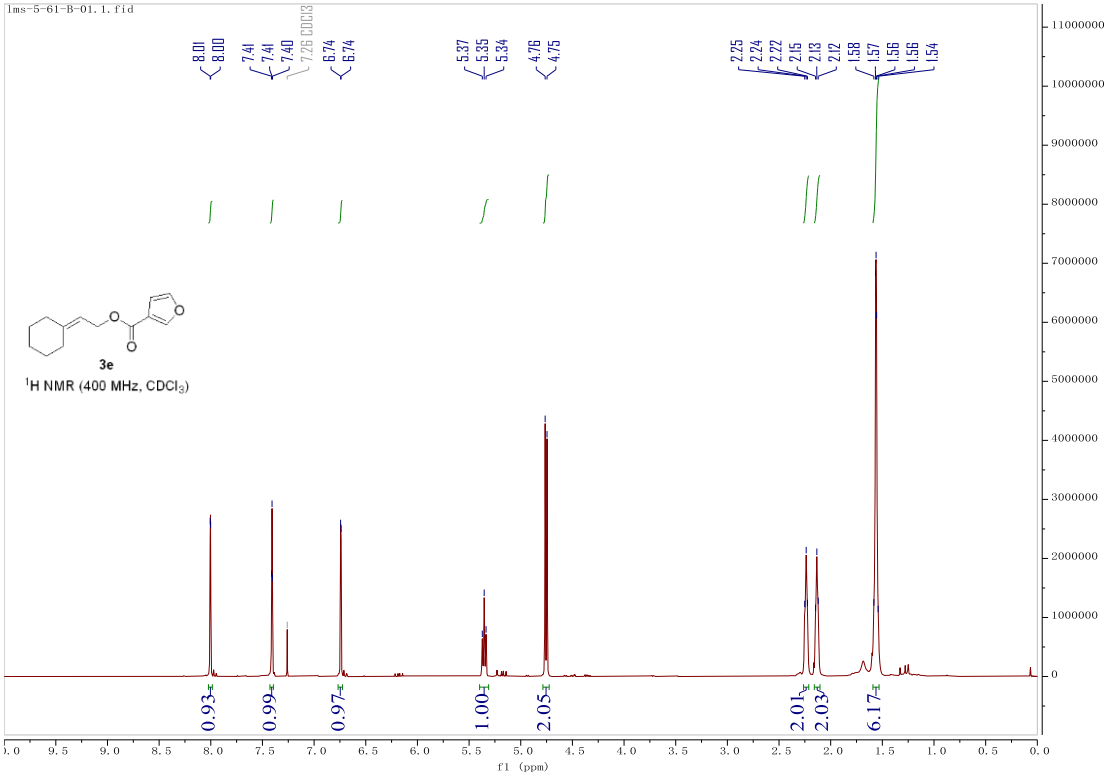
13C NMR (101 MHz, CDCl3)
f1 (ppm)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8.00
7.41
7.41
7.40
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6.74
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5.35
5.34
4.76
4.75
2.25
2.24
2.22
2.15
2.13
2.12
1.58
1.57
1.56
1.56
1.54
0.93
0.99
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1.00
2.05
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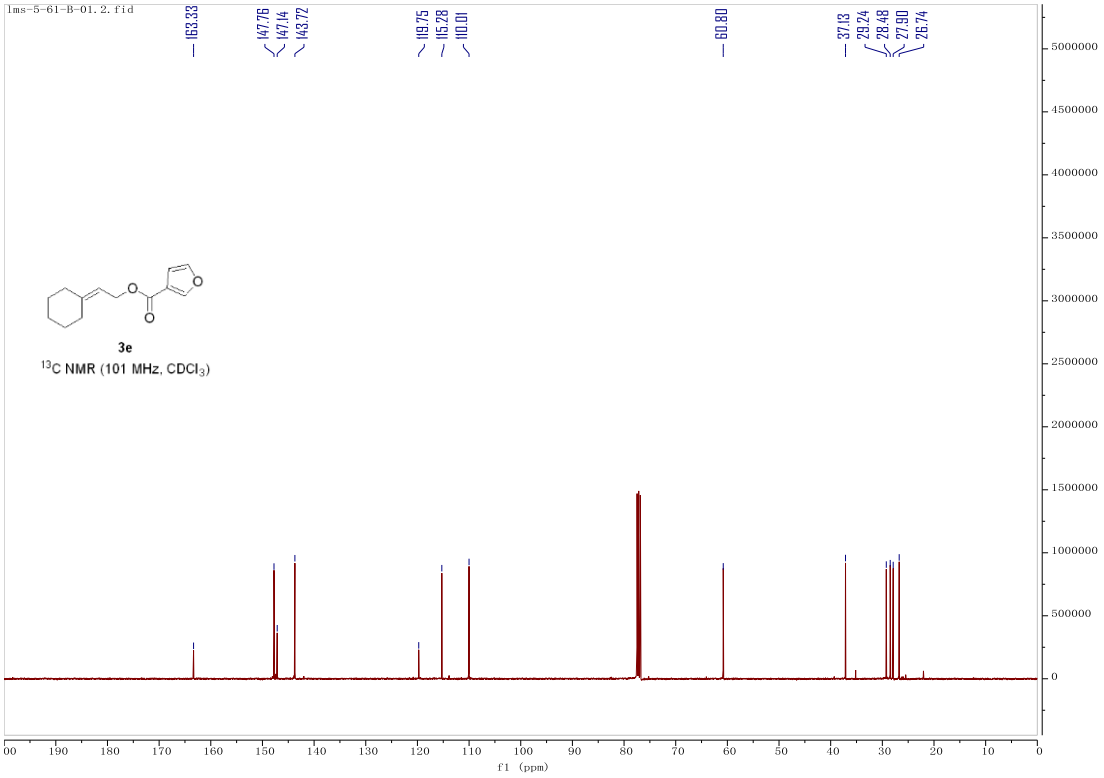
2.03
6.17
3e
1H NMR (400 MHz, CDCl3)
f1 (ppm)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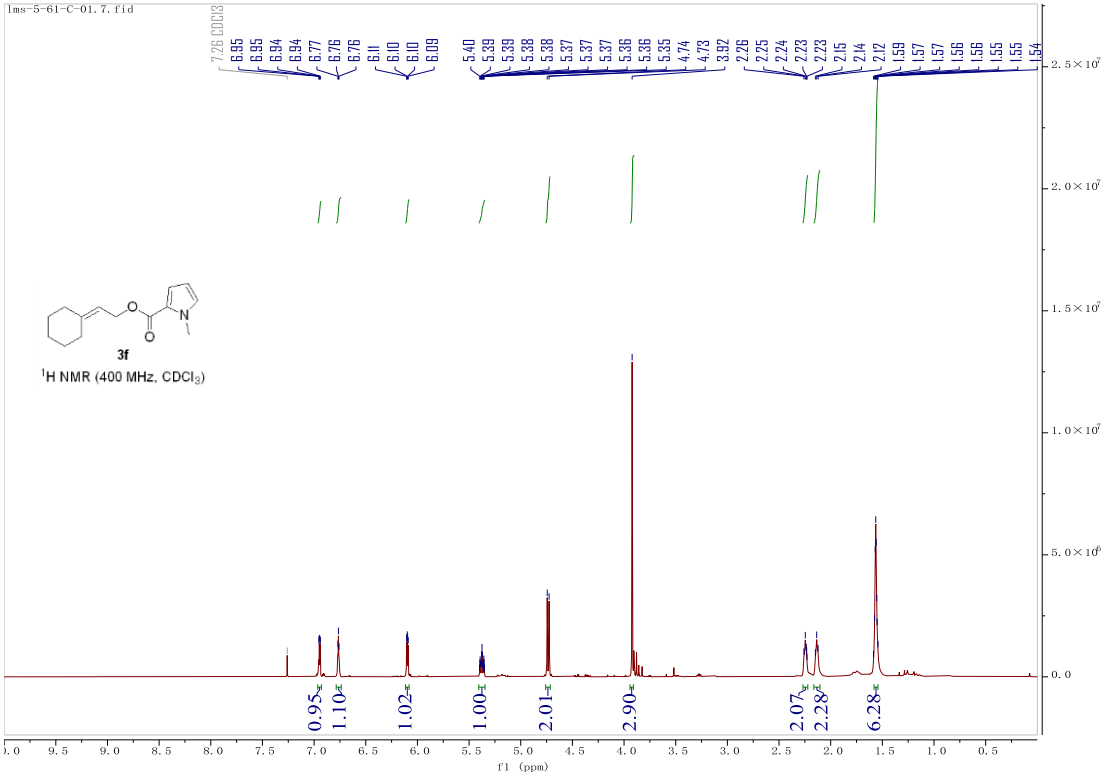
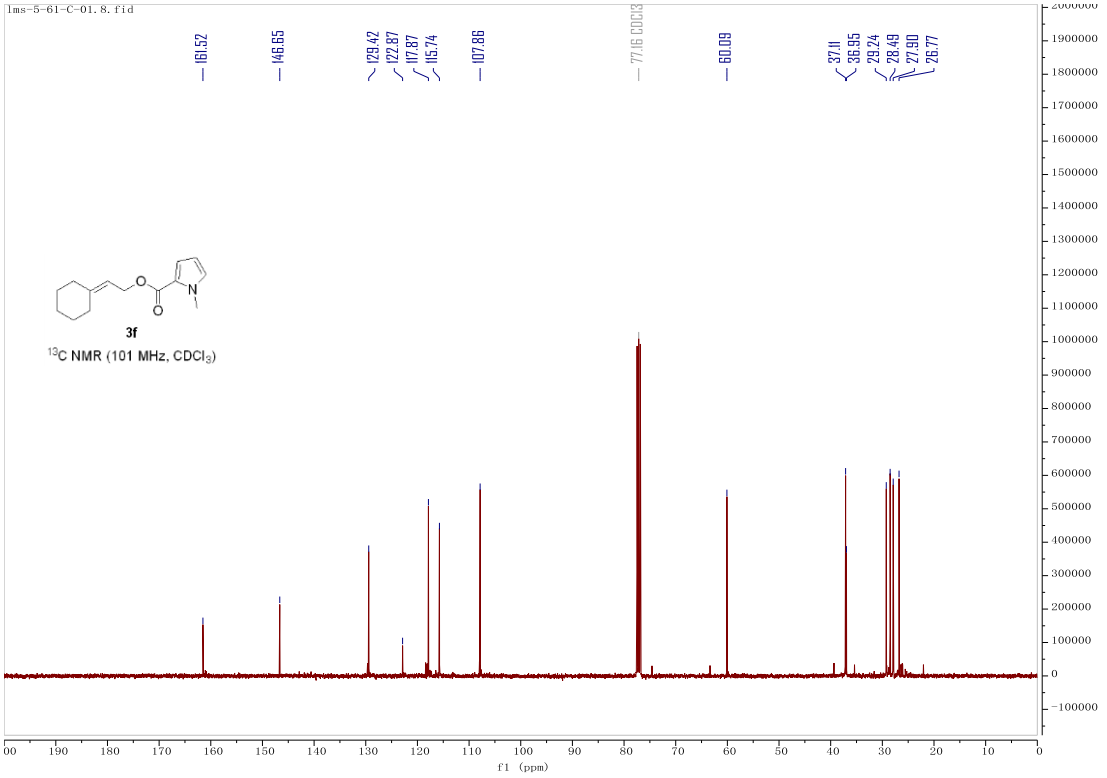
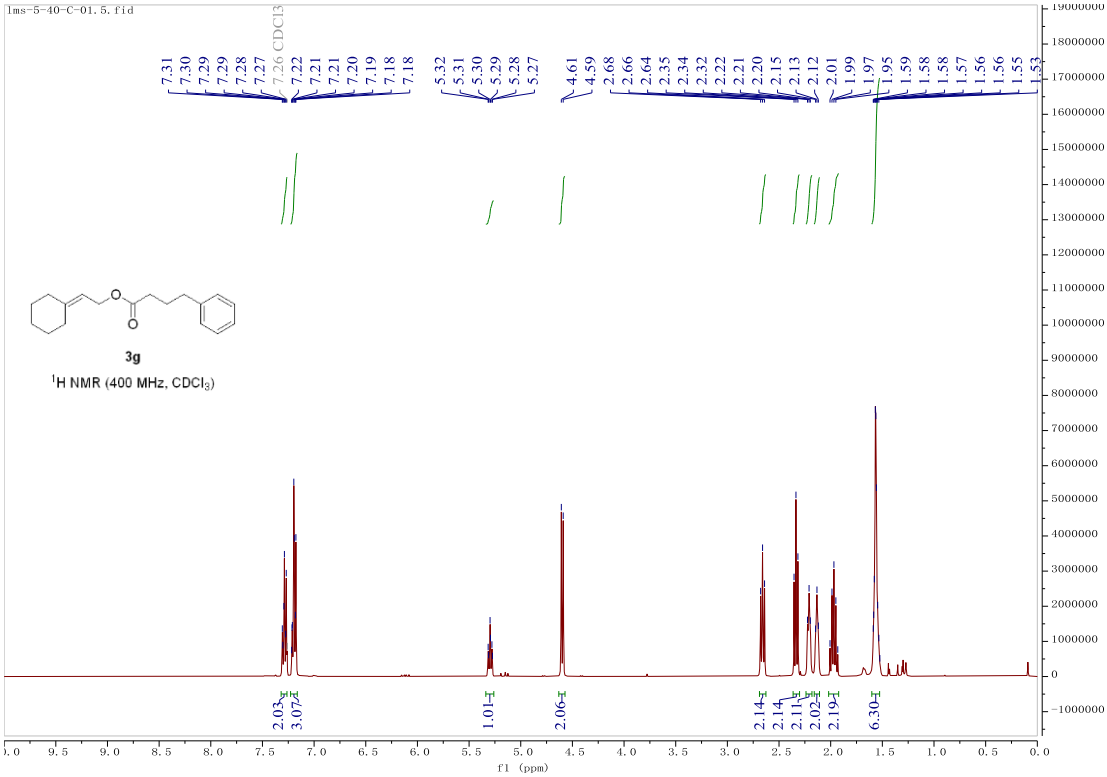
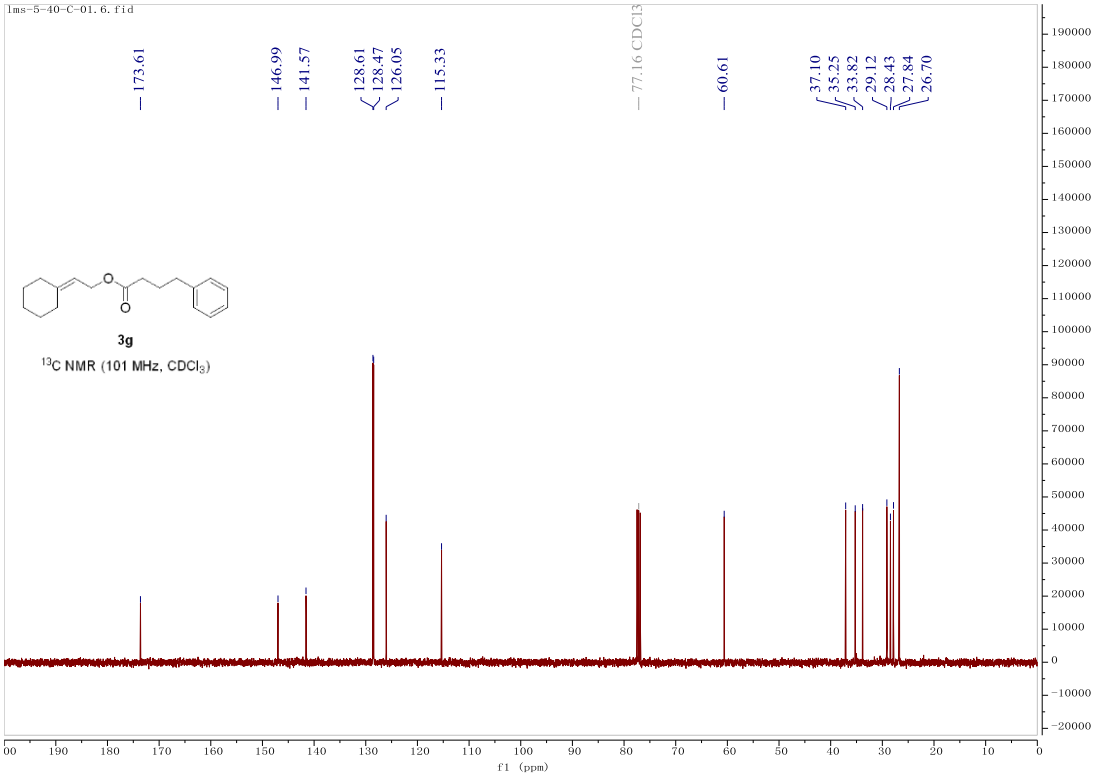
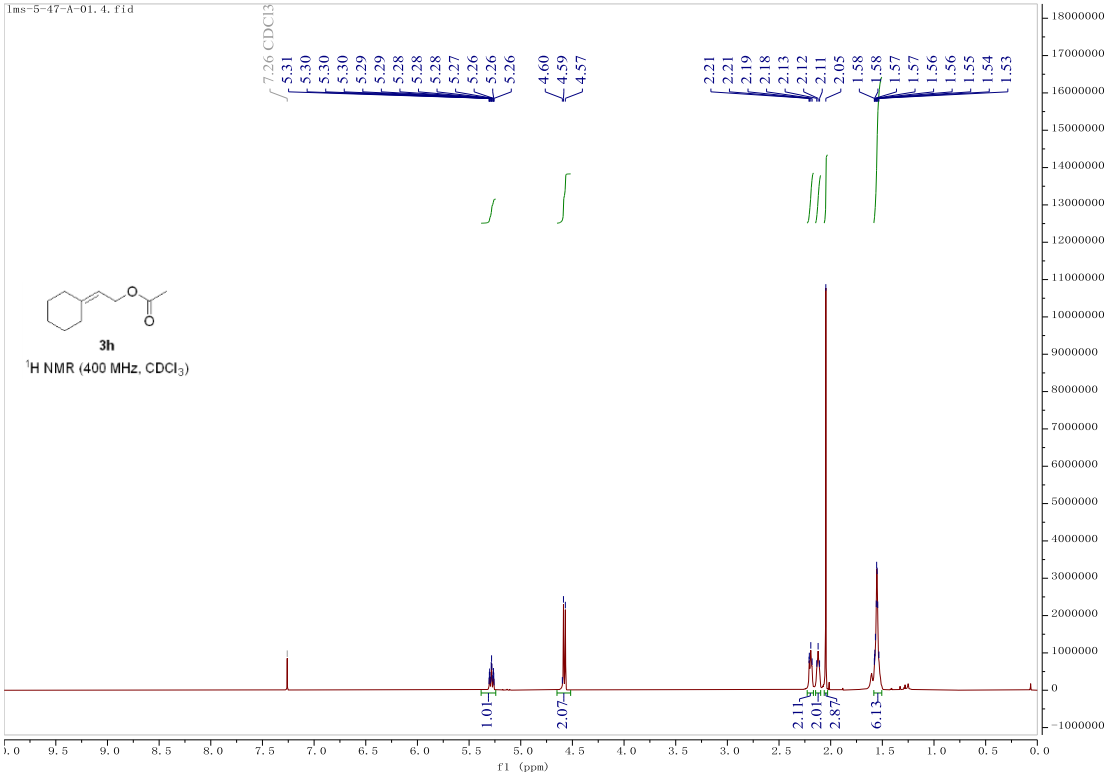
118.75
115.28
110.01
60.80
37.13
29.24
28.48
27.90
26.74
3e
13C NMR (101 MHz, CDCl3)
f1 (ppm)

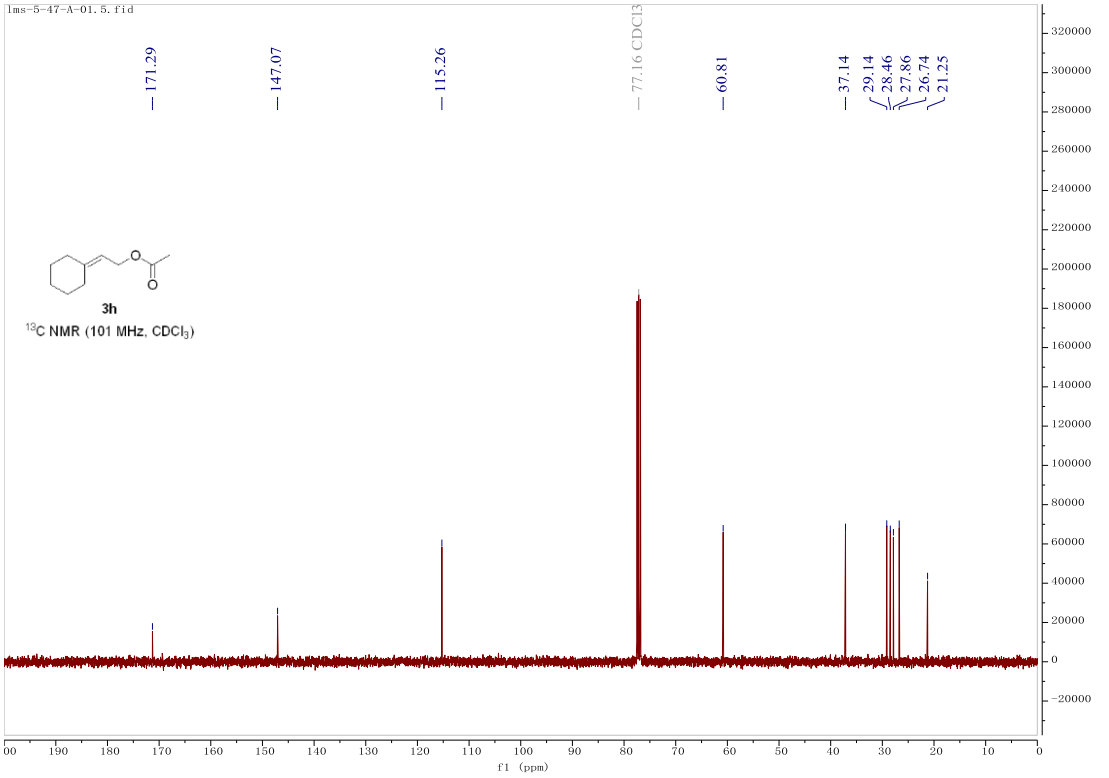

lms-5-61-C-01.7.fid
7.26 CDCl3
6.95
6.94
6.77
6.76
6.11
6.10
6.09
5.40
5.39
5.38
5.37
5.36
5.35
4.74
4.73
3.92
2.26
2.25
2.24
2.23
2.15
2.14
2.12
1.59
1.57
1.56
1.55
1.54
0.95
1.10
1.02
1.00
2.01
2.90
2.07
2.28
6.28
3f
1H NMR (400 MHz, CDCl3)
f1 (ppm)

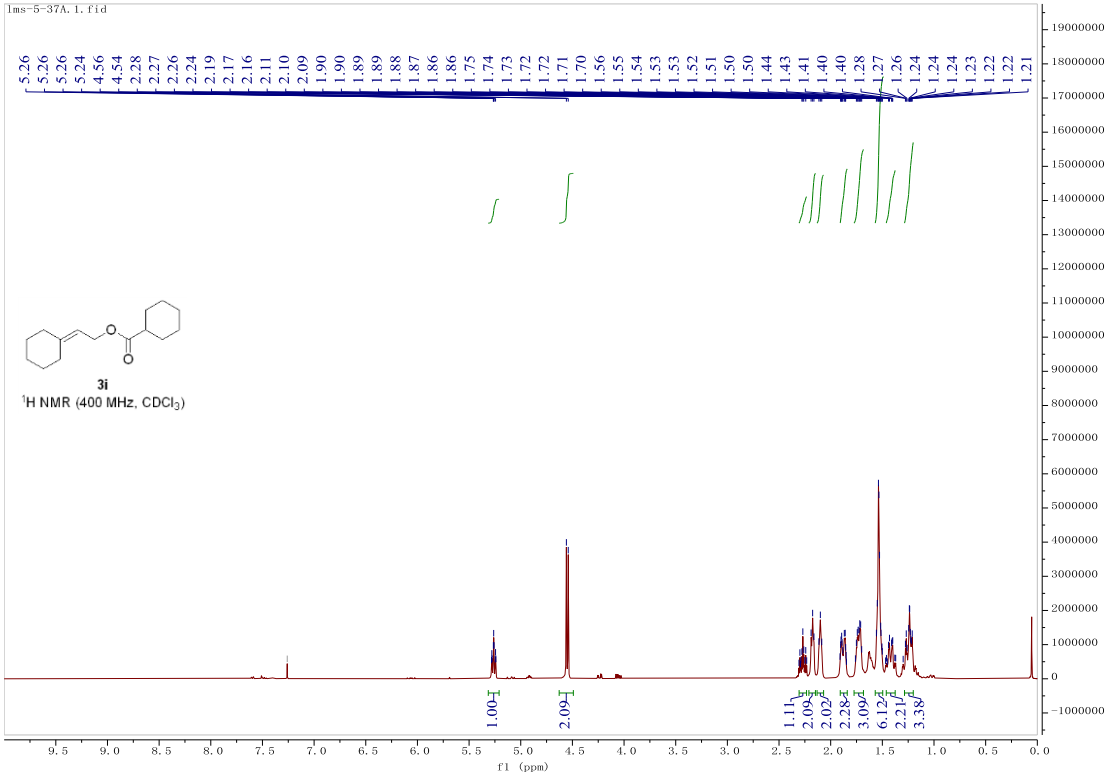

lms-5-61-C-01.8.fid
161.52
146.65
129.42
122.87
117.87
115.74
107.86
77.16 CDCl3
60.09
37.11
36.95
29.24
28.49
27.90
26.77
3f
13C NMR (101 MHz, CDCl3)
f1 (ppm)

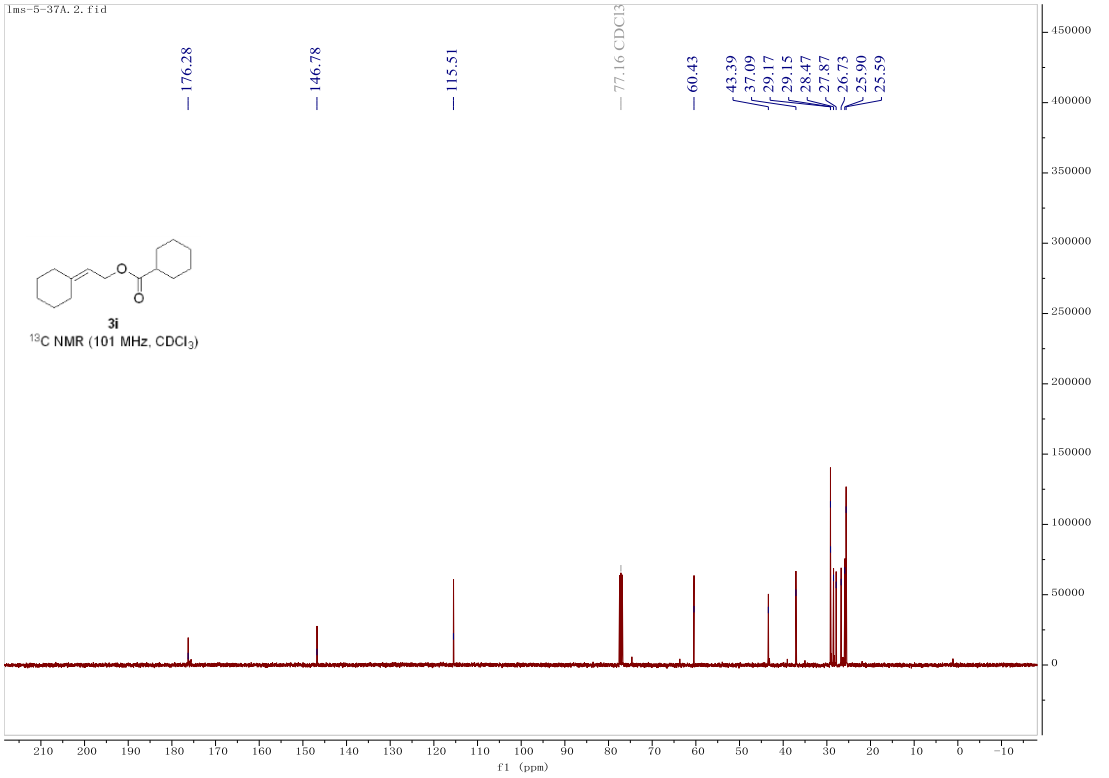

lms-5-40-C-01.5.fid
7.31
7.30
7.29
7.29
7.28
7.27
7.26 CDCl3
7.22
7.21
7.21
7.21
7.20
7.19
7.18
7.18
5.32
5.31
5.30
5.29
5.28
5.27
4.61
4.59
2.68
2.66
2.64
2.35
2.34
2.32
2.22
2.21
2.20
2.15
2.13
2.12
2.01
1.99
1.97
1.95
1.59
1.58
1.58
1.57
1.56
1.55
1.53
2.03
3.07
1.01
2.06
2.14
2.14
2.11
2.02
2.19
6.30
3g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

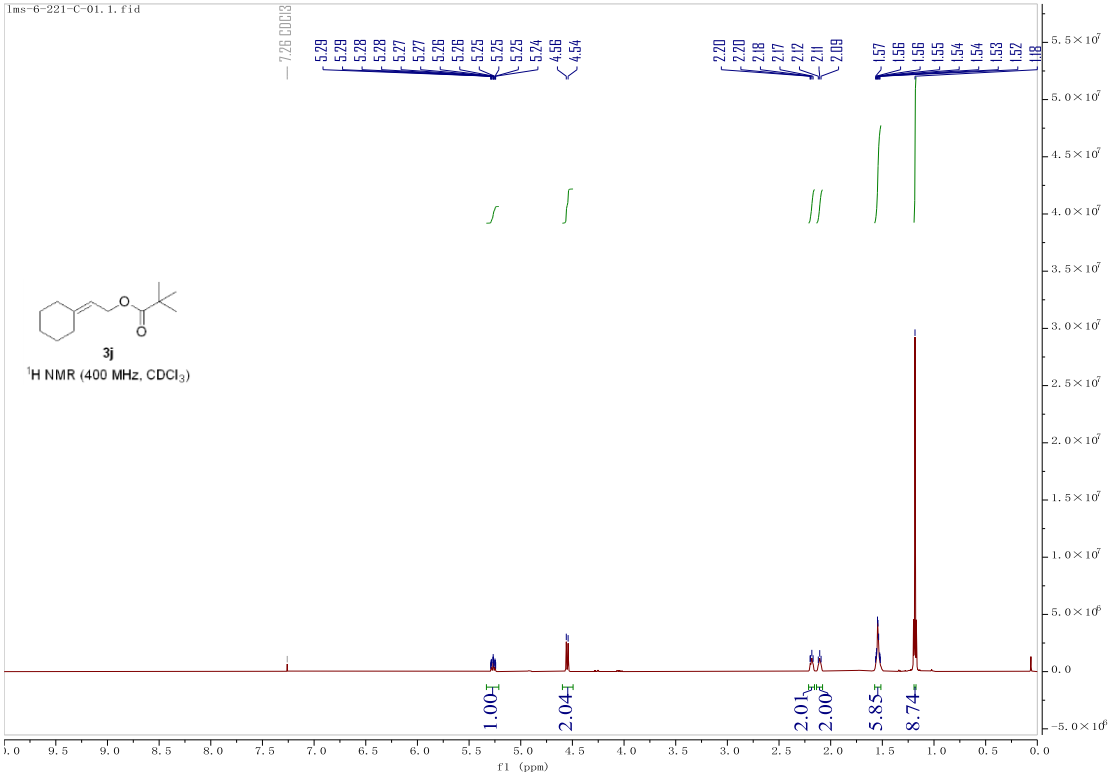

lms-5-40-C-01.6.fid
173.61
146.99
141.57
128.61
128.47
126.05
115.33
77.16 CDCl3
60.61
37.10
35.25
33.82
29.12
28.43
27.84
26.70
3g
13C NMR (101 MHz, CDCl3)
f1 (ppm)

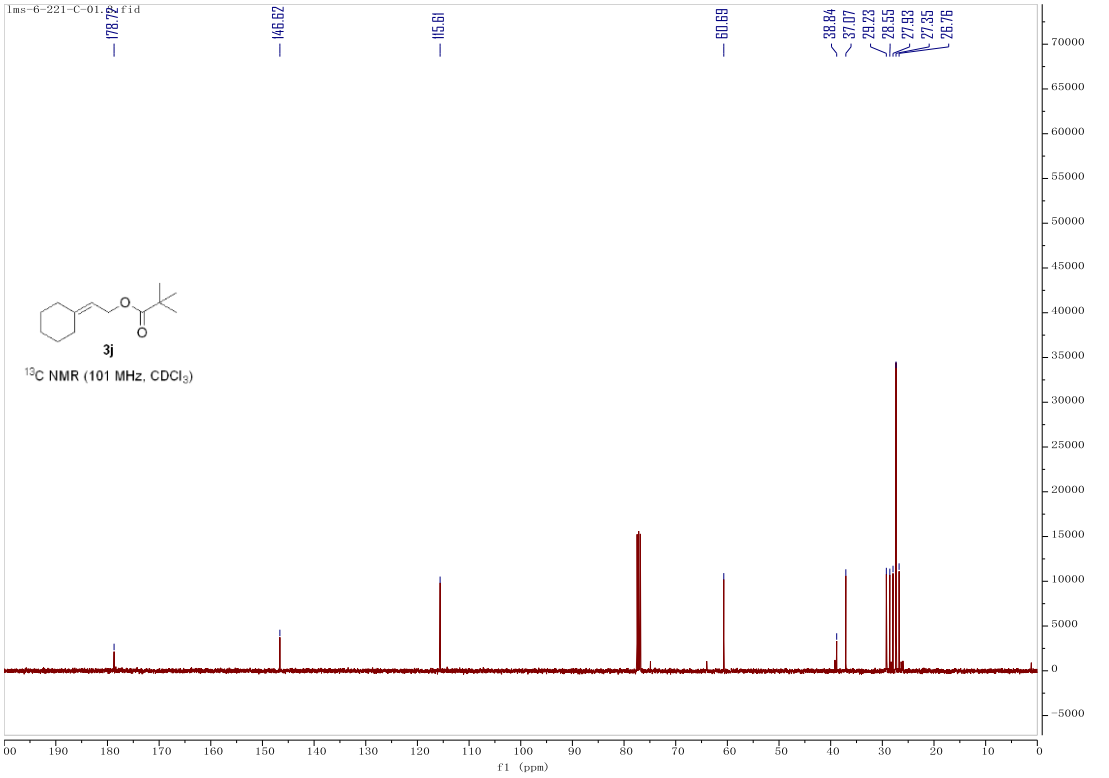

lms-5-47-A-01.4.fid
7.26 CDCl3
5.31
5.30
5.30
5.30
5.29
5.29
5.28
5.28
5.28
5.27
5.26
5.26
5.26
4.60
4.59
4.57
2.21
2.21
2.19
2.18
2.13
2.12
2.11
2.05
1.58
1.58
1.57
1.57
1.56
1.56
1.55
1.54
1.53
1.01
2.07
2.11
2.01
2.87
6.13
3h
1H NMR (400 MHz, CDCl3)
f1 (ppm)

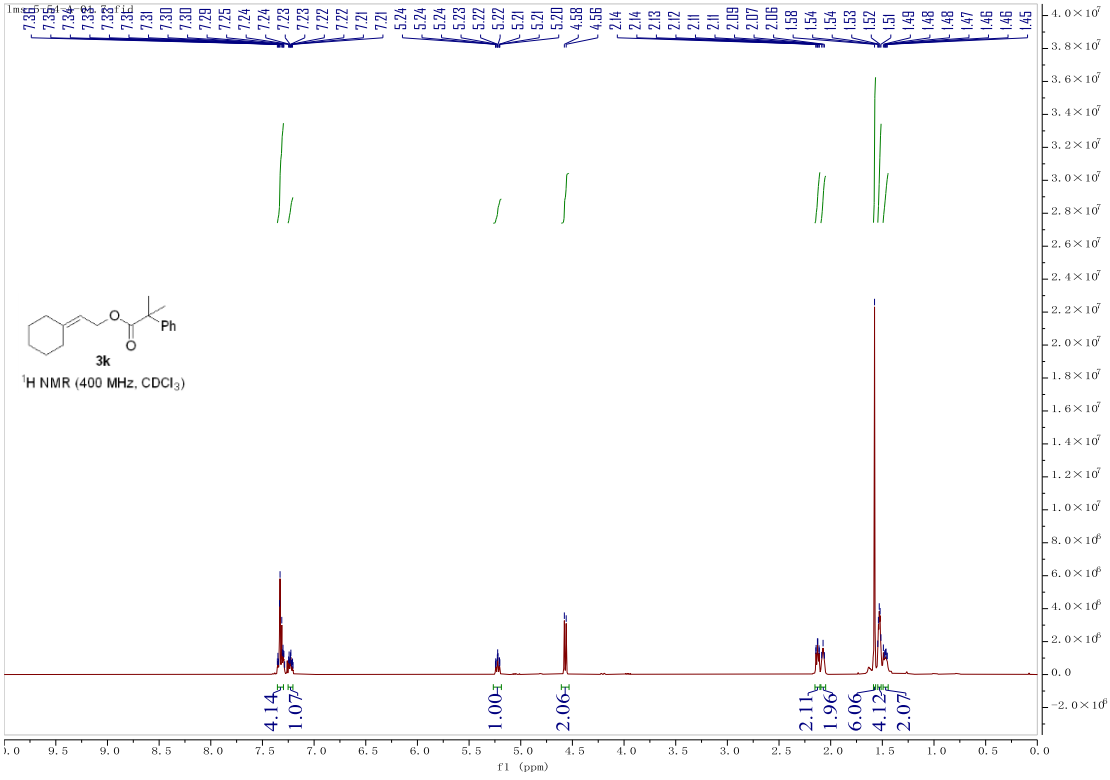

lms-5-47-A-01.5.fid
171.29
147.07
115.26
77.16 CDCl3
60.81
37.14
29.14
28.46
27.86
26.74
21.25
3h
13C NMR (101 MHz, CDCl3)
f1 (ppm)

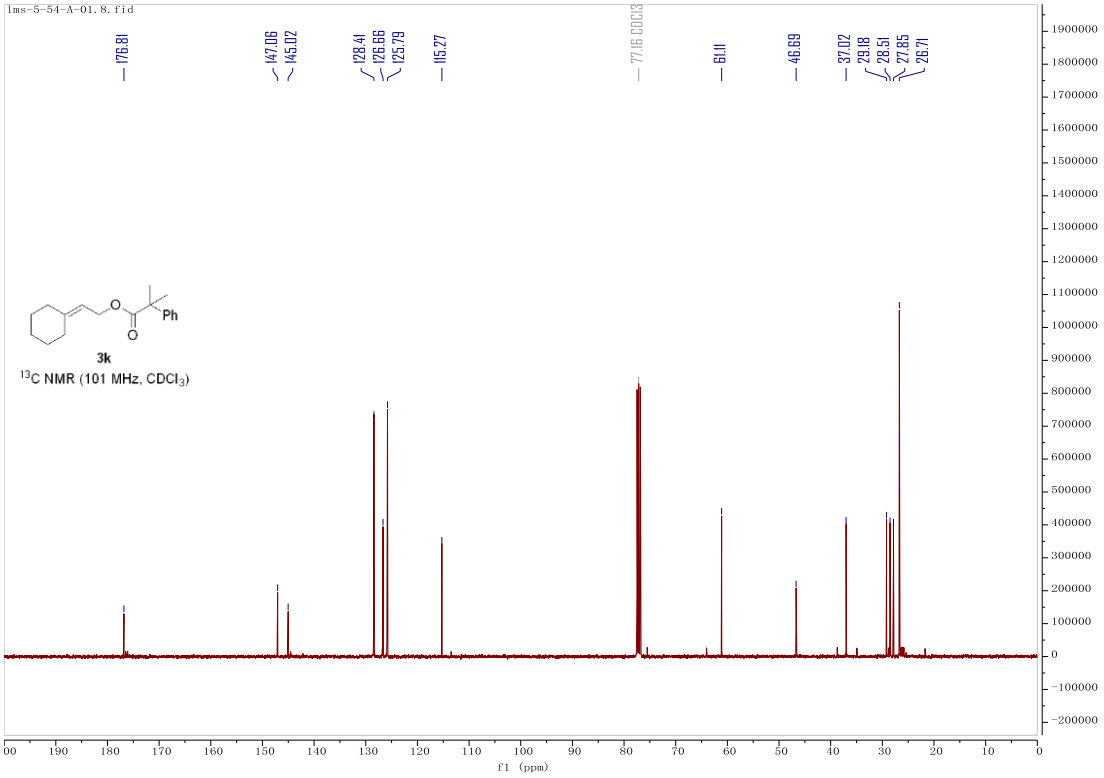

lms-5-37A.1.fid
3i
1H NMR (400 MHz, CDCl3)
1.00
2.09
1.11
2.09
2.02
2.28
3.09
6.12
2.21
3.38
f1 (ppm)

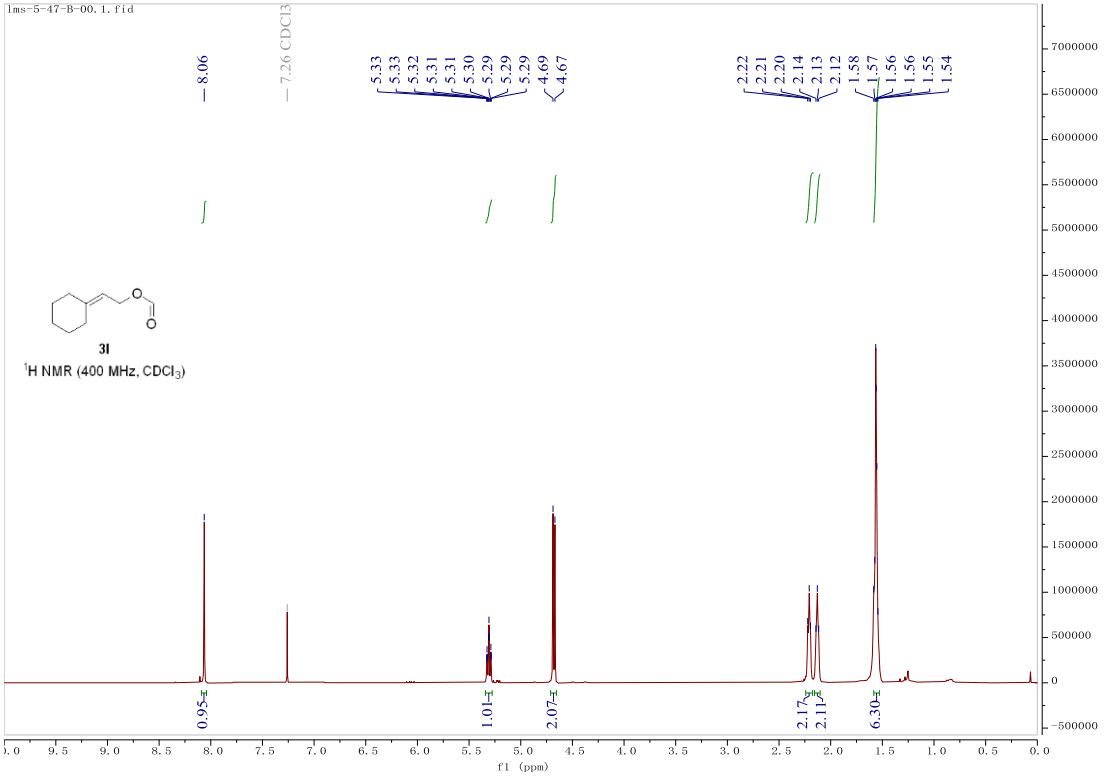

lms-5-37A.2.fid
176.28
146.78
115.51
77.16 CDCl3
60.43
43.39
37.09
29.17
29.15
28.47
27.87
26.73
25.90
25.59
3i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

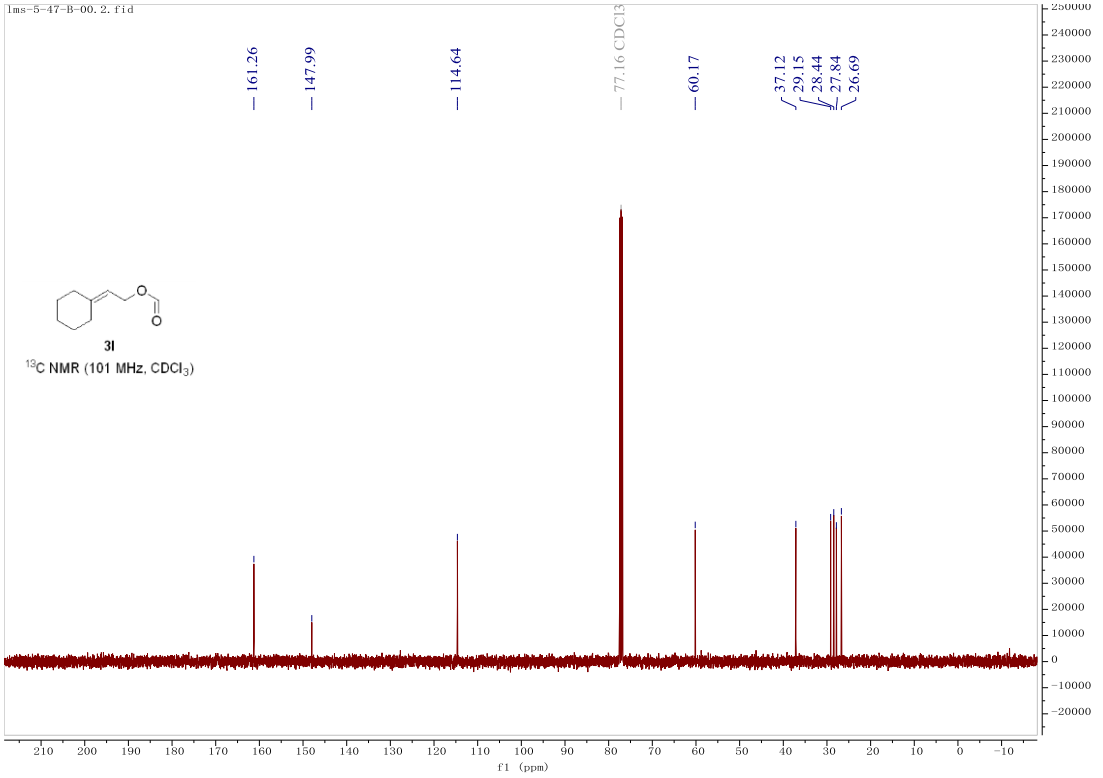

lms-6-221-C-01.1.fid
7.26 CDCl3
5.29
5.29
5.28
5.28
5.27
5.27
5.26
5.26
5.25
5.25
5.25
5.24
4.56
4.54
2.20
2.20
2.18
2.17
2.12
2.11
2.09
1.57
1.56
1.56
1.55
1.54
1.54
1.53
1.52
1.18
1.00
2.04
2.01
2.00
5.85
8.74
3j
1H NMR (400 MHz, CDCl3)
f1 (ppm)

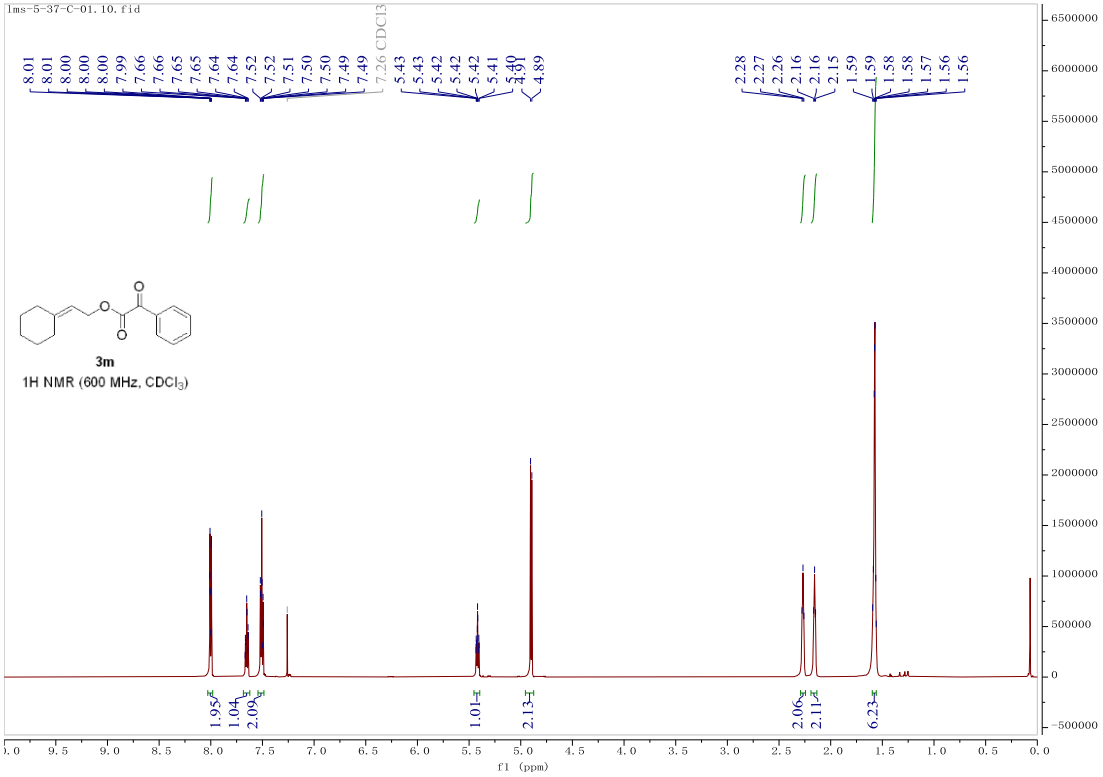

lms-6-221-C-01.1.fid
178.72
146.62
115.61
80.69
38.84
37.07
29.23
28.55
27.93
27.35
26.76
3j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

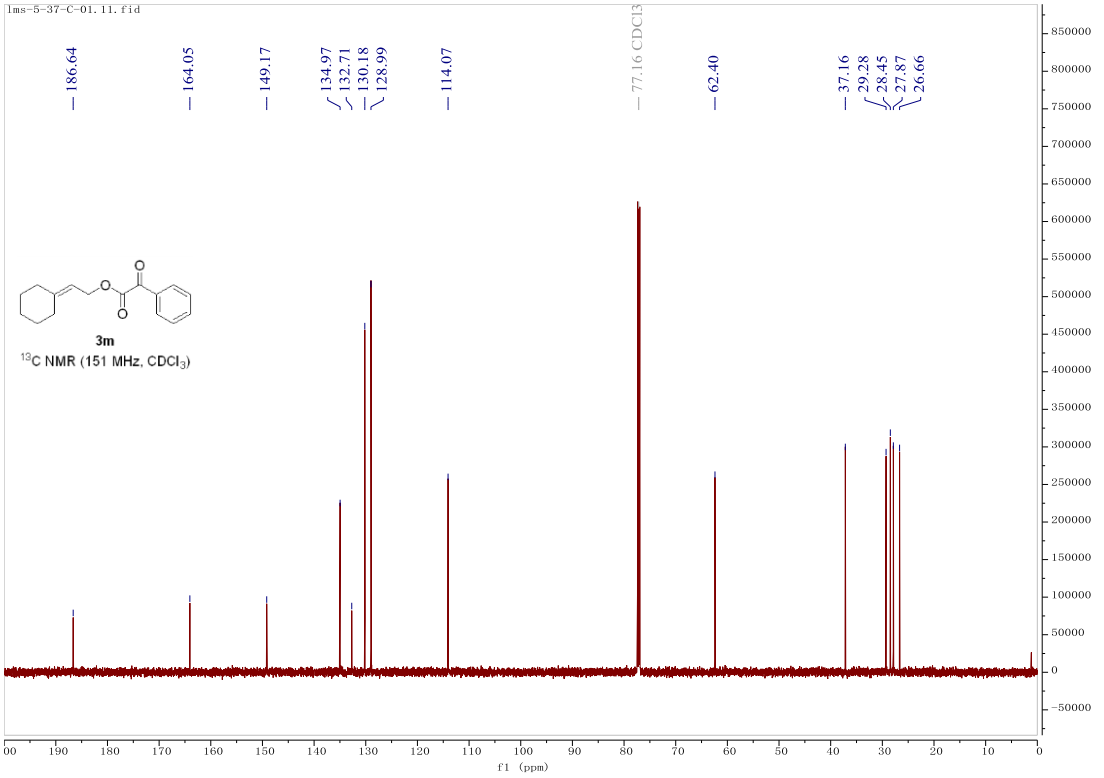

7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
5.24
5.24
5.24
5.23
5.22
5.22
5.21
5.21
5.20
4.58
4.56
2.14
2.14
2.13
2.12
2.11
2.11
2.09
2.07
2.06
1.58
1.54
1.54
1.53
1.52
1.51
1.49
1.48
1.48
1.47
1.46
1.46
1.45
Ph
3k
1H NMR (400 MHz, CDCl3)
4.14
1.07
1.00
2.06
2.11
1.96
6.06
4.12
2.07
f1 (ppm)

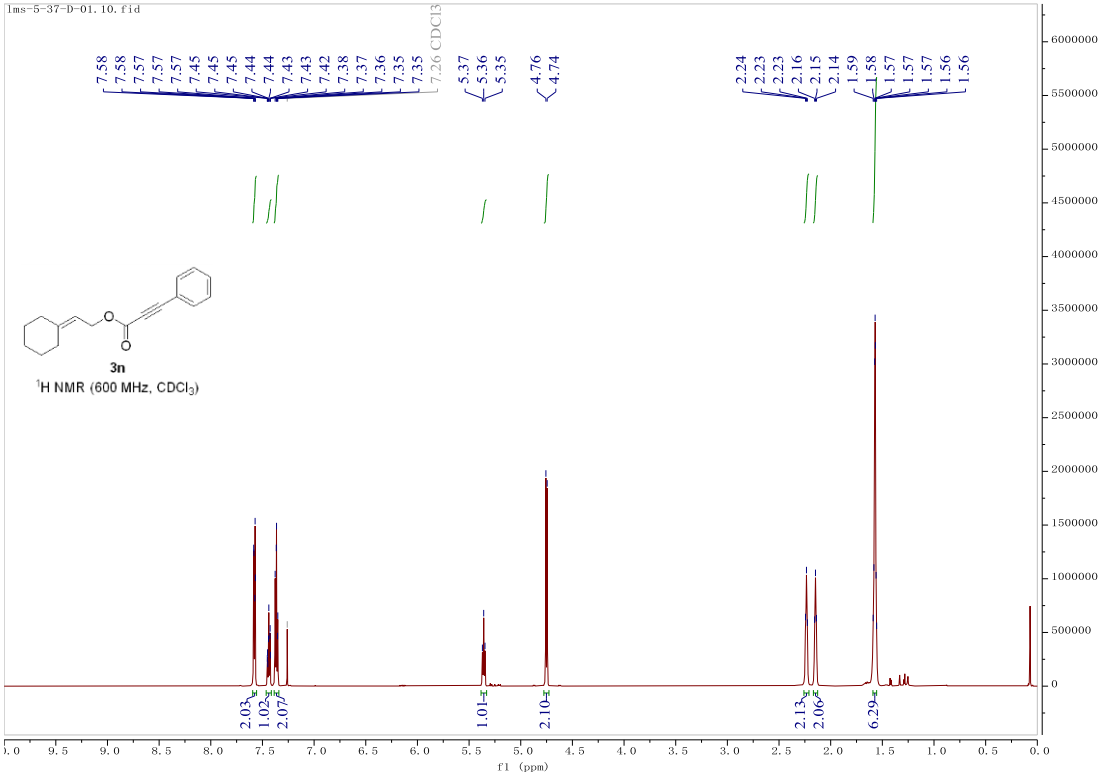

lms-5-54-A-01.8.fid
176.81
147.06
145.02
128.41
126.66
125.79
115.27
77.16 CDCl3
61.11
46.69
37.02
29.18
28.51
27.85
26.71
O
O
Ph
3k
13C NMR (101 MHz, CDCl3)
f1 (ppm)

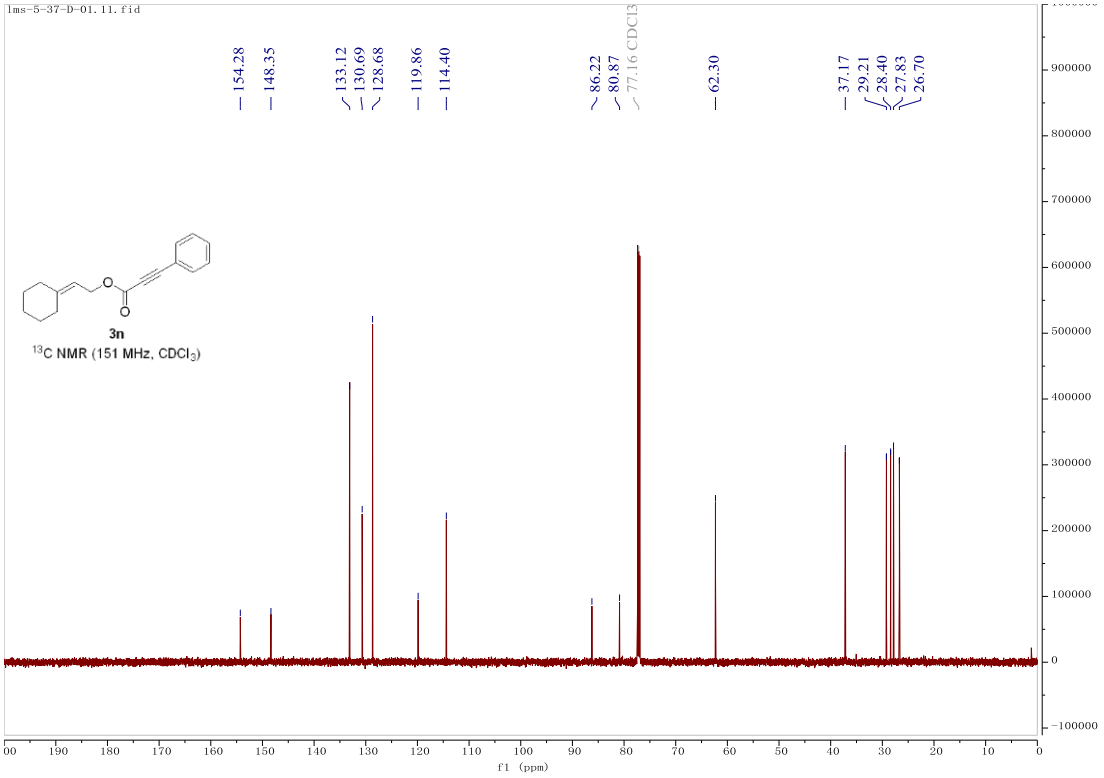

lms-5-47-B-00.1.fid
8.06
7.26 CDCl3
5.33
5.33
5.32
5.31
5.31
5.30
5.29
5.29
5.29
4.69
4.67
2.22
2.21
2.20
2.14
2.13
2.12
1.58
1.57
1.56
1.56
1.55
1.54
O
O
3l
1H NMR (400 MHz, CDCl3)
0.95
1.01
2.07
2.17
2.11
6.30
f1 (ppm)

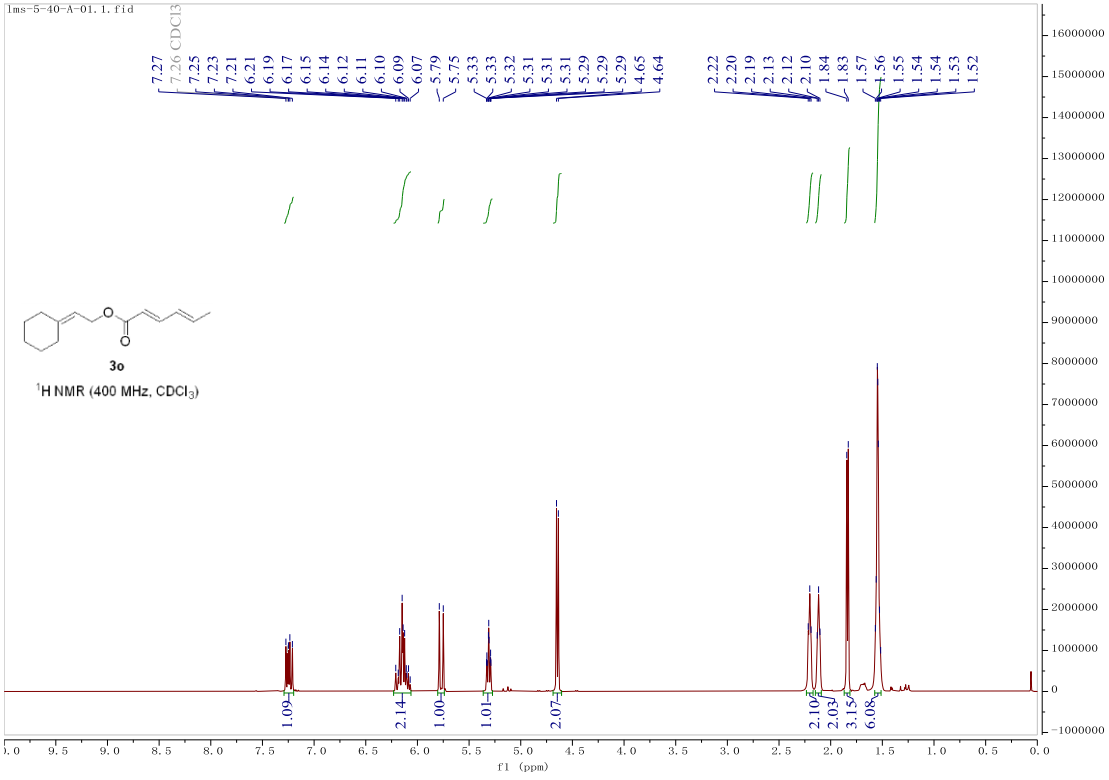

lms-5-47-B-00.2.fid
161.26
147.99
114.64
77.16 CDCl3
60.17
37.12
29.15
28.44
27.84
26.69
3l
13C NMR (101 MHz, CDCl3)
f1 (ppm)

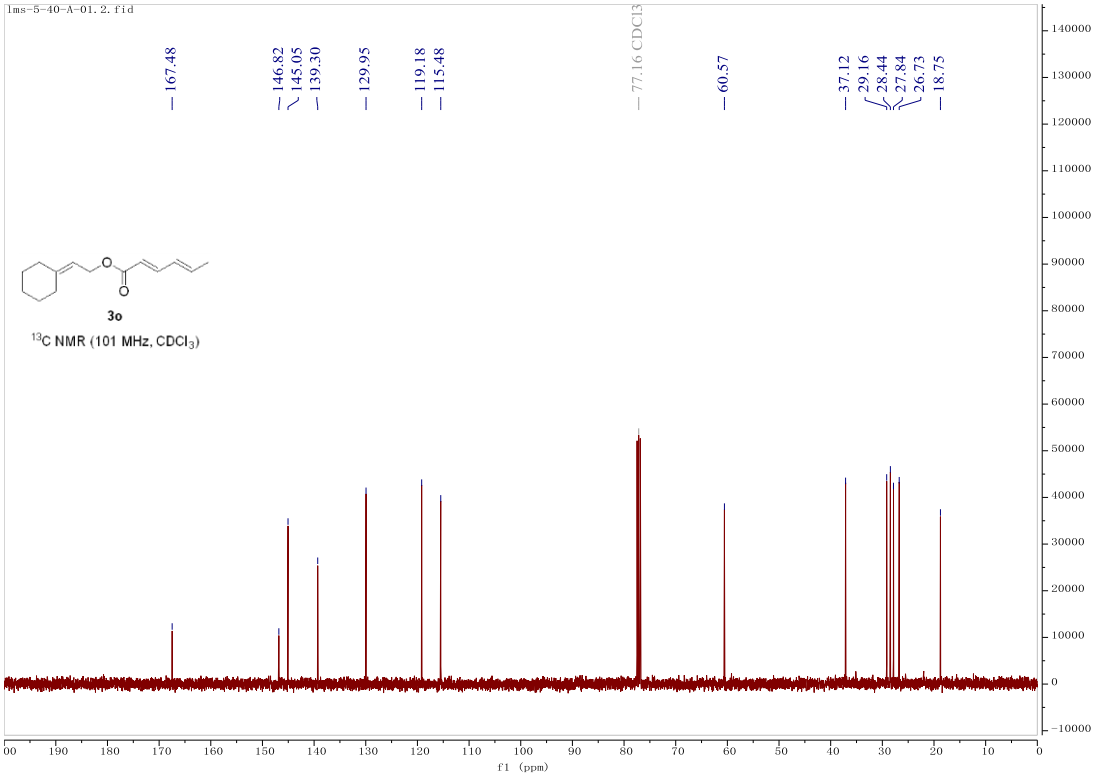

lms-5-37-C-01.10.fid
8.01
8.01
8.00
8.00
8.00
7.99
7.66
7.65
7.65
7.64
7.64
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.26 CDCl3
5.43
5.43
5.42
5.42
5.42
5.41
5.40
4.91
4.89
2.28
2.27
2.26
2.16
2.16
2.15
1.59
1.59
1.58
1.58
1.57
1.56
1.56
1.95
1.04
2.09
1.01
2.13
2.06
2.11
6.23
3m
1H NMR (600 MHz, CDCl3)
f1 (ppm)


lms-5-37-C-01.11.fid
186.64
164.05
149.17
134.97
132.71
130.18
128.99
114.07
77.16 CDCl3
62.40
37.16
29.28
28.45
27.87
26.66
3m
13C NMR (151 MHz, CDCl3)
f1 (ppm)

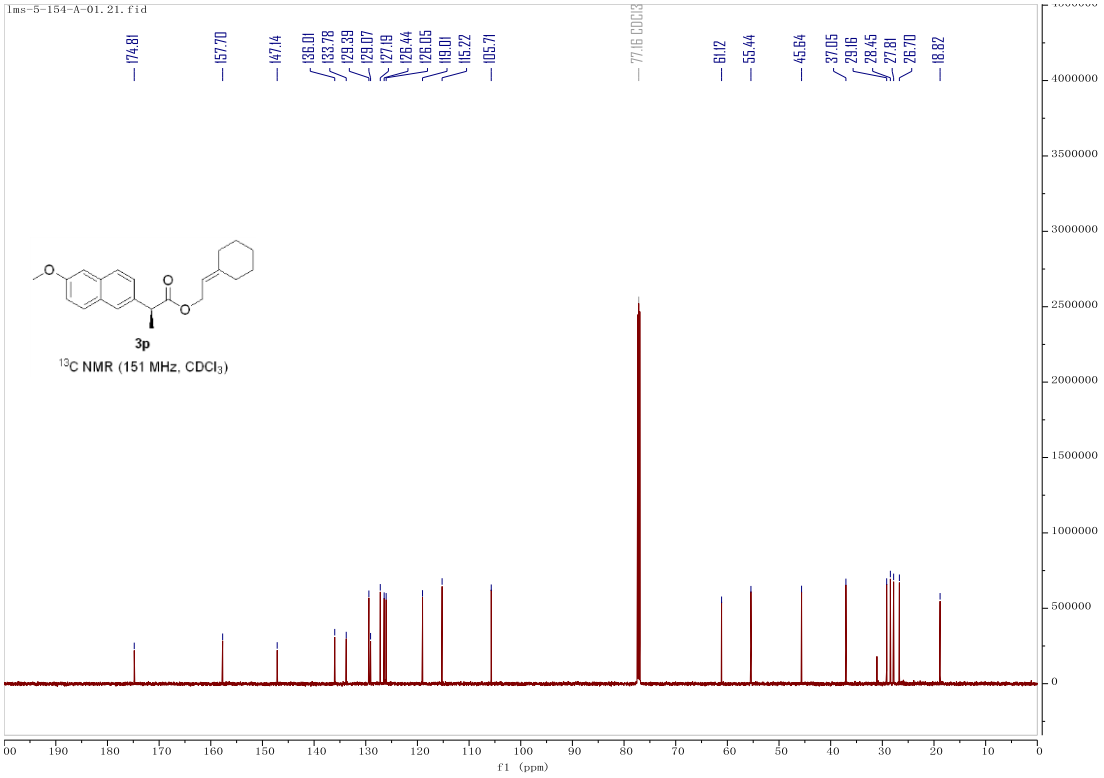

lms-5-37-D-01.10.fid
7.58
7.58
7.57
7.57
7.57
7.45
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.38
7.37
7.36
7.35
7.35
7.26 CDCl3
5.37
5.36
5.35
4.76
4.74
2.24
2.23
2.23
2.16
2.15
2.14
1.59
1.58
1.57
1.57
1.57
1.56
1.56
2.03
1.02
2.07
1.01
2.10
2.13
2.06
6.29
3n
1H NMR (600 MHz, CDCl3)
f1 (ppm)

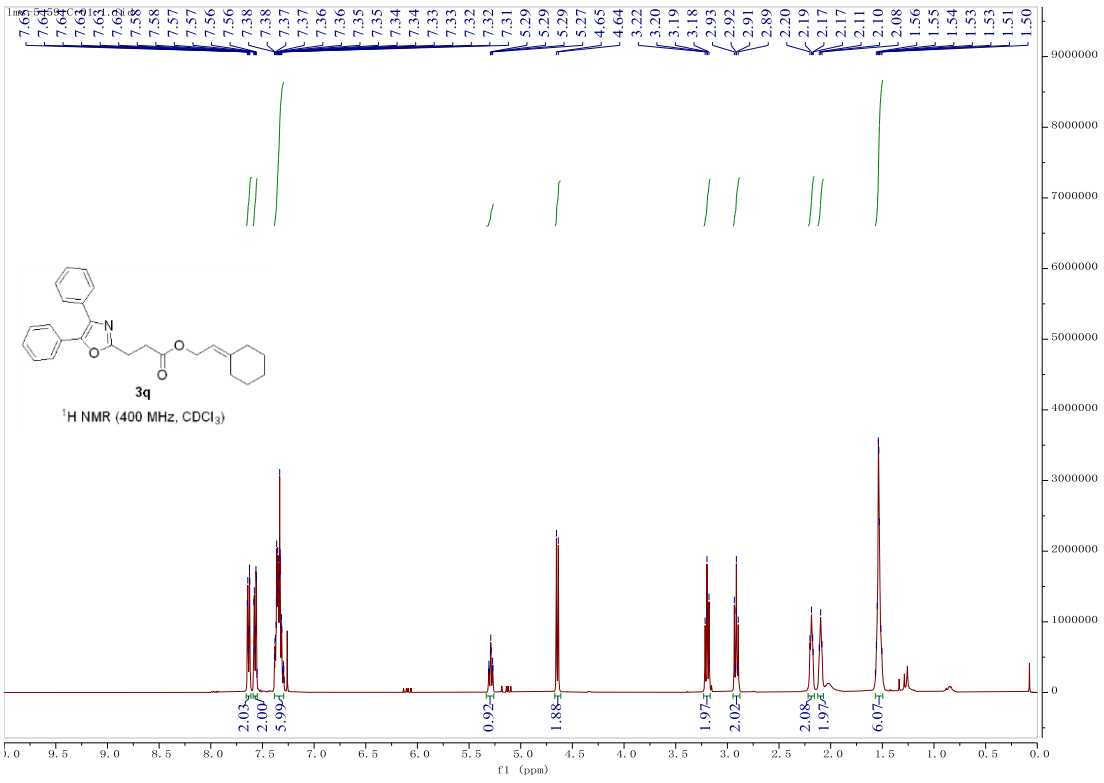

lms-5-37-D-01.11.fid
154.28
148.35
133.12
130.69
128.68
119.86
114.40
86.22
80.87
77.16 CDCl3
62.30
37.17
29.21
28.40
27.83
26.70
3n
13C NMR (151 MHz, CDCl3)
f1 (ppm)

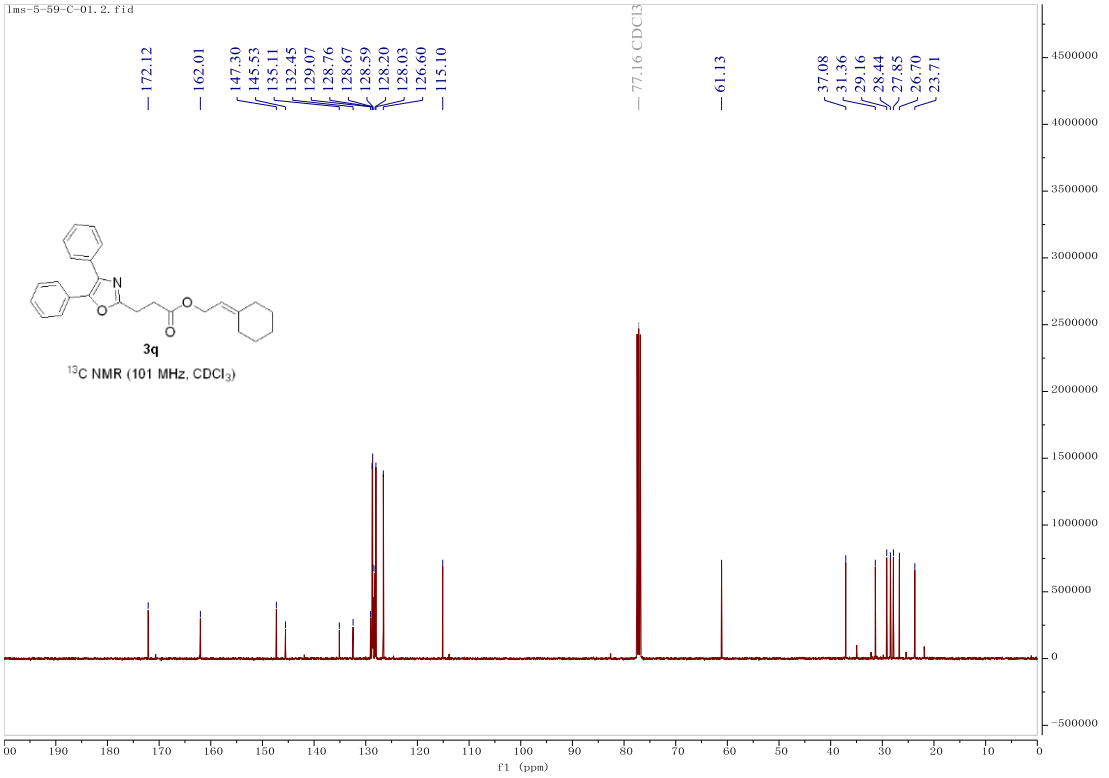

lms-5-40-A-01.1.fid
7.27
7.26 CDCl3
7.25
7.23
7.21
6.21
6.19
6.17
6.15
6.14
6.12
6.11
6.10
6.09
6.07
5.79
5.75
5.33
5.33
5.32
5.31
5.31
5.31
5.29
5.29
5.29
4.65
4.64
2.22
2.20
2.19
2.13
2.12
2.10
1.84
1.83
1.57
1.56
1.55
1.54
1.54
1.53
1.52
1.09
2.14
1.00
1.01
2.07
2.10
2.03
3.15
6.08
3o
1H NMR (400 MHz, CDCl3)
f1 (ppm)

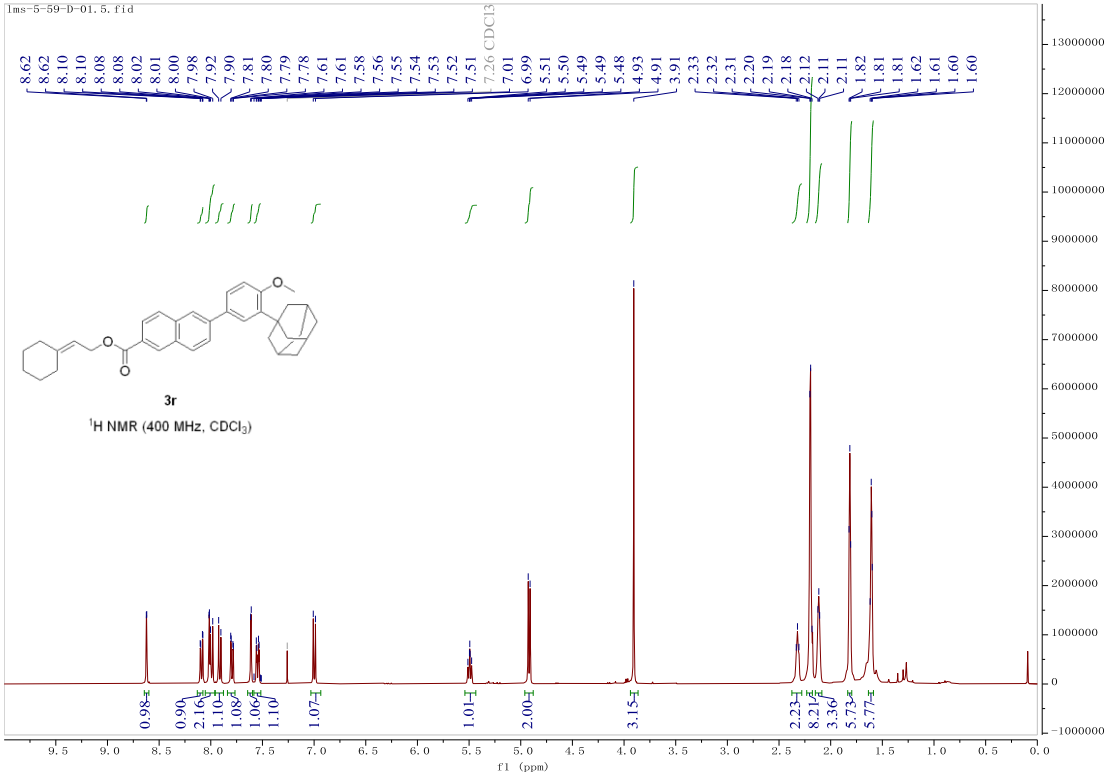

lms-5-40-A-01.2.fid
167.48
146.82
145.05
139.30
129.95
119.18
115.48
77.16 CDCl3
60.57
37.12
29.16
28.44
27.84
26.73
18.75
3o
13C NMR (101 MHz, CDCl3)
f1 (ppm)

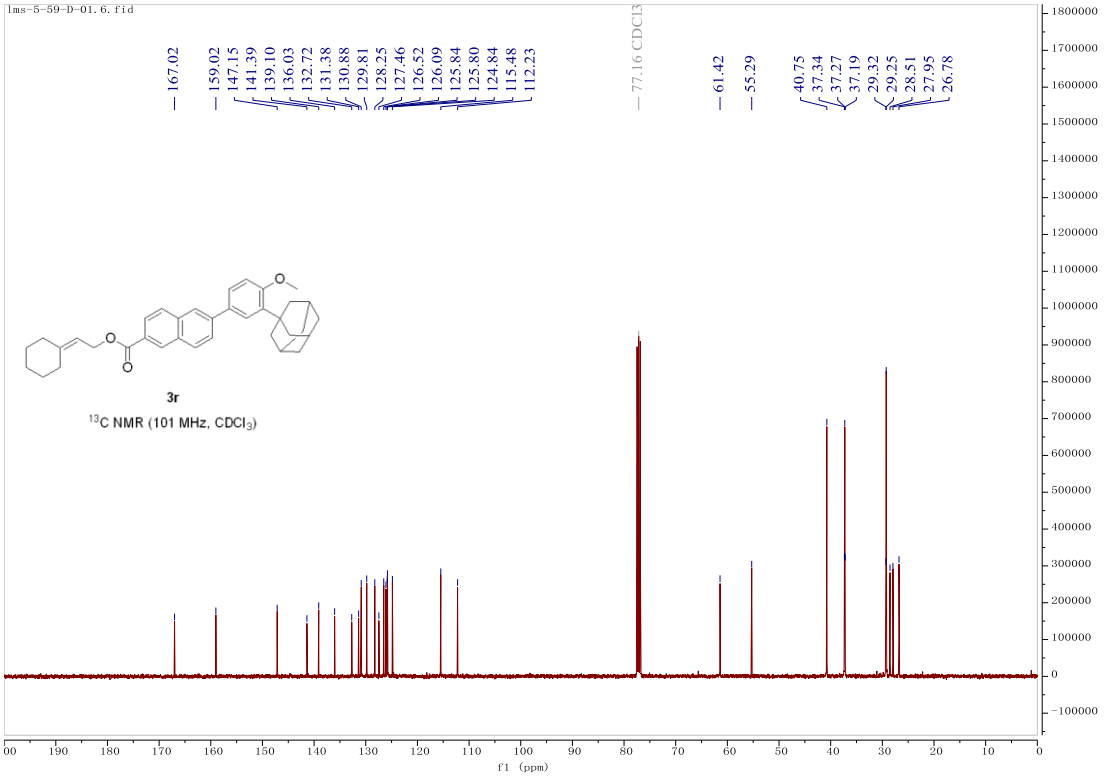

lms-5-154-A-01.20.fid
7.26 CDCl3
3p
1H NMR (600 MHz, CDCl3)
2.10
0.94
0.99
1.07
0.99
1.01
1.03
0.99
2.96
1.00
2.10
2.07
1.90
3.00
3.95
1.97
f1 (ppm)


lms-5-154-A-01.21.fid
174.81
157.70
147.14
136.01
133.78
129.39
129.07
127.19
126.44
126.05
119.01
115.22
105.71
77.16 CDCl3
61.12
55.44
45.64
37.05
29.16
28.45
27.81
26.70
18.82
3p
13C NMR (151 MHz, CDCl3)
f1 (ppm)


3q
1H NMR (400 MHz, CDCl3)
2.03
2.00
5.99
0.92
1.88
1.97
2.02
2.08
1.97
6.07
f1 (ppm)

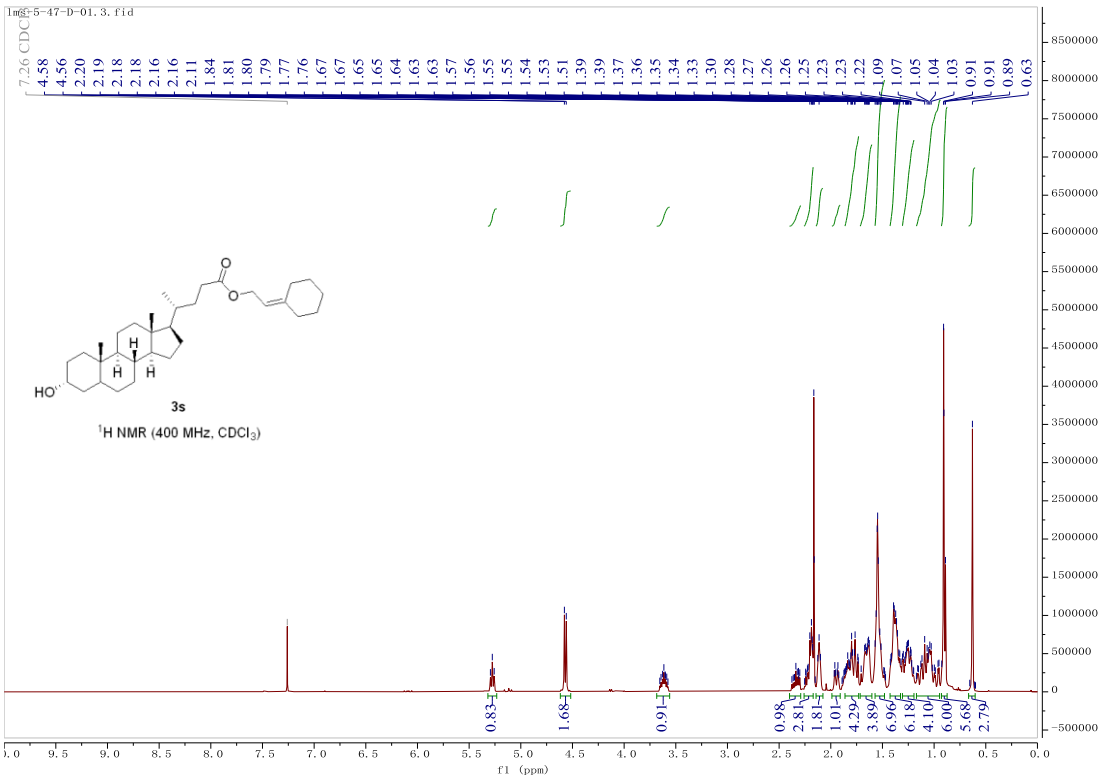

lms-5-59-C-01.2.fid
172.12
162.01
147.30
145.53
135.11
132.45
129.07
128.76
128.67
128.59
128.20
128.03
126.60
115.10
77.16 CDCl3
61.13
37.08
31.36
29.16
28.44
27.85
26.70
23.71
3q
13C NMR (101 MHz, CDCl3)
f1 (ppm)


lms-5-59-D-01.5.fid
7.26 CDCl3
3r
1H NMR (400 MHz, CDCl3)
0.98
0.90
2.16
1.10
1.08
1.06
1.10
1.07
1.01
2.00
3.15
2.23
8.21
3.36
5.73
5.77
f1 (ppm)



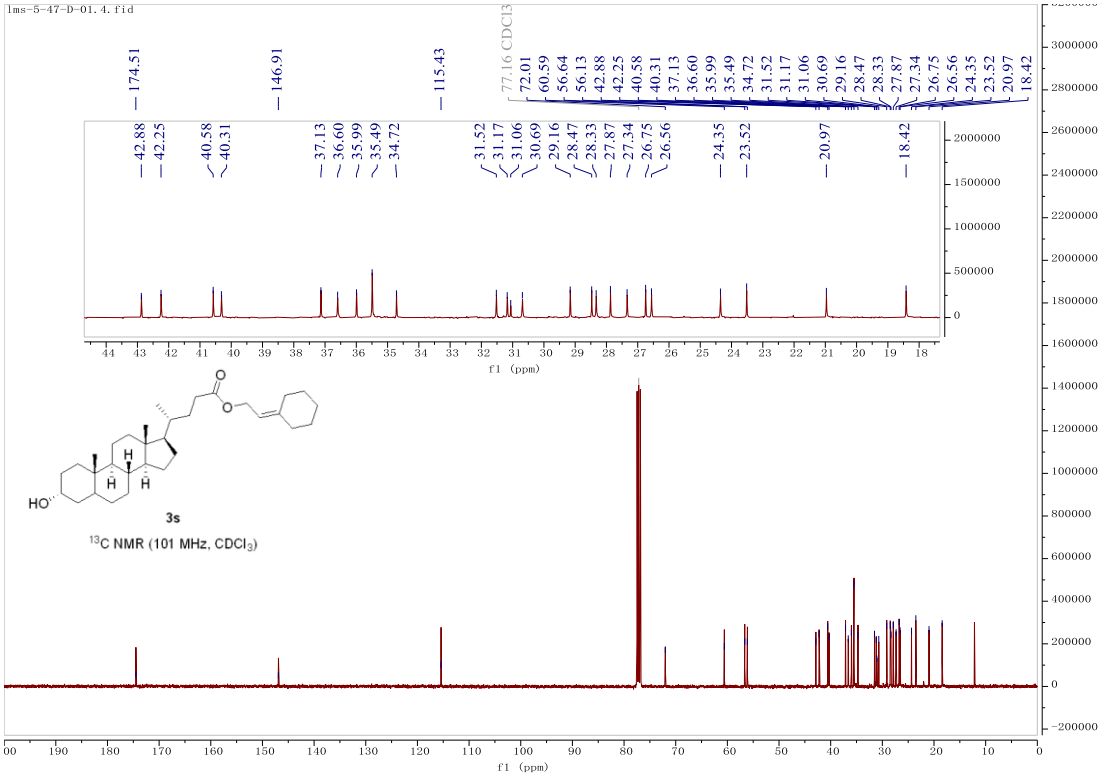
3r

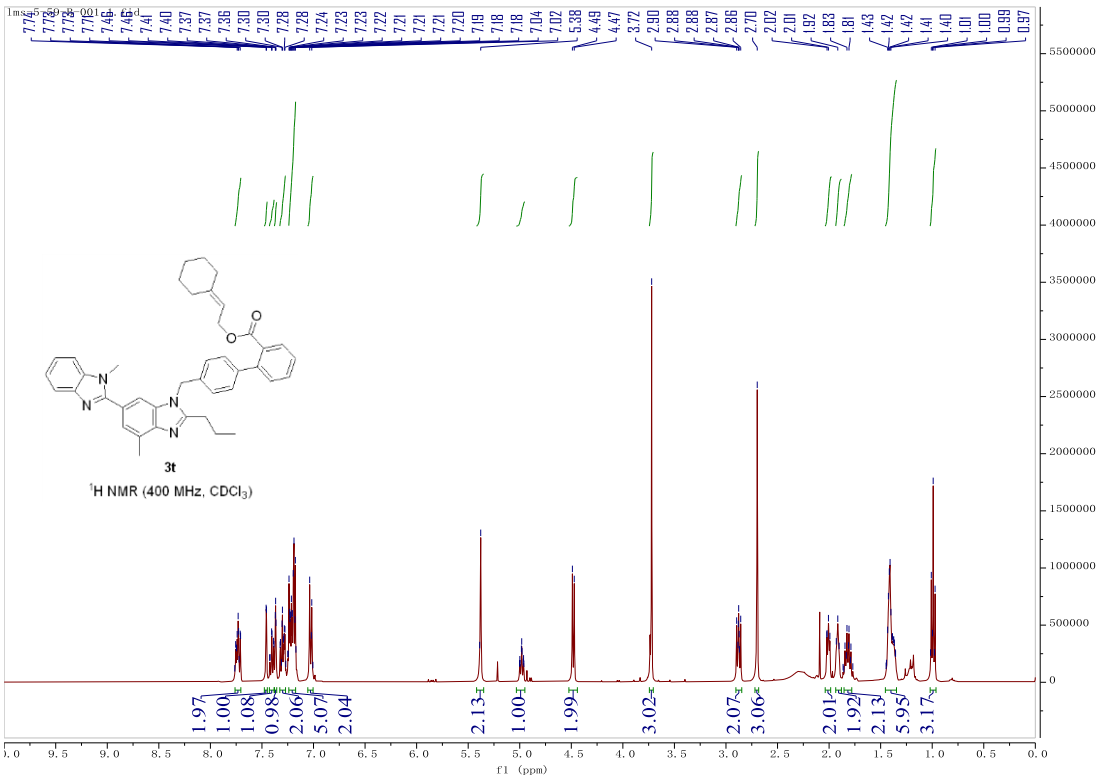
^{13}C NMR (101 MHz, $CDCl_3$)

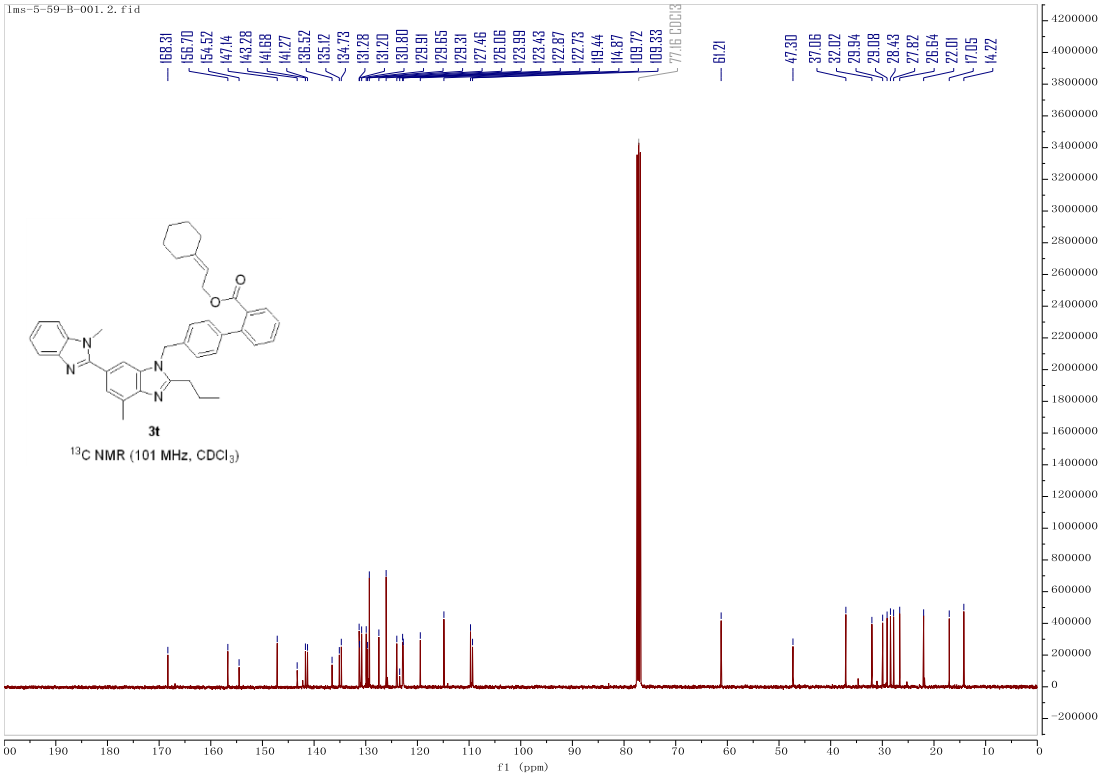


3s

^{1}H NMR (400 MHz, $CDCl_3$)

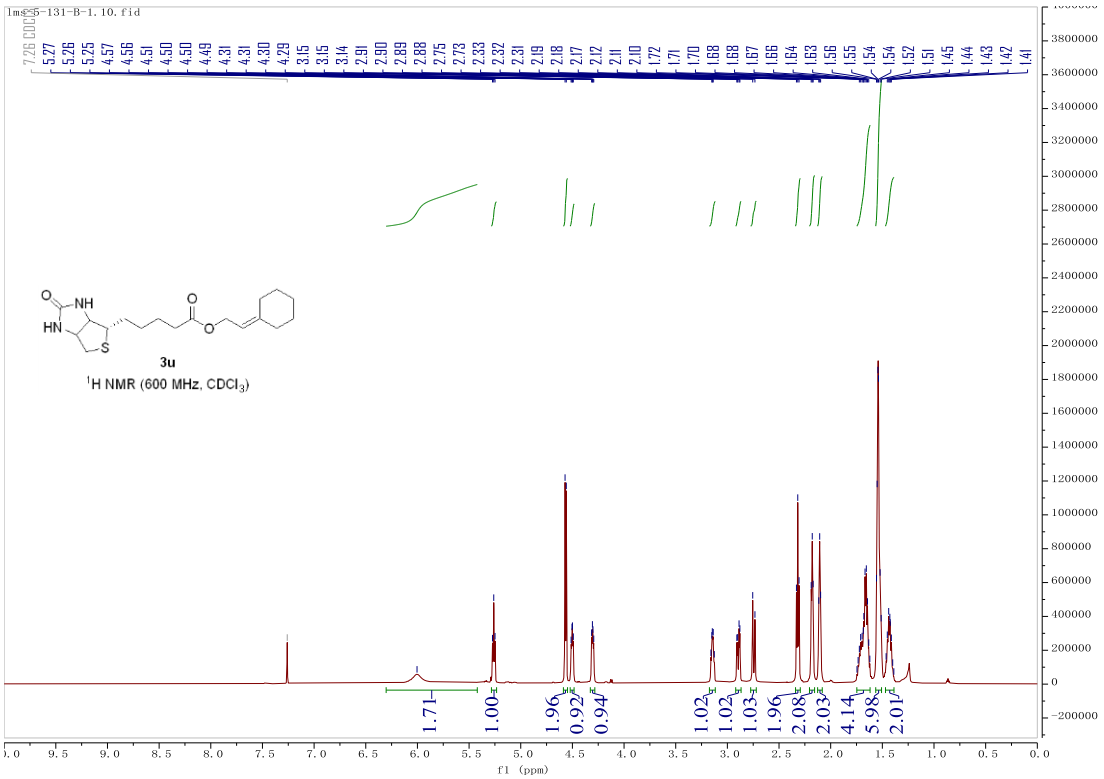

lms-5-47-D-01.4.fid
174.51
146.91
115.43
77.16 CDCl3
72.01
60.59
56.64
56.13
42.88
42.25
40.58
40.31
37.13
36.60
35.99
35.49
34.72
31.52
31.17
31.06
30.69
29.16
28.47
28.33
27.87
27.34
26.75
26.56
24.35
23.52
20.97
18.42
f1 (ppm)
HO
3s
13C NMR (101 MHz, CDCl3)


7.76
7.75
7.74
7.73
7.72
7.71
7.46
7.45
7.41
7.40
7.37
7.37
7.36
7.30
7.30
7.28
7.28
7.24
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.19
7.18
7.18
7.04
7.02
5.38
4.49
4.47
3.72
2.90
2.88
2.88
2.87
2.86
2.70
2.02
2.01
1.92
1.83
1.81
1.43
1.42
1.42
1.41
1.40
1.01
1.00
0.99
0.97
1.97
1.00
1.08
0.98
2.06
5.07
2.04
2.13
1.00
1.99
3.02
2.07
3.06
2.01
1.92
2.13
5.95
3.17
f1 (ppm)
3t
1H NMR (400 MHz, CDCl3)



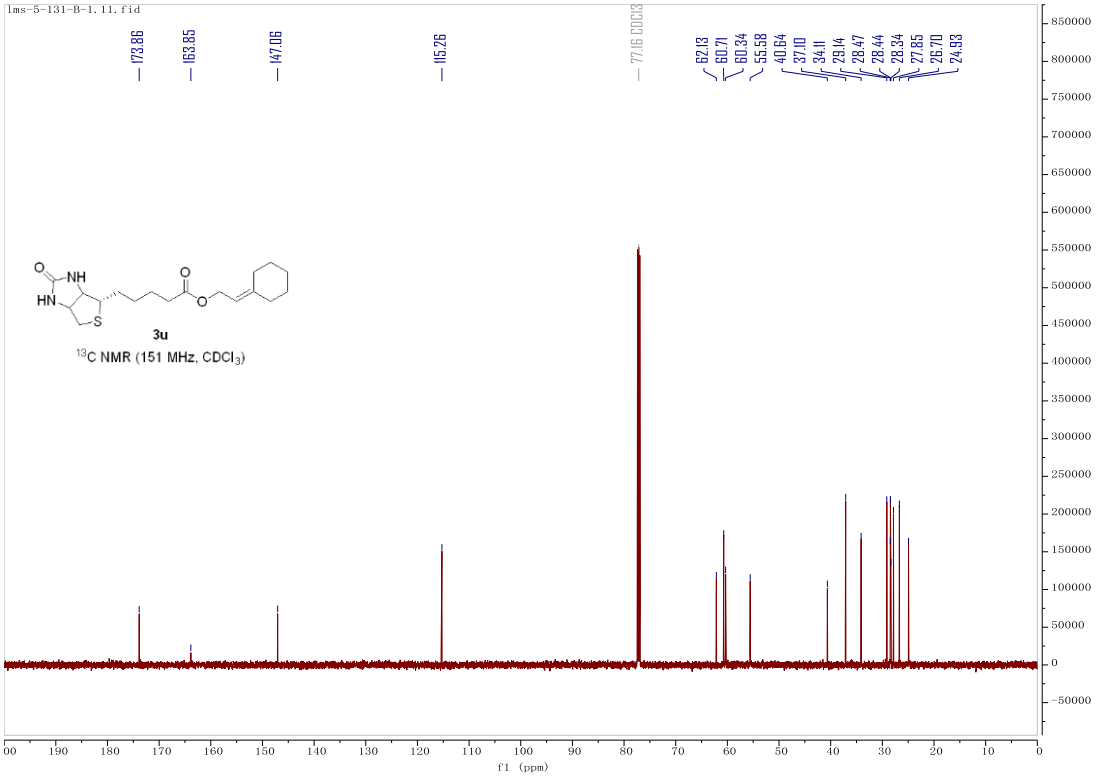
3t

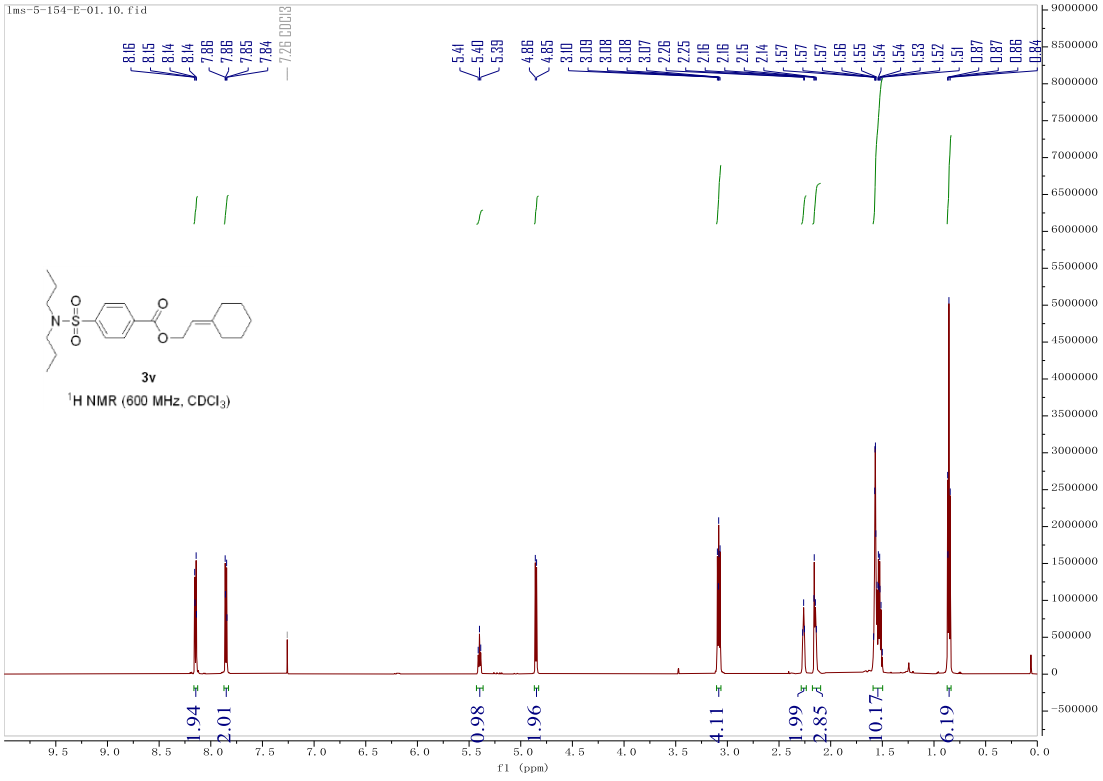
^{13}C NMR (101 MHz, $CDCl_3$)

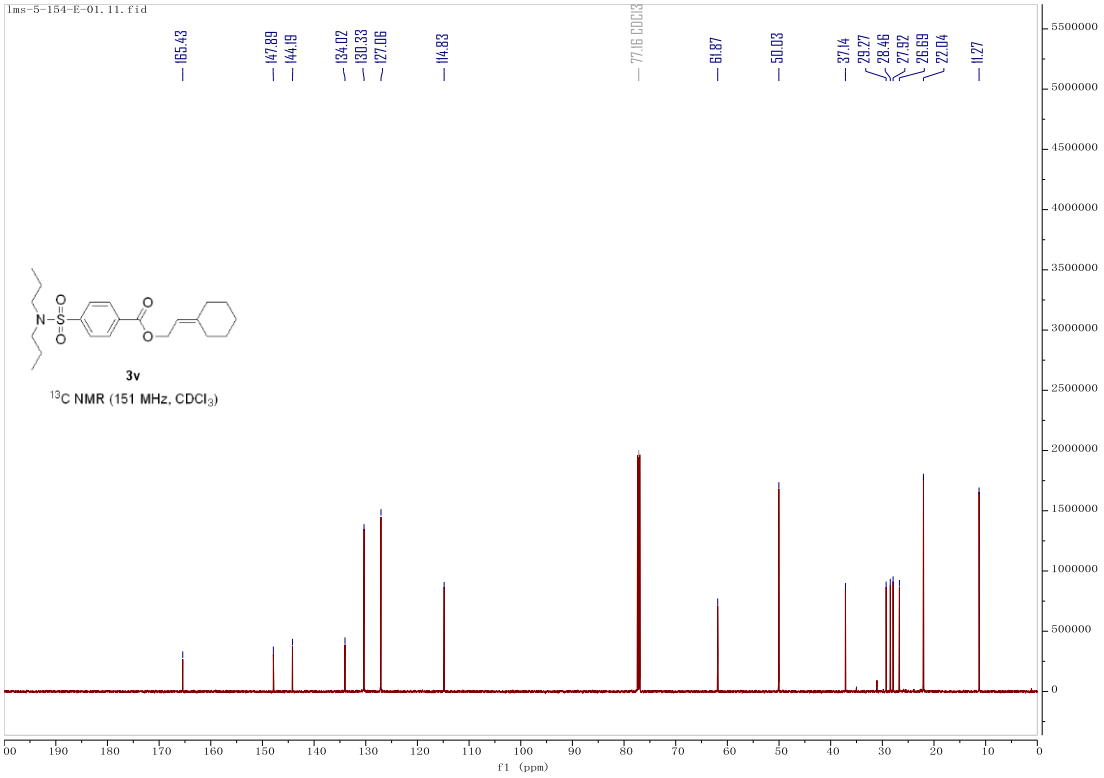


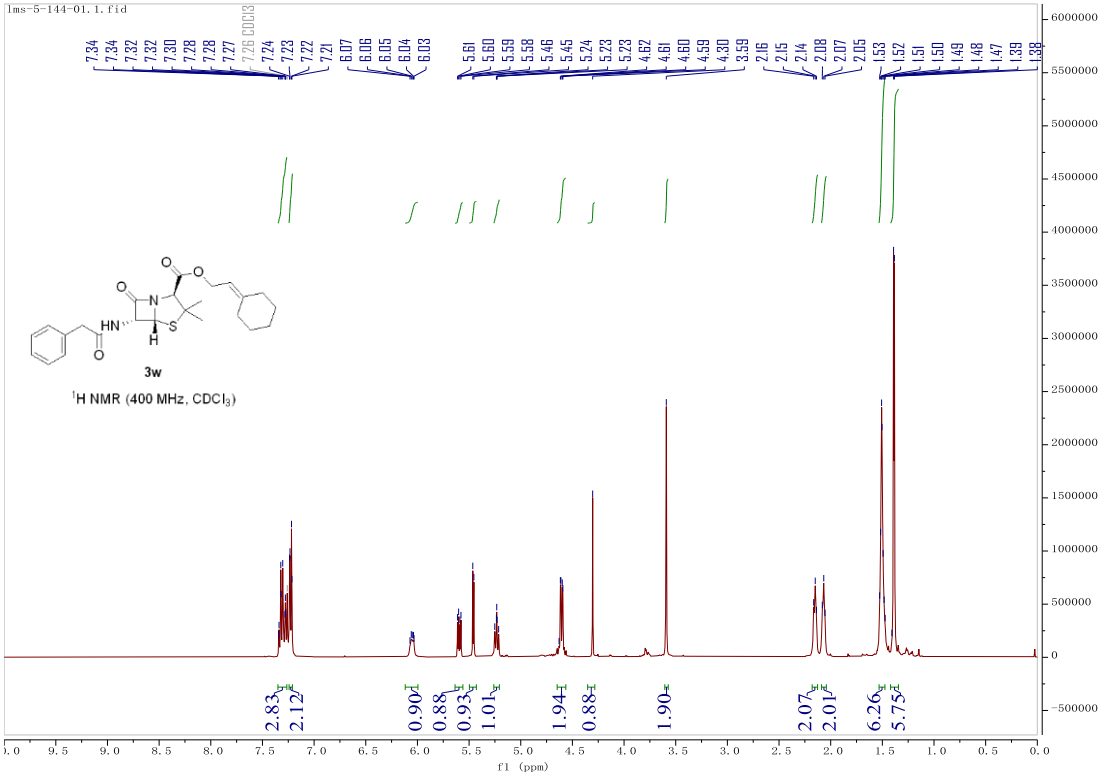
3u

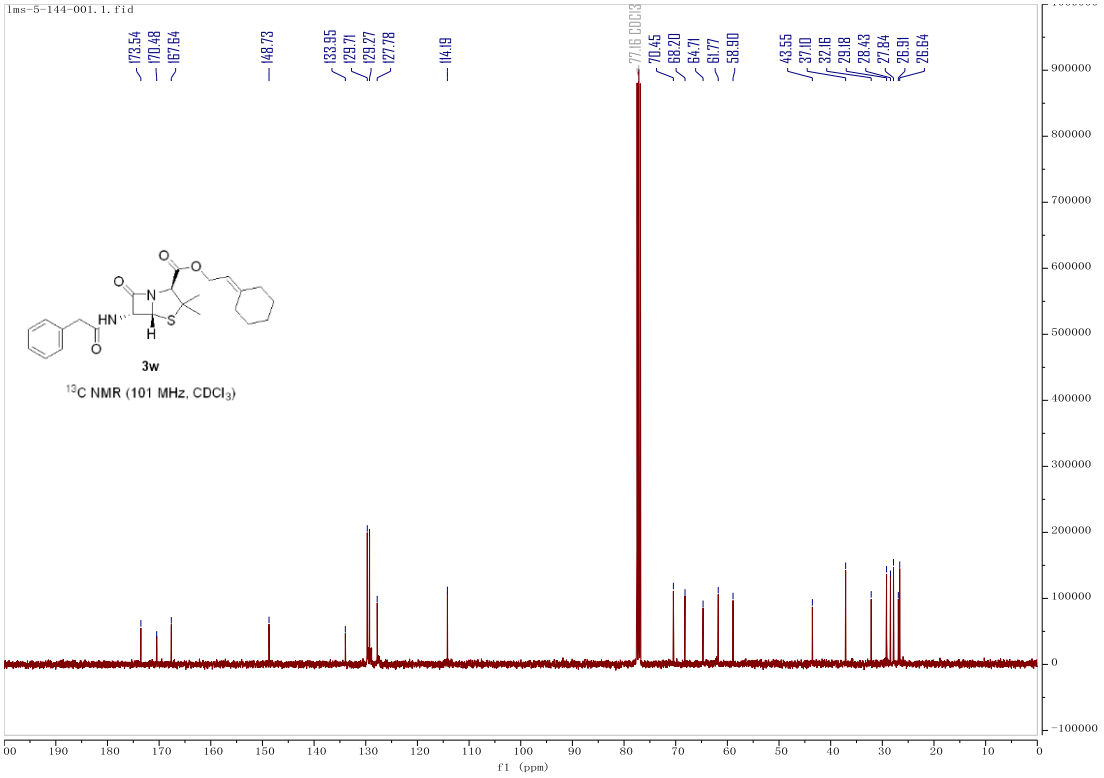
^{1}H NMR (600 MHz, $CDCl_3$)

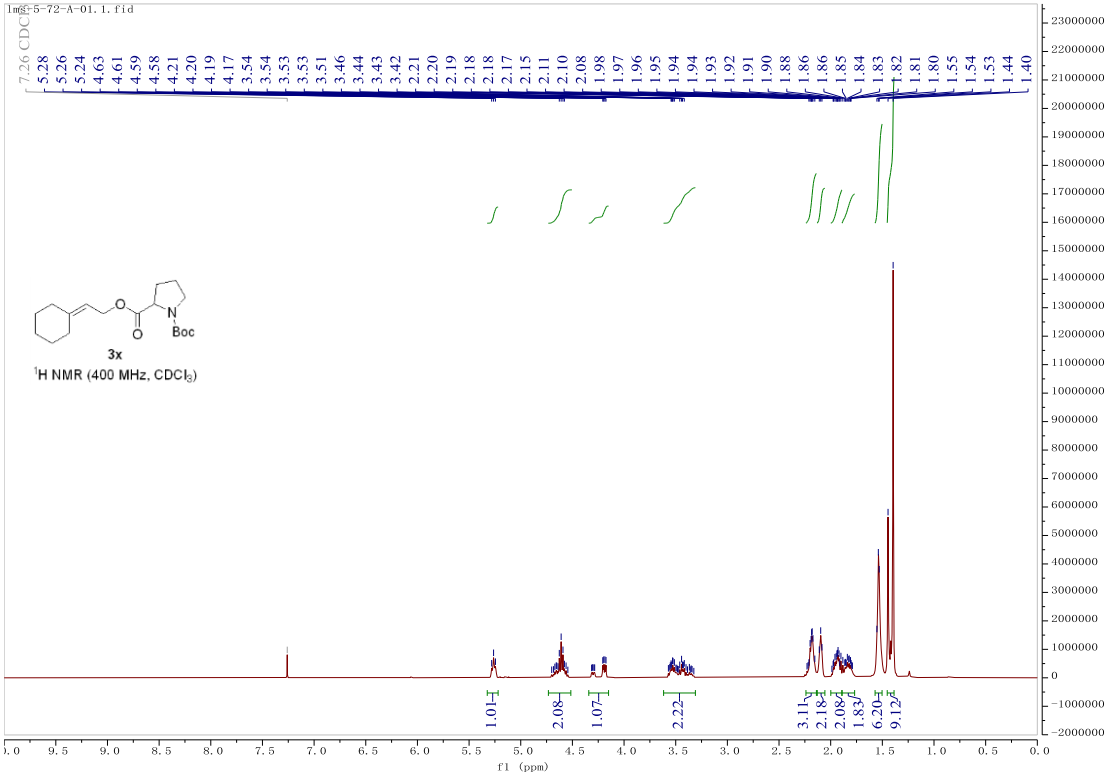

lms-5-131-B-1.11.fid
173.86
163.85
147.06
115.26
77.16 CDCl3
62.13
60.71
60.34
55.58
40.64
37.10
34.11
29.14
28.47
28.44
28.34
27.85
26.70
24.93
3u
13C NMR (151 MHz, CDCl3)
f1 (ppm)

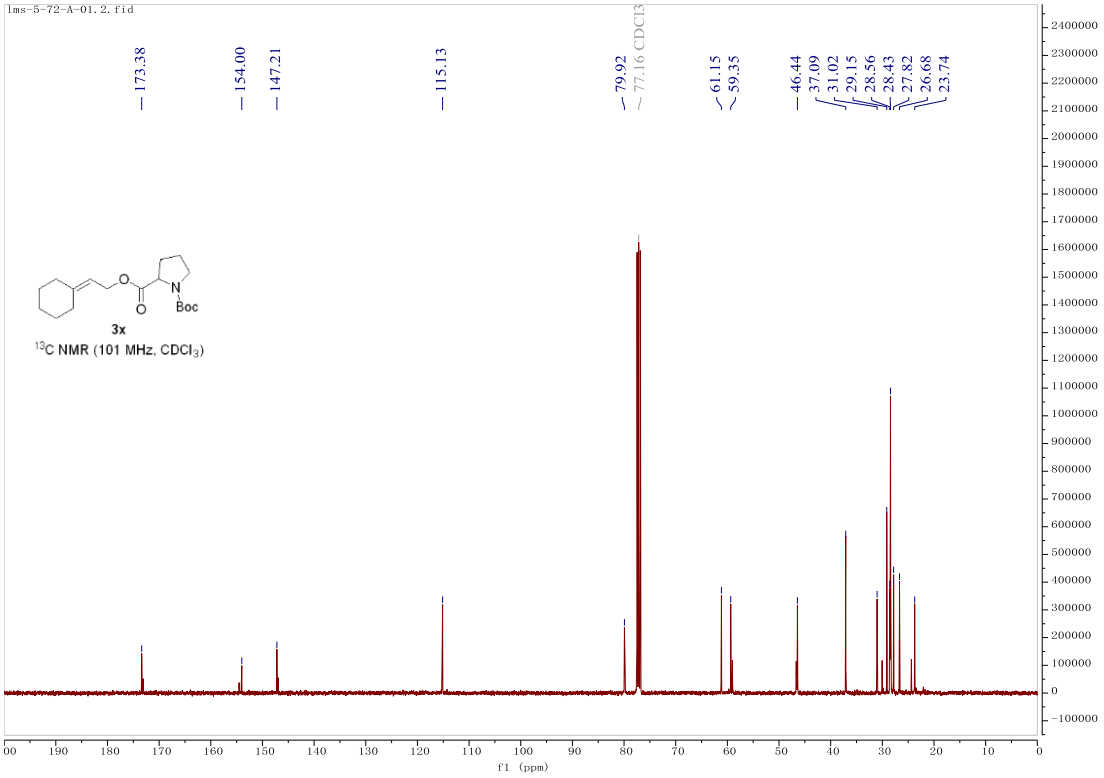

lms-5-154-E-01.10.fid
8.16
8.15
8.14
8.14
7.86
7.86
7.85
7.84
7.26 CDCl3
5.41
5.40
5.39
4.86
4.85
3.10
3.09
3.08
3.08
3.07
2.26
2.25
2.16
2.16
2.15
2.14
1.57
1.57
1.57
1.56
1.55
1.54
1.54
1.53
1.52
1.51
0.87
0.87
0.86
0.84
1.94
2.01
0.98
1.96
4.11
1.99
2.85
10.17
6.19
3v
1H NMR (600 MHz, CDCl3)
f1 (ppm)

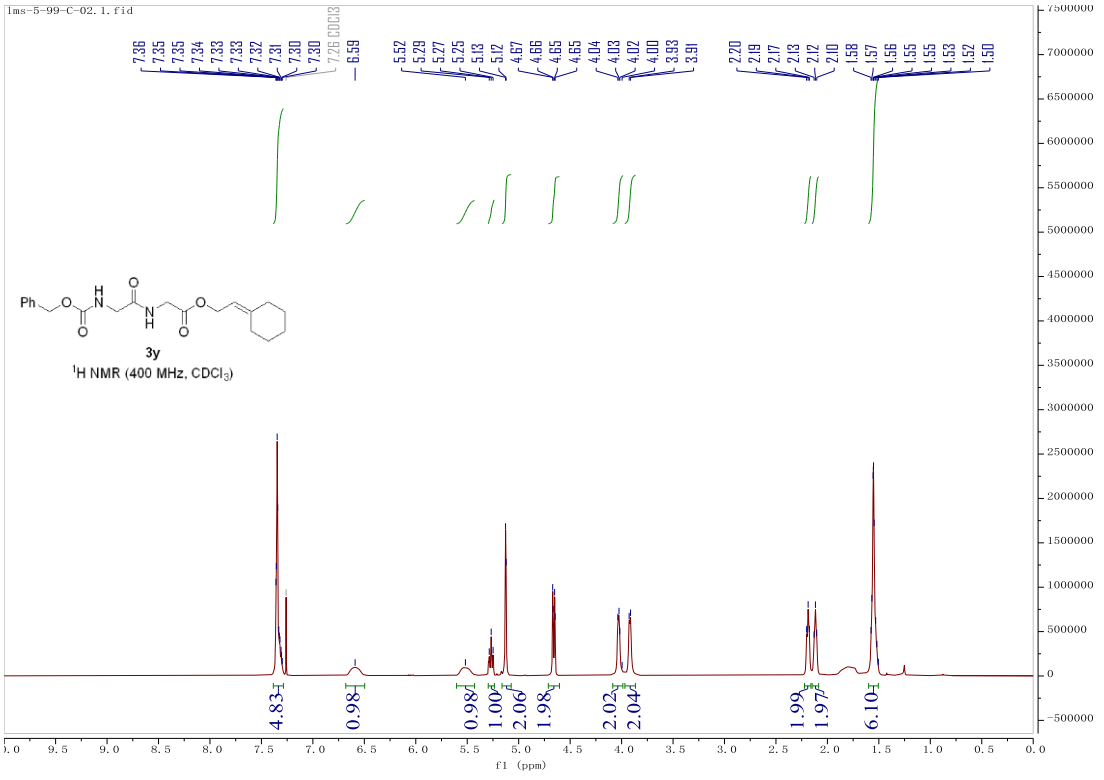

lms-5-154-E-01.11.fid
165.43
147.89
144.19
134.02
130.33
127.06
114.83
77.16 CDCl3
61.87
50.03
37.44
29.27
28.46
27.92
26.69
22.04
11.27
3v
13C NMR (151 MHz, CDCl3)
f1 (ppm)

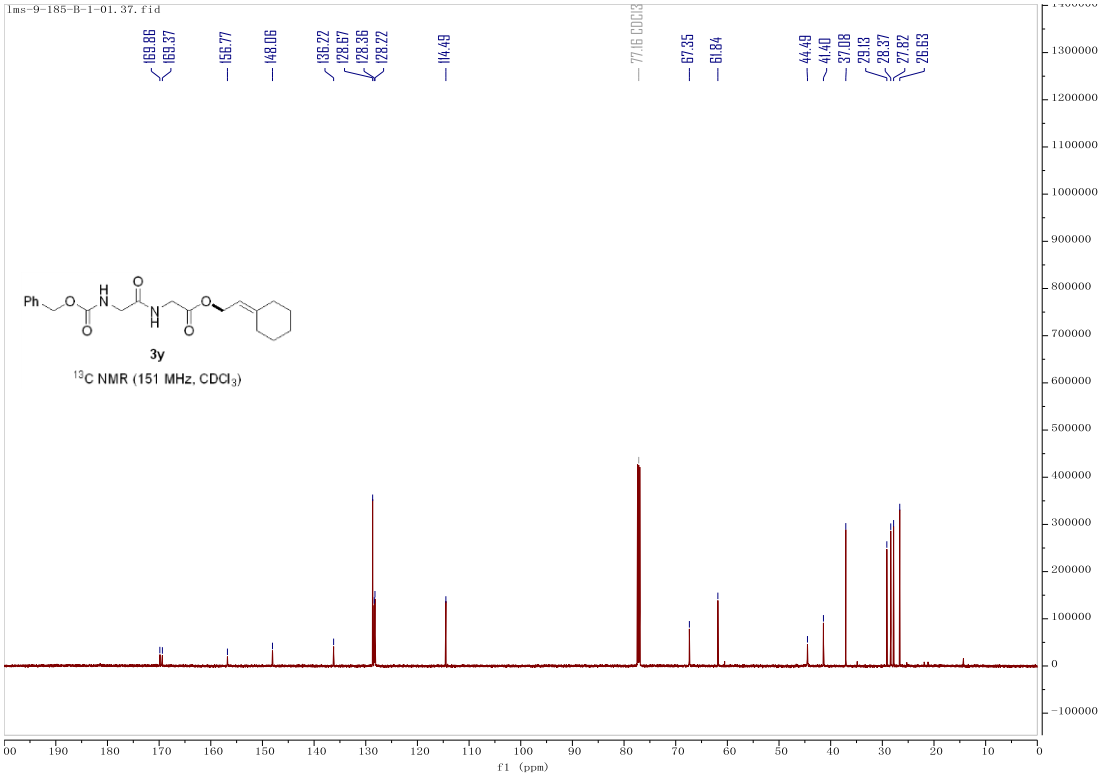

lms-5-144-01.1.fid
7.34
7.34
7.32
7.32
7.30
7.28
7.28
7.27
7.26 CDCl3
7.24
7.23
7.22
7.21
6.07
6.06
6.05
6.04
6.03
5.61
5.60
5.59
5.58
5.46
5.45
5.24
5.23
5.23
4.62
4.61
4.60
4.59
4.30
3.59
2.16
2.15
2.14
2.08
2.07
2.05
1.53
1.52
1.51
1.50
1.49
1.48
1.47
1.39
1.38
2.83
2.12
0.90
0.88
0.93
1.01
1.94
0.88
1.90
2.07
2.01
6.26
5.75
3w
1H NMR (400 MHz, CDCl3)
f1 (ppm)

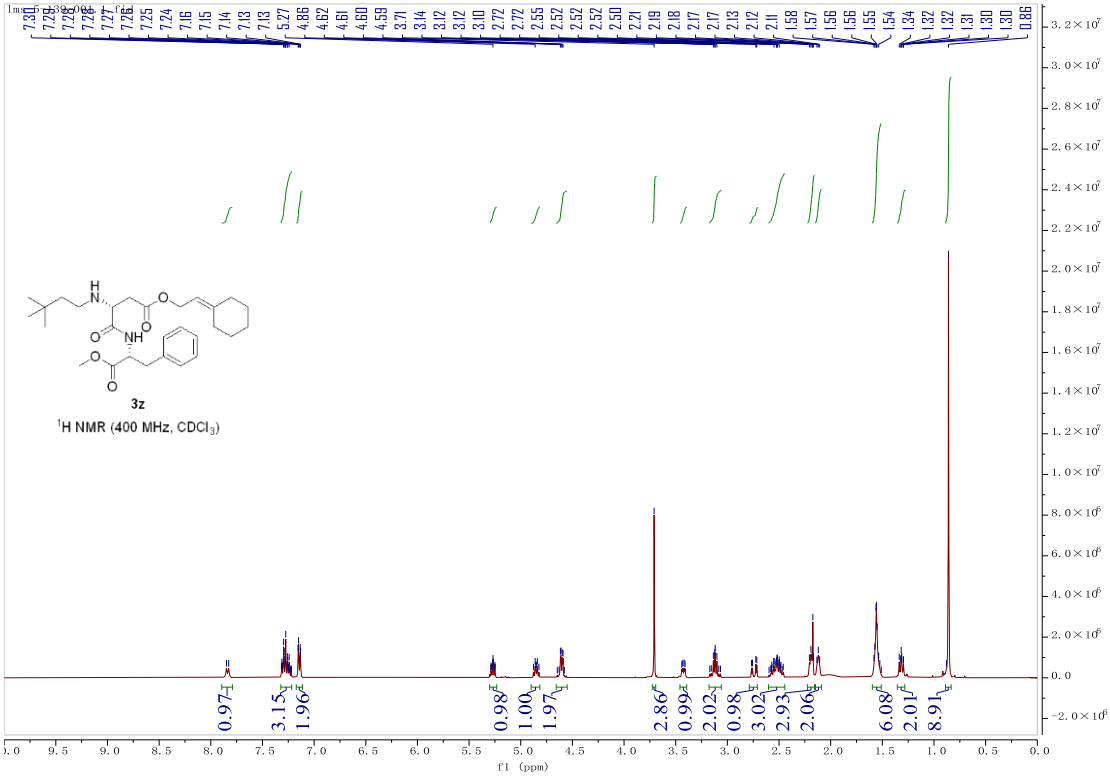

lms-5-144-001.1.fid
173.54
170.48
167.64
148.73
133.95
129.71
129.27
127.78
114.19
77.16 CDCl3
70.45
68.20
64.71
61.77
58.90
43.55
37.10
32.16
29.18
28.43
27.84
26.91
26.64
3w
13C NMR (101 MHz, CDCl3)
f1 (ppm)

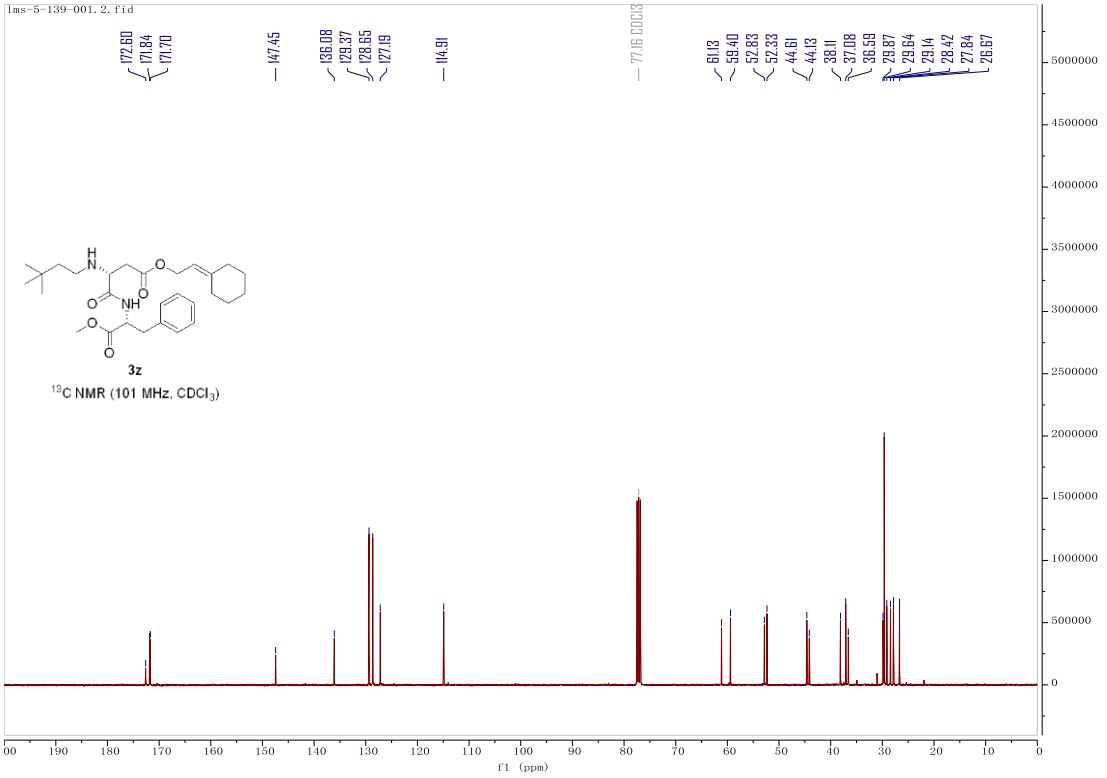

lms-5-72-A-01.1.fid
7.26 CDCl3
5.28
5.26
5.24
4.63
4.61
4.59
4.58
4.21
4.20
4.19
4.17
3.54
3.54
3.53
3.53
3.51
3.46
3.44
3.43
3.42
2.21
2.20
2.19
2.18
2.18
2.17
2.15
2.11
2.10
2.08
1.98
1.97
1.96
1.95
1.94
1.94
1.93
1.92
1.91
1.90
1.88
1.86
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.55
1.54
1.53
1.44
1.40
Boc
3x
1H NMR (400 MHz, CDCl3)
1.01
2.08
1.07
2.22
3.11
2.18
2.08
1.83
6.20
9.12
f1 (ppm)

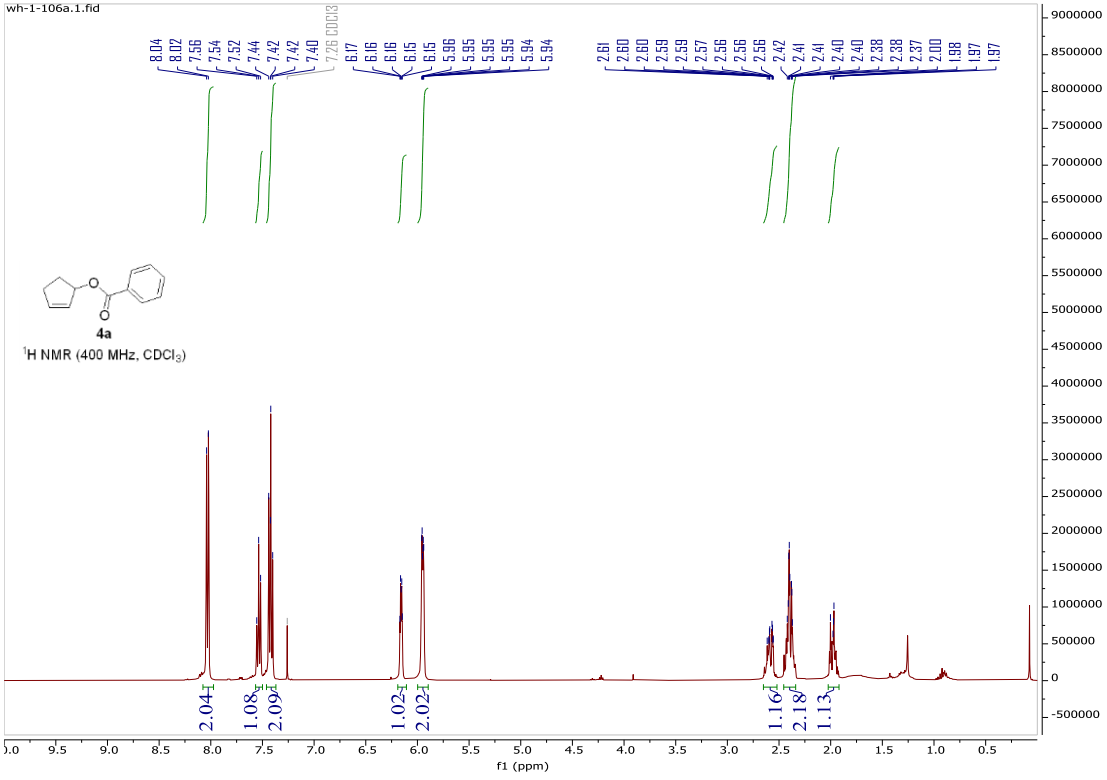

lms-5-72-A-01.2.fid
173.38
154.00
147.21
115.13
79.92
77.16 CDCl3
61.15
59.35
46.44
37.09
31.02
29.15
28.56
28.43
27.82
26.68
23.74
O
O
N
Boc
3x
13C NMR (101 MHz, CDCl3)
f1 (ppm)

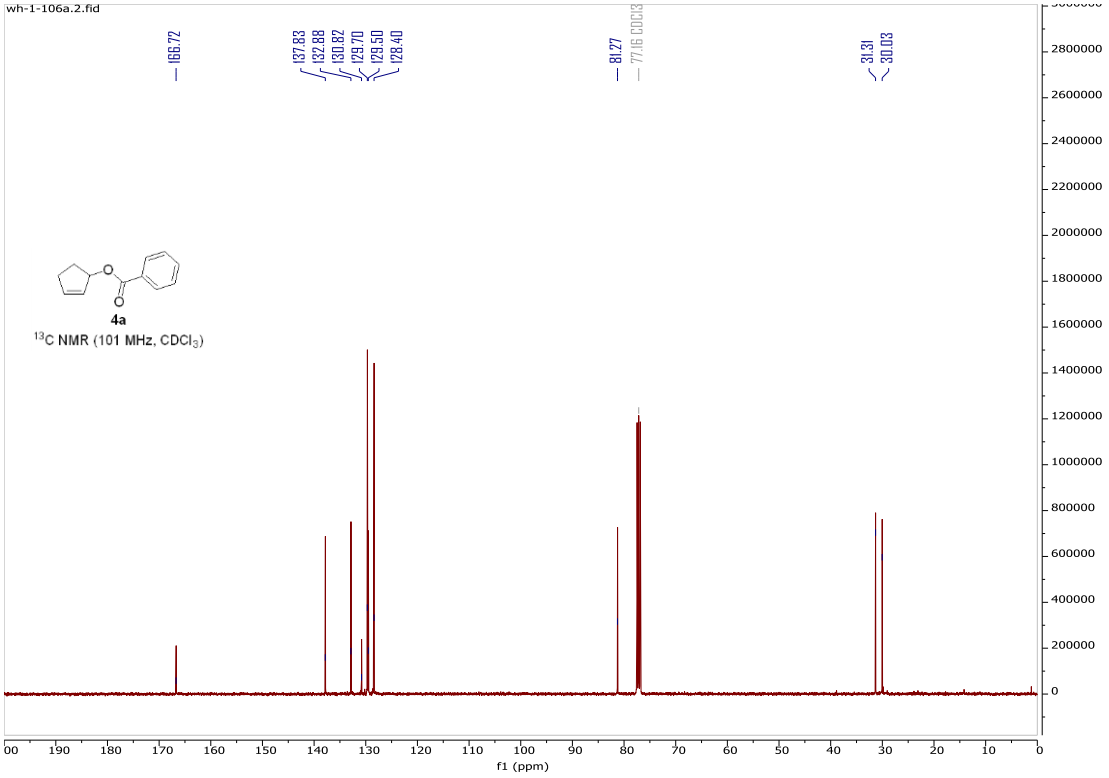

lms-5-99-C-02.1.fid
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.26 CDCl3
6.59
5.52
5.29
5.27
5.25
5.13
5.12
4.67
4.66
4.65
4.65
4.04
4.03
4.02
4.00
3.93
3.91
2.20
2.19
2.17
2.13
2.12
2.10
1.58
1.57
1.56
1.55
1.55
1.53
1.52
1.50
Ph
O
O
N
H
O
N
H
O
O
3y
1H NMR (400 MHz, CDCl3)
4.83
0.98
0.98
1.00
2.06
1.98
2.02
2.04
1.99
1.97
6.10
f1 (ppm)

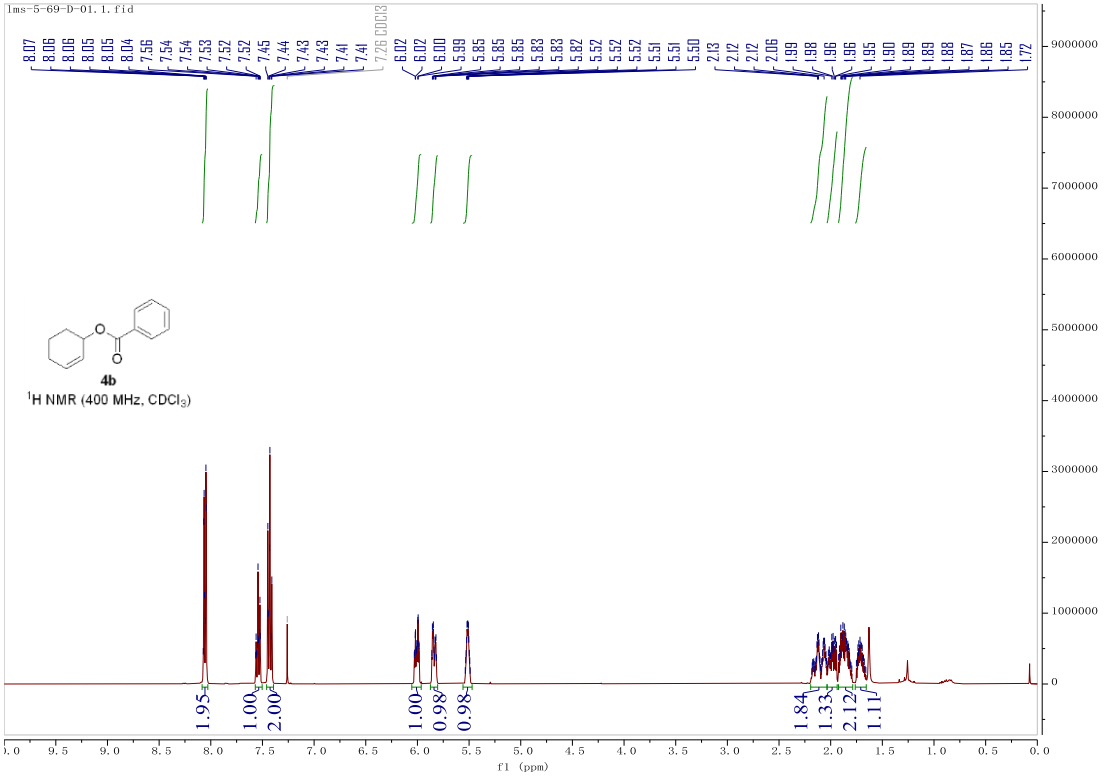

lms-9-185-B-1-01.37.fid
169.86
169.37
156.77
148.06
136.22
128.67
128.36
128.22
114.49
77.16 CDCl3
67.35
61.84
44.49
41.40
37.08
29.13
28.37
27.82
26.63
Ph
3y
13C NMR (151 MHz, CDCl3)
f1 (ppm)

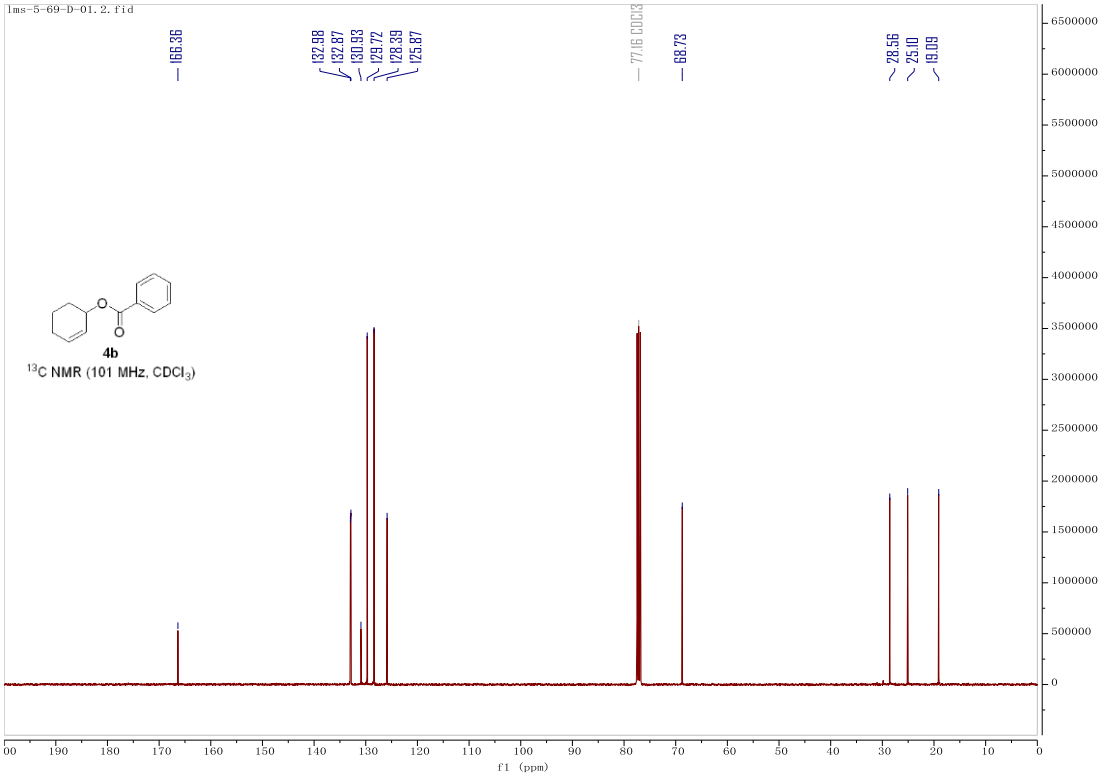

7.30
7.28
7.27
7.25
7.24
7.16
7.15
7.14
7.13
5.27
4.86
4.62
4.61
4.60
4.59
3.71
3.14
3.12
3.10
2.72
2.55
2.52
2.50
2.21
2.19
2.18
2.17
2.13
2.12
2.11
1.58
1.57
1.56
1.55
1.54
1.34
1.32
1.31
1.30
0.86
NH
3z
1H NMR (400 MHz, CDCl3)
0.97
3.15
1.96
0.98
1.00
1.97
2.86
0.99
2.02
0.98
3.02
2.93
2.06
6.08
2.01
8.91
f1 (ppm)

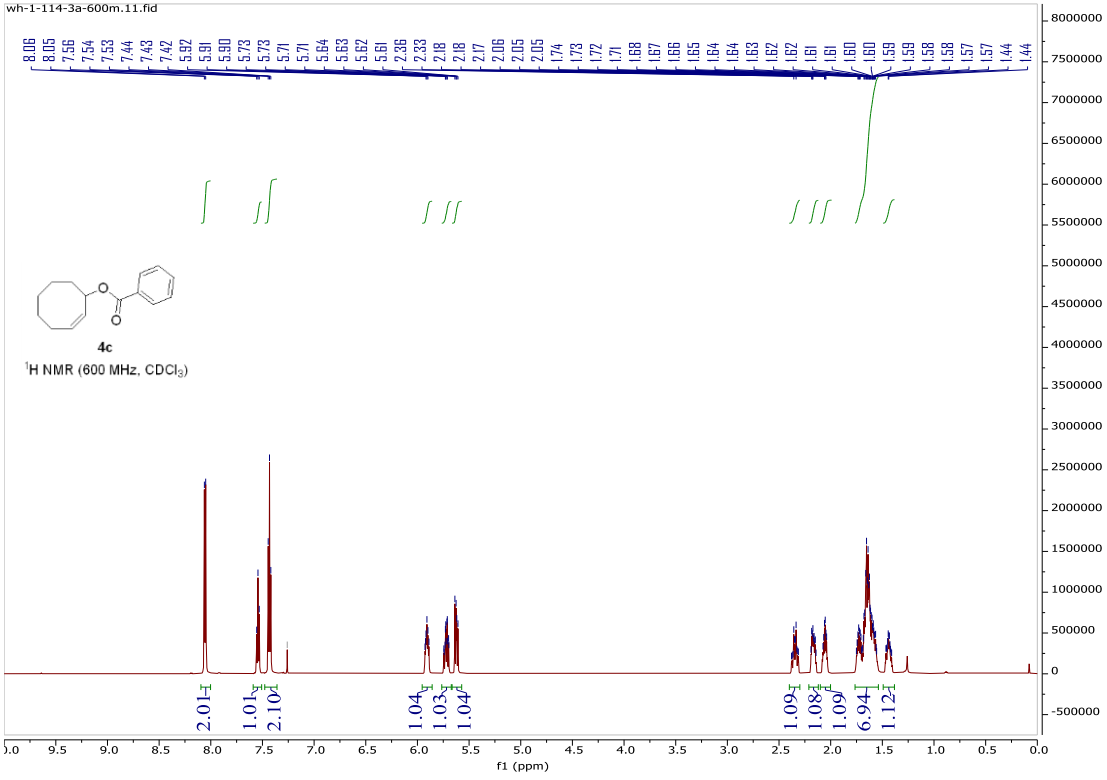

lms-5-139-001.2.fid
172.60
171.84
171.70
147.45
136.08
129.37
128.65
127.19
114.91
77.16 CDCl3
61.13
59.40
52.83
52.33
44.61
44.13
38.11
37.08
36.59
29.87
29.64
29.14
28.42
27.84
26.67
3z
13C NMR (101 MHz, CDCl3)
f1 (ppm)

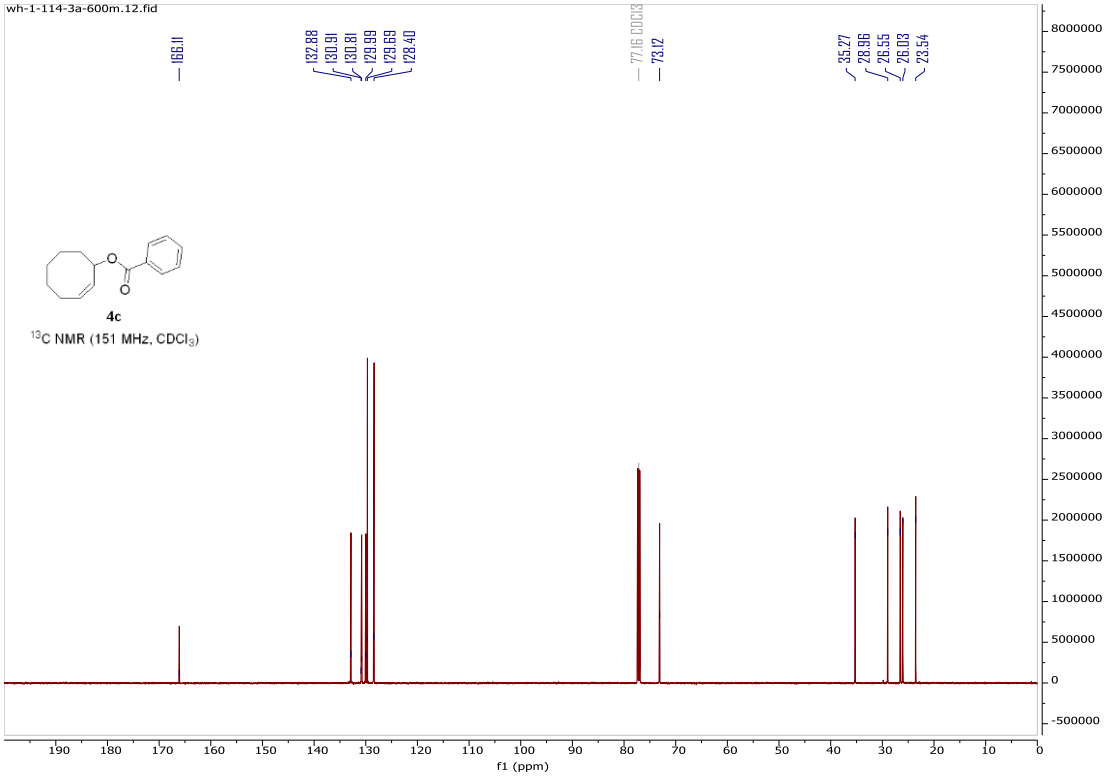

wh-1-106a.1.fid
8.04
8.02
7.56
7.54
7.52
7.44
7.42
7.42
7.40
7.26 CDCl3
6.17
6.16
6.16
6.15
6.15
5.96
5.95
5.95
5.95
5.94
5.94
2.61
2.60
2.60
2.59
2.59
2.57
2.56
2.56
2.56
2.42
2.41
2.41
2.40
2.40
2.38
2.38
2.37
2.00
1.98
1.97
1.97
4a
1H NMR (400 MHz, CDCl3)
2.04
1.08
2.09
1.02
2.02
1.16
2.18
1.13
f1 (ppm)

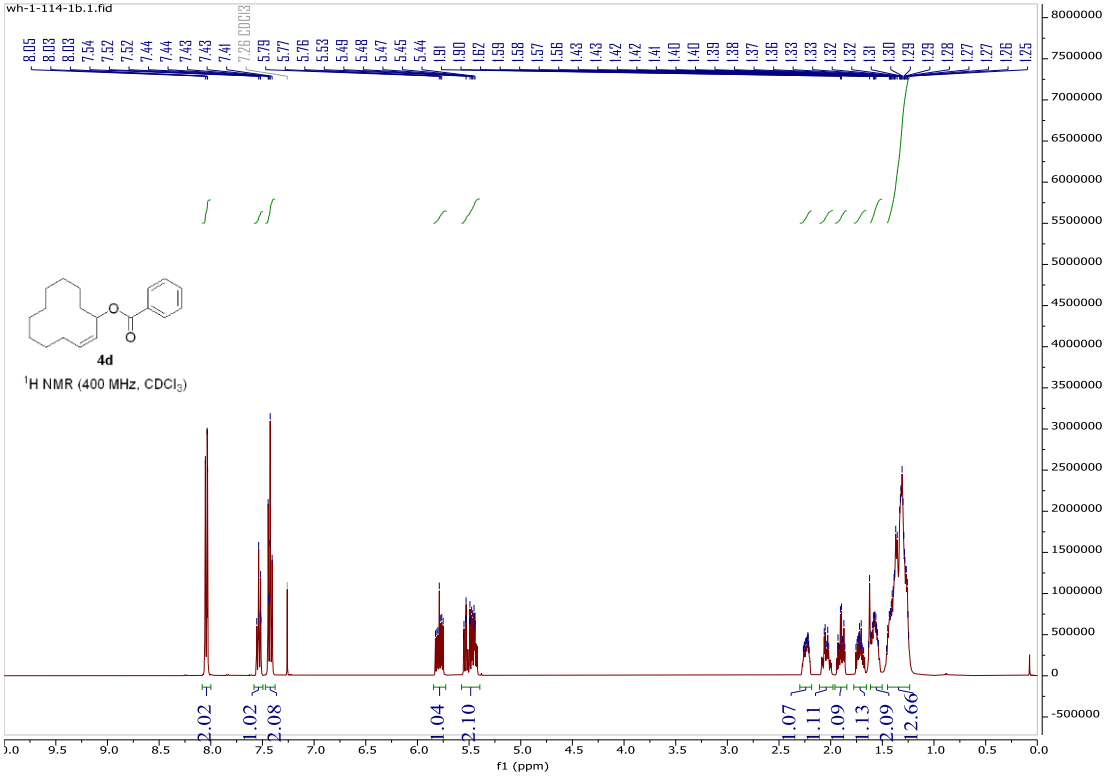

wh-1-106a.2.fid
166.72
137.83
132.88
130.82
129.70
129.50
128.40
81.27
77.16 CDCl3
31.31
30.03
4a
13C NMR (101 MHz, CDCl3)
f1 (ppm)

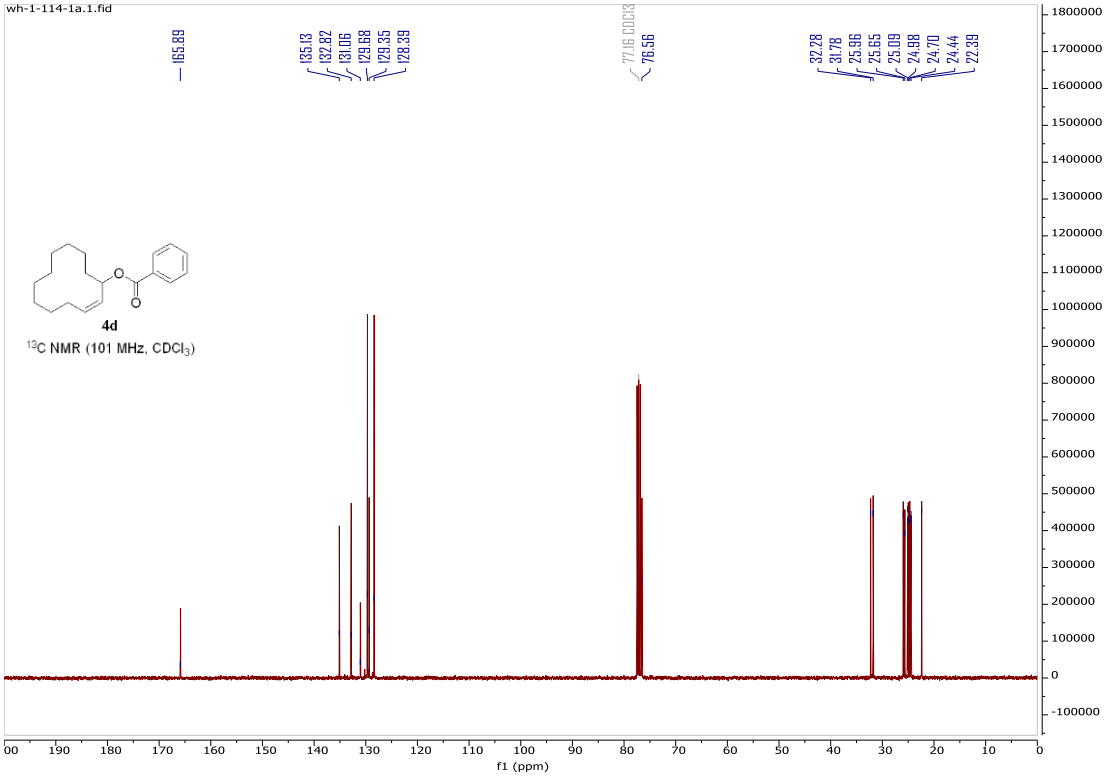

lms-5-69-D-01.1.fid
7.26 CDCl3
4b
1H NMR (400 MHz, CDCl3)
1.95
1.00
2.00
1.00
0.98
0.98
1.84
1.33
2.12
1.11
f1 (ppm)

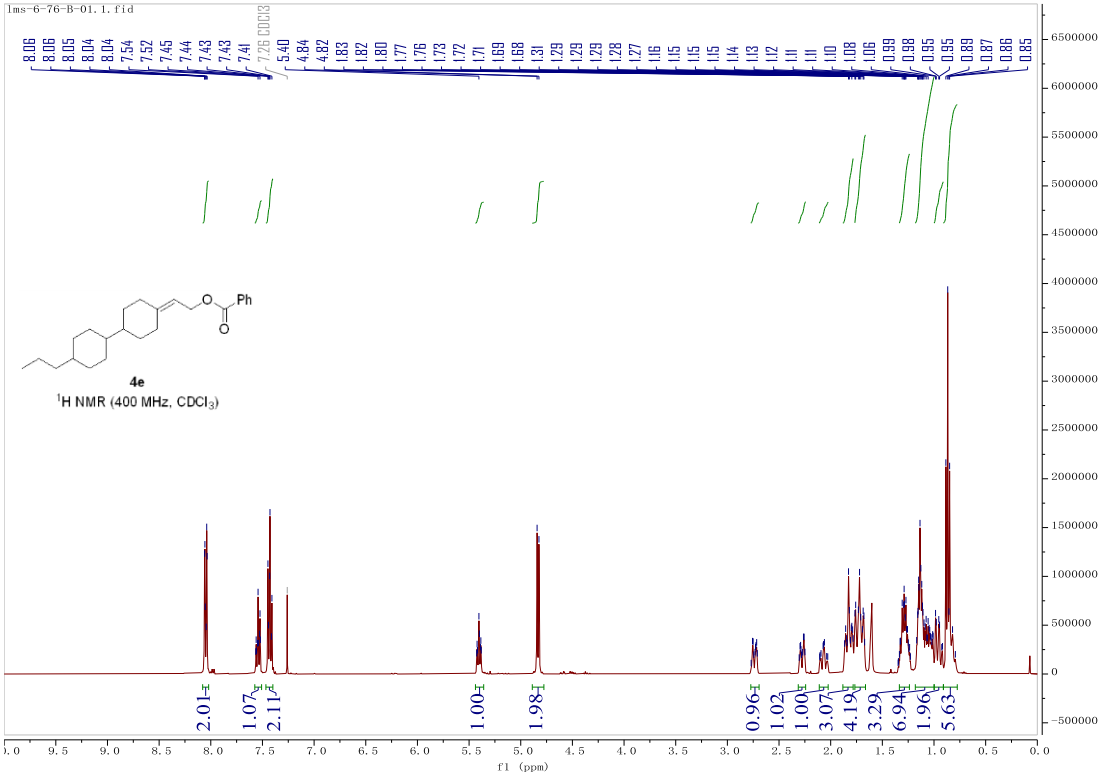

lms-5-69-D-01.2.fid
166.36
132.98
132.87
130.93
129.72
128.39
125.87
77.16 CDCl3
68.73
28.56
25.10
19.09
4b
13C NMR (101 MHz, CDCl3)
f1 (ppm)

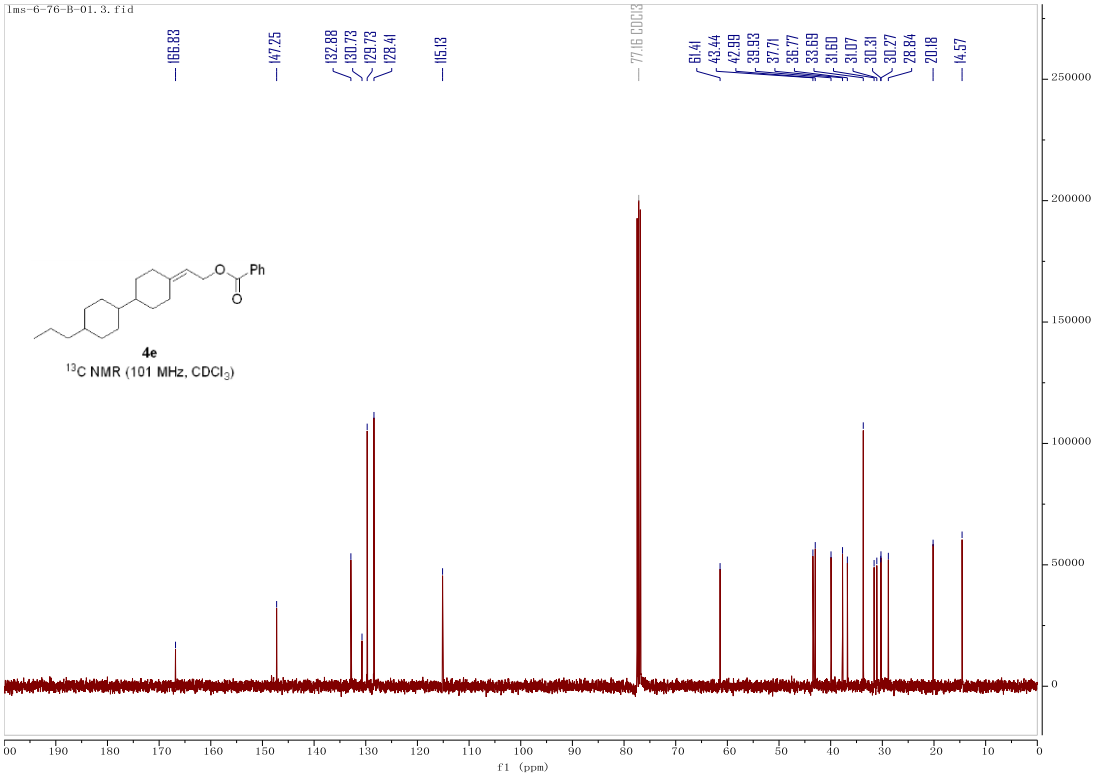

wh-1-114-3a-600m.11.fid
4c
1H NMR (600 MHz, CDCl3)
2.01
1.01
2.10
1.04
1.03
1.04
1.09
1.08
1.09
6.94
1.12
f1 (ppm)

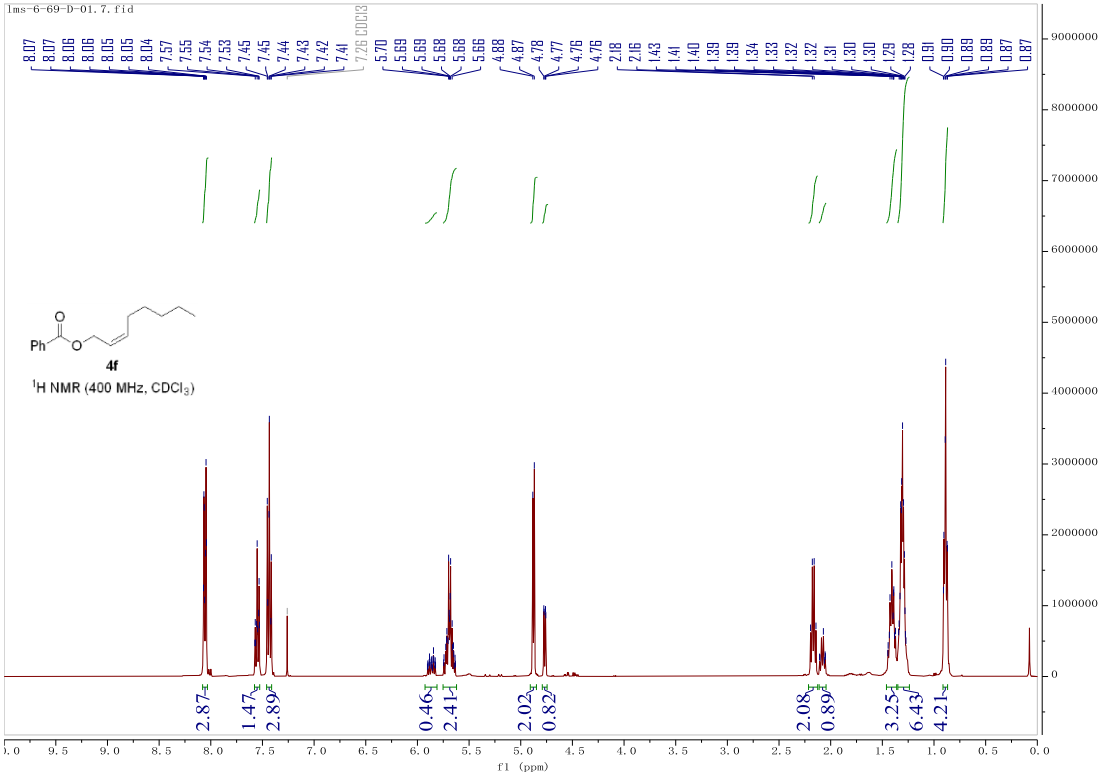

wh-1-114-3a-600m.12.fid
166.11
132.88
130.91
130.81
129.99
129.69
128.40
77.16 CDCl3
73.12
35.27
28.96
26.55
26.03
23.54
4c
13C NMR (151 MHz, CDCl3)
f1 (ppm)

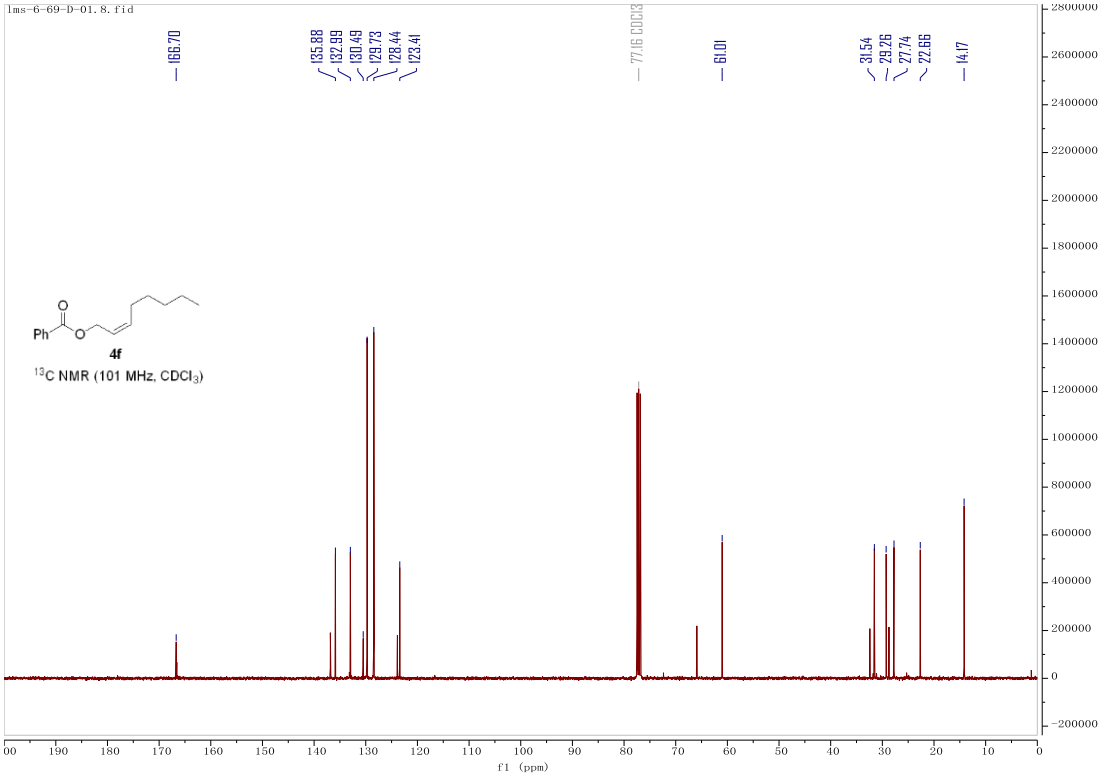

wh-1-114-1b.1.fid
7.26 CDCl3
4d
1H NMR (400 MHz, CDCl3)
2.02
1.02
2.08
1.04
2.10
1.07
1.11
1.09
1.13
2.09
12.66
f1 (ppm)

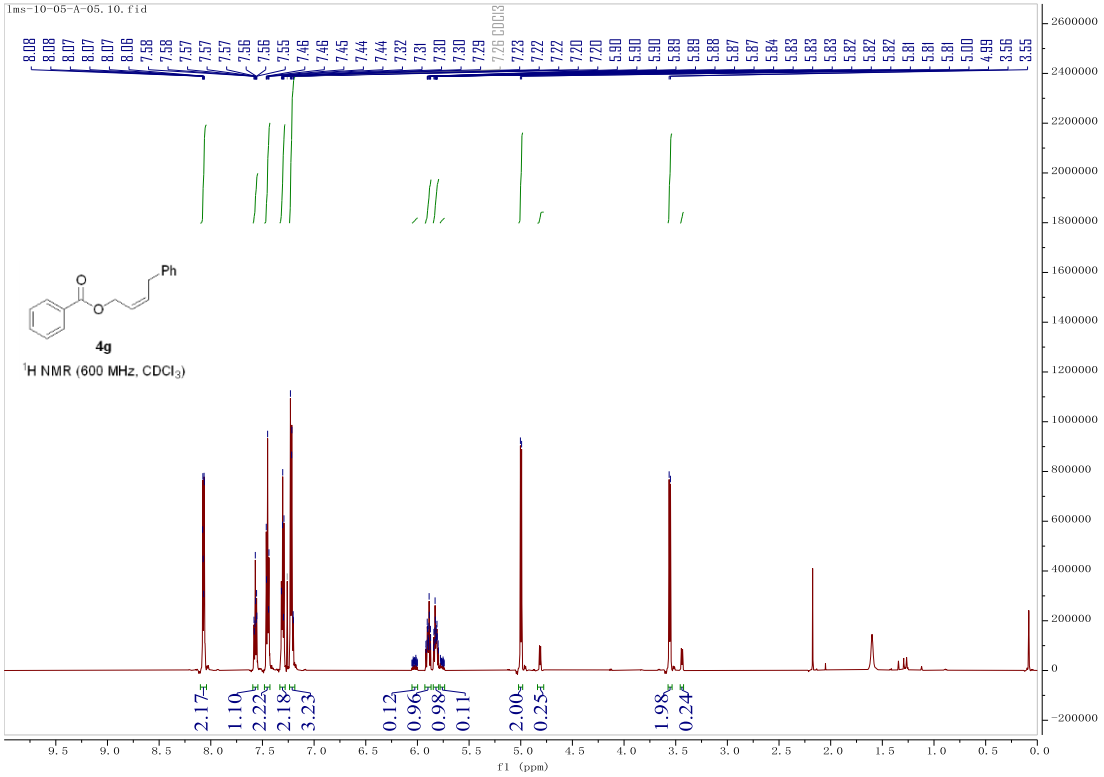

wh-1-114-1a.1.fid
165.89
135.13
132.82
131.06
129.68
129.35
128.39
77.16 CDCl3
76.56
32.28
31.78
25.96
25.65
25.09
24.98
24.70
24.44
22.39
4d
13C NMR (101 MHz, CDCl3)
f1 (ppm)

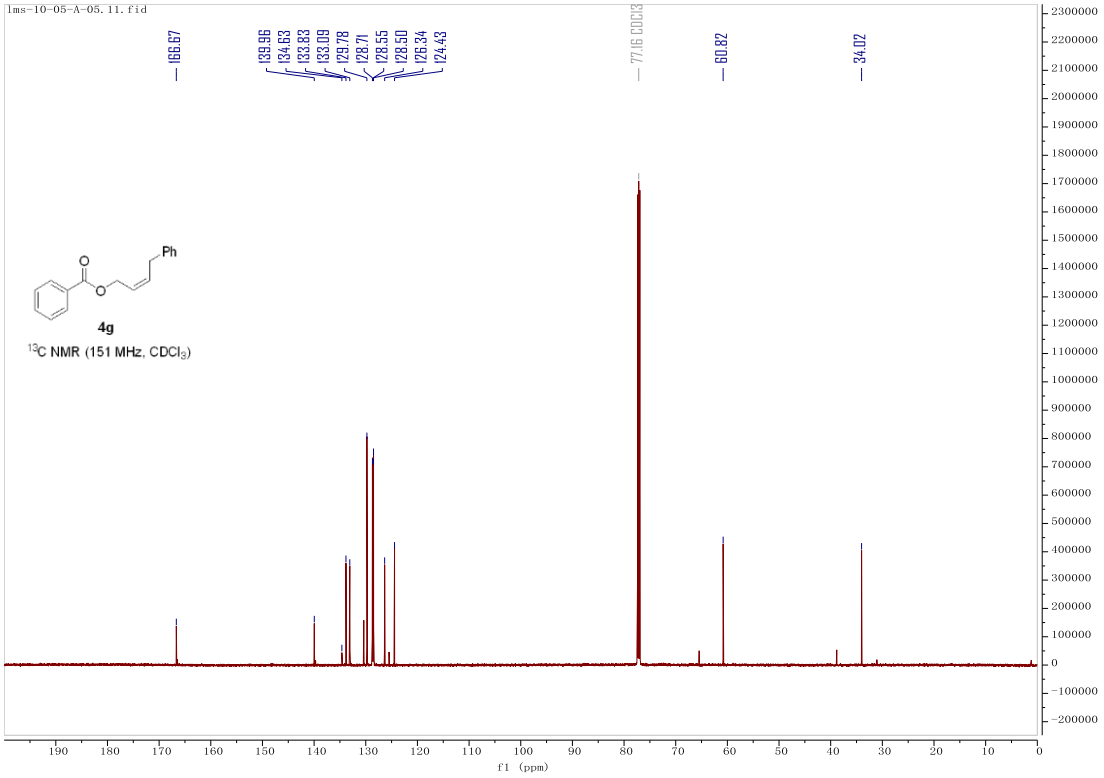

lms-6-76-B-01.1.fid
7.26 CDCl3
Ph
4e
1H NMR (400 MHz, CDCl3)
2.01
1.07
2.11
1.00
1.98
0.96
1.02
1.00
3.07
4.19
3.29
6.94
1.96
5.63
f1 (ppm)

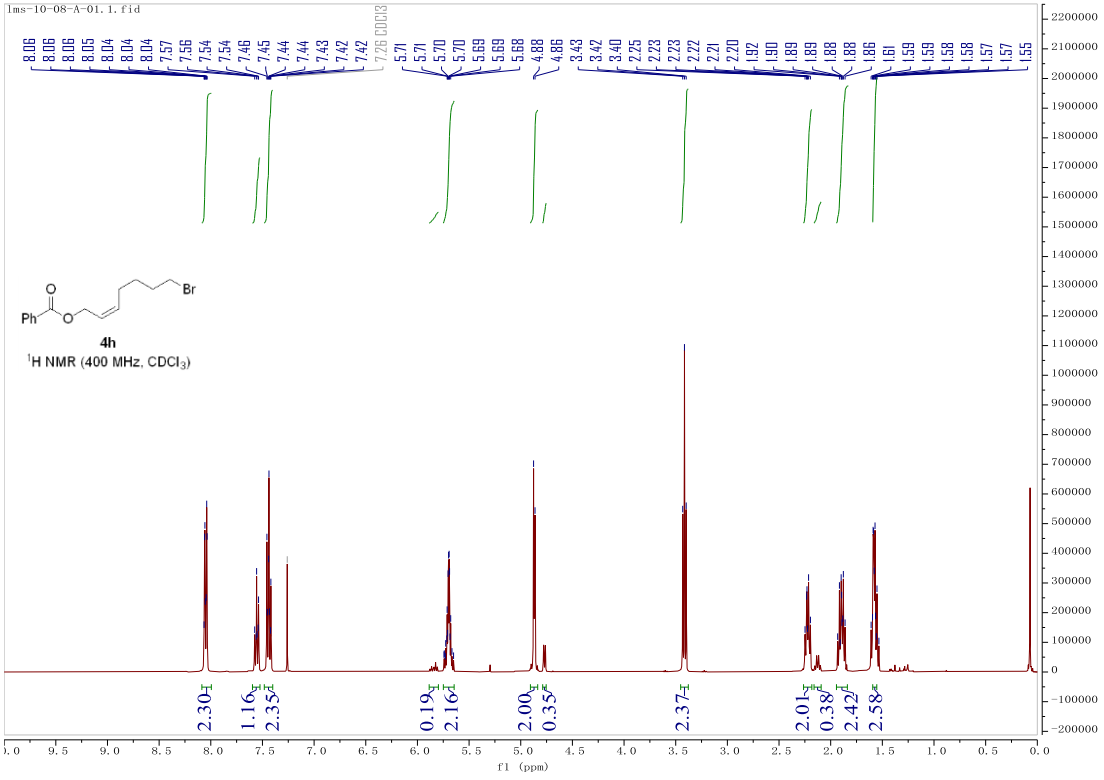

lms-6-76-B-01.3.fid
166.83
147.25
132.88
130.73
129.73
128.41
115.13
77.16 CDCl3
61.41
43.44
42.99
39.93
37.71
36.77
33.69
31.60
31.07
30.31
30.27
28.84
20.18
14.57
Ph
O
4e
13C NMR (101 MHz, CDCl3)
f1 (ppm)

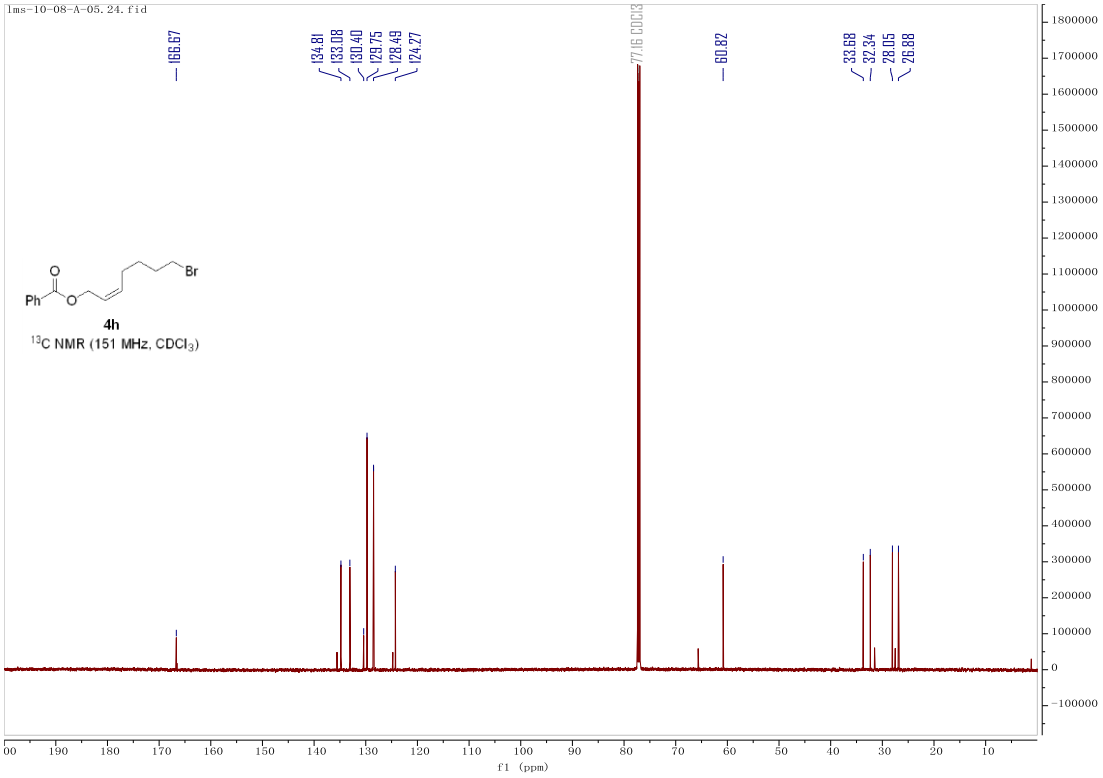

lms-6-69-D-01.7.fid
7.26 CDCl3
Ph
O
4f
1H NMR (400 MHz, CDCl3)
2.87
1.47
2.89
0.46
2.41
2.02
0.82
2.08
0.89
3.25
6.43
4.21
f1 (ppm)

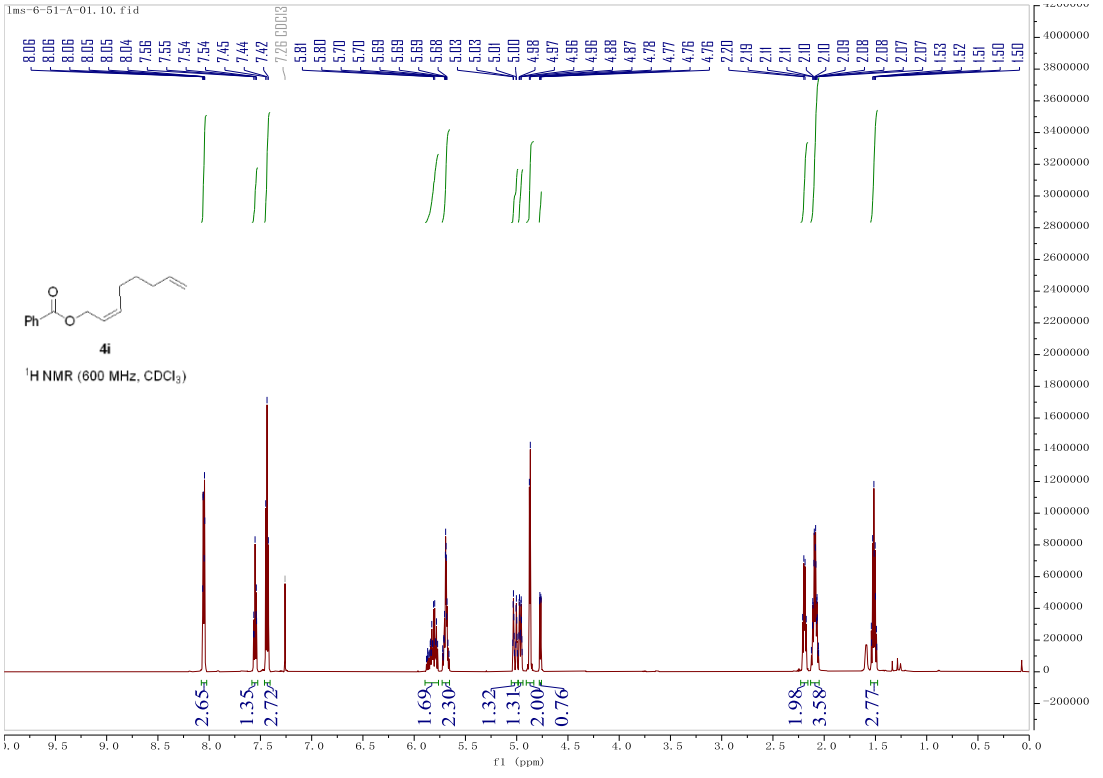

lms-6-69-D-01.8.fid
166.70
135.88
132.99
130.49
129.73
128.44
123.41
77.16 CDCl3
61.01
31.54
29.26
27.74
27.66
14.17
Ph
4f
13C NMR (101 MHz, CDCl3)
f1 (ppm)

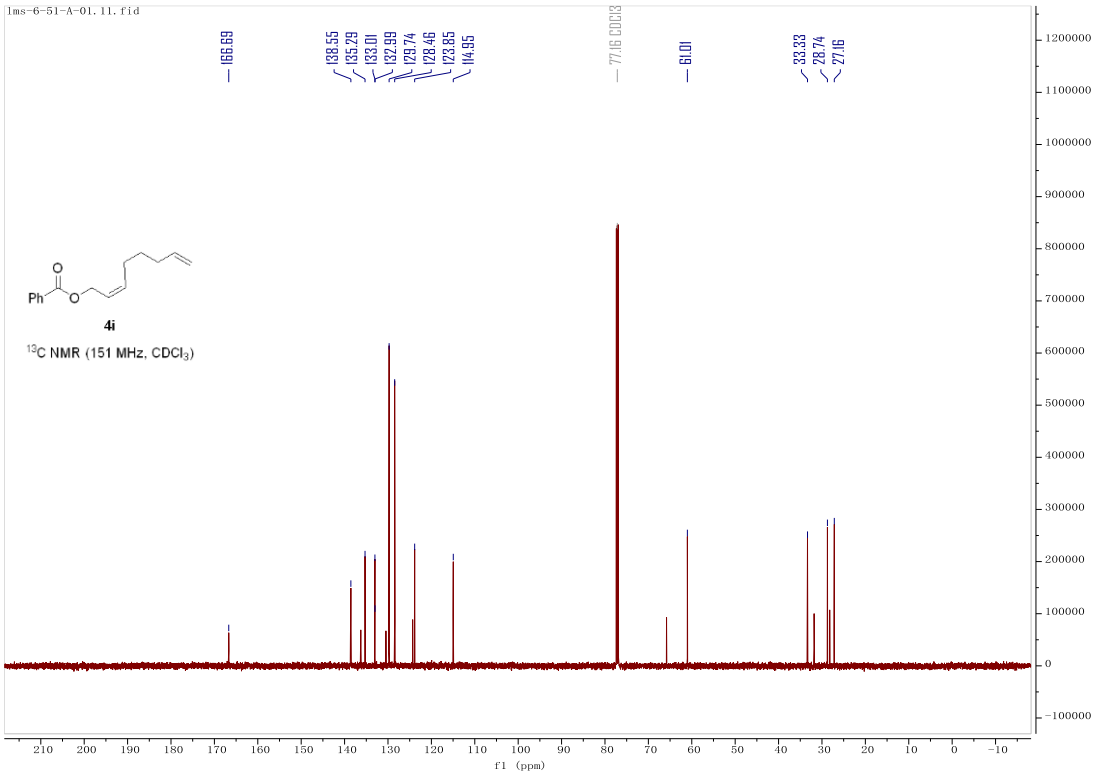

lms-10-05-A-05.10.fid
7.26 CDCl3
Ph
4g
1H NMR (600 MHz, CDCl3)
2.17
1.10
2.22
2.18
3.23
0.12
0.96
0.98
0.11
2.00
0.25
1.98
0.24
f1 (ppm)

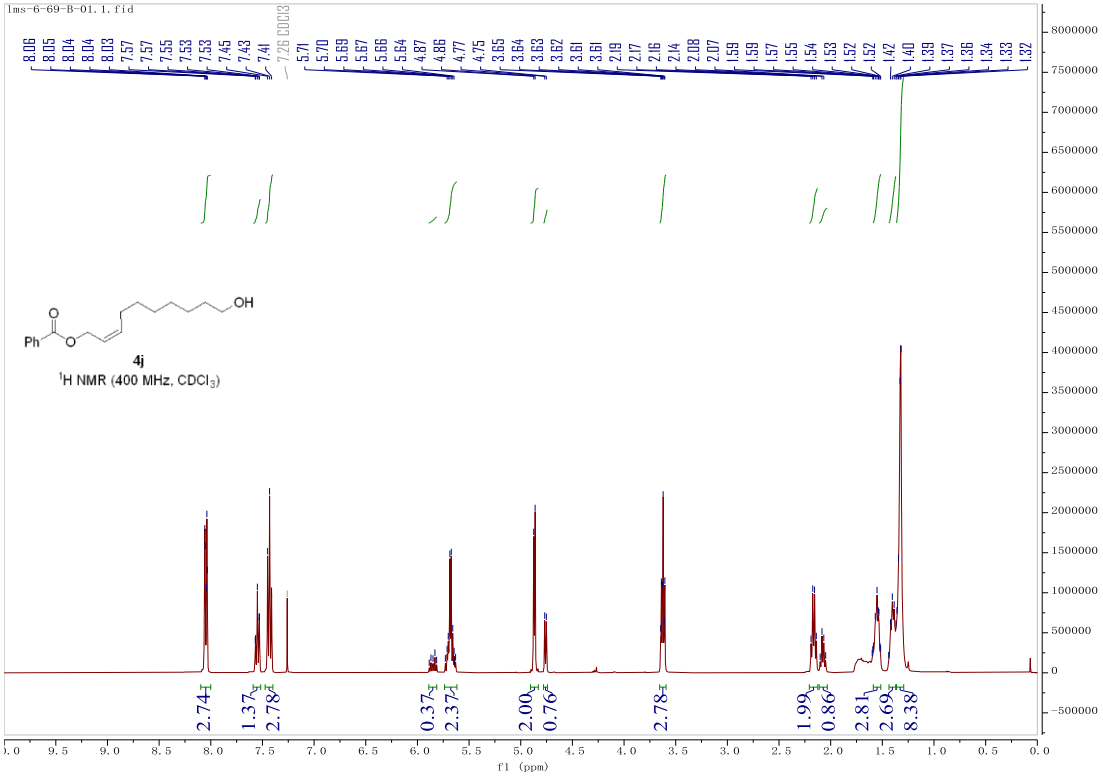

lms-10-05-A-05.11.fid
166.67
139.96
134.63
133.83
133.09
129.78
128.71
128.55
128.50
126.34
124.43
77.16 CDCl3
60.82
34.02
Ph
4g
13C NMR (151 MHz, CDCl3)
f1 (ppm)

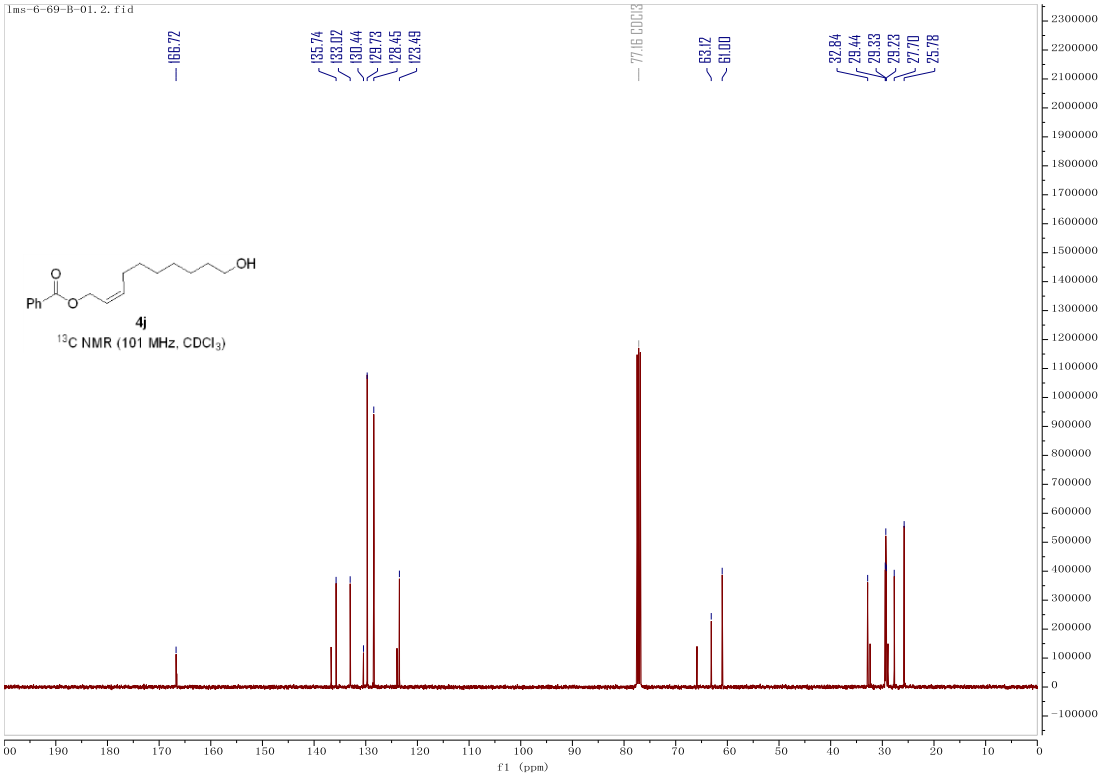

lms-10-08-A-01.1.fid
8.06
8.06
8.06
8.05
8.04
8.04
8.04
7.57
7.56
7.54
7.54
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.26 CDCl3
5.71
5.71
5.70
5.70
5.69
5.69
5.68
4.88
4.86
3.43
3.42
3.40
2.25
2.23
2.23
2.22
2.21
2.20
1.92
1.90
1.89
1.89
1.88
1.88
1.86
1.61
1.59
1.59
1.58
1.58
1.57
1.57
1.55
Br
Ph
4h
1H NMR (400 MHz, CDCl3)
2.30
1.16
2.35
0.19
2.16
2.00
0.35
2.37
2.01
0.38
2.42
2.58
f1 (ppm)

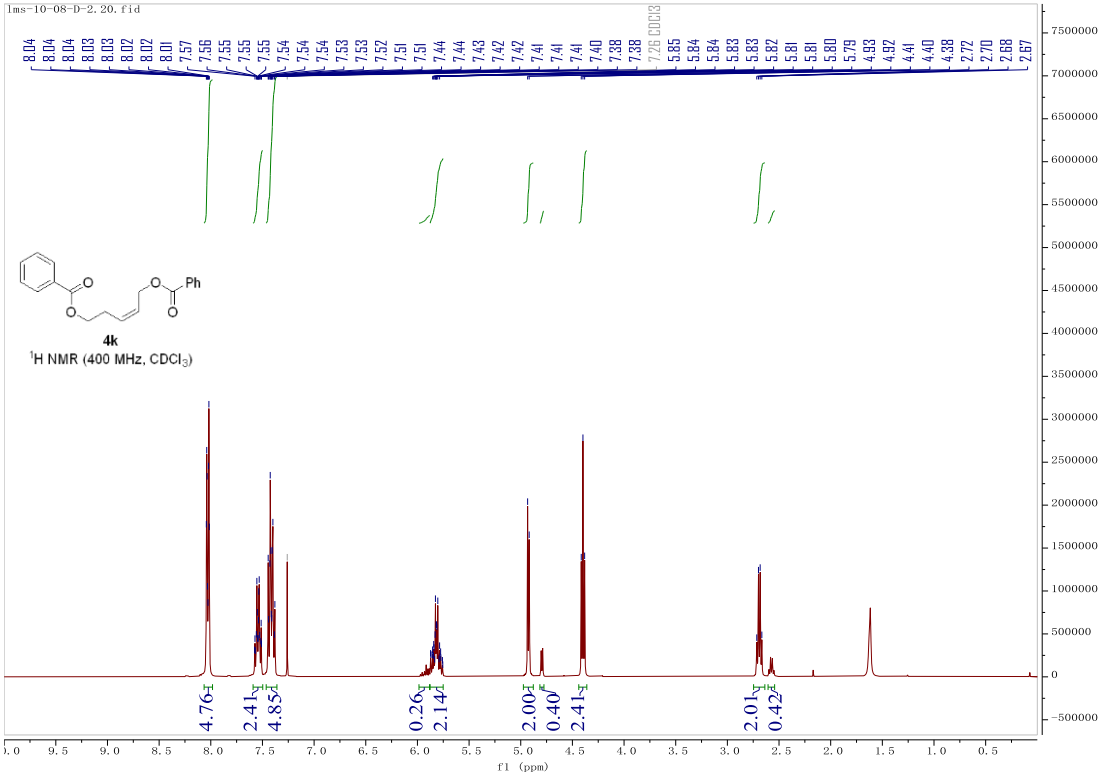

lms-10-08-A-05.24.fid
166.67
134.81
133.08
130.40
129.75
128.49
124.27
77.16 CDCl3
60.82
33.68
32.34
28.05
26.88
Ph
O
O
Br
4h
13C NMR (151 MHz, CDCl3)
f1 (ppm)

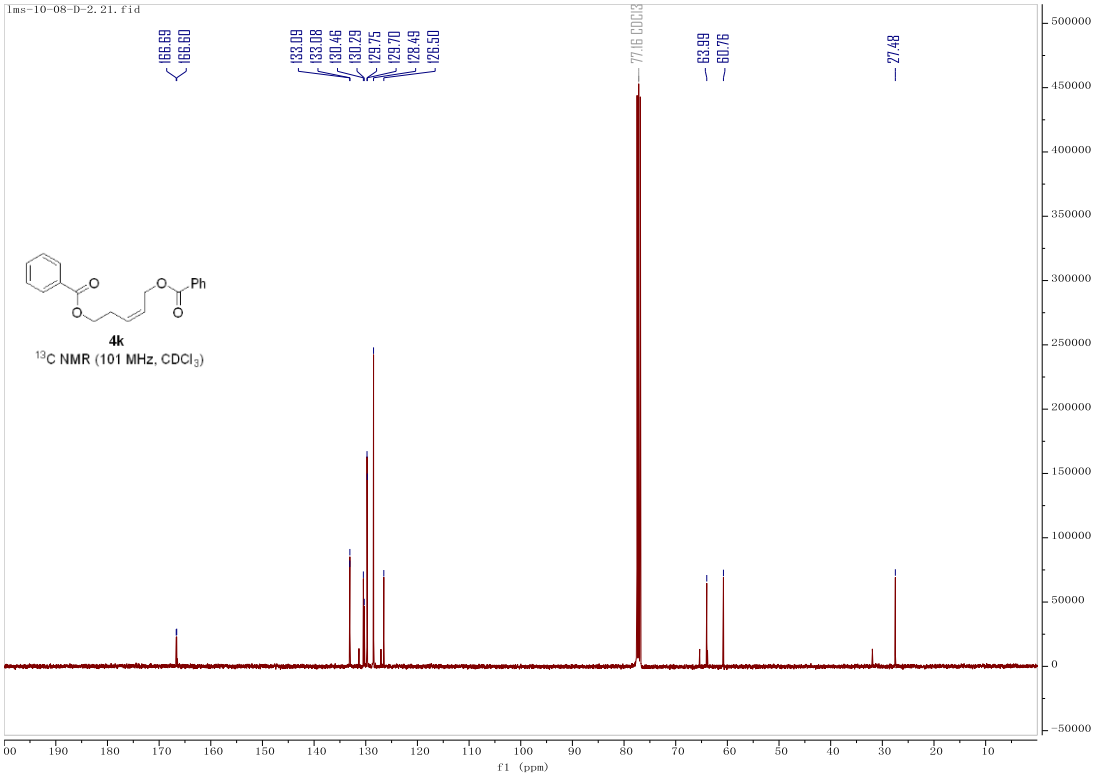

lms-6-51-A-01.10.fid
7.26 CDCl3
Ph
O
O
4i
1H NMR (600 MHz, CDCl3)
2.65
1.35
2.72
1.69
2.30
1.32
1.31
2.00
0.76
1.98
3.58
2.77
f1 (ppm)

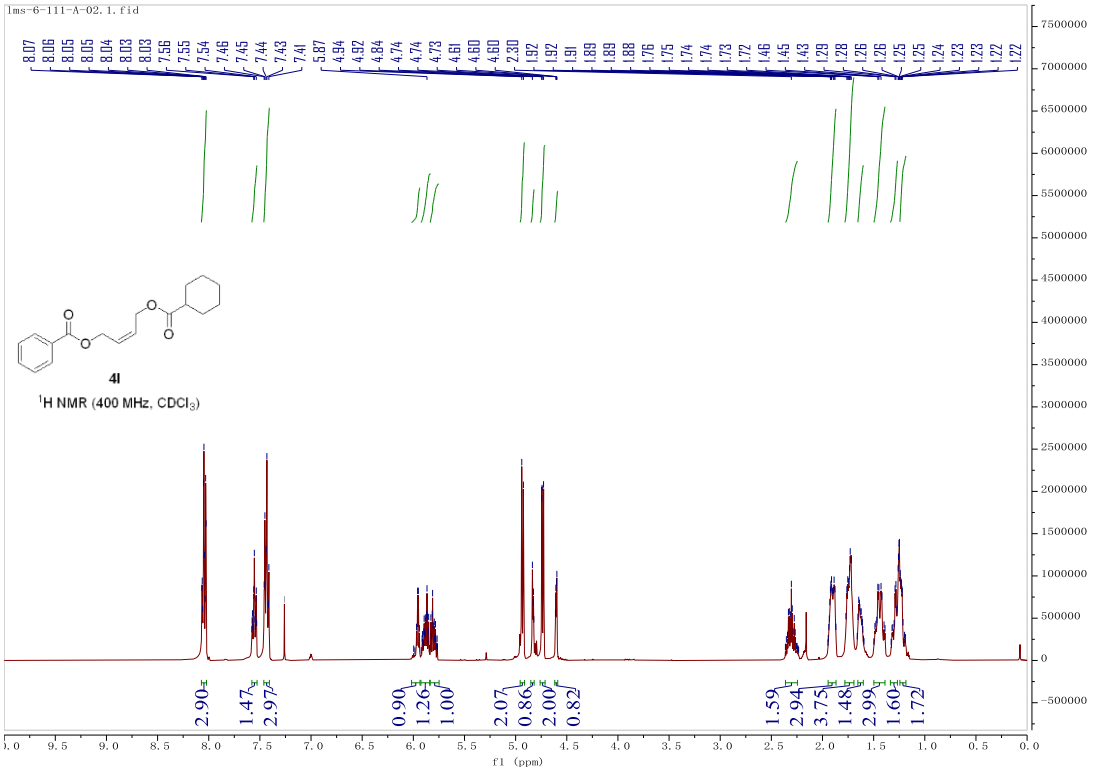

lms-6-51-A-01.11.fid
166.69
138.55
135.29
133.01
132.99
129.74
128.46
123.85
114.95
77.16 CDCl3
61.01
33.33
28.74
27.16
Ph
O
O
4i
13C NMR (151 MHz, CDCl3)
f1 (ppm)

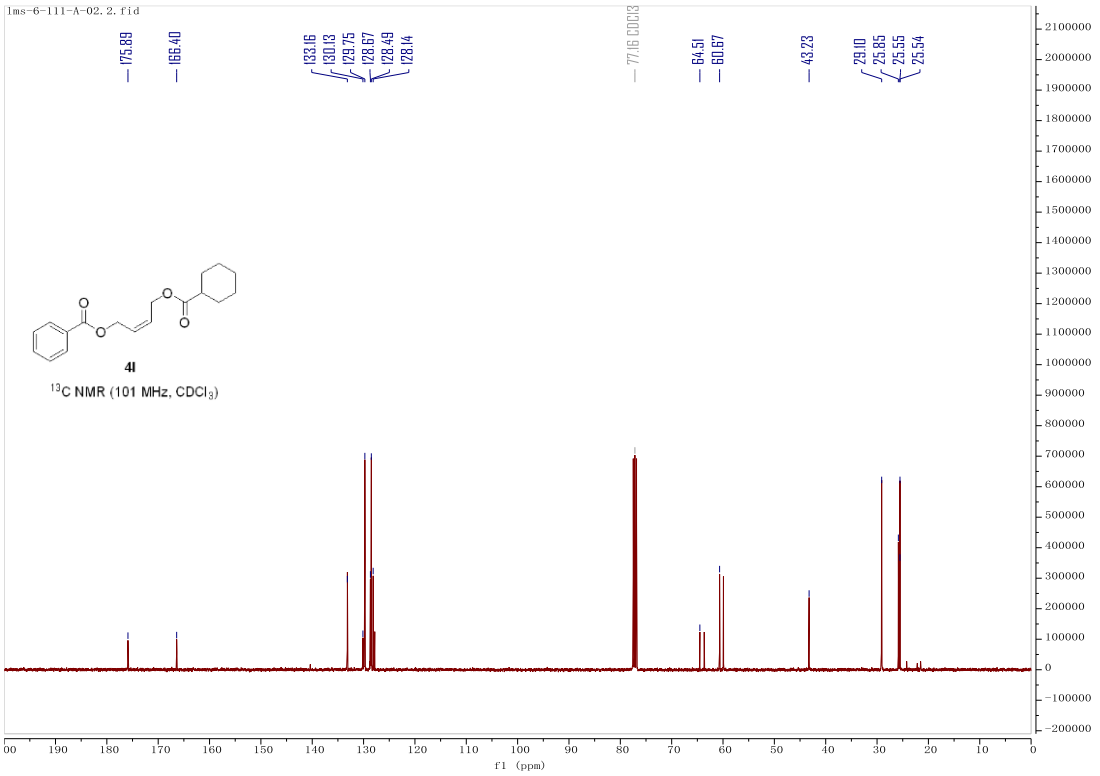

lms-6-69-B-01.1.fid
8.06
8.05
8.04
8.04
8.03
7.57
7.57
7.55
7.53
7.53
7.45
7.43
7.41
7.26 CDCl3
5.71
5.70
5.69
5.67
5.66
5.64
4.87
4.86
4.77
4.75
3.65
3.64
3.63
3.62
3.61
3.61
2.19
2.17
2.16
2.14
2.08
2.07
1.59
1.59
1.57
1.55
1.54
1.53
1.52
1.52
1.42
1.40
1.39
1.37
1.36
1.34
1.33
1.32
OH
Ph
O
O
4j
1H NMR (400 MHz, CDCl3)
2.74
1.37
2.78
0.37
2.37
2.00
0.76
2.78
1.99
0.86
2.81
2.69
8.38
f1 (ppm)

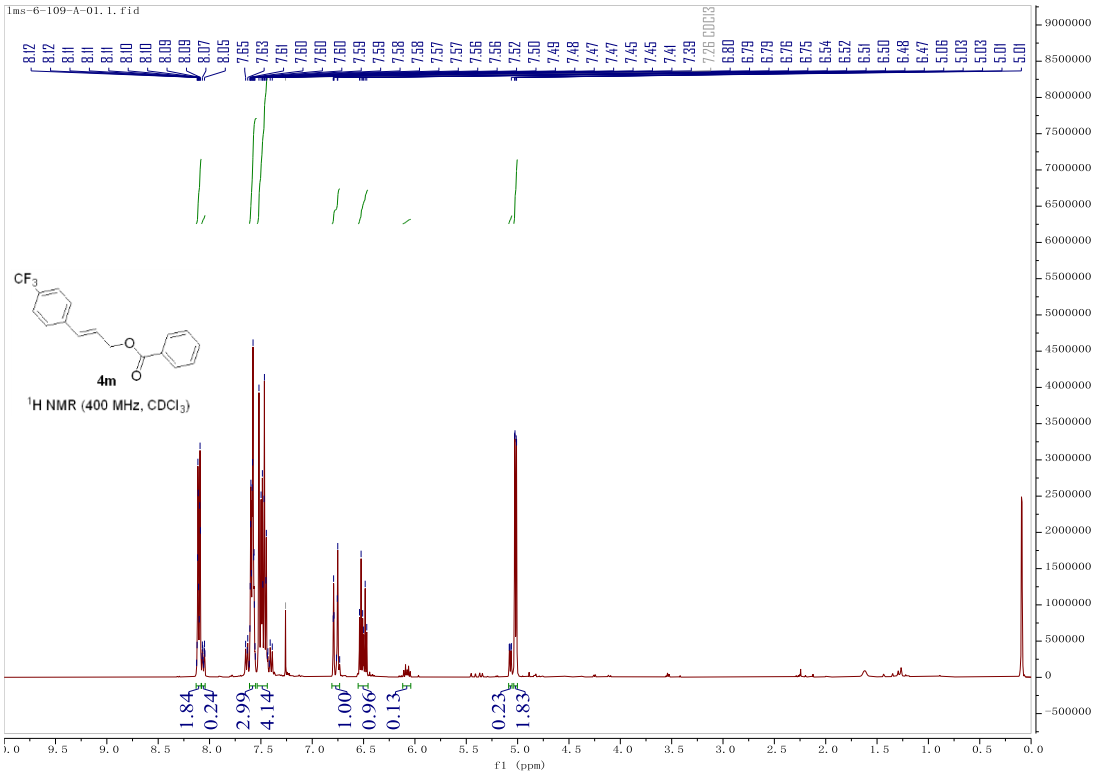

lms-6-69-B-01.2.fid
166.72
135.74
133.02
130.44
129.73
128.45
123.49
77.16 CDCl3
63.12
61.00
32.84
29.44
29.33
29.23
27.70
25.78
OH
Ph
O
O
4j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

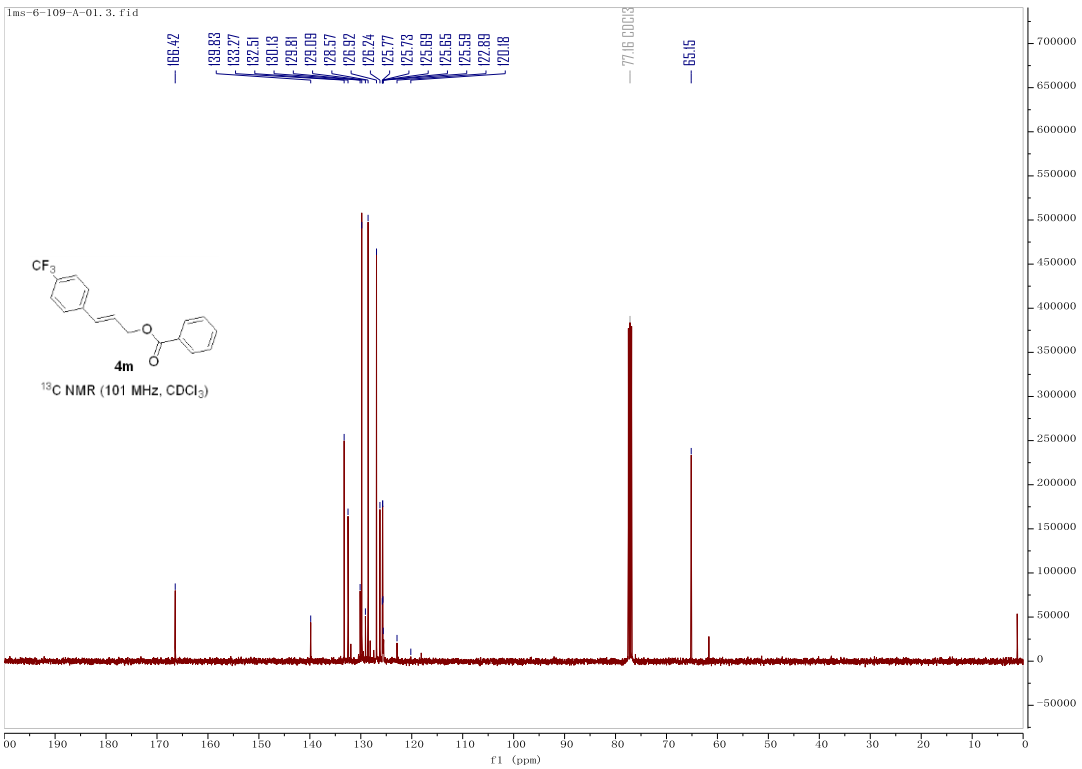

lms-10-08-D-2.20.fid
7.26 CDCl3
Ph
O
O
4k
1H NMR (400 MHz, CDCl3)
4.76
2.41
4.85
0.26
2.14
2.00
0.40
2.41
2.01
0.42
f1 (ppm)

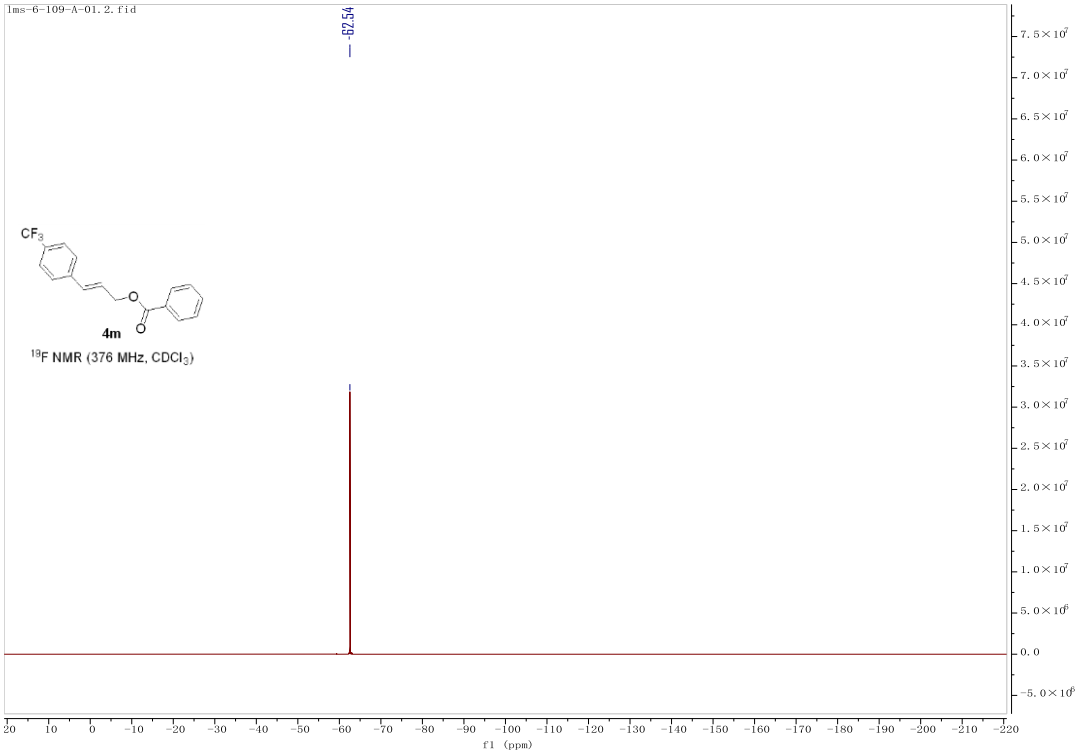

lms-10-08-D-2.21.fid
166.69
166.60
133.09
133.08
130.46
130.29
129.75
129.70
128.49
126.50
77.16 CDCl3
63.99
60.76
27.48
Ph
4k
13C NMR (101 MHz, CDCl3)
f1 (ppm)

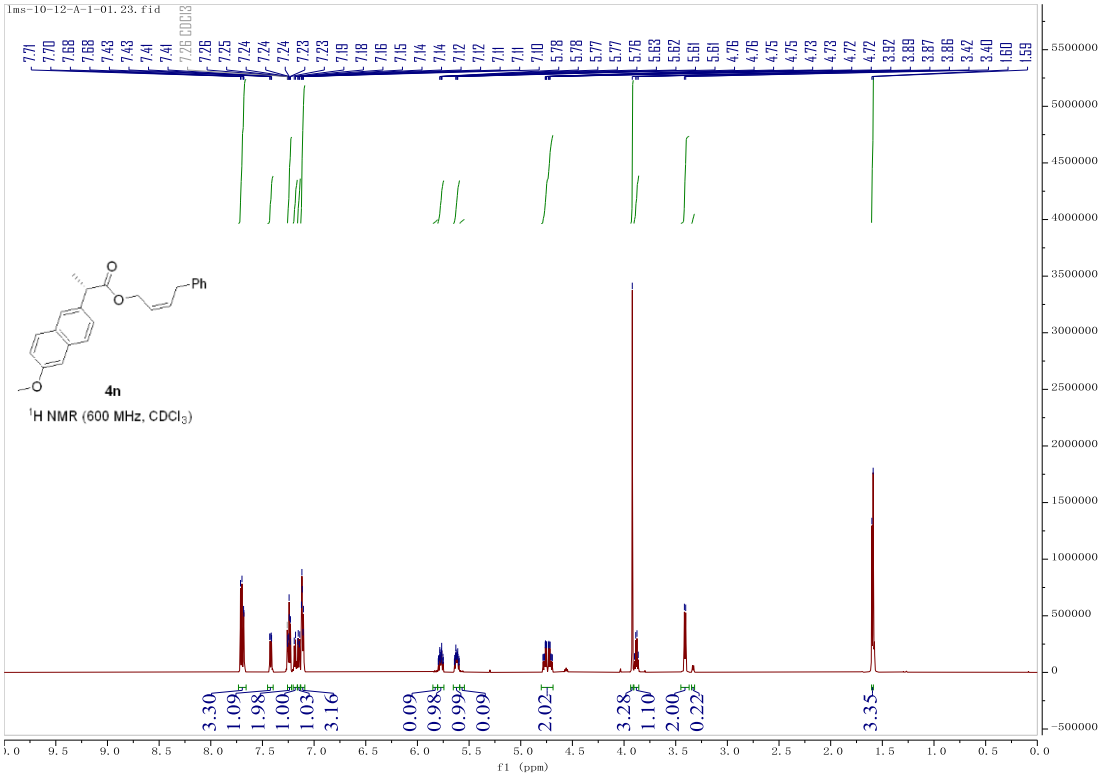

lms-6-111-A-02.1.fid
8.07
8.06
8.05
8.05
8.04
8.03
8.03
7.56
7.55
7.54
7.46
7.45
7.44
7.43
7.41
5.87
4.94
4.92
4.84
4.74
4.74
4.73
4.61
4.60
4.60
2.30
1.92
1.92
1.91
1.89
1.89
1.88
1.76
1.75
1.74
1.74
1.73
1.72
1.46
1.45
1.43
1.29
1.28
1.26
1.26
1.25
1.25
1.24
1.23
1.23
1.22
1.22
4l
1H NMR (400 MHz, CDCl3)
2.90
1.47
2.97
0.90
1.26
1.00
2.07
0.86
2.00
0.82
1.59
2.94
3.75
1.48
2.99
1.60
1.72
f1 (ppm)

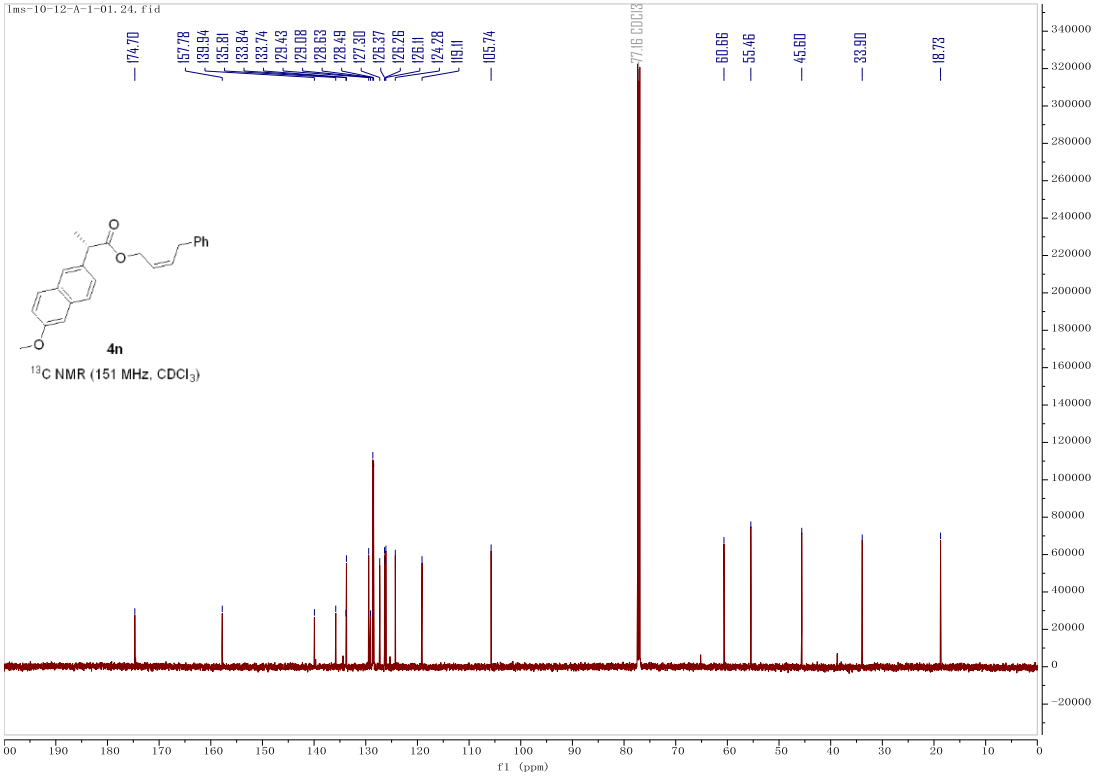

lms-6-111-A-02.2.fid
175.89
166.40
133.16
130.13
129.75
128.67
128.49
128.14
77.16 CDCl3
64.51
60.67
43.23
29.10
25.85
25.55
25.54
4l
13C NMR (101 MHz, CDCl3)
f1 (ppm)

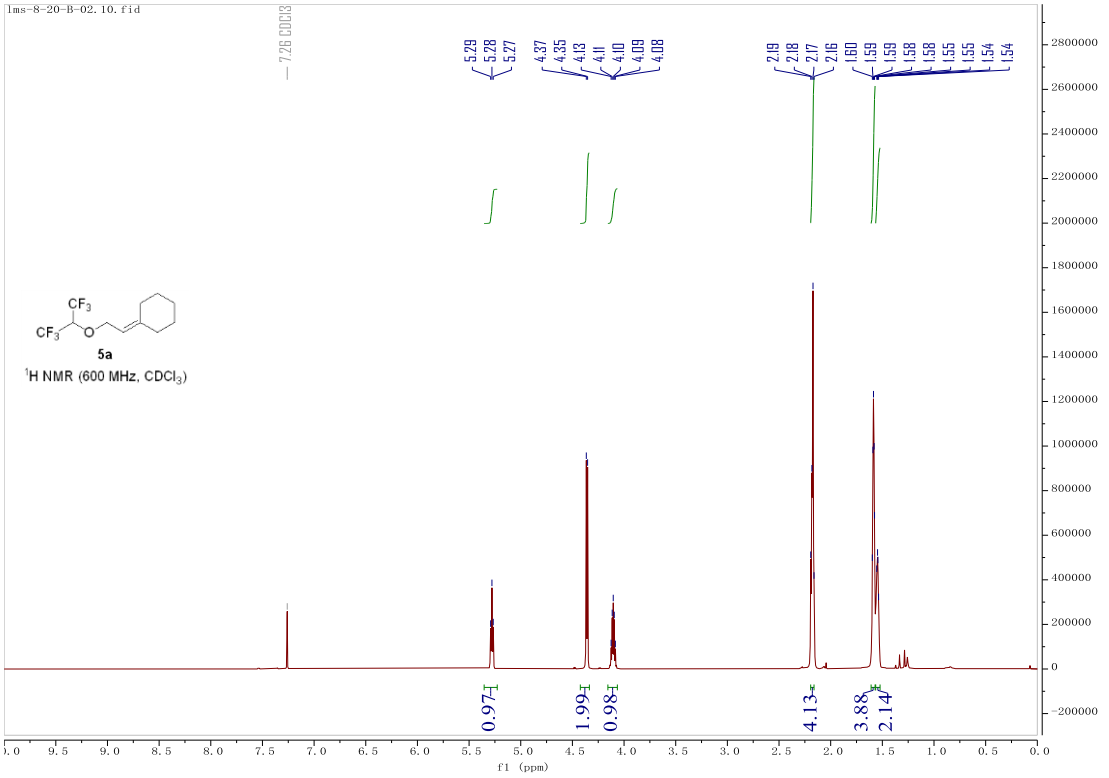

lms-6-109-A-01.1.fid
7.26 CDCl3
CF3
4m
1H NMR (400 MHz, CDCl3)
1.84
0.24
2.99
4.14
1.00
0.96
0.13
0.23
1.83
f1 (ppm)

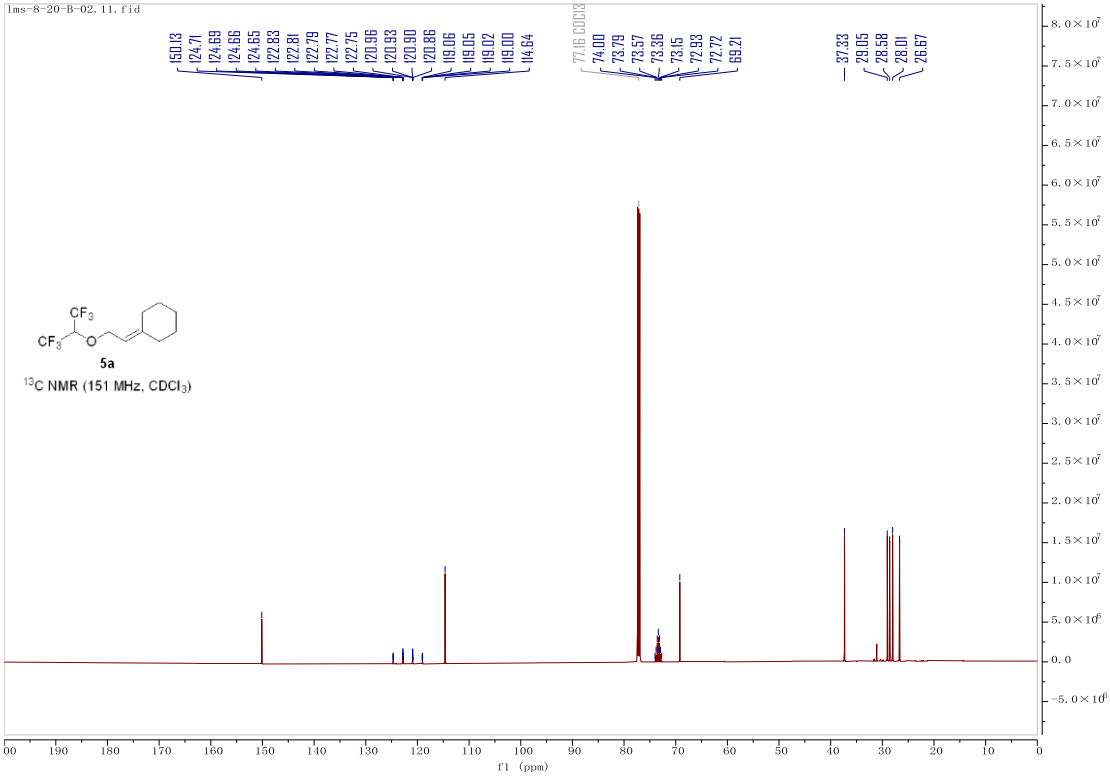

lms-6-109-A-01.3.fid
166.42
139.83
133.27
132.51
130.13
129.81
129.09
128.57
126.92
126.24
125.77
125.73
125.69
125.65
125.53
122.89
120.18
77.16 CDCl3
65.15
CF3
O
O
4m
13C NMR (101 MHz, CDCl3)
f1 (ppm)

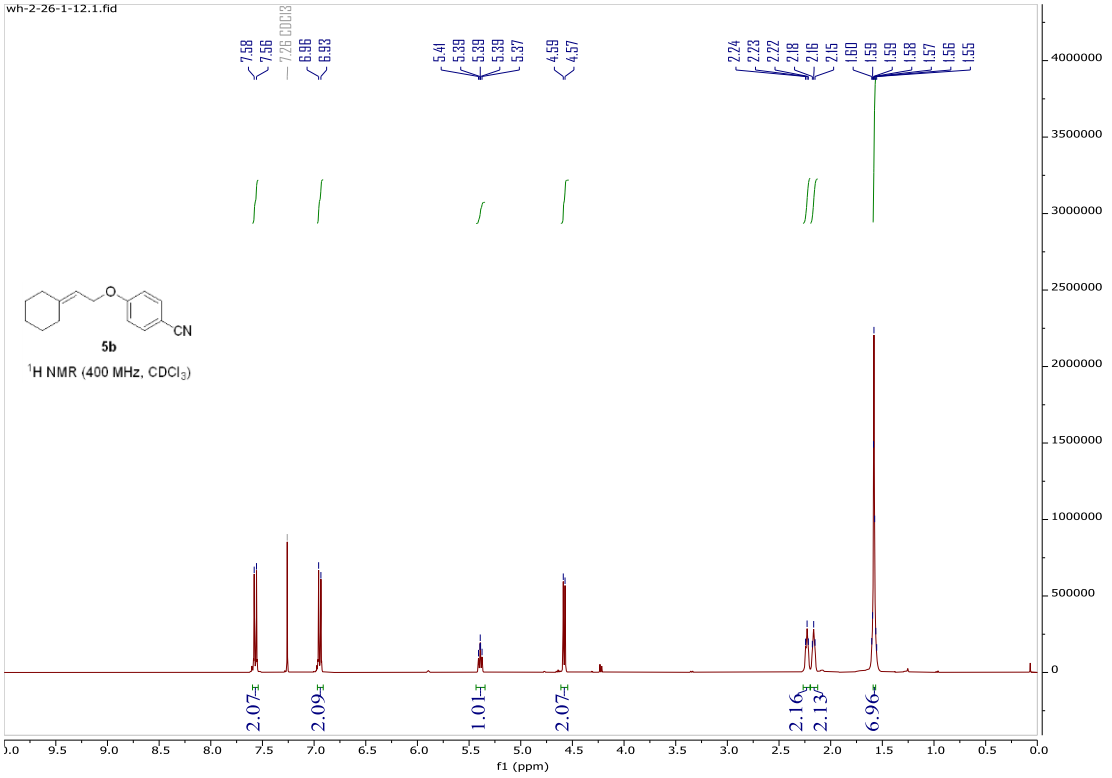

lms-6-109-A-01.2.fid
-62.54
CF3
O
O
4m
19F NMR (376 MHz, CDCl3)
f1 (ppm)

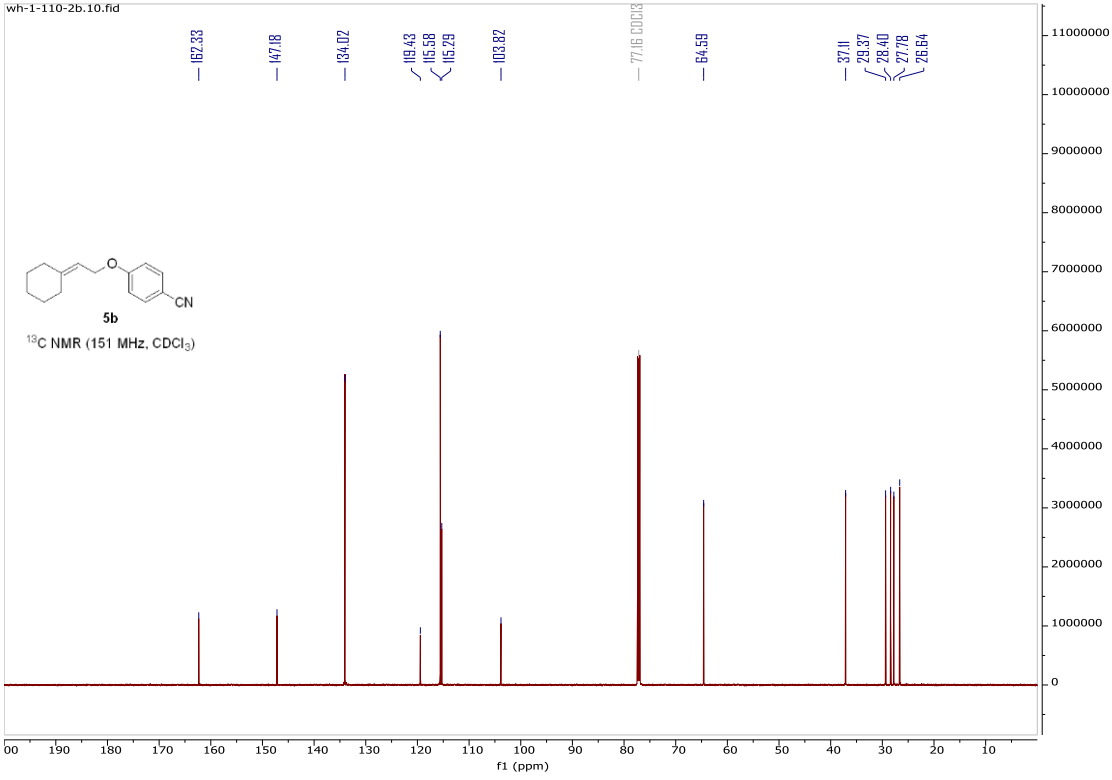

lms-10-12-A-1-01.23.fid
Ph
4n
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

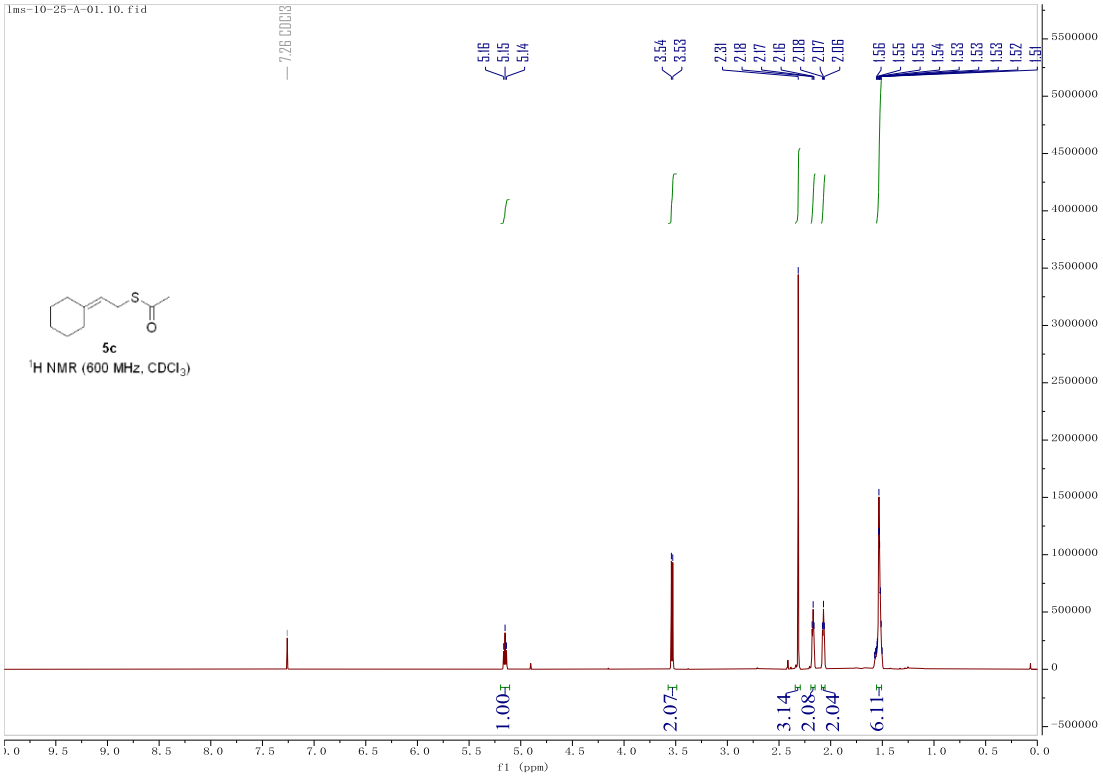

lms-10-12-A-1-01.24.fid
Ph
4n
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)


lms-8-20-B-02.10.fid
7.26 CDCl3
5.29
5.28
5.27
4.37
4.35
4.13
4.11
4.10
4.09
4.08
2.19
2.18
2.17
2.16
1.60
1.59
1.59
1.58
1.58
1.55
1.55
1.54
1.54
CF3
CF3
O
5a
1H NMR (600 MHz, CDCl3)
0.97
1.99
0.98
4.13
3.88
2.14
f1 (ppm)


lms-8-20-B-02.11.fid
150.13
124.71
124.69
124.66
124.65
122.83
122.81
122.79
122.77
122.75
120.96
120.93
120.90
120.86
119.06
119.05
119.02
119.00
114.64
77.16 CDCl3
74.00
73.79
73.57
73.38
73.15
72.93
72.72
69.21
37.33
29.05
28.58
28.01
26.67
CF3
CF3
O
5a
13C NMR (151 MHz, CDCl3)
f1 (ppm)

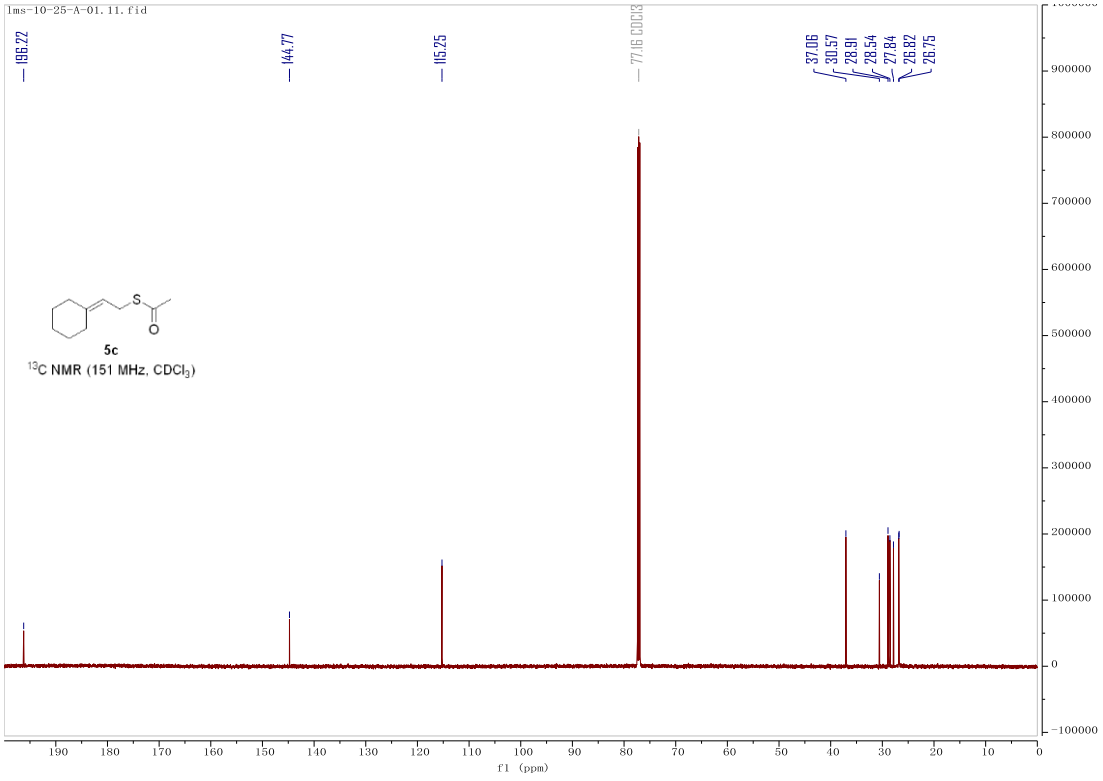

wh-2-26-1-12.1.fid
7.58
7.56
7.26 CDCl3
6.96
6.93
5.41
5.39
5.39
5.39
5.37
4.59
4.57
2.24
2.23
2.22
2.18
2.16
2.15
1.60
1.59
1.59
1.58
1.57
1.56
1.55
O
CN
5b
1H NMR (400 MHz, CDCl3)
2.07
2.09
1.01
2.07
2.16
2.13
6.96
f1 (ppm)


wh-1-110-2b.10.fid
162.33
147.18
134.02
119.43
115.58
115.29
103.82
77.16 CDCl3
64.59
37.11
29.37
28.40
27.78
26.64
O
CN
5b
13C NMR (151 MHz, CDCl3)
f1 (ppm)



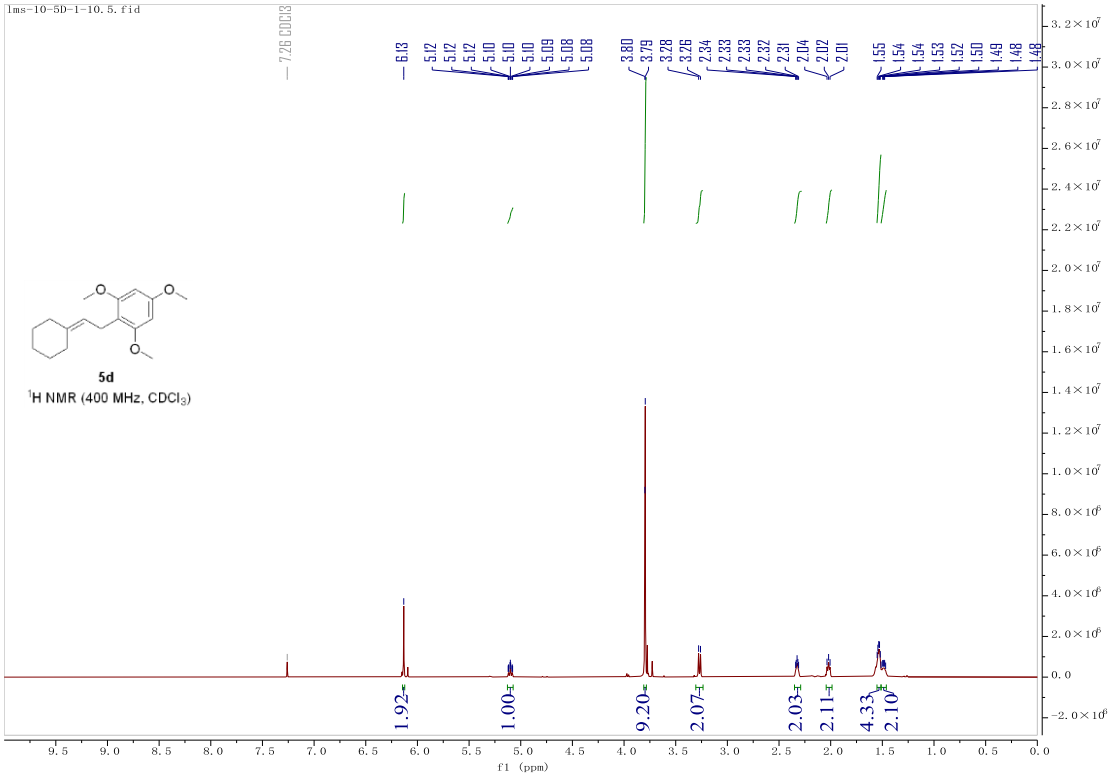
5c

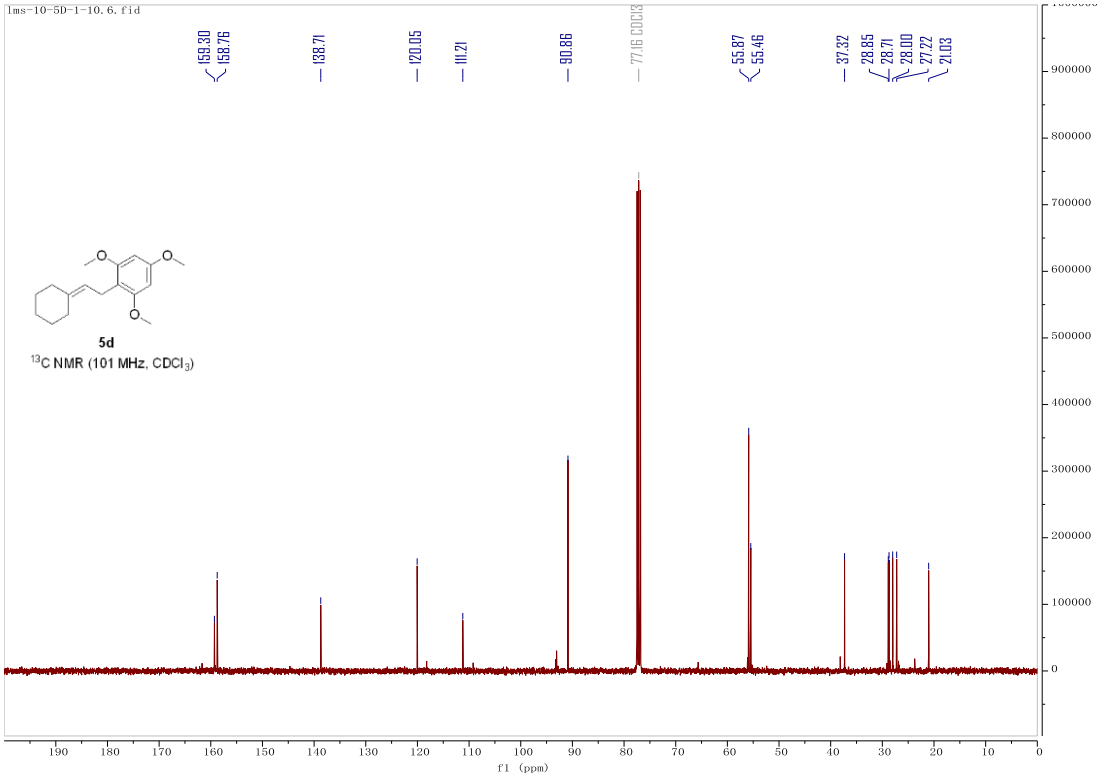
^{1}H NMR (600 MHz, $CDCl_3$)

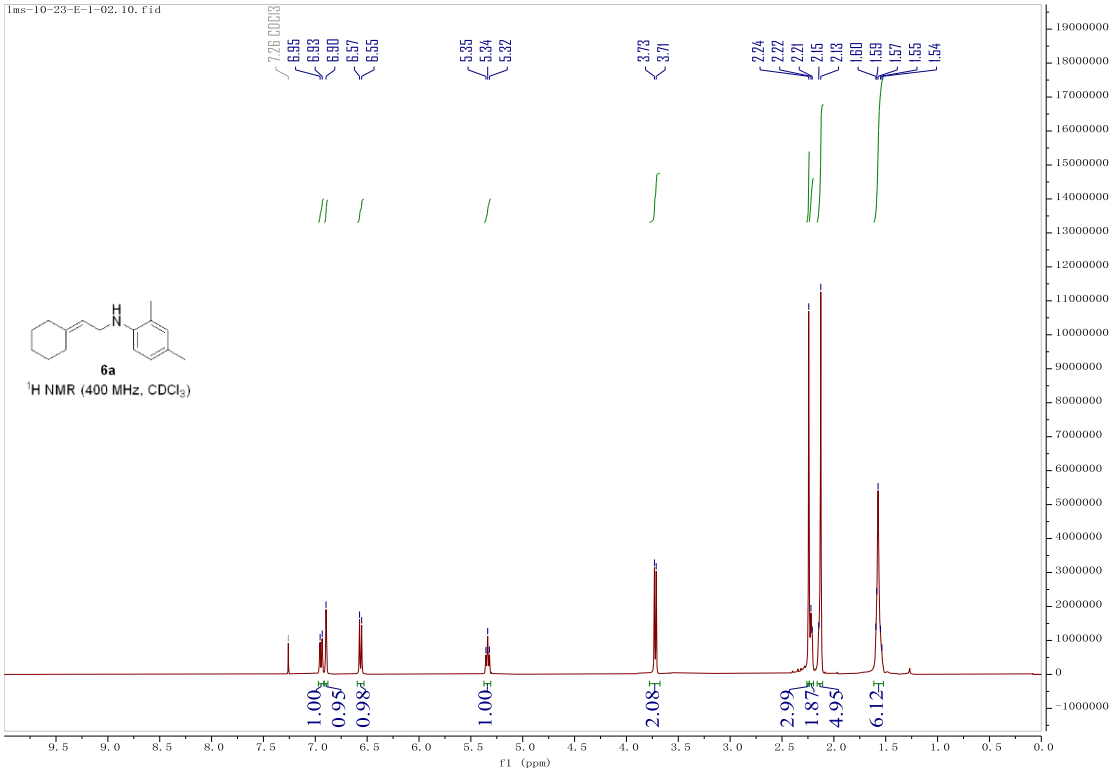


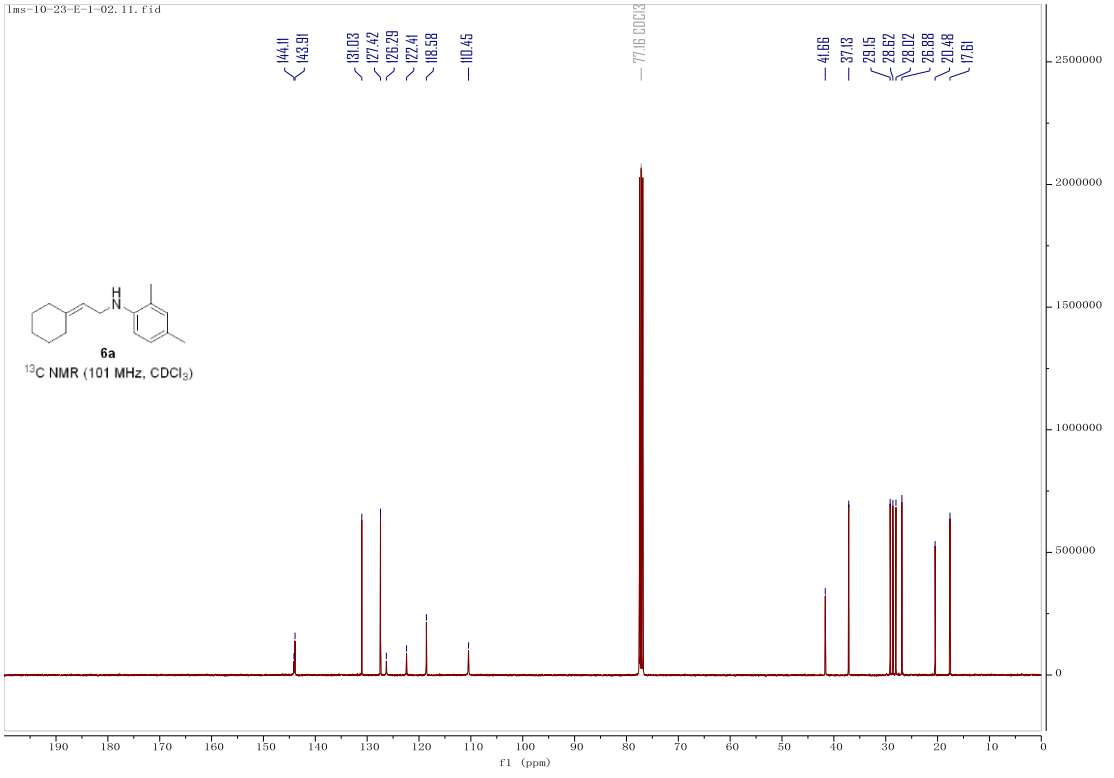
5c

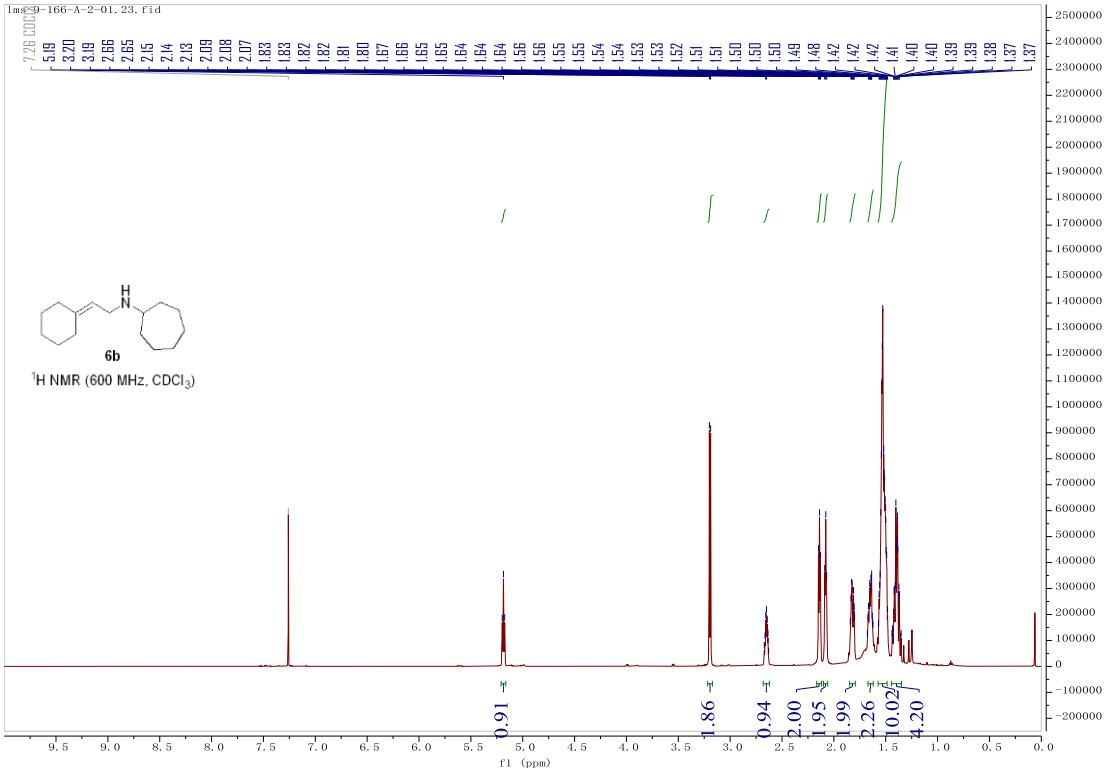
^{13}C NMR (151 MHz, $CDCl_3$)

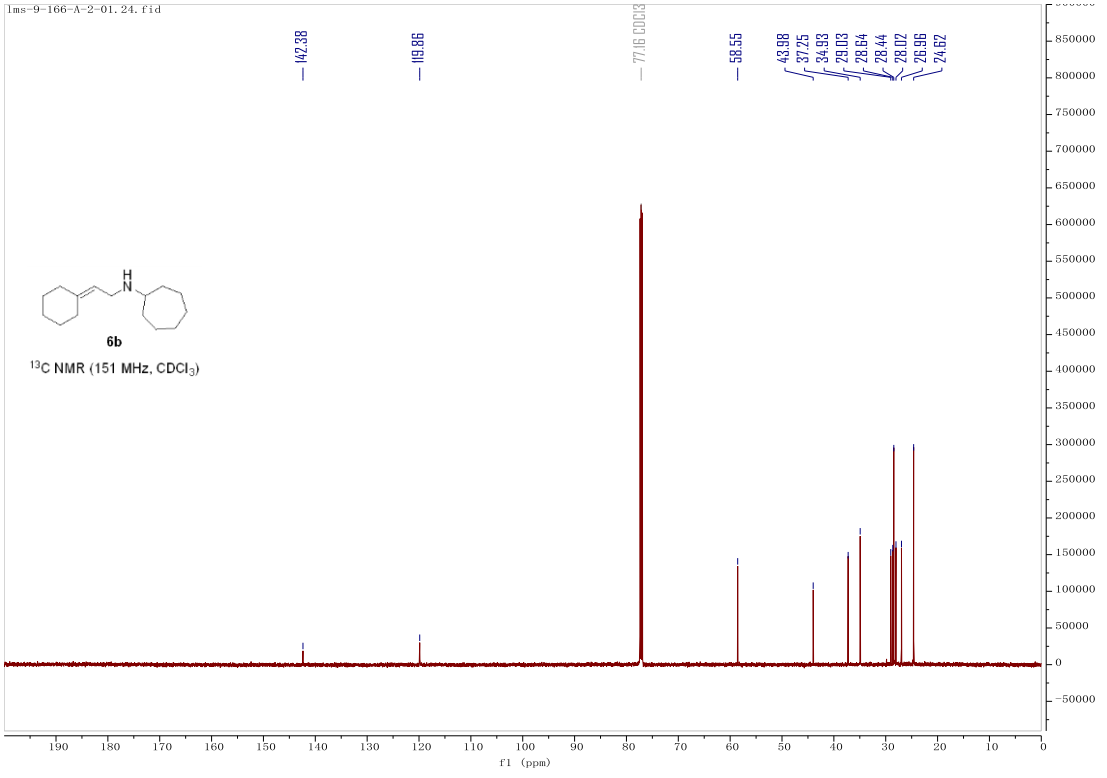

lms-10-5D-1-10.5.fid
5d
1H NMR (400 MHz, CDCl3)
1.92
1.00
9.20
2.07
2.03
2.11
4.33
2.10
f1 (ppm)

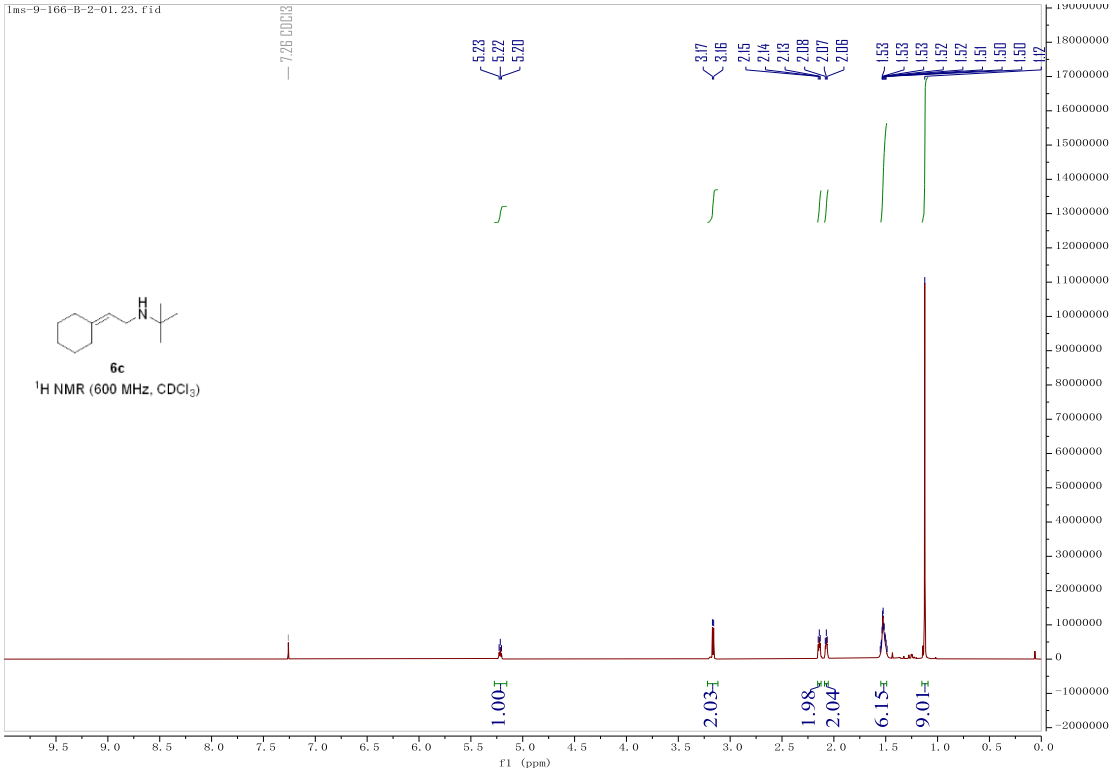

lms-10-5D-1-10.6.fid
159.30
158.76
138.71
120.05
111.21
90.86
77.16 CDCl3
55.87
55.46
37.32
28.85
28.71
28.00
27.22
21.03
5d
13C NMR (101 MHz, CDCl3)
f1 (ppm)

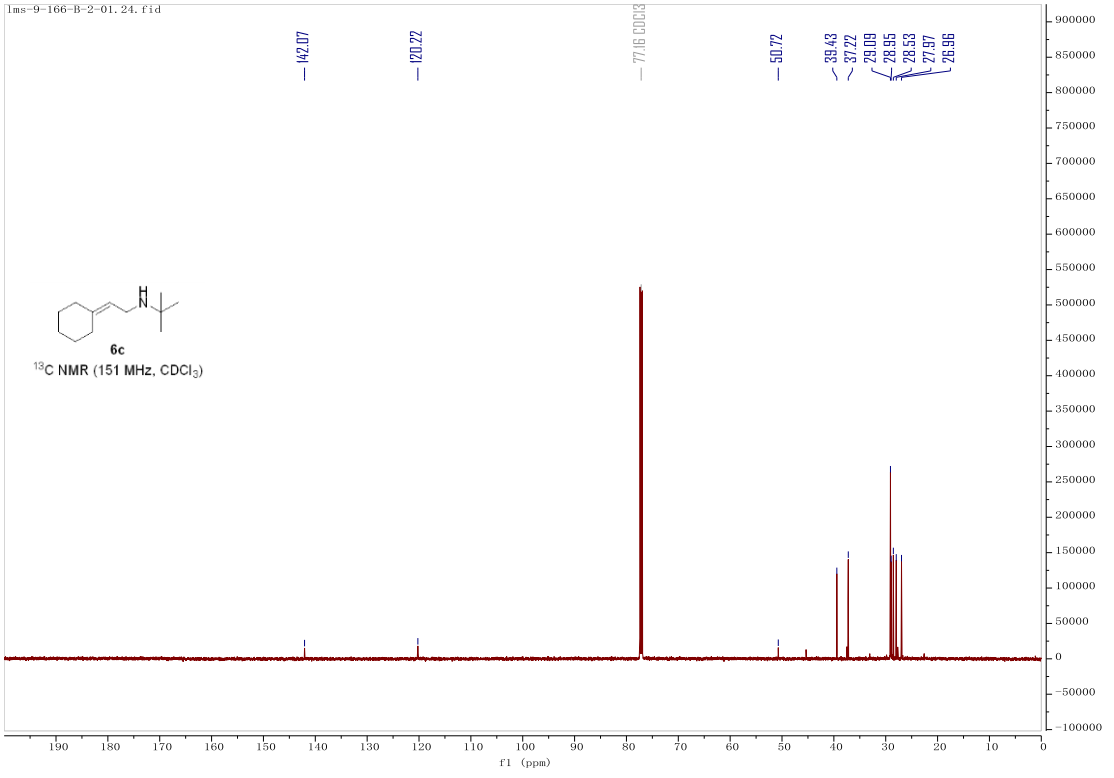

lms-10-23-E-1-02.10.fid
7.26 CDCl3
6.95
6.93
6.90
6.57
6.55
5.35
5.34
5.32
3.73
3.71
2.24
2.22
2.21
2.15
2.13
1.60
1.59
1.57
1.55
1.54
1.00
0.93
0.98
1.00
2.08
2.99
1.87
4.95
6.12
f1 (ppm)
6a
1H NMR (400 MHz, CDCl3)

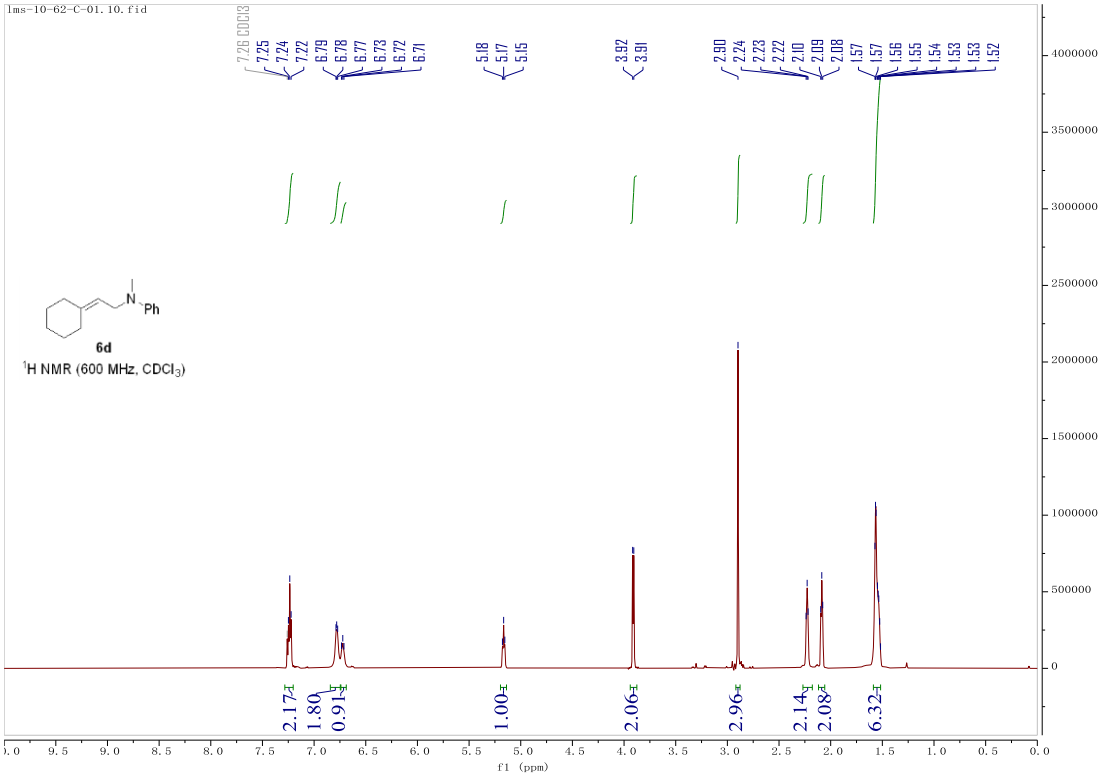

lms-10-23-E-1-02.11.fid
144.11
143.91
131.03
127.42
126.29
122.41
118.58
110.45
77.16 CDCl3
41.66
37.13
29.15
28.62
28.02
26.88
20.48
17.61
f1 (ppm)
6a
13C NMR (101 MHz, CDCl3)

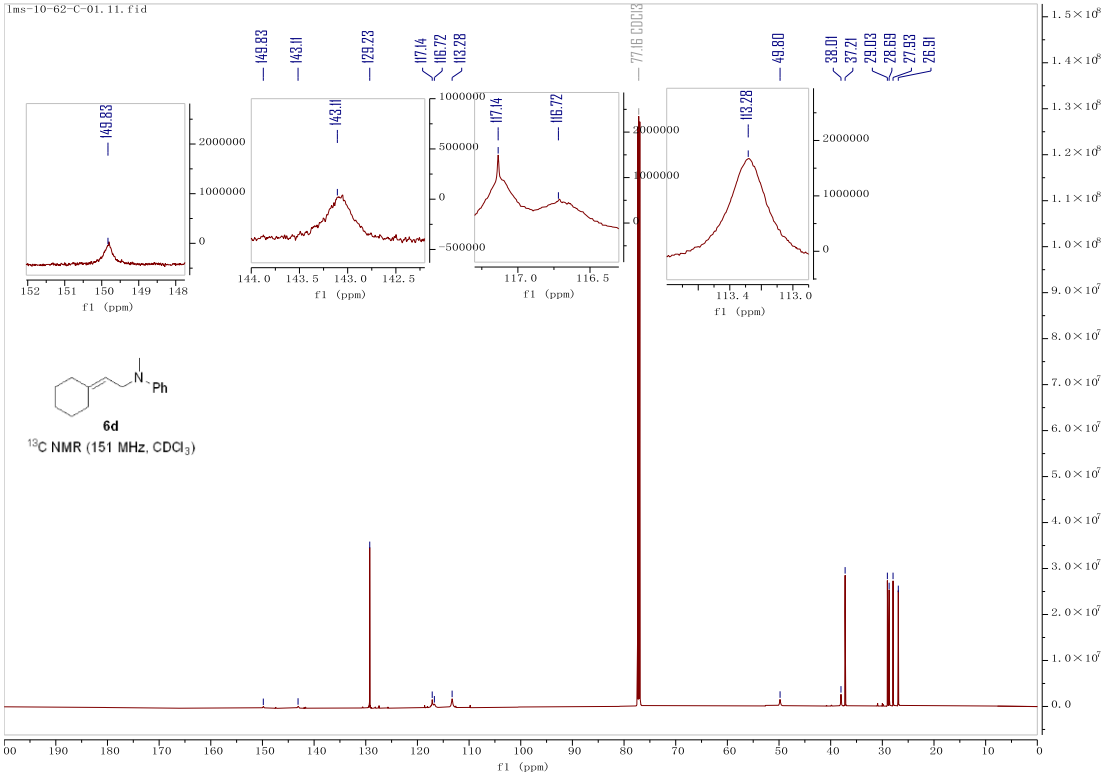

lms-9-166-A-2-01.23.fid
6b
1H NMR (600 MHz, CDCl3)
0.91
1.86
0.94
2.00
1.95
1.99
2.26
10.02
4.20
f1 (ppm)

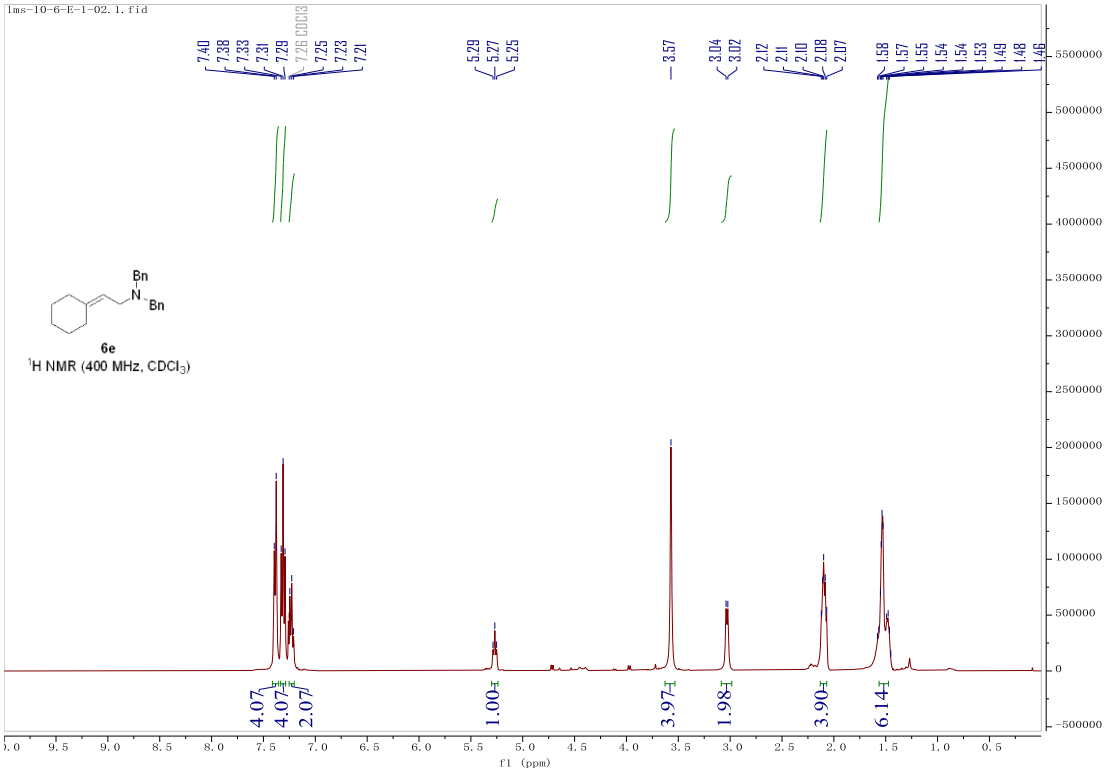

lms-9-166-A-2-01.24.fid
142.38
119.86
77.16 CDCl3
58.55
43.98
37.25
34.93
29.03
28.64
28.44
28.02
26.96
24.62
6b
13C NMR (151 MHz, CDCl3)
f1 (ppm)

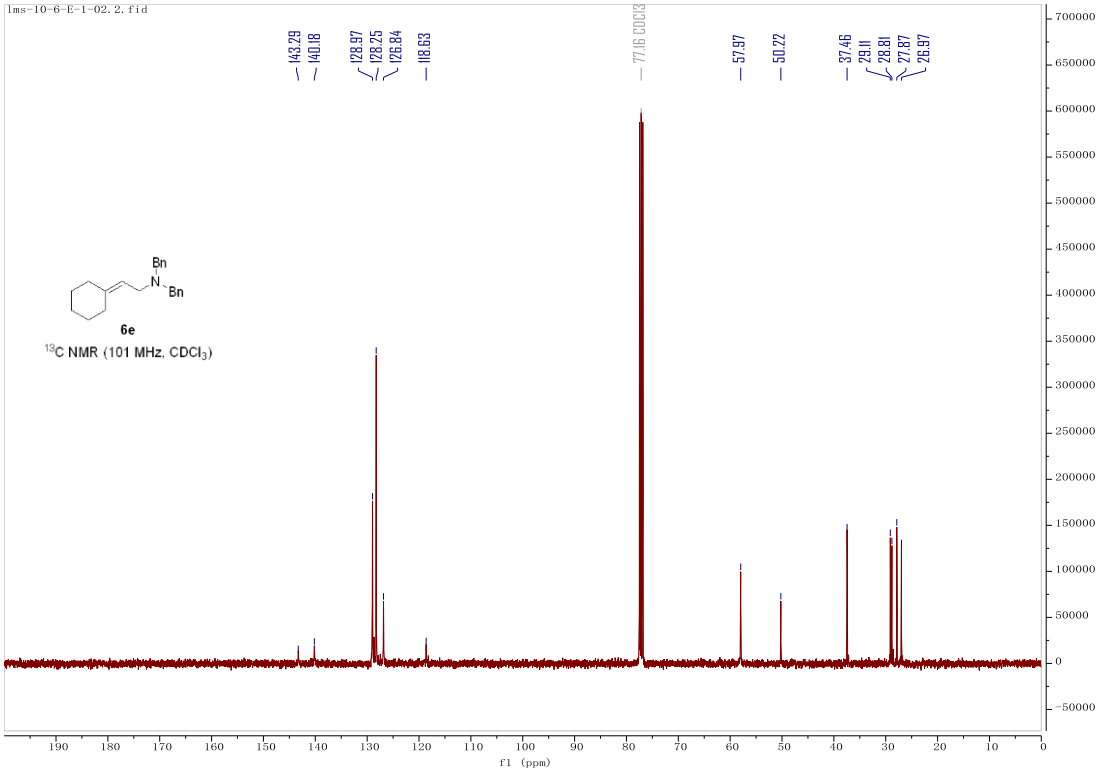

lms-9-166-B-2-01.23.fid
7.26 CDCl3
5.23
5.22
5.20
3.17
3.16
2.15
2.14
2.13
2.08
2.07
2.06
1.53
1.53
1.53
1.52
1.52
1.51
1.50
1.50
1.12
1.00
2.03
1.98
2.04
6.15
9.01
f1 (ppm)
6c
1H NMR (600 MHz, CDCl3)

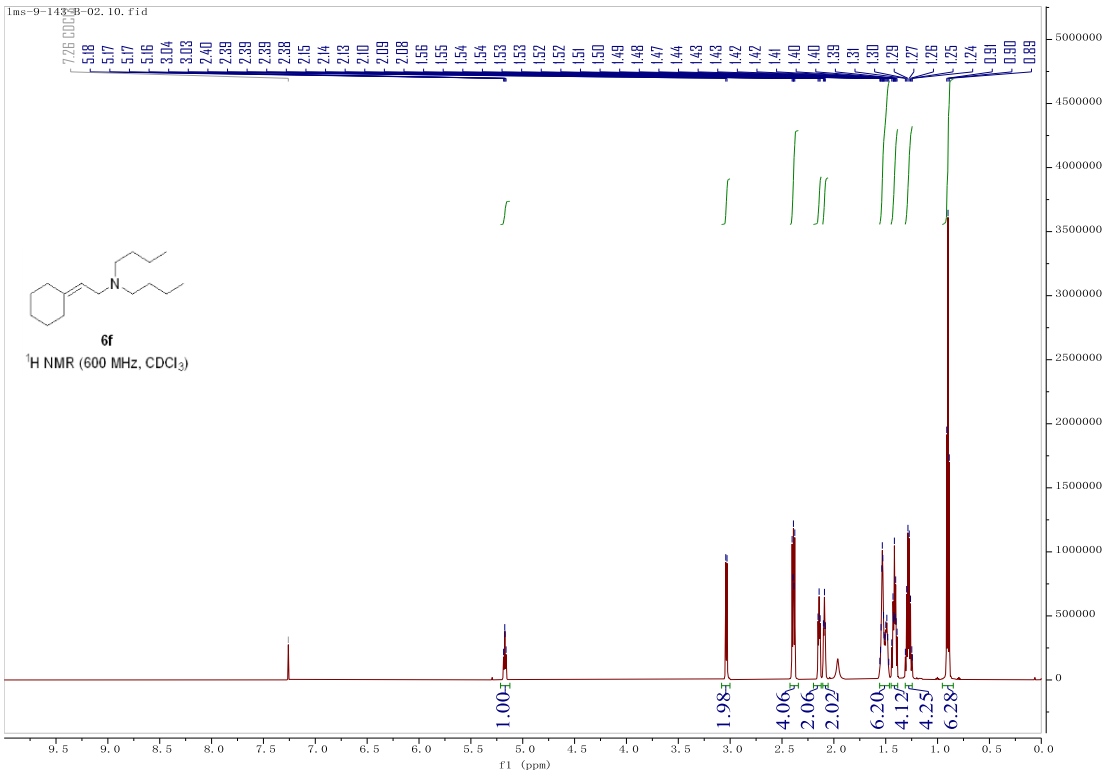

lms-9-166-B-2-01.24.fid
142.07
120.22
77.16 CDCl3
50.72
39.43
37.22
29.09
28.95
28.53
27.97
26.96
f1 (ppm)
6c
13C NMR (151 MHz, CDCl3)

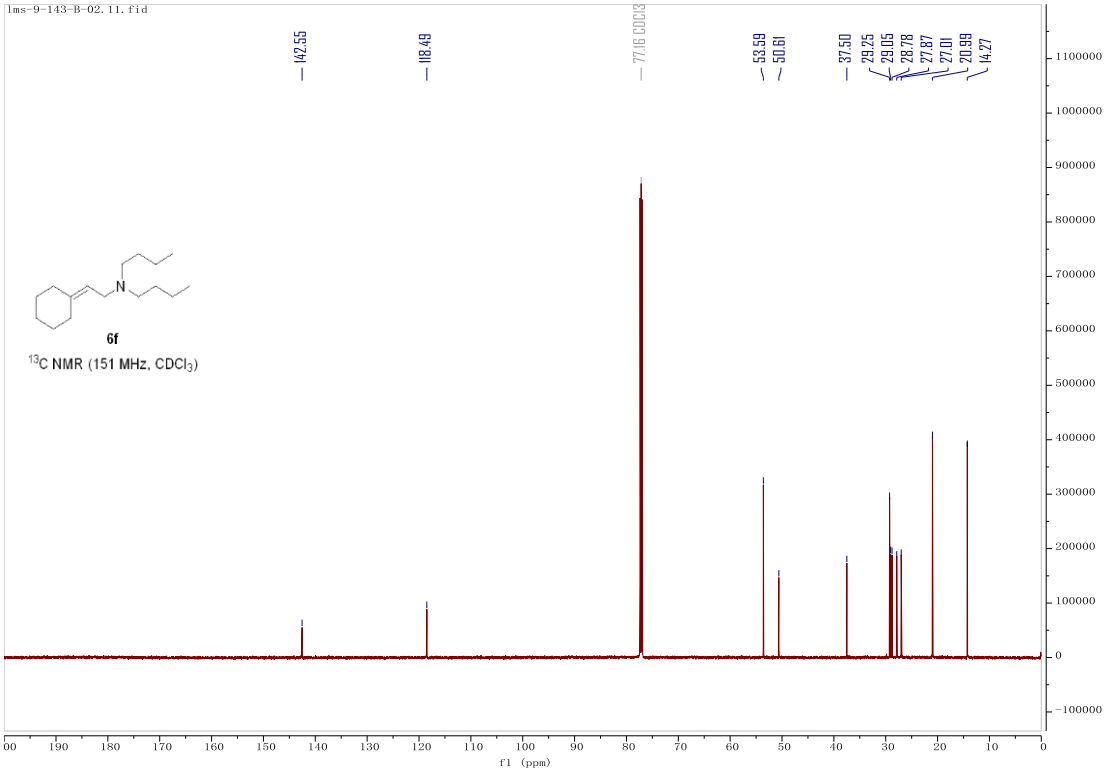

lms-10-62-C-01.10.fid
7.26 CDCl3
7.25
7.24
7.22
6.79
6.78
6.77
6.73
6.72
6.71
5.18
5.17
5.15
3.92
3.91
2.90
2.24
2.23
2.22
2.10
2.09
2.08
1.57
1.57
1.56
1.55
1.54
1.53
1.52
N
Ph
6d
1H NMR (600 MHz, CDCl3)
2.17
1.80
0.91
1.00
2.06
2.96
2.14
2.08
6.32
f1 (ppm)

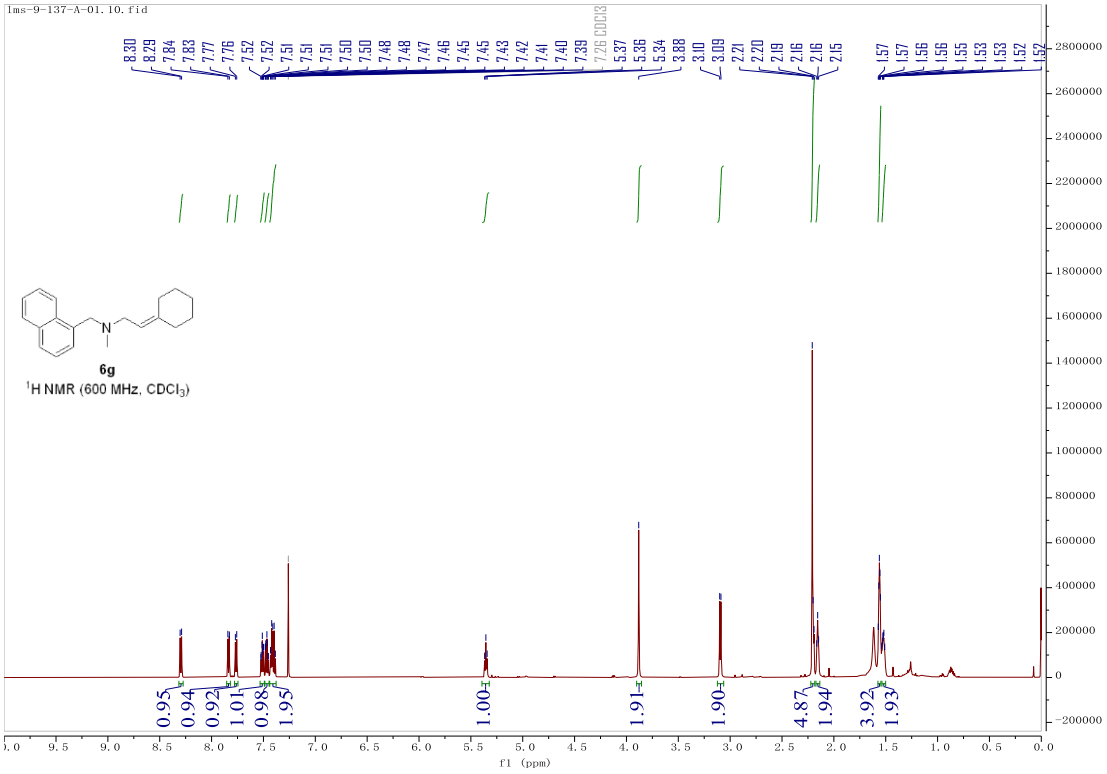

lms-10-62-C-01.11.fid
149.83
143.11
129.23
117.14
116.72
113.28
77.16 CDCl3
49.80
38.01
37.21
29.03
28.69
27.93
26.91
N
Ph
6d
13C NMR (151 MHz, CDCl3)
f1 (ppm)

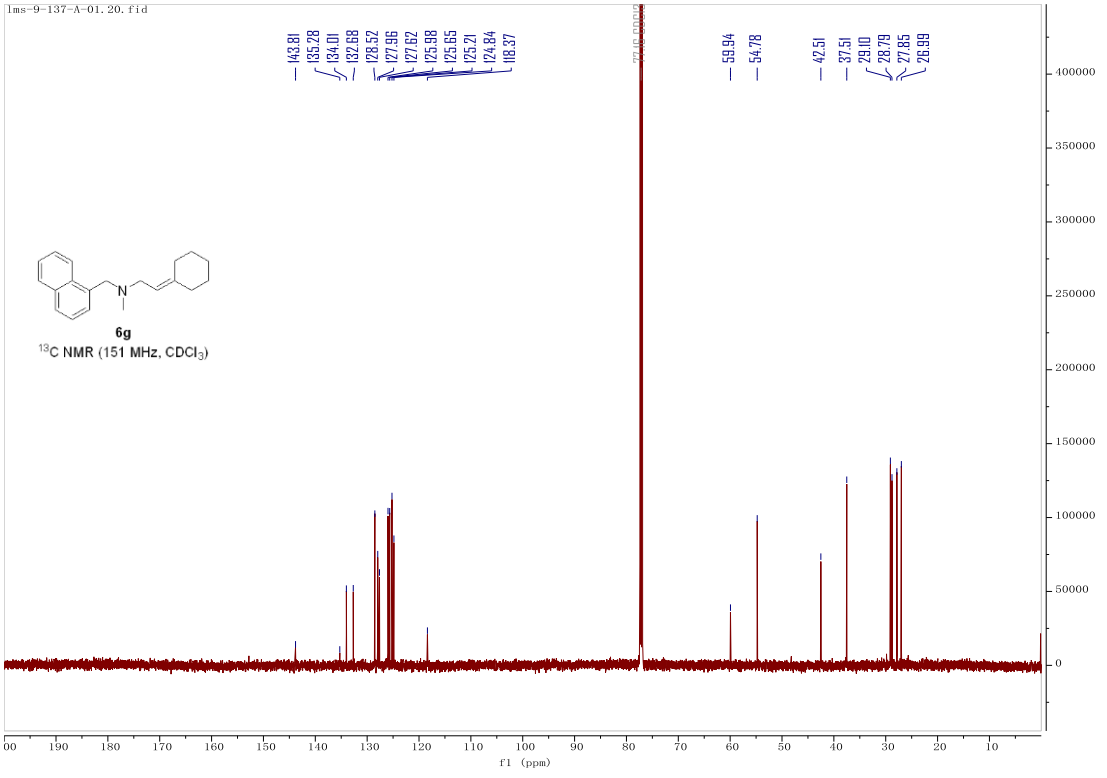

lms-10-6-E-1-02.1.fid
7.40
7.38
7.33
7.31
7.29
7.26 CDCl3
7.25
7.23
7.21
5.29
5.27
5.25
3.57
3.04
3.02
2.12
2.11
2.10
2.08
2.07
1.58
1.57
1.55
1.54
1.54
1.53
1.49
1.48
1.46
Bn
N
Bn
6e
1H NMR (400 MHz, CDCl3)
4.07
4.07
2.07
1.00
3.97
1.98
3.90
6.14
f1 (ppm)

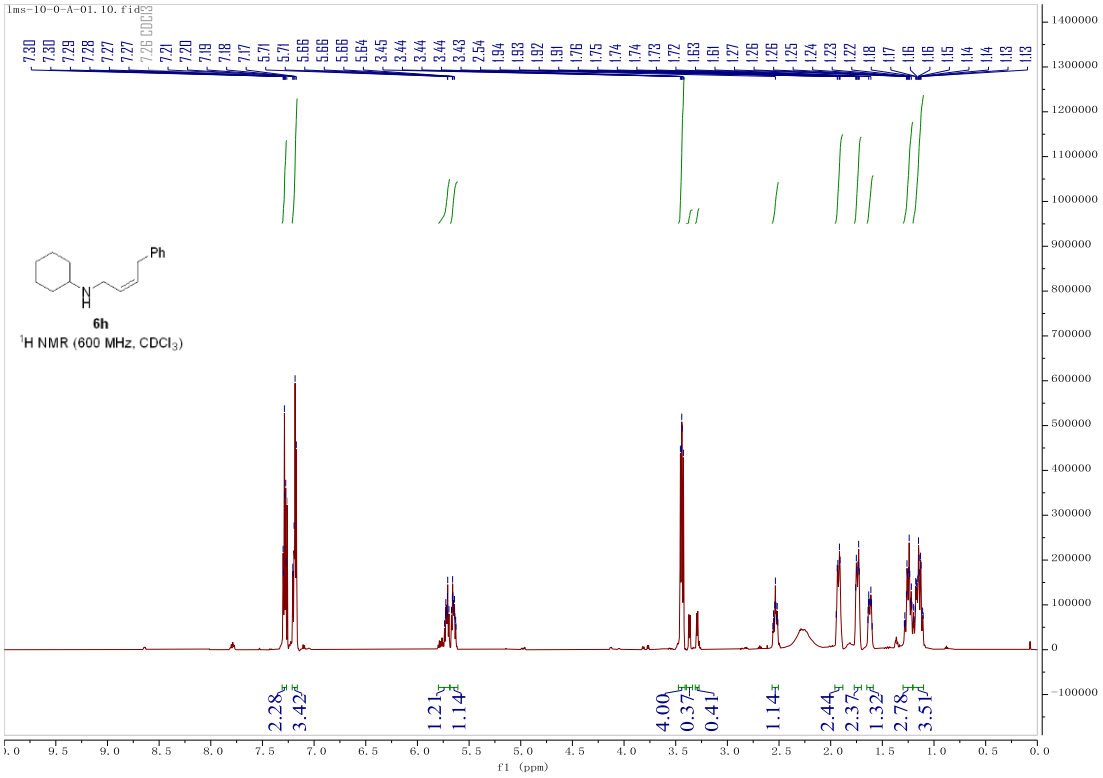

lms-10-6-E-1-02.2.fid
143.29
140.18
128.97
128.25
126.84
118.63
77.16 CDCl3
57.97
50.22
37.46
29.11
28.81
27.87
26.97
Bn
N
Bn
6e
13C NMR (101 MHz, CDCl3)
f1 (ppm)

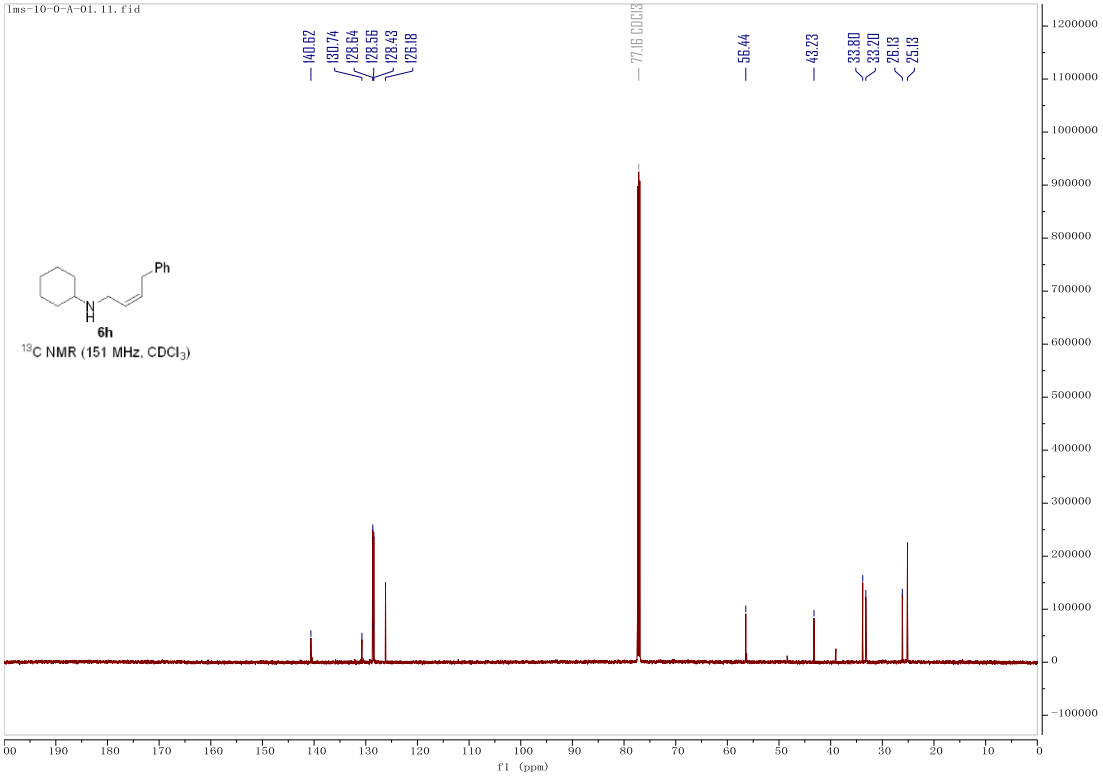

lms-9-143-B-02.10.fid
6f
1H NMR (600 MHz, CDCl3)
f1 (ppm)

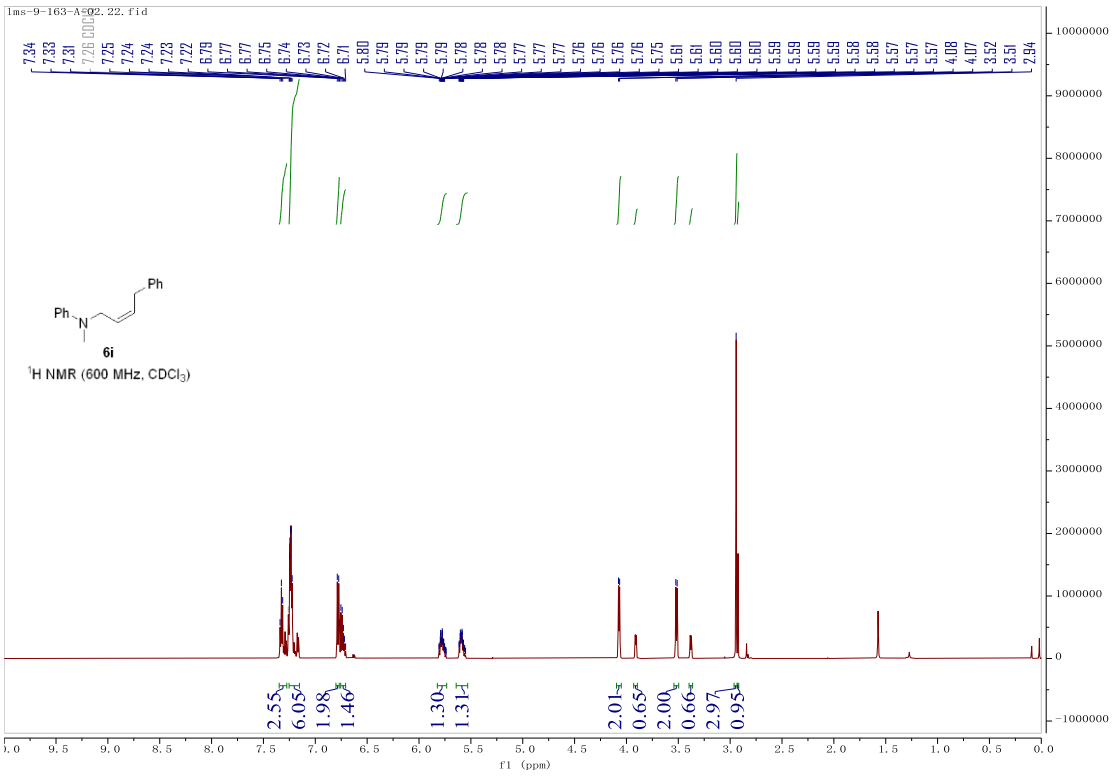

lms-9-143-B-02.11.fid
6f
13C NMR (151 MHz, CDCl3)
f1 (ppm)

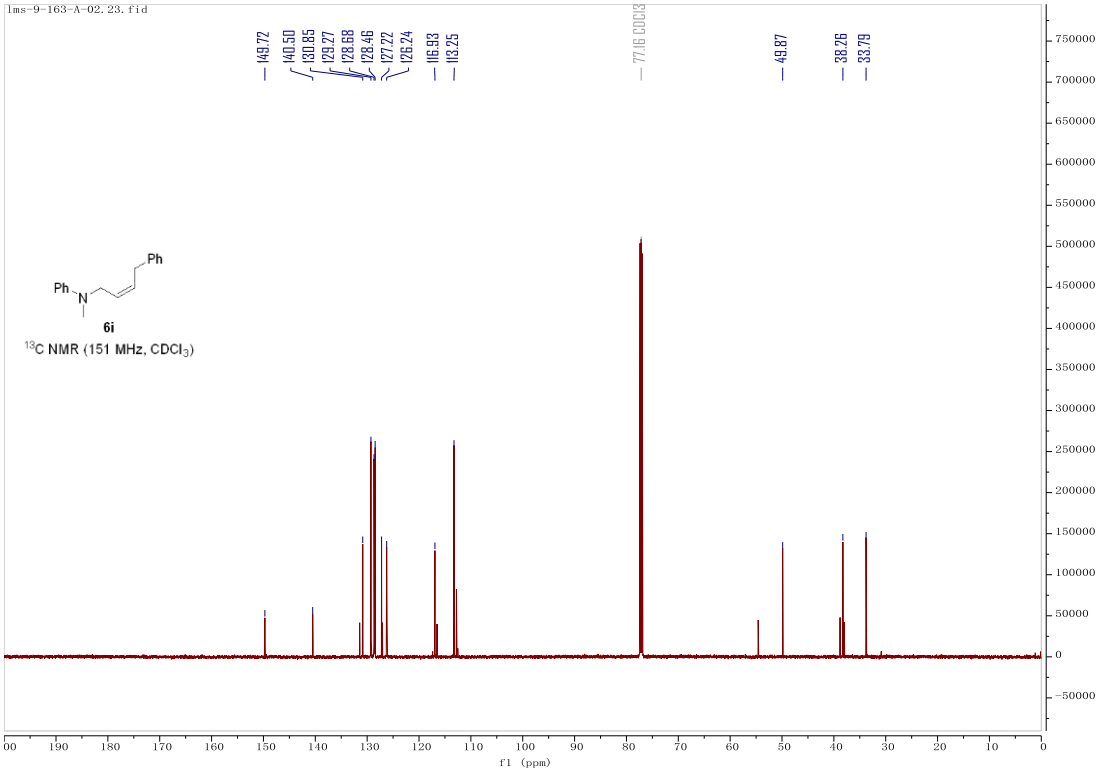

lms-9-137-A-01.10.fid
6g
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

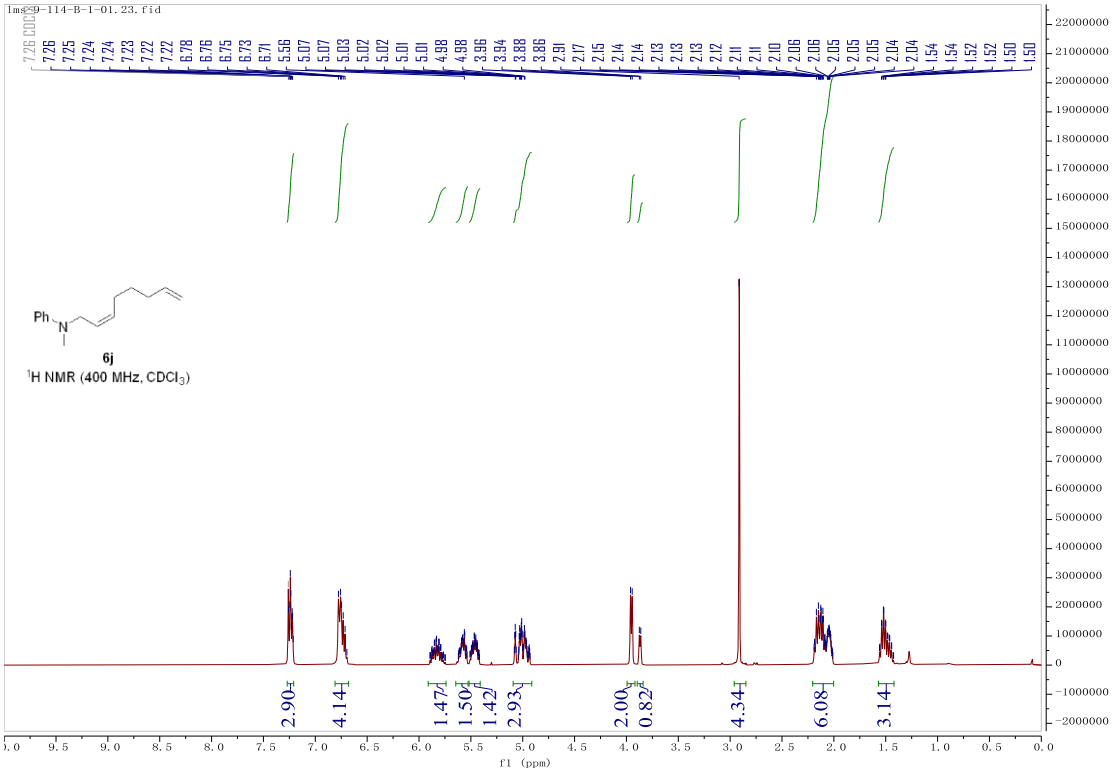

lms-9-137-A-01.20.fid
6g
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)

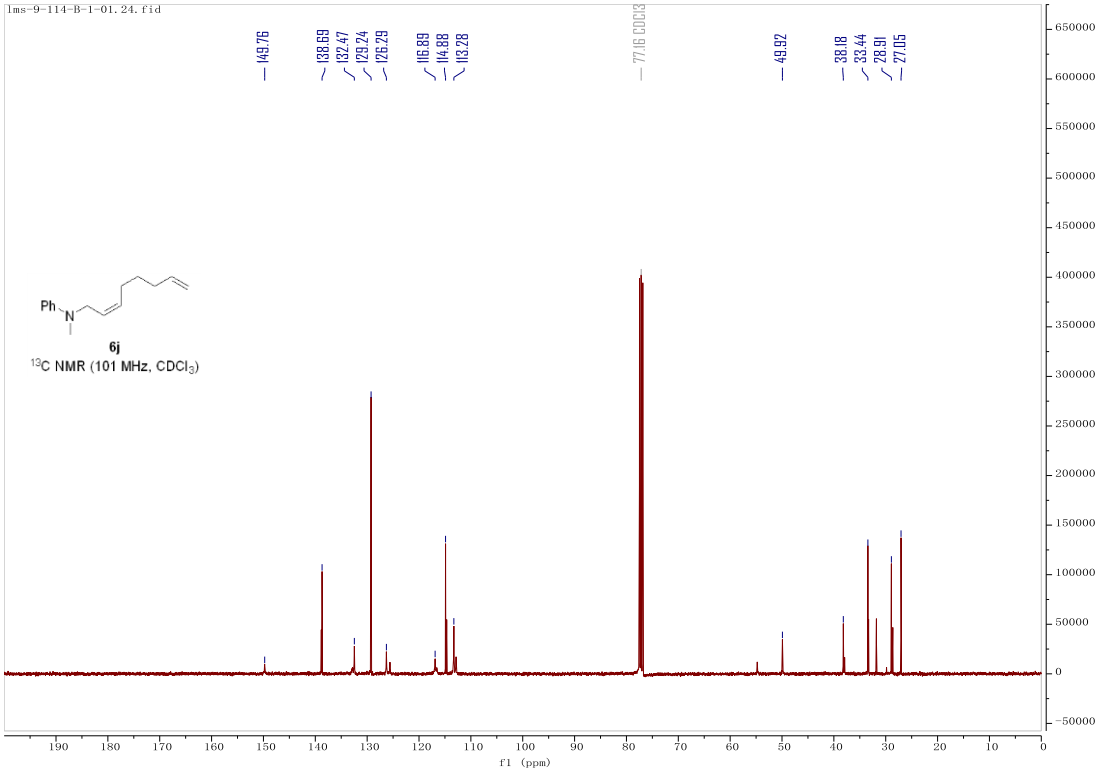

lms-10-0-A-01.10.fid
Ph
6h
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

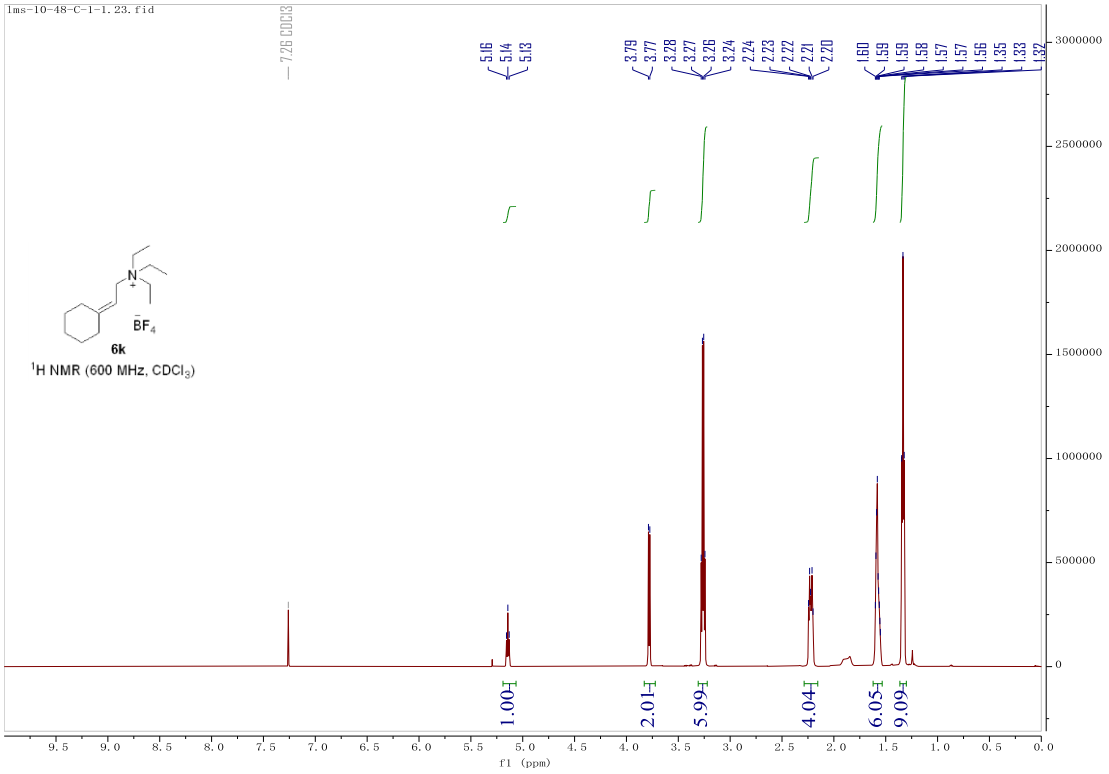

lms-10-0-A-01.11.fid
Ph
6h
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)

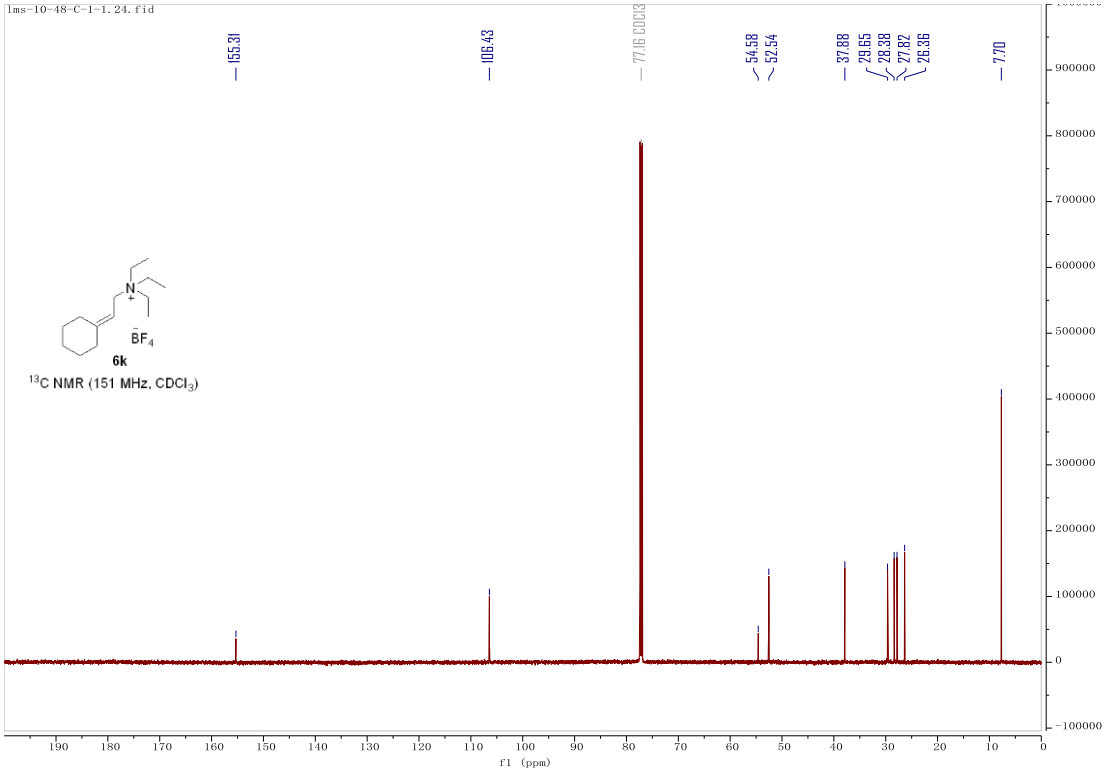

lms-9-163-A-02.22.fid
Ph
Ph
N
6i
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

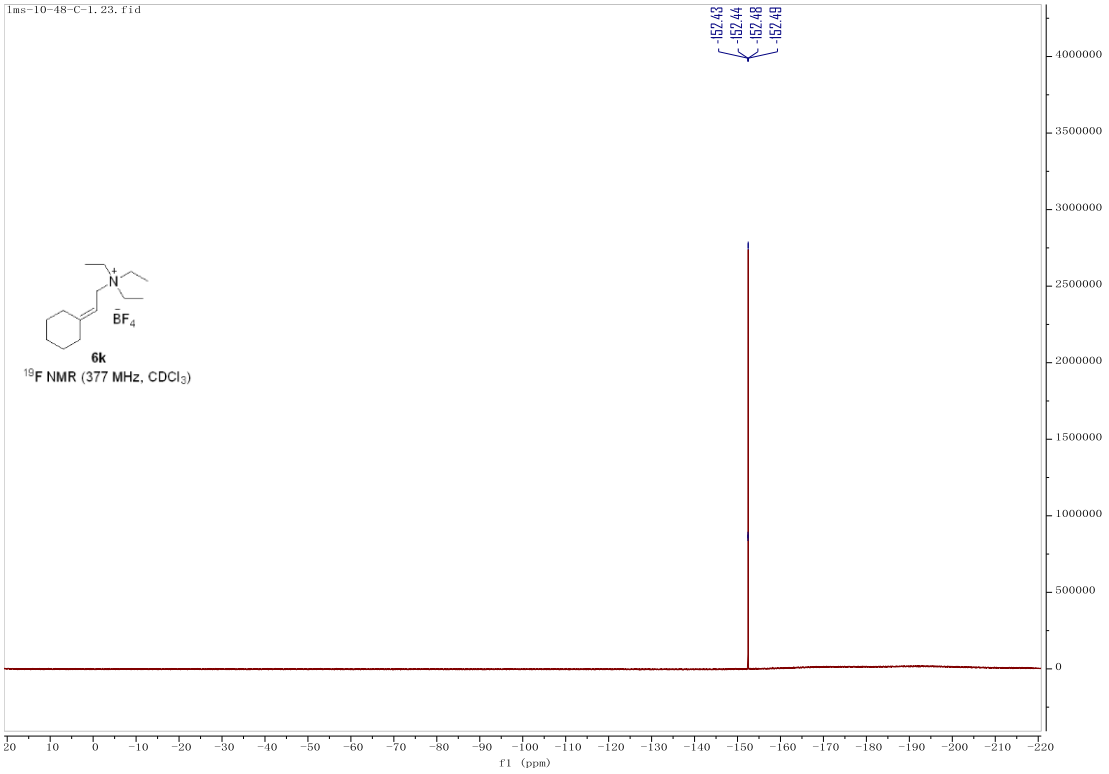

lms-9-163-A-02.23.fid
Ph
Ph
N
6i
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)

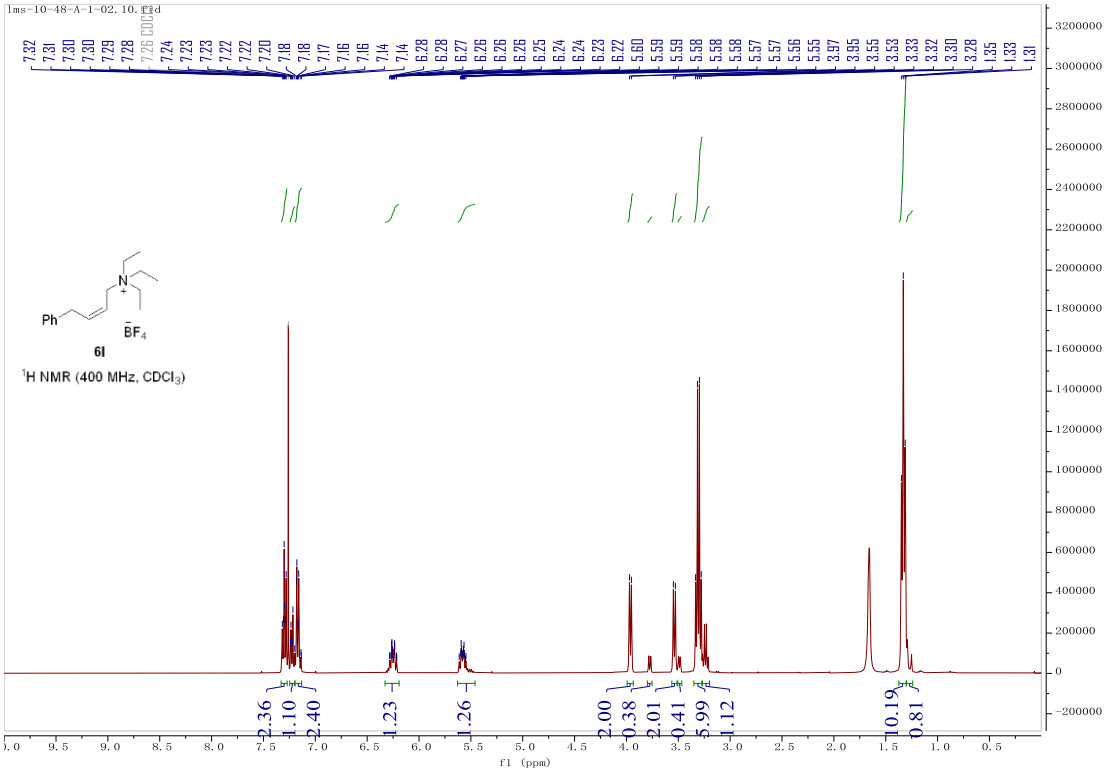

lms-9-114-B-1-01.23.fid
Ph
N
6j
1H NMR (400 MHz, CDCl3)
2.90
4.14
1.47
1.50
1.42
2.93
2.00
0.82
4.34
6.08
3.14
f1 (ppm)

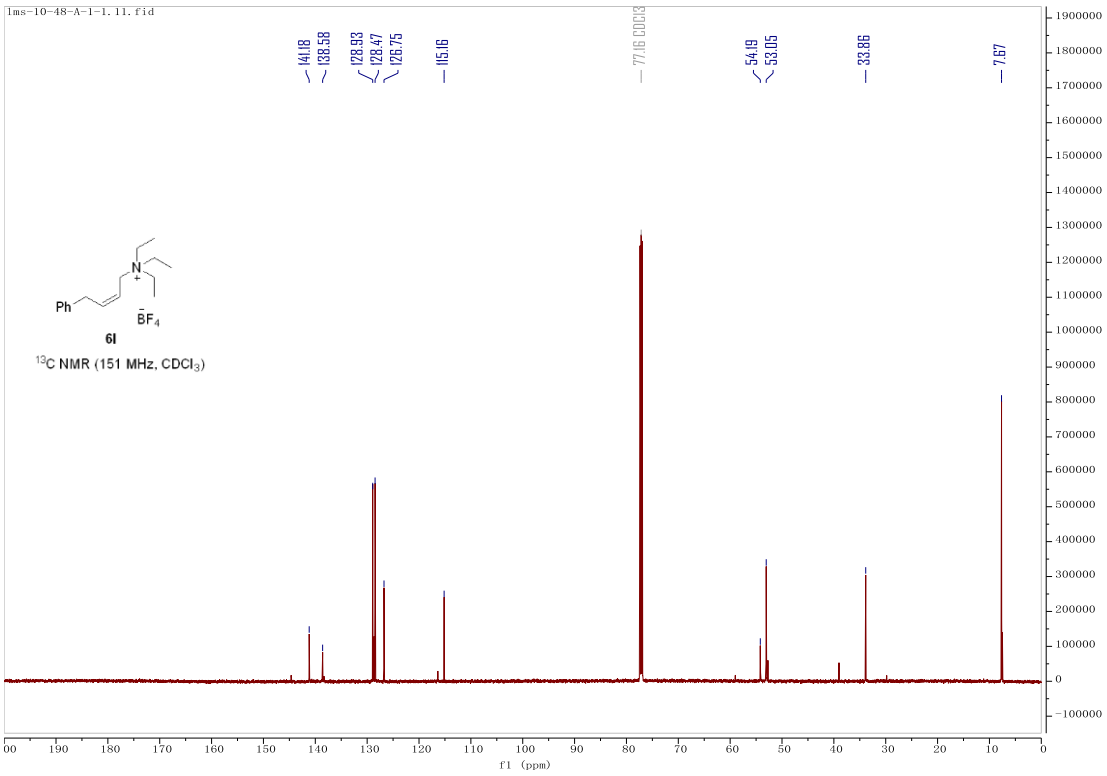

lms-9-114-B-1-01.24.fid
149.76
138.69
132.47
129.24
126.29
116.83
114.88
113.28
77.16 CDCl3
49.92
38.18
33.44
28.91
27.05
Ph
N
6j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

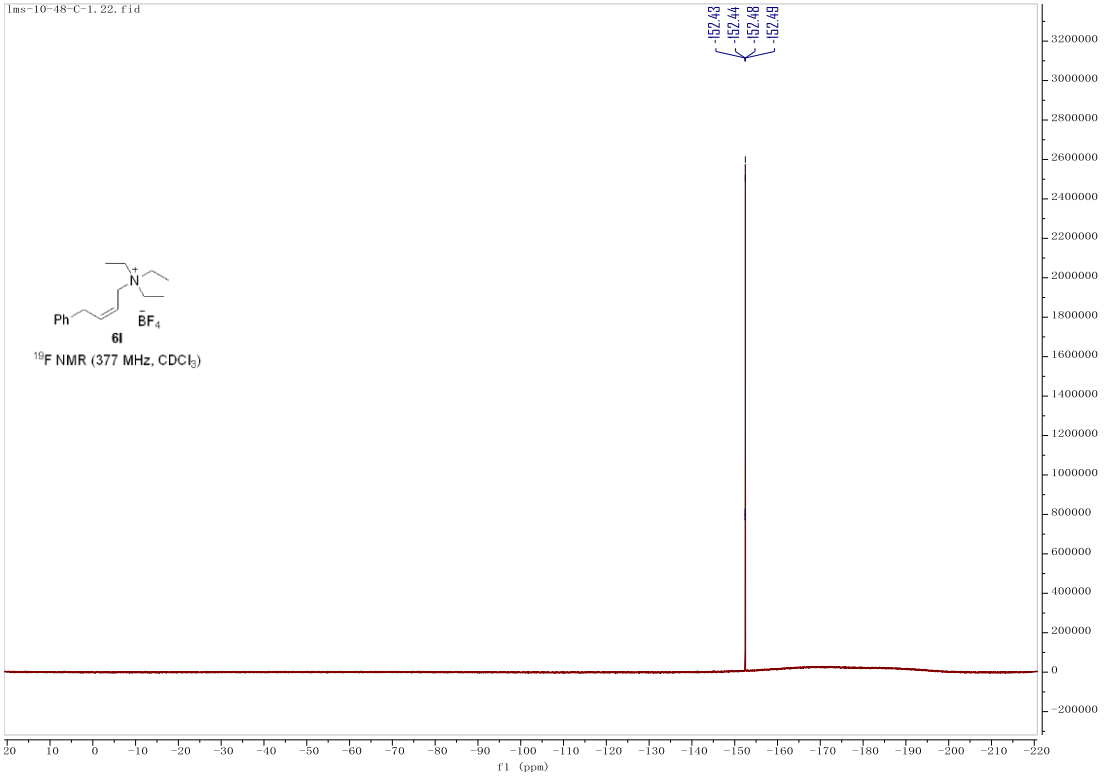

lms-10-48-C-1-1.23.fid
6k
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)

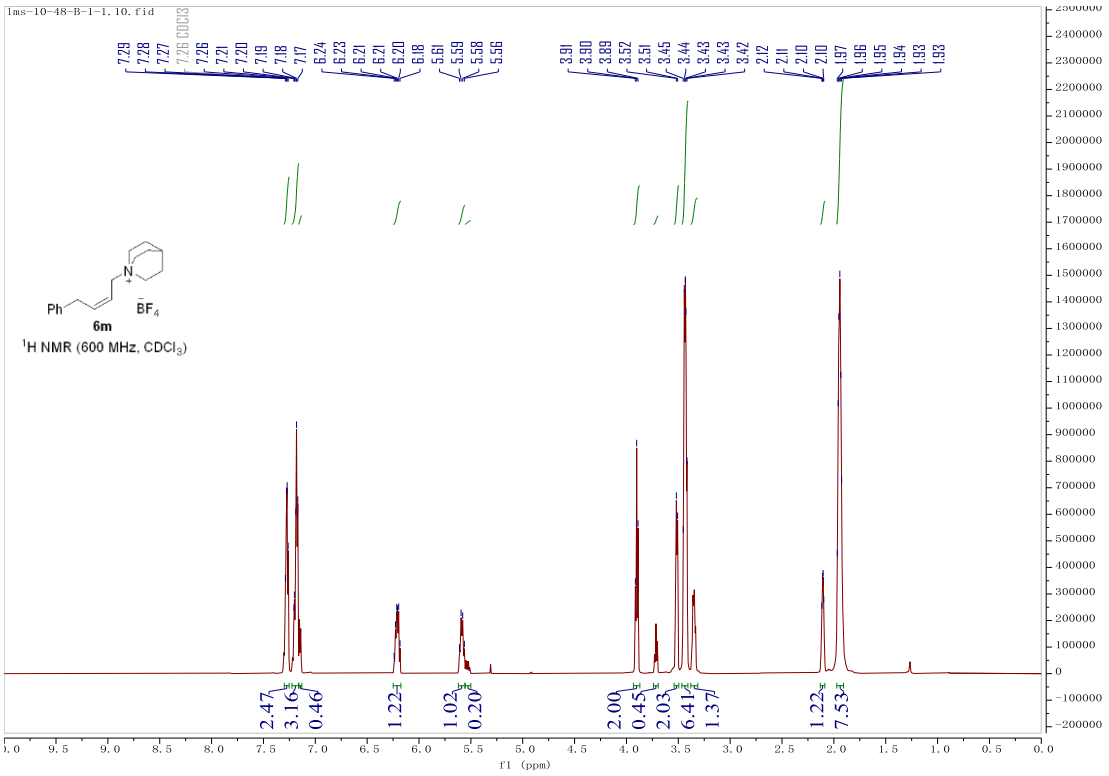

lms-10-48-C-1-1.24.fid
6k
^{13}C NMR (151 MHz, $CDCl_3$)
f1 (ppm)

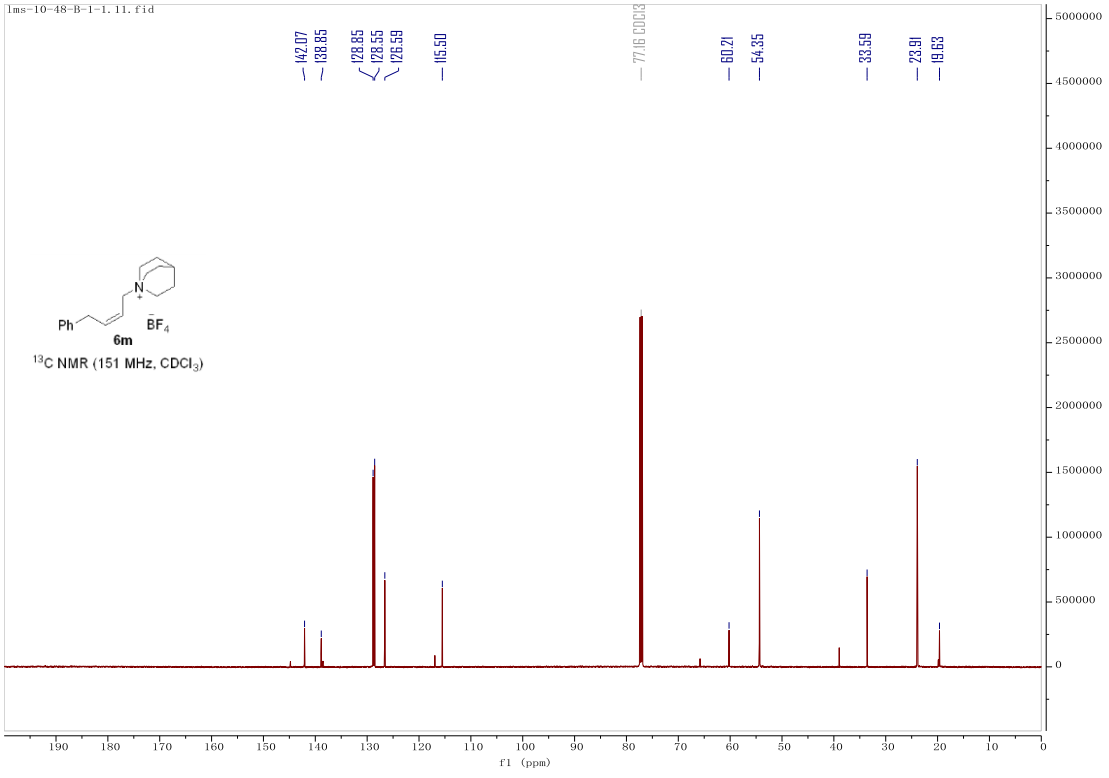

lms-10-48-C-1.23.fid
-152.43
-152.44
-152.48
-152.49
BF4
6k
19F NMR (377 MHz, CDCl3)
f1 (ppm)

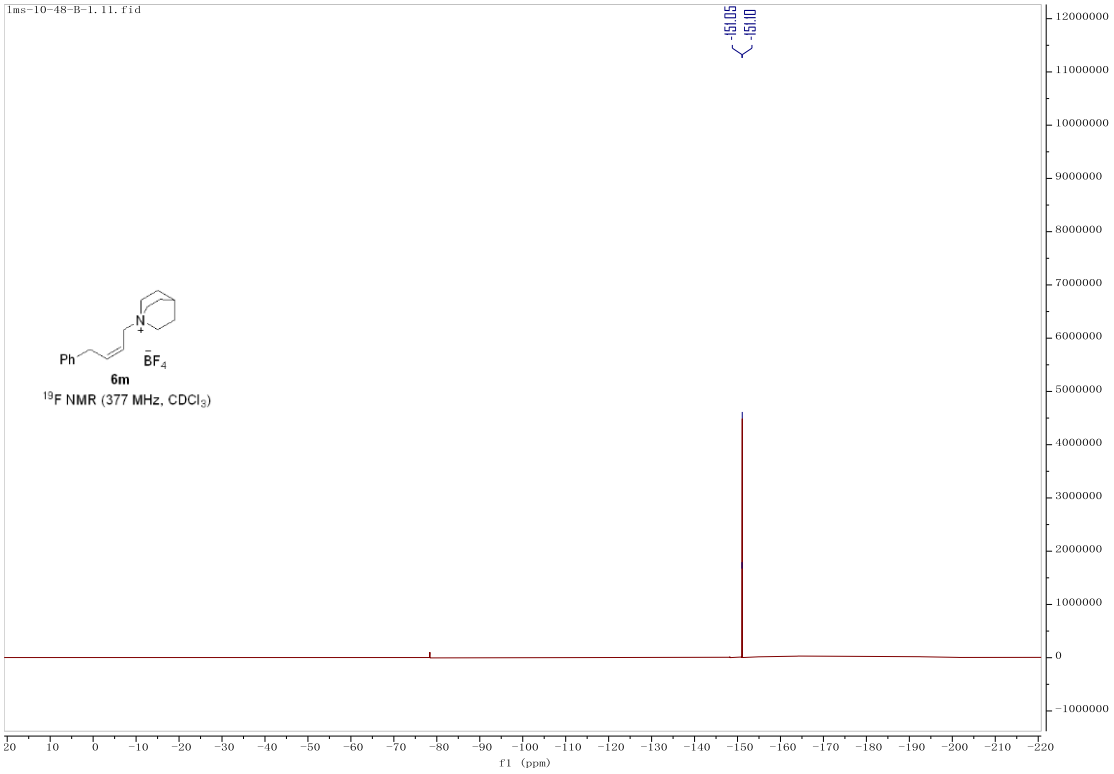

lms-10-48-A-1-02.10.fid
Ph
BF4
6l
1H NMR (400 MHz, CDCl3)
2.36
1.10
2.40
1.23
1.26
2.00
0.38
2.01
0.41
5.99
1.12
10.19
0.81
f1 (ppm)

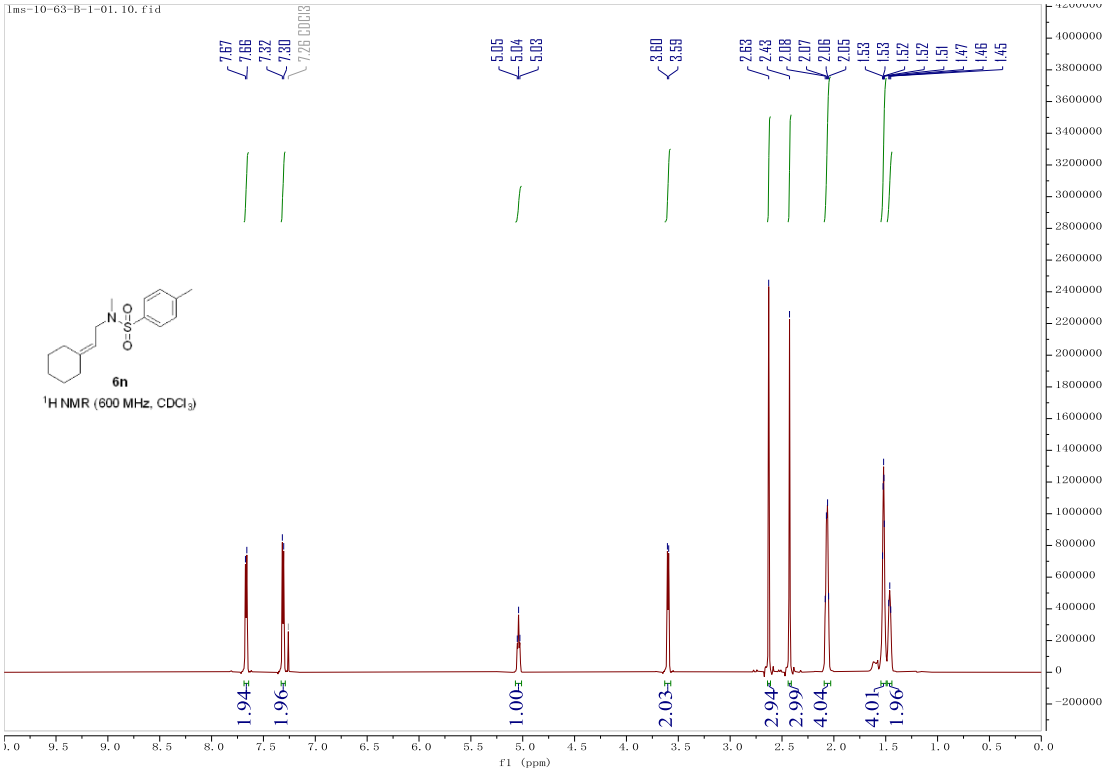

lms-10-48-A-1-1.11.fid
141.18
139.58
128.93
128.47
126.75
115.16
77.16 CDCl3
54.19
53.05
33.86
7.67
Ph
BF4
6l
13C NMR (151 MHz, CDCl3)
f1 (ppm)

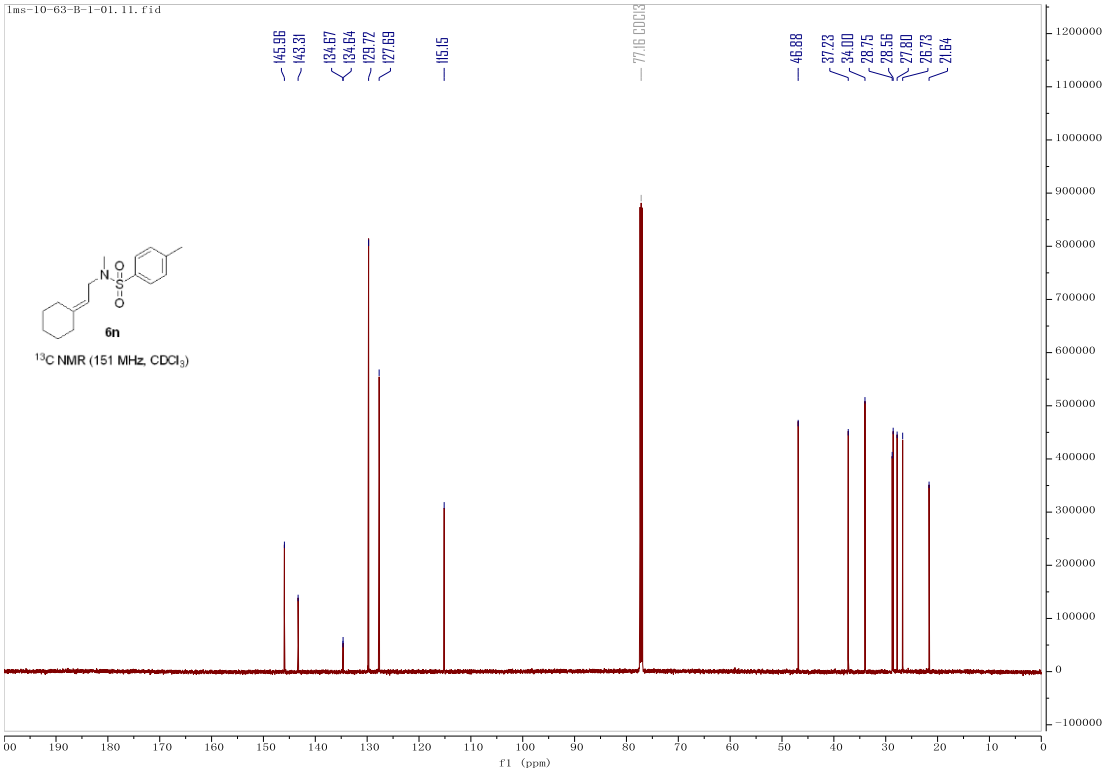

lms-10-48-C-1.22.fid
-152.43
-152.44
-152.48
-152.49
Ph
BF4
6l
19F NMR (377 MHz, CDCl3)
f1 (ppm)

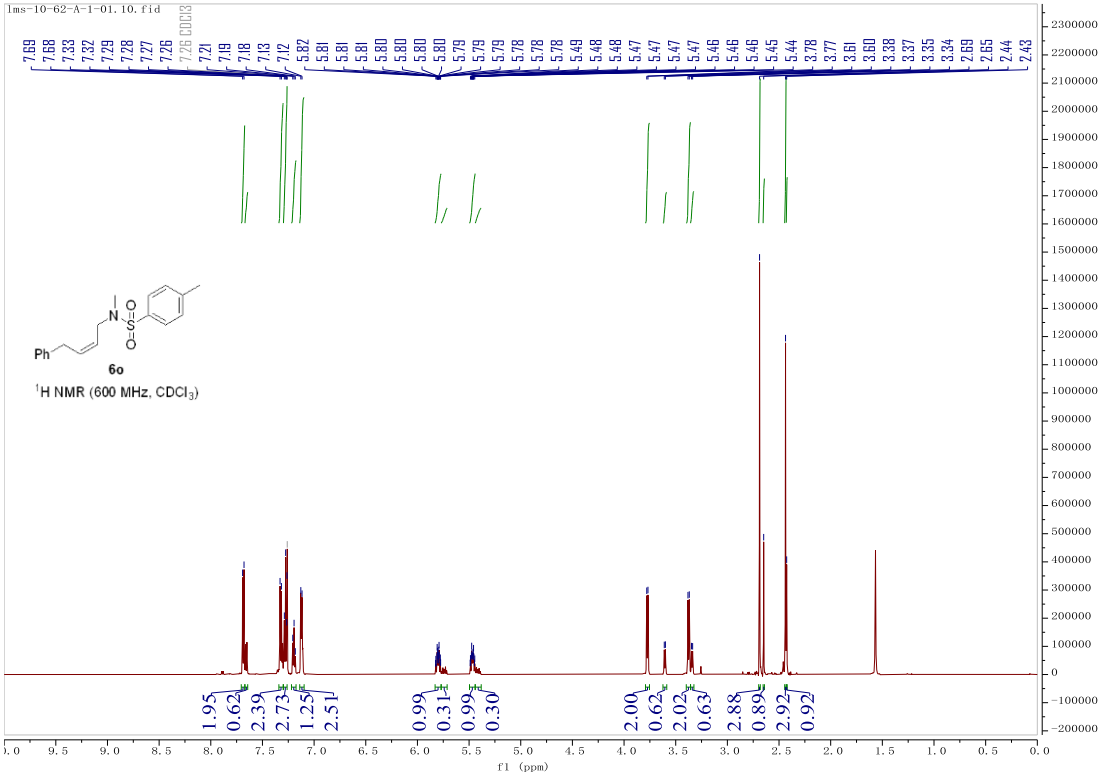

lms-10-48-B-1-1.10.fid
7.29
7.28
7.27
7.26 CDCl3
7.26
7.21
7.20
7.19
7.18
7.17
6.24
6.23
6.21
6.21
6.20
6.18
5.61
5.59
5.58
5.56
3.91
3.90
3.89
3.52
3.51
3.45
3.44
3.43
3.42
2.12
2.11
2.10
2.10
1.97
1.96
1.95
1.94
1.93
1.93
Ph
BF4
6m
1H NMR (600 MHz, CDCl3)
2.47
3.16
0.46
1.22
1.02
0.20
2.00
0.45
2.03
6.41
1.37
1.22
7.53
f1 (ppm)

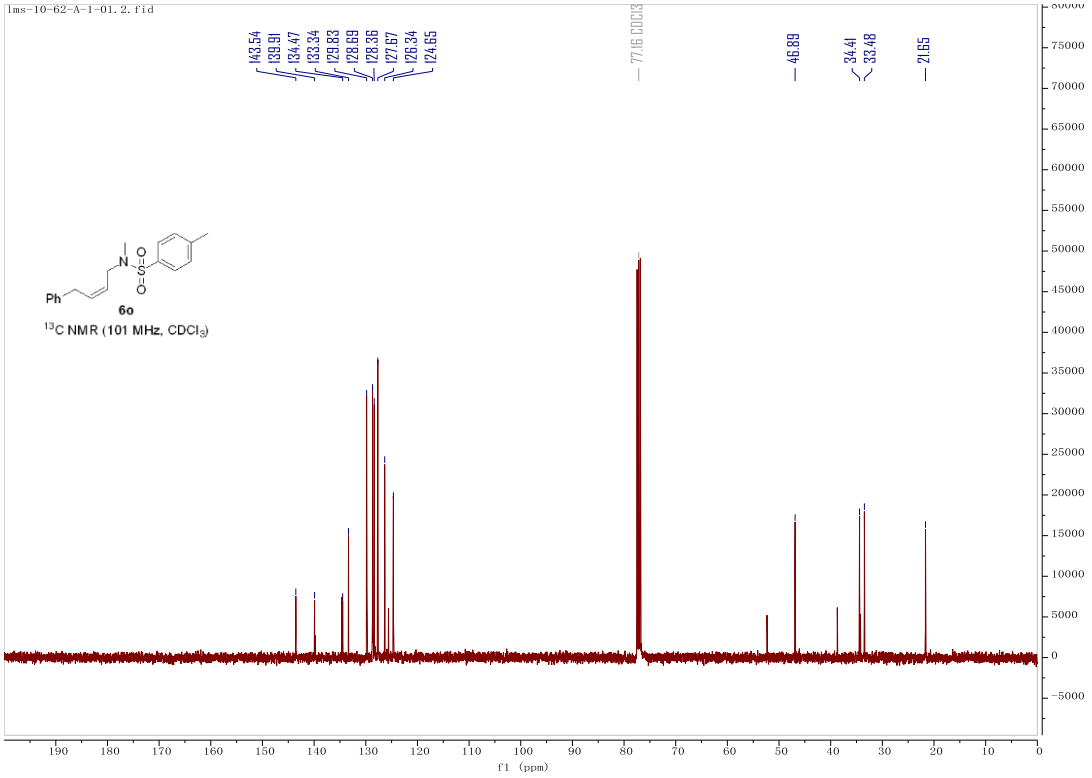

lms-10-48-B-1-1.11.fid
142.07
138.85
128.85
128.55
126.59
115.50
77.16 CDCl3
60.21
54.35
33.59
23.91
19.63
Ph
BF4
6m
13C NMR (151 MHz, CDCl3)
f1 (ppm)

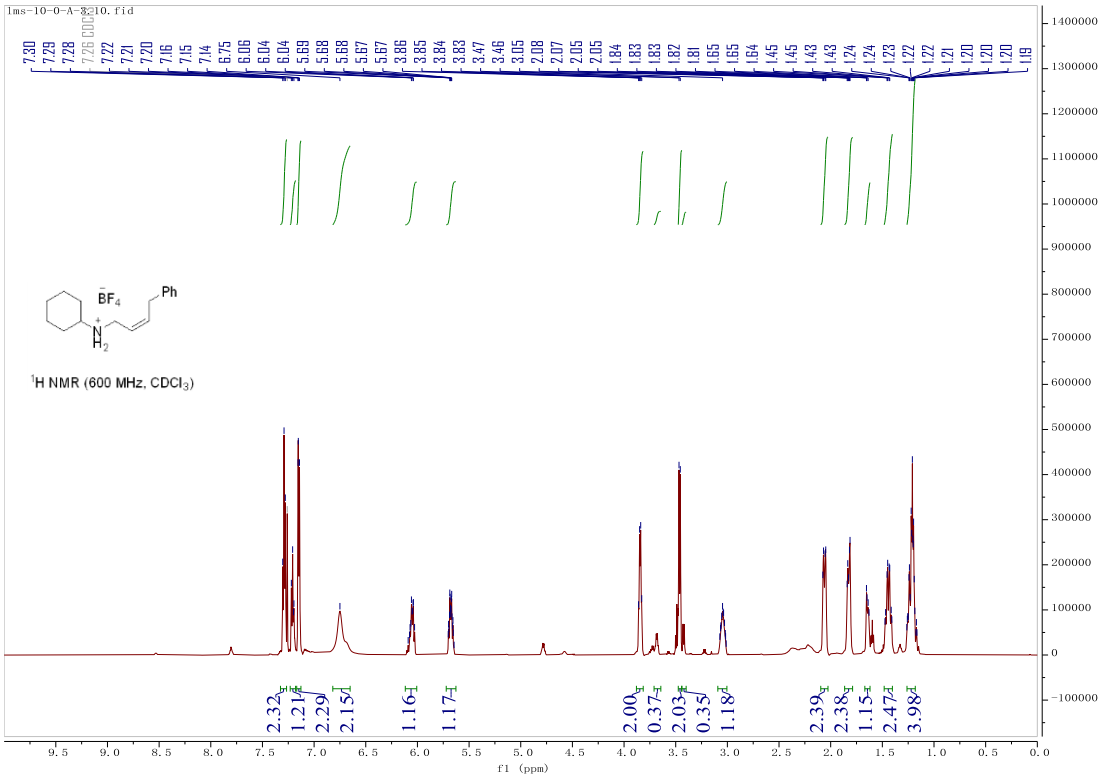

lms-10-48-B-1.11.fid
-151.05
-151.10
Ph
BF4
6m
19F NMR (377 MHz, CDCl3)
f1 (ppm)

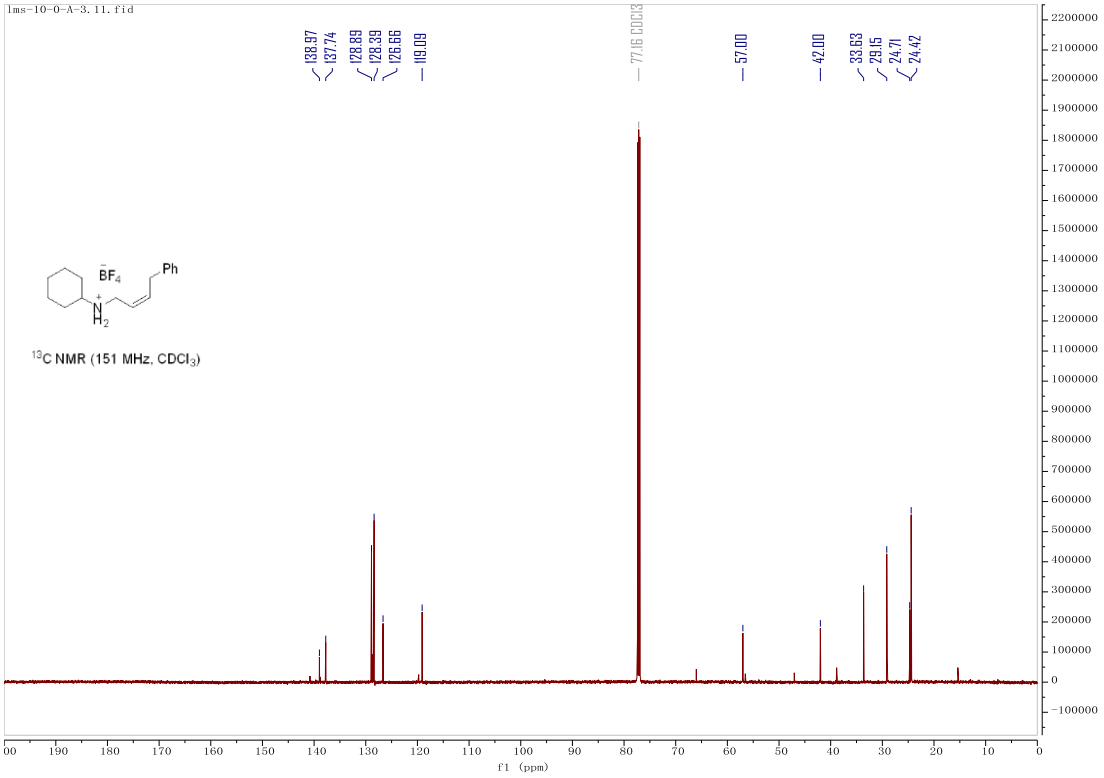

lms-10-63-B-1-01.10.fid
7.67
7.66
7.32
7.30
7.26 CDCl3
5.05
5.04
5.03
3.60
3.59
2.63
2.43
2.08
2.07
2.06
2.05
1.53
1.53
1.52
1.52
1.51
1.47
1.46
1.45
1.94
1.96
1.00
2.03
2.94
2.99
4.04
4.01
1.96
6n
1H NMR (600 MHz, CDCl3)
f1 (ppm)

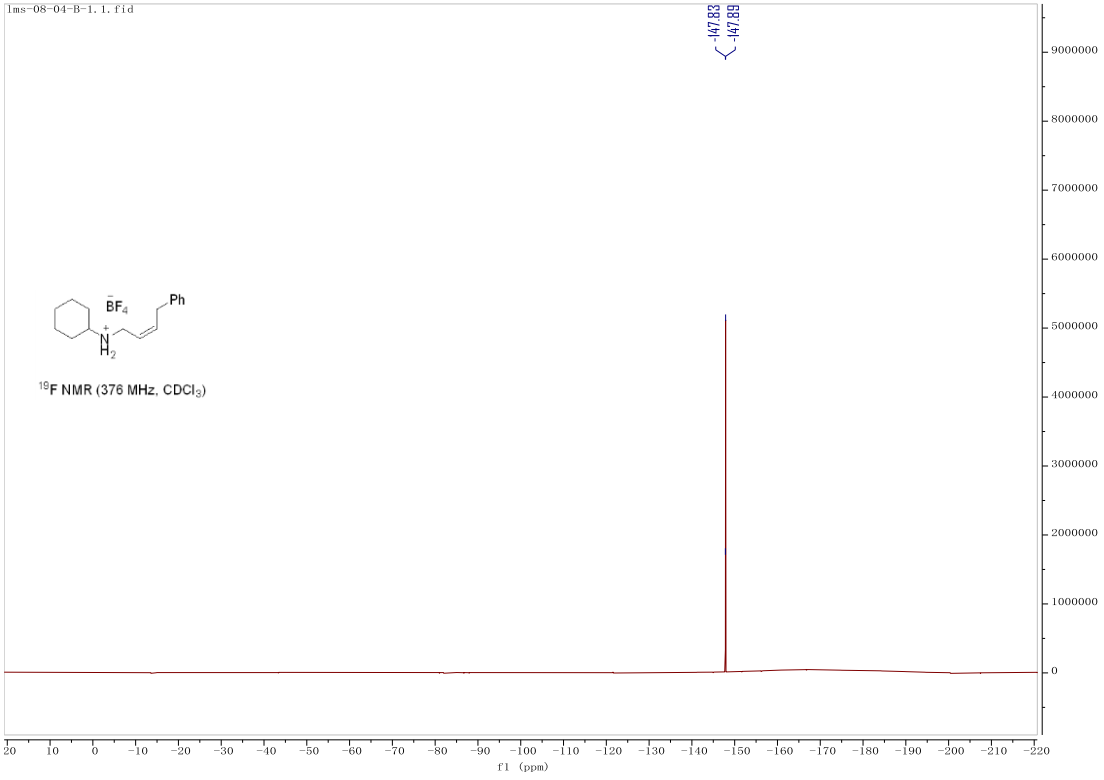

lms-10-63-B-1-01.11.fid
145.96
143.31
134.67
134.64
129.72
127.69
115.15
77.16 CDCl3
46.88
37.23
34.00
28.75
28.56
27.80
26.73
21.64
6n
13C NMR (151 MHz, CDCl3)
f1 (ppm)


lms-10-62-A-1-01.10.fid
7.26 CDCl3
Ph
6o
1H NMR (600 MHz, CDCl3)
1.95
0.62
2.39
2.73
1.25
2.51
0.99
0.31
0.99
0.30
2.00
0.62
2.02
0.63
2.88
0.89
2.92
0.92
f1 (ppm)


lms-10-62-A-1-01.2.fid
143.54
139.91
134.47
133.34
129.83
128.69
128.36
127.67
126.34
124.65
77.16 CDCl3
46.89
34.41
33.48
21.65
Ph
6o
13C NMR (101 MHz, CDCl3)
f1 (ppm)


lms-10-0-A-3-10.fid
7.30
7.29
7.28
7.26 CDCl3
7.22
7.21
7.20
7.16
7.15
7.14
6.75
6.06
6.04
6.04
5.69
5.68
5.68
5.67
5.67
3.86
3.85
3.84
3.83
3.47
3.46
3.05
2.08
2.07
2.05
2.05
1.84
1.83
1.83
1.82
1.81
1.65
1.65
1.64
1.45
1.45
1.43
1.43
1.24
1.24
1.23
1.22
1.22
1.21
1.20
1.20
1.20
1.19
BF4
Ph
1H NMR (600 MHz, CDCl3)
2.32
1.21
2.29
2.15
1.16
1.17
2.00
0.37
2.03
0.35
1.18
2.39
2.38
1.15
2.47
3.98
f1 (ppm)


lms-10-0-A-3.11.fid
138.97
137.74
128.83
128.39
126.66
119.09
77.16 CDCl3
57.00
42.00
33.83
29.15
24.71
24.42
Ph
BF4
NH2
13C NMR (151 MHz, CDCl3)
f1 (ppm)


lms-08-04-B-1.1.fid
-147.83
-147.89
Ph
BF4
NH2
19F NMR (376 MHz, CDCl3)
f1 (ppm)