Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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I. Gewneral Information

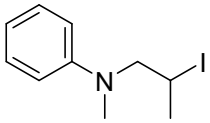
a). Materials

All the reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity ≥ 99.999%). The following chemicals were purchased and used as received: $NiBr_2$·diglyme (Aldrich), 4,4',4''-tri-tert-butyl-2,2':6',2''-terpyridine (Aldrich), cesium carbonate (99.9%, Aldrich), Anhydrous N,N-Dimethylacetamide (99.8%, HY Scientific), Anhydrous THF (HY Scientific), Anhydrous DMSO (HY Scientific), Anhydrous Toluene(HY Scientific), Anhydrous DMF(Aldrich), Triethoxysilane (95%, TCI), Diethoxymethylsilane (97%, adamas-beta),1-octyne (95%, TCI), Ethynylcyclopropane (98%, adamas-beta), 3,3-Dimethyl-1-Butyne(95%, adamas-beta), Ethynylcyclohexane (95%, bidepharmatech), 5-Hexynenitrile (98%, Alfa-Aesar), (Trimethylsilyl)acetylene (98%, Alfa-Aesar).

b). Analytical Methods

^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in $CDCl_3$unless otherwise noted; Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, AD, AS, KM columns were purchased from Daicel Chemical Industries, LTD. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

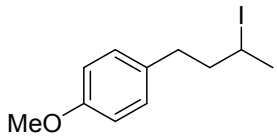
II. Preparation of Substrates



N-(2-iodopropyl)-N-methylaniline CAS:1604039-11-3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 2H), 4.44 – 4.26 (m, 1H), 3.93 – 3.77 (m, 1H), 3.56 – 3.42 (m, 1H), 2.99 (s, 3H), 1.87 (d, *J* = 6.8 Hz, 3H).

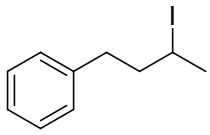
^{13}C NMR (100 MHz, CDCl3): δ 148.1, 129.3, 116.9, 111.8, 63.1, 39.8, 25.9, 25.9.



1-(3-iodobutyl)-4-methoxybenzeneCAS: 1383841-50-6

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.08 – 3.97 (m, 1H), 3.72 (s, 3H), 2.75 – 2.67 (m, 1H), 2.62 – 2.51 (m, 1H), 2.18 – 2.00 (m, 1H), 1.87 (d, *J* = 6.8 Hz, 3H), 1.80 – 1.70 (m, 1H).

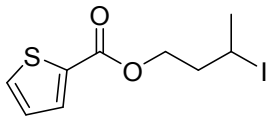
^{13}C NMR (CDCl3, 100 MHz): δ 158.0, 132.8, 129.5, 114.0, 55.3, 44.7, 35.0, 29.9, 29.1.



(3-iodobutyl)benzene CAS: 59456-20-1

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.21 – 7.16 (m, 3H), 4.16 – 4.05 (m, 1H), 2.84 – 2.80(m, 1H), 2.71 – 2.69 (m, 1H), 2.18 – 2.15 (m, 1H), 1.95 (d, *J* = 6.8 Hz, 3H), 1.92 – 1.82 (m, 1H).

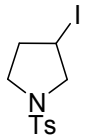
^{13}C NMR (101 MHz, CDCl3) δ 140.72, 128.50, 128.45, 126.10, 44.38, 35.81, 29.56, 28.96.



3-iodobutyl thiophene-2-carboxylate CAS: 1562423-24-8

^{1}H NMR (400 MHz, CDCl3): δ 7.80 (dd, J = 3.7, 1.3 Hz, 1H), 7.55 (dd, J = 5.0, 1.3 Hz, 1H), 7.10 (dd, J = 5.0, 3.8 Hz, 1H), 4.50 (dt, J = 11.3, 5.6 Hz, 1H), 4.35 – 4.25 (m, 2H), 2.27-2.21 (m, 1H), 2.15-2.07 (m, 1H), 2.01 (d, J = 6.9 Hz, 3H).

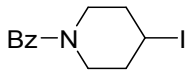
^{13}C NMR (101 MHz, CDCl3): δ 161.92, 133.53, 133.51, 132.52, 127.77, 64.79, 41.35, 28.95, 24.00.



3-iodo-1-tosylpyrrolidine: CAS: 919284-59-6

^{1}H NMR (400 MHz, CDCl3): δ7.74 (d, J = 8.19 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.15 – 4.14 (m, 1H), 3.90 (dd, J = 11.7, 5.9 Hz, 1H), 3.55 (dd, J = 11.7, 4.8 Hz, 1H), 3.43 (dd, J = 7.4, 6.1 Hz, 2H), 2.43 (s, 3H), 2.31-2.20 (m, 1H), 2.17-2.07 (m, 1H).

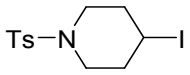
^{13}C NMR (101 MHz, CDCl3): δ 143.77, 133.91, 129.81, 127.58, 58.63, 46.97, 38.12, 21.55, 17.26.



(4-iodopiperidin-1-yl)(phenyl)methanone CAS: 244240-61-7

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 5H), 4.58 – 4.46 (m, 1H), 4.02 – 3.85 (m, 1H), 3.69 – 3.46 (m, 2H), 3.38 – 3.25 (m, 1H), 2.30 – 1.88 (m, 4H).

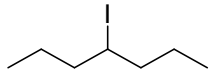
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.56, 135.71, 129.83, 128.61, 126.91, 47.71, 42.20, 37.94, 37.16, 26.78.



4-iodo-1-tosylpiperidineCAS: 289890-80-8

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.33 – 4.22 (m, 1H), 3.20 – 3.12 (m, 2H), 3.05 – 2.88 (m, 2H), 2.44 (s, 3H), 2.17 – 2.06 (m, 4H).

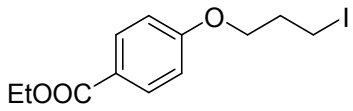
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 133.5, 129.9, 127.8, 45.8, 36.6, 25.7, 21.7.



4-iodoheptaneCAS:31294-93-6

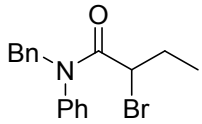
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 – 4.01 (m, 1H), 1.93 – 1.77 (m, 2H), 1.70 – 1.61 (m, 2H), 1.59 – 1.51 (m, 2H), 1.47 – 1.36 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 42.88, 40.18, 22.92, 13.41.



ethyl 4-(3-iodopropoxy)benzoateCAS:211368-04-6

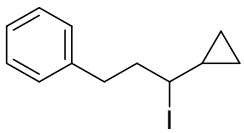
^{1}H NMR (400 MHz, CDCl3) δ 8.00 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 4.08 (td, J = 5.8, 1.3 Hz, 2H), 3.36 (td, J = 6.6, 1.0 Hz, 2H), 2.35 – 2.23 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 166.48, 162.47, 131.72, 123.31, 114.17, 67.55, 60.82, 32.89, 14.53, 2.30.



N-benzyl-2-bromo-N-phenylbutanamide CAS: 851073-30-8

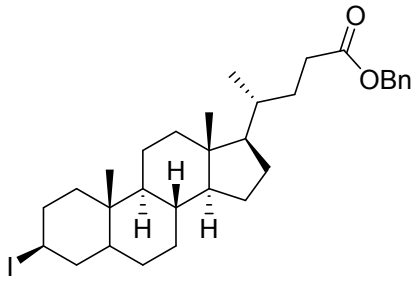
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 6.92 (m, 10H), 4.90 (s, 2H), 4.07 – 3.84 (m, 1H), 2.26 – 2.09 (m, 1H), 2.05 – 1.78 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.03, 141.11, 136.91, 129.74, 128.88, 128.63, 128.49, 128.38, 127.60, 53.57, 46.04, 28.69, 12.17.



3-cyclopropyl-3-iodopropyl)benzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.17 (m, 3H), 3.44 – 3.33 (m, 1H), 2.95 – 2.84 (m, 1H), 2.79 – 2.67 (m, 1H), 2.30 (m, 1H), 2.20 – 2.04 (m, 1H), 1.49 – 1.38 (m, 1H), 1.00 – 0.88 (m, 1H), 0.78 – 0.67 (m, 1H), 0.44 – 0.34 (m, 1H), 0.27 – 0.10 (m, 1H).

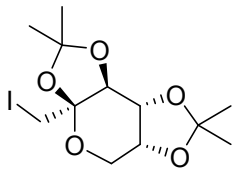


benzyl-(4R)-4-((3S,8R,9S,10S,13R,14S,17R)-3-iodo-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate[1]

Prepared using the I_2/PPh_3/imidazole method.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.15 – 5.06 (m, 2H), 5.03 – 4.97 (m, 1H), 2.40 (ddd, *J* = 15.2, 10.0, 5.0 Hz, 1H), 2.33 – 2.20 (m, 1H), 2.05 – 1.70 (m, 7H), 1.66 – 0.79 (m, 25H), 0.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.26, 136.26, 128.69, 128.38, 128.33, 66.25, 56.71, 56.13, 42.87, 41.85, 40.30, 39.67, 39.20, 37.08, 35.88, 35.81, 35.46, 32.86, 31.42, 31.11, 28.30, 27.16, 27.06, 26.58, 24.29, 23.81, 20.94, 18.40, 12.18.

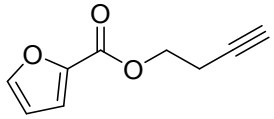
HRMS（ESI）calcd for C31H45O2INa (M+Na^+):599.2348; found: 599.2349



(3aR,5aR,8aR,8bS)-3a-(iodomethyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran　CAS: 940006-45-1

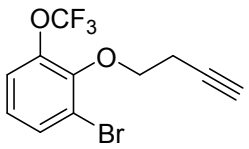
^{1}H NMR (400 MHz, CDCl3) δ 4.58 (dd, J = 7.9, 2.5 Hz, 1H), 4.31 (d, J = 2.5 Hz, 1H), 4.21 (d, J = 7.9 Hz, 1H), 3.89 (d, J = 13.0 Hz, 1H), 3.78 (d, J = 13.0 Hz, 1H), 3.51 (d, J = 10.6 Hz, 1H), 3.33 (d, J = 10.6 Hz, 1H), 1.52 (s, 3H), 1.47 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 109.39, 108.60, 100.43, 72.00, 70.85, 70.74, 62.12, 26.69, 26.14, 25.42, 24.35, 10.85.



but-3-yn-1-yl furan-2-carboxylate CAS：187152-15-4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 1H), 7.34 – 7.15 (m, 1H), 6.52 (m, 1H), 4.48 – 4.17 (m, 2H), 2.73 – 2.41 (m, 2H), 2.08 – 2.05 (m, 1H).

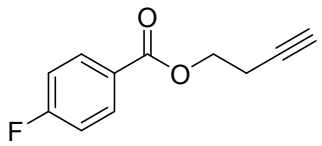


1-bromo-2-(but-3-yn-1-yloxy)-3-(trifluoromethoxy)benzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 10.0, 5.3 Hz, 1H), 6.76 (m, 2H), 4.15 (t, *J* = 7.1 Hz, 2H), 2.77 (td, *J* = 7.1, 2.7 Hz, 2H), 2.11 – 1.99 (m, 1H).

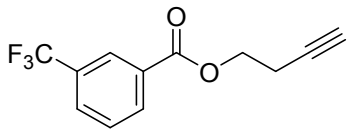
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.99.

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.81, 149.23, 133.91, 120.42 (q, *J* = 254.9 Hz), 114.53, 110.33, 107.14, 79.71, 70.54, 67.60, 19.52.



but-3-yn-1-yl 4-fluorobenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 7.91 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 4.42 (t, *J* = 6.8 Hz, 2H), 2.67 (td, *J* = 6.7, 2.6 Hz, 2H), 2.05 (t, *J* = 2.6 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.10, 164.95 (d, *J* = 74.7 Hz), 132.23 (d, *J* = 9.3 Hz), 126.18 (d, *J* = 3.0 Hz), 115.55 (d, *J*= 22.0 Hz), 79.97, 70.08, 62.70, 19.09.^{19}F NMR (376 MHz, $CDCl_3$) δ-105.43.

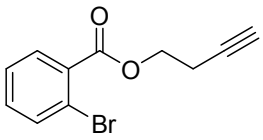


but-3-yn-1-yl 3-(trifluoromethyl)benzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.24 (t, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 9.8, 5.8 Hz, 1H), 4.47 (t, *J* = 6.8 Hz, 2H), 2.70 (td, *J* = 6.8, 2.7 Hz, 2H), 2.09 – 2.04 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.89.

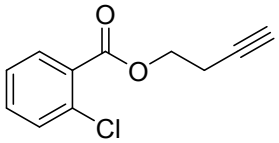
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.14, 131.24 (q, *J* = 33.0 Hz), 130.94, 129.76 (q, *J* = 3.6 Hz), 129.24, 126.75 (q, *J* = 3.9 Hz), 123.78 (q, *J* = 272.4 Hz), 79.84, 70.35, 63.20, 19.20.



but-3-yn-1-yl 2-bromobenzoateCAS: 1422056-71-0

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.67 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.41 – 7.30 (m, 2H), 4.45 (t, *J* = 6.8 Hz, 2H), 2.69 (td, *J* = 6.8, 2.6 Hz, 2H), 2.05 (t, *J* = 2.6 Hz, 1H).

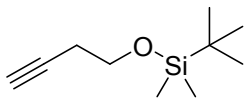
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.94, 134.53, 132.85, 131.95, 131.60, 127.32, 121.95, 80.03, 70.30, 63.28, 19.12.



but-3-yn-1-yl 2-chlorobenzoate

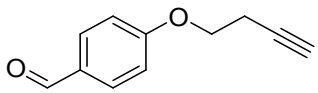
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 1H), 7.54 – 7.38 (m, 2H), 7.32 (td, *J* = 7.8, 1.7 Hz, 1H), 4.45 (t, *J* = 6.8 Hz, 2H), 2.68 (td, *J* = 6.8, 2.6 Hz, 2H), 2.05 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.43, 133.98, 132.82, 131.64, 131.23, 129.89, 126.71, 80.02, 70.26, 63.18, 19.12.



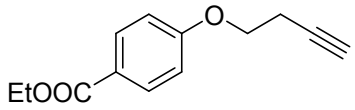
(but-3-yn-1-yloxy)(tert-butyl)dimethylsilane CAS: 78592-82-2

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (t, *J* = 7.1 Hz, 2H), 2.38 – 2.23 (m, 2H), 1.88 (t, *J* = 2.7 Hz, 1H), 0.83 – 0.79 (m, 9H), 0.05 – -0.03 (m, 6H).



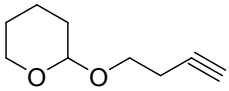
4-(but-3-yn-1-yloxy)benzaldehydeCAS:1016536-59-6

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.03 – 7.72 (m, 2H), 7.14 – 6.88 (m, 2H), 4.18 (t, *J* = 6.9 Hz, 2H), 2.73 (td, *J* = 6.9, 2.7 Hz, 2H), 2.07 (t, *J* = 2.7 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 190.93, 163.54, 132.14, 130.34, 114.95, 79.98, 70.40, 66.31, 19.56.



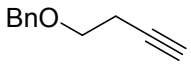
ethyl 4-(but-3-yn-1-yloxy)benzoate CAS: 1493966-83-8

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 4.35 (q, *J* = 6.9 Hz, 2H), 4.14 (t, *J* = 6.8 Hz, 2H), 2.71 (t, *J* = 6.1 Hz, 2H), 2.06 (s, 1H), 1.38 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.43, 162.18, 131.69, 123.42, 114.21, 80.16, 70.26, 66.13, 60.81, 19.57, 14.50.



2-(but-3-yn-1-yloxy)tetrahydro-2H-pyranCAS: 40365-61-5

^{1}H NMR (400 MHz, CDCl3) δ 4.66 – 4.65 (m, 1H), 3.91 – 3.80 (m, 2H), 3.61 – 3.48 (m, 2H), 2.50 (td, J = 7.0, 2.7 Hz, 2H), 1.97 (t, J = 2.7 Hz, 1H), 1.87-1.80 (m, 1H), 1.76 – 1.68 (m, 1H), 1.61 – 1.51 (m, 4H).^{13}C NMR (101 MHz, CDCl3) δ 98.79, 81.45, 69.21, 65.55, 62.24, 30.57, 25.46, 19.98, 19.42.



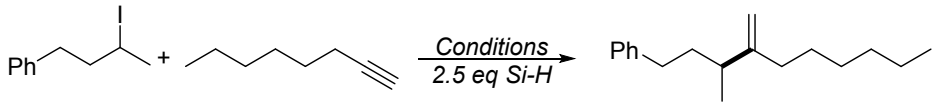
((but-3-yn-1-yloxy)methyl)benzeneCAS:22273-77-4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.26 (m, 5H), 4.57 (s, 2H), 3.61 (t, *J* = 6.9 Hz, 2H), 2.51 (td, *J* = 6.9, 2.7 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H).

III. General Experimental Procedures, Spectral Data and HPLC Analysis

Experimental Procedures for Examples Described in Table 1.

In air,catalyst (10%), base (2.5 equiv.), ligand (12%) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent was added in turn under argon atmosphere. The reaction mixture was stirred at the room temperature for 5 minutes, 0.2mmol alkyl halide and alkyne (2.0 equiv) was added were added and stirred for 5 minutes, then DEMS (Diethoxymethylsilane, 2.5 equiv)was added. The reaction was stirred at the indicated temperature for 10h. Then the reaction was diluted with EtOAc.Benzophenone was added as an internal standard. The yield was determined by GC.



1a
0.2 mmol

2a
0.4 mmol

3a

Entry	Cat.	Ligand	Base	Solvent	T (°C)	Yield (%)3a
1	$NiBr_2$·diglyme	dtbpy	NaOAc	DMAC	25	15
2	$NiBr_2$·diglyme	dtbpy	NaOAc	NMP	25	8
3	$NiBr_2$·diglyme	dtbpy	NaOAc	DMSO	25	8
4	$NiBr_2$·diglyme	dtbpy	NaOAc	DMF	25	35
5	$NiBr_2$·diglyme	dtbpy	K_2CO_3	THF	25	3
7	$NiBr_2$·diglyme	dtbpy	Na_2CO_3	DMAC	25	17
8	$NiBr_2$·diglyme	dtbpy	Cs_2CO_3	DMAC	25	65
9	$NiBr_2$·diglyme	**12%dtbpy+15% binap**	**Cs_2CO_3**	DMAC	**25**	**90(84)[i]**
10	**$NiBr_2$·diglyme**	**binap**	**Cs_2CO_3**	**DMAC**	**25**	**8**
11	$NiBr_2$·diglyme	dtbpy	LiOMe	DMAC	25	45
12	$NiBr_2$·diglyme	dtbpy	KF	DMAC	25	40
13	$NiBr_2$·diglyme	dtbpy	CsF	DMAC	25	45
14[b]	$NiBr_2$·diglyme	dtbpy	Cs_2CO_3	DMAC	25	21
15[c]	$NiBr_2$·diglyme	dtbpy	Cs_2CO_3	DMAC	25	20
16[d]	$NiBr_2$·diglyme	dtbpy	Cs_2CO_3	DMAC	25	36
17[e]	$NiBr_2$·diglyme	dtbpy	Cs_2CO_3	DMAC	25	13
18[f]	$NiBr_2$·diglyme	dtbpy	Cs_2CO_3	DMAC	25	trace
19[g]	-	dtbpy	Cs_2CO_3	DMAC	25	trace
20	$Pd(OAc)_2$	PCy3	Cs_2CO_3	Toluene	25	6

[a] GC yields after 10 hours.[b]Triethoxysilane as Si-H.[c]$(Me_2HSi)_2O$ as Si-H. [d]Ph_2SiH_2 as Si-H.

[e]polymethylhydrosiloxane **as** Si-H. [f] Et_3SiH **as** Si-H. [g]without $NiBr_2$·diglyme.[h]Isolated yield. THF = Tetrahydrofuran, NMP = 1-Methyl-2-pyrrolidinone, DMSO = Dimethyl sulfoxide, DMF = N,N-Dimethylformamide, DMAC = N,N-Dimethylacetamide

Experimental Procedures for Examples Described inTable 2.

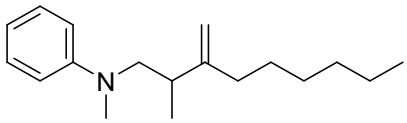
In air,$NiBr_2$·diglyme (10%), Cs_2CO_3 (2.5 equiv.), 12% dtbpyand 15% BINAP were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). 0.6 ml DMAC was added in turn under argon atmosphere. The reaction mixture was stirred at the room temperature for 5 minutes, 0.2mmol alkyl halide and alkyne (2.0 equiv)(If they were solid, adding with catalysttogether) was added were added and stirred for 5 minutes, then DEMS (Diethoxymethylsilane, 2.5 equiv) was added. The reaction was stirred at the indicated temperature for 10h. Then the reaction was diluted with EtOAc, filtered through silica gel with

copious washings. The residue was concentrated, and purified by column chromatography.

Experimental Procedures for Examples Described in Scheme3.

In air,$NiBr_2$·diglyme (10%), Cs_2CO_3 (2.5 equiv.), dtbpy (12%) and 15% BINAP were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). 20 ml DMAC was added in turn under argon atmosphere. 5 mmolalkyl halide and 7.5 mmolalkynewere added. The reaction mixture was stirred at the room temperature for 5 minutes,then DEMS (Diethoxymethylsilane) was added. The reaction was stirred at the indicated temperature for 10h. Then the reaction was diluted with EtOAc, filtered through silica gel with copious washings. The residue was concentrated, and purified by column chromatography.

Substrate scope

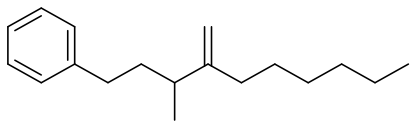


N-methyl-N-(2-methyl-3-methylenenonyl)aniline

Following general procedure, asa pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.06 (m, 2H), 6.68 (d, *J* = 7.5 Hz, 3H), 4.80 (m, 2H), 3.42 (dd, *J* = 14.6, 5.8 Hz, 1H), 3.15 (dd, *J* = 14.5, 8.6 Hz, 1H), 2.94 (s, 3H), 2.58 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.03 (d, *J* = 3.9 Hz, 2H), 1.47 – 1.39 (m, 2H), 1.29 (s, 6H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.32, 149.41, 129.24, 115.79, 111.91, 108.69, 59.04, 39.68, 38.39, 35.03, 31.95, 29.35, 28.17, 22.79, 18.22, 14.26.

HRMS (APCI) calcd for C18H30N ($M+H^+$): 260.2373; found: 260.2372

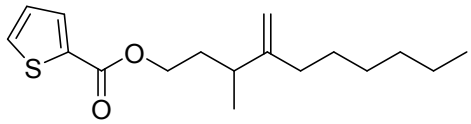


(3-methyl-4-methylenedecyl)benzene

Following general procedure, asa pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 4.86 – 4.65 (m, 2H), 2.55 (t, *J* = 8.1 Hz, 2H), 2.16 (dd, *J* = 13.7, 6.9 Hz, 1H), 2.03 – 1.92 (m, 2H), 1.68 – 1.51 (m, 2H), 1.46 – 1.37 (m, 2H), 1.36 – 1.20 (m, 6H), 1.06 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.41, 142.94, 128.39, 128.27, 125.59, 107.66, 39.71, 37.45, 33.82, 33.69, 31.87, 29.33, 28.04, 22.69, 20.24, 14.15.

HRMS (APCI)calcd for C18H29 ($M+H^+$): 245.2264; found: 245.2260



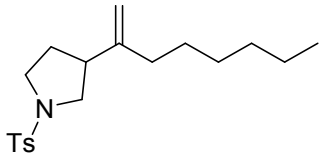
3-methyl-4-methylenedecyl thiophene-2-carboxylate

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 3.7,

1.2 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.10 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.83 – 4.70 (m, 2H), 4.36 – 4.15 (m, 2H), 2.38 – 2.26 (m, 1H), 2.02 – 1.96 (m, 2H), 1.88 (dd, *J* = 14.1, 7.3 Hz, 1H), 1.76 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.47 – 1.19 (m, 8H), 1.09 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.30, 153.47, 134.07, 133.25, 132.19, 127.71, 108.15, 63.78, 36.67, 34.23, 33.81, 31.83, 29.28, 27.99, 22.66, 20.27, 14.13.

HRMS (APCI)calcd for C17H27O2S ($M+H^+$):295.1726; found: 295.1725

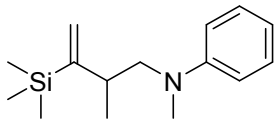


3-(oct-1-en-2-yl)-1-tosylpyrrolidine

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.72 (m, 1H), 4.63 (m, 1H), 3.52 (dd, *J* = 9.4, 7.7 Hz, 1H), 3.46 – 3.34 (m, 1H), 3.24 (td, *J* = 9.6, 6.9 Hz, 1H), 2.96 (t, *J* = 9.5 Hz, 1H), 2.63 – 2.52 (m, 1H), 2.42 (s, 3H), 2.00 – 1.69 (m, 3H), 1.71 – 1.49 (m, 1H), 1.36 – 1.13 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.19, 143.37, 134.01, 129.67, 127.50, 109.15, 52.09, 47.63, 43.86, 35.28, 31.71, 30.32, 29.02, 27.86, 22.61, 21.54, 14.09.

HRMS (APCI)calcd for C19H30O2NS ($M+H^+$):336.1992; found: 336.1991

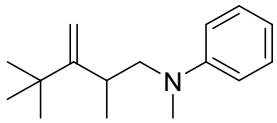


N-methyl-N-(2-methyl-3-(trimethylsilyl)but-3-en-1-yl)aniline

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.9 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 3H), 5.70 (m, 1H), 5.46 (m, 1H), 3.36 (dd, *J* = 14.6, 5.3 Hz, 1H), 3.26 – 3.13 (m, 1H), 2.93 (d, *J* = 6.5 Hz, 3H), 2.77 (dd, *J* = 14.3, 6.9 Hz, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.10 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.98, 149.46, 129.23, 124.33, 115.79, 111.95, 59.41, 39.71, 37.04, 19.60, -0.94.

HRMS (APCI)calcd for C15H26NSi ($M+H^+$):248.1829; found:248.1832

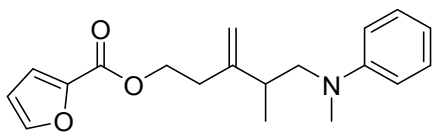


N-methyl-N-(2,4,4-trimethyl-3-methylenepentyl)aniline

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 13.5, 5.0 Hz, 2H), 6.67 (dd, *J* = 14.0, 7.7 Hz, 3H), 5.02 (m, 1H), 4.85 (m, 1H), 3.34 (dd, *J* = 14.7, 5.9 Hz, 1H), 3.24 (dd, *J* = 14.7, 9.1 Hz, 1H), 2.96 (s, 3H), 2.71 (dd, *J* = 14.4, 6.9 Hz, 1H), 1.05 (s, 9H), 0.94 (d, *J* = 12.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.27, 149.36, 129.13, 115.58, 111.68, 106.23, 60.47, 39.73, 36.97, 33.14, 28.74, 21.65.

HRMS (APCI)calcd for C16H26N ($M+H^+$):232.2060; found: 232.2059

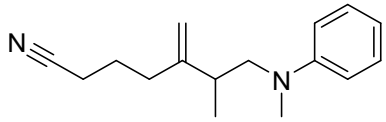


4-methyl-5-(methyl(phenyl)amino)-3-methylenepentyl furan-2-carboxylate

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.23 (dd, *J* = 13.9, 6.2 Hz, 2H), 7.16 (d, *J* = 3.4 Hz, 1H), 6.81 – 6.63 (m, 3H), 6.50 (dd, *J* = 3.3, 1.6 Hz, 1H), 4.96 (m,1H), 4.91(m,1H), 4.42 (t, *J* = 6.9 Hz, 2H), 3.41 (dd, *J* = 14.6, 6.4 Hz, 1H), 3.21 (dd, *J* = 14.6, 8.1 Hz, 1H), 2.95 (s, 3H), 2.73 – 2.64 (m, 1H), 2.50 (dd, *J* = 13.1, 6.7 Hz, 2H), 1.08 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.66, 149.34, 148.37, 146.31, 144.69, 129.16, 117.90, 115.94, 111.91, 111.83, 111.45, 63.58, 58.72, 39.47, 38.60, 33.37, 17.75.

HRMS (APCI)calcd for C19H24O3N ($M+H^+$):314.1751; found:314.1751

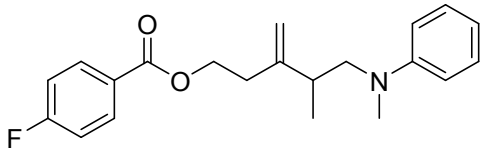


6-methyl-7-(methyl(phenyl)amino)-5-methyleneheptanenitrile

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 11.6, 4.3 Hz, 2H), 6.68 (t, *J* = 8.2 Hz, 3H),4.93 (m, 1H),4.84(m,1H), 3.40 (dd, *J* = 14.6, 6.5 Hz, 1H), 3.19 (dd, *J* = 14.6, 8.0 Hz, 1H), 2.94 (s, 3H), 2.58 (dd, *J* = 14.2, 7.1 Hz, 1H), 2.32 (t, *J* = 7.1 Hz, 2H), 2.25 – 2.11 (m, 2H), 1.92 – 1.68 (m, 2H), 1.06 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.65, 149.21, 129.20, 119.64, 116.04, 111.97, 110.34, 58.89, 39.58, 38.12, 33.52, 23.59, 18.09, 16.65.

HRMS (APCI)calcd for C16H23N2 ($M+H^+$):243.1856; found: 243.1851



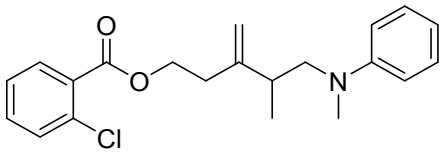
4-methyl-5-(methyl(phenyl)amino)-3-methylenepentyl 4-fluorobenzoate

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.1, 6.0 Hz, 2H), 7.31 – 7.16 (m, 2H), 7.09 (t, *J* = 8.5 Hz, 2H), 6.69 (d, *J* = 7.2 Hz, 3H), 4.95 (m, 2H), 4.43 (t, *J* = 6.9 Hz, 2H), 3.43 (dd, *J* = 14.6, 6.3 Hz, 1H), 3.21 (dd, *J* = 14.5, 8.1 Hz, 1H), 2.95 (s, 3H), 2.67 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.53 (dd, *J* = 14.4, 7.5 Hz, 2H), 1.09 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.84 (d, *J* = 253.7 Hz), 165.67, 149.31, 148.71, 132.20 (d, *J* = 9.3 Hz), 129.27, 126.64 (d, *J* = 2.9 Hz), 116.08, 115.62 (d, *J* = 22.0 Hz), 112.03, 111.45, 63.72, 58.92, 39.61, 38.57, 33.70, 17.97.

^{19}F NMR (376 MHz, $CDCl_3$) δ -105.72 (s).

HRMS (APCI)calcd for C21H25O2NF ($M+H^+$):342.1864; found: 342.1860

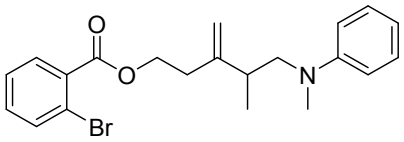


4-methyl-5-(methyl(phenyl)amino)-3-methylenepentyl 2-chlorobenzoate

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.51 – 7.36 (m, 2H), 7.30 (td, *J* = 7.7, 1.4 Hz, 1H), 7.23 (dd, *J* = 13.7, 6.4 Hz, 2H), 6.67 (t, *J* = 7.1 Hz, 3H), 4.96 (m, 2H), 4.53 – 4.37 (m, 2H), 3.42 (dd, *J* = 14.6, 6.3 Hz, 1H), 3.22 (dd, *J* = 14.6, 8.1 Hz, 1H), 2.95 (s, 3H), 2.67 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.61 – 2.42 (m, 2H), 1.09 (d, *J* = 6.9 Hz, 3H).

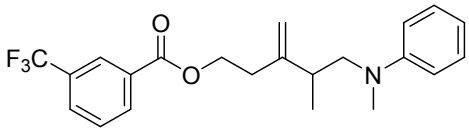
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.67, 149.25, 148.48, 133.71, 132.52, 131.35, 131.09, 130.25, 129.18,

126.59, 115.97, 111.95, 111.39, 64.03, 58.79, 39.50, 38.49, 33.48, 17.86.
HRMS (APCI)calcd for C21H25O2NCl (M+H$^+$):358.1568; found: 358.1568



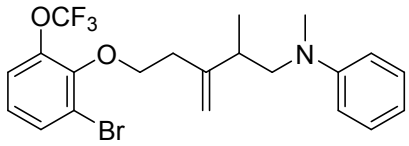
4-methyl-5-(methyl(phenyl)amino)-3-methylenepentyl 2-bromobenzoate

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.66 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.22 (t, *J* = 7.7 Hz, 2H), 6.69 (d, *J* = 7.1 Hz, 3H), 4.96 (m, 2H), 4.46 (t, *J* = 6.8 Hz, 2H), 3.42 (dd, *J* = 14.5, 6.3 Hz, 1H), 3.22 (dd, *J* = 14.6, 8.1 Hz, 1H), 2.95 (s, 3H), 2.67 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.59 – 2.47 (m, 2H), 1.09 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.15, 149.24, 148.44, 134.36, 132.53, 132.31, 131.26, 129.18, 127.18, 121.68, 115.98, 111.95, 111.41, 64.11, 58.81, 39.51, 38.48, 33.46, 17.87.
HRMS (APCI)calcd for C21H25O2NBr (M+H$^+$):402.1063; found: 402.1063



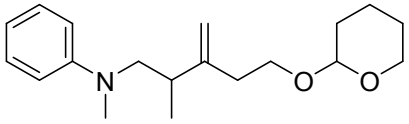
4-methyl-5-(methyl(phenyl)amino)-3-methylenepentyl 3-(trifluoromethyl)benzoate

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.20 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.23 (dd, *J* = 13.1, 5.8 Hz, 2H), 6.67 (dd, *J* = 15.3, 8.3 Hz, 3H), 4.96 (m, 2H), 4.60 – 4.40 (m, 2H), 3.48 – 3.40 (m, 1H), 3.35 – 3.15 (m, 1H), 2.96 (s, 3H), 2.68 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.53 (dt, *J* = 15.5, 7.7 Hz, 2H), 1.10 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.21, 149.23, 148.50, 132.79, 131.17, 131.06 (q, *J* = 33.1 Hz), 129.46 (q, *J* = 3.6 Hz), 129.18, 129.09, 126.52 (q, *J* = 3.8 Hz), 123.70 (q, *J* = 272.4 Hz), 116.02, 111.95, 111.48, 64.04, 58.84, 39.51, 38.50, 33.56, 17.86.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.78 (s).
HRMS (APCI)calcd for C22H25F3NO2r (M+H$^+$):392.1832; found: 392.1831



N-(5-(2-bromo-6-(trifluoromethoxy)phenoxy)-2-methyl-3-methylenepentyl)-N-methylaniline

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.6 Hz, 1H), 7.28 – 7.08 (m, 2H), 6.86 – 6.62 (m, 5H), 4.99 (m, 2H), 4.06 (dd, *J* = 12.2, 6.8 Hz, 2H), 3.44 (dd, *J* = 14.6, 6.7 Hz, 1H), 3.25 (dd, *J* = 14.6, 7.9 Hz, 1H), 2.96 (s, 3H), 2.71 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.59 (t, *J* = 6.8 Hz, 2H), 1.10 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.19, 149.33, 149.25, 148.84, 133.74, 129.30, 120.46 (q, *J* = 257.8 Hz), 116.10, 113.92, 112.07, 111.78, 110.10, 106.67, 68.55, 58.91, 39.73, 38.68, 34.02, 18.11.
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.89 (s).
HRMS (APCI)calcd for C21H24O2NBrF3 (M+H$^+$):458.0937; found: 458.0939

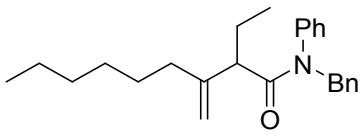


N-methyl-N-(2-methyl-3-methylene-5-((tetrahydro-2H-pyran-2-yl)oxy)pentyl)aniline

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 6.96 (m, 2H), 6.68 (t, *J* = 7.5 Hz, 3H), 4.87 (m, 2H), 4.69 – 4.46 (m, 1H), 3.88 (dd, *J* = 16.2, 8.3 Hz, 2H), 3.57 – 3.46 (m, 2H), 3.45 – 3.36 (m, 1H), 3.19 (dd, *J* = 14.6, 8.5 Hz, 1H), 2.96 (s, 3H), 2.65 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.38 (dd, *J* = 12.1, 6.8 Hz, 2H), 1.83 (dt, *J* = 9.8, 6.3 Hz, 1H), 1.75 – 1.66 (m, 1H), 1.61 – 1.47 (m, 4H), 1.07 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.68, 149.63, 149.27, 129.13, 115.76, 111.85, 110.45, 99.00, 66.73, 66.67, 62.49, 62.45, 58.65, 39.51, 39.49, 38.87, 34.43, 34.36, 30.76, 30.75, 25.48, 19.71, 19.68, 17.75, 17.74.

HRMS (APCI)calcd for C19H30O2N ($M+H^+$):304.2271; found: 304.2273

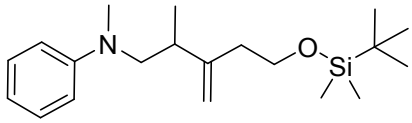


N-benzyl-2-ethyl-3-methylene-N-phenylnonanamide

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.15 (m, 8H), 6.93 (dd, *J* = 6.6, 3.0 Hz, 2H), 4.89 (m, 2H), 4.75 (s, 2H), 2.78 (dd, *J* = 9.1, 5.3 Hz, 1H), 1.94 – 1.78 (m, 2H), 1.77 – 1.66 (m, 1H), 1.59 – 1.46 (m, 1H), 1.32 – 1.08 (m, 8H), 0.85 (dt, *J* = 13.5, 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.05, 148.13, 142.38, 138.00, 129.33, 129.26, 129.02, 128.41, 127.94, 127.36, 110.98, 53.31, 51.60, 34.28, 31.87, 29.24, 27.67, 25.70, 22.74, 14.24, 12.84.

HRMS (APCI)calcd for C25H34NO ($M+H^+$):364.2635; found: 364.2631

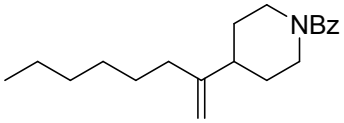


N-(5-(tert-butyldimethylsilyl)-2-methyl-3-methylenepentyl)-N-methylaniline

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.09 (m, 2H), 6.79 – 6.52 (m, 3H),4.85 (m, 1H), 4.80 (d, *J* = 0.9 Hz, 1H), 3.70 (t, *J* = 7.3 Hz, 2H), 3.39 (dd, *J* = 14.6, 6.1 Hz, 1H), 3.15 (dd, *J* = 14.6, 8.4 Hz, 1H), 2.93 (s, 3H), 2.59 (dd, *J* = 14.5, 6.9 Hz, 1H), 2.37 – 2.06 (m, 2H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.81, 149.38, 129.25, 115.87, 111.95, 110.72, 62.79, 58.83, 39.65, 38.84, 38.01, 26.10, 18.49, 17.91, -5.14.

HRMS (APCI)calcd for C20H36ONSi ($M+H^+$):334.2561; found: 334.2562

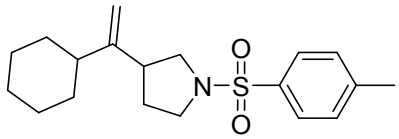


(4-(oct-1-en-2-yl)piperidin-1-yl)(phenyl)methanone

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 5H), 4.88 – 4.55 (m, 3H), 4.06 – 3.58 (m, 1H), 3.18 – 2.84 (m, 1H), 2.84 – 2.63 (m, 1H), 2.15 – 2.07 (m, 1H), 2.05 – 1.97 (m, 2H), 1.92 – 1.81 (m, 1H), 1.75 – 1.61 (m, 1H), δ 1.52 – 1.19 (m, 10H), 0.89 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.37, 152.88, 136.42, 129.53, 128.50, 126.93, 108.09, 48.42, 42.82, 42.36, 34.84, 32.07, 31.85, 31.22, 29.23, 28.19, 22.72, 14.18.

HRMS (APCI)calcd for C20H30NO ($M+H^+$):300.2322; found: 300.2318

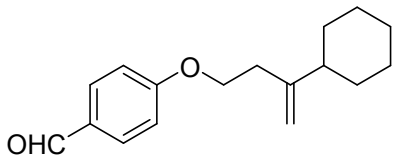


3-(1-cyclohexylvinyl)-1-tosylpyrrolidine

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.76(m,1H), 4.65 (m,1H), 3.54 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.49 – 3.31 (m, 1H), 3.28 – 3.18 (m, 1H), 2.93 (t, *J* = 9.6 Hz, 1H), 2.68 – 2.58 (m, 1H), 2.44 (s, 3H), 2.00 – 1.84 (m, 1H), 1.77 – 1.42 (m, 7H), 1.29 – 0.82 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.04, 143.47, 134.23, 129.78, 127.62, 107.83, 52.99, 47.74, 43.78, 43.35, 33.09, 33.03, 31.31, 26.82, 26.81, 26.32, 21.66.

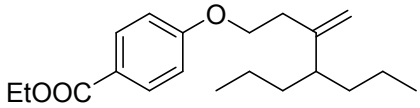
HRMS (APCI)calcd for C19H28NO2S ($M+H^+$):334.1835; found: 334.1833



4-((3-cyclohexylbut-3-en-1-yl)oxy)benzaldehyde

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.91-4.69 (m, 2H), 4.14 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.96 – 1.50 (m, 5H), 1.33 – 0.96 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 190.95, 164.15, 151.05, 132.14, 130.01, 114.94, 109.43, 67.75, 44.78, 34.07, 32.44, 26.85, 26.45.

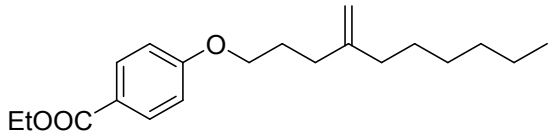
HRMS (ESI) calcd forC17H22ONa ($M+Na^+$):281.1512; found: 281.1510



Following general procedure, asa pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 4.85 (m, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.14 (t, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.18 – 1.96 (m, 1H), 1.43 – 1.14 (m, 11H), 0.88 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.55, 162.72, 148.28, 131.67, 122.94, 114.12, 111.11, 67.15, 60.74, 46.78, 36.26, 31.42, 20.72, 14.52, 14.35.

HRMS (ESI) calcd forC20H31O3 ($M+H^+$): 319.2268； found: 319.2260

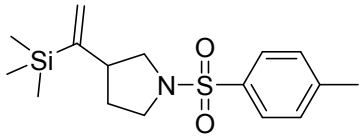


ethyl 4-((4-methylenedecyl)oxy)benzoate

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.76 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 2.12 – 1.99 (m, 2H), 1.99 – 1.80 (m, 2H), 1.50 – 1.33 (m, 5H), 1.30 (dd, *J* = 9.5, 4.4 Hz, 6H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 162.91, 149.00, 131.64, 122.83, 114.12, 109.42, 67.74, 60.75, 36.23, 32.25, 31.91, 29.22, 27.86, 27.26, 22.78, 14.53, 14.26.

HRMS (APCI) calcd for C20H31O3 ($M+H^+$):319.2268; found: 319.2267

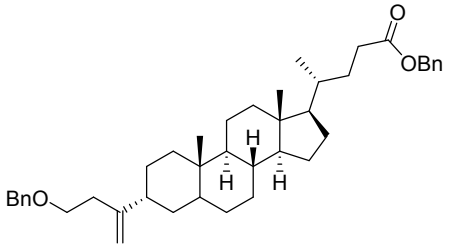


1-tosyl-3-(1-(trimethylsilyl)vinyl)pyrrolidine

Following general procedure, as a pale-yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.46 (m, 1H), 5.31 (d, *J* = 1.0 Hz, 1H), 3.52 (dd, *J* = 9.5, 7.4 Hz, 1H), 3.46 – 3.34 (m, 1H), 3.26 (td, *J* = 9.5, 6.9 Hz, 1H), 2.95 (t, *J* = 9.5 Hz, 1H), 2.69 (dd, *J* = 15.9, 8.2 Hz, 1H), 2.44 (s, 3H), 1.98 – 1.76 (m, 1H), 1.67 – 1.50 (m, 1H), 0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.72, 143.46, 134.11, 129.75, 127.57, 124.44, 53.08, 47.60, 43.40, 31.45, 21.61, -1.12.

HRMS (APCI) calcd for C16H26NO2SSi ($M+H^+$):324.1448; found: 324.1445



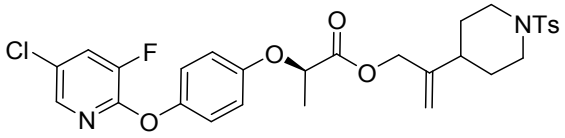
benzyl (4R)-4-((3R,8R,9S,10S,13R,14S,17R)-3-(4-(benzyloxy)but-1-en-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate.

Following general procedure, as a sticky bubble.The dr was determined to be 5:1 by NMR. The assignment of 3β configuration in the major isomer was based on the large coupling constant at 2.27 ppm, typical of an axial proton in a cyclohexane chair system[3].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.11 (m, 10H), 5.11 (d, *J* = 2.7 Hz, 2H), 4.98 – 4.89 (m, 0.29H), 4.82 – 4.66 (m, 2H), 4.59 – 4.42 (m, 2H), 3.68 – 3.51 (m, 2H), δ 2.52 – 2.19 (m, 5H), 2.00 – 1.74 (m, 5H), 1.71 – 1.49 (m, 2H), 1.47 – 1.29 (m, 9H), 1.28 – 1.14 (m, 5H), 1.14 – 0.98 (m, 6H), 0.95 – 0.84 (m, 6H), 0.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.27, 151.92, 138.61, 136.26, 128.66, 128.49, 128.35, 128.28, 127.81, 127.67, 108.35, 73.08, 69.67, 66.20, 56.58, 56.08, 45.22, 43.91, 42.86, 40.75, 40.28, 37.60, 36.00, 35.45, 35.17, 34.86, 32.88, 31.40, 31.12, 28.31, 27.63, 26.68, 26.65, 24.33, 24.10, 20.96, 18.39, 12.17.

HRMS(ESI) calcd for C42H58O3Na ($M+Na^+$): 633.4278; found: 633.4273;



2-(1-tosylpiperidin-4-yl)allyl (R)-2-(4-((5-chloro-3-fluoropyridin-2-yl)oxy)phenoxy)propanoate

Following general procedure, white solid, melting point: 201-213^{o}C.

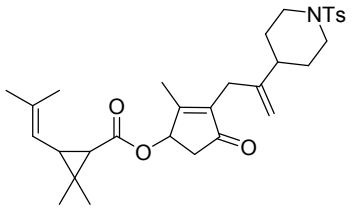
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.51 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.01 – 6.94 (m, 2H), 6.88 – 6.81 (m, 2H), 5.06 (m, 1H), 4.90 (m, 1H),

4.73 (q, *J* = 6.8 Hz, 1H), 4.65 (d, *J* = 12.9 Hz, 1H), 4.54 (d, *J* = 12.9 Hz, 1H), 3.81 (dd, *J* = 9.8, 2.0 Hz, 2H), 2.42 (s, 3H), 2.13 (ddd, *J* = 25.2, 12.0, 2.1 Hz, 2H), 1.76 – 1.65 (m, 3H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.57 – 1.45 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.29.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.88, 154.94, 151.37 (d, *J* = 11.2 Hz), 147.08, 147.08 (d, *J* = 265.8 Hz), 145.98, 143.59, 140.28 (d, *J* = 6.1 Hz), 133.16, 129.73, 127.86, 125.21, 125.03, 122.41, 115.93, 113.66, 73.17, 66.88, 46.64, 46 61, 38.50, 30.44, 30.36, 21.64, 18.74.

HRMS(ESI) calcd forC29H30ClFN2NaO6S(M+Na+): 611.1389; found: 611.1380

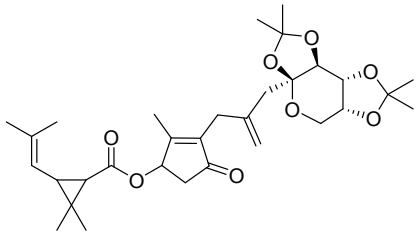


2-methyl-4-oxo-3-(2-(1-tosylpiperidin-4-yl)allyl)cyclopent-2-en-1-yl-2,2-dimethyl-3-(2-methylprop-1-en-1-yl)cyclopropane-1-carboxylate

Following general procedure, asa sticky bubble.(dr≈1:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 5.69 (dd, *J* = 27.9, 6.0 Hz, 1H), 4.88 (t, *J* = 6.5 Hz, 1H), 4.73 (m, 1H), 4.56 (m, 1H), 3.84 (d, *J* = 11.1 Hz, 2H), 3.00 – 2.67 (m, 3H), 2.42 (s, 3H), 2.20 (dd, *J* = 21.8, 11.4 Hz, 3H), 2.09 – 2.03 (m, 1H), 1.96 (t, *J* = 7.5 Hz, 3H), 1.82 (d, *J* = 12.1 Hz, 2H), 1.76 – 1.63 (m, 7H), 1.57 (t, *J* = 12.1 Hz, 2H), 1.38 (t, *J* = 4.7 Hz, 1H), 1.31 – 1.20 (m, 3H), 1.13 (d, *J* = 3.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.06, 203.99, 172.37, 172.35, 167.25, 167.16, 148.18, 143.55, 141.45, 141.39, 136.02, 135.19, 133.11, 129.71, 129.67, 127.81, 120.84, 120.77, 109.67, 72.89, 72.62, 46.75, 46.17, 42.05, 41.68, 41.42, 41.39, 34.61, 34.55, 33.33, 33.14, 30.62, 30.59, 29.29, 29.27, 27.95, 27.92, 25.67, 22.24, 22.20, 21.62, 20.60, 20.49, 18.59, 14.30, 14.18.

HRMS(ESI) calcd forC31H41NNaO5S(M+Na+): 562.2598; found: 562.2591



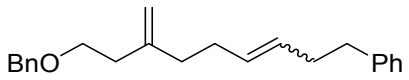
2-methyl-4-oxo-3-(2-(((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl)allyl)cyclopent-2-en-1-yl-2,2-dimethyl-3-(2-methylprop-1-en-1-yl)cyclopropane-1-carboxylate

Following general procedure, as a pale-yellow liquid.(dr≈1:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (dd, *J* = 34.6, 5.8 Hz, 1H), 4.95 (s, 1H), 4.90 (s, 1H), 4.83 (s, 1H), 4.60 (d, *J* = 7.8 Hz, 1H), 4.26 – 4.14 (m, 2H), 3.88 (d, *J* = 12.9 Hz, 1H), 3.73 (d, *J* = 12.9 Hz, 1H), 3.14 (q, *J* = 16.0 Hz, 2H), 2.93 – 2.74 (m, 1H), 2.66 (dd, *J* = 13.8, 3.0 Hz, 1H), 2.46 (d, *J* = 13.8 Hz, 1H), 2.34 – 2.18 (m, 1H), 2.13 – 2.01 (m, 4H), 1.71 (d, *J* = 4.0 Hz, 6H), 1.51 (d, *J* = 13.6 Hz, 6H), 1.36 (d, *J* = 9.8 Hz, 6H), 1.28 (d, *J* = 10.1 Hz, 4H), 1.16 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.31, 204.18, 172.46, 166.97, 166.86, 141.99, 141.88, 140.28, 140.23, 135.99, 120.94, 120.88, 116.27, 116.17, 109.12, 108.07, 108.05, 103.49, 103.44, 73.08, 73.05, 72.73,

71.01, 70.71, 61.37, 46.59, 46.48, 42.23, 41.86, 34.72, 34.68, 33.27, 33.06, 30.84, 30.79, 29.25, 29.22, 26.67, 26.08, 25.70, 25.30, 24.27, 22.29, 22.23, 20.65, 20.53, 18.63, 14.52, 14.44.

HRMS(ESI) calcd forC31H44NaO8(M+Na+): 567.2928; found: 567.2935

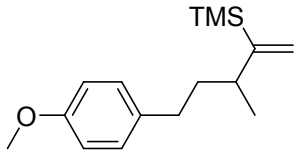


(9-(benzyloxy)-7-methylenenon-3-en-1-yl)benzene

Following general procedure, as a pale-yellow liquid.[1]H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 4H), 7.30 – 7.23 (m, 3H), 7.20 – 7.13 (m, 3H), 5.54 – 5.26 (m, 2H),4.78 (2H), 4.51 (d, *J* = 2.8 Hz, 2H), 3.69 – 3.24 (m, 2H), 2.76 – 2.53 (m, 2H), 2.45 – 2.16 (m, 4H), 2.15 – 1.88 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.29, 142.24, 138.59, 130.43, 129.96, 129.87, 129.17, 128.59, 128.49, 128.39, 128.35, 127.80, 127.67, 125.91, 125.83, 110.73, 73.06, 69.06, 36.39, 36.33, 36.28, 36.25, 36.22, 36.08, 34.56, 30.91, 29.36, 25.64.

HRMS (ESI) calcd forC23H28NaO ($M+Na^+$):343.2032; found: 343.2030

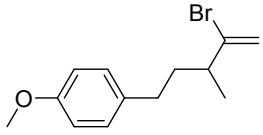


(5-(4-methoxyphenyl)-3-methylpent-1-en-2-yl)trimethylsilane

Following general procedure, as a pale-yellow liquid.[1]H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.85 (m, 2H), 6.77 – 6.61 (m, 2H), 5.55 – 5.48 (m, 1H), 5.36 – 5.19 (m, 1H), 3.69 (s, 3H), 2.46 (d, *J* = 7.6 Hz, 2H), 2.31 – 2.13 (m, 1H), 1.71 – 1.57 (m, 1H), 1.55 – 1.42 (m, 1H), 0.94 (dd, *J* = 17.8, 6.8 Hz, 3H), 0.06 – -0.07 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.73, 157.64, 135.16, 129.32, 122.98, 113.83, 55.40, 39.02, 38.69, 33.30, 21.49, -0.72.

HRMS(ESI) calcd forC16H26NaOSi ($M+Na^+$):285.1645; found: 285.1641



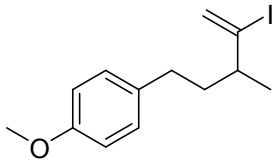
1-(4-bromo-3-methylpent-4-en-1-yl)-4-methoxybenzene

^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.91 – 6.57 (m, 2H), 5.61 (d, *J* = 1.4 Hz, 1H), 5.43 (d, *J* = 1.5 Hz, 1H), 3.78 (s, 3H), 2.60 – 2.52 (m, 1H), 2.49 – 2.41 (m, 1H), 2.37 – 2.31 (m, 1H), 1.87 – 1.69 (m, 1H), 1.64 – 1.49 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.86, 141.45, 134.19, 129.41, 116.19, 113.86, 55.37, 43.53, 37.00, 32.42, 20.32.

HRMS (ESI) calcd for C13H18BrO ($M+H^+$):269.0536; found: 269.0533

To a stirred solution of (5-(4-methoxyphenyl)-3-methylpent-1-en-2-yl)trimethylsilane in CH_2Cl_2 (3 mL) at -78 °C was added in the dark a solution of bromine in CH_2Cl_2. The mixture was stirred for 5 min at -78 °C, gradually warmed to 0 °C, at this temperature and then treated with Na_2SO_3.The aqueous layer was extracted with CH_2Cl_2 (3×). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$ and concentrated. The crude material was purified with flash chromatography.[4, 5]

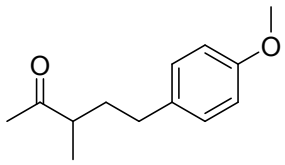


1-(4-iodo-3-methylpent-4-en-1-yl)-4-methoxybenzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.15 (dd, *J* = 1.2, 0.7 Hz, 1H), 5.78 (d, *J* = 1.4 Hz, 1H), 3.79 (s, 3H), 2.59 – 2.47 (m, 1H), 2.47 – 2.41 (m, 1H), 1.83 – 1.74 (m, 1H), 1.69 – 1.59 (m, 1H), 1.54 – 1.45 (m, 1H), 1.00 (d, *J* = 6.5 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.89, 134.21, 129.45, 124.81, 123.28, 113.89, 55.40, 45.69, 38.42, 32.41, 21.76.

HRMS (ESI) calcd for C13H18IO ($M+H^+$):317.0397; found: 317.0395

To an anhydrous CH_2Cl_2 (10 mL) solution of (5-(4-methoxyphenyl)-3-methylpent-1-en-2-yl) trimethylsilanewas added dropwise a solution of sublimationI_2in CH_2Cl_2(10 mL) at 0 °C. After stirring for 30 min, the mixture was stirred for 2 h at r.t., treated with sat. aq $Na_2S_2O_3$ (10 mL). The organic layer was washed with H_2O (2 × 10 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel.[6, 7]

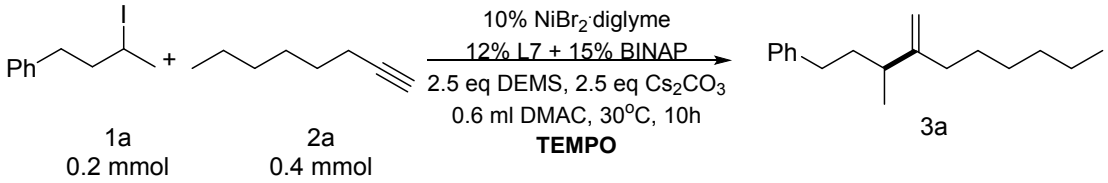


5-(4-methoxyphenyl)-3-methylpentan-2-one[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 6.99 (m, 2H), 6.93 – 6.35 (m, 2H), 3.79 (s, 3H), 2.65 – 2.43 (m, 3H), 2.12 (s, 3H), 2.05 – 1.69 (m, 1H), 1.63 – 1.48 (m, 1H), 1.12 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.78, 157.94, 133.82, 129.38, 113.92, 55.37, 46.52, 34.74, 32.55, 28.26, 16.40.

HRMS (ESI) calcd for C13H19O2 ($M+H^+$):207.1380; found: 207.1379



TEMPO	Yield %
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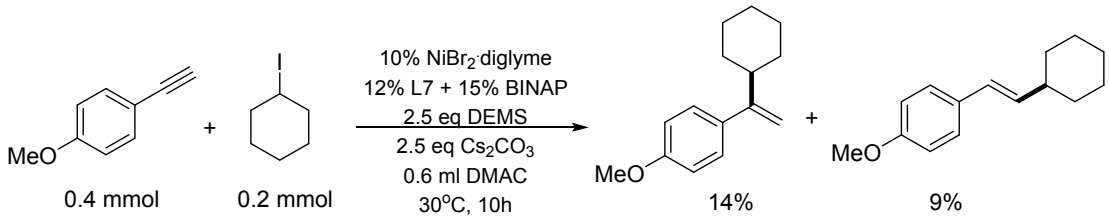
0.2 eq	55
0.5 eq	26
1.0 eq	trace



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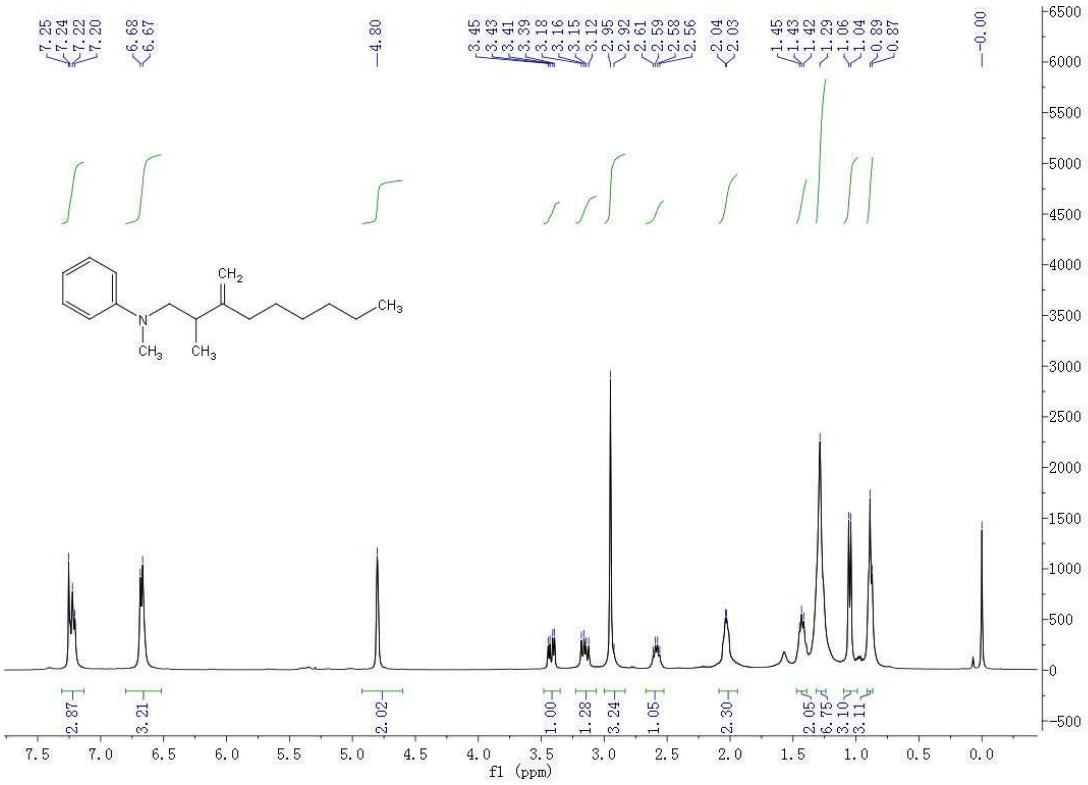
NMR Spectra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3.43
3.41
3.39
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3.15
3.12
2.95
2.92
2.61
2.59
2.58
2.56
2.04
2.03
1.45
1.43
1.42
1.29
1.06
1.04
0.89
0.87
0.00
CH2
CH3
N
CH3
CH3
2.87
3.21
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1.05
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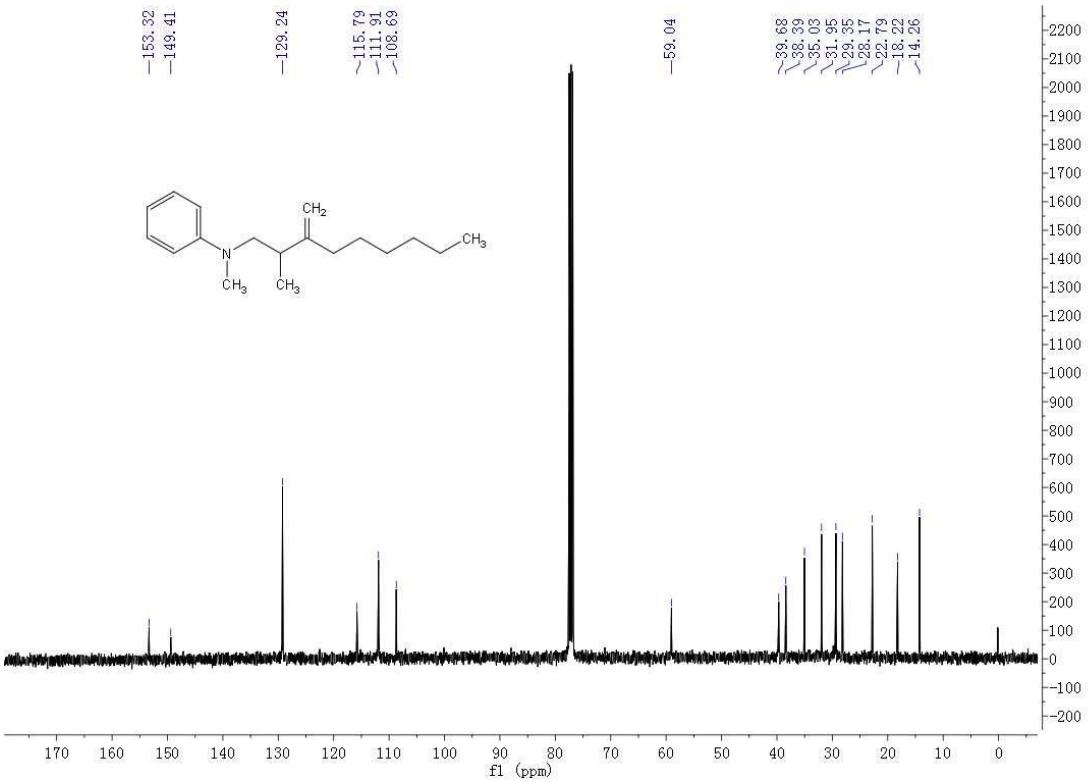
3.11
f1 (ppm)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CH3
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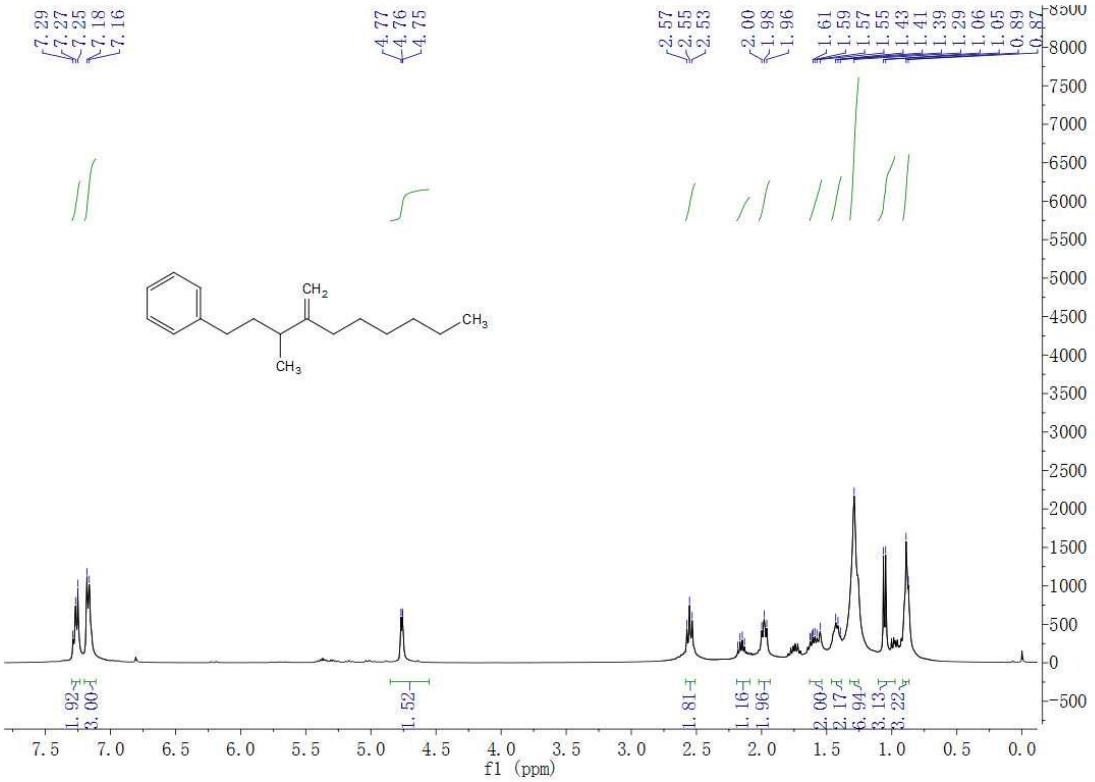
CH3
CH3
f1 (ppm)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1.59
1.57
1.55
1.43
1.41
1.39
1.29
1.06
1.05
0.89
0.87
CH2
CH3
CH3
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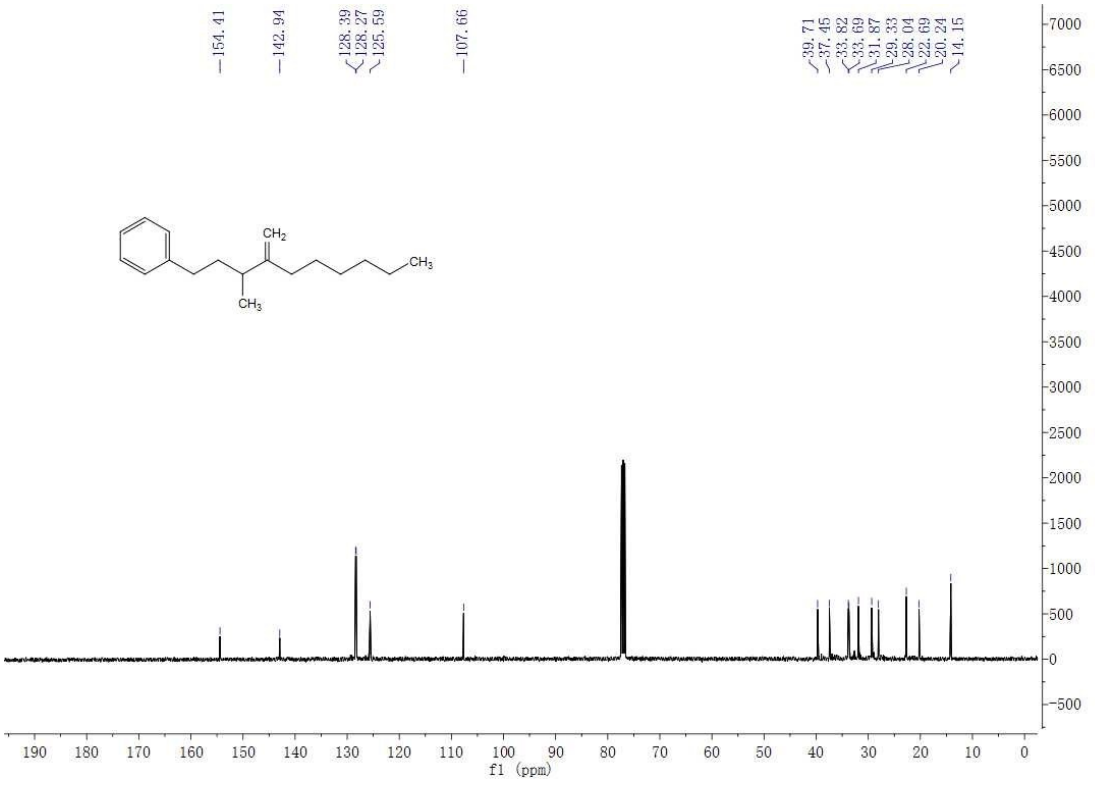
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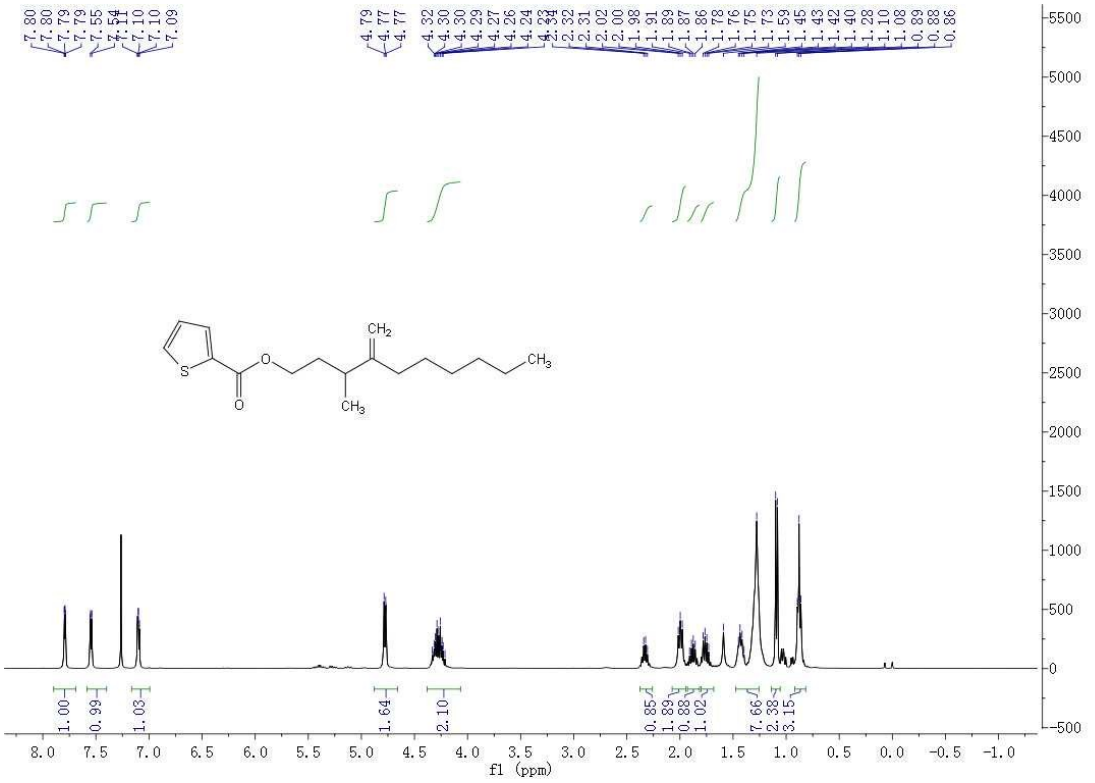
CH3
f1 (ppm)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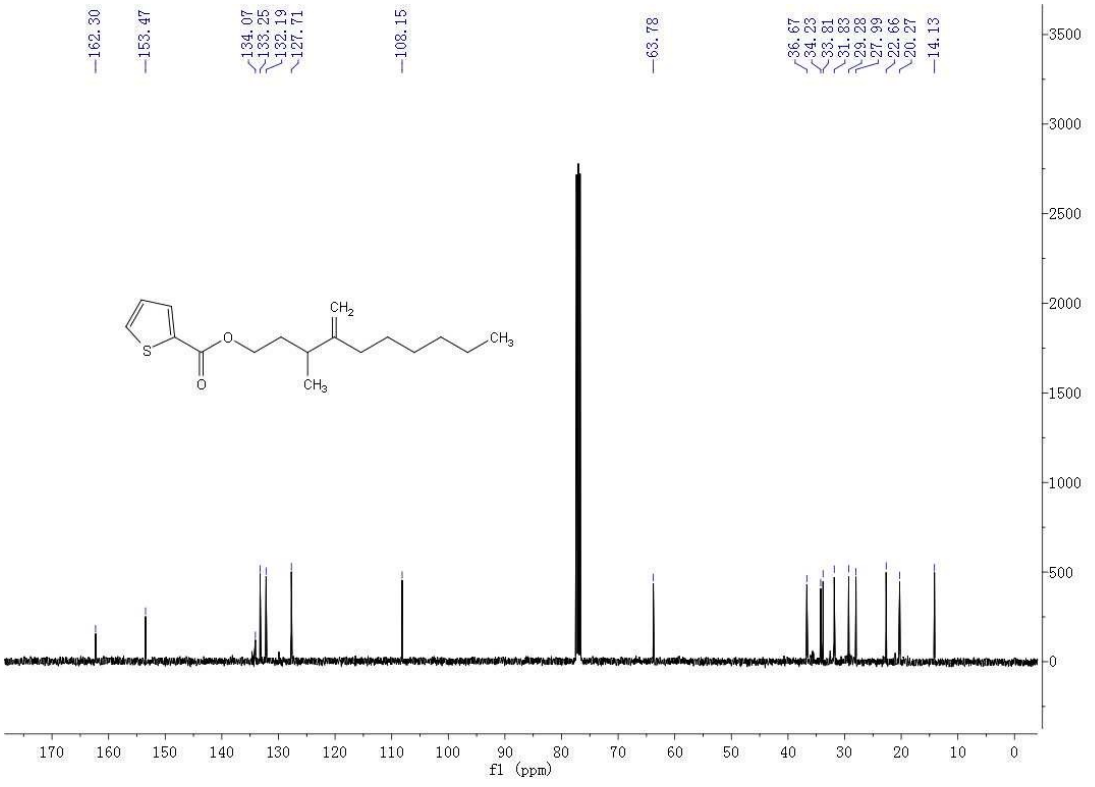
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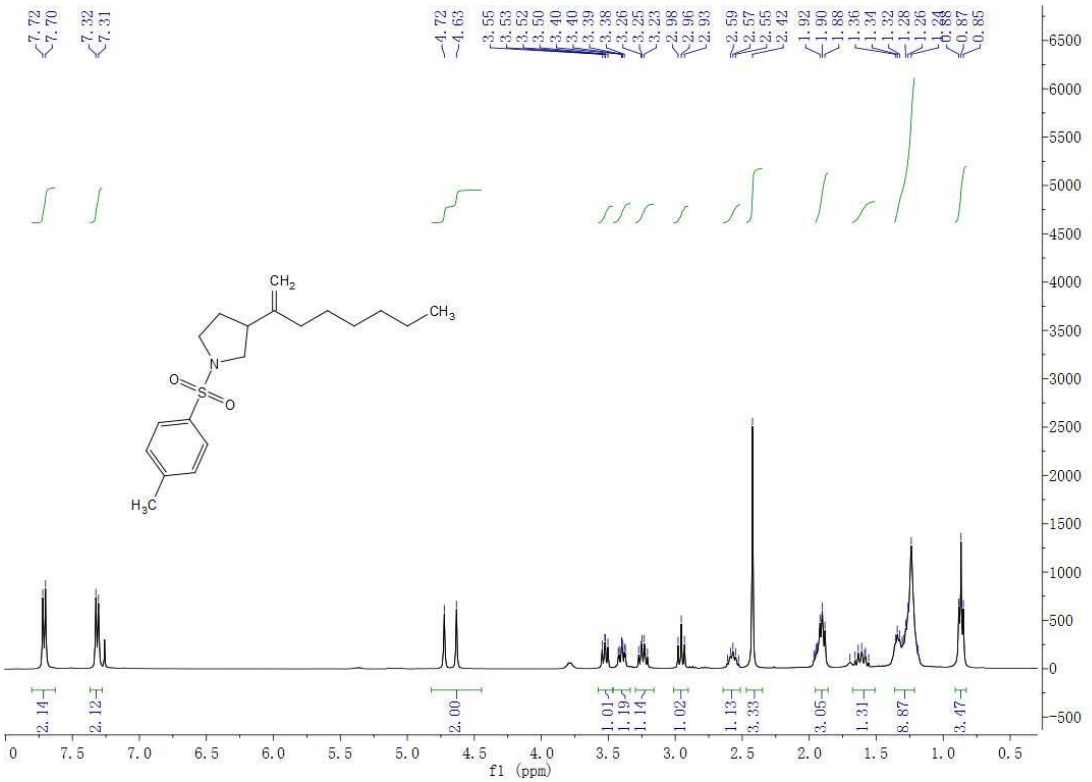
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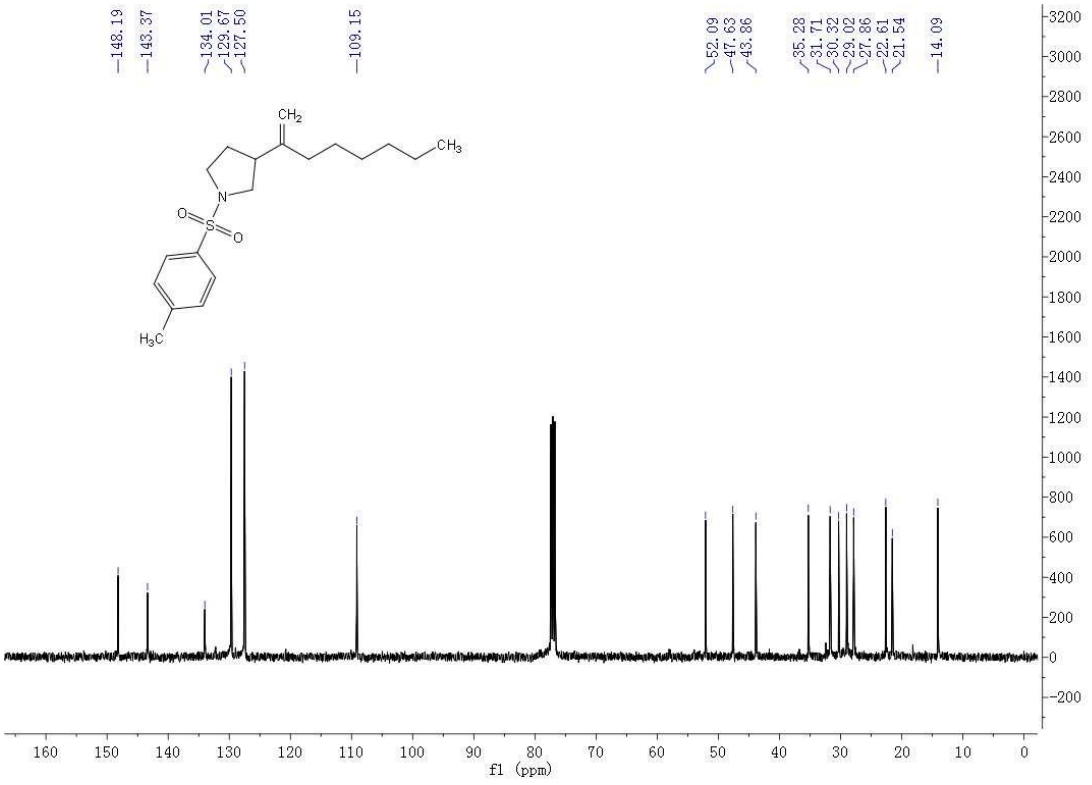
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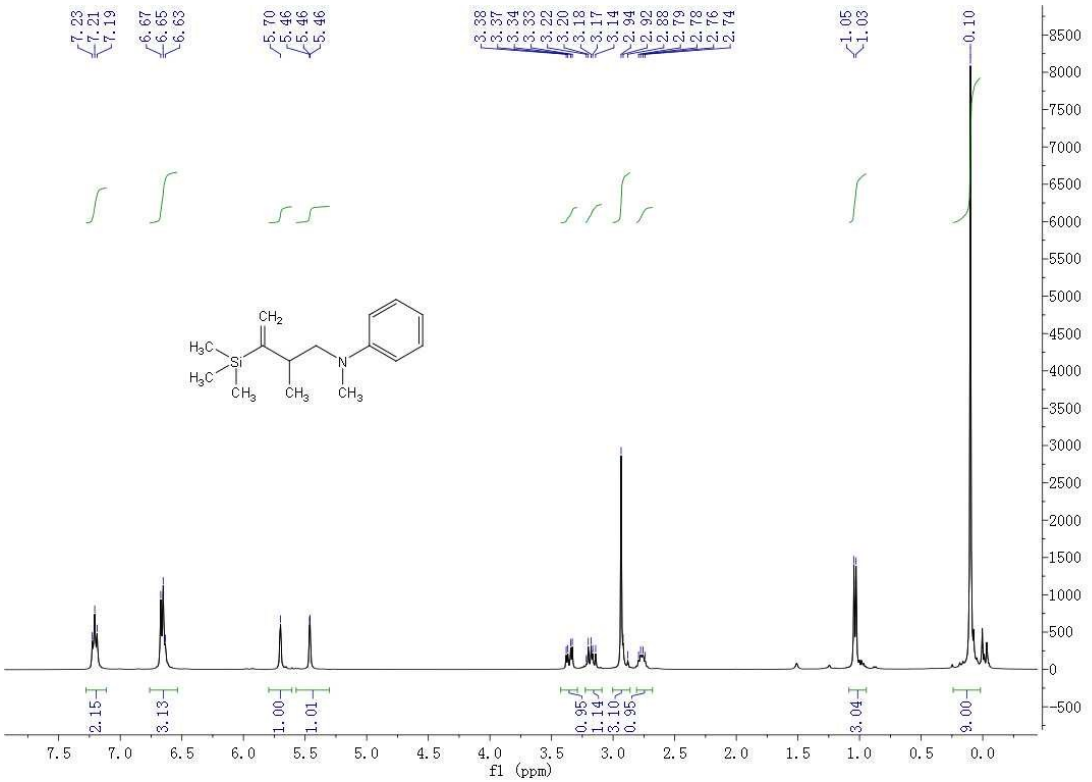
f1 (ppm)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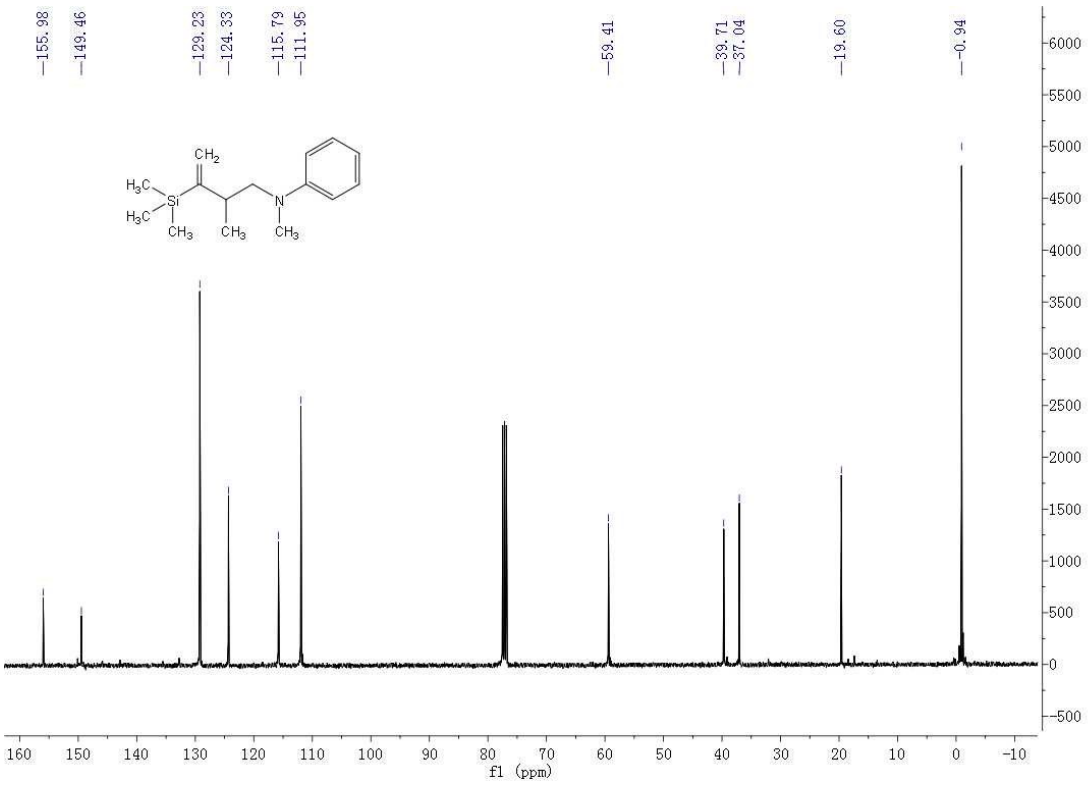
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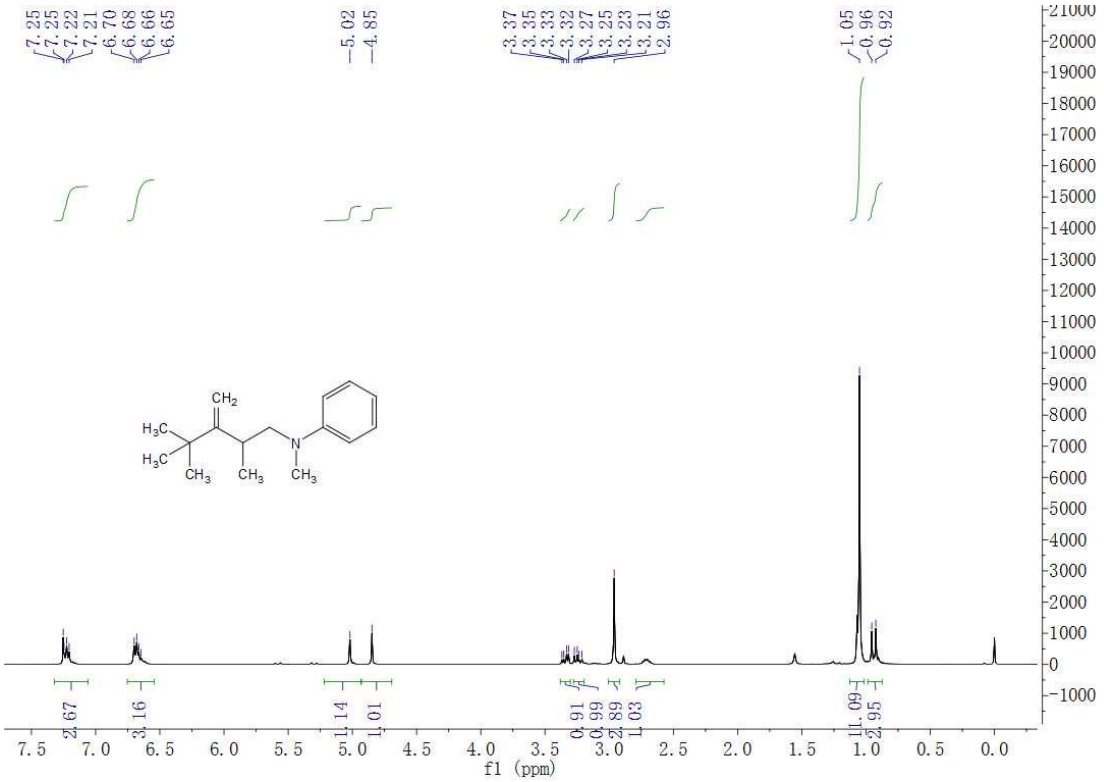
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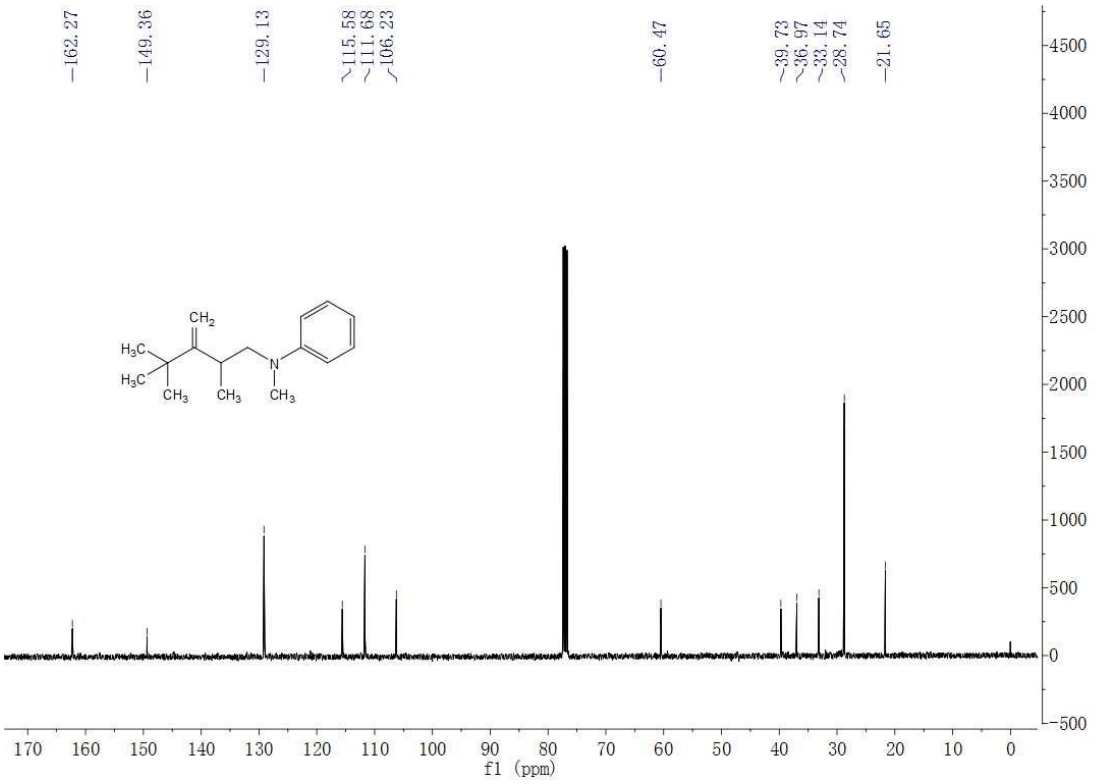
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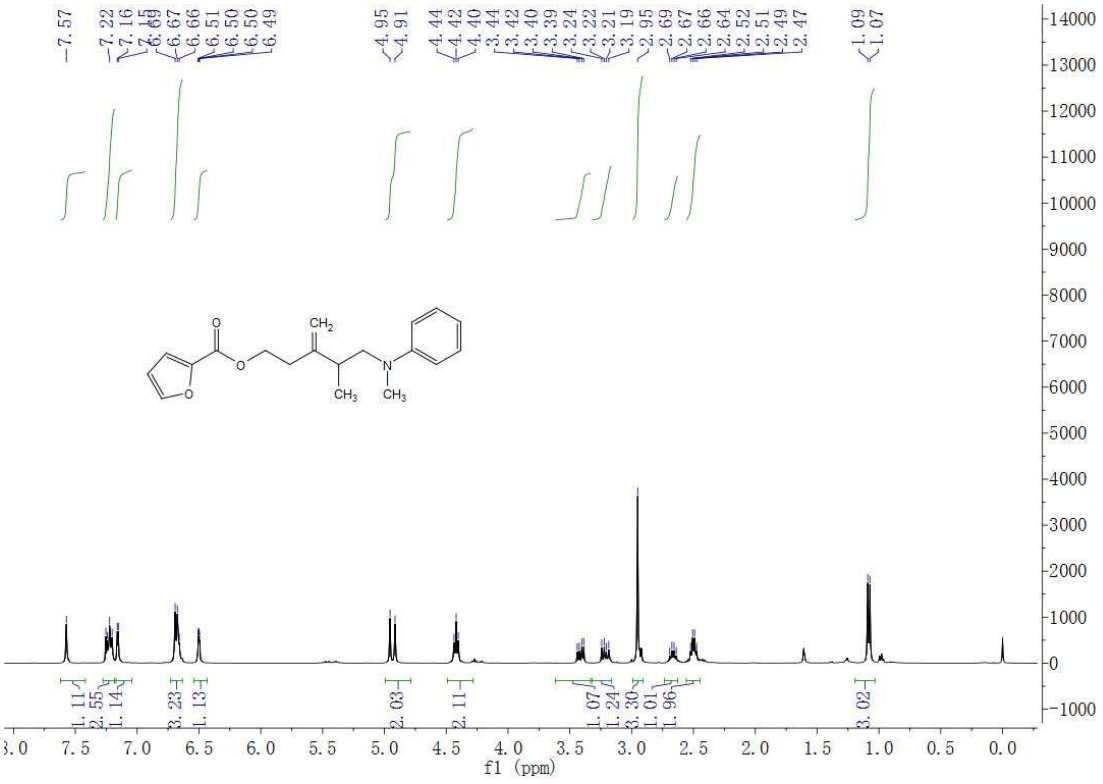
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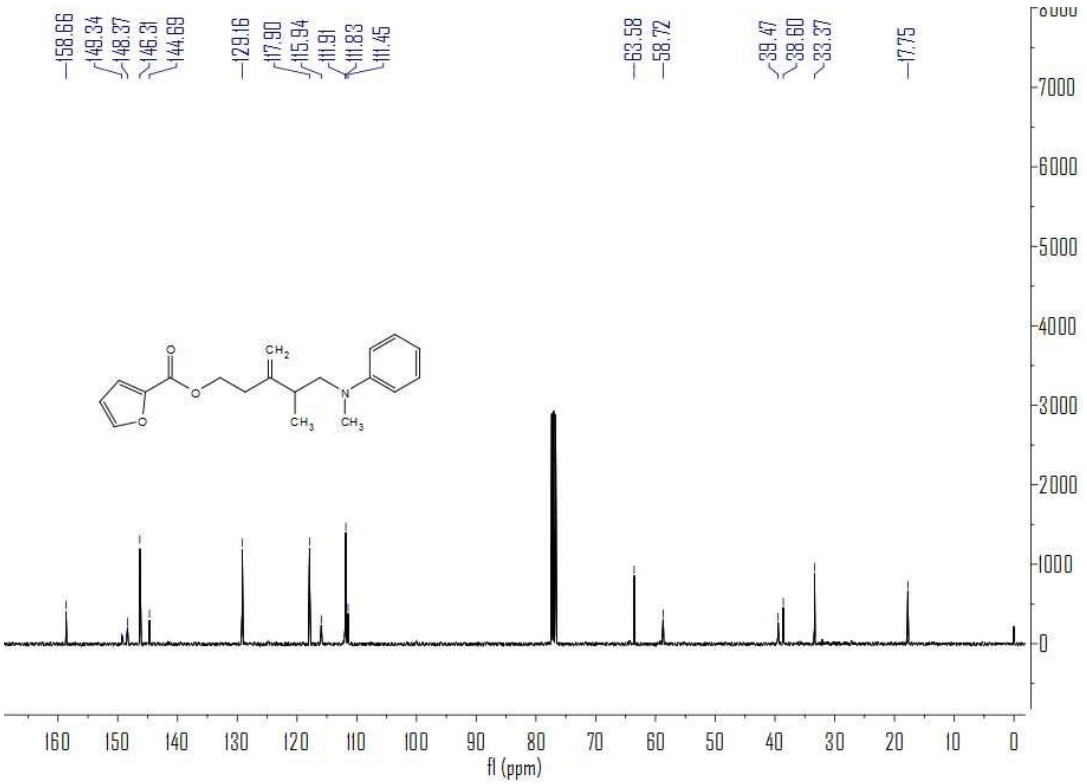
f1 (ppm)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129.16
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115.94
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111.83
111.45
63.58
58.72
39.47
38.60
33.37
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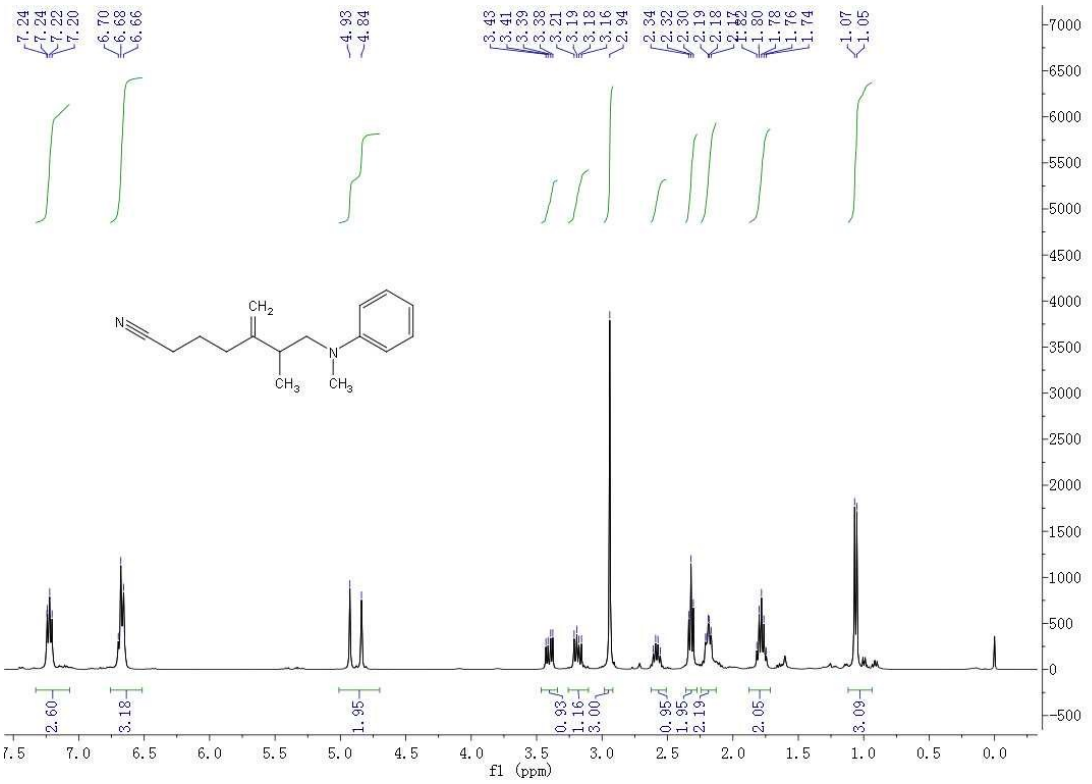
f1 (ppm)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6.66
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3.41
3.39
3.38
3.21
3.19
3.18
3.16
2.94
2.34
2.32
2.30
2.19
2.18
1.80
1.78
1.76
1.74
1.07
1.05
CH2
N
CH3
N
CH3
2.60
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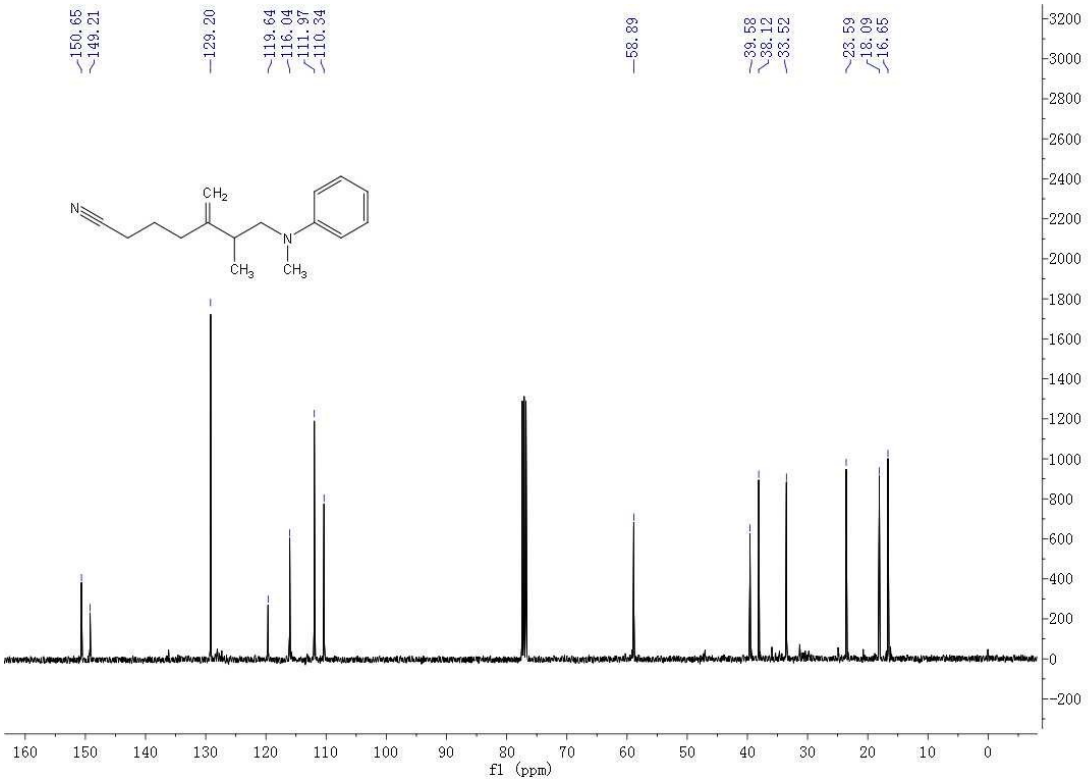
0.98
1.16
3.00
0.95
1.95
2.19
2.05
3.09
f1 (ppm)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110.34
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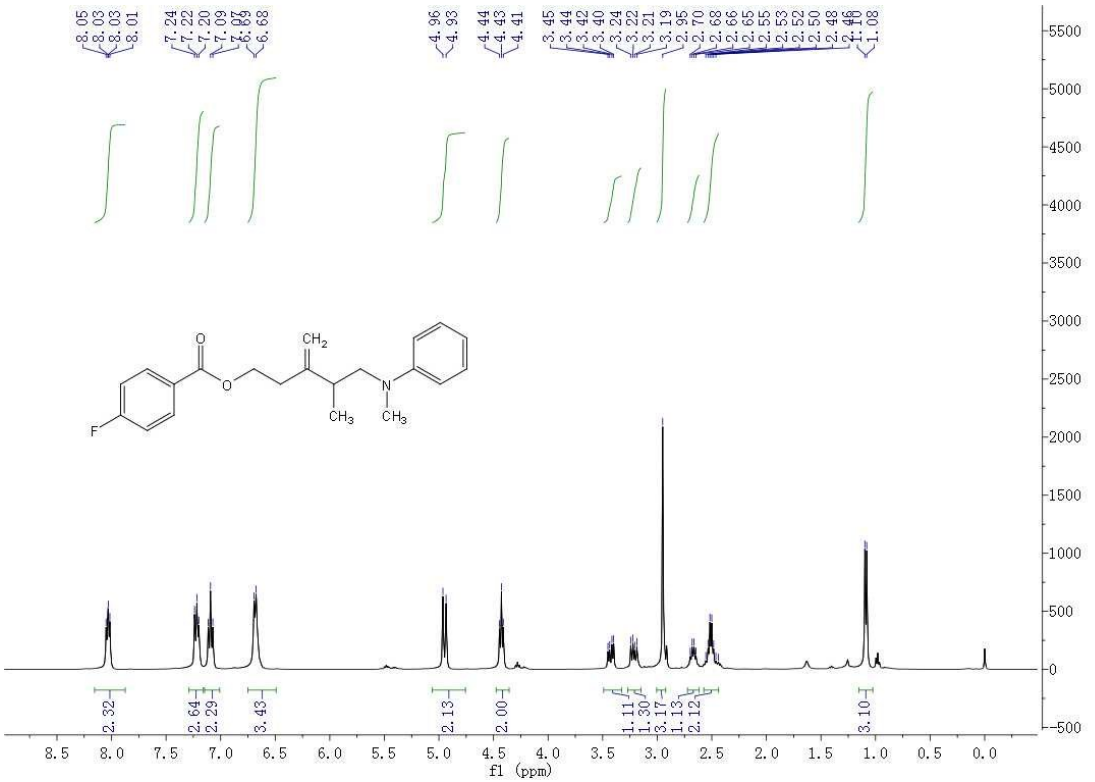
39.58
38.12
33.52
23.59
18.09
16.65
CH2
N
CH3
N
CH3
f1 (ppm)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8.03
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7.22
7.20
7.09
7.07
6.89
6.68
4.96
4.93
4.44
4.43
4.41
3.45
3.44
3.42
3.40
3.24
3.22
3.21
3.19
2.95
2.70
2.68
2.66
2.65
2.55
2.53
2.52
2.50
2.48
2.46
1.10
1.08
O
CH2
O
N
CH3
CH3
F
2.32
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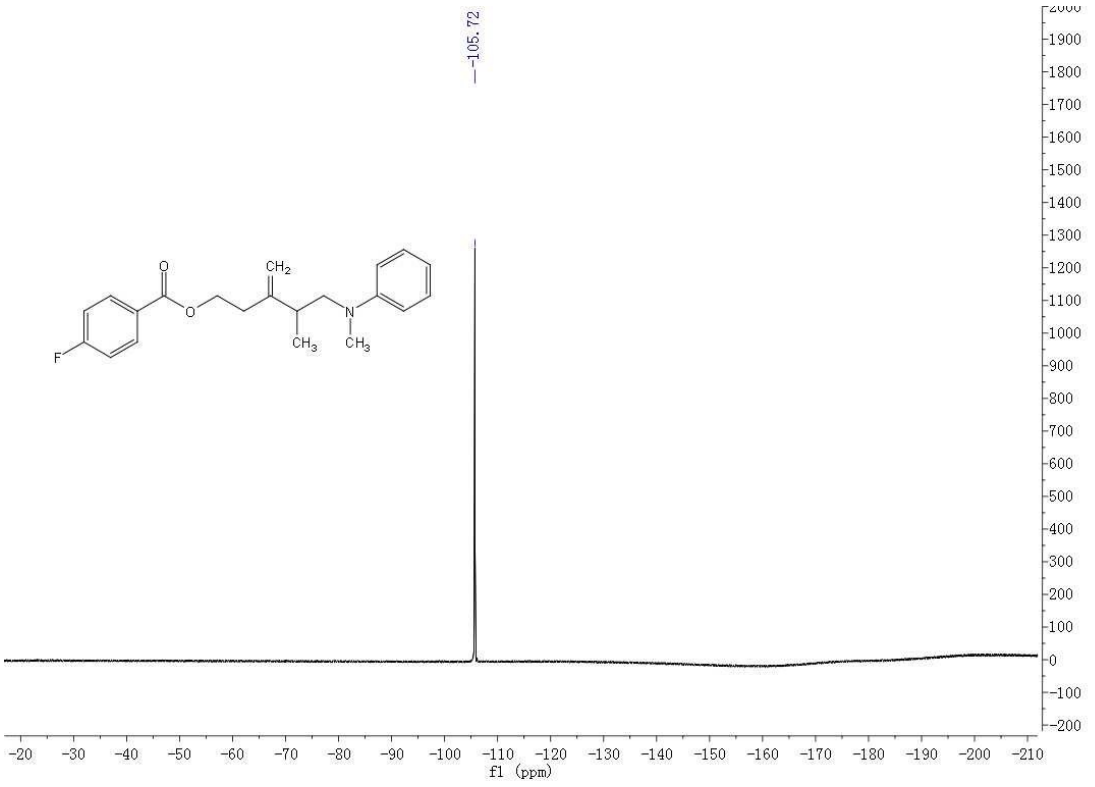
3.43
2.13
2.00
1.11
1.30
3.17
1.13
2.12
3.10
f1 (ppm)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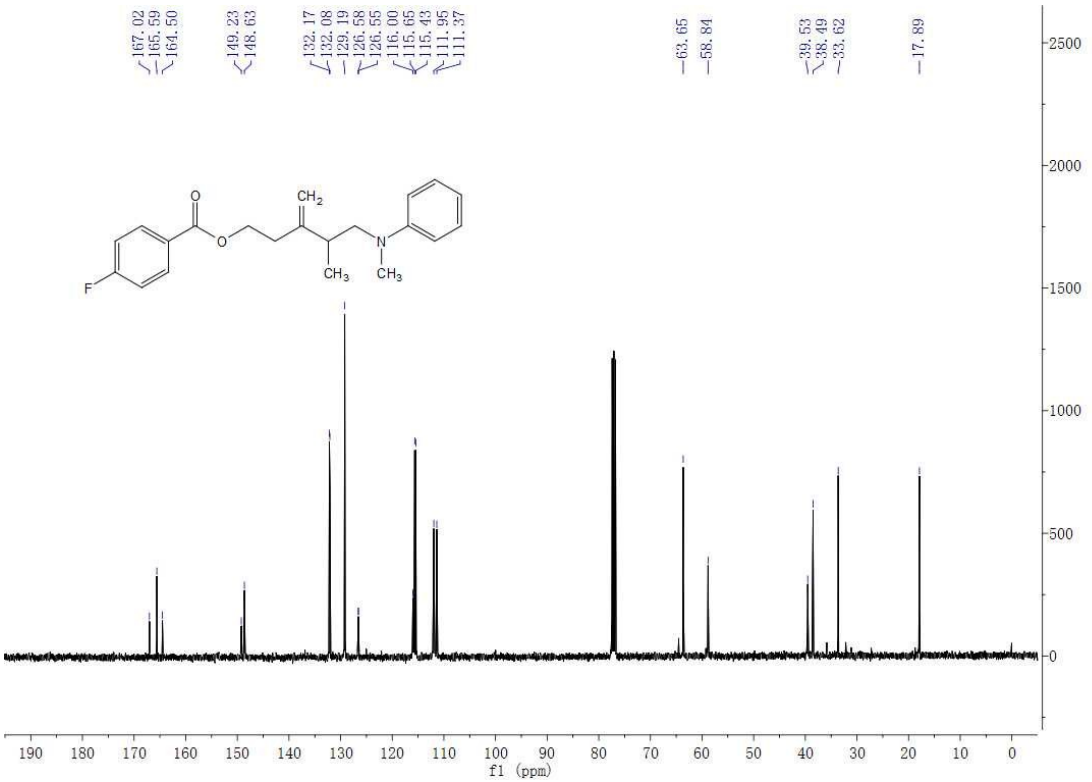
CH3
CH3
F
f1 (ppm)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132.17
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129.19
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126.55
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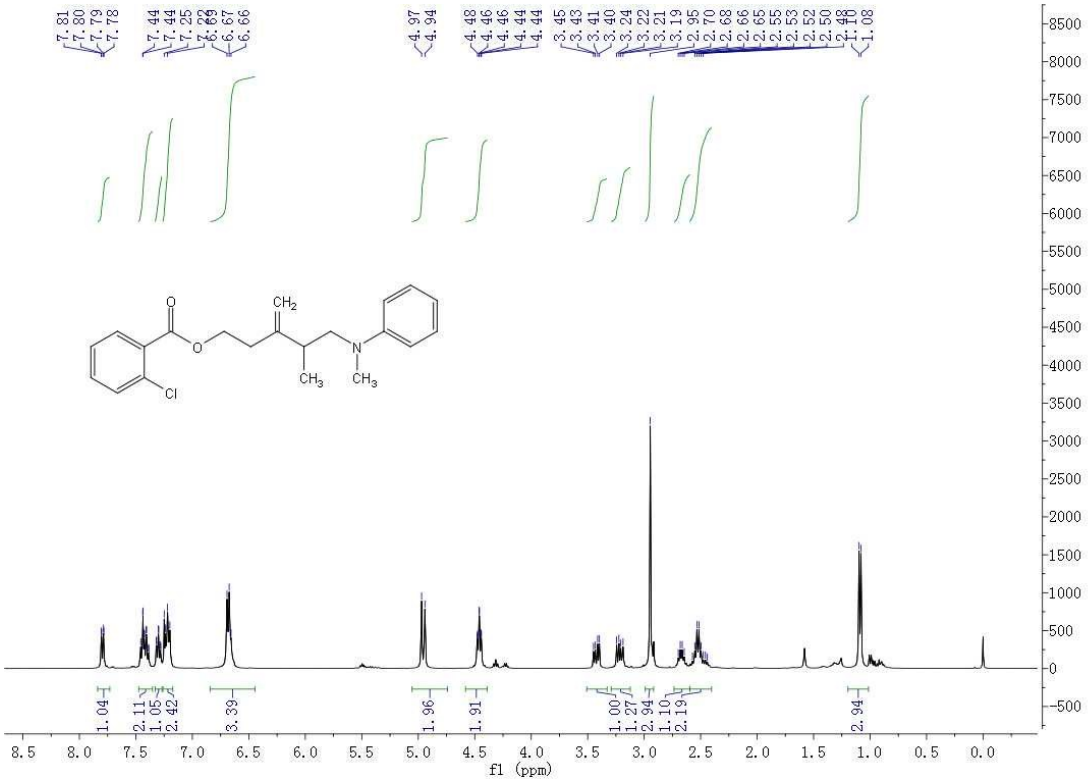
39.53
38.49
33.62
17.89
f1 (ppm)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4.46
4.44
4.44
3.45
3.43
3.41
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3.19
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2.68
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2.65
2.55
2.53
2.52
2.50
1.18
1.08
1.04
2.11
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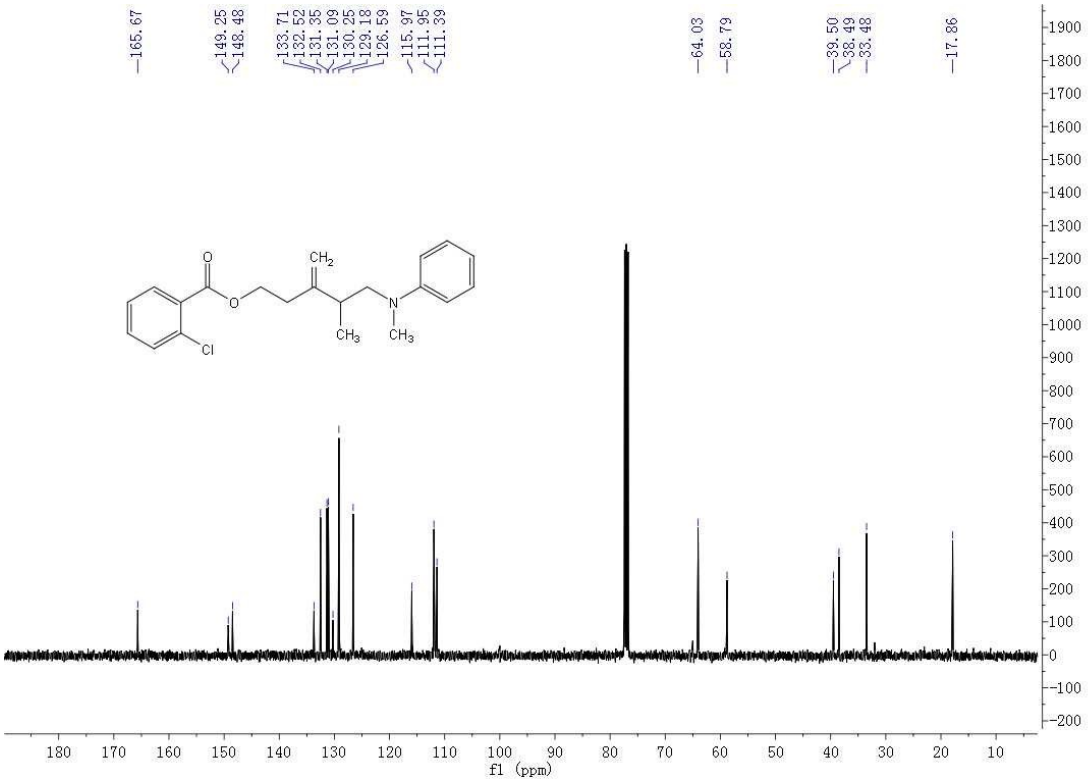
2.94
f1 (ppm)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129.18
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115.97
111.95
111.39
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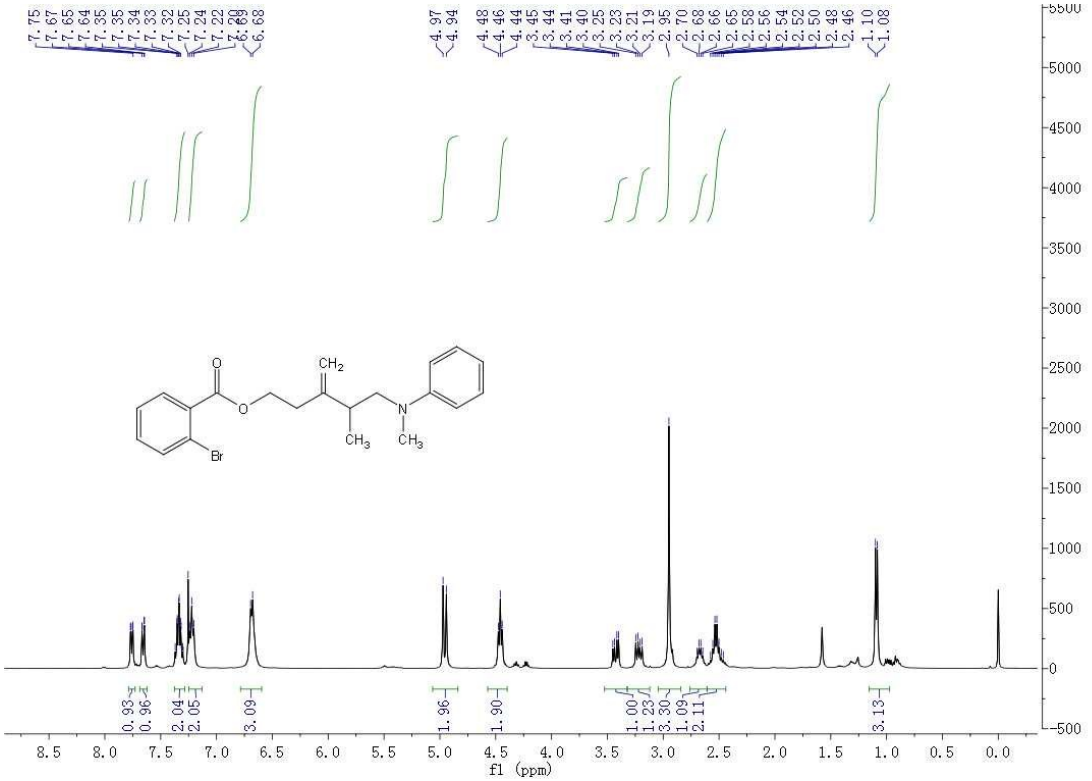
38.49
33.48
17.86
O
O
CH2
N
CH3
CH3
Cl
f1 (ppm)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7.32
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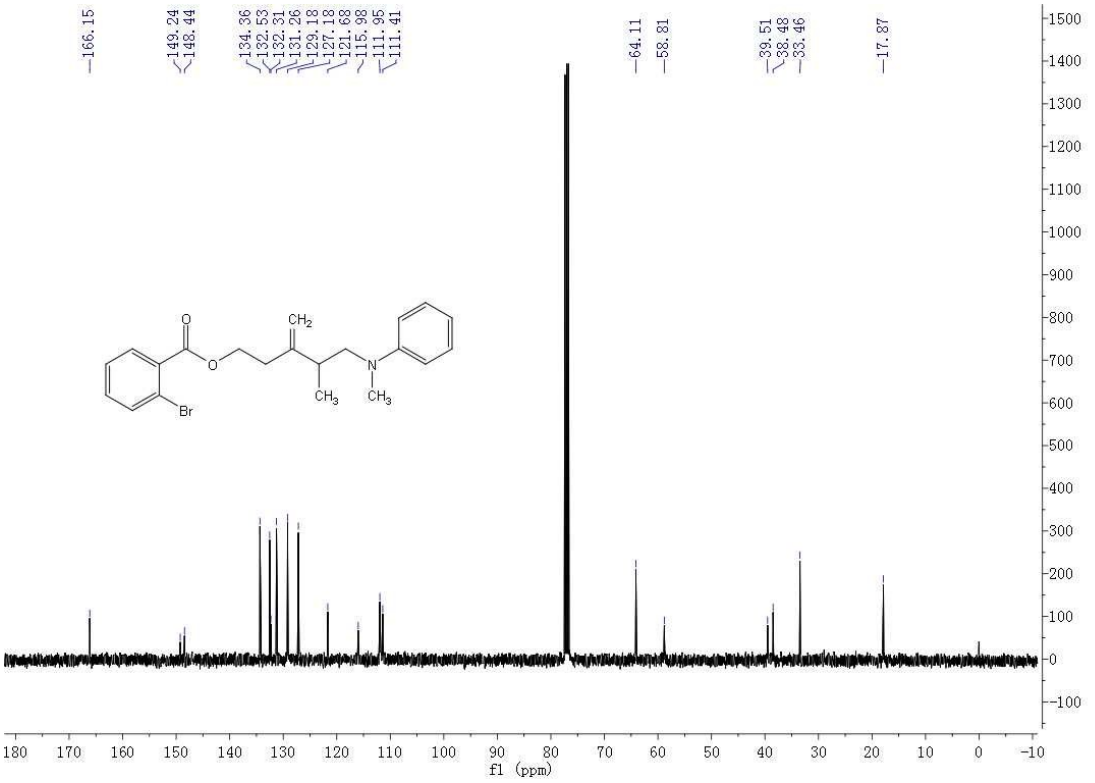
7.24
7.22
6.89
6.68
4.97
4.94
4.48
4.46
4.44
3.45
3.44
3.41
3.40
3.25
3.23
3.21
3.19
2.95
2.70
2.68
2.66
2.65
2.58
2.56
2.54
2.52
2.50
2.48
2.46
1.10
1.08
O
O
CH2
N
CH3
CH3
Br
0.93
0.96
2.04
2.05
3.09
1.96
1.90
1.00
1.23
3.30
1.09
2.11
3.13
f1 (ppm)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132.31
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129.18
127.18
121.68
115.98
111.95
111.41
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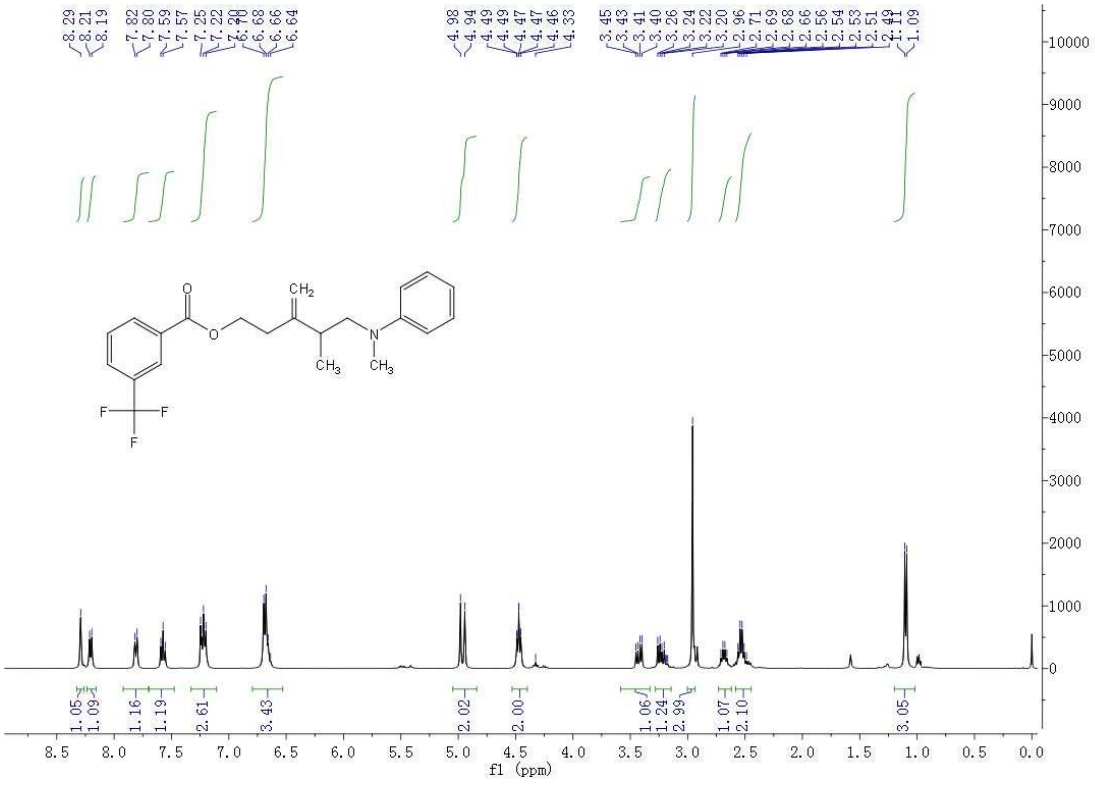
38.48
33.46
17.87
O
O
CH2
N
CH3
CH3
Br
f1 (ppm)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7.59
7.57
7.25
6.68
6.66
6.64
4.98
4.94
4.49
4.47
4.46
4.33
3.45
3.43
3.41
3.40
3.26
3.24
3.22
3.20
2.96
2.71
2.69
2.68
2.66
2.56
2.54
2.53
2.51
1.09
O
O
CH2
N
CH3
CH3
F
F
F
1.05
1.09
1.16
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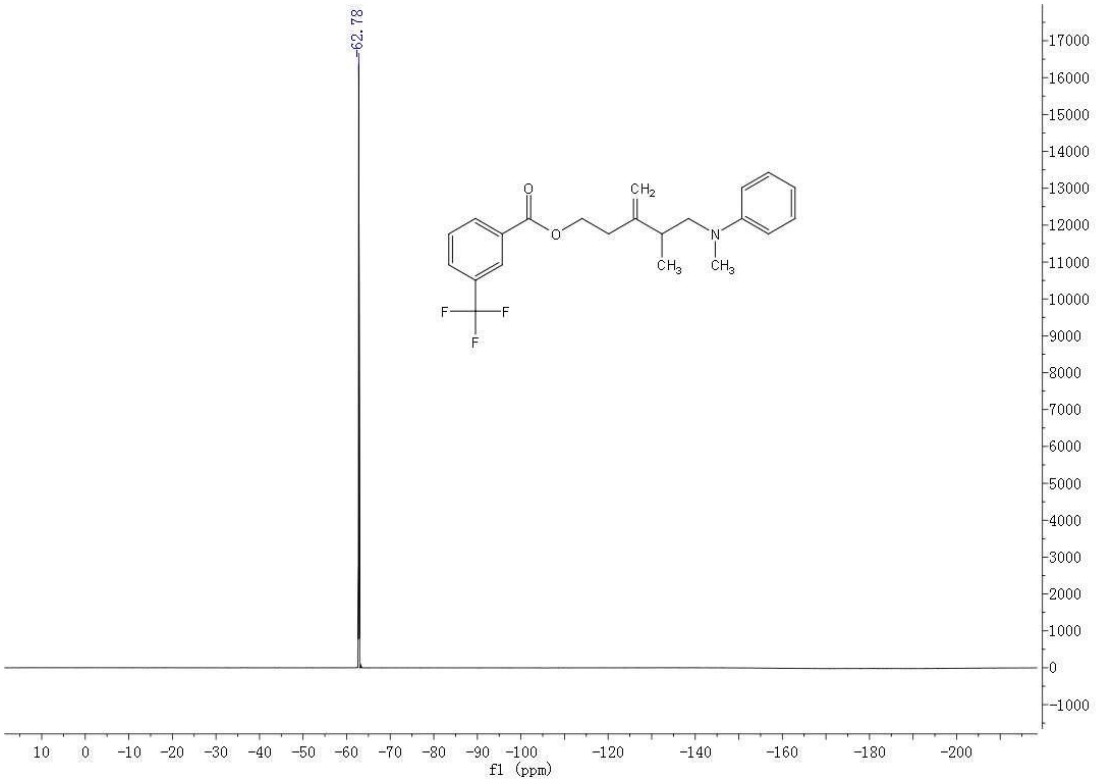
2.00
1.06
1.24
2.99
1.07
2.10
3.05
f1 (ppm)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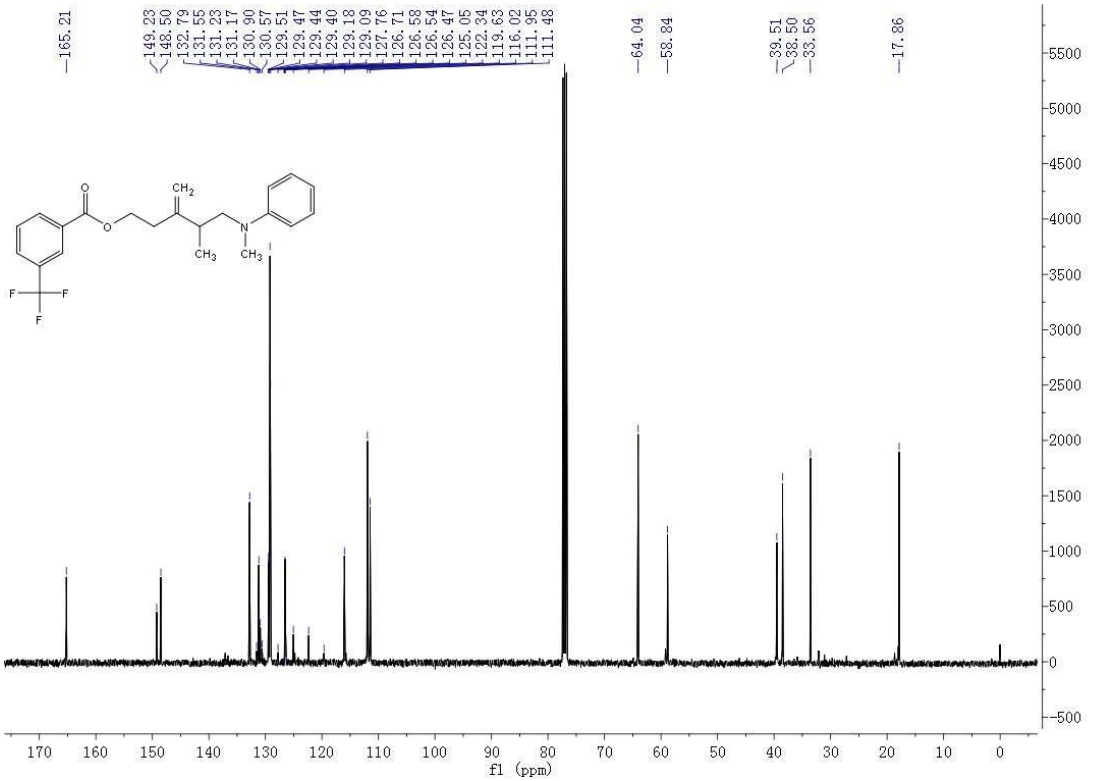
f1 (ppm)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129.44
129.40
129.18
129.09
127.76
126.71
126.58
126.54
126.47
125.05
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119.63
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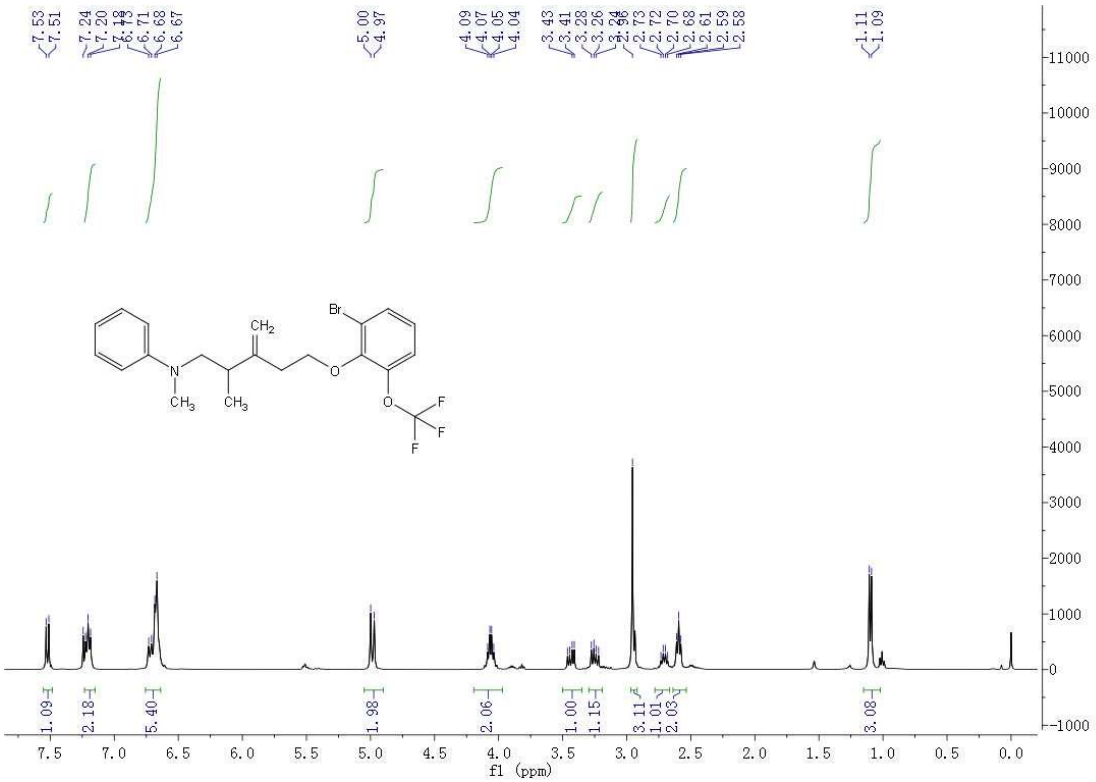
111.48
64.04
58.84
39.51
38.50
33.56
17.86
f1 (ppm)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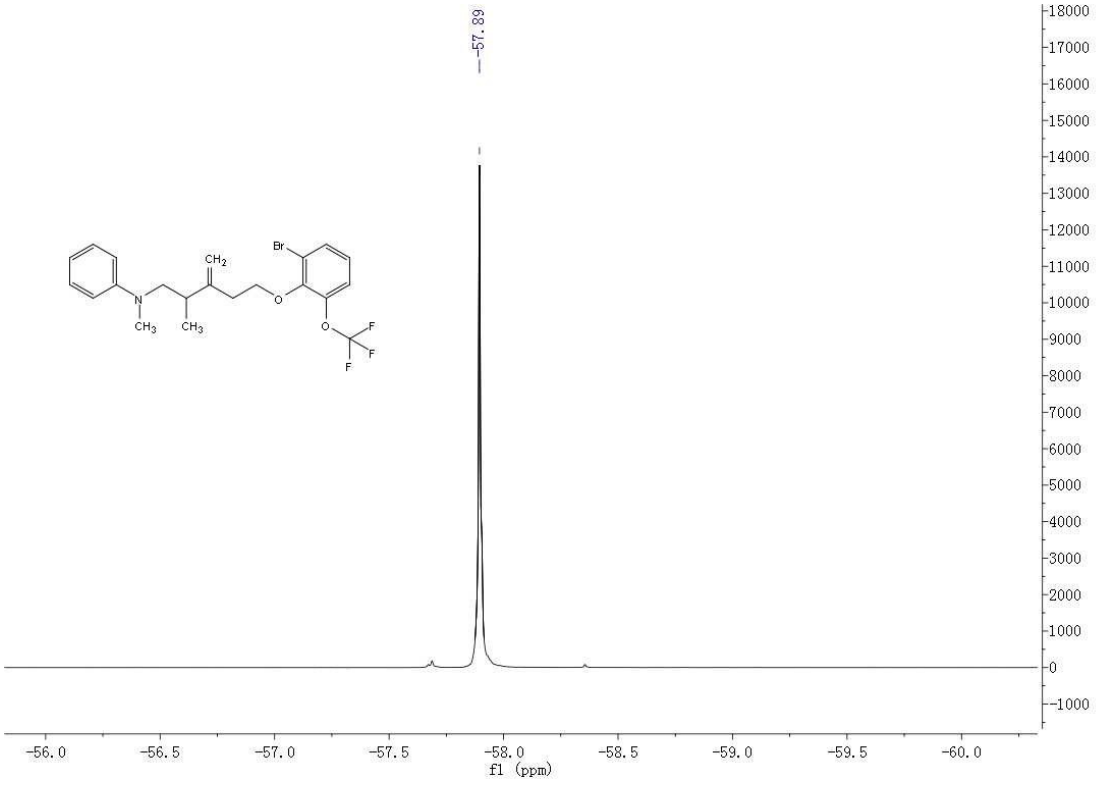
4.09
4.07
4.05
4.04
3.43
3.41
3.28
3.26
2.73
2.72
2.70
2.68
2.61
2.59
2.58
1.11
1.09
Br
CH2
N
CH3
CH3
O
O
F
F
F
1.09
2.18
5.40
1.98
2.06
1.00
1.15
3.11
1.01
2.03
3.08
f1 (ppm)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Br
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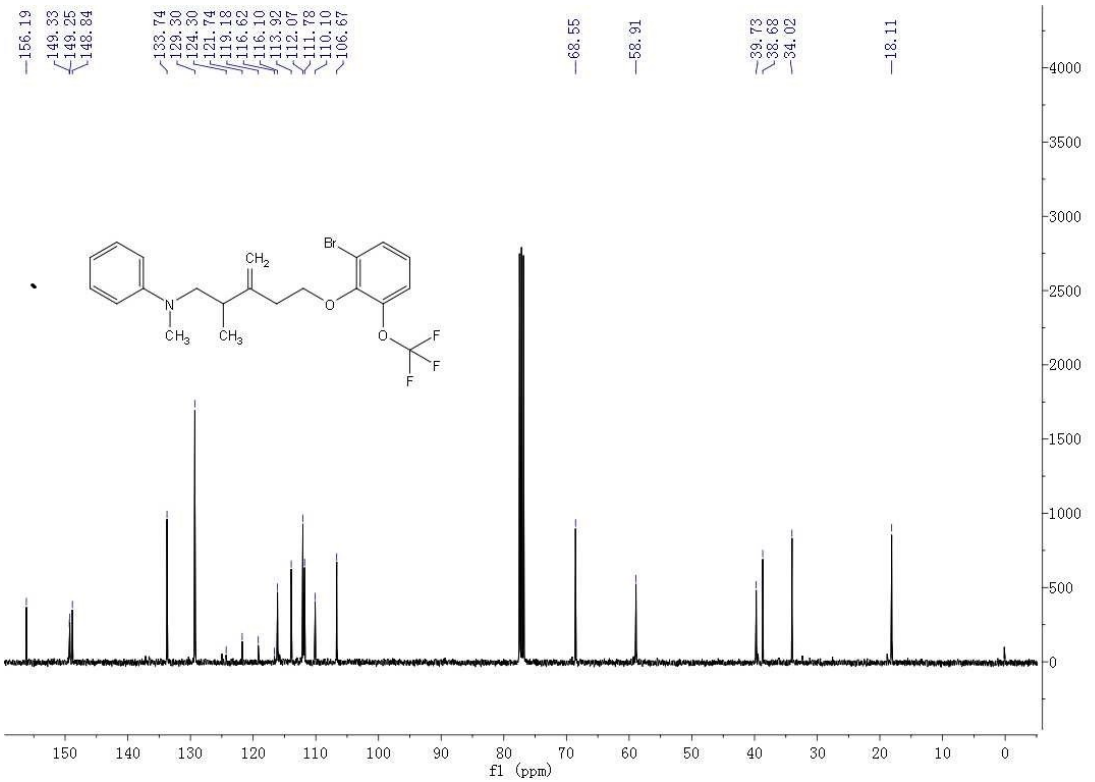
CH3
CH3
O
O
F
F
F
f1 (ppm)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116.62
116.10
113.92
112.07
111.78
110.10
106.67
68.55
58.91
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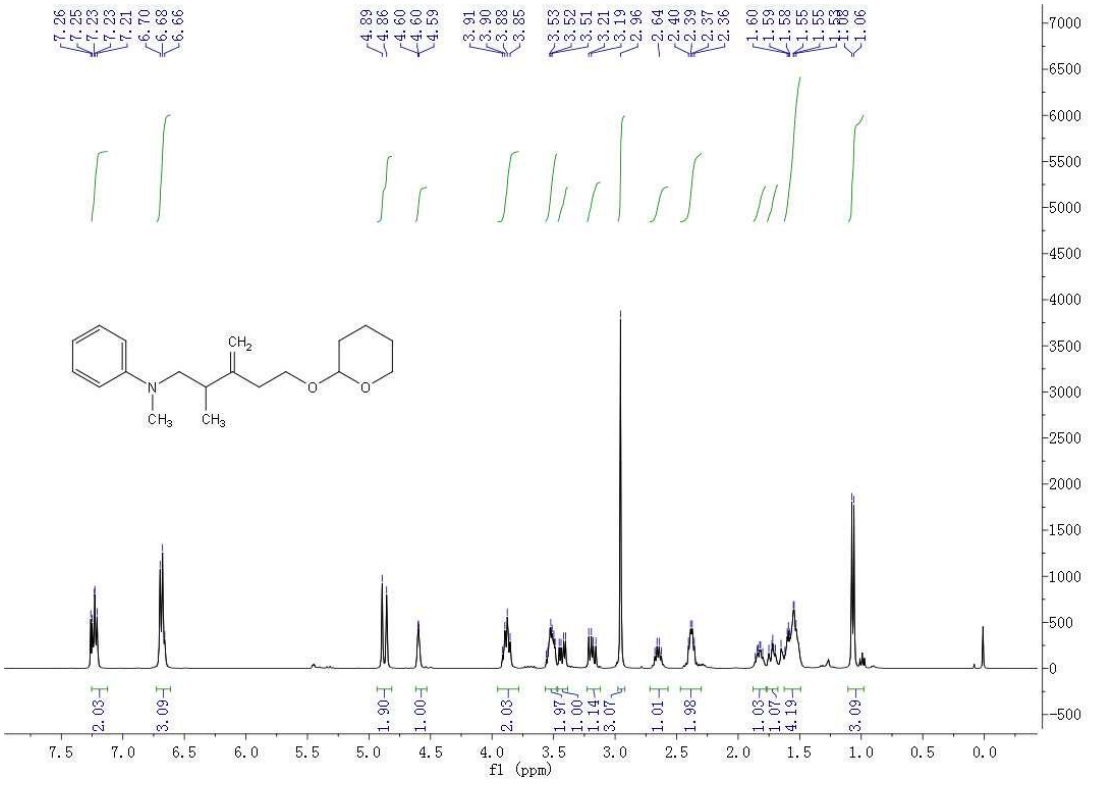
34.02
18.11
Br
CH2
N
CH3
CH3
O
O
F
F
F
f1 (ppm)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4.60
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4.59
3.91
3.90
3.88
3.85
3.53
3.52
3.51
3.21
3.19
2.96
2.64
2.40
2.39
2.37
2.36
1.60
1.59
1.58
1.55
1.55
1.06
CH2
N
CH3
CH3
O
O
2.03
3.09
1.90
1.00
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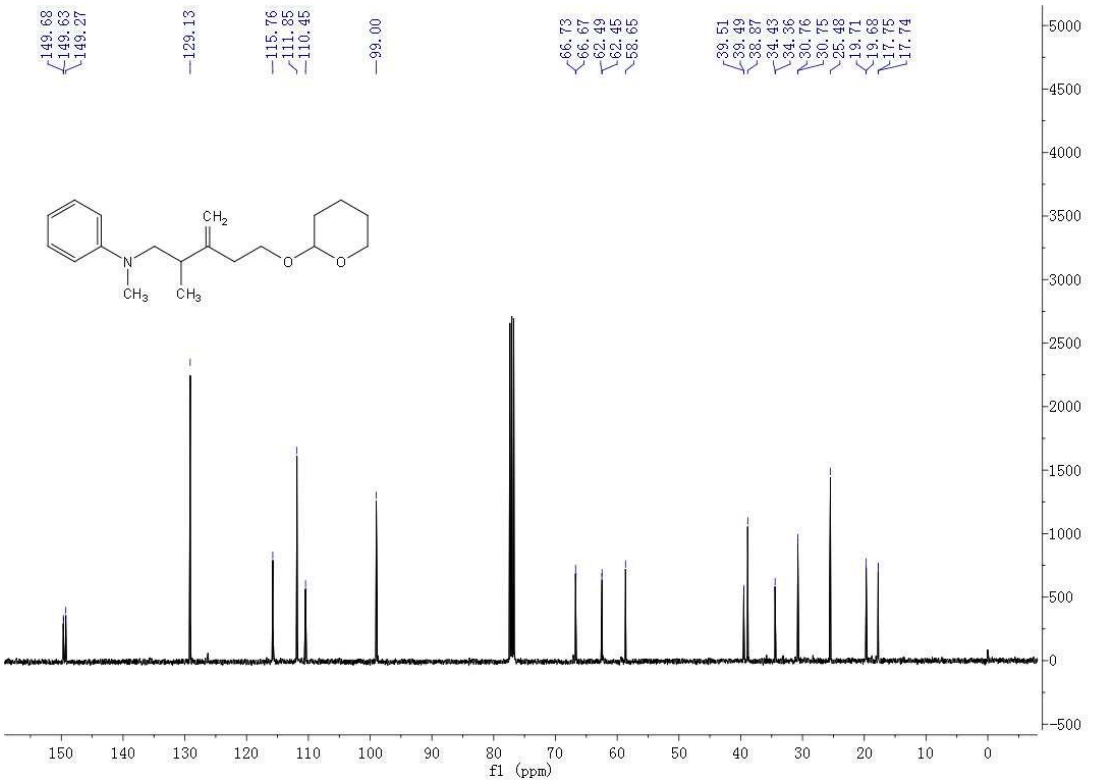
1.14
3.07
1.01
1.98
1.03
1.07
4.19
3.09
f1 (ppm)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66.67
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58.65
39.51
39.49
38.87
34.43
34.36
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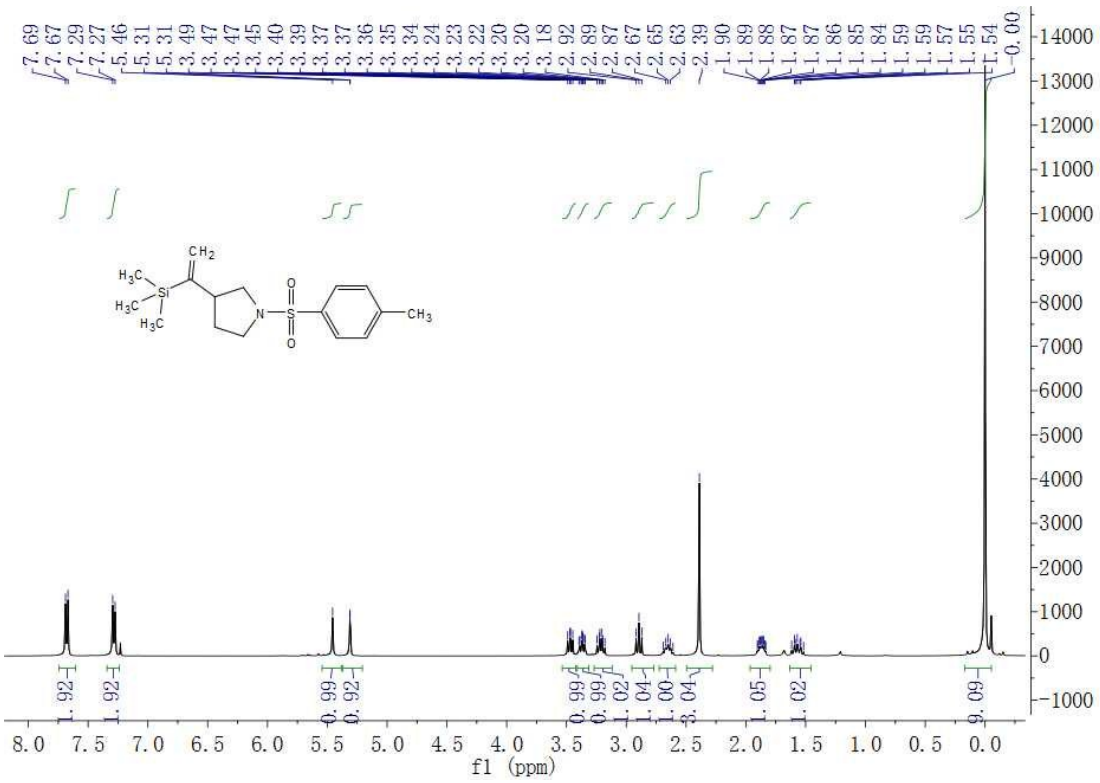
19.71
19.68
17.75
17.74
CH2
N
CH3
CH3
O
O
f1 (ppm)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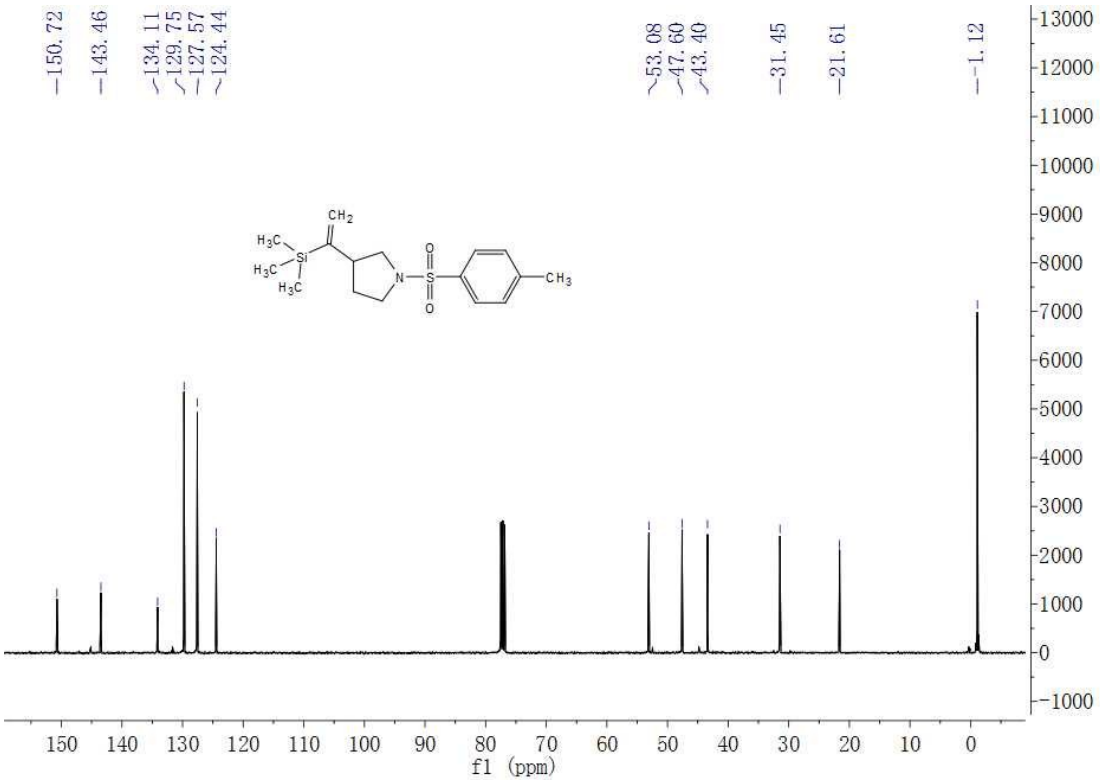
3.40
3.39
3.37
3.37
3.36
3.35
3.34
3.24
3.23
3.22
3.20
3.18
2.92
2.89
2.87
2.67
2.65
2.63
2.39
1.90
1.89
1.88
1.87
1.87
1.86
1.85
1.84
1.59
1.59
1.57
1.55
1.54
0.00
CH2
H3C
Si
H3C
H3C
N
S
O
O
CH3
1.92
1.92
0.99
0.92
0.99
0.99
1.02
1.04
1.00
3.04
1.05
1.02
9.09
f1 (ppm)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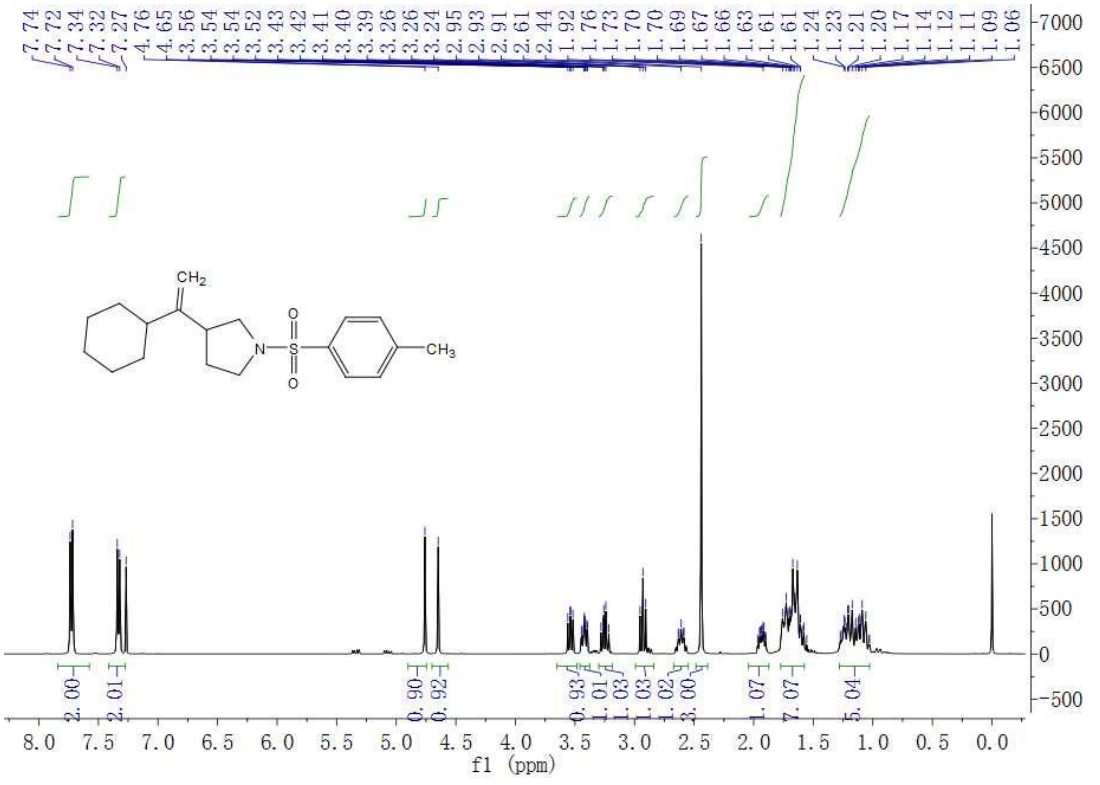
127.57
124.44
53.08
47.60
43.40
31.45
21.61
1.12
CH2
H3C
Si
H3C
H3C
N
S
O
O
CH3
f1 (ppm)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3.52
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3.42
3.41
3.40
3.39
3.26
3.26
3.24
2.95
2.93
2.91
2.61
2.44
1.92
1.76
1.73
1.70
1.70
1.69
1.67
1.66
1.63
1.61
1.61
1.24
1.23
1.21
1.20
1.17
1.14
1.12
1.11
1.09
1.06
CH2
N
S
O
O
CH3
2.00
2.01
0.90
0.92
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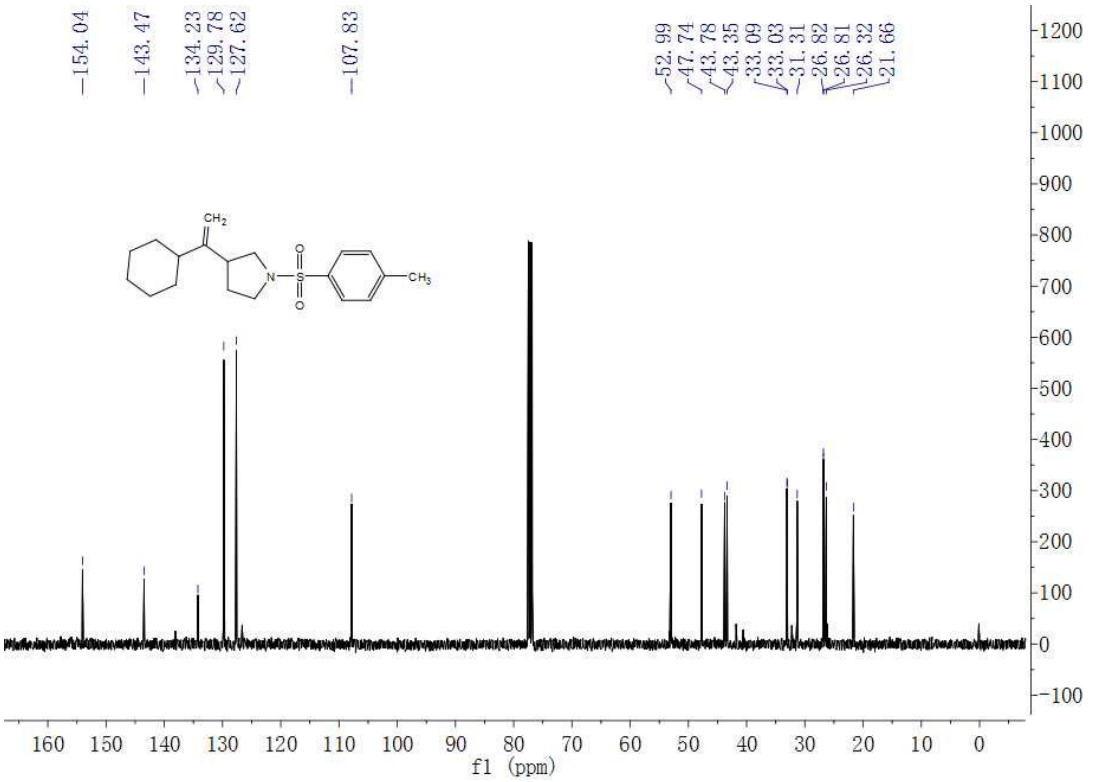
1.01
1.03
1.03
1.02
3.00
1.07
7.07
5.04
f1 (ppm)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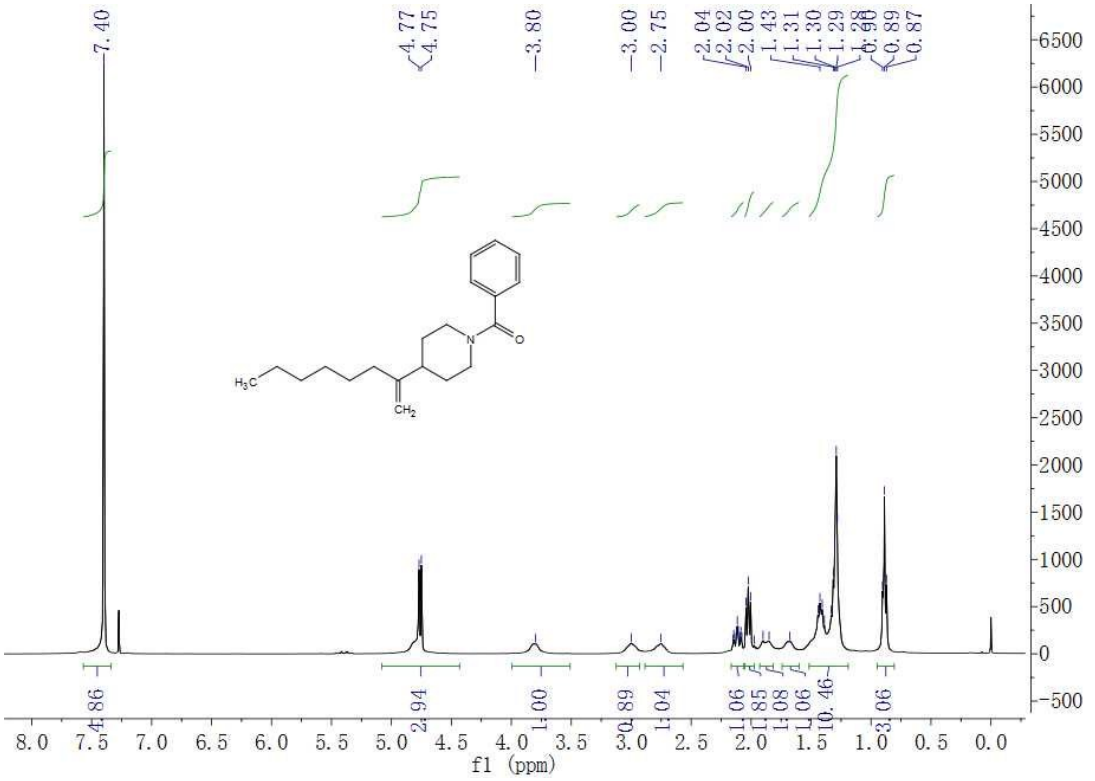
43.35
33.09
33.03
31.31
26.82
26.81
26.32
21.66
f1 (ppm)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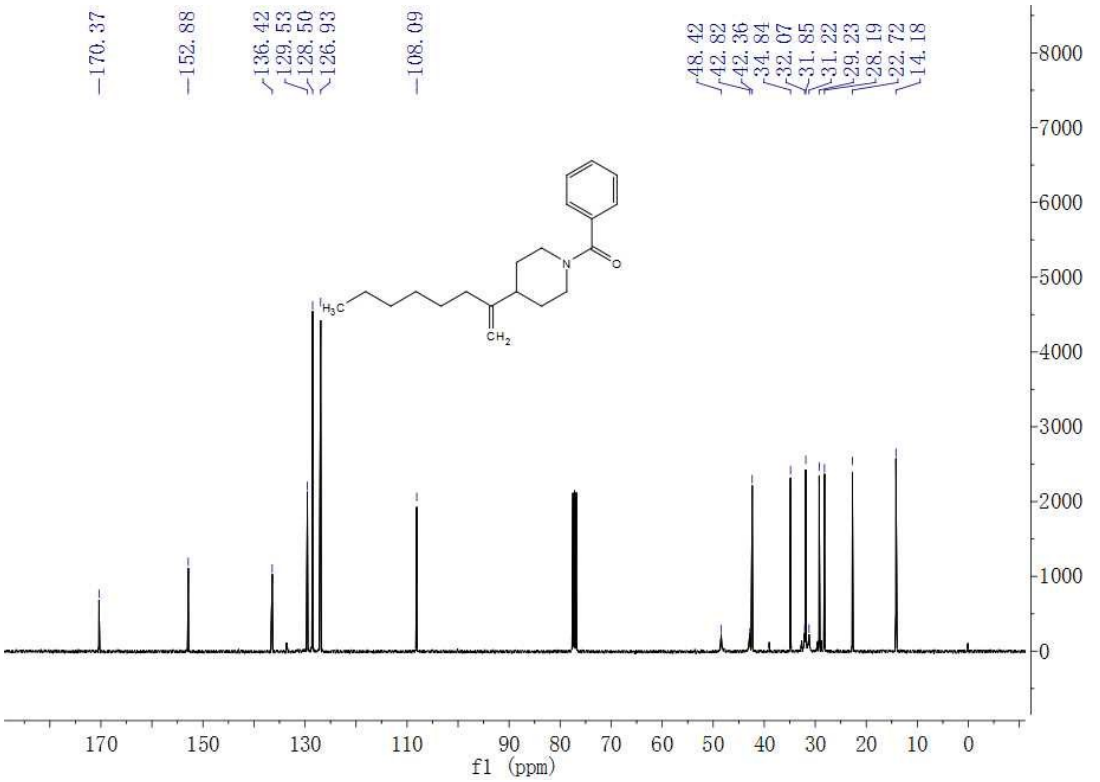
2.02
2.00
1.43
1.31
1.30
1.29
0.89
0.87
f1 (ppm)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34.84
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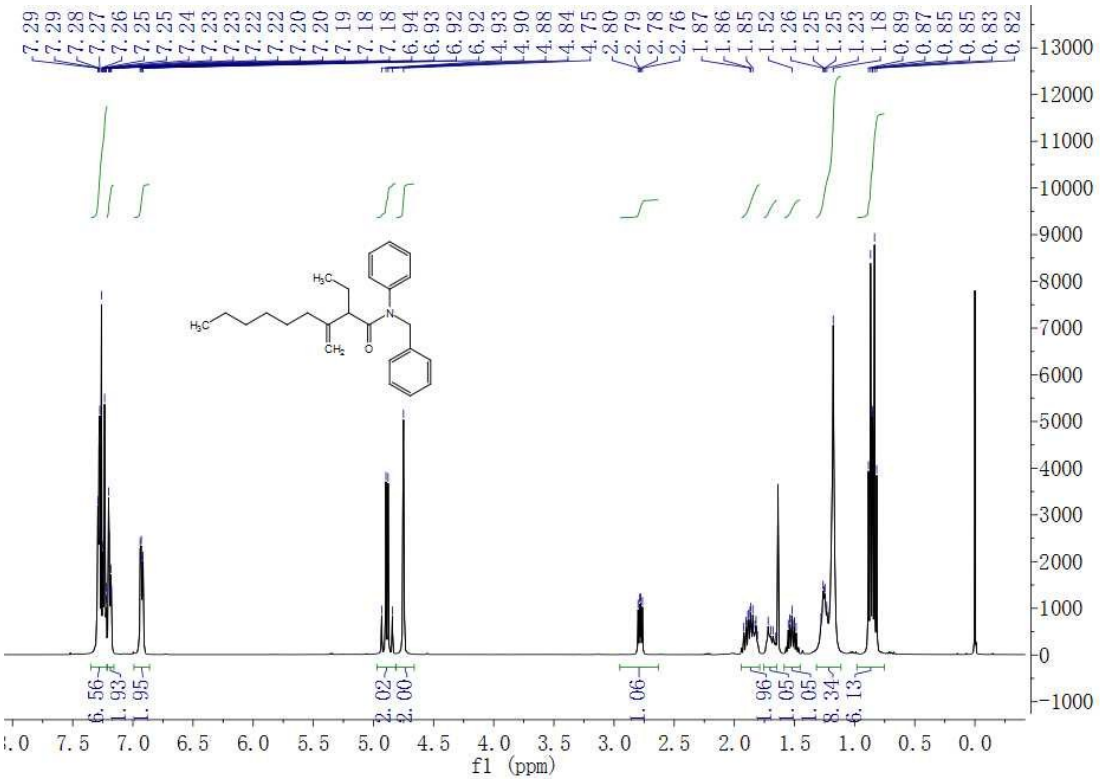
31.85
31.22
29.23
28.19
22.72
14.18
f1 (ppm)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7.18
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6.93
6.92
4.93
4.90
4.88
4.84
4.75
2.80
2.79
2.78
2.76
1.87
1.86
1.85
1.52
1.26
1.25
1.23
1.18
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0.87
0.85
0.83
0.82
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1.06
1.96
1.05
1.05
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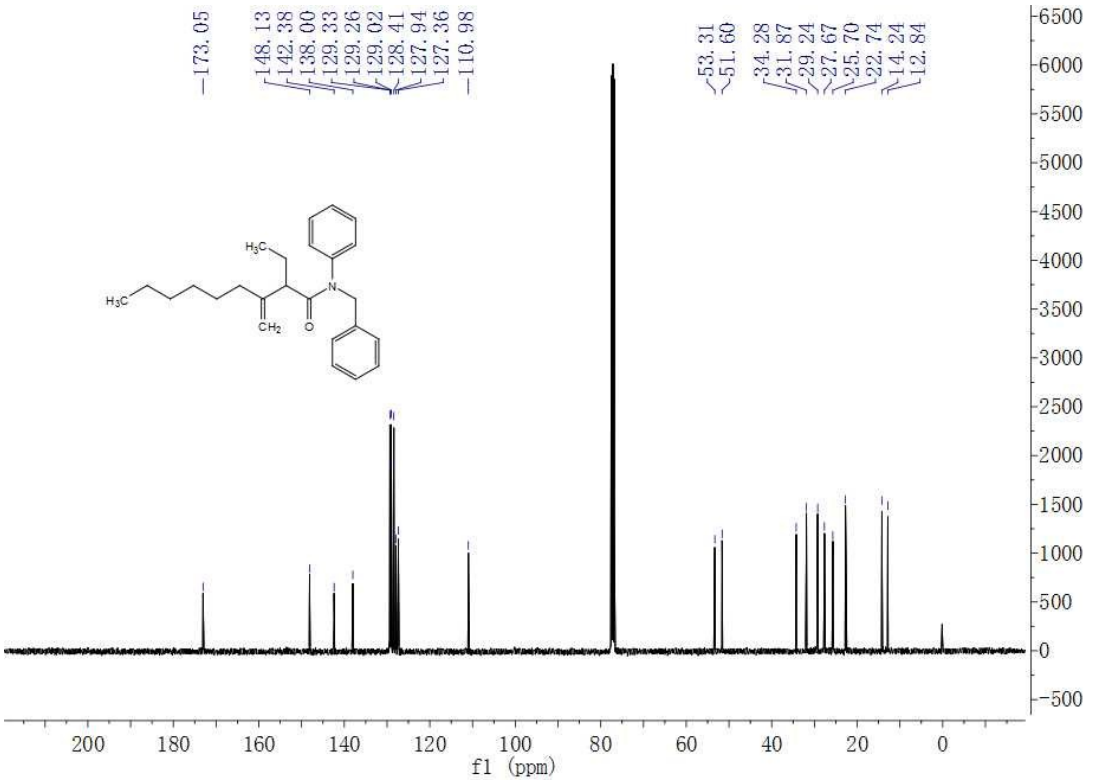
6.13
f1 (ppm)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127.36
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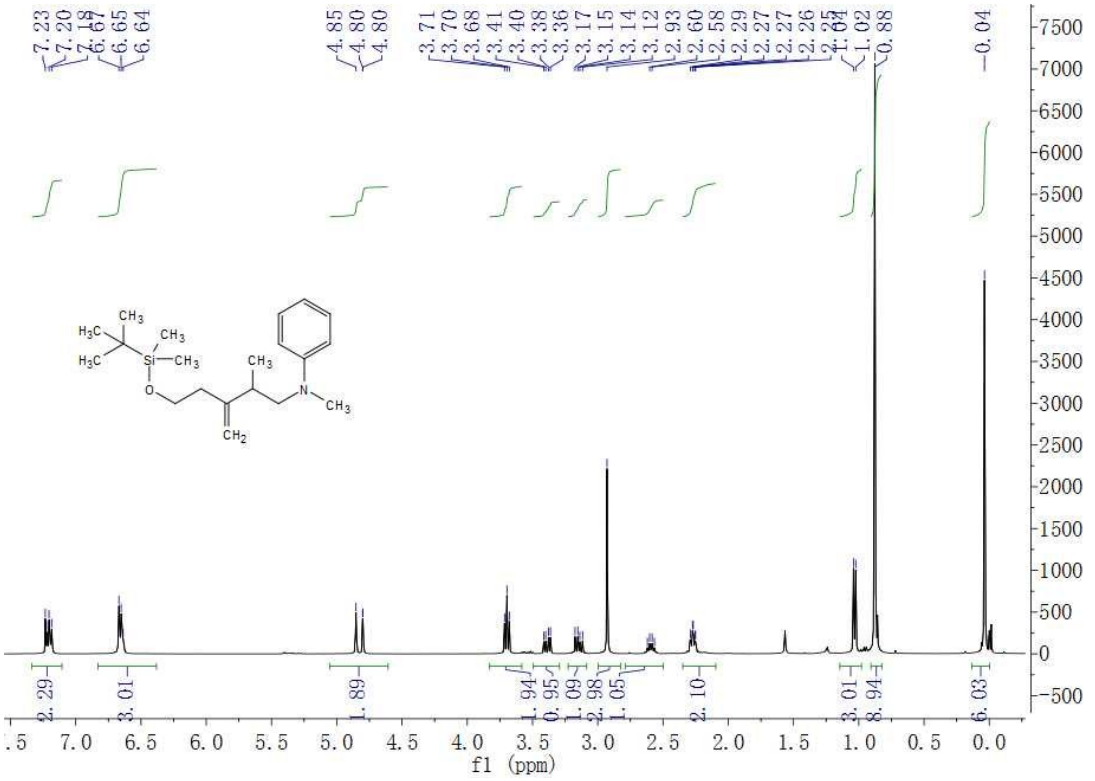
29.24
27.67
25.70
22.74
14.24
12.84
f1 (ppm)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3.15
3.14
3.12
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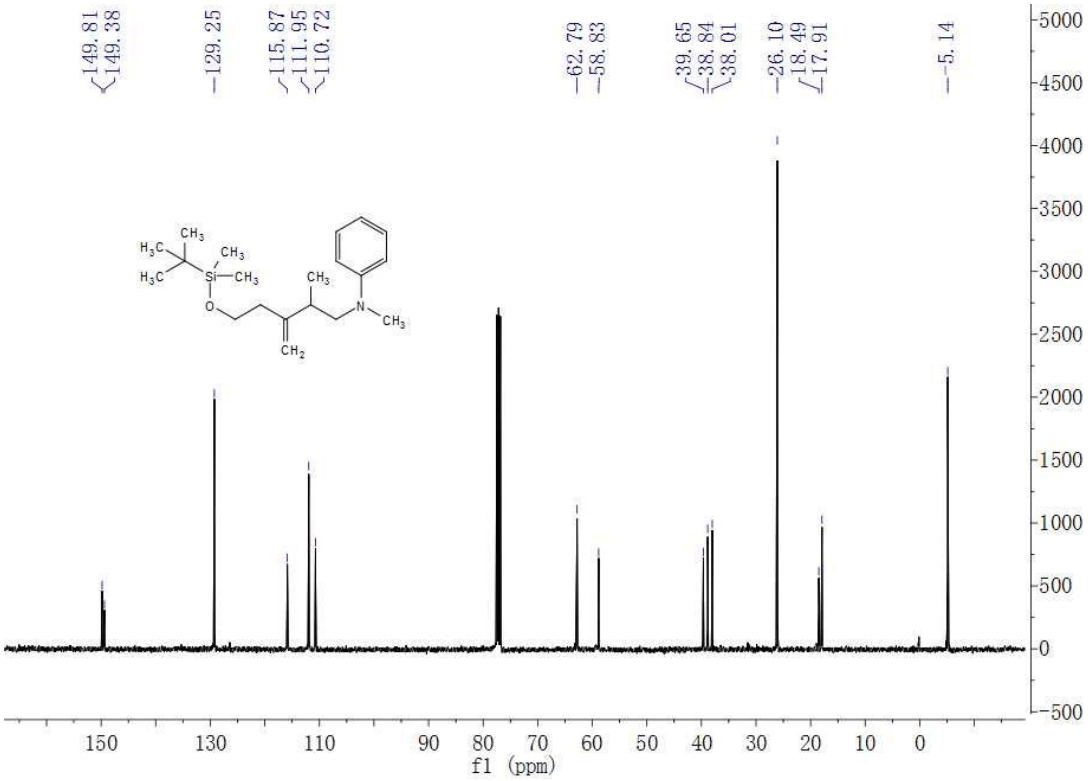
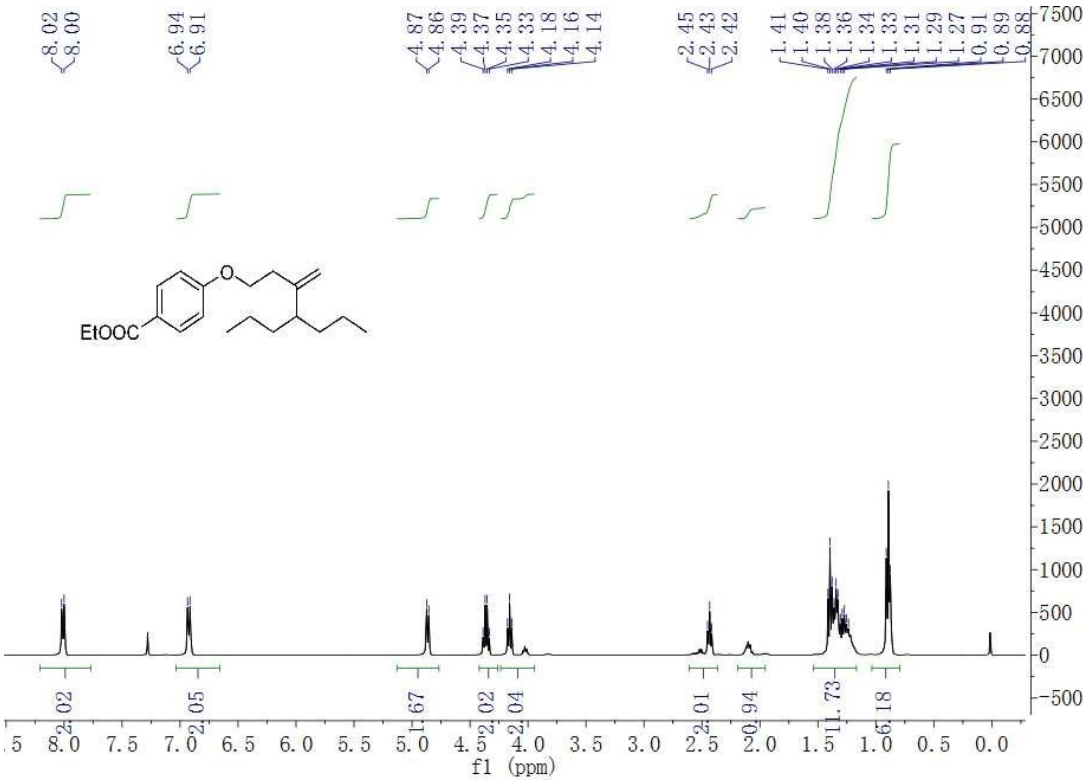
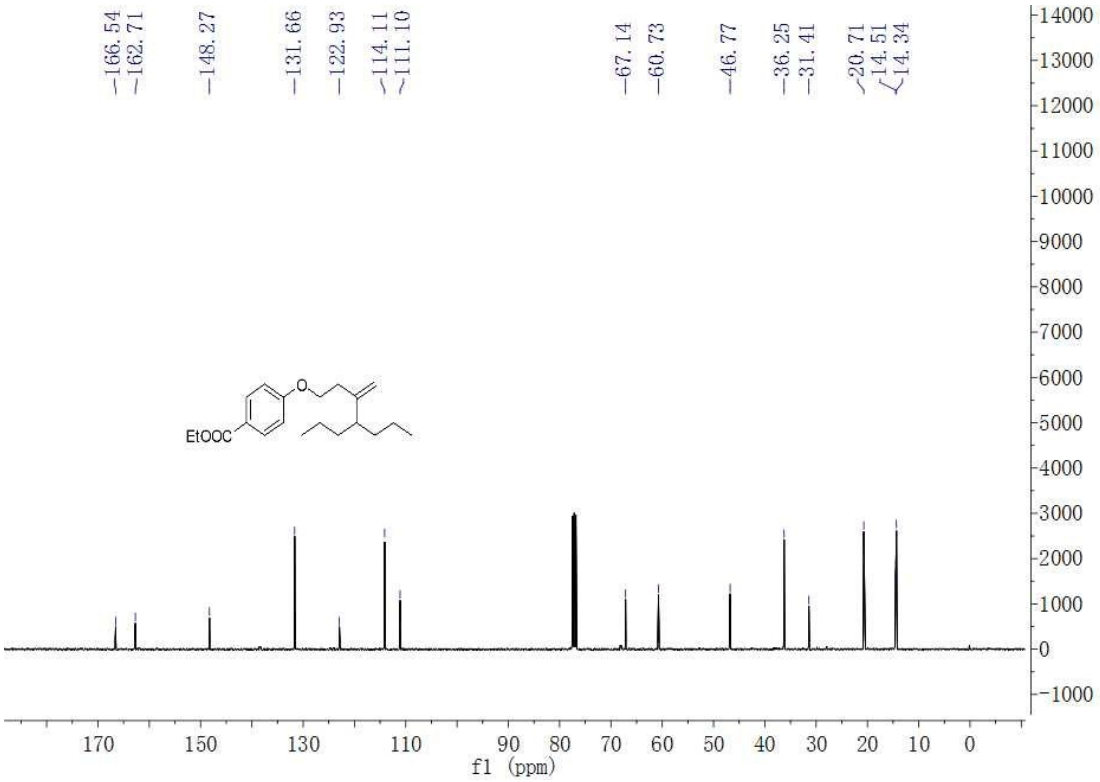
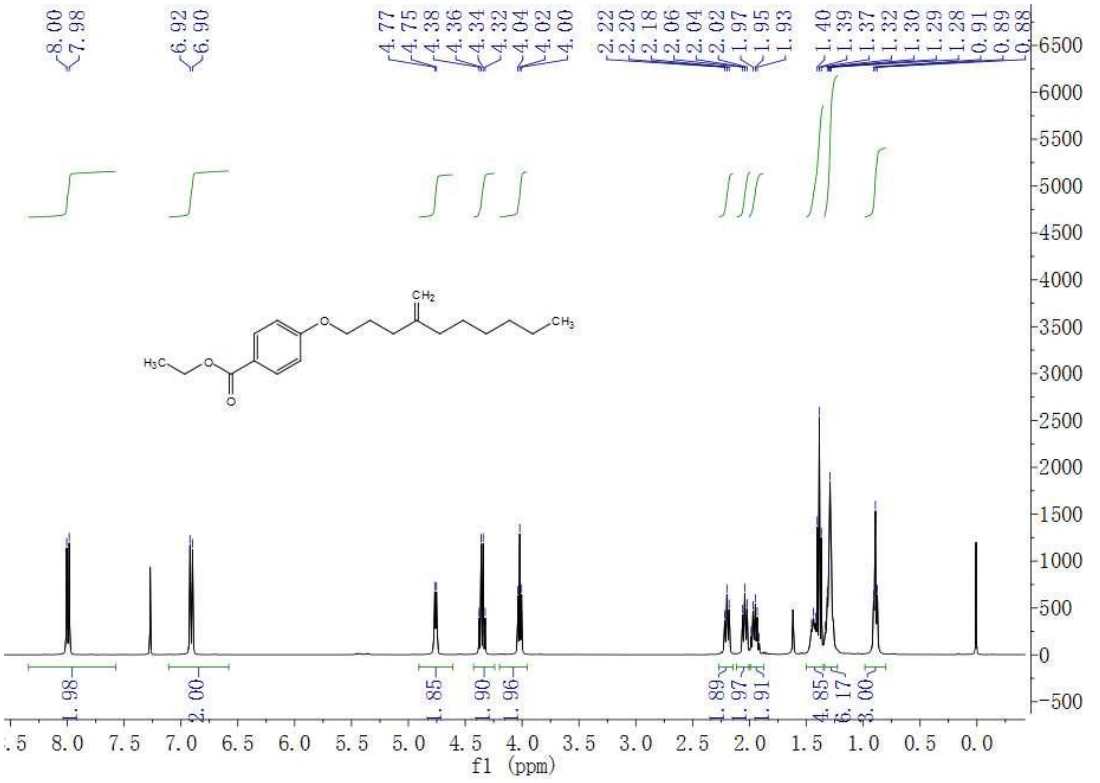
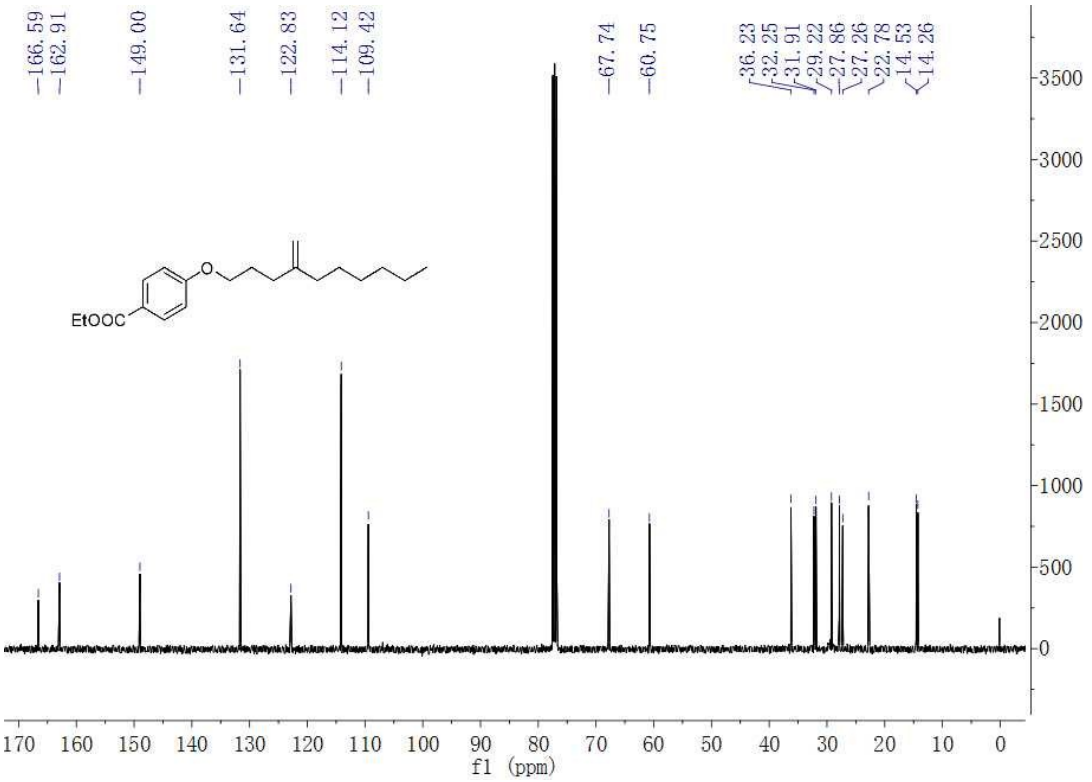
2.58
2.29
2.27
2.27
2.26
2.25
1.02
0.88
0.04
2.29
3.01
1.89
1.94
0.95
1.09
2.98
1.05
2.10
3.01
8.94
6.03
f1 (ppm)

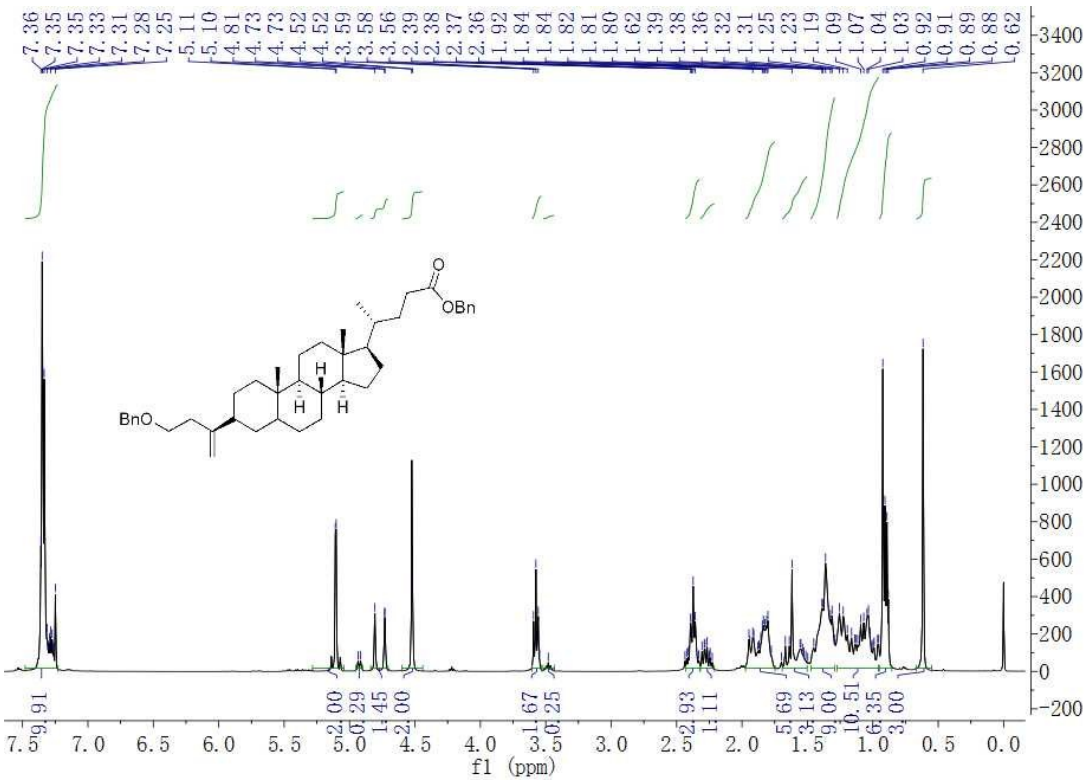

149.81
149.38
129.25
115.87
111.95
110.72
62.79
58.83
39.65
38.84
38.01
26.10
18.49
17.91
5.14
f1 (ppm)

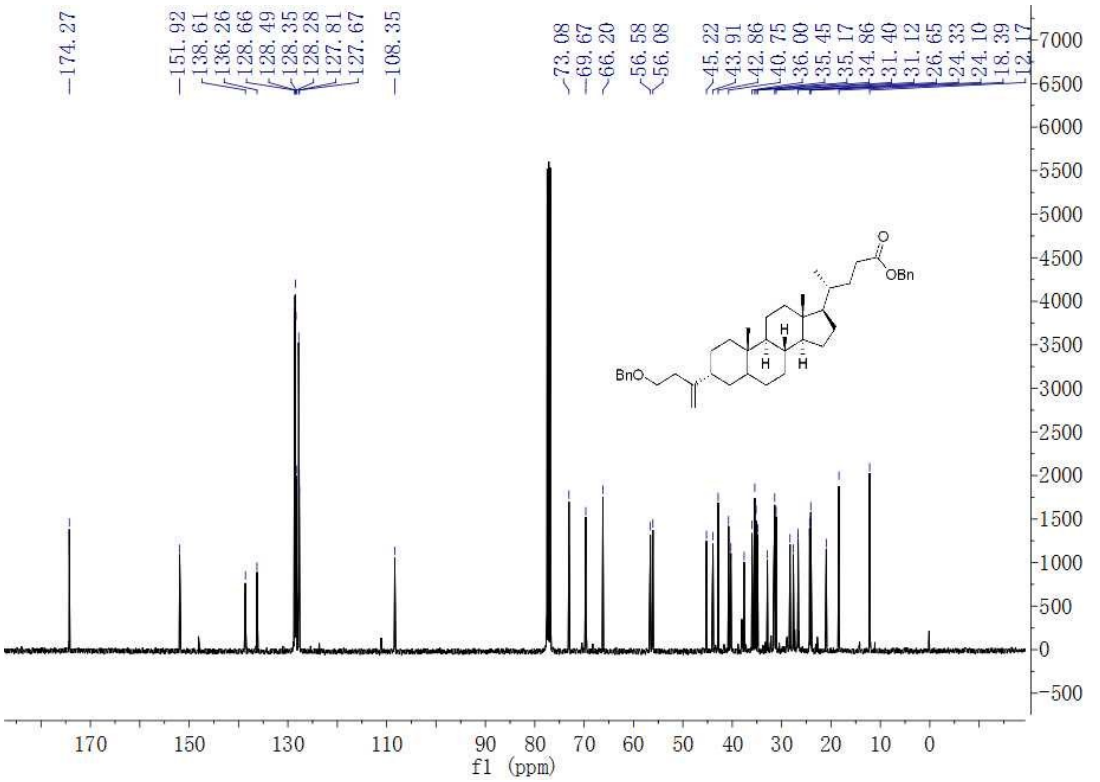

8.02
8.00
6.94
6.91
4.87
4.86
4.39
4.37
4.35
4.33
4.18
4.16
4.14
2.45
2.43
2.42
1.41
1.40
1.38
1.36
1.34
1.33
1.31
1.29
1.27
0.91
0.89
0.88
EtOOC
2.02
2.05
1.67
2.02
2.04
2.01
0.94
11.73
6.18
f1 (ppm)

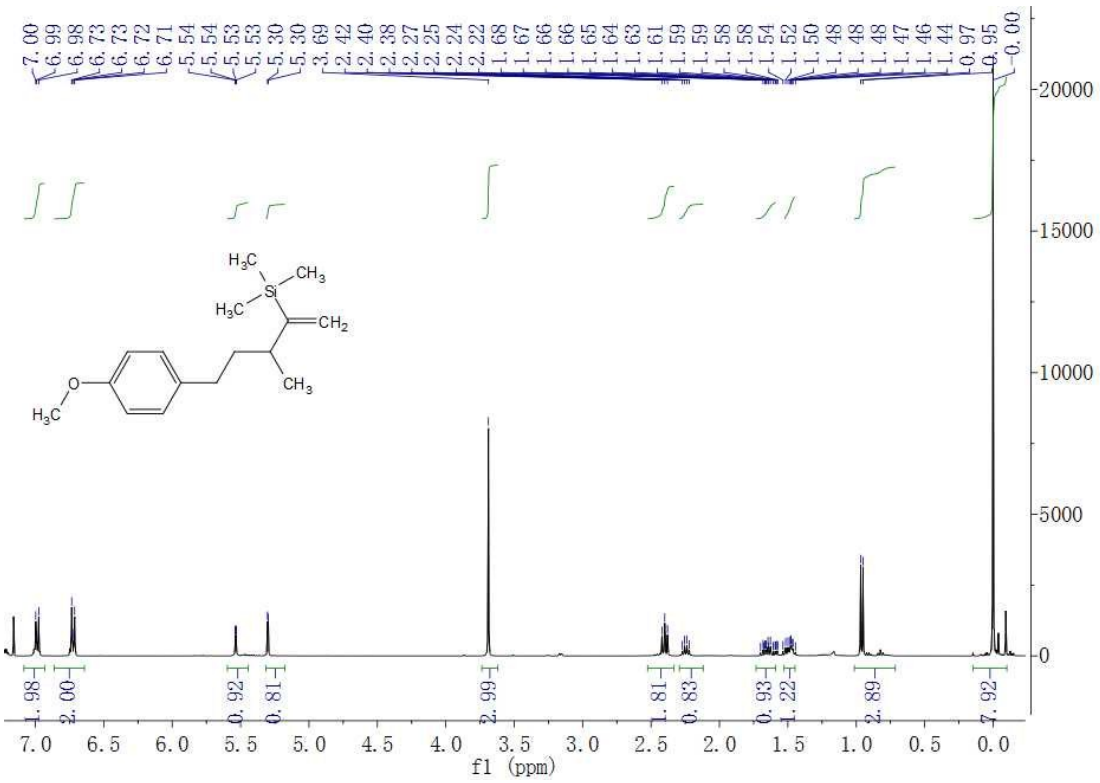

166.54
162.71
148.27
131.66
122.93
114.11
111.10
67.14
60.73
46.77
36.25
31.41
20.71
14.51
14.34
EtOOC
f1 (ppm)

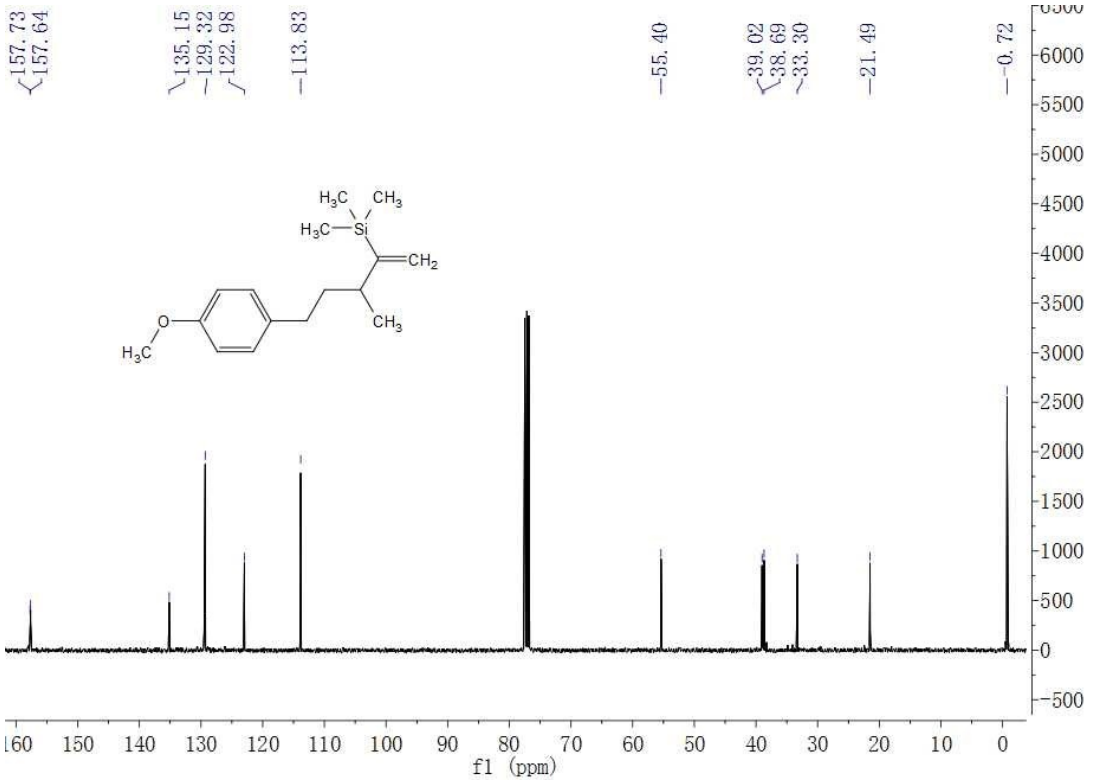

8.00
7.98
6.92
6.90
4.77
4.75
4.38
4.36
4.34
4.32
4.04
4.02
4.00
2.22
2.20
2.18
2.06
2.04
2.02
1.97
1.95
1.93
1.40
1.39
1.37
1.32
1.30
1.29
1.28
0.91
0.89
0.88
CH2
CH3
H3C
O
1.98
2.00
1.85
1.90
1.96
1.89
1.97
1.91
4.85
6.17
3.00
f1 (ppm)

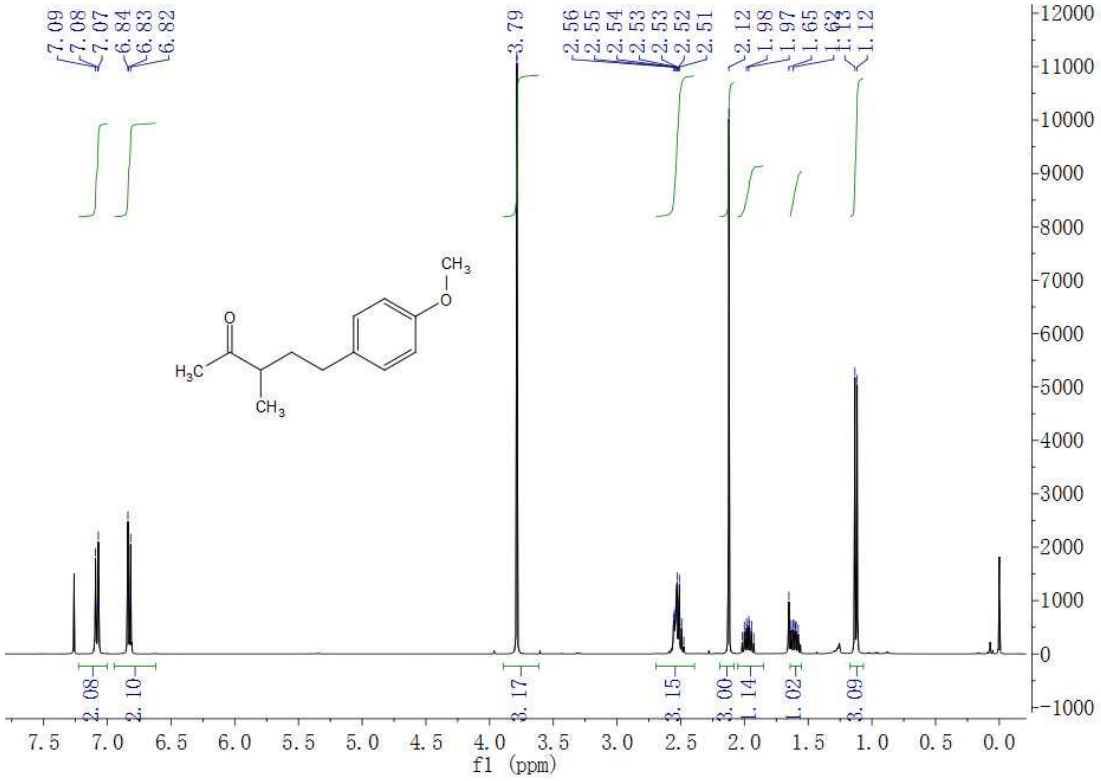

166.59
162.91
149.00
131.64
122.83
114.12
109.42
67.74
60.75
36.23
32.25
31.91
29.22
27.86
27.26
22.78
14.53
14.26
EtOOC
O
f1 (ppm)

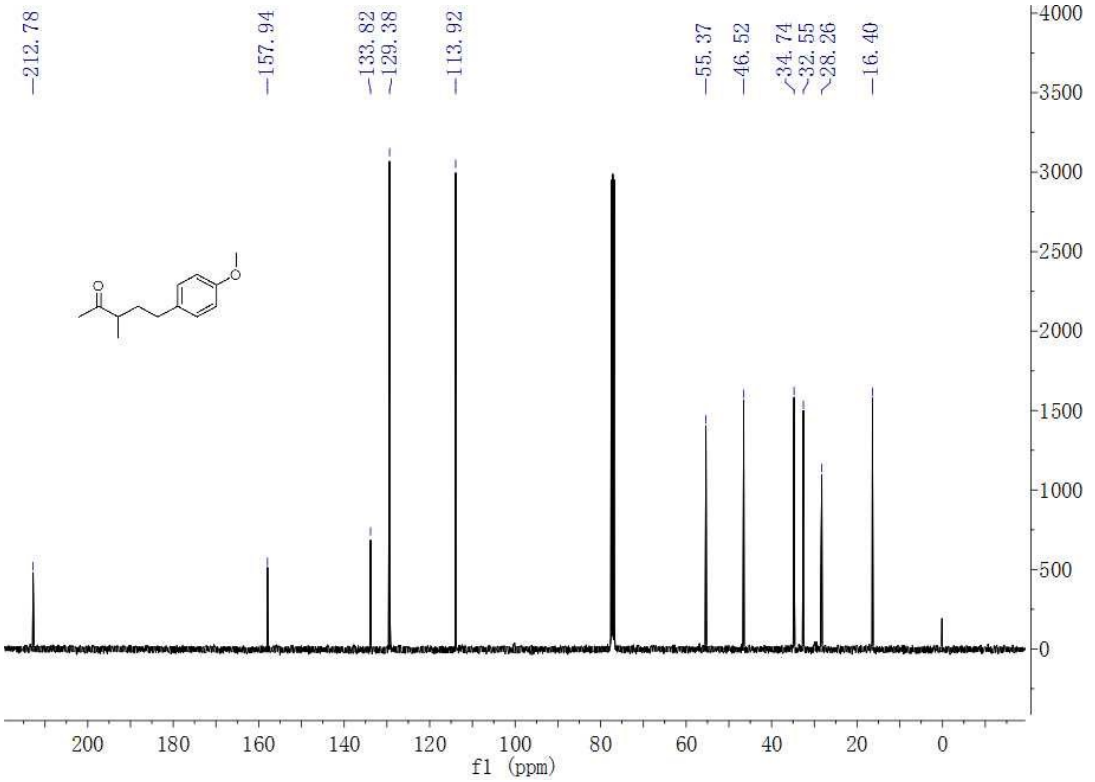

OBn
BnO
H
H
H
f1 (ppm)

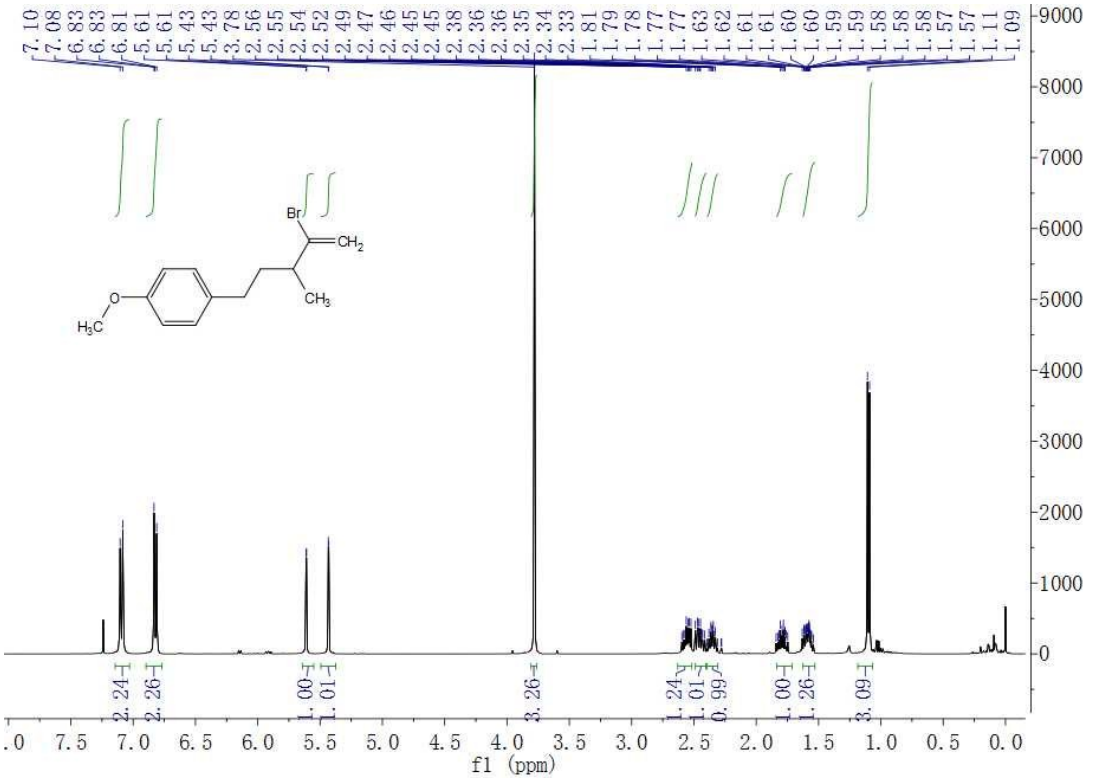

174.27
151.92
138.61
136.26
128.66
128.49
128.35
128.28
127.81
127.67
108.35
73.08
69.67
66.20
56.58
56.08
45.22
43.91
42.86
40.75
36.00
35.45
35.17
34.86
31.40
31.12
26.65
24.33
24.10
18.39
12.17
OBn
BnO
H
H
H
f1 (ppm)

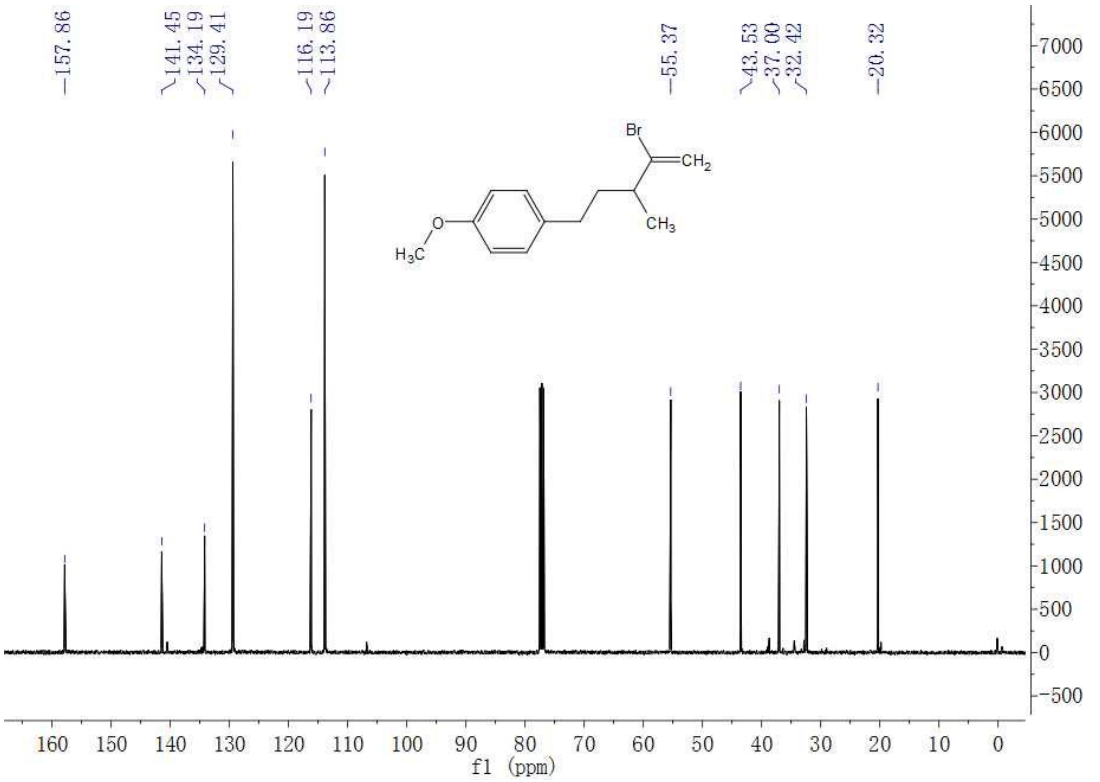

7.00
6.99
6.98
6.73
6.73
6.72
6.71
5.54
5.54
5.53
5.53
5.30
5.30
3.69
2.42
2.40
2.38
2.27
2.25
2.24
2.22
1.68
1.67
1.66
1.66
1.65
1.64
1.63
1.61
1.59
1.59
1.58
1.58
1.54
1.52
1.50
1.48
1.48
1.48
1.47
1.46
1.44
0.97
0.95
0.00
H3C
CH3
Si
H3C
CH2
CH3
O
H3C
1.98
2.00
0.92
0.81
2.99
1.81
0.83
0.93
1.22
2.89
7.92
f1 (ppm)

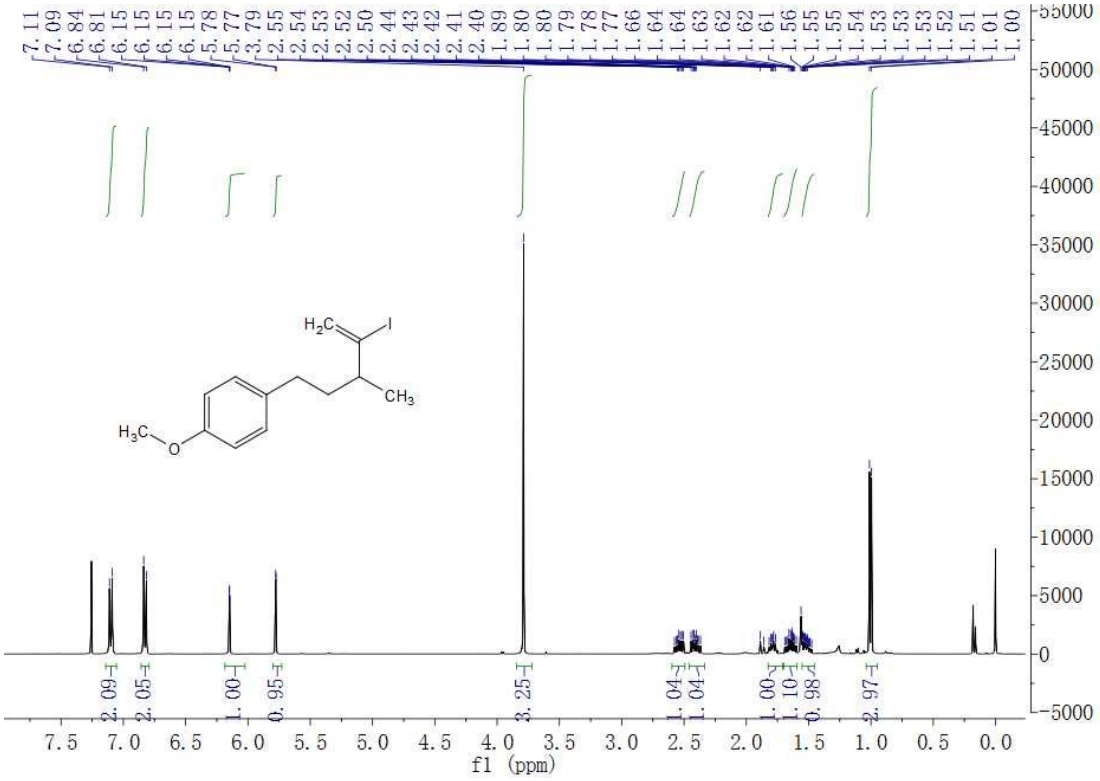

157.73
157.64
135.15
129.32
122.98
113.83
55.40
39.02
38.69
33.30
21.49
0.72
f1 (ppm)

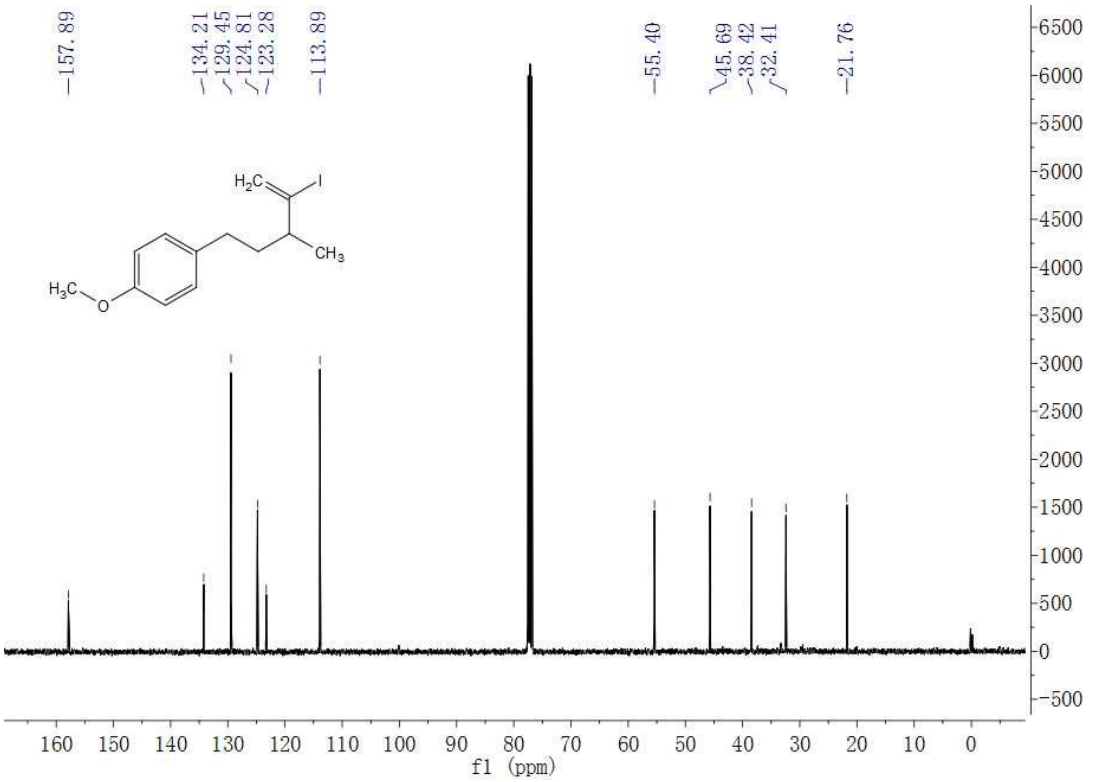

7.09
7.08
7.07
6.84
6.83
6.82
3.79
2.56
2.55
2.54
2.53
2.52
2.51
2.12
1.98
1.97
1.65
1.13
1.12
2.08
2.10
3.17
3.15
3.00
1.14
1.02
3.09
f1 (ppm)

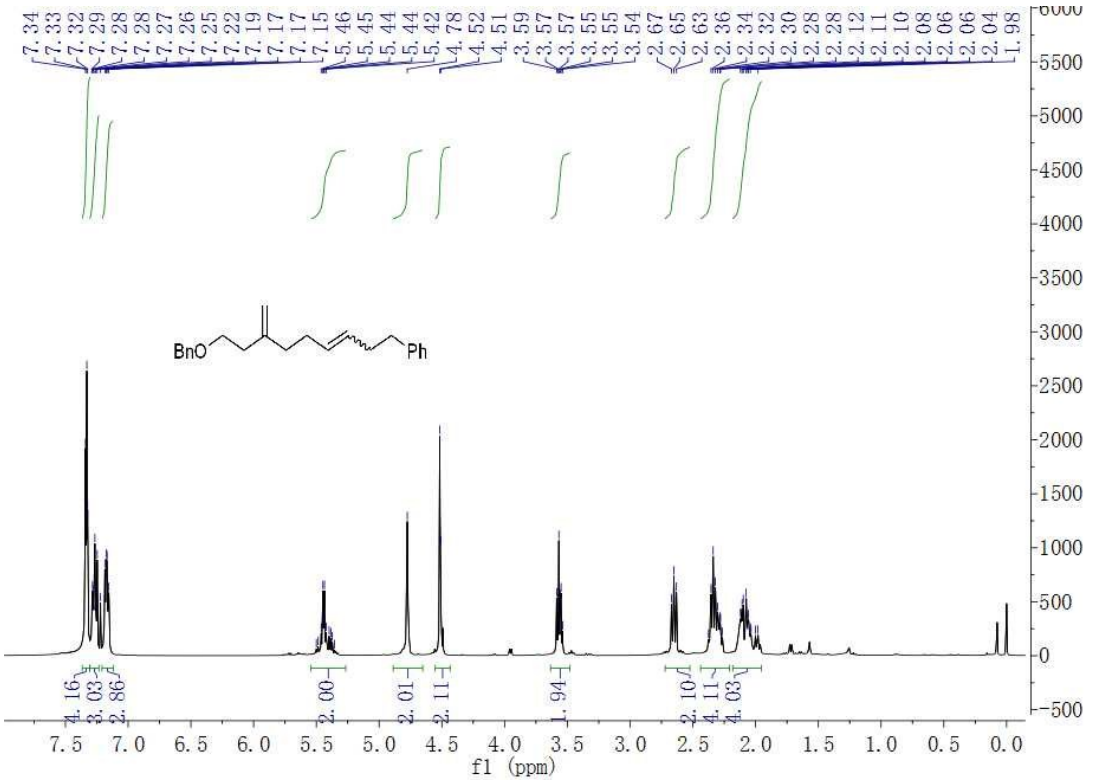

212.78
157.94
133.82
129.38
113.92
55.37
46.52
34.74
32.55
28.26
16.40
f1 (ppm)

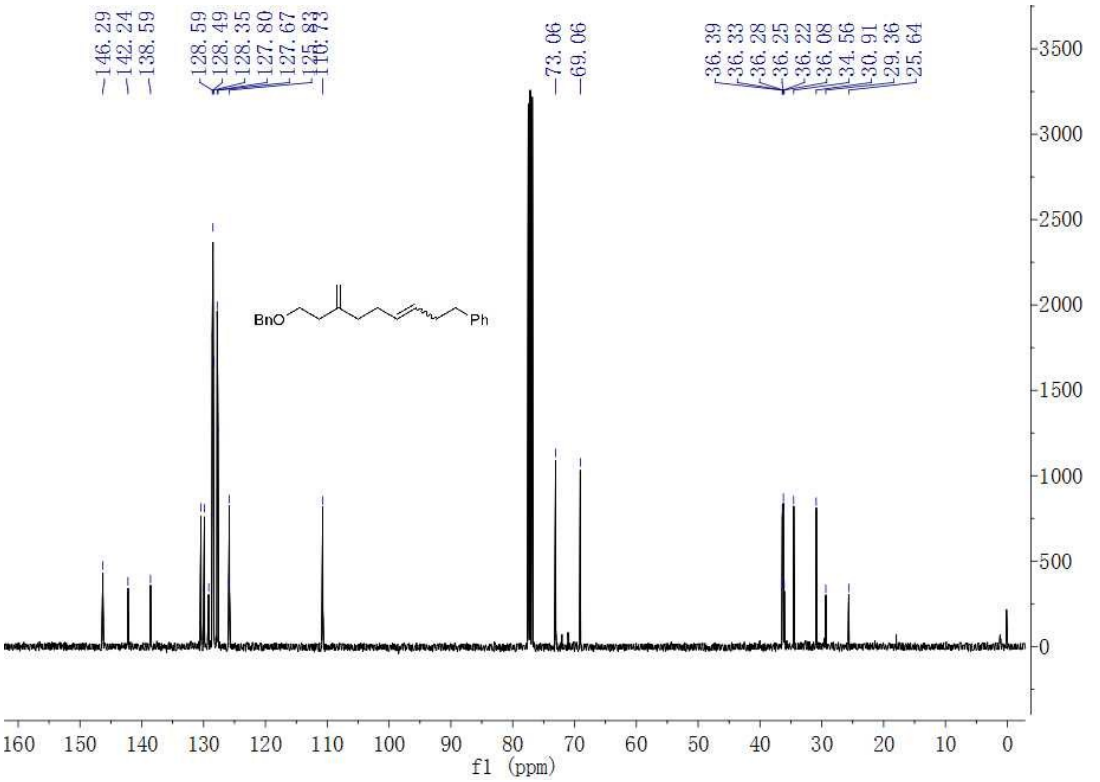

Br
CH2
CH3
O
H3C
f1 (ppm)

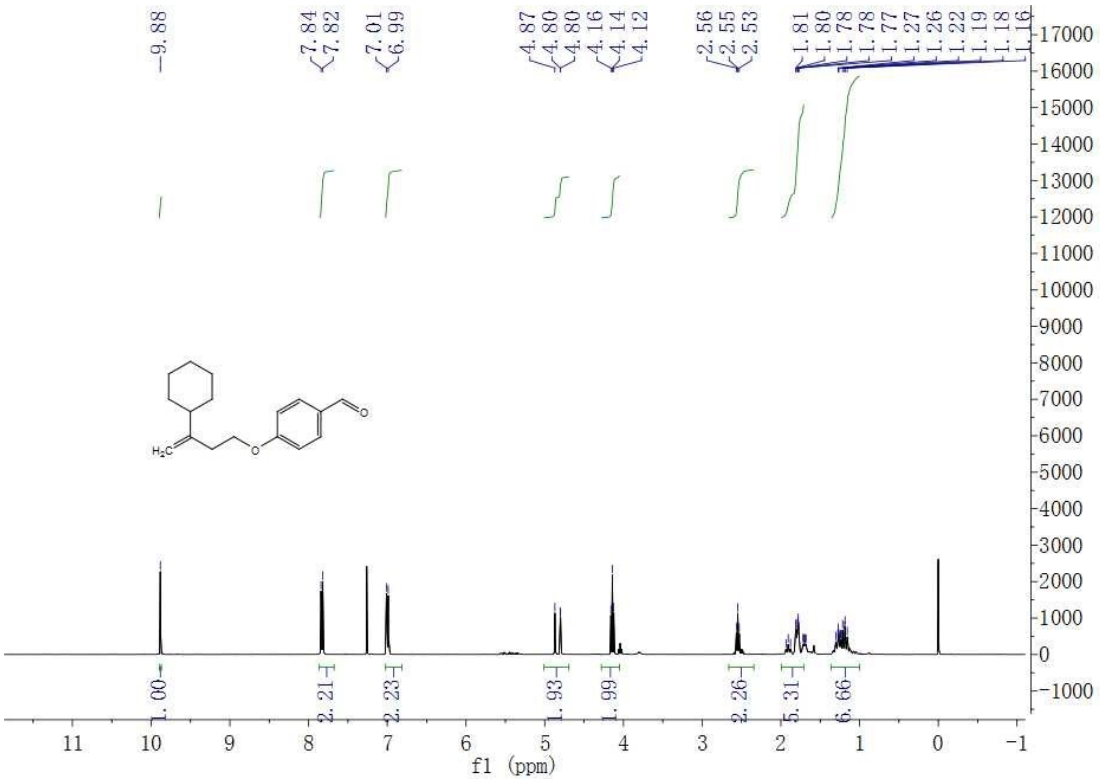

157.86
141.45
134.19
129.41
116.19
113.86
55.37
43.53
37.00
32.42
20.32
Br
CH2
CH3
O
H3C
f1 (ppm)

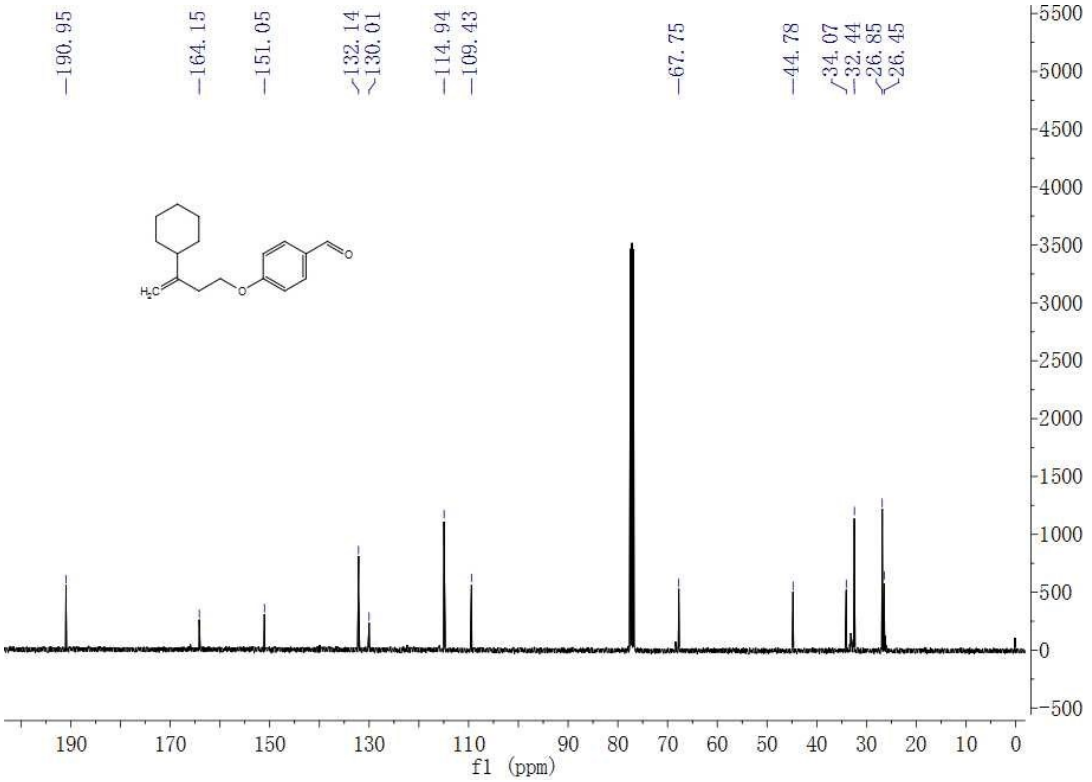

H2C
I
CH3
H3C
O
f1 (ppm)

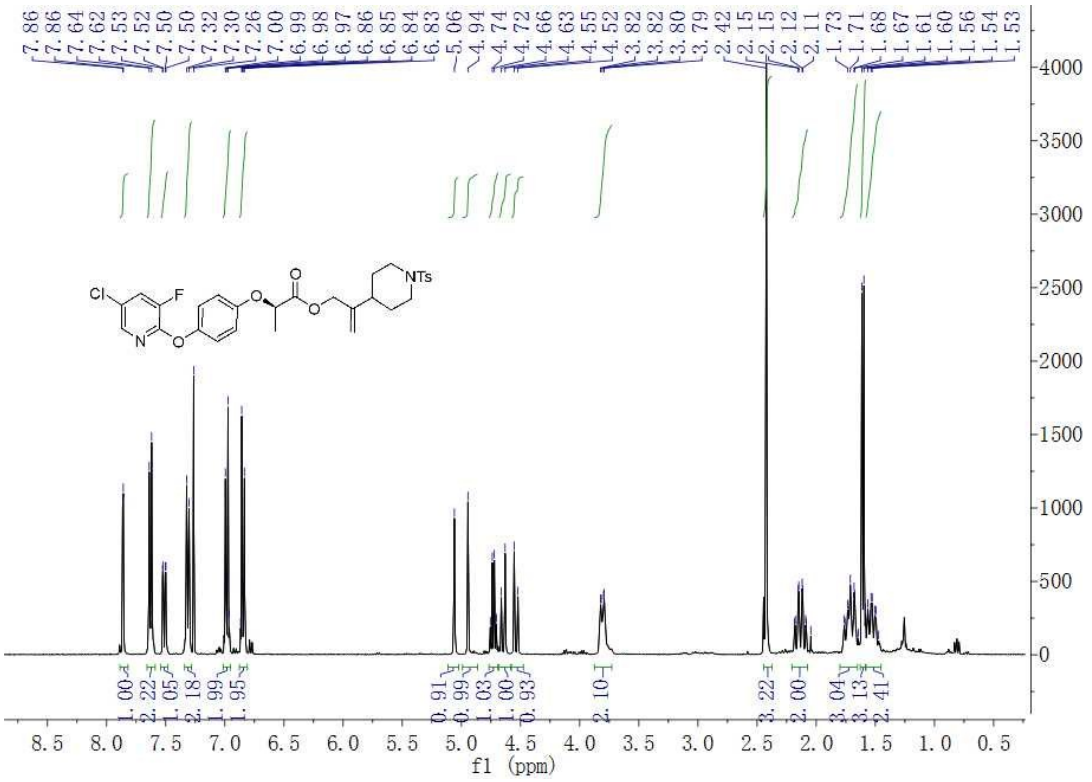

157.89
134.21
129.45
124.81
123.28
113.89
55.40
45.69
38.42
32.41
21.76
H2C
I
CH3
H3C
O
f1 (ppm)

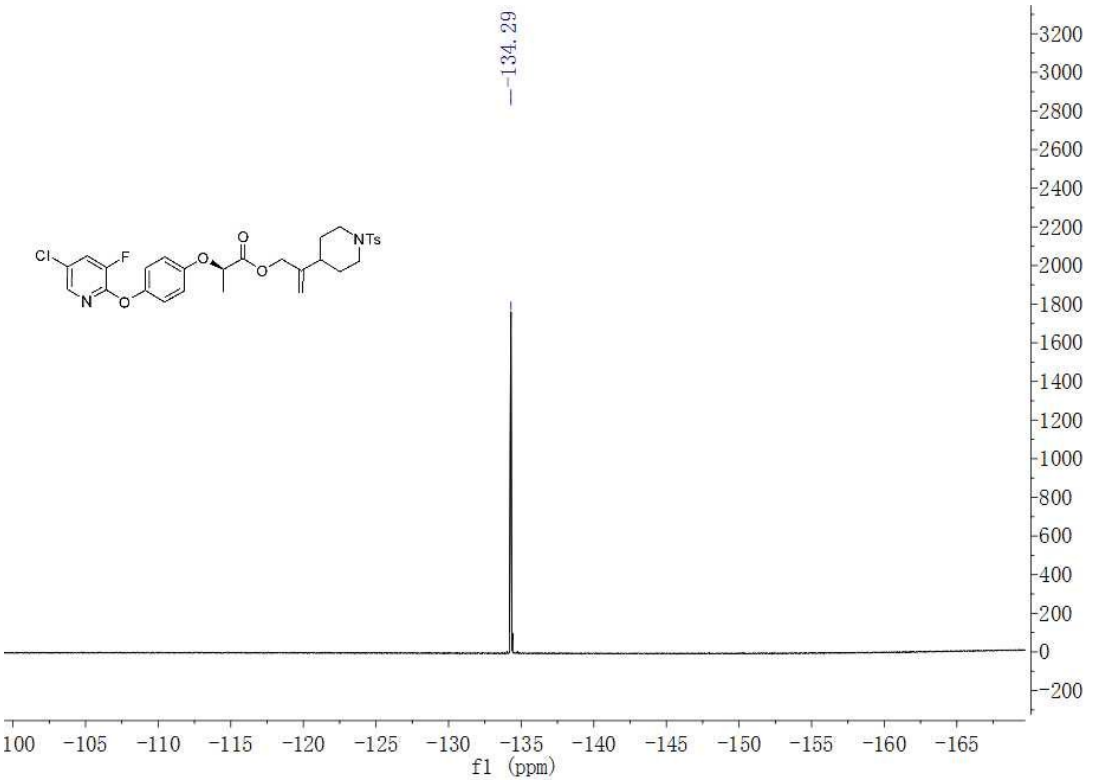

BnO
Ph
f1 (ppm)

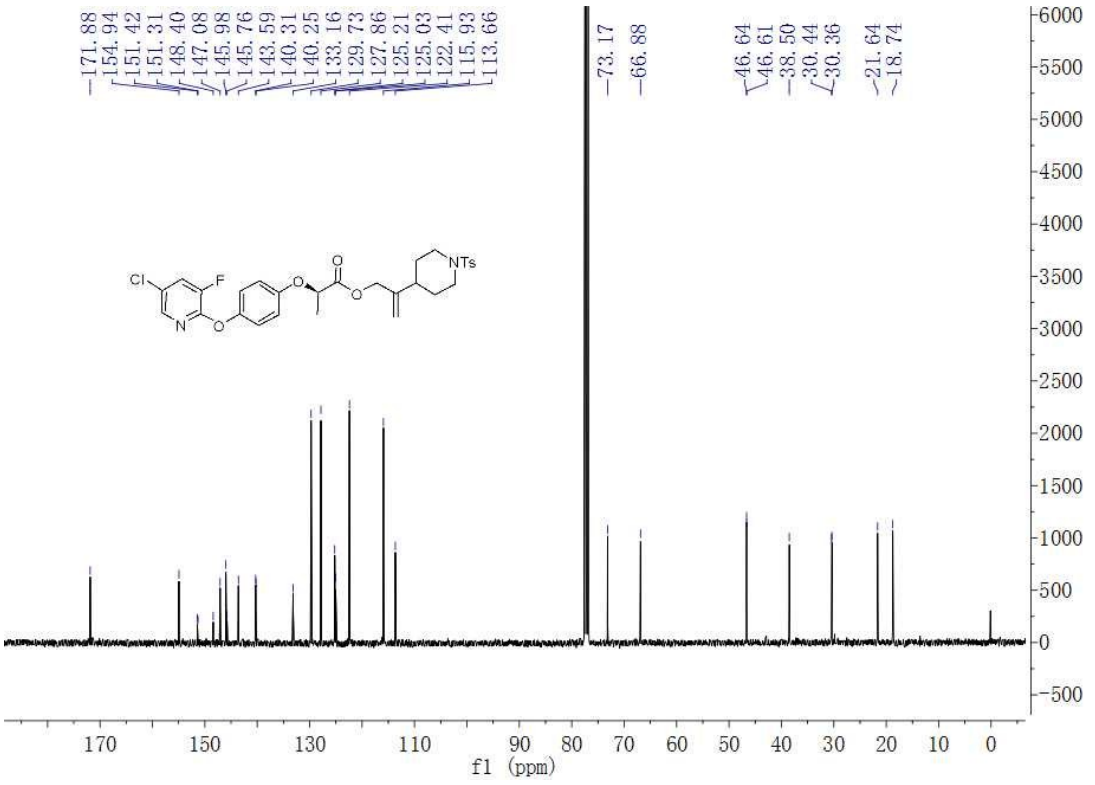

146.29
142.24
138.59
128.59
128.49
128.35
127.80
127.67
125.83
110.73
73.06
69.06
36.39
36.33
36.28
36.25
36.22
36.08
34.56
30.91
29.36
25.64
BnO
Ph
f1 (ppm)

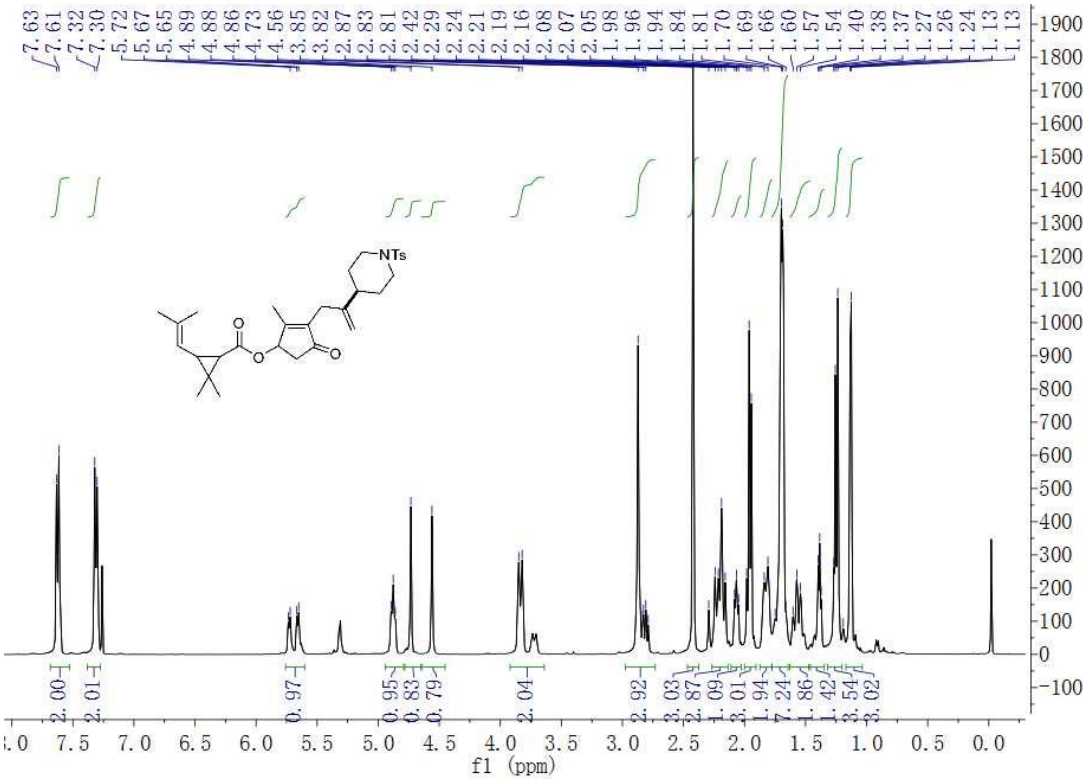

9.88
7.84
7.82
7.01
6.99
4.87
4.80
4.80
4.16
4.14
4.12
2.56
2.55
2.53
1.81
1.80
1.78
1.78
1.77
1.27
1.26
1.22
1.19
1.18
1.16
H2C
O
O
1.00
2.21
2.23
1.93
1.99
2.26
5.31
6.66
f1 (ppm)

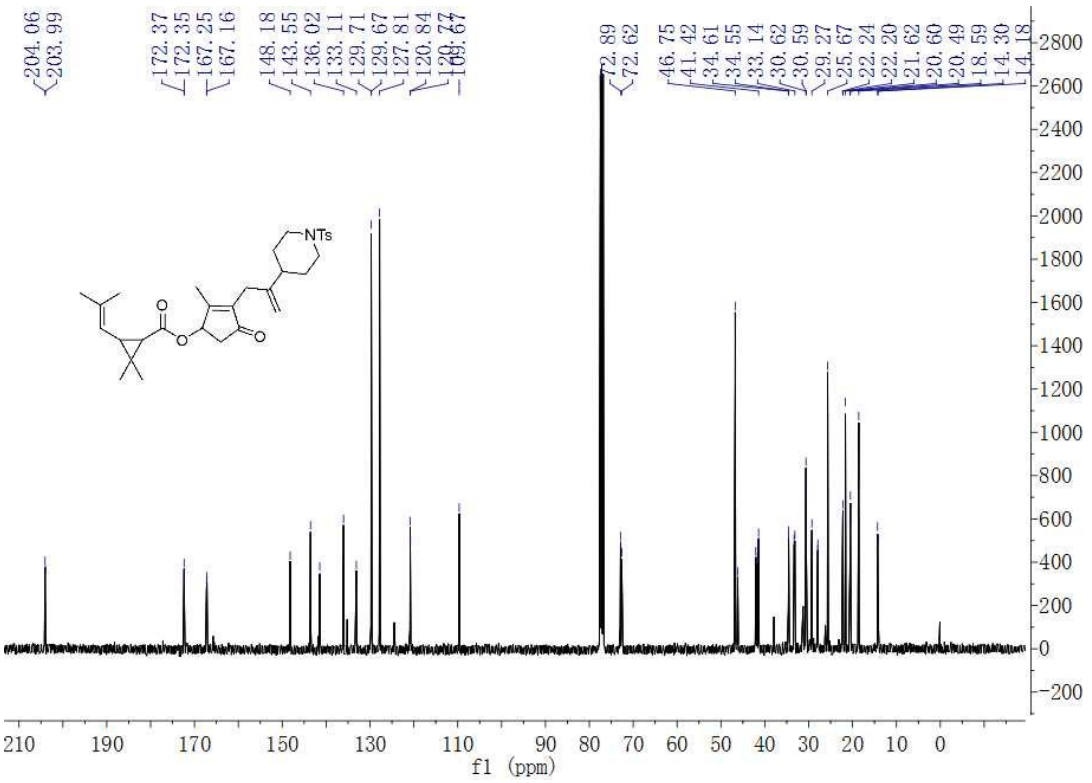

190.95
164.15
151.05
132.14
130.01
114.94
109.43
67.75
44.78
34.07
32.44
26.85
26.45
f1 (ppm)

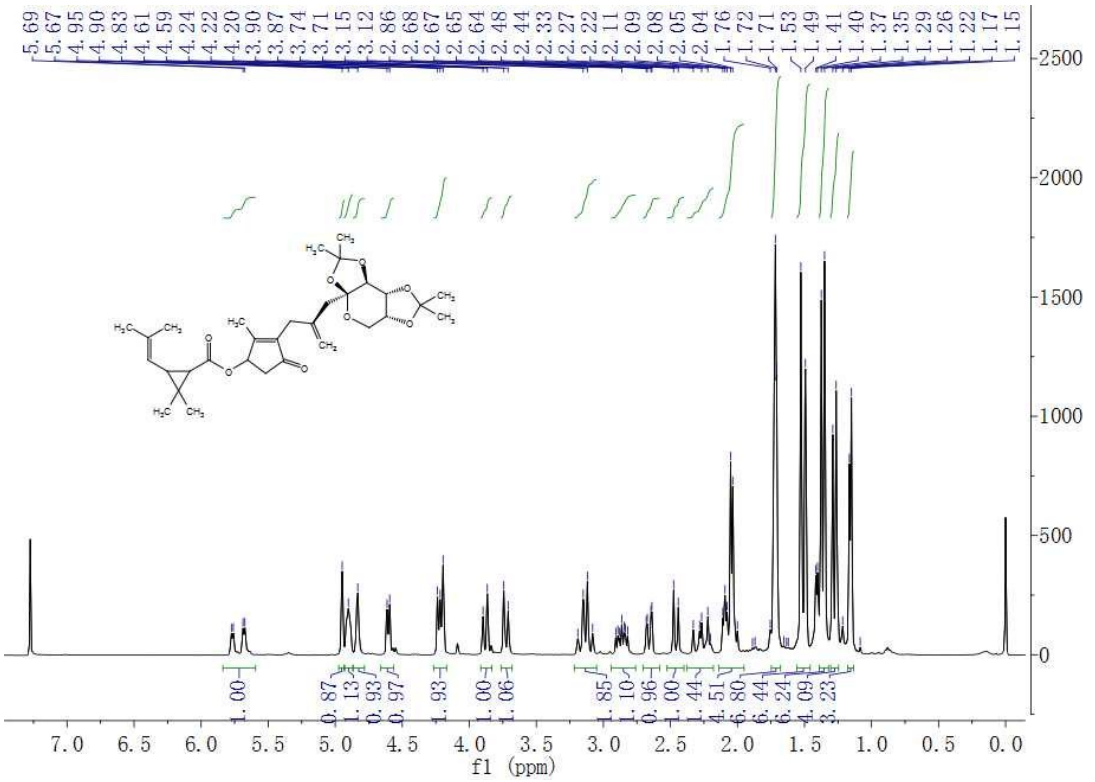

7.86
7.64
7.62
7.53
7.52
7.50
7.32
7.30
7.26
7.00
6.99
6.98
6.97
6.86
6.85
6.84
6.83
5.06
4.94
4.74
4.72
4.66
4.63
4.55
4.52
3.82
3.80
3.79
2.42
2.15
2.12
2.11
1.73
1.71
1.68
1.67
1.61
1.60
1.56
1.54
1.53
Cl
F
O
N
NTs
f1 (ppm)

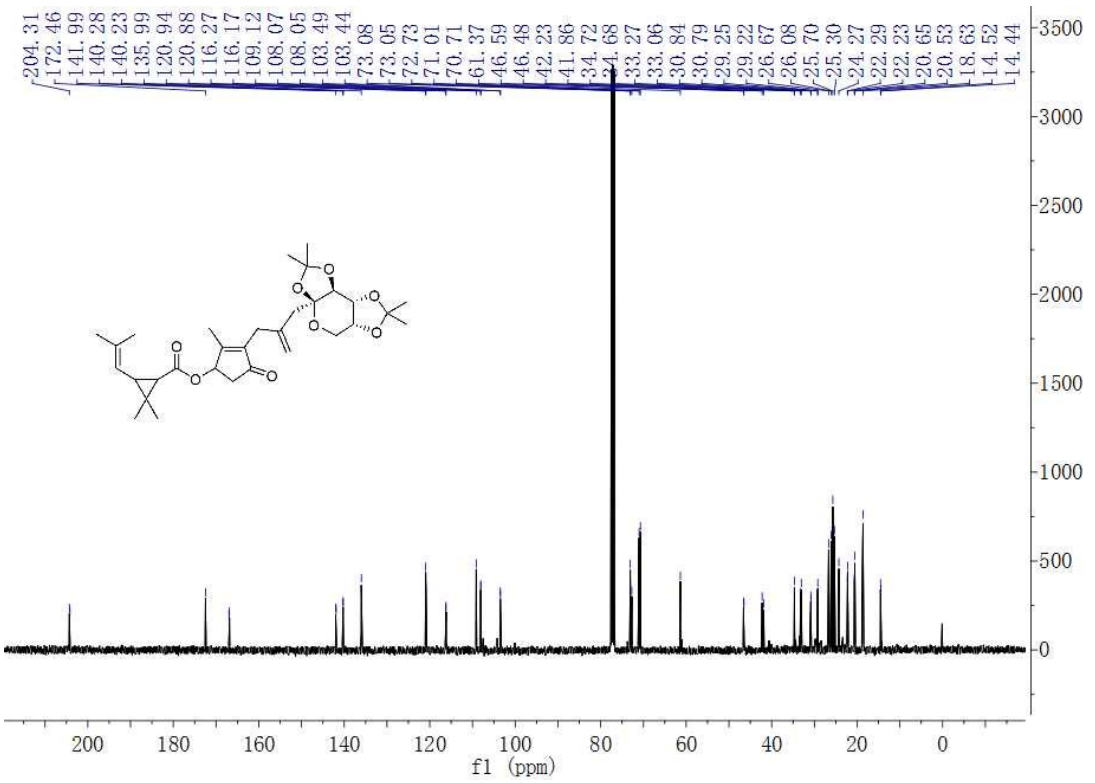

-134.29
Cl
F
O
N
O
O
O
NTs
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165
f1 (ppm)


-171.88
154.94
151.42
151.31
148.40
147.08
145.98
145.76
143.59
140.31
140.25
133.16
129.73
127.86
125.21
125.03
122.41
115.93
113.66
-73.17
-66.88
46.64
46.61
-38.50
30.44
30.36
-21.64
-18.74
Cl
F
O
N
O
O
O
NTs
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NTs
f1 (ppm)


NTs
f1 (ppm)


5.69 5.67 4.95 4.90 4.83 4.61 4.59 4.24 4.22 4.20 3.90 3.87 3.74 3.71 3.15 3.12 2.86 2.68 2.67 2.65 2.64 2.48 2.44 2.33 2.27 2.22 2.11 2.09 2.08 2.05 2.04 1.76 1.72 1.71 1.53 1.49 1.41 1.40 1.37 1.35 1.29 1.26 1.22 1.17 1.15
1.00 0.87 1.13 0.93 0.97 1.93 1.00 1.06 1.85 1.10 0.96 1.00 1.44 4.51 6.80 6.44 6.24 4.09 3.23
f1 (ppm)


204.31 172.46 141.99 140.28 140.23 135.99 120.94 120.88 116.27 116.17 109.12 108.07 108.05 103.49 103.44 73.08 73.05 72.73 71.01 70.71 61.37 46.59 46.48 42.23 41.86 34.72 34.68 33.27 33.06 30.84 30.79 29.25 29.22 26.67 26.08 25.70 25.30 24.27 22.29 22.23 20.65 20.53 18.63 14.52 14.44
f1 (ppm)