Supporting Information

Overcoming *peri*- and *ortho*-Selectivity in C−H Methylation of 1-Naphthaldehyde by Tunable Transient Ligands Strategy

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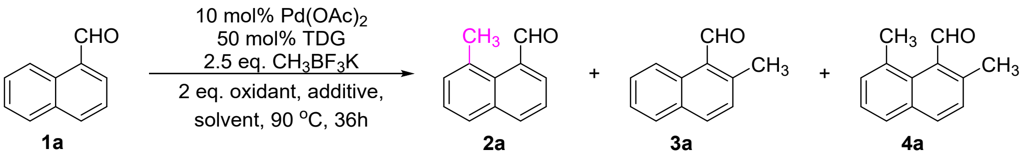
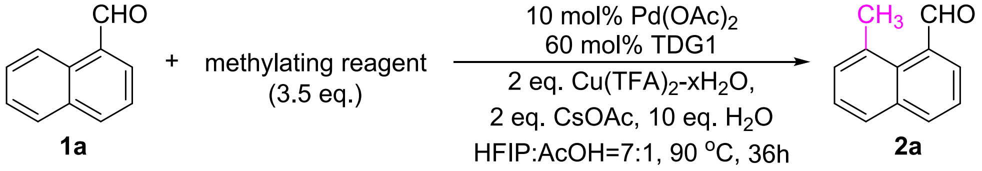
Table S1. Optimization of *peri*-C(sp2)−H methylation of 1a[a,b]



entry	additive	solvent	TDG	oxidant	**2a**(%)[b]	**3a**(%)[b]	**4a**(%)[b]
1	—	AcOH	TDG1	AgOAc	5	—	—
2	—	AcOH	TDG1	AgTFA	7	—	—
3	—	AcOH	TDG1	AgOTf	6	—	—
4	—	AcOH	TDG1	$Cu(TFA)_2$-xH_2O	22	—	2
5	—	AcOH	TDG1	$Cu(OAc)_2$	15	—	—
6	—	AcOH	TDG1	CuF_2-$2H_2O$	17	—	—
7	—	AcOH	TDG1	TBHP	8	—	—
8	—	AcOH	TDG1	$PhI(OAc)_2$	trace	—	—
9	—	AcOH	TDG1	NFSI	3	—	—
10	—	AcOH	TDG1	1- fluoro-2,4,6-trimethylpyridinium tetrafluoroborate	5	—	—
11	CsOAc(2 eq.)	AcOH	TDG1	$Cu(TFA)_2$-xH_2O	35	—	4
12	NaOAc(2 eq.)	AcOH	TDG1	$Cu(TFA)_2$-xH_2O	27	—	3
13	KOAc(2 eq.)	AcOH	TDG1	$Cu(TFA)_2$-xH_2O	30	—	3
14	TEA(2 eq.)	AcOH	TDG1	$Cu(TFA)_2$-xH_2O	33	—	3
15	CsOAc(2 eq.), H_2O(10 eq.)	AcOH	TDG1	$Cu(TFA)_2$-xH_2O	43	—	4
16	CsOAc(2 eq.), H_2O(10 eq.)	HFIP:AcOH = 7:1	TDG1	$Cu(TFA)_2$-xH_2O	48	—	4
17[c]	CsOAc(2 eq.)	HFIP:AcOH = 7:1	TDG1	$Cu(TFA)_2$-xH_2O	trace	—	—
18[d]	CsOAc(2 eq.), H_2O(10 eq.)	HFIP:AcOH = 7:1	TDG1	$Cu(TFA)_2$-xH_2O	53	—	4
19[e]	**CsOAc(2 eq.), H_2O(10 eq.)**	**HFIP:AcOH = 7:1**	**TDG1**	**$Cu(TFA)_2$-xH_2O**	**57**	**—**	**4**
20[e]	CsOAc(2 eq.), H_2O(10 eq.)	HFIP:AcOH = 7:1	NO TDG	$Cu(TFA)_2$-xH_2O	—	—	—
21[e,f]	CsOAc(2 eq.), H_2O(10 eq.)	HFIP:AcOH = 7:1	TDG1	$Cu(TFA)_2$-xH_2O	—	—	—

[a] Experiments were performed with **1** (0.3 mmol), CH_3BF_3K(0.75 mmol), $Pd(OAc)_2$ (10 mol %), TDG (50 mol %), oxidant (0.6 mmol), solvent (1.5 mL), 90 °C, sealed tube, 36 h. [b] Yields were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard. [c] $CH_3BF_3N(n\text{-}Bu)_4$ was used. [d] 3.5 eq. CH_3BF_3K was used. [e] 3.5 eq. CH_3BF_3K and 60 mol% TDG were used. [f] No $Pd(OAc)_2$.

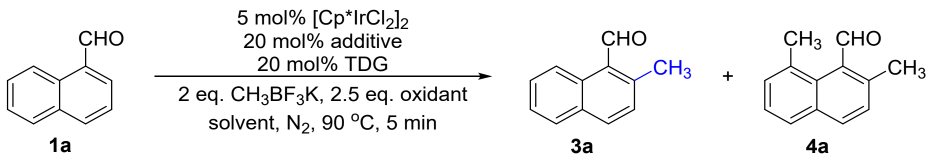
Table S2. Screening of methylating reagents in *peri*-methylation[a,b]

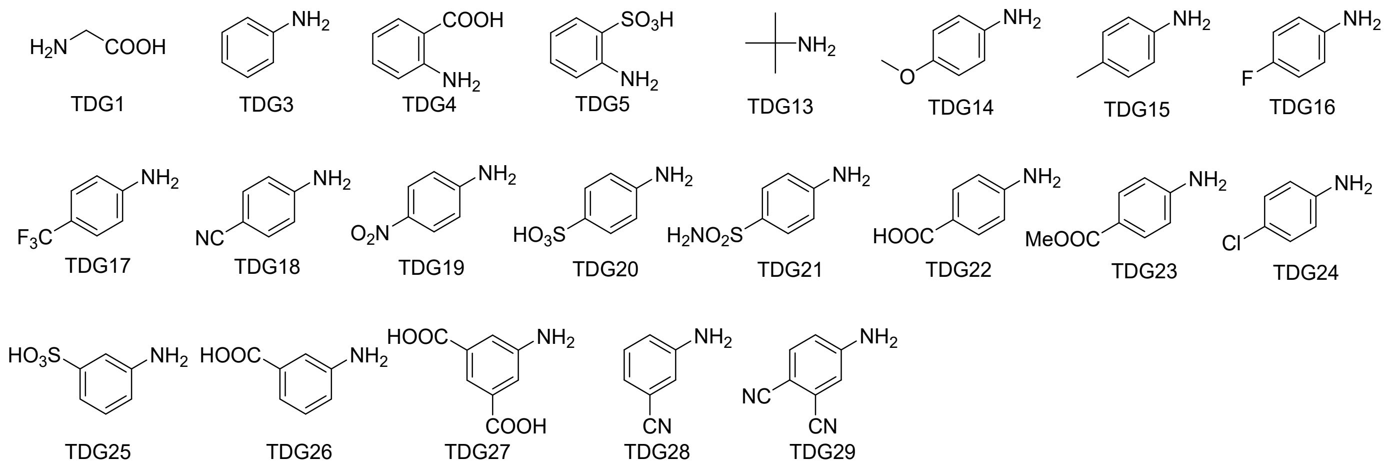


entry	methylating reagent	**2a**(%)[b]
1	$\mathbf{CH_3BF_3K}$	**57**
2	$CH_3B(OH)_2$	44
3	$(CH_3)_3B_3O_3$	45
4	2, 5, 5-trimethyl-1, 3, 2-dioxaborinane	22
5	CH_3OTs	12
7	CH_3I	15

[a]Experiments were performed with **1a** (0.3 mmol), methylating reagent (1.05 mmol), $Pd(OAc)_2$ (10 mol %), TDG1 (60 mol %), $Cu(TFA)_2$-xH_2O (0.6 mmol), CsOAc (0.6 mmol), HFIP:AcOH = 7:1 (1.5 mL), H_2O (3.0 mmol), 90 °C, sealed tube, 36 h. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.

Table S3. Optimization of *ortho*-C(sp2)−H methylation of 1a[a,b]



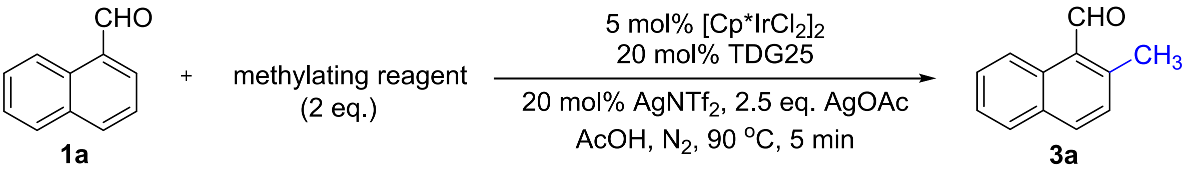


entry	additive	solvent	TDG	oxidant	**3**(%)[b]	**4**(%)[b]
1	AgNTf$_2$	AcOH	TDG3	AgOAc	65	6
2	AgNTf$_2$	DCE	TDG3	AgOAc	38	4
3	AgNTf$_2$	PhCl	TDG3	AgOAc	12	trace
4	AgNTf$_2$	AcOH	TDG3	Oxone	trace	—
5	AgNTf$_2$	AcOH	TDG3	Cu(OAc)$_2$	19	—
6	AgNTf$_2$	AcOH	TDG3	BQ	12	—
7	AgNTf$_2$	AcOH	TDG3	PhI(OAc)$_2$	trace	—
8	AgNTf$_2$	AcOH	TDG3	NFSI	33	—
9	AgNTf$_2$	AcOH	TDG3	1- fluoro-2,4,6-trimethylpyridinium tetrafluoroborate	6	—
10	AgNTf$_2$	AcOH	TDG3	Ag2O	30	3
11	AgNTf$_2$	AcOH	TDG3	AgTFA	55	5
12	AgNTf$_2$	AcOH	TDG3	AgOTf	24	2
13	AgNTf$_2$	AcOH	TDG3	AgF	32	2
14	AgBF$_4$	AcOH	TDG3	AgOAc	59	7
15	AgPF$_6$	AcOH	TDG3	AgOAc	41	5
16	AgSbF$_6$	AcOH	TDG3	AgOAc	53	5
17	AgNTf$_2$	AcOH	TDG1	AgOAc	18	—
18	AgNTf$_2$	AcOH	TDG4	AgOAc	60	6
19	AgNTf$_2$	AcOH	TDG5	AgOAc	63	5
20	AgNTf$_2$	AcOH	TDG13	AgOAc	23	—
21	AgNTf$_2$	AcOH	TDG14	AgOAc	22	3
22	AgNTf$_2$	AcOH	TDG15	AgOAc	37	4
23	AgNTf$_2$	AcOH	TDG16	AgOAc	44	5
24	AgNTf$_2$	AcOH	TDG17	AgOAc	73	4
25	AgNTf$_2$	AcOH	TDG18	AgOAc	85	2

26	AgNTf$_2$	AcOH	TDG19	AgOAc	25	—
27	AgNTf$_2$	AcOH	TDG20	AgOAc	88	2
28	AgNTf$_2$	AcOH	TDG21	AgOAc	85	4
29	AgNTf$_2$	AcOH	TDG22	AgOAc	79	2
30	AgNTf$_2$	AcOH	TDG23	AgOAc	83	3
31	AgNTf$_2$	AcOH	TDG24	AgOAc	56	5
32	**AgNTf$_2$**	**AcOH**	**TDG25**	**AgOAc**	**93**	**2**
33	AgNTf$_2$	AcOH	TDG26	AgOAc	85	2
34	AgNTf$_2$	AcOH	TDG27	AgOAc	88	3
35	AgNTf$_2$	AcOH	TDG28	AgOAc	89	2
36	AgNTf$_2$	AcOH	TDG29	AgOAc	88	2
37	AgNTf$_2$	AcOH	NO TDG	AgOAc	15(18[c])	—
38[d]	AgNTf$_2$	AcOH	TDG25	AgOAc	—	—

[a] Experiments were performed with **1** (0.3 mmol), CH_3BF_3K(0.6 mmol), $[Cp^*IrCl_2]_2$ (5 mol %), TDG (20 mol %), additive (0.06 mmol), oxidant (0.75 mmol), solvent (1.5 mL), 90 °C, sealed tube, N_2, 24 h. [b] Yields were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard. [c] 24h. [d] No $[Cp^*IrCl_2]_2$.

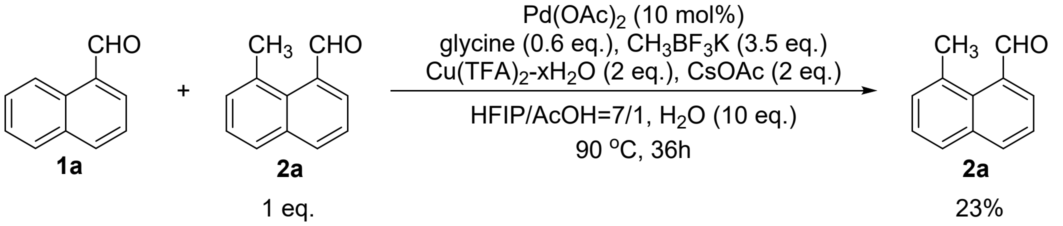
Table S4. Screening of methylating reagents in *ortho*-methylation[a,b]



entry	methylating reagent	**3a**(%)[b]
1	**CH_3BF_3K**	**93**
2	$CH_3B(OH)_2$	14
3	$(CH_3)_3B_3O_3$	18
4	2, 5, 5-trimethyl-1, 3, 2-dioxaborinane	trace
5	CH_3OTs	trace
7	CH_3I	trace

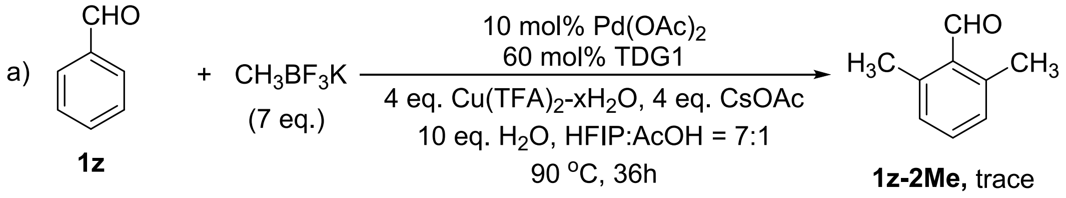
[a] Experiments were performed with **1a** (0.3 mmol), methylating reagent (0.6 mmol), $[Cp^*IrCl_2]_2$ (5 mol %), TDG25 (20 mol %), AgNTf$_2$ (0.06 mmol), AgOAc (0.75 mmol), AcOH (1.5 mL), 90 °C, N_2, sealed tube, 5 min. [b] Yields were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard.

Scheme S1. Product inhibition experiment

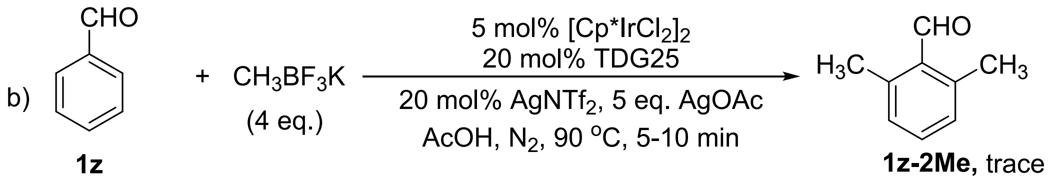


Scheme S2. Application of methylation method on benzaldehyde

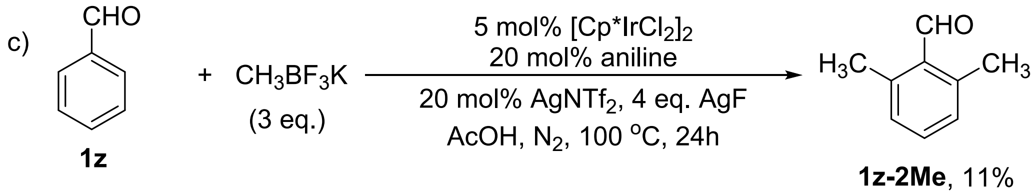
Peri-methylation method



Ortho-methylation method

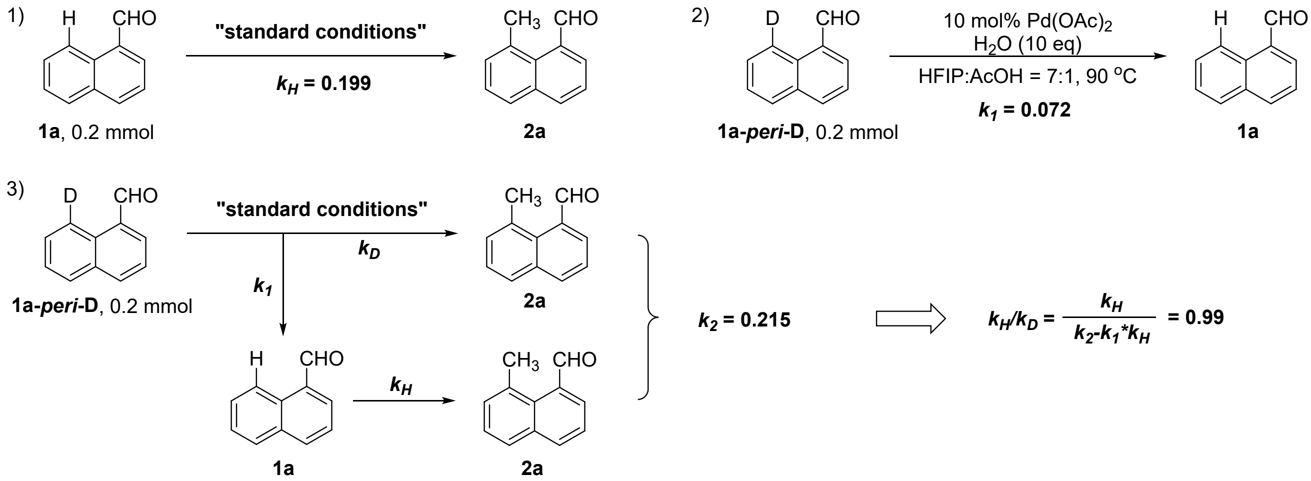


Sorensen's method [1]

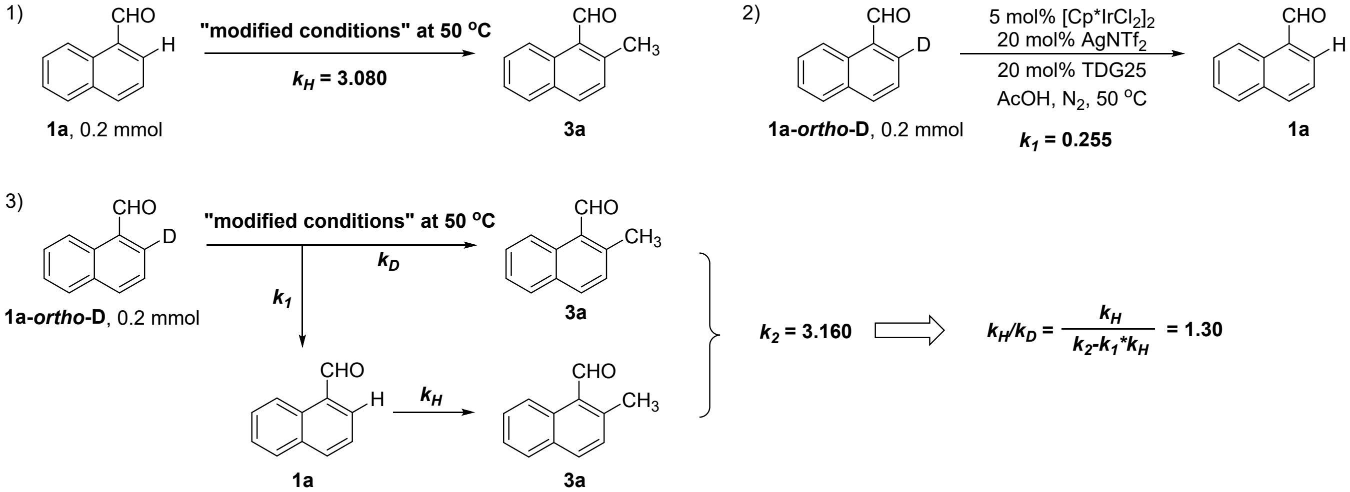


Scheme S3. Kinetic isotope effect experiments

a) *Peri*-methylation



b) *Ortho*-methylation



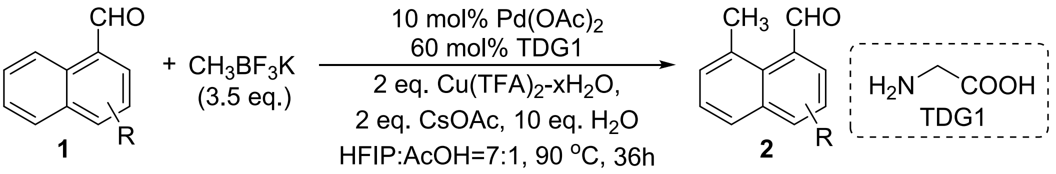
1. General materials and methods.

^{1}H (500 MHz), ^{13}C (125 MHz) NMR spectra were recorded at ambient temperature on Bruker AV-500, VNMRS 600 and Inova 400 instruments. The chemical shifts were reported in δ (ppm) using the δ 7.26 signal of $CDCl_3$ and δ 2.50 signal of DMSO-d_6 (^{1}H NMR), the δ 77.16 signal of $CDCl_3$ and δ 39.52 signal of DMSO-d_6 (^{13}C NMR) as internal standards. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HR-ESI-MS experiments were carried out using a Finnigan MAT 95 (EI/CI) or on a Thermo Fisher Scientific LTQ Orbitrap XL or Thermo Fisher Scientific Q Exactive Plus in the positive mode. All commercially available reagents were used without further purification, purchased from Acros or Aldrich and used without further purification unless otherwise noted. Solvents were predistilled according to standard laboratory methods. The progress of the reactions was monitored by analytical thin-layer chromatography (TLC) from Jiangyou Chemical Co., Ltd (Yantai, China). Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with basic potassium permanganate solution. And silica gel (200-300 mesh) for column chromatography was purchased from Haiyang Chemical Co., Ltd (Qingdao, China), particle size 0.040-0.063 mm (230-240 mesh, flash).

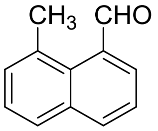
2. Computational details

All DFT-calculations were performed using Gaussian 16, Revision A.03.[2] Geometry optimizations and vibrational frequency calculations of all stationary points were computed with the M06-2X[3] functional. Each of the species was identified to be a minimum or a transition state. The electronic configuration of all the non-metal elements were described with the 6-31G(d,p) basis set, while metal elements (Pd and Ir) are treated with the effective core potential LanL2DZ basis set. All transition states were optimized using the default Berny algorithm implemented in the Gaussian 16 code. In order to get more accurate energies, single-point energies of all stationary points were computed at a larger basis set: def2-TZVP for Pd and Ir atoms and cc-pVTZ for all other atoms. All calculations were conducted in aceticacid solvent using the polarizable continuum model (PCM). For each transition state, the intrinsic reaction coordinate (IRC) analysis was performed to verify whether the transition state truly connects the reactant and the product. The intrinsic bond orbital (IBO) analysis were based on Pipek-Mezey localized orbitals calculated with Multiwfn software [4].

3. General procedure for Pd-catalyzed *peri*-C−H methylation of naphthaldehydes.

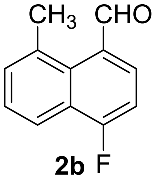


A 10-mL microwave-vial equipped with a stir bar was charged with naphthaldehyde **1** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg), glycine (TDG1) (0.18 mmol, 13.5 mg), CH_3BF_3K (1.05 mmol, 128 mg), $Cu(TFA)_2$-xH_2O (0.6 mmol, 174 mg) and CsOAc (0.6 mmol, 114 mg). HFIP:AcOH = 7:1 (1.5 mL) was added as solvent, followed by the addition of H_2O (3 mmol, 54 μL). The vial was sealed with a PTFE-lined cap, and stirred at 90 °C for 36 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting residue was purified by preparative thin layer chromatography to give desired product **2**.



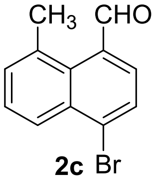
2a

8-Methyl-1-naphthaldehyde (2a). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (6:1) as the developing solvent. White solid (26.6 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.92 (s, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.1 Hz, 1H), 7.82-7.76 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.50-7.43 (m, 2H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.19, 136.32, 135.04, 134.94, 133.77, 131.17, 131.12, 129.94, 127.74, 126.42, 124.73, 25.94. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O$ 171.0804, found 171.0804.



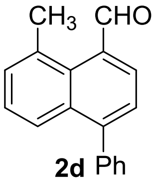
2b

4-Fluoro-8-methyl-1-naphthaldehyde (2b). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether as the developing solvent. White solid (25.9 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.83 (s, 1H), 8.12-8.06 (m, 1H), 7.99 (dd, *J* = 8.0, 6.2 Hz, 1H), 7.57-7.49 (m, 2H), 7.24-7.17 (m, 1H), 2.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.56, 162.58 (d, *J* = 260.8 Hz), 133.98 (d, *J* = 2.7 Hz), 132.92 (d, *J* = 5.0 Hz), 132.59 (d, *J* = 4.0 Hz), 132.28, 130.99 (d, *J* = 10.5 Hz), 126.80 (d, *J* = 2.0 Hz), 125.06 (d, *J* = 15.3 Hz), 119.88 (d, *J* = 8.1 Hz), 108.91 (d, *J* = 21.4 Hz), 26.08. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}FO$ 189.0710, found 189.0709.



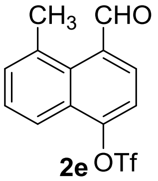
2c

4-Bromo-8-methyl-1-naphthaldehyde (2c). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (20:1) as the developing solvent. White solid (22.3 mg, 30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.28 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.61-7.48 (m, 2H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.29, 136.07, 134.28, 133.21, 132.15, 131.99, 130.46, 129.49, 129.40, 127.76, 126.96, 25.89. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}BrO$ 248.9910, found 248.9910.

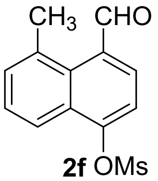


2d

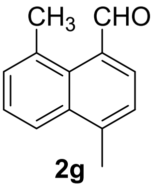
8-Methyl-4-phenyl-1-naphthaldehyde (2d). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (10:1) then petroleum ether/MTBE (80:1) as the developing solvent. Pale yellow solid (41.5 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.00 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.53-7.43 (m, 7H), 7.42-7.37 (m, 1H), 2.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.91, 146.96, 140.52, 135.61, 133.96, 133.34, 131.63, 131.02, 129.95, 129.38, 128.47, 127.97, 126.38, 126.02, 125.88, 26.14. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{15}O$ 247.1117, found 247.1121.


2e

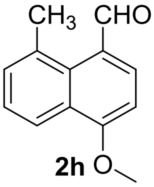
4-Formyl-5-methylnaphthalen-1-yl trifluoromethanesulfonate (2e). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (10:1) as the developing solvent. Pale yellow liquid (44 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.89 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.67-7.58 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 2.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.76, 149.31, 136.53, 134.51, 132.70, 132.56, 129.02, 128.35, 127.87, 120.19, 118.81 (q, *J* = 320.5 Hz), 116.84, 25.91. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{14}H_{12}F_3O_4S$ 333.0403, found 333.0405. $[M+CH_3]^+$ is an universal positive ion that are always found in the aromatic aldehydes with methanol as solution.[5]


2f

4-Formyl-5-methylnaphthalen-1-yl methanesulfonate (2f). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (2:1) as the developing solvent. Pale yellow solid (38.8 mg, 49%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.86 (s, 1H), 8.12 (d, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.63-7.53 (m, 3H), 3.27 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.90, 149.35, 135.37, 134.37, 132.69, 132.20, 129.62, 128.44, 127.68, 120.81, 117.14, 38.59, 25.94. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O_4S$ 265.0529, found 265.0535.

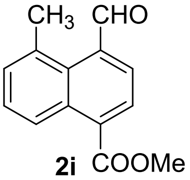

2g

4,8-Dimethyl-1-naphthaldehyde (2g). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (10:1) then petroleum ether/MTBE (60:1) as the developing solvent. Pale yellow solid (28.3 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.00-7.95 (m, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.53-7.47 (m, 2H), 7.39 (d, *J* = 7.3 Hz, 1H), 2.81 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.83, 141.97, 134.95, 134.37, 133.96, 131.30, 130.91, 129.95, 126.29, 125.95, 123.35, 26.14, 20.92. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O$ 185.0961, found 185.0957.



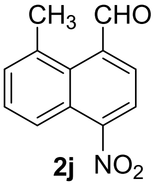
2h

4-Methoxy-8-methyl-1-naphthaldehyde (2h). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/EtOAc (20:1) as the developing solvent. Pale yellow solid (24 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 6.9 Hz, 1H), 7.47-7.41 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 4.07 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.39, 160.66, 133.76, 132.65, 132.52, 131.96, 129.08, 126.82, 125.78, 121.25, 102.96, 56.11, 26.24. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O_2$ 201.0910, found 201.0910.



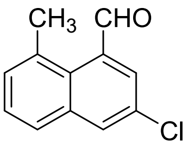
2i

Methyl 4-formyl-5-methyl-1-naphthoate (2i). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (4:1) then petroleum ether/MTBE (30:1) as the developing solvent. Pale yellow solid (37 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.87 (s, 1H), 8.63 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.58-7.52 (m, 1H), 7.50 (d, *J* = 6.9 Hz, 1H), 4.02 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.00, 167.95, 139.55, 133.87, 133.39, 132.42, 131.41, 131.20, 127.80, 127.75, 127.52, 124.81, 52.75, 25.95. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{14}H_{13}O_3$ 229.0859, found 229.0863.



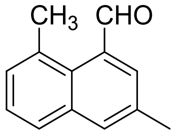
2j

8-Methyl-4-nitro-1-naphthaldehyde (2j). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (10:1) then petroleum ether/MTBE (50:1) as the developing solvent. Yellow solid (14.4 mg, 22%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.68-7.63 (m, 1H), 7.61 (d, *J* = 7.1 Hz, 1H), 2.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.94, 151.20, 140.22, 134.42, 132.34, 132.12, 129.27, 127.34, 126.25, 121.75, 121.03, 25.90. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{13}H_{12}NO_3$ 230.0812, found 230.0812.



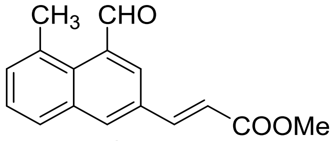
2k

3-Chloro-8-methyl-1-naphthaldehyde (2k). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (10:1) as the developing solvent. White solid (21 mg, 34%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.01 (d, J = 2.0 Hz, 1H), 7.89 (d, J = 2.1 Hz, 1H), 7.71 (d, J = 7.0 Hz, 1H), 7.53-7.46 (m, 2H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.91, 137.82, 135.91, 133.88, 132.95, 131.31, 130.86, 129.85, 129.48, 127.44, 126.98, 25.92. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{13}H_{12}ClO$ 219.0571, found 219.0575.



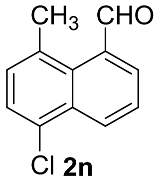
2l

3,8-Dimethyl-1-naphthaldehyde (2l). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (10:1) as the developing solvent. White solid (33.9 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.91 (s, 1H), 7.83-7.78 (m, 2H), 7.69 (d, J = 7.3 Hz, 1H), 7.44-7.37 (m, 2H), 2.80 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.41, 136.17, 135.33, 134.40, 134.07, 133.53, 131.89, 130.29, 129.55, 127.13, 126.42, 25.96, 21.13. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O$ 185.0961, found 185.0964.



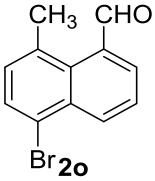
2m

Methyl (*E*)-3-(4-formyl-5-methylnaphthalen-2-yl)acrylate (2m). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (1:1) as the developing solvent. Pale yellow solid (33 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.91 (s, 1H), 8.14-8.06 (m, 2H), 7.88-7.77 (m, 2H), 7.53-7.46 (m, 2H), 6.62 (d, J = 16.0 Hz, 1H), 3.84 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.81, 167.29, 143.28, 137.04, 135.60, 135.06, 133.93, 132.31, 131.58, 130.84, 128.43, 127.36, 127.27, 119.47, 52.04, 25.77. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{16}H_{15}O_3$ 255.1016, found 255.1019.



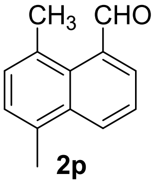
2n

5-Chloro-8-methyl-1-naphthaldehyde (2n). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether as the developing solvent. White solid (30 mg, 49%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.86 (s, 1H), 8.58-8.53 (m, 1H), 7.99-7.93 (m, 1H), 7.67-7.60 (m, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.66, 136.78, 133.09, 132.35, 131.85, 131.28, 130.88, 130.76, 130.44, 126.85, 125.86, 25.67. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}ClO$ 205.0415, found 205.0415.



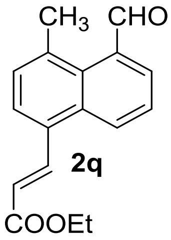
2o

5-Bromo-8-methyl-1-naphthaldehyde (2o). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (8:1) as the developing solvent. White solid (28.6 mg, 38%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.84 (s, 1H), 8.58-8.49 (m, 1H), 8.00-7.91 (m, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.67-7.58 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 2.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.52, 136.80, 133.85, 133.73, 132.91, 132.53, 131.20, 130.67, 130.48, 126.11, 122.11, 25.65. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}BrO$ 248.9910, found 248.9910.



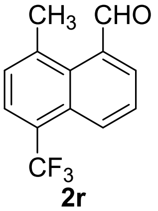
2p

5,8-Dimethyl-1-naphthaldehyde (2p). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (10:1) as the developing solvent. Pale yellow liquid (29.5 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.24 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.94 (dd, *J* = 7.1, 1.0 Hz, 1H), 7.60-7.54 (m, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 2.78 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.57, 136.83, 133.97, 133.46, 131.69, 131.48, 130.77, 130.62, 129.25, 127.46, 124.57, 25.83, 20.08. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O$ 185.0961, found 185.0958.

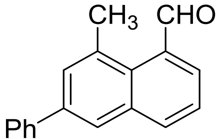


2q

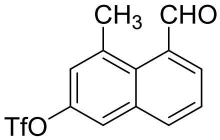
Ethyl (*E*)-3-(5-formyl-4-methylnaphthalen-1-yl)acrylate (2q). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (2:1) as the developing solvent. White solid (44.3 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.85 (s, 1H), 8.47 (d, *J* = 15.7 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 6.9 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.80 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.84, 166.81, 141.62, 136.91, 136.34, 132.66, 131.42, 131.33, 130.77, 130.03, 129.88, 125.67, 125.53, 121.77, 60.86, 26.05, 14.50. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{17}H_{17}O_3$ 269.1172, found 269.1176.


2r

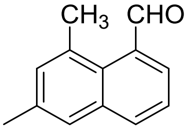
8-Methyl-5-(trifluoromethyl)-1-naphthaldehyde (2r). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/EtOAc (100:1) as the developing solvent. White solid (30 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.84 (s, 1H), 8.40 (d, J = 8.6 Hz, 1H), 7.98 (d, J = 7.1 Hz, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.72-7.65 (m, 1H), 7.52 (d, J = 7.5 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.47, 139.07, 137.05, 131.69, 130.40, 130.25, 130.22, 129.33, 126.45, 125.37 (q, J = 30.1 Hz), 125.36 (q, J = 6.1 Hz), 124.71 (q, J = 273.4 Hz), 26.10. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{10}F_3O$ 239.0678, found 239.0680.


2s

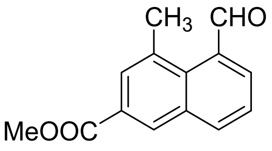
8-Methyl-6-phenyl-1-naphthaldehyde (2s). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (4:1) as the developing solvent. White solid (38.6 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.00-7.94 (m, 2H), 7.76-7.70 (m, 3H), 7.58-7.48 (m, 3H), 7.42 (t, J = 7.4 Hz, 1H), 2.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.04, 140.14, 138.88, 136.19, 135.35, 135.27, 134.33, 130.71, 130.24, 129.90, 129.06, 127.86, 127.39, 125.31, 125.14, 26.07. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{15}O$ 247.1117, found 247.1124.


2t

5-Formyl-4-methylnaphthalen-2-yl trifluoromethanesulfonate (2t). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (4:1) as the developing solvent. Pale yellow liquid (40.2 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.86 (s, 1H), 8.06 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 7.1 Hz, 1H), 7.73-7.68 (m, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.37 (s, 1H), 2.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.13, 146.89, 138.06, 136.65, 135.12, 134.85, 131.19, 130.20, 126.56, 124.04, 118.91 (q, J = 320.8 Hz), 118.52, 25.88. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{14}H_{12}F_3O_4S$ 333.0403, found 333.0417.

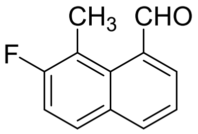

2u

6,8-Dimethyl-1-naphthaldehyde (2u). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (10:1) as the developing solvent. Pale yellow solid (25 mg, 45%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 7.1 Hz, 1H), 7.55 (s, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.32 (s, 1H), 2.78 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.27, 136.21, 136.09, 135.35, 134.45, 133.51, 129.39, 129.12, 126.75, 124.77, 25.80, 21.33. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O$ 185.0961, found 185.0962.



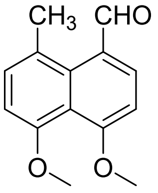
2v

Methyl 5-formyl-4-methyl-2-naphthoate (2v). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (5:1) as the developing solvent. Pale yellow solid (36.2 mg, 53%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.92 (s, 1H), 8.50 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.07-8.02 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 3.99 (s, 3H), 2.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.64, 166.81, 136.34, 136.23, 134.43, 134.26, 133.33, 131.96, 130.43, 130.13, 127.76, 125.63, 52.53, 25.96. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{14}H_{13}O_3$ 229.0859, found 229.0864.



2w

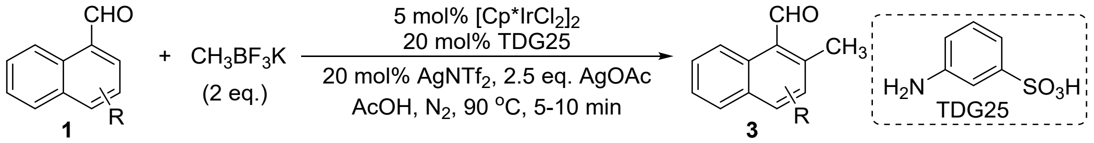
7-Fluoro-8-methyl-1-naphthaldehyde (2w). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (10:1) as the developing solvent. White solid (25.4 mg, 45%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.05-7.97 (m, 2H), 7.83-7.76 (m, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 9.0 Hz, 1H), 2.71-2.59 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.25, 160.63 (d, J = 245.8 Hz), 136.07 (d, J = 6.0 Hz), 134.85 (d, J = 5.5 Hz), 132.62 (d, J = 22.4 Hz), 131.72, 131.11, 129.53 (d, J = 10.3 Hz), 124.02 (d, J = 2.3 Hz), 118.26 (d, J = 16.4 Hz), 116.80 (d, J = 28.0 Hz), 15.89. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}FO$ 189.0710, found 189.0708.



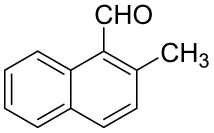
2y

4,5-Dimethoxy-8-methyl-1-naphthaldehyde (2y). The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography using petroleum ether/CH_2Cl_2 (3:1) as the developing solvent. Pale yellow solid (29 mg, 42%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 6.91-6.81 (m, 2H), 4.02 (s, 3H), 3.94 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.10, 162.64, 156.74, 135.19, 132.75, 132.09, 128.69, 125.60, 118.33, 107.46, 104.35, 56.74, 56.48, 25.55. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{14}H_{15}O_3$ 231.1016, found 231.1023.

4. General procedure for Ir-catalyzed *ortho*-C−H methylation of naphthaldehydes.

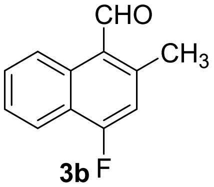


A 10-mL dry microwave-vial equipped with a stir bar was charged with naphthaldehyde **1** (0.3 mmol), $[Cp^*IrCl_2]_2$ (0.015 mmol, 12 mg), 3-Aminobenzenesulfonic acid (TDG25) (0.06 mmol, 10.4 mg), CH_3BF_3K (0.6 mmol, 73 mg), AgOAc (0.75 mmol, 125 mg) and $AgNTf_2$ (0.06 mmol, 23.3 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Degassed AcOH (1.5 mL) was added through syringe and the reaction mixture was stirred at 90 °C for 5-10 min. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography to give desired prouct **3**.



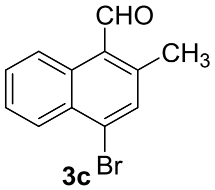
3a

2-Methyl-1-naphthaldehyde (3a). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (44.2 mg, 87%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 8.97 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.65-7.59 (m, 1H), 7.53-7.47 (m, 1H), 7.34 (d, J = 8.4 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.42, 142.74, 134.45, 132.60, 131.56, 129.88, 128.86, 128.51, 126.06, 124.46, 20.18. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O$ 171.0804, found 171.0802.



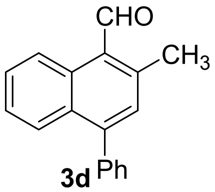
3b

4-Fluoro-2-methyl-1-naphthaldehyde (3b). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (200:1) as the eluent. White solid (50.9 mg, 90%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.85 (s, 1H), 9.05 (d, J = 8.7 Hz, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 10.9 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.86, 161.79 (d, J = 262.3 Hz), 145.12 (d, J = 9.9 Hz), 133.65 (d, J = 6.0 Hz), 129.96, 126.37 (d, J = 1.9 Hz), 125.11 (d, J = 4.0 Hz), 124.65 (d, J = 2.6 Hz), 122.73 (d, J = 15.5 Hz), 120.84 (d, J = 6.1 Hz), 113.50 (d, J = 20.3 Hz), 20.34 (d, J = 1.1 Hz). HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}FO$ 189.0710, found 189.0711.



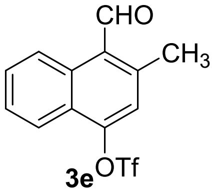
3c

4-Bromo-2-methyl-1-naphthaldehyde (3c). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (66 mg, 88%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.90 (s, 1H), 8.94 (d, *J* = 8.6 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 7.70 (s, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 2.77 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.78, 142.57, 133.87, 132.49, 131.09, 129.99, 129.54, 128.26, 127.70, 127.33, 124.75, 19.87. HRMS (ESI) m/z [M+H]$^+$calcd for C$_{12}$H$_{10}$BrO 248.9910, found 248.9910.



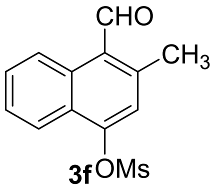
3d

2-Methyl-4-phenyl-1-naphthaldehyde (3d). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (66.3 mg, 90%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 11.01 (s, 1H), 9.07 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56-7.41 (m, 6H), 7.32 (s, 1H), 2.85 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 193.25, 146.60, 142.15, 139.87, 132.18, 131.10, 130.94, 129.85, 128.64, 128.52, 128.10, 127.85, 126.75, 126.06, 124.66, 20.23. HRMS (ESI) m/z [M+H]$^+$calcd for C$_{18}$H$_{15}$O 247.1117, found 247.1118.



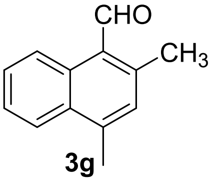
3e

4-Formyl-3-methylnaphthalen-1-yl trifluoromethanesulfonate (3e). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/CH$_2$Cl$_2$ (5:1) as the eluent. Pale yellow solid (77.1 mg, 81%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.93 (s, 1H), 8.97 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.70-7.64 (m, 1H), 7.36 (s, 1H), 2.85 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.23, 148.55, 142.57, 133.30, 130.22, 128.90, 127.81, 125.40, 124.84, 118.80 (q, *J* = 320.6 Hz), 121.32, 121.18, 20.29. HRMS (ESI) m/z [M+CH$_3$]$^+$calcd for C$_{14}$H$_{12}$F$_3$O$_4$S 333.0403, found 333.0413.



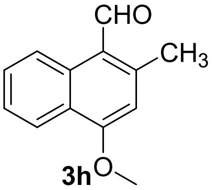
3f

4-Formyl-3-methylnaphthalen-1-yl methanesulfonate (3f). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (10:1) as the eluent. White solid (66.3 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.92 (s, 1H), 9.02 (d, *J* = 8.7 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.46 (s, 1H), 3.31 (s, 3H), 2.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.34, 148.67, 143.28, 133.27, 129.85, 127.74, 127.18, 125.97, 124.86, 121.72, 121.70, 38.64, 20.28. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O_4S$ 265.0529, found 265.0528.



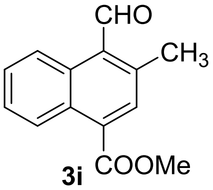
3g

2,4-Dimethyl-1-naphthaldehyde (3g). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (200:1) as the eluent. Pale yellow solid (52 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 9.10-9.00 (m, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.18 (s, 1H), 2.76 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.04, 142.83, 141.88, 131.71, 131.65, 131.01, 128.44, 127.00, 125.86, 125.01, 124.36, 20.19. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O$ 185.0961, found 185.0957.



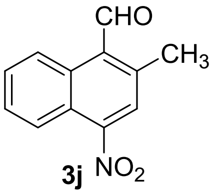
3h

4-Methoxy-2-methyl-1-naphthaldehyde (3h). The title compound was prepared according to the general procedure (TDG28 was used, 10 min) and purified by flash column chromatography over silica gel using petroleum ether/CH_2Cl_2 (4:1) as the eluent. Pale yellow solid (51.5 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.80 (s, 1H), 9.15 (d, *J* = 8.7 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.63 (t, *J* = 8.1 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 4.06 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.62, 160.00, 146.34, 133.22, 129.49, 125.48, 124.64, 124.58, 122.18, 121.87, 107.82, 55.94, 20.92. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O_2$ 201.0910, found 201.0907.

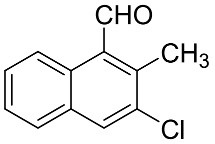


3i

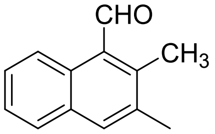
Methyl 4-formyl-3-methyl-1-naphthoate (3i). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/CH_2Cl_2 (3:1) as the eluent. Pale yellow solid (61.1 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 8.79 (d, *J* = 8.5 Hz, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H), 7.68-7.55 (m, 2H), 4.03 (s, 3H), 2.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.60, 167.53, 139.66, 132.96, 132.40, 132.09, 131.93, 130.04, 128.69, 127.33, 126.06, 124.33, 52.73, 19.97. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{15}H_{15}O_3$ 243.1016, found 243.1022.


3j

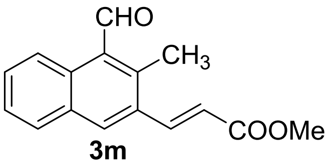
2-Methyl-4-nitro-1-naphthaldehyde (3j). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (100:1) as the eluent. Yellow solid (62.1 mg, 96%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.97 (s, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 7.93 (s, 1H), 7.78-7.68 (m, 2H), 2.83 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.74, 149.59, 139.73, 133.06, 132.63, 129.77, 128.76, 125.98, 124.56, 123.79, 123.06, 19.90. HRMS (ESI) m/z [M+CH$_3$]$^+$calcd for $C_{13}H_{12}NO_3$ 230.0812, found 230.0813.


3k

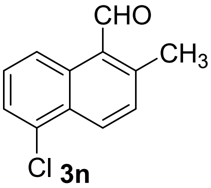
3-Chloro-2-methyl-1-naphthaldehyde (3k). The title compound was prepared according to the general procedure (TDG28 was used) and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. Pale yellow solid (48.5 mg, 79%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.91 (s, 1H), 8.70 (d, *J* = 8.6 Hz, 1H), 8.04 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 193.59, 139.12, 133.63, 133.15, 132.61, 131.38, 129.89, 128.78, 127.59, 127.02, 124.28, 16.15. HRMS (ESI) m/z [M+CH$_3$]$^+$calcd for $C_{13}H_{12}ClO$ 219.0571, found 219.0571.


3l

2,3-Dimethyl-1-naphthaldehyde (3l). The title compound was prepared according to the general procedure (TDG28 was used, 10 min) and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. Pale yellow solid (43.8mg, 79%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 11.00 (s, 1H), 8.76 (d, *J* = 8.6 Hz, 1H), 7.82 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 2.67 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 194.57, 141.54, 135.57, 134.02, 132.16, 130.18, 129.63, 127.76, 127.73, 126.03, 124.06, 20.86, 15.55. HRMS (ESI) m/z [M+H]$^+$calcd for $C_{13}H_{13}O$ 185.0961, found 185.0955.

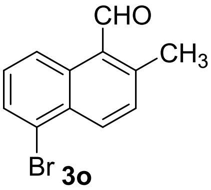

3m

Methyl (*E*)-3-(4-formyl-3-methylnaphthalen-2-yl)acrylate (3m). The title compound was prepared according to the general procedure (TDG28 was used, 10 min) and purified by flash column chromatography over silica gel using petroleum ether/CH_2Cl_2 (1:1) as the eluent. Pale yellow solid (67.9 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 8.69 (d, *J* = 8.6 Hz, 1H), 8.16-8.08 (m, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 3.85 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.14, 166.99, 142.40, 139.51, 133.42, 132.14, 131.90, 131.68, 130.45, 129.51, 129.00, 126.70, 124.22, 121.61, 52.04, 15.85. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{16}H_{15}O_3$ 255.1016, found 255.1017.



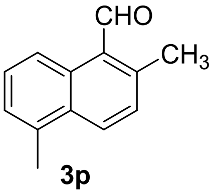
3n

5-Chloro-2-methyl-1-naphthaldehyde (3n). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (54.2 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.92 (s, 1H), 8.88 (d, *J* = 8.7 Hz, 1H), 8.41 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.54-7.47 (m, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.17, 143.23, 132.74, 132.50, 130.97, 130.44, 129.92, 128.78, 128.59, 126.48, 123.64, 20.08. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}ClO$ 205.0415, found 205.0411.



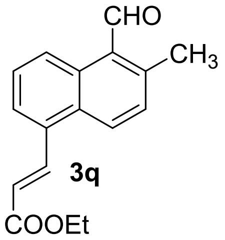
3o

5-Bromo-2-methyl-1-naphthaldehyde (3o). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (65.1 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.91 (s, 1H), 8.93 (d, *J* = 8.7 Hz, 1H), 8.38 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.49-7.39 (m, 2H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.08, 143.23, 133.19, 132.84, 131.23, 131.04, 130.28, 129.00, 128.81, 124.35, 123.44, 20.06. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}BrO$ 248.9910, found 248.9907.



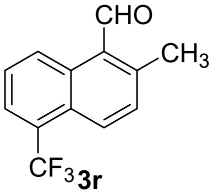
3p

2,5-Dimethyl-1-naphthaldehyde (3p). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. Pale yellow solid (51.2 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1H), 8.77 (d, *J* = 8.7 Hz, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.54-7.46 (m, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 6.9 Hz, 1H), 2.80 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.79, 141.75, 134.76, 131.89, 131.74, 130.29, 129.63, 129.03, 128.45, 126.88, 122.45, 20.22, 19.85. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O$ 185.0961, found 185.0957.



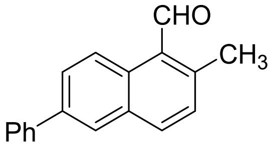
3q

Ethyl (*E*)-3-(5-formyl-6-methylnaphthalen-1-yl)acrylate (3q). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (50:1) as the eluent. Pale yellow solid (66 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.94 (s, 1H), 9.01 (d, *J* = 8.7 Hz, 1H), 8.46 (d, *J* = 15.7 Hz, 1H), 8.30 (d, *J* = 8.7 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 6.51 (d, *J* = 15.7 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.81 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.46, 166.82, 142.69, 141.42, 132.34, 131.74, 130.68, 130.49, 129.53, 129.03, 128.35, 126.70, 125.04, 121.87, 60.86, 20.02, 14.49. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{17}H_{17}O_3$ 269.1172, found 269.1176.



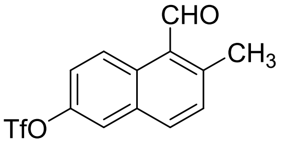
3r

2-Methyl-5-(trifluoromethyl)-1-naphthaldehyde (3r). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (150:1) as the eluent. White solid (68.5 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 9.18 (d, *J* = 8.8 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.21, 143.04, 131.95, 131.59, 130.04 (q, *J* = 2.5 Hz), 129.19, 129.13, 128.12, 127.06, 126.43 (q, *J* = 30.2 Hz), 124.71 (q, *J* = 5.9 Hz), 124.64 (q, *J* = 273.6 Hz), 19.84. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{14}H_{12}F_3O$ 253.0835, found 253.0835.



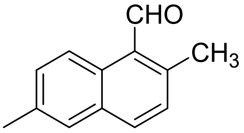
3s

2-Methyl-6-phenyl-1-naphthaldehyde (3s). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (50:1) as the eluent. White solid (60.4 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.98 (s, 1H), 9.06 (d, *J* = 8.9 Hz, 1H), 8.05-8.01 (m, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.89 (dd, *J* = 8.9, 1.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.36, 142.81, 140.42, 138.58, 134.72, 132.97, 130.66, 130.32, 129.06, 128.41, 128.36, 127.74, 127.40, 126.10, 125.11, 20.14. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{15}O$ 247.1117, found 247.1120.



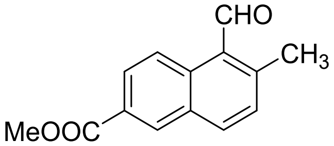
3t

5-Formyl-6-methylnaphthalen-2-yl trifluoromethanesulfonate (3t). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (50:1) as the eluent. White solid (71.6 mg, 75%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.93 (s, 1H), 9.19 (d, *J* = 9.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 2.6 Hz, 1H), 7.51 (dd, *J* = 9.5, 2.7 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 2.87 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.82, 147.15, 144.32, 134.19, 133.00, 131.79, 130.28, 128.58, 128.09, 122.15, 119.56, 118.91 (q, *J* = 320.9 Hz), 19.85. HRMS (ESI) m/z [M+CH$_3$]$^+$calcd for $C_{14}H_{12}F_3O_4S$ 333.0403, found 333.0412.



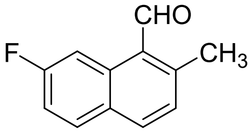
3u

2,6-Dimethyl-1-naphthaldehyde (3u). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (48 mg, 87%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.94 (s, 1H), 8.88 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 2.80 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 193.53, 141.94, 135.72, 133.97, 132.90, 131.11, 129.90, 129.73, 128.30, 127.52, 124.29, 21.50, 20.10. HRMS (ESI) m/z [M+H]$^+$calcd for $C_{13}H_{13}O$ 185.0961, found 185.0957.



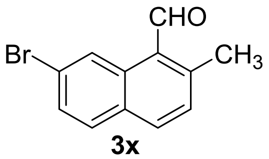
3v

Methyl 5-formyl-6-methyl-2-naphthoate (3v). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (50:1) as the eluent. Pale yellow solid (56.2 mg, 82%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.93 (s, 1H), 9.00 (d, *J* = 9.0 Hz, 1H), 8.54 (s, 1H), 8.16 (d, *J* = 10.1 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), 2.83 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 193.01, 166.90, 145.11, 135.49, 133.62, 131.77, 131.20, 130.74, 128.47, 128.14, 127.48, 124.82, 52.46, 20.30. HRMS (ESI) m/z [M+H]$^+$calcd for $C_{14}H_{13}O_3$ 229.0859, found 229.0859.



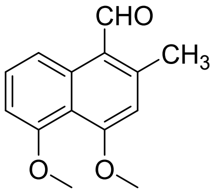
3w

7-Fluoro-2-methyl-1-naphthaldehyde (3w). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (100:1) as the eluent. Pale yellow solid (45 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.83 (dd, *J* = 12.4, 2.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.83 (dd, *J* = 8.9, 6.1 Hz, 1H), 7.34-7.28 (m, 2H), 2.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.85, 163.12 (d, *J* = 250.0 Hz), 144.57, 134.55, 132.38 (d, *J* = 10.7 Hz), 130.68 (d, *J* = 9.6 Hz), 129.73, 129.16 (d, *J* = 2.5 Hz), 127.72 (d, *J* = 5.8 Hz), 116.38 (d, *J* = 25.5 Hz), 109.23 (d, *J* = 24.2 Hz), 19.93. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}FO$ 189.0710, found 189.0706.



3x

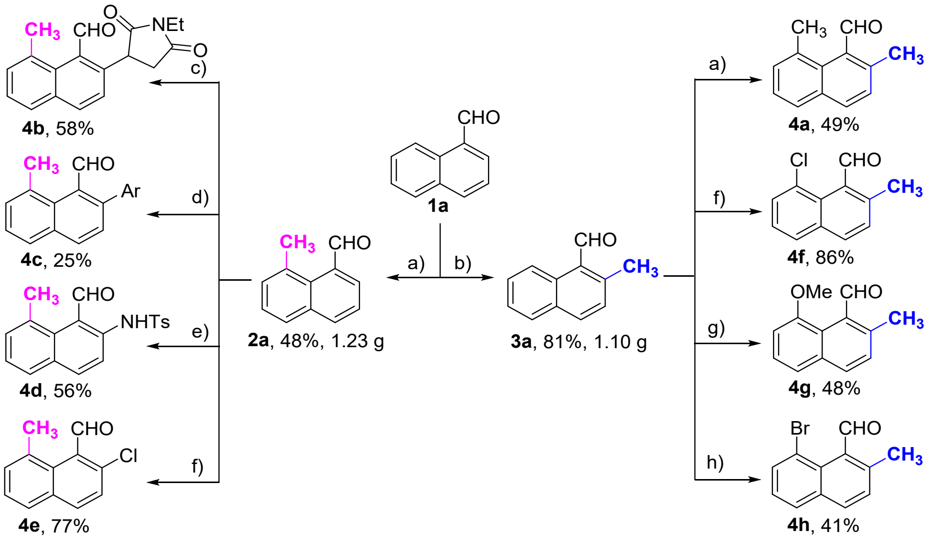
7-Bromo-2-methyl-1-naphthaldehyde (3x). The title compound was prepared according to the general procedure and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (61.1 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.86 (s, 1H), 9.26 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.57 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.77, 144.14, 134.38, 132.19, 131.04, 130.27, 129.83, 129.65, 127.44, 127.31, 123.94, 20.00. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}BrO$ 248.9910, found 248.9908.



3y

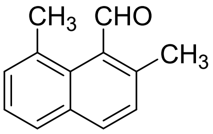
4,5-Dimethoxy-2-methyl-1-naphthaldehyde (3y). The title compound was prepared according to the general procedure (TDG29 was used, 30 min) and purified by reversed-phase column chromatography using CH_3CN/H_2O (30:70) as the eluent. Pale yellow solid (48.9 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.77 (s, 1H), 8.72 (d, *J* = 8.5 Hz, 1H), 7.51 (t, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.64 (s, 1H), 4.04 (s, 3H), 3.96 (s, 3H), 2.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.76, 161.90, 157.71, 146.10, 136.40, 129.64, 121.78, 116.93, 116.34, 109.23, 106.77, 56.46, 56.35, 20.91. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{14}H_{15}O_3$ 231.1016, found 231.1015.

5. Synthesis of diverse naphthaldehydes via sequential C−H functionalizations



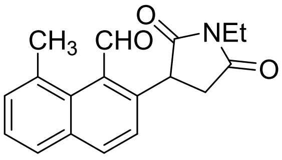
2a was prepared in 15 mmol-scale reaction according to the general *peri*-methylation procedure in 350 mL Schlenk tube and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (1.23 g, 48%).

3a was prepared in 8 mmol-scale reaction according to the general *ortho*-methylation procedure (4 h) in 100 mL Schlenk tube and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (1.10 g, 81%).



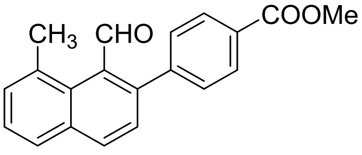
4a

2,8-dimethyl-1-naphthaldehyde (4a). A 10-mL microwave-vial equipped with a stir bar was charged with **3a** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg), glycine (0.18 mmol, 13.5 mg), CH_3BF_3K (1.05 mmol, 128 mg), $Cu(TFA)_2$-XH_2O (0.6 mmol, 174 mg) and CsOAc (0.6 mmol, 114 mg). HFIP:AcOH=7:1 (1.5 mL) was added as solvent, followed by the addition of H_2O (3 mmol, 54 μL). The vial was sealed with a PTFE-lined cap, and stirred at 90 °C for 36 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting residue was purified by preparative thin layer chromatography using petroleum ether/EtOAc (100:1) as the developing solvent. colorless liquid (27.1 mg, 49%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.98 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.73-7.67 (m, 1H), 7.40-7.35 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 2.67 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.83, 136.43, 134.27, 133.26, 133.24, 132.31, 131.21, 130.67, 129.13, 127.31, 125.67, 25.84, 20.63. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O$ 185.0961, found 185.0958.



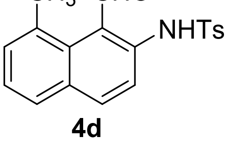
4b

2-(1-Ethyl-2,5-dioxopyrrolidin-3-yl)-8-methyl-1-naphthaldehyde (4b). A 10-mL dry microwave-vial equipped with a stir bar was charged with **2a** (0.3 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (0.015 mmol, 9.2 mg), $AgSbF_6$ (0.06 mmol, 20.5 mg), 2-methyl-3-(trifluoromethyl)aniline (0.06 mmol, 10.5 mg), 4-chlorobenzoic acid (0.15 mmol, 23.6 mg) and 1-ethyl-1*H*-pyrrole-2,5-dione (0.45 mmol). The vial was sealed with a PTFE-lined cap, and filled with N_2. DCE:HFIP = 5:1 (1.5 mL) was added through syringe and the reaction mixture was stirred at 60 °C for 36 h. Upon completion, the reaction mixture was filtered through a pad of Celite. The filtrate was quenched with saturated $NaHCO_3$ solution and extracted three times with DCM. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (6:1) as the eluent. Grey solid (51.5 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.95 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.78-7.71 (m, 1H), 7.49-7.42 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 4.53 (dd, *J* = 9.5, 5.8 Hz, 1H), 3.68 (q, *J* = 7.1 Hz, 2H), 3.29 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.84-2.73 (m, 4H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.47, 177.95, 175.90, 135.08, 134.93, 134.06, 133.99, 133.57, 131.65, 131.51, 127.62, 126.93, 125.25, 77.41, 44.40, 38.73, 34.30, 25.70, 13.23. HRMS (ESI) m/z [M+Na]$^+$calcd for $C_{18}H_{17}NNaO_3$ 318.1101, found 318.1094.



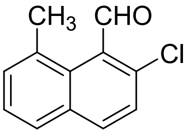
4c

Methyl 4-(1-formyl-8-methylnaphthalen-2-yl)benzoate (4c). A 10-mL dry microwave-vial equipped with a stir bar was charged with **2a** (0.3 mmol), Pd(OAc)$_2$ (0.03 mmol, 6.7 mg), methyl 4-iodobenzoate (0.6 mmol, 157.2 mg), 2-amino-2-methylpropanoic acid (0.12 mmol, 12.4 mg), and AgTFA (0.3 mmol, 66 mg) in air, followed by HFIP/TFA = 9:1 (1 mL). The reaction mixture was stirred at 110 °C for 24 h. Upon completion, the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with DCM. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (100:1) as the eluent. White solid (23.0 mg, 25%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.53-7.43 (m, 4H), 7.38 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.23, 166.90, 144.29, 140.67, 134.90, 134.54, 134.29, 132.49, 131.47, 130.33, 130.06, 129.63, 129.61, 127.27, 127.20, 126.87, 52.41, 26.51. HRMS (ESI) m/z [M+Na]$^+$calcd for $C_{20}H_{16}NaO_3$ 327.0992, found 327.1000.



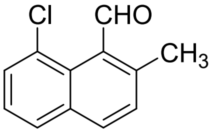
4d

N-(1-Formyl-8-methylnaphthalen-2-yl)-4-methylbenzenesulfonamide (4d). A 20-mL dry microwave-vial equipped with a stir bar was charged with **2a** (0.3 mmol), $[CpIrCl_2]_2$ (0.012 mmol, 9.6 mg), 3-trifluomethylaniline (0.12 mmol, 15 μL), 4-methylbenzenesulfonyl azide (0.6 mmol) and AgPF6 (0.072 mmol, 18 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Degassed DCE (3.0 mL) was injected into the system and the reaction mixture was stirred at 100 °C for 36 h. After cooling to room temperature, the solution was removed to a 50 mL flask. After removing the volatiles, 10 mL of THF and 5 mL of hydrochloric acid (2 M) were added. The mixture was stirred at 40 °C for 2 h (monitored by TLC) and then extracted with DCM. The combined organic phase was dried over anhydrous Na_2SO_4, concentrated, and crude product was further purified by flash chromatography on silica gel using petroleum ether/CH_2Cl_2 (1:1) as the eluent. Pale yellow solid (56.8 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.70 (s, 1H), 10.51 (s, 1H), 7.94-7.85 (m, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 7.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 8.1 Hz, 2H), 2.74 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.84, 144.35, 140.69, 137.57, 136.47, 133.17, 132.81, 132.60, 131.02, 129.87, 127.86, 127.44, 125.55, 117.28, 117.17, 25.72, 21.65. HRMS (ESI) m/z $[M+Na]^+$calcd for $C_{19}H_{17}NNaO_3S$ 362.0821, found 326.0820.



4e

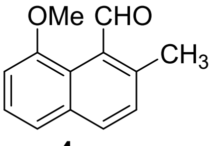
2-Chloro-8-methyl-1-naphthaldehyde (4e). A 20-mL dry microwave-vial equipped with a stir bar was charged with **2a** (0.3 mmol), NCS (0.39 mmol, 52.0 mg), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg), anthranilic acid (0.09 mmol, 12.3 mg), and AgTFA (0.03 mmol, 6.6 mg) in air, followed by DCE (3.0 mL) and TFA (3.0 mmol, 342.0 mg). The reaction mixture was stirred at 60 °C for 24 h. Upon completion, the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with DCM. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (100:1) as the eluent. White solid (47.1 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.94 (s, 1H), 7.86 (d, J = 8.7 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.48-7.36 (m, 3H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.52, 133.94, 133.57, 133.37, 133.20, 131.86, 131.38, 130.99, 127.24, 126.87, 126.72, 26.29. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}ClO$ 205.0415, found 205.0412.



4f

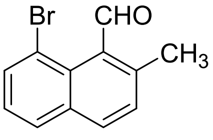
8-chloro-2-methyl-1-naphthaldehyde (4f). A 20-mL dry microwave-vial equipped with a stir bar was charged with **3a** (0.3 mmol), NCS (0.45 mmol, 60.0 mg), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg), anthranilic acid (0.09 mmol, 12.3 mg), and AgTFA (0.03 mmol, 6.6 mg) in air, followed by DCE (3.0 mL) and TFA (3.0 mmol, 342.0 mg). The reaction mixture was stirred at 60 °C for 24 h. Upon completion, the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with DCM. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (52.9

mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.12 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.45-7.30 (m, 2H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.33, 136.80, 134.10, 133.71, 131.19, 130.44, 129.58, 129.24, 129.08, 128.05, 125.92, 20.74. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}ClO$ 205.0415, found 205.0411.



4g

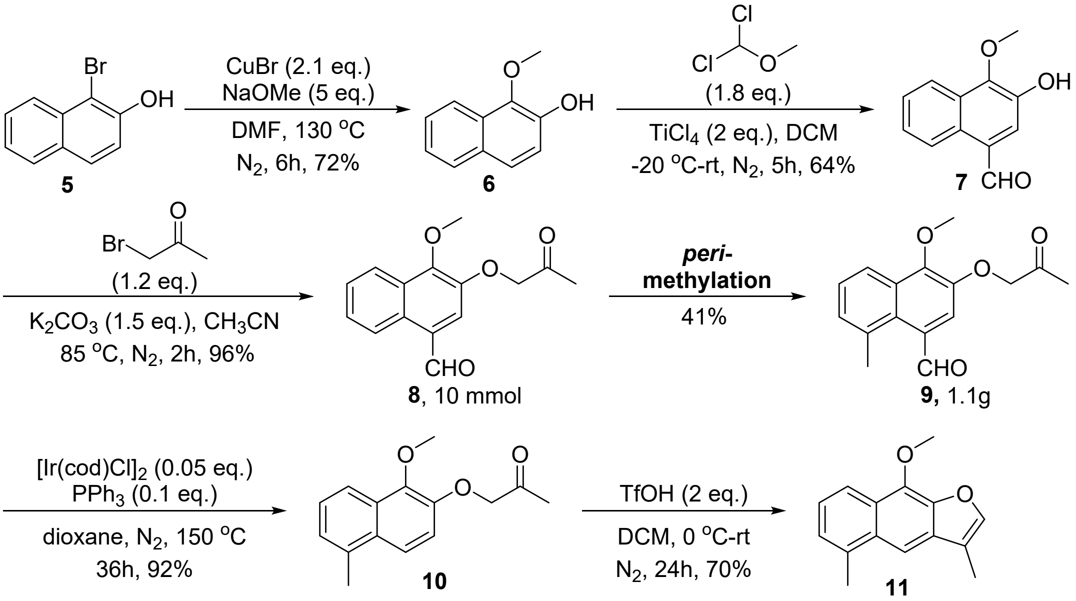
8-methoxy-2-methyl-1-naphthaldehyde (4g). A 20-mL dry microwave-vial equipped with a stir bar was charged with **3a** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg), $K_2S_2O_8$ (0.6 mmol, 162.0 mg) in air, followed by CH_2Cl_2 (3.0 mL), MeOH (6 mmol) and 3-(trifluoromethyl)aniline (0.12 mmol, 19.3 mg). The reaction mixture was stirred at 60 °C for 36 h. Upon completion, the reaction mixture was cooled to room temperature and filtered through a pad of Celite. The filtrate was quenched with saturated $NaHCO_3$ solution and extracted three times with DCM. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (100:1) as the eluent. Pale yellow solid (29.0 mg, 48%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 3.95 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.47, 155.37, 133.88, 133.56, 133.48, 130.13, 129.98, 125.93, 123.40, 121.19, 106.50, 56.06, 20.31. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{13}H_{13}O_2$ 201.0910, found 201.0911.



4h

8-bromo-2-methyl-1-naphthaldehyde (4h). A 20-mL dry microwave-vial equipped with a stir bar was charged with **3a** (0.3 mmol), NBS (0.45 mmol, 80.1 mg), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg), 2-amino-4-nitrobenzoic acid (0.15 mmol, 27.3 mg), and AgTFA (0.03 mmol, 6.6 mg) in air, followed by DCE (3.0 mL) and TfOH (0.15 mmol, 22 mg). The reaction mixture was stirred at 90 °C for 24 h. Upon completion, the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with DCM. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude residue was purified by reversed-phase column chromatography using CH_3CN/H_2O (35:65) as the eluent. Pale yellow solid (30.4 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.28 (s, 1H), 7.86-7.78 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.51, 137.38, 134.43, 134.06, 133.16, 131.49, 130.90, 130.51, 128.71, 126.41, 118.52, 20.96. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{10}BrO$ 248.9910, found 248.9909.

6. Synthetic transformation



1-Methoxynaphthalen-2-ol (6). A mixture of 1-bromonaphthalen-2-ol (40 mmol, 8.92 g), dry CuBr (44 mmol, 6.32 g), fresh prepared NaOMe (200 mmol) in MeOH (28 mL), and dry DMF (60 mL) was heated to 130 °C under N_2 for 3 h. CuBr (40 mmol, 5.74 g) was added and the reaction was stirred for another 3 h. When the starting material was consumed, the mixture was cooled to rt, neutralized with 3M HCl (60 mL) and filtered through a pad of Celite. The filtrate was extracted with ethyl acetate and the combined organic layers were washed with H_2O, brine, dried over Na_2SO_4. After removing the volatiles, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20:1) as the eluent. Pale yellow solid (5.0 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.50 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.35 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.24 (d, J = 8.8 Hz, 1H), 5.85 (s, 1H), 3.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.53, 139.73, 129.75, 128.47, 128.04, 126.49, 125.42, 123.69, 120.41, 117.59, 61.78. The characterization data is consistent with reported literature.[6]

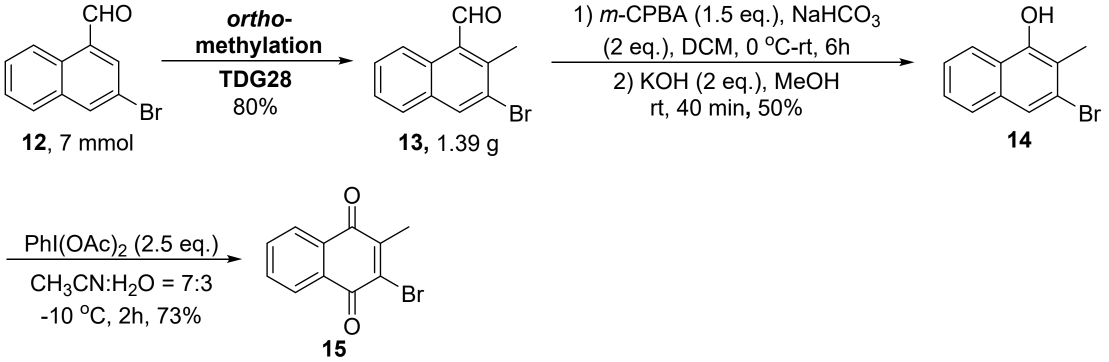
3-Hydroxy-4-methoxy-1-naphthaldehyde (7). A solution of **6** (25 mmol, 4.35 g) in DCM (50 mL) was cooled at -20 °C under N_2 and then treated dropwise with $TiCl_4$ (50 mmol) in DCM (20 mL). After stirring for 10 min at -20 °C, fresh α,α-dichloromethyl methyl ether (45 mmol) in DCM (20 mL) was added through syringe over 1 h. The reaction was allowed to slowly warm to room temperature and stirred for 5 h. The mixture was quenched by adding ice water at 0 °C and extracted with DCM twice. The combined organic layers were washed with H_2O, brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (10:1) as the eluent. Yellow solid (3.24 g, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.31 (s, 1H), 9.18 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H), 7.63-7.52 (m, 2H), 6.08 (s, 1H), 4.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.22, 145.65, 144.86, 128.81, 128.58, 127.83, 127.61, 127.50, 126.91, 125.31, 121.02, 62.14. HRMS (ESI) m/z [M-H]$^-$calcd for $C_{12}H_9O_3$ 201.0557, found 201.0559.

4-Methoxy-3-(2-oxopropoxy)-1-naphthaldehyde (8). A mixture of **7** (14 mmol, 2.83 g), K_2CO_3 (21 mmol, 2.9 g) in CH_3CN (50 mL) was heated to reflux under N_2. 1-Bromopropan-2-one (16.8 mmol, 2.3 g) was added through syringe over 30 min and the reaction mixture was stirred at 85 °C for 2 h. The mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (10:1) as the eluent. Pale yellow solid (3.47g, 96%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.33 (s, 1H), 9.08 (d, *J* = 7.5 Hz, 1H), 8.22 (d, *J* = 7.3 Hz, 1H), 7.70 (s, 1H), 7.65-7.51 (m, 2H), 4.81 (s, 2H), 4.16 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 203.97, 191.25, 150.00, 145.58, 129.63, 128.75, 128.02, 127.57, 127.33, 126.26, 124.25, 122.28, 75.10, 61.78, 26.64. HRMS (ESI) m/z [M-CH$_3$]$^-$calcd for $C_{14}H_{11}O_4$ 243.0663, found 243.0659.

4-Methoxy-8-methyl-3-(2-oxopropoxy)-1-naphthaldehyde (9). The title compound was prepared in 10 mmol-scale reaction according to the general *peri*-methylation procedure in a 330 mL tube and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (10:1) as the eluent. Pale yellow solid (1.11 g, 41%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.85 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.74 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 6.8 Hz, 1H), 4.80 (s, 2H), 4.12 (s, 3H), 2.82 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 203.90, 192.40, 148.86, 145.34, 133.56, 131.88, 130.90, 130.31, 129.02, 126.61, 121.16, 119.42, 74.40, 61.67, 26.45. HRMS (ESI) m/z [M-CH$_3$]$^-$calcd for $C_{15}H_{13}O_4$ 257.0819, found 257.0812.

1-((1-Methoxy-5-methylnaphthalen-2-yl)oxy)propan-2-one (10). A 10-mL microwave-vial equipped with a stir bar was charged with **9** (0.5 mmol, 136.2 mg), PPh$_3$ (0.05 mmol, 13.1 mg) and [Ir(cod)Cl]$_2$ (0.025 mmol, 16.8 mg). The vial was sealed with a PTFE-lined cap, and filled with N$_2$. Dry 1,4-dioxane (0.75 mL) was added through syringe and the reaction mixture was stirred at 150 °C for 36 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography using petroleum ether as the eluent. Pale yellow oil (112.3 mg, 92%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 9.2 Hz, 1H), 7.43-7.37 (m, 1H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.19 (d, *J* = 9.2 Hz, 1H), 4.75 (s, 2H), 4.03 (s, 3H), 2.66 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 205.77, 146.67, 144.24, 134.47, 129.87, 129.56, 126.34, 125.65, 120.95, 119.87, 116.59, 75.23, 61.50, 26.70, 19.64. HRMS (ESI) m/z [M+Na]$^+$calcd for $C_{15}H_{16}NaO_3$ 267.0992, found 267.0998.

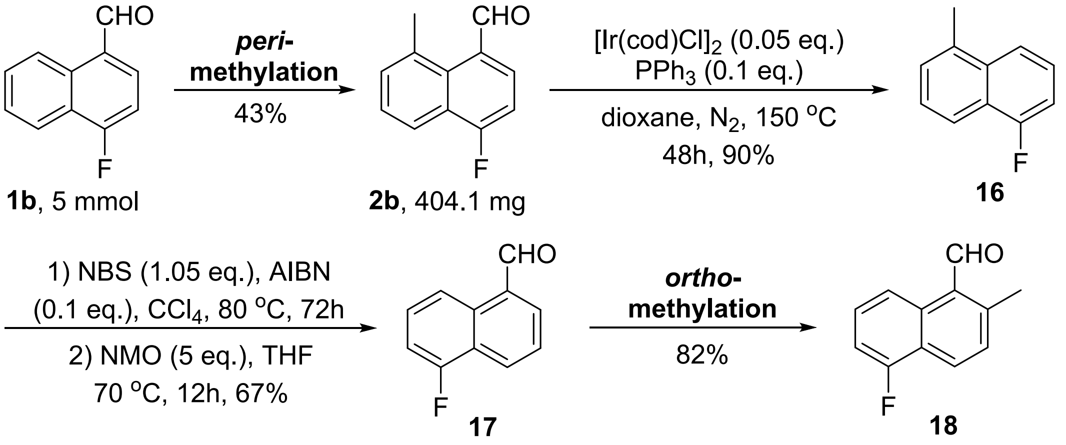
9-Methoxy-3,5-dimethylnaphtho[2,3-b]furan (11). To a solution of **10** (0.3 mmol, 73.3 mg) in DCM (1 mL) was slowly added TfOH (0.6 mmol) at 0 °C under N$_2$. Then the reaction mixture was stirred at rt for 24 h. Upon completion, the reaction mixture was quenched with saturated NaHCO$_3$ solution and extracted with DCM. The combined organic layers were washed with water, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether as the eluent. Pale yellow oil (47.3 mg, 70%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.25 (d, *J* = 8.6 Hz, 1H), 7.76 (s, 1H), 7.50 (d, *J* = 1.3 Hz, 1H), 7.37 (dd, *J* = 8.5, 6.8 Hz, 1H), 7.30 (d, *J* = 6.7 Hz, 1H), 4.38 (s, 3H), 2.79 (s, 3H), 2.36 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 143.20, 142.42, 138.67, 133.93, 131.95, 130.59, 125.13, 124.69, 123.91, 120.45, 115.81, 107.24, 60.98, 20.45, 8.14. HRMS (ESI) m/z [M+H]$^+$calcd for $C_{15}H_{15}O_2$ 227.1067, found 227.1069. The characterization data is consistent with reported literature.[7]



3-Bromo-2-methyl-1-naphthaldehyde (13). The title compound was prepared in 7 mmol-scale reaction according to the general *ortho*-methylation procedure by using TDG28 (4 h) in 100 mL Schlenk tube instead and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. White solid (1.39 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.68 (d, *J* = 8.7 Hz, 1H), 8.28 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.55-7.49 (m, 1H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.75, 140.06, 136.84, 133.11, 131.48, 130.22, 128.90, 127.56, 127.01, 124.66, 124.33, 19.28. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{13}H_{12}BrO$ 263.0066, found 263.0071.

3-Bromo-2-methylnaphthalen-1-ol (14). To a mixture of **13** (3 mmol, 747.3 mg) and $NaHCO_3$ (6 mmol, 504.1 mg) in DCM (15 mL) was added 3-chloroperbenzoic acid (4.5 mmol, 913.6 mg) at 0 °C, and the resulting mixture was stirred at rt for 6 h. Saturated $Na_2S_2O_3$ solution and $NaHCO_3$ solution were added respectively, then the mixture was stirred for 10 min. The resulting mixture was extracted with DCM and the combined organic layers were washed with H_2O, brine, dried over Na_2SO_4. After removing the volatiles, the residue was dissolved in MeOH (6 mL). The reaction was stirred at rt for 1h after a solution of KOH (6 mmol, 336.6 mg) was added. When the starting material was consumed, the mixture was adjusted to pH 3.5 with 1 M HCl and extracted with EtOAc. The combined organic layers were washed with water and brine and dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give desired prouct **14**. Pale yellow solid (355.6 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.74 (s, 1H), 7.71-7.64 (m, 1H), 7.51-7.42 (m, 2H), 5.28 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.27, 133.40, 126.86, 126.65, 125.77, 123.82, 123.61, 123.38, 121.27, 117.03, 15.89. HRMS (ESI) m/z $[M-H]^-$calcd for $C_{11}H_8BrO$ 234.9764, found 234.9768.

2-Bromo-3-methylnaphthalene-1,4-dione (15). To a solution of **14** (1 mmol, 237.1 mg) in acetonitrile/H_2O (7:3, 5 mL) was added iodobenzene diacetate (2.5 mmol, 805.3 mg) at -10 °C, and the resulting mixture was stirred at -10 °C for 2 h. To the reaction was added saturated $NaHCO_3$ solution, and the mixture was filtered through a pad of Celite. The filtrate was extracted with ethyl acetate and the combined organic layers were washed with H_2O, brine, dried over Na_2SO_4. After removing the volatiles, the residue was purified by column chromatography on silica gel using petroleum ether/CH_2Cl_2 (1:1) as the eluent. Yellow solid (184.4 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19-8.14 (m, 1H), 8.13-8.09 (m, 1H), 7.79-7.69 (m, 2H), 2.39 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 182.08, 177.65, 148.62, 139.17, 134.24, 134.02, 131.67, 131.31, 127.63, 127.24, 18.01. HRMS (ESI) m/z $[M-H]^-$calcd for $C_{11}H_6BrO_2$ 248.9557, found 248.9556.



4-Fluoro-8-methyl-1-naphthaldehyde (2b). The title compound was prepared in 5 mmol-scale reaction according to the general *peri*-methylation procedure in 100 mL tube and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (500:1) as the eluent. White solid (404.1 mg, 43%), the characterization data is the same as the batch of small scale.

1-Fluoro-5-methylnaphthalene (16). A 10-mL microwave-vial equipped with a stir bar was charged with **2b** (1 mmol, 188.2 mg), PPh$_3$ (0.1 mmol, 26.2 mg) and [Ir(cod)Cl]$_2$ (0.05 mmol, 33.6 mg). The vial was sealed with a PTFE-lined cap, and filled with N$_2$. Dry 1,4-dioxane (1.5 mL) was added through syringe and the reaction mixture was stirred at 150 °C for 48 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography using petroleum ether as the eluent. Colorless oil (143.9 mg, 90%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.99 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.48-7.41 (m, 2H), 7.37 (d, J = 6.9 Hz, 1H), 7.19-7.12 (m, 1H), 2.70 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 159.32 (d, J = 251.1 Hz), 134.35, 134.34 (d, J = 7.6 Hz), 127.66, 126.02 (d, J = 1.7 Hz), 125.48 (d, J = 8.7 Hz), 123.96 (d, J = 15.9 Hz), 120.13 (d, J = 4.1 Hz), 118.87 (d, J = 6.1 Hz), 109.33 (d, J = 20.0 Hz), 19.83.

5-fluoro-1-naphthaldehyde (17). To a solution of **16** (0.8 mmol, 128.2 mg) in CCl$_4$ (4 mL) was added NBS (0.88 mmol, 156.6 mg) followed by AIBN (0.08 mmol, 11.7 mg). After refluxed for 72 h, the resulting mixture was cooled to room temperature. Water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na$_2$SO$_4$, and filtered. The solution was removed under vacuum. The residue was dissolved in THF (5 mL) and N-methylmorpholine N-oxide (4 mmol) was added. The reaction mixture was refluxed for 12 h. After cooling to rt, water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na$_2$SO$_4$, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography using petroleum ether/EtOAc (100:1) as the eluent. White solid (93.0 mg, 67%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.38 (s, 1H), 9.02 (d, J = 8.6 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.07-8.00 (m, 1H), 7.73-7.66 (m, 1H), 7.61 (td, J = 8.2, 5.9 Hz, 1H), 7.26 (t, J = 9.0 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 193.32, 158.76 (d, J = 253.1 Hz), 137.34, 131.76 (d, J = 3.4 Hz), 131.19 (d, J = 2.3 Hz), 129.24 (d, J = 8.4 Hz), 127.69 (d, J = 6.1 Hz), 125.33 (d, J = 1.8 Hz), 124.24 (d, J = 15.5 Hz), 120.96 (d, J = 4.5 Hz), 110.90 (d, J = 19.4 Hz). HRMS (ESI) m/z [M+CH$_3$]$^+$calcd for $C_{12}H_{10}FO$ 189.0710, found 189.0702.

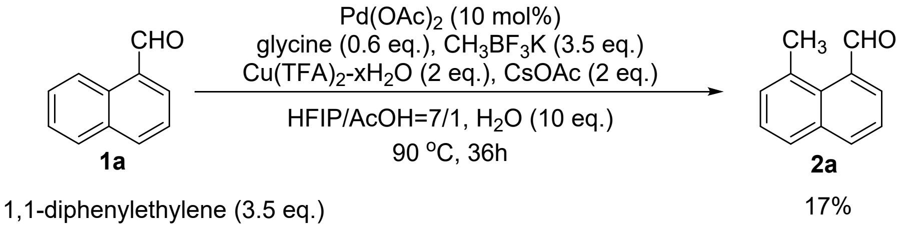
5-fluoro-2-methyl-1-naphthaldehyde (18). The title compound was prepared according to the general *ortho*-methylation procedure using **17** (0.3 mmol, 52.3 mg) as substrate and purified by flash column chromatography over silica gel using petroleum ether/EtOAc (250:1) as the eluent. Pale yellow solid (46.1

mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 8.72 (d, J = 8.7 Hz, 1H), 8.23 (d, J = 8.6 Hz, 1H), 7.53 (q, J = 7.9 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.20-7.12 (m, 1H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.19, 158.85 (d, J = 252.3 Hz), 143.55, 132.81 (d, J = 3.5 Hz), 130.23 (d, J = 1.8 Hz), 128.77 (d, J = 8.5 Hz), 128.29 (d, J = 2.3 Hz), 126.67 (d, J = 6.5 Hz), 122.99 (d, J = 16.1 Hz), 120.39 (d, J = 4.4 Hz), 109.78 (d, J = 19.2 Hz), 20.19. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{13}H_{12}FO$ 203.0867, found 203.0865.

7. Preliminary mechanistic experiments

7.1 *Peri*-methylation with Pd

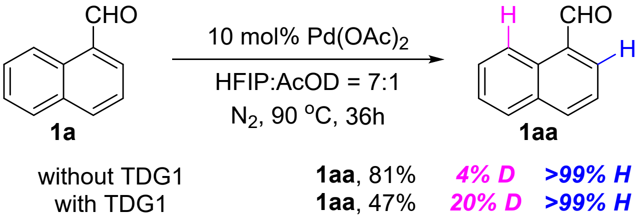
7.1.1 Radical scavenger experiment



A 10-mL microwave-vial equipped with a stir bar was charged with **1a** (0.3 mmol), 1,1-diphenylethylene (1.05 mmol, 189.4 mg), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg), glycine (TDG1) (0.18 mmol, 13.5 mg), CH_3BF_3K (1.05 mmol, 128 mg), $Cu(TFA)_2$-xH_2O (0.6 mmol, 174 mg) and CsOAc (0.6 mmol, 114 mg). HFIP:AcOH = 7:1 (1.5 mL) was added as solvent, followed by the addition of H_2O (3 mmol, 54 μL). The vial was sealed with a PTFE-lined cap, and stirred at 90 °C for 36 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting residue was purified by preparative thin layer chromatography to give desired product **2**a (8.7 mg, 17%).

7.1.2 H/D Exchange Experiments

A 10-mL microwave-vial equipped with a stir bar was charged with **1a** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg). Glycine (TDG1) (0.18 mmol, 13.5 mg) or without glycine, and HFIP:AcOD=7:1 (1.5 mL) were added subsequently. The vial was sealed with a PTFE-lined cap, and stirred at 90 °C for 36 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was concentrated and the resulting residue was purified by by column chromatography on silica gel using petroleum ether/EtOAc (50:1) as the eluent to give the remained starting materials **1aa**, in which the H/D ratio was determined by NMR as shown below.



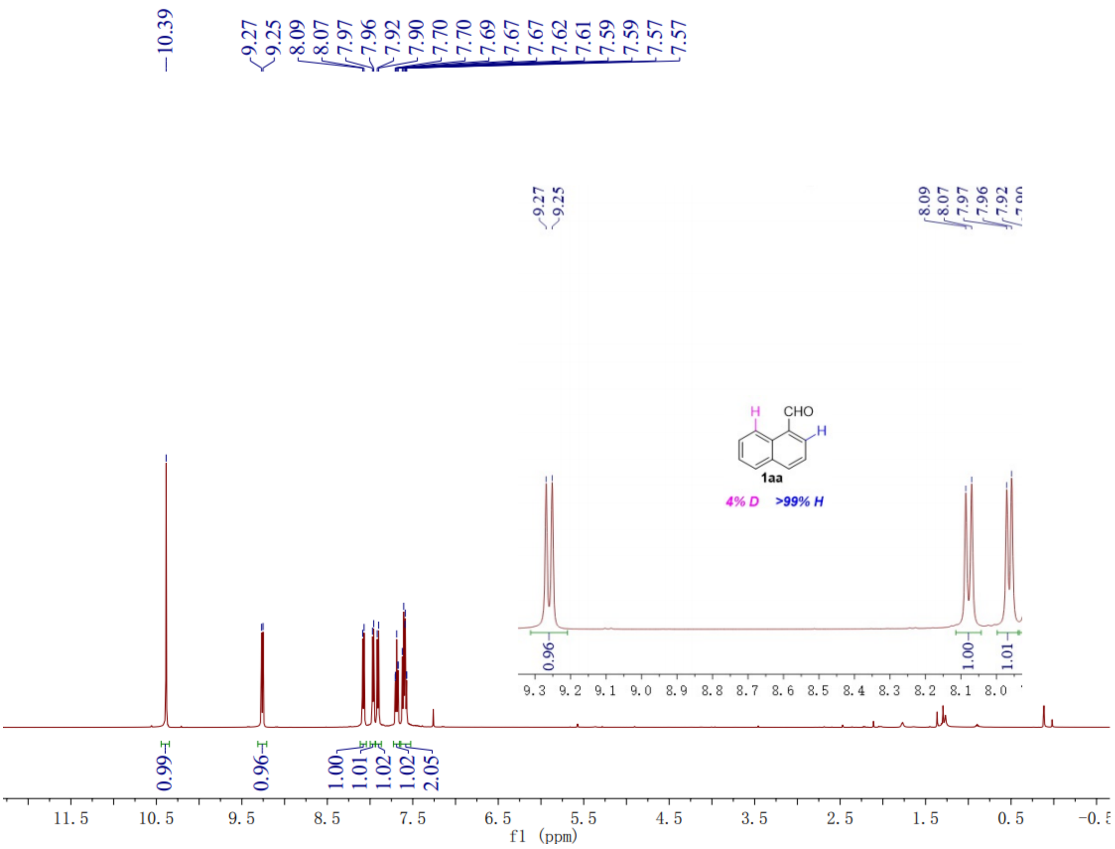


Figure S1. ^{1}H NMR of H/D exchange experiment with **1aa** in the absence of TDG1

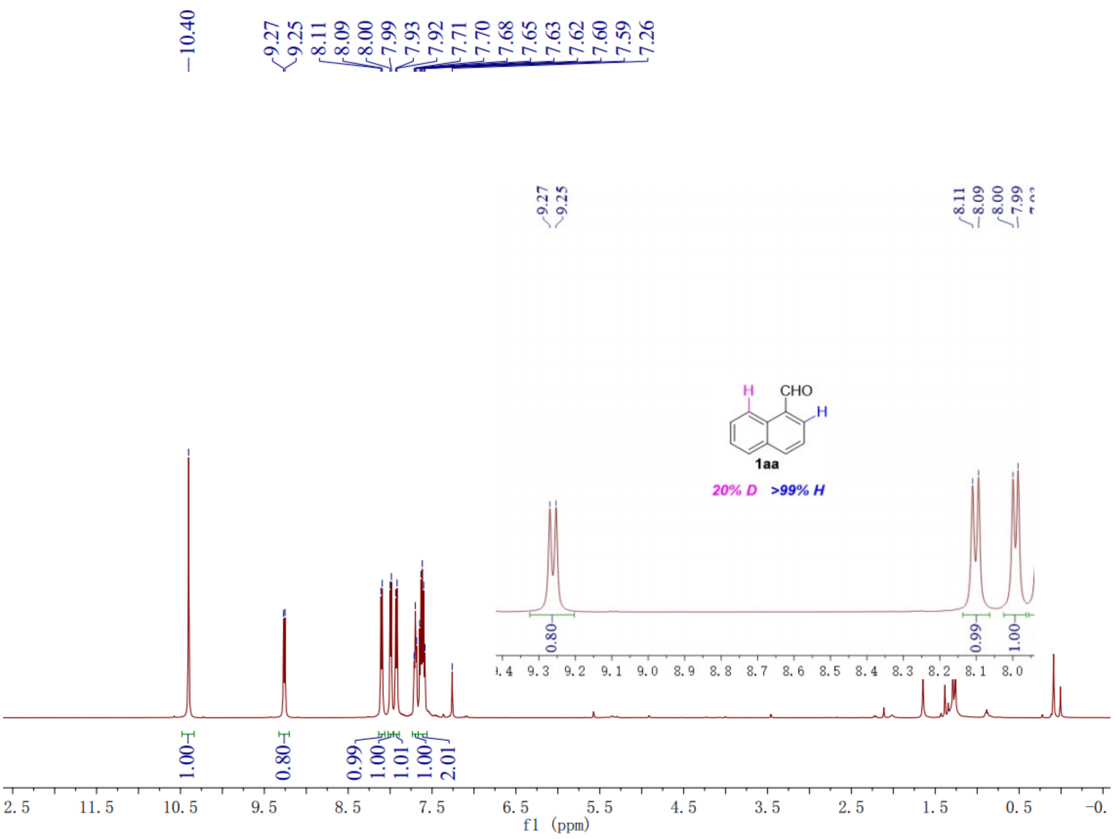
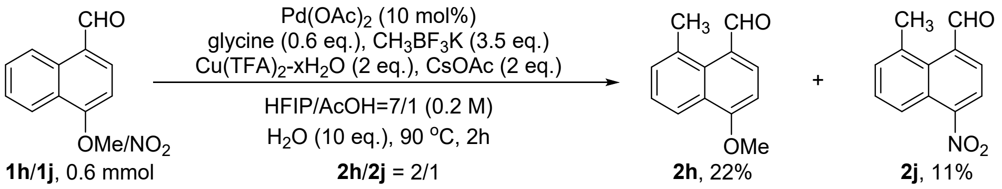
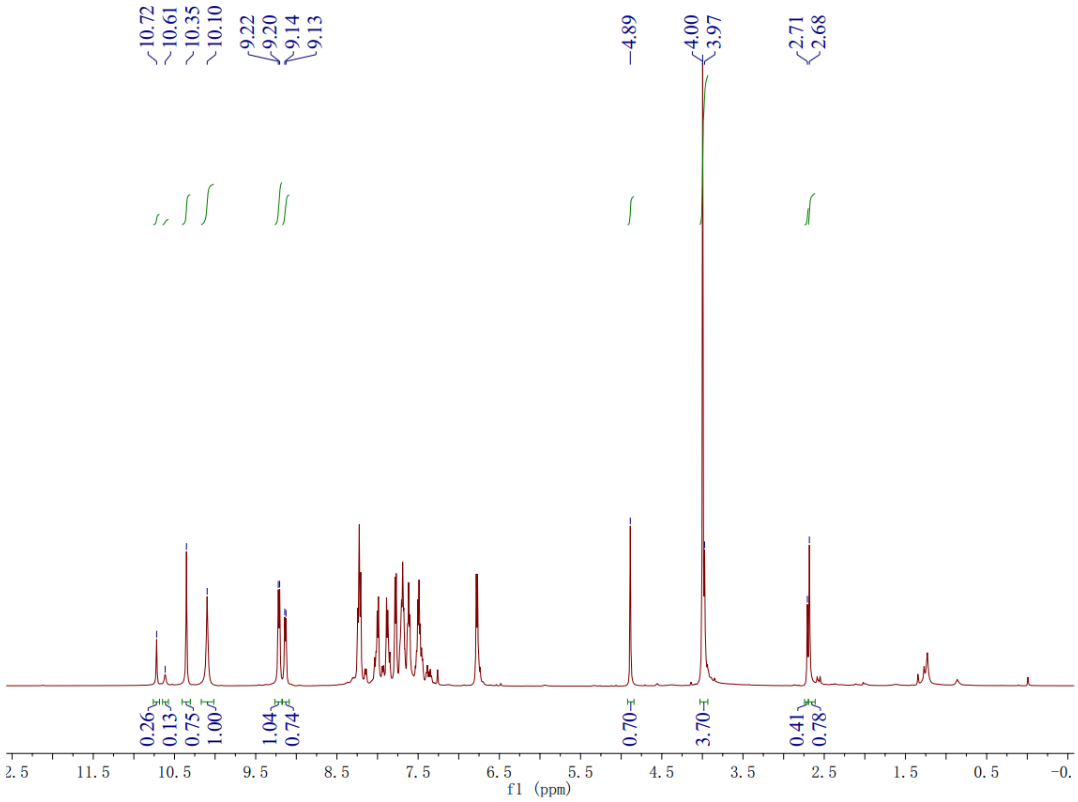


Figure S2. ^{1}H NMR of H/D exchange experiment with **1aa** in the presence of TDG1

7.1.3 Competition experiment



A 10-mL microwave-vial equipped with a stir bar was charged with **1h** (0.3 mmol), **1j** (0.3 mmol), $Pd(OAc)_2$ (0.06 mmol, 13.4 mg), glycine (TDG1) (0.36 mmol, 27 mg), CH_3BF_3K (2.1 mmol, 256 mg), $Cu(TFA)_2$-xH_2O (1.2 mmol, 348 mg) and CsOAc (1.2 mmol, 228 mg). HFIP:AcOH = 7:1 (3 mL) was added as solvent, followed by the addition of H_2O (6 mmol, 108 μL). The vial was sealed with a PTFE-lined cap, and stirred at 90 °C for 2 h. The tube was taken out into the ice water, and cold 10% NaOH aqueous (0.5 mL) was immediately added to quench the reaction, the ice water (1 mL) and EtOAc (1 mL) was added. The reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting residue was purified by column chromatography to give the mixture of **1h**, **1j**, **2h** and **2j**. Yields were determined by ^{1}H NMR analysis using CH_2Br_2 (15.7 mg) as an internal standard.



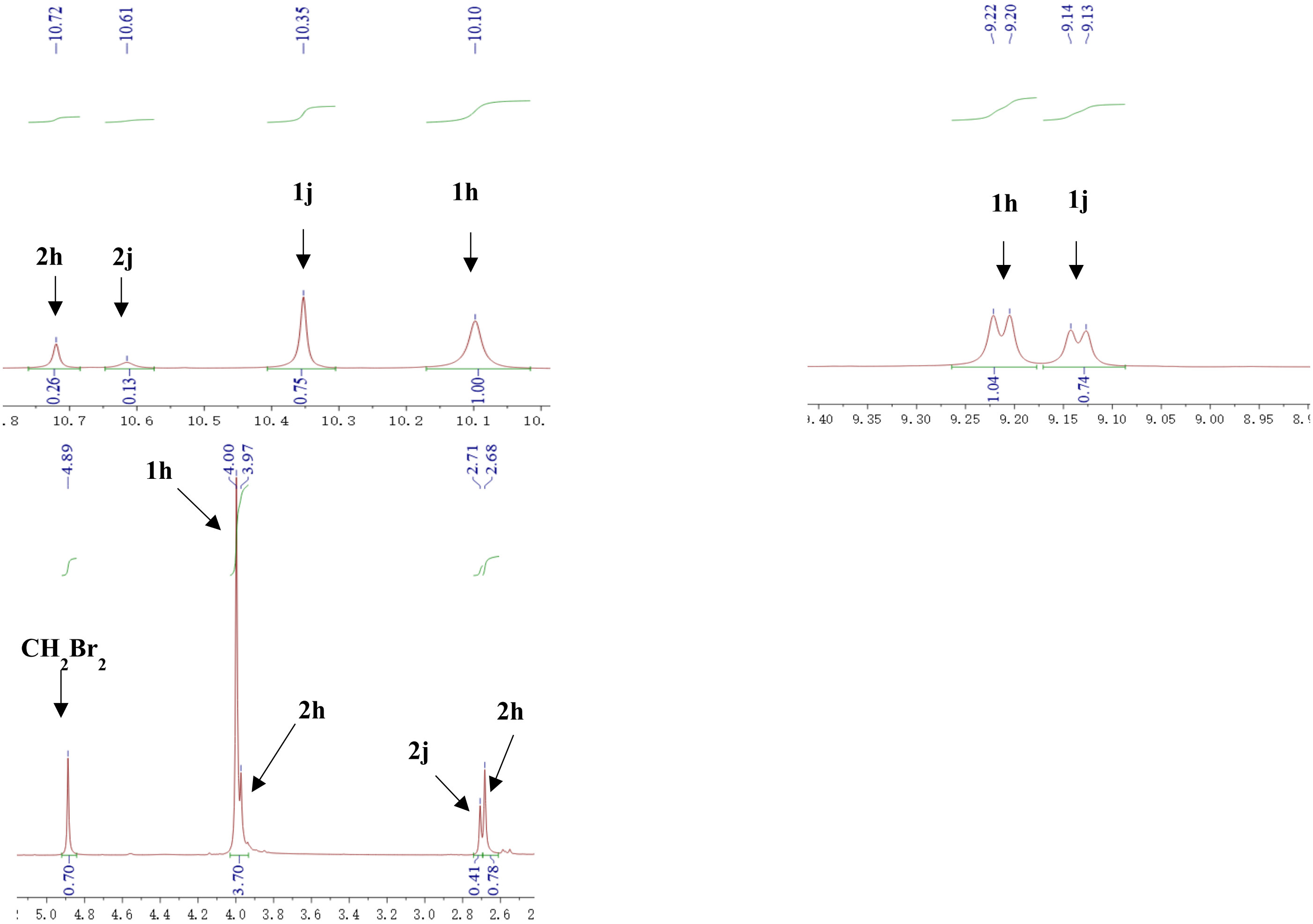
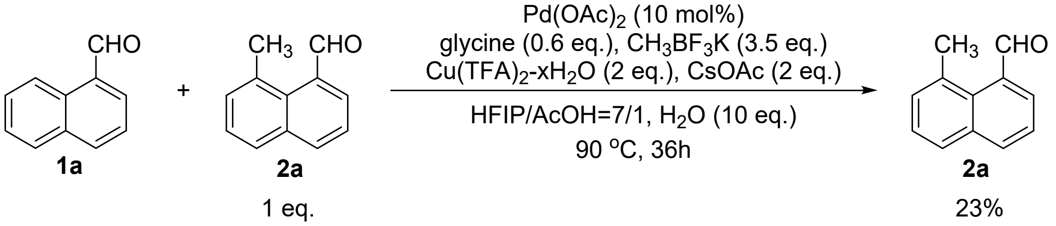


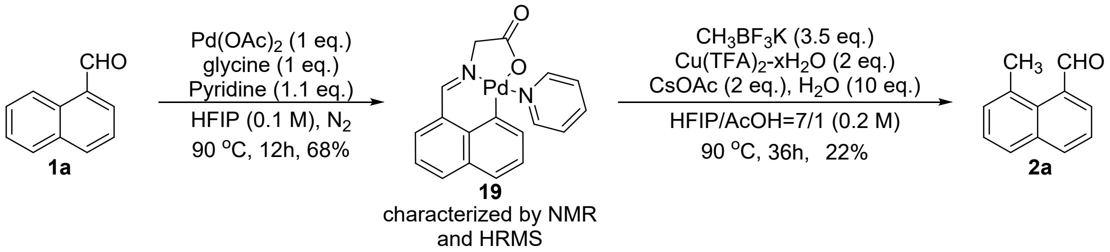
Figure S3. ^{1}H NMR of competition experiment

7.1.4 Product inhibition experiment



A 10-mL microwave-vial equipped with a stir bar was charged with **1a** (0.3 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol, 6.7 mg), glycine (TDG1) (0.18 mmol, 13.5 mg), CH_3BF_3K (1.05 mmol, 128 mg), $Cu(TFA)_2$-xH_2O (0.6 mmol, 174 mg) and CsOAc (0.6 mmol, 114 mg). HFIP:AcOH = 7:1 (1.5 mL) was added as solvent, followed by the addition of H_2O (3 mmol, 54 μL). The vial was sealed with a PTFE-lined cap, and stirred at 90 °C for 36 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting residue was purified by preparative thin layer chromatography to give desired product **2a** (12 mg, 23%).

7.1.5 Identification of reaction intermediates

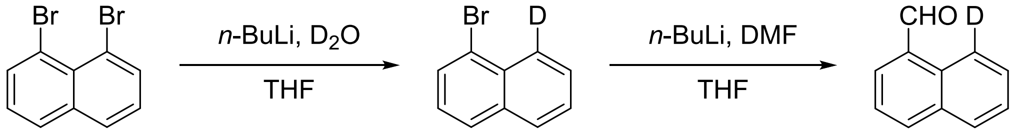


Palladacycle 19. A 10-mL microwave-vial equipped with a stir bar was charged with **1a** (0.3 mmol, 46.8 mg), $Pd(OAc)_2$ (0.3 mmol, 67.4 mg), Glycine (TDG1) (0.3 mmol, 22.5mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Pyridine (0.33 mmol, 26.1 mg) and HFIP (3 mL) was added through syringe and the reaction mixture was stirred at 90 °C for 12 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with DCM. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel using DCM/MeOH (50:1) as the eluent to afford palladacycles **19**. Yellow solid (81.1 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, J = 5.1 Hz, 2H), 8.18 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.91 (t, J = 7.7 Hz, 1H), 7.78 (d, J = 7.0 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 6.7 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 7.2 Hz, 1H), 4.79 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.36, 160.40, 153.17, 141.59, 138.49, 137.67, 137.56, 136.65, 133.02, 132.97, 127.32, 126.76, 126.11, 125.45, 124.30, 65.81. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{15}N_2O_2Pd$ 397.0163, found 397.0179.

Regeneration of compound 2a. A 10-mL microwave-vial equipped with a stir bar was charged with palladacycle **19** (0.3 mmol), CH_3BF_3K (1.05 mmol, 128.0 mg), $Cu(TFA)_2$-xH_2O (0.6 mmol, 174 mg) and CsOAc (0.6 mmol, 114 mg). HFIP:AcOH = 7:1 (1.5 mL) was added as solvent, followed by the addition of H_2O (3 mmol). The vial was sealed with a PTFE-lined cap, and stirred at 90 °C for 36 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting residue was purified by preparative thin layer chromatography using petroleum ether/EtOAc (100:1) as the developing solvent. Colorless liquid (11.5 mg, 22%), the characterization data is the same as compound **2a**.

7.1.6 Kinetic isotope effect experiments

7.1.6.1 Synthesis of **1a-*peri*-D**

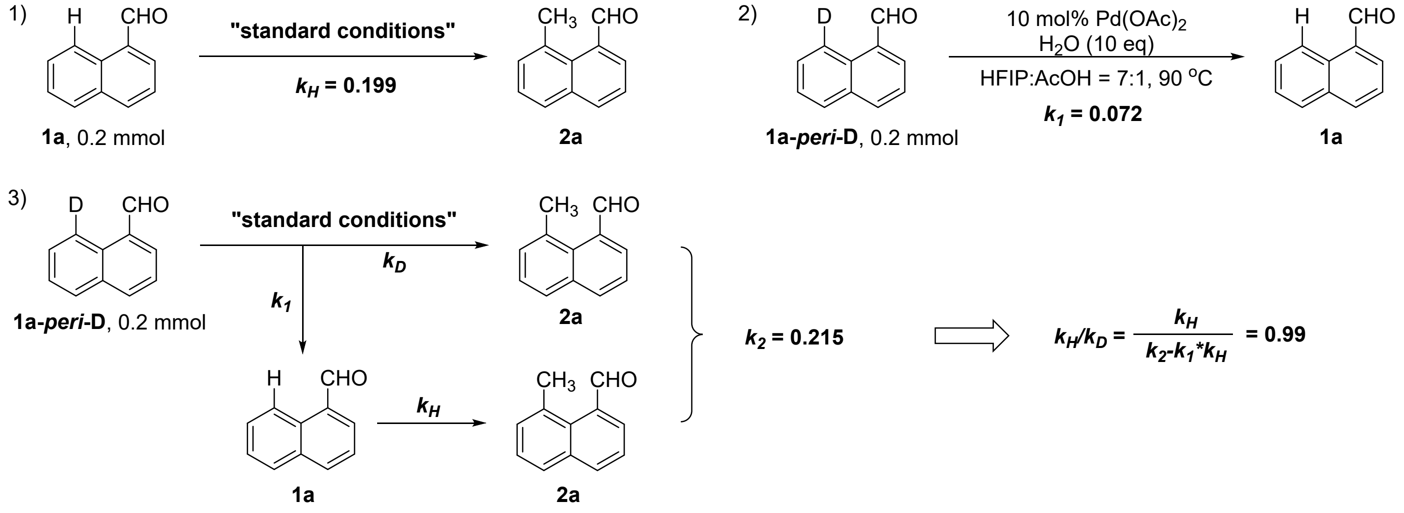


1a-*peri*-D

1-Naphthaldehyde-8-*d* (1a-*peri*-D). To a solution of 1,8-dibromonaphthalene (10 mmol) in anhydrous THF (15 mL) at -78 °C under N_2 atomosphere was dropwisely added *n*-butyl lithium solution (2.5 M in hexane, 11 mmol) over 30 min. The resulting reaction mixture was stirred at -78 °C for 1h, and then treated with D_2O (300 mmol). After warmed to room temperature, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography on silica gel using petroleum ether as the eluent without pressure to afford 1-bromonaphthalene-8-*d* as colorless oil (1.82 g, 87%).

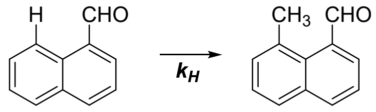
Then, to a solution of 1-bromonaphthalene-8-*d* (1.82 g, 8.75 mmol) in anhydrous THF (16 mL) at -78 °C under N_2 atomosphere was dropwisely added *n*-butyl lithium solution (2.5 M in hexane, 8.75 mmol) over 30 min. The resulting reaction mixture was stirred at -78 °C for 1h, and then treated with dry DMF (25 mmol). After warmed to room temperature, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1a-*peri*-D** as colorless oil (1.05 g, 77%, 97% D). ^1H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.11 (dd, J = 8.2, 1.1 Hz, 1H), 8.01 (dd, J = 7.0, 1.2 Hz, 1H), 7.93 (dd, J = 8.2, 1.2 Hz, 1H), 7.72-7.68 (m, 1H), 7.67-7.58 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.70, 136.85, 135.44, 133.85, 131.54, 130.57, 129.10, 128.60, 127.11, 125.01, 124.75 (t, J = 25.2 Hz).

7.1.6.2 Parallel reactions



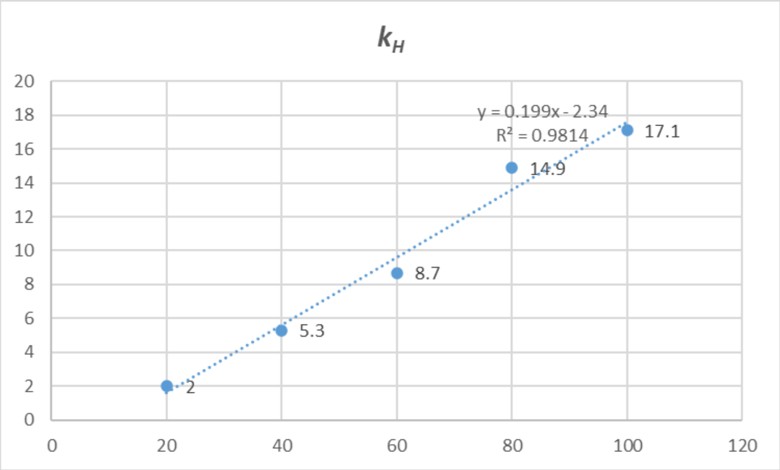
Measure of k_H or k_2: A 10-mL microwave-vial equipped with a stir bar was charged with **1a** or **1a-*peri*-D** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), glycine (TDG1) (0.12 mmol, 9 mg), CH_3BF_3K (0.7 mmol, 85.3 mg), $Cu(TFA)_2$-xH_2O (0.4 mmol, 115.8 mg) and CsOAc (0.4 mmol, 76.7 mg). HFIP:AcOH = 7:1 (1 mL) was added as solvent, followed by the addition of H_2O (2 mmol, 36 μL). Several parallel reactions were set up together. The vial was sealed with a PTFE-lined cap, and stirred at 90 °C. According to the relative reaction time, one of these tubes was taken out into the ice water, and cold 10% NaOH aqueous (0.5 mL) was immediately added to quench the reaction, the ice water (1 mL) and EtOAc (1 mL) was added. The reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Conversions were determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.

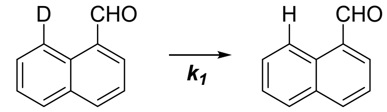
Measure of k_1: A 10-mL microwave-vial equipped with a stir bar was charged with **1a-*peri*-D** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), glycine (TDG1) (0.12 mmol, 9 mg). HFIP:AcOH = 7:1 (1 mL) was added as solvent, followed by the addition of H_2O (2 mmol, 36 μL). Several parallel reactions were set up together. The vial was sealed with a PTFE-lined cap, and stirred at 90 °C. According to the relative reaction time, one of these tubes was taken out into the ice water, and cold 10% NaOH aqueous (0.5 mL) was immediately added to quench the reaction, the ice water (1 mL) and EtOAc (1 mL) was added. The reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Conversions were determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.



1a, 0.2 mmol **2a**

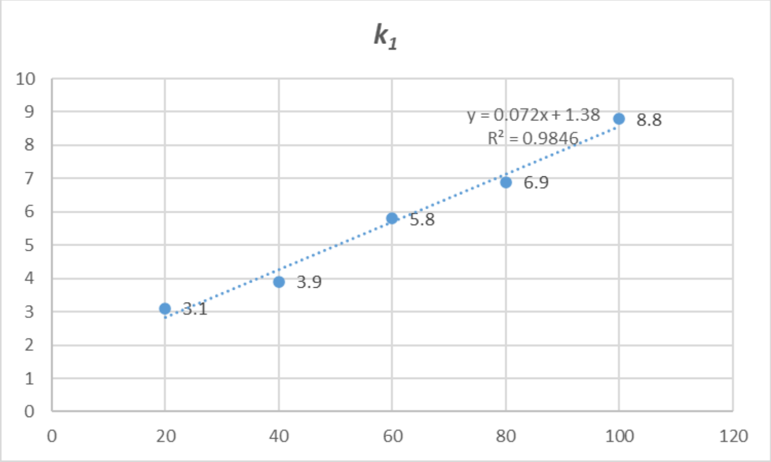
Time (min)	**Conversion (%)**
0	0
20	2.0
40	5.3
60	8.7
80	14.9
100	17.1

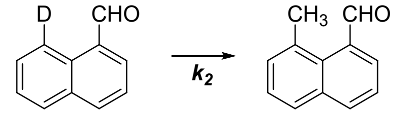




1a-*peri*-D, 0.2 mmol **1a**

Time (min)	**Conversion (%)**
0	0
20	3.1
40	3.9
60	5.8
80	6.9
100	8.8





1a-*peri*-D, 0.2 mmol **2a**

Time (min)	**Conversion (%)**
0	0
30	3.8
60	10.6
90	18.1
120	21.6
150	30.5

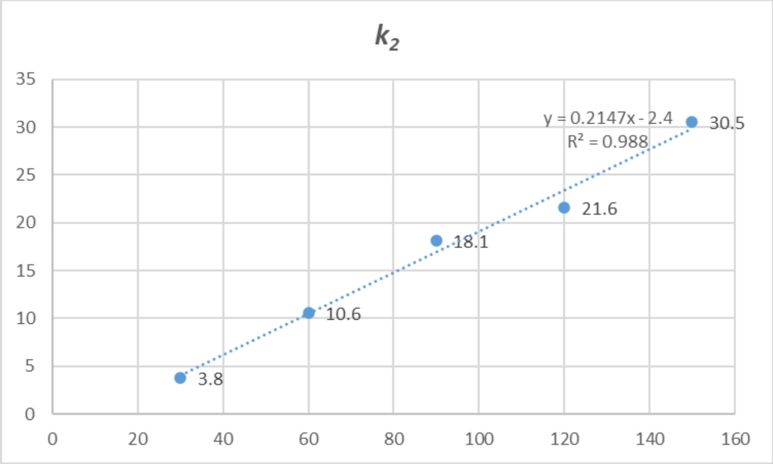
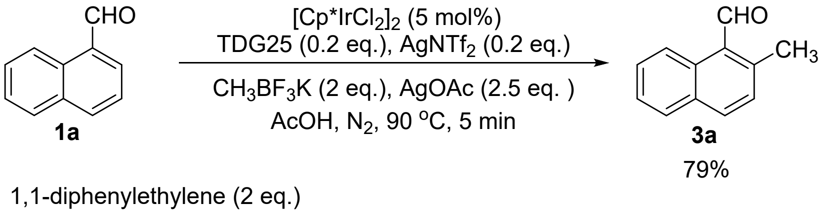


Figure S4. Parallel KIE reaction.

7.2 *Ortho*-methylation with Ir

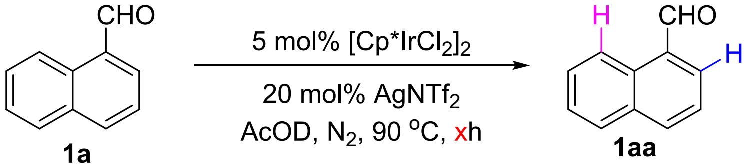
7.2.1 Radical scavenger experiment



A 10-mL dry microwave-vial equipped with a stir bar was charged with **1a** (0.3 mmol), 1,1-diphenylethylene (0.6 mmol, 108.2 mg), $[Cp^*IrCl_2]_2$ (0.015 mmol, 12 mg), 3-Aminobenzenesulfonic acid (TDG25) (0.06 mmol, 10.4 mg), CH_3BF_3K (0.6 mmol, 73 mg), AgOAc (0.75 mmol, 125 mg) and $AgNTf_2$ (0.06 mmol, 23.3 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Degassed AcOH (1.5 mL) was added through syringe and the reaction mixture was stirred at 90 °C for 5 min. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography to give desired prouct **3a** (40.5 mg, 79%).

7.2.2 H/D Exchange Experiments

A 10-mL dry microwave-vial equipped with a stir bar was charged with **1a** (0.3 mmol), $[Cp^*IrCl_2]_2$ (0.015 mmol, 12 mg), $AgNTf_2$ (0.06 mmol, 23.3 mg), 3-aminobenzenesulfonic acid (TDG25) (0.06 mmol, 10.4 mg) or without 3-aminobenzenesulfonic acid. The vial was sealed with a PTFE-lined cap, and filled with N_2. Degassed AcOD (1.5 mL) was added through syringe and the reaction mixture was stirred at 90 °C for a certain amount of time. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography using petroleum ether/EtOAc (50:1) as the eluent to give the remained starting materials **1aa**, in which the H/D ratio was determined by NMR as shown below.



without TDG25	5 min	**1aa**, 83%	***47% D***	***9% D***
with TDG25		**1aa**, 90%	***42% D***	***10% D***
without TDG25	2 h	**1aa**, 73%	***94% D***	***61% D***
with TDG25		**1aa**, 82%	***94% D***	***62% D***

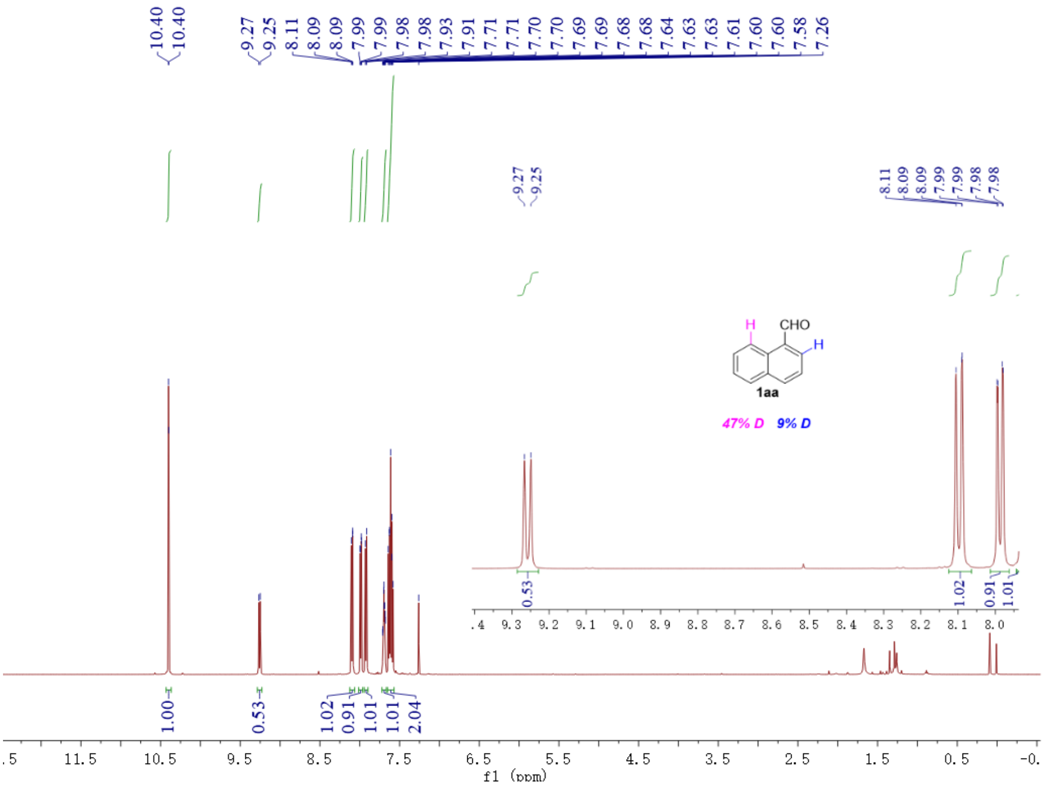


Figure S5. ^{1}H NMR of H/D exchange experiment (5 min) with **1aa** in the absence of TDG25

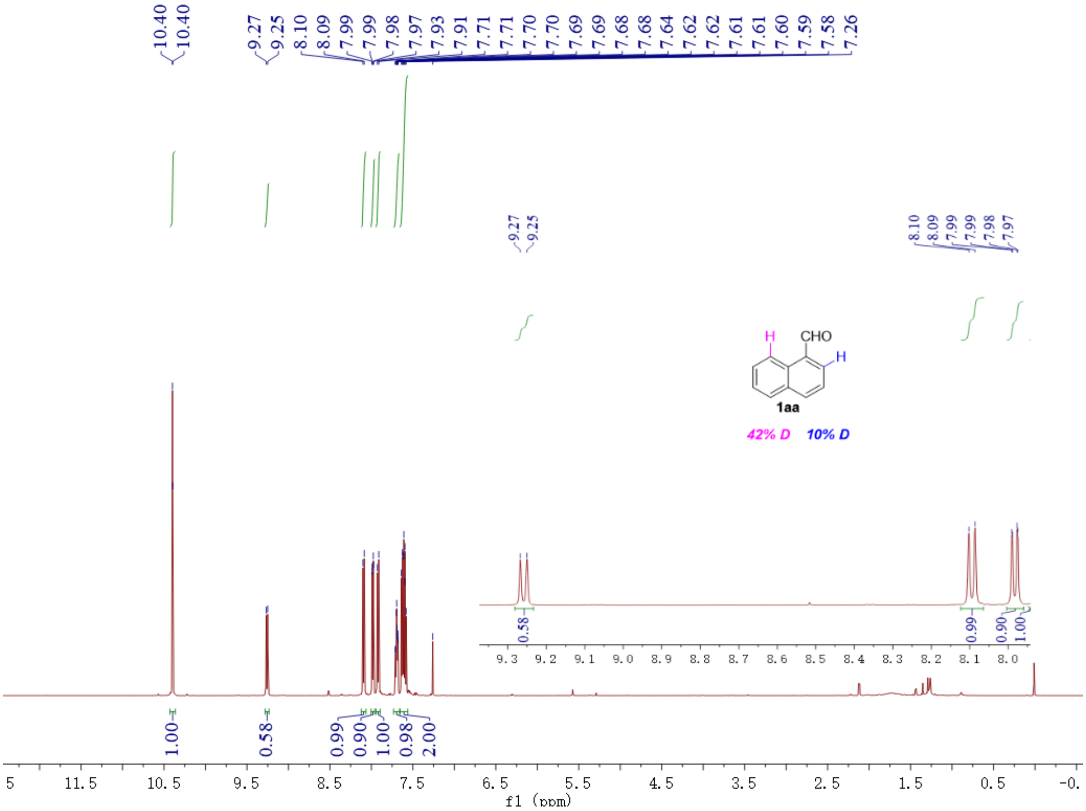


Figure S6. ^{1}H NMR of H/D exchange experiment (5 min) with **1aa** in the presence of TDG25

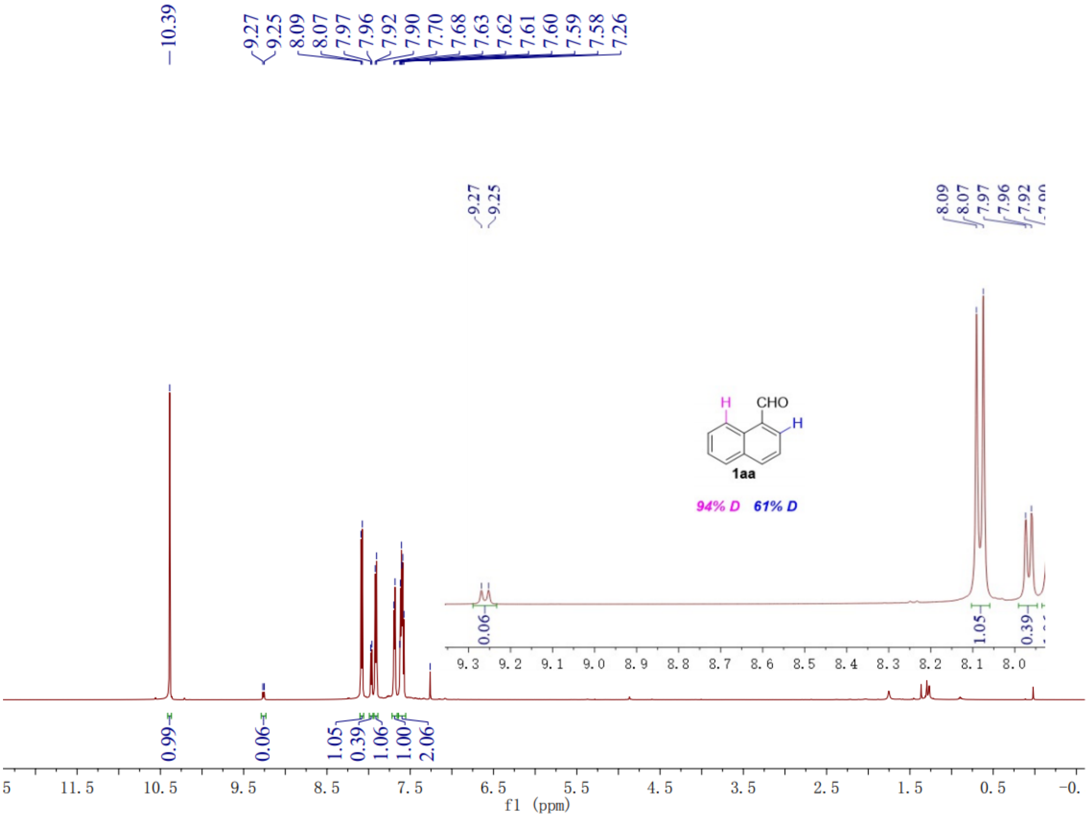


Figure S7. ^{1}H NMR of H/D exchange experiment (2 h) with **1aa** in the absence of TDG25

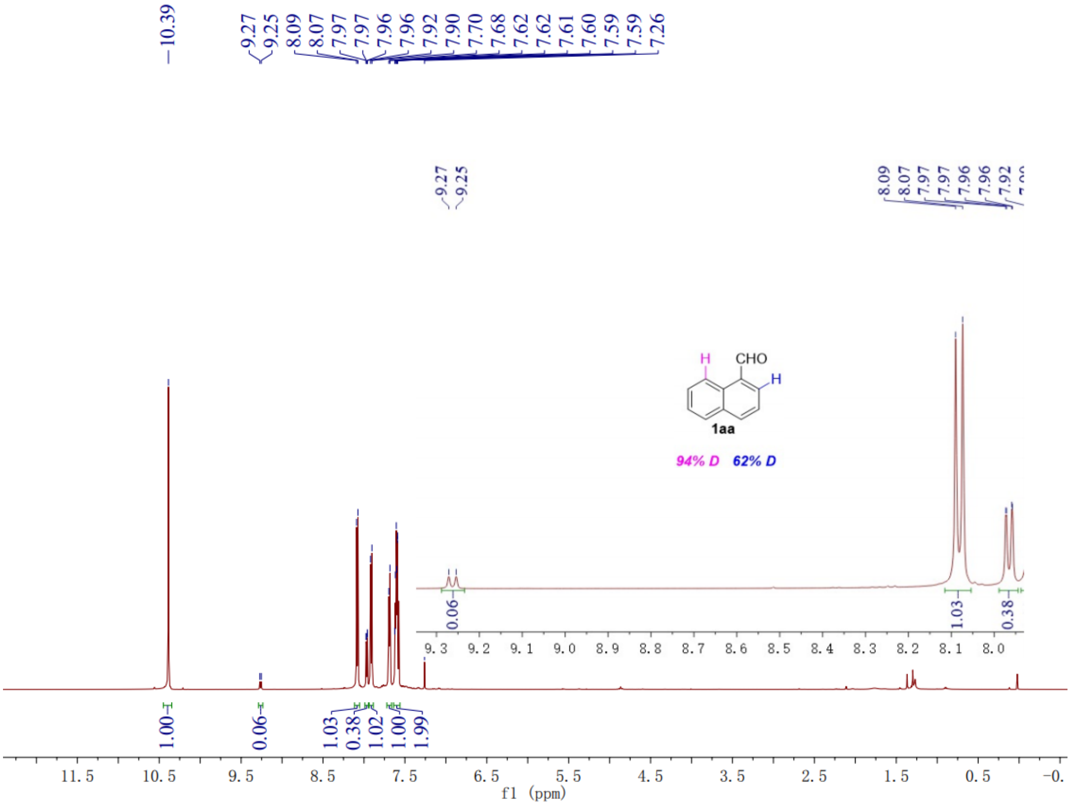
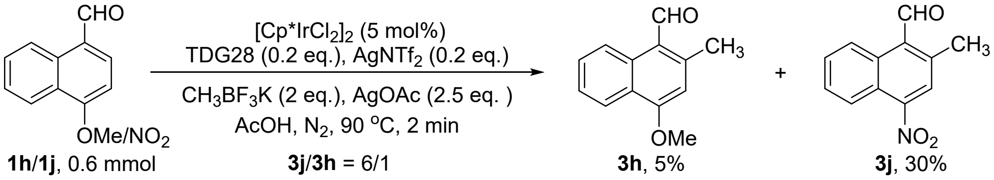
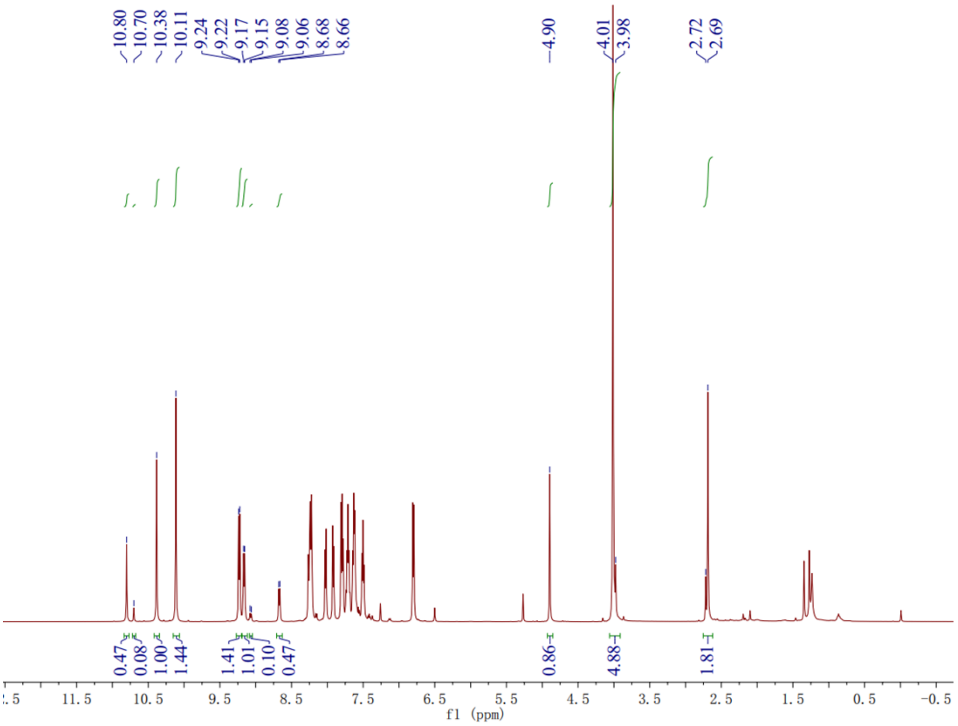


Figure S8. ^{1}H NMR of H/D exchange experiment (2 h) with **1aa** in the presence of TDG25

7.2.3 Competition experiment



A 10-mL dry microwave-vial equipped with a stir bar was charged with **1h** (0.3 mmol), **1j** (0.3 mmol), $[Cp^*IrCl_2]_2$ (0.03 mmol, 24 mg), 3-aminobenzonitrile (TDG28) (0.12 mmol, 20.9 mg), CH_3BF_3K (1.2 mmol, 146 mg), AgOAc (1.5 mmol, 250 mg) and $AgNTf_2$ (0.12 mmol, 46.6 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Degassed AcOH (3 mL) was added through syringe and the reaction mixture was stirred at 90 °C for 2 min. The tube was taken out into the ice water, and cold 10% NaOH aqueous (0.5 mL) was immediately added to quench the reaction, the ice water (1 mL) and EtOAc (1 mL) was added. The reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography to give the mixture of **1h**, **1j**, **3h** and **3j**. Yields were determined by ^{1}H NMR analysis using CH_2Br_2 (14.7 mg) as an internal standard.



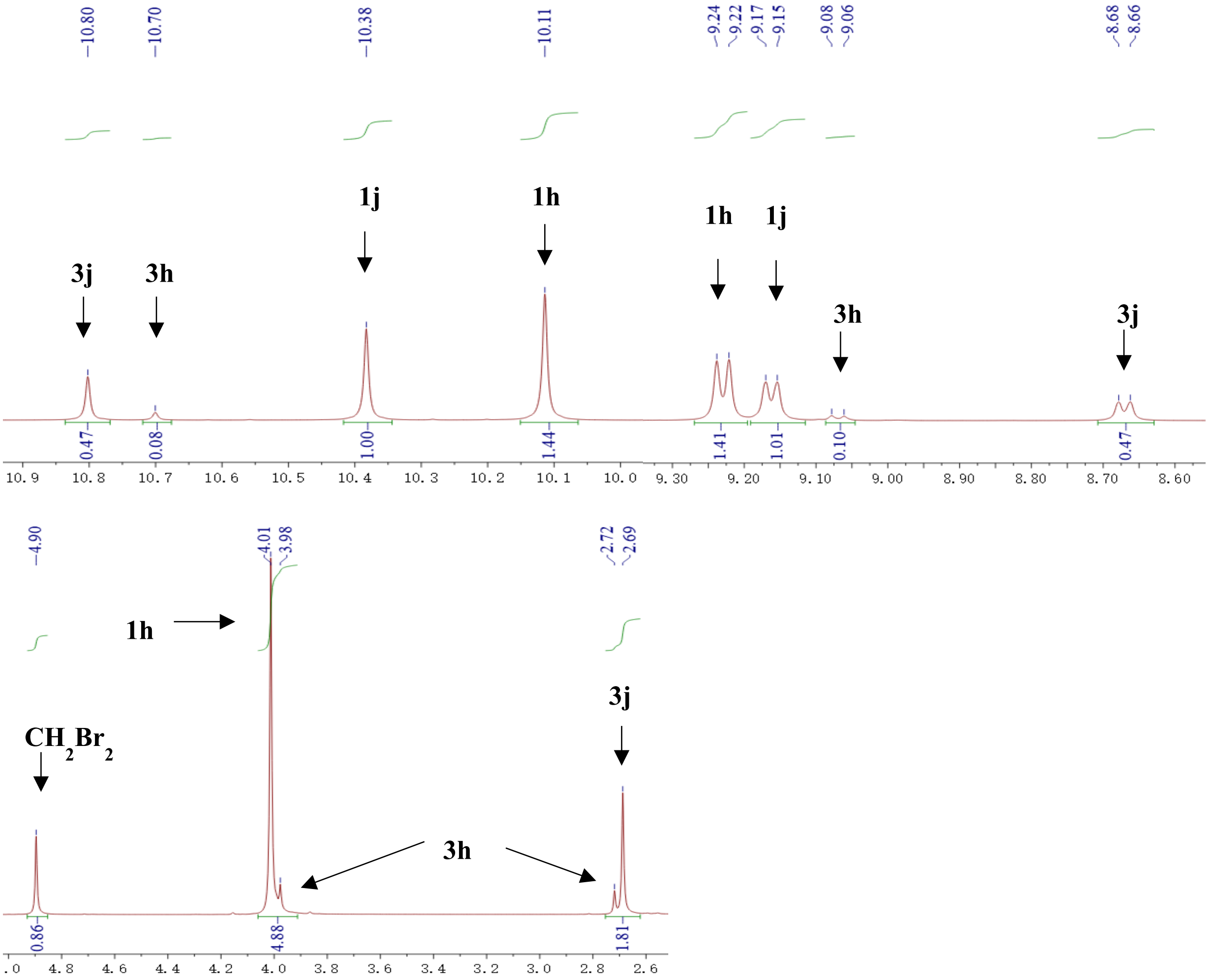
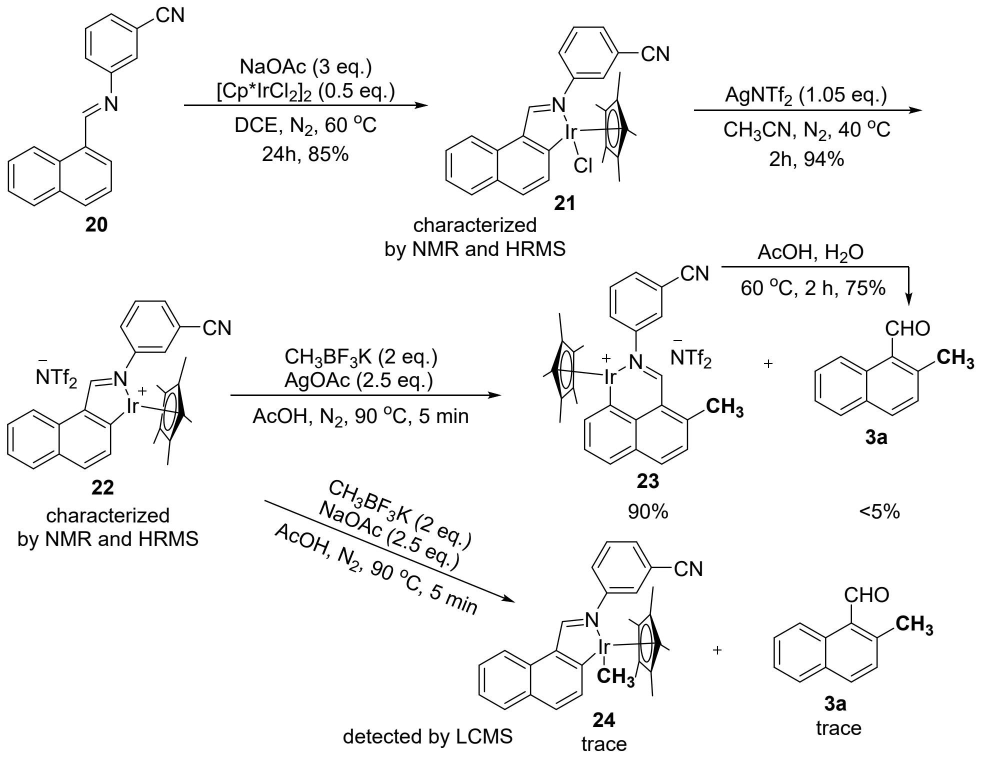


Figure S9. ^{1}H NMR of competition experiment

7.2.4 Identification of reaction intermediates



(*E*)-3-((Naphthalen-1-ylmethylene)amino)benzonitrile (20). To a solution of 1-naphthaldehyde (5 mmol, 780.9 mg) and 3-aminobenzonitrile (5 mmol, 590.7 mg) in dry DCM (10 mL) was added anhydrous $MgSO_4$ (25 mmol, 3 g). The reaction was allowed to stir at rt for 24 h. The mixture was filtered through a pad of Celite and washed with DCM (10 mL). The filtrate was concentrated under reduced pressure and the imine **20** was recrystallization from anhydrous EtOH. Grey solid (960mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (d, *J* = 8.6 Hz, 1H), 9.03 (s, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.70-7.64 (m, 1H), 7.63-7.57 (m, 2H), 7.57-7.47 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.33, 153.41, 134.05, 132.97, 131.50, 131.14, 130.80, 130.24, 129.31, 129.02, 127.99, 126.60, 125.81, 125.38, 124.41, 124.31, 118.78, 113.33.

Iridacycle 21. A 10-mL dry microwave-vial equipped with a stir bar was imine **20** (0.4 mmol, 102.5 mg), $[Cp^*IrCl_2]_2$ (0.2 mmol, 159.3 mg), NaOAc (1.2 mmol, 98.4 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Dry DCE (2 mL) was added through syringe and the reaction mixture was stirred at 60 °C for 24 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with DCM (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using DCM/EtOAc (100:1) as the eluent to afford iridacycle **21**. Red solid (210 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 1.53 (s, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.70, 173.01, 153.01, 140.04, 134.19, 134.16, 133.57, 130.66, 130.42, 130.16, 129.38, 127.68, 126.05, 124.08, 121.75, 118.21, 113.33, 90.40, 9.03. HRMS (ESI) m/z $[M-Cl]^+$calcd for $C_{28}H_{26}IrN_2$ 583.1720, found 583.1726.

Iridacycle 22. A 10-mL dry microwave-vial equipped with a stir bar was iridacycle **21** (0.2 mmol, 123.6 mg) and $AgNTf_2$ (0.21 mmol, 81.5 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Dry CH_3CN (4 mL) was added through syringe and the reaction mixture was stirred at 40 °C for 2 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with DCM (10 mL). The filtrate was concentrated under reduced pressure. The iridacycle **22** was recrystallization from anhydrous AcOH to give yellow solid (170 mg, 94%). ^1H NMR (500 MHz, DMSO-d_6) δ 9.86 (s, 1H), 8.64 (d, *J* = 8.1 Hz, 1H), 8.38 (s, 1H), 8.19 (d, *J* = 7.5 Hz, 1H), 8.07-7.92 (m, 4H), 7.87 (t, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.57 (t, *J* = 7.0 Hz, 1H), 3.35 (s, 3H), 1.56 (s, 15H). ^{13}C NMR (126 MHz, DMSO) δ 179.61, 168.96, 149.92, 142.00, 134.65, 134.01, 132.80, 131.79, 131.17, 130.36, 129.11, 128.33, 128.10, 126.71, 125.37, 123.66, 119.46 (q, *J* = 321.9 Hz), 118.04, 112.57, 97.04, 8.16, 1.12. HRMS (ESI) m/z $[M\text{-}NTf_2+CH_3OH]^+$calcd for $C_{29}H_{30}IrN_2O$ 615.1982, found 615.1937.

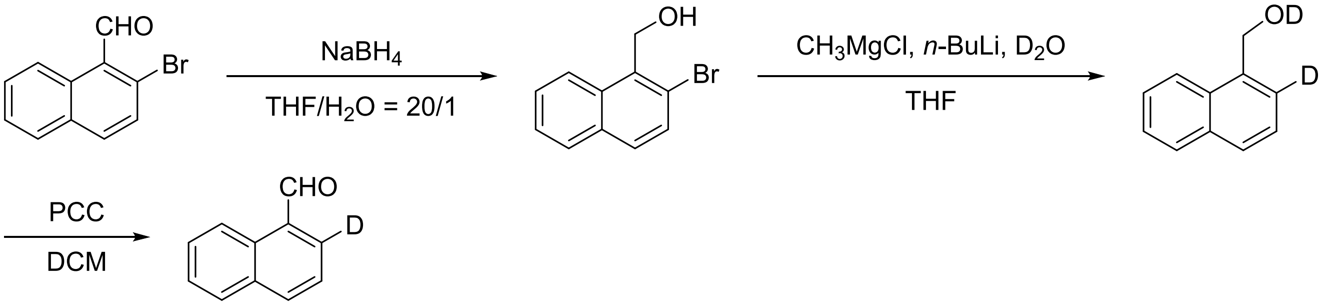
Iridacycle 23. A 10-mL dry microwave-vial equipped with a stir bar was charged with iridacycle **22** (0.15 mmol), CH_3BF_3K (0.3 mmol, 36.5 mg), AgOAc (0.38 mmol, 62.5 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Degassed AcOH (1.5 mL) was added through syringe and the reaction mixture was stirred at 90 °C for 5 min. After cooling to rt, the reaction mixture was filtered and washed with AcOH (0.5 mL). The filter cake was dissolved with DCM (5 mL) and purified by column chromatography on silica gel using DCM/EtOAc (50:1) as the eluent to afford iridacycle **23**. Yellow solid (118 mg, 90%). ^1H NMR (500 MHz, DMSO-d_6) δ 9.13 (s, 1H), 8.64 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.1 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 2.95 (s, 3H), 1.31 (s, 15H). ^{13}C NMR (126 MHz, DMSO) δ 168.48, 157.07, 148.77, 143.69, 139.77, 131.62, 130.73, 130.68, 130.63, 129.57, 128.71, 128.46, 127.31, 127.19, 126.63, 126.39, 119.48 (q, *J* = 321.9 Hz), 118.12, 112.04, 97.89, 20.70, 8.23.

Iridacycle 24. A 10-mL dry microwave-vial equipped with a stir bar was charged with iridacycle **22** (0.05 mmol), CH_3BF_3K (0.1 mmol, 12.1 mg), NaOAc (0.13 mmol, 10.2 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Degassed AcOH (0.5 mL) was added through syringe and the reaction mixture was stirred at 90 °C for 5 min. The mixture turned into black in first one minute, and then turned back to yellow quickly. LCMS(ESI) m/z $[M+H]^+$calcd for $C_{29}H_{30}IrN_2$ 599.2, found 599.2.

Regeneration of Compound 3a. A 10-mL dry microwave-vial equipped with a stir bar was charged with iridacycle **23** (0.1 mmol). AcOH (1.5 mL) and H_2O (0.5 mL) was added and the reaction mixture was stirred at 60 °C for 2 h. After cooling to rt, the reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting residue was purified by preparative thin layer chromatography using petroleum ether/EtOAc (100:1) as the developing solvent o give **3a** (12.7 mg, 75%), in which the characterization data is the same as compound **3a**.

7.2.5 Kinetic isotope effect experiments

7.2.5.1 Synthesis of **1a-*ortho*-D**

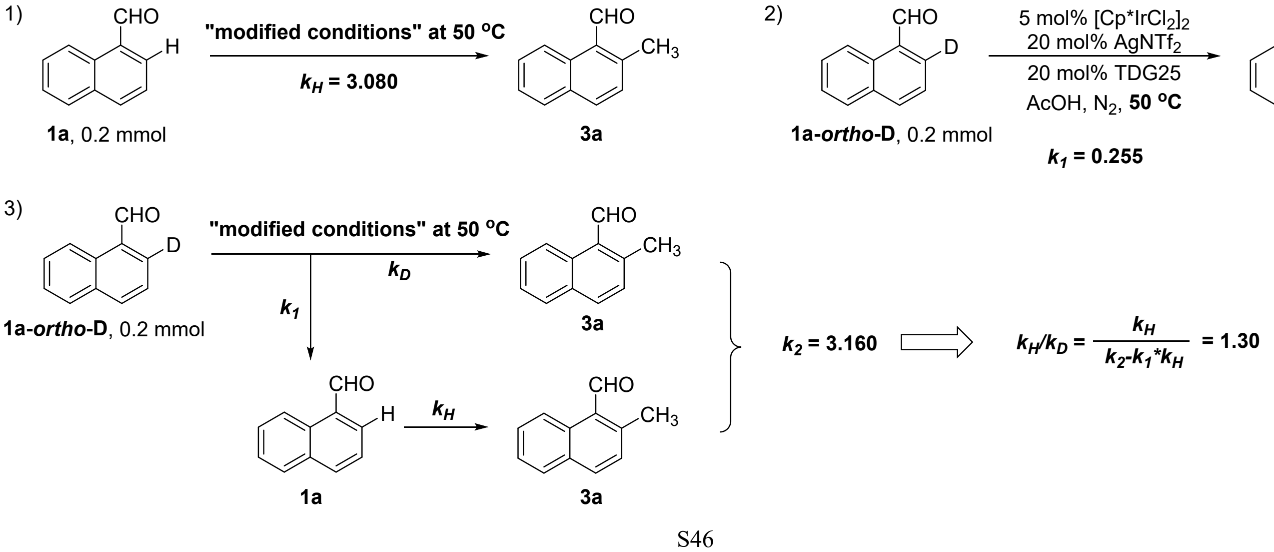


1a-*ortho*-D

1-Naphthaldehyde-2-*d* (1a-*ortho*-D). To a solution of 2-bromo-1-naphthaldehyde (8.9 mmol)[8] in THF/H_2O (20/1) (15 mL) at -0 °C was added $NaBH_4$ (8.9 mmol). The resulting reaction mixture was stirred for 30 min at rt. When the starting material was consumed, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the crude product was purified by column chromatography to afford (2-bromonaphthalen-1-yl)methanol.

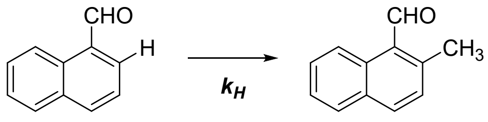
To a solution of (2-bromonaphthalen-1-yl)methanol (6.2 mmol) in dry THF (10 mL) at -10 °C under N_2 atomosphere was dropwisely added CH_3MgCl (3 M in THF, 7.4 mmol). After the reaction was stirred for 5 min, *n*-butyl lithium solution (2.5 M in hexane, 13.6 mmol) was slowly added over 30 min. The resulting reaction mixture was stirred at -10 °C for 1h, and then treated with D_2O (186 mmol). After warmed to room temperature, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum. The residue was dissolved in DCM (20 mL) and PCC (12.4 mmol) was added at rt. The mixture was stirred at room temperature for 1 h. After the reaction was completed monitored by TLC, the reaction mixture was filtered through a pad of silica gel and washed with DCM. The filtrate was then concentrated in vacuo and the resulting residue was purified by silica gel column chromatography to afford **1a-*ortho*-D** as pale yellow oil (850 mg, 81%, >99% D). ^1H NMR (500 MHz, $CDCl_3$) δ 10.39 (s, 1H), 9.26 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.72-7.66 (m, 1H), 7.64-7.56 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.59, 136.45 (t, *J* = 24.3 Hz), 135.39, 133.79, 131.40, 130.58, 129.15, 128.56, 127.04, 124.96, 124.85. The characterization data is consistent with reported literature.[9]

7.2.5.2 Parallel reactions



Measure of k_H or k_2: A 10-mL dry microwave-vial equipped with a stir bar was charged with **1a** or **1a-*ortho*-D** (0.2 mmol), $[Cp^*IrCl_2]_2$ (0.01 mmol, 8 mg), 3-aminobenzenesulfonic acid (TDG25) (0.04 mmol, 6.9 mg), CH_3BF_3K (0.4 mmol, 48.7 mg), AgOAc (0.5 mmol, 83.4 mg) and $AgNTf_2$ (0.04 mmol, 15.5 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Degassed AcOH (1 mL) was added through syringe and the vial was stirred at 50 °C. Several parallel reactions were set up together. According to the relative reaction time, one of these tubes was taken out into the ice water, and cold 10% NaOH aqueous (0.5 mL) was immediately added to quench the reaction, the ice water (1 mL) and EtOAc (1 mL) was added. The reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Conversions were determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.

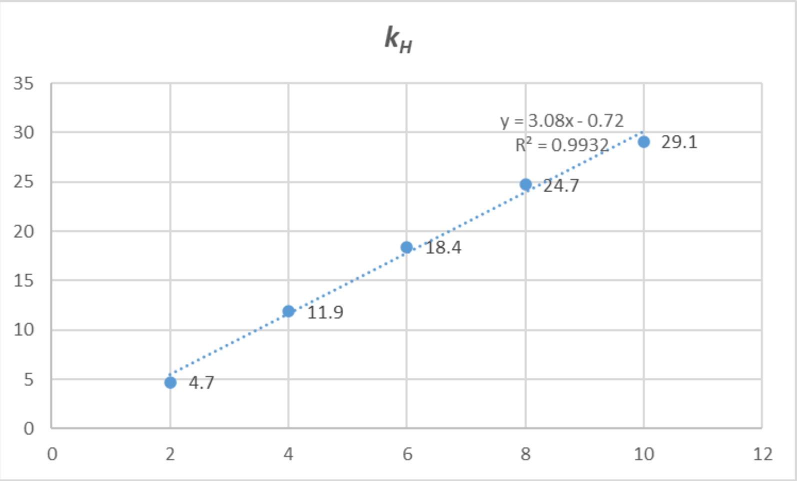
Measure of k_1: A 10-mL dry microwave-vial equipped with a stir bar was charged with **1a-*ortho*-D** (0.2 mmol), $[Cp^*IrCl_2]_2$ (0.01 mmol, 8 mg), 3-aminobenzenesulfonic acid (TDG25) (0.04 mmol, 6.9 mg), and $AgNTf_2$ (0.04 mmol, 15.5 mg). The vial was sealed with a PTFE-lined cap, and filled with N_2. Degassed AcOH (1 mL) was added through syringe and the vial was stirred at 50 °C. Several parallel reactions were set up together. According to the relative reaction time, one of these tubes was taken out into the ice water, and cold 10% NaOH aqueous (0.5 mL) was immediately added to quench the reaction, the ice water (1 mL) and EtOAc (1 mL) was added. The reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL). The filtrate was extracted with EtOAc and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Conversions were determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.

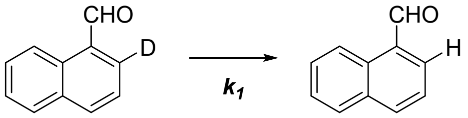


1a, 0.2 mmol

3a

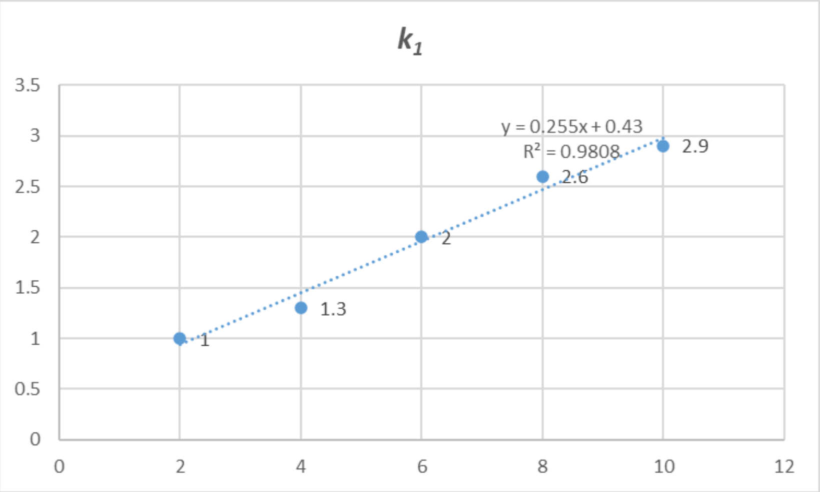
Time (min)	**Conversion (%)**
0	0
2	4.7
4	11.9
6	18.4
8	24.7
10	29.1

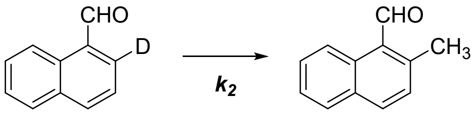




1a-*ortho*-D, 0.2 mmol **3a**

Time (min)	**Conversion (%)**
0	0
2	1.0
4	1.3
6	2.0
8	2.6
10	2.9





1a-*ortho*-D, 0.2 mmol **3a**

Time (min)	**Conversion (%)**
0	0
2	4.6
4	9.0
6	18.1
8	24.6
10	28.4

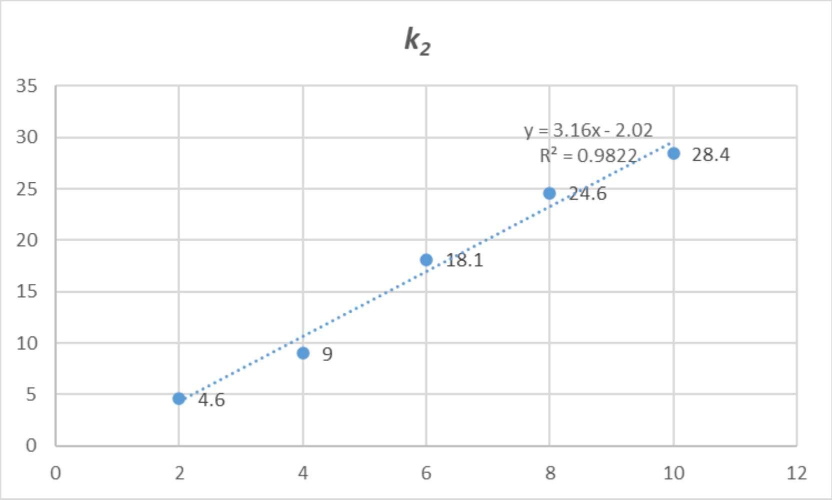
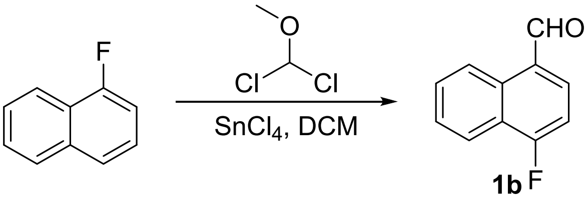


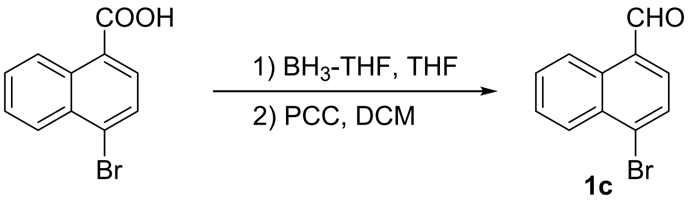
Figure S10. Parallel KIE reaction.

8. Preparation of substrates.



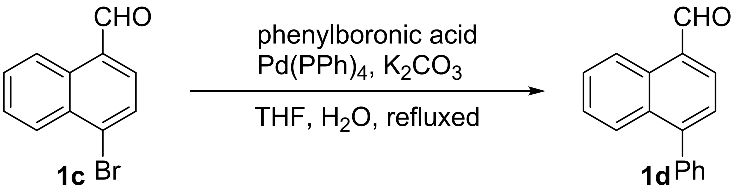
1b

4-Fluoro-1-naphthaldehyde (1b). A solution of fresh α,α-dichloromethyl methyl ether (5 mmol) in DCM (5 mL) was cooled in an ice bath and then treated dropwise with $SnCl_4$ (5 mmol) under N_2. After stirring for 45 min at 0 °C, a solution of 1-fluoronaphthalene (5 mmol) in DCM (5 mL) was added through syringe. The reaction was allowed to slowly warm to room temperature and stirred for 8 h. The mixture was poured into ice water and extracted with DCM twice. The combined organic layers were washed with H_2O, brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography to give **1b** as white solid (656 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.31 (s, 1H), 9.30 (d, J = 8.6 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.97 (dd, J = 7.9, 5.5 Hz, 1H), 7.76 (t, J = 8.4 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.28 (dd, J = 9.6, 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.28, 162.89 (d, J = 263.8 Hz), 138.03 (d, J = 10.8 Hz), 132.57 (d, J = 6.0 Hz), 130.27, 128.27 (d, J = 3.9 Hz), 127.52 (d, J = 1.9 Hz), 125.08 (d, J = 2.4 Hz), 124.00 (d, J = 15.9 Hz), 121.15 (d, J = 6.4 Hz), 109.17 (d, J = 21.4 Hz). The characterization data is consistent with reported literature.[10]

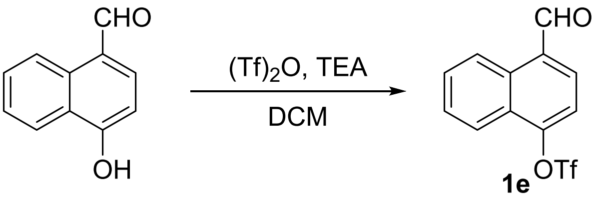


4-Bromo-1-naphthaldehyde (1c). 4-Bromonaphthalene-1-carboxylic Acid (3 mmol) was dissolved in anhydrous THF (6.0 mL) under N_2 atmosphere. BH_3-THF (2.0 M, 6.0 mmol) was added by syringe slowly. The resulting mixture was stirred at 30 °C for 8 h. The reaction mixture was quenched using a saturated aqueous solution of NH_4Cl and extracted using EtOAc. The combined organic phases were washed with brine solution, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the corresponding benzyl alcohol without further purification.

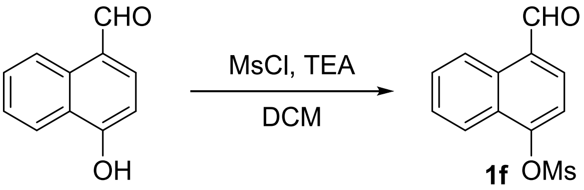
To a solution of above benzyl alcohol (3.0 mmol) in DCM (6 mL) was added PCC (6 mmol) at rt. The mixture was stirred at room temperature for 2 h. After the reaction was completed monitored by TLC, the reaction mixture was filtered through a pad of silica gel and washed with DCM. The filtrate was then concentrated in vacuo and the resulting residue was purified by silica gel column chromatography to afford **1c** as white solid (564 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 9.27 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.76-7.66 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.76, 136.23, 132.29, 131.58, 131.47, 131.06, 129.93, 129.49, 128.42, 127.88, 125.26. The characterization data is consistent with reported literature.[8]



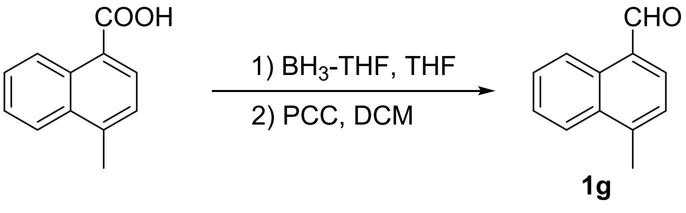
4-Phenyl-1-naphthaldehyde (1d). A two-necked flask with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (0.075 mmol), K_2CO_3 (3 mmol), compound **1c** (1.5 mmol), phenylboronic acid (1.9 mmol) under an N_2 atmosphere. THF (8 mL) and water (2 mL) were added through syringe and the reaction mixture was refluxed at 90 °C for 12 h. After cooling down to rt, water was added and the mixture extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1d** as white solid (250 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 9.37 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 7.3 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.74-7.68 (m, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.57-7.43 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.46, 147.60, 139.95, 136.31, 132.17, 131.22, 130.73, 129.91, 128.96, 128.56, 128.22, 127.09, 126.92, 126.20, 125.17. The characterization data is consistent with reported literature.[8]



4-Formylnaphthalen-1-yl trifluoromethanesulfonate (1e). A two-necked flask with a magnetic stir bar was charged with 4-hydroxy-1-naphthaldehyde (3.0 mmol) and TEA (6 mmol) at -78 °C under N_2. DCM (5mL) was added and mixture was stirred for 5 min. A solution of $(Tf)_2O$ (3.6 mmol) in DCM (5 mL) was added slowly through syringe and the reaction mixture was stirred at -78 °C for 30 min. Then the reaction was allowed to stir at rt for another 1 h. The reaction was quenched with aqueous $NaHCO_3$ and extracted with DCM twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by column chromatography to afford **1e** as pale yellow solid (490 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 9.34 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.87-7.82 (m, 1H), 7.82-7.75 (m, 1H), 7.67 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.05, 149.72, 135.81, 132.35, 131.41, 130.62, 128.93, 126.71, 125.34, 121.42, 118.83 (q, *J* = 320.4 Hz), 116.92. The characterization data is consistent with reported literature.[11]

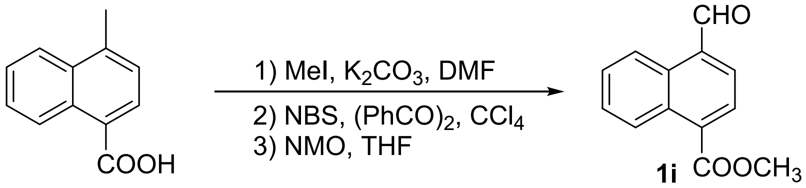


4-Formylnaphthalen-1-yl methanesulfonate (1f). 4-Hydroxy-1-naphthaldehyde (2.3 mmol) was dissolved in DCM (5.0 mL). TEA (4.6 mmol) and MsCl (3.5 mmol) were successively added at 0 °C. The reaction mixture was stirred for 1h at rt. When the starting material was consumed, the reaction was quenched with aqueous HCl and extracted with DCM twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by column chromatography to afford **1f** as white solid (528 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.34 (d, *J* = 8.6 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.83-7.77 (m, 1H), 7.76-7.69 (m, 2H), 3.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.38, 149.78, 136.58, 132.30, 130.37, 130.20, 128.28, 127.23, 125.30, 121.98, 117.18, 38.71. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{12}H_{11}O_4S$ 251.0373, found 251.0372.



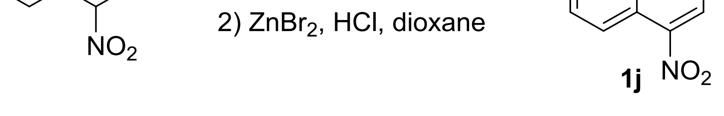
4-Methyl-1-naphthaldehyde (1g). 4-Bromonaphthalene-1-carboxylic Acid (7 mmol) was dissolved in anhydrous THF (10 mL) under N_2 atmosphere. BH_3-THF (2.0 M, 14 mmol) was added by syringe slowly. The resulting mixture was stirred at 30 °C for 8 h. The reaction mixture was quenched using a saturated aqueous solution of NH_4Cl and extracted using EtOAc. The combined organic phases were washed with brine solution, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the corresponding benzyl alcohol without further purification.

To a solution of above benzyl alcohol (7.0 mmol) in DCM (10 mL) was added PCC (14 mmol) at rt. The mixture was stirred at room temperature for 2 h. After the reaction was completed monitored by TLC, the reaction mixture was filtered through a pad of silica gel and washed with DCM. The filtrate was then concentrated in vacuo and the resulting residue was purified by silica gel column chromatography to afford **1g** as colorless oil (1.04 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 9.32 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.72-7.66 (m, 1H), 7.65-7.59 (m, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 2.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.45, 143.00, 137.01, 132.84, 130.70, 130.18, 128.75, 126.93, 126.03, 125.54, 124.51, 20.53. The characterization data is consistent with reported literature.[8]



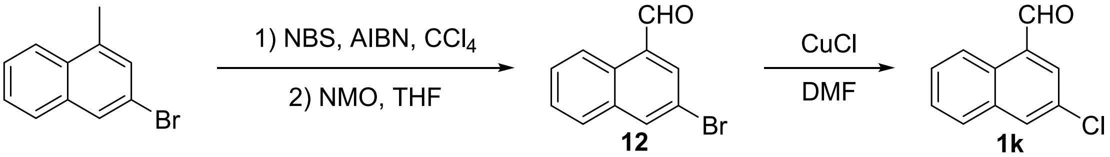
Methyl 4-formyl-1-naphthoate (1i). A mixture of 4-methyl-1-naphthoic acid (2 mmol), and K_2CO_3 (4 mmol) in DMF (1 mL) was added MeI (3 mmol) at rt. After completion of addition, the reaction was stirred for 3 h. Water was added and extracted with EtOAc for 3 times. The combined organic layers were washed with brine and dried over sodium sulfate, and concentrated under reduced pressure to afford the corresponding methyl ester without further purification.

To a solution of crude methyl ester (2 mmol) in CCl_4 (4 mL) was added NBS (2.5 mmol) followed by benzoylperoxide (0.3 mmol). After refluxed for 8 h, the resulting mixture was cooled to room temperature. Water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum. The residue was dissolved in THF (5 mL) and N-methylmorpholine N-oxide (8 mmol) was added. The reaction mixture was refluxed for 4 h. After cooling to rt, water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1i** as white solid (364 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 9.28-9.20 (m, 1H), 8.83-8.76 (m, 1H), 8.18 (d, *J* = 7.4 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 1H), 7.75-7.66 (m, 2H), 4.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.05, 167.57, 134.10, 134.05, 133.73, 131.47, 131.12, 129.21, 128.41, 128.11, 126.20, 124.91, 52.84. The characterization data is consistent with reported literature.[8]



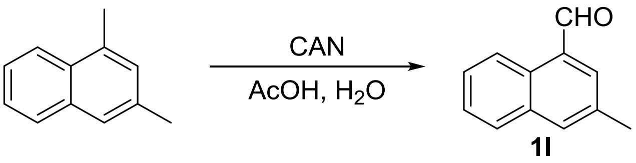
4-Nitro-1-naphthaldehyde (1j). Under nitrogen conditions, 1-nitronapthalene (1.6 mmol), tris(benzotriazol-1-yl)methane (1.6 mmol) and potassium hydroxide (10 mmol) in DMSO (16 mL) were stirred for 12 h. The solution was then poured into 15 mL of 1N HCl. The solution was extracted with DCM. The combined organic phases were washed with brine solution, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the para-[Bis(benzotriazol-1-yl)methyl]nitronapthalene without further purification.

A mixture of para-[Bis(benzotriazol-1-yl)methyl]nitronapthalene (1.6 mmol), zinc bromide (3.2 mmol), and dioxane (16 mL) were refluxed at approximately 120 °C for 30 minutes. Concentrated HCl (7 mL) was then added and the mixture was refluxed for an additional 4 hours. The mixture was then cooled to room temperature, and the solvent was concentrated in vacuo. The solution was taken up in 200 mL of water and extracted with DCM. The organic layers were washed with 5% NaOH, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography to afford **1j** as yellow solid (193 mg, 60%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.52 (s, 1H), 9.33-9.25 (m, 1H), 8.40-8.33 (m, 1H), 8.16 (d, J = 7.7 Hz, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.86-7.76 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.94, 150.98, 134.63, 133.57, 131.93, 130.38, 129.88, 125.29, 125.13, 123.25, 121.48. The characterization data is consistent with reported literature.[12]

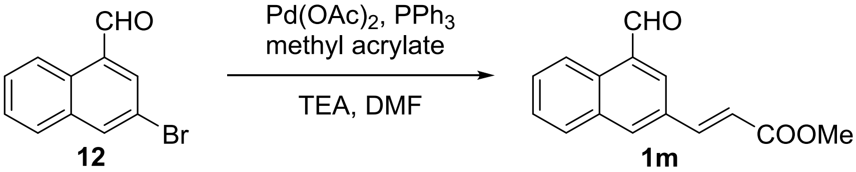


3-Chloro-1-naphthaldehyde (1k). A solution of 3-bromo-1-methylnaphthalene (21.6 mmol) in CCl_4 (40 mL) was added NBS (23.8 mmol) followed by AIBN (0.3 mmol). After refluxed for 8 h, the resulting mixture was cooled to room temperature. Water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum. The residue was dissolved in THF (80 mL) and N-methylmorpholine N-oxide (86 mmol) was added. The reaction mixture was refluxed for 4 h. After cooling to rt, water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford 3-bromo-1-naphthaldehyde **12** as pale yellow solid (2.65 g, 53%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 9.07 (d, J = 8.6 Hz, 1H), 8.12 (s, 1H), 7.92 (d, J = 1.8 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.84, 138.59, 136.72, 135.00, 132.71, 129.30, 128.93, 127.94, 127.60, 124.88, 118.55. The characterization data is consistent with reported literature.[8]

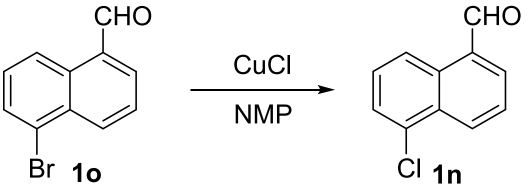
A solution of compound 3-bromo-1-naphthaldehyde (1.5 mmol) in NMP (3mL) was added CuCl (3 mmol) at rt. The reaction mixture was heated at 150 °C for 12 h in dark. After the reaction was completed monitored by TLC, water was added and the mixture extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1k** as white solid (276 mg, 96%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 9.14 (d, J = 8.6 Hz, 1H), 8.06 (d, J = 1.6 Hz, 1H), 7.91 (d, J = 2.0 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.72-7.65 (m, 1H), 7.61 (t, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.09, 136.25, 134.86, 133.60, 132.96, 130.97, 129.31, 128.98, 128.13, 127.79, 124.97. The characterization data is consistent with reported literature.[8]



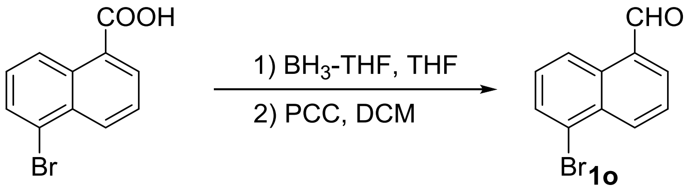
3-Methyl-1-naphthaldehyde (1l). To a solution of CAN (3.5 mmol) in 50% acetic acid (100 mL) at 85 °C by using an oil bath was dropwisely added 1,3-dimethylnaphthalene (1.0 mmol). Once the starting material was completely consumed as monitored by TLC, the reaction mixture was cooled and poured into water. The product was extracted with EtOAc twice. The combined organic phases were washed with water, brine solution, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by column chromatography to afford **1l** as yellow oil (65 mg, 38%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 9.17 (d, J = 8.5 Hz, 1H), 7.86-7.77 (m, 3H), 7.64-7.59 (m, 1H), 7.57-7.52 (m, 1H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.63, 138.81, 134.63, 134.36, 134.22, 131.36, 128.99, 128.18, 127.89, 127.05, 124.72, 21.30. The characterization data is consistent with reported literature.[8]



Methyl (*E*)-3-(4-formylnaphthalen-2-yl)acrylate (1m). A 20-mL dry microwave-vial equipped with a stir bar was charged with 3-bromo-1-naphthaldehyde **12** (2.2 mmol), $Pd(OAc)_2$ (0.22 mmol), PPh_3 (0.44 mmol), methyl acrylate (6.6 mmol), TEA (8.8 mmol). The vial was sealed with a PTFE-lined cap, and filled with N_2. DMF (3 mL) was added through syringe and the reaction mixture was stirred at 100 °C for 24 h. After cooling to rt, water was added and the mixture extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1m** as pale yellow solid (390 mg, 74%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.42 (s, 1H), 9.18 (d, J = 8.5 Hz, 1H), 8.17-8.11 (m, 2H), 7.93 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 16.0 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 6.64 (d, J = 16.0 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.08, 167.15, 143.22, 135.82, 134.18, 134.00, 132.16, 131.27, 131.11, 130.29, 129.28, 127.89, 125.07, 119.45, 52.06. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{16}H_{15}O_3$ 255.1016, found 255.1018.



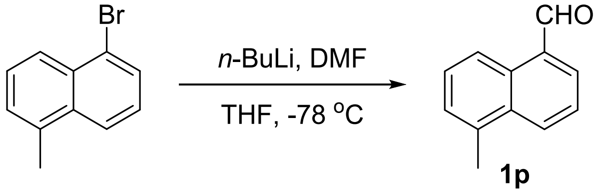
5-Chloro-1-naphthaldehyde (1n). A solution of 5-bromo-1-naphthaldehyde (3 mmol) in NMP (3mL) was added CuCl (6 mmol) at rt. The reaction mixture was heated at 150 °C for 12 h in dark. After the reaction was completed monitored by TLC, water was added and the mixture extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1n** as white solid (420 mg, 74%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.22 (d, J = 8.6 Hz, 1H), 8.61 (d, J = 8.5 Hz, 1H), 8.10-8.01 (m, 1H), 7.76 (dd, J = 8.5, 7.1 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.64-7.55 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.20, 137.30, 132.64, 131.94, 131.68, 131.58, 131.28, 129.07, 127.58, 126.12, 124.13. The characterization data is consistent with reported literature.[8]



1o

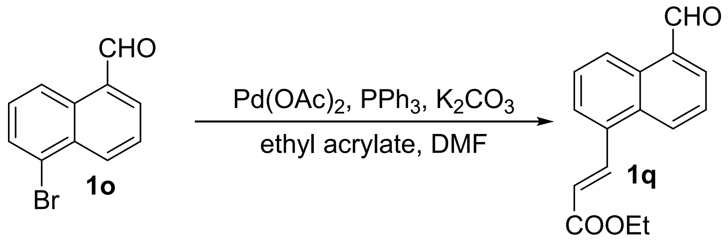
5-Bromo-1-naphthaldehyde (1o). 5-Bromonaphthalene-1-carboxylic Acid (1.5 mmol) was dissolved in anhydrous THF (3.0 mL) under N_2 atmosphere. BH_3-THF (2.0 M, 3.0 mmol) was added by syringe slowly. The resulting mixture was stirred at 30 °C for 8 h. The reaction mixture was quenched using a saturated aqueous solution of NH_4Cl and extracted using EtOAc. The combined organic phases were washed with brine solution, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the corresponding benzyl alcohol without further purification.

To a solution of above benzyl alcohol (1.5 mmol) in DCM (6 mL) was added PCC (3 mmol) at rt. The mixture was stirred at room temperature for 2 h. After the reaction was completed monitored by TLC, the reaction mixture was filtered through a pad of silica gel and washed with DCM. The filtrate was then concentrated in vacuo and the resulting residue was purified by silica gel column chromatography to afford **1o** as white solid (270 mg, 76%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.27 (d, J = 8.6 Hz, 1H), 8.58 (d, J = 8.6 Hz, 1H), 8.04 (dd, J = 7.0, 1.1 Hz, 1H), 7.90 (dd, J = 7.5, 0.8 Hz, 1H), 7.74 (dd, J = 8.5, 7.1 Hz, 1H), 7.52 (dd, J = 8.5, 7.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.08, 137.34, 134.35, 132.39, 132.06, 131.69, 131.37, 129.47, 126.38, 124.83, 123.52. The characterization data is consistent with reported literature.[8]

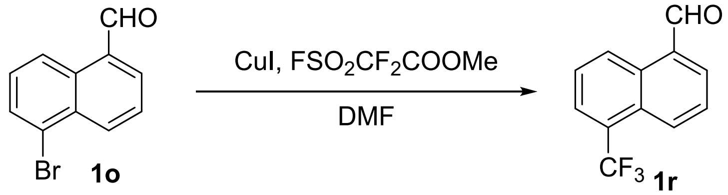


1p

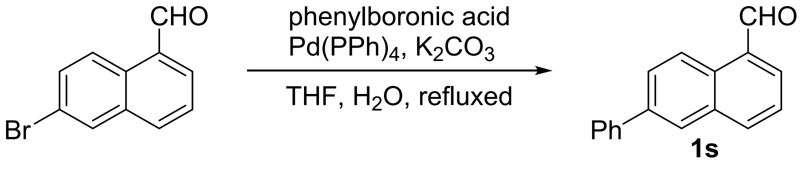
5-Methyl-1-naphthaldehyde (1p). To a solution of 1-bromo-5-methylnaphthalene[13] (1.5 mmol) in anhydrous THF at -78 °C under N_2 atomosphere was dropwisely added *n*-butyl lithium solution (1.6 M in hexane, 2.25 mmol). The resulting reaction mixture was stirred at -78 °C for 20 minutes, and then treated with anhydrous DMF (2.25 mmol) for another 15 minutes. After warmed to room temperature, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1p** as white solid (181 mg, 71%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 9.12 (d, J = 8.6 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.00 (dd, J = 7.0, 1.2 Hz, 1H), 7.67 (dd, J = 8.5, 7.1 Hz, 1H), 7.58 (dd, J = 8.6, 7.0 Hz, 1H), 7.44 (d, J = 7.0 Hz, 1H), 2.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.72, 136.03, 134.92, 133.08, 131.86, 131.35, 131.07, 128.91, 127.93, 124.79, 123.00, 20.06. The characterization data is consistent with reported literature.[14]



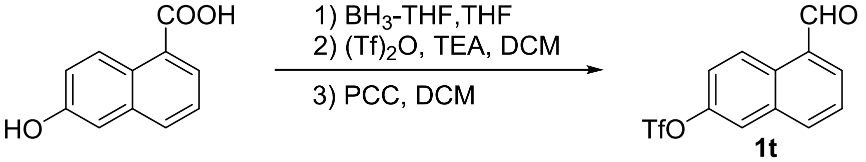
Ethyl (*E*)-3-(5-formylnaphthalen-1-yl) acrylate (1q). A 10-mL dry microwave-vial equipped with a stir bar was charged with 5-bromo-1-naphthaldehyde (3 mmol), $Pd(OAc)_2$ (0.3 mmol), PPh_3 (0.6 mmol), ethyl acrylate (4.5 mmol), K_2CO_3 (4.5 mmol). The vial was sealed with a PTFE-lined cap, and filled with N_2. DMF (3 mL) was added through syringe and the reaction mixture was stirred at 135 °C for 36 h. After cooling to rt, water was added and the mixture extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1q** as pale green solid (300 mg, 40%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.34 (d, J = 8.6 Hz, 1H), 8.52-8.44 (m, 2H), 8.03 (d, J = 7.0 Hz, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.73 (dd, J = 8.5, 7.1 Hz, 1H), 7.71-7.66 (m, 1H), 6.52 (d, J = 15.7 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.51, 166.72, 141.39, 136.88, 132.58, 131.86, 131.76, 130.97, 130.55, 128.76, 127.10, 126.08, 125.84, 122.27, 60.90, 14.48. HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{17}H_{17}O_3$ 269.1172, found 269.1175.



5-(Trifluoromethyl)-1-naphthaldehyde (1r). 5-bromo-1-naphthaldehyde (2 mmol) and CuI (6 mmol) were dissolved in anhydrous DMF (10 mL) under N_2 atmosphere. $FSO_2CF_2CO_2CH_3$ (20 mmol) was added by syringe slowly at room temperature and the reaction mixture was stirred at 130 °C by using an oil bath for 16 h. The reaction mixture was cooled and poured into water and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was purified by reversed-phase column chromatography with gradient CH_3CN/H_2O eluent to afford **1r** as white solid (150 mg, 33%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.53 (d, J = 8.7 Hz, 1H), 8.47 (d, J = 8.7 Hz, 1H), 8.08 (d, J = 7.0 Hz, 1H), 7.98 (d, J = 7.3 Hz, 1H), 7.80 (dd, J = 8.6, 7.1 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.36, 137.19, 131.86, 131.27, 131.07 (q, J = 2.6 Hz), 129.63, 129.44, 127.52, 126.82, 126.61 (q, J = 30.2 Hz), 125.75 (q, J = 6.1 Hz), 124.58 (q, J = 273.5 Hz). The characterization data is consistent with reported literature.[8]

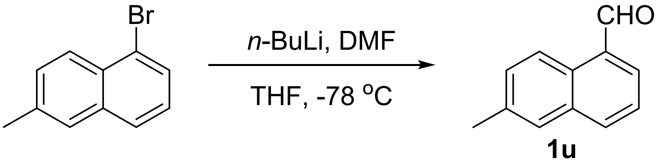


6-Phenyl-1-naphthaldehyde (1s). A two-necked flask with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (0.075 mmol), K_2CO_3 (3 mmol), 6-bromo-1-naphthaldehyde[14] (1.5 mmol), phenylboronic acid (1.8 mmol) under an N_2 atmosphere. THF (8 mL) and water (2 mL) were added through syringe and the reaction mixture was refluxed at 90 °C for 12 h. After cooling down to rt, water was added and the mixture extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1s** as white solid (300 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.42 (s, 1H), 9.33 (d, *J* = 8.9 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 1.4 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 1H), 7.97 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.69-7.64 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.67, 140.45, 139.72, 136.70, 135.63, 134.26, 131.50, 129.77, 129.11, 128.82, 127.92, 127.55, 126.24, 125.61, 125.46. HRMS (ESI) m/z $[M+H]^+$calcd for $C_{17}H_{13}O$ 233.0961, found 233.0956.



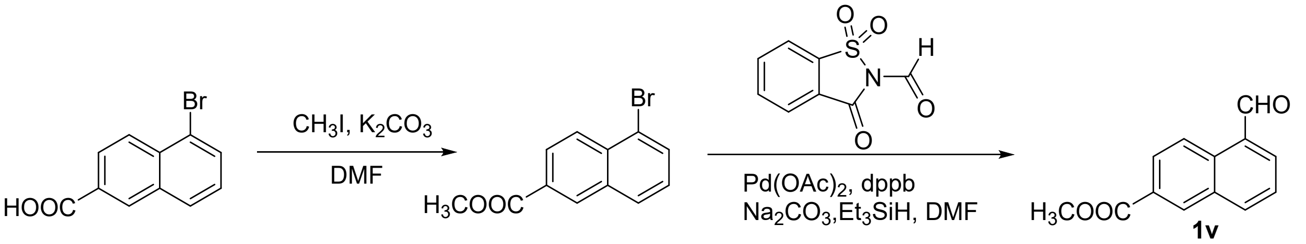
5-Formylnaphthalen-2-yl trifluoromethanesulfonate (1t). 6-Hydroxy-1-naphthoic acid (2 mmol) was dissolved in anhydrous THF (5 mL) under N_2 atmosphere. BH_3-THF (2.0 M, 6 mmol) was added by syringe slowly. The resulting mixture was stirred at 30 °C for 8 h. The reaction mixture was quenched using a saturated aqueous solution of NH_4Cl and extracted using EtOAc. The combined organic phases were washed with brine solution, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford 5-(hydroxymethyl) naphthalen-2-ol without further purification.

A two-necked flask with a magnetic stir bar was charged with 5-(hydroxymethyl) naphthalen-2-ol (2 mmol) and TEA (4 mmol) at 0 °C under N_2. DCM (5mL) was added and mixture was stirred for 5 min. A solution of $(Tf)_2O$ (2.4 mmol) in DCM (5 mL) was added slowly through syringe and the reaction mixture was stirred at 0 °C for 30 min. Then the reaction was allowed to stir at rt for 12 h. The reaction was quenched with aqueous $NaHCO_3$ and extracted with DCM twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and the residue was dissolved in DCM (6 mL). PCC (4 mmol) was added at rt. The mixture was stirred at room temperature for 2 h. After the reaction was completed monitored by TLC, the reaction mixture was filtered through a pad of silica gel and washed with DCM. The filtrate was then concentrated in vacuo and the resulting residue was purified by silica gel column chromatography to afford **1t** as white solid (236 mg, 39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 9.43 (d, *J* = 9.4 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 7.0 Hz, 1H), 7.84 (d, *J* = 2.5 Hz, 1H), 7.80-7.73 (m, 1H), 7.57 (dd, *J* = 9.4, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.22, 147.87, 138.01, 135.05, 134.37, 131.67, 129.54, 128.54, 126.95, 122.57, 119.81, 118.93 (q, *J* = 320.9 Hz). HRMS (ESI) m/z $[M+CH_3]^+$calcd for $C_{13}H_{10}F_3O_4S$ 319.0246, found 319.0245.



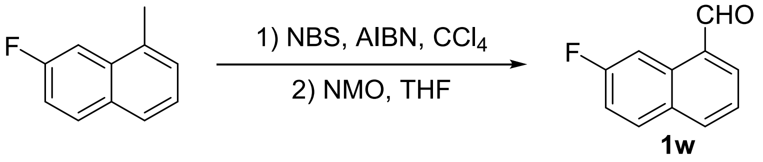
6-Methyl-1-naphthaldehyde (1u). To a solution of 1-bromo-6-methylnaphthalene (1.5 mmol) in anhydrous THF at -78 °C under N_2 atomosphere was dropwisely added n-butyl lithium solution (1.6 M in hexane, 2.25 mmol). The resulting reaction mixture was stirred at -78 °C for 20 min, and then treated with anhydrous DMF

(2.25 mmol) for another 15 min. After warmed to room temperature, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1u** as pale yellow oil (191 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 9.14 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.0 Hz, 1H), 7.68 (s, 1H), 7.62-7.56 (m, 1H), 7.55-7.49 (m, 1H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.76, 136.87, 135.97, 134.80, 134.14, 131.42, 131.39, 128.80, 127.58, 124.99, 124.76, 21.68. The characterization data is consistent with reported literature.[8]

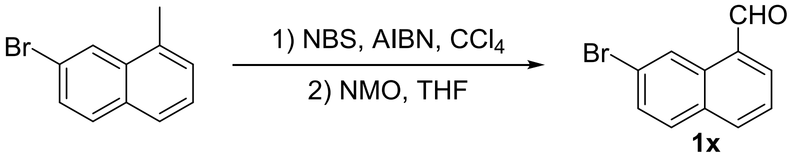


Methyl 5-formyl-2-naphthoate (1v). A mixture of 5-bromo-2-naphthoic acid (1 mmol), and K_2CO_3 (2 mmol) in DMF (1 mL) was added CH_3I (1.5 mmol) at rt. After completion of addition, the reaction was stirred for 3 h. Water was added and extracted with EtOAc for 3 times. The combined organic layers were washed with brine and dried over sodium sulfate, and concentrated under reduced pressure to afford the corresponding methyl ester without further purification.

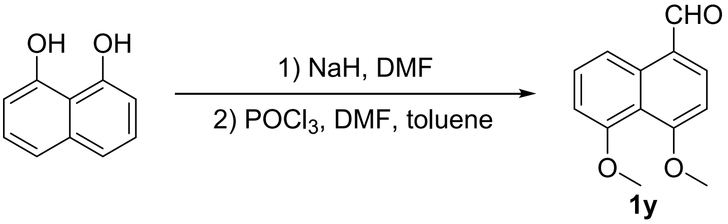
$Pd(OAc)_2$ (0.05 mmol), DPPB (0.075 mmol), *N*-formylsaccharin (1.5 mmol), methyl 5-bromo-2-naphthoate (1 mmol), and Na_2CO_3 (1.5 mmol) were added to a 10-mL test tube. The test tube was sealed by a plastic screw cap and backfilled with N_2 three times. Then, a degassed solution of Et_3SiH (1.3mmol) in DMF (2 mL) was added through syringe. Right after that, and the mixture was stirred for 10 min (this stirring is critical for the selectivity of the reaction). The mixture was warmed to 90 °C and stirred for 20 h. After cooling to rt, water was added and the mixture extracted with EtOAc twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1v** as pale green solid (140 mg, 39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 9.29 (d, *J* = 8.9 Hz, 1H), 8.69-8.61 (m, 1H), 8.25 (dd, *J* = 8.9, 1.6 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 6.8 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.23, 166.85, 138.52, 136.49, 133.14, 132.80, 131.52, 131.27, 128.55, 128.50, 125.90, 125.38, 52.56. The characterization data is consistent with reported literature.[8]



7-Fluoro-1-naphthaldehyde (1w). A solution of 7-fluoro-1-methylnaphthalene (5 mmol) in CCl_4 (10 mL) was added NBS (5.5 mmol) followed by AIBN (0.05 mmol). After refluxed for 8 h, the resulting mixture was cooled to room temperature. Water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum. The residue was dissolved in THF (10 mL) and N-methylmorpholine N-oxide (20 mmol) was added. The reaction mixture was refluxed for 4 h. After cooling to rt, water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1w** as white solid (383 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.99 (dd, *J* = 11.6, 2.4 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 7.0 Hz, 1H), 7.91 (dd, *J* = 9.0, 5.9 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.37 (td, *J* = 8.5, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.42, 163.15 (d, *J* = 248.9 Hz), 138.12, 135.25, 131.54 (d, *J* = 11.0 Hz), 131.07 (d, *J* = 6.0 Hz), 130.93, 130.85, 124.31, 117.49 (d, *J* = 25.5 Hz), 109.56 (d, *J* = 23.7 Hz). The characterization data is consistent with reported literature.[15]

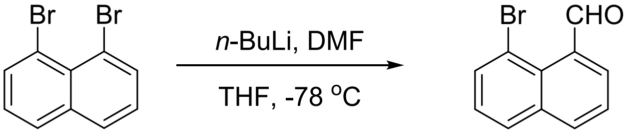


7-Bromo-1-naphthaldehyde (1x). A solution of 7-bromo-1-methylnaphthalene[13] (4.2 mmol) in CCl_4 (8 mL) was added NBS (4.6 mmol) followed by AIBN (0.04 mmol). After refluxed for 3 h, the resulting mixture was cooled to room temperature. Water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum. The residue was dissolved in THF (10 mL) and N-methylmorpholine N-oxide (17 mmol) was added. The reaction mixture was refluxed for 6 h. After cooling to rt, water was added and extracted with EtOAc twice. The combined organic phases were washed with water, brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1x** as pale yellow solid (490 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 9.49 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 6.5 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.70-7.63 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.22, 137.83, 135.22, 132.27, 131.36, 130.74, 130.62, 129.96, 127.70, 125.43, 124.30. The characterization data is consistent with reported literature.[8]



4,5-Dimethoxy-1-naphthaldehyde (1y). A 20-mL dry microwave-vial equipped with a stir bar was charged with naphthalene-1,8-diol (3 mmol). Dry DMF (6 mL) was added as solvent and then NaH (15 mmol) was slowly added at 0 °C. The reaction was stirred at 0 °C for 15 min. The vial was sealed with a PTFE-lined cap and MeI (9 mmol) was added through syringe. The mixture was stirred at 0 °C for another 15 min before heated at 60 °C for 12 h. The reaction mixture was quenched using a saturated aqueous solution of NH_4Cl and extracted using EtOAc. The combined organic phases were washed with brine solution, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the corresponding ether without further purification.

To a solution of DMF (3.6 mmol) in dry toluene (6 mL) was added $POCl_3$ (3.3 mmol) at rt. The ether (3 mmol) was added before the mixture was stirred for 5min at rt. Then reaction was stirred at 120 °C for 8 h. After the reaction was completed monitored by TLC, the mixture was poured into ice water and extracted with DCM twice. The combined organic layers were washed with H_2O, brine, dried over Na_2SO_4, and filtered. After removing the volatiles, the residue was purified by silica gel column chromatography to give **1y** as pale yellow solid (453mg, 70%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.18 (s, 1H), 8.97 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 8.2 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 4.06 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.14, 163.15, 157.76, 140.01, 135.07, 130.01, 124.58, 117.29, 117.26, 107.80, 104.37, 56.51, 56.45. HRMS (ESI) m/z [M+Na]$^+$calcd for $C_{13}H_{13}O_3$ 217.0859, found 217.0859.

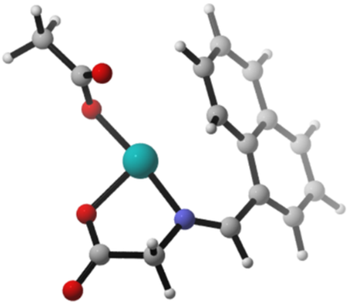


1ab

8-Bromo-1-naphthaldehyde (1ab). To a solution of 1,8-dibromonaphthalene (7 mmol) in anhydrous THF at -78 °C under N_2 atomosphere was dropwisely added n-butyl lithium solution (1.6 M in hexane, 7.7 mmol). The resulting reaction mixture was stirred at -78 °C for 30 min, and then treated with anhydrous DMF (35 mmol) for another 15 min. After warmed to room temperature, the reaction mixture was quenched with addition of aqueous NH_4Cl and extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, and filtered. The solution was removed under vacuum and purified by column chromatography to afford **1ab** as white solid (1.2 g, 72%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 11.42 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.88 (q, *J* = 7.6 Hz, 3H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) ^{13}C NMR (126 MHz, CDCl$_3$) δ 192.80, 136.28, 135.89, 133.81, 133.40, 130.67, 129.95, 129.04, 127.12, 126.11, 118.51. The characterization data is consistent with reported literature.[16]

9. Structures and cartesian coordinates of intermediates and transition states

Int1



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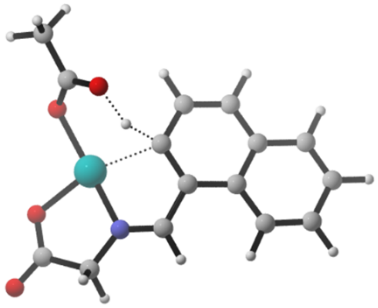
TS1



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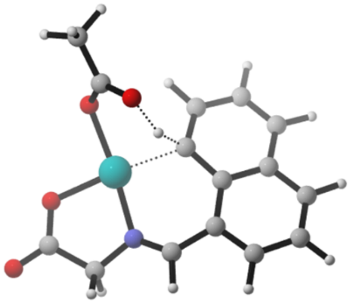
TS2



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H	4.61225200	1.69289500	-1.19476100
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C	1.82241100	-1.48858900	0.58208200
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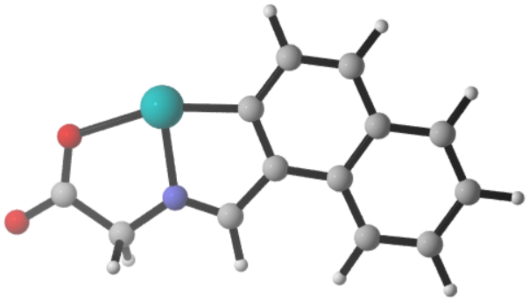

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O	4.81238200	1.58814100	-0.00074800
O	3.62576900	-0.31446100	-0.00003600
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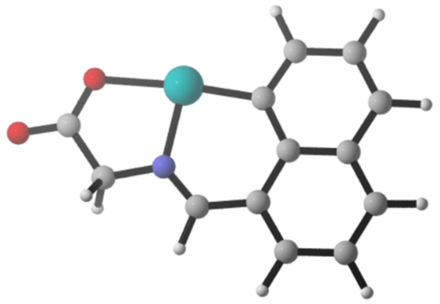
Int3



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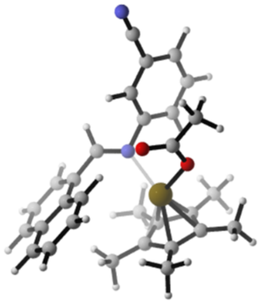
Int4



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C	2.00961700	2.23596000	-0.14872200
C	2.23529200	1.96906900	-2.54905300
H	5.00212100	3.23906500	1.21292000
H	4.20713900	2.34233100	-3.37386200
H	5.19901400	2.95568500	-1.19276800
C	3.95512200	2.95229000	1.18020600
C	1.26084800	2.18187400	1.07130600
H	1.79361100	1.73208700	-3.51171800
C	3.20919300	2.90926100	2.33123900
H	3.65173800	3.16438800	3.28728300
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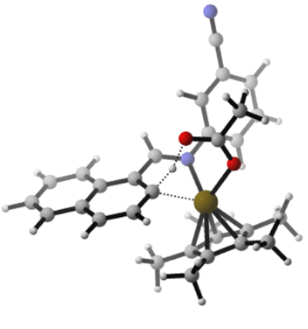
TS3



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C	-1.40828500	0.48058300	1.00843300
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C	4.75597500	1.74965500	-1.22096300
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H	-2.78439600	-4.07341000	1.01405300
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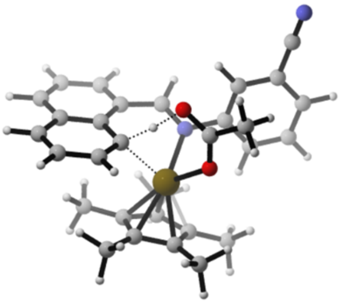
TS4



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C	-1.69198300	2.02438100	0.12505300
C	-2.16539300	0.76591500	2.13963600
H	-4.31974200	4.12016100	-0.58817100
H	-4.05942700	1.17321300	3.11412100
H	-4.75408100	2.84873800	1.42832600
C	-3.34644300	3.65170000	-0.70089600
C	-0.84658400	2.42272800	-0.95880800
H	-1.86031900	0.04455600	2.89467800
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H	-2.82464800	4.75596200	-2.45749200
C	0.50620600	1.90312300	-1.12334600
H	1.22275600	2.57017200	-1.60907400

N	0.92513300	0.74939200	-0.73765100
C	-1.24948500	3.40769200	-1.84395600
H	-0.57469200	3.71939300	-2.63613200
C	-1.30442800	1.02573600	1.08139400
H	-0.07957900	1.03424000	1.50806500
O	1.17535800	-0.98181800	1.53907800
C	1.60498200	0.00903400	2.21041400
O	1.09166300	1.15846600	2.14885300
C	2.81331900	-0.21767200	3.07709800
H	2.91797900	0.58494000	3.80466000
H	3.69468700	-0.23266000	2.42837400
H	2.74278000	-1.18664400	3.57154200
Ir	-0.37979500	-0.77111700	0.08324900
C	-2.23085800	-1.27978500	-0.92106600
C	-1.12888700	-1.59515800	-1.78214900
C	-2.10714000	-2.09721500	0.27787200
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C	2.33414000	0.51635400	-0.80789800
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H	2.81537300	2.23964000	0.39209800
C	4.19596200	-0.82487800	-1.55037300
H	2.13012300	-1.26776000	-1.96990000
C	5.08325000	0.04637900	-0.92501900
H	4.57357600	-1.68576300	-2.08993800
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H	-1.43095900	-1.54459300	-3.88887500
H	-1.21020500	0.05129900	-3.15034200
H	0.18151400	-1.01558900	-3.38456200
C	-3.37635600	-0.37547800	-1.23857900
H	-3.07573700	0.42874100	-1.91397400
H	-4.17048000	-0.95270300	-1.72195600
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C	-3.11065200	-2.21103800	1.38057600
H	-3.75502300	-1.33280000	1.42765100
H	-3.74066000	-3.08682100	1.19622000
H	-2.62856800	-2.33811200	2.35175600
C	-0.38235100	-3.85562800	1.13932000
H	-0.80466000	-3.68334800	2.12974100
H	-0.63404700	-4.87405200	0.82760300
H	0.70428800	-3.77360600	1.20595500

C	0.82727100	-3.37921200	-1.70823800
H	1.69627800	-3.38470800	-1.04549100
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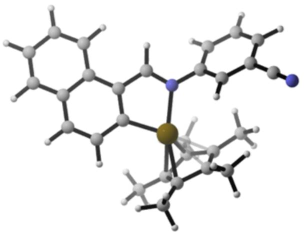
H	1.12838400	-2.99548600	-2.68451200

Int5



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C	3.52172200	1.33374900	-0.16942400
C	5.27335700	3.00812400	-0.04570200
H	4.87793900	-1.73607700	-0.87032900
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H	6.62036700	-0.04702500	-0.71186700
C	4.11124100	-0.99894600	-0.64651000
C	2.15918700	0.90305400	-0.11708500
H	5.57779100	4.03817800	0.10685200
C	2.79022100	-1.37954500	-0.56955300
H	2.52625500	-2.41802100	-0.74057600
C	1.04530500	1.81309100	0.04526200
H	1.16790500	2.89177000	0.13731600
N	-0.14818900	1.30941400	0.03118100
C	1.78042300	-0.43417500	-0.28679100
Ir	-0.21266500	-0.80037600	-0.15764000
C	-0.19953400	-2.72290700	0.81846900
C	-0.89345600	-1.70122700	1.59737300
C	-0.90976000	-2.85538400	-0.40250000
C	-2.15703800	-1.39241300	0.92200400
C	-2.14478500	-2.05577900	-0.30806900
C	-1.29775800	2.12701600	0.17135600
C	-2.38502100	1.88949800	-0.66774100
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C	-3.53392700	2.66845100	-0.52925400
H	-2.33883500	1.10726500	-1.42046300
C	-2.52161500	3.89204300	1.27564600
H	-0.53440300	3.27128100	1.82874500
C	-3.61112900	3.67403000	0.44121700
H	-2.57332600	4.65829700	2.04039600

H	-4.51554400	4.26236100	0.54044800
C	3.94366600	2.67574500	0.02692600
H	3.21812700	3.45216100	0.24318700
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H	-1.02212000	-1.88976300	3.71113600
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C	0.99724200	-3.48490000	1.28492200
H	0.68199200	-4.20554900	2.04579400
H	1.46428900	-4.04017100	0.47063600
H	1.74479900	-2.82377900	1.72824300
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H	-3.69063000	-2.92402900	-1.48953700
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C	-3.20768100	-0.49180900	1.48607600
H	-2.77090600	0.41894300	1.90528100
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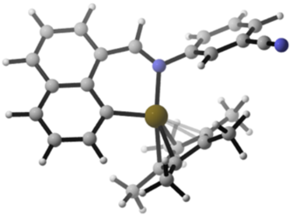
Int6



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C	2.68379400	1.15381300	-0.27583500
C	2.87410600	-1.13504800	-0.98614200
H	5.79036100	2.63123500	-0.46584200
H	4.80311700	-1.79464300	-1.70603200
H	5.90118600	0.38529600	-1.22717600
C	4.72119400	2.56067400	-0.28596900
C	1.97254600	2.33105900	0.13133200
H	2.43746100	-2.10908300	-1.17500200

C	4.01831800	3.65680400	0.15167300
H	4.51367400	4.60382500	0.32897400
C	0.54201200	2.40555800	0.24697800
H	0.12777800	3.39960600	0.42520700
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C	2.63364500	3.53910400	0.33154500
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C	2.06946600	-0.12556500	-0.45971500
Ir	0.15617000	-0.59212300	0.01800700
C	0.42594300	-2.63161800	0.73461700
C	-0.33978400	-1.82061400	1.66951600
C	-0.31827700	-2.66711800	-0.47147000
C	-1.64799200	-1.55232100	1.09141400
C	-1.61678200	-2.01330000	-0.23171000
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C	-2.20801400	2.44366700	1.29573600
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C	-3.56845100	2.73950900	1.35268300
H	-1.55164300	2.71104900	2.11842300
C	-4.41484700	2.36833000	0.31507900
H	-3.96980300	3.25439300	2.21779800
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C	-4.74111800	1.29255500	-1.87492100
N	-5.42396000	0.95035500	-2.74389400
C	0.06453500	-1.52430700	3.07423600
H	-0.29969300	-2.31880900	3.73437500
H	1.15100700	-1.47428800	3.16360300
H	-0.35814000	-0.57692000	3.41406400
C	-2.77480800	-0.88076100	1.80623900
H	-2.40744900	-0.11823800	2.49623400
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C	-2.70258500	-1.95093700	-1.25433800
H	-3.12678000	-2.95121200	-1.39056100
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H	-2.31642000	-1.62456800	-2.22369800
C	0.01837300	-3.37629800	-1.74291300
H	1.05027700	-3.72946400	-1.74991300
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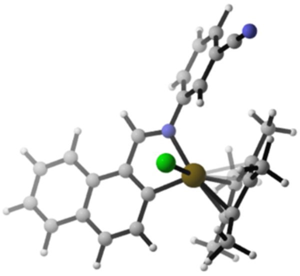

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H	6.61473900	-0.08090400	-0.56911200
C	4.08838900	-1.00268100	-0.52008800
C	2.15821800	0.93685800	-0.03647500
H	5.61880800	4.03230200	0.16256000
C	2.76683600	-1.36023000	-0.45663200
H	2.48406700	-2.39362600	-0.63255100
C	1.05526900	1.84527200	0.11086200
H	1.16479100	2.92752100	0.17051300
N	-0.13081100	1.32156200	0.11929800
C	1.75631300	-0.39770100	-0.18785000
C	-0.10410200	-2.52870800	1.19295300
C	-0.85351900	-1.47954500	1.84474700
C	-0.79690800	-2.86593000	-0.01354400
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C	-1.36923000	3.10493600	1.25240700
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H	-4.54392200	4.19020100	0.68595100
C	3.96908800	2.68426000	0.08519200
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C	1.14268800	-3.15318300	1.73360500
H	0.88328200	-3.79511400	2.58135800
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H	1.85231500	-2.39793700	2.07893500
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H	-0.66427000	-3.55861300	-2.03025600
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C	-3.09631700	-2.26788200	-1.09351800
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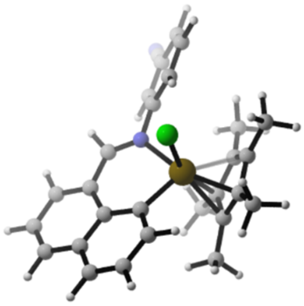

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H	5.68698600	1.87612200	0.19268000
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C	1.15448800	2.64622200	0.11917400
H	3.11854600	-1.51802700	0.67807000

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H	0.52900100	4.68427500	-0.04037900
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Ir	0.32430200	-0.69998600	0.10563700
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C	-0.14867300	-1.10018600	-1.95631000
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H	-1.59839600	-4.54931900	0.27457800
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H	-3.31493500	-1.43356000	-0.58060200
H	-2.81601700	-0.33866500	-1.87644700
H	-3.14725200	-2.03232400	-2.23930400
C	-0.25174800	-0.08529500	-3.05233000
H	-0.54291800	-0.55600000	-3.99719300
H	-0.99775100	0.67621100	-2.80979100
H	0.70454500	0.42089500	-3.20038500
C	2.36678800	-1.71529000	-2.26528100
H	3.16515500	-2.14131800	-1.65666200
H	2.34794100	-2.24078100	-3.22539300
H	2.61049600	-0.66658400	-2.44840400
C	1.53329900	-3.76948700	0.12812300
H	1.28188500	-4.77705300	-0.21904000
H	2.59187000	-3.59884700	-0.07726900
H	1.38343000	-3.72943800	1.21055700

Cl	0.47222300	-1.13018900	2.57283900

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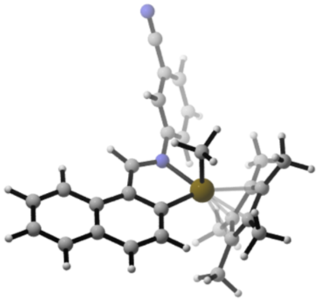

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C	4.96686000	3.26709500	0.58256300
H	4.89471700	-1.39139100	-0.72796000
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H	6.52347900	0.38226300	-0.32299100
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H	5.19454300	4.29393900	0.85063700
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C	0.81974700	1.77821100	0.42374500
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N	-0.31643300	1.13791200	0.40972900
C	1.68512900	-0.34193800	-0.14289200
Ir	-0.22308200	-0.85952300	-0.16728800
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C	-1.26868700	-2.26143300	1.37998100
C	-0.41181900	-3.00058900	-0.65049900
C	-2.25644300	-1.99878600	0.35067600
C	-1.73660800	-2.46120600	-0.87696700
C	-1.52631200	1.86339800	0.51680200
C	-1.78603500	2.94157900	-0.32725000
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H	0.23240500	-0.72604600	-2.79893400
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H	-1.76305300	-2.98853100	3.33943800
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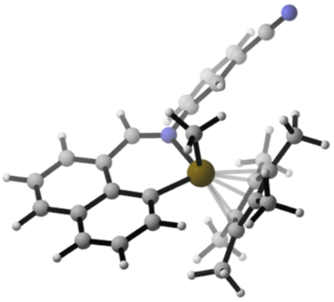

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C	2.00209500	2.32565300	0.05402600
H	2.40528600	-2.12778700	-1.17703000
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H	4.58152300	4.53646000	0.36922600
C	0.55947000	2.43020500	0.10682200
H	0.16432000	3.44225800	0.21602500
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C	2.67439100	3.52202800	0.25844900
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C	-1.66848700	1.81980200	0.14460500
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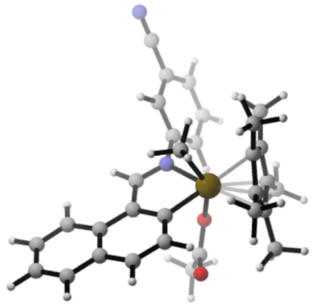
Int7



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Ir	-0.21696000	-0.75952300	-0.22249400
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C	-1.60411000	-2.01217800	-1.56904900
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H	-1.78033700	0.72633400	2.33023000
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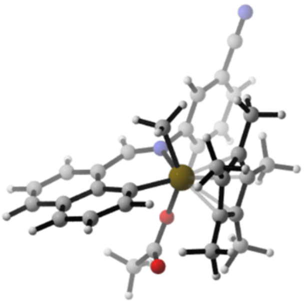
Int8



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H	2.35937300	-1.94107100	-1.57655300
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H	-1.56528600	1.93660800	2.33907800
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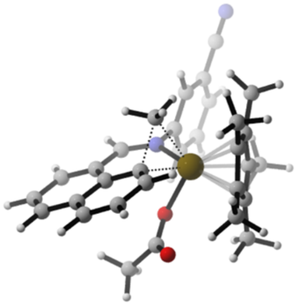
TS5



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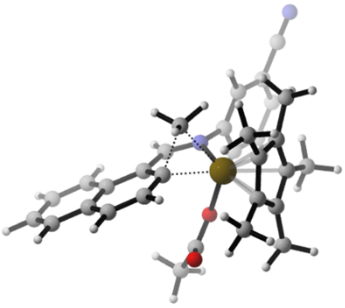
TS6



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N	-0.44504100	1.31939600	-0.27155800
C	1.60358600	-0.17576600	-0.94714000
Ir	-0.26950300	-0.76362100	-0.13867400
C	-0.44044800	-2.96930700	0.11009300
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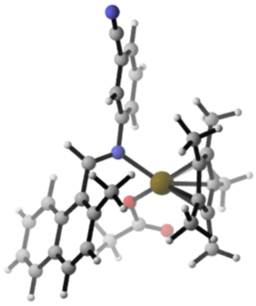

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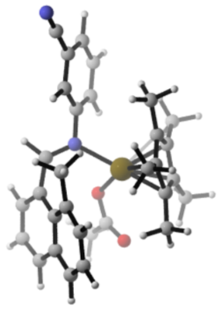

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Ir	0.05443600	0.79898000	-0.05876000
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H	-4.54150800	0.85647800	-2.73327000
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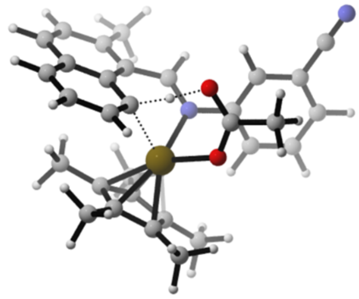
TS7



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C	-2.57354000	4.06214500	-0.97603900
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C	2.92529700	-0.89280600	2.93720100
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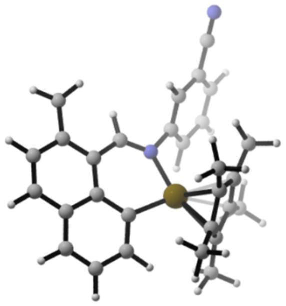
23



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C	-1.84071400	3.77131500	0.08713500
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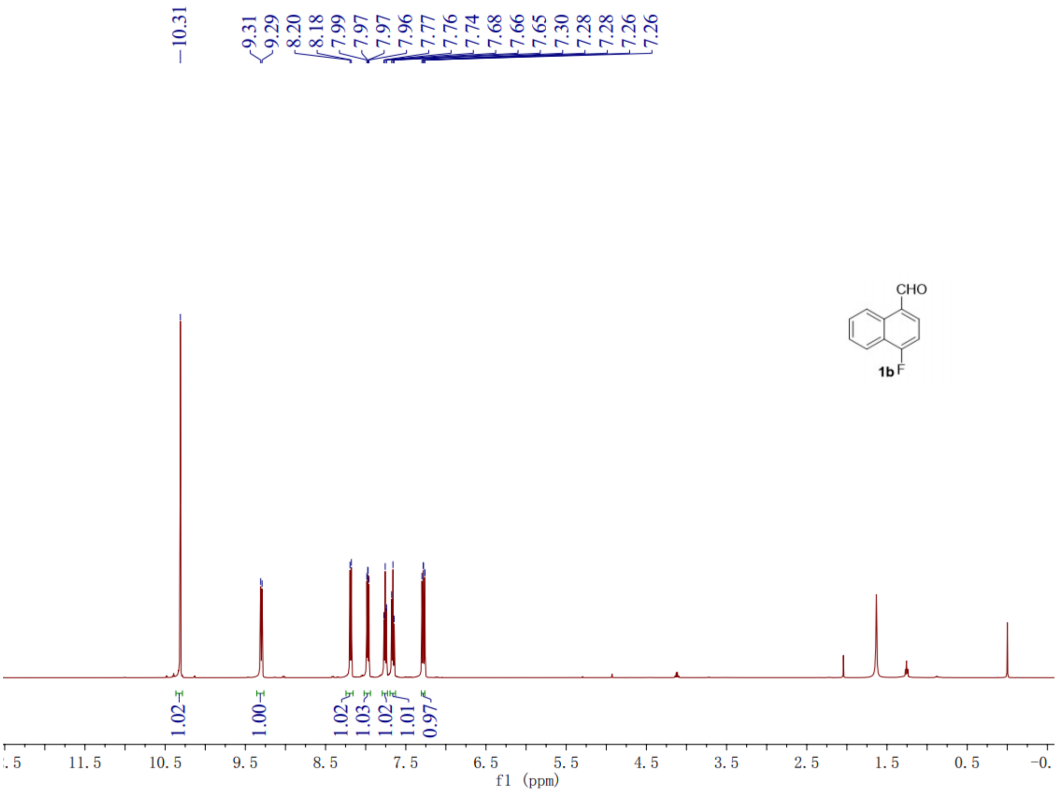
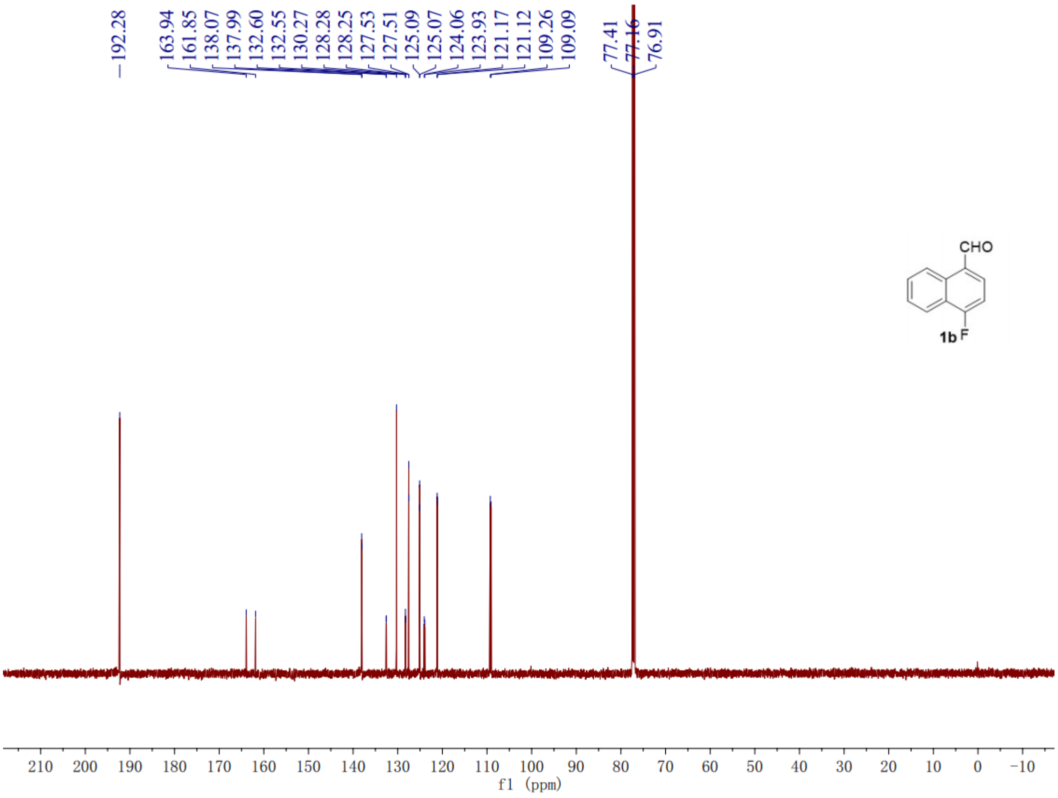
10. ^{1}H NMR, ^{13}C NMR Spectra and HRMS Spectra

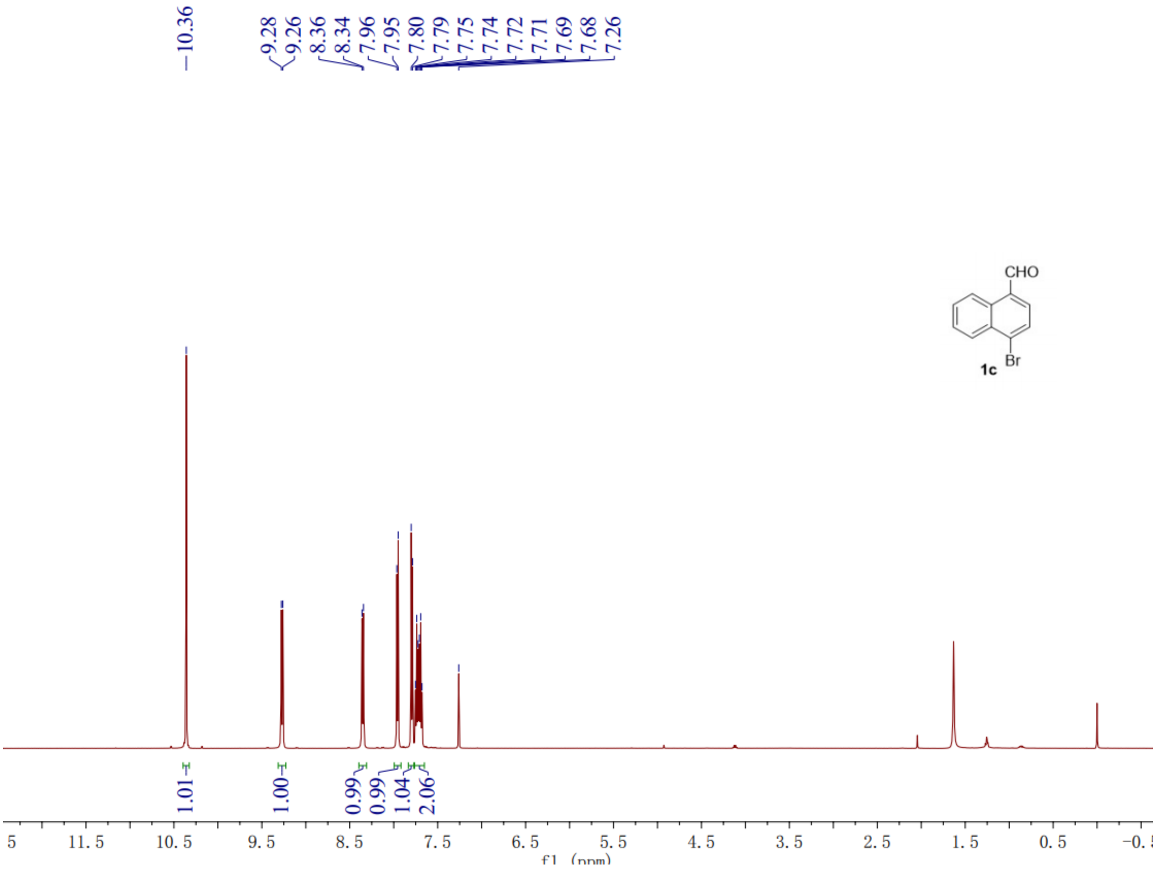
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1b



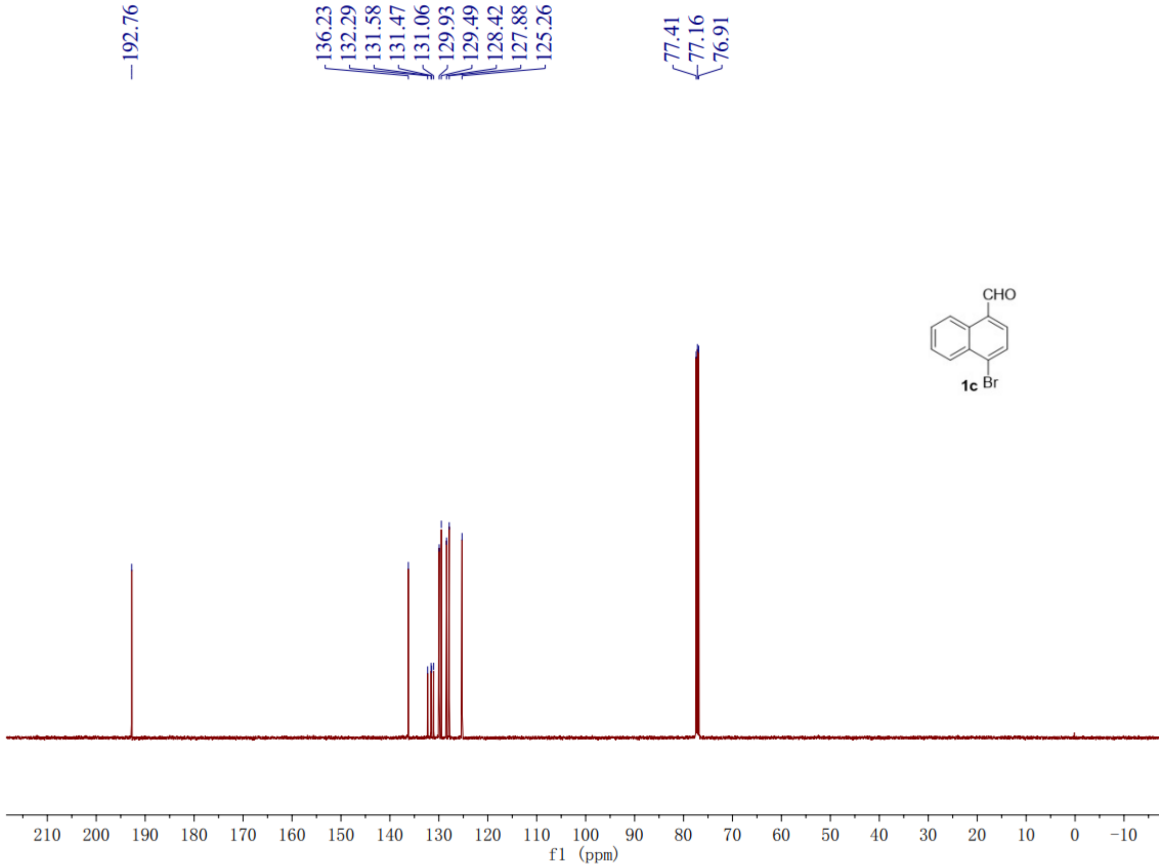
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1b



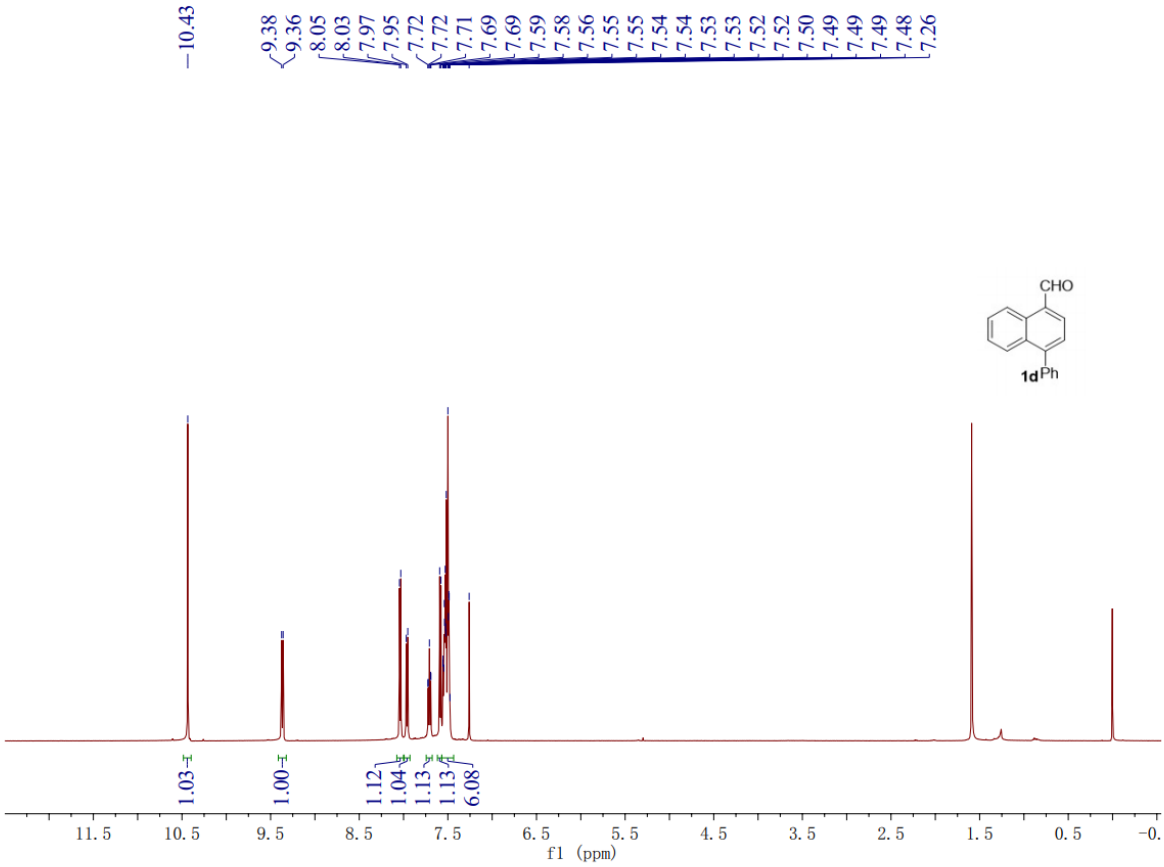
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1c



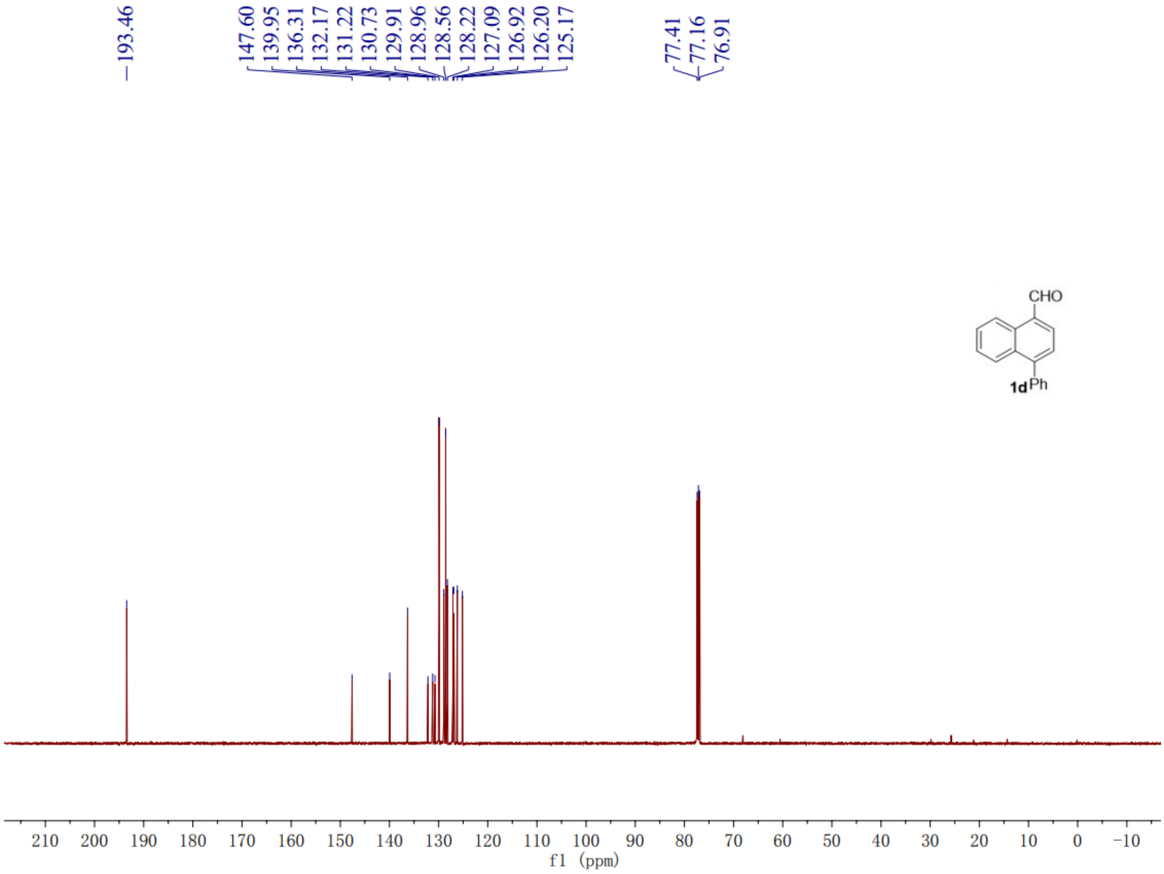
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1c



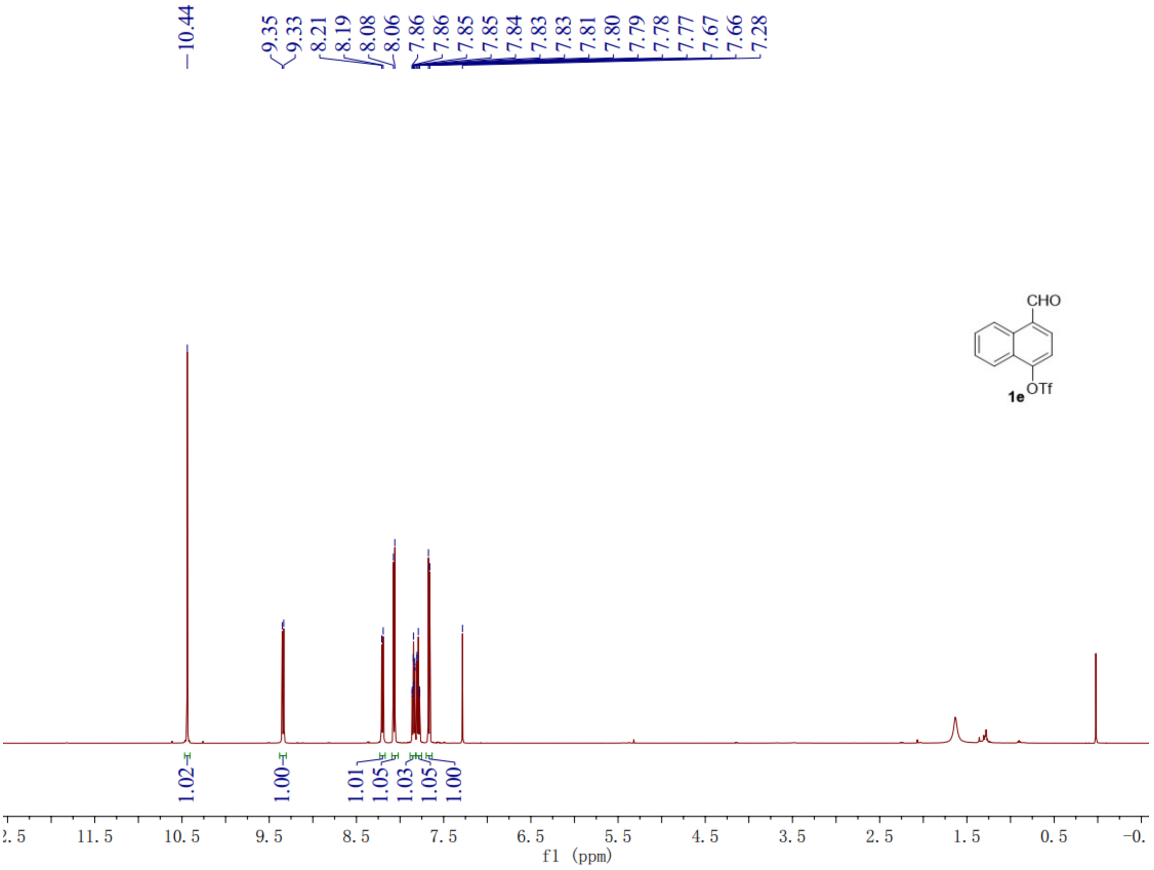
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1d



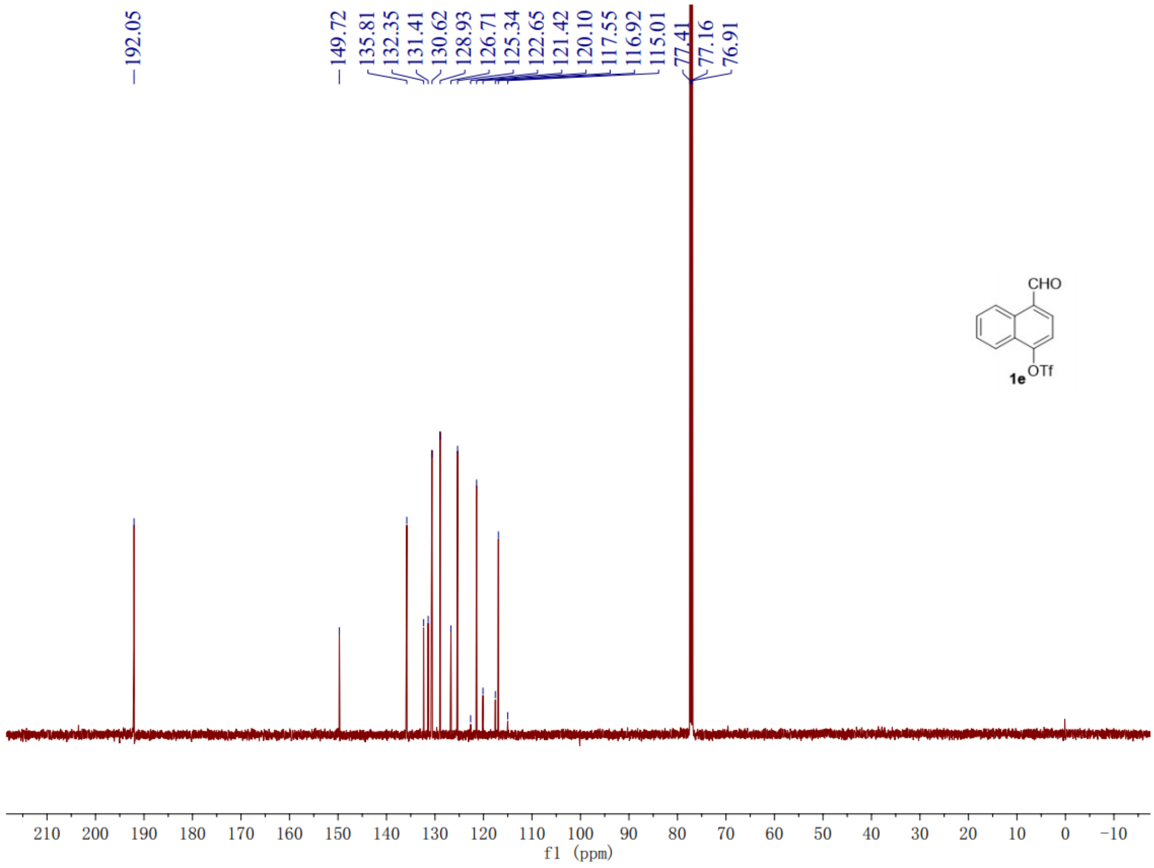
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1d



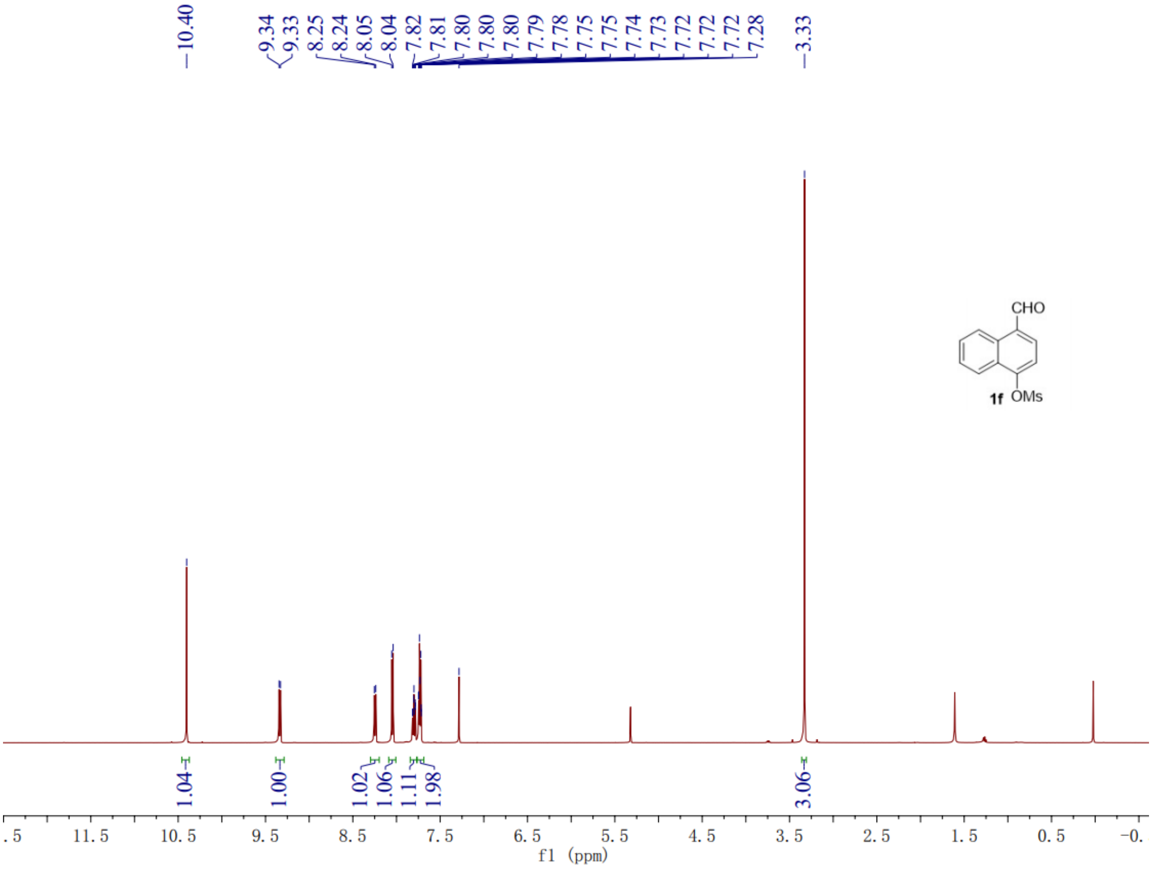
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1e



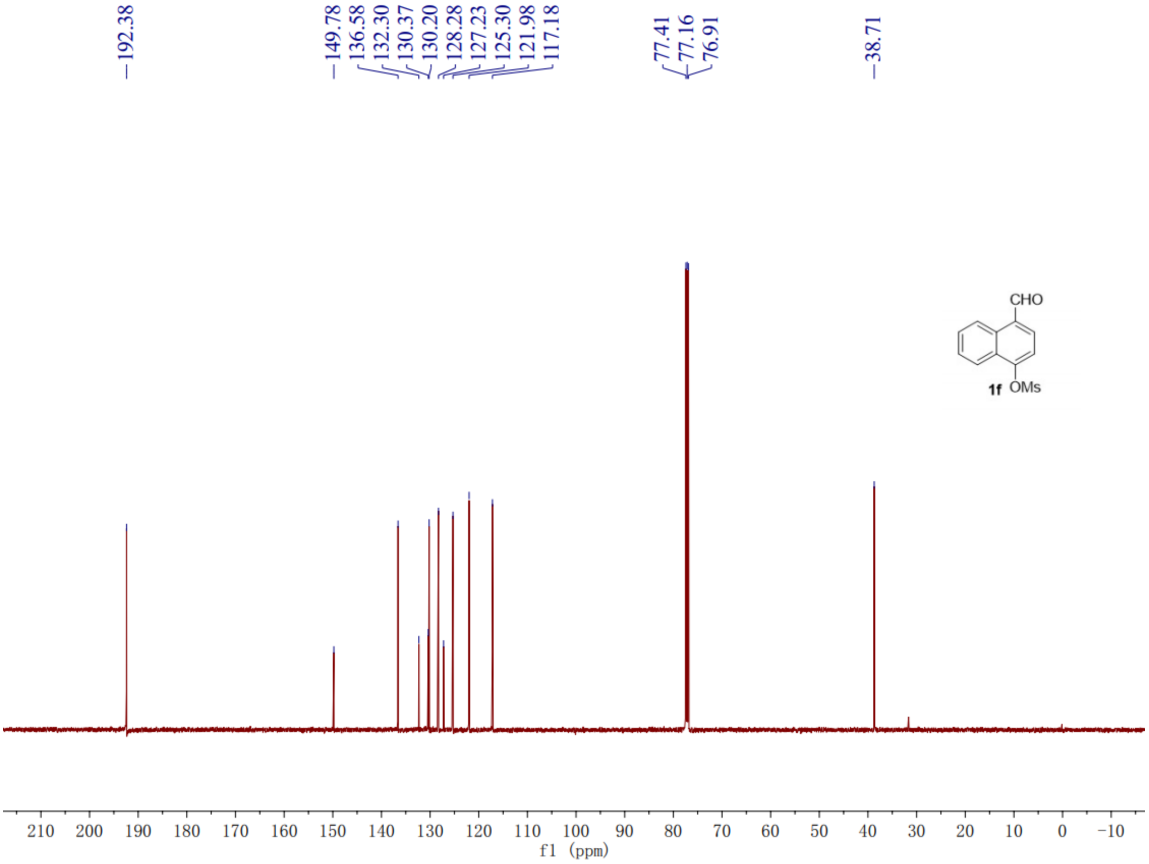
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1e



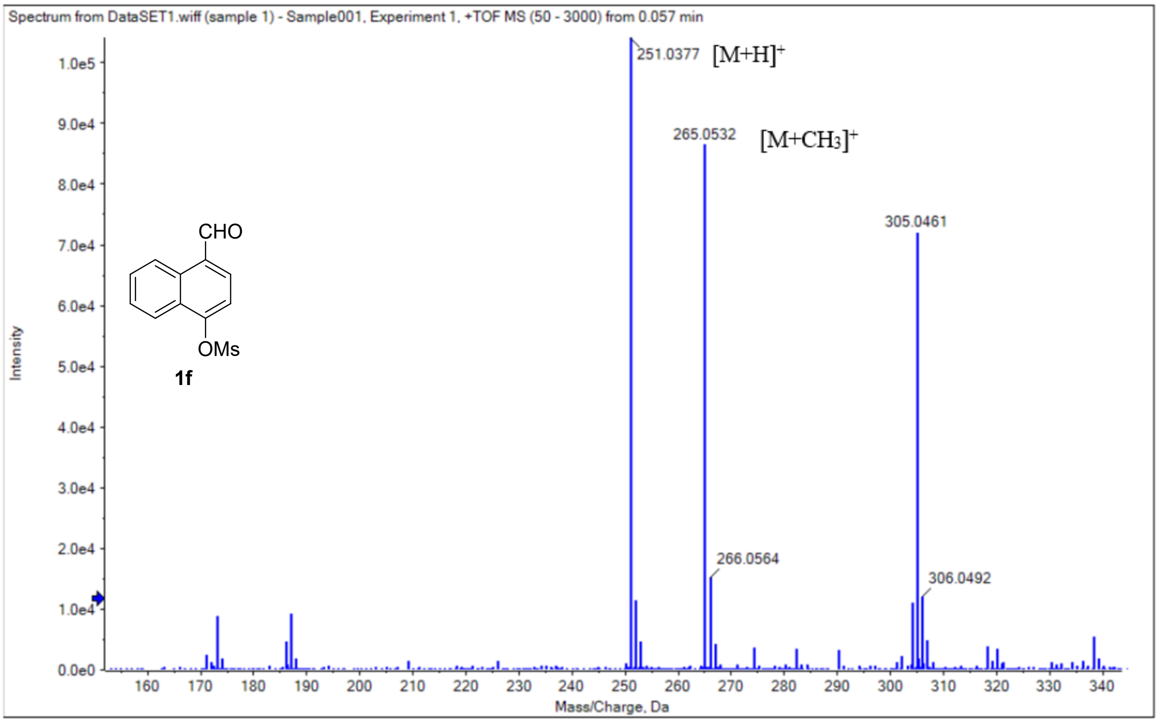
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1f



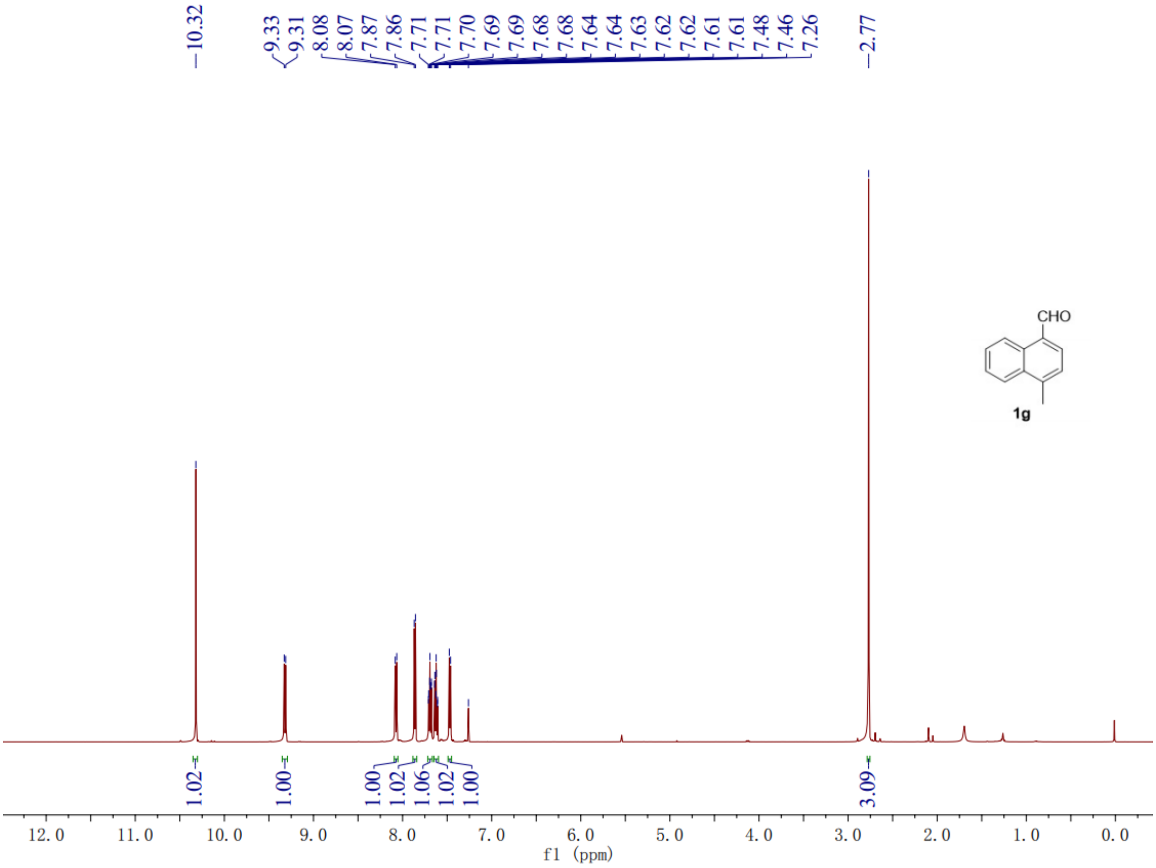
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1f



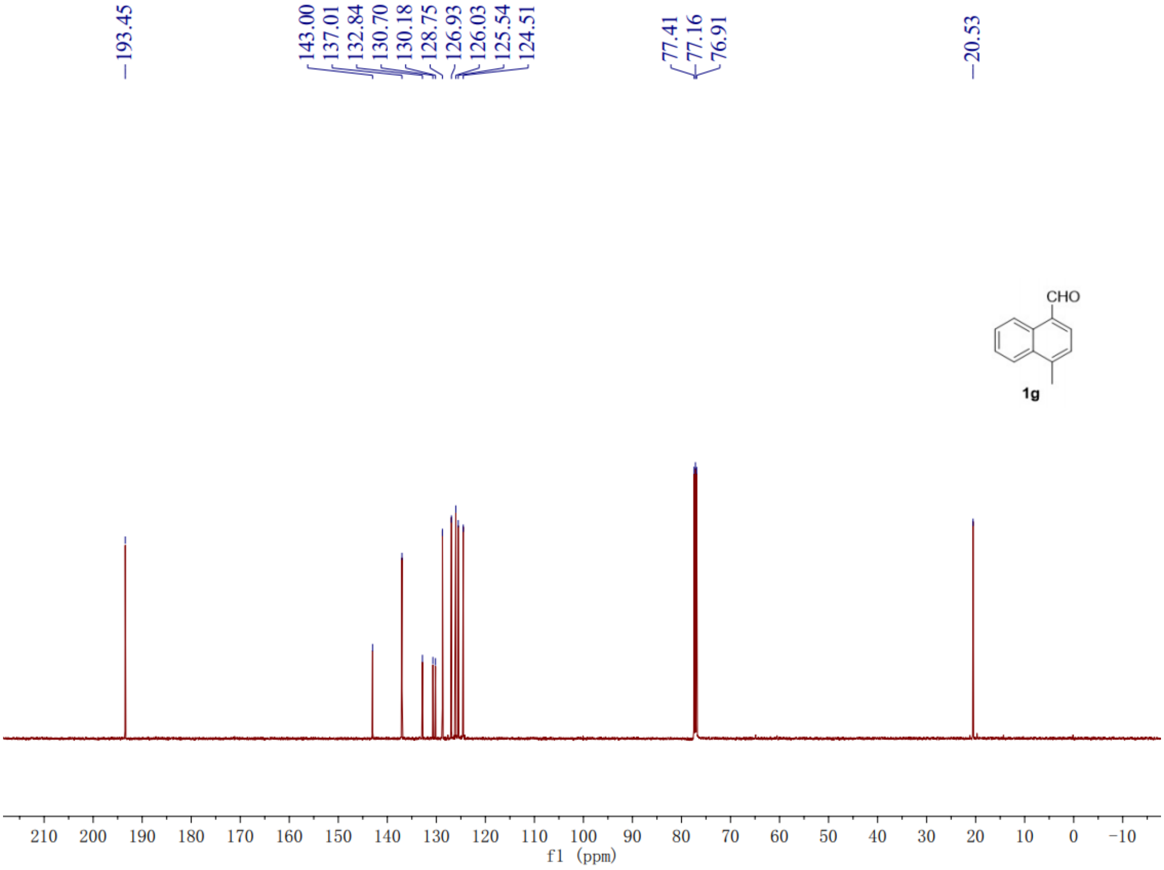
HR-ESI-MS $(M+H)^+$ of 1f



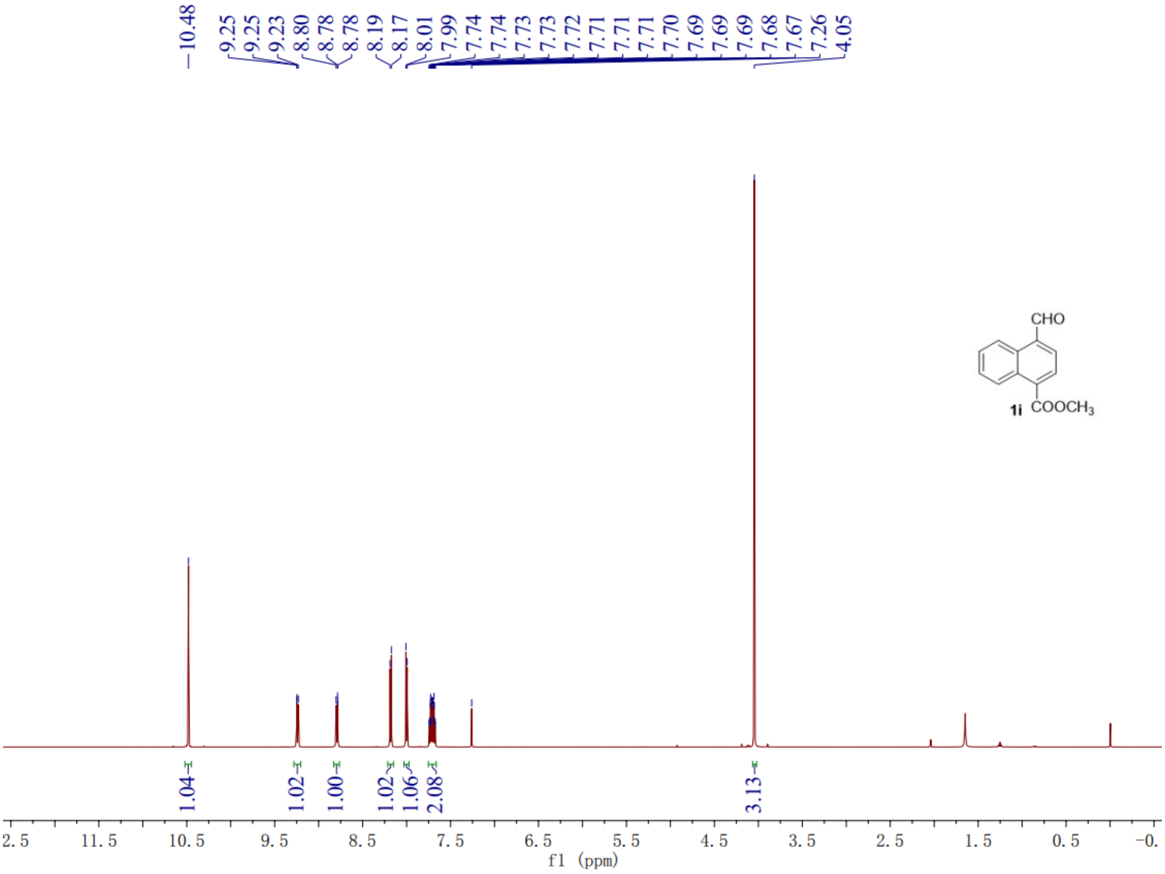
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1g



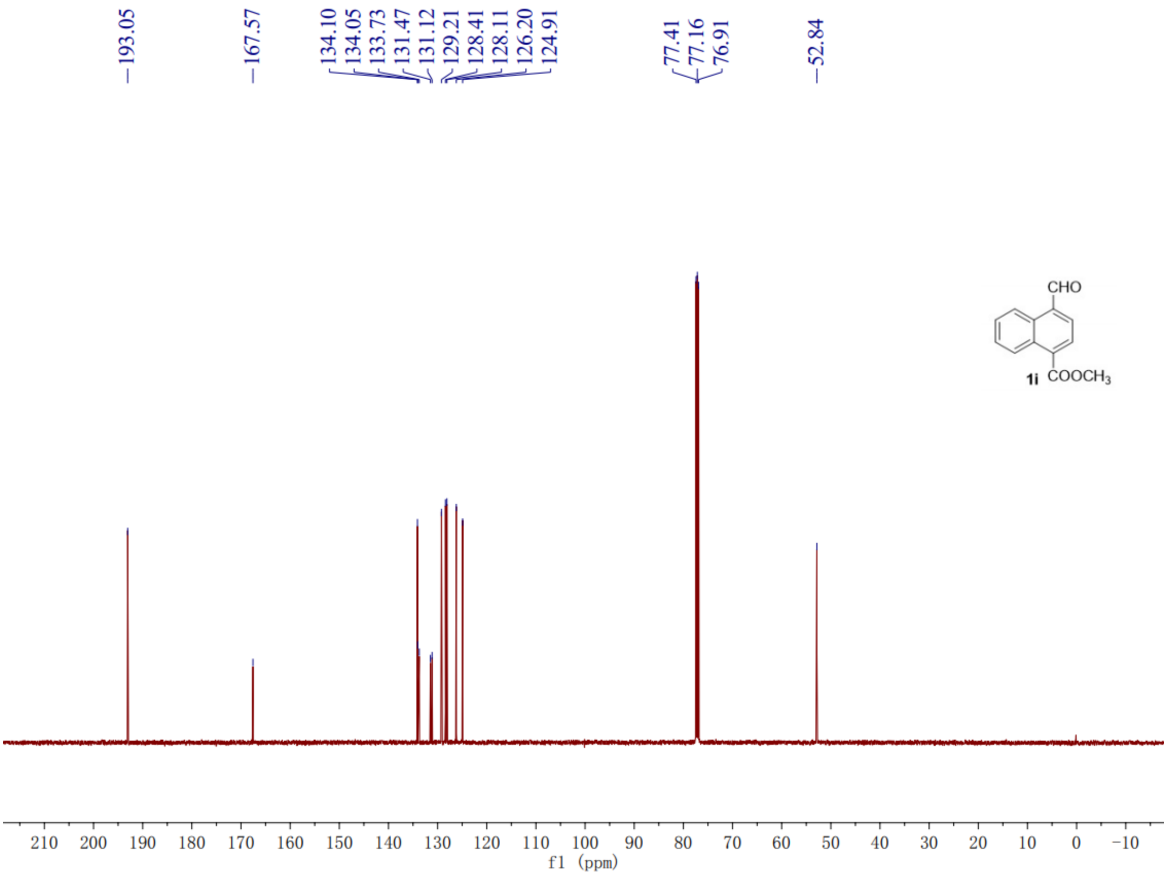
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1g



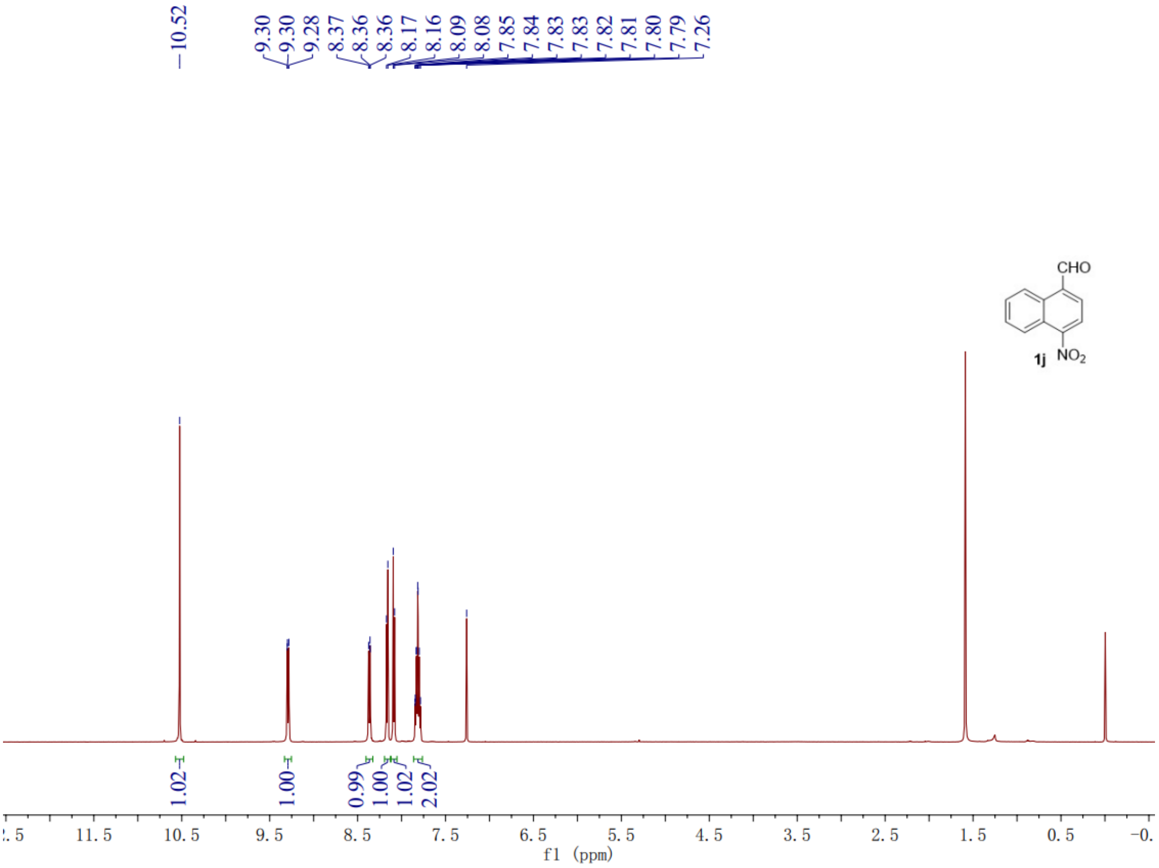
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1i



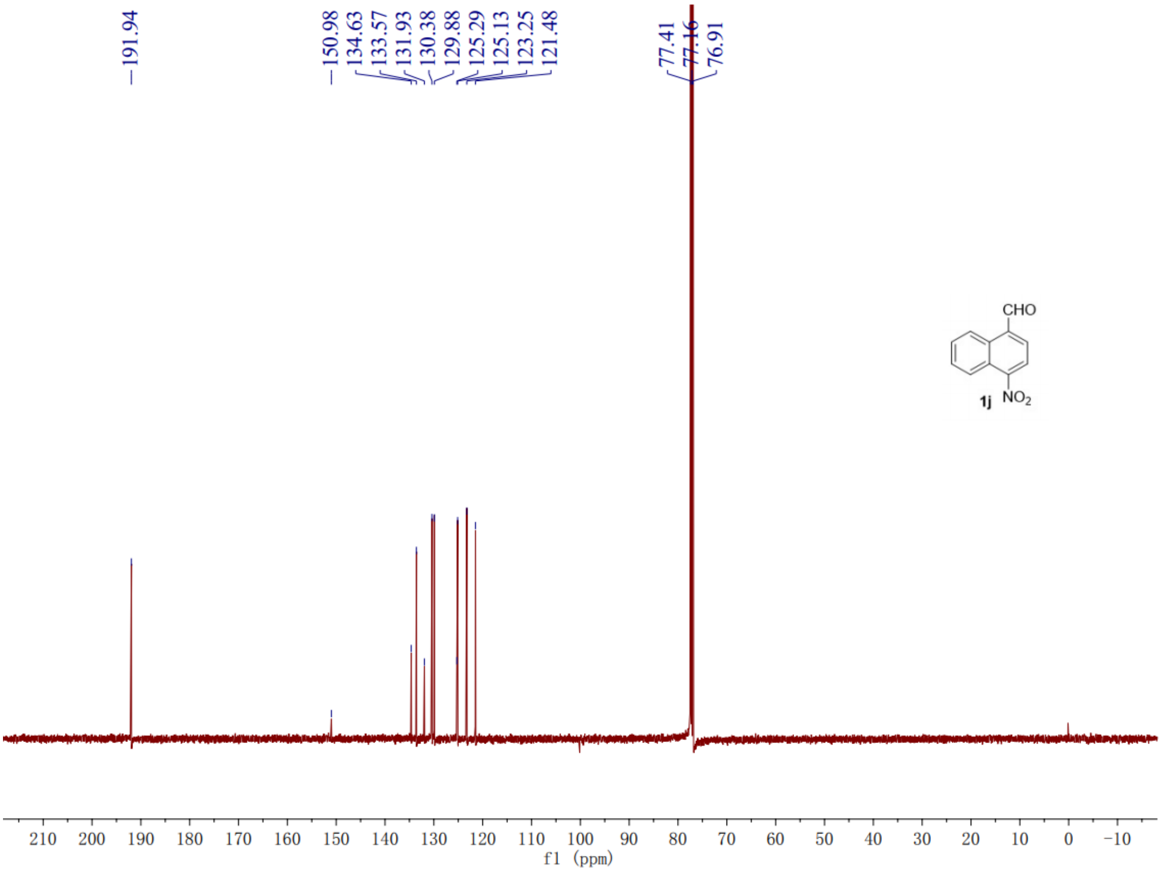
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1i



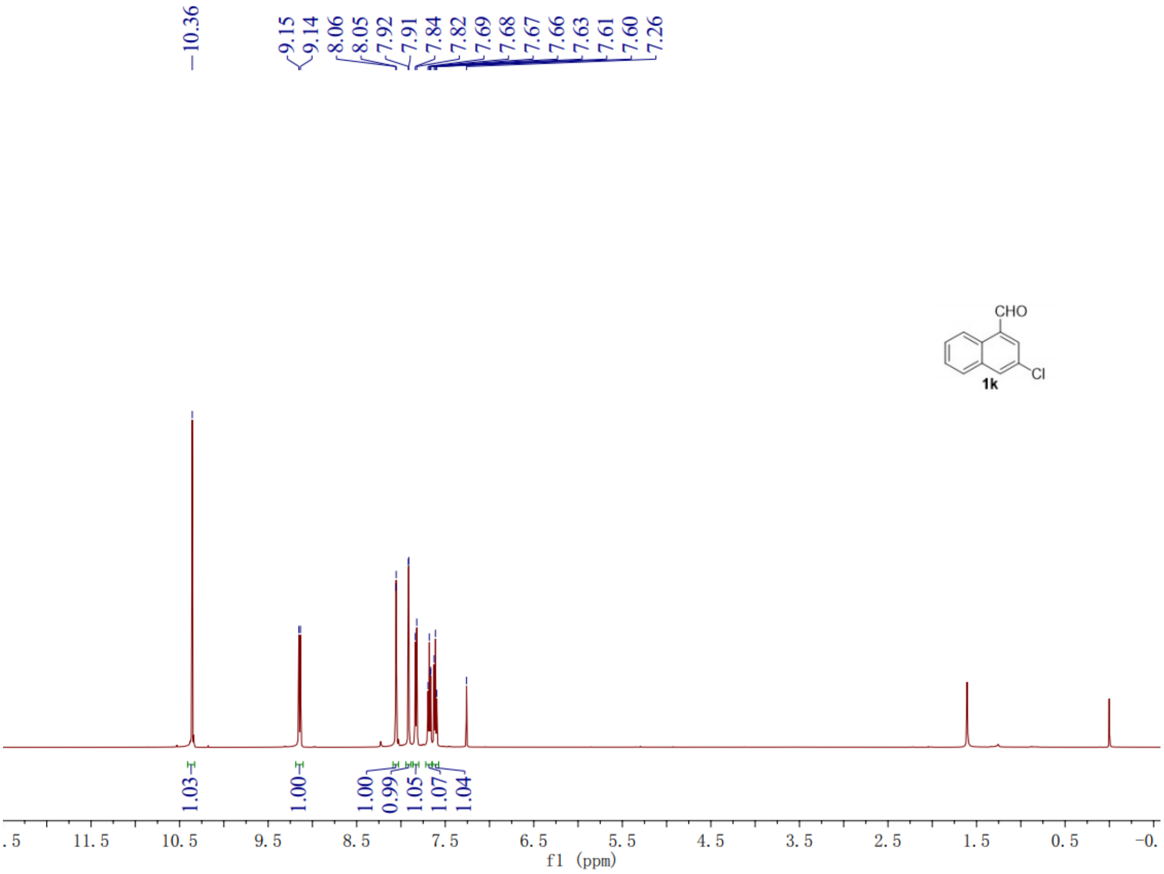
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1j



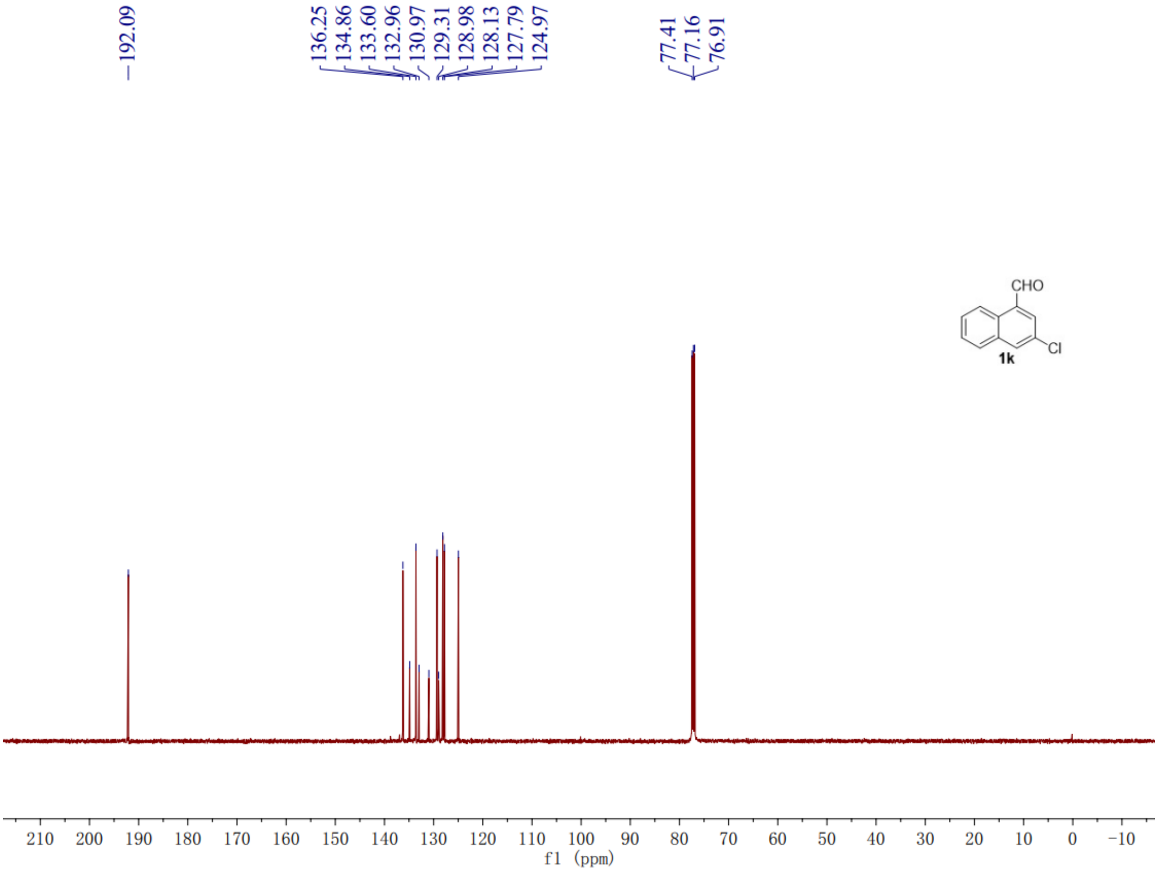
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1j



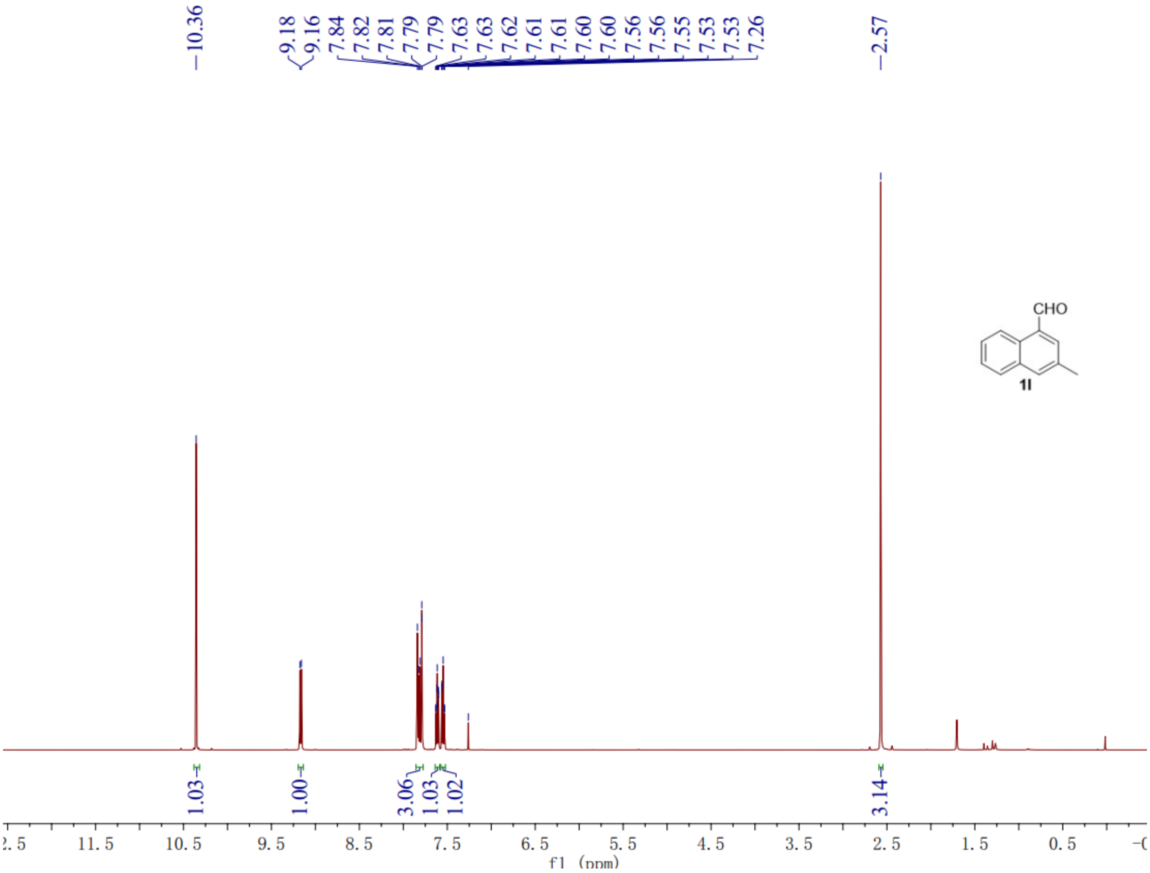
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1k



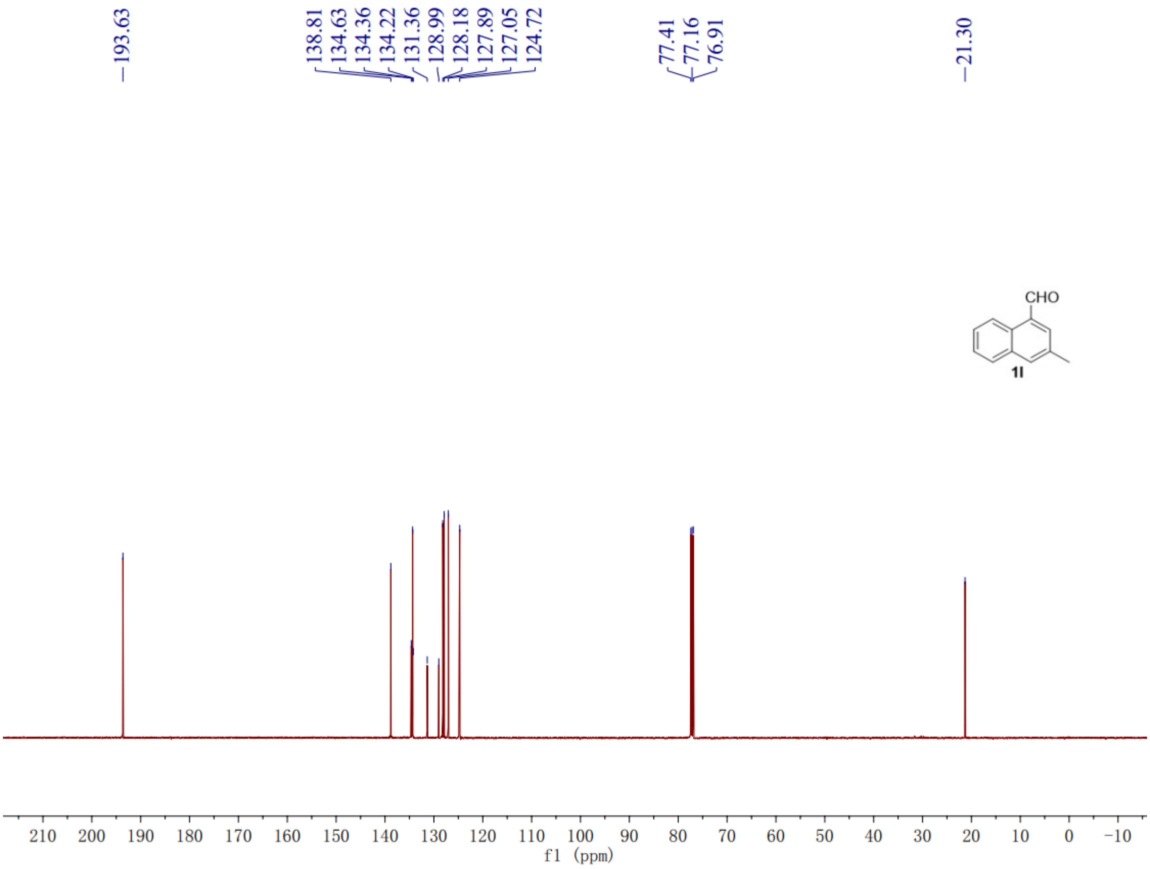
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1k



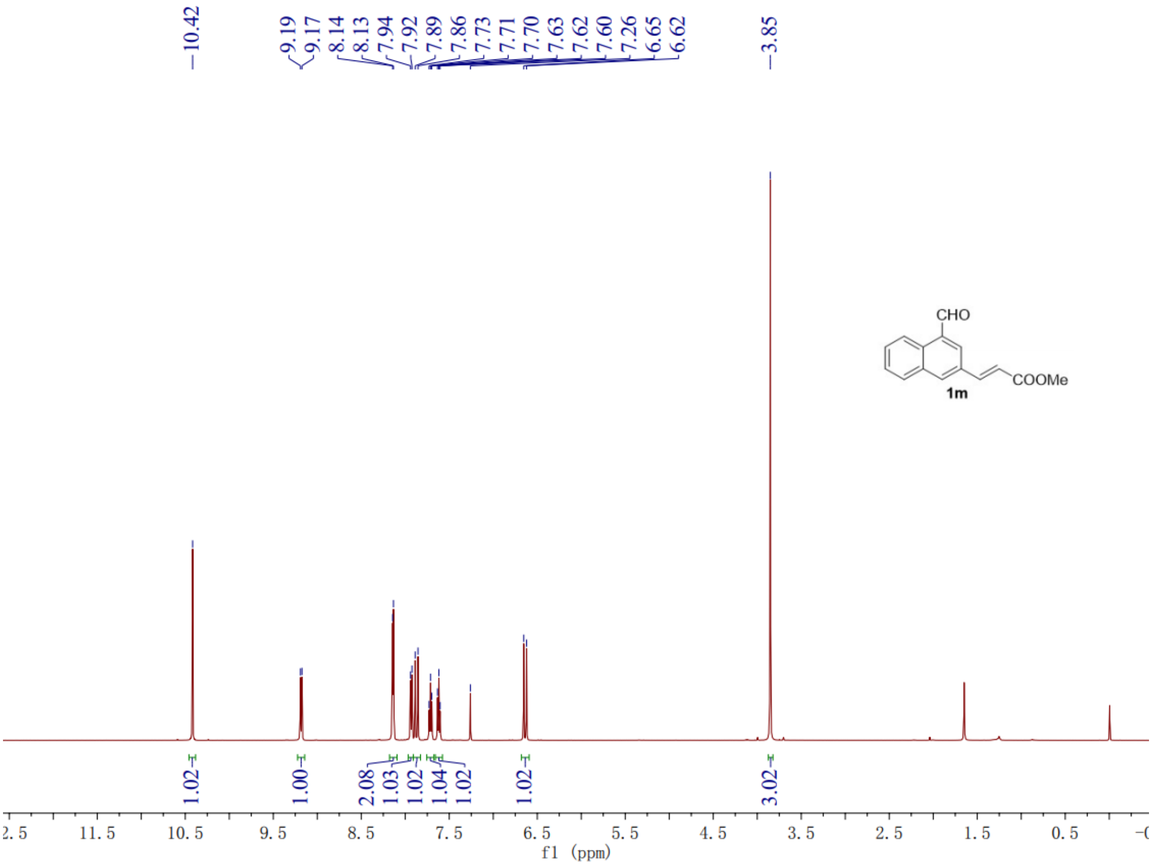
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1l



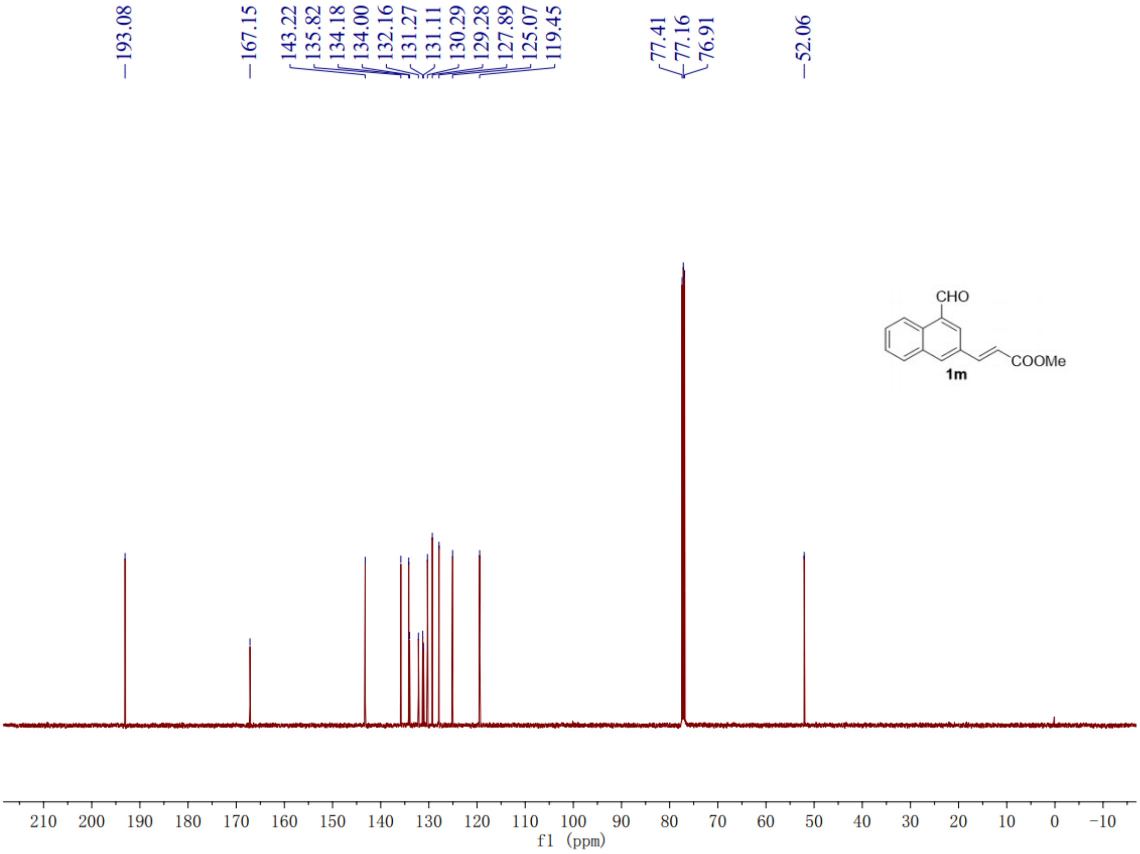
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1l



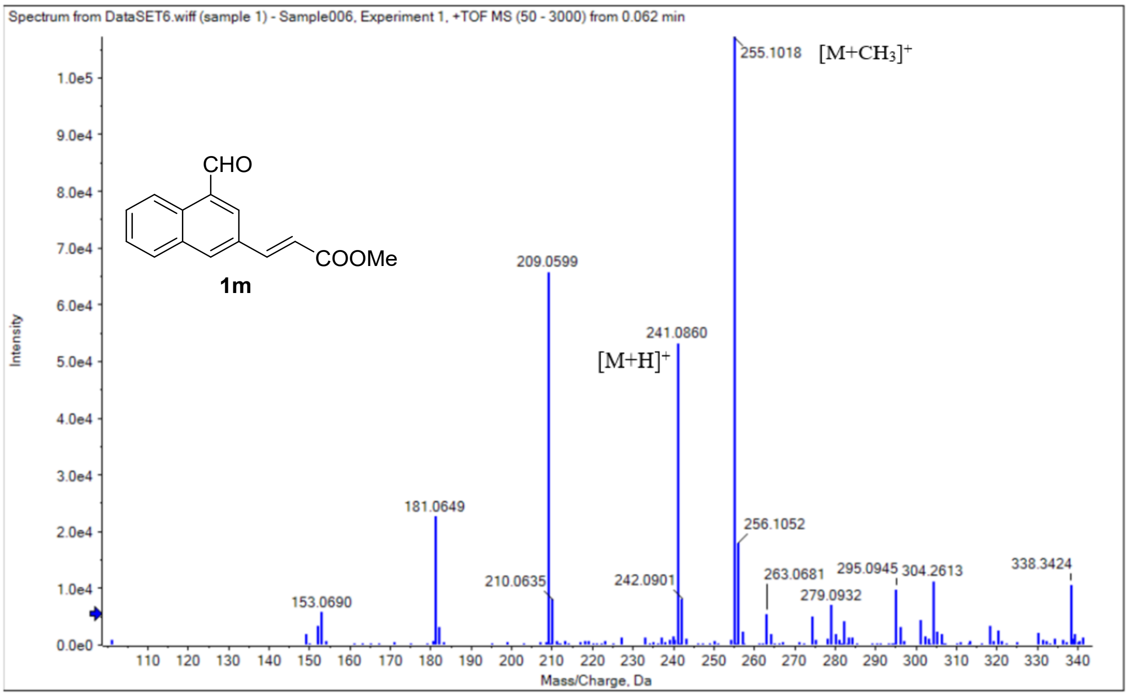
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1m



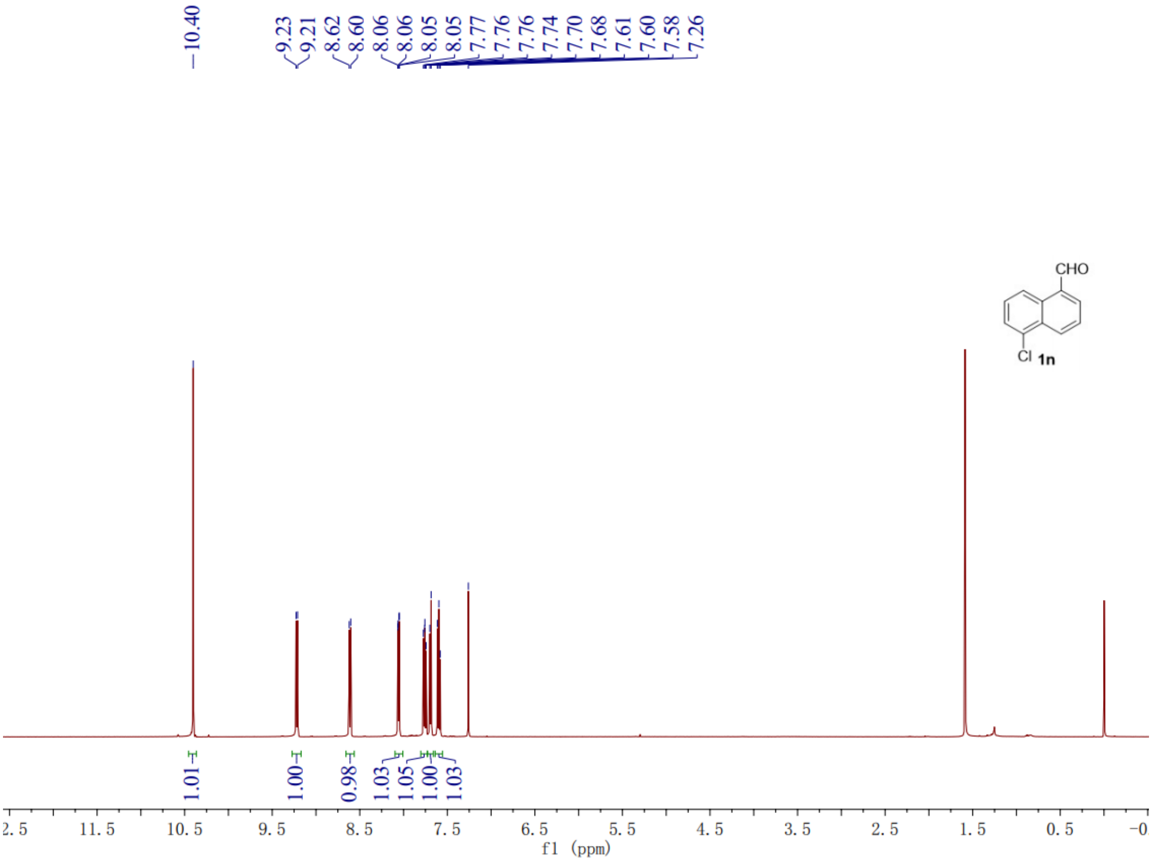
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1m



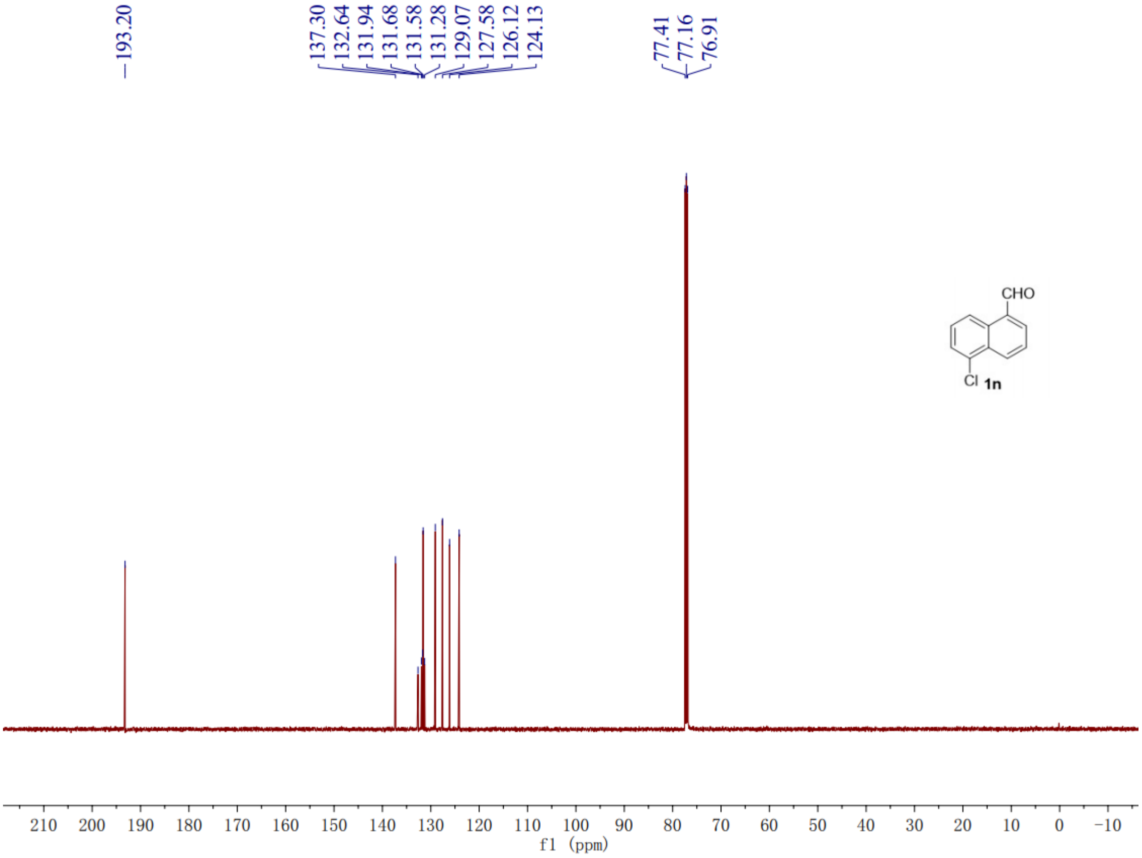
HR-ESI-MS (M+CH$_3$)$^+$ of 1m



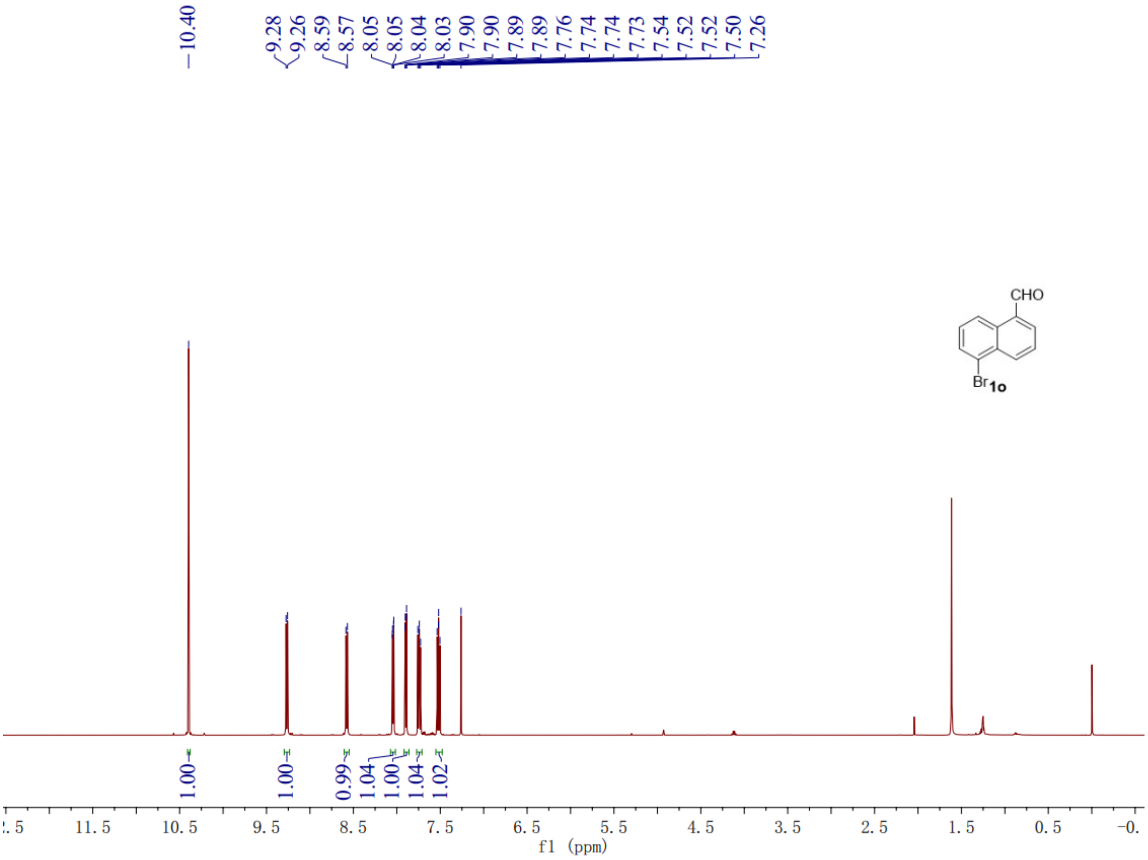
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1n



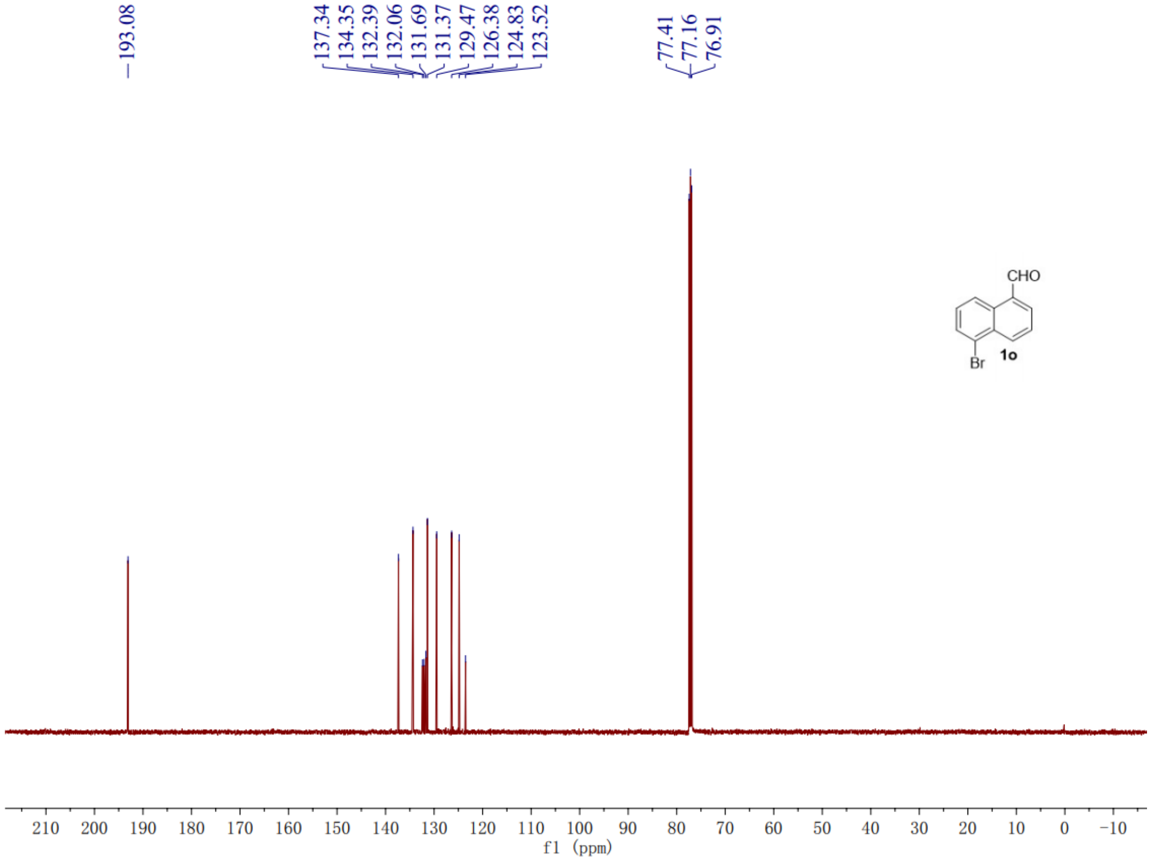
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1n



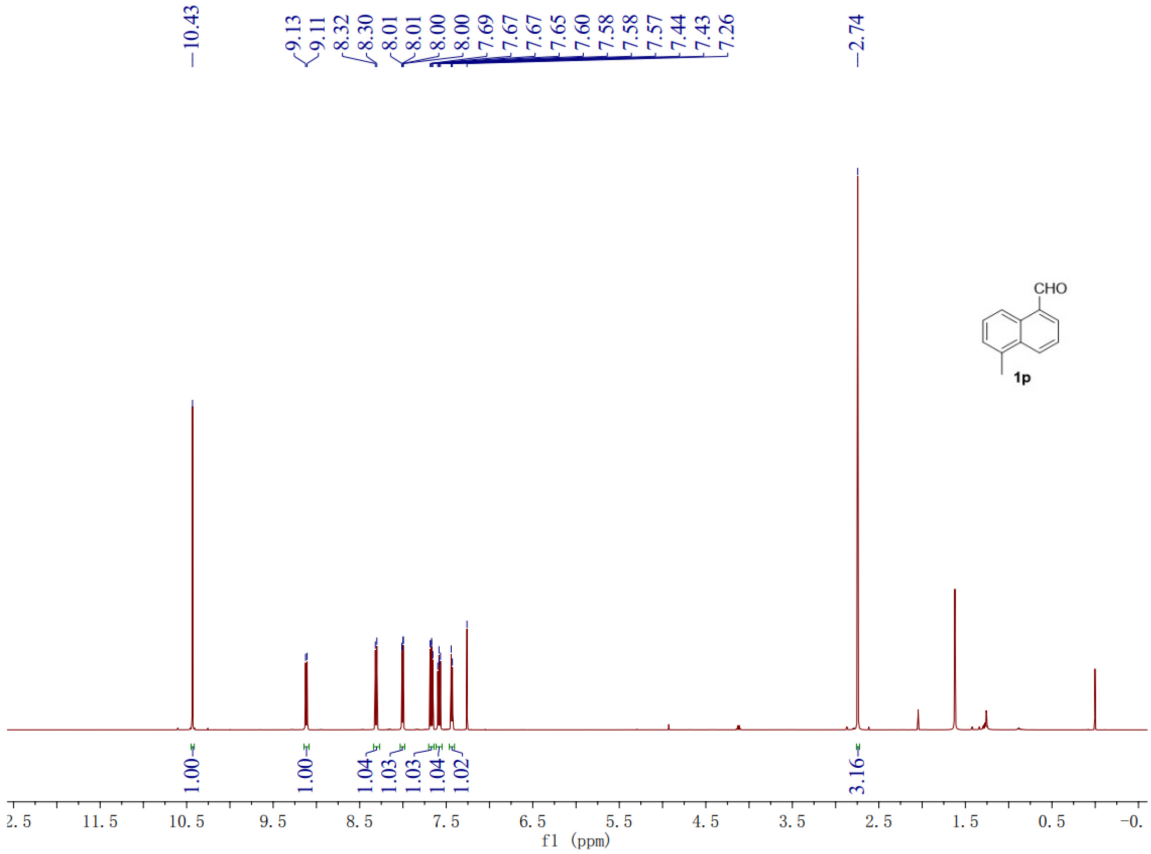
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1o



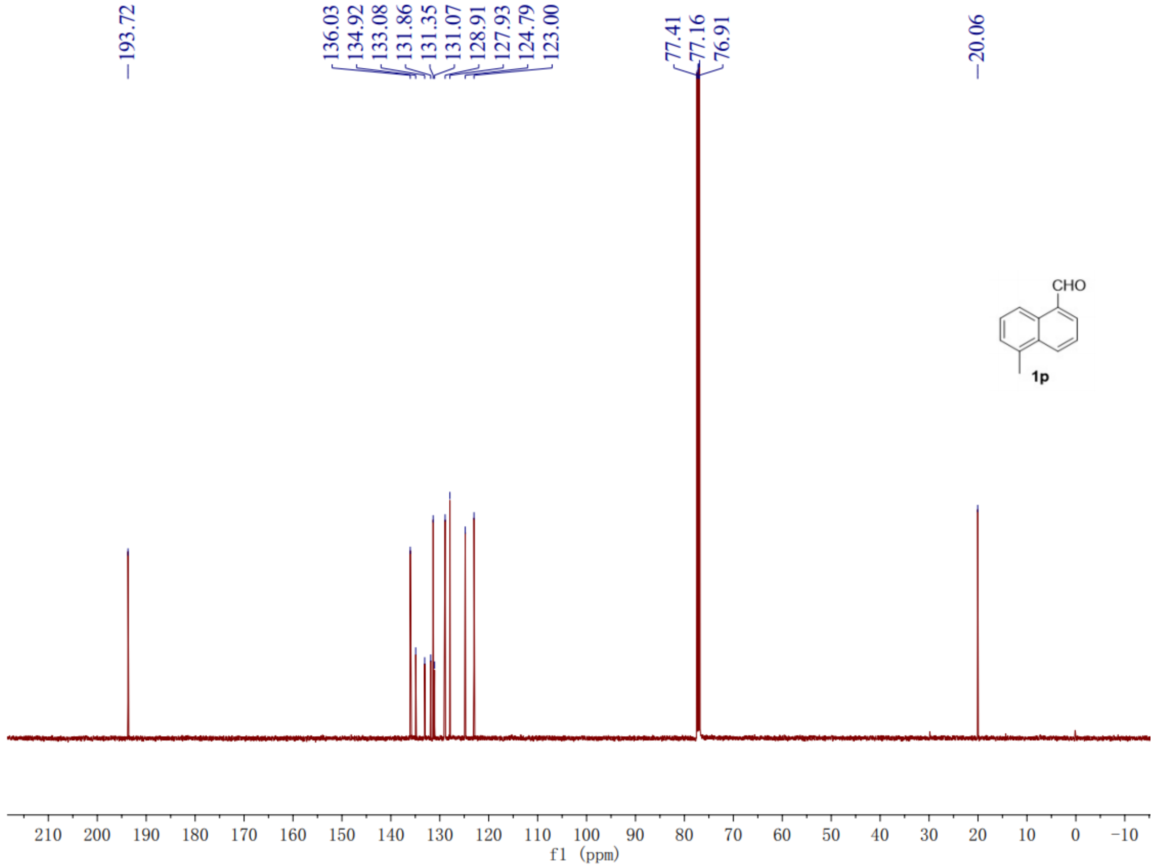
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1o



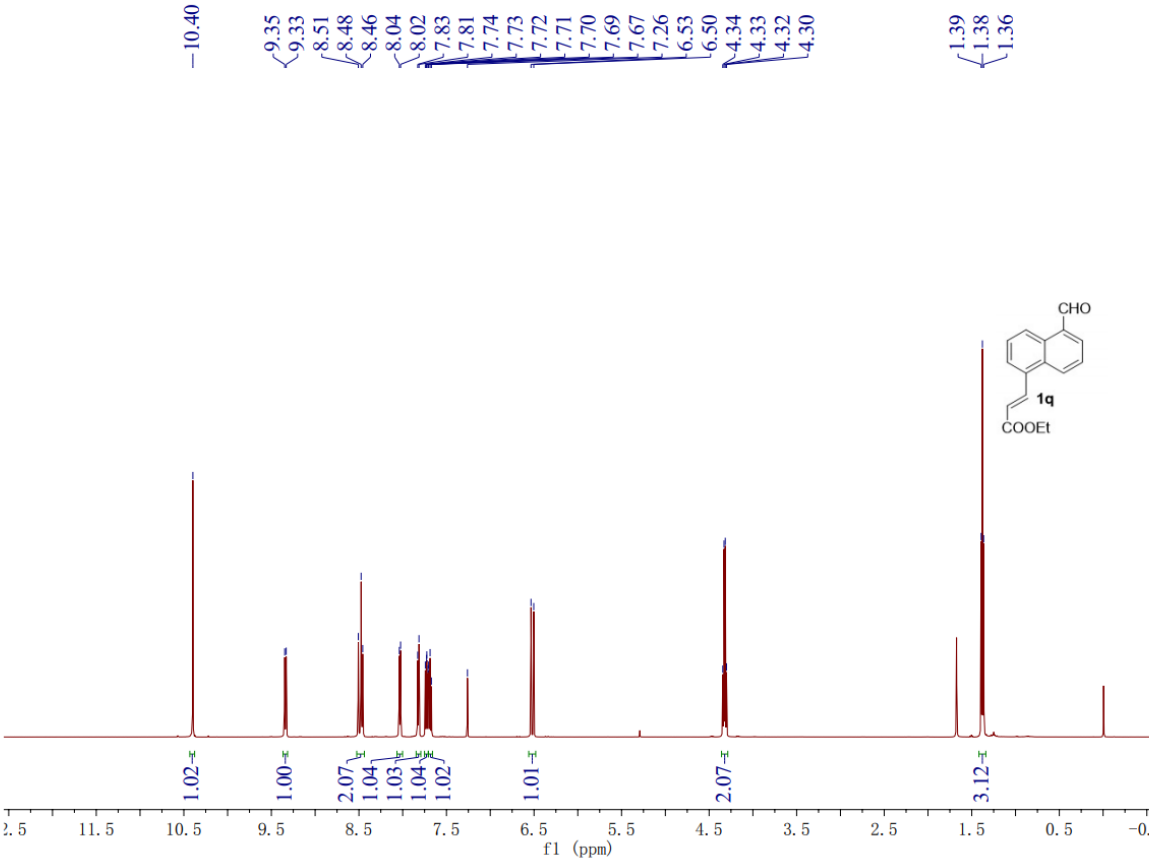
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1p



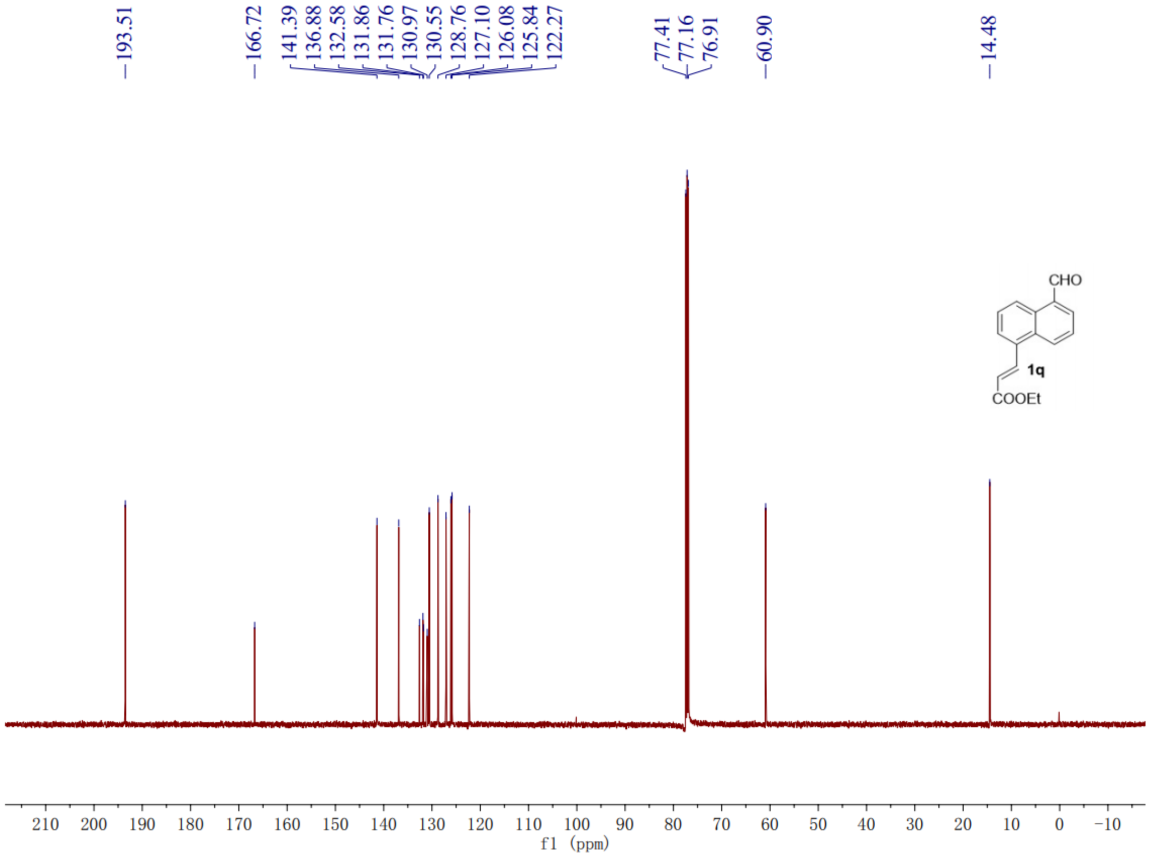
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1p



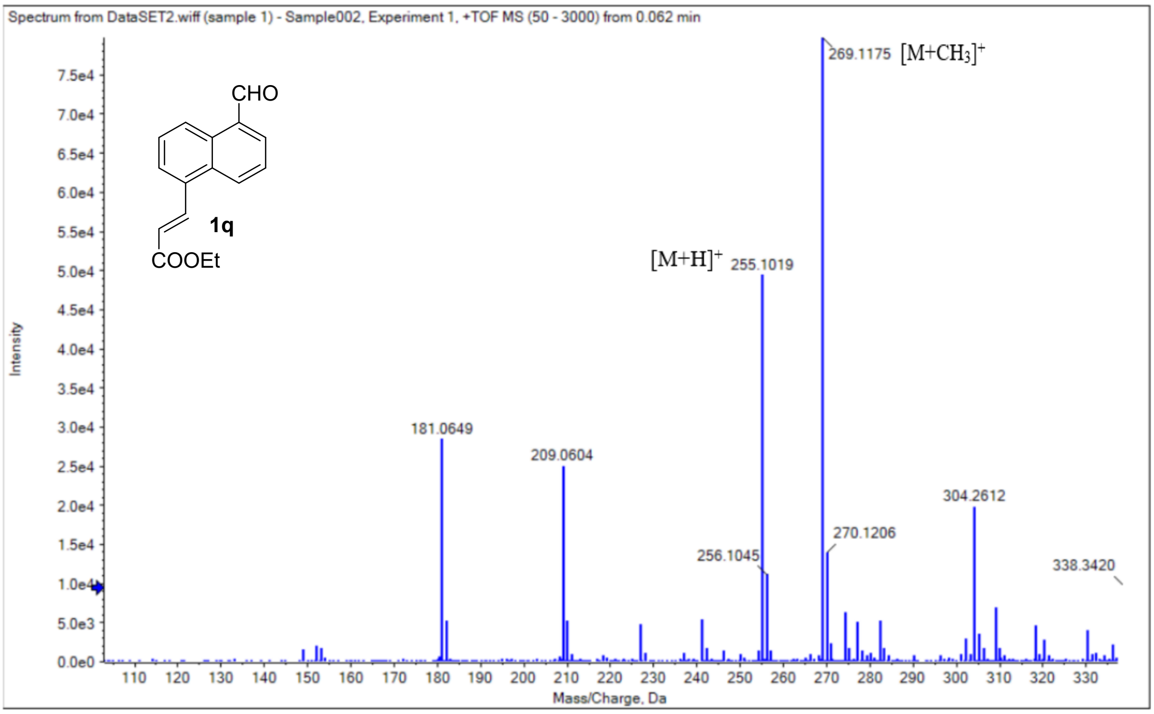
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1q



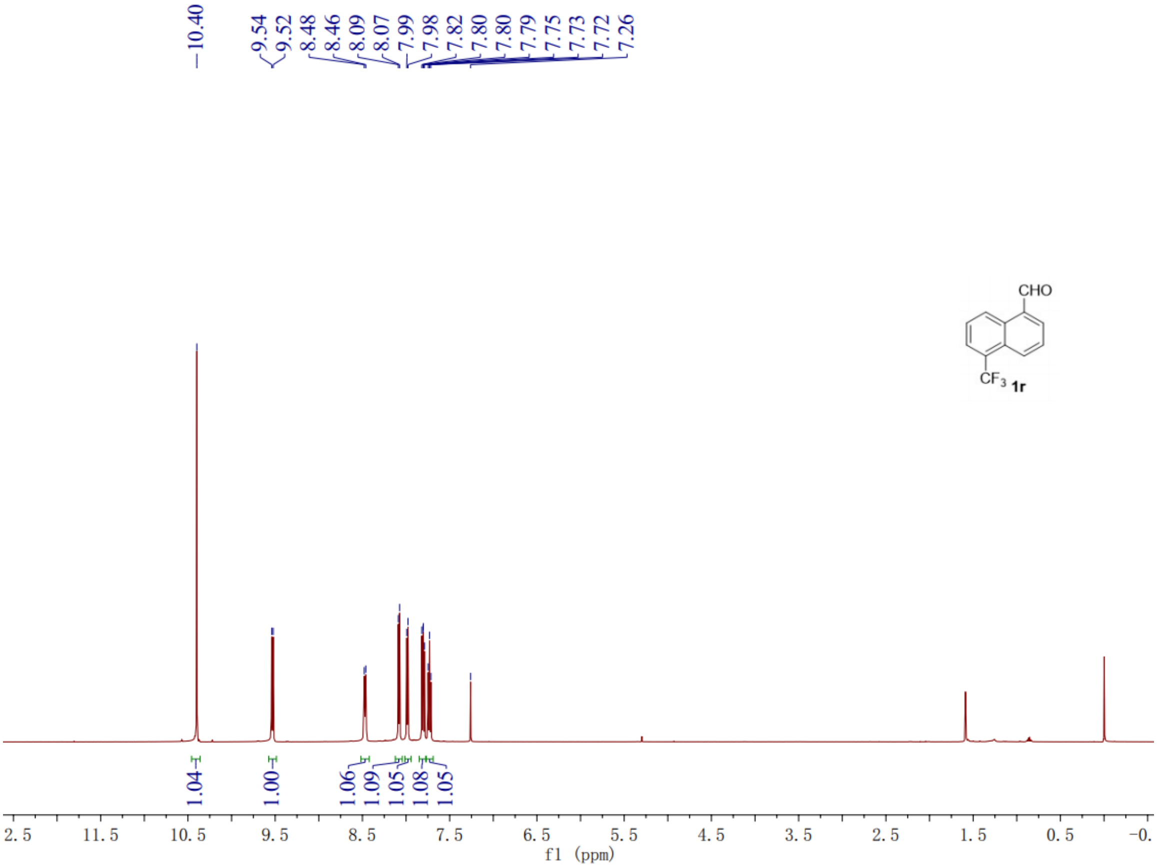
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1q



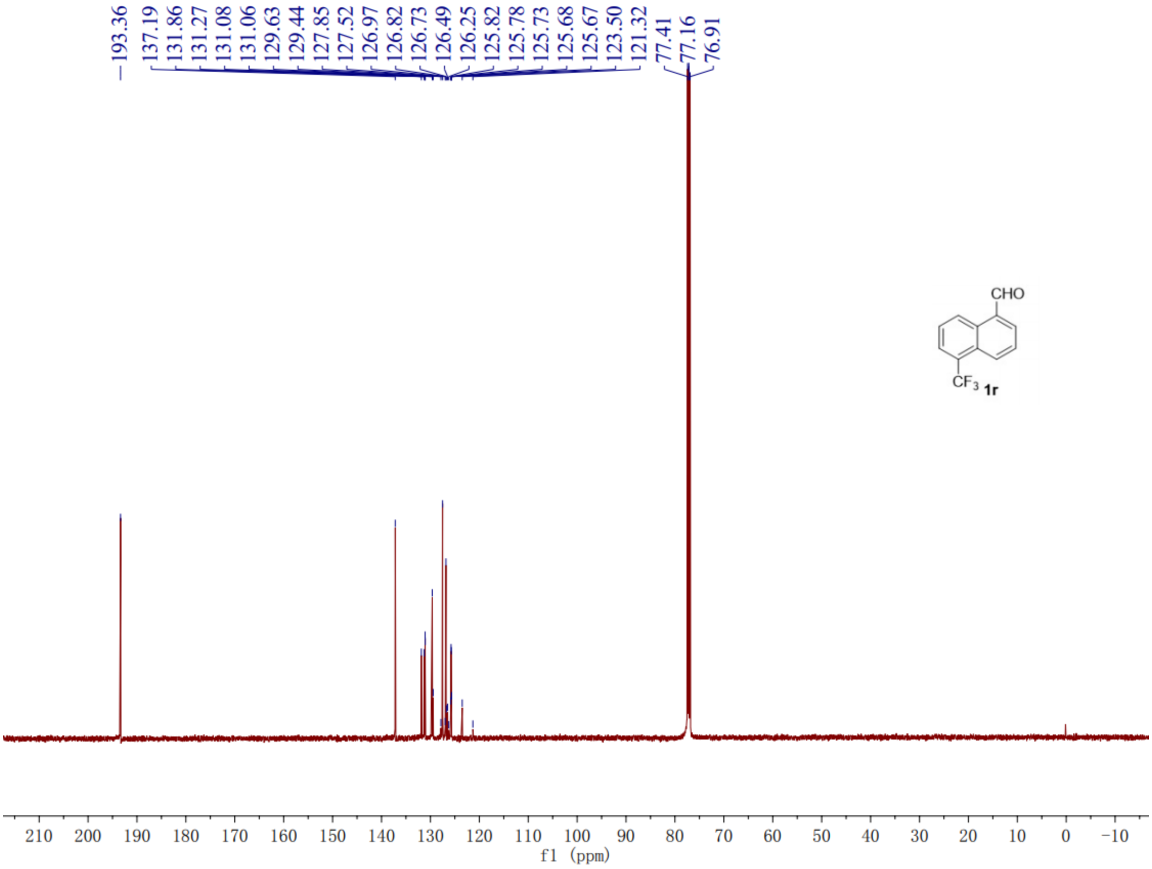
HR-ESI-MS $(M+CH_3)^+$ of 1q



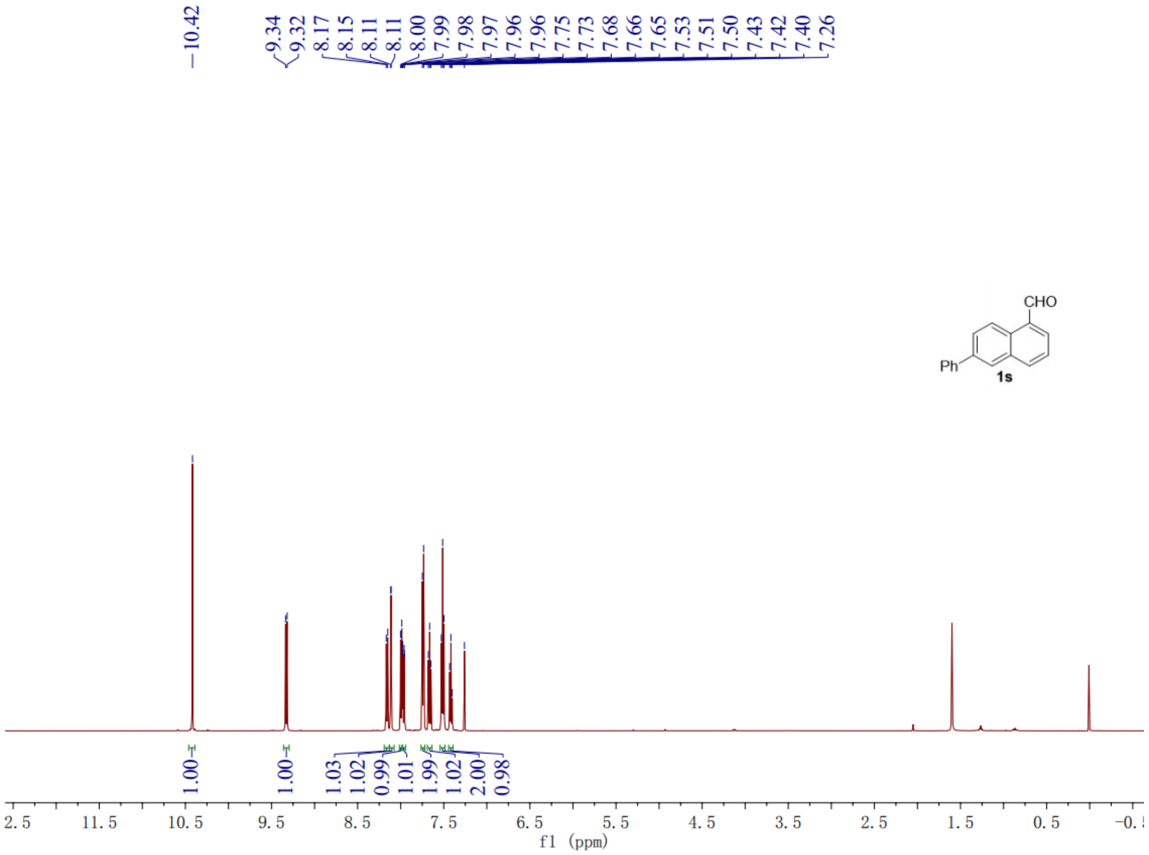
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1r



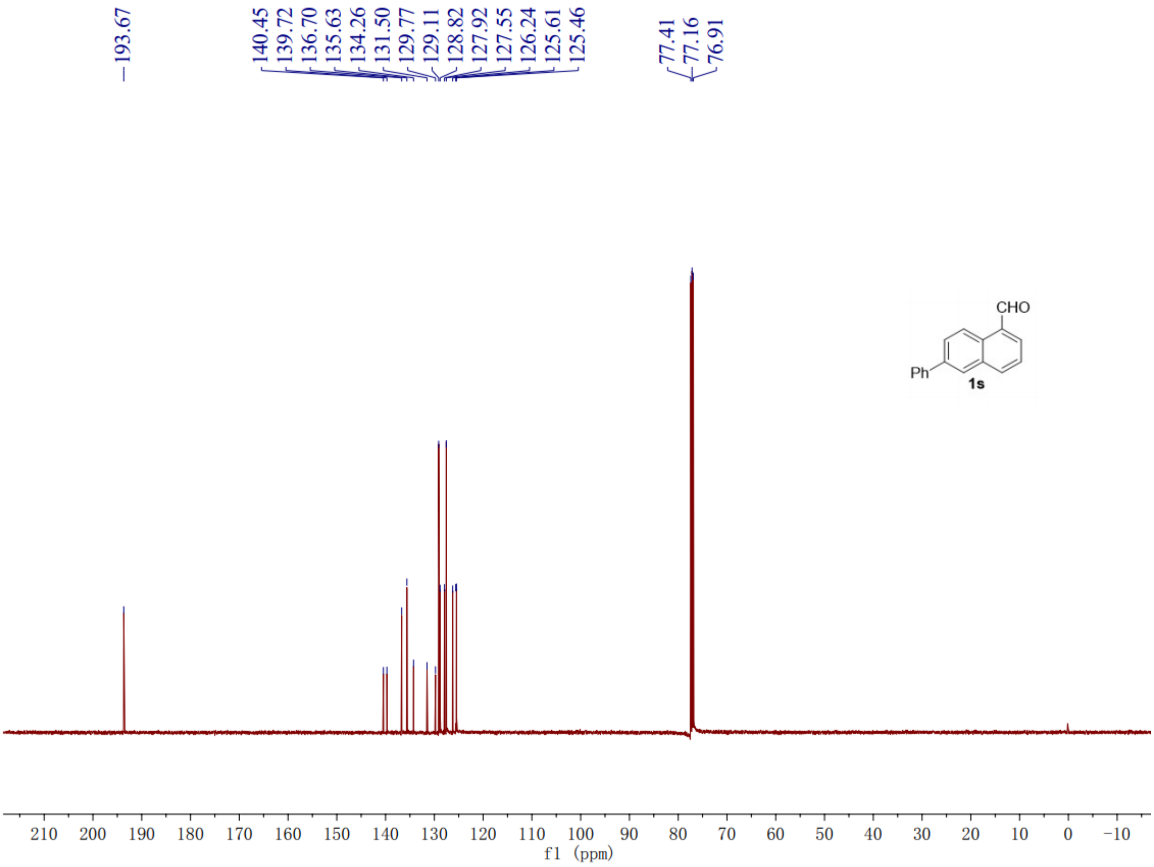
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1r



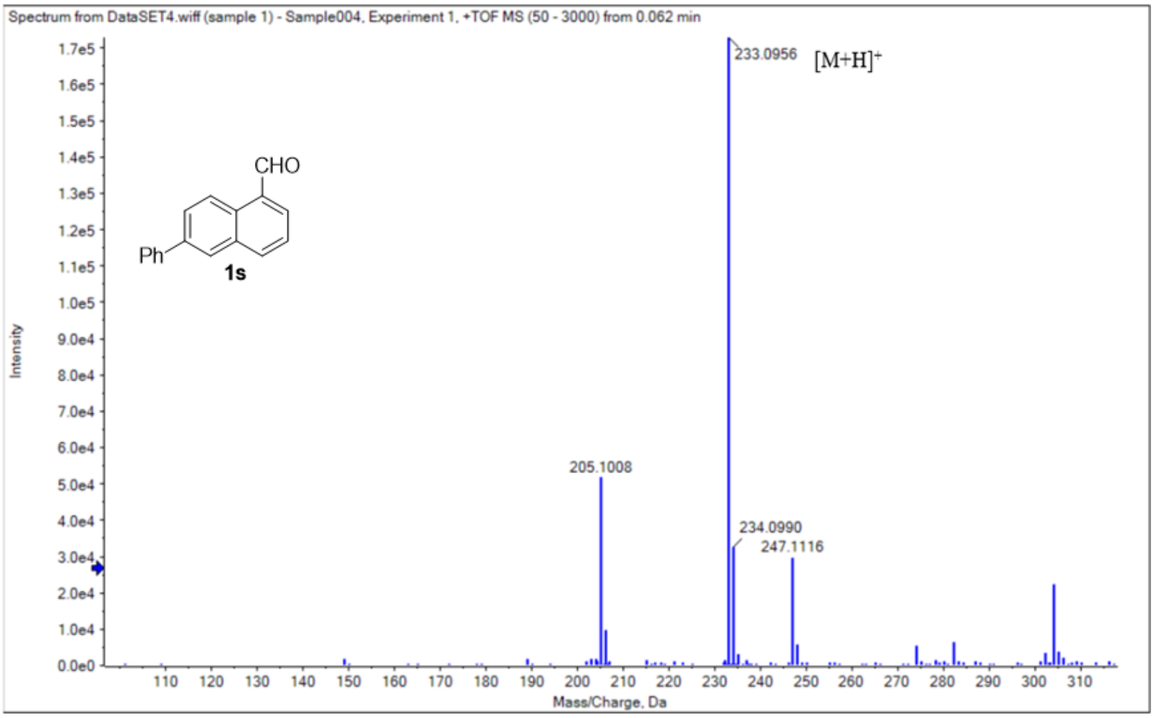
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1s



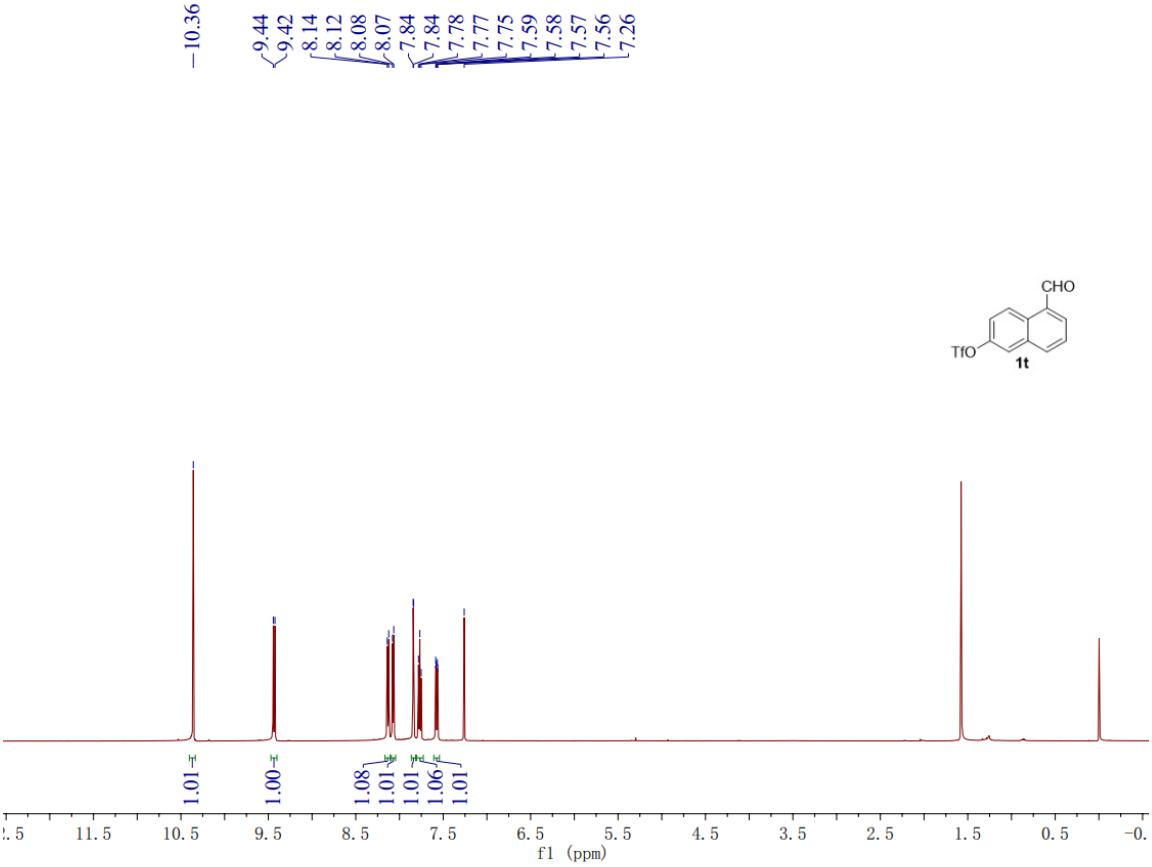
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1s



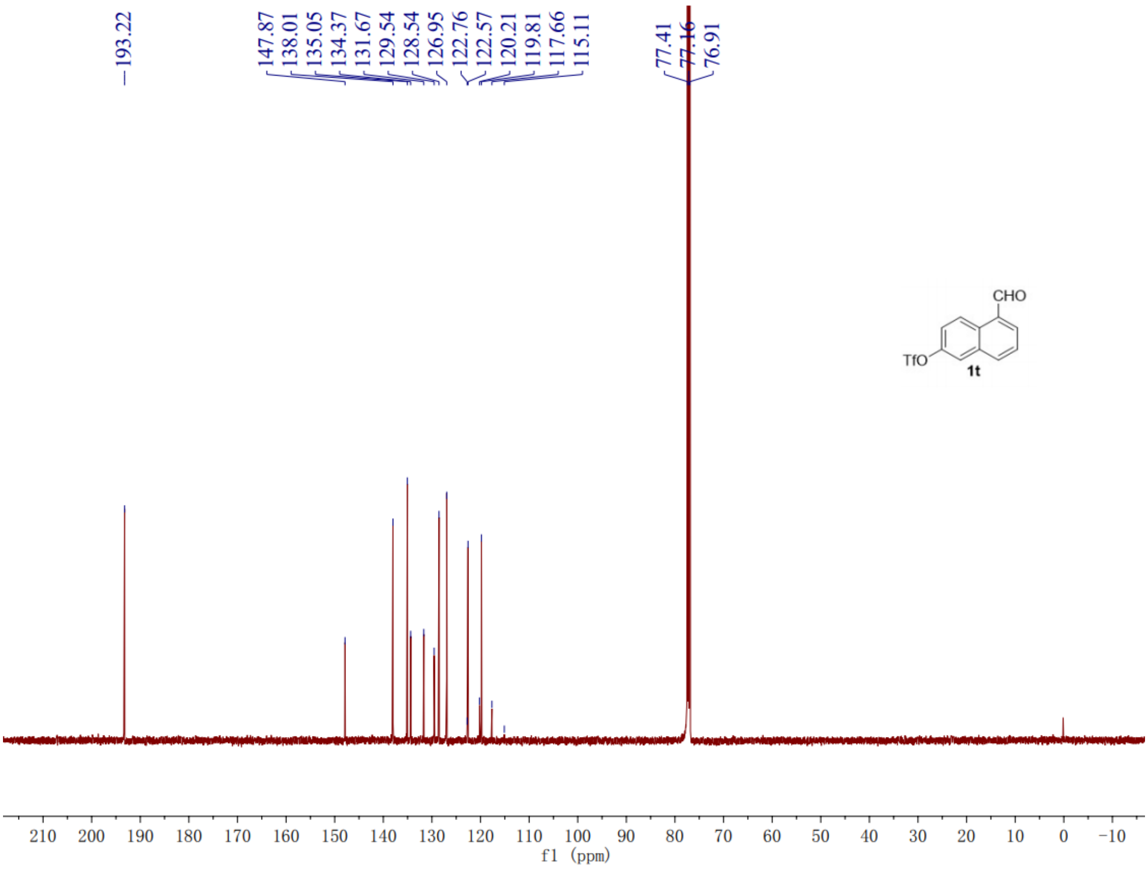
HR-ESI-MS (M+H)$^+$ of 1s



^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1t



^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1t



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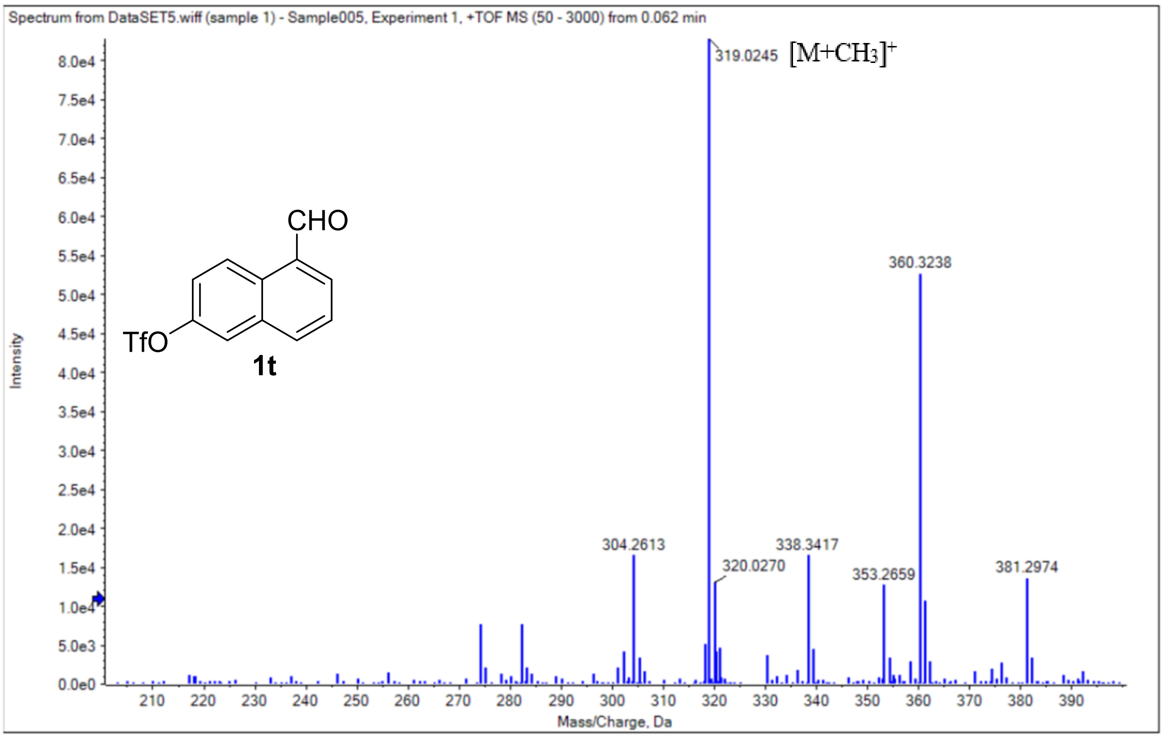
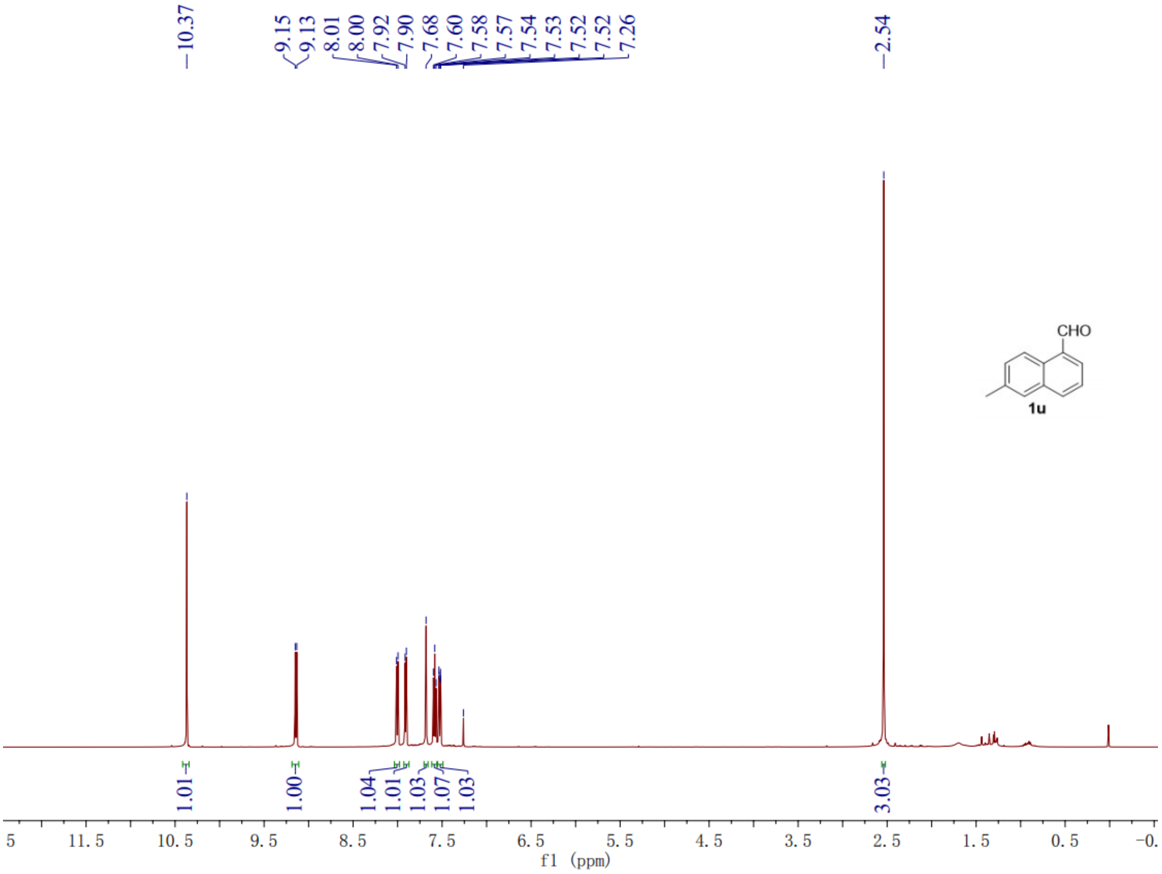
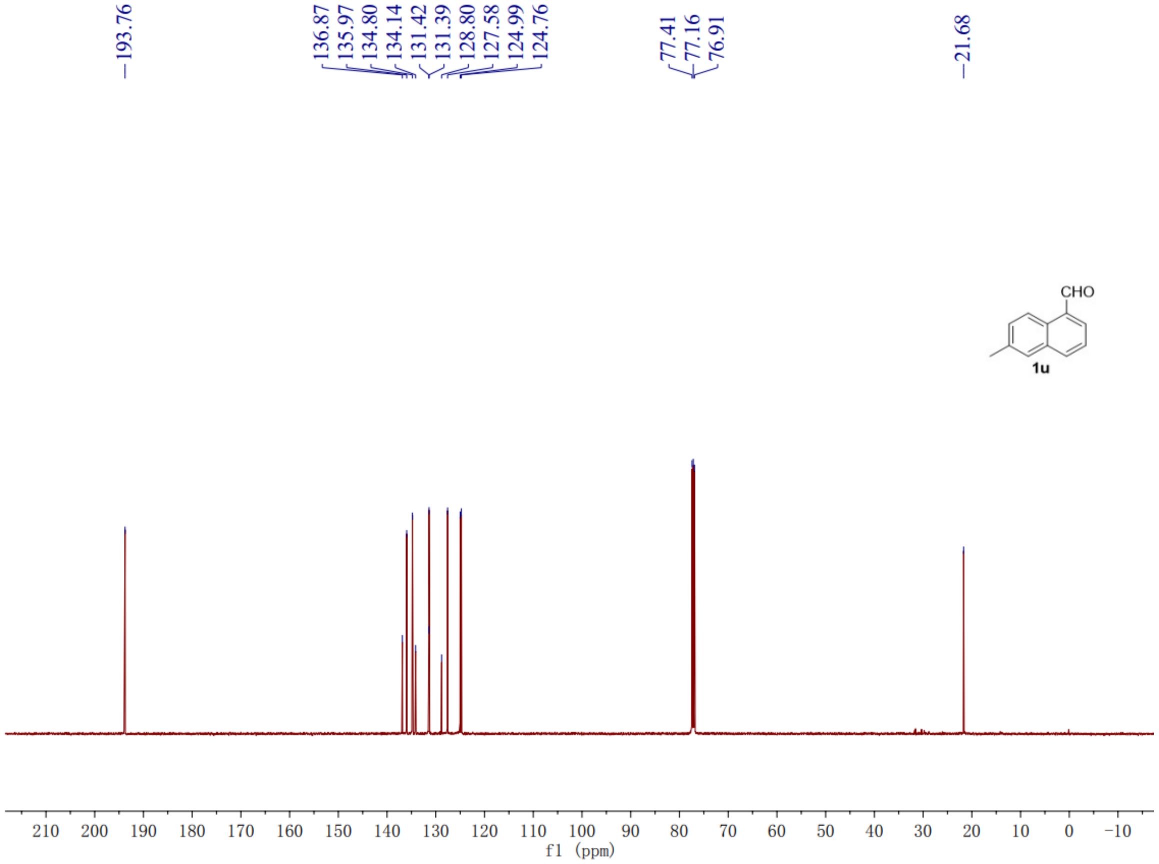


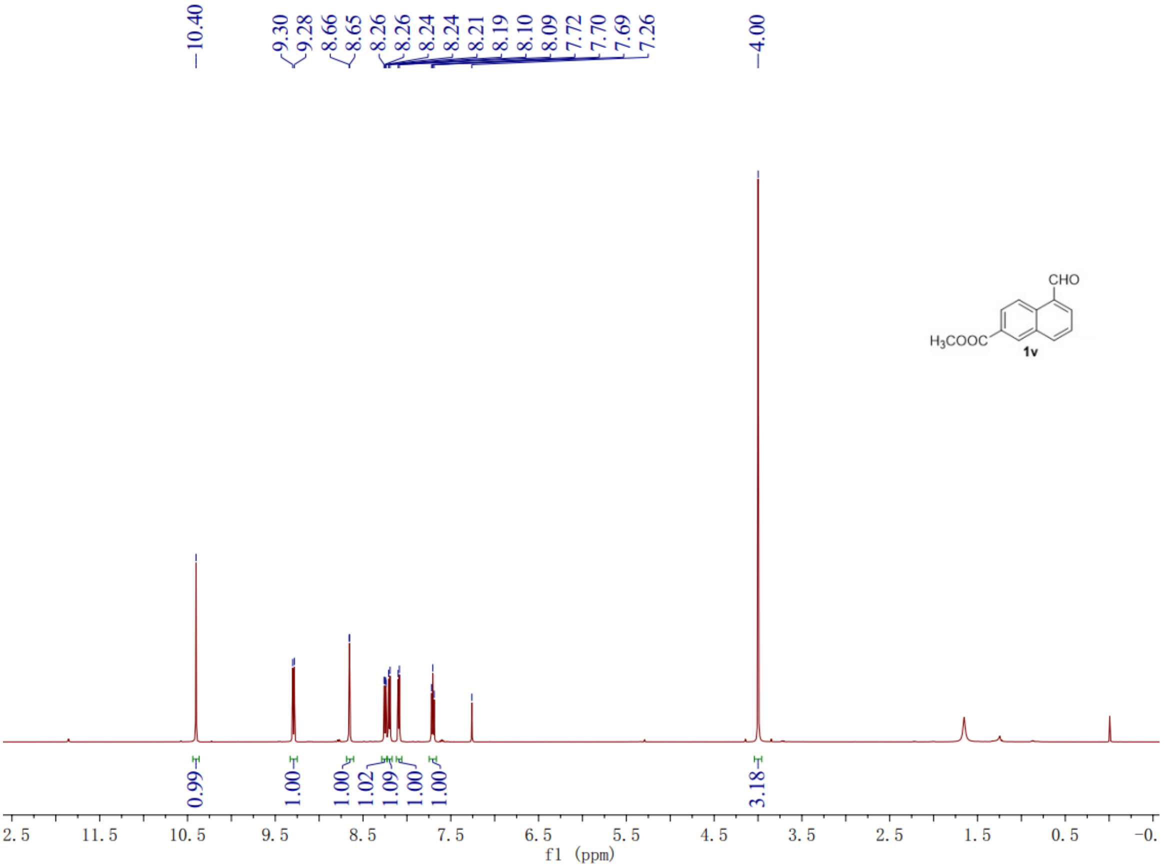
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1u



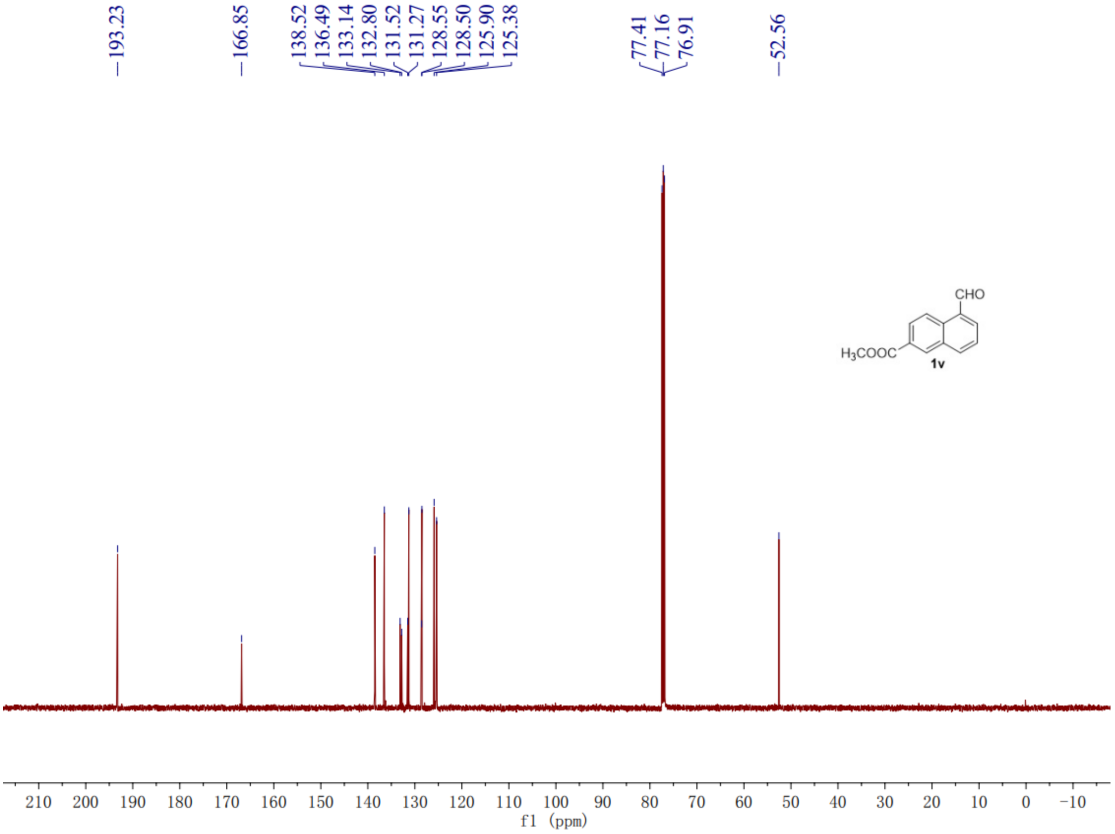
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1u



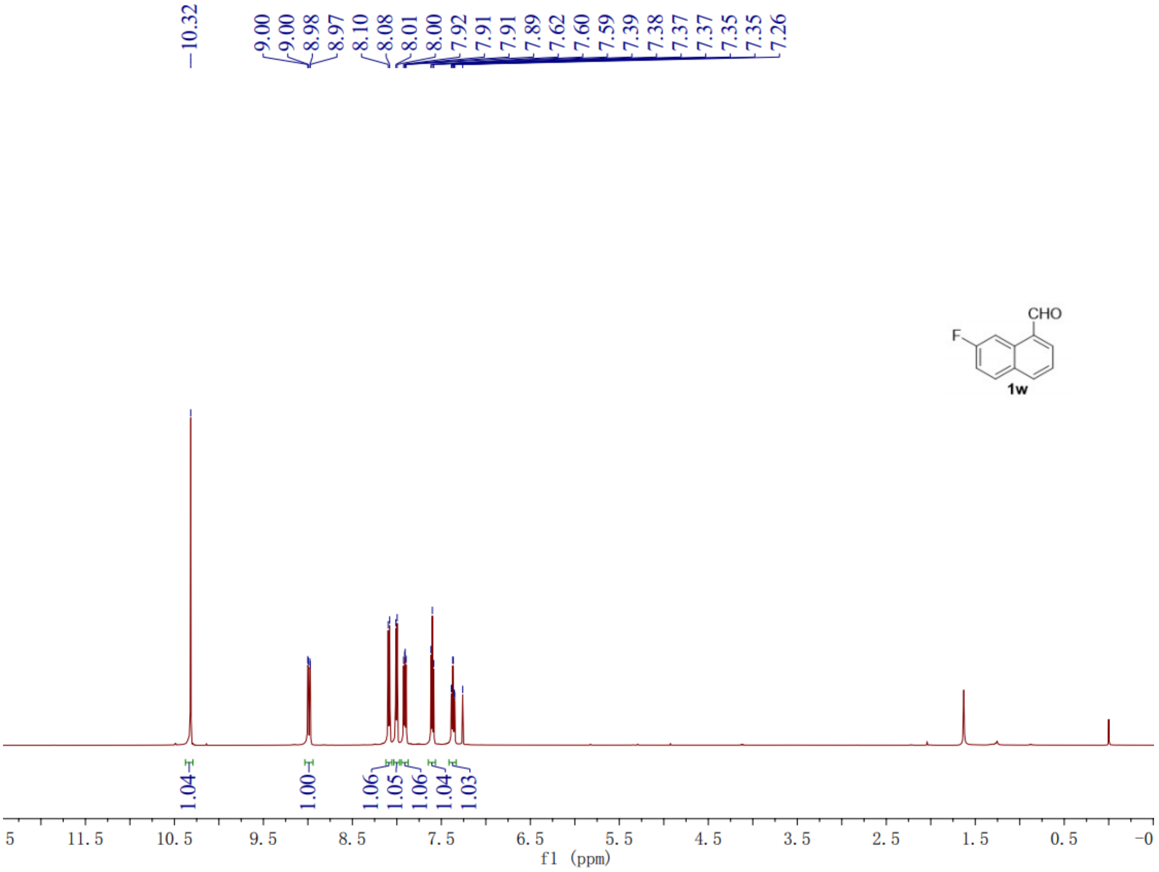
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1v



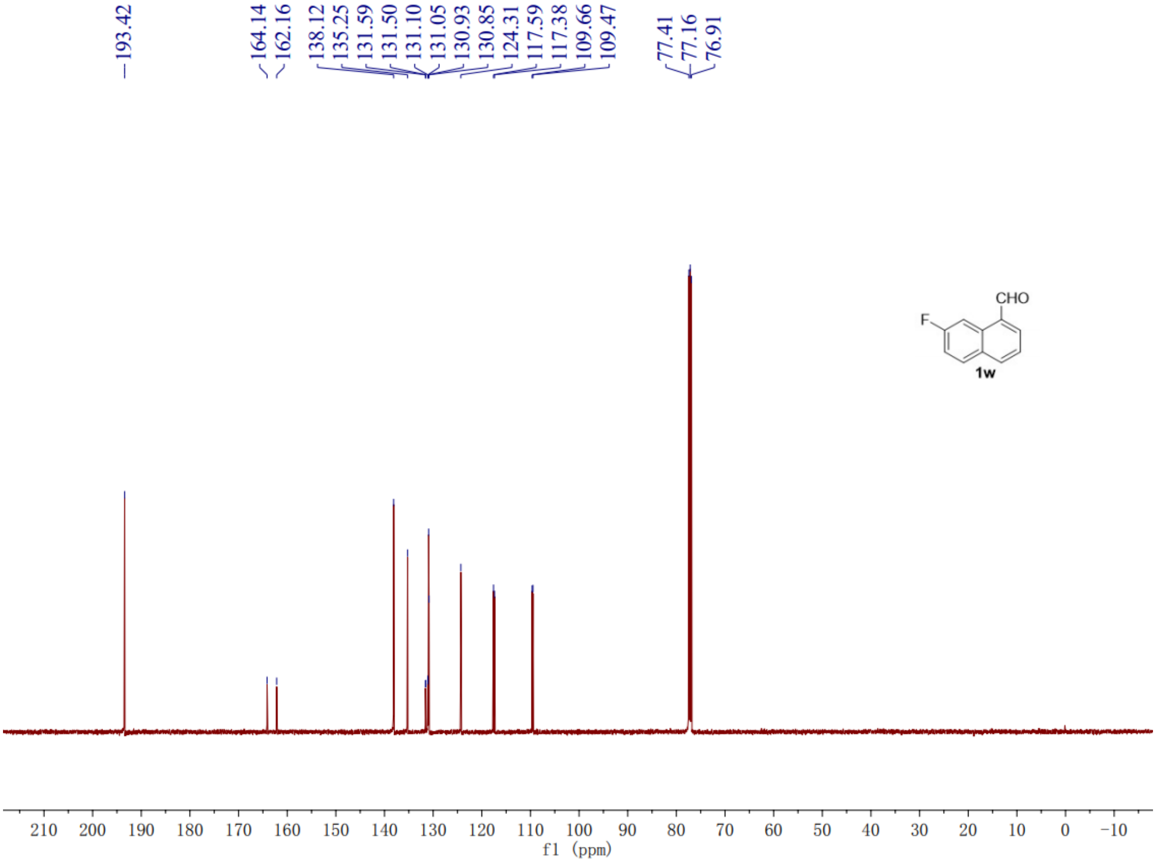
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1v



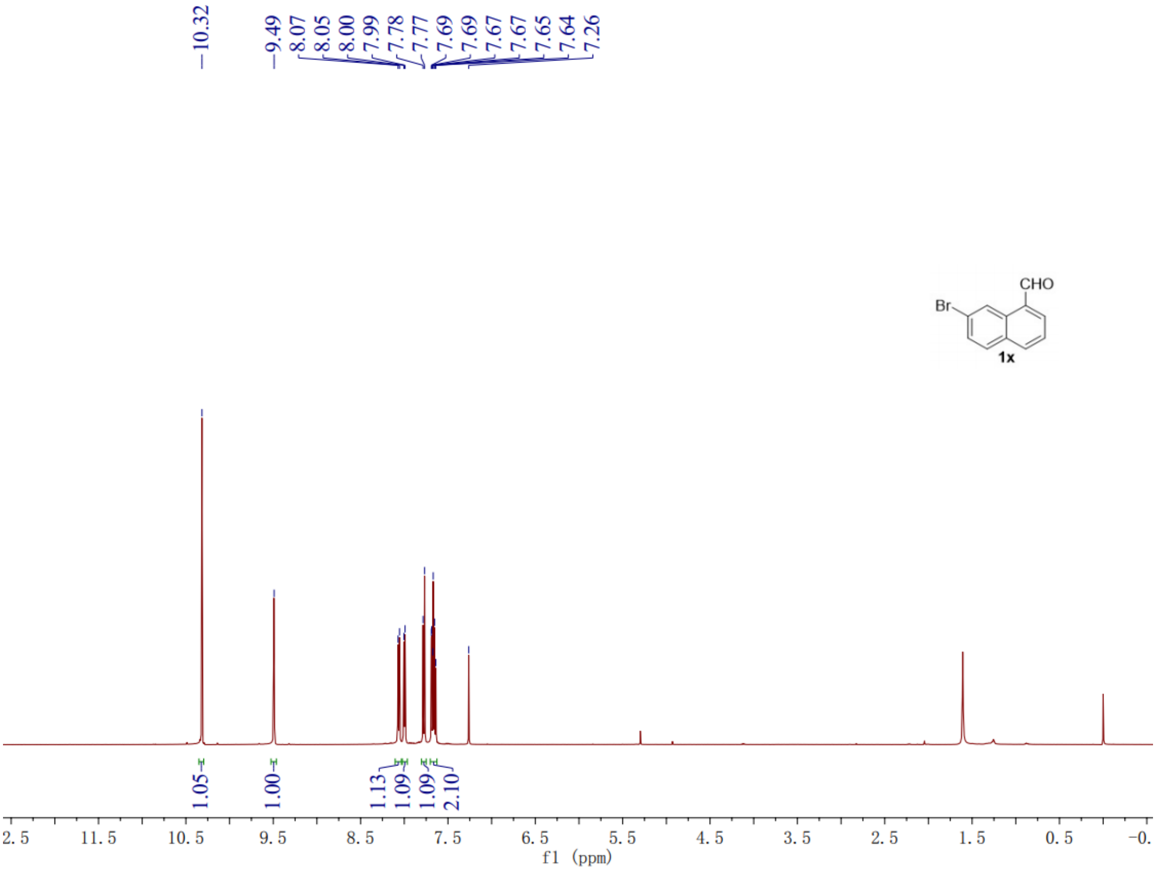
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1w



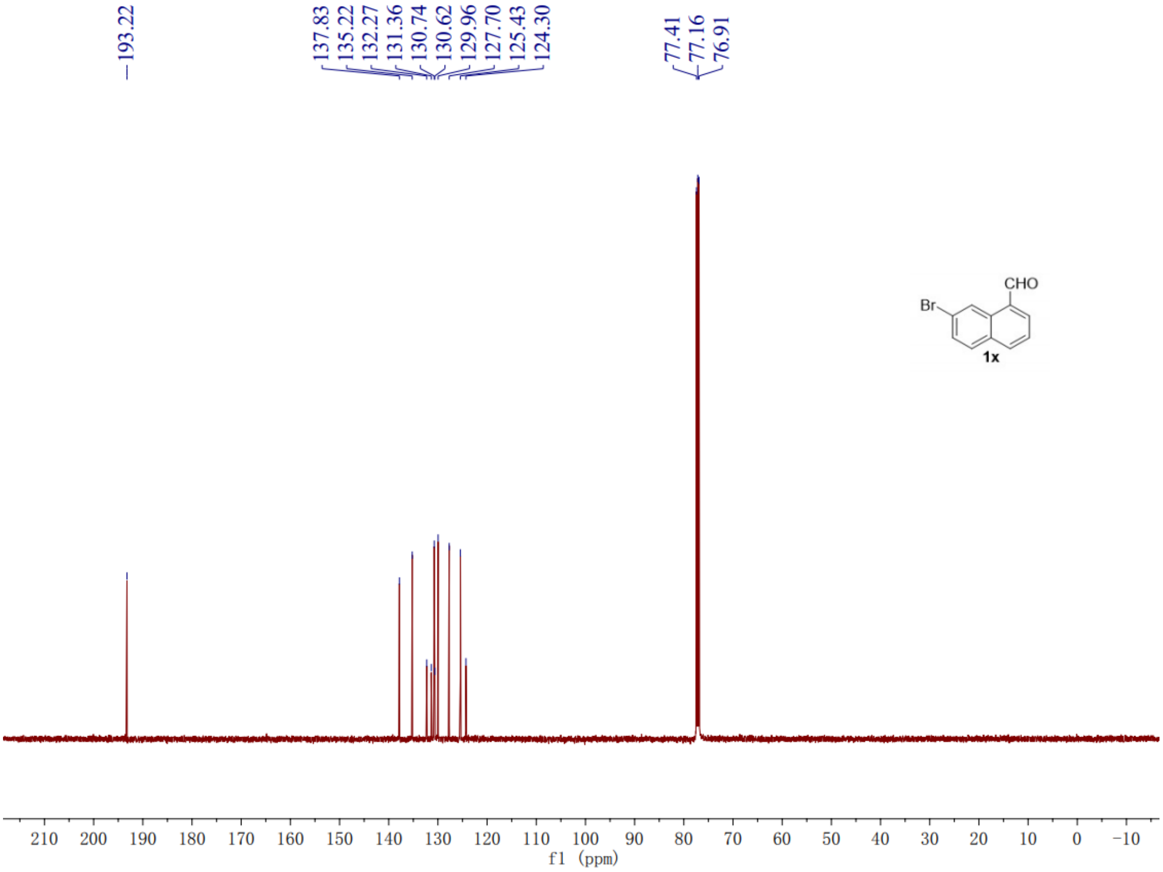
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1w



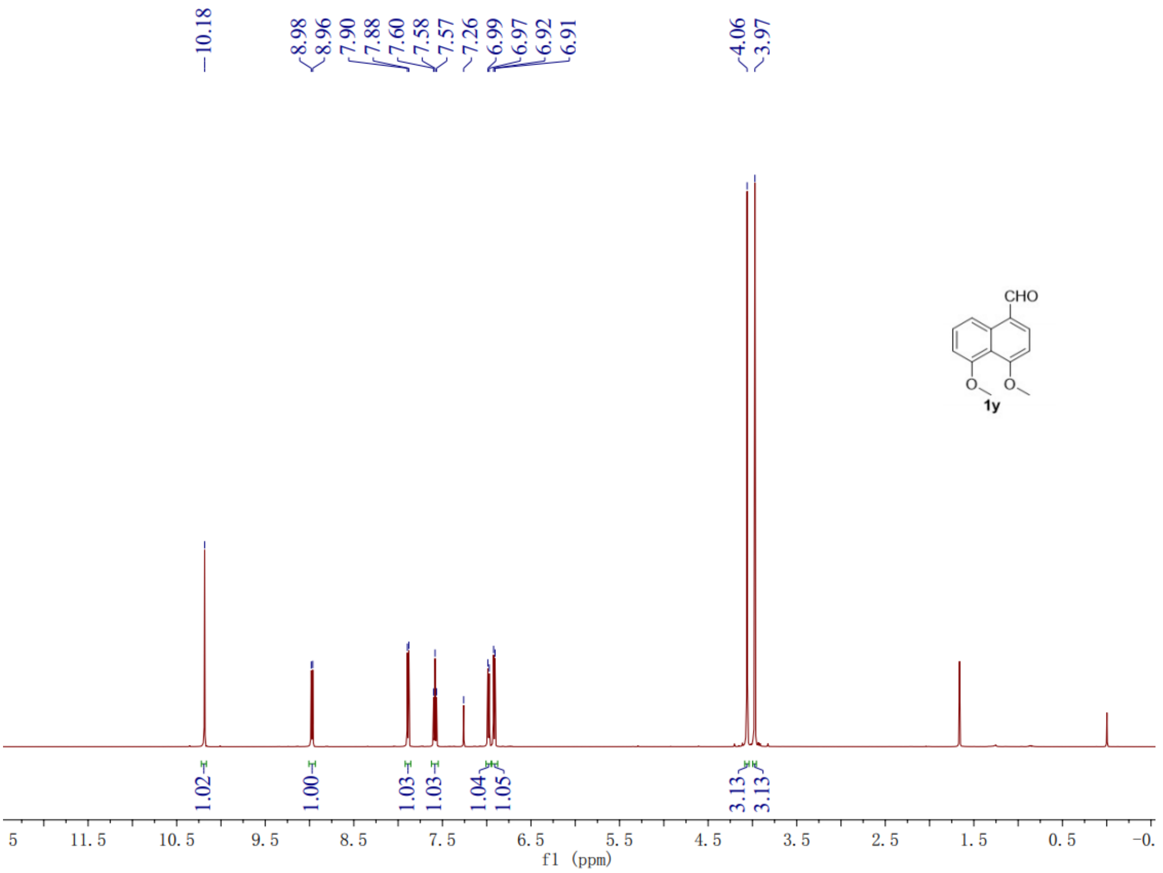
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1x



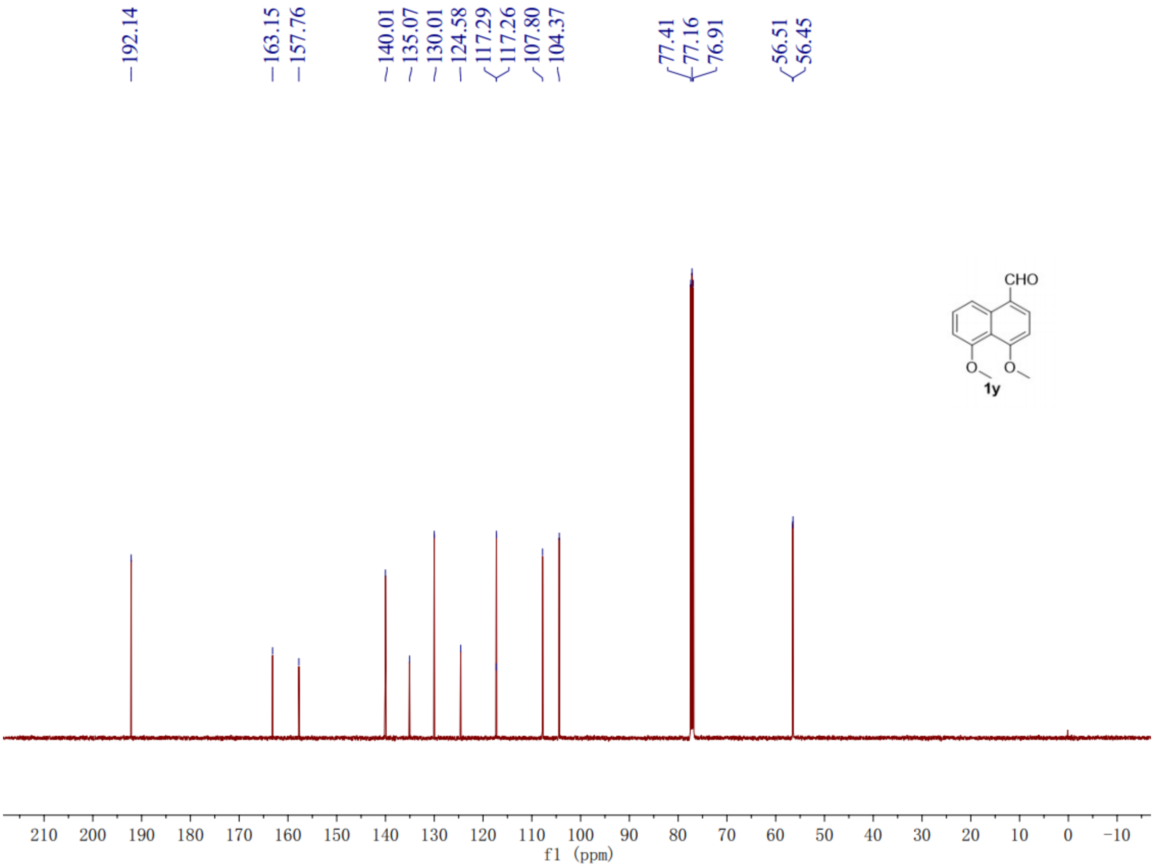
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1x



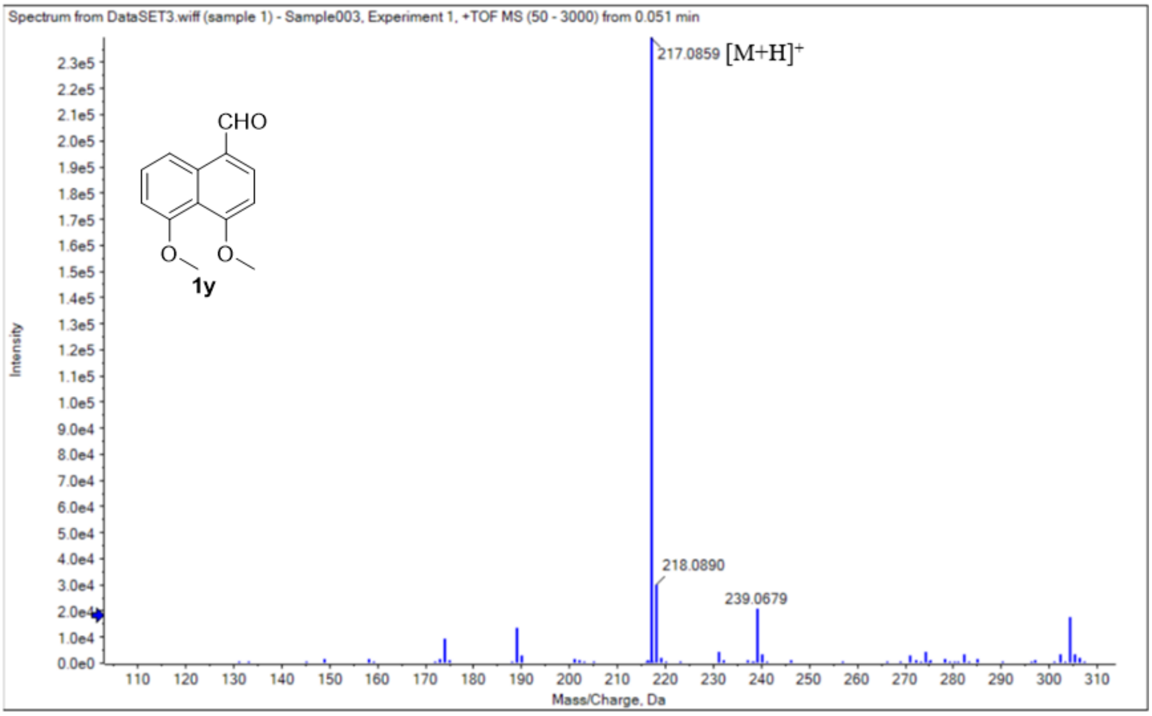
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1y



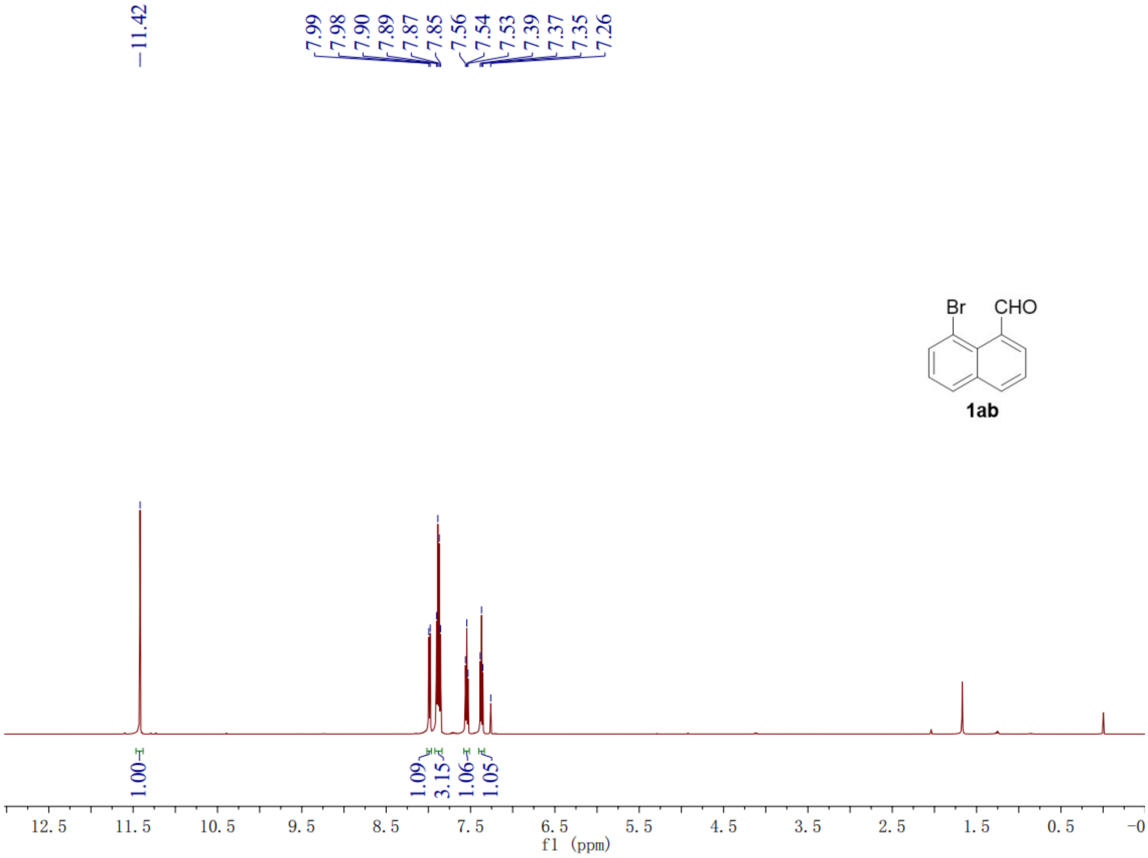
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1y



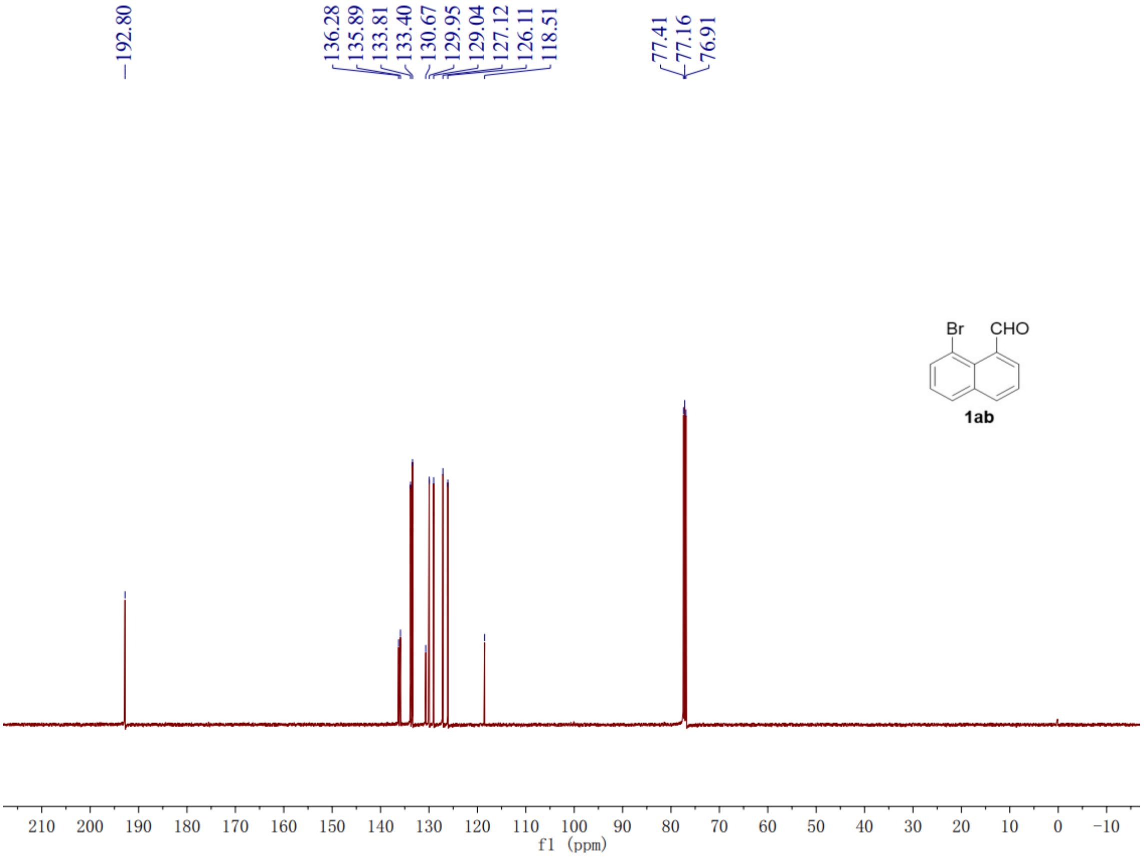
HR-ESI-MS (M+H)$^+$ of 1y



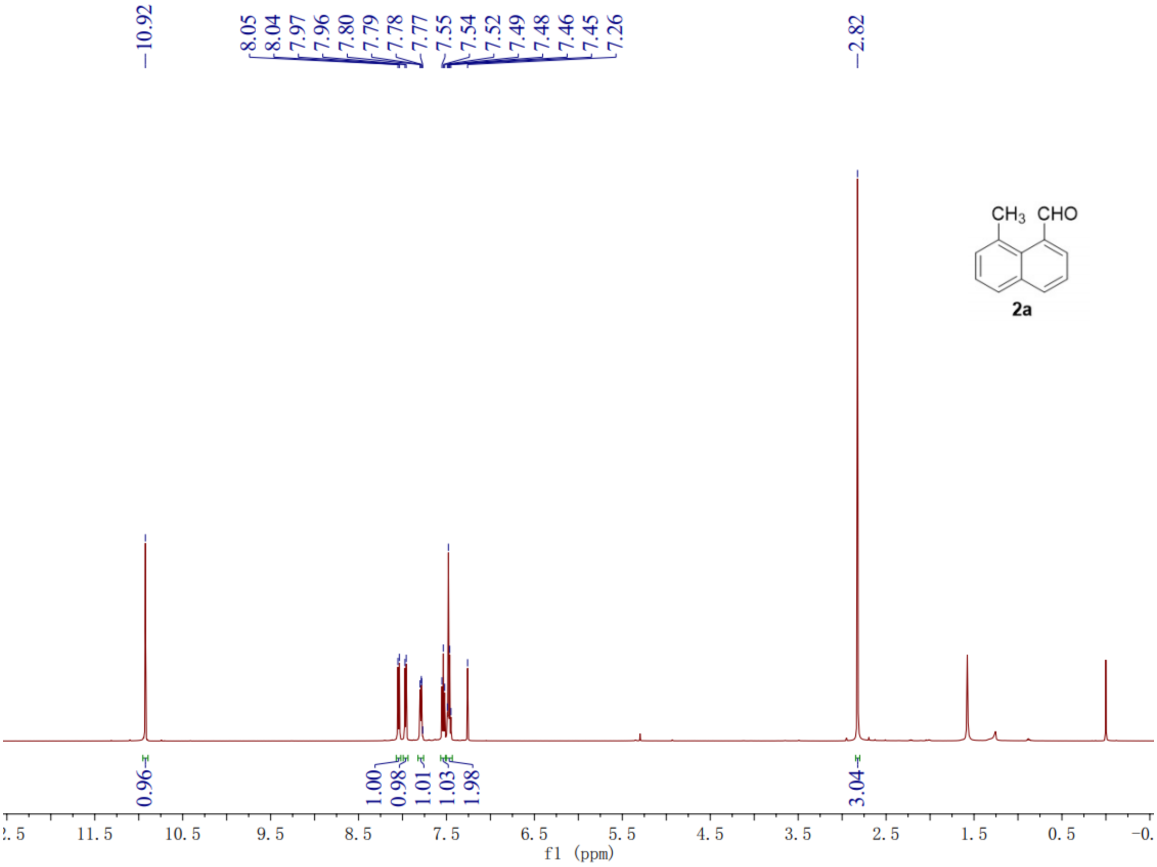
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 1ab



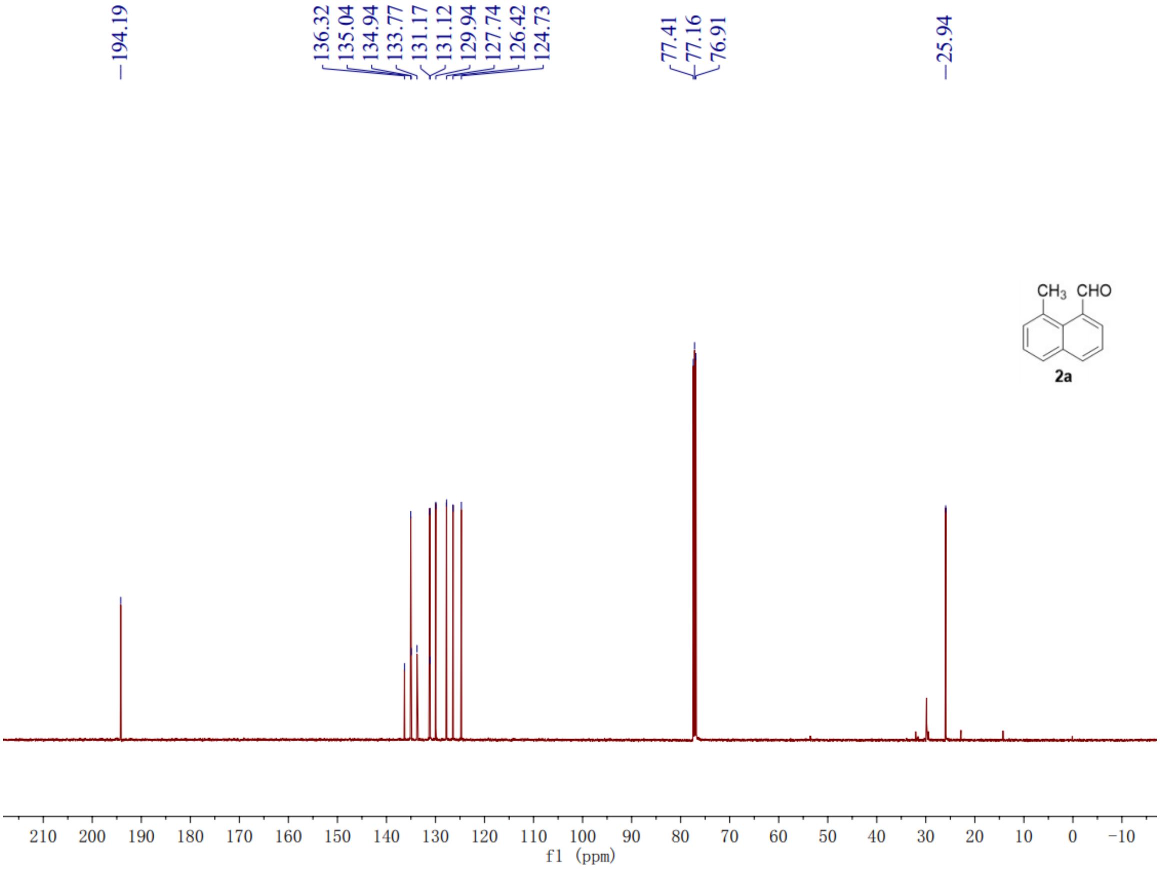
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 1ab



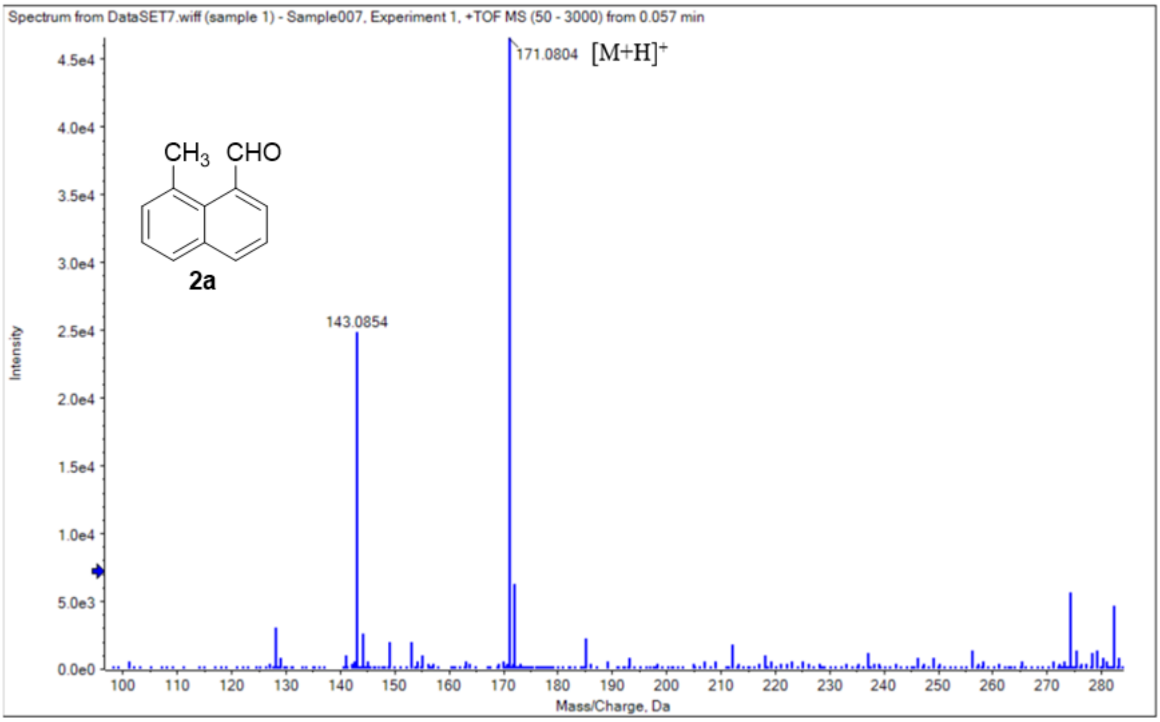
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2a



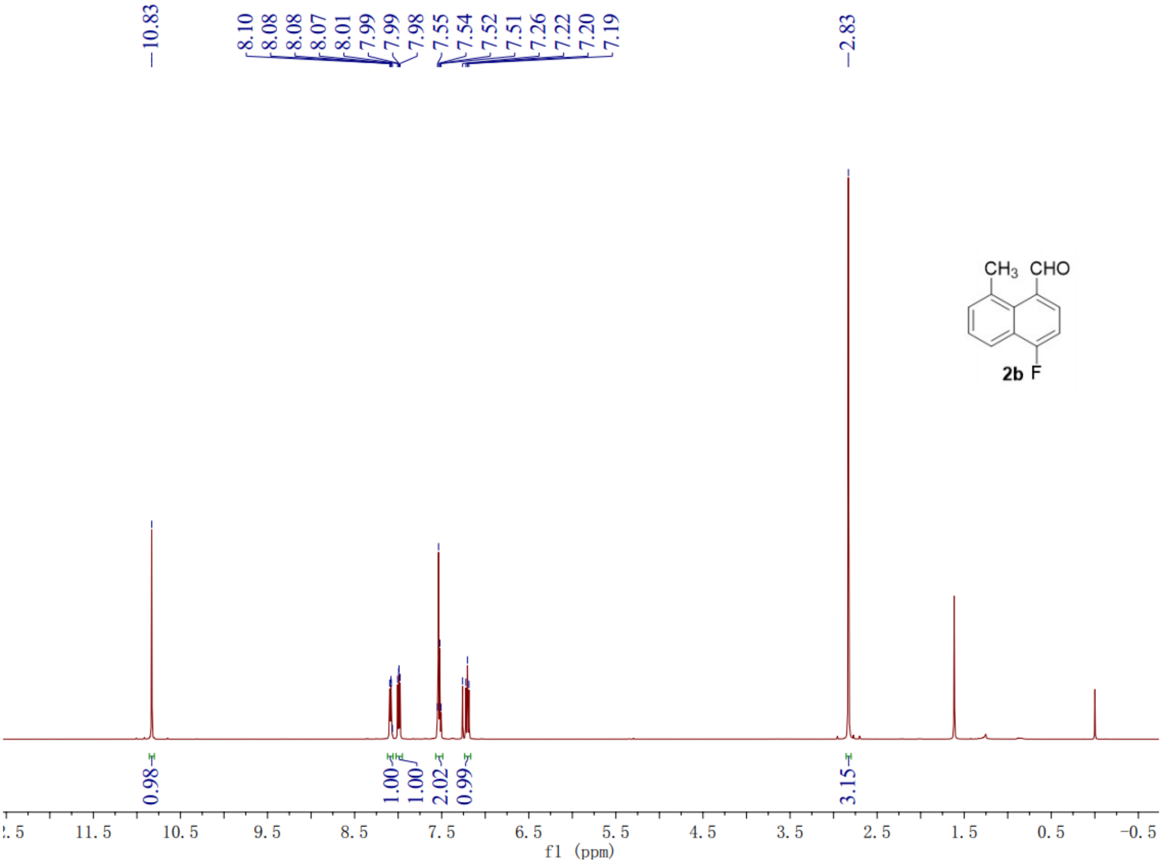
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2a



HR-ESI-MS $(M+H)^+$ of 2a

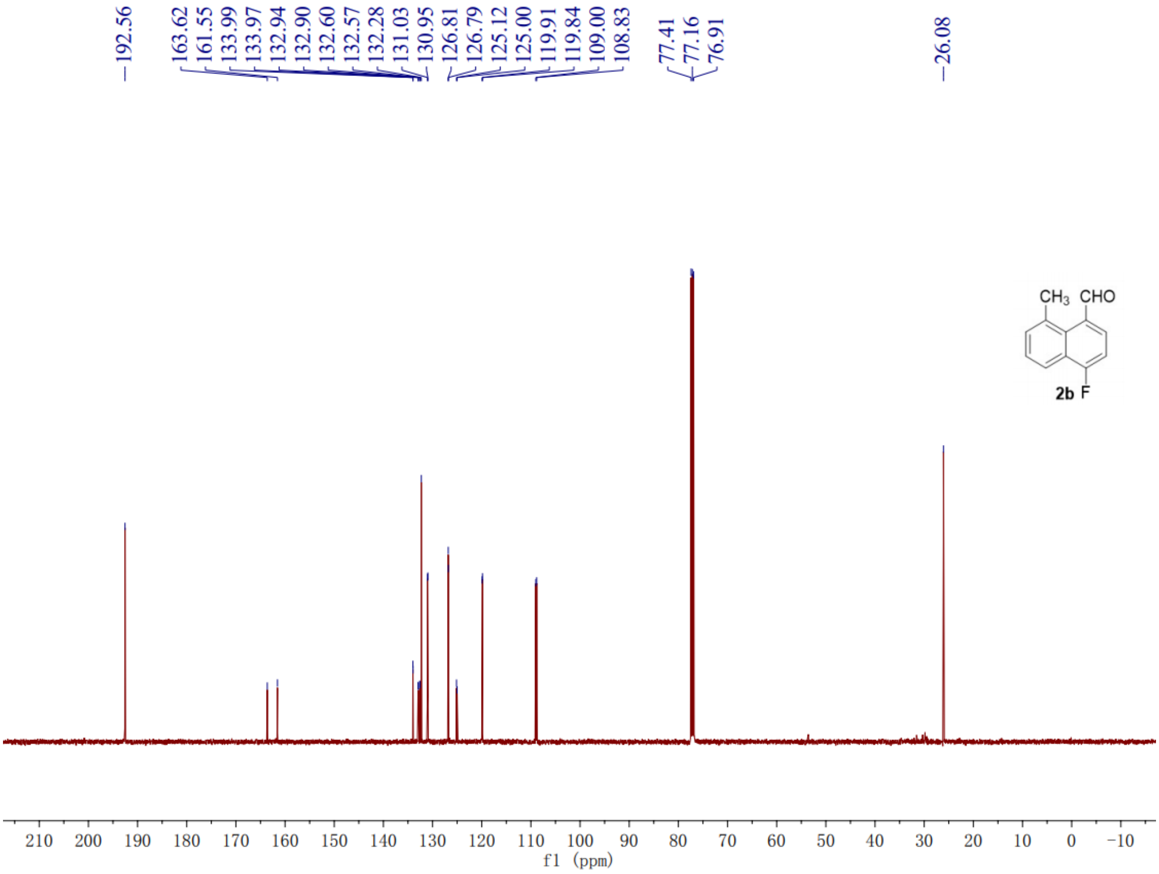


^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2b

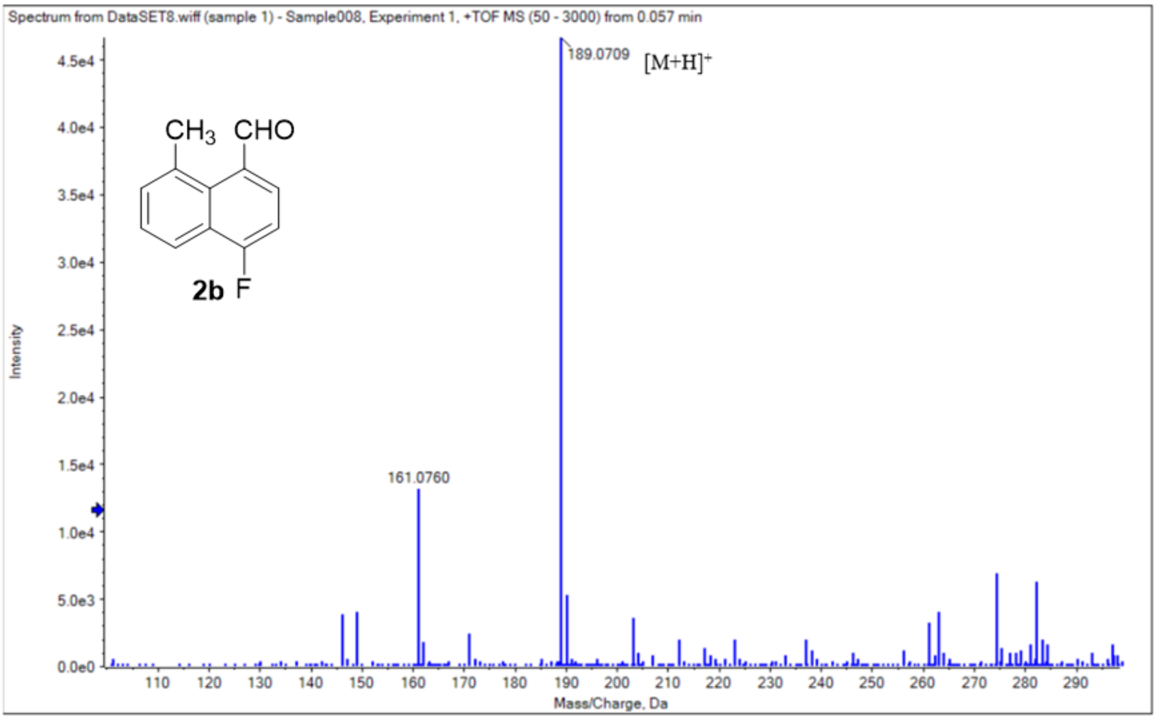


2b

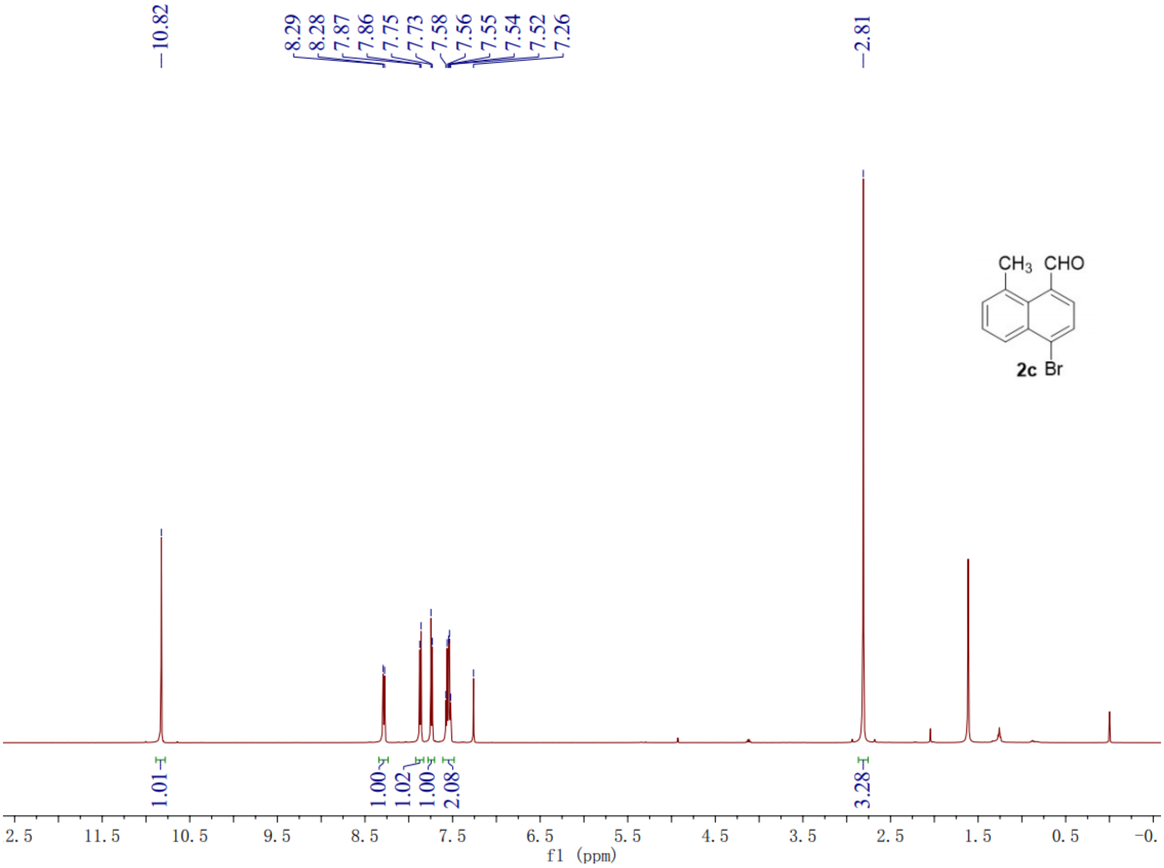
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 2b



HR-ESI-MS $(M+H)^+$ of 2b



^1H NMR spectrum ($CDCl_3$, 500 MHz) of 2c



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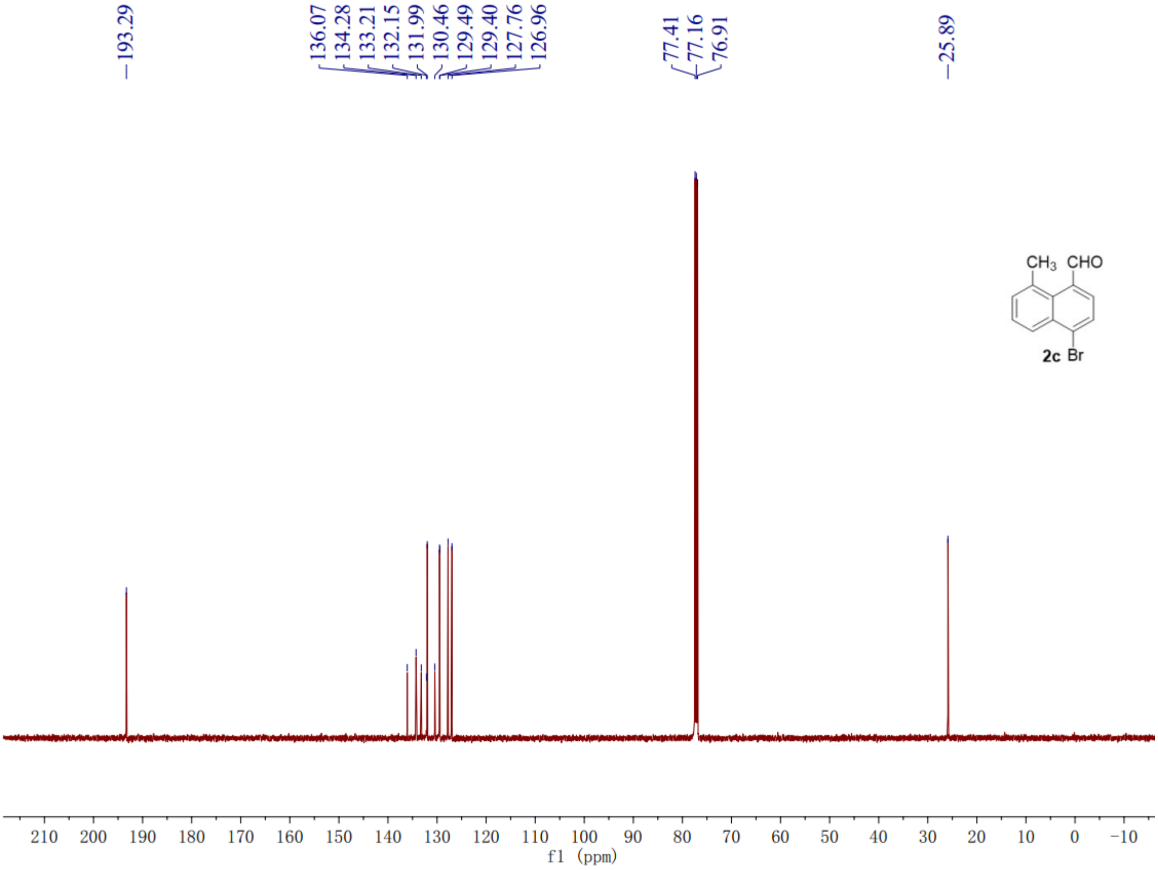
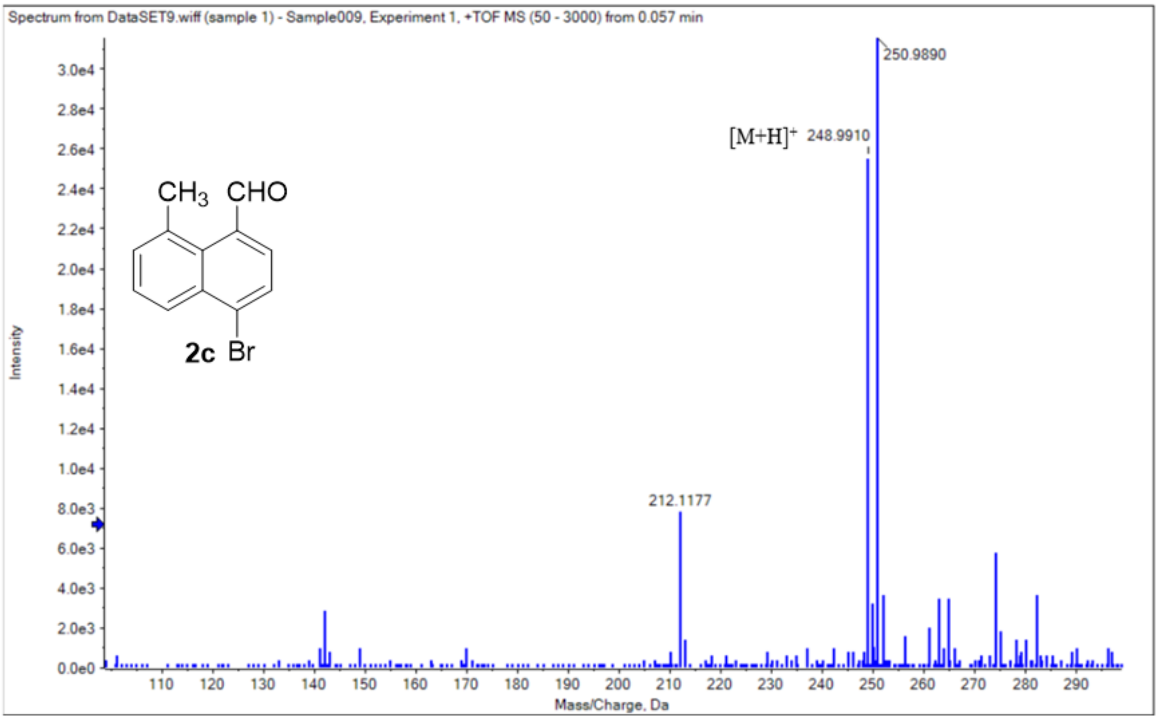
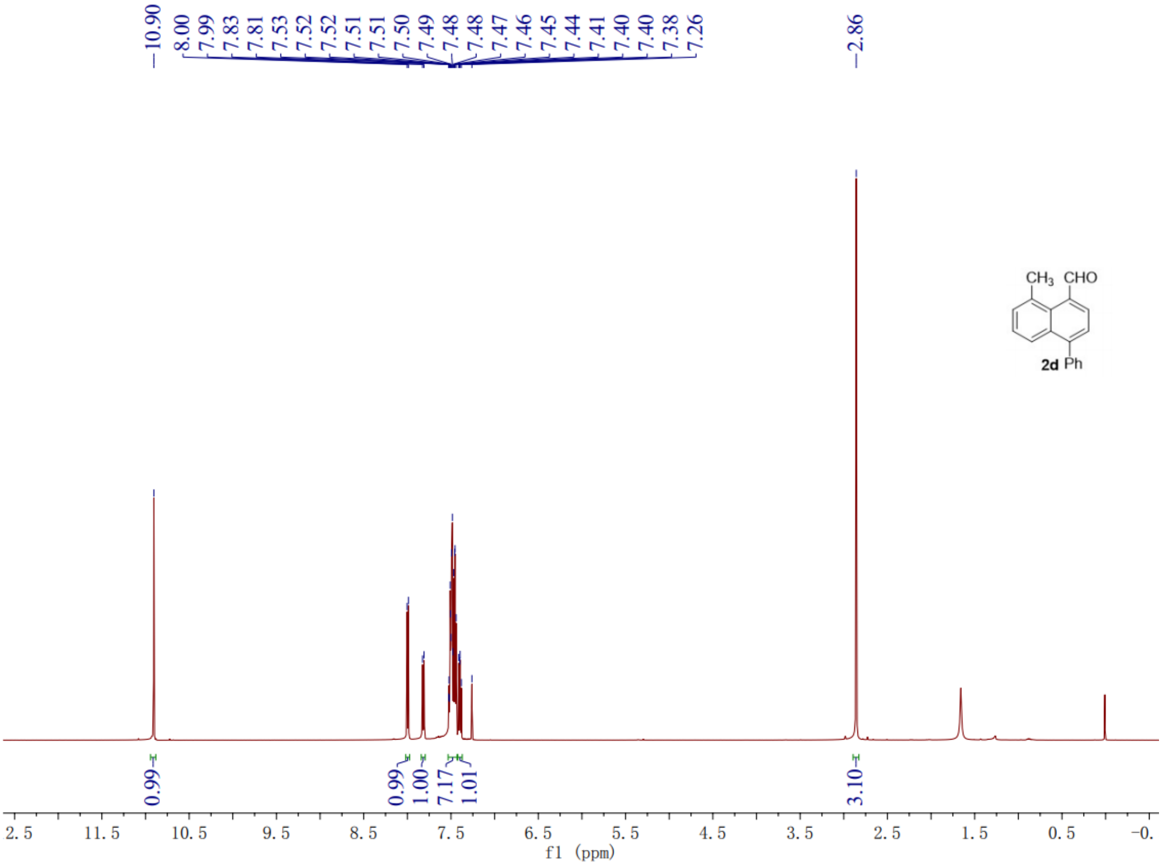


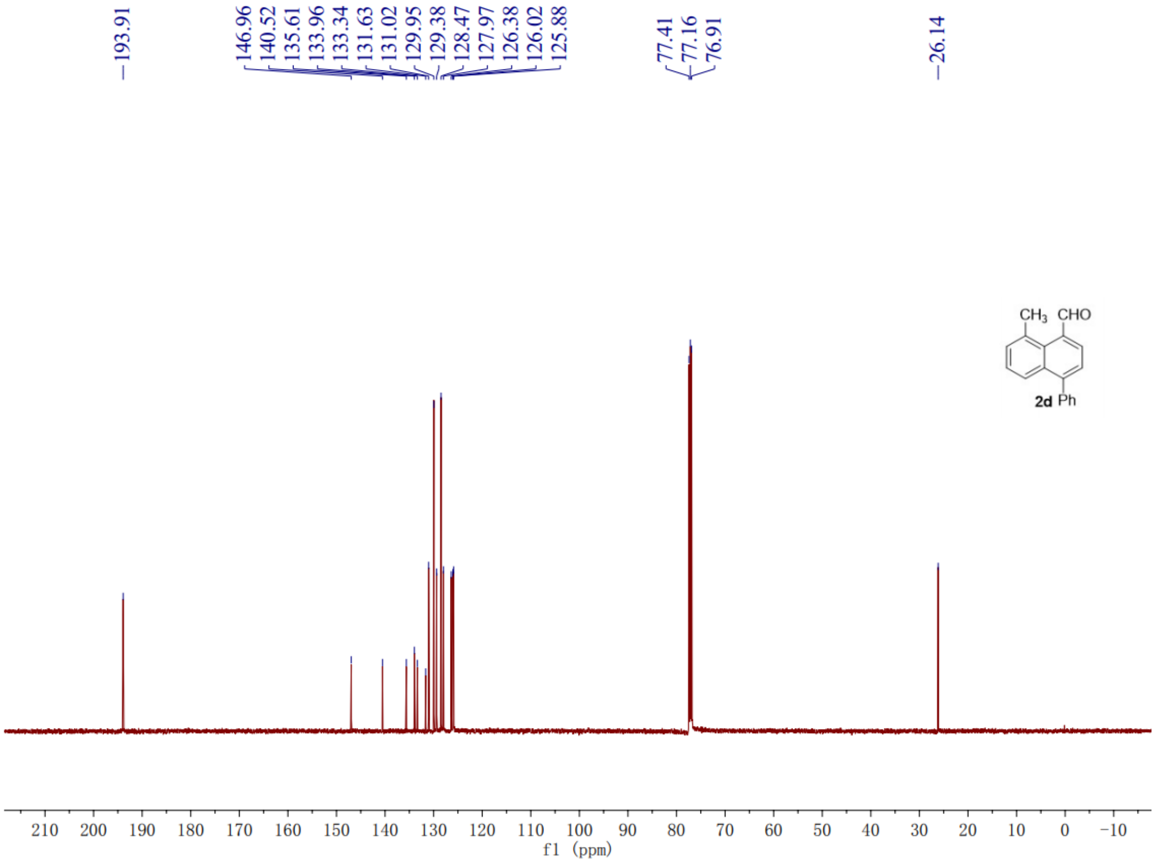
HR-ESI-MS $(M+H)^+$ of 2c



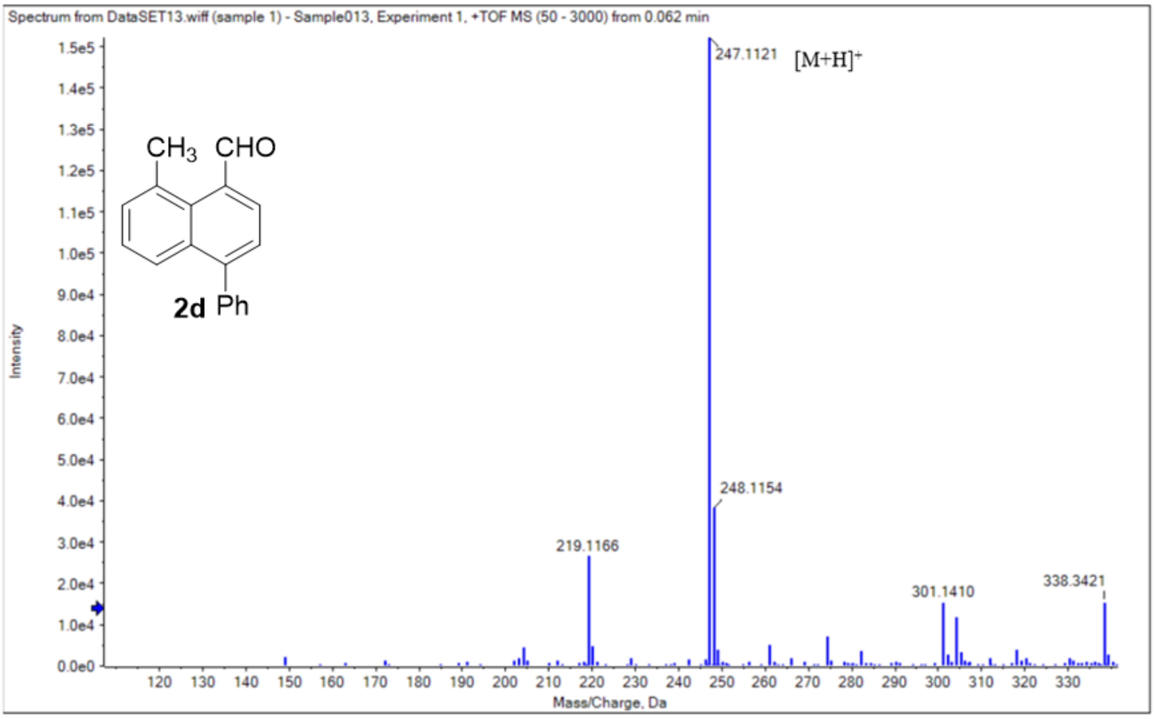
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2d



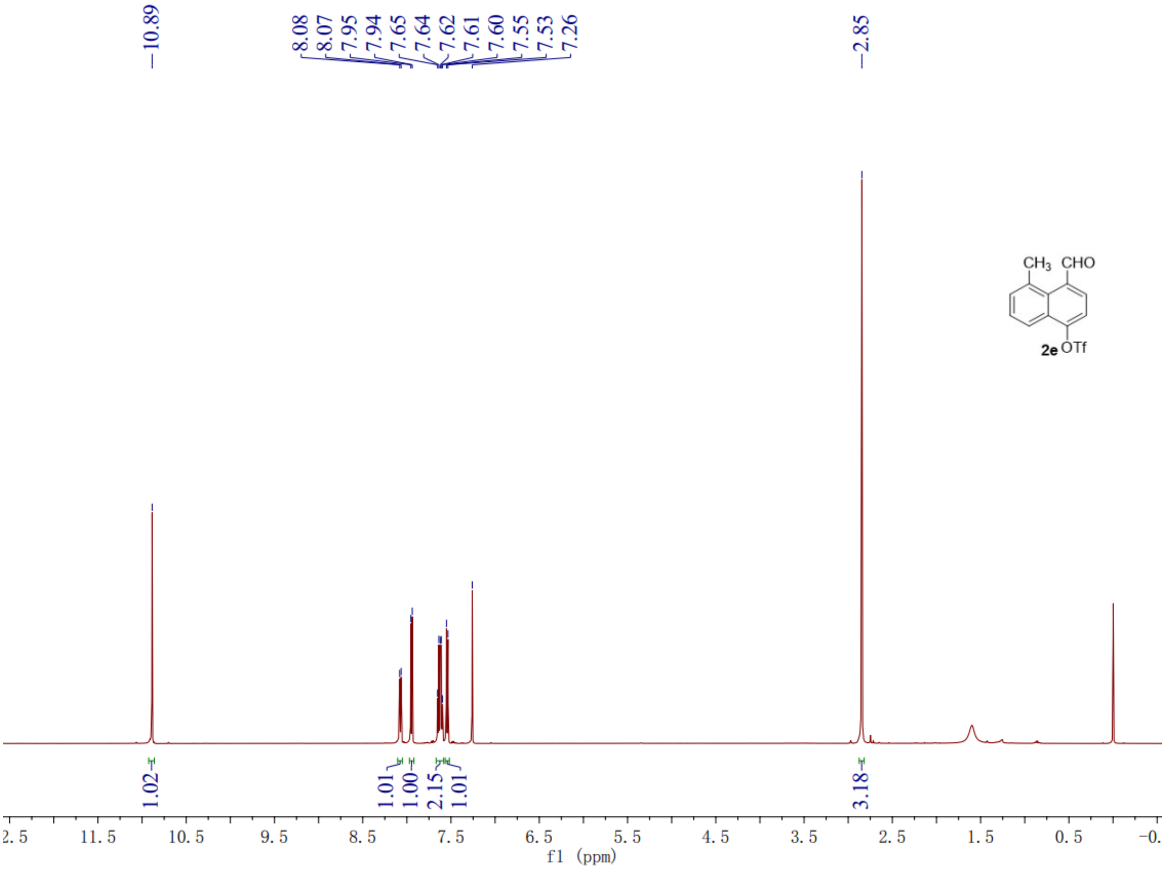
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2d



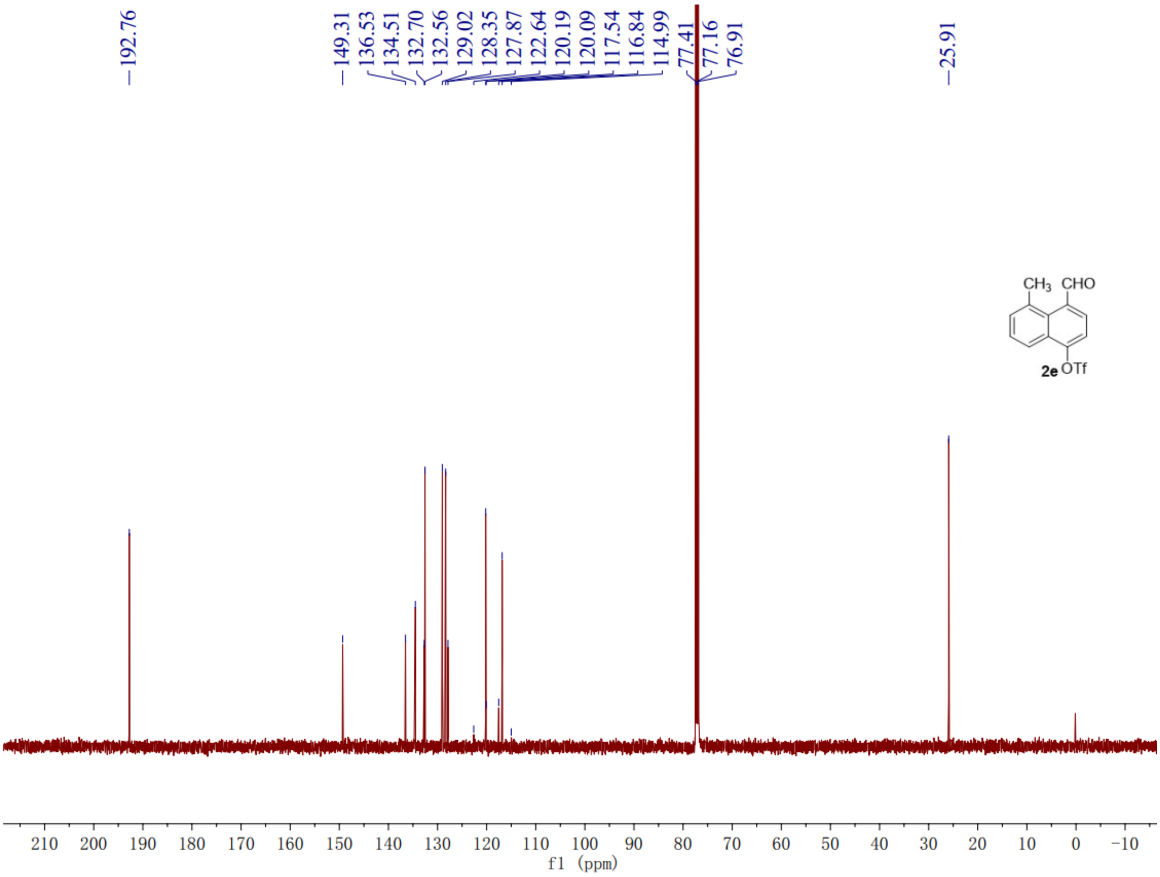
HR-ESI-MS (M+H)$^+$ of 2d



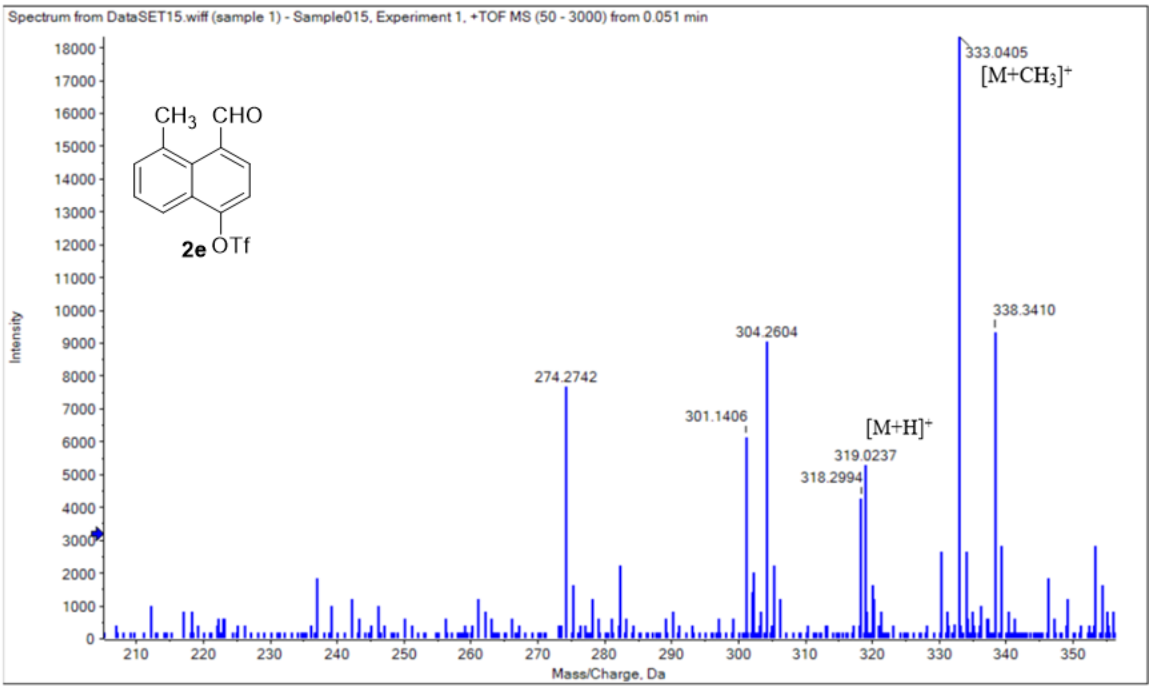
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2e



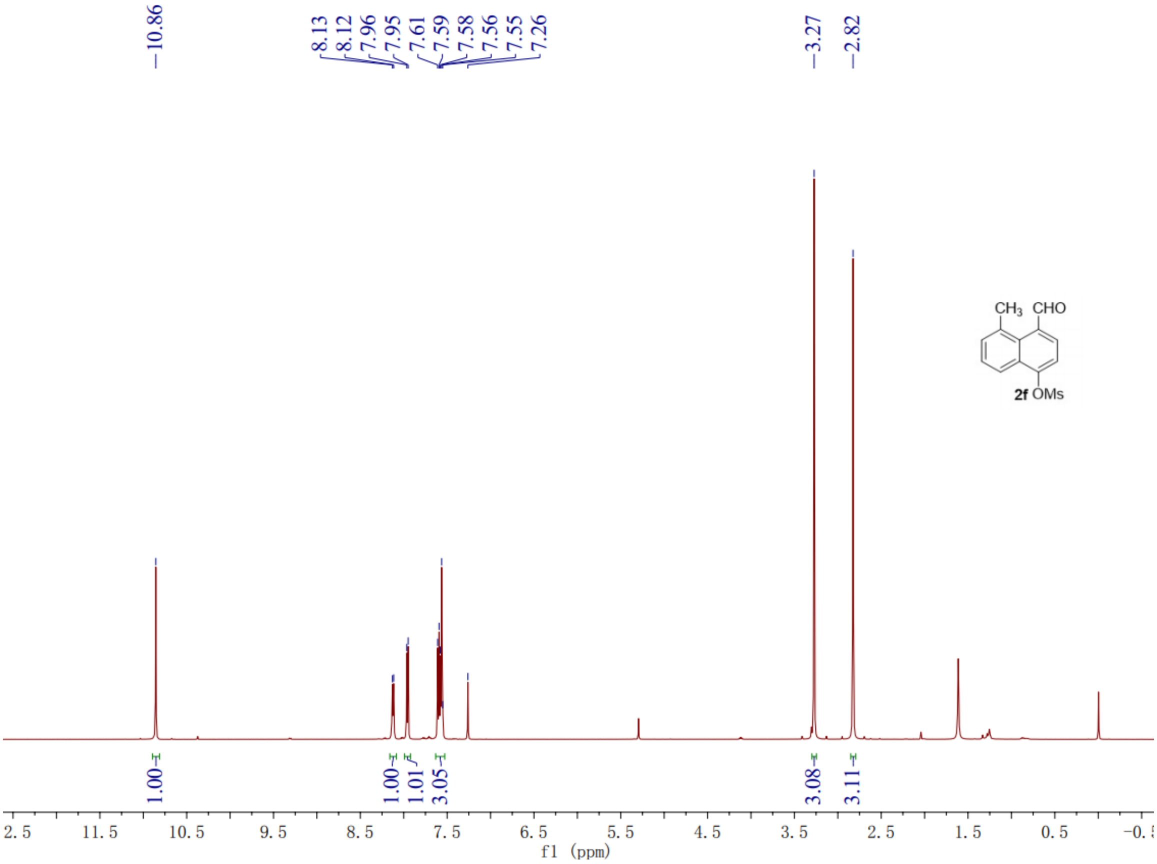
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2e



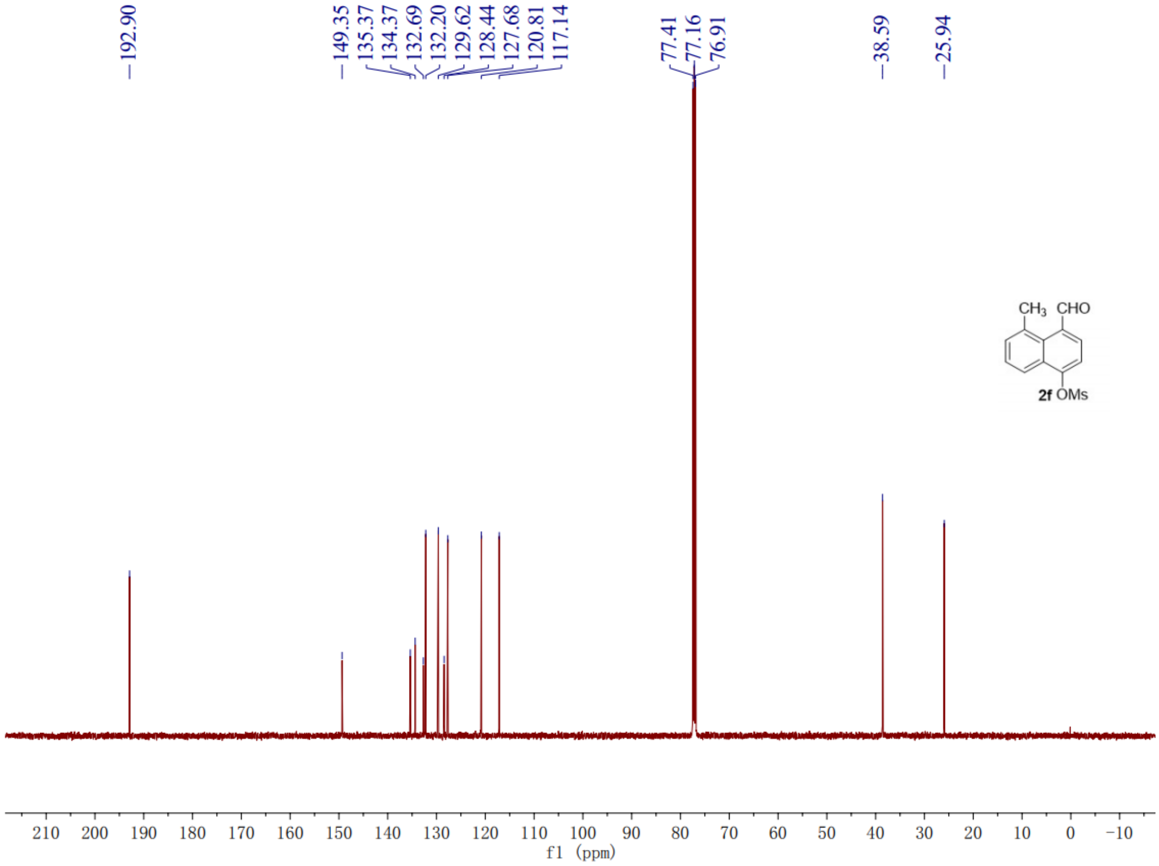
HR-ESI-MS (M+CH$_3$)$^+$ of 2e



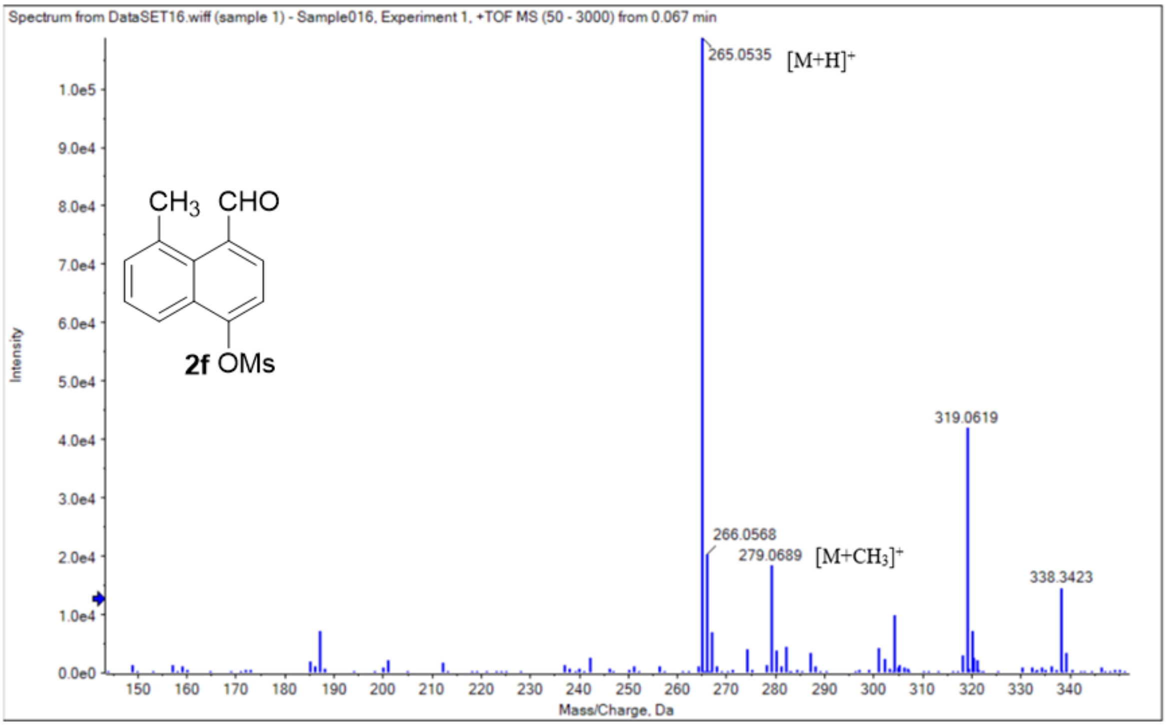
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2f



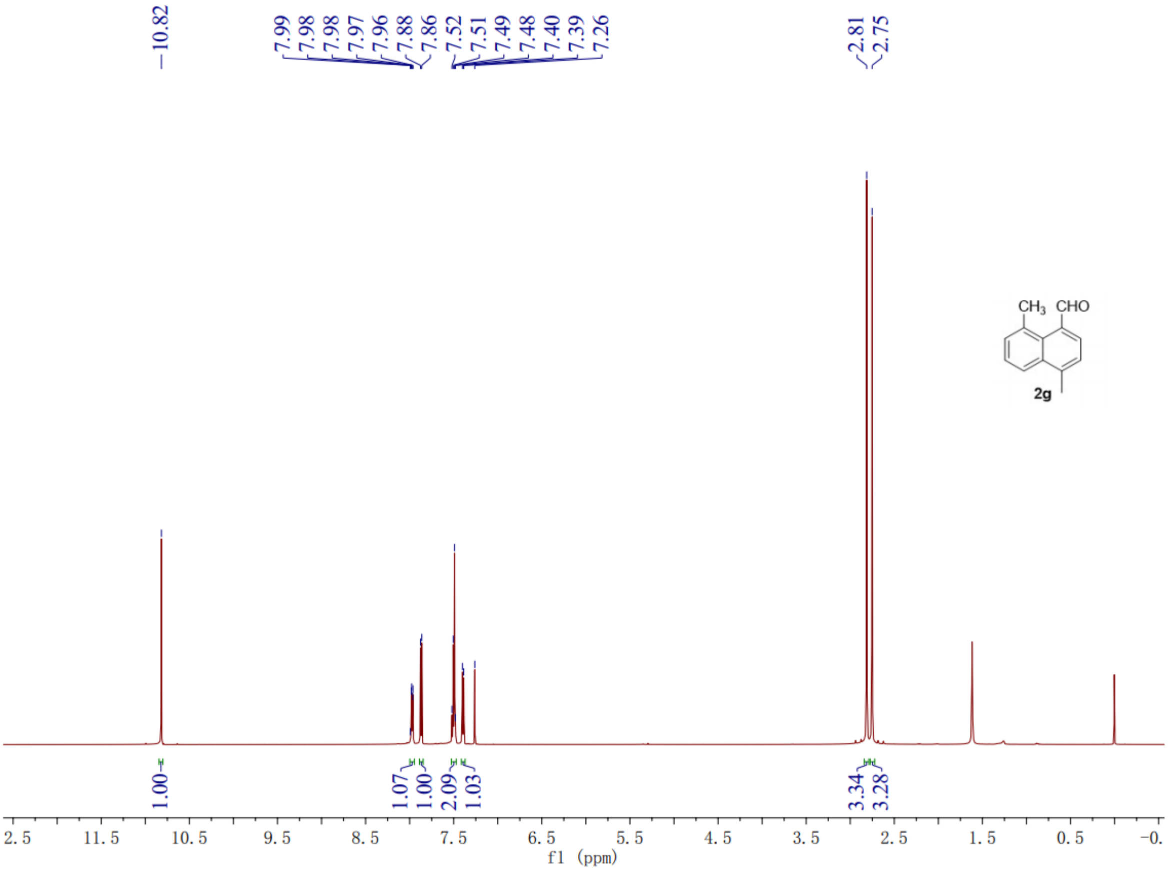
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2f



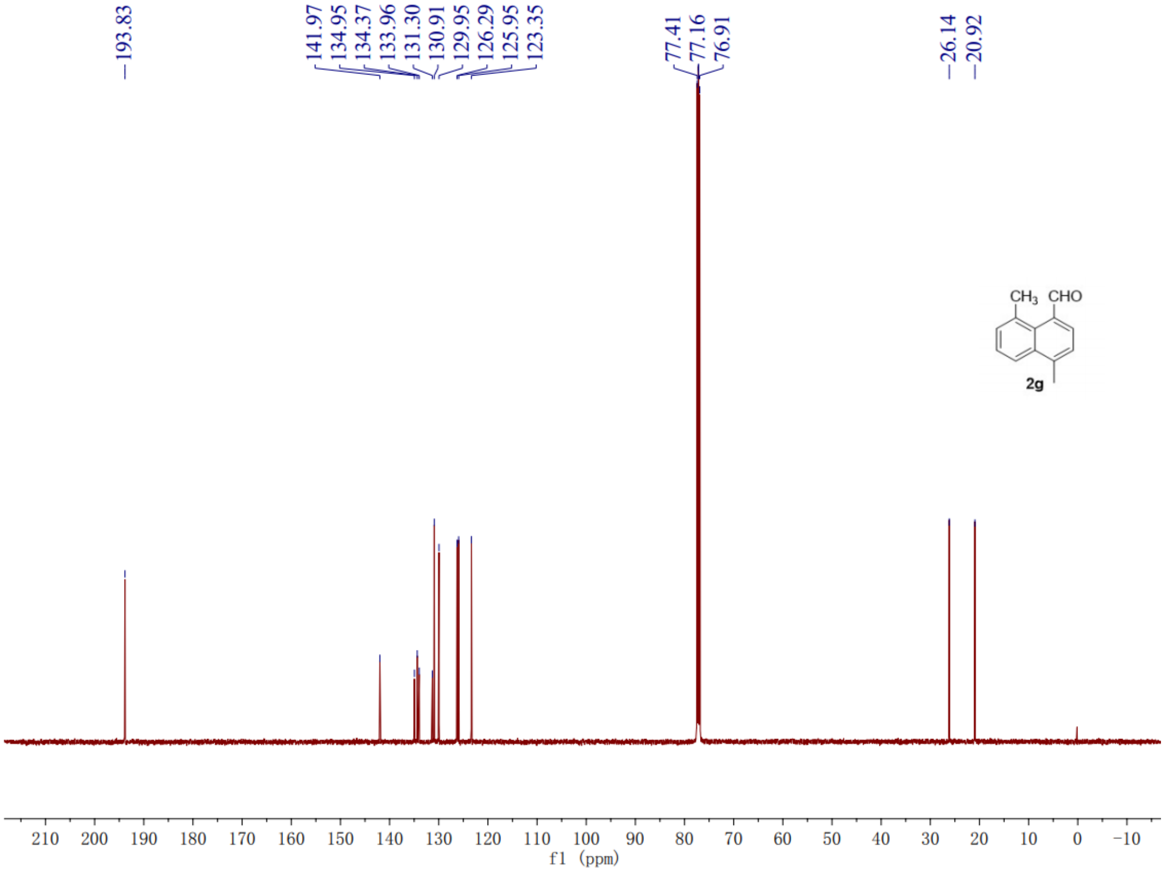
HR-ESI-MS $(M+H)^+$ of 2f



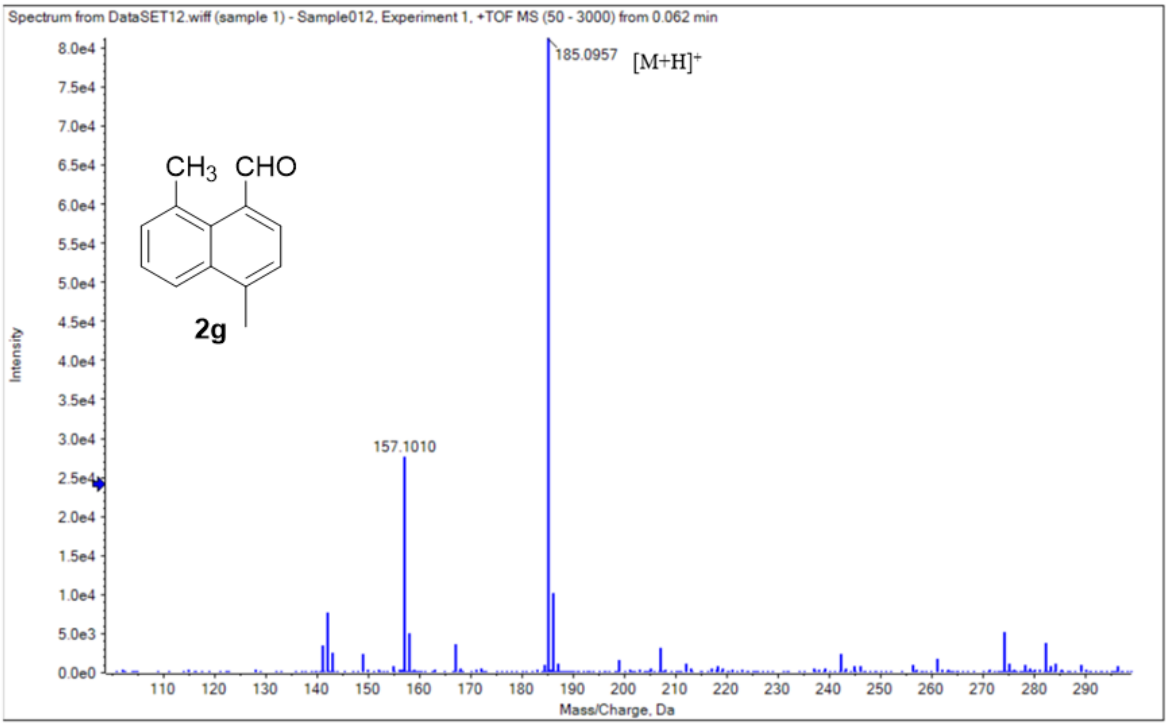
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2g



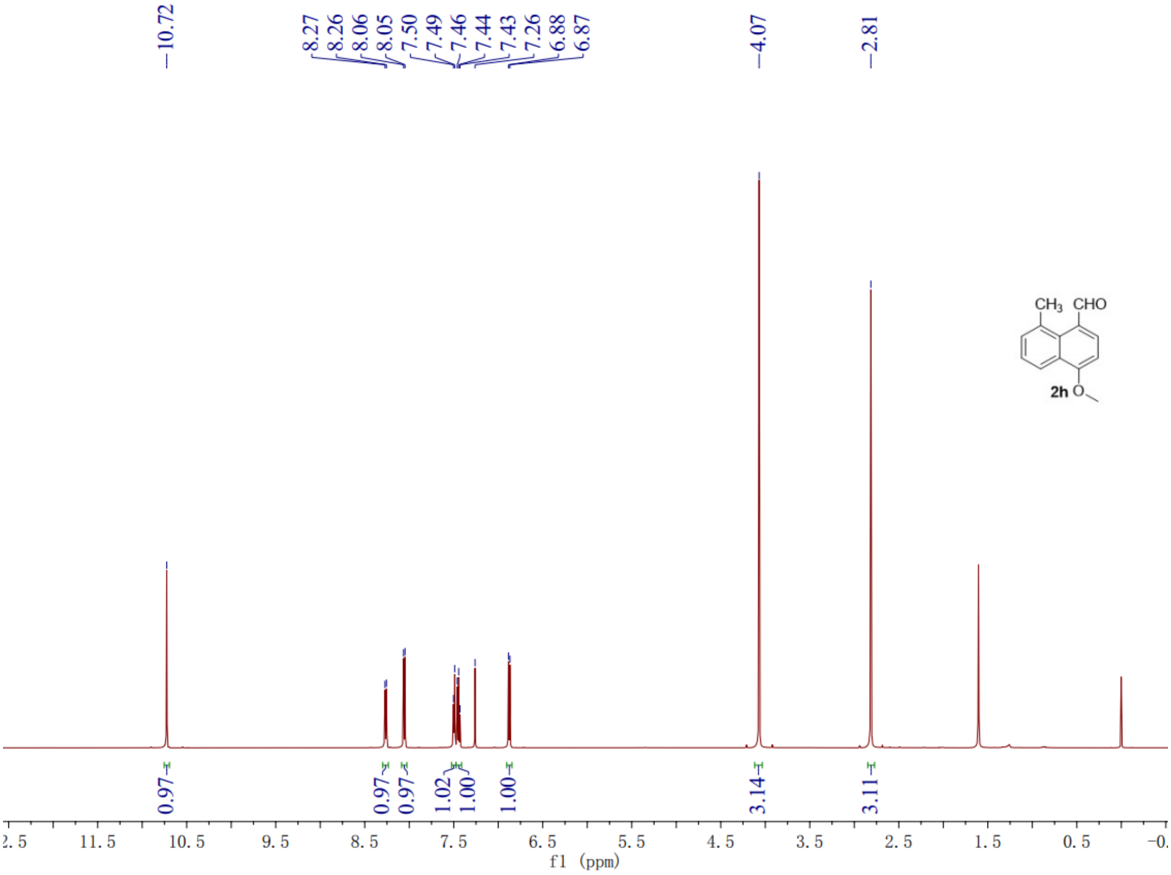
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 2g



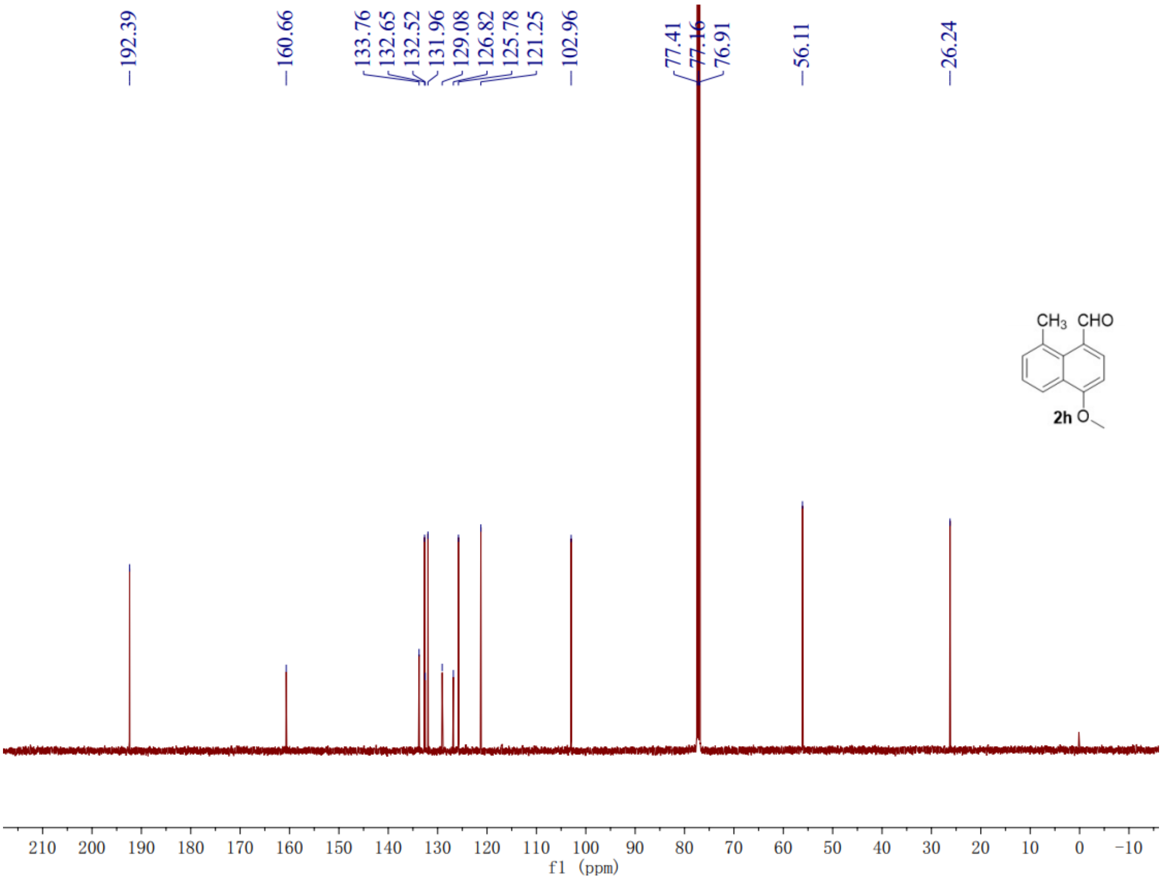
HR-ESI-MS $(M+H)^+$ of 2g



^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2h



^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2h



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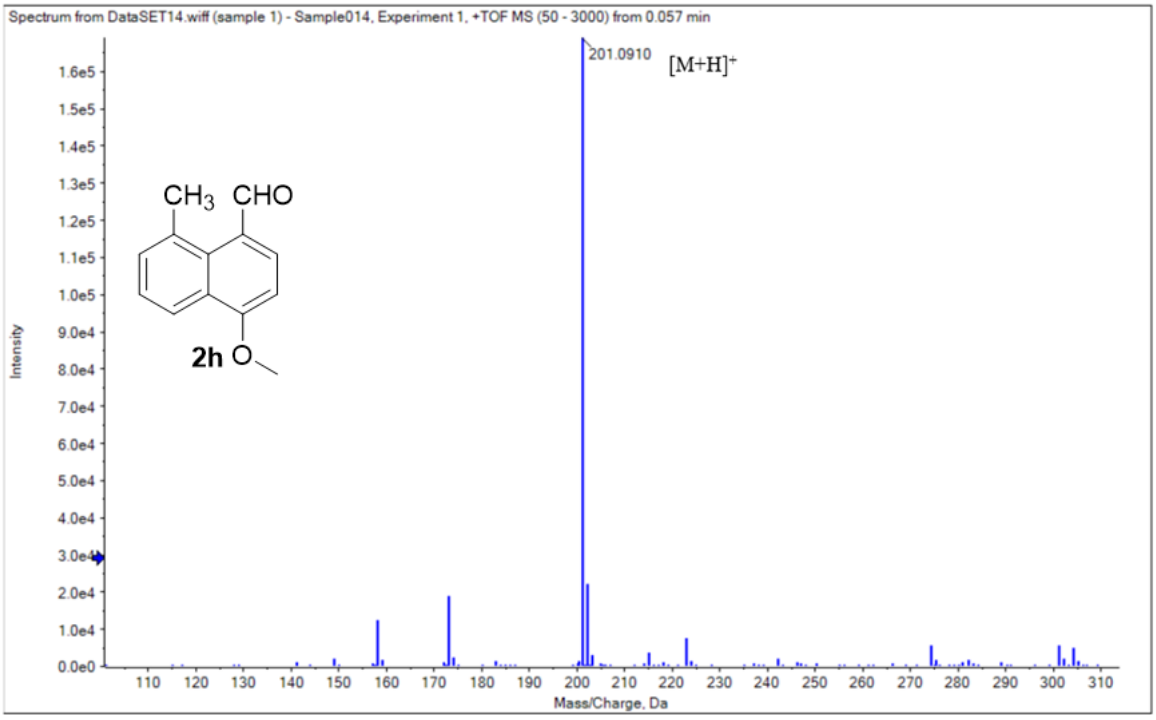
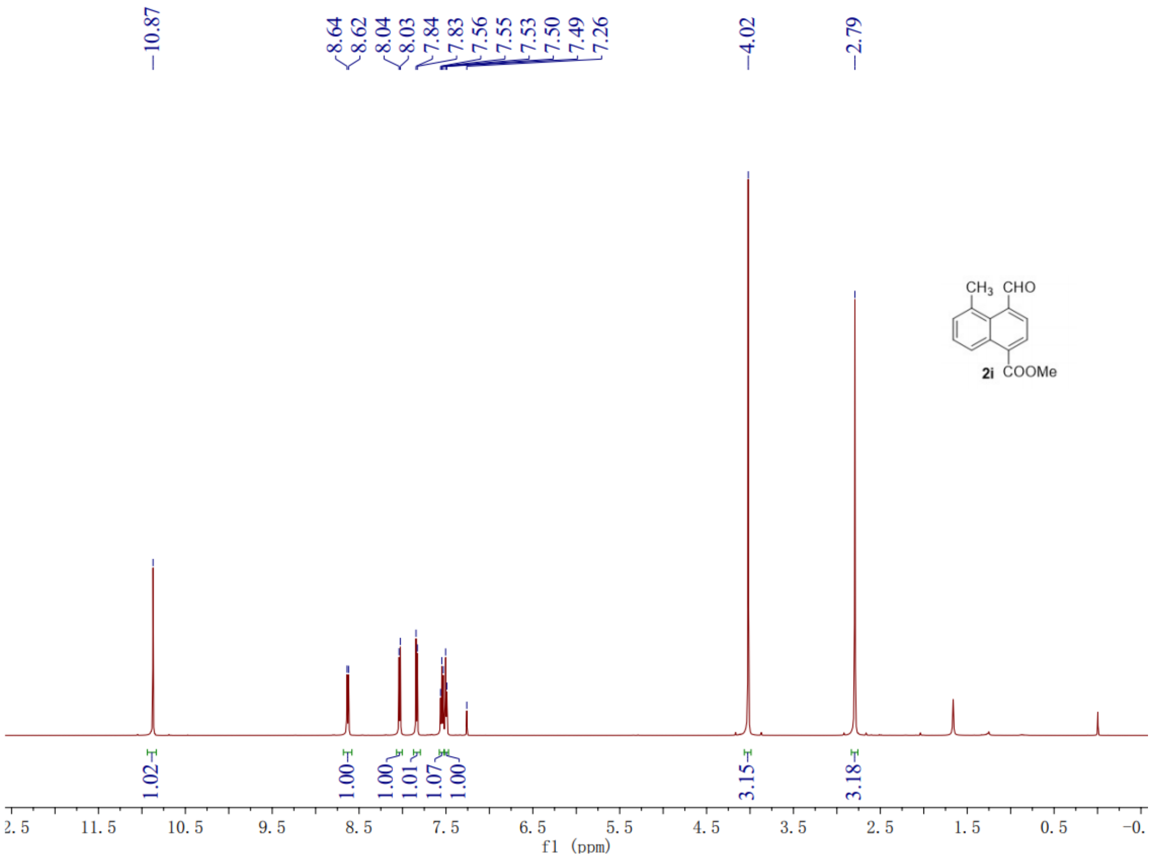
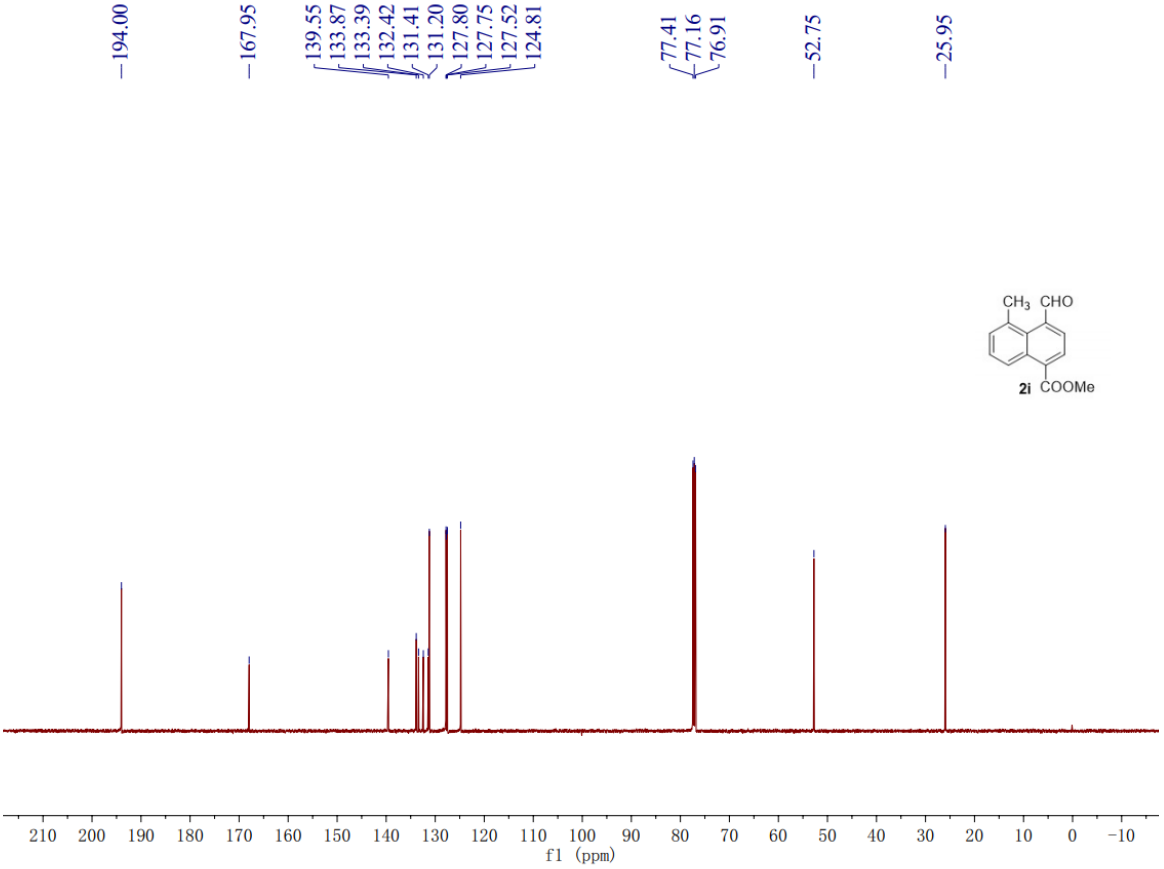


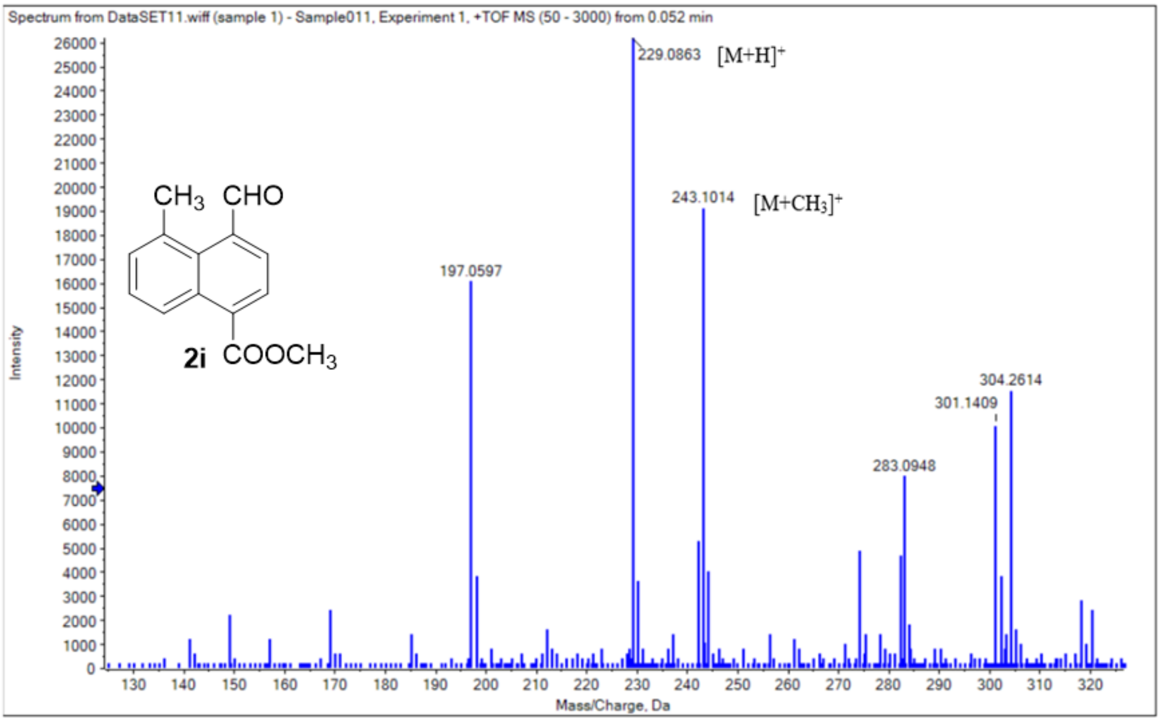
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2i



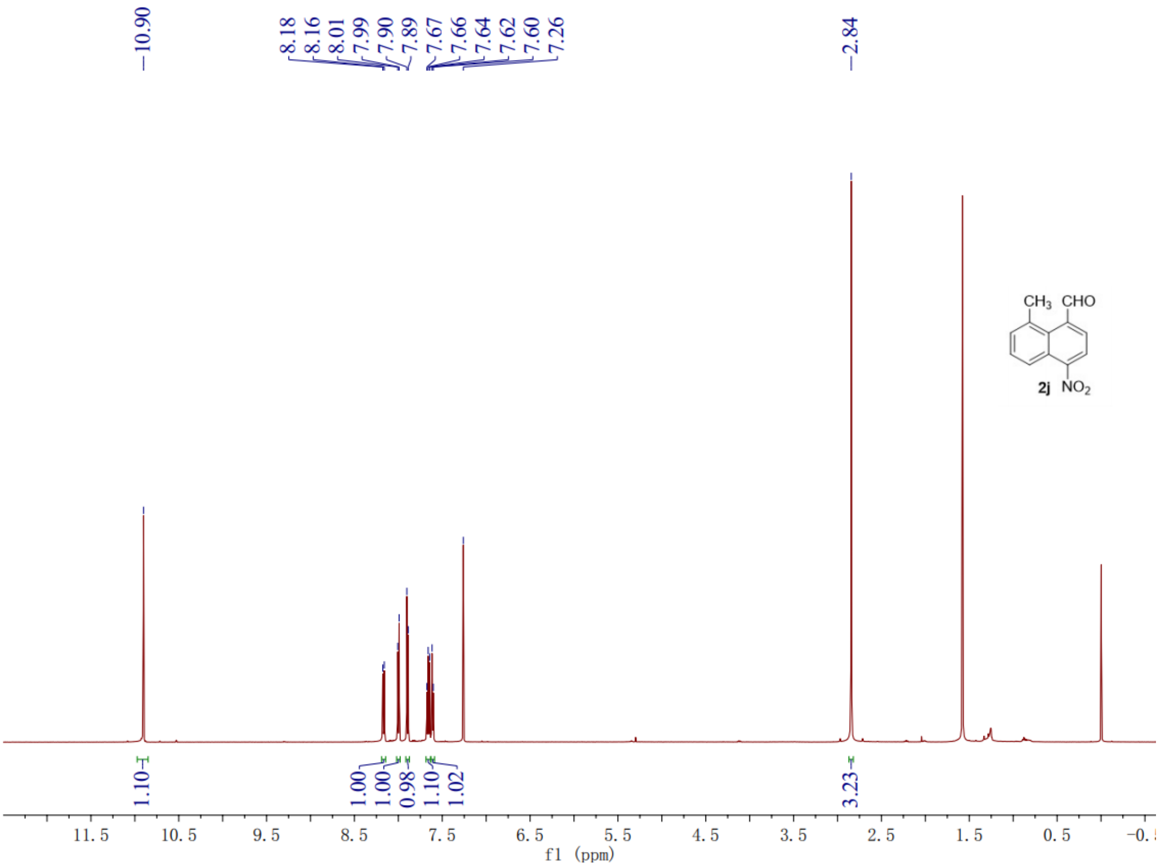
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2i



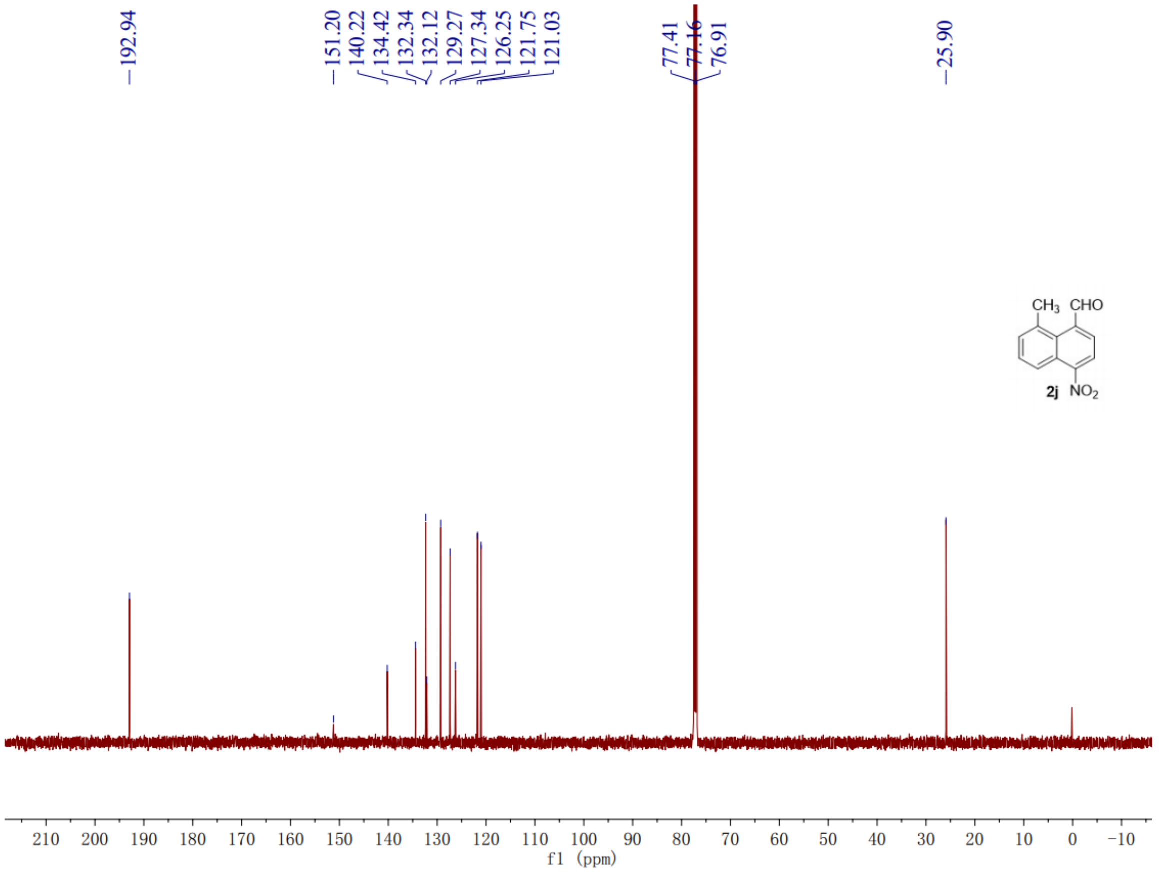
HR-ESI-MS (M+H)$^+$ of 2i



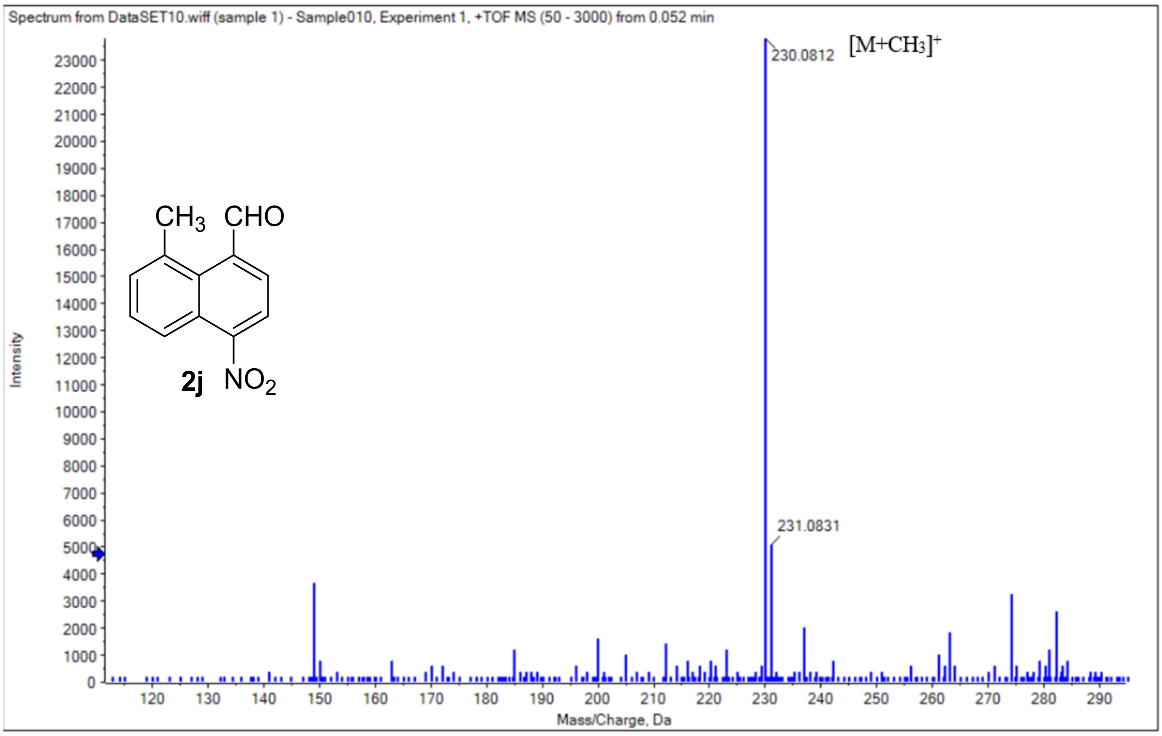
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2j



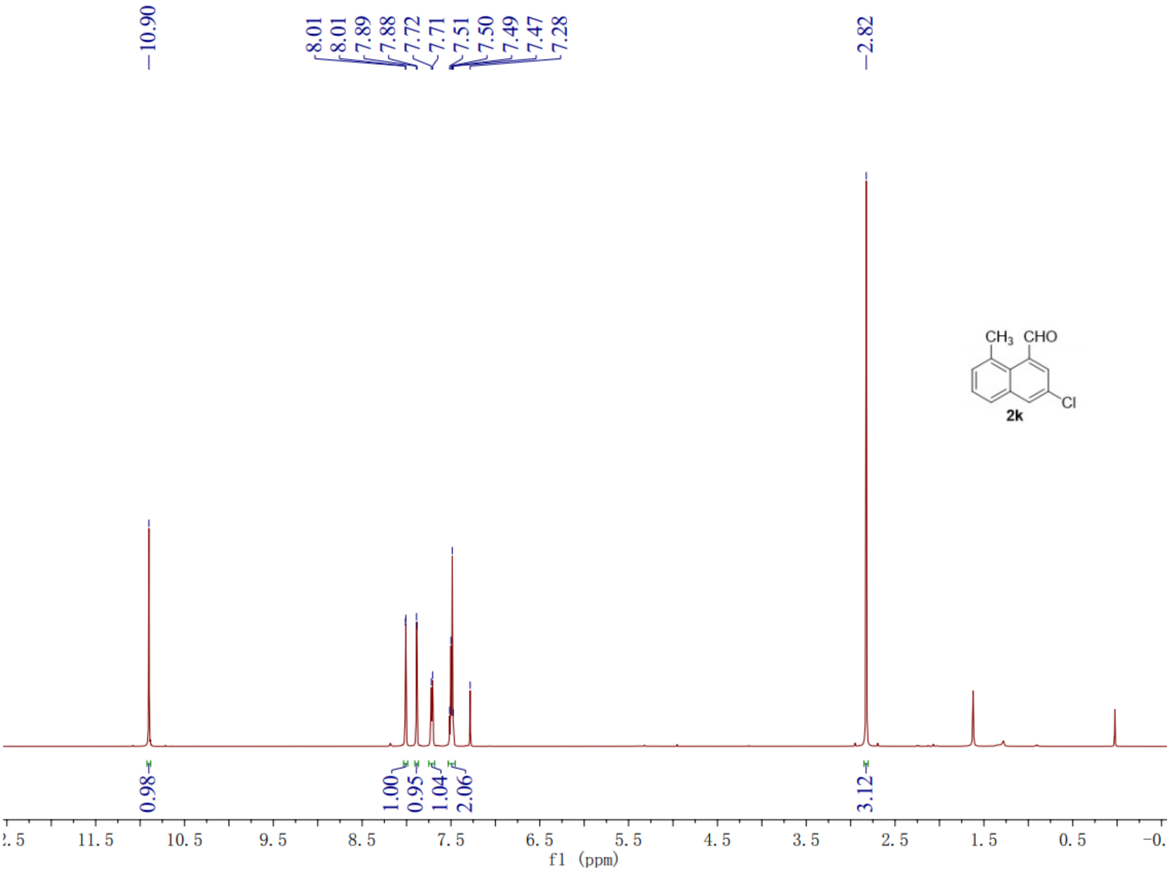
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2j



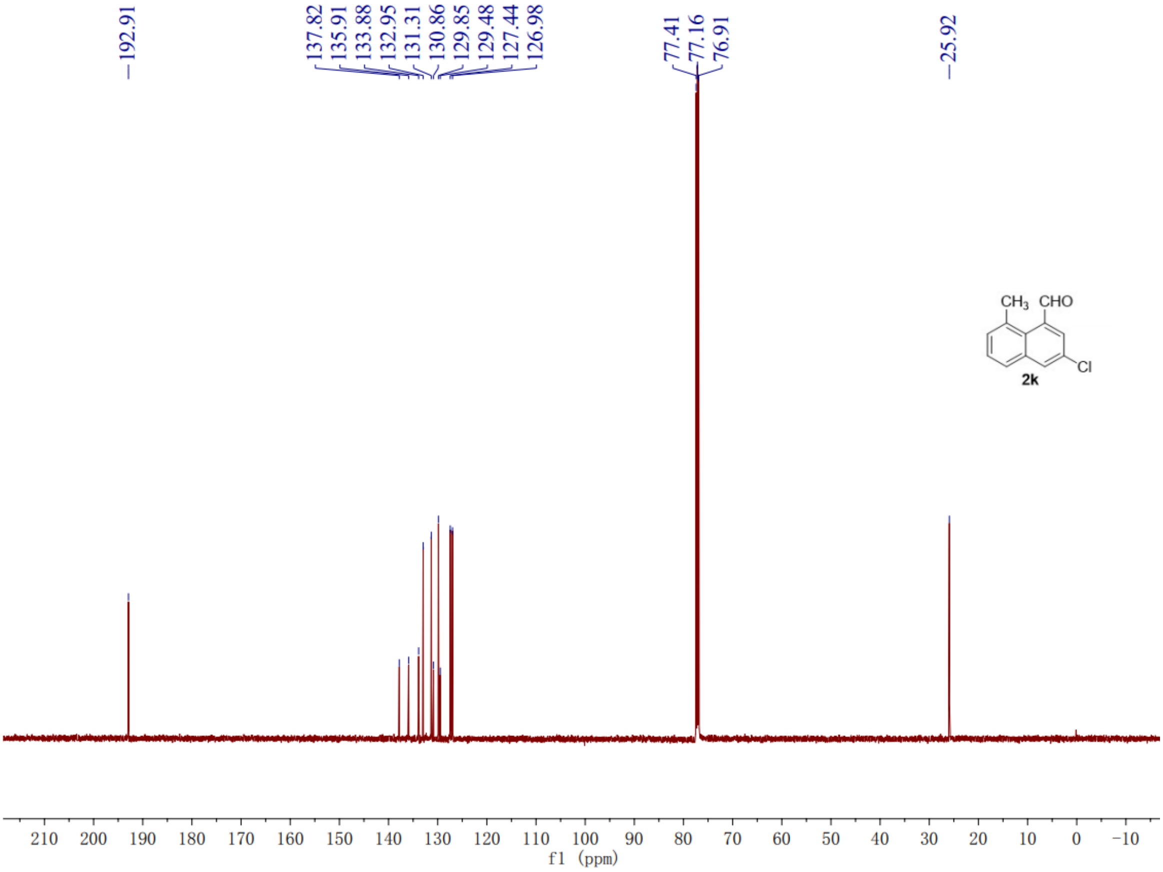
HR-ESI-MS $(M+CH_3)^+$ of 2j



^1H NMR spectrum ($CDCl_3$, 500 MHz) of 2k



^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2k



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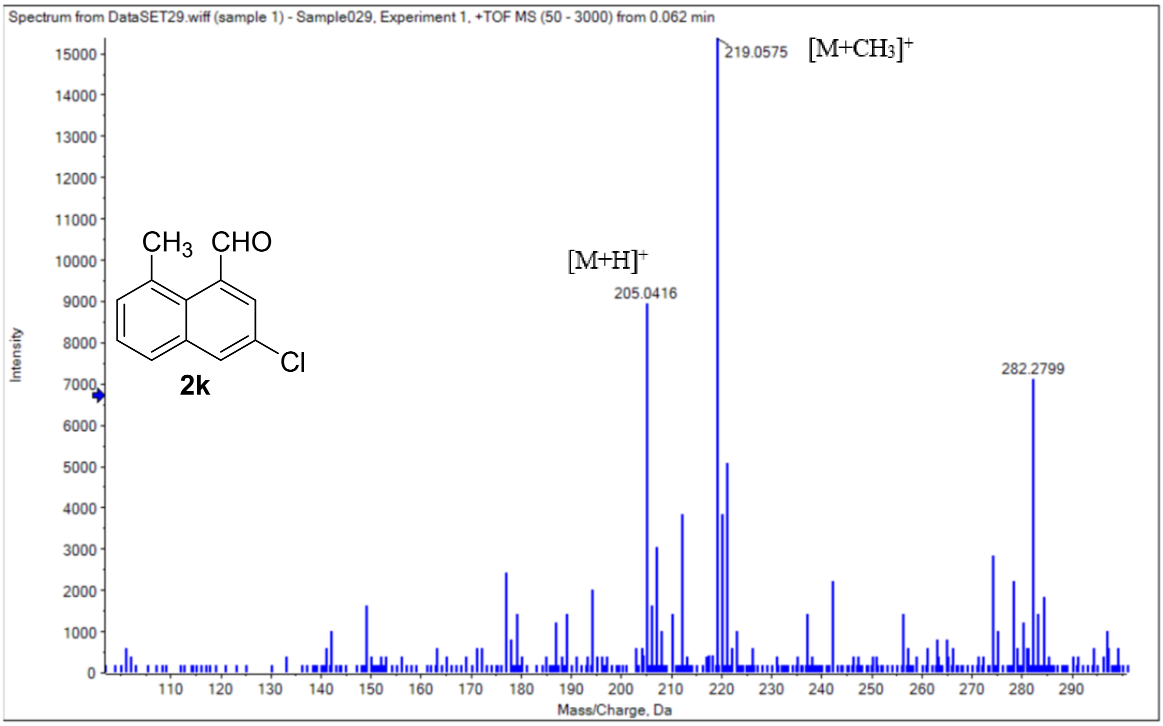
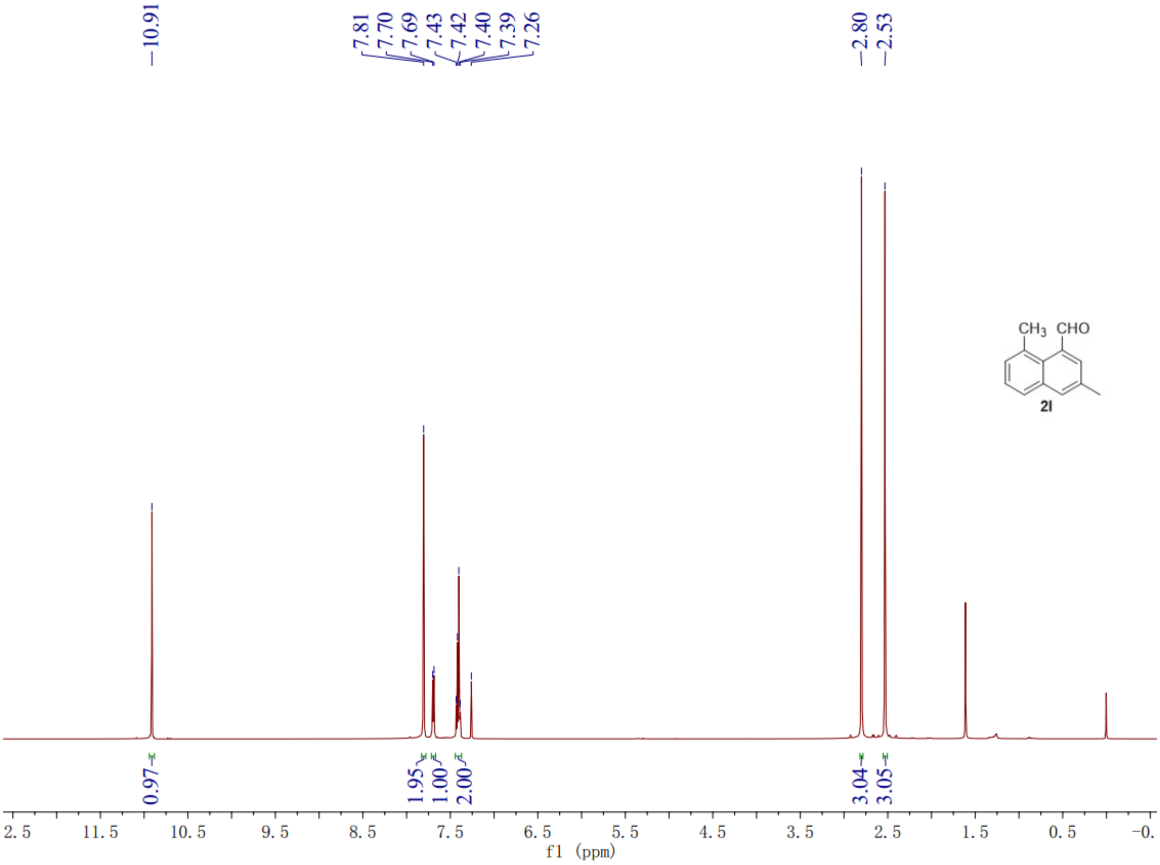
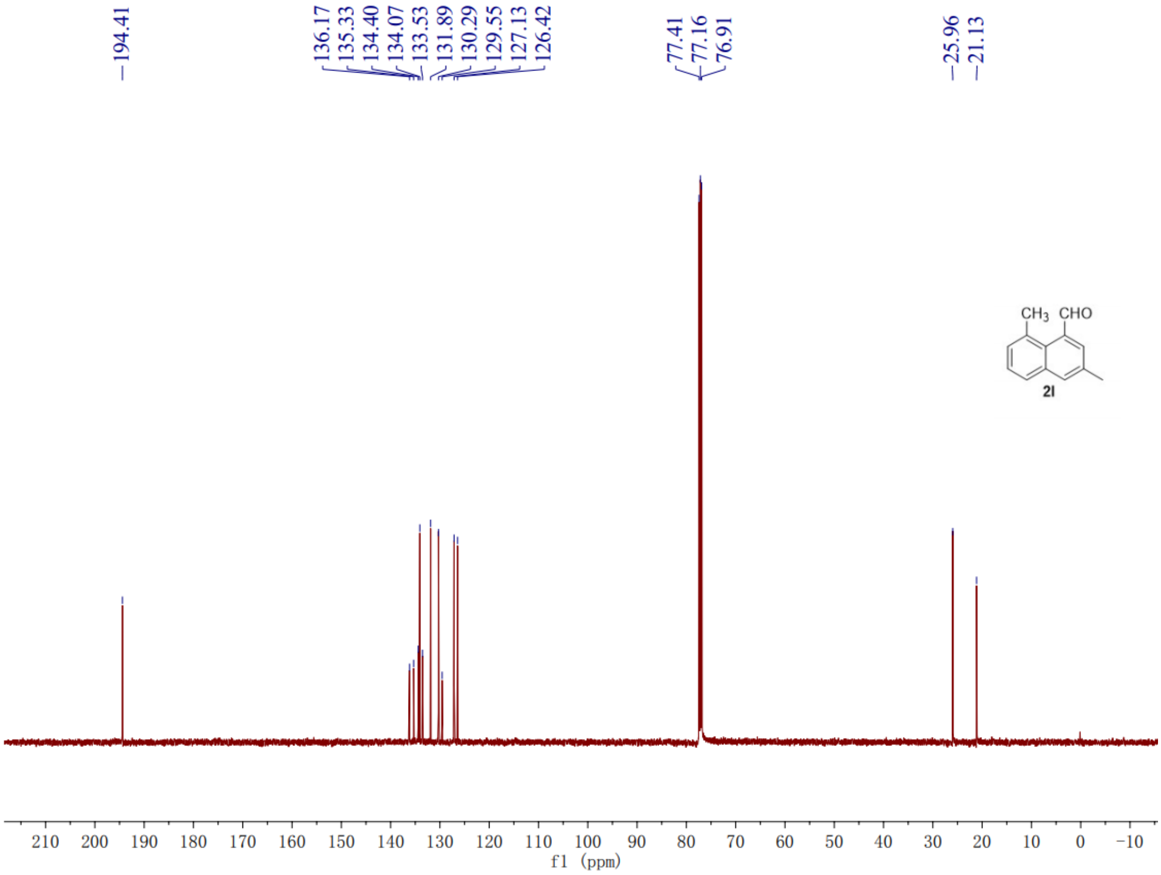


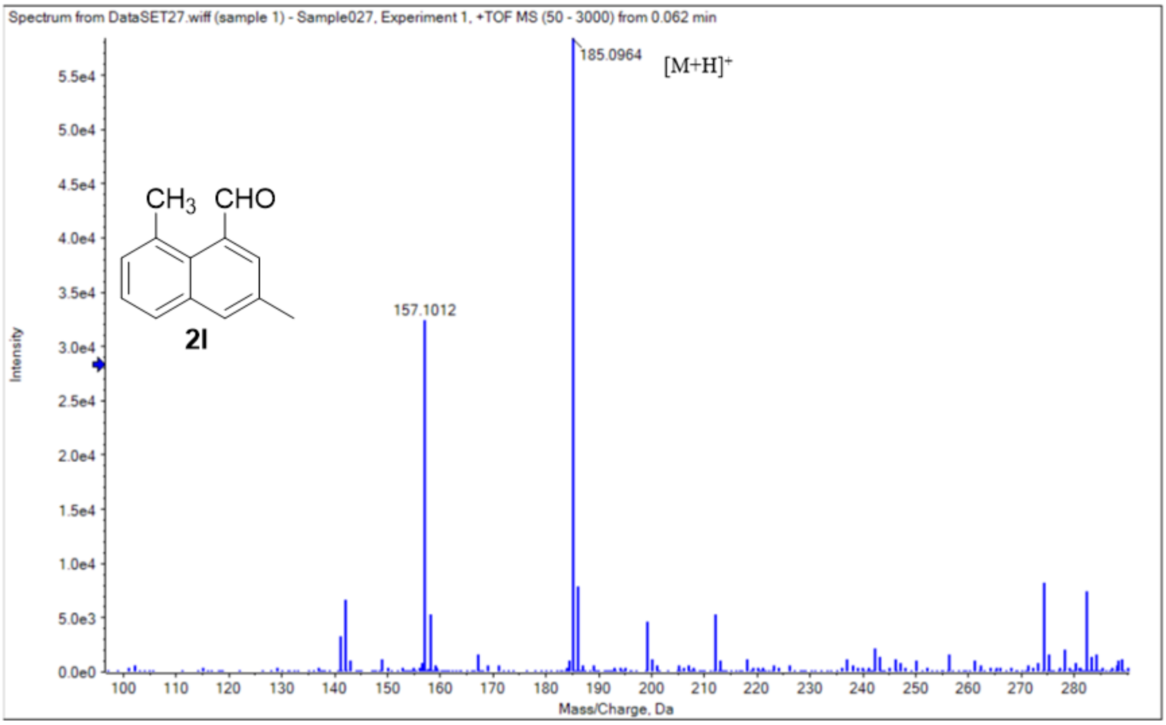
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2l



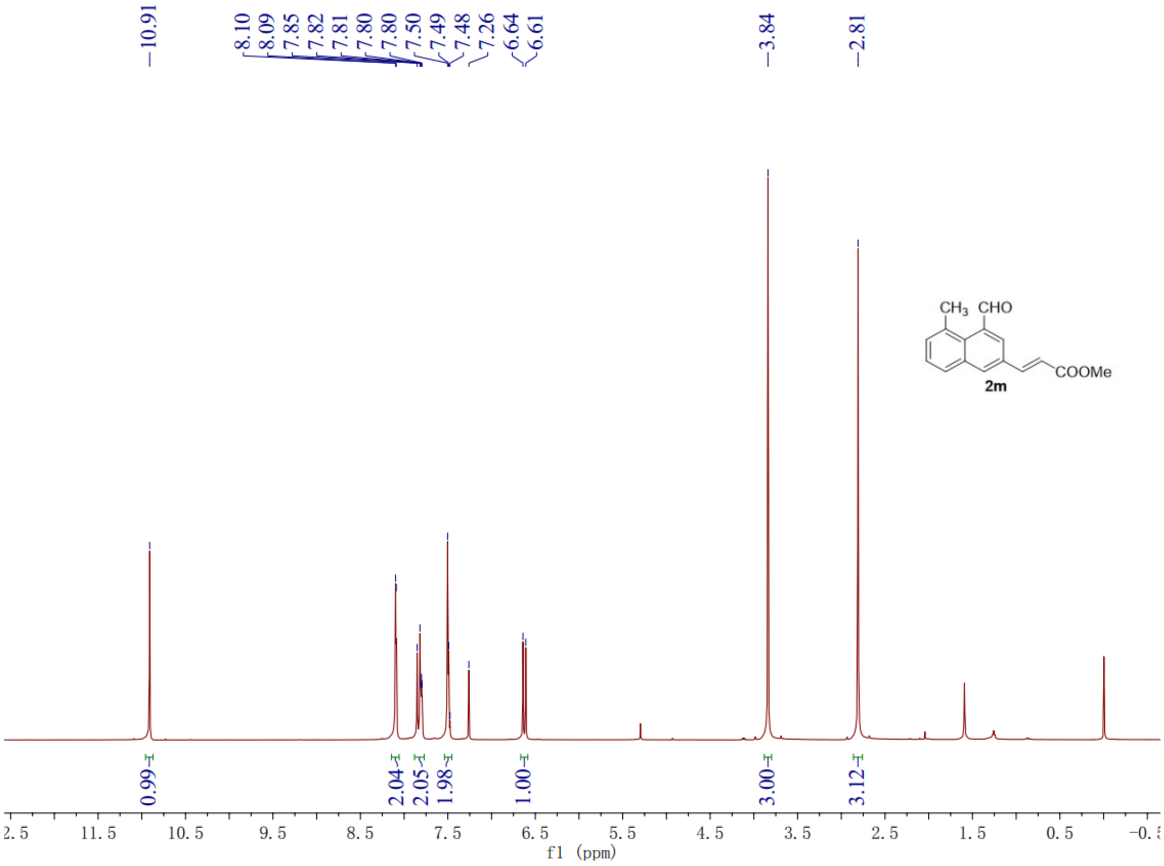
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2l



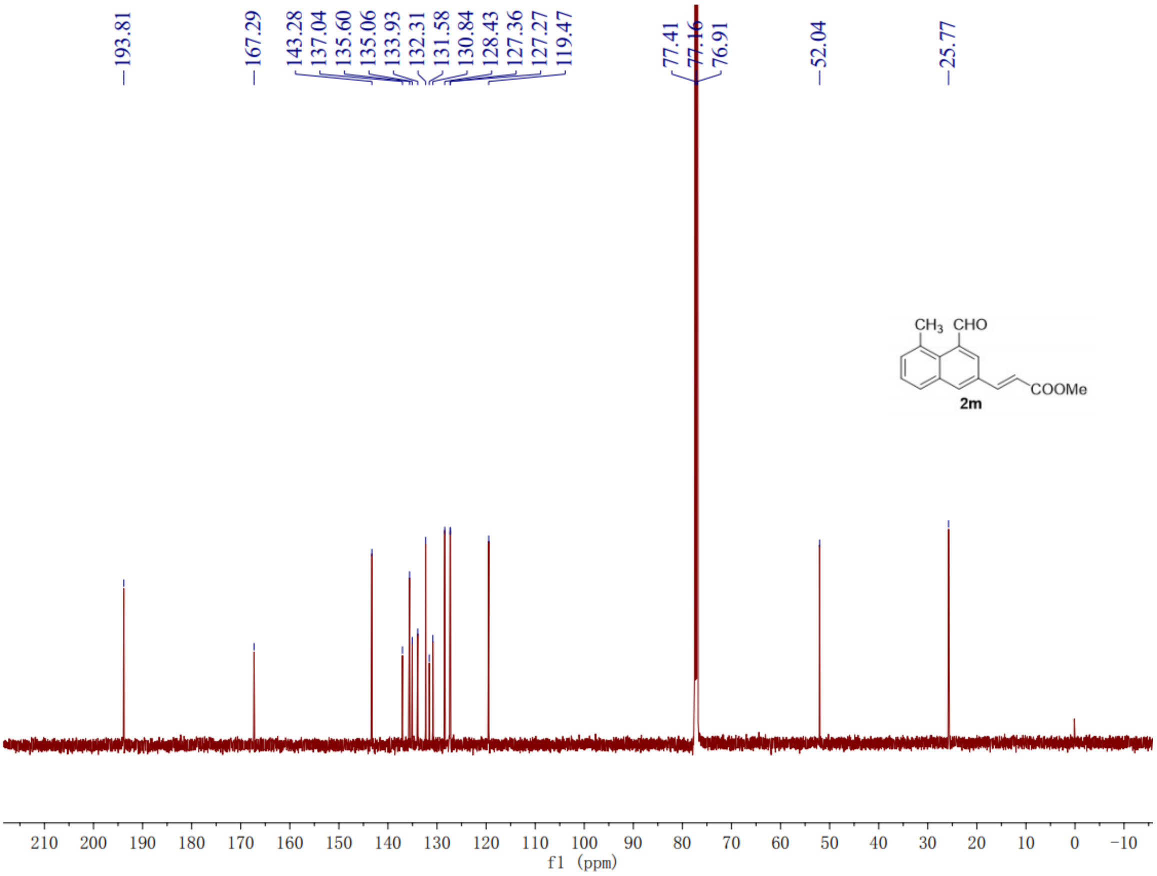
HR-ESI-MS $(M+H)^+$ of 2l



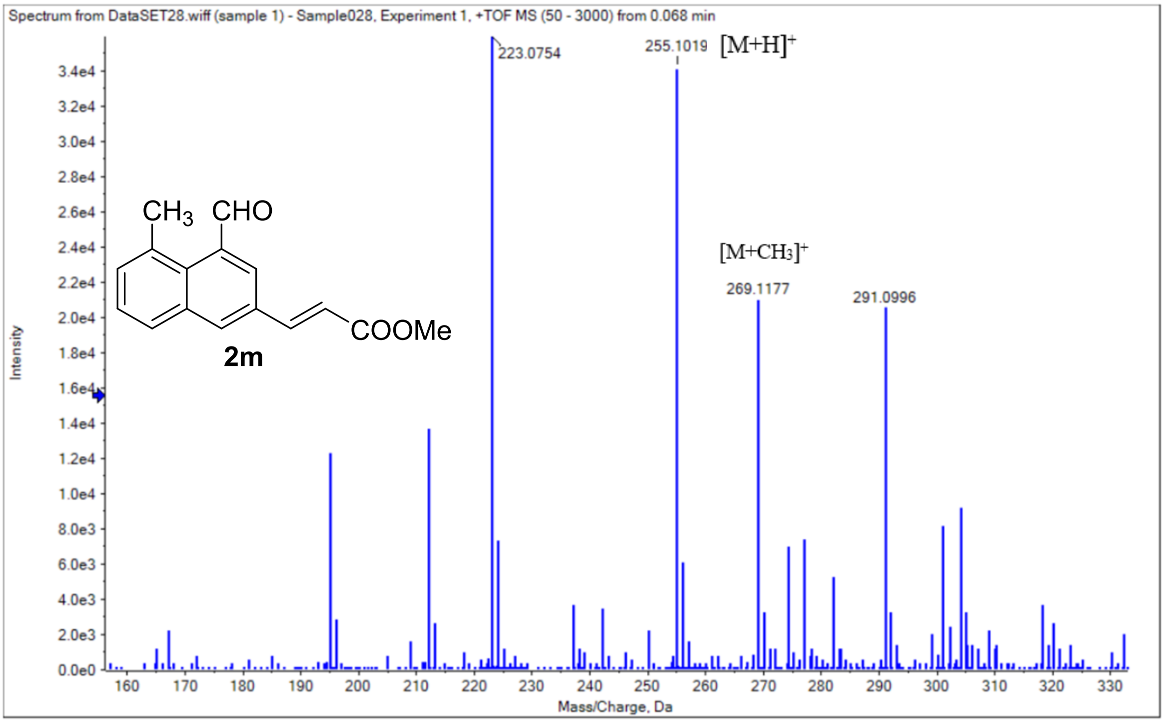
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2m



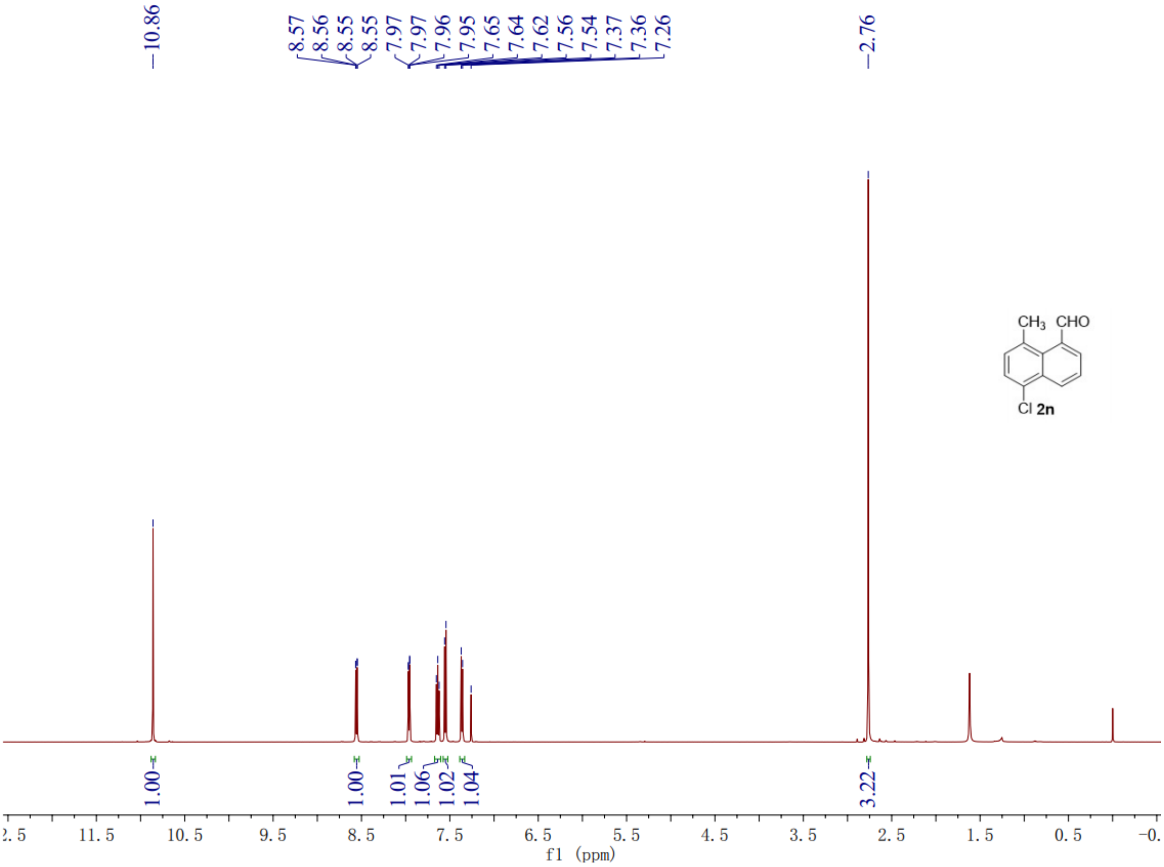
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2m



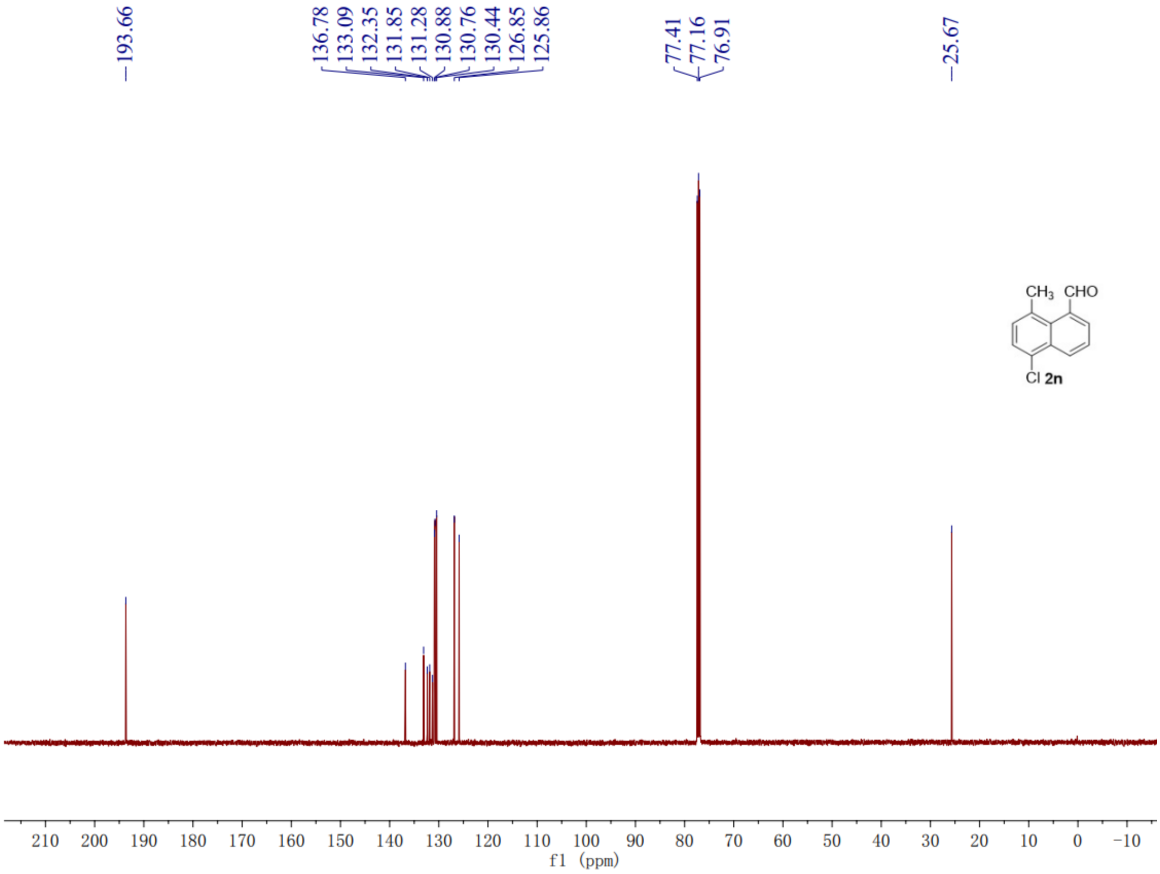
HR-ESI-MS (M+H)$^+$ of 2m



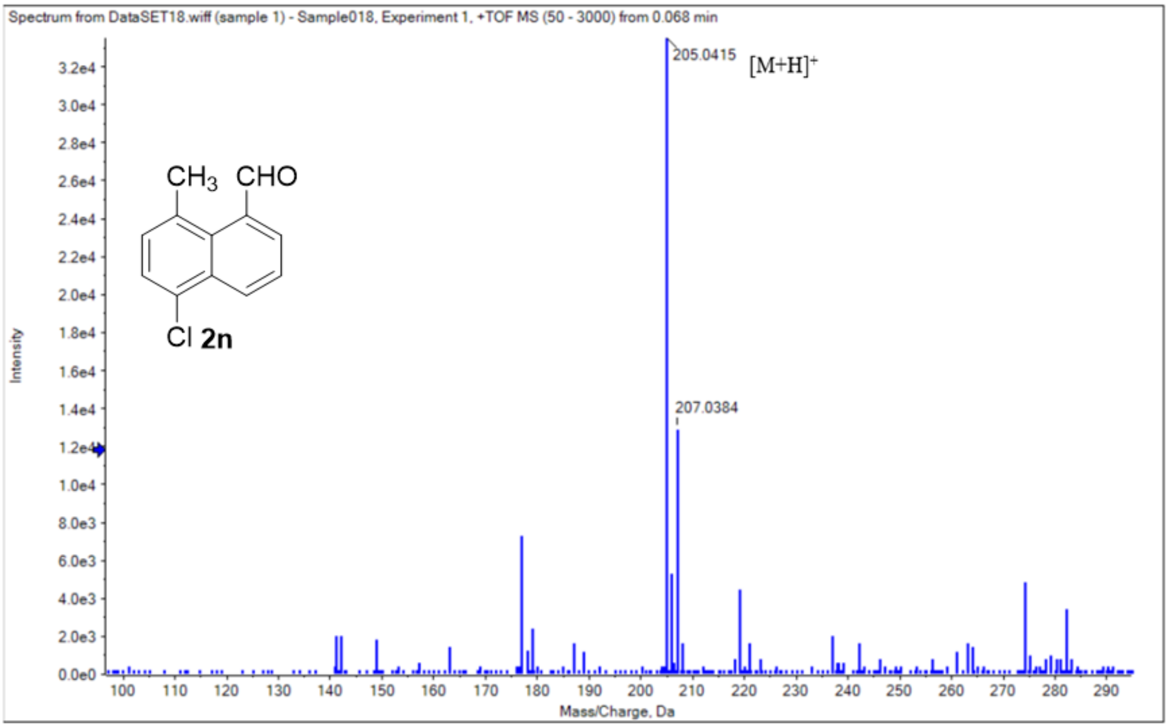
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2n



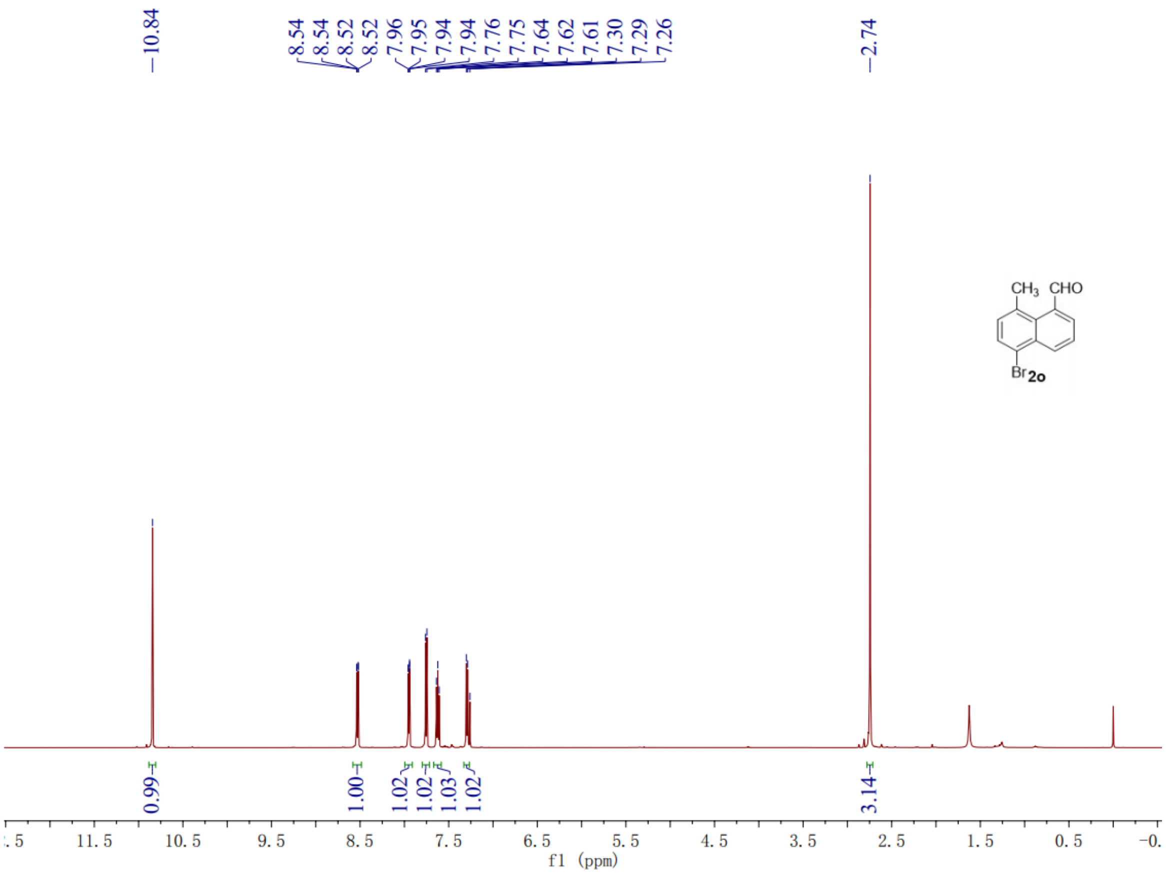
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2n



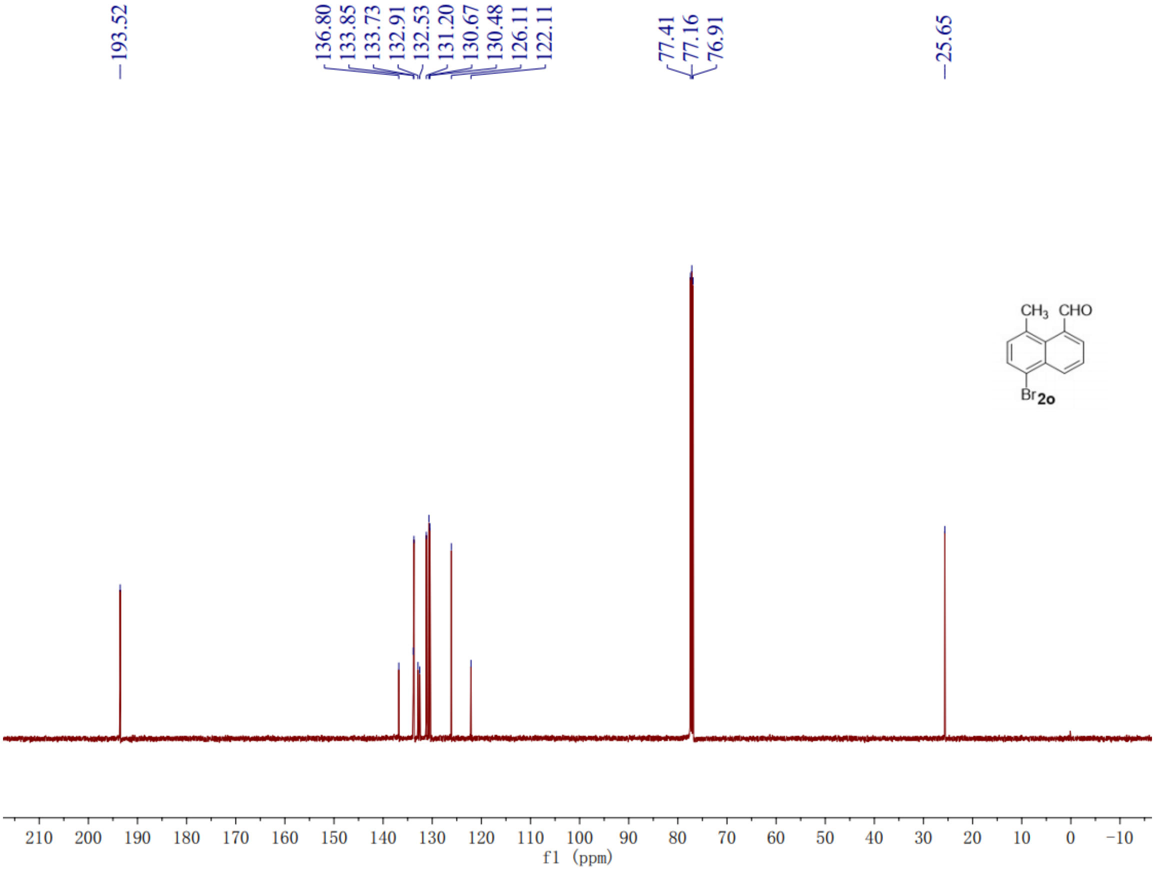
HR-ESI-MS $(M+H)^+$ of 2n



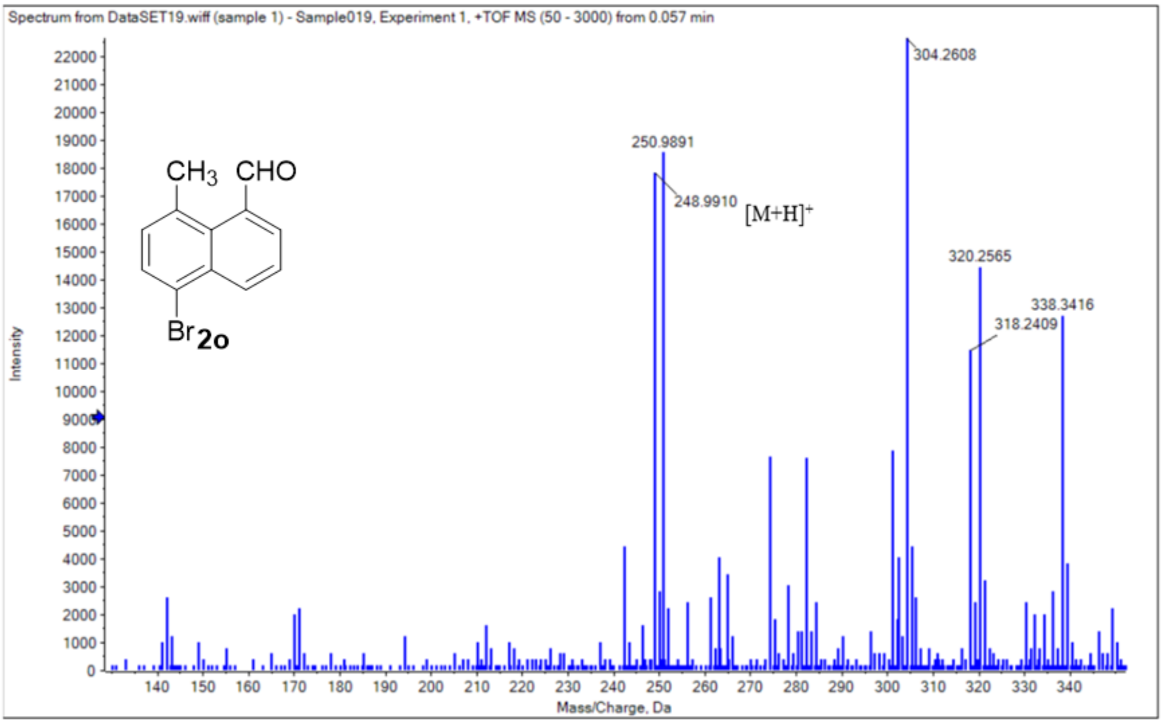
^1H NMR spectrum ($CDCl_3$, 500 MHz) of 2o



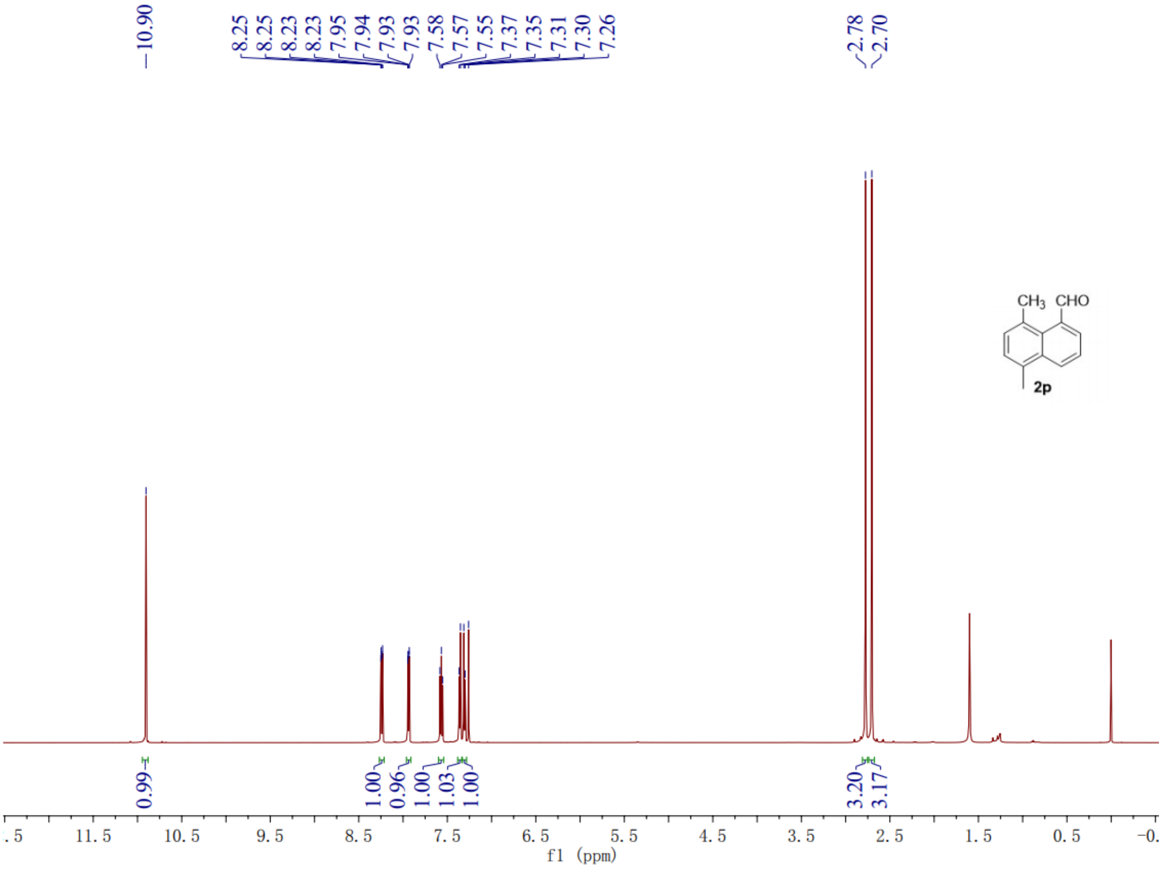
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2o



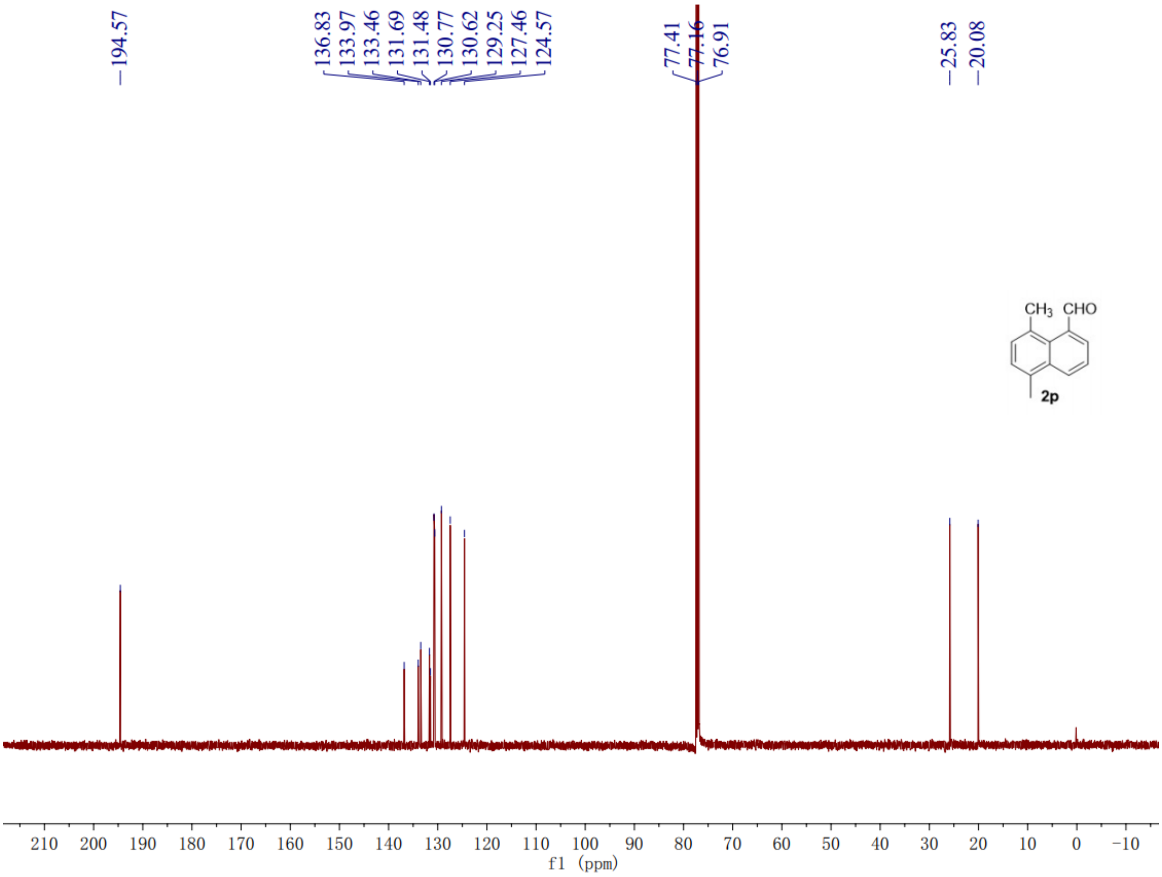
HR-ESI-MS (M+H)$^+$ of 2o



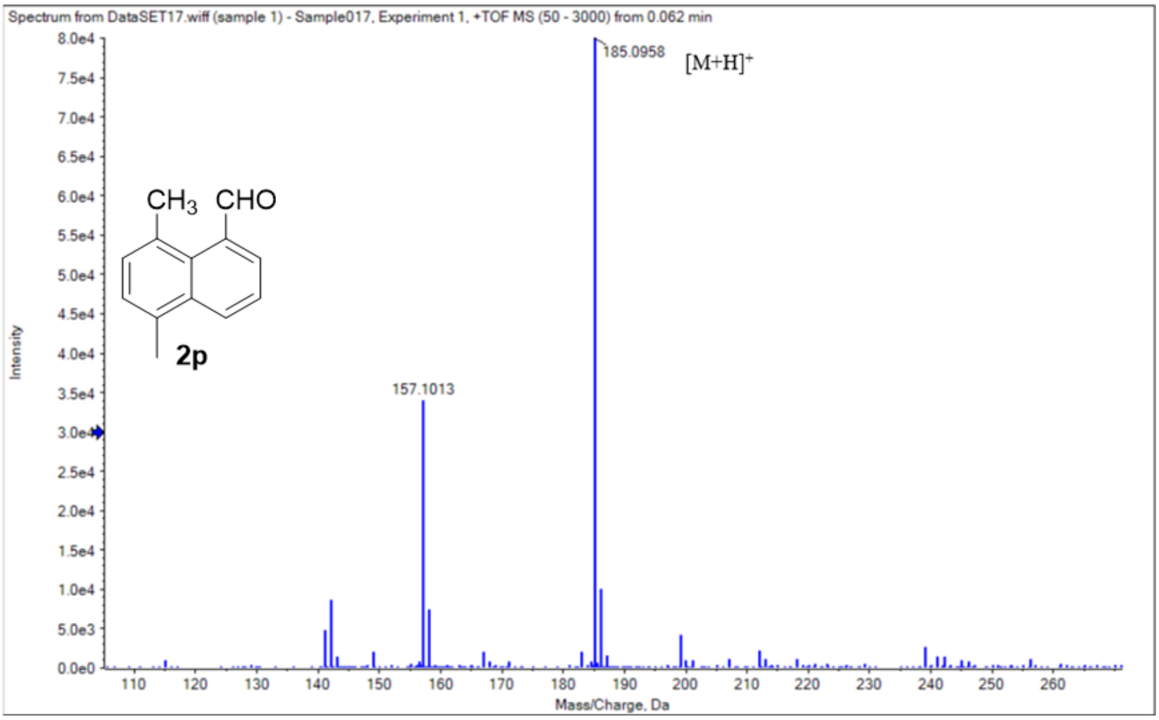
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2p



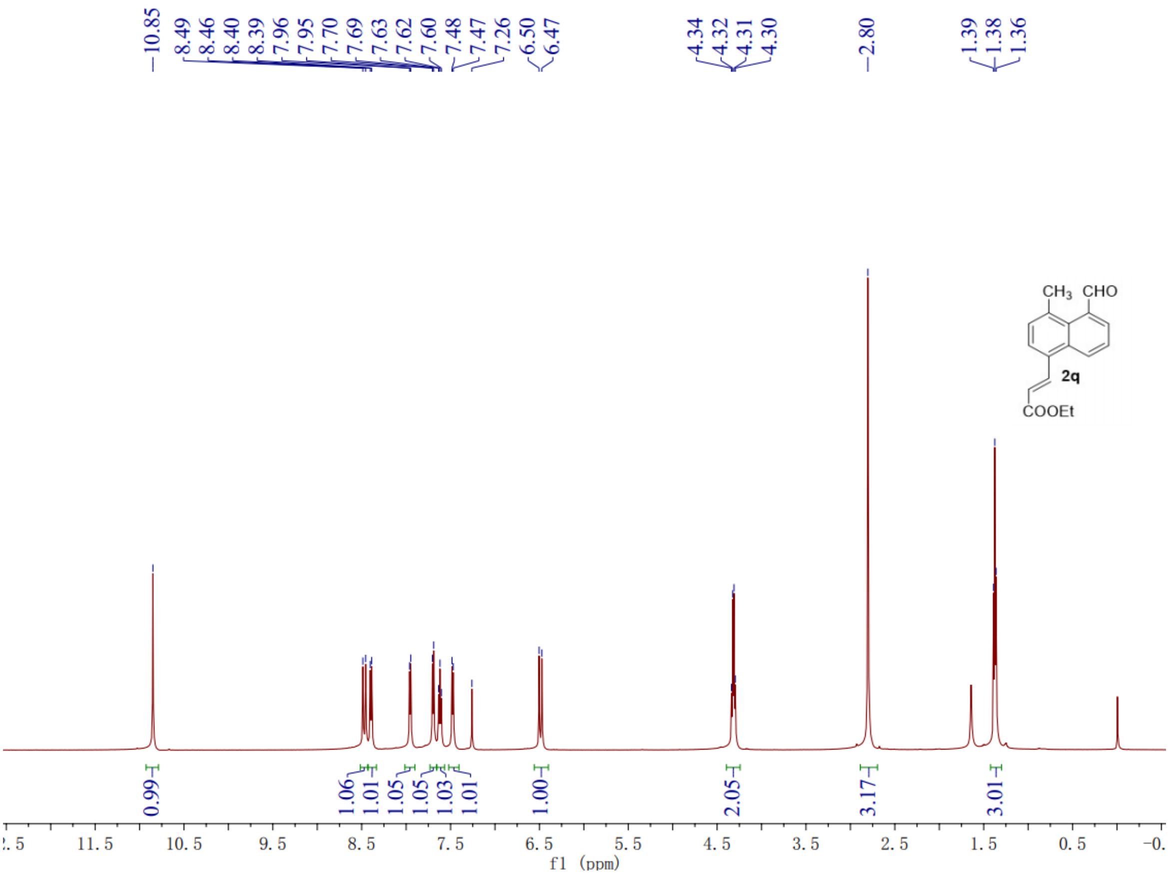
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2p



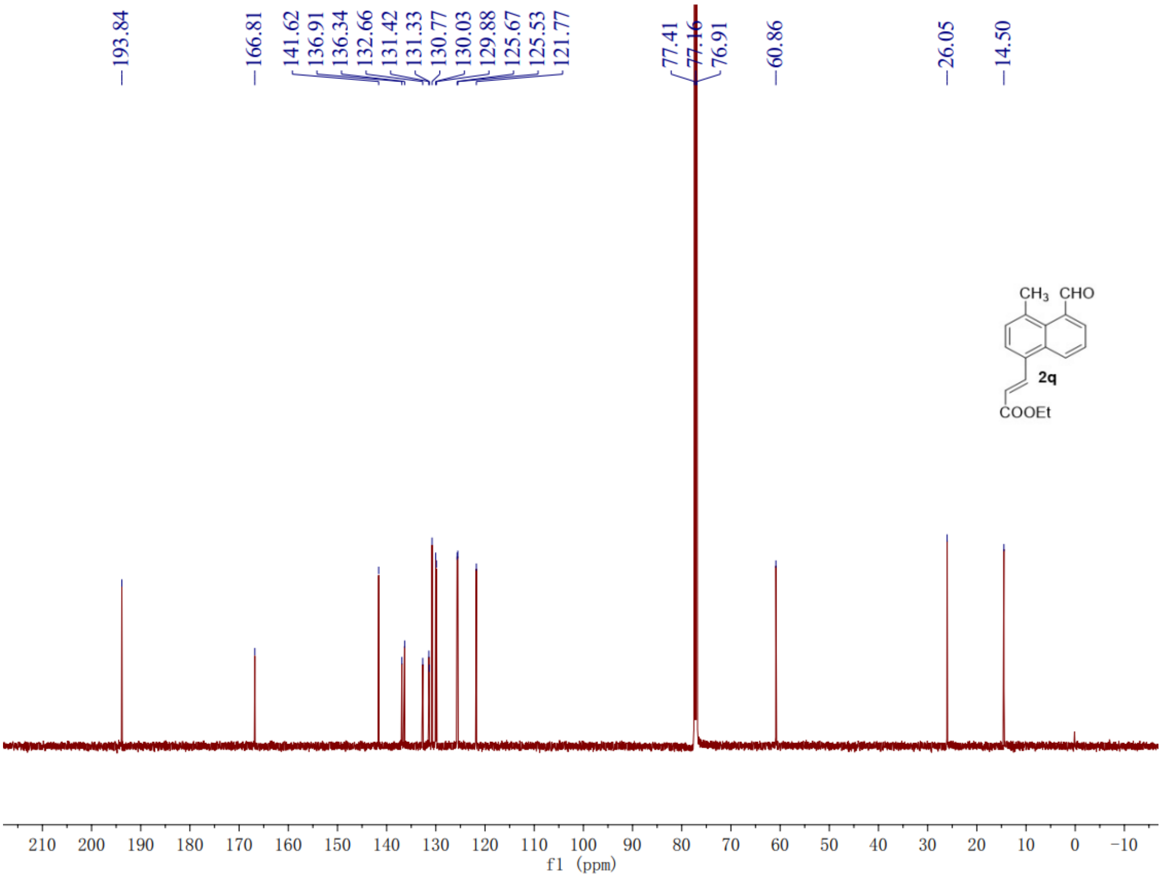
HR-ESI-MS $(M+H)^+$ of 2p



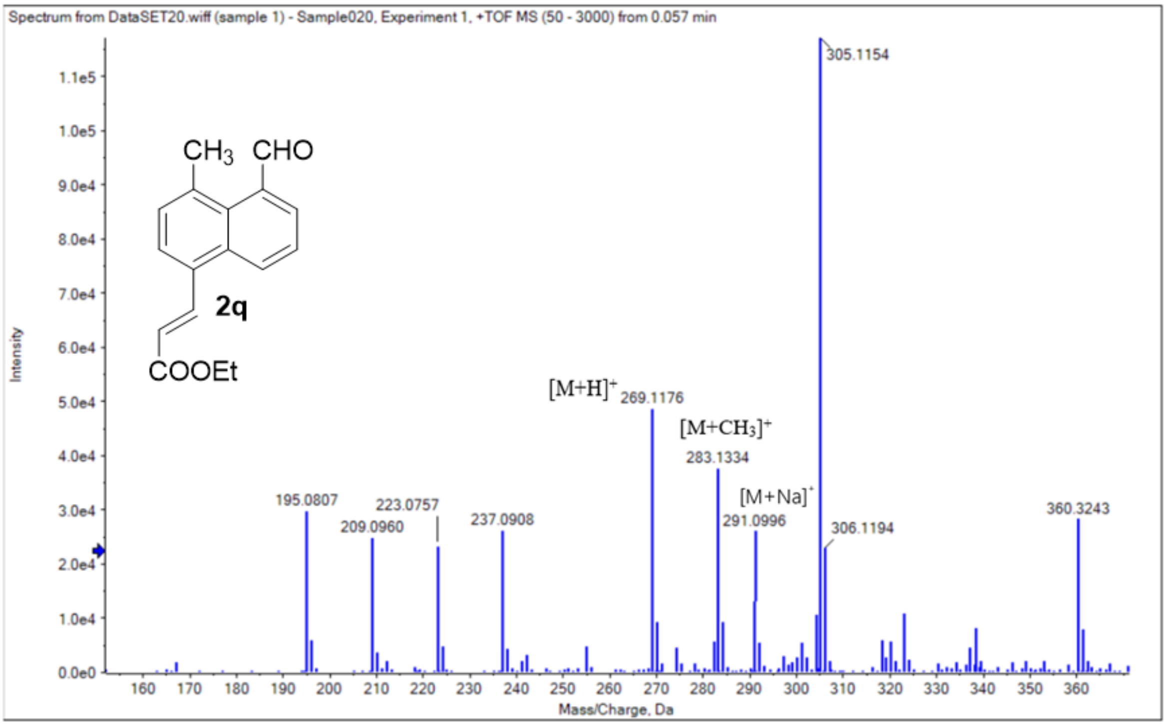
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2q



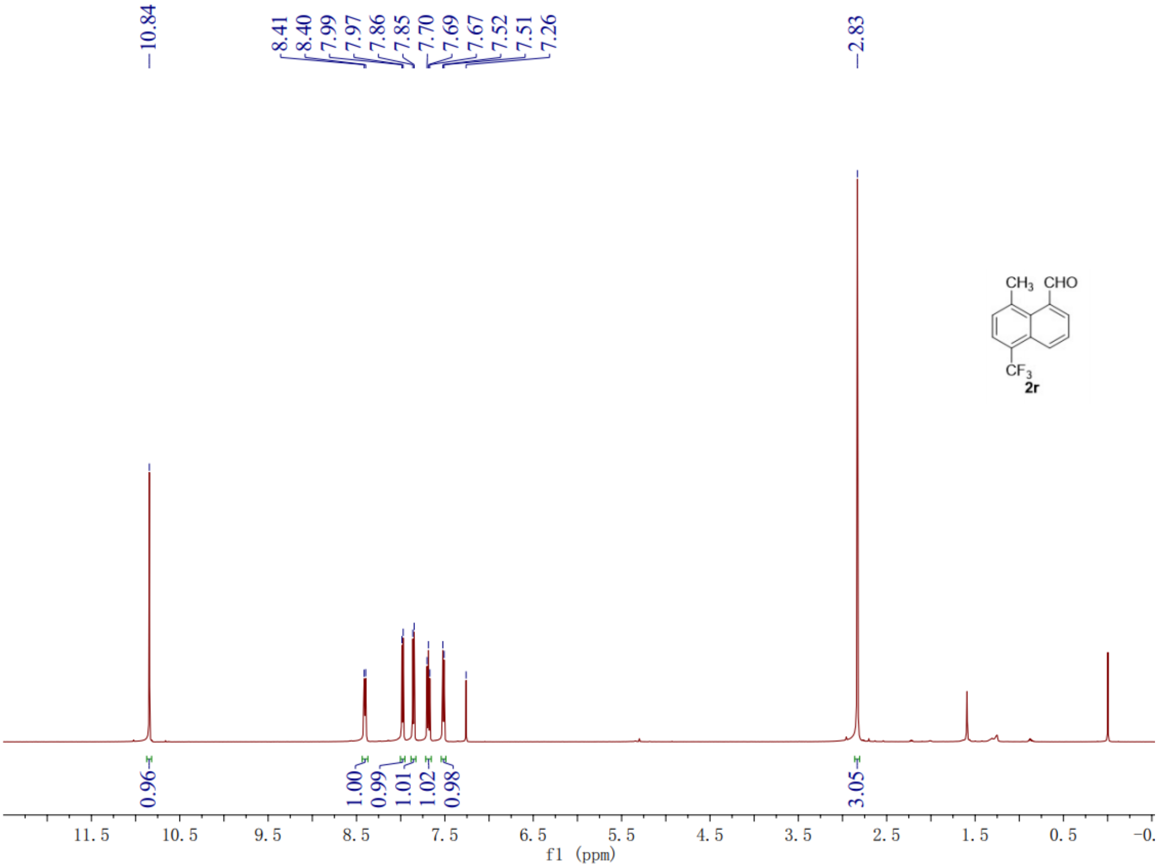
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 2q



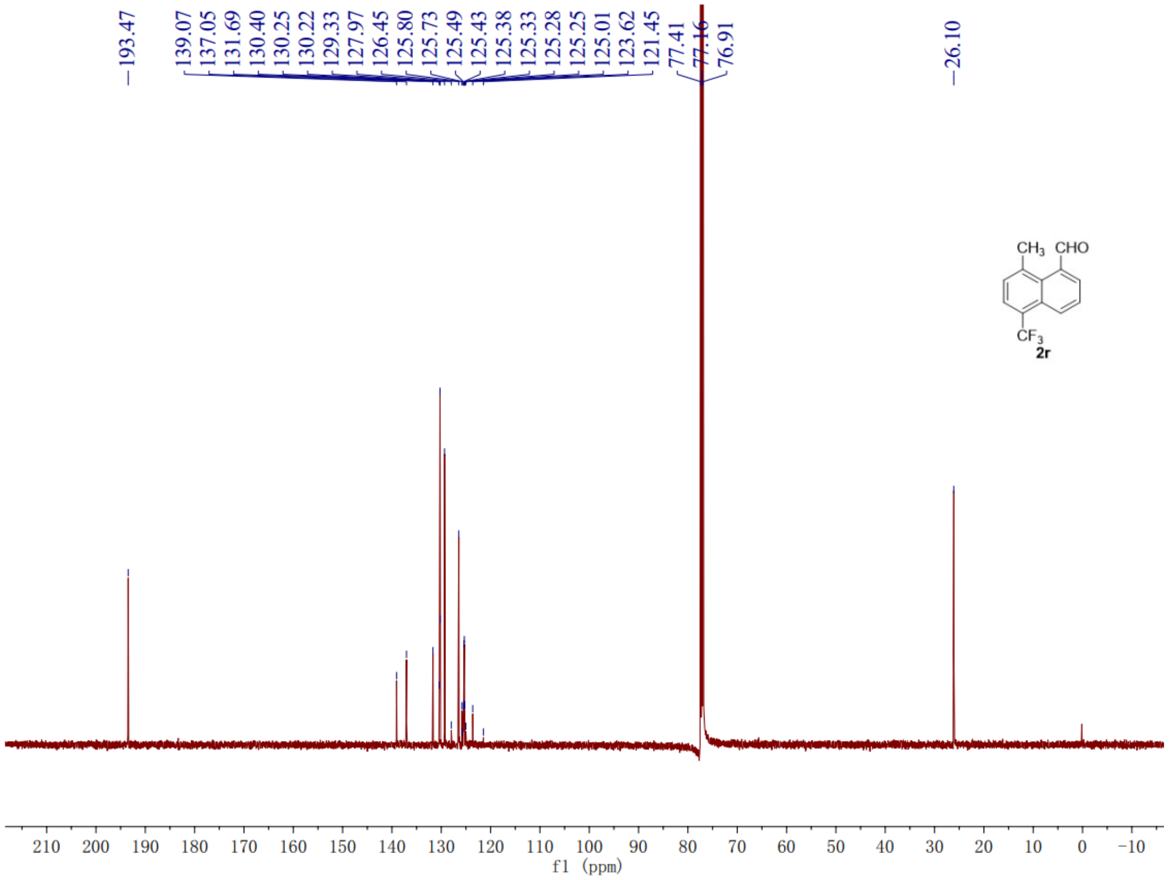
HR-ESI-MS $(M+H)^+$ of 2q



^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2r



^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2r



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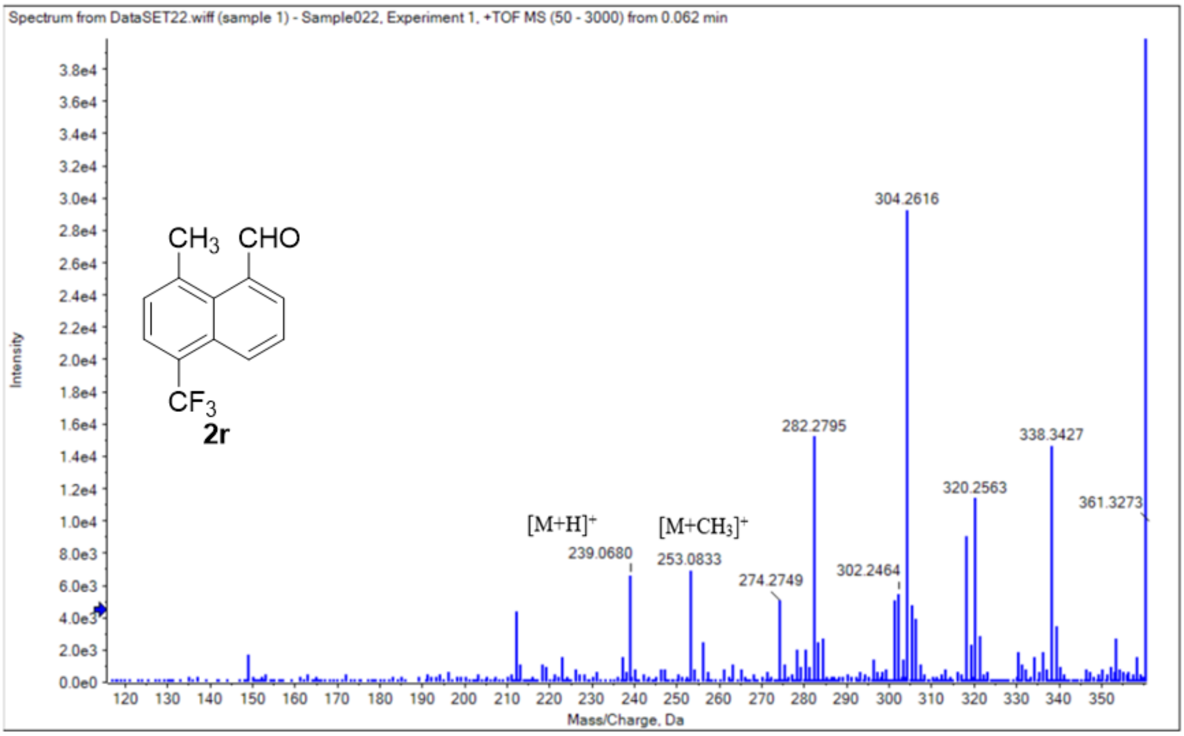
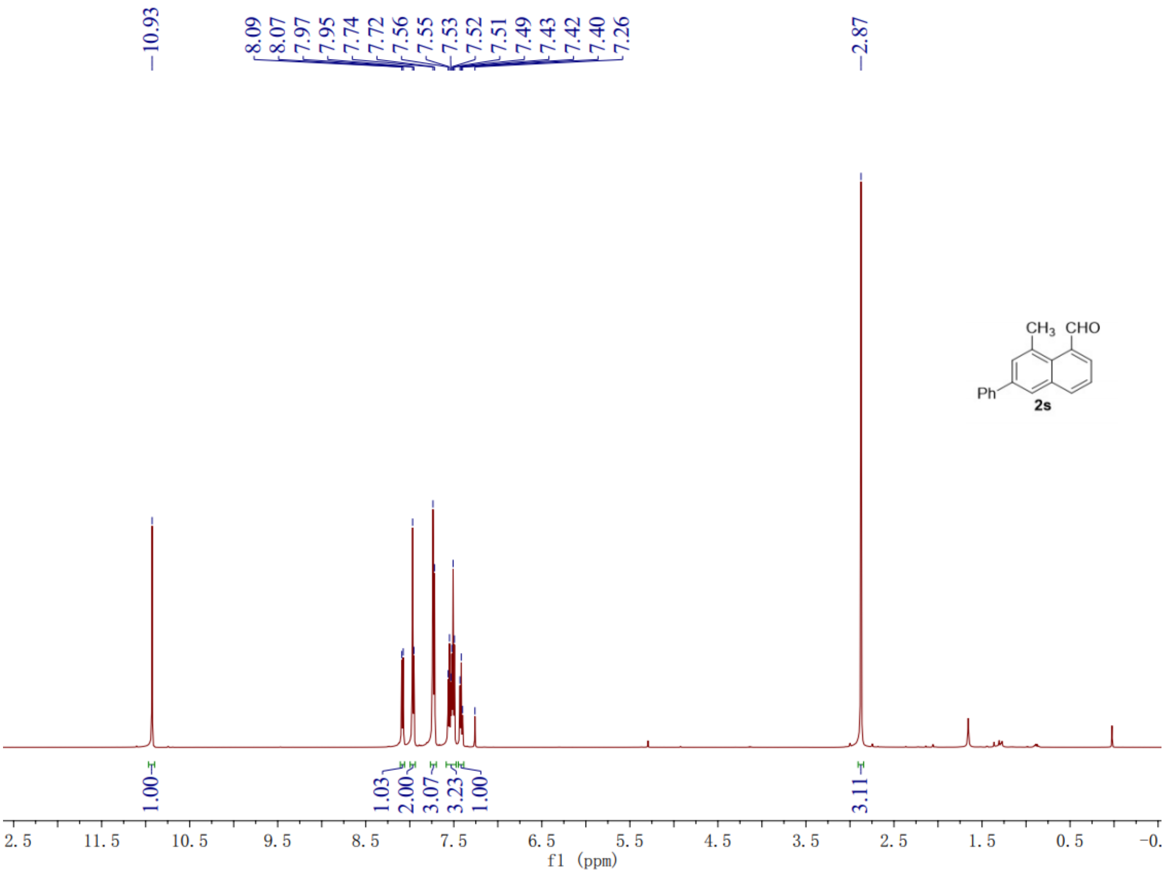
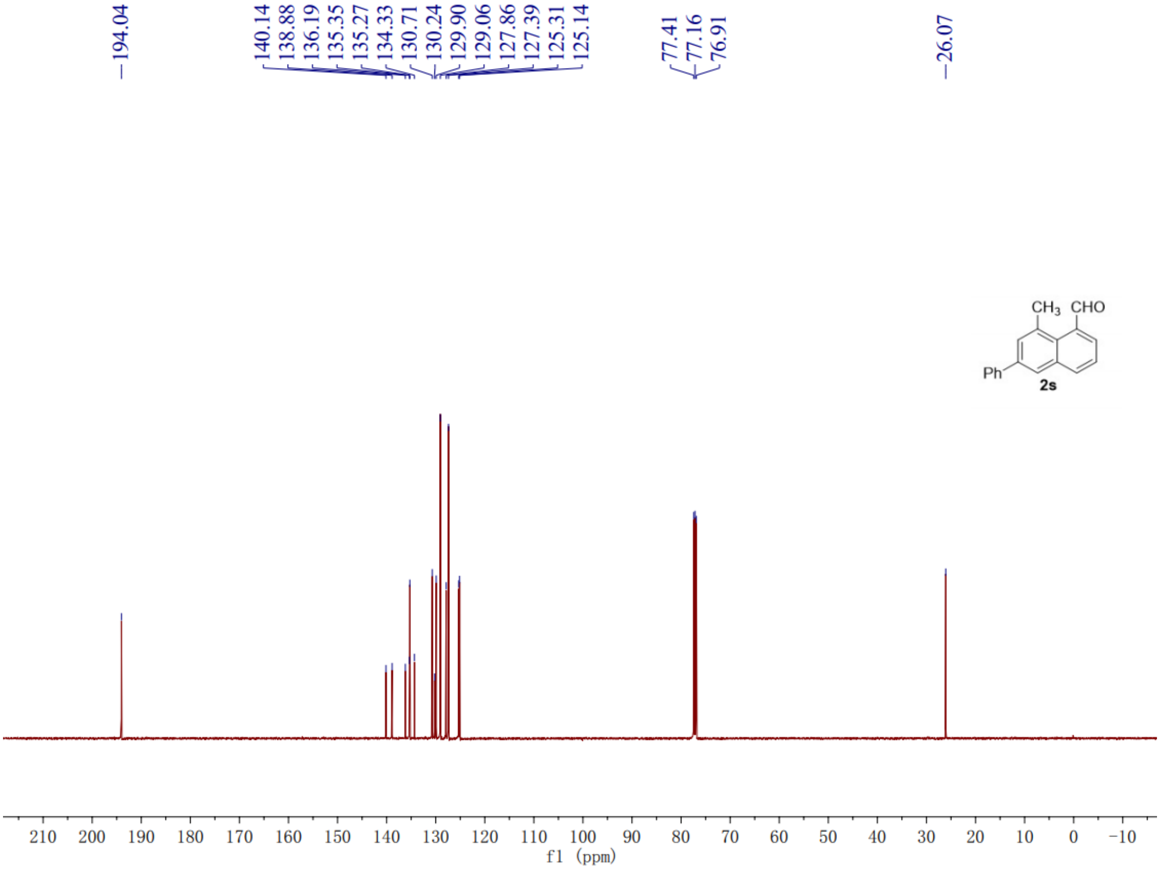


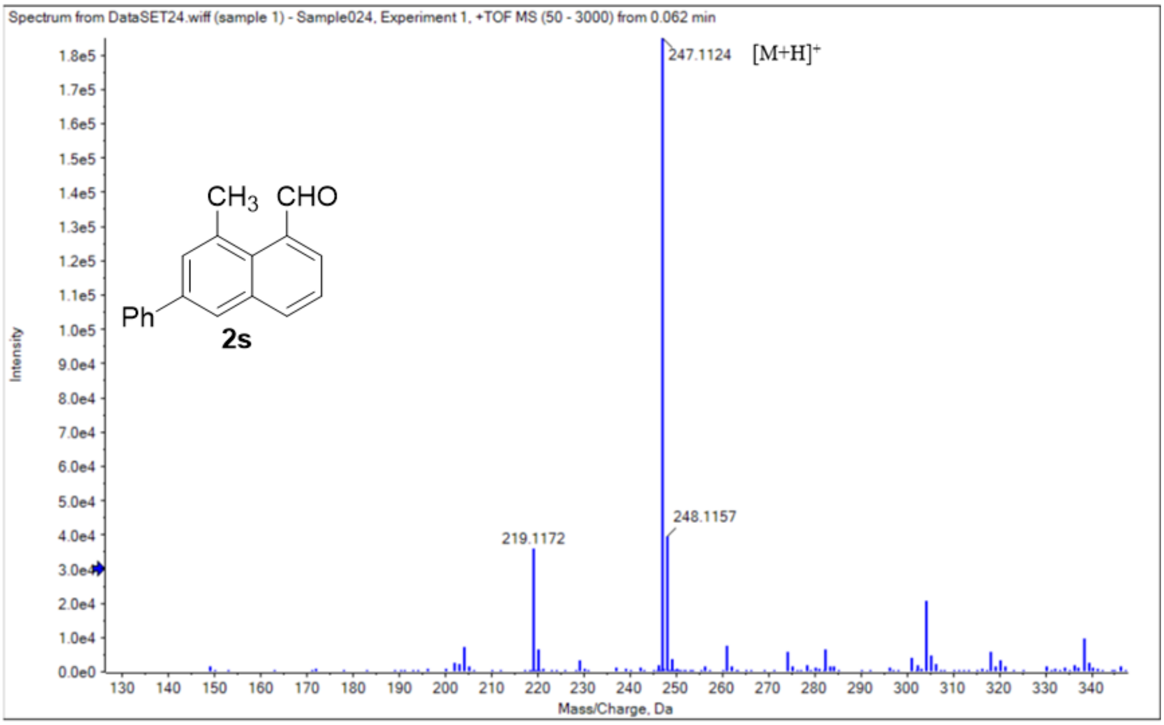
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2s



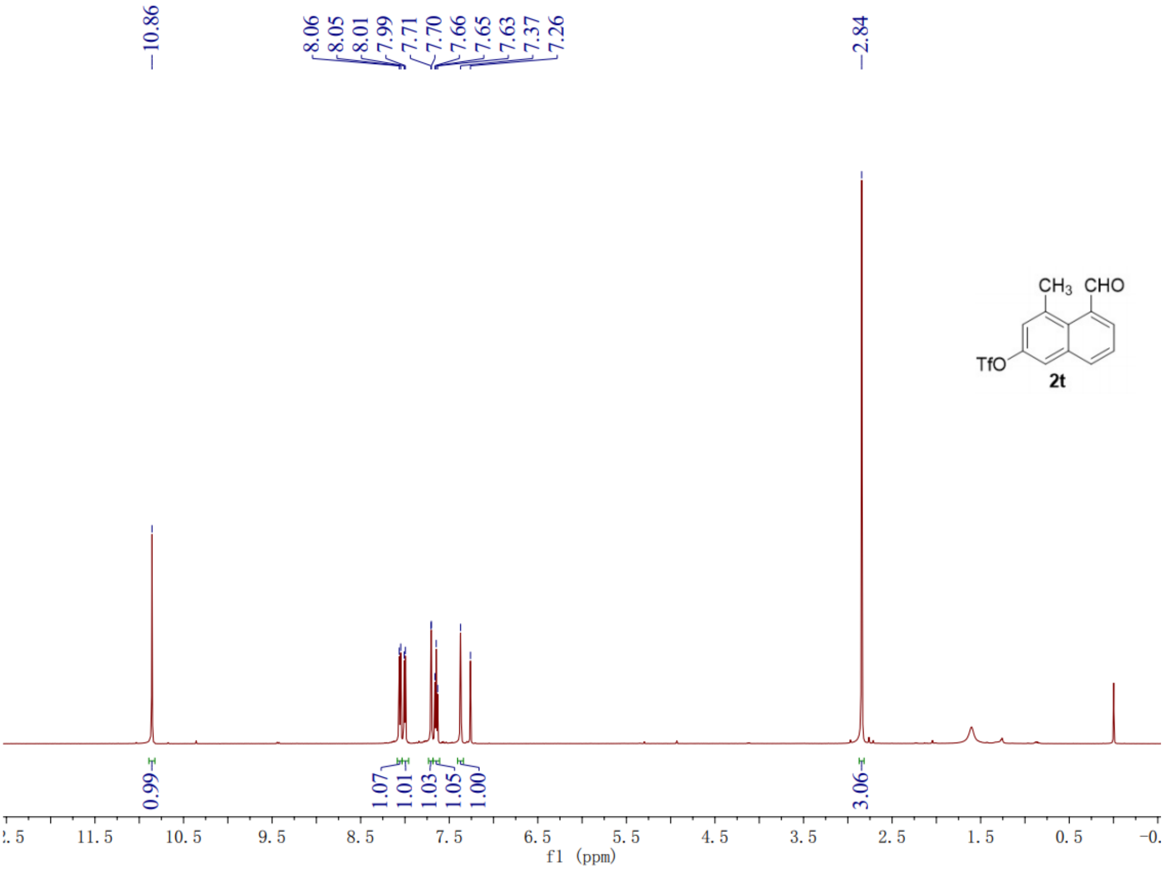
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2s



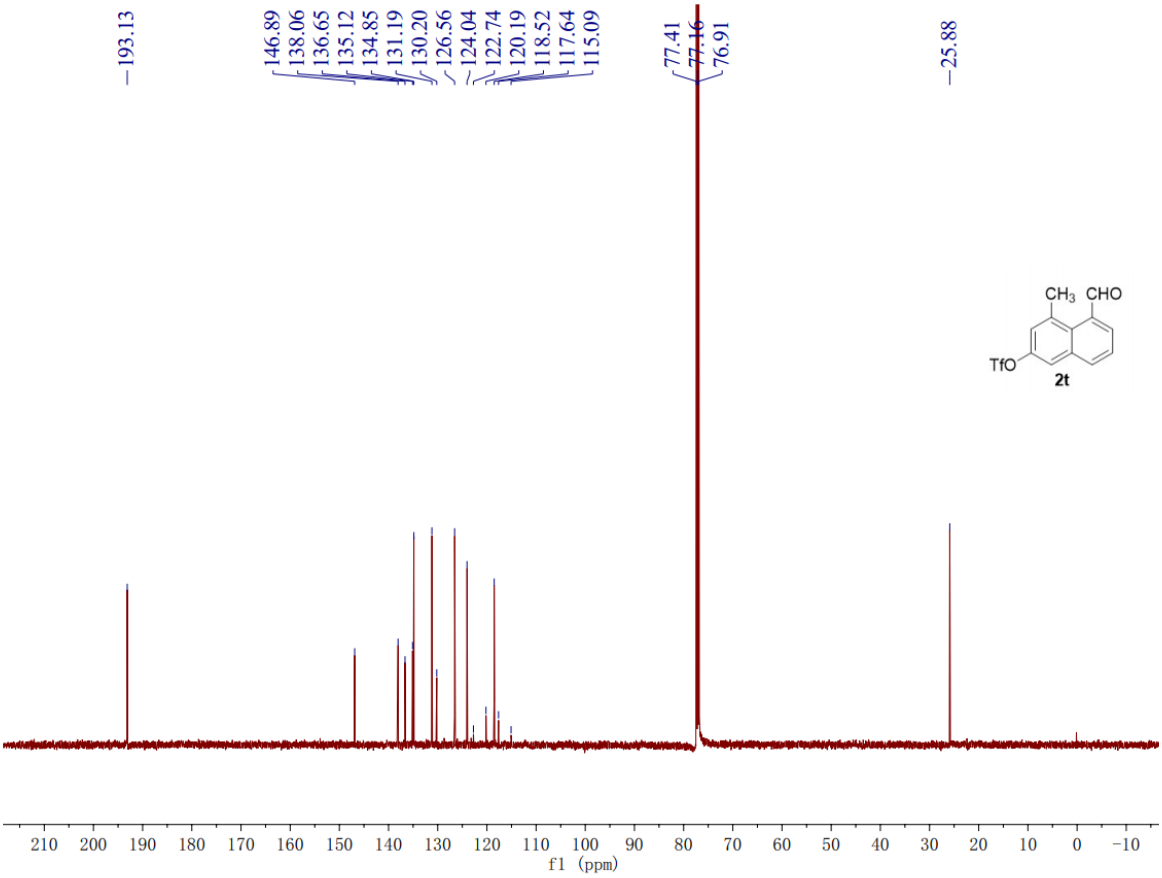
HR-ESI-MS (M+H)$^+$ of 2s



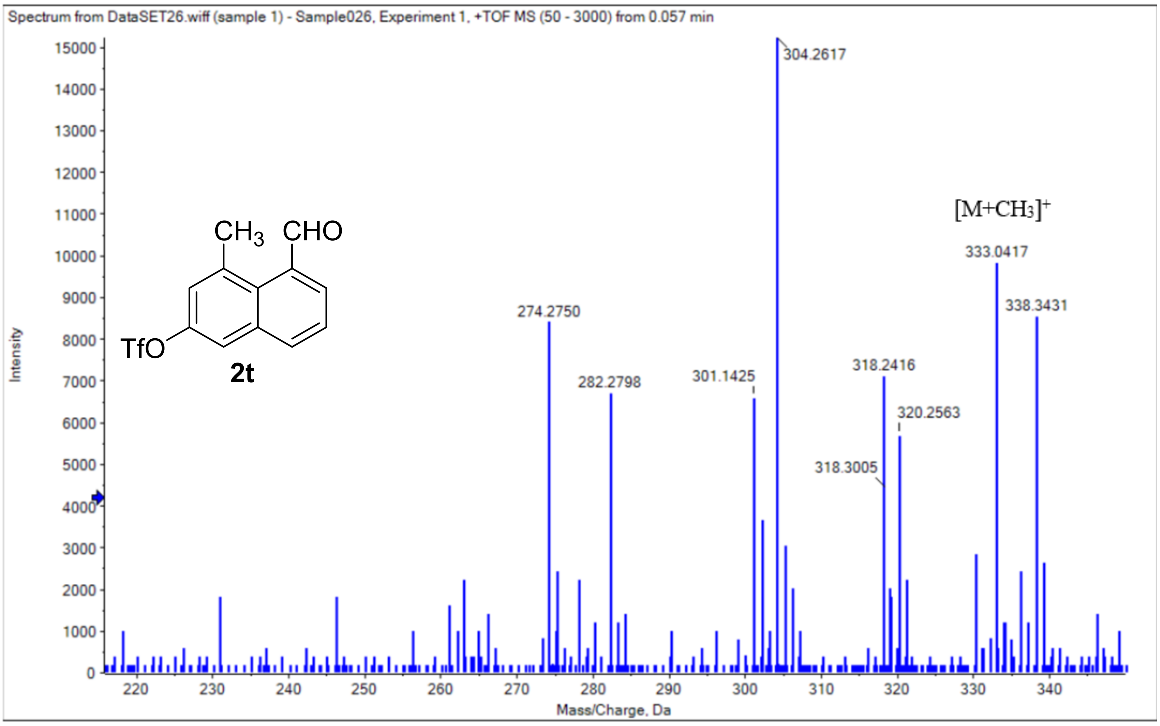
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2t



^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2t



HR-ESI-MS $(M+CH_3)^+$ of 2t



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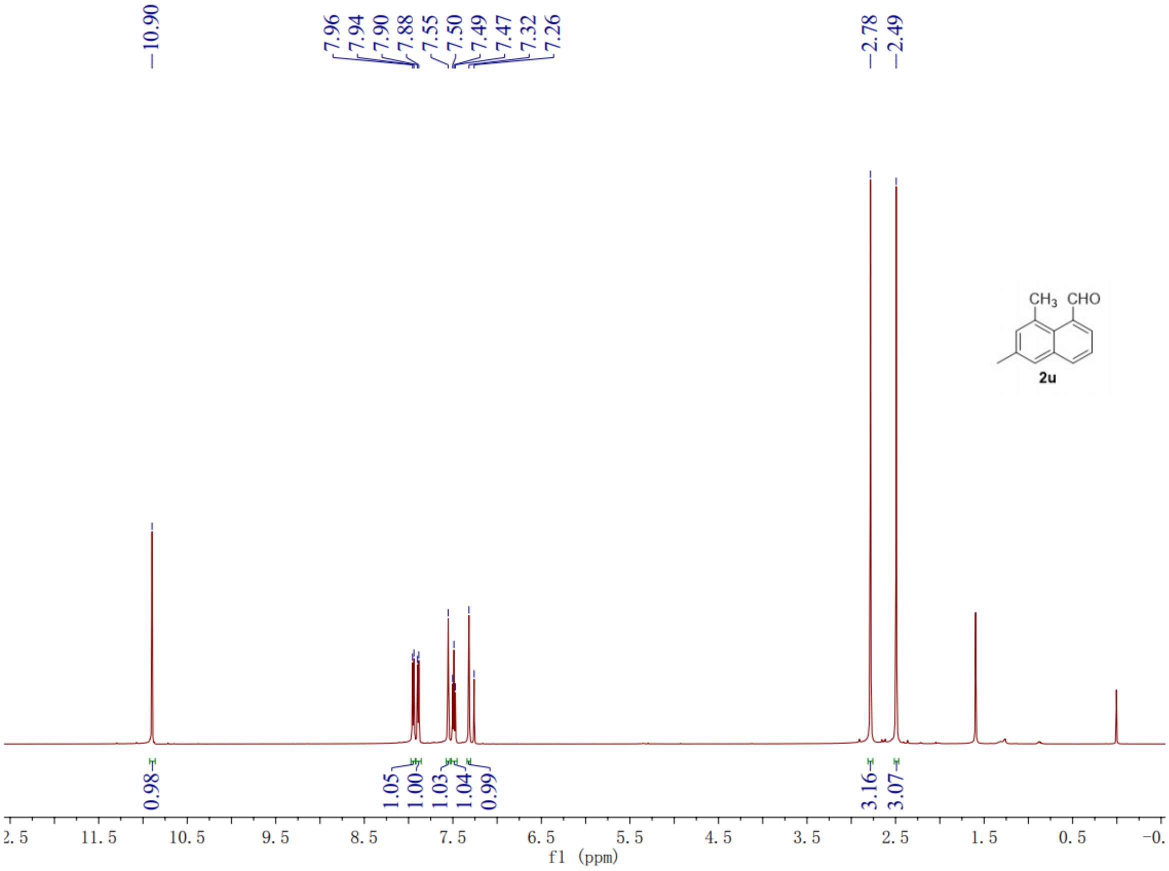
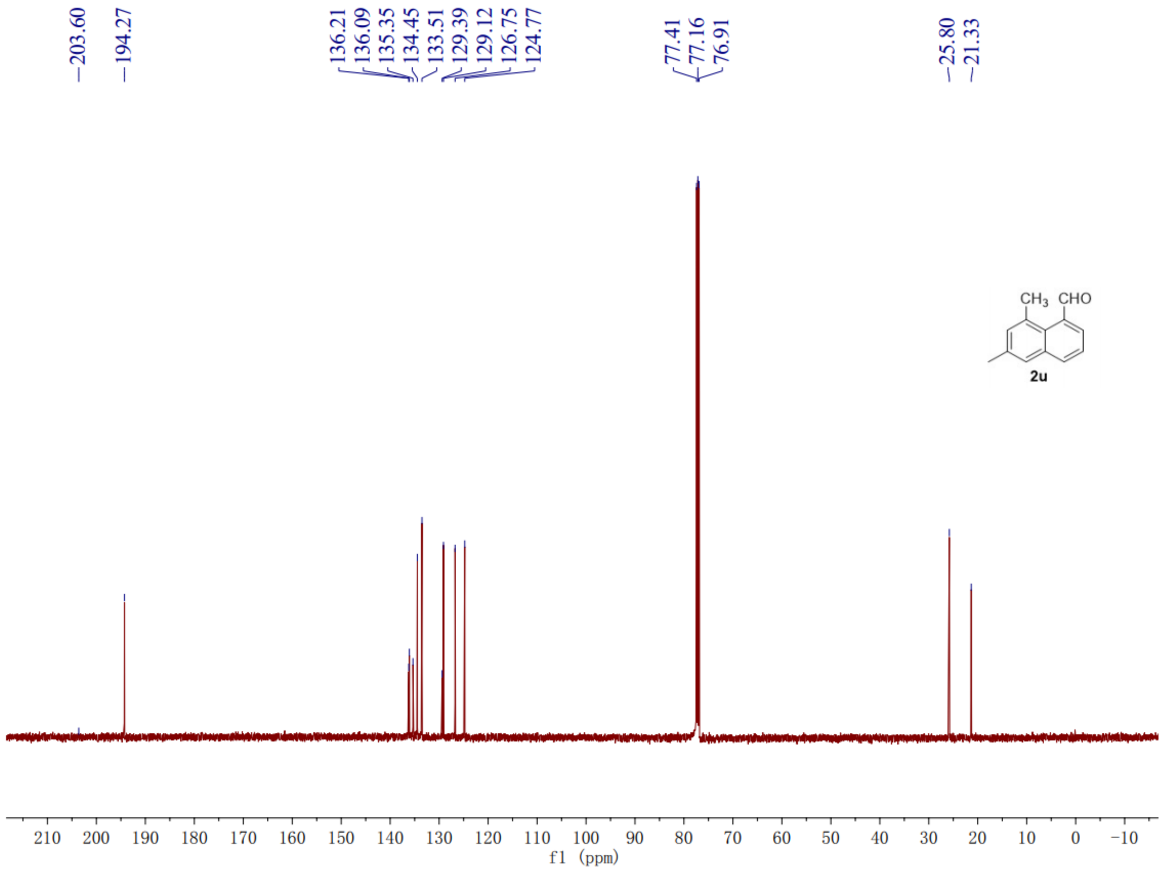
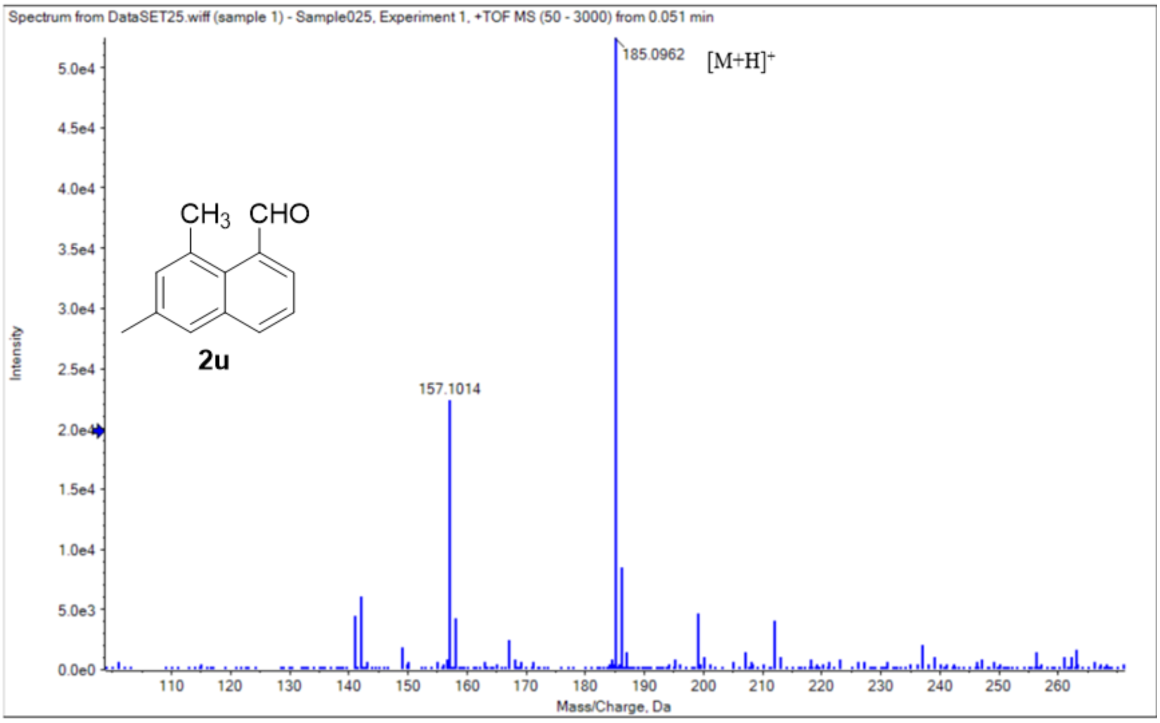


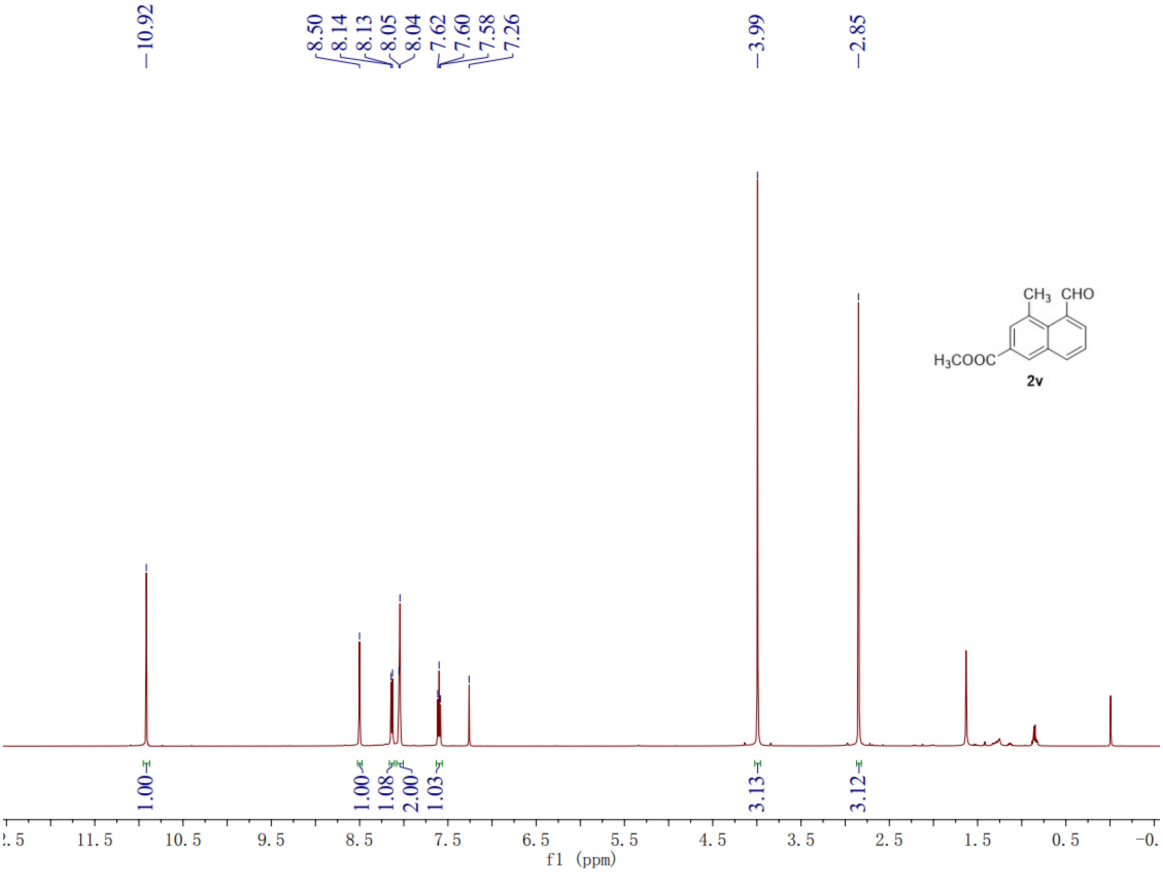
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2u



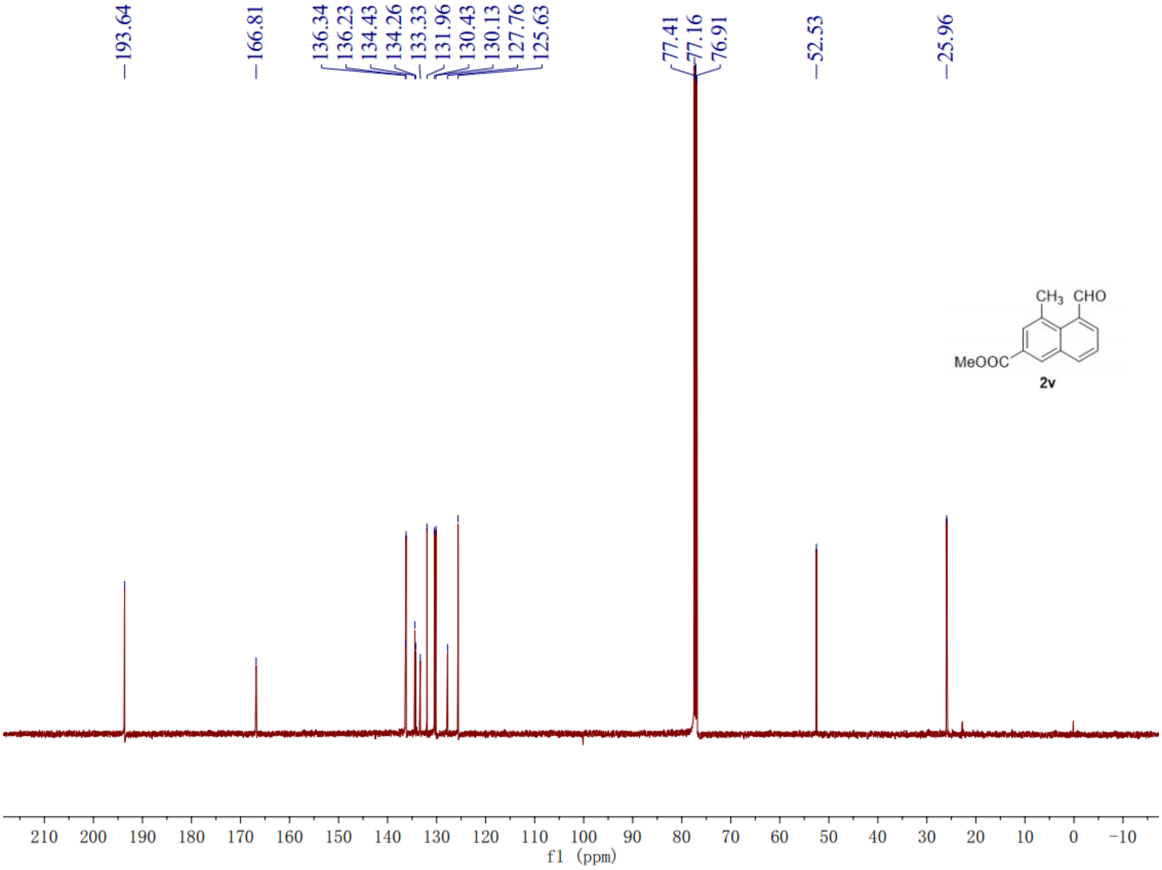
HR-ESI-MS (M+H)$^+$ of 2u



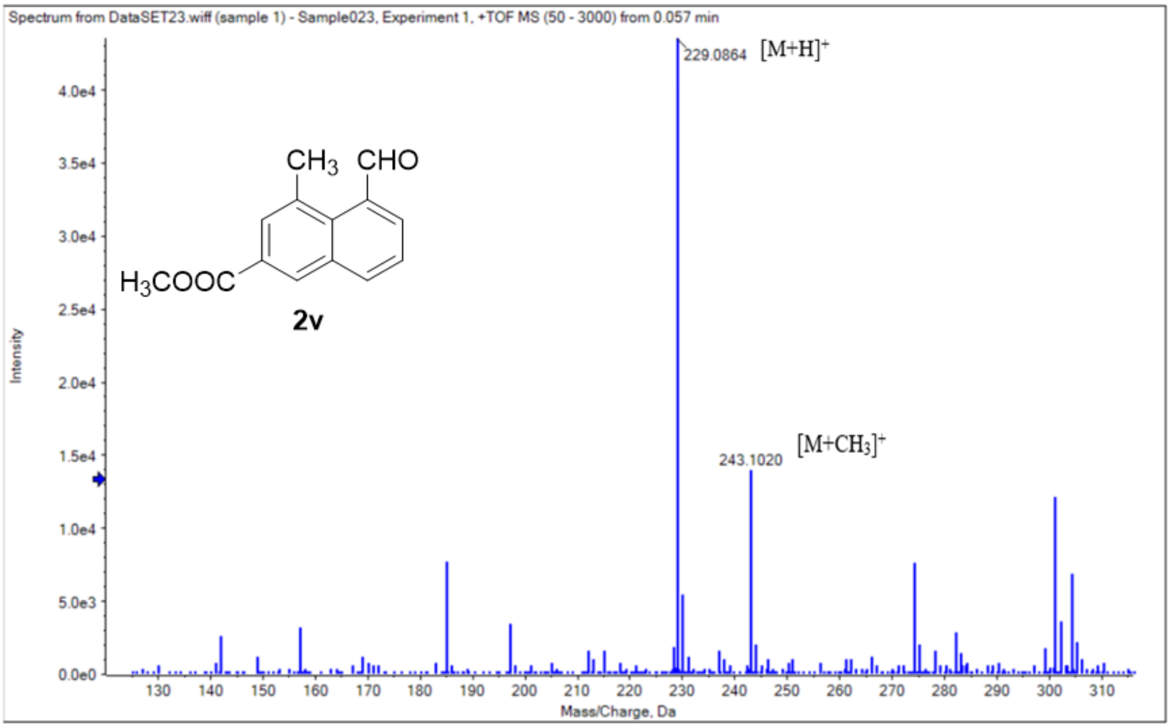
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2v



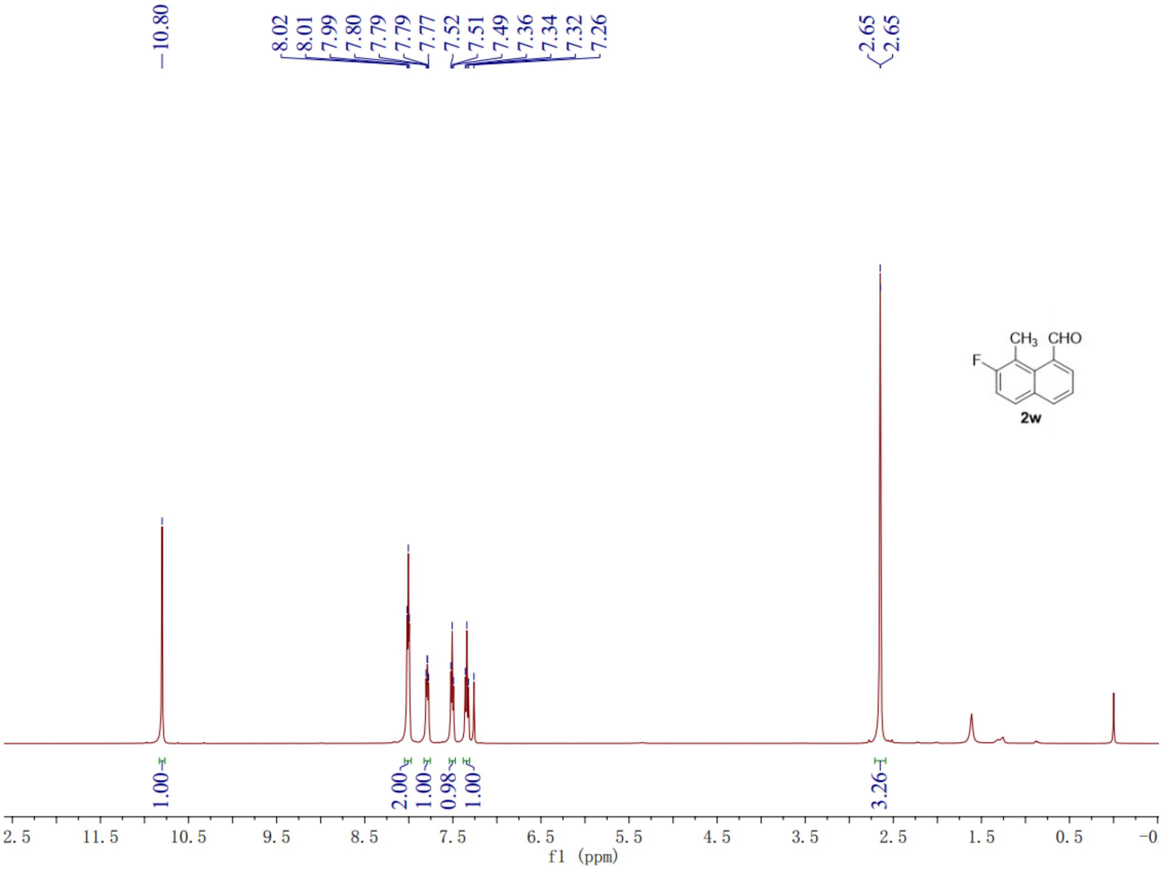
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2v



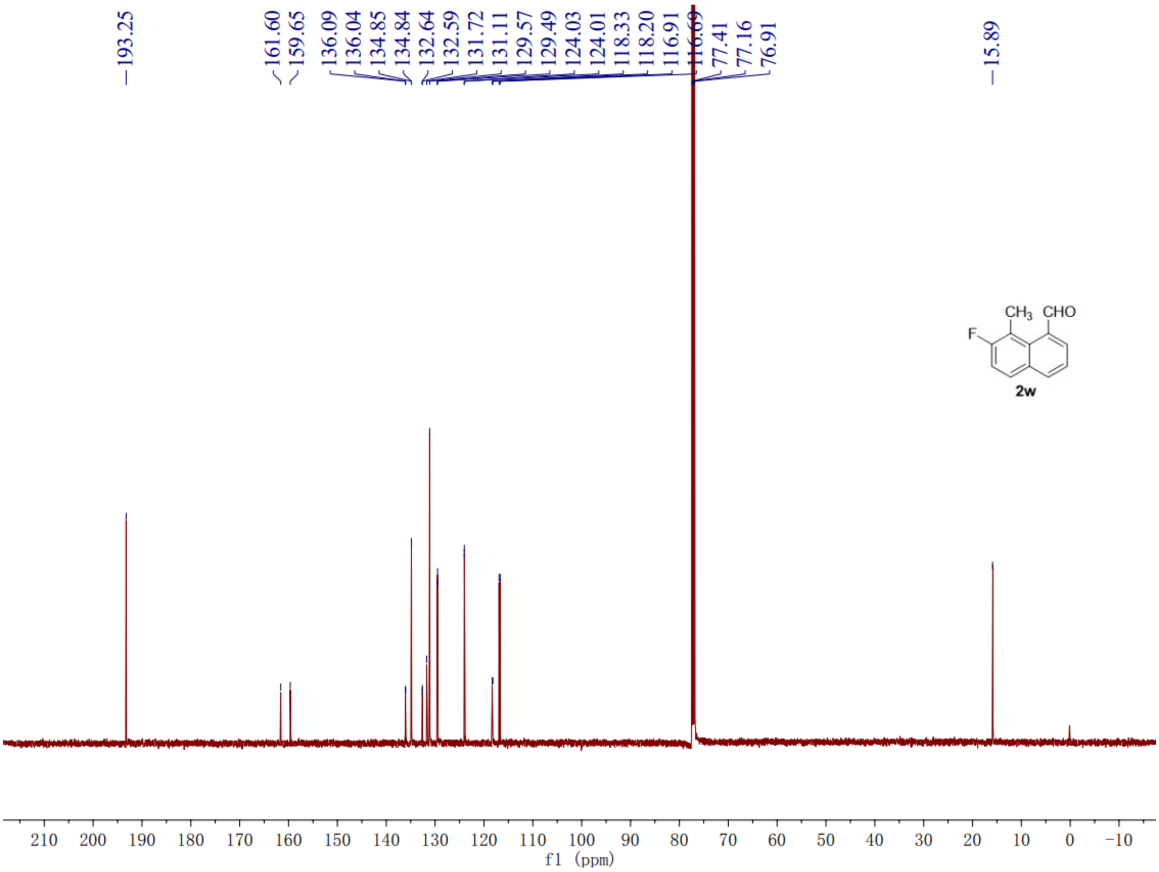
HR-ESI-MS $(M+H)^+$ of 2v



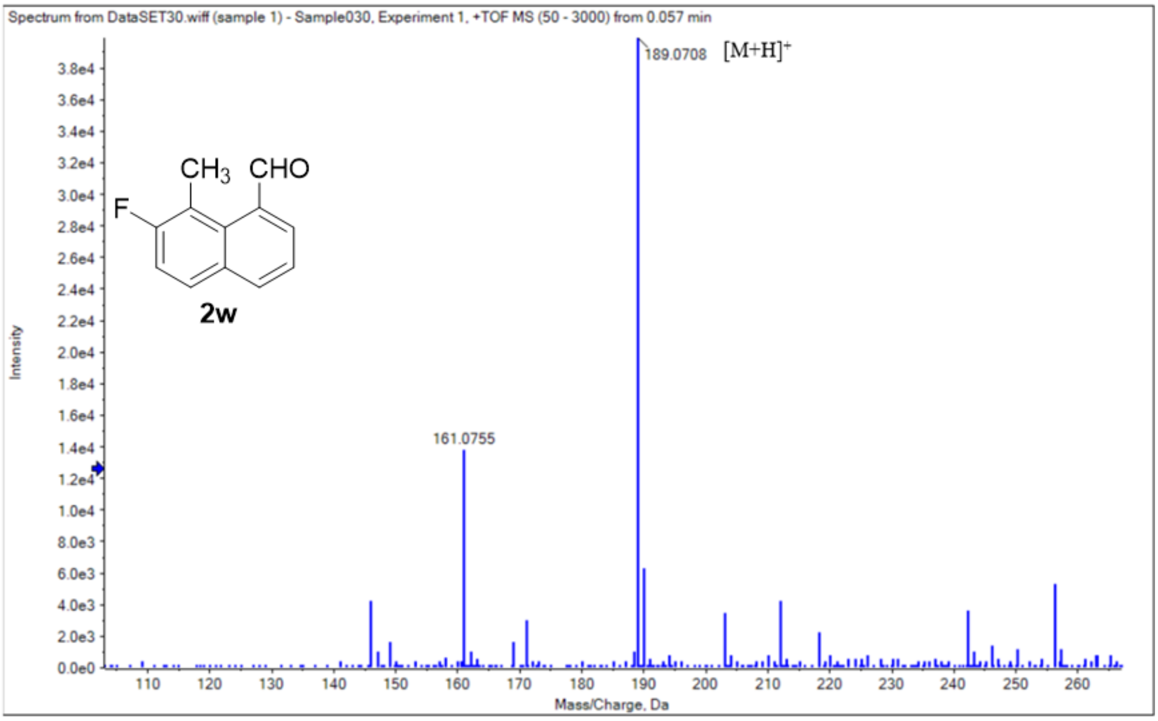
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 2w



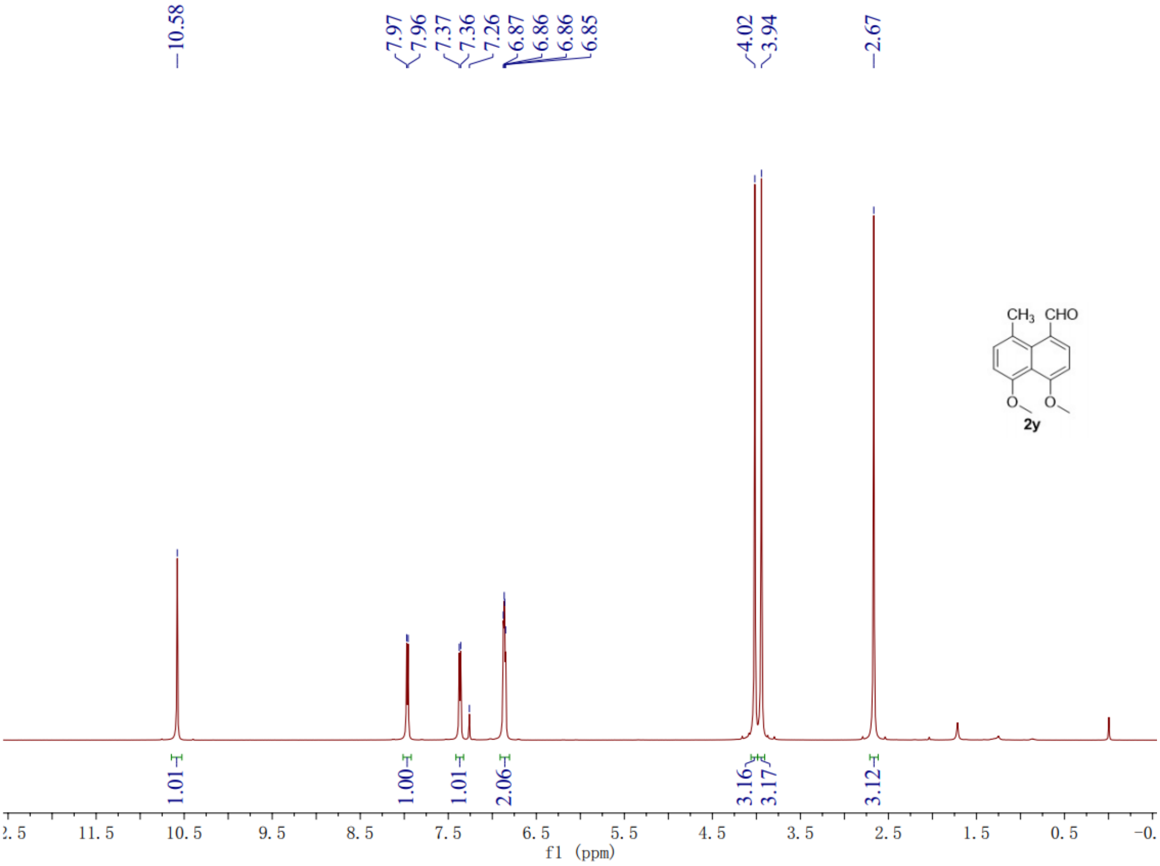
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2w



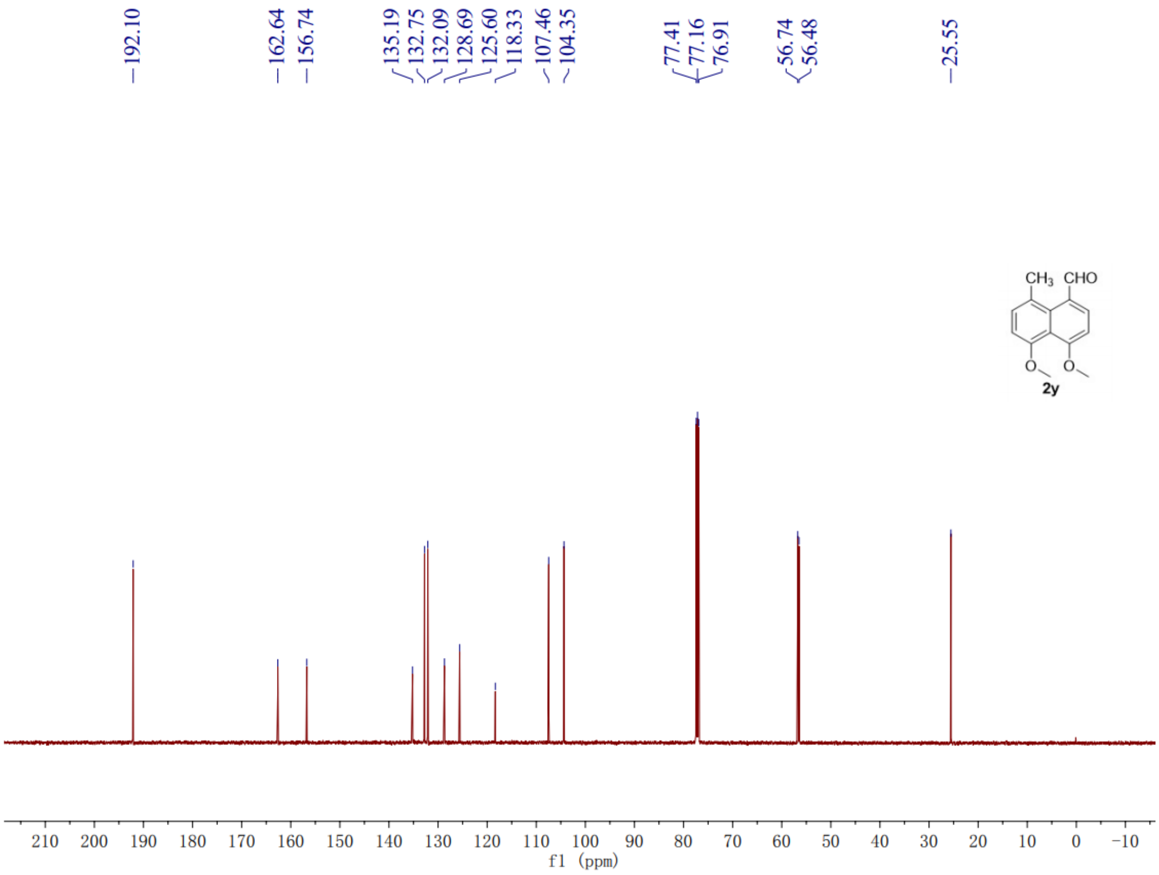
HR-ESI-MS (M+H)$^+$ of 2w



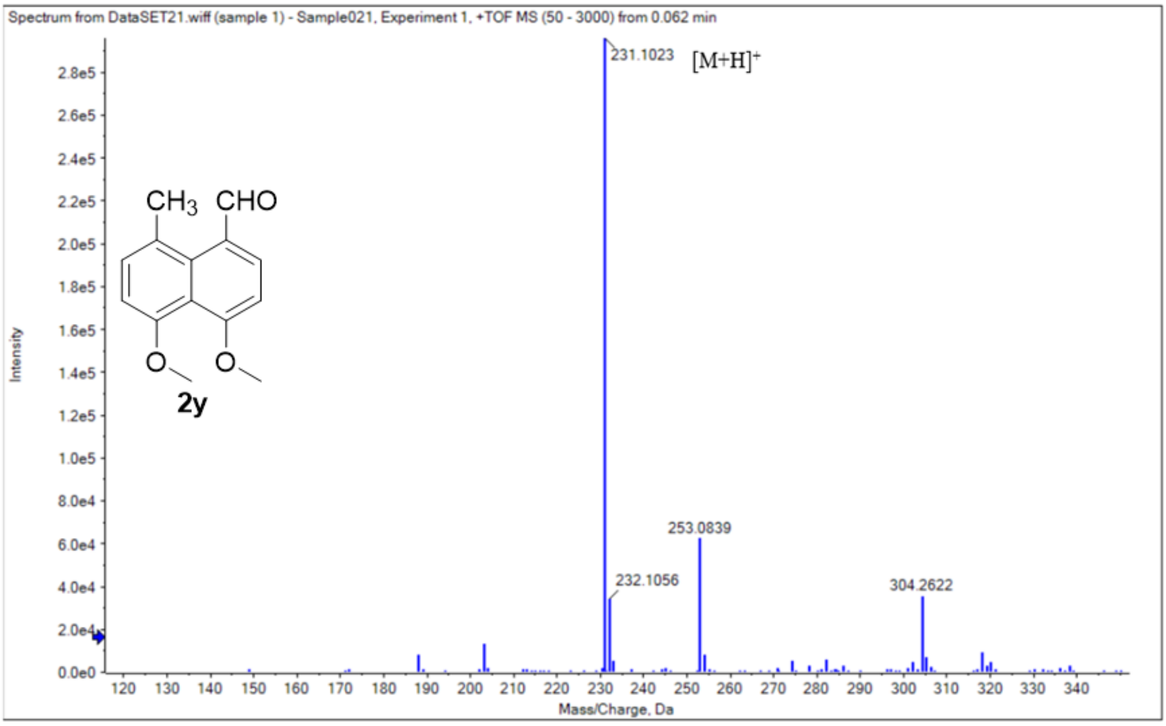
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 2y



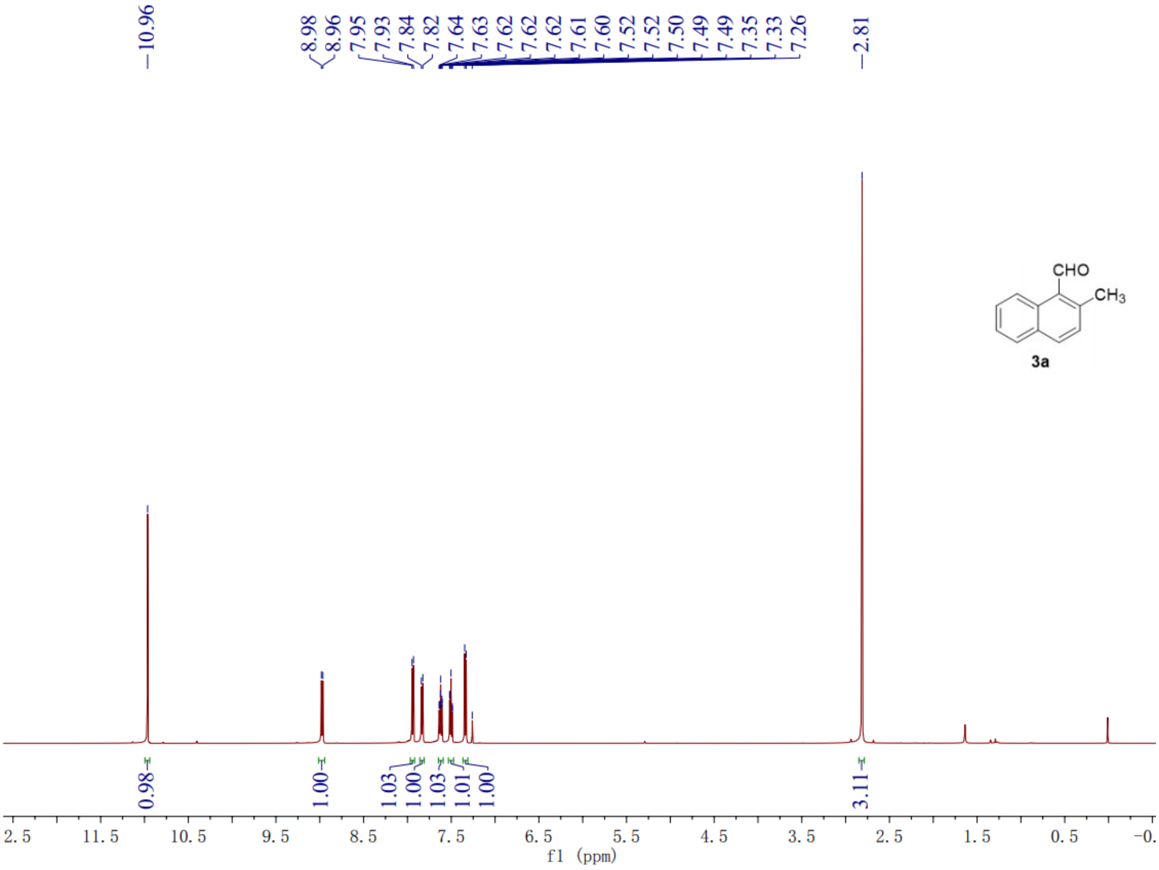
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 2y



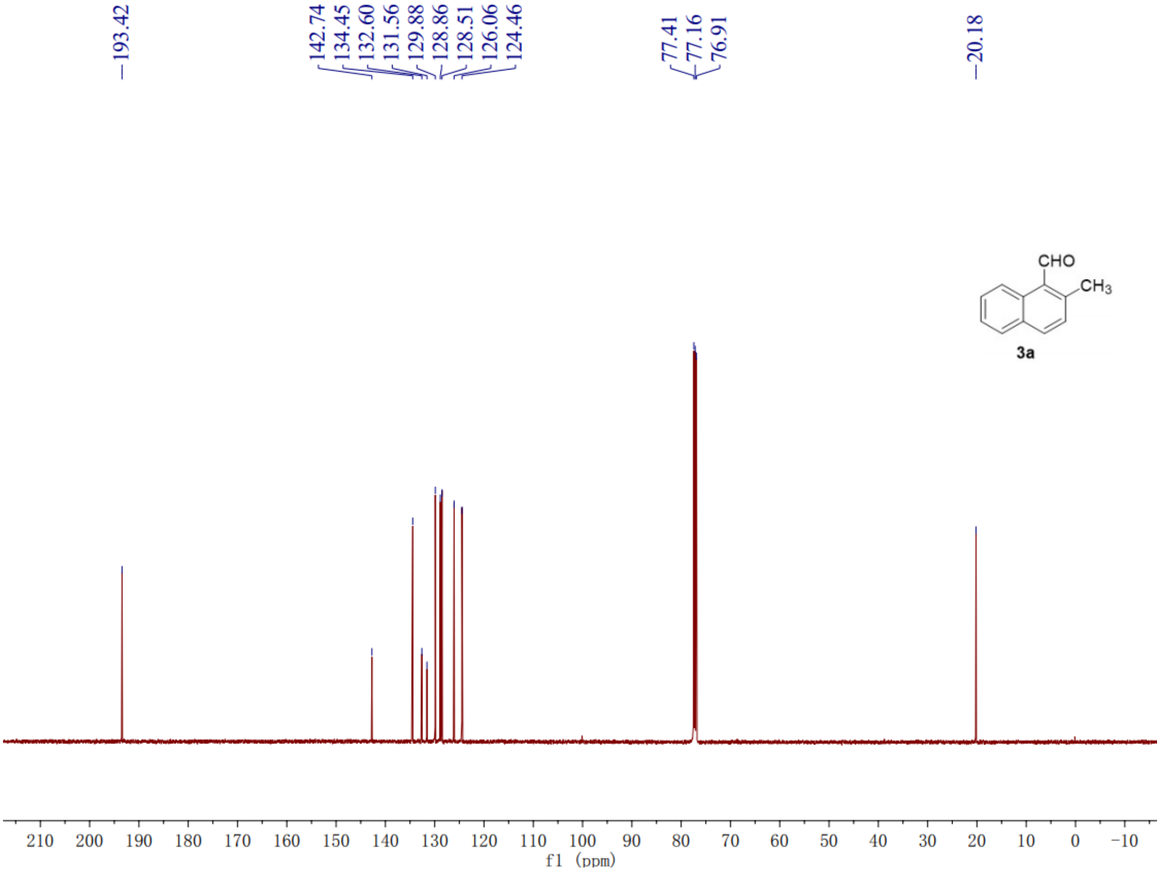
HR-ESI-MS $(M+H)^+$ of 2y



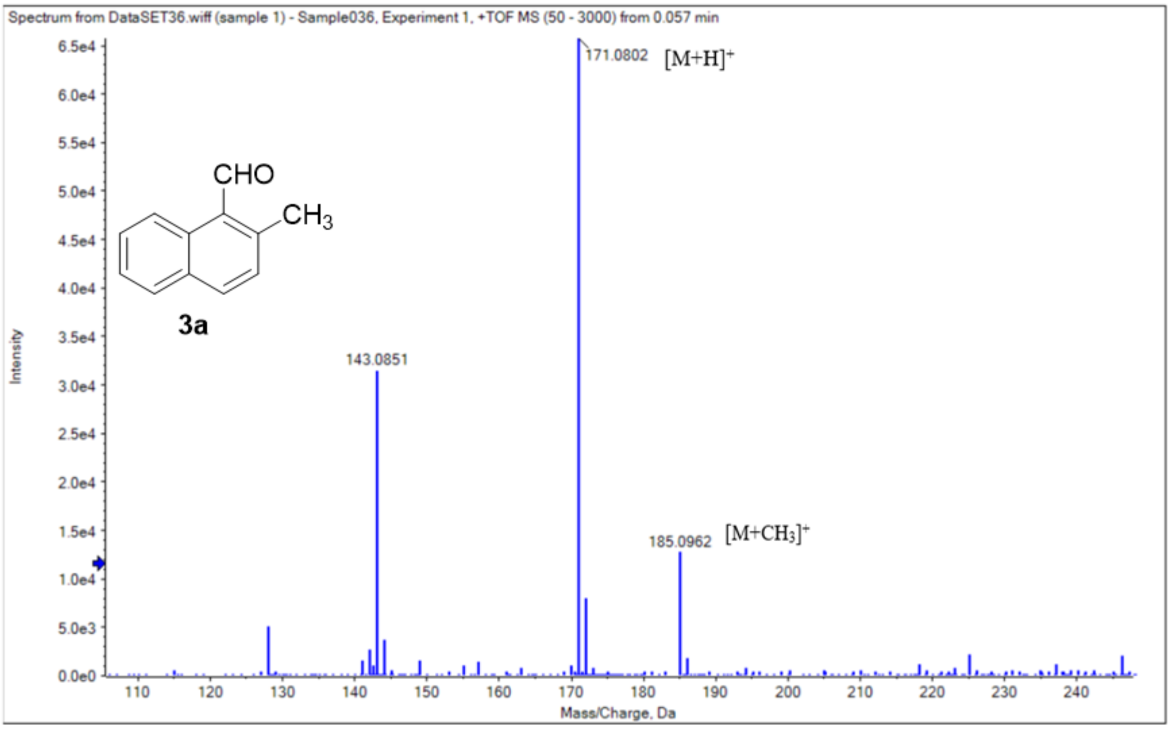
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3a



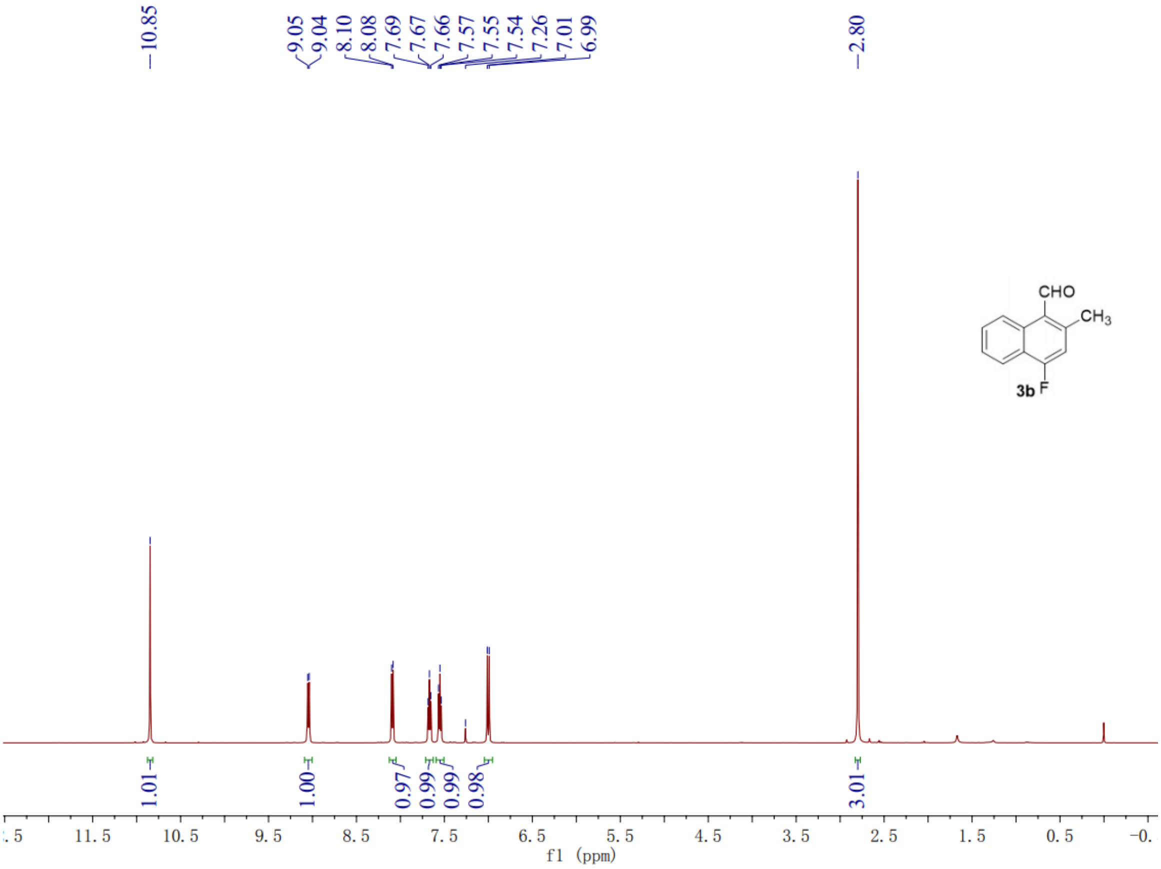
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3a



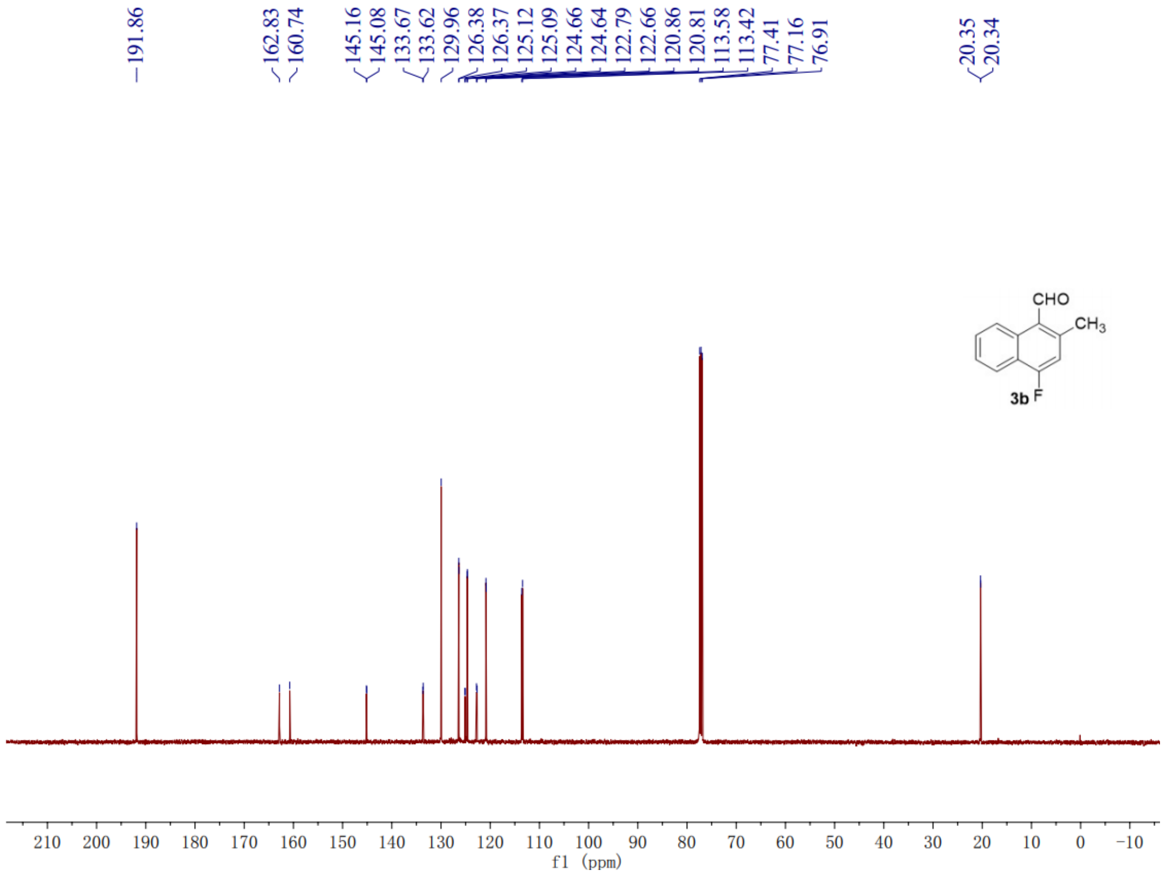
HR-ESI-MS (M+H)$^+$ of 3a



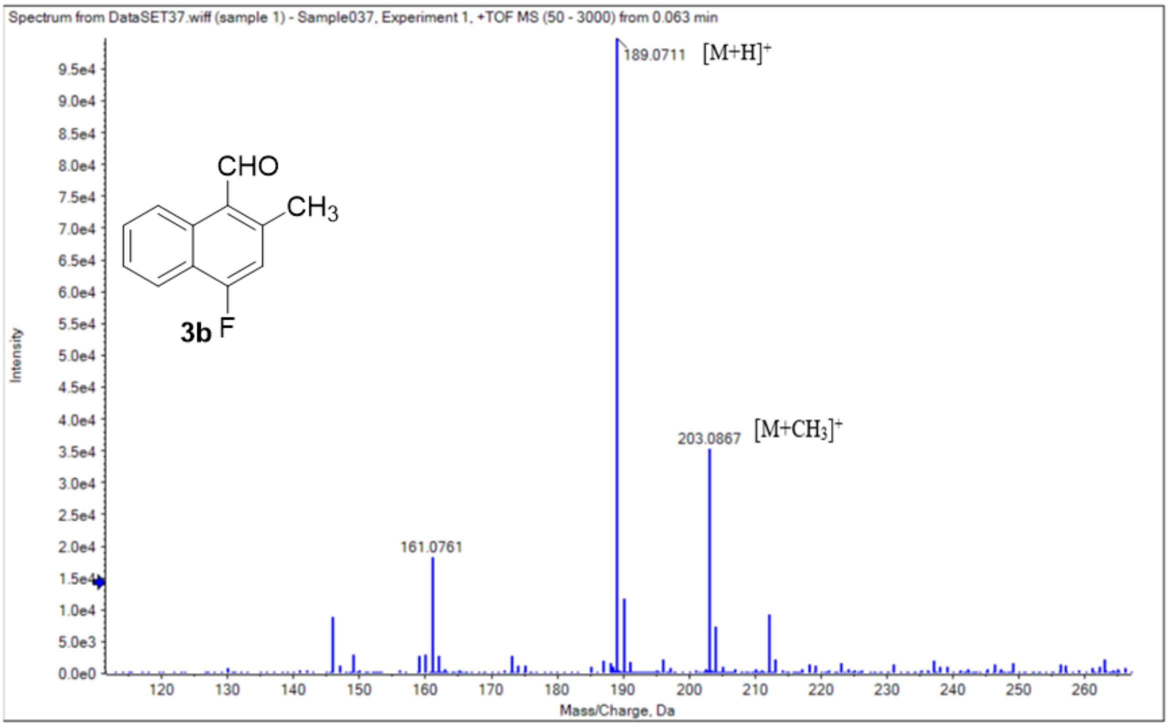
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3b



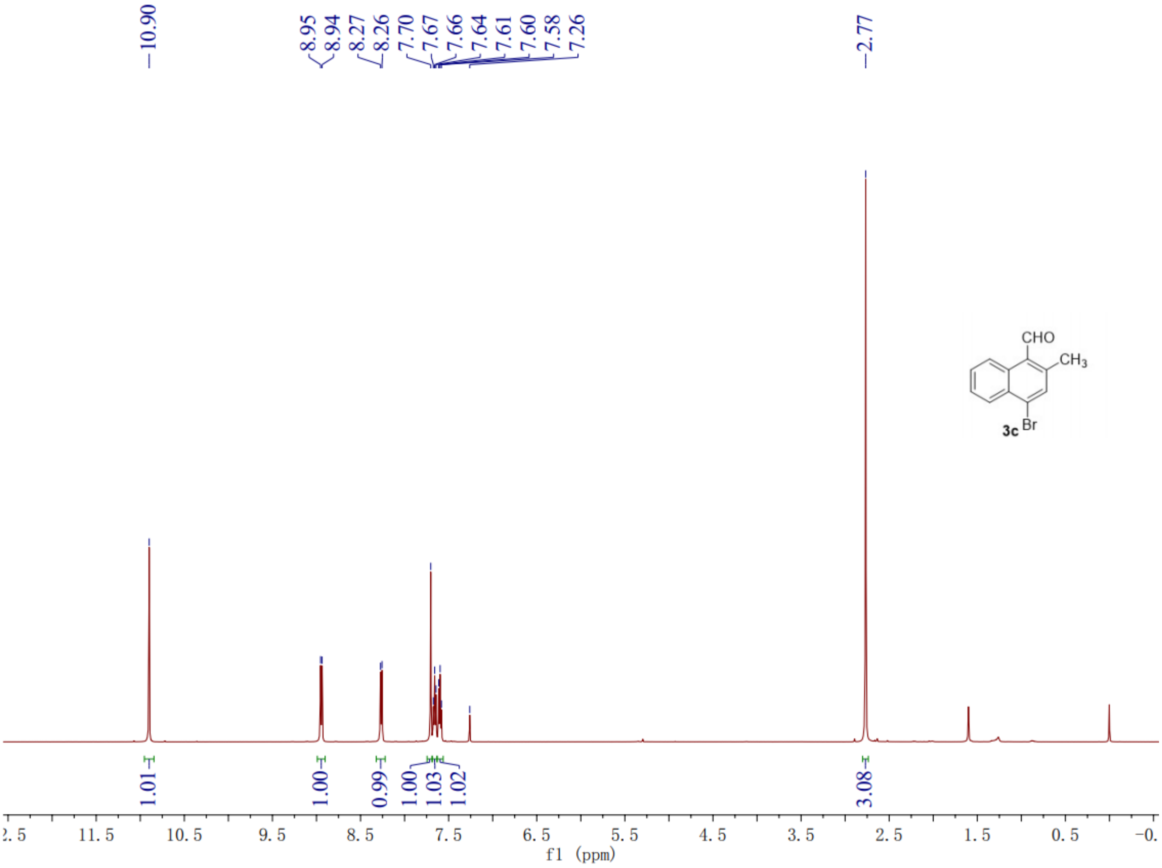
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3b



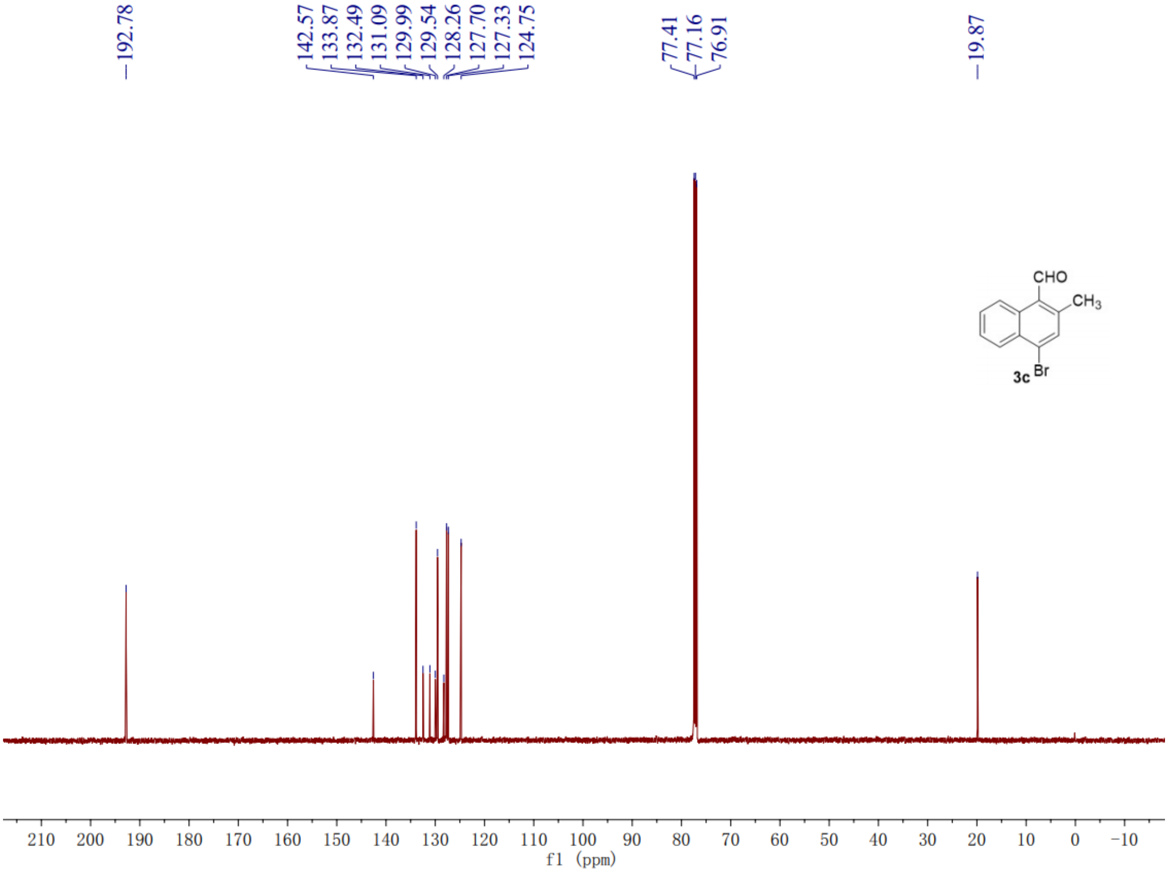
HR-ESI-MS $(M+H)^+$ of 3b



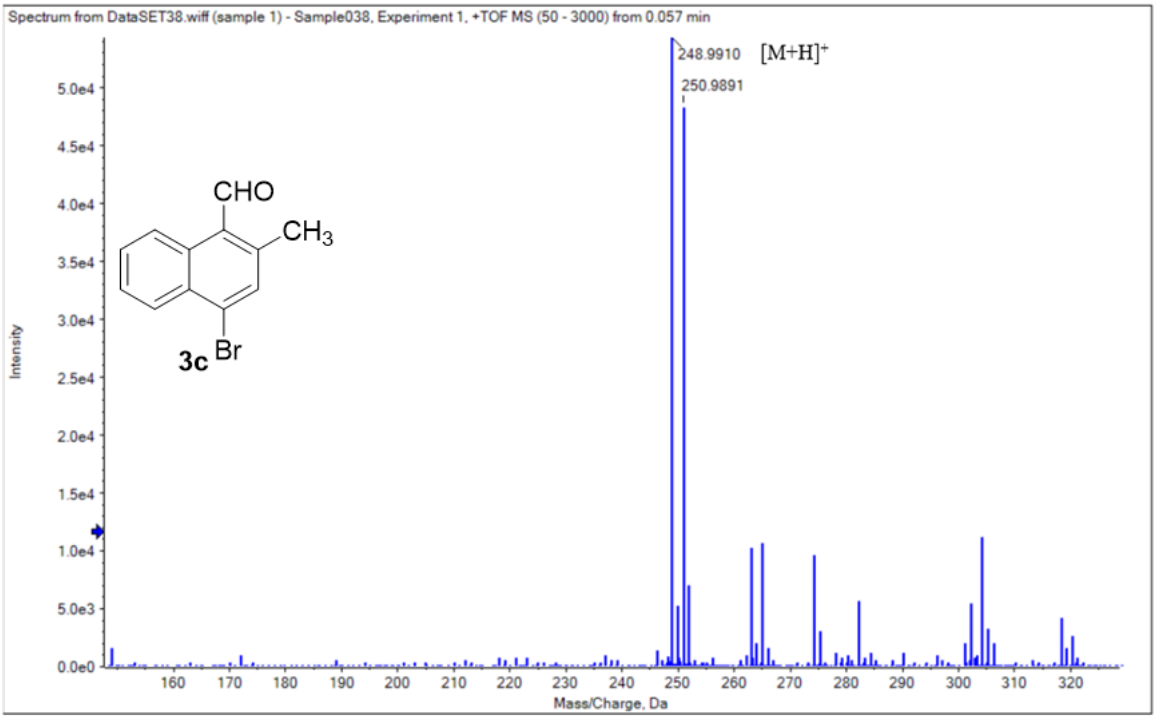
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3c



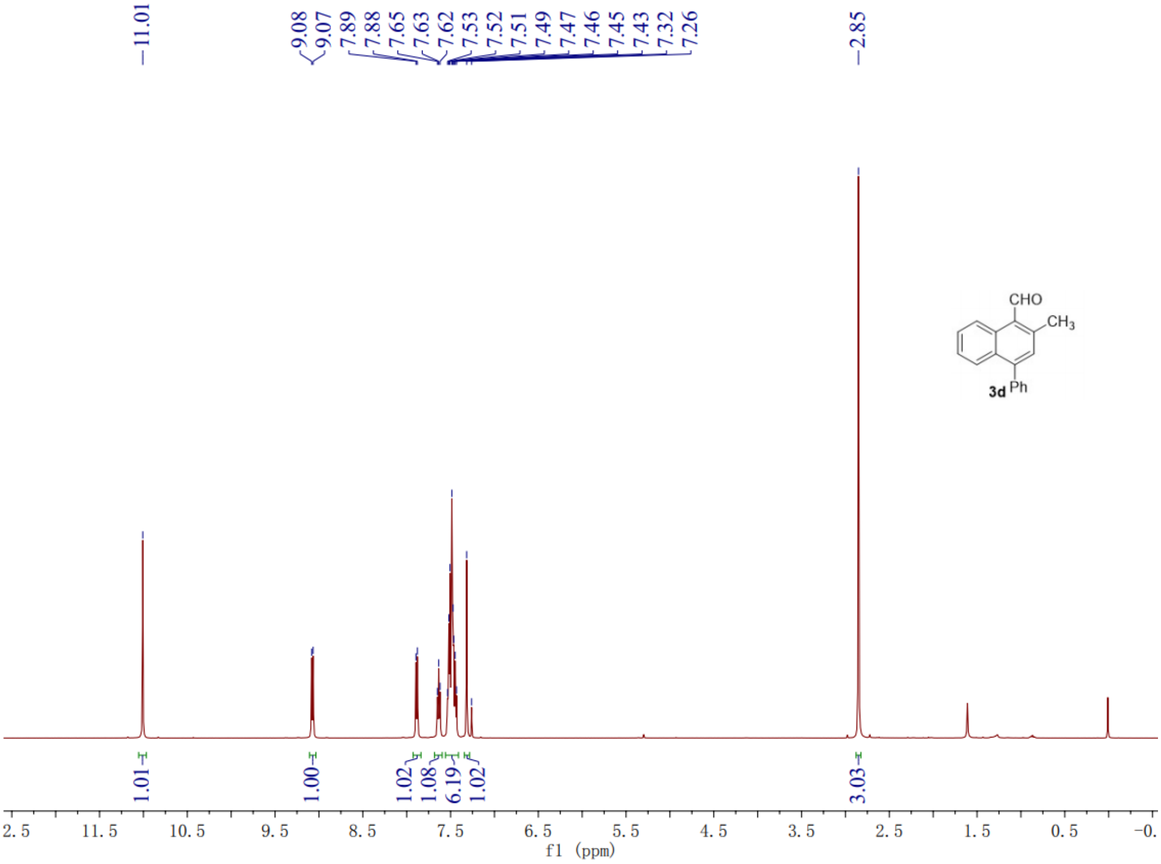
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3c



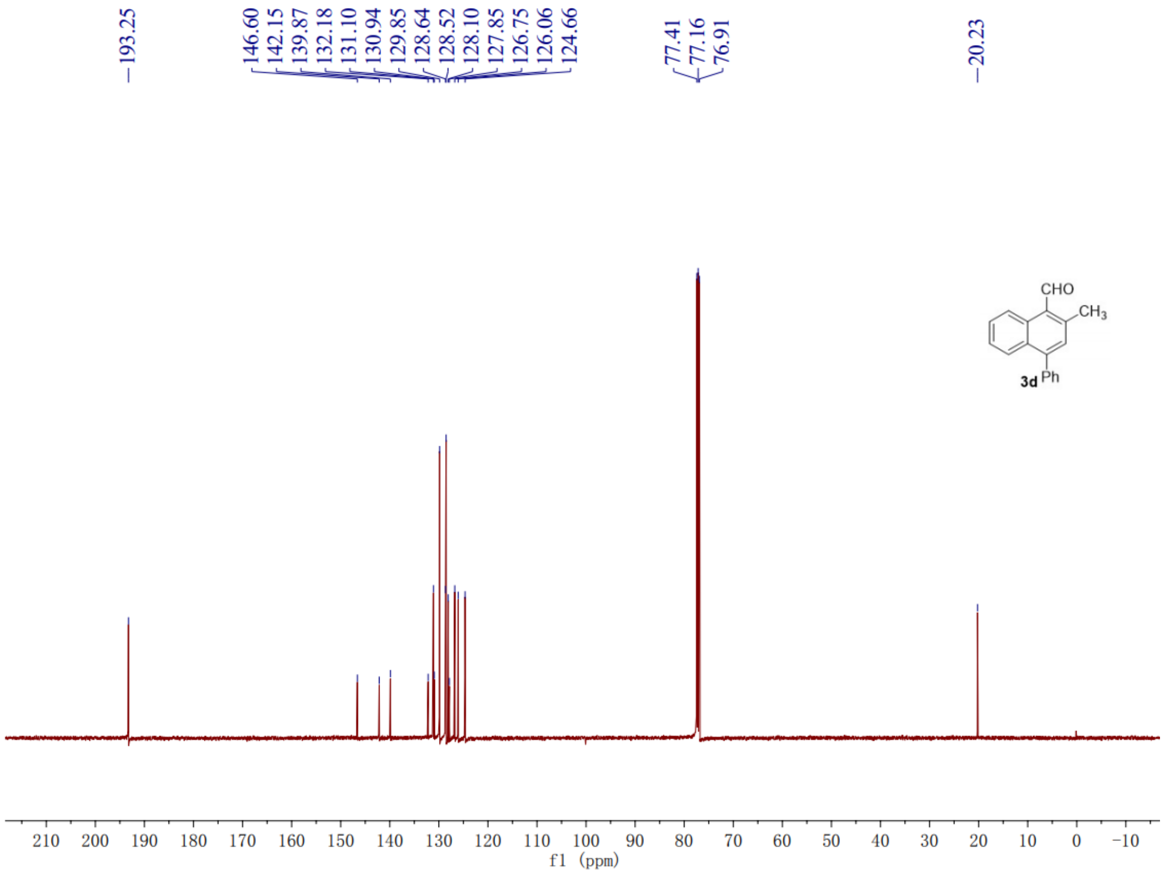
HR-ESI-MS $(M+H)^+$ of 3c



^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3d



^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 3d



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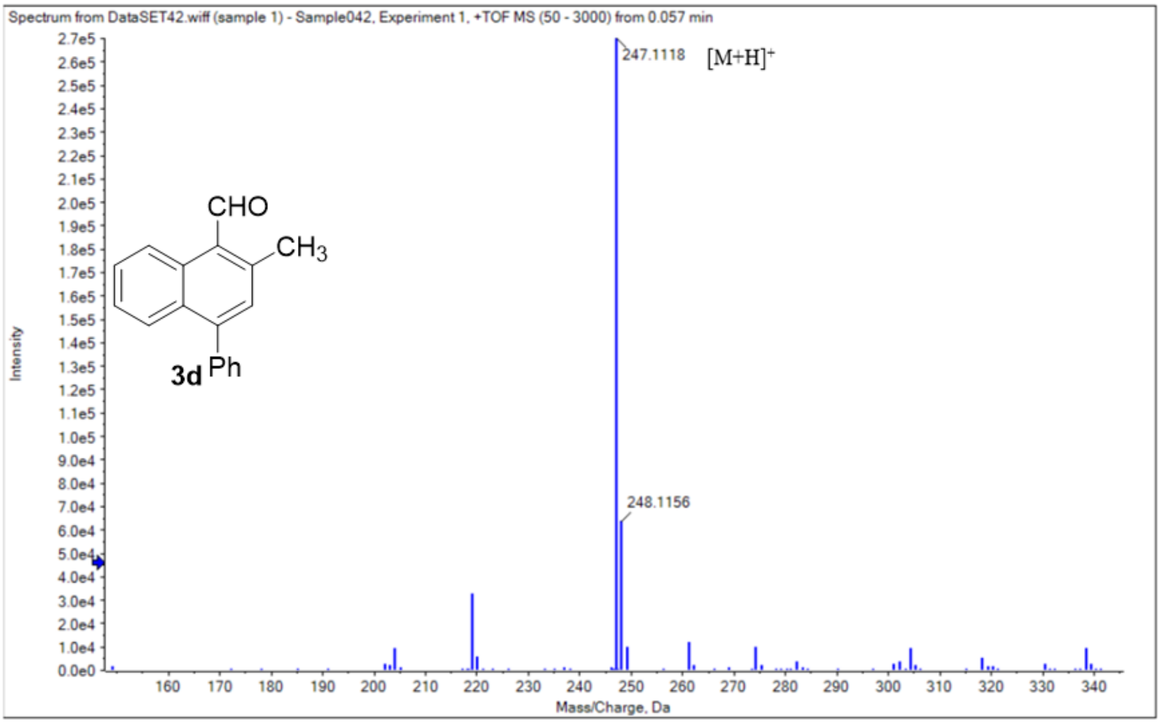

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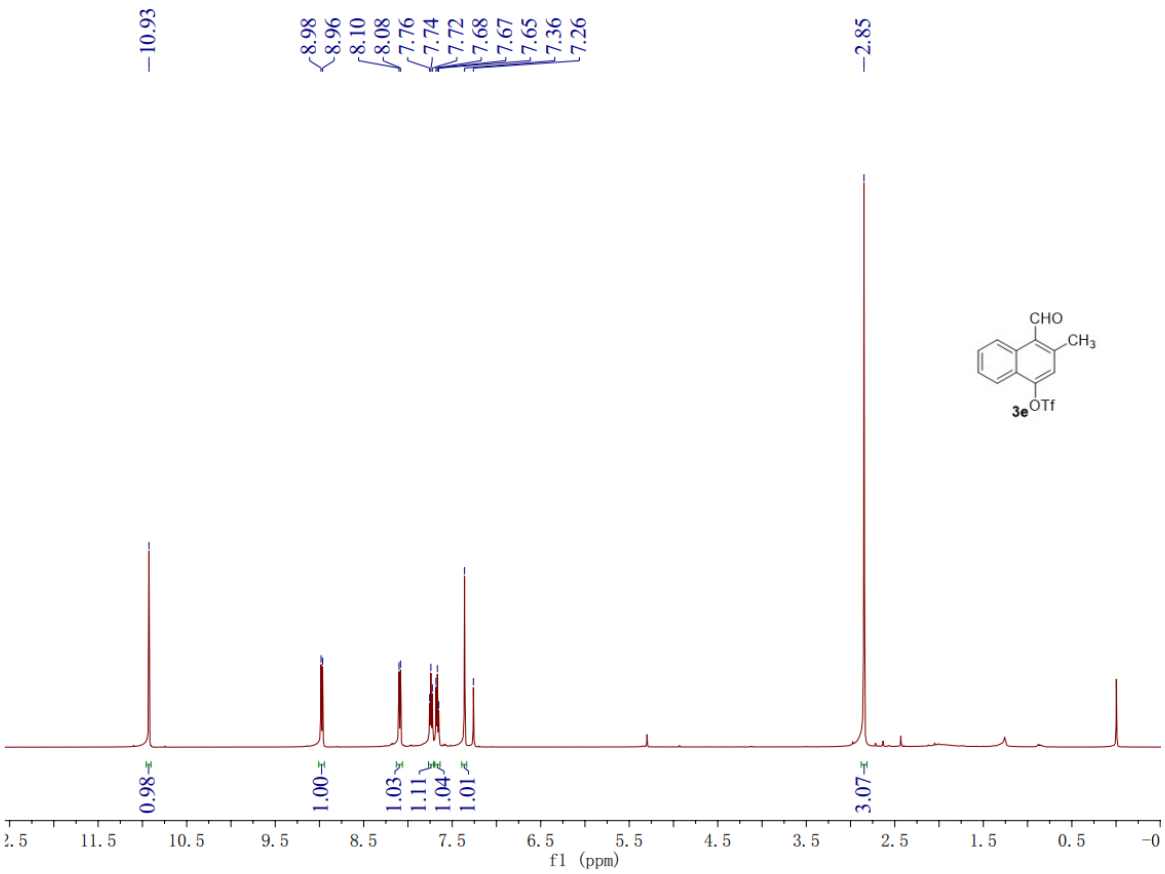
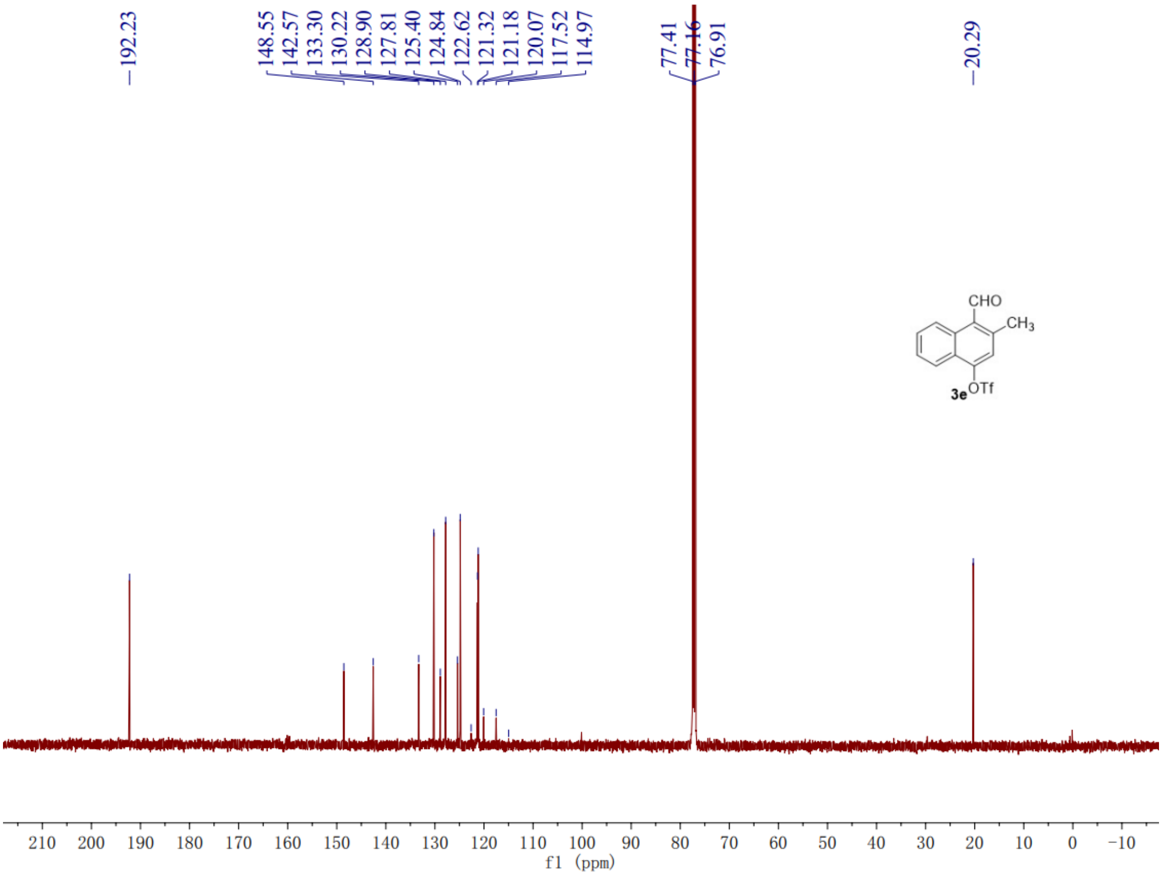


^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 3e



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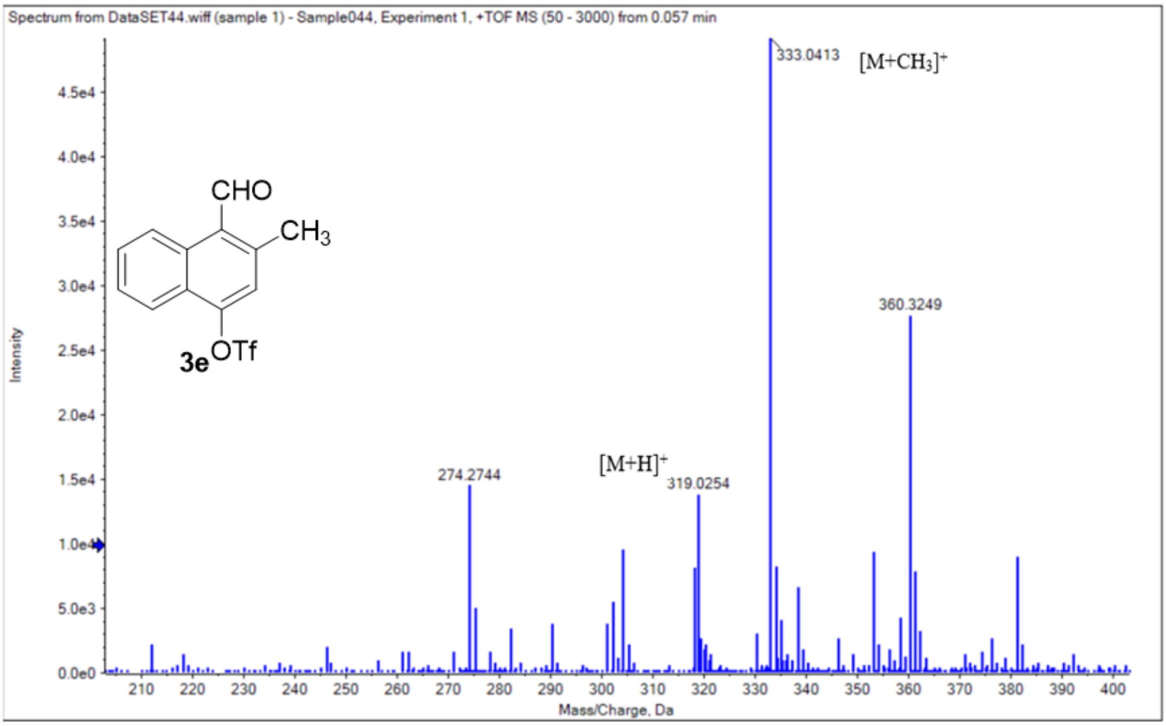

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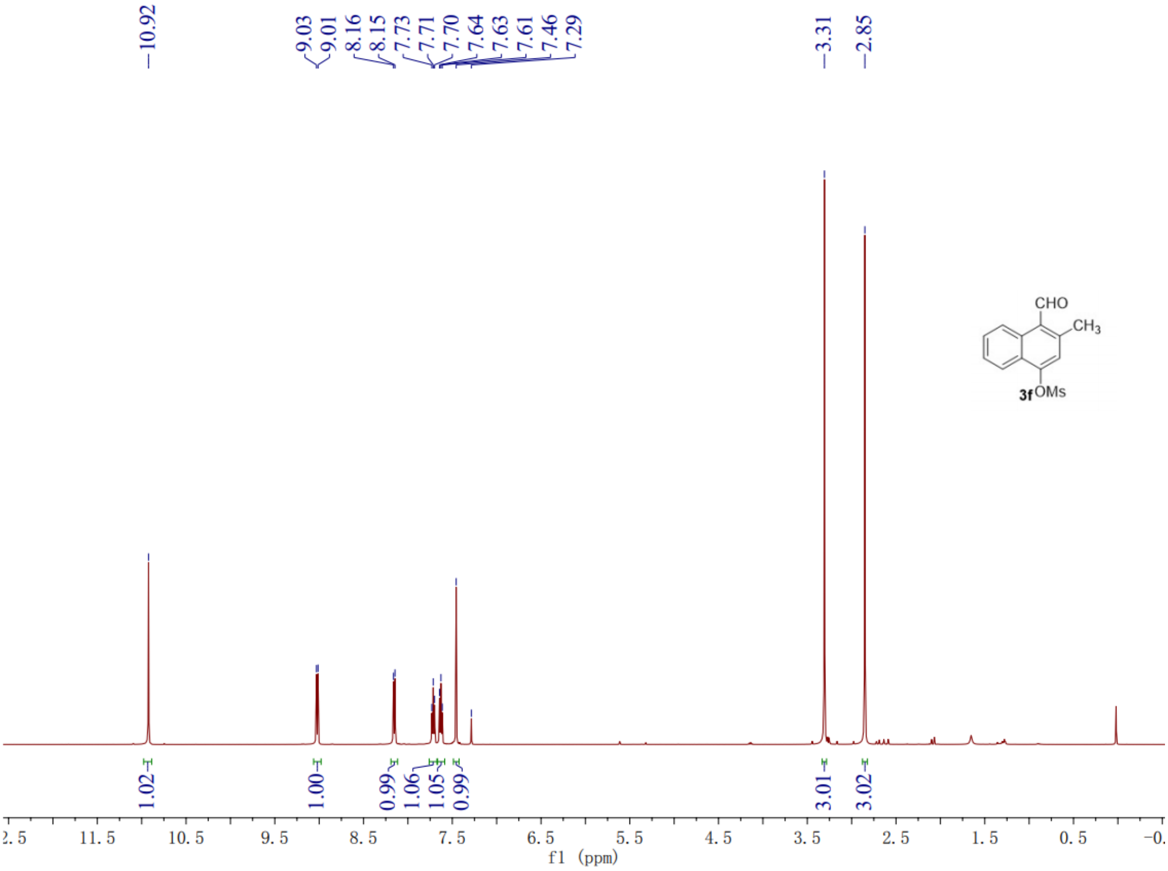
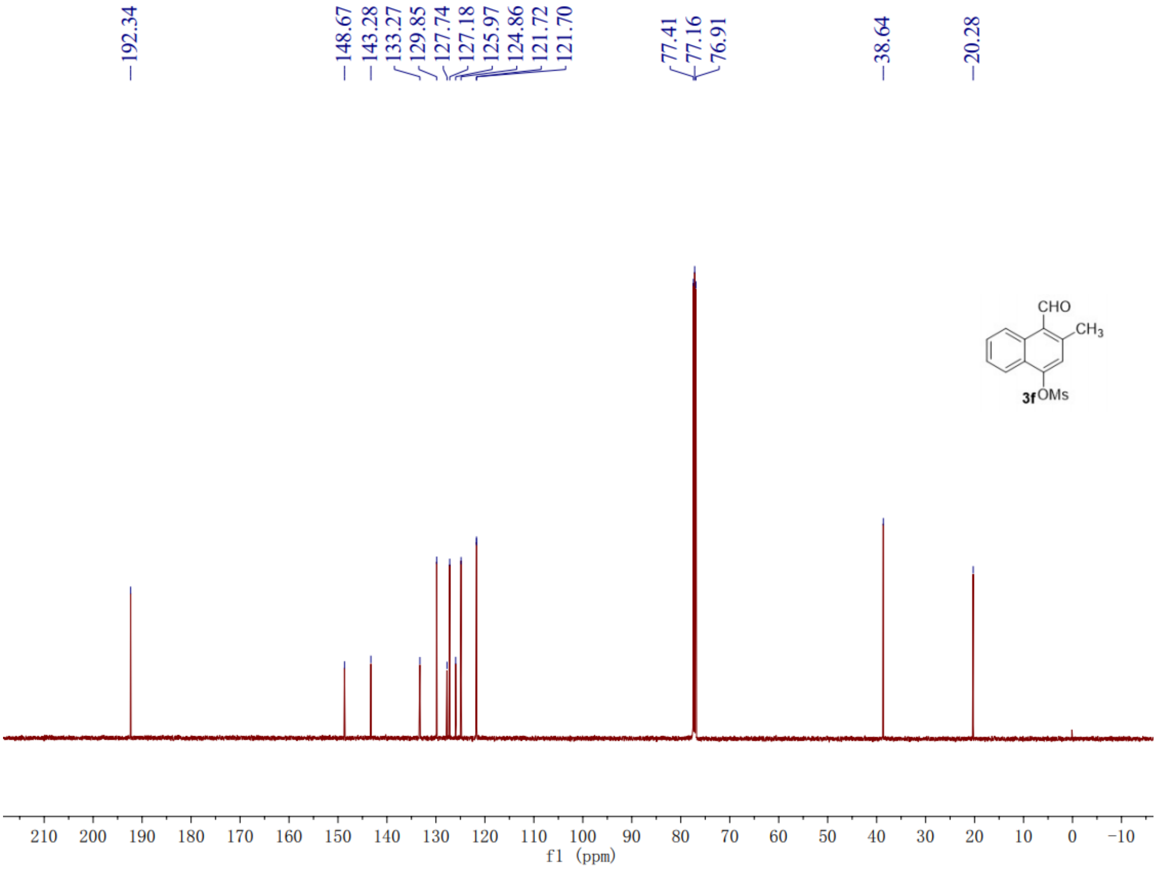


^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3f



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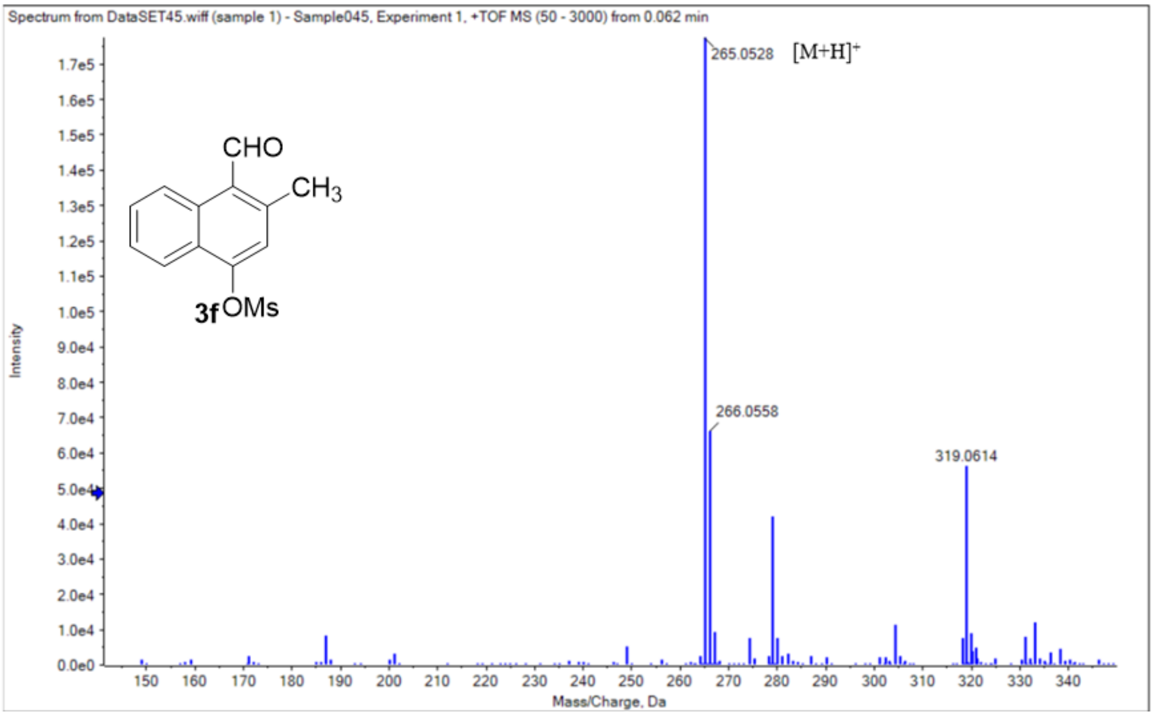
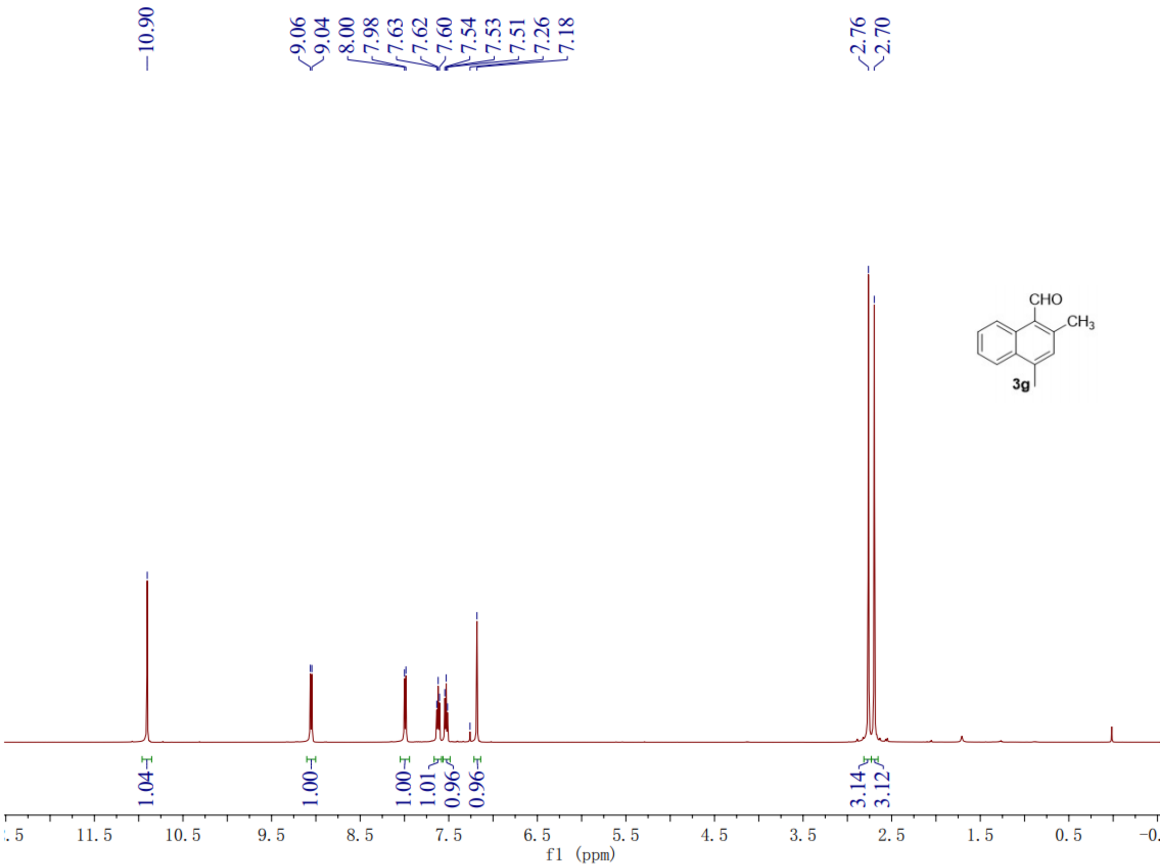
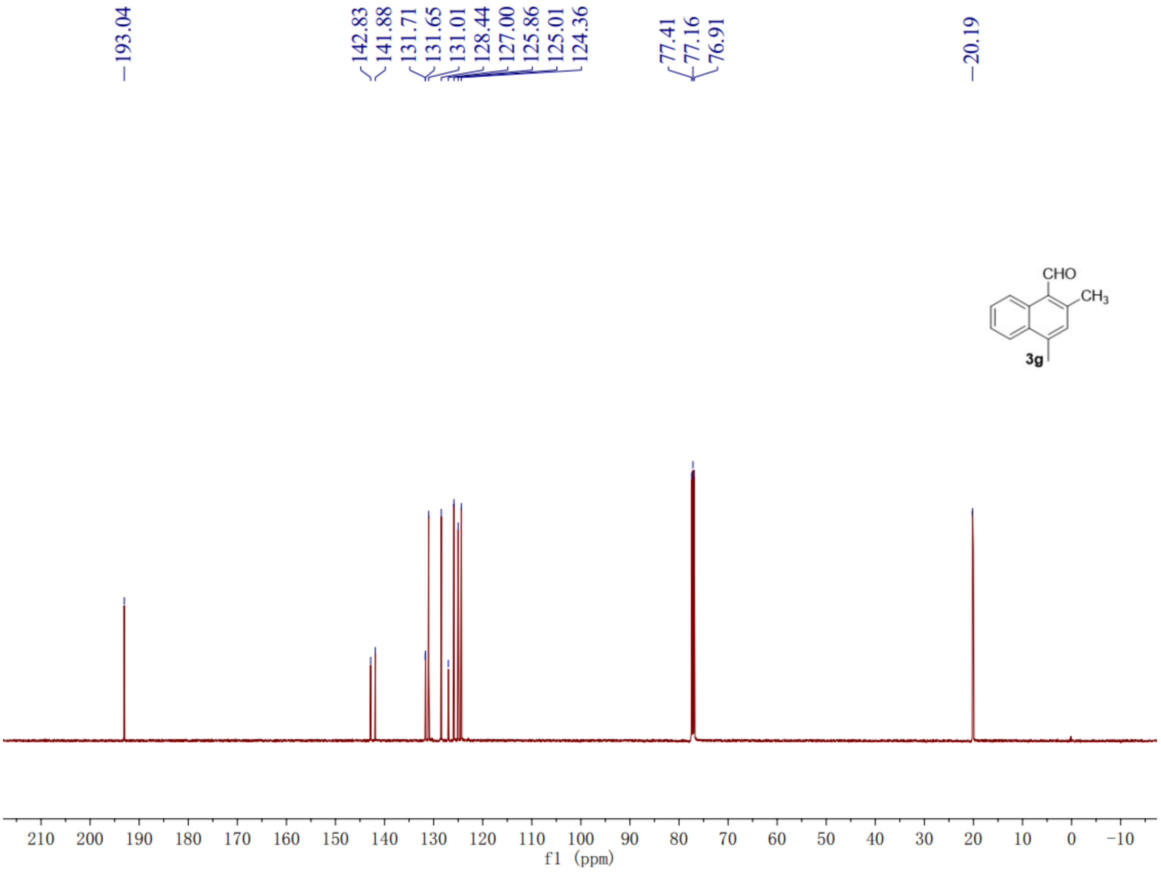


^1H NMR spectrum ($CDCl_3$, 500 MHz) of 3g



^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 3g



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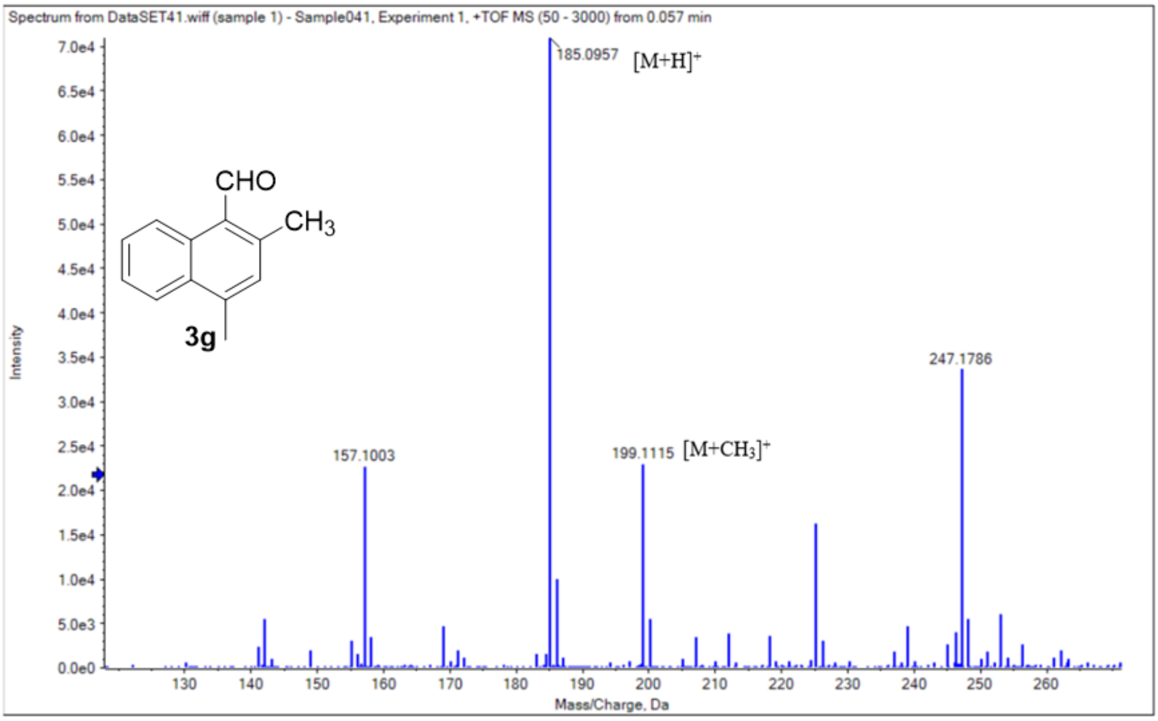
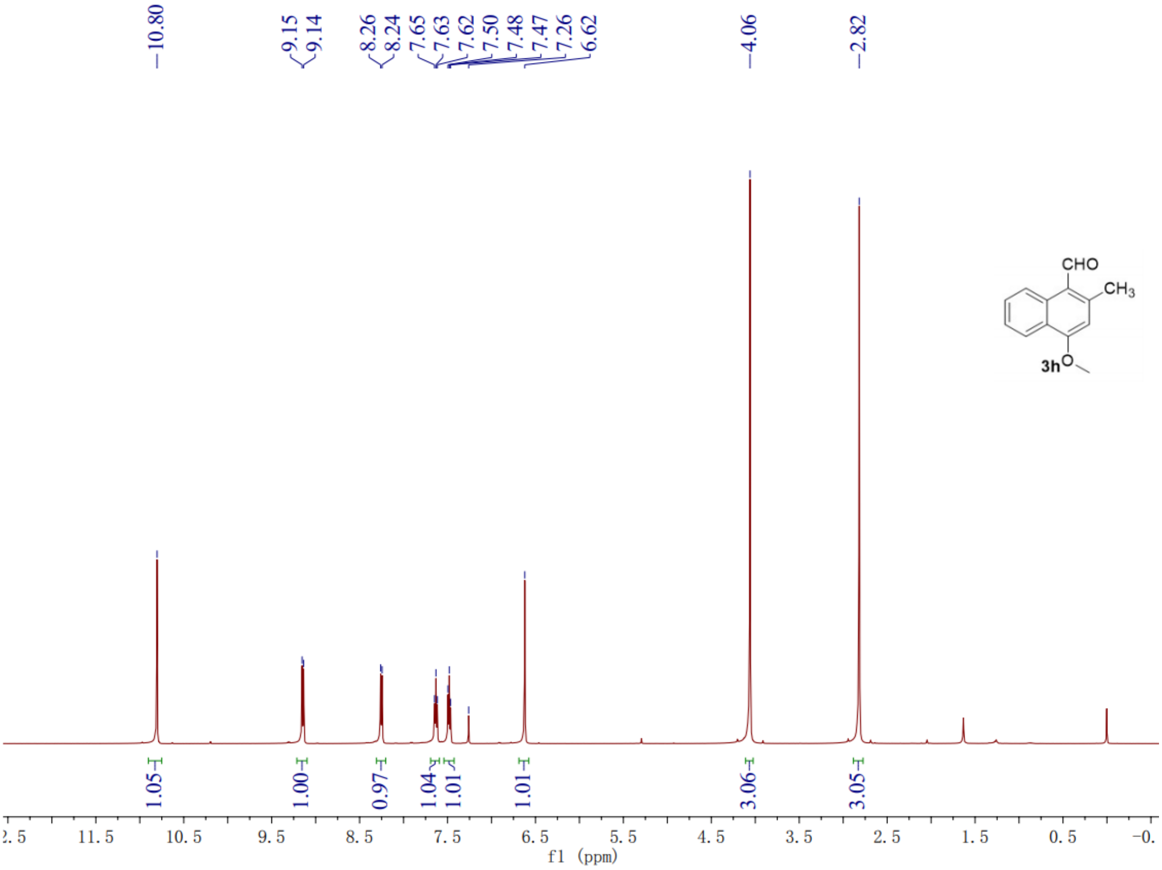
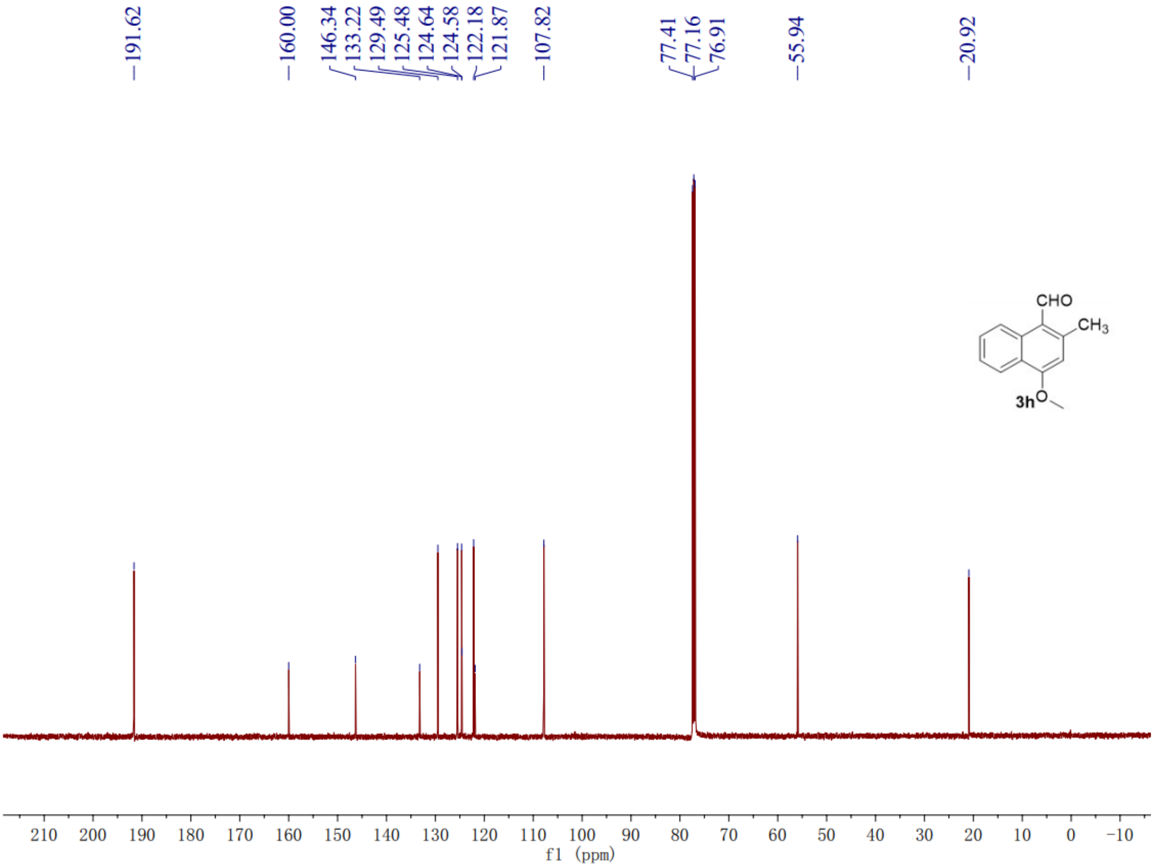


^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3h



^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 3h



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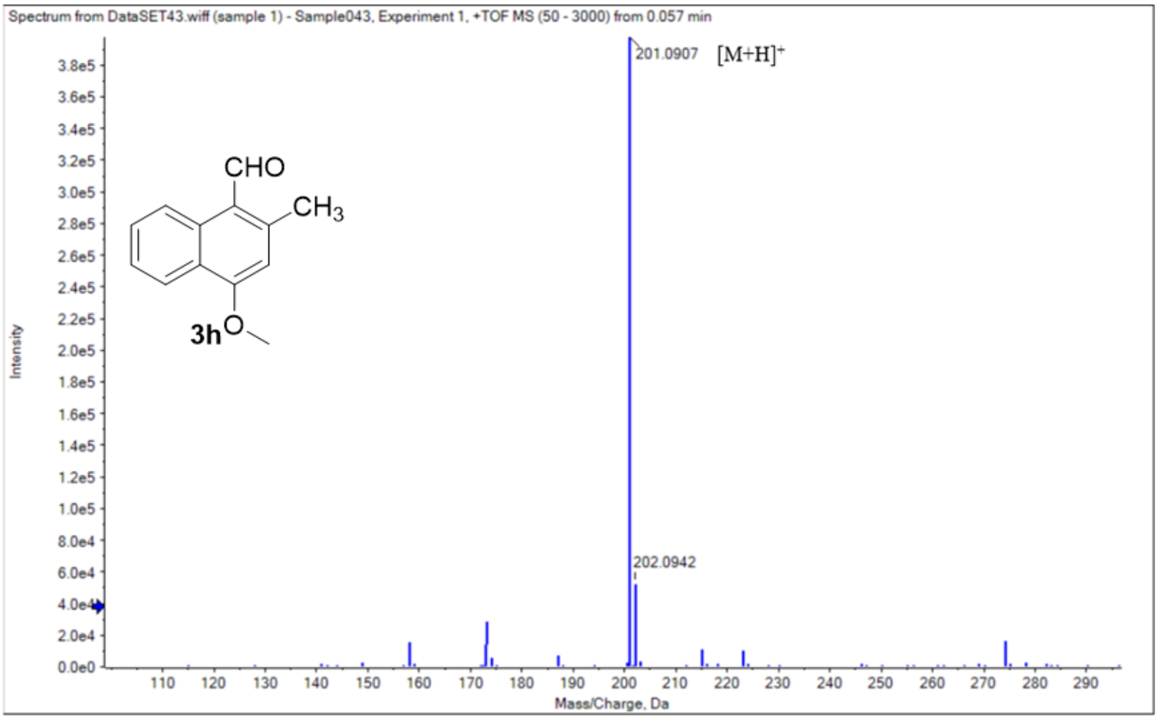
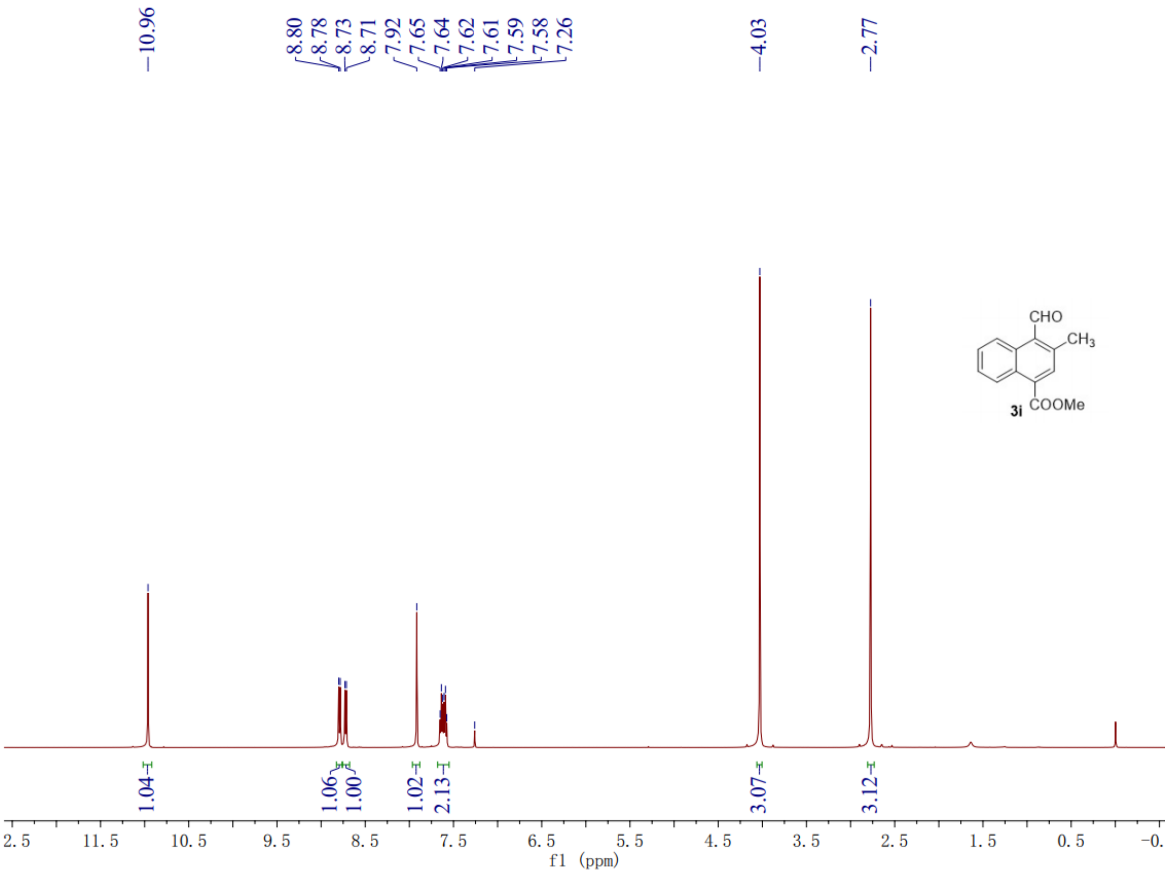
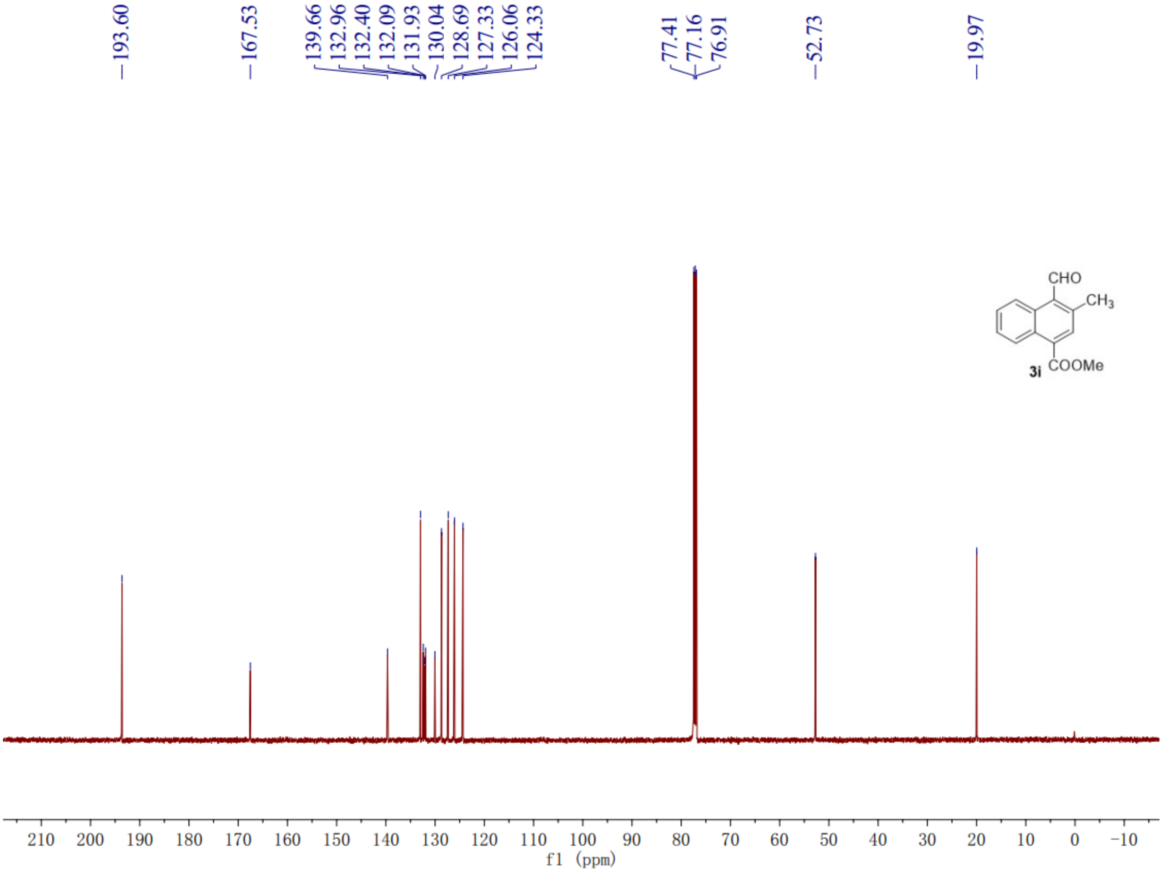


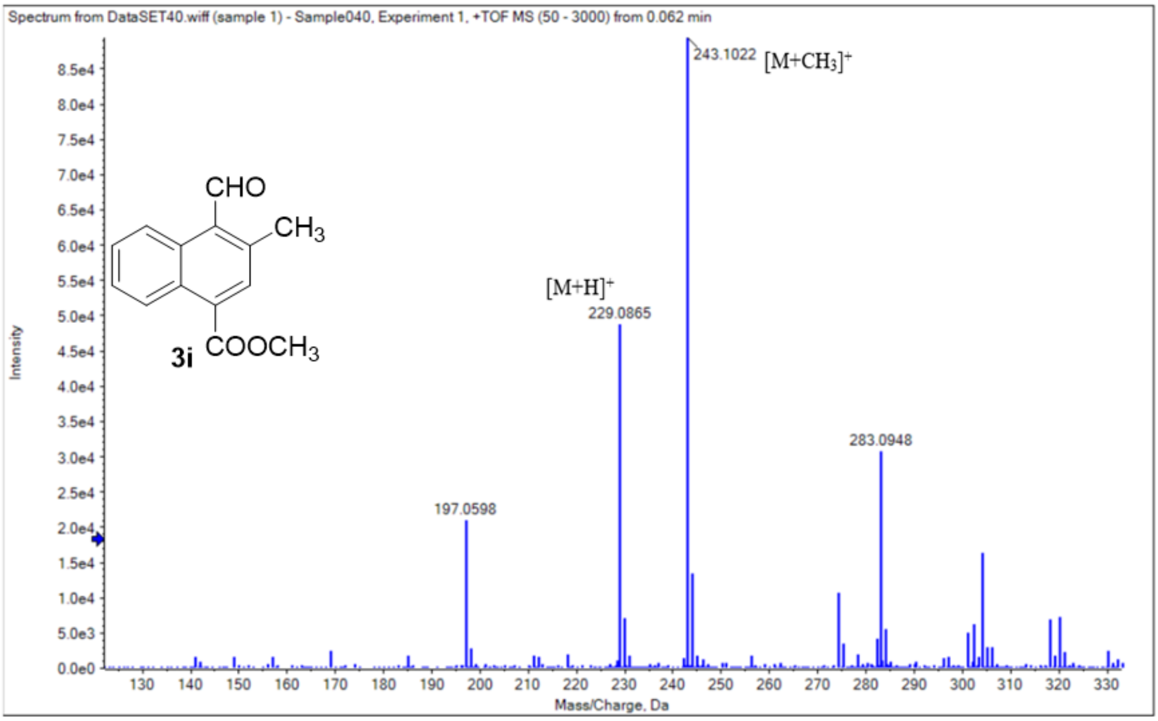
^1H NMR spectrum ($CDCl_3$, 500 MHz) of 3i



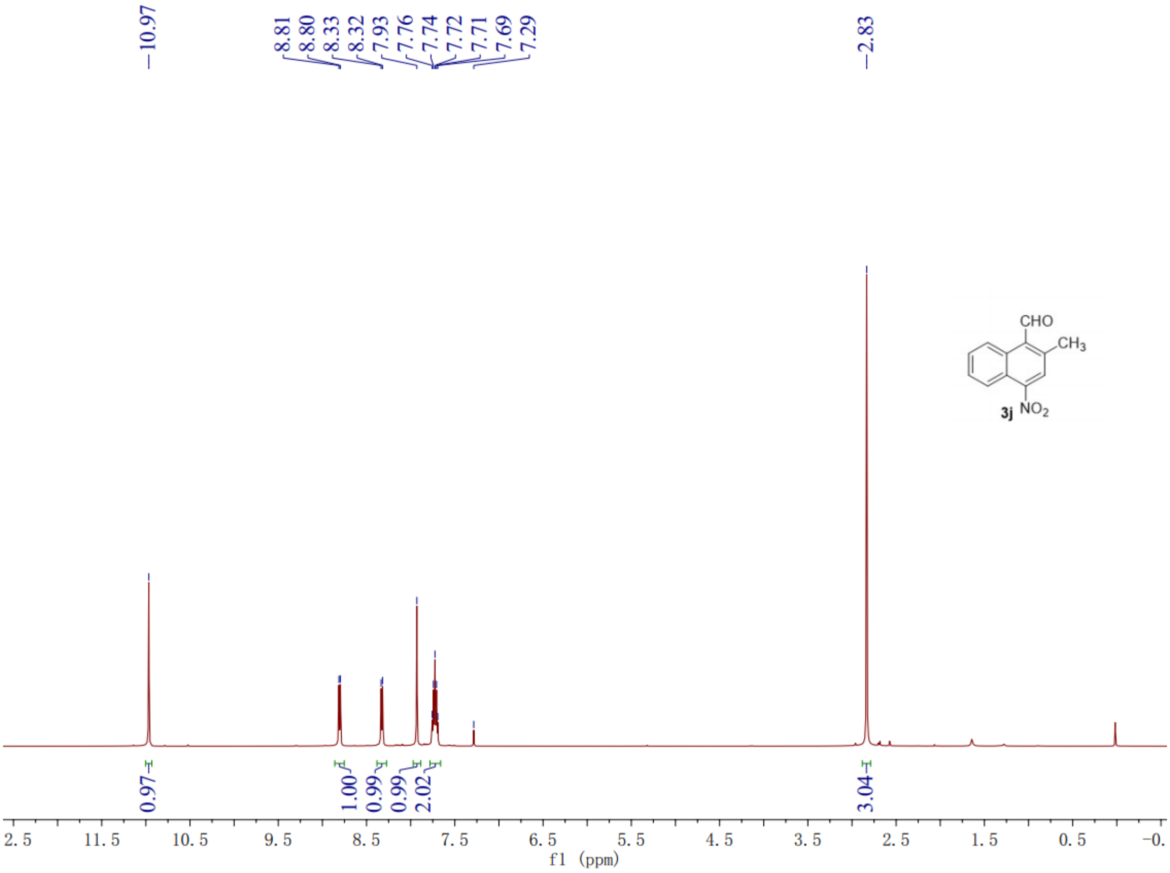
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3i



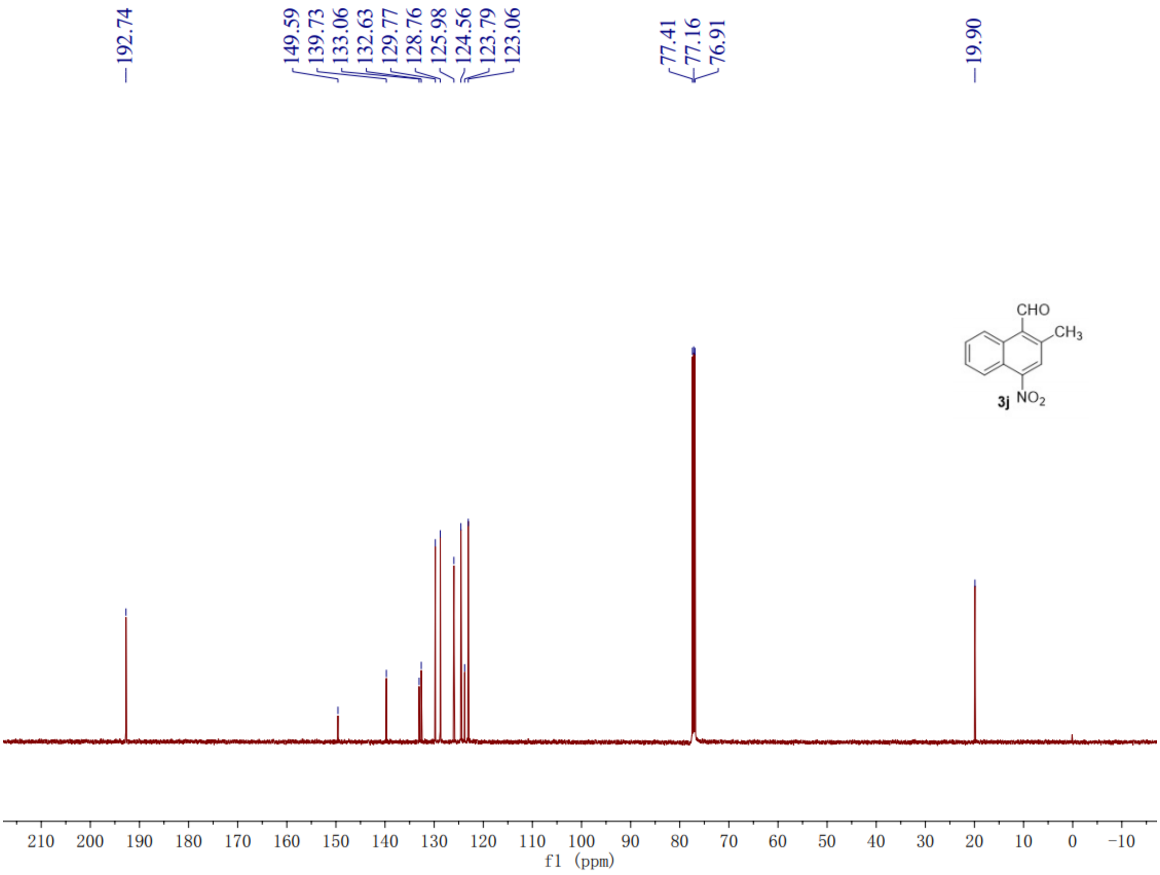
HR-ESI-MS (M+CH$_3$)$^+$ of 3i



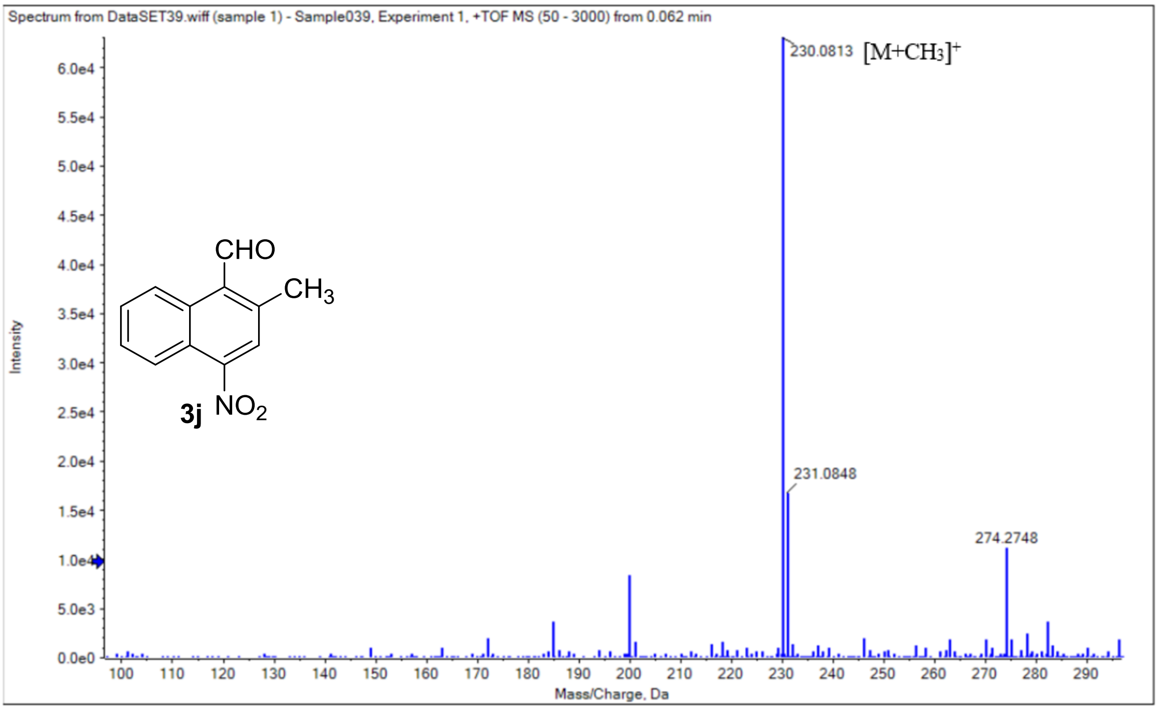
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3j



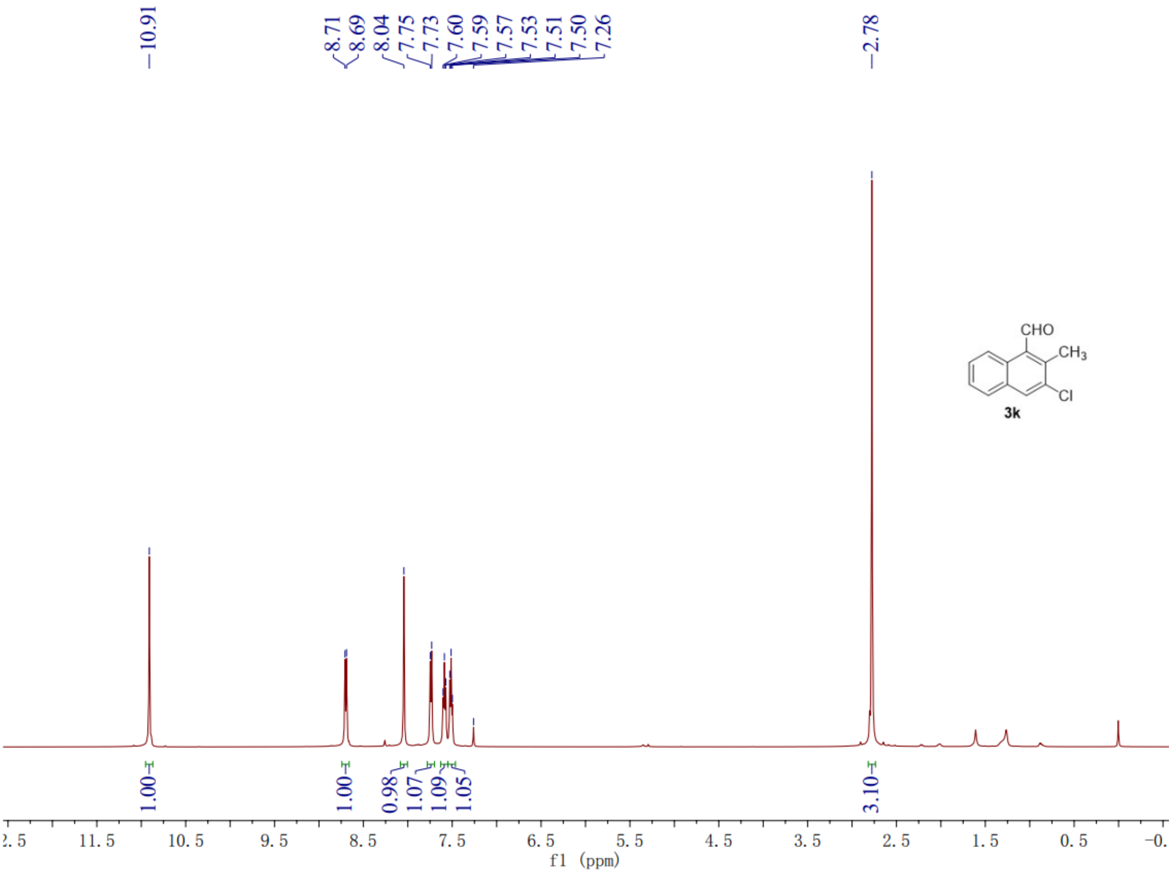
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3j



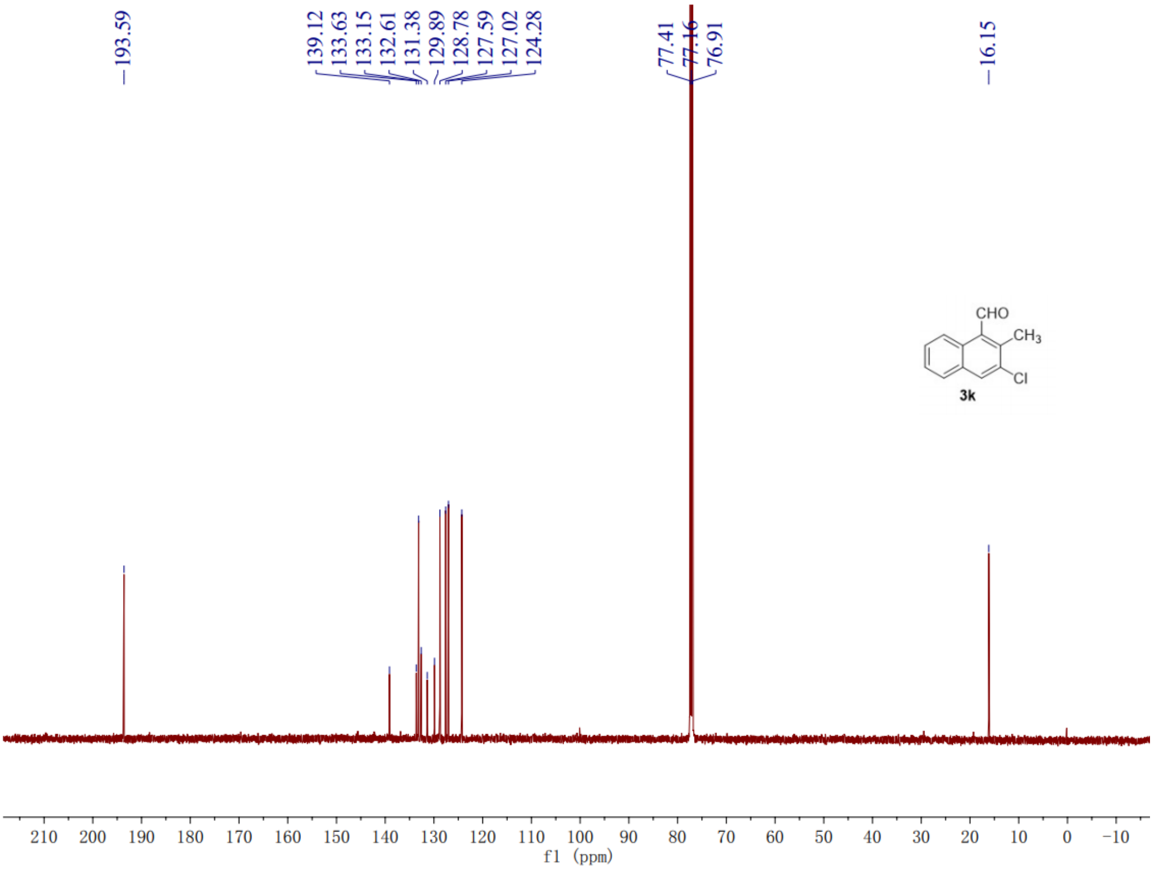
HR-ESI-MS $(M+CH_3)^+$ of 3j



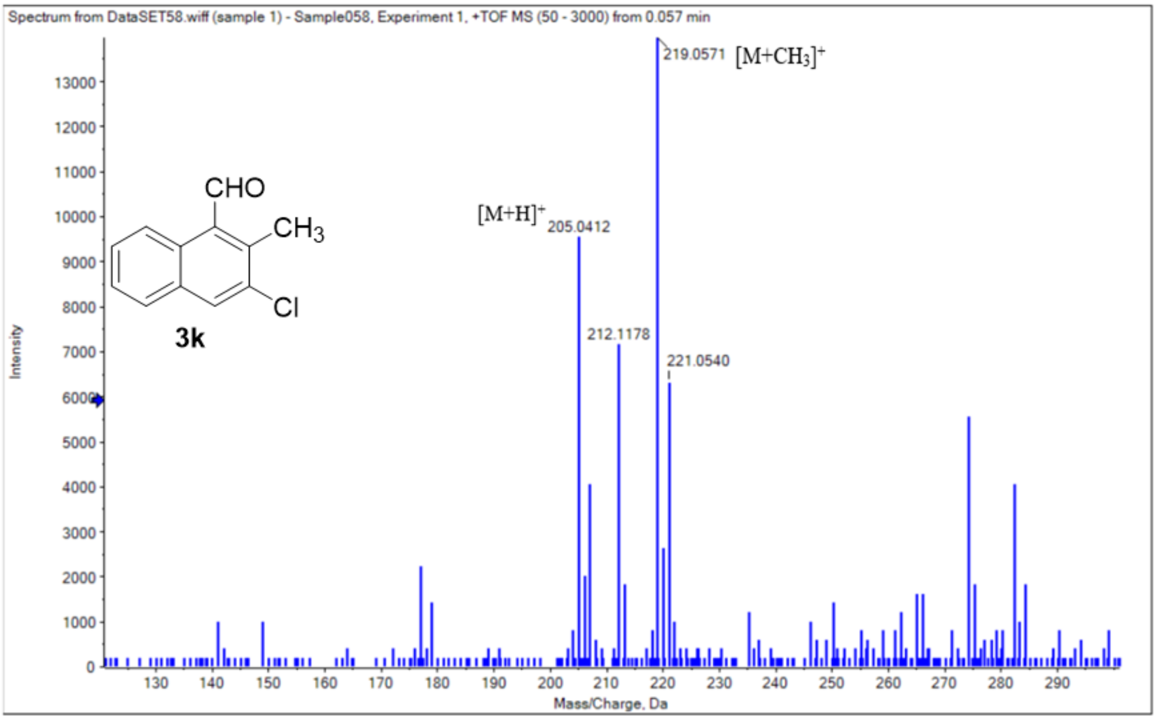
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3k



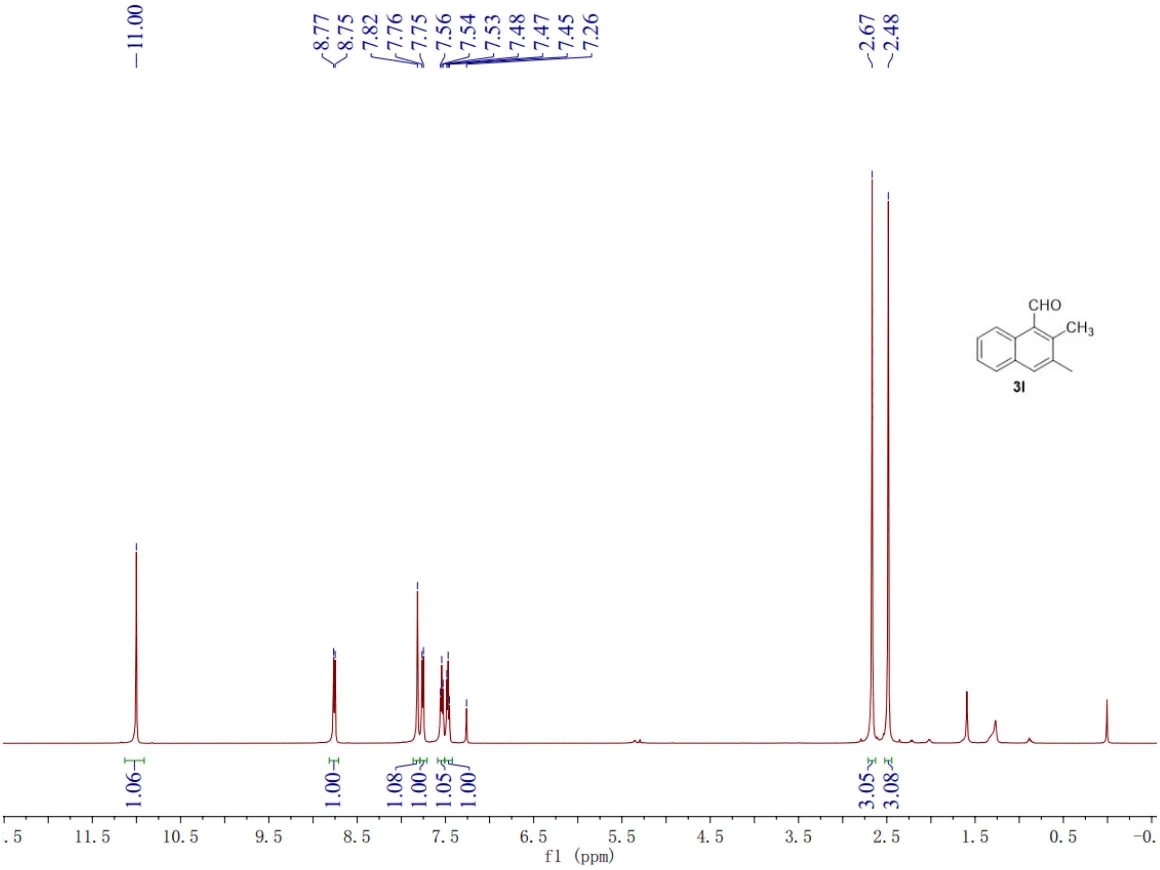
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3k



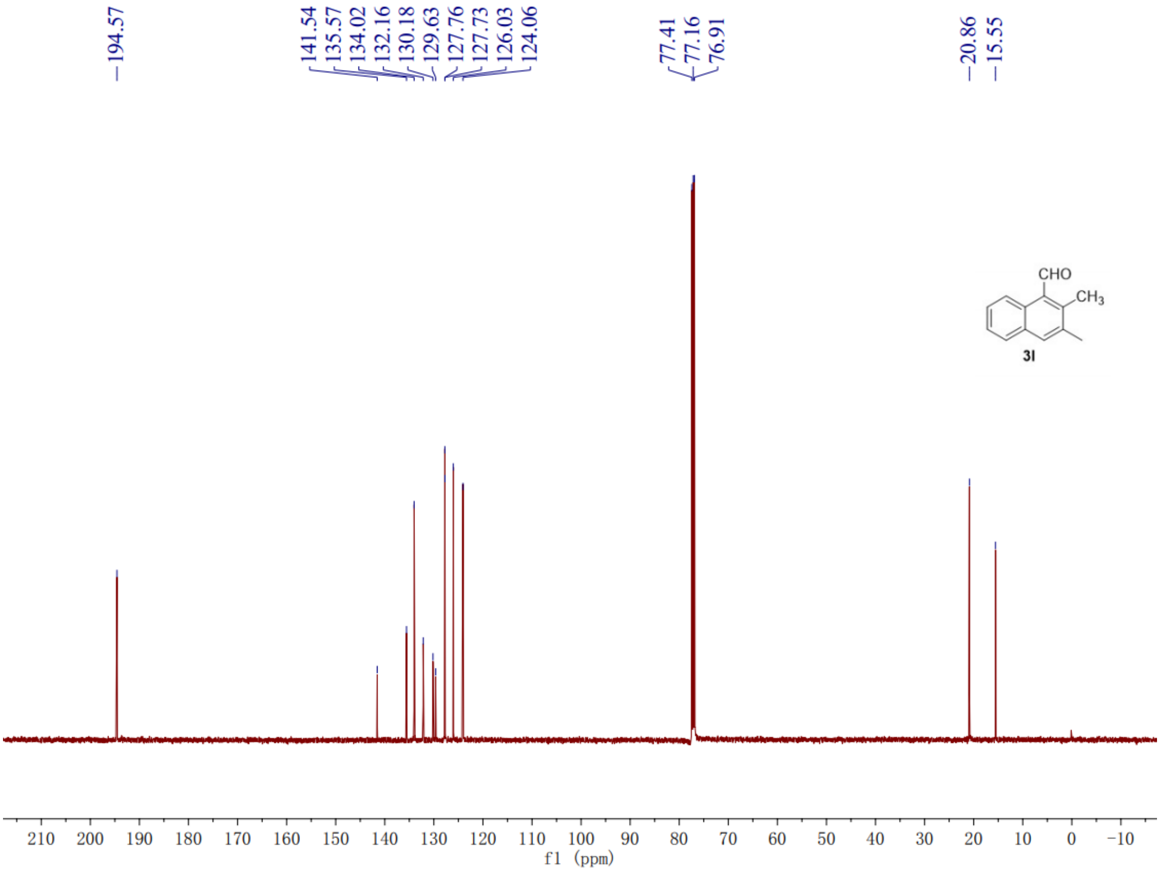
HR-ESI-MS (M+CH$_3$)$^+$ of 3k



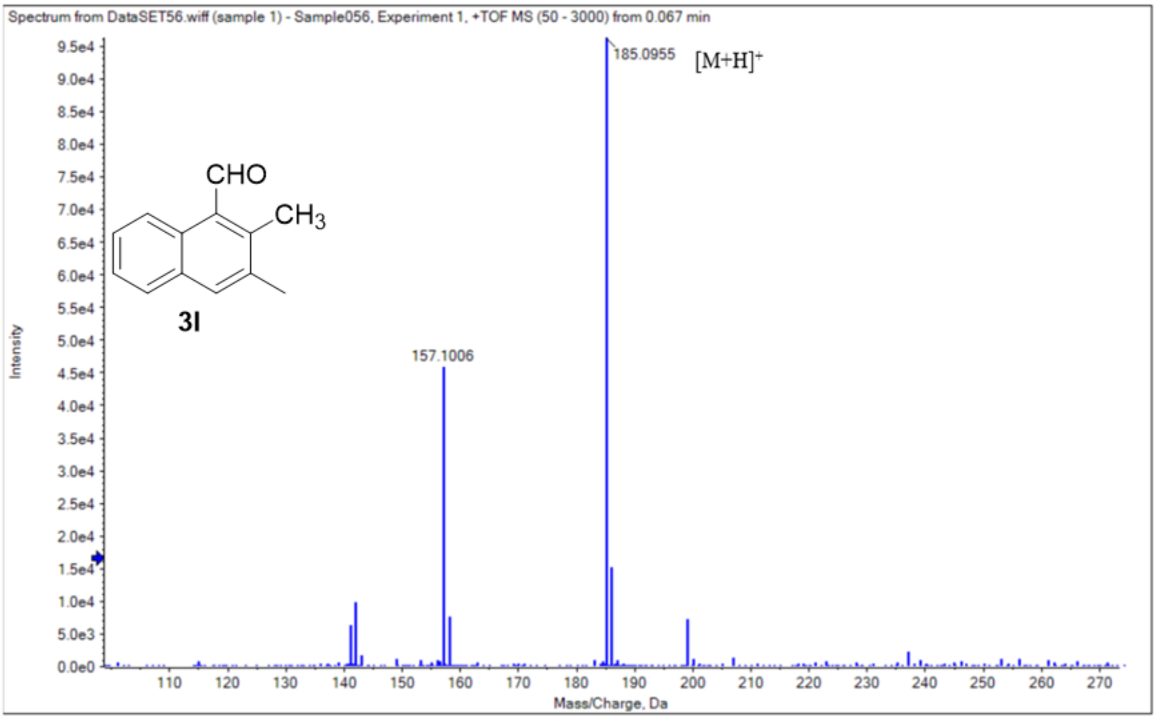
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3l



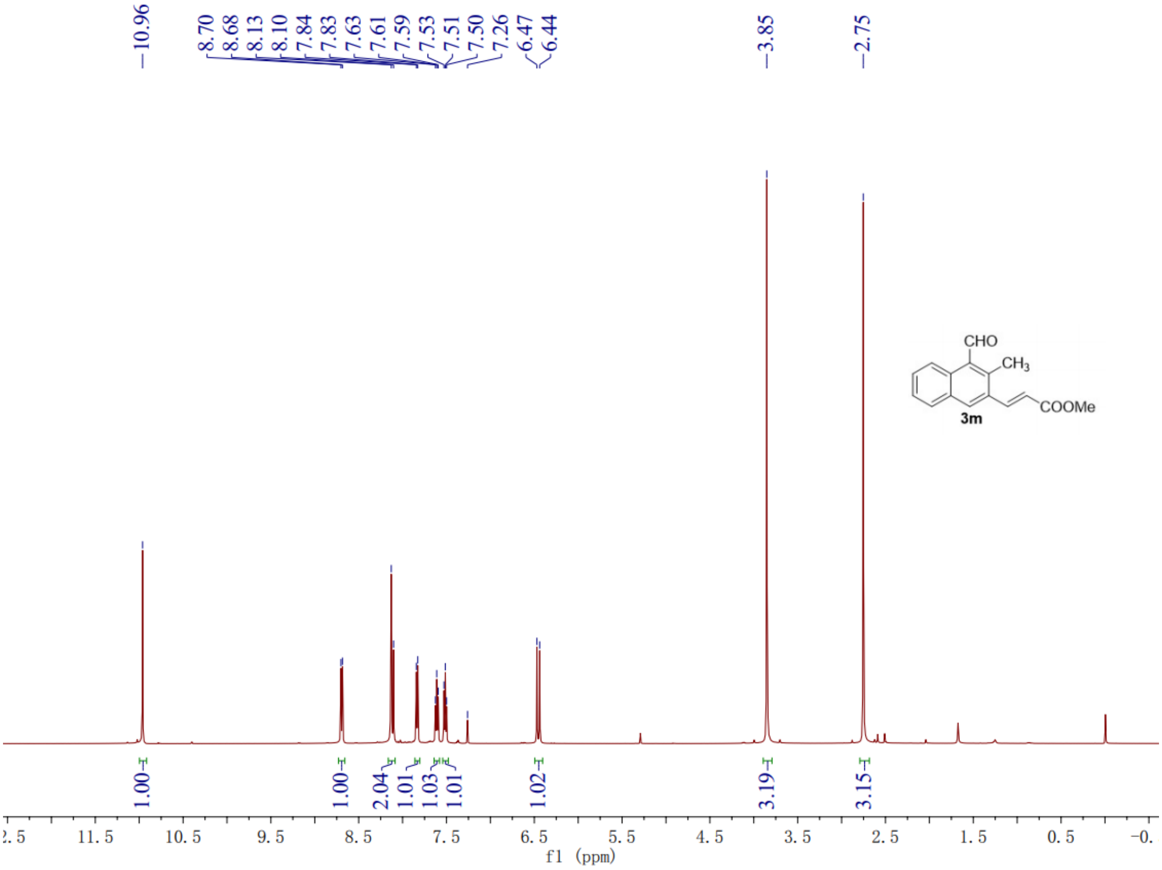
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3l



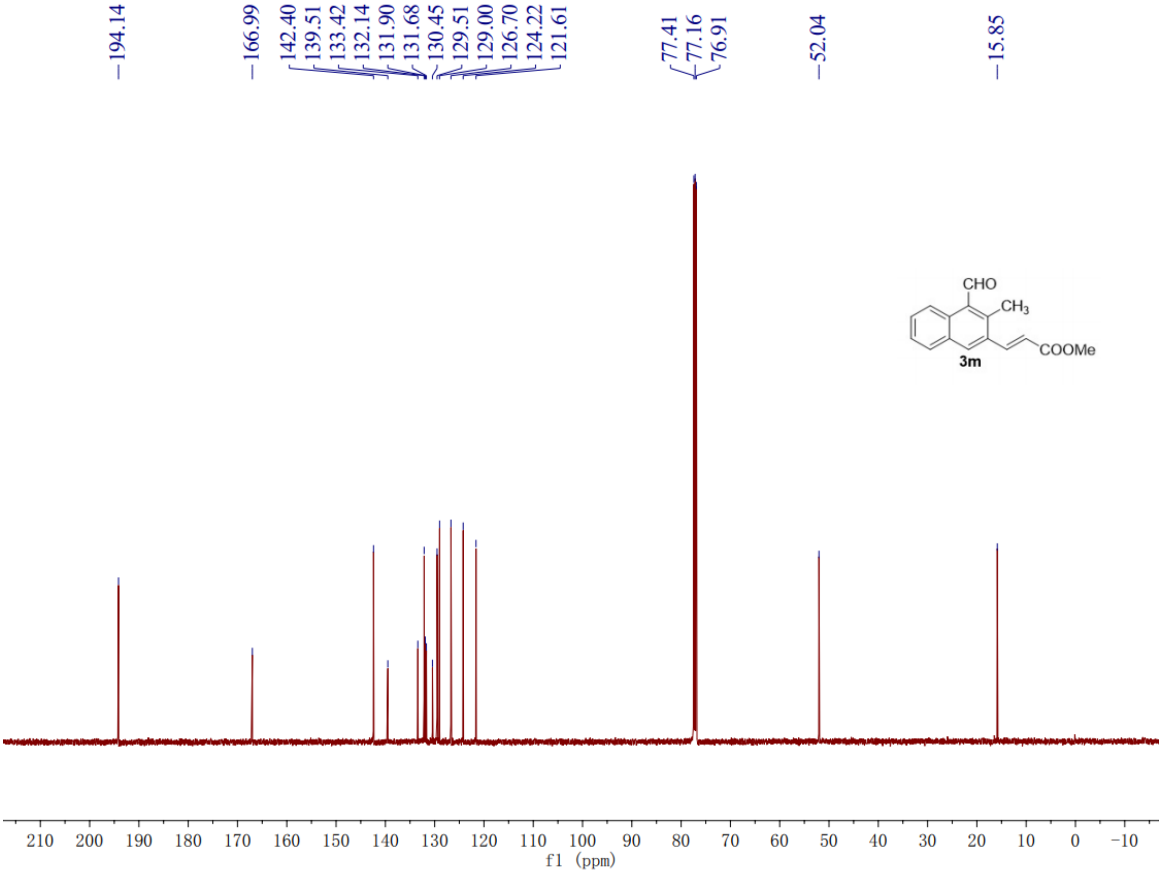
HR-ESI-MS $(M+H)^+$ of 3l



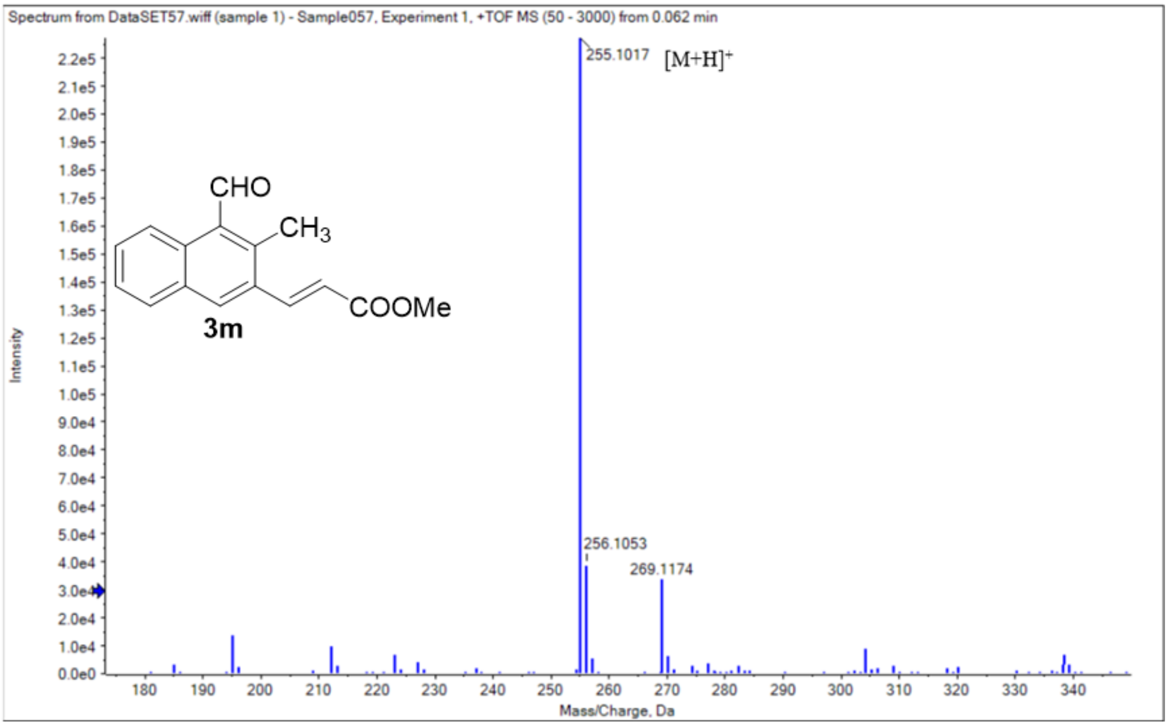
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3m



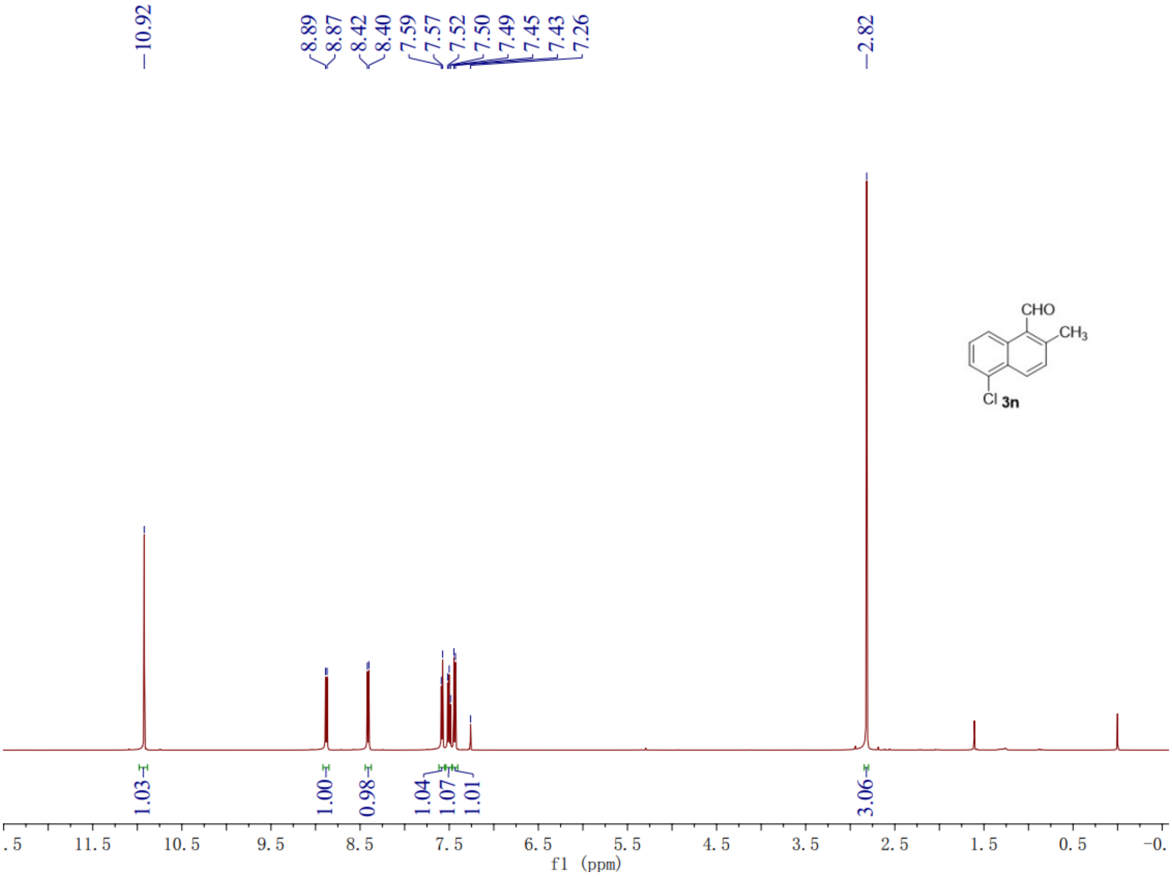
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 3m



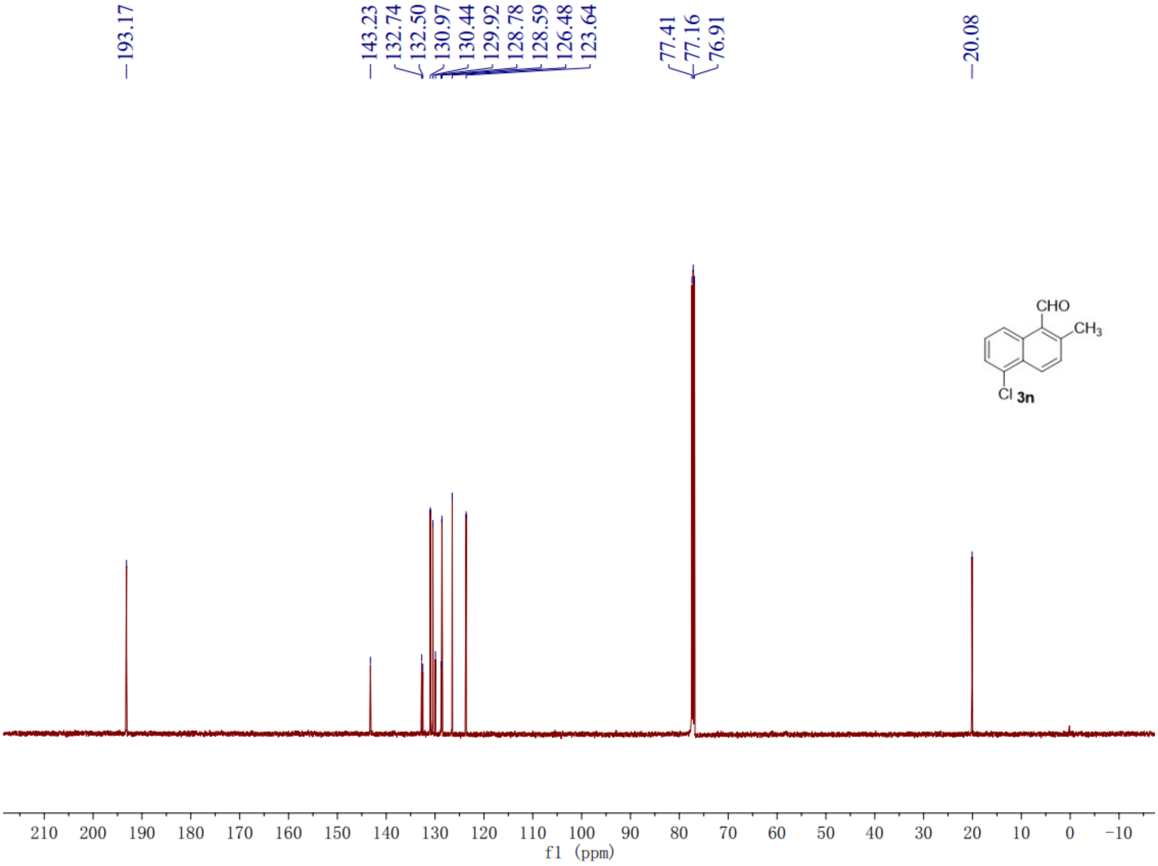
HR-ESI-MS $(M+H)^+$ of 3m



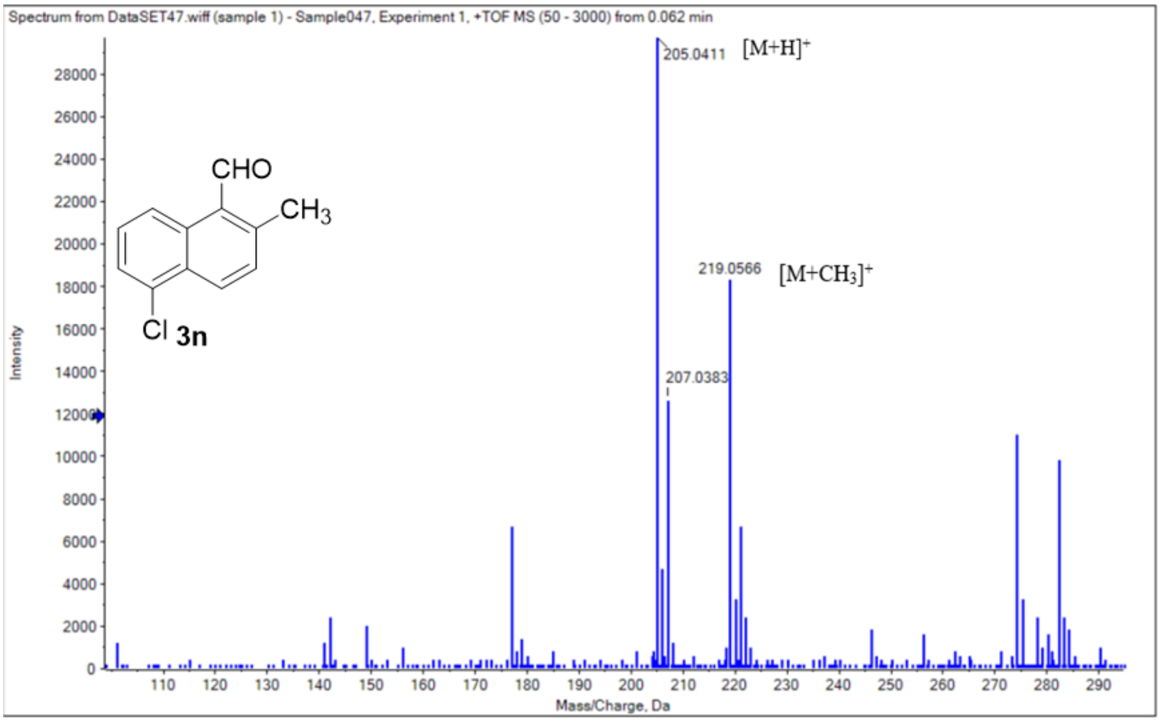
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3n



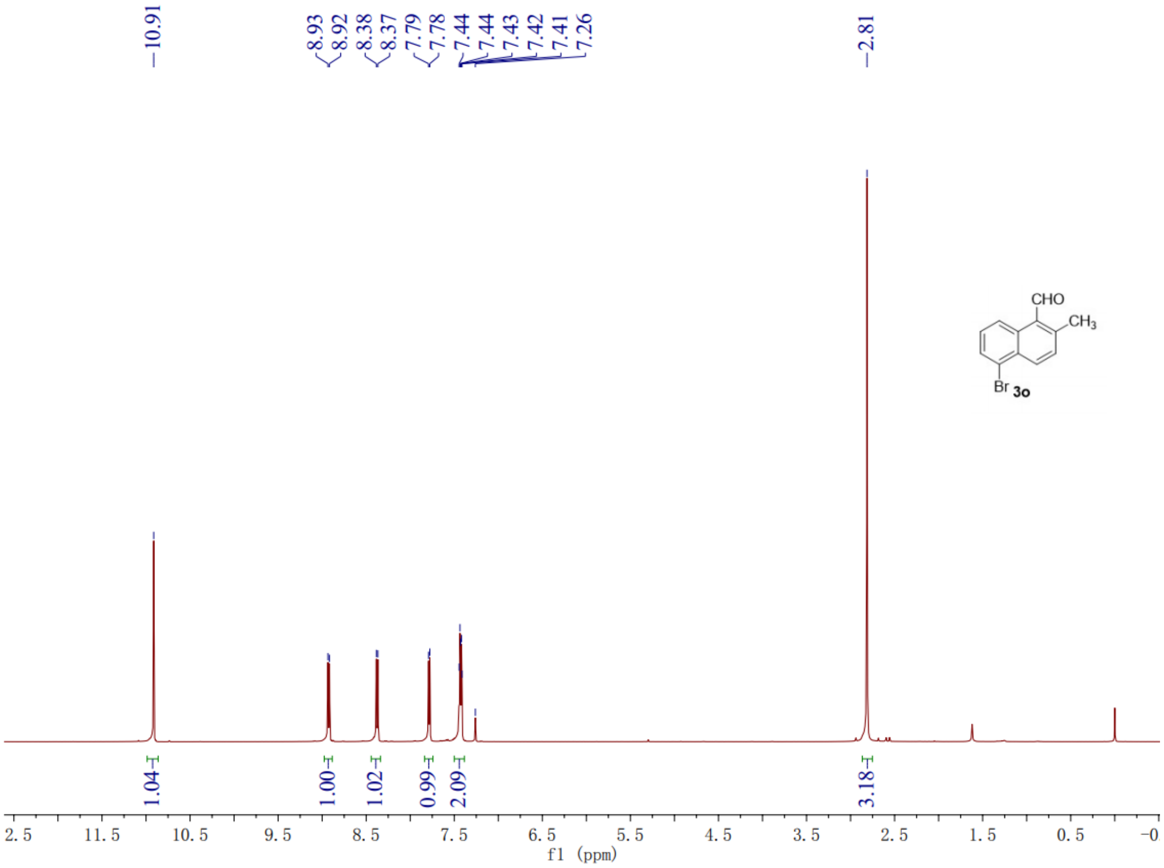
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3n



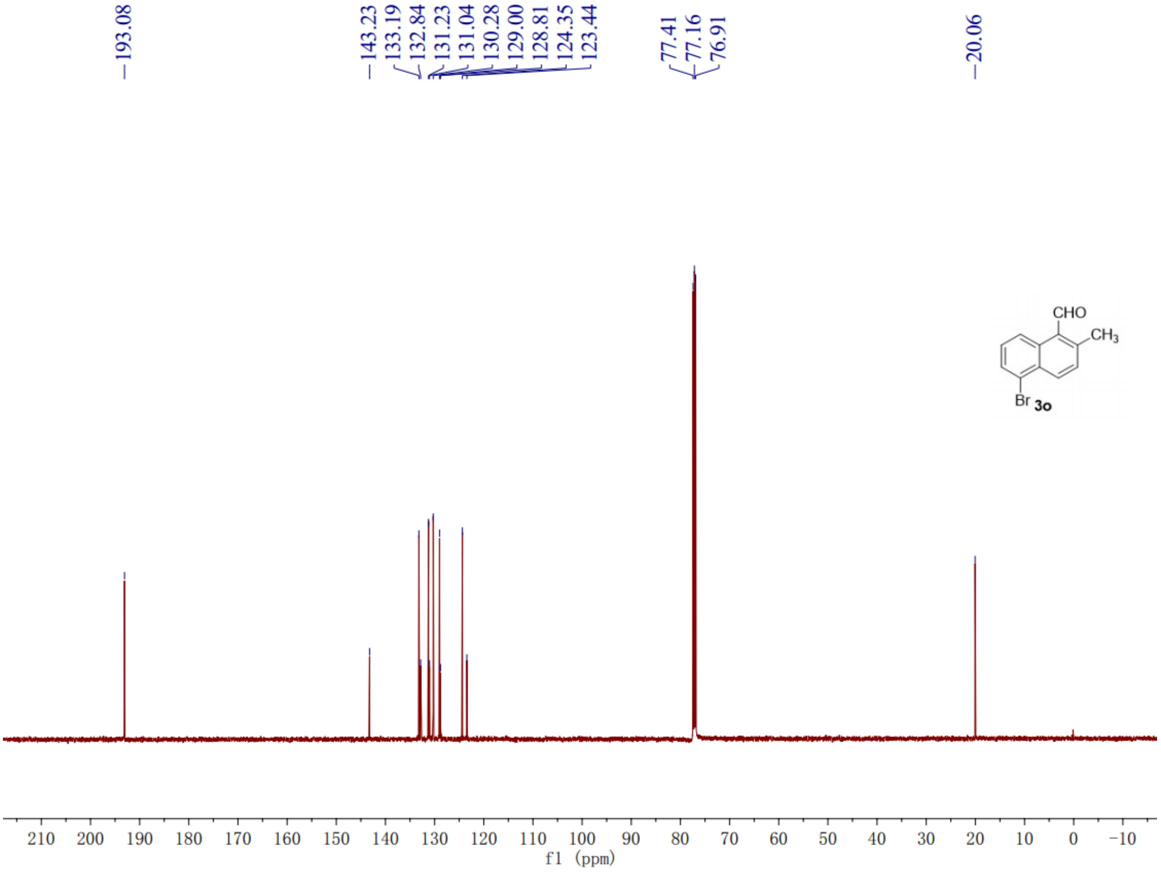
HR-ESI-MS $(M+H)^+$ of 3n



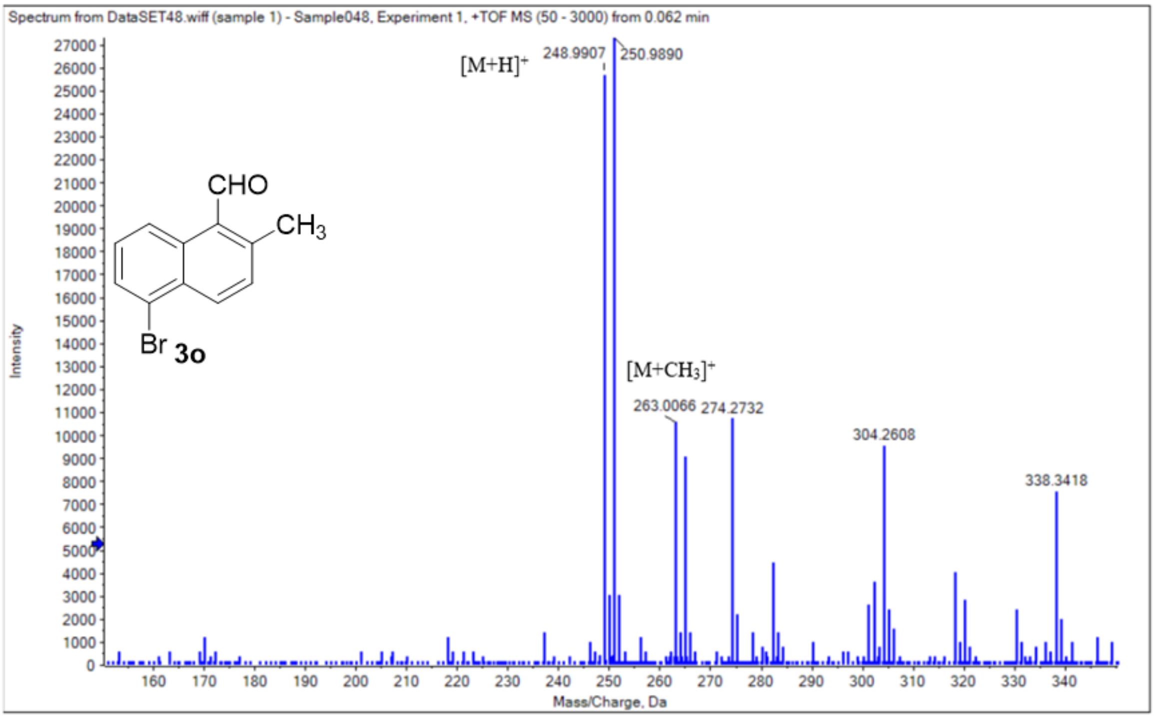
^1H NMR spectrum ($CDCl_3$, 500 MHz) of 3o



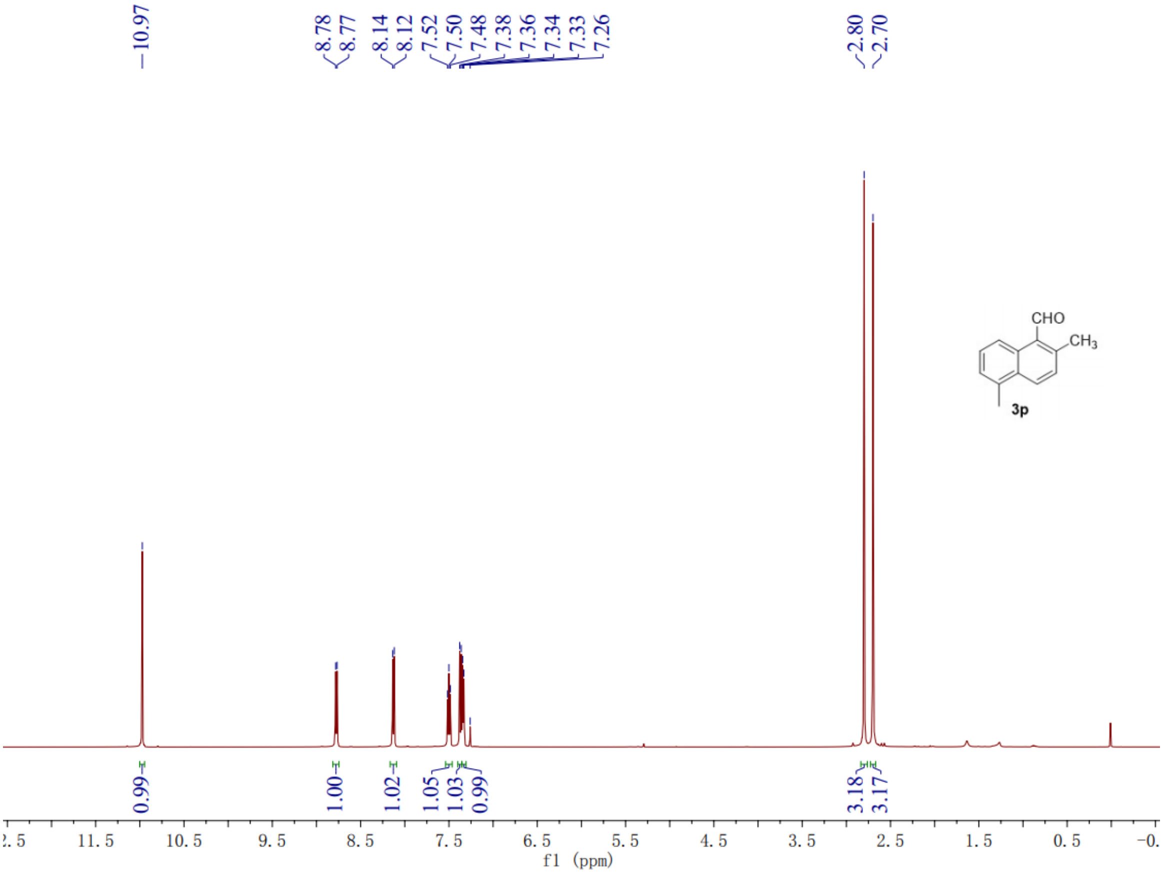
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3o



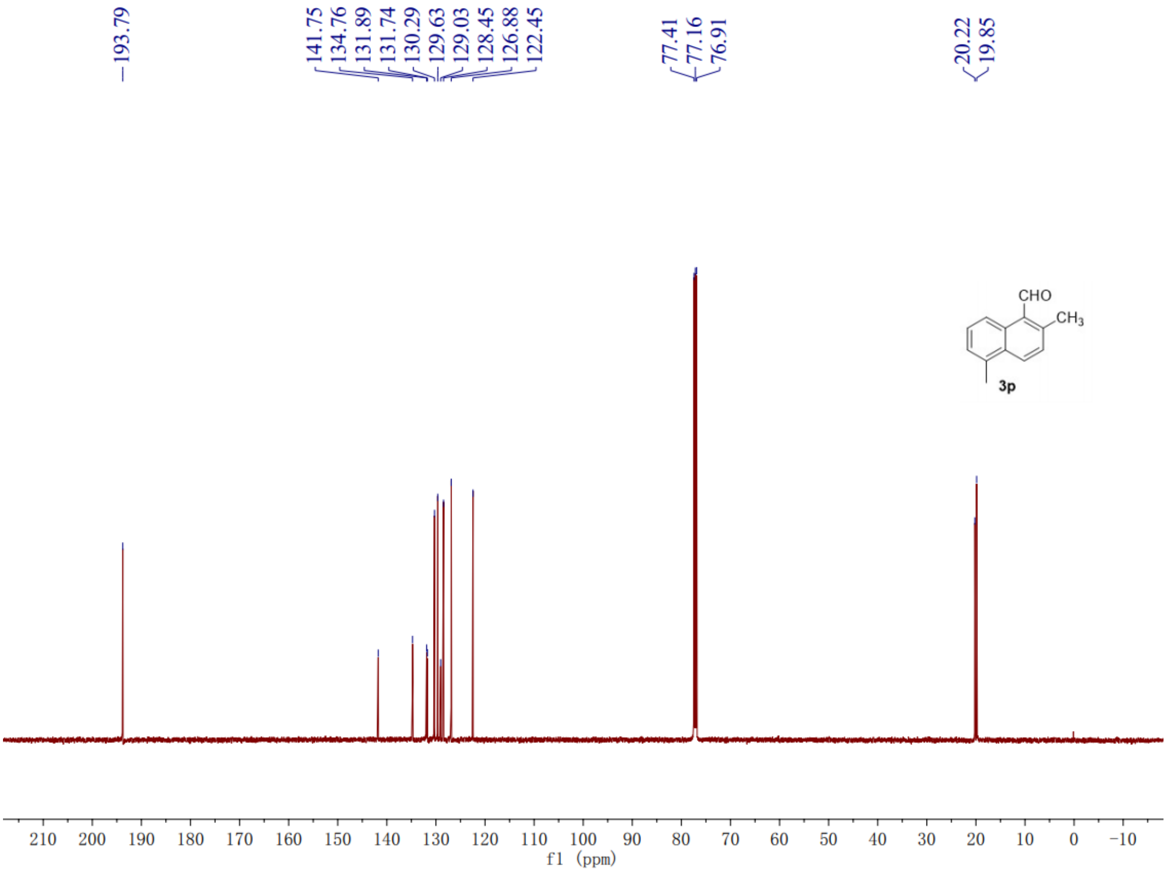
HR-ESI-MS $(M+H)^+$ of 3o



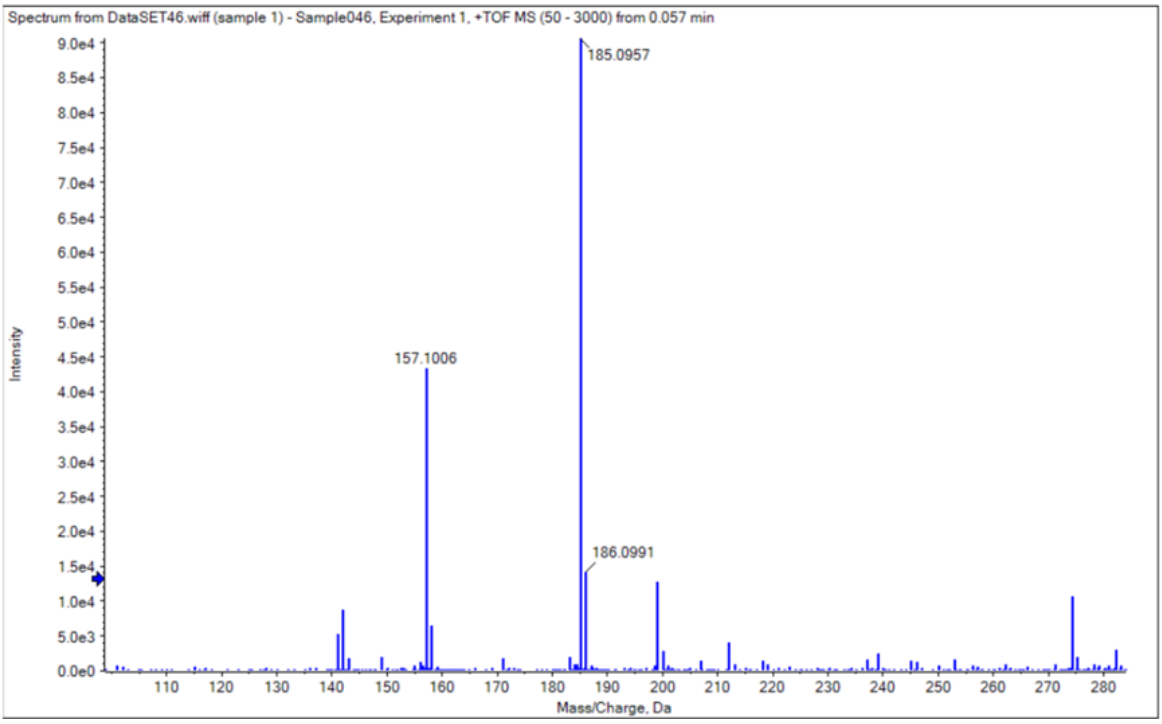
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3p



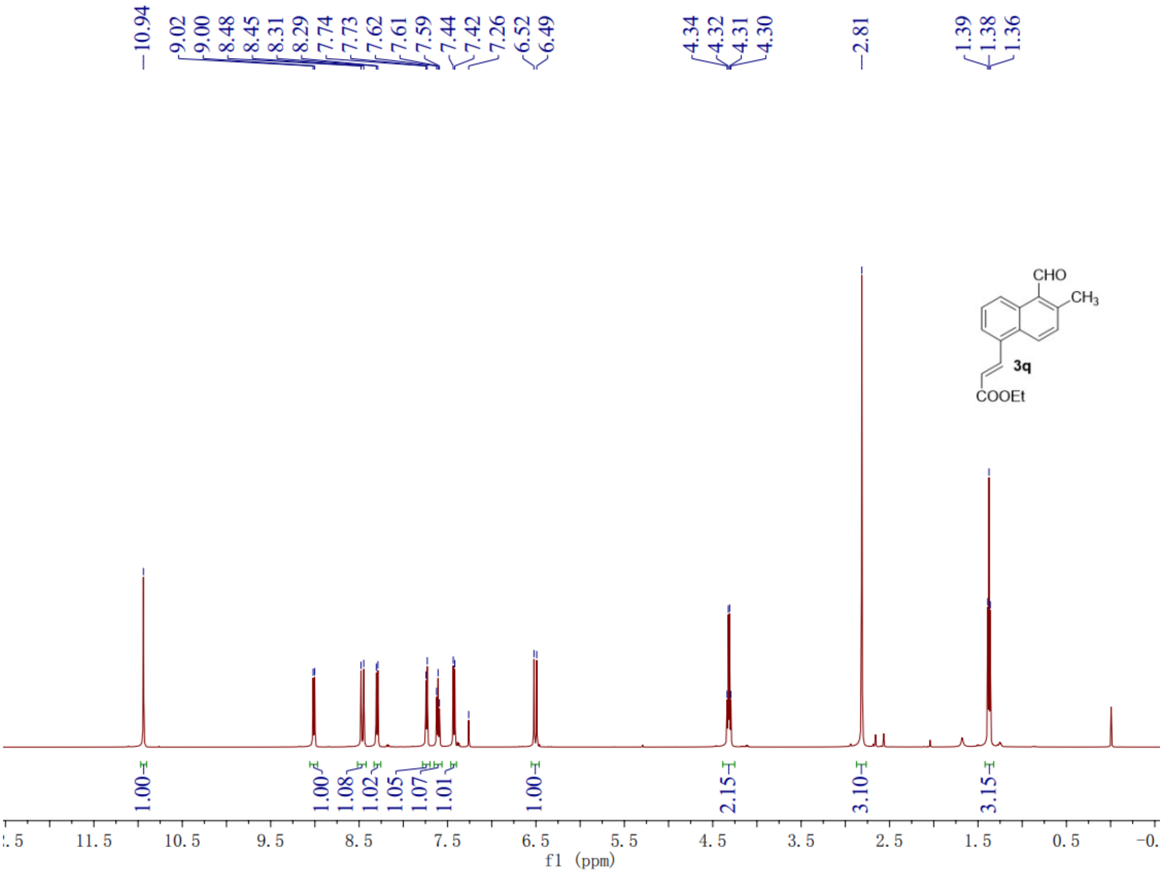
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3p



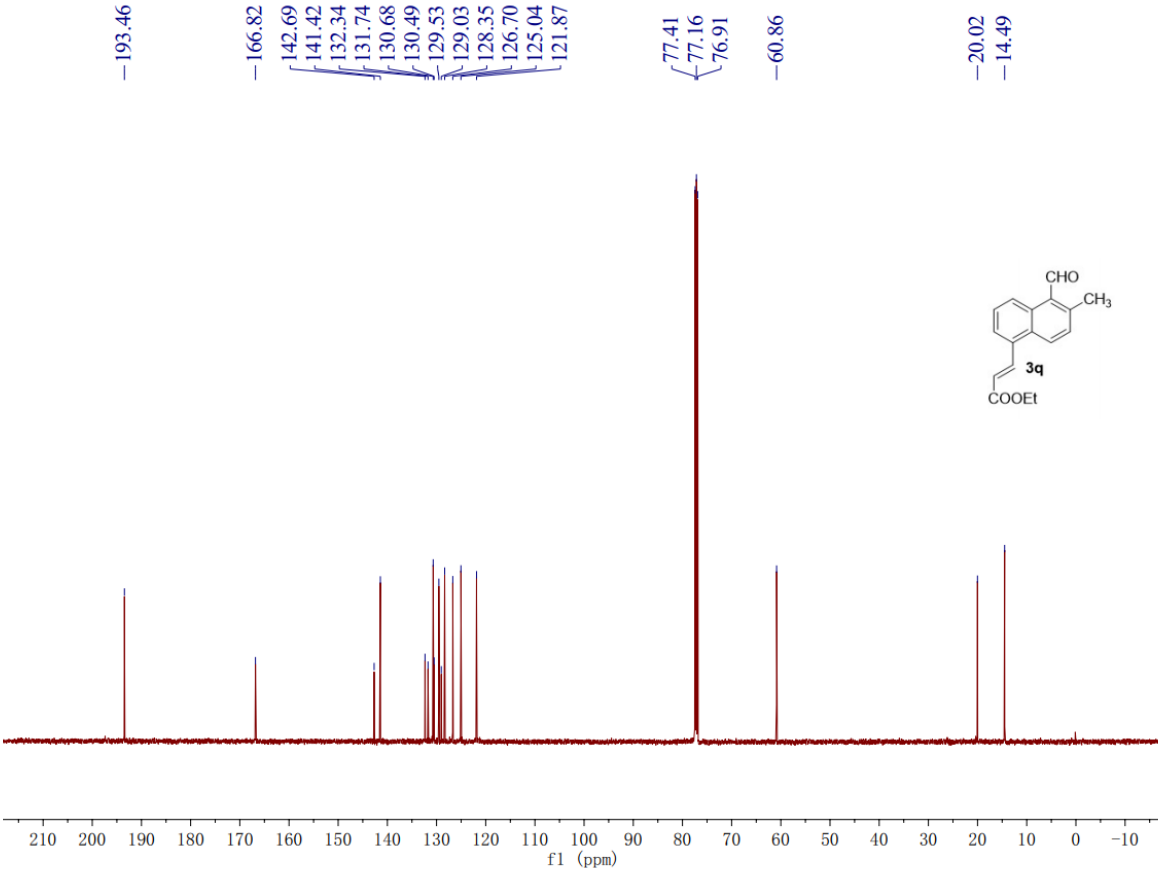
HR-ESI-MS $(M+H)^+$ of 3p



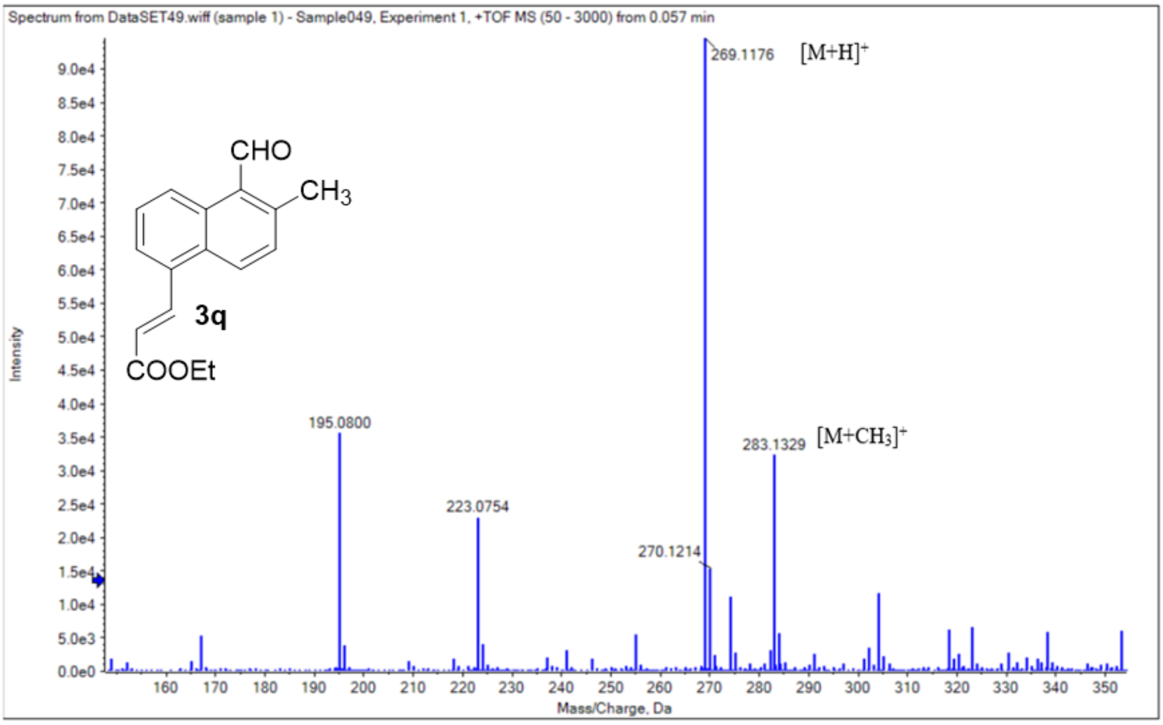
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3q



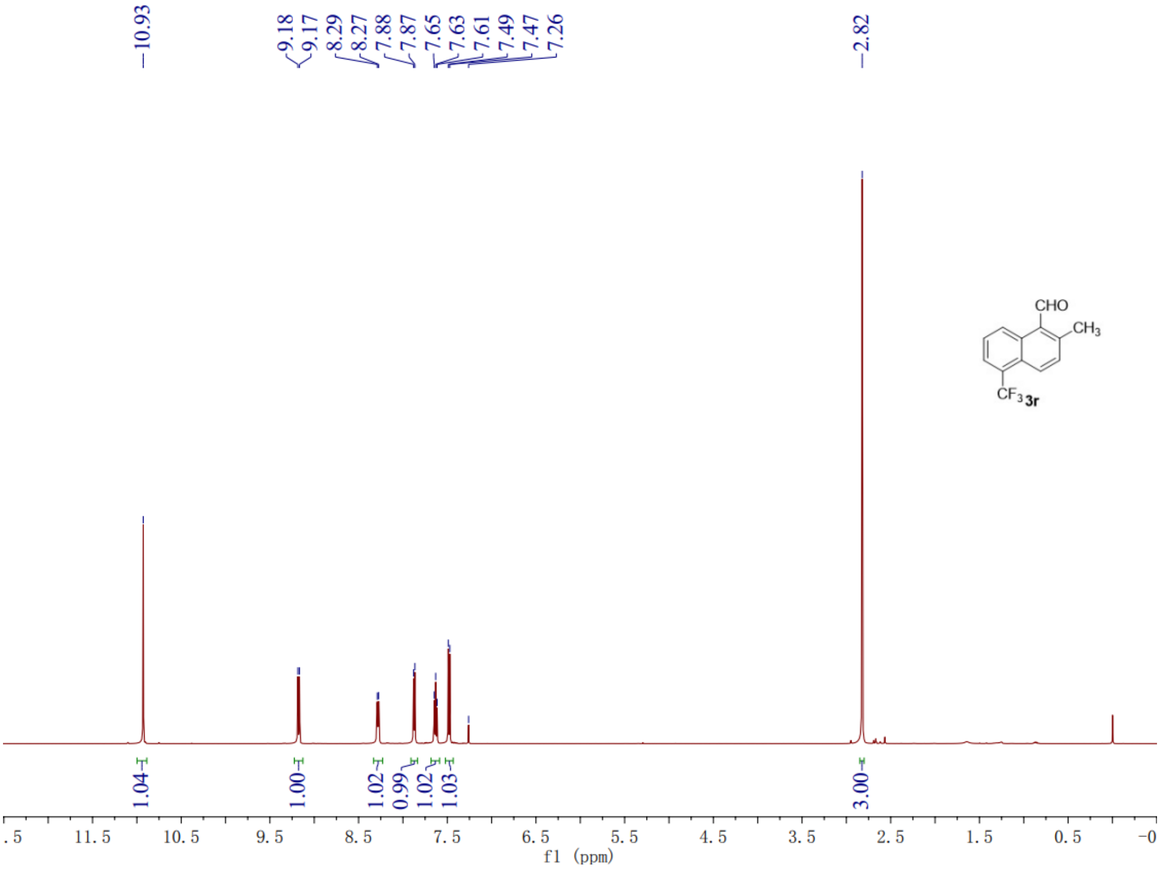
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3q



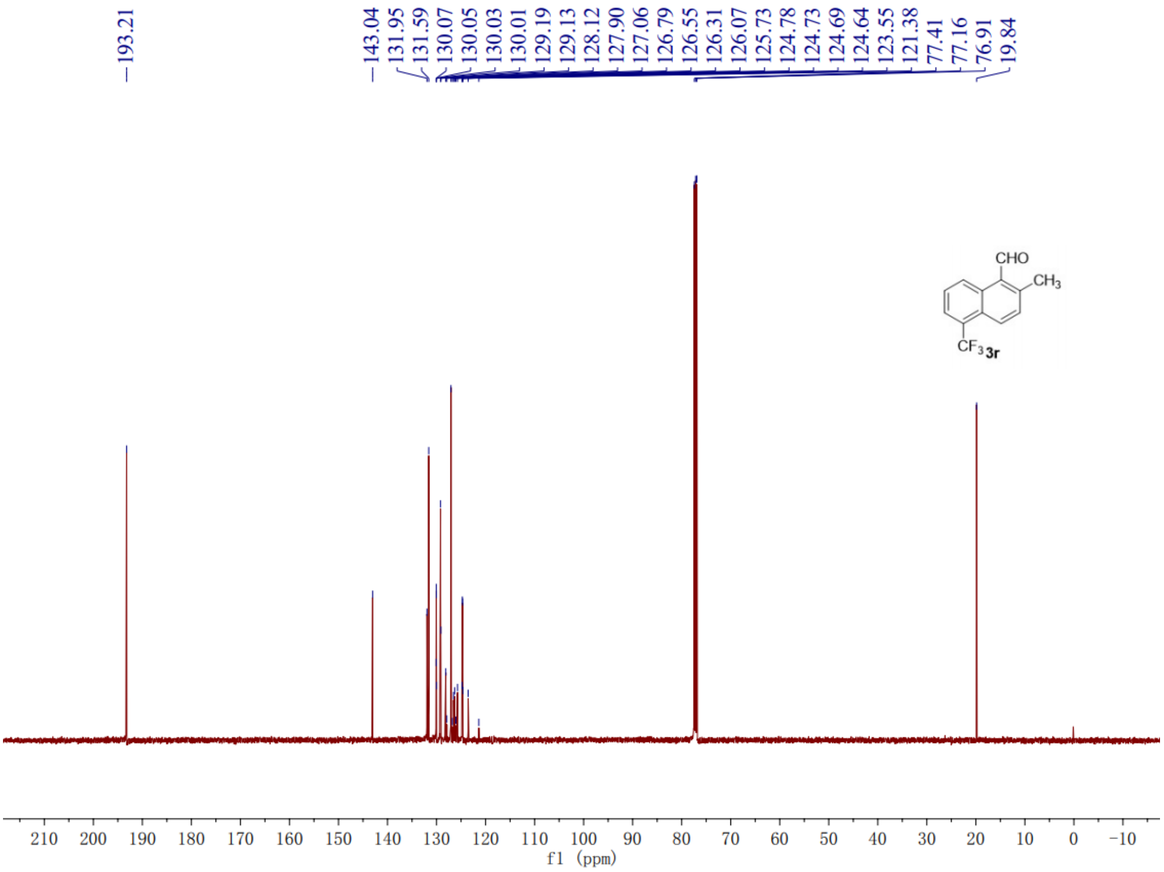
HR-ESI-MS (M+H)$^+$ of 3q



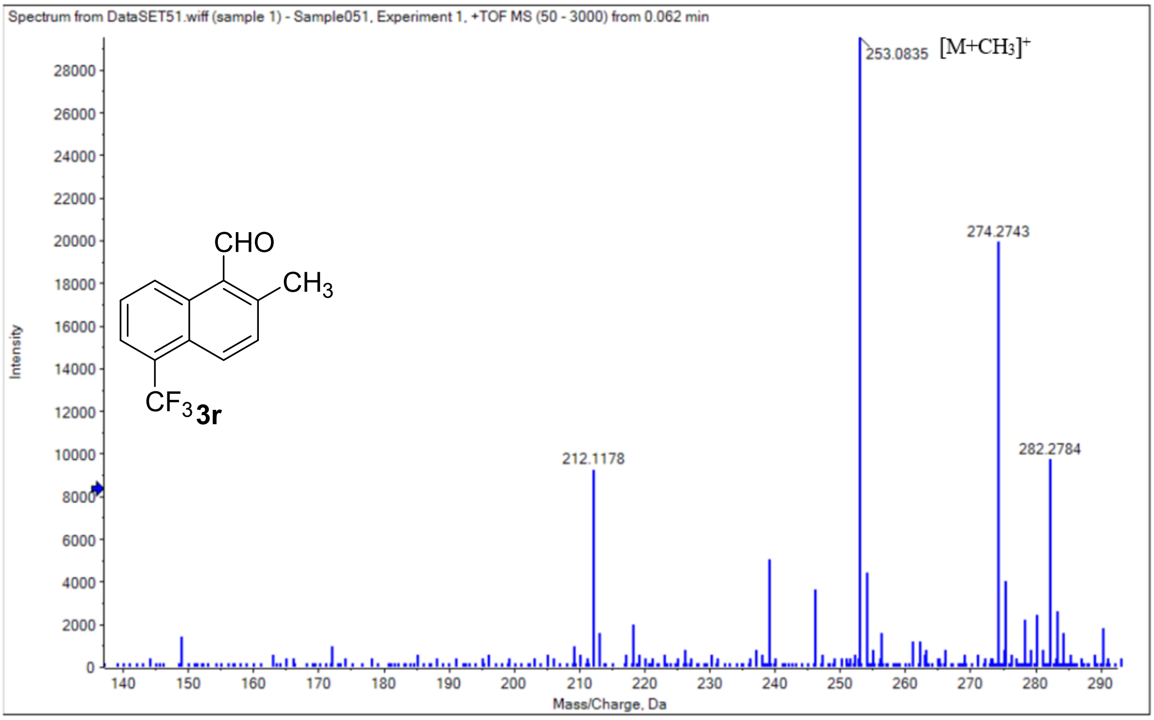
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3r



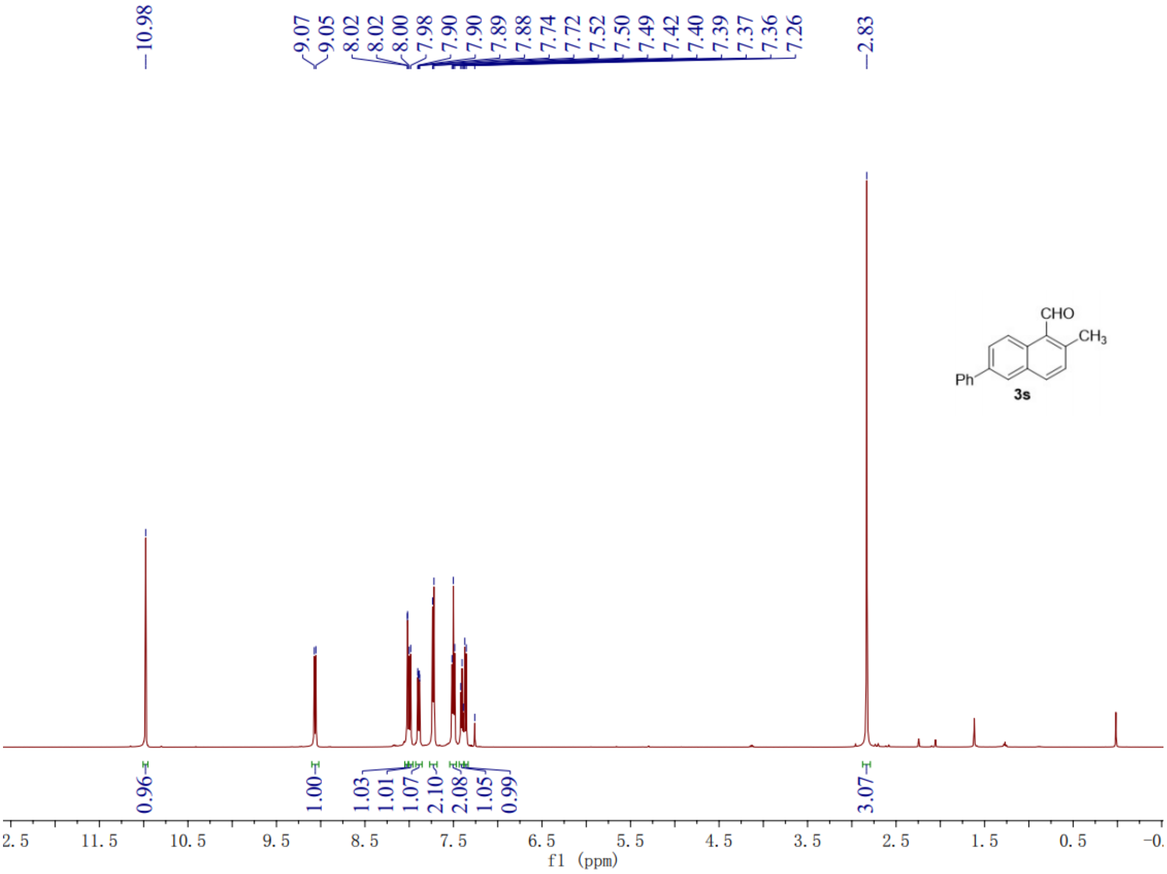
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3r



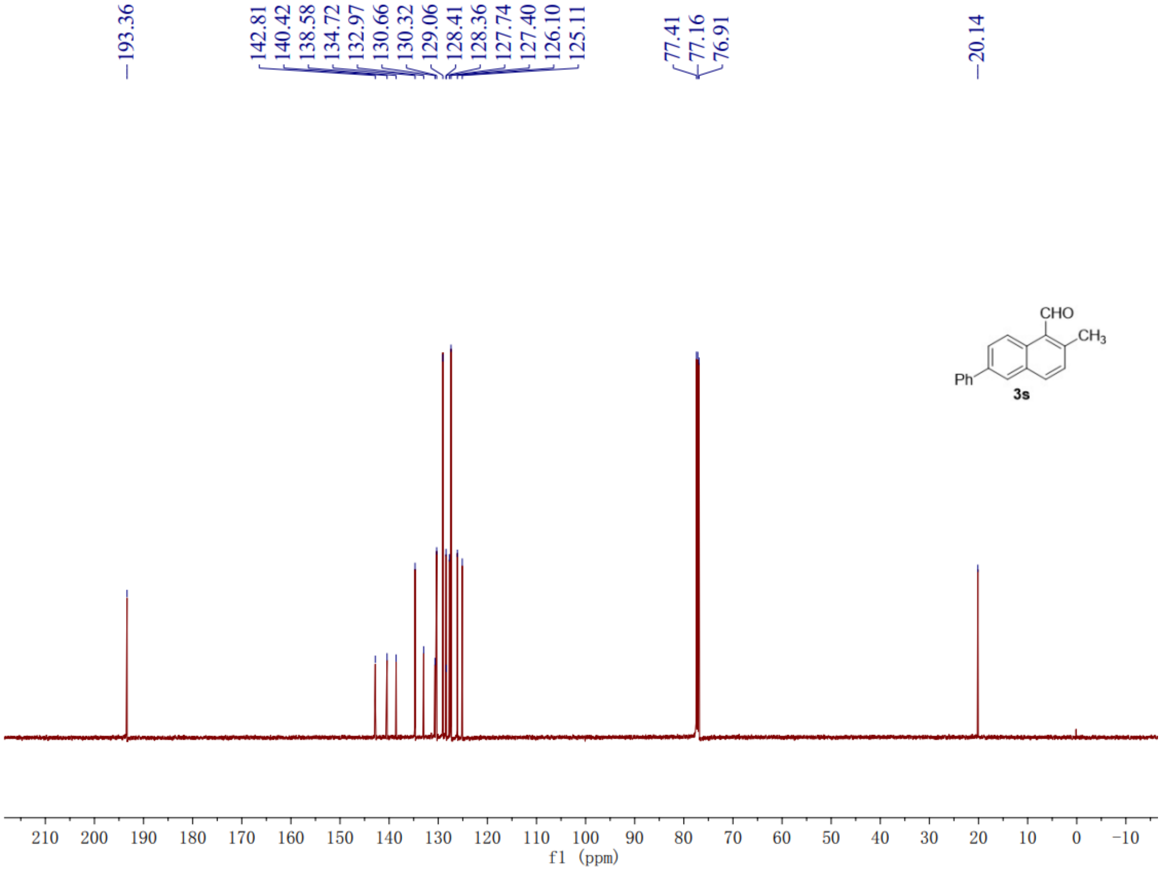
HR-ESI-MS (M+CH_3)$^+$ of 3r



^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 3s



^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3s



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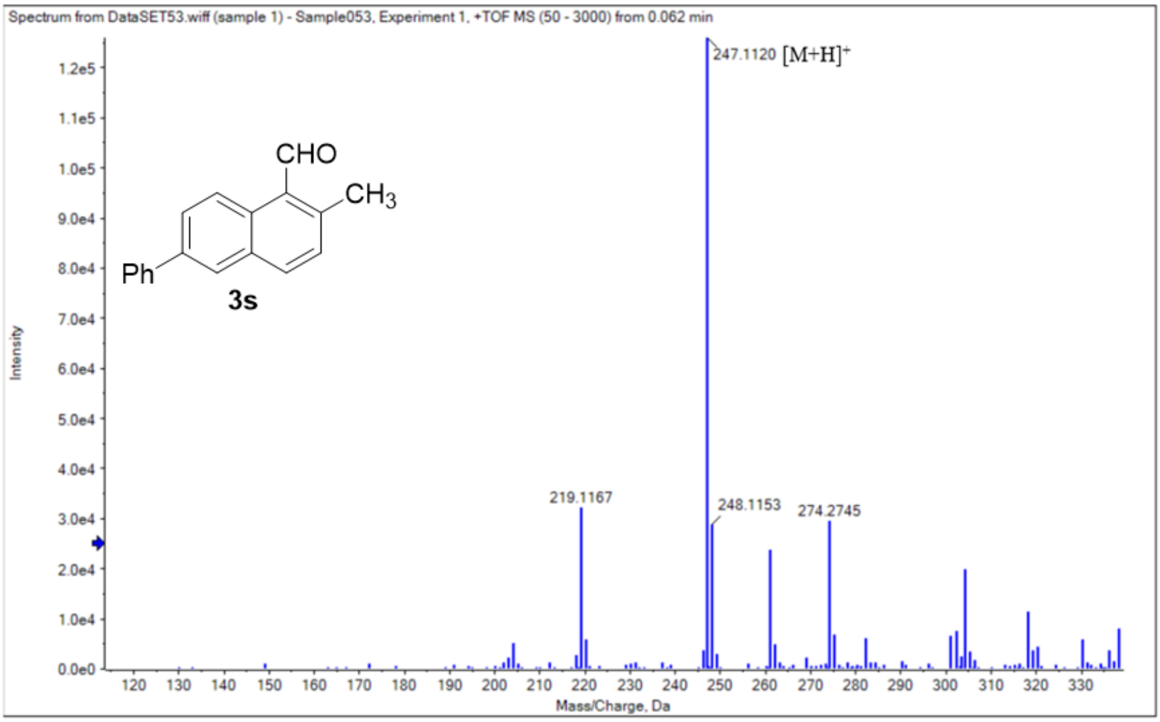
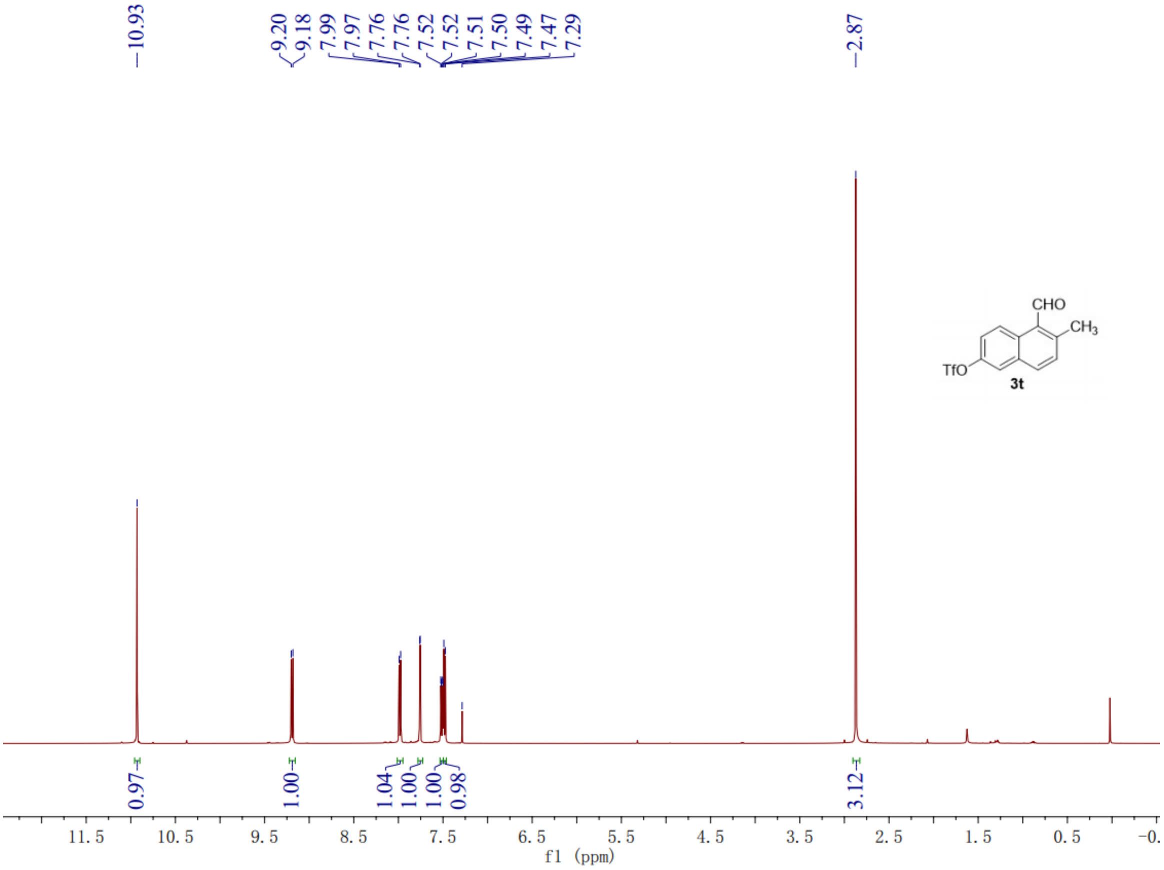
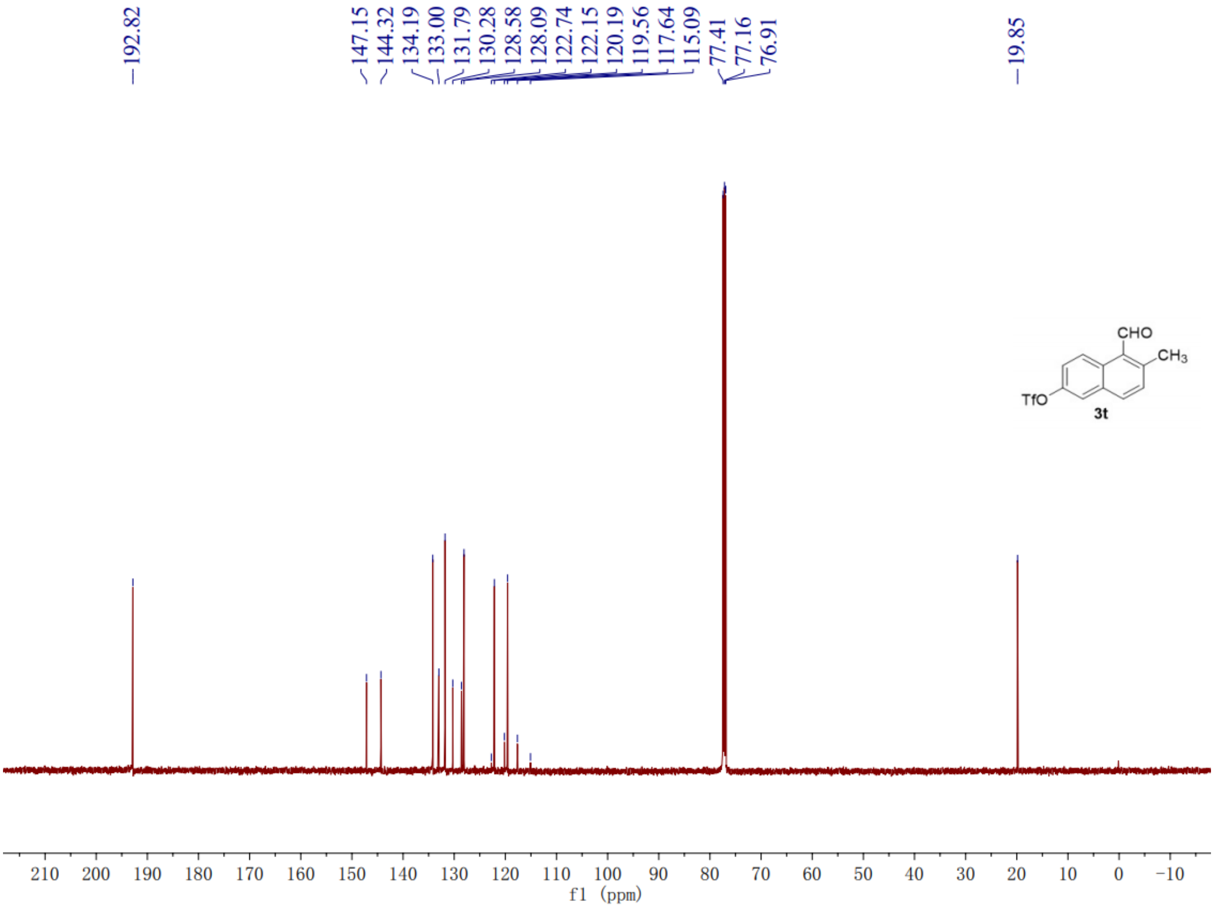


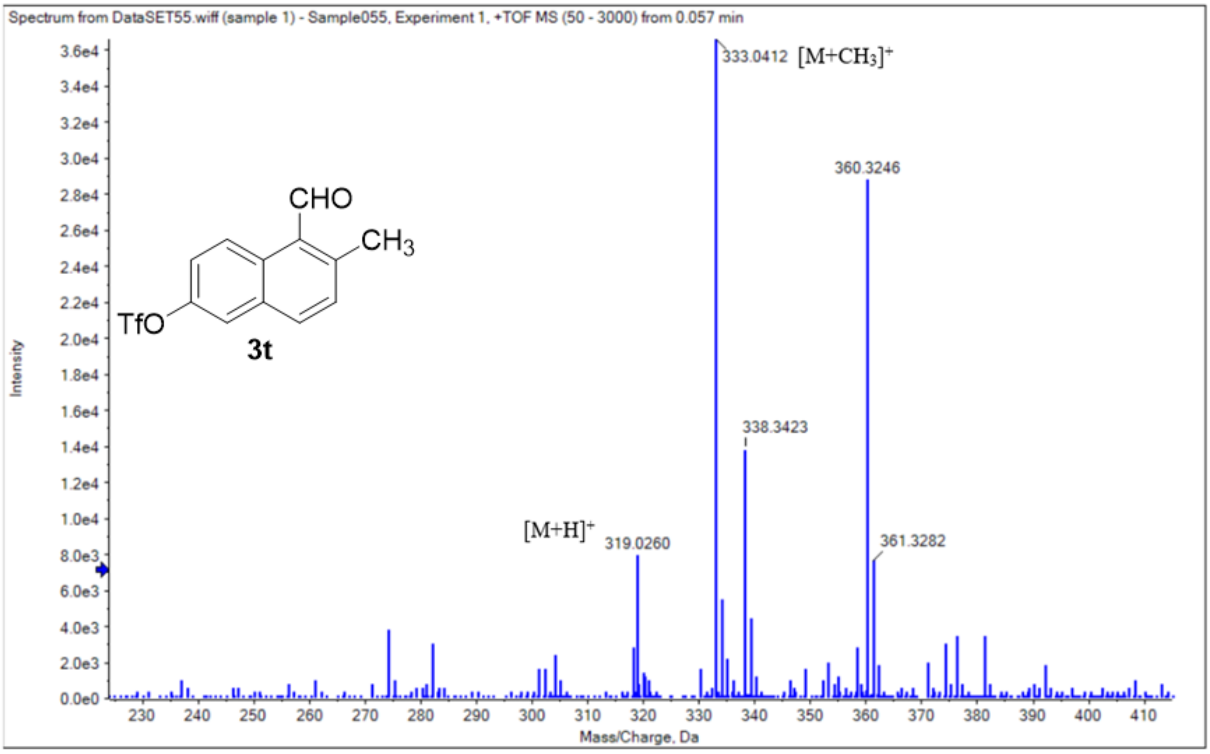
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3t



^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3t



HR-ESI-MS $(M+CH_3)^+$ of 3t



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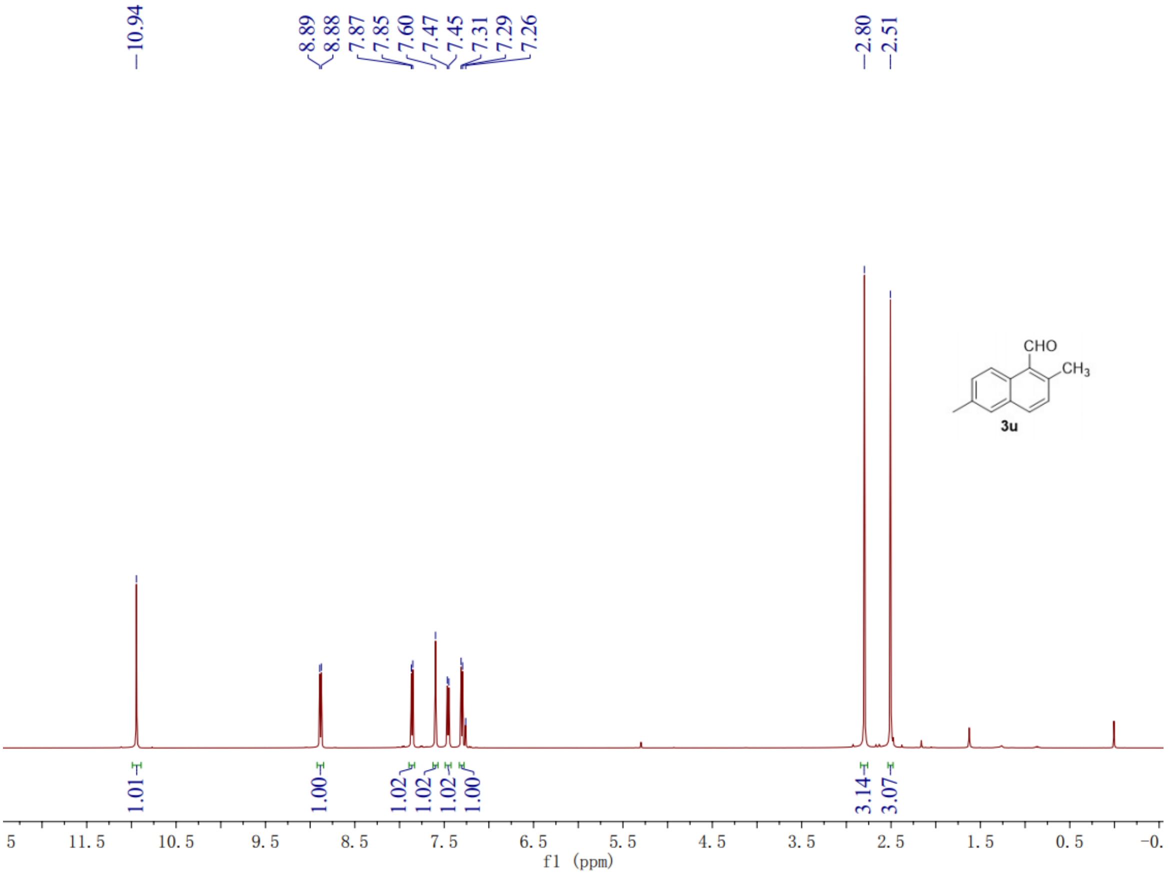
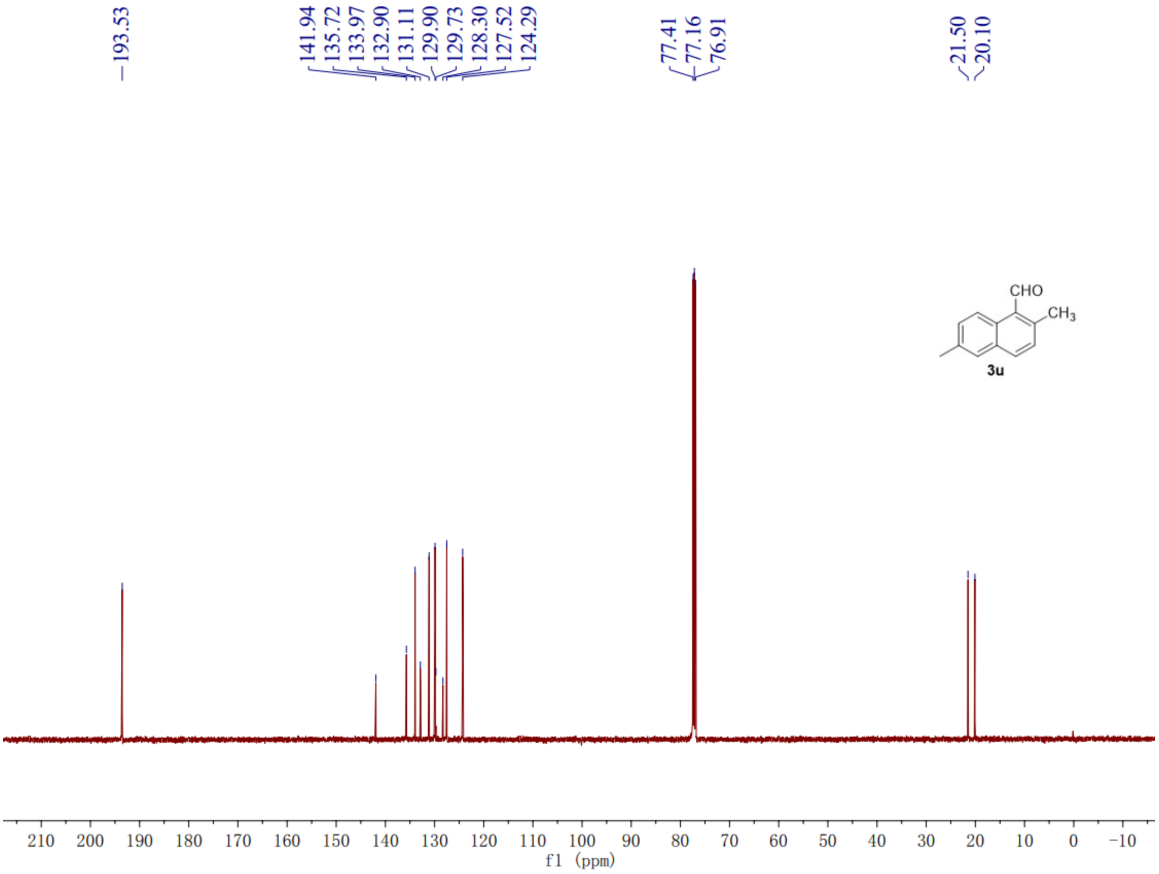


^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 3u



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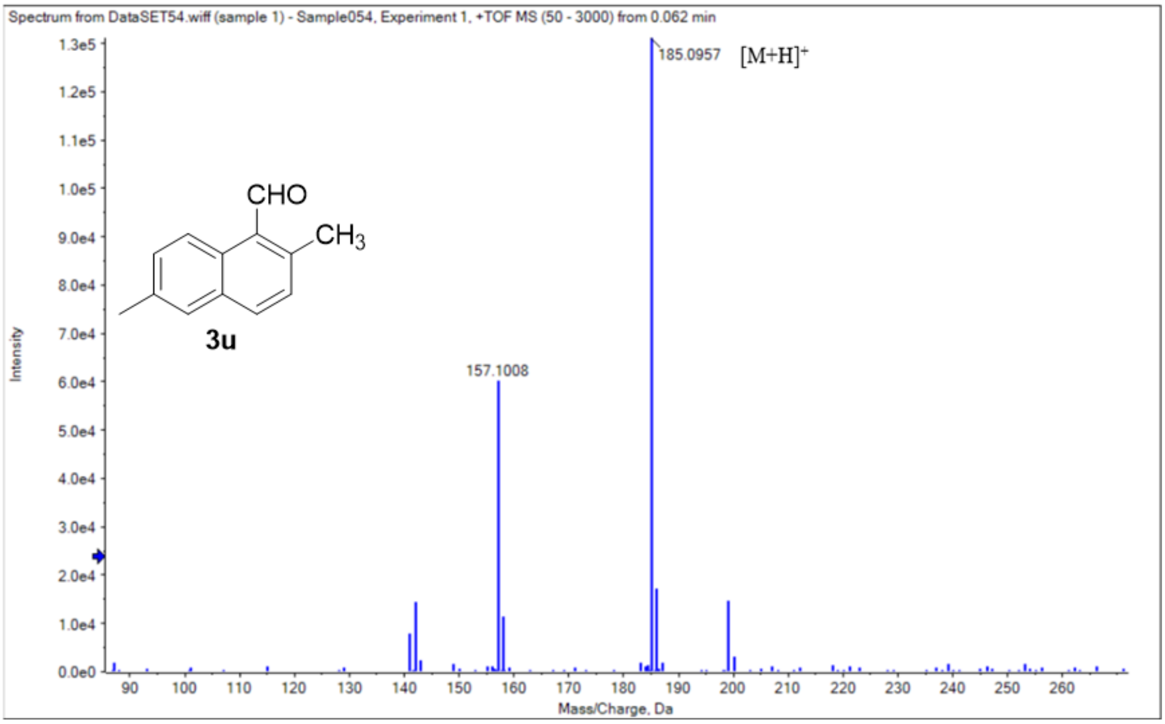

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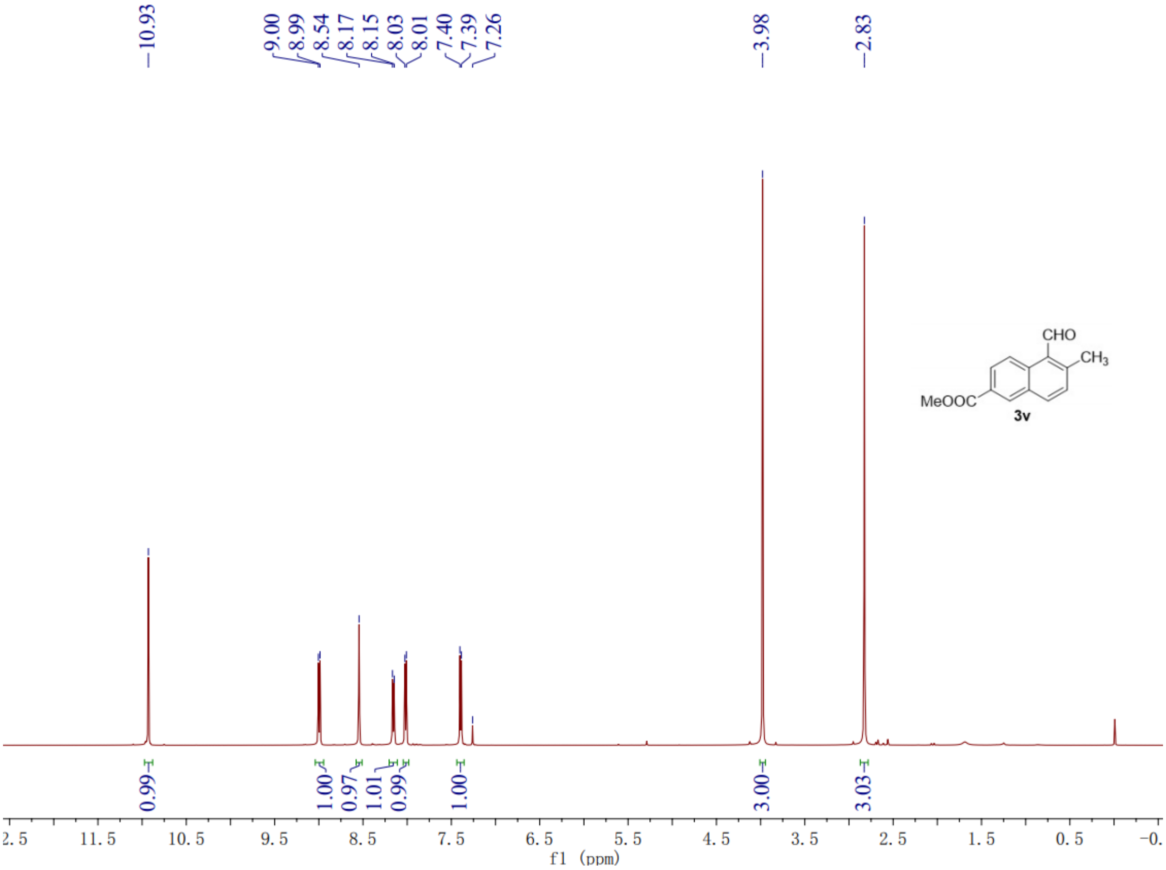
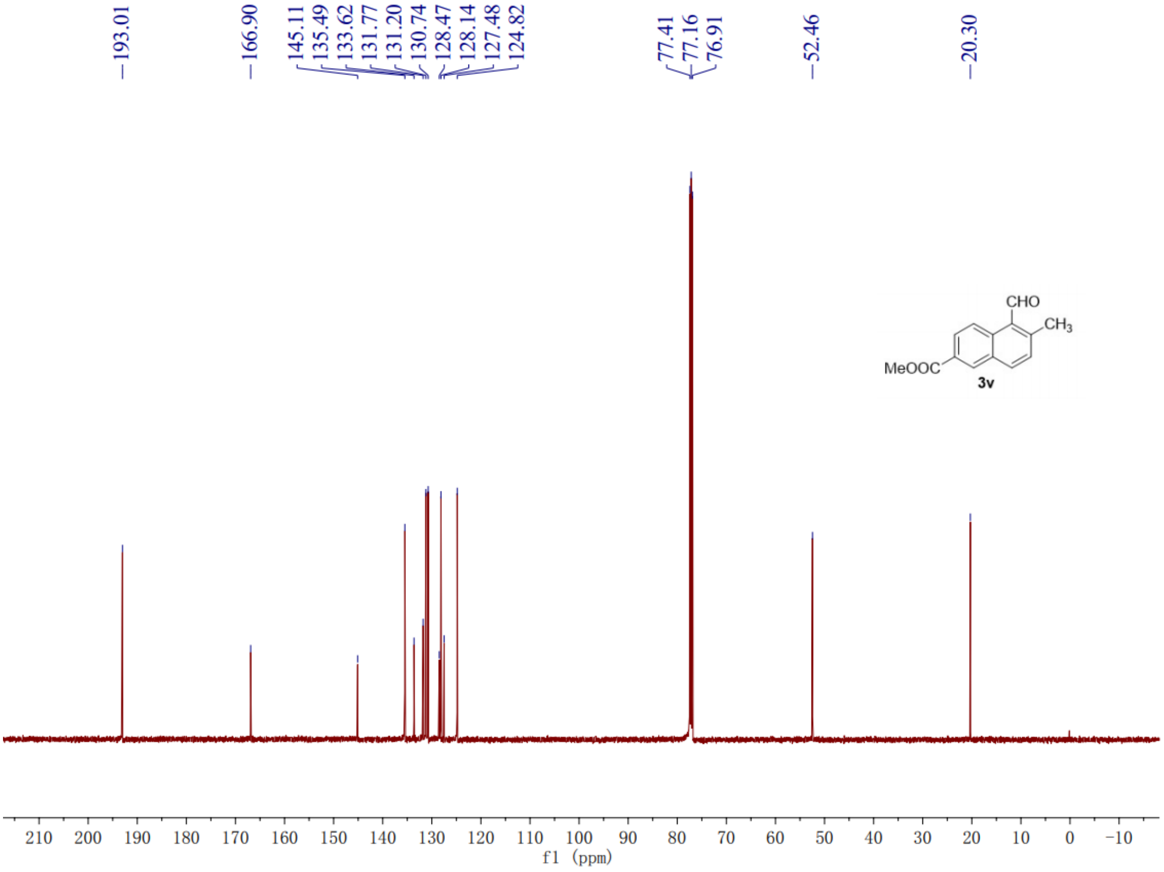
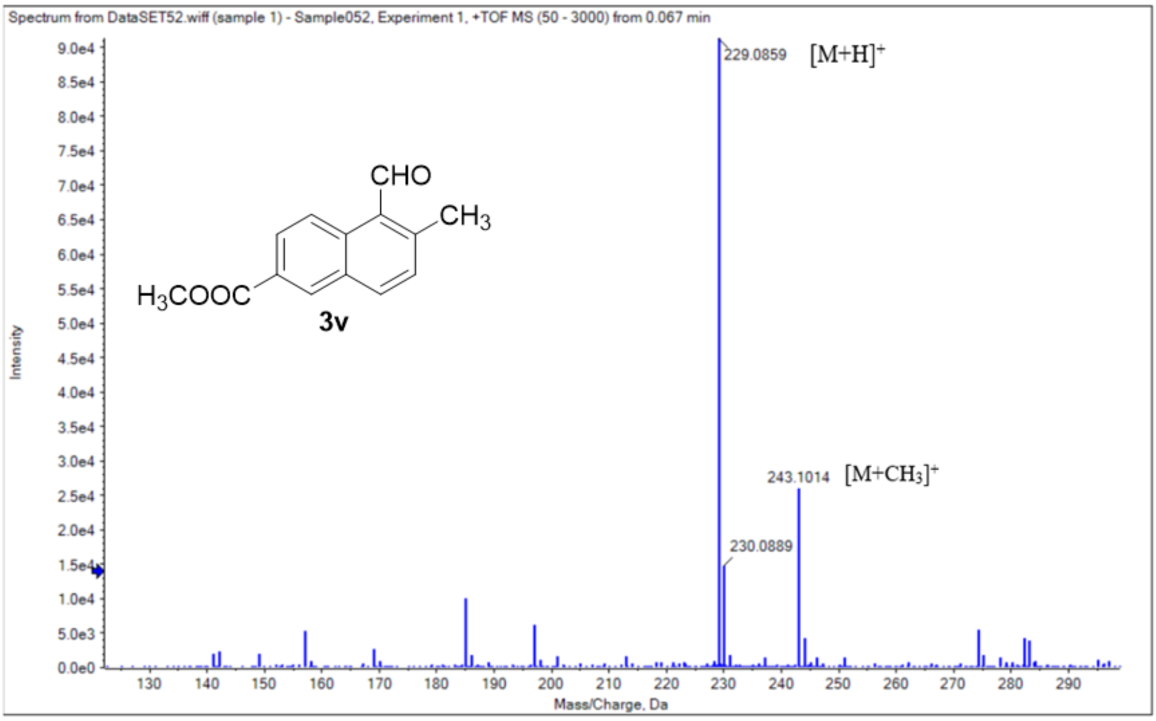


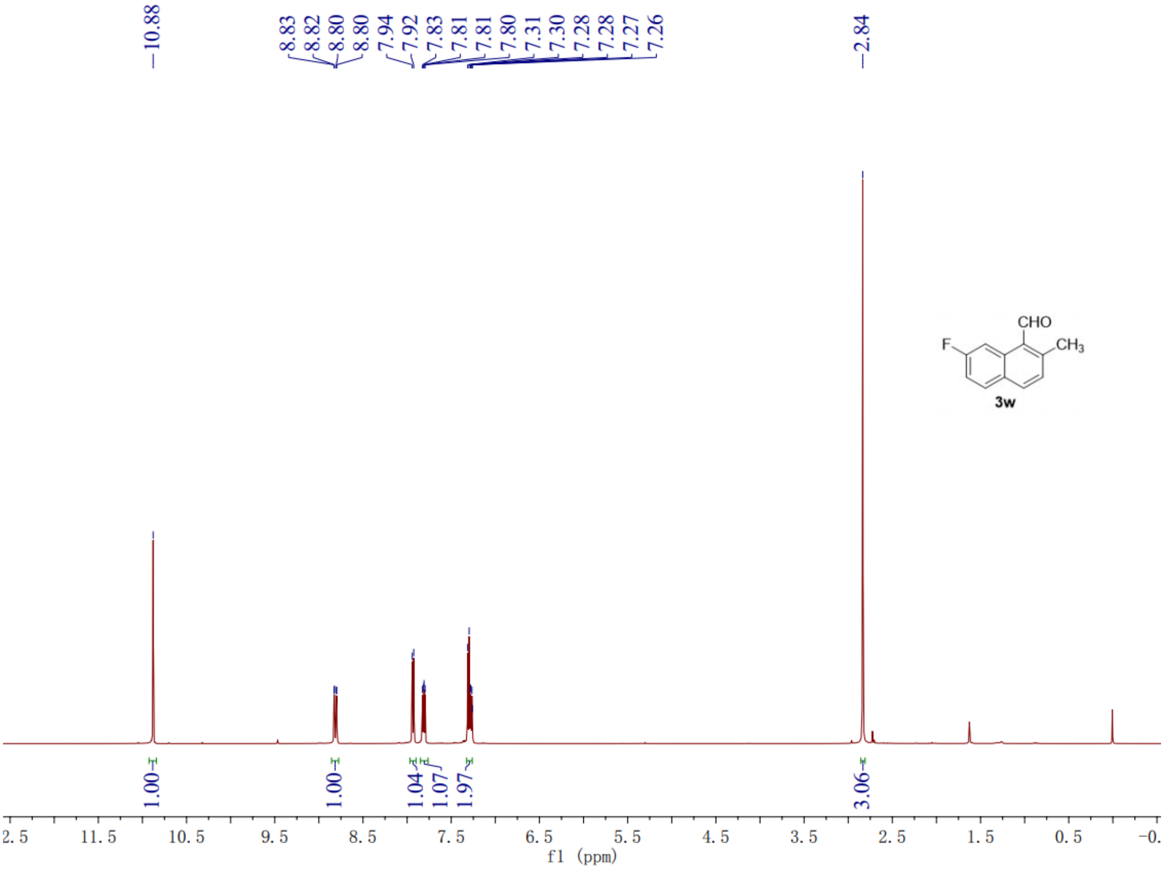
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3v



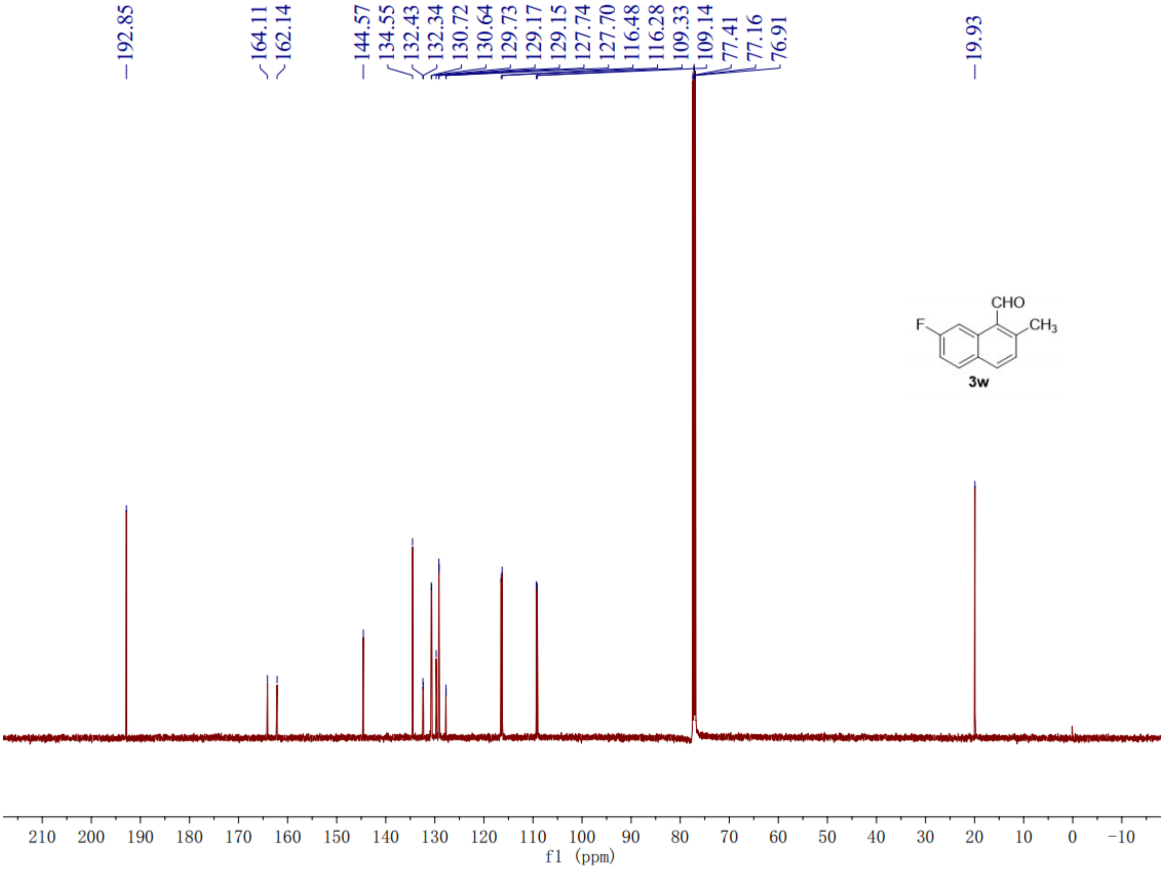
HR-ESI-MS $(M+H)^+$ of 3v



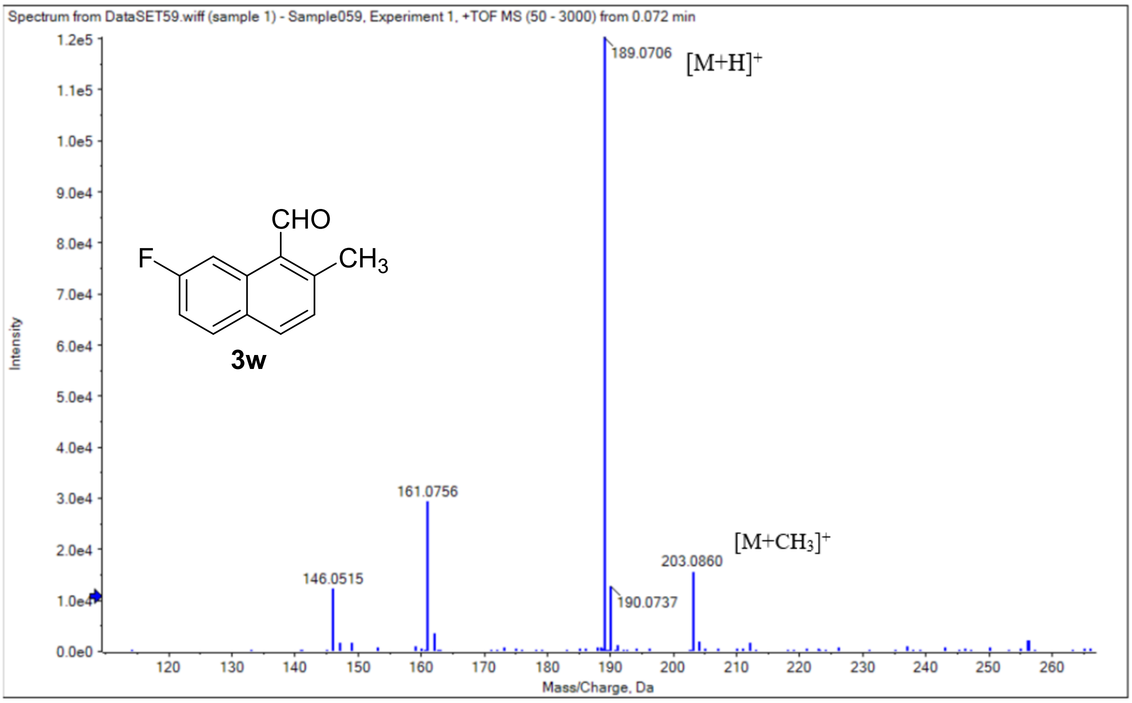
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3w



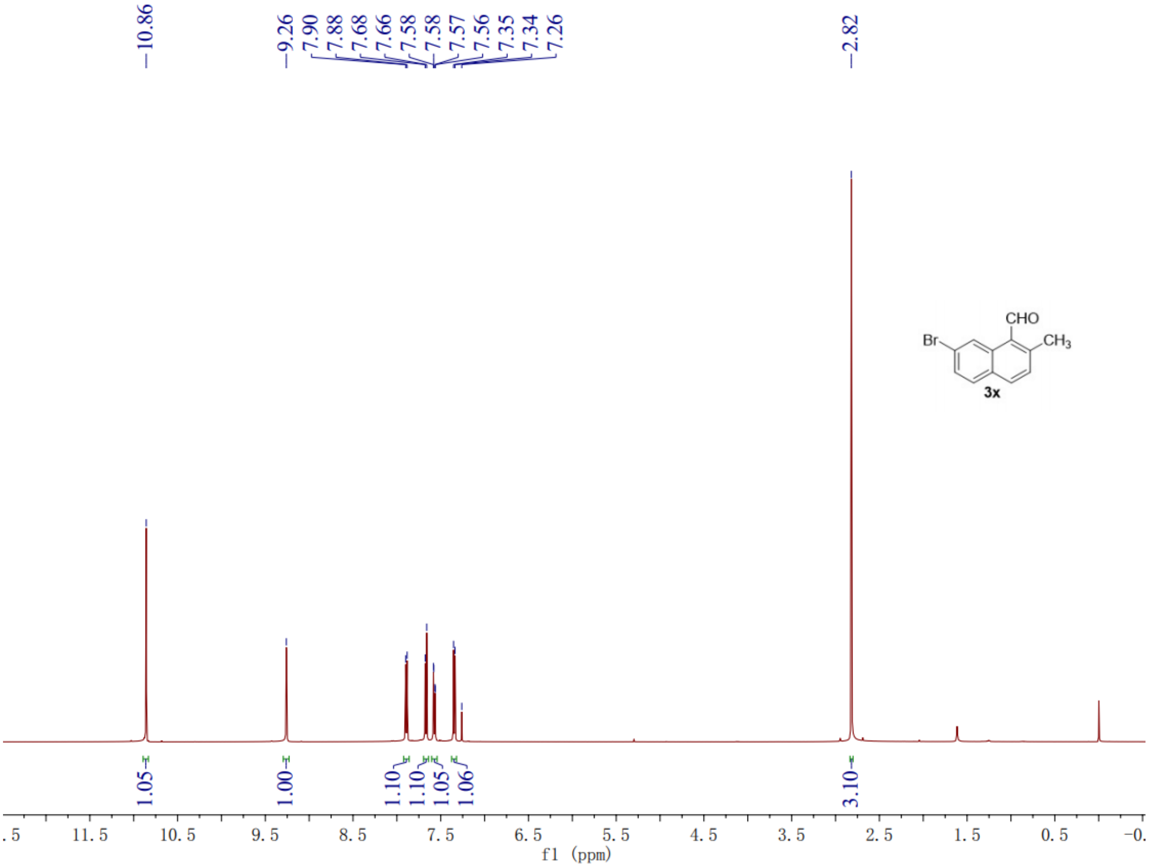
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3w



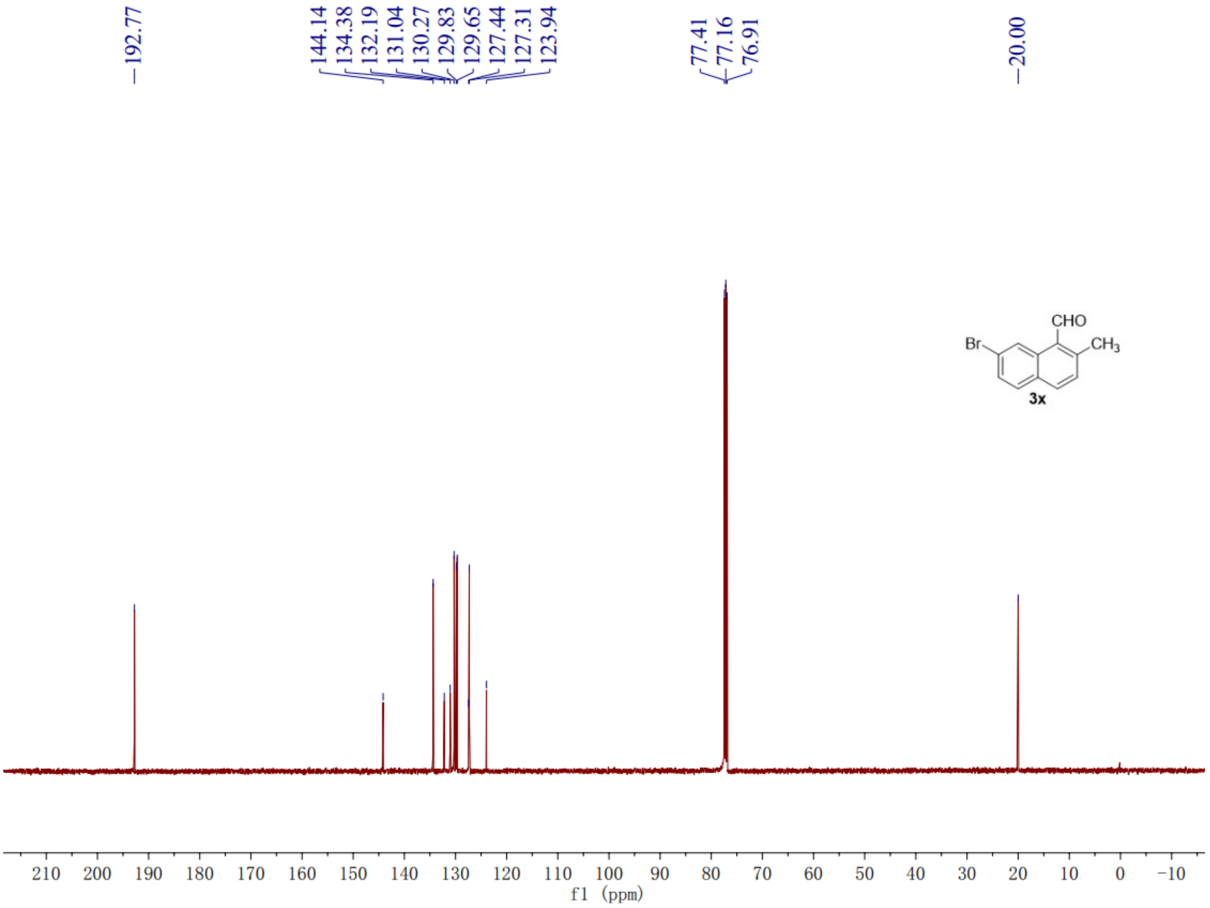
HR-ESI-MS $(M+H)^+$ of 3w



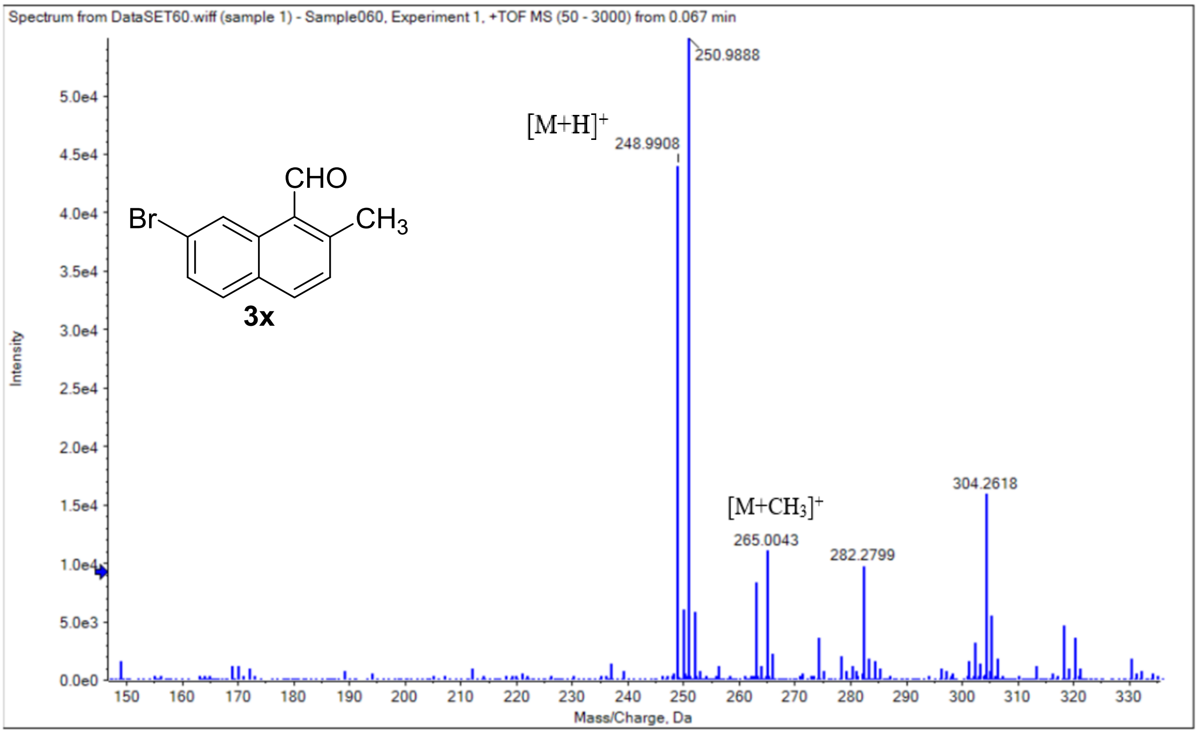
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3x



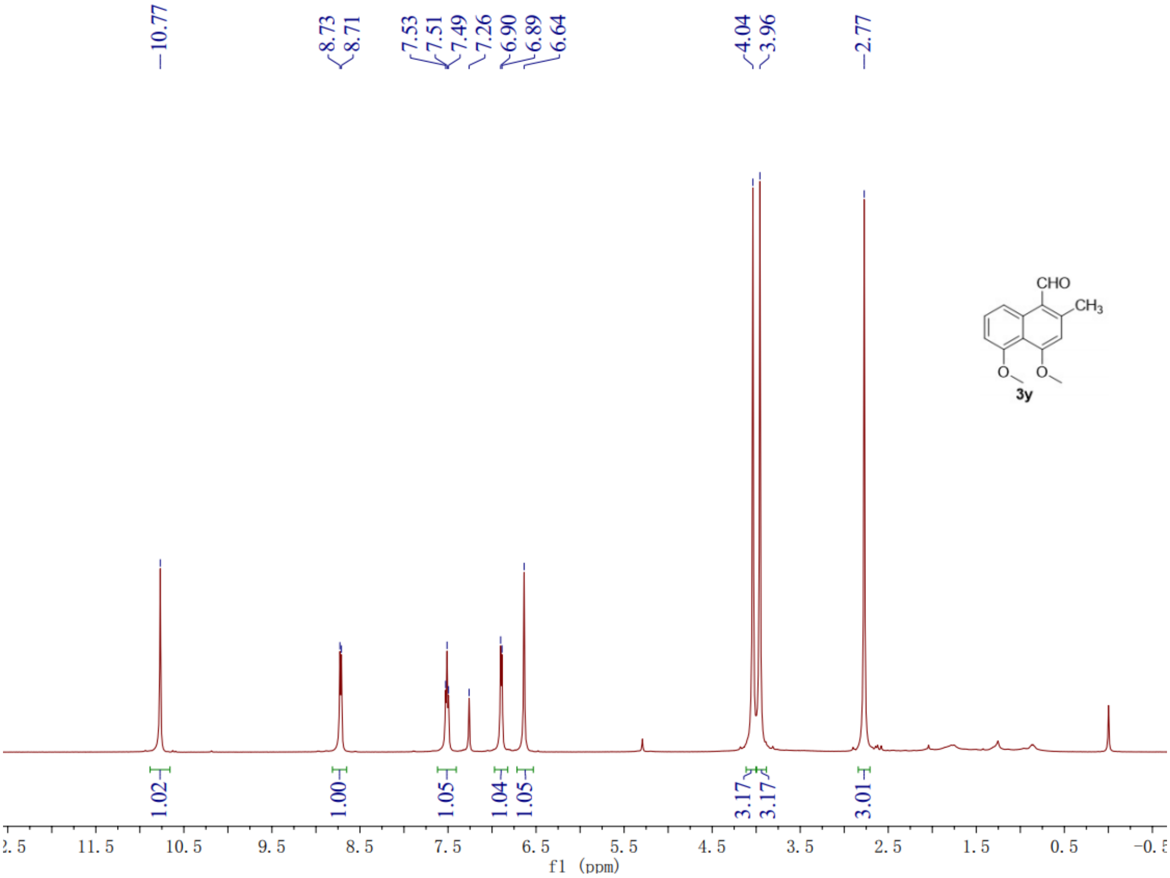
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3x



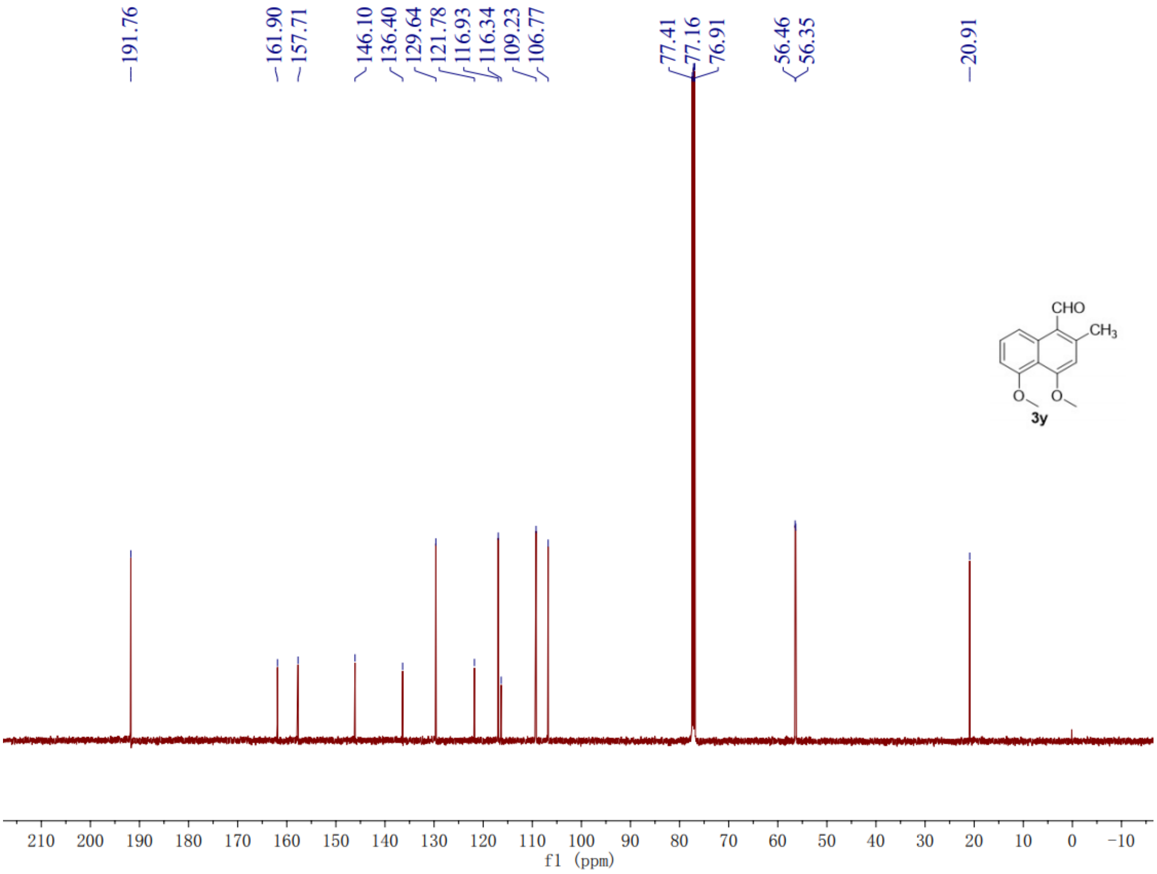
HR-ESI-MS (M+H)$^+$ of 3x



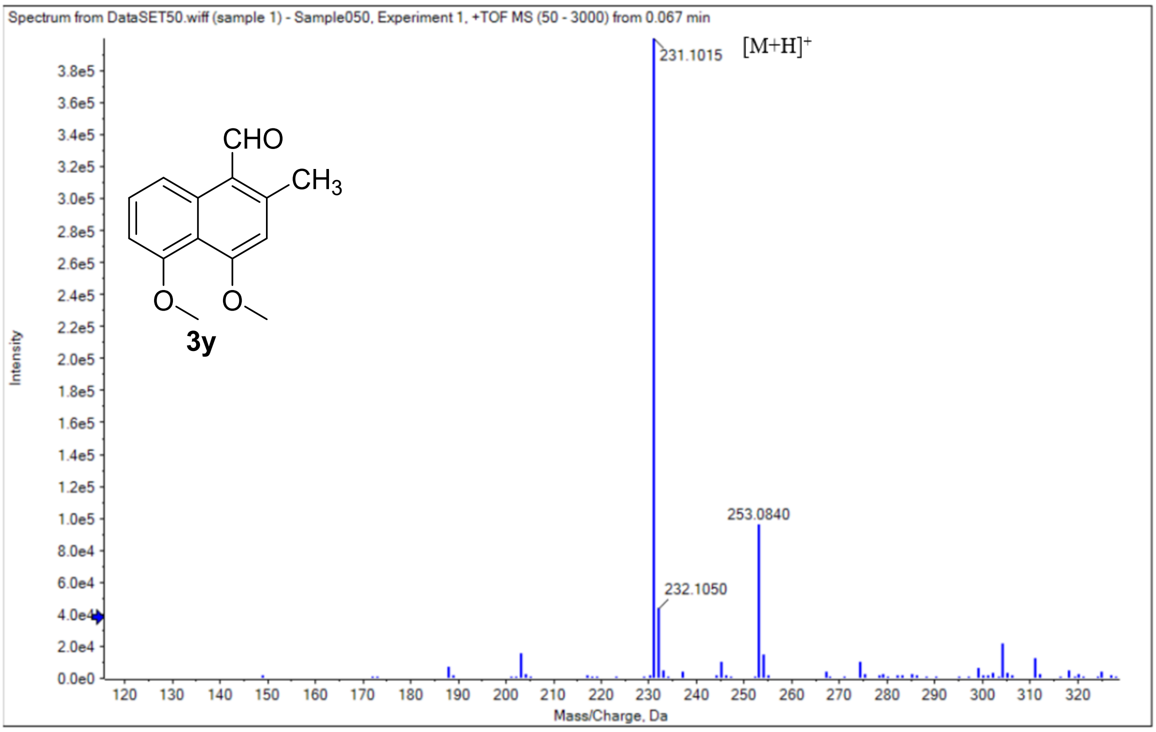
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 3y



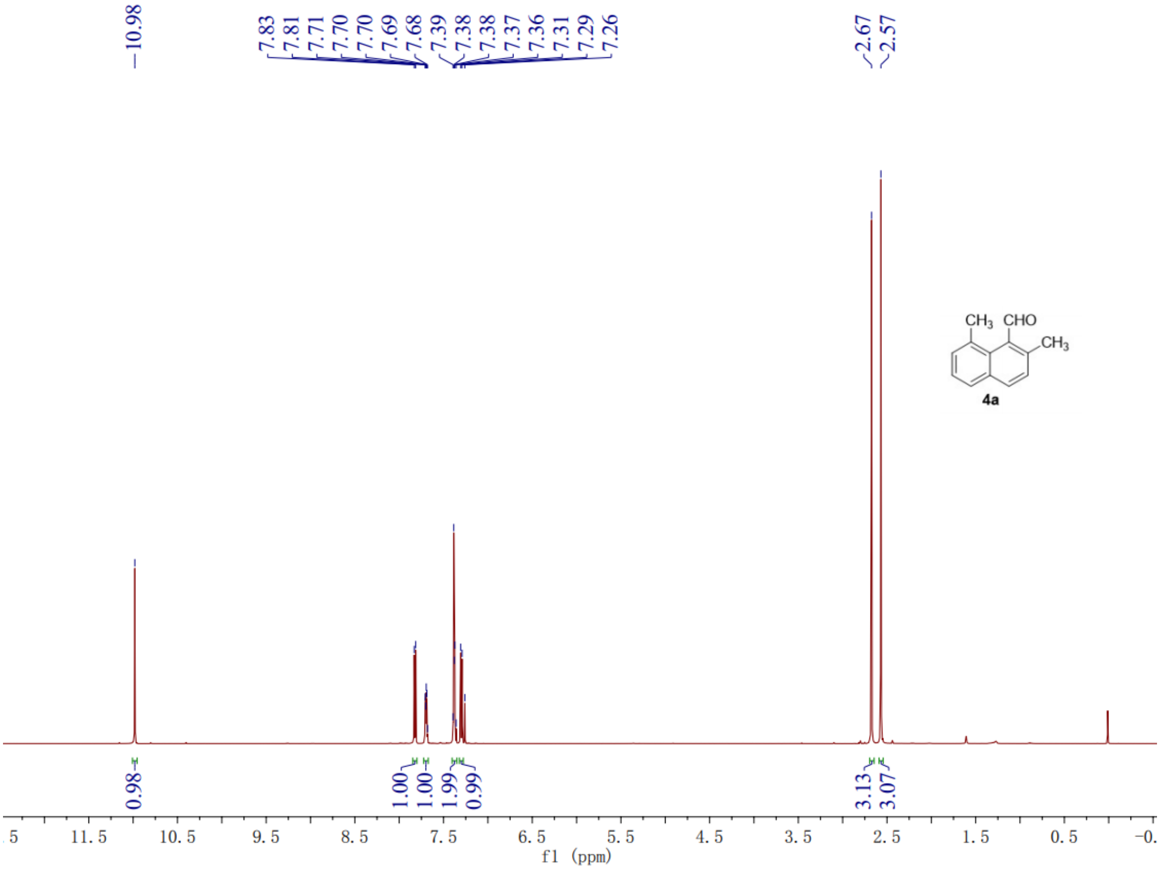
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 3y



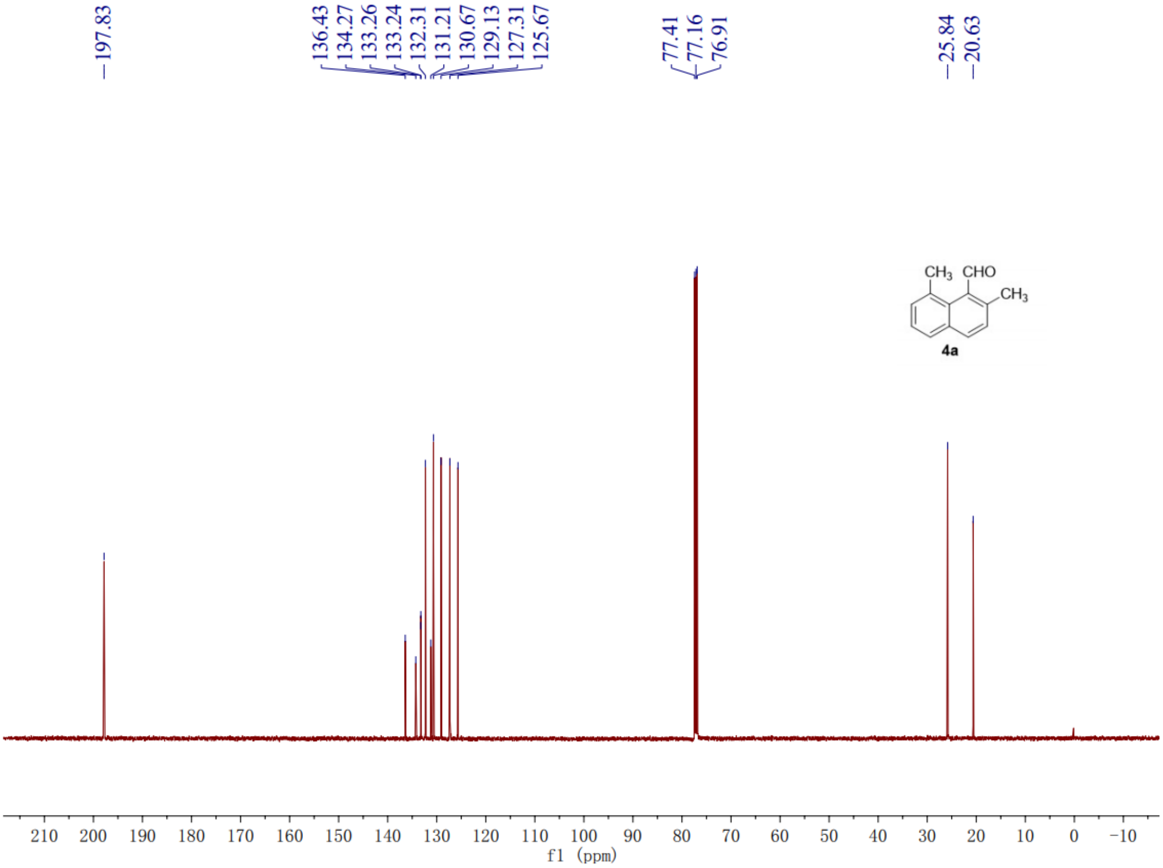
HR-ESI-MS $(M+H)^+$ of 3y



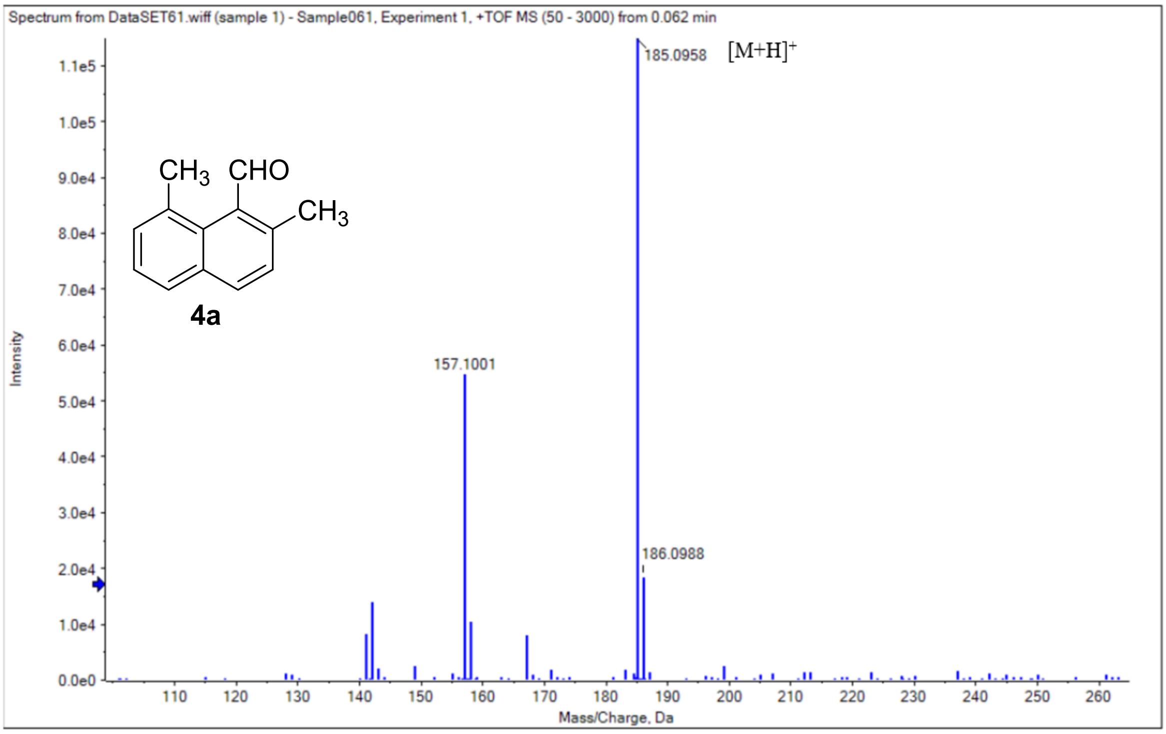
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4a



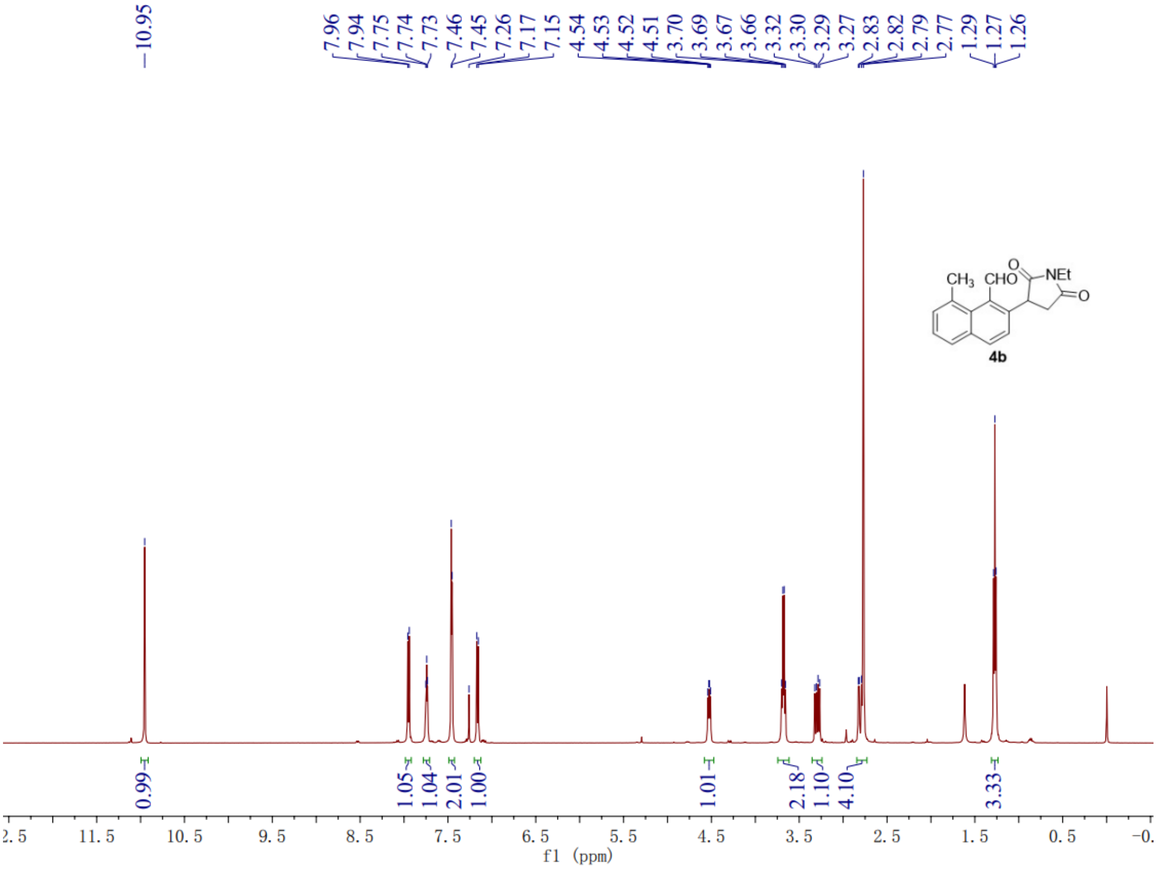
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 4a



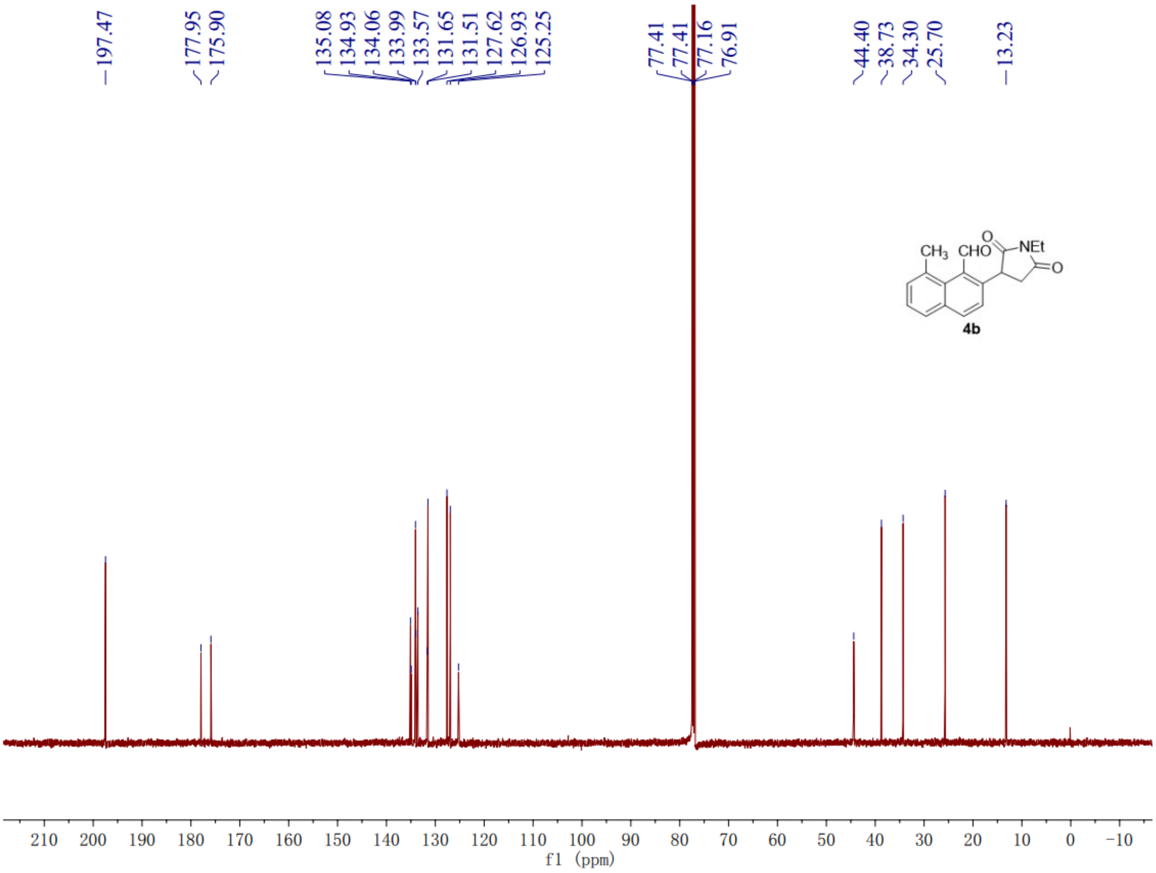
HR-ESI-MS (M+H)$^+$ of 4a



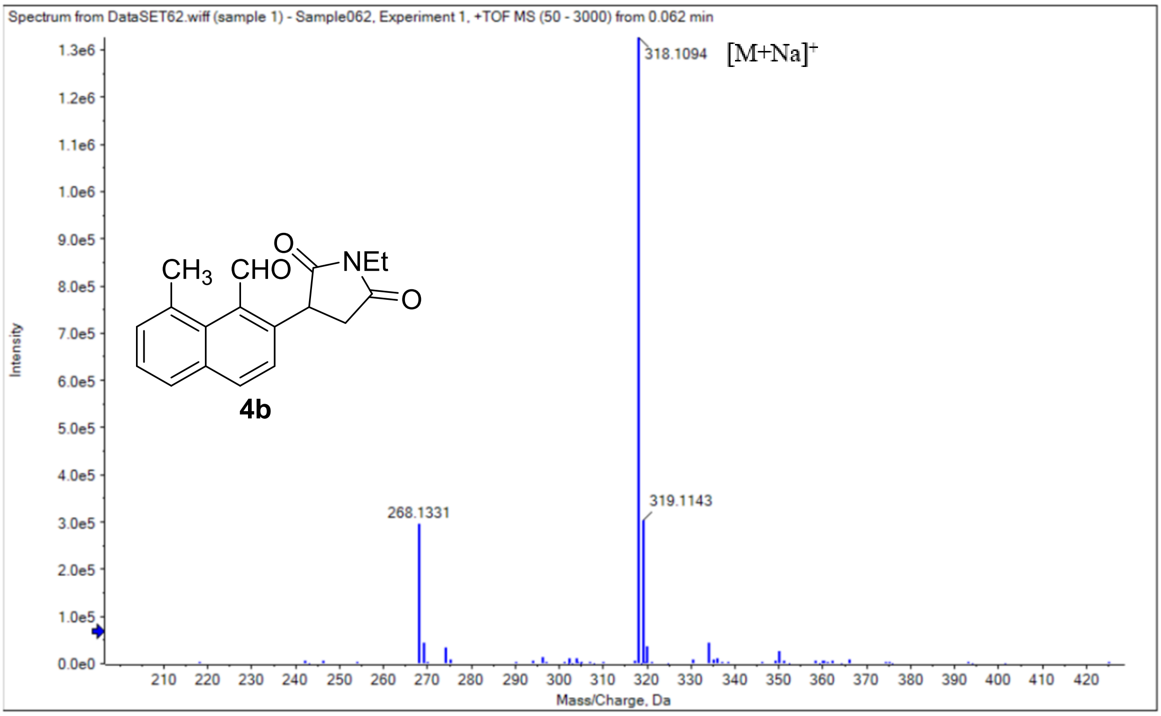
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 4b



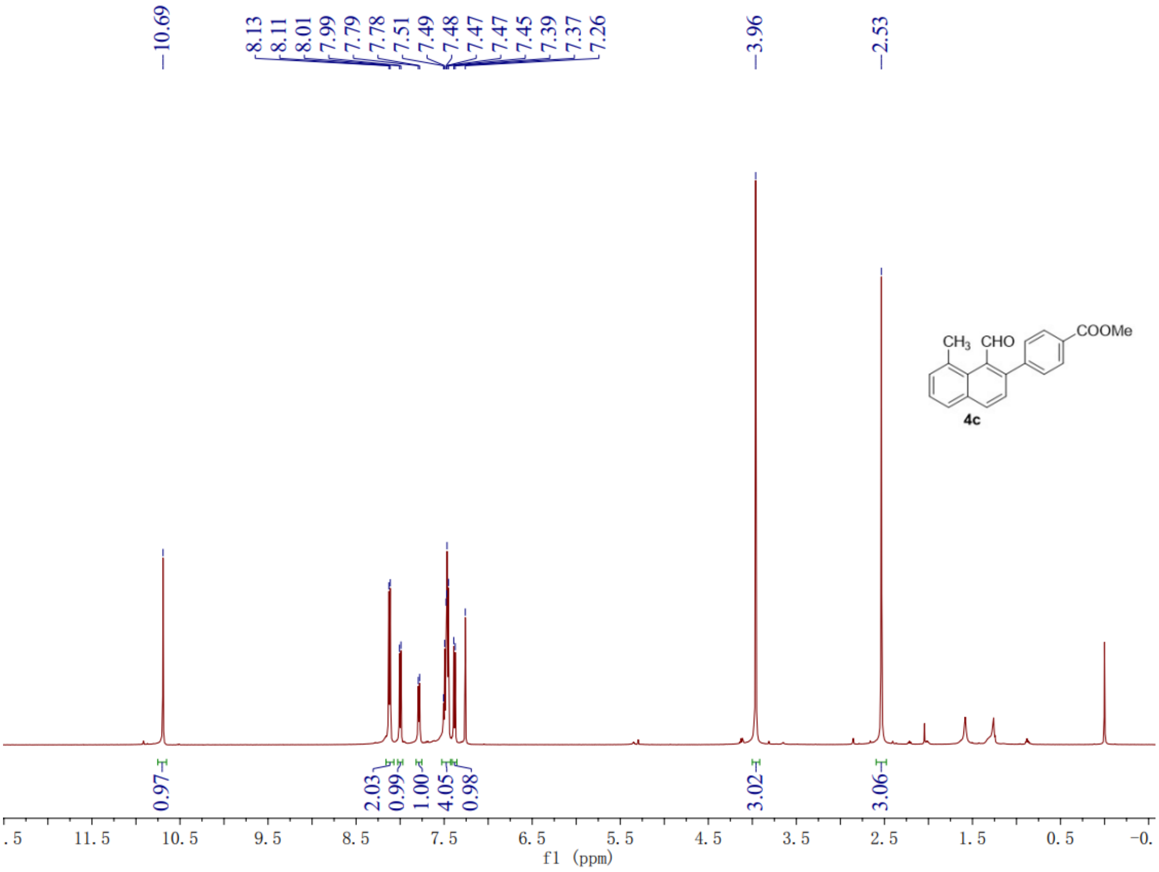
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 4b



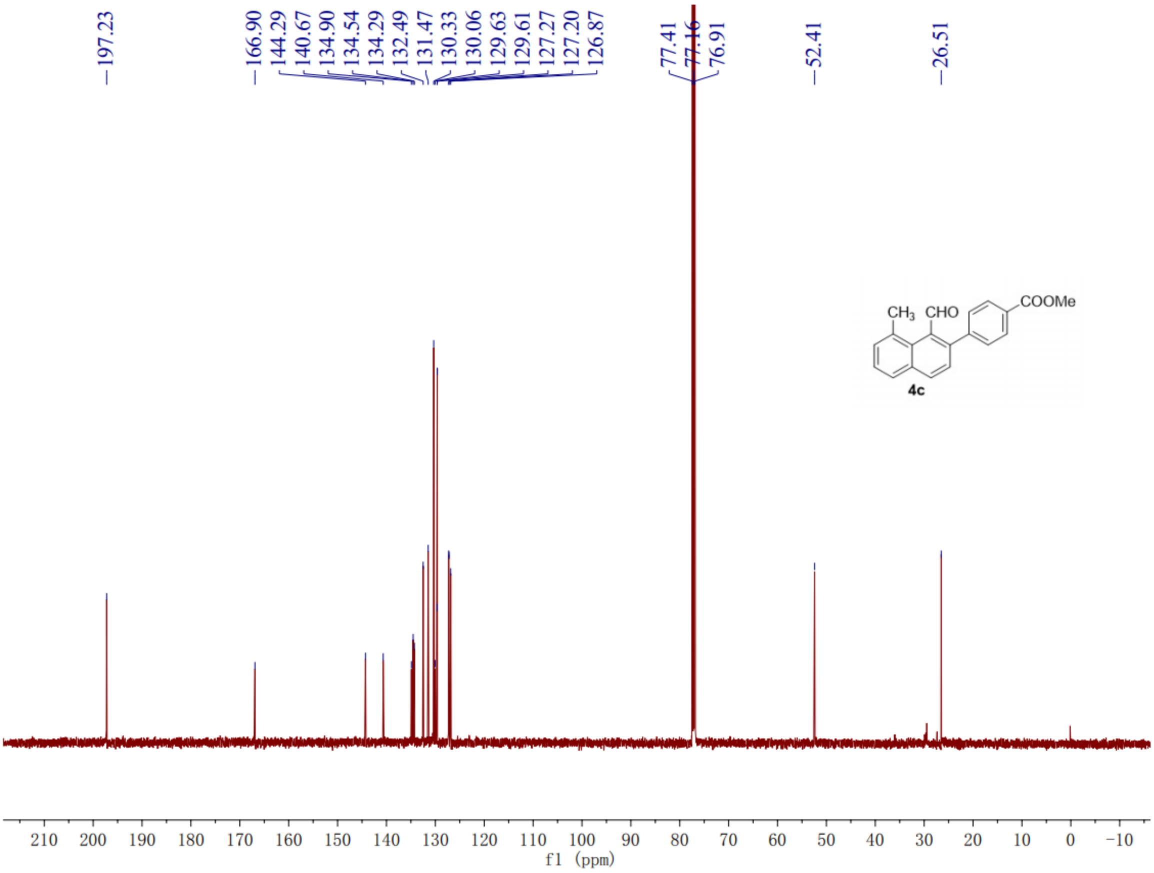
HR-ESI-MS $(M+H)^+$ of 4b



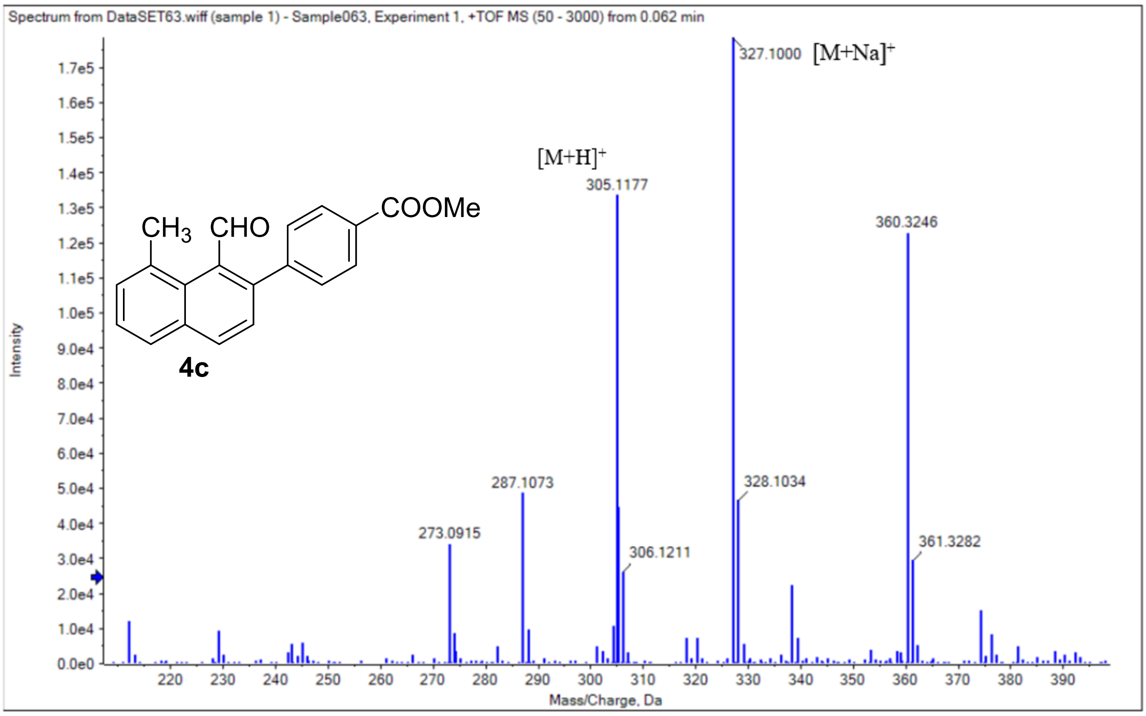
^1H NMR spectrum ($CDCl_3$, 500 MHz) of 4c



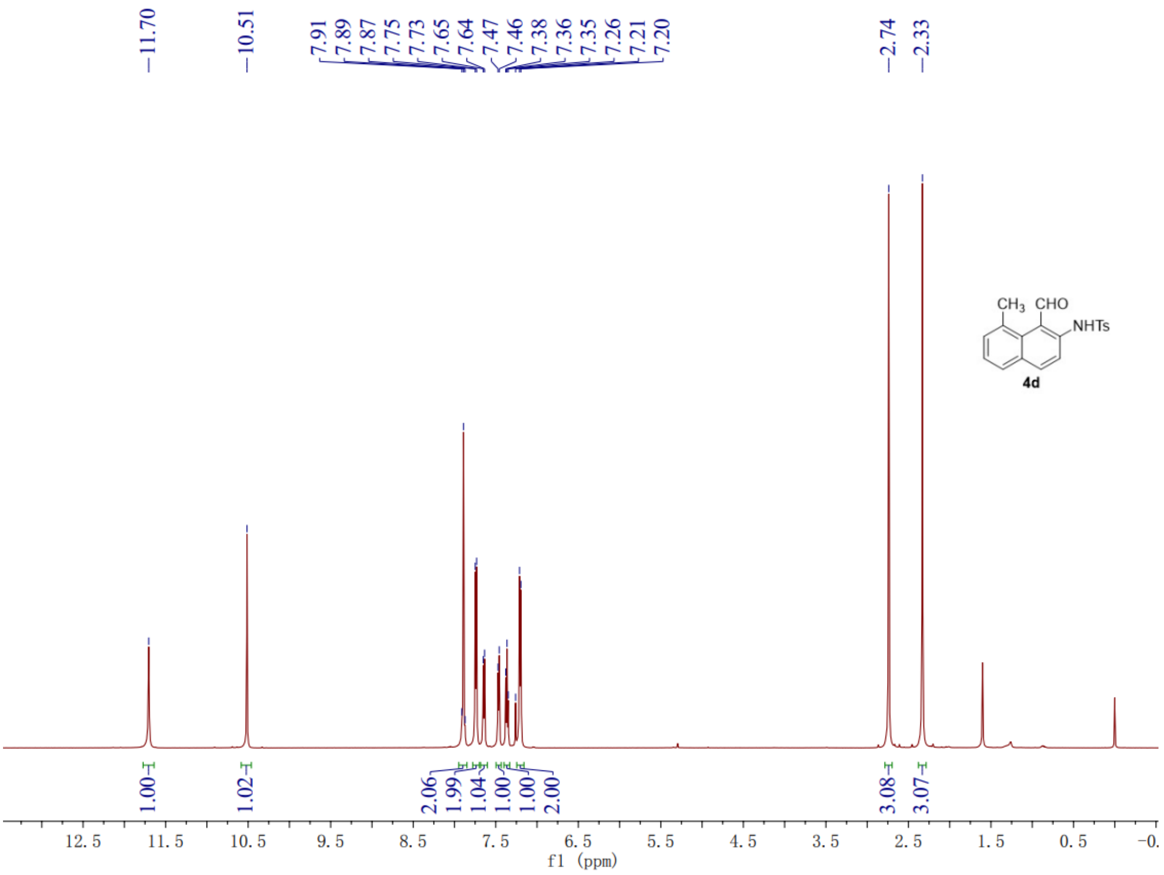
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 4c



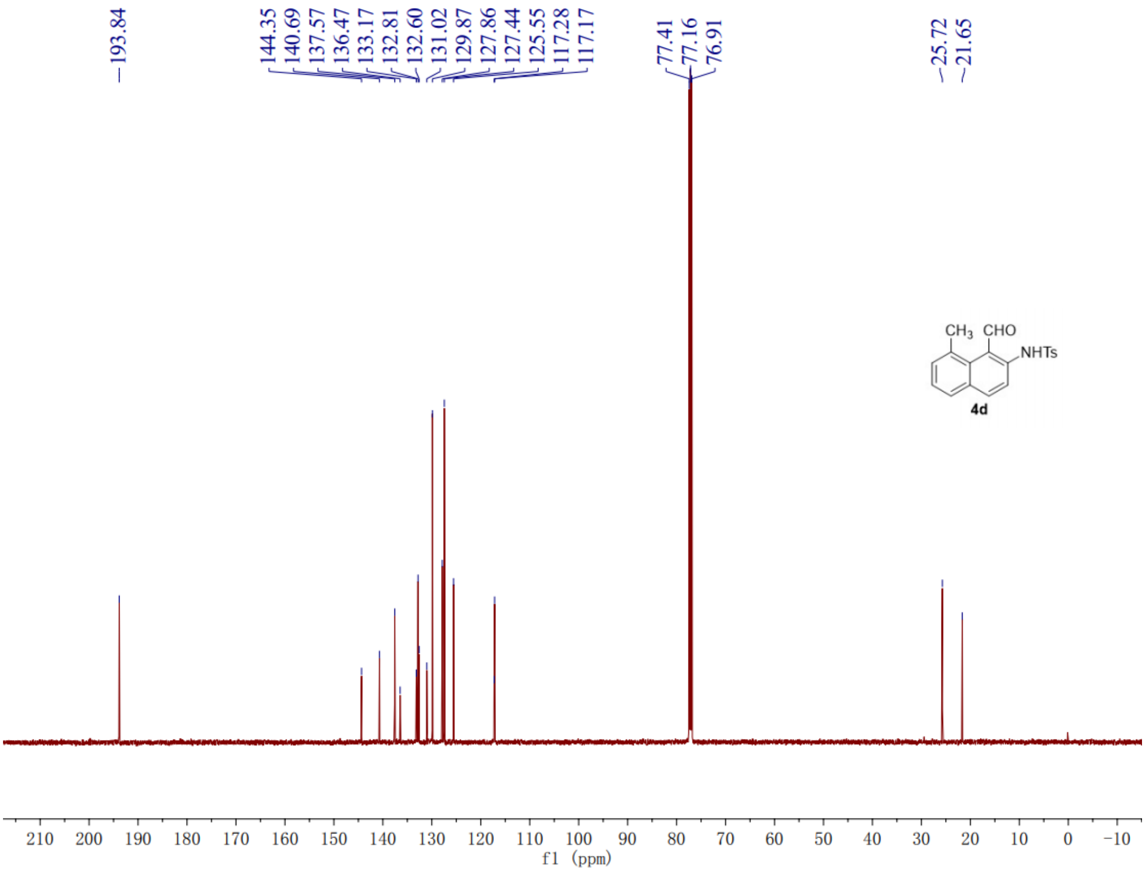
HR-ESI-MS $(M+Na)^+$ of 4c



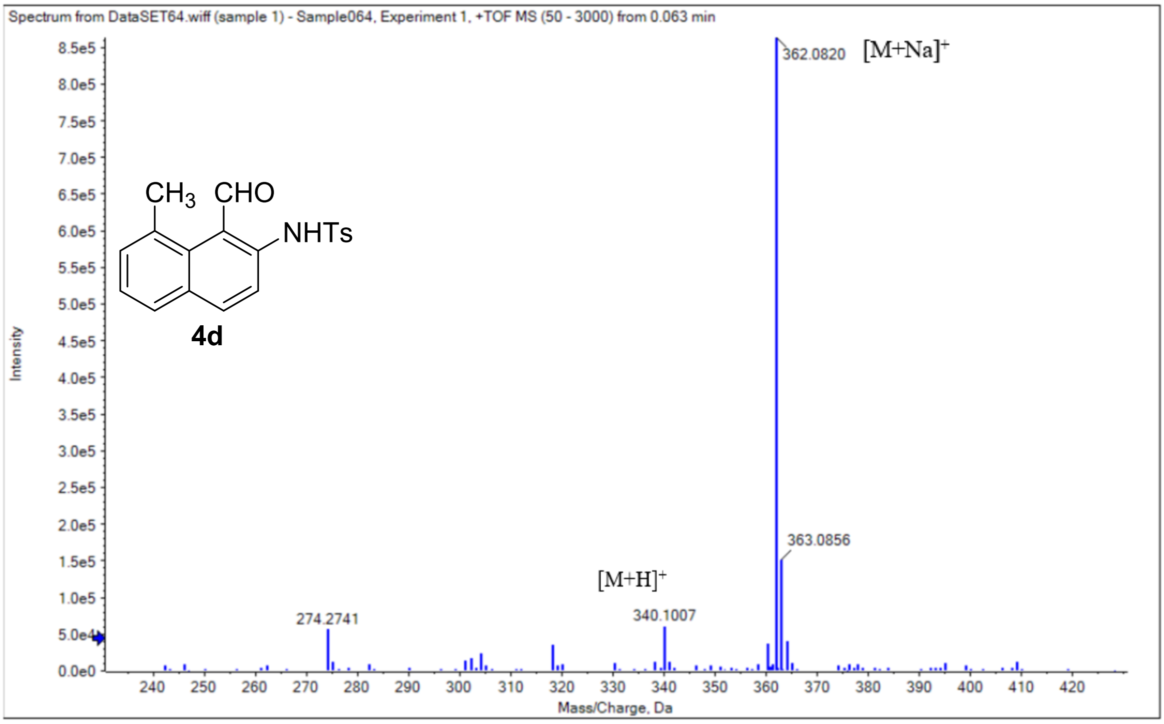
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 4d



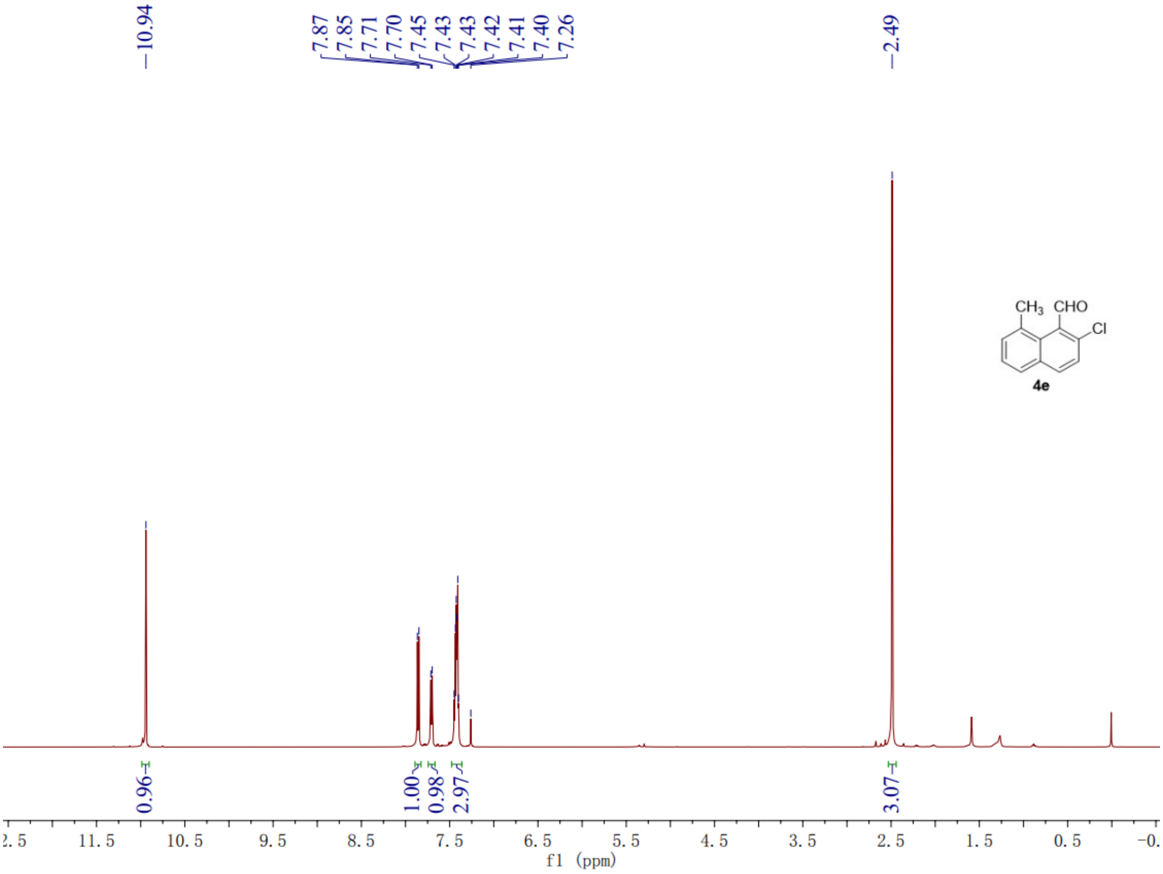
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 4d



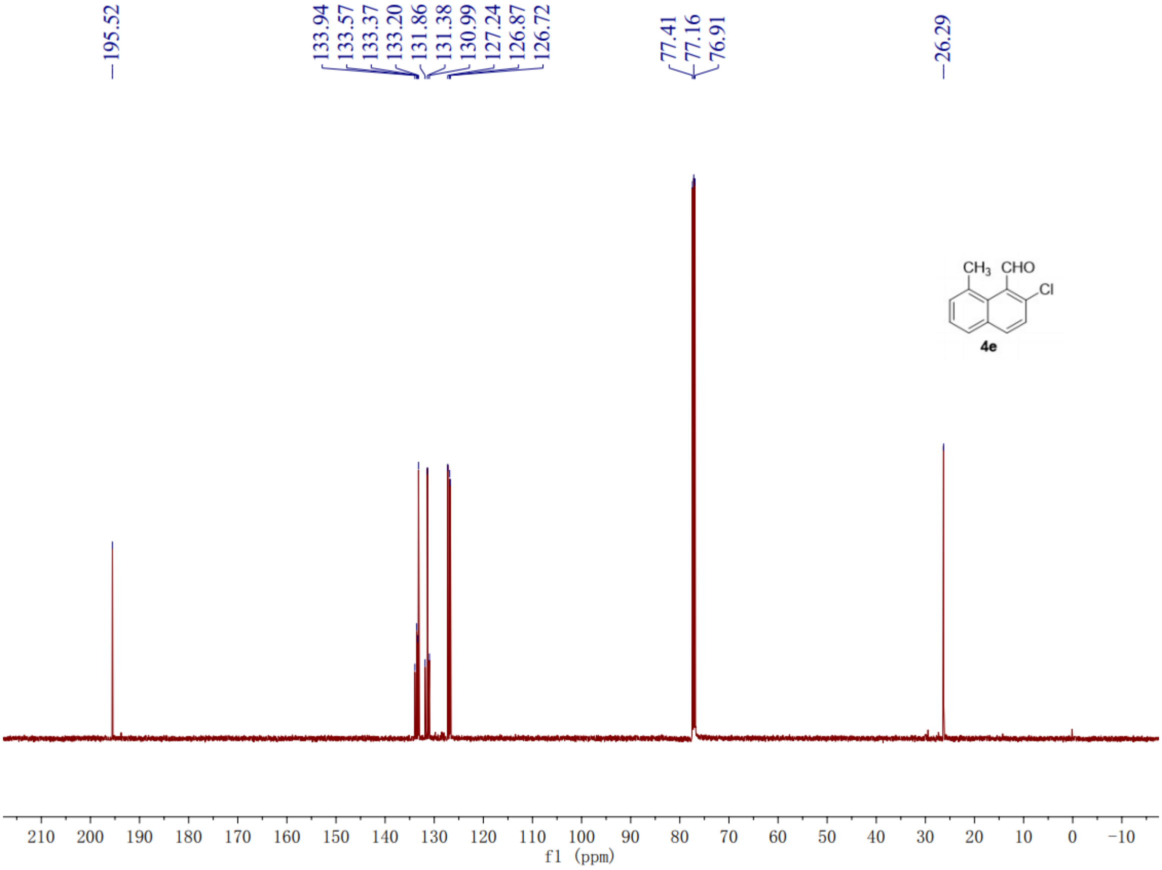
HR-ESI-MS $(M+H)^+$ of 4d



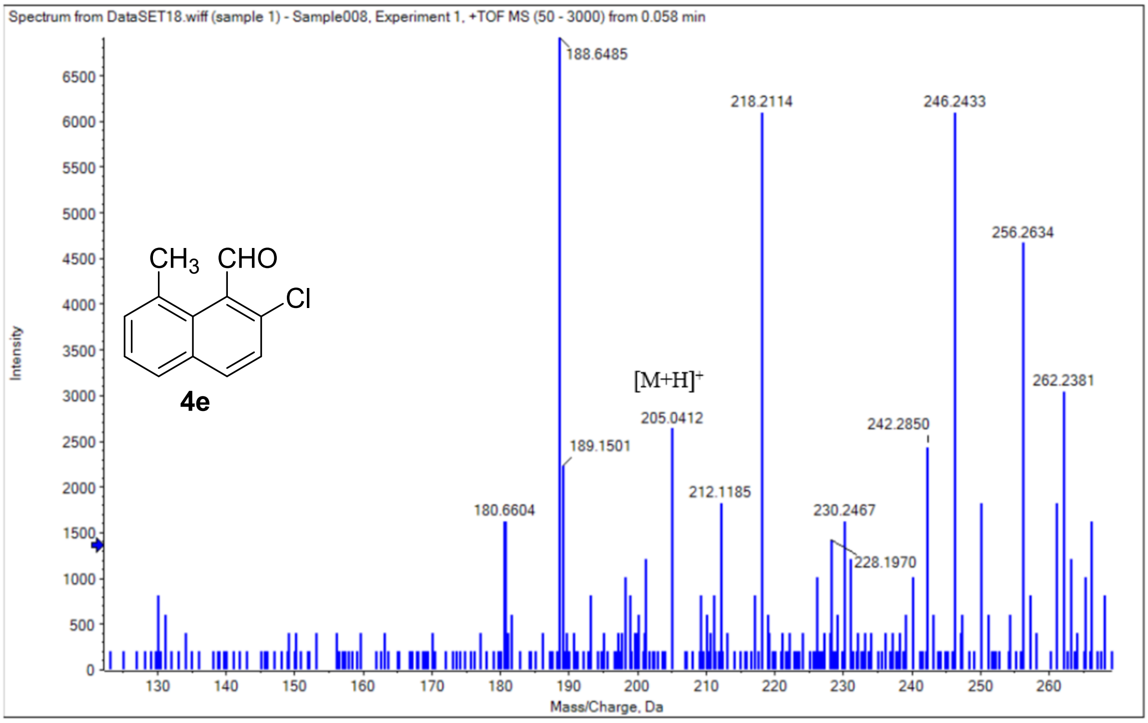
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4e



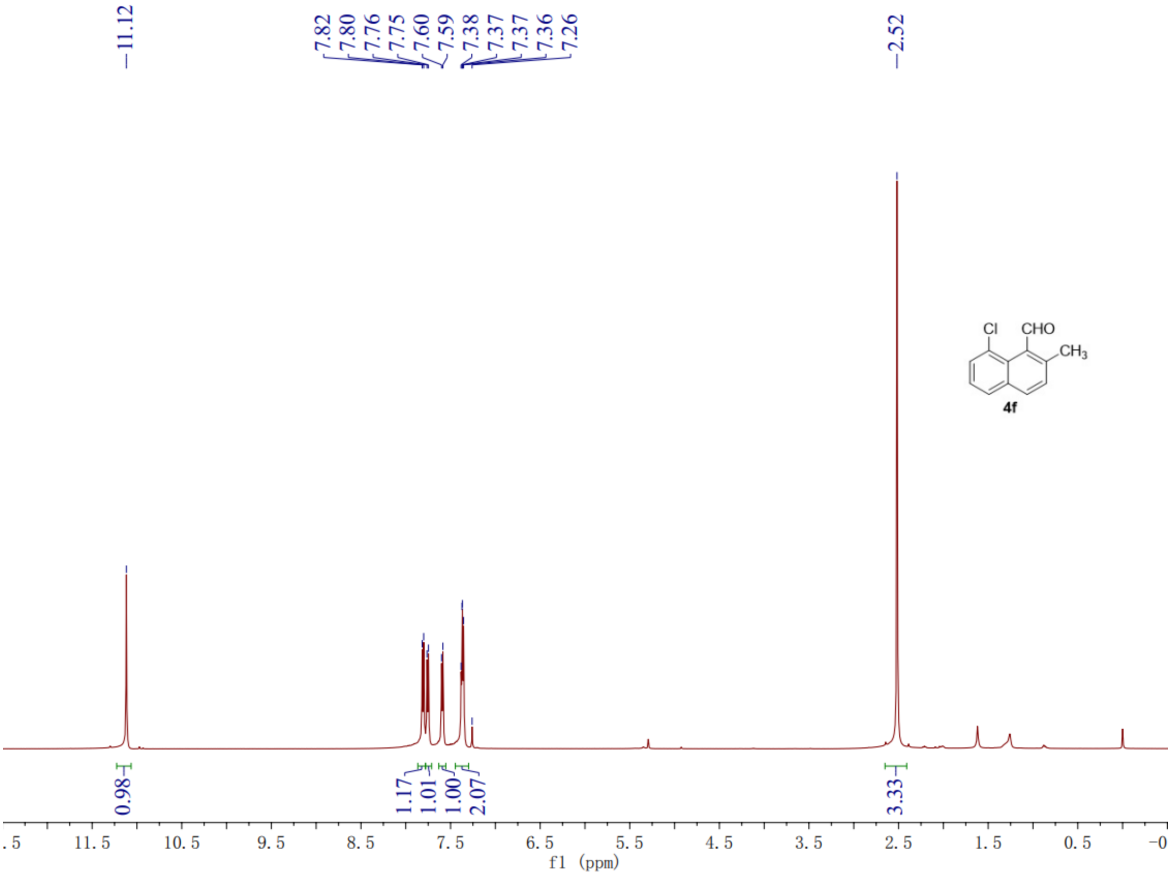
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 4e



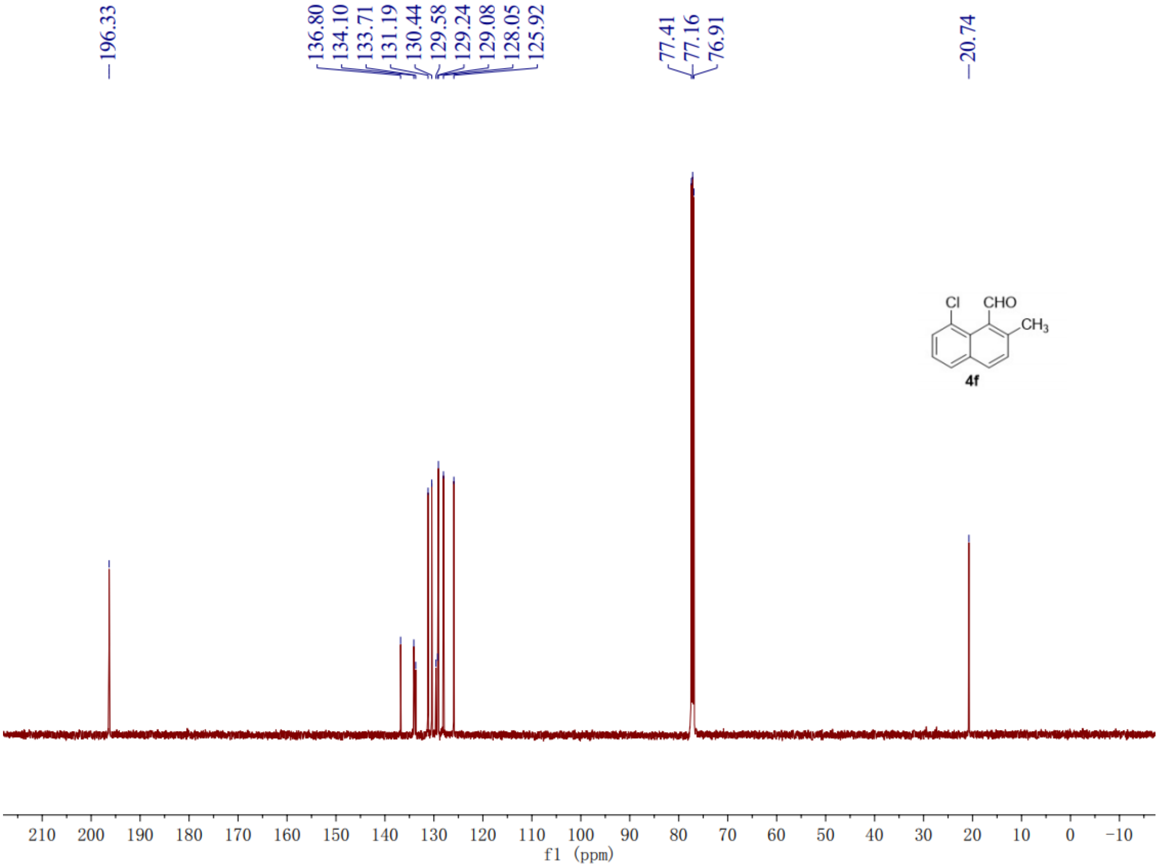
HR-ESI-MS (M+H)$^+$ of 4e



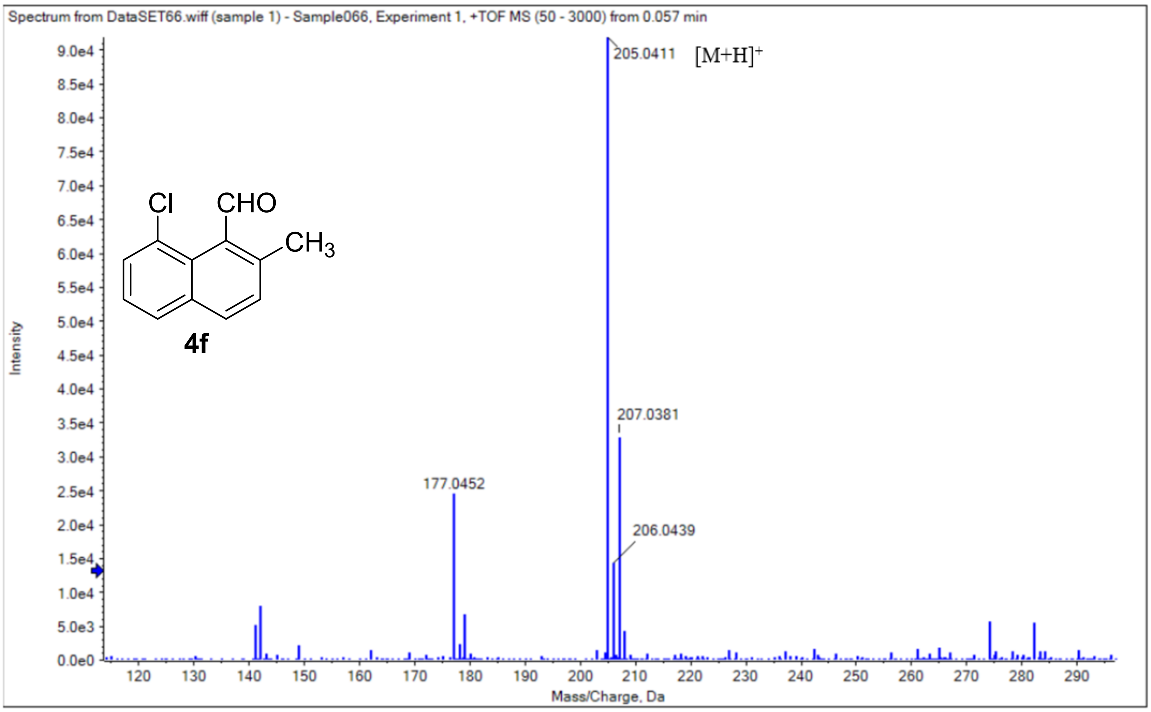
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 4f



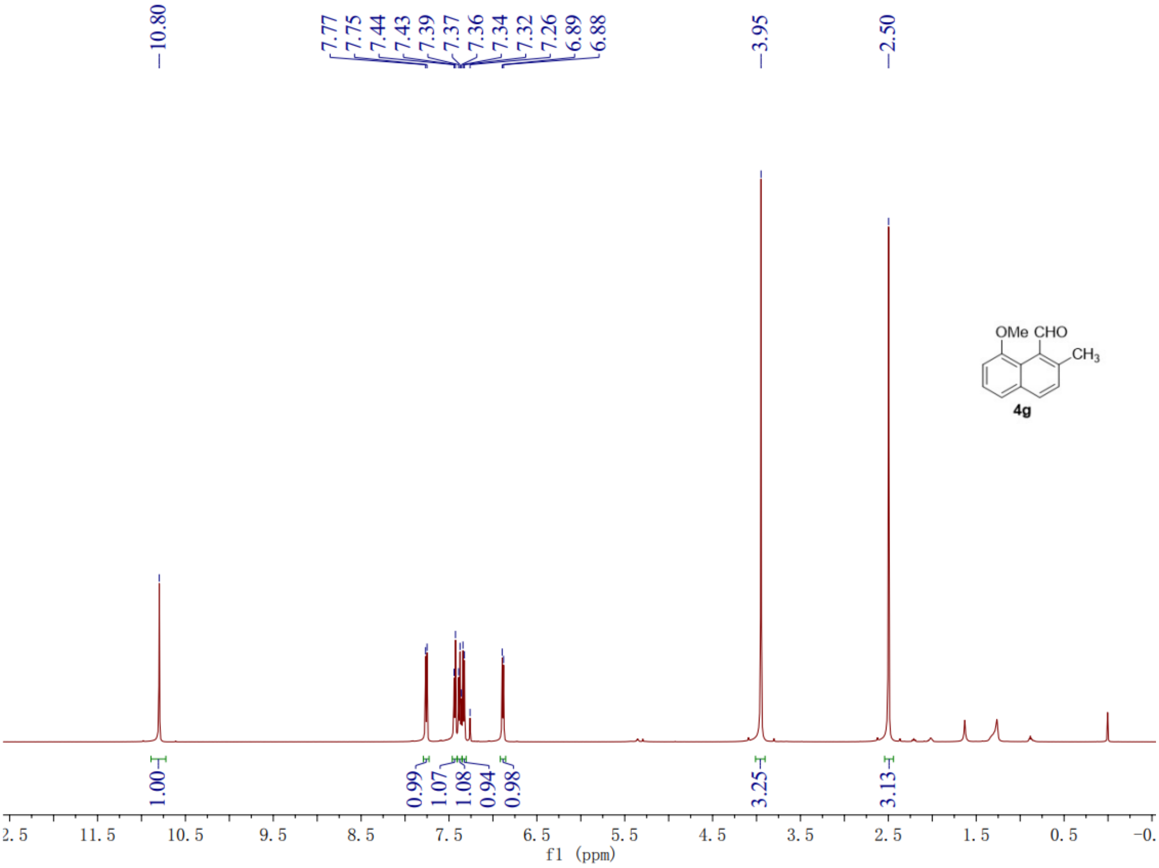
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 4f



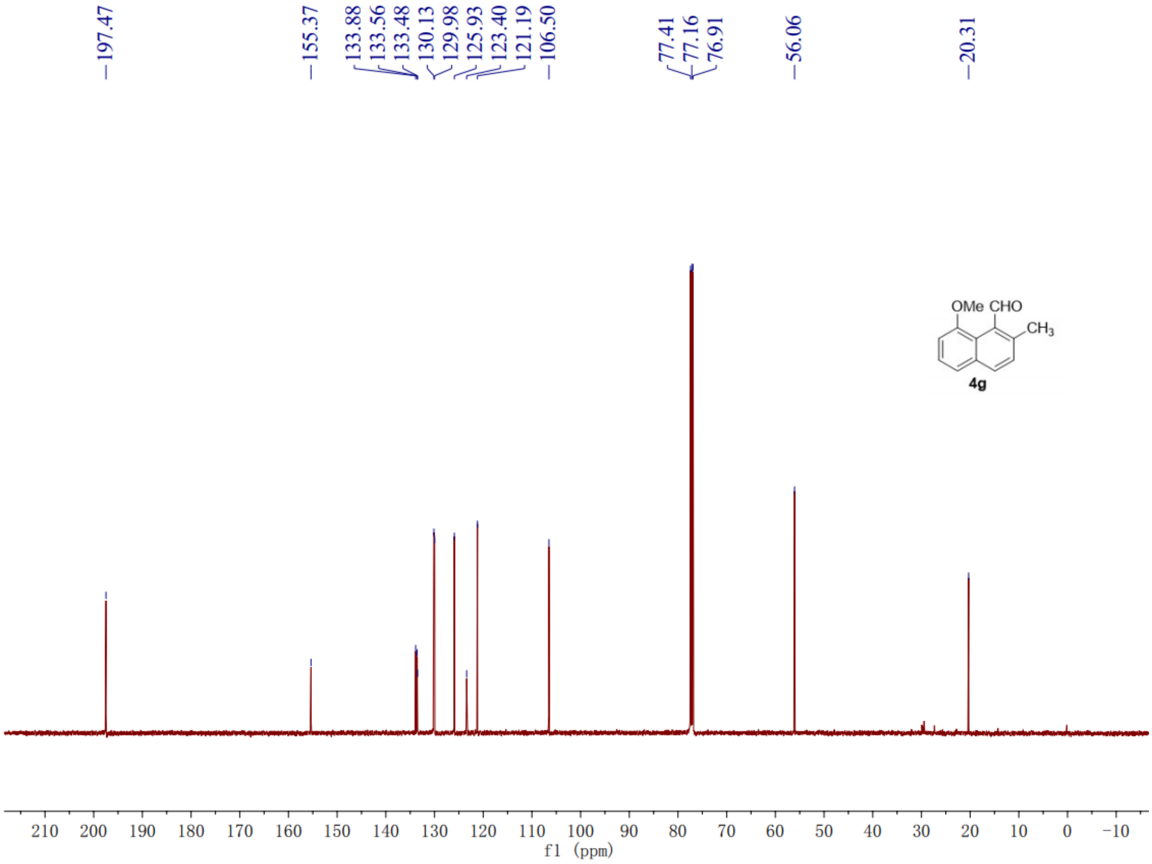
HR-ESI-MS $(M+H)^+$ of 4f



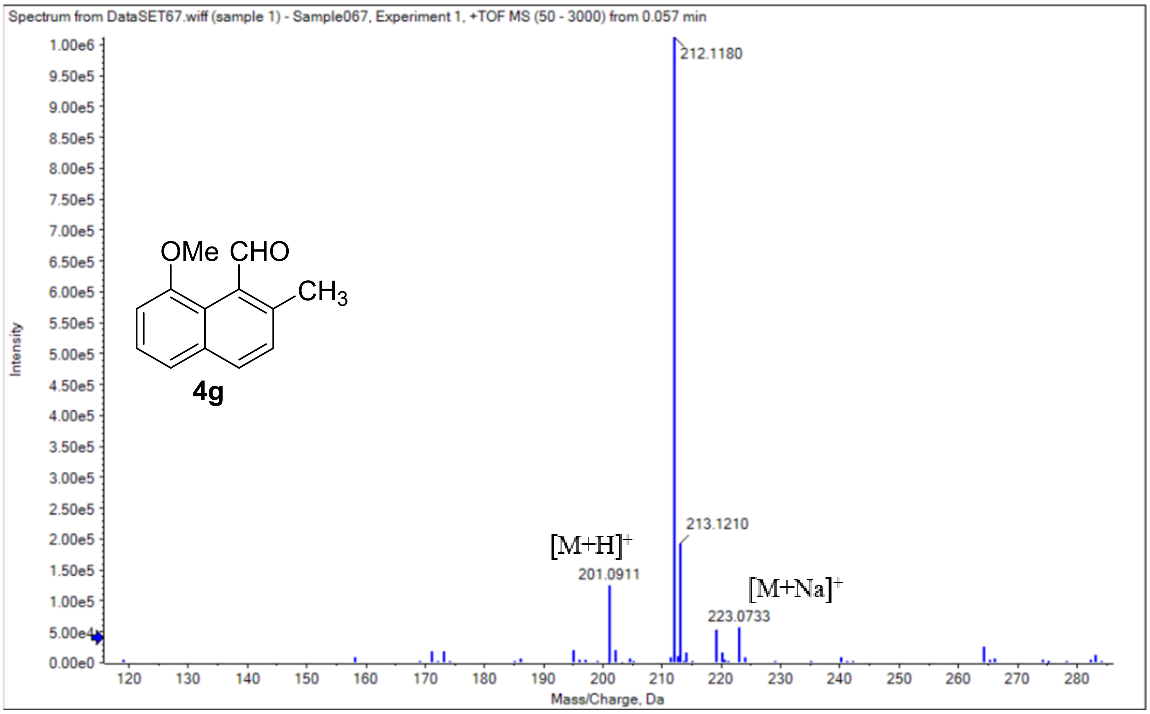
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4g



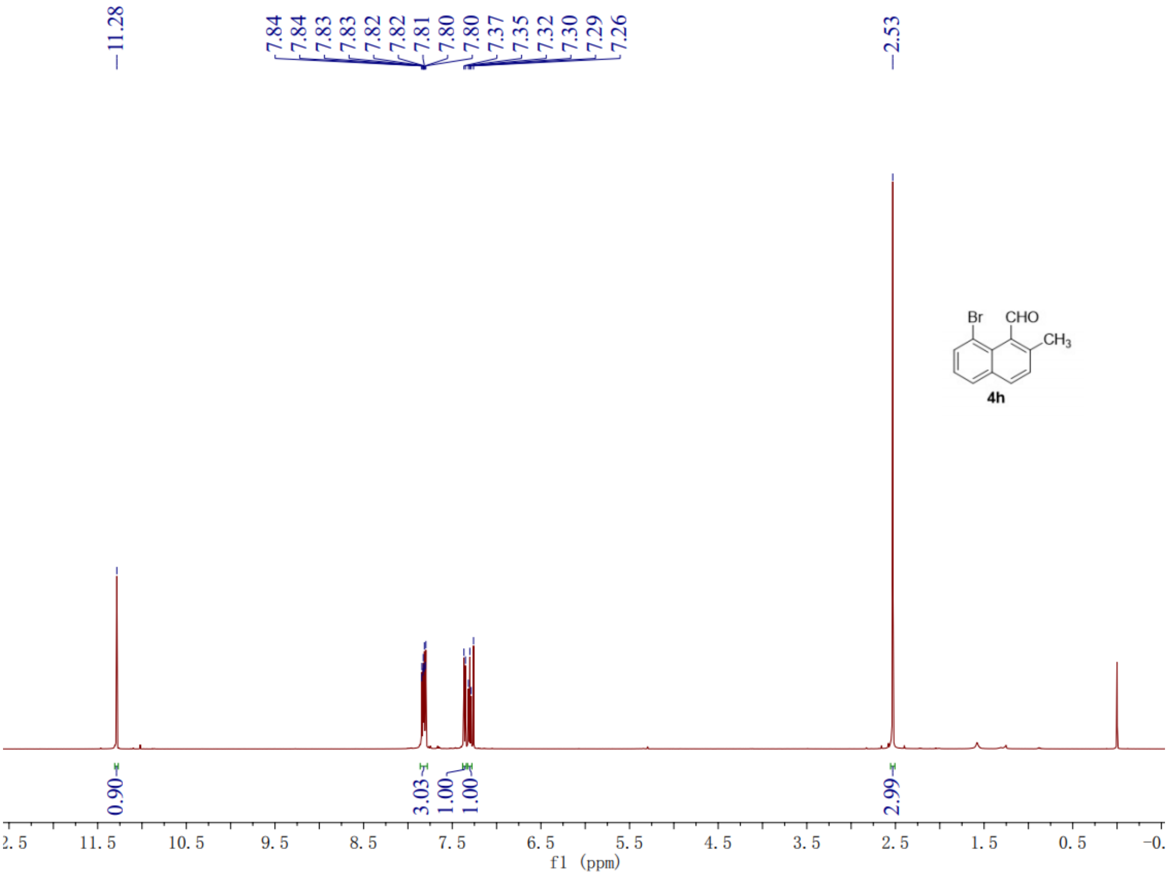
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 4g



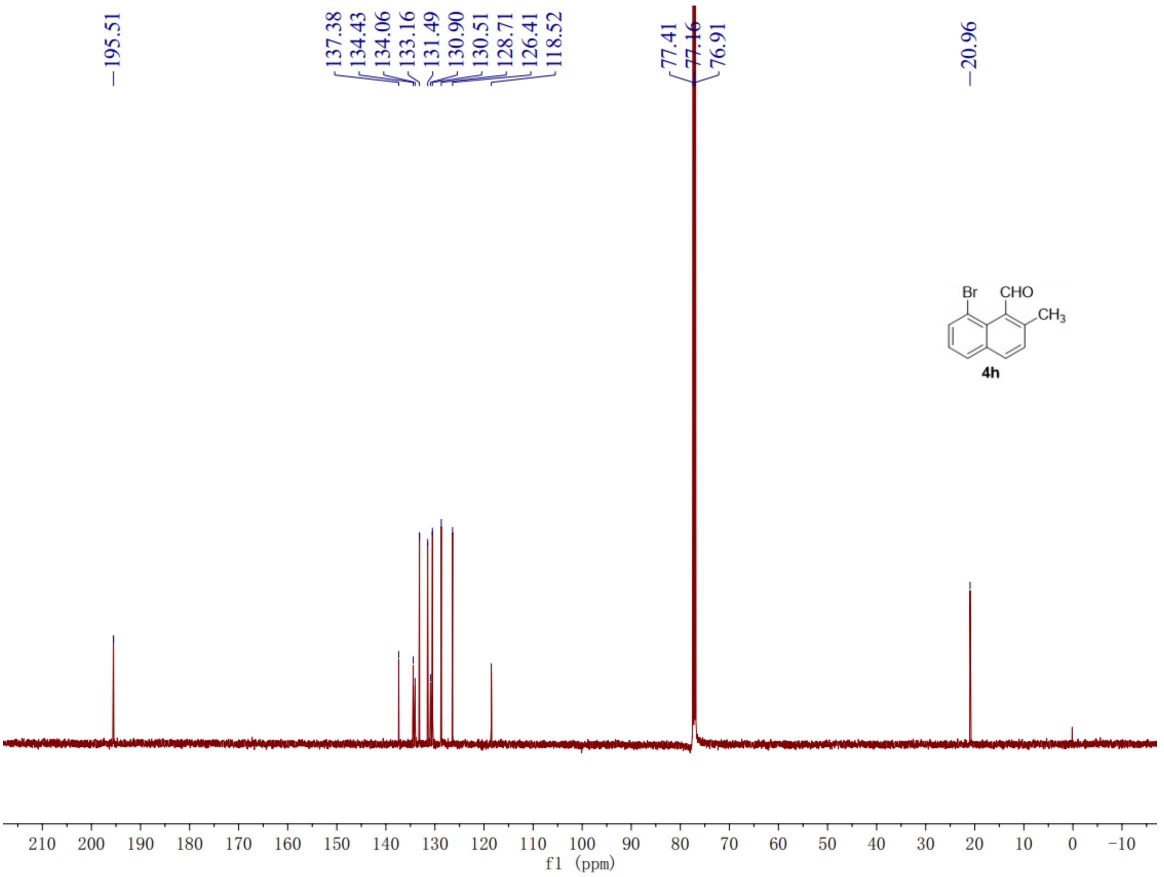
HR-ESI-MS (M+H)$^+$ of 4g



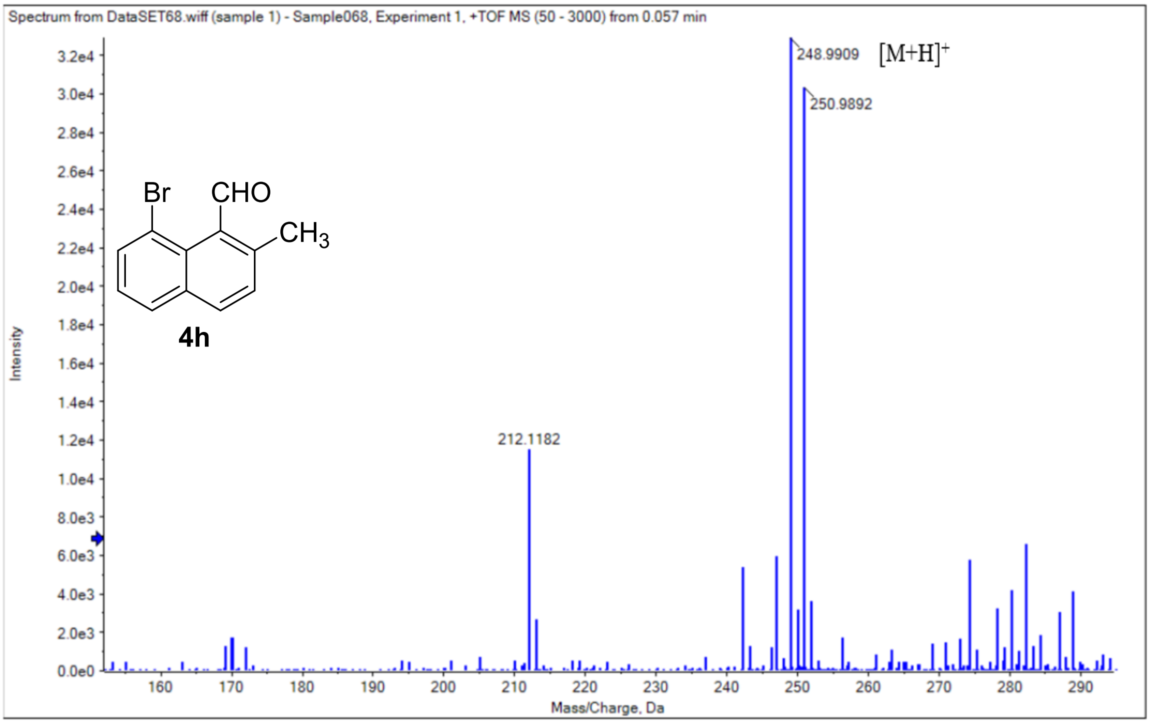
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4h



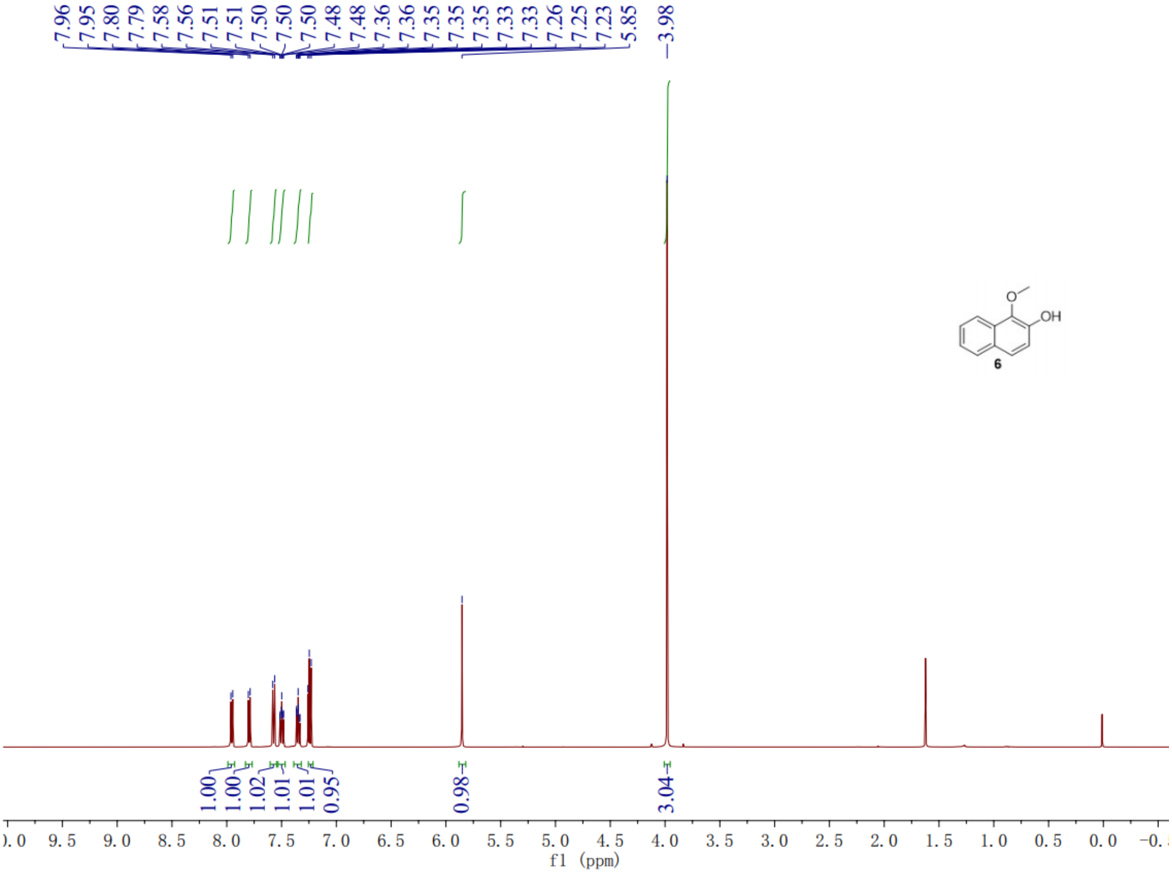
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 4h



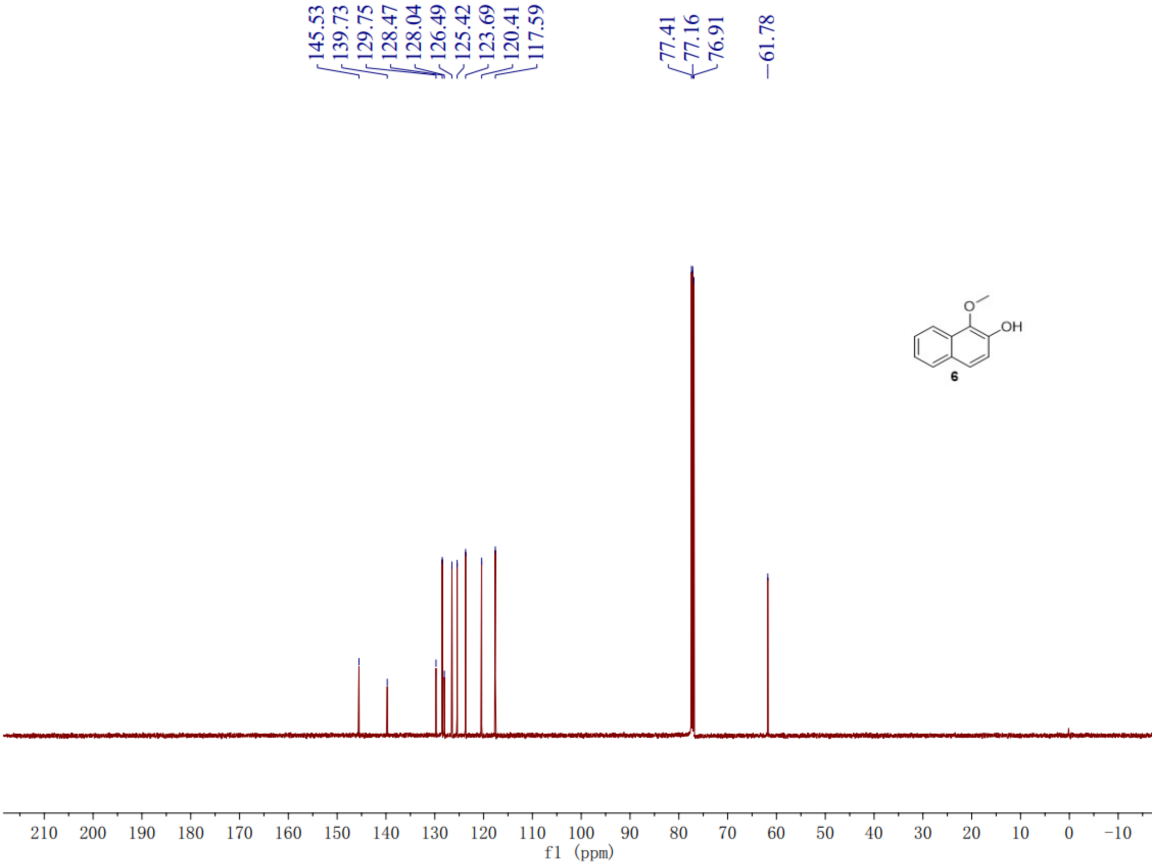
HR-ESI-MS $(M+H)^+$ of 4h



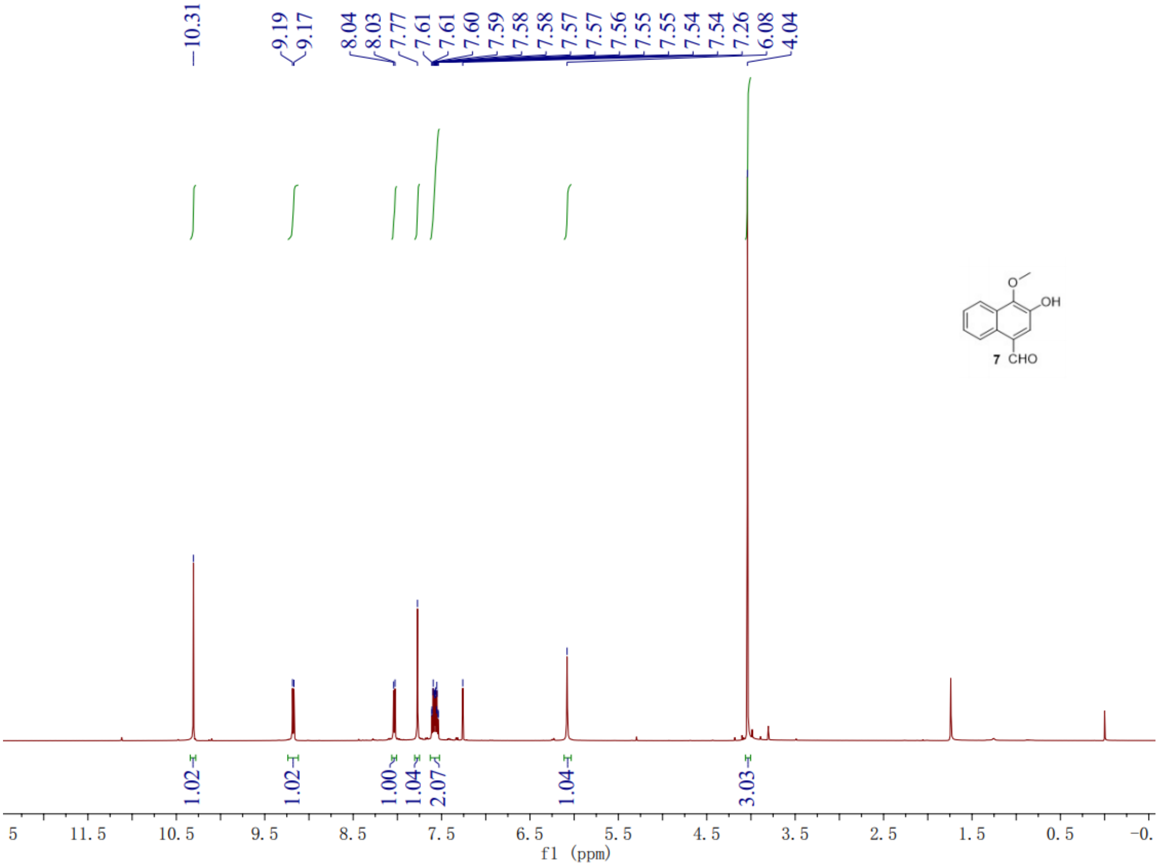
^1H NMR spectrum ($CDCl_3$, 500 MHz) of 6



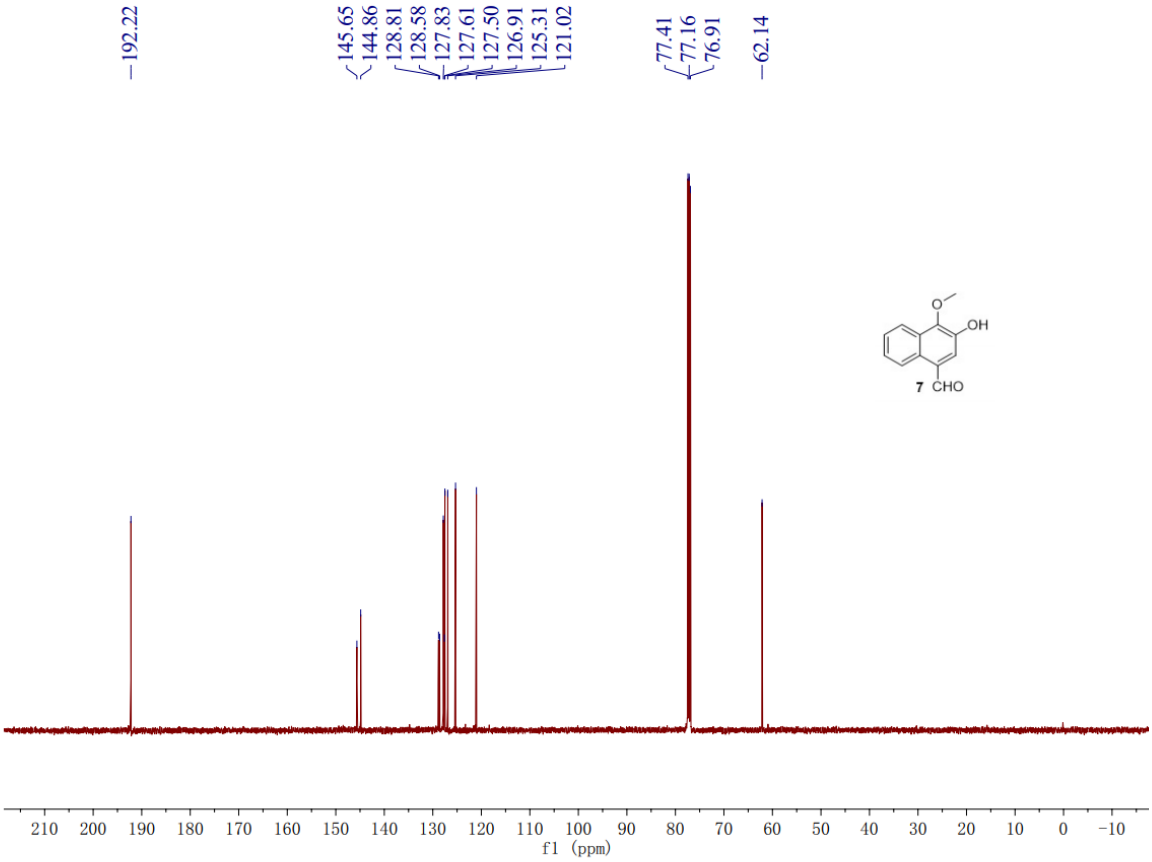
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 6



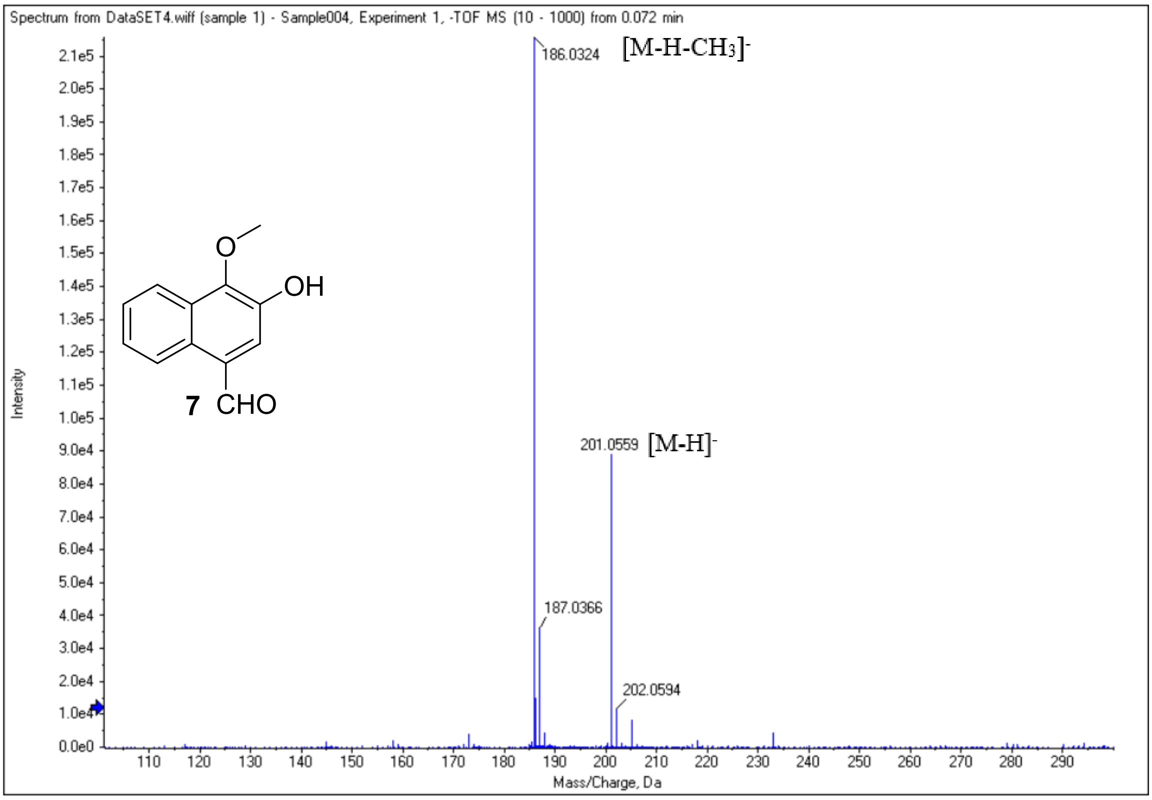
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 7



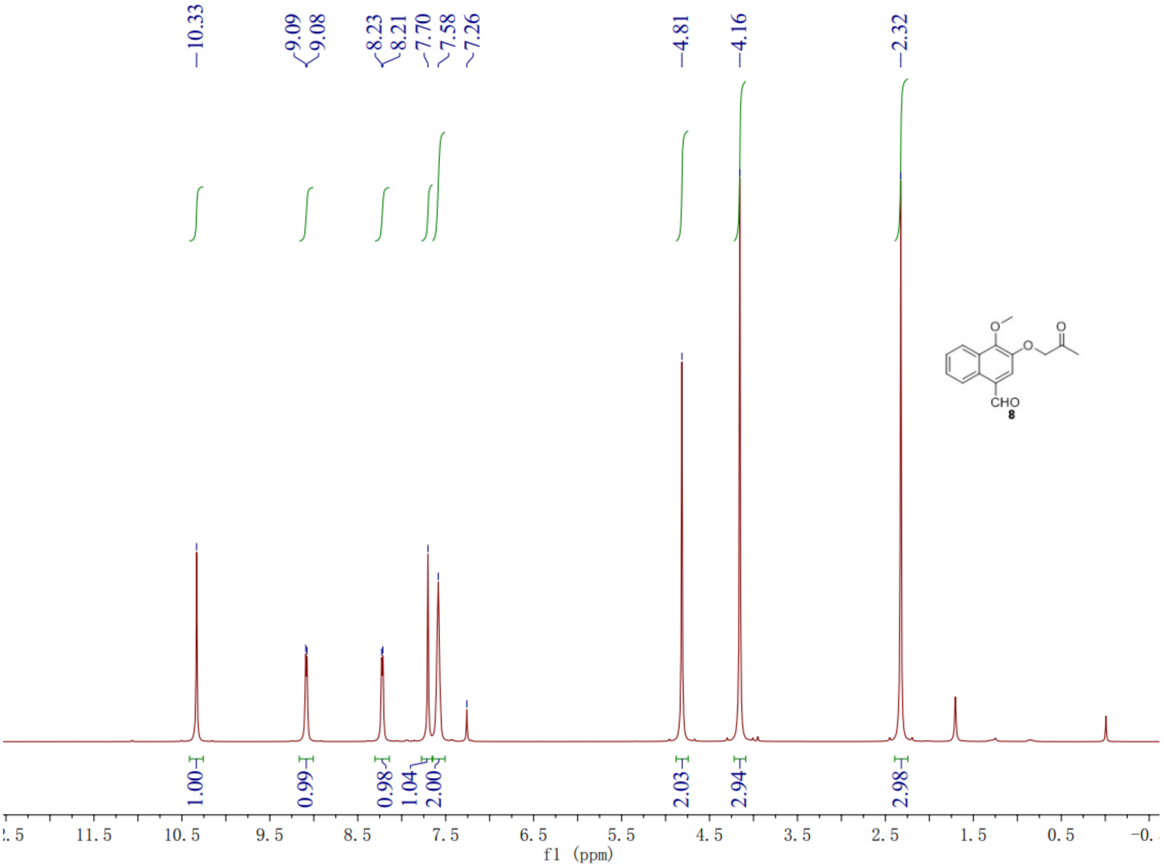
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 7



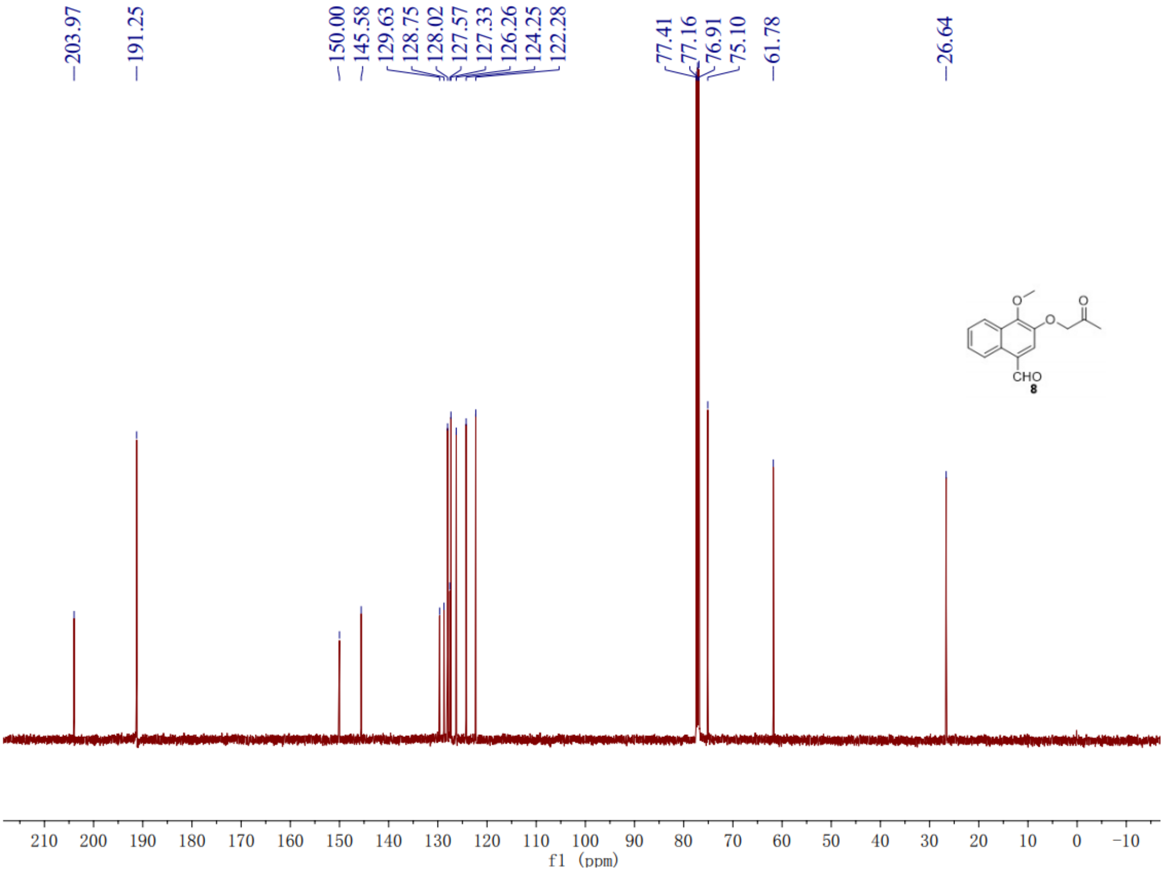
HR-ESI-MS (M-H)$^-$ of 7



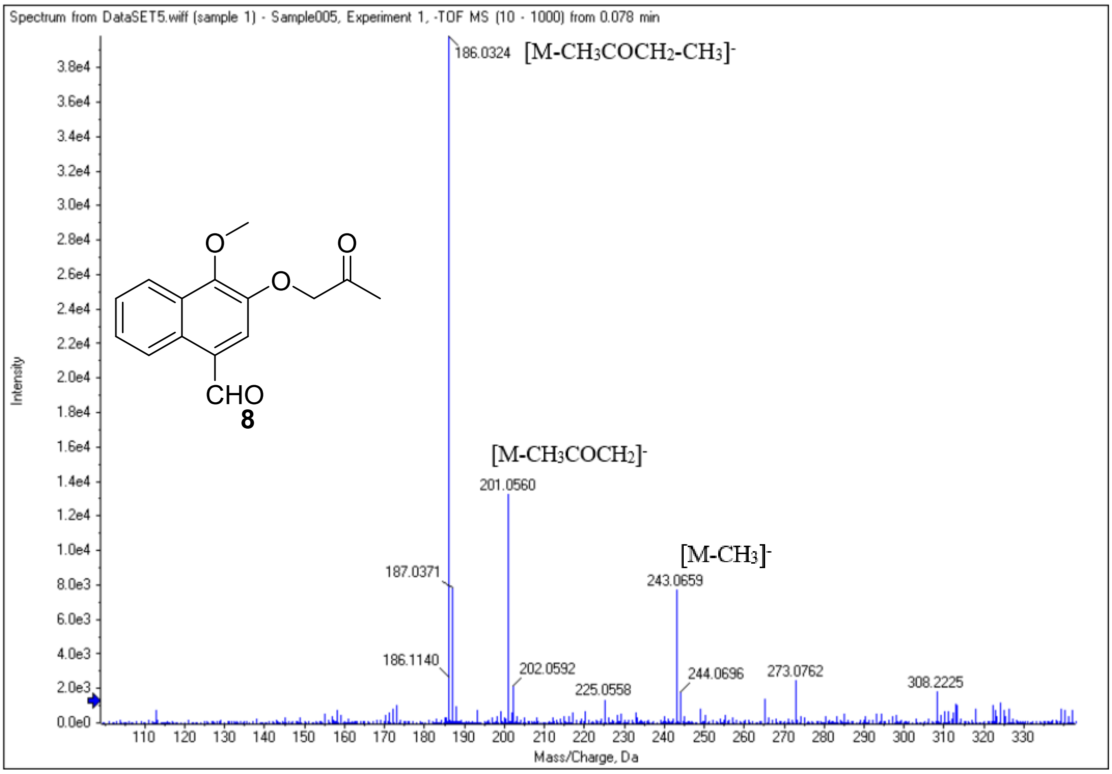
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 8



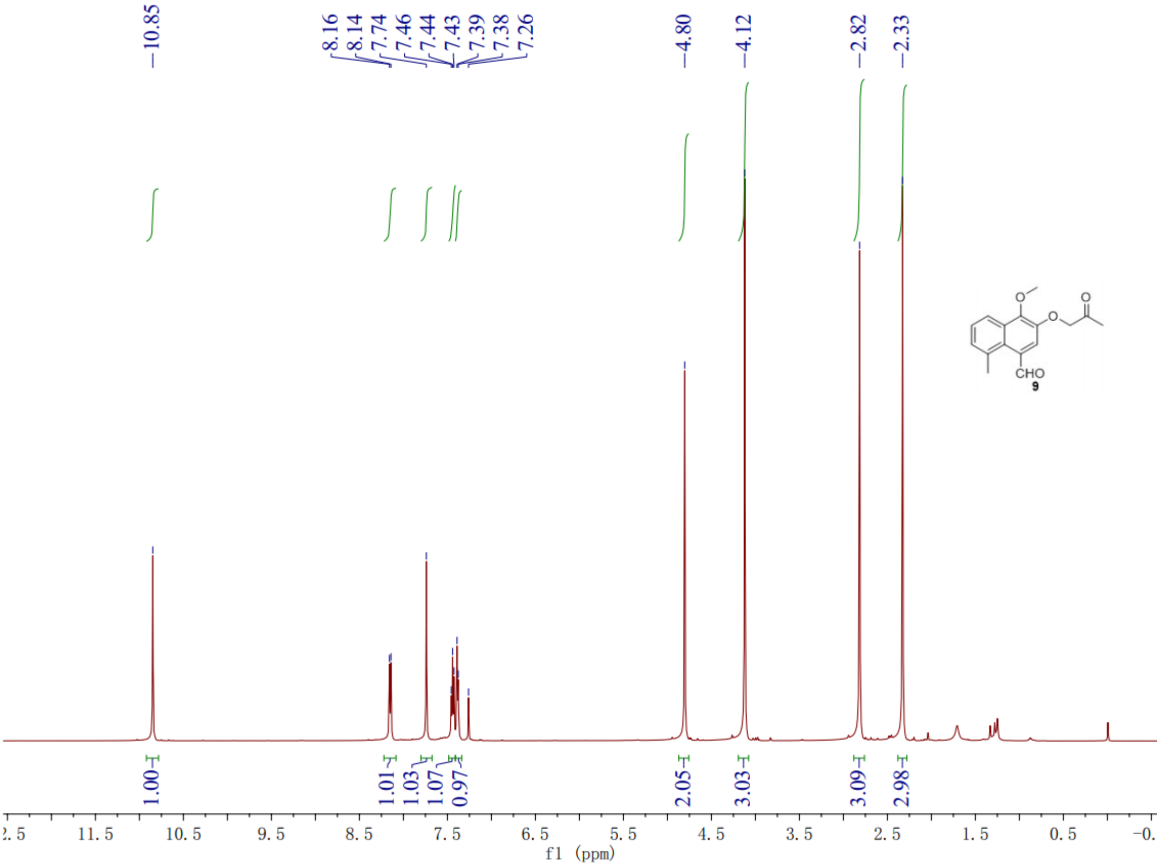
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 8



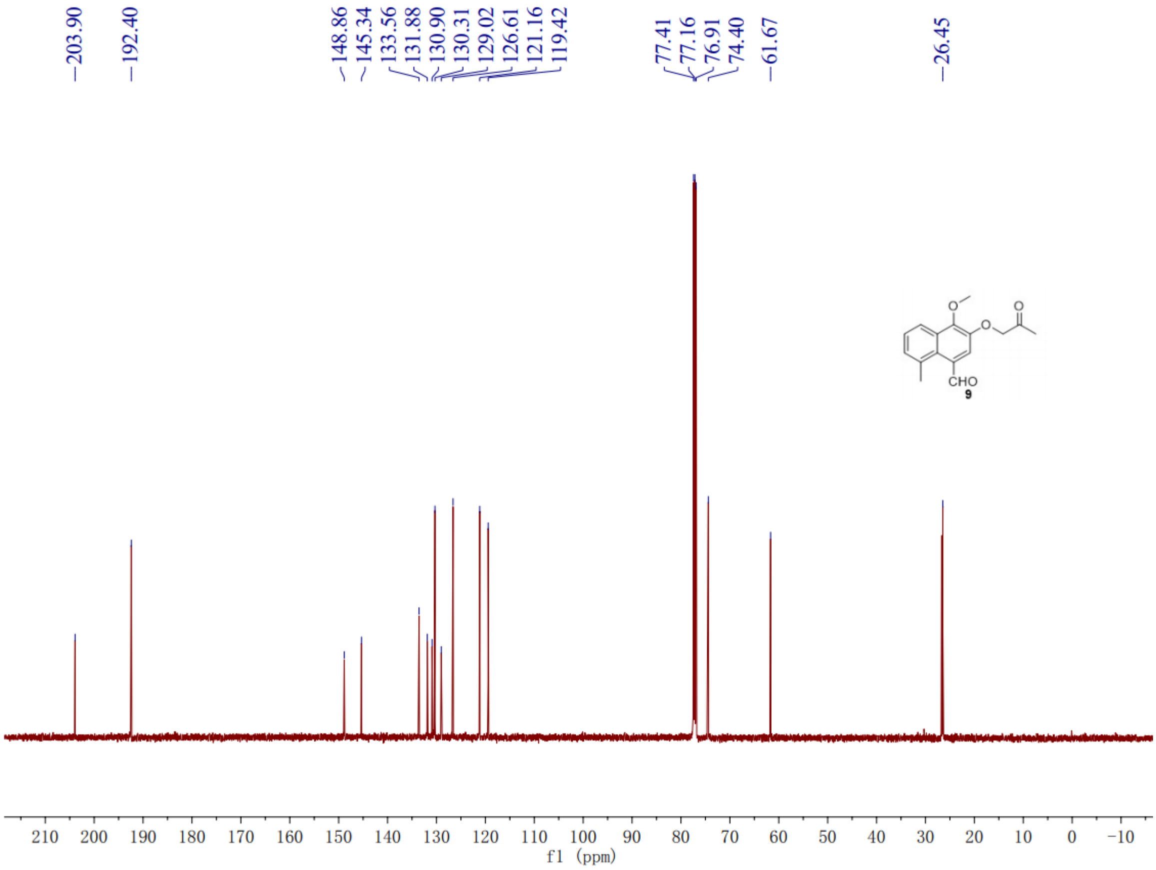
HR-ESI-MS $(M-CH_3)^-$ of 8



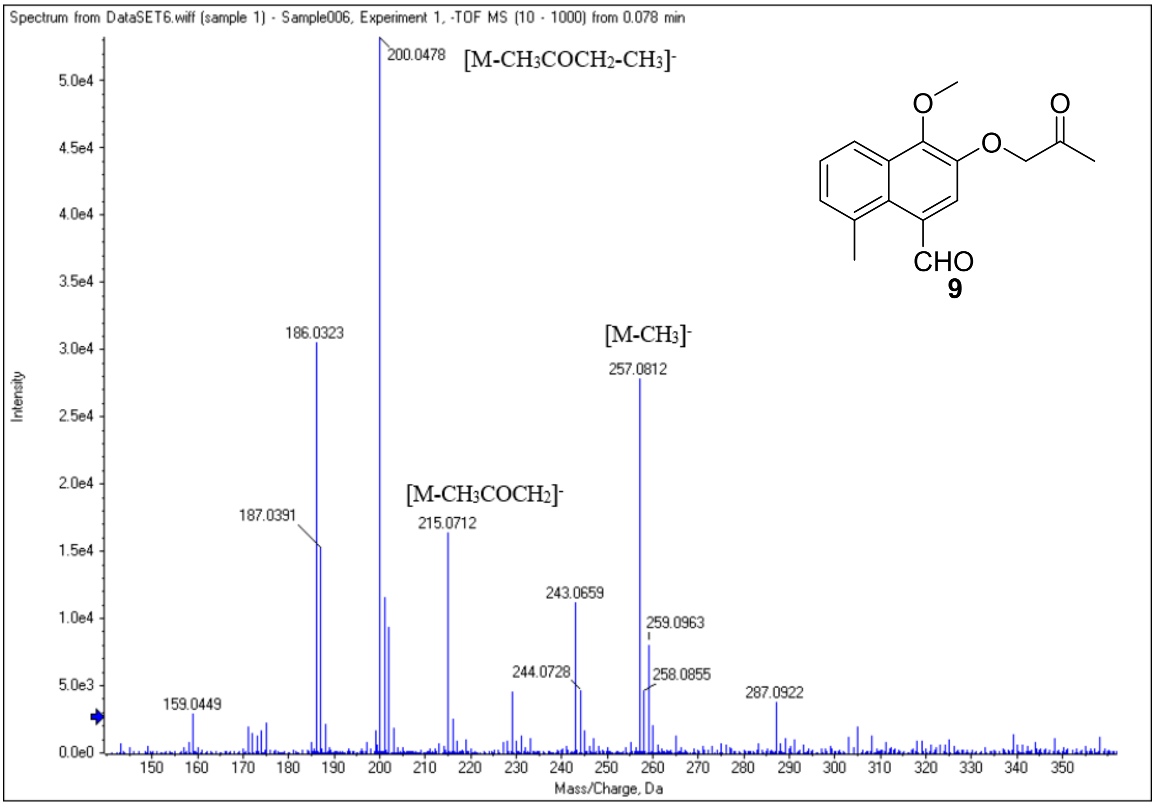
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 9



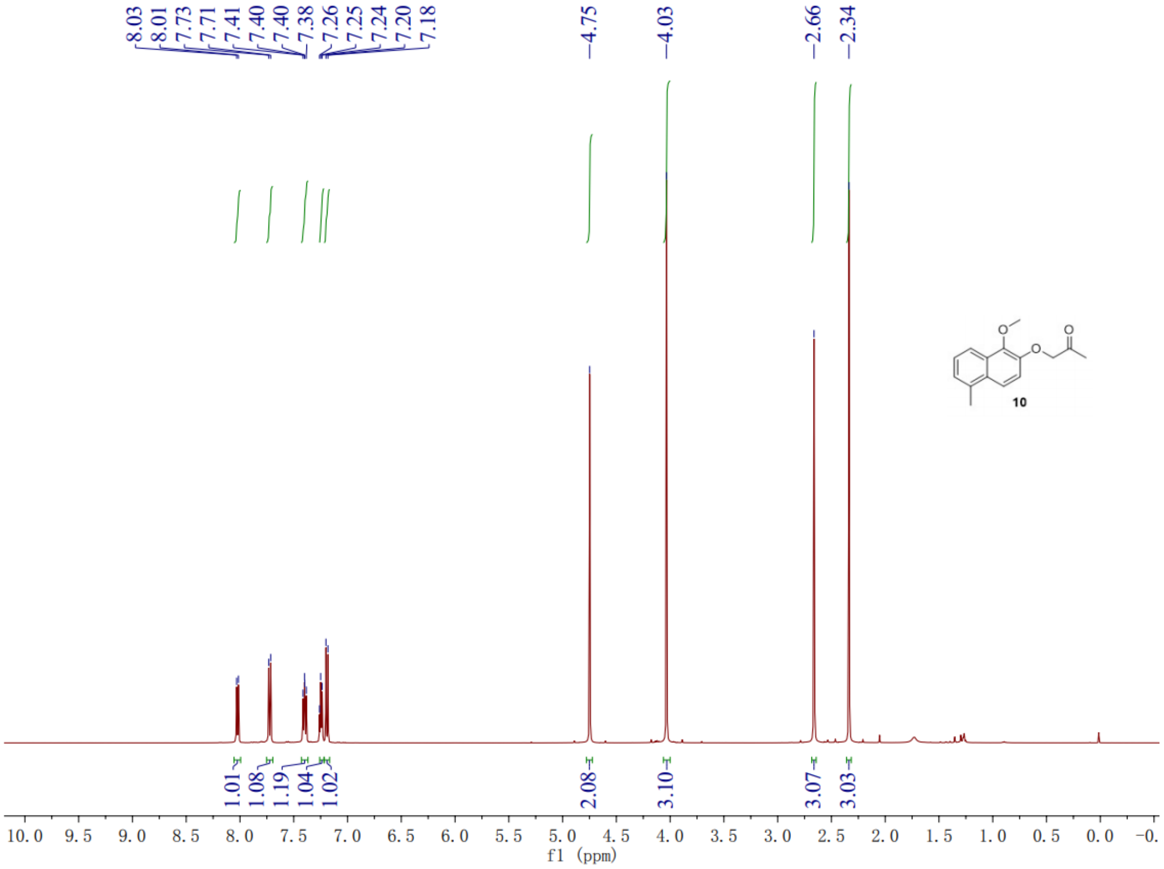
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 9



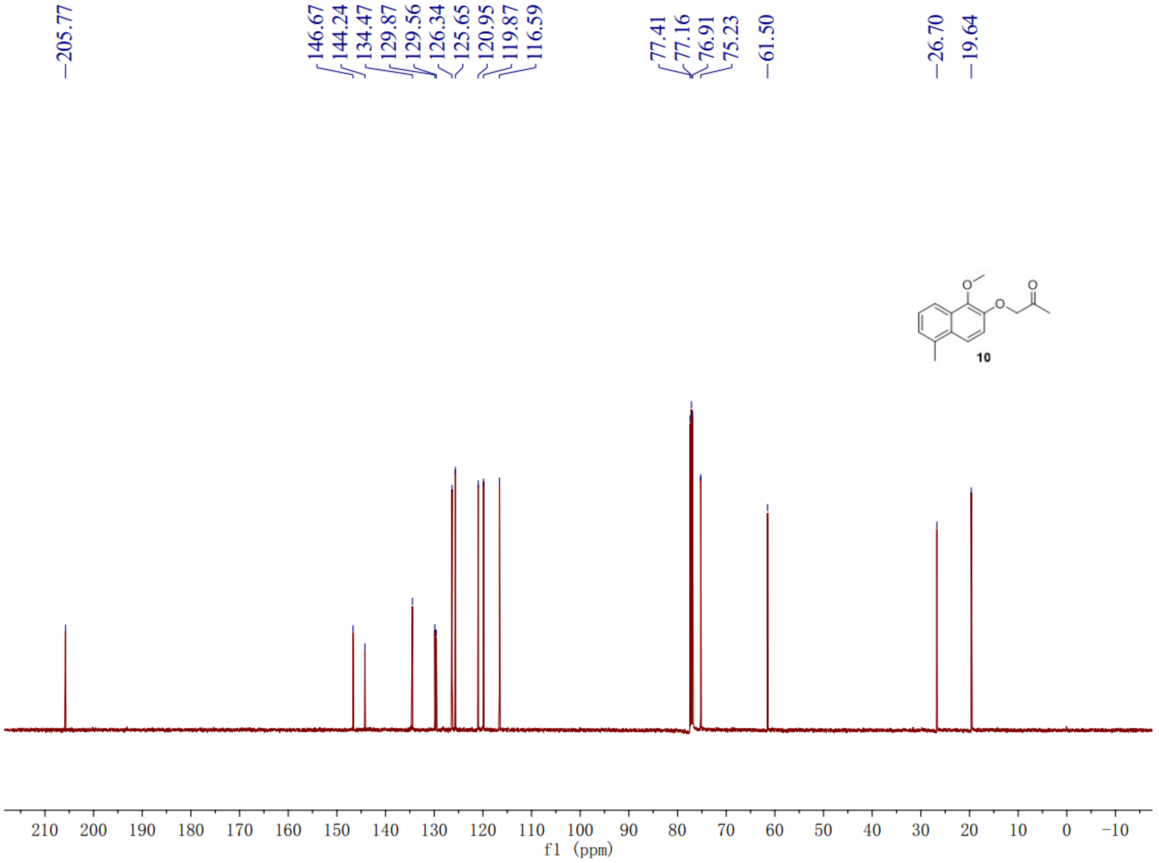
HR-ESI-MS (M-CH$_3$)$^-$ of 9



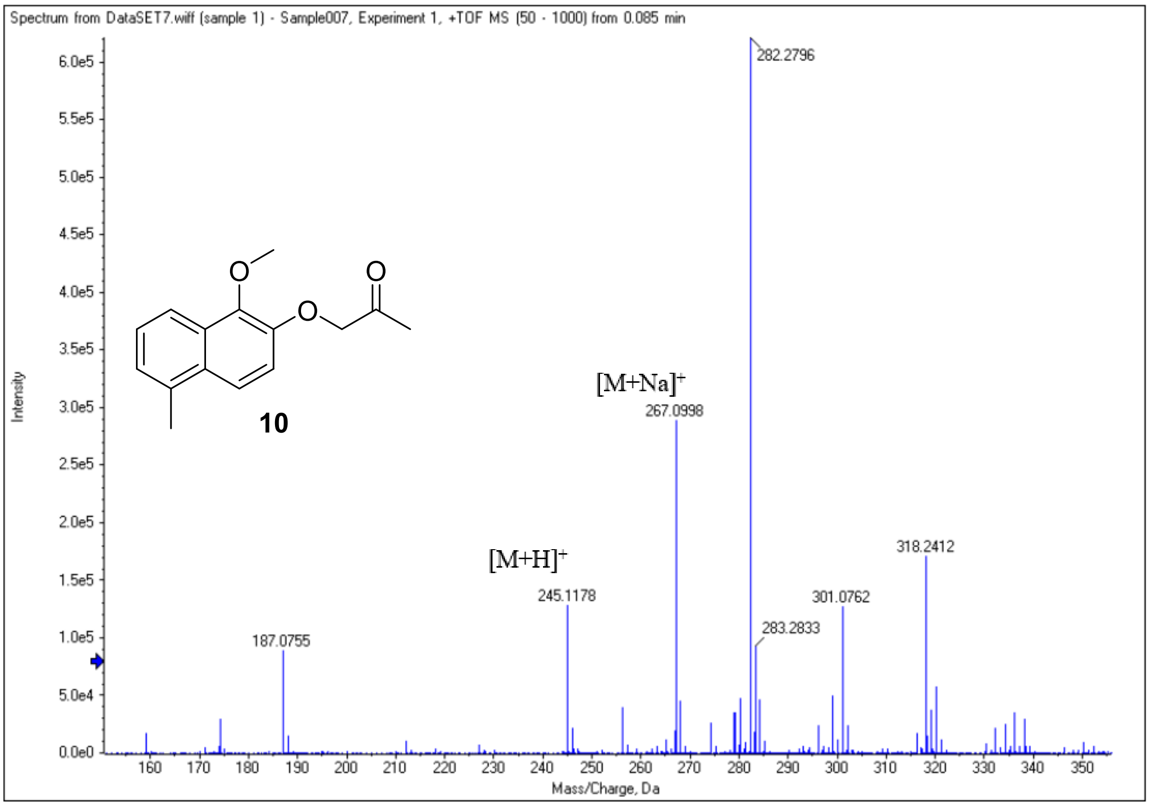
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 10



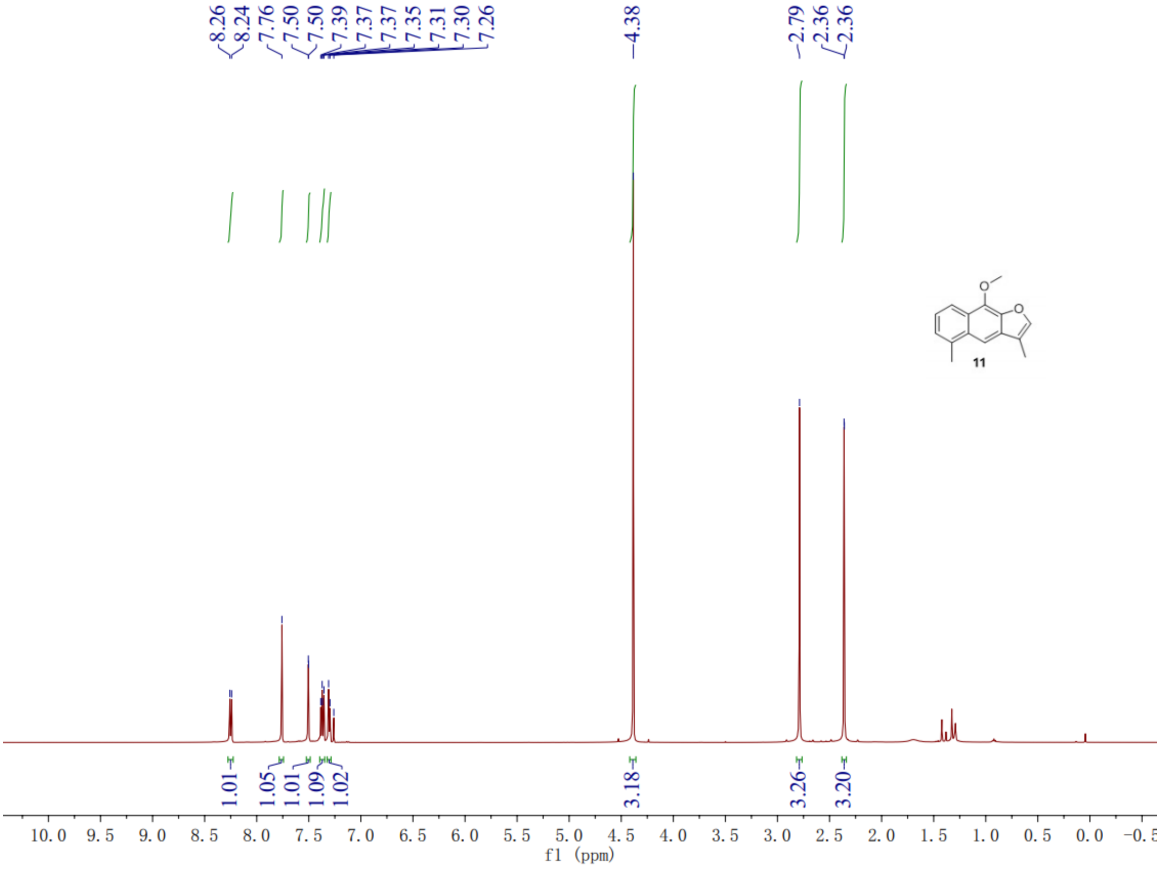
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 10



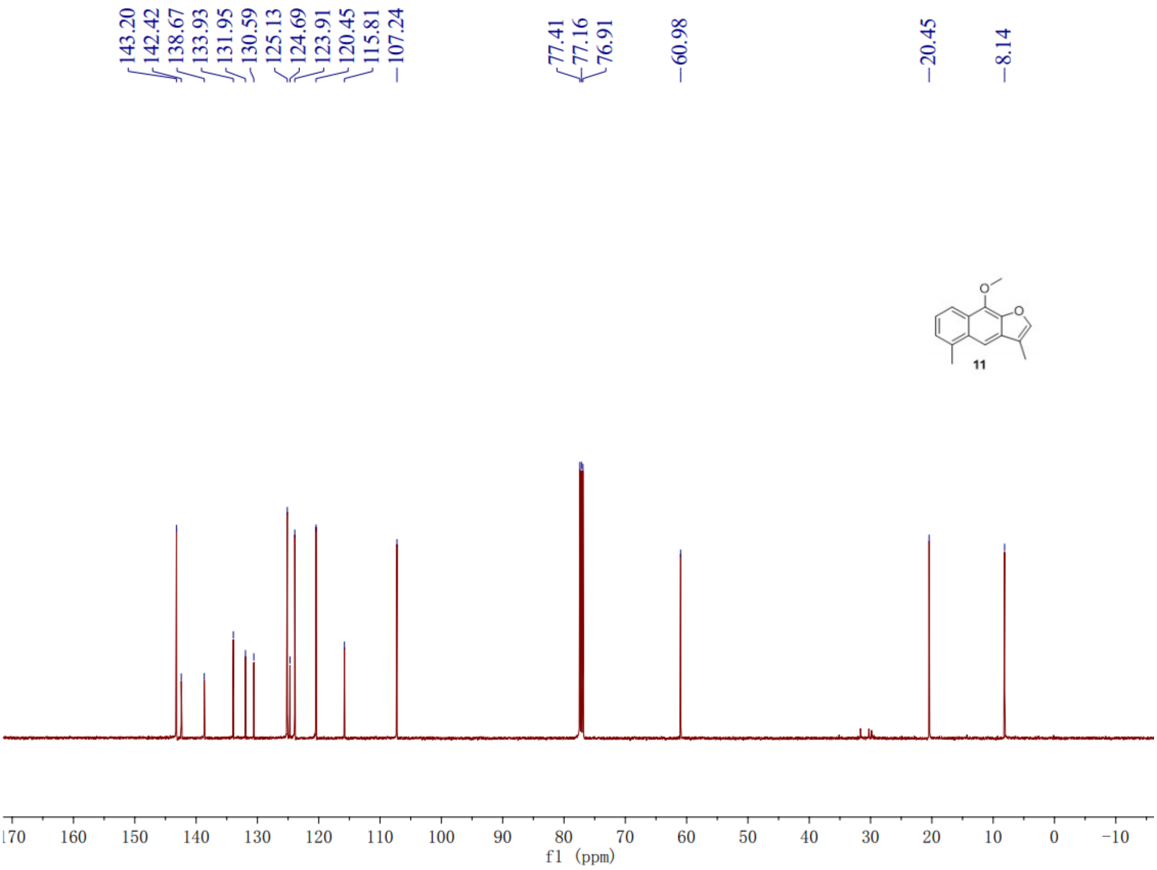
HR-ESI-MS (M+Na)$^+$ of 10



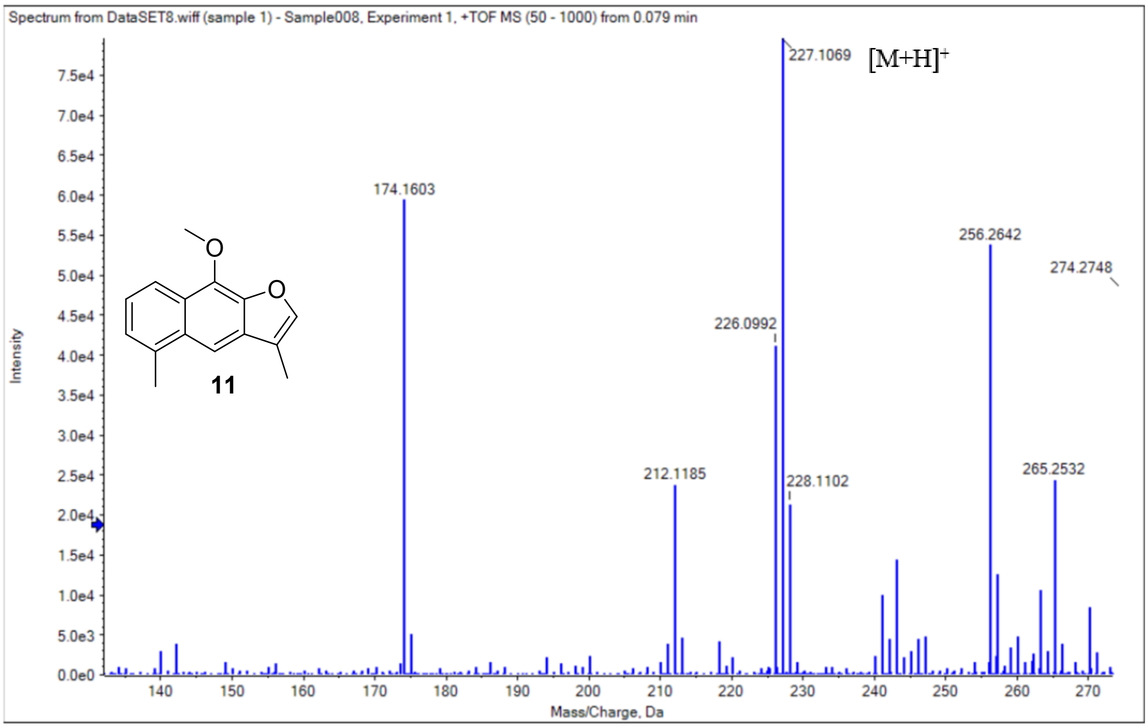
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 11



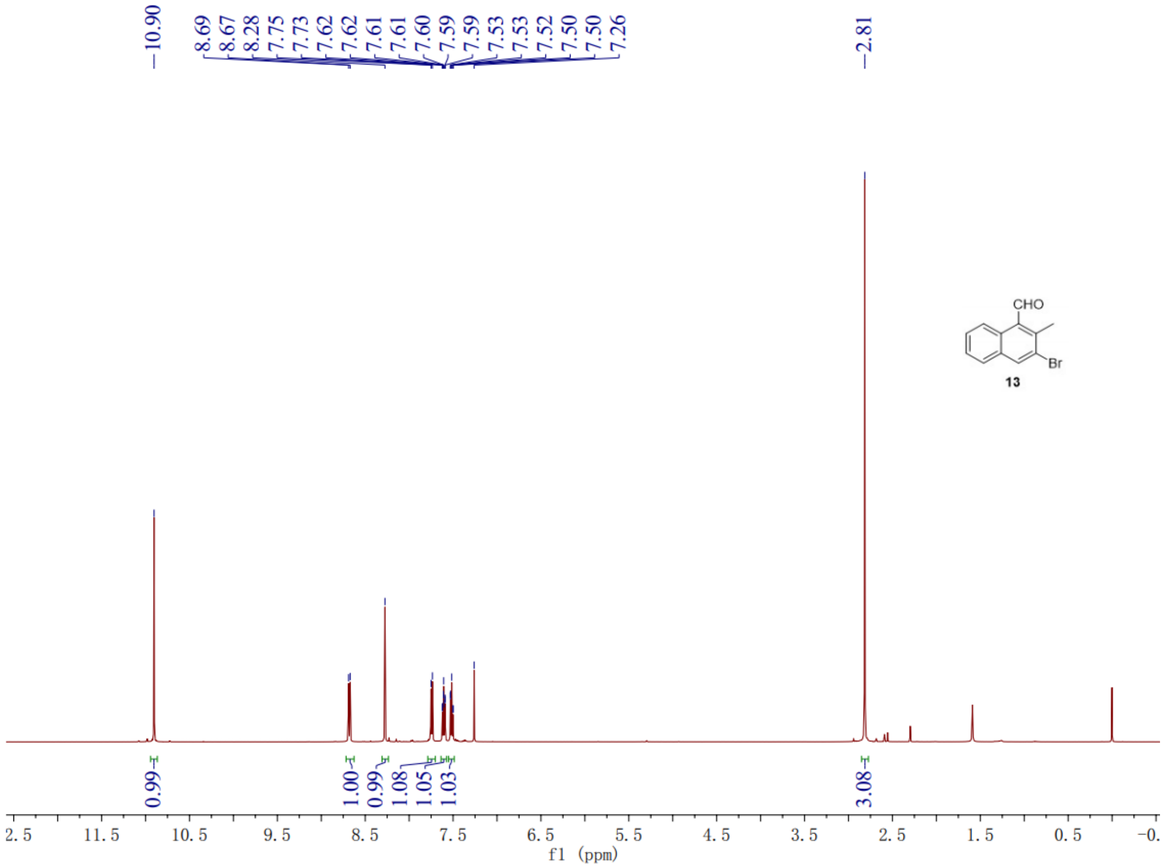
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 11



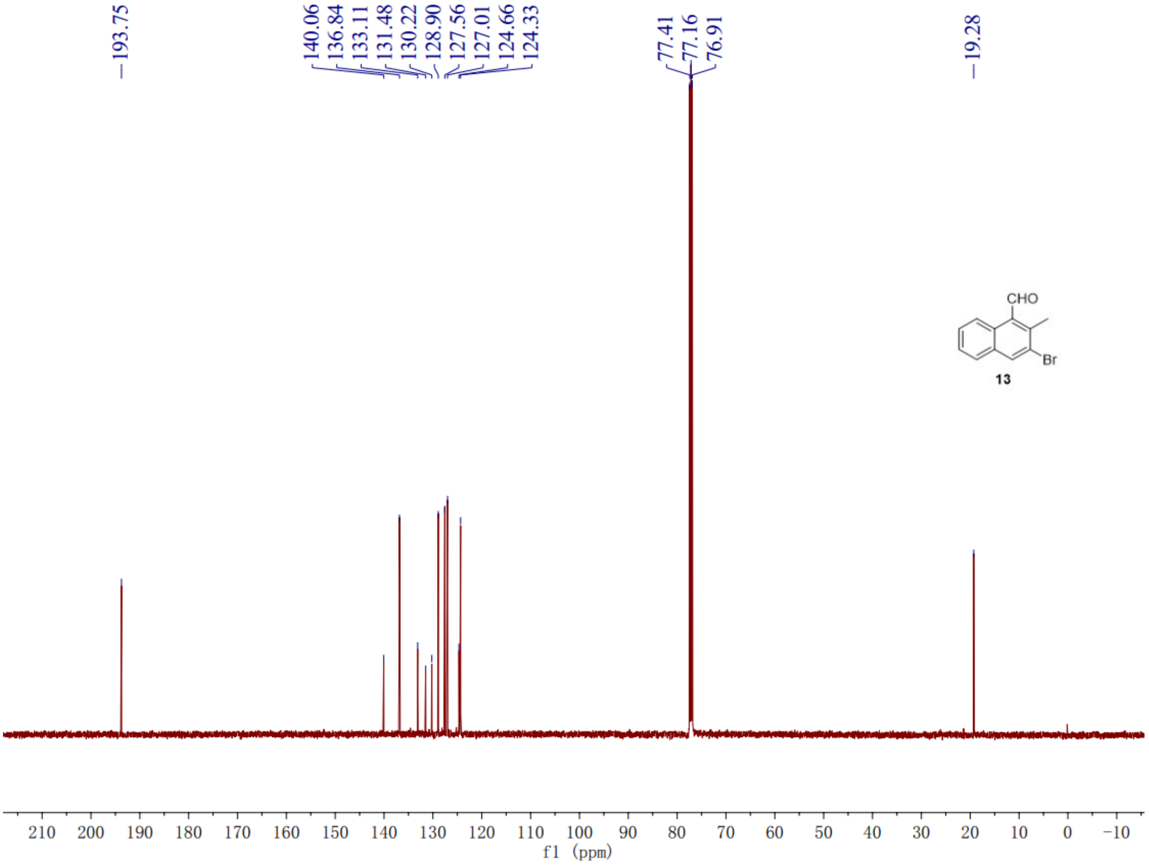
HR-ESI-MS $(M+H)^+$ of 11



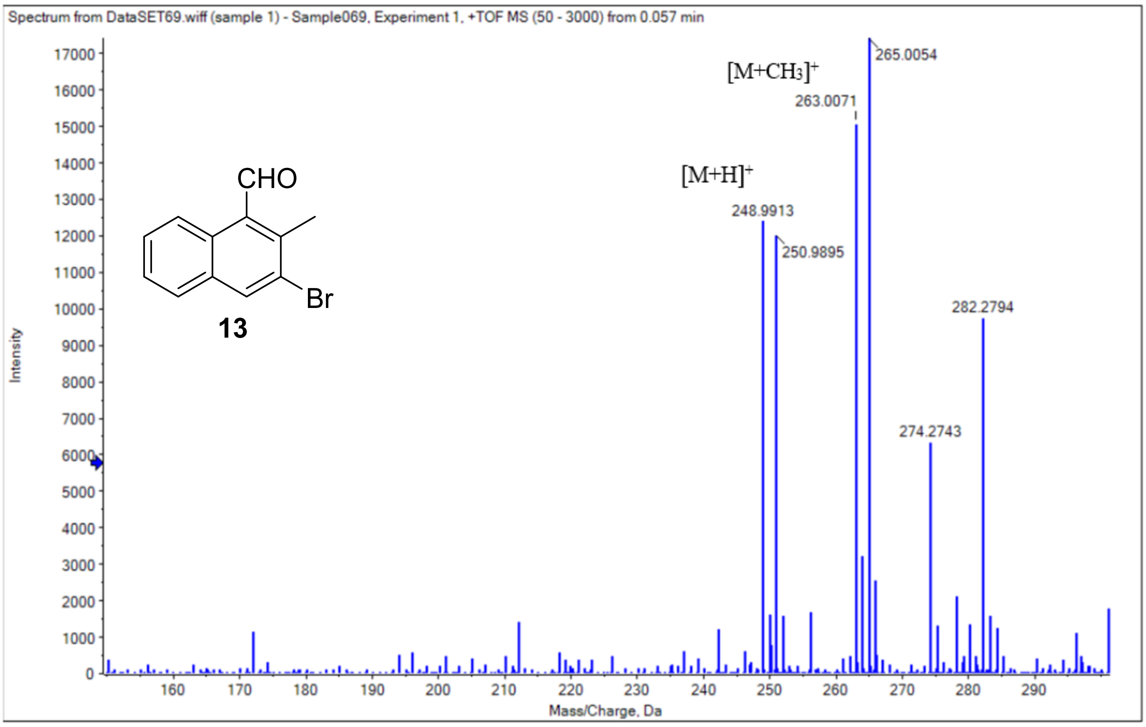
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 13



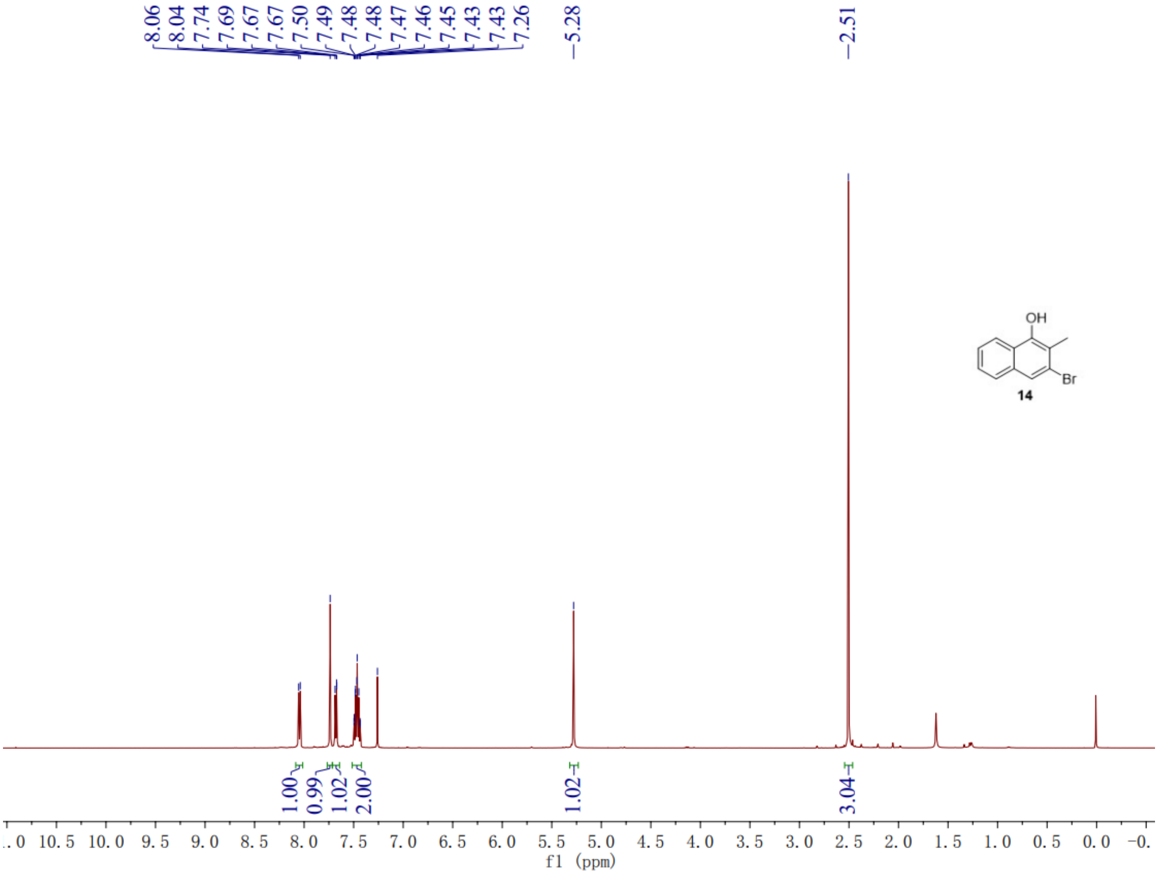
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 13



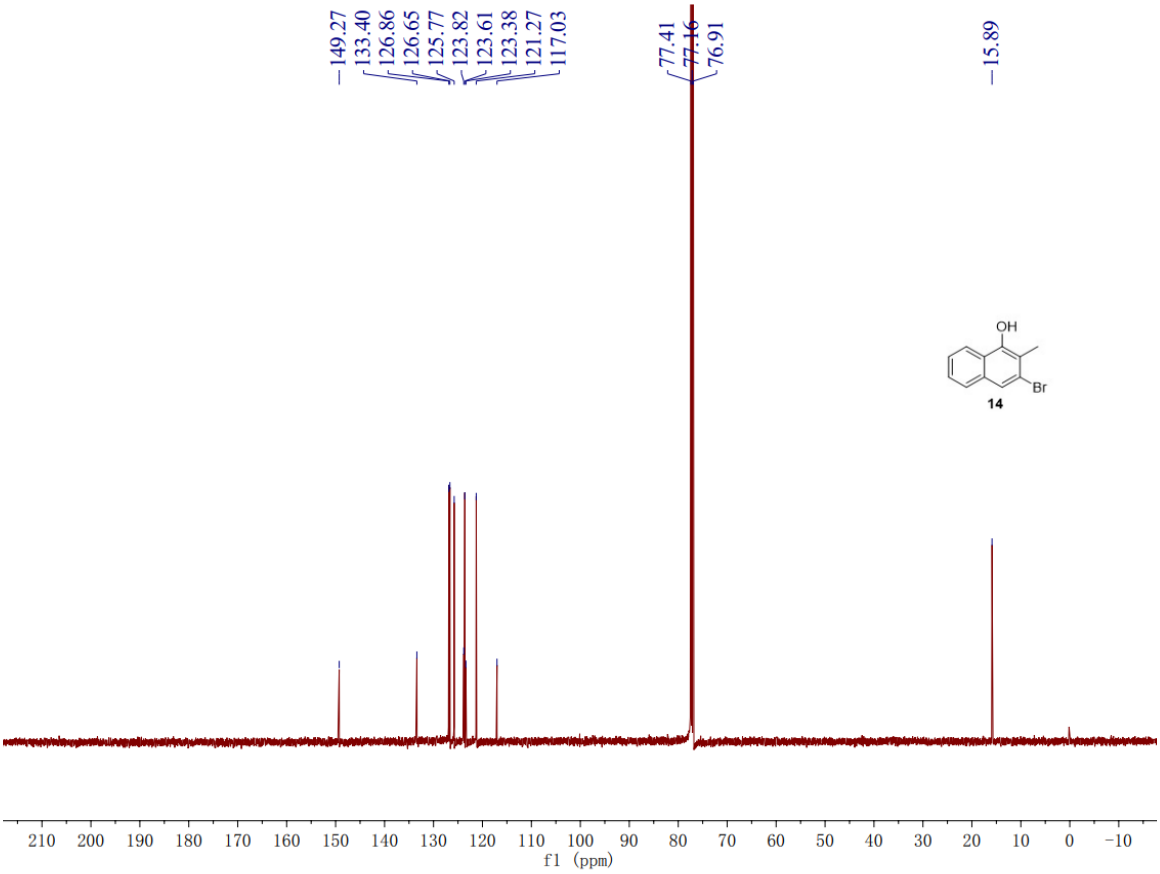
HR-ESI-MS $(M+CH_3)^+$ of 13



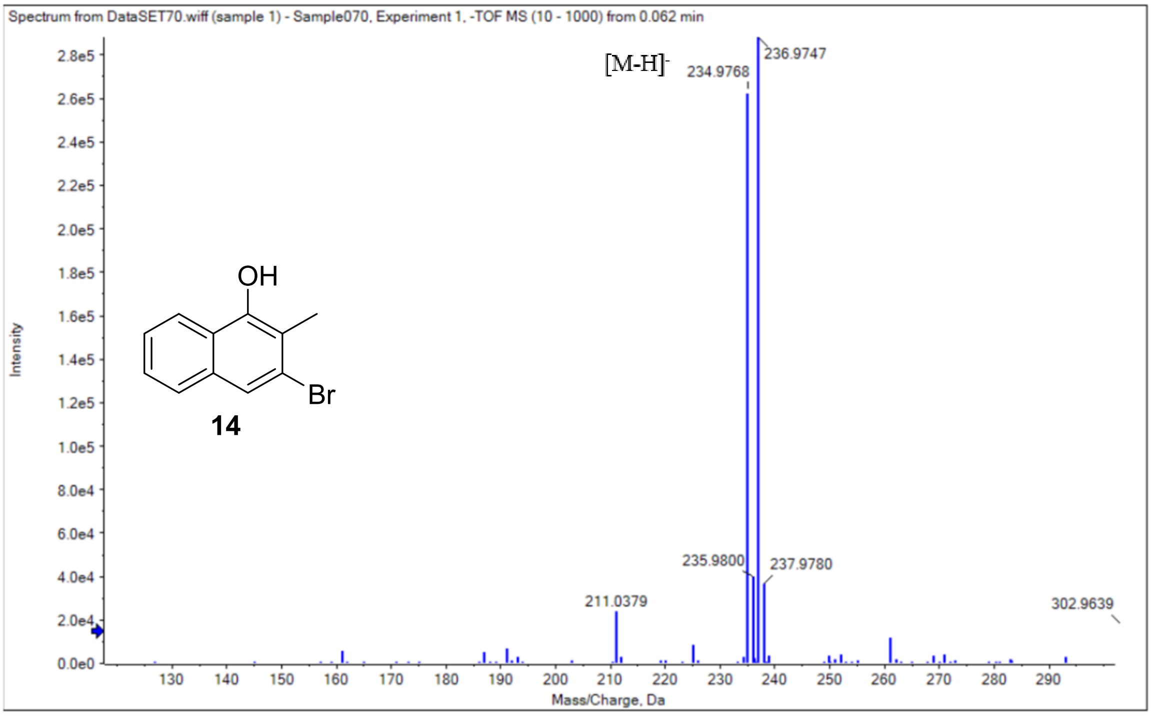
¹H NMR spectrum ($CDCl_3$, 500 MHz) of 14



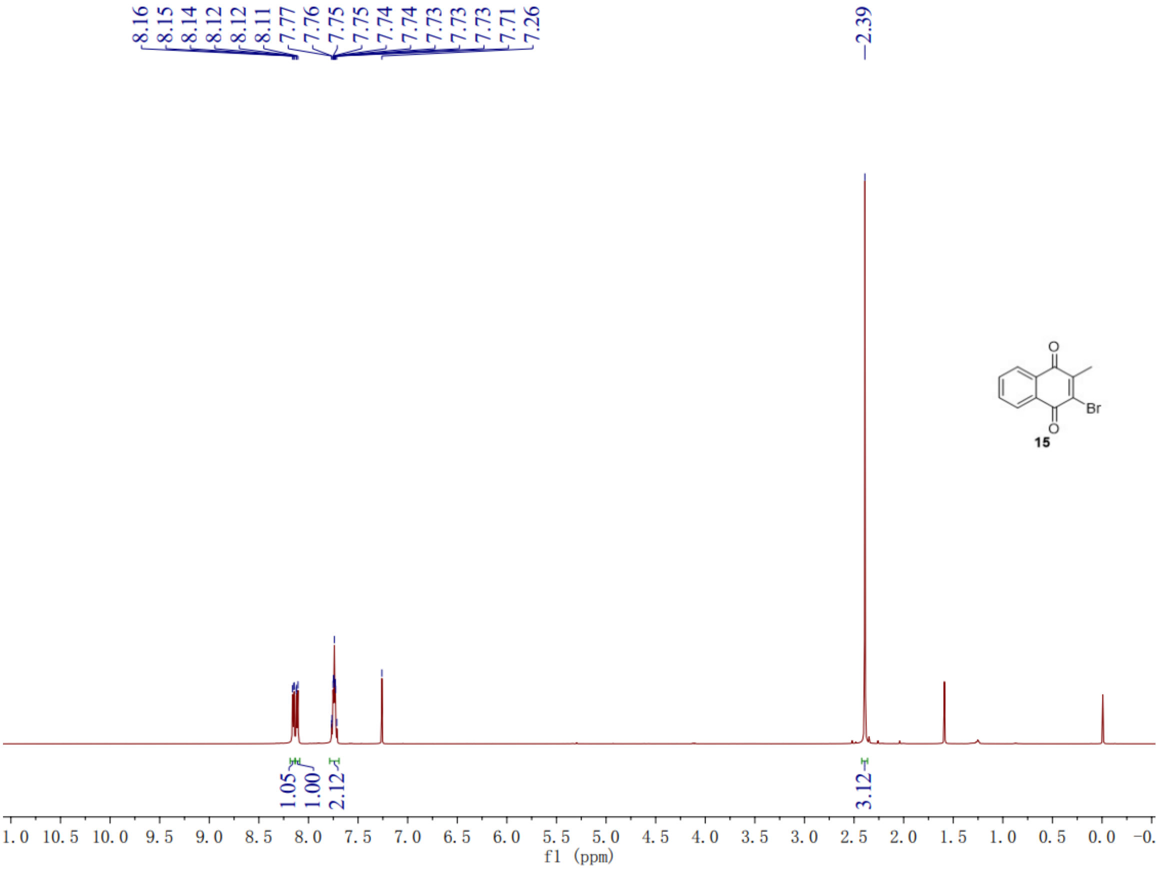
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 14



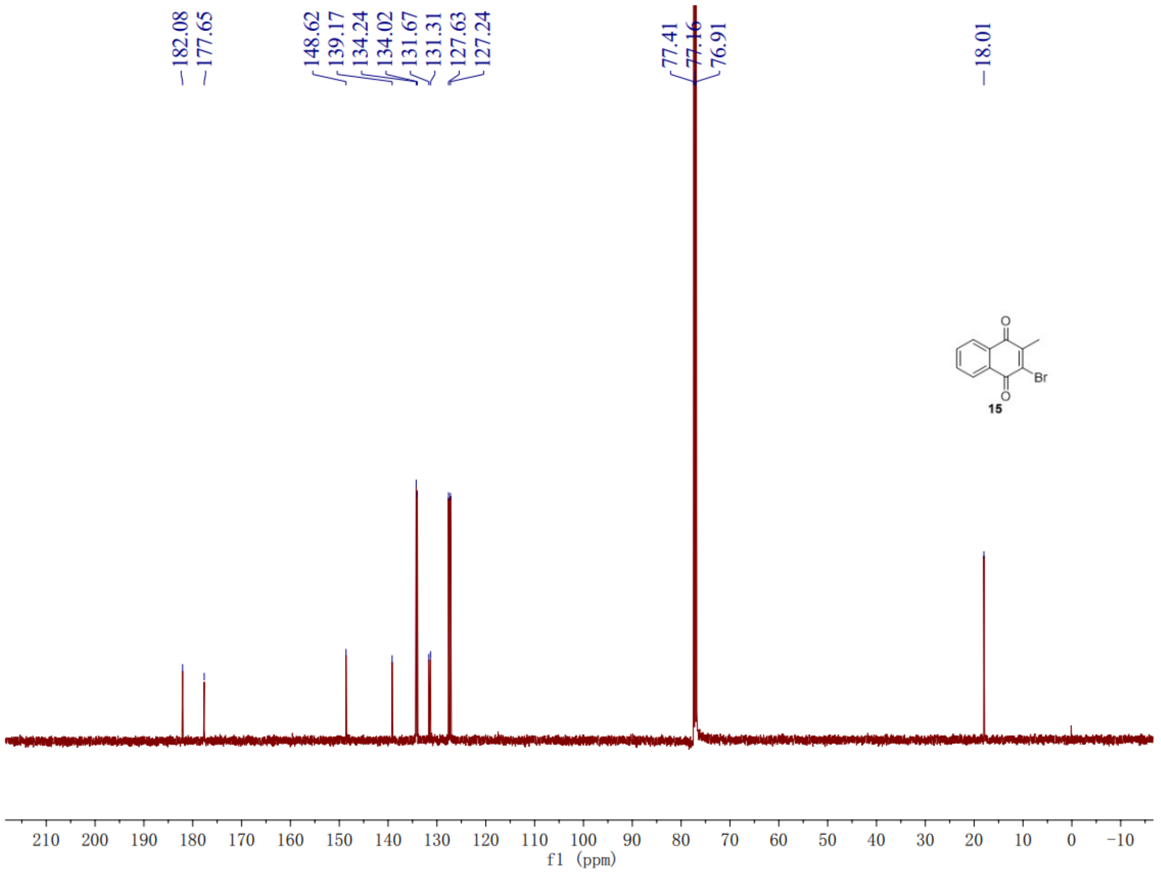
HR-ESI-MS (M-H)$^-$ of 14



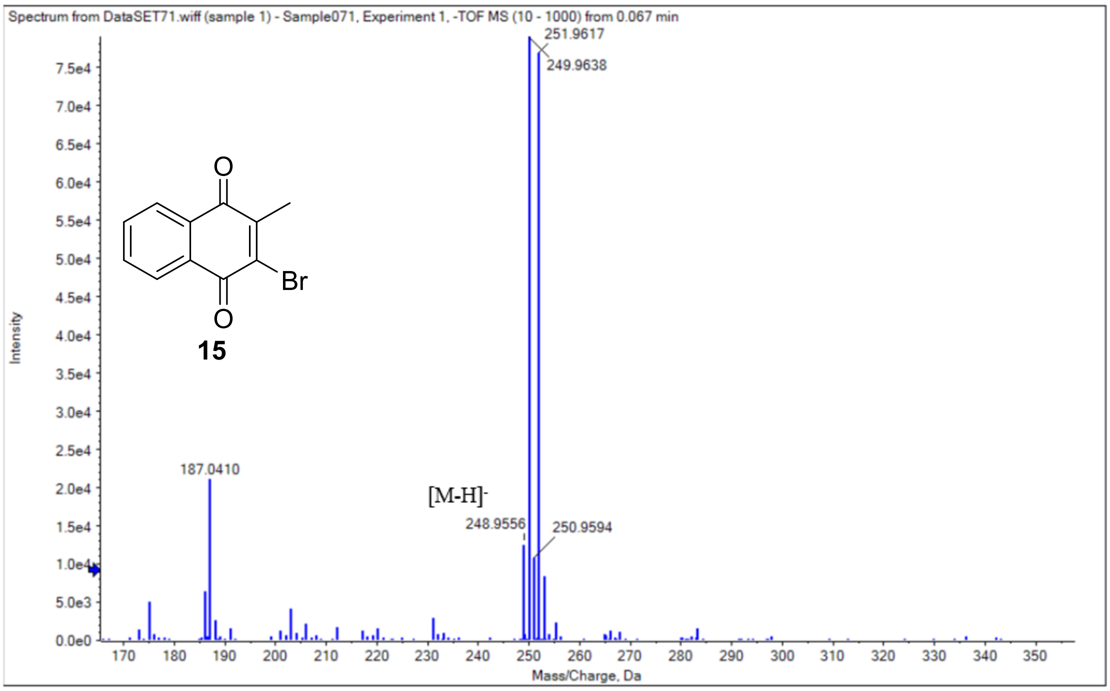
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 15



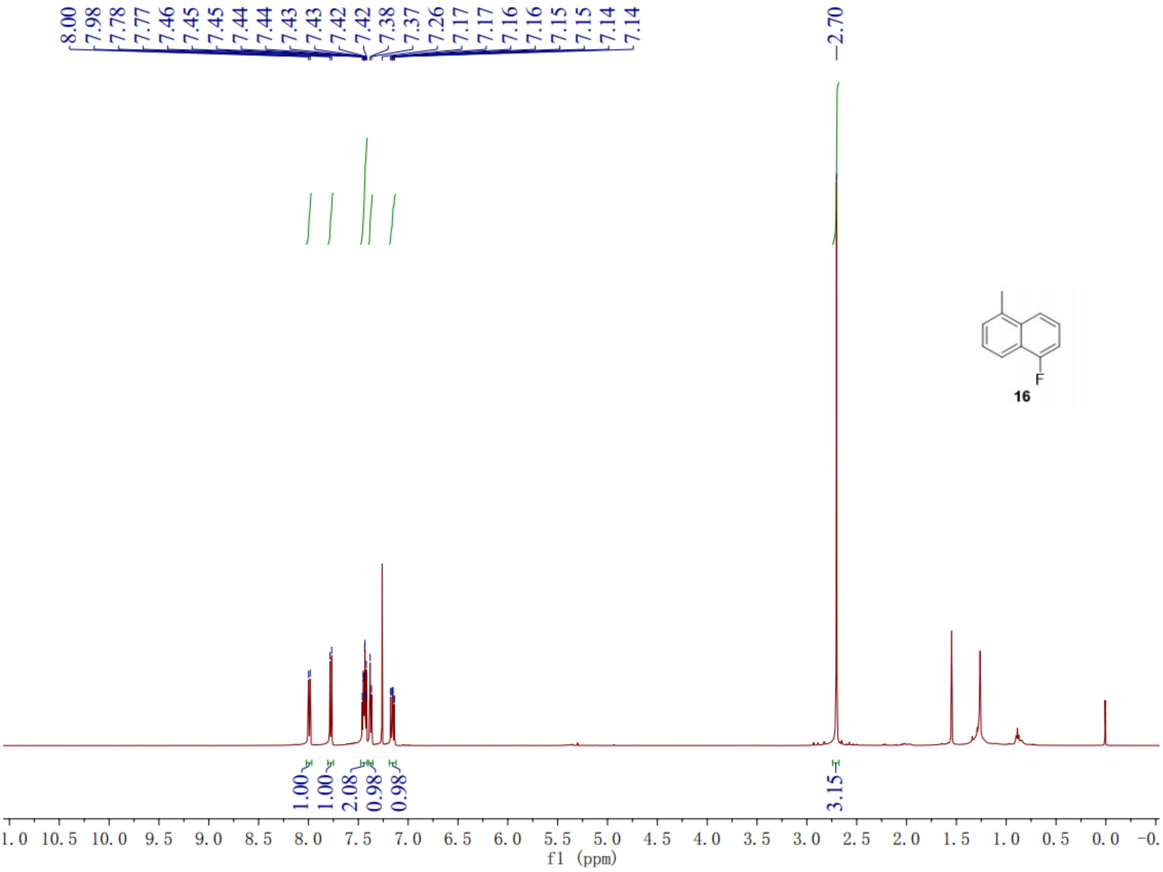
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 15



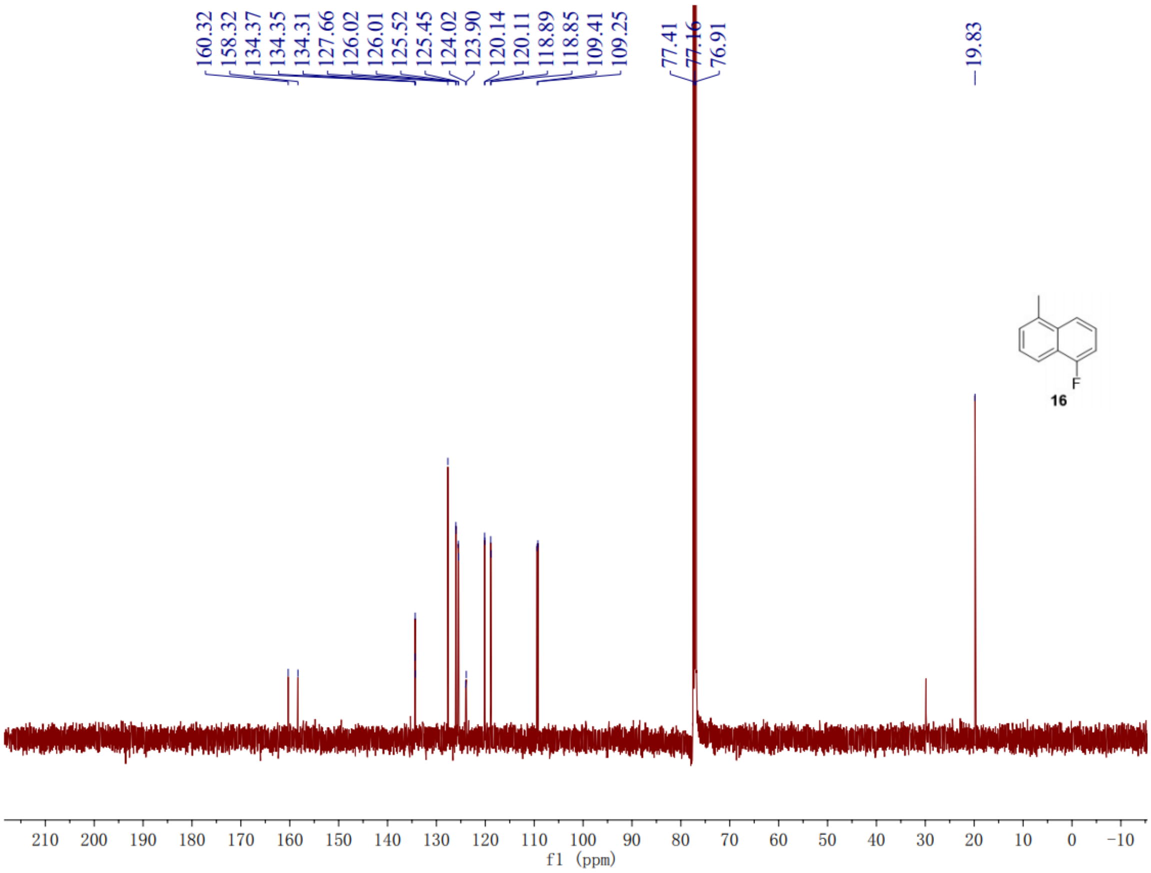
HR-ESI-MS $(M-H)^-$ of 15



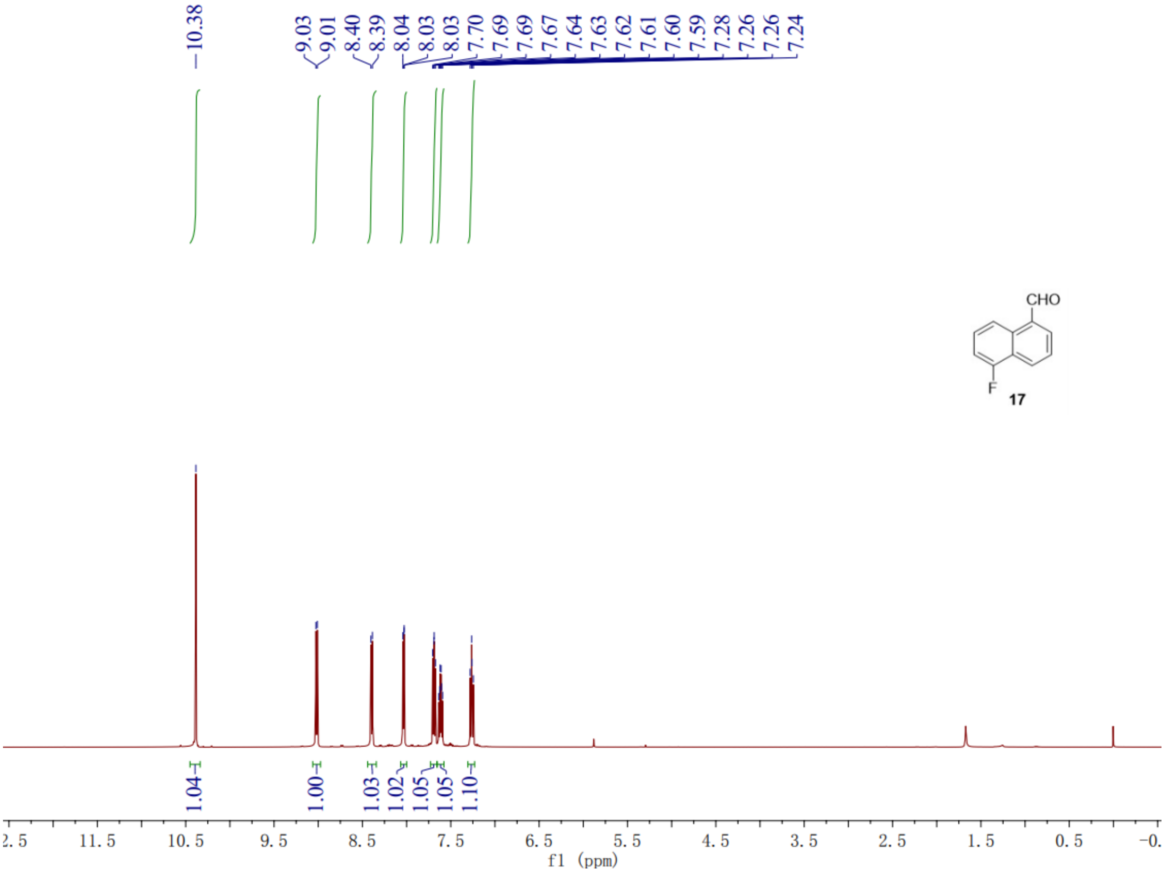
^1H NMR spectrum ($CDCl_3$, 500 MHz) of 16



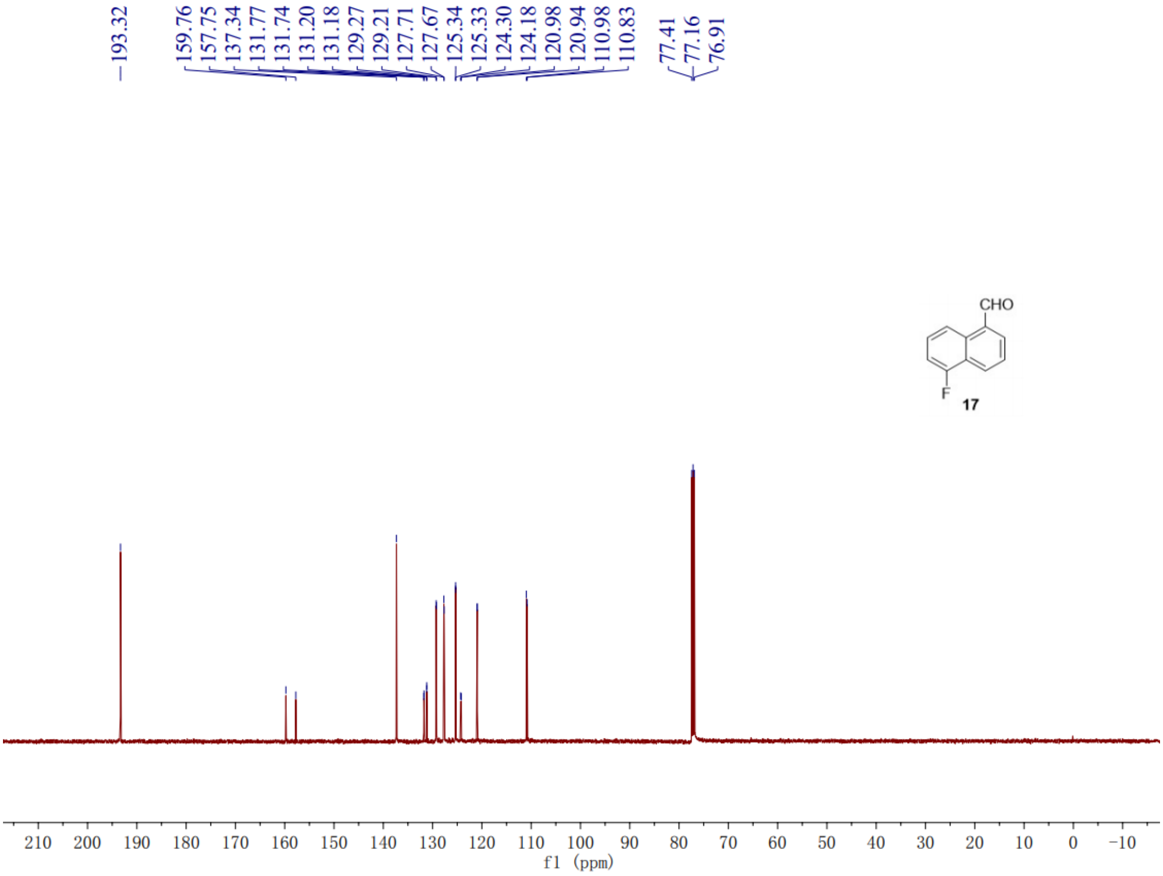
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 16



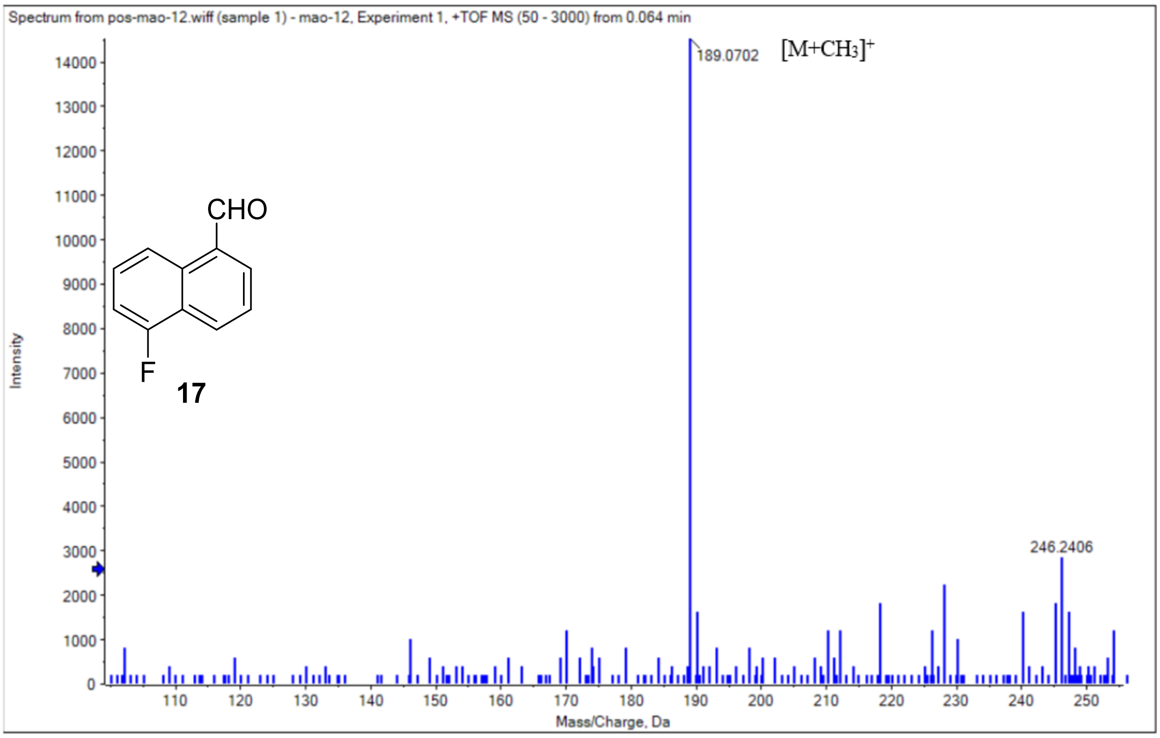
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 17



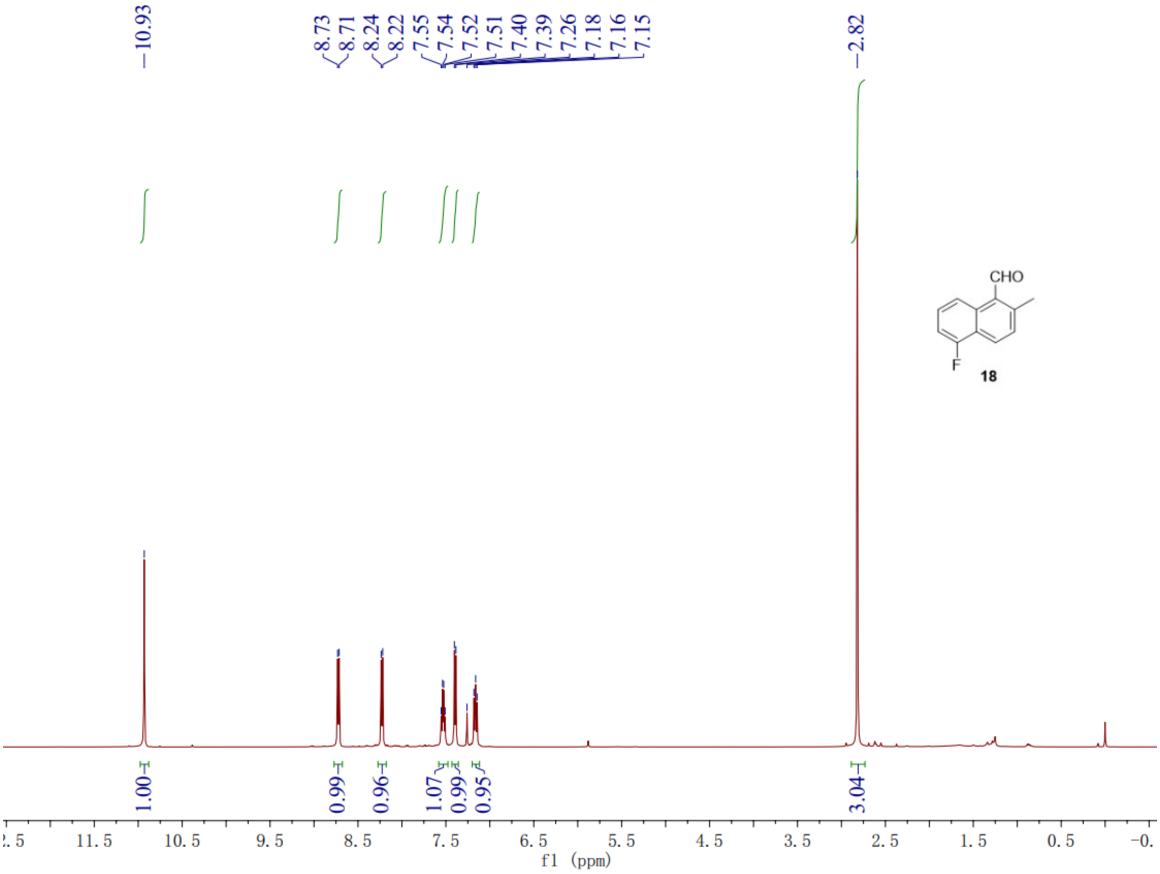
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 17



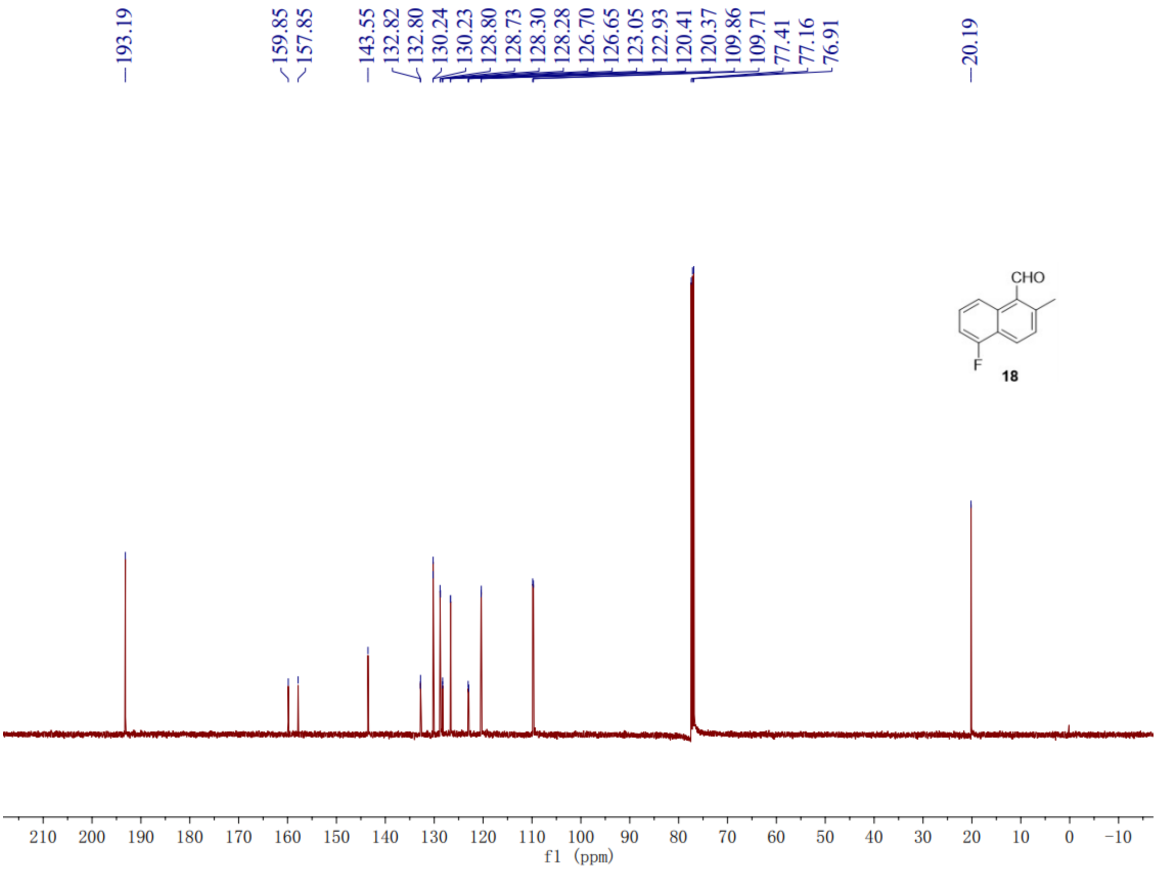
HR-ESI-MS (M+CH$_3$)$^+$ of 17



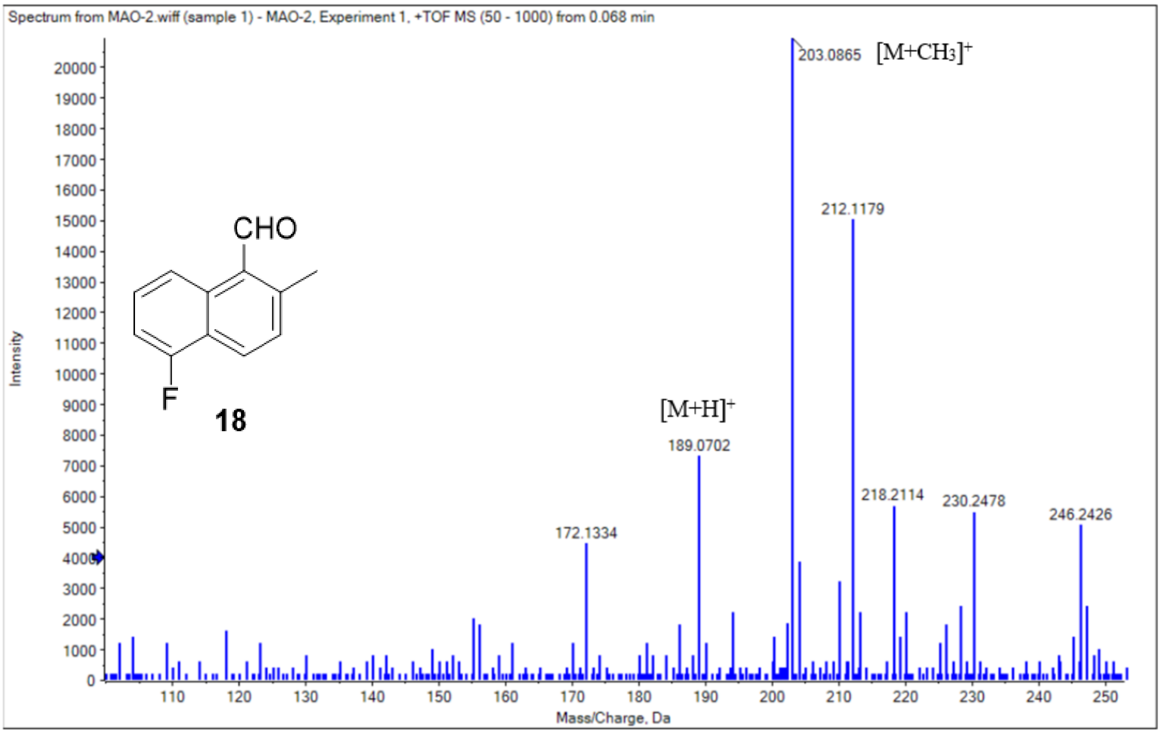
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 18



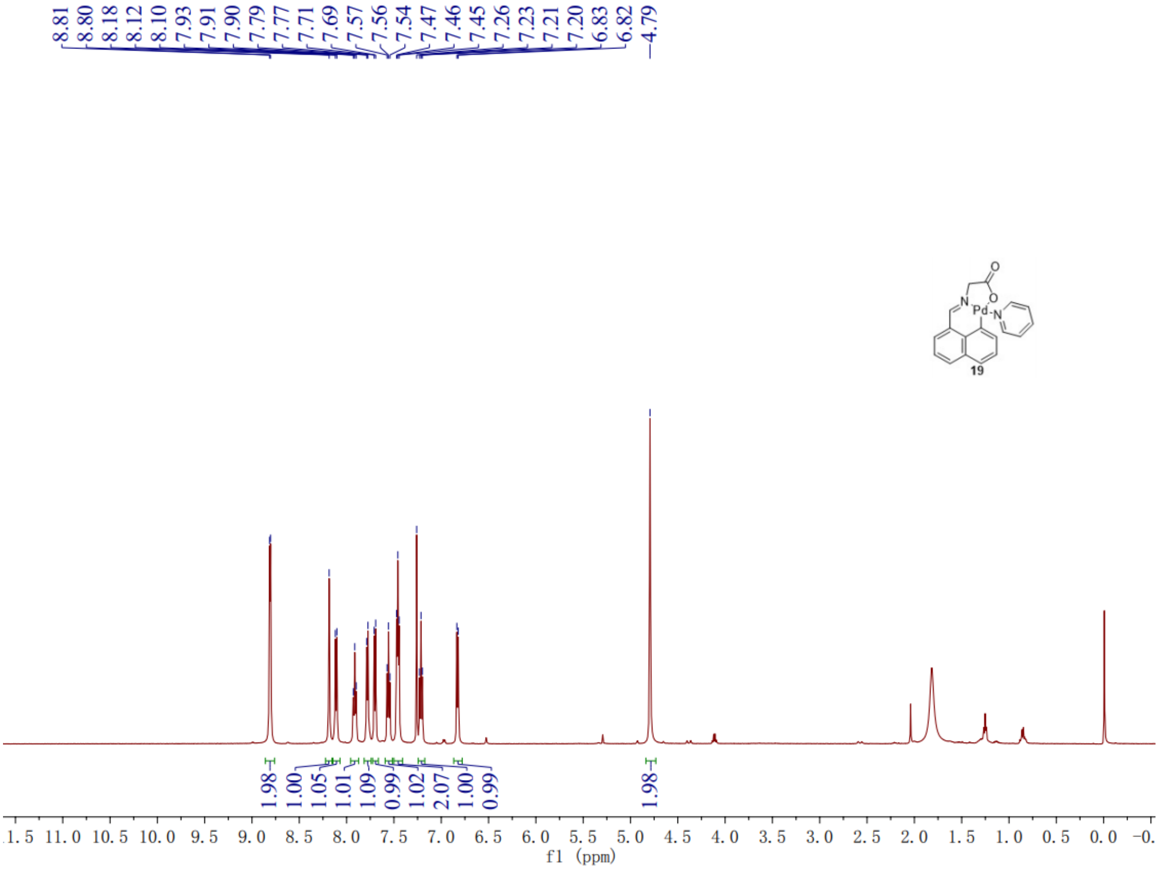
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 18



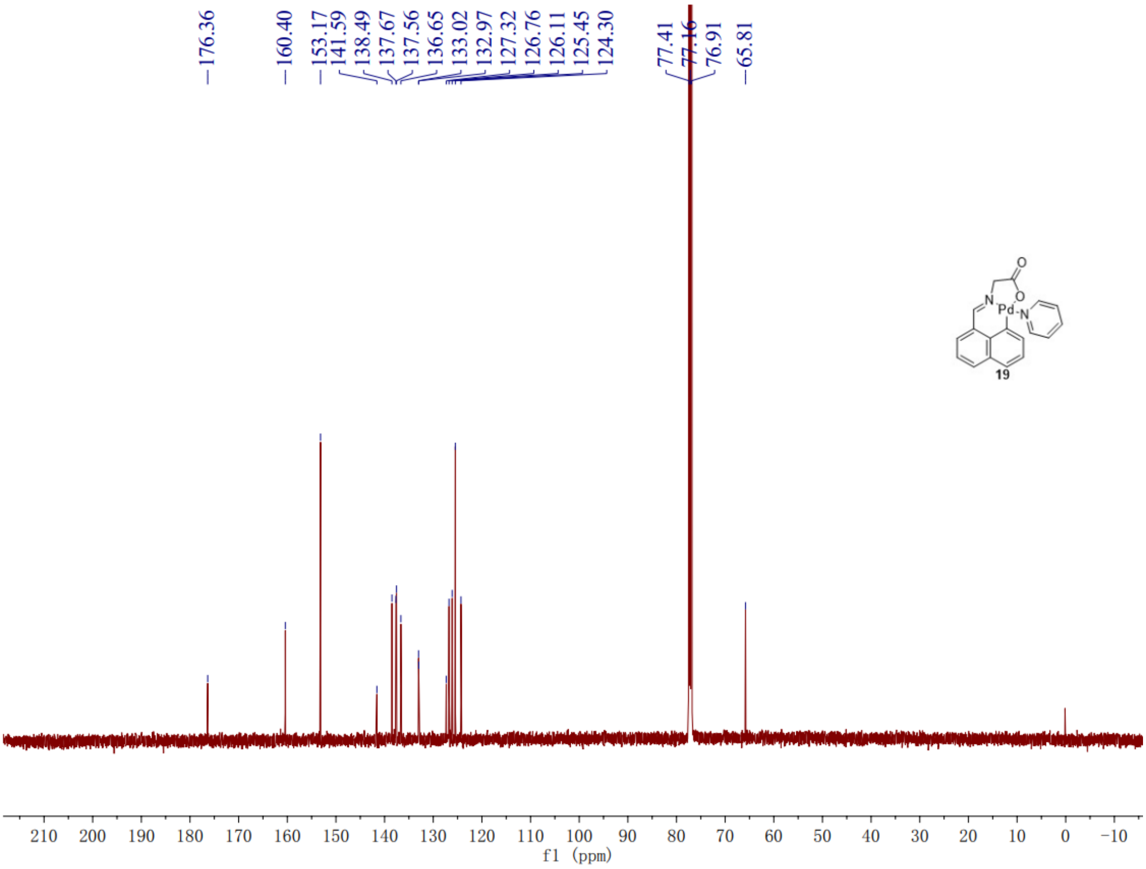
HR-ESI-MS $(M+CH_3)^+$ of 18



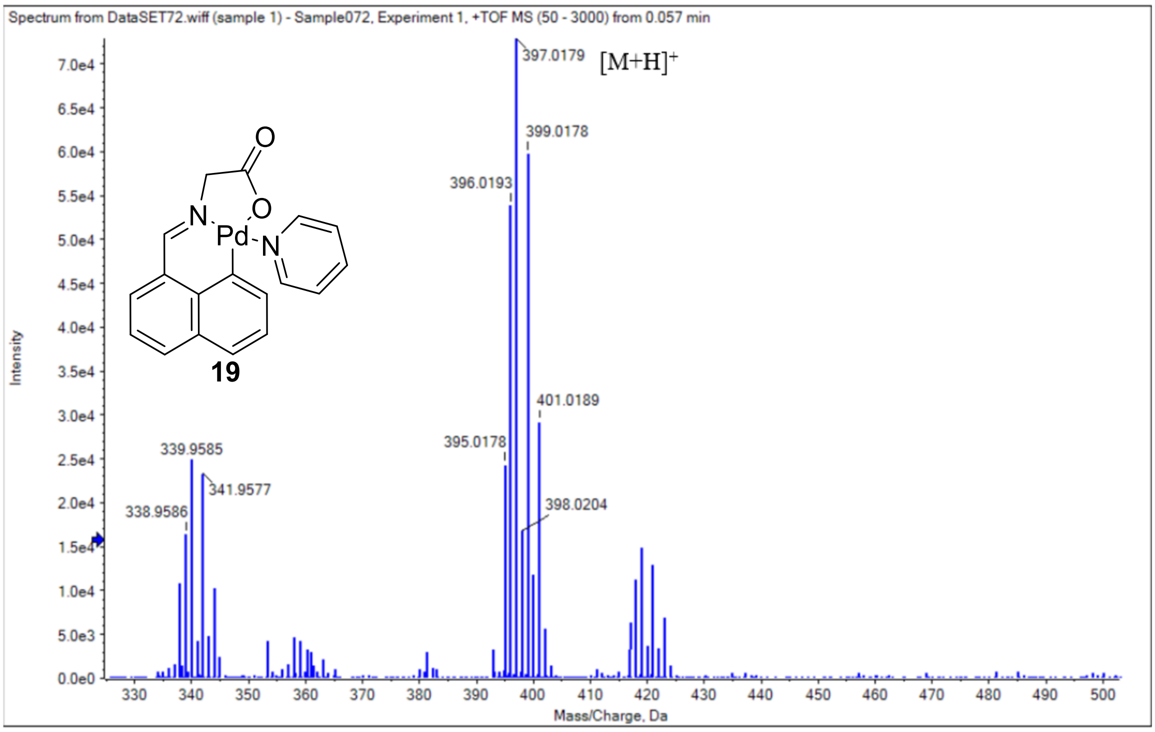
^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 19



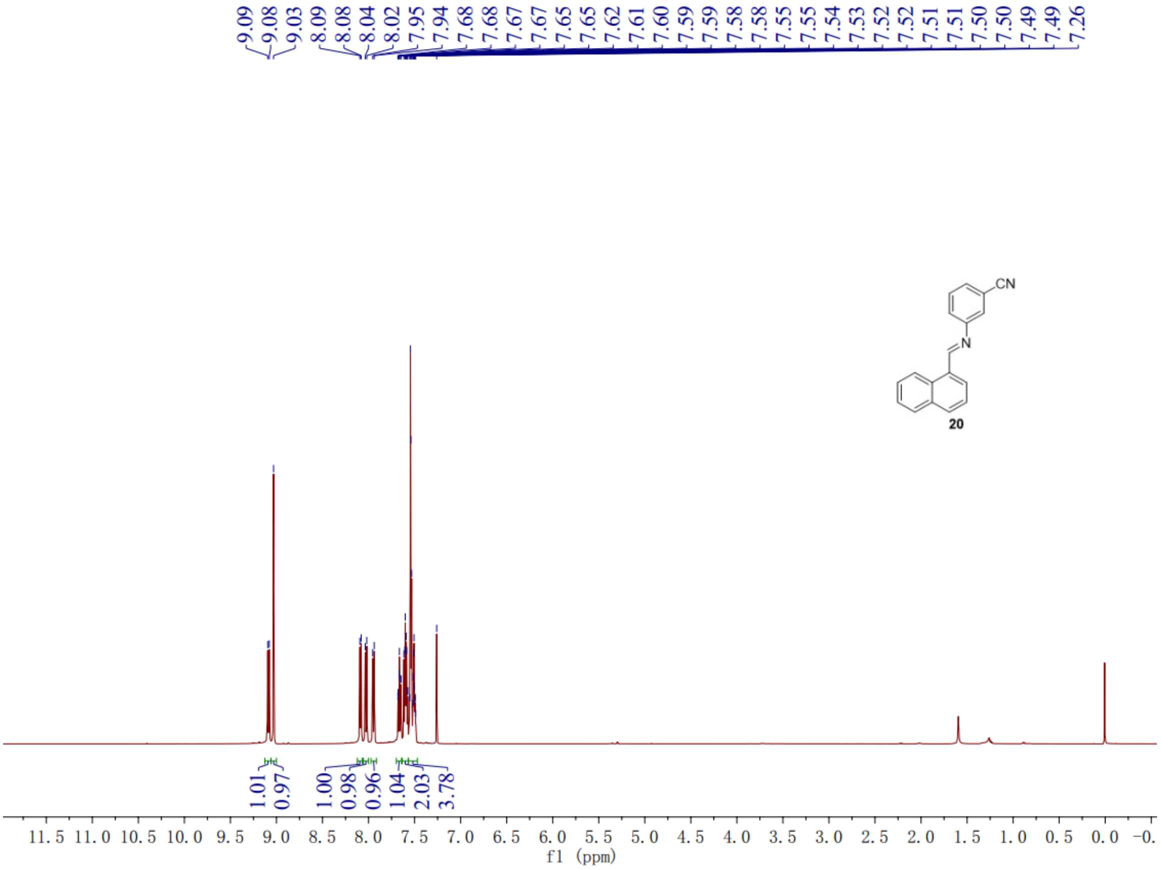
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 19



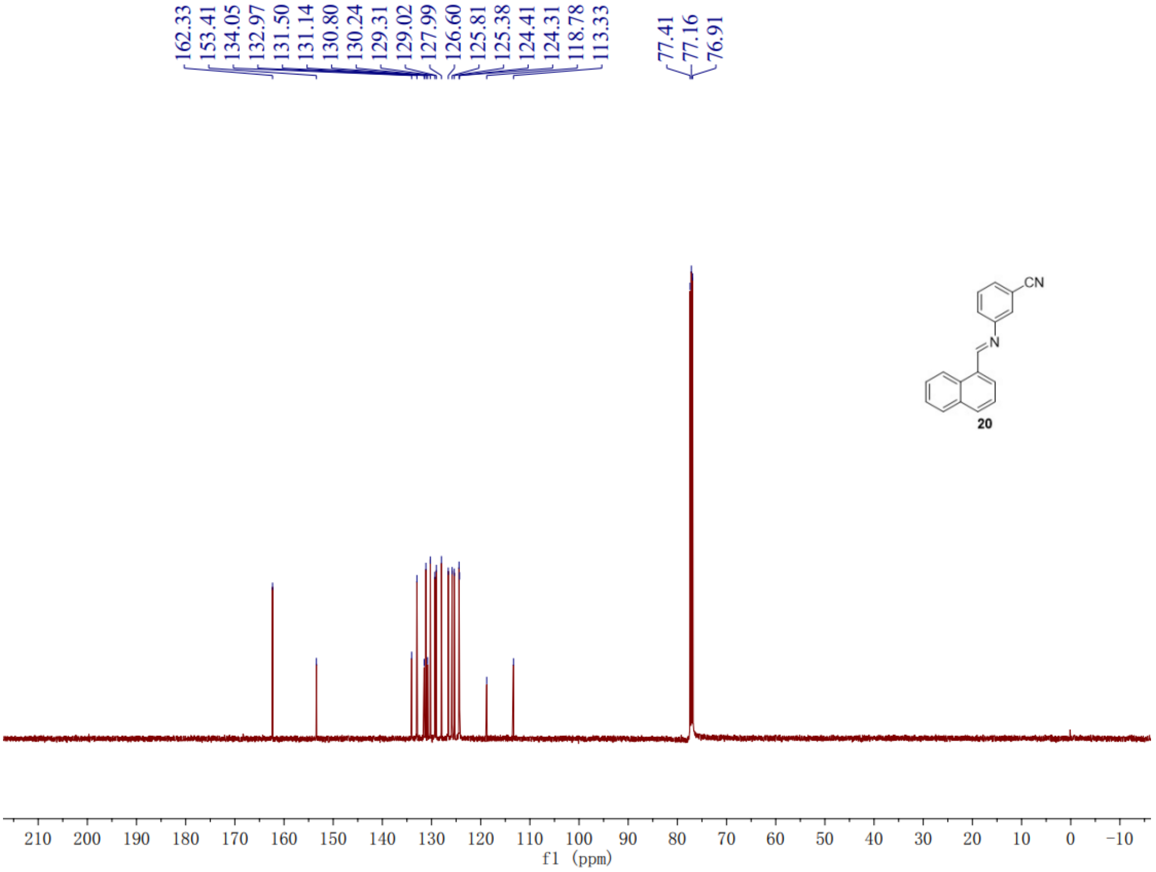
HR-ESI-MS $(M+H)^+$ of 19



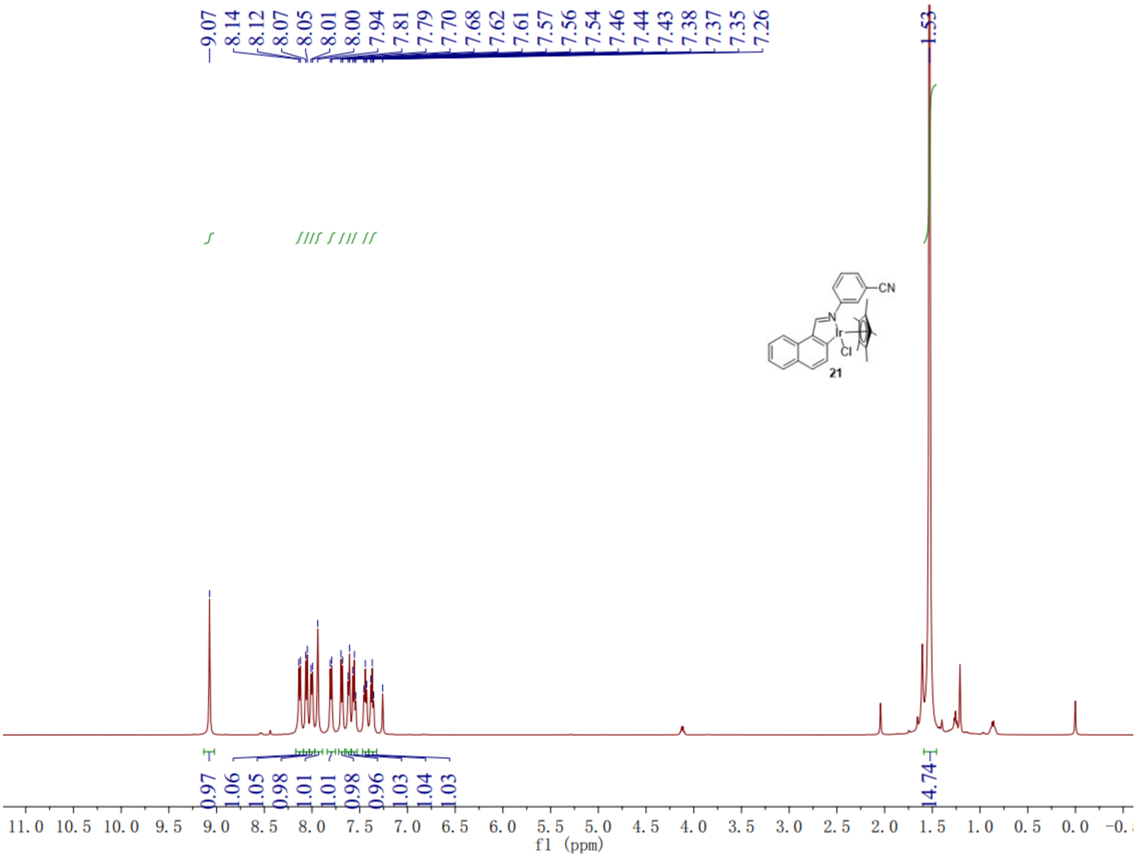
^1H NMR spectrum ($CDCl_3$, 500 MHz) of 20



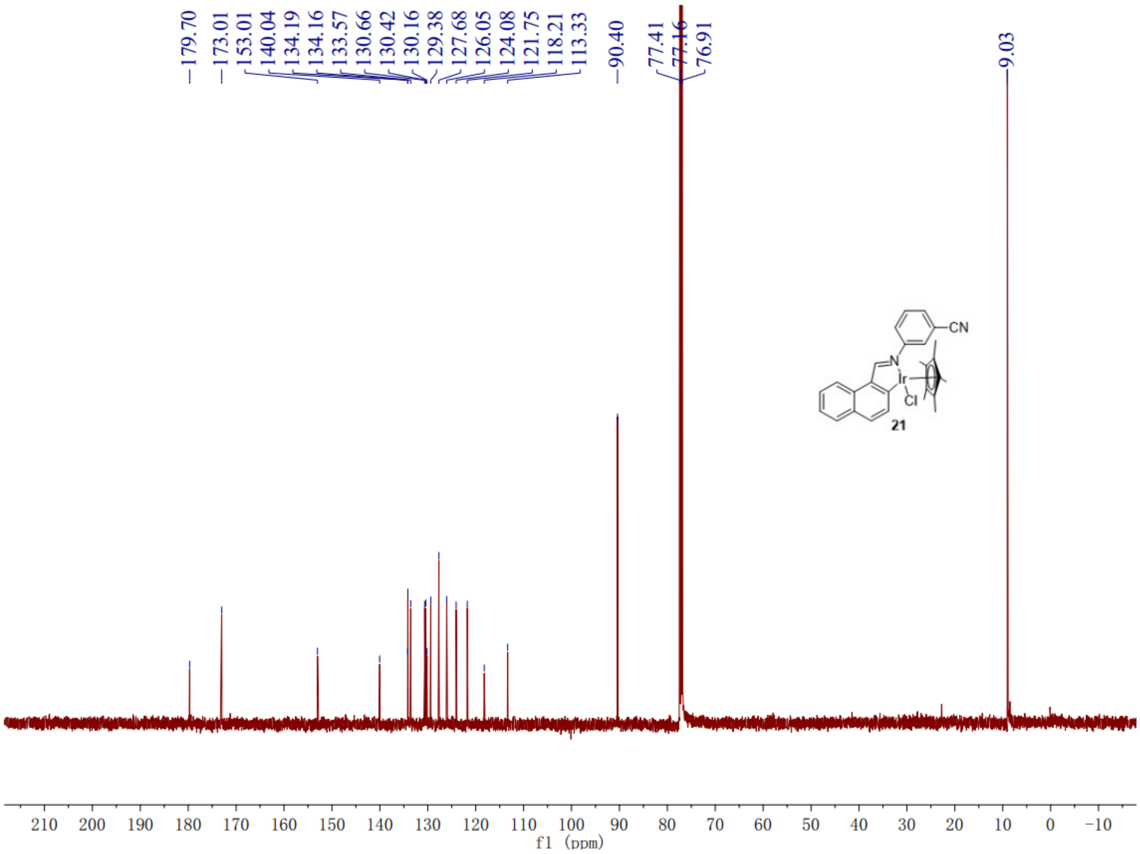
^{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 20



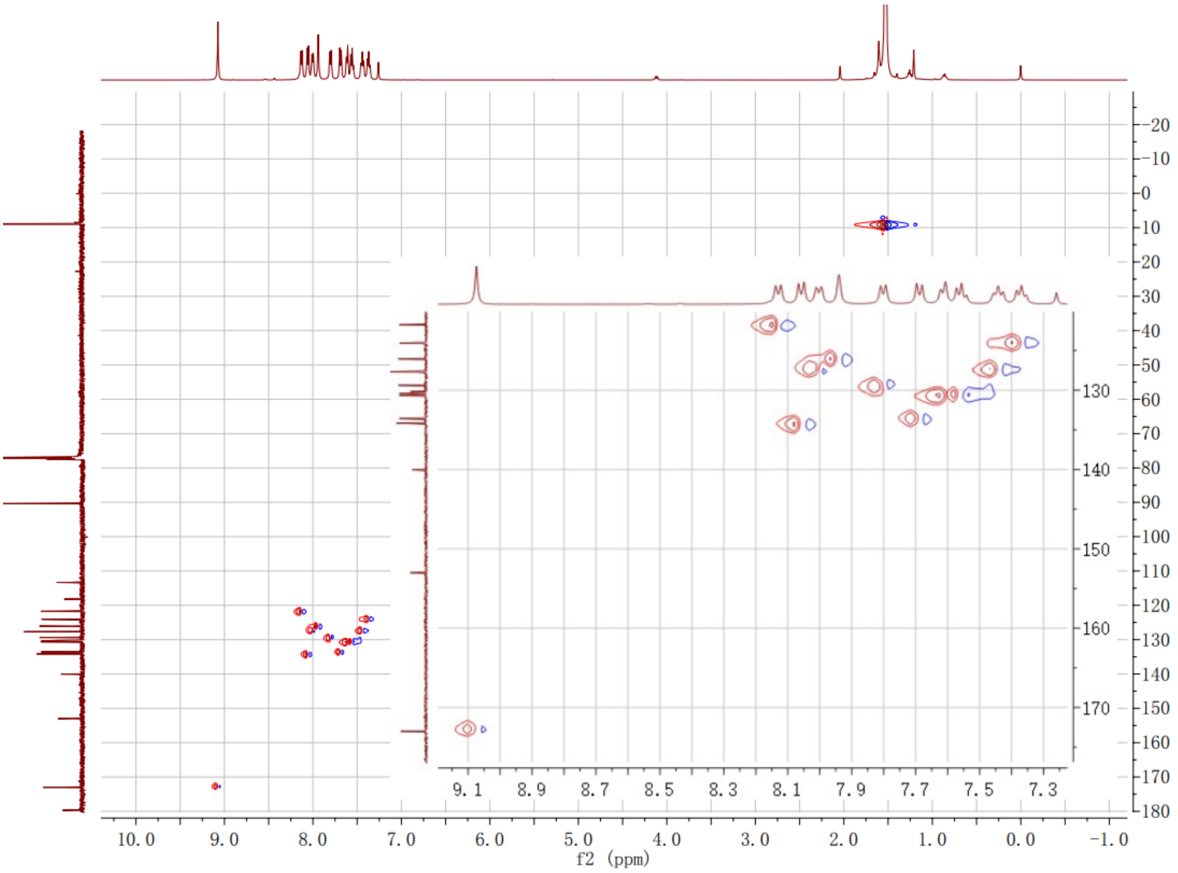
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 21



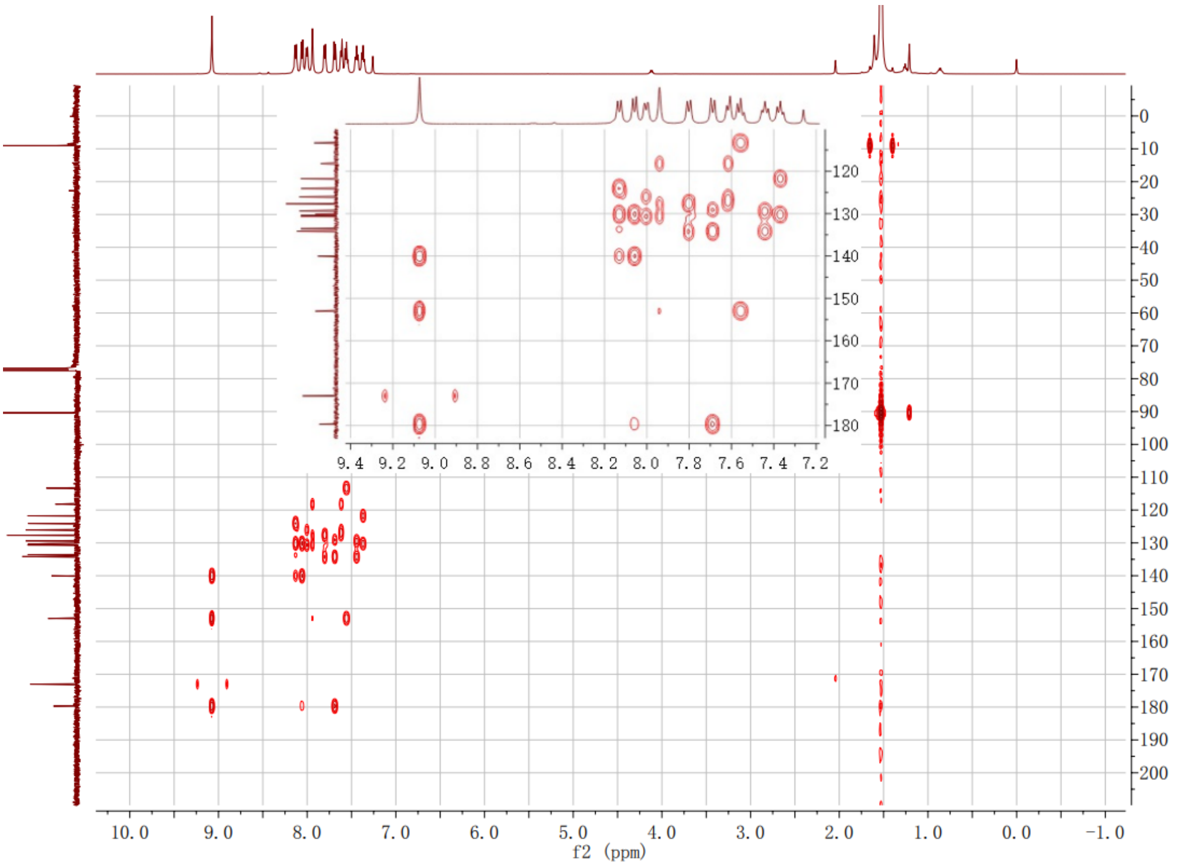
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 21



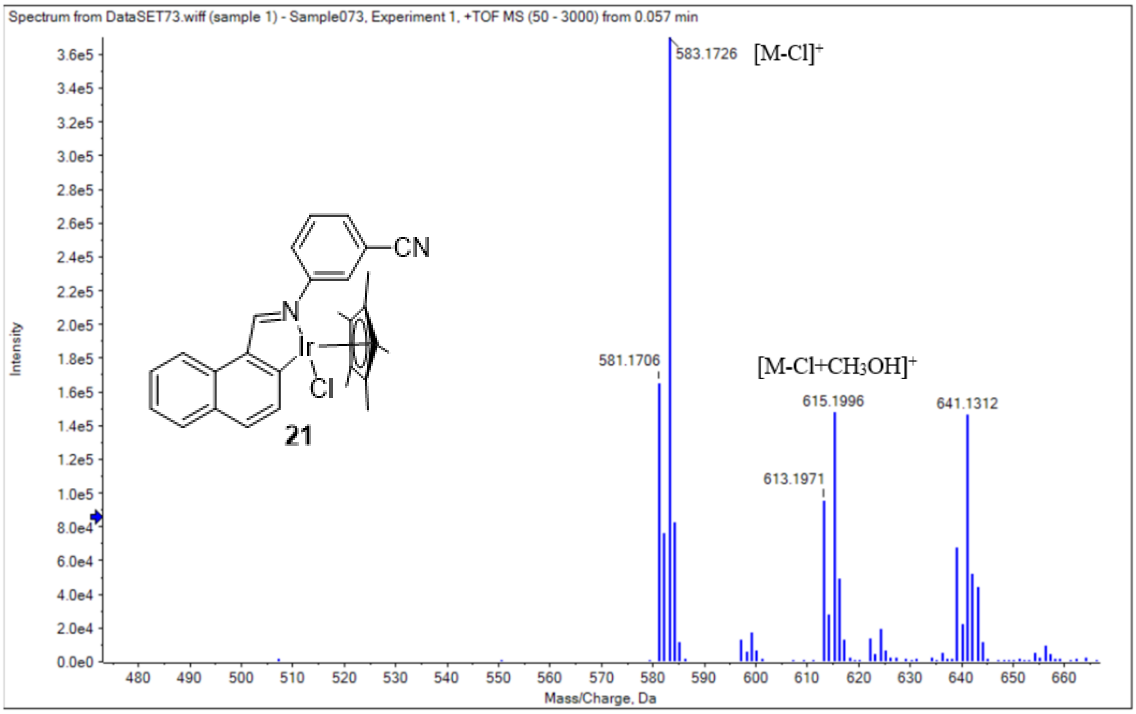
HSQC spectrum ($CDCl_3$, 500 MHz) of 21



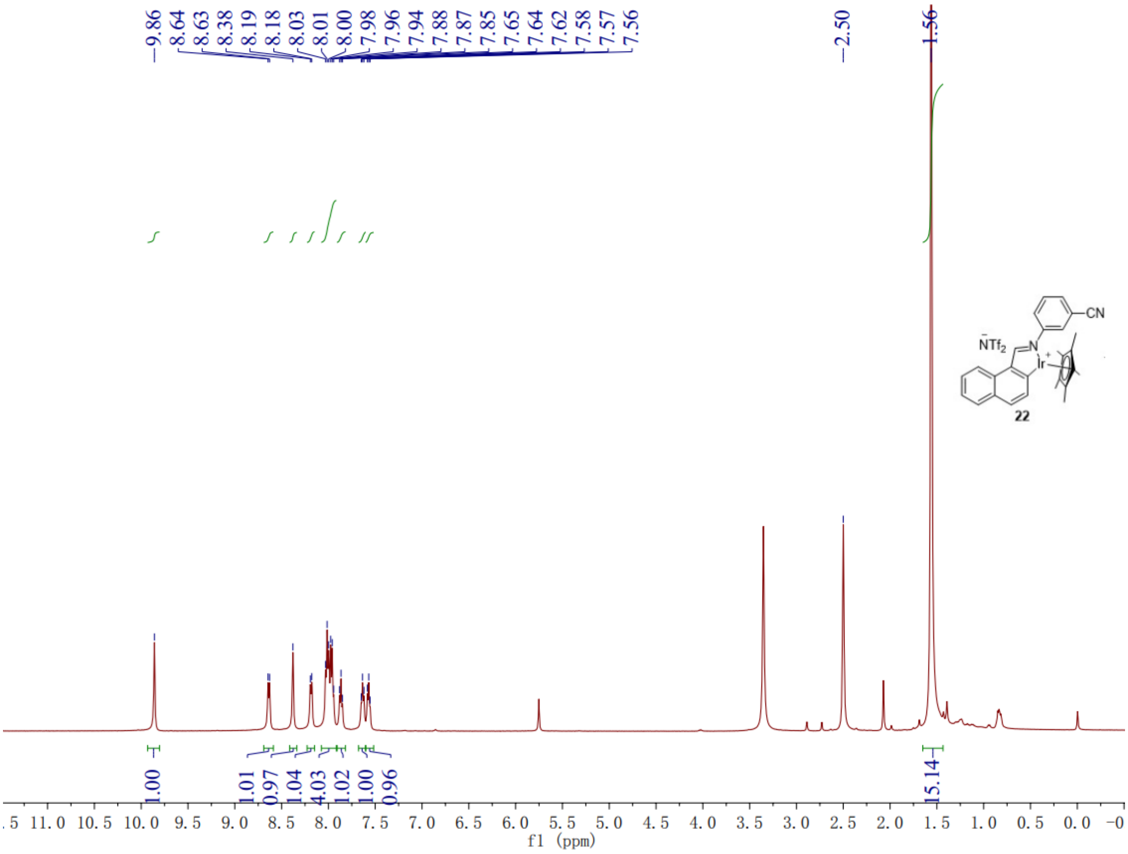
HMBC spectrum ($CDCl_3$, 500 MHz) of 21



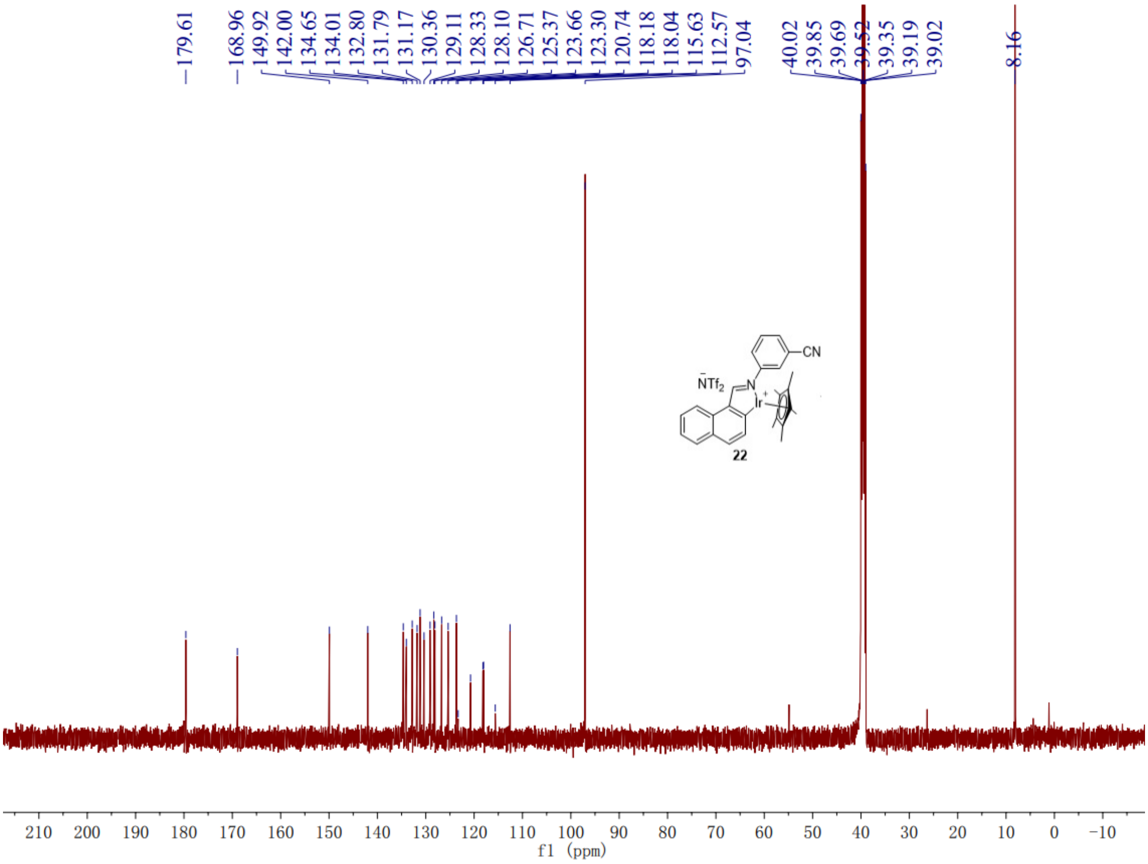
HR-ESI-MS $(M\text{-}Cl)^-$ of 21



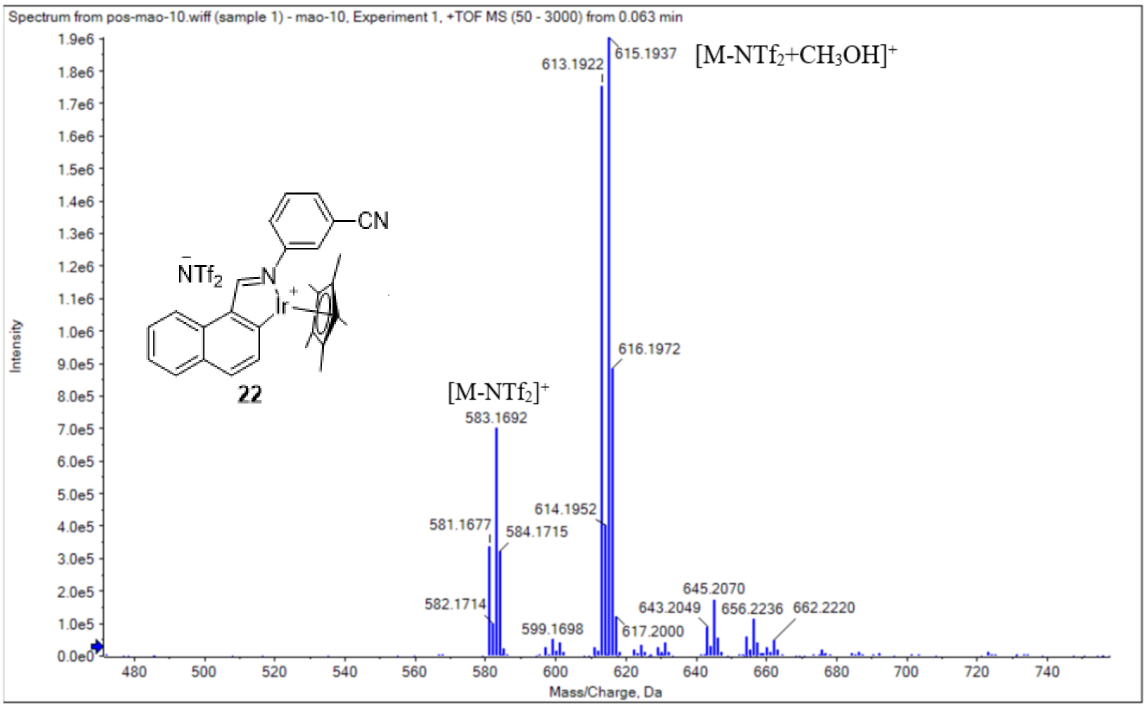
^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of 22



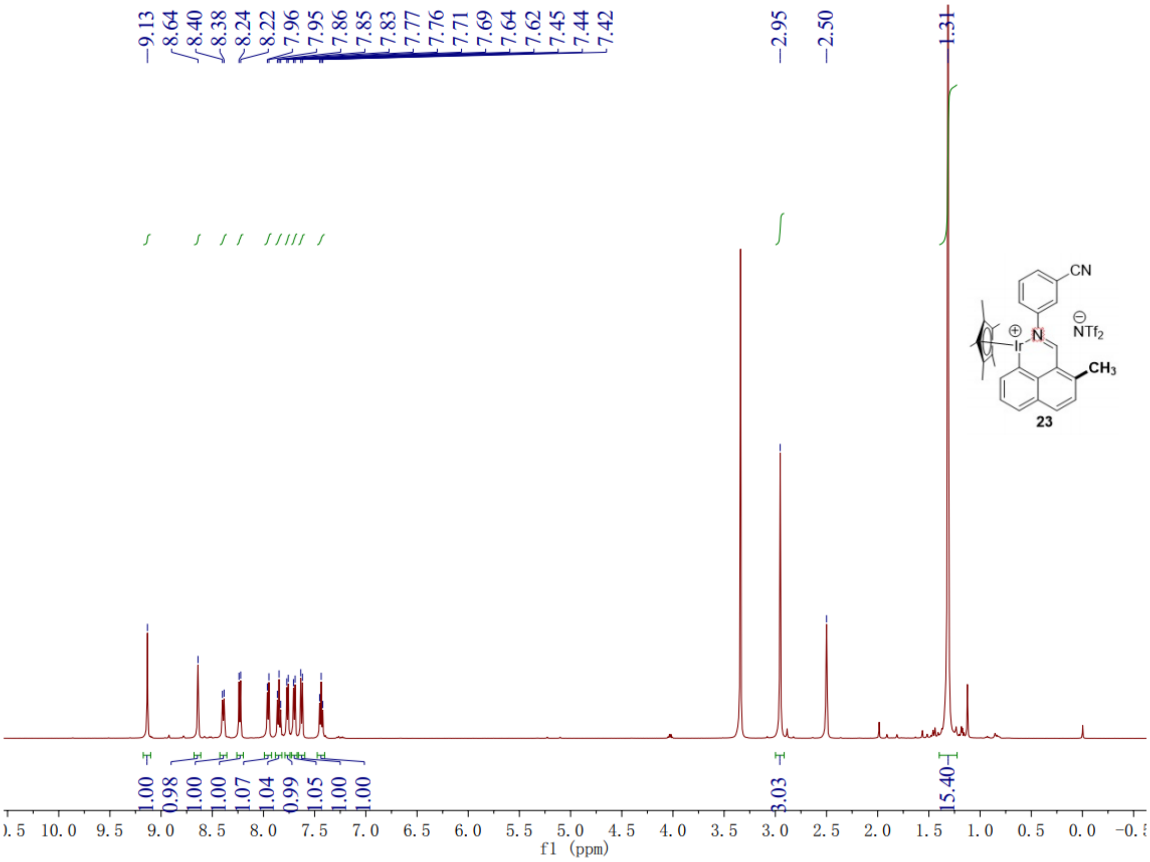
^{13}C NMR spectrum (DMSO-d_6, 126 MHz) of 22



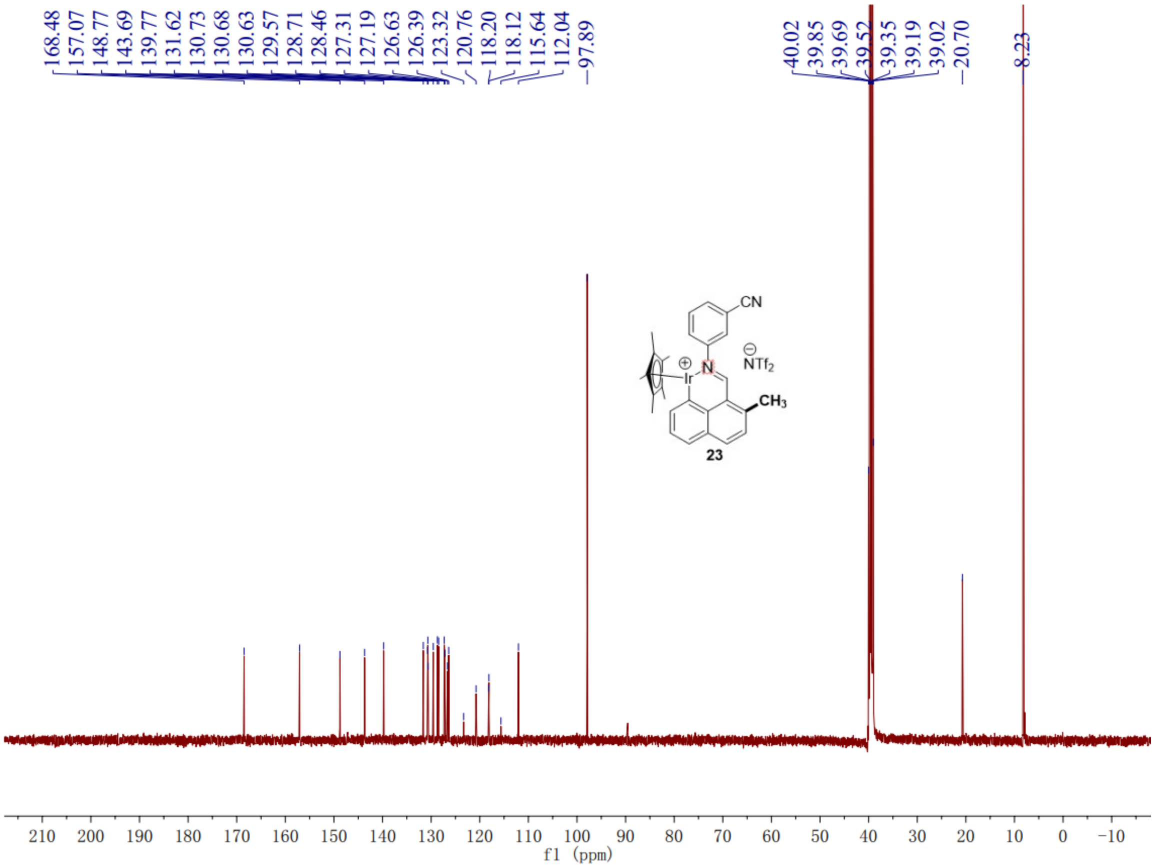
HR-ESI-MS $(M\text{-}NTf_2+CH_3OH)^+$ of 22



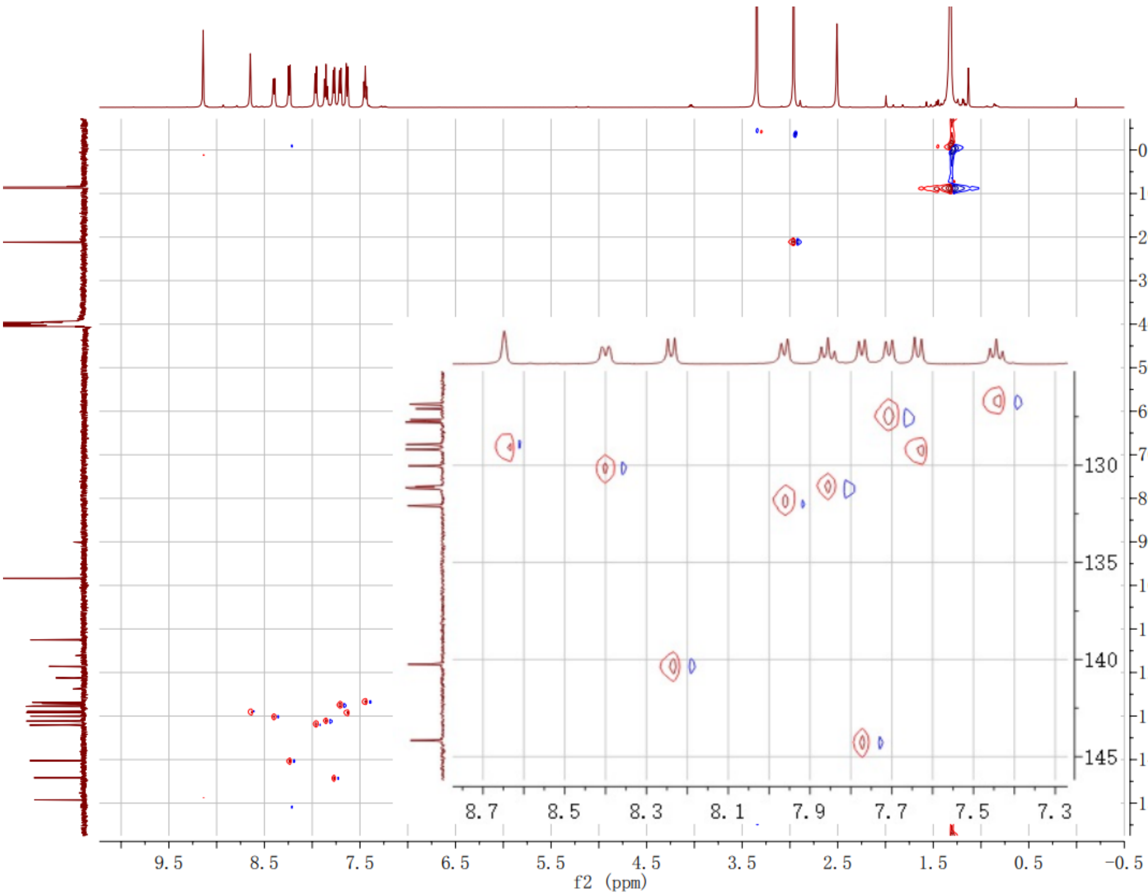
^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of 23



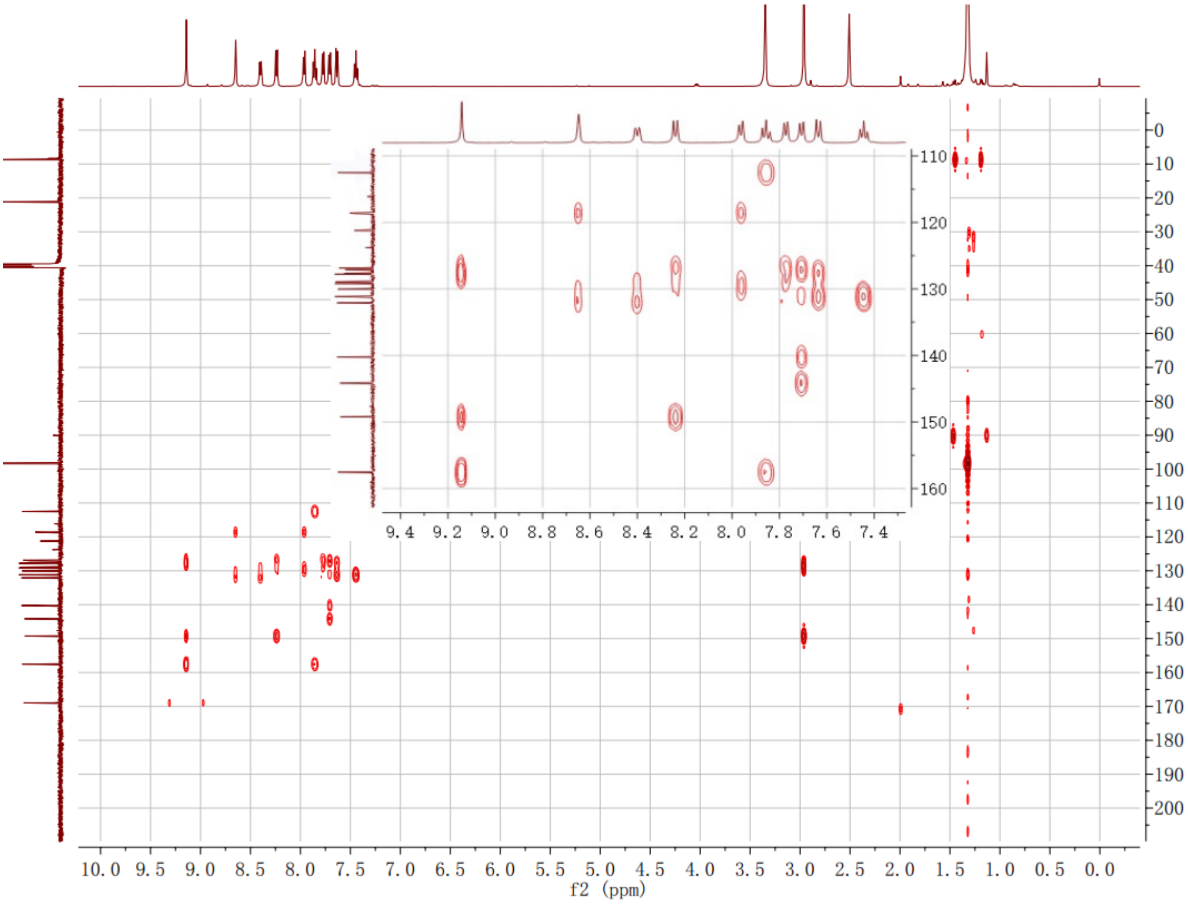
^{13}C NMR spectrum (DMSO-*d*$_6$, 126 MHz) of 23



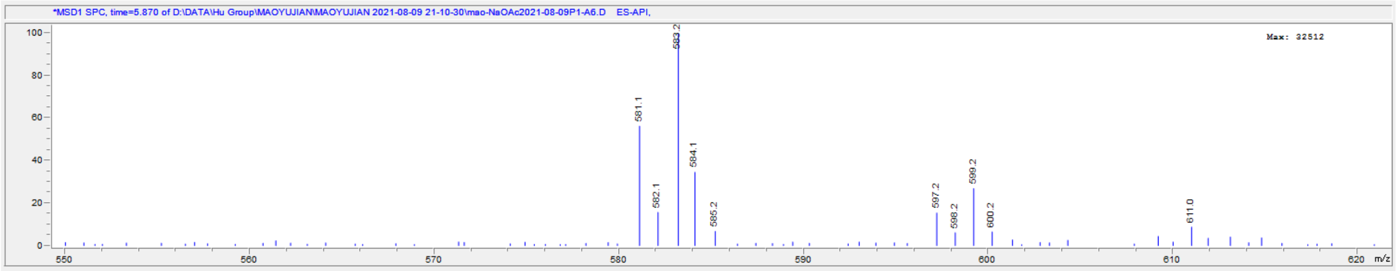
HSQC spectrum (DMSO-*d*$_6$, 500 MHz) of 23

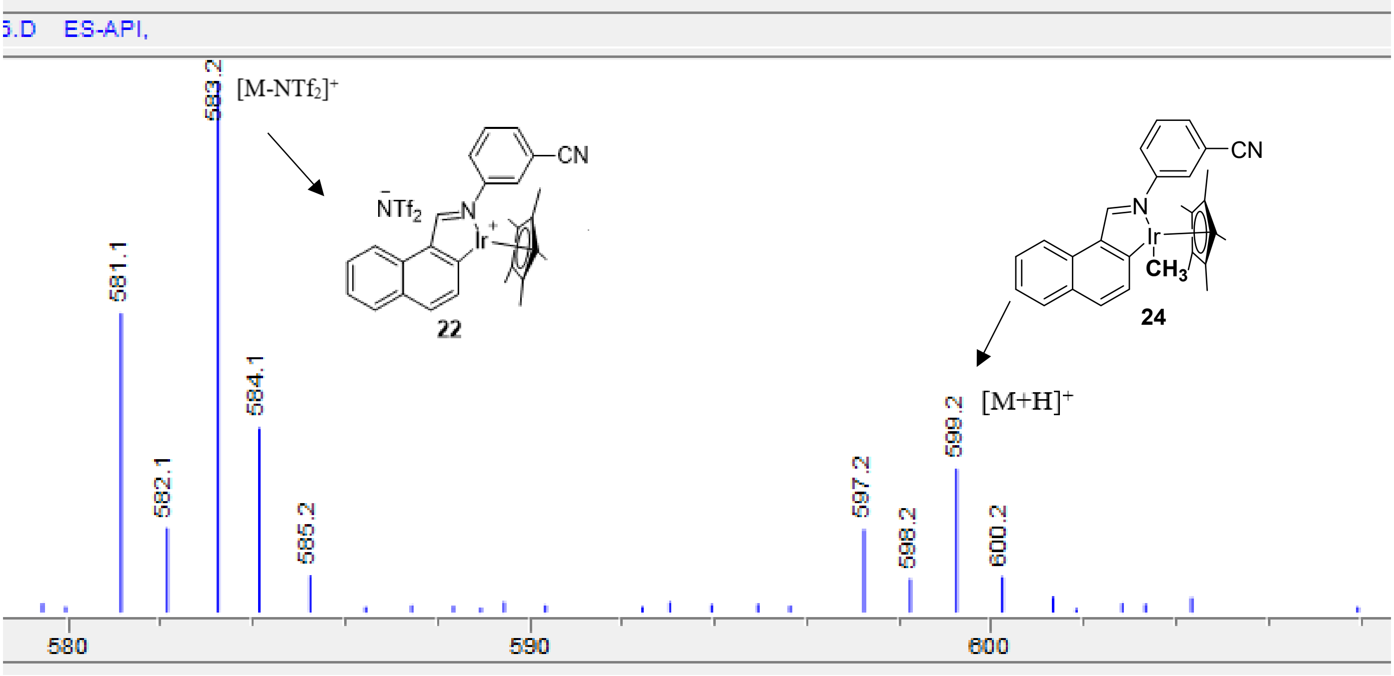


HMBC spectrum (DMSO-d_6, 500 MHz) of 23

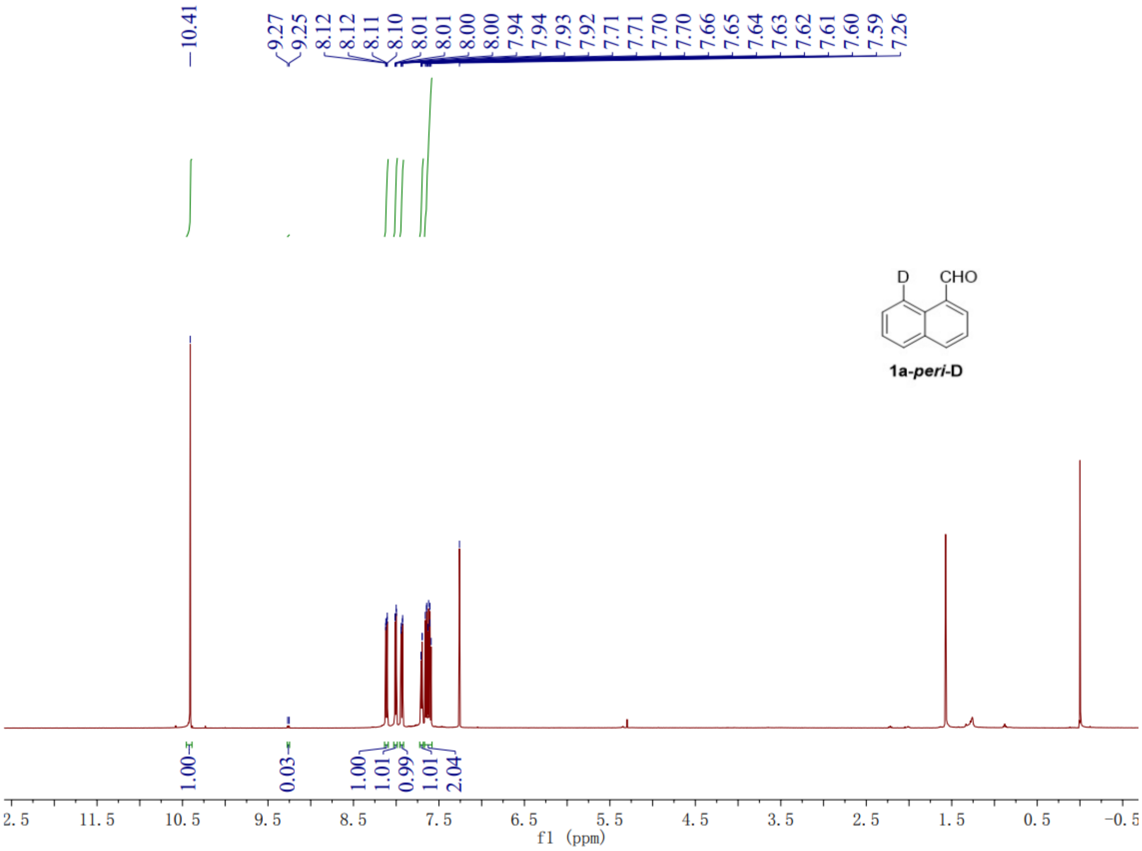


LC-ESI-MS $(M+H)^+$ of 24

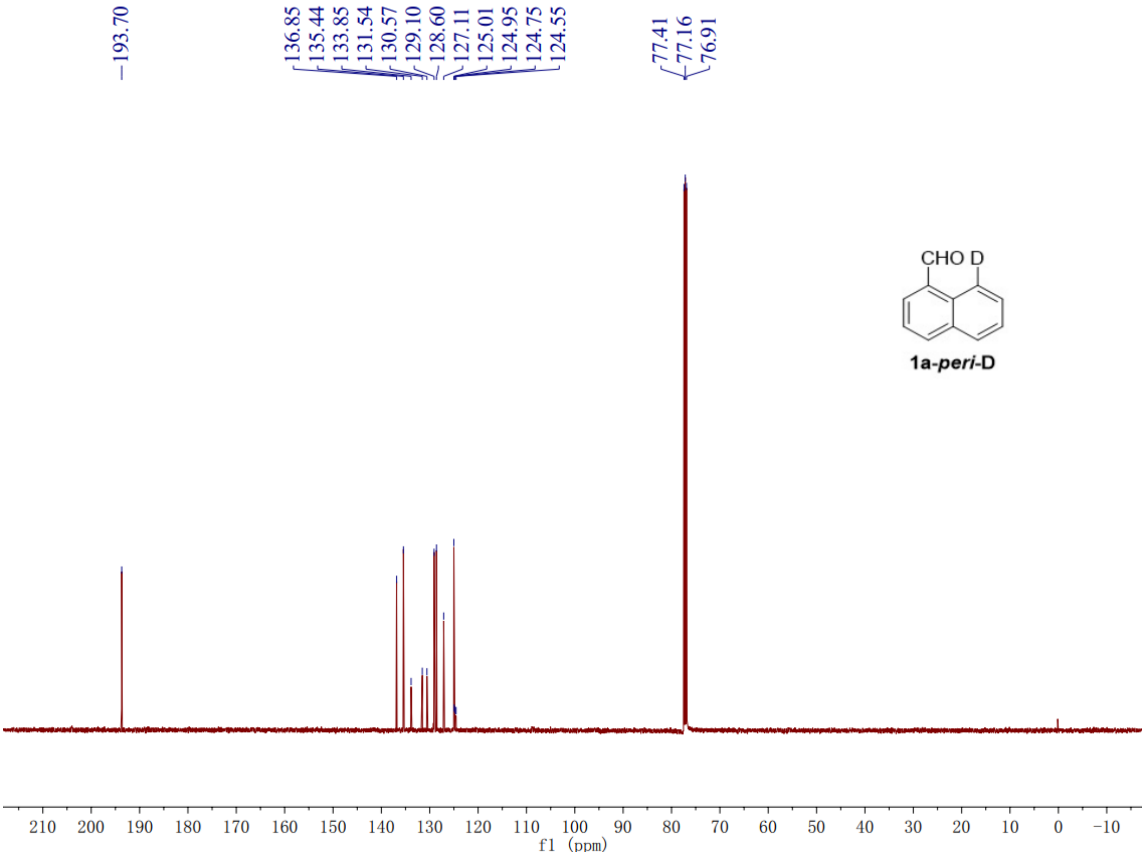




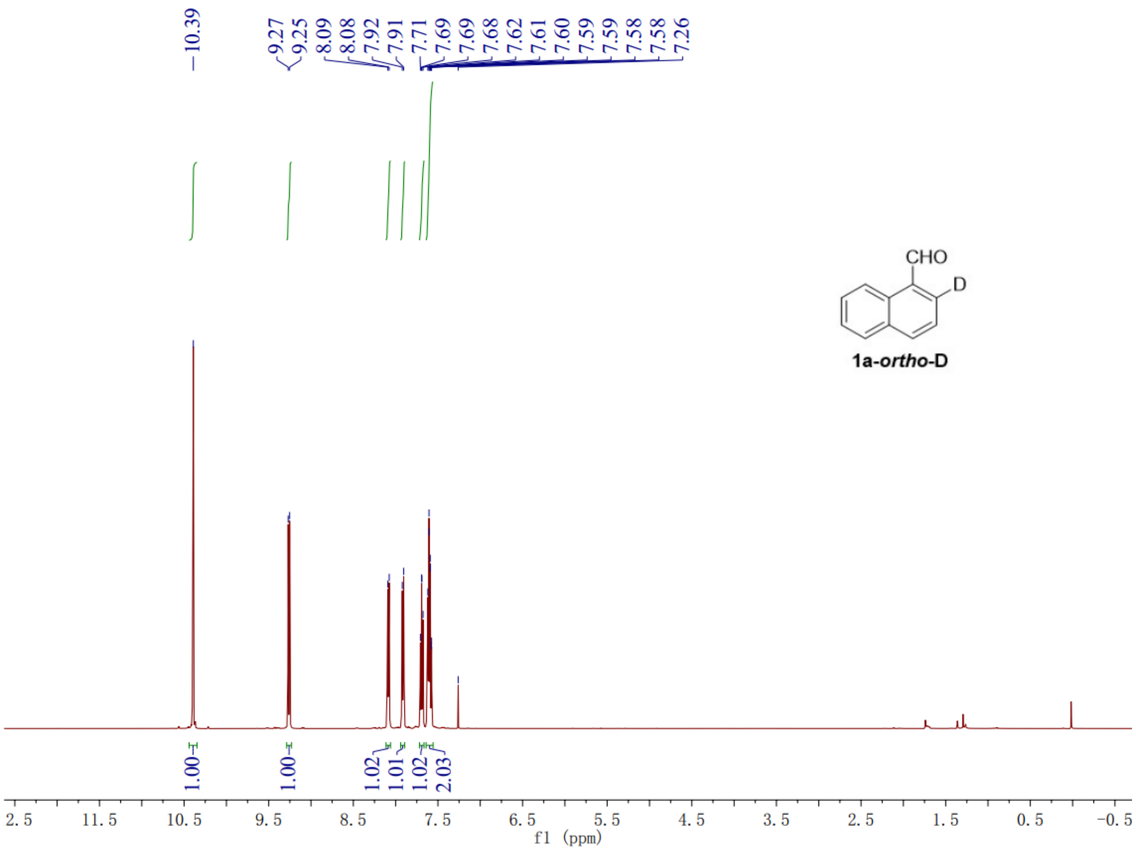
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1a-*peri*-D



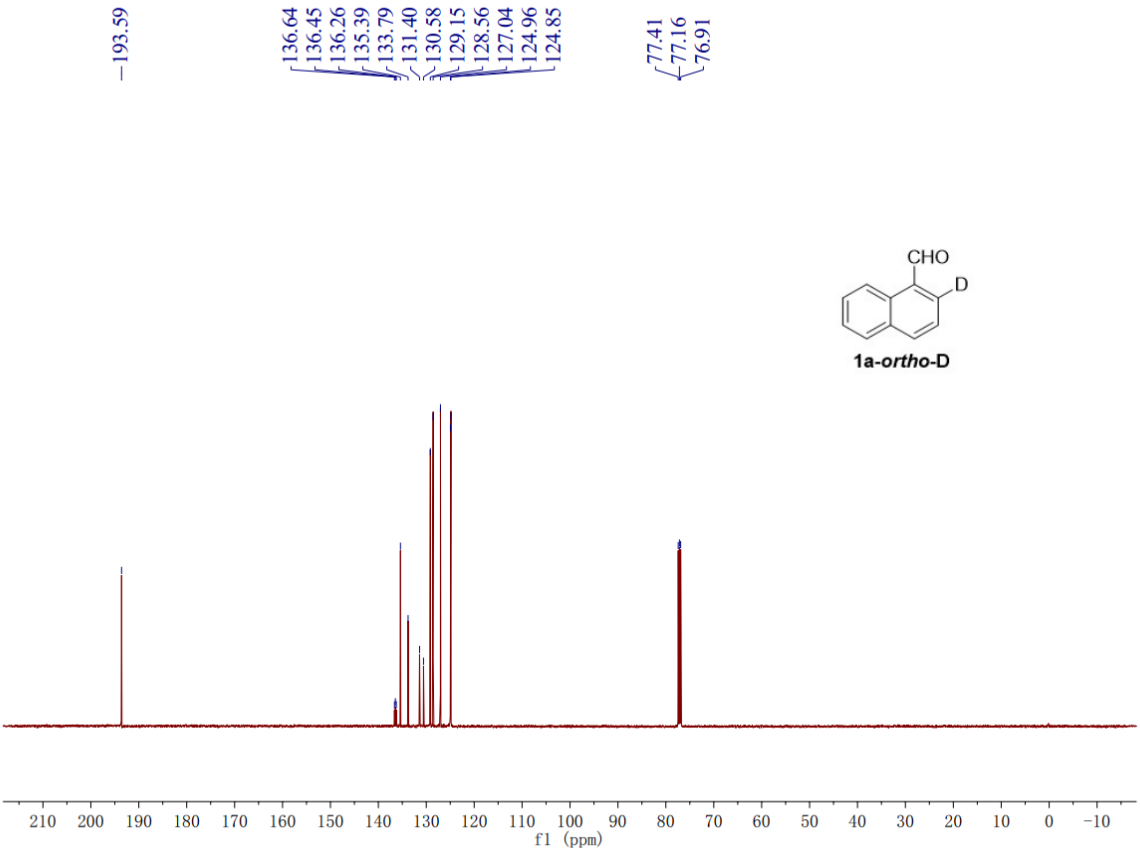
^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1a-*peri*-D



^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 1a-*ortho*-D



^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of 1a-*ortho*-D



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