Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

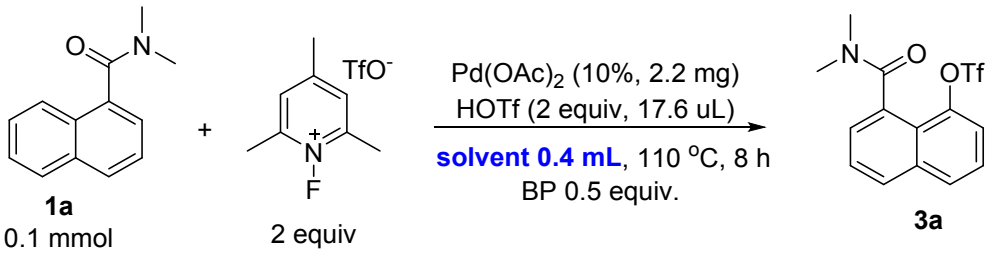
Palladium-Catalyzed Directing Group-Assisted C8-Triflation of Naphthalens

list of contents

General Remark: 1,2-Dichlorobenzene (ODCB) was purchased from commercial source and used without further treatment. $Pd(OAc)_2$, 2,4,6-trimethylpyridinium triflate and HOTf was purchased from TCI and kept in a dry place. Aryl ketones and aryl amide were commercially available or easily synthesized according to the reported method. ^1H NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts of ^1H NMR spectra were reported in parts per million relative to tetramethylsilane ($\delta = 0$).The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, br = broad. Coupling constants, J, were reported in Hertz unit (Hz). ^{19}F NMR spectra were recorded on 376 MHz spectrometers.^{13}C NMR spectra were recorded on 100 MHz spectrometers. Chemical shifts were reported in parts per million relative to the solvent resonance as the internal standard (CDCl3, δ 77.16 ppm). High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI mode.

Optimization of reaction conditions

Optimization of solvent



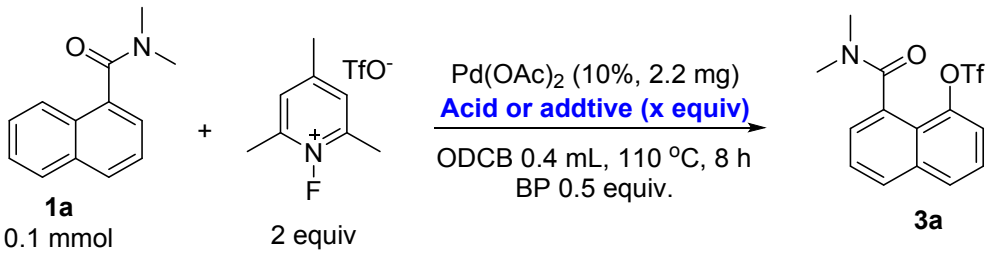
1a
0.1 mmol

2 equiv

3a

entry	Solvent	NMR yield%
1	DMSO	0
2	CH_3CN	0
3	PhMe	0
4	THF	Trace
5	NMP	0
6	CH_2Cl_2	44
7	$CHCl_3$	40
8	DCE	50
9	PhCl	60
10	ODCB	74

Optimization of Acid



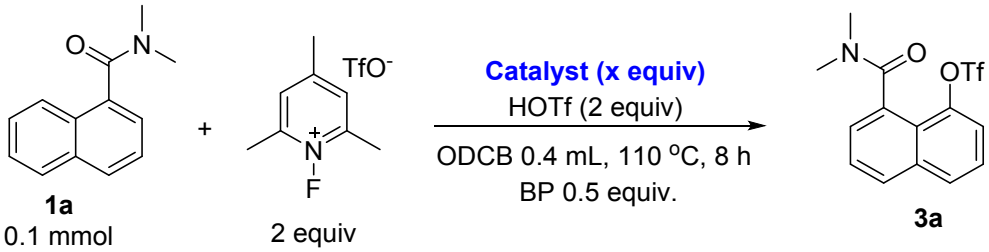
1a
0.1 mmol

2 equiv

3a

entry	Acid or other additive	Equivalent	NMR yield%
1	HOAc	2	0
2	CF_3COOH	2	0
3	KOTf	2	0
4	HOTf	2	74
5	TMSOTf	2	44
6	--	0	0
7	HOTf	1	17
8	HOTf	3	27
9	TsOH	2	0

Optimization of Catalyst



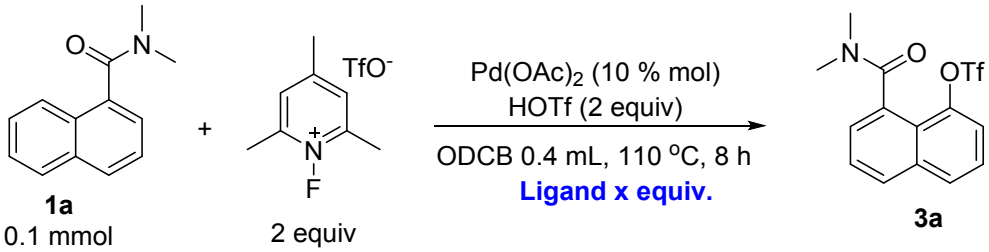
1a
0.1 mmol

2 equiv

3a

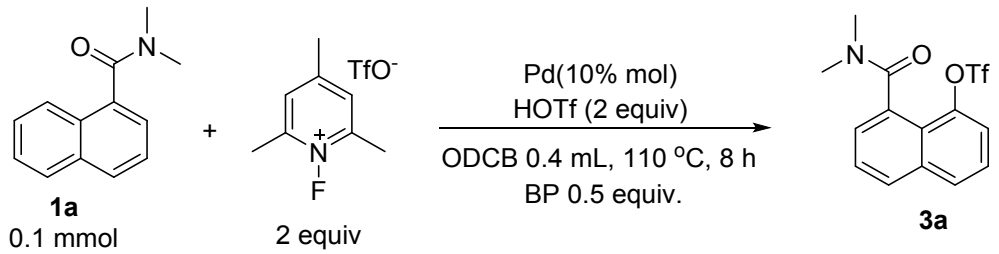
entry	Catalyst	Equivalent	NMR yield%
1	--	0	0
2	$Pd(OAc)_2$	0.05	47
3	$Pd(OAc)_2$	0.1	74
4	$Pd(OAc)_2$	0.15	56
5	$Pd(OTFA)_2$	0.1	72
6	$PdCl_2$	0.1	0
7	$Pd(OH)_2$	0.1	0
8	$Cu(OTf)_2$	0.1	0
9	$Cu(OTf)_2$	1	0
10	$IPrPdCl_2$	0.1	<5

Optimization ofLigand



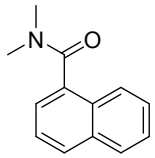
entry	Ligand	Equivalent	NMR yield%
1	--	0	0
2	BP	0.25	46
3	BP	0.5	74
4	BP	0.75	46
5	THF	0.5	0
6	DMF	0.5	0
7	NMP	0.5	0
8	CH_3CN	0.5	0
9	DMSO	0.5	0
10	BP + NMP	0.5 + 0.5	0

Optimization of Other conditions

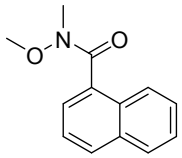


entry	Note		NMR yield%
1	Temperature	100	68
2	Temperature	120	72
3	Time	5 min	38
4	Time	10 min	46
5	Time	20 min	62
6	Time	40 min	71
7	Time	4 h	72
8	Volume of solvent	0.3 mL	70
9	Volume of solvent	0.5 mL	72

Substrate Structures:



1a



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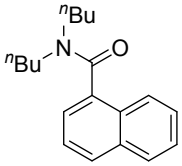

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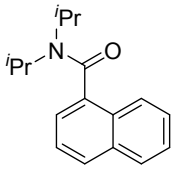

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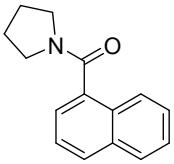

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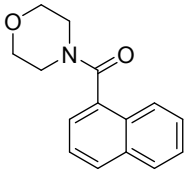

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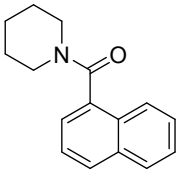

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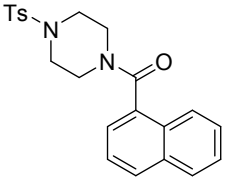

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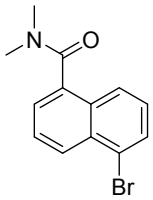

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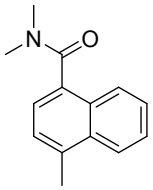

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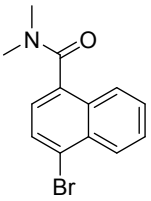

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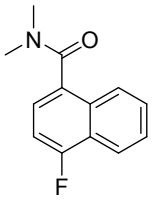

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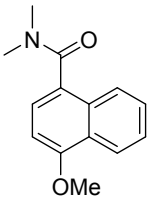

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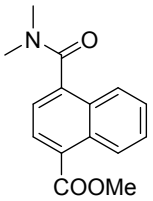

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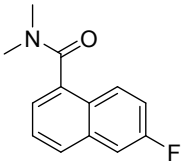

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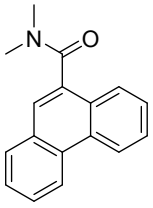

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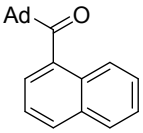

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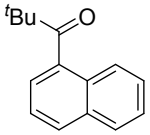

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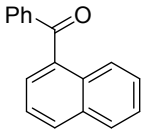

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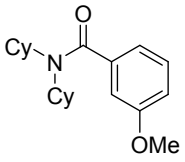
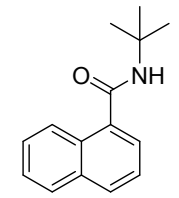
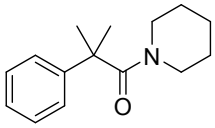
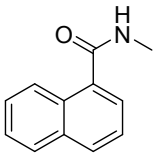
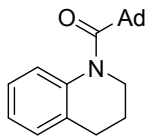
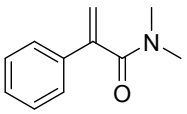
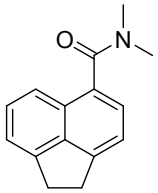
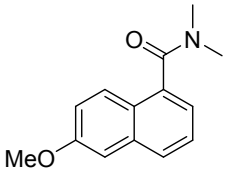
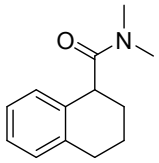
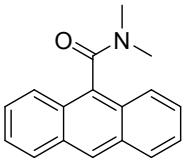
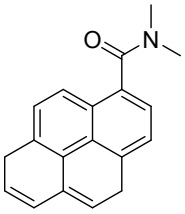
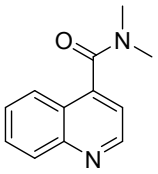
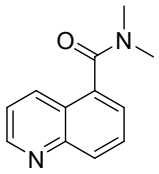
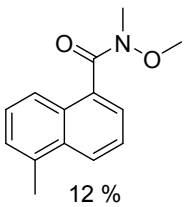
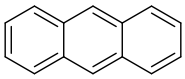
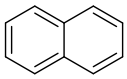
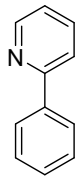
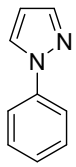
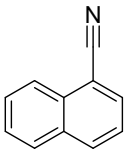
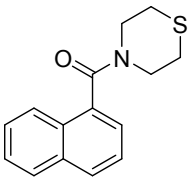
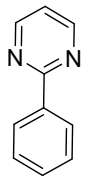


1t

Examples of unsuccessful substrate

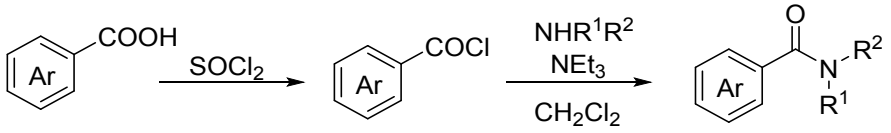














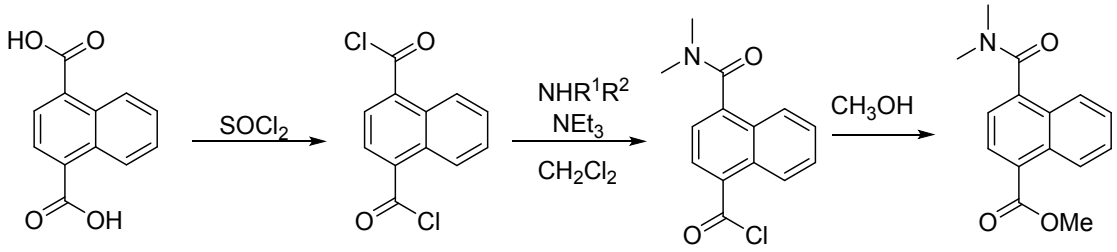
Experimental Procedures and Spectral Data

amides (1a-m, 1o, 1p1t)weresynthesized according to the reported method.

Reference: Kim, M.; Sharma,S.; Mishra,N. K.; Han, S.; Park, J.; Kim, M.; Shin, Y.; Kwak,J. H.; Hana, S. H.; Kim, I.S.*Chem. Commun.,***2014**, *50*, 11303.



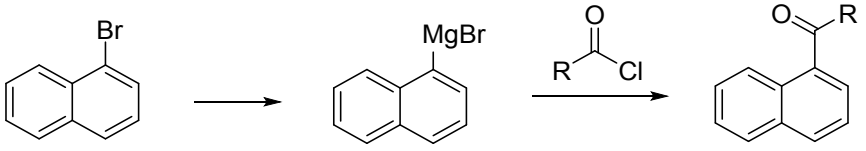
procedure for the synthesis of methyl 4-(dimethylcarbamoyl)-1-naphthoate (2n).

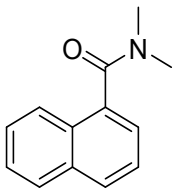


To a stirred suspension of naphthalene-1,4-dicarboxylic acid (5 mmol)in thionyl chloride (10 mL) was refluxed for overnight.The mixture was concentrated in vacuo (Bright yellow solid powder). Then Evaporation residue was dissolved in CH_2Cl_2(10mL). Themixture of Dimethylamine hydrochloride (1.1 equiv), Et_3N (3 equiv) and was added drop by drop. The reaction mixture was then stirred at room temperature for 1 hour. Then 2mL CH_3OH was added to the mixture. After stirred at room temperature for overnight.The reaction mixture was washed withdilute hydrochloric acid then H_2O and extracted with EtOAc. The organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (EA:Petroleum ether, 1:1).25% yield was obtained.

amides (1q-s) weresynthesized according to the reported method.

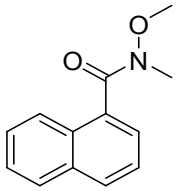
Reference: Pomares, M.; Grabuleda, X.; Jaime, C.; Virgili, A.Alvarez-Larena´, A.; Piniella, J. F.*Magn. Reson. Chem.***1999**, *37*, 885.





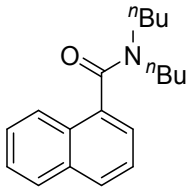
N, N-dimethyl-1-naphthamide (1a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.82 – 7.77 (m, 1H), 7.56 – 7.45 (m, 3H), 7.42 (dd, *J* = 7.0, 1.3 Hz, 1H), 3.26 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.94, 134.75, 133.48, 129.50, 129.04, 128.42, 126.98, 126.37, 125.21, 124.87, 123.90, 38.96, 34.89;HRMS Calcd for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1070, found: 200.1069.



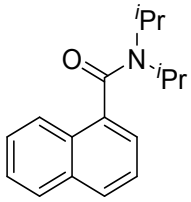
N-methoxy-N-methyl-1-naphthamide (1b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.78 (m, 3H), 7.60 – 7.38 (m, 4H), 3.38 (br, 6H);^{13}C NMR (101 MHz, $CDCl_3$) δ 169.79, 133.37, 133.18, 129.78, 129.64, 128.37, 126.94, 126.32, 124.95, 124.83, 124.37, 61.36, 33.18;HRMS Calcd for $C_{13}H_{14}O_2N$ $[M+H]^+$: 216.1019, found: 216.1016.



N, N-dibutyl-1-naphthamide (1c)

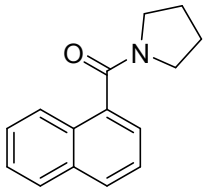
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.82 – 7.76 (m, 1H), 7.56 – 7.42 (m, 3H), 7.38 (dd, *J* = 7.0, 1.2 Hz, 1H), 3.81 (s, 1H), 3.44 (s, 1H), 3.02 (dd, *J* = 15.8, 7.8 Hz, 2H), 1.78 (tt, *J* = 15.2, 7.6 Hz, 2H), 1.54 – 1.37 (m, 4H), 1.00 (ddd, *J* = 14.7, 11.0, 5.1 Hz, 5H), 0.64 (t, *J* = 7.4 Hz, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 170.63, 135.22, 133.45, 129.65, 128.74, 128.34, 126.83, 126.30, 125.07, 124.87, 123.50, 48.50, 44.40, 30.81, 29.75, 20.50, 19.66, 14.00, 13.50;HRMS Calcd for $C_{19}H_{26}NO[M+H]^+$: 284.2009, found: 284.2008.



N,N-diisopropyl-1-naphthamide (1d)

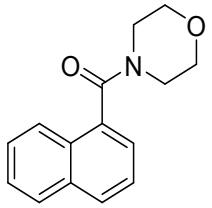
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 14.2, 7.4, 4.8 Hz, 3H), 7.57 – 7.41 (m, 3H), 7.32 (dd, *J* = 7.0, 1.1 Hz, 1H), 3.71 – 3.53 (m, 2H), 1.69 (dd, *J* = 28.4, 6.8 Hz, 6H), 1.06 (dd, *J* = 17.1, 6.7 Hz, 6H);^{13}C NMR (101 MHz, $CDCl_3$) δ 170.17, 136.65, 133.55, 129.59, 128.29, 128.22, 126.69, 126.34,

125.29, 124.92, 122.14, 51.11, 46.06, 20.87, 20.77, 20.70, 20.64;HRMS Calcd for $C_{17}H_{22}NO[M+H]^+$: 256.1696, found: 256.1694.



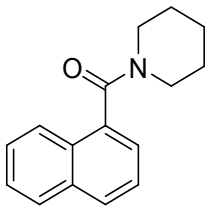
naphthalen-1-yl(pyrrolidin-1-yl)methanone (1e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.79 (m, 3H), 7.59 – 7.40 (m, 4H), 3.80 (s, 2H), 3.14 (s, 2H), 1.93 (d, *J* = 43.2 Hz, 4H);^{13}C NMR (101 MHz, $CDCl_3$) δ 171.62, 135.80, 133.56, 129.20, 129.11, 128.42, 126.97, 126.30, 125.22, 124.90, 123.75, 48.53, 45.68, 26.03, 24.65;HRMS Calcd for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1226, found: 226.1224.



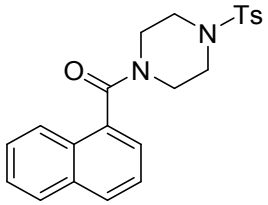
morpholino(naphthalen-1-yl)methanone (1f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 13.8, 8.3 Hz, 3H), 7.58 – 7.47 (m, 3H), 7.43 (dd, *J* = 7.0, 1.1 Hz, 1H), 4.02 (dd, *J* = 10.9, 6.3 Hz, 1H), 3.95 – 3.81 (m, 3H), 3.52 (dd, *J* = 10.7, 6.6 Hz, 2H), 3.28 – 3.14 (m, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ 169.49, 133.70, 133.49, 129.57, 129.37, 128.53, 127.16, 126.56, 125.20, 124.64, 123.94, 67.11, 67.01, 47.63, 42.21;HRMS Calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$: 242.1176, found: 242.1173.



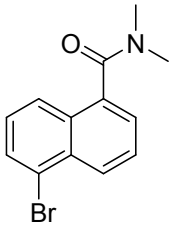
naphthalen-1-yl(piperidin-1-yl)methanone (1g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dt, *J* = 8.9, 5.4 Hz, 3H), 7.56 – 7.45 (m, 3H), 7.40 (dd, *J* = 6.9, 1.2 Hz, 1H), 3.88 (dd, *J* = 11.1, 5.4 Hz, 2H), 3.20 – 3.09 (m, 2H), 1.80 – 1.71 (m, 2H), 1.71 – 1.64 (m, 2H), 1.41 (d, *J* = 4.3 H z, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ 169.24, 134.90, 133.49, 129.66, 128.84, 128.36, 126.84, 126.37, 125.22, 124.97, 123.45, 48.33, 42.69, 26.71, 25.87, 24.58;HRMS Calcd for $C_{16}H_{18}NO$ $[M+H]^+$: 240.1383, found: 240.1380.



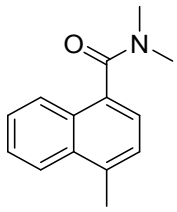
naphthalen-1-yl(4-tosylpiperazin-1-yl)methanone (1h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.1, 2.7 Hz, 2H), 7.64 (dd, *J* = 18.2, 8.3 Hz, 3H), 7.47 (dddd, *J* = 12.9, 8.1, 5.8, 1.1 Hz, 3H), 7.40 – 7.29 (m, 3H), 4.00 (dd, *J* = 21.1, 15.0 Hz, 2H), 3.37 – 3.03 (m, 4H), 2.96 – 2.75 (m, 2H), 2.48 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 169.49, 144.18, 133.47, 133.18, 132.38, 129.91, 129.62, 129.44, 128.59, 127.78, 127.15, 126.61, 125.12, 124.45, 123.94, 46.56, 46.45, 45.99, 41.10, 21.62;HRMS Calcd for $C_{22}H_{23}N_2O_3S$ $[M+H]^+$: 395.1424, found: 395.1416.



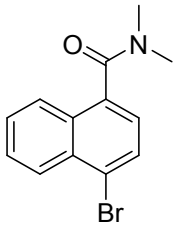
5-bromo-N, N-dimethyl-1-naphthamide (1i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.6 Hz, 1H), 7.87 – 7.73 (m, 2H), 7.61 (dd, *J* = 8.5, 7.1 Hz, 1H), 7.48 (dd, *J* = 7.0, 0.9 Hz, 1H), 7.41 – 7.32 (m, 1H), 3.26 (s, 3H), 2.80 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 170.33, 135.25, 132.05, 130.74, 130.56, 128.25, 127.27, 126.72, 124.86, 124.76, 123.37, 38.88, 34.94;HRMS Calcd for $C_{13}H_{13}BrNO[M+H]^+$: (278.0175, 280.0152), found: (278.0176, 280.0153).



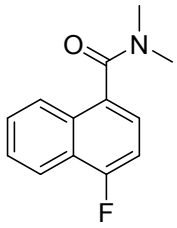
N,N,4-trimethyl-1-naphthamide (1j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 1H), 7.83 – 7.77 (m, 1H), 7.58 – 7.48 (m, 2H), 7.31 (s, 2H), 3.24 (s, 3H), 2.81 (s, 3H), 2.70 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 171.21, 135.63, 133.13, 132.61, 129.58, 126.60, 126.19, 125.89, 125.46, 124.55, 123.64, 38.95, 34.89, 19.57;HRMS Calcd for $C_{14}H_{16}NO[M+H]^+$: 214.1226, found: 214.1227.



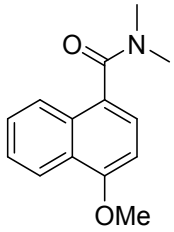
4-bromo-N,N-dimethyl-1-naphthamide (1k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.84 – 7.75 (m, 2H), 7.60 (dddd, *J* = 20.7, 8.2, 6.9, 1.3 Hz, 2H), 7.30 – 7.24 (m, 1H), 3.25 (s, 3H), 2.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.04, 134.82, 132.03, 130.68, 129.35, 127.88, 127.86, 127.69, 125.38, 124.13, 123.86, 38.88, 34.93; HRMS Calcd for $C_{13}H_{13}BrNO[M+H]^+$: (278.0175, 280.0155), found: (278.0176, 280.0154).



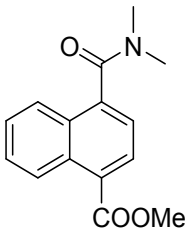
4-fluoro-N, N-dimethyl-1-naphthamide (1l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 1H), 7.85 – 7.77 (m, 1H), 7.62 – 7.54 (m, 2H), 7.37 (dd, *J* = 7.8, 5.3 Hz, 1H), 7.16 (dd, *J* = 10.2, 7.8 Hz, 1H), 3.25 (s, 3H), 2.82 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.79 – -120.95 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.28 (s), 158.99 (d, *J* = 352.7 Hz), 131.16 (d, *J* = 5.0 Hz), 130.82 (d, *J* = 4.7 Hz), 127.99 (s), 126.74 (d, *J* = 1.8 Hz), 124.88 (d, *J* = 2.8 Hz), 124.14 (d, *J* = 8.8 Hz), 123.76 (d, *J* = 16.6 Hz), 120.99 (d, *J* = 5.5 Hz), 108.91 (d, *J* = 20.6 Hz), 38.97 (s), 35.00 (s); HRMS Calcd for $C_{13}H_{13}FNO[M+H]^+$: 218.0976, found: 218.0976.



4-methoxy-N,N-dimethyl-1-naphthamide (1m)

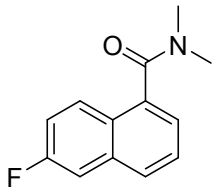
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.80 – 7.71 (m, 1H), 7.58 – 7.45 (m, 2H), 7.36 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.80 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.01 (d, *J* = 4.4 Hz, 3H), 3.03 (br, *J* = 157.3 Hz, 6H);^{13}C NMR (101 MHz, $CDCl_3$) δ 171.22, 156.08, 130.73, 127.44, 126.99, 125.63, 125.50, 124.69, 124.67, 122.40, 102.97, 55.64, 39.02, 35.02;HRMS Calcd for $C_{14}H_{16}NO_2[M+H]^+$: 230.1176, found: 230.1176.



methyl 4-(dimethylcarbamoyl)-1-naphthoate (1n)

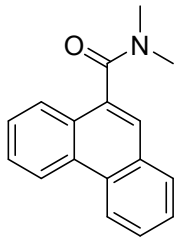
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 – 8.88 (m, 1H), 8.18 (d, *J* = 7.4 Hz, 1H), 7.86 – 7.78 (m, 1H), 7.61 (dddd, *J* = 26.8, 8.1, 6.9, 1.2 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 4.02 (s, 3H), 3.27 (s, 3H), 2.79 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 170.10, 167.60, 139.63, 131.42, 129.85, 129.45, 128.20, 128.01,

127.34, 126.28, 125.27, 122.41, 52.37, 38.74, 34.87; HRMS Calcd for $C_{15}H_{16}NO_3[M+H]^+$: 258.1125, found: 258.1125.



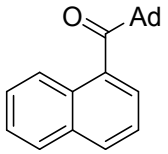
6-fluoro-N,N-dimethyl-1-naphthamide (1o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.53 – 7.46 (m, 2H), 7.37 (dd, *J* = 6.9, 0.9 Hz, 1H), 7.33 – 7.25 (m, 1H), 3.25 (s, 3H), 2.81 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.92 (td, *J* = 8.8, 5.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.54 (s), 160.74 (d, *J* = 247.4 Hz), 134.87 (s), 134.48 (d, *J* = 9.3 Hz), 128.37 (d, *J* = 5.4 Hz), 127.54 (d, *J* = 9.0 Hz), 126.54 (s), 126.33 (s), 123.14 (d, *J* = 2.6 Hz), 117.31 (d, *J* = 25.3 Hz), 111.47 (d, *J* = 20.4 Hz), 38.88 (s), 34.90 (s); HRMS Calcd for $C_{13}H_{13}ONF$ $[M+H]^+$: 218.0976, found: 218.0975.



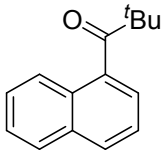
N,N-dimethylphenanthrene-9-carboxamide (1p)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 16.6, 8.2 Hz, 2H), 7.86 (ddd, *J* = 19.4, 8.0, 1.2 Hz, 2H), 7.73 – 7.66 (m, 3H), 7.66 – 7.58 (m, 2H), 3.29 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.78, 133.68, 130.88, 130.46, 130.38, 128.94, 128.31, 127.43, 127.33, 127.17, 127.05, 125.65, 124.93, 123.11, 122.63, 38.93, 34.91; HRMS Calcd for $C_{17}H_{16}NO[M+H]^+$: 250.1226, found: 250.1223.



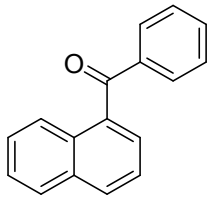
adamantan-1-yl(naphthalen-1-yl)methanone (1q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.61 – 7.56 (m, 1H), 7.47 (ddd, *J* = 15.2, 7.1, 4.6 Hz, 3H), 7.29 (dd, *J* = 7.0, 1.1 Hz, 1H), 2.04 (s, 3H), 1.99 (d, *J* = 2.7 Hz, 6H), 1.71 (dd, *J* = 9.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.98, 138.65, 133.53, 130.00, 128.78, 128.39, 126.61, 126.18, 125.60, 124.24, 122.35, 47.71, 38.55, 36.42, 27.99; HRMS Calcd for $C_{21}H_{23}O$ $[M+H]^+$: 291.1743, found: 291.1745.



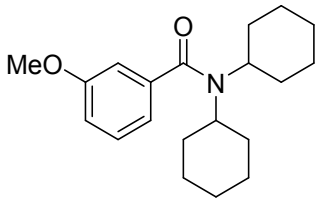
2,2-dimethyl-1-(naphthalen-1-yl)propan-1-one (1r)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 2H), 7.66 – 7.57 (m, 1H), 7.53 – 7.39 (m, 3H), 7.34 (dd, *J* = 7.0, 1.1 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.57, 138.94, 133.59, 129.93, 128.99, 128.44, 126.75, 126.23, 125.48, 124.27, 122.30, 45.55, 27.29; HRMS Calcd for $C_{15}H_{17}O[M+H]^+$: 213.1274, found: 213.1275.



naphthalen-1-yl(phenyl)methanone (1s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.3, 0.7 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.92 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.87 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.54 – 7.50 (m, 2H), 7.50 – 7.42 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.02, 138.34, 136.38, 133.74, 133.23, 131.27, 130.97, 130.42, 128.46, 128.41, 127.77, 127.26, 126.47, 125.71, 124.34; HRMS Calcd for $C_{17}H_{13}O$ $[M+H]^+$: 233.0961, found: 233.0961.

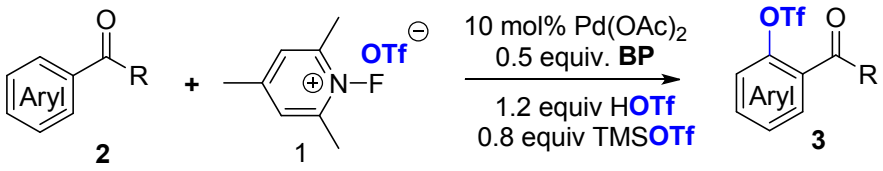


N, N-dicyclohexyl-3-methoxybenzamide (1t)

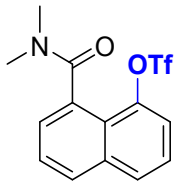
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.8 Hz, 1H), 6.92 – 6.88 (m, 1H), 6.87 – 6.79 (m, 2H), 3.82 (s, 3H), 3.36 (s, 1H), 3.03 (s, 1H), 2.61 (s, 2H), 1.87 – 1.47 (br, 12H), 1.16 (br, *J* = 57.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.04, 159.57, 140.23, 129.48, 117.69, 114.62, 110.98, 55.33, 25-32(br, 12); HRMS Calcd for $C_{20}H_{30}NO_2[M+H]^+$: 326.2271, found: 316.2272.

Procedure for C(sp2)–H Triflation

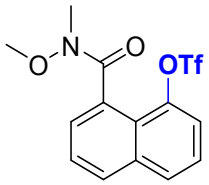


General Procedures for the C(sp2)–H Triflation: Substrate **1** (0.10 mmol), 2, 4, 6-trimethylpyridinium triflate (0.2 mmol, 58 mg), $Pd(OAc)_2$ (0.01 mmol, 2.3 mg), **L1** (0.05 mmol, 9.2 mg) were weighed into a tube (10 mL) with a magnetic stir barunder air. 1,2-dichlorobenzene (0.4 mL) was added, then HOTf(0.12 mmol, 10.5 μL) and TMSOTf (0.08 mmol, 14.5μL)were added and the tube was sealed with a cap. The reaction mixture was stirred at 110°C for 2 hours. Upon completion, the reaction mixture was cooled to room temperature and the reaction mixture was purified by flash column chromatography.



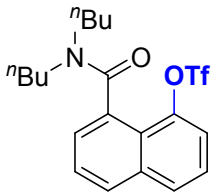
8-(dimethylcarbamoyl)naphthalen-1-yl trifluoromethanesulfonate (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.85 (m, 2H), 7.55 (ddd, *J* = 23.4, 15.8, 7.2 Hz, 4H), 3.21 (s, 3H), 2.93 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.55; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.01, 145.47, 135.81, 131.30, 129.31, 129.03, 127.24, 126.64, 125.70, 122.49, 118.67 (q, *J* = 319.1 Hz), 118.20 (q, *J* = 2.0 Hz), 39.18, 34.89; HRMS Calcd for $C_{14}H_{13}O_4NF_3S$ $[M+H]^+$: 348.0512, found: 348.0509.



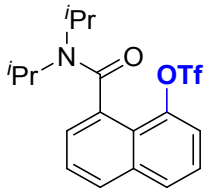
8-(methoxy(methyl)carbamoyl)naphthalen-1-yl trifluoromethanesulfonate (3b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 2H), 7.64 – 7.57 (m, 3H), 7.52 (t, *J* = 8.0 Hz, 1H), 3.45 (s, 3H), 3.28 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.52; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.51, 145.99, 135.12, 130.40, 129.51, 128.55, 127.33, 126.30, 125.51, 122.27, 118.66 (q, *J* = 319.1 Hz), 117.05 (q, *J* = 2.2 Hz), 60.76, 32.57; HRMS Calcd for $C_{14}H_{13}O_5NF_3S$ $[M+H]^+$: 364.0461, found: 364.0459.



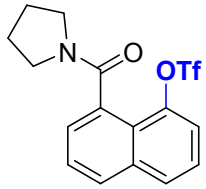
8-(dibutylcarbamoyl)naphthalen-1-yl trifluoromethanesulfonate (3c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.54 (td, *J* = 15.5, 7.6 Hz, 3H), 7.46 (d, *J* = 6.3 Hz, 1H), 4.05 (ddd, *J* = 13.5, 10.6, 5.8 Hz, 1H), 3.10 (dt, *J* = 14.8, 6.9 Hz, 3H), 1.84 (ddd, *J* = 16.2, 12.1, 6.0 Hz, 1H), 1.69 – 1.57 (m, 1H), 1.47 (ddd, *J* = 22.9, 14.3, 6.8 Hz, 4H), 1.06 (dt, *J* = 10.7, 5.3 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H), 0.69 (t, *J* = 7.3 Hz, 3H).^{19}F NMR (376 MHz, $CDCl_3$) δ -72.62; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.94, 145.89, 135.71, 131.96, 129.03, 128.82, 127.16, 126.54, 125.59, 122.19, 118.66(q, *J* = 319.1 Hz), 117.63 (q, *J* = 2.3 Hz), 49.95,45.77, 30.72, 30.15, 20.56, 19.92, 14.02, 13.55; HRMS Calcd for $C_{20}H_{25}O_4NF_3S$ $[M+H]^+$: 432.1451, found: 432.1451.



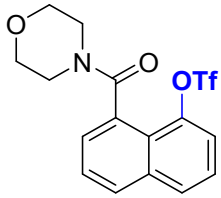
8-(diisopropylcarbamoyl)naphthalen-1-yl trifluoromethanesulfonate (3d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.50 (t, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 7.1 Hz, 1H), 3.58 (dp, *J* = 13.7, 6.7 Hz, 1H), 3.52 – 3.41 (m, 1H), 1.67 (d, *J* = 6.9 Hz, 3H), 1.58 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.7 Hz, 3H), 1.03 (d, *J* = 6.6 Hz, 3H).^{19}F NMR (376 MHz, $CDCl_3$) δ -71.78; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.50, 146.42, 135.63, 133.30, 128.73, 128.67, 126.71, 126.57, 125.43, 121.59, 118.80 (q, *J* = 320.0 Hz), 116.87 (q, *J* = 2.0 Hz), 50.88, 46.16, 20.80, 20.31, 20.25, 20.15; HRMS Calcd for $C_{18}H_{21}NF_3O_4S[M+H]^+$: 404.1138, found: 404.1134.



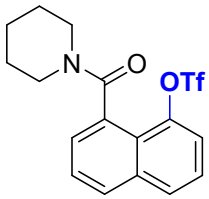
8-(pyrrolidine-1-carbonyl)naphthalen-1-yl trifluoromethanesulfonate (3e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.80 (m, 2H), 7.69 – 7.38 (m, 4H), 3.92 – 3.76 (m, 1H), 3.78 – 3.60 (m, 1H), 3.27 (t, *J* = 6.1 Hz, 2H), 2.02 – 1.66 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.34.(q, *J* = 2.0 Hz; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.28, 145.56, 135.83, 132.20, 129.43, 129.07, 127.48, 126.70, 125.63, 122.21, 118.71 (q, *J* = 319.1 Hz), 118.20 (d, *J* = 2.2 Hz), 49.07, 45.84, 25.79, 24.53; HRMS Calcd for $C_{16}H_{15}O_4NF_3S$ $[M+H]^+$: 374.0668, found: 374.0662.



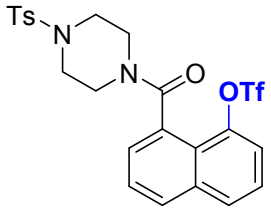
8-(morpholine-4-carbonyl)naphthalen-1-yl trifluoromethanesulfonate (3f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.91 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.51 (d, *J* = 7.3 Hz, 1H), 4.09 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.99 – 3.94 (m, 1H), 3.81 – 3.63 (m, 3H), 3.57 (ddd, *J* = 11.4, 7.1, 4.0 Hz, 1H), 3.30 (dd, *J* = 7.4, 3.1 Hz, 2H).^{19}F NMR (376 MHz, $CDCl_3$) δ -72.33; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81, 145.49, 135.79, 130.32, 129.64, 129.09, 127.35, 126.59, 125.87, 122.51, 118.67 (q, *J* = 319.2 Hz), 118.31 (q, *J* = 2.1 Hz), 77.35, 77.03, 76.71, 66.56, 66.28, 47.59, 42.11; HRMS Calcd for $C_{16}H_{15}NO_5SF_3[M+H]^+$: 390.0618, found:390.0611.



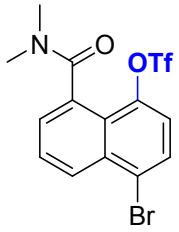
8-(piperidine-1-carbonyl)naphthalen-1-yl trifluoromethanesulfonate (3g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.89 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.55 – 7.49 (m, 3H), 4.44 – 4.35 (m, 1H), 3.39 (dt, *J* = 13.3, 4.1 Hz, 1H), 3.26 (ddd, *J* = 13.3, 10.2, 2.7 Hz, 1H), 3.11 (dt, *J* = 6.8, 4.5 Hz, 1H), 1.87 – 1.78 (m, 2H), 1.68 – 1.46 (m, 4H).^{9}F NMR (376 MHz, $CDCl_3$) δ -72.45.^{13}C NMR (101 MHz, $CDCl_3$) δ 168.50, 145.63, 135.81, 131.46, 129.18, 128.99, 126.82, 126.64, 125.65, 122.48, 120.28(q, *J* = 319.1 Hz), 118.11 (q, *J* = 2.2 Hz), 48.34, 42.57, 25.92, 25.35, 24.59; HRMS Calcd for $C_{17}H_{17}O_4NF_3S$ $[M+H]^+$: 388.0825, found: 388.0820.



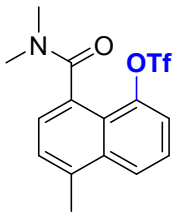
8-(4-tosylpiperazine-1-carbonyl)naphthalen-1-yl trifluoromethanesulfonate (3h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.90 (dd, *J* = 6.9, 2.4 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.48 (m, 3H), 7.42 – 7.32 (m, 3H), 4.22 – 4.06 (m, 1H), 3.89 – 3.76 (m, 1H), 3.50 – 3.30 (m, 3H), 3.12 (dd, *J* = 11.2, 3.8 Hz, 1H), 2.98 (ddd, *J* = 11.6, 8.4, 3.4 Hz, 1H), 2.78 (ddd, *J* = 11.4, 7.7, 3.5 Hz, 1H), 2.47 (d, *J* = 6.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.49; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.59, 145.37, 144.10, 135.78, 132.43, 129.93, 129.83, 129.13, 127.78, 127.18, 126.53, 125.98, 122.40, 118.67 (q, *J* = 319.5 Hz), 118.33 (q, *J* = 2.0 Hz), 46.52, 45.66, 45.48, 40.94, 21.5 (signal for one carbon could not be located); HRMS Calcd for $C_{23}H_{22}O_6N_2F_3S_2[M+H]^+$: 543.0866, found: 543.0869.



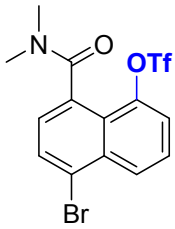
4-bromo-8-(dimethylcarbamoyl)naphthalen-1-yl trifluoromethanesulfonate (3i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.56 (d, *J* = 7.0 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 3.20 (s, 3H), 2.92 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.41; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.42, 144.94, 133.84, 131.96, 129.65, 128.92, 128.10, 128.08, 123.64, 123.15, 118.60 (q, *J* = 319.1 Hz), 118.28 (q, *J* = 2.1 Hz), 39.16, 34.89; HRMS Calcd for $C_{14}H_{12}NO_4SF_3Br[M+H]^+$: (425.9617, 427.9597), found:(425.9613, 427.9591).



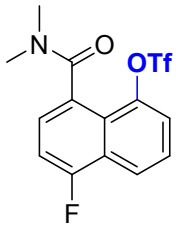
8-(dimethylcarbamoyl)-5-methylnaphthalen-1-yl trifluoromethanesulfonate (3j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 5.5, 4.0 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 3.19 (s, 3H), 2.93 (s, 3H), 2.73 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.51; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.30, 145.92, 136.00, 135.06, 129.53, 127.42, 126.99, 125.46, 125.02, 122.76, 118.68(q, *J* = 318.9 Hz), 117.87 (q, *J* = 2.1 Hz), 39.26, 34.90, 20.12; HRMS Calcd for $C_{15}H_{15}O_4NF_3S$ $[M+H]^+$: 362.0668, found: 362.0664.



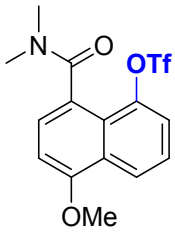
5-bromo-8-(dimethylcarbamoyl)naphthalen-1-yl trifluoromethanesulfonate (3k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.72 – 7.58 (m, 2H), 7.33 (d, *J* = 7.7 Hz, 1H), 3.19 (s, 3H), 2.93 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.42; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.20, 145.38, 134.10, 131.29, 130.91, 128.33, 127.23, 126.99, 124.06, 123.76, 118.89 (q, *J* = 2.2 Hz), 118.61 (q, *J* = 319.0 Hz), 39.15, 34.88; HRMS Calcd for $C_{14}H_{12}O_4NF_3SBr$ $[M+H]^+$: (425.9617, 427.9597), found: (425.9612, 427.9590).



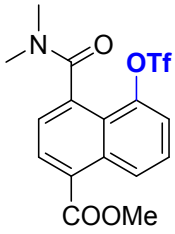
8-(dimethylcarbamoyl)-5-fluoronaphthalen-1-yl trifluoromethanesulfonate (3l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 6.5, 2.9 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.46 (dd, *J* = 7.9, 5.4 Hz, 1H), 7.34 – 7.28 (m, 1H), 3.22 (s, 3H), 2.95 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.50 (s), -118.18 (dd, *J* = 10.2, 5.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.27 (s), 158.53 (d, *J* = 255.7 Hz), 145.27,127.55 (d, *J* = 5.2 Hz), 127.37 (d, *J* = 9.0 Hz), 126.30, 124.05 (d, *J* = 4.1 Hz), 121.54 (d, *J* = 6.8 Hz), 119.34, 118.62 (q, *J* = 218.8 Hz), 110.48 (d, *J* = 20.5 Hz), 39.21 (s), 34.95 (s); HRMS Calcd for $C_{14}H_{12}O_4NF_4S$ $[M+H]^+$: 366.0418, found: 366.0419.



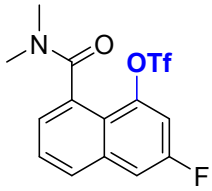
8-(dimethylcarbamoyl)-5-methoxynaphthalen-1-yl trifluoromethanesulfonate (3m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.50 (t, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 3H), 3.19 (s, 3H), 2.94 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.54; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.27, 155.84, 145.29, 128.00, 127.94, 124.94, 123.83, 123.17, 123.08, 118.93 (q, *J* = 2.0 Hz), 118.67 (q, *J* = 319.01 Hz), 104.32, 55.96, 39.29, 34.95; HRMS Calcd for $C_{15}H_{15}O_5NF_3S$ $[M+H]^+$: 378.0618, found: 378.0620.



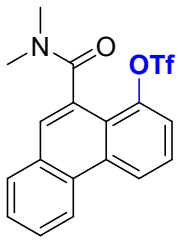
methyl 4-(dimethylcarbamoyl)-5-(((trifluoromethyl)sulfonyl)oxy)-1-naphthoate (3n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.23 (d, *J* = 7.5 Hz, 1H), 7.73 – 7.58 (m, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 4.03 (s, 3H), 3.21 (s, 3H), 2.91 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.43; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.31, 167.00, 145.61, 135.77, 133.63, 130.38, 128.50, 127.34, 126.63, 125.86, 122.94, 118.64 (q, *J* = 319.1 Hz), 118.29 (q, *J* = 2.0 Hz), 52.70, 39.00, 34.82; HRMS Calcd for $C_{16}H_{15}F_3O_6S$[M+H]$^+$: 406.0567, found: 406.0562.



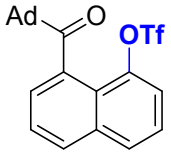
8-(dimethylcarbamoyl)-3-fluoronaphthalen-1-yl trifluoromethanesulfonate (3o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.56 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.46 – 7.39 (m, 2H), 3.20 (s, 3H), 2.91 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.48 (s), -111.18 (t, *J* = 9.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.65 (s), 158.74 (d, *J* = 248.5 Hz), 145.82 (d, *J* = 11.2 Hz), 135.58 (d, *J* = 9.8 Hz), 131.74 (s), 128.69 (d, *J* = 5.5 Hz), 127.77 (s), 126.40 (d, *J* = 2.7 Hz), 119.60 (d, *J* = 1.8 Hz), 118.58 (q, *J* = 319.0 Hz), ,112.20 (d, *J* = 19.9 Hz), 109.45 (dt, *J* = 30.0, 2.1 Hz), 39.10 (s), 34.85 (s); HRMS Calcd for $C_{14}H_{12}O_4NF_4S$[M+H]$^+$: 366.041, found: 366.0418.



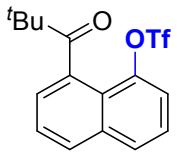
10-(dimethylcarbamoyl)phenanthren-1-yl trifluoromethanesulfonate (3p)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.2 Hz, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.80 – 7.59 (m, 5H), 3.24 (s, 3H), 3.03 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.41; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.00, 146.18, 133.51, 130.69, 129.47, 128.96, 128.77, 128.71, 128.43, 128.19, 126.79, 123.19, 123.05, 121.47, 118.69 (q, *J* = 319,1 Hz), 118.55 (q, *J* = 2.2 Hz), 39.30, 34.93; HRMS Calcd for $C_{18}H_{15}O_4NF_3S$ [M+H]$^+$: 398.0668, found: 398.0671.



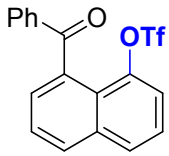
8-((3s)-adamantane-1-carbonyl)naphthalen-1-yl trifluoromethanesulfonate (3q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.90 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.62 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.58 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 7.1, 1.1 Hz, 1H), 2.08 – 1.57 (m, 15H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.89; ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.16, 145.74, 134.99, 134.96, 128.87, 128.85, 126.19, 126.07, 125.55, 122.29, 118.62 (q, *J* = 319.9 Hz), 117.37 (d, *J* = 1.8 Hz), 117.36, 38.32, 36.42, 27.96; HRMS Calcd for $C_{22}H_{22}O_4F_3S[M+H]^+$: 439.1185, found: 439.1182.



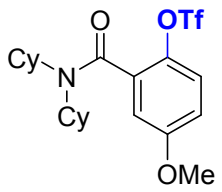
8-pivaloylnaphthalen-1-yl trifluoromethanesulfonate (3r)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 14.8, 8.2 Hz, 2H), 7.66 – 7.48 (m, 3H), 7.34 (d, *J* = 7.1 Hz, 1H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.00 (d, *J* = 3.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.85, 145.73, 135.39, 135.02, 128.98, 128.85, 126.24, 125.93, 125.63, 122.26, 118.6111 (q, *J* = 319.9 Hz), 45.94, 27.14; HRMS Calcd for $C_{16}H_{16}F_3O_4S[M+H]^+$: 361.0716, found: 361.0715.



8-benzoylnaphthalen-1-yl trifluoromethanesulfonate(3s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.01 – 7.92 (m, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.70 – 7.50 (m, 5H), 7.43 (t, *J* = 7.7 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.04; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.32, 145.03, 137.19, 135.48, 134.79, 133.46, 130.32, 130.23, 128.85, 128.63, 128.40, 126.31, 126.03, 123.26, 118.37, 118.31(q, *J* = 319.3 Hz); HRMS Calcd for $C_{18}H_{12}O_4F_3S[M+H]^+$: 381.0403, found: 381.0404.

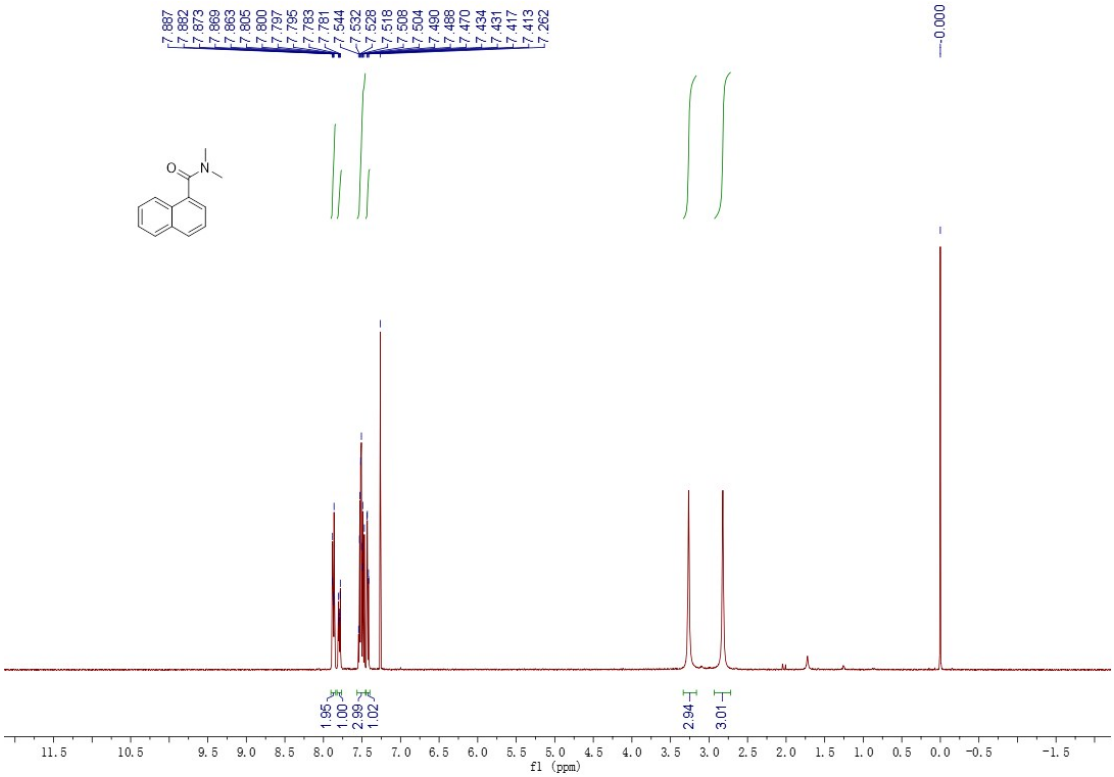


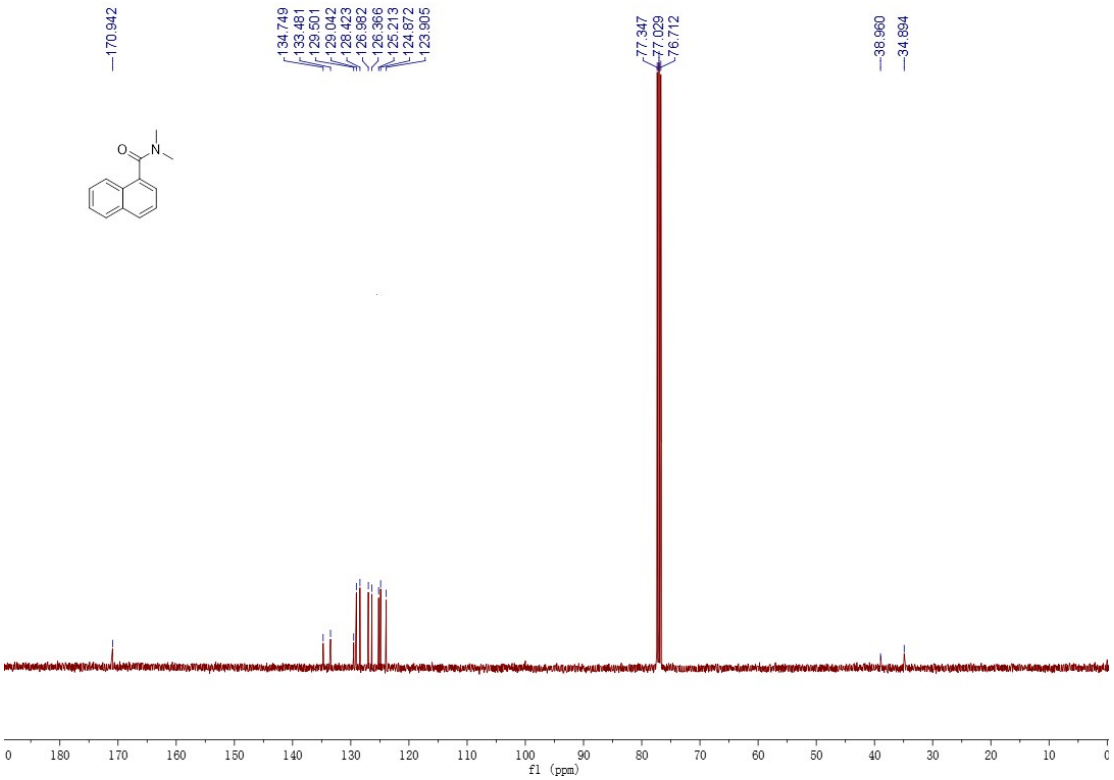
2-(dicyclohexylcarbamoyl)-4-methoxyphenyl trifluoromethanesulfonate (3t)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 4.2 Hz, 1H), 6.91 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.78 (d, *J* = 3.1 Hz, 1H), 3.82 (s, 3H), 3.20 (tt, *J* = 11.7, 3.4 Hz, 1H), 3.12 – 2.99 (m, 1H), 2.73 – 2.50 (m, 2H), 1.85 (s, 2H), 1.73 (d, *J* = 8.2 Hz, 2H), 1.65 (d, *J* = 16.4 Hz, 4H), 1.54 (d, *J* = 12.3 Hz, 2H), 1.50 – 1.46 (m, 1H), 1.31 – 1.23 (m, 4H), 1.05 (dd, *J* = 13.7, 5.8 Hz, 3H).^{9}F NMR (376 MHz, $CDCl_3$) δ -73.65; ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.81, 158.80, 138.54, 133.52, 122.70, 115.21, 112.35, 118.49 (q, *J* = 320.4 Hz) 60.16, 56.51, 55.89, 31.57, 30.81, 29.69, 29.41, 26.67, 26.57, 25.63, 25.56, 25.23, 25.10; HRMS Calcd for $C_{21}H_{29}O_5NF_3S$ $[M+H]^+$: 464.1713, found: 464.1711.

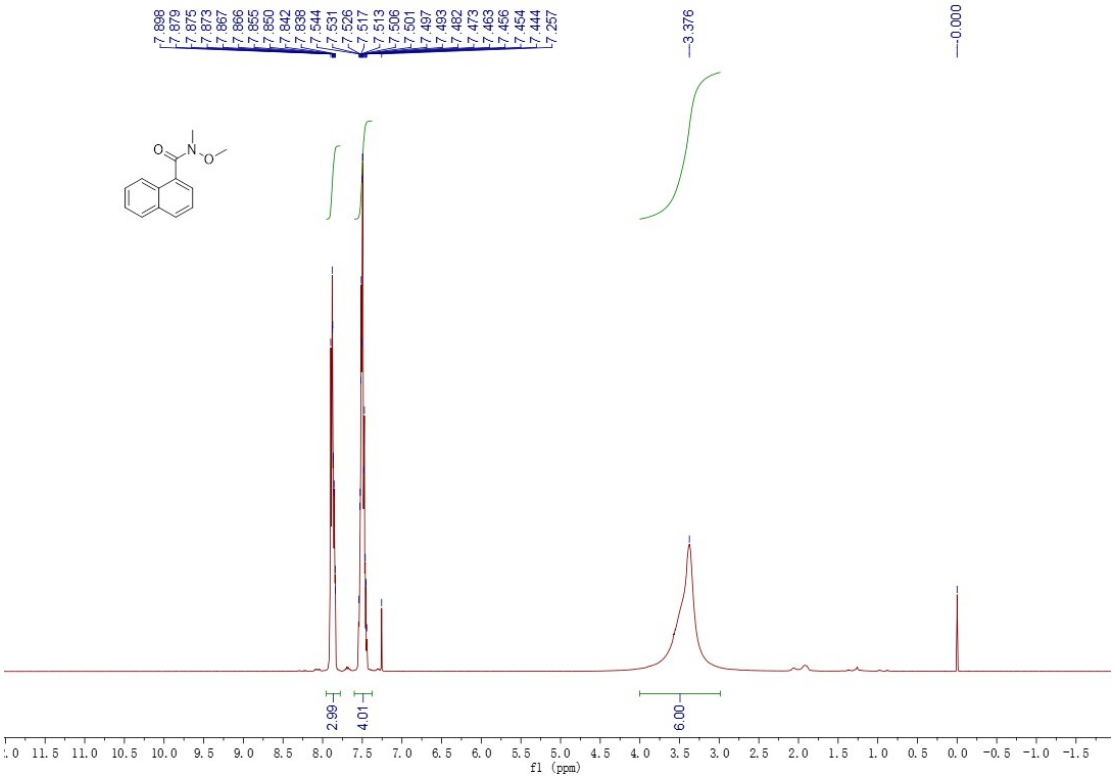
NMR Spectra of Compounds

1a





1b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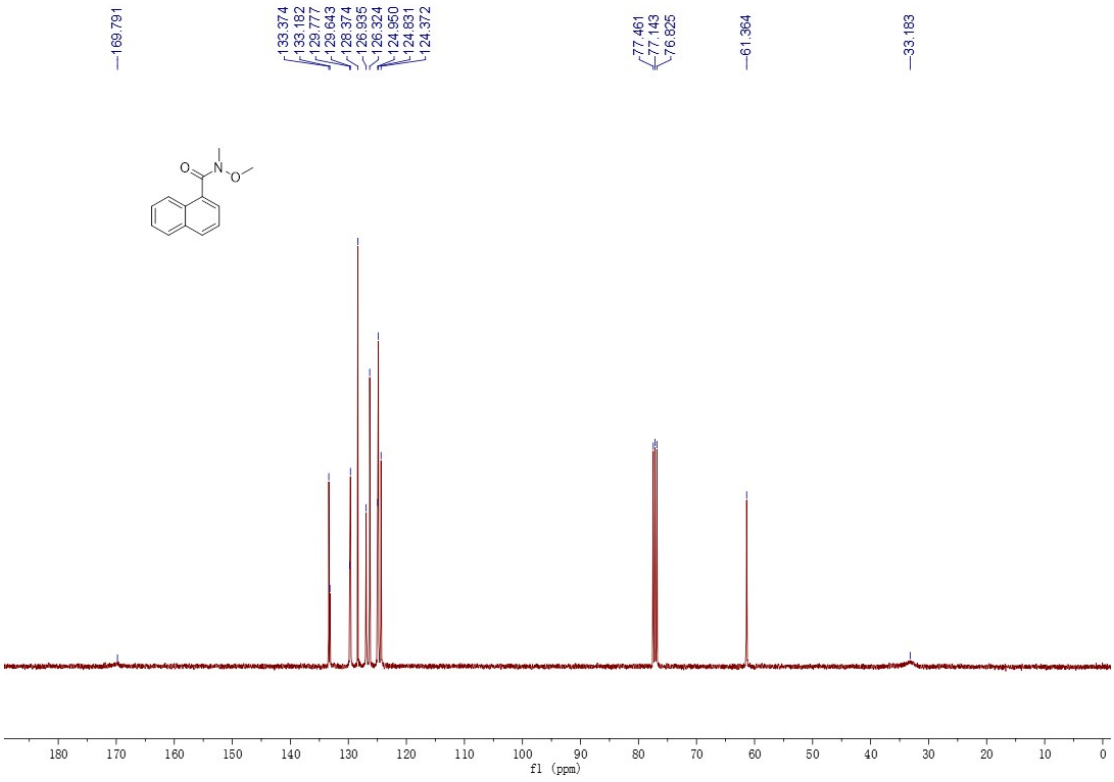
7.855
7.850
7.842
7.838
7.544
7.531
7.526
7.517
7.513
7.506
7.501
7.497
7.493
7.482
7.473
7.463
7.456
7.454
7.444
7.257
3.376
0.000
2.99
4.01
6.00
f1 (ppm)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128.374
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126.324
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124.372
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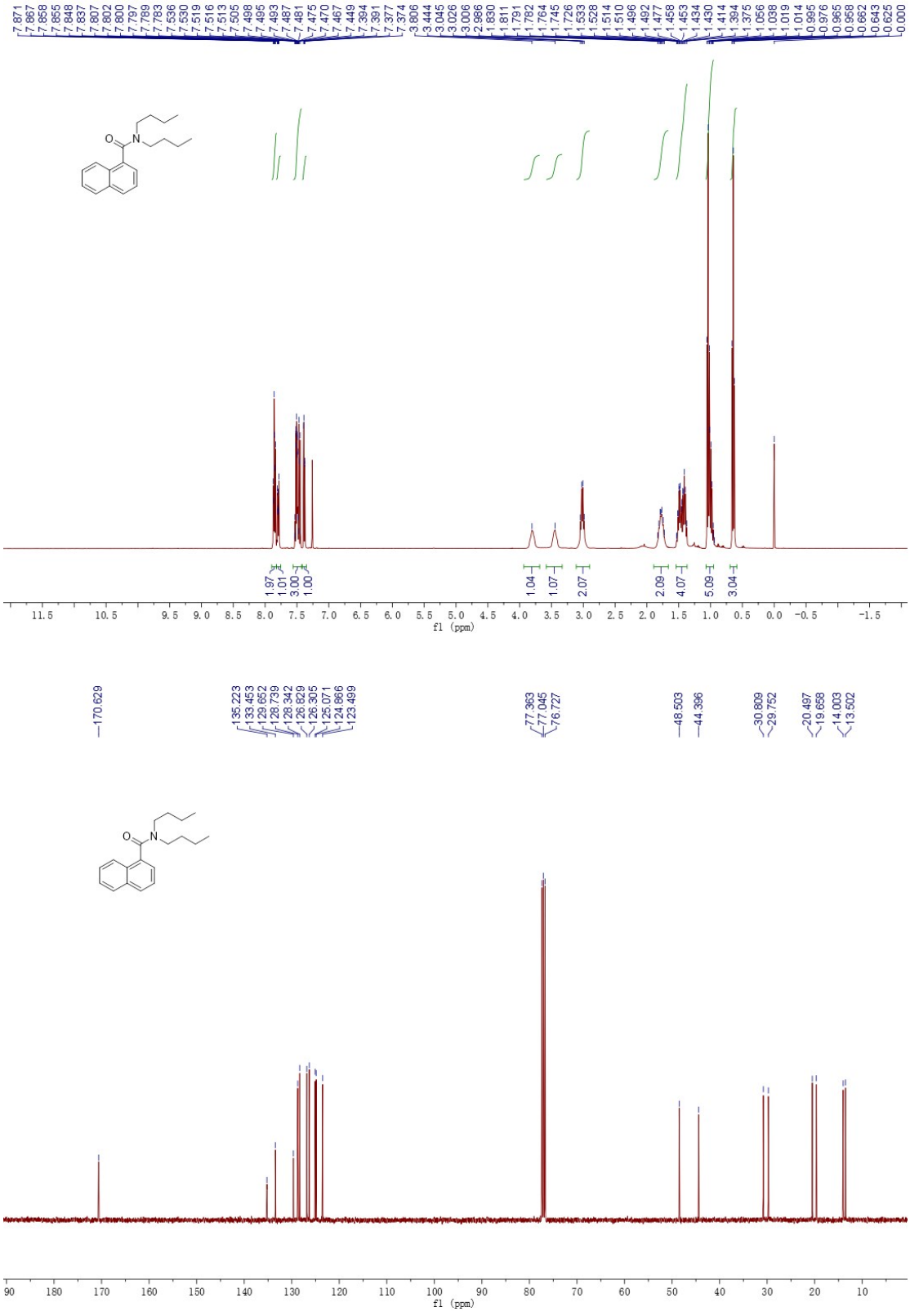
76.825
61.364
33.183
f1 (ppm)

1c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7.802
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7.797
7.789
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7.530
7.519
7.516
7.513
7.505
7.498
7.495
7.493
7.487
7.481
7.475
7.470
7.467
7.449
7.394
7.391
7.377
7.374
3.806
3.444
3.045
3.026
3.006
2.986
1.830
1.811
1.791
1.782
1.764
1.745
1.726
1.533
1.528
1.514
1.510
1.496
1.492
1.477
1.458
1.453
1.434
1.430
1.414
1.394
1.375
1.056
1.038
1.019
1.014
0.995
0.976
0.965
0.958
0.662
0.643
0.625
0.000
1.97
1.01
3.00
1.00
1.04
1.07
2.07
2.09
4.07
5.09
3.04
f1 (ppm)
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135.223
133.453
129.652
128.739
128.342
126.829
126.305
125.071
124.866
123.499
77.363
77.045
76.727
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44.396
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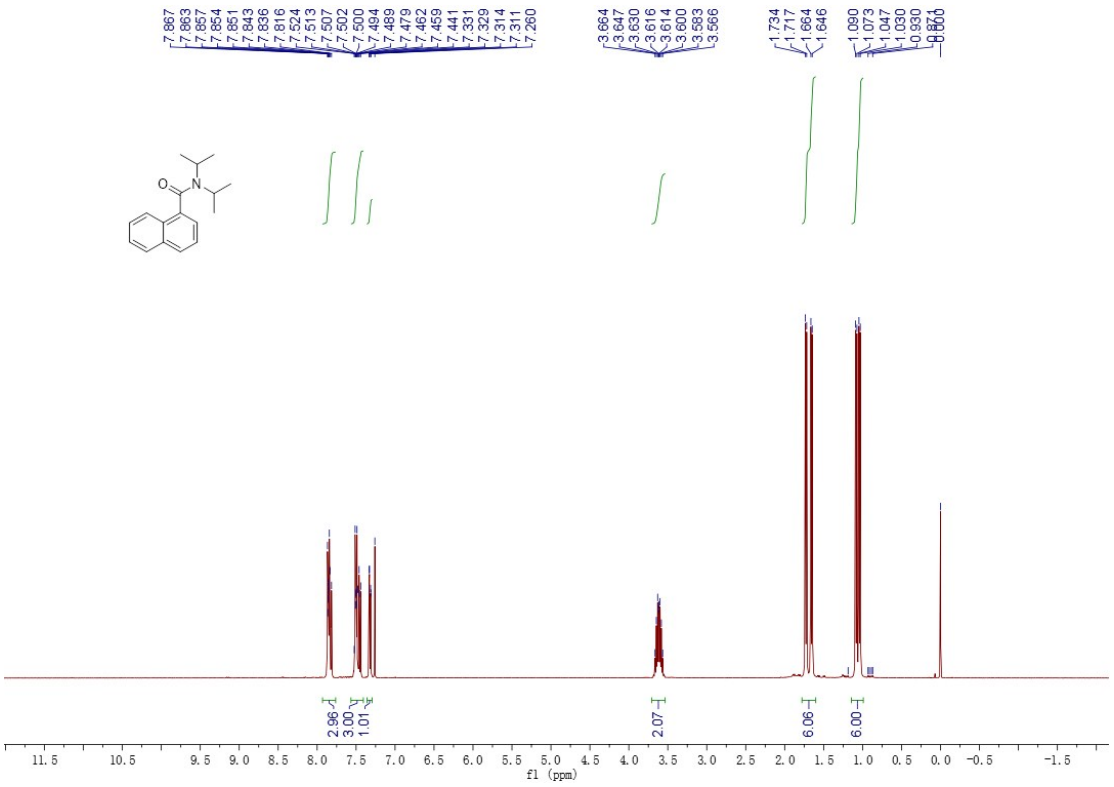
29.752
20.497
19.658
14.003
13.502
f1 (ppm)

1d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7.857
7.854
7.851
7.843
7.836
7.816
7.524
7.513
7.507
7.502
7.500
7.494
7.489
7.479
7.462
7.459
7.441
7.331
7.329
7.314
7.311
7.260
3.664
3.647
3.630
3.616
3.614
3.600
3.583
3.566
1.734
1.717
1.664
1.646
1.090
1.073
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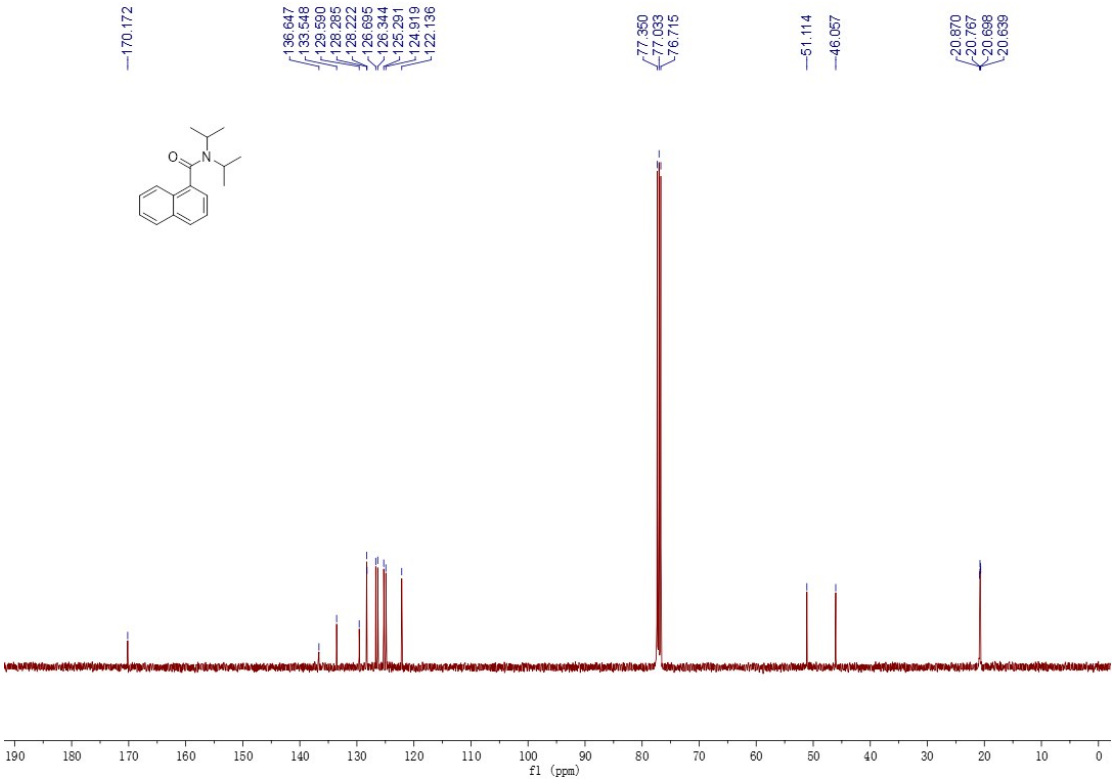
1.030
0.930
2.96
3.00
1.01
2.07
6.06
6.00
f1 (ppm)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128.285
128.222
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125.291
124.919
122.136
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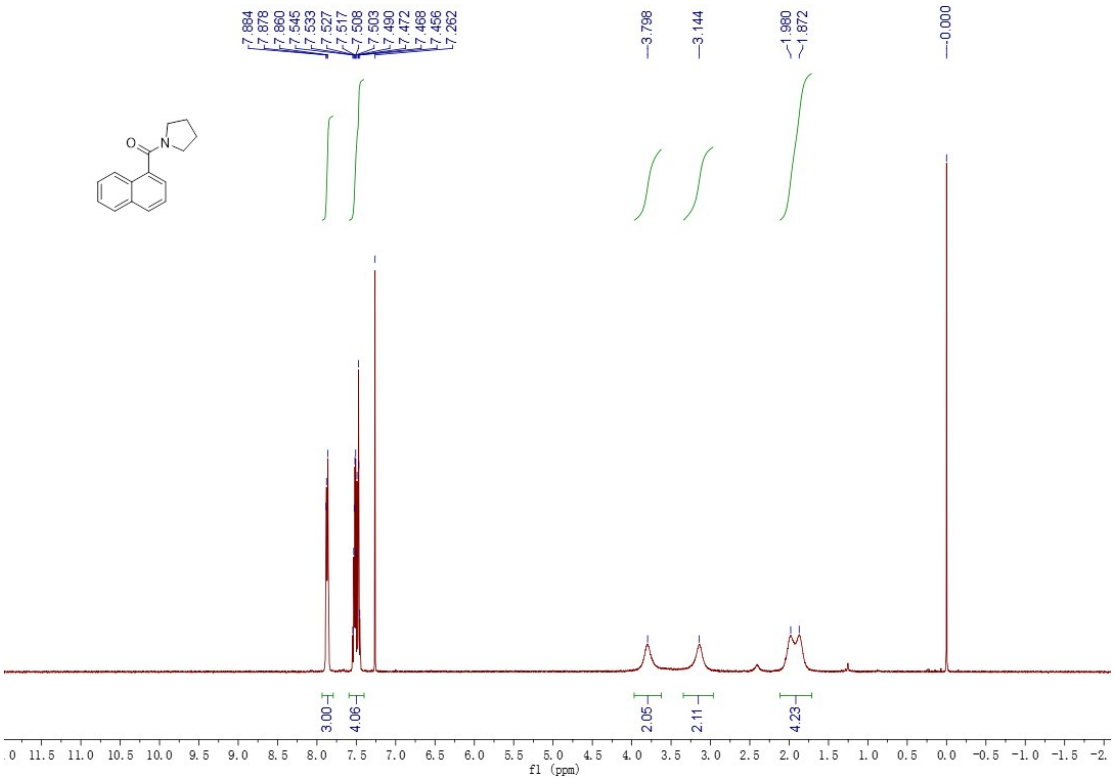
77.033
76.715
51.114
46.057
20.870
20.767
20.698
20.639
f1 (ppm)

1e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7.517
7.508
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7.490
7.472
7.468
7.456
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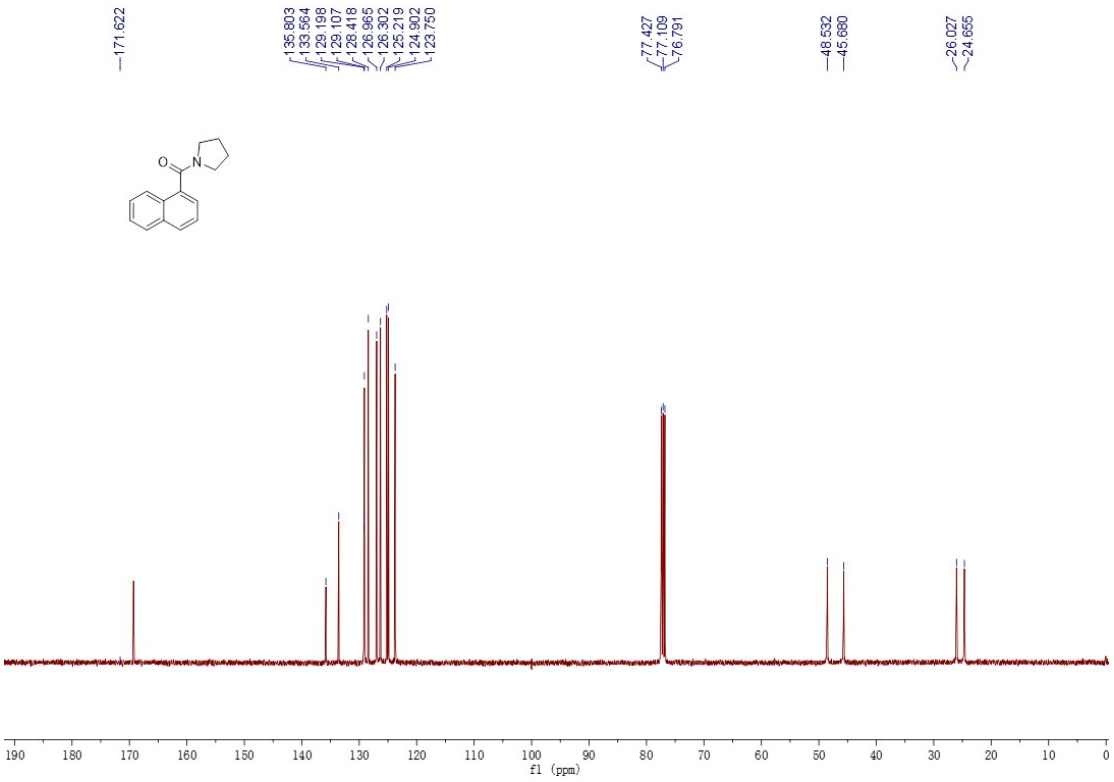
1.980
1.872
0.000
3.00
4.06
2.05
2.11
4.23
f1 (ppm)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126.302
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77.427
77.109
76.791
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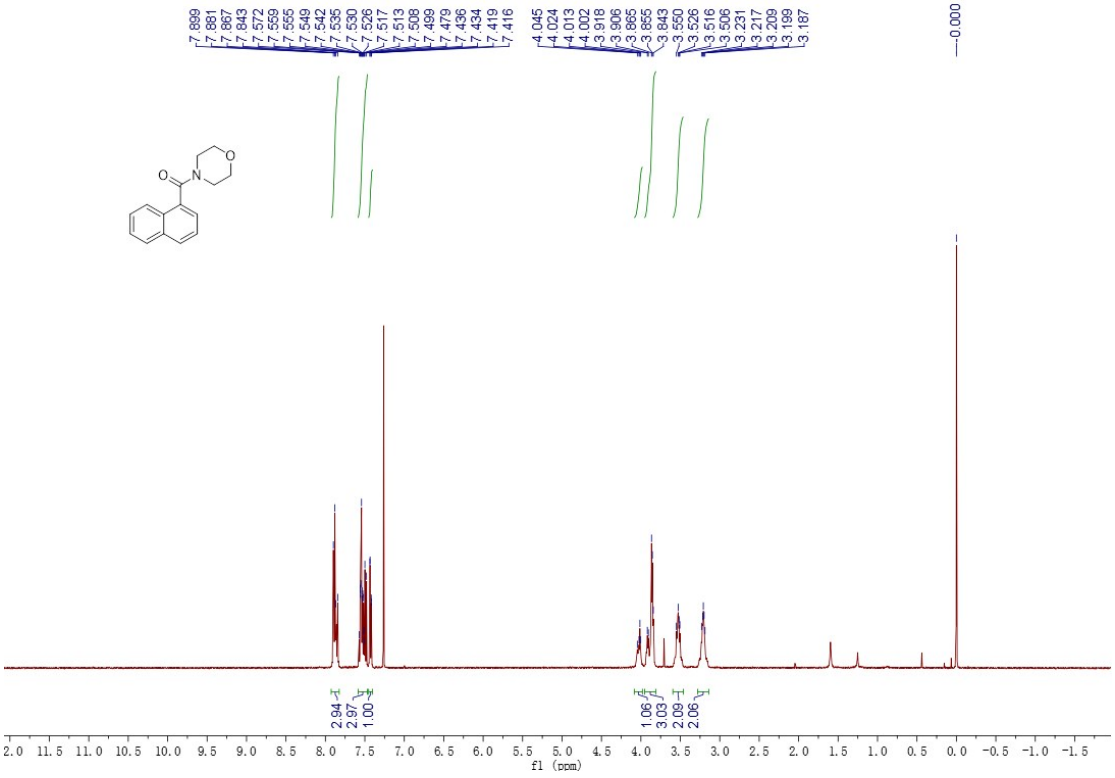
45.680
26.027
24.655
f1 (ppm)

1f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7.555
7.549
7.542
7.536
7.530
7.526
7.517
7.513
7.508
7.499
7.479
7.436
7.434
7.419
7.416
4.045
4.024
4.013
4.002
3.918
3.906
3.885
3.855
3.843
3.550
3.526
3.516
3.506
3.231
3.217
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3.199
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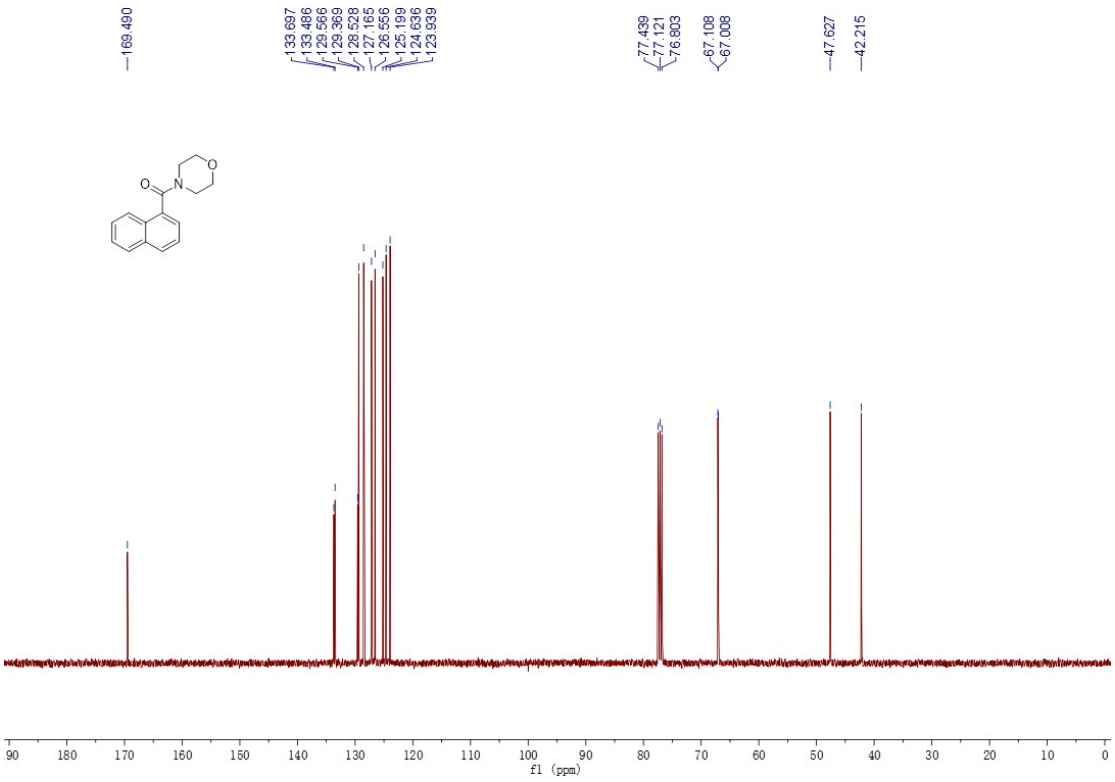
2.97
1.00
1.06
3.03
2.09
2.06
f1 (ppm)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129.369
128.528
127.165
126.556
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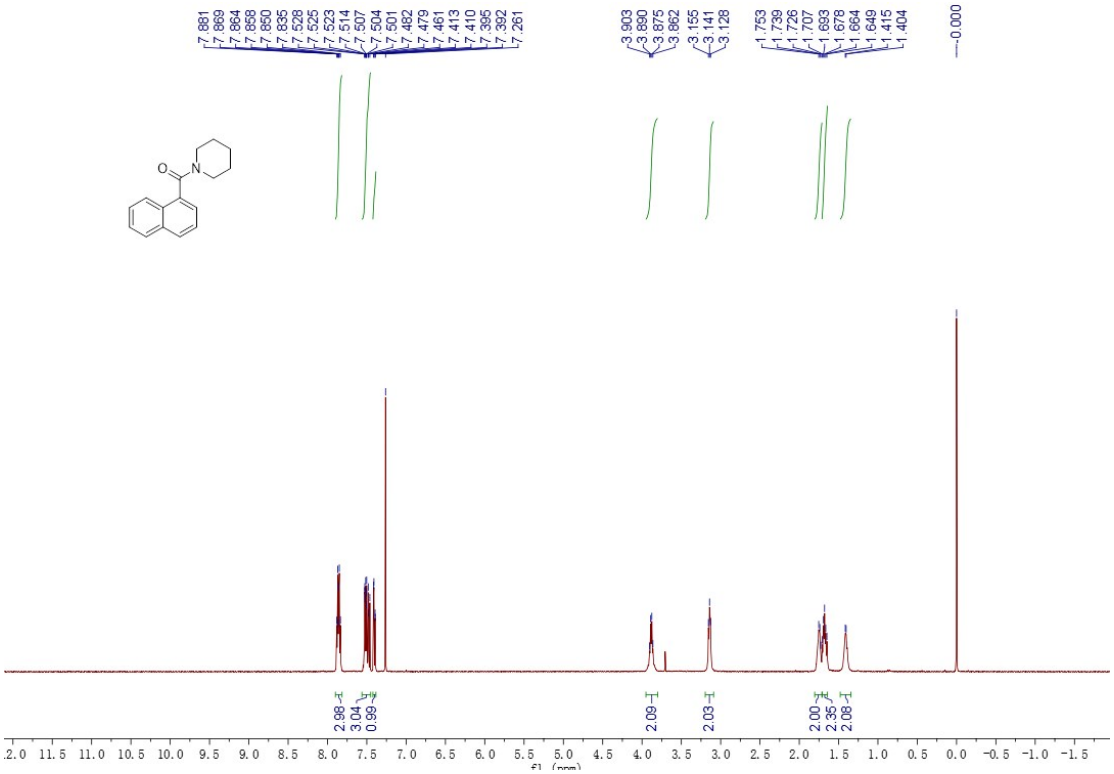
77.121
76.803
67.108
67.008
47.627
42.215
f1 (ppm)

1g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7.501
7.482
7.479
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7.410
7.395
7.392
7.261
3.903
3.890
3.875
3.862
3.155
3.141
3.128
1.753
1.739
1.726
1.707
1.693
1.678
1.664
1.649
1.415
1.404
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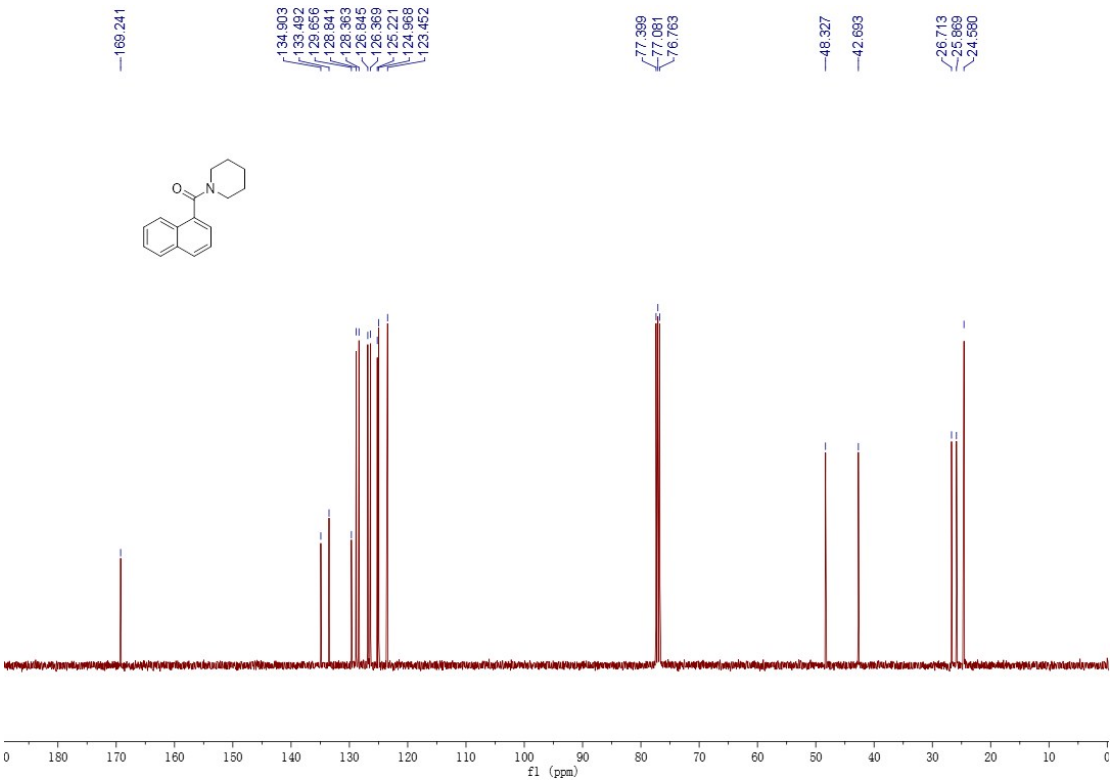
3.04
0.99
2.09
2.03
2.00
2.35
2.08
f1 (ppm)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25.869
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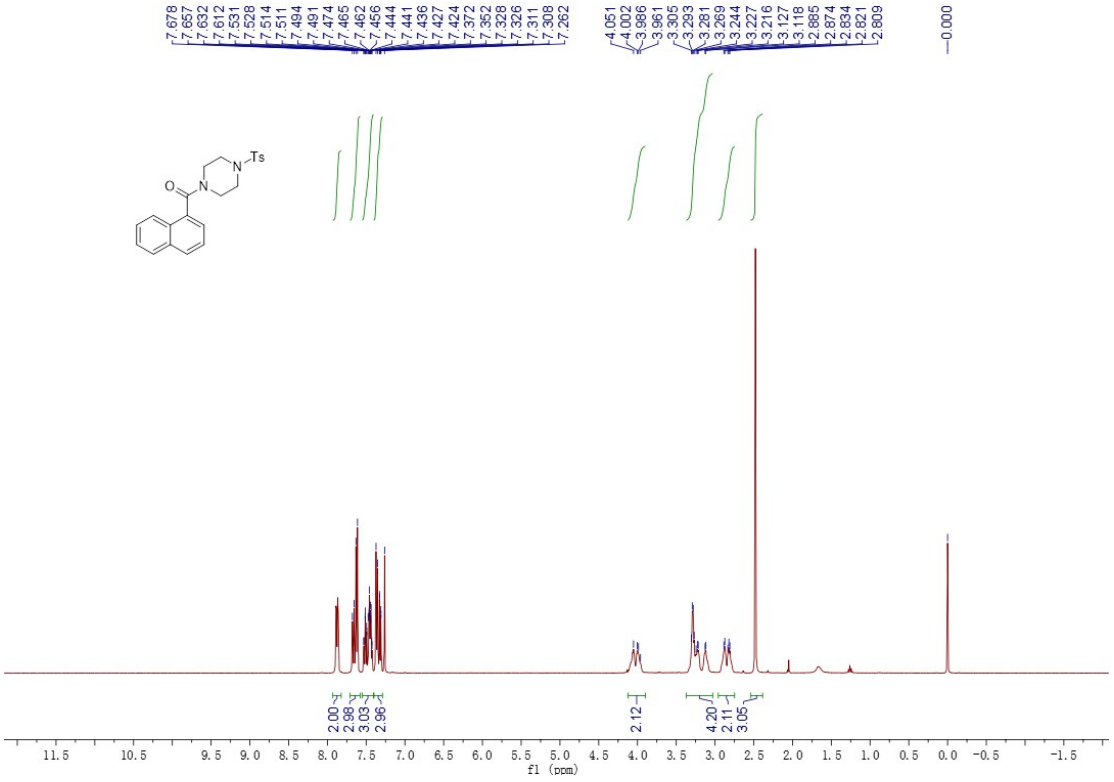
f1 (ppm)

1h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7.511
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7.491
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7.462
7.456
7.444
7.441
7.436
7.427
7.424
7.372
7.362
7.328
7.326
7.311
7.308
7.262
4.051
4.002
3.986
3.961
3.305
3.293
3.281
3.269
3.244
3.227
3.216
3.127
3.118
2.885
2.874
2.834
2.821
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Ts
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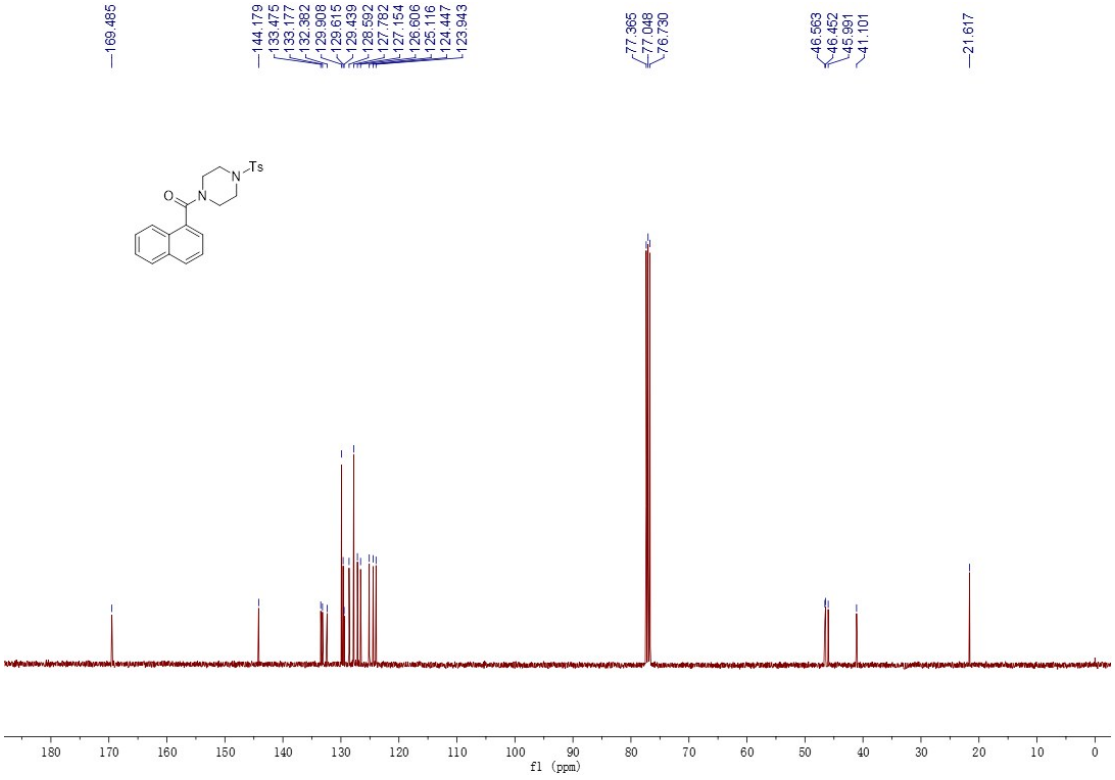
3.03
2.96
2.12
4.20
2.11
3.05
f1 (ppm)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128.592
127.782
127.154
126.606
125.116
124.447
123.943
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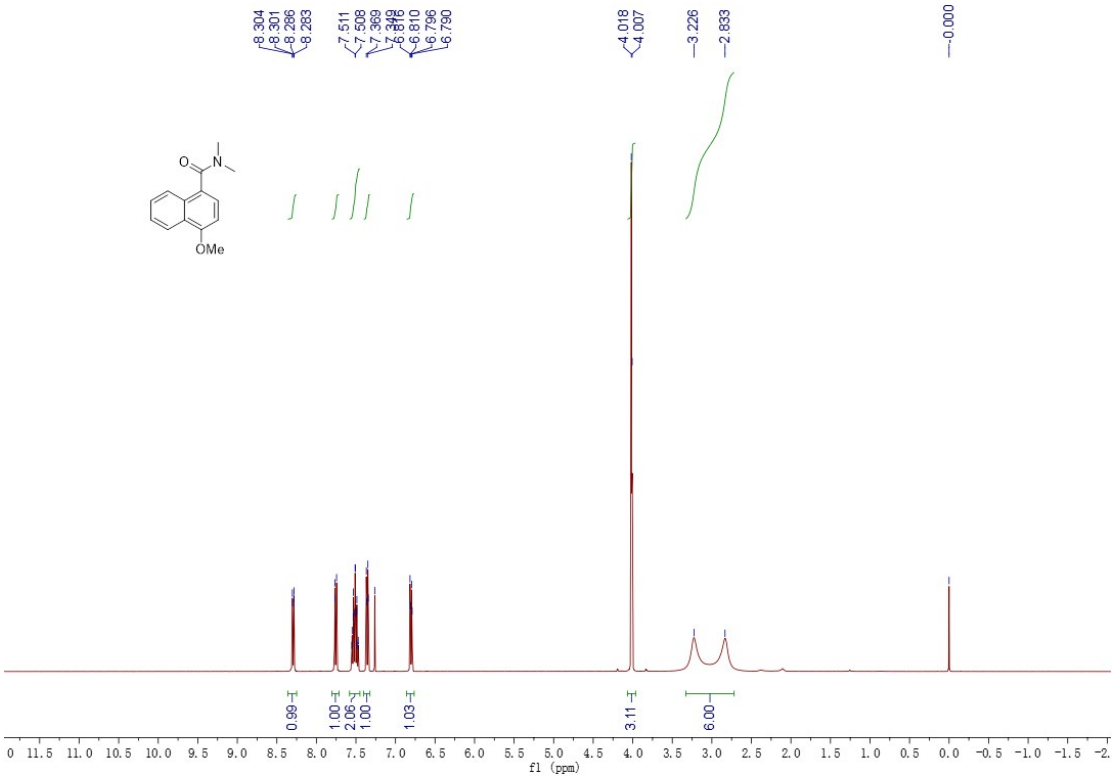
77.048
76.730
46.563
46.452
45.991
41.101
21.617
Ts
f1 (ppm)

1i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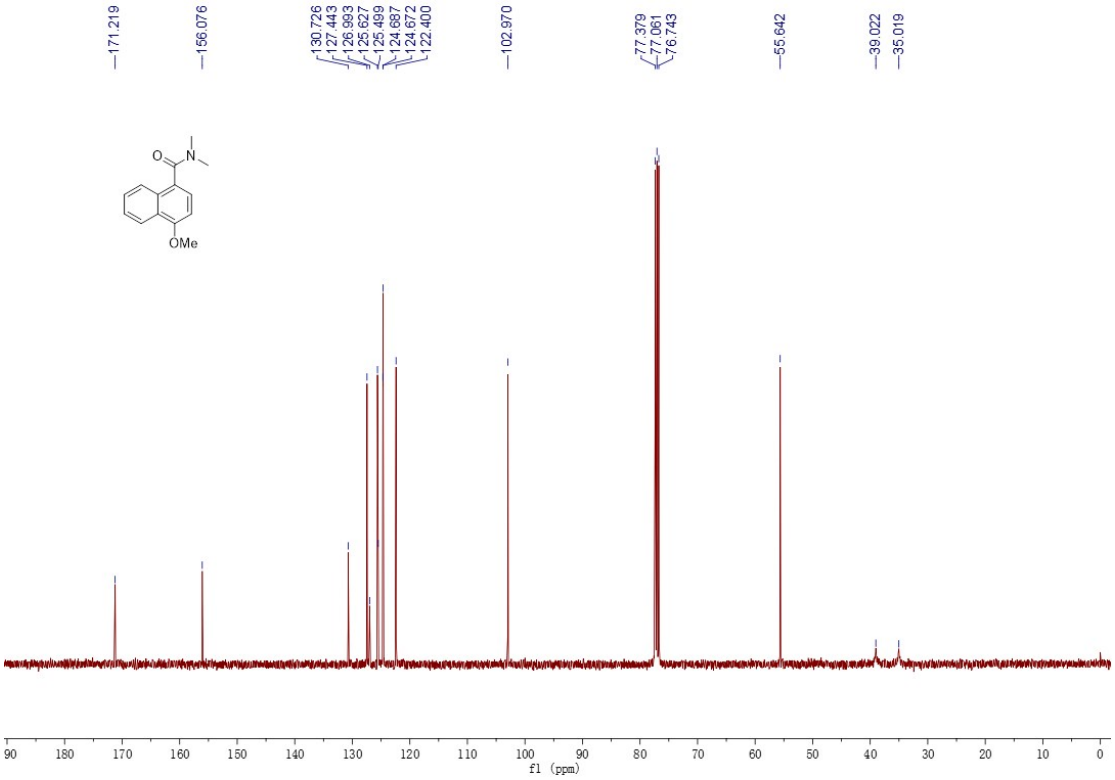
7.346
6.816
6.810
6.796
6.790
4.018
4.007
3.226
2.833
0.000
O
N
OMe
0.99
1.00
2.06
1.00
1.03
3.11
6.00
f1 (ppm)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77.061
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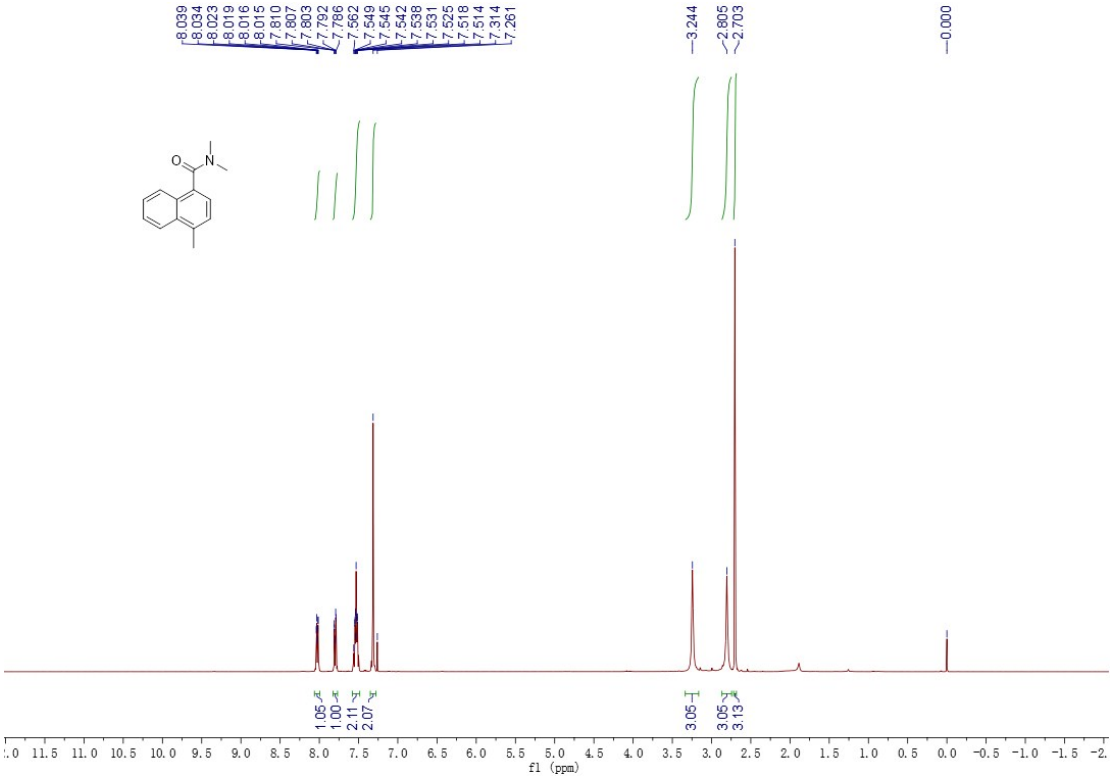
55.642
39.022
35.019
O
N
OMe
f1 (ppm)

1j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7.549
7.545
7.542
7.538
7.531
7.525
7.518
7.514
7.314
7.261
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1.00
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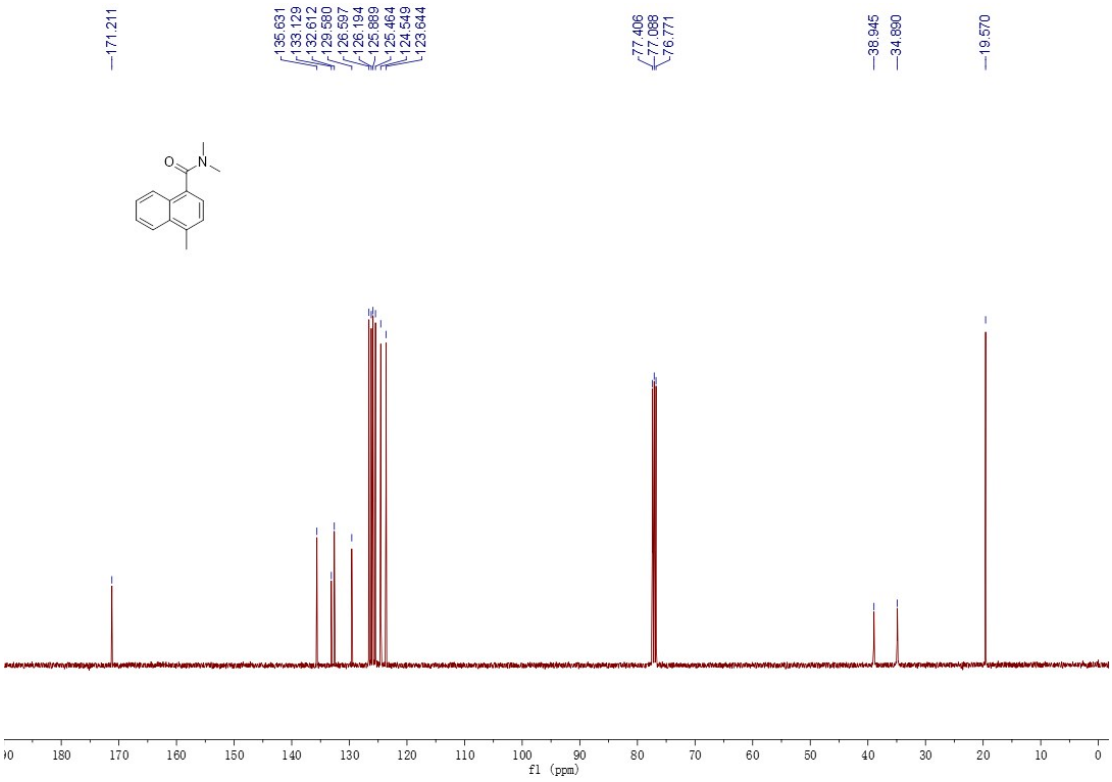
2.07
3.05
3.05
3.13
f1 (ppm)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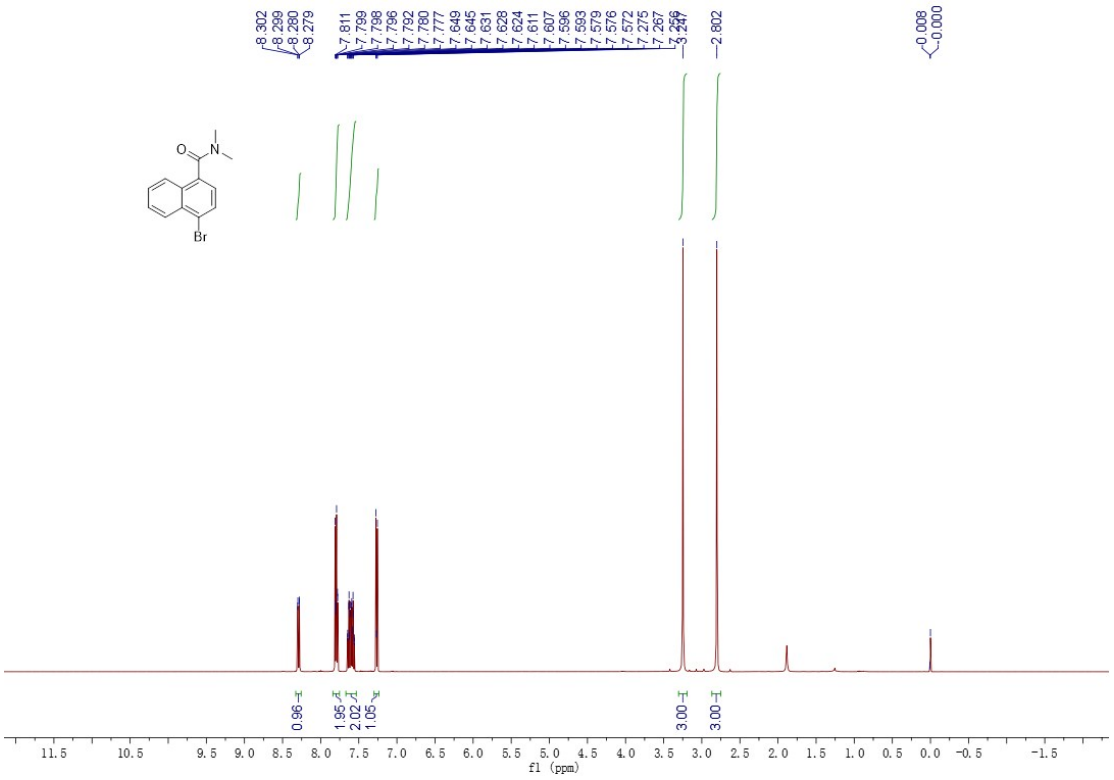
19.570
f1 (ppm)

1k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8.279
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7.780
7.777
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7.645
7.631
7.628
7.624
7.611
7.607
7.596
7.593
7.579
7.576
7.572
7.275
7.267
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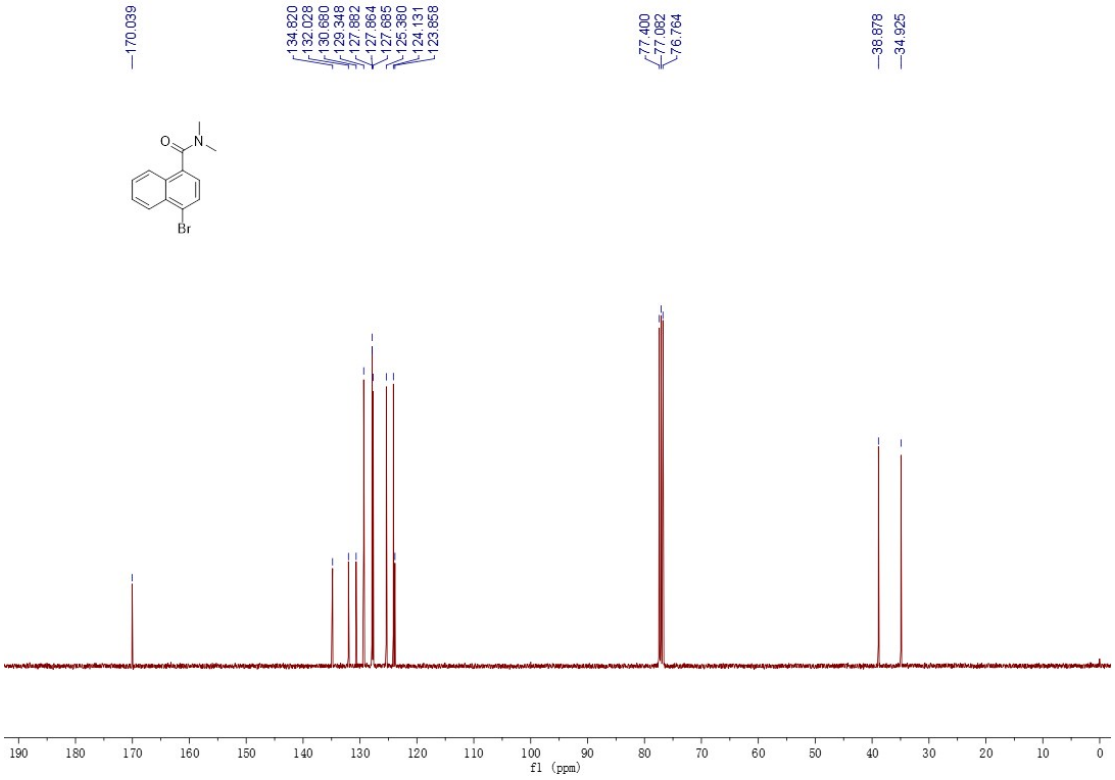
0.000
O
N
Br
0.96
1.95
2.02
1.05
3.00
3.00
f1 (ppm)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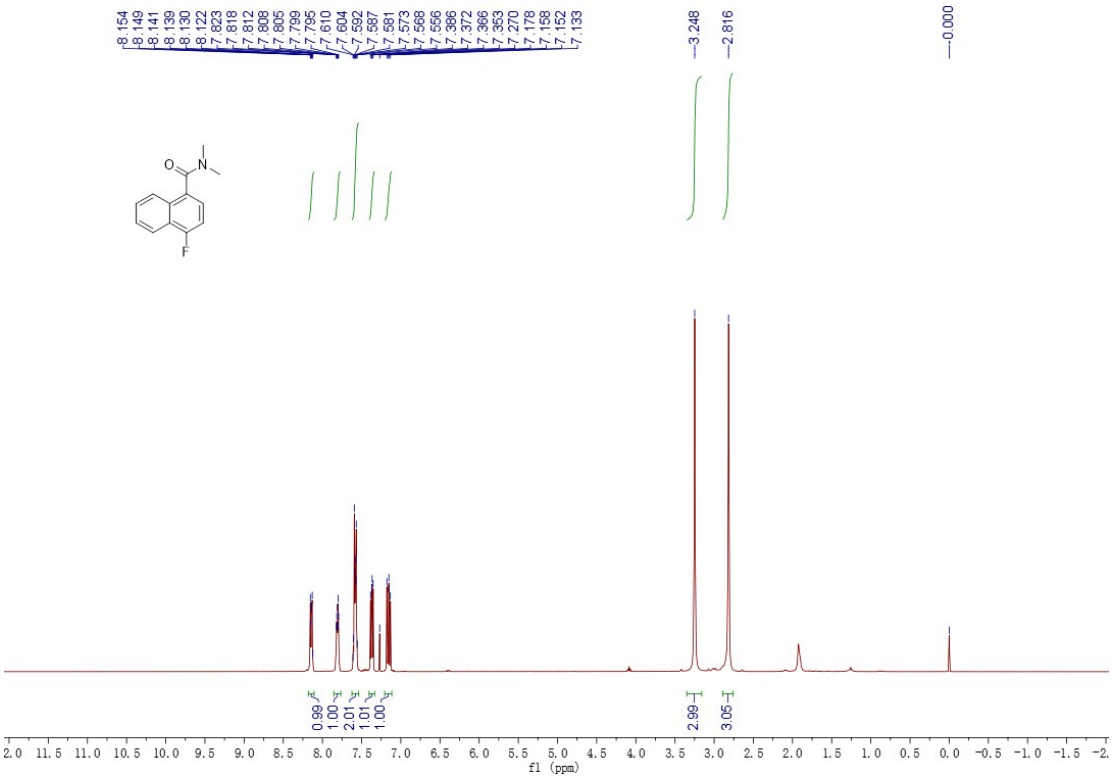
76.764
38.878
34.925
O
N
Br
f1 (ppm)

1l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7.587
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7.366
7.353
7.270
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7.158
7.152
7.133
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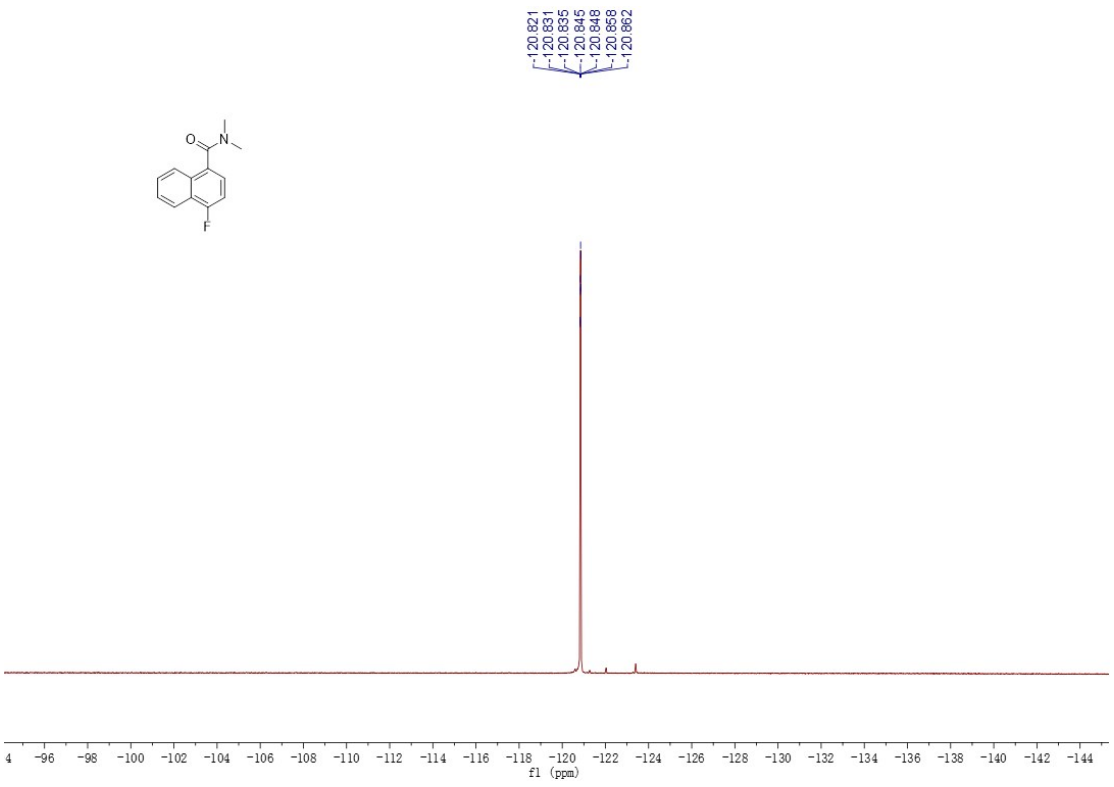
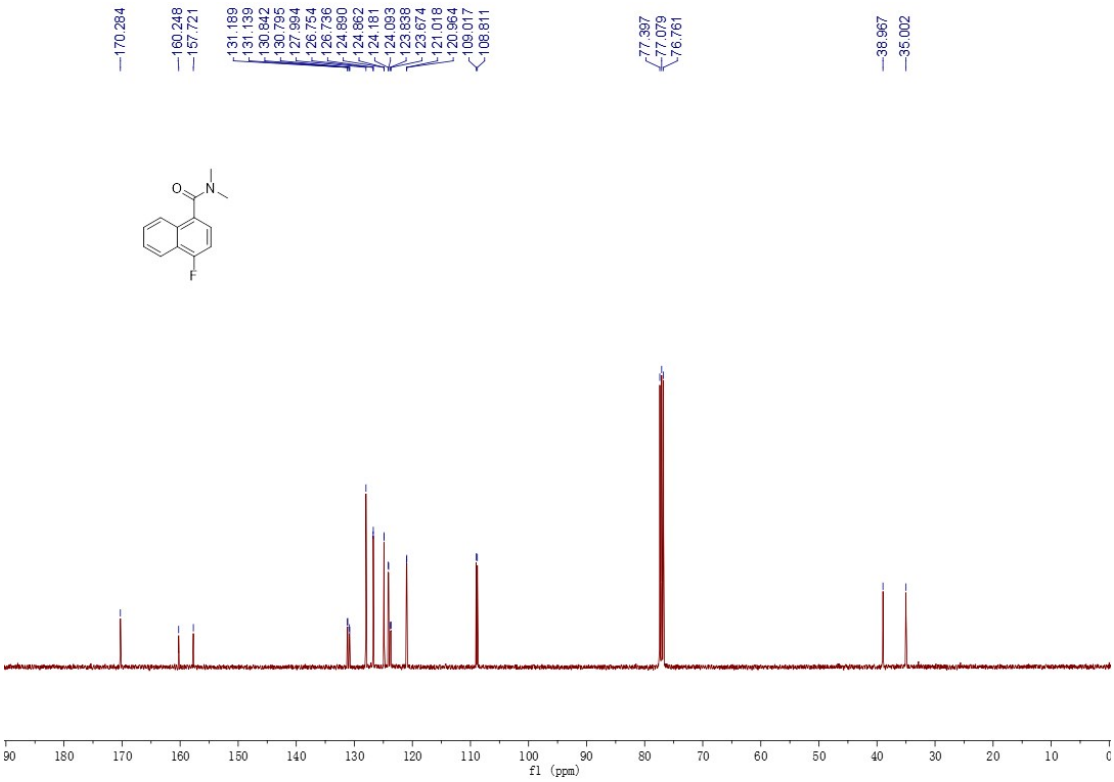
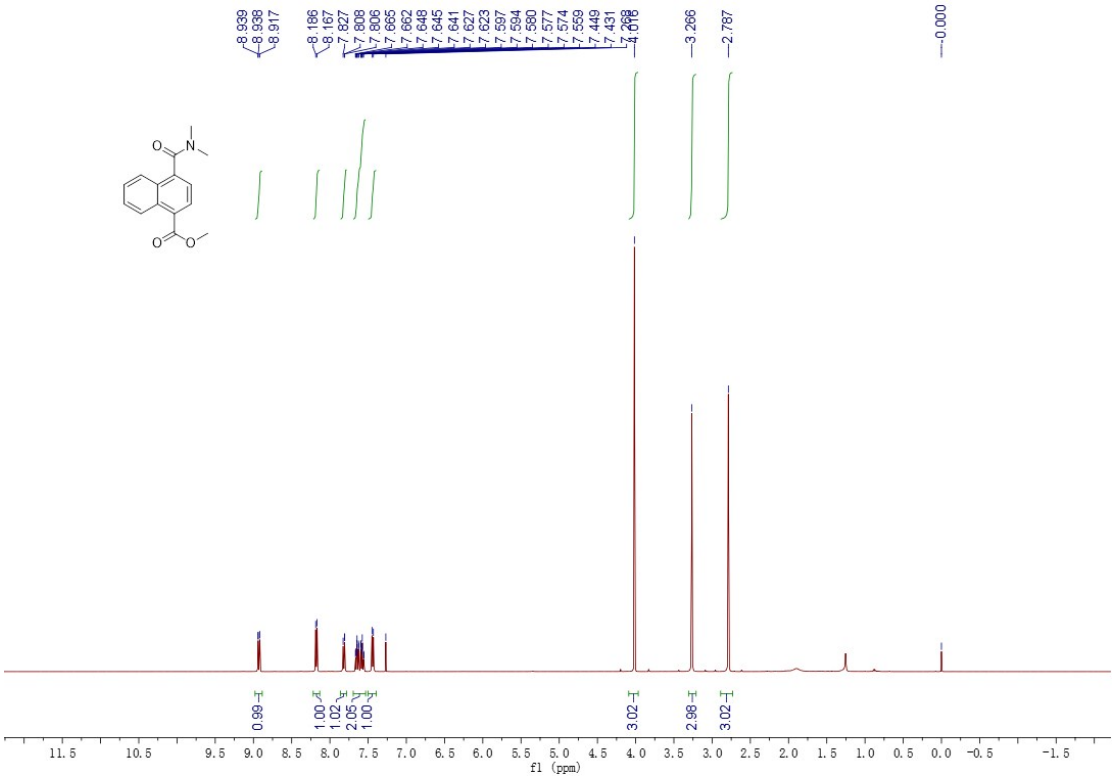
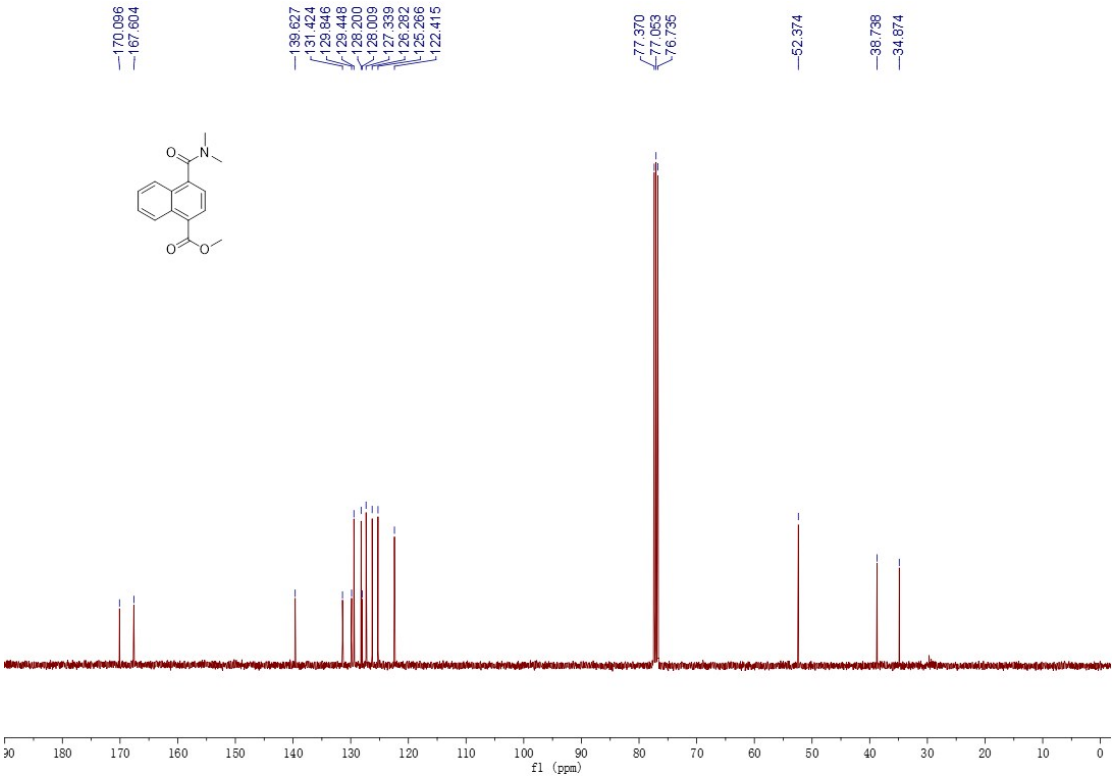
2.816
0.000
0.99
1.00
2.01
1.01
1.00
2.99
3.05
f1 (ppm)


120.821
120.831
120.835
120.845
120.848
120.858
120.862
f1 (ppm)

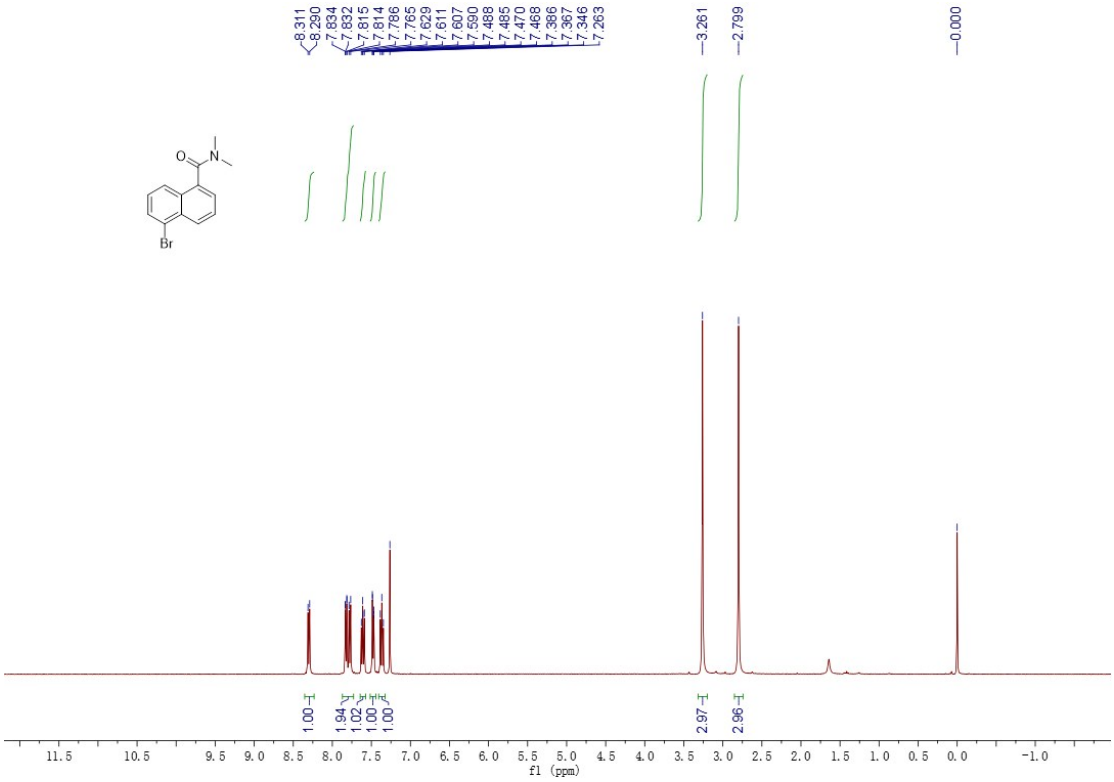

170.284
160.248
157.721
131.189
131.139
130.842
130.795
127.994
126.754
126.736
124.890
124.862
124.181
124.093
123.838
123.674
121.018
120.964
109.017
108.811
77.397
77.079
76.761
38.967
35.002
O
N
F
f1 (ppm)

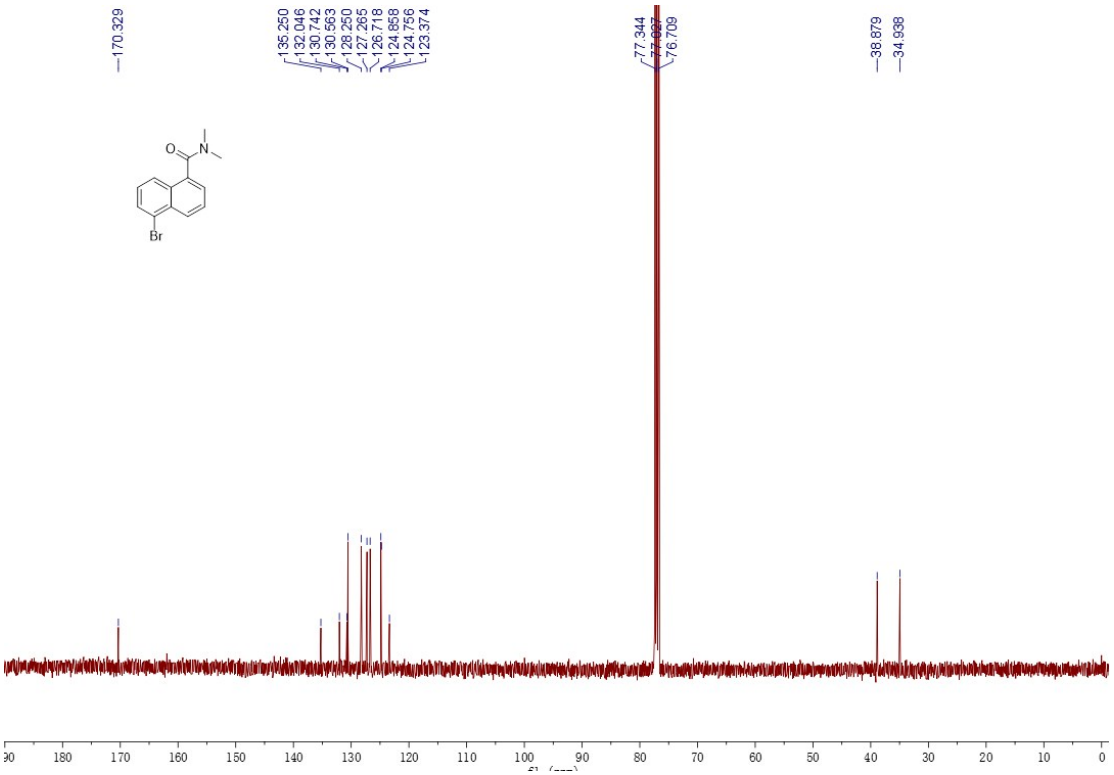
1m


8.939
8.938
8.917
8.186
8.167
7.827
7.808
7.806
7.665
7.662
7.648
7.645
7.641
7.627
7.623
7.597
7.594
7.580
7.577
7.574
7.559
7.449
7.431
4.016
3.266
2.787
0.000
0.99
1.00
1.02
2.05
1.00
3.02
2.98
3.02
f1 (ppm)

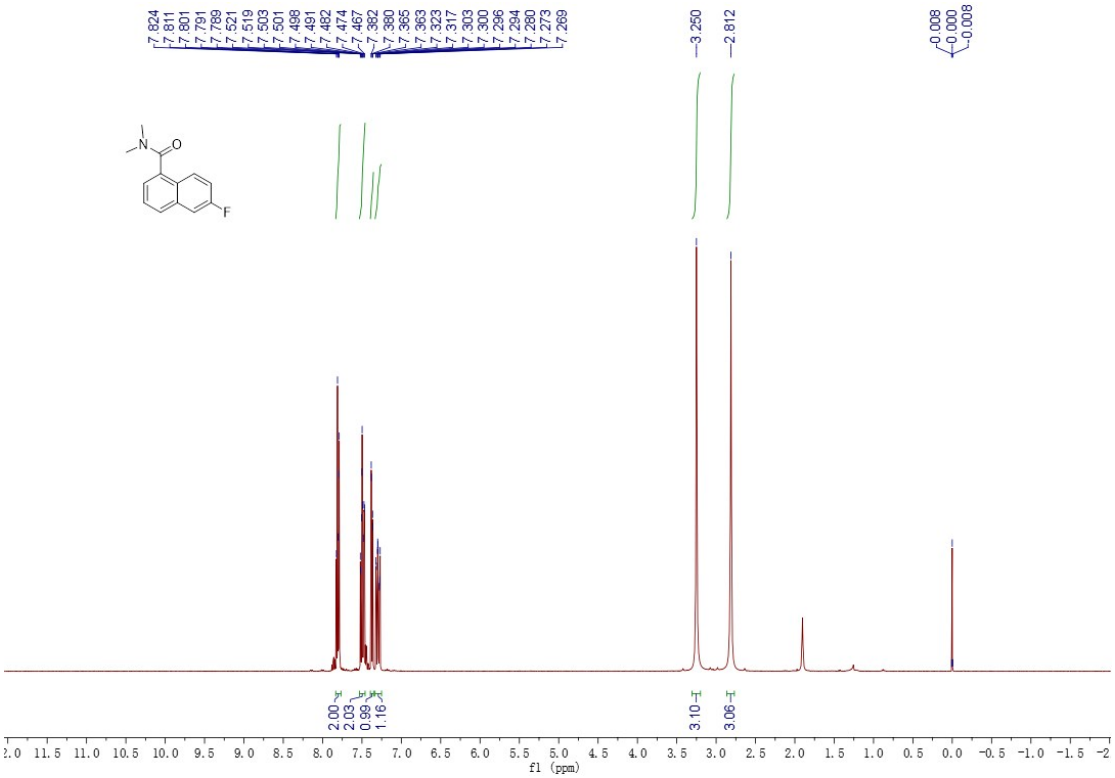

170.096
167.604
139.627
131.424
129.846
129.448
128.200
128.009
127.339
126.282
125.266
122.415
77.370
77.053
76.735
52.374
38.738
34.874
f1 (ppm)

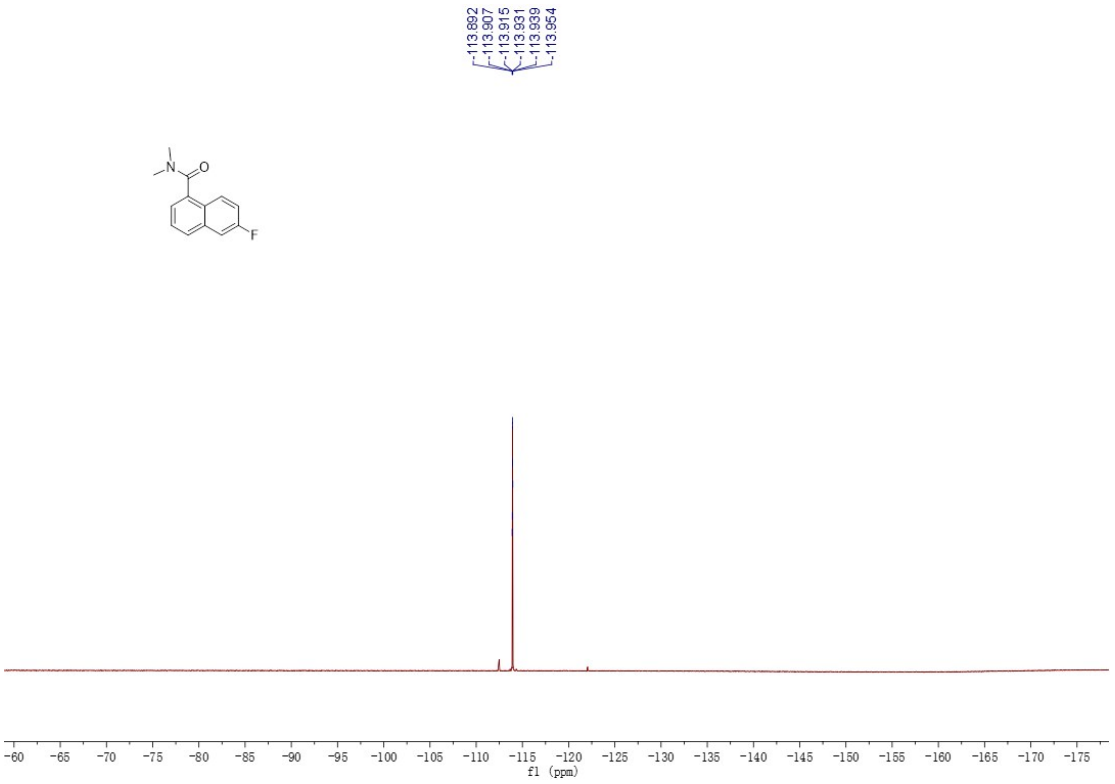
1n

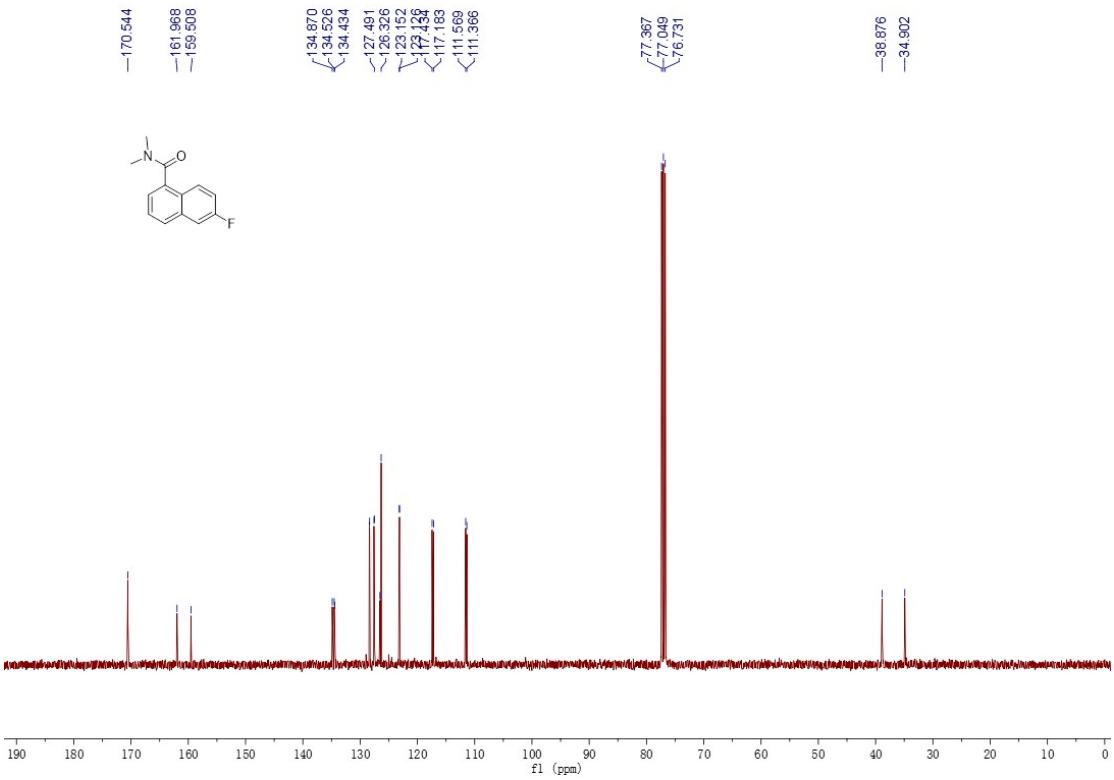

8.311
8.290
7.834
7.832
7.815
7.814
7.786
7.765
7.629
7.611
7.607
7.590
7.488
7.485
7.470
7.468
7.386
7.367
7.346
7.263
3.261
2.799
0.000
1.00
1.94
1.02
1.00
1.00
2.97
2.96
f1 (ppm)


170.329
135.250
132.046
130.742
130.563
128.250
127.265
126.718
124.858
124.756
123.374
77.344
77.032
76.709
38.879
34.938

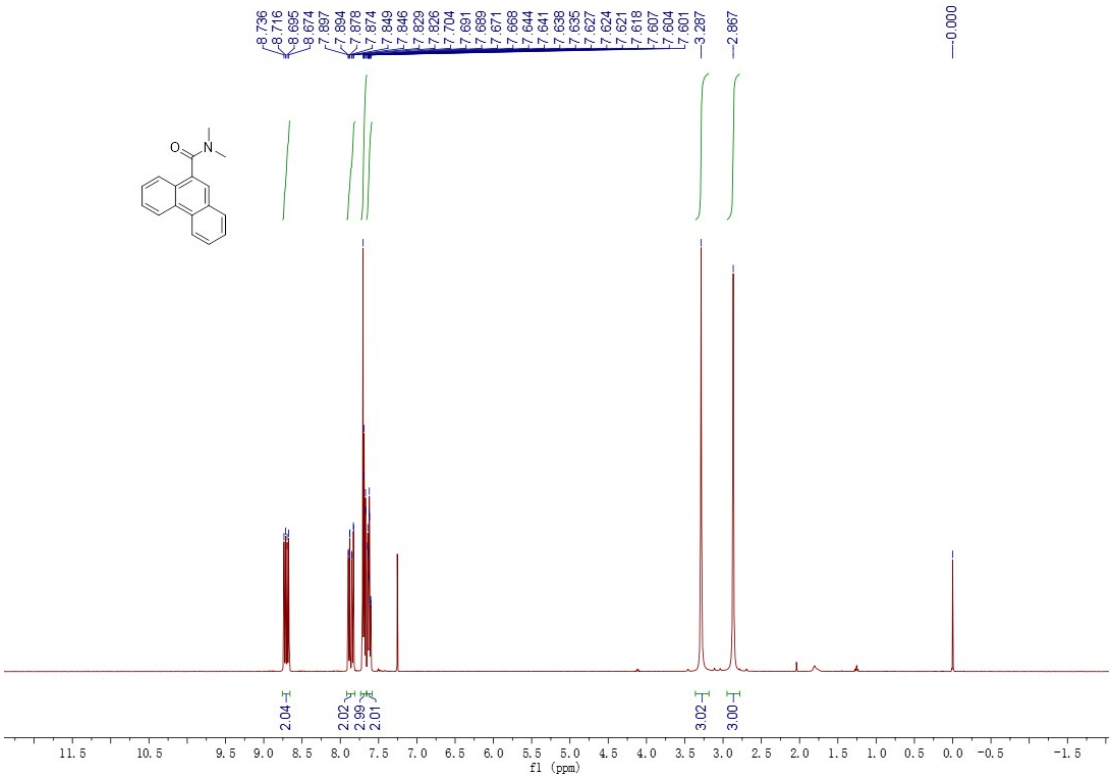
1o

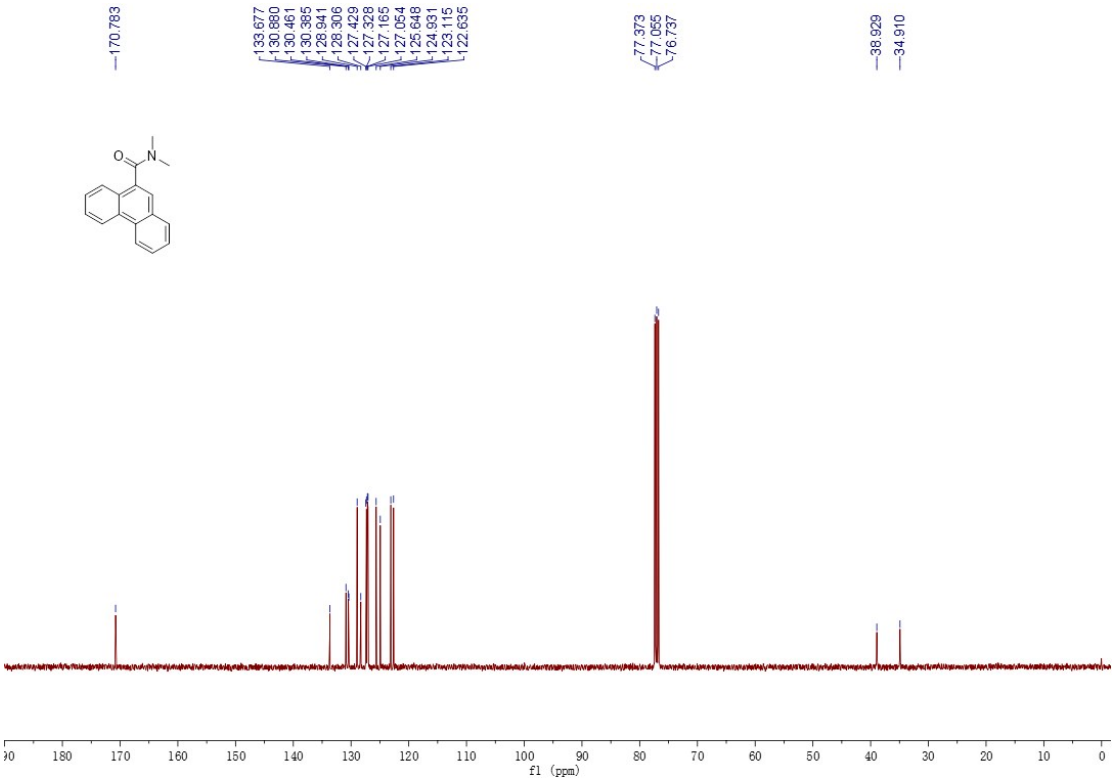

7.824
7.811
7.801
7.791
7.789
7.521
7.519
7.503
7.501
7.498
7.491
7.462
7.474
7.467
7.382
7.380
7.365
7.363
7.323
7.317
7.303
7.300
7.296
7.294
7.280
7.273
7.269
3.250
2.812
0.008
0.000
-0.008
2.00
2.03
0.99
1.16
3.10
3.06
f1 (ppm)


-113.892
-113.907
-113.915
-113.931
-113.939
-113.954
f1 (ppm)

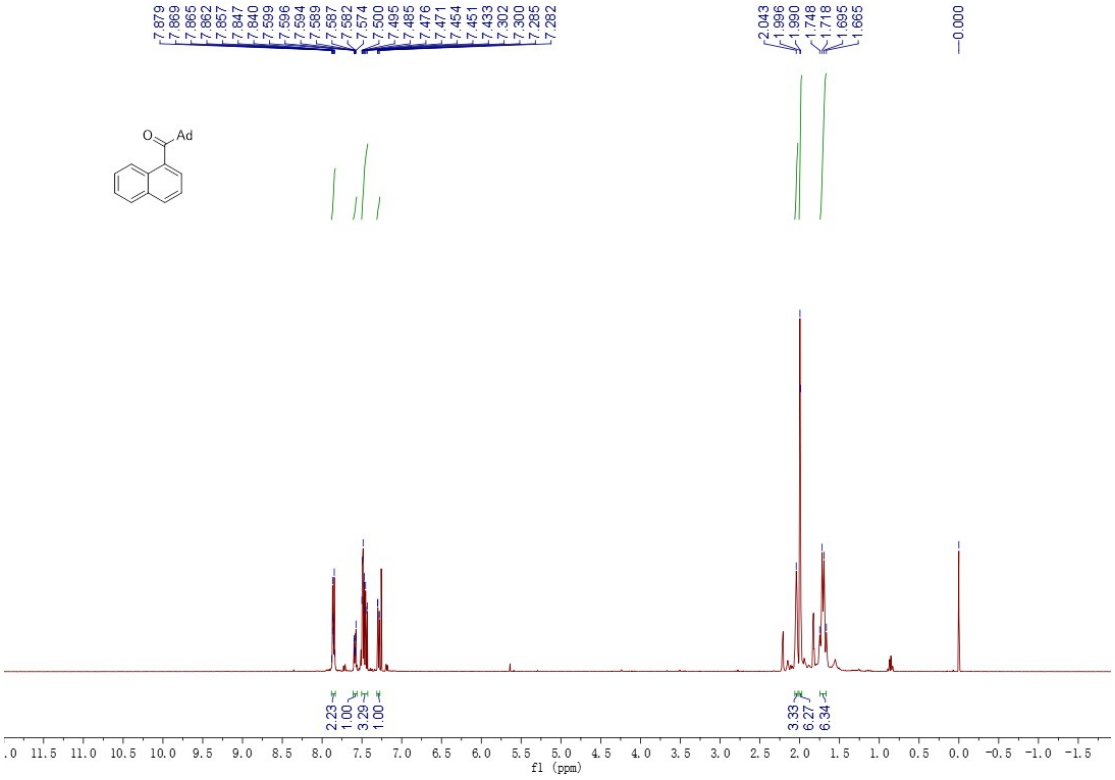

170.544
161.968
159.508
134.870
134.526
134.434
127.491
126.326
123.152
123.126
117.434
117.183
111.569
111.366
77.367
77.049
76.731
38.876
34.902
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

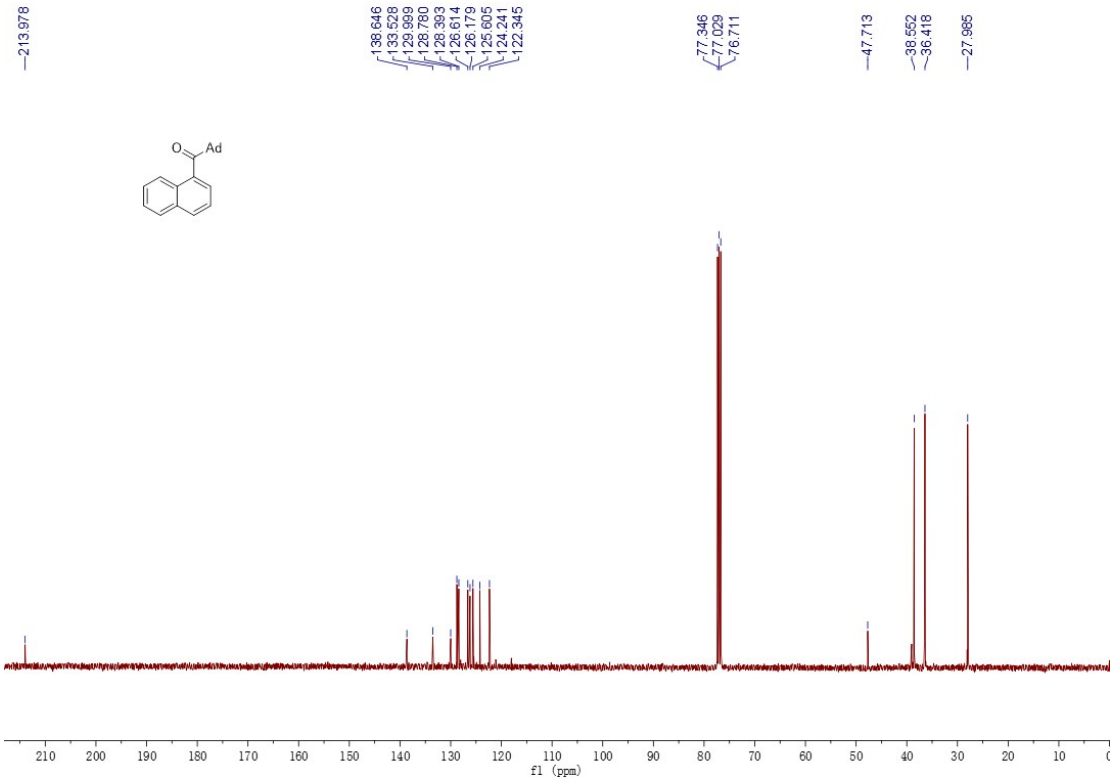
1p


8.736
8.716
8.695
8.674
7.897
7.894
7.878
7.874
7.849
7.846
7.829
7.826
7.704
7.691
7.689
7.671
7.668
7.644
7.641
7.638
7.635
7.627
7.624
7.621
7.618
7.607
7.604
7.601
3.287
2.867
0.000
2.04
2.02
2.99
2.01
3.02
3.00
f1 (ppm)

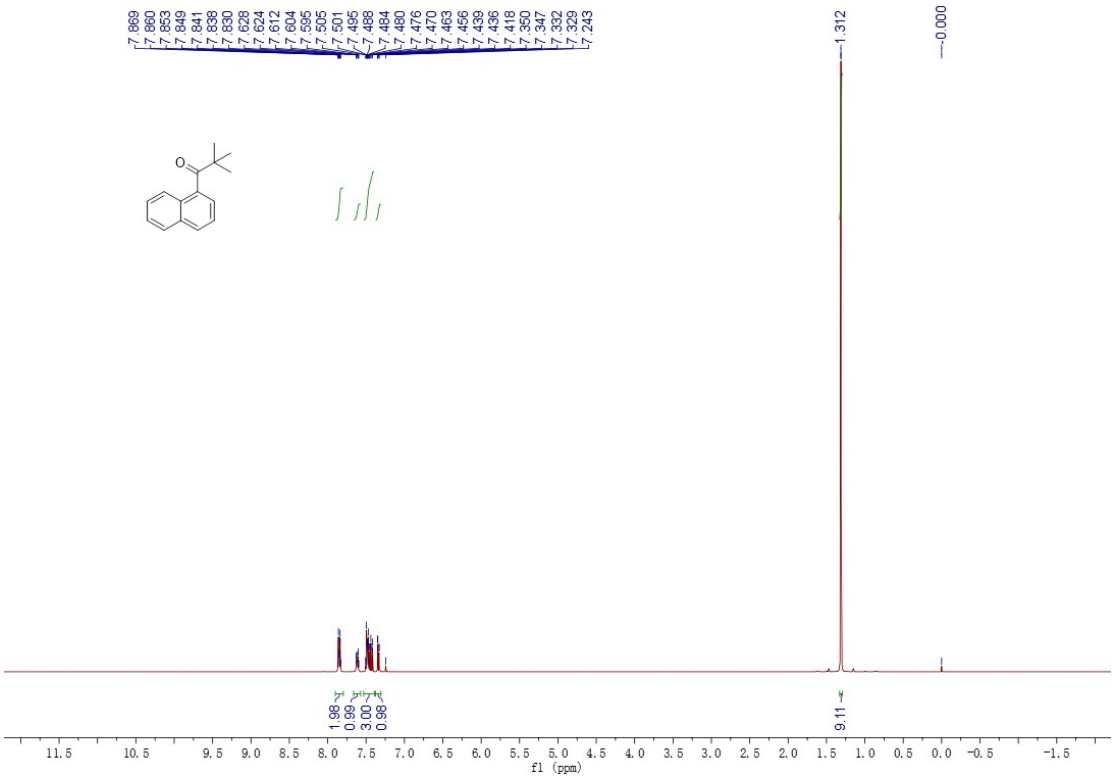

170.783
133.677
130.880
130.461
130.385
128.941
128.306
127.429
127.328
127.165
127.054
125.648
124.931
123.115
122.635
77.373
77.055
76.737
38.929
34.910
f1 (ppm)

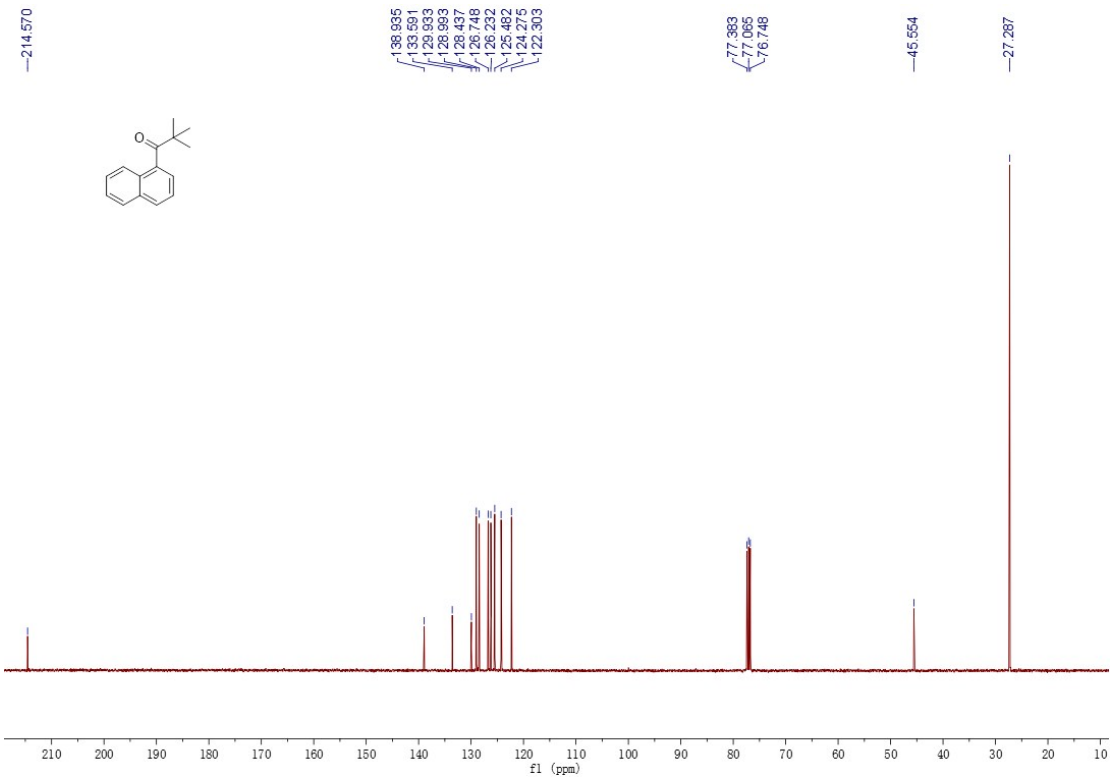
1q


7.879
7.869
7.865
7.862
7.857
7.847
7.840
7.599
7.596
7.594
7.589
7.587
7.582
7.574
7.500
7.495
7.485
7.476
7.471
7.454
7.451
7.433
7.302
7.300
7.285
7.282
2.043
1.996
1.990
1.748
1.718
1.695
1.665
0.000
Ad
2.23
1.00
3.29
1.00
3.33
6.27
6.34
f1 (ppm)

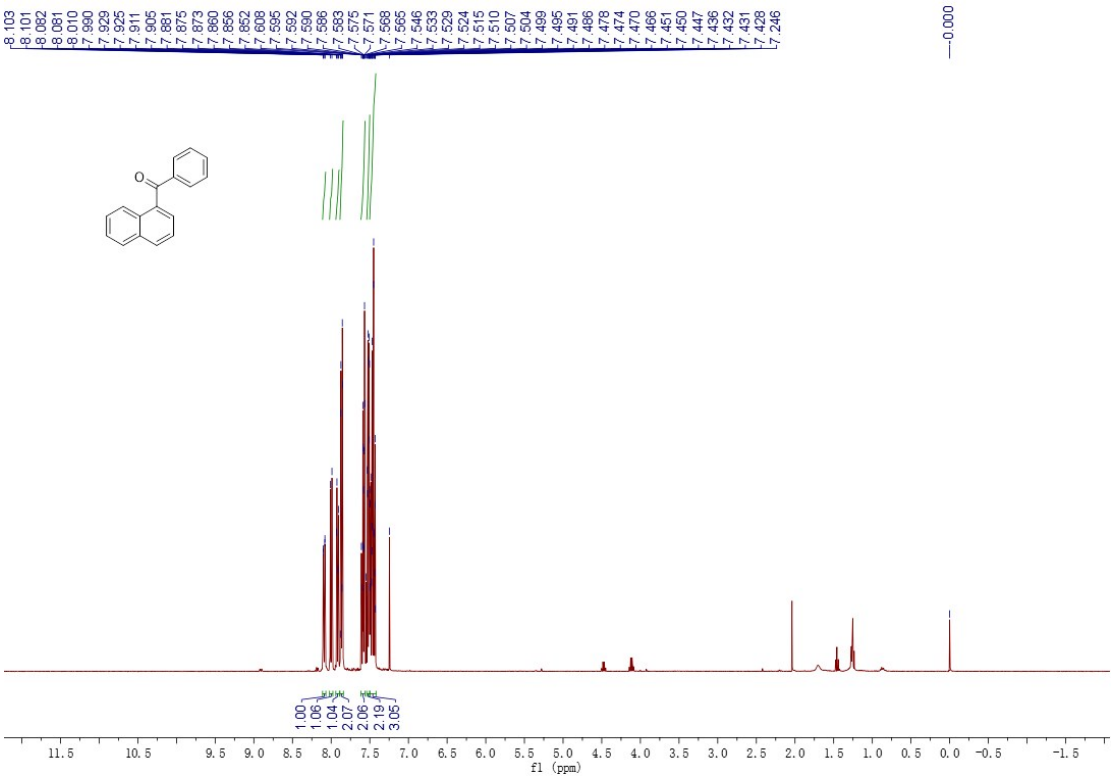

213.978
138.646
133.528
129.999
128.780
128.393
126.614
126.179
125.605
124.241
122.345
77.346
77.029
76.711
47.713
38.552
36.418
27.985
Ad
f1 (ppm)

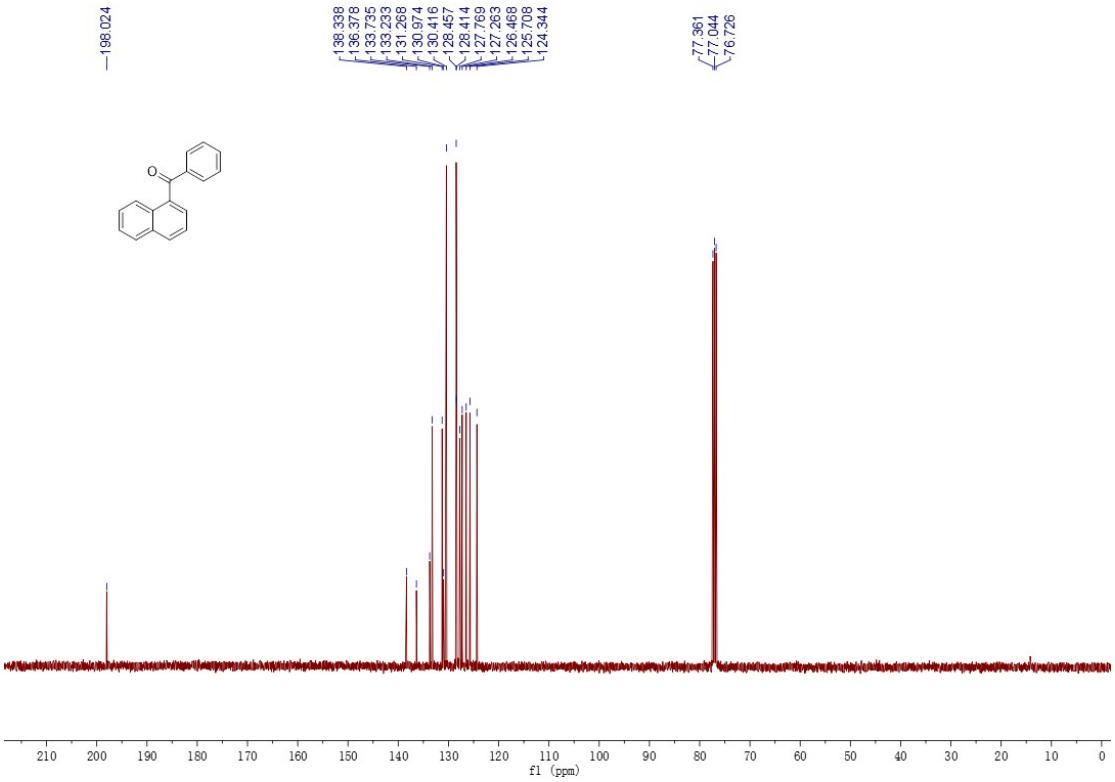
1r


7.869
7.860
7.853
7.849
7.841
7.838
7.830
7.628
7.624
7.612
7.604
7.595
7.505
7.501
7.495
7.488
7.484
7.480
7.476
7.470
7.463
7.456
7.439
7.436
7.418
7.350
7.347
7.332
7.329
7.243
1.312
0.000
O
1.98
0.99
3.00
0.98
9.11
f1 (ppm)

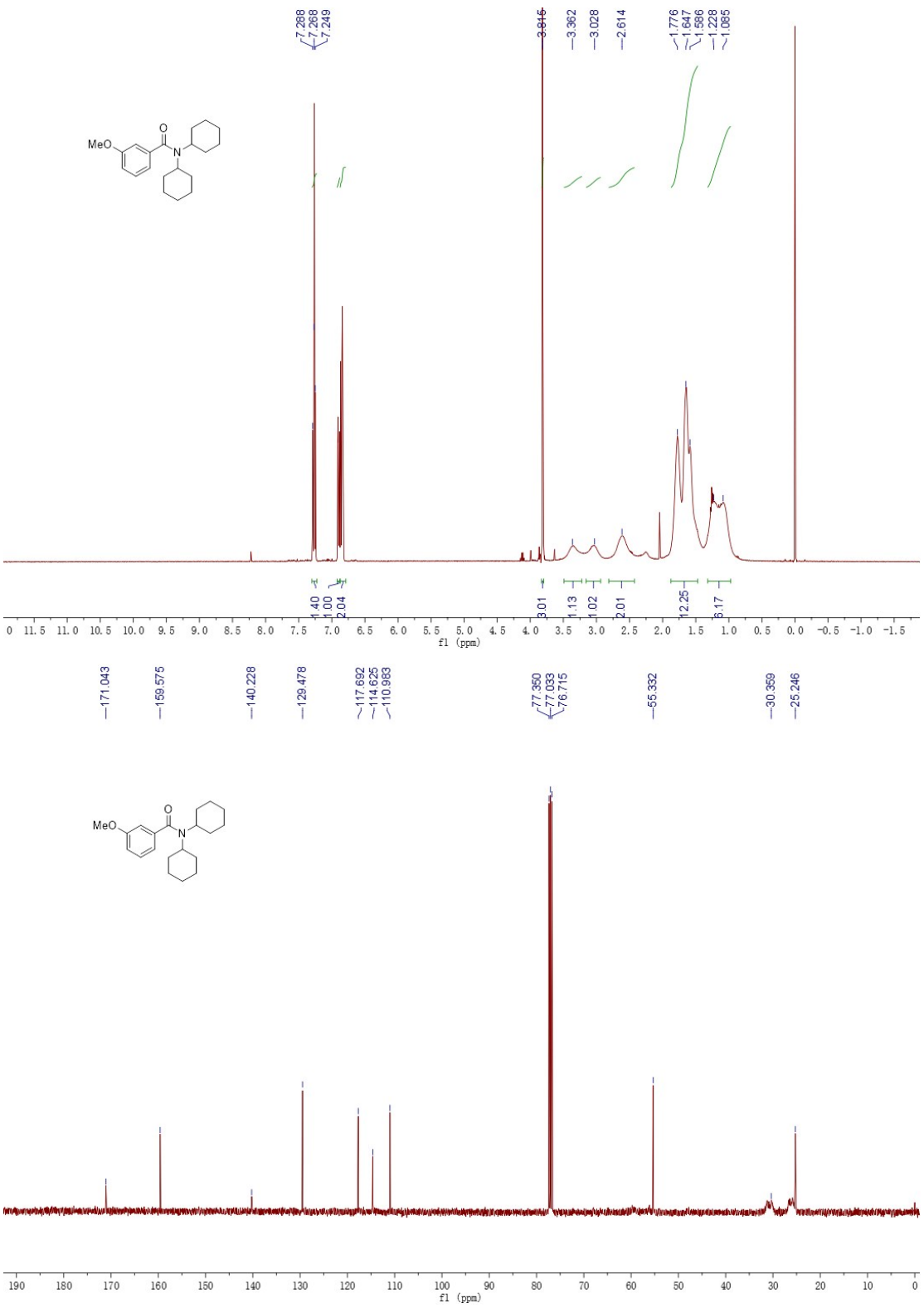

214.570
138.935
133.591
129.933
128.993
128.437
126.748
126.232
125.482
124.275
122.303
77.383
77.065
76.748
45.554
27.287
O
f1 (ppm)

1s

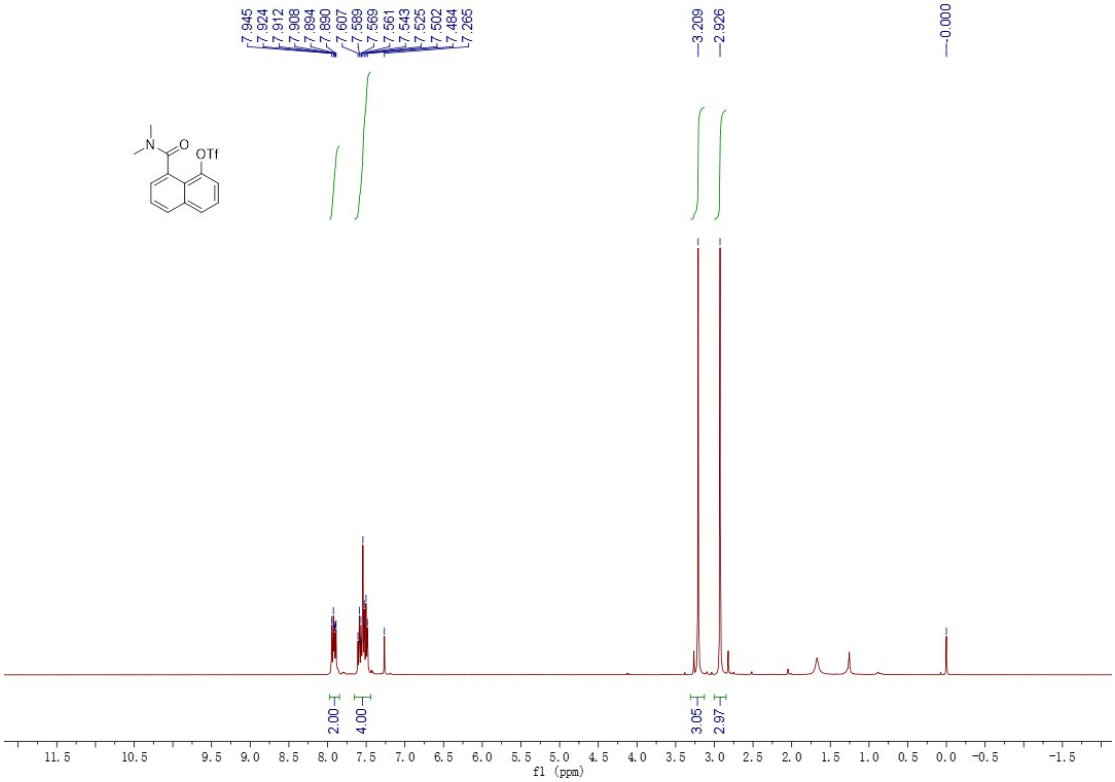

8.103
8.101
8.082
8.081
8.010
7.990
7.929
7.925
7.911
7.905
7.881
7.875
7.873
7.860
7.856
7.852
7.608
7.595
7.592
7.590
7.586
7.583
7.575
7.571
7.568
7.565
7.546
7.533
7.529
7.524
7.515
7.510
7.507
7.504
7.499
7.495
7.491
7.486
7.478
7.474
7.470
7.466
7.451
7.450
7.447
7.436
7.432
7.431
7.428
7.246
0.000
1.00
1.06
1.04
2.07
2.06
2.19
3.05
f1 (ppm)

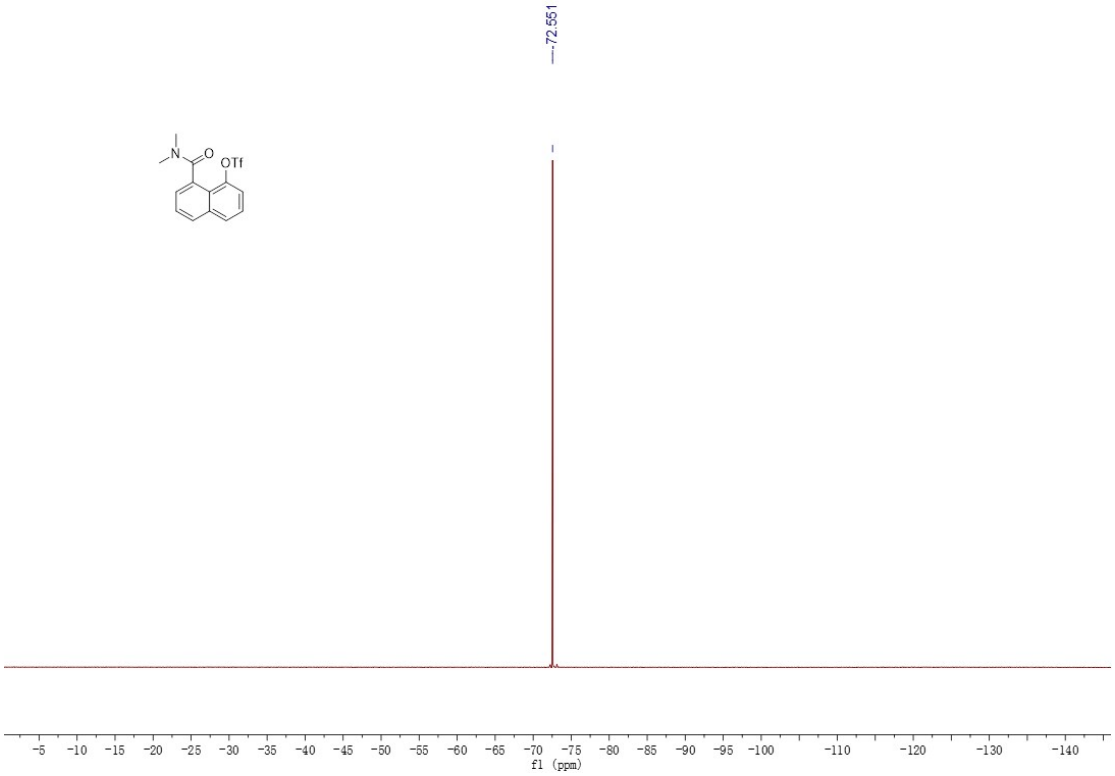

198.024
138.338
136.378
133.735
133.233
131.268
130.974
130.416
128.457
128.414
127.769
127.263
126.468
125.708
124.344
77.361
77.044
76.726
f1 (ppm)

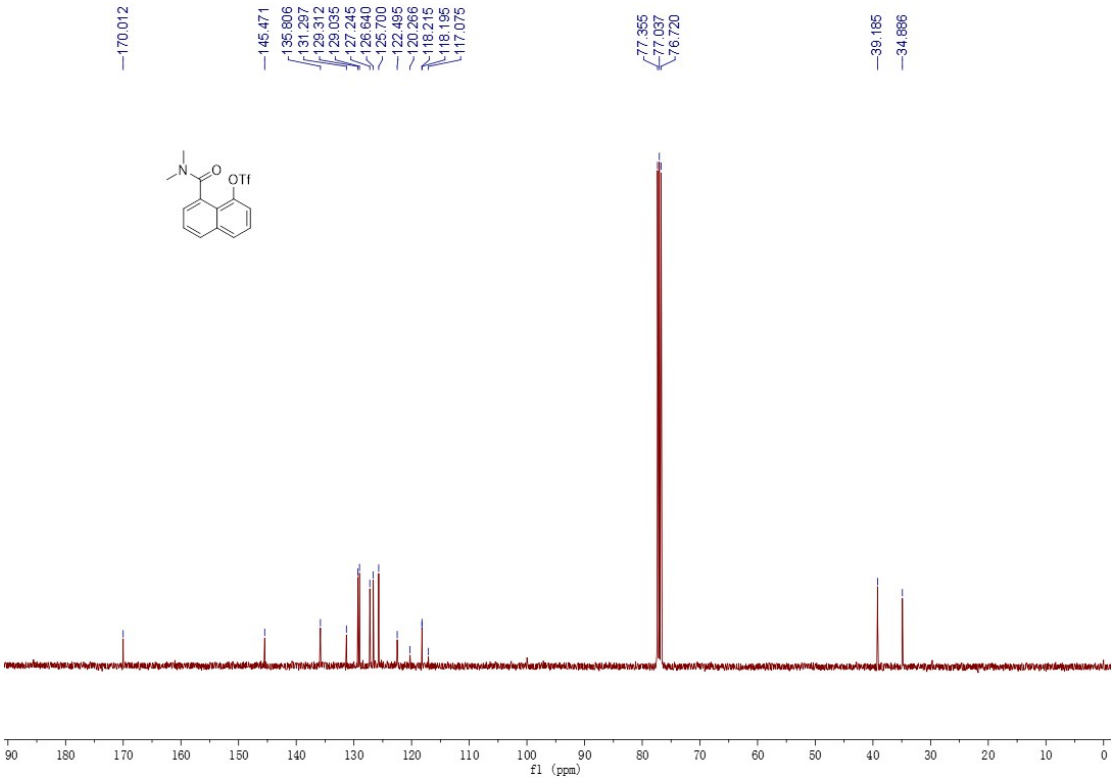
1t


7.288
7.268
7.249
3.815
3.362
3.028
2.614
1.776
1.647
1.586
1.228
1.085
MeO
O
N
1.40
1.00
2.04
3.01
1.13
1.02
2.01
12.25
6.17
f1 (ppm)
171.043
159.575
140.228
129.478
117.692
114.625
110.983
77.350
77.033
76.715
55.332
30.359
25.246
MeO
O
N
f1 (ppm)

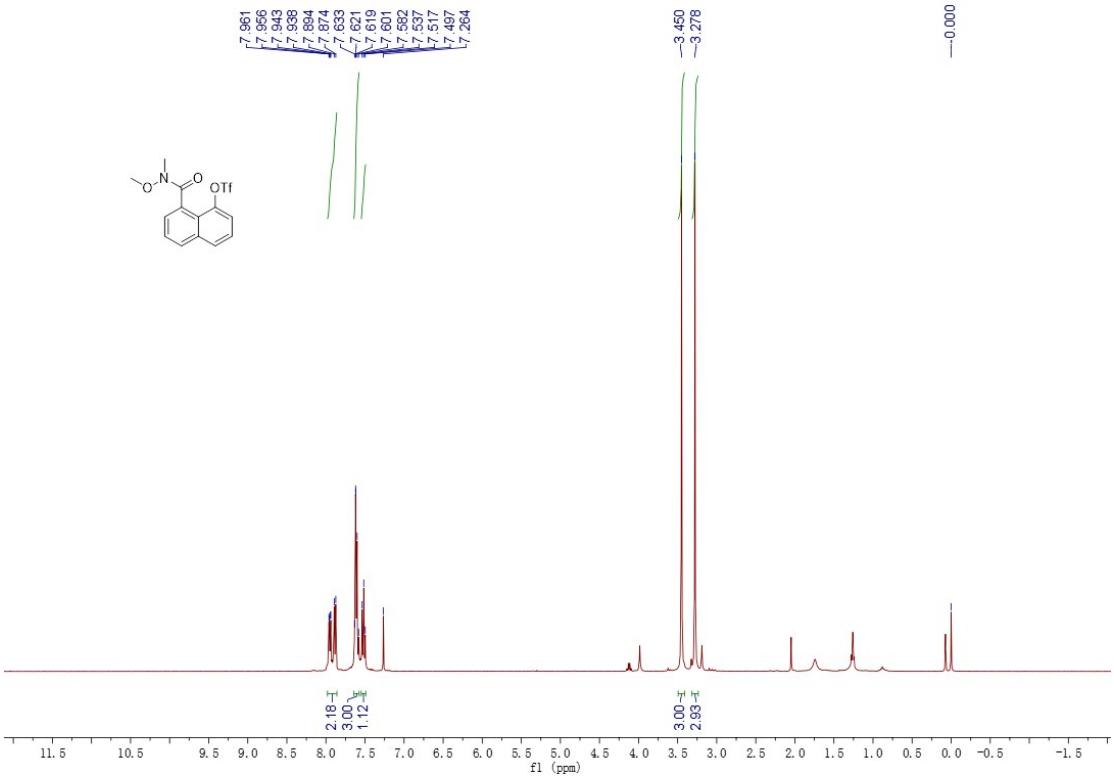
3a

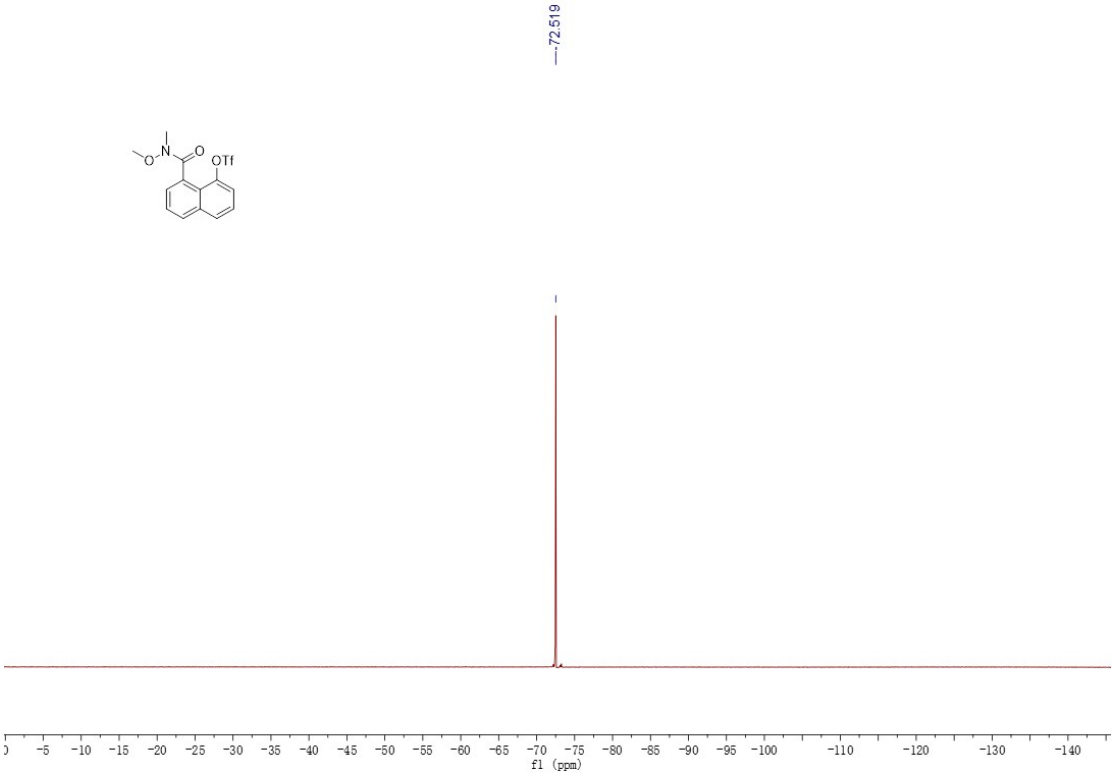

7.945
7.924
7.912
7.908
7.894
7.890
7.607
7.589
7.569
7.561
7.543
7.525
7.502
7.484
7.265
3.209
2.926
0.000
OTf
2.00
4.00
3.05
2.97
f1 (ppm)

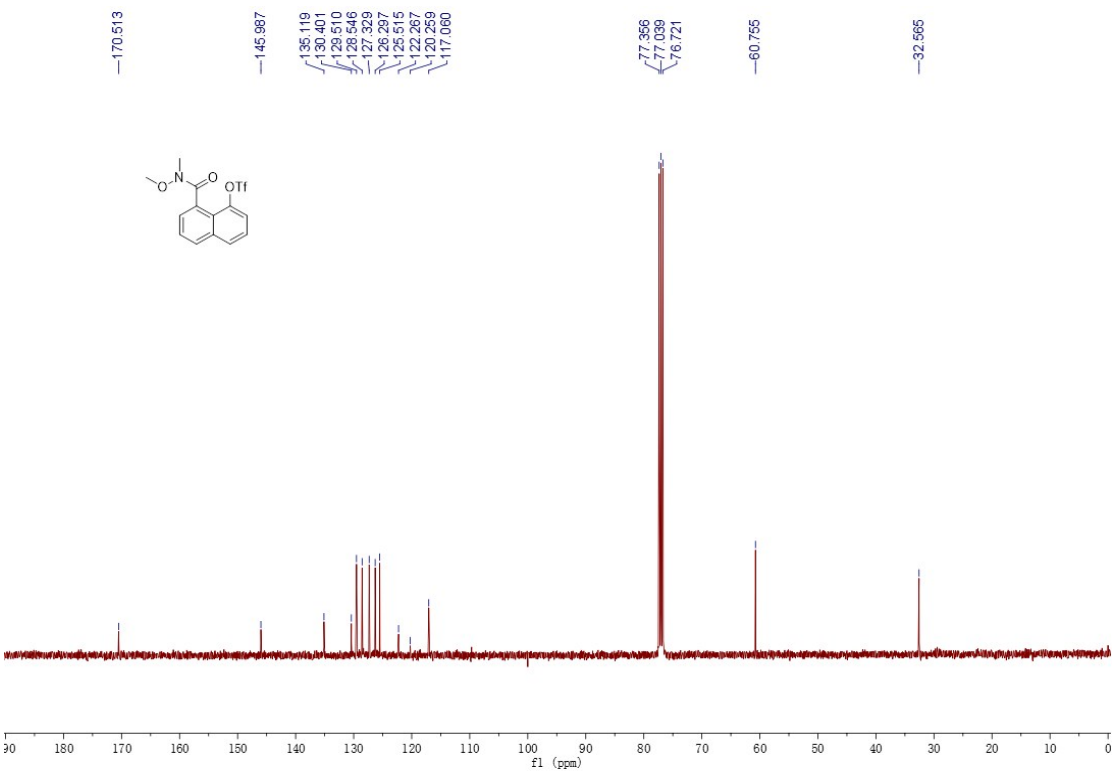

-72.551
OTf
f1 (ppm)


170.012
145.471
135.806
131.297
129.312
129.035
127.245
126.640
125.700
122.495
120.266
118.215
118.195
117.075
77.355
77.037
76.720
39.185
34.886
N
O
OTf
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

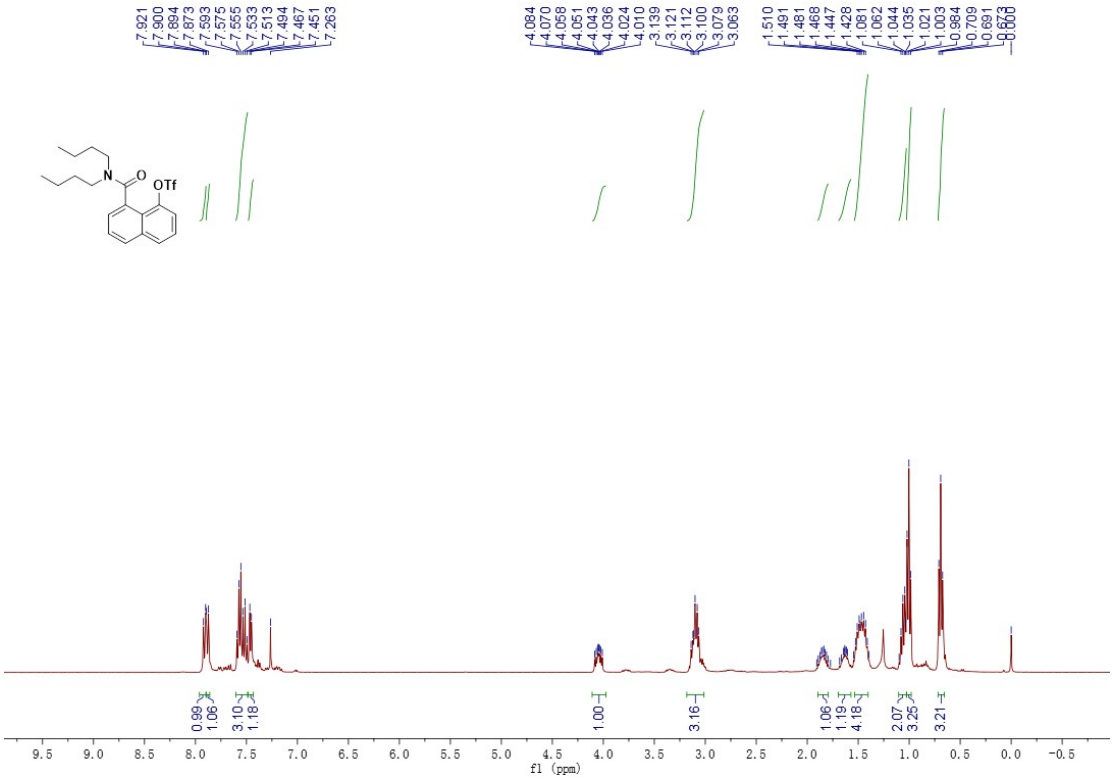
3b

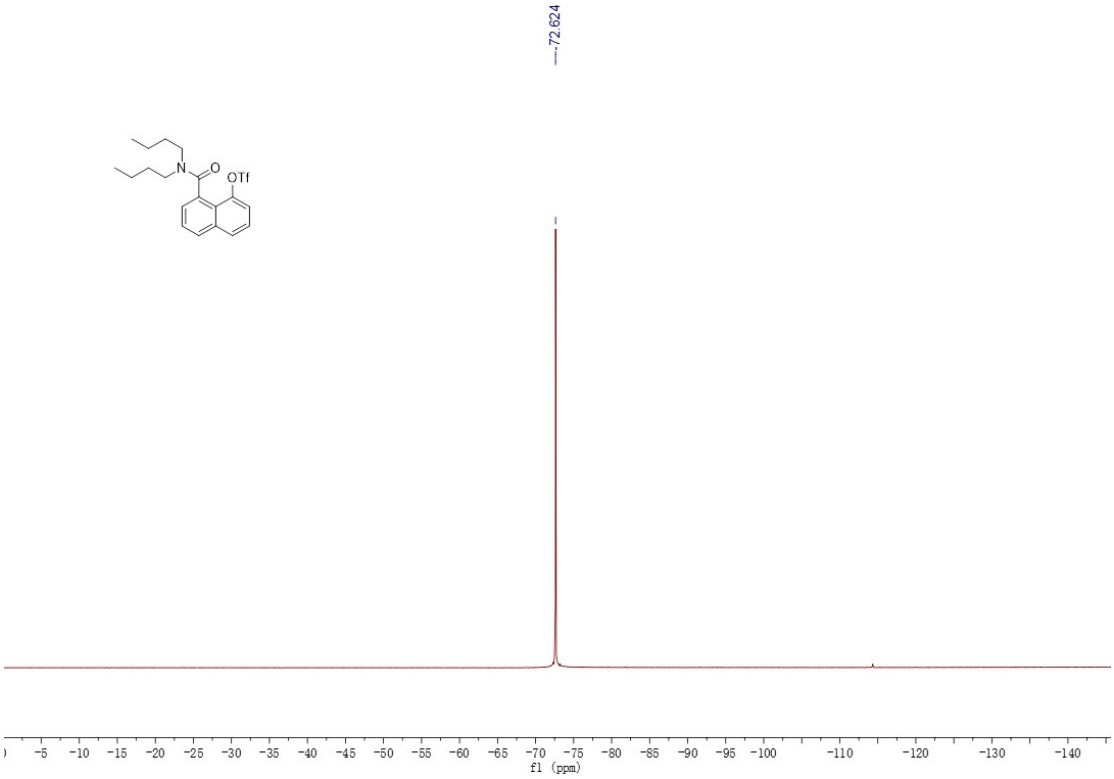

7.961
7.956
7.943
7.938
7.894
7.874
7.633
7.621
7.619
7.601
7.582
7.537
7.517
7.497
7.264
3.450
3.278
0.000
OTf
2.18
3.00
1.12
3.00
2.93
f1 (ppm)

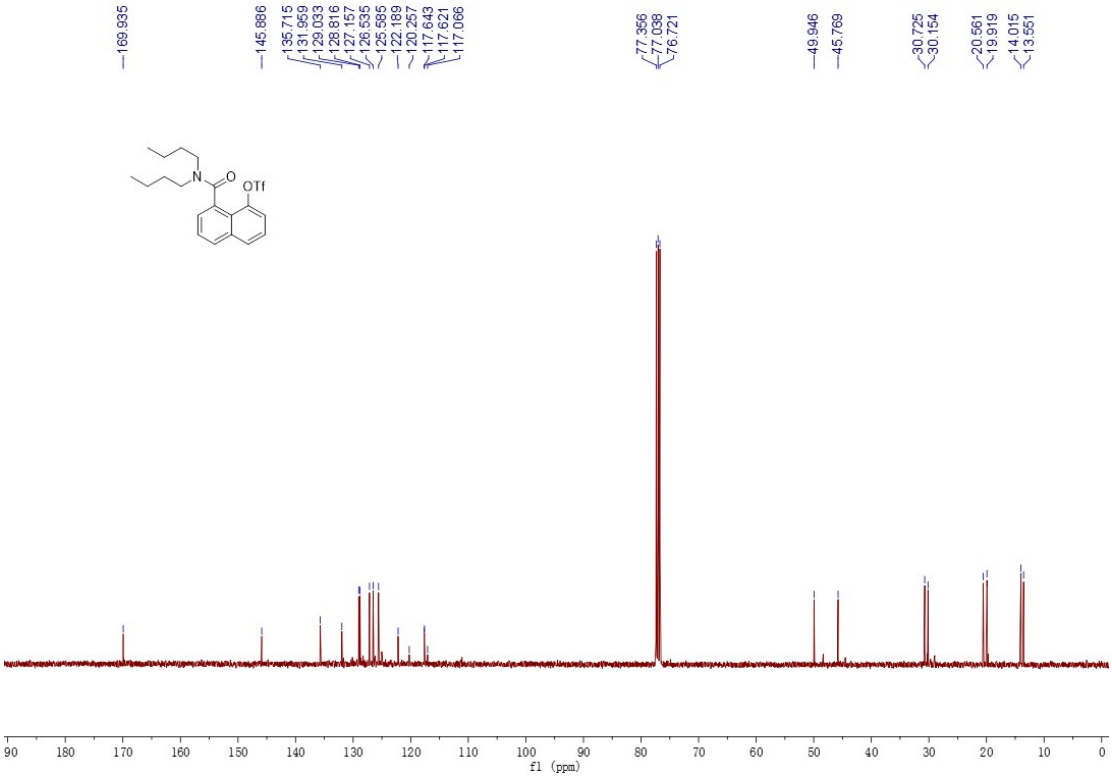

-72.519
OTf
f1 (ppm)


170.513
145.987
135.119
130.401
129.510
128.546
127.329
126.297
125.515
122.267
120.259
117.060
77.356
77.099
76.721
60.755
32.565
OTf
f1 (ppm)

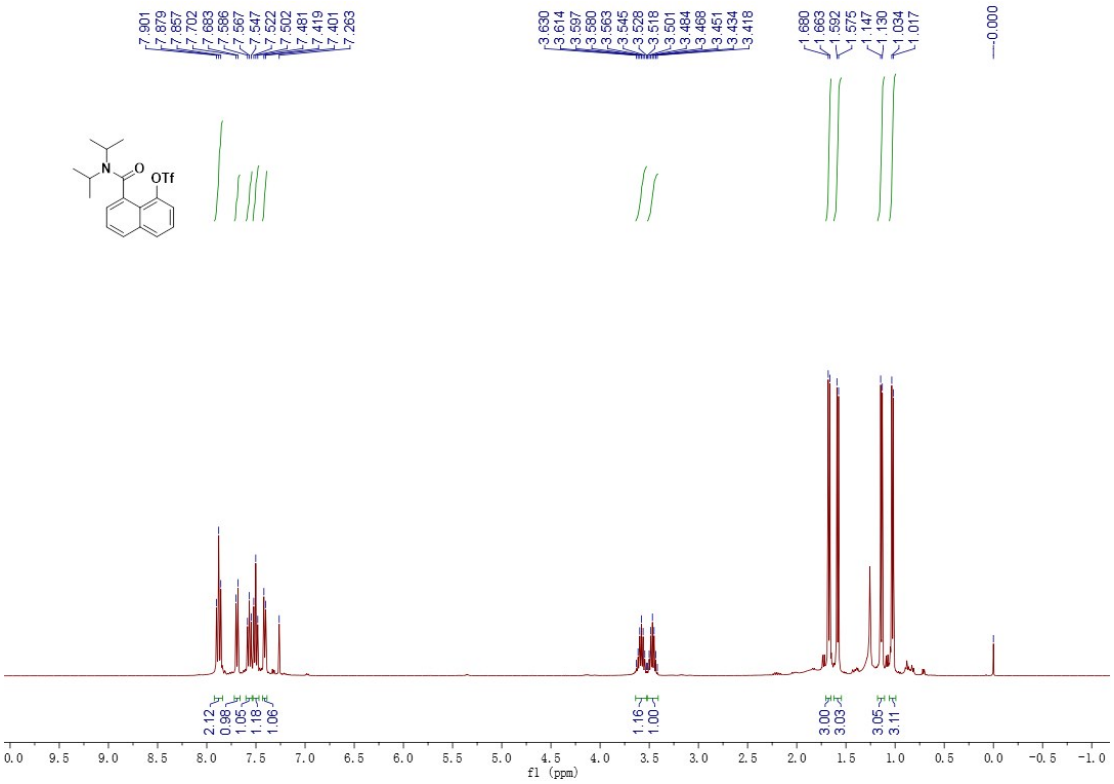
3c

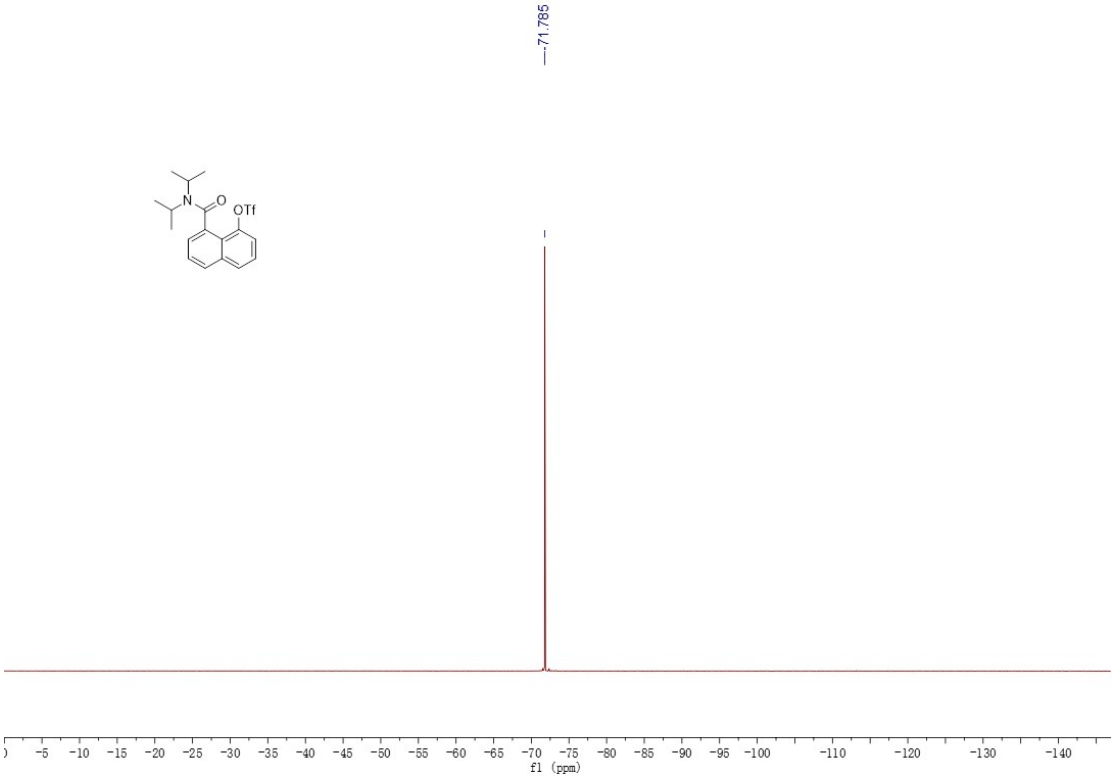

7.921
7.900
7.894
7.873
7.593
7.575
7.555
7.533
7.513
7.494
7.467
7.451
7.263
4.084
4.070
4.058
4.051
4.043
4.036
4.024
4.010
3.139
3.121
3.112
3.100
3.079
3.063
1.510
1.491
1.481
1.468
1.447
1.428
1.081
1.062
1.044
1.035
1.021
1.003
0.984
0.709
0.691
OTf
0.99
1.08
3.10
1.18
1.00
3.16
1.06
1.19
4.18
2.07
3.25
3.21
f1 (ppm)

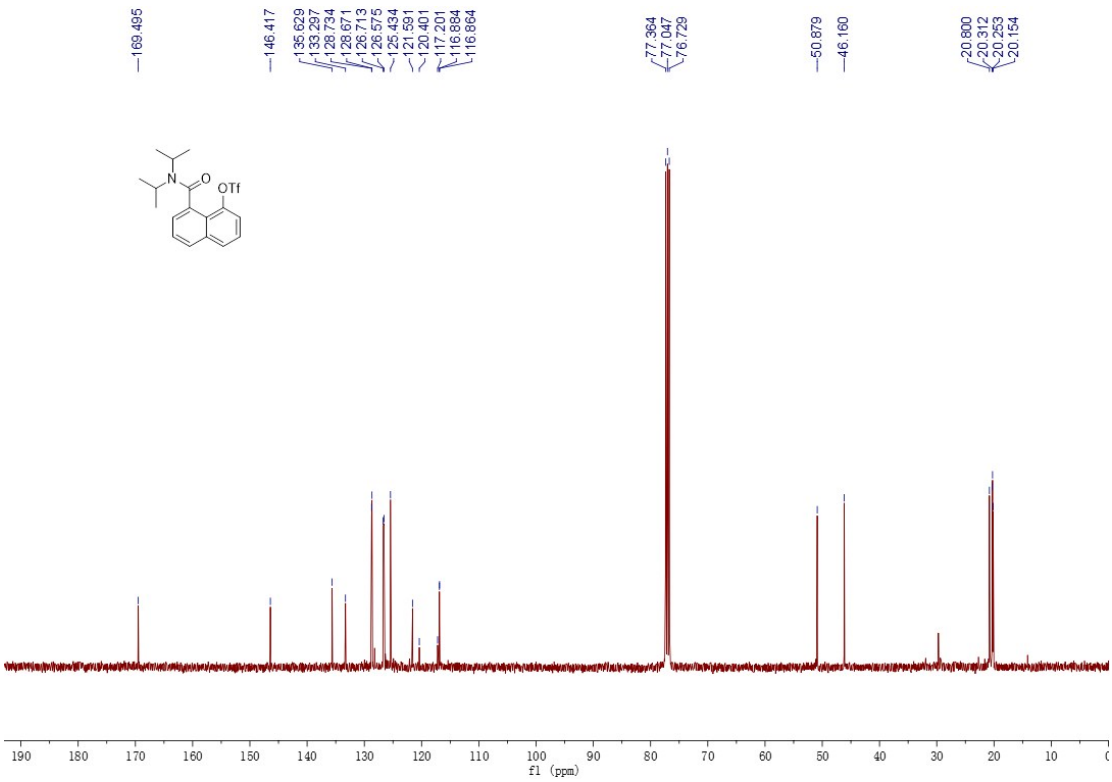

-72.624
OTf
f1 (ppm)


169.935
145.886
135.715
131.959
129.033
128.816
127.157
126.535
125.385
122.189
120.257
117.643
117.621
117.066
77.356
77.038
76.721
49.946
45.769
30.725
30.154
20.561
19.919
14.015
13.551
N
O
OTf
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

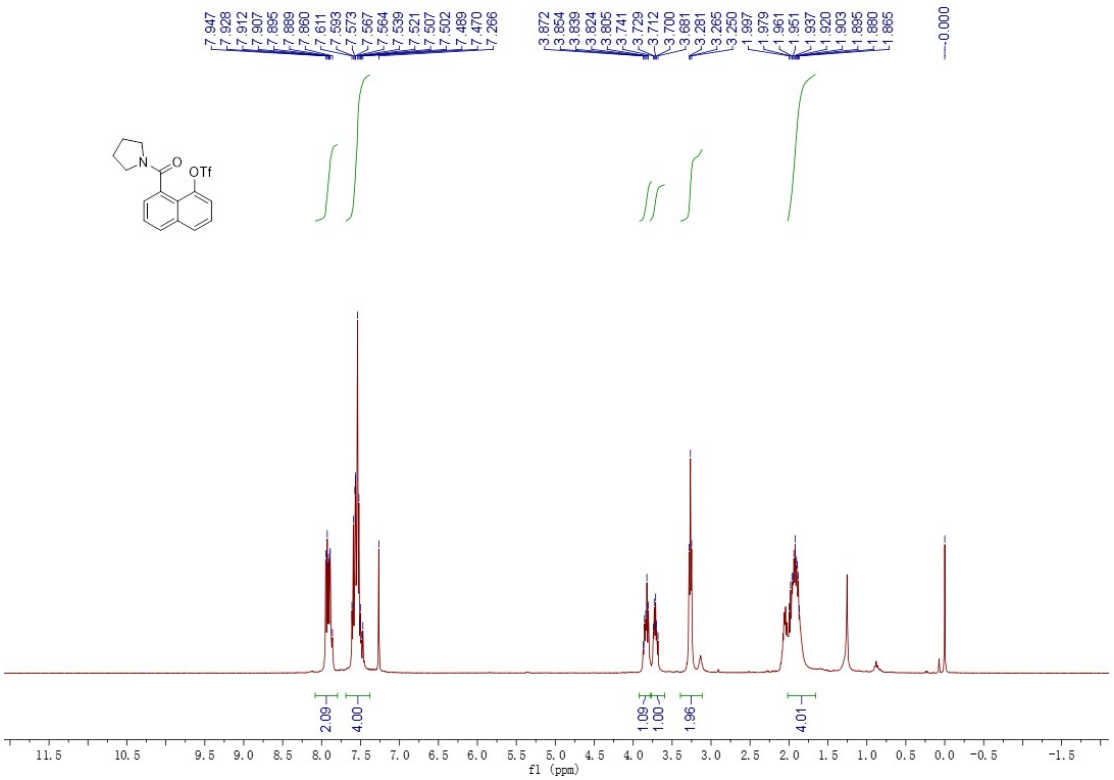
3d


7.901
7.879
7.857
7.702
7.683
7.586
7.567
7.547
7.522
7.502
7.481
7.419
7.401
7.263
3.630
3.614
3.597
3.580
3.563
3.545
3.528
3.518
3.501
3.484
3.468
3.451
3.434
3.418
1.680
1.663
1.592
1.575
1.147
1.130
1.034
1.017
0.000
OTf
2.12
0.98
1.05
1.18
1.06
1.16
1.00
3.00
3.03
3.05
3.11
f1 (ppm)


71.785
OTf
f1 (ppm)


169.495
146.417
135.629
133.297
128.734
128.671
126.713
126.575
125.434
121.591
120.401
117.201
116.884
116.864
77.364
77.047
76.729
50.879
46.160
20.800
20.312
20.253
20.154
OTf
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3e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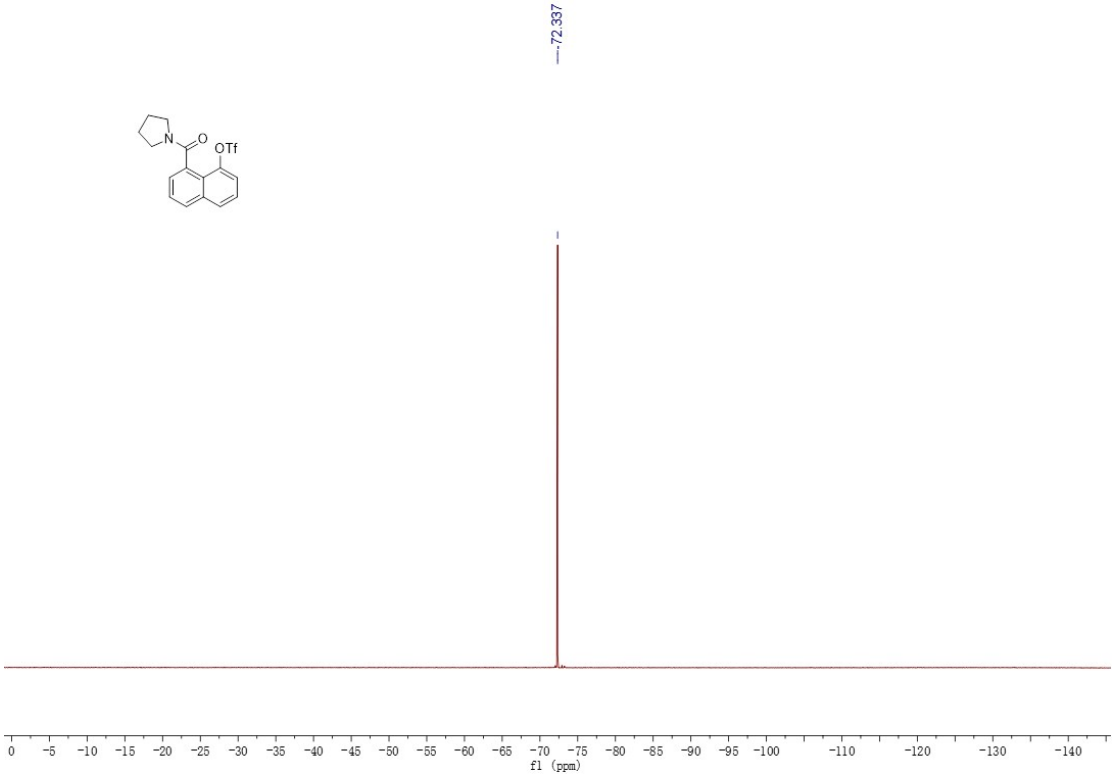
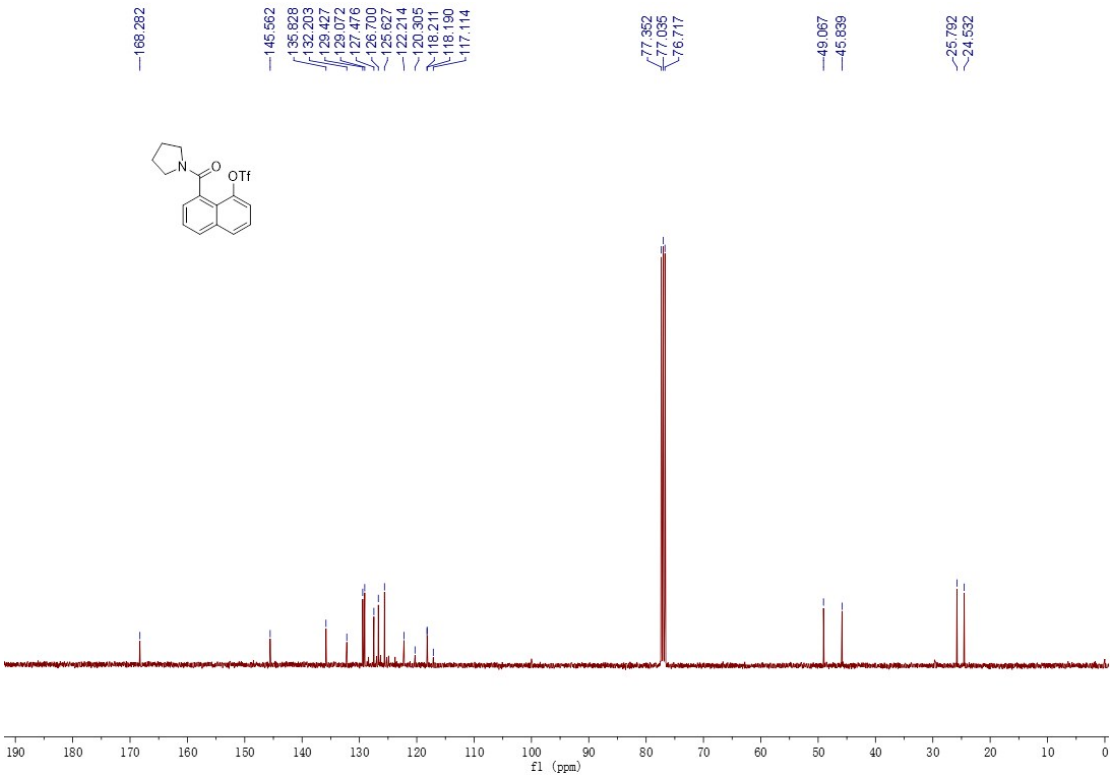
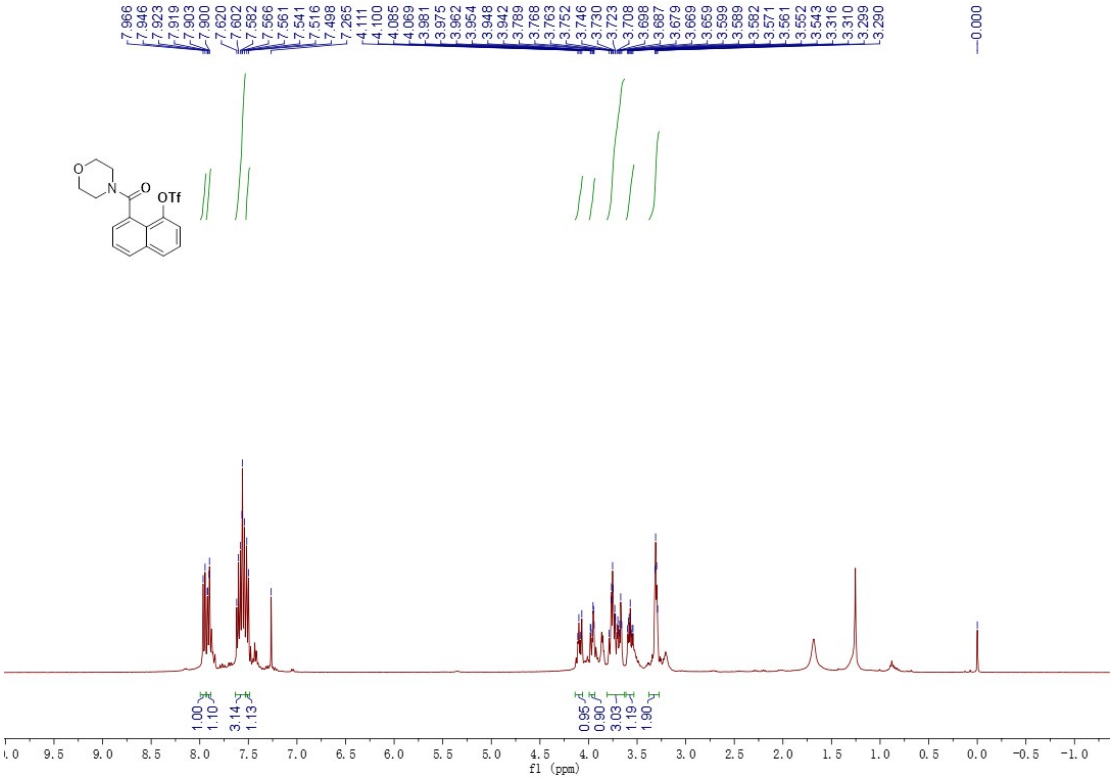
7.928
7.912
7.907
7.895
7.889
7.860
7.611
7.593
7.573
7.567
7.564
7.539
7.521
7.507
7.502
7.489
7.470
7.266
3.872
3.854
3.839
3.824
3.805
3.741
3.729
3.712
3.700
3.681
3.281
3.265
3.250
1.997
1.979
1.961
1.951
1.937
1.920
1.903
1.895
1.880
1.865
0.000
OTf
2.09
4.00
1.09
1.00
1.96
4.01
f1 (ppm)


-72.337
OTf
f1 (ppm)


168.282
145.562
135.828
132.203
129.427
129.072
127.476
126.700
125.627
122.214
120.305
118.211
118.190
117.114
77.352
77.035
76.717
49.067
45.839
25.792
24.532
OTf
N
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3f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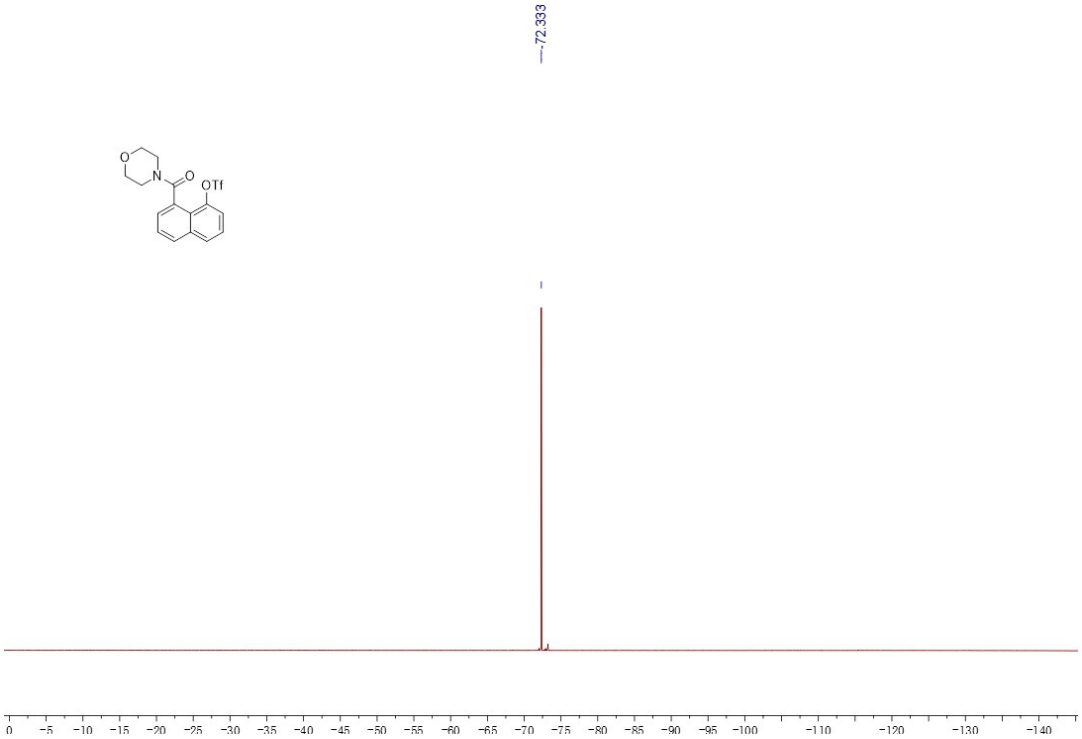
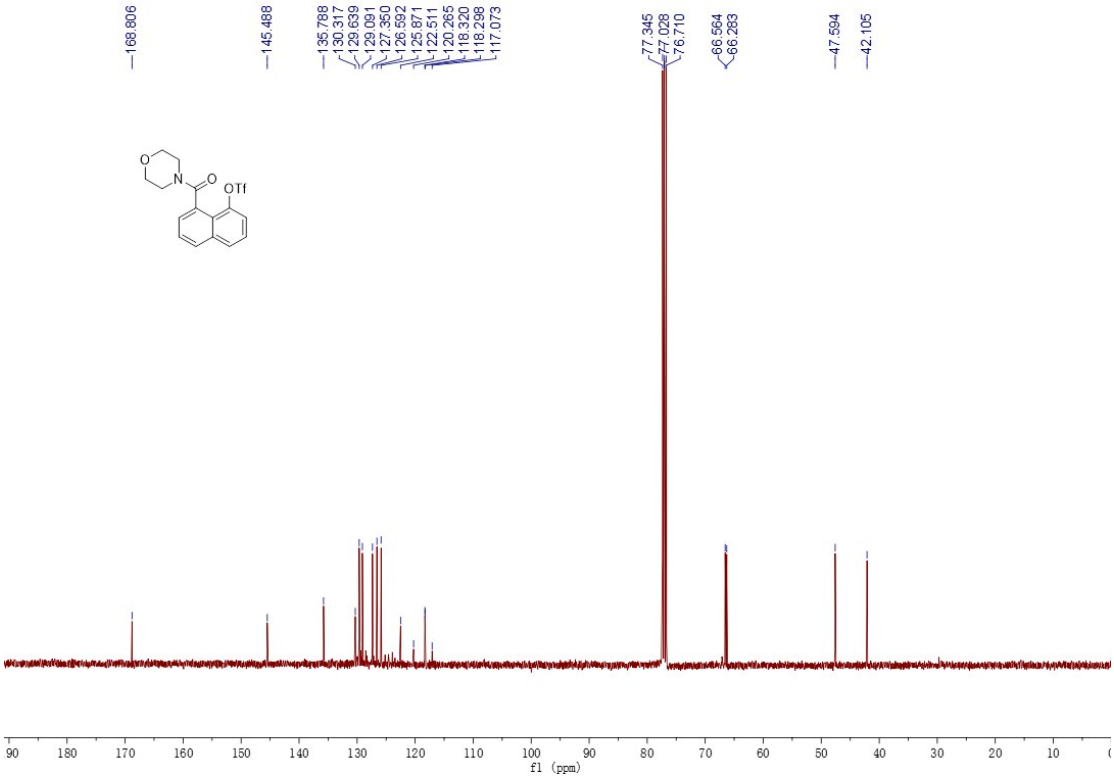
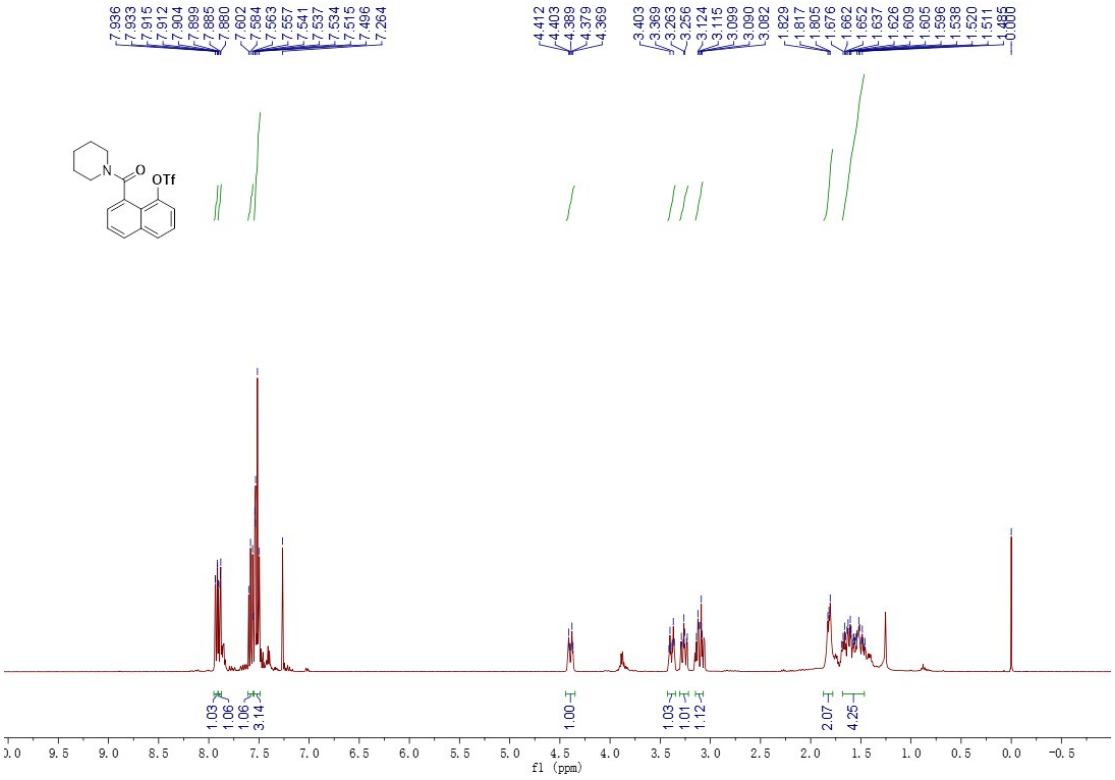
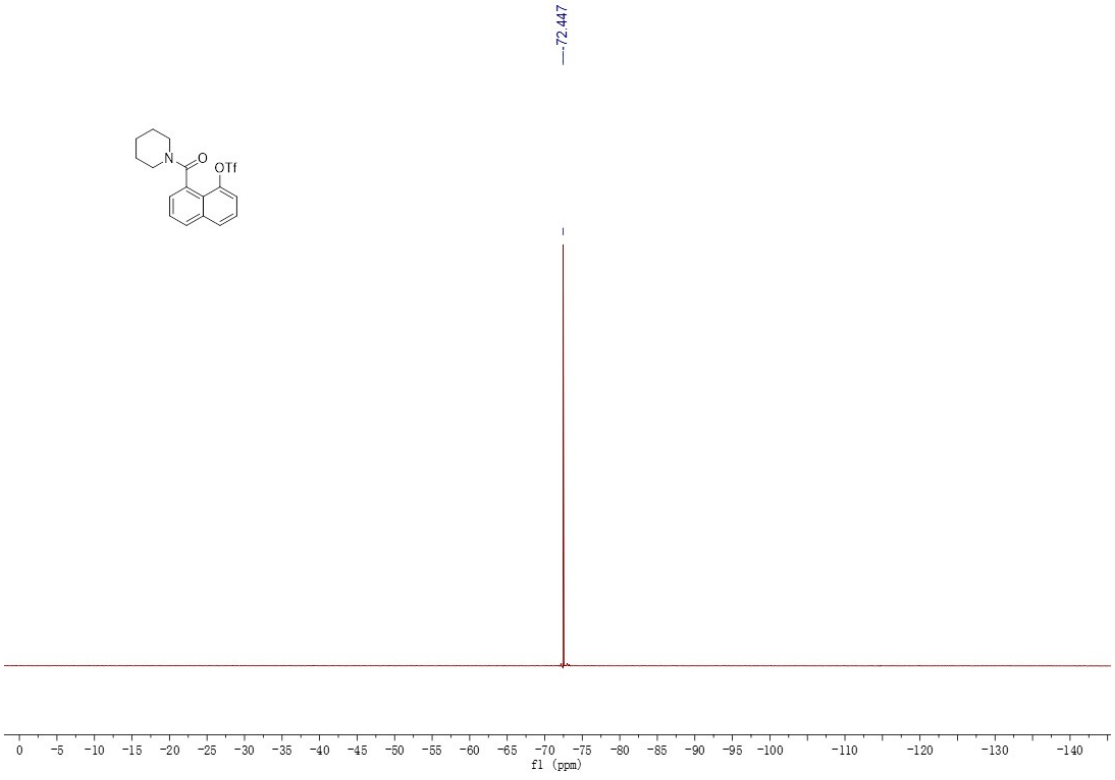
7.946
7.923
7.919
7.903
7.900
7.620
7.602
7.582
7.566
7.561
7.541
7.516
7.498
7.265
4.111
4.100
4.085
4.069
3.981
3.975
3.962
3.954
3.948
3.942
3.789
3.768
3.763
3.752
3.746
3.730
3.723
3.708
3.698
3.687
3.679
3.669
3.659
3.599
3.589
3.582
3.571
3.561
3.552
3.543
3.316
3.310
3.299
3.290
0.000
O
N
O
OTf
1.00
1.10
3.14
1.13
0.95
0.90
3.03
1.19
1.90
f1 (ppm)

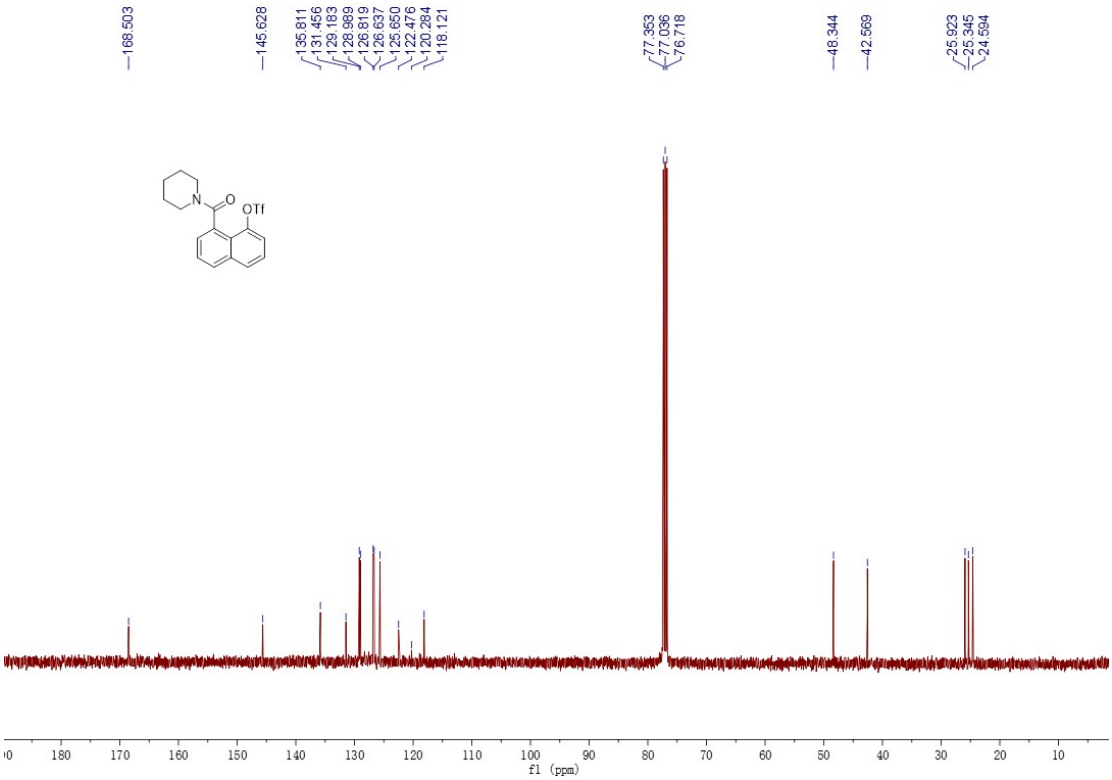

-72.333
O
N
O
OTf


168.806
145.488
135.788
130.317
129.639
129.091
127.350
126.592
125.871
122.511
120.265
118.320
118.298
117.073
77.345
77.028
76.710
66.564
66.283
47.594
42.105
OTf
f1 (ppm)

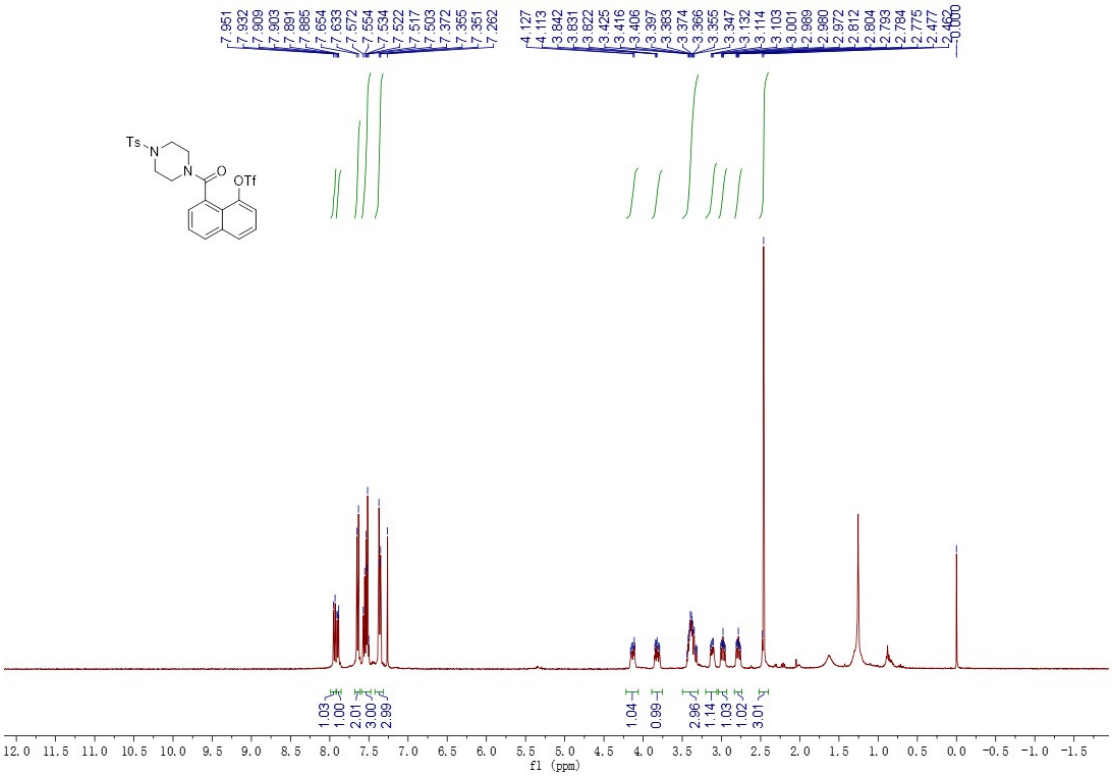
3g


7.936
7.933
7.915
7.912
7.904
7.899
7.885
7.880
7.602
7.584
7.563
7.557
7.541
7.537
7.534
7.515
7.496
7.264
4.412
4.403
4.389
4.379
4.369
3.403
3.369
3.263
3.256
3.124
3.115
3.099
3.090
3.082
1.829
1.817
1.805
1.676
1.662
1.652
1.637
1.626
1.609
1.605
1.596
1.538
1.520
1.511
0.000
OTf
1.03
1.06
1.06
3.14
1.00
1.03
1.01
1.12
2.07
4.25
f1 (ppm)


-72.447
OTf
f1 (ppm)


168.503
145.628
135.811
131.456
129.183
128.989
126.819
126.637
125.650
122.476
120.284
118.121
77.353
77.036
76.718
48.344
42.569
25.923
25.345
24.594
N
O
OTf
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3h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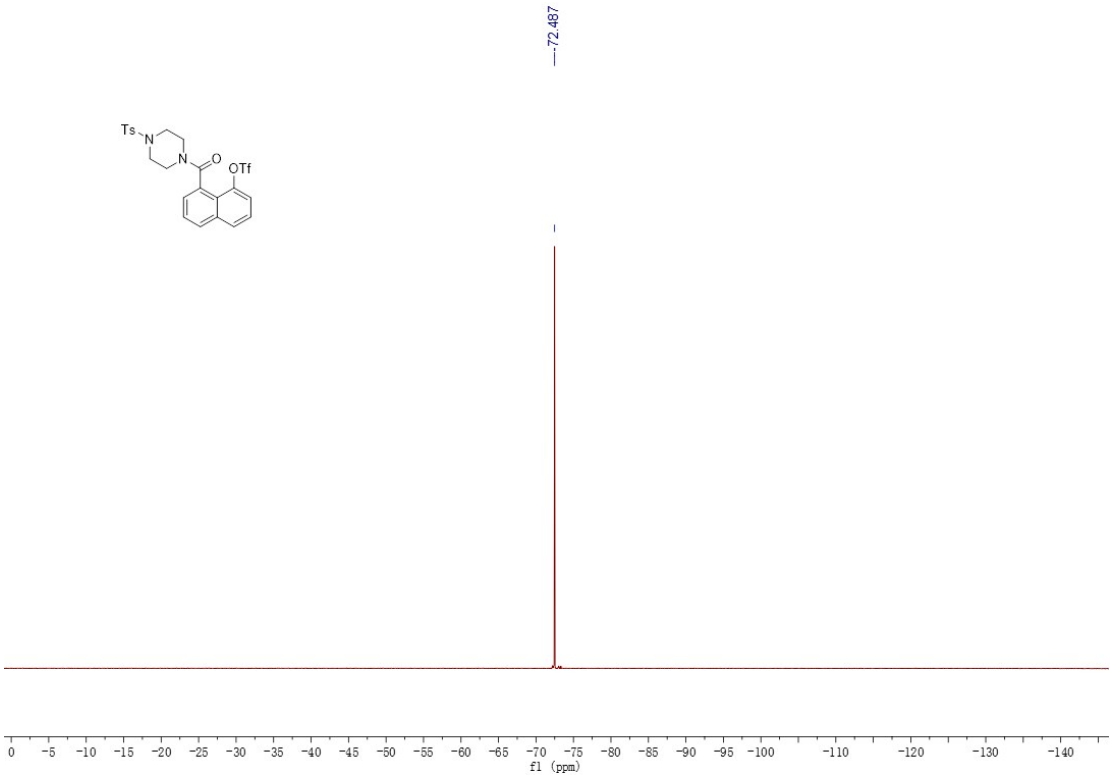
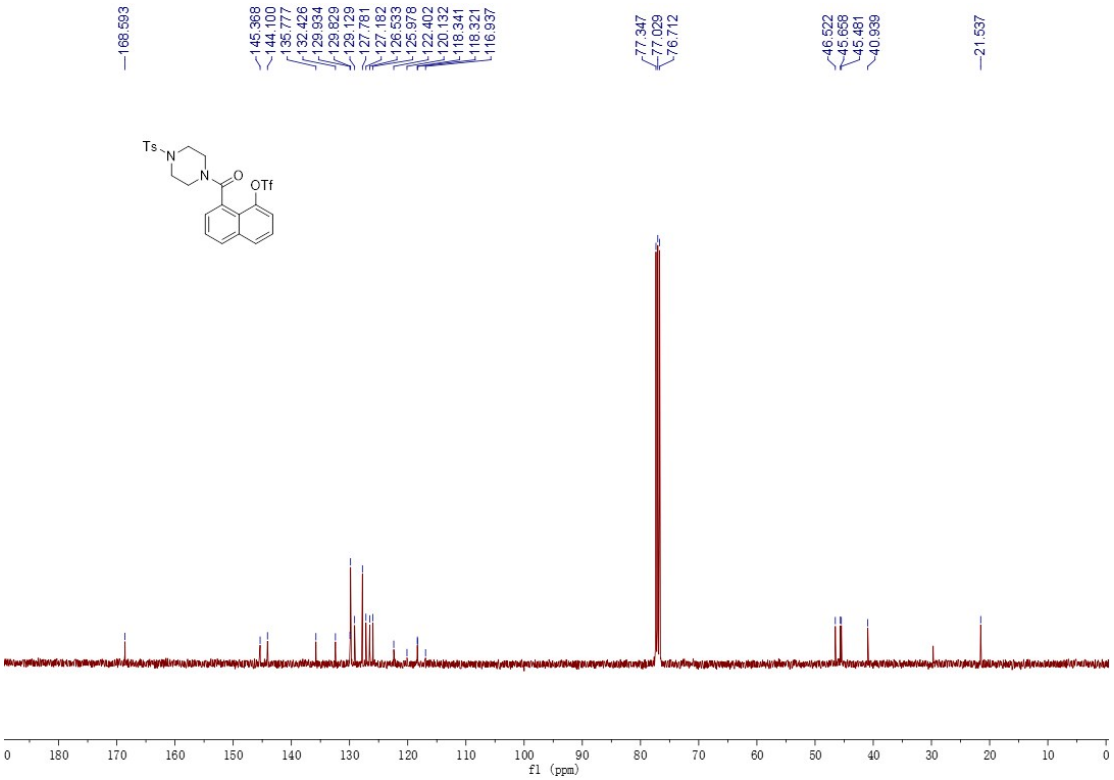
7.932
7.909
7.903
7.891
7.885
7.654
7.633
7.572
7.554
7.534
7.522
7.517
7.503
7.372
7.355
7.351
7.262
4.127
4.113
3.842
3.831
3.822
3.425
3.416
3.406
3.397
3.383
3.374
3.366
3.355
3.347
3.132
3.114
3.103
3.001
2.989
2.980
2.972
2.812
2.804
2.793
2.784
2.775
2.477
2.462
0.000
Ts
N
N
O
OTf
1.03
1.00
2.01
3.00
2.99
1.04
0.99
2.96
1.14
1.03
1.02
3.01
f1 (ppm)


-72.487
Ts
N
N
O
OTf
f1 (ppm)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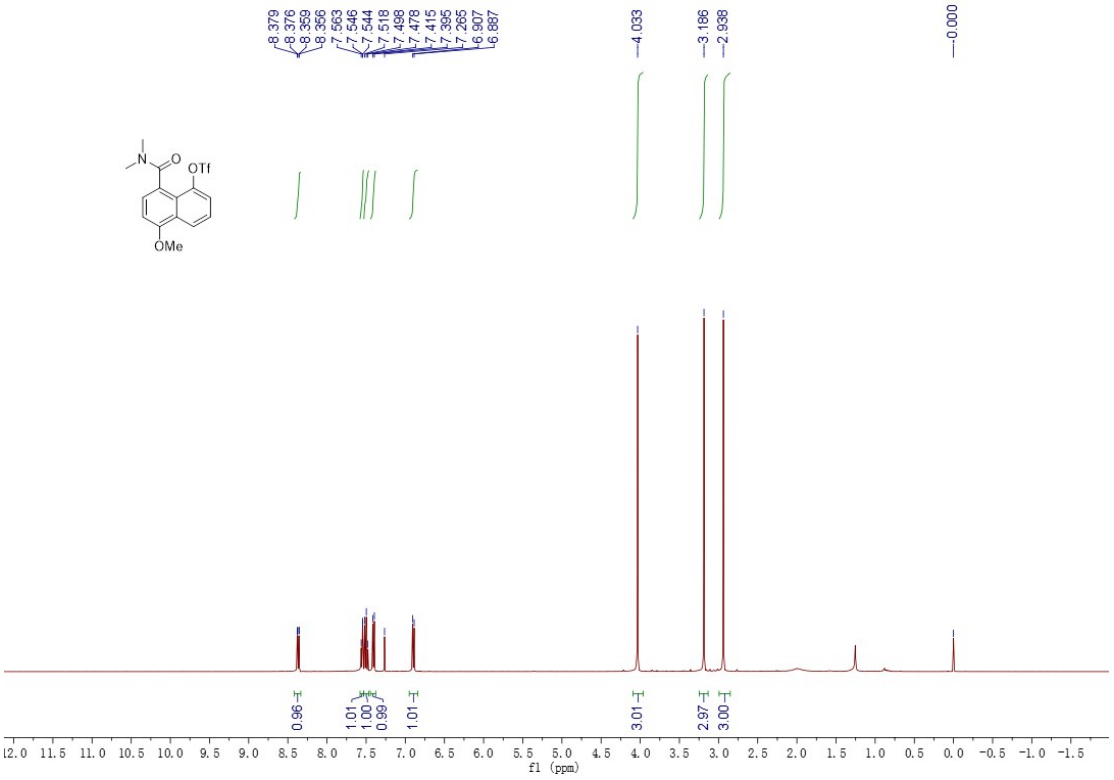
132.426
129.934
129.829
129.129
127.781
127.182
126.533
125.978
122.402
120.132
118.341
118.321
116.937
77.347
77.029
76.712
46.522
45.658
45.481
40.939
21.537
Ts
N
N
O
OTf
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3i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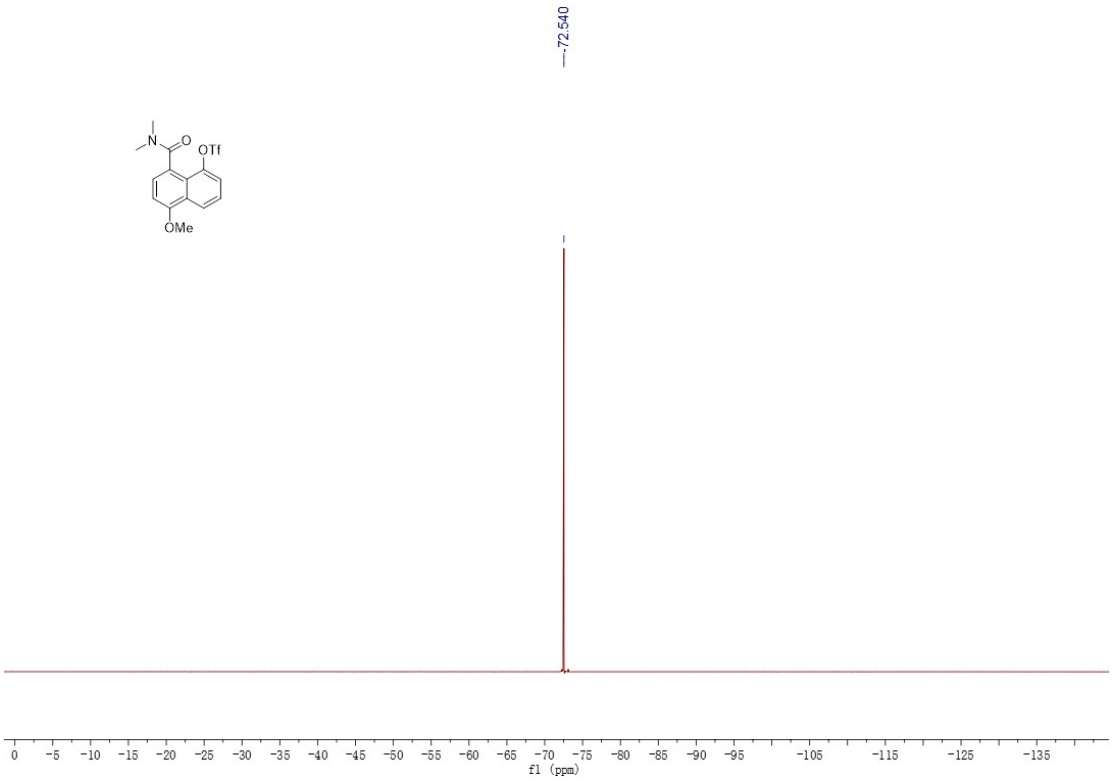
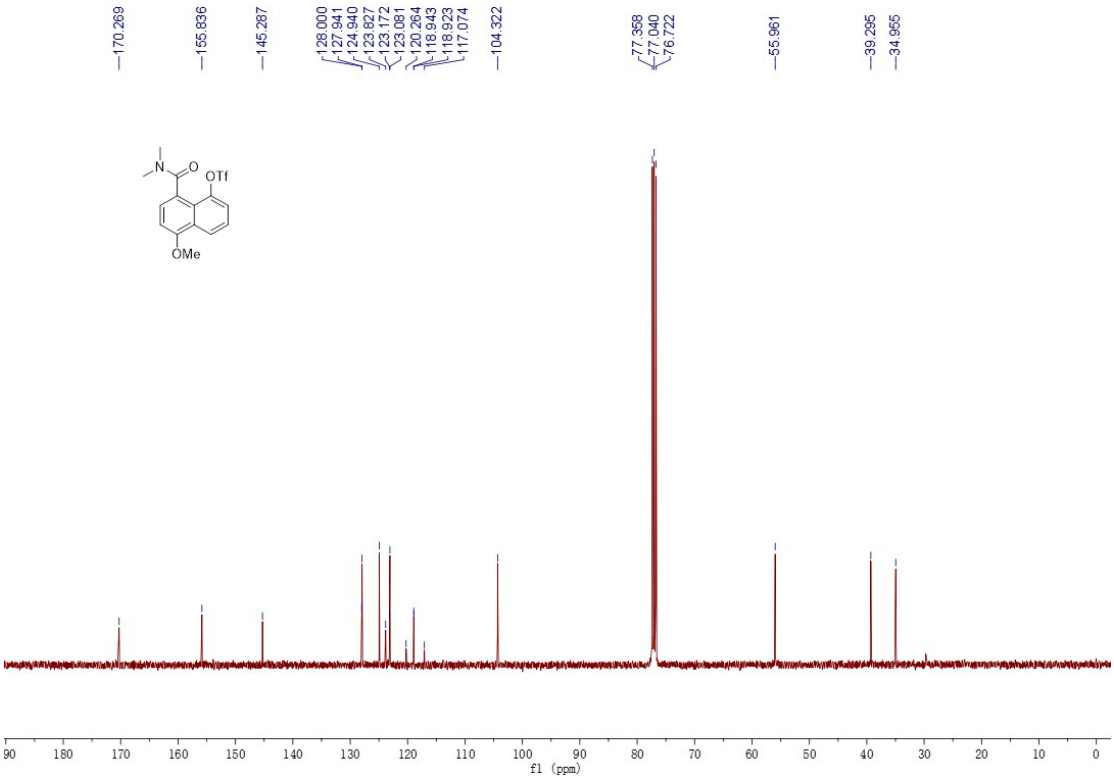
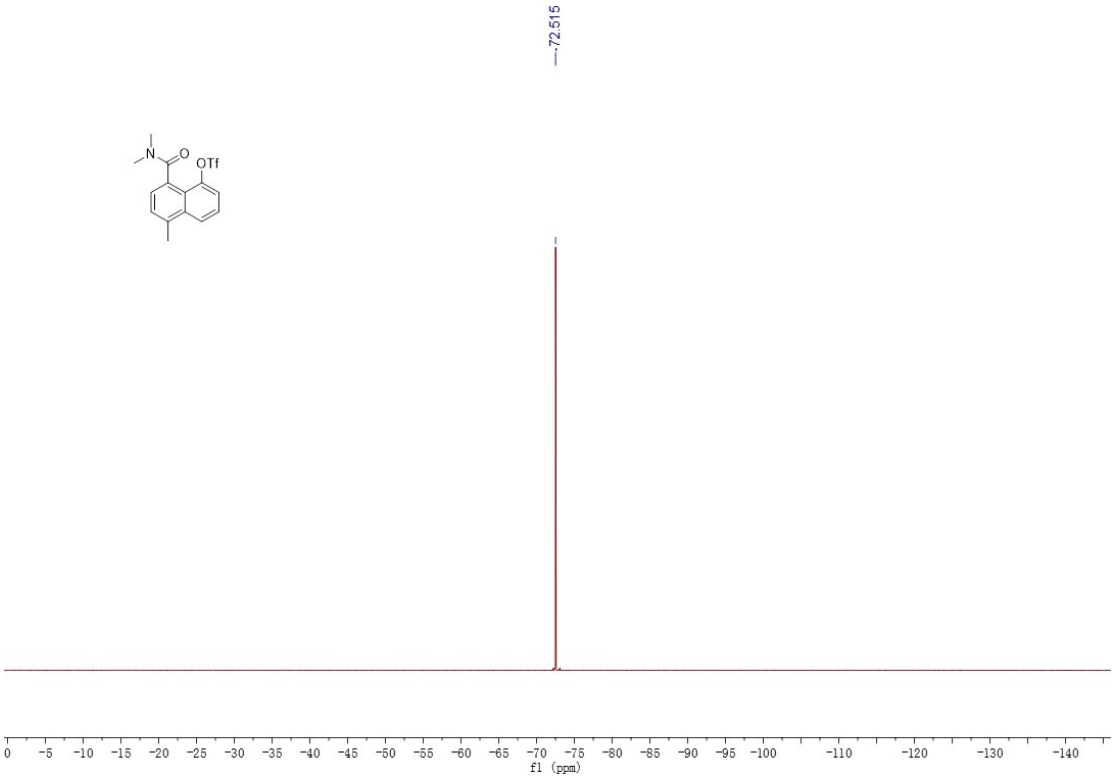
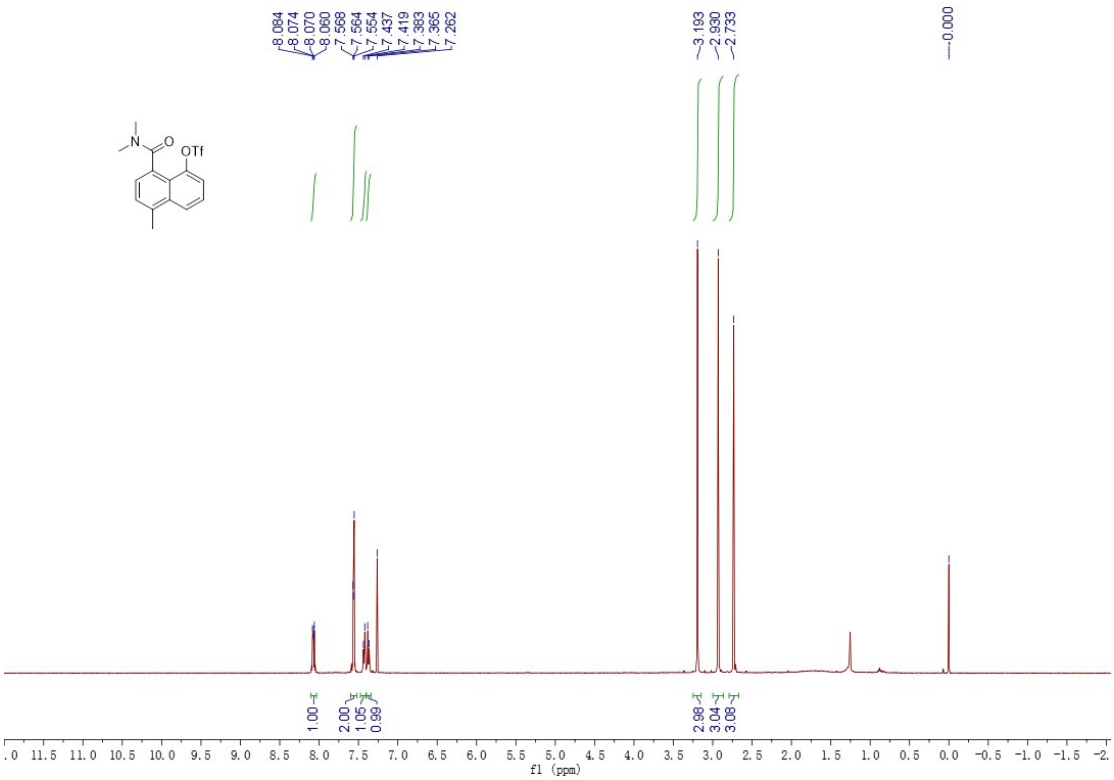
8.376
8.359
8.356
7.563
7.546
7.544
7.518
7.498
7.478
7.415
7.395
7.265
6.907
6.887
4.033
3.186
2.938
0.000
OTf
OMe
0.96
1.01
1.00
0.99
1.01
3.01
2.97
3.00
f1 (ppm)


-72.540
OTf
OMe
f1 (ppm)


170.269
155.836
145.287
128.000
127.941
124.940
123.627
123.172
123.081
120.264
118.943
118.923
117.074
104.322
77.358
77.040
76.722
55.961
39.295
34.955
N
O
OTf
OMe
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3j


-72.515
OTf
f1 (ppm)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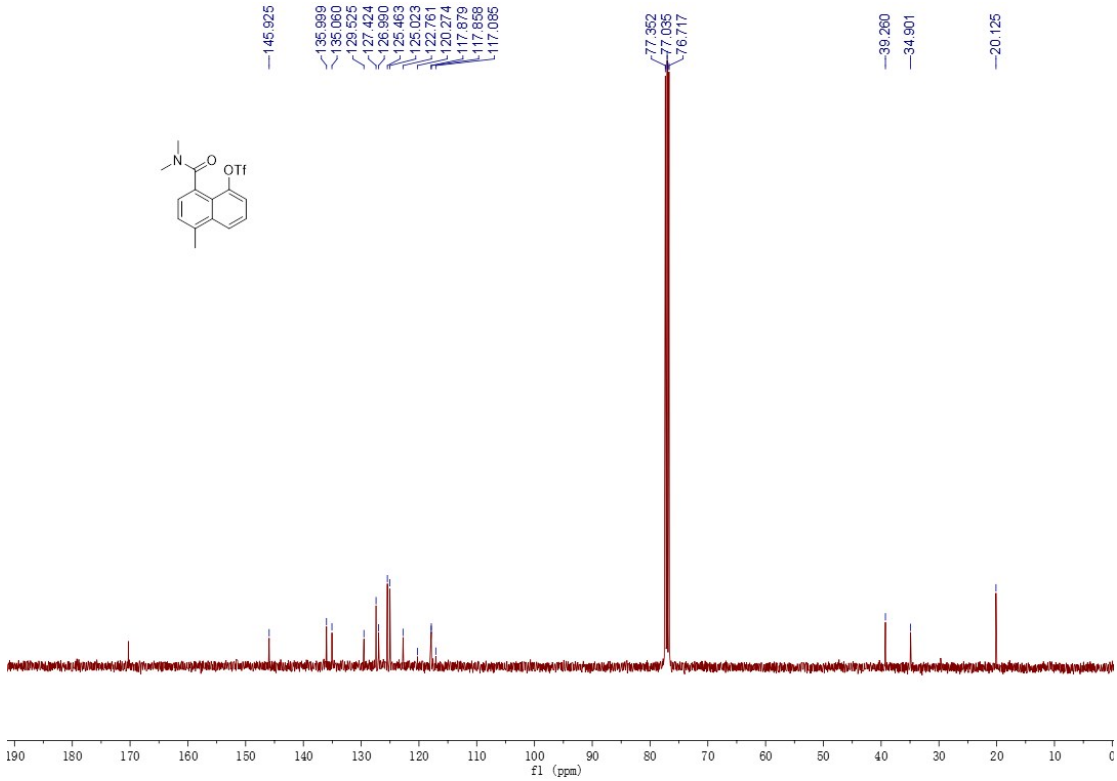
8.074
8.070
8.060
7.568
7.564
7.554
7.437
7.419
7.383
7.365
7.262
3.193
2.930
2.733
0.000
OTf
1.00
2.00
1.05
0.99
2.98
3.04
3.08
f1 (ppm)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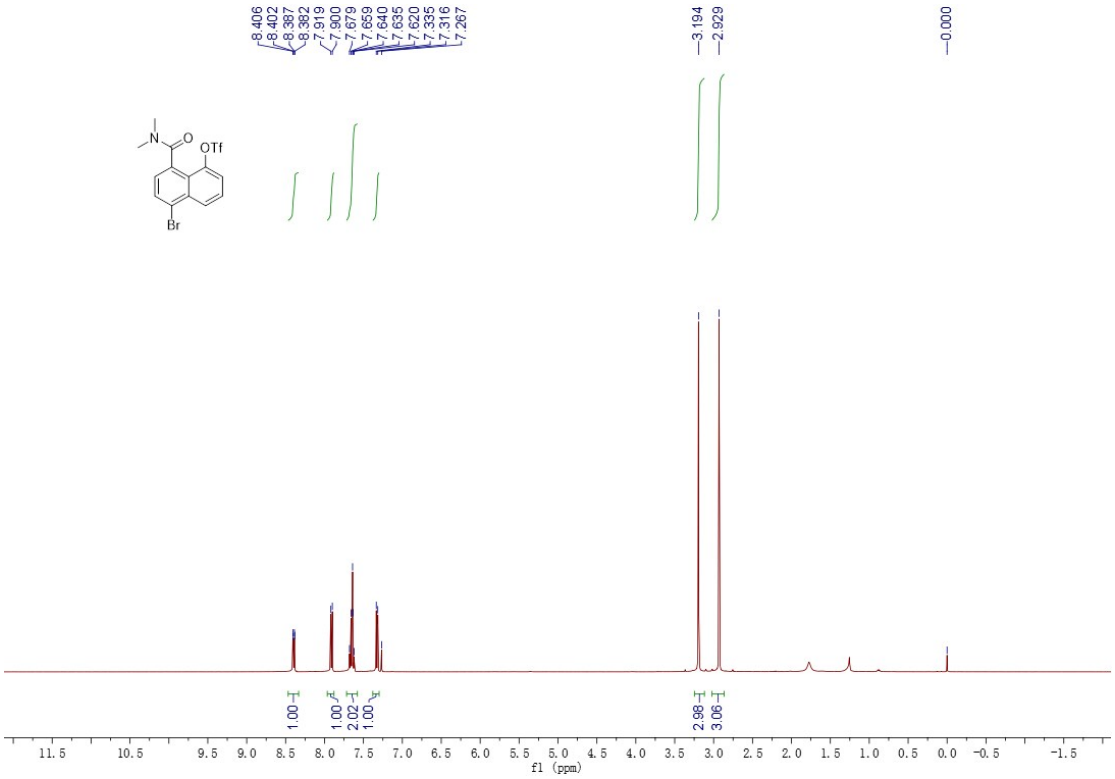
135.060
129.525
127.424
126.990
125.463
125.023
122.761
120.274
117.879
117.858
117.085
77.352
77.035
76.717
39.260
34.901
20.125
OTf
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3k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8.402
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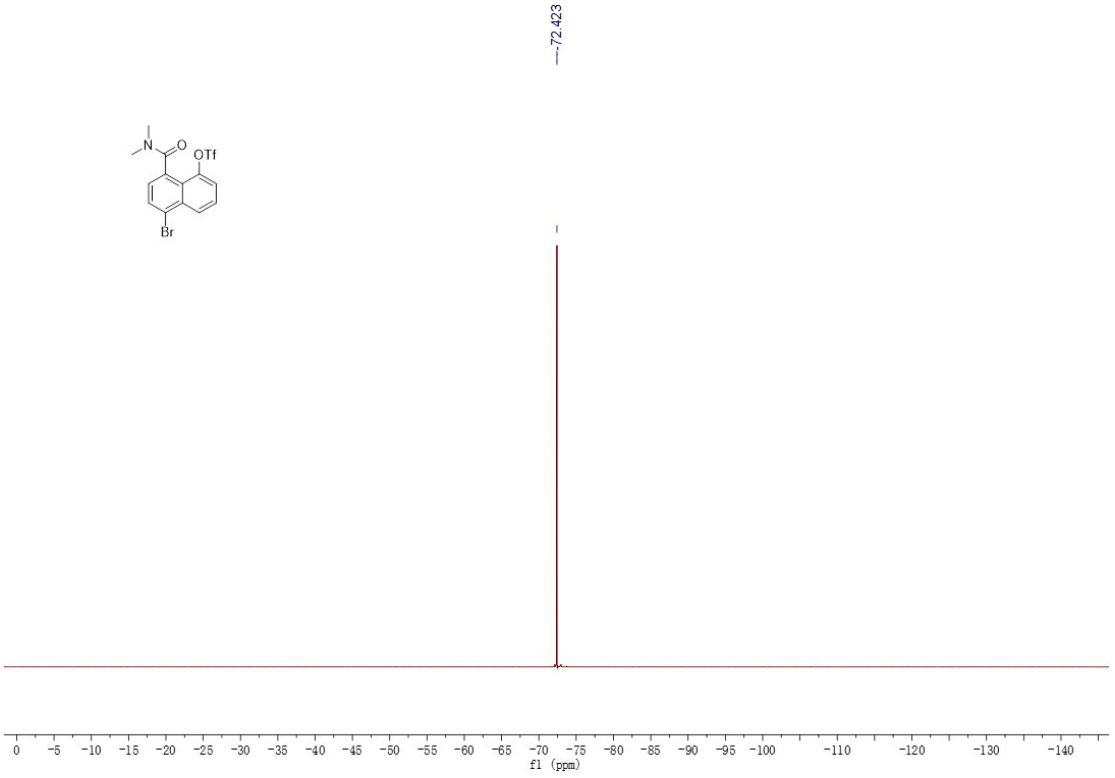
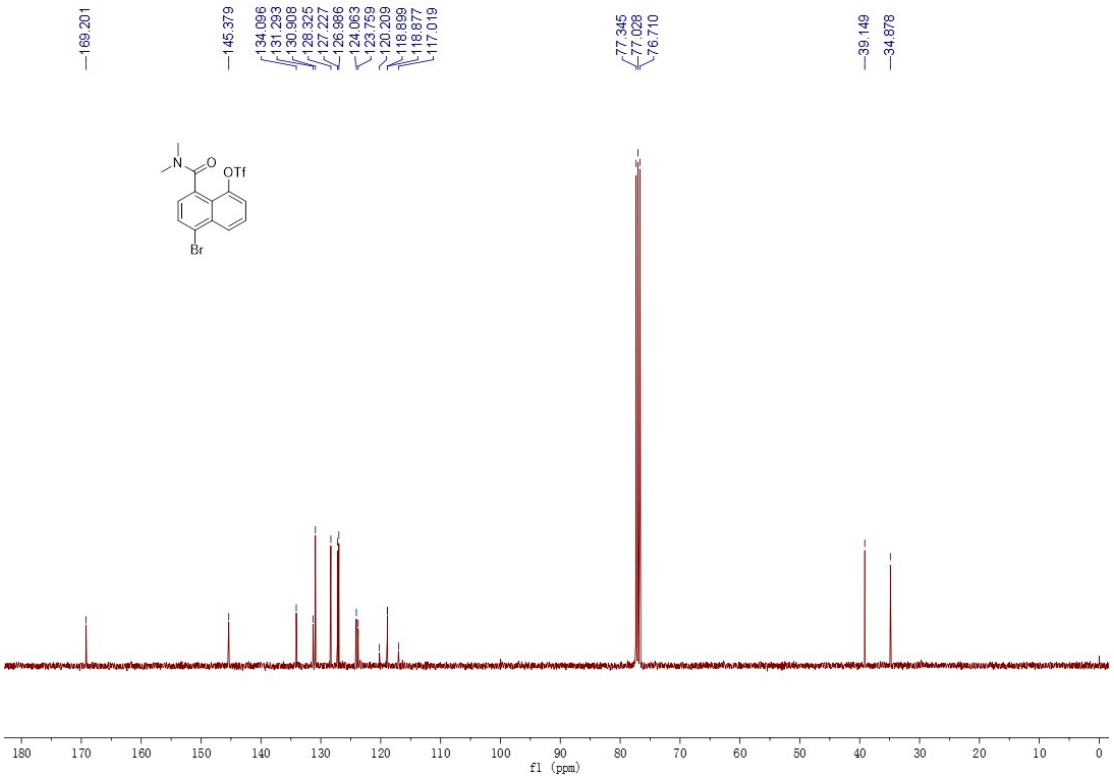
8.382
7.919
7.900
7.679
7.659
7.640
7.635
7.620
7.335
7.316
7.267
3.194
2.929
0.000
OTf
Br
1.00
1.00
2.02
1.00
2.98
3.06
f1 (ppm)


-72.423
OTf
Br
f1 (ppm)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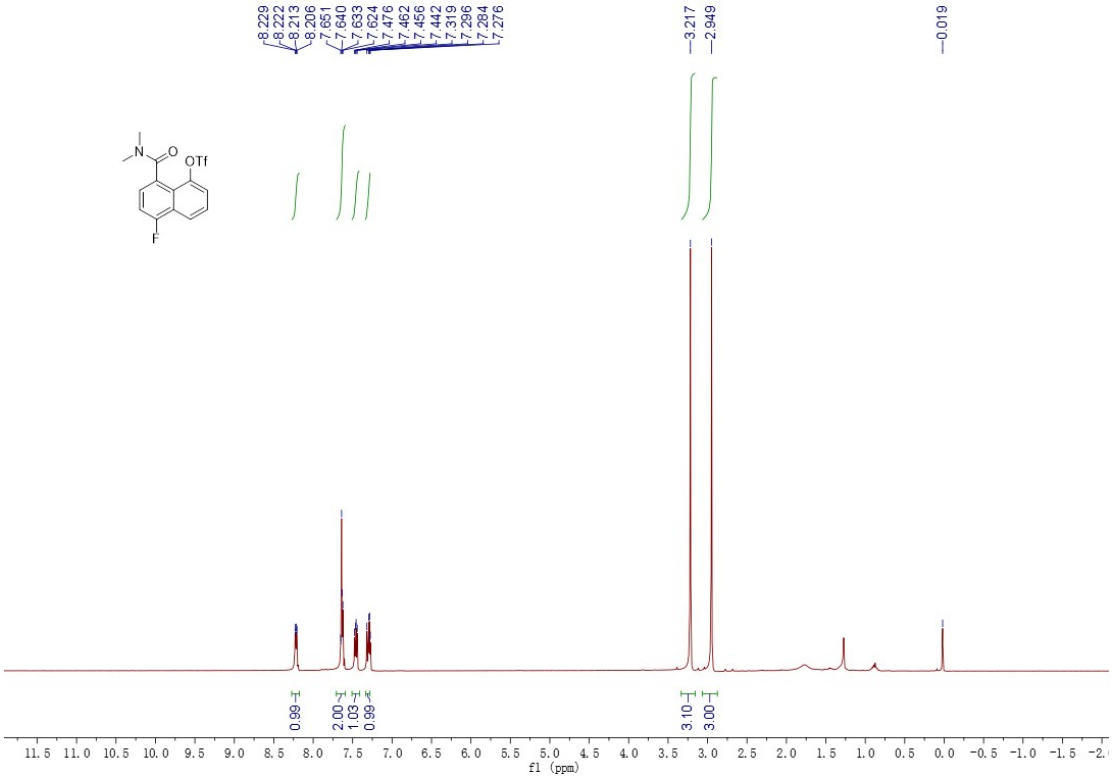
145.379
134.096
131.293
130.908
128.325
127.227
126.986
124.063
123.759
120.209
118.899
118.877
117.019
77.345
77.028
76.710
39.149
34.878
N
O
OTf
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3l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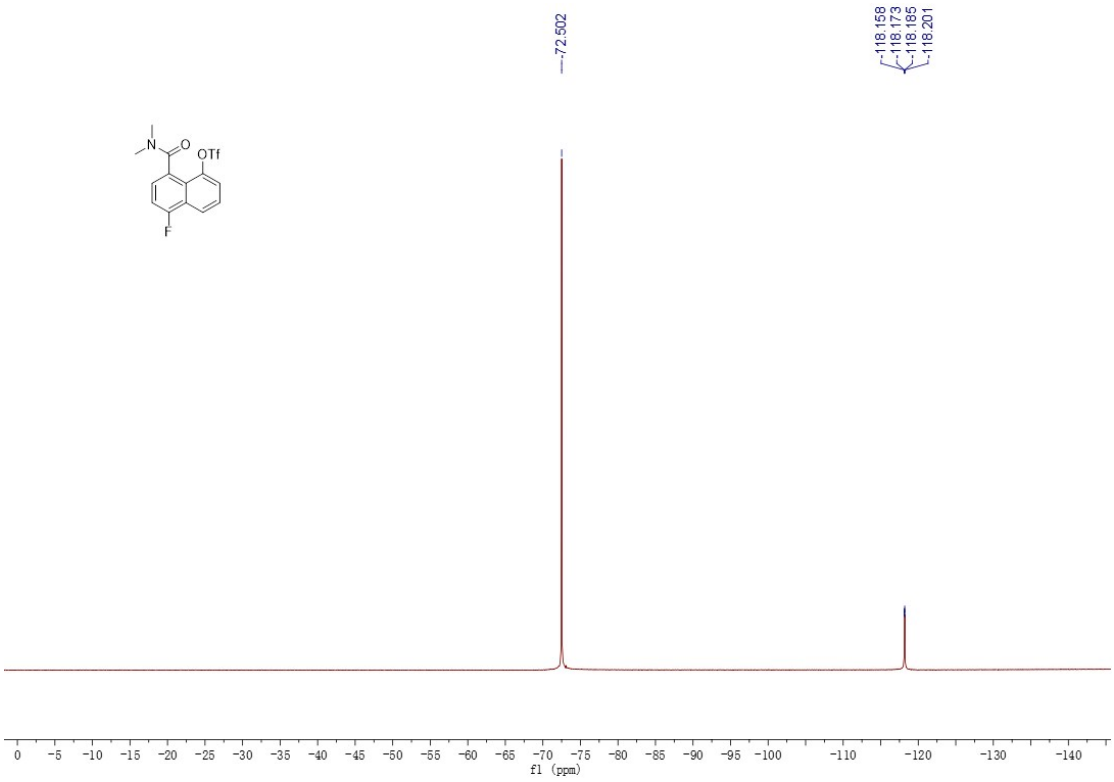
8.222
8.213
8.206
7.651
7.640
7.633
7.624
7.476
7.462
7.456
7.442
7.319
7.296
7.284
7.276
3.217
2.949
0.019
OTf
F
0.99
2.00
1.03
0.99
3.10
3.00
f1 (ppm)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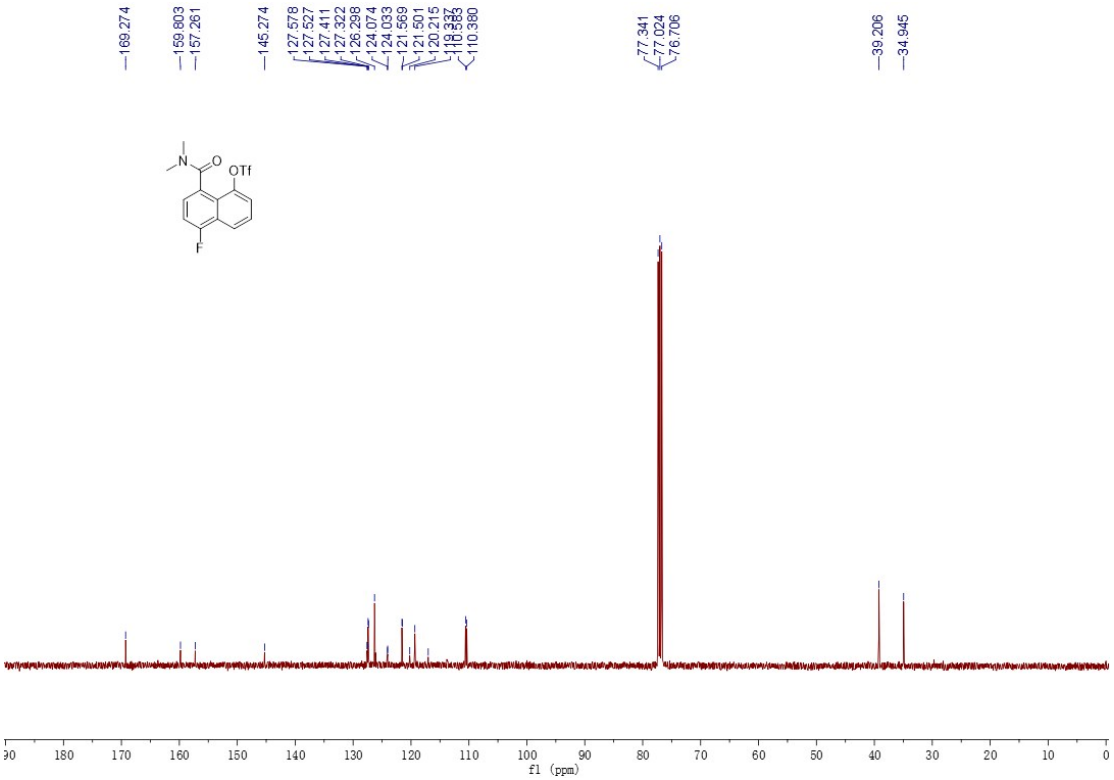
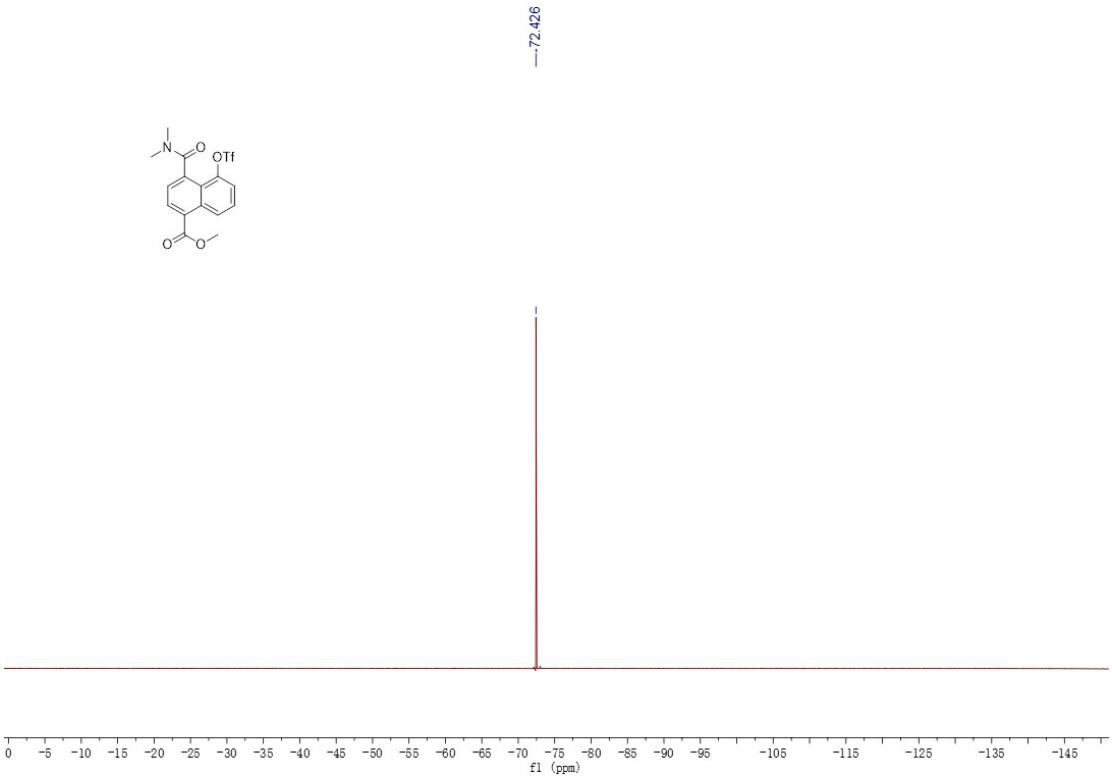
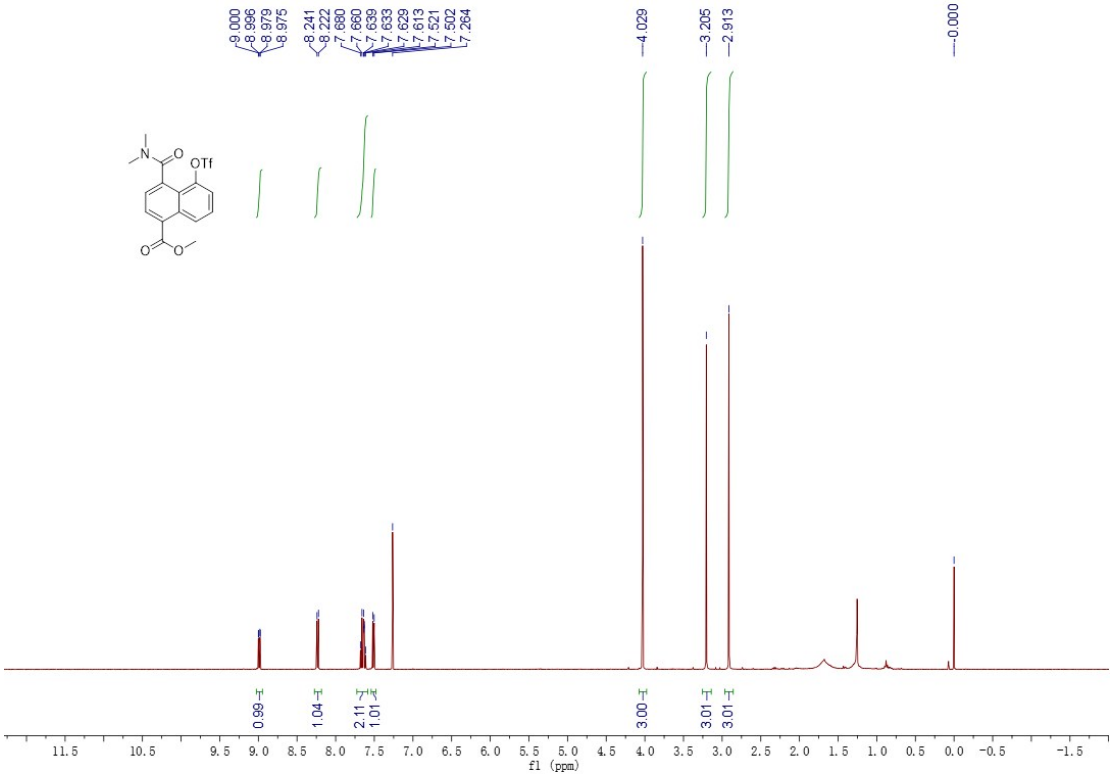
-118.158
-118.173
-118.185
-118.201
OTf
F
f1 (ppm)


169.274
159.803
157.261
145.274
127.578
127.527
127.411
127.322
126.298
124.074
124.033
121.569
121.501
120.215
110.380
77.341
77.024
76.706
39.206
34.945
OTf
F
f1 (ppm)

3m


-72.426
OTf
f1 (ppm)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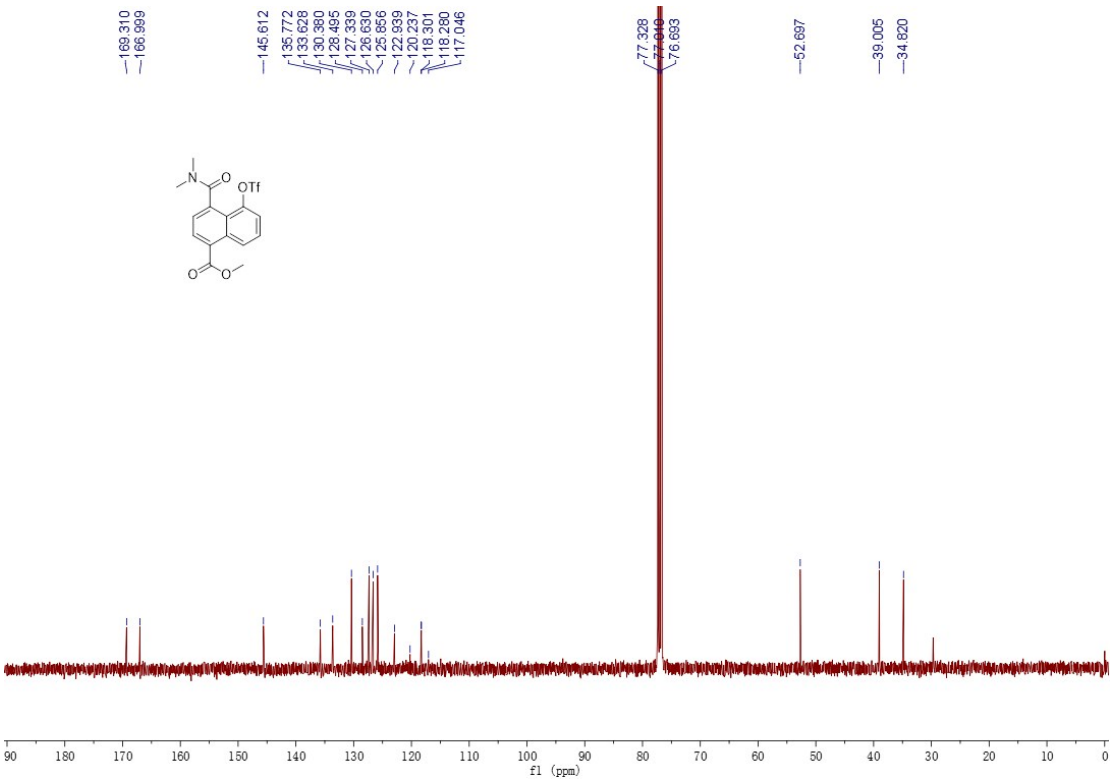
8.979
8.975
8.241
8.222
7.680
7.660
7.639
7.633
7.629
7.613
7.521
7.502
7.264
4.029
3.205
2.913
0.000
OTf
0.99
1.04
2.11
1.01
3.00
3.01
3.01
f1 (ppm)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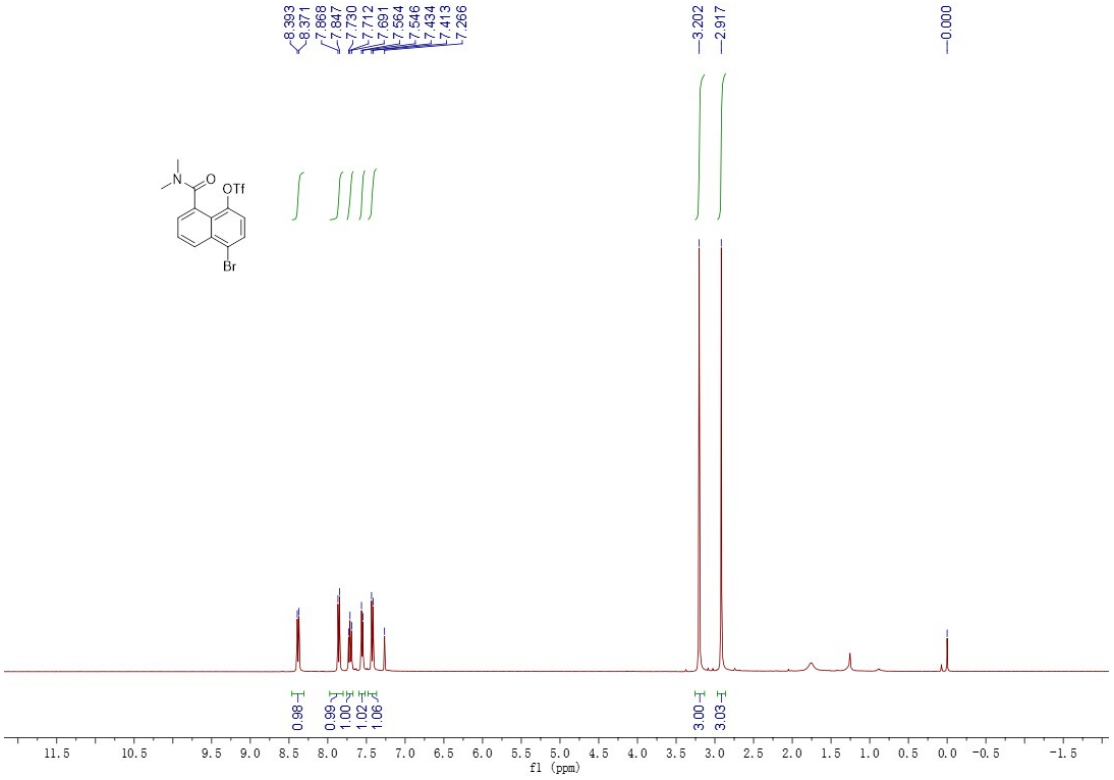
133.628
130.380
128.495
127.339
126.630
125.856
122.939
120.237
118.301
118.280
117.046
77.328
76.693
52.697
39.005
34.820
OTf
f1 (ppm)

3n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8.371
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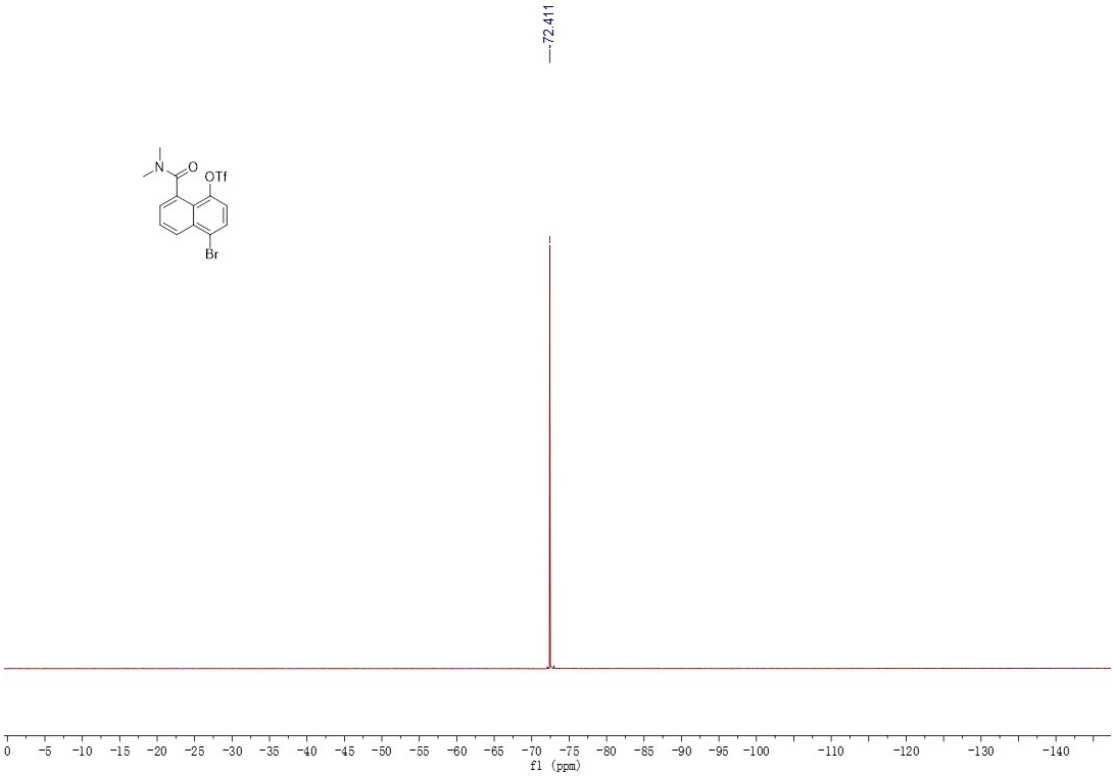
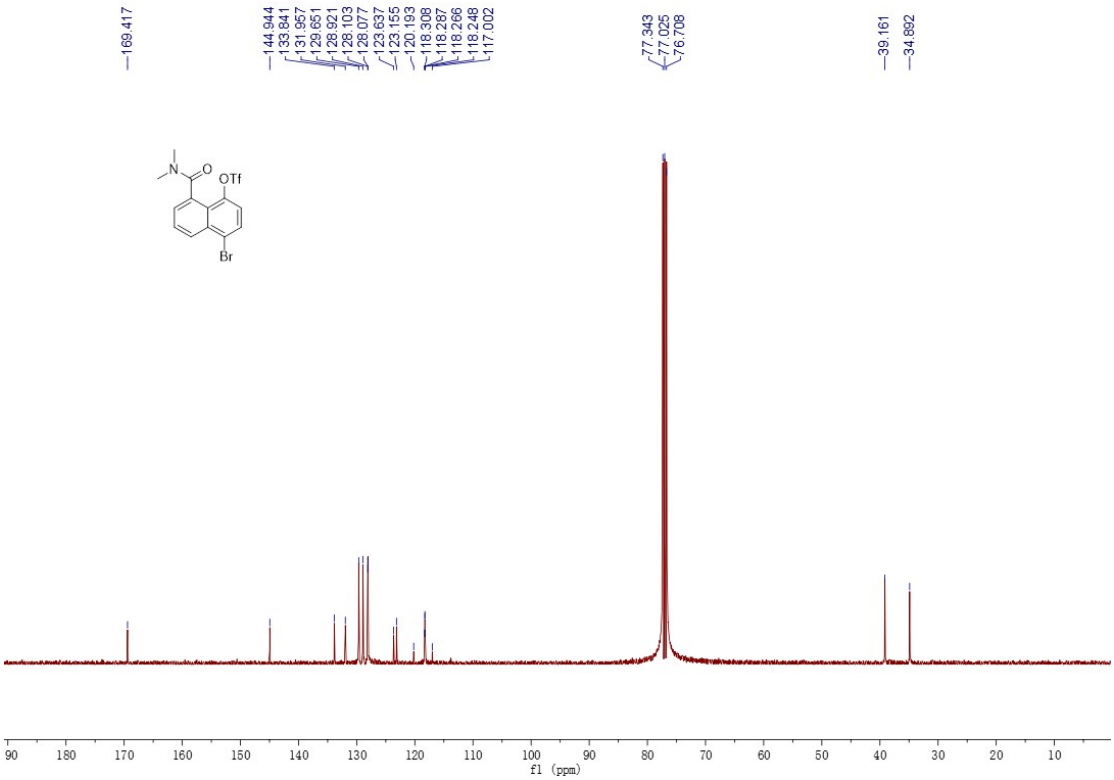
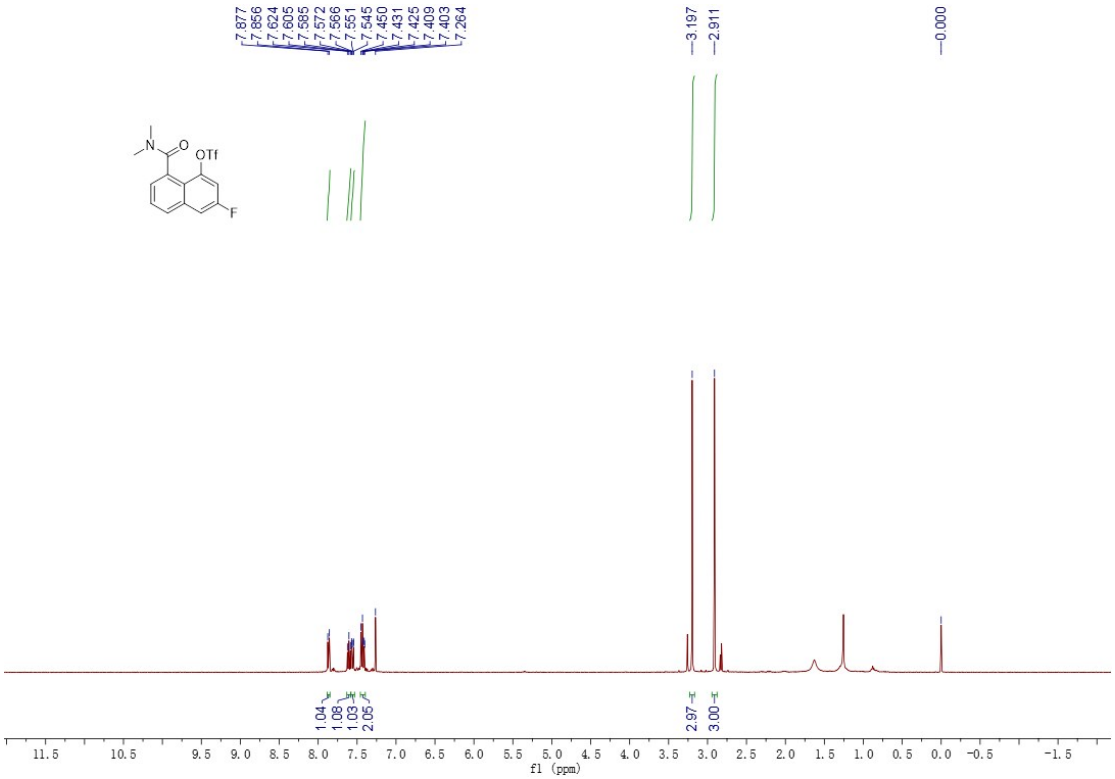
7.847
7.730
7.712
7.691
7.564
7.546
7.434
7.413
7.266
3.202
2.917
0.000
OTf
Br
0.98
0.99
1.00
1.02
1.06
3.00
3.03
f1 (ppm)


-72.411
OTf
Br
f1 (ppm)


169.417
144.944
133.841
131.957
129.651
128.921
128.103
128.077
123.637
123.155
120.193
118.308
118.287
118.266
118.248
117.002
77.343
77.025
76.708
39.161
34.892
OTf
Br
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3o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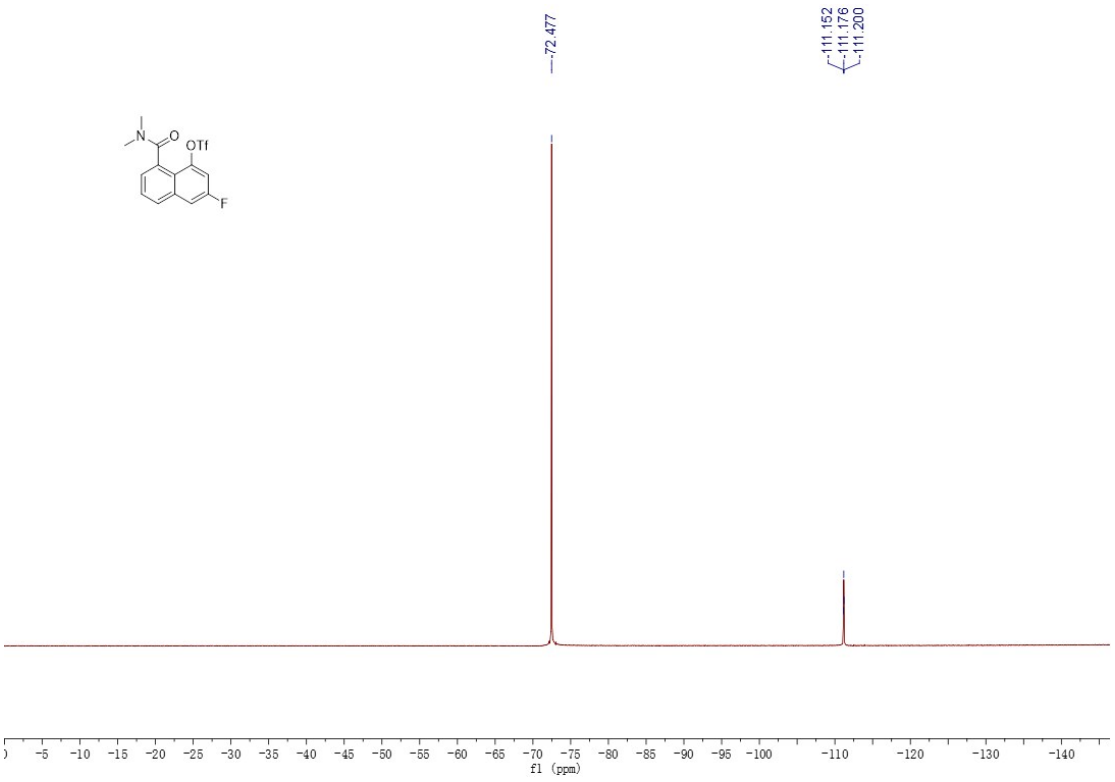
7.572
7.566
7.551
7.545
7.450
7.431
7.425
7.409
7.403
7.264
3.197
2.911
0.000
OTf
F
1.04
1.08
1.03
2.05
2.97
3.00
f1 (ppm)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-111.176
-111.200
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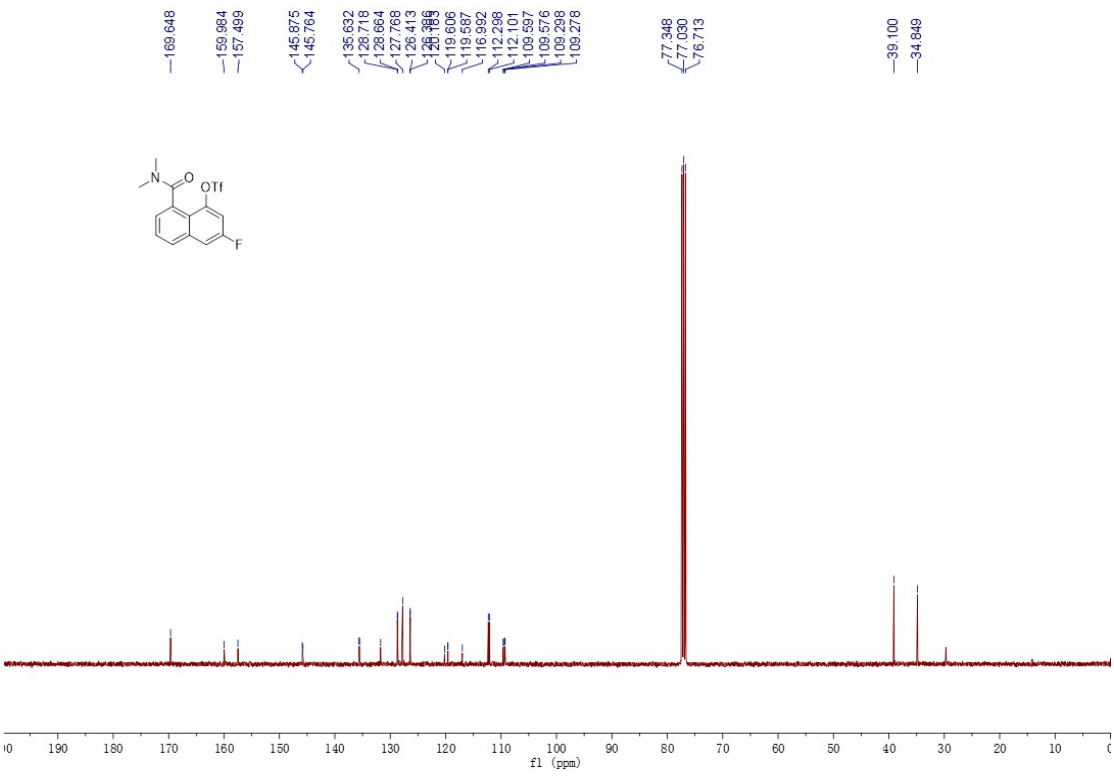
F
f1 (ppm)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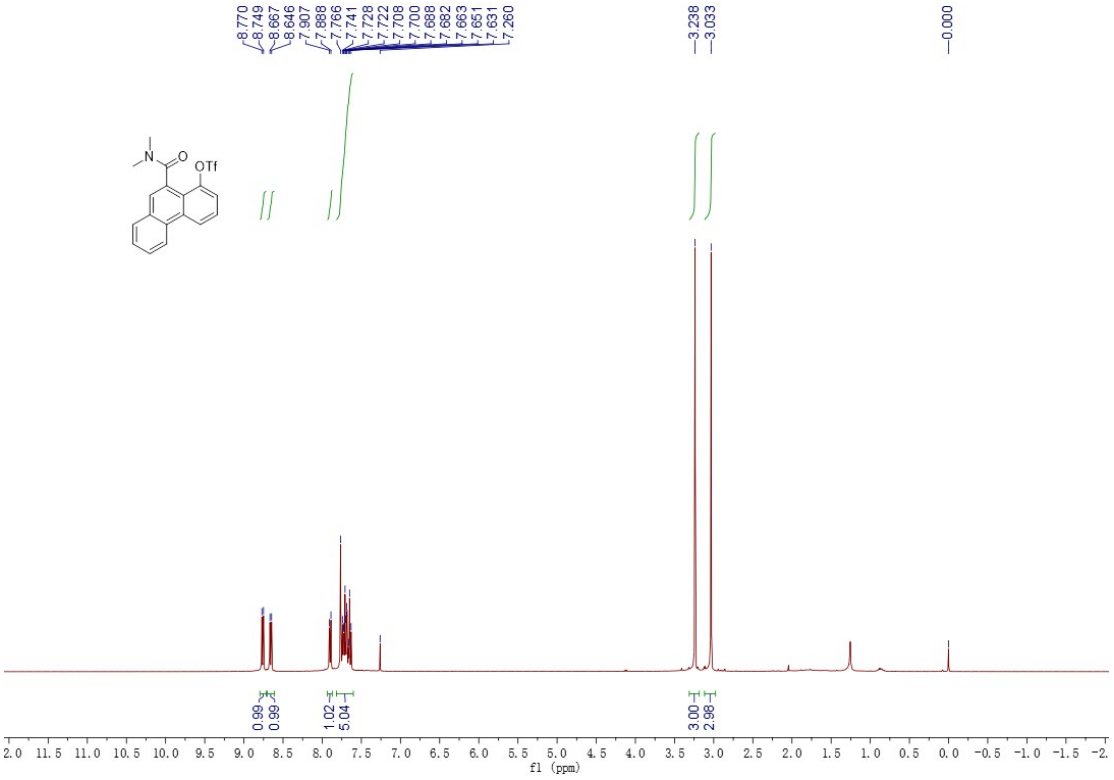
159.984
157.499
145.875
145.764
135.632
128.718
128.664
127.788
126.413
119.606
119.587
116.992
112.298
112.101
109.597
109.576
109.298
109.278
77.348
77.030
76.713
39.100
34.849
N
O
OTf
F
f1 (ppm)

3p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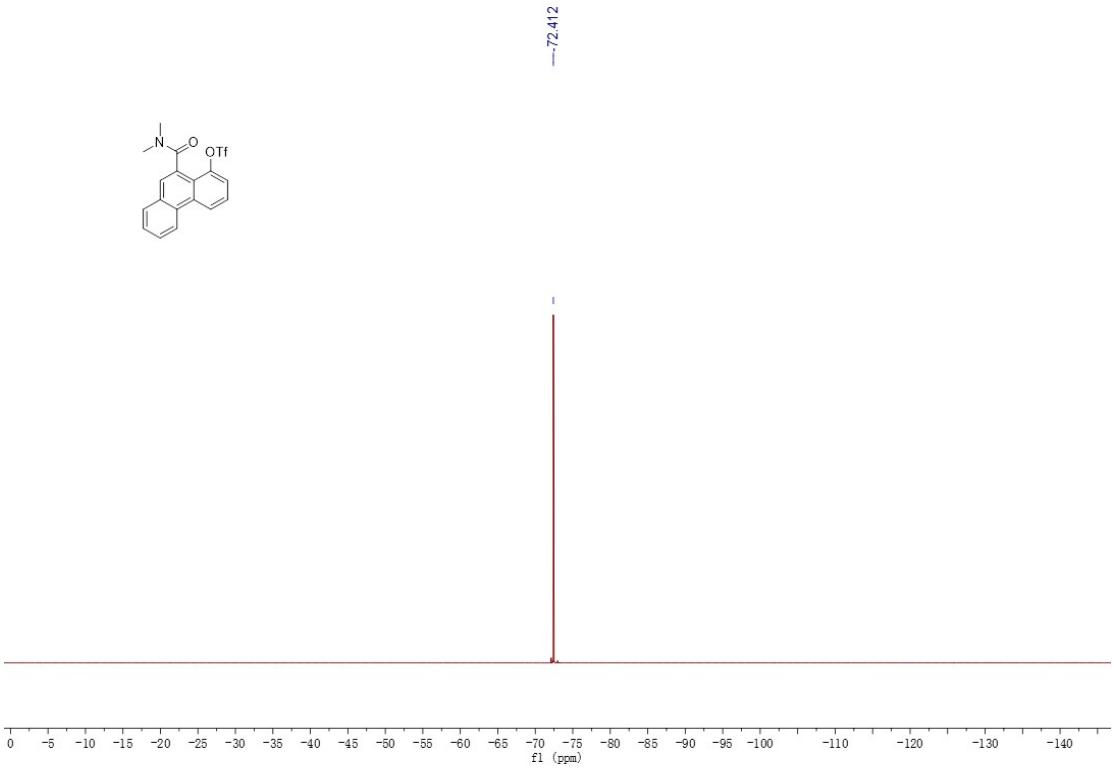
8.667
8.646
7.907
7.888
7.766
7.741
7.728
7.722
7.708
7.700
7.688
7.682
7.663
7.651
7.631
7.260
3.238
3.033
0.000
OTf
0.99
0.99
1.02
5.04
3.00
2.98
f1 (ppm)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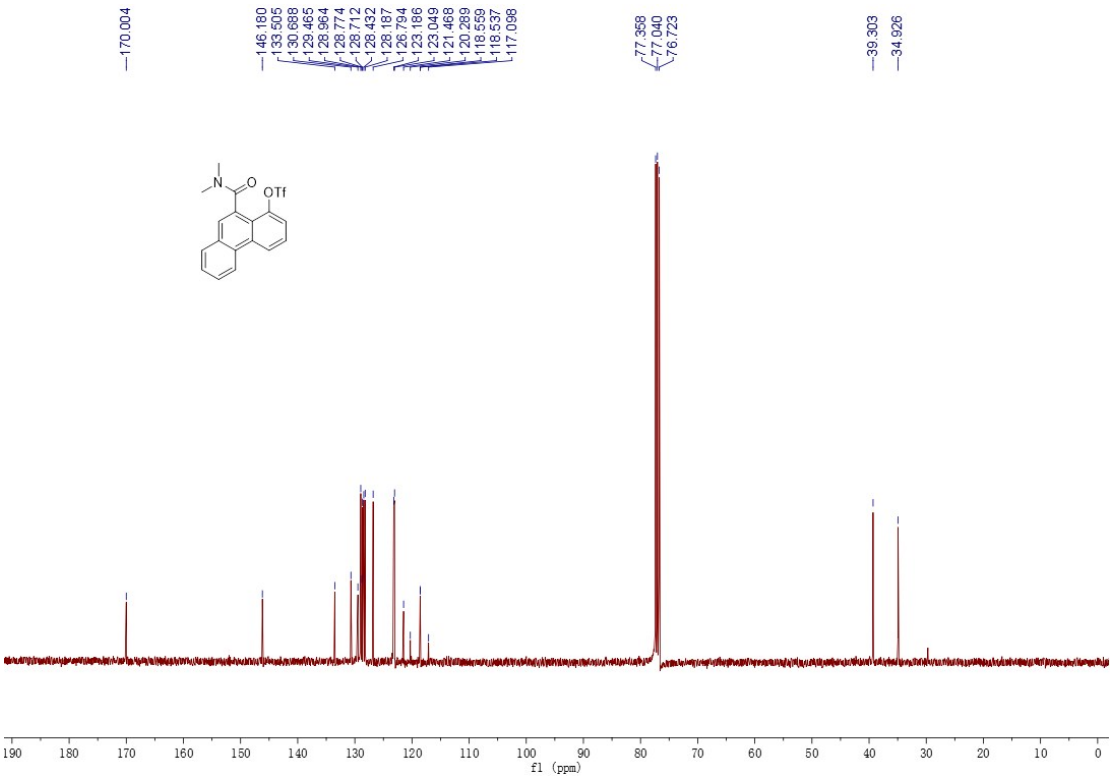
OTf
f1 (ppm)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129.465
128.964
128.774
128.712
128.432
128.187
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123.186
123.049
121.468
120.289
118.559
118.537
117.098
77.358
77.040
76.723
39.303
34.926
N
O
OTf
190
180
170
160
150
140
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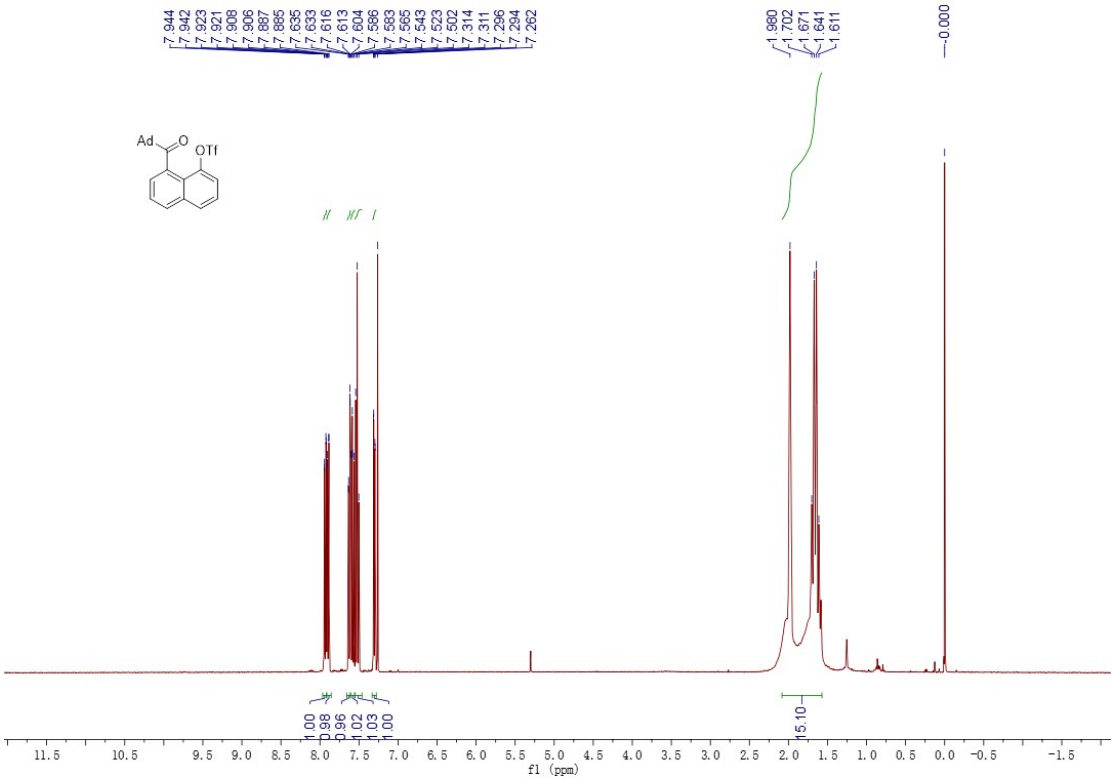
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3q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7.633
7.616
7.613
7.604
7.586
7.583
7.565
7.543
7.523
7.502
7.314
7.311
7.296
7.294
7.262
1.980
1.702
1.671
1.641
1.611
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Ad
O
OTf
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0.98
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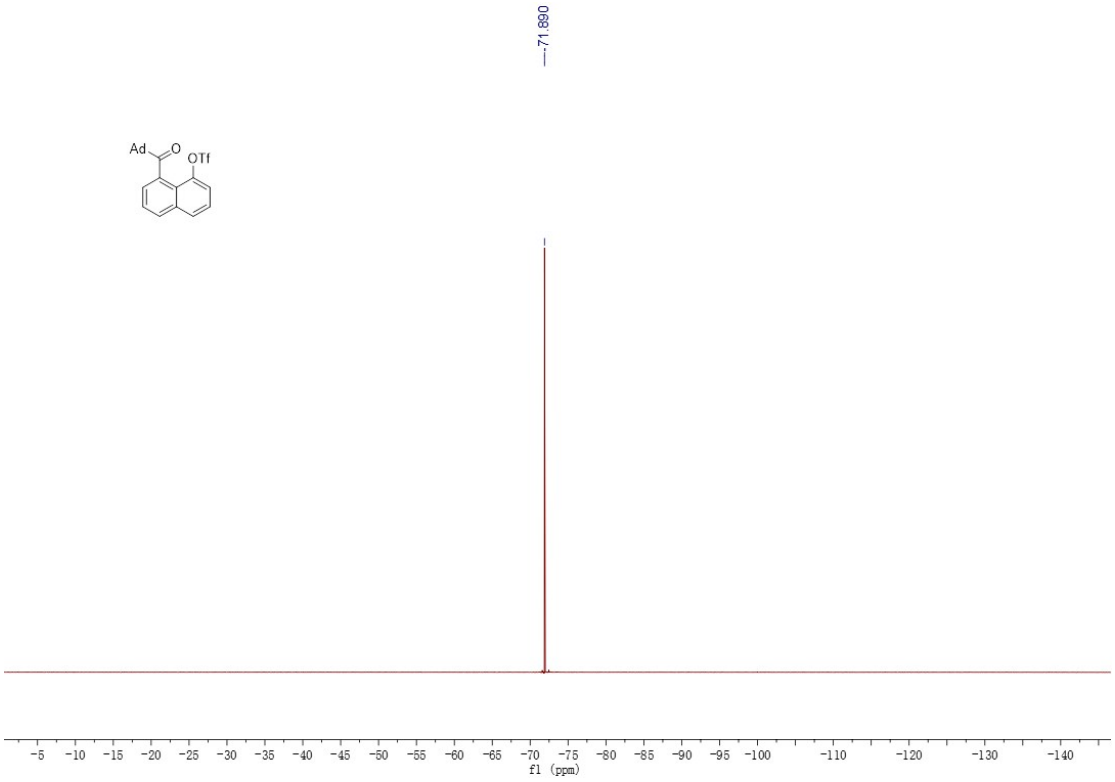
1.03
1.00
15.10
f1 (ppm)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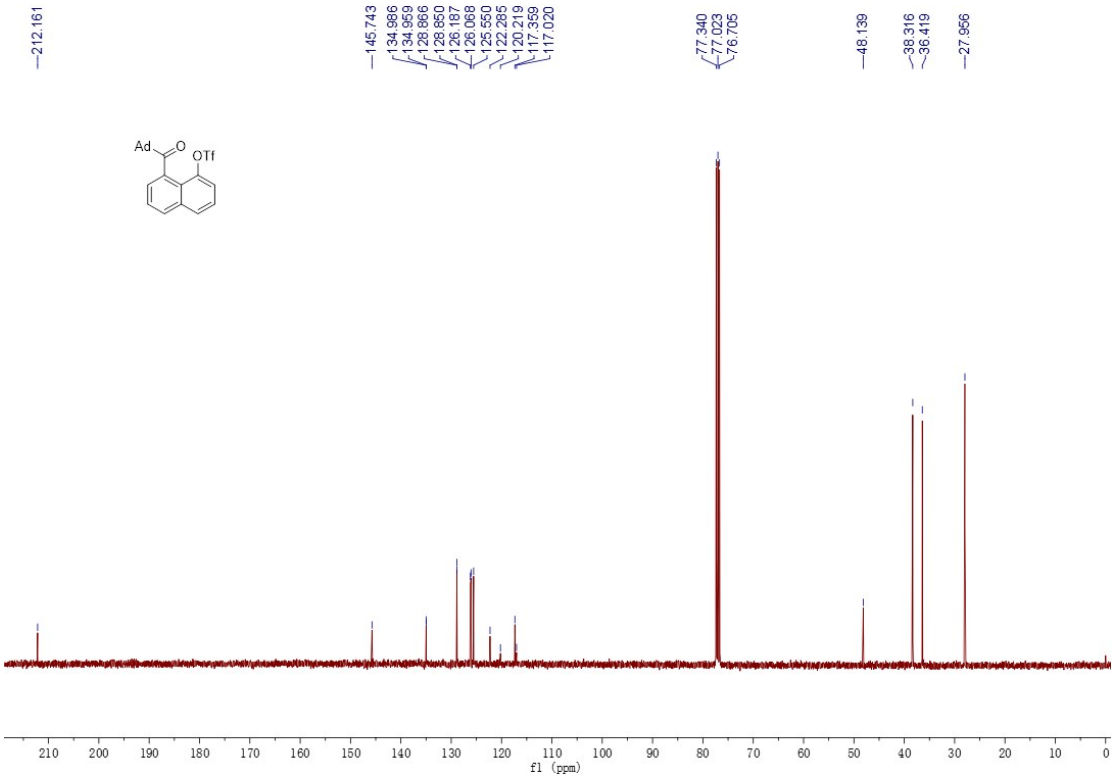
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134.959
128.866
128.850
126.187
126.068
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122.285
120.219
117.359
117.020
77.340
77.023
76.705
48.139
38.316
36.419
27.956
Ad
O
OTf
210
200
190
180
170
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140
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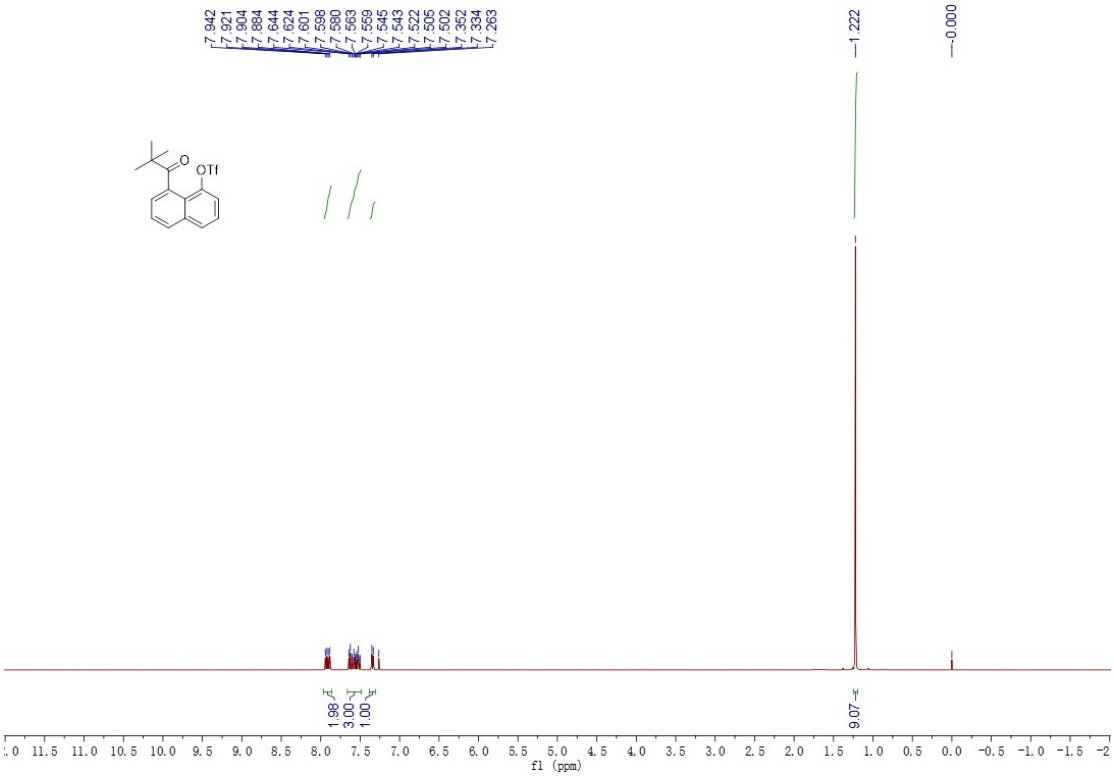
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3r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7.601
7.598
7.580
7.563
7.559
7.545
7.543
7.522
7.505
7.502
7.352
7.334
7.263
1.222
0.000
OTf
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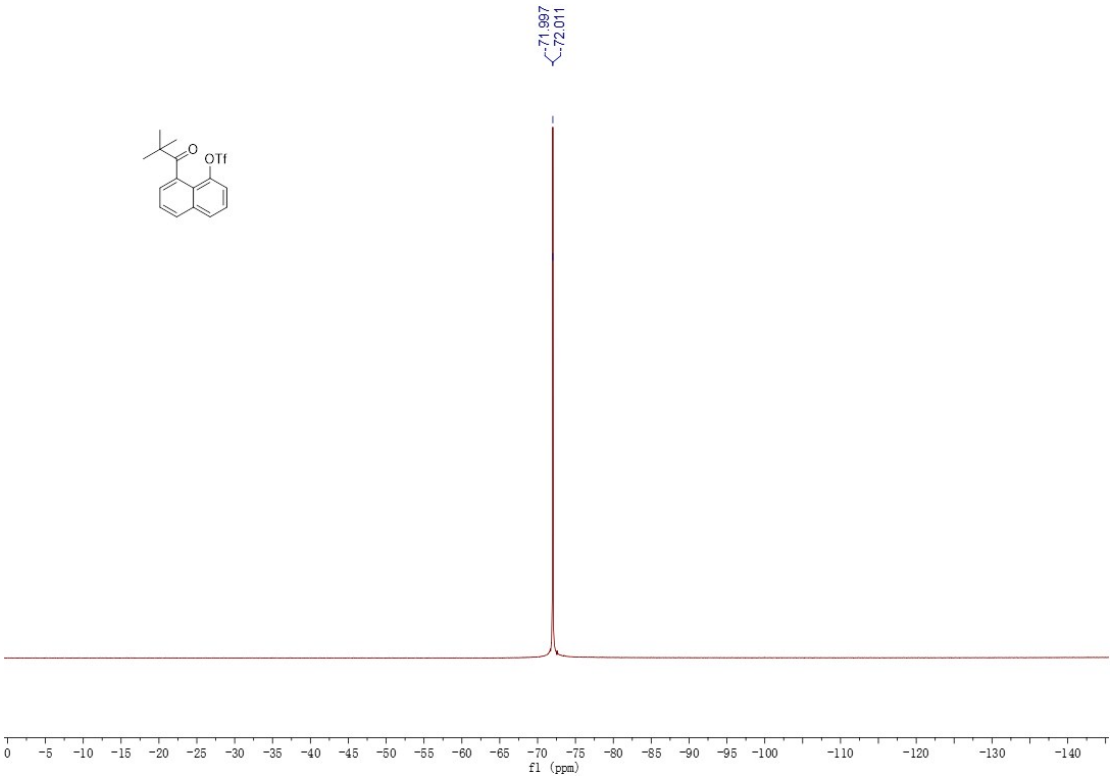
3.00
1.00
9.07
f1 (ppm)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-72.011
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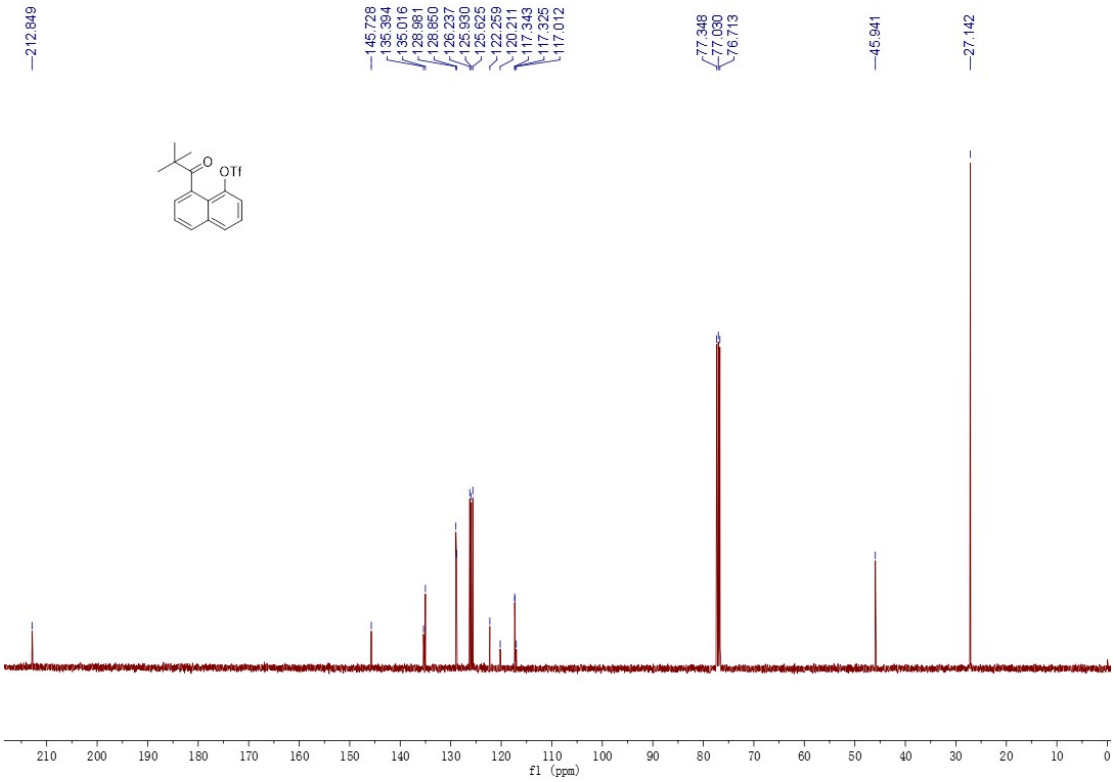
f1 (ppm)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135.016
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128.850
126.237
125.930
125.625
122.259
120.211
117.343
117.325
117.012
77.348
77.030
76.713
45.941
27.142
O
OTf
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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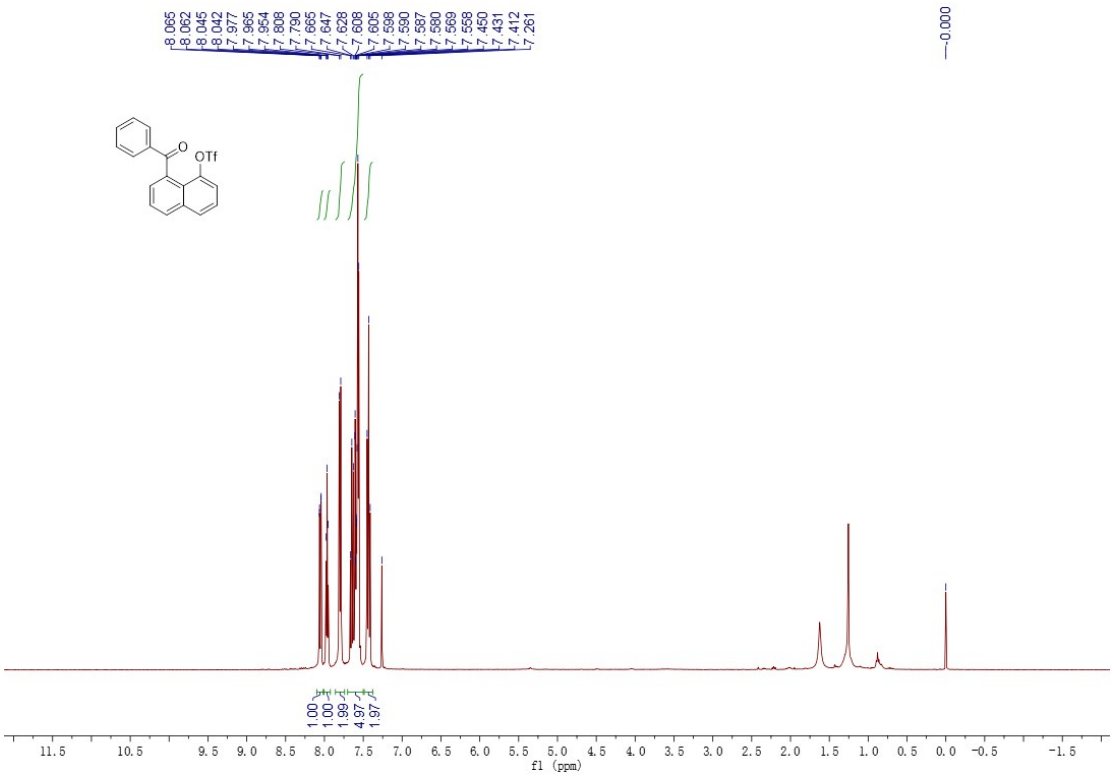
60
50
40
30
20
10
0
f1 (ppm)

3s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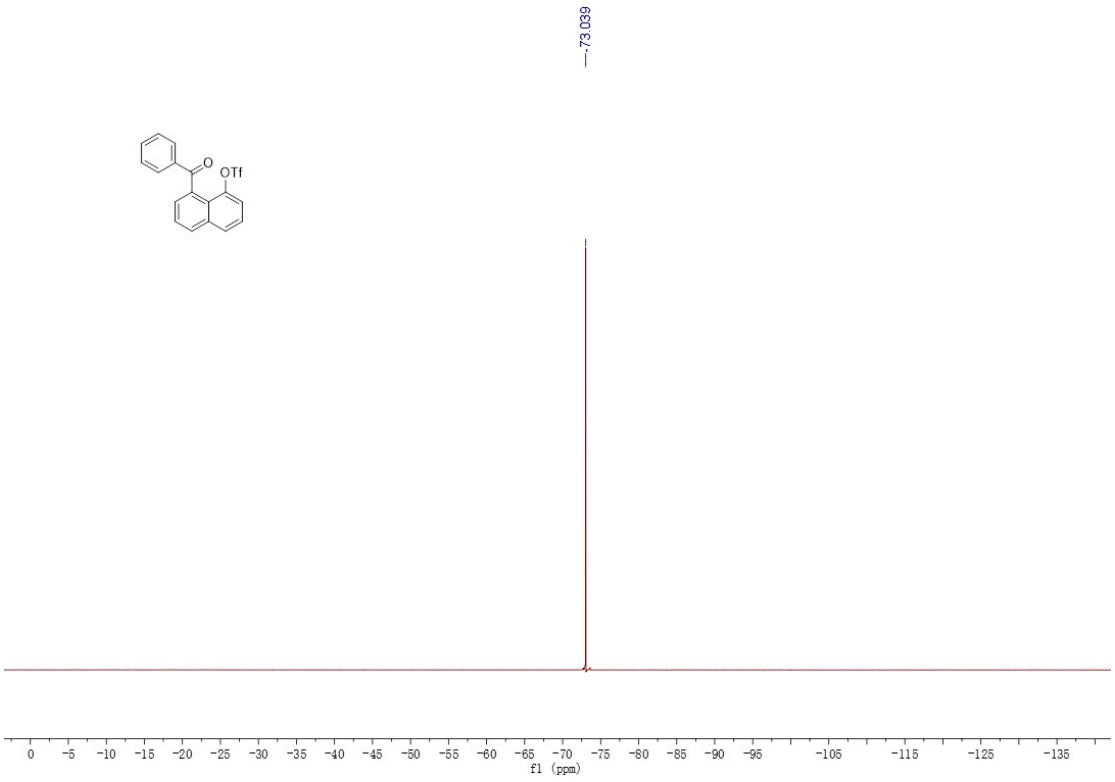
7.965
7.954
7.808
7.790
7.665
7.647
7.628
7.608
7.605
7.598
7.590
7.587
7.580
7.569
7.558
7.450
7.431
7.412
7.261
0.000
OTf
1.00
1.00
1.99
4.97
1.97
f1 (ppm)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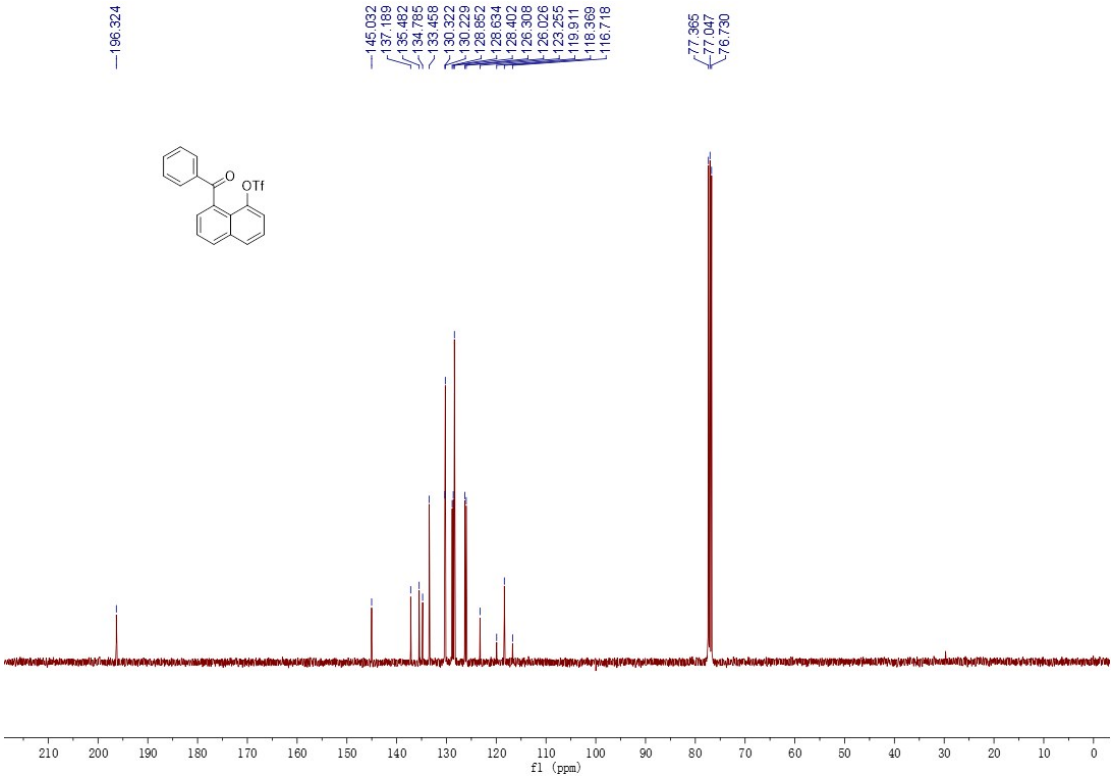
OTf
f1 (ppm)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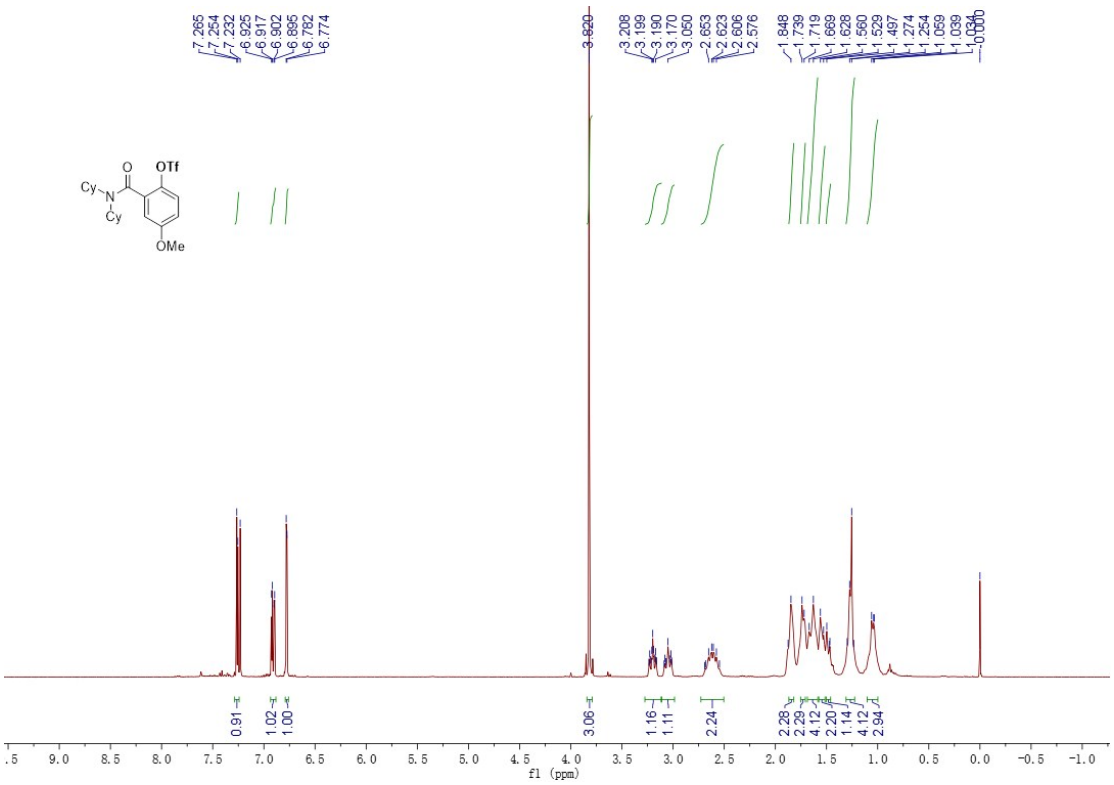
137.189
135.482
134.785
133.458
130.322
130.229
128.852
128.634
128.402
126.308
126.026
123.255
119.911
118.369
116.718
77.365
77.047
76.730
O
OTf
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3t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6.782
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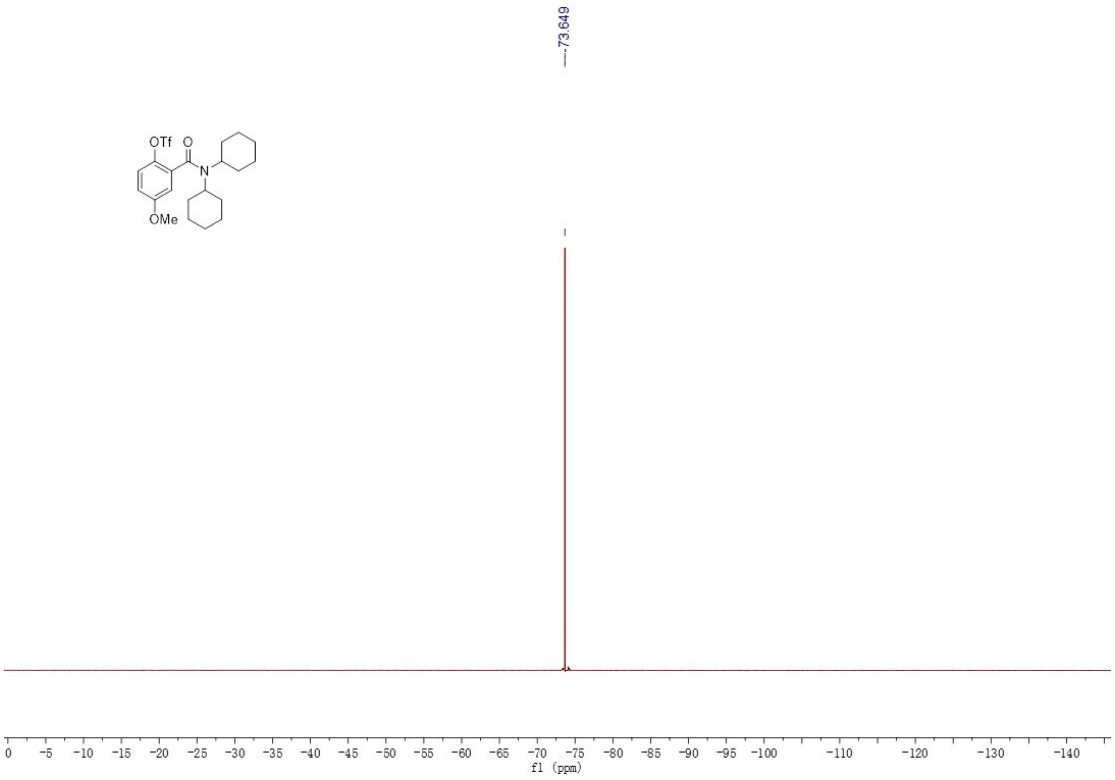
3.820
3.208
3.199
3.190
3.170
3.050
2.653
2.623
2.606
2.576
1.848
1.739
1.719
1.669
1.628
1.560
1.529
1.497
1.274
1.254
1.069
1.039
1.034
0.000
OTf
O
Cy
N
Cy
OMe
0.91
1.02
1.00
3.06
1.16
1.11
2.24
2.28
2.29
4.12
2.20
1.14
4.12
2.94
f1 (ppm)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OTf
O
N
OMe
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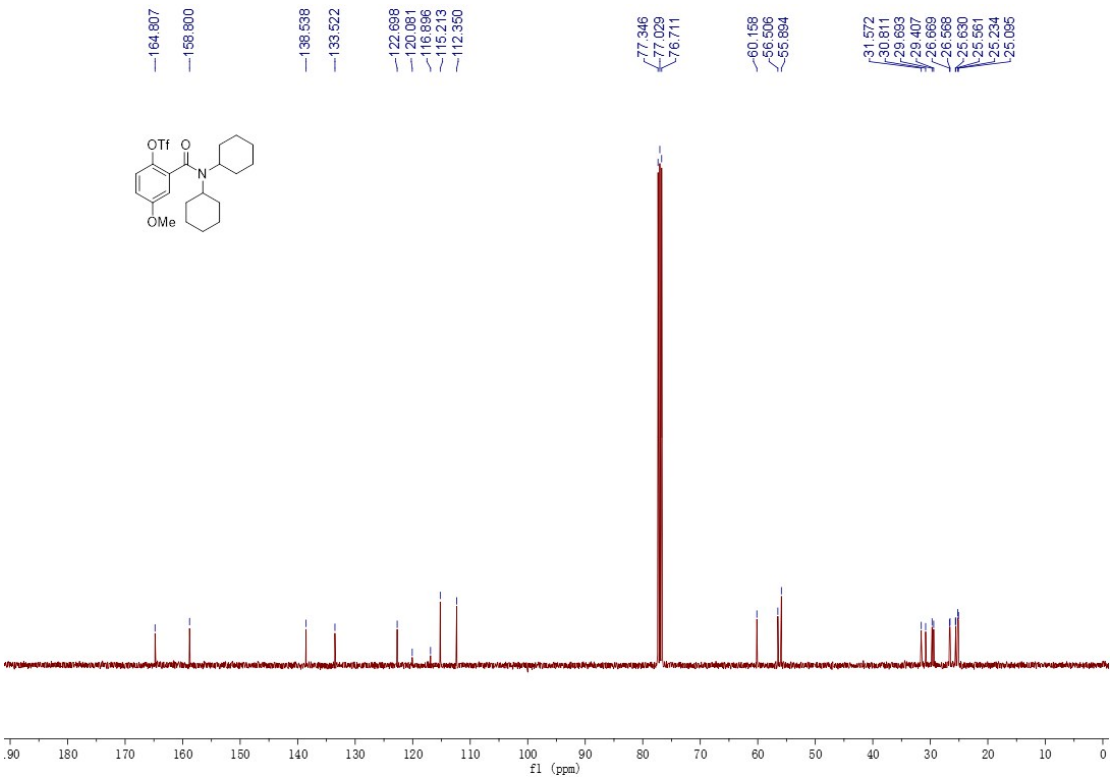
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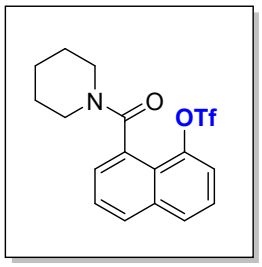
133.522
122.698
120.081
116.896
115.213
112.350
77.346
77.029
76.711
60.158
56.506
55.894
31.572
30.811
29.693
29.407
26.669
26.568
25.630
25.561
25.234
25.095
OTf
O
N
OMe
f1 (ppm)

X-ray Crystallographic Data of 3g



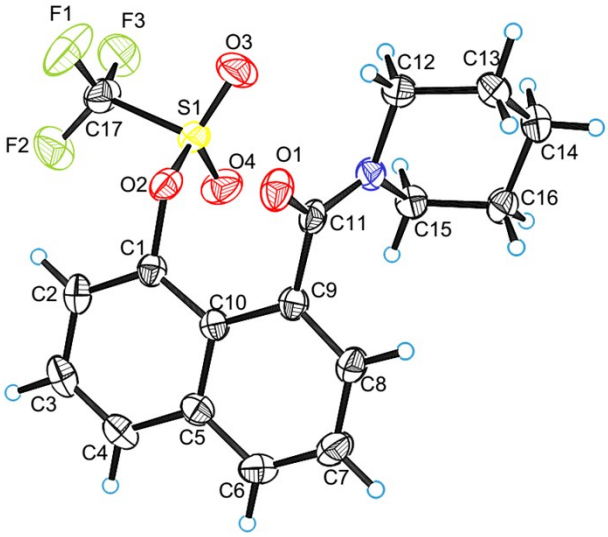


Table 1 Crystal data and structure refinement for 3g.

Identification code	3g
Empirical formula	$C_{17}H_{16}F_3NO_4S$
Formula weight	387.37
Temperature/K	289(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.3925(8)
b/Å	9.5682(9)
c/Å	10.9216(10)
α/°	73.528(8)
β/°	66.260(9)
γ/°	85.458(7)
Volume/Å^3	860.90(15)
Z	2
ρ_{calc}g/cm^3	1.494
μ/mm^{-1}	0.242
F(000)	400.0
Crystal size/mm^3	0.410 × 0.400 × 0.370
Radiation	MoKα (λ = 0.71073)
2Θ range for data	5.958 to 58.23

collection/°	
Index ranges	$-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-14 \leqslant l \leqslant 13$
Reflections collected	7934
Independent reflections	3951 [R_{int} = 0.0321, R_{sigma} = 0.0492]
Data/restraints/parameters	3951/0/235
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1306
Final R indexes [all data]	R_1 = 0.0819, wR_2 = 0.1518
Largest diff. peak/hole / e Å^{-3}	0.23/-0.37

Table 2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 3g.U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	6616.0(8)	3343.3(7)	6947.8(6)	53.5(2)
O1	10006.2(18)	3294.2(18)	8183.9(16)	53.3(4)
O2	8204.5(18)	4167.4(17)	6466.3(16)	47.9(4)
F2	6620(2)	4554(2)	4466.1(19)	94.6(6)
N1	7585(2)	2669.0(19)	9874.1(18)	44.9(5)
F3	5351(3)	2550(2)	5544(2)	98.5(6)
O3	6778(3)	1882(2)	7609(2)	86.4(7)
C9	8368(2)	5237(2)	8691(2)	39.9(5)
F1	7825(3)	2597(3)	4639(2)	117.9(8)
O4	5352(2)	4165(2)	7546(2)	76.6(6)
C10	8322(2)	6167(2)	7424(2)	37.7(5)
C5	8333(3)	7710(2)	7227(2)	45.9(5)
C11	8705(3)	3643(2)	8882(2)	40.6(5)
C1	8282(2)	5704(2)	6314(2)	41.1(5)
C6	8295(3)	8261(3)	8304(3)	55.6(6)
C15	6029(3)	3011(3)	10758(2)	47.8(6)
C17	6624(4)	3270(3)	5282(3)	65.0(8)
C8	8341(3)	5848(3)	9697(2)	49.3(6)
C2	8411(3)	6637(3)	5067(2)	52.5(6)

C13	7673(3)	514(3)	11702(3)	59.3(7)
C16	5805(3)	2478(3)	12270(2)	52.7(6)
C7	8280(3)	7357(3)	9518(3)	58.3(7)
C14	6083(3)	858(3)	12669(3)	61.4(7)
C12	7883(3)	1108(3)	10196(3)	57.1(7)
C4	8401(3)	8664(3)	5947(3)	55.5(6)
C3	8480(3)	8145(3)	4887(3)	60.6(7)

Table 3 Anisotropic Displacement Parameters (Å2×103) for 3g.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	75.2(5)	46.4(4)	47.5(4)	-16.0(3)	-30.9(3)	2.4(3)
O1	50.7(10)	65.0(11)	40.2(9)	-17.1(8)	-15.3(7)	18.5(8)
O2	56.3(10)	52.1(10)	46.0(9)	-22.7(8)	-27.1(8)	13.6(8)
F2	138.2(17)	83.0(12)	82.3(13)	4.3(10)	-78.3(12)	-14.1(11)
N1	56.2(12)	39.2(10)	36.1(10)	-9.8(8)	-17.0(8)	9.8(9)
F3	134.9(17)	92.3(13)	95.1(14)	-13.0(11)	-75.2(13)	-28.7(12)
O3	153(2)	46.4(11)	86.1(15)	-3.4(10)	-82.4(15)	-5.3(12)
C9	38.9(12)	44.7(12)	37.0(11)	-10.9(9)	-16.7(9)	3.1(9)
F1	135.3(18)	164(2)	103.0(16)	-94.7(16)	-66.7(14)	62.6(16)
O4	60.5(12)	79.4(14)	82.0(14)	-41.8(11)	-5.7(10)	-5.1(10)
C10	34.7(11)	40.1(12)	36.3(11)	-8.8(9)	-13.4(9)	1.8(9)
C5	41.8(12)	42.8(13)	49.7(14)	-9.3(10)	-16.7(10)	-0.8(10)
C11	48.9(13)	47.6(13)	30.6(11)	-12.5(9)	-21.4(9)	9.8(10)
C1	39.7(12)	45.4(13)	37.7(12)	-11(1)	-15.9(9)	6(1)
C6	62.2(16)	43.9(14)	67.2(18)	-20.1(13)	-28.6(13)	-0.6(12)
C15	44.4(13)	50.0(14)	47.3(14)	-12.6(11)	-17.4(10)	4.4(10)
C17	88(2)	65.0(18)	66.1(18)	-25.2(15)	-52.1(16)	13.8(16)
C8	59.6(15)	54.9(15)	40.5(12)	-15.4(11)	-25.4(11)	3.1(12)
C2	50.6(14)	68.0(17)	34.6(12)	-7.7(11)	-16.7(10)	1.2(12)
C13	84.7(19)	41.4(14)	51.0(15)	-7.6(11)	-31.1(14)	10.6(13)
C16	53.2(14)	57.5(15)	41.2(13)	-16.6(11)	-11(1)	4.2(12)
C7	70.7(17)	60.2(16)	58.1(16)	-27.3(13)	-32.0(13)	1.0(13)
C14	77.3(19)	59.0(17)	41.5(14)	-5.3(12)	-21.7(13)	-4.6(14)
C12	80.8(19)	41.7(14)	48.5(14)	-15.3(11)	-26.0(13)	15.9(13)

C4	56.4(15)	43.0(14)	58.3(16)	1.4(12)	-23.2(12)	-5.1(11)
C3	58.9(16)	62.7(17)	45.9(15)	8.4(12)	-20.3(12)	-7.7(13)

Table 4 Bond Lengths for 3g.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O4	1.4050(19)	F1	C17	1.298(3)
S1	O3	1.4074(19)	C10	C1	1.418(3)
S1	O2	1.5633(17)	C10	C5	1.431(3)
S1	C17	1.838(3)	C5	C6	1.406(3)
O1	C11	1.231(2)	C5	C4	1.416(3)
O2	C1	1.436(3)	C1	C2	1.364(3)
F2	C17	1.298(3)	C6	C7	1.358(3)
N1	C11	1.347(3)	C15	C16	1.514(3)
N1	C15	1.464(3)	C8	C7	1.400(3)
N1	C12	1.466(3)	C2	C3	1.404(4)
F3	C17	1.315(3)	C13	C12	1.514(3)
C9	C8	1.374(3)	C13	C14	1.517(3)
C9	C10	1.433(3)	C16	C14	1.518(3)
C9	C11	1.505(3)	C4	C3	1.357(4)

Table 5 Bond Angles for 3g.

Atom	Atom	Atom	Angle/	Atom	Atom	Atom	Angle/
O4	S1	O3	122.76(15)	N1	C11	C9	117.74(18)
O4	S1	O2	111.47(10)	C2	C1	C10	123.6(2)
O3	S1	O2	106.90(12)	C2	C1	O2	117.6(2)
O4	S1	C17	107.90(14)	C10	C1	O2	118.64(18)
O3	S1	C17	103.82(13)	C7	C6	C5	121.3(2)
O2	S1	C17	101.76(12)	N1	C15	C16	109.72(18)
C1	O2	S1	121.16(13)	F1	C17	F2	108.9(3)
C11	N1	C15	126.00(18)	F1	C17	F3	108.9(3)

C11	N1	C12	120.56(19)	F2	C17	F3	107.4(2)
C15	N1	C12	113.40(19)	F1	C17	S1	110.71(19)
C8	C9	C10	119.2(2)	F2	C17	S1	112.7(2)
C8	C9	C11	117.54(19)	F3	C17	S1	108.1(2)
C10	C9	C11	122.55(19)	C9	C8	C7	122.0(2)
C1	C10	C5	115.7(2)	C1	C2	C3	119.0(2)
C1	C10	C9	126.0(2)	C12	C13	C14	110.8(2)
C5	C10	C9	118.3(2)	C15	C16	C14	110.8(2)
C6	C5	C4	120.8(2)	C6	C7	C8	119.7(2)
C6	C5	C10	119.4(2)	C13	C14	C16	111.0(2)
C4	C5	C10	119.8(2)	N1	C12	C13	110.73(19)
O1	C11	N1	123.2(2)	C3	C4	C5	121.3(2)
O1	C11	C9	118.9(2)	C4	C3	C2	120.3(2)

Table 6 Torsion Angles for 3g.

A	B	C	D	Angle/	A	B	C	D	Angle/
O4	S1	O2	C1	-16.21(19)	C11	N1	C15	C16	-119.1(2)
O3	S1	O2	C1	-152.86(16)	C12	N1	C15	C16	58.6(3)
C17	S1	O2	C1	98.58(17)	O4	S1	C17	F1	176.2(2)
C8	C9	C10	C1	-177.4(2)	O3	S1	C17	F1	-52.1(3)
C11	C9	C10	C1	12.7(3)	O2	S1	C17	F1	58.8(2)
C8	C9	C10	C5	3.3(3)	O4	S1	C17	F2	53.9(3)
C11	C9	C10	C5	-166.54(19)	O3	S1	C17	F2	-174.4(2)
C1	C10	C5	C6	176.9(2)	O2	S1	C17	F2	-63.4(2)
C9	C10	C5	C6	-3.8(3)	O4	S1	C17	F3	-64.6(2)
C1	C10	C5	C4	-3.8(3)	O3	S1	C17	F3	67.1(2)
C9	C10	C5	C4	175.50(19)	O2	S1	C17	F3	178.02(18)
C15	N1	C11	O1	178.8(2)	C10	C9	C8	C7	-0.4(3)
C12	N1	C11	O1	1.3(3)	C11	C9	C8	C7	169.9(2)
C15	N1	C11	C9	2.8(3)	C10	C1	C2	C3	-4.6(3)
C12	N1	C11	C9	-174.76(19)	O2	C1	C2	C3	179.6(2)
C8	C9	C11	O1	-103.7(2)	N1	C15	C16	C14	-56.2(3)
C10	C9	C11	O1	66.3(3)	C5	C6	C7	C8	1.5(4)
C8	C9	C11	N1	72.5(3)	C9	C8	C7	C6	-2.0(4)
C10	C9	C11	N1	-117.5(2)	C12	C13	C14	C16	-53.5(3)

C5	C10	C1	C2	6.8(3)	C15	C16	C14	C13	54.8(3)
C9	C10	C1	C2	-172.5(2)	C11	N1	C12	C13	120.0(2)
C5	C10	C1	O2	-177.49(17)	C15	N1	C12	C13	-57.8(3)
C9	C10	C1	O2	3.2(3)	C14	C13	C12	N1	54.1(3)
S1	O2	C1	C2	-87.2(2)	C6	C5	C4	C3	178.2(2)
S1	O2	C1	C10	96.8(2)	C10	C5	C4	C3	-1.0(4)
C4	C5	C6	C7	-177.9(2)	C5	C4	C3	C2	3.5(4)
C10	C5	C6	C7	1.4(4)	C1	C2	C3	C4	-0.8(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3g.

Atom	*x*	*y*	*z*	U(eq)
H6	8279	9263	8183	67
H15A	5249	2543	10618	57
H15B	5904	4056	10507	57
H8	8364	5241	10521	59
H2	8452	6278	4347	63
H13A	8475	942	11847	71
H13B	7783	-534	11917	71
H16A	4755	2661	12855	63
H16B	6524	3013	12424	63
H7	8230	7738	10229	70
H14A	6011	556	13618	74
H14B	5284	316	12623	74
H12A	8937	954	9594	68
H12B	7173	586	10021	68
H4	8391	9666	5830	67
H3	8581	8792	4038	73

Computational Details

Methods

All theoretical calculations were performed with the Gaussian09 program[1]. All the structures involved in this study were optimized in the gas phase as minima or transition states by the density functional B3LYP method. As to the basis sets, the LANL2DZ effective core potential[2] with an extra f-polarization function(ζ(f) = 1.42) was used for Pd, and the 6-31G(d)[3] basis set was used for all other atoms (C, H, S, O and F). Frequency calculations were carried out at the same level of theory to get the thermodynamic corrections and to confirm whether the structures are minima (with no imaginary frequency) or transition states (with only one imaginary frequency). To take the solvent effect into accounts, solution phase single-point energies were computed at the B3LYP functional on the optimized structures using the SMD model. o-DiChloroBenzene is used as solvent, according to the experimental conditions. Herein, the SDD20 basis set is used for Pd and 6-311G+(d,p) basis set is used for the other atoms.

In this study, the solution phase single-point energies with thegas-phase Gibbs free energy corrections were used to describe all the reaction energetics. All these energies correspond to the reference stateof 1 mol/L, 298 K.

Gibbs Free Energy Corrections and Electronic Energies in Solvate of related compounds and Transition States

	Thermal Correction of Gibbs Free Energies (Hartree)	Electronic Energy in solvent (Hartree)
$Pd(OTf)_2BP$	0.184017	-2628.010377
5	0.428154	-3383.899901
6	0.442634	-4245.646758
TS1	0.423842	-3383.867454
TS2	0.424471	-3383.852932
TS3	0.440354	-4245.606599
2,4,6-Collidine	0.134561	-366.3553405
1r	0.155469	-1427.795319
3r	0.237057	-1617.652416
7	0.21992	-755.9249151
HF	-0.007433	-100.490527
HOTf	0.005378	-962.2230513
2	0.134561	-366.3553405

Cartesian Coordinates of Intermediates and Transition States

$Pd(OTf)_2BP$

Pd	-0.62831900	0.16642700	-0.06919800
O	1.39973900	0.33114000	-0.30205600
C	2.33372800	-0.49648600	-0.15760500
C	3.67782800	0.06544500	0.05746100
C	4.84573600	-0.68176700	-0.19153100
C	3.78152400	1.40696000	0.48346000
C	6.09627100	-0.10013100	-0.00308700
H	4.77226500	-1.70129700	-0.55400300
C	5.03585000	1.97421800	0.67713300
H	2.87578400	1.97956900	0.65941400
C	6.19189200	1.22361900	0.43584100
H	6.99533200	-0.67486100	-0.20477900
H	5.11412100	3.00348300	1.01383700
H	7.16976800	1.67339100	0.58479600
C	2.08798300	-1.95417400	-0.22466700
C	1.20423800	-2.45386300	-1.19750900
C	2.69056600	-2.83894600	0.68626700
C	0.93729100	-3.81798100	-1.26359900
H	0.74899700	-1.77220300	-1.90975800
C	2.39814200	-4.20023900	0.63145700
H	3.35535400	-2.45481700	1.45333300
C	1.52829000	-4.69090800	-0.34553900
H	0.26295800	-4.19867700	-2.02471100
H	2.84676000	-4.87711700	1.35242300
H	1.30890700	-5.75393300	-0.39030000
O	-2.68157800	-0.12912900	0.34279200
S	-2.46605200	-1.50799800	0.96266400
O	-0.94426500	-1.62822700	1.03314100
O	-3.23255800	-1.85854700	2.13951800
C	-2.95753400	-2.70584500	-0.38443300
F	-2.66952800	-3.94508100	0.01066600
F	-2.28187100	-2.43146600	-1.50492400
F	-4.26178400	-2.59490100	-0.61302500
O	-0.73232200	1.86000400	-1.13861500
S	-0.29224300	3.20761400	-0.48123700
O	0.52970600	3.00377700	0.71693100
O	0.13568900	4.13766500	-1.51970400
C	-1.93115000	3.83231100	0.14524200
F	-2.43121100	2.96720800	1.03621900
F	-1.75595400	5.01627700	0.73829800

F	-2.79232500	3.96798900	-0.86383200

5

C	-4.82869	1.33144	-0.95385
C	-3.6489	0.72842	-0.51223
C	-3.11702	-0.3938	-1.25792
C	-3.9409	-0.95714	-2.30336
C	-5.13683	-0.30082	-2.68162
C	-5.55319	0.85187	-2.05288
H	-5.21194	2.19642	-0.43603
C	-1.87864	-1.03639	-1.06527
C	-3.54804	-2.14824	-2.96656
H	-5.72012	-0.72514	-3.49492
H	-6.4549	1.36502	-2.37057
C	-2.37333	-2.77915	-2.64247
C	-1.50269	-2.19812	-1.69129
H	-4.199	-2.54763	-3.73925
H	-2.07503	-3.6984	-3.13637
H	-0.54829	-2.66108	-1.47842
Pd	-0.48595	-0.10224	0.01062
C	-3.05303	1.13531	0.76357
O	-1.91825	0.74476	1.12806
C	-3.76116	1.99224	1.85151
C	-5.16549	1.43665	2.19413
H	-5.57362	2.01223	3.03203
H	-5.88102	1.49311	1.3726
H	-5.10128	0.39003	2.51207
C	-3.81427	3.47416	1.38975
H	-4.49245	3.65688	0.55334
H	-4.15803	4.08584	2.23126
H	-2.81937	3.82637	1.09787
C	-2.92117	1.94404	3.14919
H	-2.80771	0.9218	3.52066
H	-1.92038	2.35661	3.00371
H	-3.43154	2.5362	3.91591
O	1.17489	0.97981	1.2258
C	1.98057	1.8625	0.88002
C	3.43184	1.61487	1.02845
C	4.37231	2.6611	1.032
C	3.86657	0.28757	1.21116
C	5.7264	2.38373	1.20404
H	4.0421	3.68786	0.91738
C	5.22163	0.01854	1.37214

H	3.13653	-0.5145	1.2207
C	6.15217	1.06299	1.36851
H	6.44826	3.19561	1.21239
H	5.55285	-1.00771	1.50156
H	7.20982	0.84777	1.49767
C	1.47571	3.18034	0.39366
C	0.46409	3.81615	1.12948
C	1.97327	3.78729	-0.76894
C	-0.02392	5.05715	0.72509
H	0.08922	3.33929	2.03024
C	1.45558	5.01265	-1.18915
H	2.72026	3.27251	-1.36224
C	0.4675	5.65435	-0.43956
H	-0.78208	5.56213	1.31837
H	1.82552	5.46614	-2.10434
H	0.08032	6.61758	-0.76127
O	1.04967	-0.92359	-0.98538
S	1.61235	-0.3348	-2.33572
O	0.66555	-0.43773	-3.4422
O	2.38467	0.89115	-2.13802
C	2.86126	-1.70275	-2.58247
F	3.51874	-1.46131	-3.72211
F	2.24225	-2.88088	-2.67743
F	3.7317	-1.73495	-1.5742
O	-0.4913	-1.5831	1.42037
S	0.51792	-2.77253	1.49247
O	0.36139	-3.71665	0.38306
O	1.86187	-2.37147	1.90516
C	-0.25816	-3.58977	2.97972
F	-1.53362	-3.90261	2.72904
F	0.41849	-4.71039	3.24948
F	-0.20662	-2.7821	4.04161
F	-0.60507	1.35635	-1.20359

TS1

C	-4.90183	1.38209	-0.48003
C	-3.55919	1.07831	-0.70138
C	-3.2279	-0.10793	-1.45885
C	-4.31704	-0.92275	-1.96129
C	-5.65442	-0.55487	-1.67108
C	-5.94896	0.57085	-0.94058
H	-5.15941	2.25334	0.10059
C	-1.96173	-0.63233	-1.77503
C	-4.07126	-2.07516	-2.74762

H	-6.45014	-1.19373	-2.04484
H	-6.97657	0.83886	-0.71823
C	-2.7888	-2.44952	-3.06866
C	-1.69707	-1.68839	-2.6032
H	-4.9225	-2.64601	-3.10599
H	-2.59317	-3.31733	-3.6903
H	-0.68308	-1.94682	-2.88097
Pd	-0.40714	-0.13102	-0.3709
C	-2.54142	1.94585	-0.08485
O	-1.38753	1.54134	0.16279
C	-2.76349	3.42911	0.33099
C	-3.49483	3.50105	1.69917
H	-3.47543	4.53915	2.04846
H	-4.54119	3.18829	1.66037
H	-2.98629	2.88165	2.44366
C	-3.5083	4.22345	-0.76859
H	-4.54401	3.91471	-0.9195
H	-3.5164	5.28218	-0.48783
H	-2.98967	4.14006	-1.7302
C	-1.37487	4.08653	0.51847
H	-0.79348	3.59888	1.30322
H	-0.78879	4.04649	-0.40475
H	-1.52134	5.13714	0.79034
O	1.5076	1.40841	0.56934
C	2.73843	1.5058	0.57355
C	3.55118	0.73826	1.5623
C	4.81317	1.18051	1.99552
C	2.99659	-0.41936	2.13627
C	5.51082	0.47229	2.97353
H	5.23835	2.09058	1.5856
C	3.70378	-1.13279	3.09953
H	2.01572	-0.75284	1.81824
C	4.96126	-0.68893	3.52069
H	6.481	0.82857	3.3091
H	3.27103	-2.03391	3.52474
H	5.50885	-1.2447	4.27751
C	3.39976	2.43834	-0.39229
C	2.72405	3.61418	-0.75386
C	4.62865	2.13971	-1.00064
C	3.28117	4.49277	-1.67905
H	1.76448	3.82626	-0.29336
C	5.1736	3.0093	-1.94547
H	5.13298	1.20909	-0.76423
C	4.50779	4.19057	-2.27812

H	2.75878	5.40926	-1.94045
H	6.11529	2.76013	-2.42664
H	4.93877	4.87064	-3.0082
O	0.72639	-1.75259	-0.83592
S	1.91209	-1.71534	-1.84857
O	1.48696	-2.12251	-3.19221
O	2.76677	-0.5385	-1.69682
C	2.86009	-3.16161	-1.1475
F	3.9624	-3.33656	-1.88391
F	2.11981	-4.27	-1.19579
F	3.21264	-2.91809	0.11556
O	-0.42672	-0.85879	1.51271
S	-1.5185	-1.85235	2.01671
O	-2.5058	-2.17094	0.98399
O	-0.91516	-2.90495	2.82414
C	-2.40787	-0.7444	3.22225
F	-2.96894	0.29224	2.56531
F	-3.37868	-1.431	3.82907
F	-1.5693	-0.26234	4.13841
F	-0.56249	0.60274	-2.20693

TS2

C	-4.69112	1.59594	-1.37787
C	-3.51825	1.04313	-0.86967
C	-3.0852	-0.24266	-1.36085
C	-3.86478	-0.88279	-2.39705
C	-5.03306	-0.24157	-2.88285
C	-5.44702	0.9687	-2.38276
H	-5.01578	2.56581	-1.0324
C	-1.95078	-0.98692	-0.96477
C	-3.48686	-2.14527	-2.92134
H	-5.59916	-0.73806	-3.66644
H	-6.34152	1.45154	-2.76273
C	-2.37328	-2.79856	-2.45234
C	-1.59784	-2.22974	-1.42043
H	-4.10434	-2.58904	-3.69634
H	-2.07429	-3.76098	-2.85424
H	-0.73395	-2.74784	-1.0337
Pd	-0.1998	0.28998	-0.47272
C	-2.6955	1.8952	0.02305
O	-1.45267	1.83992	0.01087
C	-3.2776	2.93823	1.01646
C	-4.5759	2.42725	1.68437
H	-4.85321	3.12044	2.48594

H	-5.42632	2.35415	1.00372
H	-4.42123	1.44174	2.13653
C	-3.49073	4.29931	0.30321
H	-4.28268	4.28324	-0.45059
H	-3.76599	5.04868	1.05347
H	-2.56657	4.63059	-0.18178
C	-2.22697	3.15545	2.13352
H	-2.01652	2.22386	2.66606
H	-1.28309	3.53354	1.73726
H	-2.62317	3.88071	2.85215
O	1.49398	1.48603	1.16905
C	2.68423	1.62263	0.86186
C	3.72481	0.79774	1.54194
C	5.06217	1.2148	1.64961
C	3.32817	-0.40554	2.152
C	5.98756	0.43802	2.34609
H	5.37296	2.15505	1.20647
C	4.2588	-1.18543	2.83175
H	2.29295	-0.71742	2.07592
C	5.58926	-0.7656	2.93117
H	7.01778	0.77273	2.43224
H	3.94714	-2.12184	3.28611
H	6.3132	-1.37477	3.46646
C	3.06887	2.63697	-0.16576
C	2.34999	3.84183	-0.21169
C	4.07486	2.39837	-1.11472
C	2.65497	4.80827	-1.16556
H	1.55863	4.00548	0.51325
C	4.35891	3.35763	-2.08696
H	4.58964	1.4443	-1.12425
C	3.66074	4.5664	-2.10663
H	2.10658	5.74654	-1.18326
H	5.1213	3.15578	-2.83414
H	3.89236	5.31581	-2.85915
O	1.16727	-1.19923	-0.54792
S	2.00639	-1.51533	-1.83381
O	1.16607	-1.73679	-3.01018
O	3.22616	-0.71941	-1.93273
C	2.5491	-3.21062	-1.27398
F	3.33694	-3.74523	-2.21172
F	1.47953	-4.00716	-1.10815
F	3.221	-3.14372	-0.1241
O	-1.54225	-0.70759	0.82182
S	-1.28658	-1.85965	1.91904

O	-1.59777	-3.17962	1.39117
O	-0.06073	-1.5937	2.65206
C	-2.71238	-1.36698	3.02618
F	-3.84492	-1.31943	2.31826
F	-2.82971	-2.27185	3.99413
F	-2.48305	-0.1664	3.56386
F	0.61107	1.18694	-1.91716

HF

F	0.	0.	0.09348
H	0.	0.	-0.84134

HOTf

S	0.85161	-0.14841	0.07663
C	-1.00619	0.0091	-0.00109
F	-1.5401	-0.92186	0.78477
F	-1.35803	1.221	0.43279
F	-1.42216	-0.15939	-1.25121
O	1.26264	0.18284	1.4333
O	1.21399	-1.37541	-0.59988
O	1.24802	1.0937	-0.90518
H	1.4968	1.8532	-0.3426

6

C	4.77339	-0.33766	-1.36547
C	3.48817	0.01757	-0.94821
C	3.22476	0.14095	0.47017
C	4.34923	0.06041	1.37451
C	5.62401	-0.29698	0.87399
C	5.82916	-0.53459	-0.46688
H	4.97814	-0.46437	-2.41669
C	1.98965	0.3697	1.10202
C	4.18636	0.33049	2.75763
H	6.44564	-0.38428	1.58021
H	6.80509	-0.83022	-0.83739
C	2.95946	0.66879	3.26927
C	1.8223	0.67036	2.42748
H	5.05898	0.26882	3.40158
H	2.83203	0.89803	4.32245
H	0.84748	0.88275	2.84746
Pd	0.30856	0.09067	0.04015
C	2.47819	0.37469	-1.94387
O	1.26502	0.51686	-1.6521
C	2.75326	0.70416	-3.43818

C	3.07435	-0.5998	-4.21725
H	3.13874	-0.3551	-5.28303
H	4.01485	-1.07515	-3.93206
H	2.27265	-1.33513	-4.09009
C	3.87276	1.76761	-3.56639
H	4.85889	1.41277	-3.26221
H	3.93801	2.07721	-4.61497
H	3.63077	2.65159	-2.96727
C	1.47193	1.30577	-4.06393
H	0.63444	0.60431	-4.0319
H	1.16573	2.22449	-3.55617
H	1.68117	1.54418	-5.112
O	-1.54152	-0.40411	-1.31662
C	-2.76649	-0.36812	-1.52806
C	-3.48332	-1.66379	-1.68794
C	-4.56358	-1.81797	-2.57466
C	-3.00806	-2.77982	-0.97656
C	-5.16121	-3.06652	-2.7404
H	-4.91562	-0.96932	-3.15221
C	-3.62368	-4.01879	-1.12952
H	-2.1694	-2.66805	-0.29944
C	-4.698	-4.16538	-2.01236
H	-5.98593	-3.18193	-3.43833
H	-3.257	-4.8696	-0.56276
H	-5.17118	-5.13603	-2.13662
C	-3.48613	0.92143	-1.65875
C	-2.7665	2.06121	-2.05229
C	-4.85175	1.04522	-1.34455
C	-3.40078	3.29522	-2.1536
H	-1.70972	1.97457	-2.27084
C	-5.48156	2.28409	-1.43611
H	-5.40531	0.18277	-0.9902
C	-4.76004	3.4077	-1.84792
H	-2.82635	4.16693	-2.45065
H	-6.53183	2.37573	-1.17394
H	-5.25446	4.37312	-1.91825
O	-0.76332	-0.52913	1.6335
S	-1.88601	0.29179	2.36823
O	-1.31577	1.28032	3.2869
O	-2.99414	0.66372	1.49484
C	-2.48509	-1.13892	3.41401
F	-3.47815	-0.69048	4.18858
F	-1.50045	-1.59898	4.18356
F	-2.94255	-2.11684	2.63444

O	0.82254	-1.82905	-0.33858
S	0.93562	-2.99486	0.71185
O	1.69732	-2.62322	1.90086
O	-0.30987	-3.74649	0.84043
C	2.07689	-4.04664	-0.32902
F	3.22525	-3.39357	-0.55441
F	2.34266	-5.17422	0.33369
F	1.51094	-4.34705	-1.49925
O	-0.24523	2.02338	0.27232
S	0.54374	3.2641	-0.27355
C	0.24075	4.40196	1.17582
F	0.82838	5.57342	0.9128
F	-1.06242	4.58865	1.35199
F	0.77774	3.87923	2.27828
O	-0.12535	3.86127	-1.42952
O	1.99199	3.04262	-0.3384

TS3

C	-4.56939	-0.06997	-1.99787
C	-3.38824	0.20009	-1.30906
C	-3.35492	-0.01664	0.1165
C	-4.5336	-0.5478	0.76389
C	-5.68653	-0.82254	-0.01376
C	-5.71279	-0.58297	-1.36605
H	-4.60352	0.06362	-3.06761
C	-2.29184	0.19943	1.01191
C	-4.55746	-0.78783	2.16196
H	-6.55714	-1.23166	0.49171
H	-6.59876	-0.80125	-1.95309
C	-3.46444	-0.51553	2.94663
C	-2.30031	0.03598	2.36784
H	-5.46751	-1.185	2.60105
H	-3.47324	-0.7019	4.01528
H	-1.44746	0.28244	2.98041
Pd	-0.27359	-0.12719	0.10095
C	-2.1935	0.52947	-2.10857
O	-1.03805	0.24527	-1.72838
C	-2.21923	1.22115	-3.49904
C	-3.25712	2.36848	-3.54317
H	-3.11745	2.92799	-4.47416
H	-4.29577	2.0344	-3.51367
H	-3.10394	3.06409	-2.71058
C	-2.45311	0.16096	-4.60888
H	-3.46356	-0.25582	-4.61515

H	-2.28507	0.63379	-5.58261
H	-1.7455	-0.66806	-4.50382
C	-0.82427	1.84959	-3.74254
H	-0.57393	2.57706	-2.96491
H	-0.03417	1.09731	-3.76327
H	-0.84054	2.36695	-4.70747
O	1.88427	0.8853	-1.08153
C	3.10625	0.74669	-1.20545
C	3.98964	1.94505	-1.05921
C	5.1803	2.09188	-1.79021
C	3.56797	2.98546	-0.21387
C	5.9384	3.25698	-1.67317
H	5.49966	1.30539	-2.46641
C	4.34009	4.13683	-0.08304
H	2.64237	2.87316	0.34011
C	5.52437	4.27651	-0.81344
H	6.85081	3.36794	-2.25277
H	4.01681	4.9283	0.58757
H	6.12147	5.17936	-0.71438
C	3.69177	-0.58912	-1.51368
C	2.90599	-1.52085	-2.21159
C	4.97168	-0.96573	-1.07077
C	3.39529	-2.79544	-2.47972
H	1.91008	-1.24162	-2.53329
C	5.45349	-2.24846	-1.3275
H	5.57341	-0.26799	-0.49767
C	4.67007	-3.16108	-2.03779
H	2.77061	-3.50484	-3.01372
H	6.43576	-2.5382	-0.96478
H	5.04865	-4.1602	-2.23734
O	0.75432	-0.19702	1.82925
S	0.99743	-1.50942	2.66042
O	-0.24739	-2.24085	2.90219
O	2.20799	-2.21848	2.26763
C	1.39787	-0.63046	4.25913
F	1.6541	-1.54506	5.19786
F	0.3479	0.1088	4.65531
F	2.45796	0.16218	4.11519
O	-1.22271	1.69796	0.47175
S	-0.85656	2.93892	1.42313
O	-1.69561	2.95572	2.61264
O	0.581	3.13546	1.50394
C	-1.52961	4.23494	0.25109
F	-2.80604	3.96806	-0.04187

F	-1.44832	5.42218	0.84623
F	-0.81472	4.24897	-0.87471
O	0.29402	-2.00674	-0.36504
S	-0.6381	-2.90123	-1.2462
C	-0.1471	-4.55536	-0.53413
F	-0.85309	-5.50134	-1.16563
F	1.15228	-4.7702	-0.73536
F	-0.41788	-4.59585	0.76476
O	-0.2186	-2.90875	-2.6512
O	-2.05793	-2.69844	-0.94067

2,4,6-Collidine

C	-0.70153100	-1.15366700	-0.00087500
C	0.69712200	-1.19291400	0.00925900
C	1.42548800	0.00016500	0.01134200
C	0.69687200	1.19305400	0.00930700
C	-0.70179900	1.15352600	-0.00085300
N	-1.38784300	-0.00013600	-0.00617000
H	1.21321600	-2.14983500	0.01751200
H	1.21280900	2.15005900	0.01756500
C	-1.52594500	2.41889300	-0.00216200
H	-0.89692800	3.31442800	-0.00293700
H	-2.17795400	2.44894400	-0.88264300
H	-2.17832200	2.45108300	0.87804600
C	2.93481700	0.00029300	-0.00880000
H	3.31151700	-0.00304900	-1.04028200
H	3.34217300	0.88956300	0.48360500
H	3.34241400	-0.88573300	0.48926900
C	-1.52543900	-2.41919000	-0.00214800
H	-0.89625800	-3.31460700	-0.00392000
H	-2.17705400	-2.45199200	0.87861500
H	-2.17821900	-2.44887100	-0.88206000

1r

C	-2.03596400	0.95927500	0.94228200
C	-2.87311000	-0.14431100	0.98692500
C	-3.05924700	-0.96936900	-0.13300400
C	-2.38710800	-0.64505000	-1.31302500
C	-1.52324800	0.44163600	-1.37603600
N	-1.45015000	1.19028900	-0.25563400
H	-3.36552200	-0.36698100	1.92696000
H	-2.47646900	-1.26930200	-2.19450100
C	-0.70722600	0.84744500	-2.55946400
H	0.35075400	0.82464400	-2.28530000

H	-0.87654900	0.14215200	-3.37428600
H	-0.96693500	1.85718600	-2.89559400
C	-3.91848500	-2.20088700	-0.04570500
H	-4.34054800	-2.46734200	-1.01888600
H	-3.30772700	-3.04729100	0.29399600
H	-4.73589800	-2.07299400	0.67015900
C	-1.73520400	1.88060900	2.07801800
H	-2.36337100	1.62461800	2.93307500
H	-0.68000200	1.75056100	2.34134300
H	-1.90774600	2.92618900	1.80416000
F	-0.62379100	2.27305000	-0.31826600
S	1.33374100	-0.78133600	0.61360800
C	2.82688300	-0.03717500	-0.20338500
F	3.68154300	0.46584600	0.69649000
F	3.47741400	-0.94238600	-0.94698700
F	2.45537000	0.97762000	-1.02703300
O	1.86018100	-1.89729800	1.40876600
O	0.78042700	0.36676300	1.38261800
O	0.48972300	-1.15600100	-0.55724500

3r

C	-2.81051200	-0.42791300	1.36858800
C	-1.67972200	-0.32044400	0.57771600
C	-1.36326800	0.93867700	-0.02478900
C	-2.28660400	2.03091100	0.13127000
C	-3.44889500	1.85461400	0.92758500
C	-3.69700000	0.65652100	1.55144200
H	-3.02621000	-1.37503800	1.85418300
C	-0.18342300	1.20973700	-0.78001200
C	-2.03134800	3.27310500	-0.50898100
H	-4.13375700	2.69134700	1.03724900
H	-4.57772400	0.52972900	2.17432400
C	-0.91112800	3.45107800	-1.28376700
C	0.02810700	2.40550800	-1.42680500
H	-2.74673400	4.08049700	-0.37769800
H	-0.72939200	4.39647600	-1.78565700
H	0.92097000	2.54854900	-2.02016000
C	-0.86288800	-1.59601700	0.42453800
O	-0.13203300	-1.94159600	1.33510900
C	-1.13458900	-2.53447300	-0.77663800
C	-1.60532600	-1.79795000	-2.04311000
H	-1.84655200	-2.53273900	-2.82016700
H	-2.50580500	-1.20176000	-1.86137300

H	-0.82795600	-1.13950600	-2.44114200
C	-2.26228200	-3.49130900	-0.30396700
H	-3.19602100	-2.95361600	-0.10356400
H	-2.46542600	-4.22905800	-1.08902300
H	-1.96614100	-4.02864000	0.60316600
C	0.13327900	-3.35648200	-1.07210900
H	0.94622100	-2.71766300	-1.43108800
H	0.48069100	-3.87175500	-0.17314500
H	-0.08104400	-4.10432500	-1.84451800
O	0.73694400	0.14741500	-0.91046300
S	2.35889600	0.31306200	-0.61292700
O	2.95135100	-0.86014800	-1.22466900
O	2.80409000	1.66717900	-0.90033500
C	2.44878000	0.11519700	1.26218800
F	2.51397500	-1.16541900	1.57539000
F	3.55761200	0.73639800	1.66294800
F	1.38737300	0.68803800	1.82270800

7

C	0.01685600	2.18105600	-0.29648400
C	0.11952100	0.80336100	-0.34789400
C	-1.05238900	0.01019800	-0.14573000
C	-2.30796200	0.65336300	0.12445700
C	-2.35038600	2.07137800	0.19040500
C	-1.21503300	2.81784700	-0.01832200
H	0.89775900	2.78883900	-0.48220700
C	-1.07006700	-1.40629900	-0.21688500
C	-3.47640500	-0.13471400	0.31166000
H	-3.30086500	2.55500100	0.40055300
H	-1.25698700	3.90268900	0.02180700
C	-3.42509500	-1.50729300	0.23022700
C	-2.20035300	-2.16111600	-0.03974900
H	-4.41656200	0.37047400	0.51593400
H	-4.32362600	-2.10065500	0.37121800
H	-2.13476400	-3.24144400	-0.11133700
C	1.47508400	0.21032600	-0.70597100
O	1.80381000	0.16848400	-1.87640200
C	2.47140100	-0.17275600	0.41501600
C	1.78802400	-0.52138200	1.74851900
H	2.55130900	-0.72805400	2.50802800
H	1.16713700	0.30178100	2.11785300
H	1.16067700	-1.41215300	1.65638700
C	3.36978800	1.07550500	0.61543100
H	2.79329400	1.93641200	0.97428500

H	4.14152300	0.85804000	1.36341500
H	3.86529400	1.35432100	−0.32030700
C	3.33535000	−1.35093600	−0.07082700
H	2.72664900	−2.25209500	−0.19817600
H	3.80161900	−1.11927700	−1.03160900
H	4.12196800	−1.56754900	0.66139000
F	0.10056600	−2.04504800	−0.46657200

2

C	-2.03596400	0.95927500	0.94228200
C	-2.87311000	-0.14431100	0.98692500
C	-3.05924700	-0.96936900	-0.13300400
C	-2.38710800	-0.64505000	-1.31302500
C	-1.52324800	0.44163600	-1.37603600
N	-1.45015000	1.19028900	-0.25563400
H	-3.36552200	-0.36698100	1.92696000
H	-2.47646900	-1.26930200	-2.19450100
C	-0.70722600	0.84744500	-2.55946400
H	0.35075400	0.82464400	-2.28530000
H	-0.87654900	0.14215200	-3.37428600
H	-0.96693500	1.85718600	-2.89559400
C	-3.91848500	-2.20088700	-0.04570500
H	-4.34054800	-2.46734200	-1.01888600
H	-3.30772700	-3.04729100	0.29399600
H	-4.73589800	-2.07299400	0.67015900
C	-1.73520400	1.88060900	2.07801800
H	-2.36337100	1.62461800	2.93307500
H	-0.68000200	1.75056100	2.34134300
H	-1.90774600	2.92618900	1.80416000
F	-0.62379100	2.27305000	-0.31826600
S	1.33374100	-0.78133600	0.61360800
C	2.82688300	-0.03717500	-0.20338500
F	3.68154300	0.46584600	0.69649000
F	3.47741400	-0.94238600	-0.94698700
F	2.45537000	0.97762000	-1.02703300
O	1.86018100	-1.89729800	1.40876600
O	0.78042700	0.36676300	1.38261800
O	0.48972300	-1.15600100	-0.55724500