Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

for

N-Aminophthalimide-Mediated Aerobic Deborohydroxylation of Boronic Acid in Air

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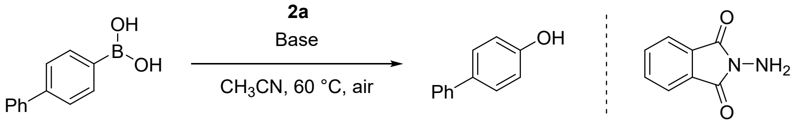
(A) General information

All reactions were carried out by standard procedures under air condition at room temperature unless stated otherwise. All boronic acid materials are commercially available unless stated otherwise. All solvents were freshly distilled prior to use in synthesis unless otherwise noted. Flash column chromatography was performed using silica gel (200-300 mesh). ^{1}H, ^{13}C and ^{19}F NMR spectra were measured on Brucker Avance IIDMX 400 MHz spectrometers (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR and 289 MHz for ^{19}F NMR). Chemical shifts are reported in parts per million (ppm) relative to TMS (0.00) for the ^{1}H NMR, residual signals in solvents ($CDCl_3$ at δ 77.16 ppm) for the ^{13}C NMR and CDF_3 (0.00 ppm) for the ^{19}F NMR measurements. Coupling constant (*J*) are quoted in Hz.

(B) Optimization of Reaction Conditions

1. Base Optimization



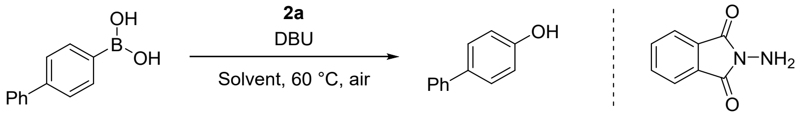
1a **3a** **2a**

Under air atmosphere, dry CH_3CN (2.0 mL) was added to an oven-dried reaction tube charged with arylboronic acid **1a** (1.0 equiv, 0.2 mmol), *N*-aminophthalimide **2a** (1.2 equiv, 0.24 mmol), Base (1.2 equiv, 0.24 mmol) and a stirring bar; then the reaction mixture was stirred at 60 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give the desired product **3a**.

Table S1. Base Optimization.

Entry	Base	Time (h)	Yield of **3a** (%)
1	**DBU**	**22**	**67**
2	DABCO	24	trace
3	Et_3N	24	0
4	K_2CO_3	24	0
5	Cs_2CO_3	24	12
6	t-BuOK	24	0
7	KOH	24	0

2. Solvent Optimization



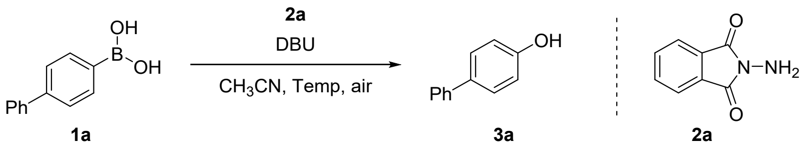
1a **3a** **2a**

Under air atmosphere, dry solvent (2.0 mL) was added to an oven-dried reaction tube charged with arylboronic acid **1a** (1.0 equiv, 0.2 mmol), *N*-aminophthalimide **2a** (1.2 equiv, 0.24 mmol), DBU (1.2 equiv, 0.24 mmol) and a stirring bar; then the reaction mixture was stirred at 60 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give the desired product **3a**.

Table S2. Solvent Optimization.

Entry	Solvent	Time (h)	Yield of **3a** (%)
1	**CH_3CN**	**22**	**67**
2	DMF	24	59
3	DMA	24	44
4	EtOAc	24	47
5	CH_3NO_2	24	30
6	$ClCH_2CN$	24	0
7	toluene	24	32
8	PhF	23	29
9	PhCl	33	33
10	DCE	24	21
11	CH_3OH	24	0
12	HFIP	24	0
13	DME	27	33
14	THF	24	48
15	1,4-dioxane	36	52

3. Temperature Optimization

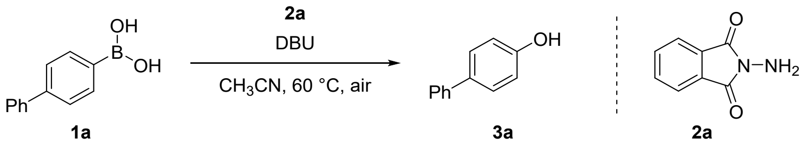


Under air atmosphere, dry CH_3CN (2.0 mL) was added to an oven-dried reaction tube charged with arylboronic acid **1a** (1.0 equiv, 0.2 mmol), *N*-aminophthalimide **2a** (1.2 equiv, 0.24 mmol), DBU (1.2 equiv, 0.24 mmol) and a stirring bar; then the reaction mixture was stirred at different temperature heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give the desired product **3a**.

Table S3. Temperature Optimization.

Entry	Temp (°C)	Time (h)	Yield of **3a** (%)
1	rt	24	trace
2	40	26	58
3	**60**	**22**	**67**
4	reflux	16	51

4. Reactant ratio Optimization

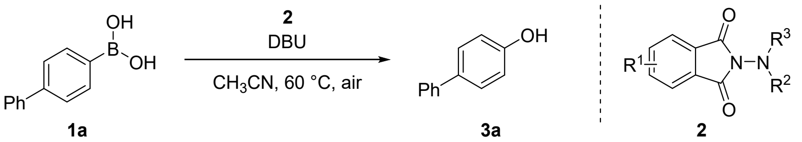


Under air atmosphere, dry CH_3CN (2.0 mL) was added to an oven-dried reaction tube charged with arylboronic acid **1a** (1.0 equiv, 0.2 mmol), *N*-aminophthalimide **2a** (x equiv), DBU (y equiv) and a stirring bar; then the reaction mixture was stirred at 60 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give the desired product **3a**.

Table S4. Reactant ratio Optimization.

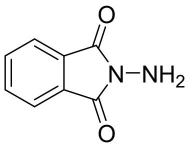
Entry	1a:2a:base	Time (h)	Yield of **3a** (%)
1	1:1.2:1.2	22	67
2	1:1.5:1.5	18	77
3	**1:1.5:2**	**12**	**90**
4	1:2:2	18	85

5. Mediator Optimization

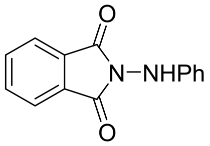


Under air atmosphere, dry CH_3CN (2.0 mL) was added to an oven-dried reaction tube charged with arylboronic acid **1a** (1.0 equiv, 0.2 mmol), *N*-aminophthalimide **2** (1.5 equiv, 0.3 mmol), DBU (2 equiv, 0.4 mmol) and a stirring bar; then the reaction mixture was stirred at 60 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give the desired product **3a**.

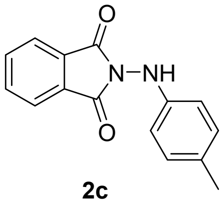
Table S5. Mediator Optimization.



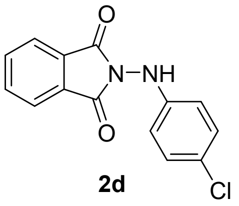
2a



2b



2c



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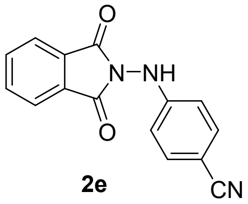

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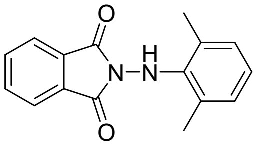
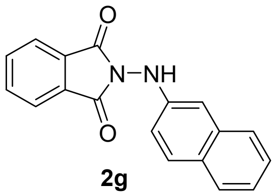
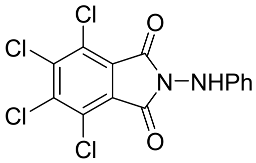


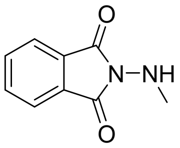
2f



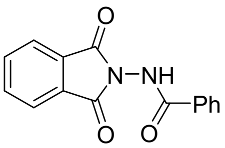
2g



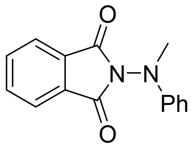
2h



2i



2j



2k

Entry	**2**	Time (h)	Yield of **3a** (%)
1	**2a**	12	90
2	**2b**	9	95
3	**2c**	3	95
4	**2d**	10	91
5	**2e**	12	80
6	**2f**	**3**	**98**
7	**2g**	12	95
8	**2h**	36	72
9	**2i**	9	75
10	**2j**	48	8
11	**2k**	24	0

(C) Computational details

All data in this study were calculated with the Gaussian 16 software package (ref. 22 in the main body, similarly hereinafter). The structures were optimized at the B3LYP-GD3(BJ)/6-31G+(d,p) level (ref 23) in conjunction with the SMD solvation model (ref 24) in acetonitrile. Vibrational frequency analysis was computed at the same level to ensure that the minimum points have no imaginary frequency and the transition states have only one imaginary frequency. Accurate single-point energies were obtained at M06-2X-GD3/def2-tzvpd level (ref 25) in conjunction with the SMD solvation model in acetonitrile.

Ref 22: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

	E (hartree)	ΔE (hartree)	ΔE (kcal/mol)
9’	-1126.5842199	0.0000000	0
TS1	-1126.5391734	0.0450465	28.2
FLP	-1126.659358	-0.0751381	-47.1
14’	-1126.7177743	-0.1335544	-83.8

	Thermal correction to Gibbs Free Energy	G (hartree)	ΔG (hartree)	ΔG (kcal/mol)
9’	0.203489	-1126.3807309	0	0
TS1	0.199755	-1126.3394184	0.0413125	25.9
14’	0.204545	-1126.5132293	-0.1324984	-83.1

XYZ Coordinates for optimized structures: 9’

Number of imaginary frequencies: 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.504824	2.304802	-1.371033
2	6	0	2.867767	3.028556	-0.354751
3	6	0	2.131683	2.375673	0.645591
4	6	0	2.054663	0.991683	0.580965
5	6	0	2.687993	0.267955	-0.437284
6	6	0	3.425954	0.904328	-1.423813
7	6	0	1.349523	0.031029	1.467866
8	7	0	1.608764	-1.238514	0.920675
9	6	0	2.415267	-1.182654	-0.231042
10	8	0	2.813654	-2.140164	-0.865283
11	8	0	0.722199	0.229981	2.493310
12	7	0	1.003023	-2.415016	1.354798
13	8	0	-0.098857	-2.744261	0.560615
14	8	0	-1.122536	-1.672500	0.656928
15	5	0	-1.442436	-1.121351	-0.732177
16	8	0	-0.278009	-0.549677	-1.417239
17	8	0	-1.957027	-2.182687	-1.601525
18	6	0	-2.545241	0.035391	-0.338739
19	6	0	-3.858158	0.005918	-0.842057
20	6	0	-4.789108	1.012966	-0.555373
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22	6	0	-3.127207	2.146393	0.778660
23	6	0	-2.210840	1.131302	0.483361
24	1	0	4.067857	2.836813	-2.131441
25	1	0	2.944354	4.111186	-0.342235
26	1	0	1.636835	2.931942	1.434836
27	1	0	3.918075	0.343164	-2.211311
28	1	0	0.655787	-2.212681	2.297492
29	1	0	-0.164564	0.375199	-1.171291
30	1	0	-2.515112	-2.775310	-1.084696
31	1	0	-4.154061	-0.822392	-1.482200
32	1	0	-5.794938	0.957740	-0.965742
33	1	0	-5.142632	2.876036	0.484359
34	1	0	-2.832780	2.976963	1.416304
35	1	0	-1.212792	1.191106	0.910860

TS1

Number of imaginary frequencies: 1

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      4          6           0        2.746758   -0.917439   -0.329512
      5          6           0        3.454925    0.211285    0.100037
      6          6           0        4.658838    0.095301    0.777928
      7          6           0        1.508260   -0.453472   -1.009555
      8          7           0        1.533314    0.941928   -0.940294
      9          6           0        2.698679    1.426393   -0.319685
     10          8           0        2.996874    2.598742   -0.181801
     11          8           0        0.632503   -1.111876   -1.556918
     12          7           0        0.572976    1.806880   -1.519383
     13          8           0       -0.288736    2.332621   -0.595442
     14          8           0       -1.730211    1.114129   -0.218636
     15          5           0       -1.574243    0.426168    0.997038
     16          8           0       -0.670066   -0.666295    1.138115
     17          8           0       -1.697539    1.111576    2.242863
     18          6           0       -3.181277   -0.092199    0.276155
     19          6           0       -3.269480   -1.242725   -0.518349
     20          6           0       -4.513696   -1.812269   -0.806110
     21          6           0       -5.686470   -1.215811   -0.326628
     22          6           0       -5.605781   -0.044633    0.436313
     23          6           0       -4.359295    0.522641    0.720921
     24          1           0        6.079659   -1.331043    1.551176
     25          1           0        4.828615   -3.318865    0.797021
     26          1           0        2.662561   -3.074494   -0.428915
     27          1           0        5.208328    0.970621    1.108446
     28          1           0        0.047569    1.210267   -2.166661
     29          1           0       -0.518048   -1.074035    0.276335
     30          1           0       -2.139706    1.957422    2.102438
     31          1           0       -2.368028   -1.707116   -0.909689
     32          1           0       -4.568891   -2.715600   -1.408379
     33          1           0       -6.654129   -1.654305   -0.553508
     34          1           0       -6.512390    0.428714    0.804893
     35          1           0       -4.309956    1.436276    1.307515
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FLP of **10** and **11'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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5	6	0	-3.493692	-0.170368	0.049012
6	6	0	-4.692797	-0.066933	0.735555
7	6	0	-1.527536	0.497235	-1.009824
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13	8	0	0.054218	-2.357937	-0.435889
14	8	0	2.163168	-0.756223	-0.047060
15	5	0	1.282969	-0.639643	1.039277
16	8	0	0.483437	0.471880	1.171672
17	8	0	1.433452	-1.397518	2.177618
18	6	0	3.357201	-0.059272	-0.041533
19	6	0	3.429829	1.197222	-0.649410
20	6	0	4.651836	1.872391	-0.681213
21	6	0	5.792681	1.298041	-0.110815
22	6	0	5.708614	0.038233	0.491710
23	6	0	4.492062	-0.644993	0.528842
24	1	0	-6.080177	1.346099	1.593737
25	1	0	-4.789101	3.344273	0.943675
26	1	0	-2.628648	3.120810	-0.296857
27	1	0	-5.263017	-0.946510	1.016421
28	1	0	0.100363	-1.077591	-1.929888
29	1	0	0.434437	0.965540	0.339885
30	1	0	1.967658	-2.182247	2.004670
31	1	0	2.540028	1.627735	-1.097356
32	1	0	4.714574	2.848040	-1.155469
33	1	0	6.740505	1.827228	-0.138981
34	1	0	6.593950	-0.413226	0.931191
35	1	0	4.416548	-1.626663	0.985425

14’

Number of imaginary frequencies: 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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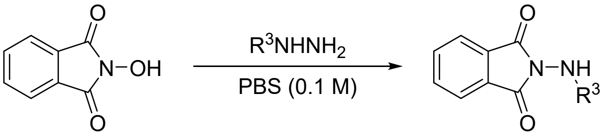
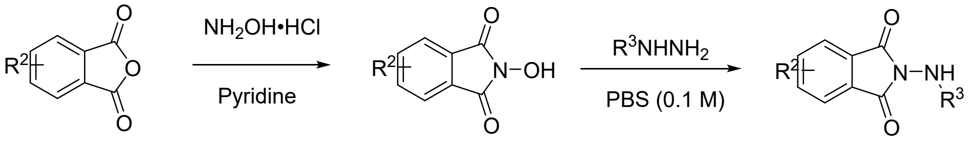
5	6	0	3.677137	0.166448	-0.240347
6	6	0	5.056033	0.203863	-0.096693
7	6	0	1.509239	-0.706454	-0.210172
8	7	0	1.450351	0.634163	-0.615236
9	6	0	2.727203	1.228744	-0.674046
10	8	0	2.958878	2.373038	-1.015328
11	8	0	0.540503	-1.446662	-0.105797
12	7	0	0.297811	1.337693	-0.992115
13	8	0	-0.278245	1.995124	0.139113
14	8	0	-2.230810	0.774940	-0.374044
15	5	0	-1.430283	1.285082	0.819545
16	8	0	-1.051305	0.204811	1.699426
17	8	0	-2.118991	2.286906	1.598429
18	6	0	-3.324860	0.001597	-0.295131
19	6	0	-3.820559	-0.555614	-1.491932
20	6	0	-4.964664	-1.354313	-1.488355
21	6	0	-5.644764	-1.619978	-0.293150
22	6	0	-5.156796	-1.068011	0.896879
23	6	0	-4.012923	-0.265198	0.906800
24	1	0	6.771566	-0.980893	0.452357
25	1	0	5.483058	-3.031619	0.919661
26	1	0	2.997593	-3.067149	0.649172
27	1	0	5.621747	1.106521	-0.302784
28	1	0	-0.385498	0.630348	-1.283148
29	1	0	-0.692502	-0.528768	1.182071
30	1	0	-2.257391	3.072042	1.055146
31	1	0	-3.290331	-0.349002	-2.417718
32	1	0	-5.325599	-1.772141	-2.424856
33	1	0	-6.534645	-2.242476	-0.290080
34	1	0	-5.672515	-1.262153	1.834332
35	1	0	-3.640447	0.156542	1.831310

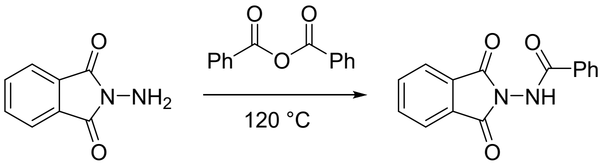
(D) Procedures for starting materials



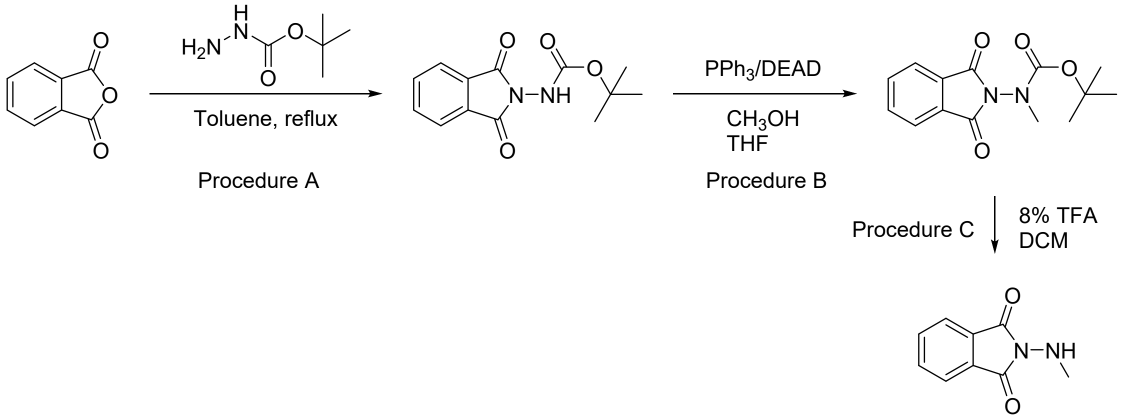
(1)



(2)



(3)



(4)

Route 1: To a solution of *N*-hydroxyphthalimide (489 mg, 3.0 mmol, 1.0 equiv) in pH 7.0 phosphate buffer (30 mL) was added phenylhydrazine (0.293 mL, 3.0 mmol, 1.0 equiv) at room temperature. The mixture was stirred for 15 h at room temperature and then filtered and washed with water. The solid was filtered and dissolved with ethyl acetate (150 mL), and then the solution was washed with 5% aq. HCl (30 mL for twice) and the organic phase was dried with brine and $MgSO_4$, filtered and concentrated in vacuo and purified by silica gel column chromatography (PE:EtOAc = 2:1) to give product as a bright yellow solid.[1]

Route 2: To a solution of anhydride (1.0 equiv, 3.5 mmol) and hydroxylamine hydrochloride (2.0 equiv, 7.0 mmol) in pyridine (10 mL) was heated at 80 ℃ for 4 h and then cooled to room temperature. The mixture was diluted by adding 20 mL water and acidified to pH 2 with concentrated HCl. The precipitate was filtrated and washed with water. The filtrate was dried in vacuo and purified by recrystallization with EtOH. The next step is the same as route 1 to get the product.[2]

Route 3: *N*-Aminophthalimide (165 mg, 1 mmol) was mixed with benzoic anhydride (1130 mg, 5 mmol) in a round bottom flask and warmed to 120 °C, forming a homogeneous yellow solution which turned colorless as heating was continued for 1 h. Afterwards, the reaction mixture was cooled to room temperature, forming colorless prismatic needles. The excess anhydride was drawn off and the residue was washed with a small amount of cold ether to get the product.[3]

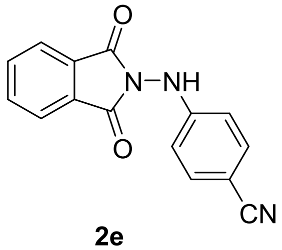
Route 4: Produce A: To a suspension *tert*-butylcarbazate (1 equiv) in toluene, phthalic anhydride (1 equiv) was added. The suspension was refluxed in a two-neck round bottom flask fitted with a Dean-Stark trap for 4 h. The mixture was cooled to room temperature and concentrated. The crude product was purified by column chromatography using hexanes and ethyl acetate as the eluting solvent.[4]

Produce B: To a solution of *N*-*tert*butyloxycarbonylaminophthalimide (1 equiv), PPh_3 (1.5 equiv) and methanol (3 equiv) in anhydrous THF and under N_2 atmosphere was added one portion of Diethyl azodicarboxylate (DEAD) (1.5 equiv) under stirring at 0-5 °C. The resulting solution was stirred overnight and concentrated under vacuum. The crude was purified by column chromatography on silica gel using hexanes and ethyl acetate.[4]

Produce C: To a solution of *N*-alkyl-*N*-*tert*butyloxycarbonylaminophthalimide (1 equiv) in anhydrous CH_2Cl_2 was added trifluoroacetic acid (8% TFA in CH_2Cl_2) (25 equiv) dropwise at 0 °C. The mixture was brought to room temperature and stirred overnight. After completion, the solution was concentrated under vacuum. The crude was dissolved in ethyl acetate and the organic layer was sequentially washed with water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine (2 × 10 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. After concentrating the organic layer, the desired compound was purified by column chromatography on silica gel using hexanes and ethyl acetate mixture.[4]

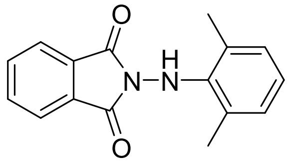
The spectra data of **2b, 2c, 2d, 2g, 2h, 2i, 2j, 2k,** were consistent with literature reported.[1]

The spectral data of compounds **2e, 2f, 2l** were shown below.



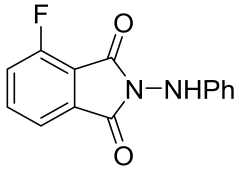
2e

4-((1,3-dioxoisoindolin-2-yl)amino)benzonitrile **(2e)**: 73% yield, yellow solid. m.p. 267.0-267.8 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.32 (s, 1H), 8.12 – 7.86 (m, 4H), 7.61 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 166.59, 151.27, 135.54, 134.15, 130.17, 124.13, 120.13, 112.79, 101.34. HRMS (ESI) m/z calcd for $C_{15}H_{10}N_3O_2^+$ $[M + H]^+$ 264.0768, found 267.0774.



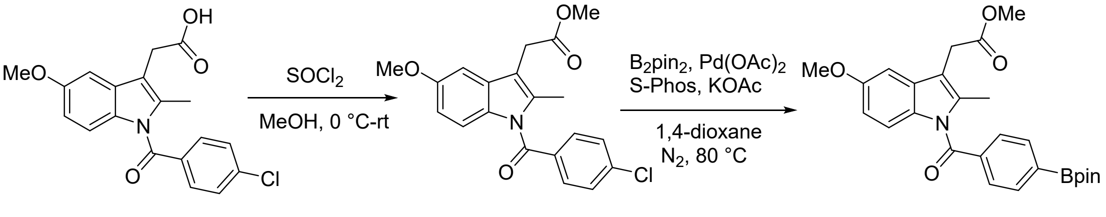
2f

2-((2,6-dimethylphenyl)amino)isoindoline-1,3-dione **(2f)**: 63% yield, yellow solid. m.p 175.3-175.8 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.91 (s, 4H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 167.52, 142.90, 135.60, 129.68, 129.41, 127.72, 123.84, 122.68, 18.80. HRMS (ESI) m/z calcd for $C_{15}H_{12}N_2O_2^+$ $[M + H]^+$ 267.1128, found 267.1132.



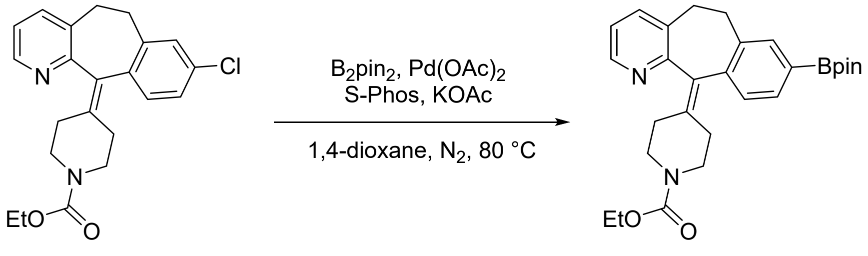
2l

4-fluoro-2-(phenylamino)isoindoline-1,3-dione **(2l)**: 70% yield, yellow solid. m.p 190.1-190.3 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.80 (m, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 8.4 Hz, 1H), 7.36 – 7.20 (m, 2H), 7.04 – 6.95 (m, 1H), 6.92 – 6.81 (m, 2H), 6.30 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.33 (d, *J* = 2.9 Hz), 163.18, 157.71 (d, *J* = 267.1 Hz), 145.51, 137.36 (d, *J* = 7.8 Hz), 131.95, 129.40, 123.19 (d, *J* = 19.6 Hz), 122.54, 120.21 (d, *J* = 3.6 Hz), 115.93 (d, *J* = 12.7 Hz). 114.29. HRMS (ESI) m/z calcd for $C_{14}H_{10}FN_2O_2^+$ [M + H]$^+$ 257.0721, found 257.0727.



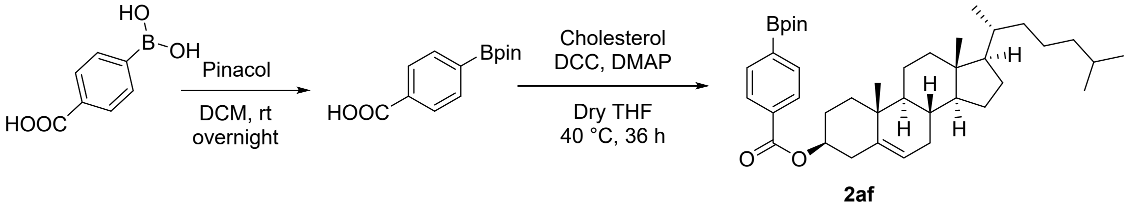
2ad

Methyl 2-(1-(4-chlorobenzene)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**2ad**): $SOCl_2$ (7.7 mmol, 1.5 mL) was dropwise added to a solution of Indometacin (4 mmol, 1.43 g) and MeOH (10 mL) at 0 °C. Subsequently, the temperature is from 0 °C to rt. After the reaction, the reaction mixture was concentrated under reduced pressure to give ester as a white solid. Then, A mixture of ester (1 mmol, 372 mg), bis(pinacolato)diboron (B_2pin_2, 3 mmol, 762 mg), $Pd(OAc)_2$ (4 mol%, 9 mg), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 10 mol%, 41 mg), KOAc (3 mol, 295 mg) was stirred in 1, 4-dioxane (4 mL) under N_2 atmosphere at 80 °C. After the reaction, the reaction mixture was diluted with H_2O and extracted with ethyl acetate (×3). The combined organics were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude mixture was chromatographed on silica gel using petroleum ether/ethyl acetate (PE/EA = 10/1) as eluent to give **2ad**. [5]



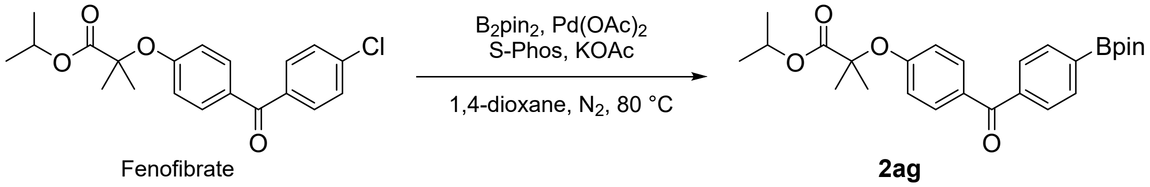
2ae

Ethyl 4-(8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6-dihydro-11Hbenzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (**2ae**): A mixture of Loratadine (1 mmol, 383 mg), bis(pinacolato)diboron (B_2pin_2, 3 mmol, 762 mg), $Pd(OAc)_2$ (4 mol%, 9 mg), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 10 mol%, 41 mg), KOAc (3 mol, 295 mg) was stirred in 1,4-dioxane (4 mL) under N_2 atmosphere at 80 °C. After the reaction, the reaction mixture was diluted with H_2O and extracted with ethyl acetate (×3). The combined organics were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude mixture was chromatographed on silica gel using petroleum ether/ethyl acetate (PE/EA = 1/1) as eluent to give **2ae**. [5]



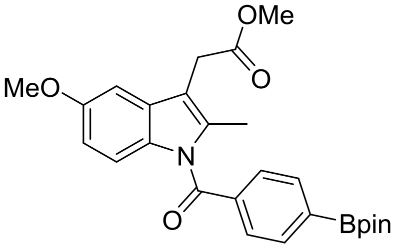
(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**2af**): 4-boronobenzoic acid (3 mmol), pinacol (3.3 mmol) were dispersed in 40 mL DCM. The reaction mixture was stirred at room temperature for overnight. Then, the reaction solution was filtered to remove all solid impurities. The solid was rinsed by DCM 3 times. The combined solution was concentrated to get the product.

Under nitrogen, a 20-mL vial was charged with Acid (3.0 mmol), Cholesterol (3.6 mmol), DCC (4.5 mmol), DMAP (0.60 mmol) and dry THF (10 mL). The vial was sealed with a Teflon-lined cap and stirred at 40 °C for 1.5 d. The reaction was quenched with water (20 mL) and extracted with ethyl acetate (20 mL × 3). The organic layer was condensed, and the residue was purified by flash column chromatography (hexane/ethyl acetate = 40/1) to afford the **2af** as white solid. [6]

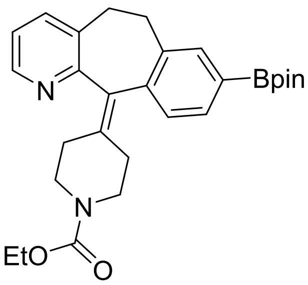


Isopropyl 2-methyl-2-(4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoyl) phenoxy) propanoate (**2ag**): A mixture of Fenofibrate (1 mmol, 361 mg), bis(pinacolato)diboron (B_2pin_2, 3 mmol, 762 mg), $Pd(OAc)_2$ (4 mol%, 9 mg), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 10 mol%, 41 mg), KOAc (3 mol, 295 mg) was stirred in 1,4-dioxane (4 mL) under N_2 atmosphere at 80 °C. After the reaction, the reaction mixture was diluted with H_2O and extracted with ethyl acetate (×3). The combined organics were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude mixture was chromatographed on silica gel using petroleum ether/ethyl acetate (PE/EA = 10/1) as eluent to give **2ag**. [5]

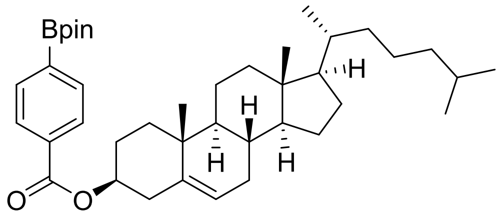
The spectral data of compounds **2ad, 2ae, 2af, 2ag** were shown below.



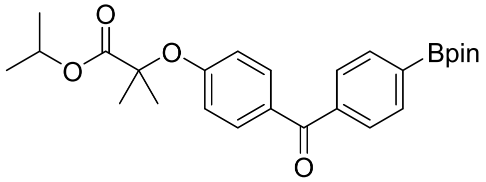
methyl 2-(5-methoxy-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1H-indol-3-yl)acetate (**2ad**): 70% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.64 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 3.66 (s, 2H), 2.36 (s, 3H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.44, 169.54, 156.05, 137.96, 136.10, 135.00, 130.97, 130.65, 128.67, 115.24, 112.41, 111.60, 101.25, 84.38, 55.75, 52.18, 30.22, 24.94, 13.47.



ethyl 4-(8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (**2ae**): 53% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 4.6 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 7.7, 4.7 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.87 – 3.70 (m, 2H), 3.54 – 3.25 (m, 2H), 3.18 – 3.06 (m, 2H), 2.95 – 2.74 (m, 2H), 2.55 – 2.24 (m, 4H), 1.31 (s, 12H), 1.24 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.10, 155.57, 146.57, 142.51, 137.60, 137.07, 136.92, 135.41, 133.73, 132.58, 128.69, 122.17, 83.83, 61.33, 44.92, 31.89, 31.61, 30.82, 30.58, 24.91, 24.85, 14.74.

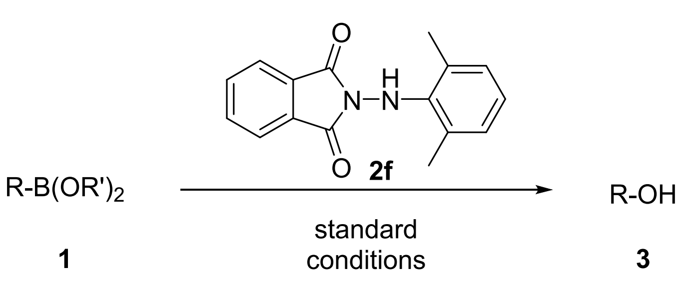


(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**2af**): 31% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 5.54 – 5.31 (m, 1H), 5.08 – 4.71 (m, 1H), 2.47 (d, *J* = 8.1 Hz, 2H), 2.10 – 1.67 (m, 6H), 1.63 – 1.43 (m, 8H), 1.36 (s, 12H), 1.24 – 0.96 (m, 14H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.7, 1.8 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.07, 139.73, 134.64, 133.09, 128.61, 122.82, 84.19, 74.74, 56.76, 56.20, 50.11, 42.39, 39.81, 39.58, 38.26, 37.11, 36.72, 36.25, 35.86, 32.00, 31.95, 28.30, 28.08, 27.93, 24.94, 24.36, 23.90, 22.89, 22.63, 21.12, 19.45, 18.79, 11.93.



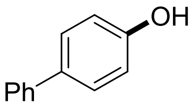
isopropyl 2-methyl-2-(4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)phenoxy)propanoate: 66% yield (**2ag**); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.07 (p, *J* = 6.3 Hz, 1H), 1.64 (s, 6H), 1.35 (s, 12H), 1.19 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.69, 173.17, 159.68, 140.43, 134.54, 132.12, 130.58, 128.73, 117.18, 84.19, 79.41, 69.35, 25.43, 24.93, 21.55.

(E) General procedure for deborohydroxylation of arylboronic acids

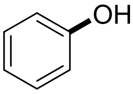


Under air atmosphere, dry CH_3CN (2.0 mL) was added to an oven-dried reaction tube charged with arylboronic acid **1** (1.0 equiv, 0.2 mmol), **2f** (1.5 equiv, 0.3 mmol), DBU (2.0 equiv, 0.4 mmol) and a stirring bar; then the reaction mixture was stirred at 60 °C heated by oil bath. Upon the completion of the reaction, the mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (4 mL). The mixture was then extracted with diethyl ether (10 mL) for three times. The combined organic phase was continually washed with 10 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give the desired product **3**.

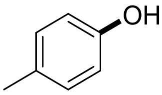
(F) Characterization of products



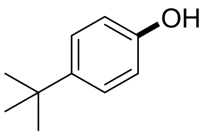
1,1'-biphenyl]-4-ol (**3a**)[10]: 98% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 2H), 4.97 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.09, 140.79, 134.51, 134.07, 128.79, 128.46, 126.77, 115.69.



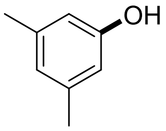
Phenol (**3b**)[10]: 92% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (t, *J* = 7.1 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 2H), 5.14 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.49, 129.75, 120.88, 115.37.



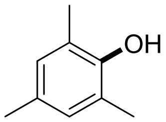
p-cresol (**3c**)[10]: 92% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 5.19 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.29, 130.12, 129.99, 115.16, 20.52.



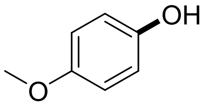
4-(tert-butyl)phenol (**3d**)[10]: 86% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.93 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.13, 143.62, 126.51, 114.82, 34.14, 31.60.



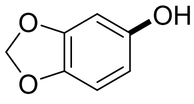
3,5-dimethylphenol (**3e**)[12]: 83% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.63 (s, 1H), 6.51 (s, 2H), 4.78 (s, 1H), 2.31 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.43, 139.61, 122.62, 113.08, 21.31.



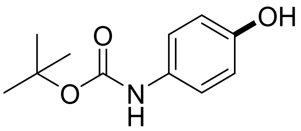
2,4,6-trimethylphenol (**3f**)[12]: 93% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.71 (s, 1H), 4.38 (s, 1H), 2.14 (s, 3H), 2.13 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 149.94, 129.36, 129.18, 122.85, 20.46, 15.90.



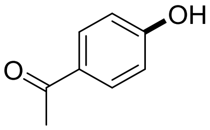
4-methoxyphenol (**3g**)[12]: 99% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.96 – 6.61 (m, 4H), 4.99 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.74, 149.55, 116.14, 114.96, 55.91.



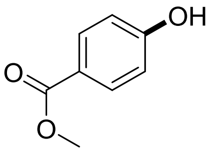
benzo[*d*][1,3]dioxol-5-ol (**3h**)[5]: 83% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.69 (d, *J* = 8.3 Hz, 1H), 6.47 (d, *J* = 2.5 Hz, 1H), 6.31 – 6.27 (m, 1H), 5.95 (s, 2H), 4.79 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 150.69, 148.34, 141.63, 108.20, 106.70, 101.23, 98.35.



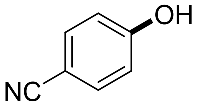
tert-butyl(4-hydroxyphenyl)carbamate (**3i**)[15]: 81% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.39 (s, 1H), 5.49 (s, 1H), 1.55 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.74, 152.24, 130.83, 121.64, 115.82, 80.56, 28.44.



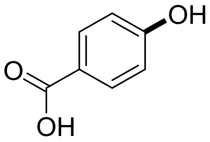
1-(4-hydroxyphenyl)ethan-1-one (**3j**)[10]; 85% yield: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.76 (s, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 198.70, 161.42, 131.31, 129.63, 115.62, 26.39.



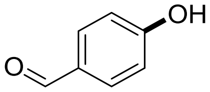
methyl 4-hydroxybenzoate (**3k**)[10]: 86% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.74 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.44, 160.27, 132.01, 122.38, 115.33, 52.13.



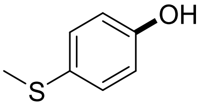
4-hydroxybenzonitrile (**3l**)[10]: 87% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.30 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 159.90, 134.37, 119.25, 116.45, 103.58.



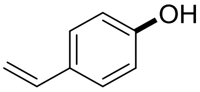
4-hydroxybenzoic acid (**3m**)[5]: 92% yield,^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 12.46 (s, 1H), 10.25 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.40, 166.86, 136.79, 126.56, 120.37.



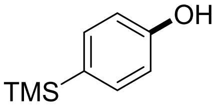
4-hydroxybenzaldehyde (**3n**)[5]: 68% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.71 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.51, 161.86, 132.66, 129.76, 116.11.



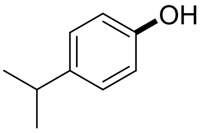
4-(methylthio)phenol (**3o**)[11]: 79% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 5.02 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.09, 130.43, 128.94, 116.13, 18.11.



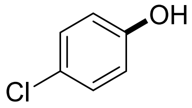
4-vinylphenol (**3p**)[5]: 70% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.64 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.60 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 4.95 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.29, 136.18, 130.73, 127.67, 115.43, 111.73.



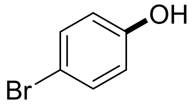
4-(trimethylsilyl)phenol (**3q**)[12]: 90% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.3 Hz, 2H), 6.83 (d, *J* = 7.2 Hz, 2H), 5.15 (s, 1H), 0.23 (d, *J* = 1.2 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.20, 135.02, 131.68, 114.95, -0.88.



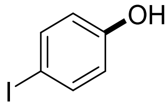
4-isopropylphenol (**3r**)[12]: 91% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 4.96 (s, 1H), 2.86 (p, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.49, 141.29, 127.52, 115.15, 33.33, 24.27.



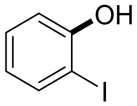
4-chlorophenol (**3s**)[12]: 85% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.9 Hz, 1H), 6.76 (d, *J* = 8.9 Hz, 1H), 5.37 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.08, 129.62, 125.79, 116.76.



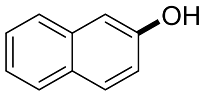
4-bromophenol (**3t**)[5]: 84% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 6.7 Hz, 1H), 6.76 (d, *J* = 6.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.56, 132.56, 117.27, 113.04.



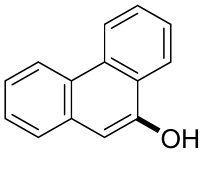
4-iodophenol (**3u**)[5]: 86% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.8 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 5.11 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.36, 138.53, 117.89, 82.81.



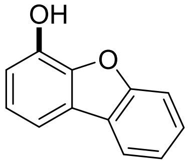
2-iodophenol (**3v**)[12]: 88% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.76 – 6.68 (m, 1H), 5.31 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.84, 138.32, 130.29, 122.50, 115.22, 85.82.



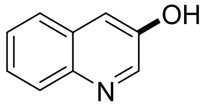
naphthalen-2-ol (**3w**)[5]: 80% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (t, *J* = 8.5 Hz, 2H), 7.67 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.36 – 7.30 (m, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.10 (dd, *J* = 8.8, 2.6 Hz, 1H), 5.28 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.39, 134.65, 129.93, 129.00, 127.84, 126.61, 126.44, 123.70, 117.82, 109.58.



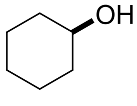
phenanthren-9-ol (**3x**)[5]: 81% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 8.1 Hz, 1H), 8.62 – 8.56 (m, 1H), 8.39 – 8.27 (m, 1H), 7.77 – 7.61 (m, 3H), 7.57 – 7.45 (m, 2H), 6.99 (s, 1H), 5.33 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.54, 132.71, 131.60, 127.29, 127.01, 126.79, 126.48, 125.58, 124.35, 122.77, 122.65, 122.40, 106.16.



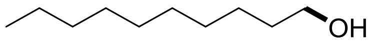
dibenzo[*b*,*d*]furan-4-ol (**3y**)[5]: 88% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.77 (m, 1H), 7.53 – 7.44 (m, 1H), 7.41 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.25 (t, *J* = 7.5, 1.0 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.93 (dd, *J* = 7.9, 1.1 Hz, 1H), 5.51 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.11, 144.12, 141.19, 127.34, 125.82, 124.65, 123.75, 123.06, 121.09, 113.68, 112.88, 111.85.



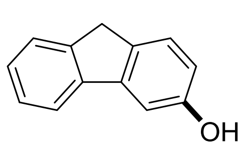
quinolin-3-ol (**3z**)[11]: 73% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.32 (s, 1H), 8.60 (d, *J* = 2.6 Hz, 1H), 8.04 – 7.87 (m, 1H), 7.85 – 7.69 (m, 2H), 7.61 – 7.46 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 151.39, 144.41, 142.93, 129.54, 129.11, 127.22, 127.03, 126.34, 115.78.



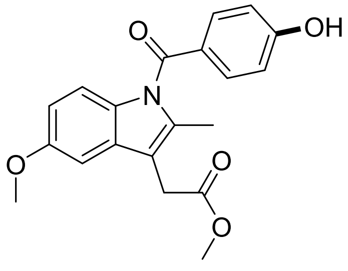
Cyclohexanol (**3aa**)[10]: 46% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.71 – 3.51 (m, 1H), 2.00 – 1.84 (m, 2H), 1.76 – 1.68 (m, 2H), 1.63 – 1.44 (m, 1H), 1.38 – 1.13 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.31, 35.56, 25.49, 24.18.



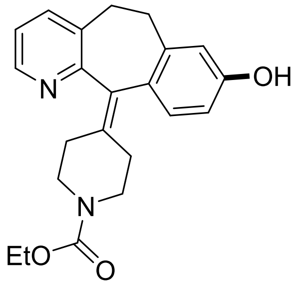
decan-1-ol (**3ab**)[11]: 60% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.64 (t, *J* = 6.6 Hz, 2H), 1.63 – 1.52 (m, 2H), 1.49 (s, 1H), 1.40 – 1.18 (m, 14H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 63.12, 32.84, 31.95, 29.67, 29.61, 29.49, 29.38, 25.79, 22.73, 14.17.



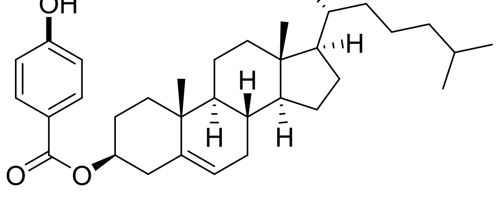
9H-fluoren-3-ol (**3ac**)[14]: 90% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.35 (m, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.94 – 6.84 (m, 1H), 5.02 (s, 1H), 3.89 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.03, 145.43, 142.67, 141.62, 135.01, 126.80, 125.72, 124.92, 120.75, 119.09, 114.14, 112.28, 36.94.



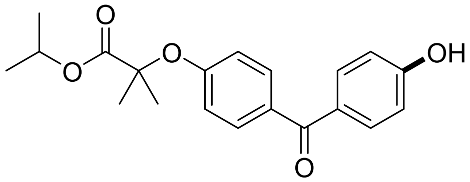
methyl 2-(1-(4-hydroxybenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**3ad**)[5]: 60% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.56 (s, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.80 (s, 2H), 3.78 (s, 3H), 3.65 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 171.71, 168.85, 162.81, 155.66, 136.03, 132.88, 131.06, 130.53, 125.72, 116.12, 114.54, 111.86, 111.65, 101.78, 55.89, 52.27, 29.69, 13.19.



ethyl 4-(8-hydroxy-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (**3ae**)[5]: 62% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 – 8.30 (m, 1H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.12 (dd, *J* = 7.7, 4.9 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 6.62 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.87 – 3.71 (m, 1H), 3.71 – 3.58 (m, 1H), 3.43 – 3.24 (m, 2H), 3.17 – 3.03 (m, 2H), 2.95 – 2.66 (m, 2H), 2.53 – 2.10 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.00, 156.89, 155.62, 145.59, 138.95, 138.11, 136.69, 134.52, 134.12, 130.26, 129.80, 122.40, 116.53, 113.36, 61.40, 44.75, 32.09, 31.57, 30.57, 14.72.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-hydroxybenzoate: 81% yield (**3af**)[13]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 5.51 – 5.34 (m, 1H), 4.94 – 4.76 (m, 1H), 2.45 (d, *J* = 8.1 Hz, 2H), 2.07 – 1.77 (m, 7H), 1.73 – 1.43 (m, 7H), 1.42 – 1.29 (m, 10H), 1.19 –1.13 (m, 3H), 1.03 – 0.98 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.90, 159.74, 139.75, 131.91, 123.42, 122.78, 115.14, 74.44, 56.75, 56.20, 50.09, 42.38, 39.58, 38.33, 37.09, 36.71, 35.86, 31.99, 31.94, 28.29, 28.07, 27.99, 23.90, 22.87, 22.62, 21.11, 19.43, 18.77, 11.92.



isopropyl 2-(4-(4-hydroxybenzoyl)phenoxy)-2-methylpropanoate (**3ag**)[5]: 75% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 4.8 Hz, 2H), 7.69 (d, *J* = 4.5 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.09 (p, *J* = 6.3 Hz, 1H), 1.65 (s, 6H), 1.21 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.29, 173.48, 160.39, 159.29, 132.71, 131.91, 131.20, 130.10, 117.35, 115.27, 79.45, 69.53, 25.43, 21.56.

All the^{19}F NMR were conducted in MeCN without adding deuterium reagent.

(G) References

(1) B. Holmes, J. Lee, K. A. Landon, A. Benavides-Serrato, T. Bashir, M. E. Jung, A. Lichtenstein and J. Gera, *J. Biol. Chem*., 2016, **291**, 14146-14159.

(2) Y. Li, J. Zhang, D. Li and Y. Chen, *Org. Lett*., 2018, **20**, 3296-3299.

(3) R. Samanta, J. O. Bauer, C. Strohmann and A. P. Antonchick, *Org. Lett*., 2012, **14**, 5518–5521.

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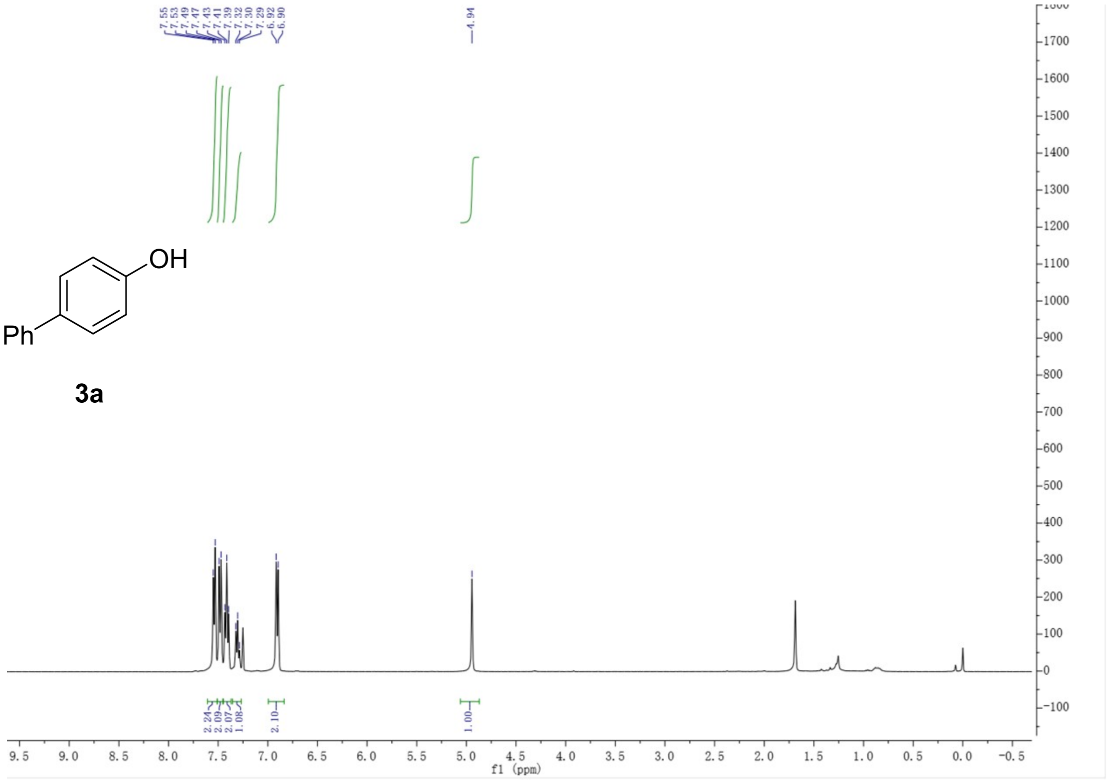
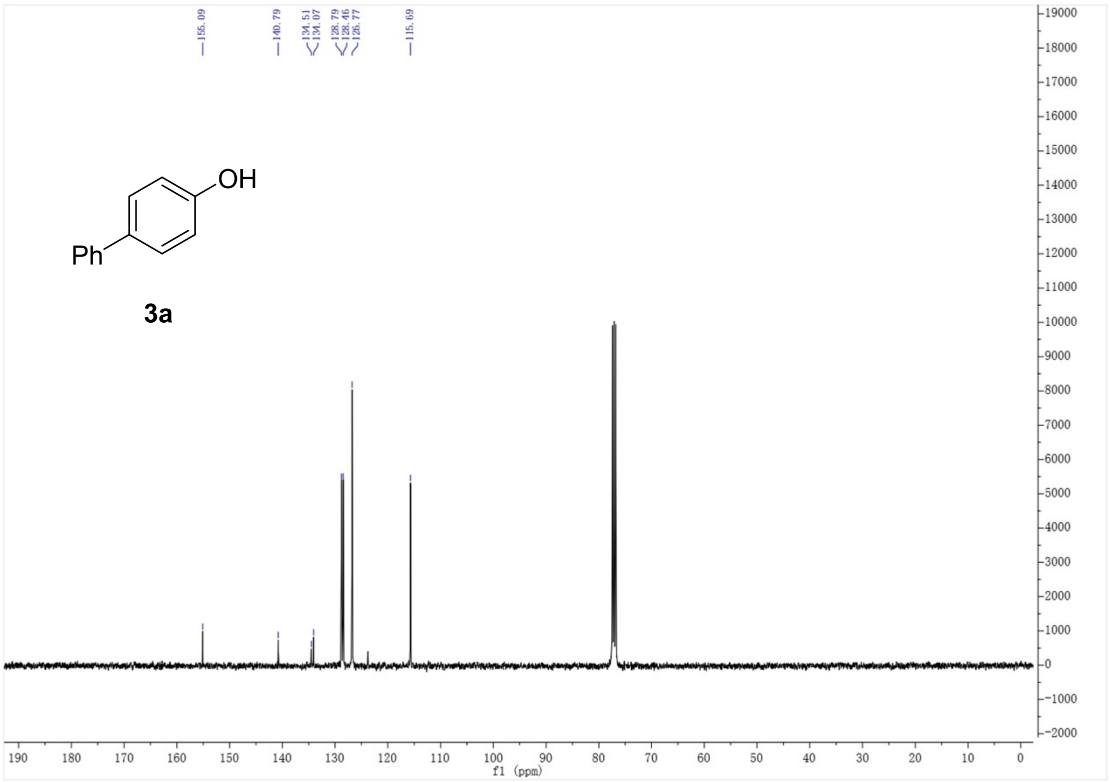
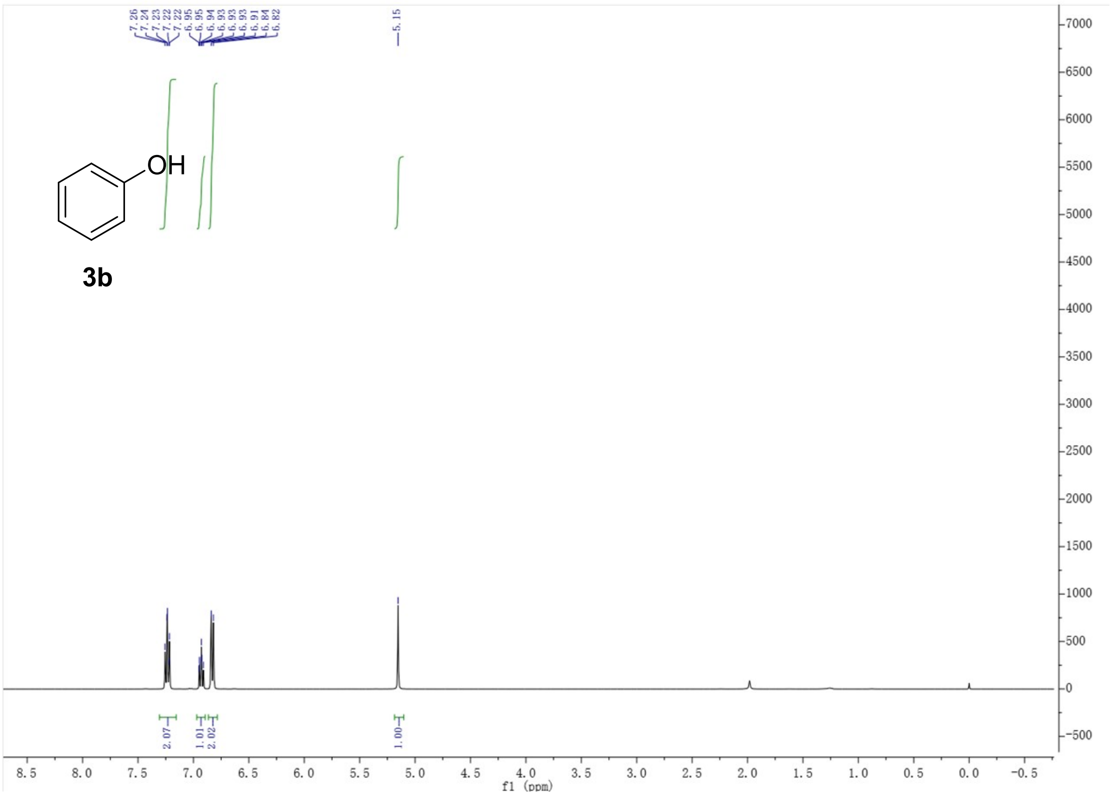
(H) NMR spectra



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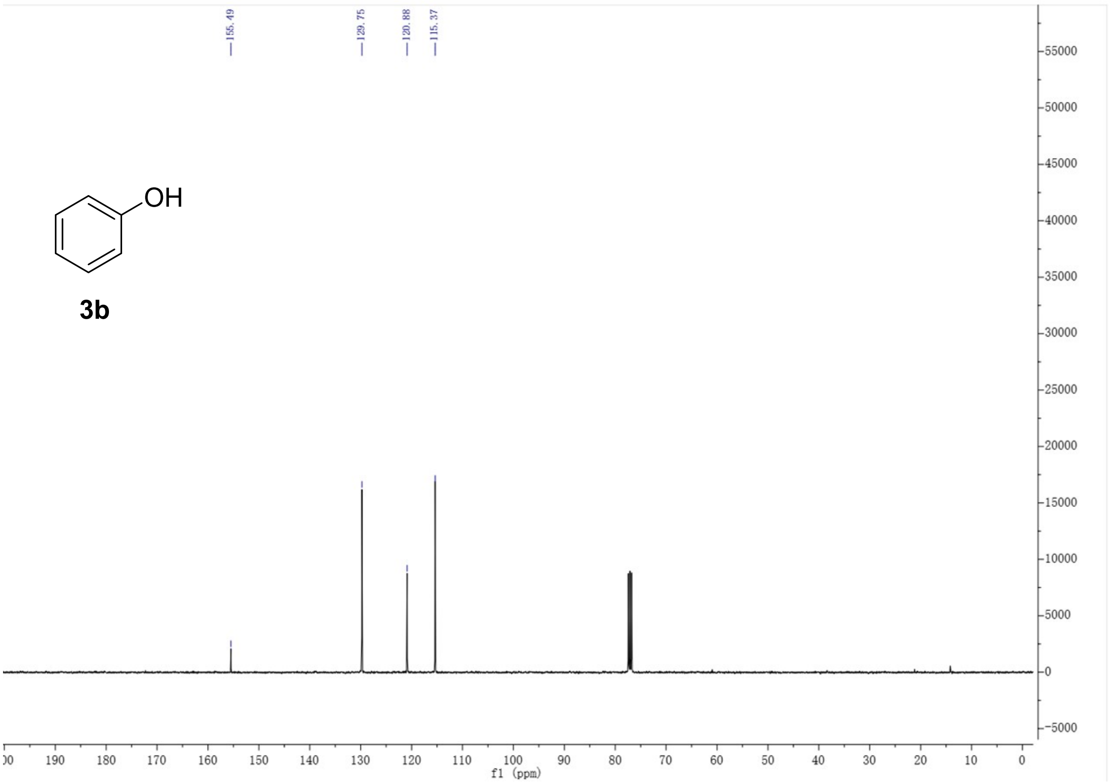
7.23
7.22
7.22
6.95
6.95
6.94
6.93
6.93
6.93
6.91
6.84
6.82
5.15
OH
3b
2.07
1.01
2.02
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500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129.75
120.88
115.37
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3b
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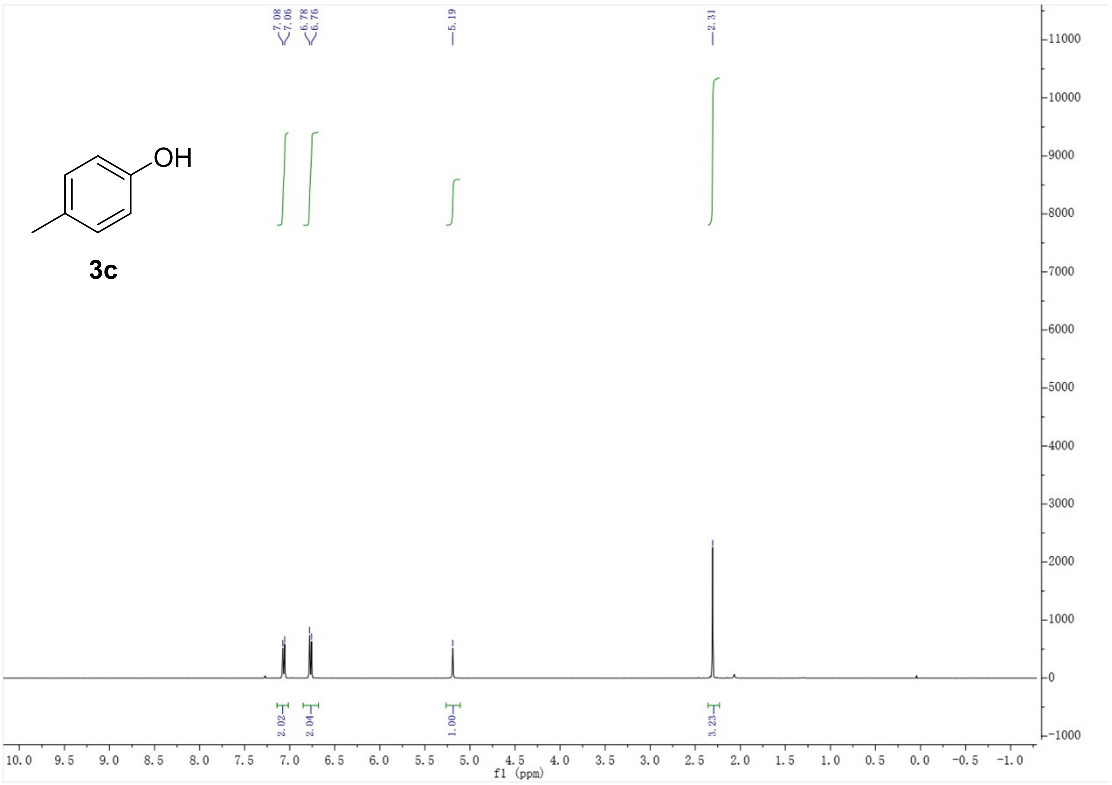
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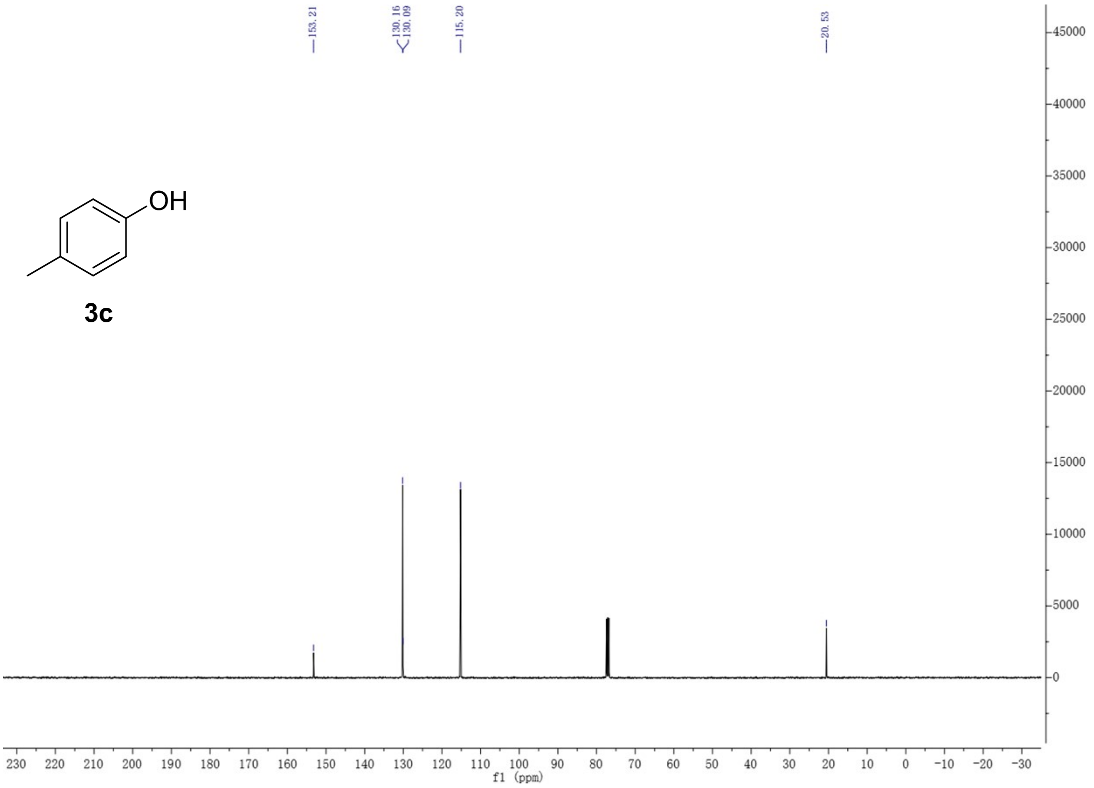
5.19
2.31
OH
2.02
2.04
1.00
3.23
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

3c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130.09
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20.53
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40000
35000
30000
25000
20000
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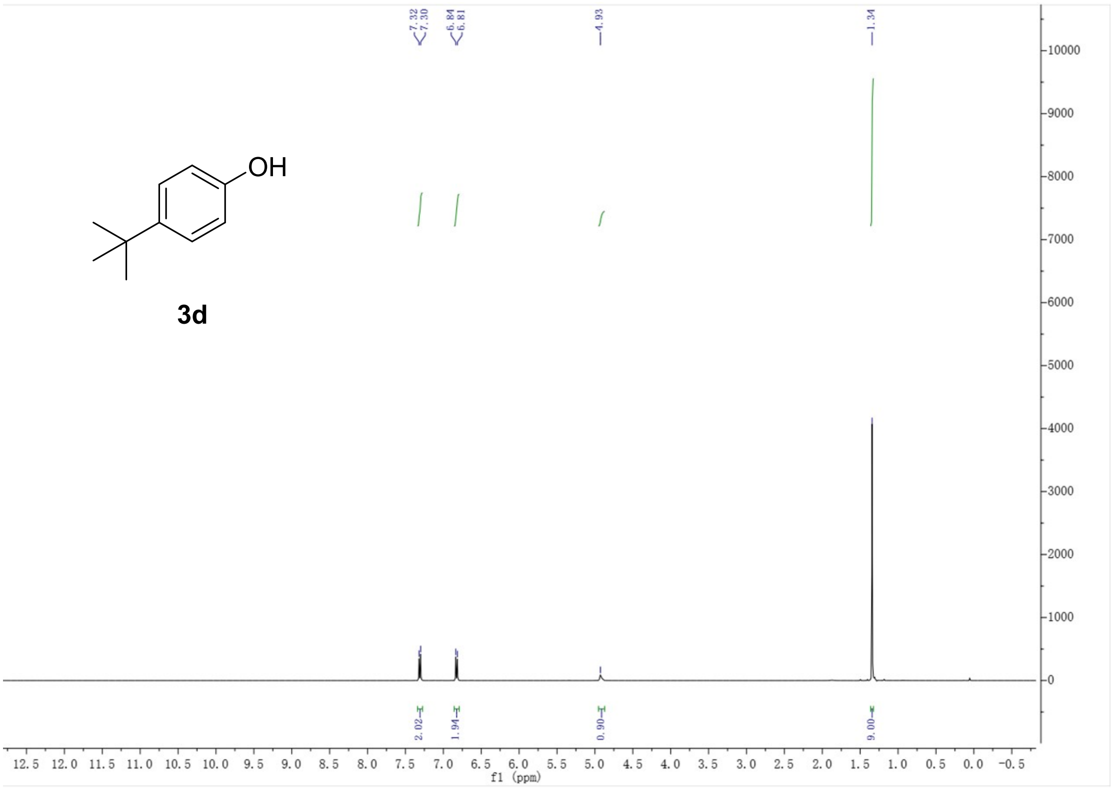
5000
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

3c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4.93
1.34
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3d
2.02
1.94
0.90
9.00
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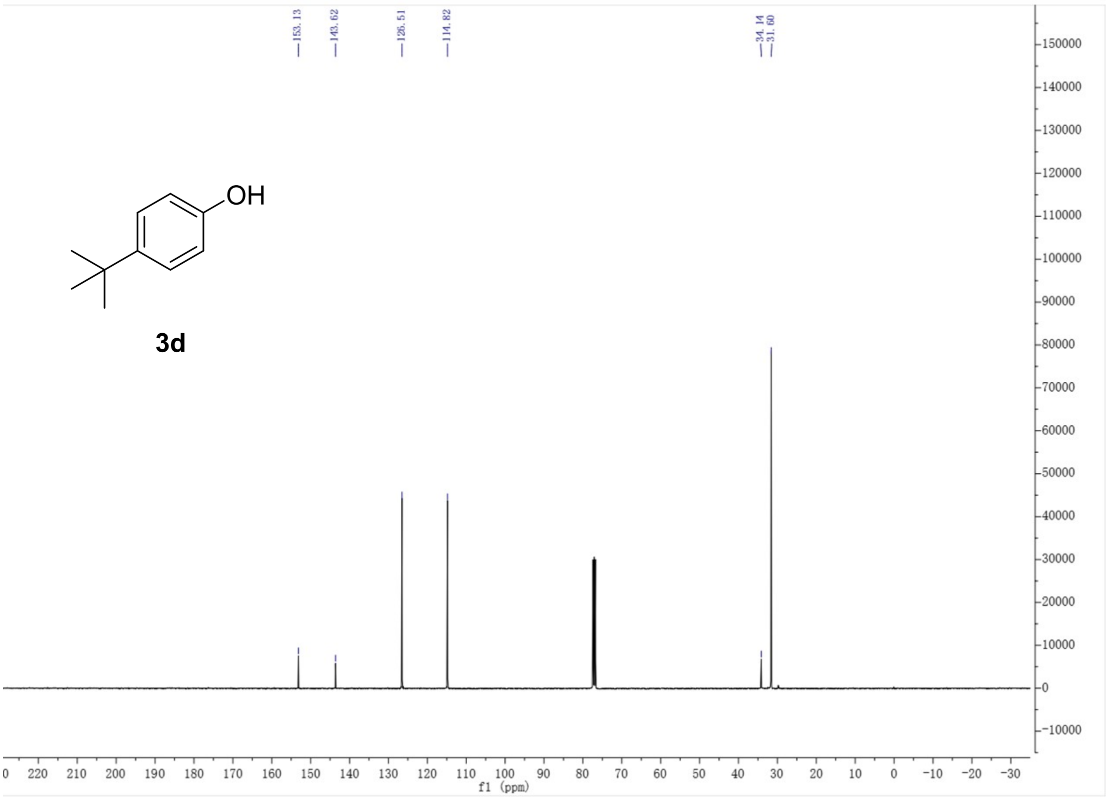
7000
6000
5000
4000
3000
2000
1000
0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143.62
126.51
114.82
34.14
31.60
OH
3d
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f1 (ppm)
150000
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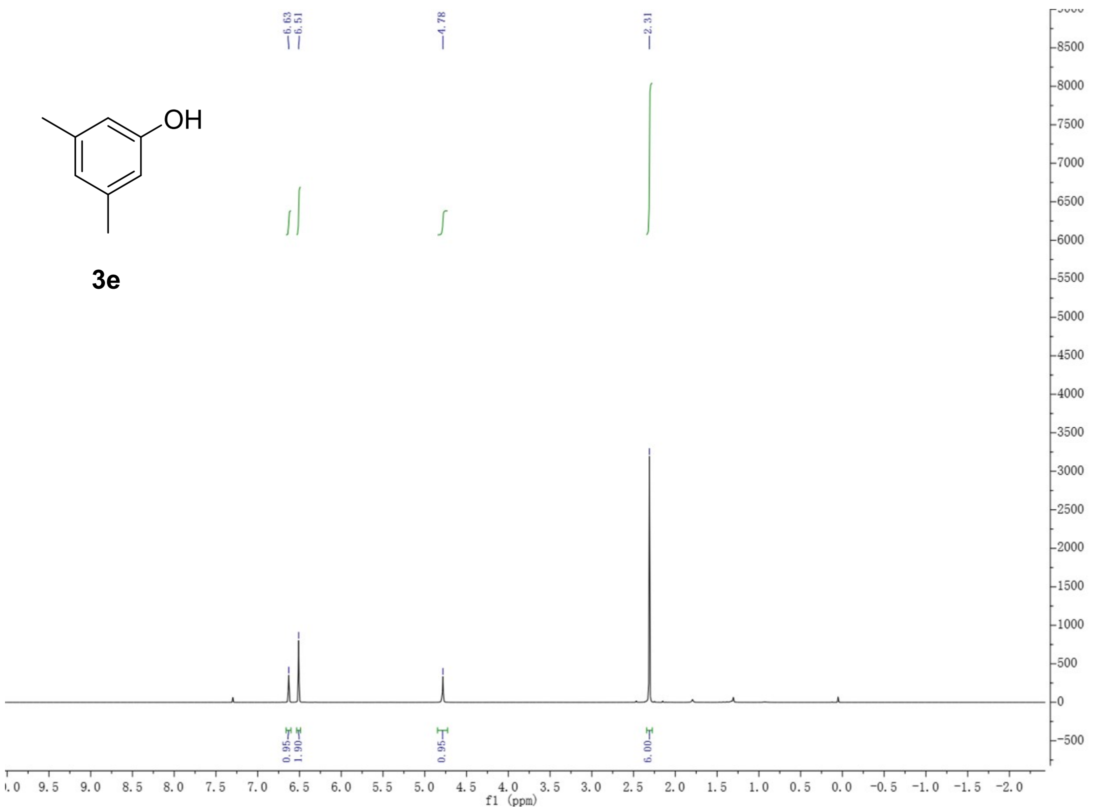
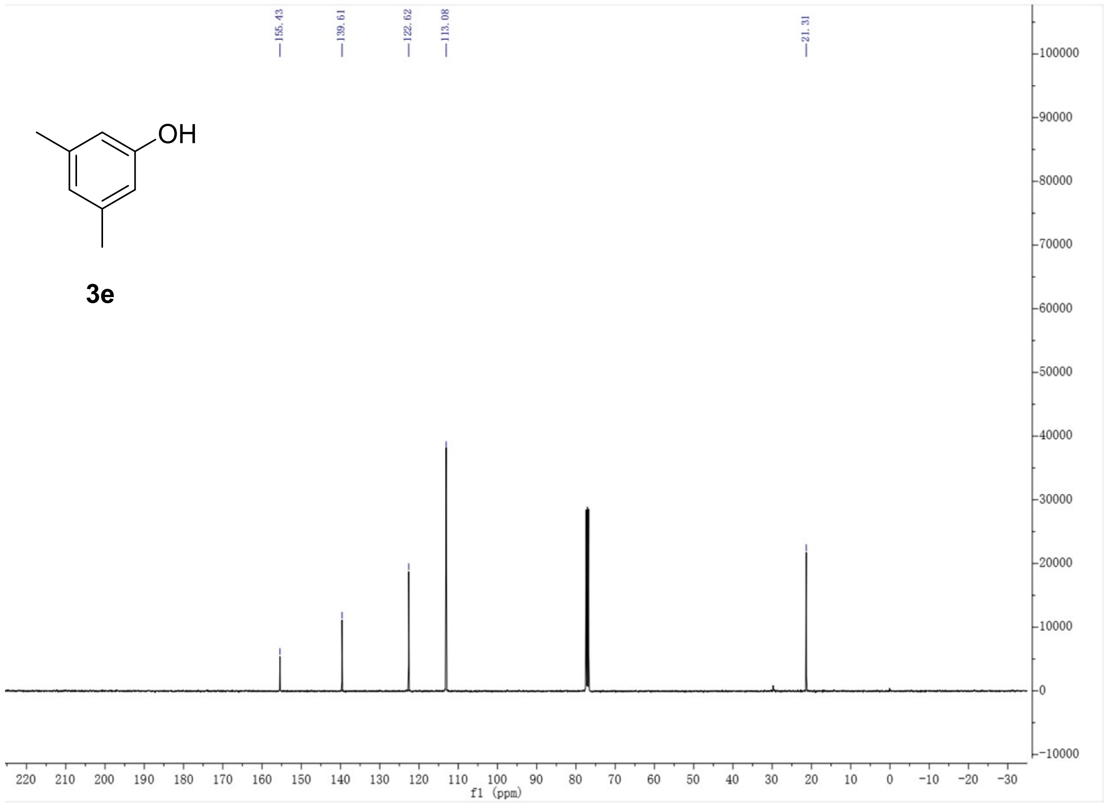
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000



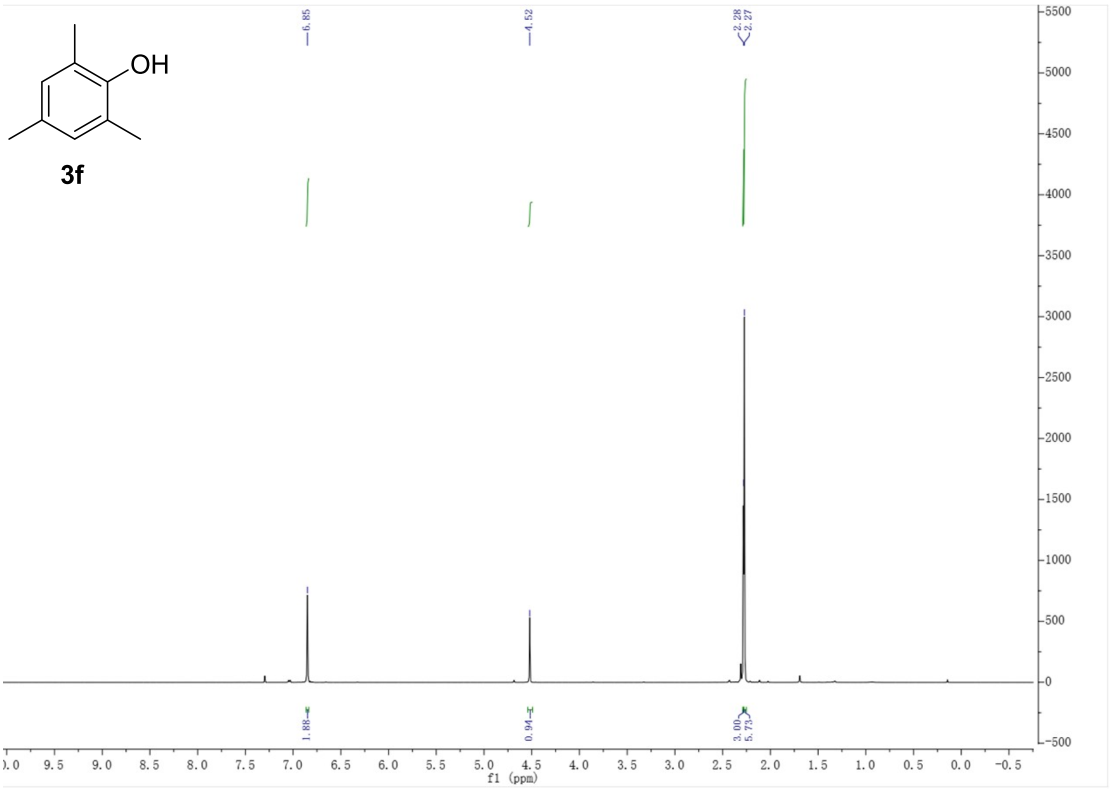
3e

6.63
6.51
4.78
2.31
0.95
1.90
0.95
6.00
f1 (ppm)
OH



3e

155.43
139.61
122.62
113.08
21.31
f1 (ppm)
OH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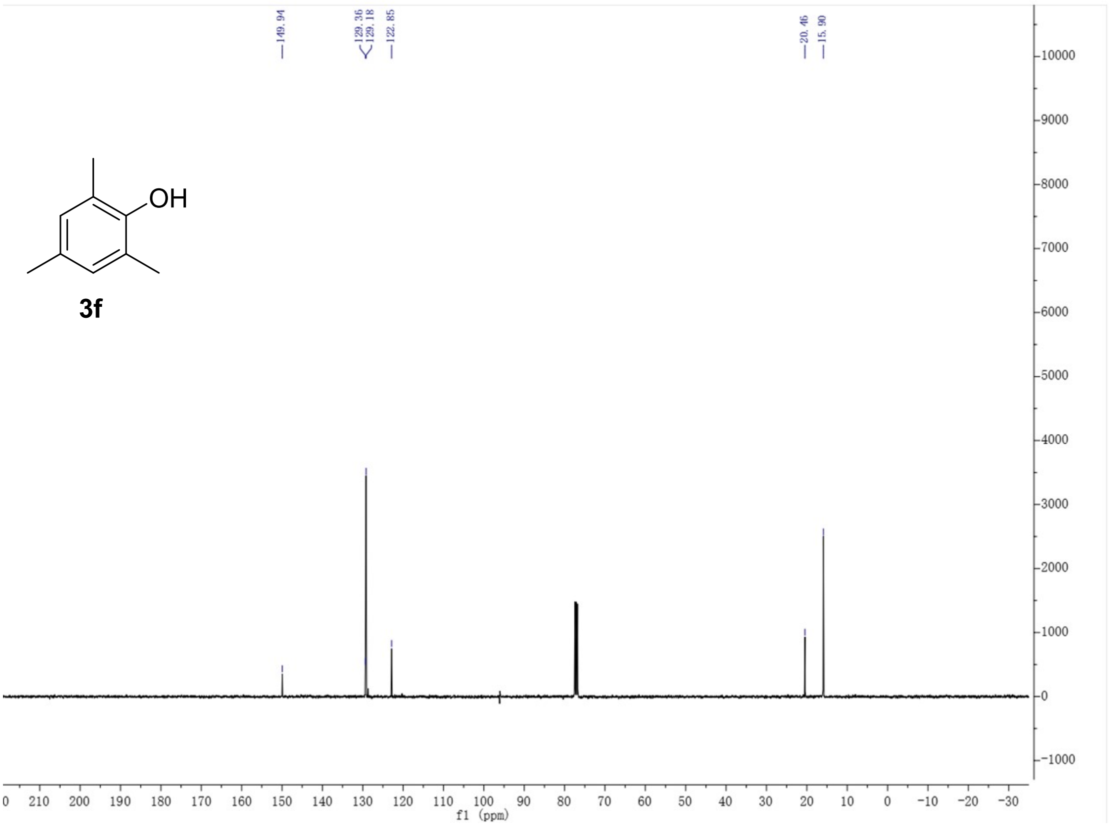
4.52
2.28
2.27
1.88
0.94
3.00
5.73
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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3f
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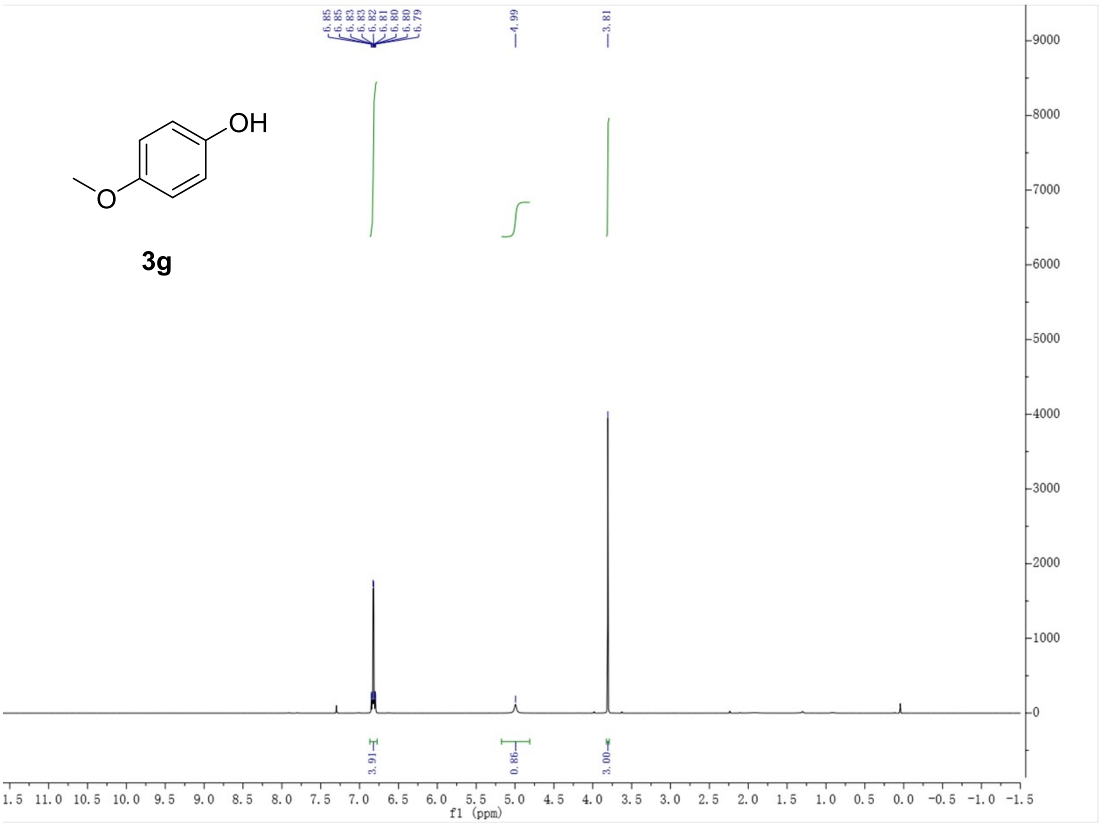
129.36
129.18
122.85
20.46
15.90
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)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OH
O
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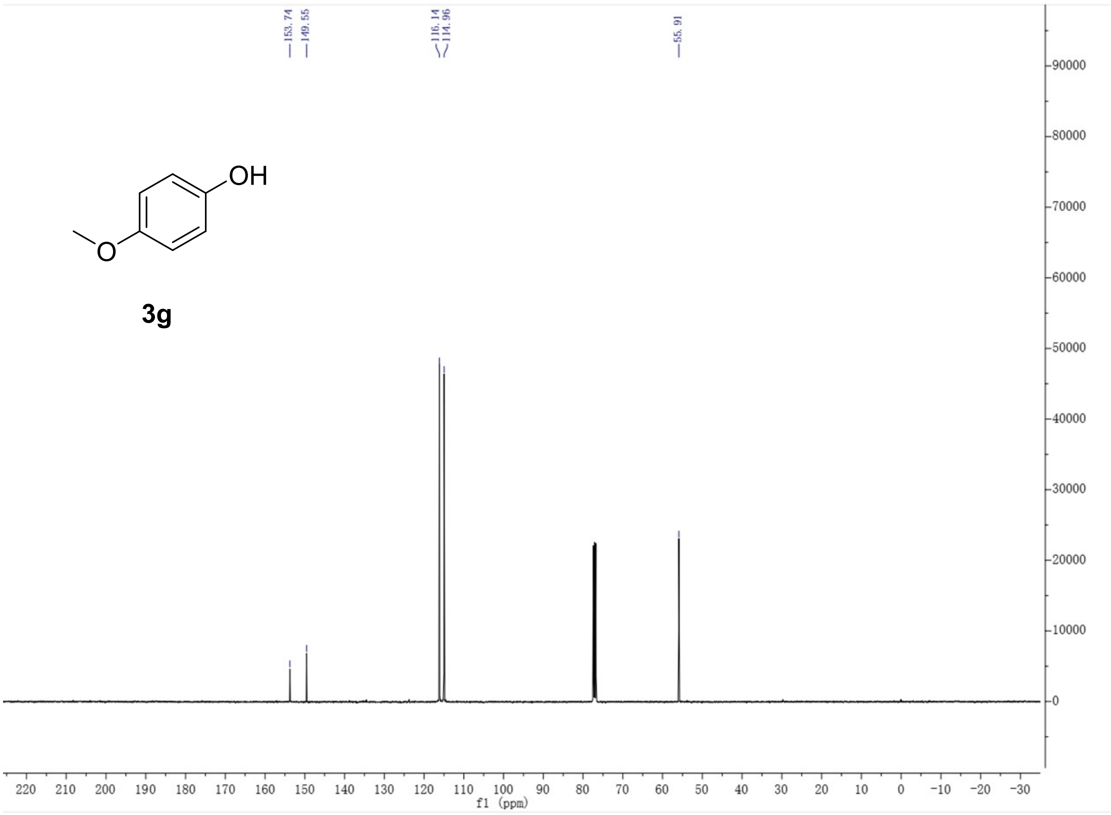
6.83
6.83
6.82
6.81
6.80
6.80
6.79
4.99
3.81
3.91
0.86
3.00
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)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O
153.74
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55.91
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50000
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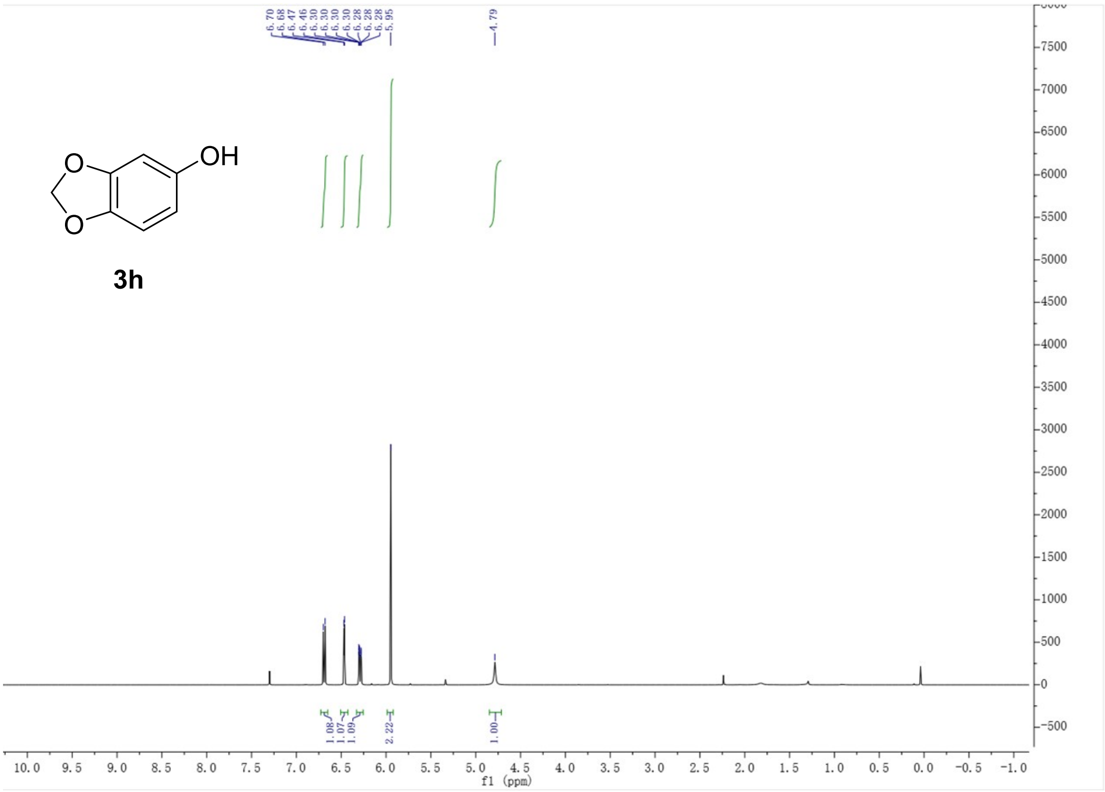
30000
20000
10000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)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6.30
6.30
6.30
6.28
6.28
6.28
5.95
4.79
OH
O
O
3h
1.08
1.07
1.09
2.22
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
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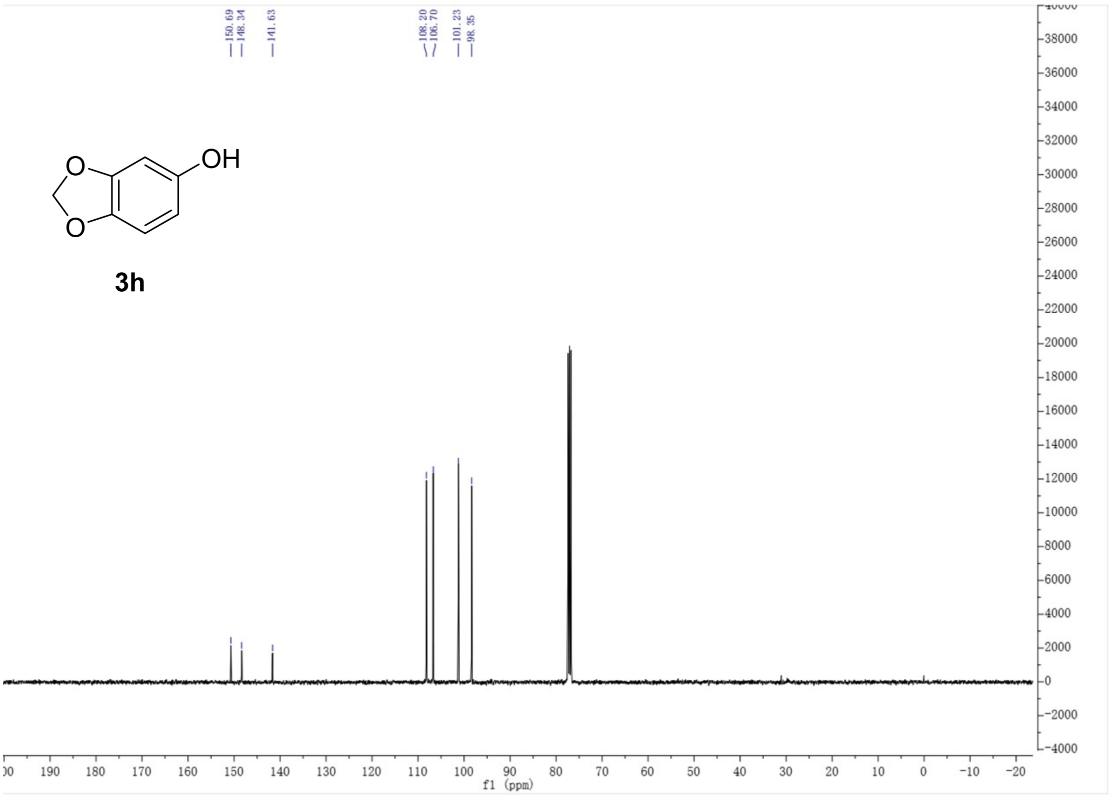
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141.63
108.20
106.70
101.23
98.35
OH
O
O
3h
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
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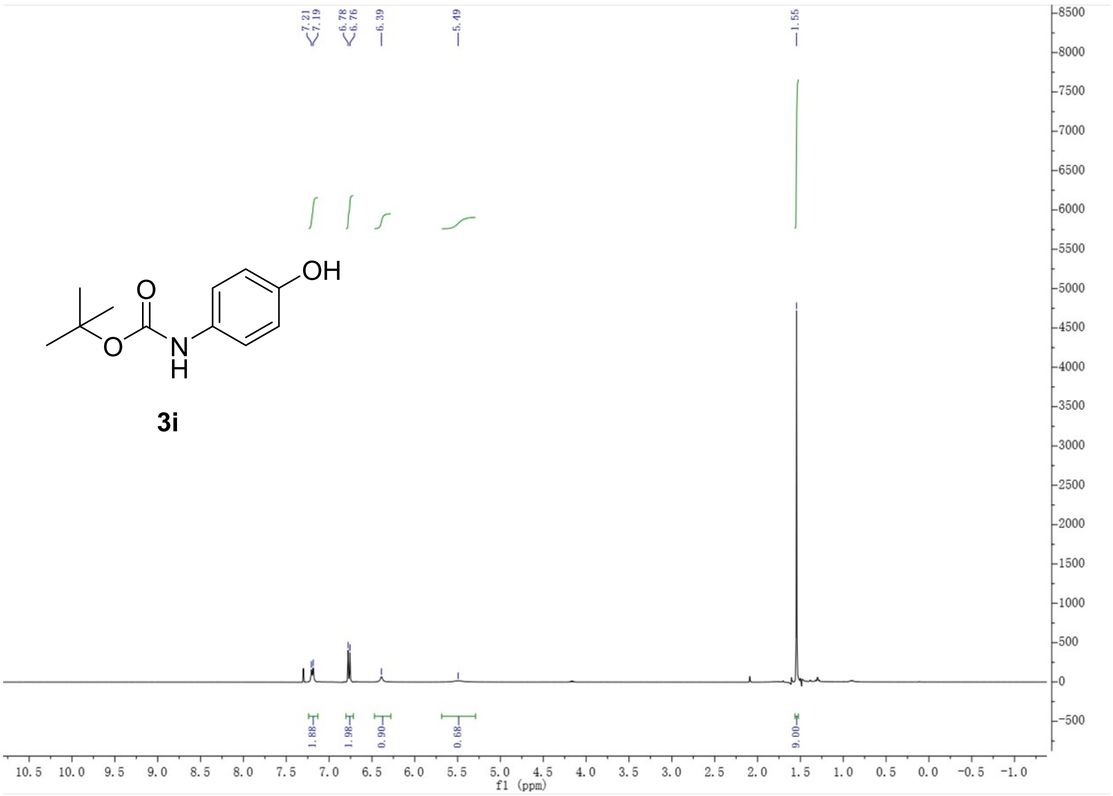
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O
O
N
H
3i
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1.98
0.90
0.68
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
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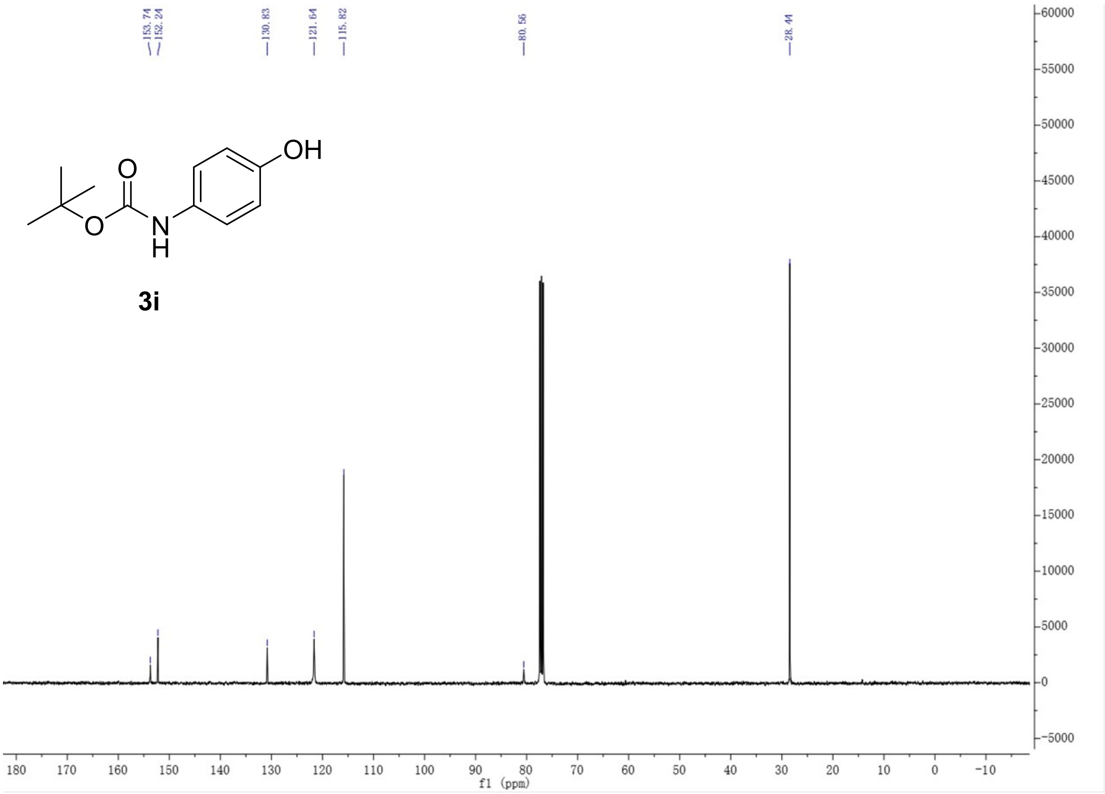
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121.64
115.82
80.56
28.44
OH
O
O
N
H
3i
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f1 (ppm)
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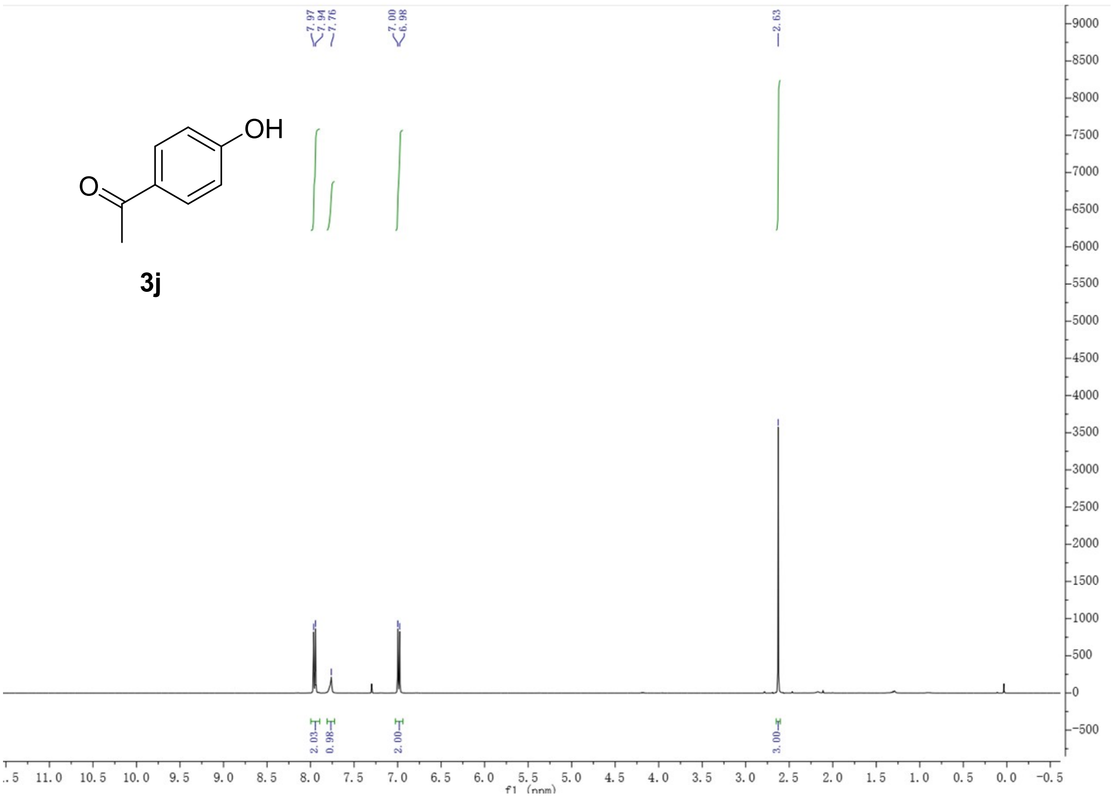
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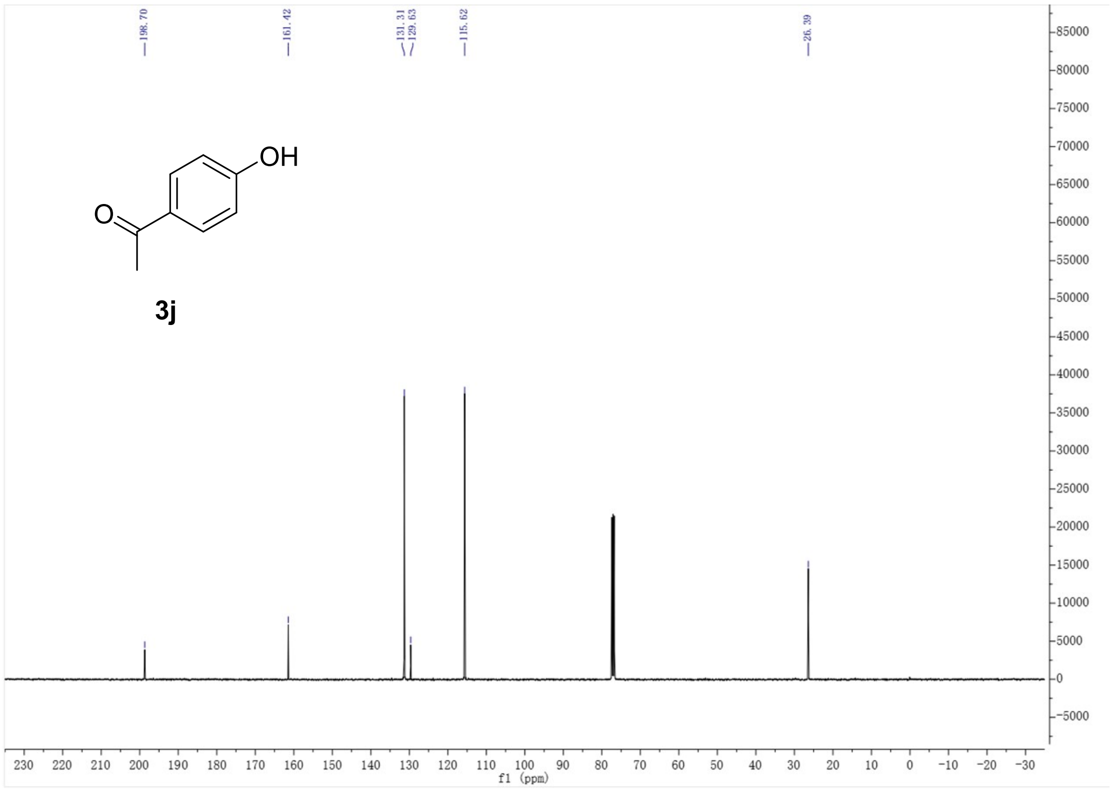
7.94
7.76
7.00
6.98
2.63
OH
O
3j
2.03
0.98
2.00
3.00
f1 (ppm)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
9000 8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500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161.42
131.31
129.63
115.62
26.39
OH
O
3j
f1 (ppm)
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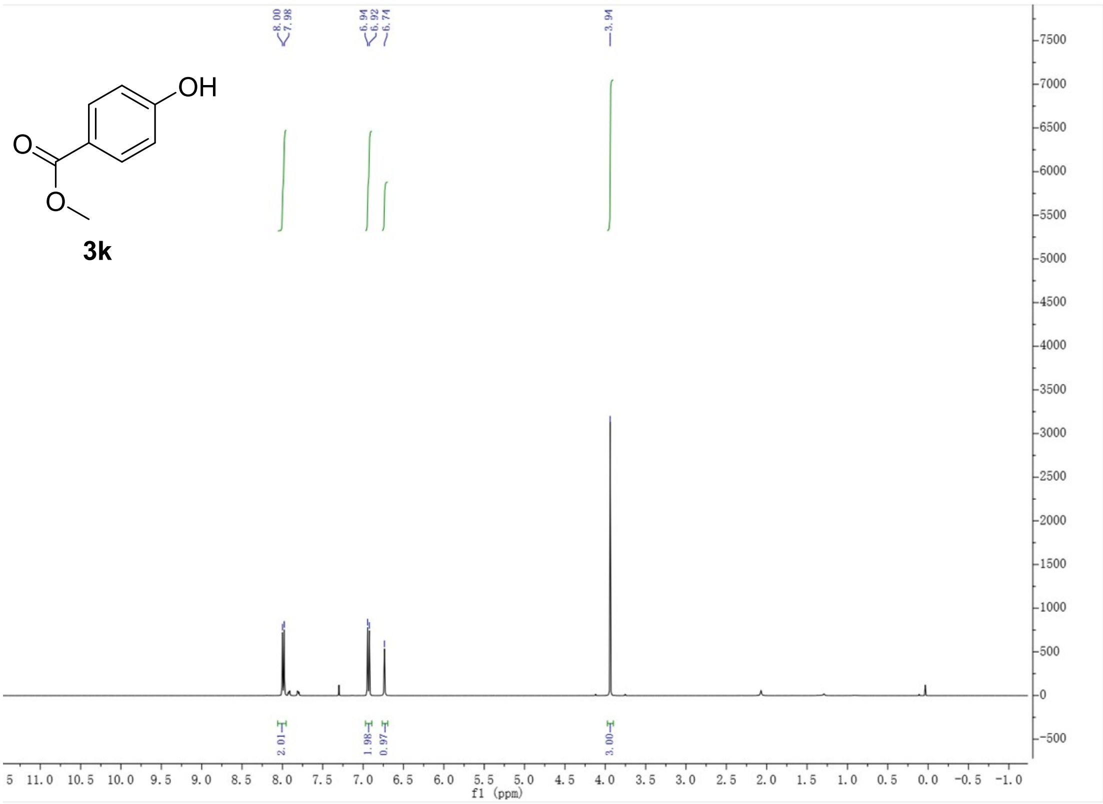
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O
O
3k
8.00
7.98
6.94
6.92
6.74
3.94
2.01
1.98
0.97
3.00
f1 (ppm)
5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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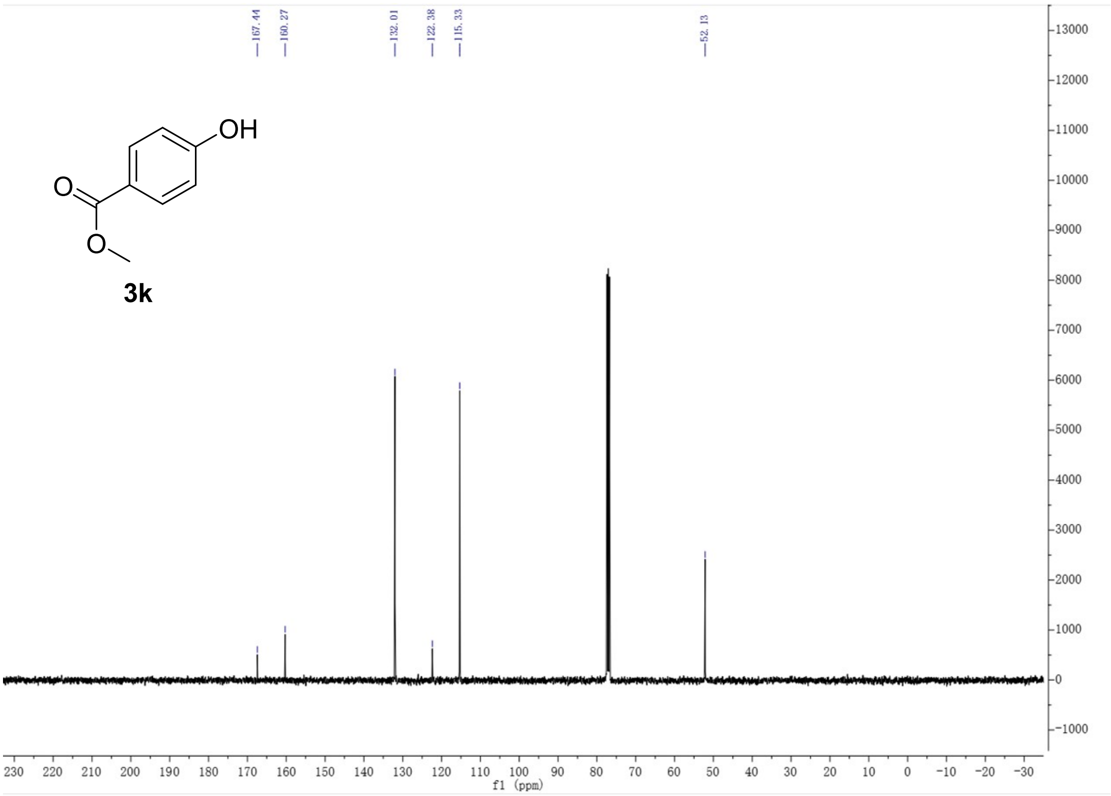
OH
O
O
3k
167.44
160.27
132.01
122.38
115.33
52.13
f1 (ppm)
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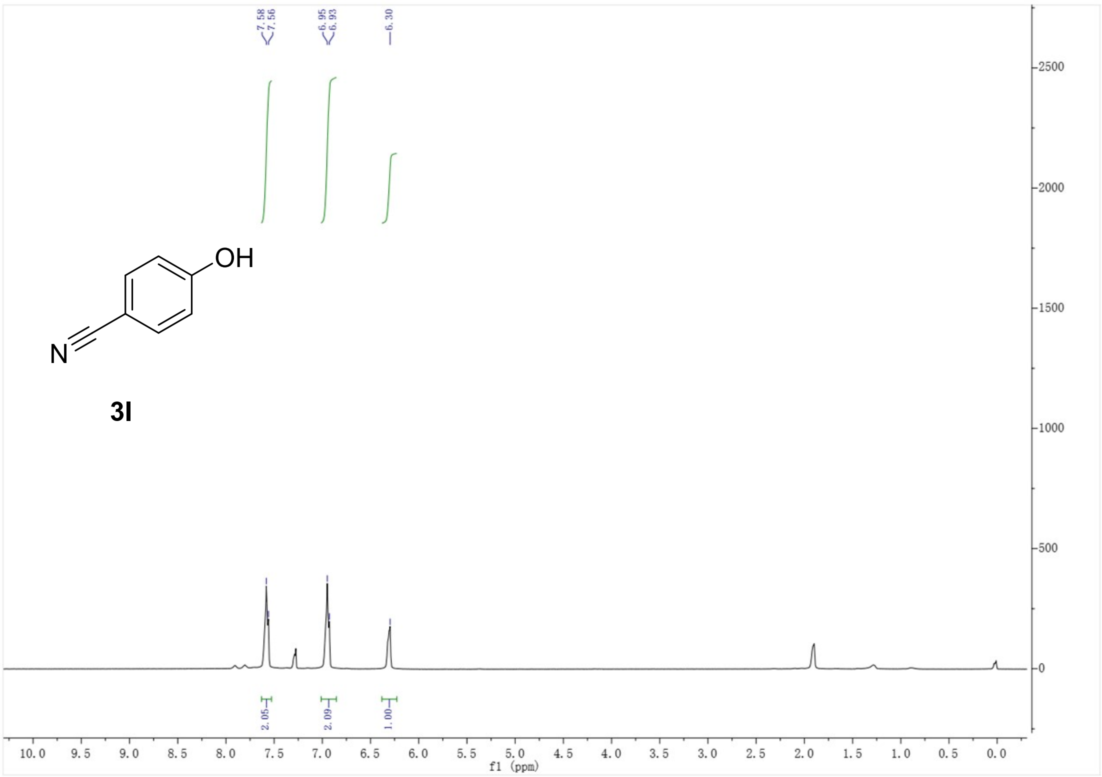
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7.56
6.95
6.93
6.30
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N
3l
2.05
2.09
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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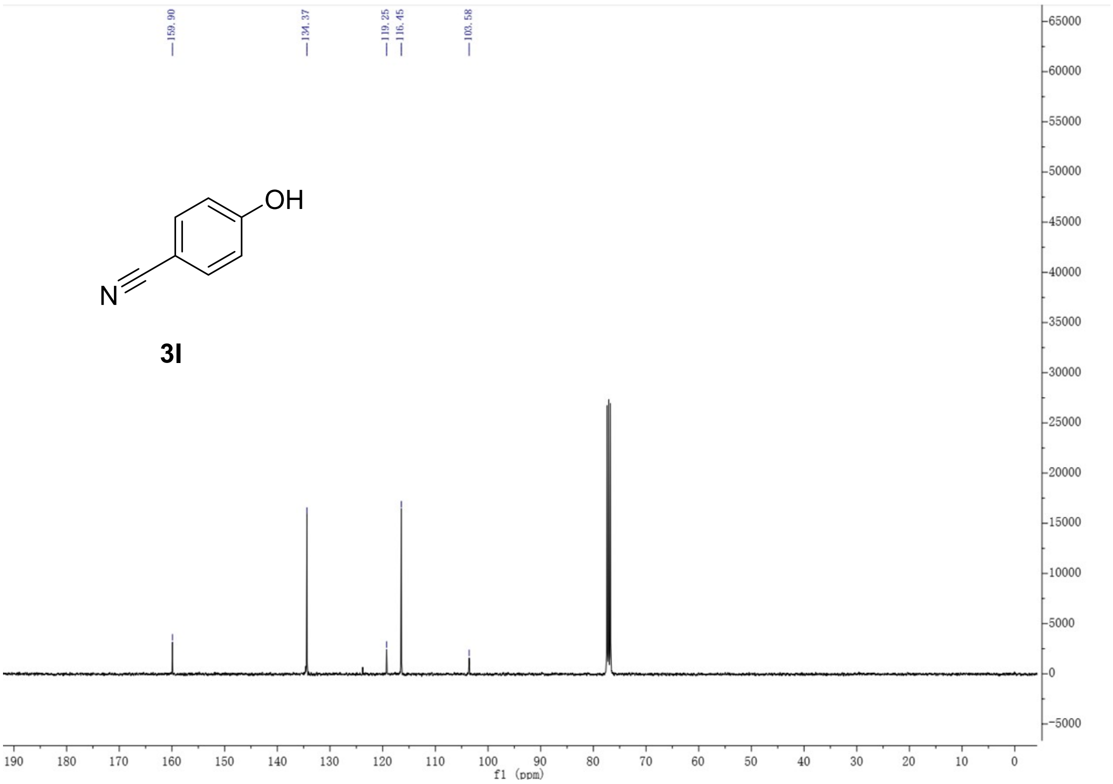
2000
1500
1000
500
0


159.90
134.37
119.25
116.45
103.58
OH
N
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
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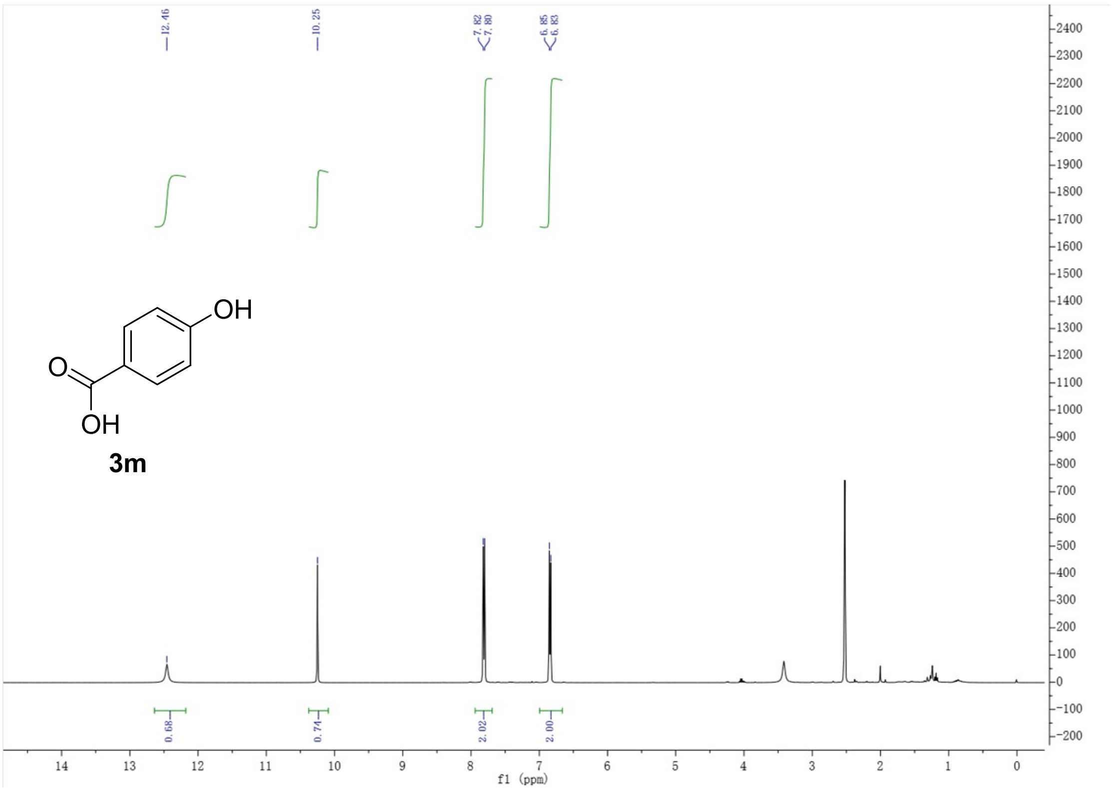
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000


12.46
10.25
7.82
7.80
6.85
6.83
OH
O
OH
3m
0.68
0.74
2.02
2.00
f1 (ppm)
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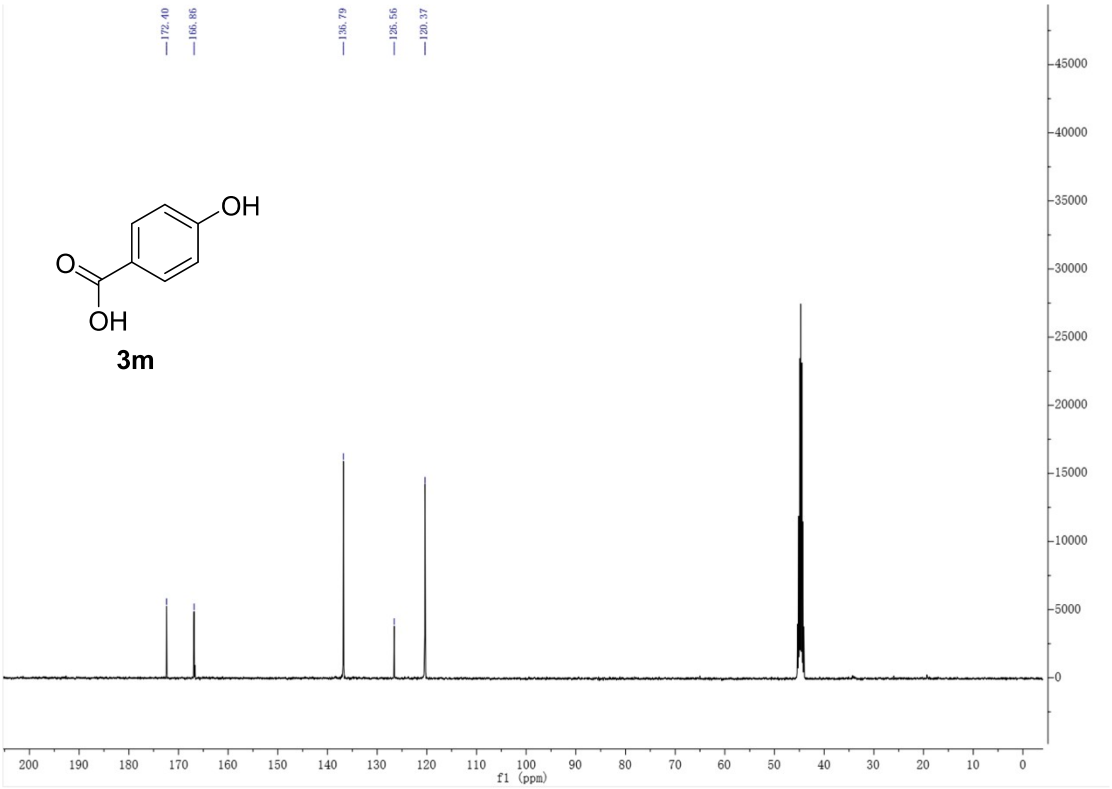
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136.79
126.56
120.37
OH
O
OH
3m
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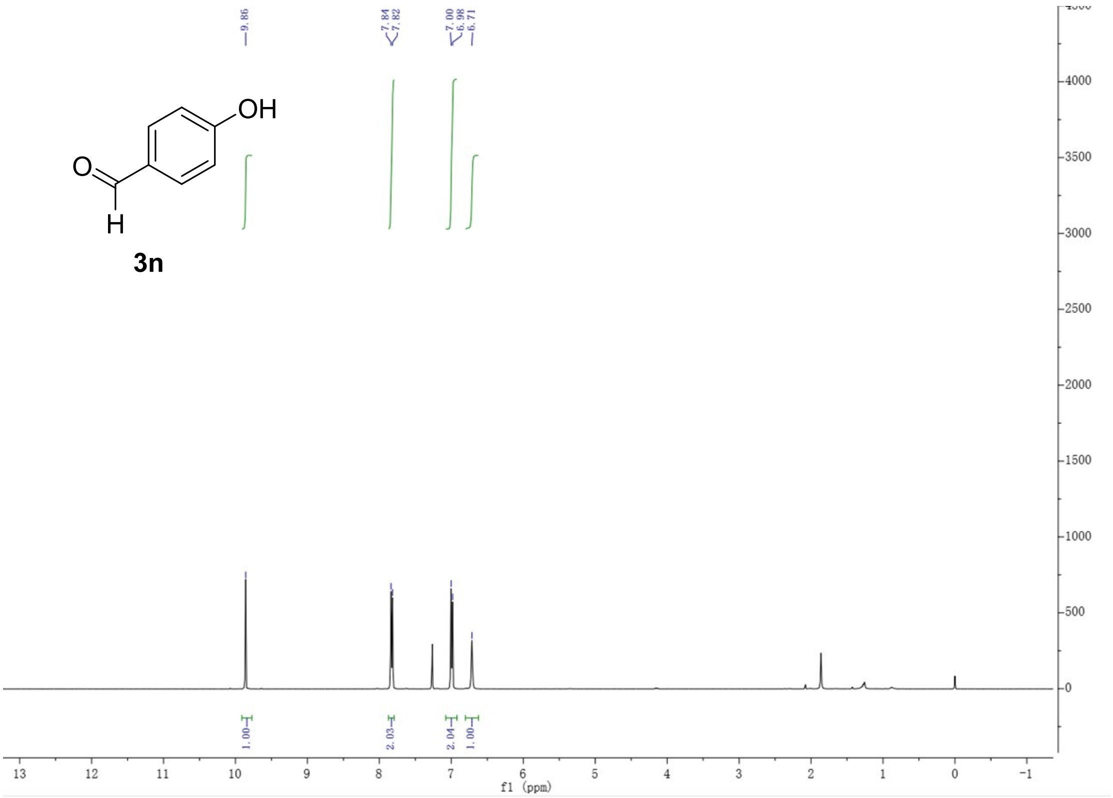
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7.00
6.98
6.71
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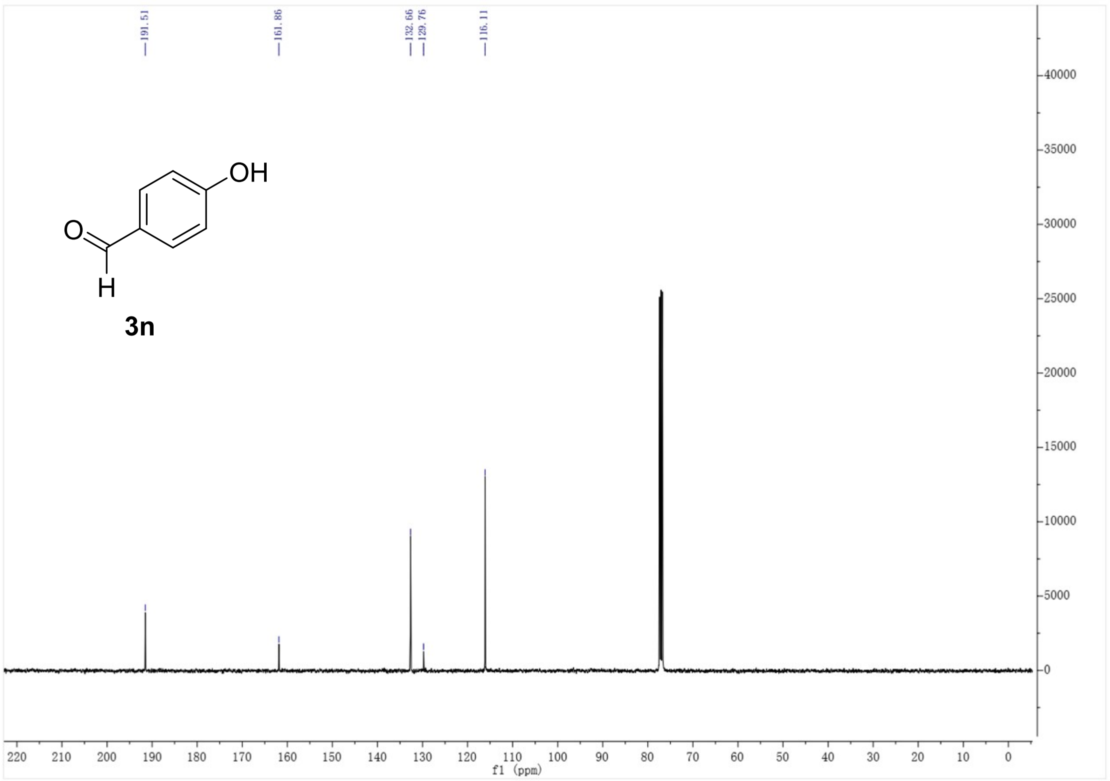
O
H
3n
1.00
2.03
2.04
1.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0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132.66
129.76
116.11
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O
H
3n
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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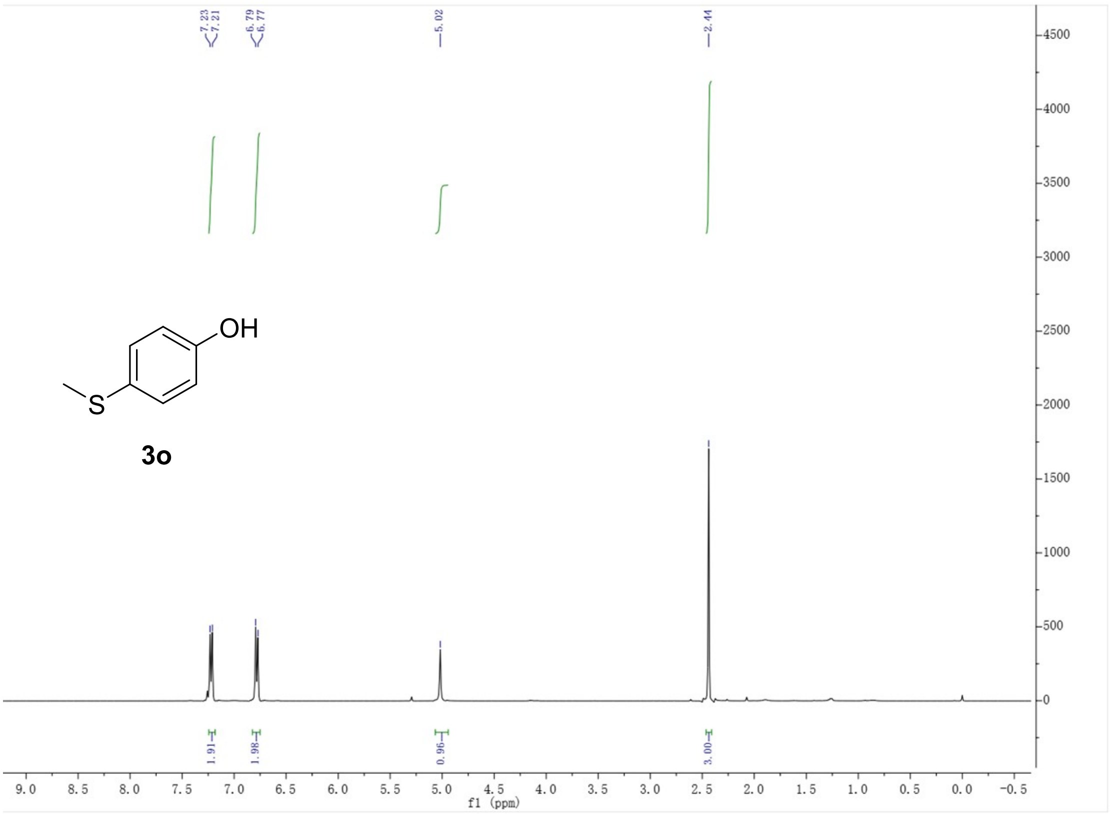
40000
35000
30000
25000
20000
15000
10000
5000
0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6.79
6.77
5.02
2.44
OH
S
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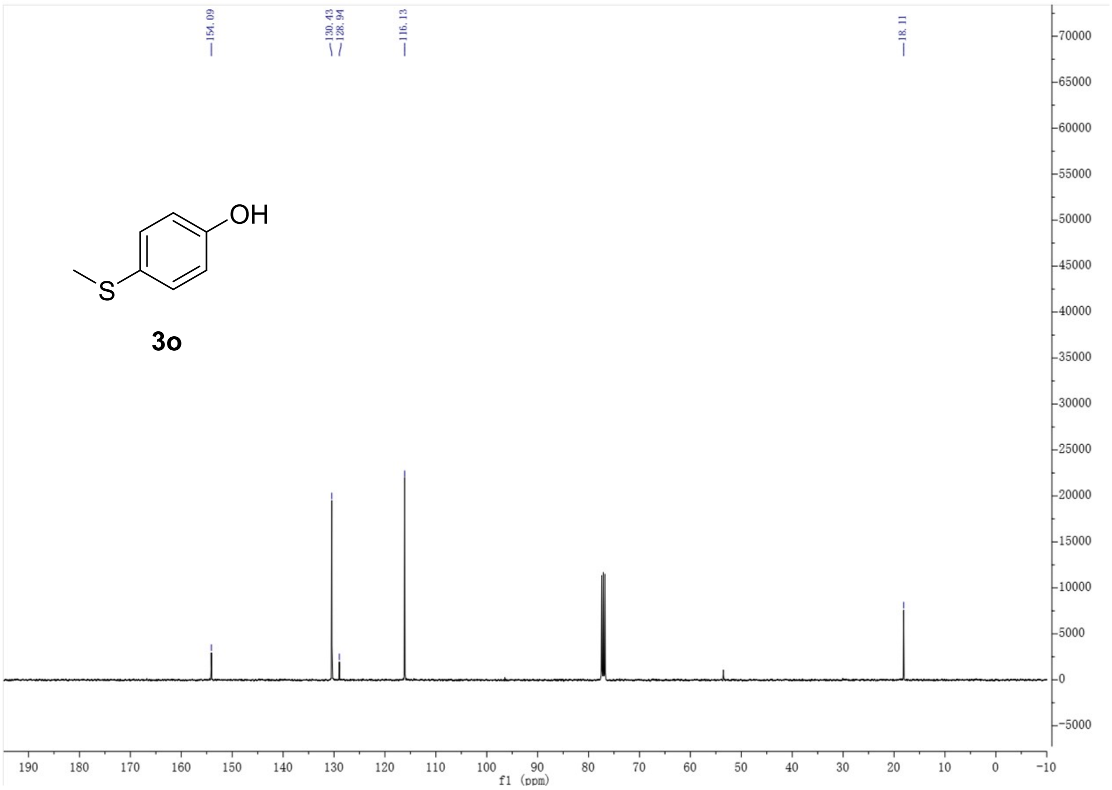
1.98
0.96
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
4500 4000 3500 3000 2500 2000 1500 1000 500 0


154.09
130.43
128.94
116.13
18.11
OH
S
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
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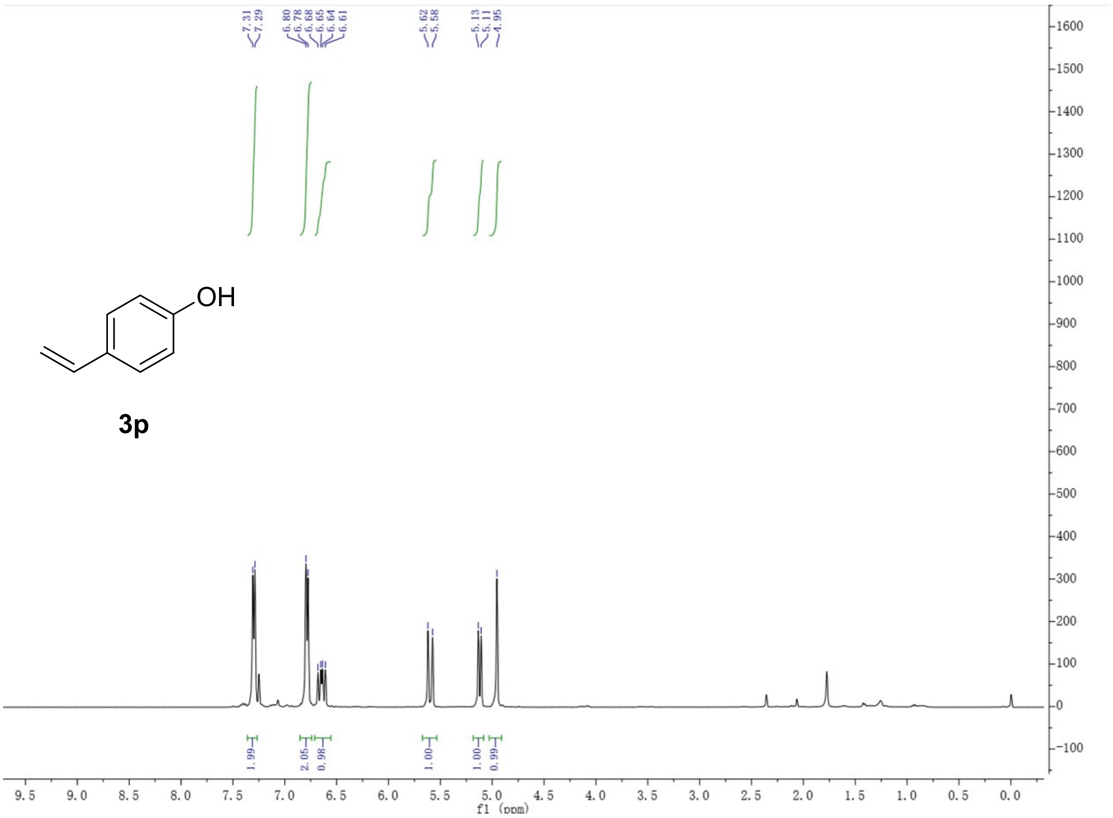
70000 65000 60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 −5000


3p
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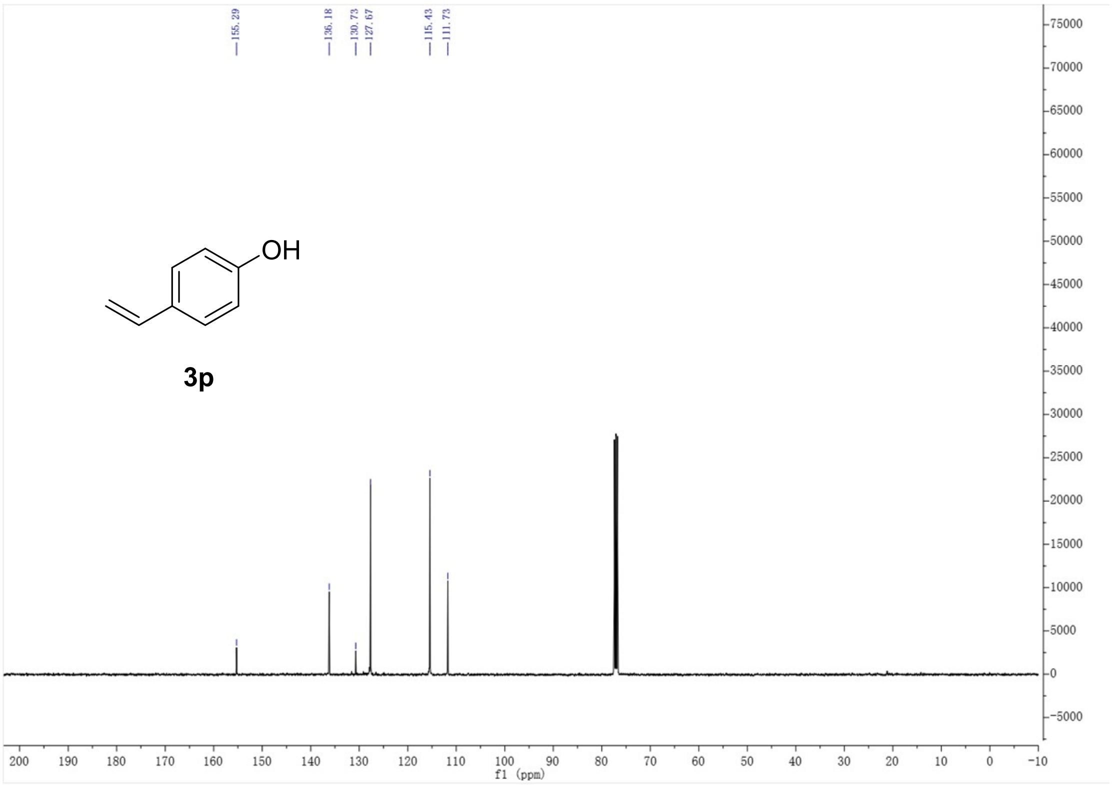
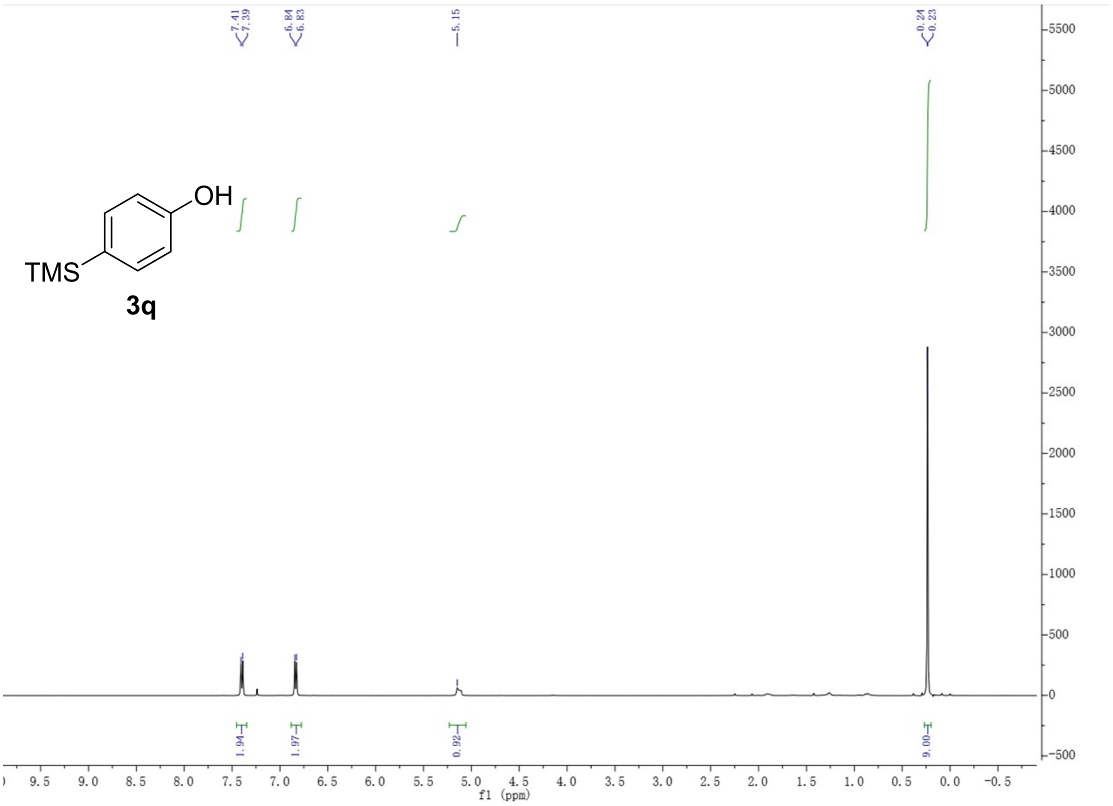
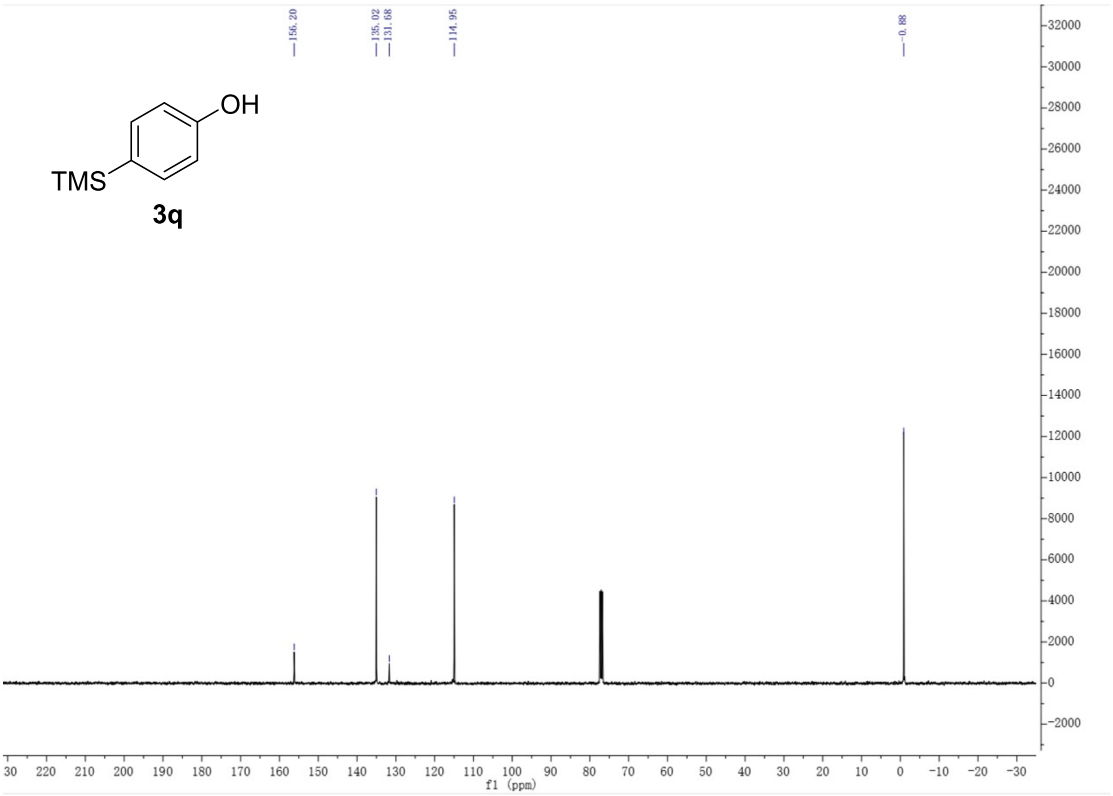
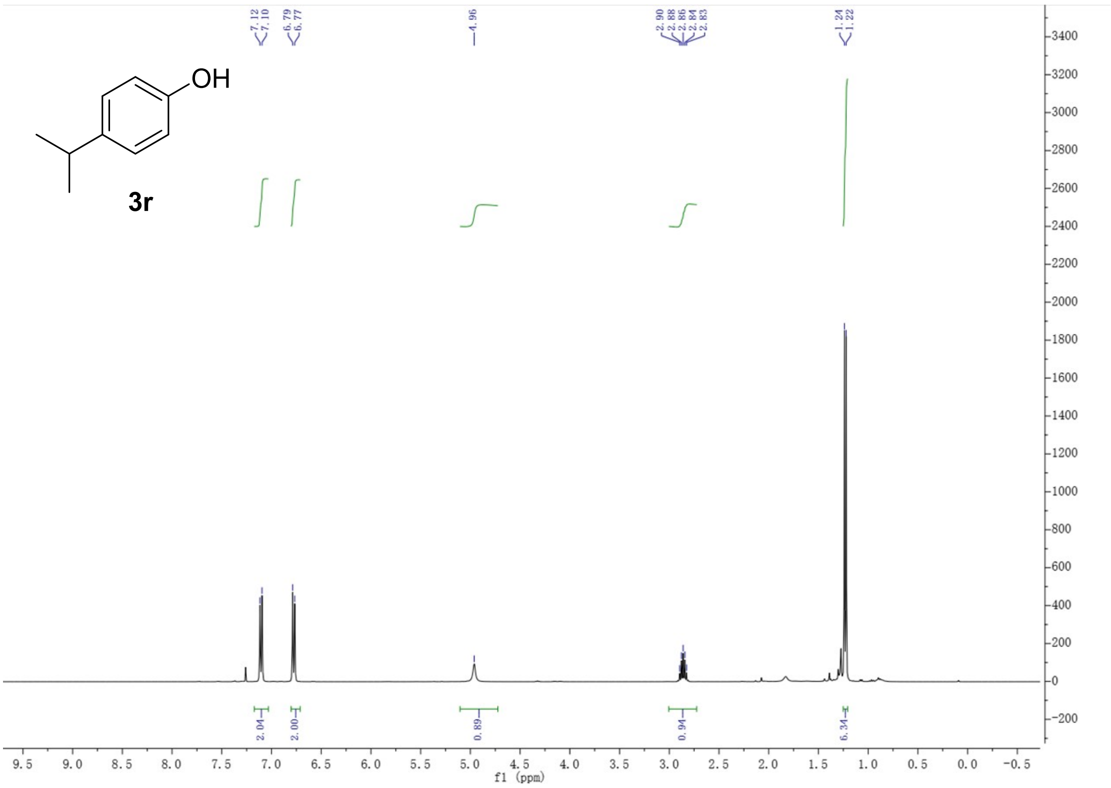
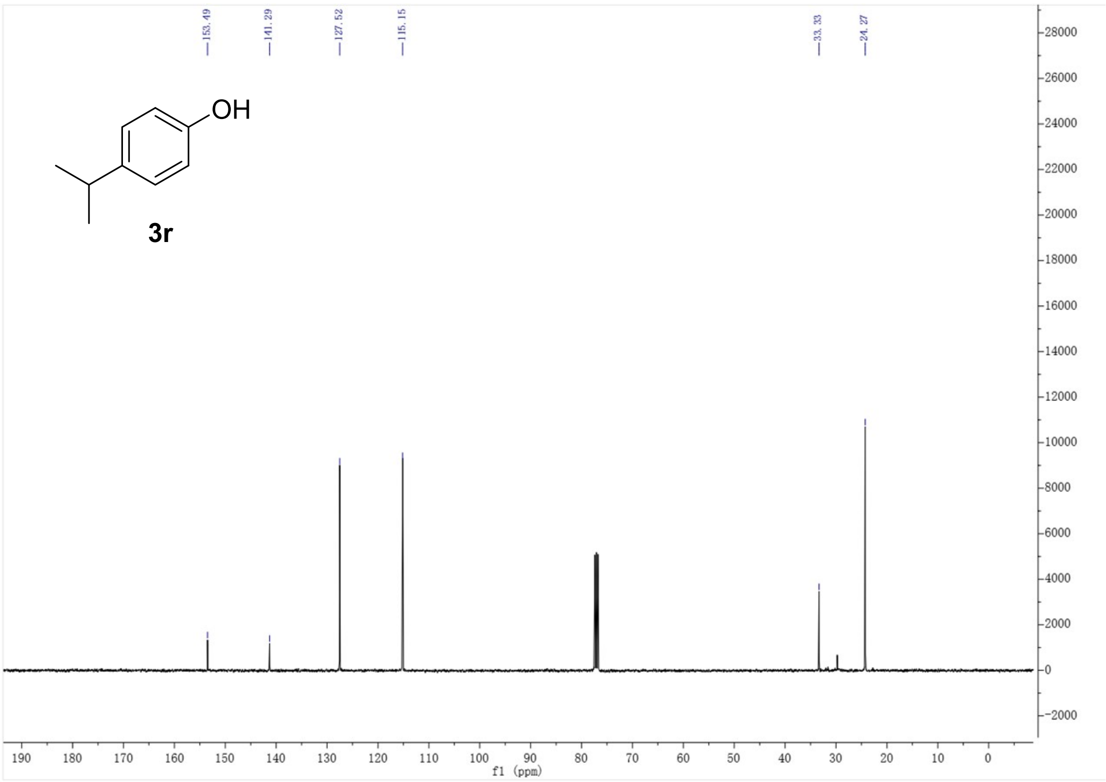
7.29
6.80
6.78
6.68
6.65
6.64
6.61
5.62
5.58
5.13
5.11
4.95
OH
1.99
2.05
0.98
1.00
1.00
0.99
f1 (ppm)

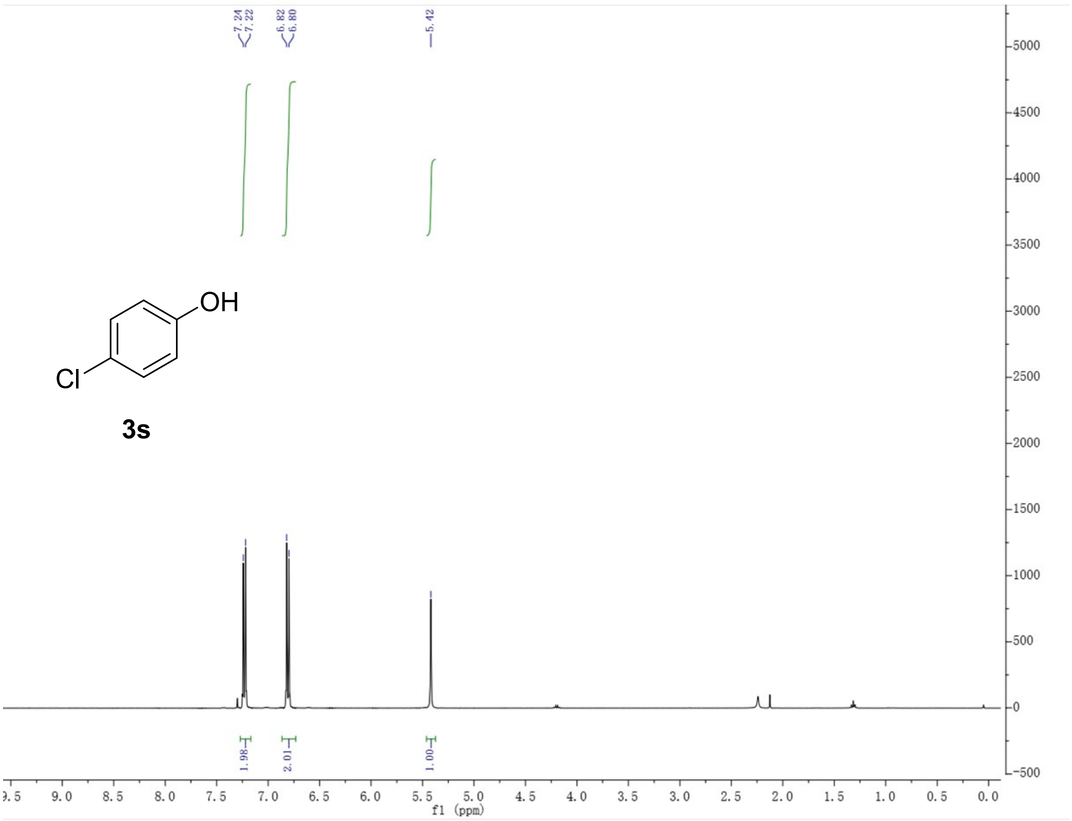

3p
155.29
136.18
130.73
127.67
115.43
111.73
OH
f1 (ppm)

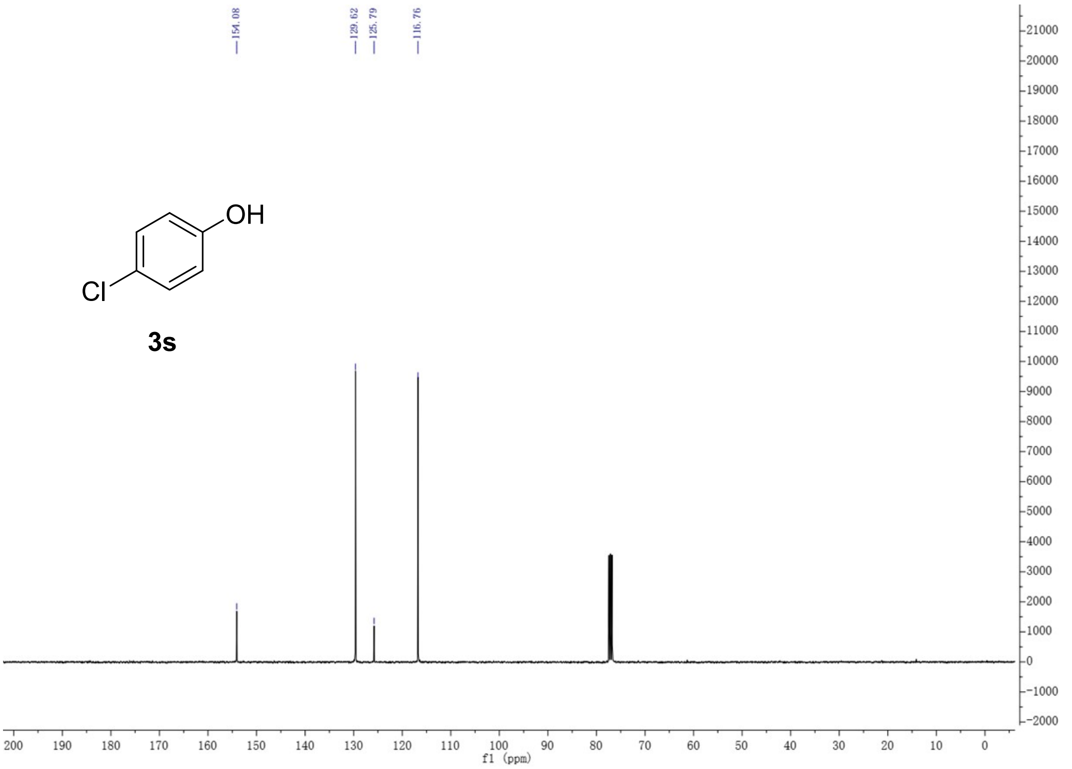

7.41
7.39
6.84
6.83
5.15
0.24
0.23
OH
TMS
3q
1.94
1.97
0.92
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

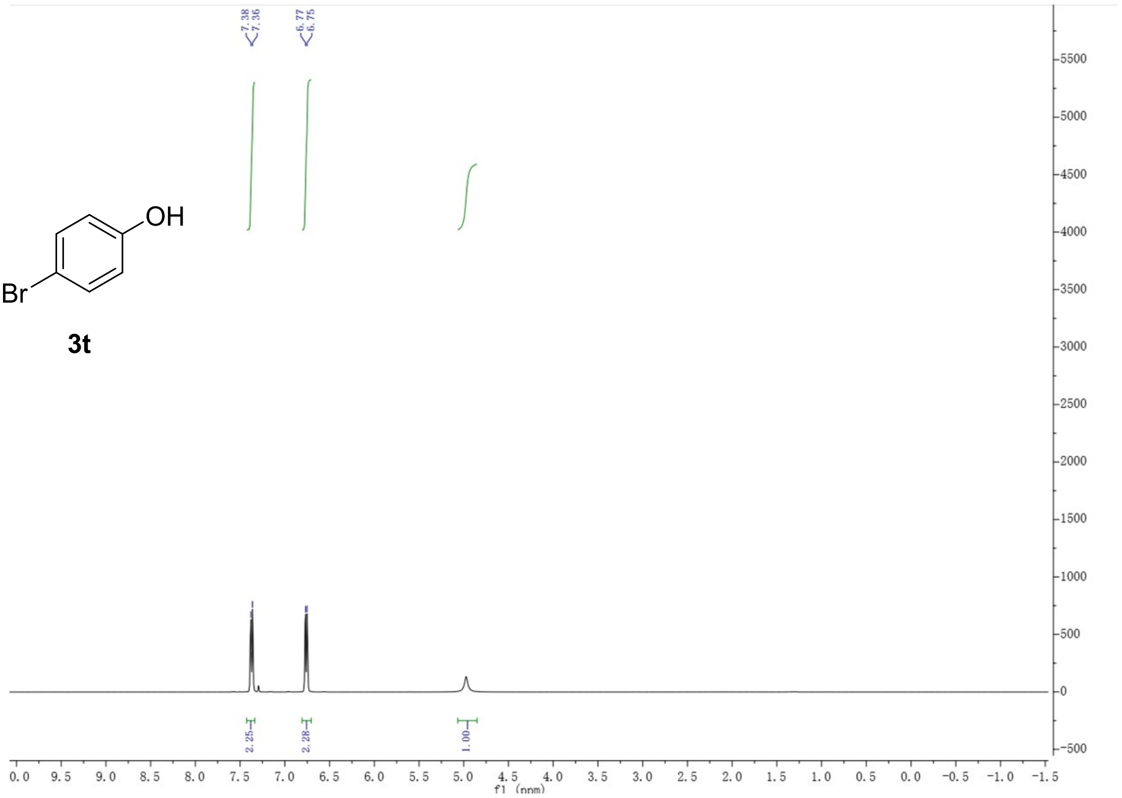

156.20
135.02
131.68
114.95
-0.88
OH
TMS
3q
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)
32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000

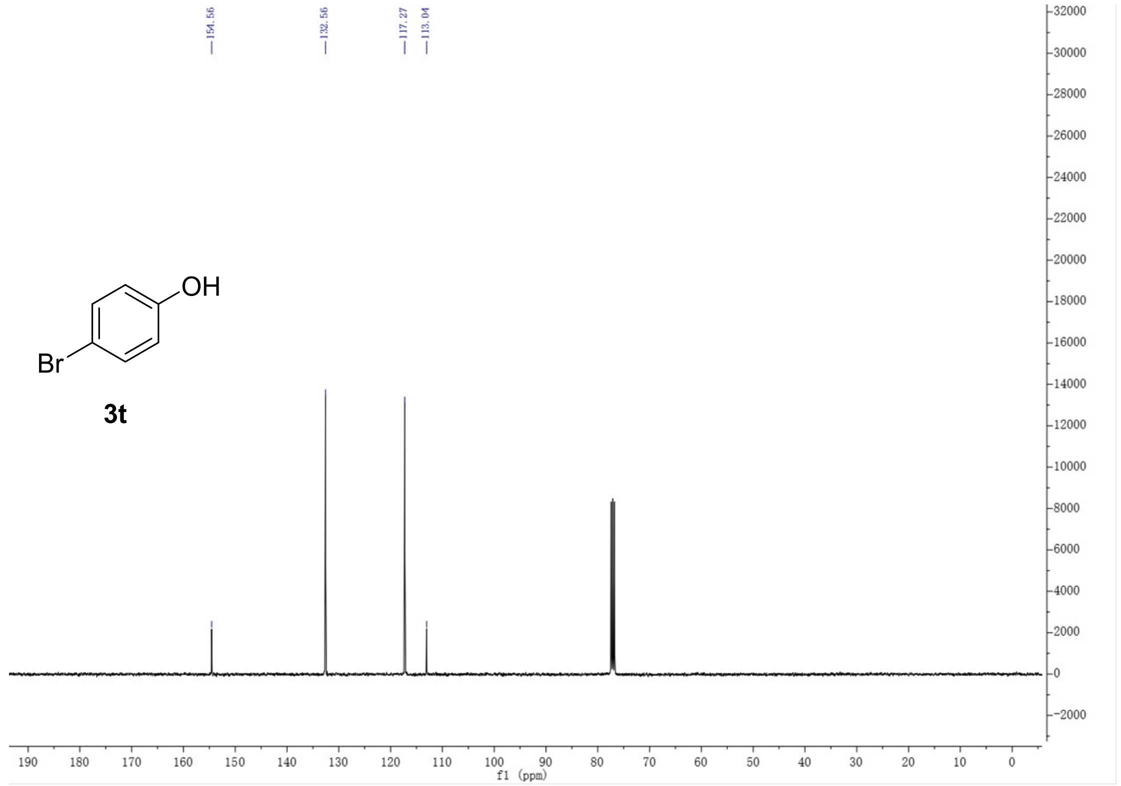

7.12
7.10
6.79
6.77
4.96
2.90
2.88
2.86
2.84
2.83
1.24
1.22
OH
3r
2.04
2.00
0.89
0.94
6.34
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

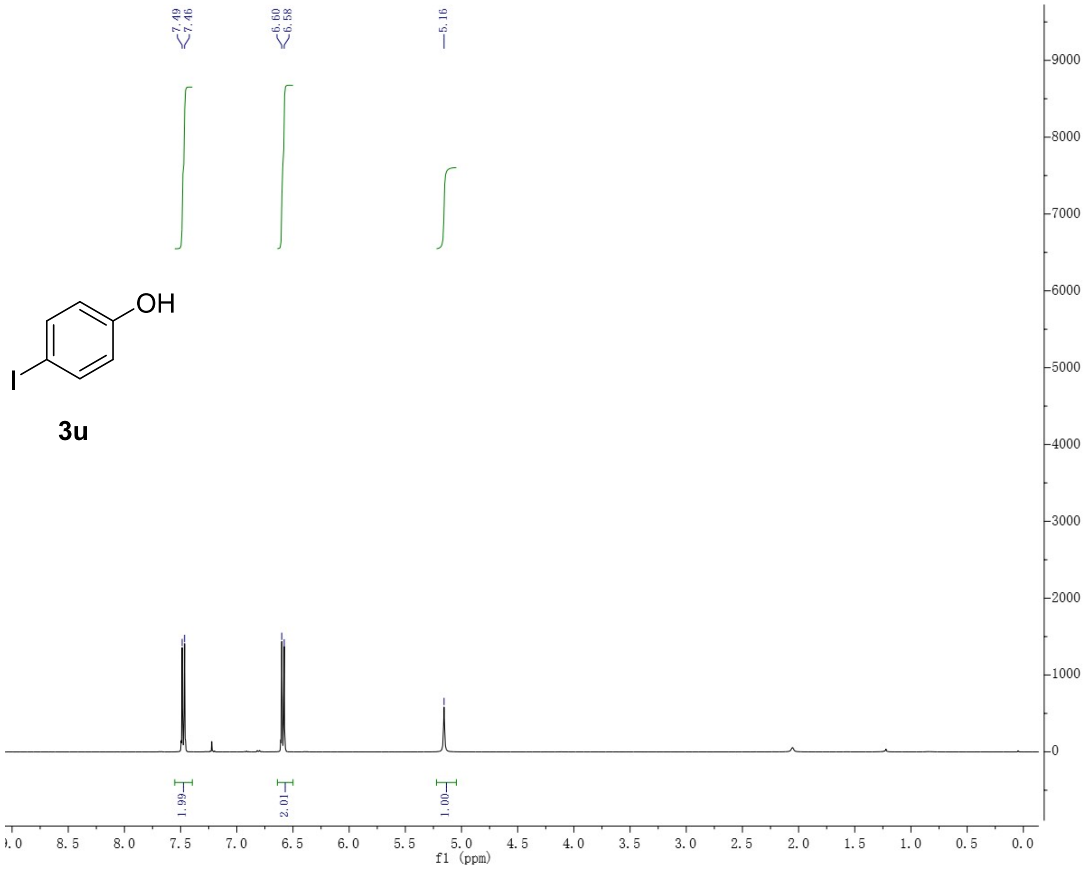

153.49
141.29
127.52
115.15
33.33
24.27
OH
3r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000


7.24
7.22
6.82
6.80
5.42
OH
Cl
3s
1.98
2.01
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

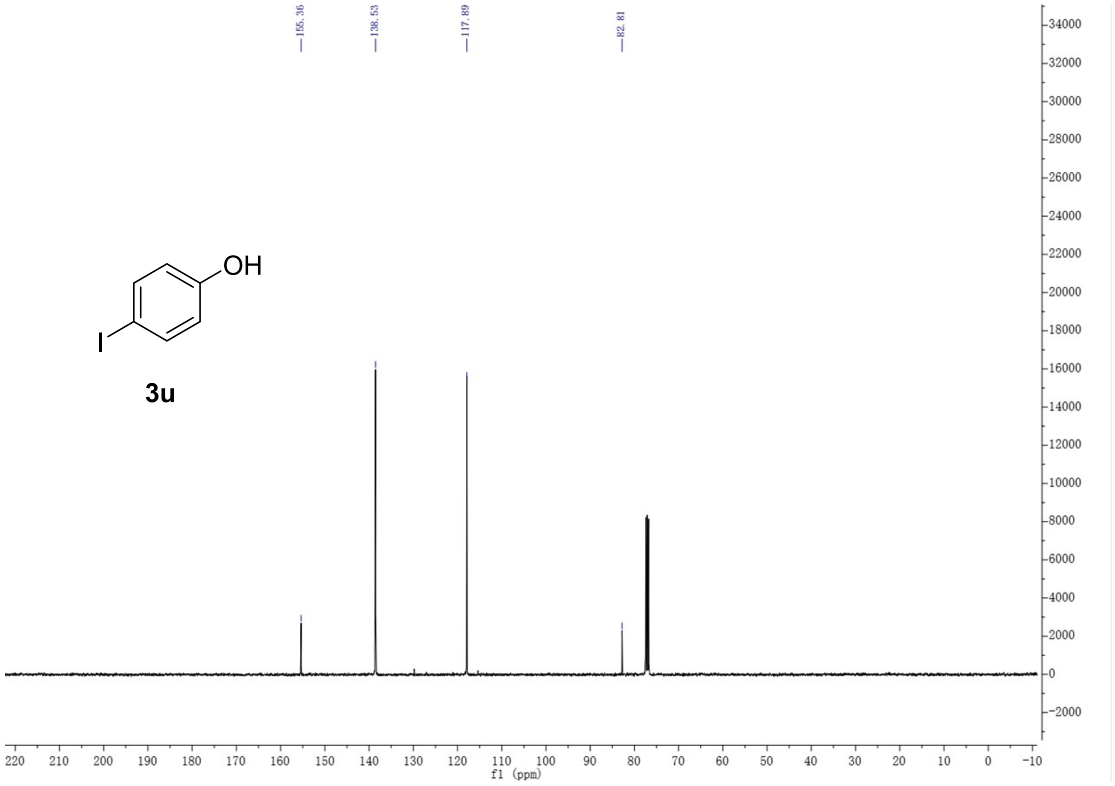

154.08
129.62
125.79
116.76
OH
Cl
3s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
21000 20000 19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000 -2000


7.38
7.36
6.77
6.75
OH
Br
3t
2.25
2.28
1.00
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 −500

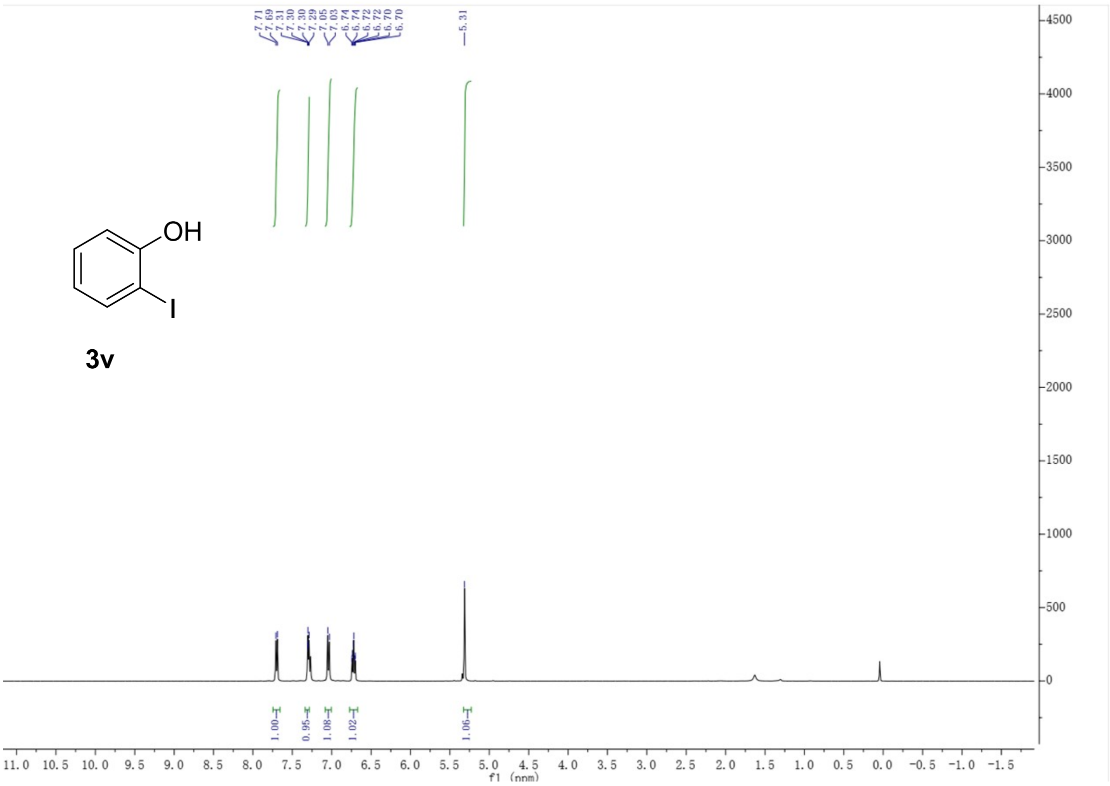

154.56
132.56
117.27
113.04
OH
Br
3t
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 −2000


7.49
7.46
6.60
6.58
5.16
OH
I
1.99
2.01
1.00
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

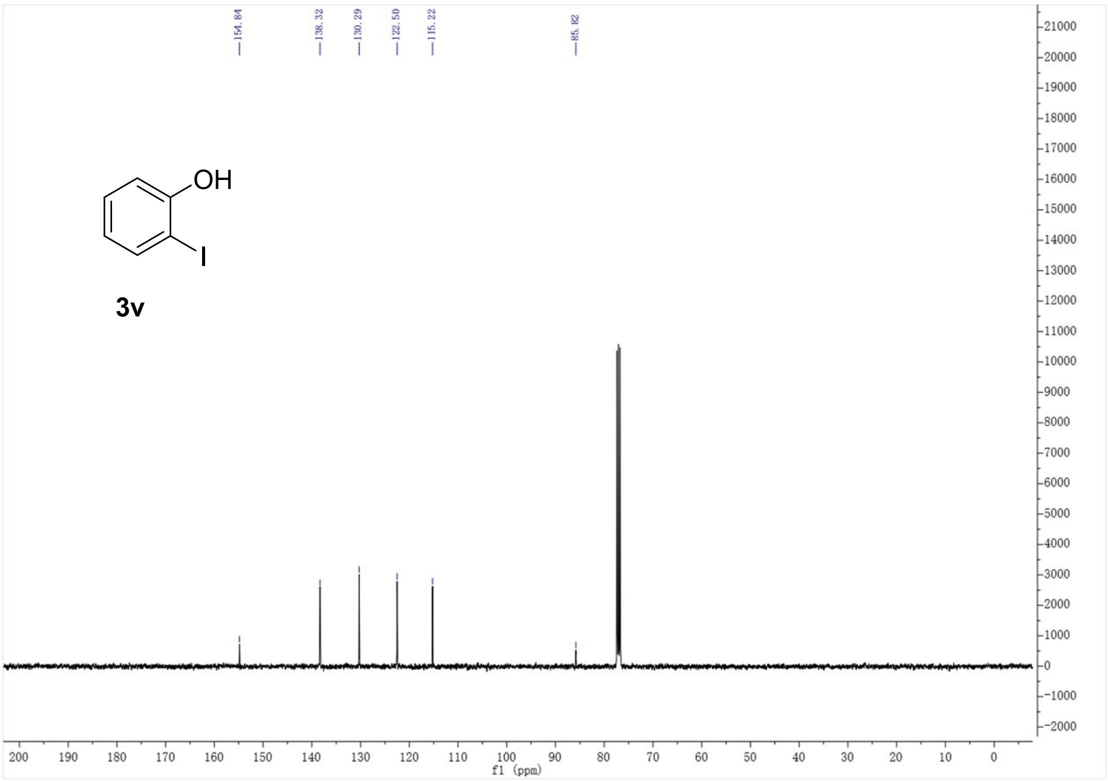
3u


155.36
138.53
117.89
82.81
OH
I
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

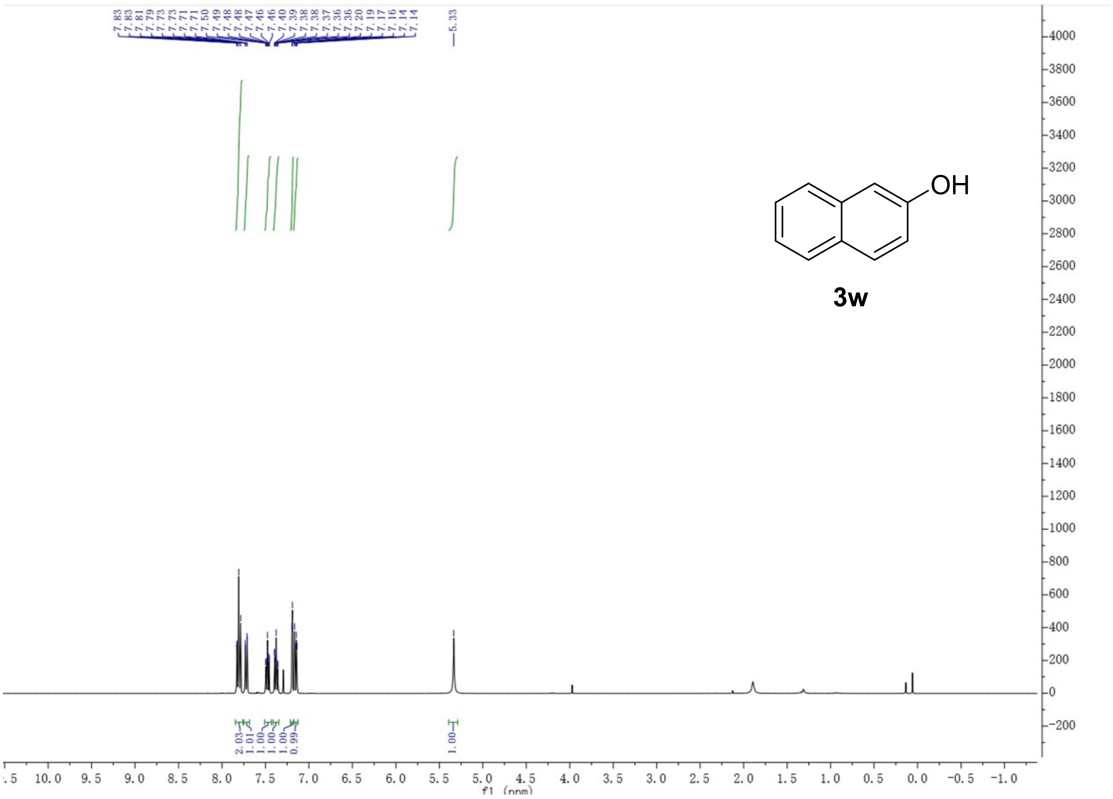
3u

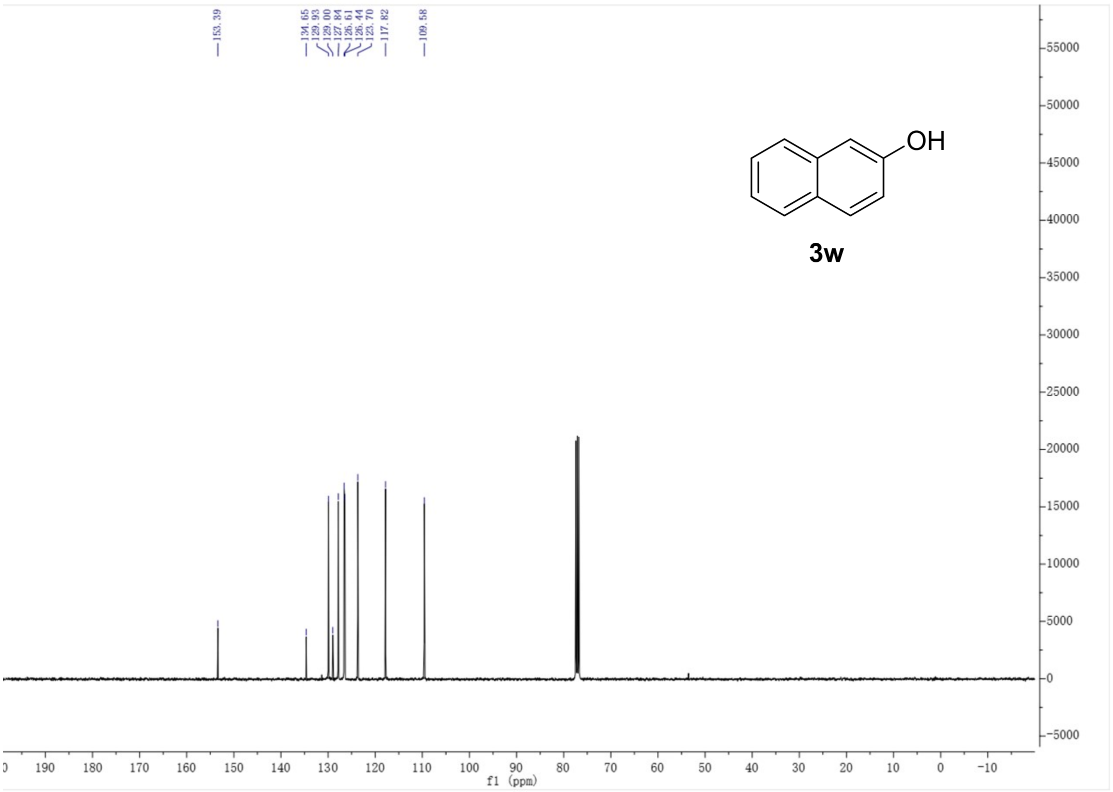

7.71
7.69
7.31
7.30
7.30
7.29
7.05
7.03
6.74
6.74
6.72
6.72
6.70
6.70
5.31
OH
I
1.00
0.95
1.08
1.02
1.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0

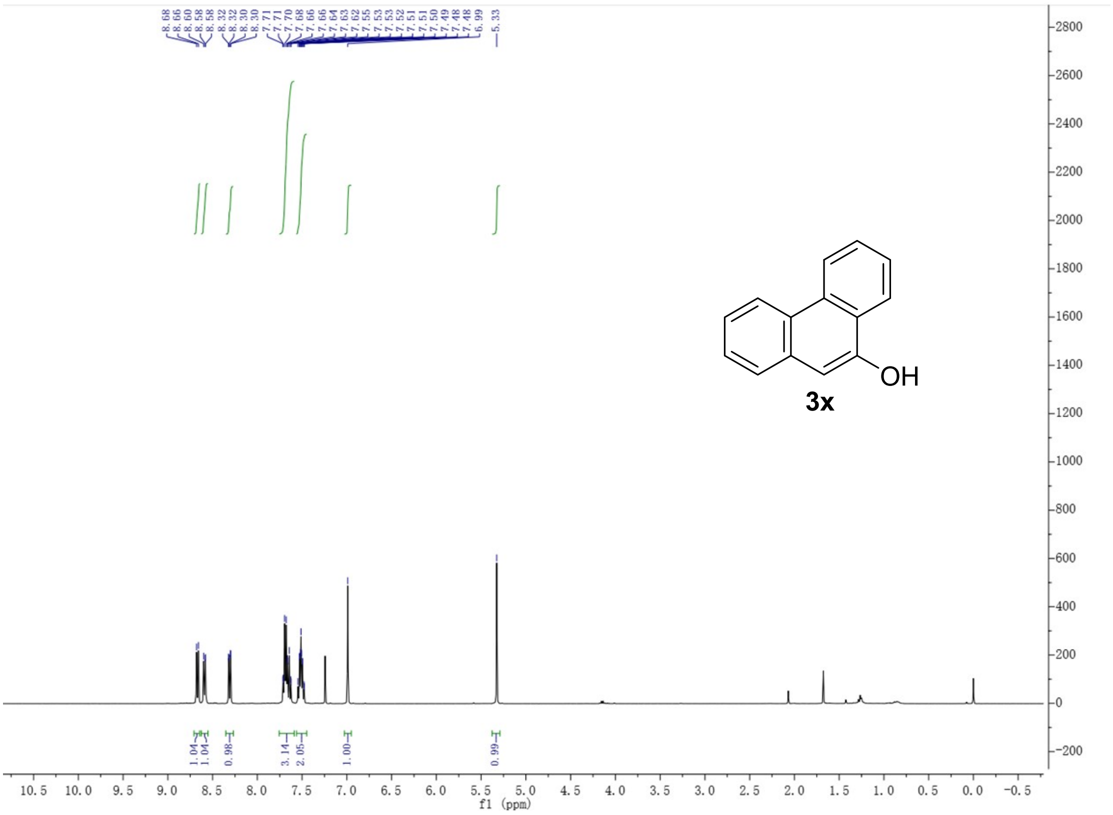
3v

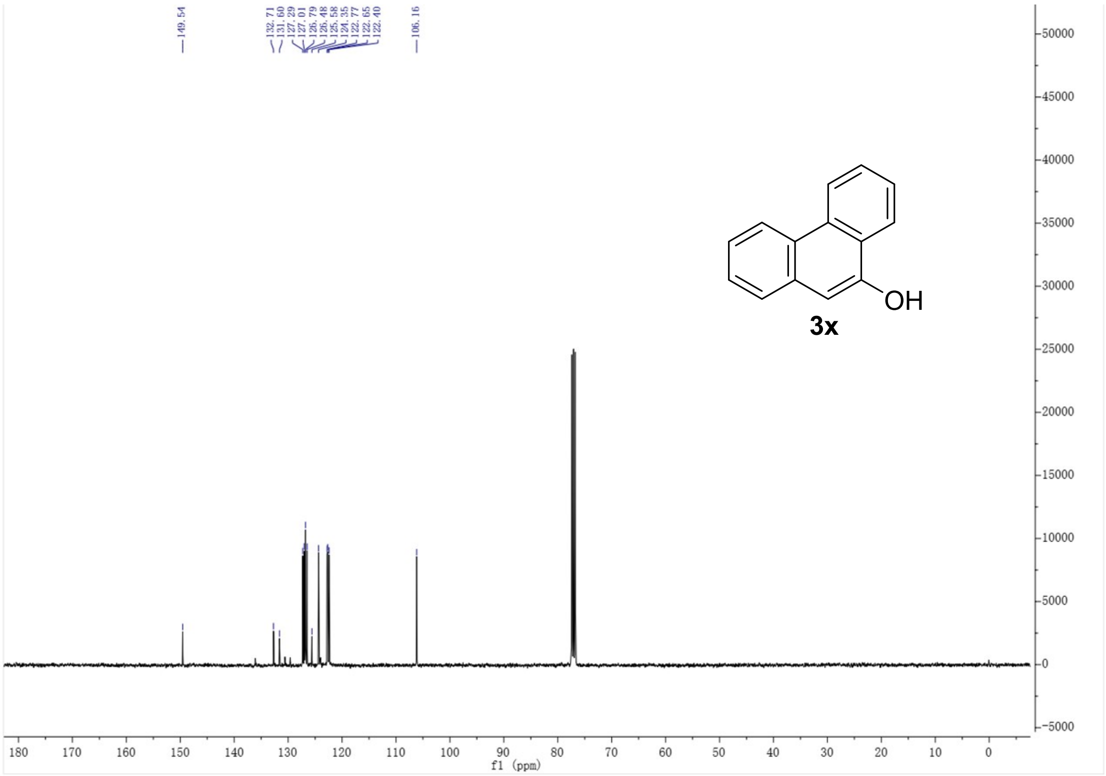

154.84
138.32
130.29
122.50
115.22
85.82
OH
I
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
−2000

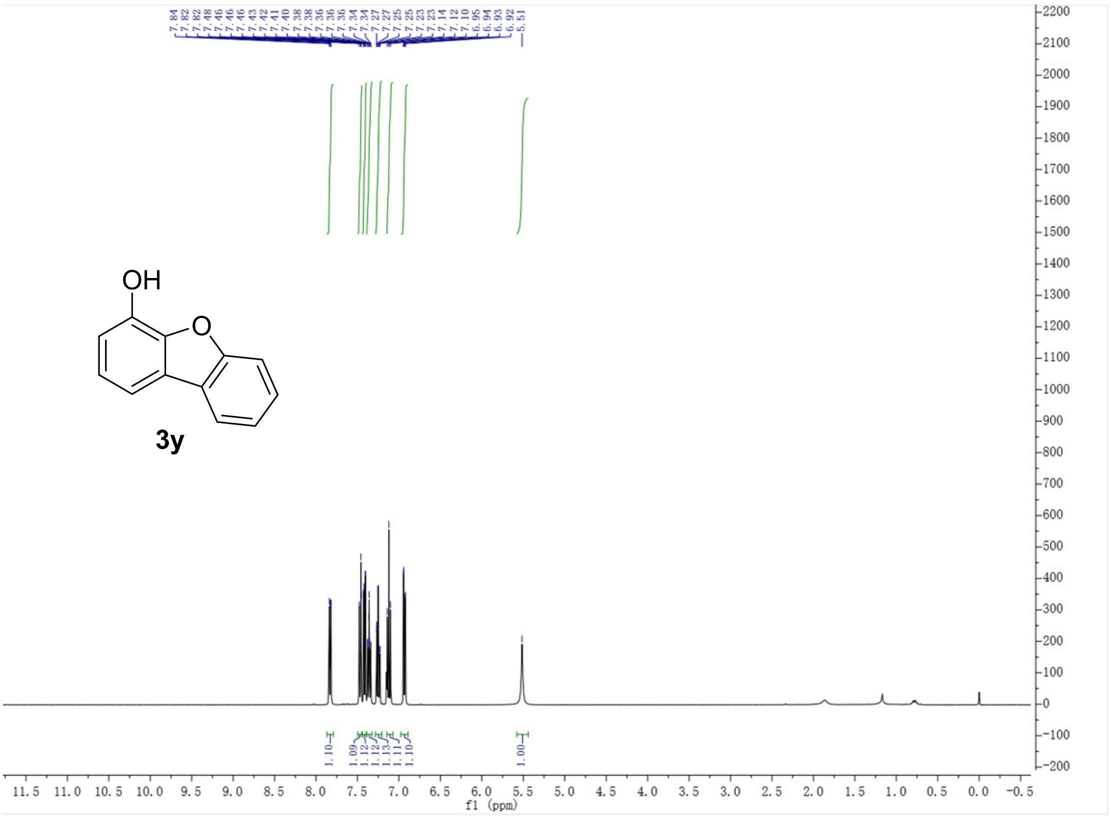
3v

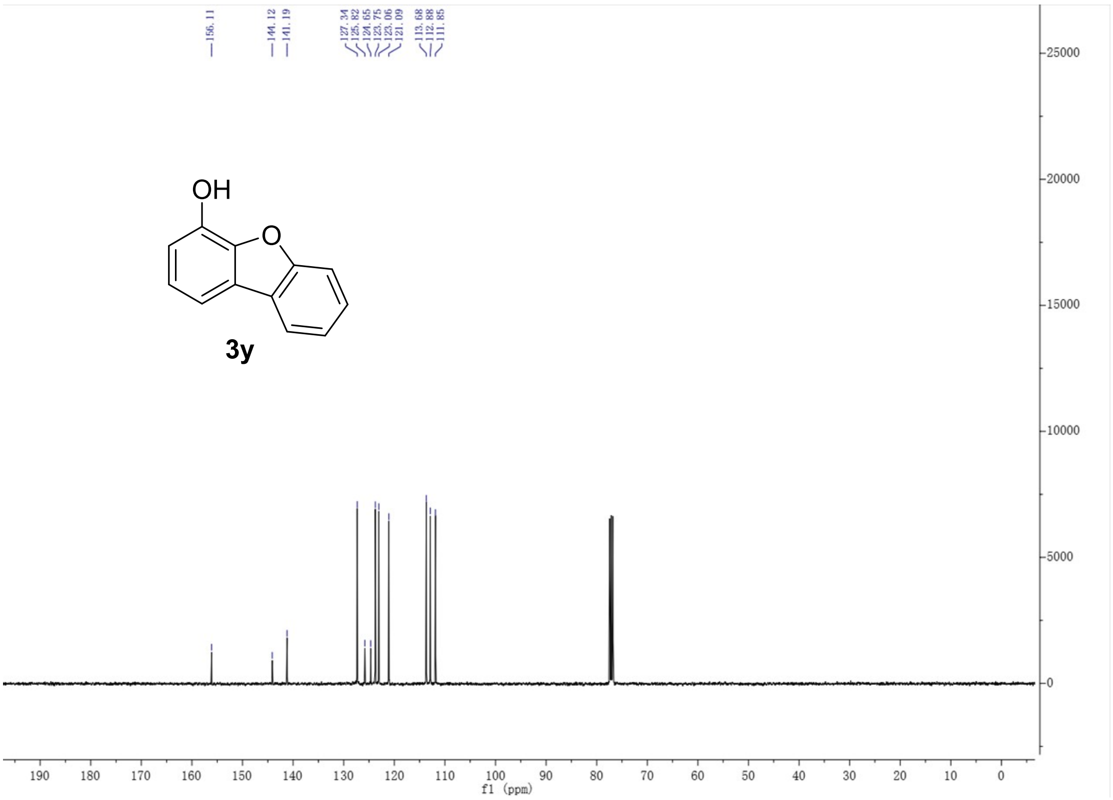

7.83
7.83
7.81
7.79
7.73
7.73
7.71
7.71
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.20
7.19
7.17
7.16
7.14
7.14
5.33
2.03
1.01
1.00
1.00
1.00
0.99
1.00
OH
3w
f1 (ppm)

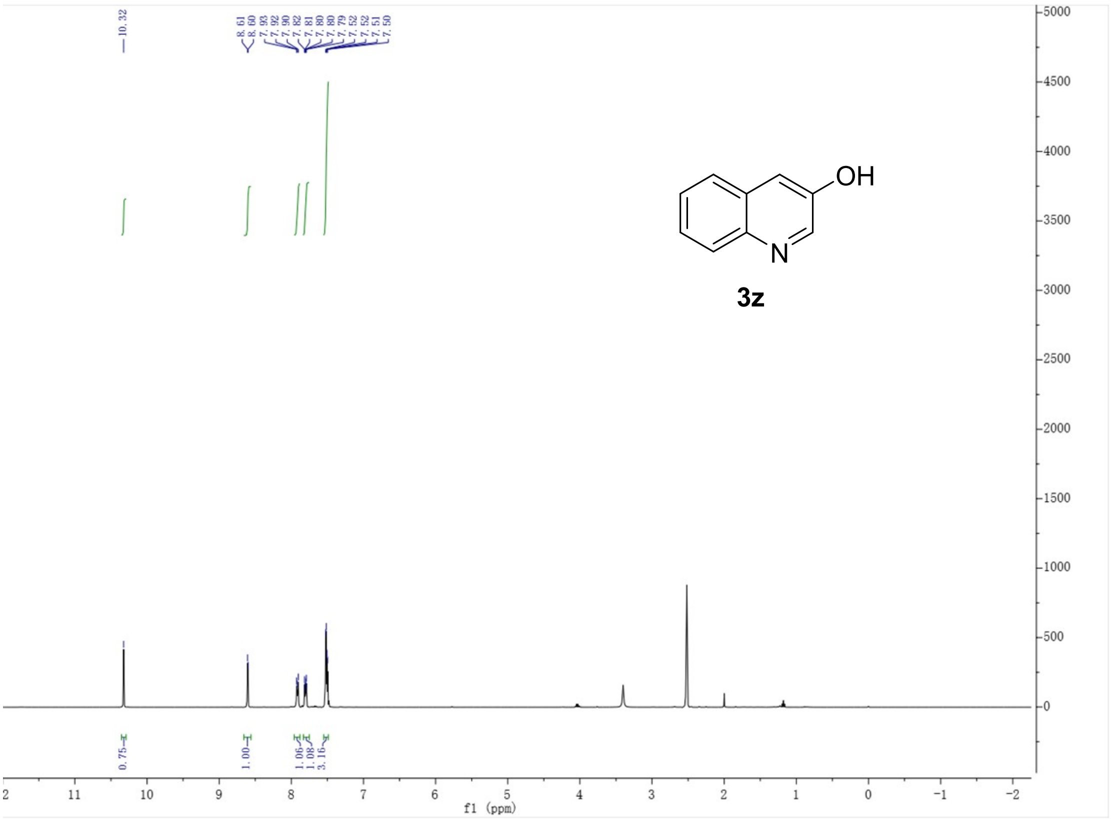

153.39
134.65
129.93
129.00
127.84
126.61
126.44
123.70
117.82
109.58
OH
3w
f1 (ppm)

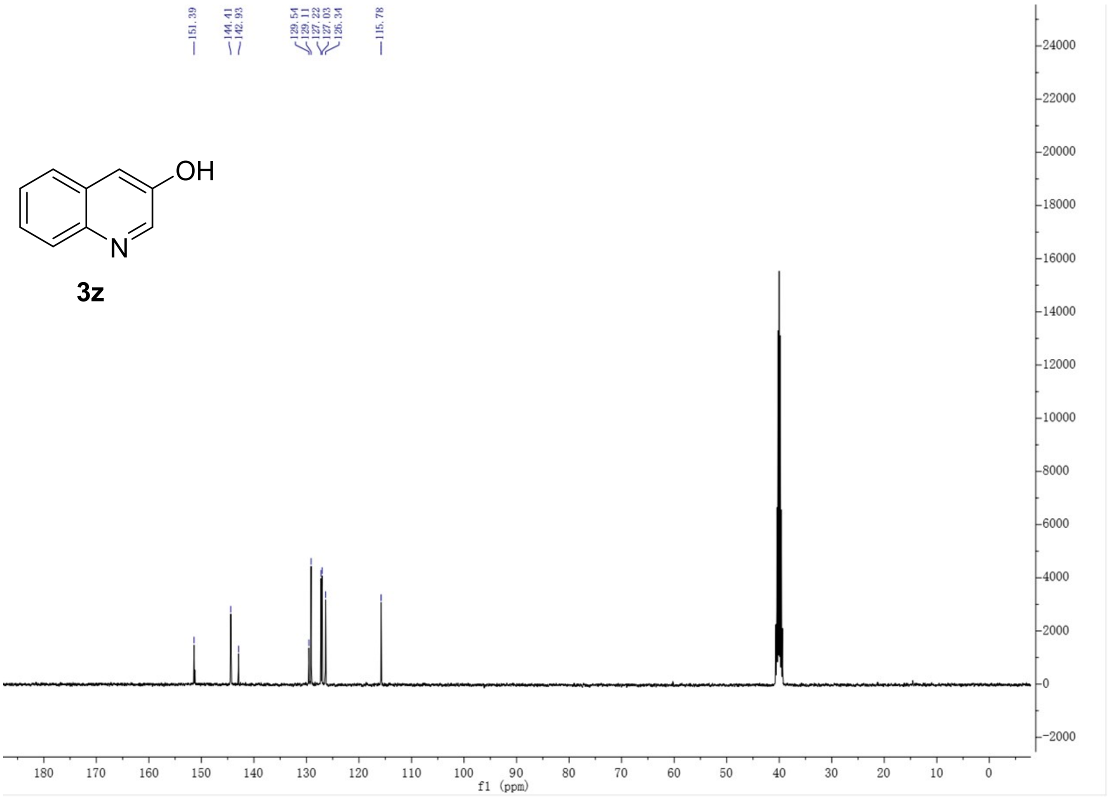

8.68
8.66
8.60
8.58
8.58
8.32
8.32
8.30
8.30
7.71
7.71
7.70
7.68
7.66
7.66
7.64
7.63
7.62
7.55
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.48
7.48
6.99
5.33
OH
3x
1.04
1.04
0.98
3.14
2.05
1.00
0.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

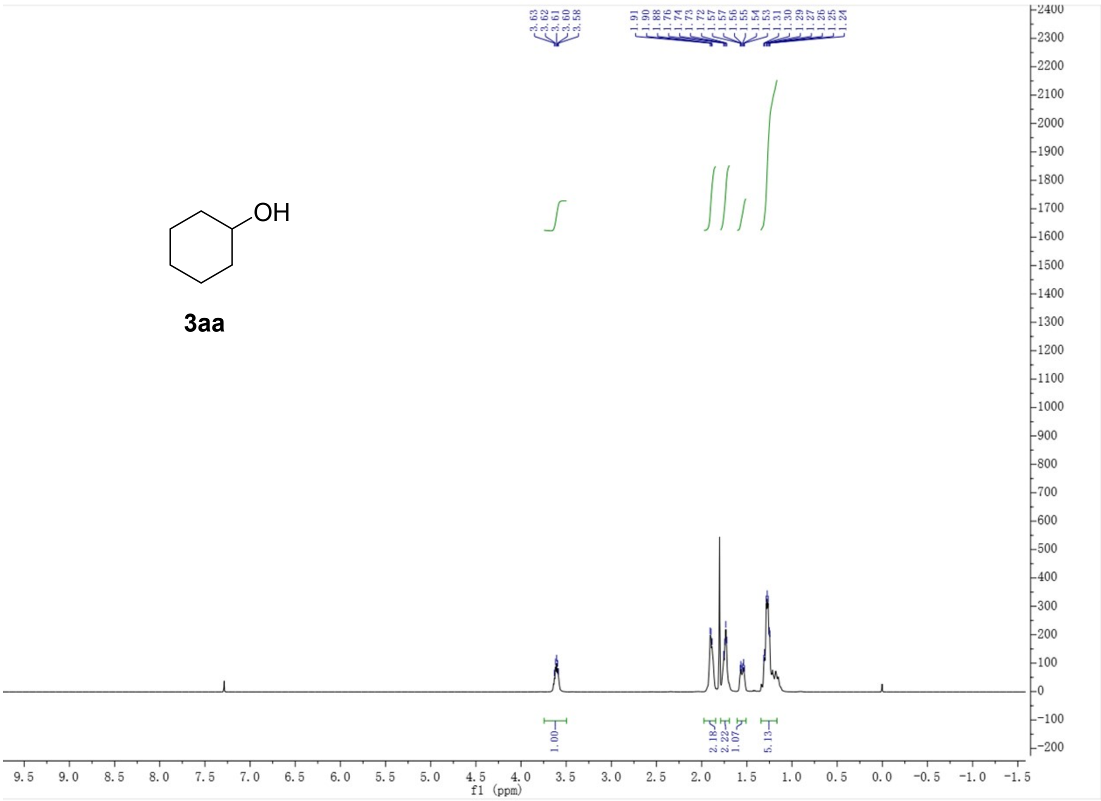

149.54
132.71
131.60
127.29
127.01
126.79
126.48
125.58
124.35
122.77
122.65
122.40
106.16
OH
3x
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

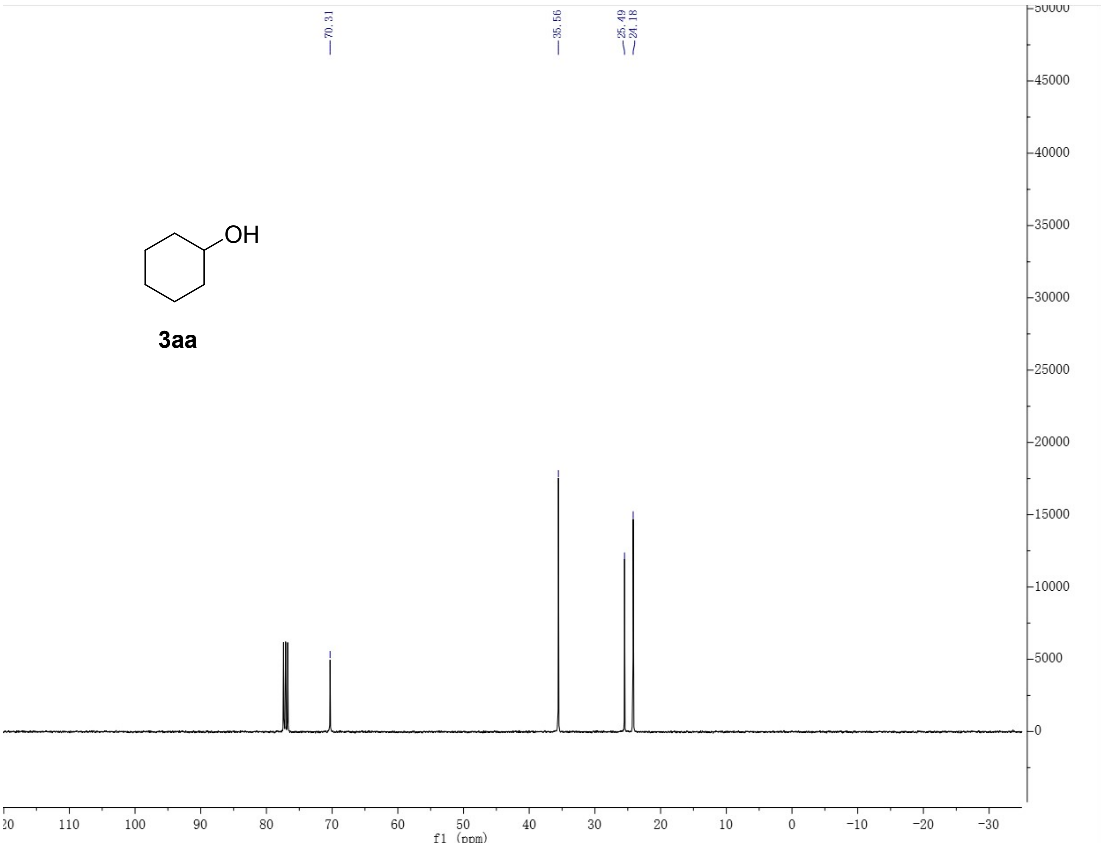

7.84
7.82
7.82
7.48
7.46
7.46
7.46
7.43
7.42
7.41
7.40
7.38
7.38
7.36
7.36
7.36
7.34
7.34
7.27
7.27
7.25
7.25
7.23
7.23
7.14
7.12
7.10
6.95
6.94
6.93
6.92
5.51
OH
O
3y
1.10
1.09
1.12
1.12
1.13
1.11
1.10
1.00
f1 (ppm)

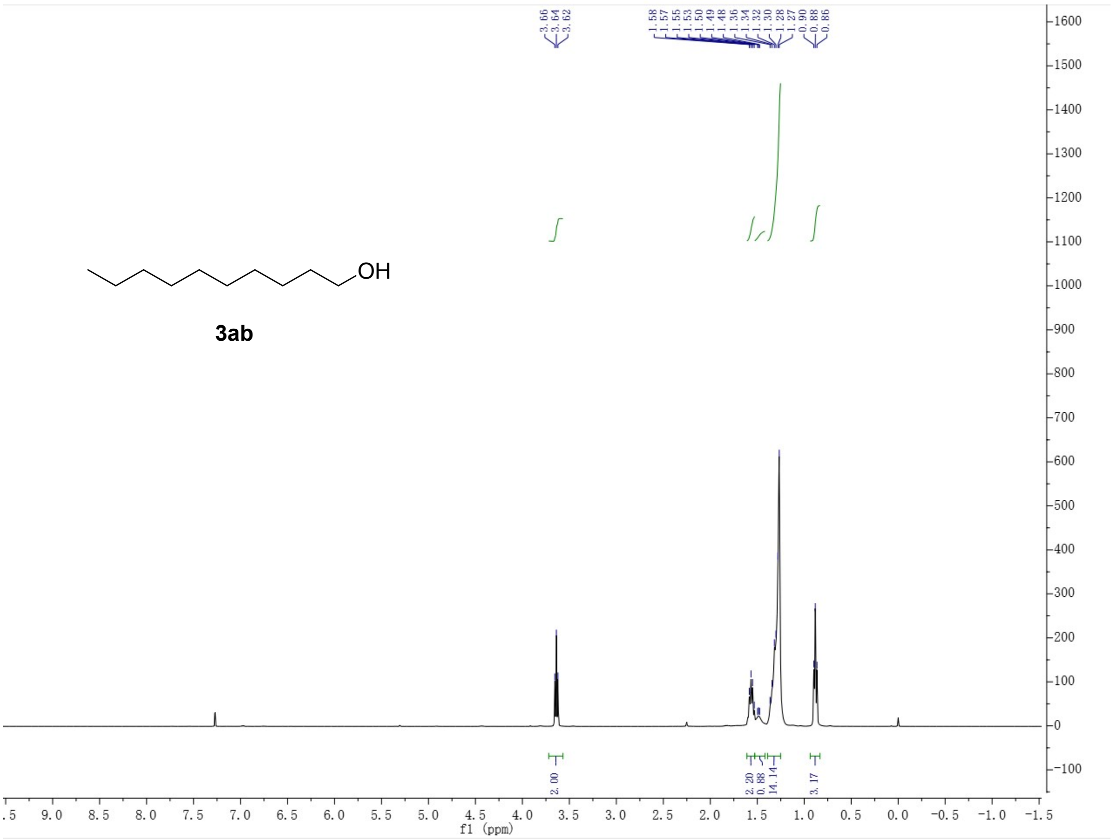

156.11
144.12
141.19
127.34
125.82
124.65
123.75
123.06
121.09
113.68
112.88
111.85
OH
O
3y
f1 (ppm)

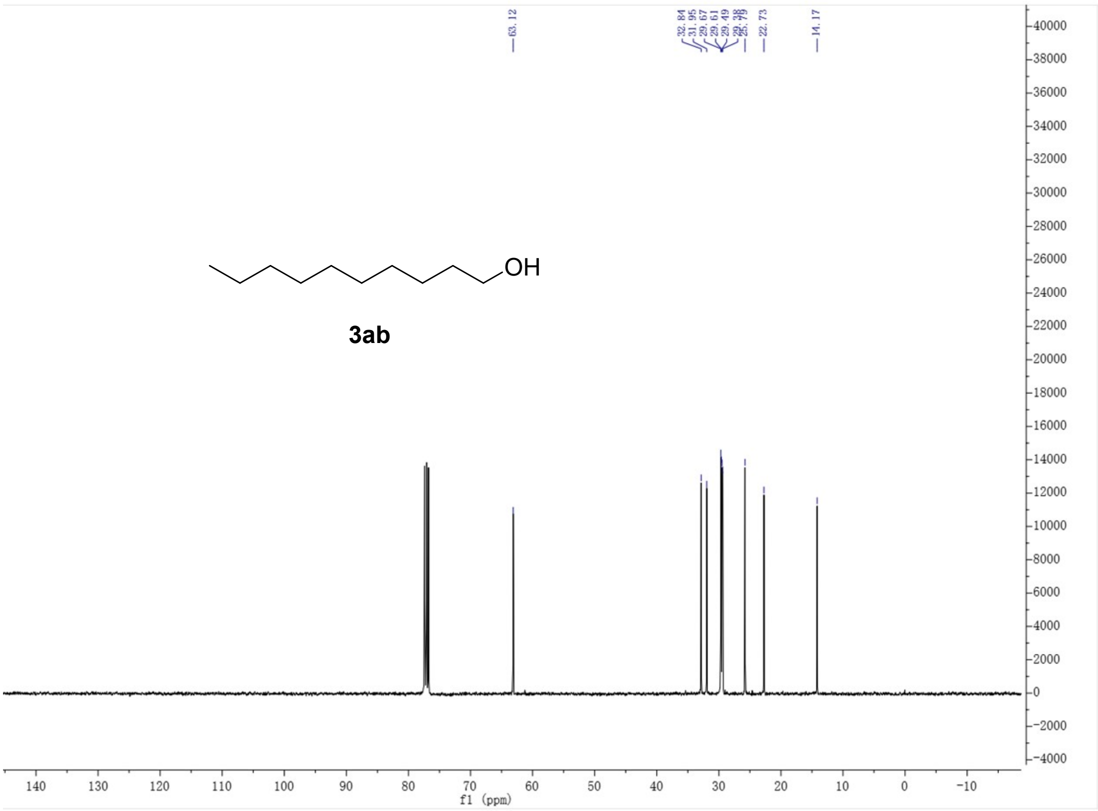

10.32
8.61
8.60
7.93
7.92
7.90
7.82
7.81
7.80
7.80
7.79
7.52
7.52
7.51
7.50
OH
N
3z
0.75
1.00
1.06
1.08
3.16
f1 (ppm)
2
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0

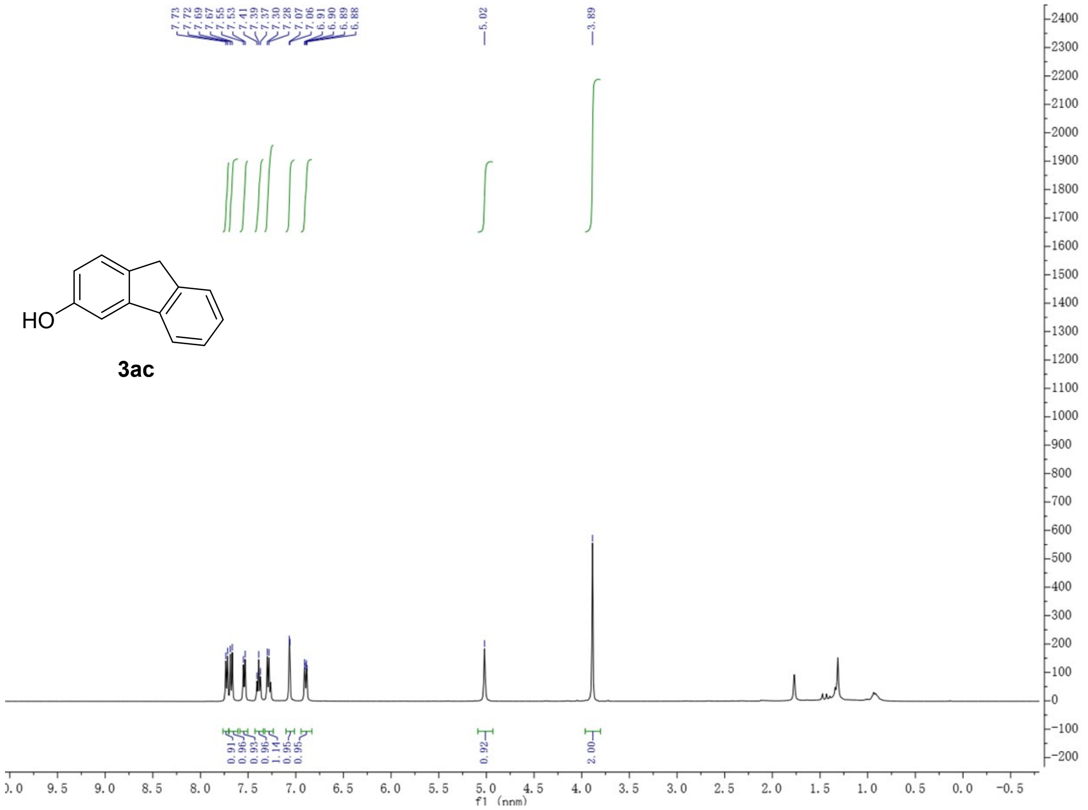

151.39
144.41
142.93
129.54
129.11
127.22
127.03
126.34
115.78
OH
N
3z
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

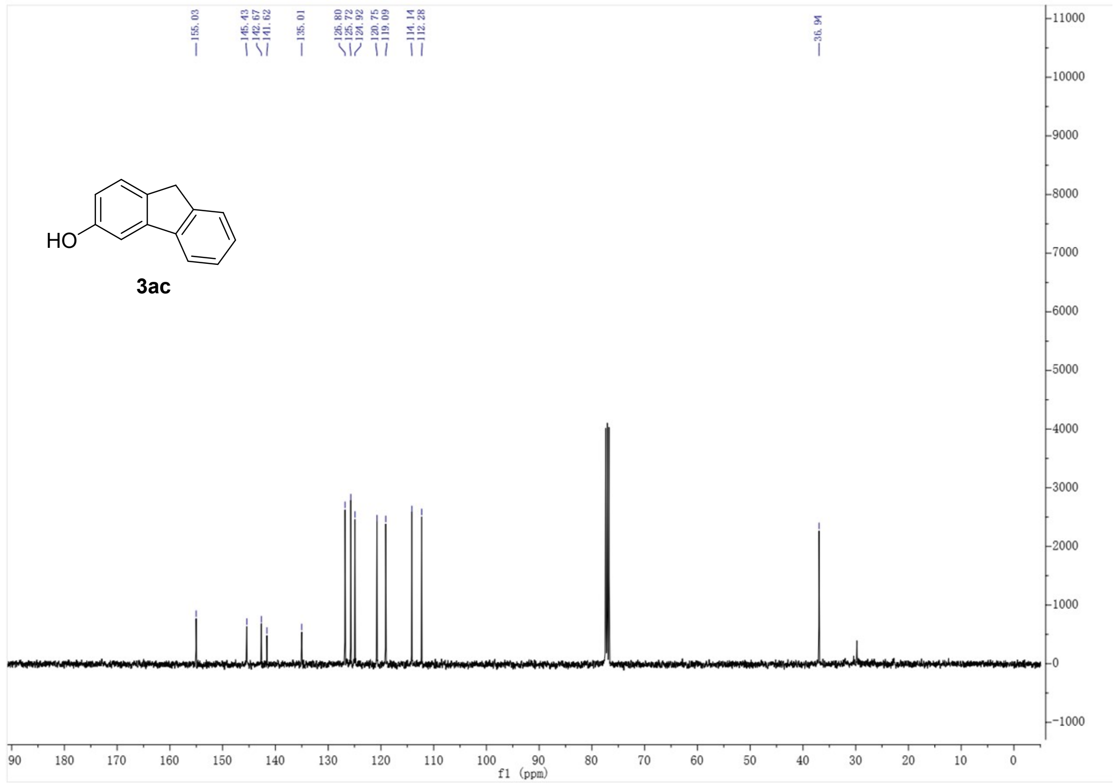

3.63
3.62
3.61
3.60
3.58
1.91
1.90
1.88
1.76
1.74
1.73
1.72
1.57
1.57
1.56
1.55
1.54
1.53
1.31
1.30
1.29
1.27
1.26
1.25
1.24
OH
3aa
1.00
2.18
2.22
1.07
5.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)
2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

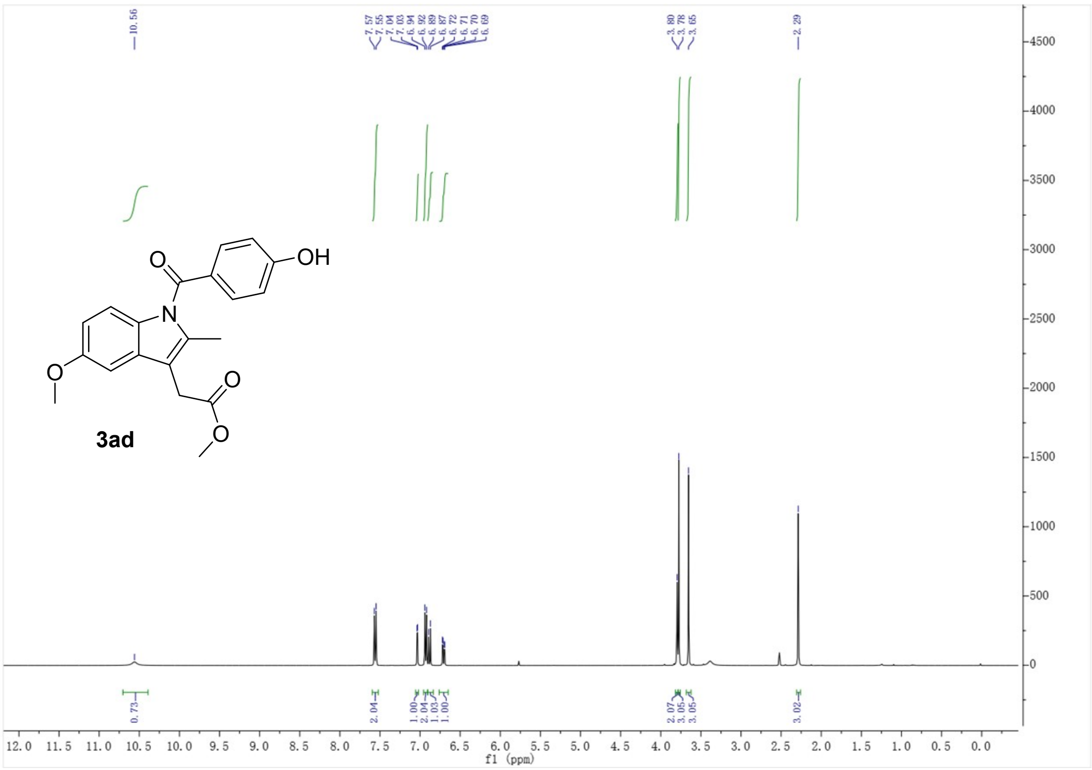

70.31
35.56
25.49
24.18
OH
3aa
20 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)
50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0

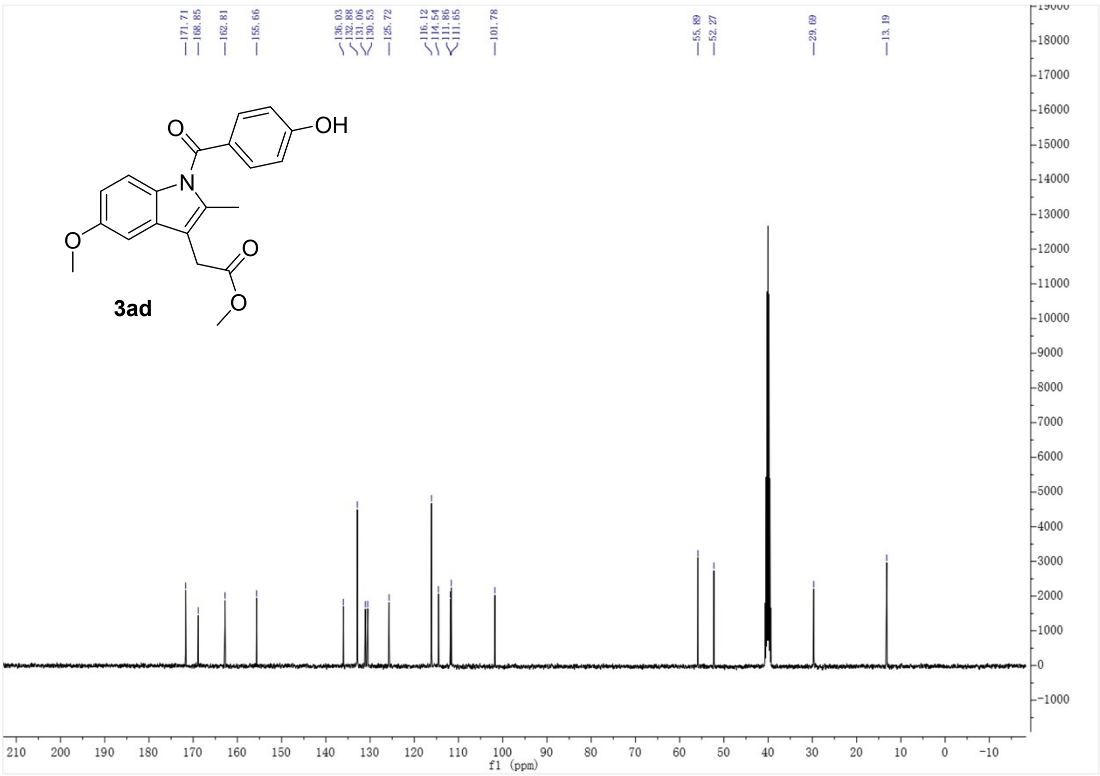

3.66
3.64
3.62
1.58
1.57
1.55
1.53
1.50
1.49
1.48
1.36
1.34
1.32
1.30
1.28
1.27
0.90
0.88
0.86
OH
3ab
2.00
2.20
0.88
14.14
3.17
f1 (ppm)

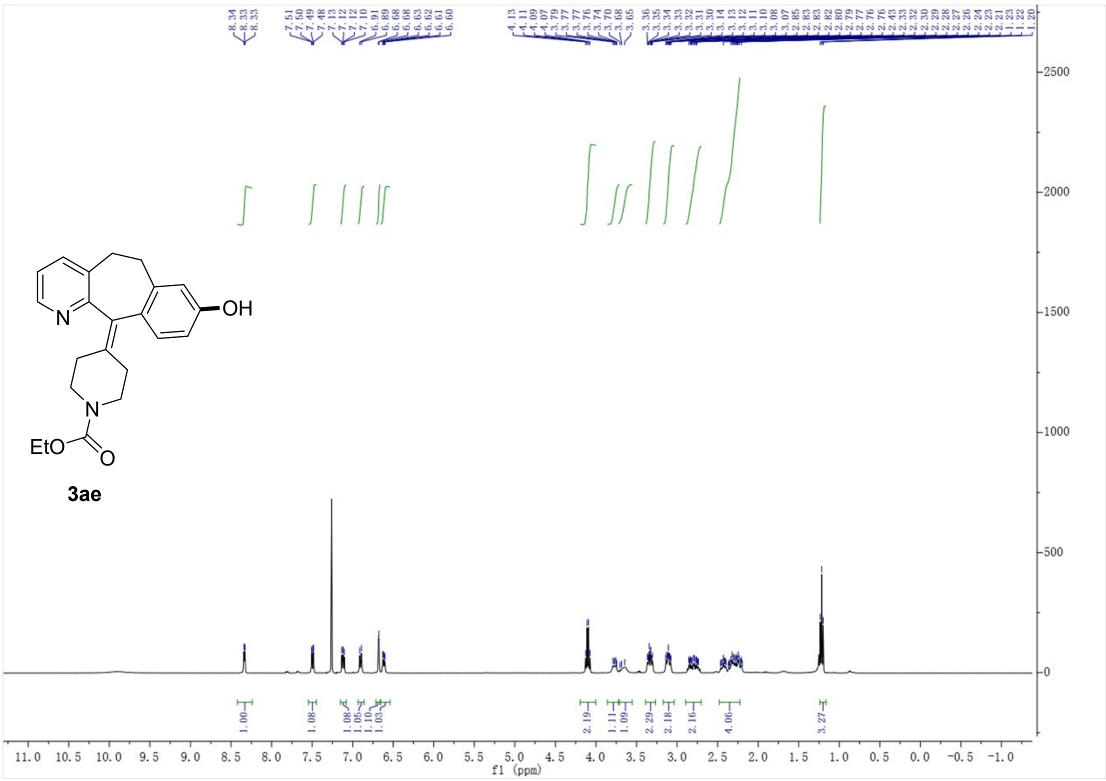

63.12
32.84
31.95
29.67
29.61
29.49
29.38
25.79
22.73
14.17
OH
3ab
f1 (ppm)

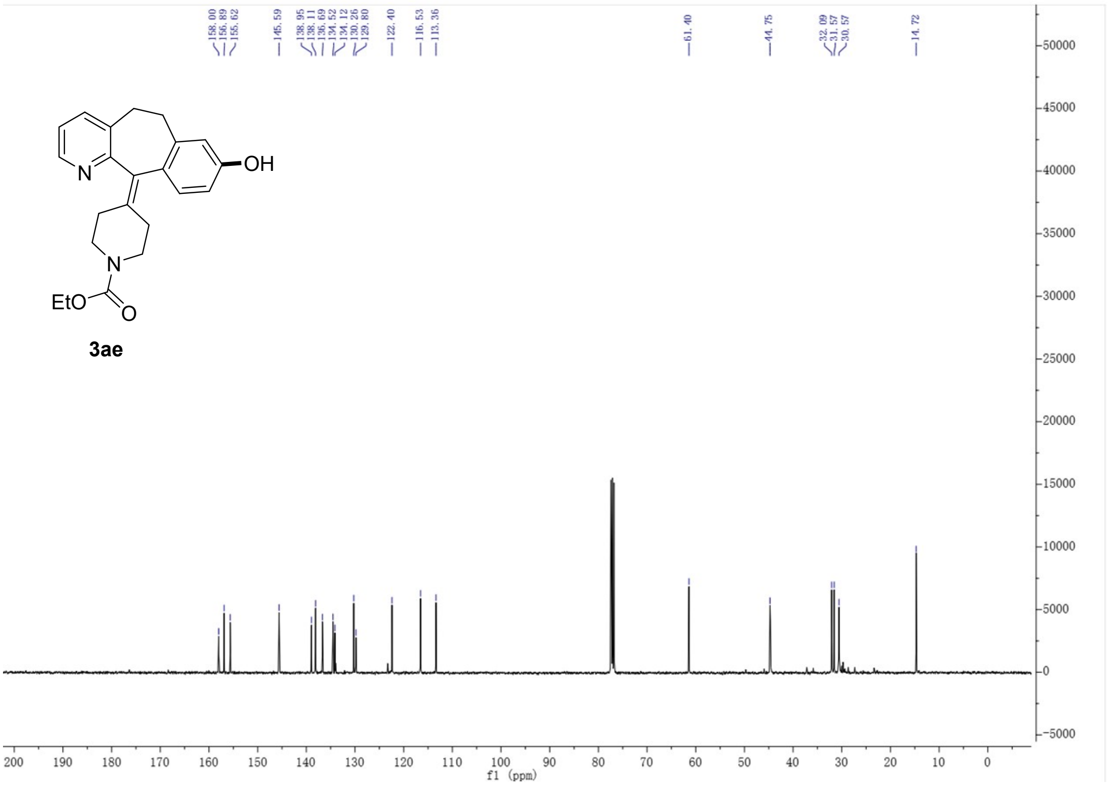

7.73
7.72
7.69
7.67
7.55
7.53
7.41
7.39
7.37
7.30
7.28
7.07
7.06
6.91
6.90
6.89
6.88
5.02
3.89
HO
3ac
0.91
0.96
0.93
0.96
1.14
0.95
0.95
0.92
2.00
f1 (ppm)

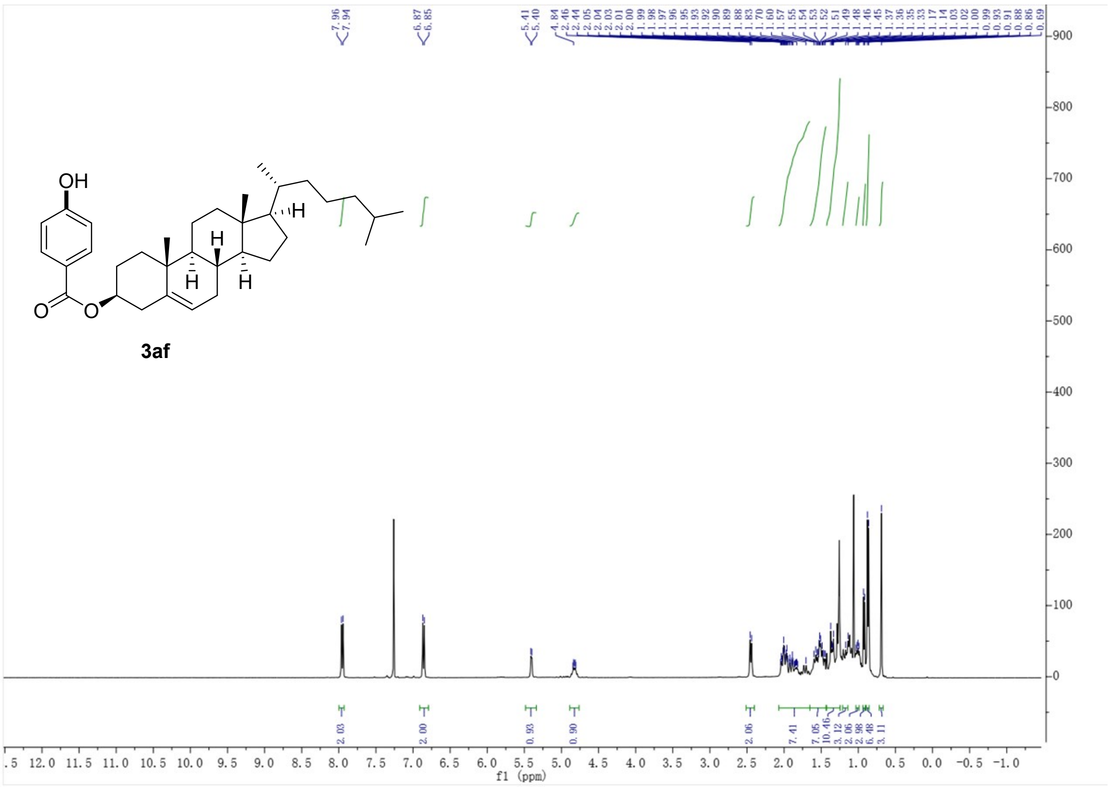

155.03
145.43
142.67
141.62
135.01
126.80
125.72
124.92
120.75
119.09
114.14
112.28
36.94
HO
3ac
f1 (ppm)

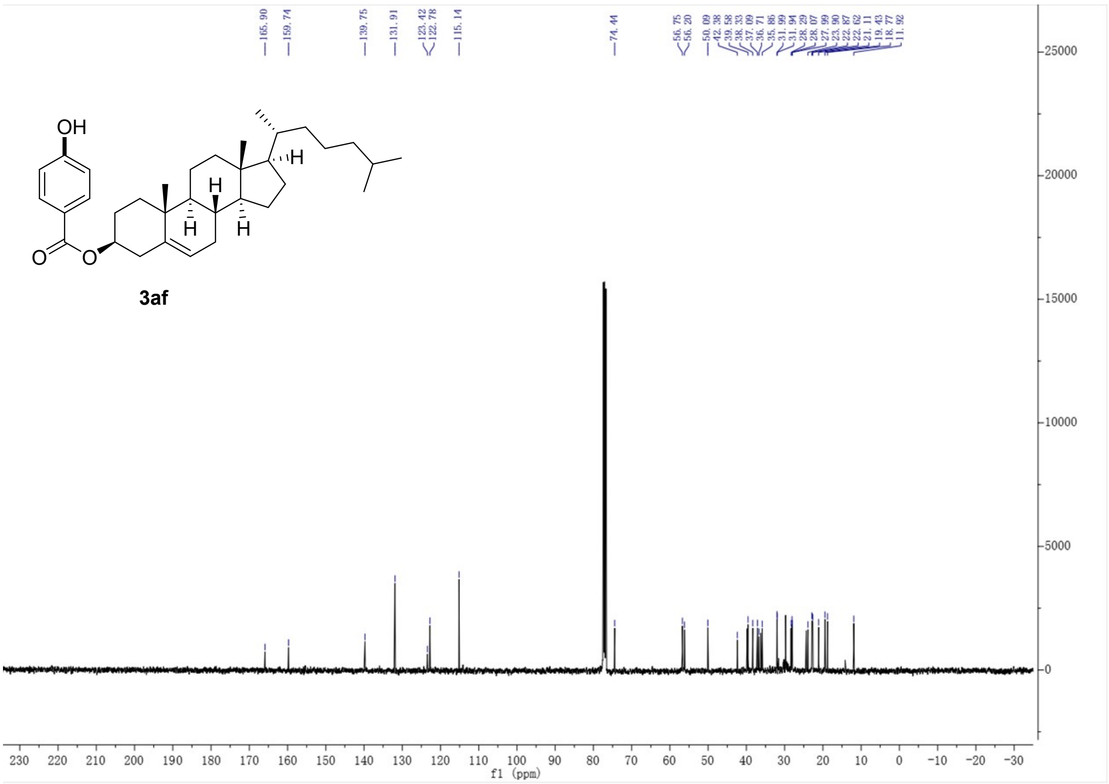

10.56
7.57
7.55
7.04
7.03
6.94
6.92
6.89
6.87
6.72
6.71
6.70
6.69
3.80
3.78
3.65
2.29
OH
O
N
O
O
O
3ad
0.73
2.04
1.00
2.04
1.03
1.00
2.07
3.05
3.05
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0

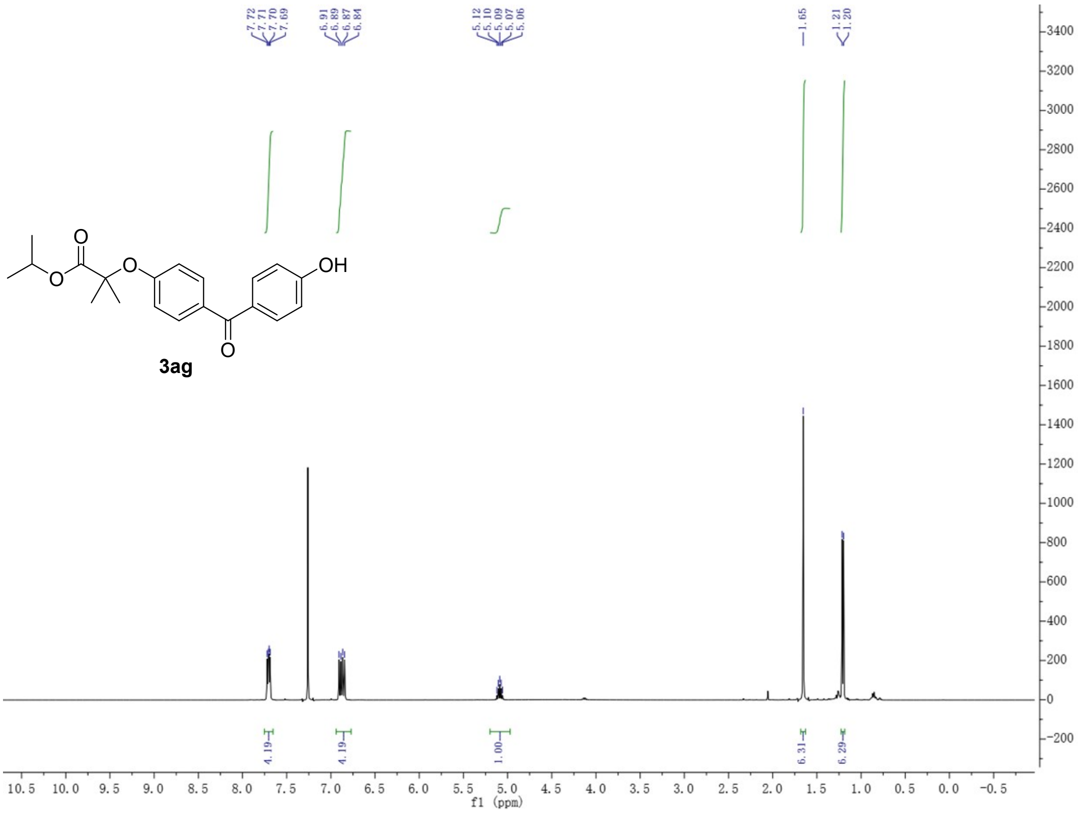

171.71
168.85
162.81
155.66
136.03
132.88
131.06
130.53
125.72
116.12
114.54
111.86
111.65
101.78
55.89
52.27
29.69
13.19
OH
O
N
O
O
O
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


3ae
8.34
8.33
8.33
7.51
7.50
7.49
7.48
7.13
7.12
7.12
7.10
6.91
6.89
6.68
6.68
6.63
6.62
6.61
6.60
4.13
4.11
4.09
4.07
3.79
3.77
3.77
3.76
3.74
3.70
3.68
3.65
3.36
3.35
3.34
3.33
3.32
3.31
3.30
3.14
3.13
3.12
3.11
3.10
3.08
3.07
2.85
2.83
2.83
2.82
2.80
2.79
2.77
2.76
2.43
2.33
2.32
2.30
2.29
2.28
2.27
2.26
2.24
2.23
2.21
1.23
1.22
1.20
1.00
1.08
1.08
1.05
1.10
1.03
2.19
1.11
1.09
2.29
2.18
2.16
4.06
3.27
N
OH
N
EtO
O
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
2500
2000
1500
1000
500
0

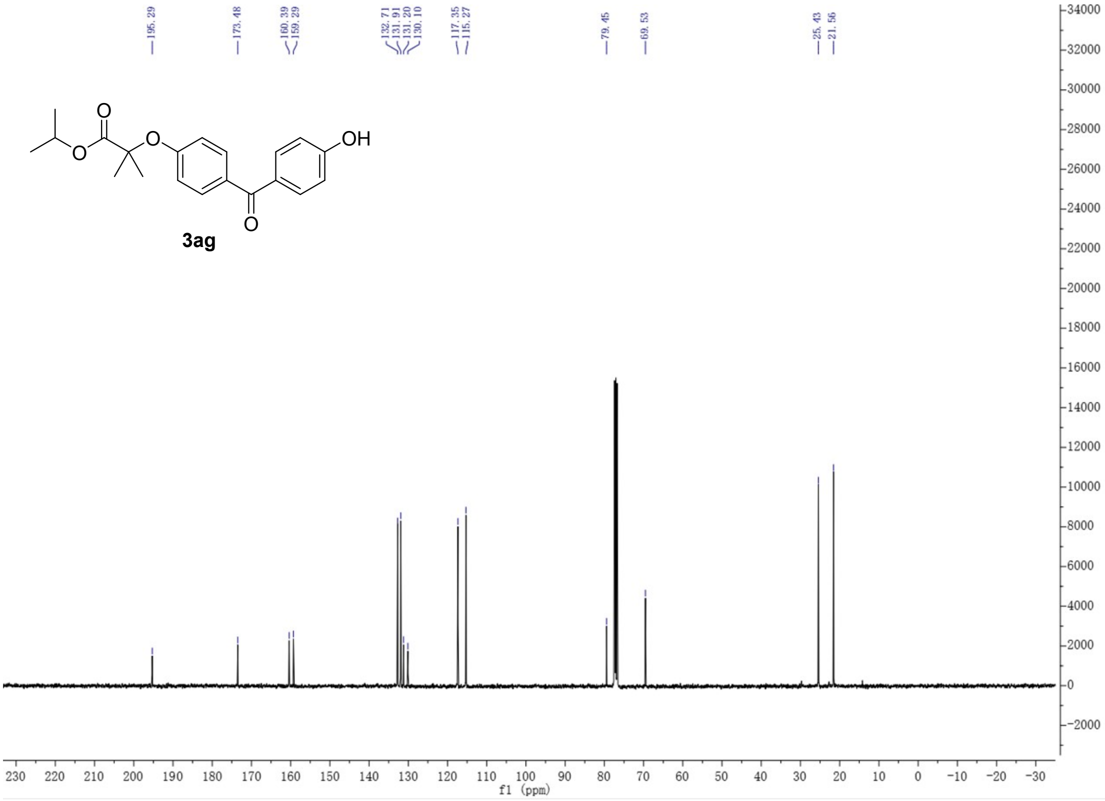

3ae
158.00
156.89
155.62
145.59
138.95
138.11
136.69
134.52
134.12
130.26
129.80
122.40
116.53
113.36
61.40
44.75
32.09
31.57
30.57
14.72
N
OH
N
EtO
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000


7.96
7.94
6.87
6.85
5.41
5.40
4.84
2.46
2.44
2.05
2.04
2.03
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.93
1.92
1.90
1.89
1.88
1.83
1.70
1.60
1.57
1.55
1.54
1.53
1.52
1.51
1.49
1.48
1.46
1.45
1.37
1.36
1.35
1.33
1.17
1.14
1.03
1.02
1.00
0.99
0.93
0.91
0.88
0.86
0.69
OH
H
H
H
H
O
O
3af
2.03
2.00
0.93
0.90
2.06
7.41
7.05
10.46
3.12
2.06
2.98
6.48
3.11
f1 (ppm)
900
800
700
600
500
400
300
200
100
0

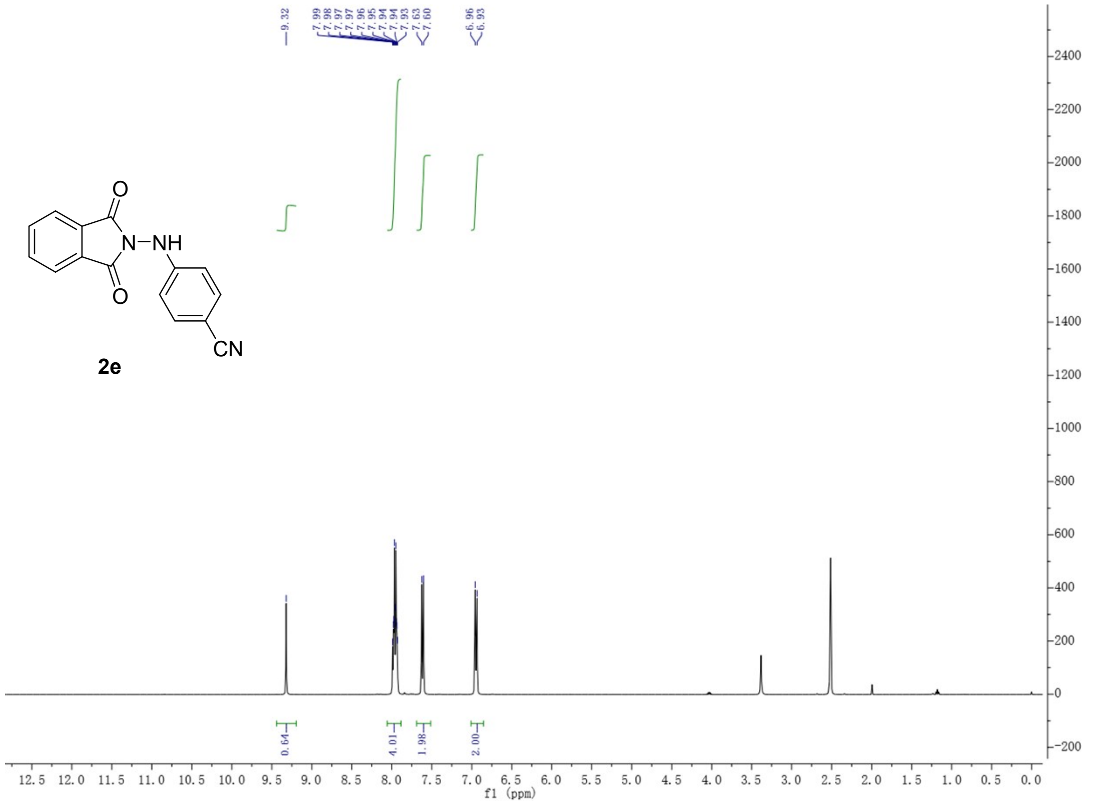

165.90
159.74
139.75
131.91
123.42
122.78
115.14
74.44
56.75
56.20
50.09
42.38
39.58
38.33
37.09
36.71
35.86
31.99
31.94
28.29
28.07
27.99
23.90
22.87
22.62
21.11
19.43
18.77
11.92
OH
H
H
H
H
O
O
3af
f1 (ppm)
25000
20000
15000
10000
5000
0

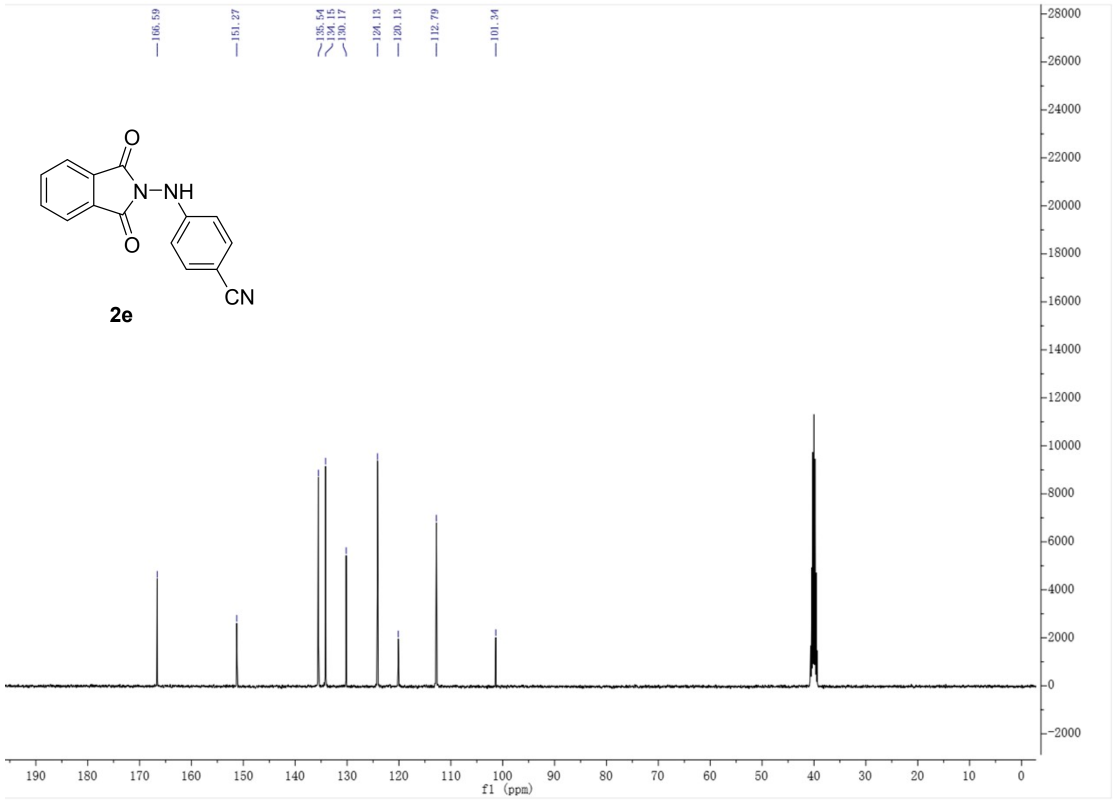


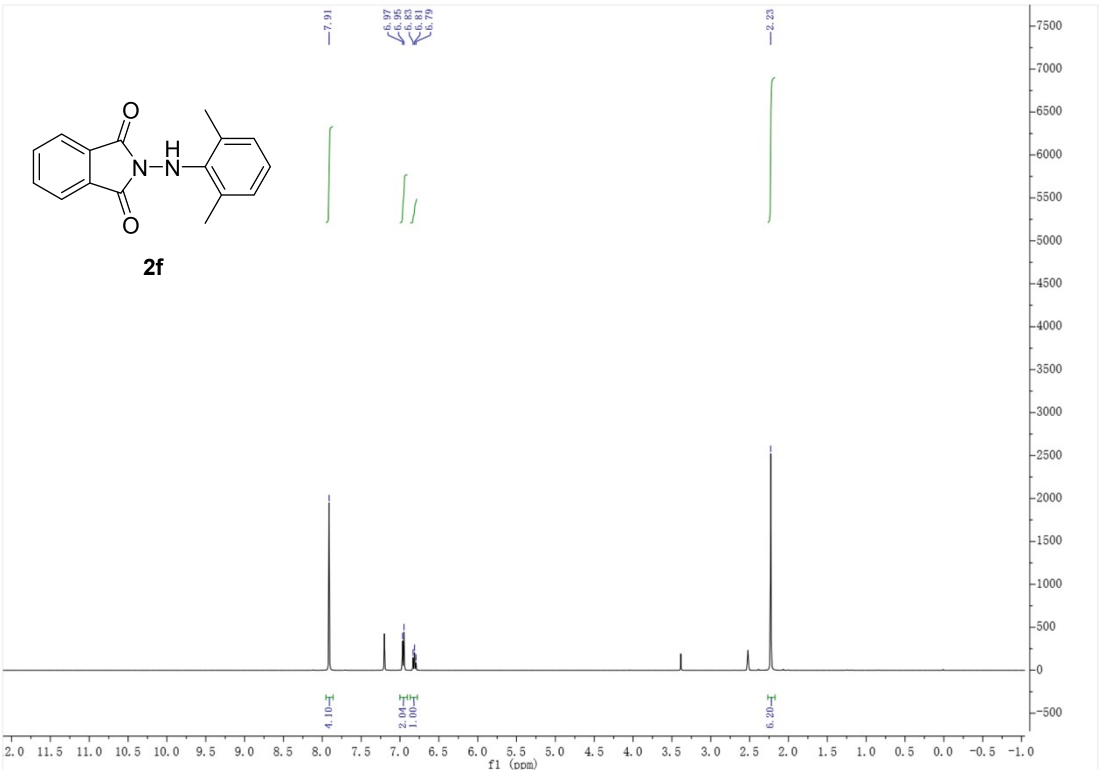
7.72
7.71
7.70
7.69
6.91
6.89
6.87
6.84
5.12
5.10
5.09
5.07
5.06
1.65
1.21
1.20
OH
O
O
O
O
3ag
4.19
4.19
1.00
6.31
6.29
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 −200



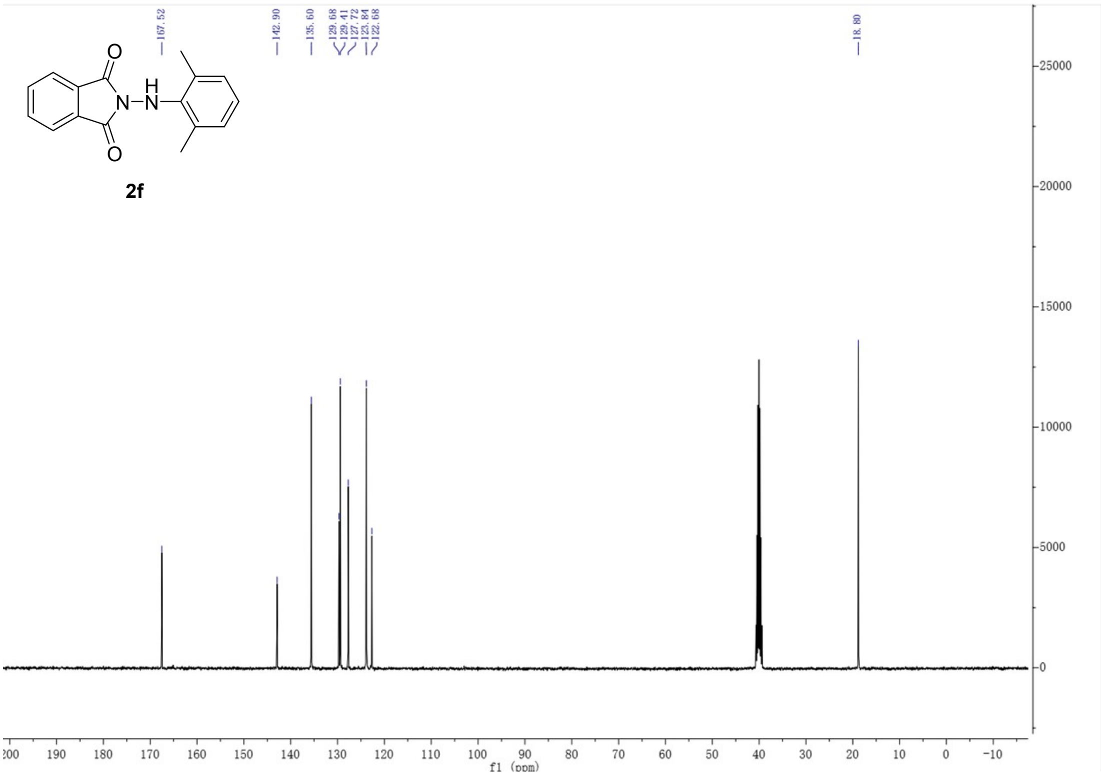
195.29
173.48
160.39
159.29
132.71
131.91
131.20
130.10
117.35
115.27
79.45
69.53
25.43
21.56
OH
O
O
O
O
3ag
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)
34000 32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 −2000


9.32
7.99
7.98
7.97
7.97
7.96
7.95
7.94
7.94
7.93
7.63
7.60
6.96
6.93
O
N–NH
O
CN
2e
0.64
4.01
1.98
2.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

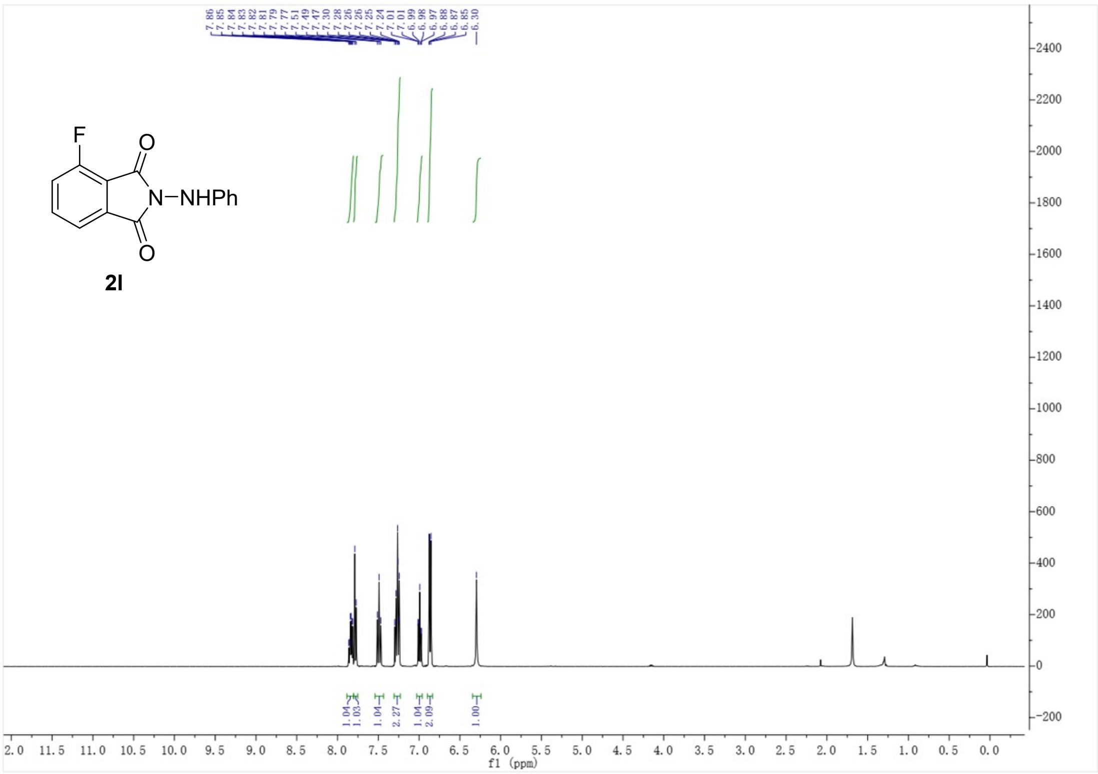

166.59
151.27
135.54
134.15
130.17
124.13
120.13
112.79
101.34
O
N–NH
O
CN
2e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

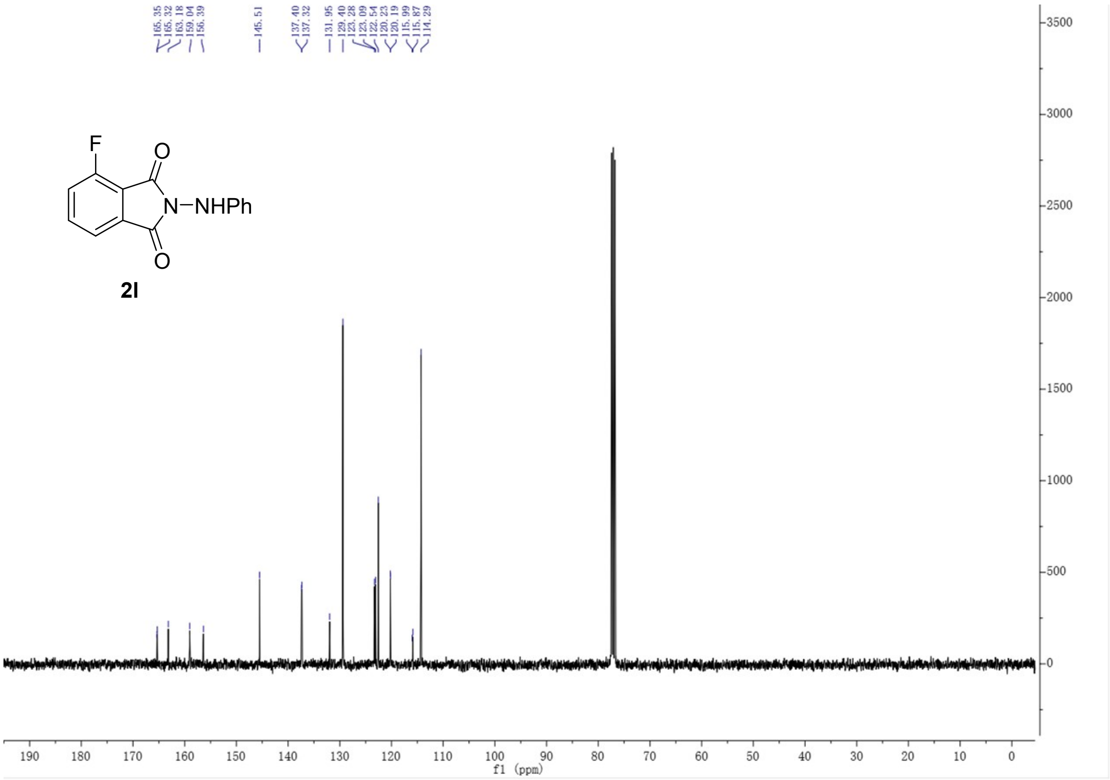

2f

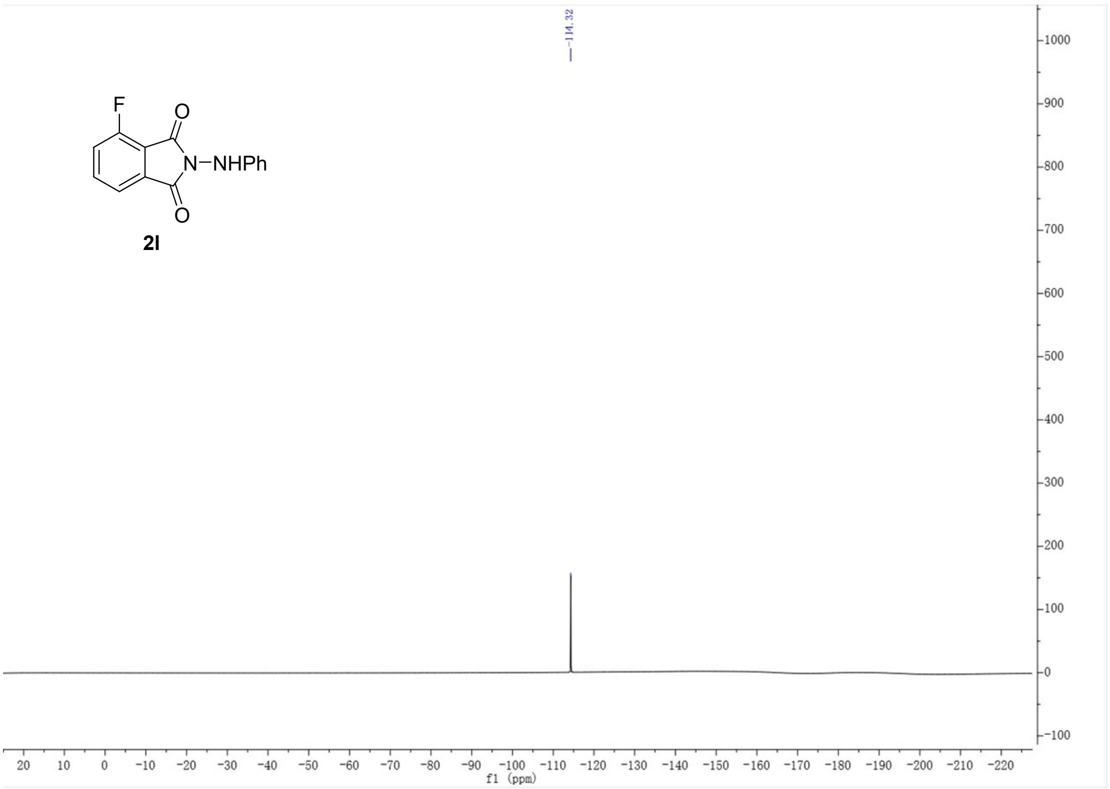
O
N
H
N
O
7.91
6.97
6.95
6.83
6.81
6.79
2.23
4.10
2.04
1.00
6.20
f1 (ppm)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

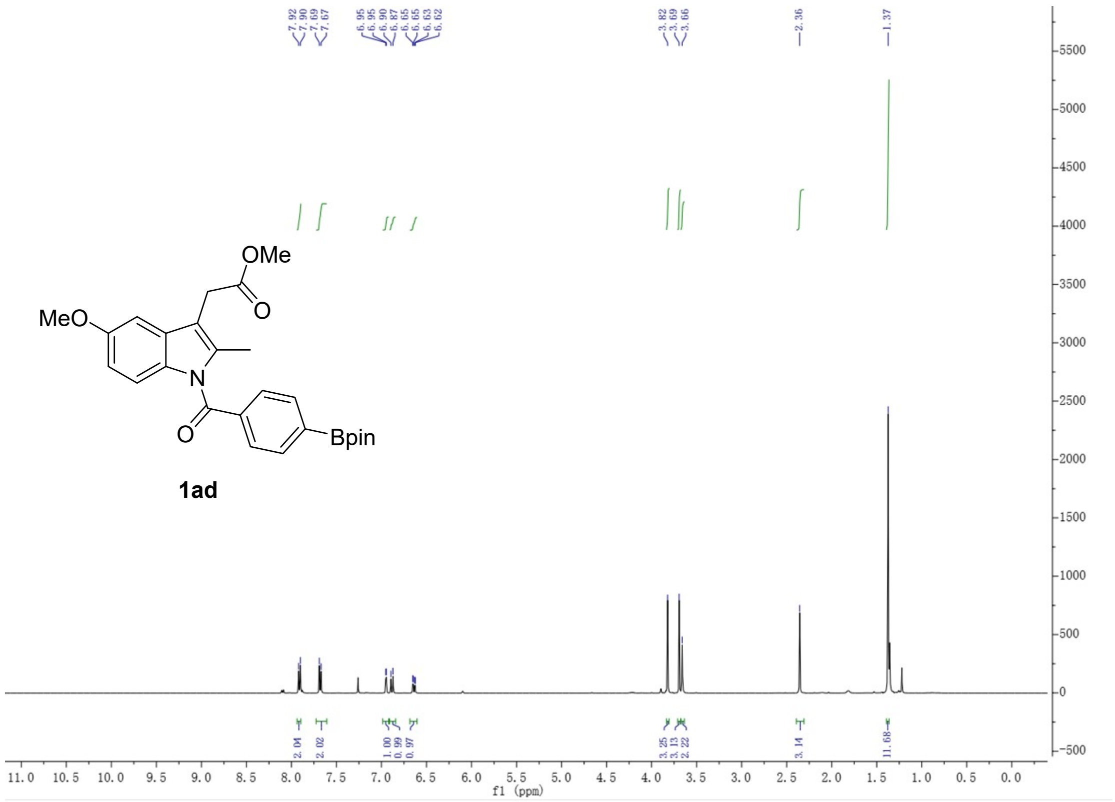

2f

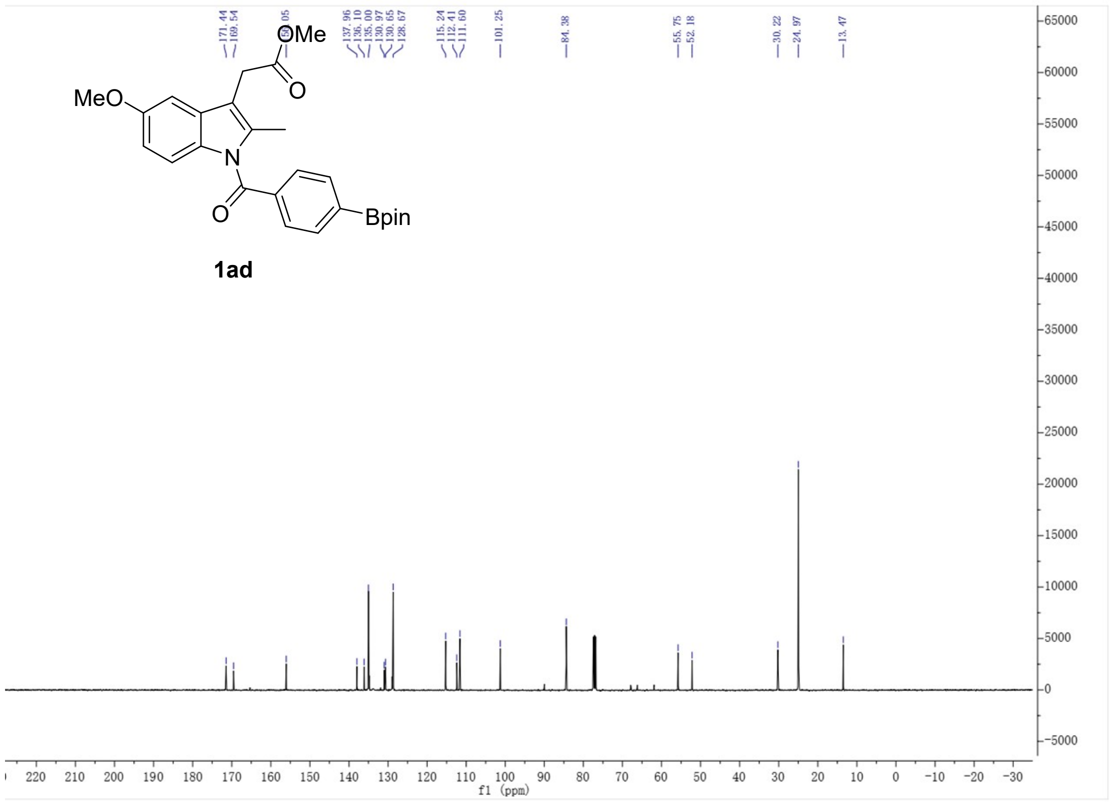
O
N
H
N
O
167.52
142.90
135.60
129.68
129.41
127.72
123.84
122.68
18.80
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
25000 20000 15000 10000 5000 0

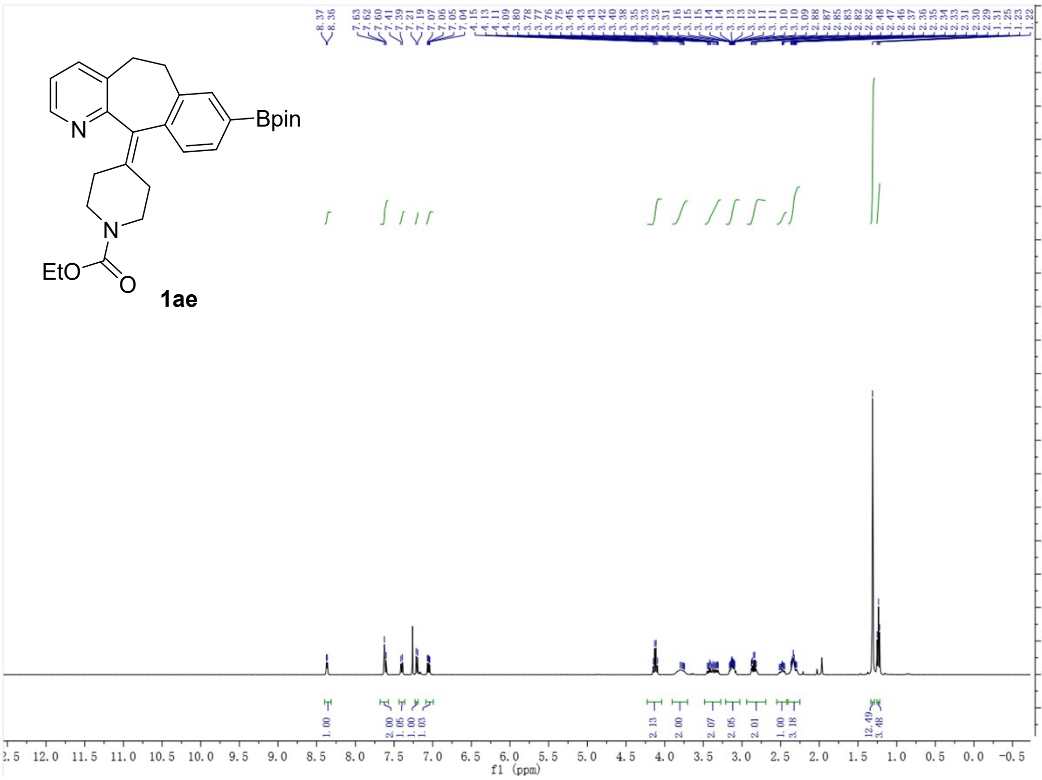

7.86
7.85
7.84
7.83
7.82
7.81
7.79
7.77
7.51
7.49
7.47
7.30
7.28
7.26
7.26
7.25
7.24
7.01
7.01
6.99
6.98
6.97
6.88
6.87
6.85
6.30
F
O
N−NHPh
O
2l
1.04
1.03
1.04
2.27
1.04
2.09
1.00
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.35
165.32
163.18
159.04
156.39
145.51
137.40
137.32
131.95
129.40
123.28
123.09
122.54
120.23
120.19
115.99
115.87
114.29
F
O
N−NHPh
O
2l
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
O
N−NHPh
O
2l
−114.32
1000
900
800
700
600
500
400
300
200
100
0
−100
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

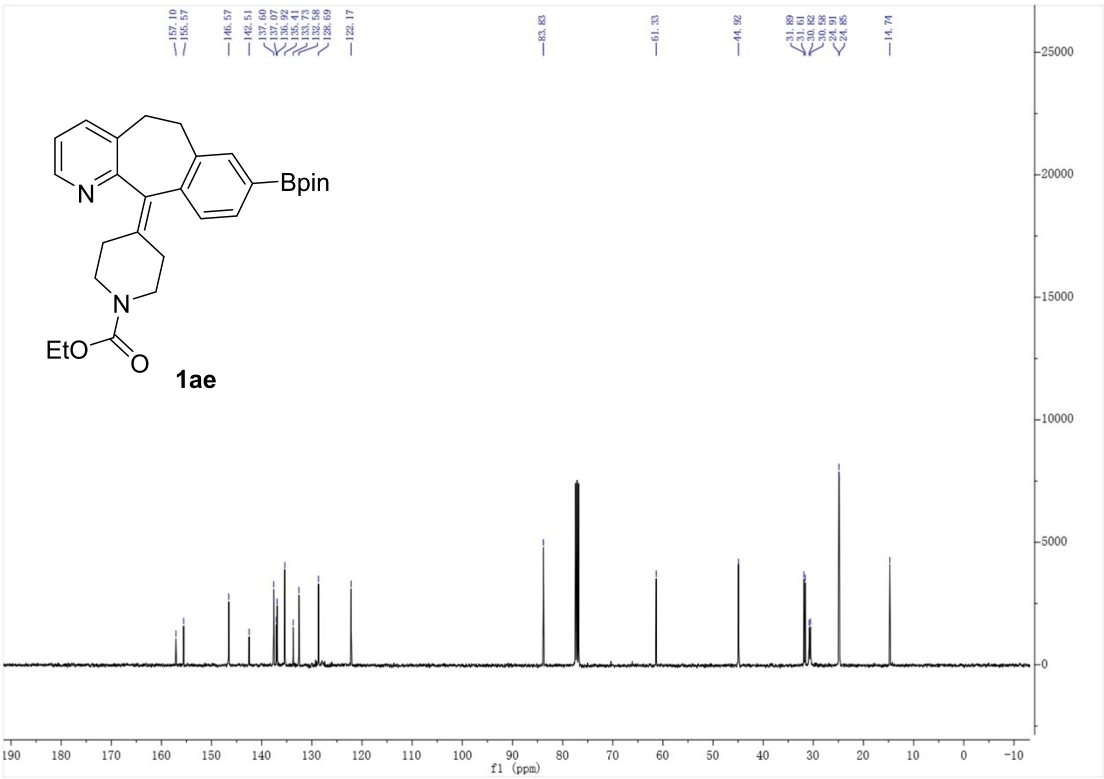

7.92
7.90
7.69
7.67
6.95
6.95
6.90
6.87
6.65
6.65
6.63
6.62
3.82
3.69
3.66
2.36
1.37
OMe
MeO
N
O
O
Bpin
1ad
2.04
2.02
1.00
0.99
0.97
3.25
3.13
2.22
3.14
11.68
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


171.44
169.54
156.05
137.96
136.10
135.00
130.97
130.65
128.67
115.24
112.41
111.60
101.25
84.38
55.75
52.18
30.22
24.97
13.47
OMe
MeO
N
O
O
Bpin
1ad
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000



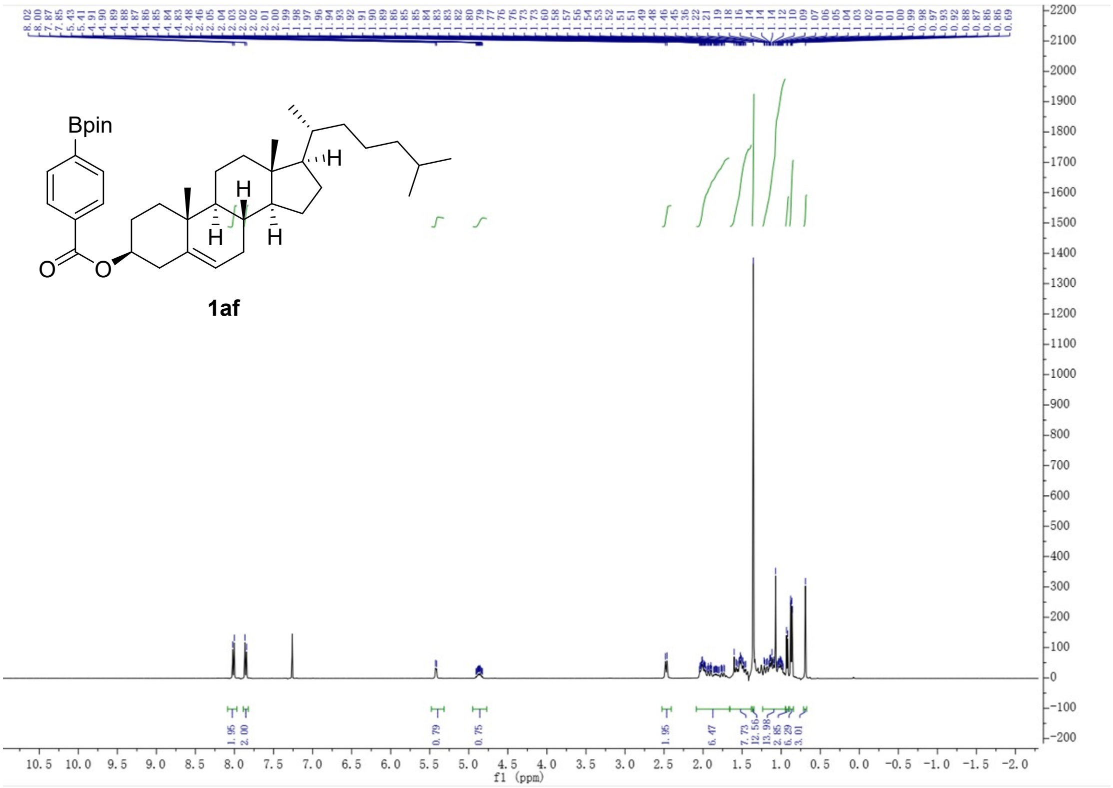
1ae

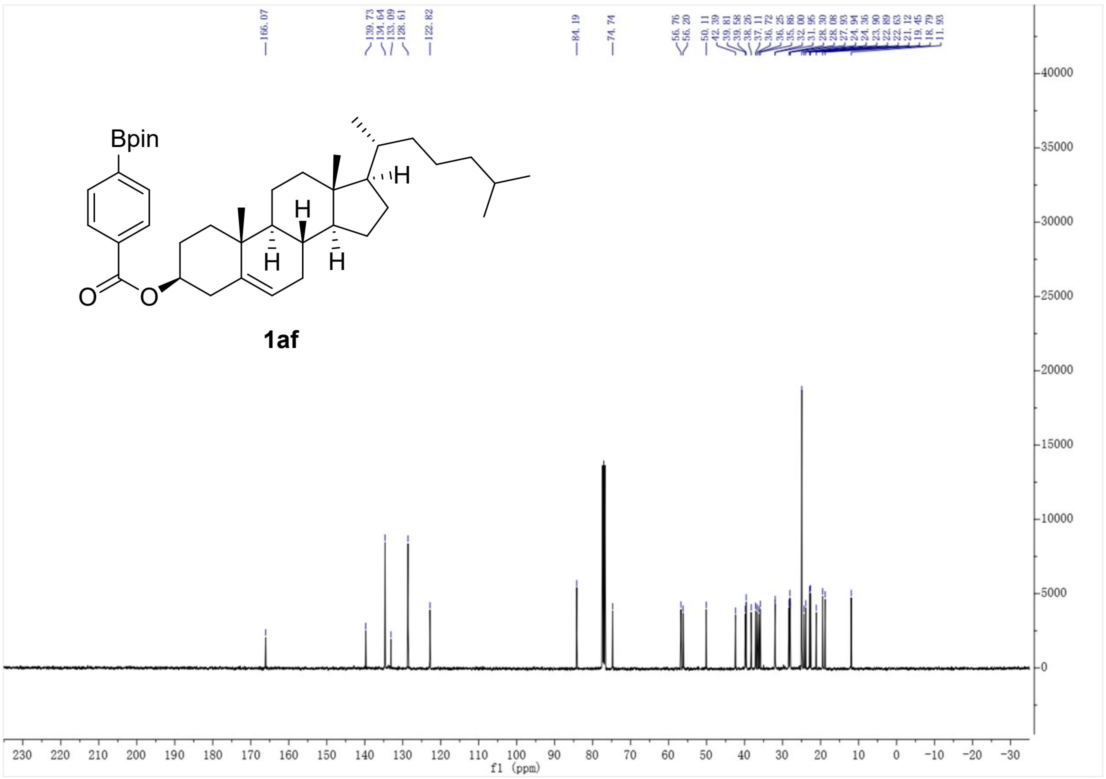
Bpin
N
EtO
O
8.37
8.36
7.63
7.62
7.60
7.41
7.39
7.21
7.19
7.07
7.06
7.05
7.04
4.15
4.13
4.11
4.09
3.80
3.78
3.77
3.76
3.75
3.45
3.43
3.43
3.42
3.40
3.38
3.35
3.33
3.32
3.31
3.16
3.15
3.15
3.14
3.14
3.13
3.13
3.12
3.11
3.11
3.10
3.10
3.09
2.88
2.87
2.85
2.83
2.82
2.82
2.48
2.47
2.46
2.37
2.36
2.35
2.34
2.33
2.31
2.30
2.29
1.31
1.25
1.23
1.22
1.00
2.00
1.05
1.00
1.03
2.13
2.00
2.07
2.05
2.01
1.00
3.18
12.49
3.48
f1 (ppm)

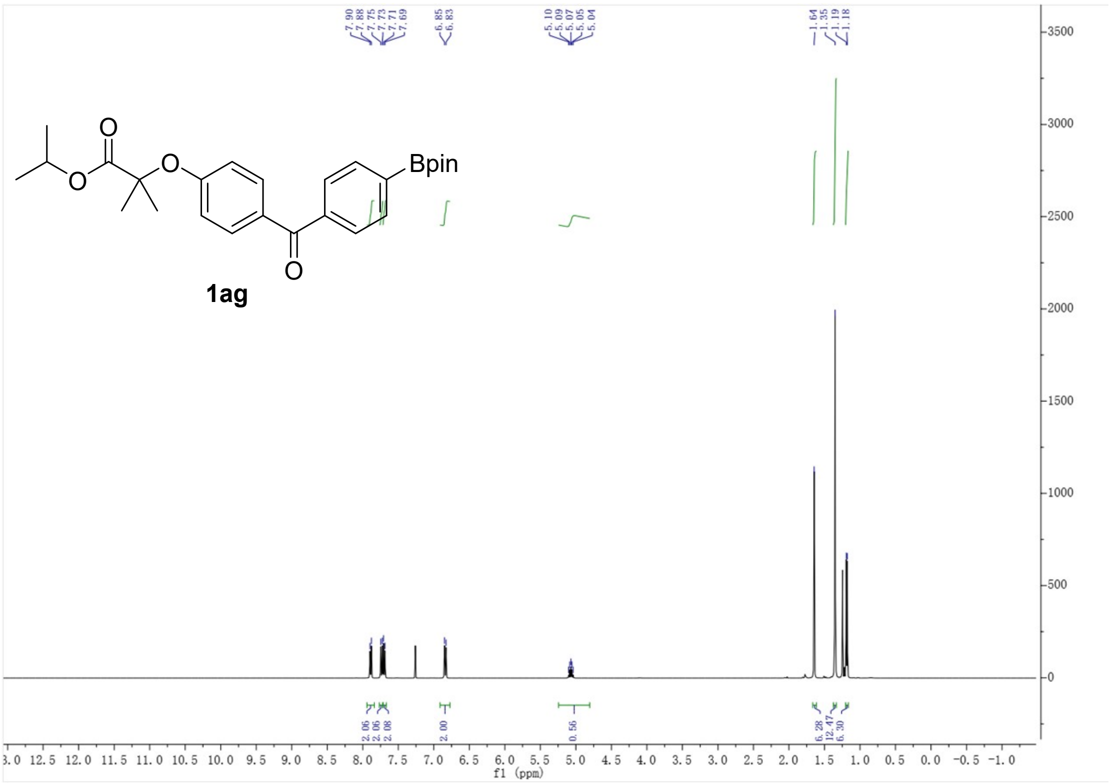


1ae

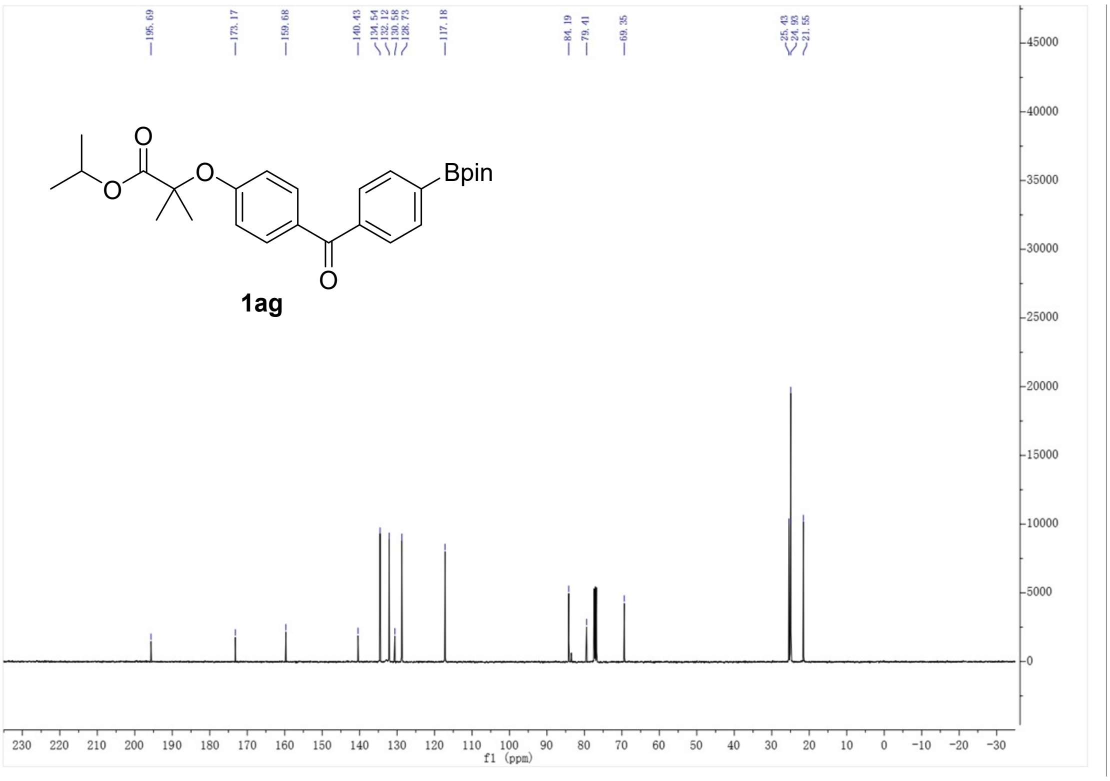
Bpin
N
EtO
O
157.10
155.57
146.57
142.51
137.60
137.07
136.92
135.41
133.73
132.58
128.69
122.17
83.83
61.33
44.92
31.89
31.61
30.82
30.58
24.91
24.85
14.74
f1 (ppm)


8.02
8.00
7.87
7.85
5.43
5.41
4.91
4.90
4.89
4.88
4.87
4.86
4.85
4.84
4.83
2.48
2.46
2.05
2.04
2.03
2.02
2.02
2.01
2.00
1.99
1.98
1.97
1.96
1.94
1.93
1.92
1.91
1.90
1.89
1.86
1.85
1.85
1.84
1.83
1.83
1.82
1.80
1.79
1.77
1.76
1.76
1.73
1.73
1.60
1.58
1.57
1.56
1.54
1.53
1.52
1.51
1.51
1.49
1.48
1.46
1.45
1.36
1.22
1.21
1.19
1.18
1.16
1.14
1.14
1.14
1.12
1.10
1.09
1.07
1.06
1.05
1.04
1.03
1.02
1.01
1.01
1.00
0.99
0.98
0.97
0.93
0.92
0.88
0.87
0.86
0.86
0.69
Bpin
H
H
H
H
O
O
1af
1.95
2.00
0.79
0.75
1.95
6.47
7.73
12.56
13.98
2.85
6.29
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)
2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200


166.07
139.73
134.64
133.09
128.61
122.82
84.19
74.74
56.76
56.20
50.11
42.39
39.81
39.58
38.26
37.11
36.72
36.25
35.86
32.00
31.95
28.30
28.08
27.93
24.94
24.36
23.90
22.89
22.63
21.12
19.45
18.79
11.93
Bpin
H
H
H
H
O
O
1af
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)
40000 35000 30000 25000 20000 15000 10000 5000 0


7.90
7.88
7.75
7.73
7.71
7.69
6.85
6.83
5.10
5.09
5.07
5.05
5.04
1.64
1.35
1.19
1.18
Bpin
O
O
O
O
2.06
2.06
2.08
2.00
0.56
6.28
12.47
6.30
f1 (ppm)

1ag


195.69
173.17
159.68
140.43
134.54
132.12
130.58
128.73
117.18
84.19
79.41
69.35
25.43
24.93
21.55
Bpin
O
O
O
O
f1 (ppm)

1ag