C(sp^3)–H Hydroxylation of Fluorenes, Oxindoles and Benzofuranones with $Mg(NO_3)_2$-$HP(O)Ph_2$ Oxidation System

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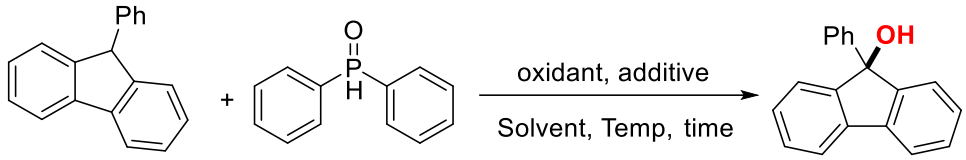
SUPPORTING INFORMATION

Content

EXPERIMENTAL SECTION

General Information. ^{1}H NMR and ^{13}C NMR, spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 126 MHz respectively using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. Melting points were uncorrected. High-resolution mass spectrometry (HRMS) was performed on an ESI-TOF spectrometer. Fluorene derivatives were prepared according to the literature procedure.[1] Substituted oxindoles and benzofuranones were synthesized according to the reported procedure.[2] Chemicals were commercially available and used without purification. Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

1.1 Optimization of the Reaction Conditions[a]



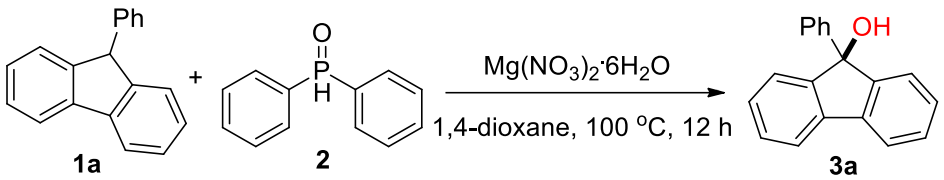
1a **2a** **3a**

entry	oxidant (4 eq)	additive (2 eq)	solvent	*t* (°C)	time (h)	yield (%)
1	DTBP	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	100	24	87
2	DTBP	/	1,4-dioxane	100	24	trace
3	DTBP	TfOH	1,4-dioxane	100	24	trace
4	DTBP	$AlCl_3$	1,4-dioxane	100	24	trace
5	DTBP	LDA	1,4-dioxane	100	24	trace
6	DTBP	$NaNO_2$	1,4-dioxane	100	24	trace
7	DTBP	KO^{t}Bu	1,4-dioxane	100	24	trace
8	DTBP	K_3PO_4	1,4-dioxane	100	24	23
9	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	100	24	91
10	DDQ	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	100	24	72
11	TBPB	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	100	24	53
12	H_2O_2	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	100	24	43
13	BPO	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	100	24	70
14	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	CH_3CN	100	24	81
15	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	DCE	100	24	72
16	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	CH_2Cl_2	100	24	69
17	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	$CHCl_3$	100	24	84
18	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	DMSO	100	24	24
19	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	DMF	100	24	69
20	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	120	24	89
21	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	80	24	90
22	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	50	24	81
23	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	80	8	83
24	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	80	12	91
25	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	80	18	88
26	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$	1,4-dioxane	80	5	63
27	TBHP	$Mg(NO_3)_2{\cdot}6H_2O$ (1)	1,4-dioxane	100	12	90
28	/	$Mg(NO_3)_2{\cdot}6H_2O$ (1)	1,4-dioxane	100	12	92
29	$NaNO_2$	/	1,4-dioxane	100	12	trace
30	/	$Mg(NO_3)_2{\cdot}6H_2O$ (1.5)	1,4-dioxane	100	12	88
31	/	$Mg(NO_3)_2{\cdot}6H_2O$ (1)	1,4-dioxane	100	12	82,[b] 87,[c] 0[d]
32	/	$Mg(NO_3)_2{\cdot}6H_2O$ (1)	1,4-dioxane	100	12	0-72[e]
33	/	/	1,4-dioxane	100	12	0
34	/	$Al(NO_3)_3{\cdot}9H_2O$ (1)	1,4-dioxane	100	12	37
35	/	$Fe(NO_3)_3{\cdot}9H_2O$ (1)	1,4-dioxane	100	12	42

36	/	$Cu(NO_3)_2{\cdot}6H_2O$ (1)	1,4-dioxane	100	12	66
37	/	$Co(NO_3)_2{\cdot}6H_2O$ (1)	1,4-dioxane	100	12	trace
38	/	$Cr(NO_3)_3{\cdot}9H_2O$ (1)	1,4-dioxane	100	12	trace

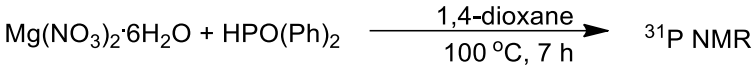
[a] Reaction condition: **1a** (0.25 mmol), **2a** (0.5 mmol), oxidant (4 equiv), additive (2 equiv), solvent (2 mL), under air; isolated yield; DTBP: Di-*t*-butyl peroxide; TBHP: *tert*-Butyl hydroperoxide; TBPB: *tert*-Butyl peroxybenzoate; BPO: Dibenzoyl peroxide. [b] **2a** (0.25 mmol). [c] **2a** (0.75 mmol). [d] without **2a**. [e] Cs_2CO_3, KOH, benzoic acid, pivalic acid, $BF_3{\cdot}OEt_2$, TsOH, trifluoroethanol, PPh_3, diethyl phosphite were employed respectively instead of **2a.**

1.2 Control Experiments[a]

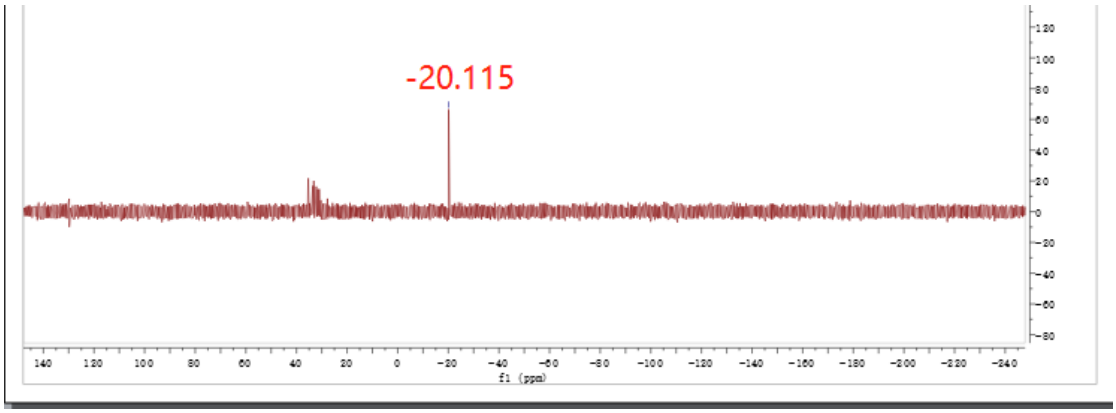


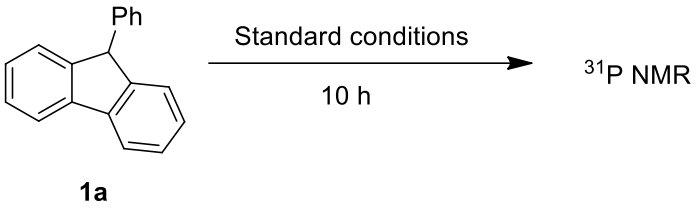
Entry	**2** (2 eq)	Catalyst (1 eq)	T (°C)	t (h)	yield
10	$HPPh_2$ instead of **2**	$Mg(NO_3)_2{\cdot}6H_2O$	100	12	0
11	Diphenylphosphinic acid instead of **2**	$Mg(NO_3)_2{\cdot}6H_2O$	100	12	72
12	**2**	HNO_3 instead of $Mg(NO_3)_2{\cdot}6H_2O$	100	12	67

[a] Reaction condition: **1a** (0.25 mmol), **2a** (0.5 mmol), catalyst (1 equiv), 1,4-dioxane (2 mL), under air; isolated yield;



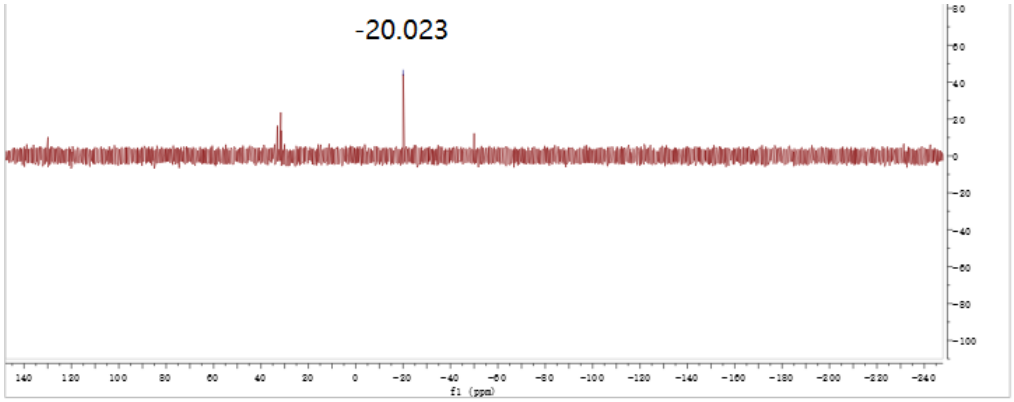
(Note: around 25 ppm is the known $HPO(Ph)_2$ peak, without substrate **1a**, new peak -20.115 ppm showed up, and according to literature, $HPPh_2$ is around -39.65 ppm)

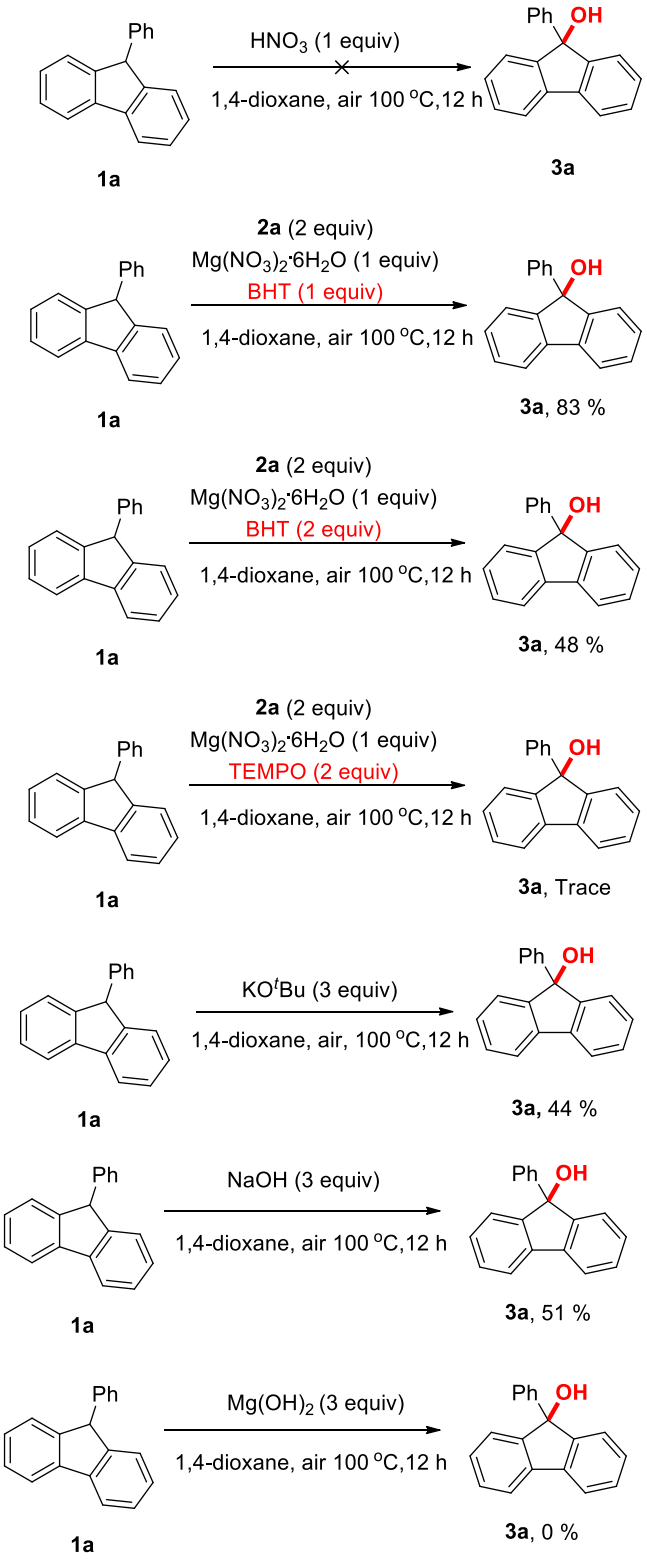




1a

(Note: when adding substrate **1a**, similar new peak -20.023 ppm showed up under optimized conditions, and according to literature, $HPPh_2$ is around -39.65 ppm)

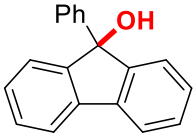




Note: these control experiments may indicate more than one mechanism (radical pathway and oxygen in air) may be involved in this interesting reaction. More efforts are being done to figure this mechanism out.

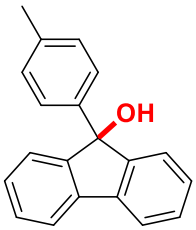
Characterization Data of Products

General procedure A. 9-phenyl-9H-fluorene **1** (0.25 mmol, 1 equiv), Diarylphosphine Oxides **2a** (0.50 mmol, 2 equiv), $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv), dry 1,4-dioxane (2 mL) and a stir bar were added to a sealed tube. After being stirred at 100 °C for 12 h, the mixture was evaporated under vacuum. The corresponding product **3** was isolated by silica column chromatography with a hexane/ethyl acetate mixture as eluent.



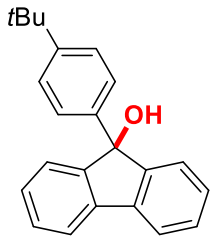
9-phenyl-9H-fluoren-9-ol (**3a**)

General procedure A was followed using **1a** (60.58 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3a** (59.41 mg) in 92% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 2H), 7.41–7.30 (m, 6H), 7.29–7.20 (m, 5H), 2.82–2.21 (m, 1H). HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{19}H_{14}NaO$ 281.0942, found 281.0940. Spectral data match those previously reported.[3]



9-(p-tolyl)-9H-fluoren-9-ol (**3b**)

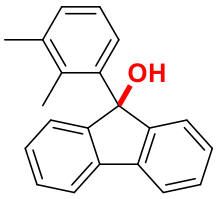
General procedure A was followed using **1b** (64.09 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3b** (62.64 mg) in 97% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.6, 3.2 Hz, 2H), 7.40–7.30 (m, 4H), 7.29–7.20 (m, 4H), 7.07 (dt, *J* = 8.2, 2.9 Hz, 2H), 2.59–2.42 (m, 1H), 2.30 (q, *J* = 3.9, 2.6 Hz, 3H). HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{20}H_{16}NaO$ 295.1099, found 295.1096. Spectral data match those previously reported.[3]



9-(4-(tert-butyl)phenyl)-9H-fluoren-9-ol (**3c**)

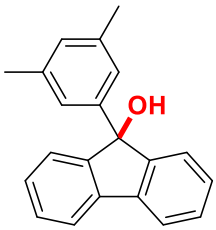
General procedure A was followed using **1c** (74.61 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3c** (57.38 mg) in 73% yield as a white solid. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.9, 1.2 Hz, 2H), 7.38–7.33 (m, 4H), 7.32–7.27 (m, 3H), 7.27–7.22 (m, 3H), 2.46 (s, 1H), 1.27 (s, 9H). HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{23}H_{22}NaO$ 337.1568, found 337.1570. Spectral data match those previously reported.[4]



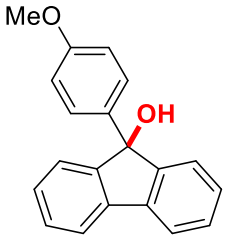
9-(2,3-dimethylphenyl)-9H-fluoren-9-ol (**3d**)

General procedure A was followed using **1d** (67.59 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3d** (58.71 mg) in 82% yield as a white solid. R_f =0.20 (20% EtOAc/hexane). M.p. 103-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.61 (m, 2H), 7.38–7.30 (m, 4H), 7.24–7.21 (m, 2H), 7.17 (d, *J* = 1.9 Hz, 1H), 7.12–7.06 (m, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 2.44 (d, *J* = 3.8 Hz, 1H), 2.19 (d, *J* = 5.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 140.6, 139.6, 136.4, 135.6, 129.5, 129.0, 128.5, 126.5, 124.8, 122.9, 120.1, 83.5, 20.0, 19.5. IR (film) 3529, 2735, 1610, 1325, 1260, 650. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{21}H_{18}NaO$ 309.1255, found 309.1253.



9-(3,5-dimethylphenyl)-9H-fluoren-9-ol (**3e**)

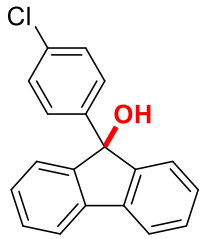
General procedure A was followed using **1e** (67.59 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3e** (44.39 mg) in 62% yield as a white solid. R_f =0.20 (20% EtOAc/hexane). M.p. 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.63 (m, 2H), 7.39–7.31 (m, 4H), 7.25–7.22 (m, 2H), 7.02–6.97 (d, *J* = 1.6 Hz, 2H), 6.83–6.80 (m, 1H), 2.43 (d, *J* = 2.3 Hz, 1H), 2.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 143.0, 139.6, 137.7, 129.1, 129.0, 128.5, 124.8, 123.1, 120.1, 83.6, 21.5. IR (film) 3470, 2837, 1410, 1350, 1180, 767, 744. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{21}H_{18}NaO$ 309.1255, found 309.1260.



9-(4-methoxyphenyl)-9H-fluoren-9-ol (**3f**)

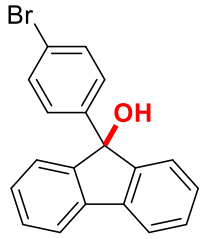
General procedure A was followed using **1f** (68.09 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h.

Chromatography (10% EtOAc/hexane) afforded **3f** (69.92 mg) in 97% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.62 (m, 2H), 7.36–7.29 (m, 5H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.25–7.20 (m, 2H), 6.84–6.71 (m, 2H), 3.73 (s, 3H), 2.53 (s, 1H). HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{20}H_{16}NaO_2$ 311.1048, found 311.1051. Spectral data match those previously reported.[5]



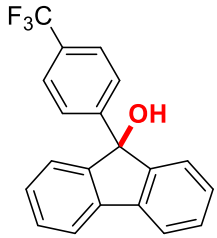
9-(4-chlorophenyl)-9H-fluoren-9-ol (**3g**)

General procedure A was followed using **1g** (69.19 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3g** (61.48 mg) in 84% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.66 (m, 2H), 7.37 (td, *J* = 7.2, 1.7 Hz, 2H), 7.32–7.26 (m, 4H), 7.26–7.19 (m, 4H), 2.50 (s, 1H). HRMS (ESI-TOF) m/z [M - H]$^-$ Calcd for $C_{19}H_{12}ClO$ 291.0577, found 291.0582. Spectral data match those previously reported.[3]



9-(4-bromophenyl)-9H-fluoren-9-ol (**3h**)

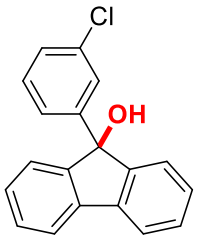
General procedure A was followed using **1h** (80.30 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3h** (60.70 mg) in 72% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.62 (m, 2H), 7.39–7.32 (m, 4H), 7.28–7.20 (m, 6H), 2.49 (s, 1H). HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{19}H_{13}BrNaO$ 359.0047, found 359.0048. Spectral data match those previously reported.[3]



9-(4-(trifluoromethyl)phenyl)-9H-fluoren-9-ol (**3i**)

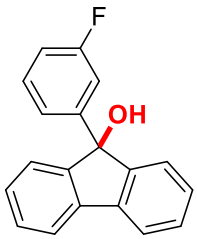
General procedure A was followed using **1i** (77.58 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3i** (35.90 mg) in 44% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.65–7.57 (m, 4H), 7.53 (td, *J* = 7.6, 1.1 Hz, 2H),

7.41–7.30 (m, 4H). HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{20}H_{13}F_3NaO$ 349.0816, found 349.0810. Spectral data match those previously reported.[3]



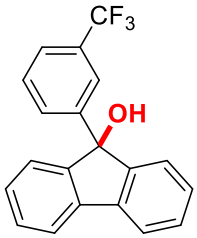
9-(3-chlorophenyl)-9H-fluoren-9-ol (**3j**)

General procedure A was followed using **1j** (69.19 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3j** (63.68 mg) in 87% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.43 (q, *J* = 1.4 Hz, 1H), 7.38–7.32 (m, 2H), 7.28–7.22 (m, 3H), 7.22–7.11 (m, 4H), 2.57 (s, 1H). HRMS (ESI-TOF) m/z [M - H]$^-$ Calcd for $C_{19}H_{12}ClO$ 291.0577, found 291.0587. Spectral data match those previously reported.[3]



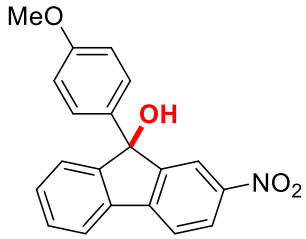
9-(3-fluorophenyl)-9H-fluoren-9-ol (**3k**)

General procedure A was followed using **1k** (65.08 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3k** (55.91 mg) in 81% yield as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dt, *J* = 7.5, 0.9 Hz, 2H), 7.55–7.44 (m, 4H), 7.42–7.36 (m, 2H), 7.30–7.21 (m, 4H), 2.50 (s, 1H). HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{19}H_{13}FNaO$ 299.0848, found 299.0847. Spectral data match those previously reported.[5]



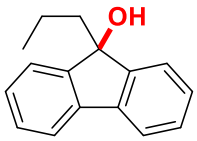
9-(3-(trifluoromethyl)phenyl)-9H-fluoren-9-ol (**3l**)

General procedure A was followed using **1l** (77.58 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3l** (74.24 mg) in 91% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, *J* = 1.8 Hz, 1H), 7.72–7.65 (m, 2H), 7.53–7.46 (m, 1H), 7.42–7.26 (m, 7H), 7.25–7.20 (m, 1H), 2.55 (s, 1H). HRMS (ESI-TOF) m/z [M - H]$^-$ Calcd for $C_{20}H_{12}F_3O$ 325.0840, found 325.0847. Spectral data match those previously reported.[4]



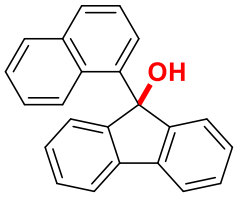
9-(4-methoxyphenyl)-2-nitro-9H-fluoren-9-ol (**3m**)

General procedure A was followed using **1m** (79.34 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3m** (73.34 mg) in 88% yield as a yellow solid. R_f =0.30 (40% EtOAc/hexane). M.p. 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dt, *J* = 8.4, 1.5 Hz, 1H), 8.13 (d, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.49–7.33 (m, 3H), 7.31–7.23 (m, 2H), 6.83–6.74 (m, 2H), 3.75 (s, 3H), 2.78 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 151.9, 151.7, 147.9, 145.8, 137.2, 133.6, 130.5, 129.7, 126.5, 125.2, 121.5, 120.34, 113.9, 83.1, 55.3. IR (film) 3490, 2958, 1510, 1329, 1249, 770, 753. HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{20}H_{15}NNaO_4$ 356.0899, found 356.0896.



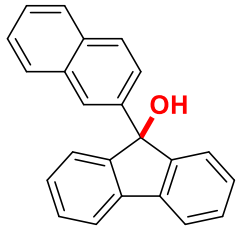
9-propyl-9H-fluoren-9-ol (**3n**)

General procedure A was followed using **1n** (52.78 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3n** (49.35 mg) in 88% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.54 (m, 2H), 7.50–7.43 (m, 2H), 7.37–7.23 (m, 4H), 2.34–1.99 (m, 3H), 0.88 (m, 2H), 0.74 (t, *J* = 7.1 Hz, 3H). HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{16}H_{16}NaO$ 247.1099, found 247.1098. Spectral data match those previously reported.[6]



9-(naphthalen-1-yl)-9H-fluoren-9-ol (**3o**)

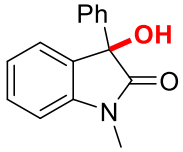
General procedure A was followed using **1o** (73.10 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3o** (71.69 mg) in 93% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.2 Hz, 1H), 7.78 (td, *J* = 15.8, 8.0 Hz, 5H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.36 (td, *J* = 7.5, 1.4 Hz, 2H), 7.16–7.04 (m, 4H), 6.87 (d, *J* = 7.9 Hz, 2H), 2.47 (s, 1H). HRMS (ESI-TOF) m/z $[M - H]^-$ Calcd for $C_{23}H_{15}O$ 307.1123, found 307.1129. Spectral data match those previously reported.[3]



9-(naphthalen-2-yl)-9H-fluoren-9-ol (**3p**)

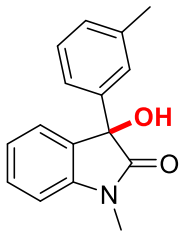
General procedure A was followed using **1p** (73.10 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **3p** (57.82 mg) in 75% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.8 Hz, 1H), 7.77 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.67 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.64–7.53 (m, 3H), 7.42–7.31 (m, 2H), 7.31–7.20 (m, 4H), 7.13 (td, *J* = 7.5, 1.1 Hz, 2H), 7.05 (dd, *J* = 8.6, 1.8 Hz, 1H), 2.68 (s, 1H). HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{23}H_{16}NaO$ 331.1099, found 331.1096. Spectral data match those previously reported.[4]

General procedure B. 9-phenylfluorene **4** (0.25 mmol, 1 equiv), diarylphosphine oxides **2a** (0.50 mmol, 2 equiv), $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv), dry 1,4-dioxane (2 mL) and a stir bar were added to a sealed tube. After being stirred at 100 °C for 12 h, the mixture was evaporated under vacuum. The corresponding product **5** was isolated by silica column chromatography with a hexane/ethyl acetate mixture as eluent.



3-hydroxy-1-methyl-3-phenylindolin-2-one (**5a**)

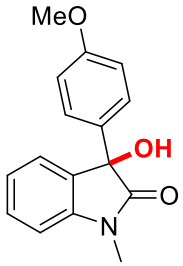
General procedure B was followed using **4a** (55.82 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (13% EtOAc/hexane) afforded **5a** (56.83 mg) in 95% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.25 (m, 7H), 7.09 (td, *J* = 7.6, 0.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H). HRMS (EI) calcd for $C_{15}H_{13}NO_2$ $[M]^+$ m/z= 239.0946; found 239.0944. Spectral data match those previously reported.[7]



3-hydroxy-1-methyl-3-(m-tolyl)indolin-2-one (**5b**)

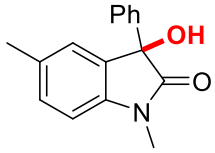
General procedure B was followed using **4b** (59.33 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (13% EtOAc/hexane) afforded **5b** (51.29 mg) in 81% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (td, *J* = 7.8, 1.2 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.24–7.20 (m, 2H), 7.16 (d,

J = 8.1 Hz, 1H), 7.12–7.06 (m, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.27 (s, 3H), 3.13 (s, 1H), 2.32 (s, 3H). HRMS (EI) calcd for $C_{16}H_{15}NO_2$ $[M]^+$ m/z= 253.1103; found 253.1112. Spectral data match those previously reported.[8]



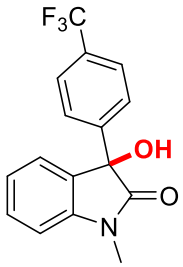
3-hydroxy-3-(4-methoxyphenyl)-1-methylindolin-2-one (**5c**)

General procedure B was followed using **4c** (63.33 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (13% EtOAc/hexane) afforded **5c** (58.57 mg) in 87% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.29 (m, 4H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.24 (s, 3H), 3.12 (s, 1H). HRMS (EI) calcd for $C_{16}H_{15}NO_3$ $[M]^+$ m/z= 269.1052; found 269.1050. Spectral data match those previously reported.[7]



3-hydroxy-1,5-dimethyl-3-phenylindolin-2-one (**5d**)

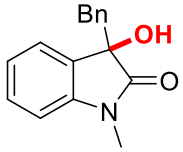
General procedure B was followed using **4d** (59.33 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (13% EtOAc/hexane) afforded **5d** (59.53 mg) in 94% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.9 Hz, 2H), 7.35–7.27 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.10 (s, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 3.24 (d, *J* = 3.3 Hz, 4H), 2.30 (s, 3H). HRMS (EI) calcd for $C_{16}H_{15}NO_2$ $[M]^+$ m/z= 253.1103; found 253.1096. Spectral data match those previously reported.[7]



3-hydroxy-1-methyl-3-(4-(trifluoromethyl)phenyl)indolin-2-one (**5e**)

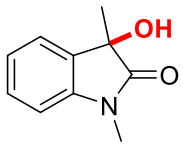
General procedure B was followed using **4e** (72.82 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (13% EtOAc/hexane) afforded **5e** (32.45 mg) in 48% yield as a white solid. ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.38 (td, *J* = 7.8, 1.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.97 (s, 1H), 3.24 (s, 3H). HRMS (EI) calcd for $C_{16}H_{12}F_3NO_2$ $[M]^+$ m/z= 307.0820; found 307.0820. Spectral data match those previously reported.[7]



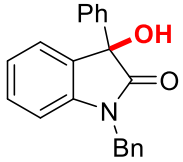
3-benzyl-3-hydroxy-1-methylindolin-2-one (**5f**)

General procedure B was followed using **4f** (59.33 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (13% EtOAc/hexane) afforded **5f** (27.86 mg) in 44% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.22 (m, 1H), 7.18–7.10 (m, 4H), 7.06–7.03 (m, 1H), 6.97–6.92 (m, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 3.30 (d, *J* = 12.9 Hz, 1H), 3.12 (d, *J* = 12.9 Hz, 1H), 3.01 (s, 3H), 2.80 (s, 1H). HRMS (EI) calcd for $C_{16}H_{15}NO_2$ $[M]^+$ m/z= 253.1103; found 253.1089. Spectral data match those previously reported.[8]



3-hydroxy-1,3-dimethylindolin-2-one (**5g**)

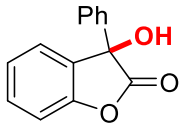
General procedure B was followed using **4g** (40.30 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (13% EtOAc/hexane) afforded **5g** (25.69 mg) in 58% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 1H), 7.33 (td, *J* = 7.8, 1.2 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.20 (s, 3H), 2.73 (s, 1H), 1.61 (s, 3H). HRMS (EI) calcd for $C_{10}H_{11}NO_2$ $[M]^+$ m/z= 177.0790; found 177.0780. Spectral data match those previously reported.[9]



N-benzyl-3-hydroxy-3-phenylindolin-2-one (**5h**)

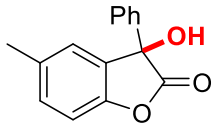
General procedure B was followed using **4h** (74.84 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (13% EtOAc/hexane) afforded **5h** (59.13 mg) in 75% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.8 Hz, 2H), 7.38–7.27 (m, 9H), 7.23 (td, *J* = 7.8, 1.2 Hz, 1H), 7.05 (td, *J* = 7.6, 0.8 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 5.05 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H),

3.33 (s, 1H). HRMS (EI) calcd for $C_{21}H_{17}NO_2$ $[M]^+$ m/z= 315.1259; found 315.1240. Spectral data match those previously reported.[7]



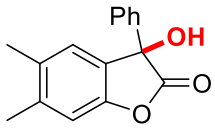
3-hydroxy-3-phenylbenzofuran-2(3H)-one (**5i**)

General procedure B was followed using **4i** (52.56 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (12% EtOAc/hexane) afforded **5i** (32.34 mg) in 57% yield as a yellow oil. R_f =0.28 (20% EtOAc/hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.33 (m, 7H), 7.24–7.19 (m, 2H), 3.21 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 153.5, 138.9, 131.2, 129.4, 129.2, 129.1, 125.5, 125.4, 125.3, 111.6, 77.3. IR (film) 3448, 2961, 1814, 1619, 1487, 1246, 1072, 1049. HRMS (EI) calcd for $C_{14}H_{10}O_3$ $[M]^+$ m/z= 226.0630; found 226.0630.



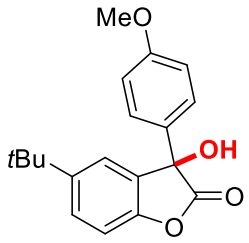
3-hydroxy-5-methyl-3-phenylbenzofuran-2(3H)-one (**5j**)

General procedure B was followed using **4j** (56.06 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (12% EtOAc/hexane) afforded **5j** (40.84 mg) in 68% yield as a yellow oil. R_f =0.25 (20% EtOAc/hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.33 (m, 5H), 7.22–7.18 (m, 1H), 7.14–7.12 (m, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 3.23 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.7, 151.4, 139.1, 135.1, 131.6, 129.3, 129.1, 129.0, 125.8, 125.5, 111.2, 21.2. IR (film) 3447, 2960, 1619, 1449, 1281, 1164, 1031, 890, 762, 640. HRMS (EI) calcd for $C_{15}H_{12}O_3$ $[M]^+$ m/z= 240.0786; found 240.0784.



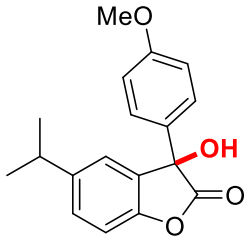
3-hydroxy-5,6-dimethyl-3-phenylbenzofuran-2(3H)-one (**5k**)

General procedure B was followed using **4k** (59.57 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (12% EtOAc/hexane) afforded **5k** (31.79 mg) in 50% yield as a colorless oil. R_f =0.25 (20% EtOAc/hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.31 (m, 5H), 7.21 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.19 (s, 1H), 2.23 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.6, 151.8, 138.2, 135.9, 134.2, 132.0, 129.0, 128.9, 127.4, 125.3, 108.4, 77.8, 19.3, 14.9. IR (film) 3448, 2923, 1603, 1476, 1053, 973, 650. HRMS (EI) calcd for $C_{16}H_{14}O_3$ $[M]^+$ m/z= 254.0943; found 254.0945.



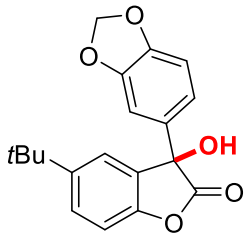
5-(tert-butyl)-3-hydroxy-3-(4-methoxyphenyl)benzofuran-2(3H)-one (**5l**)

General procedure B was followed using **4l** (74.09 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (13% EtOAc/hexane) afforded **5l** (47.64 mg) in 61% yield as a yellow oil. R_f =0.35 (40% EtOAc/hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.37 (d, *J* = 2.1 Hz, 1H), 7.36–7.33 (m, 2H), 7.10 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 3.17 (s, 1H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 160.2, 151.3, 148.7, 131.0, 128.8, 128.1, 127.2, 122.2, 114.4, 110.9, 77.1, 55.5, 35.0, 31.6. IR (film) 3430, 2961, 1813, 1486, 1253, 1071, 825. HRMS (EI) calcd for $C_{19}H_{20}O_4$ $[M]^+$ m/z= 312.1362; found 312.1348.



3-hydroxy-5-isopropyl-3-(4-methoxyphenyl)benzofuran-2(3H)-one (**5m**)

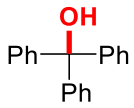
General procedure B was followed using **4m** (70.58 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (14% EtOAc/hexane) afforded **5m** (40.28 mg) in 54% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.9 Hz, 2H), 7.28 (d, *J* = 1.9 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 3.13 (s, 1H), 2.94-2.88 (m, 1H), 1.23 (dd, *J* = 6.9, 4.4 Hz, 6H). HRMS (EI) calcd for $C_{18}H_{18}O_4$ $[M]^+$ m/z= 298.1205; found 298.1206. Spectral data match those previously reported.[10]



3-(benzo[d][1,3]dioxol-5-yl)-5-(tert-butyl)-3-hydroxybenzofuran-2(3H)-one (**5n**)

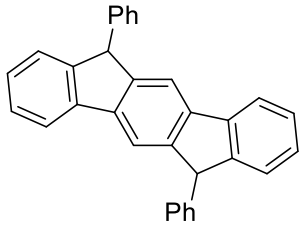
General procedure B was followed using **4n** (77.59 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (12% EtOAc/hexane) afforded **5n** (31.00 mg) in 38% yield as a colorless oil. R_f =0.35 (30% EtOAc/hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.36 (d, *J* = 1.9 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 1.6 Hz, 1H), 6.85–6.76 (m, 2H), 6.04–5.92 (m, 2H), 1.31 (s,

9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.6, 151.2, 148.8, 148.4, 132.8, 128.6, 128.3, 122.1, 119.5, 111.0, 108.5, 106.5, 101.6, 77.2, 35.0, 31.6, 29.8. IR (film) 3466, 2960, 1814, 1487, 1245, 1072, 814. HRMS (EI) calcd for $C_{19}H_{18}O_5$ $[M]^+$ m/z= 326.1154; found 326,1145.



Triphenylmethanol (**10**)

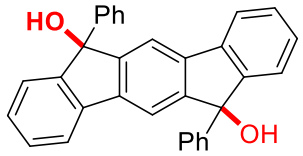
General procedure B was followed using triphenylmethane (61.08 mg, 0.25 mmol), **2a** (101.09 mg, 0.50 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (64.10 mg, 0.25 mmol, 1 equiv) in 1,4-dioxane (2 mL) at 100 °C for 12 h. Chromatography (8% EtOAc/hexane) afforded **10** (20.18 mg) in 31% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.25 (m, 15H), 2.77 (s, 1H). HRMS (EI) calcd for $C_{19}H_{16}O$ $[M]^+$ m/z= 260.1201; found 260.1181.



6,12-diphenyl-6,12-dihydroindeno[1,2-b]fluorine (**12**)

This compound was synthesized from 1,4-dibromo-2,5-dimethylbenzene (5 mmol scale) in 4 steps according to a modified known procedure,[10] affording **12** in 30% yield (609.79 mg, pale yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 5.9 Hz, 4H), 7.35–7.24 (m, 10H), 7.23–7.11 (m, 6H), 5.07 (s, 2H). HRMS (ESI-TOF) m/z $[M + Na]^+$ Calcd for $C_{32}H_{22}Na$ 429.1619, found 429.1607. Spectral data match those previously reported.[11]

Preparation of the 6,12-diphenyl-6,12-dihydroindeno[1,2-b]fluorene-6,12-diol (13). 6,12-diphenyl-6,12-dihydroindeno[1,2-b]fluorene **12** (1 mmol, 1 equiv), Diarylphosphine Oxides **2a** (2 mmol, 2 equiv), $Mg(NO_3)_2{\cdot}6H_2O$ (256.40 mg, 1 mmol, 1 equiv), dry 1,4-dioxane (10 mL) and a stir bar were added to a sealed tube. After being stirred at 100 °C for indicate time, the mixture was evaporated under vacuum. The corresponding product **13** was isolated by silica column chromatography with a petroleum ether/ethyl acetate mixture as eluent.

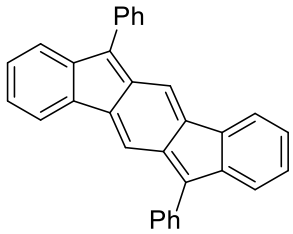


6,12-diphenyl-6,12-dihydroindeno[1,2-b]fluorene-6,12-diol (**13**)

General procedure C was followed using **12** (438.53 mg, 1 mmol), **2a** (404.39 mg, 2 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (256.40 mg, 1 mmol, 1 equiv) in 1,4-dioxane (10 mL) at 100 °C for 12 h. Chromatography (10% EtOAc/hexane) afforded **13** (206.11 mg) in 47% yield as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85–7.75 (m, 2H), 7.67 (s, 2H), 7.37–7.30 (m, 6H), 7.28–7.17 (m, 10H), 6.41 (s, 2H).

HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{32}H_{22}NaO_2$ 461.1517, found 461.1520. Spectral data match those previously reported.[11]

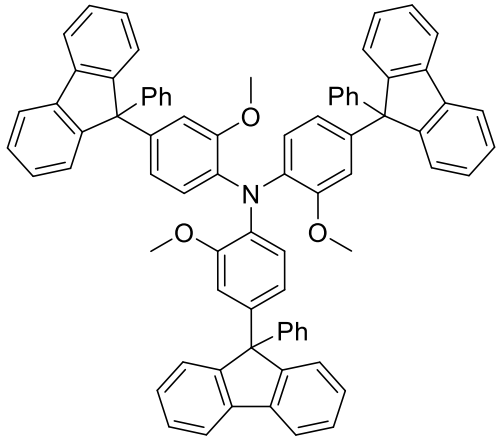
Preparation of the 6,12-diphenylindeno[1,2-b]fluorine (14). 6,12-diphenyl-6,12-dihydroindeno[1,2-b]fluorene-6,12-diol (**13**) (153.48g, 0.35 mmol) was redissolved in 40 mL toluene and degassed with Ar for 10 min. $SnCl_2$ (0.27 g, 1.42 mmol) was added to the mixture and warmed to 65 ℃ overnight. The solution was then filtered and the filtrate evaporated to dryness. The corresponding product **14** was isolated by silica column chromatography with a petroleum ether/ethyl acetate mixture as eluent.[12]



6,12-diphenylindeno[1,2-b]fluorine (**14**)

General procedure D was followed using **13** (153.48 mg, 0.35 mmol), $SnCl_2$ (0.27 g, 1.42 mmol) in toluene (40 mL) at 65 ^{o}C for 12 h. Chromatography (10% EtOAc/hexane) afforded **14** (101.94 mg) in 77% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.60 (m, 4H), 7.58–7.52 (m, 4H), 7.49–7.44 (m, 2H), 7.42–7.39 (m, 2H), 7.37 (s, 2H), 7.27 (dd, *J* = 2.8, 1.6 Hz, 2H), 7.10–7.01 (m, 4H). HRMS (ESI-TOF) m/z [M + Na]$^+$ Calcd for $C_{32}H_{20}Na$ 427.1463, found 427.1460. Spectral data match those previously reported.[12]

Preparation of the tris(2-methoxy-4-(9-phenyl-9H-fluoren-9-yl)phenyl)amine (16). 2,2',2''-Trimethoxytriphenylamine (**15**) (0.42 g, 1.25 mmol) and 9-phenyl-9-fluorenol (**3a**) (1 g, 3.87 mmol) were redissolved in 40 mL 1,4-dioxane. Trifluoromethanesulfonic acid (CF_3SO_3H, 0.48 g, 3.19 mmol) was added to the mixture and warmed to 80 ℃ and kept at this temperature for 4 h. The solution was then filtered and the filtrate evaporated to dryness. The corresponding product **16** was isolated by silica column chromatography with a petroleum ether/ethyl acetate mixture as eluent.[13]



tris(2-methoxy-4-(9-phenyl-9H-fluoren-9-yl)phenyl)amine (**16**)

General procedure E was followed using **15** (0.42 g, 1.25 mmol), **3a** (1 g, 3.87 mmol), CF_3SO_3H (0.48 g, 3.19 mmol) in 1,4-dioxane (40 mL) at 80 °C for 4 h. Chromatography (20% EtOAc/hexane) afforded **16** (369.36 mg) in 28% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 6H), 7.37 (d, *J* = 7.6 Hz, 6H), 7.31 (td, *J* = 7.5, 1.2 Hz, 6H), 7.25–7.16 (m, 7H), 7.15 (s, 15H), 6.67–6.52 (m, 8H), 3.24 (s, 9H).Spectral data match those previously reported.[13]

Reference

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Copies of ^{1}H NMR and ^{13}C NMR

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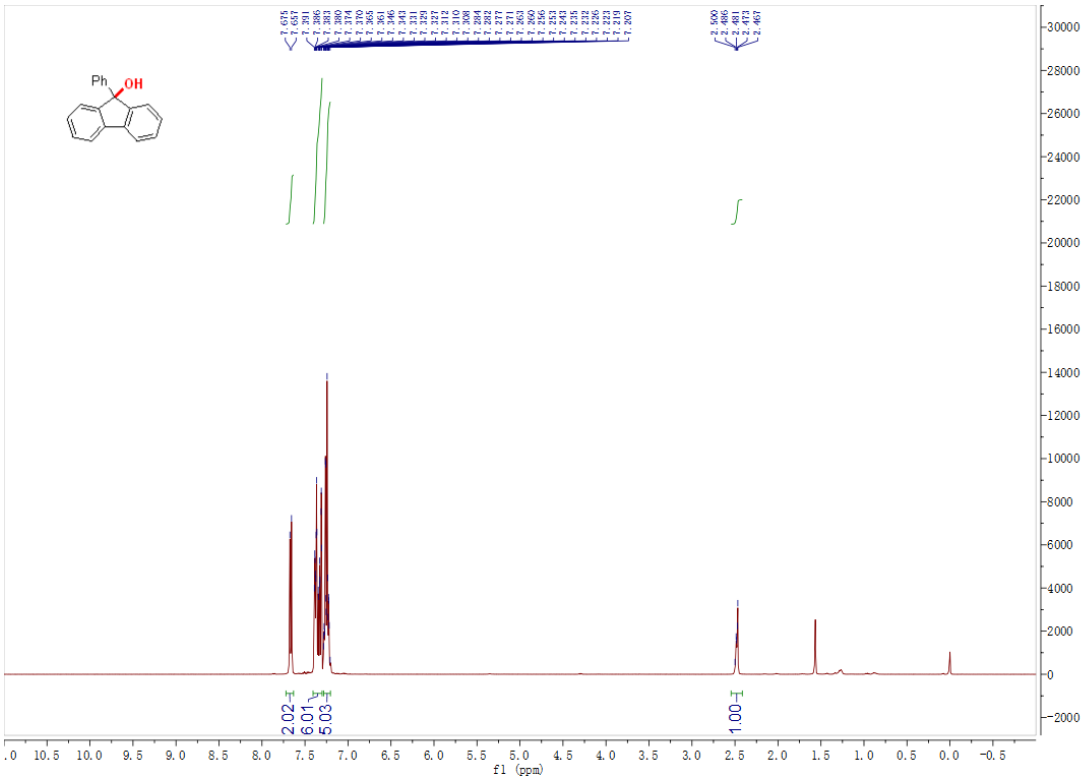

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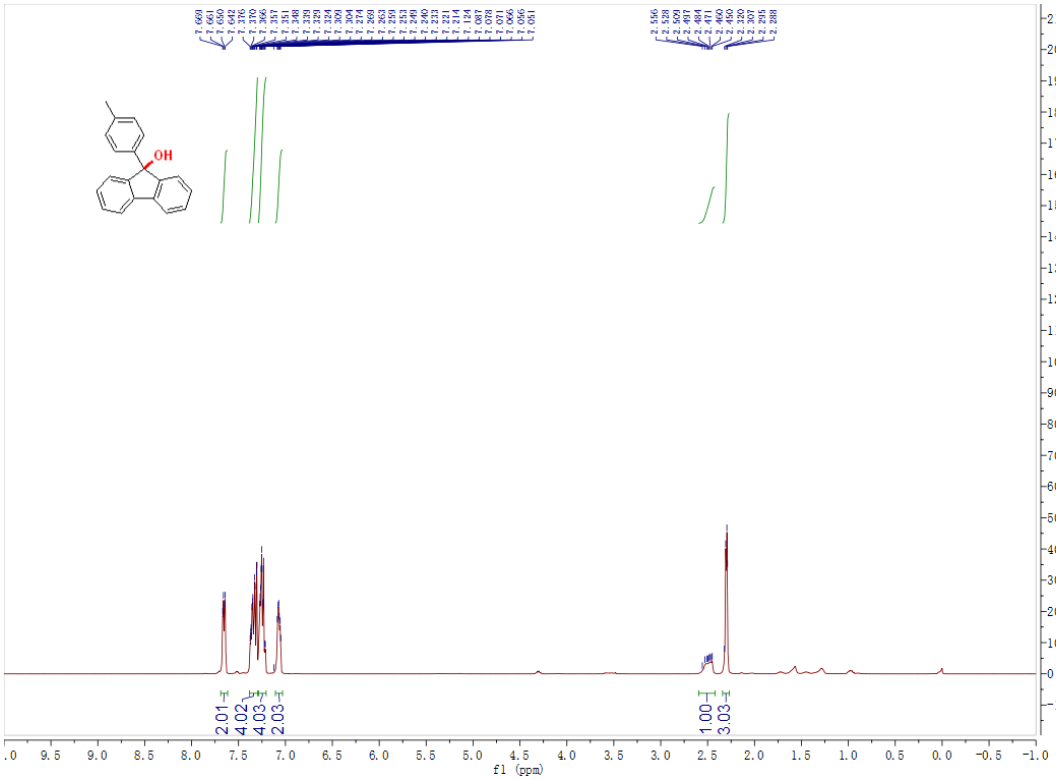

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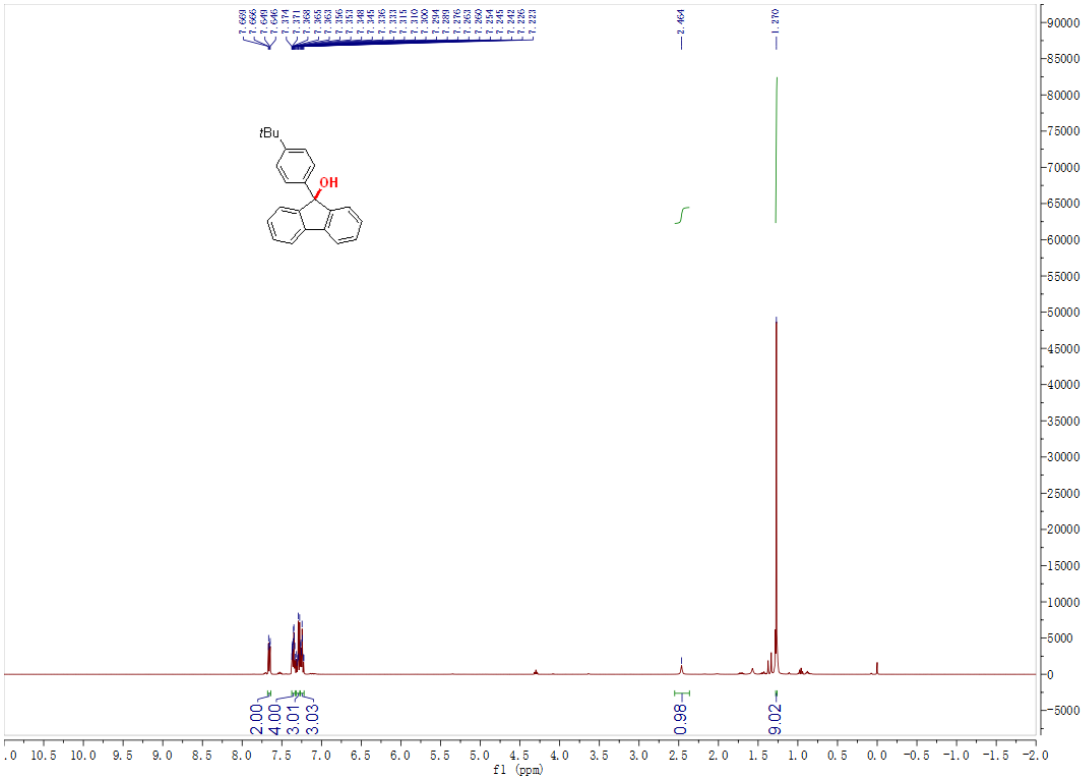
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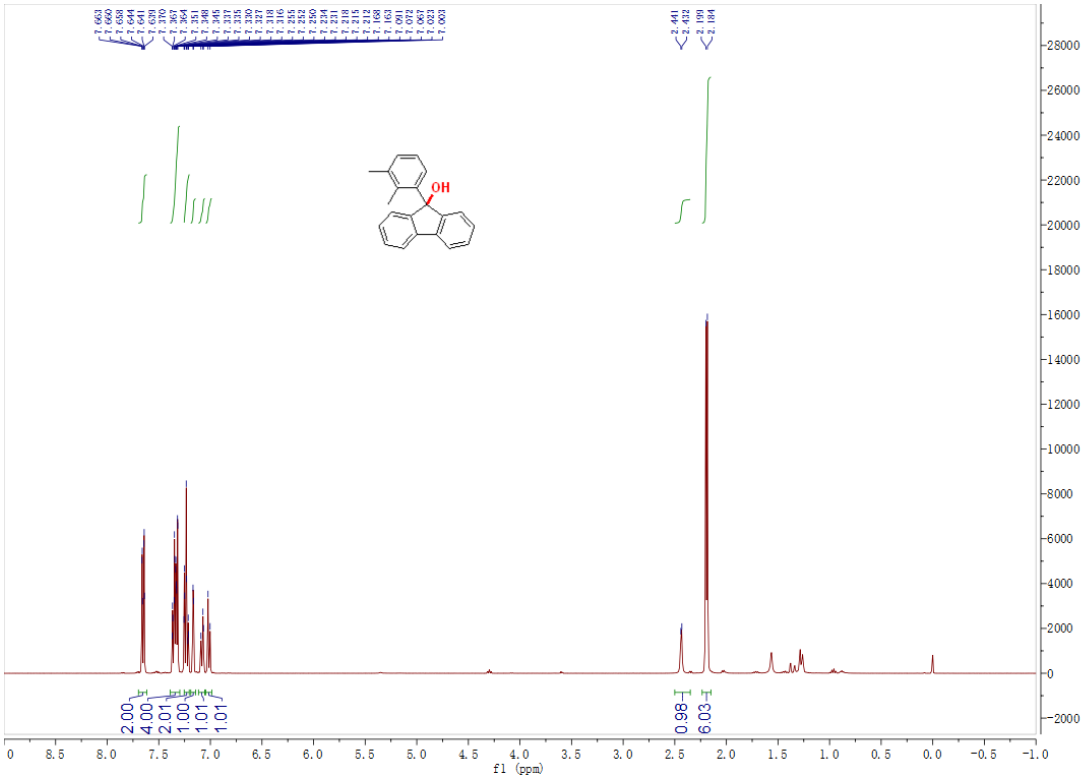
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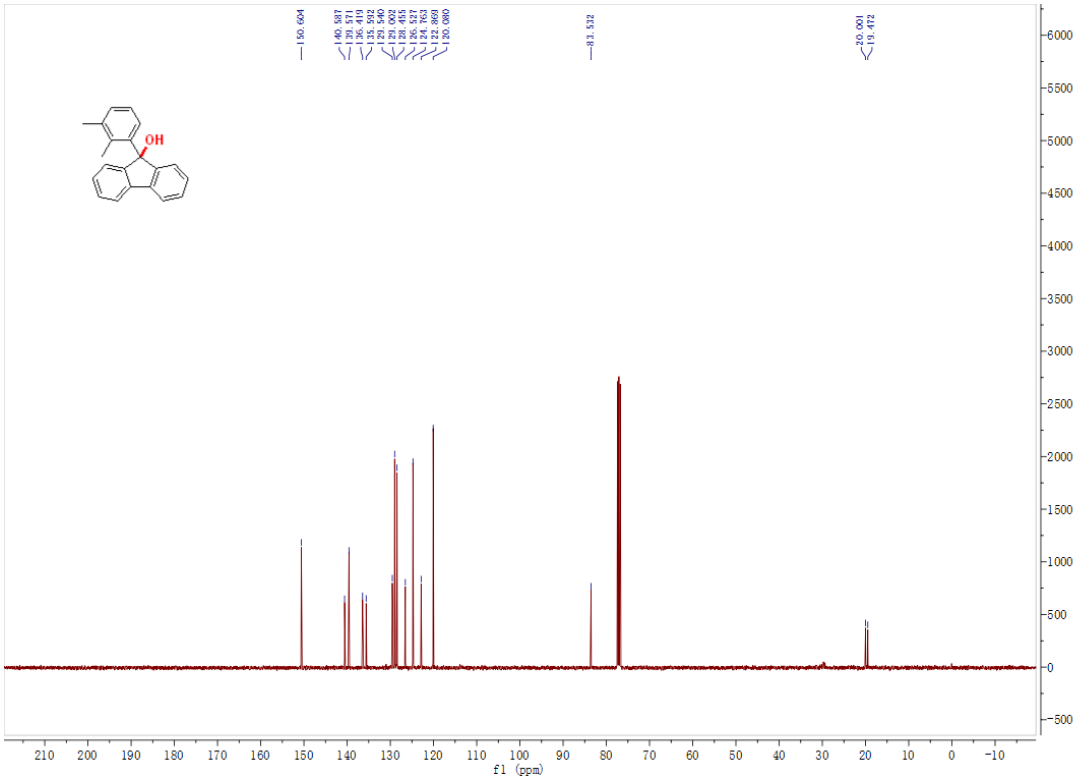
f1 (ppm)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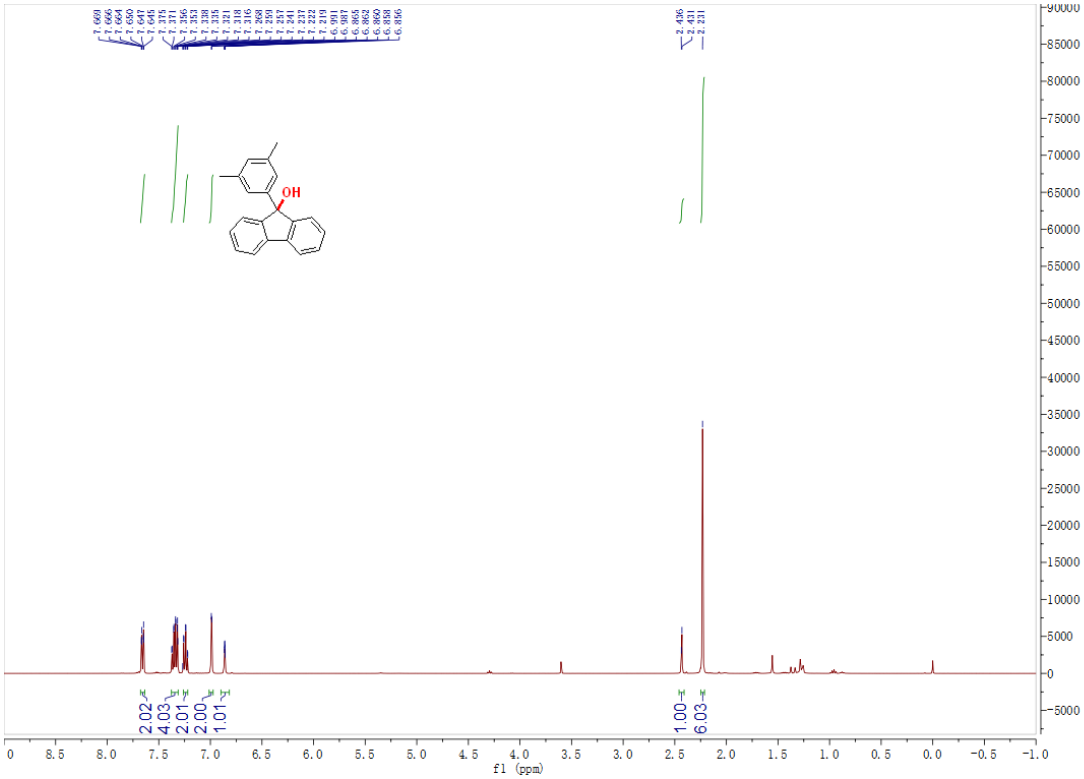
19.472
OH
f1 (ppm)

3e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7.222
7.219
6.991
6.987
6.865
6.865
6.860
6.858
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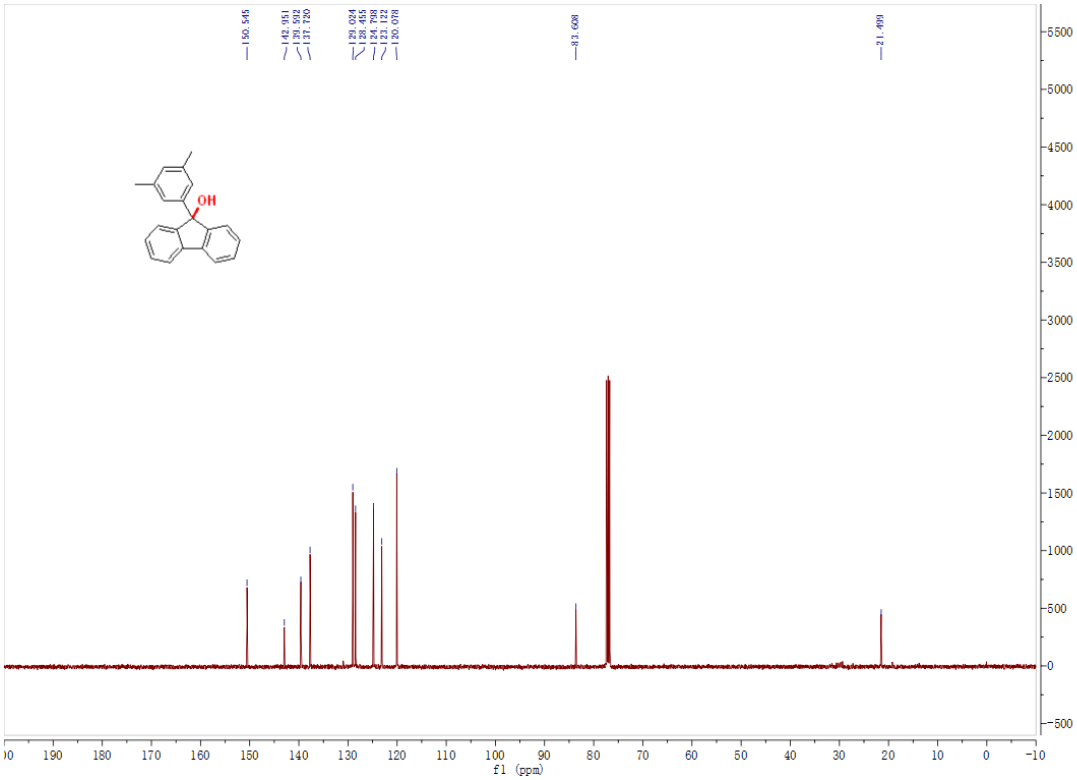
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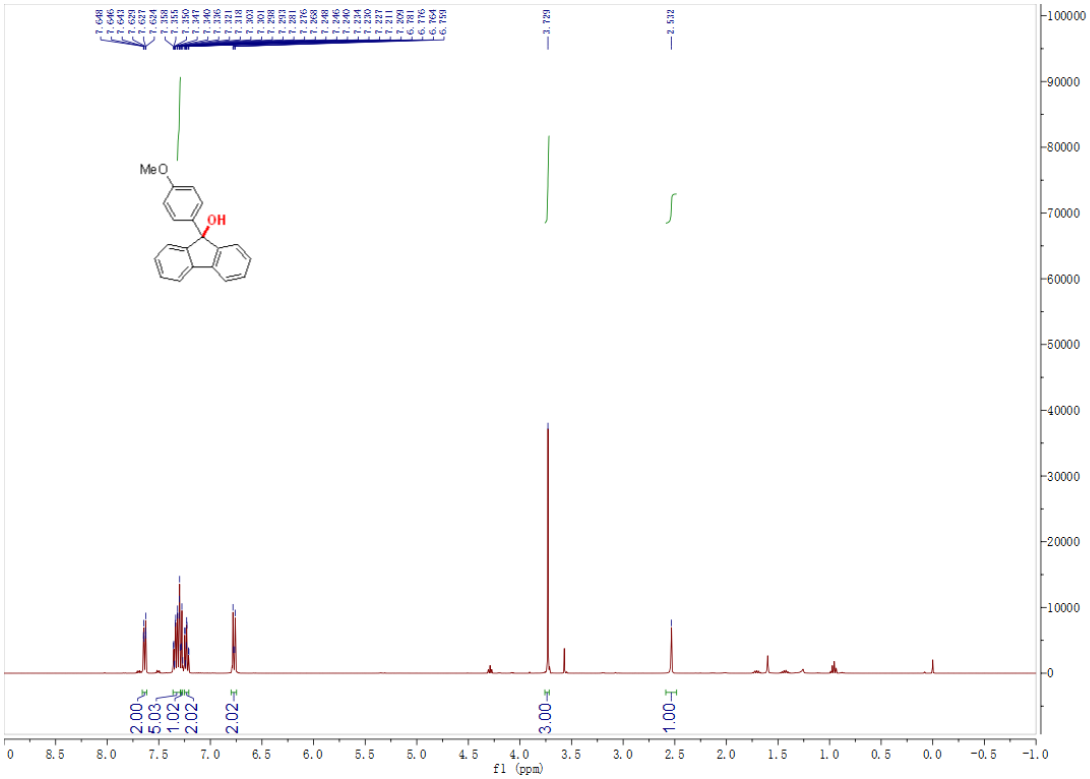
3f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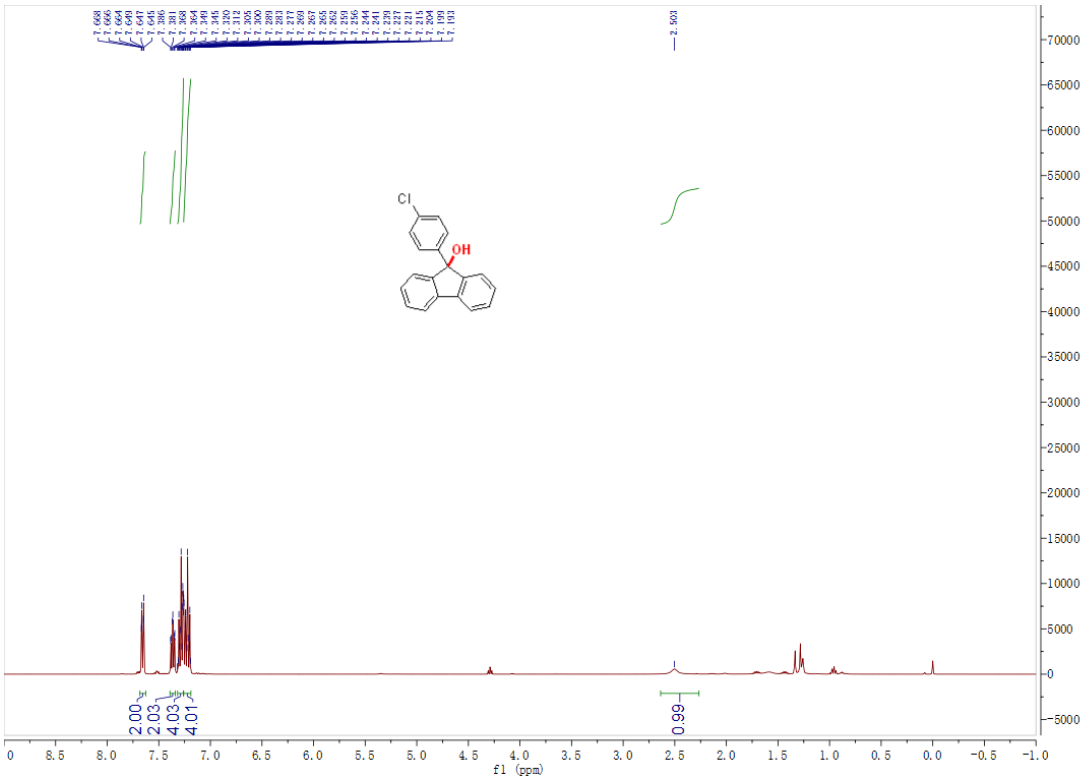
3g



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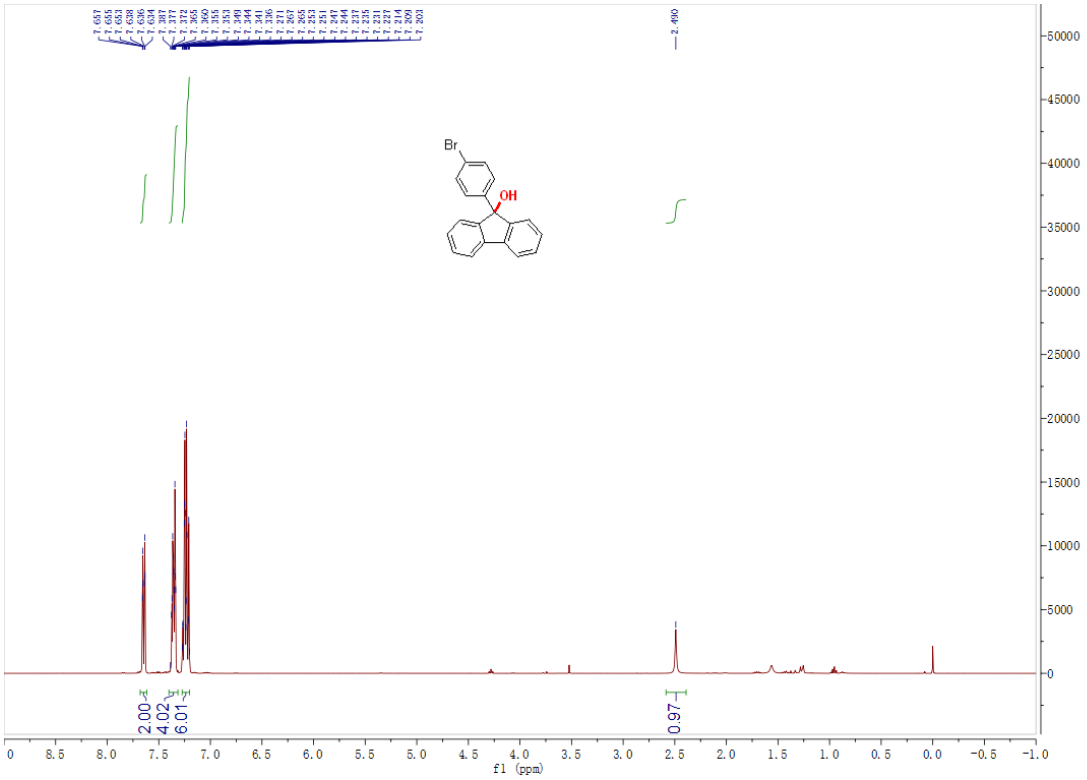

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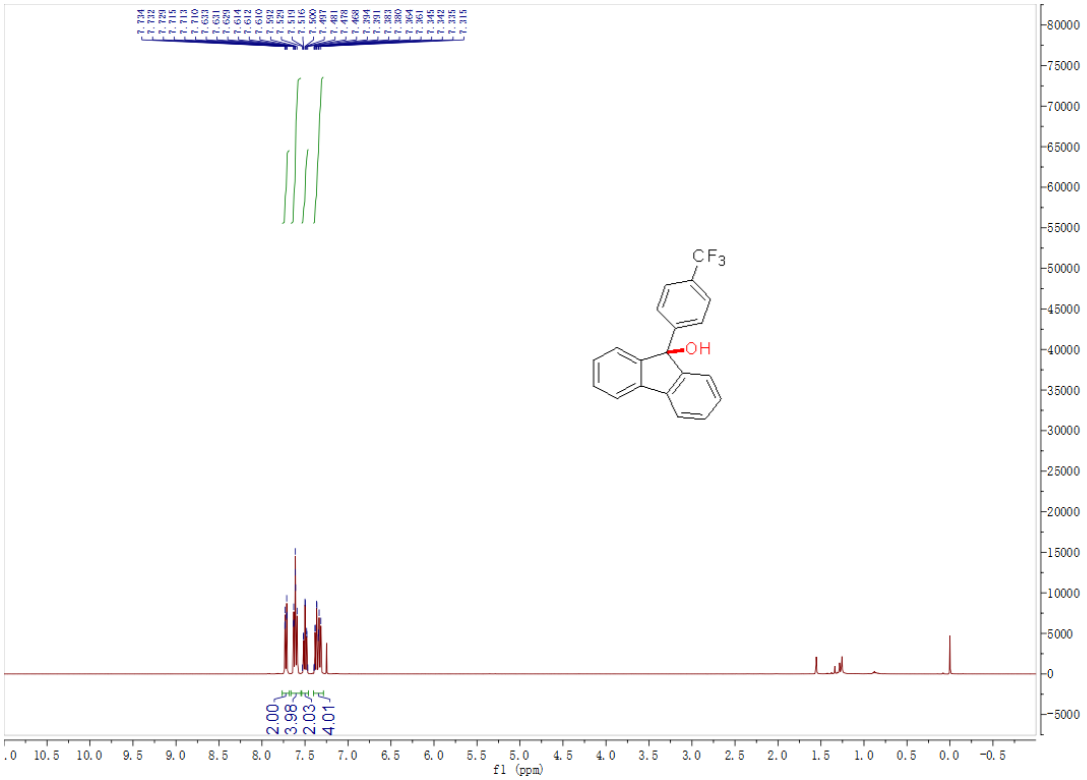

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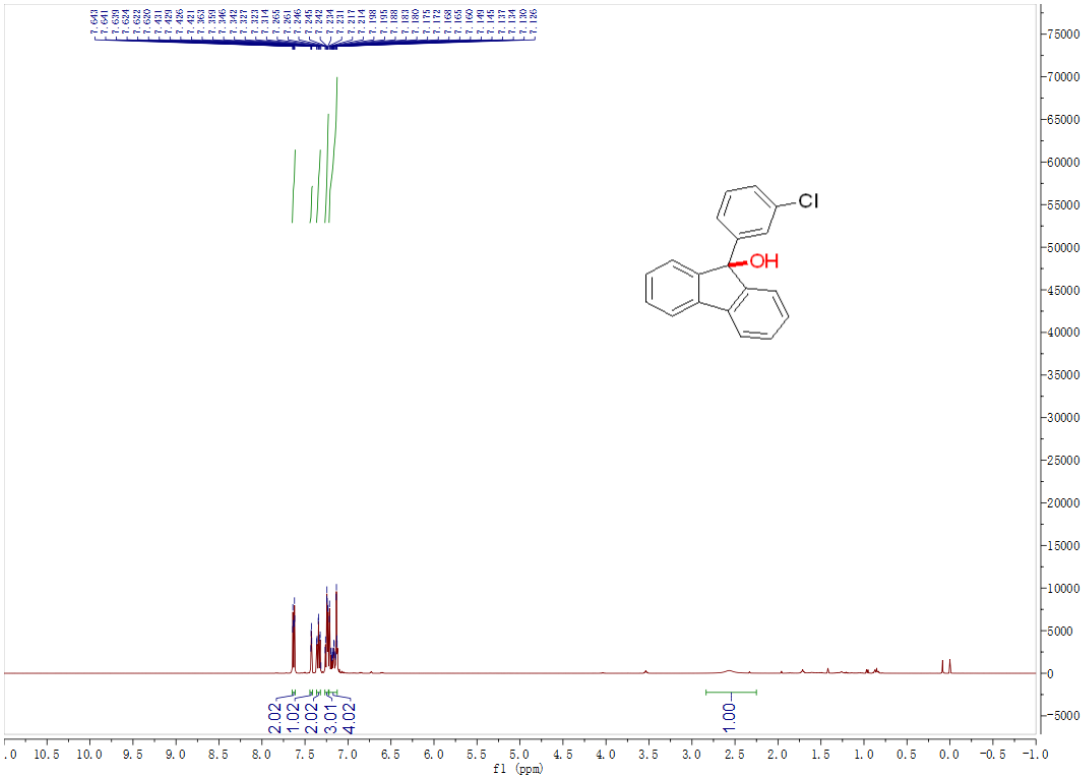

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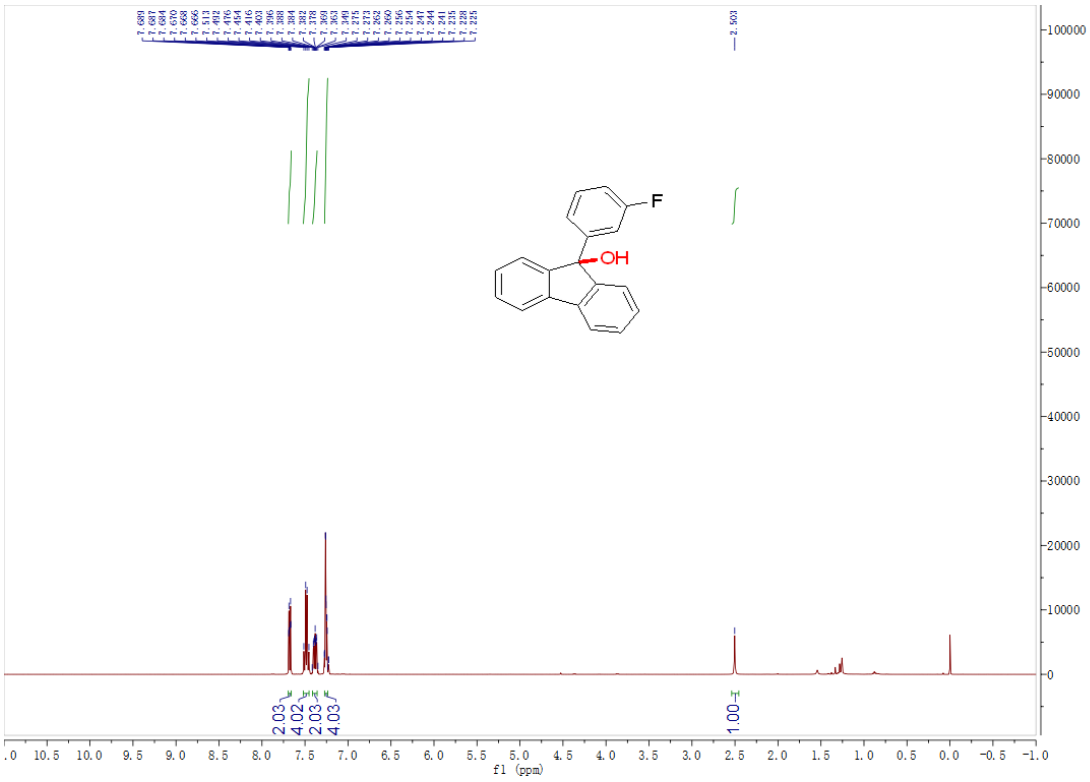
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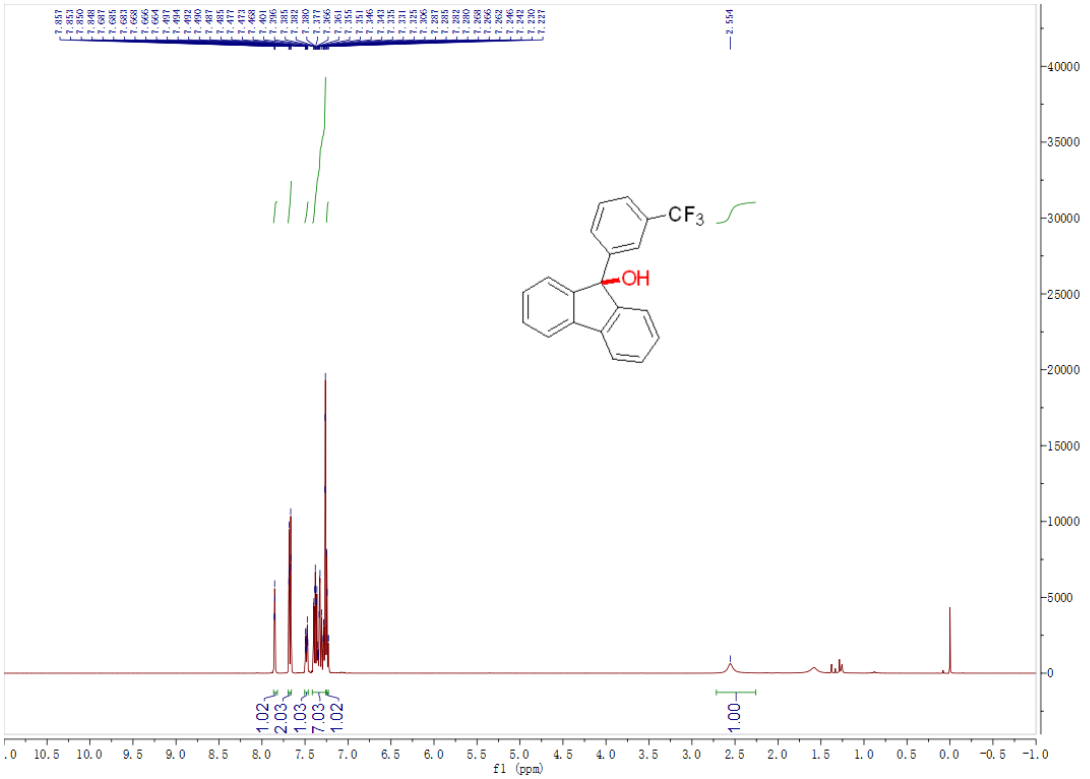
f1 (ppm)

3l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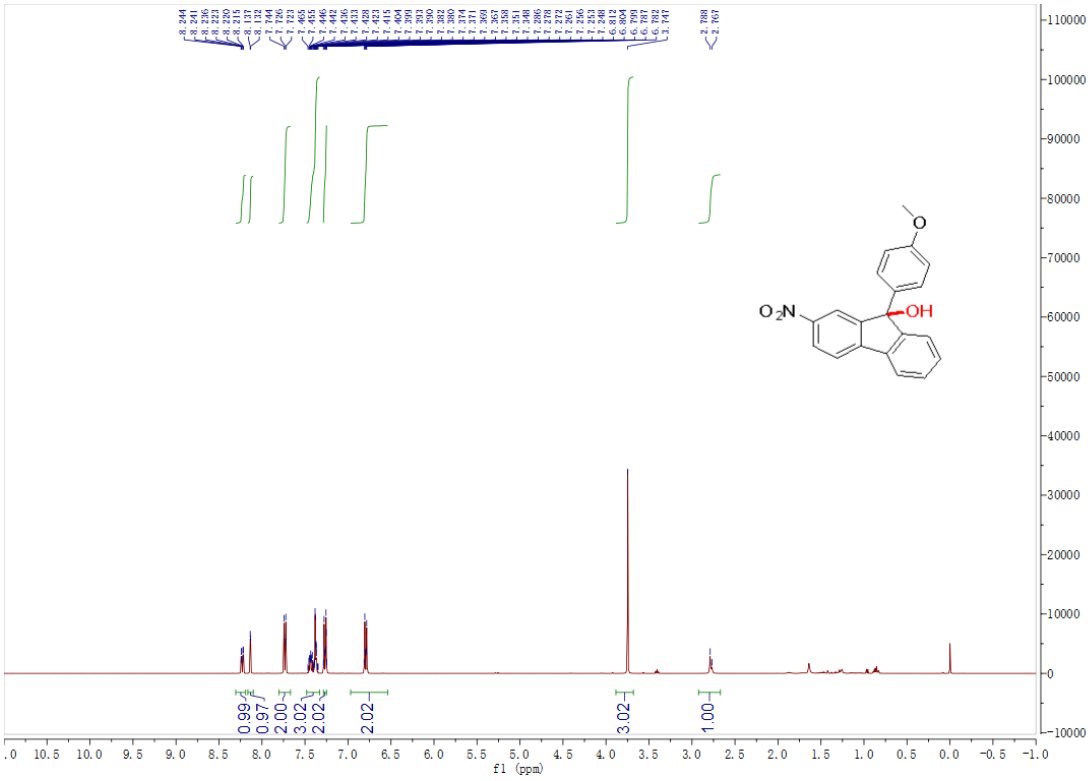
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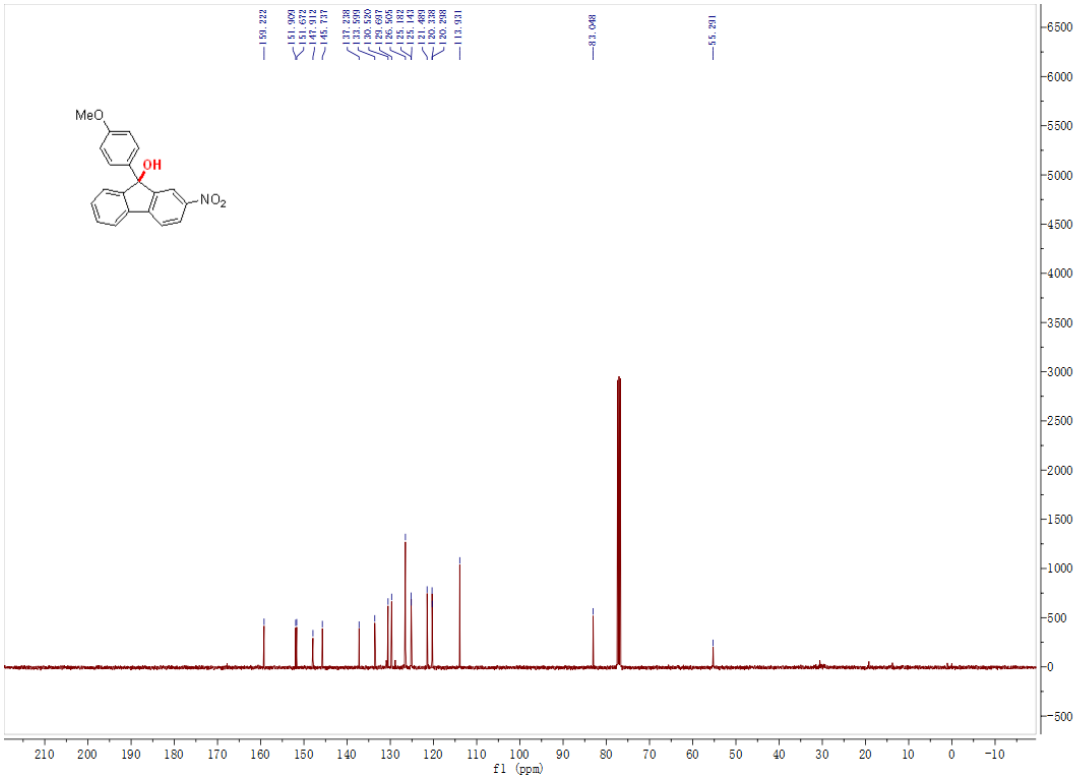
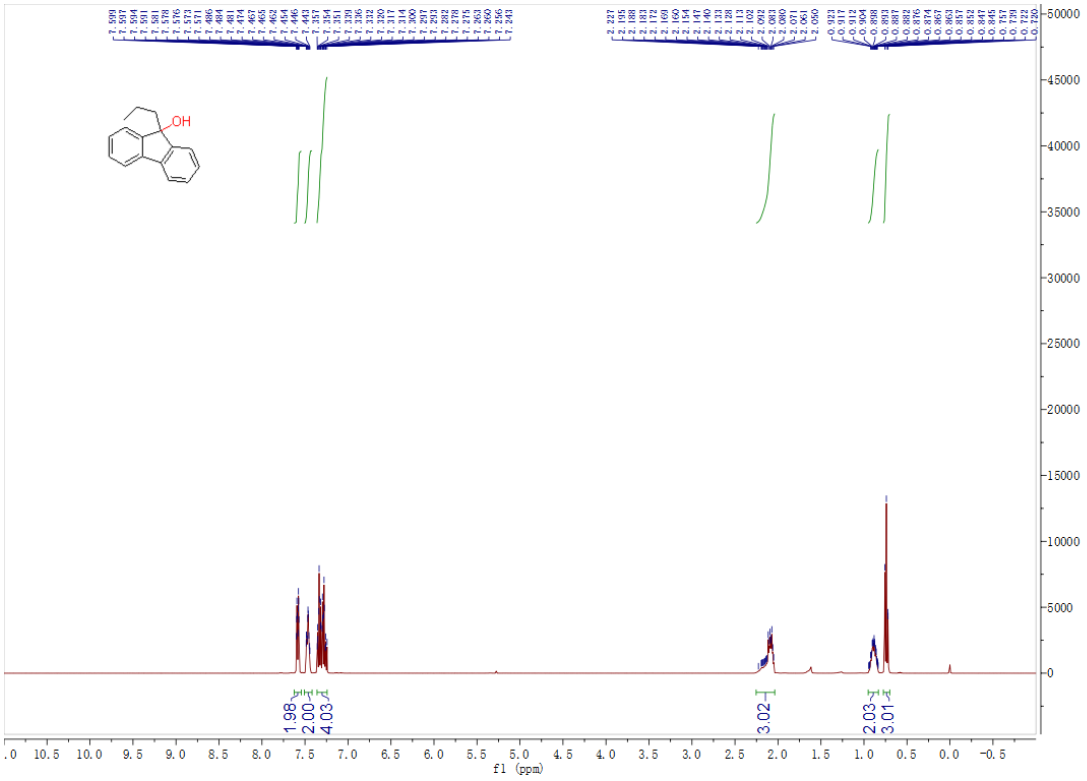
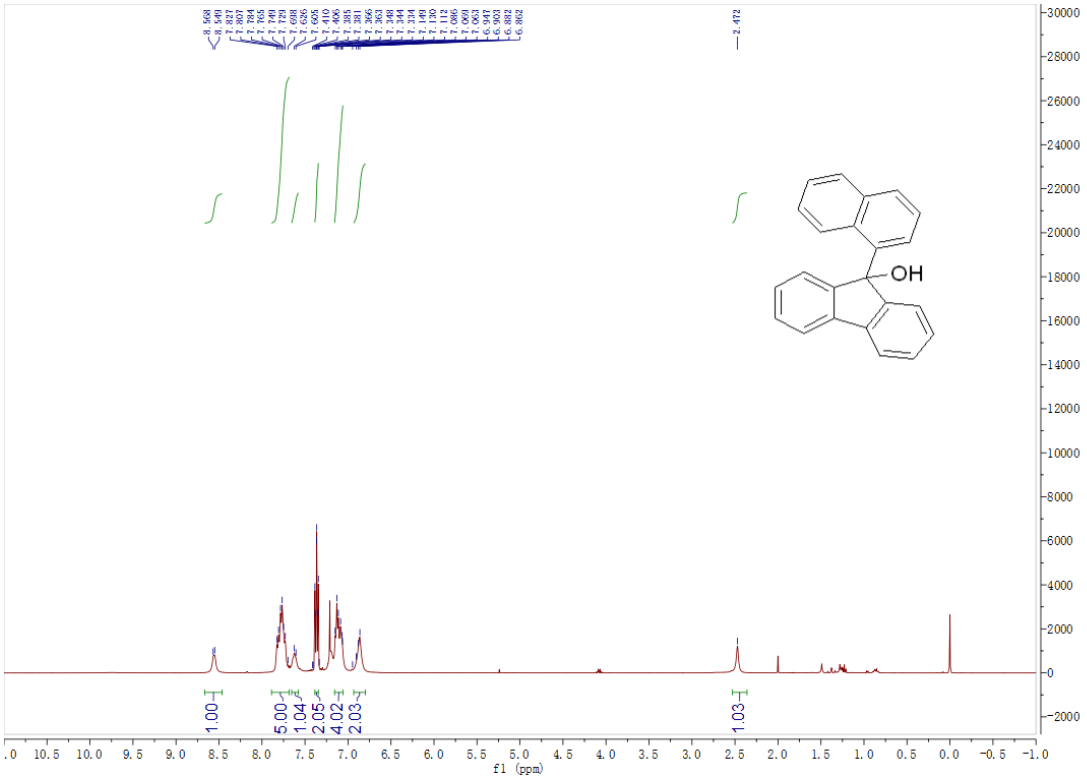
1.00
f1 (ppm)


MeO
OH
NO2
159.222
151.909
151.672
147.912
145.737
137.238
133.599
130.529
129.697
126.505
125.182
125.143
124.460
120.338
120.298
113.931
83.048
55.291
f1 (ppm)

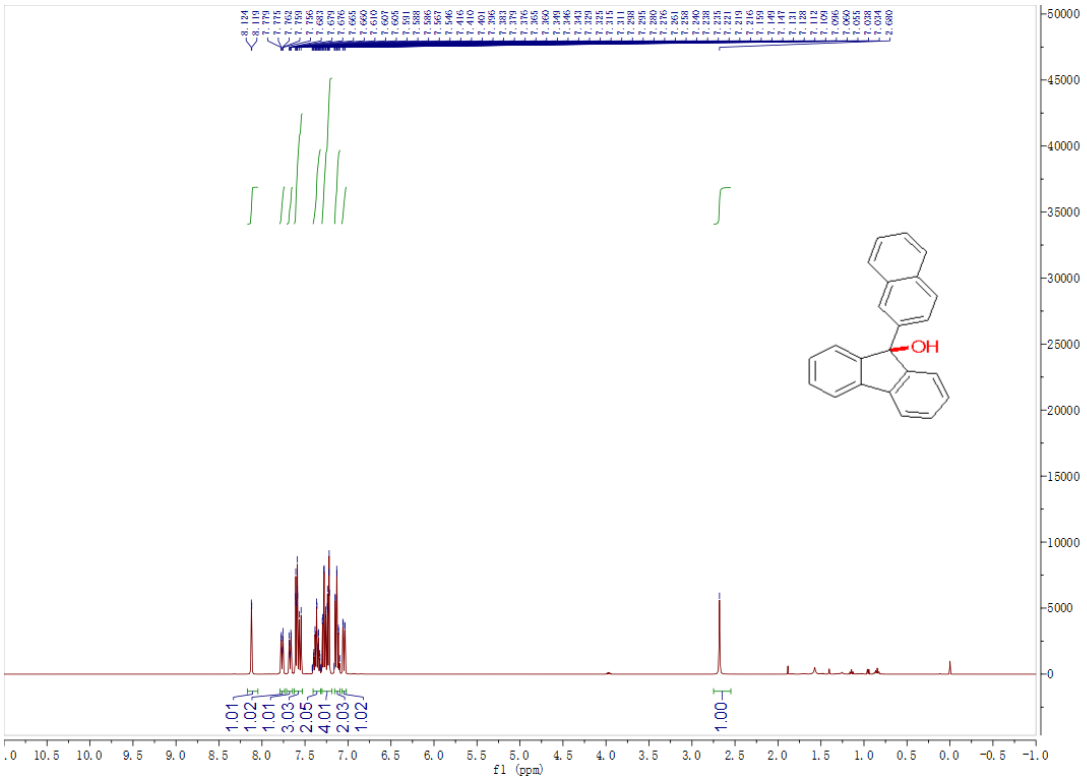
3n


OH
1.98
2.00
4.03
3.02
2.03
3.01
f1 (ppm)

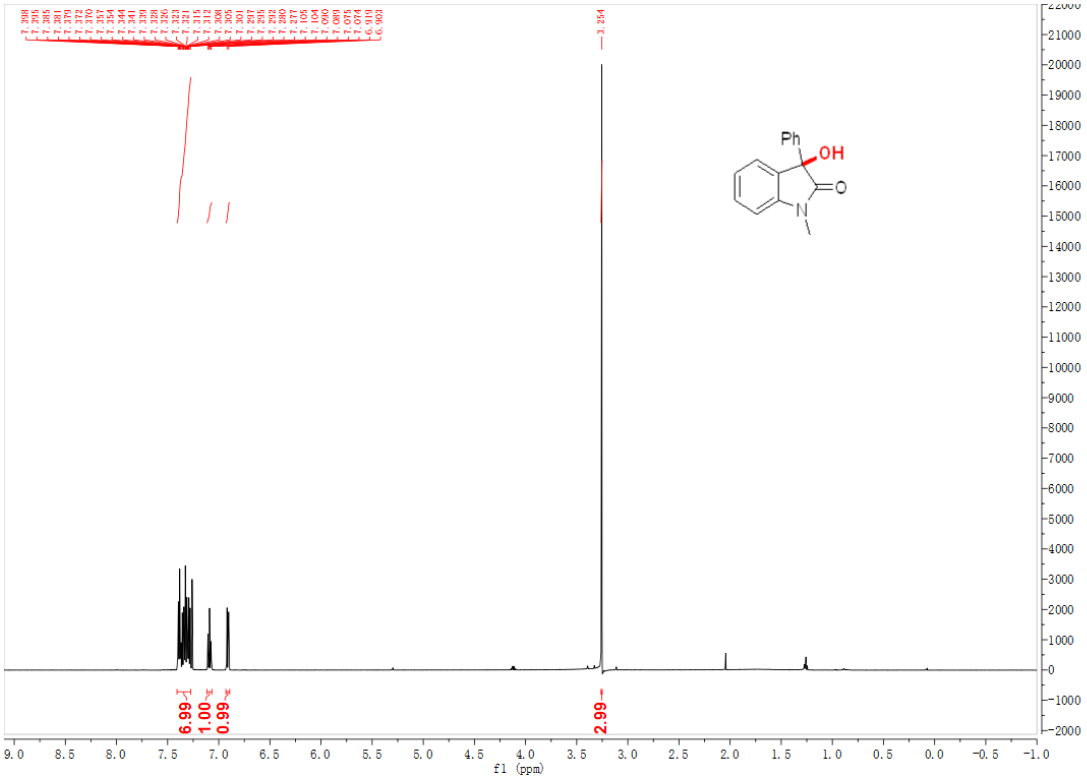
3o


OH
1.00
5.00
1.04
2.05
4.02
2.03
1.03
f1 (ppm)

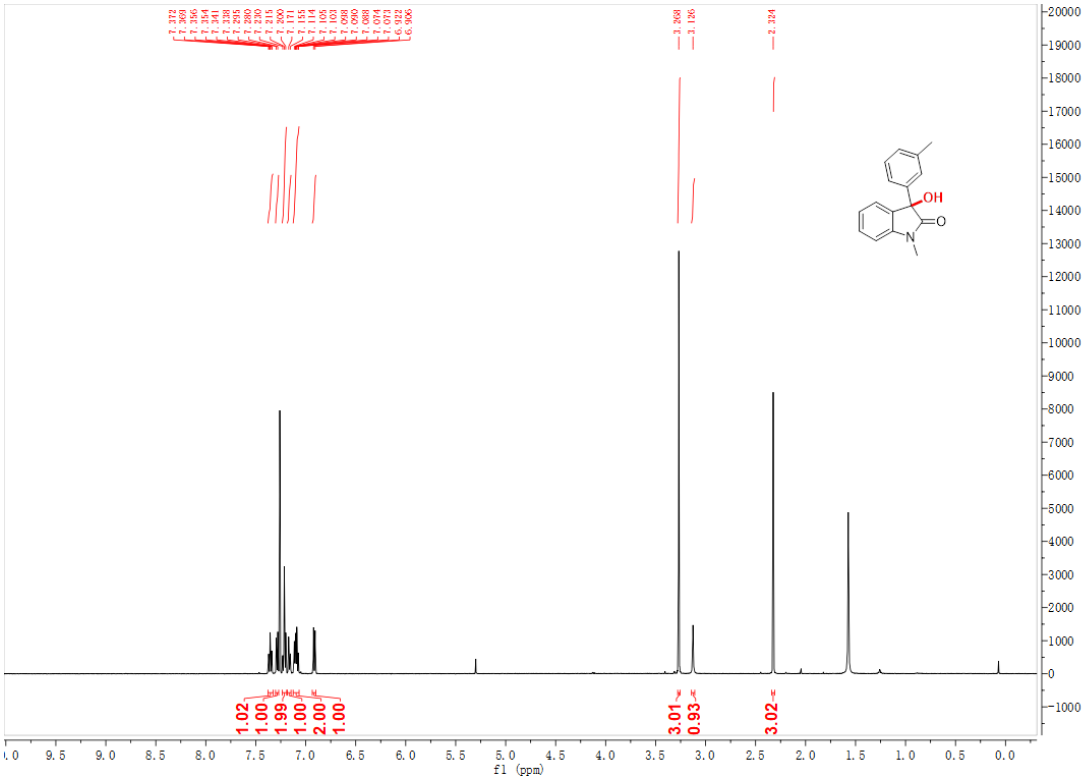
3p


OH
1.01
1.02
1.01
3.03
2.05
4.01
2.03
1.02
1.00
f1 (ppm)

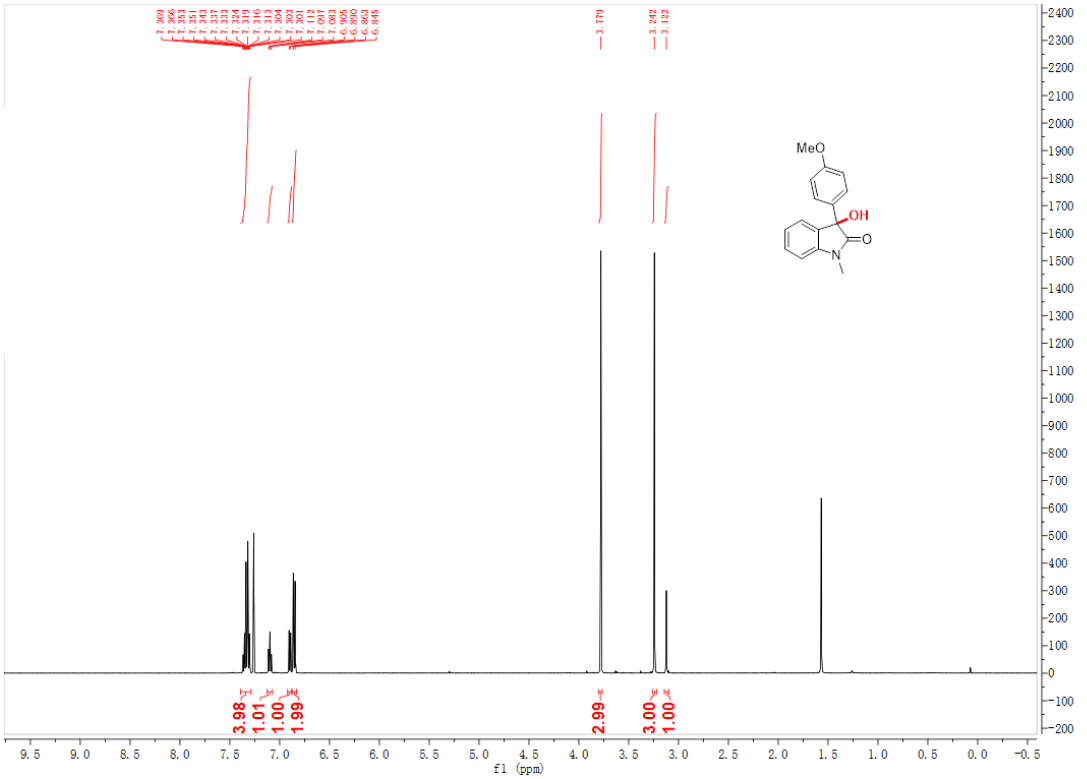
5a


Ph
OH
O
N
6.99
1.00
0.99
2.99
f1 (ppm)

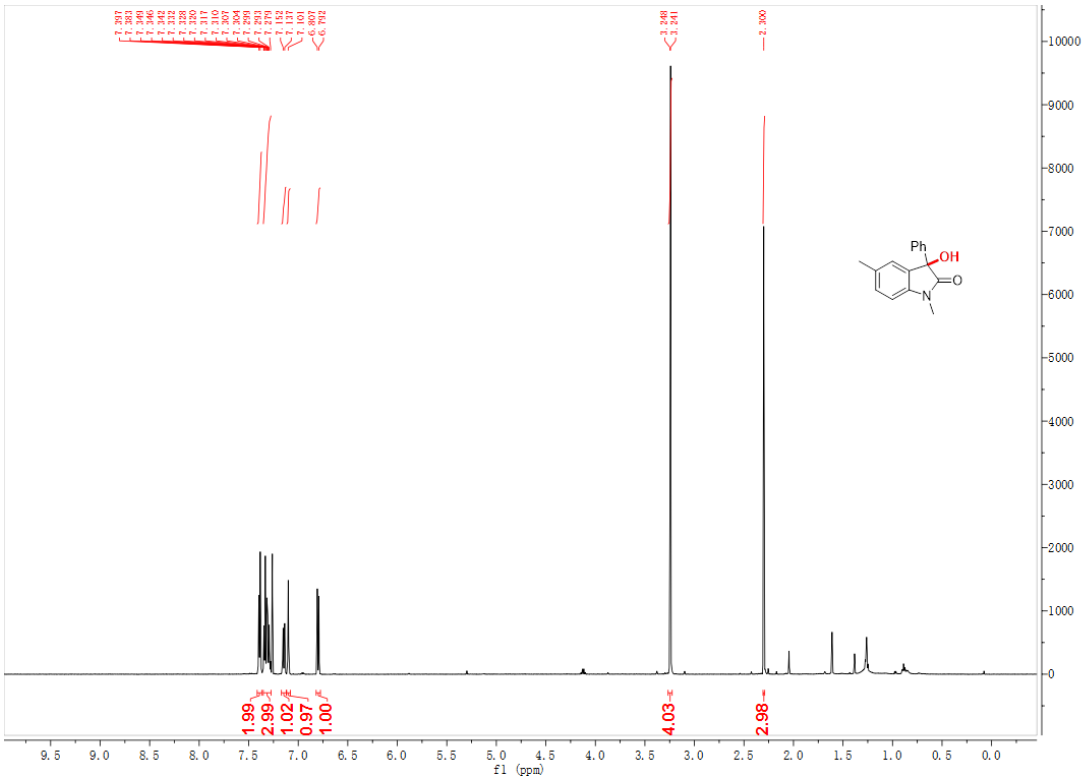
5b


7.372
7.369
7.356
7.354
7.341
7.338
7.293
7.280
7.230
7.215
7.200
7.171
7.155
7.114
7.105
7.103
7.098
7.090
7.086
7.074
7.073
6.922
6.905
3.268
3.126
2.324
OH
O
N
1.02
1.00
1.99
1.00
2.00
1.00
3.01
0.93
3.02
f1 (ppm)

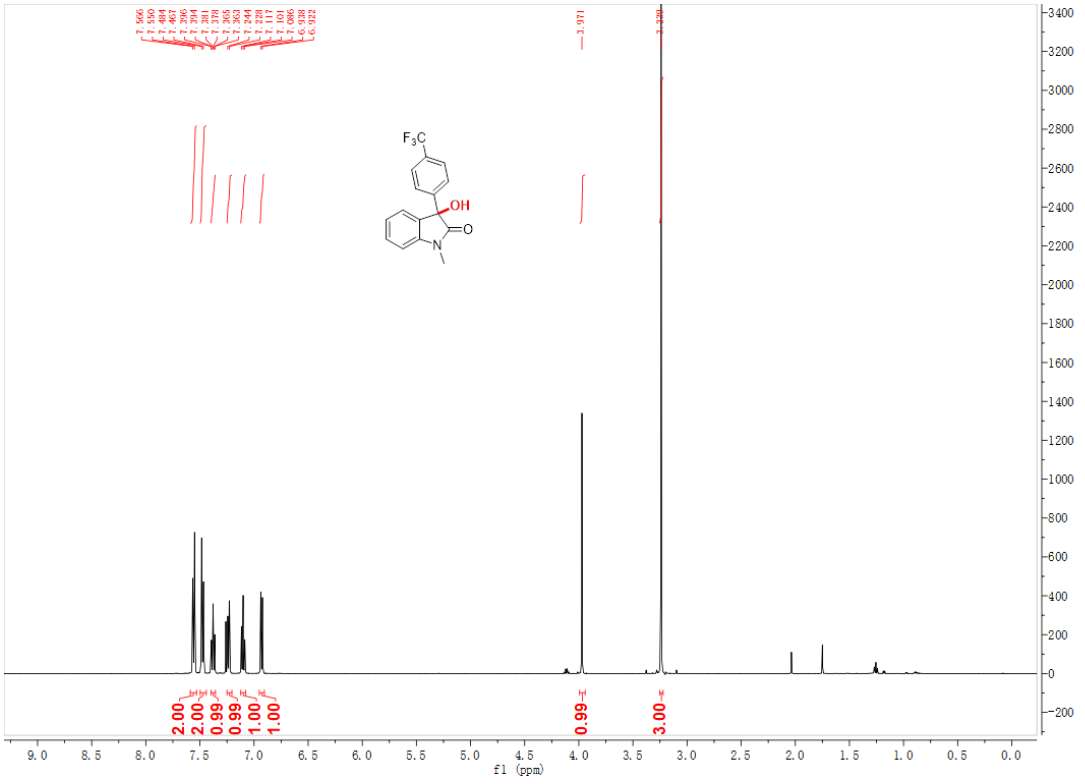
5c


7.369
7.366
7.353
7.351
7.343
7.337
7.333
7.324
7.319
7.316
7.313
7.304
7.303
7.301
7.113
7.097
7.083
6.905
6.899
6.893
6.845
3.779
3.242
3.122
MeO
OH
O
N
3.98
1.01
1.00
1.99
2.99
3.00
1.00
f1 (ppm)

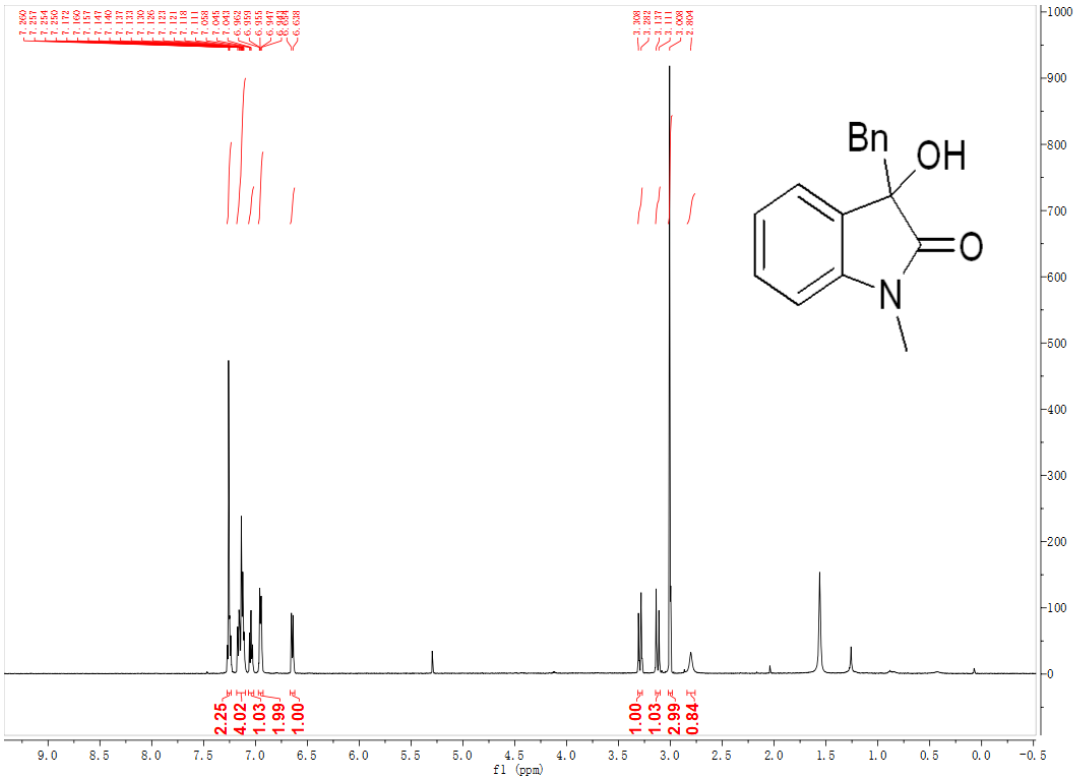
5d



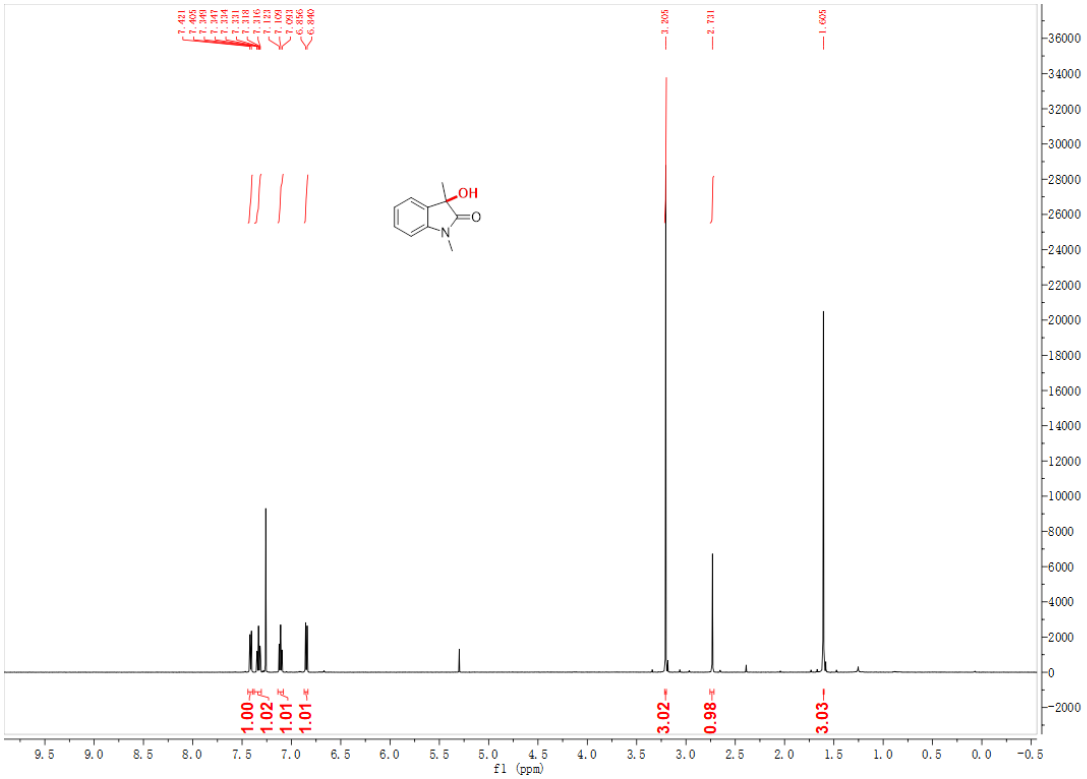
5e



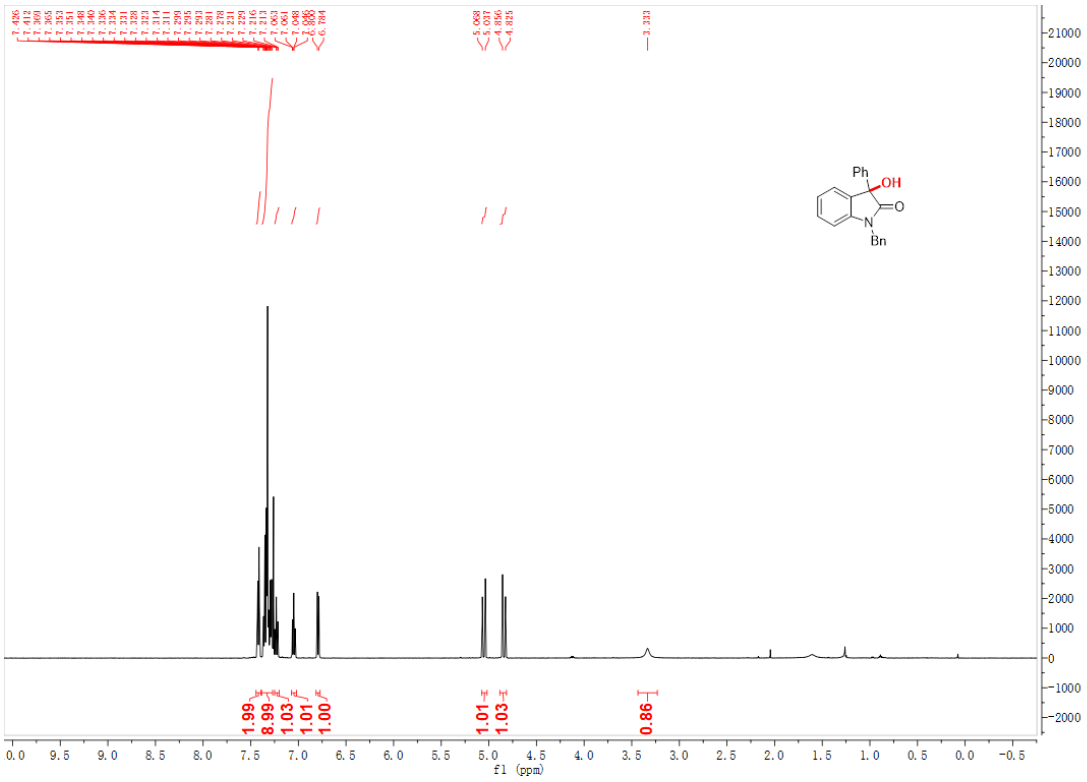
5f


Bn
OH
O
N
2.25
4.02
1.03
1.99
1.00
1.00
1.03
2.99
0.84
f1 (ppm)

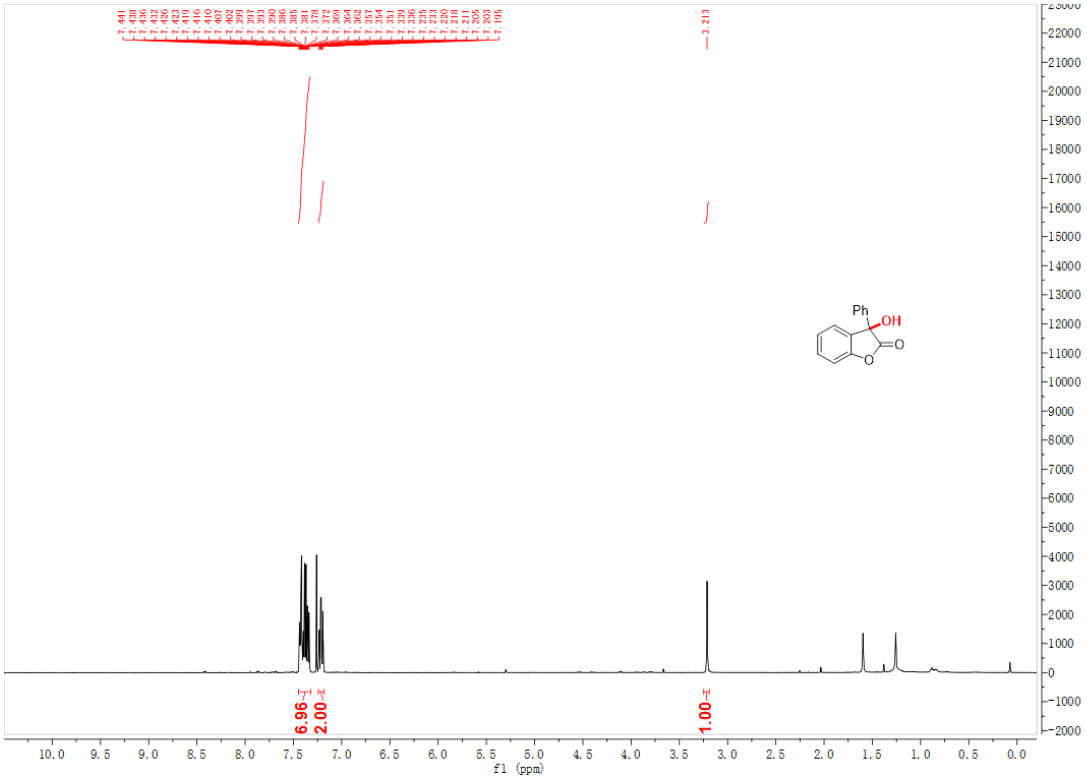
5g

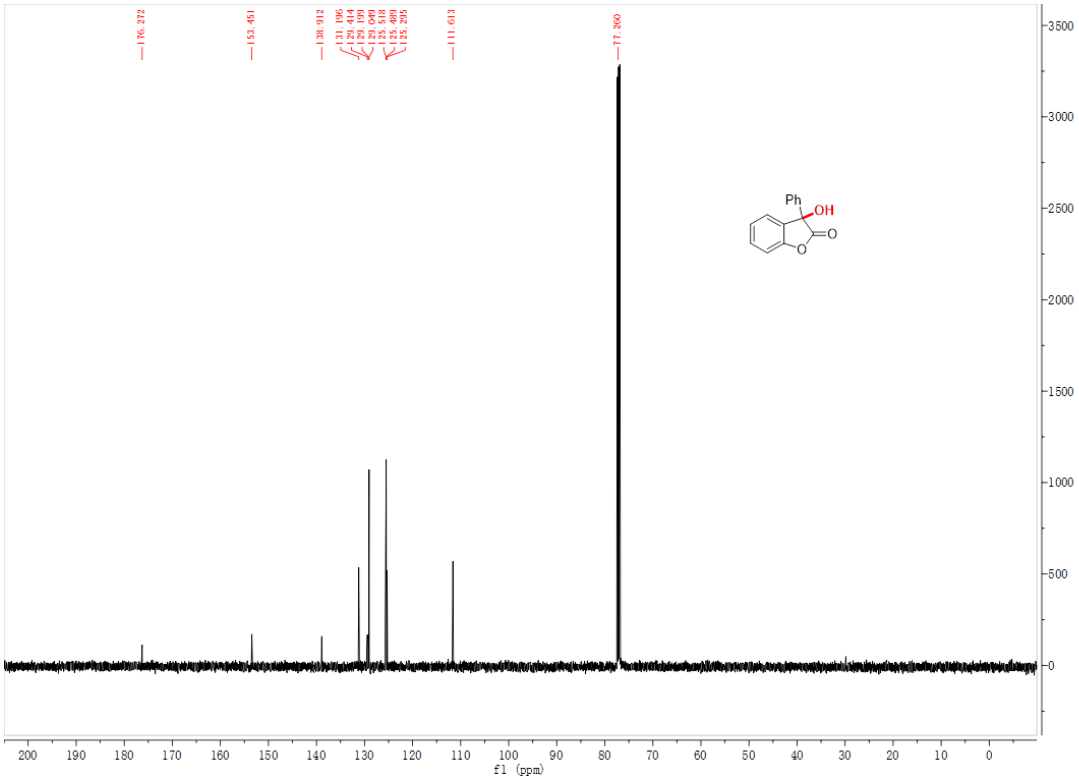

OH
O
N
3.205
2.731
1.605
1.00
1.02
1.01
1.01
3.02
0.98
3.03
f1 (ppm)

5h

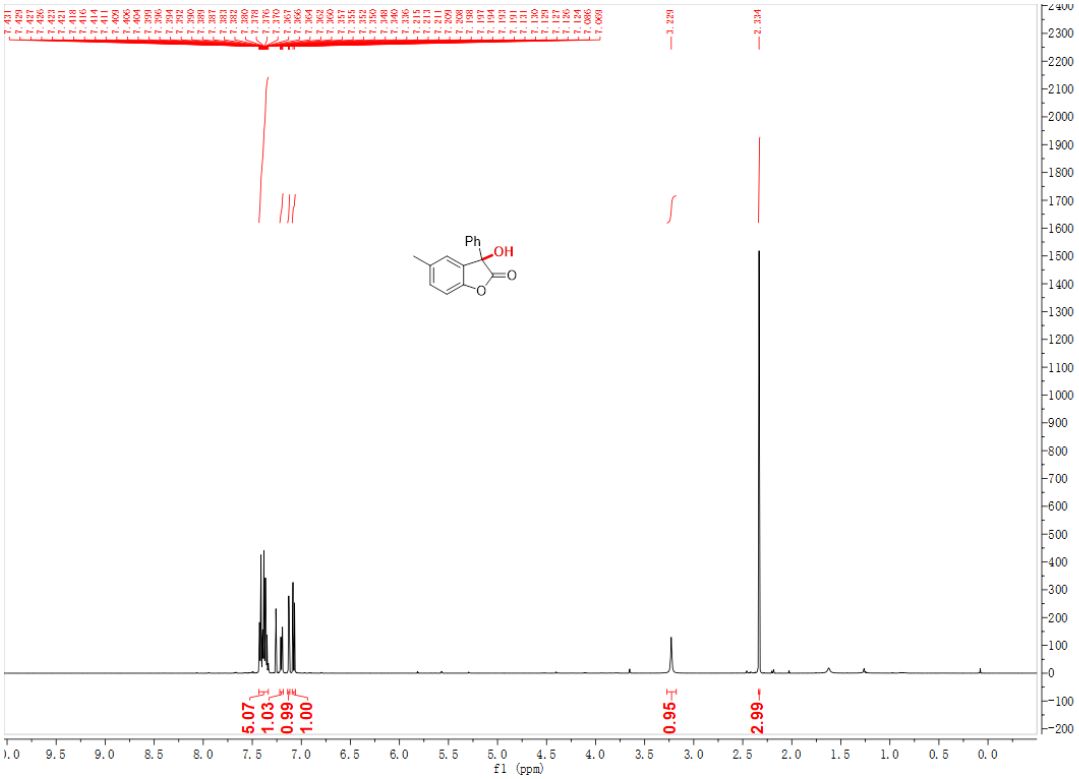

Ph
OH
O
N
Bn
1.99
8.99
1.03
1.01
1.00
1.01
1.03
0.86
f1 (ppm)

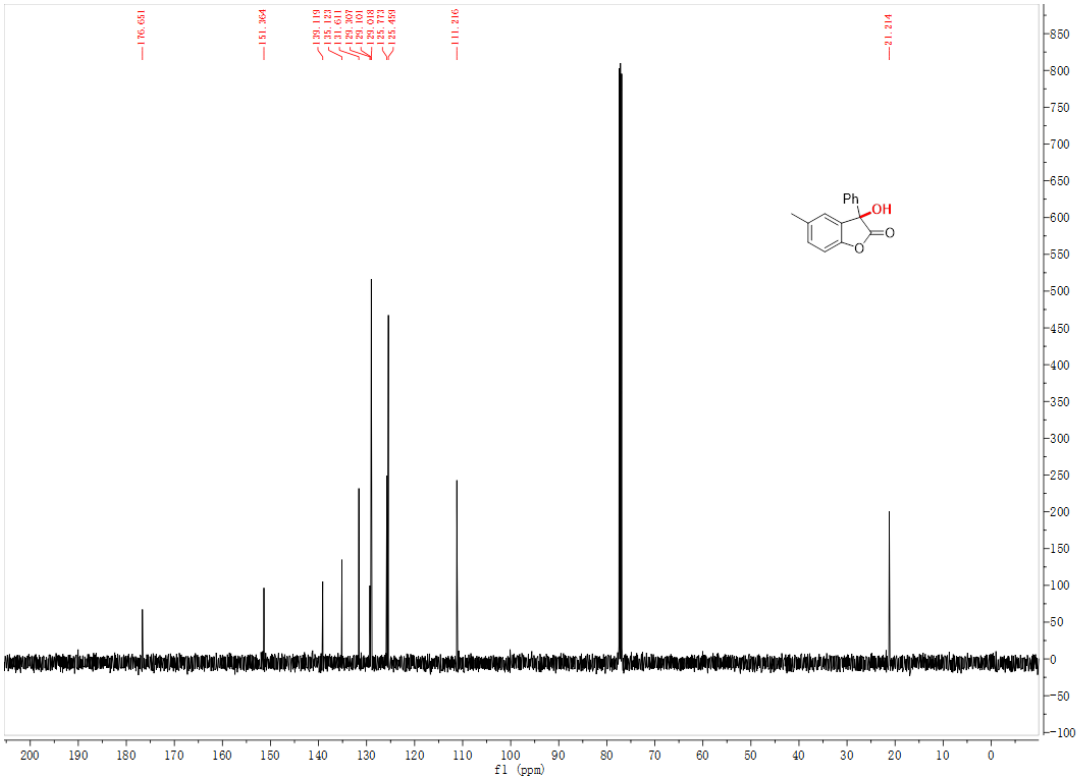
5i


Ph
OH
O
O
6.96
2.00
1.00
f1 (ppm)

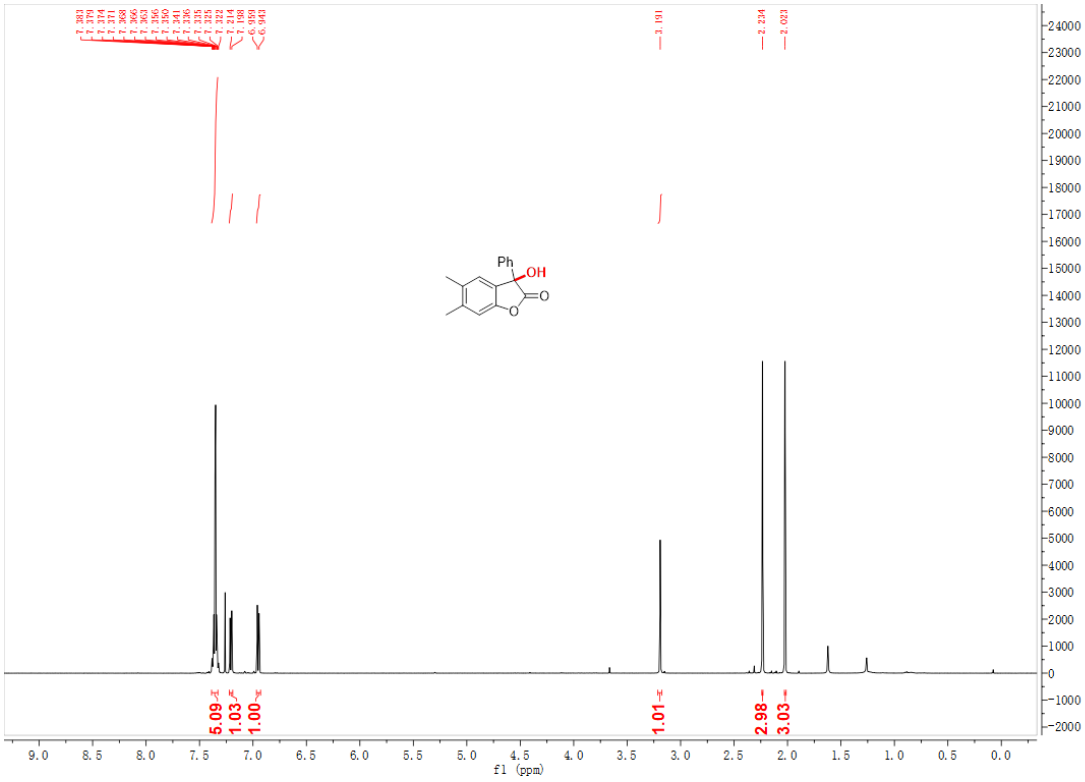

176.372
153.451
138.912
131.195
129.414
129.199
129.060
125.918
125.600
125.295
111.613
77.260
Ph
OH
O
O
f1 (ppm)

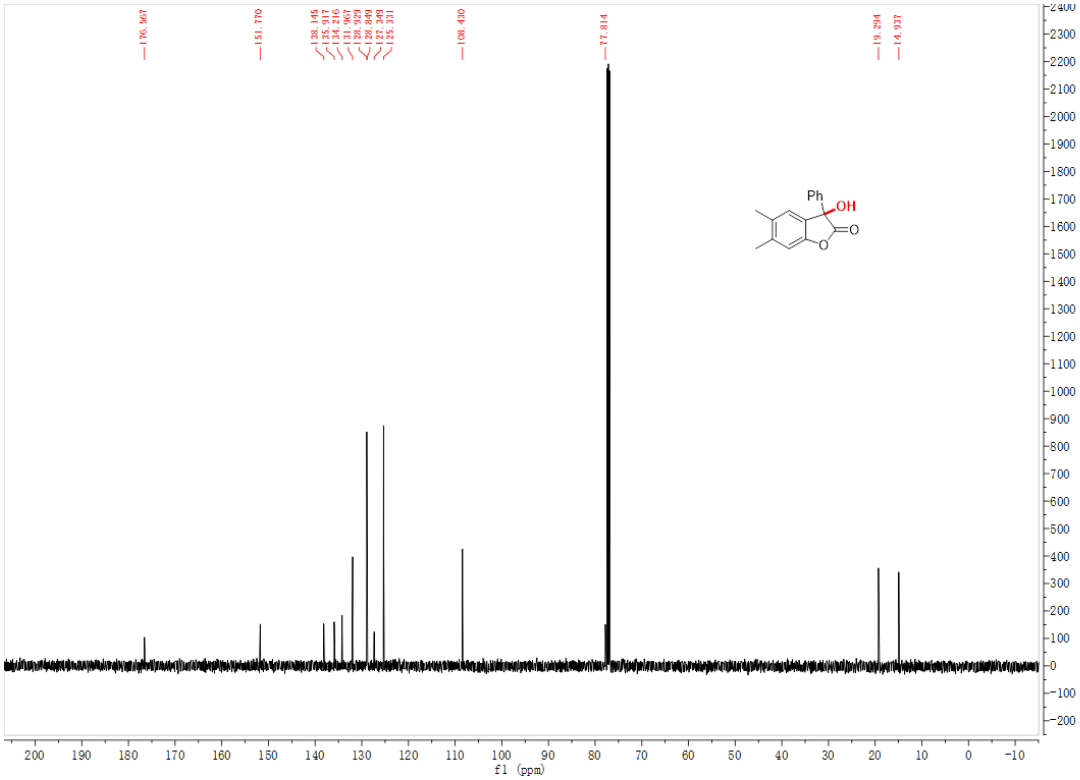
5j


3.229
2.334
Ph
OH
O
O
5.07
1.03
0.99
1.00
0.95
2.99
f1 (ppm)

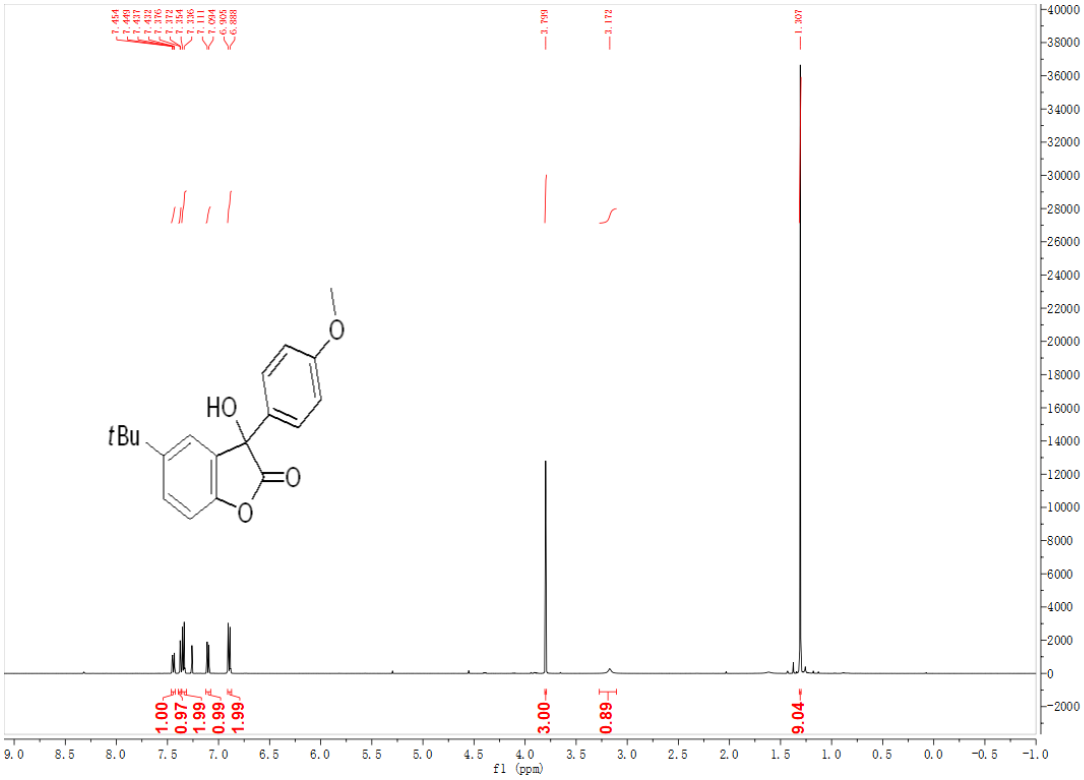

176.651
151.364
139.119
135.123
131.641
129.307
129.101
129.018
125.773
125.469
111.216
21.214
Ph
OH
O
O
f1 (ppm)

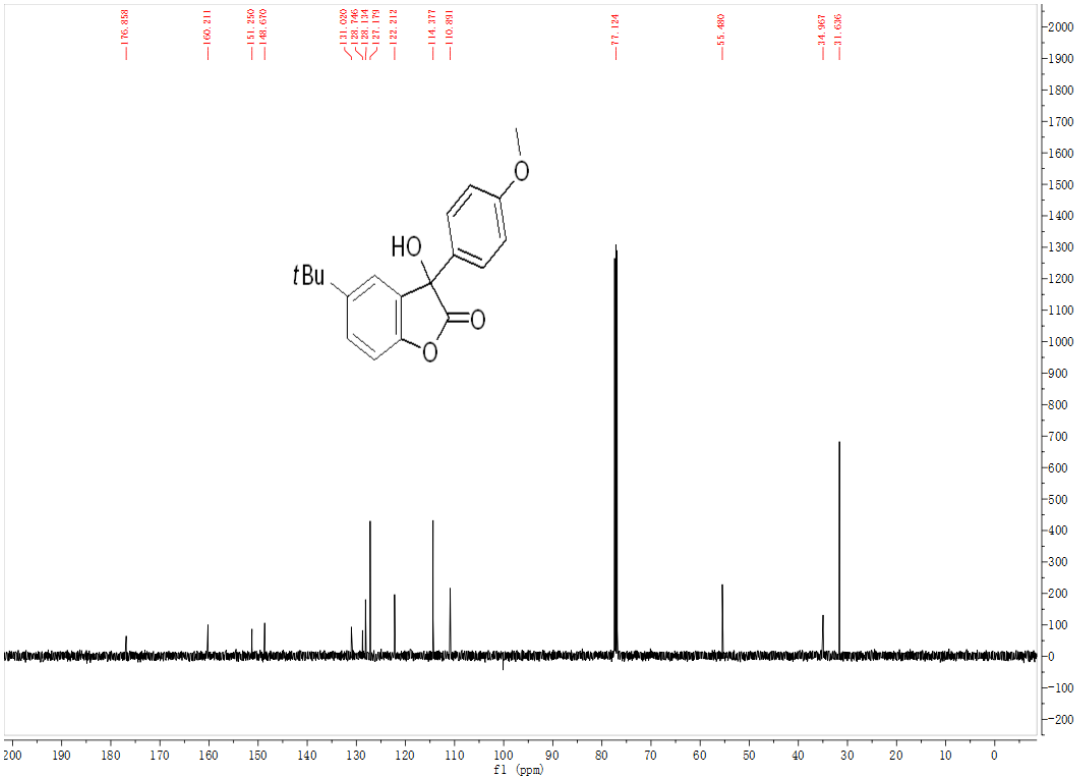
5k


7.383
7.379
7.374
7.371
7.368
7.366
7.363
7.356
7.350
7.341
7.336
7.335
7.325
7.322
7.214
7.198
6.950
6.943
3.101
2.234
2.023
5.09
1.03
1.00
1.01
2.98
3.03
Ph
OH
O
O
f1 (ppm)

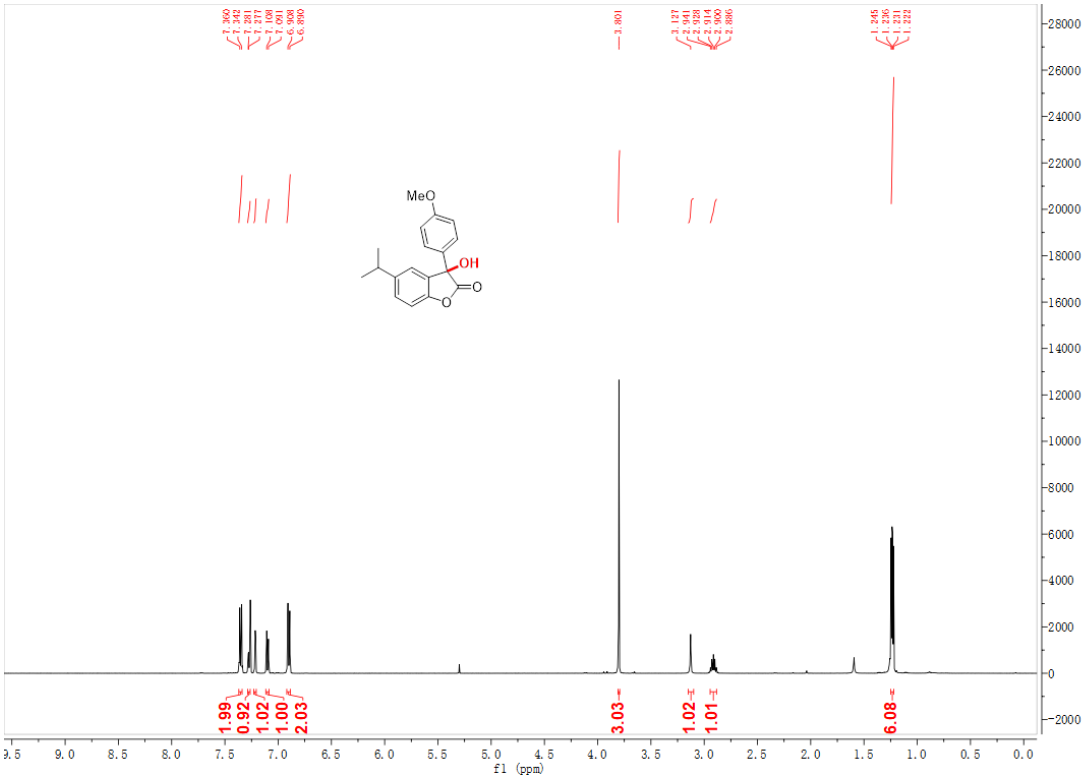

176.567
151.770
138.145
135.917
134.316
131.967
128.929
128.849
127.360
125.331
108.430
77.814
19.294
14.937
Ph
OH
O
f1 (ppm)

5l

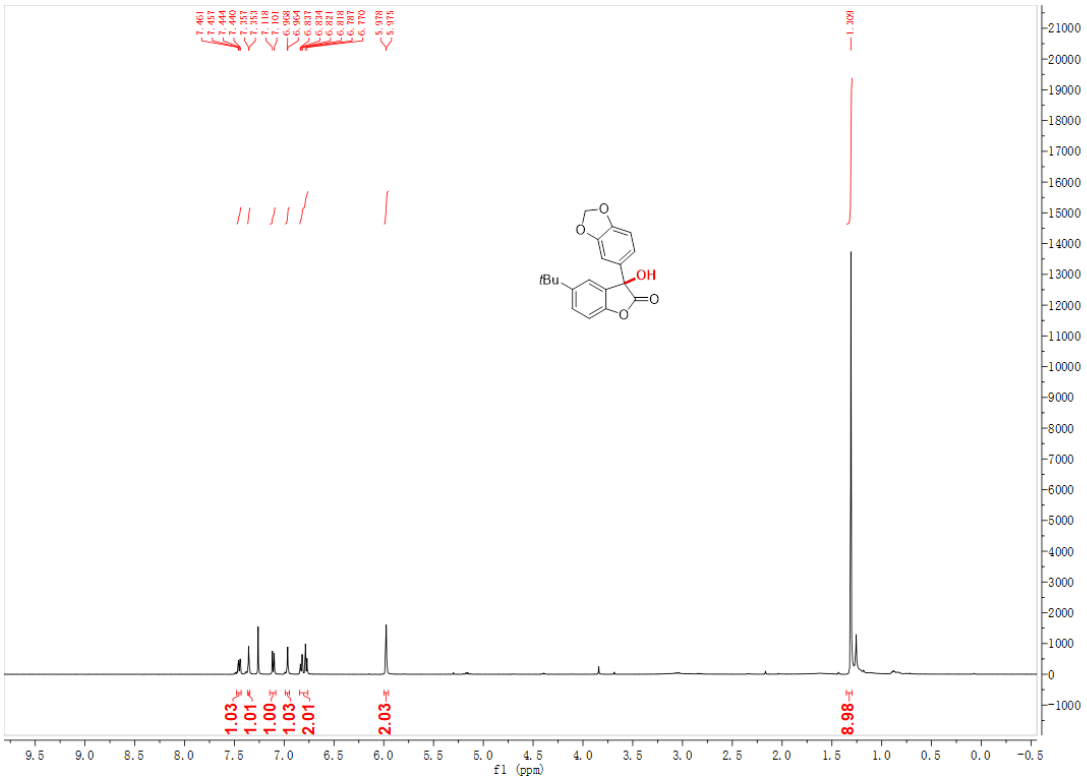

7.464
7.460
7.437
7.432
7.376
7.372
7.354
7.336
7.111
7.094
6.905
6.888
3.799
3.172
1.307
HO
tBu
O
O
1.00
0.97
1.99
0.99
1.99
3.00
0.89
9.04
f1 (ppm)

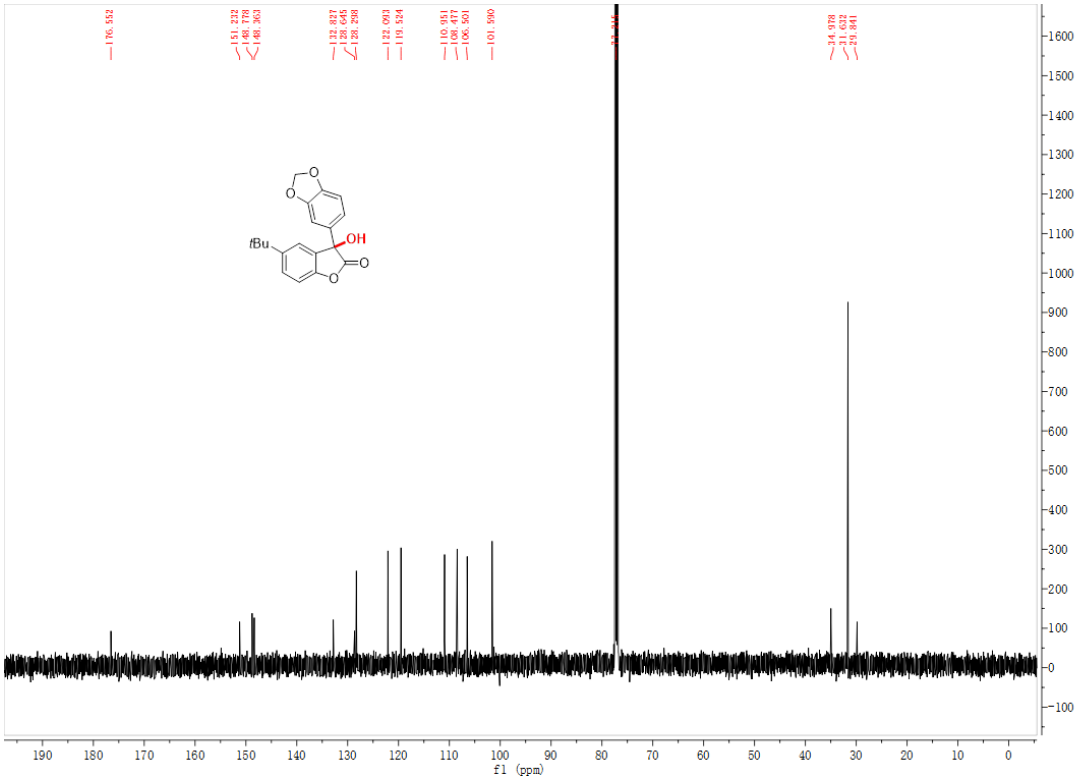

176.858
160.211
151.250
148.670
131.020
128.746
128.144
127.170
122.212
114.377
110.891
77.124
55.480
34.967
31.636
HO
tBu
O
O
O
f1 (ppm)

5m

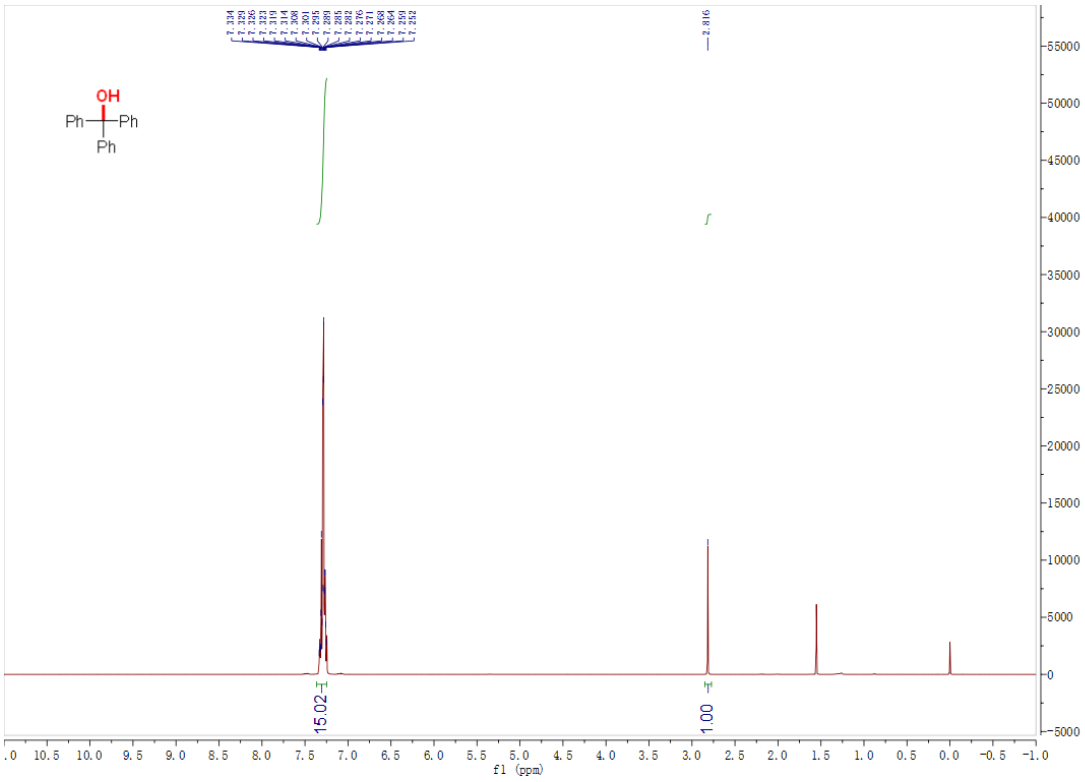

7.360
7.342
7.281
7.277
7.108
7.091
6.908
6.890
3.801
3.137
2.941
2.928
2.914
2.900
2.886
1.245
1.236
1.231
1.222
MeO
OH
O
O
1.99
0.92
1.02
1.00
2.03
3.03
1.02
1.01
6.08
f1 (ppm)

5n

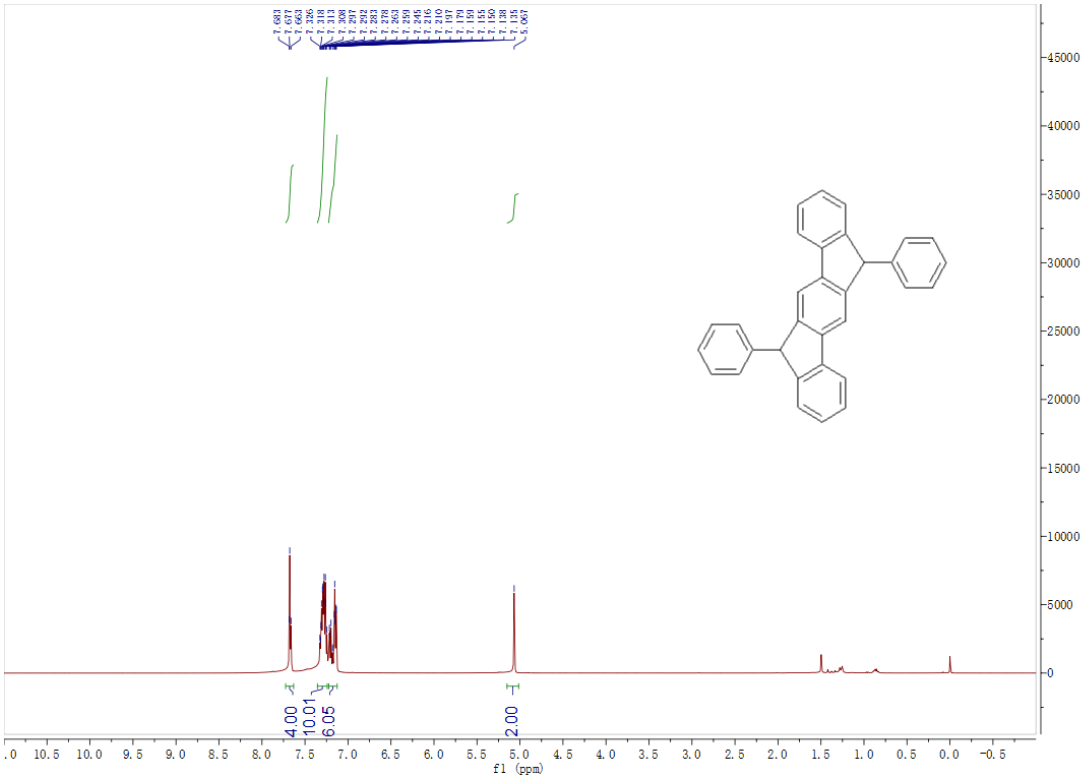

7.461
7.457
7.444
7.440
7.357
7.353
7.118
7.101
6.968
6.964
6.837
6.834
6.821
6.818
6.797
6.793
6.770
5.978
5.975
1.309
OH
tBu
O
1.03
1.01
1.00
1.03
2.01
2.03
8.98
f1 (ppm)


176.552
151.232
148.778
148.363
132.827
128.645
128.298
122.093
119.524
110.951
108.477
106.501
101.590
34.978
31.632
29.841
OH
tBu
O
f1 (ppm)

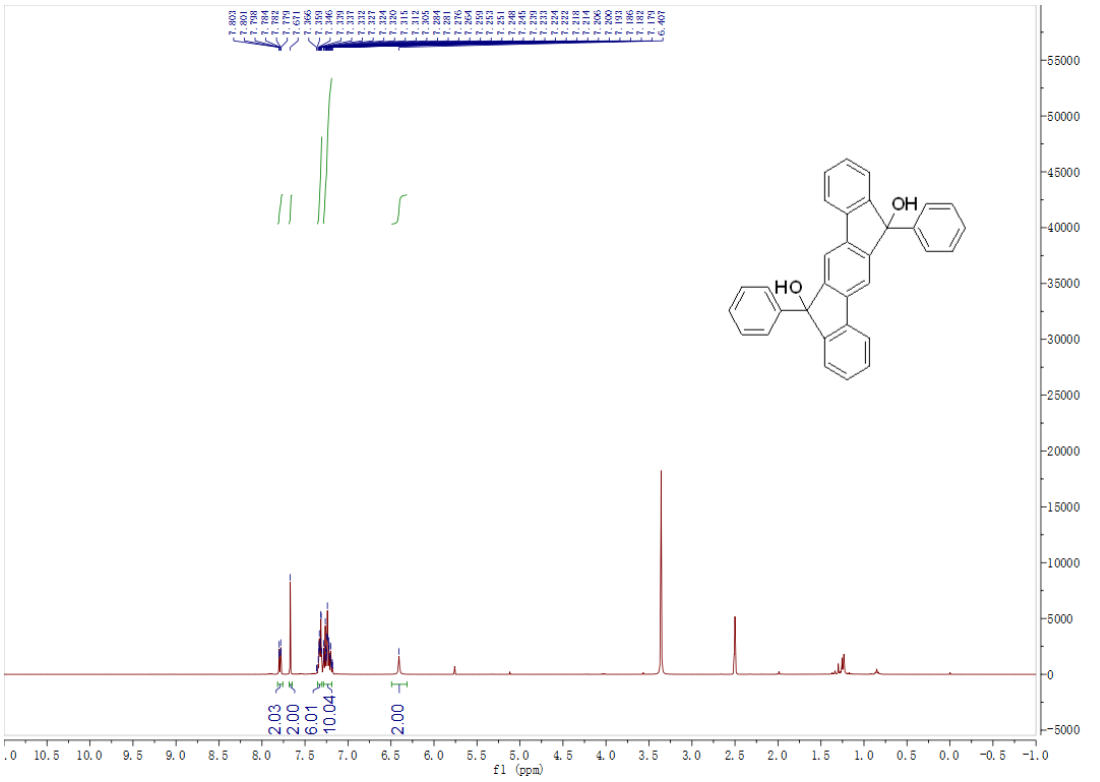
10



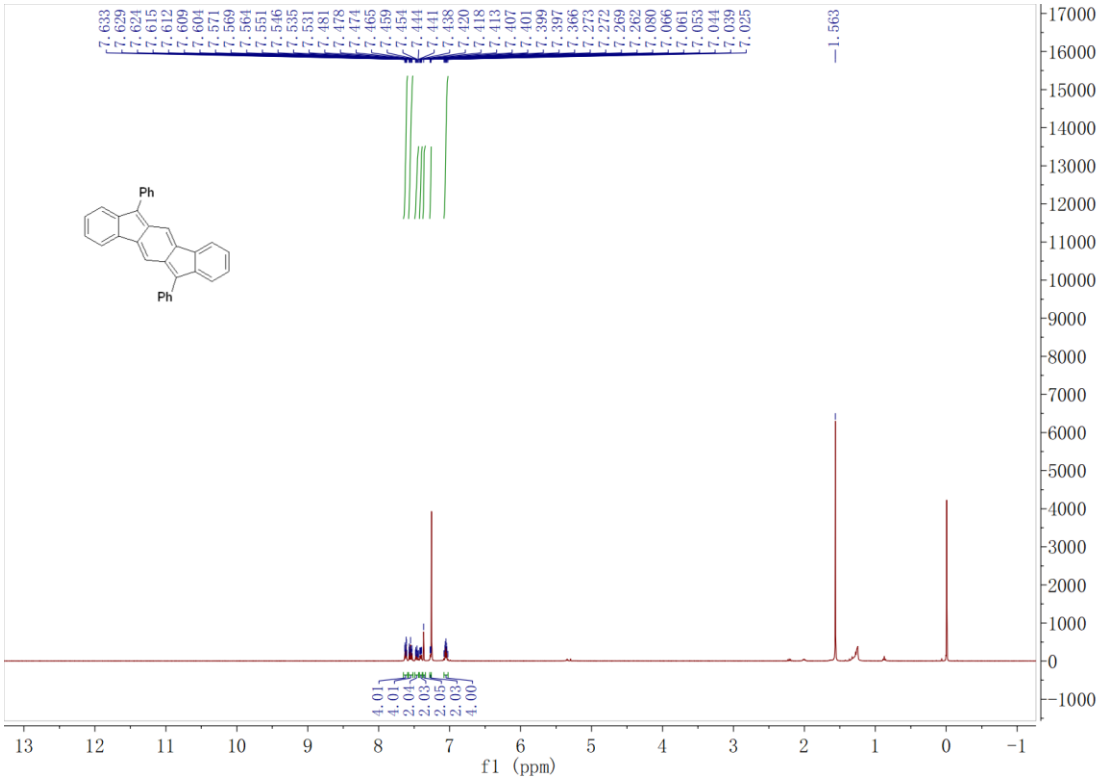
12



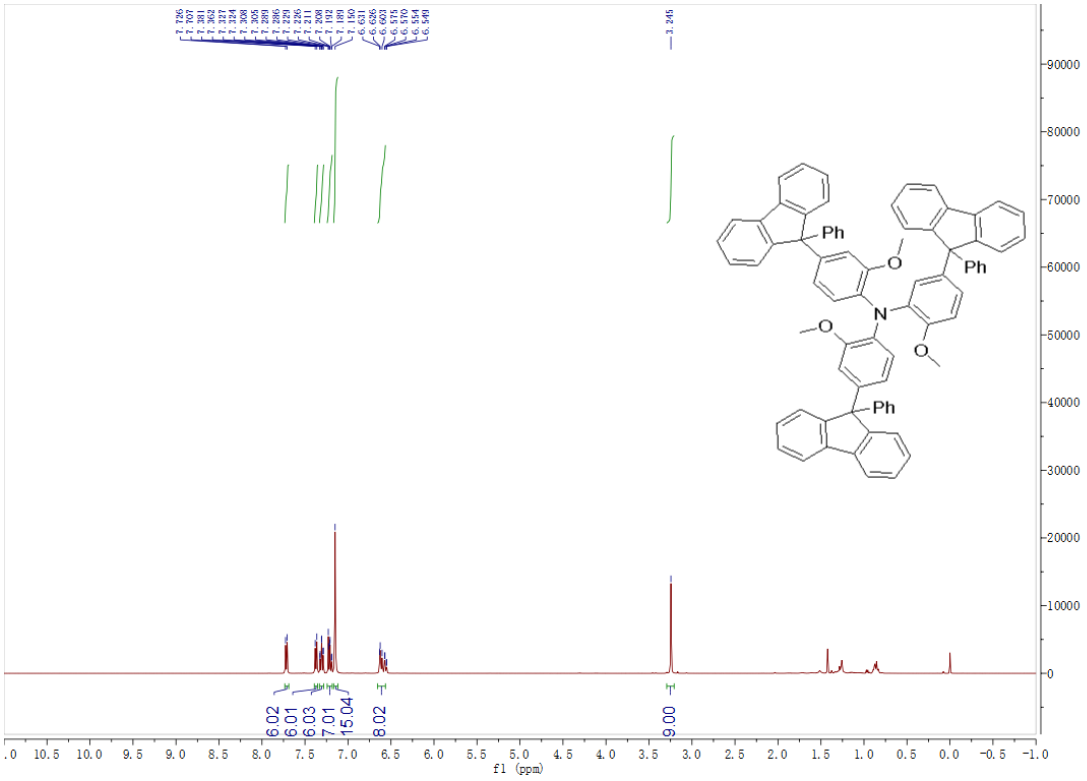
13


OH
HO
2.03
2.00
6.01
10.04
2.00
f1 (ppm)

14


Ph
Ph
1.563
4.01
4.01
2.04
2.03
2.05
2.03
4.00
f1 (ppm)

16


7.726
7.707
7.381
7.362
7.327
7.324
7.308
7.295
7.289
7.286
7.229
7.225
7.211
7.208
7.192
7.189
7.170
7.167
6.631
6.625
6.603
6.575
6.570
6.554
6.549
3.245
Ph
Ph
Ph
O
N
O
O
6.02
6.01
6.03
7.01
15.04
8.02
9.00
f1 (ppm)