Supplementary Materials

Enantioselective synthesis of 3-arylindole atropisomers *via* organocatalytic indolization of iminoquinones

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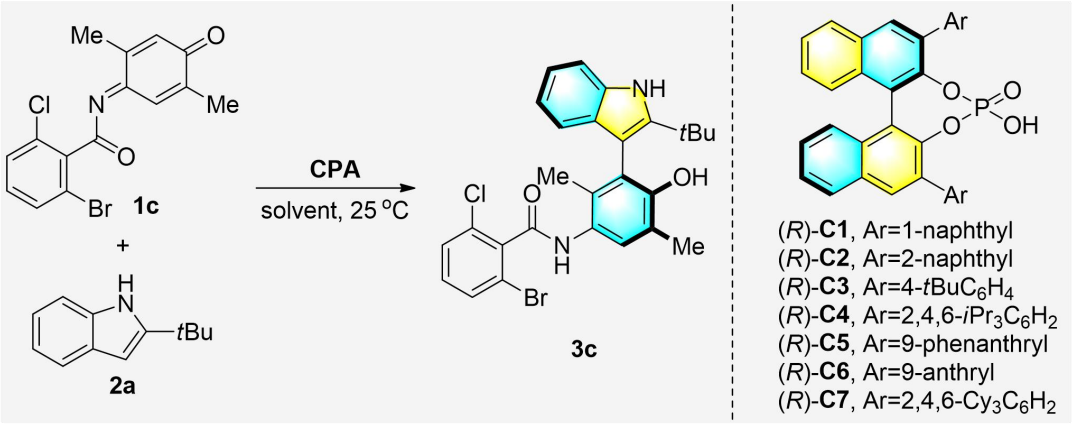
General information

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Dichloromethane was dried over calcium hydride overnight then distilled priori to use. Toluene and THF were distilled over sodium/benzophenone priori to use. Reactions were monitored by TLC on silica gel 60 F254 plates. Visualization on TLC was achieved by use of UV light (254 nm). Column chromatography was performed using Tsingdao silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer operating at 400 MHz for proton and 100 MHz for carbon in $CDCl_3$, acetone-d_6 or DMSO-d_6, and internally referenced to tetramethylsilane signal or residual protio solvent signals. Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Enantioselectivities were recorded on Agilent HPLC using CHIRALPAK columns. The chiral stationary phase was Daicel Chiralpak IA, IC, ID, IE, IG, AD-H, AD-3 or OD-3 column (Ø = 0.46 cm, length = 25.0 cm). IA, IC, ID, IE, IG, AD-H, AD-3 or OD-3 column columns were purchased from Daicel Chemical Industries (Shanghai, China). UV absorption was monitored at 214 nm, 254 nm, 260 nm, 273 nm or 280 nm. High Resolution Mass Spectrometry was performed on a Agilent Technologies 6230 TOF LC/MS under the conditions of electrospray ionization (ESI) in both positive and negative mode. X-ray crystallography analysis of single crystal was performed on an Agilent SuperNova-CCD X-Ray diffractometer.

Table S1. Reaction optimization of 1c with 2-*tert*-butylindole 2a[a]



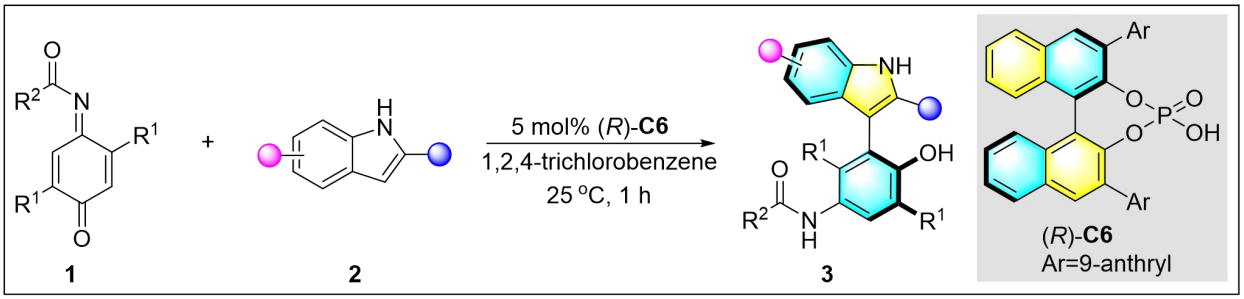
Entry	**CPA**	Solvent	Yield (%)[b]	*ee* (%)[c]
1	(*R*)-**C1**	toluene	60	82
2	(*R*)-**C2**	toluene	86	78
3	(*R*)-**C3**	toluene	89	83
4	(*R*)-**C4**	toluene	50	82
5	(*R*)-**C5**	toluene	87	83
6	(*R*)-**C6**	toluene	76	90
7	(*R*)-**C7**	toluene	46	88
8	(*R*)-**C6**	CH_2Cl_2	74	87
9	(*R*)-**C6**	$ClCH_2CH_2Cl$	64	74
10	(*R*)-**C6**	$PhCF_3$	61	88
11	(*R*)-**C6**	1,2,4-trichlorobenzene	80	94
12[d]	(*R*)-**C6**	1,2,4-trichlorobenzene	84	94
13[e]	(*R*)-**C6**	1,2,4-trichlorobenzene	86	94
14[f]	(*R*)-**C6**	1,2,4-trichlorobenzene	86	94
15[g]	(*R*)-**C6**	1,2,4-trichlorobenzene	81	93
16[h]	(*R*)-**C6**	1,2,4-trichlorobenzene	86	94

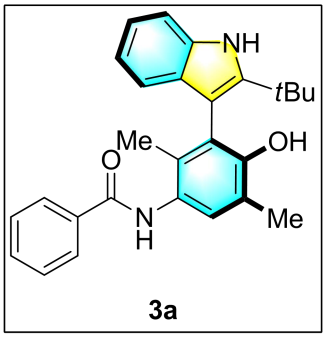
[a]Reaction conditions: **1c** (0.10 mmol), **2a** (0.10 mmol), 5 mol% of **CPA**, solvent (2 mL), at 25 °C for 1 h unless noted otherwise. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Reaction conditions: **1c** (0.12 mmol), **2a** (0.10 mmol) in 1,2,4-trichlorobenzene (2 mL) with 5 mol% of (*R*)-**C6**. [e]Reaction conditions: **1c** (0.14 mmol), **2a** (0.10 mmol) in 1,2,4-trichlorobenzene (2 mL) with 5 mol% of (*R*)-**C6**. [f]Reaction conditions: **1c** (0.16

mmol), **2a** (0.10 mmol) in 1,2,4-trichlorobenzene (2 mL) with 5 mol% of (*R*)-**C6**. [g]Reaction conditions: **1c** (0.14 mmol), **2a** (0.10 mmol) in 1,2,4-trichlorobenzene (2 mL) with 2.5 mol% of (*R*)-**C6**. [h]Reaction conditions: **1c** (0.14 mmol), **2a** (0.10 mmol) in 1,2,4-trichlorobenzene (2 mL) with 7.5 mol% of (*R*)-**C6**.

General procedure for atropselective synthesis of axially chiral 3-arylindoles 3

Chiral phosphoric acid (*R*)-**C6** (5 mol%), **1** (0.28 mmol) and **2** (0.20 mmol) were added to a Schlenk tube, then 4 mL 1,2,4-trichlorobenzene was added via syringe in one portion. When the reaction was completed (about 1 h) and the mixture was purified by preparative TLC (CH_2Cl_2/PE = 5/1 to 6/1) to give the pure products **3**.





3a

N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)benzamide **3a**

88% yield, 78% *ee*.

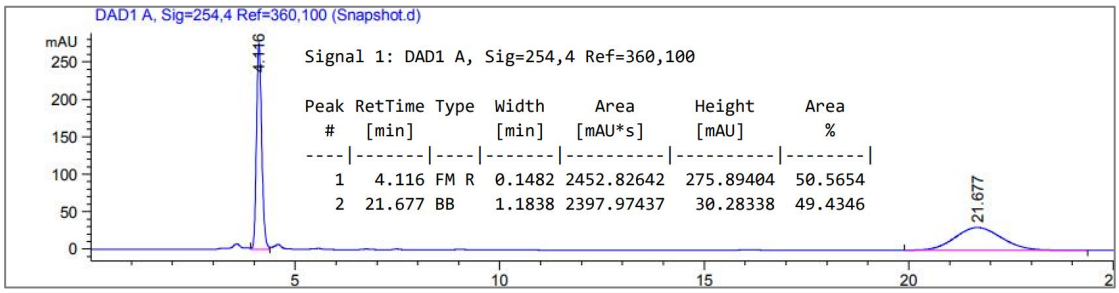
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.65 (s, 1H), 7.59 (s, 1H), 7.56 – 7.47 (m, 3H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.08 – 7.01 (m, 2H), 5.01 (s, 1H), 2.29 (s, 3H), 1.96 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.08, 150.97, 145.46, 135.28, 135.10, 131.75, 130.13, 129.23, 128.88, 127.72, 127.17, 126.64, 122.35, 122.05, 121.52, 120.26, 119.01, 110.56, 103.46, 33.44, 30.15, 16.24, 15.65.

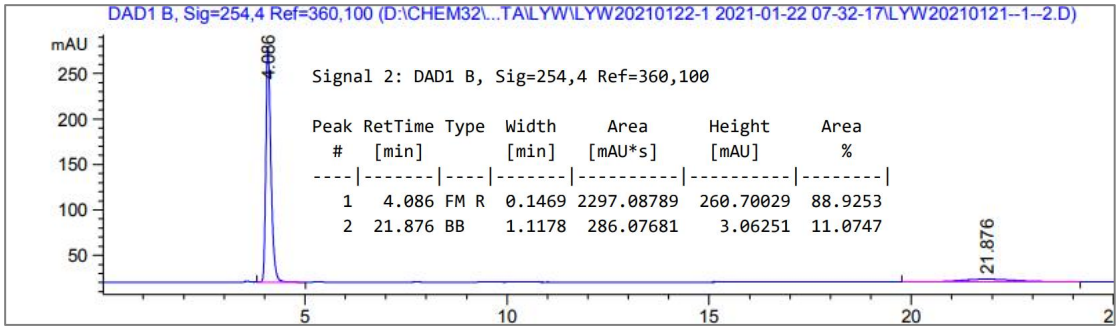
HRMS (ESI) Calcd for $C_{27}H_{29}N_2O_2^+$ $[M+H]^+$ 413.2224; Found: 413.2210.

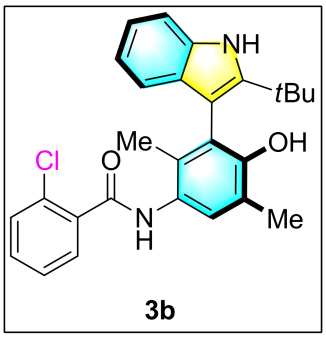
HPLC condition: Chiralpak AD-H (hexane/*i*PrOH = 70/30, 1.0 mL/min, t_R (major) = 4.1 min, t_R (minor) = 21.9 min.)

HPLC spectrum of racemic **3a**



HPLC spectrum of **3a**





3b

N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-2-chlorobenzamide **3b**

85% yield, 86% *ee*.

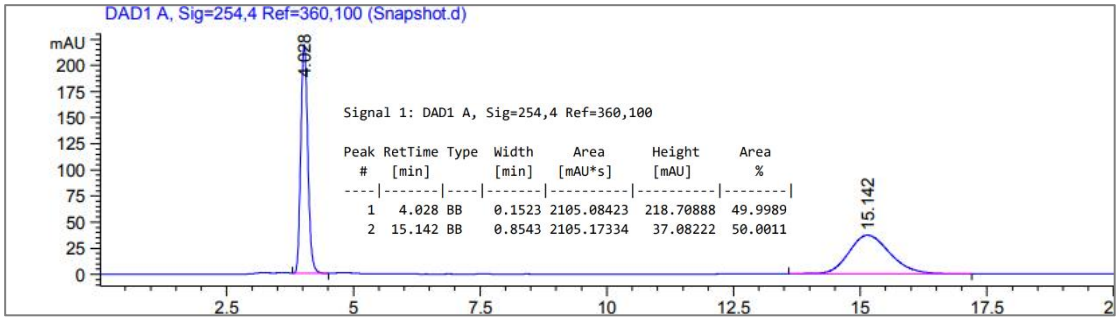
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.27 (s, 1H), 8.88 (s, 1H), 7.69 – 7.62 (m, 1H), 7.52 – 7.41 (m, 3H), 7.40 (s, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.11 – 7.03 (m, 1H), 6.95 – 6.86 (m, 2H), 6.56 (s, 1H), 2.26 (s, 3H), 1.98 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 165.85, 152.83, 146.07, 138.58, 136.64, 132.71, 131.52, 131.38, 130.59, 130.28, 130.03, 128.34, 128.11, 127.87, 123.35, 121.98, 121.33, 119.80, 119.02, 111.47, 104.59, 34.14, 30.43, 16.47, 16.15.

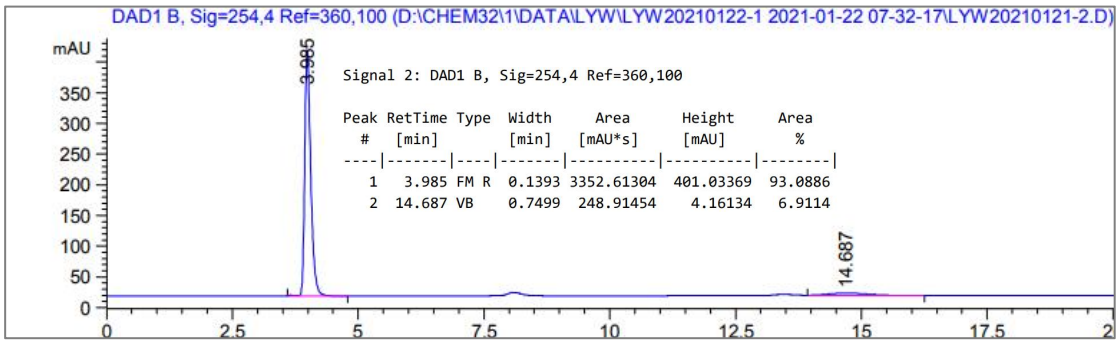
HRMS (ESI) Calcd for $C_{27}H_{28}ClN_2O_2^+$ $[M+H]^+$ 447.1834; Found: 447.1827.

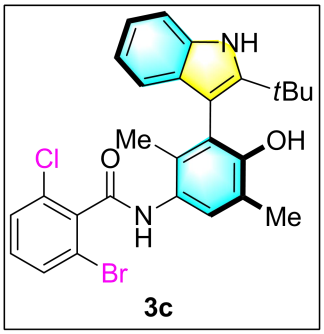
HPLC condition: Chiralpak AD-H (hexane/*i*PrOH = 70/30, 1.0 mL/min, t_R (major) = 4.0 min, t_R (minor) = 14.7 min.)

HPLC spectrum of racemic **3b**



HPLC spectrum of **3b**





3c

2-Bromo-N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3c**

86% yield, 94% *ee*. > 99% *ee* after recrystallization.

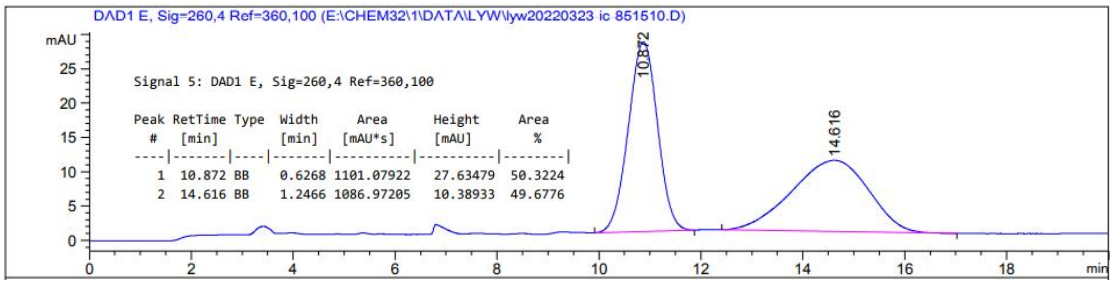
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.26 (s, 1H), 9.05 (s, 1H), 7.64 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.48 (s, 1H), 7.38 – 7.34 (m, 2H), 7.11 – 7.05 (m, 1H), 6.92 (d, *J* = 4.0 Hz, 2H), 6.52 (s, 1H), 2.28 (s, 3H), 2.05 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.23, 152.94, 146.09, 140.11, 136.66, 132.83, 132.68, 132.11, 131.87, 130.26, 129.44, 128.07, 127.86, 123.44, 122.00, 121.41, 121.34, 119.84, 119.01, 111.50, 104.48, 34.14, 30.44, 16.49, 16.24.

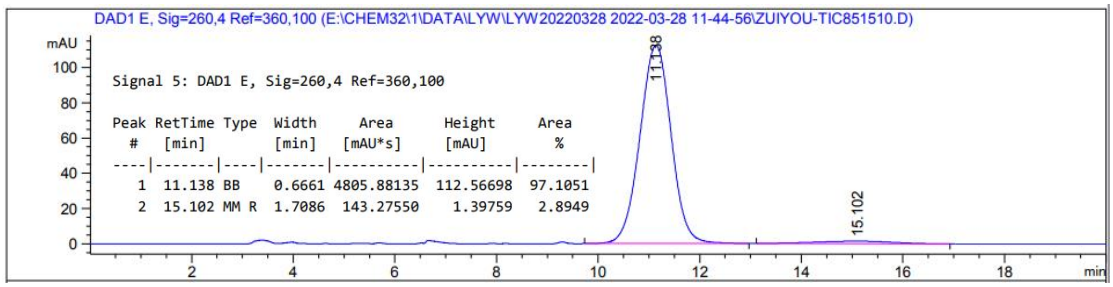
HRMS (ESI) Calcd for $C_{27}H_{27}BrClN_2O_2^+$ $[M+H]^+$ 525.0939; Found: 525.0936.

HPLC condition: Chiralpak IC (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 11.1 min, t_R (minor) = 15.1 min.)

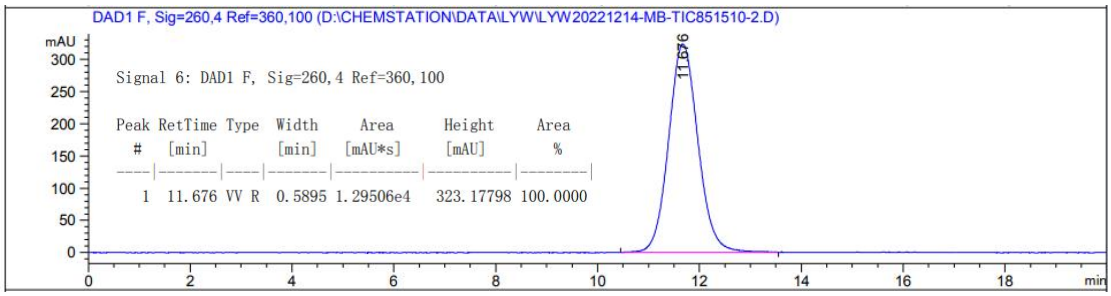
HPLC spectrum of racemic **3c**

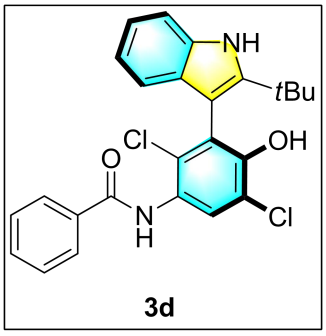


HPLC spectrum of **3c**



HPLC spectrum of **3c** (after recrystallization)





N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-2,5-dichloro-4-hydroxyphenyl)benzamide **3d**

34% yield, 33% *ee*.

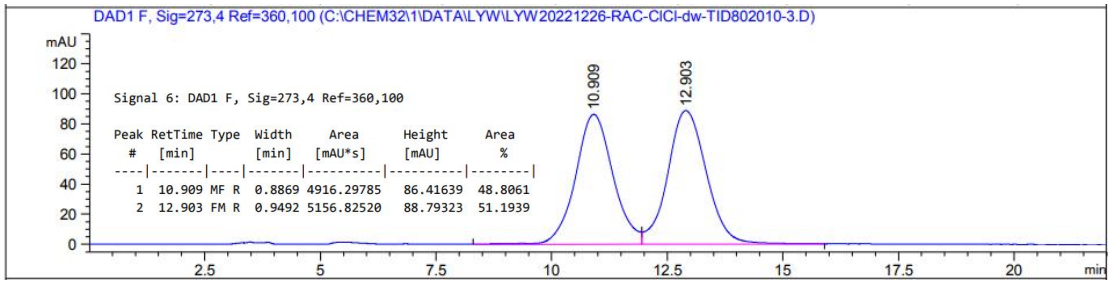
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.42 (s, 1H), 8.36 (s, 1H), 7.94 – 7.91 (m, 2H), 7.60 – 7.56 (m, 1H), 7.53 – 7.49 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.10 – 7.05 (m, 2H), 5.40 (s, 1H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.36, 147.96, 145.72, 134.96, 134.63, 132.32, 129.09, 128.33, 128.24, 127.17, 124.16, 123.47, 122.70, 122.33, 120.65, 118.91, 118.48, 110.81, 101.80, 33.53, 30.12.

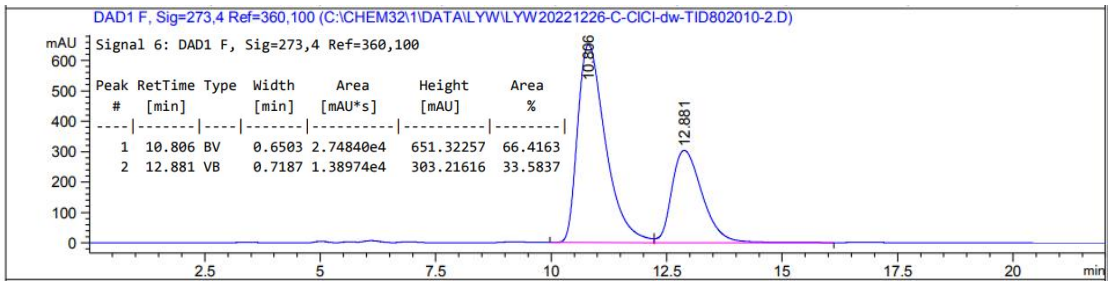
HRMS (ESI) Calcd for $C_{25}H_{23}Cl_2N_2O_2^+$ $[M+H]^+$ 453.1131; Found: 453.1122.

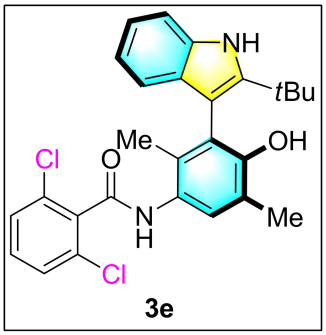
HPLC condition: Chiralpak ID (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 10.8 min, t_R (minor) = 12.9 min.)

HPLC spectrum of racemic **3d**



HPLC spectrum of **3d**





3e

N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-2,6-dichlorobenzamide **3e**

90% yield, 91% *ee*.

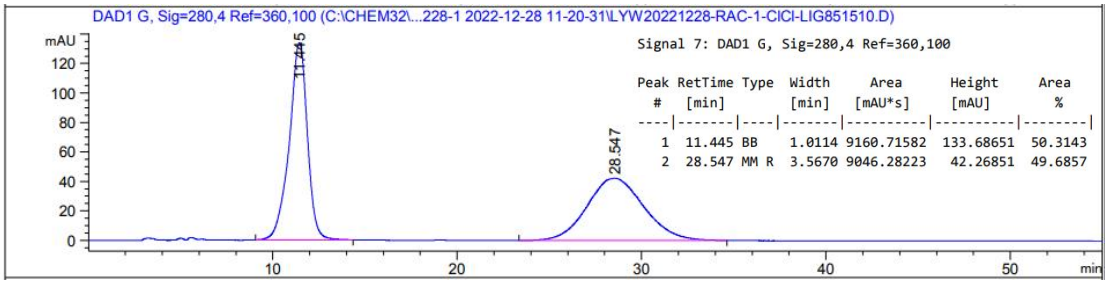
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.91 (s, 1H), 10.00 (s, 1H), 7.55 – 7.53 (m, 2H), 7.47 – 7.42 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.23 (s, 1H), 7.15 (s, 1H), 7.08 – 7.04 (m, 1H), 6.91 – 6.87 (m, 1H), 6.82 (d, J = 7.8 Hz, 1H), 2.23 (s, 3H), 1.89 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 162.48, 152.18, 144.43, 136.97, 135.58, 132.26, 131.33, 131.01, 128.98, 128.18, 127.17, 126.29, 123.27, 120.50, 120.46, 118.41, 117.81, 110.74, 103.98, 33.26, 30.01, 16.52, 15.71.

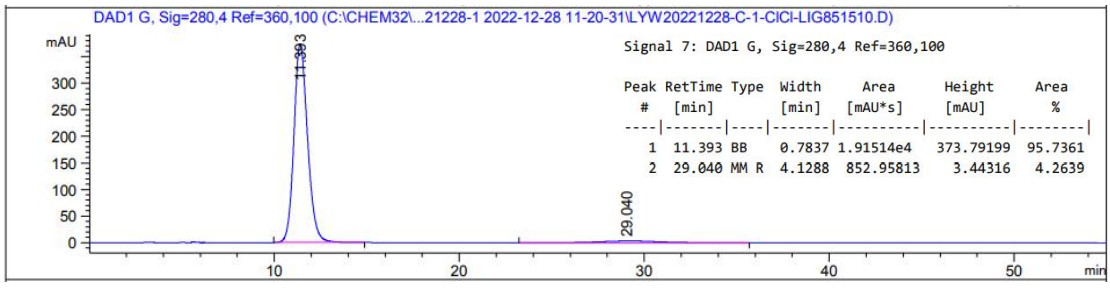
HRMS (ESI) Calcd for $C_{27}H_{27}Cl_2N_2O_2^+$ $[M+H]^+$ 481.1444; Found: 481.1439.

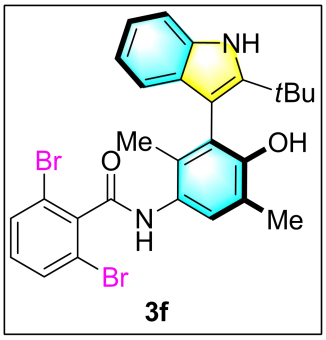
HPLC condition: Chiralpak IG (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 11.4 min, t_R (minor) = 29.0 min.)

HPLC spectrum of racemic **3e**



HPLC spectrum of **3e**





2,6-Dibromo-N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)benzamide **3f**

88% yield, 91% *ee*.

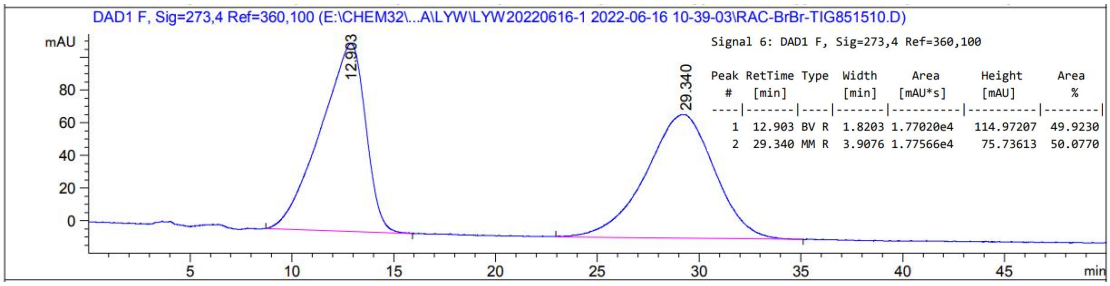
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.90 (s, 1H), 9.92 (s, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 8.1 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.07 – 7.03 (m, 1H), 6.90 – 6.86 (m, 1H), 6.82 (d, J = 7.8 Hz, 1H), 2.22 (s, 3H), 1.91 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 164.44, 152.06, 144.39, 140.63, 135.54, 132.22, 131.71, 131.56, 128.97, 127.01, 126.34, 123.18, 120.46, 120.30, 120.16, 118.36, 117.81, 110.70, 103.97, 33.23, 30.00, 16.54, 15.81.

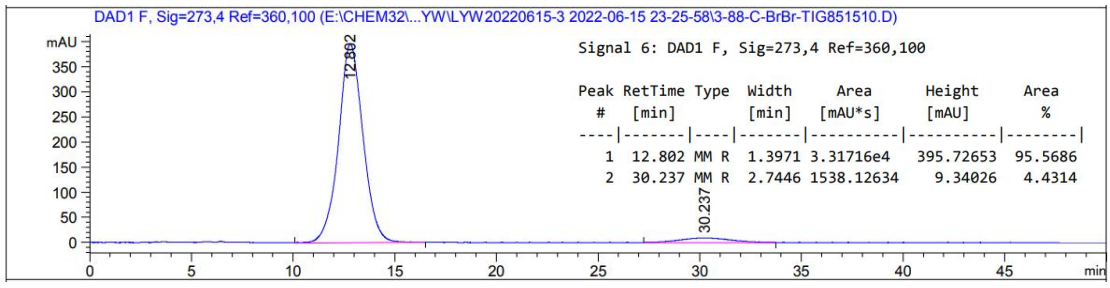
HRMS (ESI) Calcd for $C_{27}H_{27}Br_2N_2O_2^+$ $[M+H]^+$ 569.0434; Found: 569.0432.

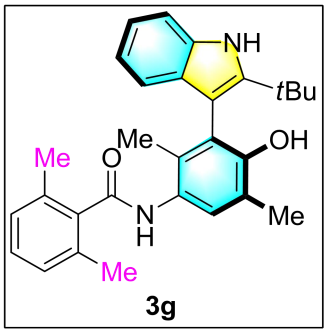
HPLC condition: Chiralpak IG (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 12.8 min, t_R (minor) = 30.2 min.)

HPLC spectrum of racemic **3f**



HPLC spectrum of **3f**





3g

N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-2,6-dimethylbenzamide **3g**

85% yield, 84% *ee*.

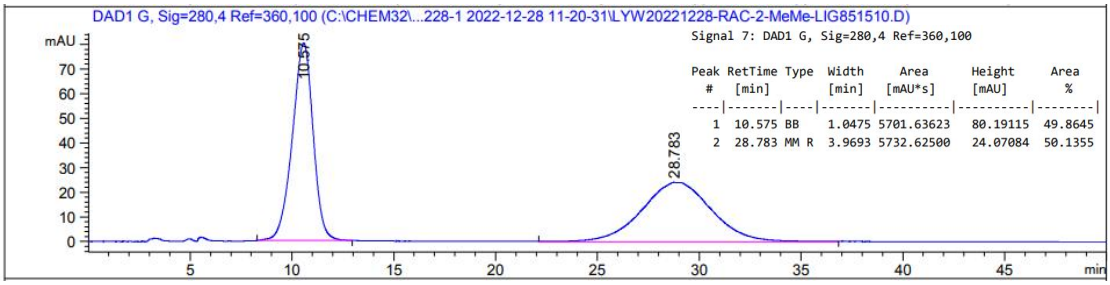
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.36 (s, 1H), 8.81 (s, 1H), 7.44 (s, 1H), 7.36 – 7.34 (m, 1H), 7.19 – 7.15 (m, 1H), 7.10 – 7.05 (m, 3H), 6.95 – 6.90 (m, 2H), 6.50 (s, 1H), 2.43 (s, 6H), 2.29 (s, 3H), 2.02 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 169.20, 152.68, 146.08, 139.85, 136.65, 134.85, 132.68, 130.25, 128.98, 128.47, 128.24, 128.05, 123.37, 121.94, 121.28, 119.77, 119.00, 111.50, 104.49, 34.12, 30.45, 19.56, 16.50, 16.36.

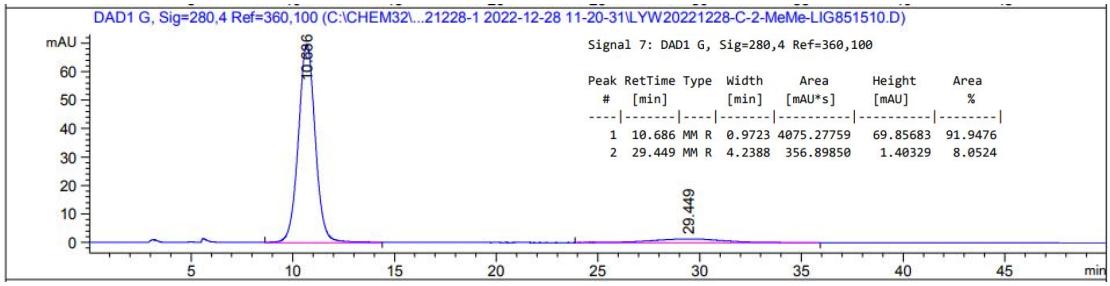
HRMS (ESI) Calcd for $C_{29}H_{33}N_2O_2^+$ $[M+H]^+$ 441.2537; Found: 441.2533.

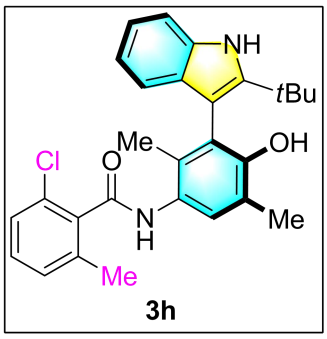
HPLC condition: Chiralpak IG (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 10.7 min, t_R (minor) = 29.4 min.)

HPLC spectrum of racemic **3g**



HPLC spectrum of **3g**





3h

N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-2-chloro-6-methylbenzamide **3h**

94% yield, 91% *ee*.

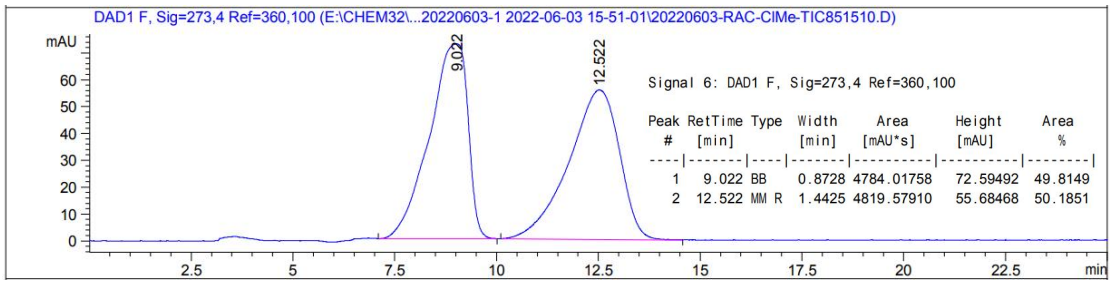
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.36 (s, 1H), 9.00 (s, 1H), 7.46 (s, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 4.9 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.10 – 7.06 (m, 1H), 6.95 – 6.90 (m, 2H), 6.52 (s, 1H), 2.48 (s, 3H), 2.29 (s, 3H), 2.05 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 166.18, 152.80, 146.06, 138.79, 137.86, 136.62, 132.80, 131.14, 130.38, 130.18, 129.35, 128.18, 128.08, 127.32, 123.41, 121.93, 121.32, 119.76, 118.94, 111.51, 104.38, 34.09, 30.43, 19.56, 16.49, 16.26.

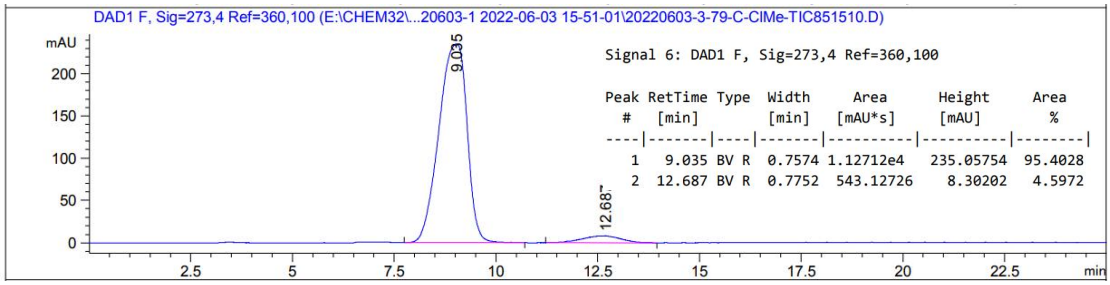
HRMS (ESI) Calcd for $C_{28}H_{30}ClN_2O_2^+$ $[M+H]^+$ 461.1990; Founded: 461.1987.

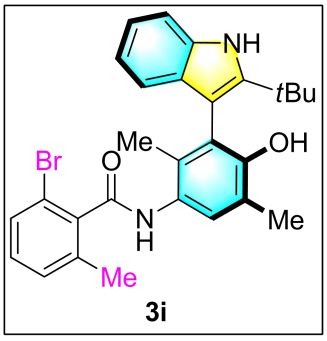
HPLC condition: Chiralpak IC (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 9.0 min, t_R (minor) = 12.7 min.)

HPLC spectrum of racemic **3h**



HPLC spectrum of **3h**





3i

2-Bromo-N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-methylbenzamide **3i**

92% yield, 90% *ee*.

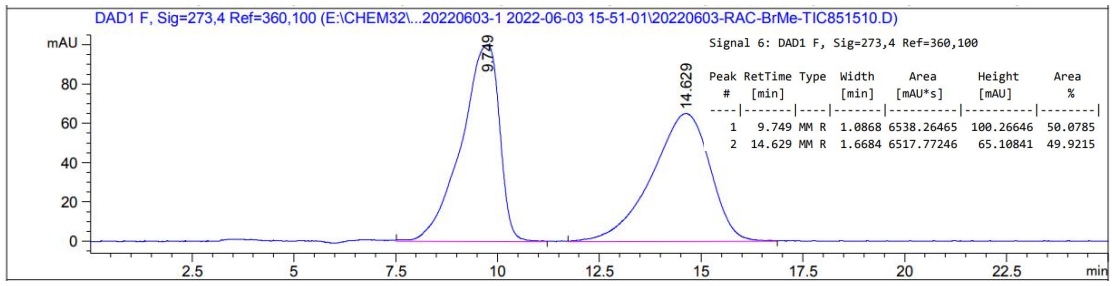
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.35 (s, 1H), 8.96 (s, 1H), 7.50 (s, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.95 – 6.90 (m, 2H), 6.51 (s, 1H), 2.49 (s, 3H), 2.29 (s, 3H), 2.06 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 167.02, 152.76, 146.06, 140.85, 137.94, 136.61, 132.72, 130.66, 130.53, 130.19, 129.88, 128.09, 123.38, 121.93, 121.28, 120.12, 119.76, 118.95, 111.50, 104.38, 34.08, 30.43, 19.81, 16.50, 16.32.

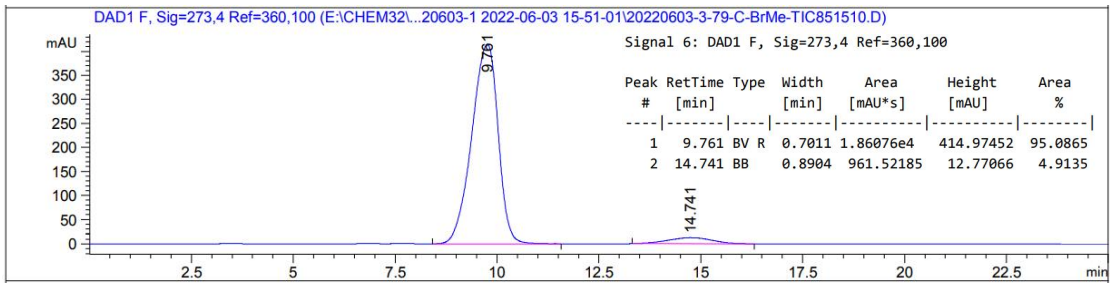
HRMS (ESI) Calcd for $C_{28}H_{30}BrN_2O_2^+$ $[M+H]^+$ 505.1485; Found: 505.1483.

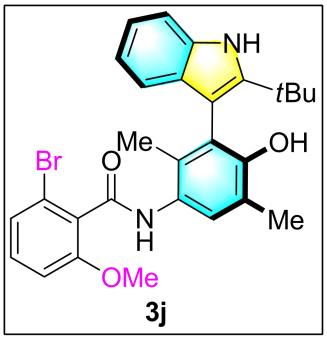
HPLC condition: Chiralpak IC (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 9.8 min, t_R (minor) = 14.7 min.)

HPLC spectrum of racemic **3i**



HPLC spectrum of **3i**





3j

2-Bromo-N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-methoxybenzamide **3j**

80% yield, 86% *ee*. Reaction time: 4 h.

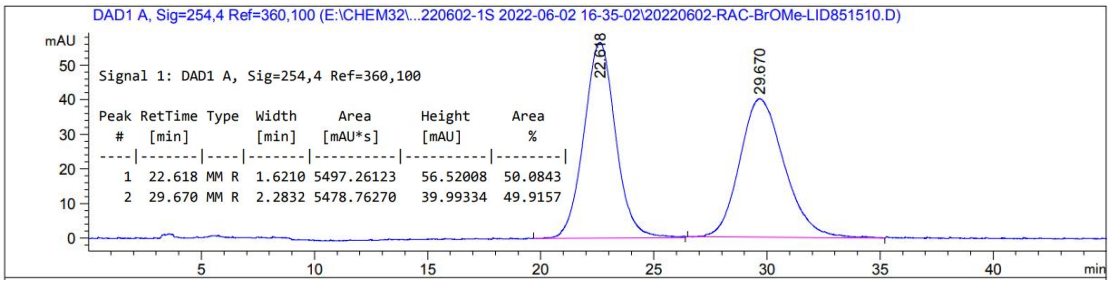
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.35 (s, 1H), 8.82 (s, 1H), 7.46 (s, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.28 (t, J = 8.2 Hz, 1H), 7.21 (dd, J = 8.0, 0.8 Hz, 1H), 7.09 – 7.05 (m, 2H), 6.92 – 6.91 (m, 2H), 6.46 (s, 1H), 3.85 (s, 3H), 2.28 (s, 3H), 2.04 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.66, 158.41, 152.62, 146.04, 136.64, 132.76, 131.54, 130.73, 130.19, 128.32, 128.21, 125.08, 123.32, 121.90, 121.12, 120.96, 119.73, 118.96, 111.52, 111.25, 104.45, 56.48, 34.09, 30.43, 16.49, 16.10.

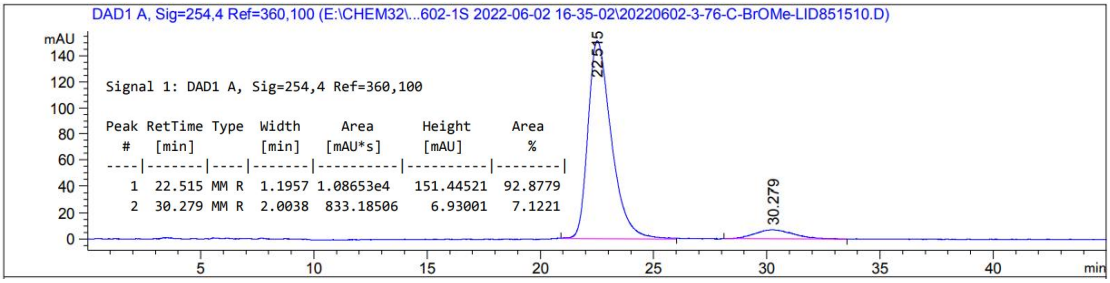
HRMS (ESI) Calcd for $C_{28}H_{30}BrN_2O_3^+$ $[M+H]^+$ 521.1434; Found: 521.1423.

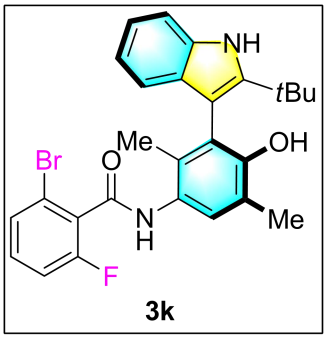
HPLC condition: Chiralpak ID (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 22.5 min, t_R (minor) = 30.3 min.)

HPLC spectrum of racemic **3j**



HPLC spectrum of **3j**





2-Bromo-N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-fluorobenzamide

3k

89% yield, 91% *ee*.

^{1}H NMR (400 MHz, Acetone-d_6) δ 10.32 (s, 1H), 9.19 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.43 – 7.36 (m, 2H), 7.29 – 7.24 (m, 1H), 7.11 – 7.05 (m, 1H), 6.92 (d, *J* = 3.8 Hz, 2H), 6.57 (s, 1H), 2.29 (s, 3H), 2.03 (s, 3H), 1.35 (s, 9H).

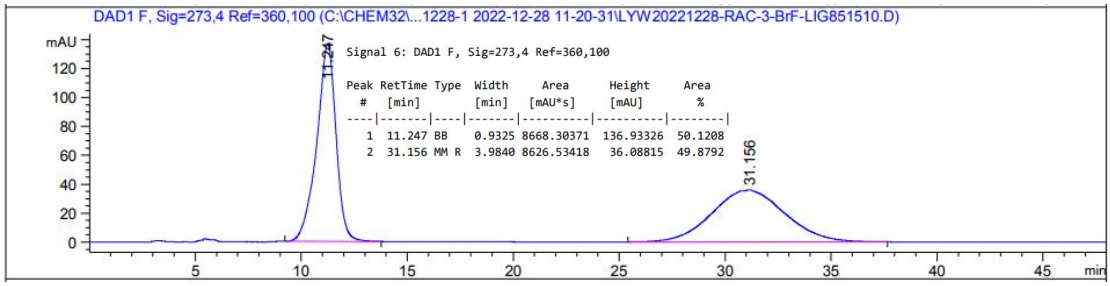
^{13}C NMR (100 MHz, Acetone-d_6) δ 162.33, 161.37, 158.89, 152.98, 146.06, 136.61, 132.77, 132.34, 132.25, 130.16, 129.73, 129.50, 129.35, 129.32, 128.10, 127.76, 123.46, 121.95, 121.42, 121.13, 121.07, 119.79, 118.92, 115.78, 115.56, 111.49, 104.35, 34.09, 30.41, 16.47, 16.11.

^{19}F NMR (376 MHz, Acetone-d_6) δ -114.34.

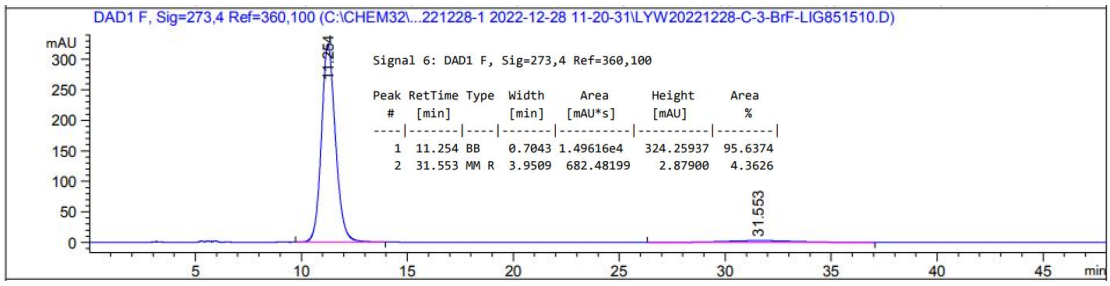
HRMS (ESI) Calcd for $C_{27}H_{27}BrFN_2O_2^+$ $[M+H]^+$ 509.1234; Found: 509.1234.

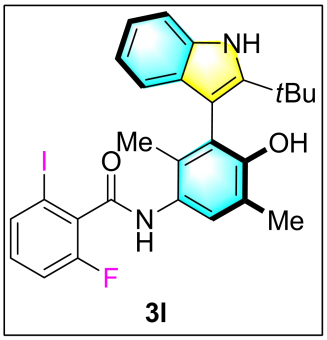
HPLC condition: Chiralpak IG (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 11.3 min, t_R (minor) = 31.6 min.)

HPLC spectrum of racemic **3k**



HPLC spectrum of **3k**





3l

N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-2-fluoro-6-iodobenzamide **3l** 85% yield, 90% *ee*.

^{1}H NMR (400 MHz, Acetone-d_6) δ 10.11 (s, 1H), 8.92 (s, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.28 (s, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.07 – 6.97 (m, 2H), 6.89 – 6.83 (m, 1H), 6.71 (d, J = 3.8 Hz, 2H), 6.34 (s, 1H), 2.07 (s, 3H), 1.83 (s, 3H), 1.13 (s, 9H).

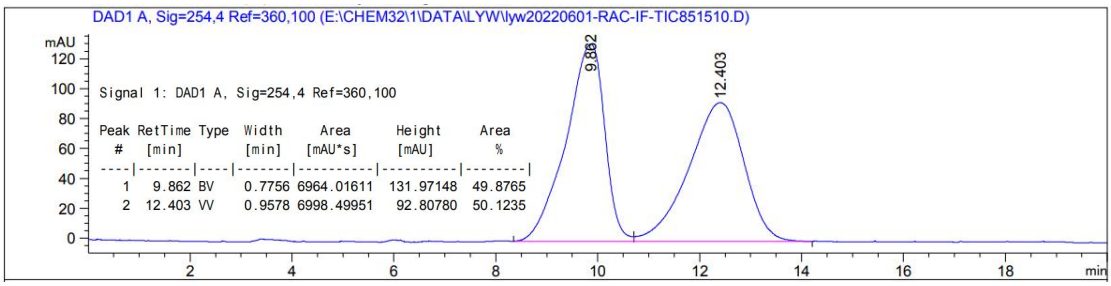
^{13}C NMR (100 MHz, Acetone-d_6) δ 164.15, 160.55, 158.06, 152.90, 146.03, 136.57, 135.79, 135.75, 133.54, 133.32, 132.70, 132.64, 132.56, 130.13, 128.03, 127.76, 123.42, 121.92, 121.33, 119.76, 118.90, 116.40, 116.18, 111.49, 104.31, 94.39, 94.36, 34.06, 30.41, 16.50, 16.17.

^{19}F NMR (376 MHz, Acetone-d_6) δ -113.54.

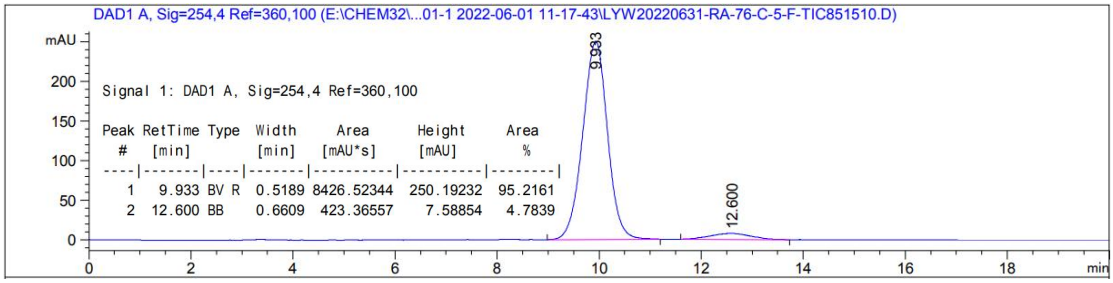
HRMS (ESI) Calcd for $C_{27}H_{27}FIN_2O_2^+$ $[M+H]^+$ 557.1096; Found: 557.1088.

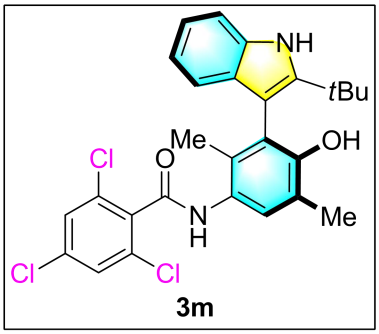
HPLC condition: Chiralpak IC (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 9.9 min, t_R (minor) = 12.6 min.)

HPLC spectrum of racemic **3l**



HPLC spectrum of **3l**





N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-2,4,6-trichlorobenzamide

3m

93% yield, 94% *ee*.

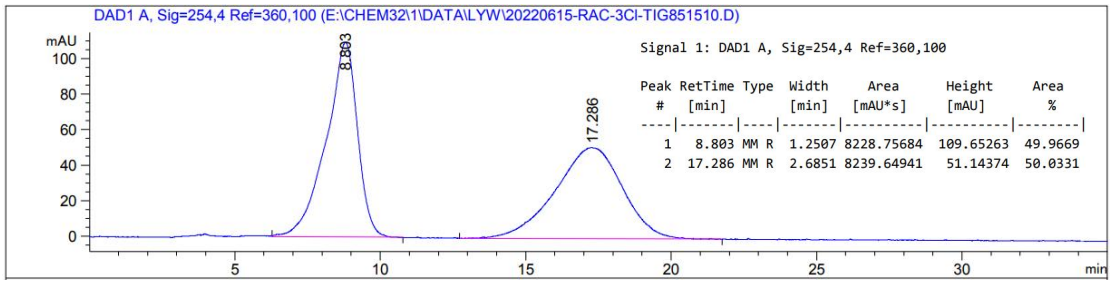
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.30 (s, 1H), 9.22 (s, 1H), 7.58 (s, 2H), 7.43 (s, 1H), 7.37 – 7.35 (m, 1H), 7.11 – 7.05 (m, 1H), 6.92 (d, *J* = 3.8 Hz, 2H), 6.57 (s, 1H), 2.28 (s, 3H), 2.02 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 162.61, 153.03, 146.06, 136.98, 136.60, 135.67, 133.66, 132.73, 130.16, 128.74, 127.93, 127.52, 123.48, 121.96, 121.49, 119.80, 118.92, 111.48, 104.31, 34.09, 30.41, 16.47, 16.16.

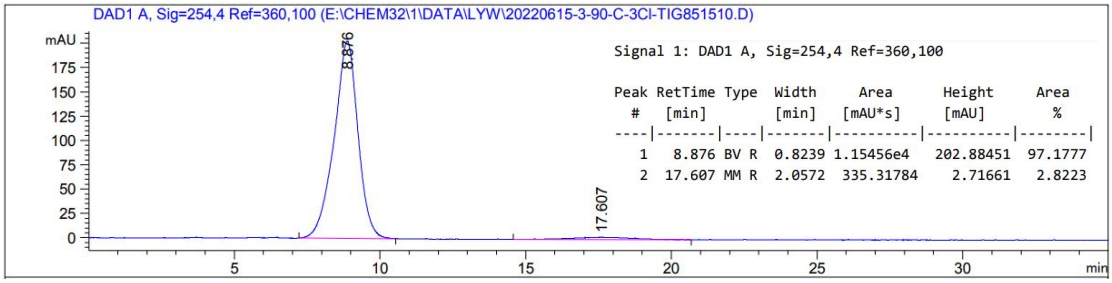
HRMS (ESI) Calcd for $C_{27}H_{26}Cl_3N_2O_2^+$ $[M+H]^+$ 515.1054; Found: 515.1055.

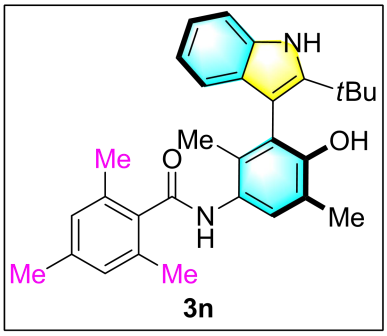
HPLC condition: Chiralpak IG (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 8.9 min, t_R (minor) = 17.6 min.)

HPLC spectrum of racemic **3m**



HPLC spectrum of **3m**





N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-2,4,6-trimethylbenzamide

3n

90% yield, 87% *ee*.

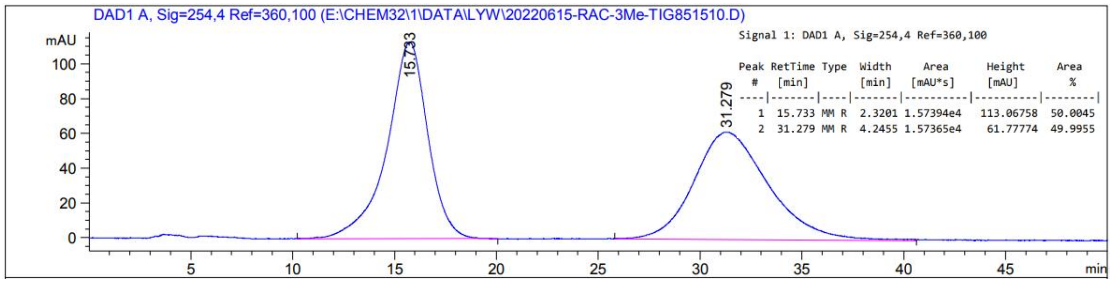
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.40 (s, 1H), 8.77 (s, 1H), 7.43 (s, 1H), 7.36 – 7.33 (m, 1H), 7.10 – 7.05 (m, 1H), 6.96 – 6.88 (m, 4H), 6.47 (s, 1H), 2.39 (s, 6H), 2.29 (s, 3H), 2.28 (s, 3H), 2.03 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 169.51, 152.62, 146.08, 138.39, 137.10, 136.65, 134.79, 132.66, 130.21, 128.69, 128.55, 128.21, 123.36, 121.91, 121.23, 119.74, 118.97, 111.52, 104.43, 34.10, 30.45, 21.10, 19.52, 16.50, 16.35.

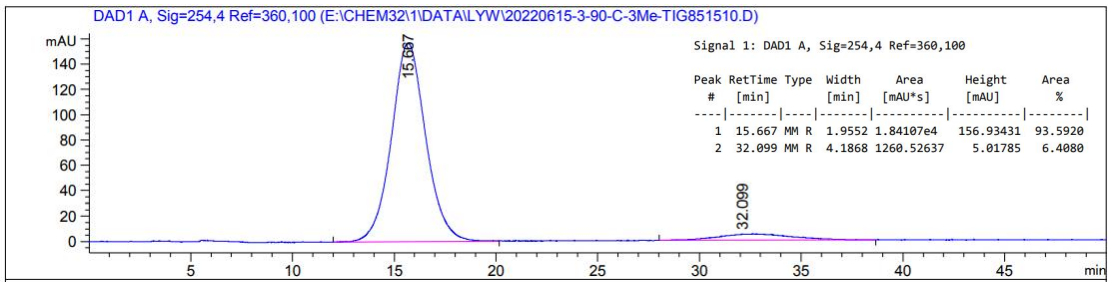
HRMS (ESI) Calcd for $C_{30}H_{35}N_2O_2^+$ $[M+H]^+$ 455.2693; Found: 455.2687.

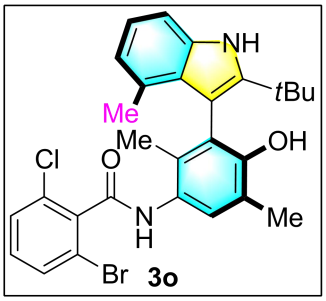
HPLC condition: Chiralpak IG (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 15.7 min, t_R (minor) = 32.1 min.)

HPLC spectrum of racemic **3n**



HPLC spectrum of **3n**





3o

2-Bromo-N-(3-(2-(*tert*-butyl)-4-methyl-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3o**

74% yield, 83% *ee*.

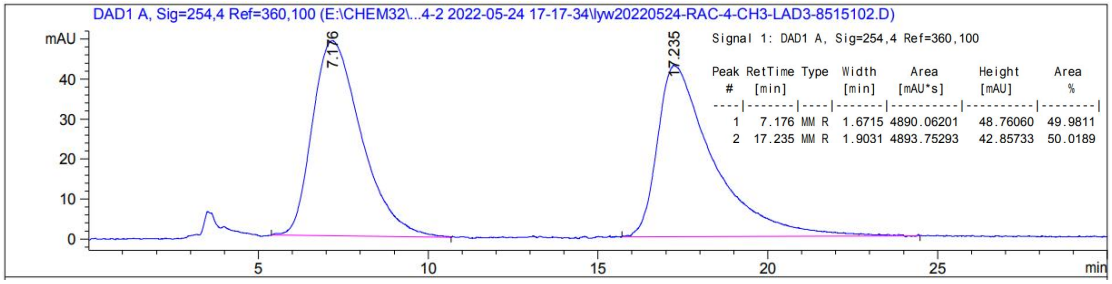
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.09 (s, 1H), 8.92 (s, 1H), 7.46 – 7.04 (m, 5H), 6.77 (s, 1H), 6.46 (s, 2H), 2.12 (s, 3H), 1.91 (s, 3H), 1.73 (s, 3H), 1.17 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.24, 153.35, 145.18, 140.01, 136.68, 133.42, 132.60, 132.07, 131.84, 130.80, 129.39, 128.08, 127.73, 127.50, 125.60, 121.76, 121.30, 121.29, 120.99, 109.66, 104.31, 34.14, 30.52, 18.92, 16.68, 16.49.

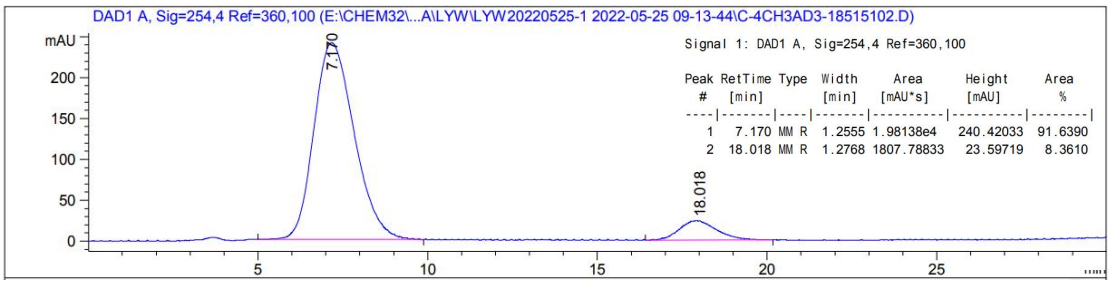
HRMS (ESI) Calcd for $C_{28}H_{29}B_rClN_2O_2^+$ $[M+H]^+$ 539.1095; Found: 539.1093.

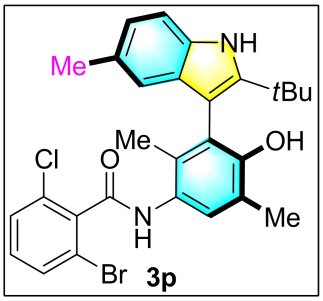
HPLC condition: Chiralpak AD-3 (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 7.2 min, t_R (minor) = 18.0 min.)

HPLC spectrum of racemic **3o**



HPLC spectrum of **3o**





2-Bromo-N-(3-(2-(*tert*-butyl)-5-methyl-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3p**

83% yield, 93% *ee*.

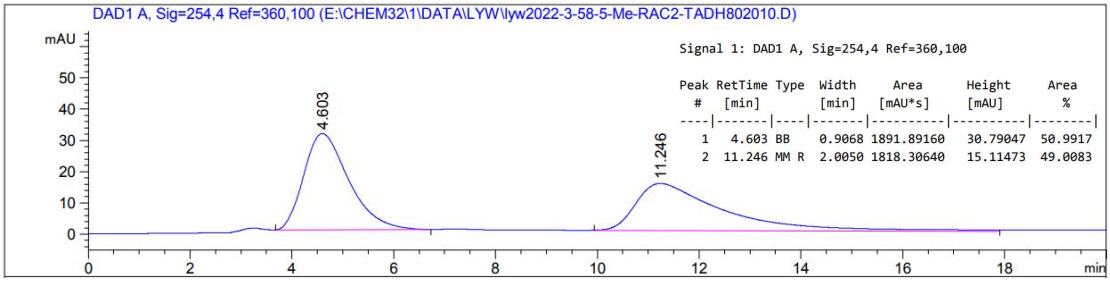
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.15 (s, 1H), 9.05 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.35 (t, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.70 (s, 1H), 6.48 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 2.04 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.21, 152.88, 146.16, 140.10, 134.97, 132.79, 132.66, 132.11, 131.87, 130.48, 129.43, 128.69, 127.99, 127.85, 123.60, 123.54, 121.33, 121.31, 118.58, 111.27, 103.89, 34.11, 30.44, 21.50, 16.49, 16.27.

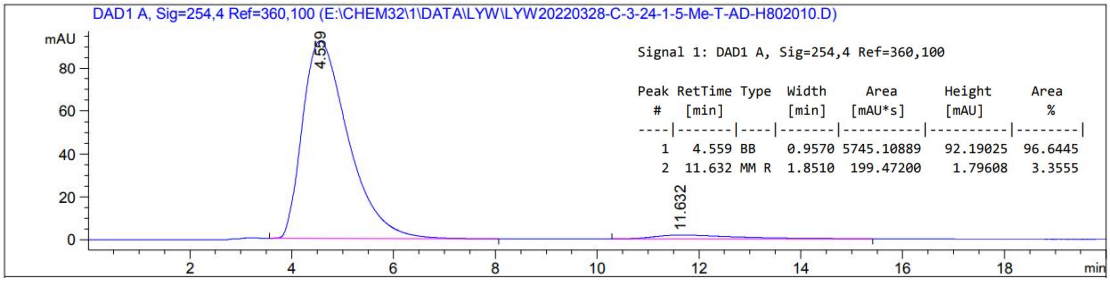
HRMS (ESI) Calcd for $C_{28}H_{29}B_rClN_2O_2^+$ $[M+H]^+$ 539.1095; Found: 539.1095.

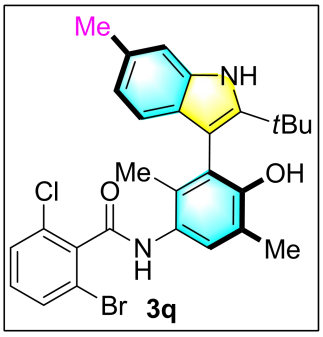
HPLC condition: Chiralpak AD-H (hexane/*i*PrOH = 80/20, 1.0 mL/min, t_R (major) = 4.6 min, t_R (minor) = 11.6 min.)

HPLC spectrum of racemic **3p**



HPLC spectrum of **3p**





3q

2-Bromo-N-(3-(2-(*tert*-butyl)-6-methyl-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3q**

81% yield, 91% *ee*.

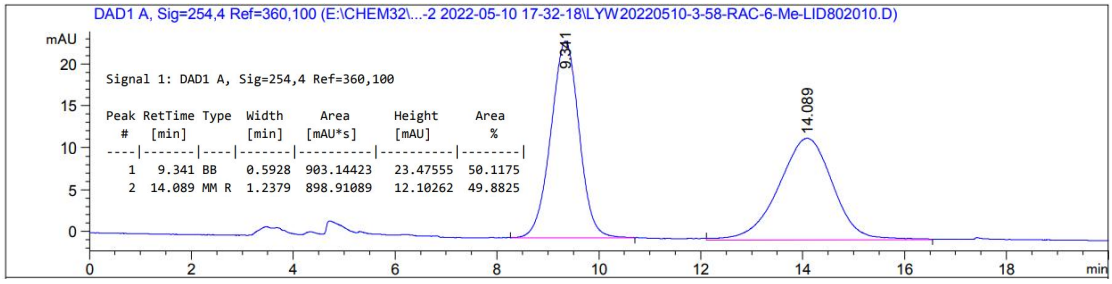
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.16 (s, 1H), 9.10 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.34 (t, J = 8.1 Hz, 1H), 7.16 (s, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 6.46 (s, 1H), 2.40 (s, 3H), 2.29 (s, 3H), 2.06 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.30, 152.81, 145.32, 139.98, 137.05, 132.75, 132.61, 132.06, 131.86, 131.35, 129.39, 128.04, 127.94, 127.75, 123.60, 121.45, 121.29, 121.24, 118.71, 111.47, 104.02, 34.05, 30.44, 21.77, 16.48, 16.21.

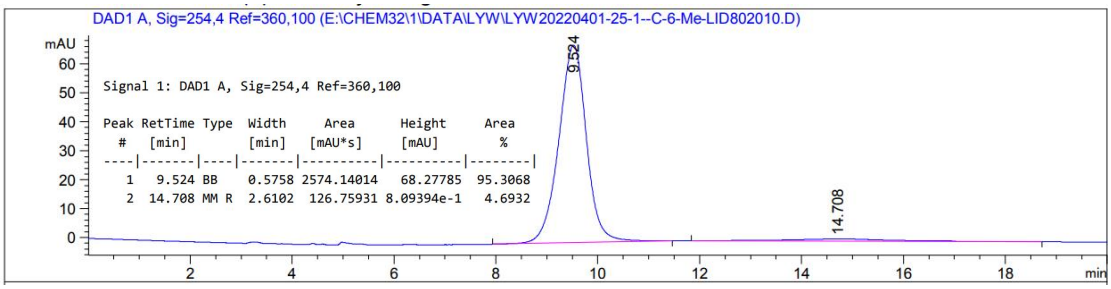
HRMS (ESI) Calcd for $C_{28}H_{29}BrClN_2O_2^+$ $[M+H]^+$ 539.1095; Found: 539.1096.

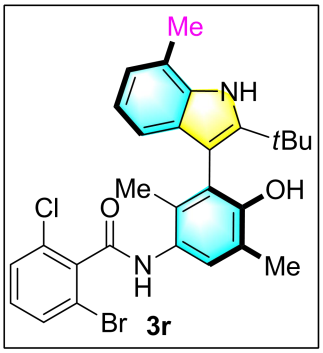
HPLC condition: Chiralpak ID (hexane/*i*PrOH = 80/20, 1.0 mL/min, t_R (major) = 9.5 min, t_R (minor) = 14.7 min.)

HPLC spectrum of racemic **3q**



HPLC spectrum of **3q**





3r

2-Bromo-N-(3-(2-(*tert*-butyl)-7-methyl-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3r**

78% yield, 91% *ee*. Reaction time: 5 h.

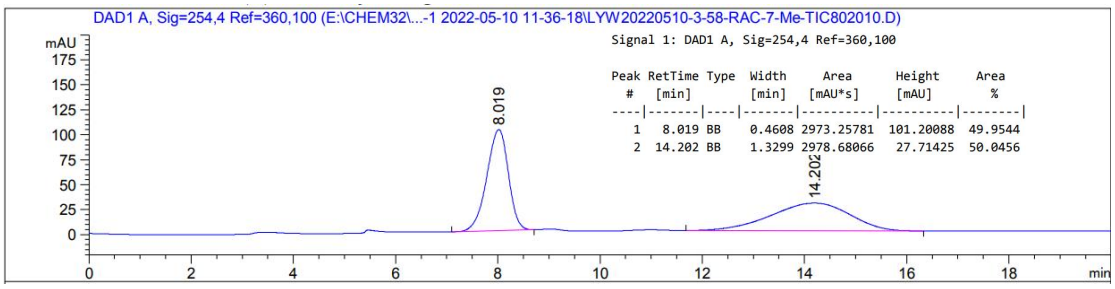
^{1}H NMR (400 MHz, Acetone-d_6) δ 9.88 (s, 1H), 9.07 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.46 (s, 1H), 7.34 (t, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 7.0 Hz, 1H), 6.83 (t, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.53 (s, 1H), 2.50 (s, 3H), 2.27 (s, 3H), 2.04 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.24, 152.85, 145.89, 140.03, 136.11, 132.74, 132.63, 132.07, 131.85, 129.86, 129.40, 127.99, 127.75, 123.74, 122.97, 121.31, 120.71, 120.14, 116.79, 105.01, 34.24, 30.53, 17.17, 16.50, 16.22.

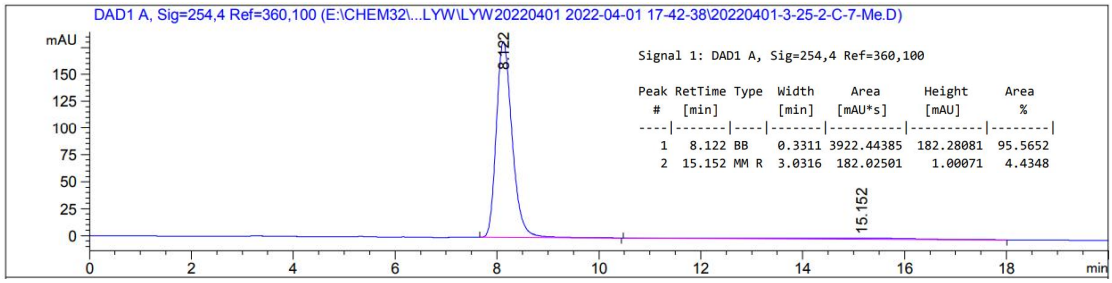
HRMS (ESI) Calcd for $C_{28}H_{29}BrClN_2O_2^+$ $[M+H]^+$ 539.1095; Found: 539.1092.

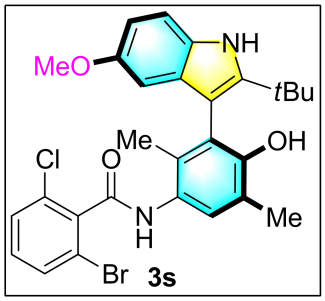
HPLC condition: Chiralpak IC (hexane/*i*PrOH = 80/20, 1.0 mL/min, t_R (major) = 8.1min, t_R (minor) = 15.2 min.)

HPLC spectrum of racemic **3r**



HPLC spectrum of **3r**





2-Bromo-N-(3-(2-(*tert*-butyl)-5-methoxy-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3s**

88% yield, 92% *ee*.

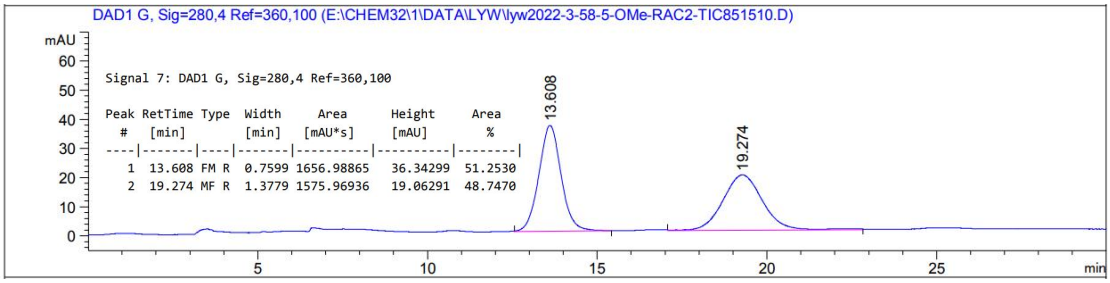
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.17 (s, 1H), 9.12 (s, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.34 (t, J = 8.1 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 6.74 (dd, J = 8.7, 2.5 Hz, 1H), 6.52 (s, 1H), 6.43 (d, J = 2.4 Hz, 1H), 3.62 (s, 3H), 2.29 (s, 3H), 2.07 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.30, 155.06, 152.89, 146.77, 139.96, 132.86, 132.60, 132.06, 131.87, 131.62, 130.64, 129.39, 128.03, 127.80, 123.44, 121.34, 121.28, 112.22, 111.84, 104.17, 100.87, 55.87, 34.11, 30.39, 16.51, 16.19.

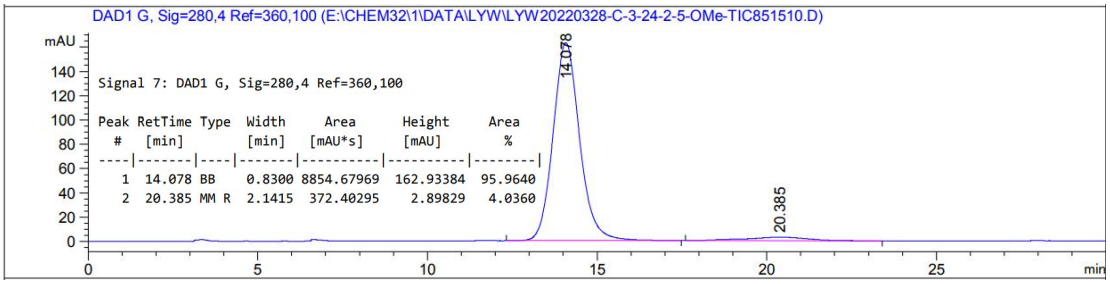
HRMS (ESI) Calcd for $C_{28}H_{29}B_rClN_2O_3^+$ $[M+H]^+$ 555.1045; Found: 555.1042.

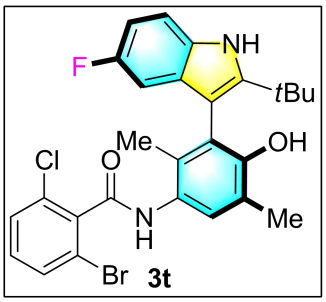
HPLC condition: Chiralpak IC (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 14.1 min, t_R (minor) = 20.4 min.)

HPLC spectrum of racemic **3s**



HPLC spectrum of **3s**





2-Bromo-N-(3-(2-(*tert*-butyl)-5-fluoro-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3t**

86% yield, 93% *ee*.

^{1}H NMR (400 MHz, Acetone-d_6) δ 10.42 (s, 1H), 9.15 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.37 – 7.33 (m, 2H), 6.89 – 6.84 (m, 1H), 6.67 (s, 1H), 6.59 (dd, J = 9.7, 2.6 Hz, 1H), 2.29 (s, 3H), 2.07 (s, 3H), 1.34 (s, 9H).

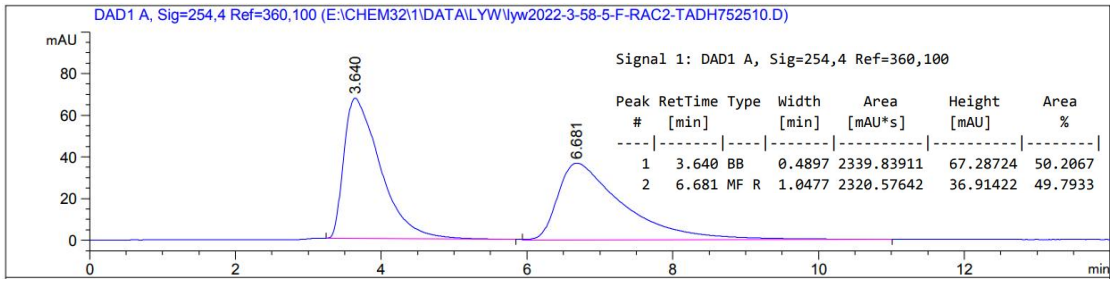
^{13}C NMR (100 MHz, Acetone-d_6) δ 164.40, 159.75, 157.44, 152.97, 148.32, 139.90, 133.11, 132.84, 132.61, 132.06, 131.90, 130.81, 130.72, 129.39, 128.28, 127.80, 122.86, 121.63, 121.27, 112.42, 112.33, 109.83, 109.57, 104.89, 104.84, 103.50, 103.27, 34.19, 30.29, 16.51, 16.21.

^{19}F NMR (376 MHz, Acetone-d_6) δ -126.69.

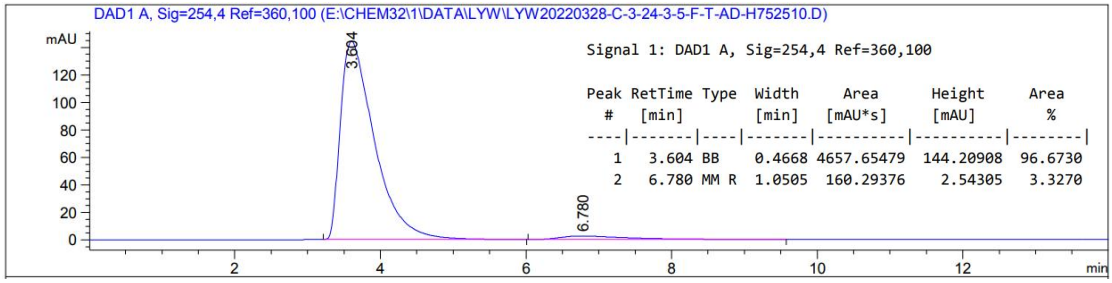
HRMS (ESI) Calcd for $C_{27}H_{26}B_rClFN_2O_2^+$ $[M+H]^+$ 543.0845; Found: 543.0843.

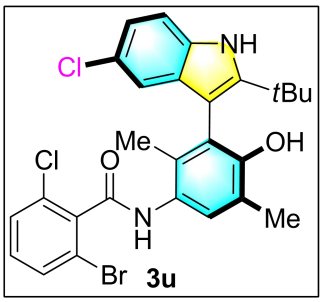
HPLC condition: Chiralpak AD-H (hexane/*i*PrOH = 75/25, 1.0 mL/min, t_R (major) = 3.6 min, t_R (minor) = 6.8 min.)

HPLC spectrum of racemic **3t**



HPLC spectrum of **3t**





3u

2-Bromo-N-(3-(2-(*tert*-butyl)-5-chloro-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3u**

90% yield, 95% *ee*.

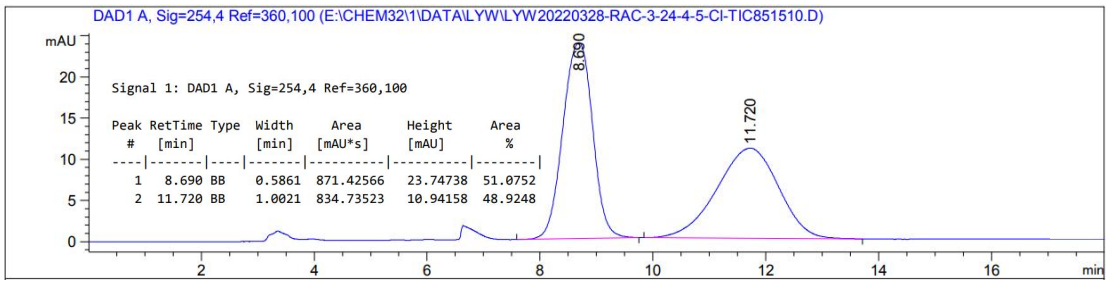
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.47 (s, 1H), 9.08 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.38 – 7.34 (m, 2H), 7.05 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.71 (s, 1H), 2.28 (s, 3H), 2.04 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.27, 153.03, 148.08, 140.04, 135.08, 132.83, 132.66, 132.12, 131.91, 131.64, 129.44, 128.39, 127.93, 125.13, 122.64, 121.87, 121.78, 121.32, 118.06, 112.91, 104.71, 34.23, 30.28, 16.51, 16.27.

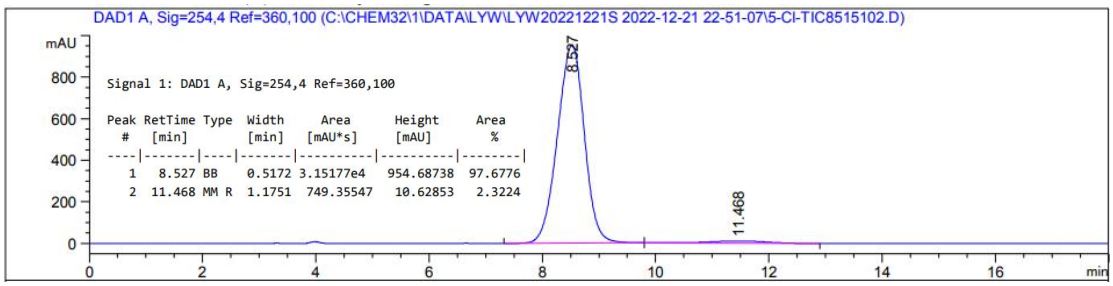
HRMS (ESI) Calcd for $C_{27}H_{26}B_rCl_2N_2O_2^+$ $[M+H]^+$ 559.0549; Found: 559.0551.

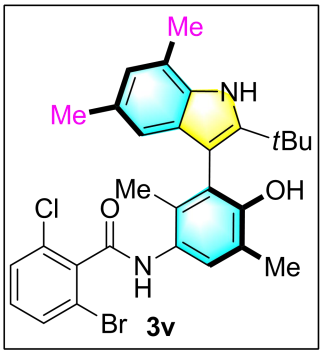
HPLC condition: Chiralpak IC (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 8.5 min, t_R (minor) = 11.5 min.)

HPLC spectrum of racemic **3u**



HPLC spectrum of **3u**





2-Bromo-N-(3-(2-(*tert*-butyl)-5,7-dimethyl-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3v**

63% yield, 89% *ee*. Reaction time: 2 h.

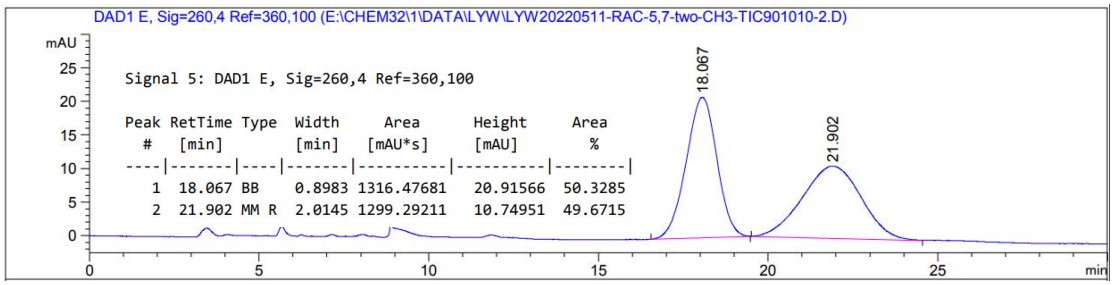
^{1}H NMR (400 MHz, Acetone-d_6) δ 9.77 (s, 1H), 9.05 (s, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.46 (s, 1H), 7.35 (t, J = 8.1 Hz, 1H), 6.74 (s, 1H), 6.54 (s, 1H), 6.46 (s, 1H), 2.47 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.04 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.21, 152.80, 145.98, 140.09, 134.47, 132.73, 132.65, 132.10, 131.86, 130.14, 129.42, 128.99, 127.94, 127.81, 124.69, 123.93, 121.32, 121.25, 120.44, 116.36, 104.49, 34.25, 30.54, 21.42, 17.10, 16.48, 16.24.

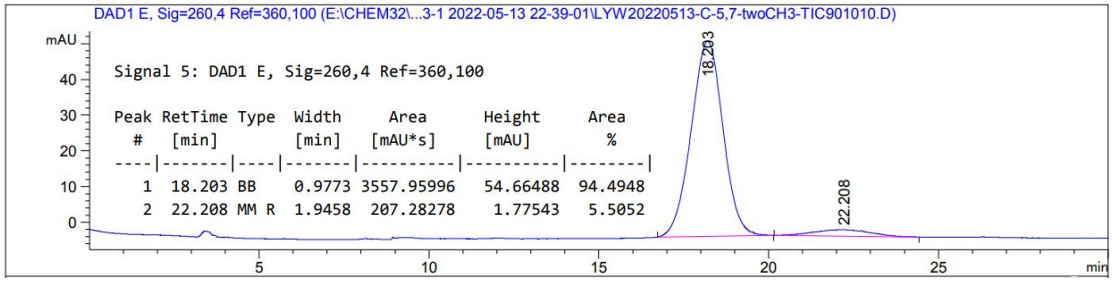
HRMS (ESI) Calcd for $C_{29}H_{31}B_rClN_2O_2^+$ $[M+H]^+$ 553.1252; Found: 553.1249.

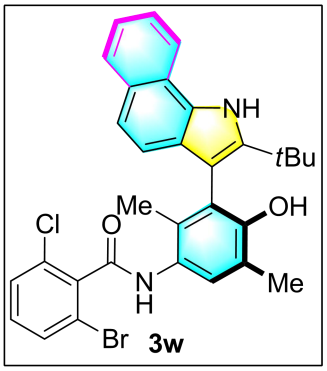
HPLC condition: Chiralpak IC (hexane/*i*PrOH = 90/10, 1.0 mL/min, t_R (major) = 18.2 min, t_R (minor) = 22.2 min.)

HPLC spectrum of racemic **3v**



HPLC spectrum of **3v**





2-Bromo-N-(3-(2-(*tert*-butyl)-1*H*-benzo[*g*]indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **3w**

40% yield, 94% *ee*. 0.40 mmol of **1h** was used. Reaction time: 6 h.

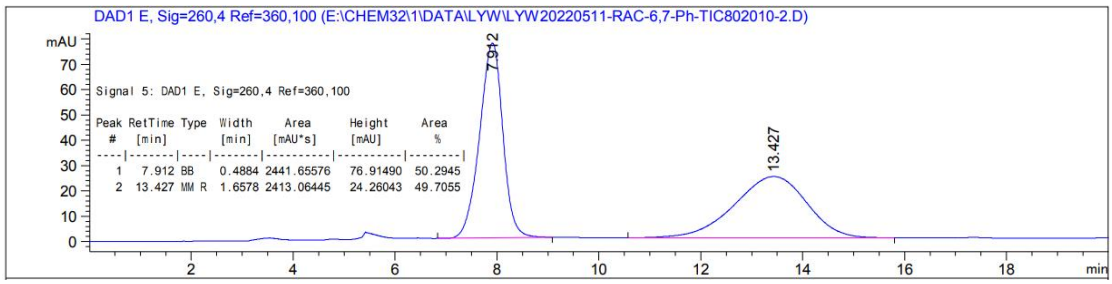
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.82 (s, 1H), 9.12 (s, 1H), 8.48 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.41 – 7.33 (m, 3H), 7.05 (d, J = 8.5 Hz, 1H), 6.64 (s, 1H), 2.30 (s, 3H), 2.09 (s, 3H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.35, 153.03, 144.52, 140.06, 132.85, 132.68, 132.12, 131.89, 131.37, 131.07, 131.00, 129.44, 129.36, 128.19, 127.83, 125.93, 124.14, 123.52, 122.88, 121.53, 121.34, 121.30, 120.76, 119.63, 106.64, 34.35, 30.74, 16.52, 16.34.

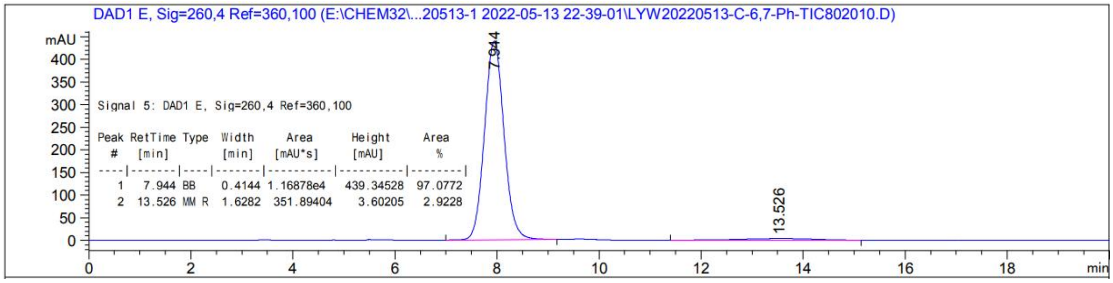
HRMS (ESI) Calcd for $C_{31}H_{29}B_rClN_2O_2^+$ $[M+H]^+$ 575.1095; Found: 575.1087.

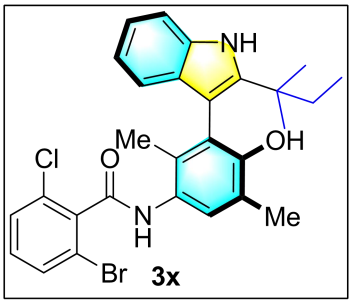
HPLC condition: Chiralpak IC (hexane/*i*PrOH = 80/20, 1.0 mL/min, t_R (major) = 7.9 min, t_R (minor) = 13.5 min.)

HPLC spectrum of racemic **3w**



HPLC spectrum of **3w**





3x

2-Bromo-6-chloro-N-(4-hydroxy-2,5-dimethyl-3-(2-(*tert*-pentyl)-1*H*-indol-3-yl)phenyl)benzamide **3x**

71% yield, 95% *ee*.

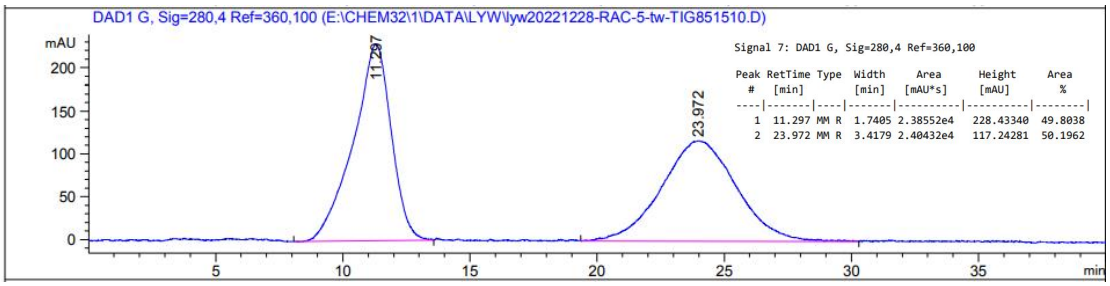
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.29 (s, 1H), 9.10 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.38 – 7.33 (m, 2H), 7.10 – 7.06 (m, 1H), 6.93 (d, J = 4.1 Hz, 2H), 6.33 (s, 1H), 2.28 (s, 3H), 2.07 (s, 3H), 1.83 – 1.68 (m, 2H), 1.32 (s, 3H), 1.24 (s, 3H), 0.80 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.28, 152.78, 144.99, 140.00, 136.74, 132.80, 132.63, 132.08, 131.87, 130.18, 129.40, 128.01, 127.87, 123.46, 122.02, 121.30, 121.28, 119.81, 118.93, 111.50, 105.44, 37.78, 36.74, 27.80, 27.19, 16.47, 16.30, 9.85.

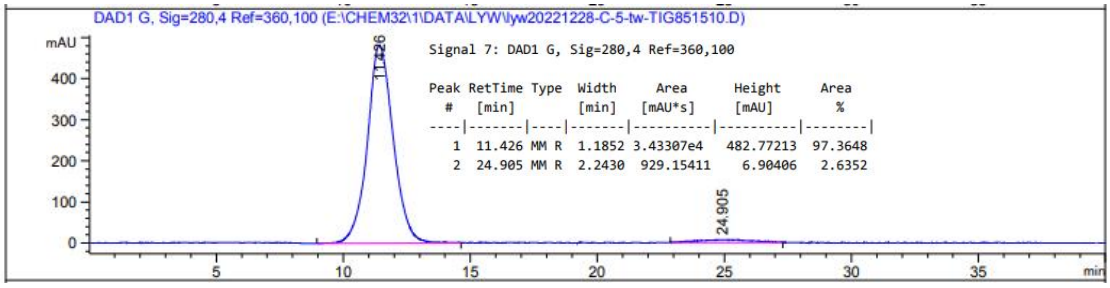
HRMS (ESI) Calcd for $C_{28}H_{29}B_rClN_2O_2^+$ $[M+H]^+$ 539.1095; Found: 539.1092.

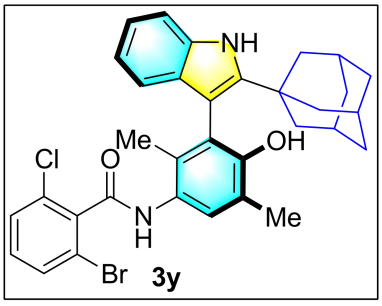
HPLC condition: Chiralpak IG (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 11.4 min, t_R (minor) = 24.9 min.)

HPLC spectrum of racemic **3x**



HPLC spectrum of **3x**





3y

N-(3-(2-(adamantan-1-yl)-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-2-bromo-6-chlorobenzamide **3y**

86% yield, 92% *ee*.

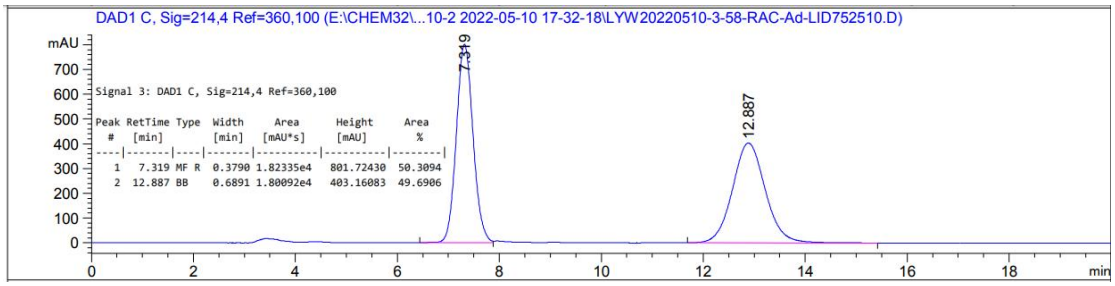
^{1}H NMR (400 MHz, Acetone-d_6) δ 10.35 (s, 1H), 9.16 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.41 – 7.35 (m, 2H), 7.12 – 7.08 (m, 1H), 6.94 (d, J = 4.2 Hz, 2H), 6.47 (s, 1H), 2.32 (s, 3H), 2.11 (s, 9H), 1.96 (s, 3H), 1.76 – 1.67 (m, 6H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.35, 152.79, 146.30, 139.95, 136.53, 132.74, 132.61, 132.05, 131.86, 130.10, 129.38, 127.94, 127.68, 123.56, 121.92, 121.29, 121.21, 119.69, 118.91, 111.55, 103.96, 42.14, 37.23, 36.46, 29.29, 16.54, 16.33.

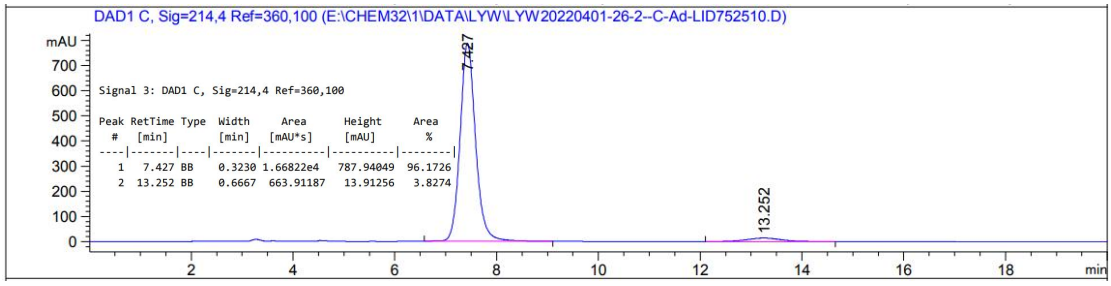
HRMS (ESI) Calcd for $C_{33}H_{33}B_rClN_2O_2^+$ $[M+H]^+$ 603.1408; Found: 603.1399.

HPLC condition: Chiralpak ID (hexane/*i*PrOH = 75/25, 1.0 mL/min, t_R (major) = 7.4min, t_R (minor) = 13.3 min.)

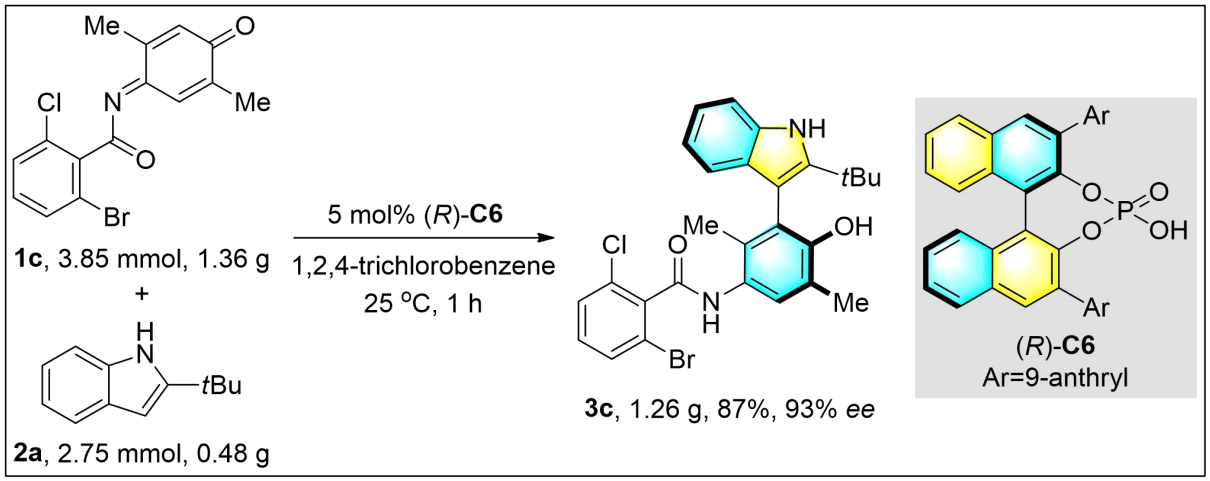
HPLC spectrum of racemic **3y**



HPLC spectrum of **3y**

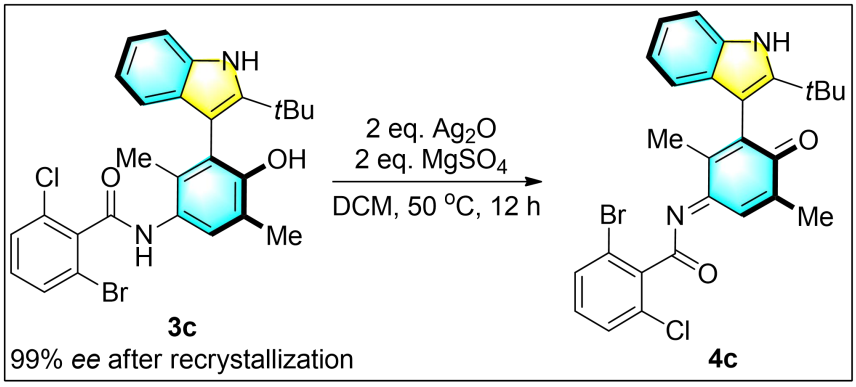


Synthesis of 3c in gram-scale under the optimized reaction conditions

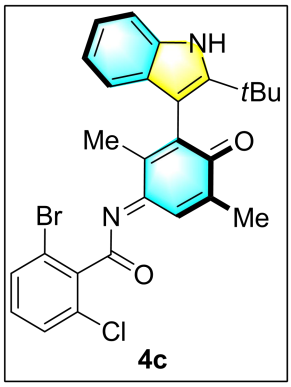


To a 100 mL round-bottom flask with a magnetic stirring bar were sequentially added (*R*)-**C6** (5 mol%, 96.3 mg), **2a** (2.75 mmol, 0.48 g) and 1,2,4-trichlorobenzene (15 mL). A solution of **1c** (3.85 mmol, 1.36 g) in 1,2,4-trichlorobenzene (40 mL) was added dropwise to the mixture. After stirred at 25 °C for 1 h, the mixture was concentrated and purified by silica gel column chromatography (PE to PE/EtOAc = 8/1) to afford the pure product **3c** (1.26 g, 87% yield, 93% *ee*).

Oxidation reaction of 3c



Ag_2O (1.2 mmol, 0.28 g) and $MgSO_4$ (1.2 mmol, 0.14 g) were added to a solution of **3c** (0.6 mmol, 0.32 g) in anhydrous DCM (12 mL). The reaction was stirred at 50 °C for 12 h. After filtration, the filtrate was evaporated in vacuo to give the pure product **4c**.



2-Bromo-N-(3-(2-(*tert*-butyl)-1*H*-indol-3-yl)-2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-chlorobenzamide **4c**

90% yield, 99% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.02 – 6.99 (m, 1H), 2.10 (s, 3H), 1.98 (s, 3H), 1.31 (s, 9H).

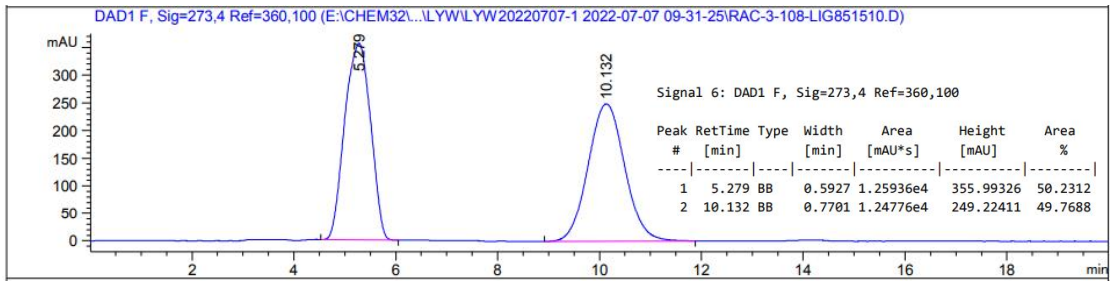
^{13}C NMR (100 MHz, $CDCl_3$) δ 186.58, 177.94, 158.85, 146.04, 143.88, 141.21, 137.03, 134.75, 132.19, 131.89, 131.56, 129.19, 128.32, 121.86, 120.57, 119.96, 118.26, 110.65, 104.31, 33.33, 30.43, 16.74, 15.89.

HRMS (ESI) Calcd for $C_{27}H_{25}BrClN_2O_2^+$ $[M+H]^+$ 523.0782; Found: 523.0769.

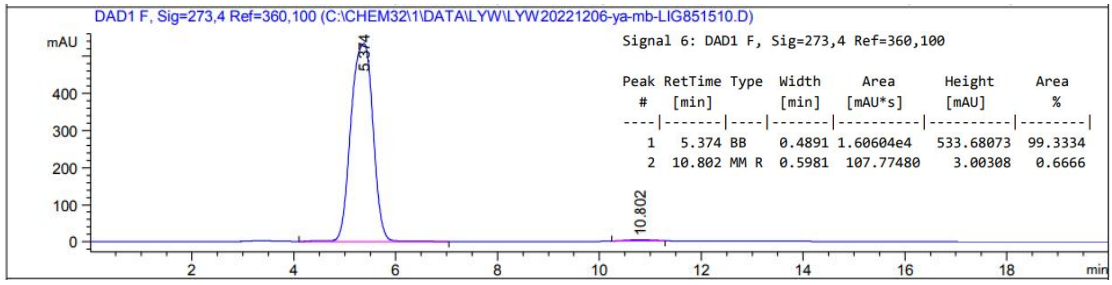
HPLC condition: Chiralpak IG (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 5.4 min, t_R

(minor) = 10.8 min.)

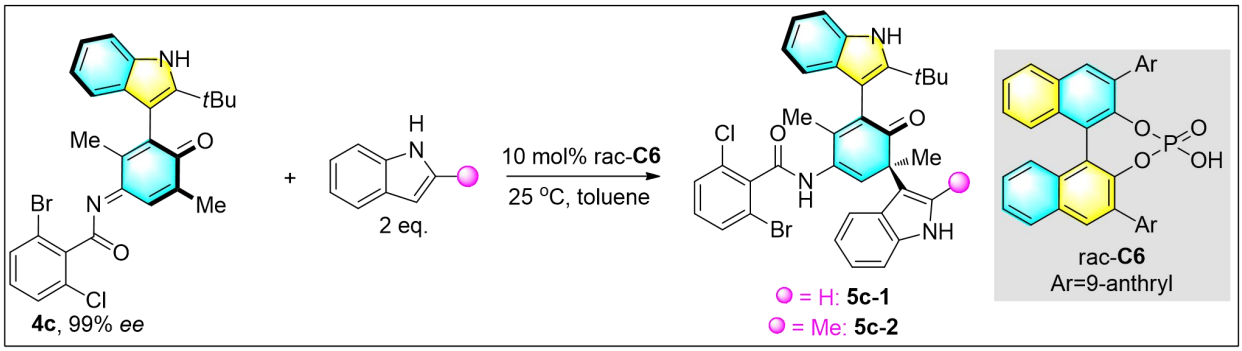
HPLC spectrum of racemic **4c**



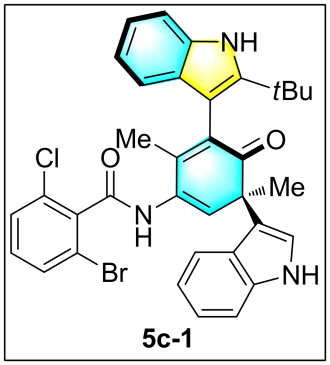
HPLC spectrum of **4c**



Nucleophilic addition of indoles with 4c



Racemic **C6** (10 mol%, 7.0 mg), **4c** (0.10 mmol, 52.4 mg) and indoles (0.20 mmol) were added to a Schlenk tube, then 2 mL toluene was added via syringe in one portion. When the reaction was completed (about 1 h), the mixture was purified by silica gel column chromatography (PE/EtOAc = 4/1) to give the pure products **5c-1** and **5c-2**.



2-Bromo-N-(5-(2-(*tert*-butyl)-1*H*-indol-3-yl)-3-(1*H*-indol-3-yl)-3,6-dimethyl-4-oxocyclohexa-1,5-dien-1-yl)-6-chlorobenzamide **5c-1**

89% yield, 99% *ee*.

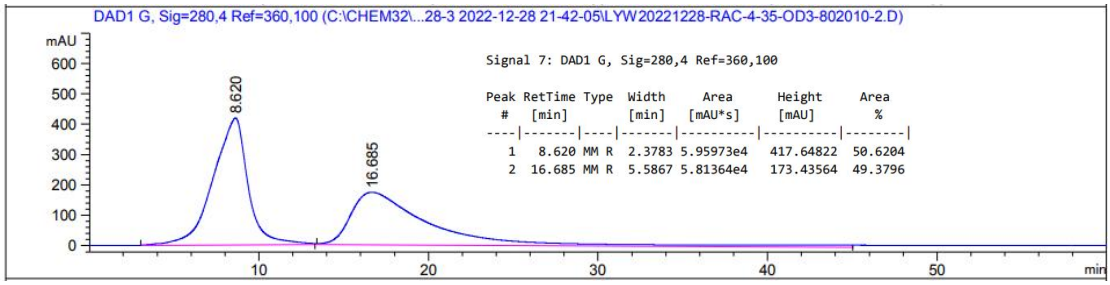
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.07 (s, 1H), 10.82 (s, 1H), 10.08 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.61 - 7.56 (m, 2H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.79 – 6.71 (m, 2H), 6.61 (s, 1H), 2.01 (s, 3H), 1.75 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 200.41, 164.59, 150.00, 143.91, 139.35, 138.20, 136.68, 135.18, 131.65, 131.36, 131.07, 130.84, 129.25, 128.71, 128.27, 125.69, 123.06, 121.15, 120.38, 120.16, 119.77, 118.51, 118.26, 117.53, 115.69, 111.59, 110.58, 104.24, 49.36, 33.21, 30.01, 24.63, 18.35.

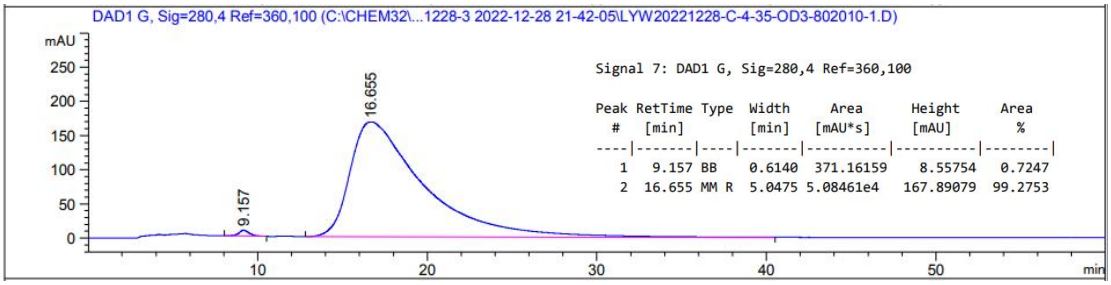
HRMS (ESI) Calcd for $C_{35}H_{32}BrClN_3O_2^+$ $[M+H]^+$ 640.1361; Found: 640.1358.

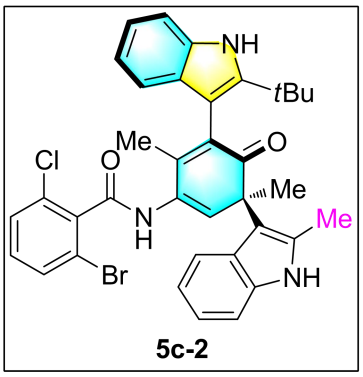
HPLC condition: Chiralpak OD-3 (hexane/*i*PrOH = 80/20, 1.0 mL/min, t_R (major) = 16.7 min, t_R (minor) = 9.2 min.)

HPLC spectrum of racemic **5c-1**



HPLC spectrum of **5c-1**





5c-2

2-Bromo-N-(5-(2-(*tert*-butyl)-1*H*-indol-3-yl)-3,6-dimethyl-3-(2-methyl-1*H*-indol-3-yl)-4-oxocyclohexa-1,5-dien-1-yl)-6-chlorobenzamide **5c-2**

78% yield, 99% *ee*.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.91 (s, 1H), 10.84 (s, 1H), 10.05 (s, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.31 (d, J =

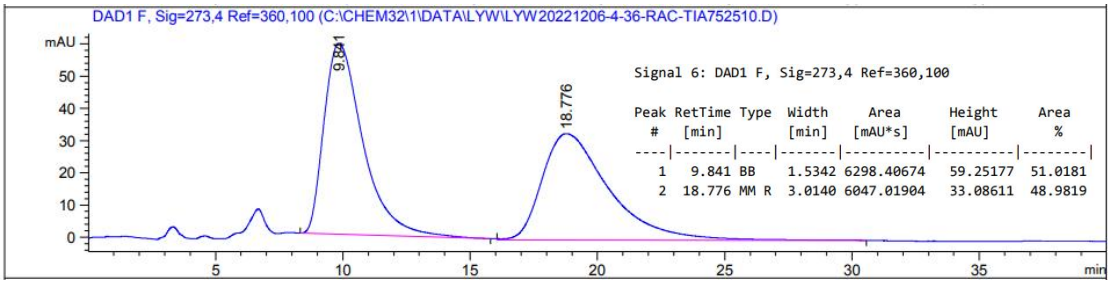
7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 6.99 – 6.94 (m, 3H), 6. 92 – 6.85 (m, 2H), 6.61 (s, 1H), 2.42 (s, 3H), 2.01 (s, 3H), 1.89 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 201.56, 164.58, 150.37, 143.99, 140.51, 138.22, 135.21, 134.79, 132.97, 131.64, 131.37, 131.08, 130.63, 128.72, 128.46, 128.15, 127.90, 120.42, 120.18, 119.93, 119.31, 118.46, 118.42, 117.63, 110.72, 110.60, 110.12, 104.32, 51.20, 33.22, 30.03, 26.00, 18.45, 13.67.

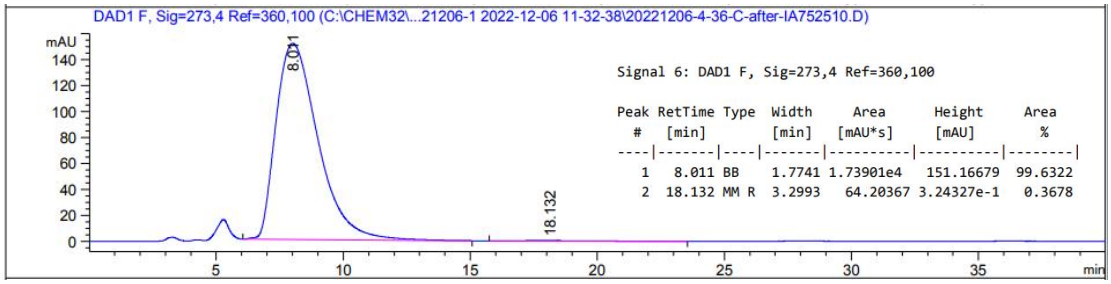
HRMS (ESI) Calcd for $C_{36}H_{34}BrClN_3O_2^+$ $[M+H]^+$ 654.1517; Found: 654.1496.

HPLC condition: Chiralpak IA (hexane/*i*PrOH = 75/25, 1.0 mL/min, t_R (major) = 8.0 min, t_R (minor) = 18.1 min.)

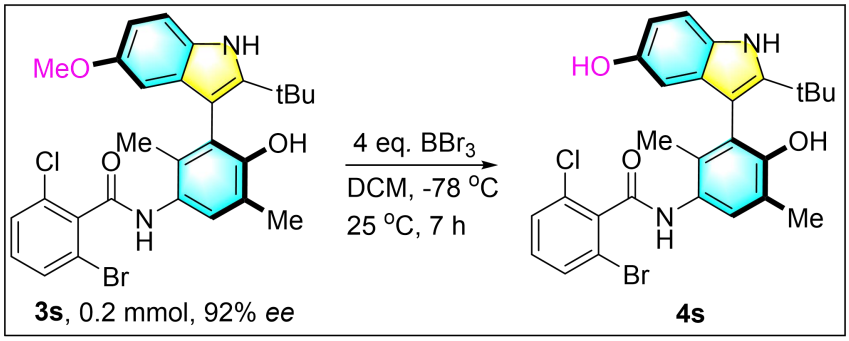
HPLC spectrum of racemic **5c-2**



HPLC spectrum of **5c-2**

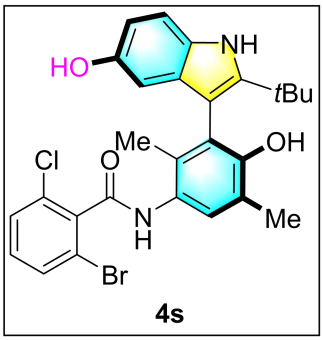


Demethylation reaction of 3s



3s, 0.2 mmol, 92% *ee* **4s**

BBr_3 (0.8 mmol, 1.0 M in DCM, 8 mL) in anhydrous DCM (8 mL) was added dropwise to **3s** (0.2 mmol, 111.2 mg) in anhydrous DCM (4 mL) at -78 °C and the mixture was stirred at 25 °C for 7 h. Then H_2O was added to quench the reaction, and the mixture was purified by preparative TLC (PE/EtOAc = 4/1) to give the pure product **4s**.



4s

2-Bromo-N-(3-(2-(*tert*-butyl)-5-hydroxy-1*H*-indol-3-yl)-4-hydroxy-2,5-dimethylphenyl)-6-chlorobenzamide **4s**

70% yield, 92% *ee*.

^{1}H NMR (400 MHz, Acetone-d_6) δ 9.97 (s, 1H), 9.00 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 2.5 Hz, 2H), 7.36 (t, J = 8.1 Hz, 1H), 7.17 (d, J = 8.6 Hz, 1H), 6.66 (dd, J = 8.5, 2.0 Hz, 1H), 6.40 (s, 1H), 6.30 (d, J = 1.7 Hz, 1H), 2.26 (s, 3H), 2.03 (s, 3H), 1.32 (s, 9H).

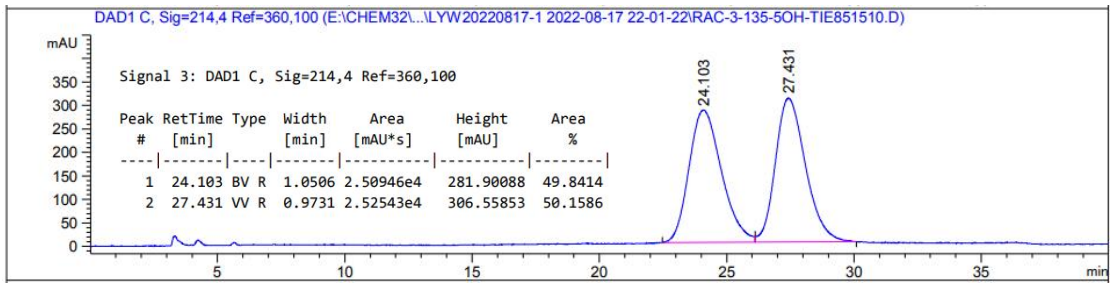
^{13}C NMR (100 MHz, Acetone-d_6) δ 164.26, 152.83, 152.00, 146.73, 140.13, 132.86, 132.70, 132.13, 131.88, 131.22, 131.09, 129.45, 128.00, 127.86, 123.74, 121.35, 121.28, 111.96, 103.66, 103.17, 34.12, 30.43, 16.45, 16.23.

HRMS (ESI) Calcd for $C_{27}H_{27}BrClN_2O_3^+$ $[M+H]^+$ 541.0888; Found: 541.0886.

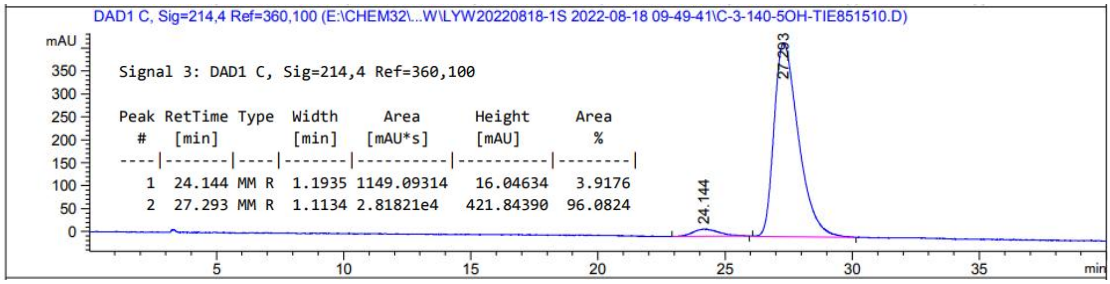
HPLC condition: Chiralpak IE (hexane/*i*PrOH = 85/15, 1.0 mL/min, t_R (major) = 27.3 min, t_R

(minor) = 24.1 min.)

HPLC spectrum of racemic **4s**



HPLC spectrum of **4s**



Single-crystal X-ray crystallography of compound 3s

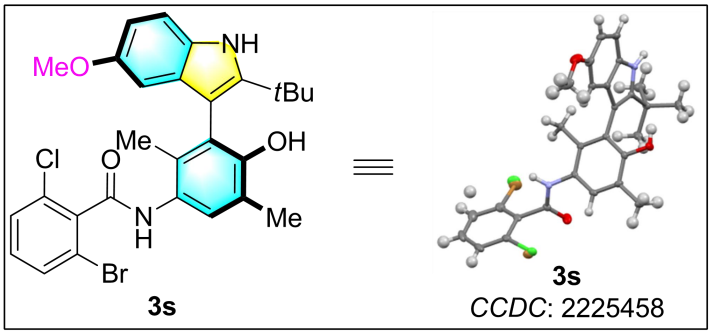


Table 1 Crystal data and structure refinement for LYW202205255OMe_0m.

Identification code	LYW202205255OMe_0m
Empirical formula	$C_{32}H_{36}BrClN_2O_5$
Formula weight	643.99
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.9695(5)
b/Å	14.2146(6)
c/Å	18.3960(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3129.9(2)
Z	4
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	2.915
F(000)	1336.0
Crystal size/mm^3	0.2 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.86 to 136.874
Index ranges	$-11 \le h \le 14$, $-17 \le k \le 17$, $-21 \le l \le 22$

Reflections collected	27867
Independent reflections	5722 [R_{int} = 0.0251, R_{sigma} = 0.0228]
Data/restraints/parameters	5722/2/387
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0186, wR_2 = 0.0475
Final R indexes [all data]	R_1 = 0.0188, wR_2 = 0.0476
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.27
Flack parameter	0.006(3)

Single-crystal X-ray crystallography of compound 5c-1

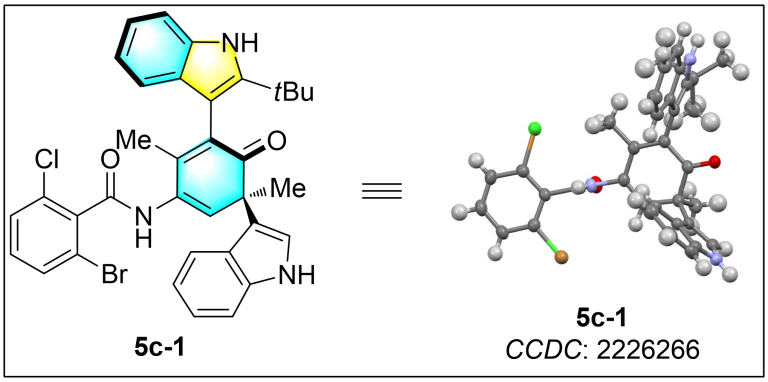


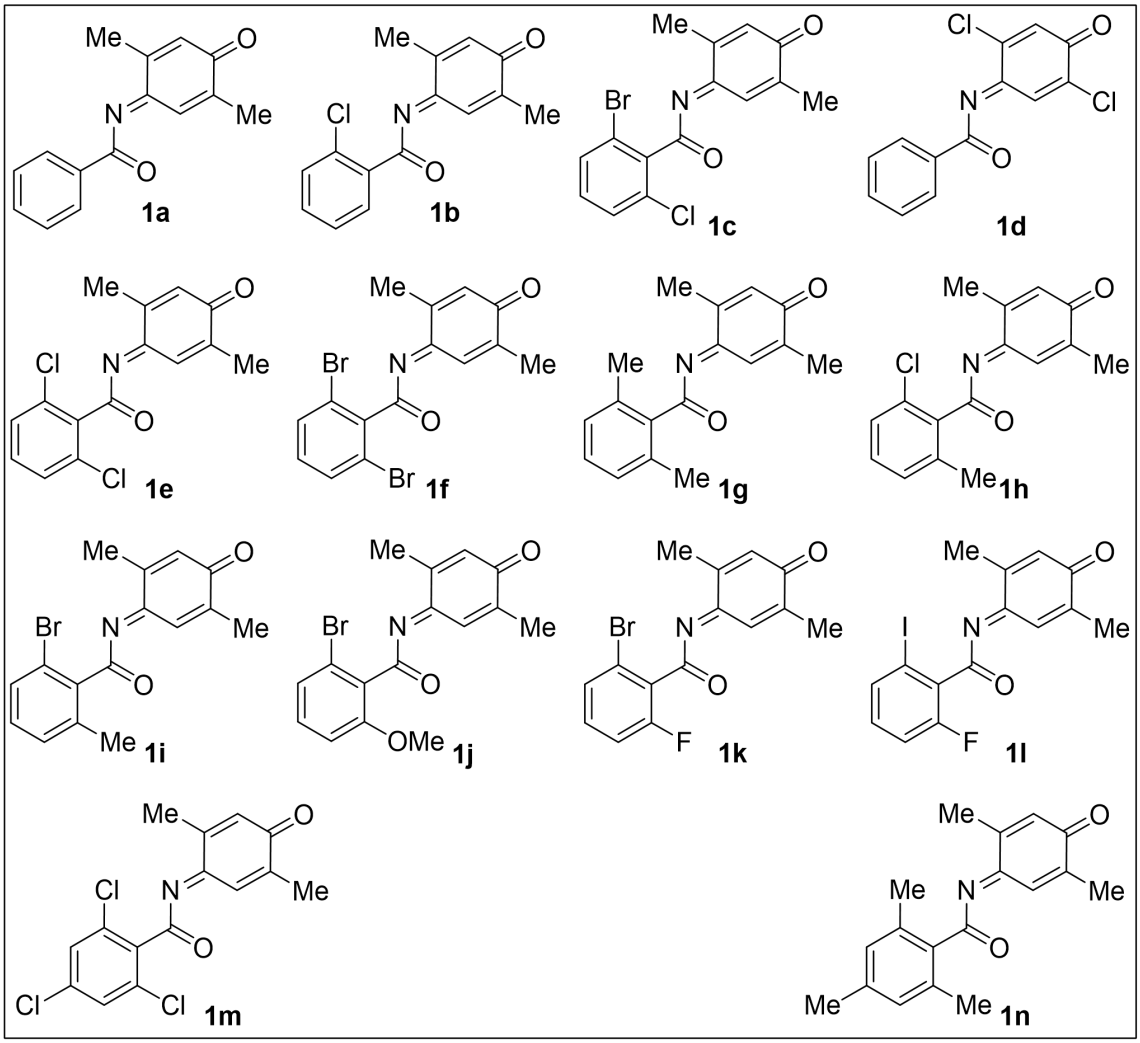
Table 1 Crystal data and structure refinement for LYW2022102701_0m.

Identification code	LYW2022102701_0m
Empirical formula	$C_{35}H_{31}BrClN_3O_2$
Formula weight	640.99
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.5966(6)
b/Å	15.9032(7)
c/Å	17.3382(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3473.3(3)
Z	4
ρ_{calc}g/cm^3	1.226
μ/mm^{-1}	2.572
F(000)	1320.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.676 to 137.02

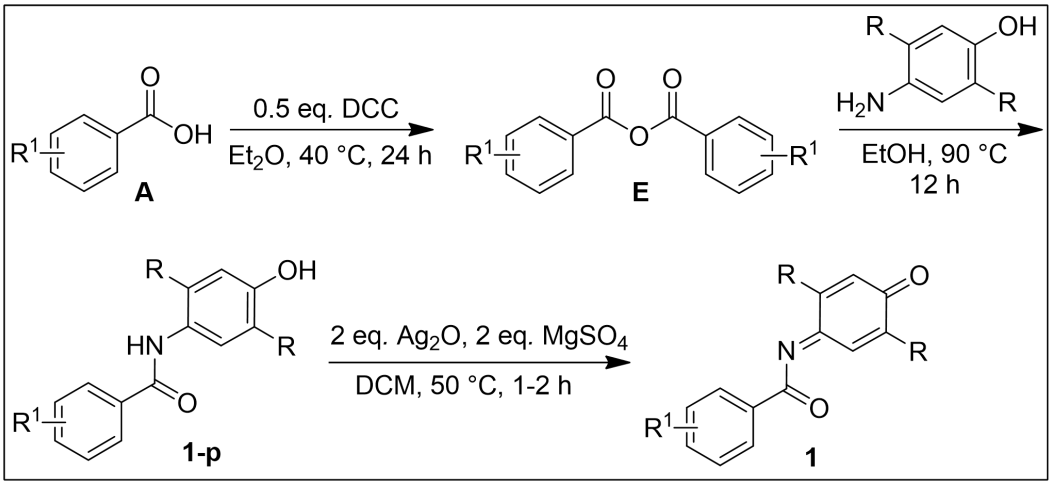
Index ranges	$-14 \leq h \leq 15$, $-19 \leq k \leq 19$, $-20 \leq l \leq 20$
Reflections collected	91774
Independent reflections	6369 [R_{int} = 0.0269, R_{sigma} = 0.0108]
Data/restraints/parameters	6369/0/385
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0313, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0313, wR_2 = 0.0851
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.18
Flack parameter	0.007(3)

Synthetic procedures and characterization of raw materials

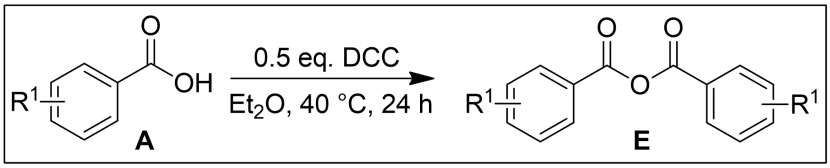
Supplementary Figure 1. Iminoquinones 1 involved in the manuscript.



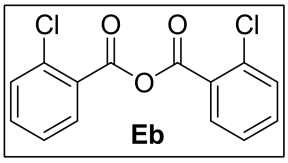
Synthetic route for the preparation of 1



Synthetic procedure for the preparation of E



Dicyclohexylcarbodiimide (DCC, 15 mmol, 3.09 g) was added to a solution of carboxylic acid **A** (30 mmol) in Et_2O (150 mL). The reaction mixture was stirred at 40 °C for 24 h and cooled to room temperature. After filtration, the filtrate was evaporated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/CH_2Cl_2 = 2/1) to give the pure products **E**.

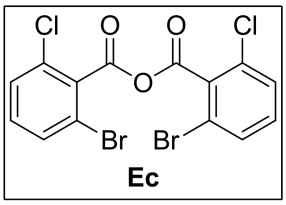


2-Chlorobenzoic anhydride **Eb**

56% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 2H), 7.54 – 7.52 (m, 4H), 7.43 – 7.36 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.46, 135.19, 134.34, 132.68, 131.75, 127.92, 127.06.



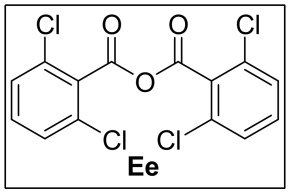
Ec

2-Bromo-6-chlorobenzoic anhydride **Ec**

62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.41 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.30 – 7.26 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.04, 133.66, 132.31, 132.27, 131.28, 128.68, 120.02.



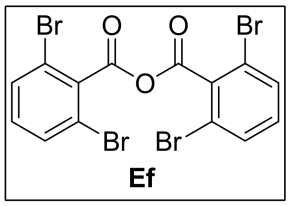
Ee

2,6-Dichlorobenzoic anhydride **Ee**

38% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.48, 132.36, 132.13, 131.51, 128.21.



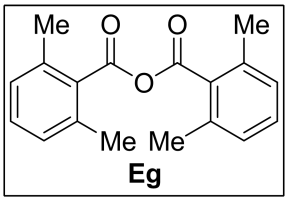
Ef

2,6-Dibromobenzoic anhydride **Ef**

42% yield

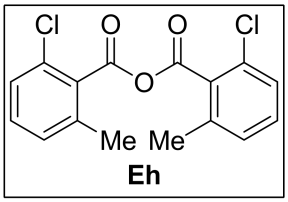
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 4H), 7.19 (t, *J* = 8.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.63, 135.67, 132.52, 131.75, 119.97.



Eg

Eg was synthesized according to literature method[1].



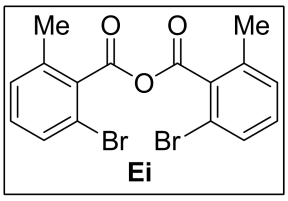
Eh

2-Chloro-6-methylbenzoic anhydride **Eh**

85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.17 (d, *J* = 7.1 Hz, 2H), 2.49 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.82, 137.95, 131.70, 131.40, 131.13, 128.87, 127.19, 19.75.



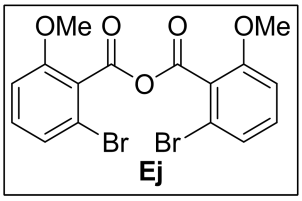
Ei

2-Bromo-6-methylbenzoic anhydride **Ei**

55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.22 – 7.16 (m, 4H), 2.48 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.24, 137.85, 133.91, 131.54, 130.25, 129.35, 119.07, 19.92.



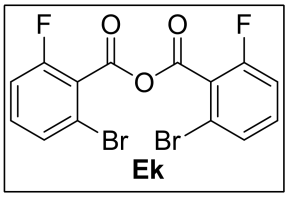
Ej

2-Bromo-6-methoxybenzoic anhydride **Ej**

32% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.32, 157.93, 132.36, 124.73, 124.13, 119.96, 110.26, 56.37.



Ek

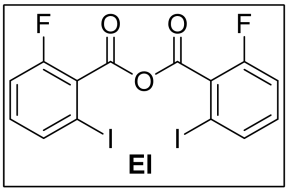
2-Bromo-6-fluorobenzoic anhydride **Ek**

50% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.14 (t, *J* = 8.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.60, 159.04, 157.76, 133.65, 133.63, 133.59, 133.57, 133.54, 133.51, 129.31, 129.29, 129.27, 122.24, 122.07, 121.07, 115.55, 115.53, 115.50, 115.35, 115.32, 115.30.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.18.



El

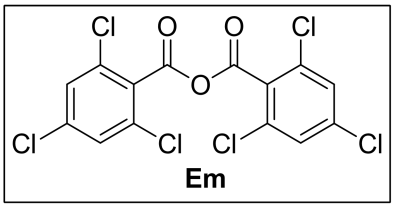
2-Fluoro-6-iodobenzoic anhydride **El**

83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.4, 1.5 Hz, 2H), 7.22 – 7.13 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.02, 158.91, 158.45, 135.90, 135.86, 135.84, 135.83, 135.79, 134.03, 134.00, 133.97, 133.95, 133.92, 133.89, 125.70, 125.54, 116.34, 116.31, 116.28, 116.13, 116.10, 116.08, 92.91.

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.13.

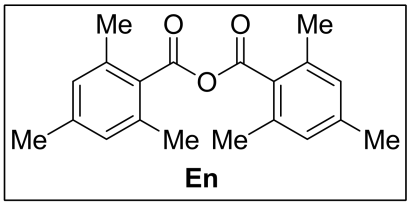


2,4,6-Trichlorobenzoic anhydride **Em**

87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.62, 137.68, 133.15, 129.85, 128.40.



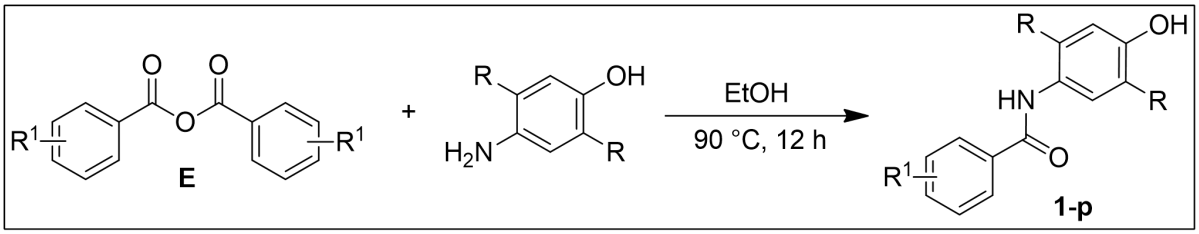
2,4,6-Trimethylbenzoic anhydride **En**

80% yield.

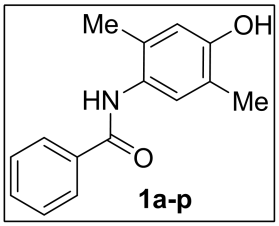
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 4H), 2.43 (s, 12H), 2.31 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.47, 140.84, 136.39, 128.96, 128.94, 21.28, 20.15.

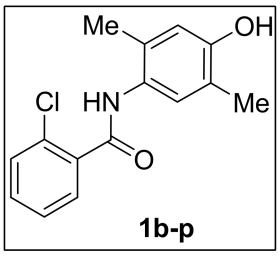
Synthetic procedure for the preparation of 1-p



Benzoic anhydride **E** (10 mmol) was added to the solution of 4-amino-2,5-diRphenol (10 mmol) in EtOH (30 mL) at 25 °C in one portion. The mixture was stirred at 90 °C for 12 h, cooled to room temperature and evaporated in vacuo. The residue was washed with CH_2Cl_2 to give the pure products **1-p**.



1a-p was synthesized according to literature method[2].

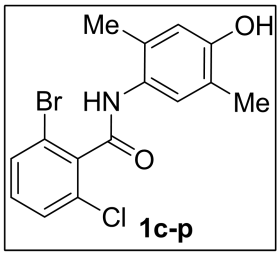


2-Chloro-N-(4-hydroxy-2,5-dimethylphenyl)benzamide **1b-p**.

69% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.68 (s, 1H), 9.19 (s, 1H), 7.58 – 7.53 (m, 2H), 7.50 – 7.42 (m, 2H), 7.03 (s, 1H), 6.66 (s, 1H), 2.16 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 165.25, 153.52, 137.40, 131.79, 130.74, 129.92, 129.60, 128.92, 128.67, 127.17, 126.69, 121.21, 116.02, 17.73, 15.58.

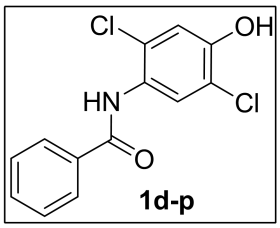


2-Bromo-6-chloro-N-(4-hydroxy-2,5-dimethylphenyl)benzamide **1c-p**

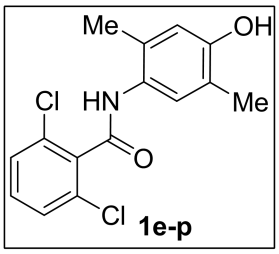
92% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.88 (s, 1H), 9.23 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.05 (s, 1H), 6.66 (s, 1H), 2.20 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 163.46, 153.60, 138.73, 131.71, 131.32, 131.27, 131.13, 128.62, 128.33, 126.22, 121.27, 120.25, 116.04, 17.83, 15.63.



1d-p was synthesized according to literature method[3].

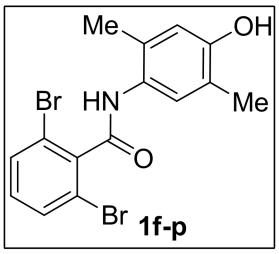


2,6-Dichloro-N-(4-hydroxy-2,5-dimethylphenyl)benzamide **1e-p**

88% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 9.23 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.01 (s, 1H), 6.65 (s, 1H), 2.17 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 162.46, 153.64, 136.85, 131.71, 131.26, 131.06, 128.39, 128.20, 126.17, 121.32, 116.04, 17.76, 15.61.

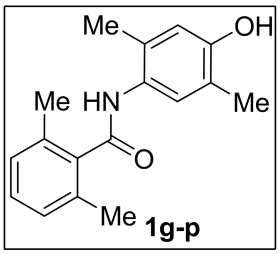


2,6-Dibromo-N-(4-hydroxy-2,5-dimethylphenyl)benzamide **1f-p**

61% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.86 (s, 1H), 9.24 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 6.65 (s, 1H), 2.22 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 164.49, 153.57, 140.54, 131.76, 131.72, 131.66, 128.29, 126.26, 121.22, 120.14, 116.03, 17.96, 15.71.

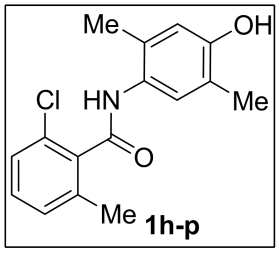


N-(4-hydroxy-2,5-dimethylphenyl)-2,6-dimethylbenzamide **1g-p**.

90% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.57 (s, 1H), 9.19 (s, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.99 (s, 1H), 6.64 (s, 1H), 2.35 (s, 6H), 2.16 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 168.09, 153.42, 138.85, 133.66, 131.71, 128.75, 128.10, 127.21, 126.97, 121.24, 116.02, 19.09, 18.04, 15.64.

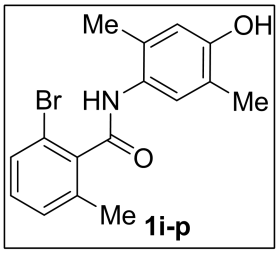


2-Chloro-N-(4-hydroxy-2,5-dimethylphenyl)-6-methylbenzamide **1h-p**

57% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 9.18 (s, 1H), 7.36 – 7.31 (m, 2H), 7.27 – 7.25 (m, 1H), 7.00 (s, 1H), 6.64 (s, 1H), 2.39 (s, 3H), 2.17 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 165.06, 153.48, 137.72, 136.54, 131.69, 129.73, 129.62, 128.60, 128.54, 126.54, 126.44, 121.22, 115.99, 19.02, 17.83, 15.56.

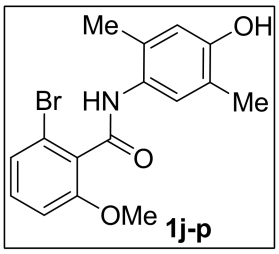


2-Bromo-N-(4-hydroxy-2,5-dimethylphenyl)-6-methylbenzamide **1i-p**

58% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.70 (s, 1H), 9.19 (s, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.02 (s, 1H), 6.63 (s, 1H), 2.39 (s, 3H), 2.18 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 165.98, 153.49, 139.75, 136.64, 131.66, 129.94, 129.59, 129.11, 128.47, 126.54, 121.19, 119.11, 115.99, 19.28, 17.95, 15.62.

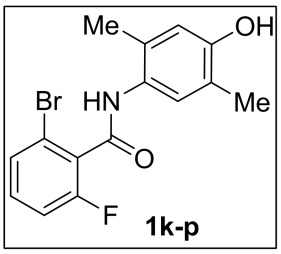


2-Bromo-N-(4-hydroxy-2,5-dimethylphenyl)-6-methoxybenzamide **1j-p**

80% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.56 (s, 1H), 9.15 (s, 1H), 7.32 (t, J = 8.2 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 8.3 Hz, 1H), 6.99 (s, 1H), 6.62 (s, 1H), 3.82 (s, 3H), 2.16 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 163.71, 157.14, 153.30, 131.64, 130.83, 129.53, 128.52, 126.75, 124.03, 121.01, 119.70, 115.94, 110.89, 56.22, 17.66, 15.61.



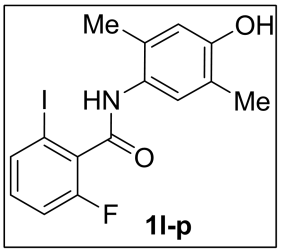
2-Bromo-6-fluoro-N-(4-hydroxy-2,5-dimethylphenyl)benzamide **1k-p**

88% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 9.22 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.00 (s, 1H), 6.65 (s, 1H), 2.16 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.40, 159.91, 157.44, 153.63, 131.73, 131.64, 131.59, 128.52, 128.48, 128.37, 128.29, 126.20, 121.31, 120.00, 119.95, 116.03, 115.21, 115.00, 17.65, 15.57.

^{19}F NMR (376 MHz, DMSO-d_6) δ -113.49.



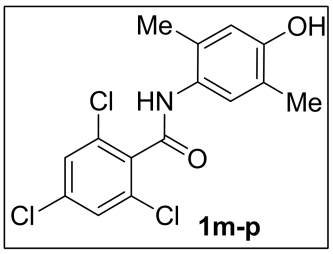
2-Fluoro-N-(4-hydroxy-2,5-dimethylphenyl)-6-iodobenzamide **1l-p**

65% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.83 (s, 1H), 9.20 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 8.7 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.04 (s, 1H), 6.65 (s, 1H), 2.17 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 163.33, 159.17, 156.70, 153.55, 134.67, 134.64, 132.31, 132.09, 131.97, 131.89, 131.54, 128.25, 126.30, 121.19, 116.02, 115.61, 115.39, 94.92, 94.88, 17.72, 15.60.

^{19}F NMR (376 MHz, DMSO-d_6) δ -113.00.

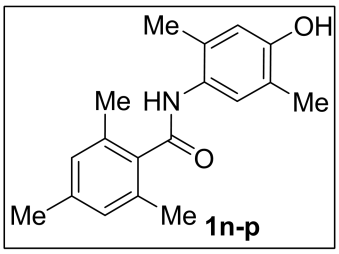


2,4,6-Trichloro-N-(4-hydroxy-2,5-dimethylphenyl)benzamide **1m-p**

70% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 9.23 (s, 1H), 7.79 (s, 2H), 7.02 (s, 1H), 6.65 (s, 1H), 2.16 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.69, 153.65, 135.87, 134.35, 132.16, 131.51, 128.19, 127.97, 125.95, 121.35, 116.06, 17.69, 15.56.



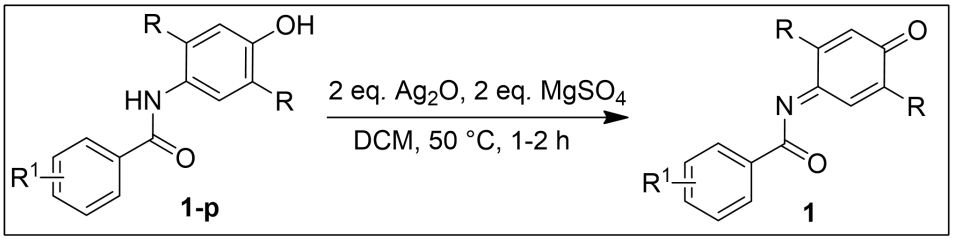
N-(4-hydroxy-2,5-dimethylphenyl)-2,4,6-trimethylbenzamide **1n-p**

54% yield.

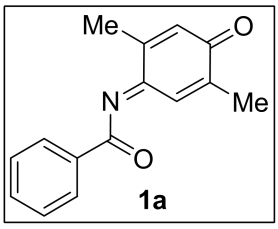
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.46 (s, 1H), 9.14 (s, 1H), 6.98 (s, 1H), 6.89 (s, 2H), 6.64 (s, 1H), 2.31 (s, 6H), 2.26 (s, 3H), 2.15 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 168.21, 153.32, 137.13, 136.14, 133.55, 131.62, 128.68, 127.72, 127.06, 121.15, 115.98, 20.66, 18.99, 17.96, 15.56.

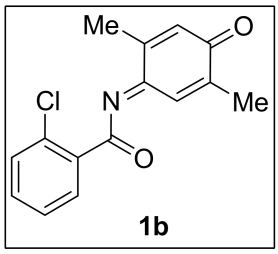
Synthetic procedure for the preparation of 1



Ag_2O (10 mmol, 2.32 g) and $MgSO_4$ (10 mmol, 1.20 g) were added to a solution of **1-p** (5 mmol) in anhydrous DCM (25 mL). The mixture was stirred at 50 °C for 1-2 h and cooled to room temperature and filtered. The filtrate was evaporated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EtOAc = 30/1 to 15/1) and recrystallization (PE/ CH_2Cl_2) to give the pure products **1**.



1a was synthesized according to literature method[2].



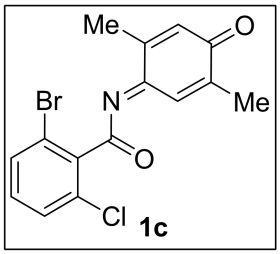
(*E*)-2-Chloro-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide **1b**

75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 1H), 7.48 – 7.47 (m, 2H), 7.40 – 7.36 (m, 1H), 6.80 (q, *J* = 1.6 Hz, 1H), 6.56 (q, *J* = 1.5 Hz, 1H), 2.24 (d, *J* = 1.4 Hz, 3H), 1.98 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.03, 179.14, 157.36, 148.01, 143.69, 133.59, 133.55, 132.86, 132.32, 132.22, 131.65, 128.30, 127.12, 17.60, 15.96.

HRMS (ESI) Calcd for $C_{15}H_{13}ClNO_2^+$ $[M+H]^+$ 274.0629; Founded:274.0625.



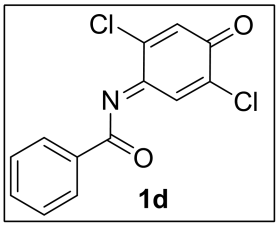
(*E*)-2-Bromo-6-chloro-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide **1c**

28% yield.

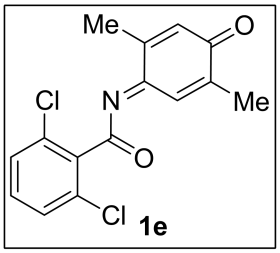
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.40 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.33 (q, *J* = 1.6 Hz, 1H), 7.23 (t, *J* = 8.1 Hz, 1H), 6.55 (q, *J* = 1.5 Hz, 1H), 2.16 (d, *J* = 1.5 Hz, 3H), 2.04 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.18, 177.86, 158.53, 148.25, 143.67, 136.72, 133.22, 132.15, 131.90, 131.68, 129.19, 128.44, 120.50, 17.47, 16.04.

HRMS (ESI) Calcd for $C_{15}H_{12}BrClNO_2^+$ $[M+H]^+$ 351.9734; Found: 351.9731.



1d was synthesized according to literature method[3].



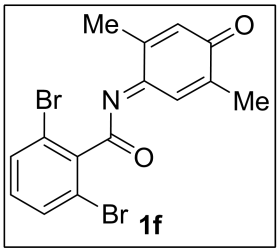
(*E*)-2,6-Dichloro-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide **1e**

39% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.20 – 7.18 (m, 1H), 6.47 (q, *J* = 1.5 Hz, 1H), 2.07 (d, *J* = 1.6 Hz, 3H), 1.96 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.11, 177.27, 158.26, 148.16, 143.70, 134.82, 133.20, 132.30, 131.43, 128.68, 128.38, 17.42, 16.03.

HRMS (ESI) Calcd for $C_{15}H_{12}Cl_2NO_2^+$ $[M+H]^+$ 308.0240; Founded: 308.0237.



1f

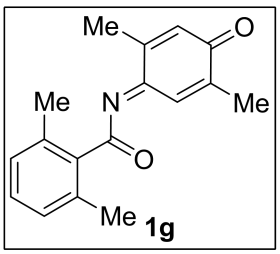
(*E*)-2,6-Dibromo-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide **1f**

12% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.41 (q, *J* = 1.6 Hz, 1H), 7.15 (t, *J* = 8.1 Hz, 1H), 6.55 (q, *J* = 1.5 Hz, 1H), 2.16 (d, *J* = 1.2 Hz, 3H), 2.04 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.20, 178.39, 158.85, 148.31, 143.60, 138.51, 133.22, 132.39, 131.91, 128.47, 120.34, 17.50, 16.02.

HRMS (ESI) Calcd for $C_{15}H_{12}Br_2NO_2^+$ $[M+H]^+$ 395.9229; Founded: 395.9228.



1g

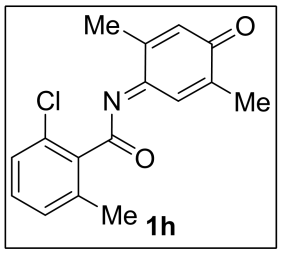
(*E*)-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-2,6-dimethylbenzamide **1g**

68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.96 (q, *J* = 1.6 Hz, 1H), 6.51 (d, *J* = 1.0 Hz, 1H), 2.49 (s, 6H), 2.16 (d, *J* = 1.0 Hz, 3H), 1.99 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.87, 184.04, 155.38, 148.30, 143.42, 135.92, 135.36, 132.72, 130.25, 128.67, 127.86, 20.96, 17.54, 16.05.

HRMS (ESI) Calcd for $C_{17}H_{18}NO_2^+$ $[M+H]^+$ 268.1332; Founded: 268.1332.



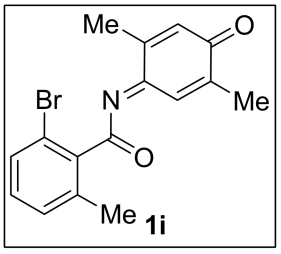
(*E*)-2-Chloro-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-methylbenzamide **1h**

49% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 3H), 7.24 – 7.22 (m, 1H), 6.58 (s, 1H), 2.59 (s, 3H), 2.19 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.14, 180.77, 157.11, 148.03, 143.44, 138.49, 135.08, 133.05, 130.91, 130.19, 129.39, 128.65, 127.50, 20.57, 17.49, 16.01.

HRMS (ESI) Calcd for $C_{16}H_{15}ClNO_2^+$ $[M+H]^+$ 288.0786; Founded: 288.0782.



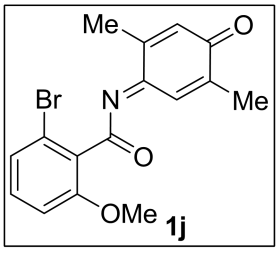
(*E*)-2-Bromo-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-methylbenzamide **1i**

61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 1.0 Hz, 1H), 7.22 – 7.15 (m, 2H), 6.52 (s, 1H), 2.53 (s, 3H), 2.13 (d, J = 1.5 Hz, 3H), 2.03 (d, J = 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.14, 181.22, 157.39, 148.04, 143.37, 138.61, 137.00, 133.04, 131.11, 130.72, 129.91, 128.76, 118.56, 20.79, 17.50, 15.96.

HRMS (ESI) Calcd for $C_{16}H_{15}BrNO_2^+$ $[M+H]^+$ 332.0281; Founded: 332.0278.

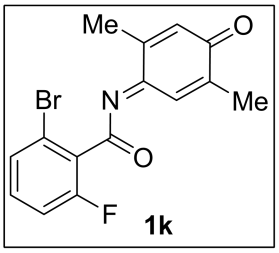


(*E*)-2-Bromo-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-methoxybenzamide **1j**
58% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 3H), 6.89 – 6.85 (m, 1H), 6.51 (s, 1H), 3.80 (s, 3H), 2.14 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.29, 179.41, 157.16, 156.21, 148.37, 142.50, 132.80, 131.90, 129.17, 127.14, 125.66, 120.66, 110.24, 56.05, 17.41, 15.97.

HRMS (ESI) Calcd for $C_{16}H_{15}BrNO_3^+$ $[M+H]^+$ 348.0230; Founded: 348.0225.



1k

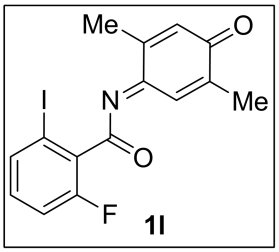
(*E*)-2-Bromo-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-fluorobenzamide **1k**
62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.1 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.13 – 7.06 (m, 2H), 6.54 (s, 1H), 2.16 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.99, 176.57, 161.11, 158.58, 157.27, 148.02, 143.81, 133.12, 132.75, 132.65, 129.63, 129.60, 128.53, 128.50, 126.11, 125.92, 120.71, 120.67, 115.56, 115.34, 17.43, 16.01.

HRMS (ESI) Calcd for $C_{15}H_{12}BrFNO_2^+$ $[M+H]^+$ 336.0030; Founded: 336.0026.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.59.



1l

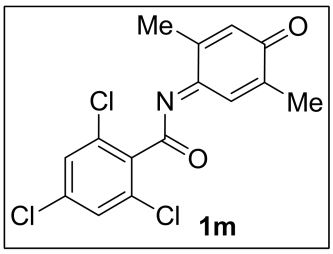
(*E*)-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-2-fluoro-6-iodobenzamide **1l**
49% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 1H), 7.16 – 7.06 (m, 3H), 6.53 (s, 1H), 2.17 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.01, 177.73, 160.49, 157.96, 157.14, 148.05, 143.78, 136.44, 136.40, 133.23, 133.14, 133.08, 129.38, 129.20, 128.72, 128.69, 116.38, 116.16, 93.38, 93.36, 17.52, 16.00.

HRMS (ESI) Calcd for $C_{15}H_{12}FINO_2^+$ $[M+H]^+$ 383.9891; Founded:383.9885.

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.57.



1m

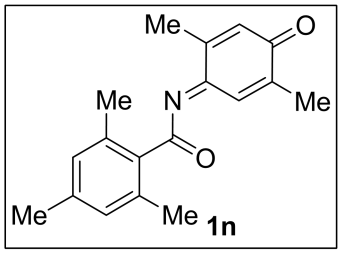
(*E*)-2,4,6-Trichloro-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzamide **1m**

15% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.21 (q, *J* = 1.6 Hz, 1H), 6.55 (q, *J* = 1.6 Hz, 1H), 2.14 (d, *J* = 1.2 Hz, 3H), 2.03 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.03, 176.46, 158.63, 148.03, 143.97, 136.76, 133.38, 133.33, 133.02, 128.80, 128.21, 17.41, 16.06.

HRMS (ESI) Calcd for $C_{15}H_{11}Cl_3NO_2^+$ $[M+H]^+$ 341.9850; Founded: 341.9848.



1n

(*E*)-N-(2,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-2,4,6-trimethylbenzamide **1n**

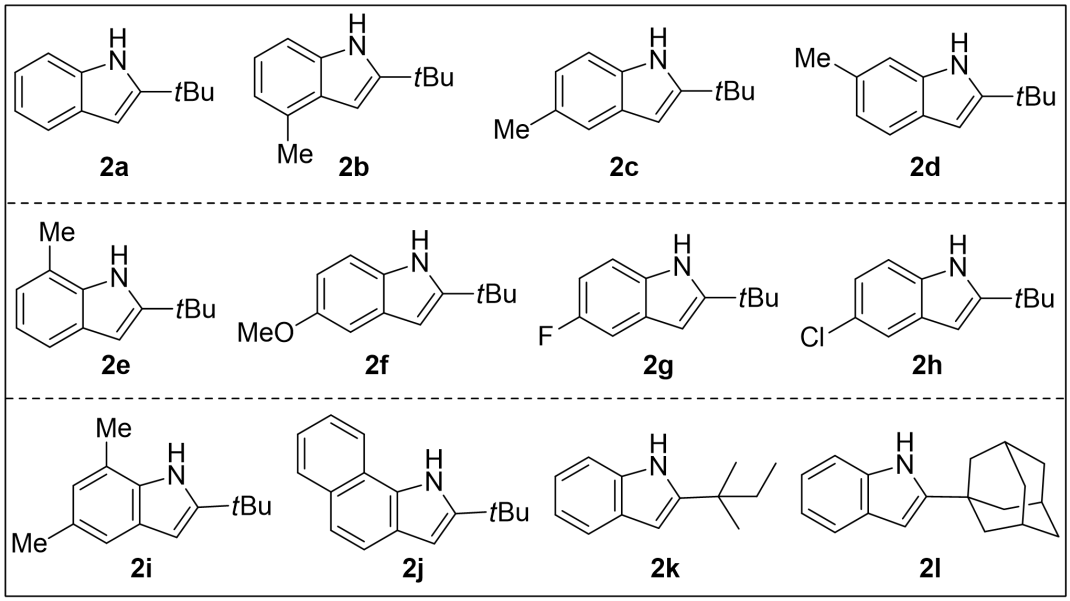
63% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 3H), 6.52 (s, 1H), 2.48 (s, 6H), 2.29 (s, 3H), 2.17 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.99, 184.25, 155.09, 148.44, 143.35, 140.70, 136.38, 132.69, 132.49, 129.67, 128.04, 21.28, 21.20, 17.63, 16.12.

HRMS (ESI) Calcd for $C_{18}H_{20}NO_2^+$ $[M+H]^+$ 282.1489; Founded: 282.1486.

Supplementary Figure 2. Indoles 2 involved in the manuscript.



Indoles **2a**-**2l** were synthesized according to literature methods[4-7].

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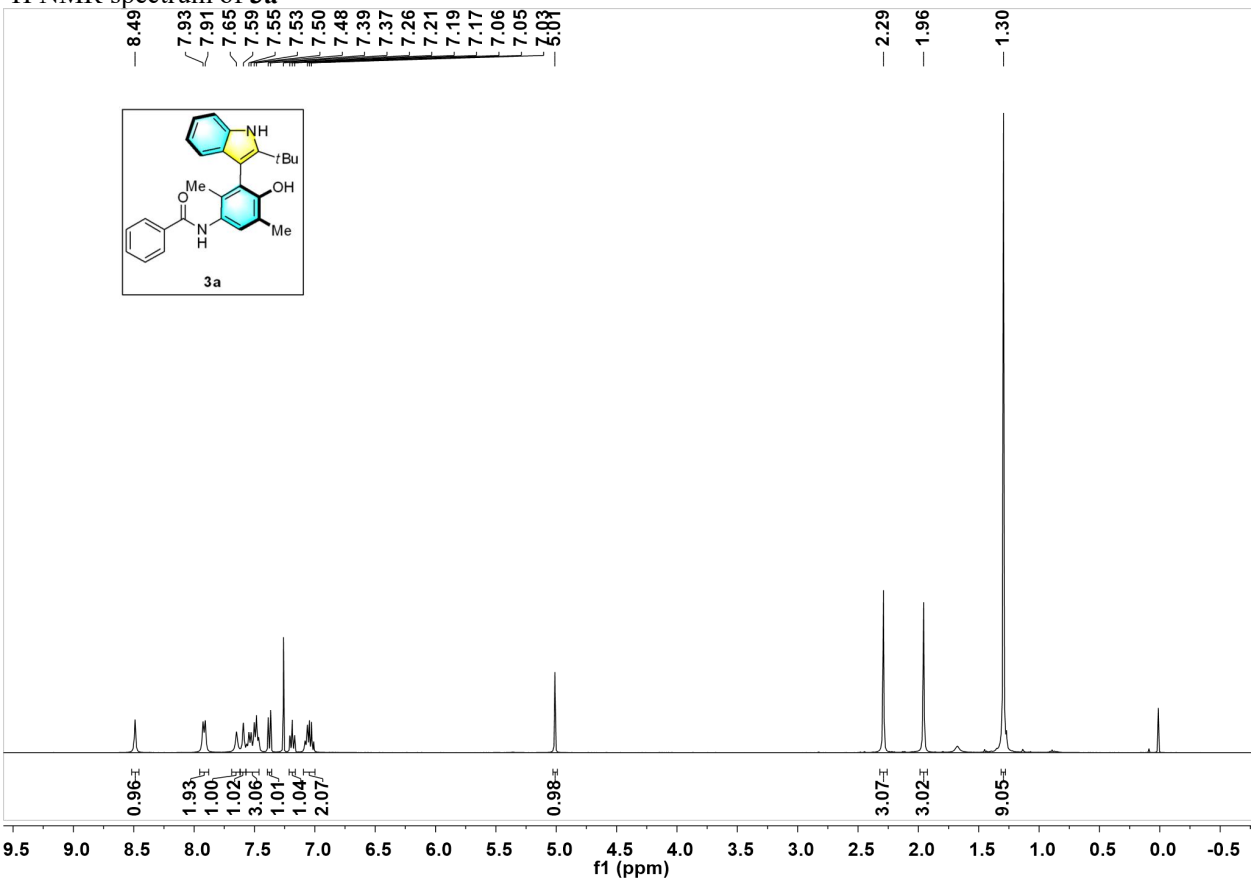
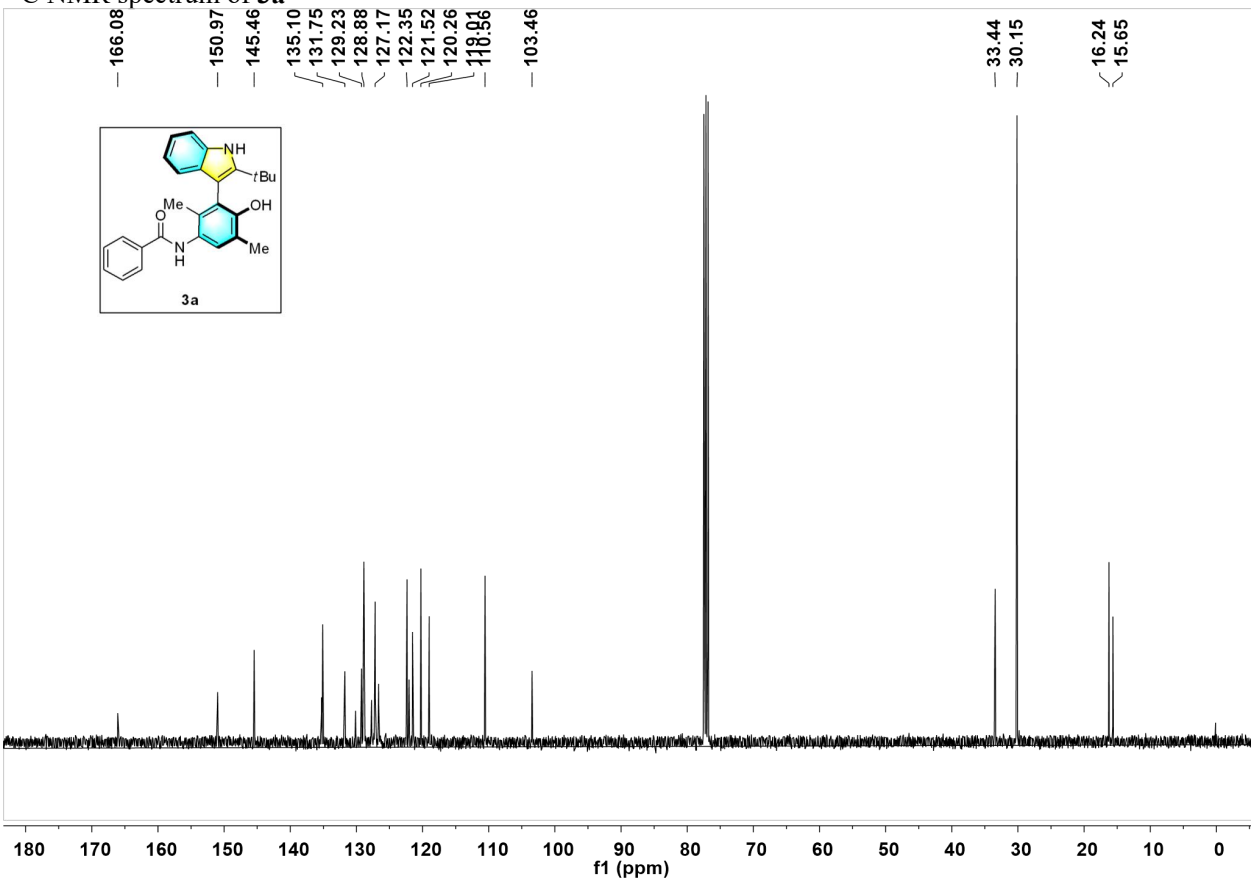
NMR spectra

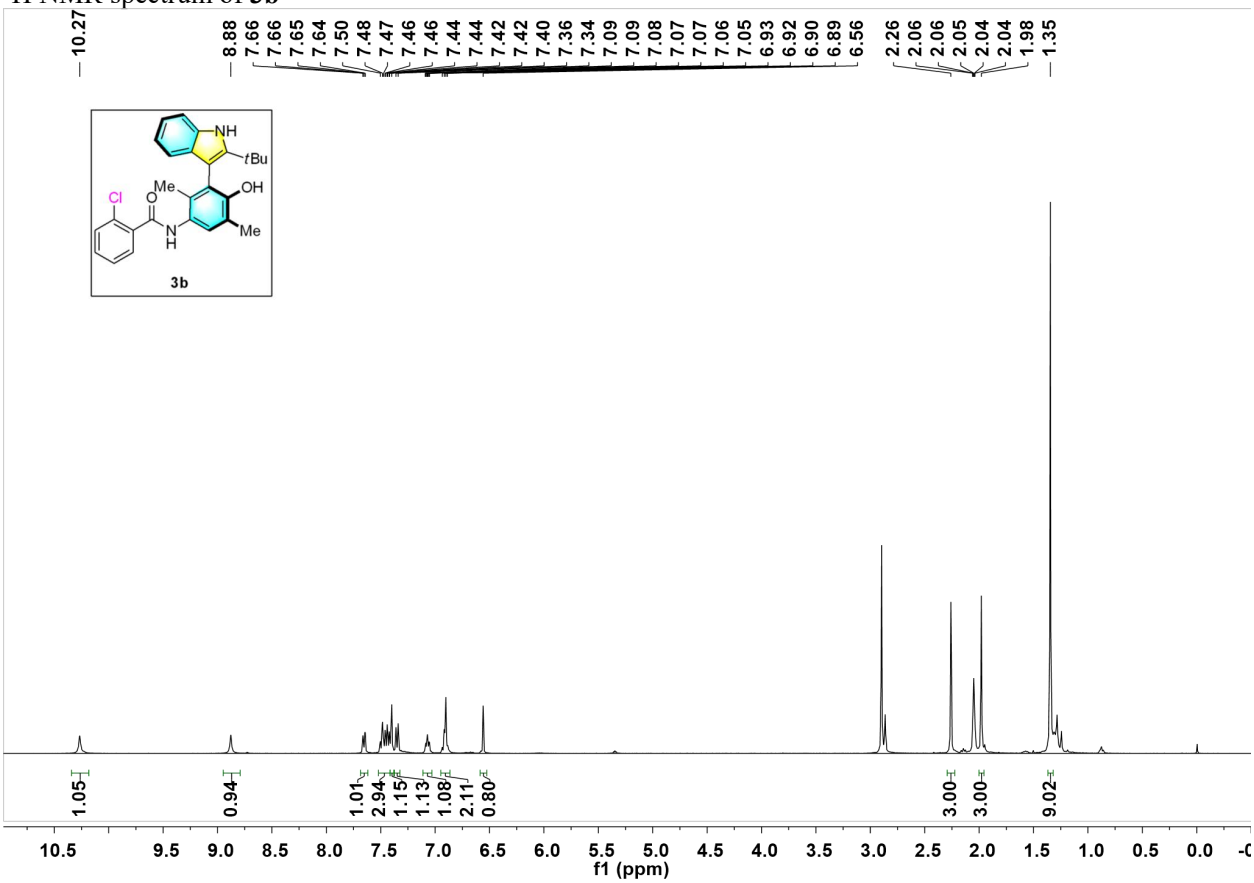
^{1}H NMR spectrum of **3a**



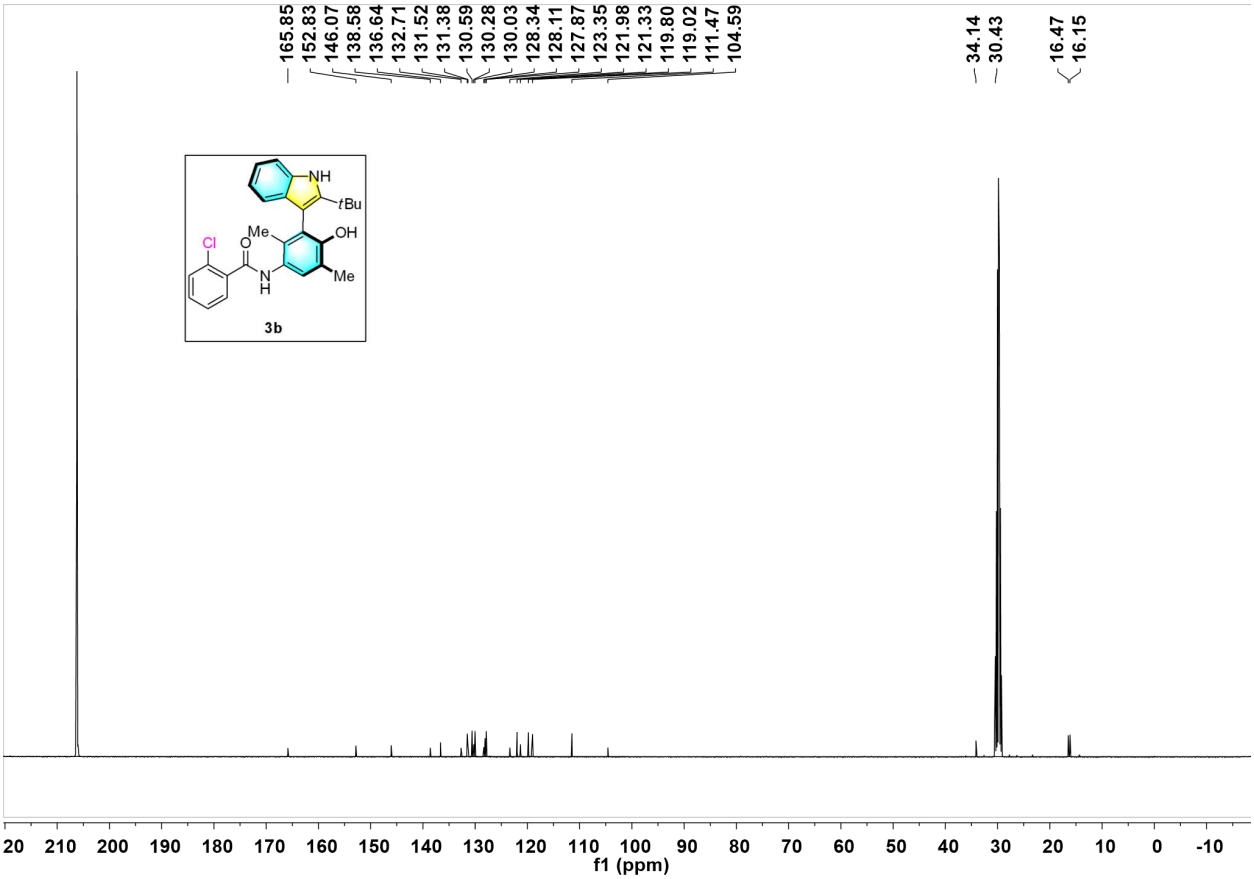
^{13}C NMR spectrum of **3a**



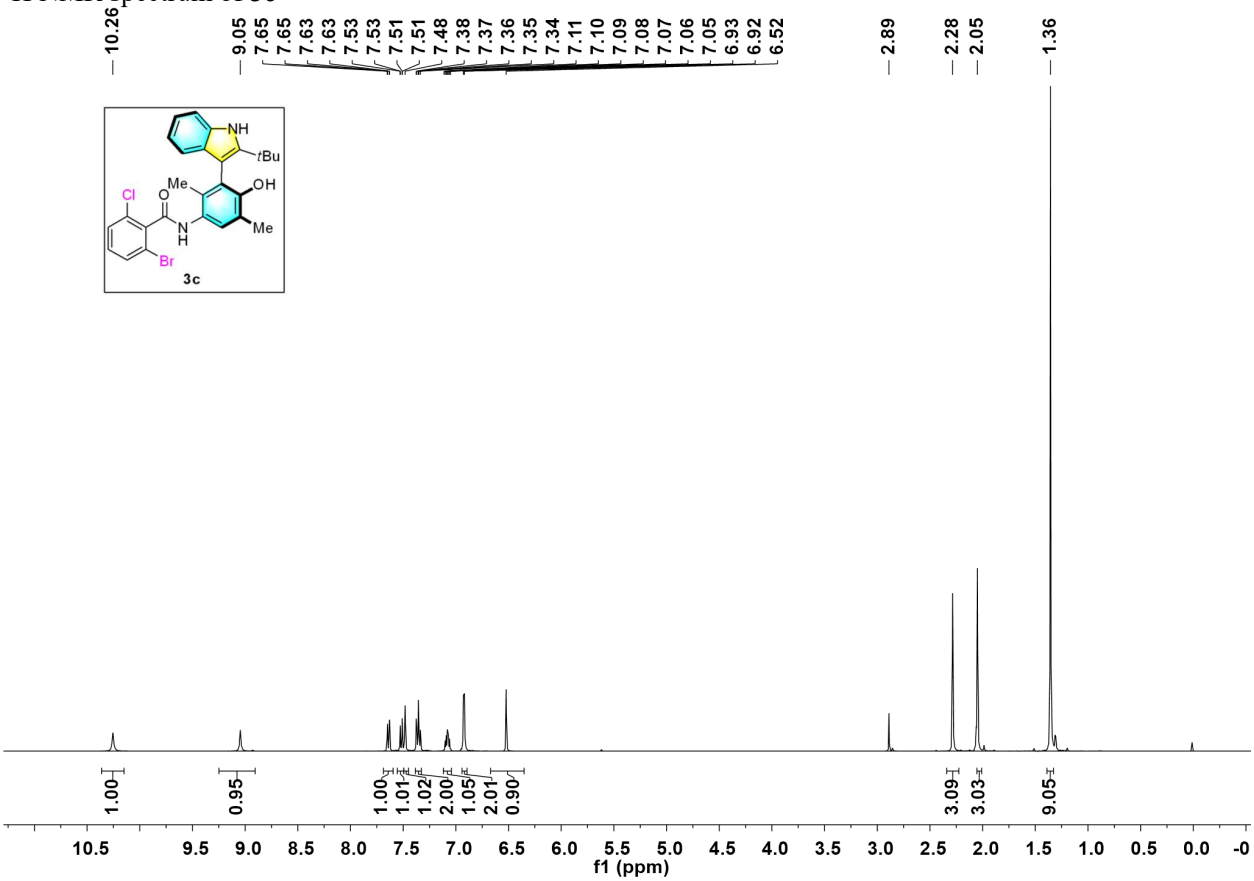
^{1}H NMR spectrum of **3b**



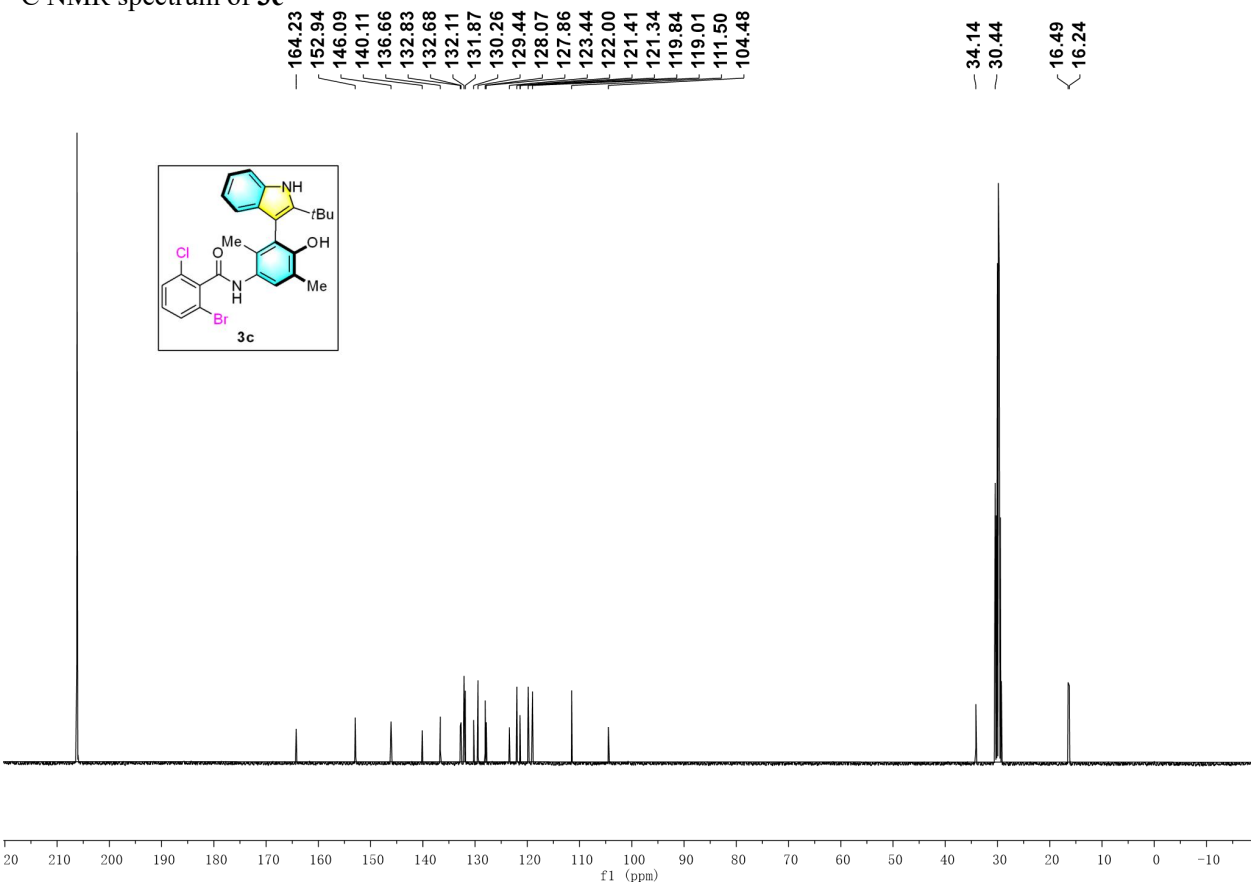
^{13}C NMR spectrum of **3b**



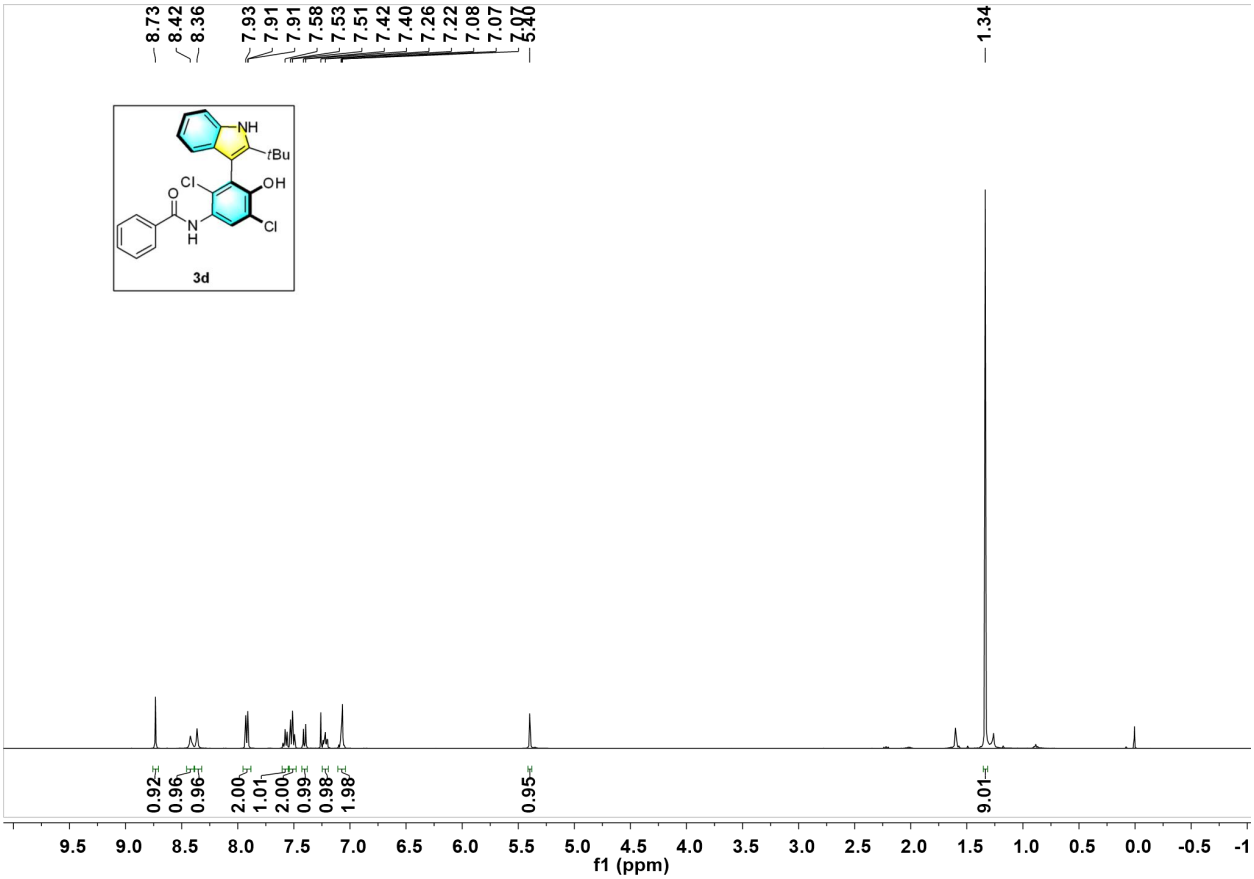
^{1}H NMR spectrum of **3c**



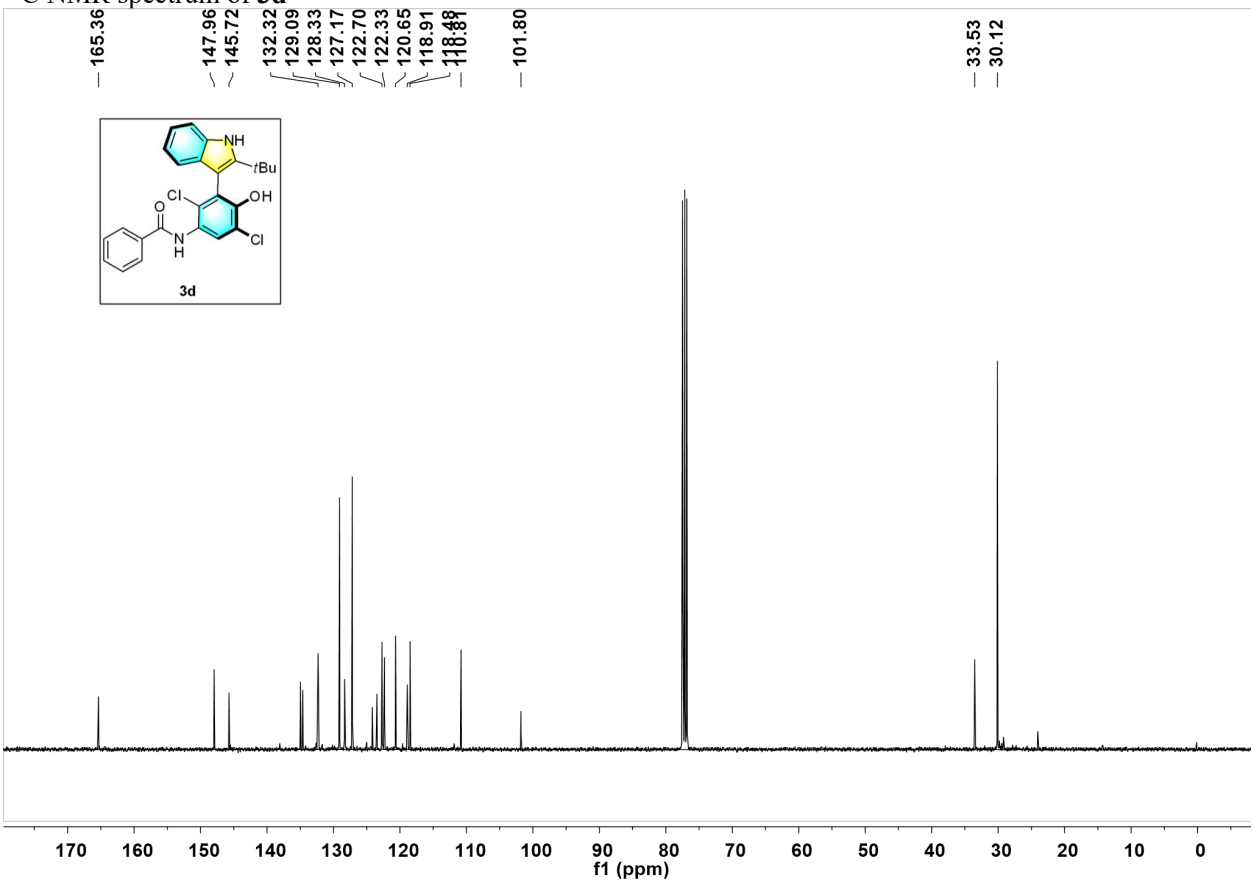
^{13}C NMR spectrum of **3c**



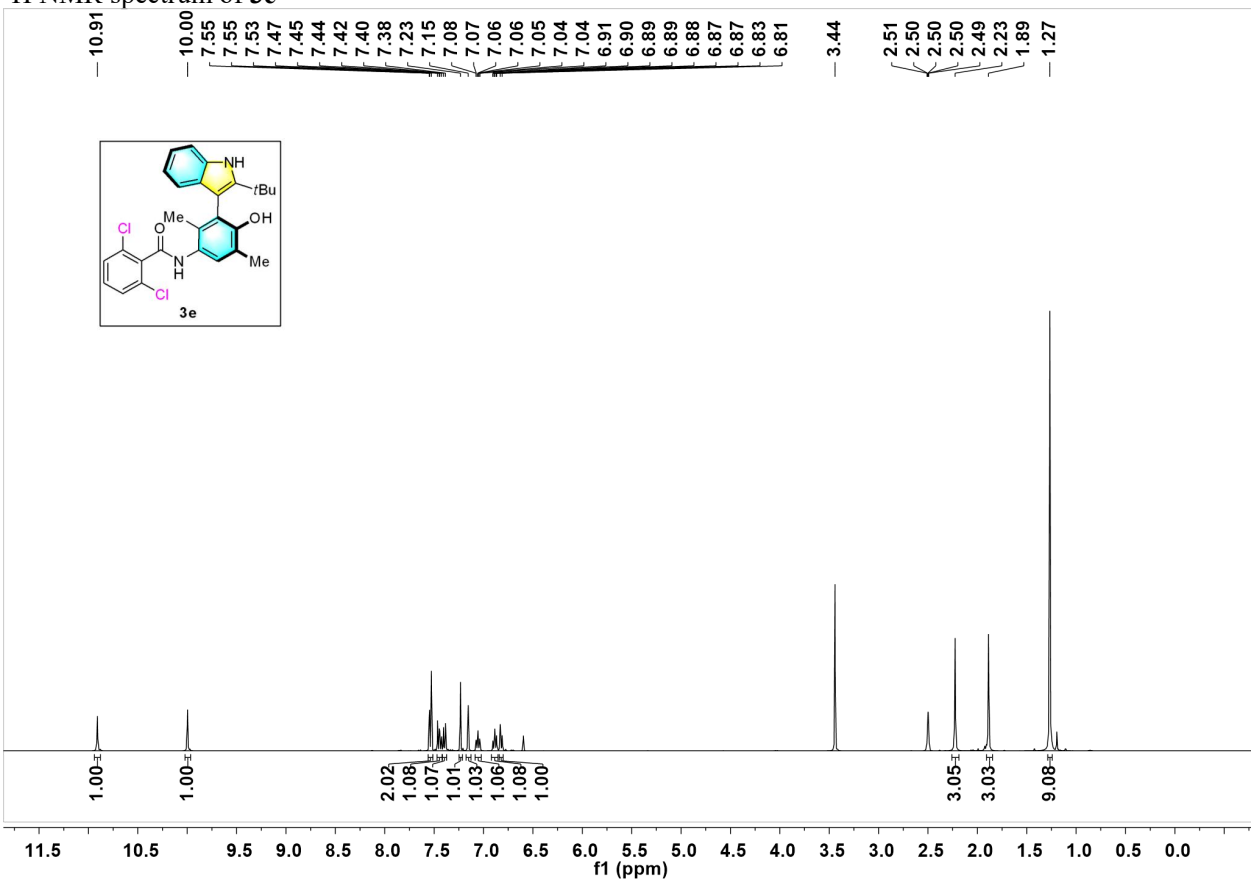
^{1}H NMR spectrum of **3d**



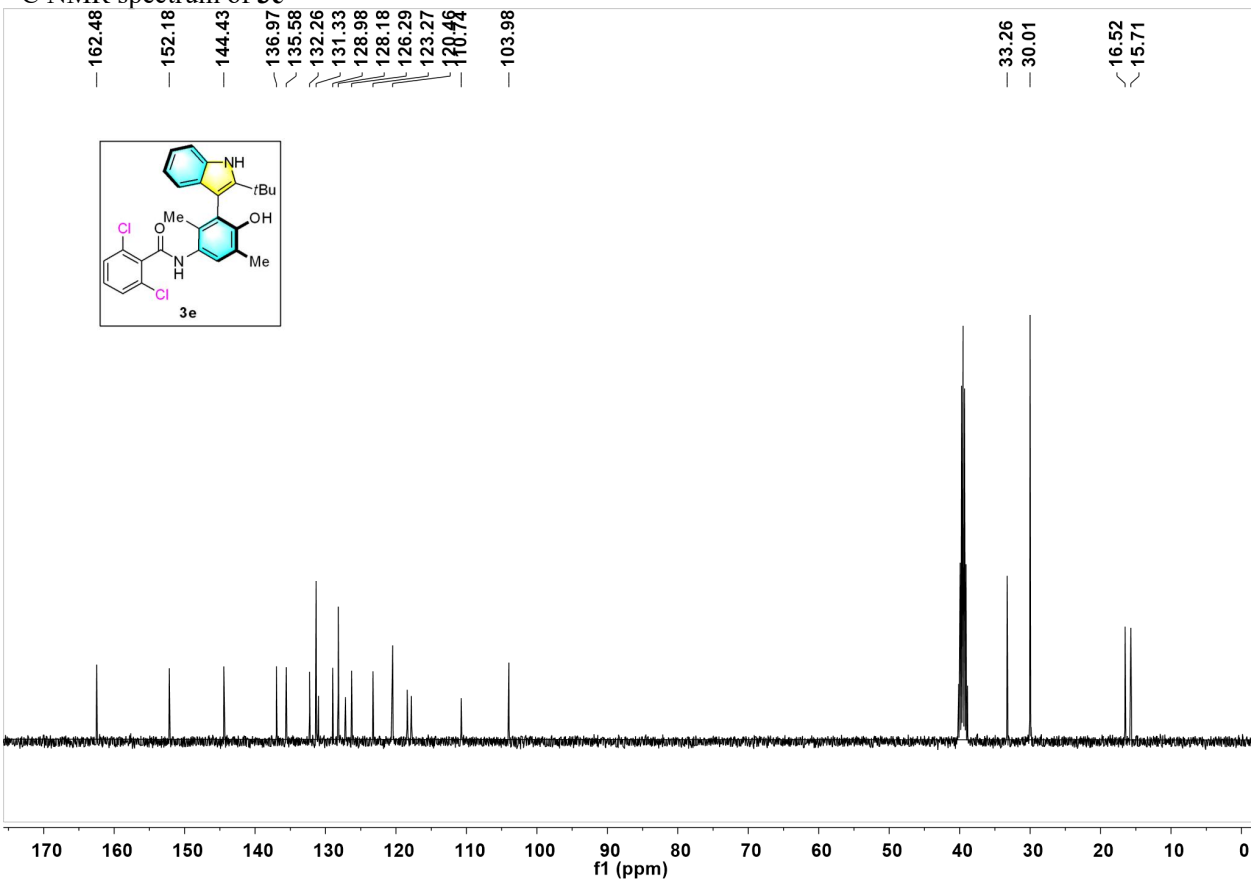
^{13}C NMR spectrum of **3d**



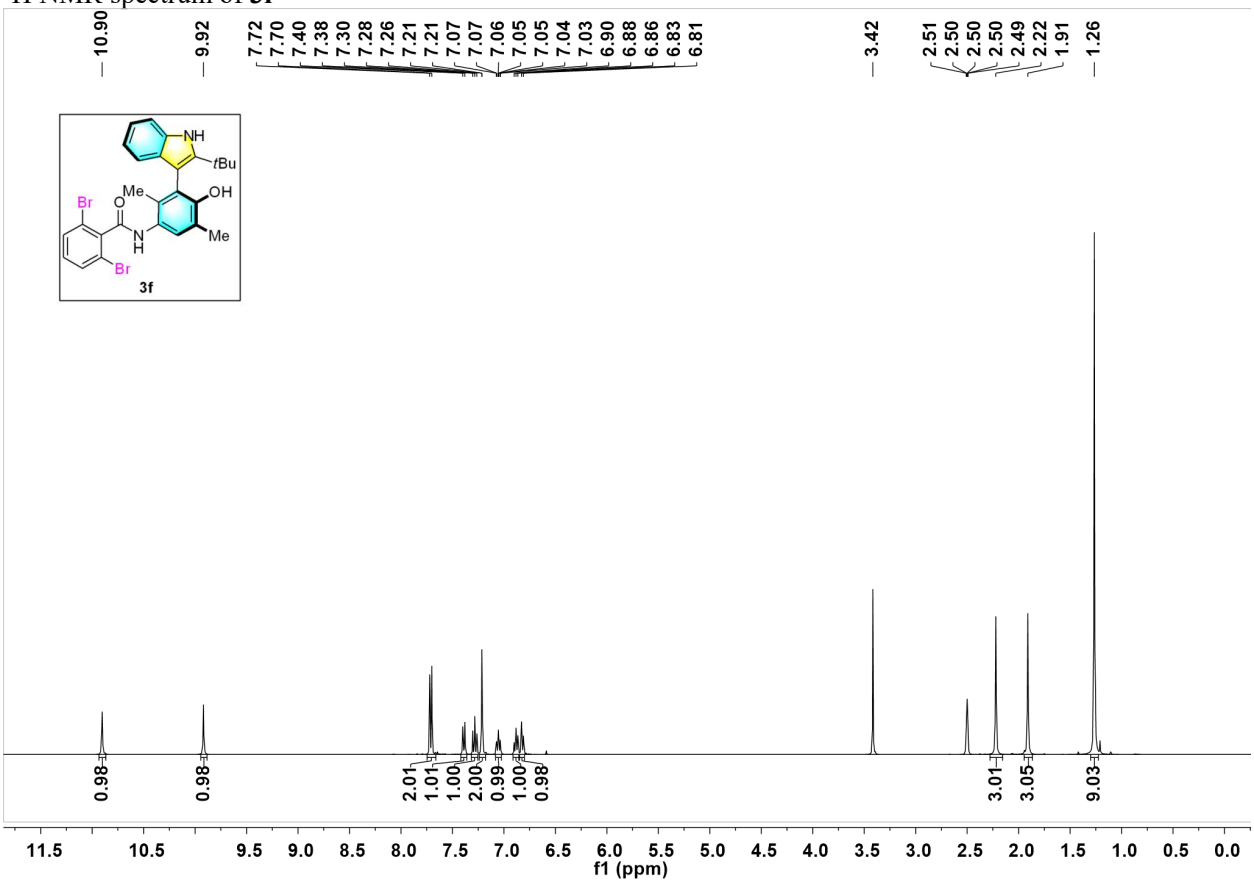
^{1}H NMR spectrum of **3e**



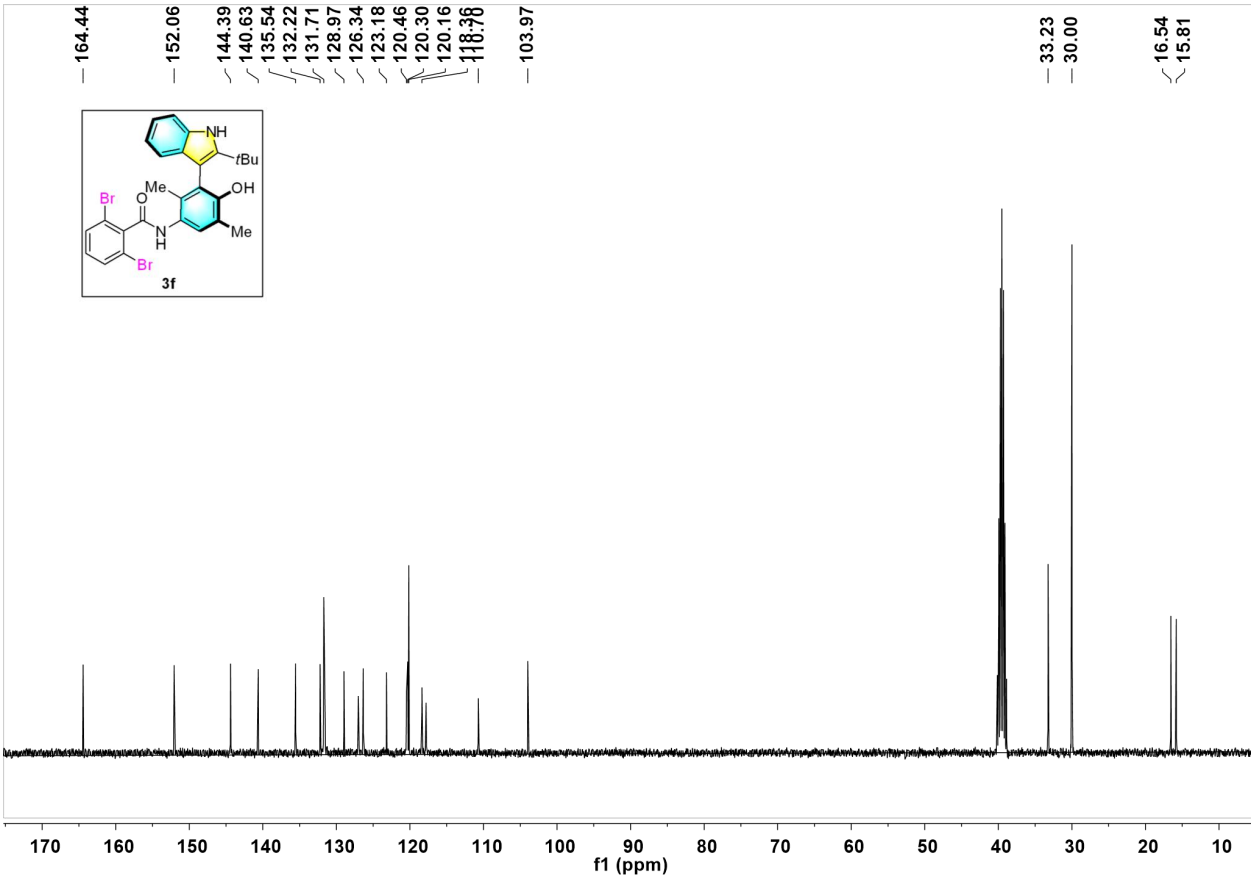
^{13}C NMR spectrum of **3e**



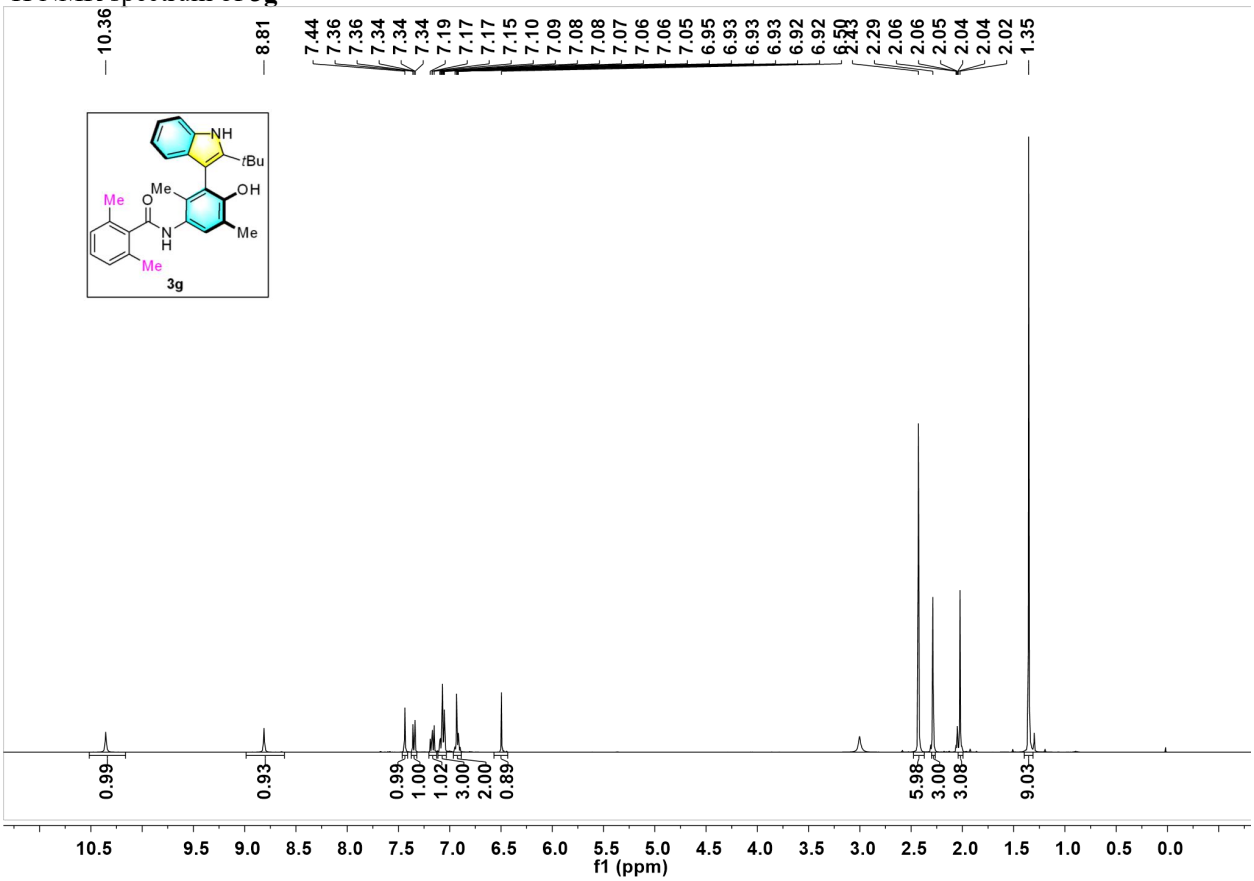
^{1}H NMR spectrum of **3f**



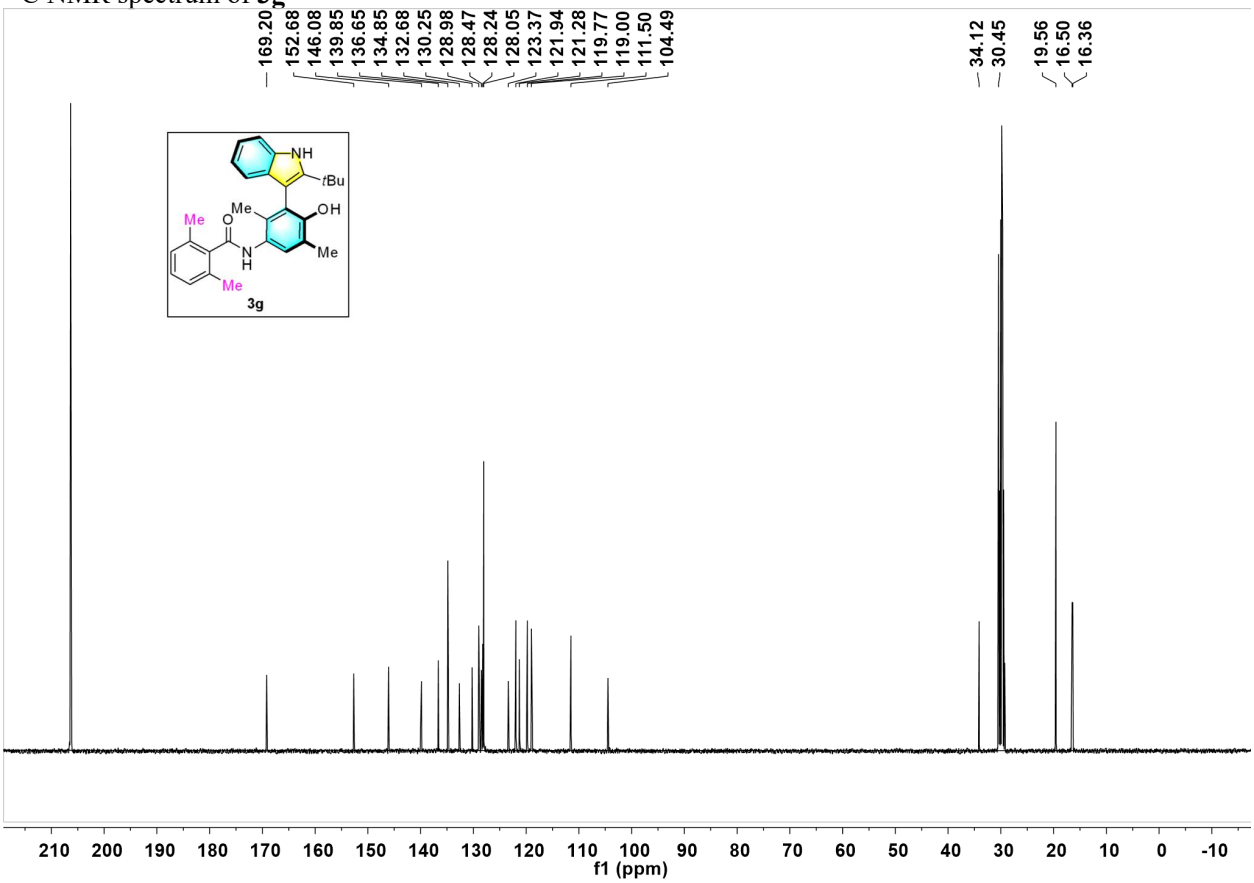
^{13}C NMR spectrum of **3f**



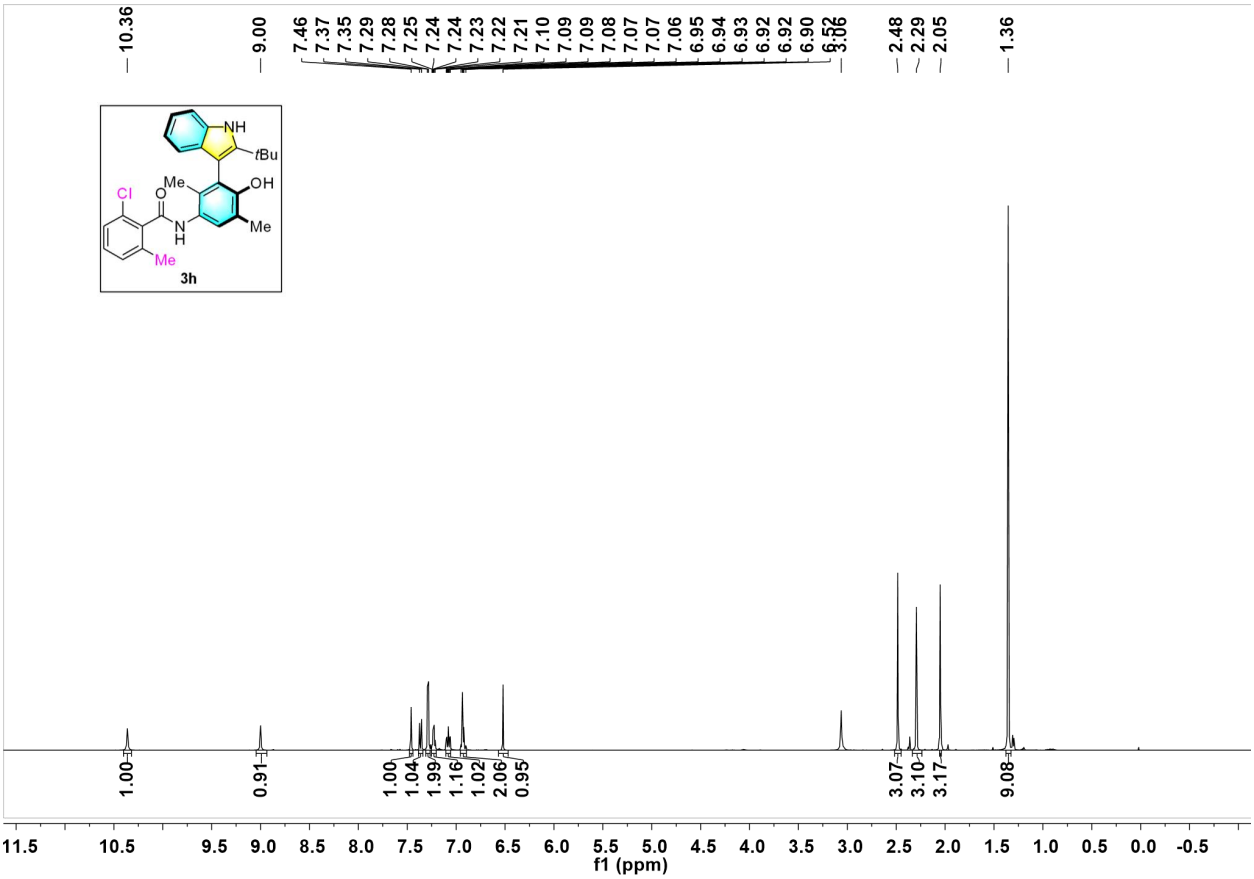
^{1}H NMR spectrum of **3g**



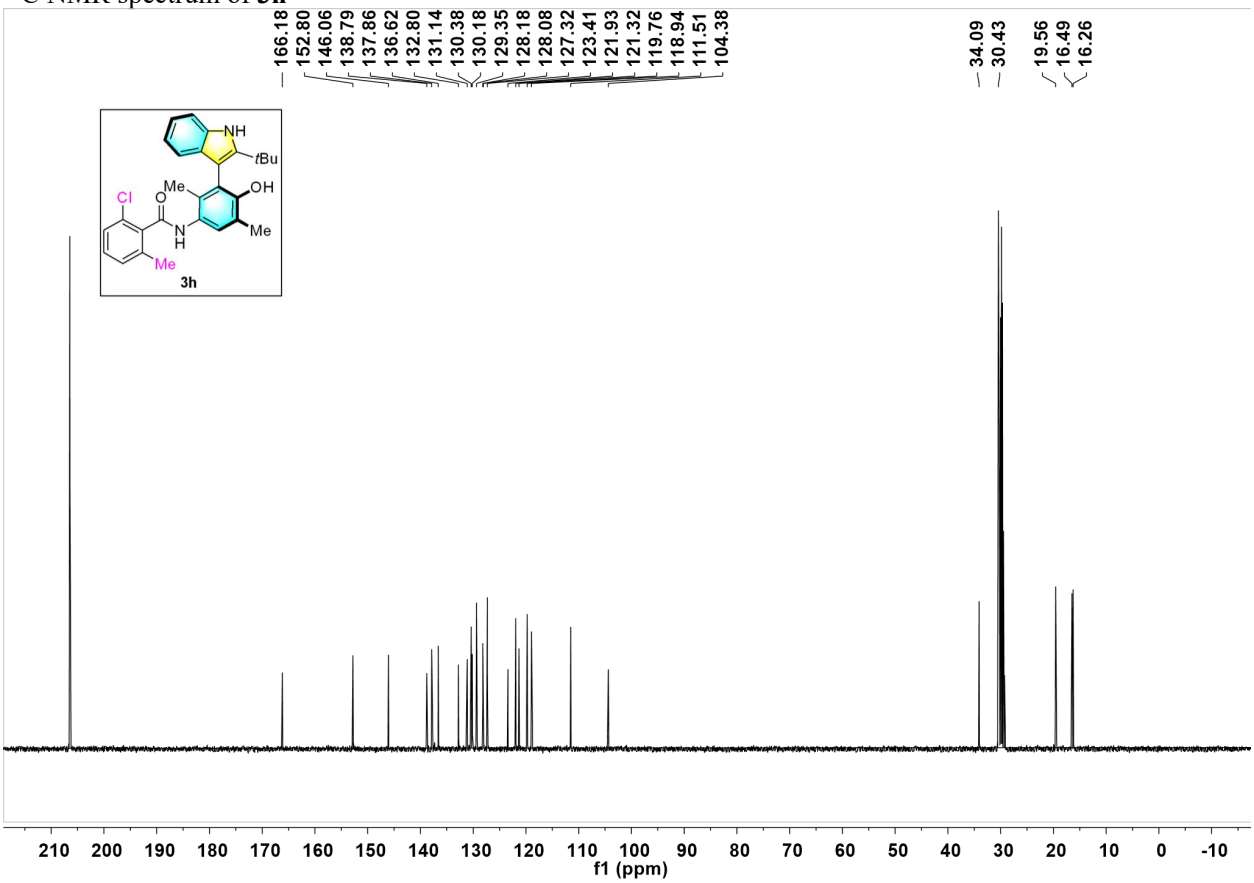
^{13}C NMR spectrum of **3g**



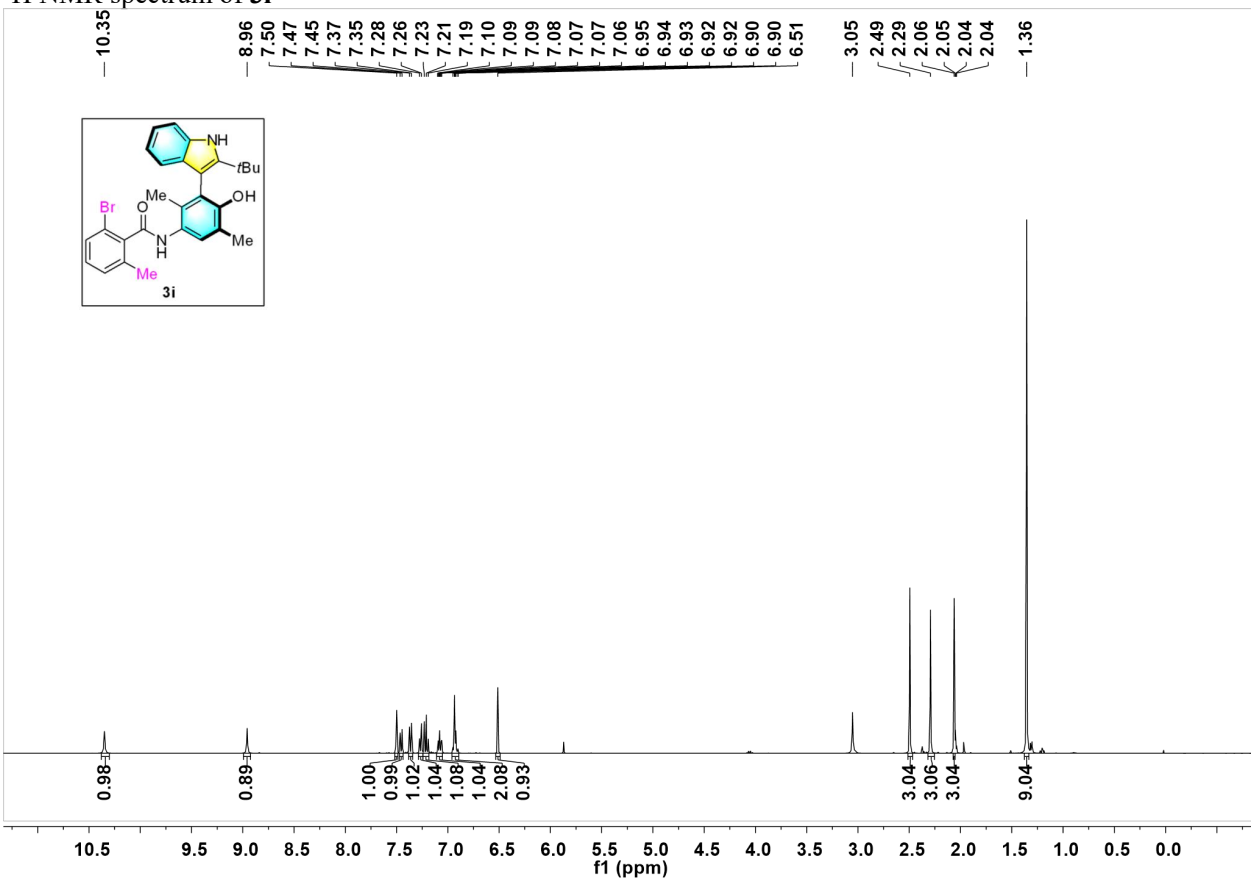
^{1}H NMR spectrum of **3h**



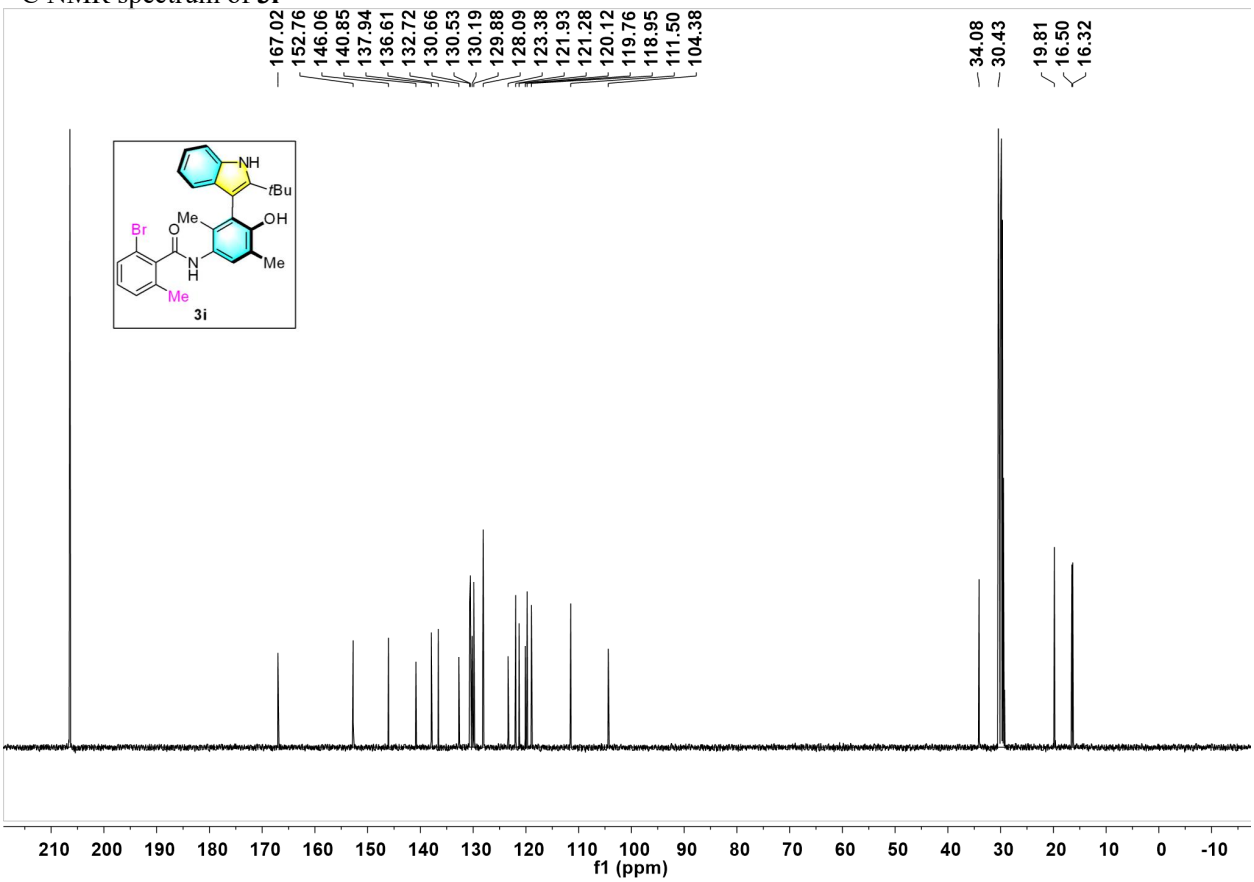
^{13}C NMR spectrum of **3h**



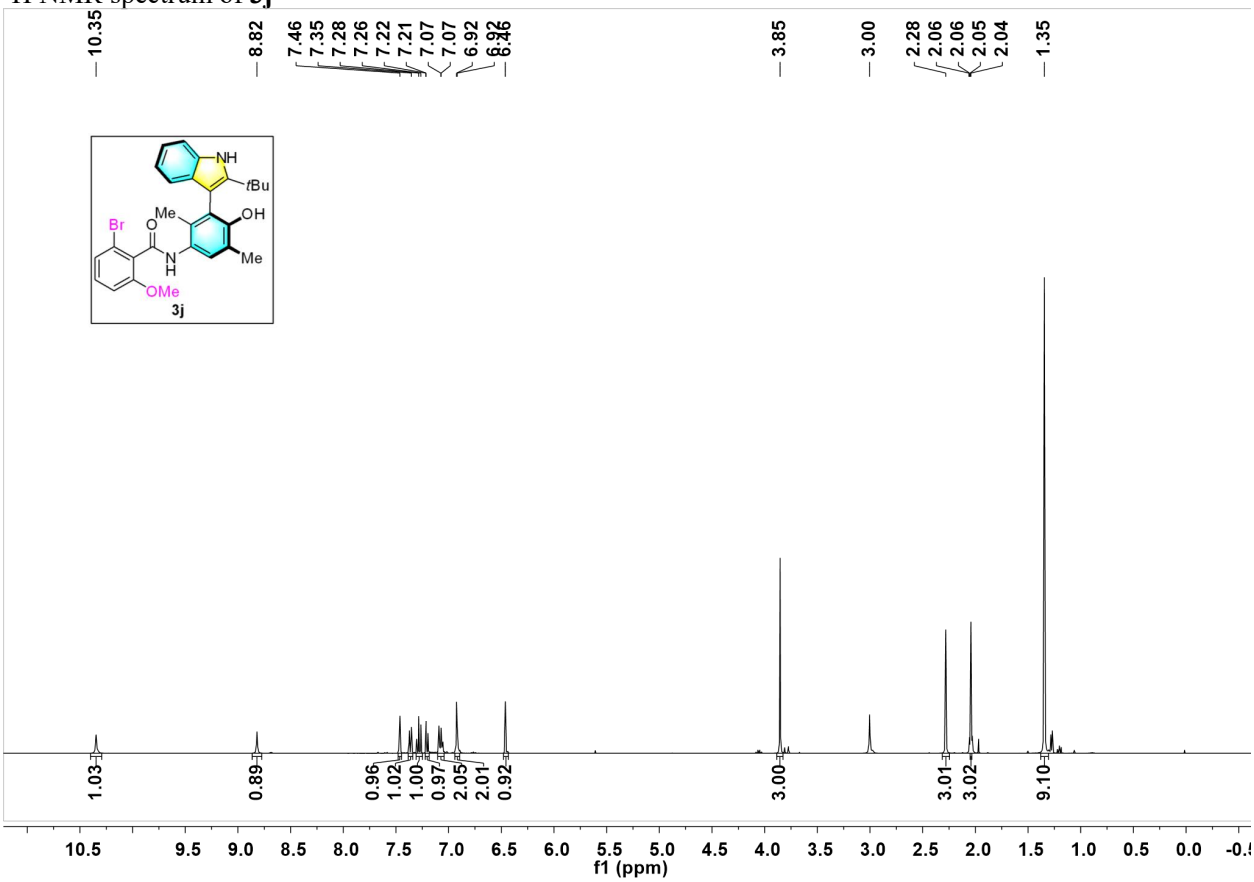
^{1}H NMR spectrum of **3i**



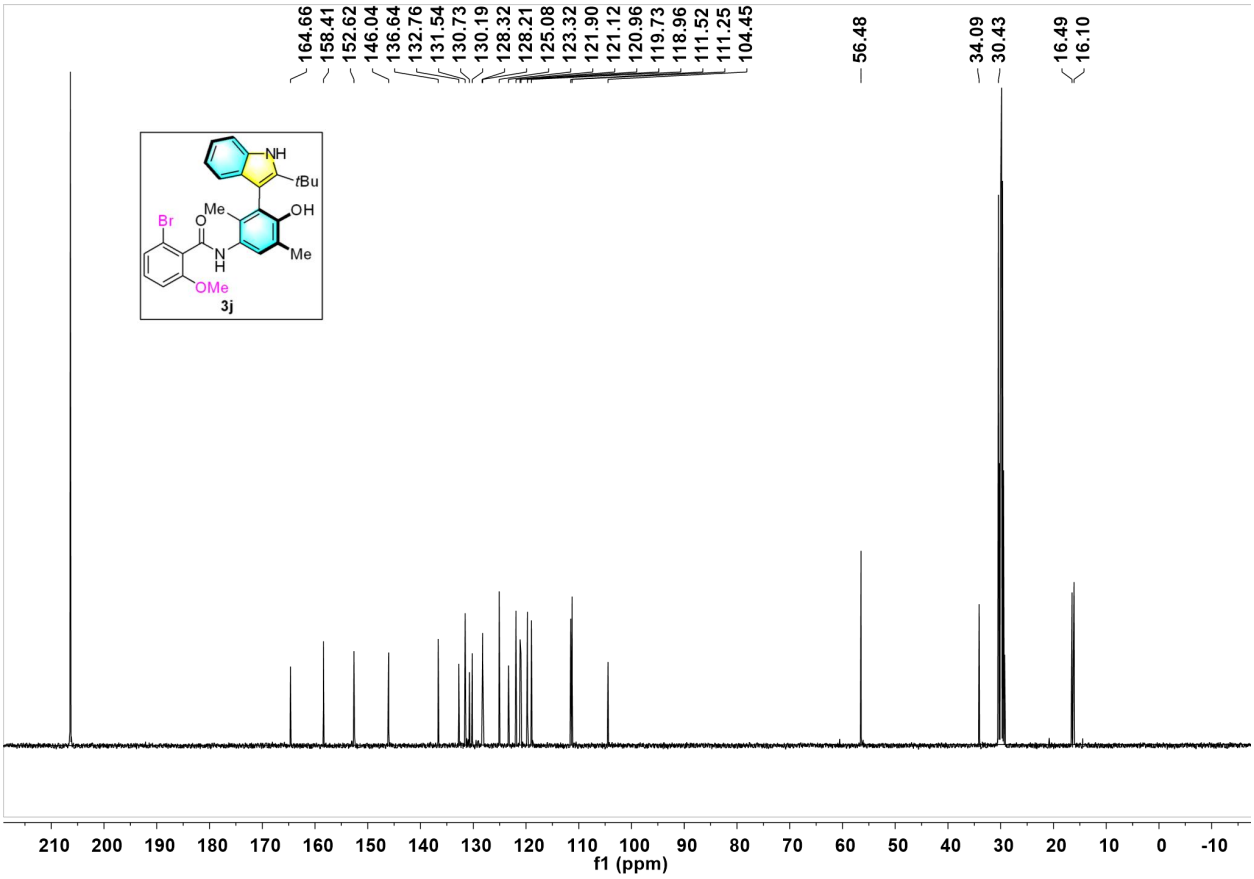
^{13}C NMR spectrum of **3i**



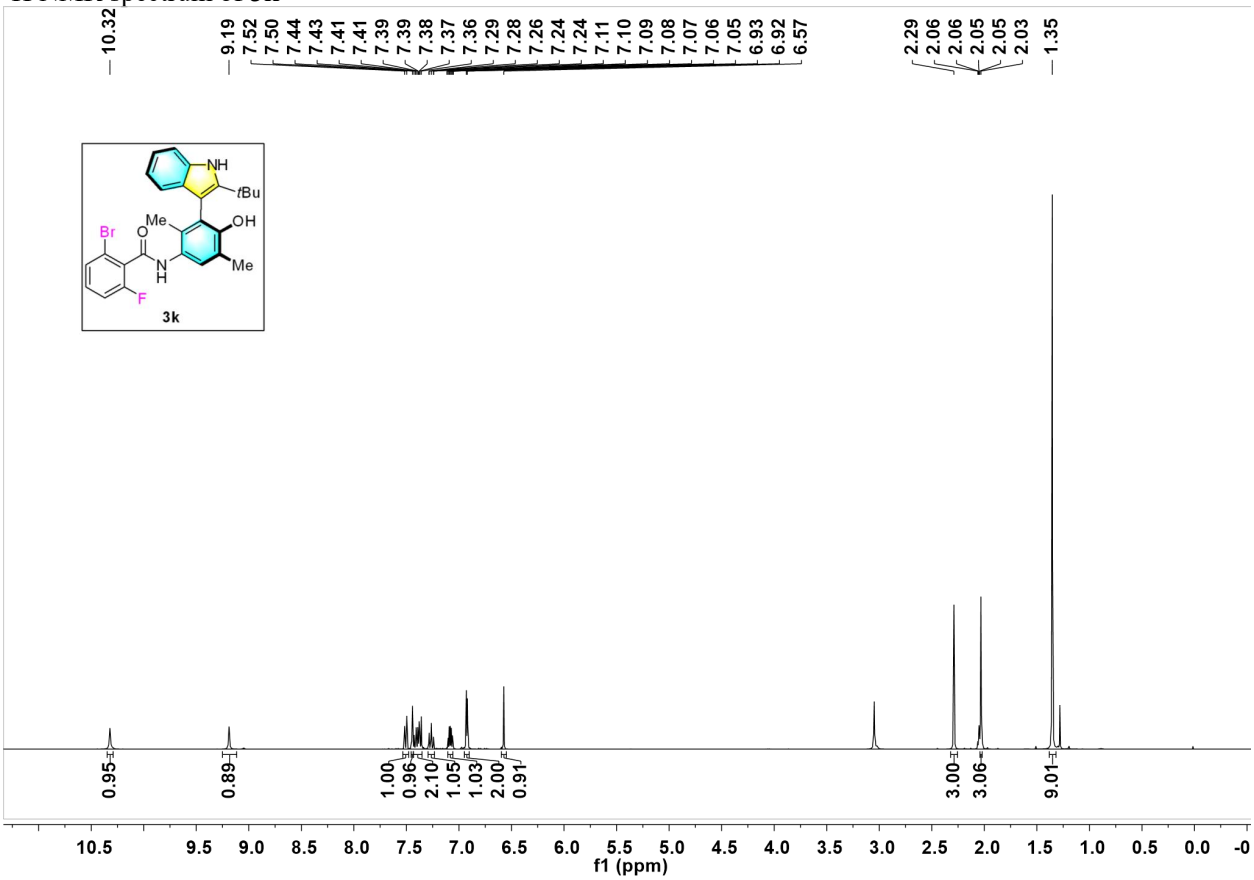
^{1}H NMR spectrum of **3j**



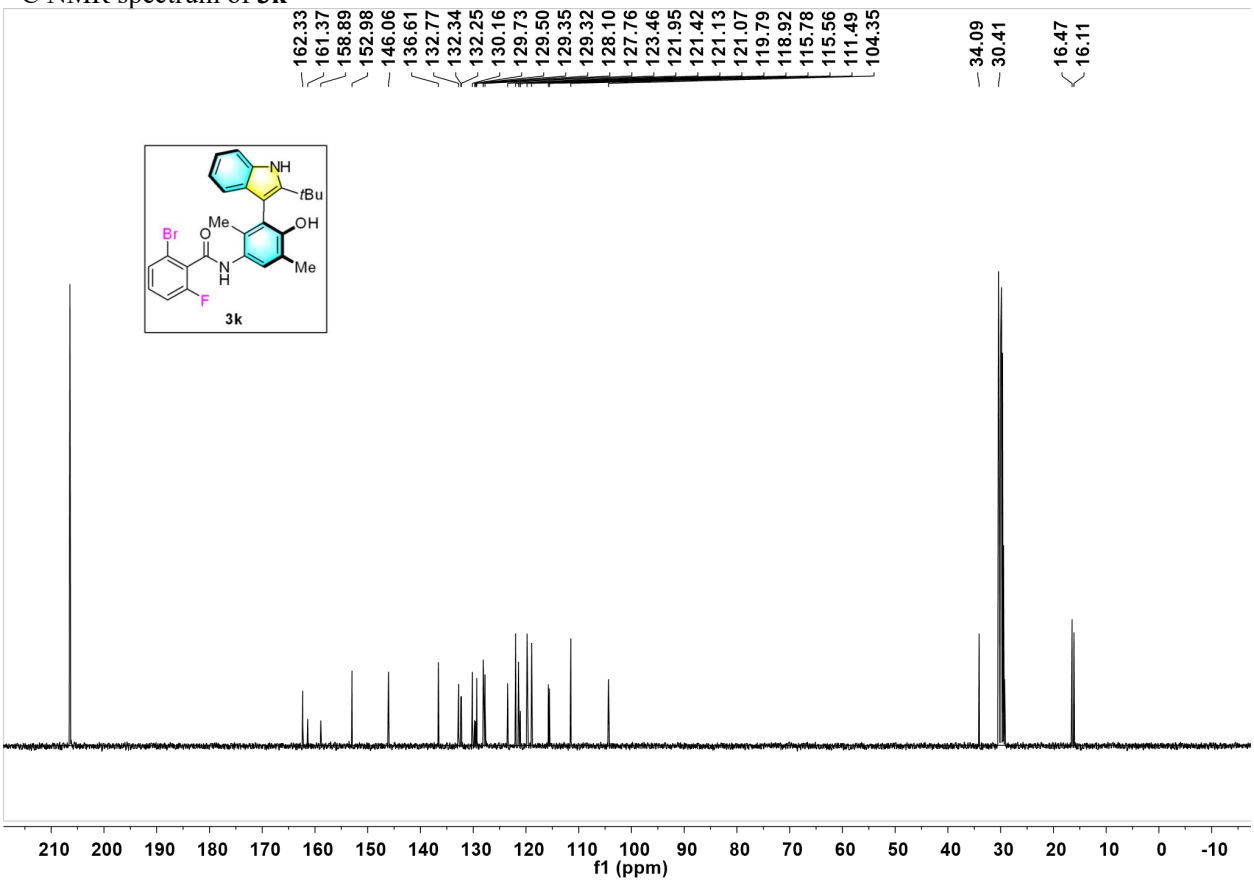
^{13}C NMR spectrum of **3j**



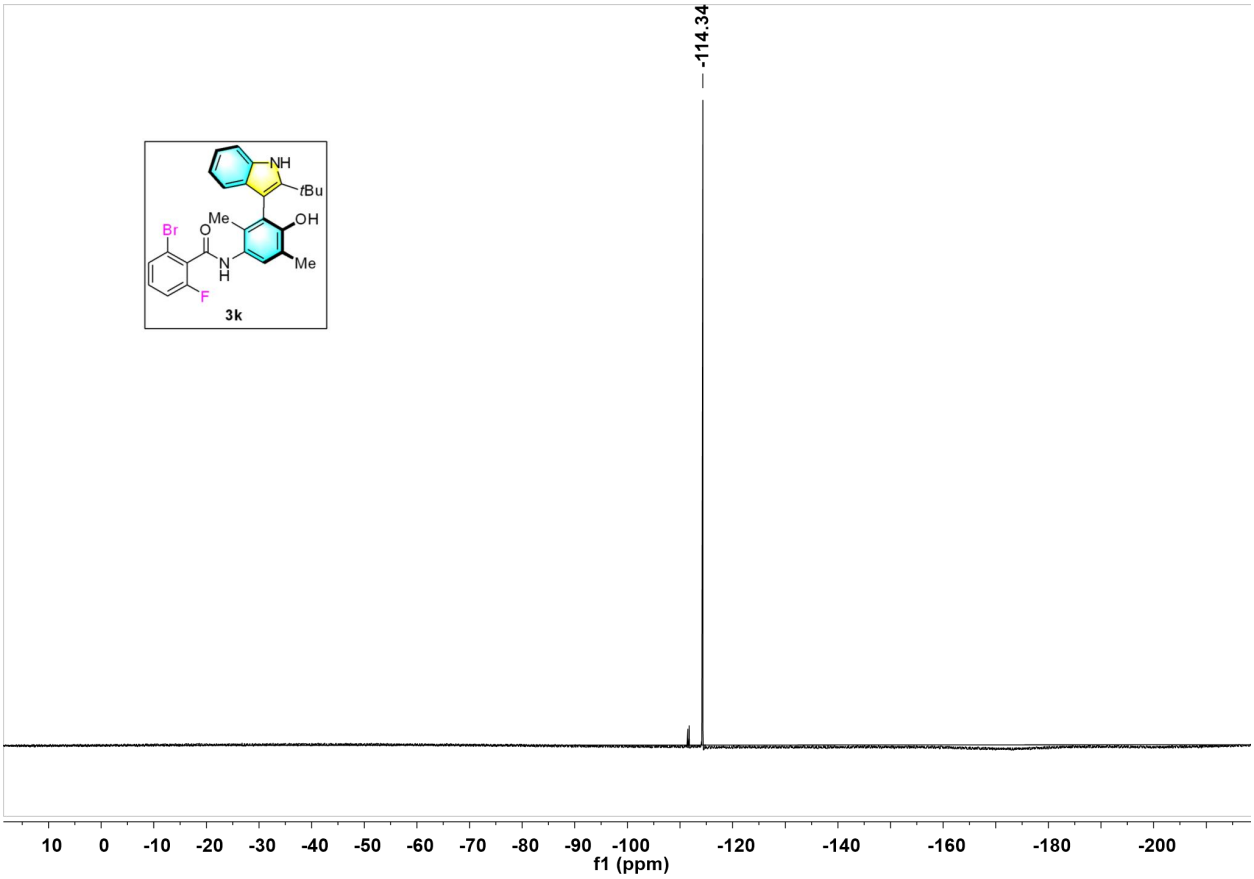
^{1}H NMR spectrum of **3k**



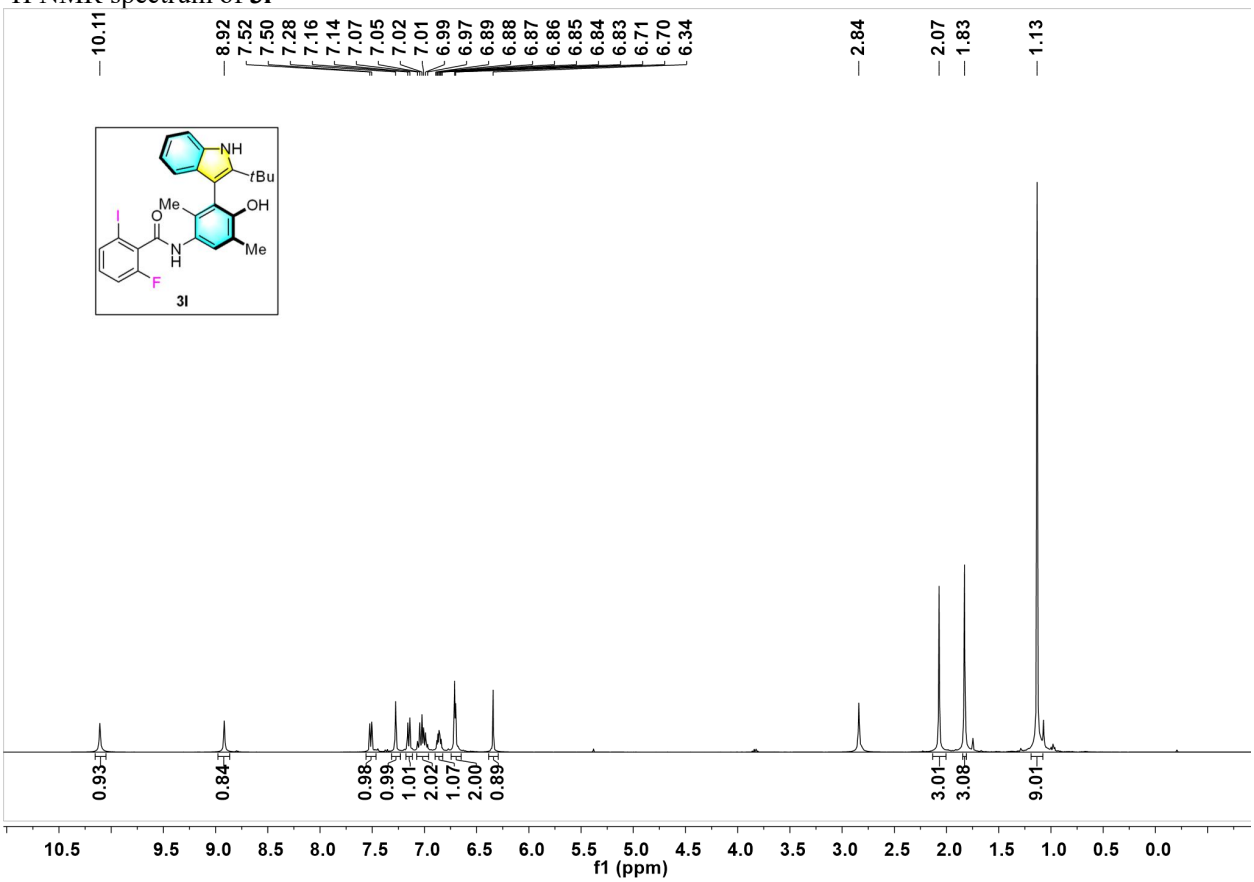
^{13}C NMR spectrum of **3k**



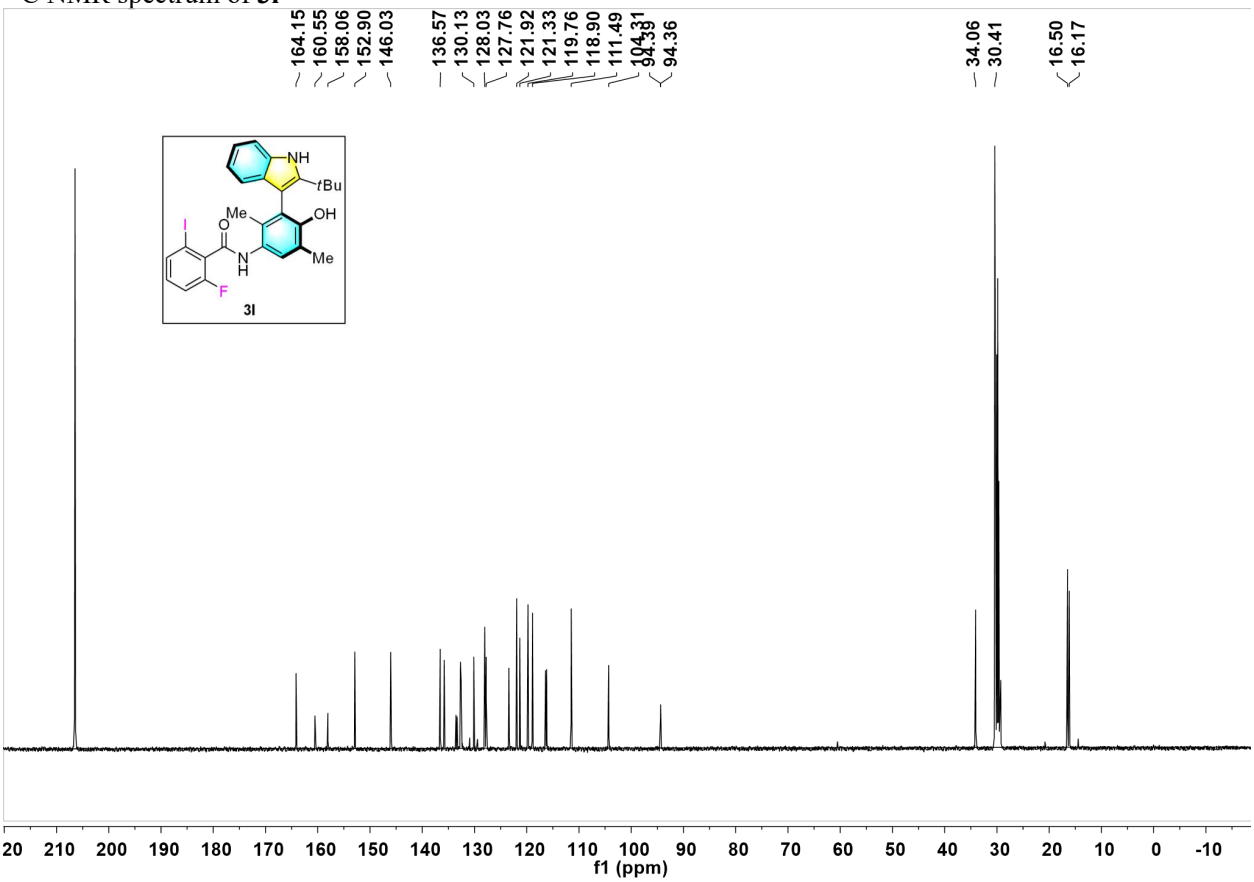
^{19}F NMR spectrum of **3k**


-114.34
NH
tBu
Br
O
Me
OH
N
H
Me
F
3k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

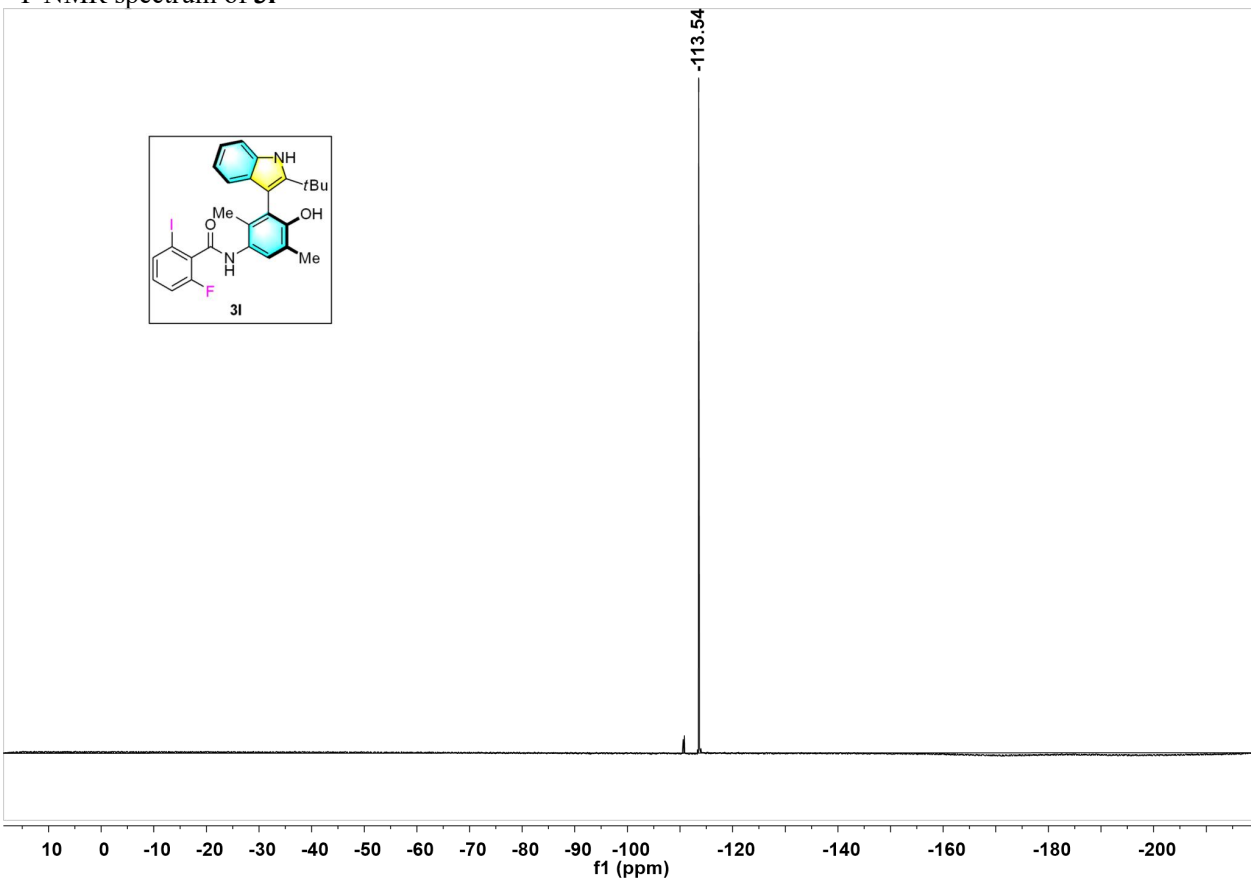
^{1}H NMR spectrum of **3l**



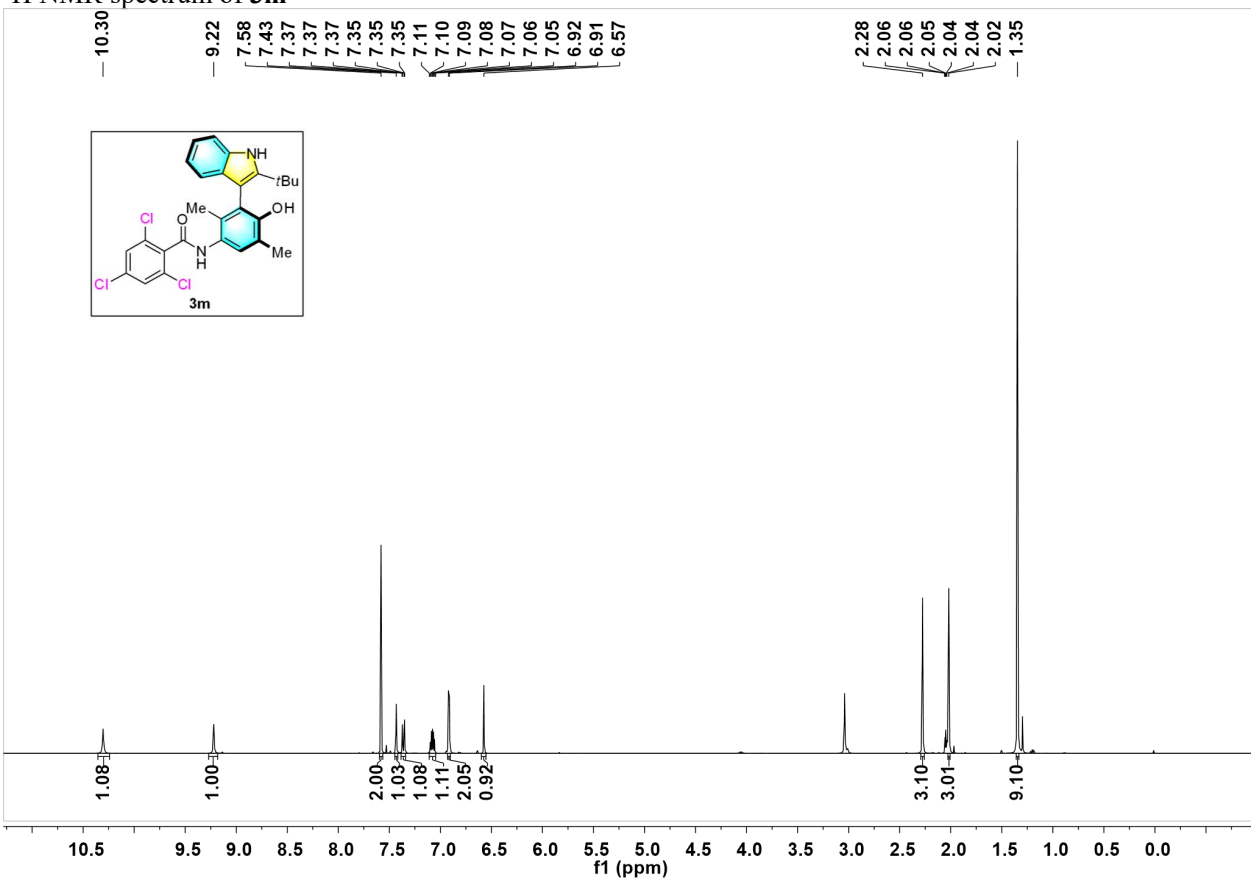
^{13}C NMR spectrum of **3l**



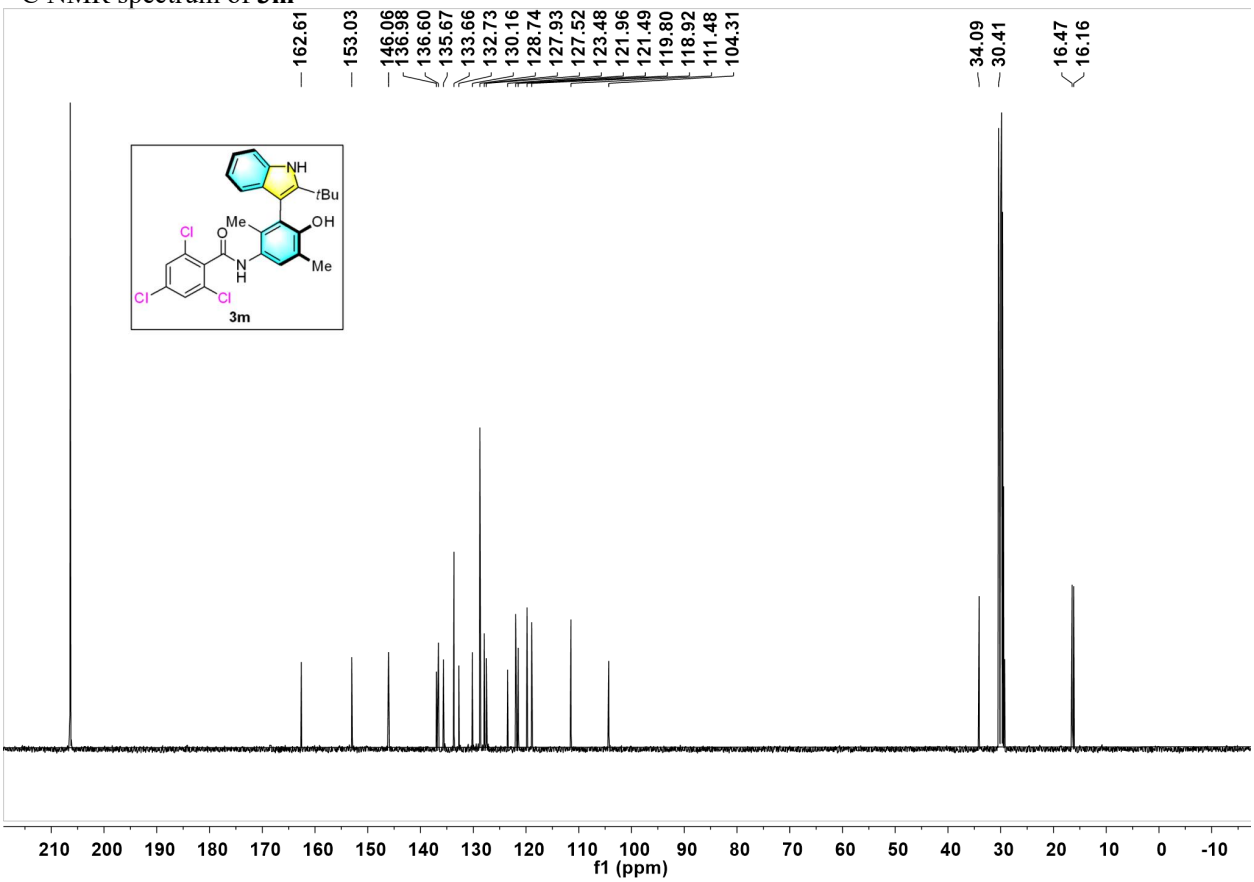
^{19}F NMR spectrum of **3l**



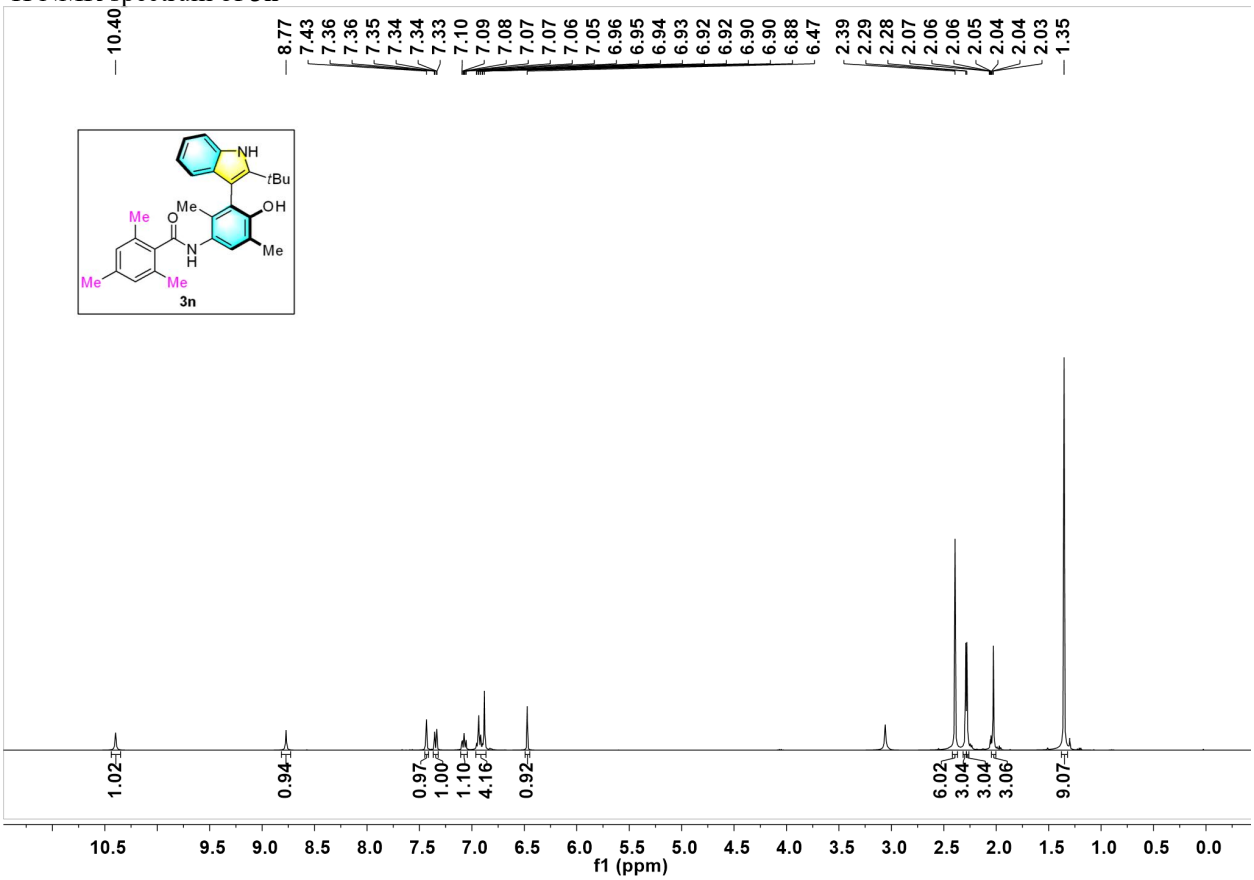
^{1}H NMR spectrum of **3m**



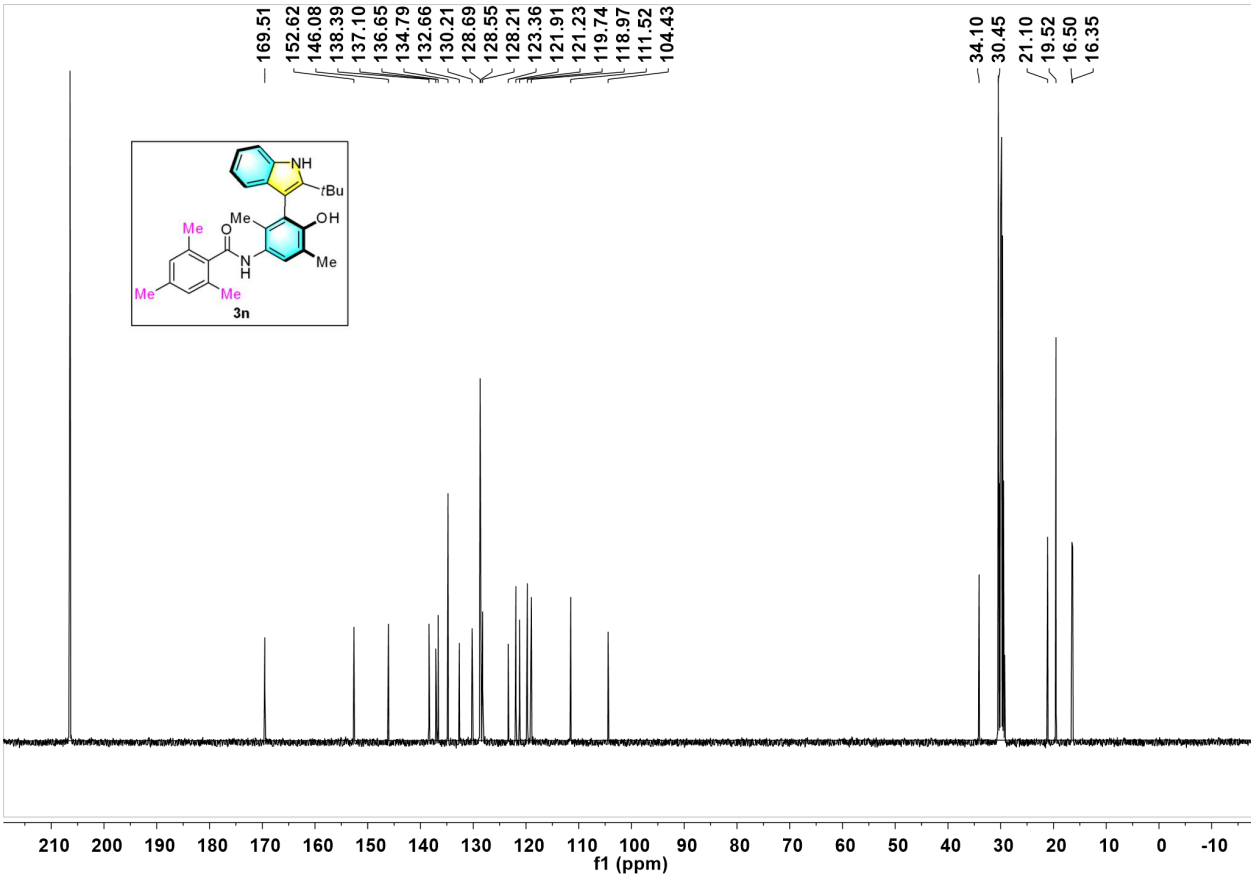
^{13}C NMR spectrum of **3m**



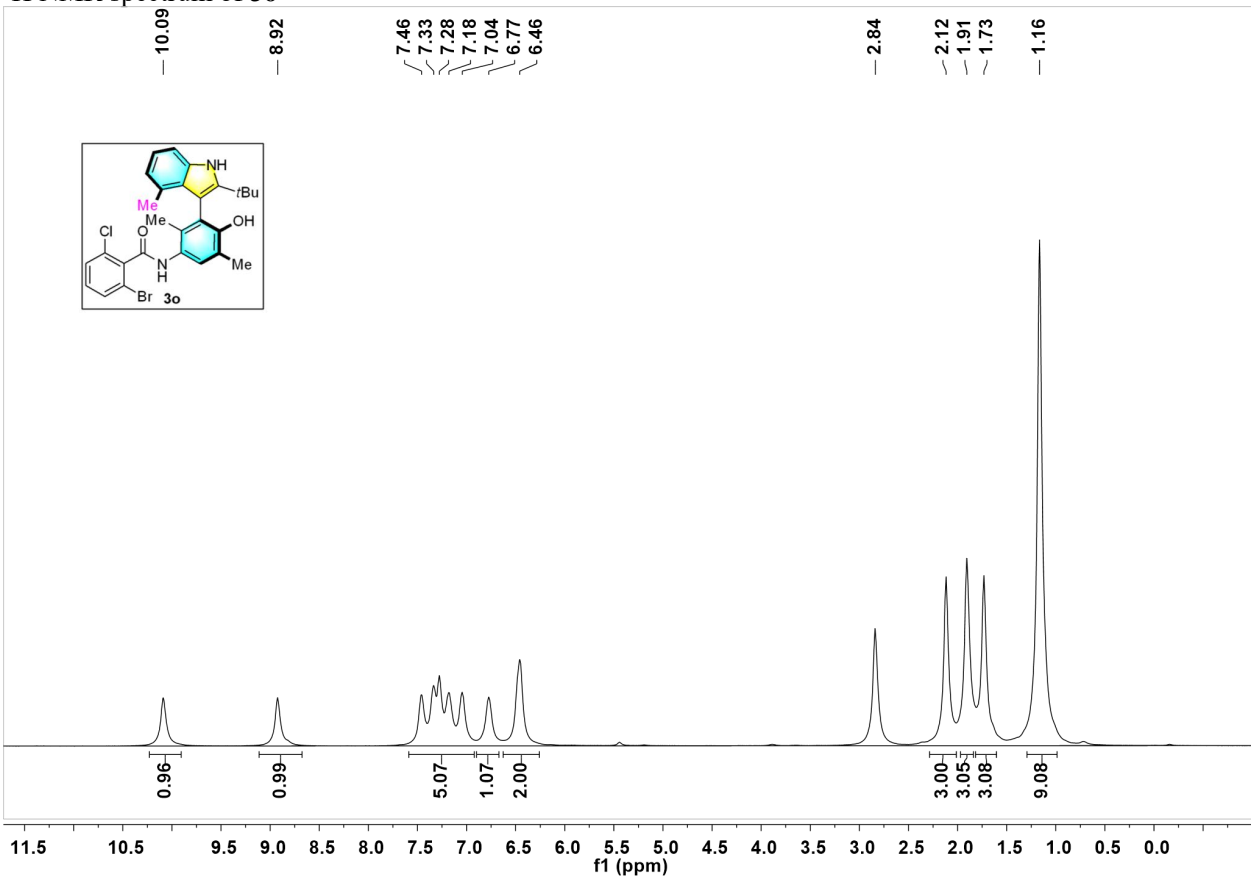
^{1}H NMR spectrum of **3n**



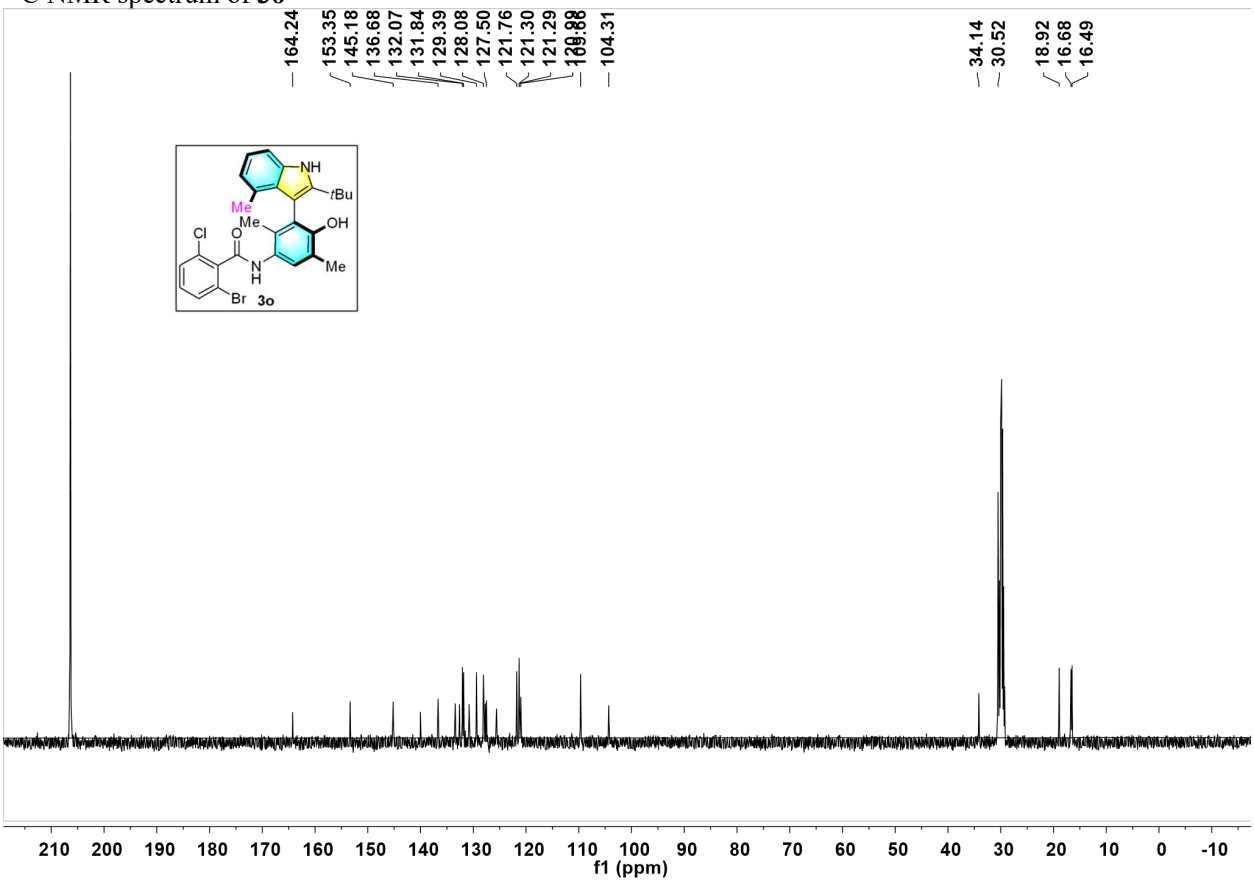
^{13}C NMR spectrum of **3n**



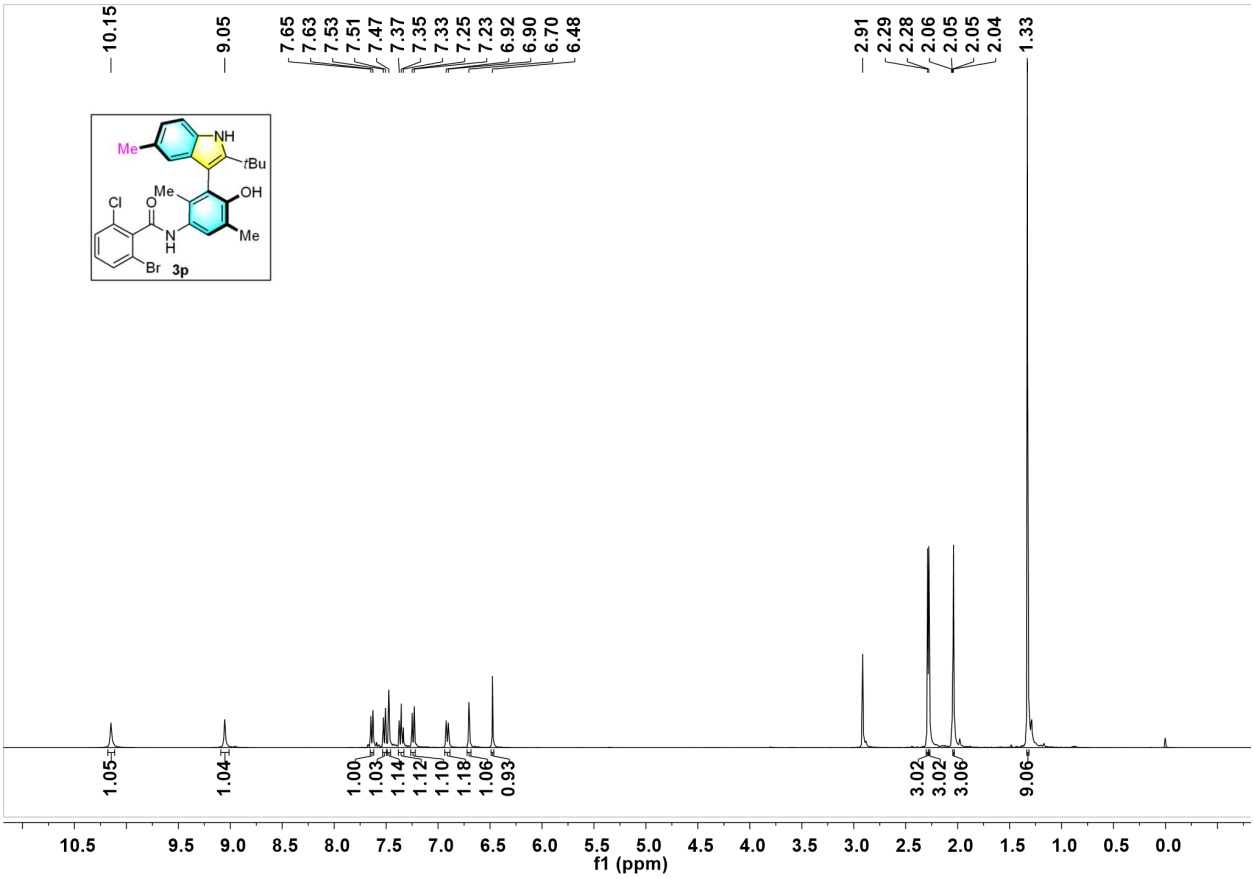
^{1}H NMR spectrum of **3o**



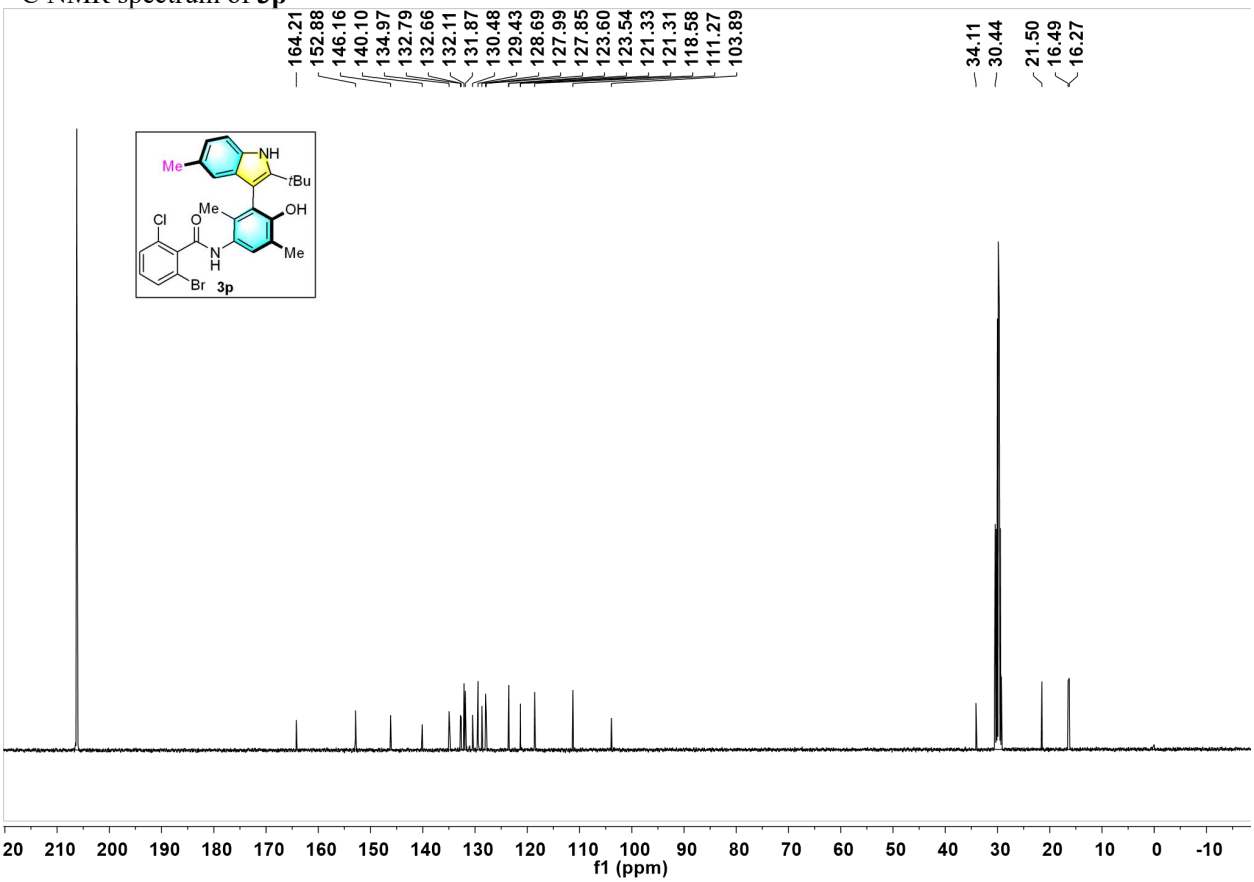
^{13}C NMR spectrum of **3o**



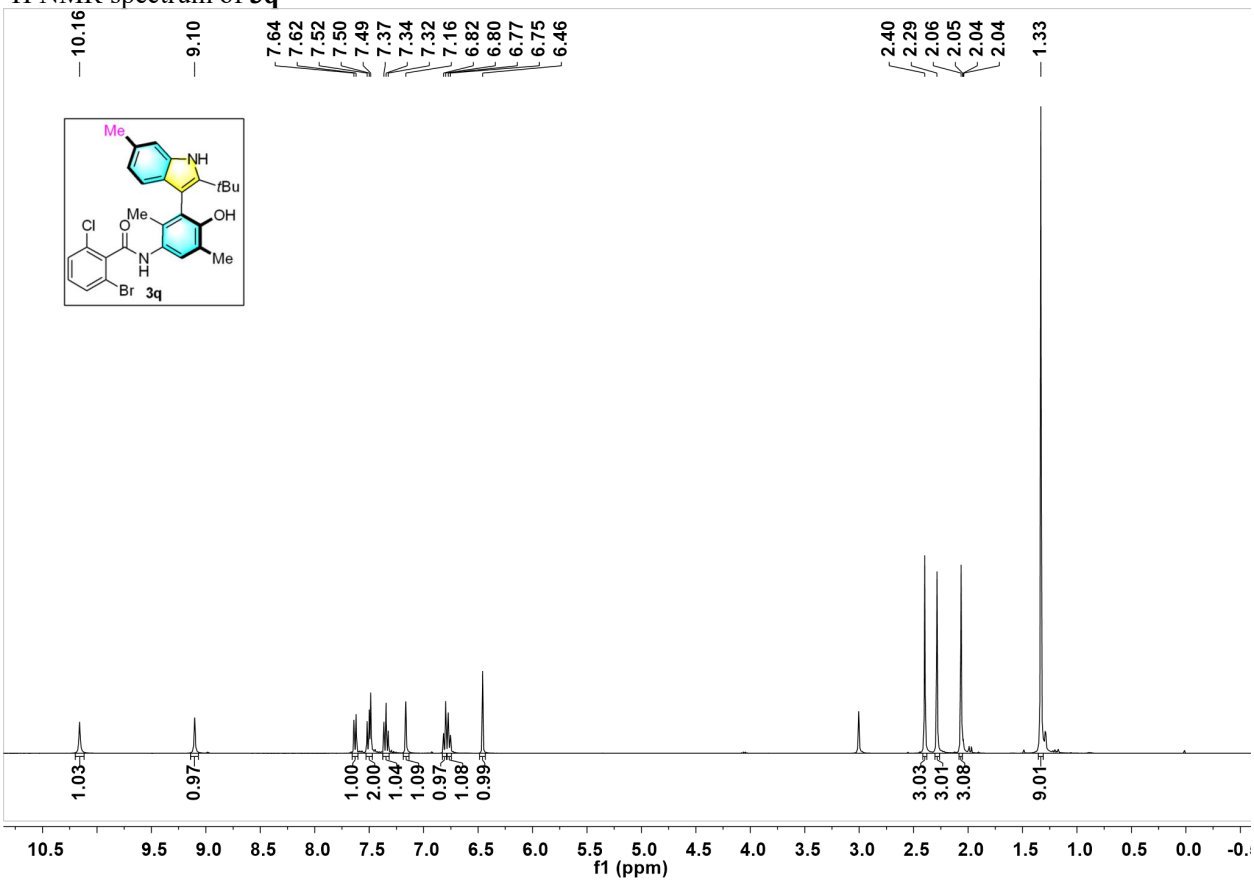
^{1}H NMR spectrum of **3p**



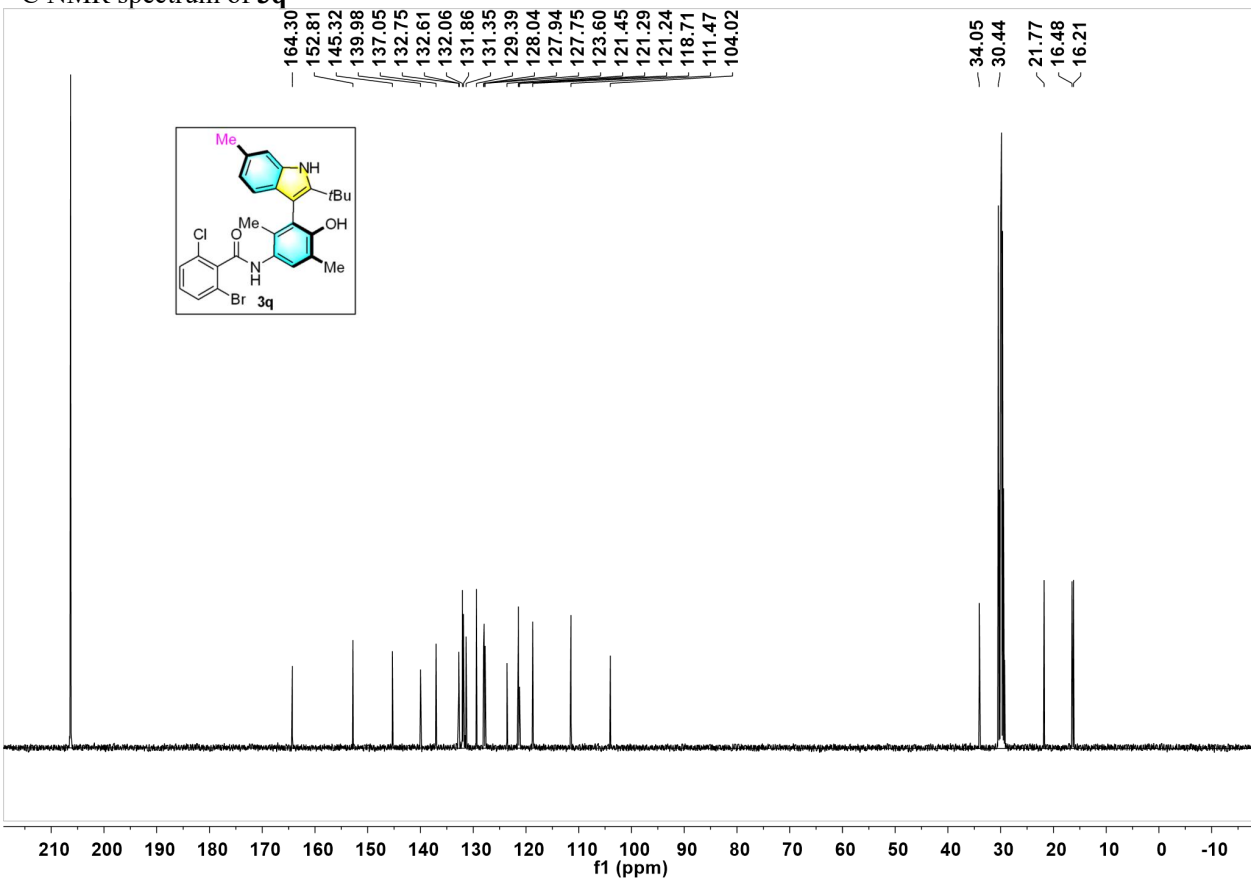
^{13}C NMR spectrum of **3p**



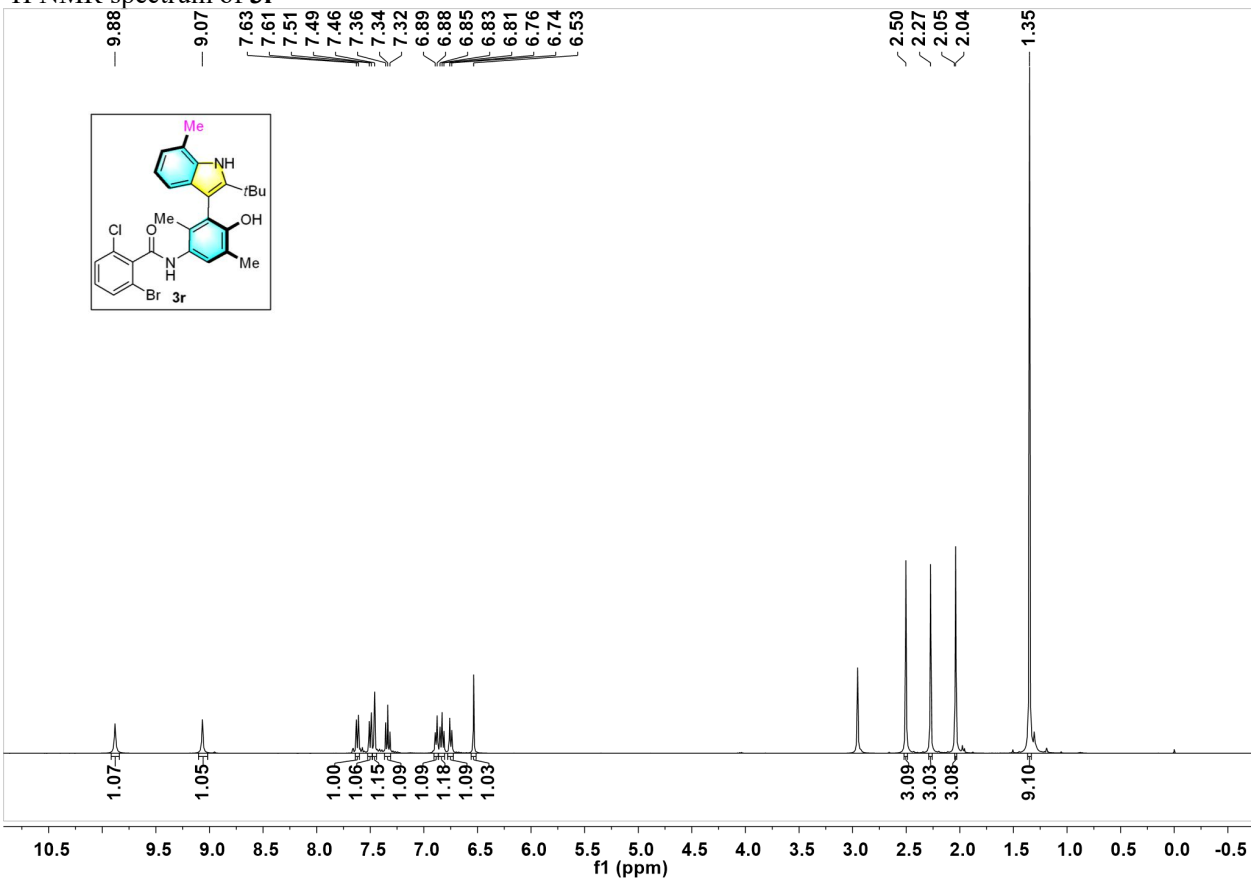
^{1}H NMR spectrum of **3q**



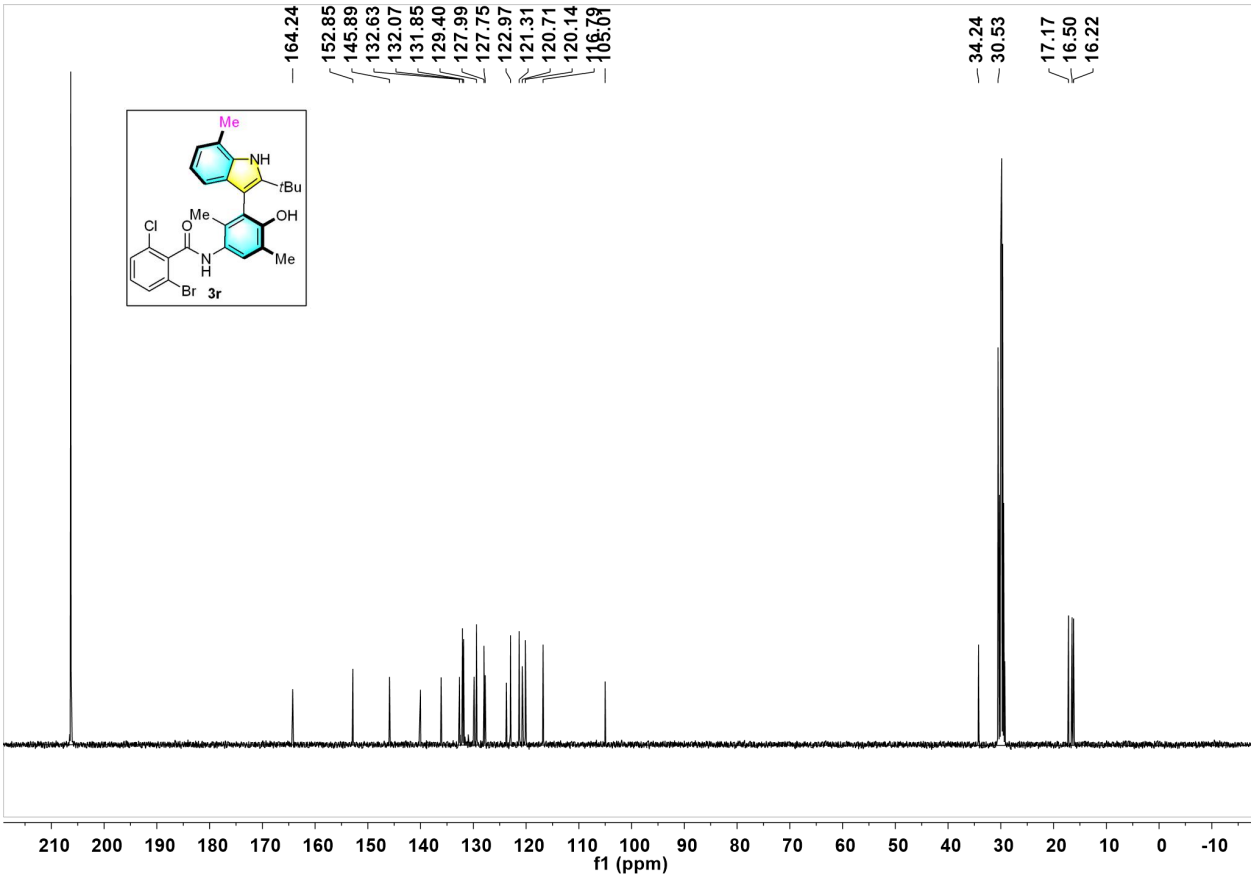
^{13}C NMR spectrum of **3q**



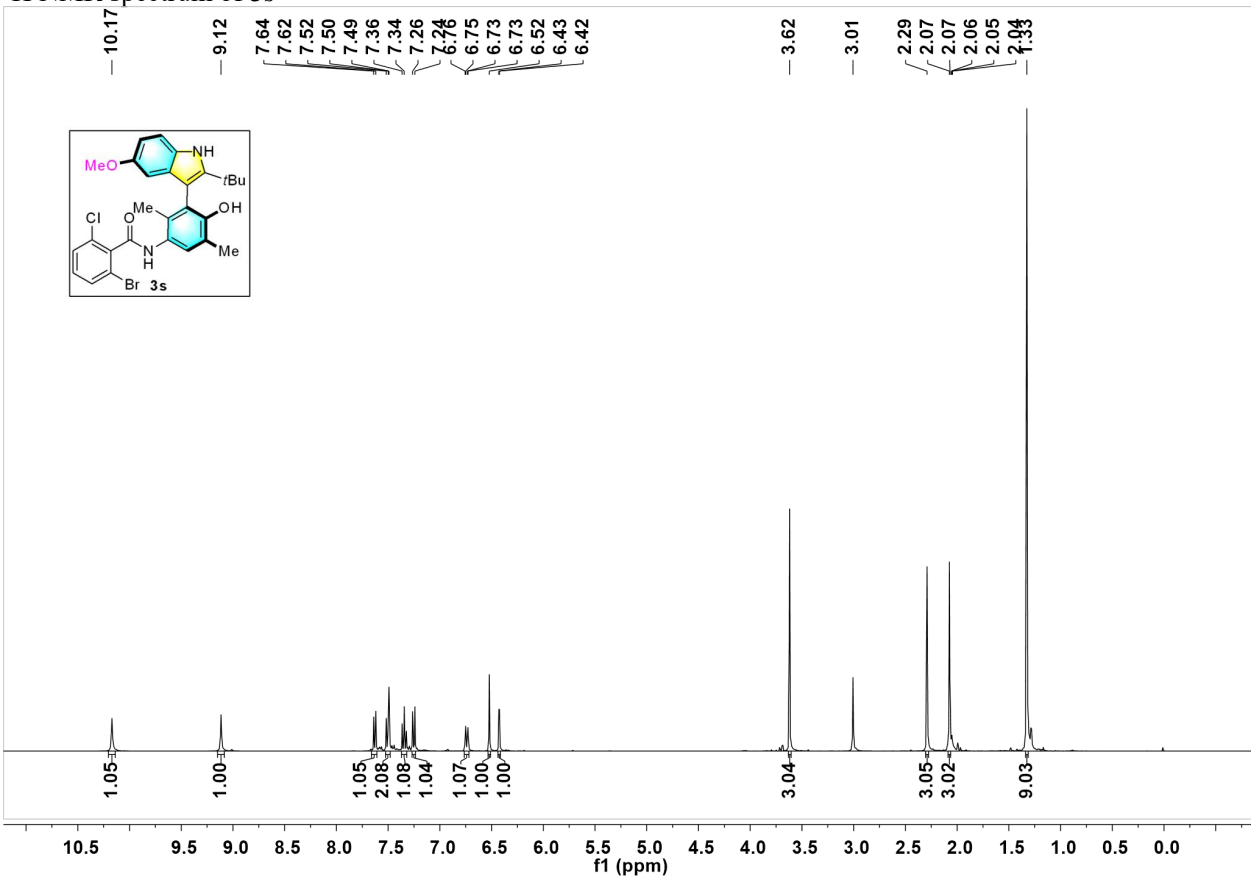
^{1}H NMR spectrum of **3r**



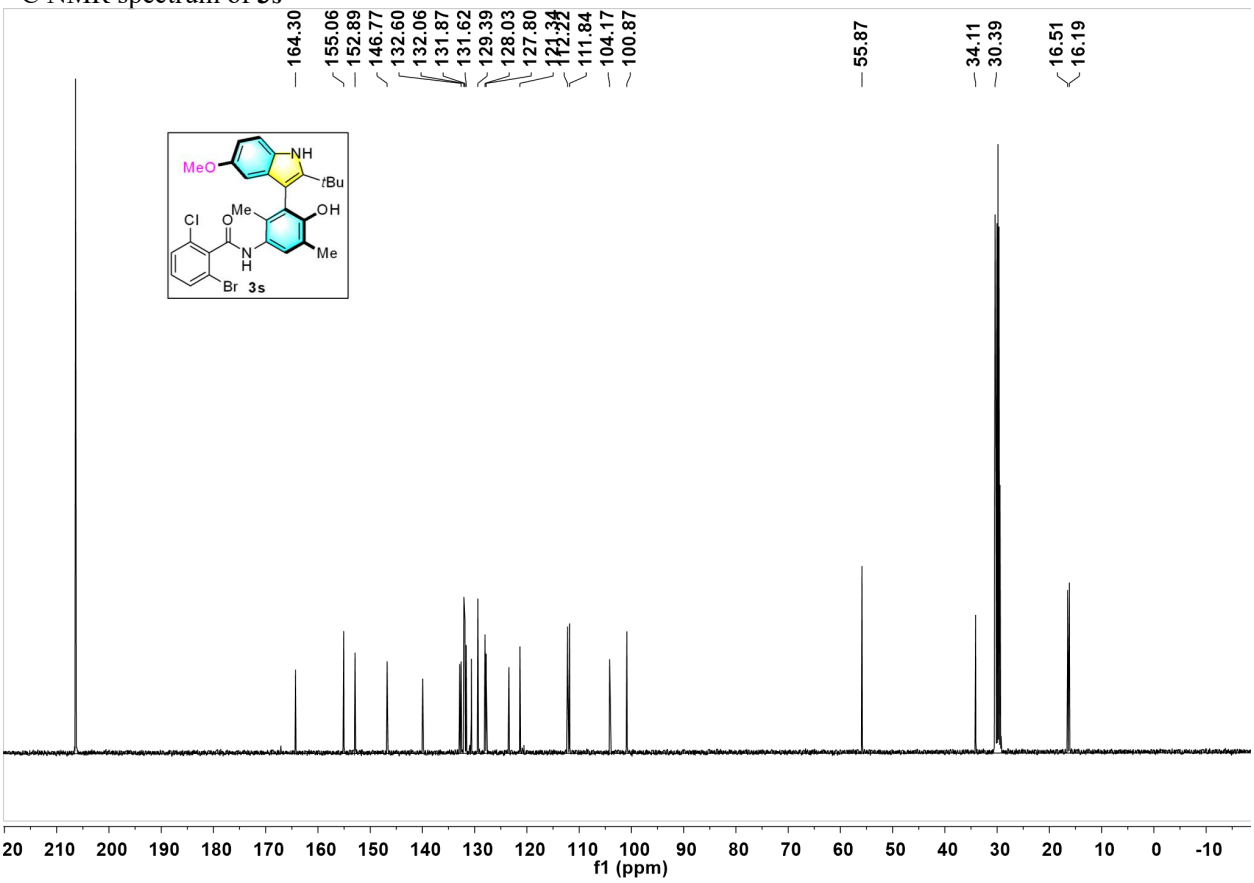
^{13}C NMR spectrum of **3r**



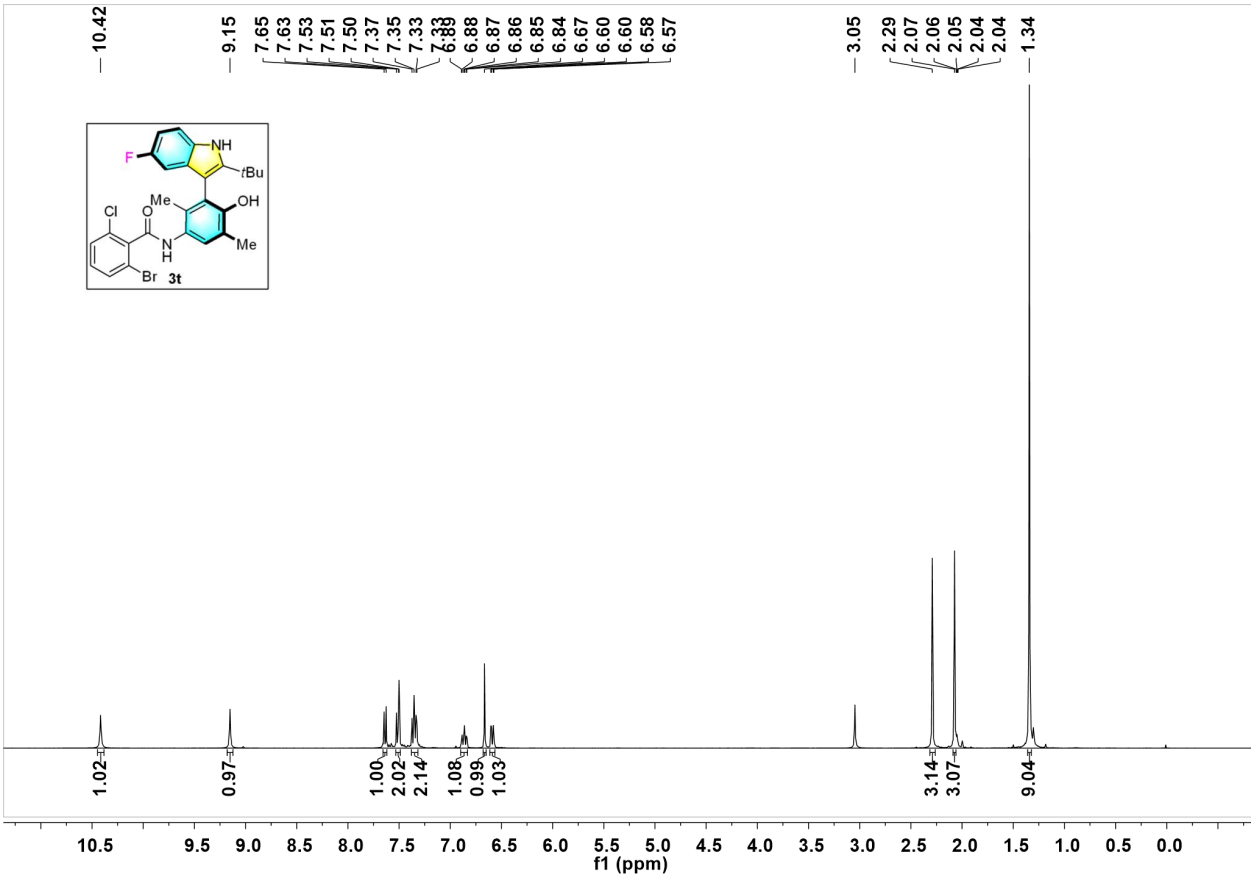
^{1}H NMR spectrum of **3s**



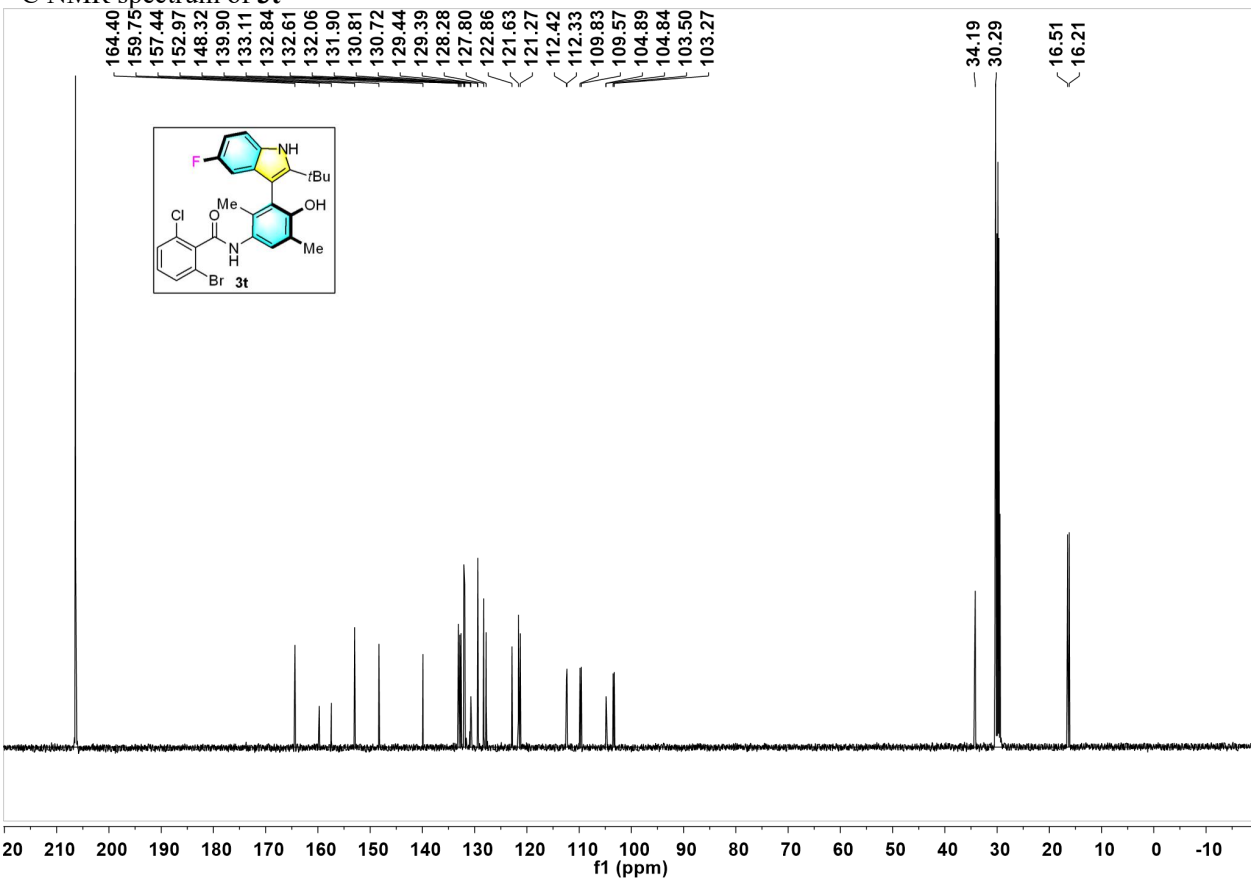
^{13}C NMR spectrum of **3s**



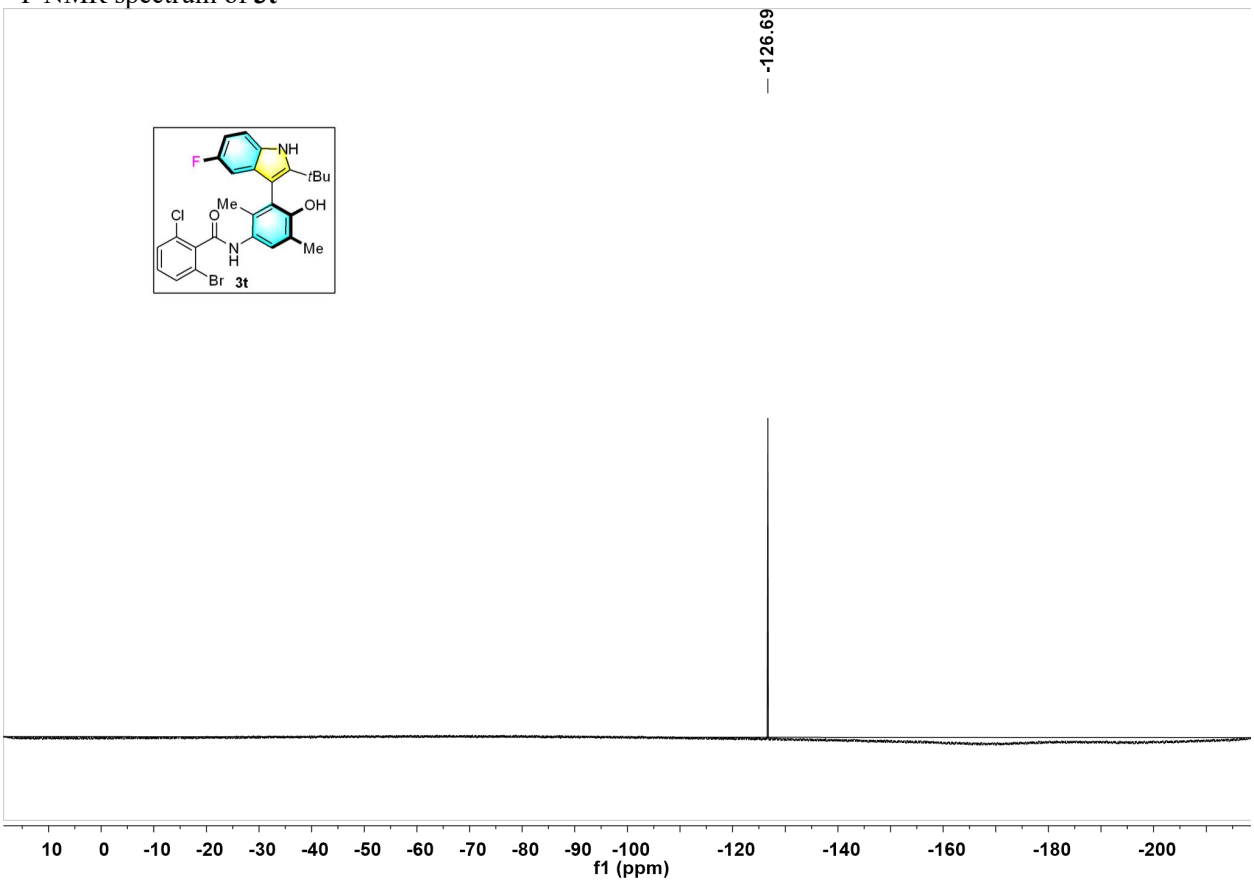
^{1}H NMR spectrum of **3t**



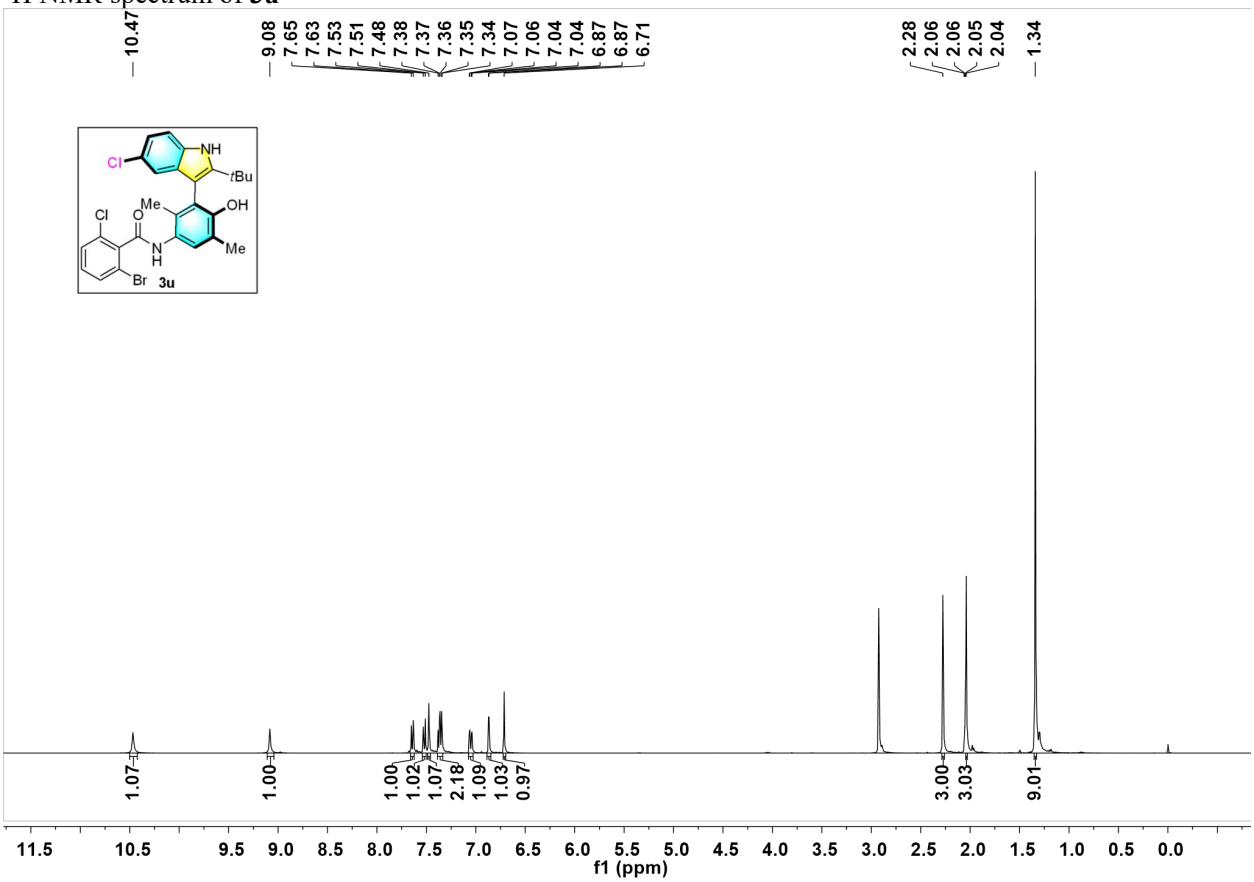
^{13}C NMR spectrum of **3t**



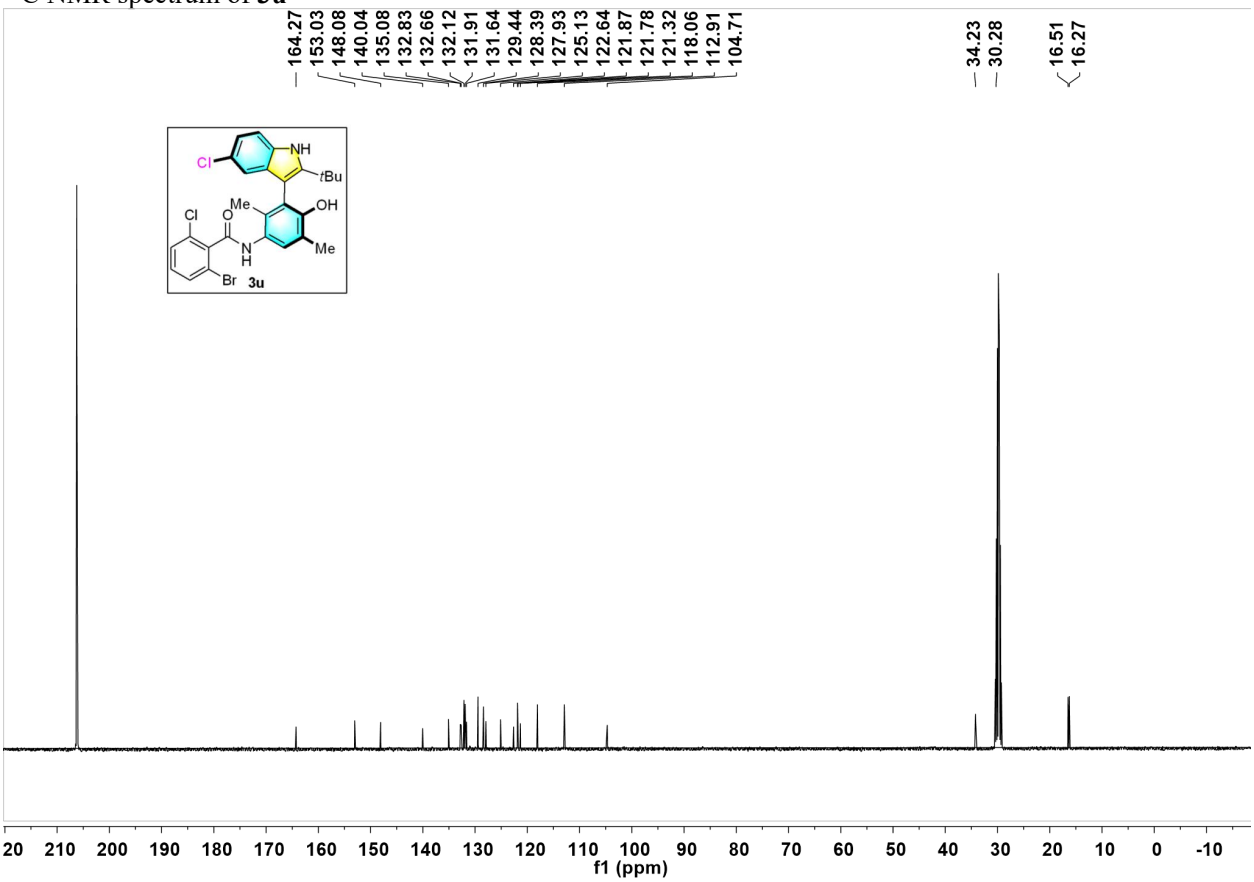
^{19}F NMR spectrum of **3t**



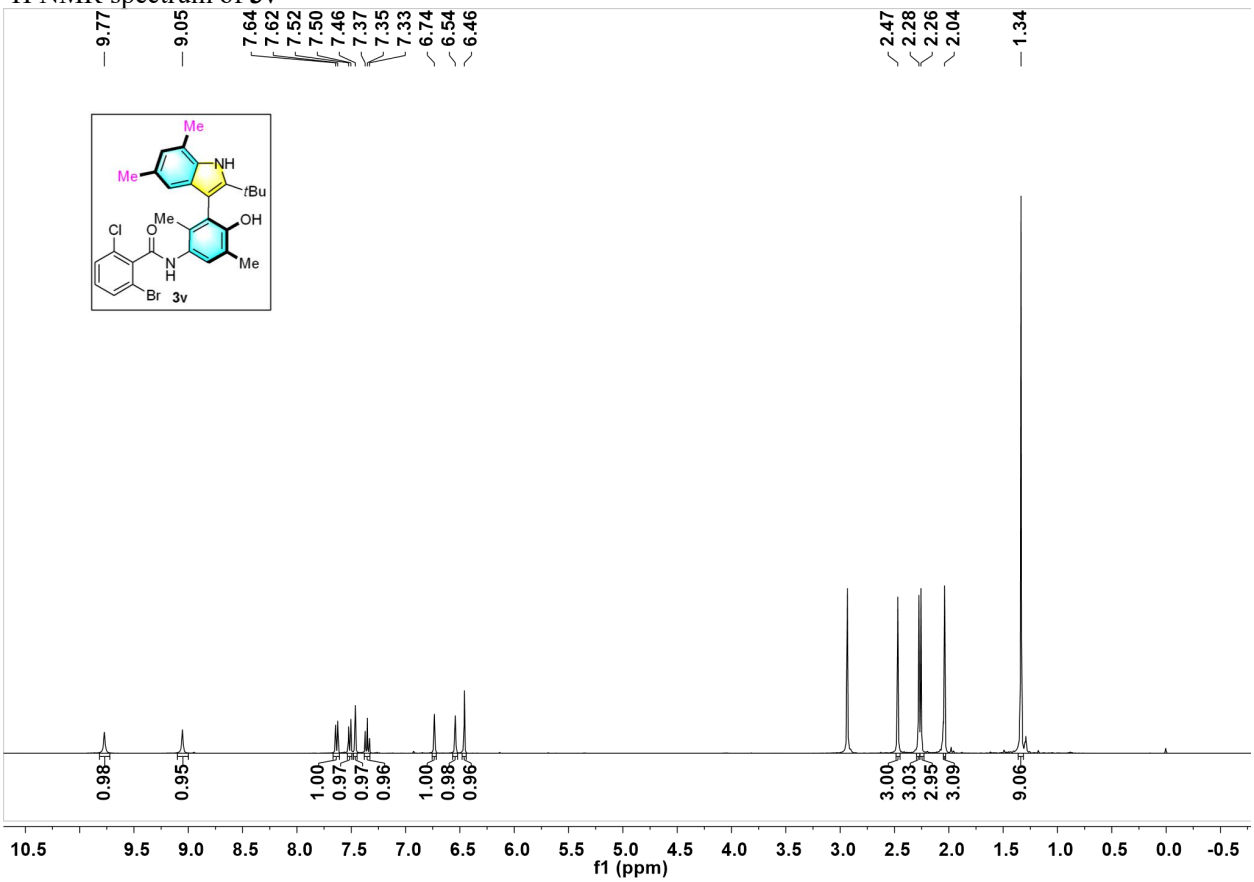
[1]H NMR spectrum of **3u**



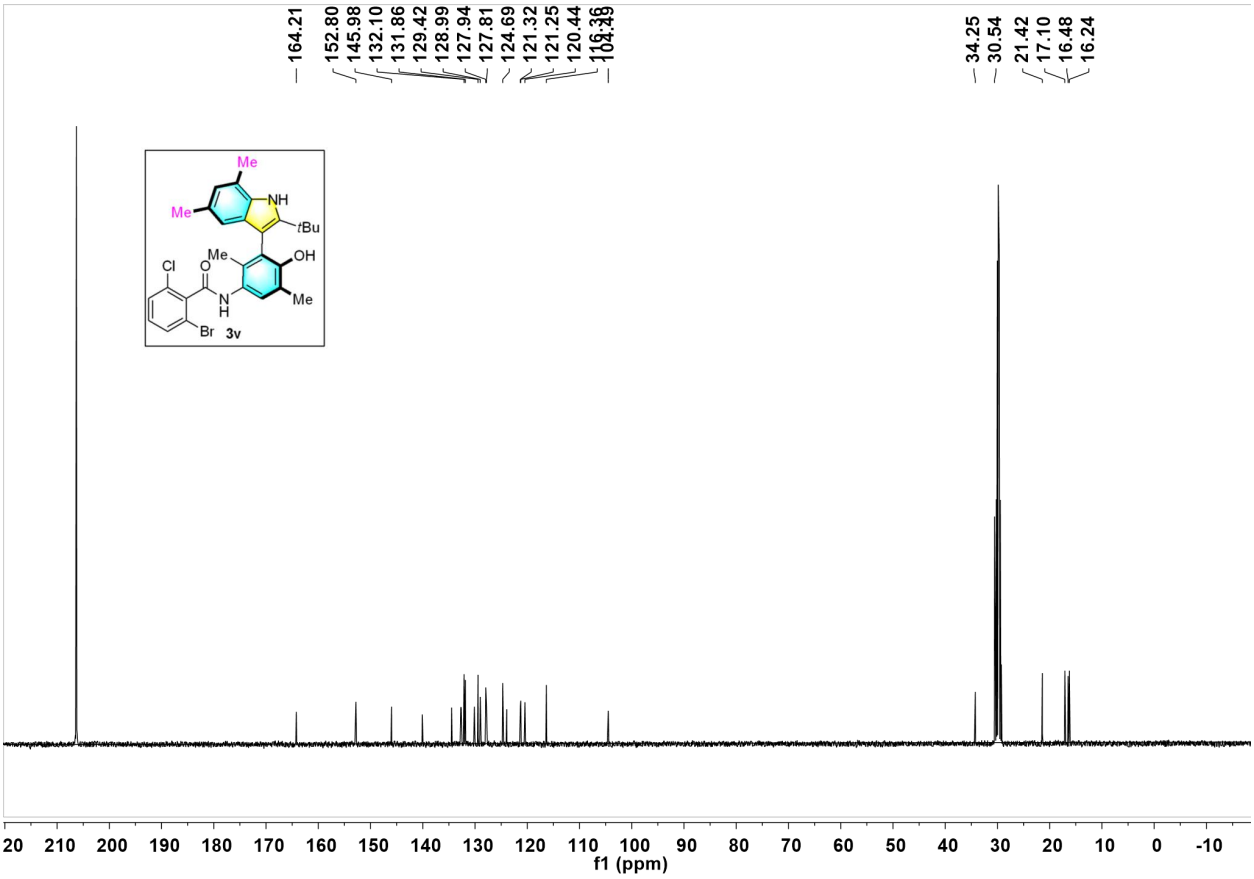
[13]C NMR spectrum of **3u**



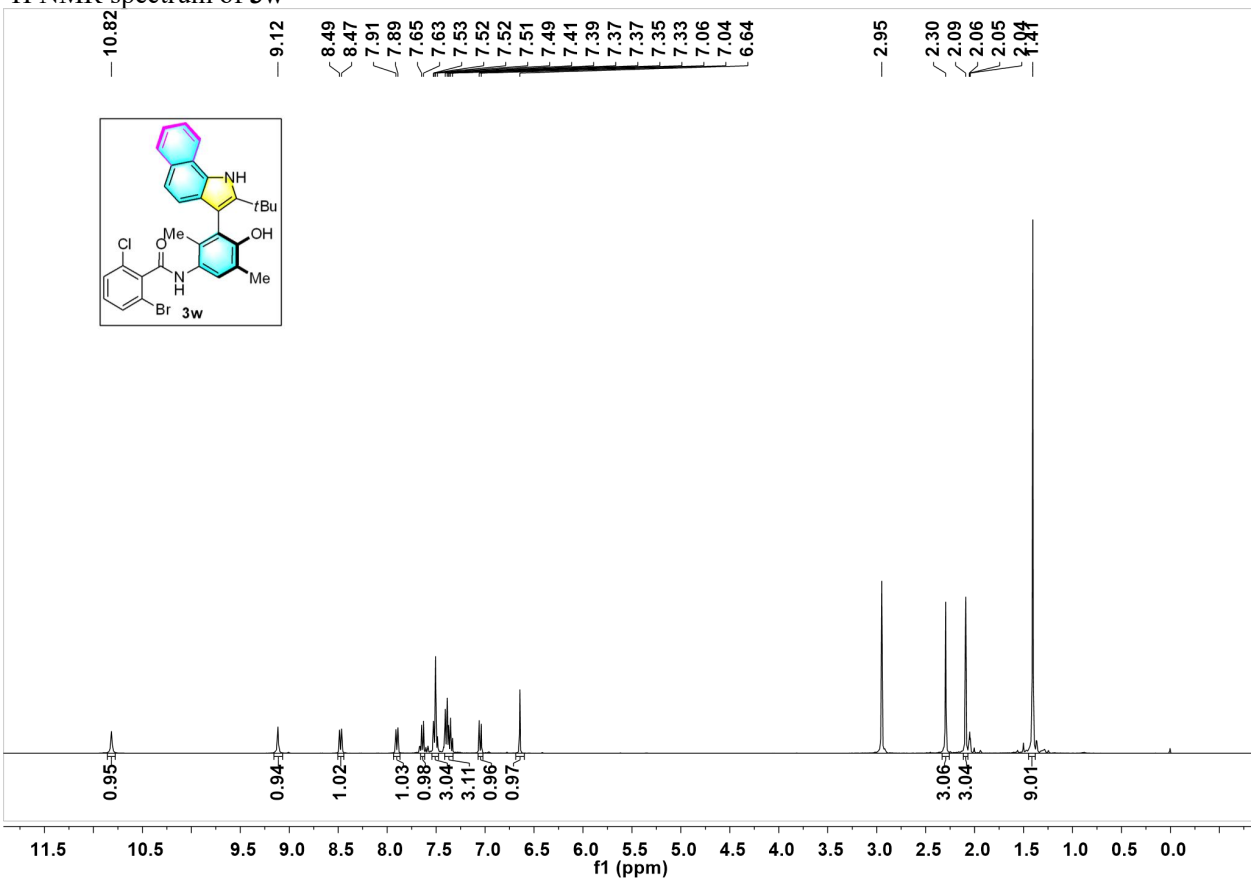
^{1}H NMR spectrum of **3v**



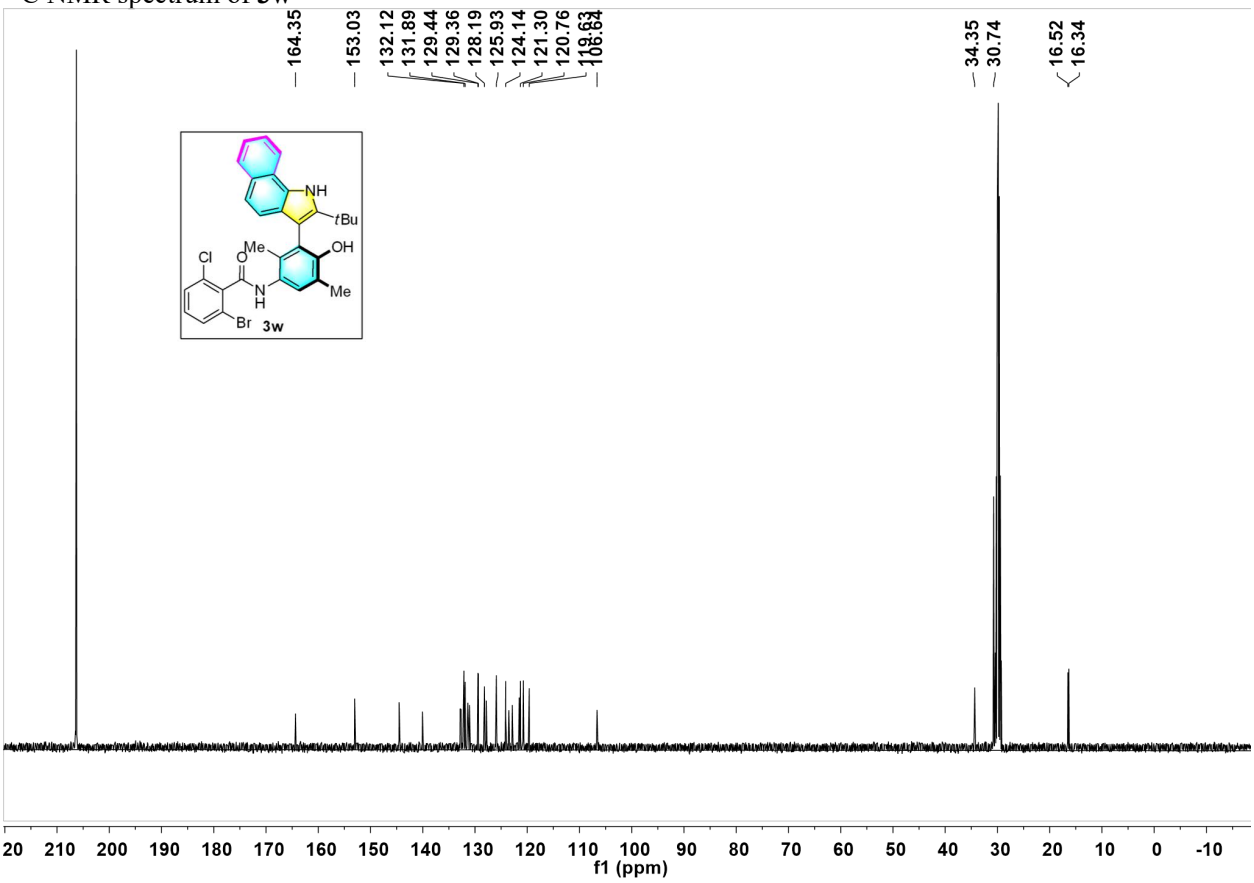
^{13}C NMR spectrum of **3v**



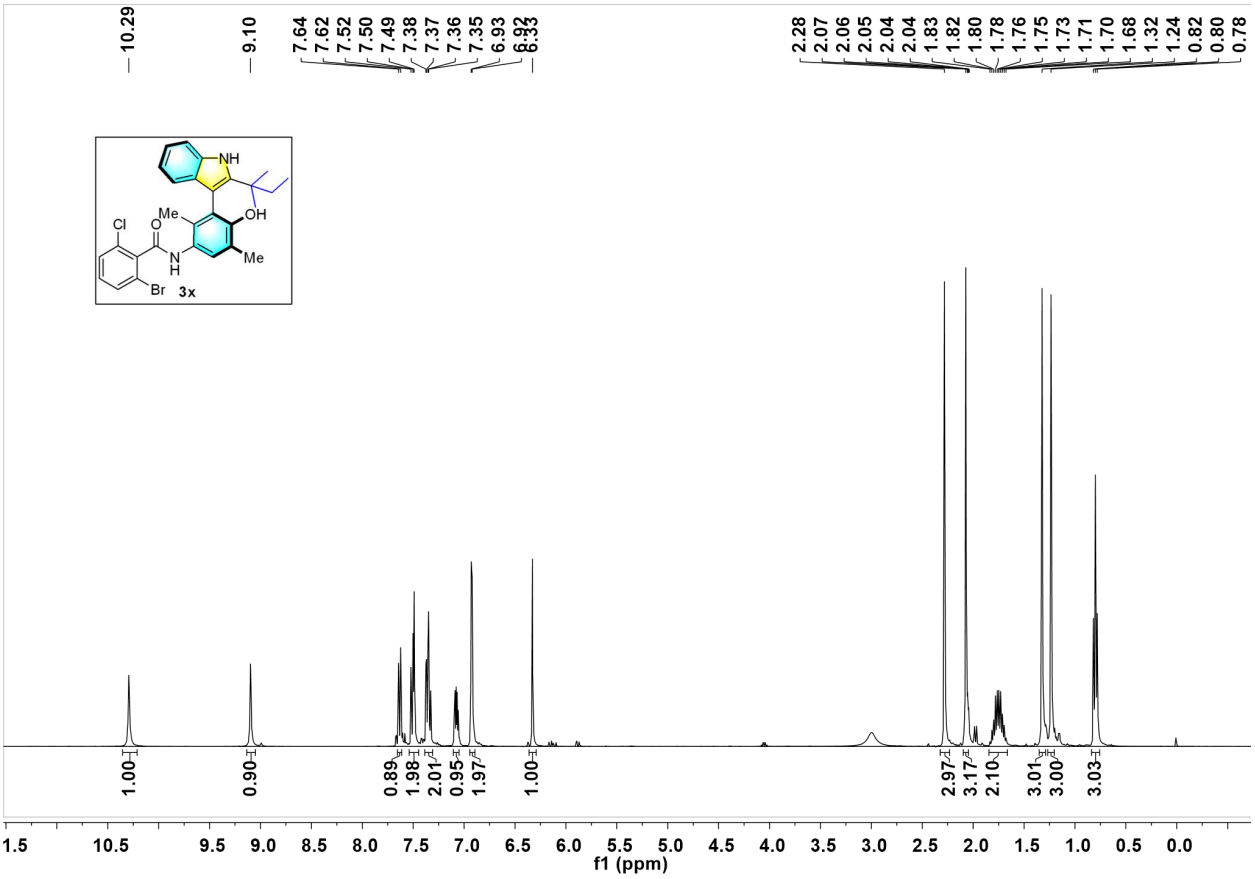
^{1}H NMR spectrum of **3w**



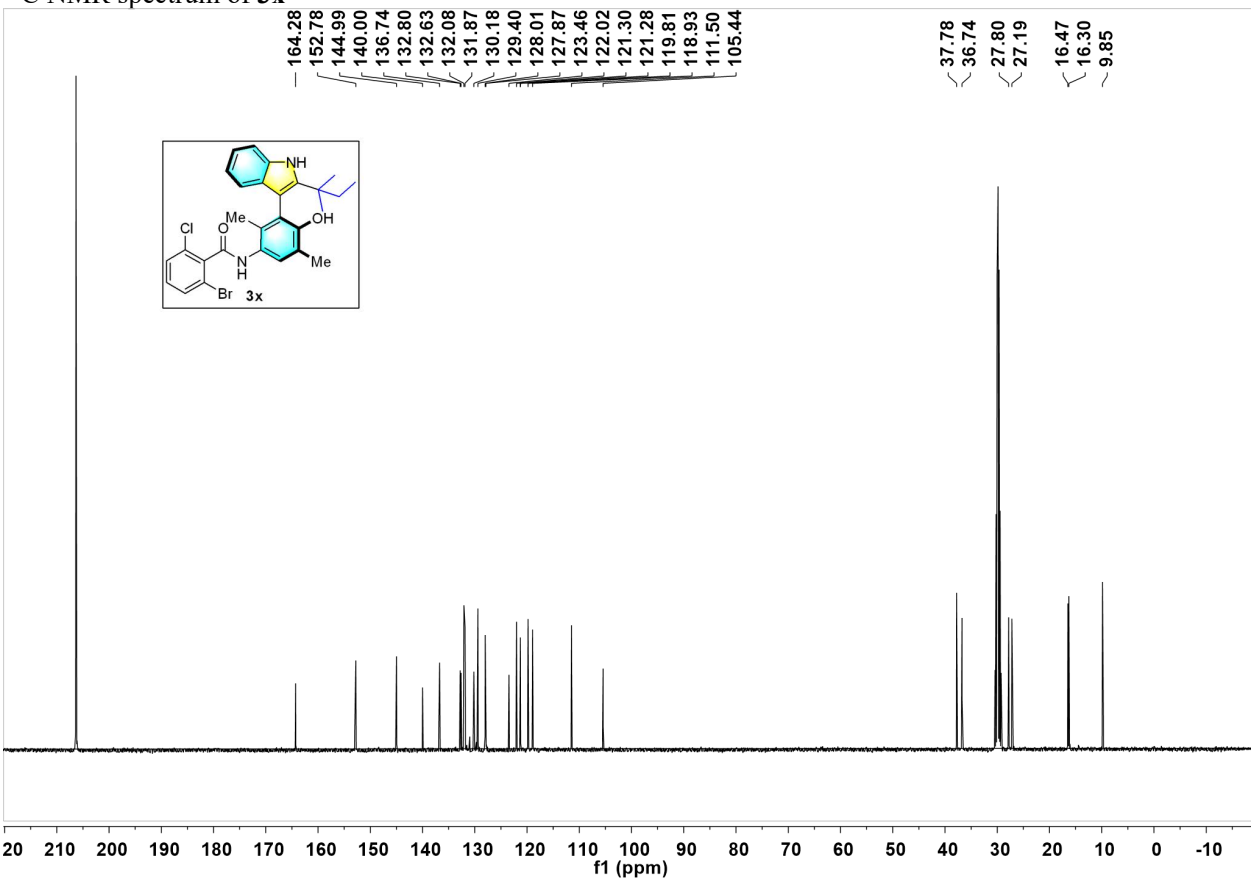
^{13}C NMR spectrum of **3w**



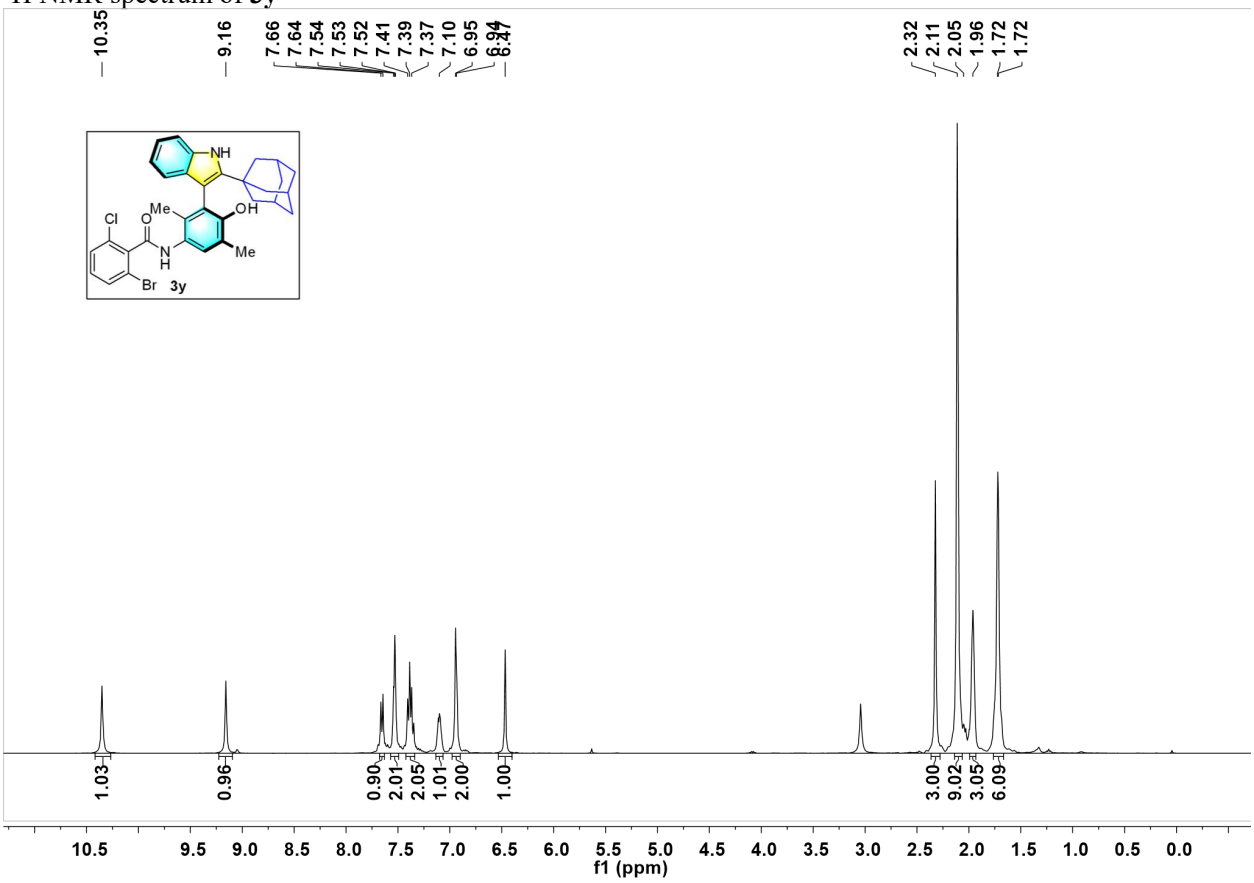
^{1}H NMR spectrum of **3x**



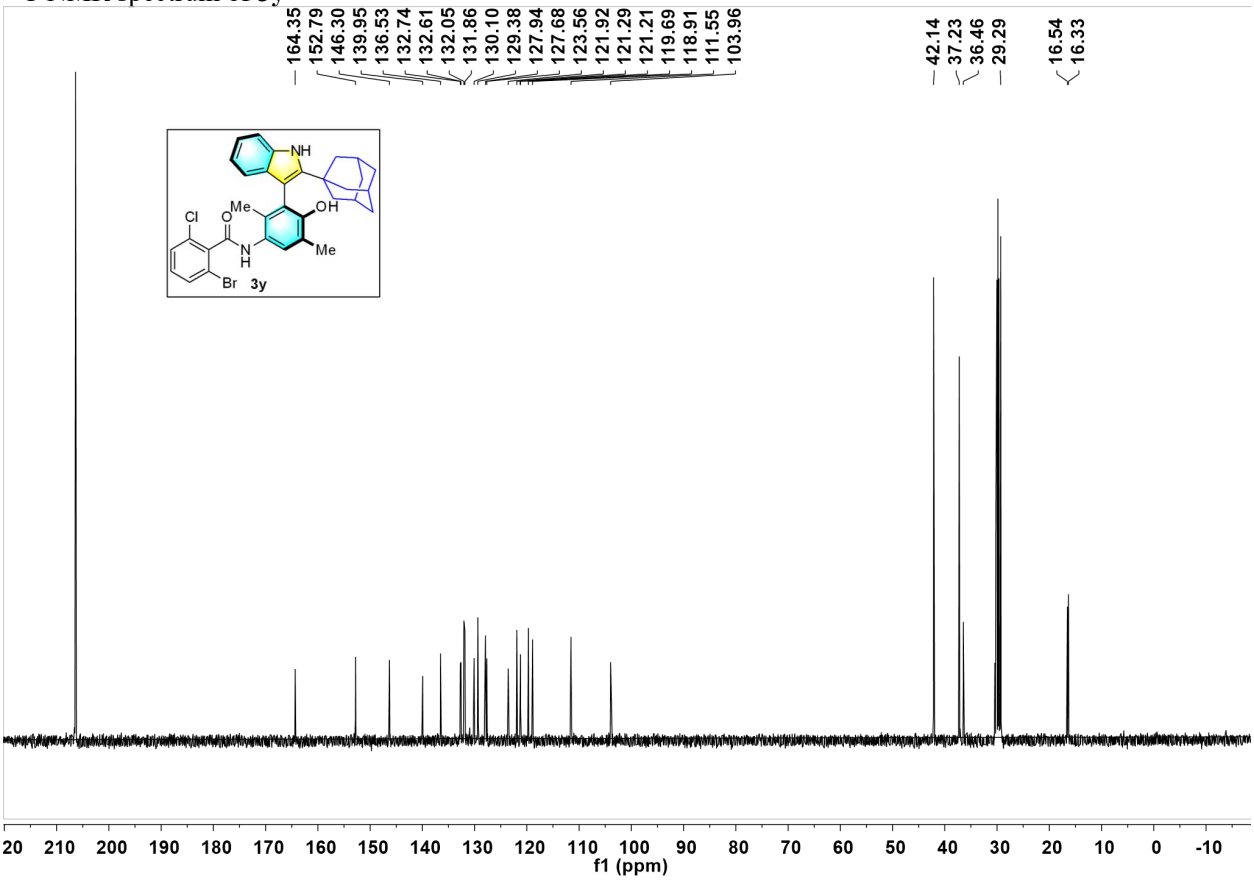
^{13}C NMR spectrum of **3x**



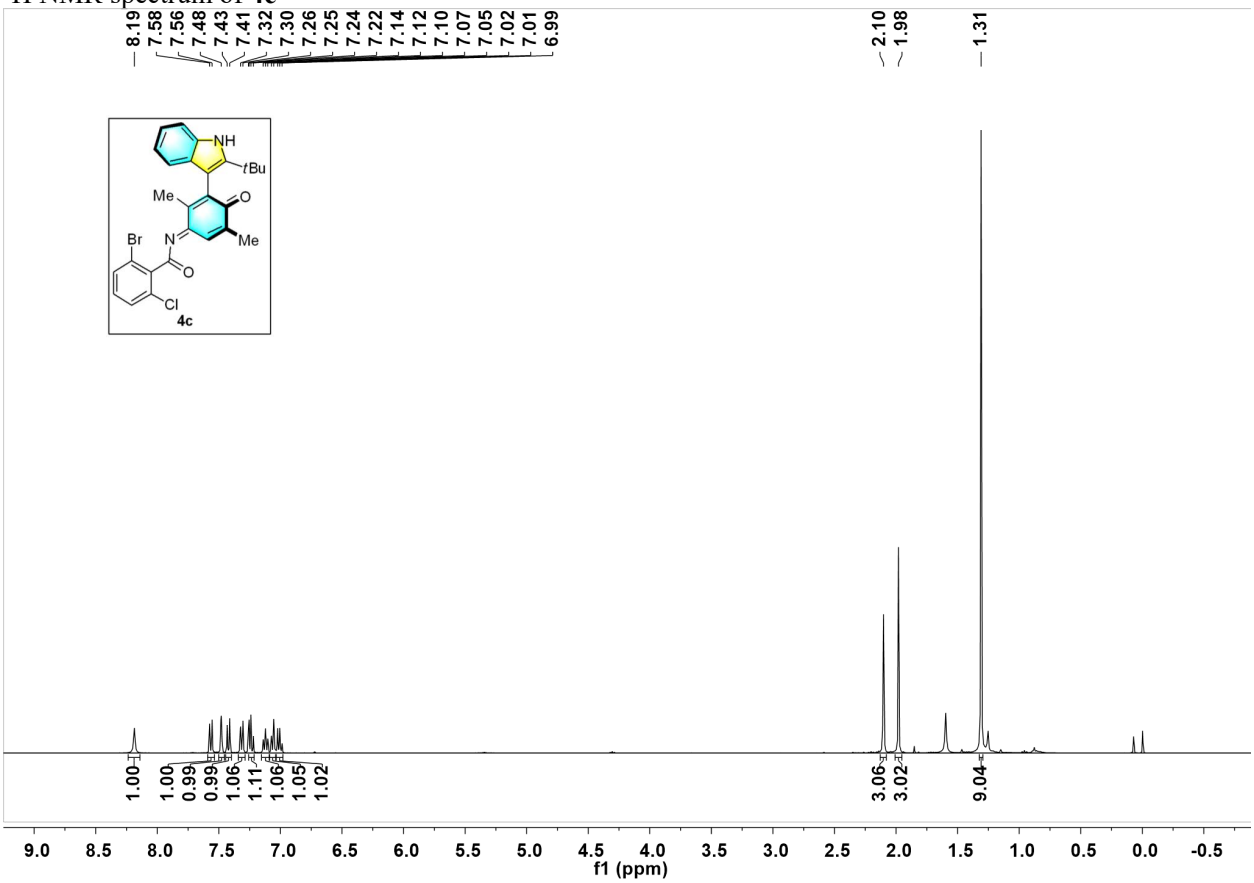
^{1}H NMR spectrum of **3y**



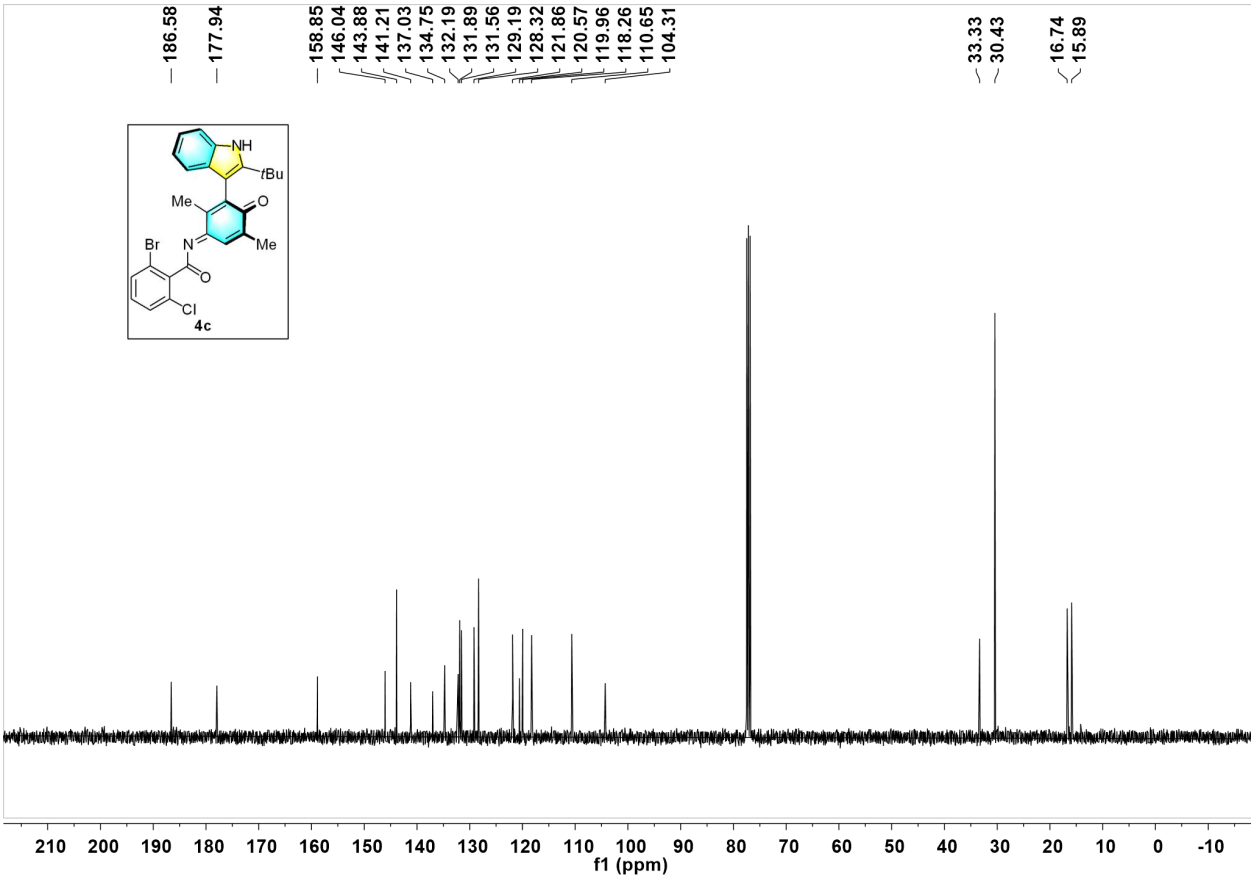
^{13}C NMR spectrum of **3y**



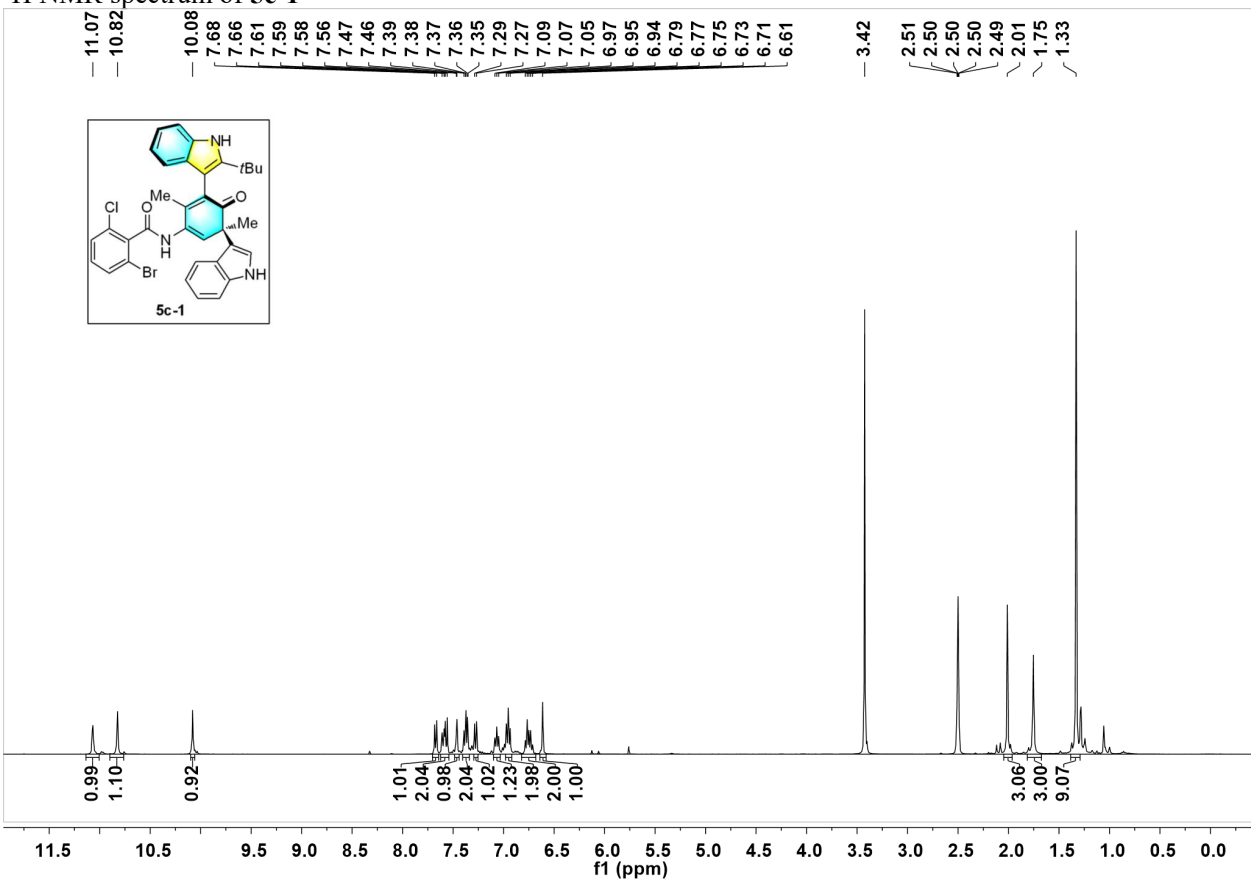
^{1}H NMR spectrum of **4c**



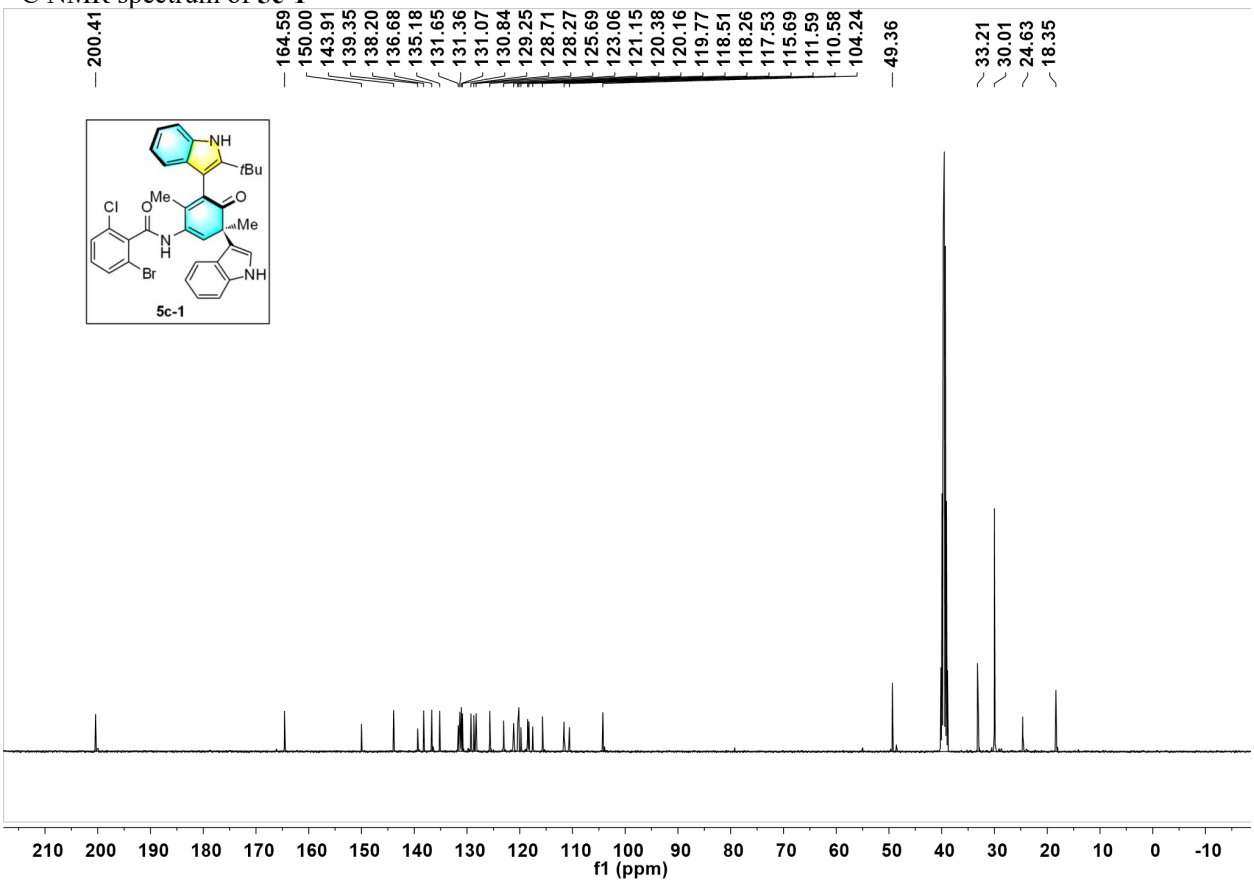
^{13}C NMR spectrum of **4c**



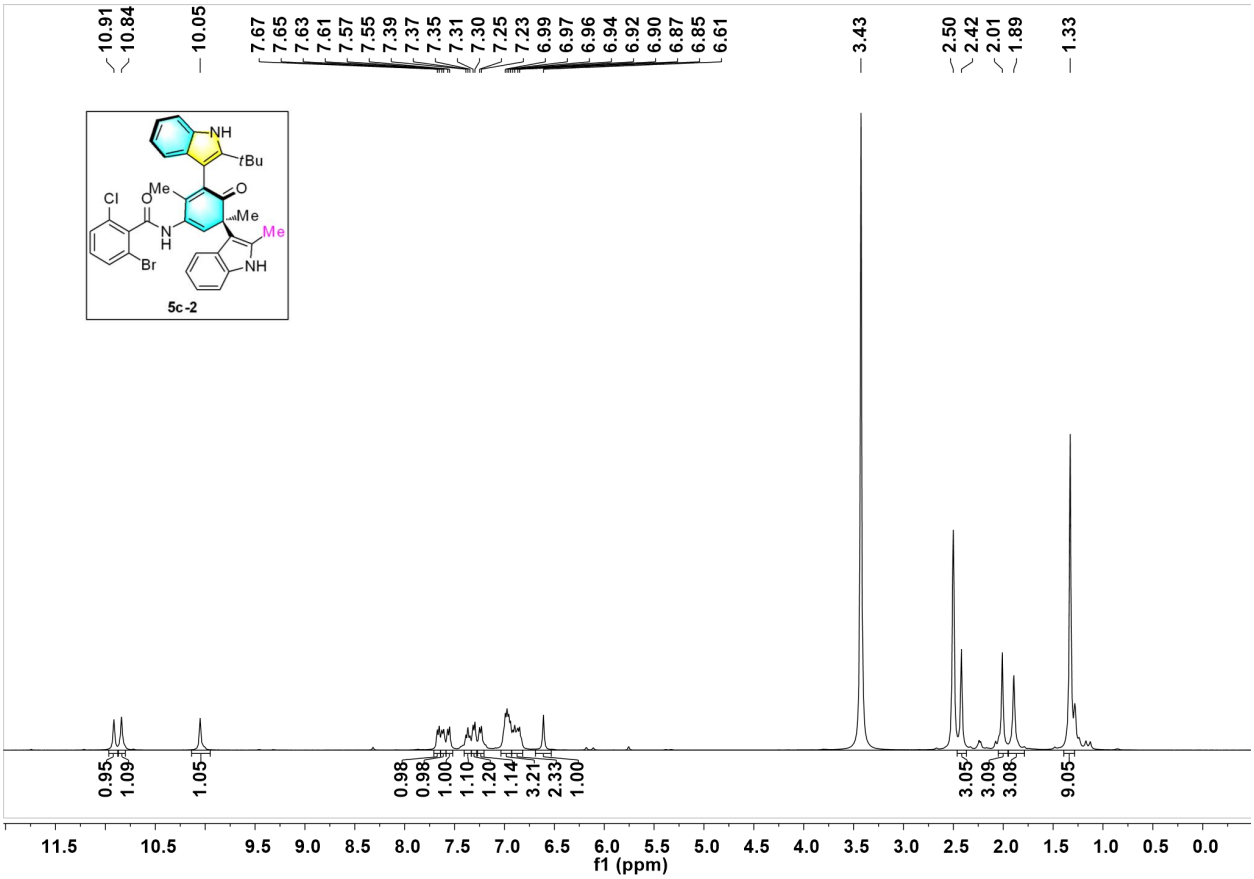
^{1}H NMR spectrum of **5c-1**



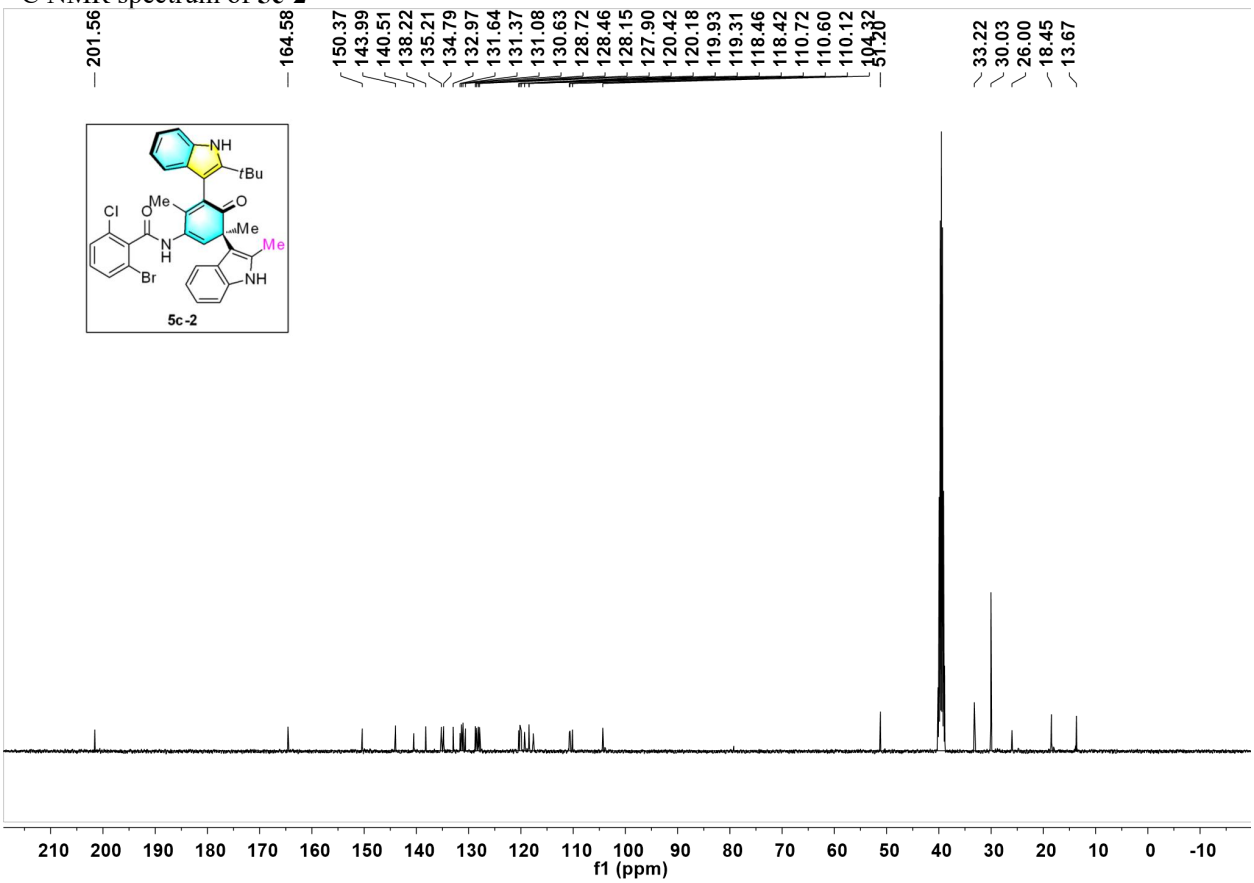
^{13}C NMR spectrum of **5c-1**



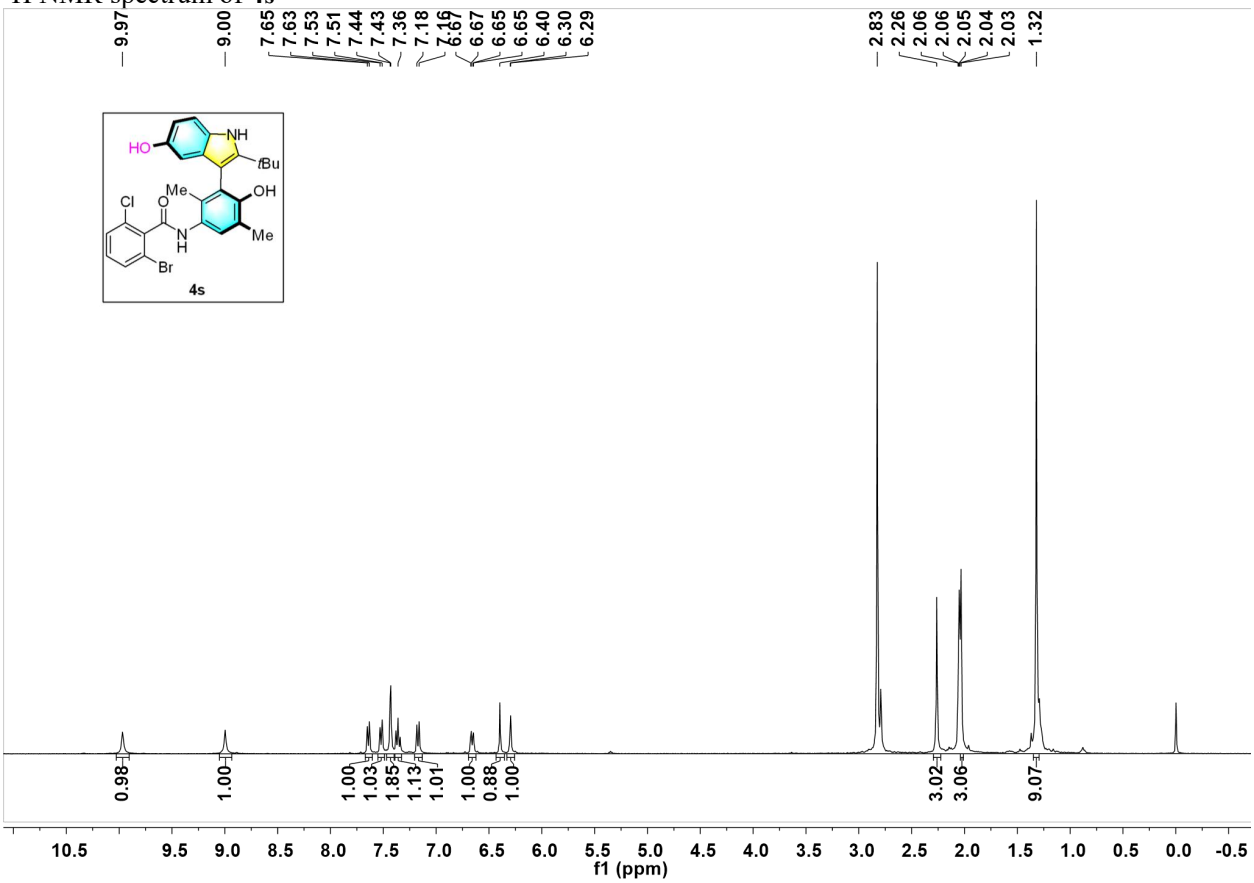
^{1}H NMR spectrum of **5c-2**



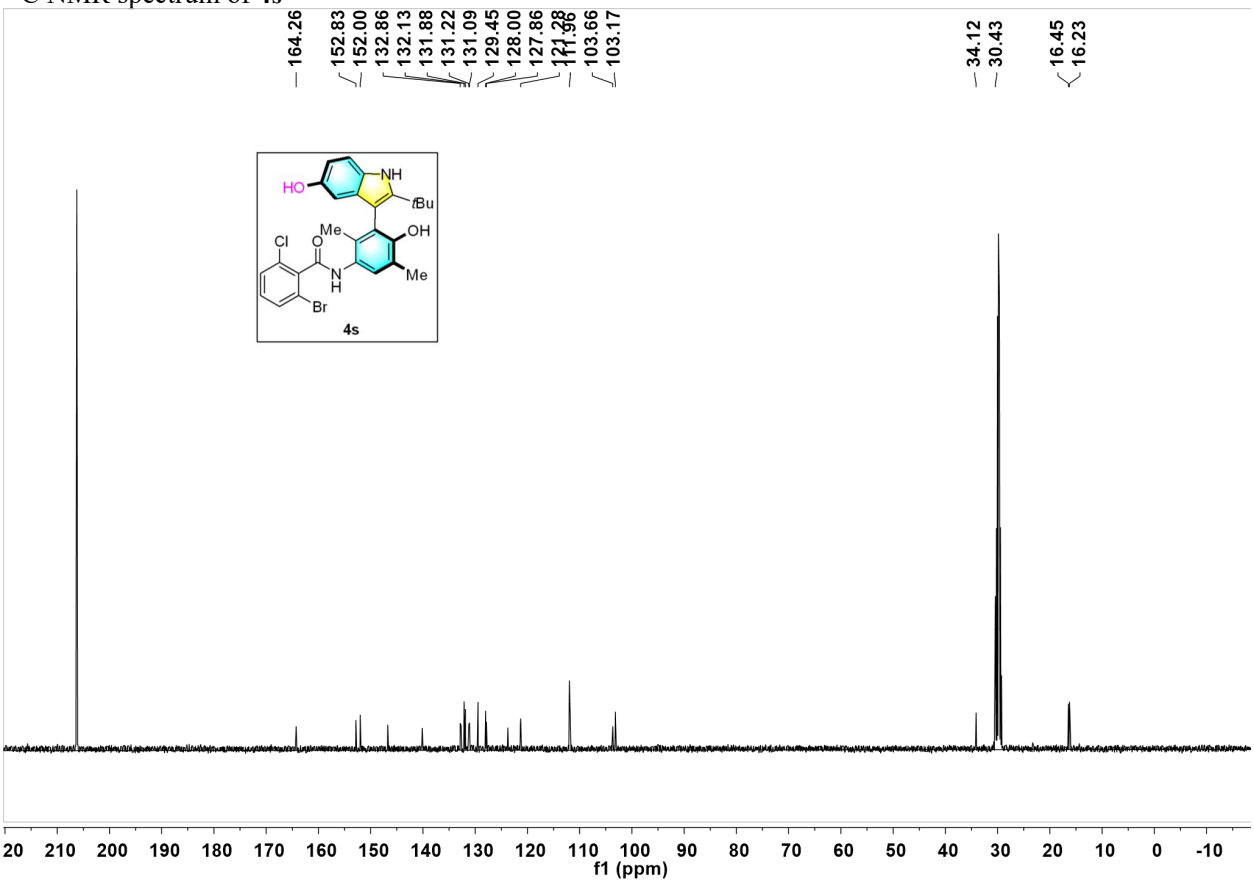
^{13}C NMR spectrum of **5c-2**



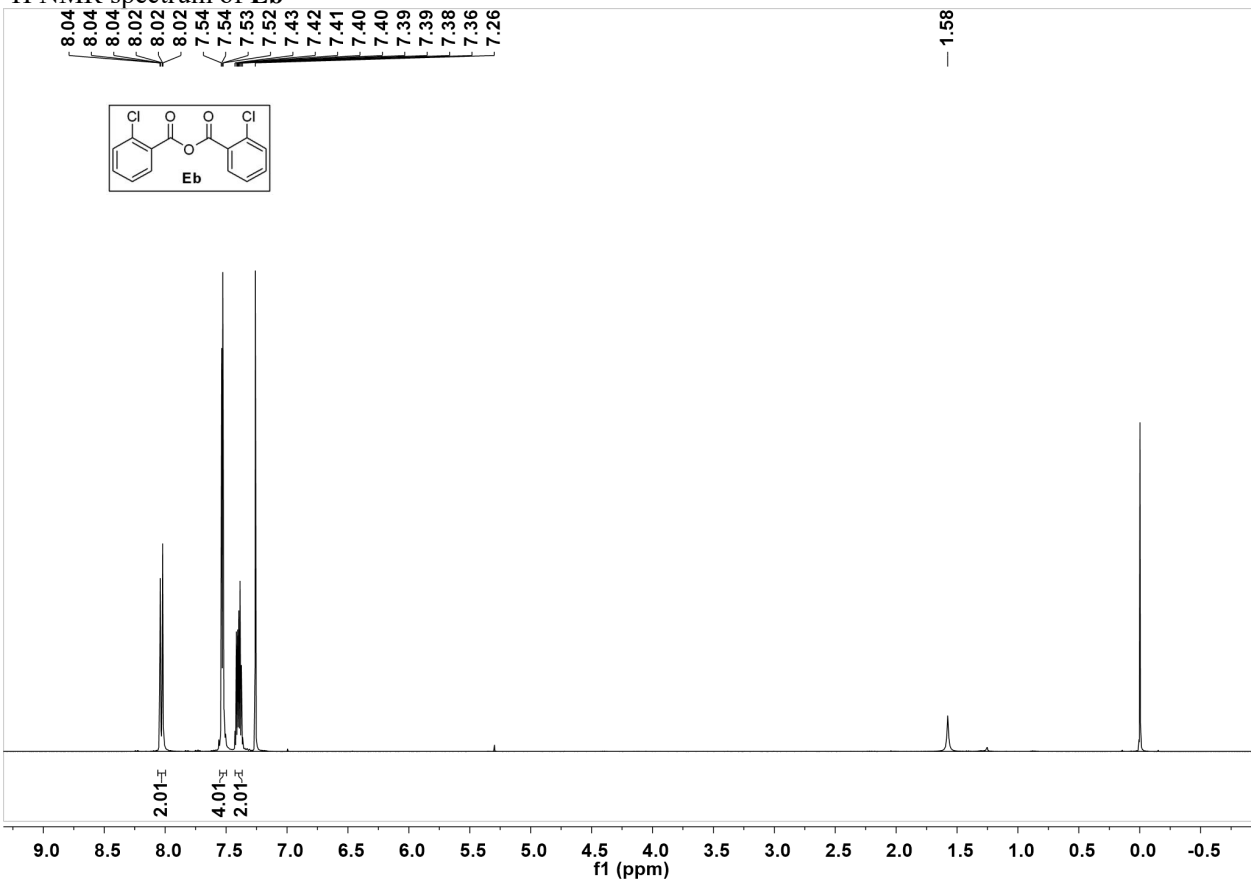
^{1}H NMR spectrum of **4s**



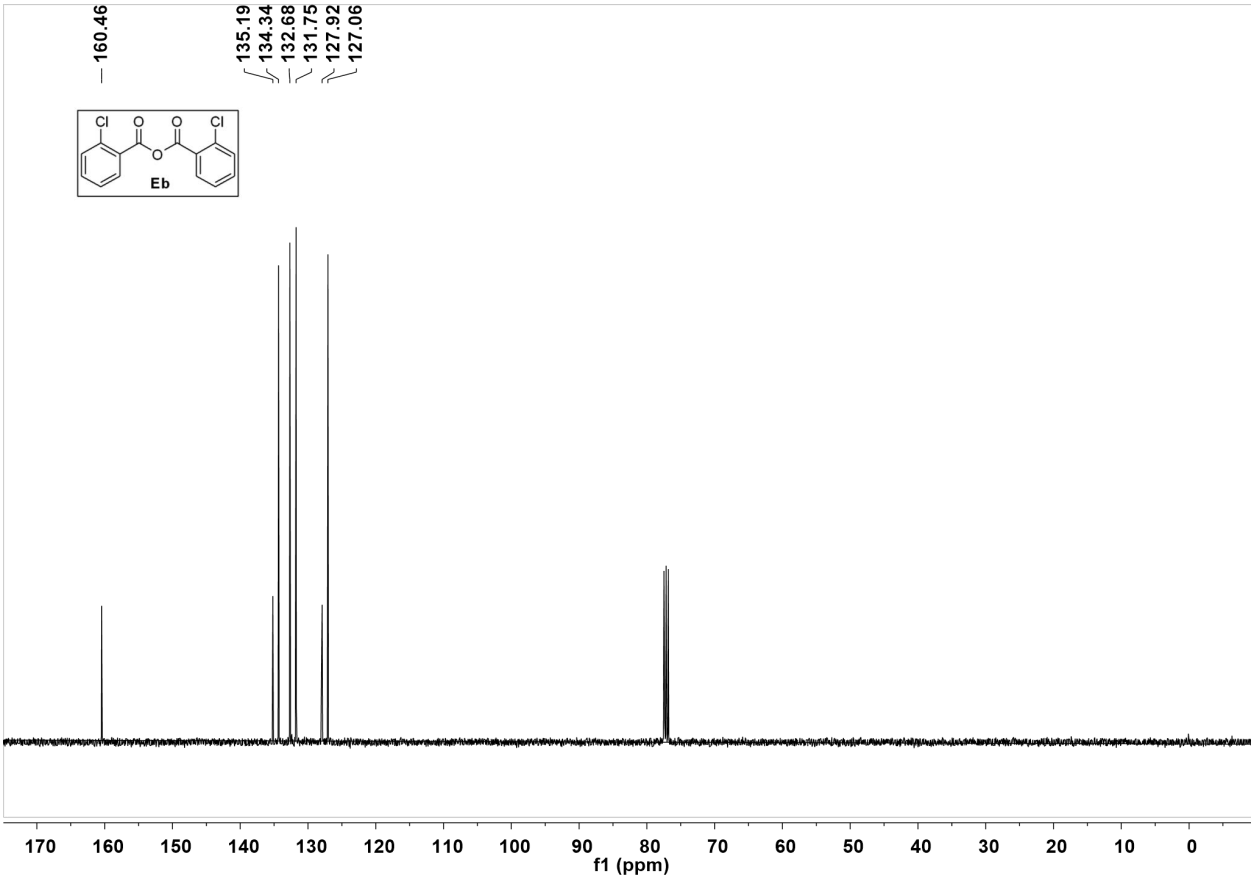
^{13}C NMR spectrum of **4s**



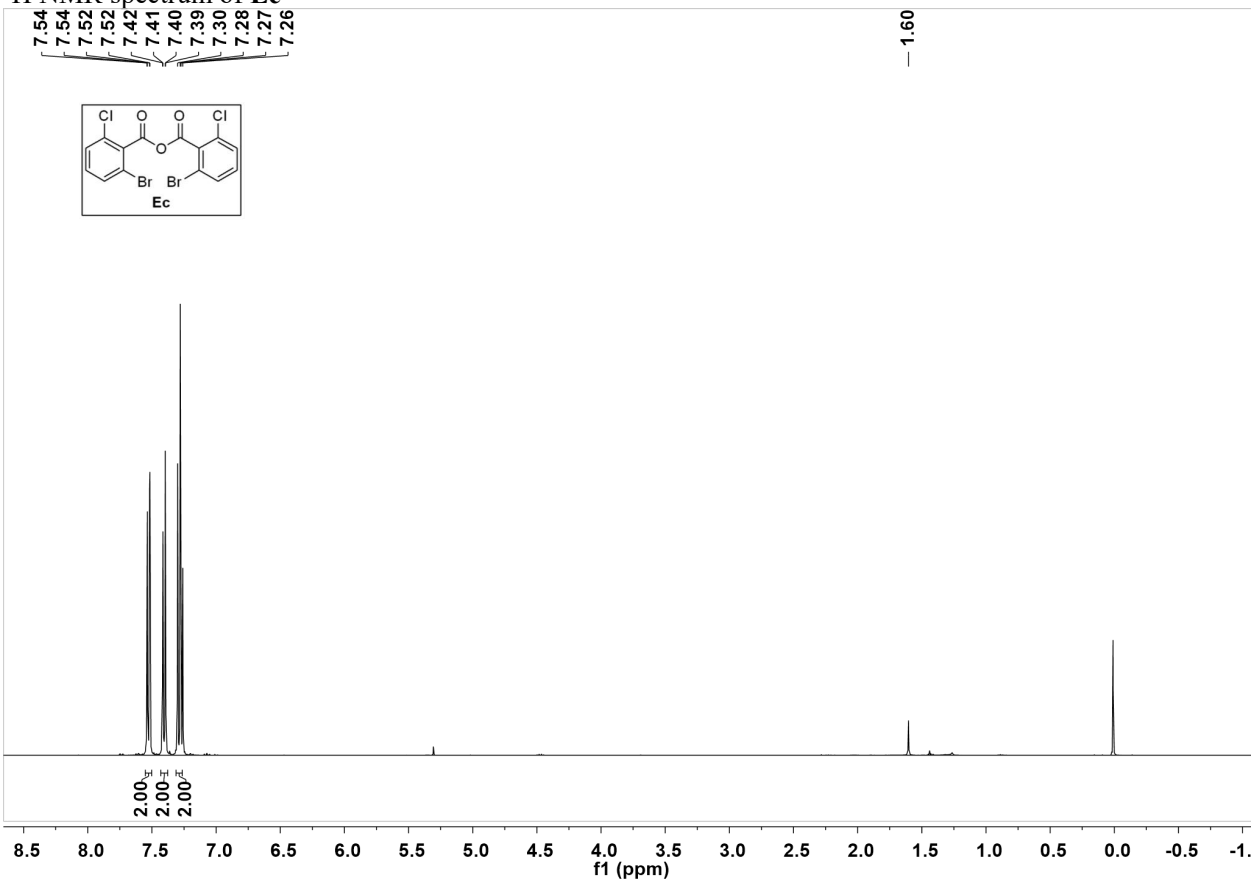
^{1}H NMR spectrum of **Eb**



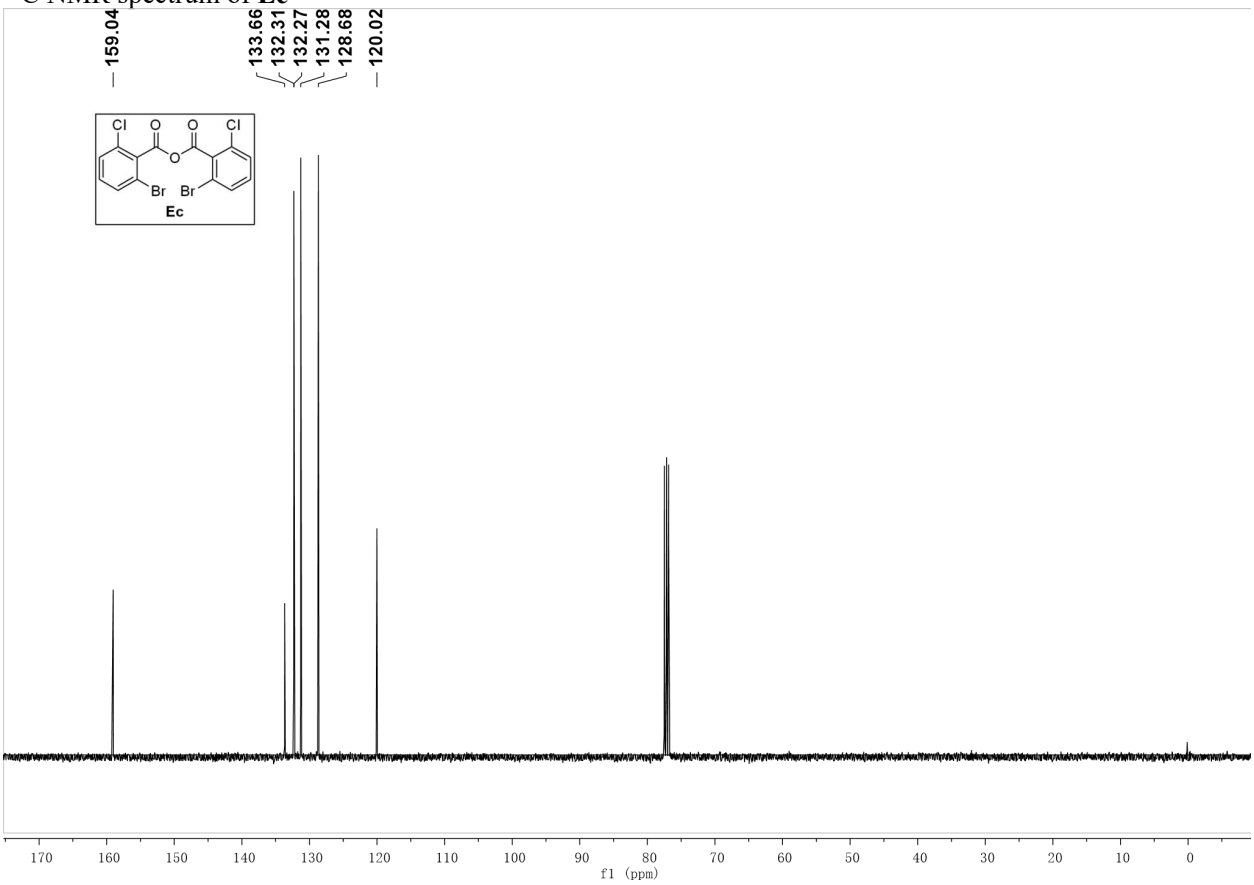
^{13}C NMR spectrum of **Eb**



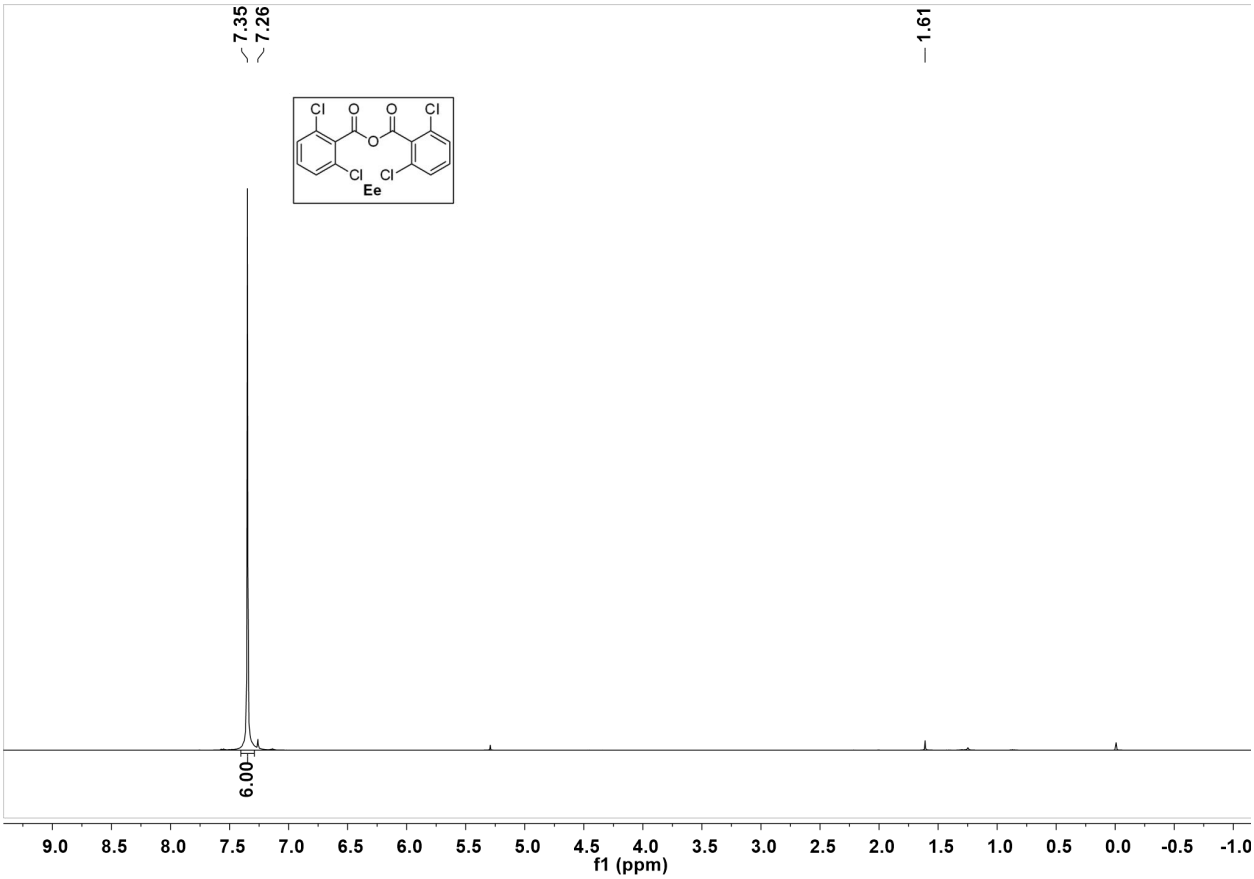
^{1}H NMR spectrum of **Ec**



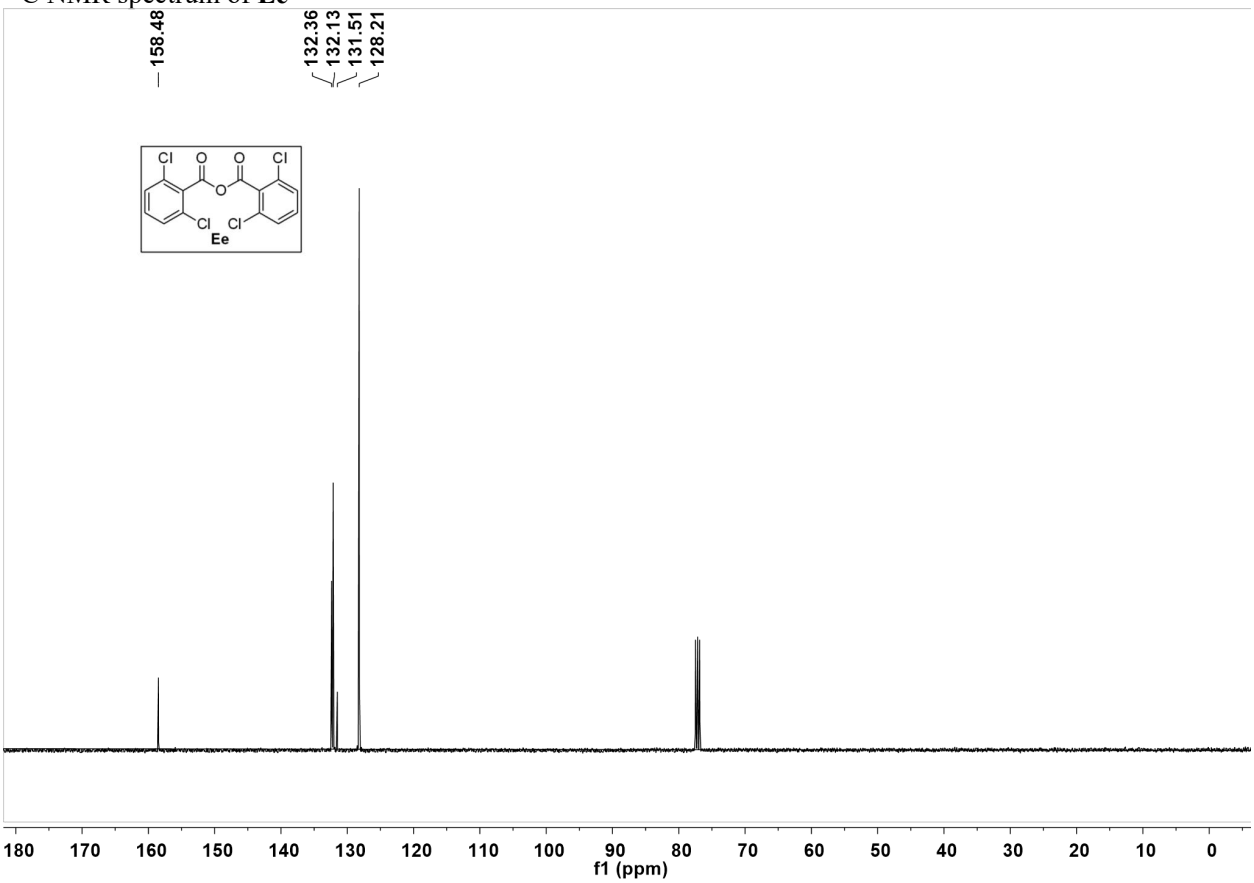
^{13}C NMR spectrum of **Ec**



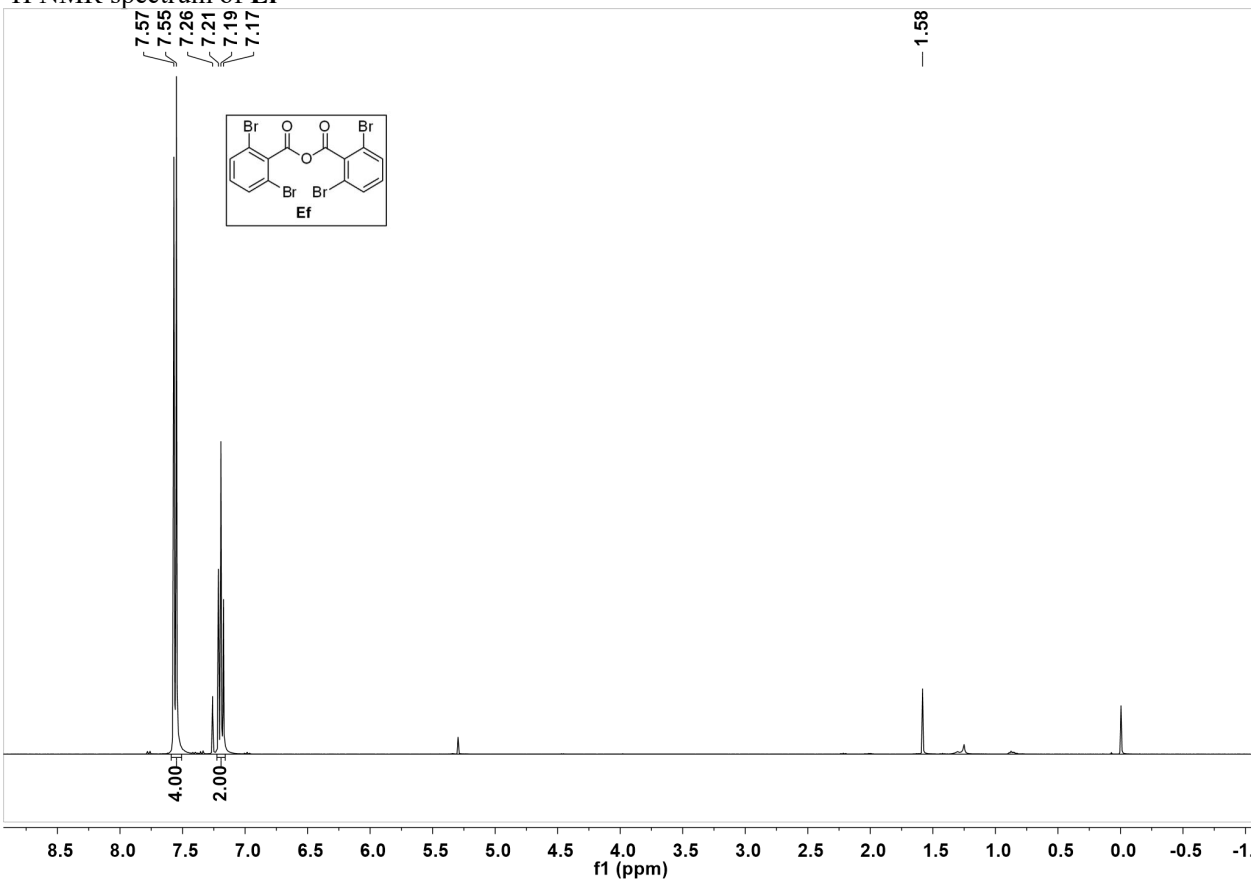
^{1}H NMR spectrum of **Ee**



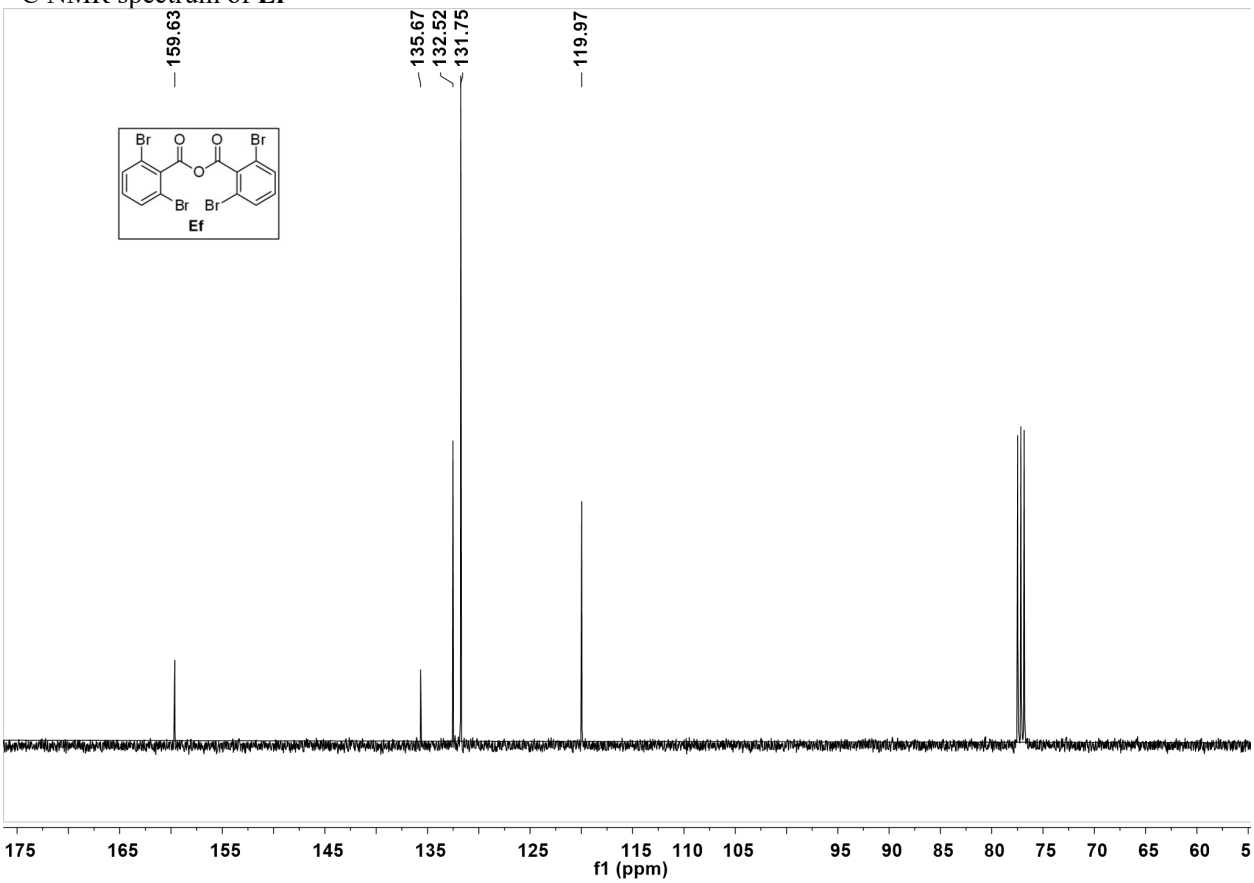
^{13}C NMR spectrum of **Ee**



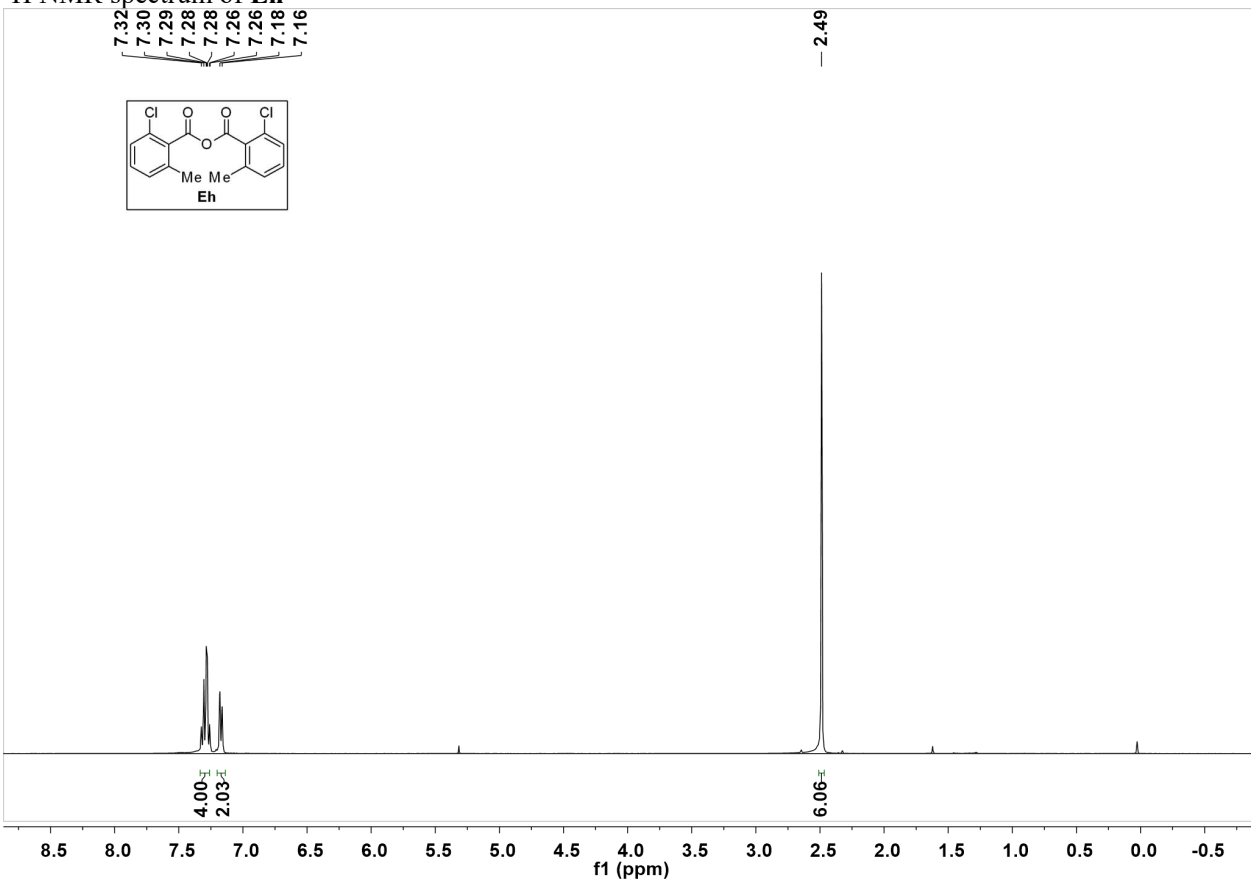
^{1}H NMR spectrum of **Ef**



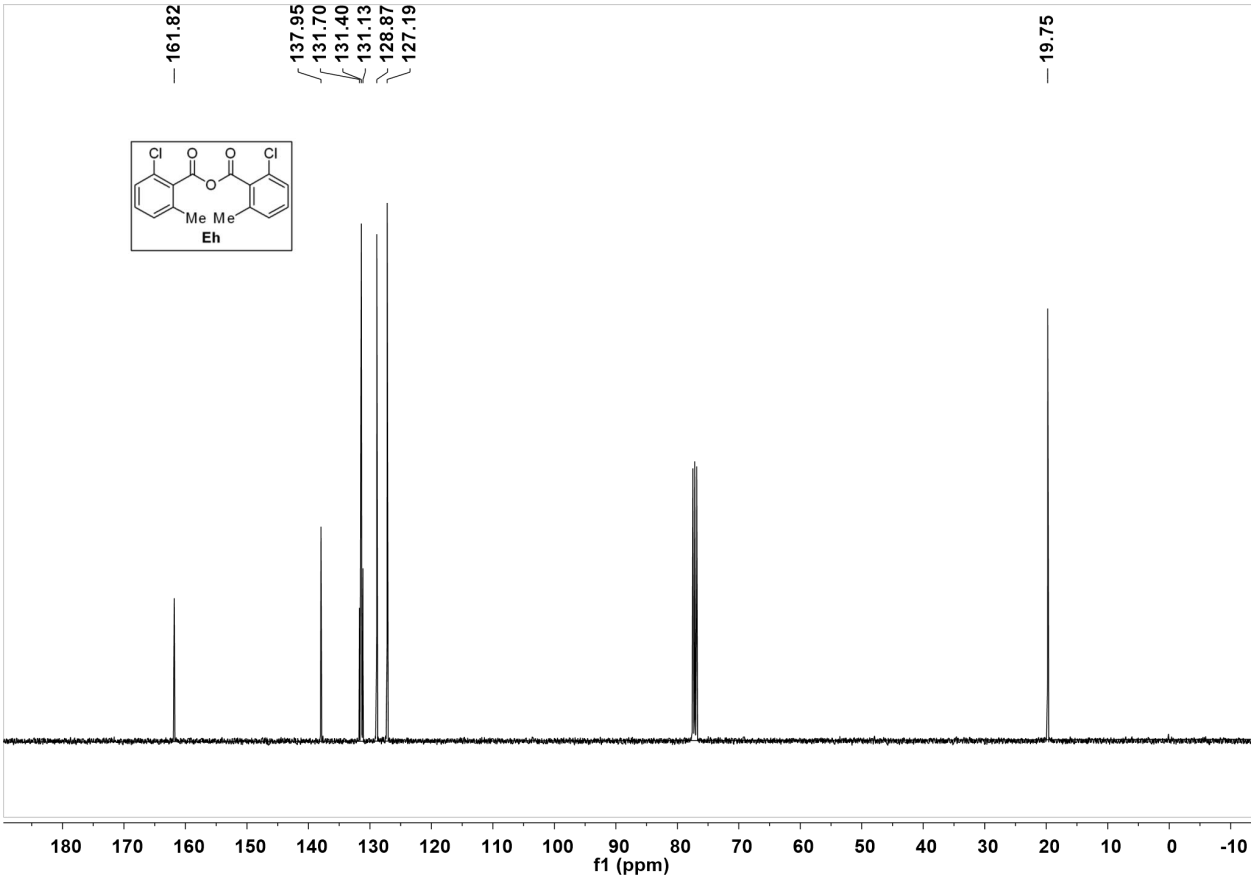
^{13}C NMR spectrum of **Ef**



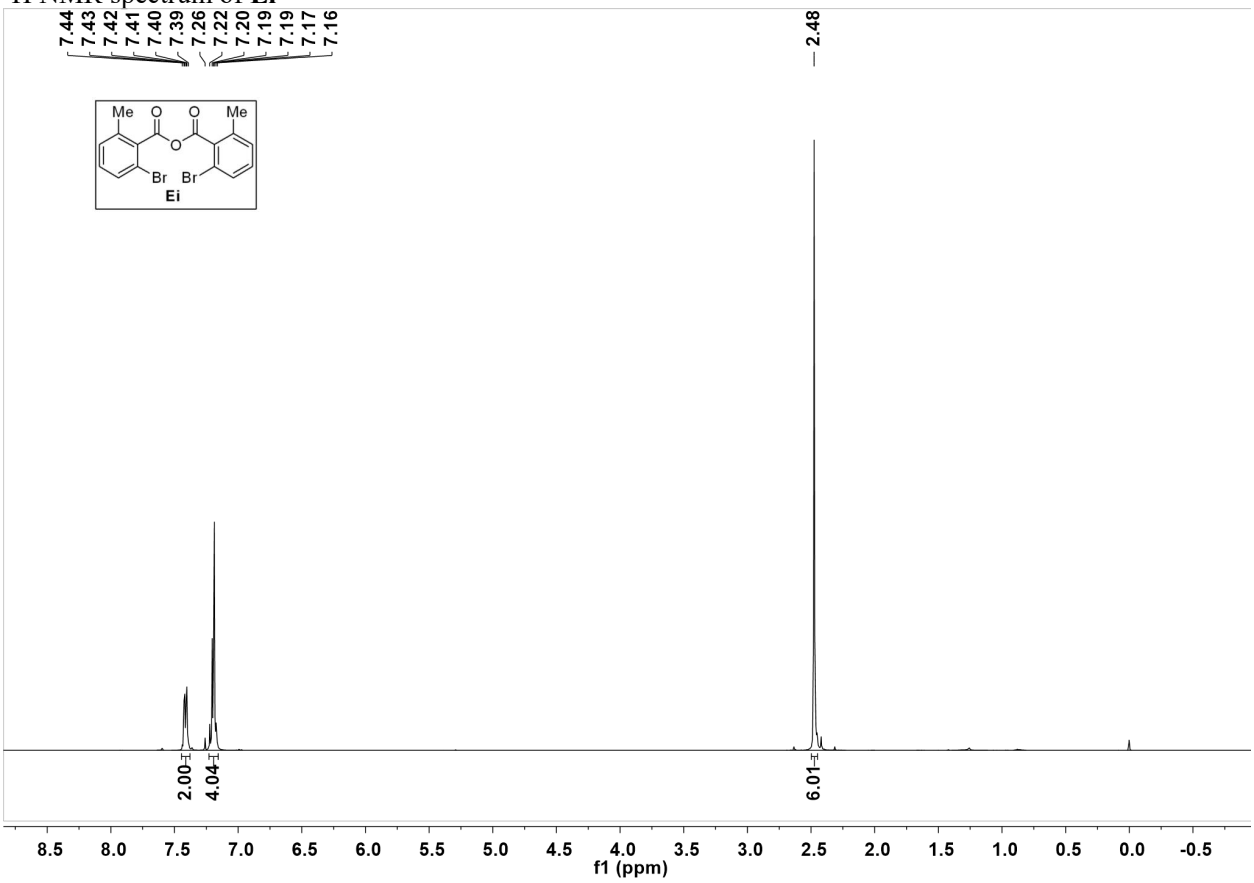
^{1}H NMR spectrum of **Eh**



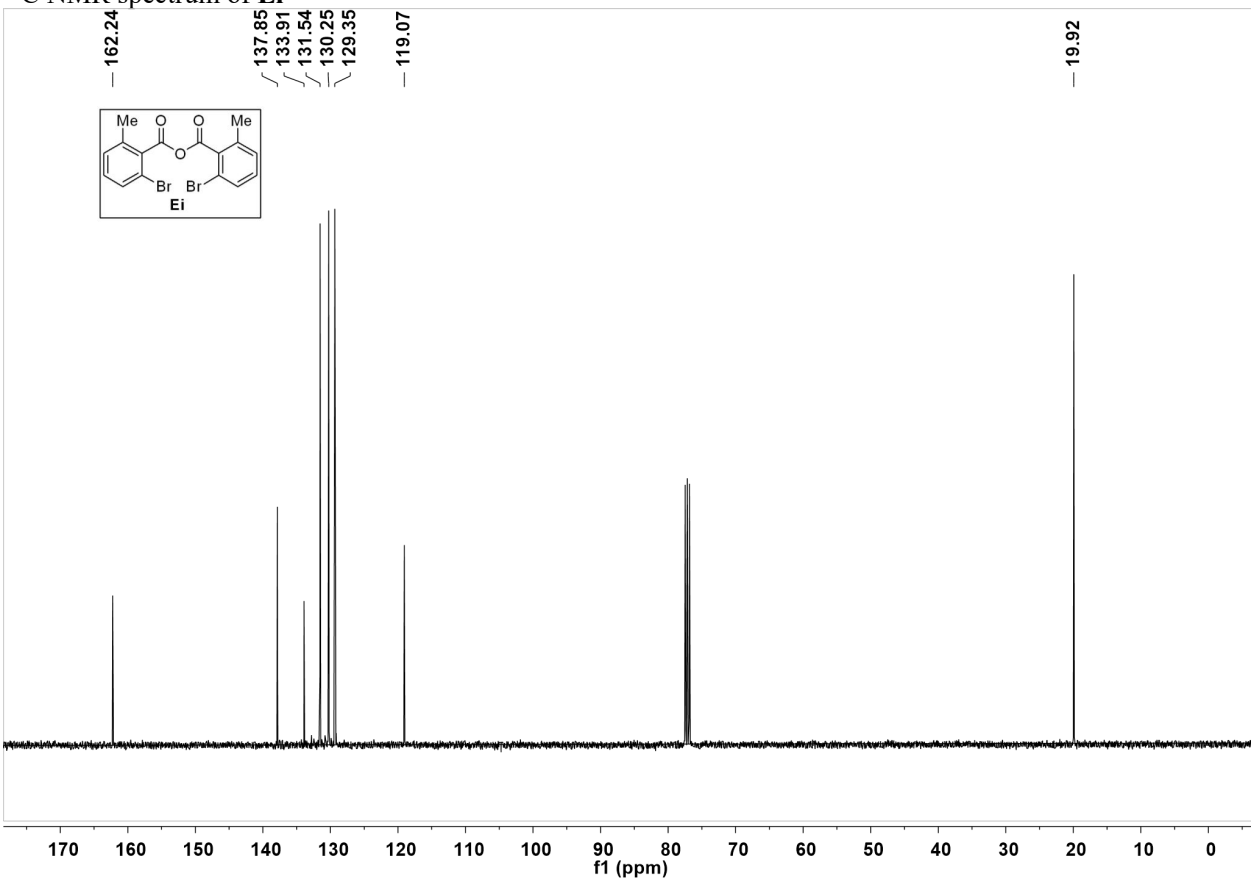
^{13}C NMR spectrum of **Eh**



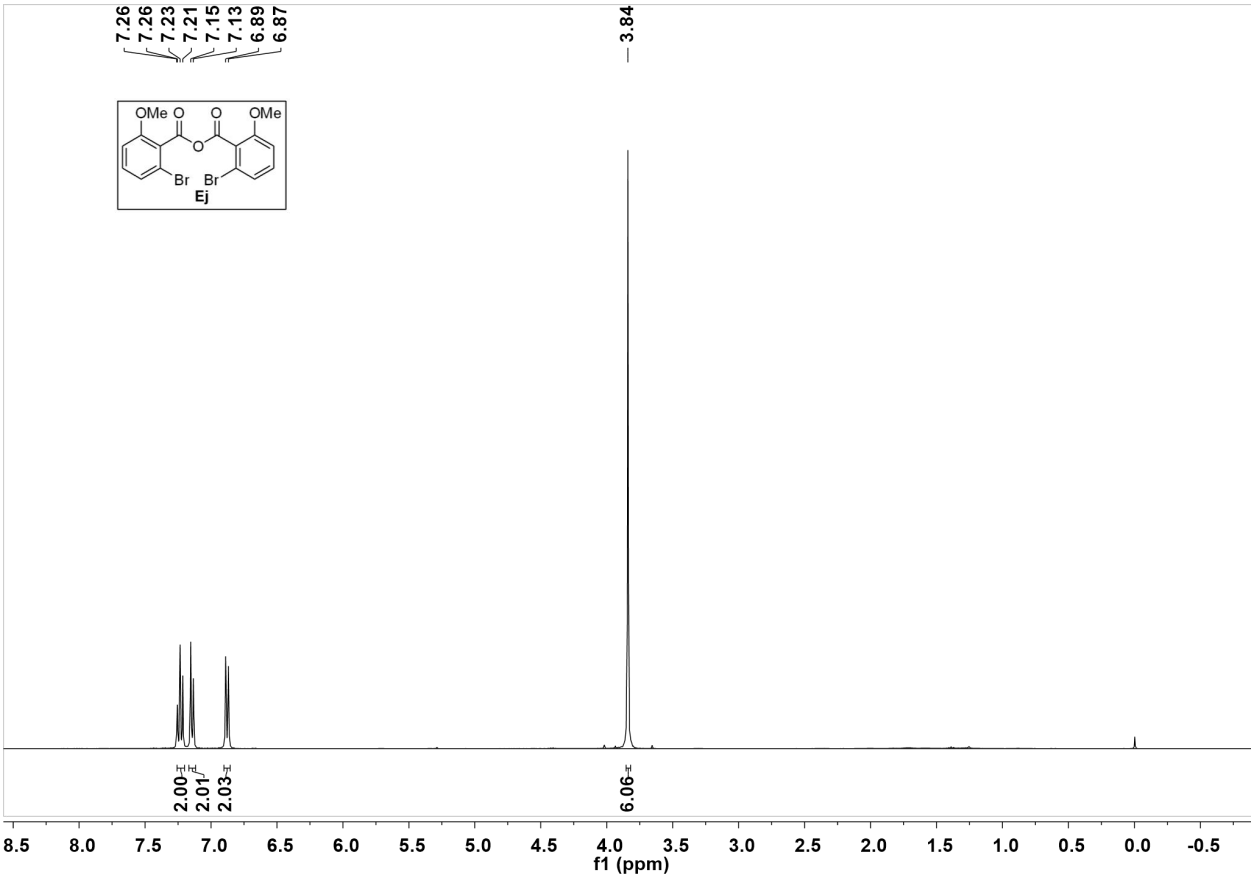
^{1}H NMR spectrum of **Ei**



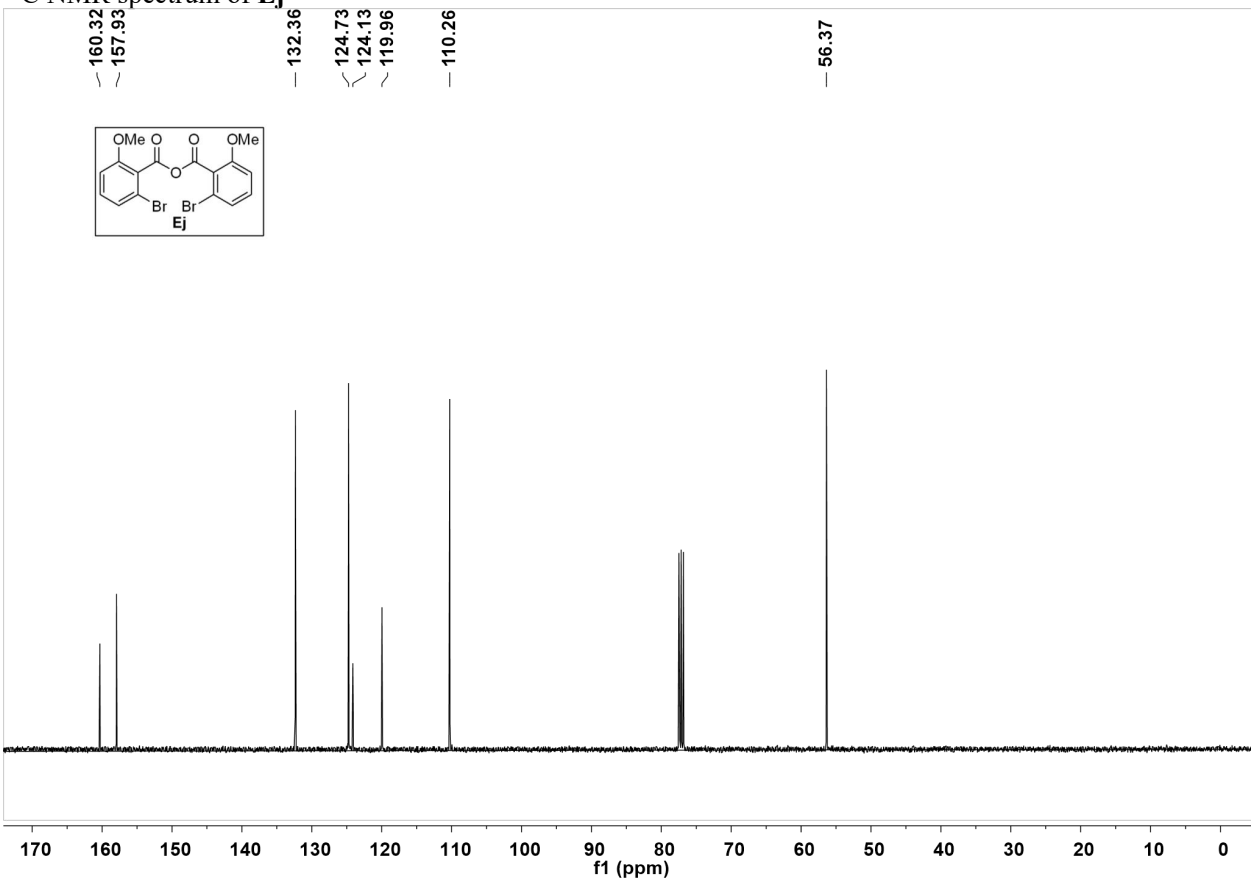
^{13}C NMR spectrum of **Ei**



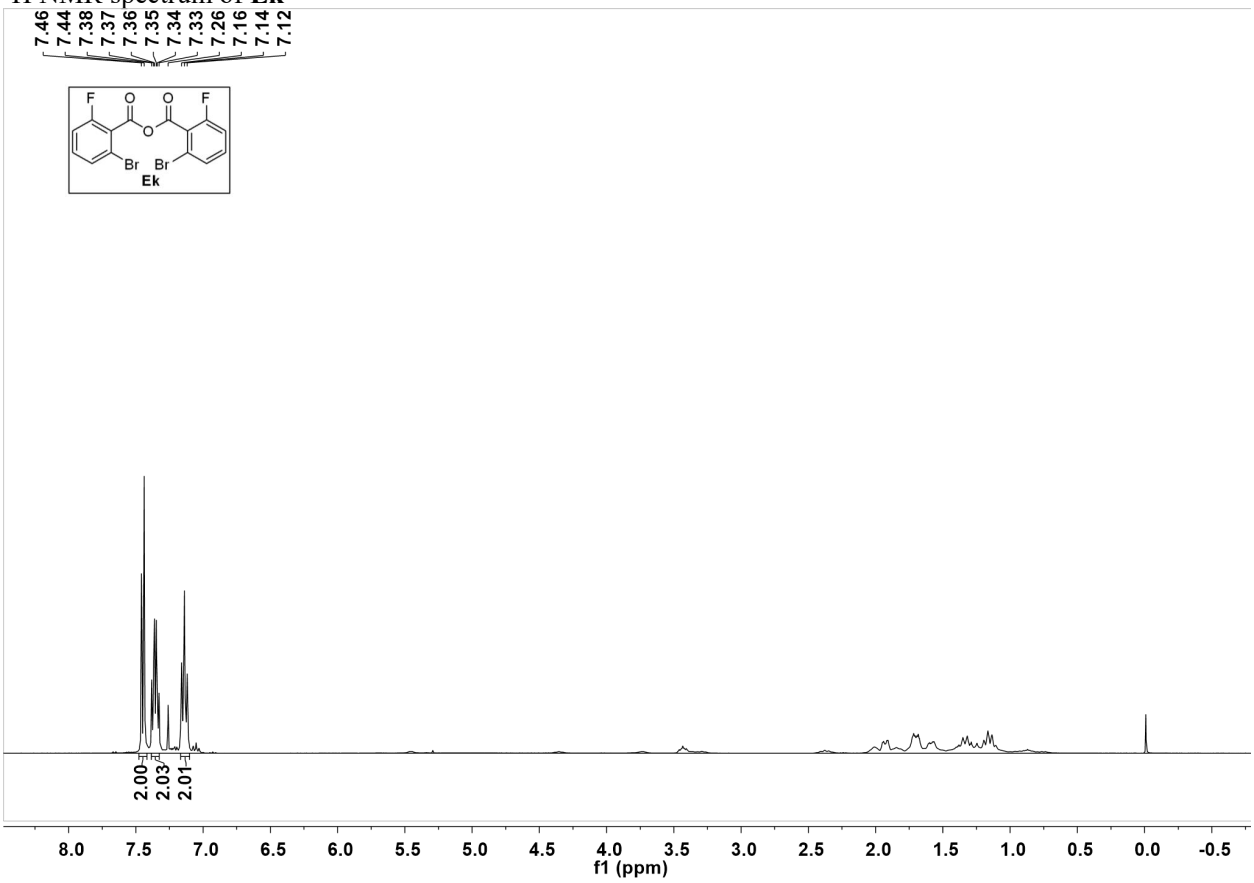
^{1}H NMR spectrum of **Ej**



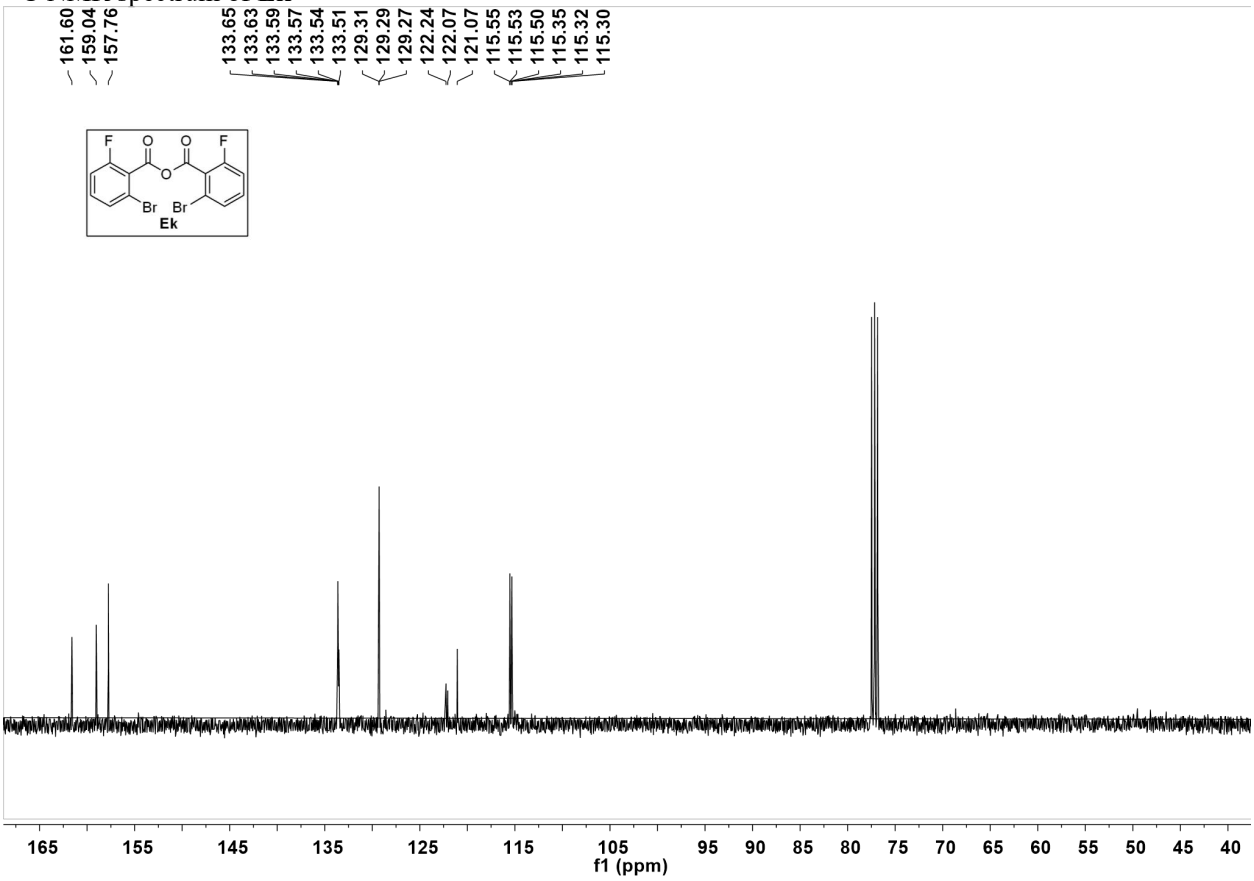
^{13}C NMR spectrum of **Ej**



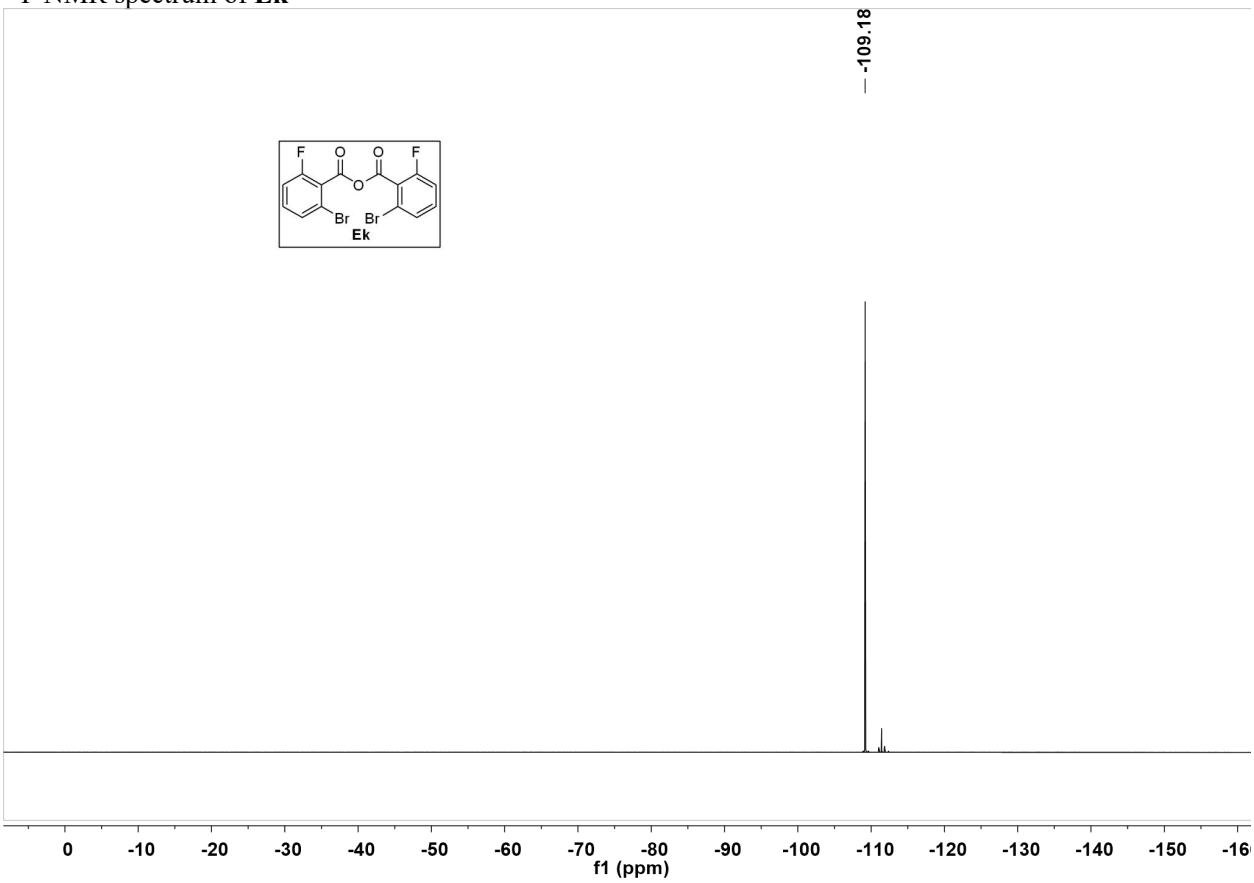
^{1}H NMR spectrum of **Ek**



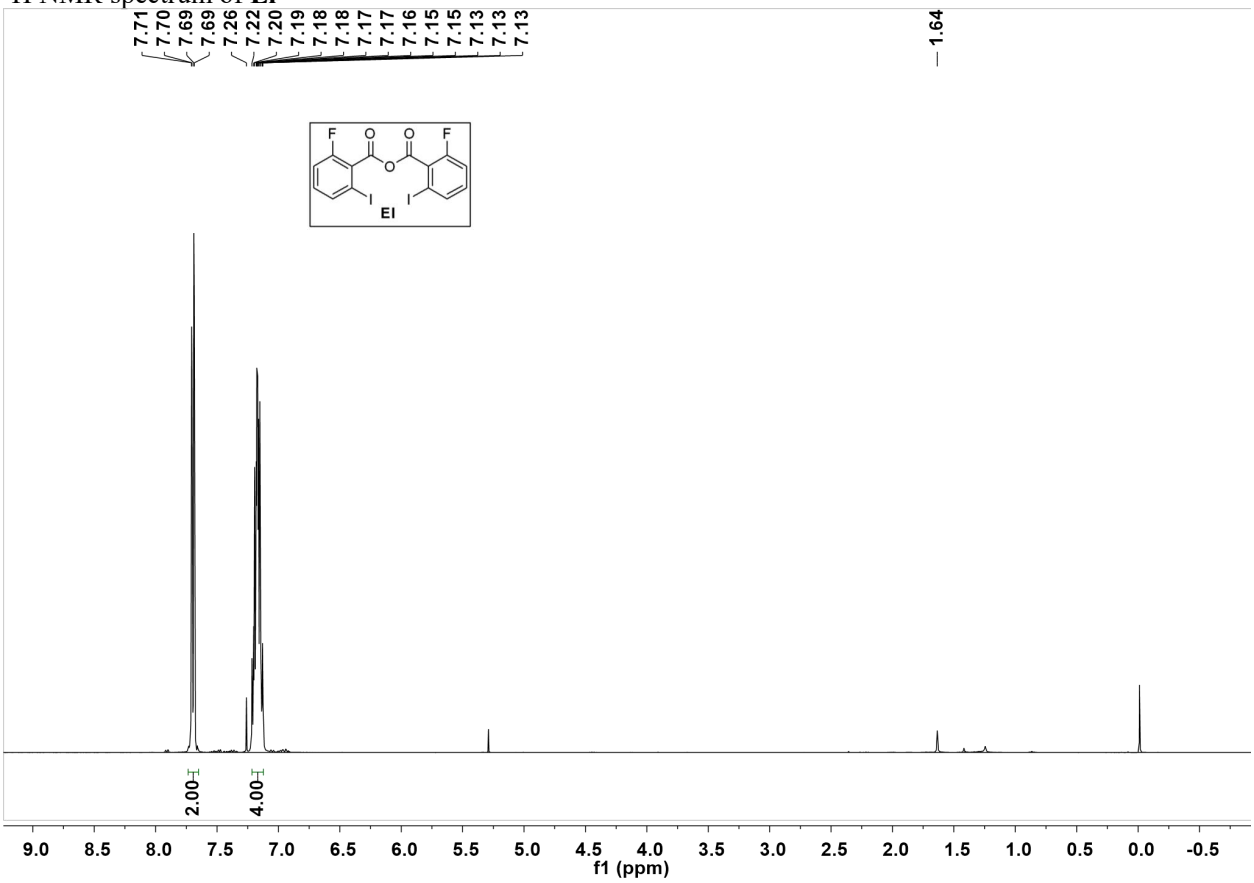
^{13}C NMR spectrum of **Ek**



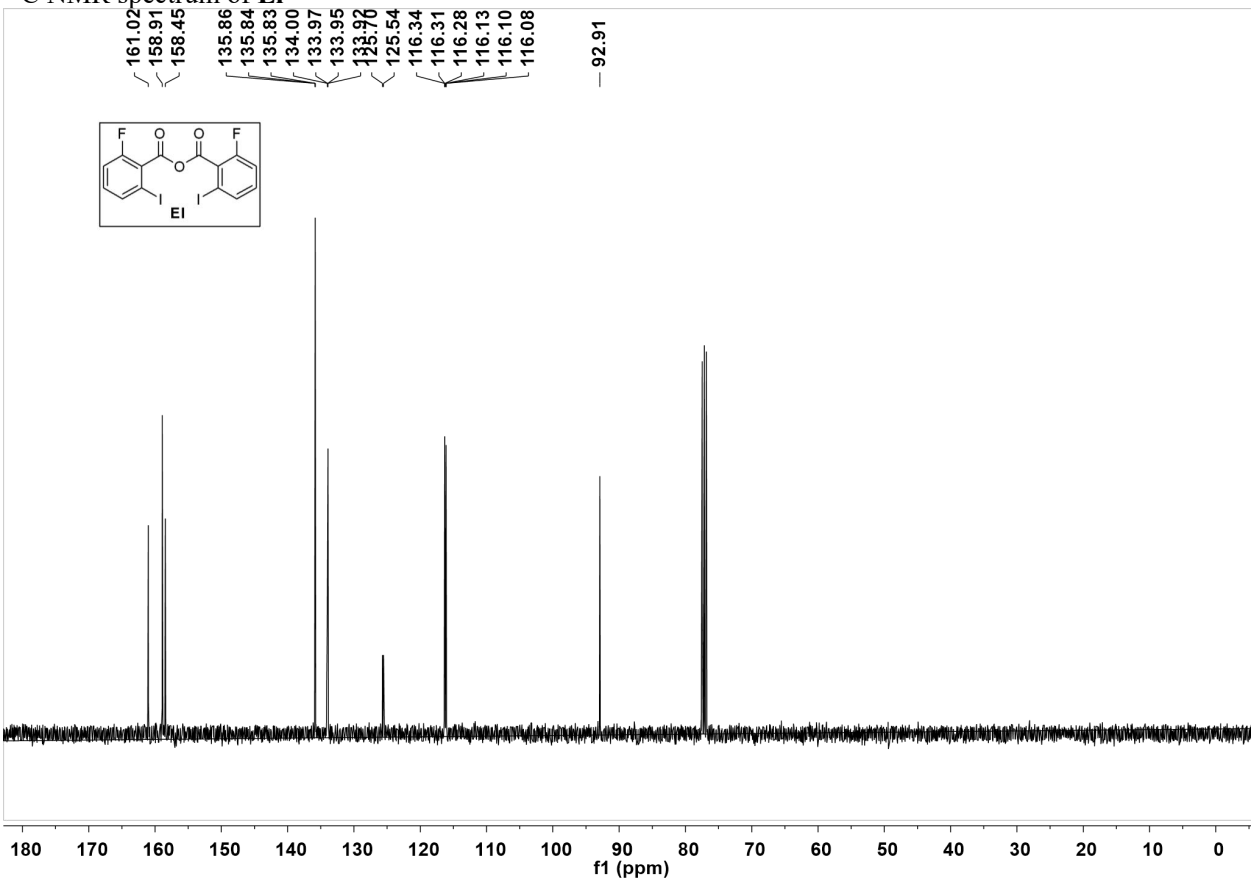
^{19}F NMR spectrum of **Ek**



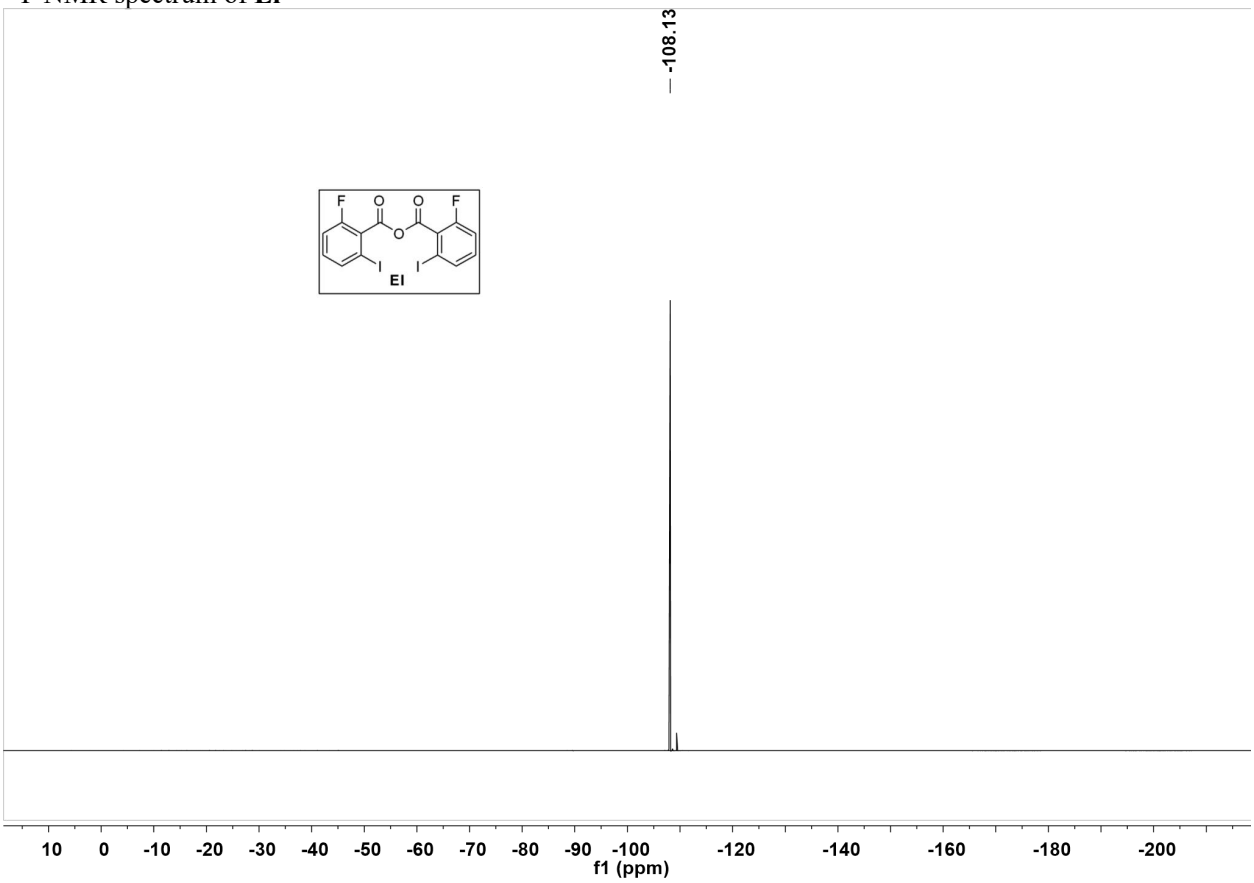
^{1}H NMR spectrum of **El**



^{13}C NMR spectrum of **El**



^{19}F NMR spectrum of **EI**



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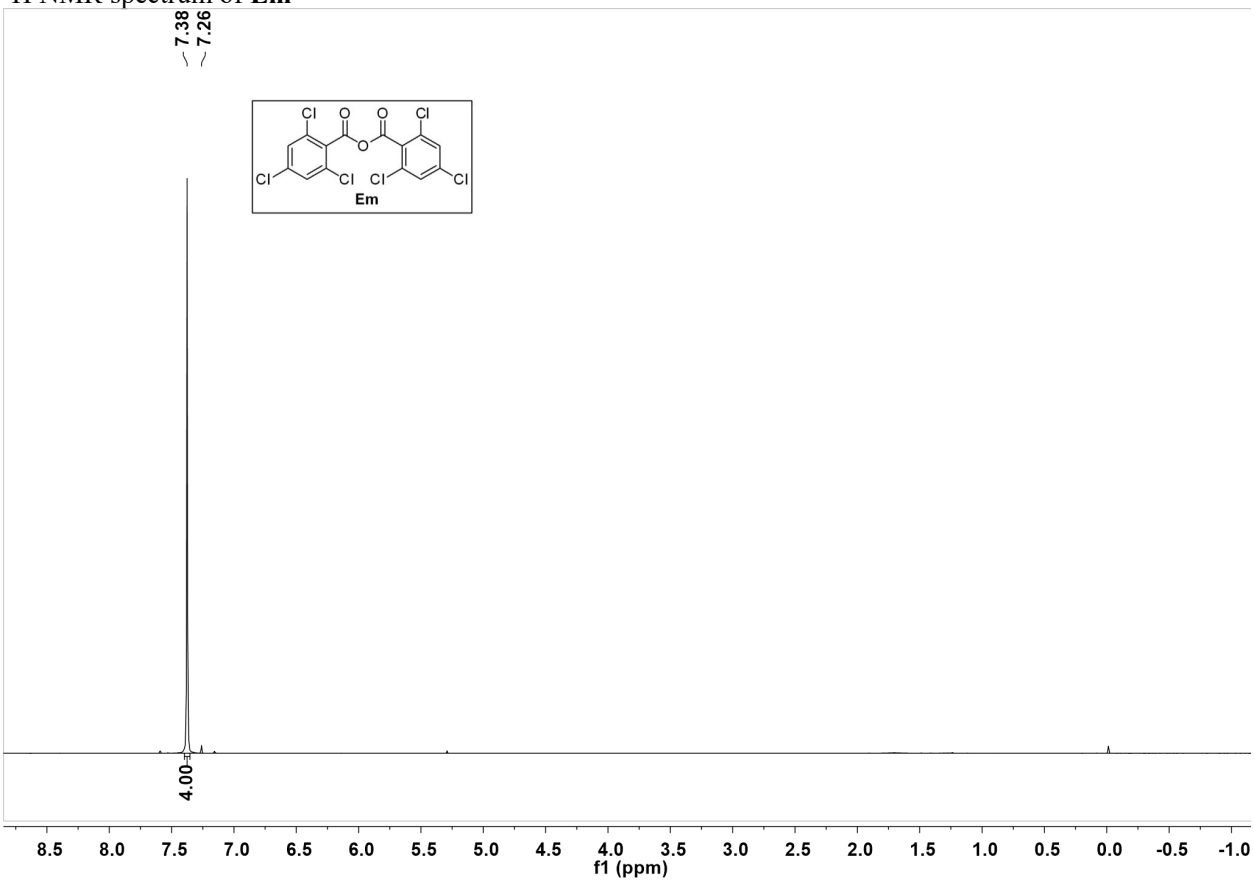
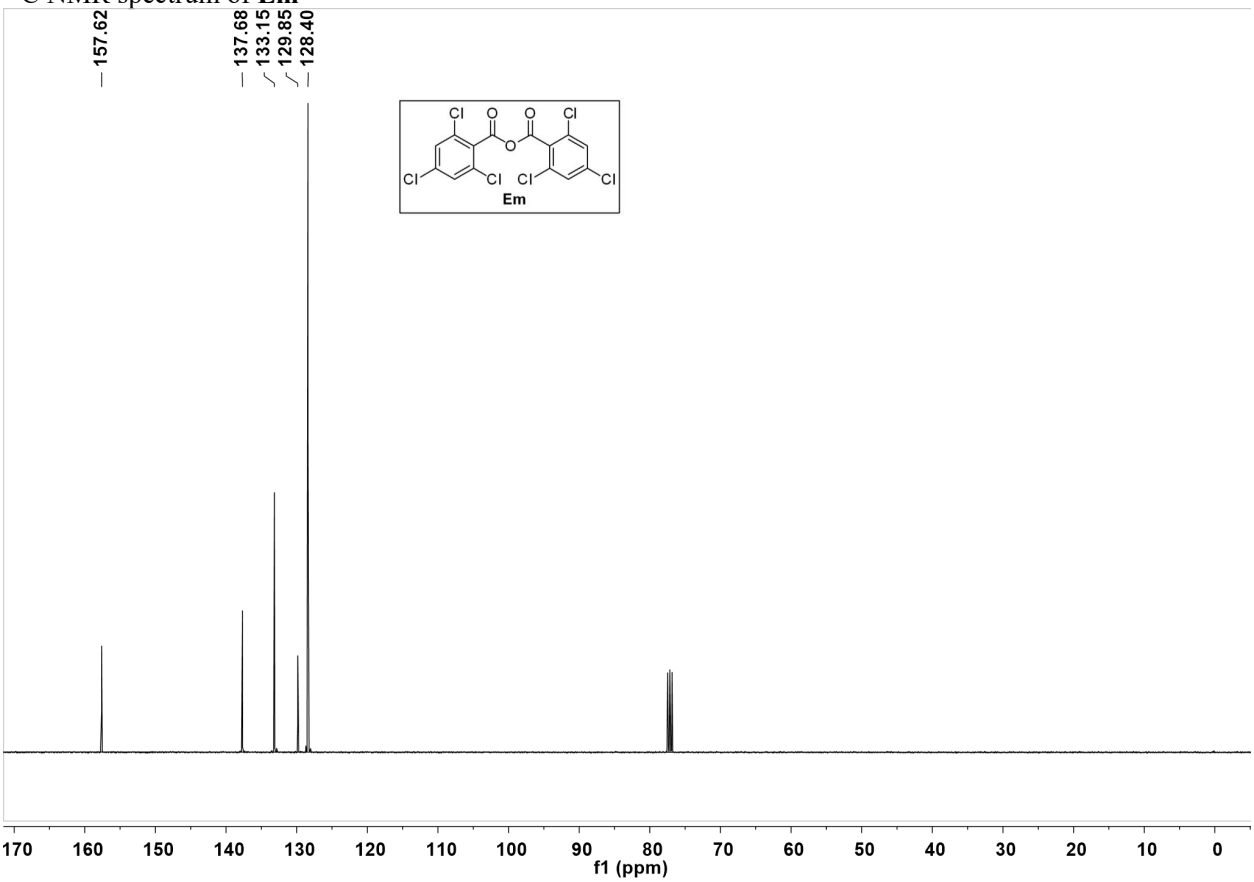
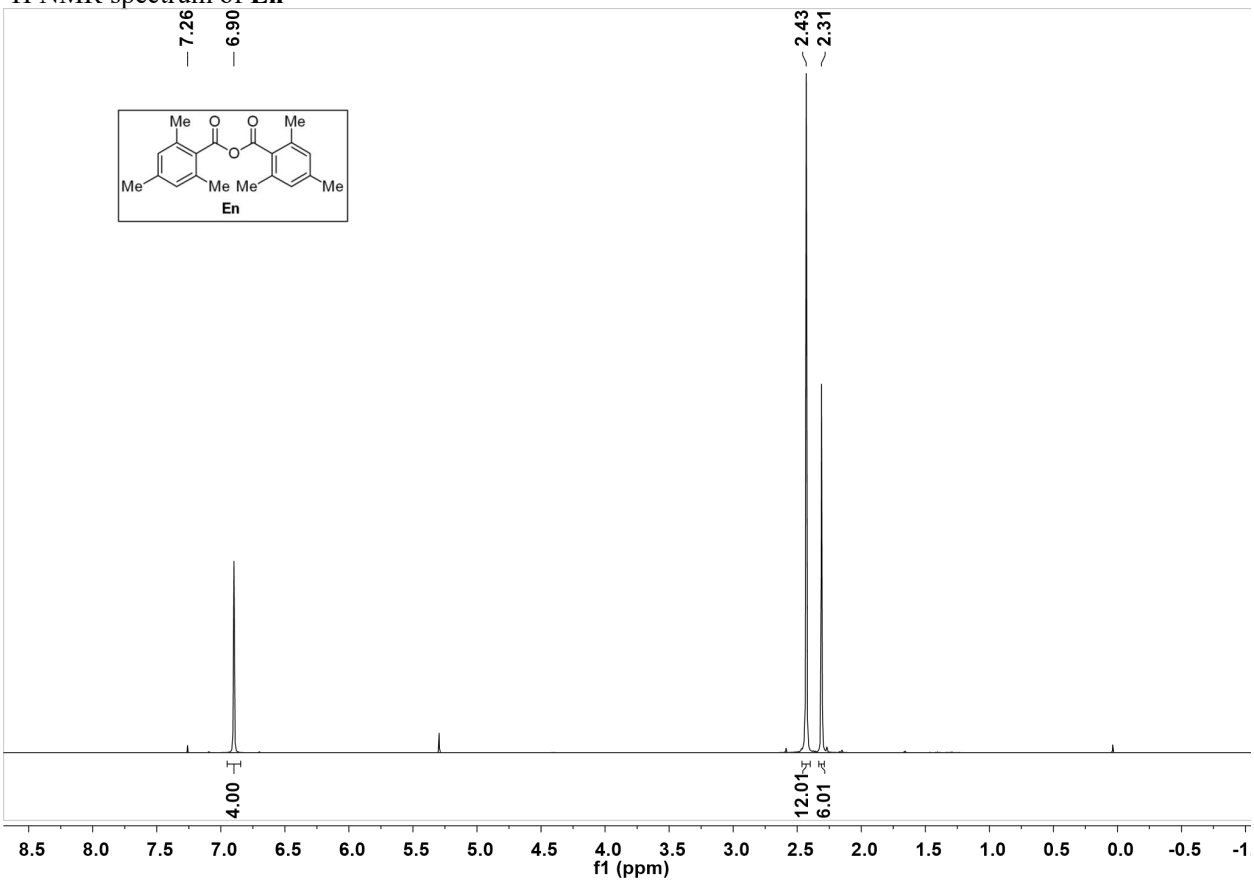


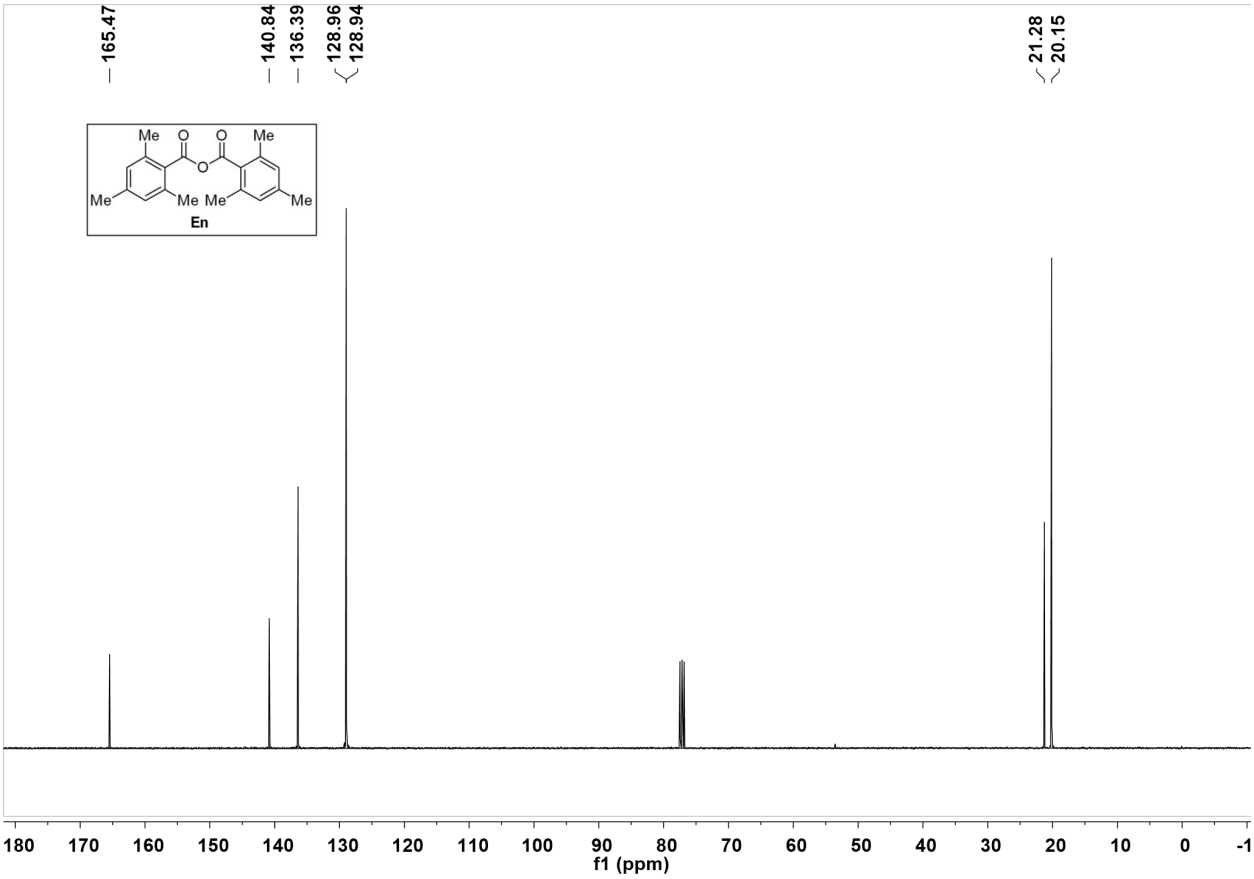
^{13}C NMR spectrum of **Em**



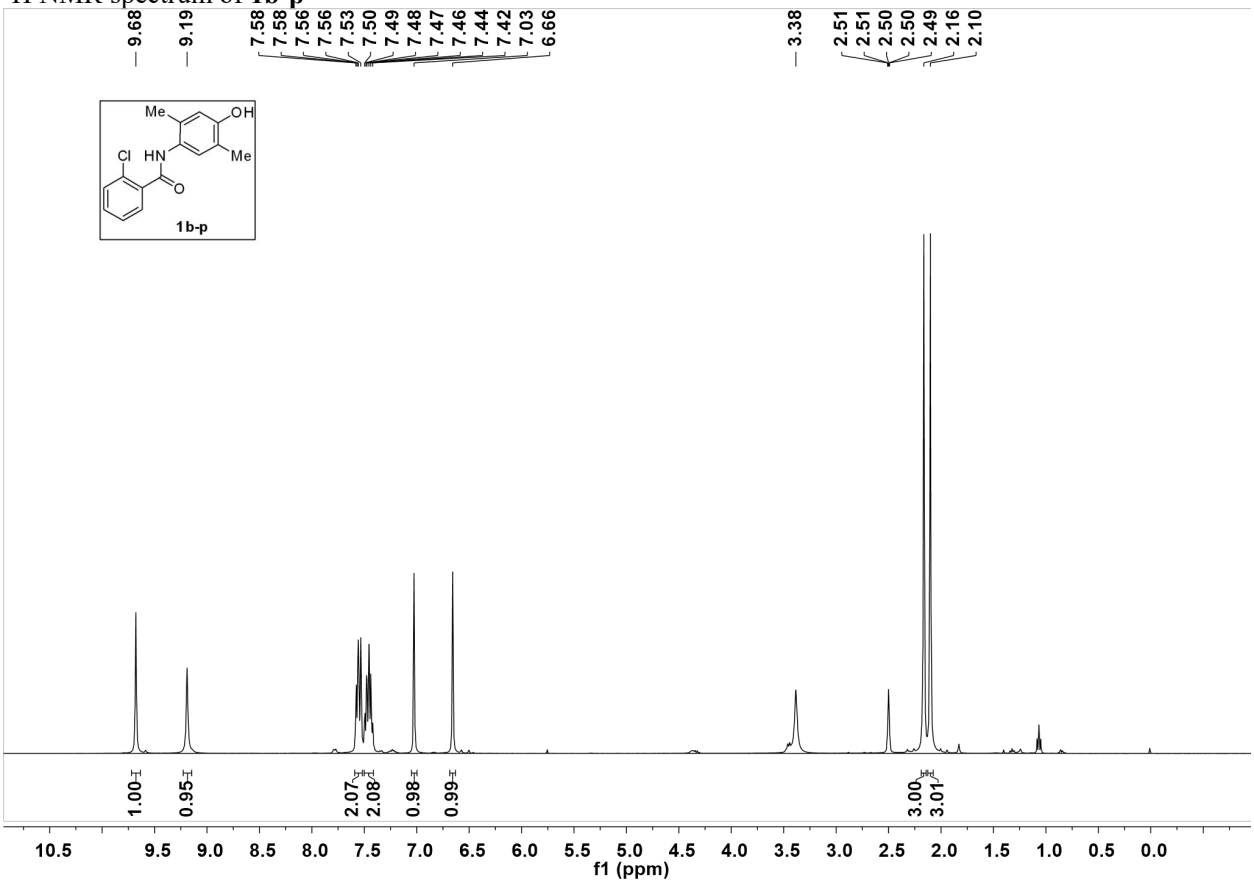
^{1}H NMR spectrum of **En**



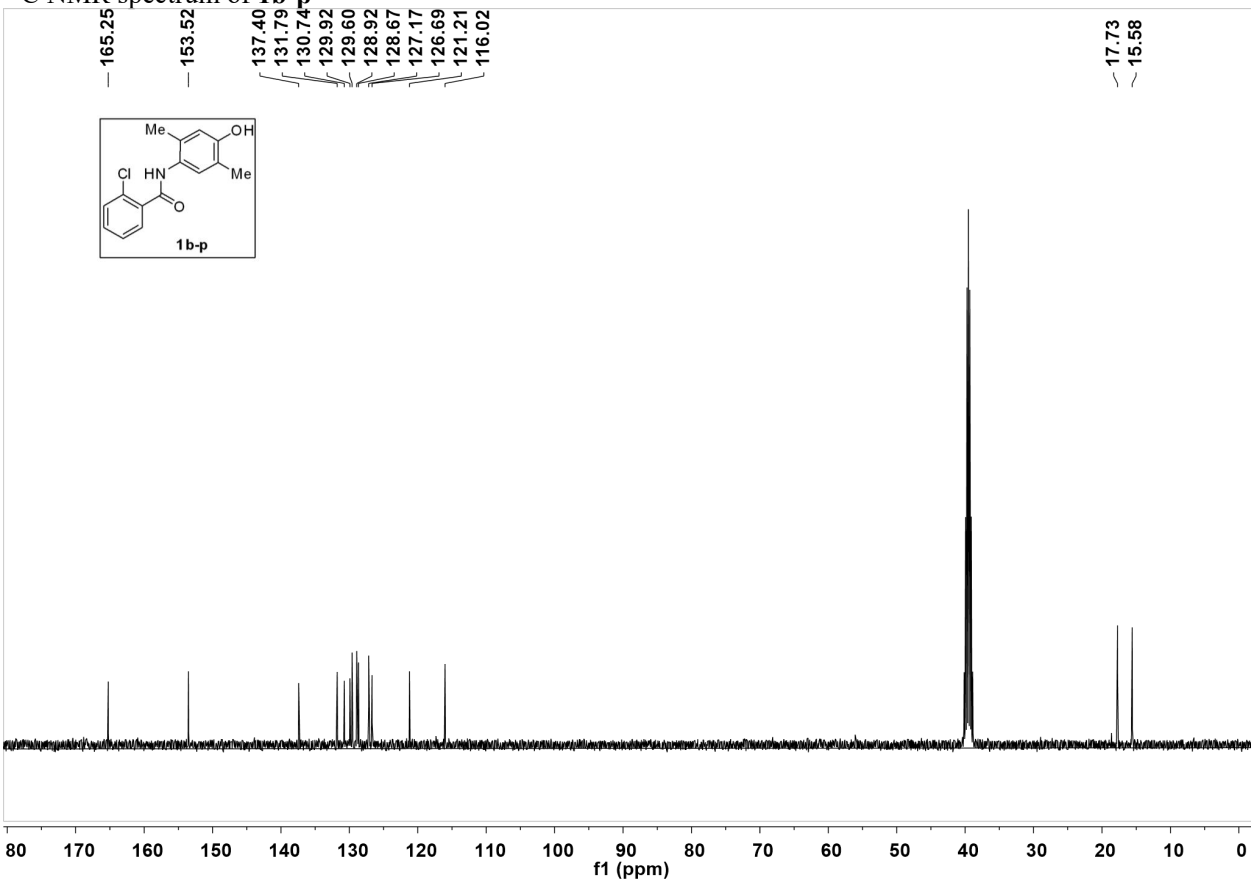
^{13}C NMR spectrum of **En**



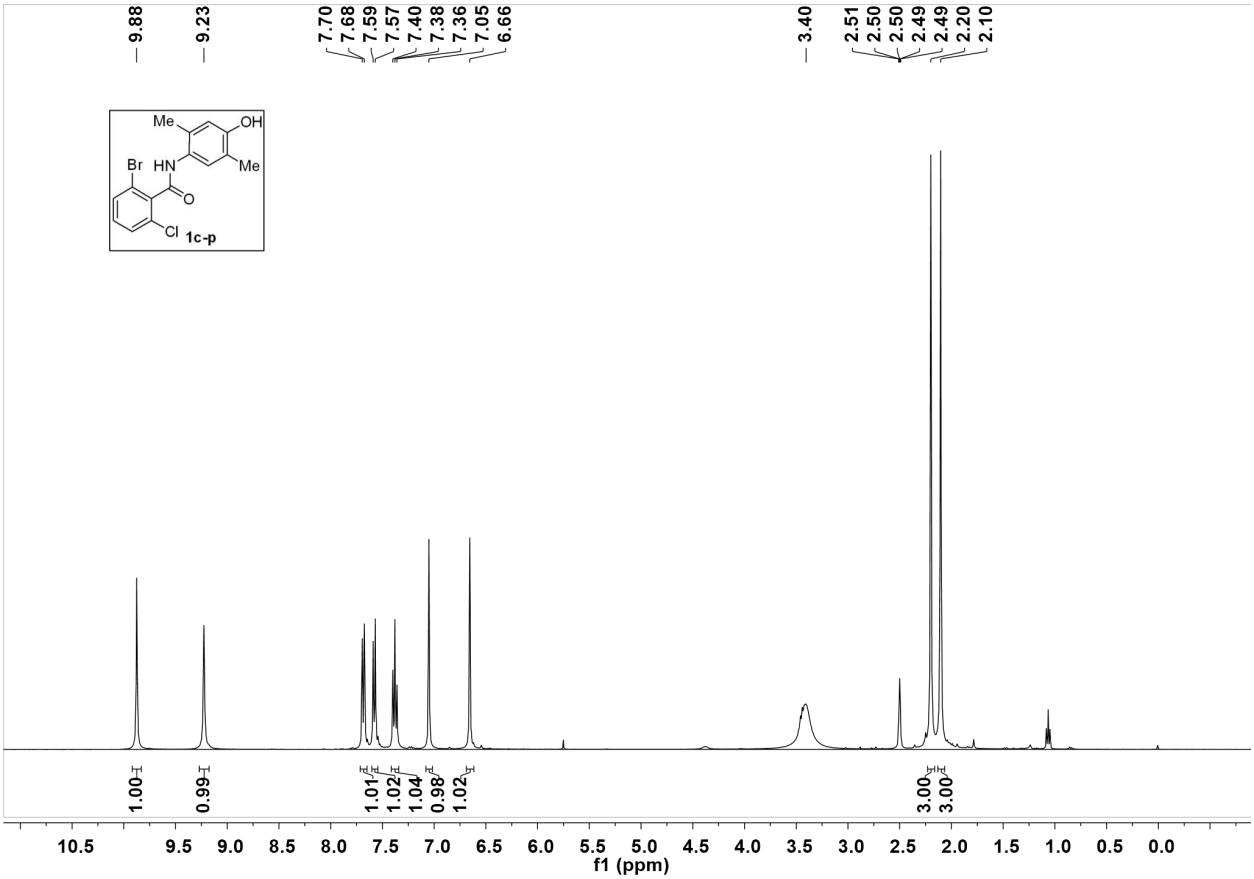
^{1}H NMR spectrum of **1b-p**



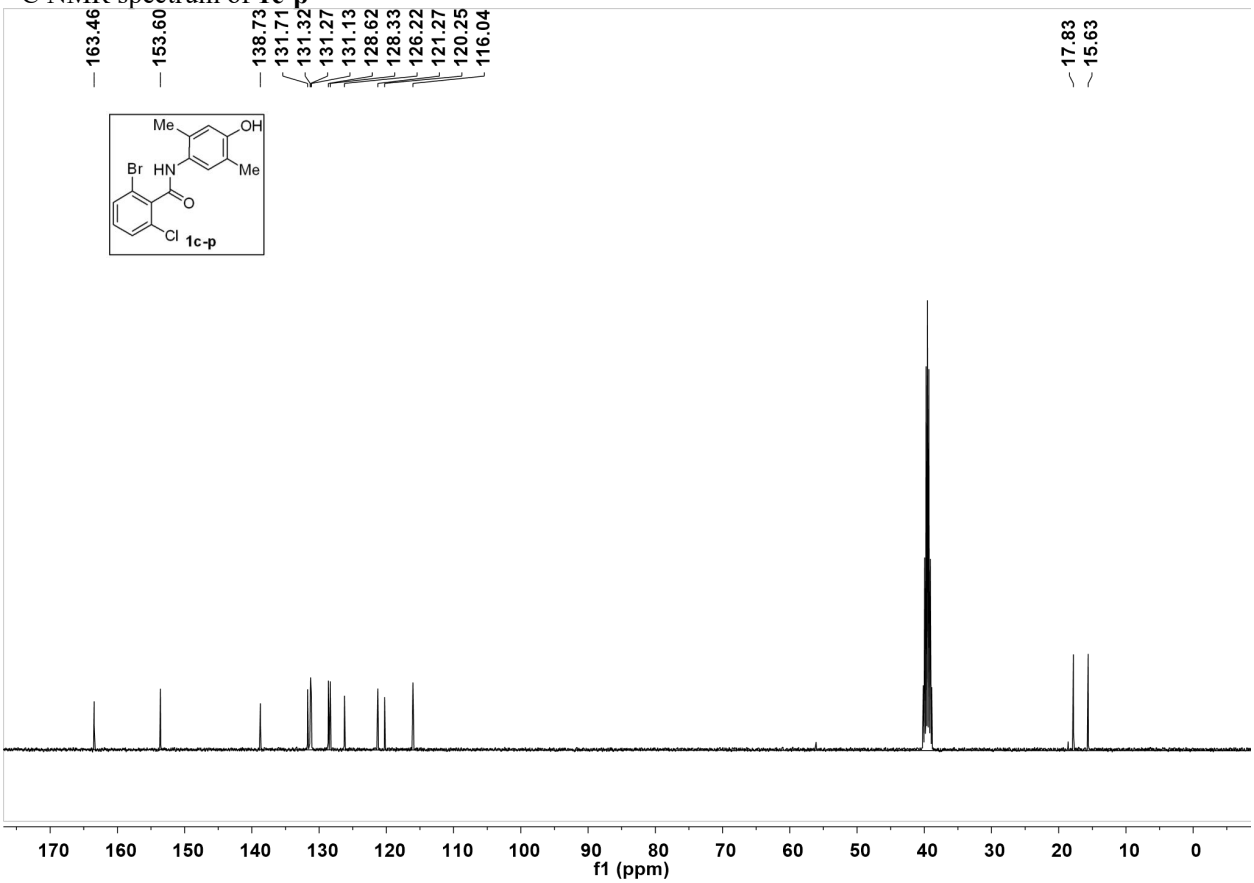
^{13}C NMR spectrum of **1b-p**



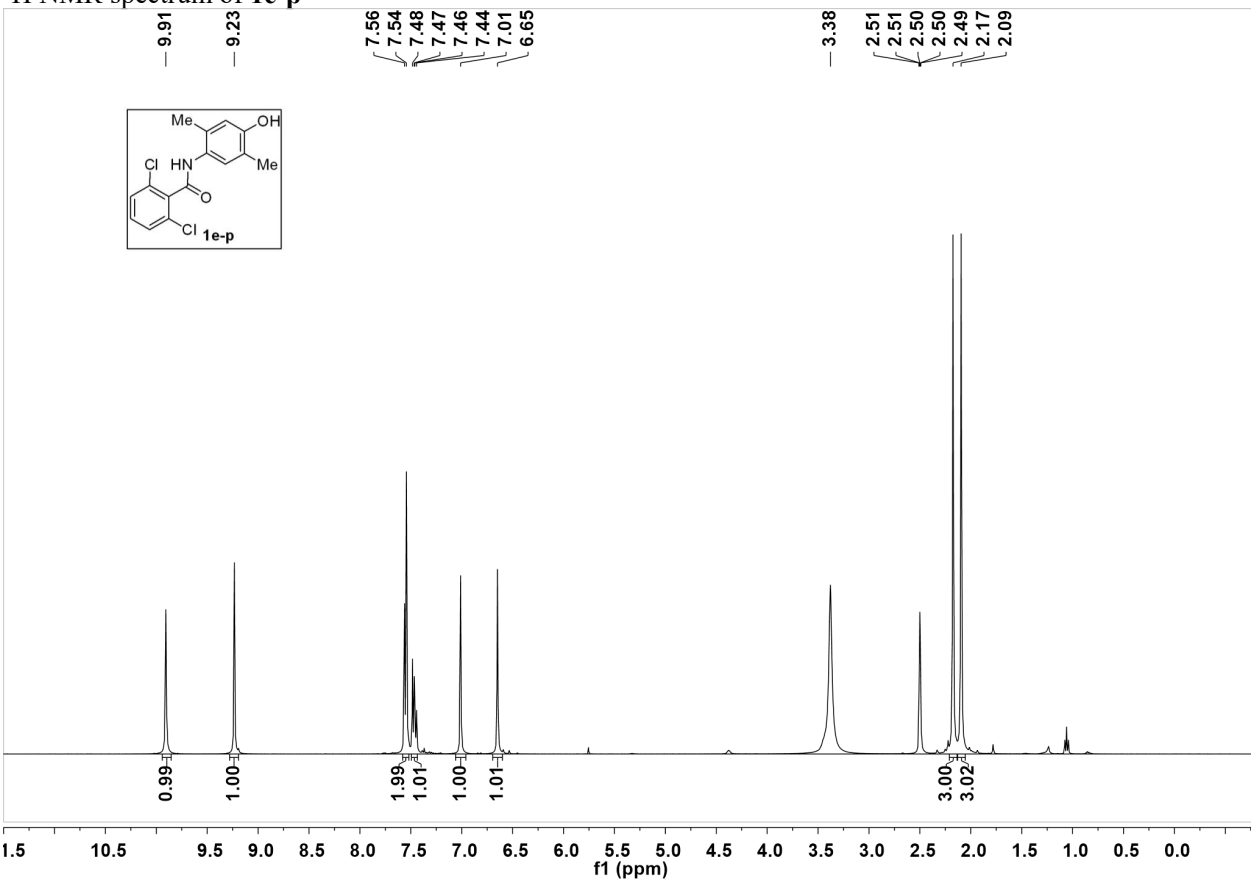
^{1}H NMR spectrum of **1c-p**



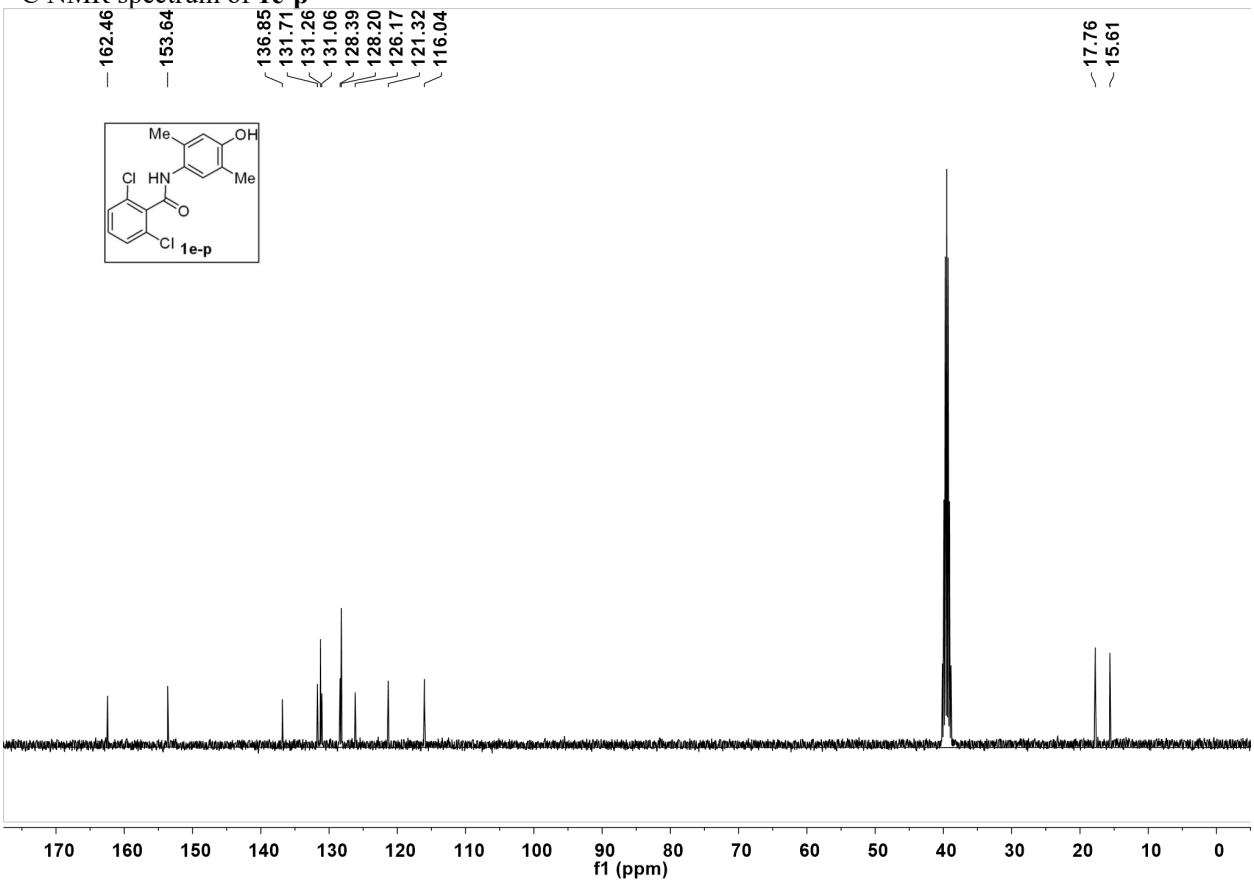
^{13}C NMR spectrum of **1c-p**



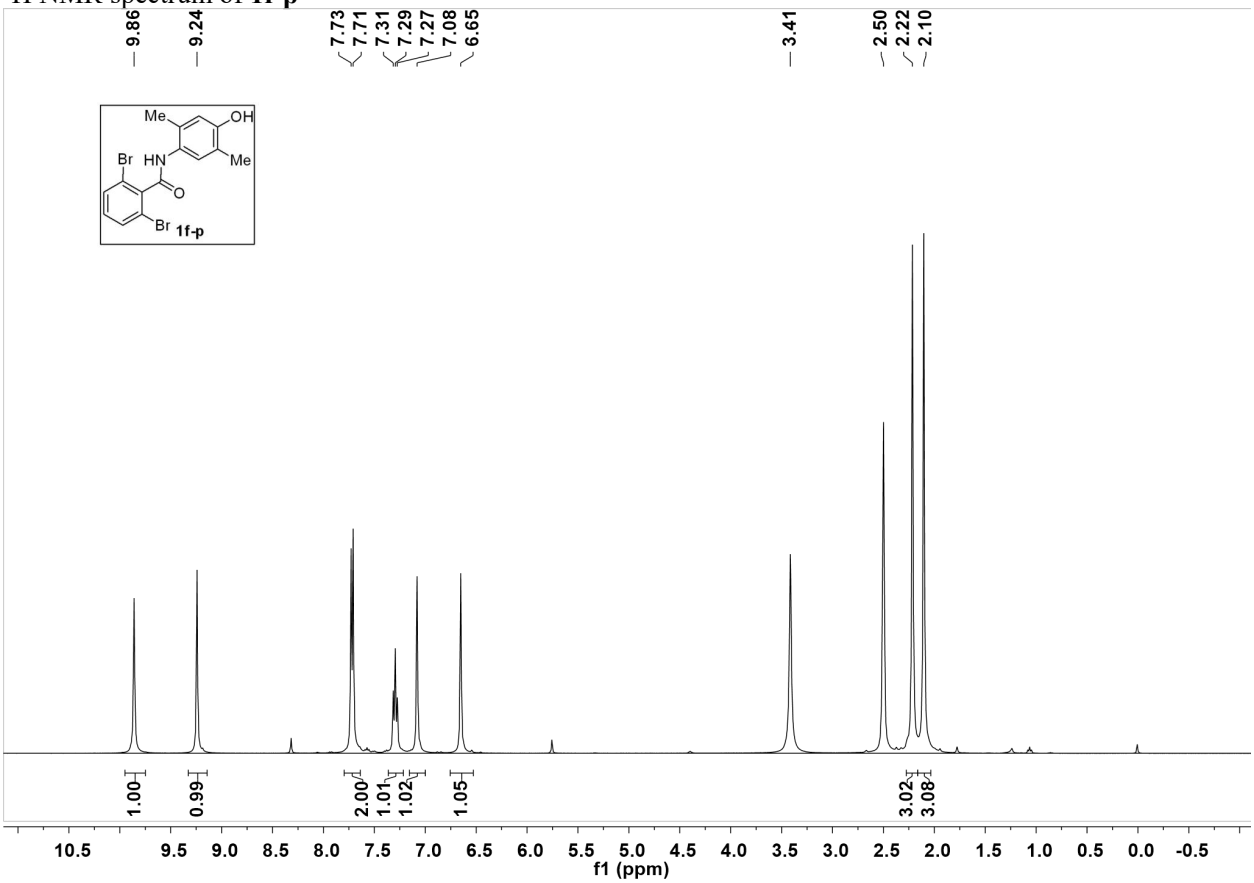
[1]H NMR spectrum of **1e-p**



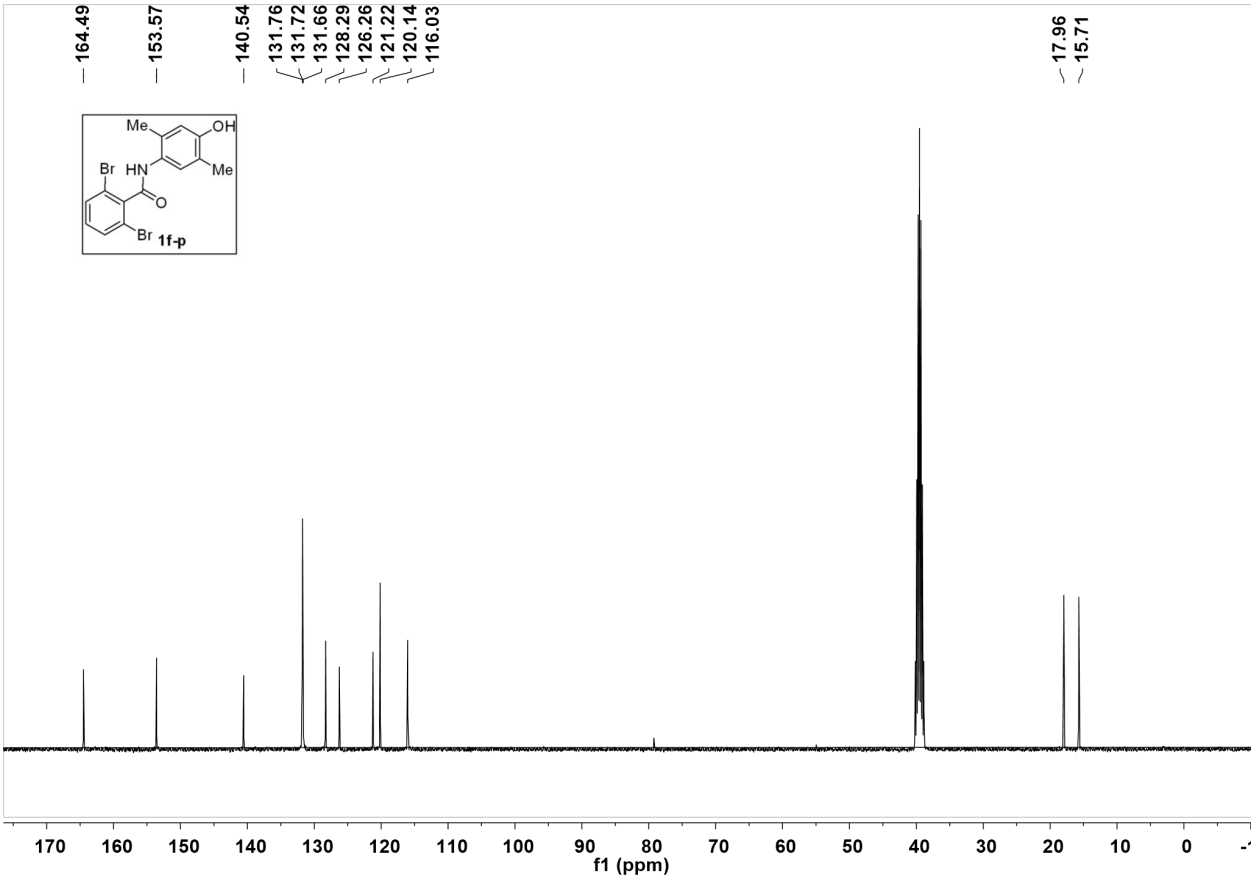
[13]C NMR spectrum of **1e-p**



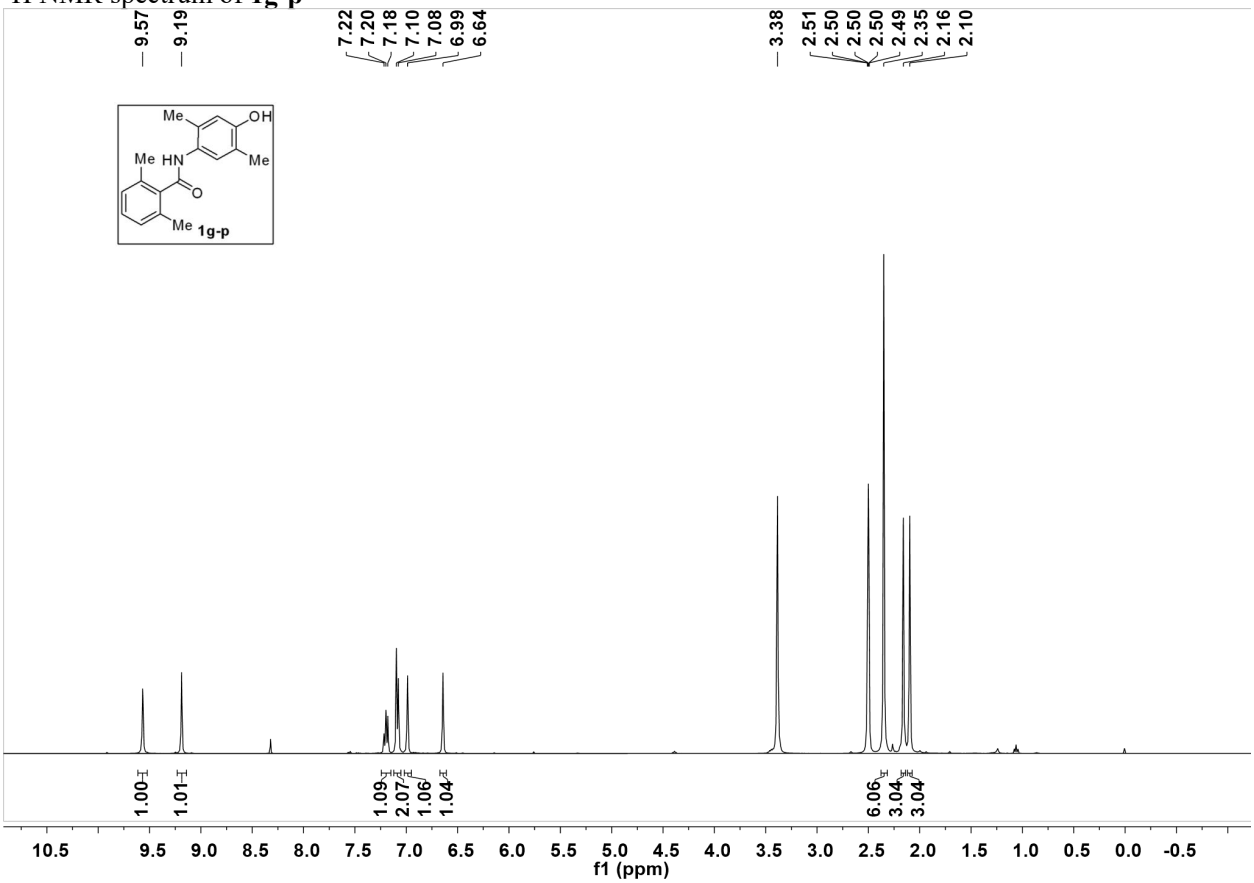
^{1}H NMR spectrum of **1f-p**



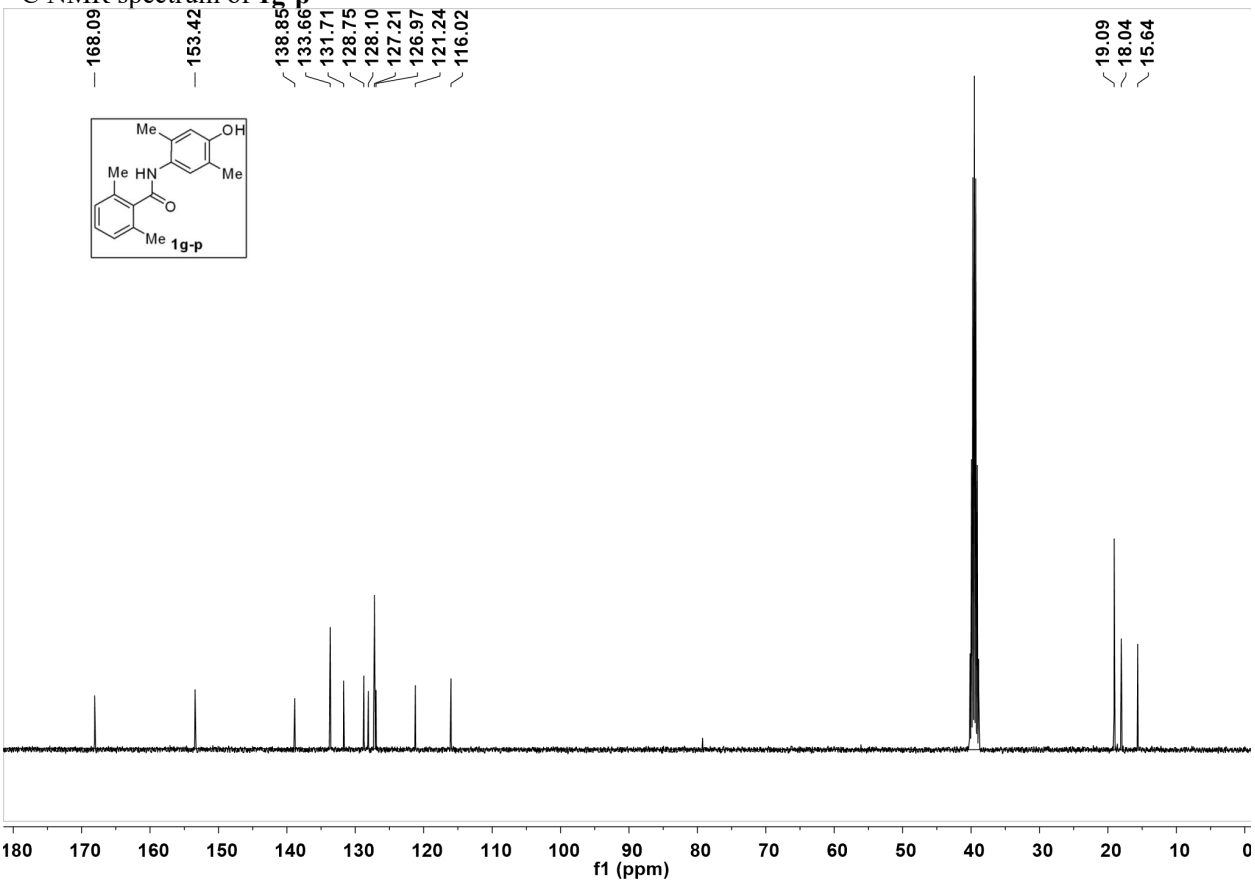
^{13}C NMR spectrum of **1f-p**



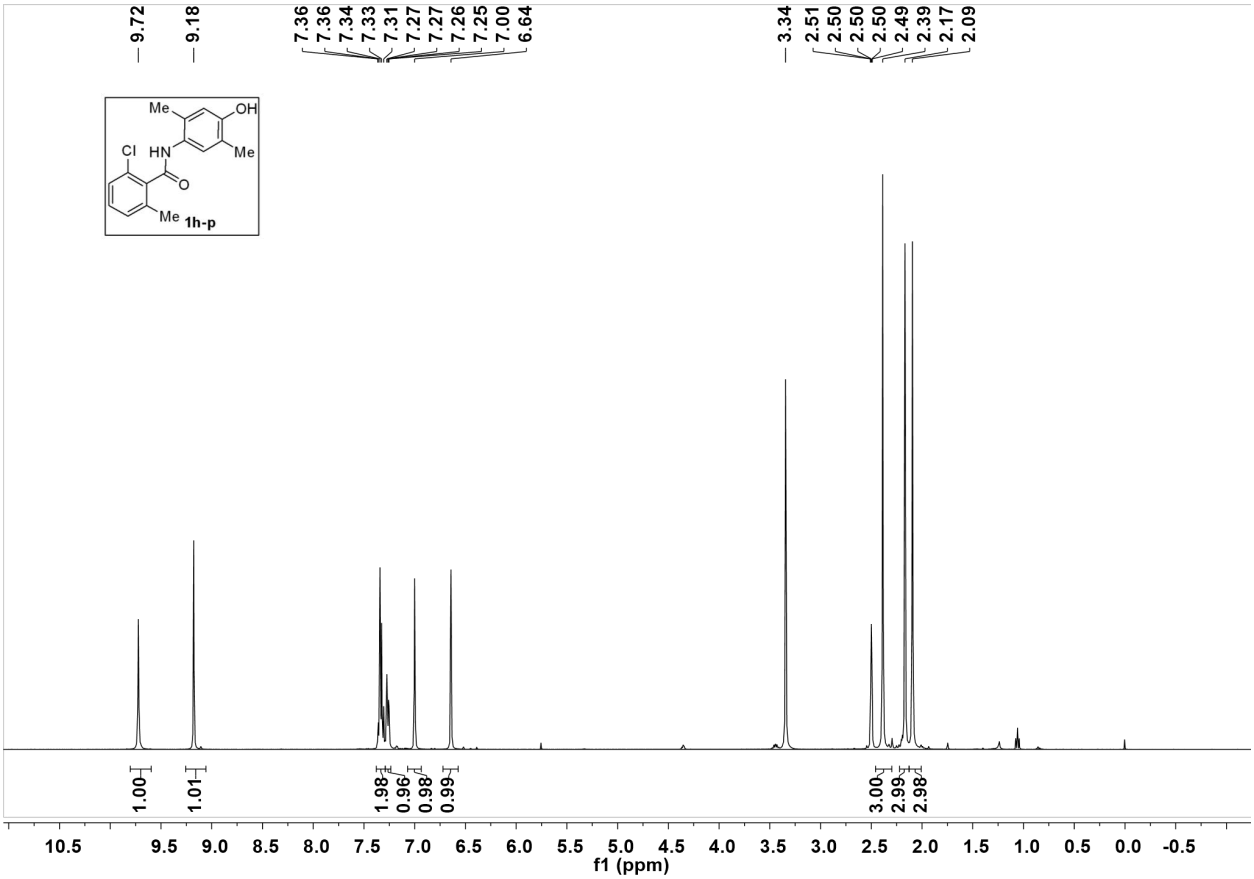
^{1}H NMR spectrum of **1g-p**



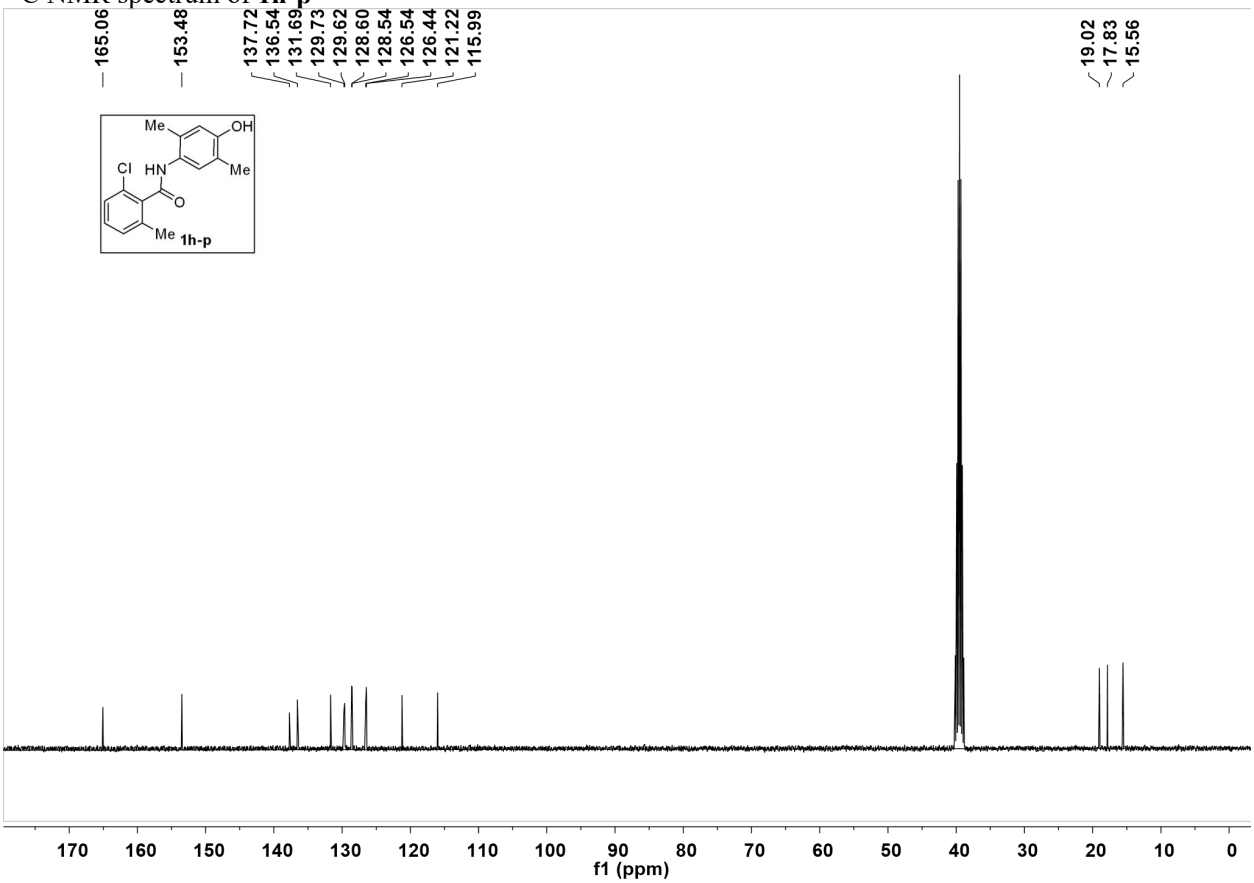
^{13}C NMR spectrum of **1g-p**



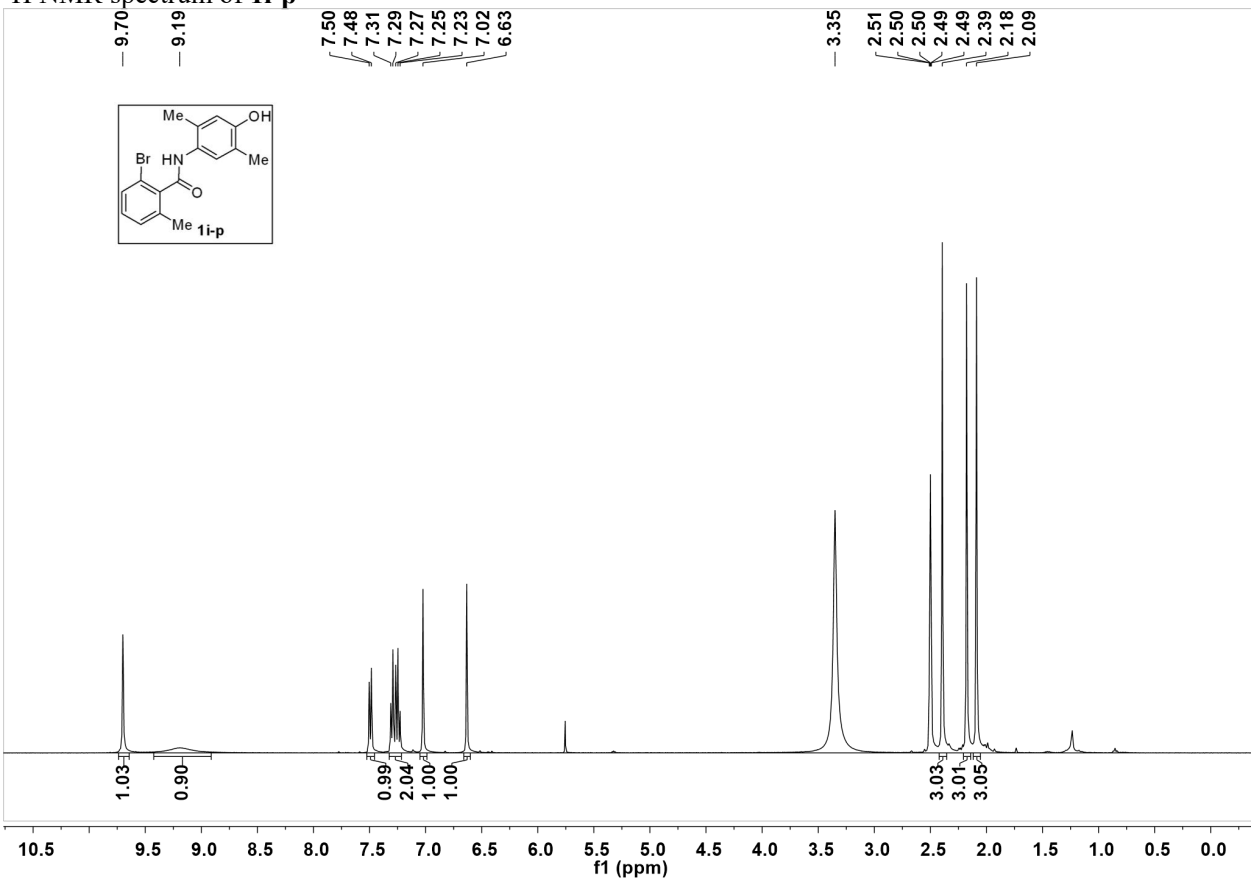
^{1}H NMR spectrum of **1h-p**



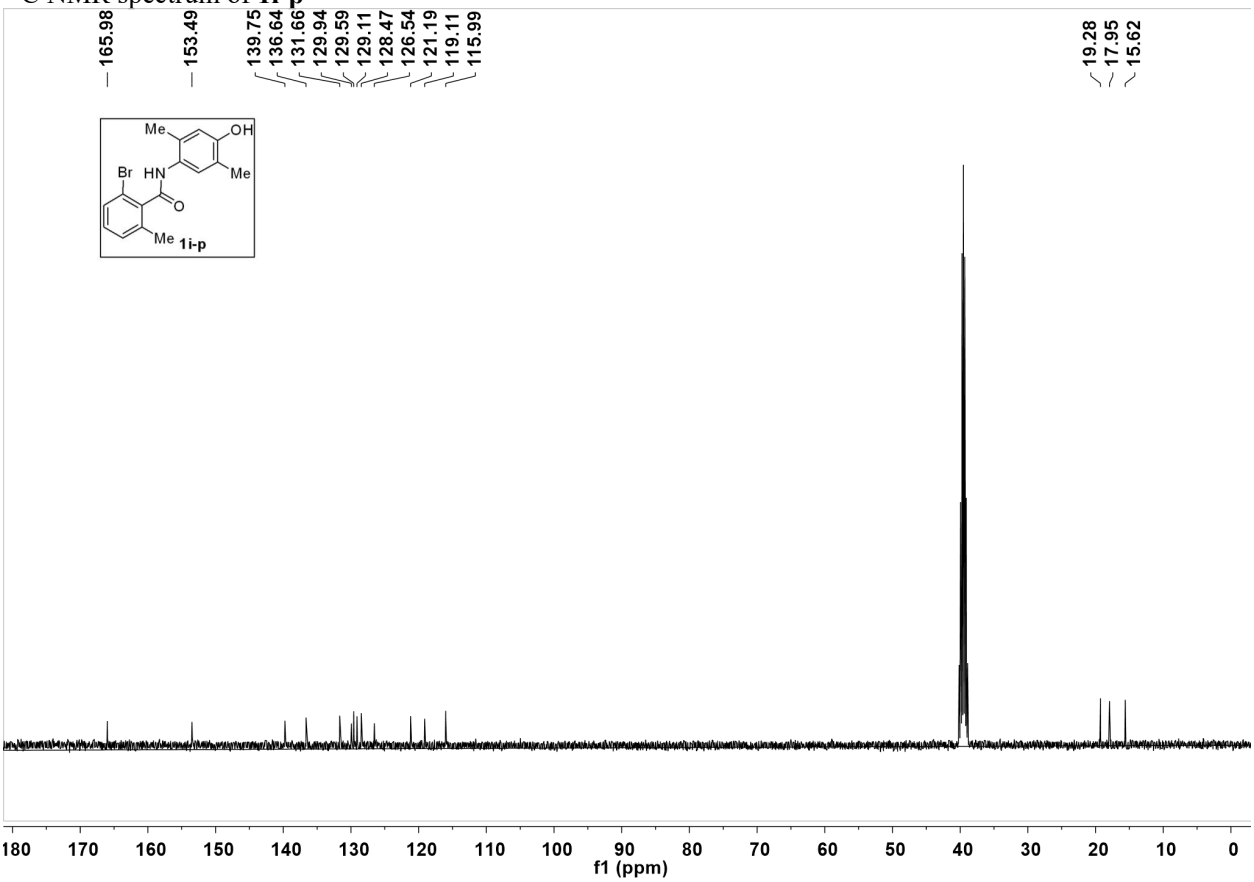
^{13}C NMR spectrum of **1h-p**



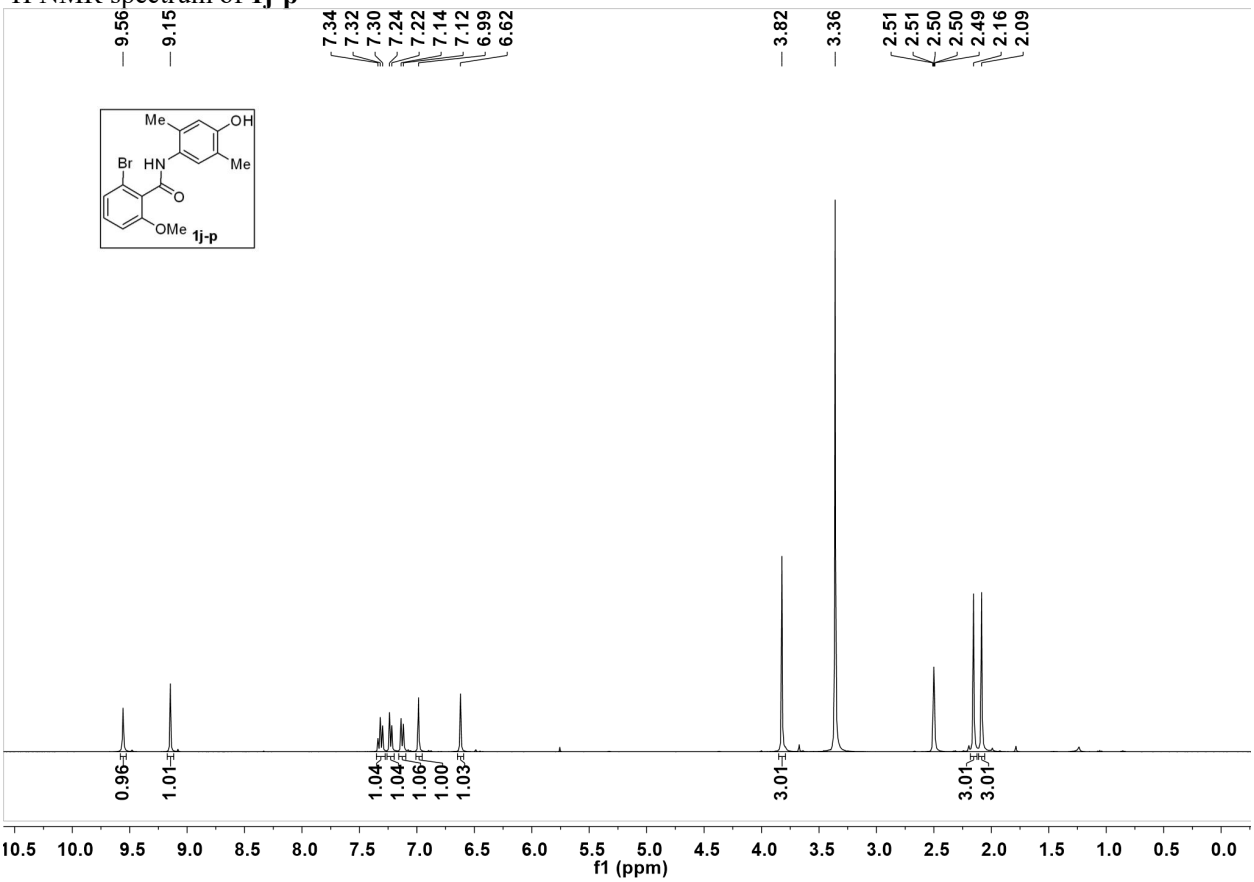
^{1}H NMR spectrum of **1i-p**



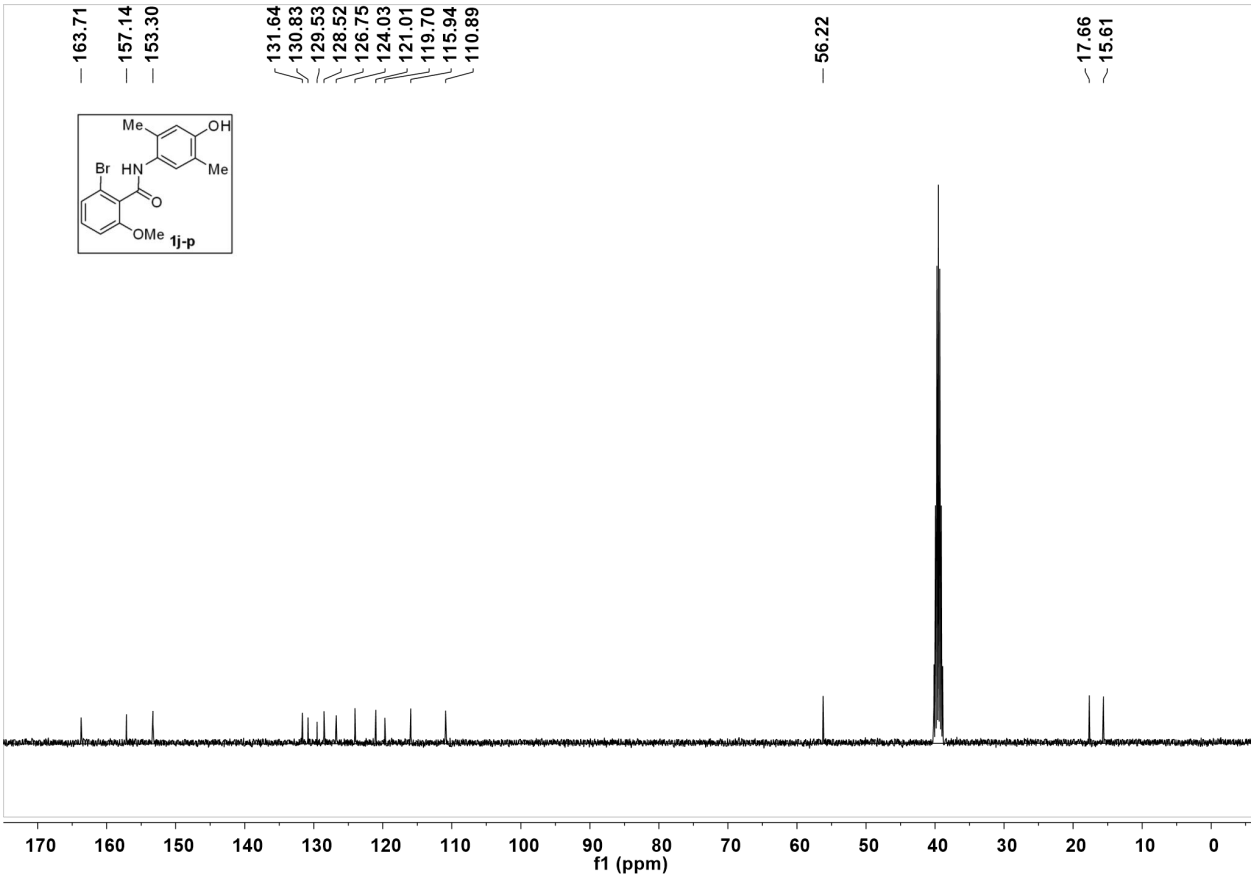
^{13}C NMR spectrum of **1i-p**



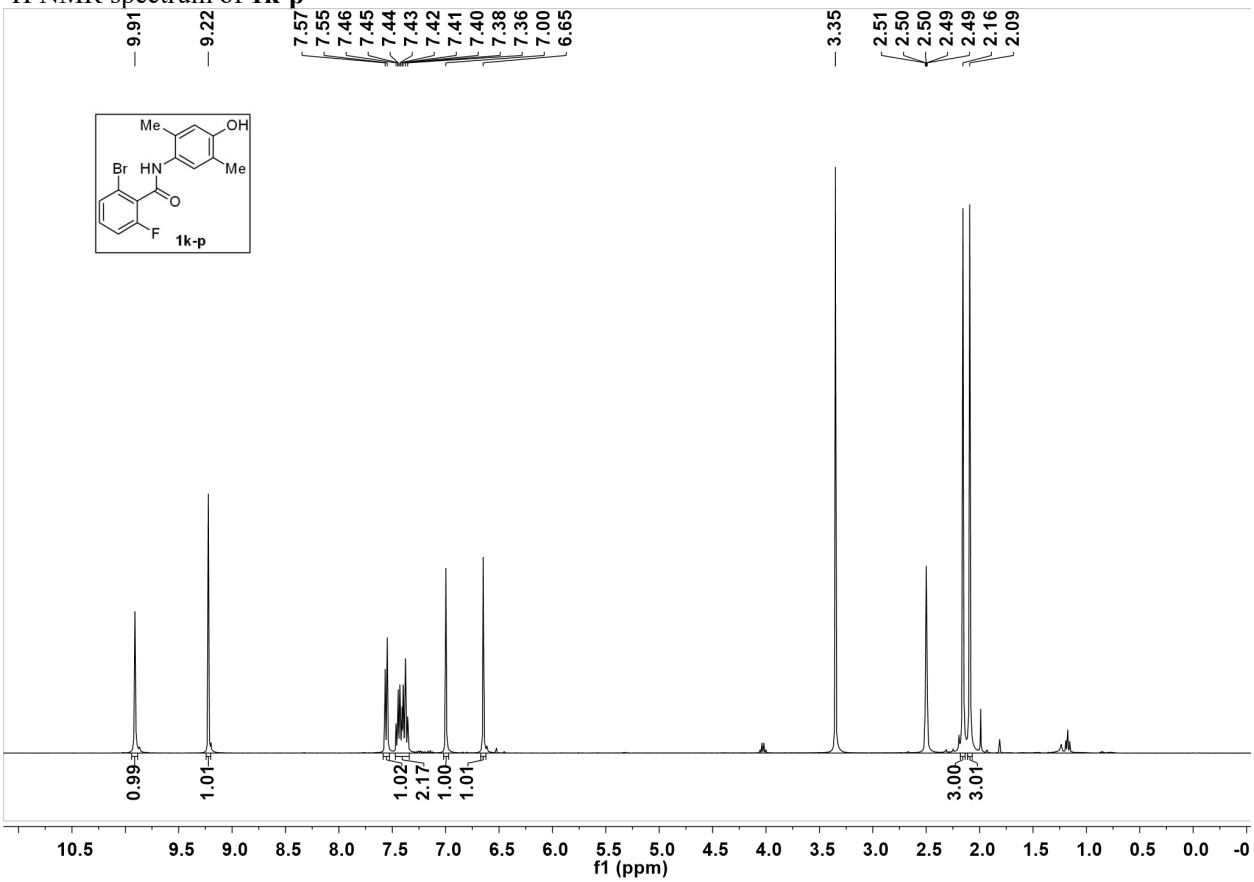
^{1}H NMR spectrum of **1j-p**



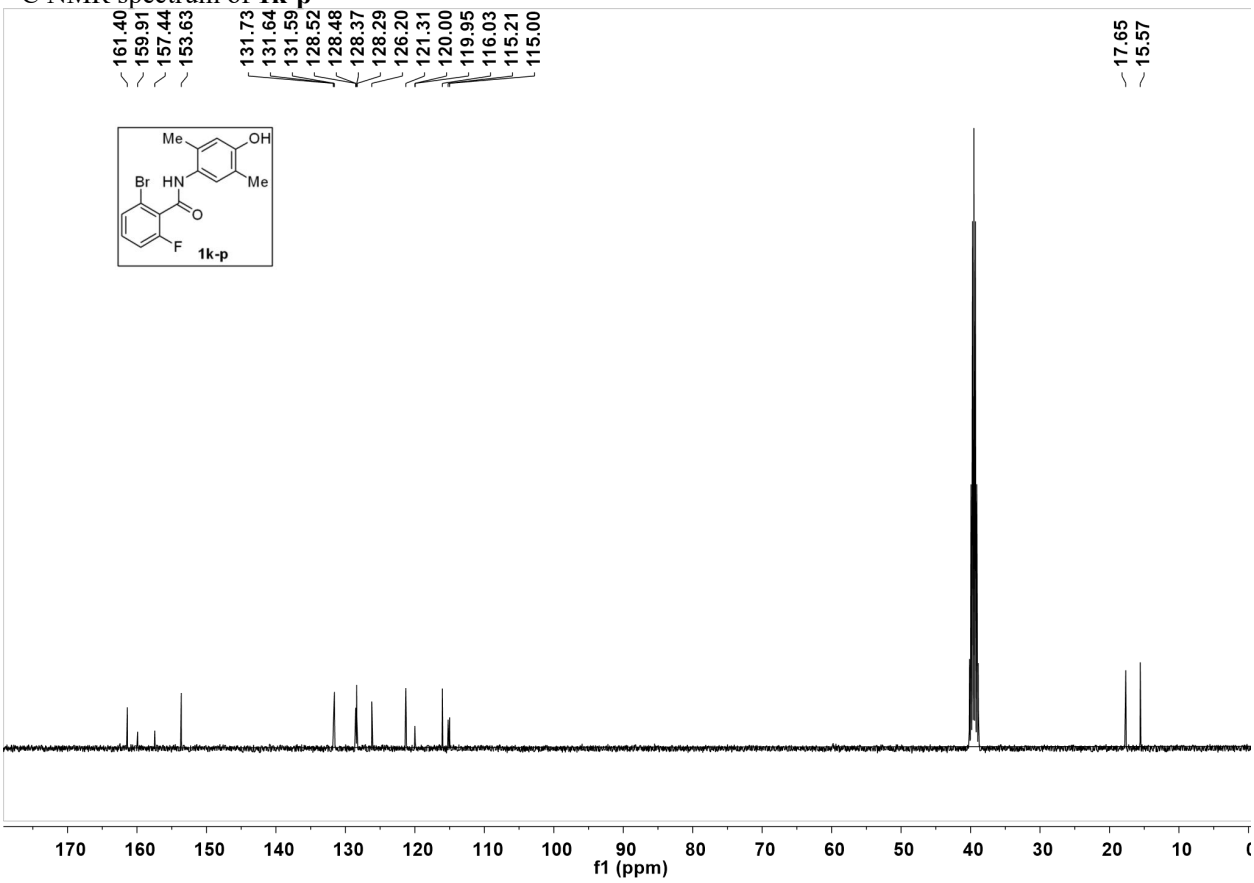
^{13}C NMR spectrum of **1j-p**



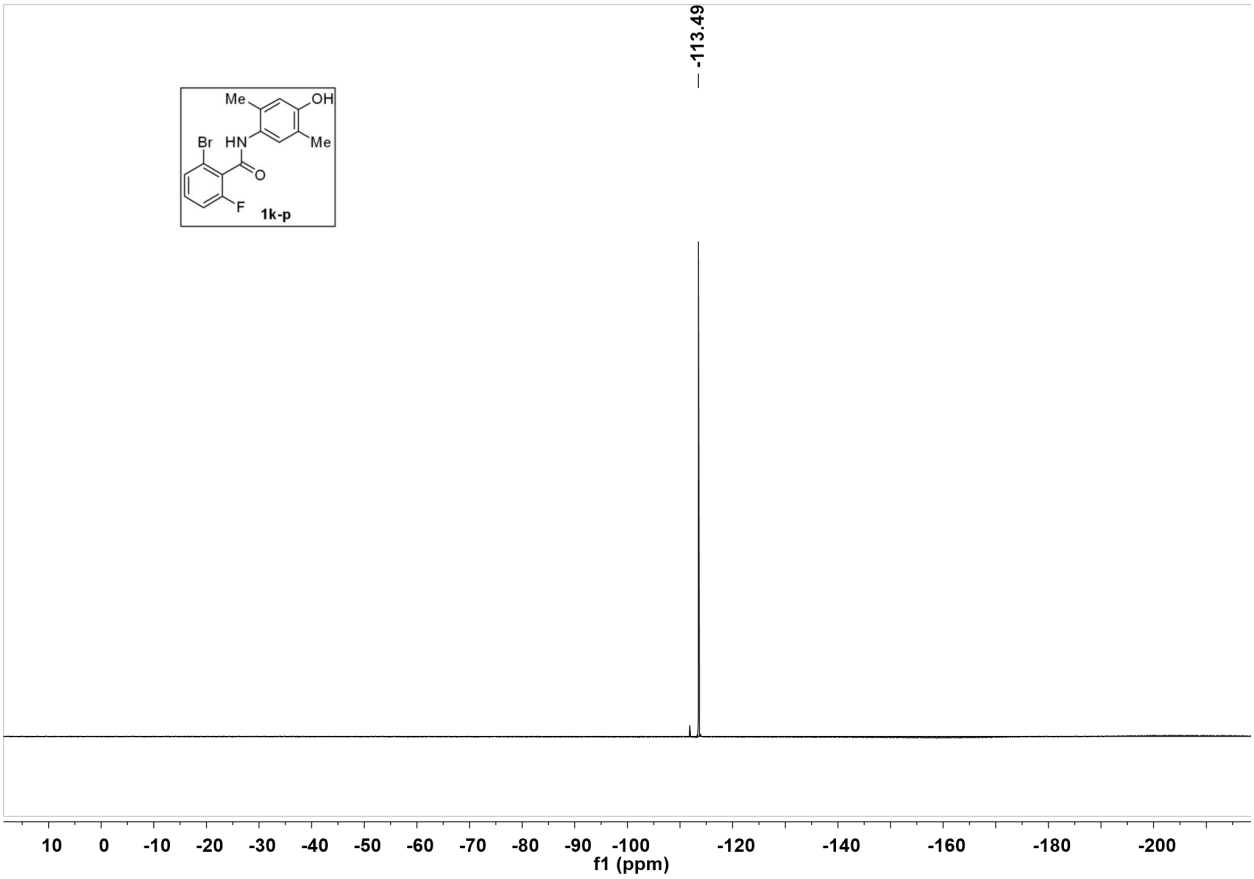
^{1}H NMR spectrum of **1k-p**



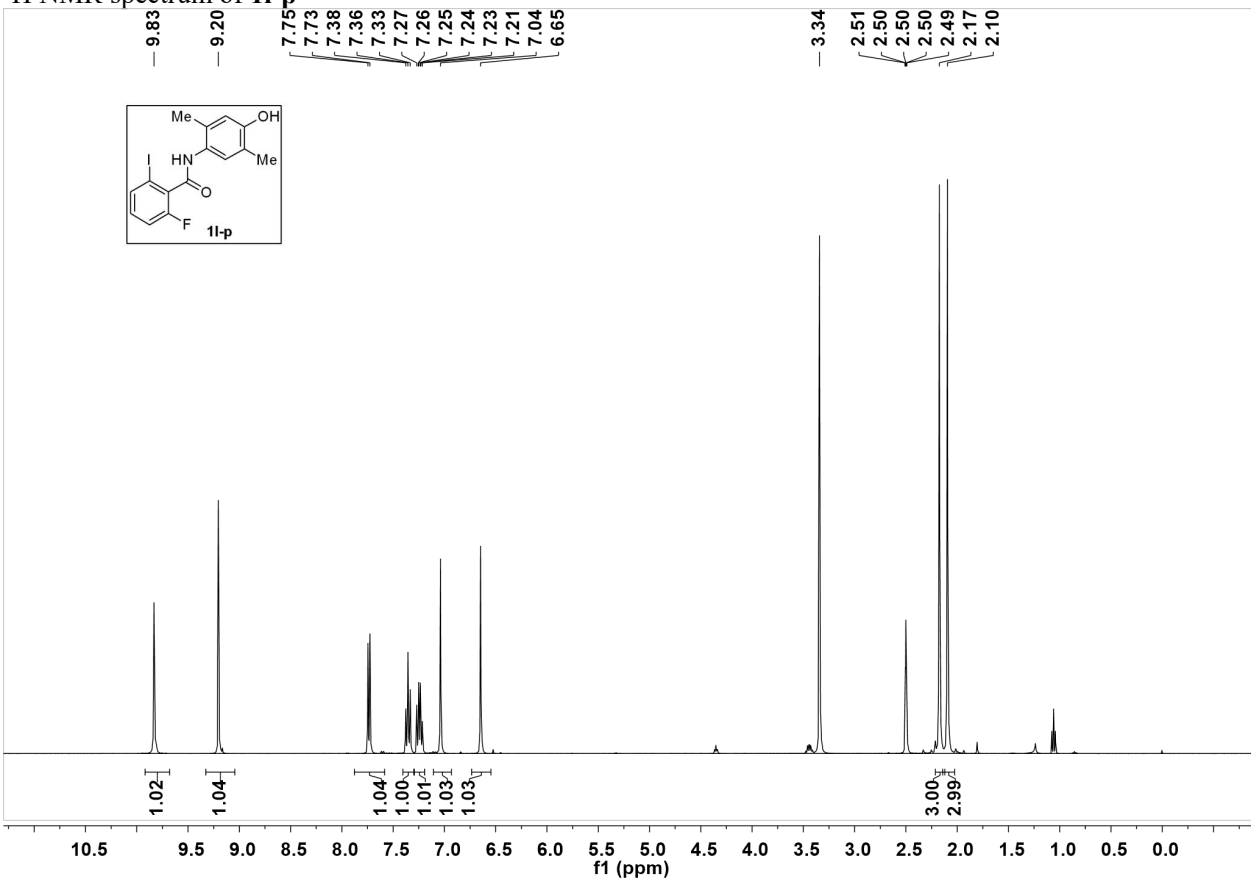
^{13}C NMR spectrum of **1k-p**



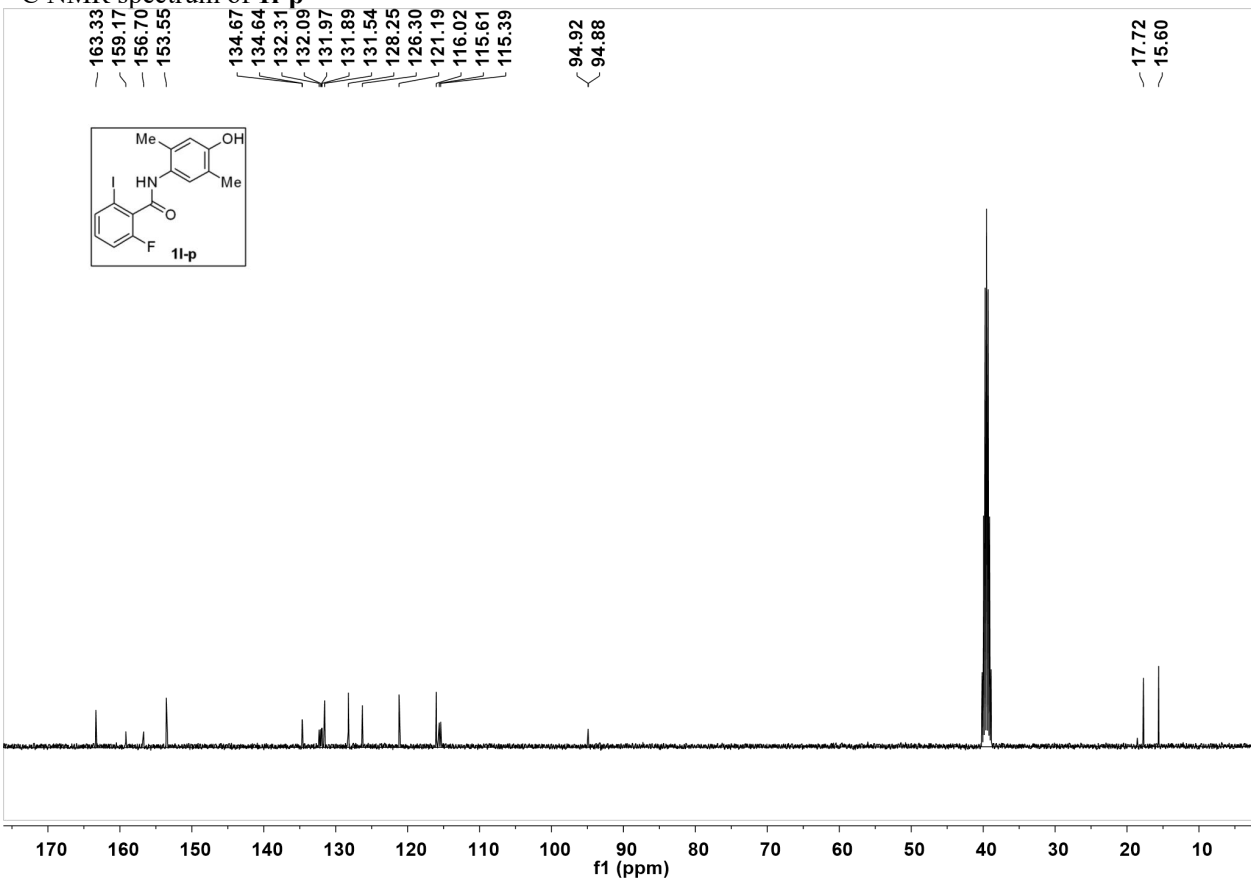
^{19}F NMR spectrum of **1k-p**


-113.49
Me
OH
Br
HN
Me
O
F
1k-p
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

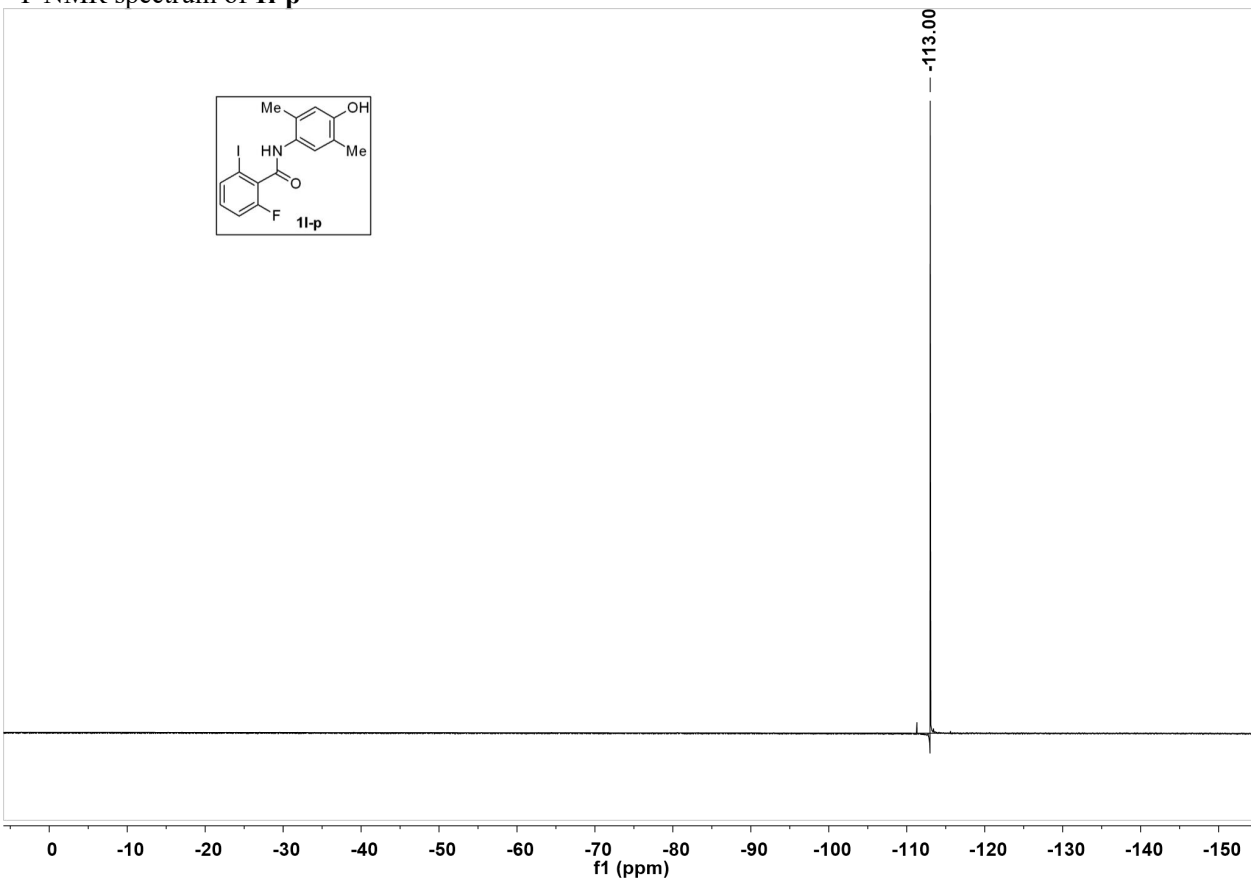
^{1}H NMR spectrum of **1l-p**



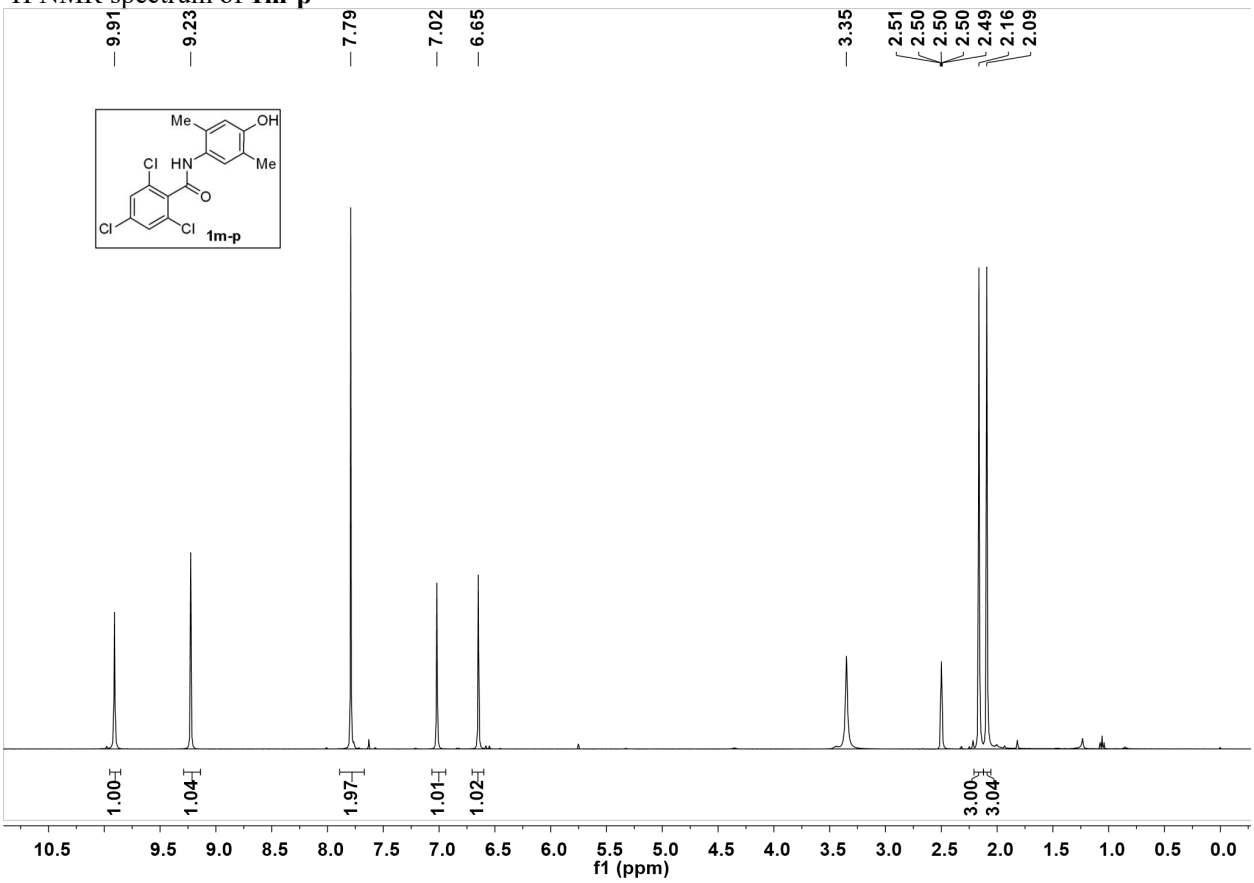
^{13}C NMR spectrum of **1l-p**



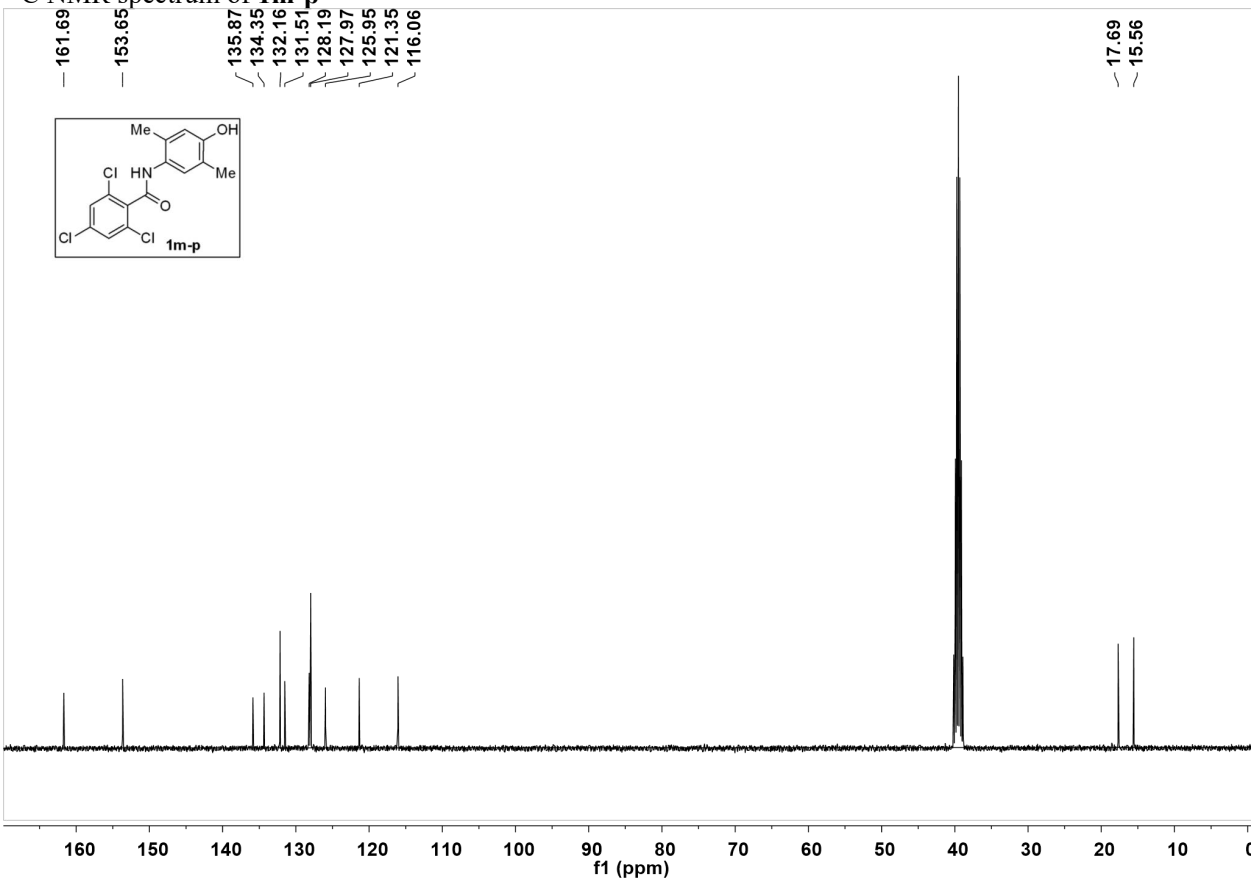
^{19}F NMR spectrum of **1l-p**



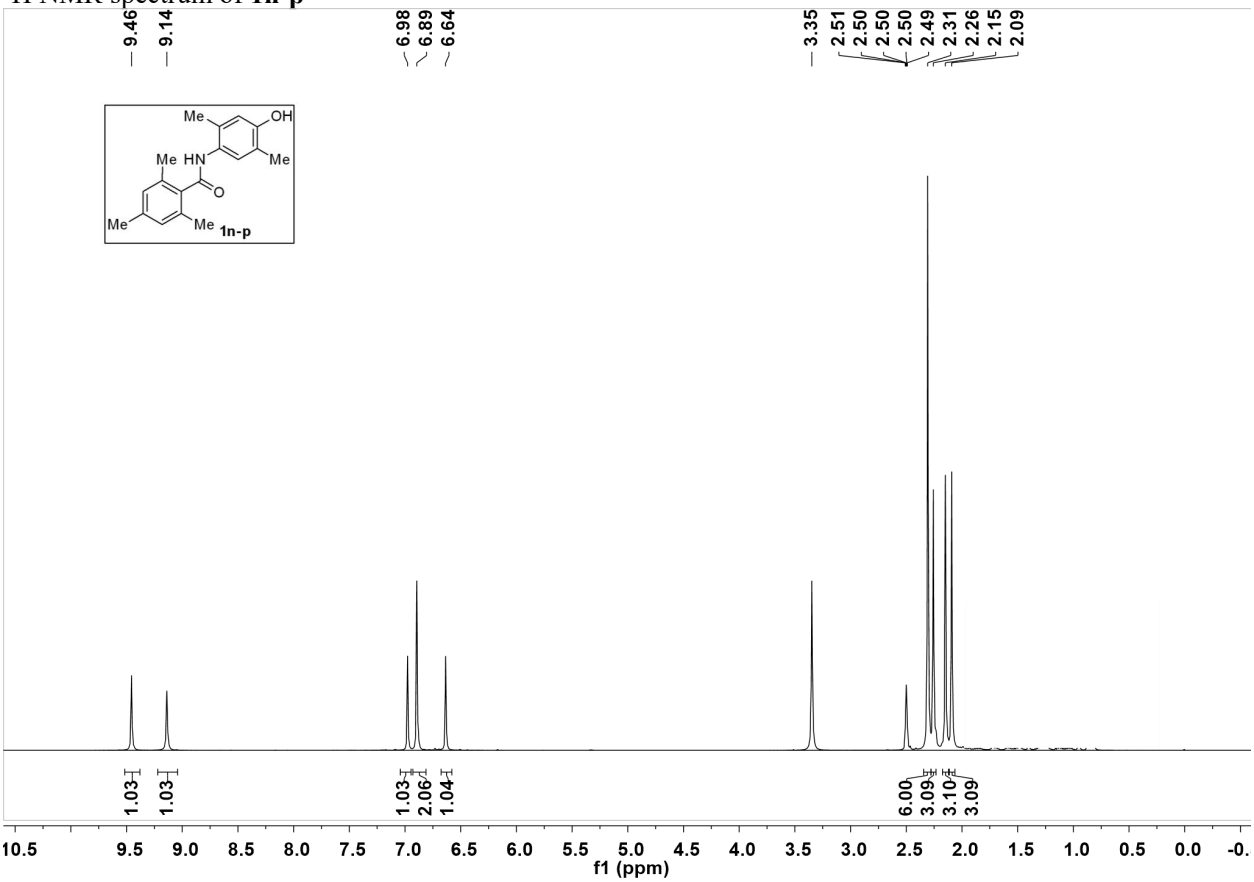
^{1}H NMR spectrum of **1m-p**



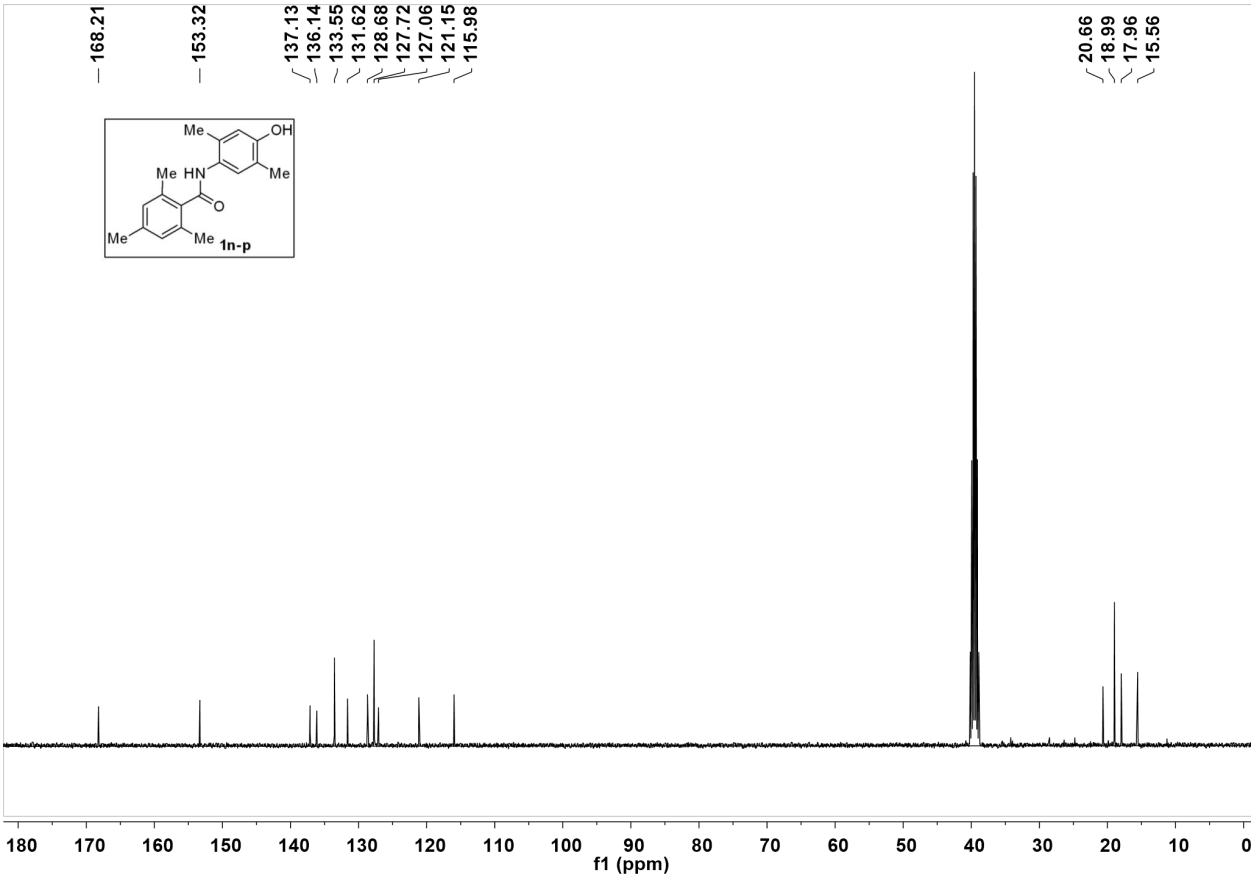
^{13}C NMR spectrum of **1m-p**



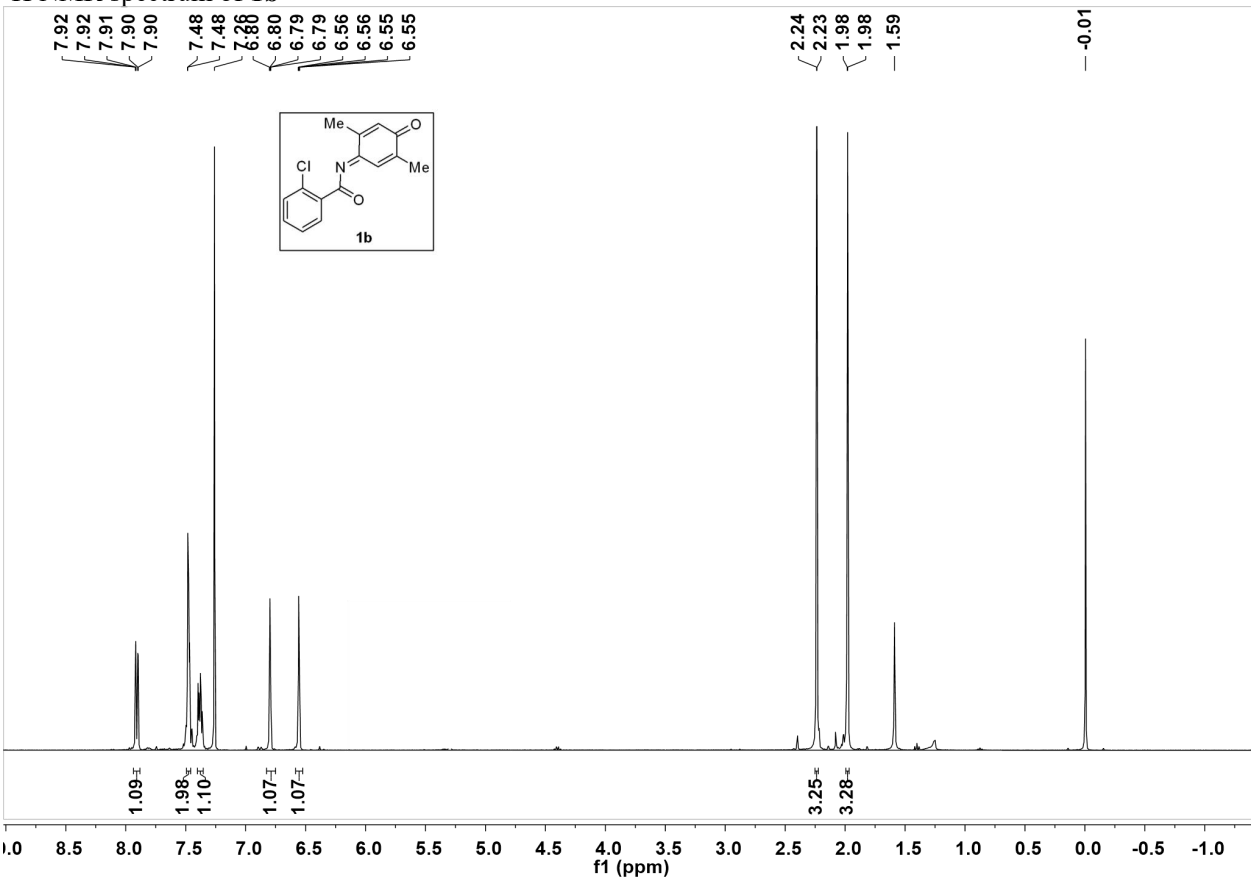
^{1}H NMR spectrum of **1n-p**



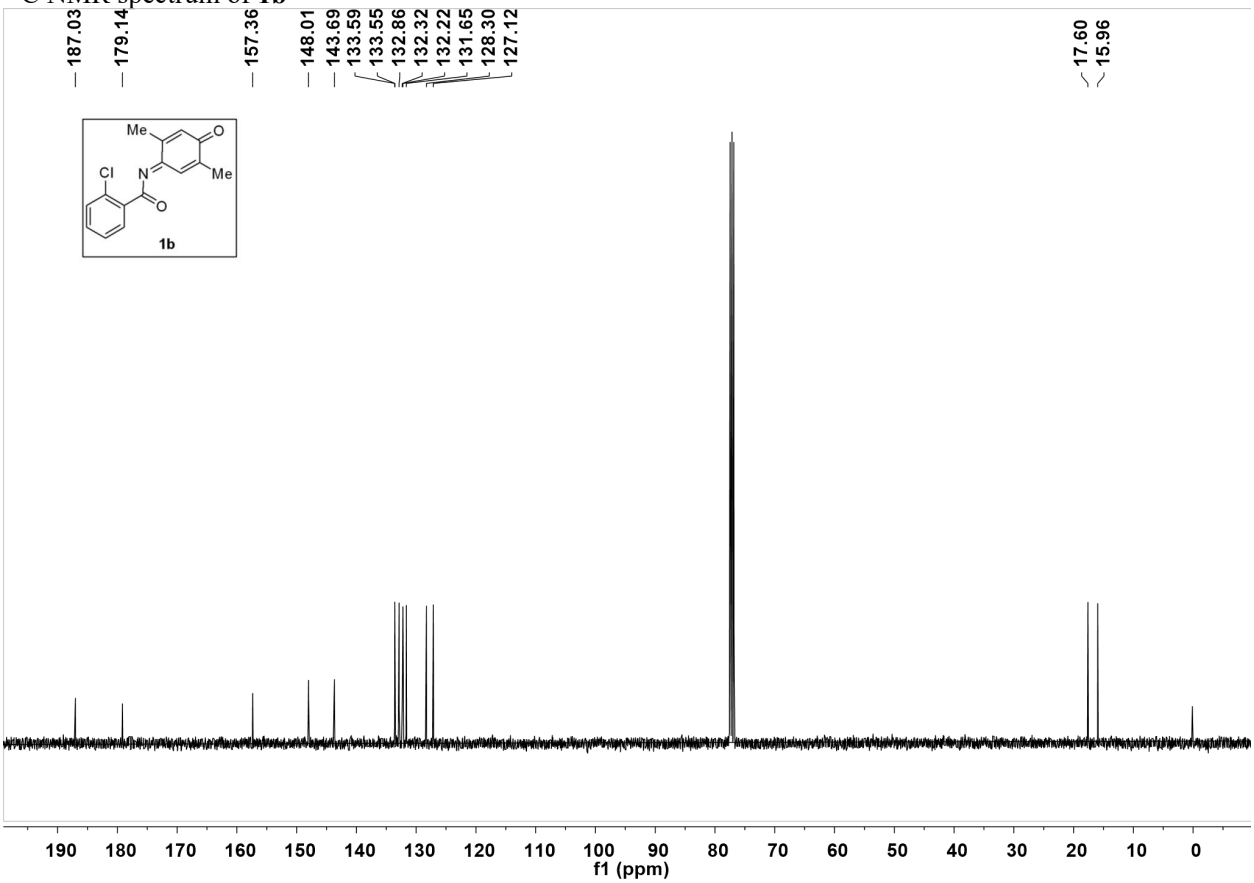
^{13}C NMR spectrum of **1n-p**



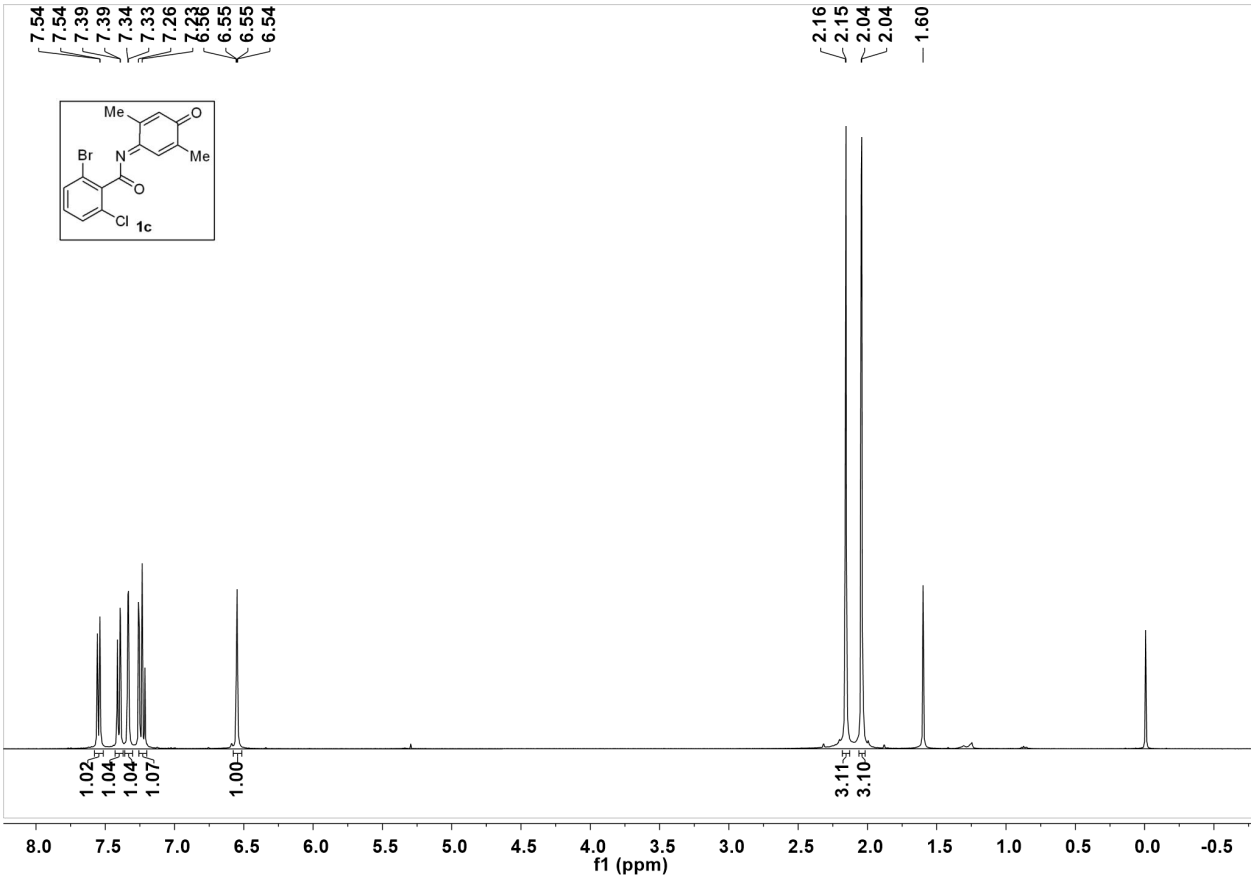
^{1}H NMR spectrum of **1b**



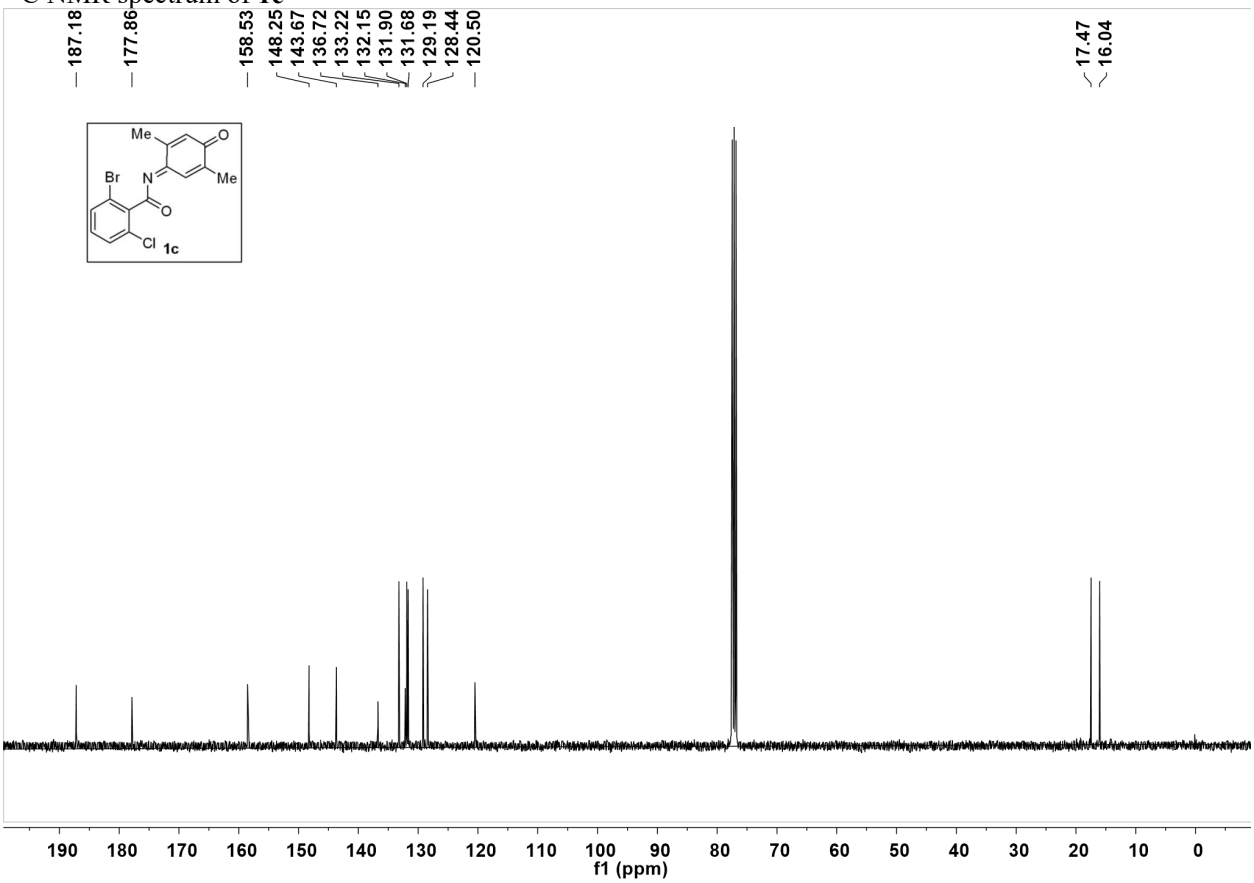
^{13}C NMR spectrum of **1b**



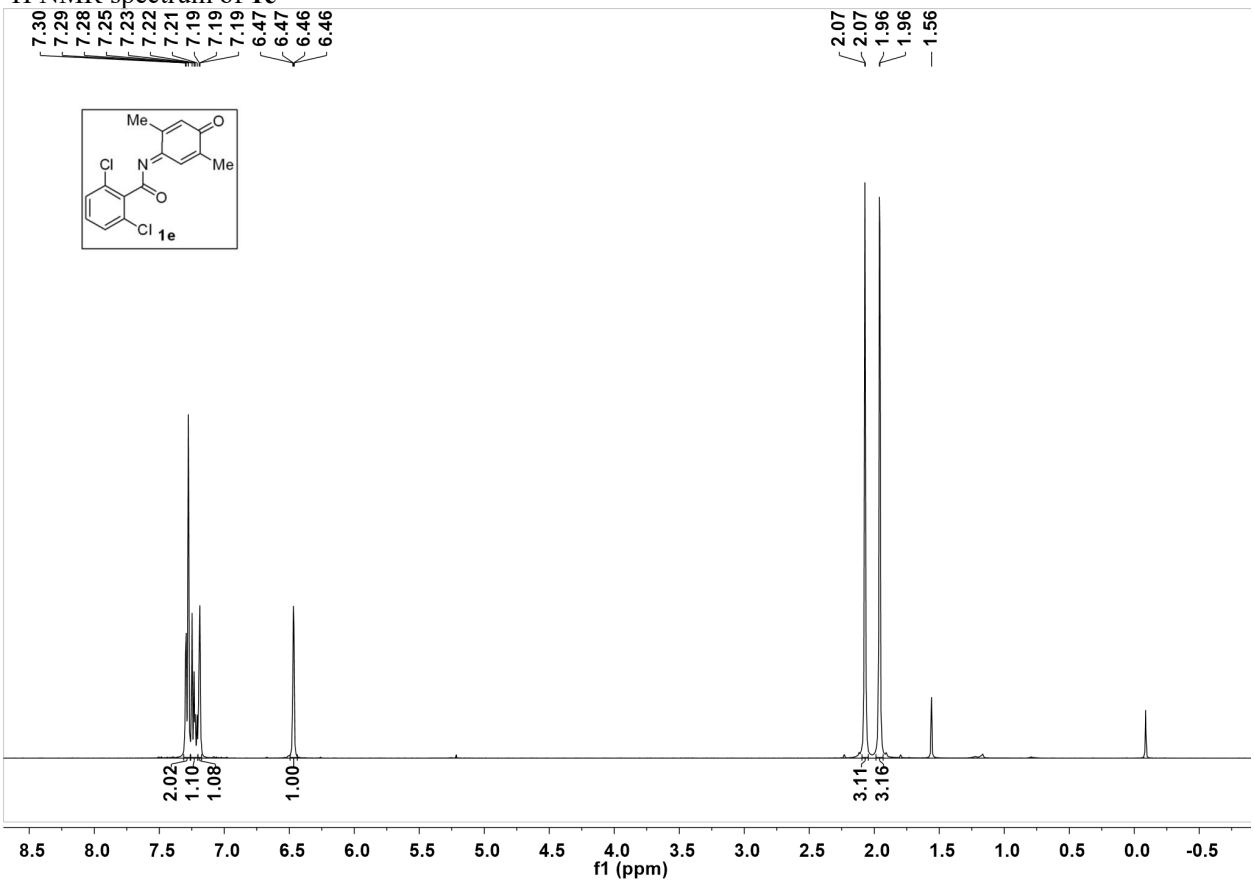
^{1}H NMR spectrum of **1c**



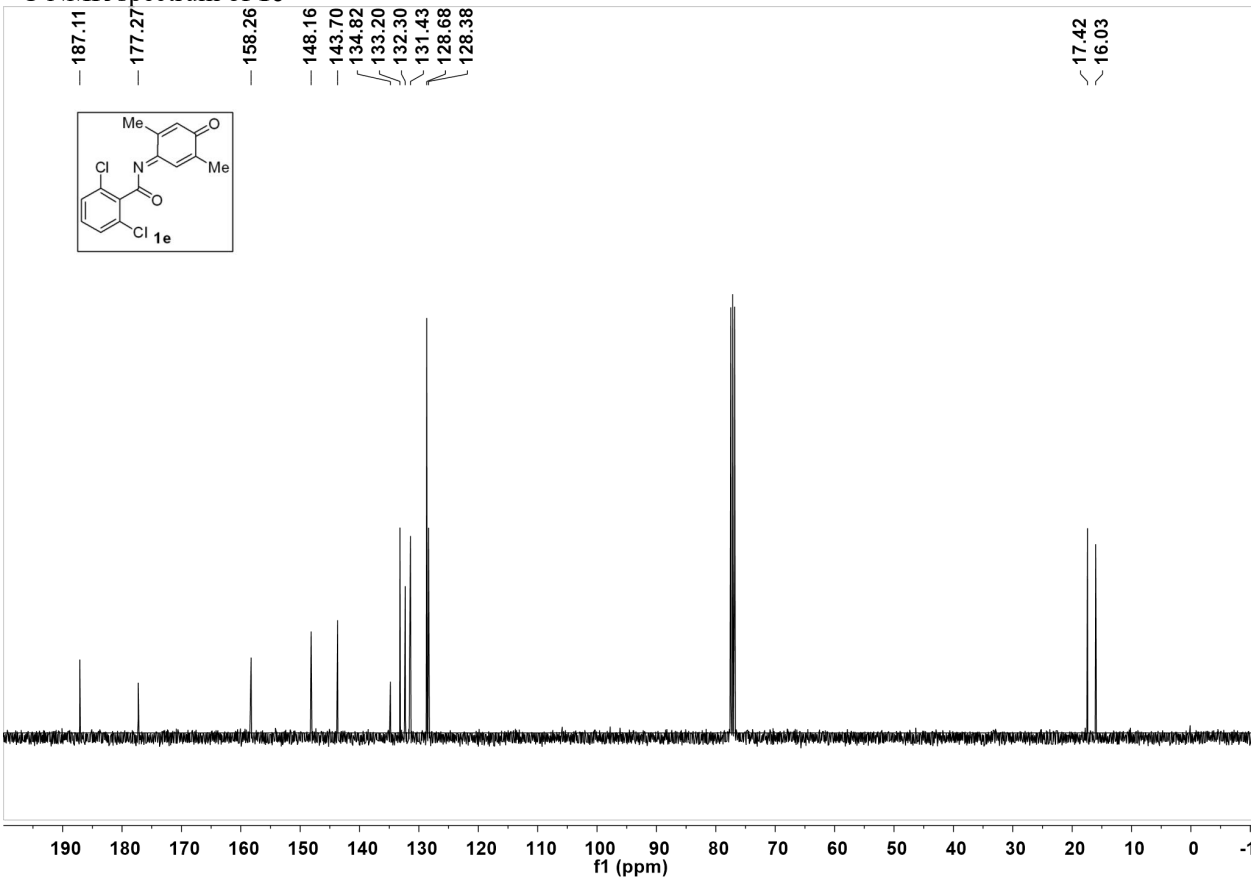
^{13}C NMR spectrum of **1c**



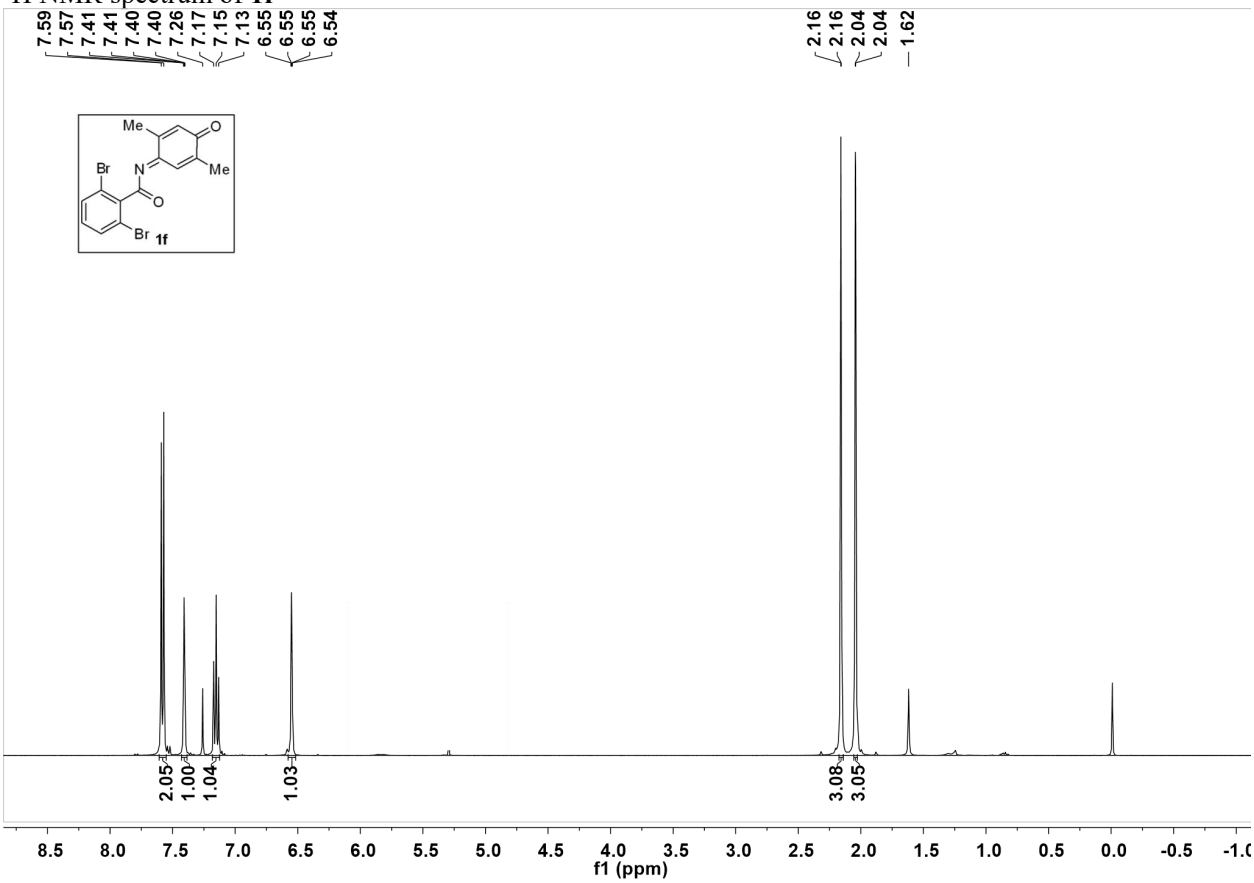
^{1}H NMR spectrum of **1e**



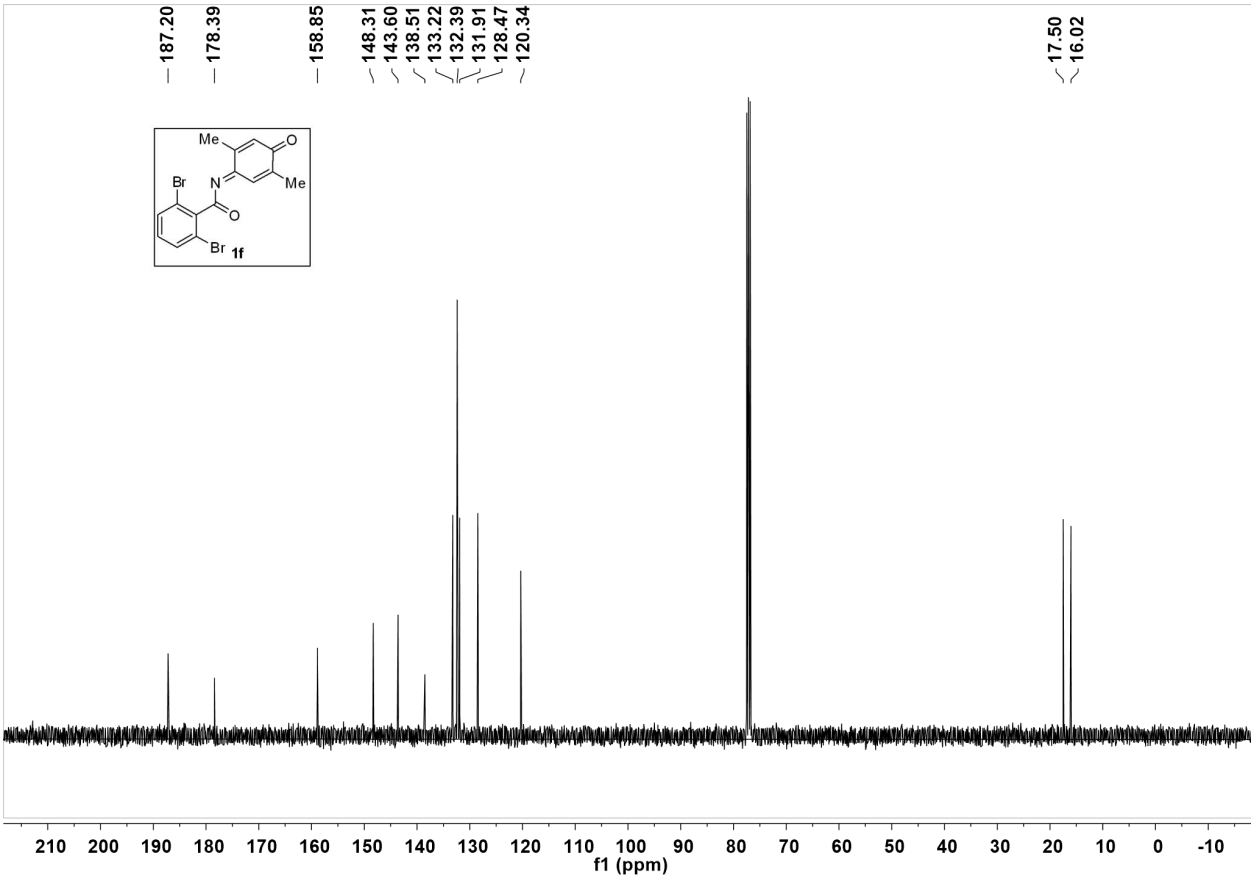
^{13}C NMR spectrum of **1e**



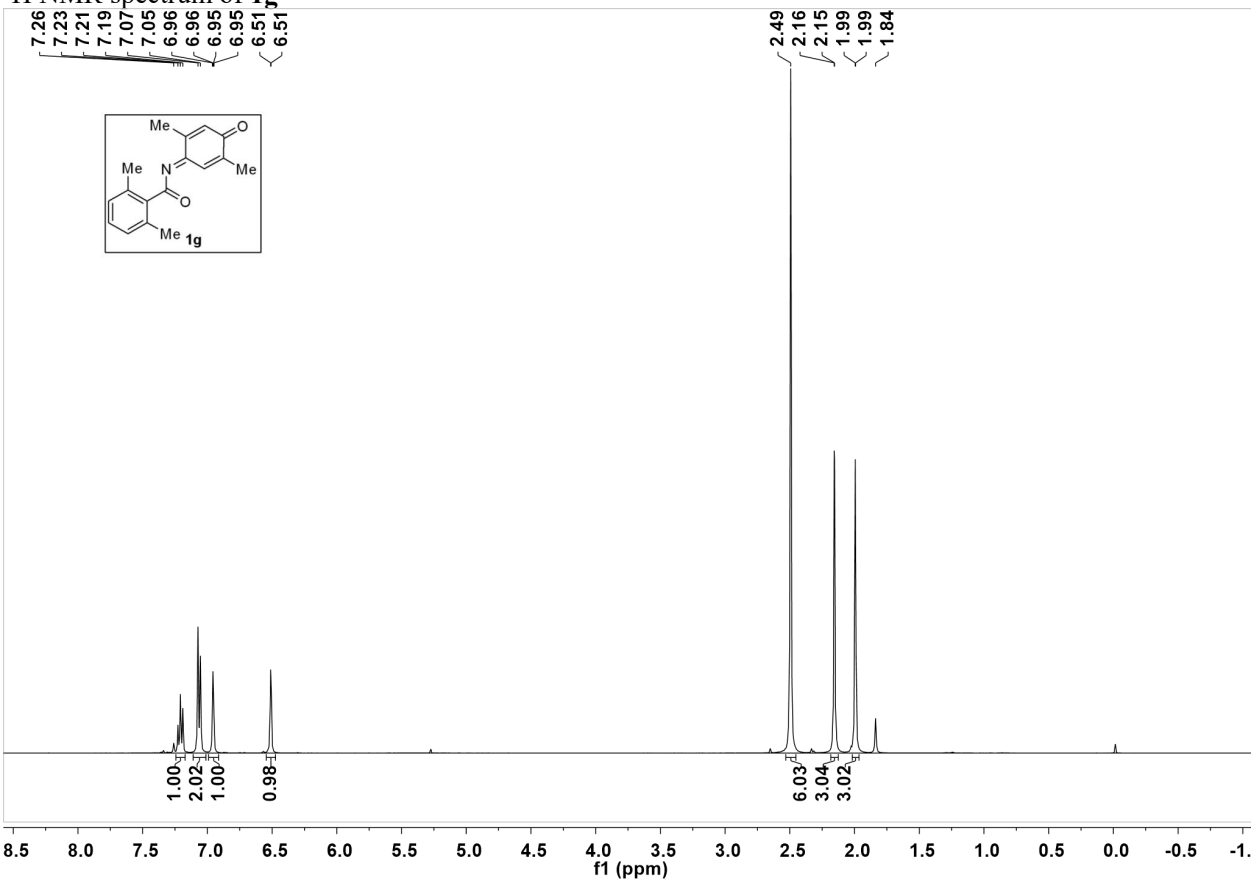
^{1}H NMR spectrum of **1f**



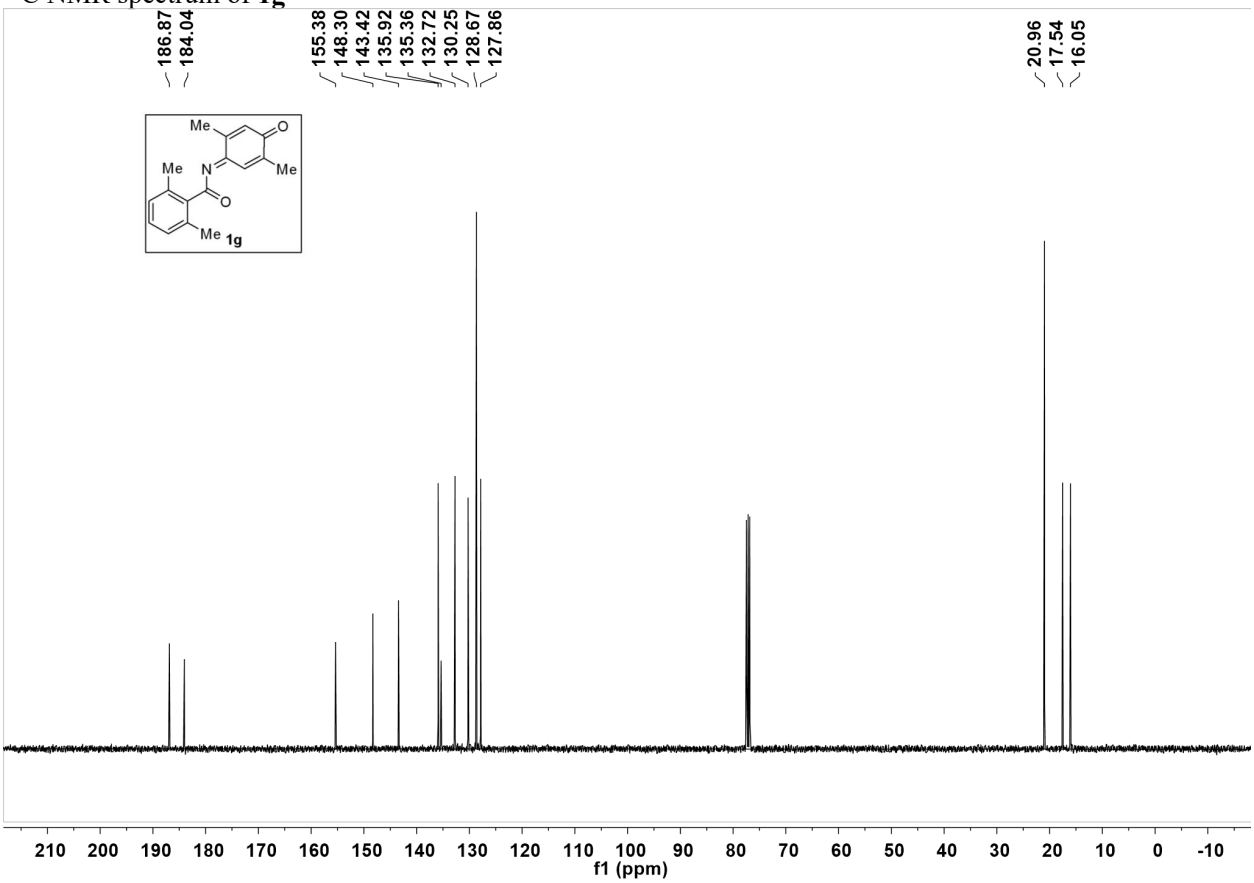
^{13}C NMR spectrum of **1f**



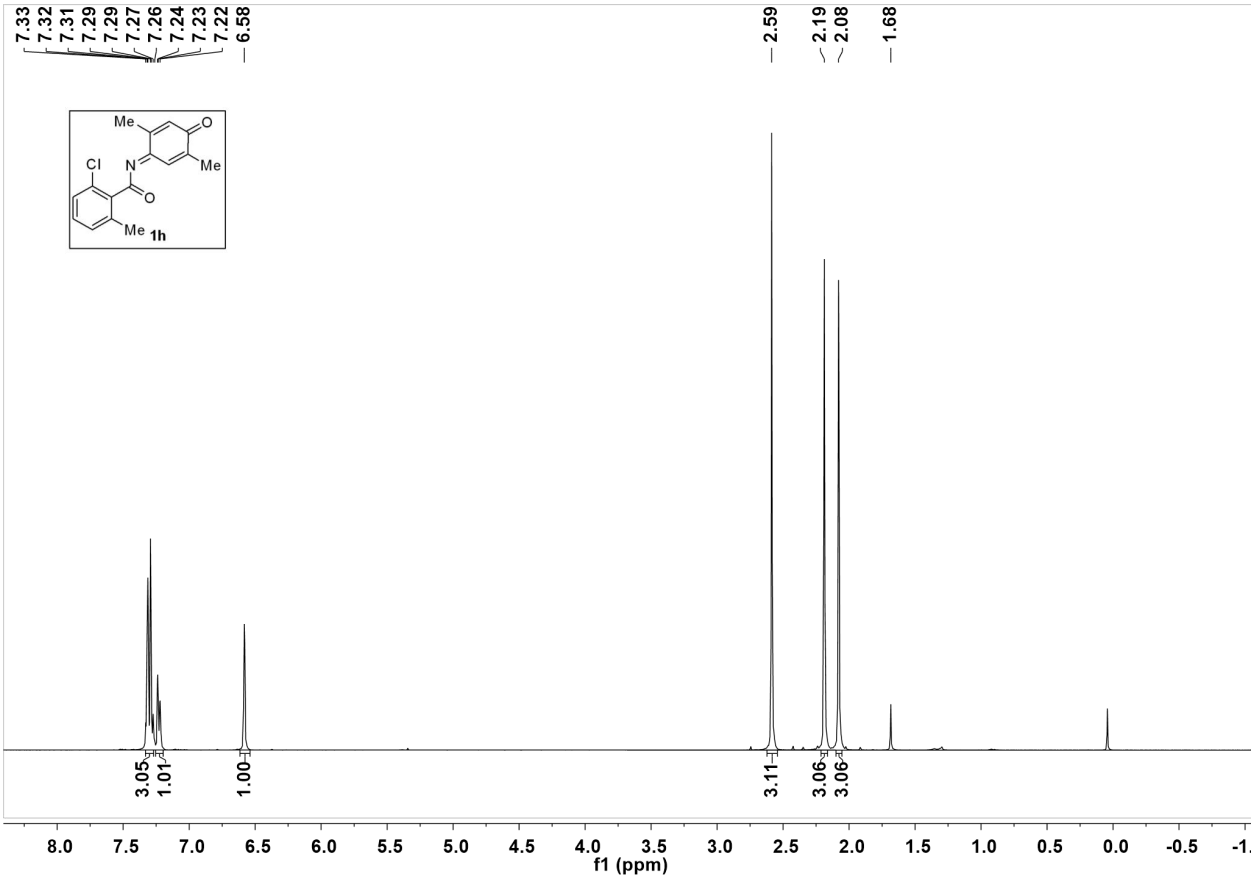
^{1}H NMR spectrum of **1g**



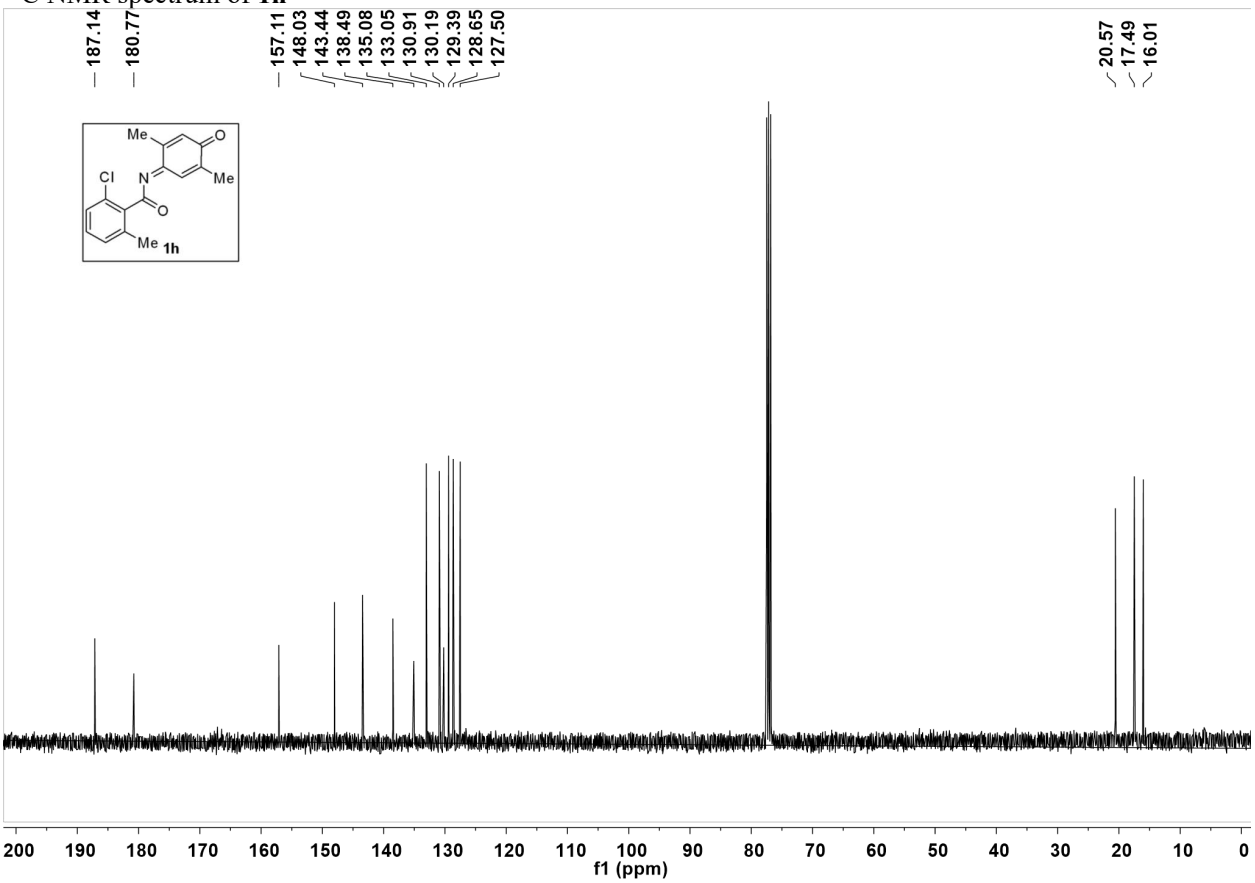
^{13}C NMR spectrum of **1g**



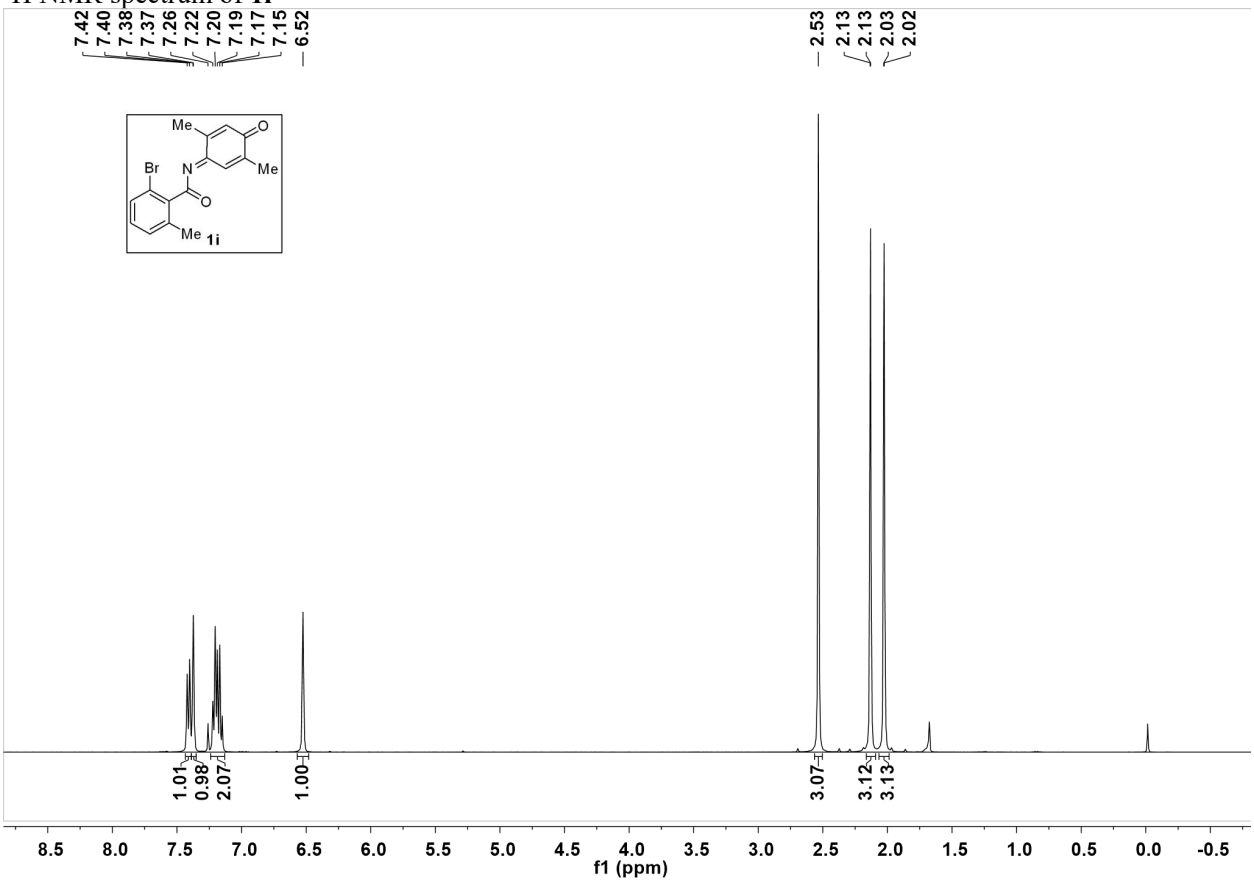
^{1}H NMR spectrum of **1h**



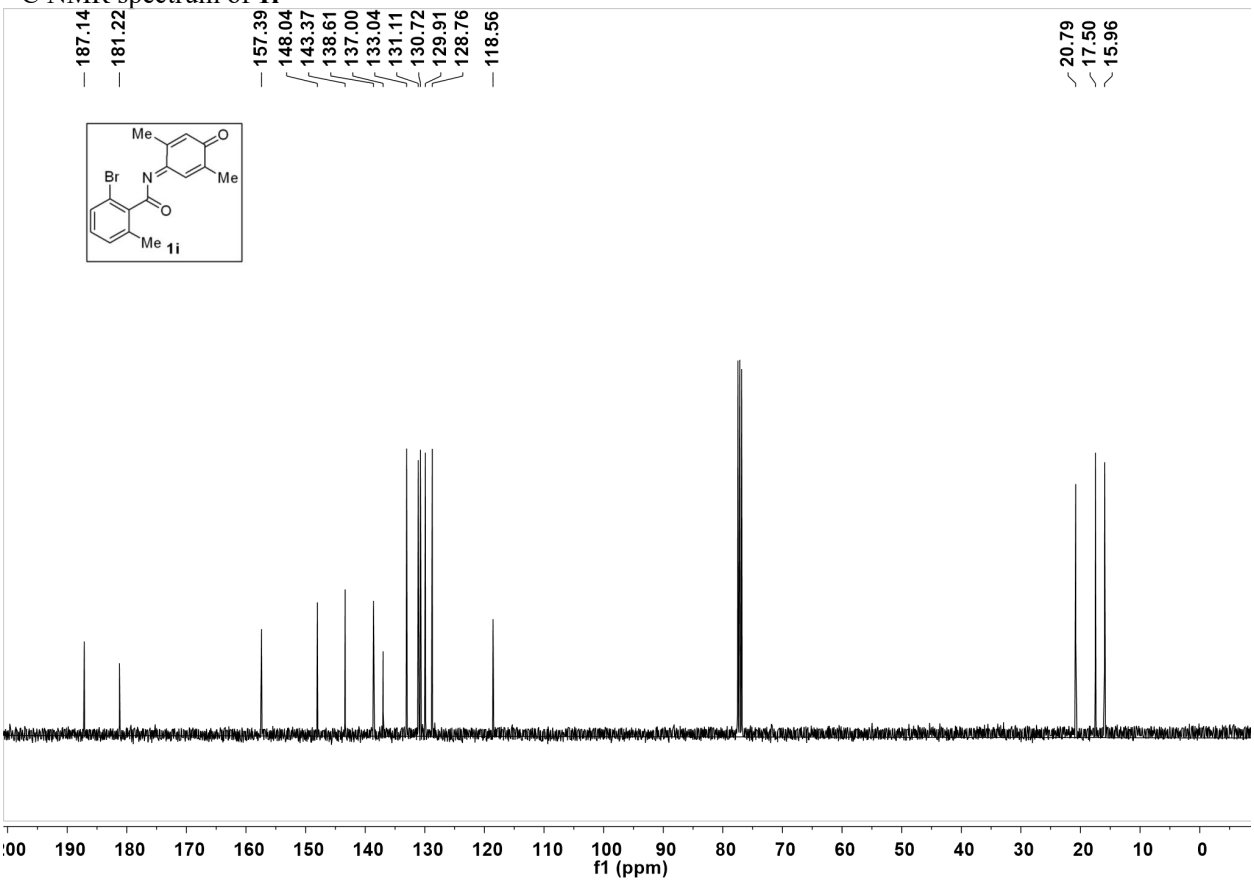
^{13}C NMR spectrum of **1h**



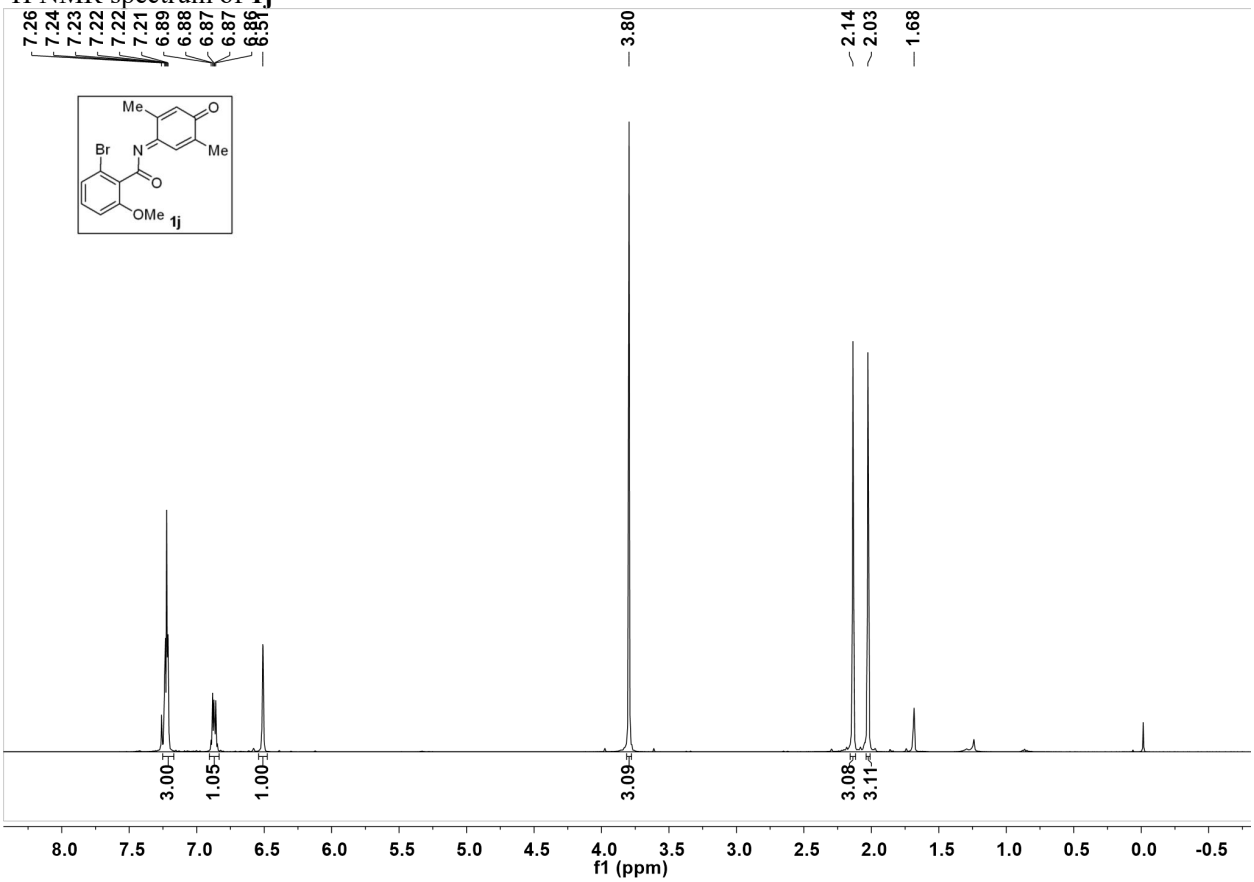
^{1}H NMR spectrum of **1i**



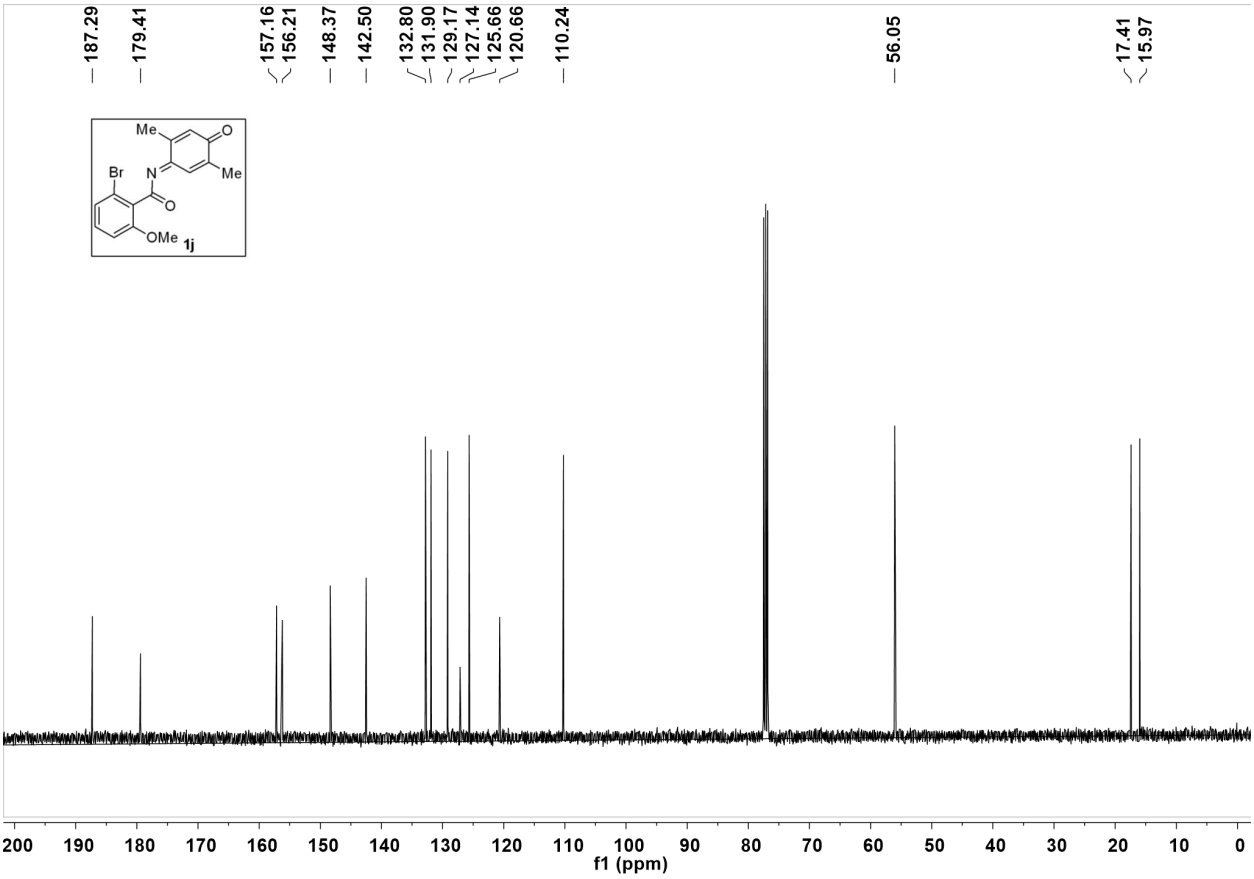
^{13}C NMR spectrum of **1i**



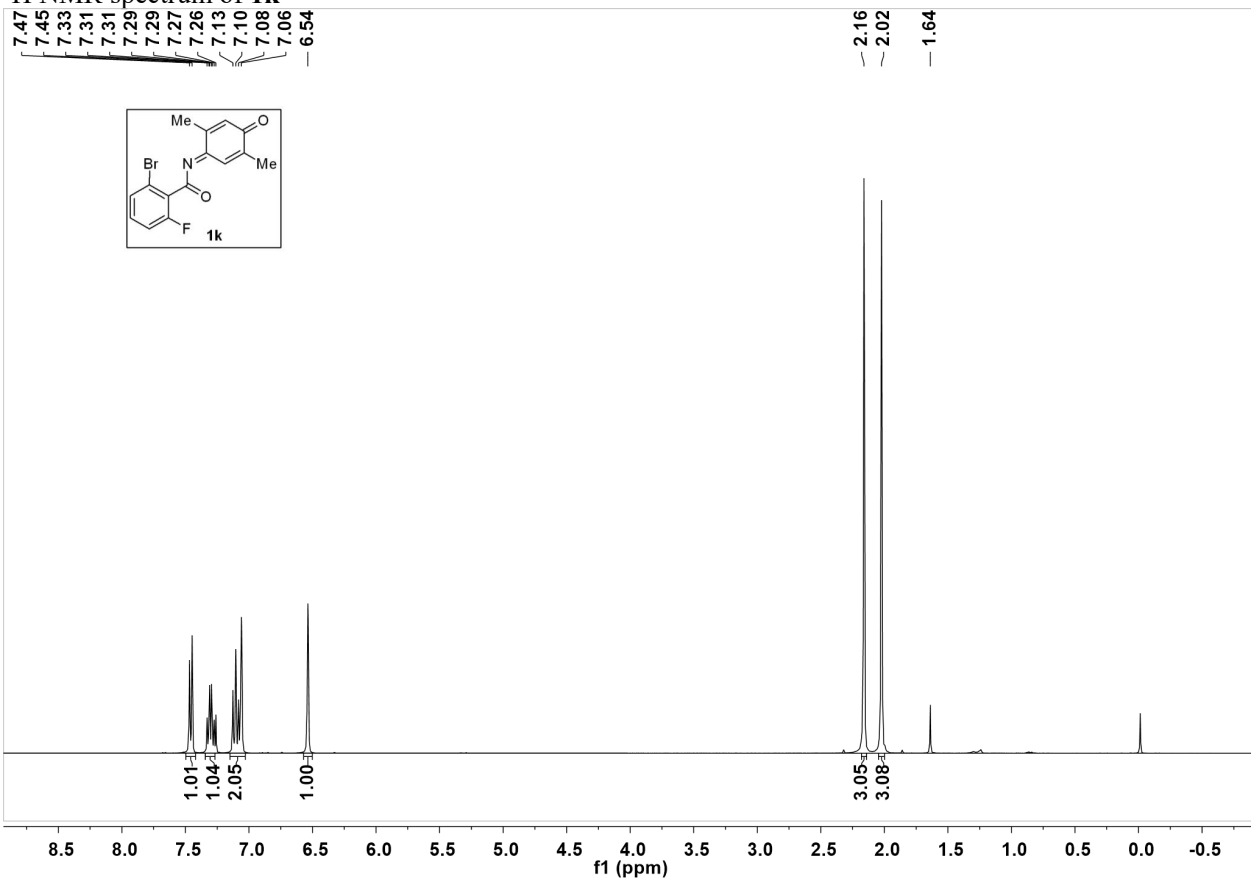
^{1}H NMR spectrum of **1j**



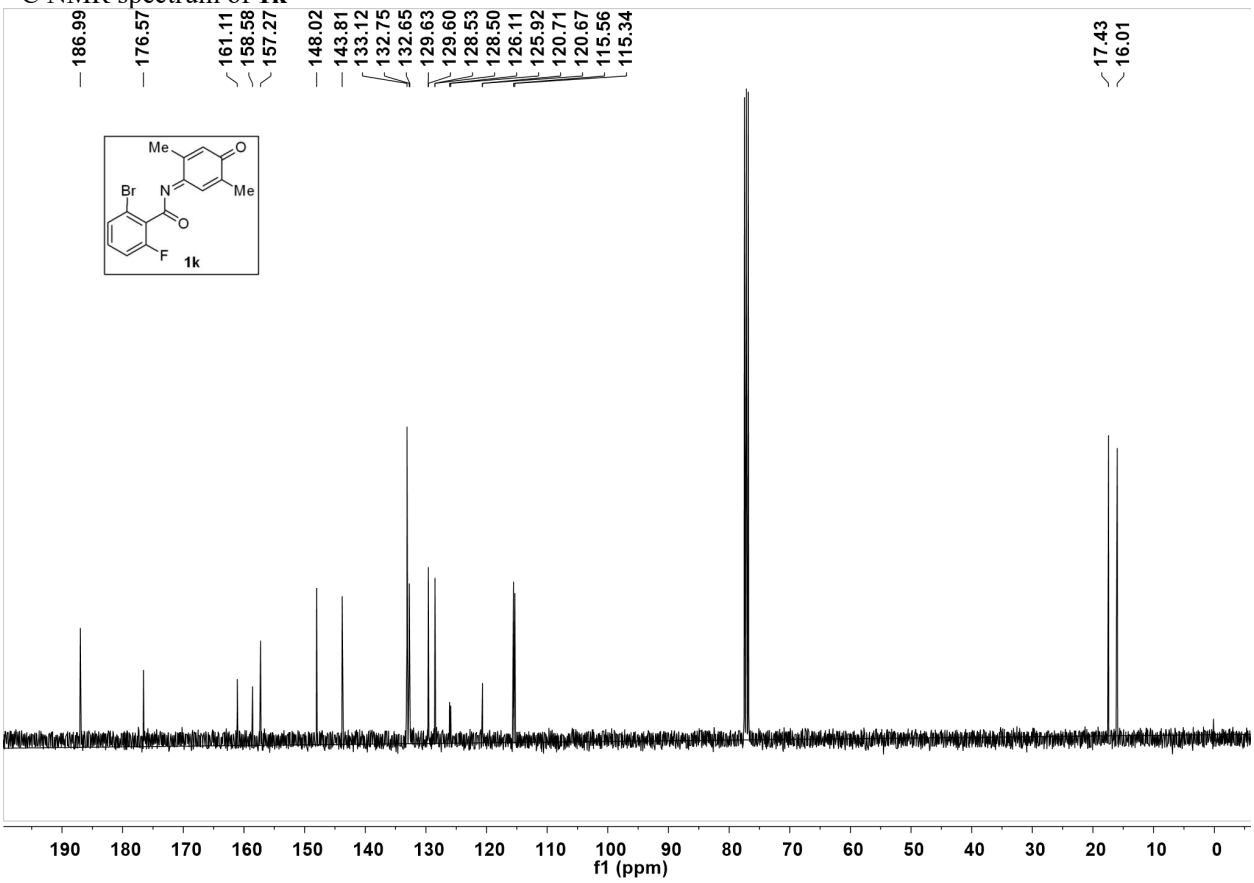
^{13}C NMR spectrum of **1j**



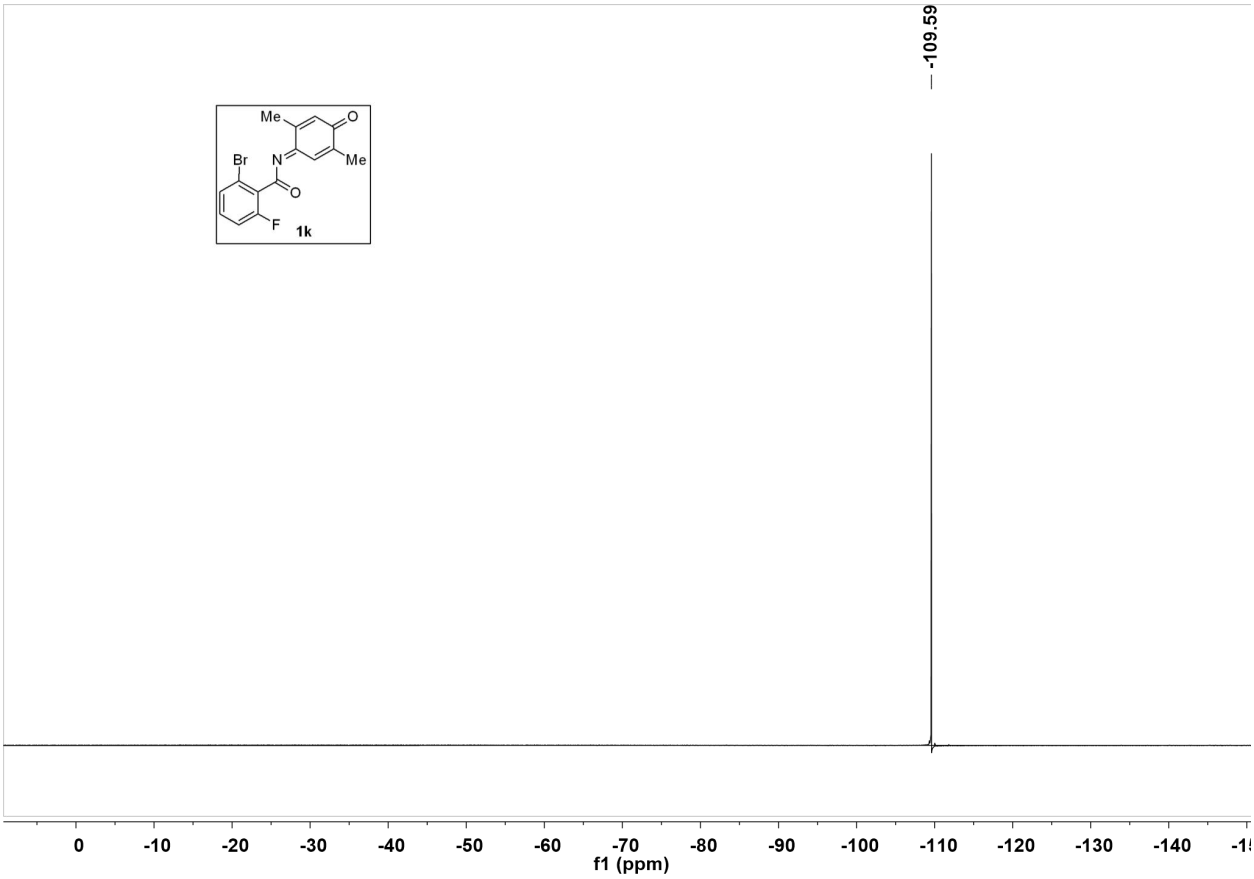
^{1}H NMR spectrum of **1k**



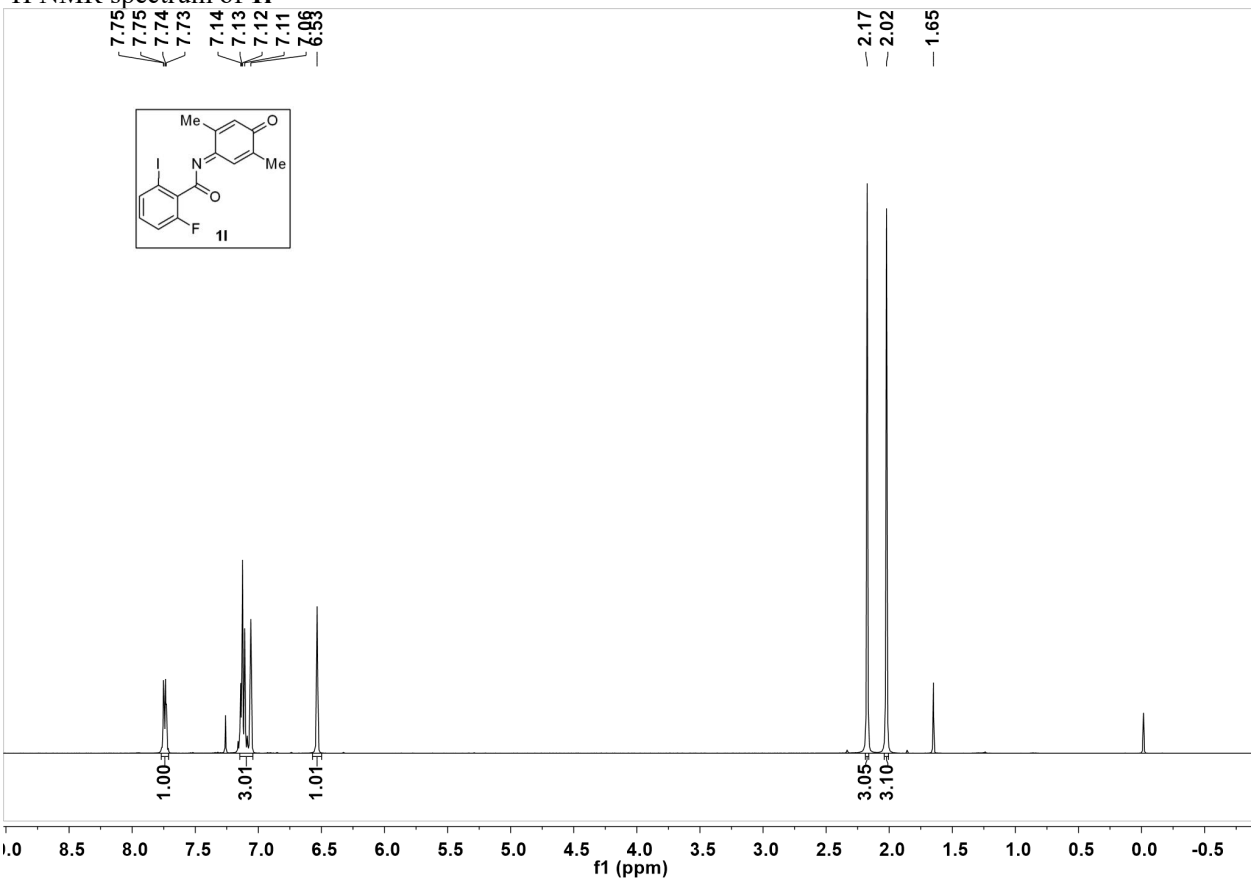
^{13}C NMR spectrum of **1k**



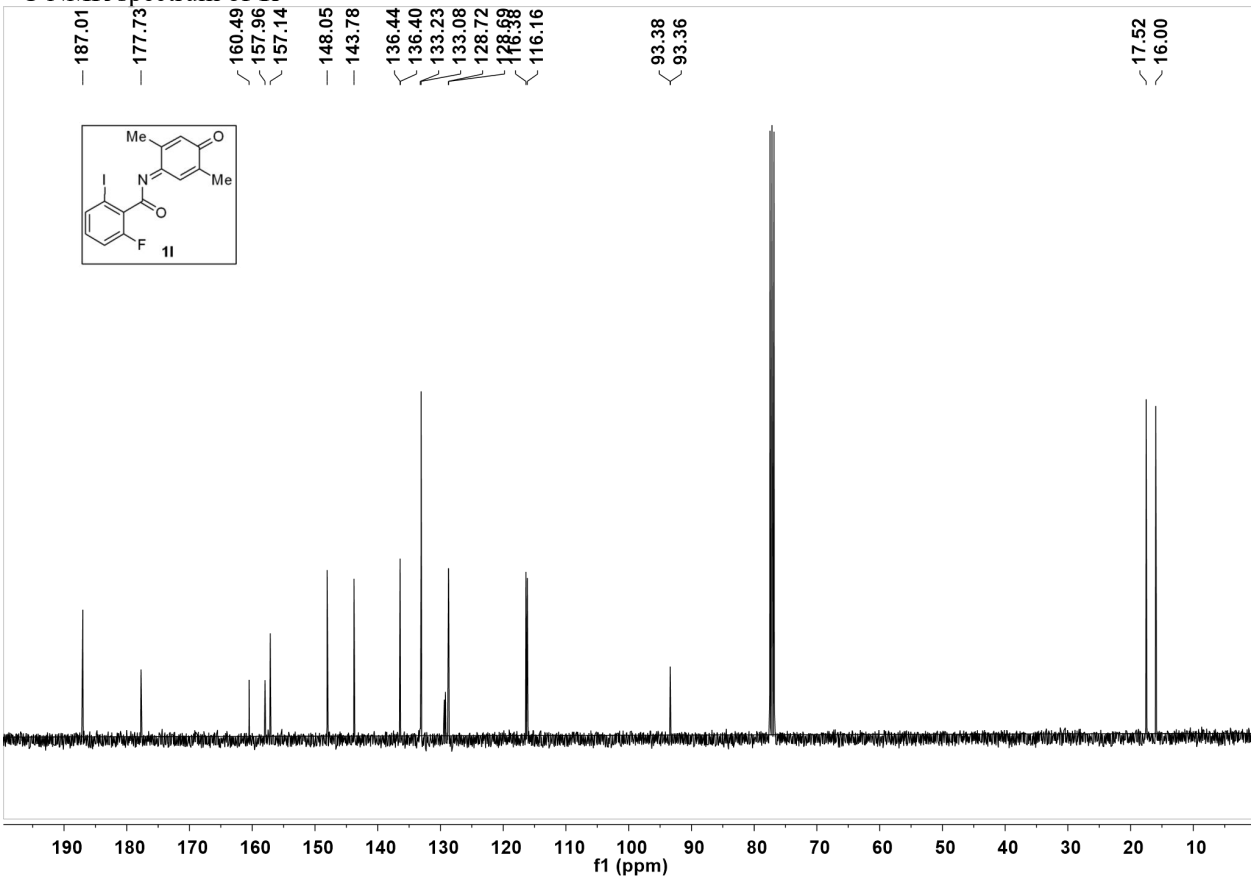
^{19}F NMR spectrum of **1k**


-109.59
Me
O
Br
N
Me
O
F
1k
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

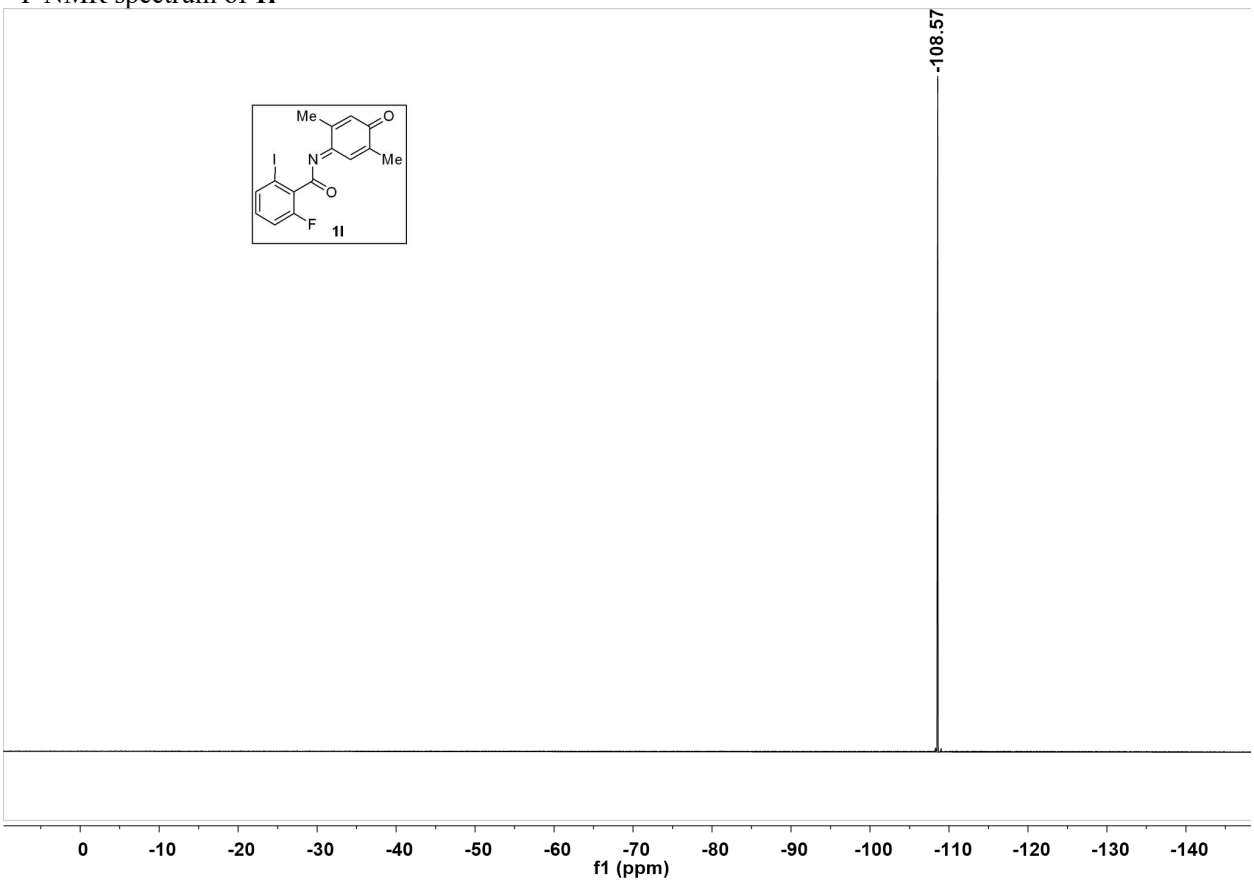
^{1}H NMR spectrum of **1l**



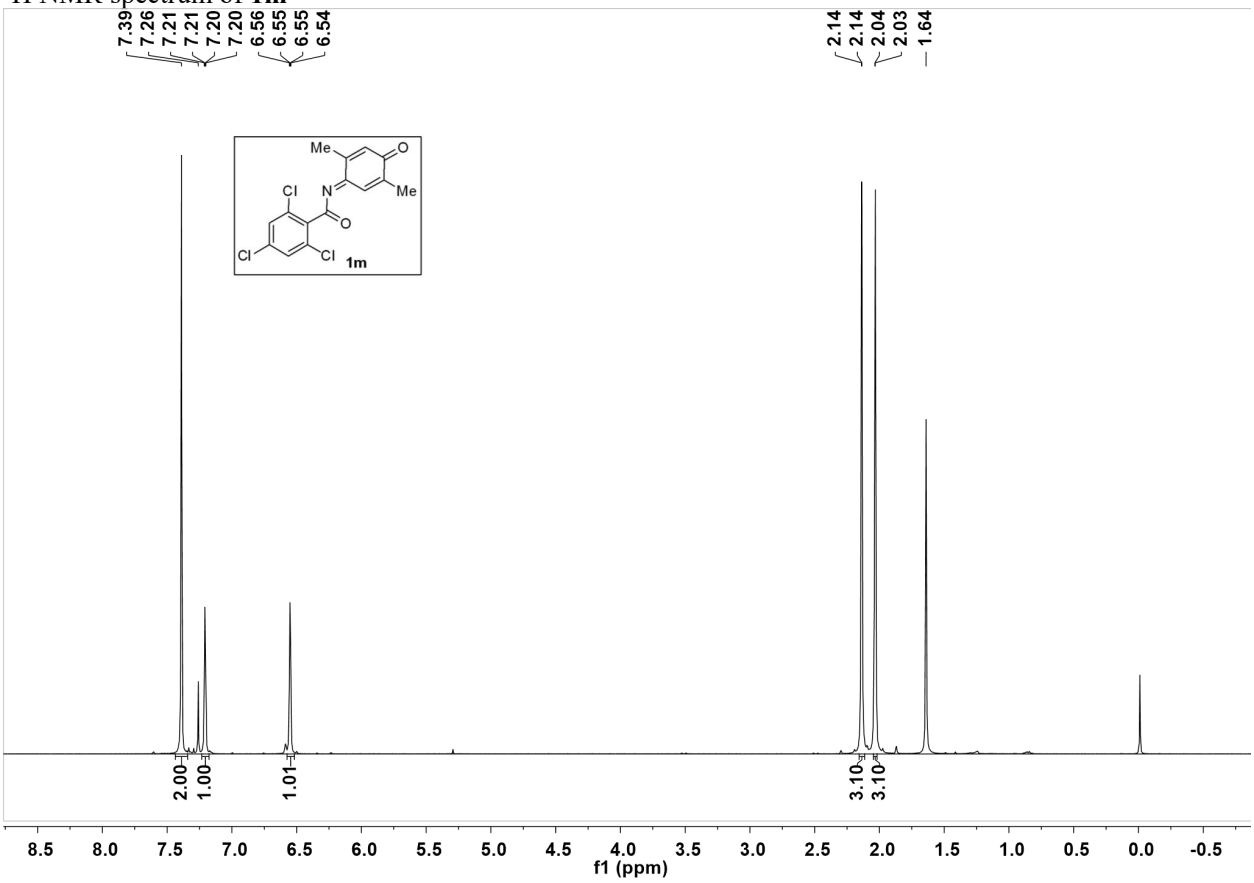
^{13}C NMR spectrum of **1l**



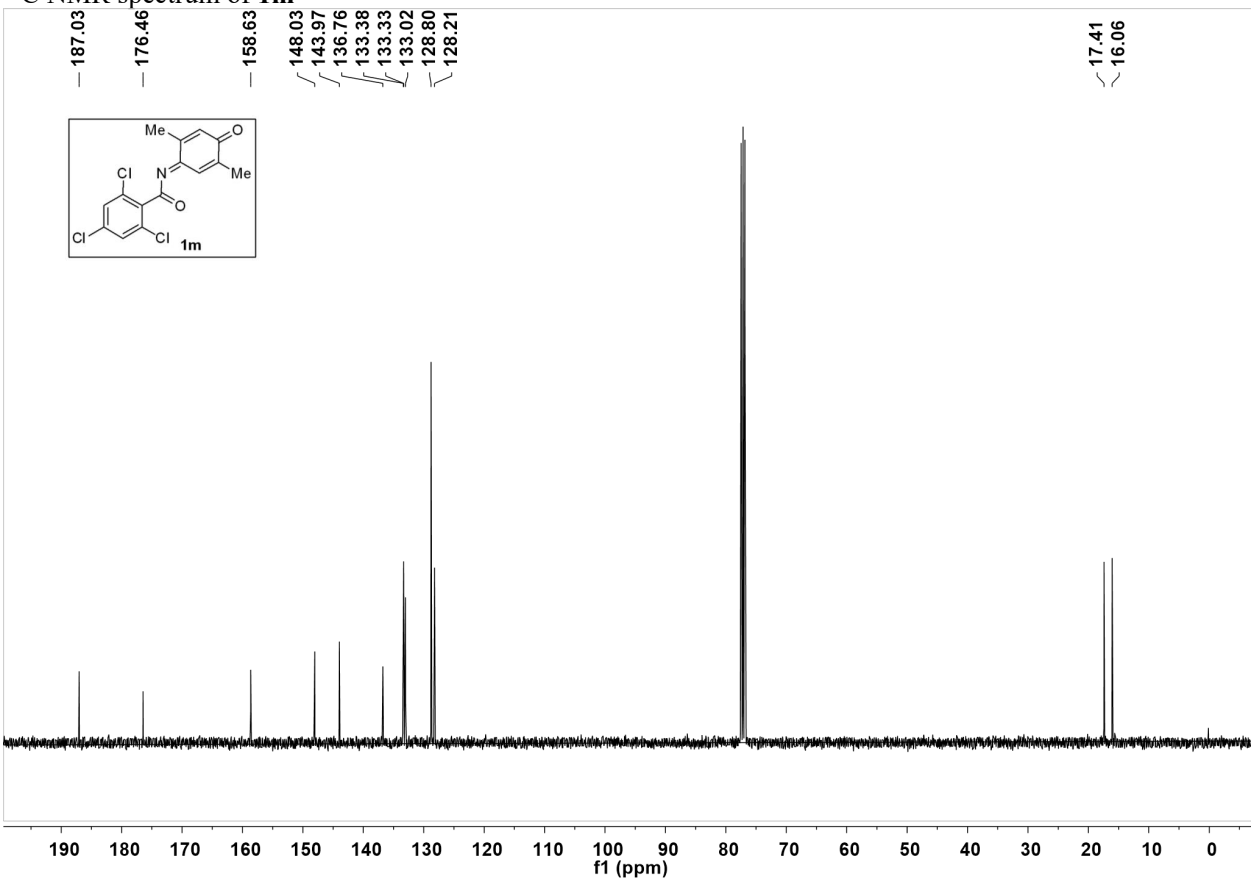
^{19}F NMR spectrum of **1l**



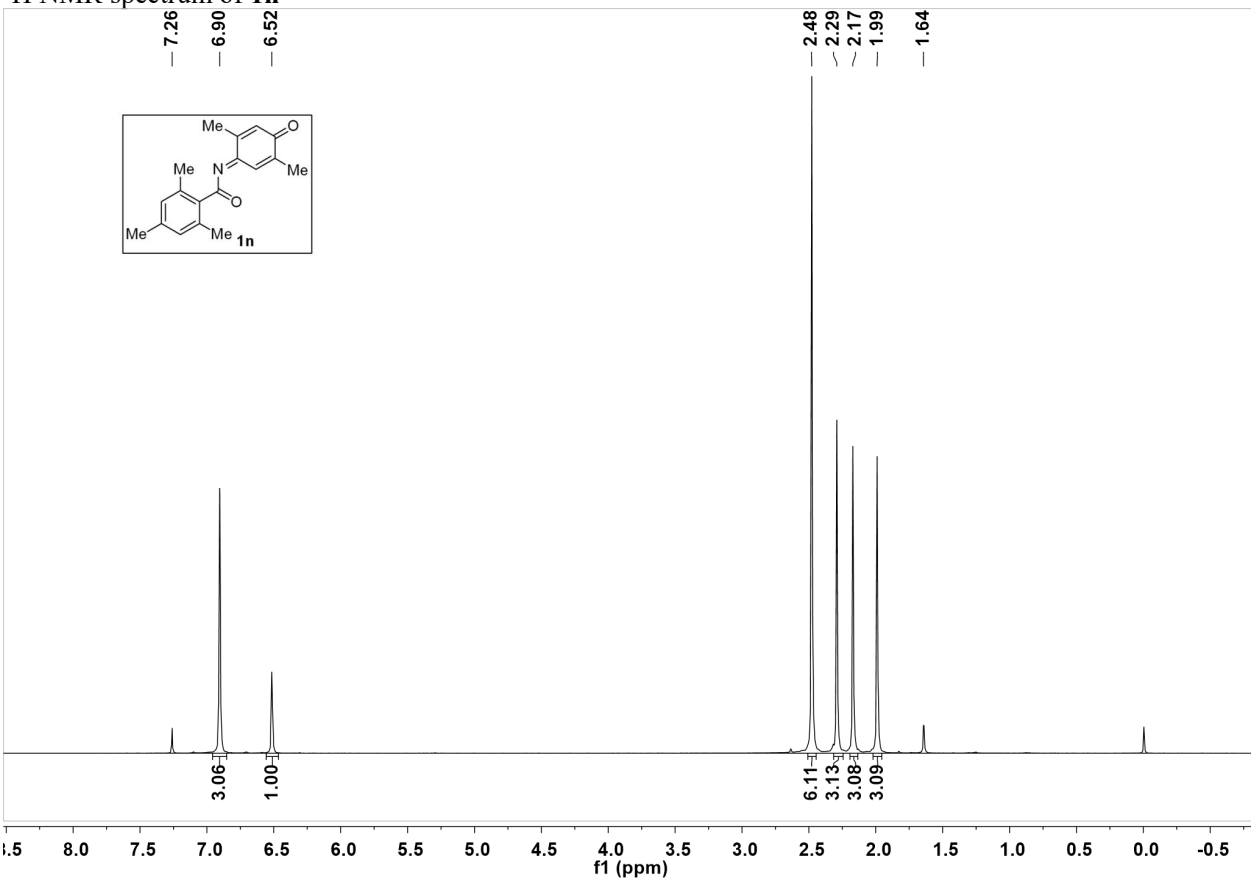
^{1}H NMR spectrum of **1m**



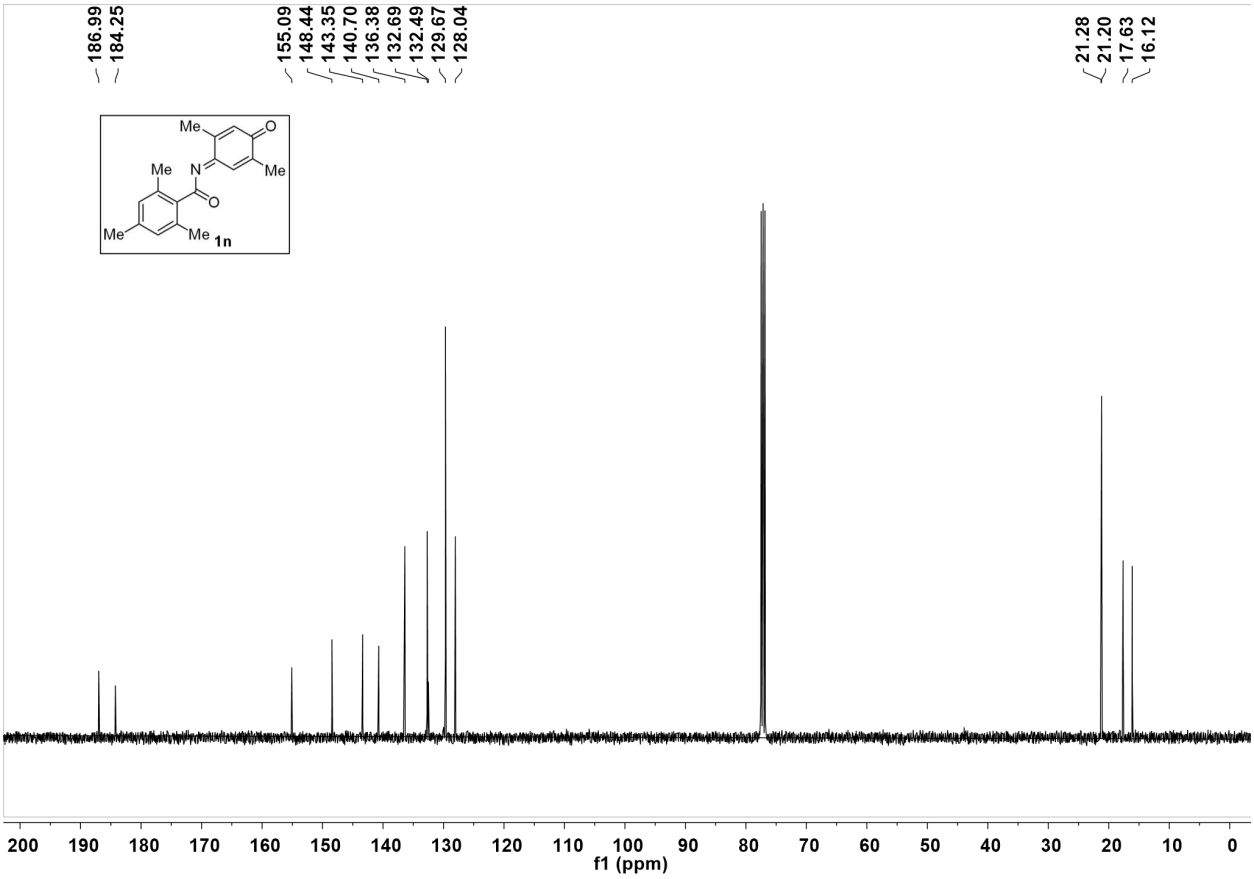
^{13}C NMR spectrum of **1m**



^{1}H NMR spectrum of **1n**



^{13}C NMR spectrum of **1n**


186.99
184.25
155.09
148.44
143.35
140.70
136.38
132.69
132.49
129.67
128.04
21.28
21.20
17.63
16.12
Me
O
Me
N
Me
O
Me
Me
1n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)