SUPPORTING INFORMATION

Rh(II)/Phosphoric acid co-catalyzed three-component reaction of diazo-ketones with alcohols and azonaphthalenes: Access to indole derivatives via a formal [3+2]-cycloaddition

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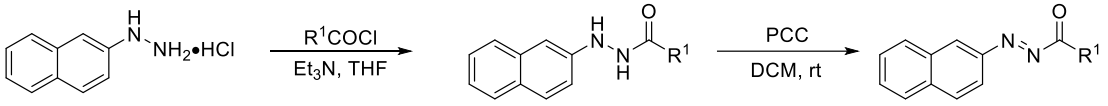
Table of Contents

1. General Information

All reactions were carried out in oven-dried glassware. Solvents were dried by the standard methods. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO-*d*6 on a 400 or 500 MHz spectrometer; chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI or CI Source).

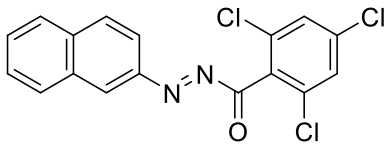
Materials: CH_2Cl_2 & $ClCH_2CH_2Cl$ was distilled over calcium hydride (CaH_2) prior to use. 4 Å molecular sieves were dried in a Muffle furnace at 250 ℃ over 5 hrs. Alcohols and phosphoric acid **4a, 4d, 4e, 4f** was commercial available, diazo ketones **1** were prepared according to the literature procedures [1] and **3** were synthesized similarly to the literature.[2] Phosphoric acid **4b, 4c** were prepared according to the literature.[3] All small scale reactions were carried out under argon atmosphere in a well-dried glassware. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 ºC was used. Silica gel (300–400 mesh) were used for column chromatography (20–30 g per one gram of crude material).

2. General Procedure for the Preparation of Azonaphthalenes 3.



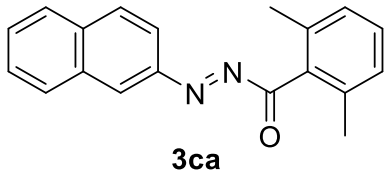
3

To a solution of 2-Naphthylhydrazine hydrochloride (2.0 g, 10.0 mmol) in THF (20.0 mL) was added Et_3N (3.1 mL, 22.0 mmol). The mixture was cooled to 0℃ and the corresponding chloroformate or substituted benzoyl chloride (11.0 mmol) was added dropwise under stirring. The reaction mixture was then stirred for additional 15 min at 0 ℃ and 1 h at room temperature. Then reaction was then quenched with water (20 mL) and extracted with CH_2Cl_2 (5 x 10 mL), the organic layers were combined and washed with saturated aq. $NaHCO_3$ (50 mL) and brine (50 mL). After dried over Na_2SO_4 and concentrated to ~20 mL, PCC (3.2 g, 15.0 mmol) was then added in and stirred at room temperature until hydrazide completely consumed (monitored by TLC). The reaction mixture was then filtered through celite and the filtrate was concentrated and purified by silica gel flash chromatography (n-Hexanes: EtOAc = 100:1 to 20:1) to afford pure products **3** as solid.



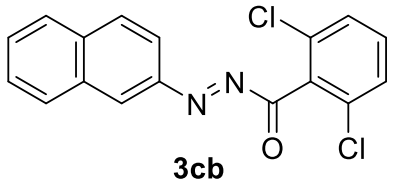
3c

(*E*)-(Naphthalen-2-yldiazenyl)(2,4,6-trichlorophenyl)methanone (3c). 44% yield. Dark red solid, mp = 115.1-117.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.00 (d, *J* = 6.7 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.39 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2, 149.6, 136.8, 136.5, 134.7, 134.2, 133.1, 132.9, 130.3, 129.9, 129.8, 128.2, 128.0, 127.5, 115.5; HRMS (TOF MS CI^+) calculated for$C_{17}H_9Cl_3N_2O$ $[M+H]^+$: 362.9853, found: 362.9851.



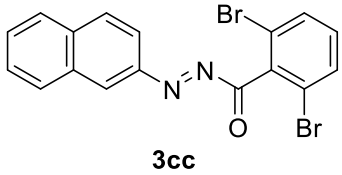
3ca

(*E*)-(2,6-Dimethylphenyl) (naphthalen-2-yldiazenyl) methanone (3ca). 63% yield. Dark red solid, mp = 213.8-214.9 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.96 – 7.89 (comp, 3H), 7.66 – 7.58 (comp , 2H), 7.31 – 7.28 (m, 1H), 7.13 (d, *J* = 7.4 Hz, 2H), 2.46 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2, 149.6, 136.0, 135.8, 134.9, 133.2, 132.1, 130.2, 129.9, 129.5, 129.0, 128.1, 127.8, 127.2, 115.6, 2, 20.6; HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{16}N_2O$ $[M+H]^+$: 289.1335, found: 289.1338.



3cb

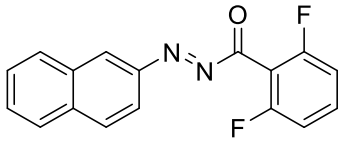
(*E*)-(2,6-Dichlorophenyl) (naphthalen-2-yldiazenyl) methanone (3cb). 51% yield. Dark red solid, mp = 152.9-154.2 ºC . ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.02 (t, *J* = 6.5 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.0, 149.6, 136.7, 135.5, 134.3, 133.1, 132.3, 131.3, 130.2, 129.7 (two carbon signals overlapped), 128.2, 127.8, 127.4, 115.6; HRMS (TOF MS CI$^+$) calculated for $C_{17}H_{10}Cl_2N_2O$ $[M+H]^+$: 329.0243, found: 329.0244.



3cc

(*E*)-(2,6-Dibromophenyl) (naphthalen-2-yldiazenyl) methanone (3cc). 51% yield. Dark red solid, mp = 129.1-131.3 ºC . ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.00 (d, *J* = 3.0 Hz, 2H), 7.91 – 7.86 (m, 2H), 7.66 – 7.56 (m, 4H), 7.20 (td, *J* = 8.1, 3.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 149.7, 139.8, 136.7, 134.5, 133.1, 131.7,

131.3, 130.2, 129.7 (two carbon signals overlapped), 128.18, 127.4, 120.1, 115.5; HRMS (TOF MS CI$^+$) calculated for $C_{17}H_{10}Br_2N_2O$ [M+H]$^+$: 416.9233, found: 416.9237.



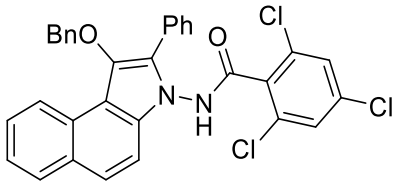
3cd

(*E*)-(2,6-Difluorophenyl)(naphthalen-2-yldiazenyl)methanone. 56% yield. Dark red solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.07 – 7.98 (m, 2H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.65 (m, 1H), 7.60 (m, 1H), 7.57 – 7.52 (m, 1H), 7.04 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, δ 161.31 (d, J = 257.9 Hz), 149.5, 136.3, 134.4 (d, *J* = 10.6 Hz), 134.3 (d, *J* = 10.5 Hz) 133.1, 132.8, 130.1, 129.6, 129.3, 128.1, 127.3, 115.7, 112.3 (d, *J* = 21.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.65; HRMS (TOF MS CI$^+$) calculated for $C_{17}H_{10}F_2N_2O$ [M+H]$^+$: 297.0834, found: 297.0839.

3. General Procedure for the Annulation of diazo-ketones with alcohols and azonaphthalenes.

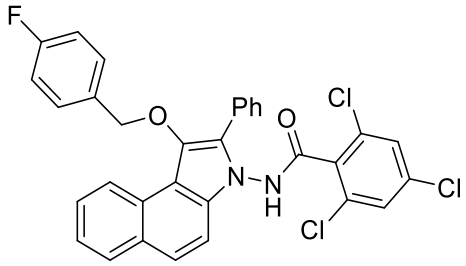
To a 10 mL oven-dried vial with a magnetic stirring bar was added azo compounds **3** (0.2 mmol), alcohol **2** (0.24 mmol), $Rh_2(OAc)_4$ (1.12 mg, 2.5 mol%), acid **4c** (5.0 mol%), 4Å molecular sieves (100 mg) and anhydrous DCE (1.0 mL) in sequence under atmosphere of argon. The reaction mixture was stirred at 0 °C for 10 minutes and diazo ketones **1** (0.30 mmol) in anhydrous DCE (1.0 mL) were added to the above mixture for 1.0 h via a syringe pump. After completion of the addition, the reaction was running for additional 10 minutes under these conditions. When the reaction was completed (monitored by TLC), the reaction mixture was filtered through celite and the filtrate was concentrated and purified by silica gel flash chromatography (n-Hexanes: EtOAc: CH_2Cl_2 = 15:1:1 to 5:1:1) to afford pure products **5-7** as viscous solid or liquid.

4. NMR data for Compounds 5, 6, 7



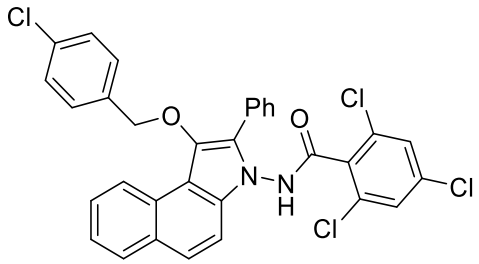
5c

***N*-[1-(Benzyloxy)-2-phenyl-3*H*-benzo[*e*]indol-3-yl]-2,4,6-trichlorobenzamide (5c).** 83 mg, 70% yield. White solid, mp = 223.9-225.9 °C; ^{1}H NMR (400 MHz, DMSO) δ 12.20 (s, 1H), 8.60 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.72 (comp, 4H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.53 – 7.40 (comp, 4H), 7.34 (s, 5H), 4.92 (d, *J* = 11.1 Hz, 1H), 4.82 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 137.5, 137.3, 136.2, 133.0, 132.9, 131.9, 130.5, 129.9, 129.1, 128.9, 128.8, 128.5, 128.5, 128.2, 127.3, 126.9, 124.8, 124.3, 123.6, 113.5, 111.7, 75.9; HRMS (TOF MS CI$^+$) calculated for $C_{32}H_{21}Cl_3N_2O_2$ $[M+Na]^+$: 593.0561, found: 593.0569.



5d

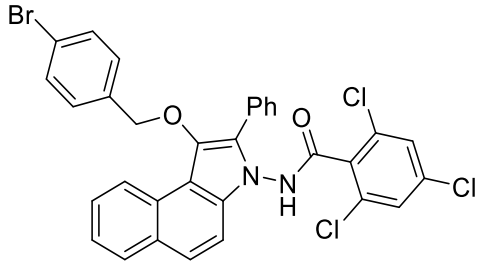
2,4,6-Trichloro-*N*-{1-[(4-fluorobenzyl)oxy]-2-phenyl-3*H*-benzo[*e*]indol-3-yl}benzamide (5d). 79.8 mg, 68% yield. White solid, mp = 209.6-211.8 ºC; ^{1}H NMR (500 MHz, DMSO) δ 12.19 (s, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.83 – 7.72 (comp, 4H), 7.61 (t, *J* = 7.3 Hz, 3H), 7.48 (t, *J* = 7.4 Hz, 3H), 7.44 – 7.40 (m, 1H), 7.31 (dd, *J* = 8.4, 5.7 Hz, 2H), 7.12 (t, *J* = 8.9 Hz, 2H), 4.92 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 162.4 (d, *J* = 244.1 Hz), 137.2, 136.2, 133.5, 133.1, 132.9, 132.0, 130.8, 130.5, 129.9, 129.1 (two carbon signals overlapped), 128.8, 128.7, 128.4, 128.4, 127.3, 126.9, 124.8, 124.3, 123.6, 115.4 (d, *J* = 21.4 Hz), 113.6, 111.7, 75.1.; ^{19}F NMR (376 MHz, DMSO) δ -114.14; HRMS (TOF MS CI^{+}) calculated for $C_{32}H_{20}Cl_3FN_2O_2$ $[M+H]^{+}$: 589.0647, found: 589.0642.



5e

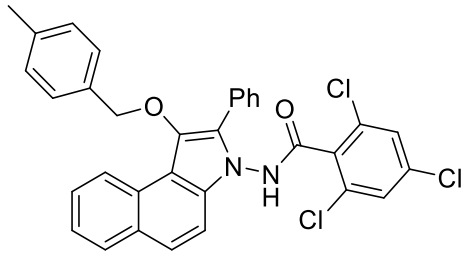
2,4,6-Trichloro-*N*-{1-[(4-chlorobenzyl)oxy]-2-phenyl-3*H*-benzo[*e*]indol-3-yl}benzamide (5e). 79.7 mg, 66% yield. White solid, mp = 221.1-223.4 ºC; ^{1}H NMR (400 MHz, DMSO) δ 12.20 (s, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 10.2 Hz, 4H), 7.61 (t, *J* = 7.3 Hz, 3H), 7.48 (t, *J* = 7.2 Hz, 3H), 7.43 – 7.39 (m, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.94 (d, *J* = 11.2 Hz, 1H), 4.82 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 163.0, 137.1, 136.1, 133.1, 133.0, 132.9, 132.0, 130.5, 130.3, 129.9, 129.1, 129.0, 128.6, 128.7, 128.4, 127.3, 127.0, 124.8, 124.3, 123.6, 113.5, 111.7, 75.0; HRMS (TOF MS CI^{+}) calculated for

$C_{32}H_{20}Cl_4N_2O_2$ [M+H]$^+$: 605.0352, found: 605.0363.



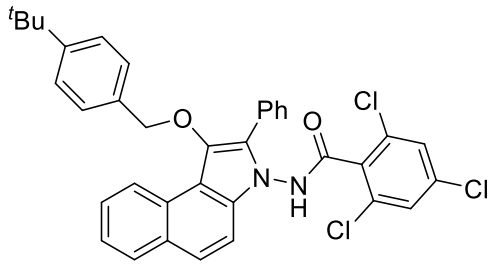
5f

***N*-{1-[(4-bromobenzyl)oxy]-2-phenyl-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5f).** 88 mg, 68% yield. White solid, mp = 215.1-217.3 ºC; ^{1}H NMR (400 MHz, DMSO) δ 12.18 (s, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.85 – 7.72 (comp, 4H), 7.63 – 7.58 (comp, 3H), 7.48 (t, *J* = 8.9 Hz, 5H), 7.43 – 7.39 (comp, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.80 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 137.1, 136.6, 136.2, 133.0, 132.9, 132.0, 131.7, 130.6, 130.5, 129.9, 129.1, 129.1, 128.8, 128.7, 128.40 127.3, 127.0, 124.8, 124.3, 123.6, 121.7, 113.5, 111.7, 75.0; HRMS (TOF MS CI$^+$) calculated for $C_{32}H_{20}Cl_3BrN_2O_2$ [M-H]$^-$: 646.9701, found: 646.9703.



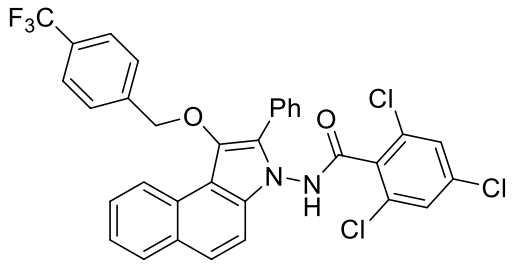
5g

2,4,6-Trichloro-*N*-{1-[(4-methylbenzyl)oxy]-2-phenyl-3*H*-benzo[*e*]indol-3-yl}benzamide (5g). 75.9 mg, 65% yield. White solid, mp = 222.5-224.5 ºC; ^{1}H NMR (500 MHz, DMSO) δ 12.19 (s, 1H), 8.62 (d, *J* = 6.8 Hz, 1H), 8.00 (d, *J* = 6.6 Hz, 1H), 7.78 (d, *J* = 19.8 Hz, 4H), 7.66 (s, 2H), 7.60 (s, 1H), 7.50 (s, 3H), 7.43 (s, 1H), 7.19 (s, 2H), 7.14 (s, 2H), 4.87 (d, *J* = 9.6 Hz, 1H), 4.77 (d, *J* = 9.3 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 137.8, 137.5, 136.2, 134.3, 133.1, 132.9, 132.0, 130.5, 129.9, 129.4, 129.2, 129.1, 128.8, 128.7, 128.6, 128.4, 128.2, 127.4, 126.9, 124.7, 124.3, 123.6, 113.6, 111.69, 75.8, 21.3; HRMS (TOF MS CI$^+$) calculated for $C_{33}H_{23}Cl_3N_2O_2$ [M+Na]$^+$: 607.0717, found: 607.0710.



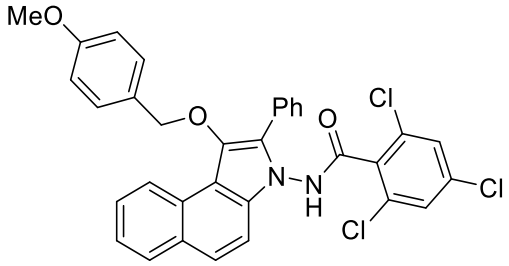
5h

***N*-{1-[(4-(Tert-butyl)benzyl)oxy]-2-phenyl-3*H*-benzo[e]indol-3-yl}-2,4,6-trichlorobenzamide (5h).** 56.3 mg, 45% yield. White solid, mp = 224.4-225.9 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.19 (s, 1H), 8.64 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 9.5 Hz, 4H), 7.67 (d, *J* = 7.1 Hz, 2H), 7.62 (dd, *J* = 11.6, 4.5 Hz, 1H), 7.49 (td, *J* = 7.1, 3.8 Hz, 3H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.78 (d, *J* = 10.9 Hz, 1H), 1.28 (d, *J* = 2.7 Hz, 9H); ^{13}C NMR (100MHz, DMSO) δ 162.9, 151.0, 137.5, 136.2, 134.3, 133.1, 133.0, 132.0, 130.5, 129.9, 129.1 (two carbon signals overlapped), 128.8, 128.7, 128.4, 127.4, 126.9, 126.8, 125.6, 125.2, 124.7, 124.3, 123.7, 113.6, 111.7, 75.8, 34.8, 31.6; HRMS (TOF MS CI^{+}) calculated for $C_{36}H_{29}Cl_3N_2O_2$ [M+H]$^{+}$: 627.1367, found: 627.1363.



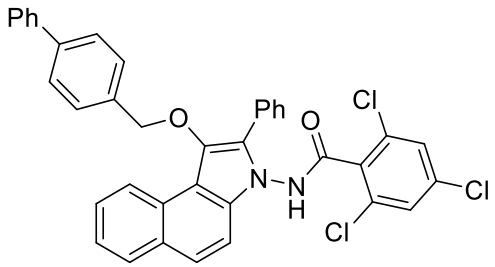
5i

2,4,6-Trichloro-*N*-{2-phenyl-1-[(4-(trifluoromethyl)benzyl)oxy]-3*H*-benzo[*e*]indol-3-yl}benzamide (5i). 81.6 mg, 64% yield; White solid, mp = 214.6-216.6 ºC;^{1}H NMR (400 MHz, DMSO) δ 12.20 (s, 1H), 8.55 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 17.6, 8.9 Hz, 4H), 7.69 – 7.55 (comp, 5H), 7.54 – 7.35 (comp, 6H), 5.09 (d, *J* = 12.0 Hz, 1H), 4.93 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 163.0, 141.9, 137.0, 136.2, 133.0, 132.9, 132.0, 130.5, 129.9, 129.2, 129.1, 128.9, 128.8, 128.7, 128.5, 128.4, 127.2, 127.0, 126.0, 125.6 (q, *J* = 3.6 Hz), 124.9, 124.3, 123.5, 123.3, 113.4, 111.7, 75.0.; ^{19}F NMR (376 MHz, DMSO) δ -60.99; HRMS (TOF MS CI^{+}) calculated for $C_{33}H_{20}Cl_3F_3N_2O_2$ [M+H]$^{+}$: 639.0615, found: 639.0623.



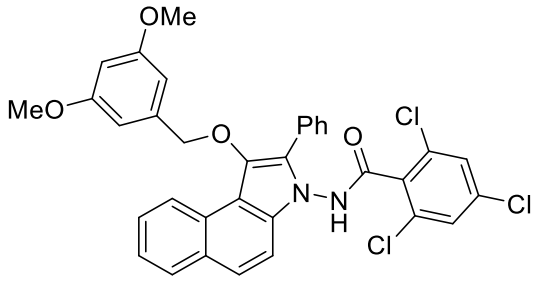
5j

2,4,6-Trichloro-*N*-{1-[(4-methoxybenzyl)oxy]-2-phenyl-3*H*-benzo[*e*]indol-3-yl}benzamide (5j). 76.8 mg, 64% yield. White solid, mp = 255.8-256.8 ℃; ^{1}H NMR (500 MHz, DMSO) δ 12.19 (s, 1H), 8.64 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 19.9 Hz, 4H), 7.67 (d, *J* = 6.4 Hz, 2H), 7.62 (m, 1H), 7.51 (s, 3H), 7.44 (d, *J* = 6.3 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 7.3 Hz, 2H), 4.85 (d, *J* = 10.4 Hz, 1H), 4.75 (d, *J* = 10.5 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 159.6, 137.4, 136.2, 133.1, 132.9, 132.0, 130.5, 130.3, 129.9, 129.2, 129.2, 129.1, 128.8, 128.7, 128.4, 128.3, 127.4, 126.9, 124.7, 124.3, 123.7, 114.2, 113.7, 111.7, 75.7, 55.6; HRMS (TOF MS CI^{+}) calculated for $C_{33}H_{23}Cl_3N_2O_3$ [M+H]$^{+}$: 601.0847, found: 601.0853.



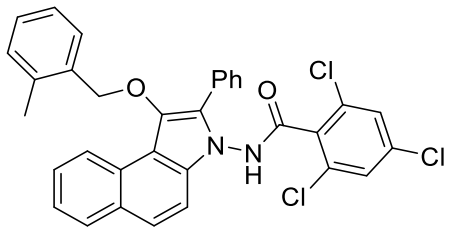
5k

***N*-{1-[(1,1'-Biphenyl)-4-ylmethoxy]-2-phenyl-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5k).** 80.1 mg, 62% yield. White solid, mp = 232.5-234.5 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.23 (s, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.79 (s, 2H), 7.70 – 7.59 (comp, 8H), 7.50 – 7.36 (comp, 10H), 4.99 (d, *J* = 11.3 Hz, 1H), 4.87 (d, *J* = 11.3 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 140.4, 140.3, 137.4, 136.4, 136.2, 133.1, 132.9, 132.0, 130.6, 129.9, 129.4, 129.1, 128.8, 128.7, 128.4, 128.0, 127.5, 127.4, 127.2, 127.1, 127.02, 126.97, 126.9, 124.8, 124.3, 123.7, 113.6, 111.7, 75.6; HRMS (TOF MS CI^{+}) calculated for $C_{38}H_{25}Cl_3N_2O_2$ [M+H]$^{+}$: 647.1054. found: 647.1051.



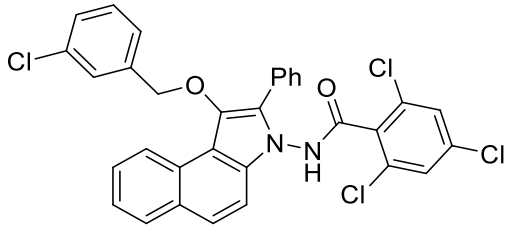
5l

2,4,6-Trichloro-*N*-{1-[(3,5-dimethoxybenzyl)oxy]-2-phenyl-3*H*-benzo[*e*]indol-3-yl}benzamide (5l). 79.4 mg, 63% yield. White solid, mp = 231.7-233.5 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.21 (s, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 4H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 3H), 7.45 – 7.41 (m, 1H), 6.47 (s, 2H), 6.42 (s, 1H), 4.86 (d, *J* = 11.3 Hz, 1H), 4.78 (d, *J* = 11.2 Hz, 1H), 3.68 (s, 6H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 160.8, 139.5, 137.4, 136.2, 133.1, 131.9, 130.6, 129.9, 129.1, 128.8, 128.5, 128.1, 127.4, 126.9, 124.8, 124.3, 123.7, 113.6, 111.7, 106.1, 100.4, 75.7, 55.6; HRMS (TOF MS CI^{+}) calculated for $C_{34}H_{25}Cl_3N_2O_4$ [M+H]$^{+}$: 631.0953, found: 631.0956.



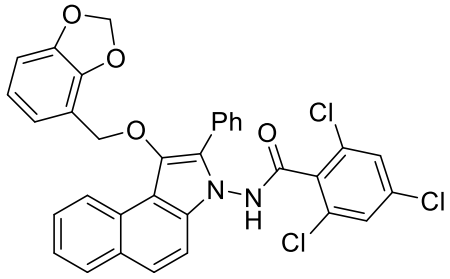
5m

2,4,6-trichloro-N-(1-((2-methylbenzyl)oxy)-2-phenyl-3H-benzo[e]indol-3-yl)benzamide (5m). 60.7 mg, 52% yield. White solid, mp = 221.5-223.5 ℃; ^{1}H NMR (500 MHz, DMSO) δ 12.18 (s, 1H), 8.61 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.77 (s, 4H), 7.60 (dd, *J* = 20.2, 7.0 Hz, 3H), 7.47 (s, 3H), 7.42 (d, *J* = 6.2 Hz, 1H), 7.33 (d, *J* = 5.8 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 6.1 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 11.0 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 137.5, 136.9, 136.2, 135.4, 133.1, 133.0, 131.8, 130.9, 130.5, 129.9, 129.3, 129.1, 128.8, 128.7, 128.5, 128.4, 127.4, 126.8, 126.3, 124.7, 124.3, 123.6, 113.4, 111.7, 74.2, 18.7; RMS (TOF MS CI^{+}) calculated for $C_{33}H_{23}Cl_3N_2O_2$ [M+H]$^{+}$: 585.0898, found: 585.0883.



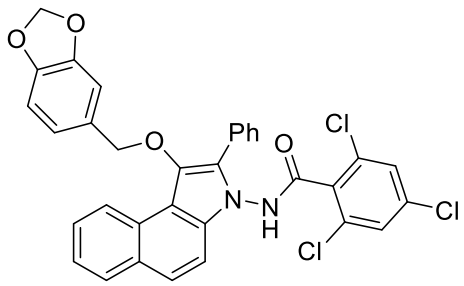
5n

2,4,6-Trichloro-*N*-{1-[(3-chlorobenzyl)oxy]-2-phenyl-3*H*-benzo[*e*]indol-3-yl}benzamide (5n). 74.9 mg, 62% yield. White solid, mp = 205.9-208.1 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.22 (s, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.78 (s, 4H), 7.62 (dd, *J* = 15.2, 7.7 Hz, 3H), 7.49 (t, *J* = 7.3 Hz, 3H), 7.44 – 7.40 (comp, 1H), 7.36 – 7.29 (comp, 3H), 7.26 (d, *J* = 5.1 Hz, 1H), 4.98 (d, *J* = 11.6 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 163.0, 139.7, 137.2, 136.2, 133.5, 133.1, 132.9, 131.9, 130.6, 130.6, 129.9, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.2, 127.3, 127.0, 126.9, 124.8, 124.3, 123.6, 113.47, 111.7, 75.1; HRMS (TOF MS CI^{+}) calculated for $C_{32}H_{20}Cl_4N_2O_4$ [M+H]$^{+}$: 605.0352, found: 605.0359.



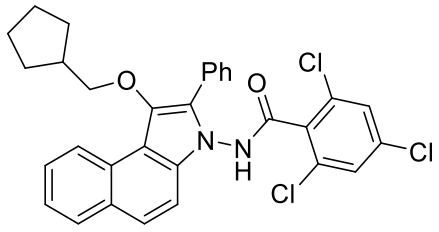
5o

***N*-[1-(Benzo[d][1,3]dioxol-4-ylmethoxy)-2-phenyl-3*H*-benzo[e]indol-3-yl]-2,4,6-trichlorobenzamide (5o).** 79.8 mg, 65% yield. White solid, mp = 150.2-152.2 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.19 (s, 1H), 8.69 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.87 – 7.71 (comp, 3H), 7.67 – 7.59 (comp, 3H), 7.54 – 7.44 (comp, 4H), 7.41 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 5.98 (d, *J* = 6.1 Hz, 2H). 4.89 (d, *J* = 10.9 Hz, 1H), 4.79 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 162.9, 147.5, 146.3, 137.1, 136.2, 133.0, 132.9, 131.9, 130.5, 129.9, 129.0, 128.8, 128.7, 128.5, 128.3, 127.3, 126.8, 124.7, 124.3, 123.9, 123.1, 121.8, 118.3, 113.7, 111.7, 109.1, 101.4, 70.1, 55.4; HRMS (TOF MS CI^{+}) calculated for $C_{33}H_{21}Cl_3N_2O_4$ [M+H]$^{+}$: 615.0640, found: 615.0637.



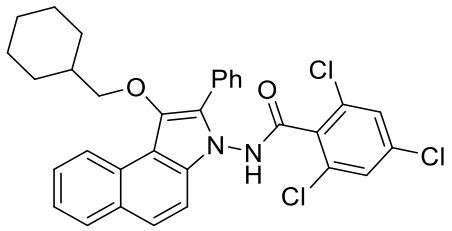
5p

***N*-[1-(Benzo[d][1,3]dioxol-5-ylmethoxy)-2-phenyl-3*H*-benzo[e]indol-3-yl]-2,4,6-trichlorobenzamide (5p).** 92.1 mg, 75% yield. White solid, mp = 172.3-175.1 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.19 (s, 1H), 8.61 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.73 (comp, 4H), 7.63 (d, *J* = 7.1 Hz, 3H), 7.49 (t, *J* = 6.6 Hz, 3H), 7.42 (t, J = 7.2 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.99 (d, *J* = 3.4 Hz, 2H), 4.84 (d, *J* = 10.9 Hz, 1H), 4.71 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 162.9, 147.7, 147.6, 137.2, 136.2, 133.0, 132.9, 132.0, 130.9, 130.6, 129.9, 129.1, 129.1, 128.8, 128.7, 128.5, 128.4, 127.3, 126.9, 124.7, 124.3, 123.7, 122.5, 113.6, 111.68, 109.2, 108.4, 101.5, 75.8; HRMS (TOF MS CI^{+}) calculated for $C_{33}H_{21}Cl_3N_2O_4$ [M+H]$^{+}$: 615.0640, found：615.0641.



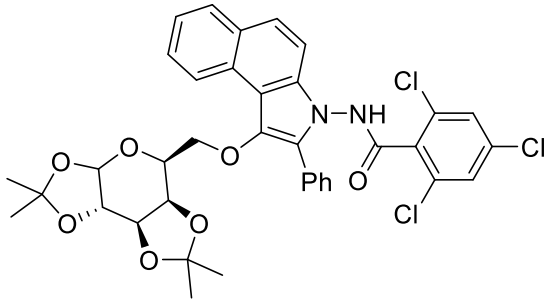
5q

2,4,6-Tichloro-*N*-[-(cyclopentylmethoxy)-2-phenyl-3*H*-benzo[*e*]indol-3-yl]enzamide (5q). 51.4 mg, 45% yield. White solid, mp = 238.1-240.5 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.15 (s, 1H), 8.60 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.87 – 7.70 (comp, 4H), 7.63 (t, *J* = 7.3 Hz, 3H), 7.49 (q, *J* = 7.0 Hz, 3H), 7.41 (t, *J* = 7.3 Hz, 1H), 3.78 – 3.71 (m, 1H), 3.63 (t, *J* = 8.1 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.46 (s, 4H), 1.30 – 1.17 (m, 3H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 138.0, 136.2, 133.1, 133.0, 131.9, 130.6, 129.8, 129.2, 129.1, 128.8, 128.7, 128.3, 127.9, 127.4, 126.8, 124.6, 124.2, 123.7, 113.5, 111.7, 78.3, 29.4, 25.3; HRMS (TOF MS CI^{+}) calculated for $C_{31}H_{25}Cl_3N_2O_2$ [M+H]$^{+}$: 563.1054, found: 563.1052.



5r

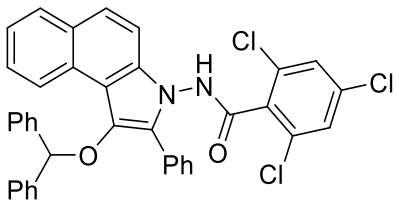
2,4,6-Tichloro-*N*-[-(cyclohexylmethoxy)-2-phenyl-3*H*-benzo[*e*]indol-3-yl]enzamide (5r). 50.6 mg, 45% yield. White solid, mp = 250.2-252.2 ℃; ^{1}H NMR (500 MHz, DMSO) δ 12.16 (s, 1H), 8.59 (d, *J* = 6.7 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.77 (comp, 4H), 7.64 (t, *J* = 7.3 Hz, 3H), 7.49 (d, *J* = 6.6 Hz, 3H), 7.42 (d, *J* = 6.0 Hz, 1H), 3.71 (s, 1H), 3.58 (s, 1H), 1.74 – 1.56 (m, 6H), 1.15 (d, *J* = 24.5 Hz, 3H), 0.96 (d, *J* = 9.6 Hz, 2H); ^{13}C NMR (125 MHz, DMSO) δ 162.95, 138.04, 136.1, 131.9, 130.6, 129.8, 129.2 129.1 128.8 128.6, 128.3, 127.9, 127.3, 126.9 124.6, 124.2, 123.7 113.5, 111.7 79.7, 38.1, 29.8, 29.8 26.4, 25.8; HRMS (TOF MS CI^{+}) calculated for $C_{32}H_{27}Cl_3N_2O_2$ [M+H]$^{+}$: 577.1211, found: 577.1210.



5s

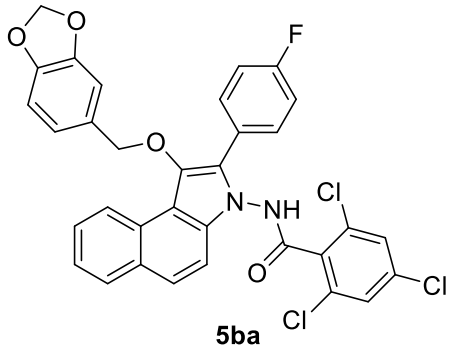
2,4,6-Trichloro-*N*-{2-phenyl-1-[((5*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methoxy}-3*H*-benzo[*e*]indol-3-yl)benzamide (5s). 90.9 mg, 63% yield. White solid, mp = 242.6-245.3℃; ^{1}H NMR (500 MHz, DMSO, 70 ºC) δ 11.91 (s, 1H), 8.77 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.71 (comp, 2H), 7.67 (comp, 4H), 7.56 (m, 1H), 7.46 (q, *J* = 7.0 Hz, 3H), 7.41 (m, 1H), 5.45 (s, 1H), 4.55 (d, *J* = 7.5 Hz, 1H), 4.32 (d, *J* = 2.5 Hz, 1H), 4.23 (d, *J* = 7.7 Hz, 1H), 4.15 – 4.03 (m, 2H), 3.84 (m, 1H), 1.48 – 1.26 (m, 12H); ^{13}C NMR (125 MHz, DMSO, 70 ºC) δ δ 162.8, 136.1, 133.2, 133.18, 132.1, 130.7, 130.0, 129.4, 128.8, 128.7, 128.6, 128.4, 127.5, 126.6, 124.7, 124.5, 124.2, 113.6, 111.7, 109.1, 108.4,

96.2, 72.8, 72.5, 70.9, 70.8, 70.7, 67.0, 66.6, 26.4, 26.3, 25.4, 25.0; HRMS (TOF MS CI$^+$) calculated for $C_{37}H_{33}Cl_3N_2O_7$ [M+Na]$^+$: 745.1246, found: 745.1258.



5t

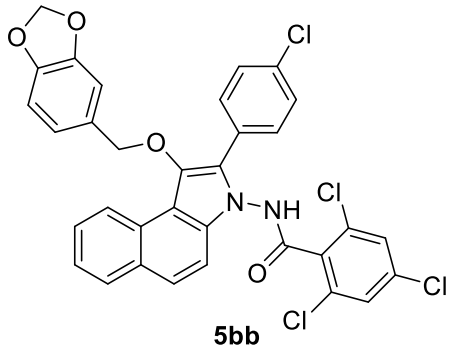
***N*-[1-(Benzhydryloxy)-2-phenyl-3*H*-benzo[*e*]indol-3-yl]-2,4,6-trichlorobenzamide (5t).** 52.9 mg, 41% yield. White solid, mp = 165.9-168.4℃; ^{1}H NMR (400 MHz, DMSO) δ 12.01 (s, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.86 – 7.65 (m, 4H), 7.52-7.50 (m, 1H), 7.49 – 7.44 (m, 1H), 7.38 (t, *J* = 5.3 Hz, 5H), 7.23-7.20 (m, 5H), 7.17 – 7.08 (m, 5H), 6.02 (s, 1H); ^{13}C NMR (125 MHz, DMSO) δ 162.8, 141.5, 141.2, 136.1, 135.5, 133.0, 131.9, 131.1, 129.9, 129.6, 129.1, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.5, 127.1, 126.7, 124.7, 124.2, 123.8, 113.6, 111.6, 85.3; HRMS (TOF MS CI$^+$) calculated for $C_{38}H_{25}Cl_3N_2O_2$ [M+Na]$^+$: 669.0874, found: 669.0881.



5ba

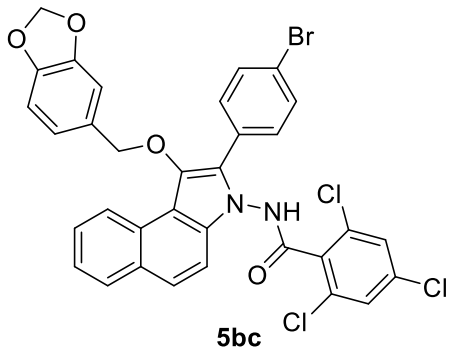
***N*-{1-[Benzo[*d*][1,3]dioxol-5-ylmethoxy]-2-(4-fluorophenyl)-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5ba).** 74.5 mg, 59% yield. White solid, mp = 224.1-226.3℃; ^{1}H NMR (400 MHz, DMSO) δ 12.27 (s, 1H), 8.61 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.85 – 7.75 (comp, 4H), 7.66 (d, *J* = 1.6 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 6.78 – 6.75 (m, 1H), 6.72 (s, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.00 (d, *J* = 4.7 Hz, 2H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.71 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 163.4, 163.0, 161.5, 147.6, 137.0, 136.2, 133.0, 132.9, 132.8, 132.7, 132.0, 130.8, 129.9, 129.1, 128.8, 127.7, 127.4, 127.0,

125.5, 125.3, 124.8, 124.3, 123.7, 122.7, 115.7, 115.5, 113.6, 111.7, 109.4, 108.3, 101.5, 75.9; ^{19}F NMR (376 MHz, DMSO) δ -113.70; HRMS (TOF MS CI$^+$) calculated for $C_{33}H_{20}Cl_3FN_2O_4$ [M+H]$^+$: 633.0545, found: 633.0545.



5bb

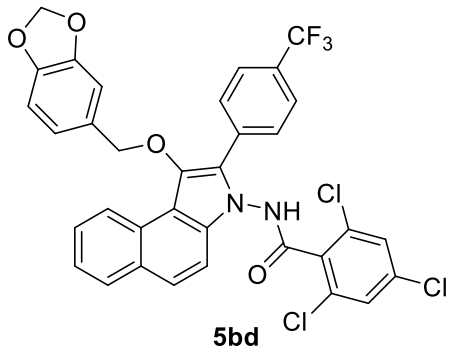
***N*-{1-[Benzo[*d*][1,3]dioxol-5-ylmethoxy]-2-(4-chlorophenyl)-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5bb).** 79.1 mg, 61% yield. White solid, mp = 219.1-221.3℃; ^{1}H NMR (400 MHz, DMSO) δ 12.21 (s, 1H), 8.60 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.1 Hz, 1H), 7.79 (comp, 4H), 7.54 (comp, 6H), 6.82 – 6.71 (comp, 2H), 6.65 (d, *J* = 6.5 Hz, 1H), 5.99 (d, *J* = 10.2 Hz, 2H), 4.90 (d, *J* = 10.4 Hz, 1H), 4.71 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 162.9, 147.6 (two carbon signals overlapped), 137.2, 136.3, 133.1, 133.0, 132.8, 132.4, 132.1, 130.6, 129.9, 129.2, 128.8, 128.6, 128.0, 127.6, 127.4, 127.0, 125.0, 124.4, 123.7, 122.8, 113.7, 111.7, 109.4, 108.3, 101.5, 76.0; HRMS (TOF MS CI$^+$) calculated for $C_{33}H_{20}Cl_4N_2O_4$ [M+Na]$^+$: 671.0069, found: 671.0052.



5bc

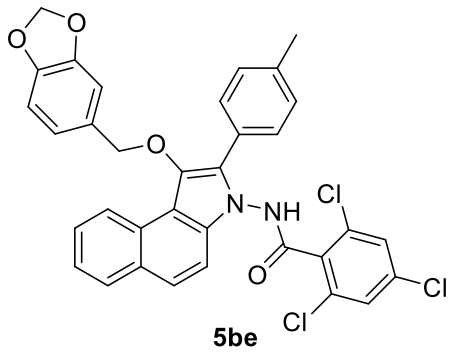
***N*-{1-[Benzo[*d*][1,3]dioxol-5-ylmethoxy]-2-(4-bromophenyl)-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5bc).** 80.1 mg, 64% yield. White solid, mp = 223.6-225.8℃; ^{1}H NMR (500 MHz, DMSO) δ 12.23 (s, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.85 – 7.76 (comp, 4H), 7.67 (d, *J* = 8.0 Hz, 3H), 7.51 (d, *J* = 8.2

Hz, 3H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.00 (d, *J* = 11.5 Hz, 2H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 162.9, 147.63, 147.59, 137.2, 136.3, 133.0, 132.8, 132.5, 132.4, 131.5, 130.6, 129.9, 129.2, 128.8, 128.3, 127.7, 127.3, 127.1, 125.1, 124.4, 123.7, 122.8, 121.7, 113.7, 111.7, 109.4, 108.2, 101.5, 76.0; HRMS (TOF MS CI$^+$) calculated for $C_{33}H_{20}BrCl_3N_2O_4$ [M-H]$^-$: 690.9599, found: 690.9589.



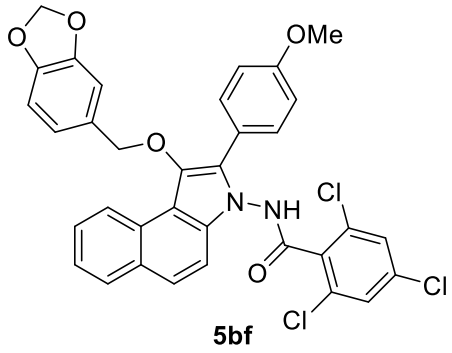
5bd

***N*-{1-[Benzo[*d*][1,3]dioxol-5-ylmethoxy]-2-[4-(trifluoromethyl)phenyl]-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5bd).** 84.5 mg, 62% yield. White solid, mp = 228.6-230.9℃; ^{1}H NMR (400 MHz, DMSO) δ 12.27 (s, 1H), 8.61 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.85 – 7.75 (comp, 4H), 7.66 (comp, 2H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 6.76 (dd, *J* = 14.6, 7.9 Hz, 2H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.00 (d, *J* = 4.7 Hz, 2H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.71 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 162.3, 147.1, 147.0, 137.1, 135.7, 132.6, 132.40, 132.36, 132.1, 130.4, 129.8, 129.4, 128.7, 128.3, 127.1, 126.8, 126.6, 125.4, 124.9, 124.8 (q, *J* = 3.5 Hz). 124.0, 123.2, 123.1, 122.5, 113.1, 111.2, 109.0, 107.6, 100.9, 75.4.; ^{19}F NMR (376 MHz, DMSO) δ -61.00; HRMS (TOF MS CI$^+$) calculated for $C_{34}H_{20}Cl_3F_3N_2O_4$ [M+H]$^+$: 683.0514, found: 683.0529.



5be

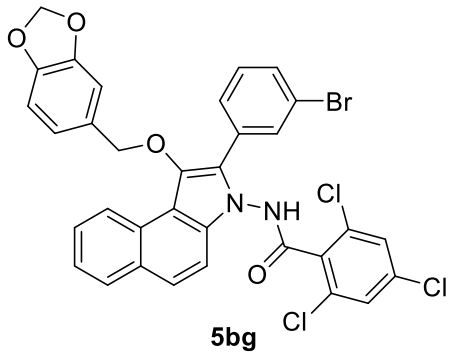
***N*-{1-[Benzo[*d*][1,3]dioxol-5-ylmethoxy]-2-(*p*-tolyl)-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5be).** 80.4 mg, 64% yield. White solid, mp = 225.5-227.8 ℃; ^{1}H NMR (500 MHz, DMSO) δ 12.18 (s, 1H), 8.66 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.85 – 7.74 (comp, 4H), 7.65 – 7.61 (m, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 10.4 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.01 (d, *J* = 5.7 Hz, 2H), 4.85 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 147.7, 147.6, 137.8, 137.0, 136.2, 133.1, 133.0, 131.8, 131.0, 130.5, 129.9, 129.2, 129.1, 128.8, 128.5, 127.4, 126.8, 126.3, 124.5, 124.2, 123.7, 122.5, 113.7, 111.7, 109.2, 108.4, 101.5, 75.7, 21.5; HRMS (TOF MS CI^{+}) calculated for $C_{34}H_{23}Cl_3N_2O_4$ $[M+H]^{+}$: 629.0796, found: 629.0799.



5bf

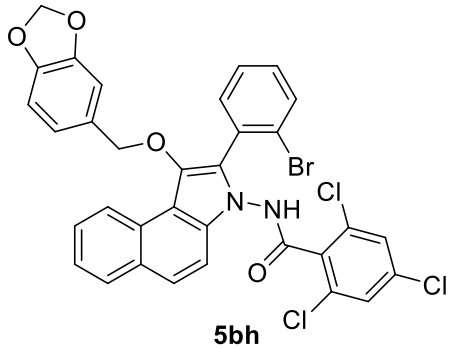
***N*-{1-[Benzo[*d*][1,3]dioxol-5-ylmethoxy]-2-(4-methoxyphenyl)-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5bf)**. 87.5 mg, 68% yield. White solid, mp = 223.2-225.7 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.12 (s, 1H), 8.60 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.74 (s, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.79 (s, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.99 (d, *J* = 5.4 Hz, 2H),

4.83 (d, J = 10.8 Hz, 1H), 4.72 (d, J = 10.9 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 162.9, 159.7, 147.7, 147.5, 136.7, 136.2, 133.04, 132.98, 132.0, 131.5, 131.1, 129.8, 129.0, 128.8, 128.3, 127.3, 126.8, 124.3, 124.2, 123.7, 122.5, 121.4, 114.2, 113.6, 111.6, 109.2, 108.4, 101.5, 75.7, 55.8; HRMS (TOF MS CI$^+$) calculated for $C_{34}H_{23}Cl_3N_2O_5$ $[M+H]^+$: 645.0745, found: 645.0745.



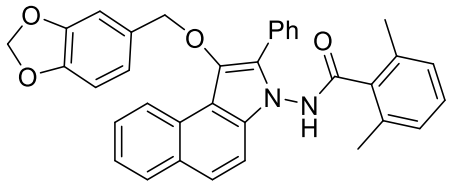
5bg

***N*-{1-[Benzo[*d*][1,3]dioxol-5-ylmethoxy]-2-(3-bromophenyl)-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5bg). 75.1 mg, 60% yield.** White solid, mp = 149.2-151.0℃; ^{1}H NMR (500 MHz, DMSO) δ 12.27 (s, 1H), 8.62 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.85 – 7.76 (comp, 4H), 7.69 – 7.65 (comp, 2H), 7.60 (comp, 2H), 7.53 – 7.49 (m, 1H), 7.43 (t, J = 7.8 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 6.73 (s, 1H), 6.65 (d, J = 7.8 Hz, 1H), 6.01 (d, J = 5.7 Hz, 2H), 4.92 (d, J = 11.0 Hz, 1H), 4.73 (d, J = 11.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 147.7, 147.6, 137.4, 136.3, 133.0, 132.8, 132.5, 131.2, 130.9, 130.6, 130.5, 129.9, 129.4, 129.2, 128.9, 127.3, 127.1, 125.3, 124.5, 123.6, 122.9, 122.0, 113.6, 111.7, 109.5, 108.2, 101.5, 76.0; HRMS (TOF MS CI$^+$) calculated for $C_{33}H_{20}BrCl_3N_2O_4$ $[M+H]^+$: 692.9745, found: 692.9771.



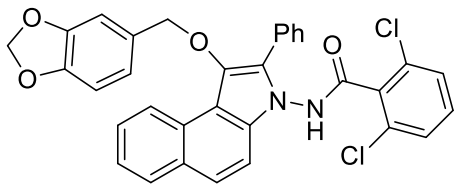
5bh

***N*-{1-[Benzo[*d*][1,3]dioxol-5-ylmethoxy]-2-(2-bromophenyl)-3*H*-benzo[*e*]indol-3-yl}-2,4,6-trichlorobenzamide (5bh).** 70.1 mg, 56% yield. White solid, mp = 200.9-202.6℃; ^{1}H NMR (500 MHz, DMSO) δ 12.20 (s, 1H), 8.64 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.78 (comp, 3H), 7.65 (t, *J* = 6.9 Hz, 3H), 7.52 – 7.47 (comp, 3H), 7.42 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 1.4 Hz, 1H), 6.73 (dd, J = 7.9, 1.4 Hz, 1H), 6.00 (dd, *J* = 5.2, 0.8 Hz, 2H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 163.0, 147.7, 147.6, 137.2, 136.2, 133.1, 132.9, 132.0, 130.9, 130.6, 129.9, 129.2, 129.1, 128.8, 128.7, 128.5, 128.4, 127.4, 126.9, 124.7, 124.3, 123.7, 122.5, 113.7, 111.7, 109.2, 108.4, 101.5, 75.8; HRMS (TOF MS CI^{+}) calculated for $C_{33}H_{20}BrCl_3N_2O_4$ [M+H]$^{+}$: 692.9745, found: 692.9771.



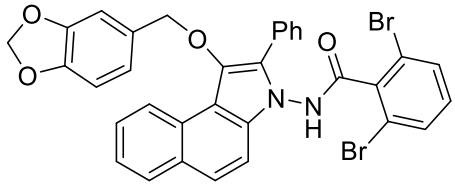
5ca

***N*-(1-(Benzo[*d*][1,3]dioxol-5-yloxy)-2-phenyl-3*H*-benzo[*e*]indol-3-yl)-2,6-dimethylbenzamide (5ca).** 57.8 mg, 55% yield. White solid, mp = 213.8-215.5 ℃; ^{1}H NMR (400 MHz, DMSO) δ 11.78 (s, 1H), 8.64 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.65 (dd, *J* = 10.8, 8.2 Hz, 4H), 7.50 (comp, 4H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.83 (comp, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.00 (d, *J* = 5.5 Hz, 2H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.70 (d, *J* = 10.9 Hz, 1H), 2.00 (s, 6H); ^{13}C NMR (125 MHz, DMSO) δ 168.8, 147.7, 147.6, 137.04, 137.00, 135.4, 135.0, 132.2, 132.1, 131.0, 130.5, 129.8, 129.6, 129.5, 129.1, 128.9, 128.7, 128.5, 128.4, 127.9, 127.5, 126.9, 124.5, 124.2, 123.7, 122.5, 113.60, 113.56, 111.4, 109.2, 108.4, 101.5, 75.9, 21.1, 19.1. HRMS (TOF MS CI^{+}) calculated for $C_{35}H_{28}N_2O_4$ [M+H]$^{+}$: 541.2122, found: 541.2119.



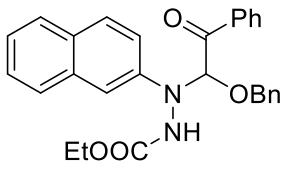
5cb

***N*-(1-(Benzo[*d*][1,3]dioxol-5-yloxy)-2-phenyl-3*H*-benzo[*e*]indol-3-yl)-2,6-dichlorobenzamide (5cb).** 72.4 mg, 64% yield. White solid, mp = 215.9-217.5 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.16 (s, 1H), 8.60 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.77 (s, 2H), 7.63 (d, *J* = 6.4 Hz, 4H), 7.50 (d, *J* = 6.8 Hz, 5H), 7.42 (d, *J* = 6.4 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.77 (s, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.99 (s, 2H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.71 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 167.2, 147.6, 147.6, 137.1, 133.8, 132.7, 132.1, 131.9, 130.9, 130.5, 129.8, 129.1, 129.1, 128.9, 128.6, 128.5, 128.3, 127.3, 126.9, 124.6, 124.3, 123.6, 122.5, 113.5, 111.7, 109.2, 108.4, 101.5, 75.8; HRMS (TOF MS CI^{+}) calculated for $C_{33}H_{22}Cl_2N_2O_4$ [M+H]$^{+}$: 581.1029, found: 581.1034.



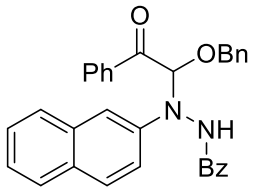
5cc

***N*-(1-(Benzo[*d*][1,3]dioxol-5-yloxy)-2-phenyl-3*H*-benzo[*e*]indol-3-yl)-2,6-dibromobenzamide (5cc).** 65.4 mg, 50% yield. White solid, mp = 129.4-131.2 ℃; ^{1}H NMR (400 MHz, DMSO) δ 12.16 (s, 1H), 8.60 (d, *J* = 8.1 Hz, 1H), 7.98 (dd, *J* = 16.1, 8.6 Hz, 2H), 7.76 (t, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.1 Hz, 4H), 7.49 (t, *J* = 7.4 Hz, 3H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.74 (s, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.99 (d, *J* = 4.6 Hz, 2H), 4.85 (d, *J* = 10.9 Hz, 1H), 4.66 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 165.2, 147.6, 147.6, 137.5, 137.1, 133.2, 132.5, 132.2, 130.9, 130.8, 129.8, 129.4, 129.0, 128.8, 128.3, 127.3, 126.8, 124.4, 124.2, 123.6, 122.5, 113.5, 112.44, 109.2, 108.4, 101.4, 75.8; HRMS (TOF MS CI^{+}) calculated for $C_{33}H_{22}Br_2N_2O_4$ [M+H]$^{+}$: 669.0019, found: 668.9896.



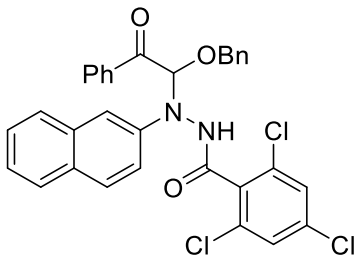
6a

Ethyl 2-(1-(benzyloxy)-2-oxo-2-phenylethyl)-2-(naphthalen-2-yl)hydrazine-1-carboxylate (6a). 56.3 mg, 62% yield, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.66 (t, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.44 (comp, 2H), 7.35 – 7.29 (comp, 6H), 7.25 – 7.15 (comp, 4H), 6.08 (s, 1H), 5.16 – 4.89 (m, 2H), 4.12 (d, *J* = 5.8 Hz, 2H), 1.24 – 1.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 156.7, 145.3, 136.8, 134.3, 134.0, 133.7, 129.6, 129.5, 129.4, 129.0, 128.72, 128.66, 128.5, 128.3, 127.7, 127.3, 126.7, 124.3, 117.5, 111.3, 71.7, 61.8, 14.7; HRMS (TOF MS CI$^+$) calculated for $C_{28}H_{26}N_2O_4$ [M+Na]$^+$: 477.1785, found: 477.1781.



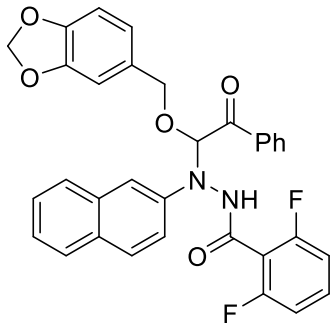
6b

***N′*-(1-(Benzyloxy)-2-oxo-2-phenylethyl)-*N′*-(naphthalen-2-yl)benzohydrazide (6b).** 70.01 mg, 72% yield. Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.63 – 7.59 (comp, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.38 (comp, 3H), 7.33 (d, *J* = 6.4 Hz, 3H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.23 (s, 5H), 7.18 (d, *J* = 10.8 Hz, 3H), 6.19 (s, 1H), 5.01 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.3, 166.1, 143.5, 135.4, 133.4, 133.1, 133.0, 132.7, 131.9, 131.0, 128.5, 128.4, 128.3, 128.0, 127.7, 127.6, 127.4, 127.3, 127.2, 126.5, 126.4, 126.0, 125.5, 125.5, 125.3, 123.2, 122.5, 116.6, 114.9, 110.4, 86.6, 70.6; HRMS (TOF MS CI$^+$) calculated for $C_{32}H_{26}N_2O_3$ [M+Na]$^+$: 509.1836, found: 509.1835.



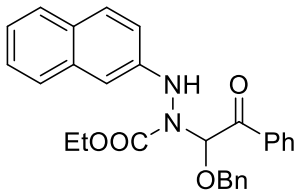
6c

***N*'-(1-(Benzyloxy)-2-oxo-2-phenylethyl)-2,4,6-trichloro-*N*'-(naphthalen-2-yl)benzohydrazide (6c)**. 23 mg, 32% yield. Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 3H), 7.54 (dd, *J* = 18.2, 10.9 Hz, 4H), 7.34 – 7.29 (m, 5H), 7.24 – 7.17 (m, 5H), 6.70 (s, 2H), 5.00 (s, 1H), 4.90 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 169.8, 142.2, 136.1, 136.0, 135.6, 134.7, 134.6, 134.0, 133.7, 133.6, 132.7（two carbon signals overlap）, 129.5, 128.9, 128.7, 128.5, 128.2, 127.5, 126.7, 126.4, 126.3, 123.9, 116.5, 116.4, 110.5, 80.6, 71.8. HRMS (TOF MS CI$^+$) calculated for $C_{32}H_{23}Cl_3N_2O_3$ $[M+Na]^+$: 611.0666, found: 611.0669.



6d

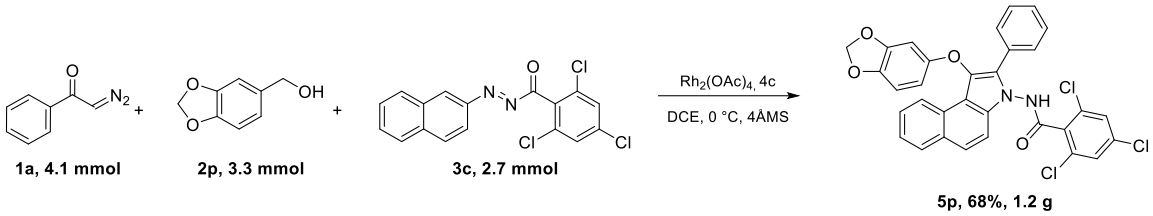
***N*'-(1-(Benzo[*d*][1,3]dioxol-5-ylmethoxy)-2-oxo-2-phenylethyl)-2,6-difluoro-*N*'-(naphthalen-2-yl)benzohydrazide.** 91.7 mg, 81% yield. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.80 (comp, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.61 (comp, 1H), 7.49 – 7.35 (comp, 7H), 7.08 – 6.96 (comp, 4H), 6.85 (m, 1H), 6.30 (s, 1H), 6.00 (d, *J* = 6.7 Hz, 2H), 5.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 160.4, 160.3 (d, *J* = 252.9 Hz), 147.9, 147.9, 144.1, 134.4, 134.2, 134.1, 132.3 (d, *J* = 10.1 Hz), 132.2 (d, *J* = 10.1 Hz), 130.1, 129.7, 129.5, 129.4, 128.6, 127.5, 127.2, 126.6, 124.4, 123.7, 117.4, 112.1 (d, *J* = 21.0 Hz), δ 112.1 (d, *J* = 15.1 Hz), 111.7, 110.1, 108.3, 101.2, 71.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.01.



7a

Ethyl 1-(1-(benzyloxy)-2-oxo-2-phenylethyl)-2-(naphthalen-2-yl)hydrazine-1-carboxylate (7a). 27.2 mg, 30% yield, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 2H), 7.44-7.42 (m, 5H), 7.39-7.36 (m, 4H), 7.25 (d, *J* = 7.3 Hz, 1H), 6.94 (s, 2H), 6.73 (s, 1H), 6.10 (s, 1H), 4.93 (s, 2H), 4.24 (s, 2H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 157.3, 144.6, 136.7, 135.0, 134.2, 133.6, 129.3, 129.3, 128.9, 128.8, 128.7, 128.6 (two carbon signals overlapped), 128.3, 127.6, 126.6, 126.2, 123.3, 116.2, 108.4, 71.6, 63.3, 14.4; HRMS (TOF MS CI$^+$) calculated for $C_{28}H_{26}N_2O_4$ $[M+Na]^+$: 477.1785, found: 477.1788.

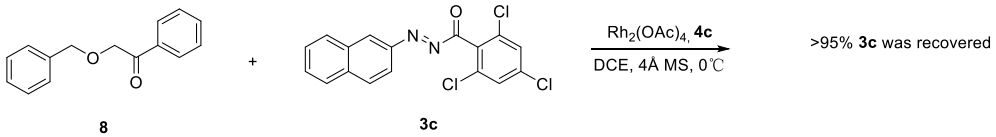
5. General Procedure for Scale up



To a 50-mL oven-dried round-bottom flask with a magnetic stirring bar, Azonaphthalenes compounds **3c** (0.991 g, 2.7 mmol), Piperonyl alcohol **2p** (0.502 g, 3.3 mmol), $Rh_2(OAc)_4$ (11.9 mg, 1.0 mol%), **4c** (85.92 mg, 5.0 mol%), 4 Å molecular sieves (1.35 g) and anhydrous DCE (15.0 mL) were added in sequence under atmosphere of argon, the mixture was stirred at 0 ℃ for 10 minutes. **1a** (0.589 g, 4.1 mmol) in anhydrous DCE (15.0 mL) was then added to the above mixture via a syringe pump for 1.0 h at 0 ℃ under argon atmosphere. When reaction was completed (monitored by TLC), the crude reaction mixture was evaporated in *vacuo* after filtration. The residue was purified by flash column chromatography on silica gel (Hexanes: EtOAc: CH_2Cl_2 = 15:1:1 to 5:1:1) to give the pure product **5p** 68% yield (1.20 g) as yellow solid.

6. Control Experiment：

Control reaction (a):



To a 10-mL oven-dried vial with a magnetic stirring bar, compound **8** (0.12 mmol), Azonaphthalenes compound **3c** (0.10 mmol), $Rh_2(OAc)_4$ (2.5 mol%), 4Å molecular sieves (100 mg) and anhydrous DCE (1 mL) were added in sequence under atmosphere of argon, the mixture was stirred at 0 ℃ for 1 hour. The crude reaction mixture was then evaporated in *vacuo* after filtration. Crude NMR showed more than 95% of starting material **3c** remained (1,3,5-trimethoxybenzene (0.10 mmol) was used as the internal standard), after flash column chromatography on silica gel (Hexanes: EtOAc = 50:1 to

20:1), > 95% of **3c** was recovered. (Figure S1).

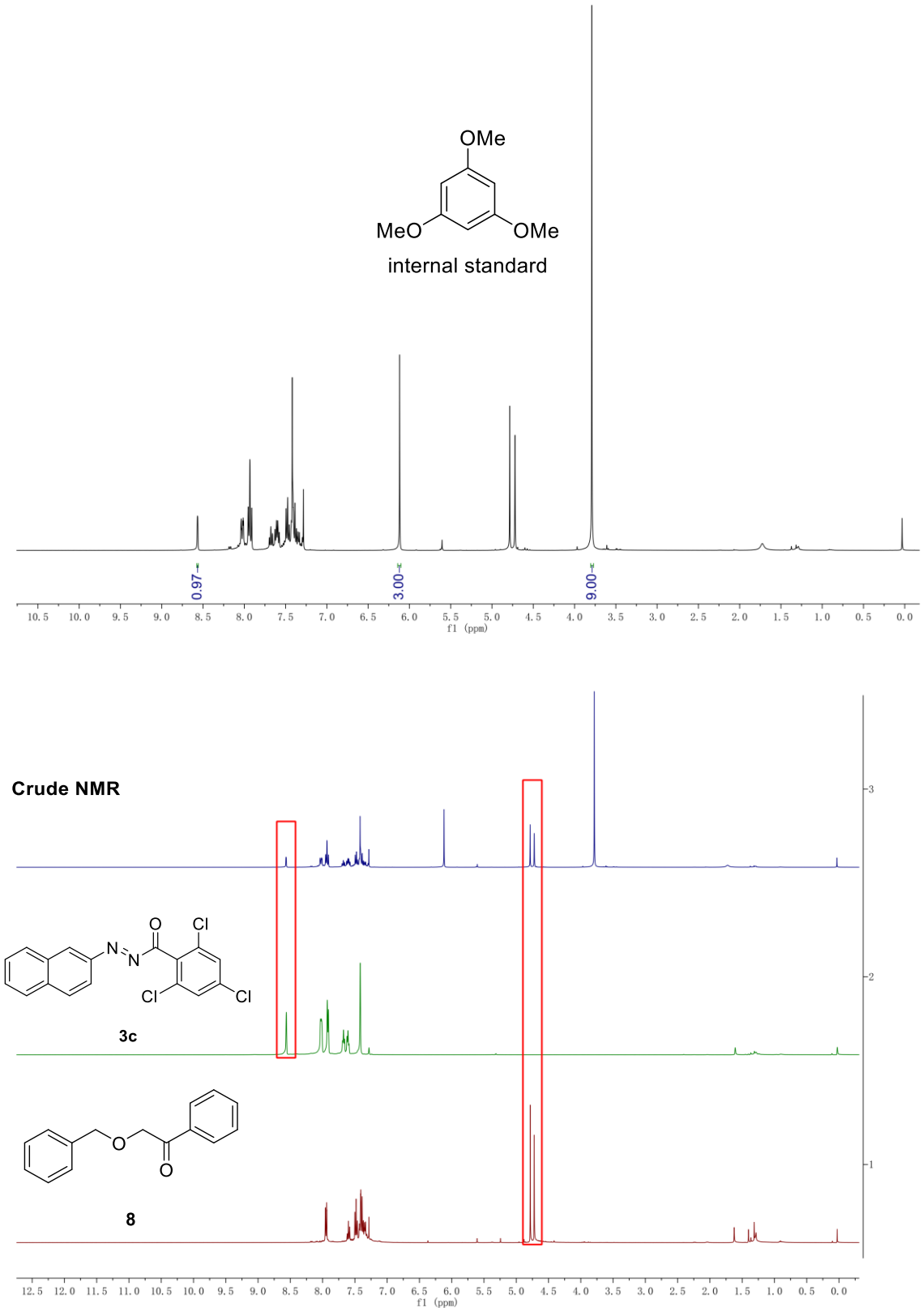
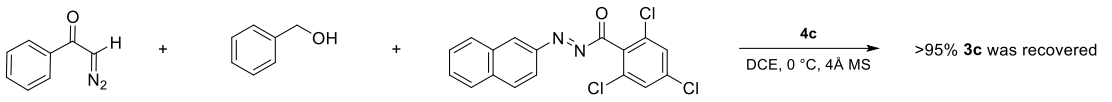


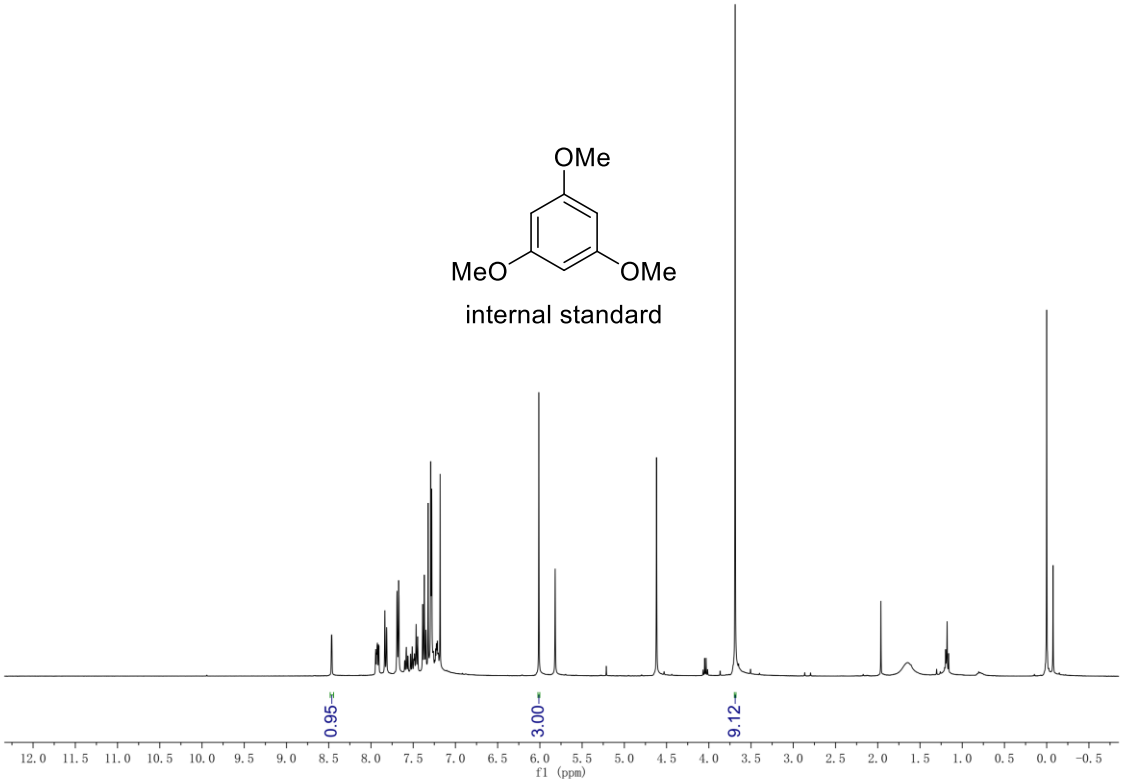
Figure S1

Control reaction (b):



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

To a 10-mL oven-dried vial with a magnetic stirring bar, Benzyl alcohol **2a** (0.12 mmol), Azonaphthalenes compound **3c** (0.10 mmol), **4c** (5.0 mol%), 4 Å molecular sieves (100 mg) and anhydrous DCE (1 mL) were added in sequence under atmosphere of argon, the mixture was stirred at 0 ℃ for 10 minutes, and **1a** (0.15 mmol) in anhydrous DCE (1 mL) were added to the above mixture via a syringe pump for 1 h at 0 ℃ under argon atmosphere. The crude reaction mixture was evaporated in *vacuo* after filtration. Crude NMR showed more than 95% of starting material **3c** remained (1,3,5-trimethoxybenzene (0.10 mmol) was used as the internal standard), after flash column chromatography on silica gel (Hexanes: EtOAc = 50:1 to 20:1), > 95% of **3c** was recovered.(Figure S2).



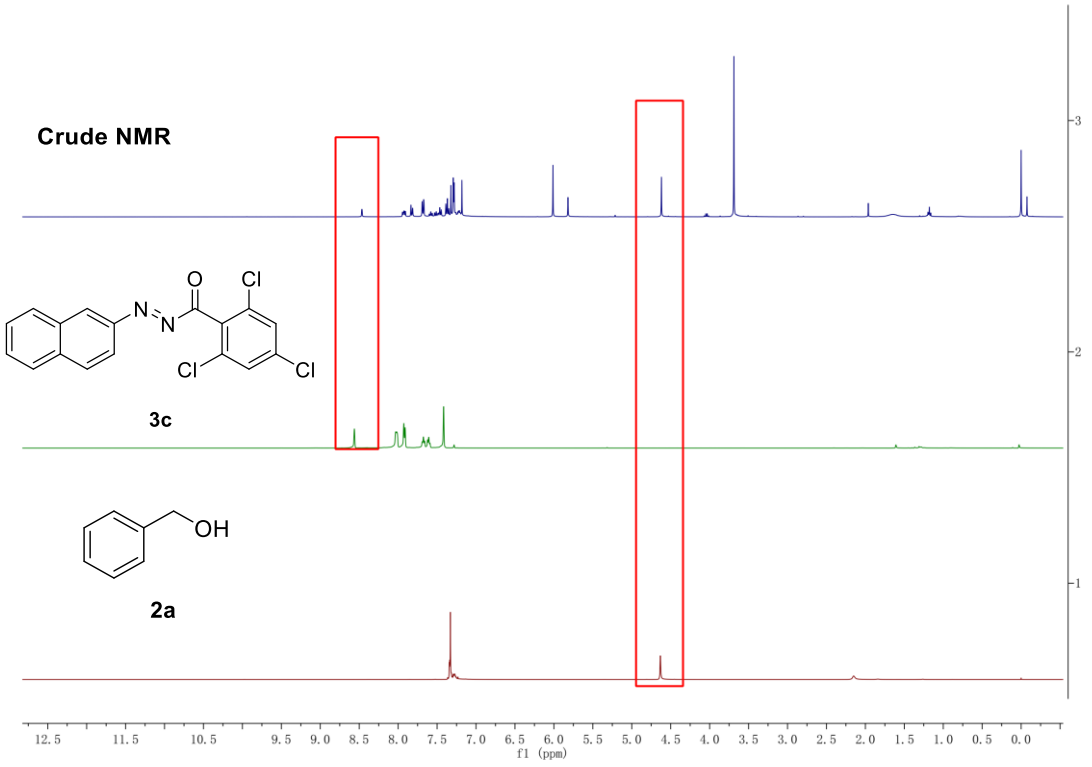
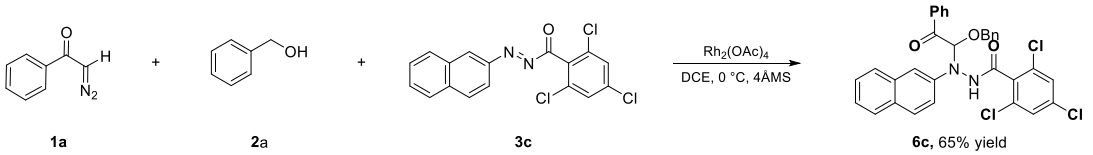


Figure S2

Control reaction (c):



To a 10-mL oven-dried vial with a magnetic stirring bar, Benzyl alcohol **2a** (13.0 mg, 0.12 mmol), Azonaphthalenes compound **3c** (36.3 mg, 0.1 mmol), $Rh_2(OAc)_4$ (1.1 mg, 2.5 mol%), 4Å molecular sieves (100 mg) and anhydrous DCE (1 mL) were added in sequence under atmosphere of argon, the mixture was stirred at 0 ℃ for 10 minutes, and **1a** (21.9 mg, 0.15 mmol) in anhydrous DCE (1 mL) were added to the above mixture via a syringe pump for 1 h at 0 ℃ under argon atmosphere. The crude reaction mixture was evaporated in *vacuo* after filtration and the residue was purified by flash column chromatography on silica gel (Hexanes : EtOAc = 20:1 to 15:1) to give the pure product **6c** in 65% yield (38.23 mg).

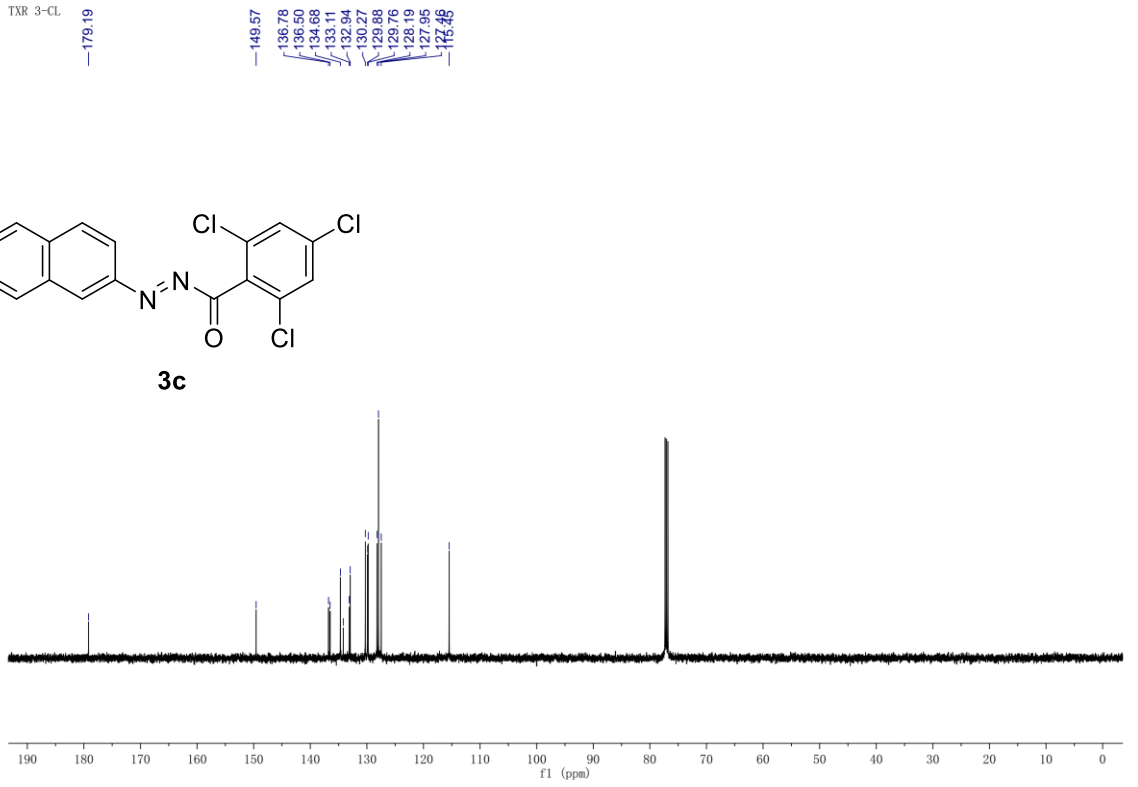
7. Reference:

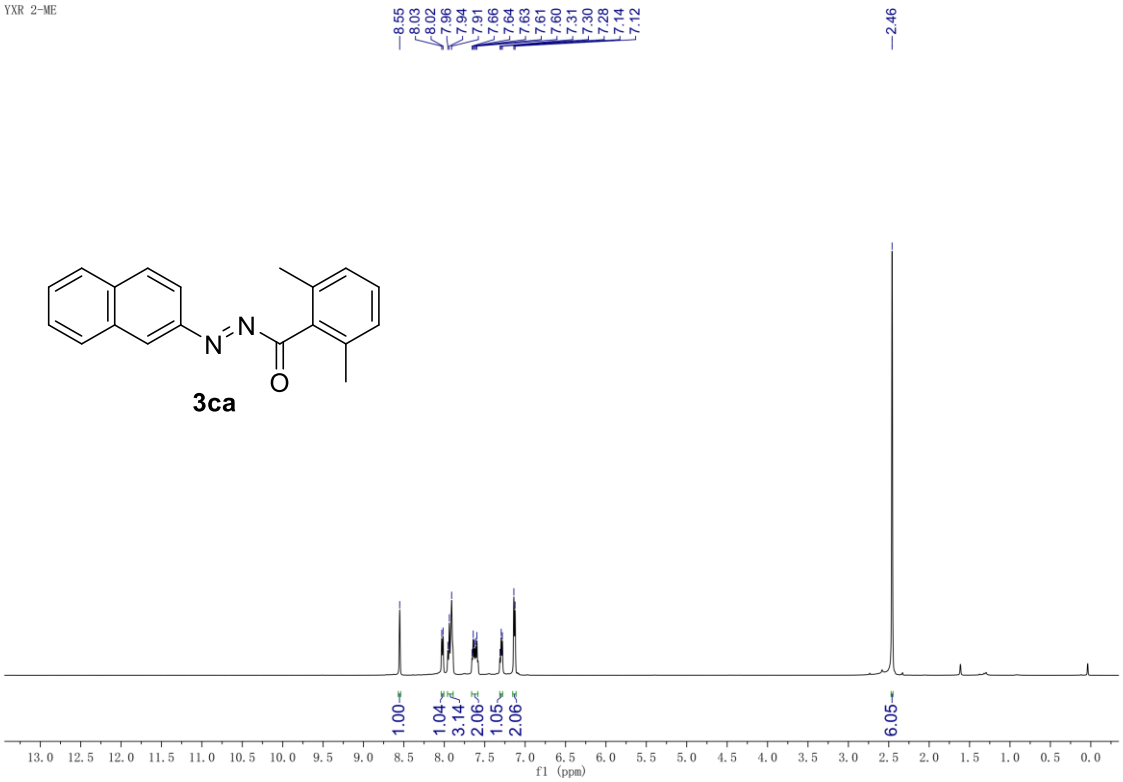
[1] B. S. Kale, H. Fu. Lee, R. S. Liu, *Adv. Synth. Catal*. **2017**, 359, 402 – 409.

[2] L. W. Qi, J. H. Mao, J. Zhang, B. Tan, *Nat. Chem.* **2018**, *10*, 58-64.

[3] D. Uraguchi, M. Terada, *J. Am. Chem. Soc.* **2004**, *126*, 5356-5357.

8. NMR Spectra for Compounds 3, 5, 6, 7

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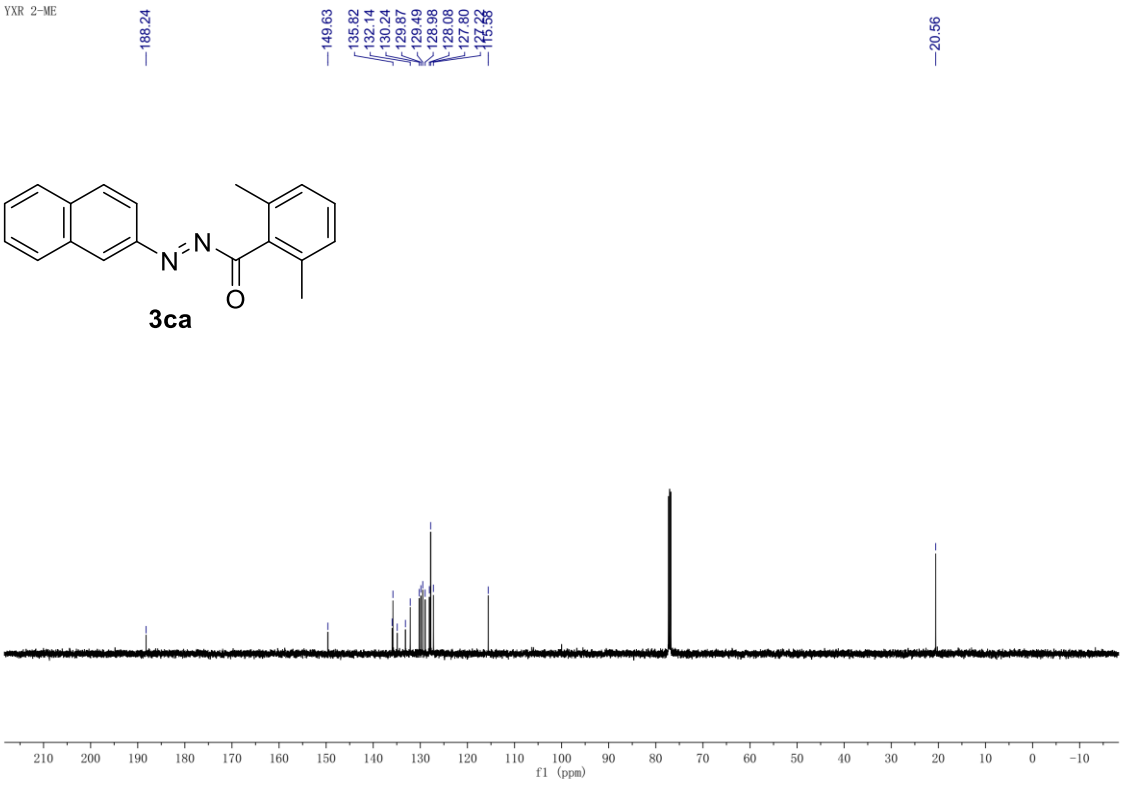
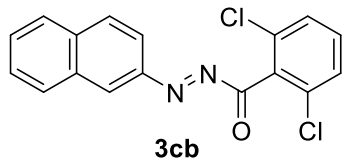
8.02
7.96
7.94
7.91
7.66
7.64
7.63
7.61
7.60
7.31
7.30
7.28
7.14
7.12
2.46
3ca
1.00
1.04
3.14
2.06
1.05
2.06
6.05
f1 (ppm)

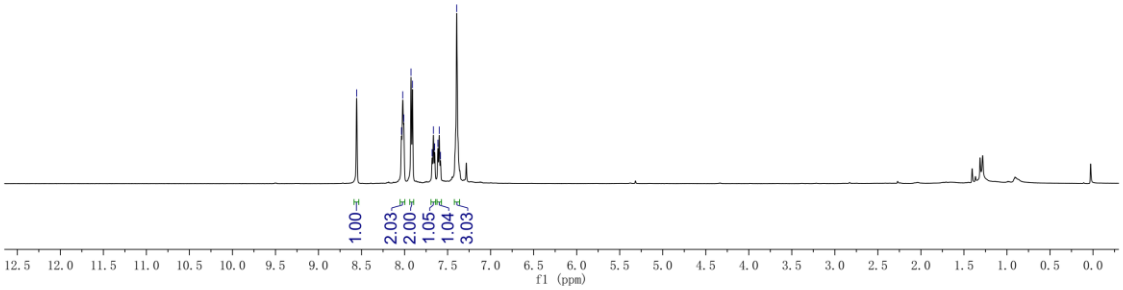

YXR 2-ME
188.24
149.63
135.82
132.14
130.24
129.87
129.49
128.98
128.08
127.80
20.56
3ca
f1 (ppm)

YXR 2-CL

8.56
8.04
8.02
8.01
7.93
7.91
7.68
7.67
7.65
7.61
7.60
7.58
7.39

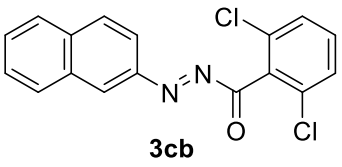


3cb



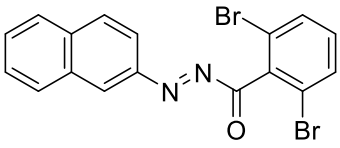
YXR 2-CL

179.95
149.61
136.66
134.26
132.25
131.30
130.20
129.68
128.17
127.78
115.38

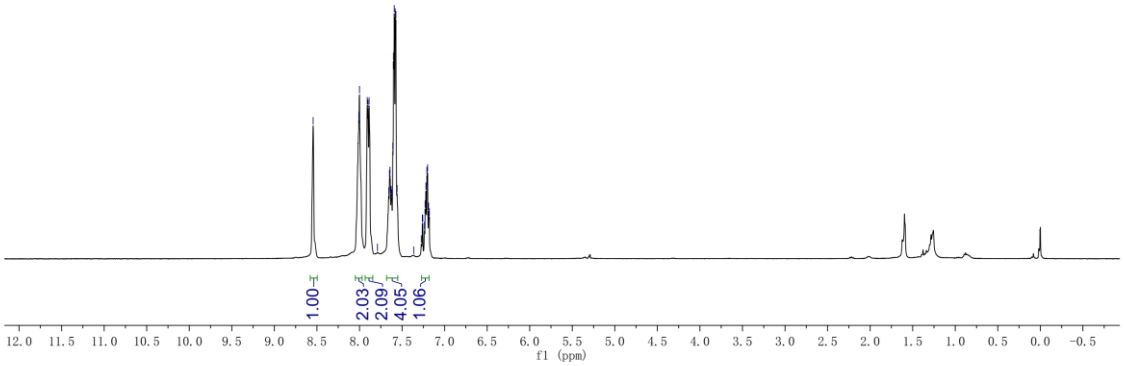


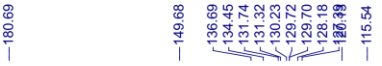
3cb


8.54
8.01
8.00
7.91
7.90
7.89
7.79
7.66
7.65
7.64
7.64
7.63
7.62
7.61
7.60
7.59
7.58
7.58
7.57
7.56
7.36
7.27
7.26
7.26
7.24
7.23
7.22
7.21
7.20
7.19
7.18


Br
N
N
O
Br

3cc


1.00
2.03
2.09
4.05
1.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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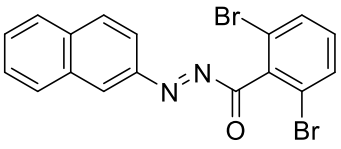
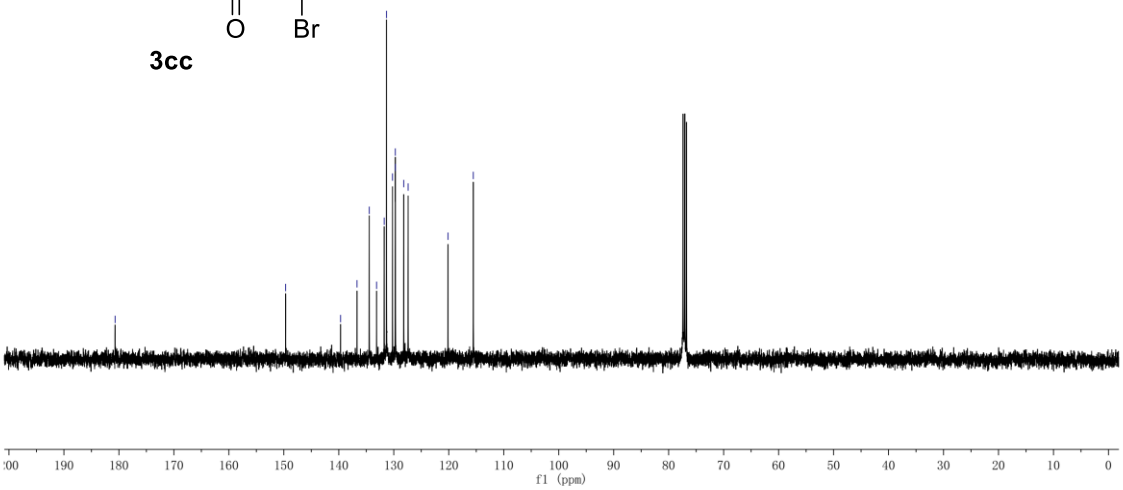
149.68
136.69
134.45
131.74
131.32
130.23
129.72
129.70
128.18
115.54


Br
N
N
O
Br

3cc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f1 (ppm)


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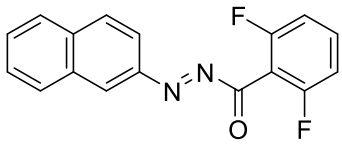
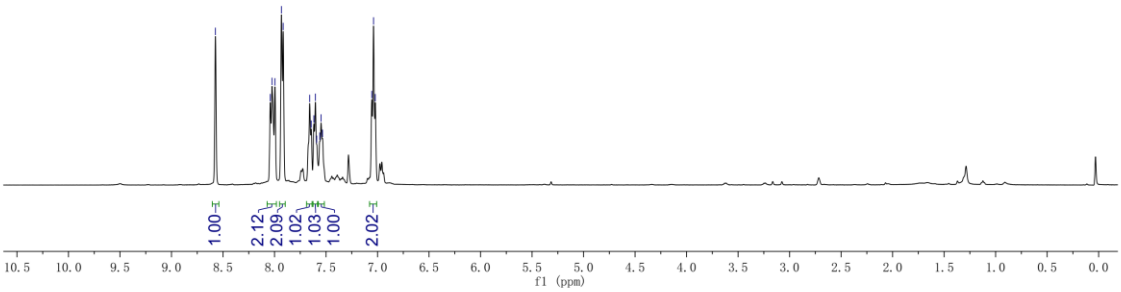
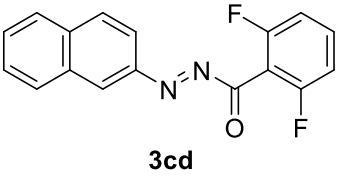
8.04
8.02
8.00
7.93
7.92
7.66
7.60
7.55
7.06
7.04
7.02


F
N
N
O
F

3cd

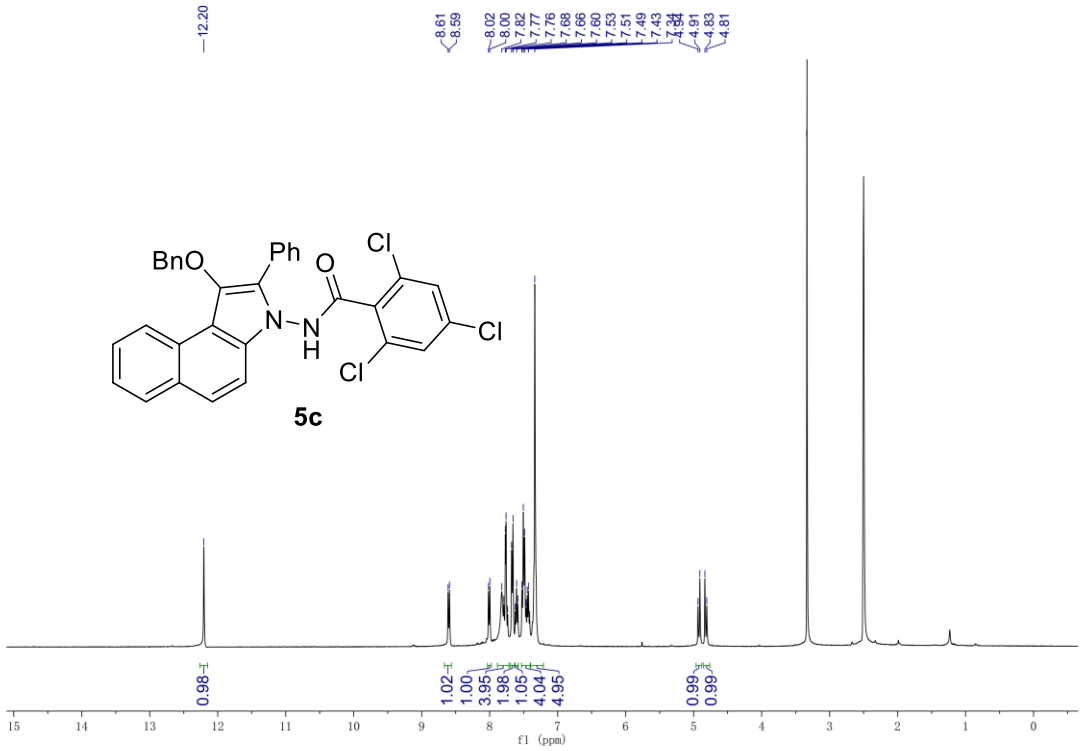

1.00
2.12
2.09
1.02
1.03
1.00
2.02
f1 (ppm)


177.69
162.34
162.29
160.29
149.53
136.31
134.35
133.14
132.82
130.05
129.63
129.31
128.12
112.36
112.33
112.19
112.16


F
N
N
O
F

3cd

f1 (ppm)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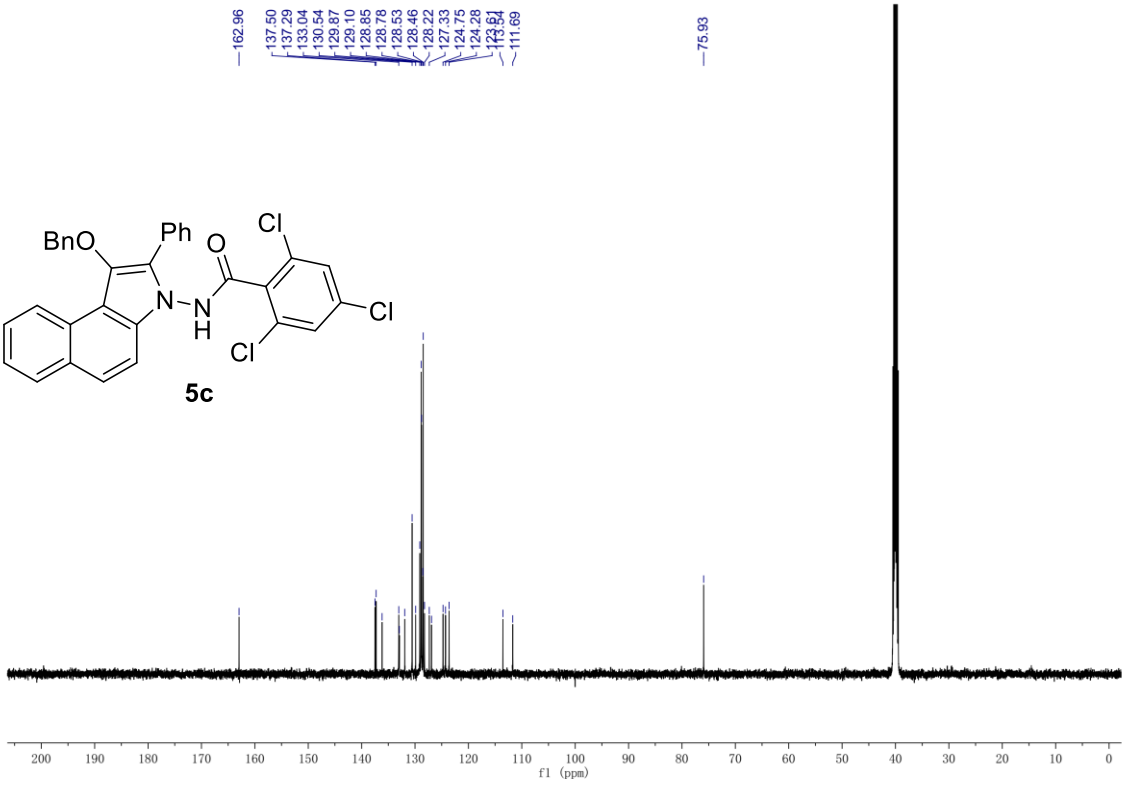
8.00
7.82
7.77
7.76
7.68
7.66
7.60
7.53
7.51
7.49
7.43
4.91
4.83
4.81
BnO
Ph
O
N
N
H
Cl
Cl
Cl
5c
0.98
1.02
1.00
3.95
1.98
1.05
4.04
4.95
0.99
0.99
f1 (ppm)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137.50
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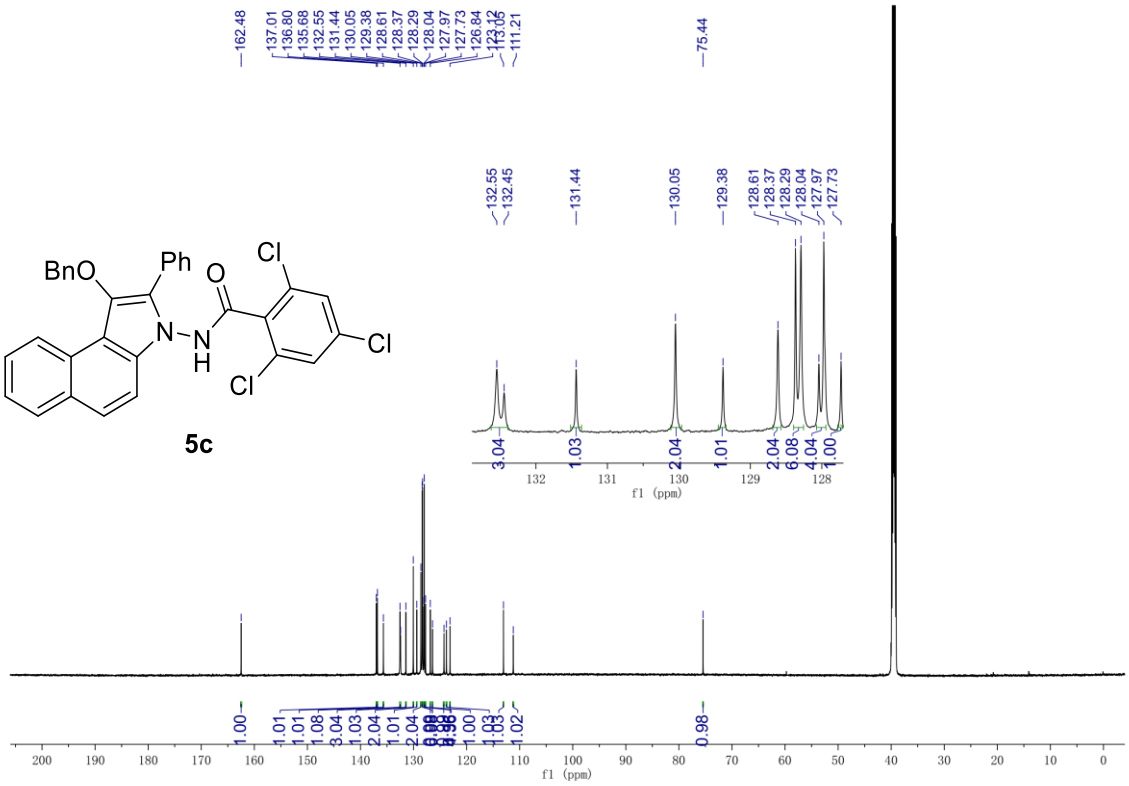
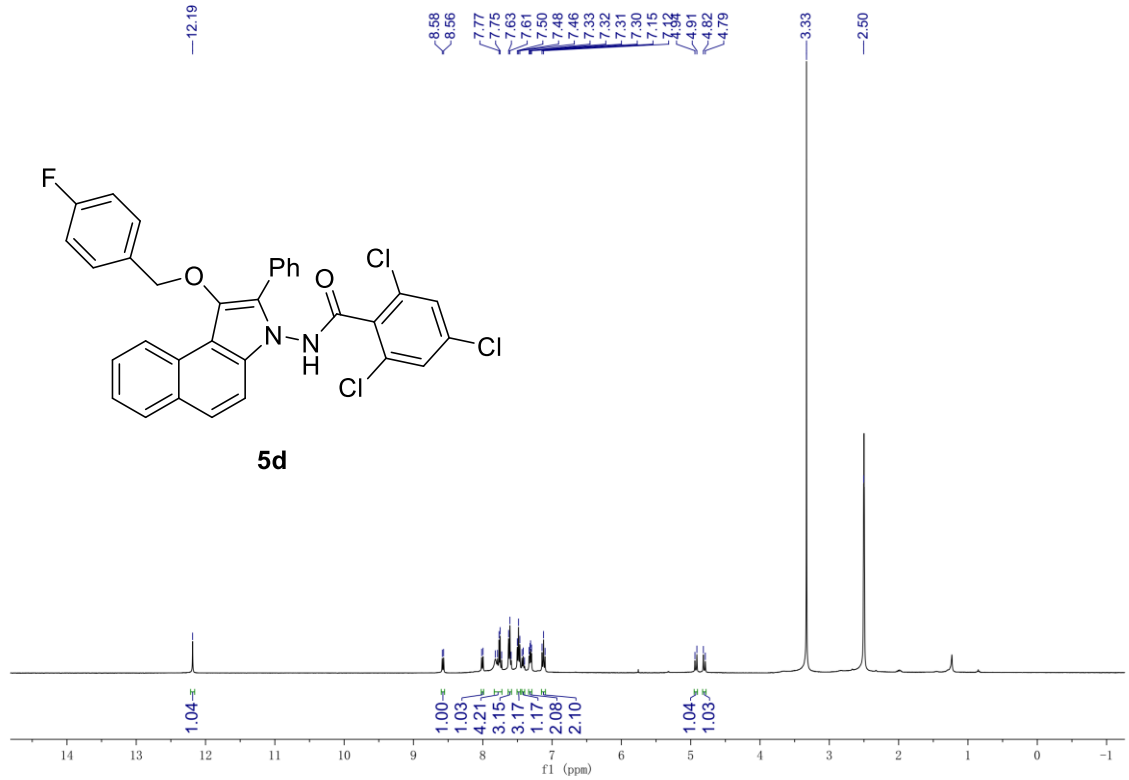
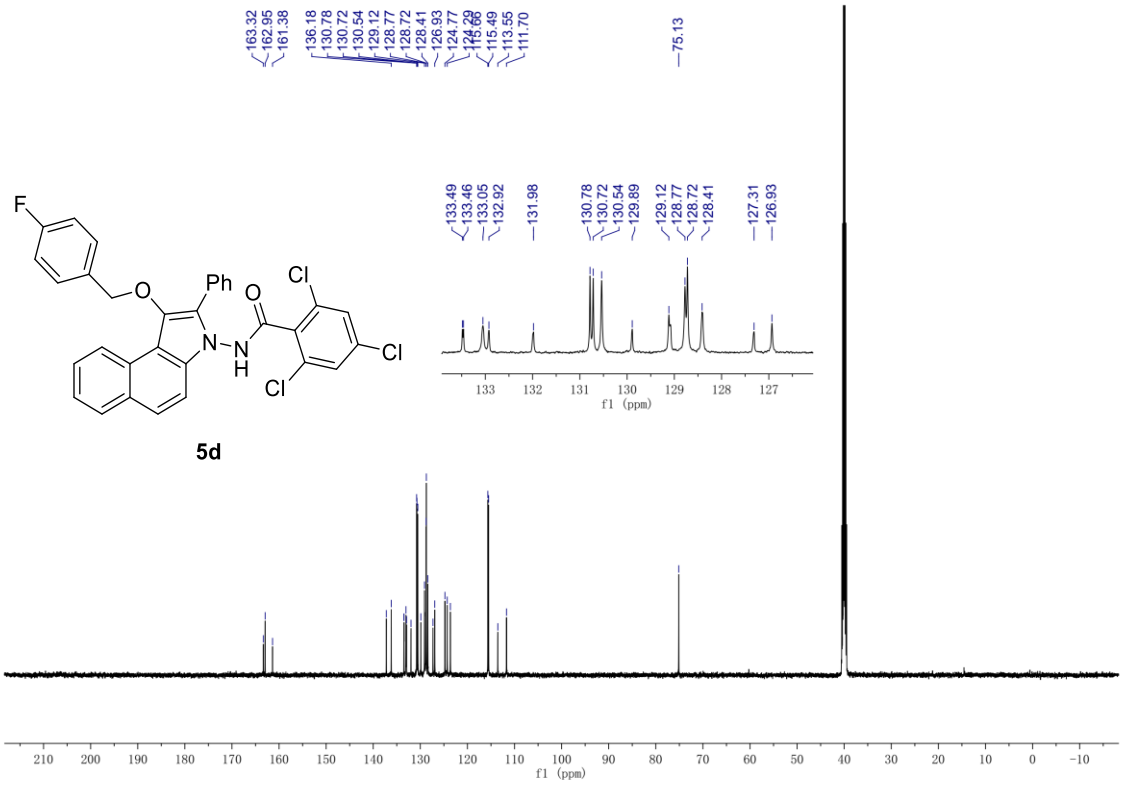
130.54
129.87
129.10
128.85
128.78
128.53
128.46
128.22
127.33
124.75
124.28
111.69
75.93
BnO
Ph
O
N
N
H
Cl
Cl
Cl
5c
f1 (ppm)

Quantitative ^{13}C spectrum for compound **5c:**



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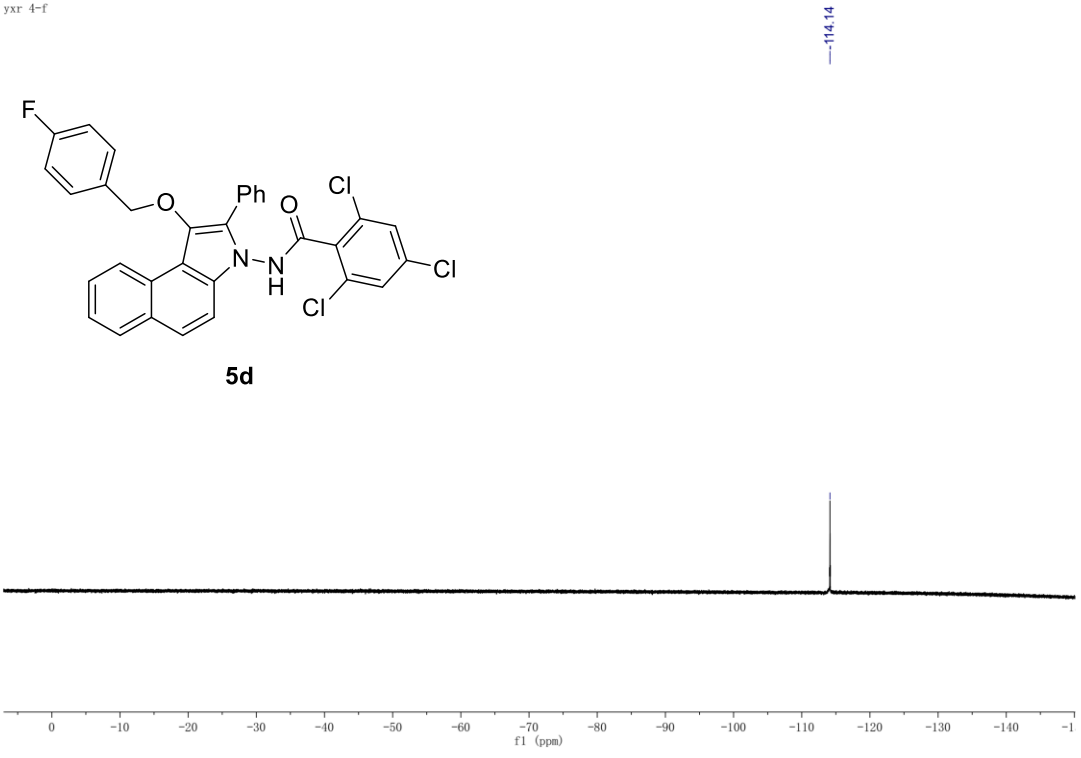
161.38
136.18
130.78
130.72
130.54
129.12
128.77
128.72
128.41
126.93
124.77
115.49
113.55
111.70
75.13
133.49
133.46
133.05
132.92
131.98
130.78
130.72
130.54
129.89
129.12
128.77
128.72
128.41
127.31
126.93
F
O
Ph
O
N
N
H
Cl
Cl
Cl
f1 (ppm)
f1 (ppm)

5d

yxr 4-f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O
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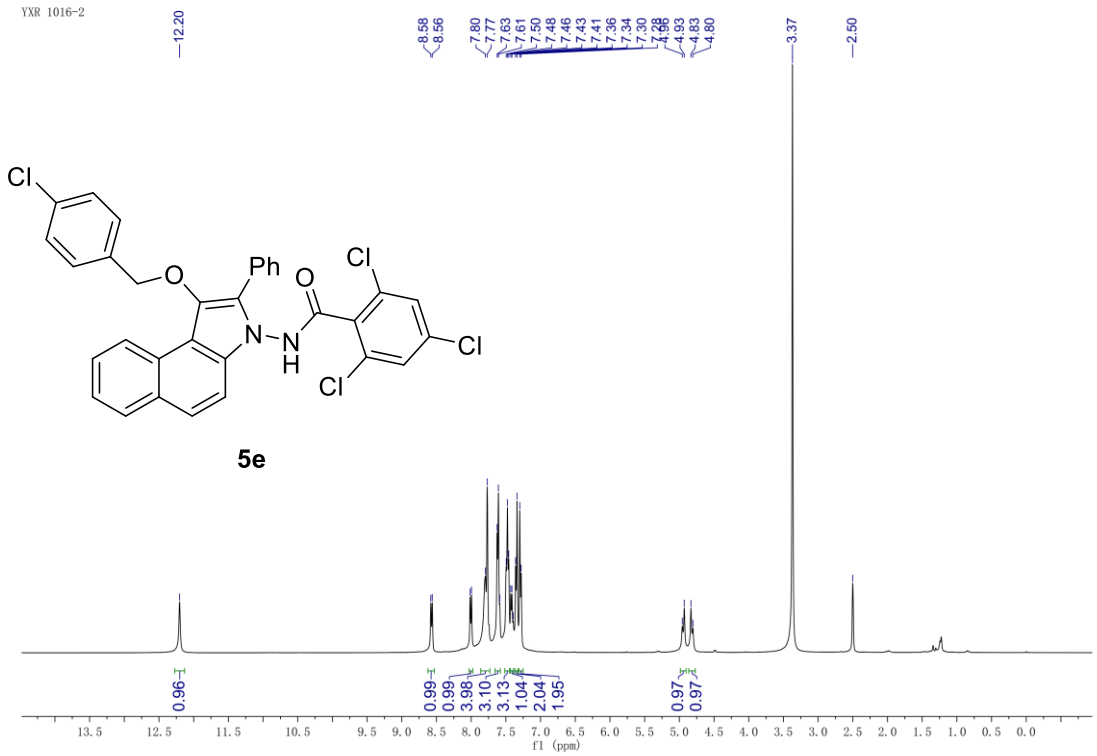
H
Cl
Cl
Cl
f1 (ppm)

5d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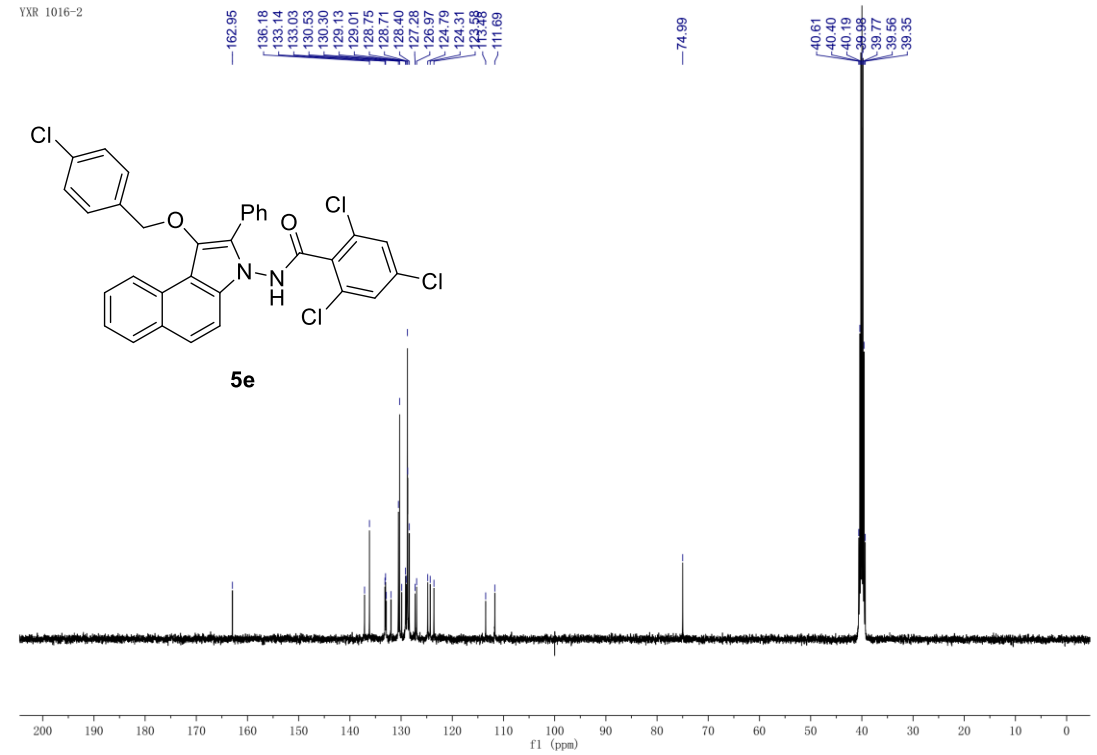
7.80
7.77
7.63
7.61
7.50
7.48
7.46
7.43
7.41
7.36
7.34
7.30
4.93
4.83
4.80
3.37
2.50
Cl
O
Ph
N
N
H
O
Cl
Cl
Cl
5e
0.96
0.99
0.99
3.98
3.10
3.13
1.04
2.04
1.95
0.97
0.97
f1 (ppm)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136.18
133.14
133.03
130.53
130.30
129.13
129.01
128.75
128.71
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127.28
126.97
124.79
124.31
123.58
123.38
111.69
74.99
40.61
40.40
40.19
39.98
39.77
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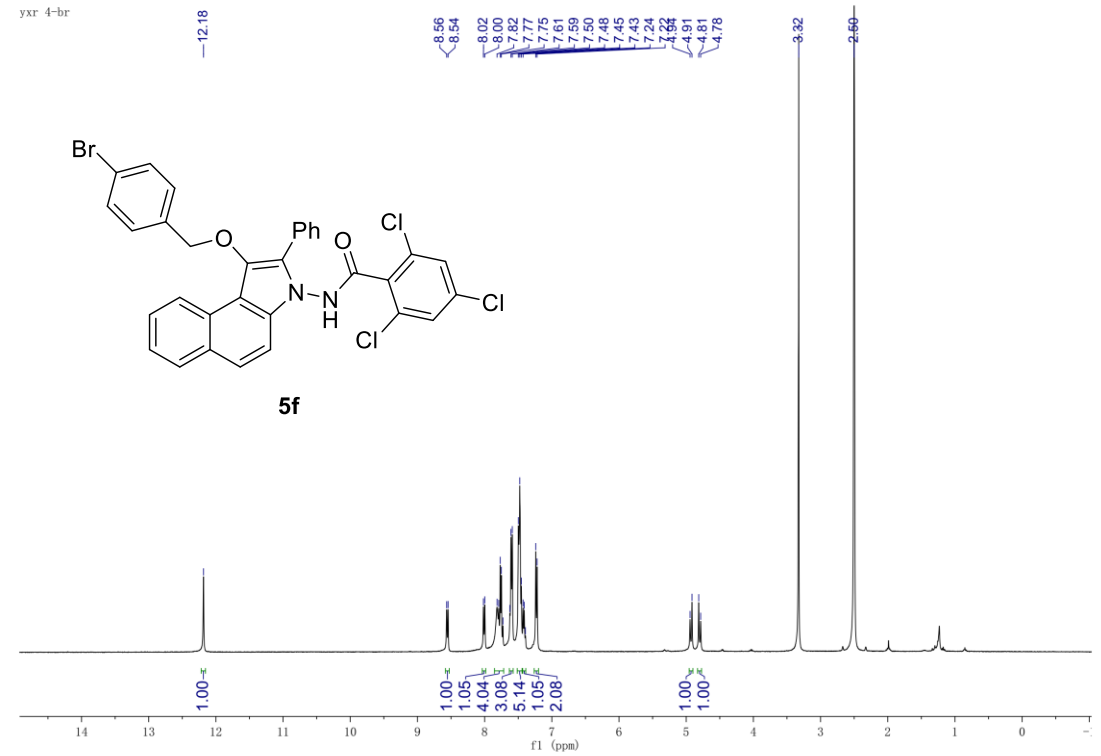
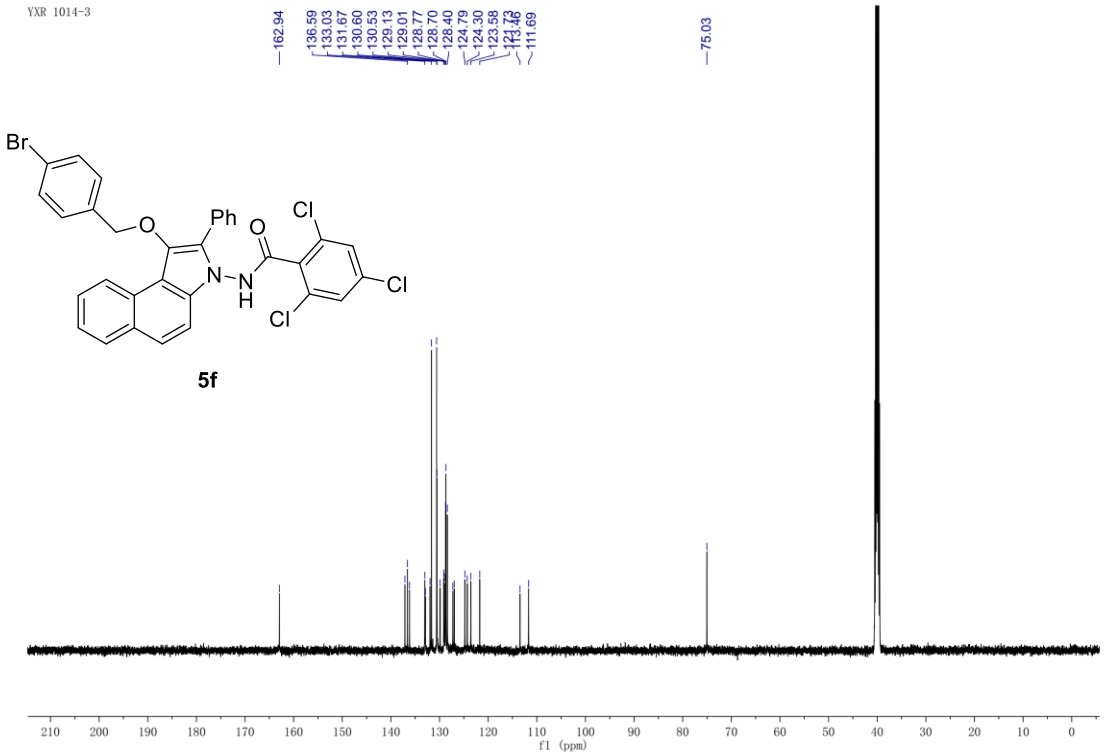
39.35
Cl
O
Ph
N
N
H
O
Cl
Cl
Cl
5e
f1 (ppm)


yxr 4-br
12.18
8.56
8.54
8.02
8.00
7.82
7.77
7.75
7.61
7.59
7.50
7.48
7.45
7.43
7.24
4.91
4.81
4.78
3.32
2.60
Br
O
Ph
O
Cl
N
N
H
Cl
Cl
1.00
1.00
1.05
4.04
3.08
5.14
1.05
2.08
1.00
1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

5f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129.01
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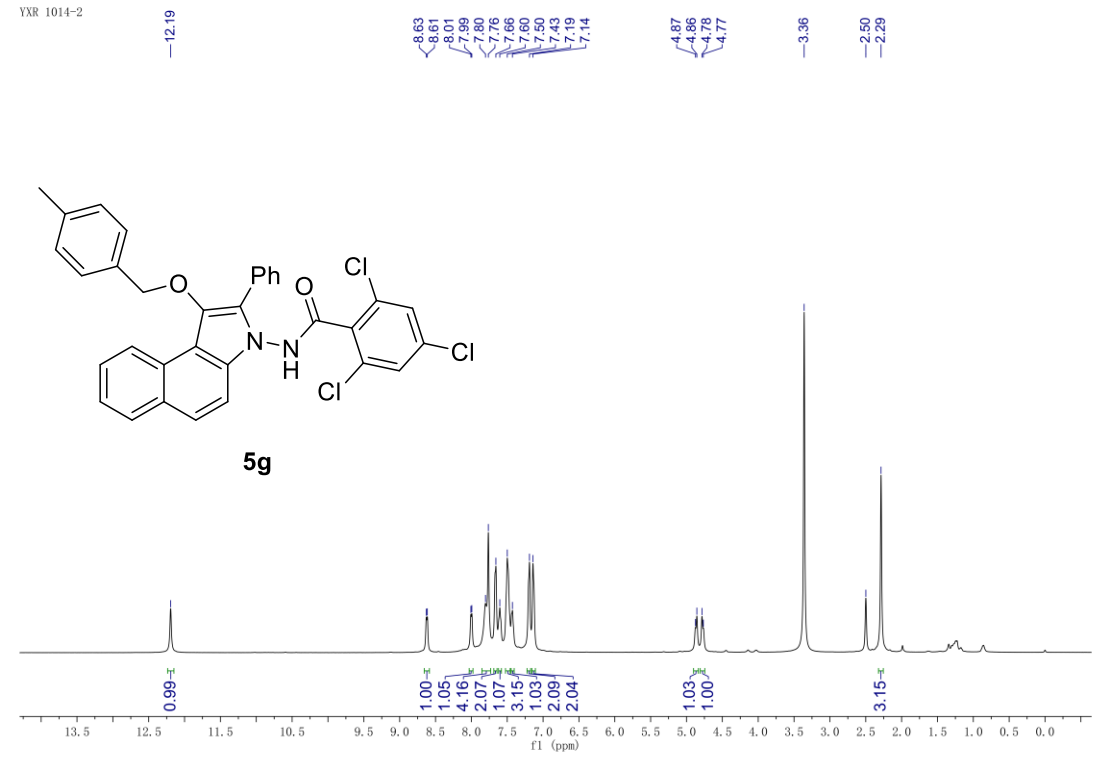
128.70
128.40
124.79
124.30
123.58
111.69
75.03
Br
O
Ph
O
Cl
N
N
H
Cl
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5f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8.01
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7.66
7.60
7.50
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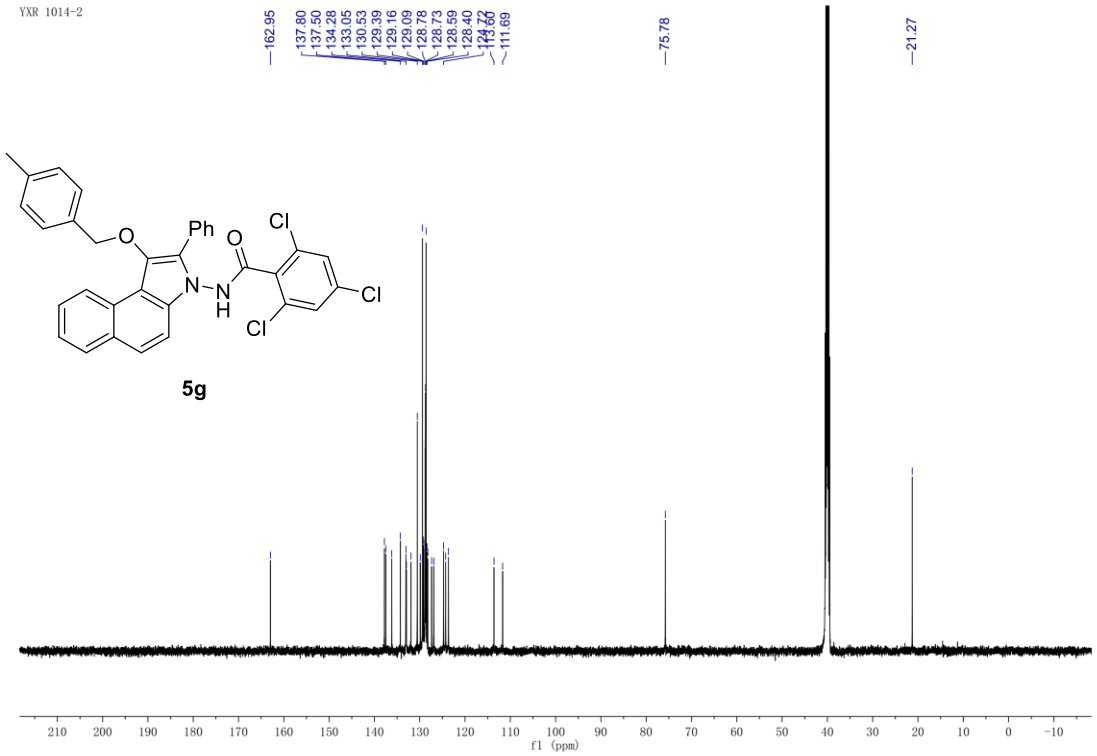
7.19
7.14
4.87
4.86
4.78
4.77
3.36
2.50
2.29
Ph
O
N
N
H
O
Cl
Cl
Cl
5g
0.99
1.00
1.05
4.16
2.07
1.07
3.15
1.03
2.09
2.04
1.03
1.00
3.15
f1 (ppm)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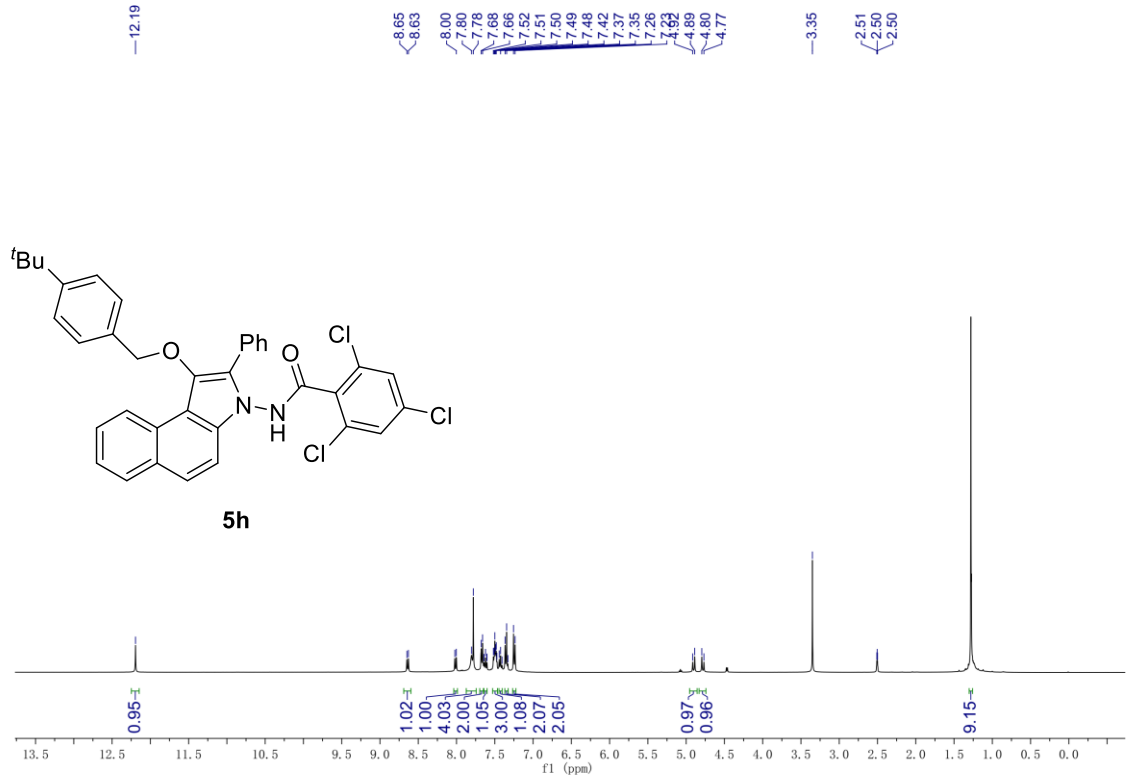
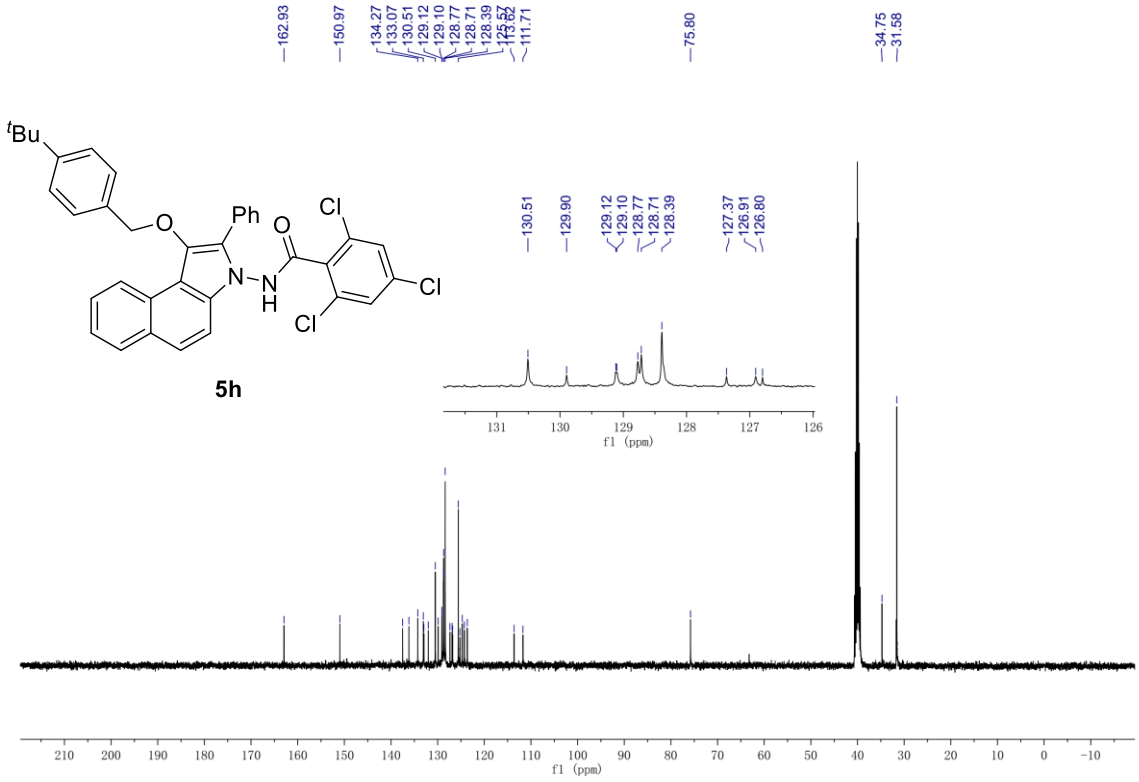
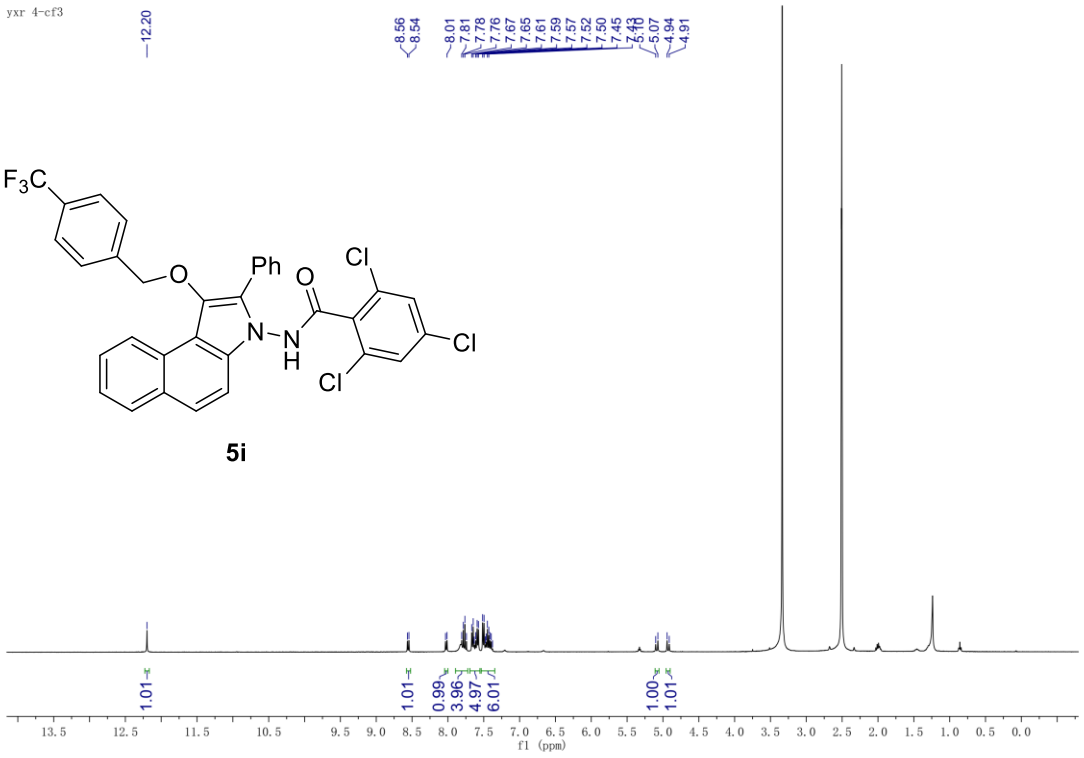
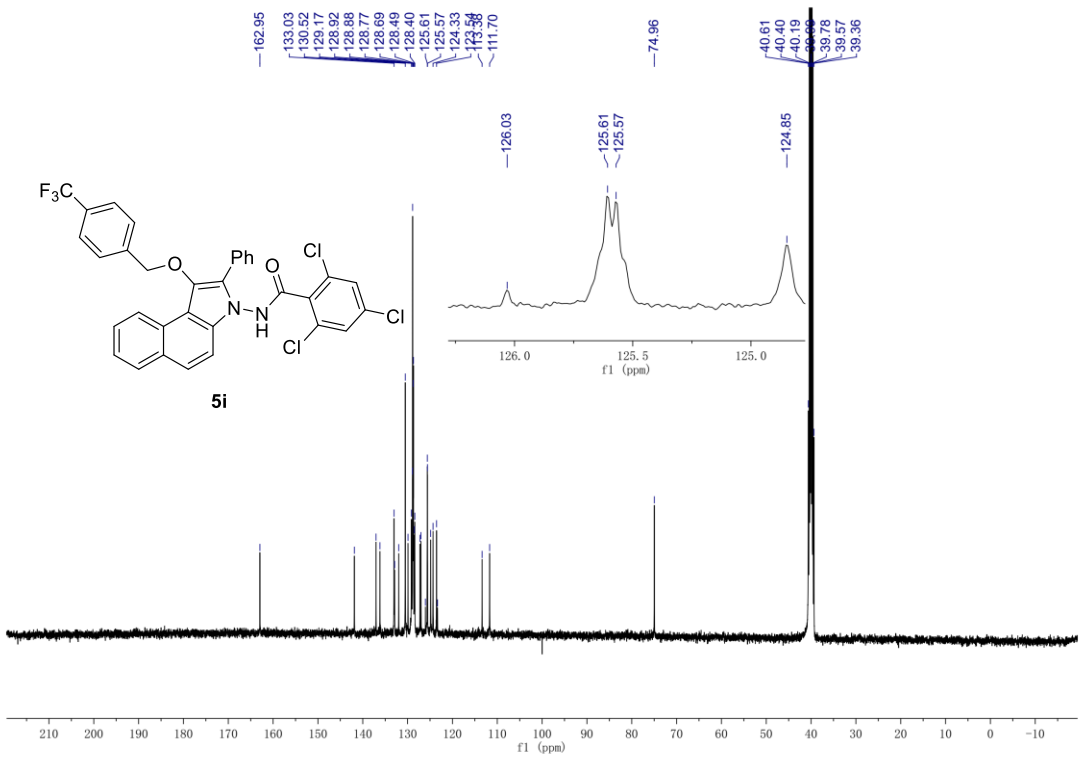
162.95
137.80
137.50
134.28
133.05
130.53
129.39
129.16
129.09
128.78
128.73
128.59
128.40
111.69
75.78
21.27
Ph
O
N
N
H
O
Cl
Cl
Cl
5g
f1 (ppm)

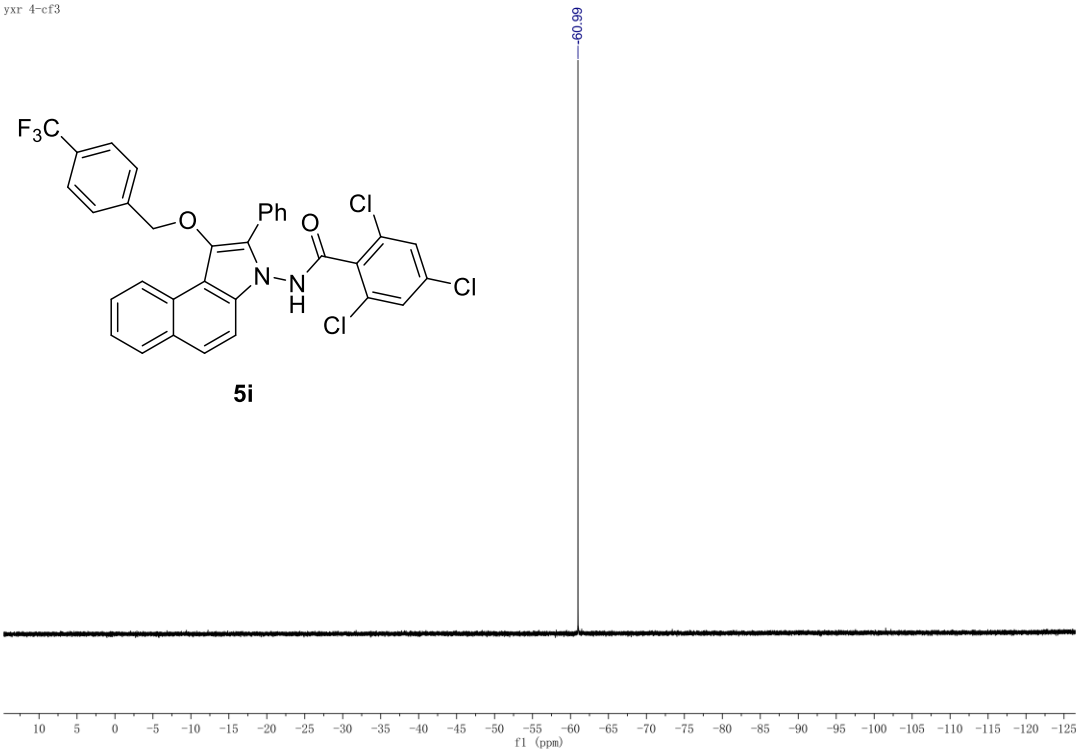

12.19
8.65
8.63
8.00
7.80
7.78
7.68
7.66
7.52
7.51
7.50
7.49
7.48
7.42
7.37
7.35
7.26
4.89
4.80
4.77
3.35
2.51
2.50
2.50
tBu
O
Ph
N
N
H
O
Cl
Cl
Cl
5h
0.95
1.02
1.00
4.03
2.00
1.05
3.00
1.08
2.07
2.05
0.97
0.96
9.15
f1 (ppm)


162.93
150.97
134.27
133.07
130.51
129.12
129.10
128.77
128.71
128.39
125.57
113.62
111.71
75.80
34.75
31.58
130.51
129.90
129.12
129.10
128.77
128.71
128.39
127.37
126.91
126.80
tBu
O
Ph
N
N
H
O
Cl
Cl
Cl
5h
f1 (ppm)
f1 (ppm)


yxr 4-cf3
12.20
8.56
8.54
8.01
7.81
7.78
7.76
7.67
7.65
7.61
7.59
7.57
7.52
7.50
7.45
5.18
5.07
4.94
4.91
F3C
O
Ph
N
N
H
O
Cl
Cl
Cl
5i
1.01
1.01
0.99
3.96
4.97
6.01
1.00
1.01
f1 (ppm)

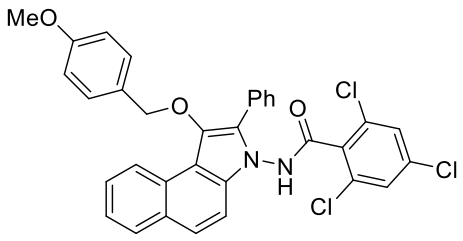

162.95
133.03
130.52
129.17
128.92
128.88
128.77
128.69
128.49
128.40
125.61
125.57
124.33
123.54
123.38
111.70
74.96
40.61
40.40
40.19
39.78
39.57
39.36
126.03
125.61
125.57
124.85
126.0
125.5
125.0
f1 (ppm)
F3C
O
Ph
N
N
H
O
Cl
Cl
Cl
5i
f1 (ppm)

yxr 4-cf3

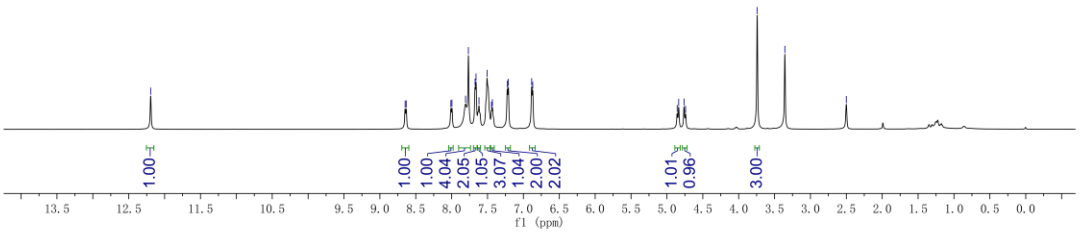


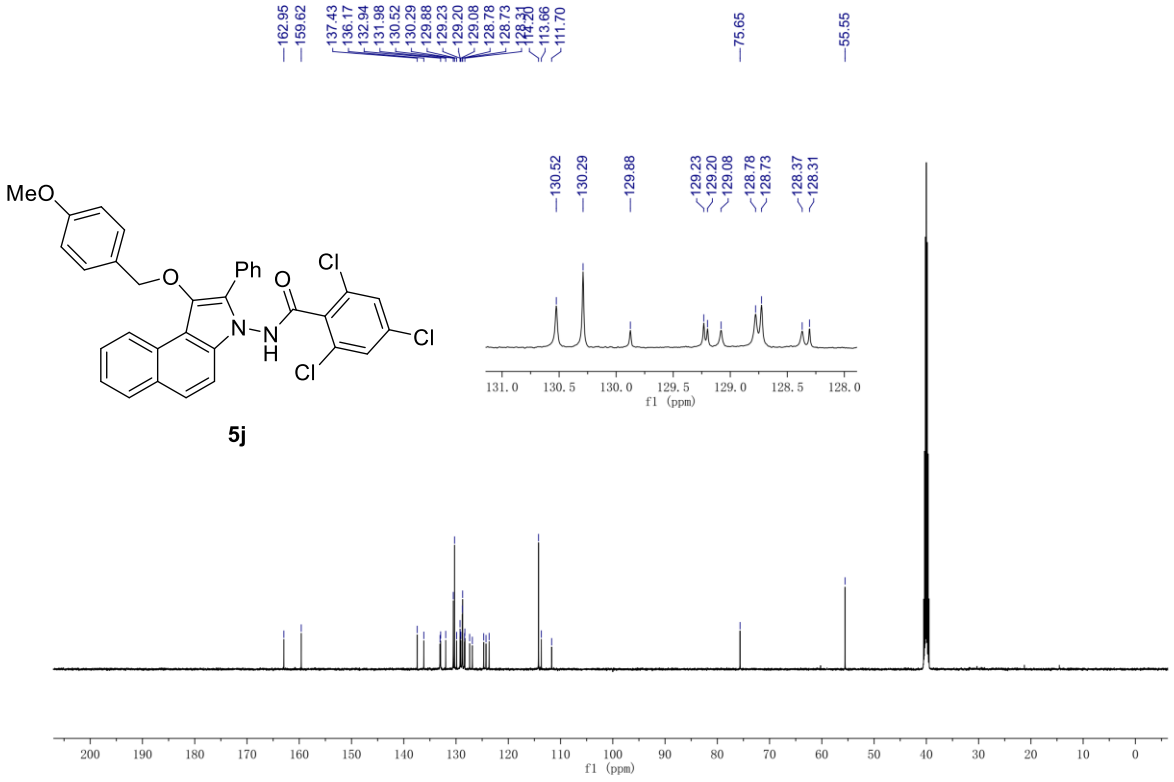
5i

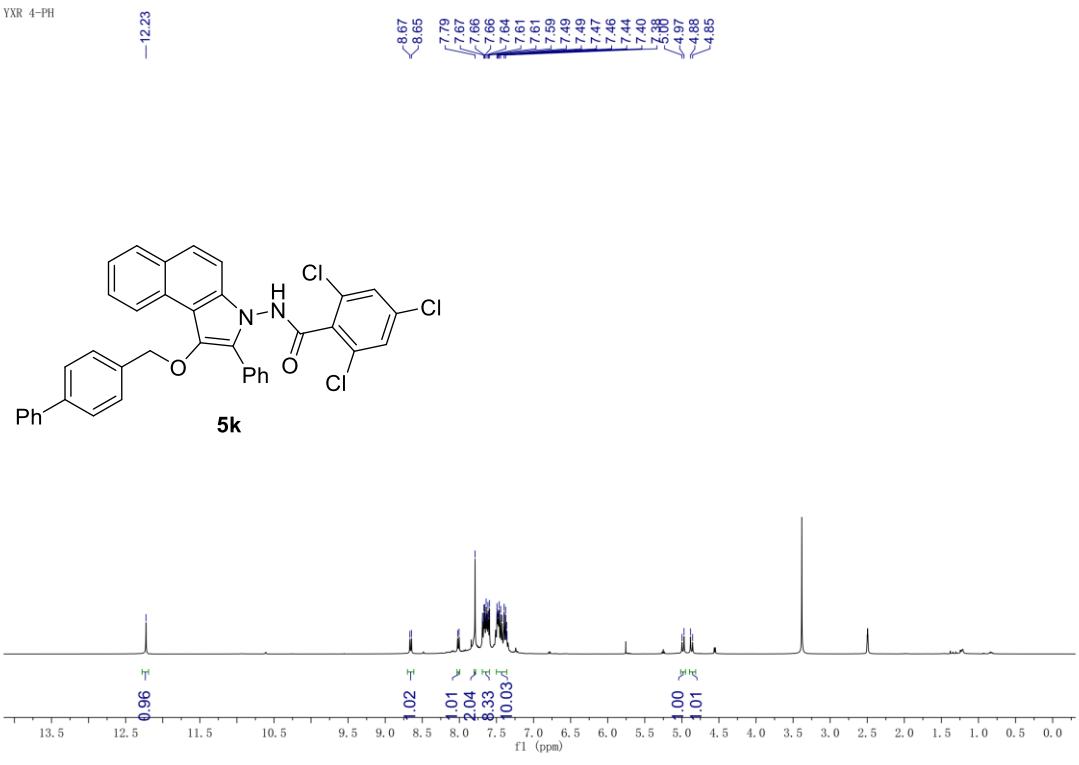
YXR 1014-6

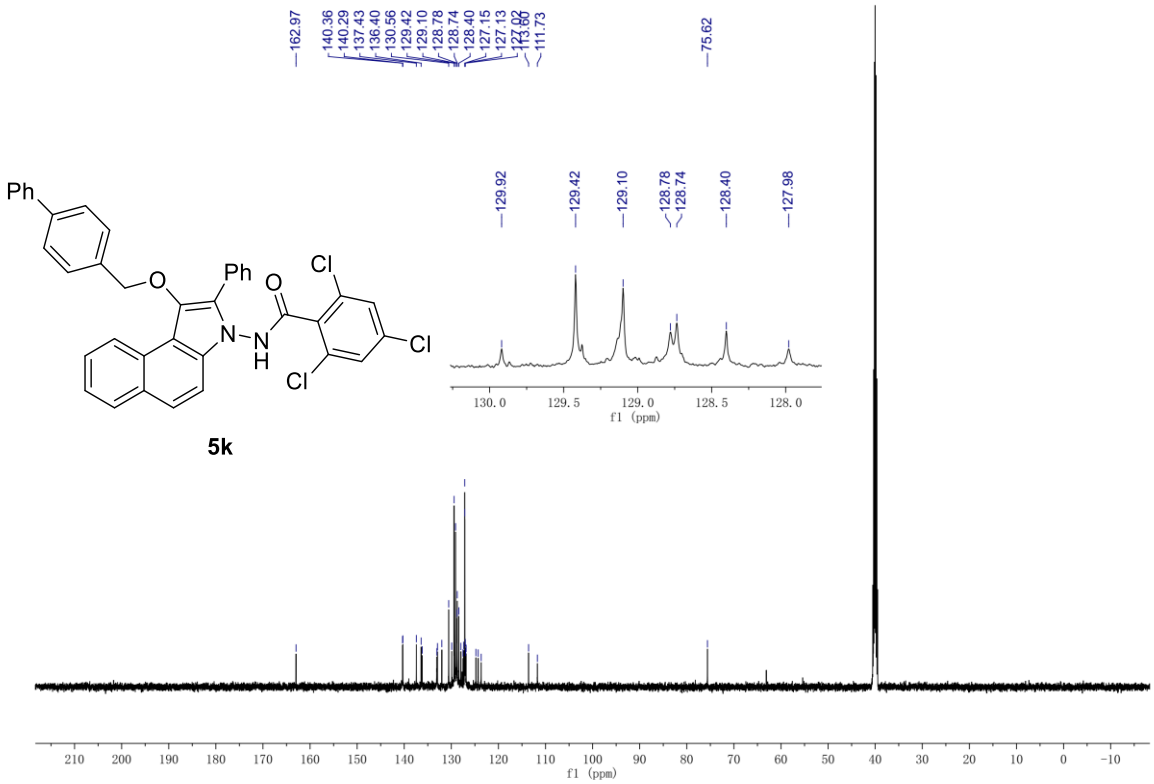


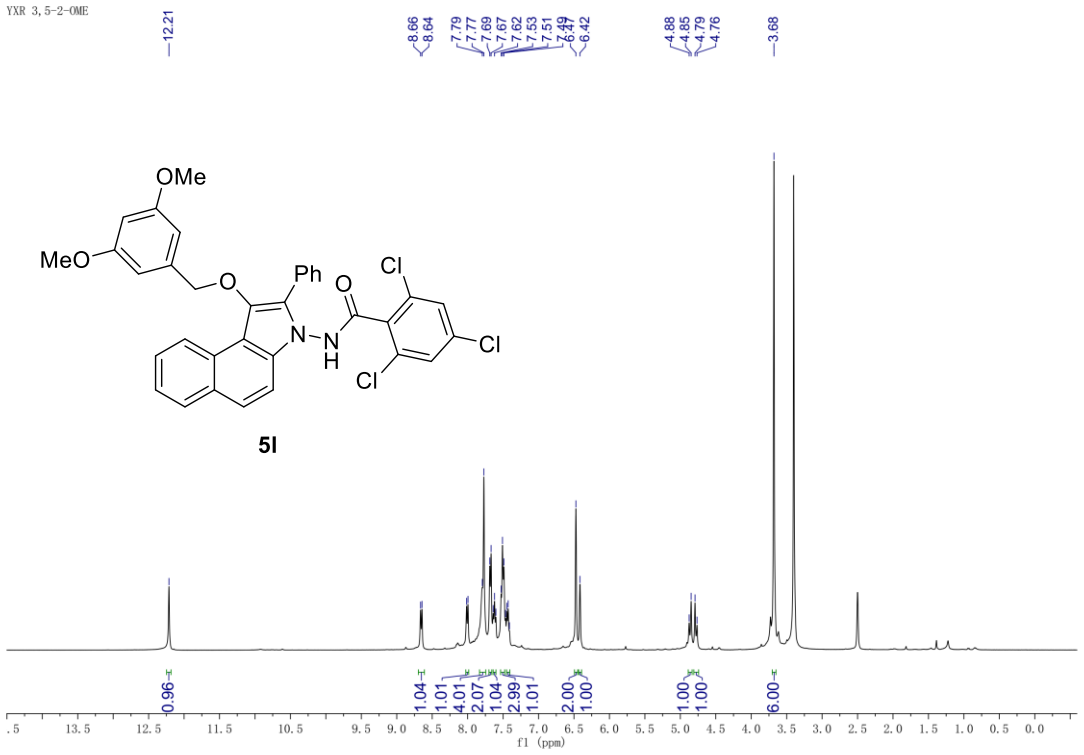
5j

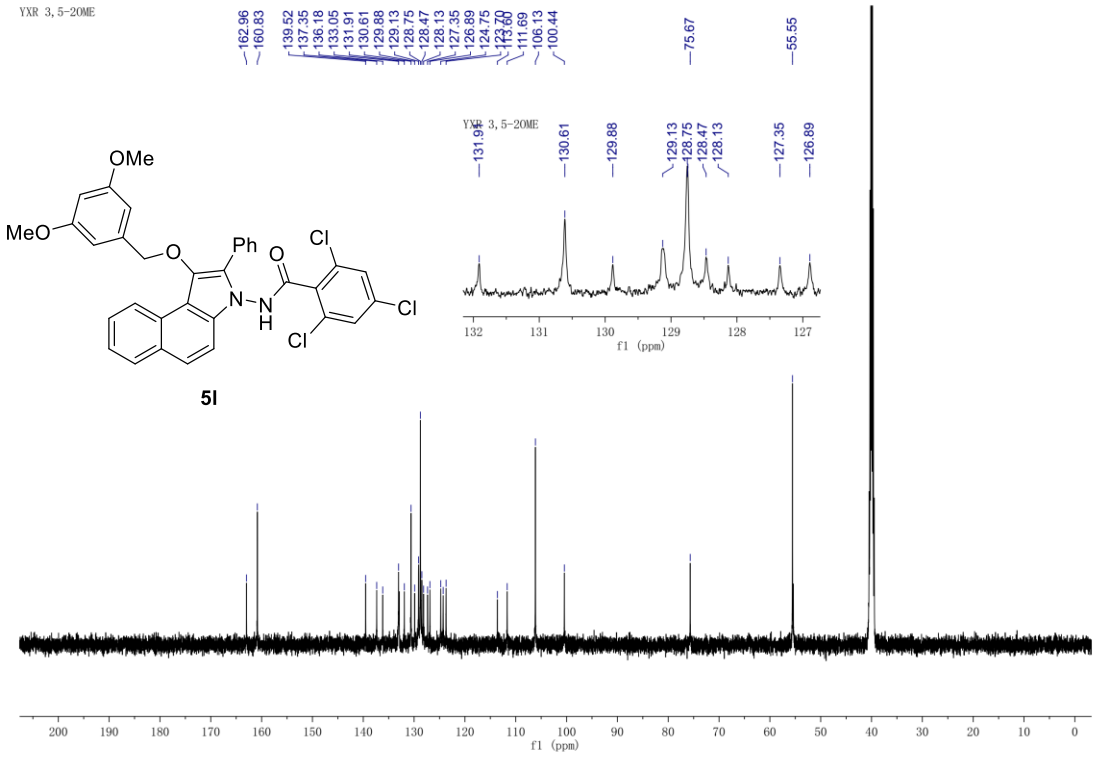



162.95
159.62
137.43
136.17
132.94
131.98
130.52
130.29
129.88
129.23
129.20
129.08
128.78
128.73
128.31
128.20
113.66
111.70
75.65
55.55
MeO
O
Ph
N
N
H
O
Cl
Cl
Cl
5j
130.52
130.29
129.88
129.23
129.20
129.08
128.78
128.73
128.37
128.31
131.0
130.5
130.0
129.5
129.0
128.5
128.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

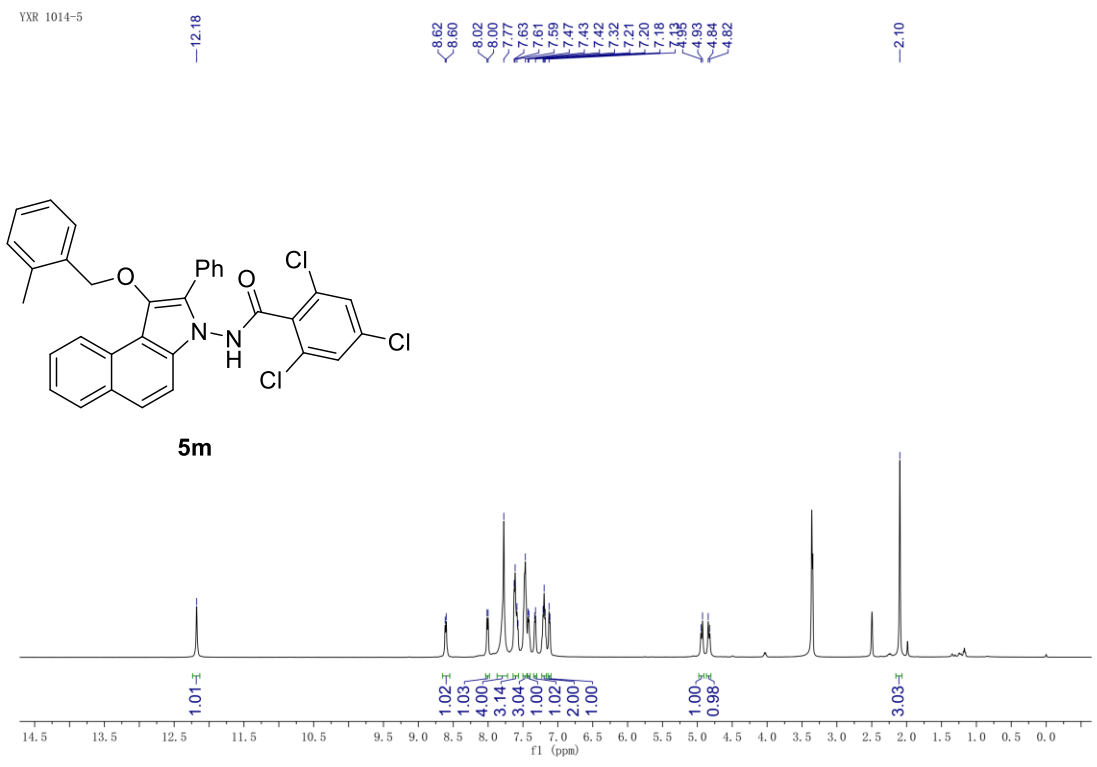

YXR 4-PH
12.23
8.67
8.65
7.79
7.67
7.66
7.66
7.64
7.61
7.61
7.59
7.49
7.49
7.47
7.46
7.44
7.40
5.08
4.97
4.88
4.85
N
H
N
O
Cl
Cl
Cl
O
Ph
Ph
5k
0.96
1.02
1.01
2.04
8.33
10.03
1.00
1.01
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.97
140.36
140.29
137.43
136.40
130.56
129.42
129.10
128.78
128.74
128.40
127.15
127.13
111.73
75.62
129.92
129.42
129.10
128.78
128.74
128.40
127.98
Ph
O
Ph
N
N
H
O
Cl
Cl
Cl
5k
130.0
129.5
129.0
128.5
128.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

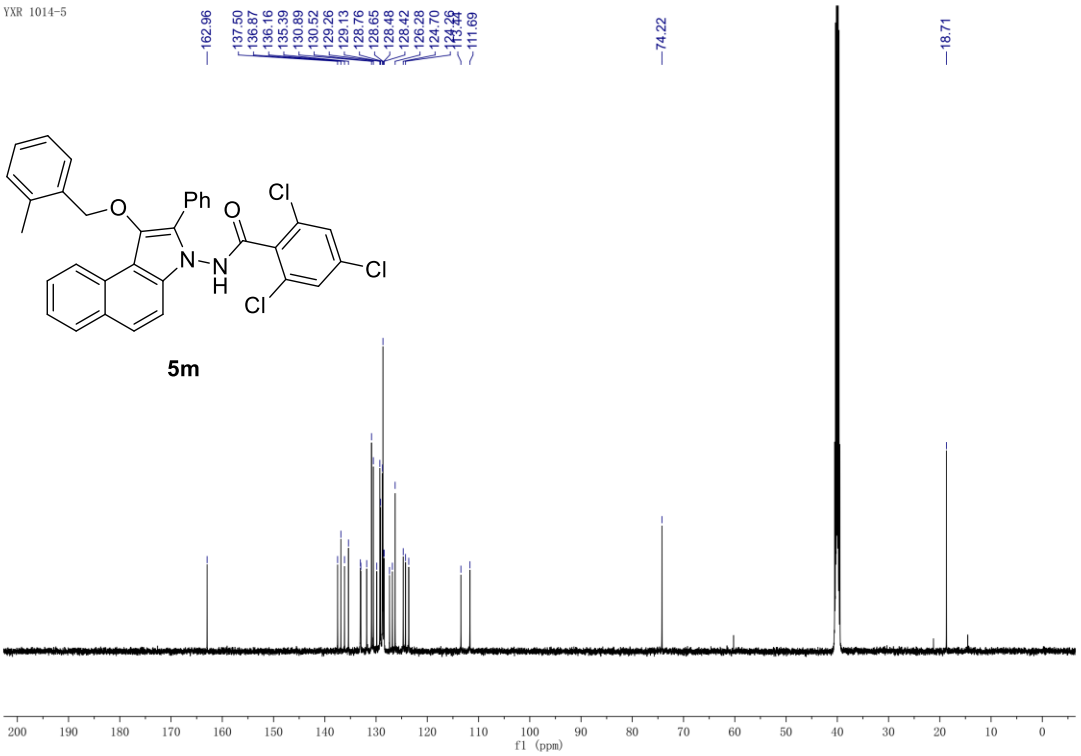

YXR 3,5-2-OME
12.21
8.66
8.64
7.79
7.77
7.69
7.67
7.62
7.53
7.51
6.42
4.88
4.85
4.79
4.76
3.68
OMe
MeO
O
Ph
O
N
N
H
Cl
Cl
Cl
5l
0.96
1.04
1.01
4.01
2.07
1.04
2.99
1.01
2.00
1.00
1.00
1.00
6.00
.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

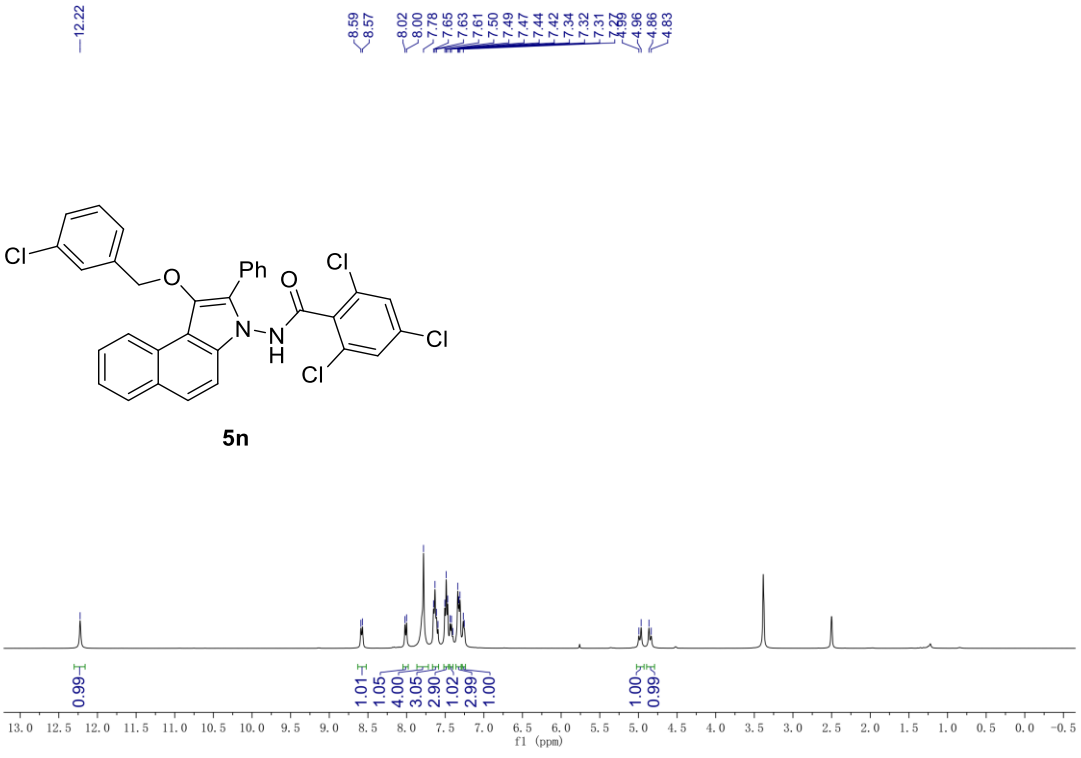

YXR 3,5-2OME
162.96
160.83
139.52
137.35
136.18
133.05
131.91
130.61
129.88
129.13
128.75
128.47
128.13
127.35
126.89
124.75
123.70
113.60
111.69
106.13
100.44
75.67
55.55
YXR 3,5-2OME
131.91
130.61
129.88
129.13
128.75
128.47
128.13
127.35
126.89
132
131
130
129
128
127
f1 (ppm)
OMe
MeO
O
Ph
O
N
N
H
Cl
Cl
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

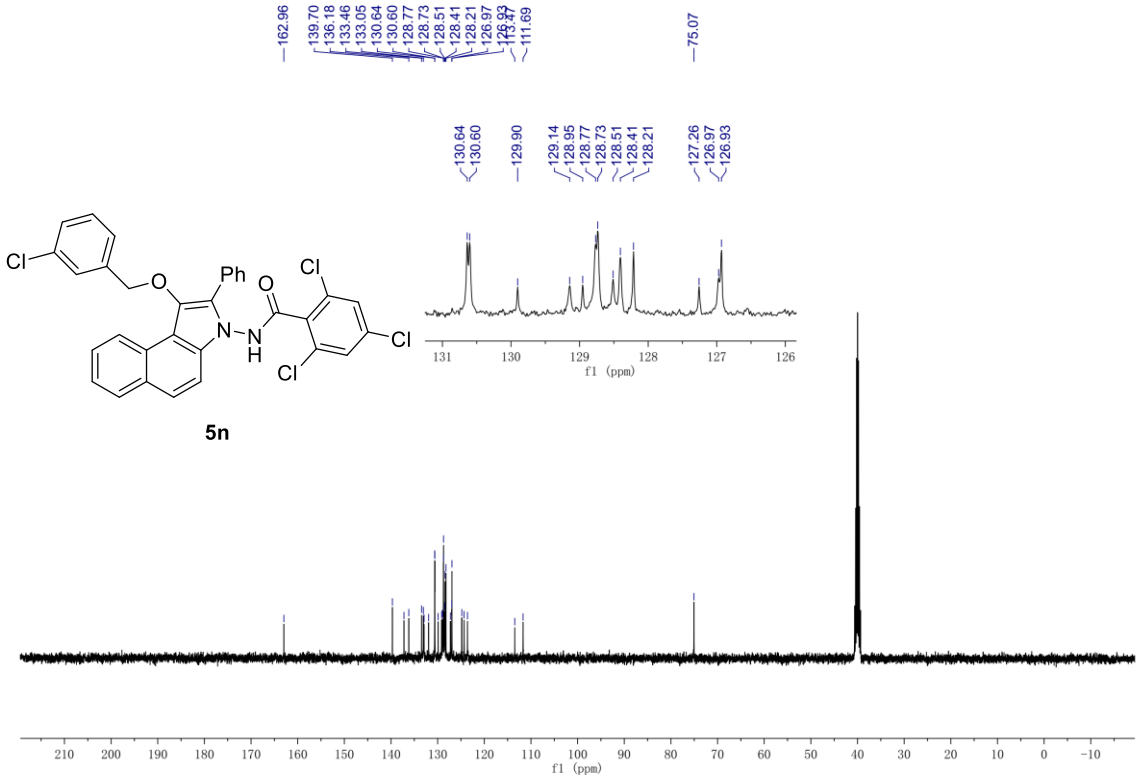
5l


YXR 1014-5
12.18
8.62
8.60
8.02
8.00
7.77
7.63
7.61
7.59
7.47
7.43
7.42
7.32
7.21
7.20
7.18
4.93
4.84
4.82
2.10
Ph
O
O
N
N
H
Cl
Cl
Cl
1.01
1.02
1.03
4.00
3.14
3.04
1.00
1.02
2.00
1.00
1.00
0.98
3.03
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

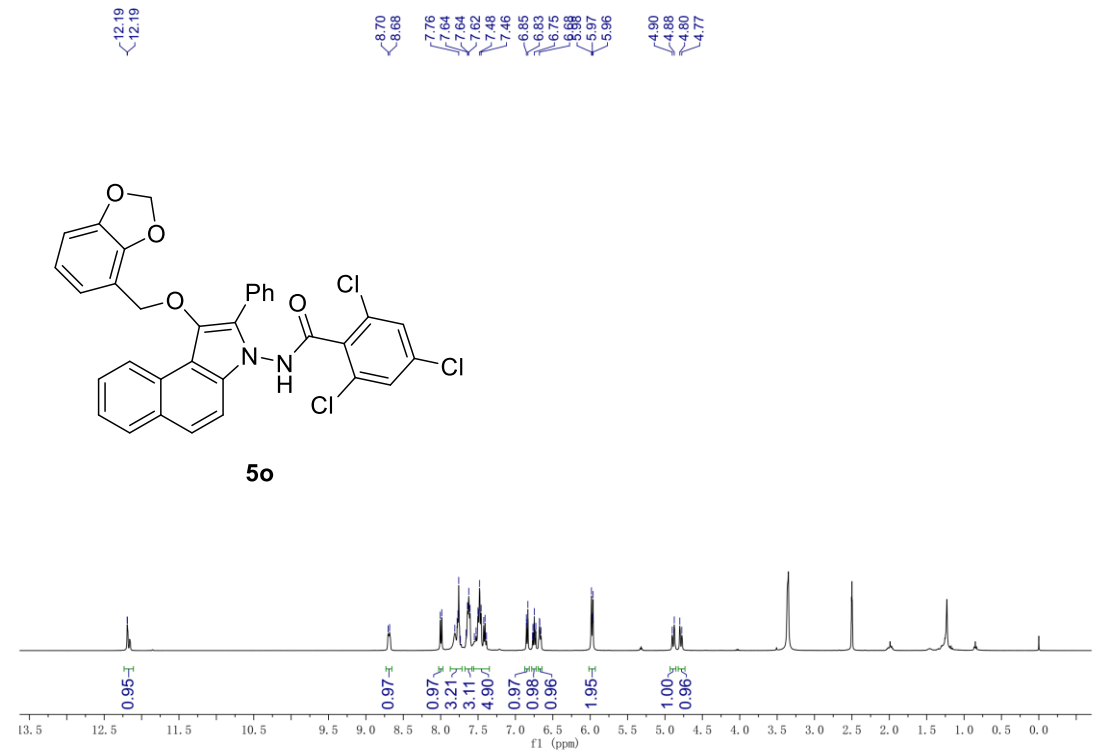
5m


YXR 1014-5
162.96
137.50
136.87
136.16
135.39
130.89
130.52
129.26
129.13
128.76
128.65
128.48
128.42
126.28
124.70
111.69
74.22
18.71
Ph
O
N
N
H
Cl
Cl
Cl
5m
f1 (ppm)

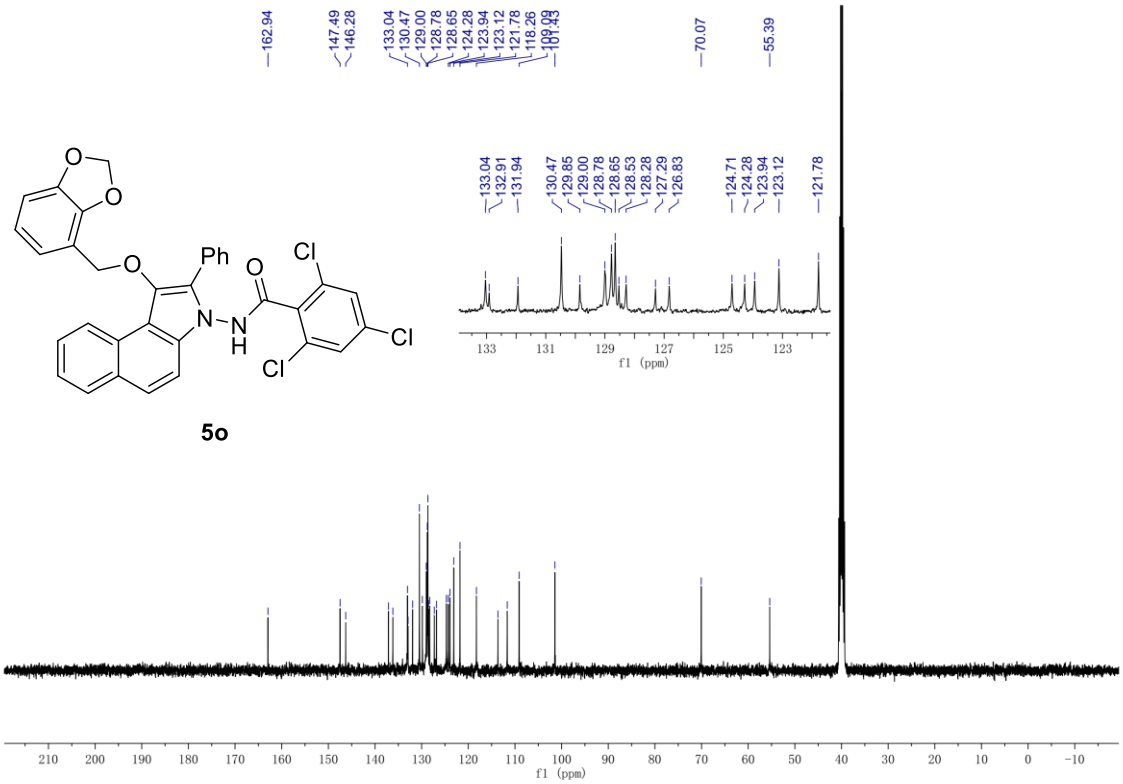

12.22
8.59
8.57
8.02
8.00
7.78
7.65
7.63
7.61
7.50
7.49
7.47
7.44
7.42
7.34
7.32
7.31
4.96
4.86
4.83
Cl
Ph
O
N
N
H
Cl
Cl
Cl
5n
0.99
1.01
1.05
4.00
3.05
2.90
1.02
2.99
1.00
1.00
0.99
f1 (ppm)


162.96
139.70
136.18
133.46
133.05
130.64
130.60
128.77
128.73
128.51
128.41
128.21
126.97
126.93
111.69
75.07
130.64
130.60
129.90
129.14
128.95
128.77
128.73
128.51
128.41
128.21
127.26
126.97
126.93
Cl
O
Ph
N
N
H
O
Cl
Cl
Cl
131
130
129
128
127
126
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

5n


12.19
12.19
8.70
8.68
7.76
7.64
7.64
7.62
7.48
7.46
6.85
6.83
6.75
5.97
5.96
4.90
4.88
4.80
4.77
O
O
O
Ph
N
N
H
O
Cl
Cl
Cl
0.95
0.97
0.97
3.21
3.11
4.90
0.97
0.98
0.96
1.95
1.00
0.96
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

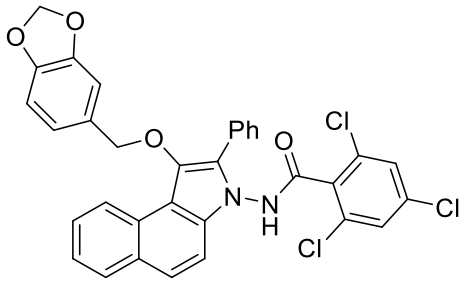
5o


162.94
147.49
146.28
133.04
130.47
129.00
128.78
128.65
124.28
123.94
123.12
121.78
118.26
70.07
55.39
Ph
O
N
H
Cl
Cl
Cl
133.04
132.91
131.94
130.47
129.85
129.00
128.78
128.65
128.53
128.28
127.29
126.83
124.71
124.28
123.94
123.12
121.78
f1 (ppm)

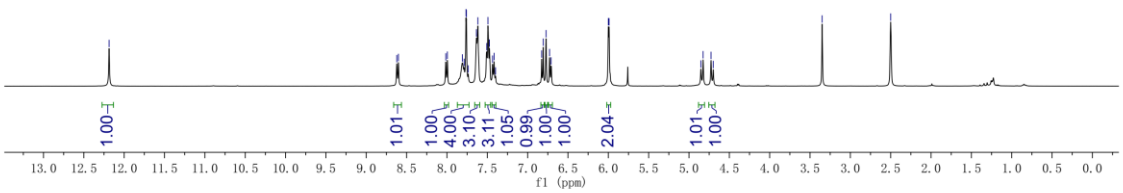
5o

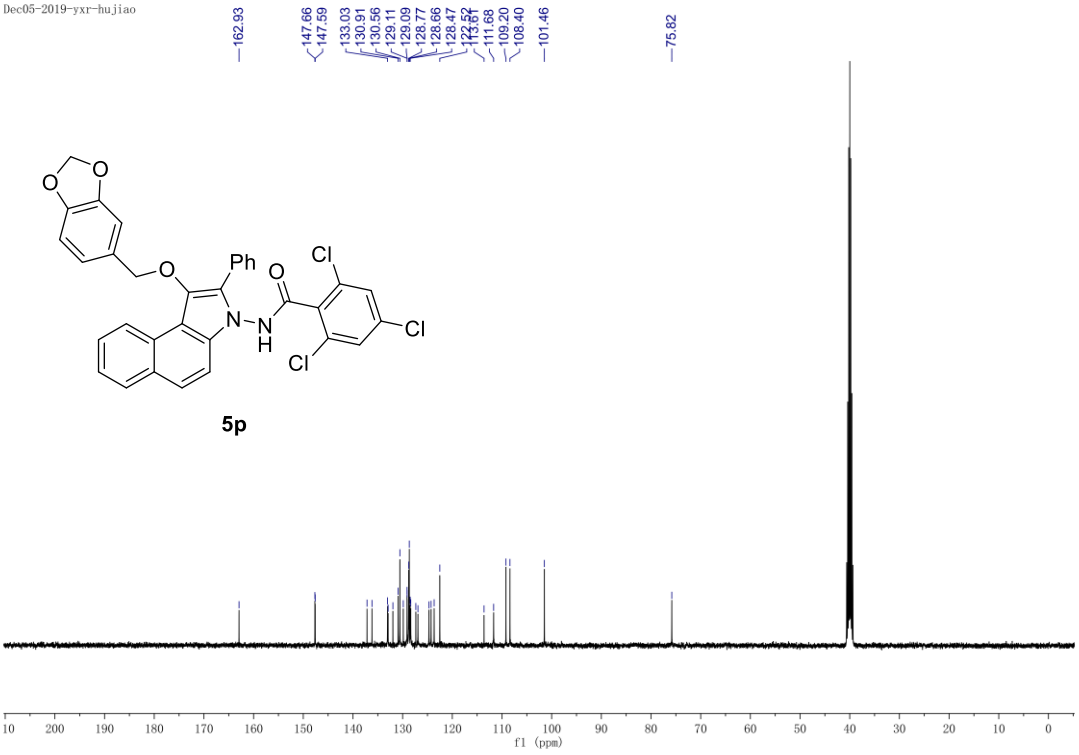
f1 (ppm)

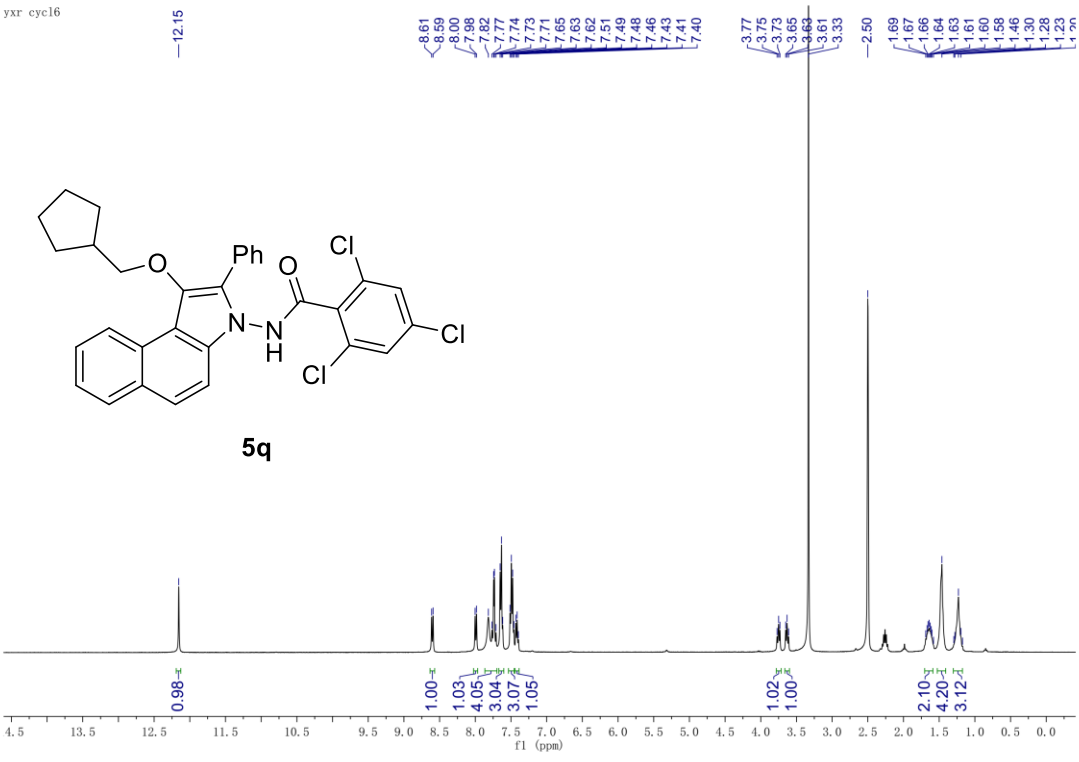

12.19
8.62
8.60
7.76
7.76
7.63
7.62
7.49
7.47
6.83
6.81
6.77
6.73
6.00
5.99
4.85
4.82
4.73
4.70
3.35
2.50

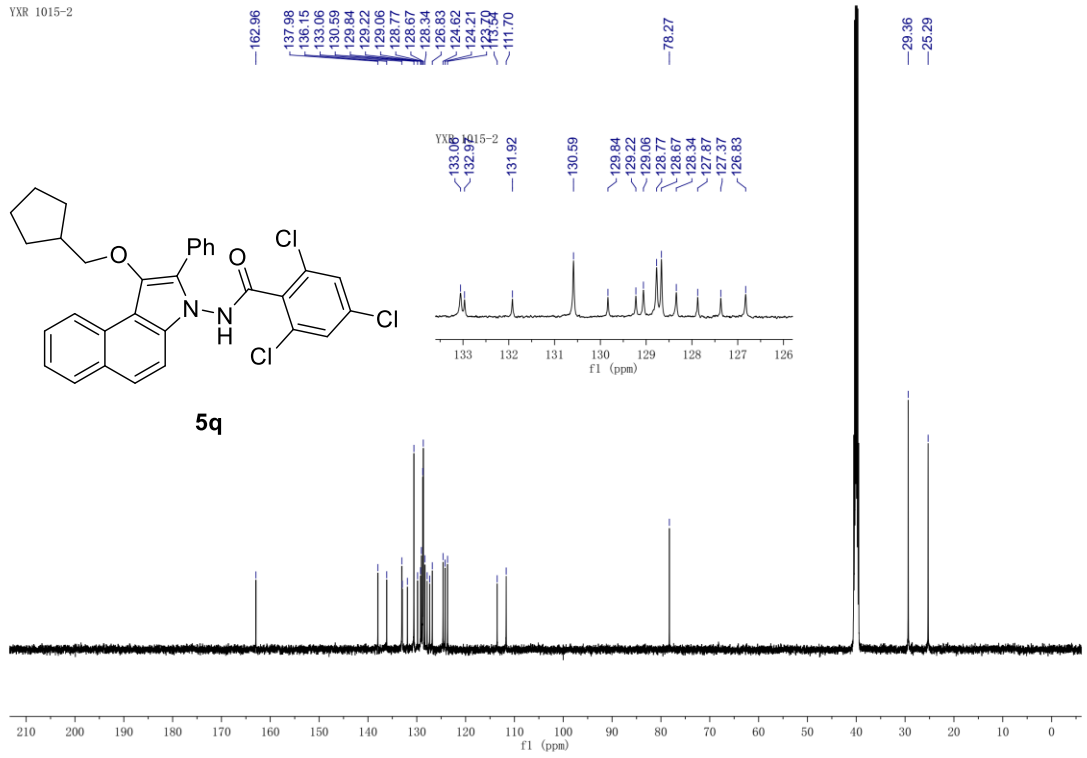

O
O
O
Ph
N
H
O
Cl
Cl
Cl

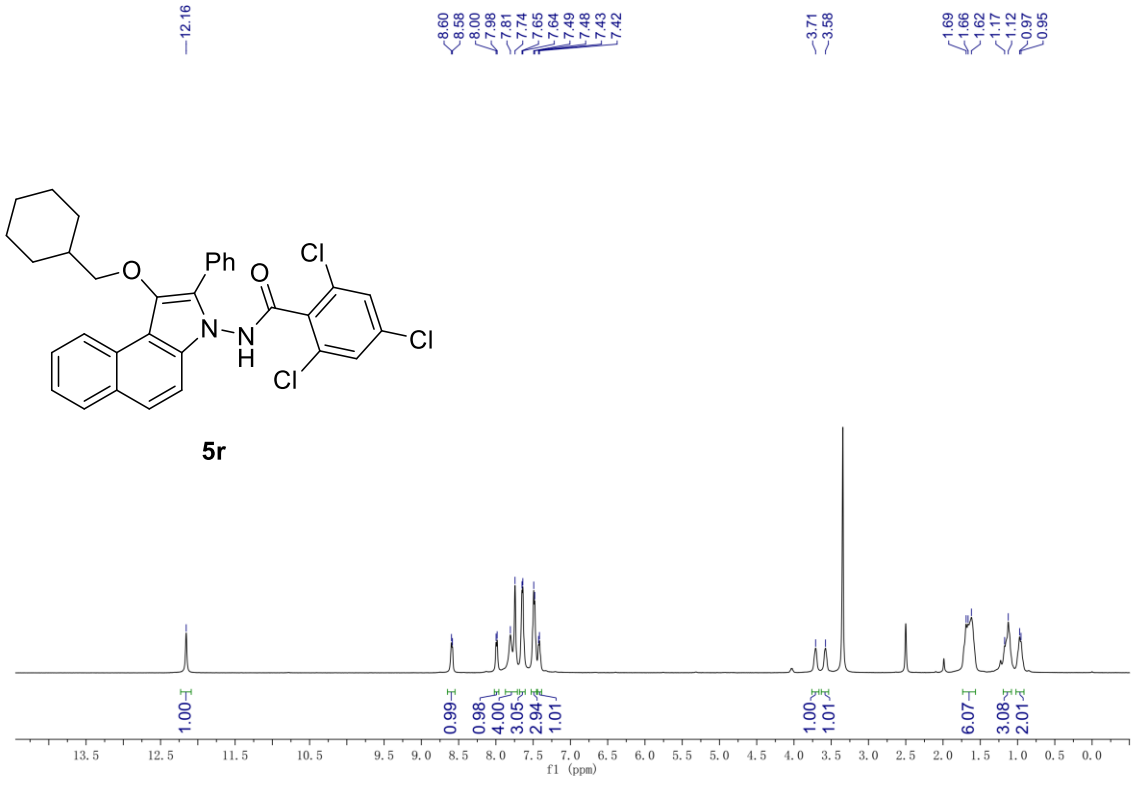
5p

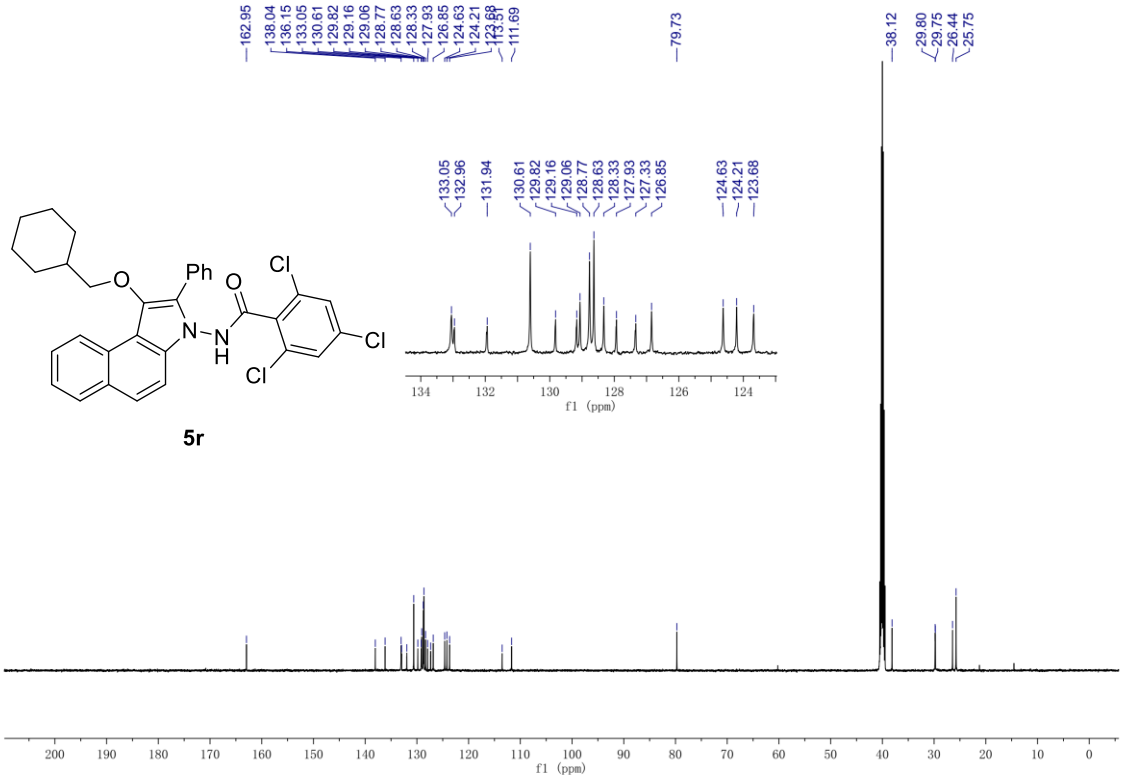

1.00
1.01
1.00
4.00
3.10
3.11
1.05
0.99
1.00
1.00
2.04
1.01
1.00
f1 (ppm)

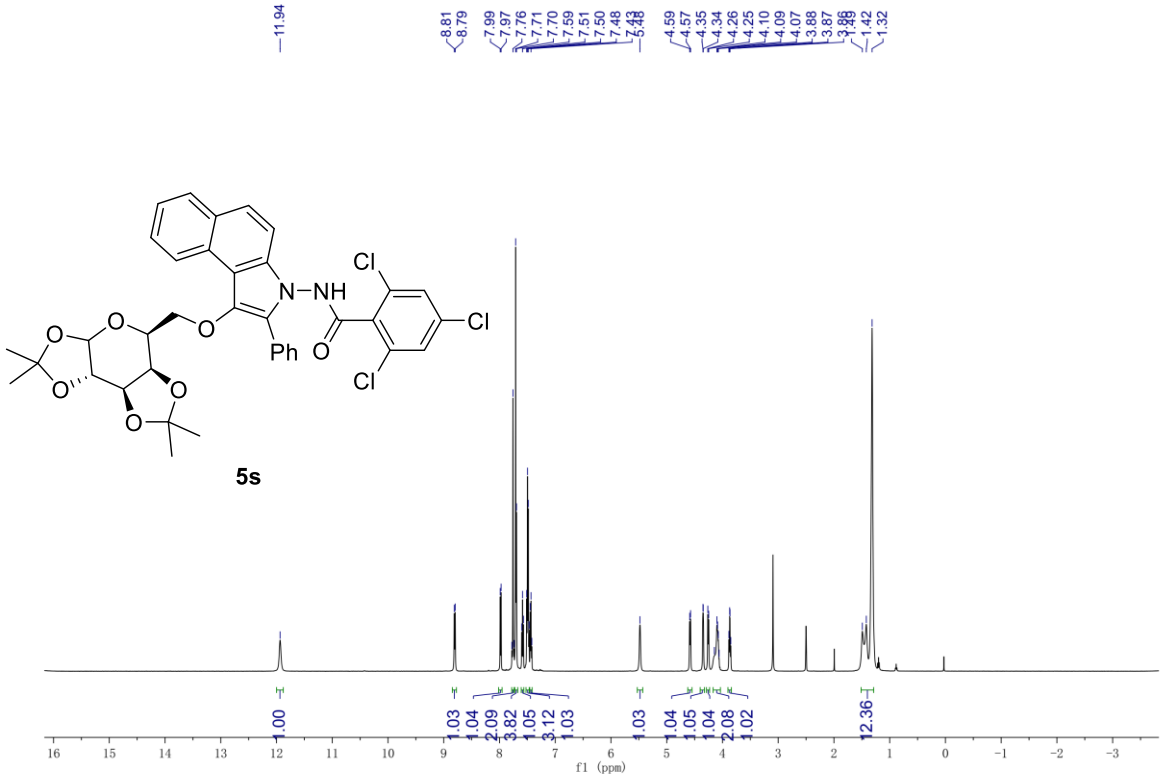

Dec05-2019-yxr-hujiao
162.93
147.66
147.59
133.03
130.91
130.56
129.11
129.09
128.77
128.66
128.47
123.52
123.51
111.68
109.20
108.40
101.46
75.82
O
O
O
Ph
N
N
H
O
Cl
Cl
Cl
5p
f1 (ppm)

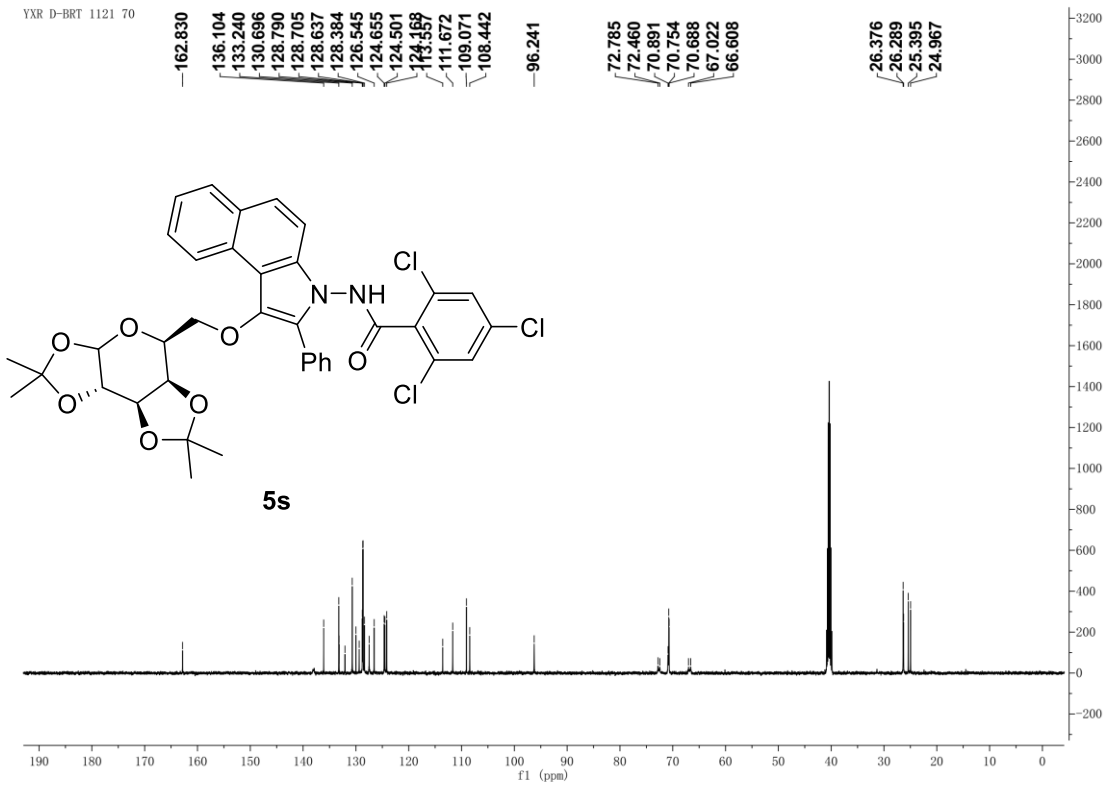

yxr cycl6
12.15
8.61
8.59
8.00
7.98
7.82
7.77
7.74
7.73
7.71
7.65
7.63
7.62
7.51
7.49
7.48
7.46
7.43
7.41
7.40
3.77
3.75
3.73
3.65
3.63
3.61
3.33
2.50
1.69
1.67
1.66
1.64
1.63
1.61
1.60
1.58
1.46
1.30
1.28
1.23
0.98
1.00
1.03
4.05
3.04
3.07
1.05
1.02
1.00
2.10
4.20
3.12
O
Ph
O
N
N
H
Cl
Cl
Cl
5q
f1 (ppm)

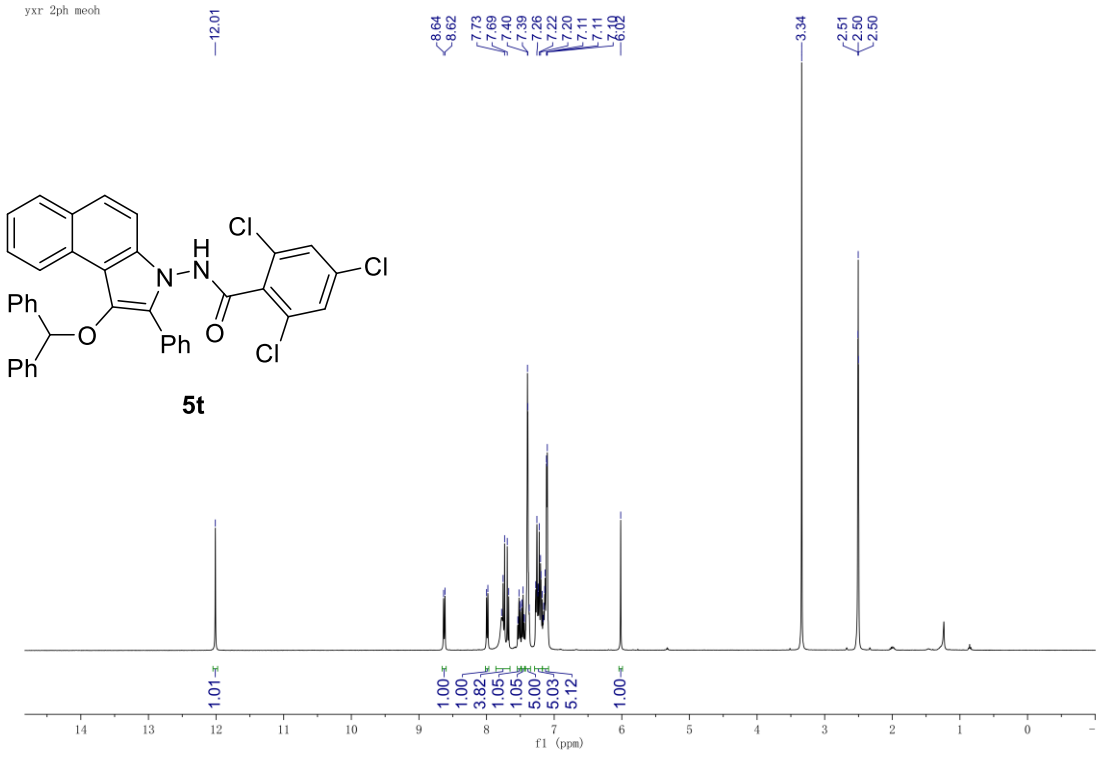

YXR 1015-2
162.96
137.98
136.15
133.06
130.59
129.84
129.22
129.06
128.77
128.67
128.34
126.83
124.62
124.21
123.70
113.54
111.70
78.27
29.36
25.29
YXR 1015-2
133.06
132.92
131.92
130.59
129.84
129.22
129.06
128.77
128.67
128.34
127.87
127.37
126.83
f1 (ppm)
Ph
O
N
N
H
O
Cl
Cl
Cl
5q
f1 (ppm)

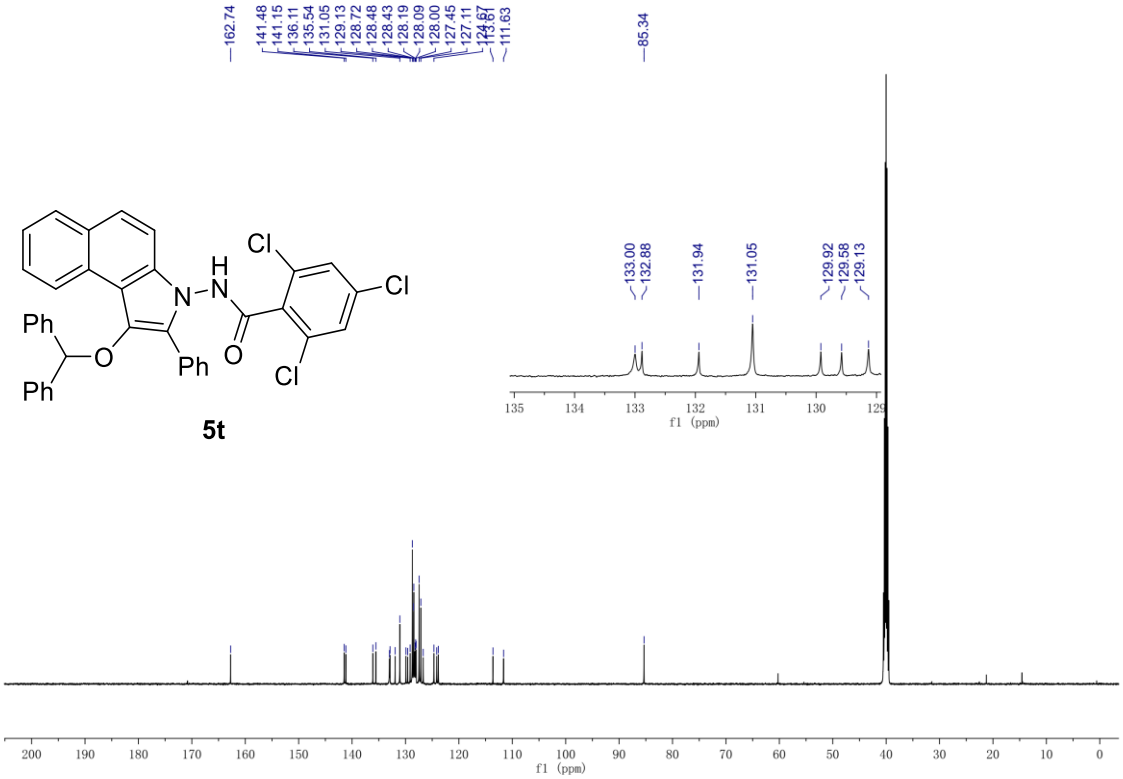

12.16
8.60
8.58
8.00
7.98
7.81
7.74
7.65
7.64
7.49
7.48
7.43
7.42
3.71
3.58
1.69
1.66
1.62
1.17
1.12
0.97
0.95
Ph
O
N
N
H
O
Cl
Cl
Cl
5r
1.00
0.99
0.98
4.00
3.05
2.94
1.01
1.00
1.01
6.07
3.08
2.01
f1 (ppm)


162.95
138.04
136.15
133.05
130.61
129.82
129.16
129.06
128.77
128.63
128.33
127.93
126.85
124.63
124.21
111.69
79.73
38.12
29.80
29.75
26.44
25.75
Ph
O
N
N
H
O
Cl
Cl
Cl
5r
f1 (ppm)

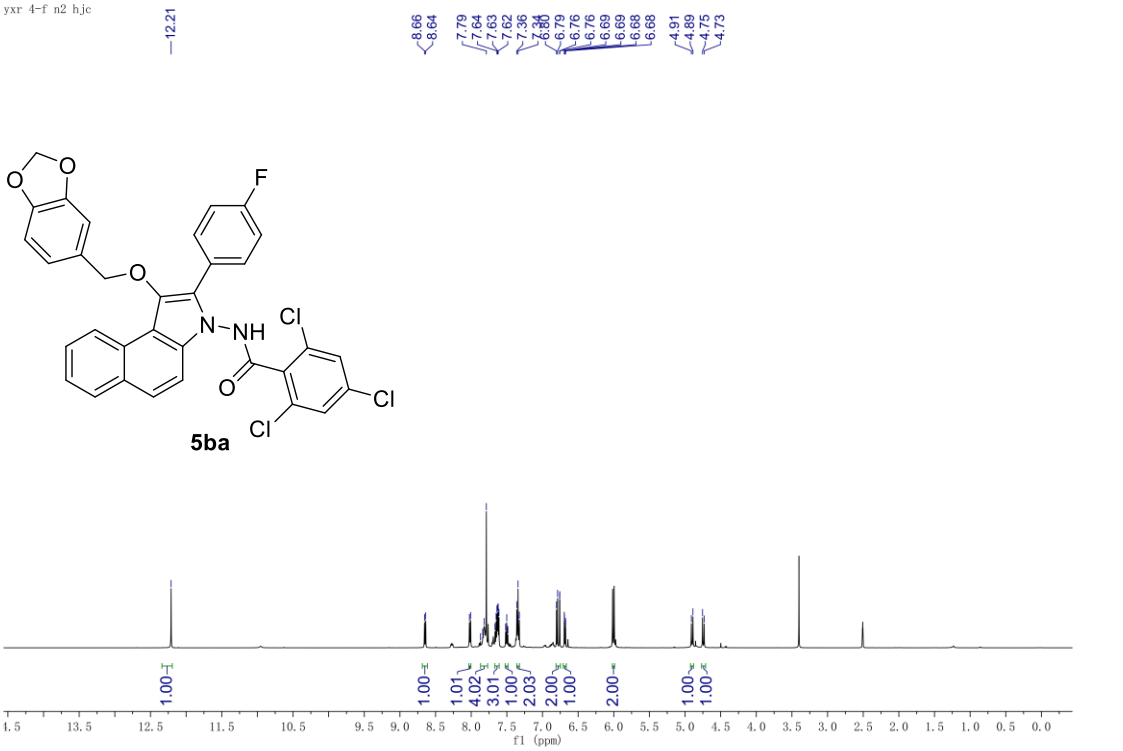

11.94
8.81
8.79
7.99
7.97
7.76
7.71
7.70
7.59
7.51
7.50
7.48
4.59
4.57
4.35
4.34
4.26
4.25
4.10
4.09
4.07
3.88
3.87
1.42
1.32
N–NH
O
O
O
O
O
O
Ph
O
Cl
Cl
Cl
5s
1.00
1.03
1.04
2.09
3.82
1.05
3.12
1.03
1.03
1.04
1.05
1.04
2.08
1.02
12.36
f1 (ppm)


YXR D-BRT 1121 70
162.830
136.104
133.240
130.696
128.790
128.705
128.637
128.384
126.545
124.655
124.501
124.168
113.557
111.672
109.071
108.442
96.241
72.785
72.460
70.891
70.754
70.688
67.022
66.608
26.376
26.289
25.395
24.967
Cl
N–NH
Cl
O
O
Ph
O
O
O
O
Cl
5s
f1 (ppm)

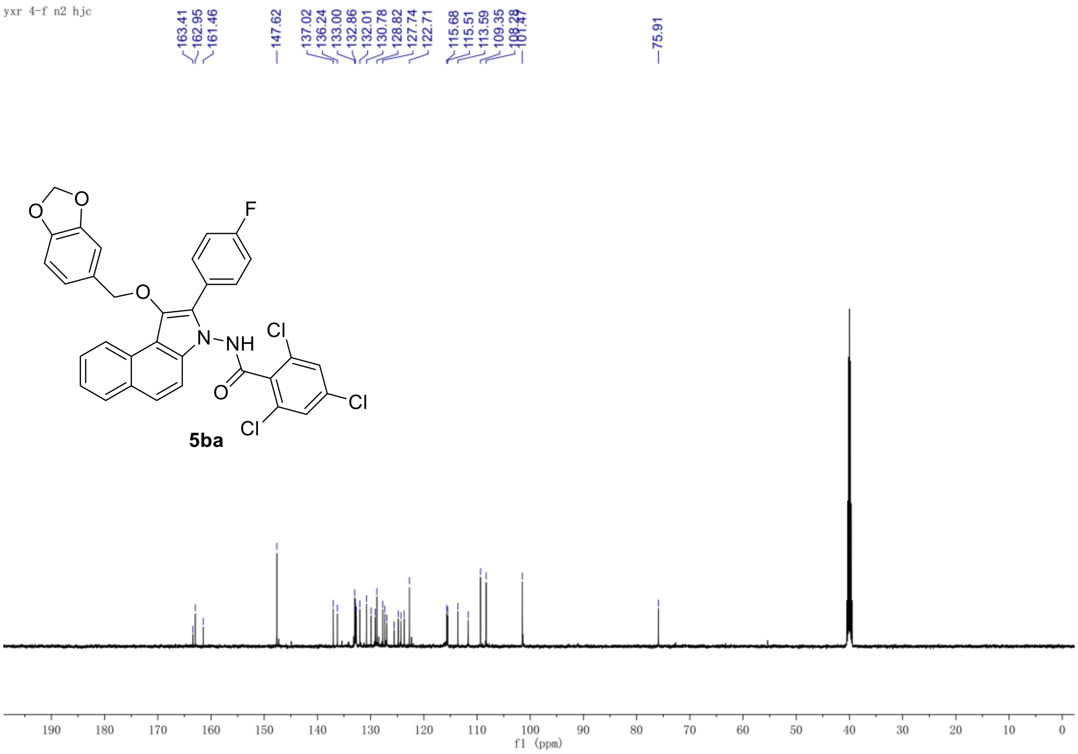

yxr 2ph meoh
12.01
8.64
8.62
7.73
7.69
7.40
7.39
7.26
7.22
7.20
7.11
7.11
6.02
3.34
2.51
2.50
2.50
Cl
H
N–N
Cl
Ph
O
Ph
O
Ph
Cl
5t
1.01
1.00
1.00
3.82
1.05
1.05
5.00
5.03
5.12
1.00
f1 (ppm)

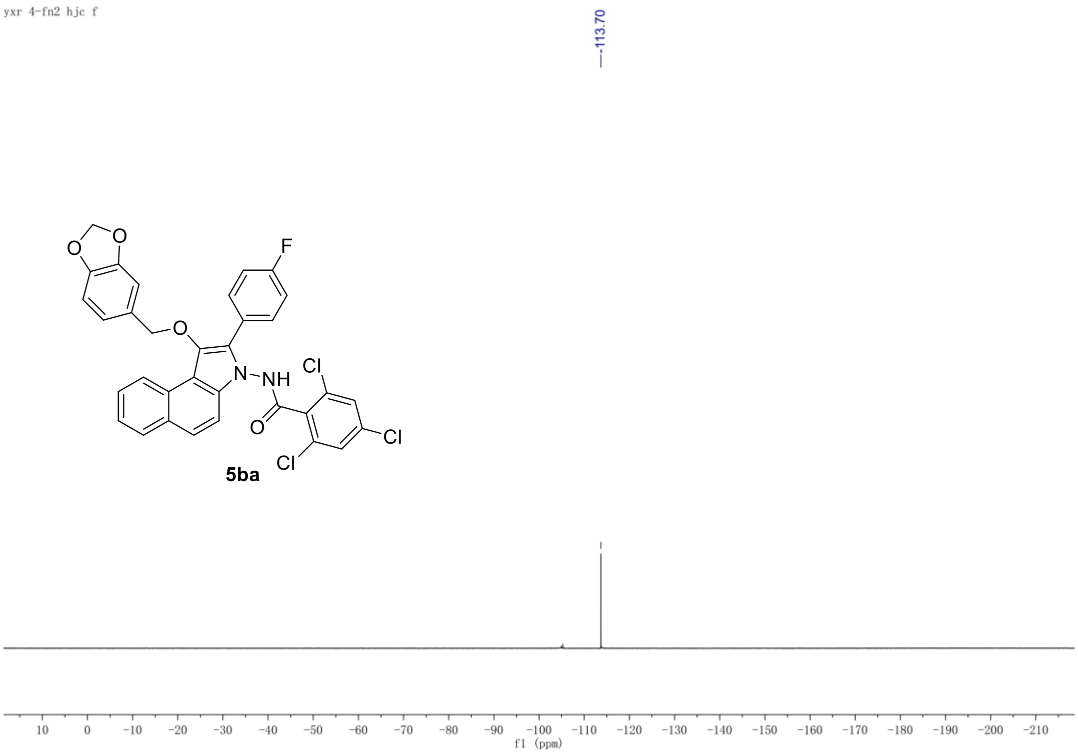

162.74
141.48
141.15
136.11
135.54
131.05
129.13
128.72
128.48
128.43
128.19
128.09
128.00
127.45
127.11
111.63
85.34
133.00
132.88
131.94
131.05
129.92
129.58
129.13
Cl
Cl
Cl
H
N
N
O
O
Ph
Ph
Ph
Ph
f1 (ppm)

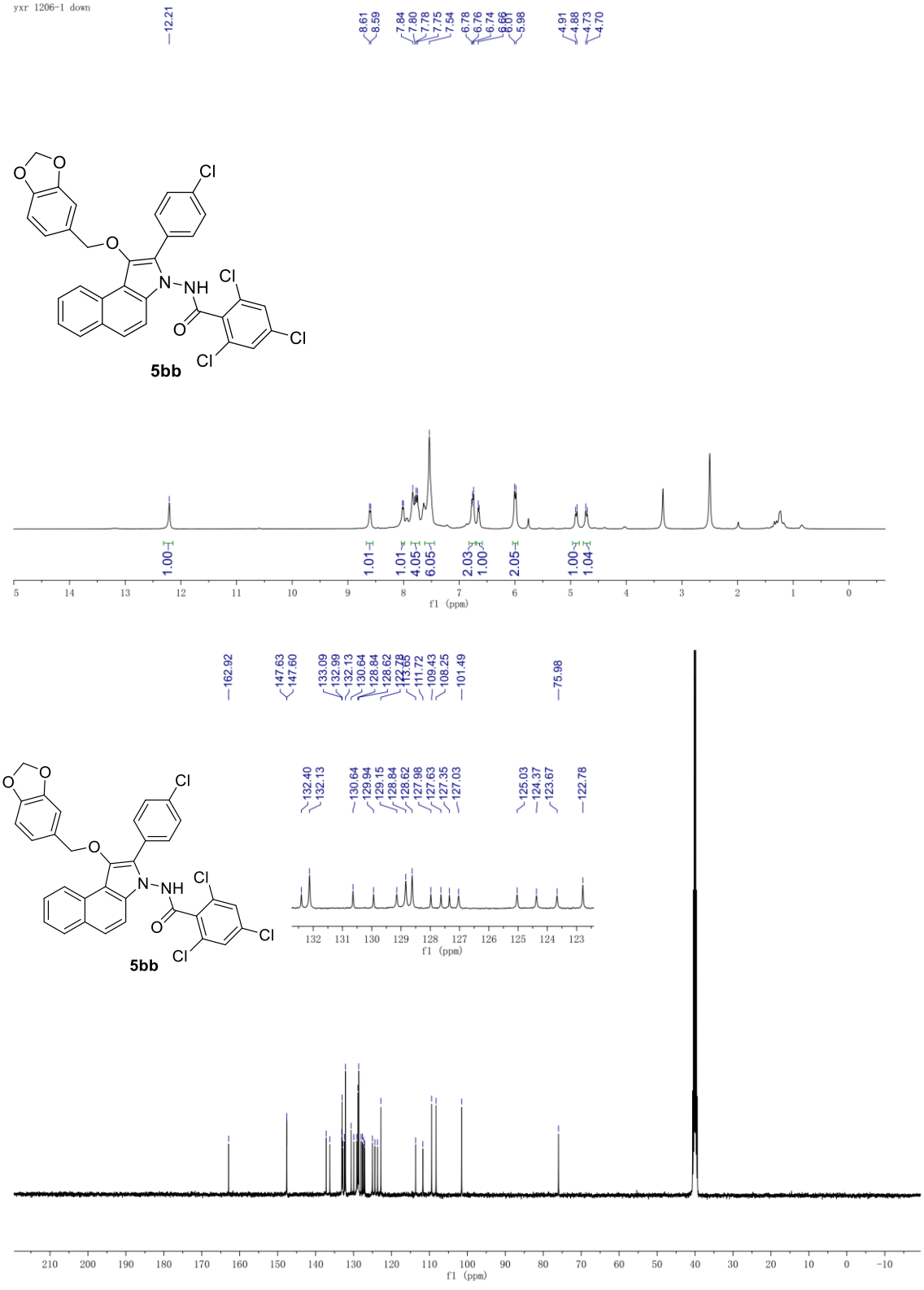
5t

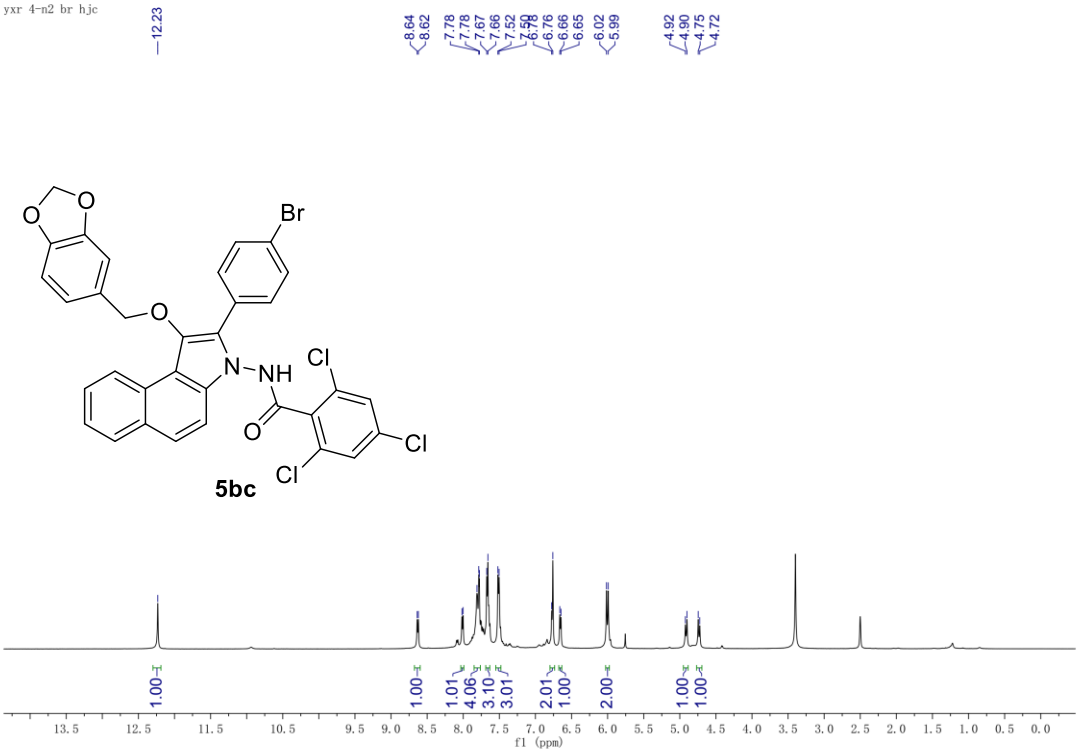

yxr 4-f n2 hjc
12.21
8.66
8.64
7.79
7.64
7.63
7.62
7.36
6.79
6.76
6.69
6.68
4.91
4.89
4.75
4.73
F
O
O
O
N
NH
Cl
Cl
Cl
O
1.00
1.00
1.01
4.02
3.01
1.00
2.03
2.00
1.00
2.00
1.00
1.00
f1 (ppm)

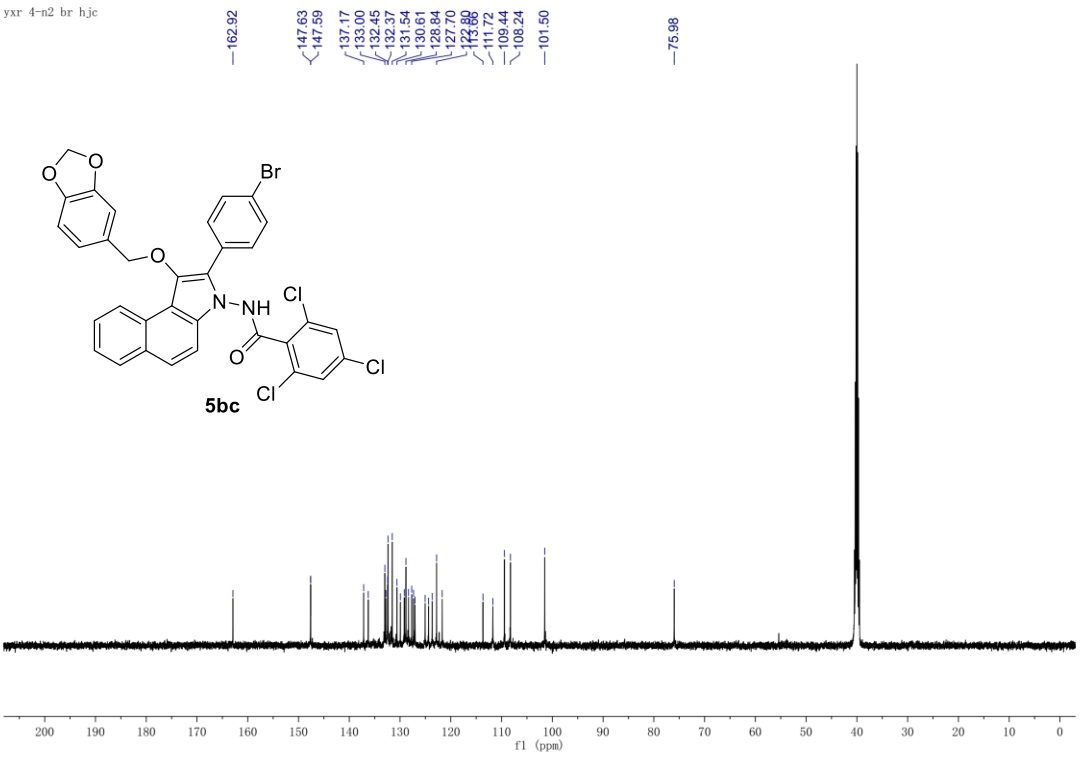
5ba

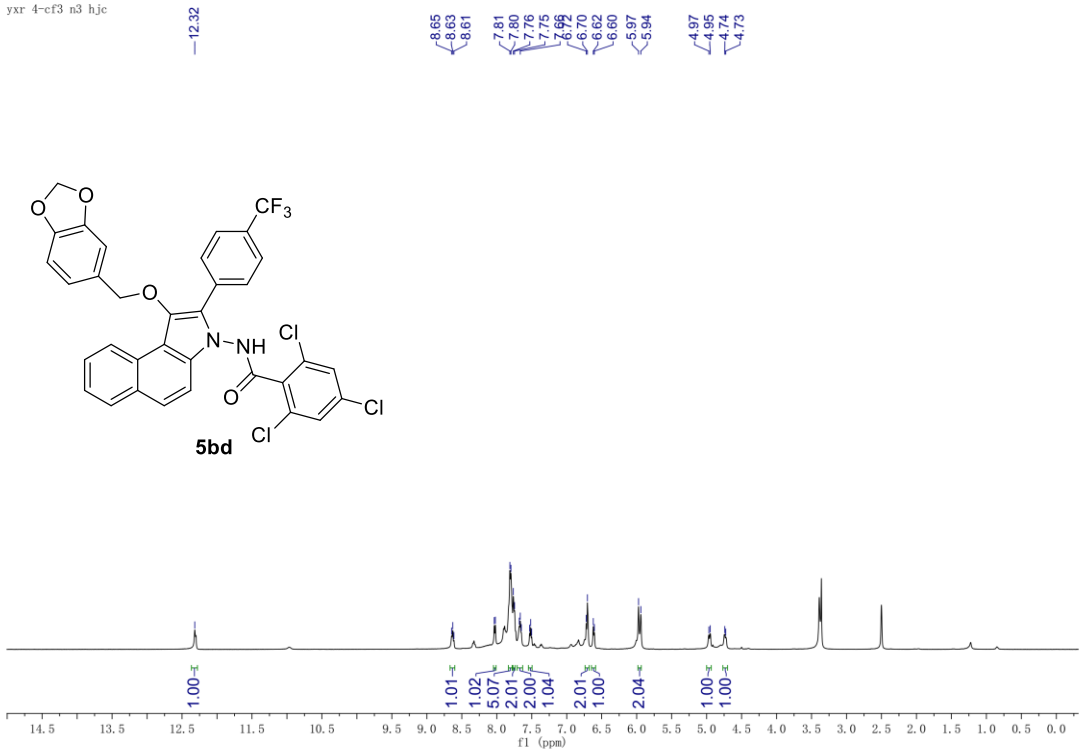

yxr 4-f n2 hjc
163.41
162.95
161.46
147.62
137.02
136.24
133.00
132.86
132.01
130.78
128.82
127.74
122.71
115.68
115.51
113.59
109.35
101.47
75.91
F
O
O
O
N
NH
Cl
Cl
Cl
O
5ba
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

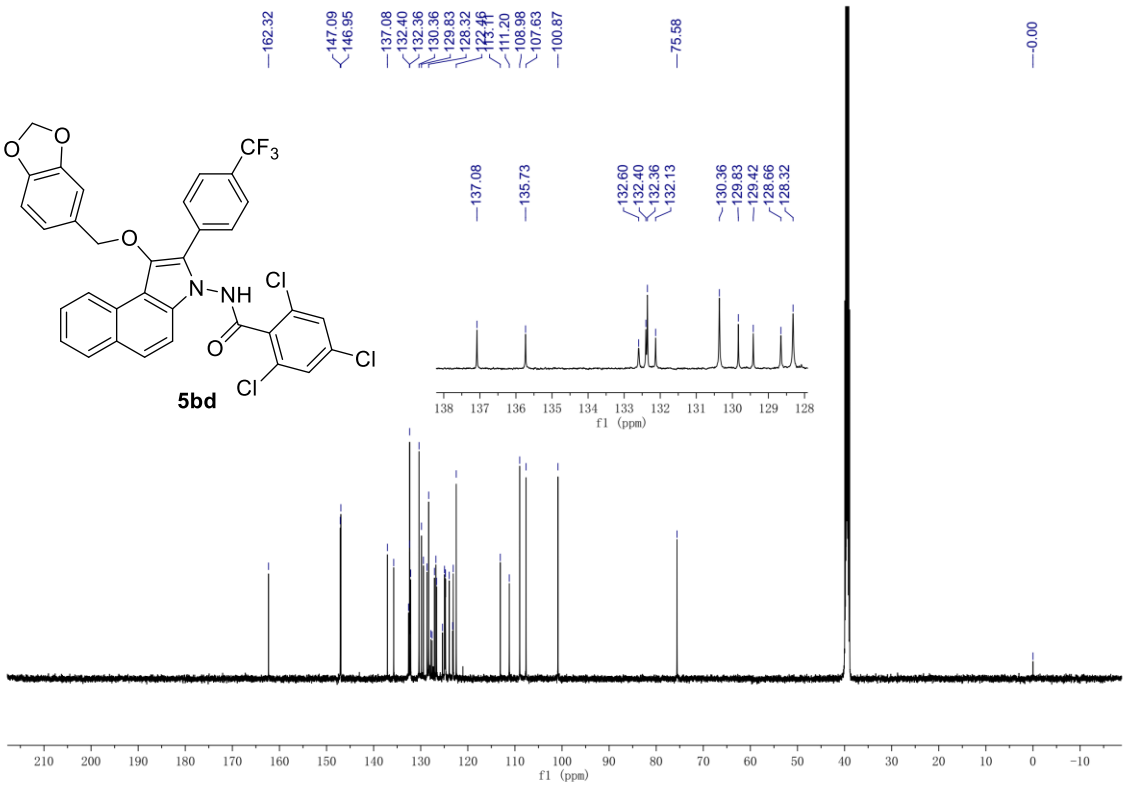

yxr 4-fn2 hjc f
-113.70
F
O
O
O
N
NH
Cl
Cl
Cl
O
5ba
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

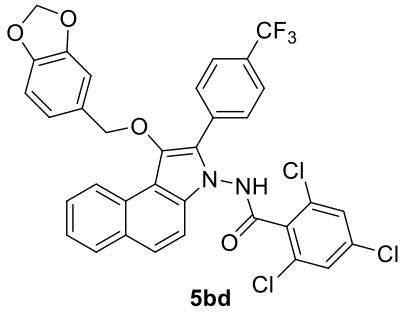

yxr 1206-1 down
12.21
8.61
8.59
7.84
7.80
7.78
7.75
7.54
6.78
6.76
6.74
5.98
4.91
4.88
4.73
4.70
5bb
1.00
1.01
1.01
4.05
6.05
2.03
1.00
2.05
1.00
1.04
f1 (ppm)
162.92
147.63
147.60
133.09
132.99
132.13
130.64
128.84
128.62
111.72
109.43
108.25
101.49
75.98
132.40
132.13
130.64
129.94
129.15
128.84
128.62
127.98
127.63
127.35
127.03
125.03
124.37
123.67
122.78
5bb
f1 (ppm)
f1 (ppm)


yxr 4-n2 br hjc
12.23
8.64
8.62
7.78
7.78
7.67
7.66
7.52
7.50
6.78
6.76
6.66
6.65
6.02
5.99
4.92
4.90
4.75
4.72
Br
O
O
O
N
NH
O
Cl
Cl
Cl
5bc
1.00
1.00
1.01
4.06
3.10
3.01
2.01
1.00
2.00
1.00
1.00
f1 (ppm)

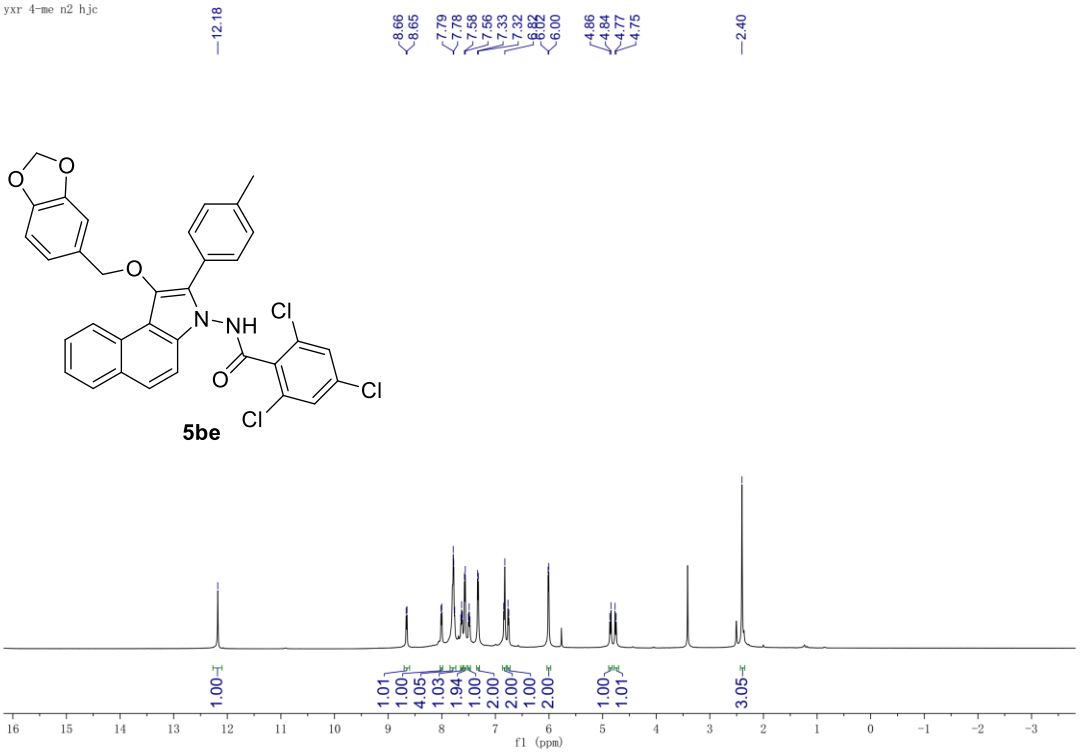

yxr 4-n2 br hjc
162.92
147.63
147.59
137.17
133.00
132.45
132.37
131.54
130.61
128.84
127.70
111.72
109.44
108.24
101.50
75.98
Br
O
O
O
N
NH
O
Cl
Cl
Cl
5bc
f1 (ppm)

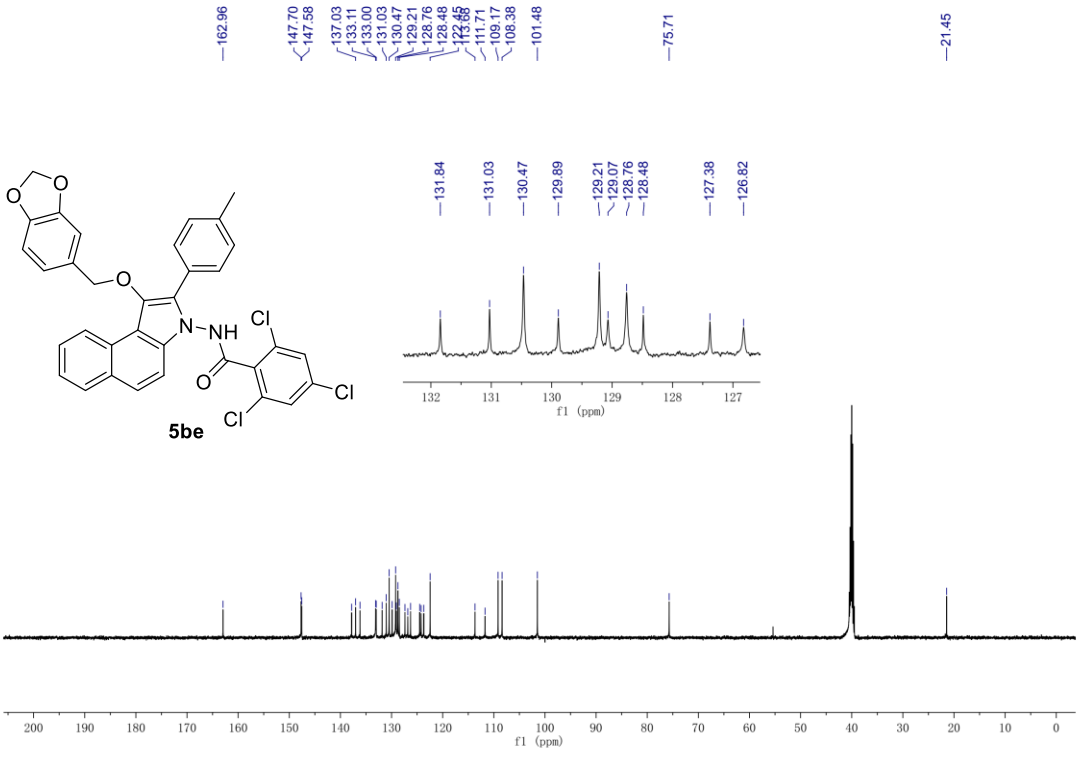

yxr 4-cf3 n3 hjc
12.32
8.65
8.63
8.61
7.81
7.80
7.76
7.75
6.70
6.62
6.60
5.97
5.94
4.97
4.95
4.74
4.73
CF3
O
O
O
N
NH
Cl
Cl
Cl
O
5bd
1.00
1.01
1.02
5.07
2.01
2.00
1.04
2.01
1.00
2.04
1.00
1.00
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

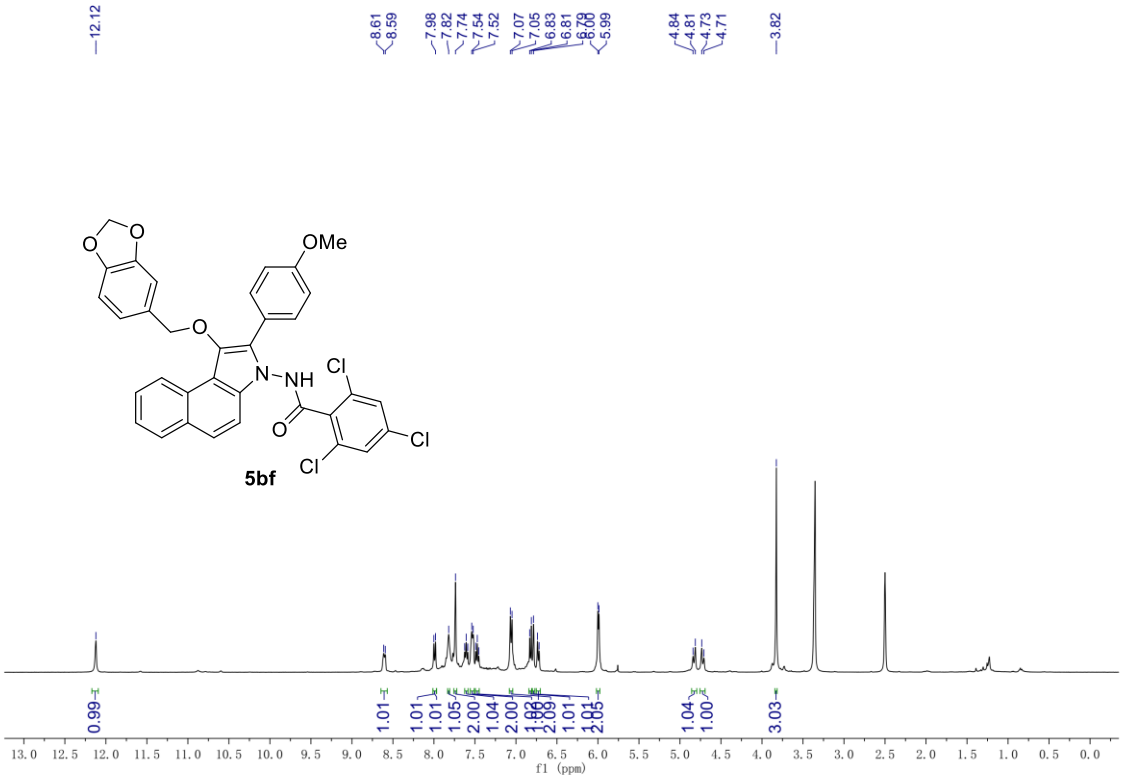

162.32
147.09
146.95
137.08
132.40
132.36
130.36
129.83
128.32
111.20
108.98
107.63
100.87
75.58
0.00
137.08
135.73
132.60
132.40
132.36
132.13
130.36
129.83
129.42
128.66
128.32
f1 (ppm)
f1 (ppm)

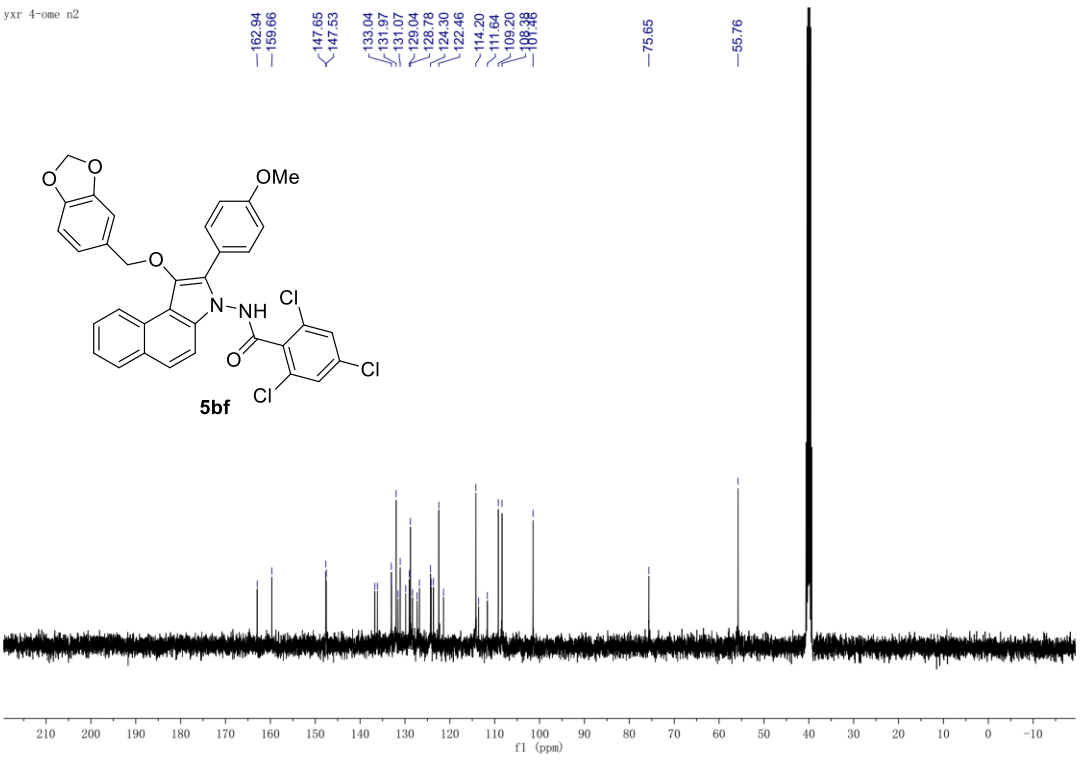

5bd

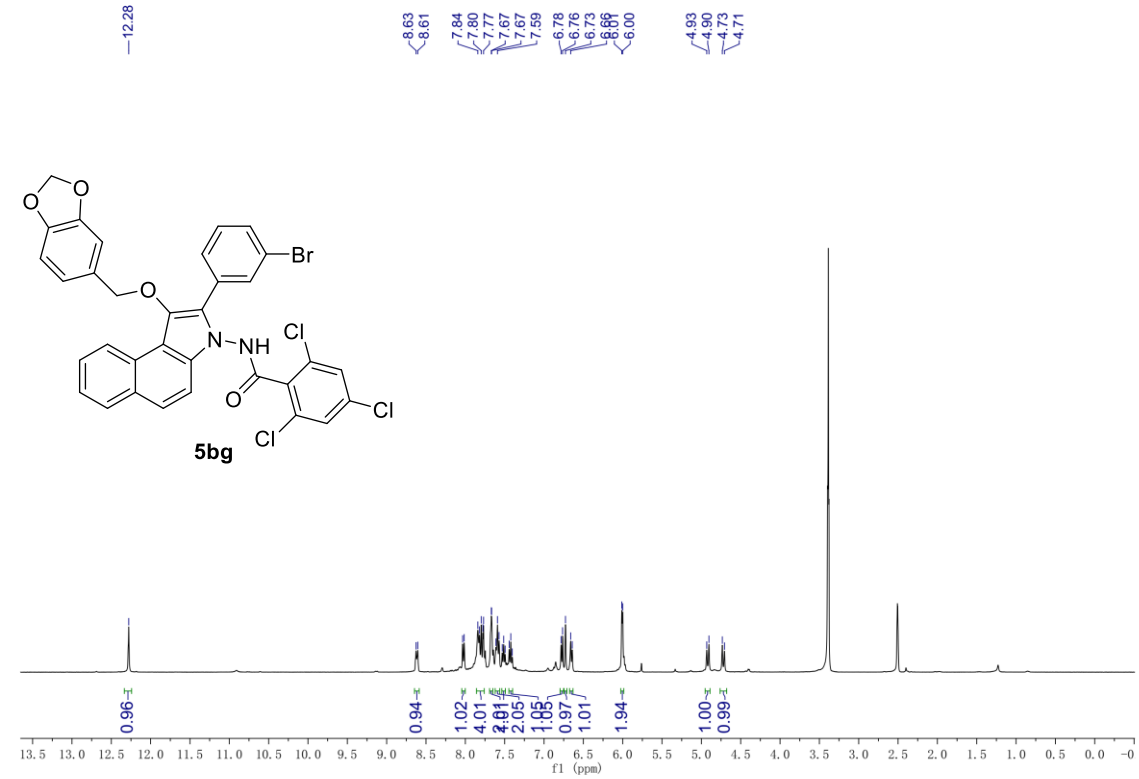
60.97
f1 (ppm)

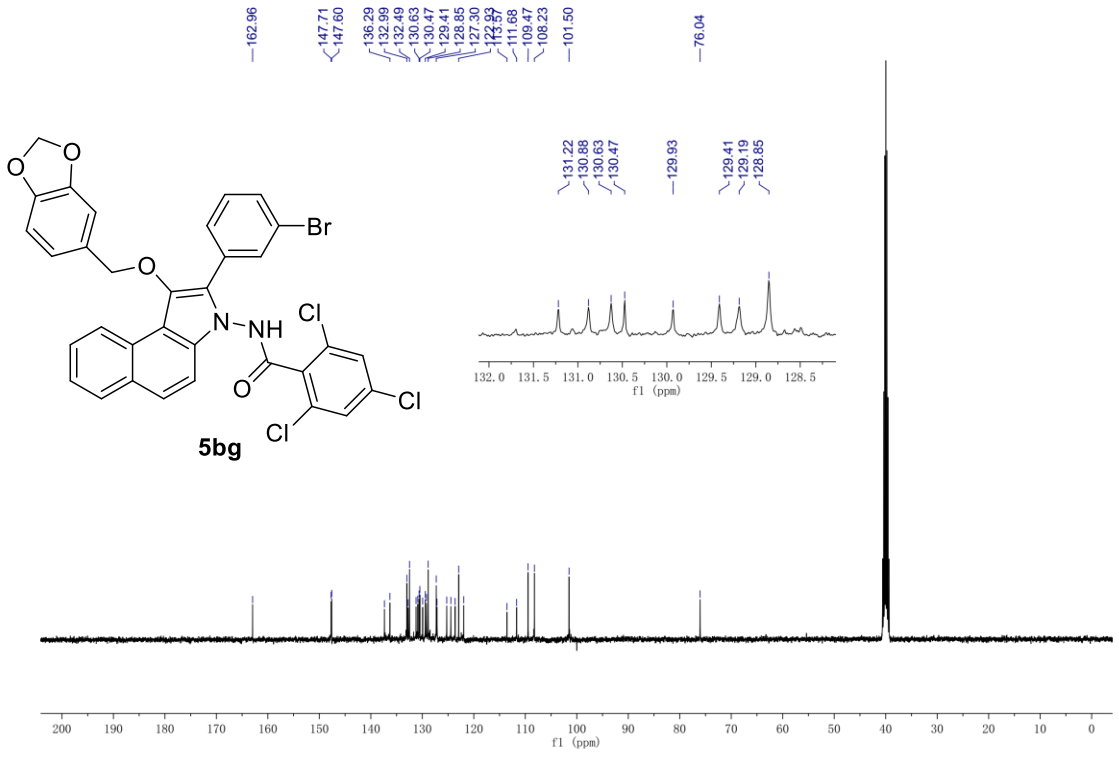

yxr 4-me n2 hjc
12.18
8.66
8.65
7.79
7.78
7.58
7.56
7.33
7.32
6.00
4.86
4.84
4.77
4.75
2.40
O
O
O
N
NH
O
Cl
Cl
Cl
5be
1.00
1.01
1.00
4.05
1.03
1.94
1.00
2.00
2.00
1.00
2.00
1.00
1.01
3.05
f1 (ppm)

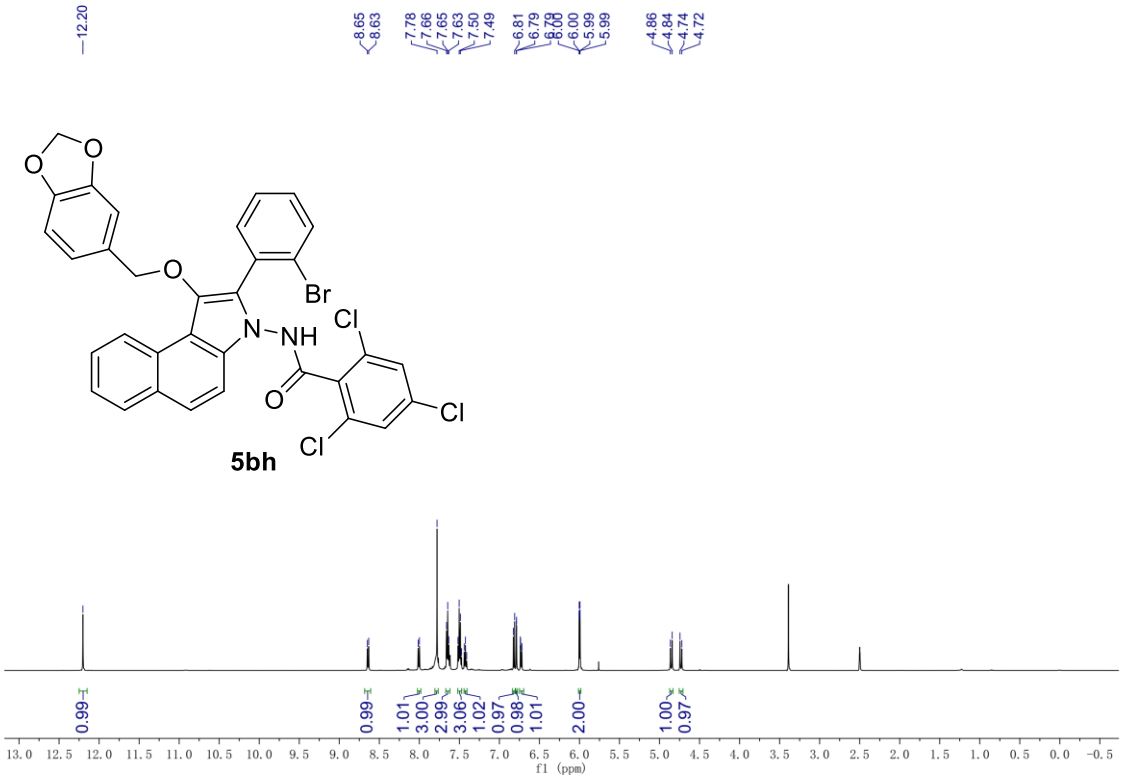

162.96
147.70
147.58
137.03
133.11
133.00
131.03
130.47
129.21
128.76
128.48
111.71
109.17
108.38
101.48
75.71
21.45
131.84
131.03
130.47
129.89
129.21
129.07
128.76
128.48
127.38
126.82
O
O
O
N
NH
O
Cl
Cl
Cl
5be
f1 (ppm)
f1 (ppm)

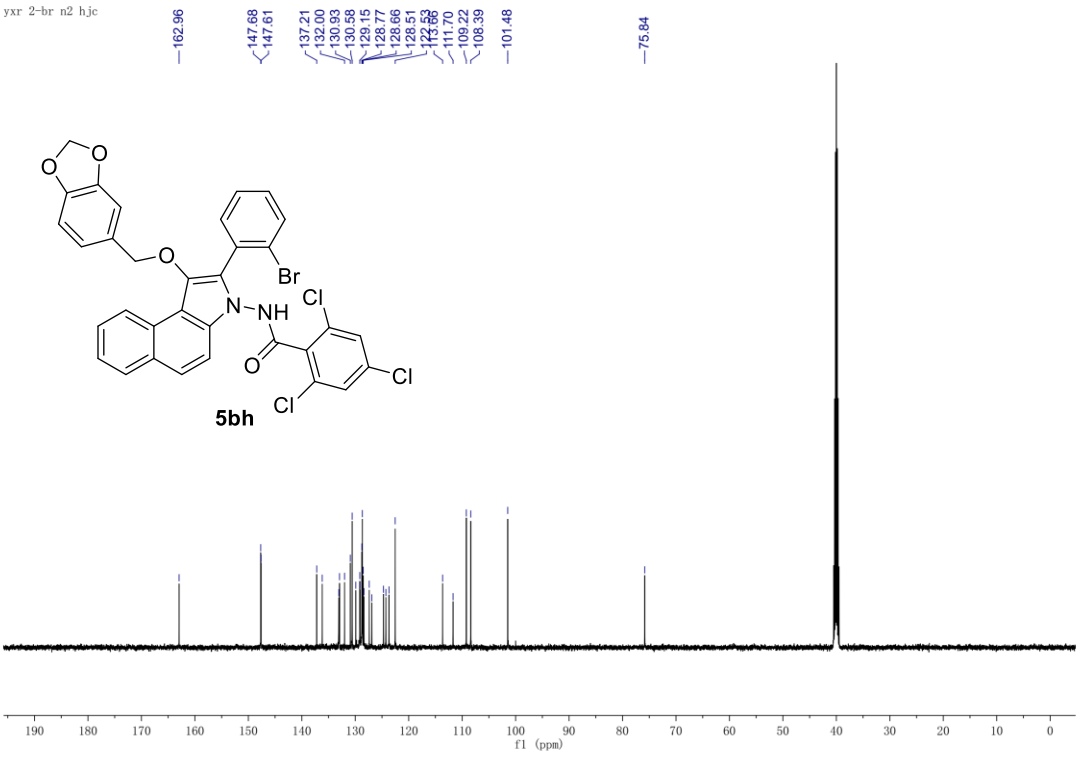

12.12
8.61
8.59
7.98
7.82
7.74
7.54
7.52
7.07
7.05
6.83
6.81
6.79
6.00
5.99
4.84
4.81
4.73
4.71
3.82
OMe
O
O
N
NH
Cl
Cl
Cl
O
5bf
0.99
1.01
1.01
1.01
1.05
2.00
1.04
2.00
2.09
1.01
2.05
1.04
1.00
3.03
f1 (ppm)


yxr 4-ome n2
162.94
159.66
147.65
147.53
133.04
131.97
131.07
129.04
128.78
124.30
122.46
114.20
111.64
109.20
75.65
55.76
OMe
O
O
N
NH
Cl
Cl
Cl
O
5bf
f1 (ppm)


12.28
8.63
8.61
7.84
7.80
7.77
7.67
7.59
6.78
6.76
6.73
6.00
4.93
4.90
4.73
4.71
Br
Cl
Cl
Cl
N
NH
O
O
O
5bg
0.96
0.94
1.02
4.01
2.05
1.05
0.97
1.01
1.94
1.00
0.99
f1 (ppm)


162.96
147.71
147.60
136.29
132.99
132.49
130.63
130.47
129.41
128.85
127.30
111.68
109.47
108.23
101.50
76.04
131.22
130.88
130.63
130.47
129.93
129.41
129.19
128.85
Br
Cl
Cl
Cl
N
NH
O
O
O
5bg
f1 (ppm)
f1 (ppm)


12.20
8.65
8.63
7.78
7.66
7.65
7.63
7.50
7.49
6.81
6.79
6.78
6.00
5.99
5.99
4.86
4.84
4.74
4.72
O
O
O
Br
N
NH
Cl
O
Cl
Cl
5bh
0.99
0.99
1.01
3.00
2.99
3.06
1.02
0.97
0.98
1.01
2.00
1.00
0.97
f1 (ppm)


yxr 2-br n2 hjc
162.96
147.68
147.61
137.21
132.00
130.93
130.58
129.15
128.77
128.66
128.51
111.70
109.22
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75.84
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O
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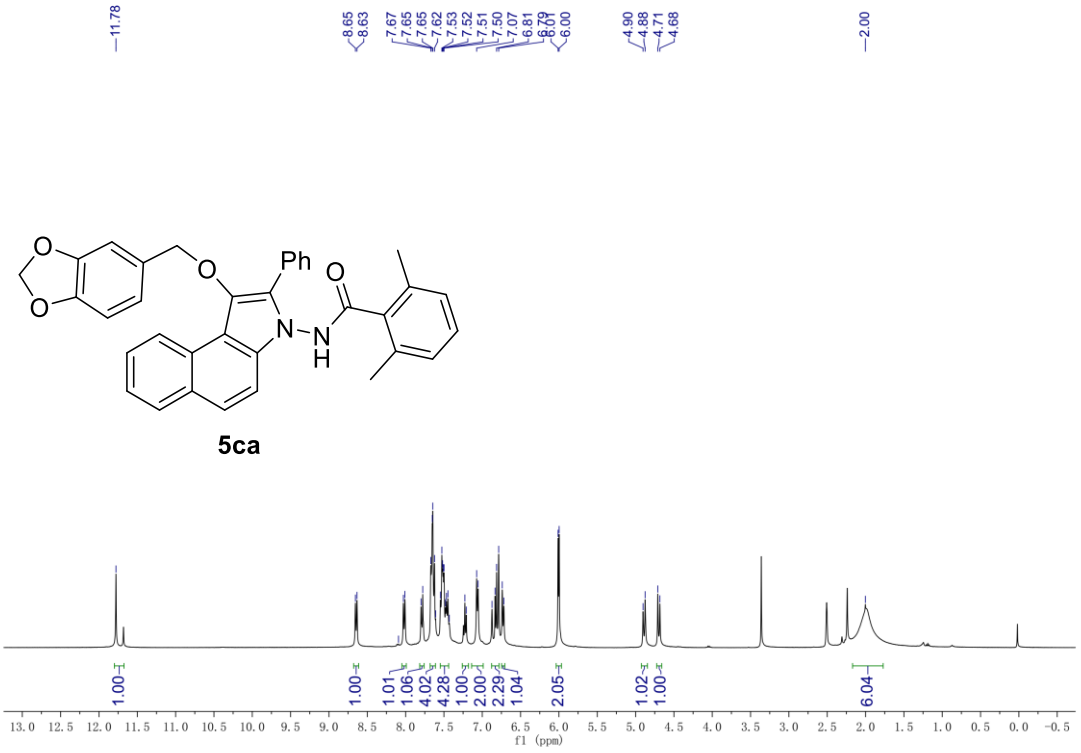
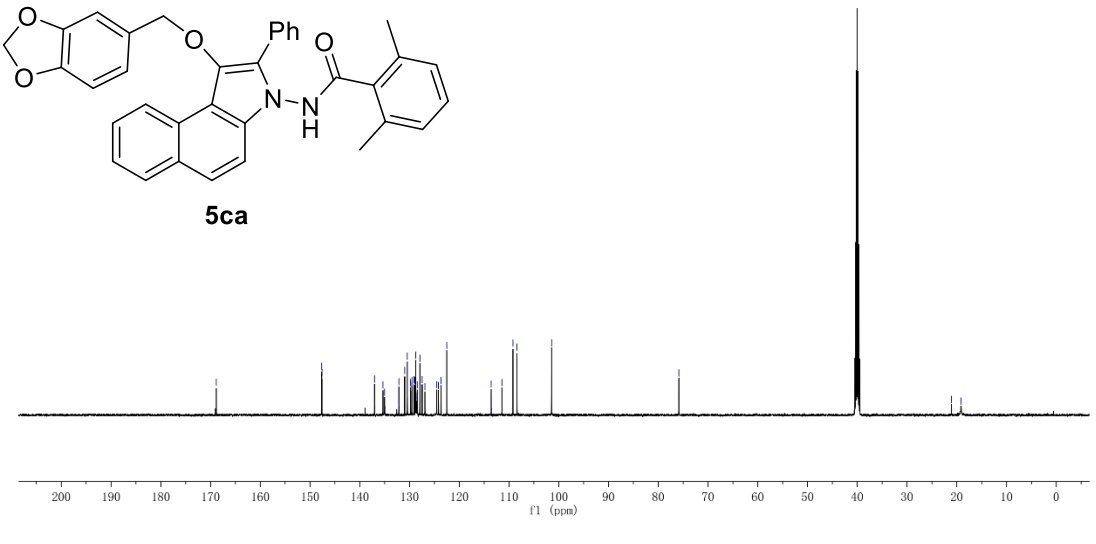
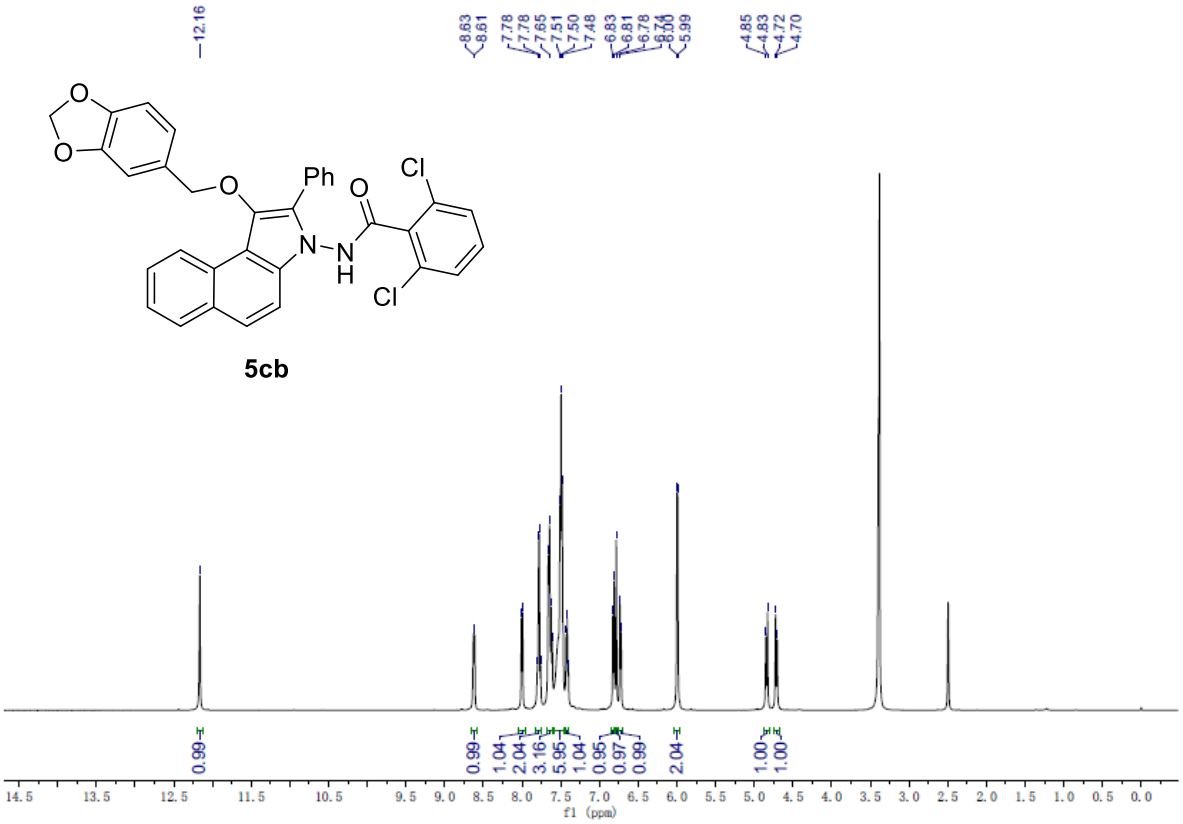
Br
N
NH
Cl
O
Cl
Cl
5bh
f1 (ppm)


11.78
8.65
8.63
7.67
7.65
7.65
7.62
7.53
7.52
7.51
7.50
7.07
6.81
6.79
6.77
6.00
4.90
4.88
4.71
4.68
2.00
Ph
O
O
O
N
N
H
1.00
1.00
1.01
1.06
4.02
4.28
1.00
2.00
2.29
1.04
2.05
1.02
1.00
6.04
f1 (ppm)

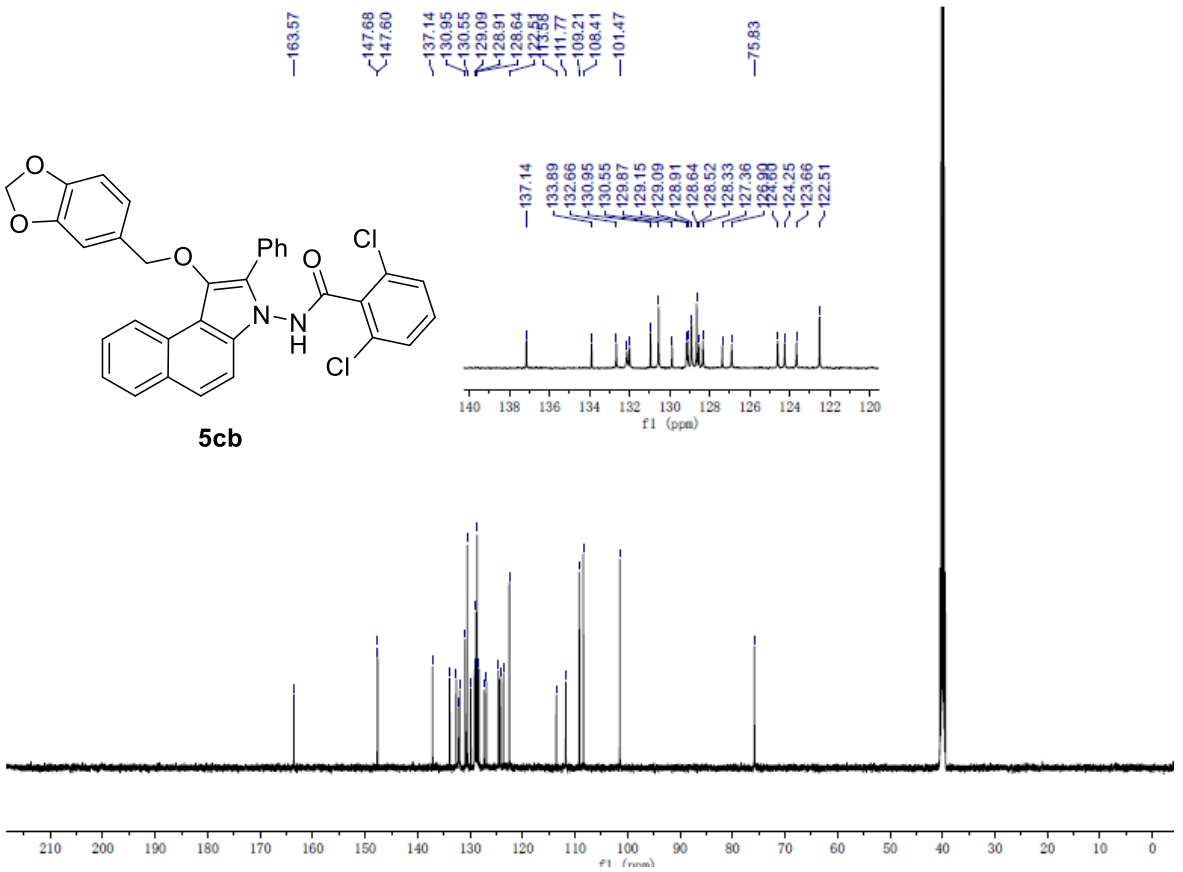
5ca


168.83
147.66
147.59
137.04
130.97
130.45
129.08
128.74
127.92
127.46
122.51
113.60
111.43
109.22
108.38
101.46
75.86
21.08
19.13
Ph
O
O
O
N
N
H
f1 (ppm)

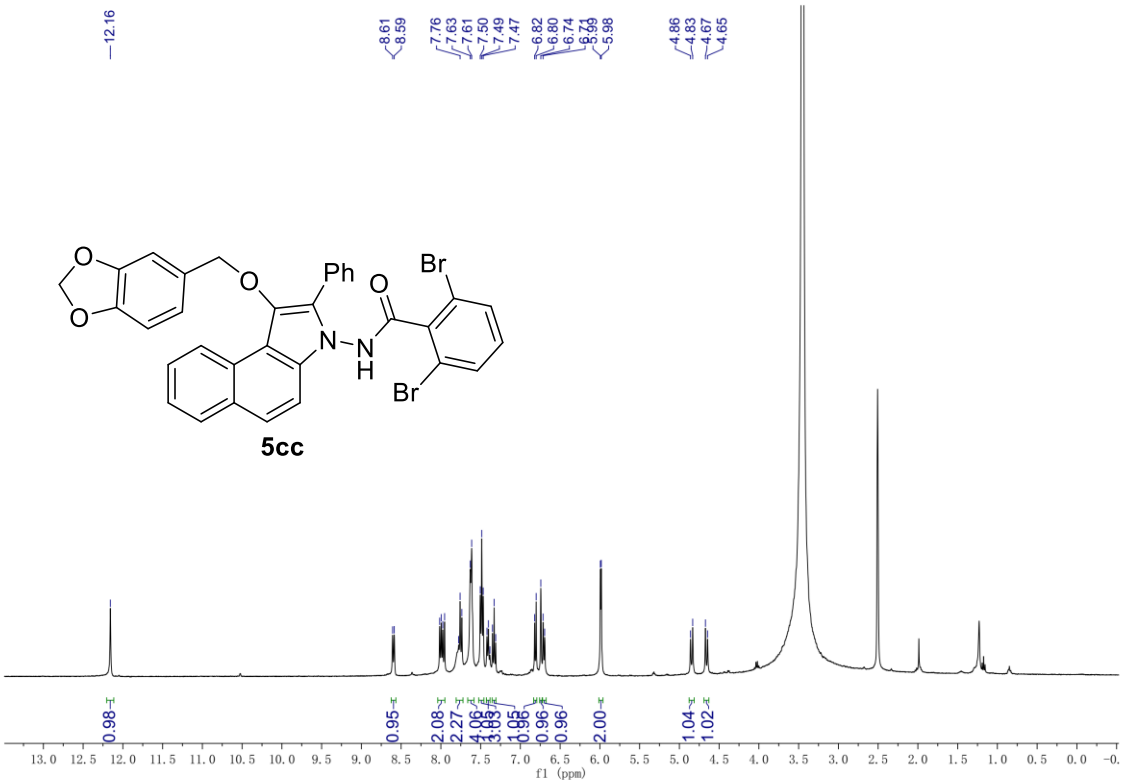
5ca

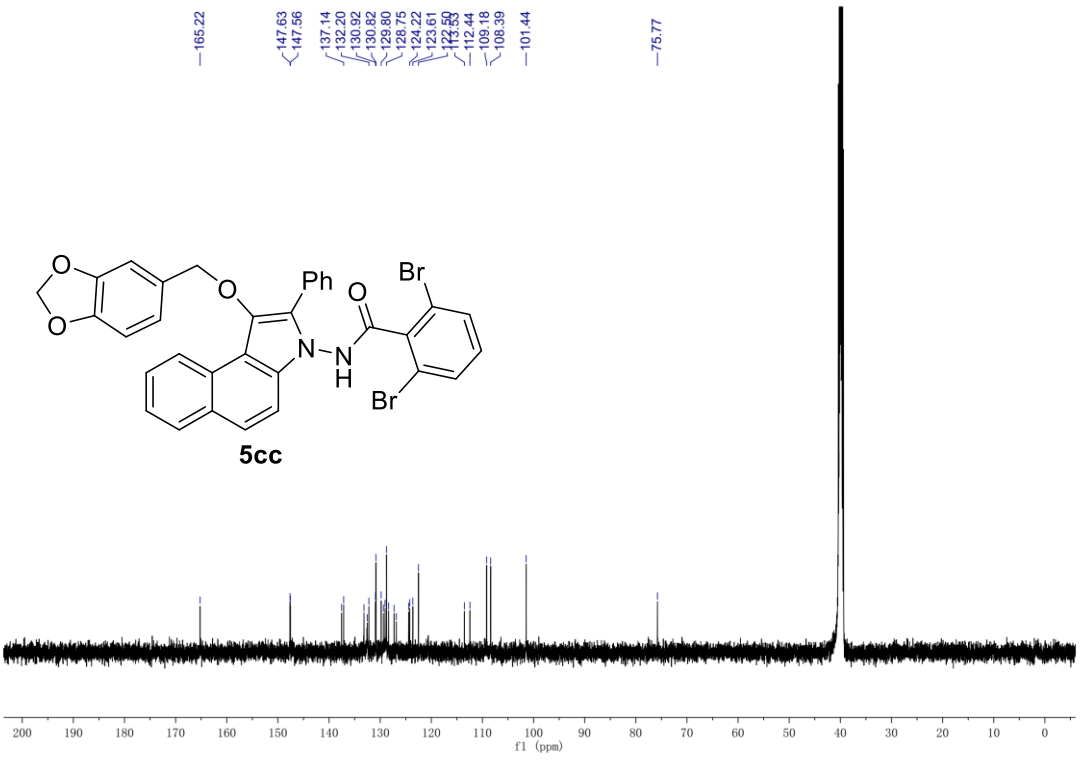

12.16
8.63
8.61
7.78
7.78
7.65
7.51
7.50
7.48
6.83
6.81
6.78
6.74
6.00
5.99
4.85
4.83
4.72
4.70
O
O
O
Ph
O
N
N
H
Cl
Cl
0.99
0.99
1.04
2.04
3.16
5.95
1.04
0.95
0.97
0.99
2.04
1.00
1.00
14.5 13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

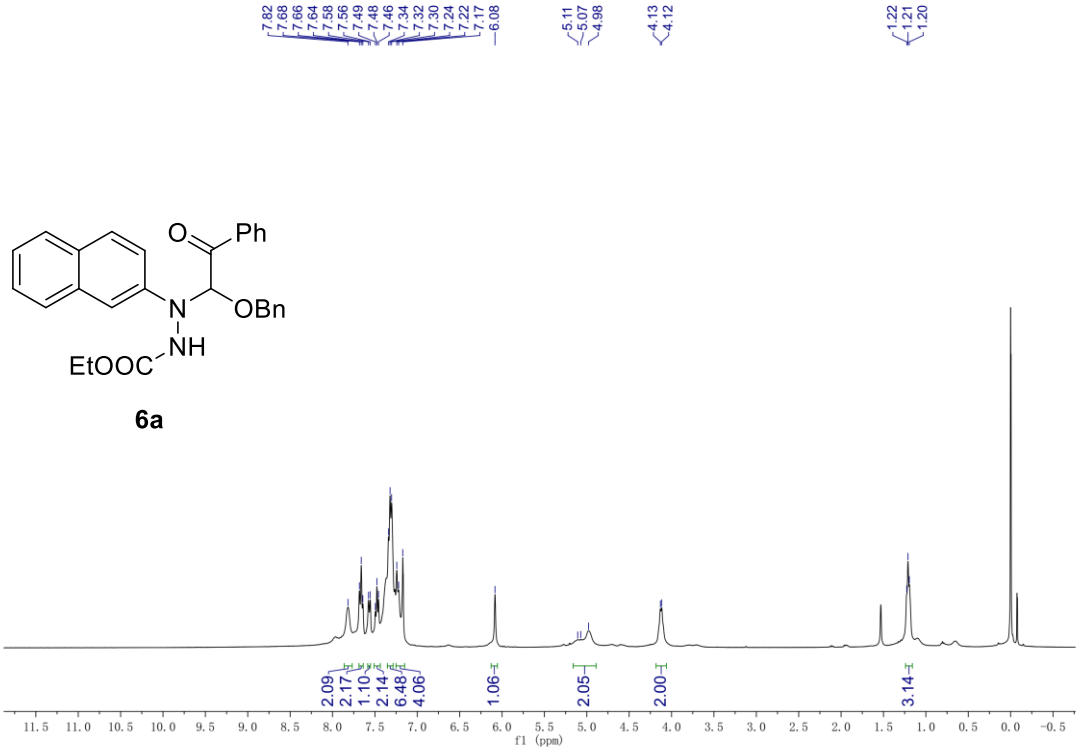
5cb


163.57
147.68
147.60
137.14
130.95
130.55
129.09
128.91
128.64
122.51
113.58
111.77
109.21
108.41
101.47
75.83
O
O
O
Ph
O
N
N
H
Cl
Cl
137.14
133.89
132.66
130.95
130.55
129.87
129.15
129.09
128.91
128.64
128.52
128.33
127.36
124.25
123.66
122.51
140 138 136 134 132 130 128 126 124 122 120
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

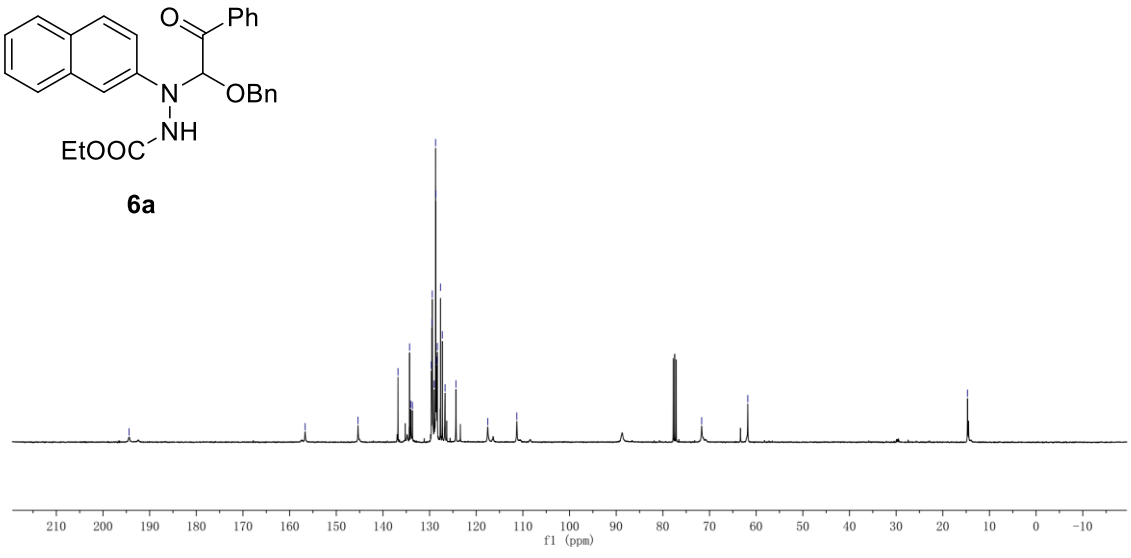
5cb


12.16
8.61
8.59
7.76
7.63
7.61
7.50
7.49
7.47
6.82
6.80
6.74
6.71
5.99
5.98
4.86
4.83
4.67
4.65
O
O
O
Ph
N
N
H
O
Br
Br
5cc
0.98
0.95
2.08
2.27
1.05
0.96
0.96
2.00
1.04
1.02
f1 (ppm)


165.22
147.63
147.56
137.14
132.20
130.92
130.82
129.80
128.75
124.22
123.61
112.44
109.18
108.39
101.44
75.77
O
O
O
Ph
N
N
H
O
Br
Br
5cc
f1 (ppm)

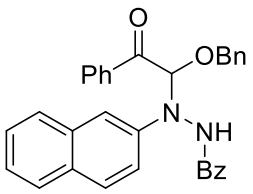

7.82
7.68
7.66
7.64
7.58
7.56
7.49
7.48
7.46
7.34
7.32
7.30
7.24
7.22
7.17
6.08
5.11
5.07
4.98
4.13
4.12
1.22
1.21
1.20
O
Ph
N
OBn
NH
EtOOC
2.09
2.17
1.10
2.14
6.48
4.06
1.06
2.05
2.00
3.14
f1 (ppm)

6a

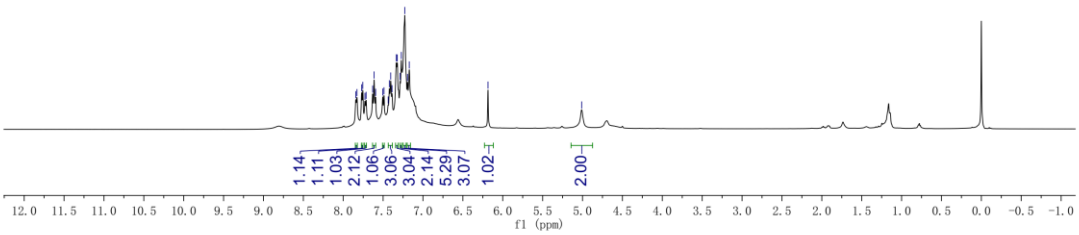

194.40
156.68
145.34
129.50
129.42
128.72
128.66
128.34
127.67
111.30
71.68
61.80
14.71
O
Ph
N
OBn
NH
EtOOC
f1 (ppm)

6a

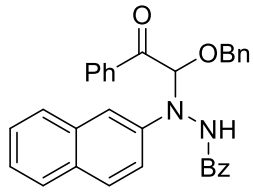

7.84
7.83
7.77
7.75
7.73
7.71
7.63
7.61
7.59
7.50
7.49
7.44
7.42
7.40
7.39
7.33
7.32
7.29
7.27
7.23
7.19
7.17
6.19
5.01


O
Ph
OBn
N
NH
Bz

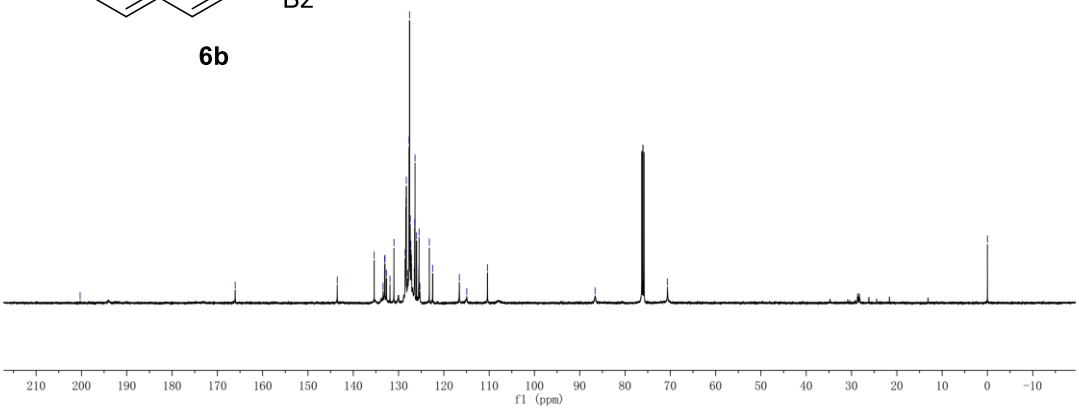
6b

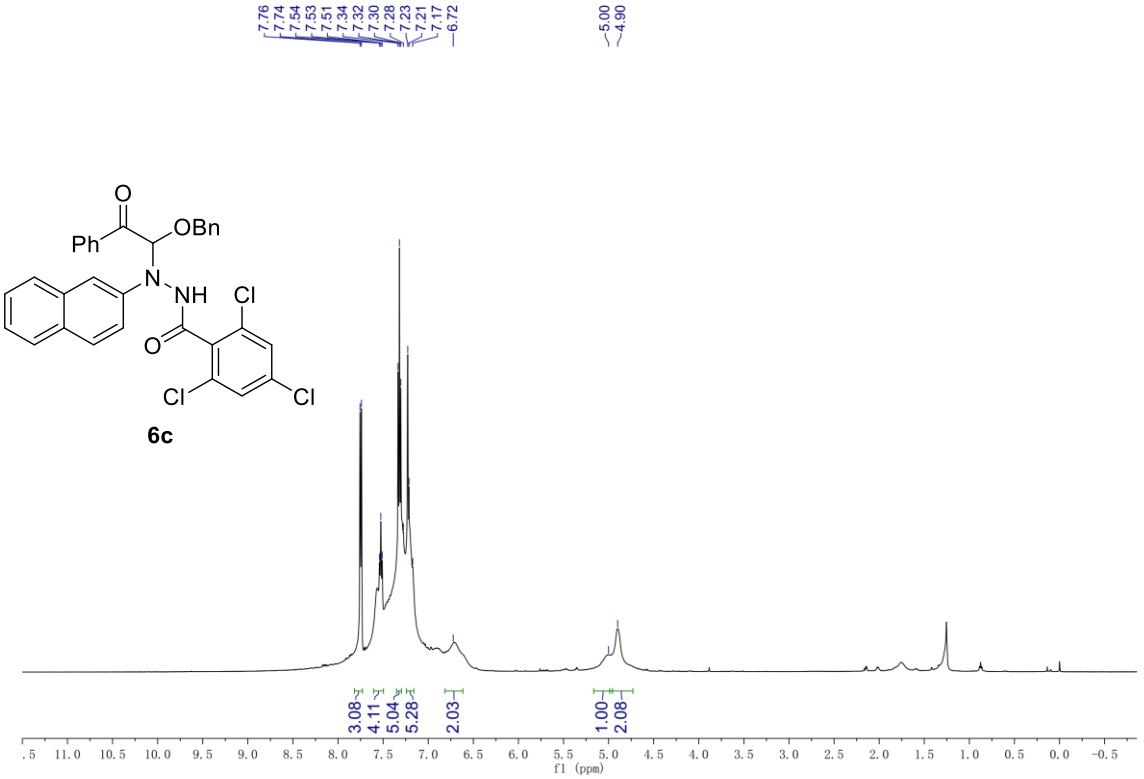

1.14
1.11
1.03
2.12
1.06
3.06
3.04
2.14
5.29
3.07
1.02
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

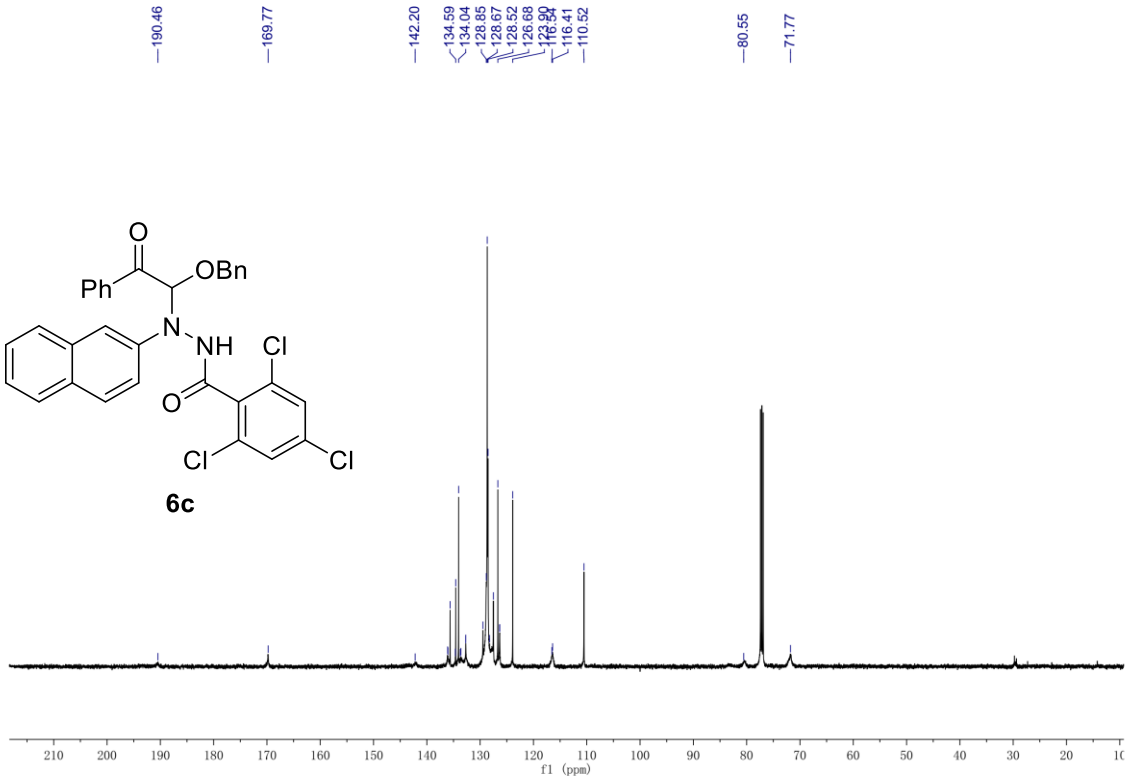

200.29
166.06
143.53
135.38
132.99
131.02
128.54
128.38
128.29
127.69
127.57
127.42
127.28
127.15
126.45
126.36
126.04
125.47
86.50
70.62
0.00

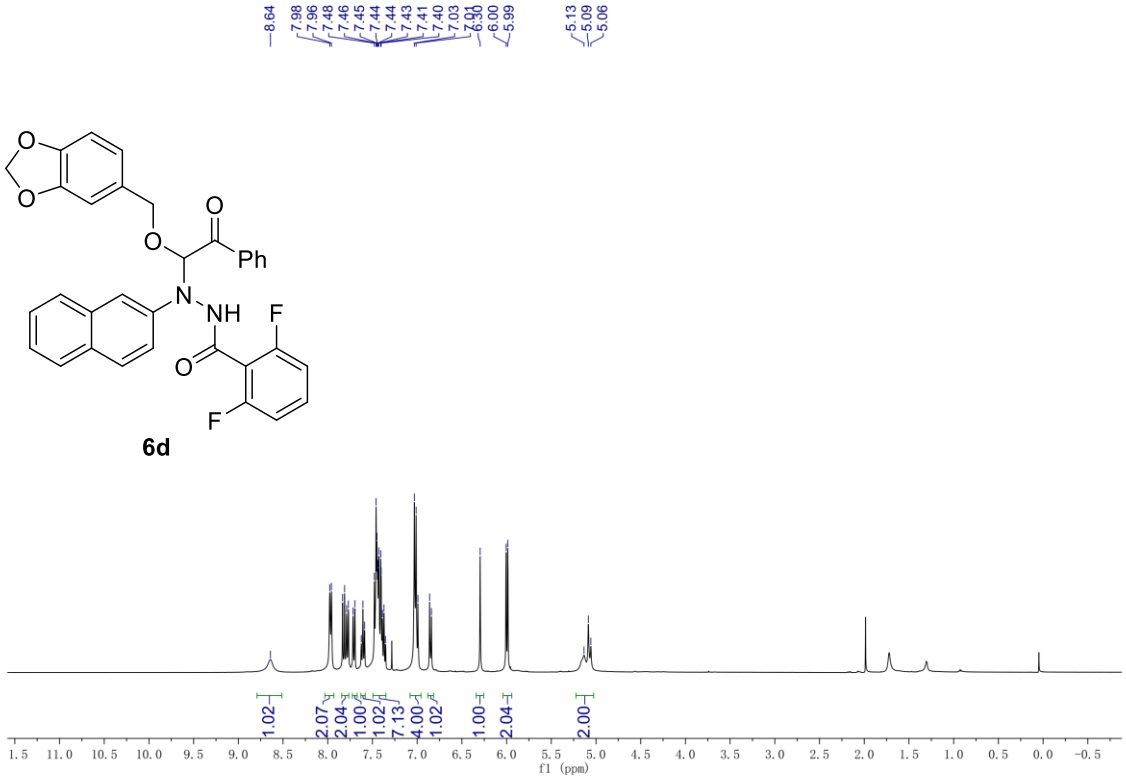

O
Ph
OBn
N
NH
Bz

6b

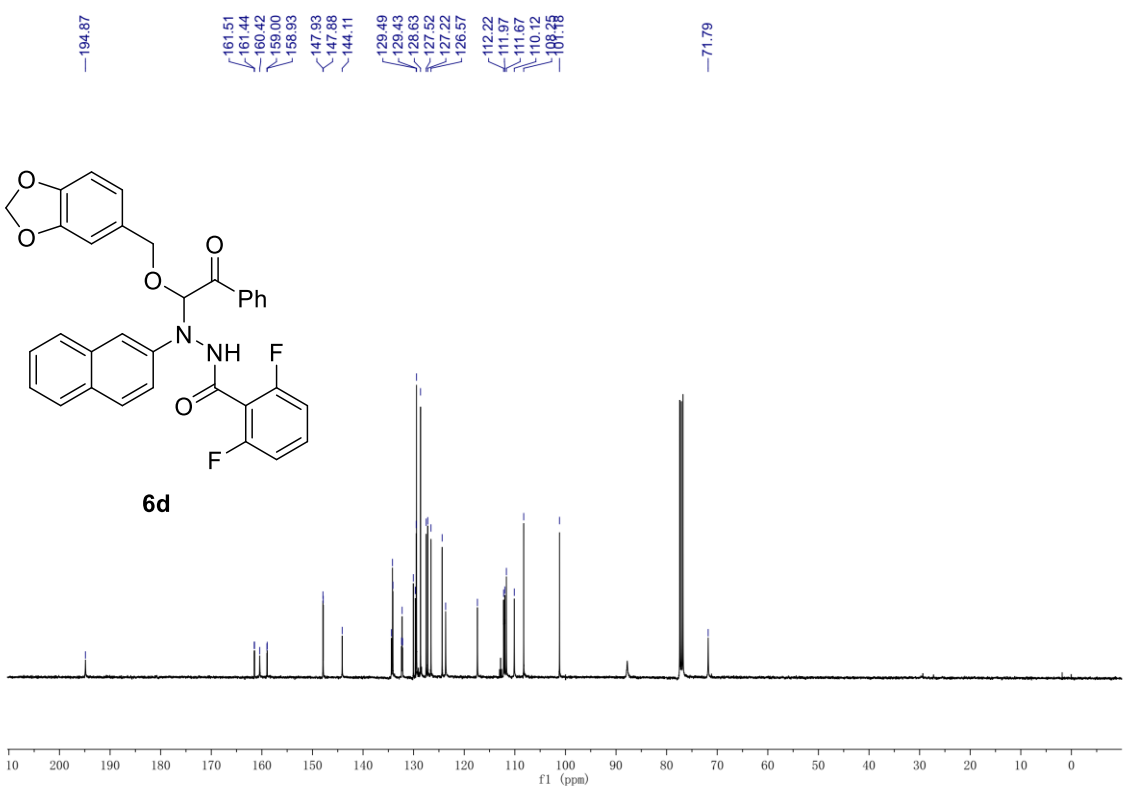

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.76
7.74
7.54
7.53
7.51
7.34
7.32
7.30
7.28
7.23
7.21
7.17
6.72
5.00
4.90
O
Ph
OBn
N
NH
Cl
O
Cl
Cl
6c
3.08
4.11
5.04
5.28
2.03
1.00
2.08
f1 (ppm)

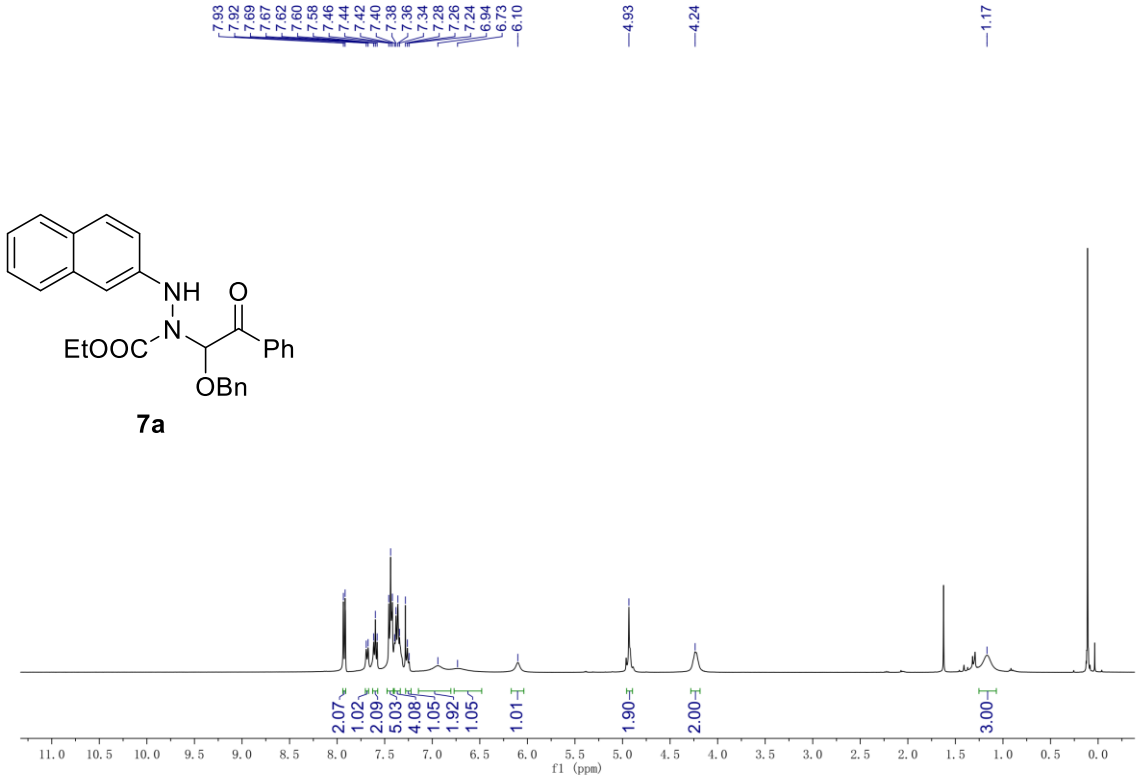

190.46
169.77
142.20
134.59
134.04
128.85
128.67
128.52
126.68
116.41
110.52
80.55
71.77
O
Ph
OBn
N
NH
Cl
O
Cl
Cl
6c
f1 (ppm)


8.64
7.98
7.96
7.48
7.46
7.45
7.44
7.44
7.43
7.41
7.40
7.03
7.01
6.30
6.00
5.99
5.13
5.09
5.06
O
O
O
Ph
N
NH
F
O
F
1.02
2.07
2.04
1.00
1.02
7.13
4.00
1.02
1.00
2.04
2.00
f1 (ppm)

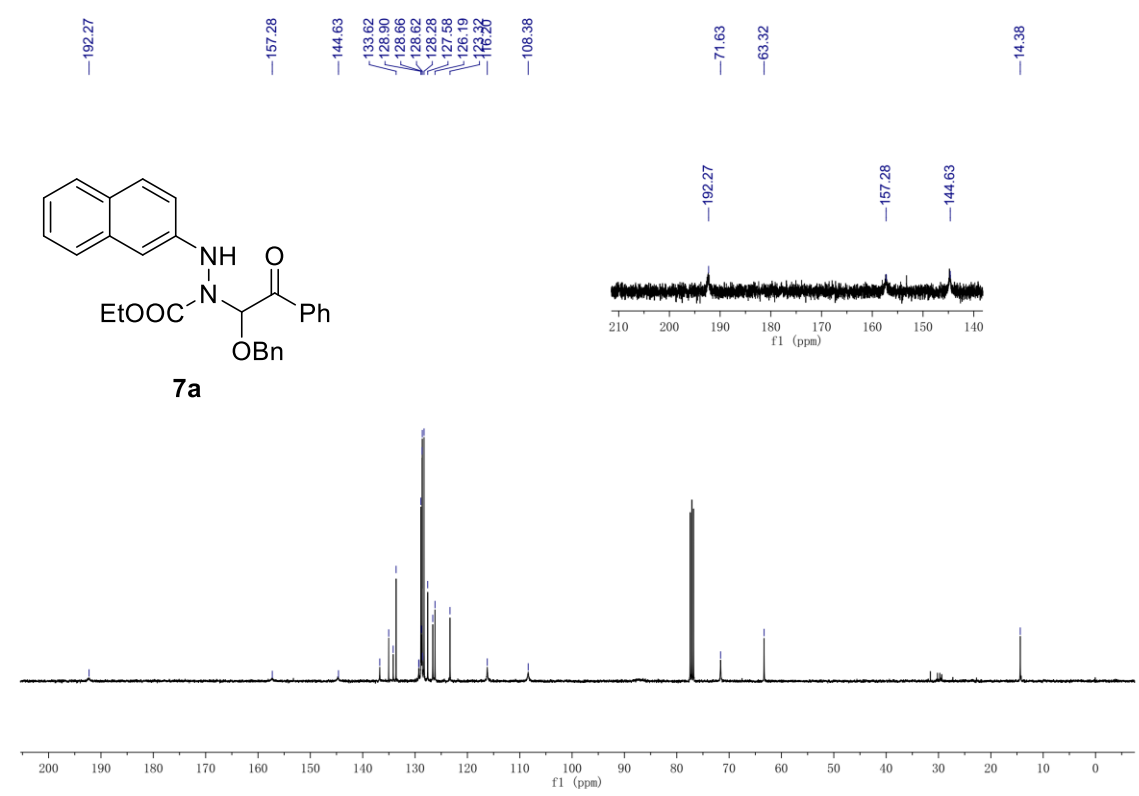
6d


194.87
161.51
161.44
160.42
159.00
158.93
147.93
147.88
144.11
129.49
129.43
128.63
127.52
127.22
126.57
112.22
111.97
111.67
110.12
101.18
71.79
O
O
O
Ph
N
NH
F
O
F
f1 (ppm)

6d


7.93
7.92
7.69
7.67
7.62
7.60
7.58
7.46
7.44
7.42
7.40
7.38
7.36
7.34
7.28
7.26
7.24
6.94
6.73
6.10
4.93
4.24
1.17
NH
O
N
EtOOC
Ph
OBn
2.07
1.02
2.09
5.03
4.08
1.05
1.92
1.05
1.01
1.90
2.00
3.00
f1 (ppm)

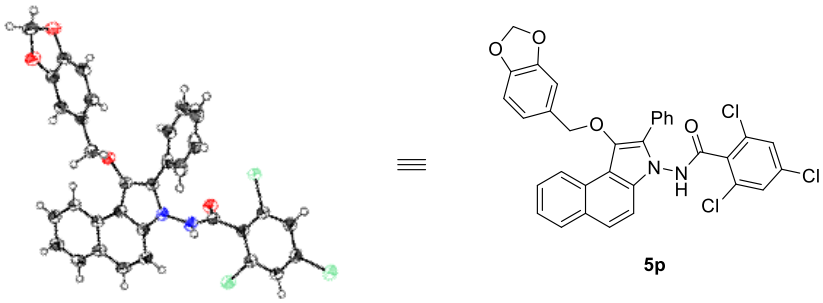
7a


192.27
157.28
144.63
133.62
128.90
128.66
128.62
128.28
127.58
126.19
108.38
71.63
63.32
14.38
NH
O
N
EtOOC
Ph
OBn
f1 (ppm)

7a

9. Single-Crystal X-ray Diffraction of 5p, 5t and 7a

Crystallographic Data for Compound **5p** (CCDC No. 2026832):



Bond precision: C-C = 0.0041 A Wavelength=1.54184

Cell: a=14.0142(4) b=21.0380(5) c=9.3503(3)
alpha=90 beta=90.176(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	2756.74(14)	2756.74(14)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C33 H21 Cl3 N2 O4	C33 H21 Cl3 N2 O4
Sum formula	C33 H21 Cl3 N2 O4	C33 H21 Cl3 N2 O4
Mr	615.87	615.87
Dx,g cm-3	1.484	1.484
Z	4	4
Mu (mm-1)	3.375	3.375
F000	1264.0	1264.0
F000'	1271.68	
h,k,lmax	17,26,11	17,26,11
Nref	5827	5747
Tmin,Tmax	0.817,0.845	0.755,1.000
Tmin'	0.363	

Correction method= # Reported T Limits: Tmin=0.755 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.986 Theta(max)= 76.979

R(reflections)= 0.0542(4720) wR2(reflections)= 0.1261(5747)

S = 1.060 Npar= 379

Alert level C

PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00409 Ang.
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	8.436 Check
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	2.787 Check

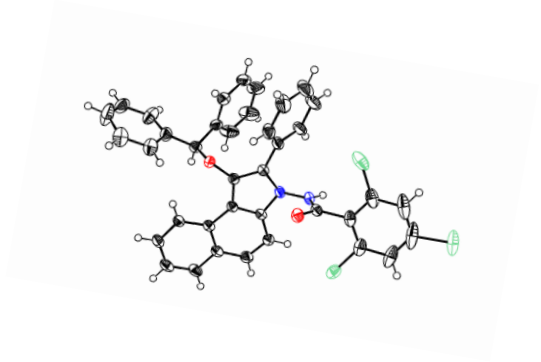
Alert level G

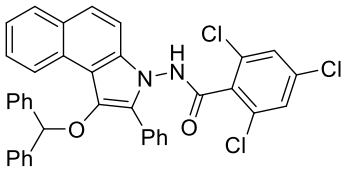
PLAT007_ALERT_5_G	Number of Unrefined Donor-H Atoms	1 Report
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O26	106.0 Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O28	105.1 Degree
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	79 Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	1 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	5 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Crystallographic Data for Compound **5t** (CCDC No. 1964942)





5t

Bond precision: C-C = 0.0052 A Wavelength=1.54184

Cell: a=26.6744(1) b=26.6744(1) c=18.1796(1)
alpha=90 beta=90 gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	12935.22(12)	12935.22(12)
Space group	I 41/a	I 41/a
Hall group	-I 4ad	-I 4ad
Moiety formula	4(C38 H25 Cl3 N2 O2), S [+ solvent]	4(C38 H25 Cl3 N2 O2), S
Sum formula	C152 H100 Cl12 N8 O8 S [+ solvent]	C152 H108 Cl12 N8 O8 S
Mr	2623.86	2631.92
Dx,g cm-3	1.347	1.351
Z	4	4
Mu (mm-1)	3.012	3.012
F000	5408.0	5440.0
F000'	5439.87	
h,k,lmax	33,33,22	33,33,22
Nref	6838	6752
Tmin,Tmax	0.510,0.547	0.771,1.000
Tmin'	0.386	

Correction method= # Reported T Limits: Tmin=0.771 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.987 Theta(max)= 77.023

R(reflections)= 0.0770(6576) wR2(reflections)= 0.1989(6752)

S = 1.061 Npar= 418

Alert level C

DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.

PLAT094_ALERT_2_C	Ratio of Maximum / Minimum Residual Density	2.37	Report
PLAT097_ALERT_2_C	Large Reported Max. (Positive) Residual Density	1.61	eA-3
PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	3.1	Ratio
PLAT230_ALERT_2_C	Hirshfeld Test Diff for C00Q --C015 .	6.3	s.u.
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of	C019	Check
PLAT336_ALERT_2_C	Long Bond Distance for ..... C012 -Cl2A	1.868	Ang.
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.0052	Ang.
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	4.644	Check
PLAT918_ALERT_3_C	Reflection(s) with I(obs) much Smaller I(calc) .	3	Check

Alert level G

FORMU01_ALERT_1_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and _chemical_formula_moiety. This is
usually due to the moiety formula being in the wrong format.
Atom count from _chemical_formula_sum: C152 H108 Cl12 N8 O8 S1
Atom count from _chemical_formula_moiety:C152 H100 Cl12 N8 O8 S1

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C152 H108 Cl12 N8 O8 S1
Atom count from the _atom_site data: C152 H100 Cl12 N8 O8 S1

CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.

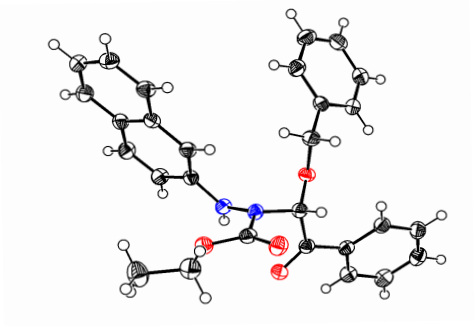
CELLZ01_ALERT_1_G WARNING: H atoms missing from atom site list. Is this intentional?
From the CIF: _cell_formula_units_Z 4
From the CIF: _chemical_formula_sum C152 H108 Cl12 N8 O8 S
TEST: Compare cell contents of formula and atom_site data

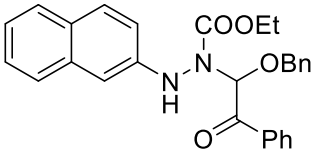
atom	Z*formula	cif sites	diff
C	608.00	608.00	0.00
H	432.00	400.00	32.00
Cl	48.00	48.00	0.00
N	32.00	32.00	0.00
O	32.00	32.00	0.00
S	4.00	4.00	0.00

PLAT007_ALERT_5_G	Number of Unrefined Donor-H Atoms	1	Report
PLAT041_ALERT_1_G	Calc. and Reported SumFormula Strings Differ	Please	Check
PLAT068_ALERT_1_G	Reported F000 Differs from Calcd (or Missing)...	Please	Check
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	58.76	Why ?
PLAT143_ALERT_4_G	s.u. on c - Axis Small or Missing	0.00010	Ang.
PLAT301_ALERT_3_G	Main Residue Disorder .....(Resd 1)	2%	Note
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in ..... Resd 2	0.25	Check
PLAT605_ALERT_4_G	Largest Solvent Accessible VOID in the Structure	31	A**3
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	69	Note
PLAT868_ALERT_4_G	ALERTS Due to the Use of _smtbx_masks Suppressed	!	Info
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	85	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	3	Info
PLAT992_ALERT_5_G	Repd & Actual _reflns_number_gt Values Differ by	1	Check

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
10 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
17 **ALERT level G** = General information/check it is not something unexpected

Crystallographic Data for Compound **7a** (CCDC No. 1965474)





7a

Bond precision: C-C = 0.0020 A Wavelength=1.54184

Cell: a=10.5825(1) b=10.9351(2) c=20.5330(3)
alpha=90 beta=94.269(1) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	2369.50(6)	2369.50(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C28 H26 N2 O4	C28 H26 N2 O4
Sum formula	C28 H26 N2 O4	C30 H26 N0.25 O4
Mr	454.51	454.01
Dx,g cm-3	1.274	1.273
Z	4	4
Mu (mm-1)	0.691	0.671
F000	960.0	959.0
F000'	962.92	
h,k,lmax	13,13,25	13,13,25
Nref	4975	4708
Tmin,Tmax	0.851,0.935	0.564,1.000
Tmin'	0.818	

Correction method= # Reported T Limits: Tmin=0.564 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.946 Theta(max)= 76.542

R(reflections)= 0.0429(4214) wR2(reflections)= 0.1325(4708)

S = 0.783 Npar= 308

Alert level C

```
GOODF01_ALERT_2_C  The least squares goodness of fit parameter lies
           outside the range 0.80 <> 2.00
           Goodness of fit given =      0.783
PLAT041_ALERT_1_C Calc. and Reported SumFormula    Strings  Differ      Please Check
PLAT043_ALERT_1_C Calculated and Reported Mol. Weight Differ by ..       0.50 Check
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)...      Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          4 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          2 Check
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  1.00A   From N11            0.45 eA-3
PLAT976_ALERT_2_C Check Calcd Resid. Dens.  0.97A   From N11           -0.54 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H11             -0.39 eA-3
```

Alert level G

```
FORMU01_ALERT_1_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and _chemical_formula_moiety. This is
           usually due to the moiety formula being in the wrong format.
           Atom count from _chemical_formula_sum:   C30 H26 N0.25 O4
           Atom count from _chemical_formula_moiety:C28 H26 N2 O4
FORMU01_ALERT_2_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and the formula from the _atom_site* data.
           Atom count from _chemical_formula_sum:C30 H26 N0.25 O4
           Atom count from the _atom_site data:  C28 H26 N2 O4
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: Large difference may be due to a
           symmetry error - see SYMMG tests
          From the CIF: _cell_formula_units_Z    4
          From the CIF: _chemical_formula_sum  C30 H26 N0.25 O4
          TEST: Compare cell contents of formula and atom_site data

          atom    Z*formula  cif sites diff
          C        120.00    112.00    8.00
          H        104.00    104.00    0.00
          N          1.00      8.00   -7.00
          O         16.00     16.00    0.00
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............          1 Report
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.10 Report
PLAT793_ALERT_4_G Model has Chirality at C17         (Centro SPGR)          S Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        264 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          8 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  9 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 10 ALERT level G = General information/check it is not something unexpected

  6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  7 ALERT type 2 Indicator that the structure model may be wrong or deficient
  3 ALERT type 3 Indicator that the structure quality may be low
  2 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```