Supporting information

Ruthenium Porphyrin Catalyzed Diimination of Indoles with Aryl Azides as Nitrene Source

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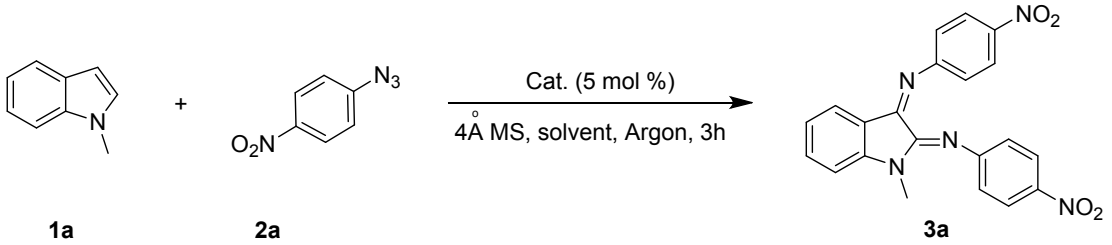
Experimental Section

General Information. All reactions were performed under argon atmosphere unless indicated otherwise. Molecular sieves were dried at 400℃ for 3 h prior to use. All anhydrous solvents used in the reactions were dried and freshly distilled. All manipulations with air-sensitive reagents were carried out under a dry argon atmosphere. Metal porphyrin catalysts and organic azides were synthesized according to previously reported methods. All ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV300 or AV400 NMR spectrometers with tetramethylsilane (TMS) as internal reference. Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. Mass spectra were obtained on a HP5989A spectrometer (EI), an IonSpec 4.7 Tesla FTMS spectrometer (MALDI). X-ray diffraction data were collected on Bruker SMART 1000 CCD diffractometer with graphite monochromatized MoKα radiation. Preparative thin layer chromatography was performed on pre-coated silica gel 60 F254 plates.

General procedure for screening of catalysts and reaction conditions

To an oven-dried Schlenk flask equipped with a rubber seal was added 1-methyl indole (0.2 mmol), 4-nitrophenyl azide (0.6 mmol), catalyst (5 mol %) and 200 mg of 4Å molecular sieve. The flask was evacuated and backfilled with argon three times. Then freshly distilled 1,2-dichloroethane (2 mL) was added via syringe. The reaction mixture was stirred at reflux for 3h. The mixture was cooled down to room temperature and filtered through a plug of celite. The filtrate was concentrated by rotary evaporator and the residue was purified by flash chromatography on a silica gel column (eluent: Hexane/EA = 4:1) to give the corresponding red solid product.

Table S1 Screening of catalysts and reaction conditions [a]



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

Entry	Catalyst	solvent	Temp.	Conv.(%)[b]	Yield(%)[c]
1	[Ru(TTP)(CO)]	DCE	85	78	80
2	[Ru(F_{20}-TPP)(CO)]	DCE	85	46	21
3	[Ru(TDCPP)(CO)]	DCE	85	81	47
4	[$Rh_2(OAc)_4$]	DCE	85	NR[d]	
5	[$Cu(OTf)_2$]	DCE	85	NR	
6	[Fe(TTP)Cl]	DCE	85	NR	
7	[Co(TTP)]	DCE	85	NR	
8	[Ru(TTP)(CO)]	CH_2Cl_2	40	39	42
9	[Ru(TTP)(CO)]	DCE	25	34	33
11	[Ru(TTP)(CO)]	Toluene	85	94	70
12	[Ru(TTP)(CO)]	MeCN	85	82	45
13	none	DCE	85	NR	

[a] Conditions: N-methylindole (0.2 mmol), 4-nitrophenylazide (0.6 mmol), catalyst (5 mol %), 200 mg of 4ÅMS, 2 mL of solvent, argon; [b] Conv. was based on N-methylindole by ^{1}H-NMR; [c] Isolated yield based on N-methylindole conversion. [d] No reaction.

General procedure for [Ru(TTP)CO]-catalyzed diimination of indoles with 4-nitrophenyl azide or 3,5-bis(trifluoromethyl)phenyl azide

To an oven-dried Schlenk flask equipped with a rubber seal was added indole (0.2 mmol), azide (0.4 mmol), [Ru(TTP)CO] (5 mol %) and 200 mg of 4Å molecular sieve. The flask was evacuated and backfilled with argon three times. Then freshly distilled

1,2-dichloroethane (2 mL) was added via syringe. The reaction mixture was stirred at reflux. When azide was completely consumed (monitored by TLC), another portion of azide (0.25 mmol) was added into the reaction mixture. The reaction mixture was continuously stirred until all of the azide was consumed. The mixture was cooled down to room temperature and filtered through a plug of celite. The filtrate was concentrated by rotary evaporator and the residue was purified by flash chromatography on a silica gel column (eluent: Hexane/EA = 5:1~3:1 or Hexane/DCM = 2:1~1:1) to give the corresponding red solid product.

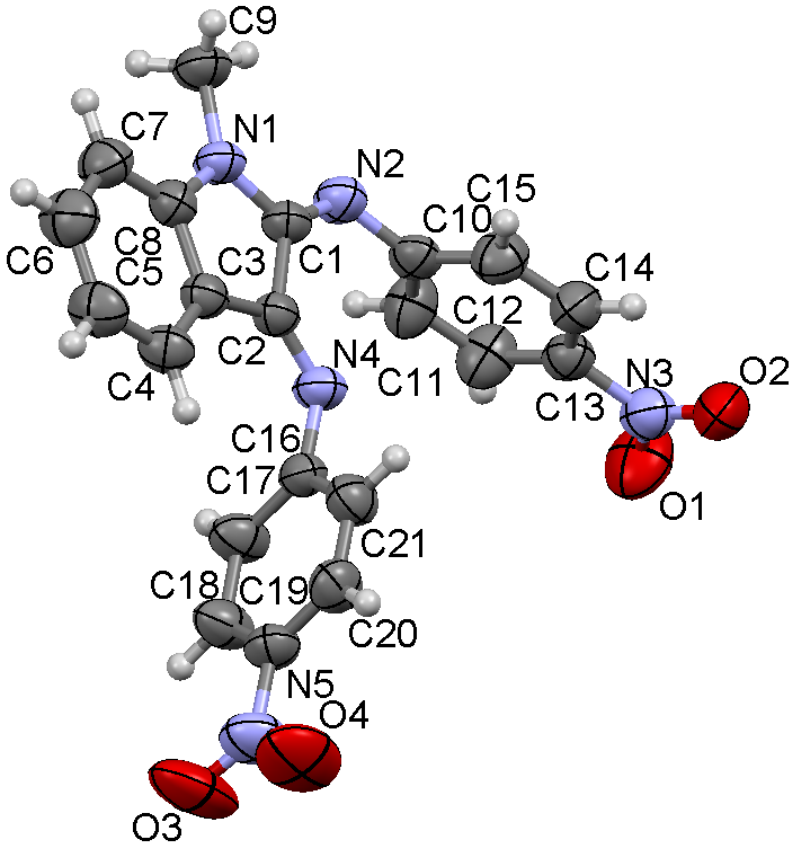
Stoichiometric reaction of [Ru(TPP)(NAr)$_2$] (Ar= 3,5-bis(trifluoromethyl)phenyl) 5 with 1-methylindole

To an oven-dried Schlenk flask was added 0.05 mmol of 1-methylindole and 0.025 mmol of complex **5**. The flask was evacuated and backfilled with argon three times. Freshly distilled DCE (2 mL) was added via syringe. The mixture was stirred at reflux under argon atmosphere for 1.5h. After complex **5** was completely consumed, the reaction mixture was concentrated by rotary evaporator. The residue was purified by silica gel column chromatography (eluent: hexane/DCM = 5:1) to give the product **3b** in 35% yield.

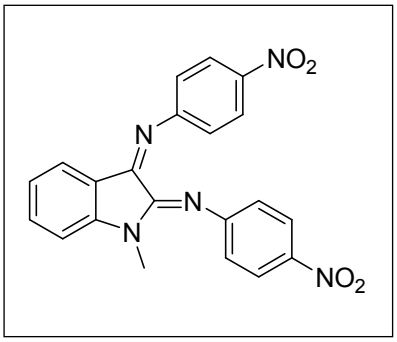
Control reaction of 1-methylindole with 3,5- bis(trifluoromethyl)phenyl azide and 4-nitroaniline

To an oven-dried Schlenk flask equipped with a rubber seal was added 1-methylindole (0.2 mmol), 3,5-bis(trifluoromethyl)phenyl azide (0.4 mmol), 4-nitroaniline (0.4 mmol) and [Ru(TTP)CO] (5mol %) and 200 mg of 4Å molecular sieve. The flask was evacuated and backfilled with argon three times. Then freshly distilled 2ml of 1,2-dichloroethane was added via syringe. The reaction mixture was stirred at reflux under atmosphere for 6h. After azide was completely consumed (monitored by TLC) the mixture was cooled down to room temperature and filtered through a plug of celite. The filtrate was concentrated by rotary evaporator and purified by silica gel columu chromatography (eluent: Hexane/DCM = 5:1) to give the product **3b** in 65% yield based on 80% conversion of indole.

Figure S1 X-ray Crystal Structure of **3a** (Solvent is not included). CCDC 973563 for **3a** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif)



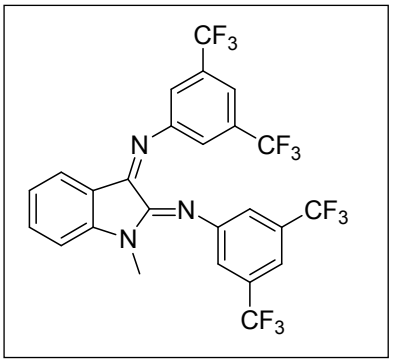
Characterizations of Products



1-Methyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22(d, *J* = 8.72 Hz, 2H), 8.14(d, *J* = 8.80 Hz, 2H), 7.40(t, *J* = 7.78 Hz, 1H), 6.98(d, *J* = 8.60 Hz, 2H), 6.88(d, *J* = 8.04 Hz, 1H), 6.80(d, *J* = 7.52 Hz, 2H), 6.67(t, *J* = 7.58 Hz, 1H), 6.44(d, *J* = 7.52 Hz, 1H), 3.36(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 155.3, 150.8, 147.7, 144.7, 143.1, 135.2, 126.7, 125.7, 125.4, 125.1, 121.4, 120.3, 117.7, 115.8, 109.2, 27.9.

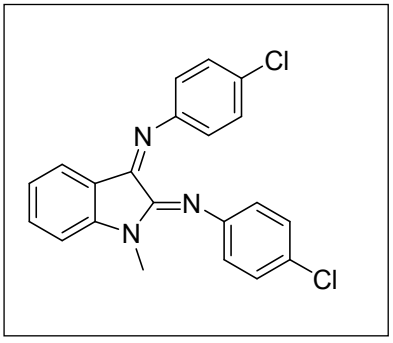
HRMS-EI (m/z), Calcd for, $C_{21}H_{15}N_5O_4$ $[M]^+$ 401.1124; found: 401.1076.



3-(3,5-Bis(trifluoromethyl)phenylimino)-1-methylindolin-2-ylidene)-3,5-bis(trifluoromethyl)benzenamine(3b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64(s, 1H), 7.46-7.38 (m. 4H), 7.14(s, 2H), 6.90(d, *J* = 8.03 Hz, 1H), 6.68(t, *J* = 7.32 Hz, 1H), 6.41(d, *J* = 6.88 Hz, 1H), 3.39(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.62, 150.85, 150.53, 149.17, 135.45, 133.14(q, $J_{(CF3)}$ = 33.40 Hz), 131.95(q, $J_{(CF3)}$ = 32.70 Hz), 127.44(d, $J_{(C-F)}$ = 57.90 Hz), 126.31, 124.74(d, $J_{(C-F)}$ = 57.80 Hz), 122.03(d, $J_{(C-F)}$ = 58.10 Hz), 121.44, 121.15, 119.29(d, $J_{(C-F)}$ = 58.30 Hz), 118-117(m, *C-F*), 116.14, 115.74, 109.42, 27.66;

HRMS-EI (m/z), Calcd for, $C_{25}H_{13}N_3F_{12}$ $[M]^+$ 583.0918; found: 583.0898.

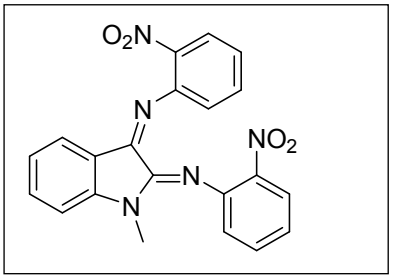


4-chloro-N-(3-(4-chlorophenylimino)-1-methylindolin-2-ylidene)benzenamine(3c)

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.33-7.29(m, 3H), 7.19 (d, *J* = 8.07 Hz, 2H), 6.89-6.82(m, 3H), 6.68-6.49(m, 4H), 3.32(s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 150.88, 149.11, 148.61, 138.21, 134.44, 129.88,

128.89, 127.40, 126.76, 122.20, 121.98, 121.62, 120.61, 119.03, 116.63, 108.95, 30.07;

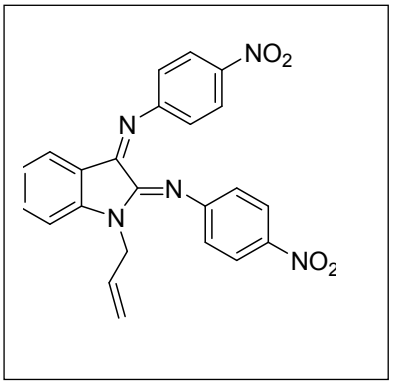
HRMS-EI (m/z), Calcd for, $C_{21}H_{15}N_3Cl_2$ $[M]^+$ 379.0643; found: 379.0608.



1-Methyl-3-(2-nitrophenylimino)indolin-2-ylidene)-2-nitrobenzenamine(3e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04(dd, *J* = 8.31, 1.21 Hz, 1H), 7.93(dd, *J* = 8.30, 1.35 Hz, 1H), 7.50(td, *J* = 8.32, 1.30 Hz, 1H), 7.42(td, *J* = 8.36, 1.39 Hz, 1H), 7.37(td, *J* = 7.84, 1.07 Hz, 1H), 7.21(td, *J* = 8.44, 1.22 Hz, 1H), 7.05(dd, *J* = 8.10, 1.15 Hz, 1H), 6.99(td, *J* = 8.38, 1.25 Hz, 1H), 6.88(d, *J* = 8.03 Hz, 1H), 6.76(dd, *J* = 8.02, 1.10 Hz, 1H), 6.63(t, *J* = 7.67 Hz, 1H), 6.42(d, *J* = 7.42 Hz, 1H), 3.41(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.02, 150.73, 148.39, 145.43, 144.94, 139.64, 138.10, 134.89, 134.65, 133.91, 125.96, 125.43, 124.95, 124.58, 123.84, 122.28, 121.02, 119.46, 116.32, 109.04, 29.69;

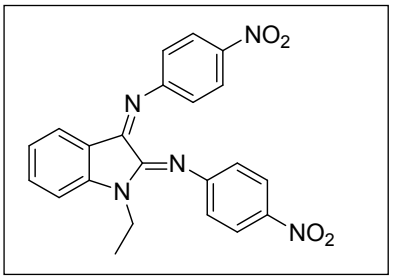
HRMS-EI (m/z), Calcd for, $C_{21}H_{15}N_5O_4$ $[M]^+$ 401.1124; found: 401.1077.



1-Allyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21(d, *J* = 8.76 Hz, 2H), 8.12(d, *J* = 8.84 Hz, 2H), 7.36(t, *J* = 7.80 Hz, 1H), 6.97(d, *J* = 8.84 Hz, 2H), 6.87(d, *J* = 8.08 Hz, 1H), 6.81(d, *J* = 8.44 Hz, 2H), 6.66(t, *J* = 7.64 Hz, 1H), 6.46(d, *J* = 7.68 Hz, 1H), 5.95-5.89(m, 1H), 5.35-5.28(m, 2H), 4.49(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.27, 155.32, 152.49, 150.05, 146.93, 144.60, 143.07, 135.16, 130.82, 126.69, 126.49, 125.66, 125.06, 121.42, 120.22, 117.87, 117.67, 115.78, 110.02, 43.70;

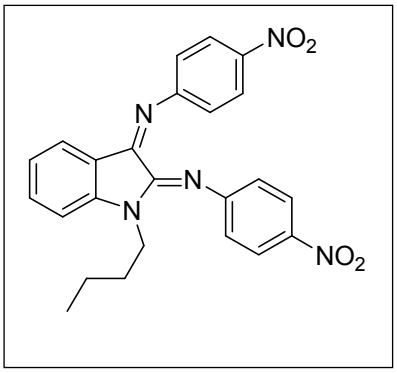
HRMS-EI (m/z), Calcd for, $C_{23}H_{17}N_5O_4$ $[M]^+$ 427.1281; found: 427.1280.



1-Ethyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4b)

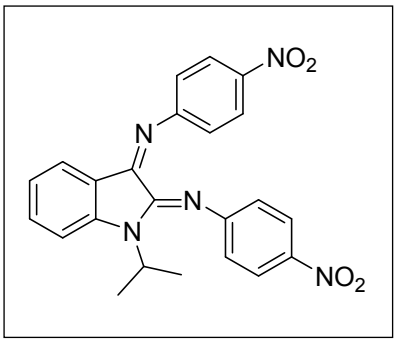
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21(d, *J* = 8.80 Hz, 2H), 8.12(d, *J* = 8.92 Hz, 2H), 7.37(t, *J* = 7.88 Hz, 1H), 6.97(d, *J* = 8.80 Hz, 2H), 6.89(d, *J* = 8.04 Hz, 1H), 6.80(d, *J* = 8.56 Hz, 2H), 6.64(t, *J* = 7.68 Hz, 1H), 6.44(d, *J* = 7.68 Hz, 1H), 3.92-3.90(m, 2H), 1.35(t, *J* = 7.04 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.59, 155.37, 152.48, 149.92, 146.86, 144.61, 143.03, 135.21, 126.87, 125.68, 125.11, 121.20, 120.24, 117.66, 115.90, 109.28, 36.14, 12.11;

HRMS-EI (m/z), Calcd for, $C_{22}H_{17}N_5O_4$ $[M]^+$ 415.1281; found: 415.1275.



1-Butyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21(d, *J* = 8.80 Hz, 2H), 8.12(d, *J* = 8.88 Hz, 2H), 7.37(t, *J* = 7.72 Hz, 1H), 6.96(d, *J* = 8.76 Hz, 2H), 6.88(d, *J* = 8.08 Hz, 1H), 6.80(d, *J* = 8.60 Hz, 2H), 6.64(t, *J* = 7.64 Hz, 1H), 6.44(d, *J* = 7.72 Hz, 1H), 3.84(t, *J* = 6.93 Hz, 2H), 1.80-1.72(m, 2H), 1.49-1.44(m, 2H), 1.00(t, *J* = 7.28 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.66, 155.38, 152.19, 150.36, 147.22, 144.61, 142.99, 135.17, 126.80, 125.67, 125.12, 121.14, 120.17, 117.66, 115.79, 109.46, 41.19, 29.22, 20.41, 13.96; HRMS-EI (m/z), Calcd for, $C_{24}H_{21}N_5O_4$ $[M]^+$ 443.1594; found: 443.1585.

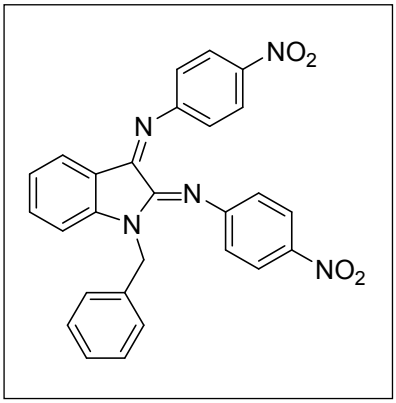


1-Isopropyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20(d, *J* = 8.76 Hz, 2H), 8.12(d, *J* = 8.84 Hz, 2H), 7.34(t, *J* = 7.84 Hz, 1H), 7.05(d, *J* = 8.16 Hz, 1H), 6.93(d, *J* = 8.88 Hz, 2H), 6.76(d, *J* = 8.72 Hz, 2H), 6.62(t, *J* = 7.64 Hz, 1H), 6.45(d, *J* = 7.76 Hz, 1H), 4.90-4.80(m, 1H), 1.60(d, *J* = 6.96 Hz, 6H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 156.83, 155.35, 151.96, 149.51, 146.86, 144.56, 142.87, 134.92, 126.98, 125.73, 125.21, 120.82, 119.92, 117.51, 116.16, 110.02, 45.05, 19.11;

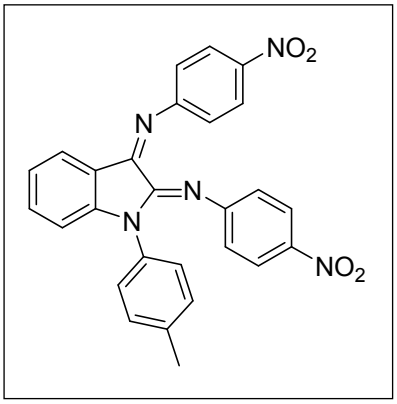
HRMS-EI (m/z), Calcd for, $C_{23}H_{19}N_5O_4$ $[M]^+$ 429.1437; found: 429.1325.



1-Benzyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4e)

^1H NMR (300 MHz, $CDCl_3$) δ 8.23(d, *J* = 8.91 Hz, 2H), 8.13(d, *J* = 8.91 Hz, 2H), 7.40-7.27(m, 7H), 6.97(d, *J* = 8.91 Hz, 2H), 6.82(d, *J* = 7.83 Hz, 2H), 6.65(t, *J* = 7.57 Hz, 1H), 6.46(d, *J* = 7.56 Hz, 1H), 5.09(s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.17, 155.31, 150.13, 147.38, 144.77, 143.25, 135.71, 135.23, 129.09, 128.04, 127.40, 126.83, 125.76, 125.16, 121.58, 120.23, 117.73, 115.95, 110.15, 45.14;

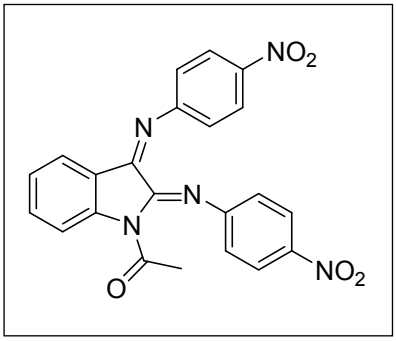
HRMS-EI (m/z), Calcd for, $C_{27}H_{19}N_5O_4$ $[M]^+$ 477.1437; found: 477.1404.



4-Nitro-N-(3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)benzenamine(4f)

^1H NMR (400 MHz, $CDCl_3$): δ 8.29(d, *J* = 5.72 Hz, 2H), 7.92(br, 2H), 7.40-6.90(br, 7H), 6.90-6.60(m, 4H), 6.57(br, 1H), 2.33(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.26, 144.70, 142.85, 139.01, 138.08, 135.03, 132.26, 130.44, 127.51, 126.97, 126.52, 125.68, 124.35, 122.21, 120.36, 117.97, 115.91, 113.39, 110.88, 110.69, 21.18;

HRMS-EI (m/z), Calcd for, $C_{27}H_{19}N_5O_4$ $[M]^+$ 477.1437; found: 477.1407.

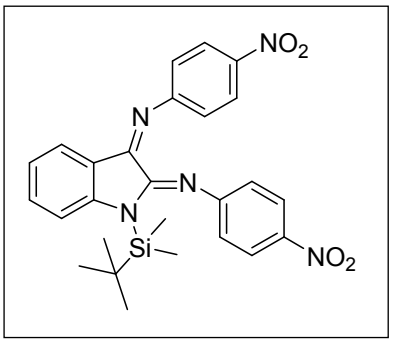


2,3-Bis(4-nitrophenylimino)indolin-1-yl)ethanone(4g)

^1H NMR (400 MHz, $CDCl_3$) δ 8.52(d, *J* = 8.36 Hz, 1H), 8.22(d, *J* = 8.88 Hz, 2H), 8.18(d, *J* = 8.92 Hz, 2H), 7.52-7.51(m, 1H), 6.97-6.93(m, 3H), 6.75(d, *J* = 8.84 Hz, 2H), 6.63(d, *J* = 7.84 Hz, 1H), 2.84(s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.62, 154.50, 154.46, 150.18, 146.99, 146.38, 144.89, 143.64, 135.54, 125.97, 125.93, 125.33, 124.92, 118.56, 118.41, 117.44, 117.27, 28.19;

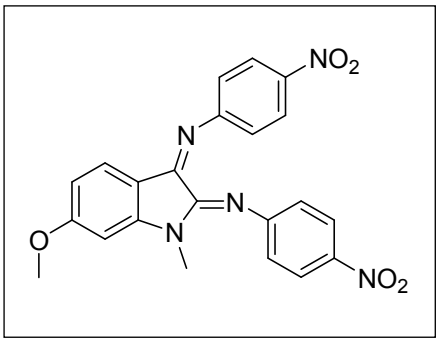
HRMS-EI (m/z), Calcd for, $C_{22}H_{15}N_5O_5$ $[M]^+$ 429.1073; found: 429.1044.



1-(*tert*-Butyldimethylsilyl)-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine (4h)

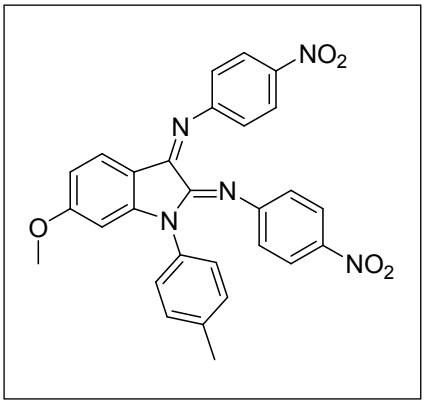
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19(d, *J* = 7.92 Hz, 2H), 8.12(d, *J* = 7.96 Hz, 2H), 7.29(t, *J* = 7.80 Hz, 1H), 7.10(d, *J* = 7.10 Hz, 1H), 6.85(d, *J* = 8.04 Hz, 2H), 6.76(d, *J* = 8.00 Hz, 2H), 6.64(t, *J* = 7.54 Hz, 1H), 6.48(d, *J* = 7.76 Hz, 1 H), 1.10(s, 9H), 0.61(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 155.4, 154.2, 152.7, 152.3, 144.4, 142.7, 134.8, 126.7, 125.7, 125.2, 121.2, 118.9, 118.5, 117.5, 114.4, 31.6, 27.0, - 1.9;

HRMS-EI (m/z), Calcd for, $C_{26}H_{27}N_5O_4Si$ $[M]^+$ 501.1832; found: 501.1799.



6-Methoxy-1-methyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20(d, *J* = 8.72 Hz, 2H), 8.13(d, *J* = 8.88 Hz, 2H), 6.97(d, *J* = 8.72 Hz, 2H), 6.78(d, *J* = 6.68 Hz, 2H), 6.38-6.34(m, 2H), 6.15(d, *J* = 8.52 Hz, 1H), 3.83(s, 3H), 3.32(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.63, 155.97, 152.99, 148.63, 144.41, 143.11, 128.47, 125.68, 125.08, 120.72, 120.37, 118.11, 109.19, 107.71, 106.46, 95.75, 55.96, 29.83; HRMS-EI (m/z), Calcd for, $C_{22}H_{17}N_5O_5$ $[M]^+$ 431.1230; found: 431.1178.

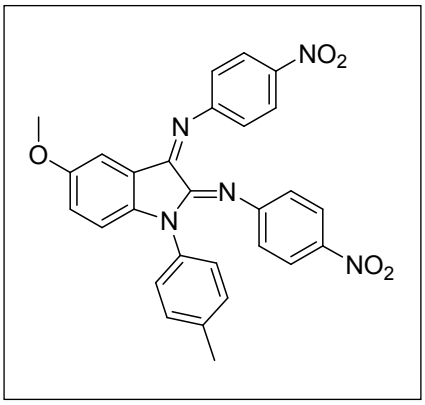


N-(6-methoxy-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine(4j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25(br, 2H), 7.93(br, 2H), 7.60-6.60(m/br, 8H), 6.48(br, 1H),

6.22(d, J = 8.28 Hz, 1H), 6.13(br, 1H), 3.70(s, 3H), 2.32(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.43, 156.82, 153.55, 147.48, 144.43, 142.78, 139.04, 132.24, 130.50, 128.35, 127.63, 125.68, 124.30, 120.41, 118.44, 113.12, 109.28, 107.92, 96.72, 55.87, 21.25;

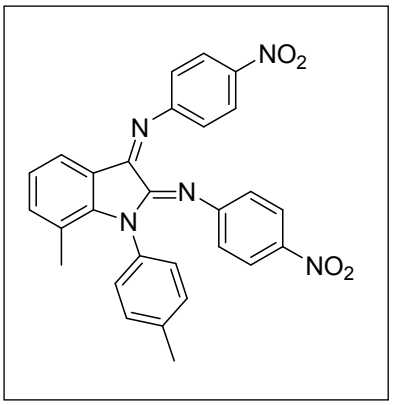
HRMS-EI (m/z), Calcd for, $C_{28}H_{21}N_5O_5$ $[M]^+$ 507.1543; found: 507.1499.



N-(5-methoxy-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine(4k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27(d, J = 8.76 Hz, 2H), 7.91(d, J = 8.36 Hz, 2H), 7.14(br, 4H), 6.99(d, J = 8.16 Hz, 2H), 6.87(dd, J = 8.80, 2.52 Hz, 1H), 6.77(d, J = 8.00 Hz, 2H), 6.60(d, J = 8.76 Hz, 1H), 6.22(br, 1H), 3.49(s, 3H), 2.32(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.10, 145.54, 144.73, 142.86, 138.93, 132.64, 131.03 130.47, 127.49, 126.92, 126.49, 125.71, 124.31, 121.10, 120.55, 118.23, 113.51, 111.70, 111.49, 55.79, 21.27;

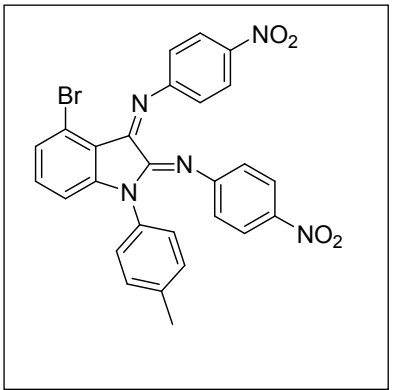
HRMS-EI (m/z), Calcd for, $C_{28}H_{21}N_5O_5$ $[M]^+$ 507.1543; found: 507.1507.



7-Methyl-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine(4l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22(d, J = 8.80 Hz, 2H), 8.01(d, J = 6.76 Hz, 2H), 7.30(br, 4H), 7.08(d, J = 7.60 Hz, 1H), 6.86(br, 4H), 6.61(t, J = 7.70 Hz, 1H), 6.43(br, 1H), 2.41(s, 3H), 1.68(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.94, 148.77, 144.59, 142.78, 139.44, 138.87, 135.38, 130.11, 129.50, 126.47, 125.81, 124.56, 123.70, 122.59, 122.10, 119.93, 117.71, 113.50, 21.39, 19.07.

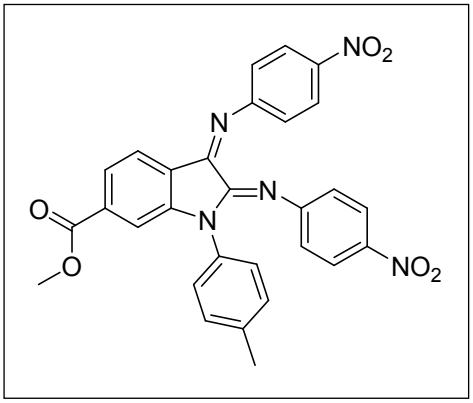
HRMS-EI (m/z), Calcd for, $C_{28}H_{21}N_5O_4$ $[M]^+$ 491.1594; found: 491.1550.



4-Bromo-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine(4m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14(d, *J* = 8.96 Hz, 2H), 7.61(d, *J* = 8.94 Hz, 2H), 7.27(d, *J* = 8.15 Hz, 1H), 7.17(t, *J* = 8.01 Hz, 1H), 6.96(d, *J* = 8.95 Hz, 2H), 6.91(d, *J* = 8.09 Hz, 2H), 6.80(d, *J* = 8.22 Hz, 2H), 6.50(d, *J* = 7.93 Hz, 1H), 6.22(d, *J* = 8.91 Hz, 2H), 2.17(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.25, 152.77, 152.26, 152.02, 143.30, 142.43, 139.43, 139.38, 134.68, 131.96, 130.24, 128.18, 127.73, 124.97, 123.62, 119.92, 119.63, 118.88, 117.03, 109.03, 21.00;

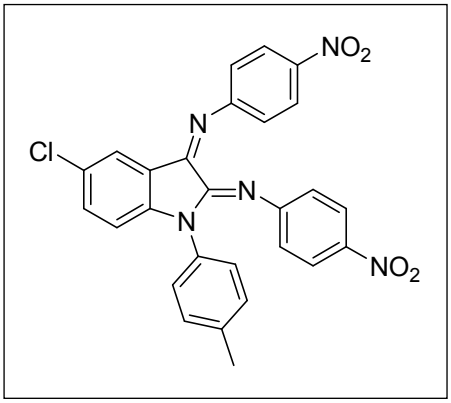
HRMS-EI (m/z), Calcd for, $C_{27}H_{18}BrN_5O_4$ $[M]^+$ 555.0542; found: 555.0539.



Methyl 1-methyl-2,3-bis(4-nitrophenylimino) indoline-6-carboxylate(4n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30(br, 2H), 7.96(br, 2H), 7.5-6.7(br/m, 10H), 6.60(br/m, 1H), 3.84(s, 3H), 2.35(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.57, 151.29, 145.00, 143.05, 139.40, 135.80, 131.95, 130.75, 127.52, 127.03, 126.44, 125.82, 124.60, 123.45, 120.38, 118.99, 117.85, 113.46, 111.76, 111.37, 52.79, 21.31;

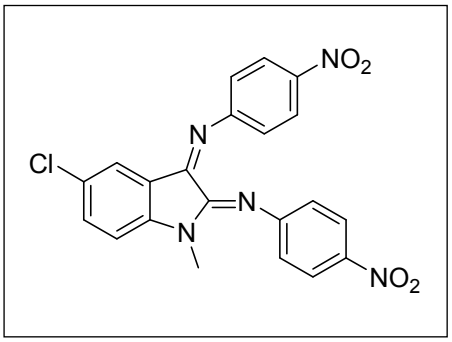
HRMS-EI (m/z), Calcd for, $C_{29}H_{21}N_5O_6$ $[M]^+$ 535.1492; found: 535.1462.



5-Chloro-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine(4o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26(d, *J* = 8.84 Hz, 2H), 7.93(d, *J* = 8.64 Hz, 2H), 7.25-7.15(m, 5H), 6.95(d, *J* = 8.56 Hz, 2H), 6.77(d, *J* = 8.28 Hz, 2H), 6.68(br, 1H), 6.62(d, *J* = 8.56 Hz, 1H), 2.34(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.11, 149.79, 144.92, 143.04, 139.35, 134.81, 132.02, 130.65, 127.47, 126.97, 126.05, 125.84, 125.31, 124.48, 120.22, 117.86, 113.45, 112.27, 111.88, 21.27;

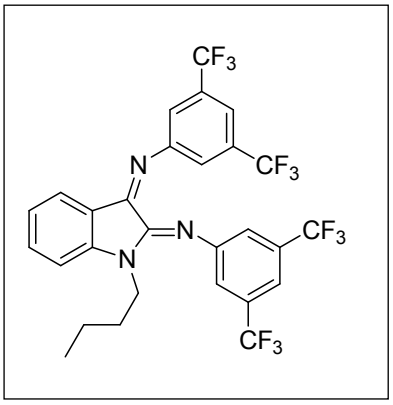
HRMS-EI (m/z), Calcd for, $C_{27}H_{18}N_5O_4Cl$ $[M]^+$ 511.1047; found: 511.1011.



N-(5-chloro-1-methyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4p)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24(d, J = 8.68 Hz, 2H), 8.13(d, J = 8.76 Hz, 2H), 7.36(dd, J = 8.52, 1.76 Hz, 1H), 6.96(d, J = 8.60 Hz, 2H), 6.83(d, J = 8.52 Hz, 2H), 6.79(d, J = 7.96 Hz, 1H), 6.42(s, 1H), 3.35(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.99, 154.49, 152.52, 149.26, 147.30, 144.90, 143.28, 134.95, 126.57, 126.30, 125.82, 125.17, 120.17, 117.57, 116.58, 110.33, 28.01;

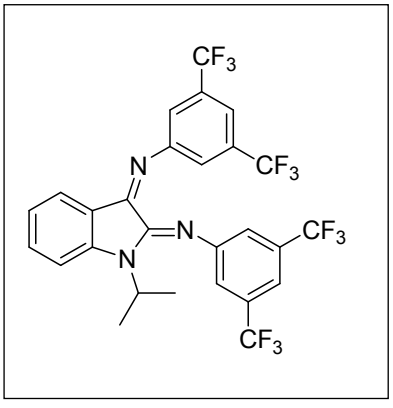
HRMS-EI (m/z), Calcd for, $C_{21}H_{14}N_5O_4Cl$ $[M]^+$ 435.0734; found: 435.0704.



3-(3,5-Bis(trifluoromethyl)phenylimino)-1-butylindolin-2-ylidene)-3,5-bis(trifluoromethyl)benzenamine(4q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64(s, 1H), 7.46-7.37 (m, 4H), 7.16(s, 2H), 6.90(d, *J* = 8.07 Hz, 1H), 6.66(t, *J* = 7.49 Hz, 1H), 6.41(d, *J* = 6.88 Hz, 1H), 3.88(s, 2H), 1.79(t, *J* = 6.68 Hz, 2H), 1.57-1.47 (m, 2H), 1.03(t, *J* = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.68, 150.71, 150.63, 150.51, 148.68, 135.36, 133.15(q, $J_{(CF3)}$ = 33.40 Hz), 131.96(q, $J_{(CF3)}$ = 32.70 Hz), 127.49(d, $J_{(C-F)}$ = 58.40 Hz), 126.44, 124.78(d, $J_{(C-F)}$ = 58.90 Hz), 122.07(d, $J_{(C-F)}$ = 59.20 Hz), 121.22, 121.06, 119.31(d, $J_{(C-F)}$ = 59.50 Hz), 118.24-117.93(m, *C-F*), 116.01-115.80(m, *C-F*), 109.62, 41.18, 29.27, 20.50, 13.96;

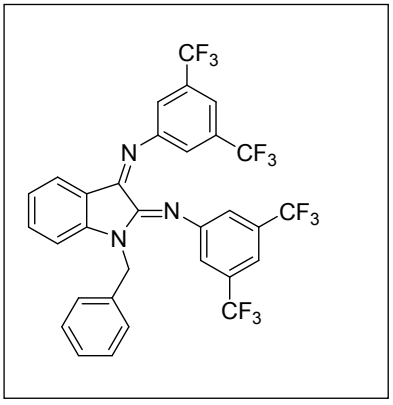
HRMS-EI (m/z), Calcd for, $C_{28}H_{19}N_3F_{12}$ $[M]^+$ 625.1387; found: 625.1356.



3-(3,5-Bis(trifluoromethyl)phenylimino)-1-isopropylindolin-2-ylidene)-3,5-bis(trifluoromethyl)benzenamine(4r)

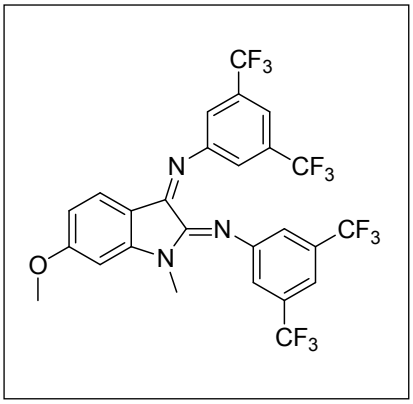
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63(s, 1H), 7.44(s, 1H), 7.39-7.34(m, 3H), 7.13(s, 2H), 7.08(d, *J* = 8.18

Hz, 1H), 6.65(t, *J* = 7.62 Hz, 1H), 6.42(d, *J* = 7.22 Hz, 1H), 4.93- 4.89(m, 1H), 1.61(d, *J* = 7.05 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.55, 150.87, 150.67, 149.62, 148.33, 135.10, 133.15(q, $J_{(CF3)}$ = 33.40 Hz), 131.98(q, $J_{(CF3)}$ = 32.80 Hz), 127.51(d, $J_{(C-F)}$ = 60.40 Hz), 126.62, 124.79(d, $J_{(C-F)}$ = 60.80 Hz), 122.08(d, $J_{(C-F)}$ = 61.10 Hz), 120.89, 120.81, 119.37(d, $J_{(C-F)}$ = 61.60 Hz), 118.13-117.78(m, *C-F*), 116.18-115.77(m, *C-F*), 111.16, 45.04, 19.06; HRMS-EI (m/z), Calcd for, $C_{27}H_{17}N_3F_{12}$ $[M]^+$ 611.1231; found: 611.1221



3-(3,5-Bis(trifluoromethyl)phenylimino)-1-benzylindolin-2-ylidene)-3,5-bis(trifluoromethyl)benzenamine(4s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67(s, 1H), 7.49-7.39 (m, 7H), 7.36-7.31(m, 2H), 7.20(s, 2H), 6.85(d, *J* = 8.06 Hz, 1H), 6.68(t, *J* = 7.50 Hz, 1H), 6.46(d, *J* = 6.99 Hz, 1H), 5.14(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.51, 150.53, 150.29, 150.19, 148.90, 135.72, 135.42, 133.17(q, $J_{(CF3)}$ = 33.50 Hz), 131.95(q, $J_{(CF3)}$ = 32.80 Hz), 129.13, 128.03, 127.46(d, $J_{(C-F)}$ = 56.40 Hz), 127.36, 126.40, 124.76(d, $J_{(C-F)}$ = 56.90 Hz), 122.04(d, $J_{(C-F)}$ = 57.10 Hz), 121.63, 121.11, 119.29(d, $J_{(C-F)}$ = 57.60 Hz), 118.36-117.97(m, *C-F*), 116.29-115.86(m, *C-F*), 110.32, 45.00; HRMS-EI (m/z), Calcd for, $C_{31}H_{17}N_3F_{12}$ $[M]^+$ 659.1231; found: 659.1216.



3-(3,5-Bis(trifluoromethyl)phenylimino)-6-methoxy-1-methylindolin-2-ylidene)-3,5-bis(trifluoromethyl)benzenamine(4t)

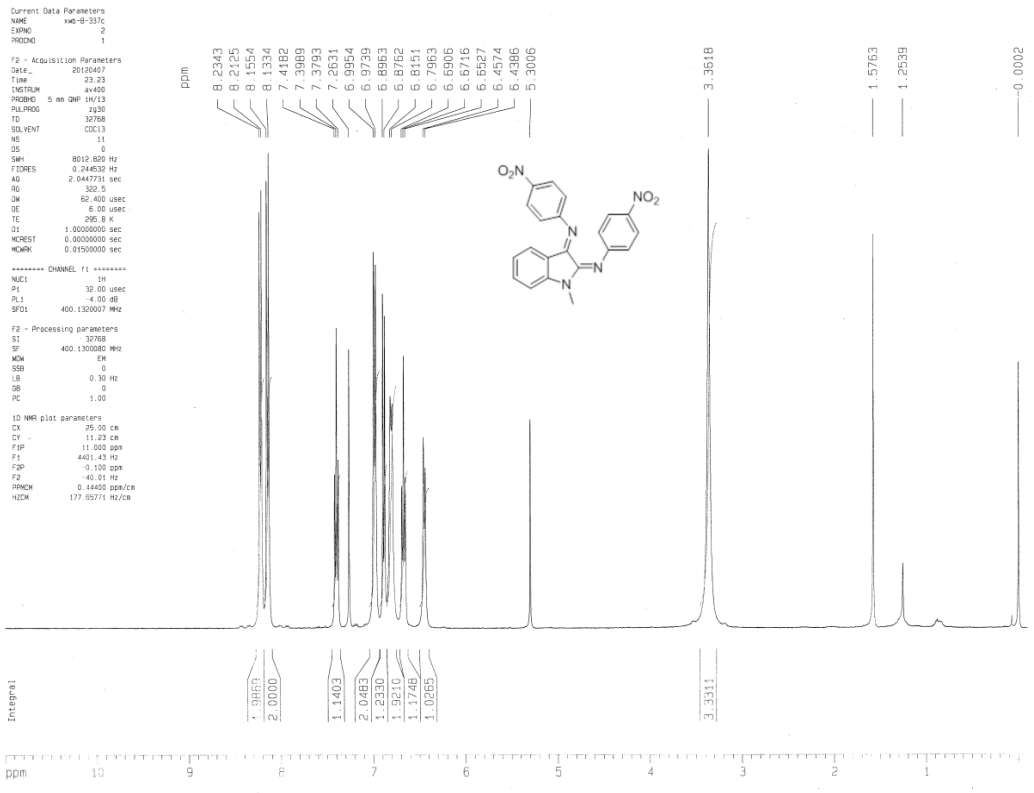
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60(s, 1H), 7.45(s, 1H), 7.41(s, 2H), 7.12(s, 2H), 6.36-6.32(m, 2H), 6.17(d, *J* = 8.32 Hz, 1H), 3.84(s, 3H), 3.35(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 153,08, 152.60, 151.04, 150.43, 150.06, 133.03(q, $J_{(CF3)}$ = 33.20 Hz), 131.84(q, $J_{(CF3)}$ = 32.80 Hz), 128.10, 127.52(d, $J_{(C-F)}$ = 52.90 Hz),

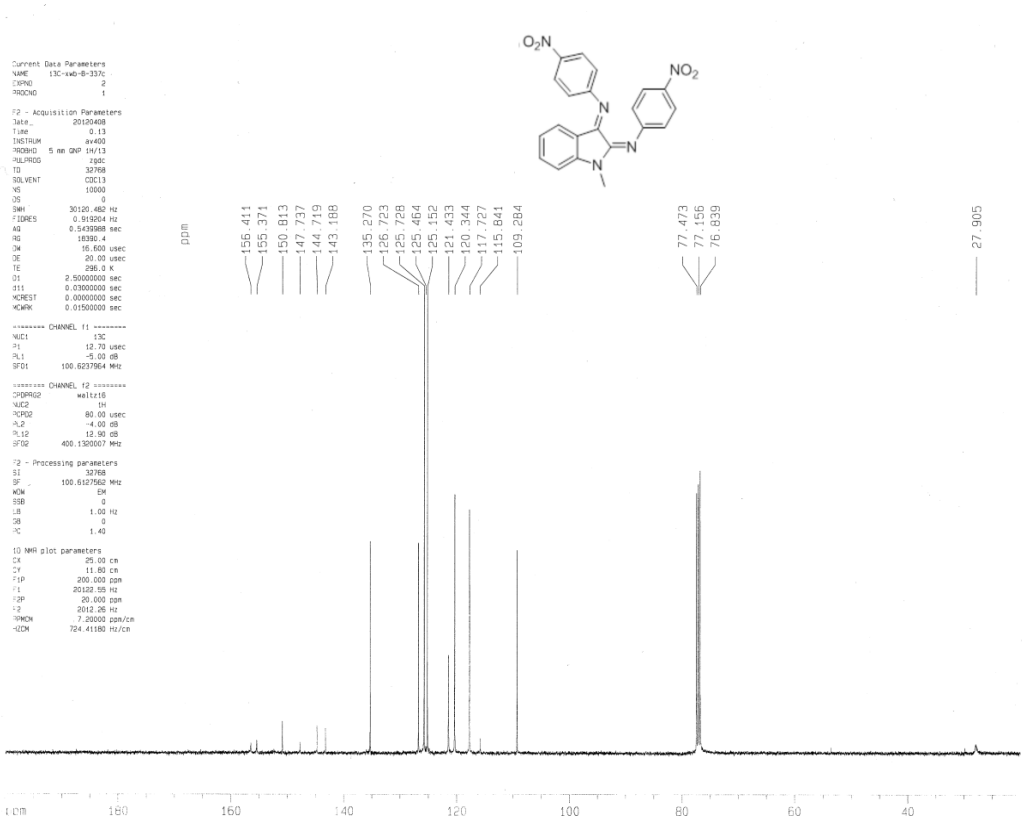
124.78(d, $J_{(C-F)}$ = 53.40 Hz), 122.06(d, $J_{(C-F)}$ = 53.70 Hz), 121.17, 119.37(d, $J_{(C-F)}$ = 53.60 Hz), 118.31, 116.11, 106.49, 95.89, 55.98, 29.87;

HRMS-EI (m/z), Calcd for, $C_{26}H_{15}N_3OF_{12}$ $[M]^+$ 613.1024; found: 613.0994.

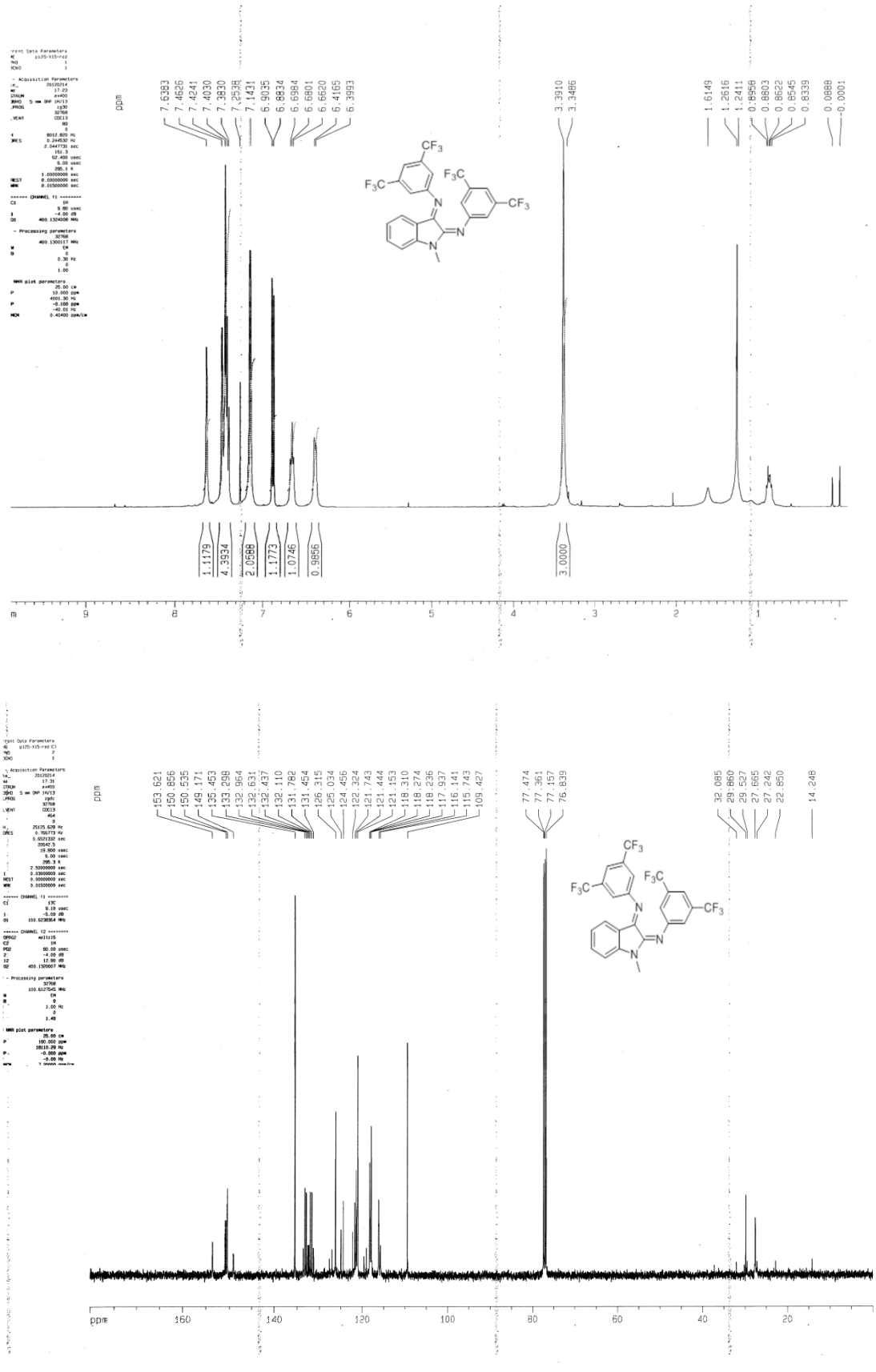
NMR Spectra of products

1-Methyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine (3a)

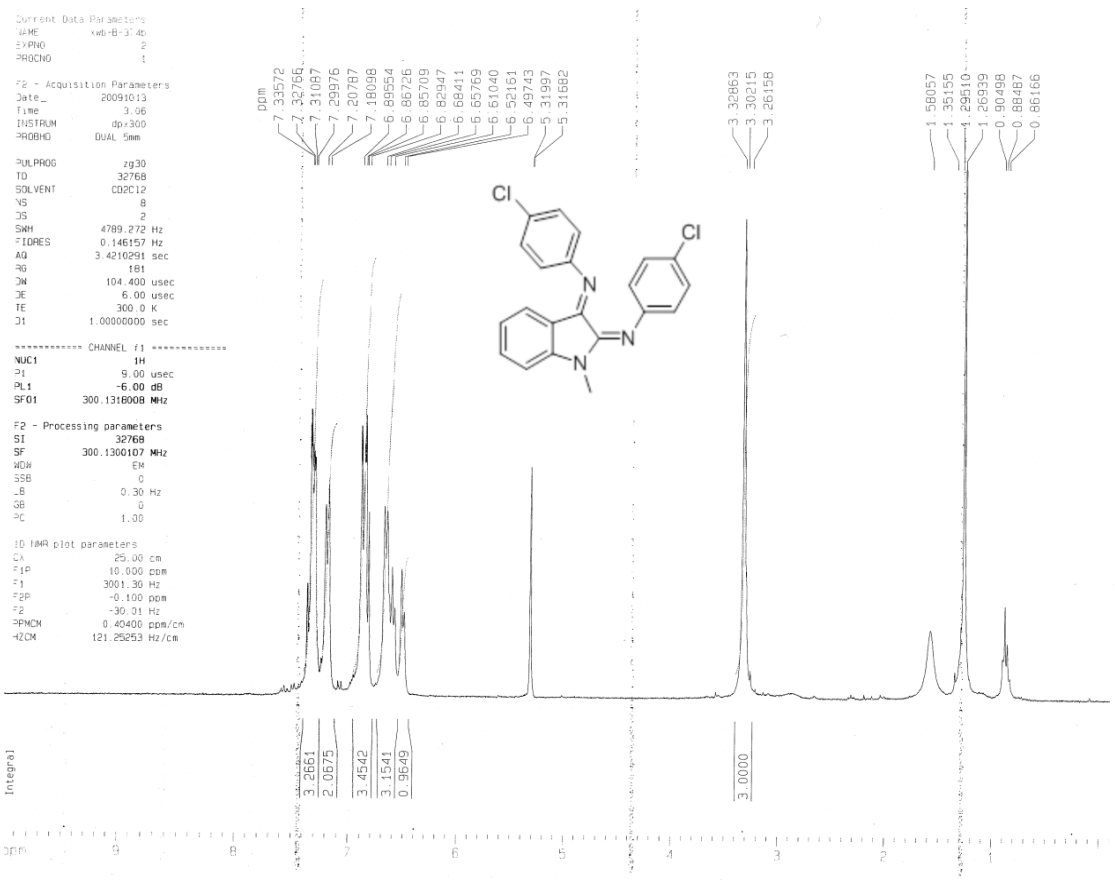




3-(3,5-Bis(trifluoromethyl)phenylimino)-1-methylindolin-2-ylidene)-3,5-bis(trifluoromethyl)benzenamine(3b)



4-chloro-N-(3-(4-chlorophenylimino)-1-methylindolin-2-ylidene)benzenamine(3c)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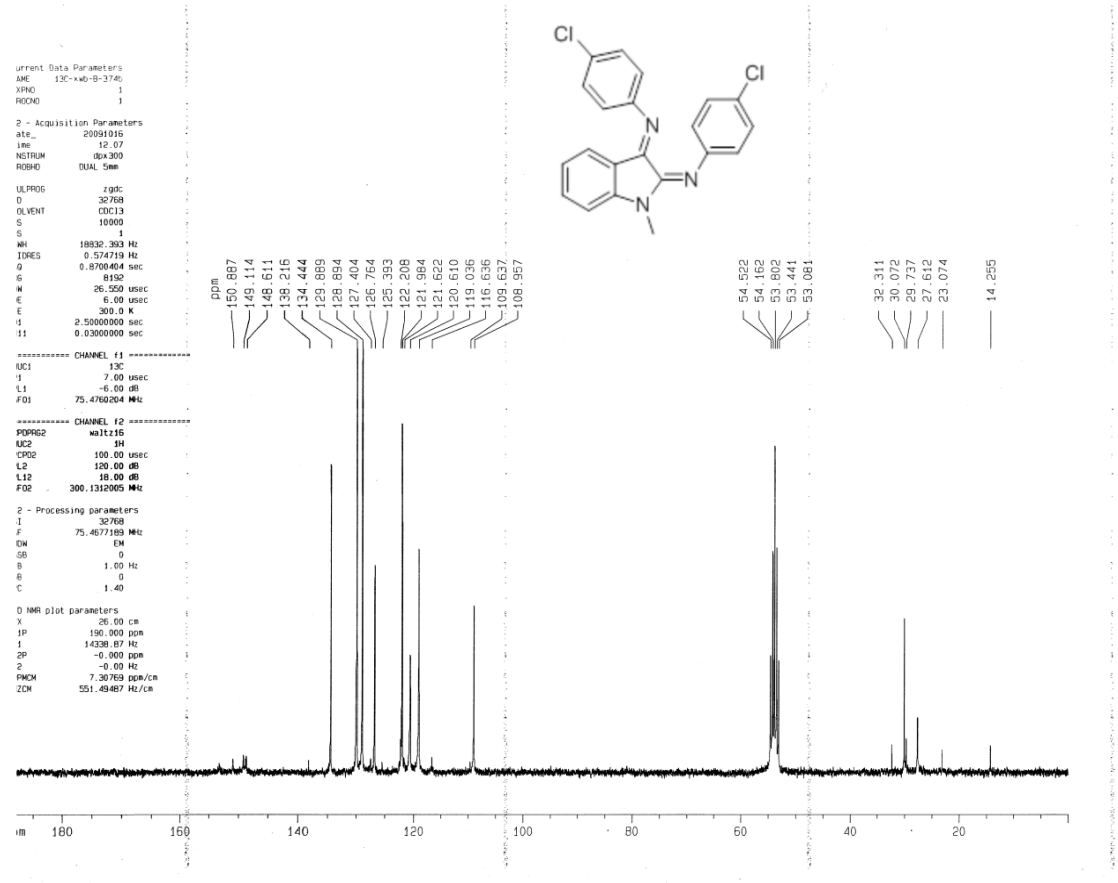
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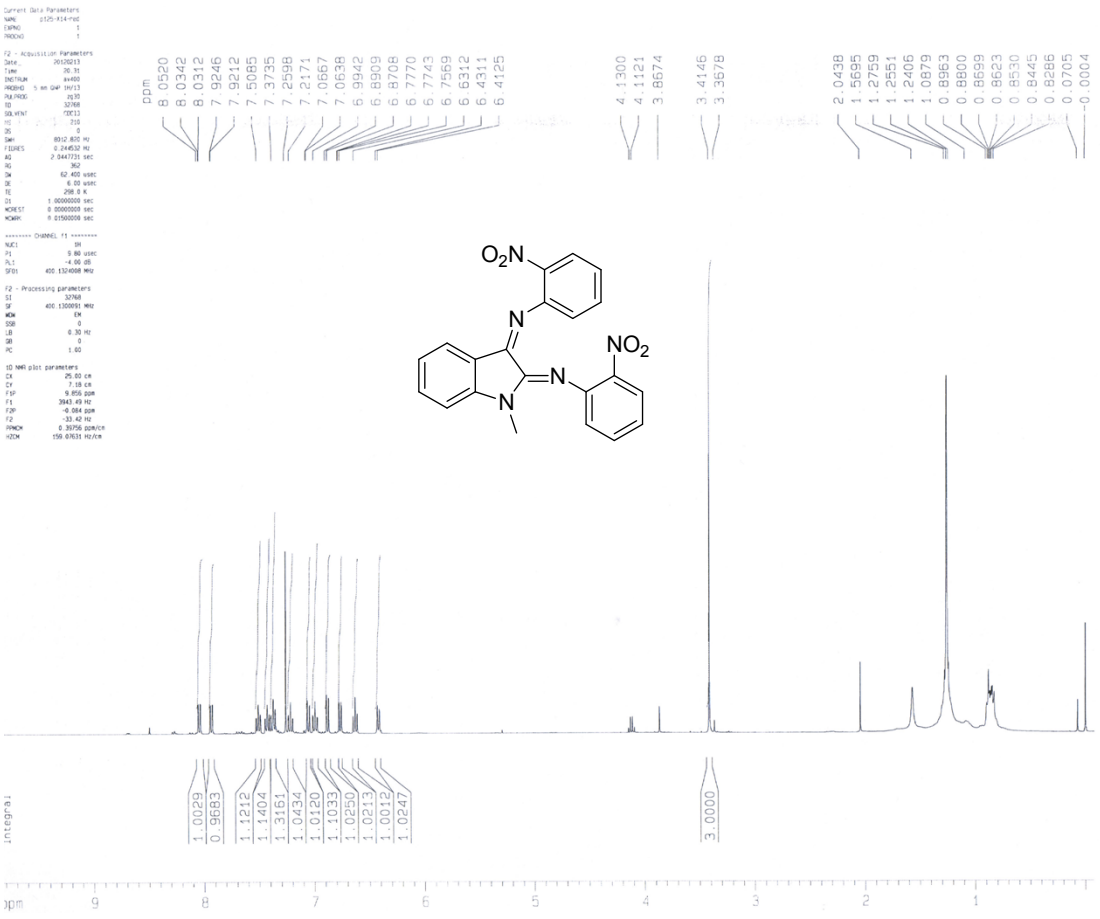
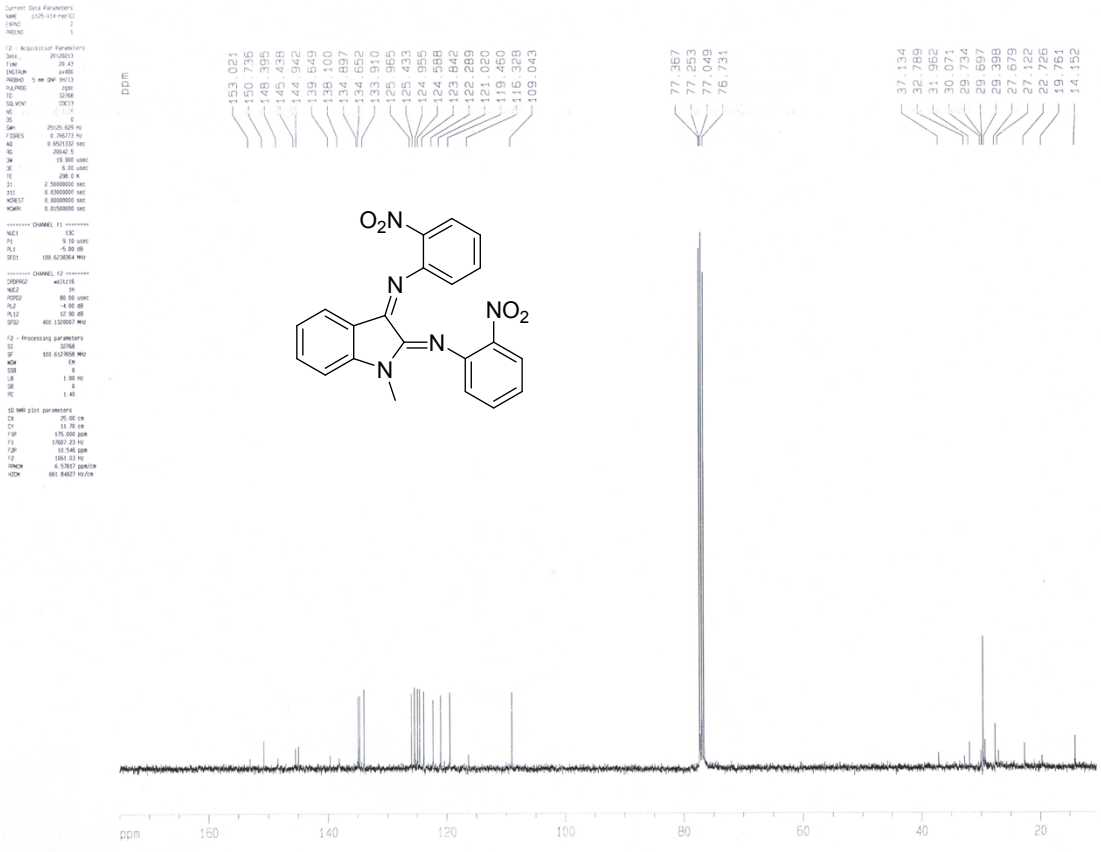
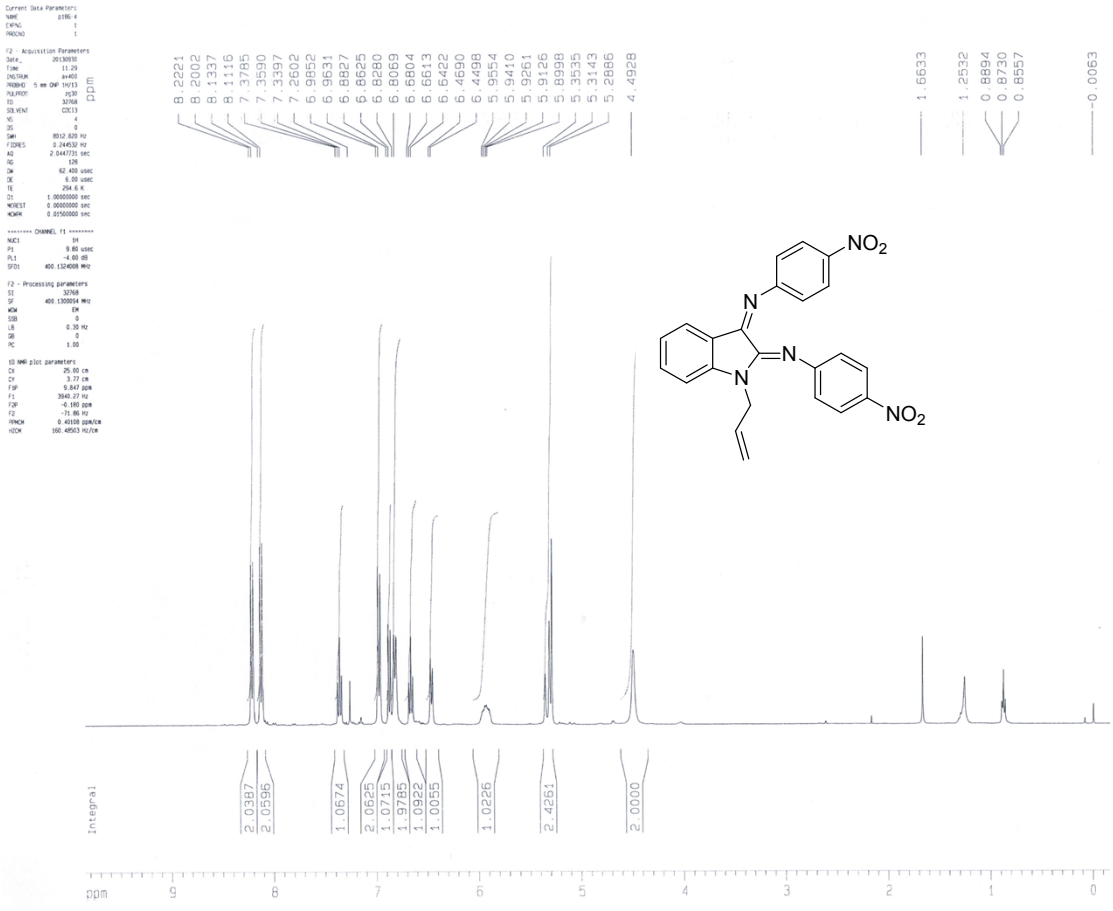
1-Methyl-3-(2-nitrophenylimino)indolin-2-ylidene)-2-nitrobenzenamine(3e)





1-Allyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4a)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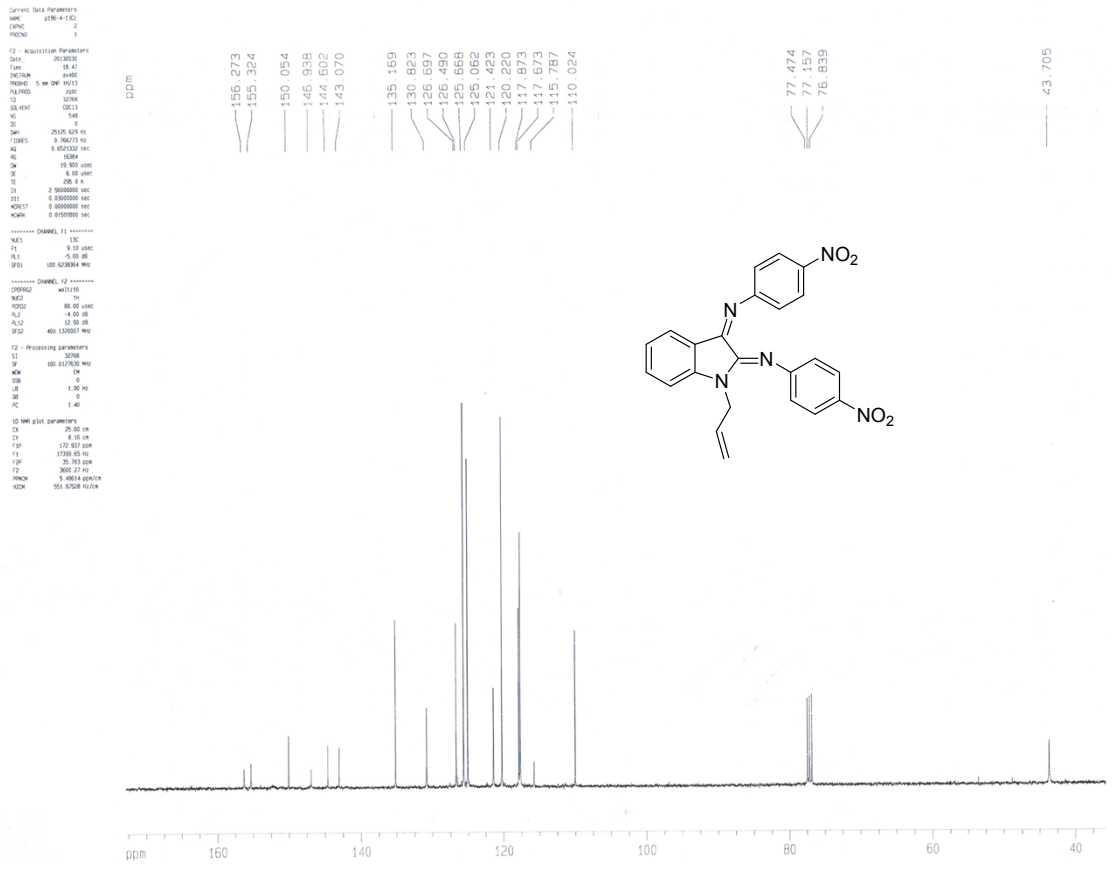
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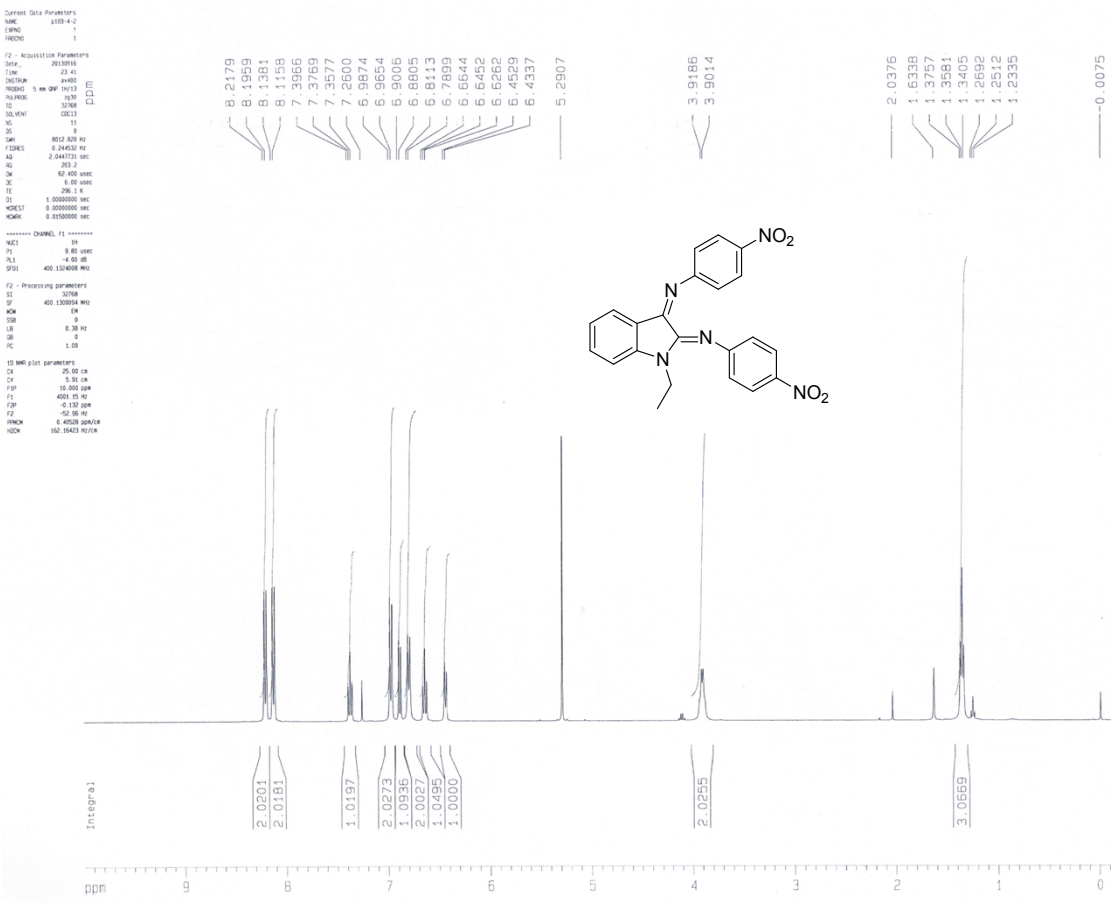
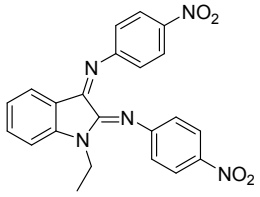
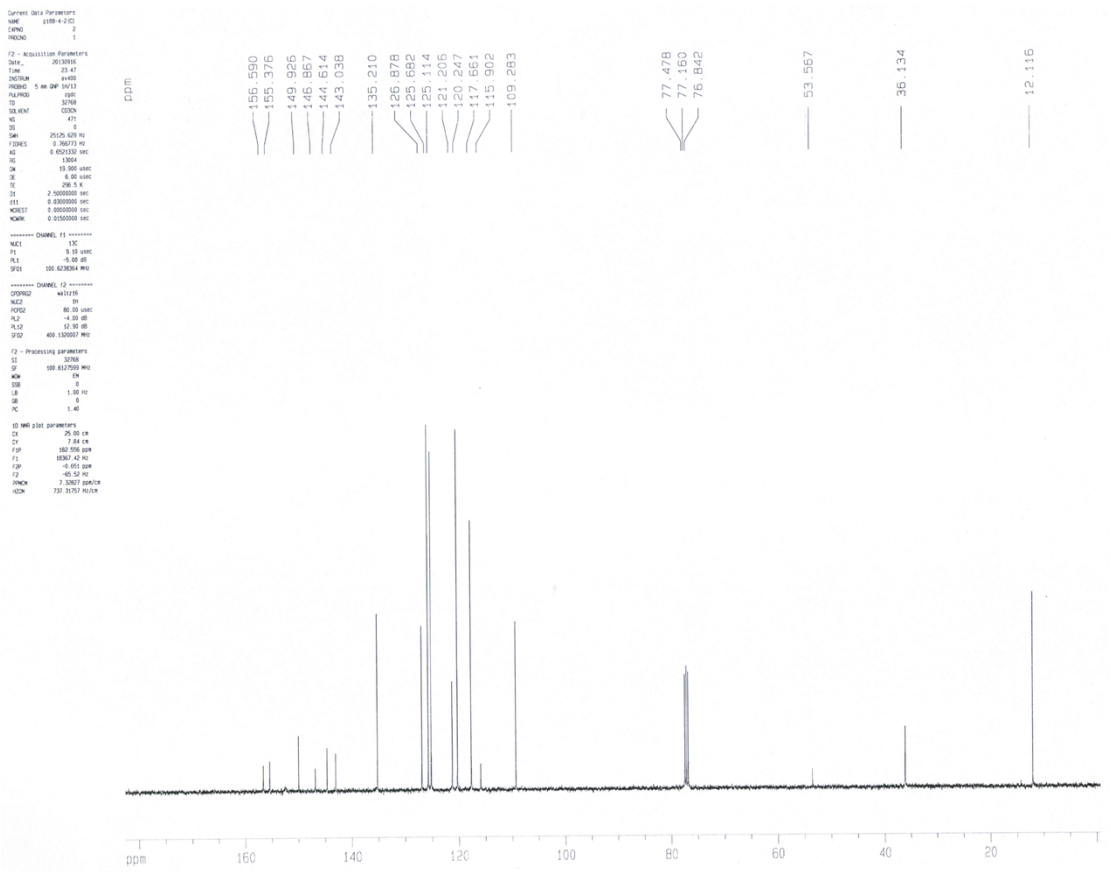
ppm
NO2
N
N
N
NO2
ppm
160
140
120
100
80
60
40

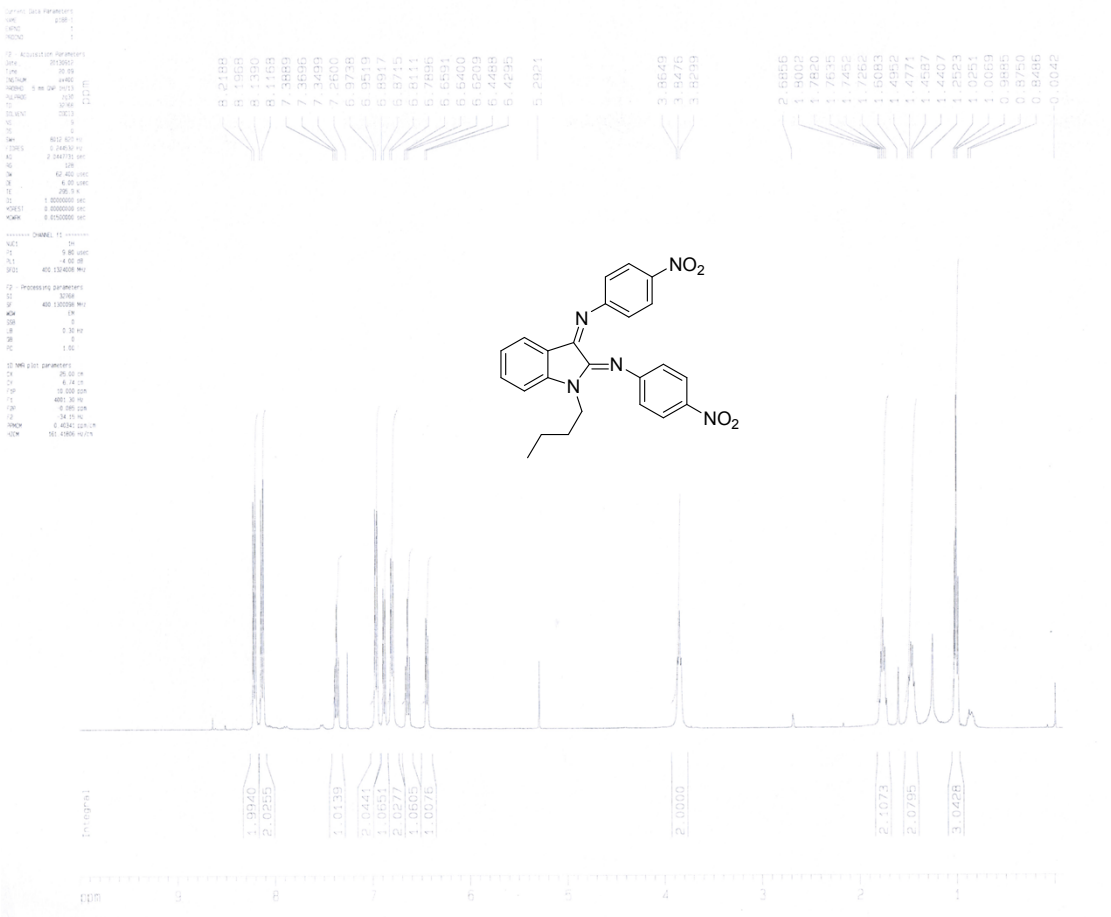
1-Ethyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4b)

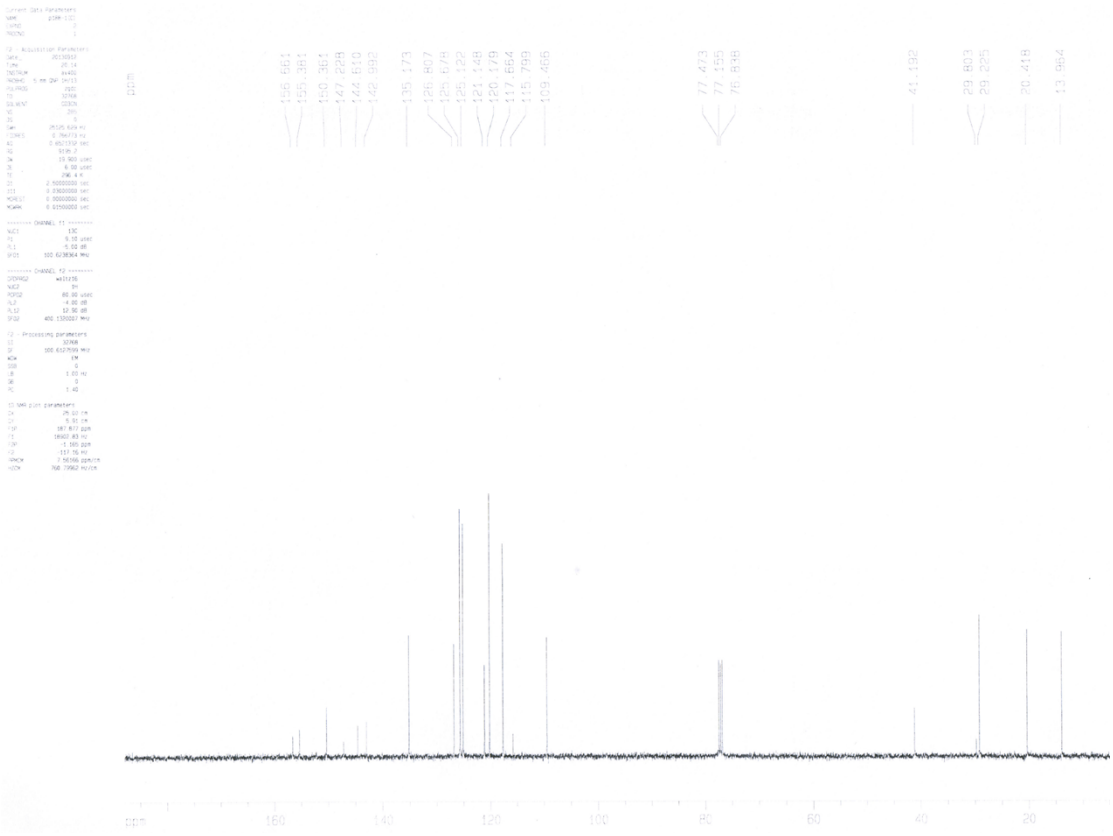




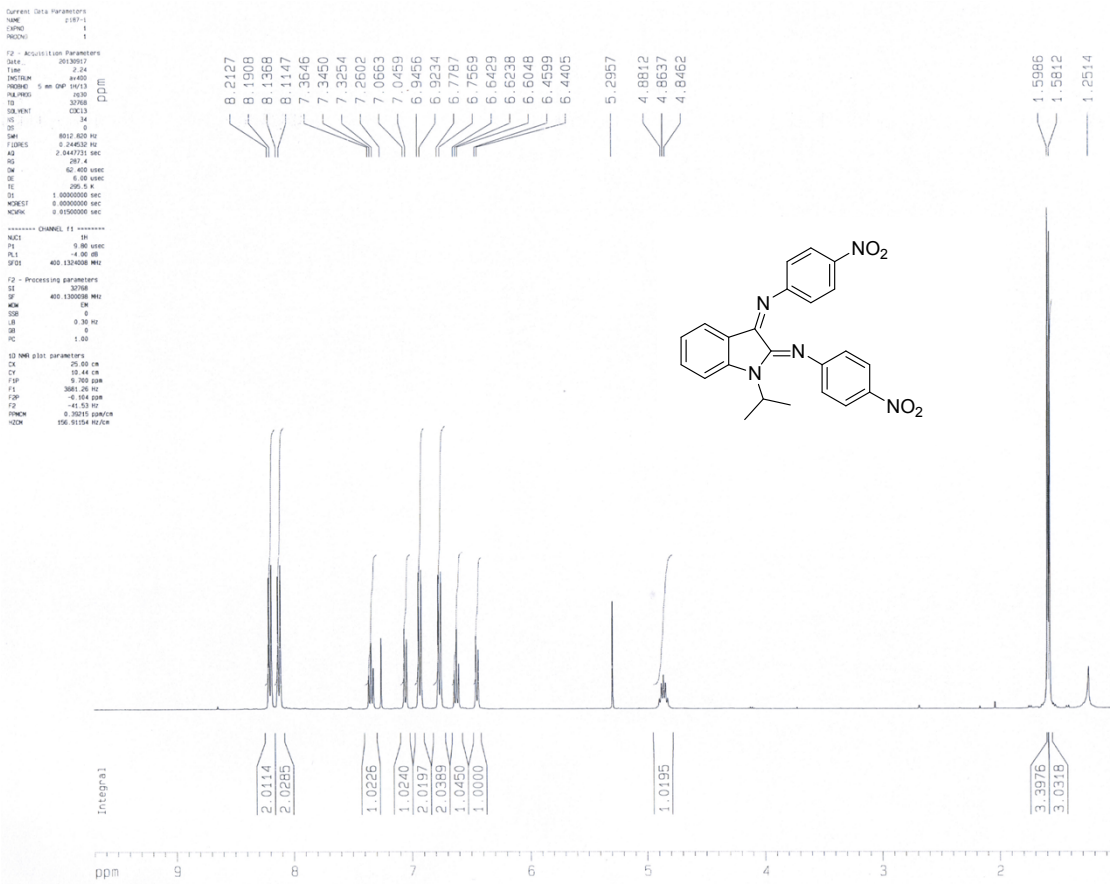


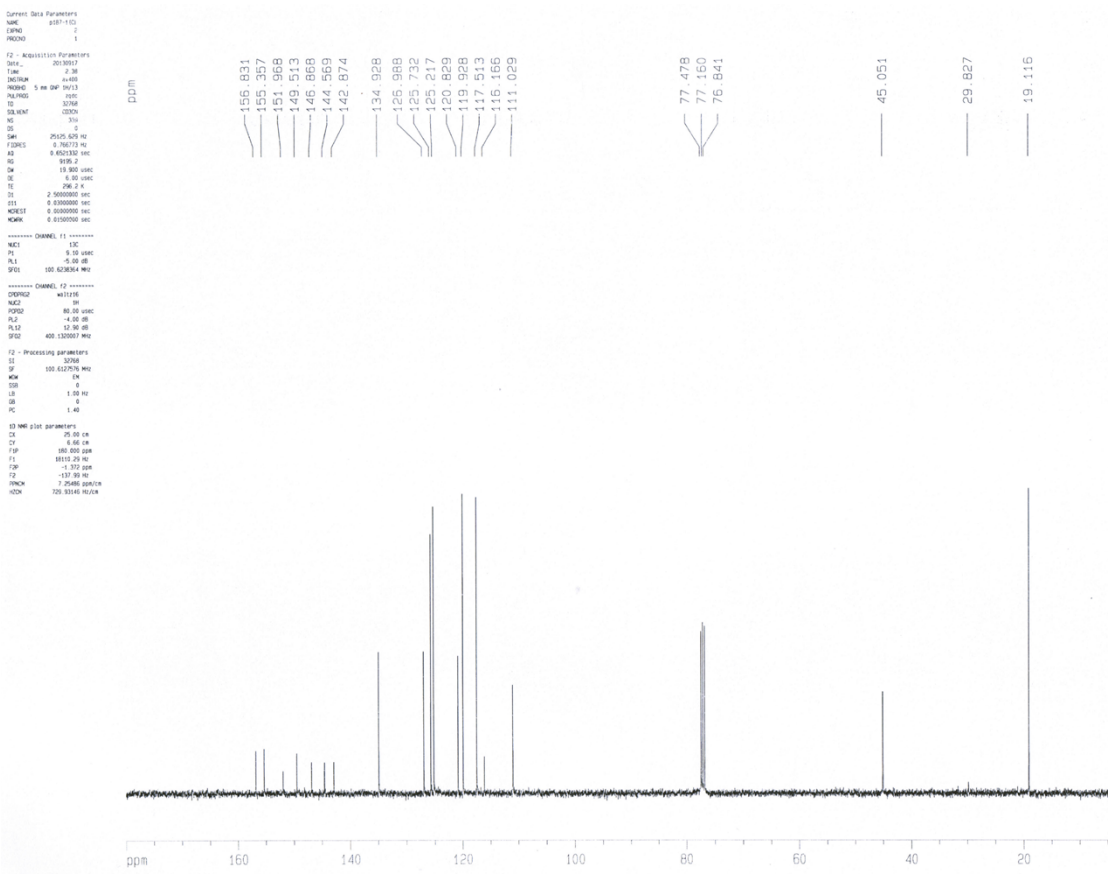
1-Butyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4c)



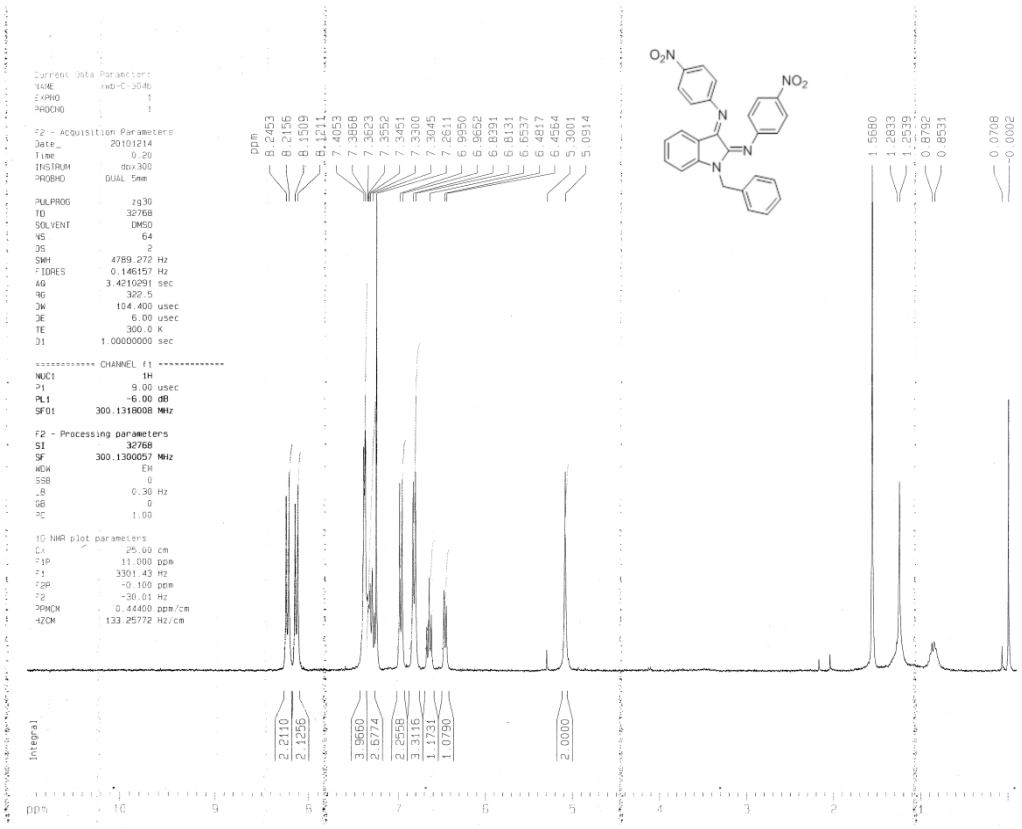


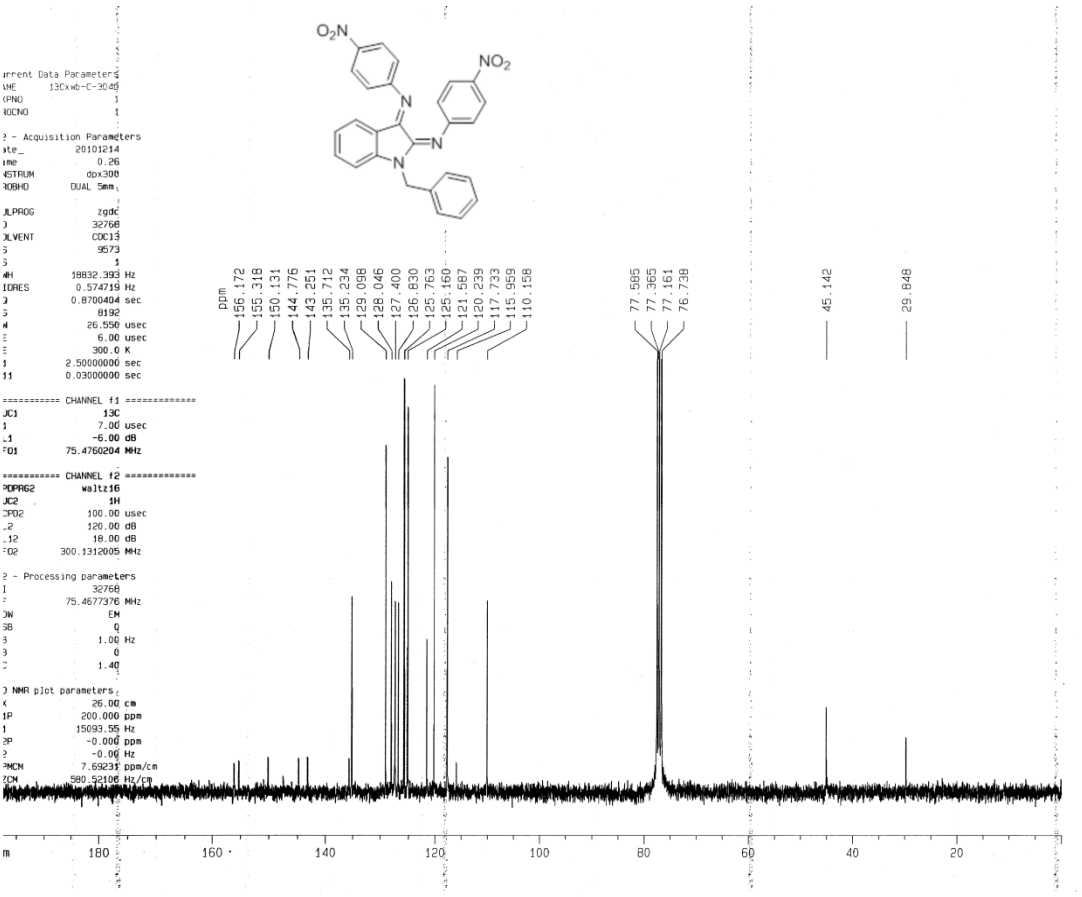
1-Isopropyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4d)



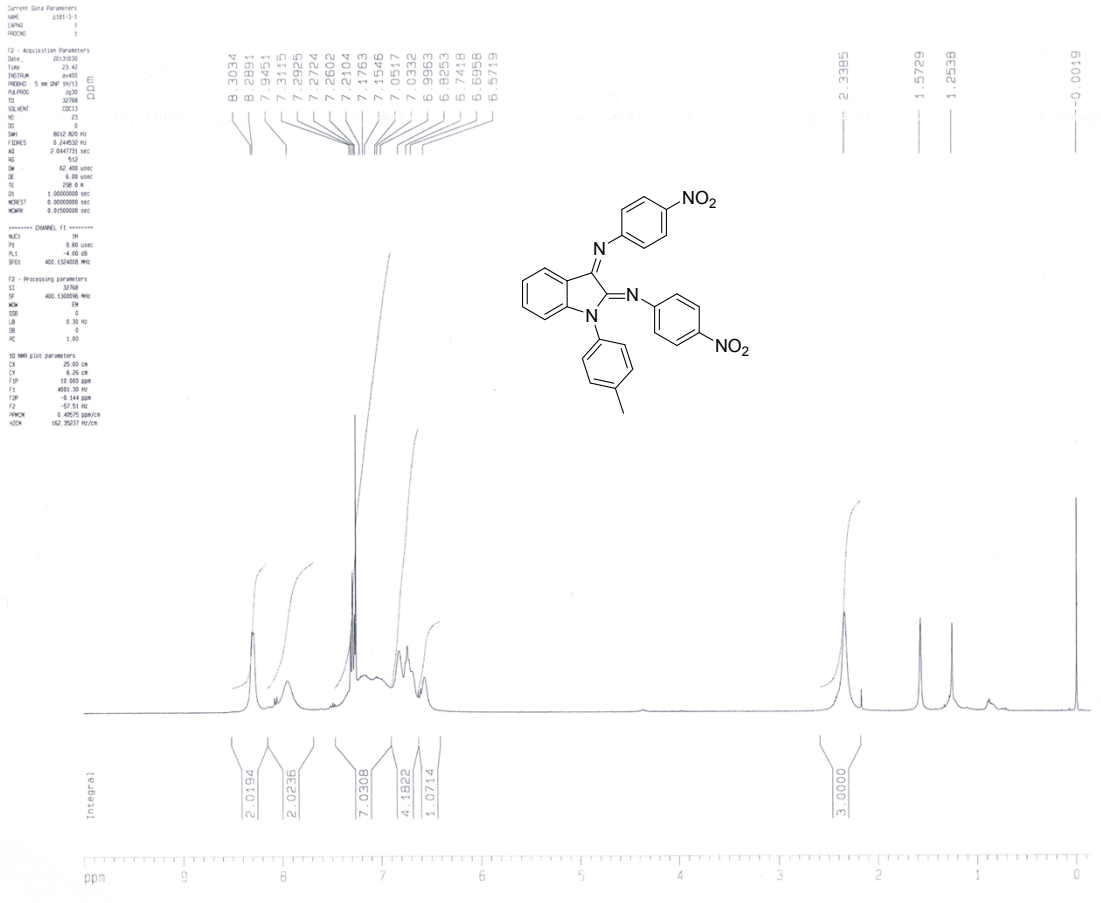


1-Benzyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4e)





4-Nitro-N-(3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)benzenamine(4f)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7.0517
7.0332
6.9963
6.8253
6.7418
6.6958
6.5719
2.3385
1.5729
1.2538
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NO2
Integral
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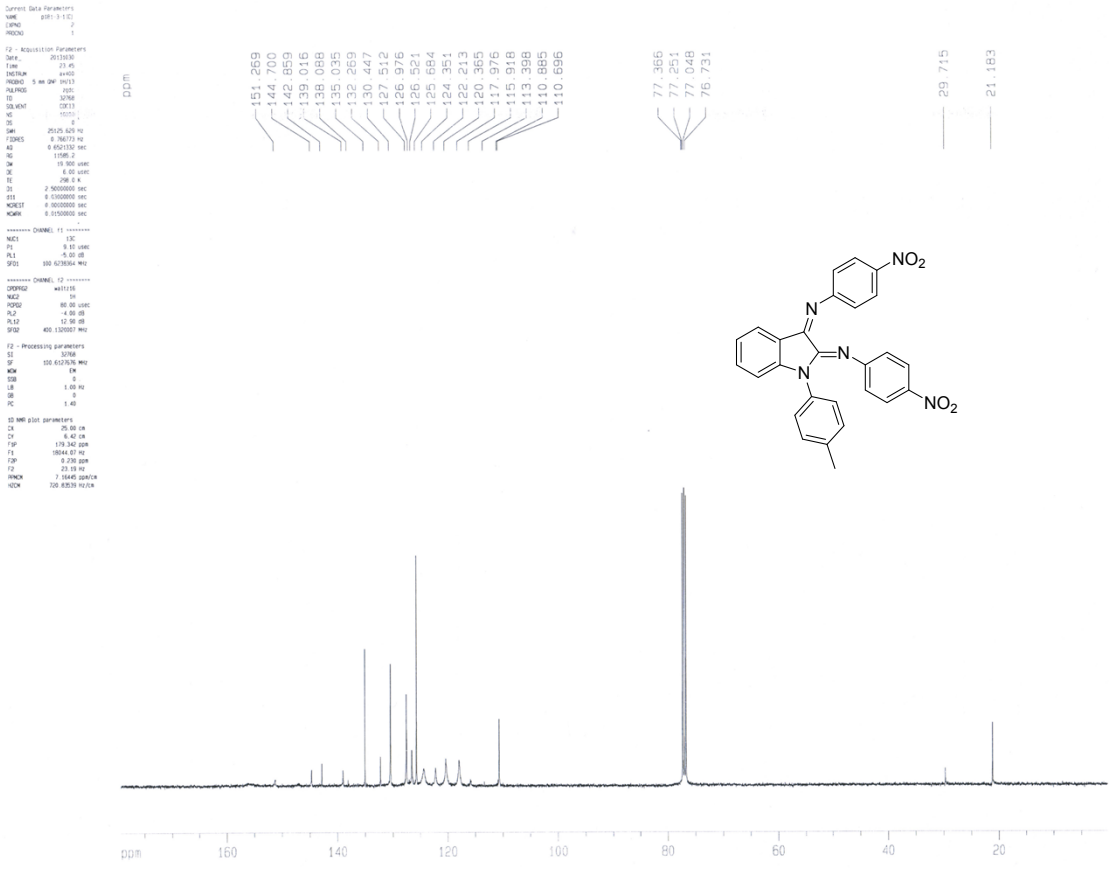
ppm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135.035
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122.213
120.365
117.976
115.918
113.398
110.885
110.696
77.366
77.251
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76.731
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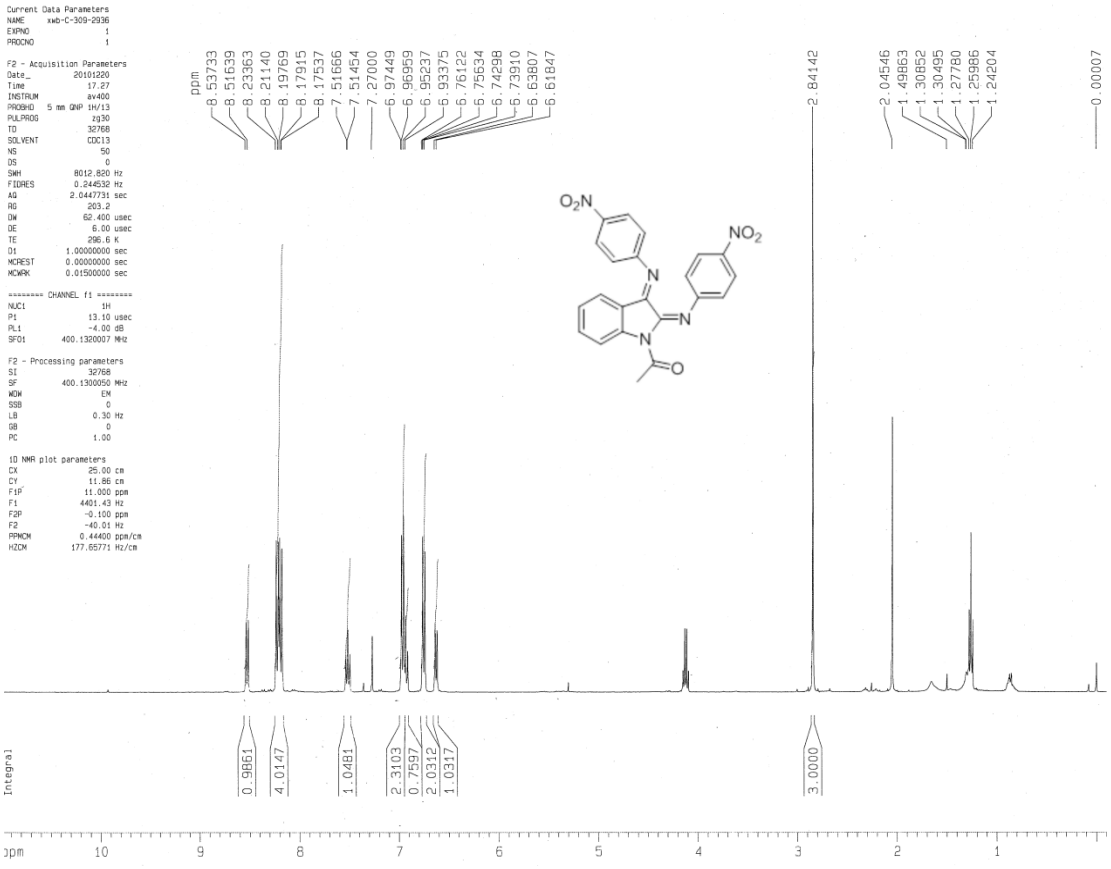
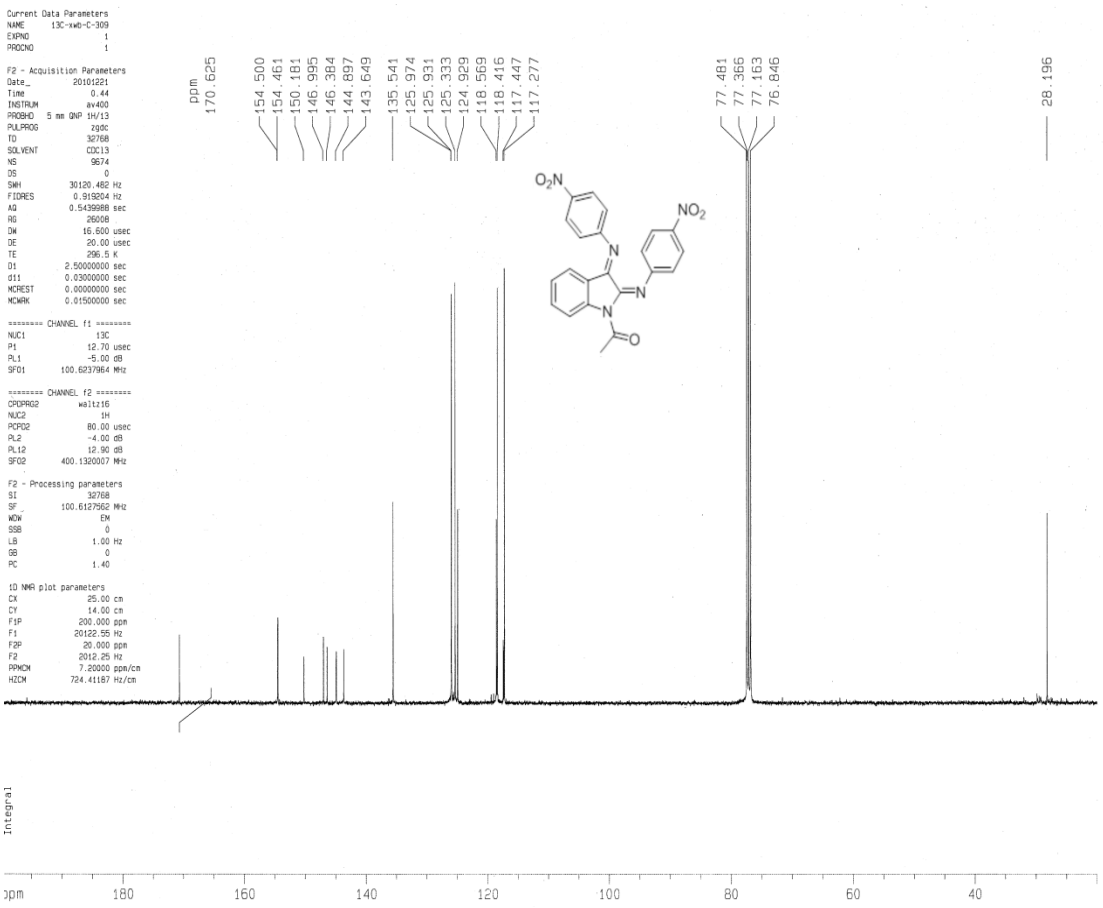
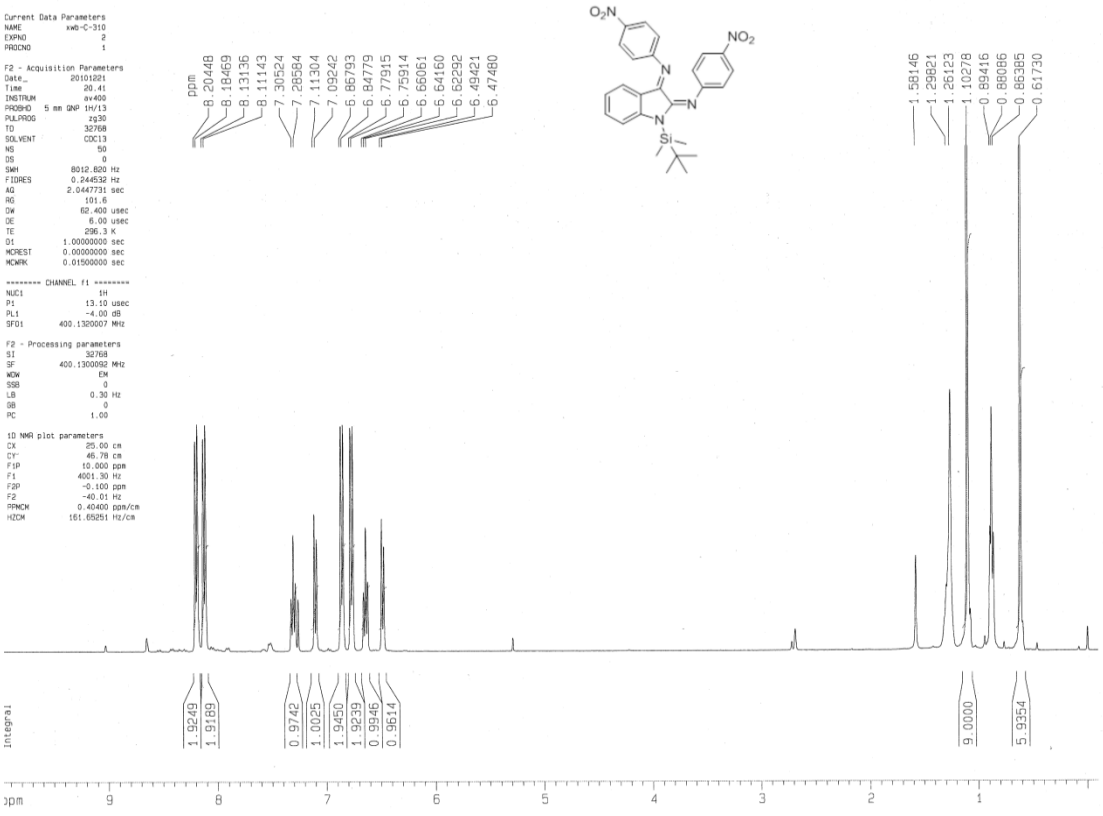
NO2
NO2
ppm

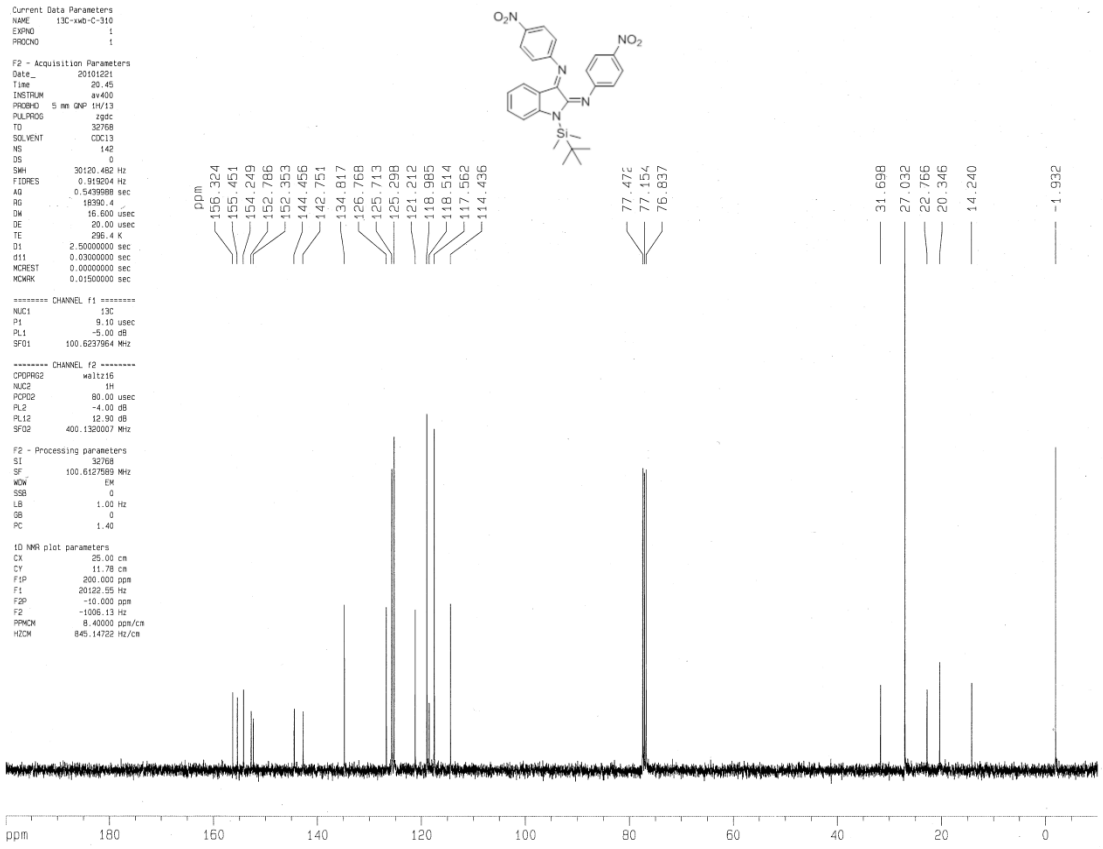
2,3-Bis(4-nitrophenylimino)indolin-1-yl)ethanone(4g)





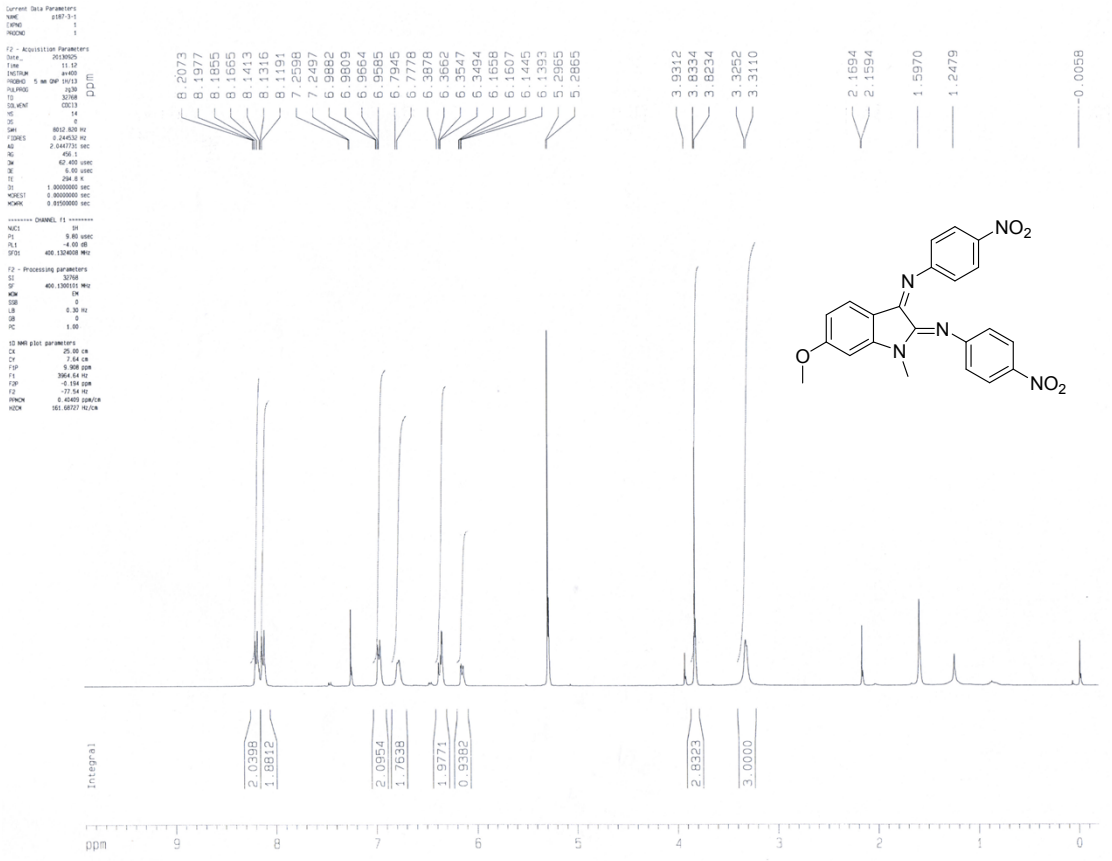
1-(*tert*-Butyldimethylsilyl)-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine (4h)

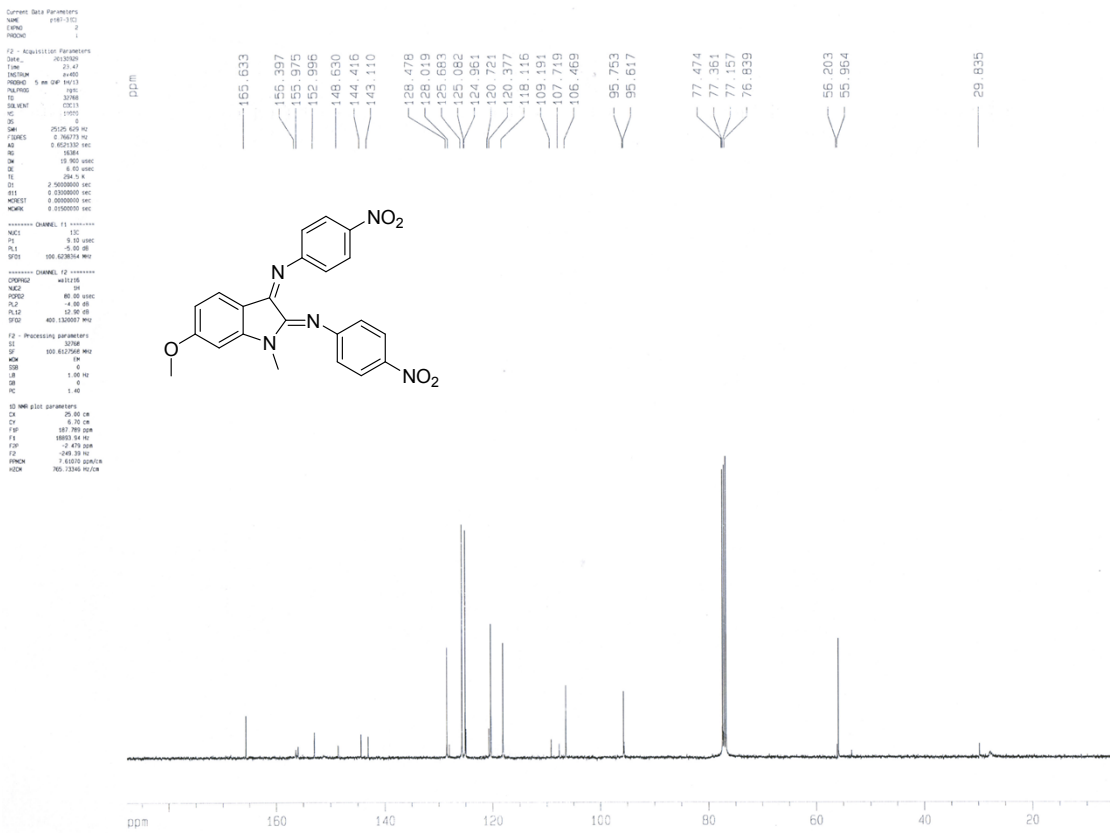




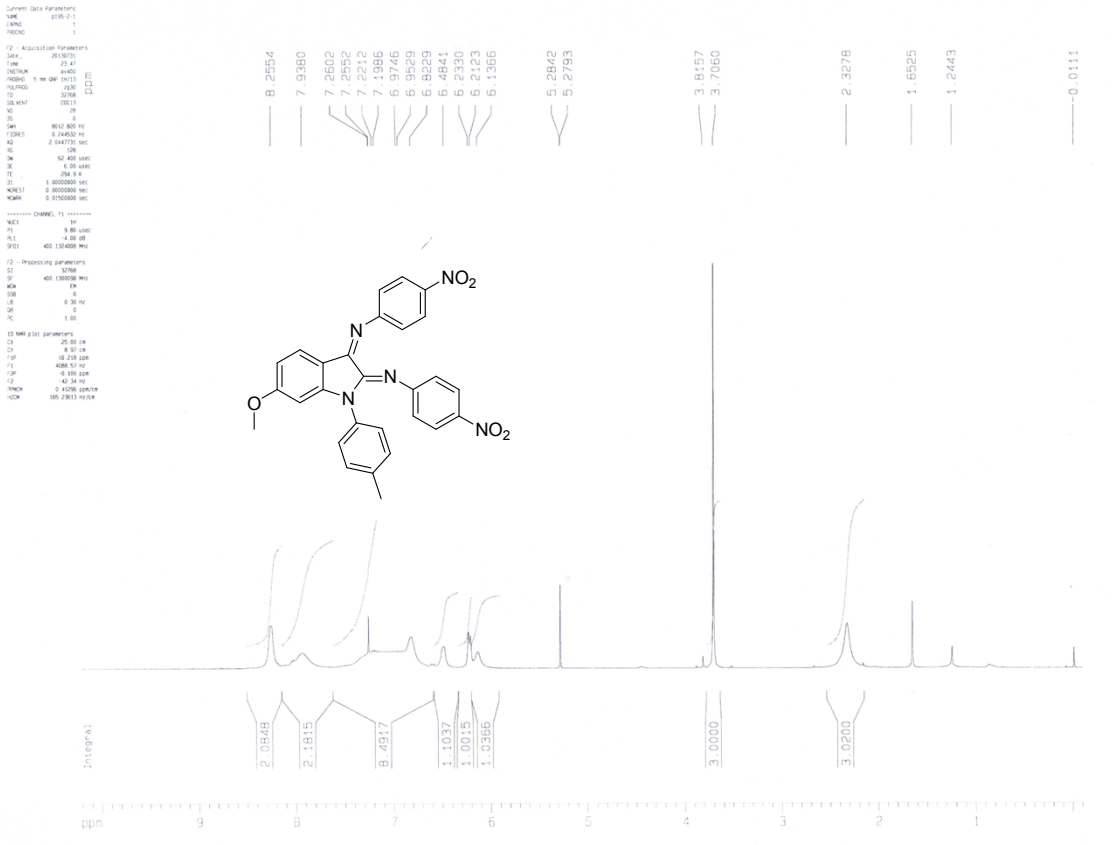
6-Methoxy-1-methyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-

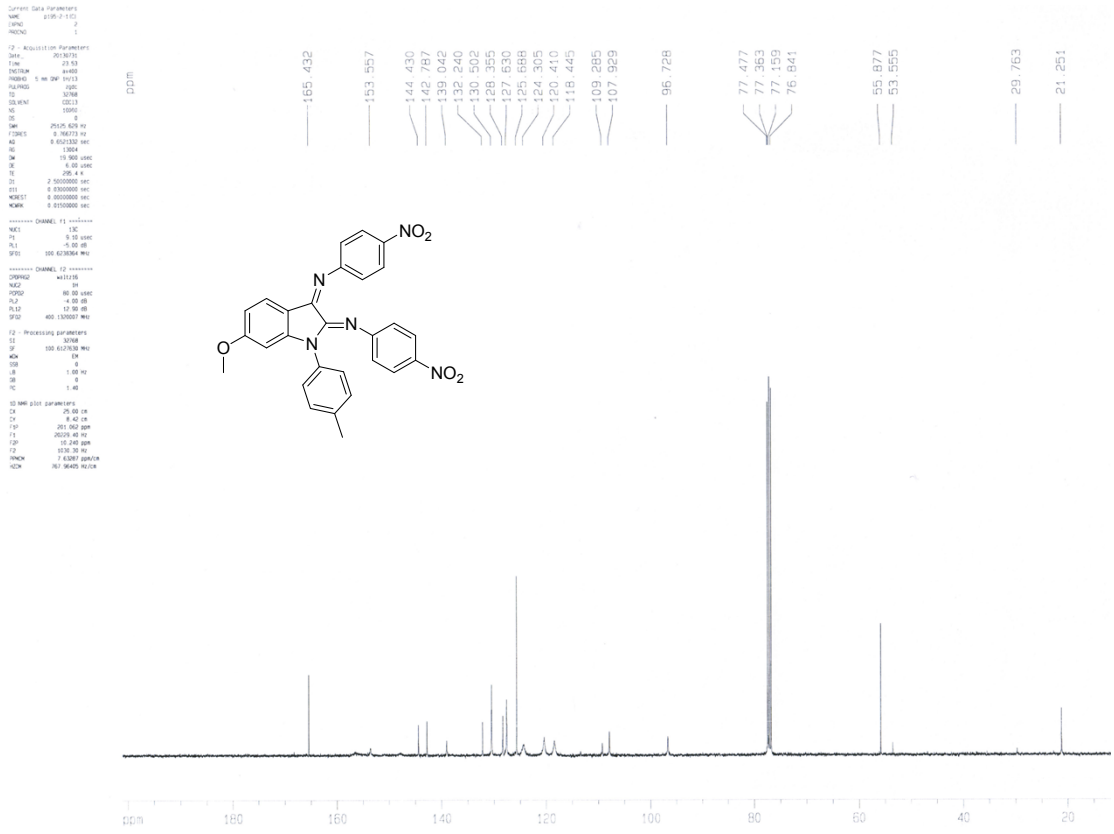
nitrobenzenamine(4i)



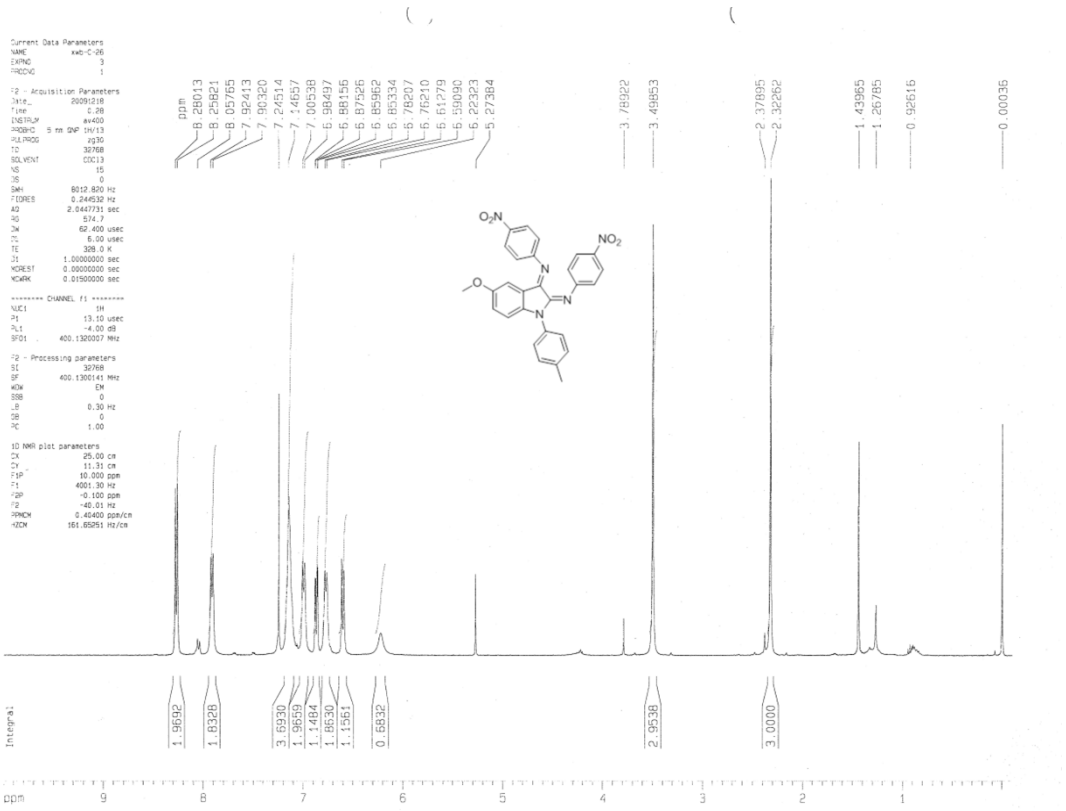


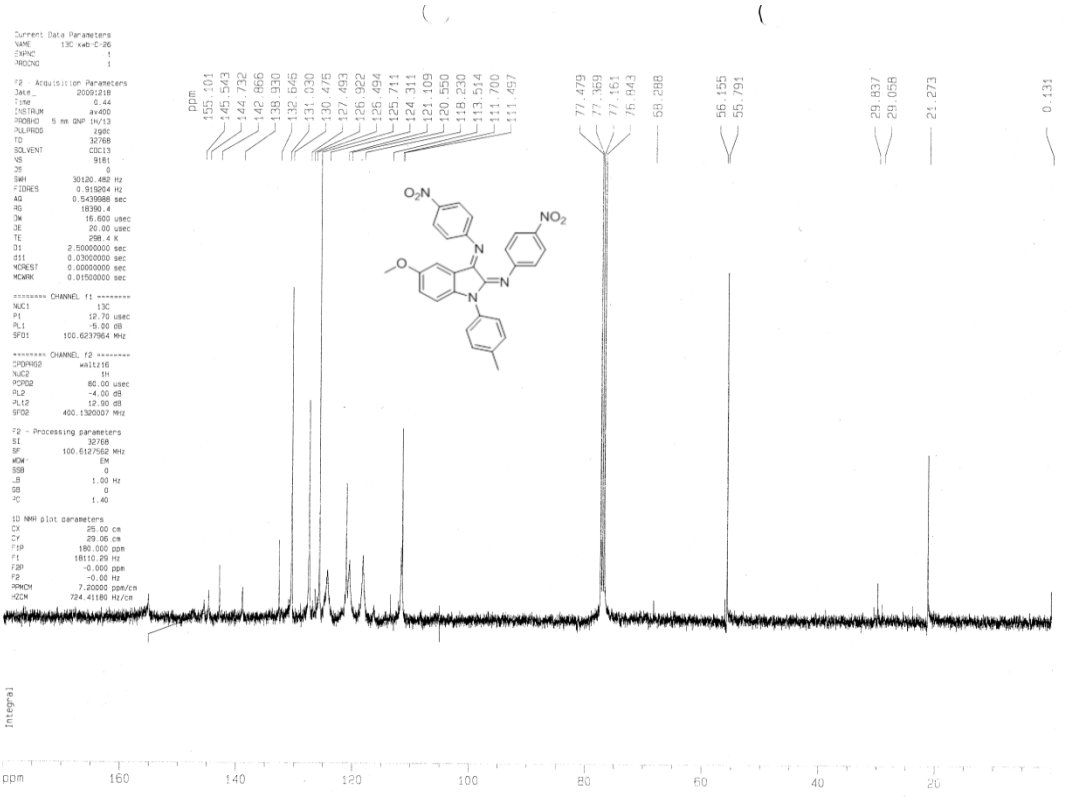
N-(6-methoxy-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine(4j)



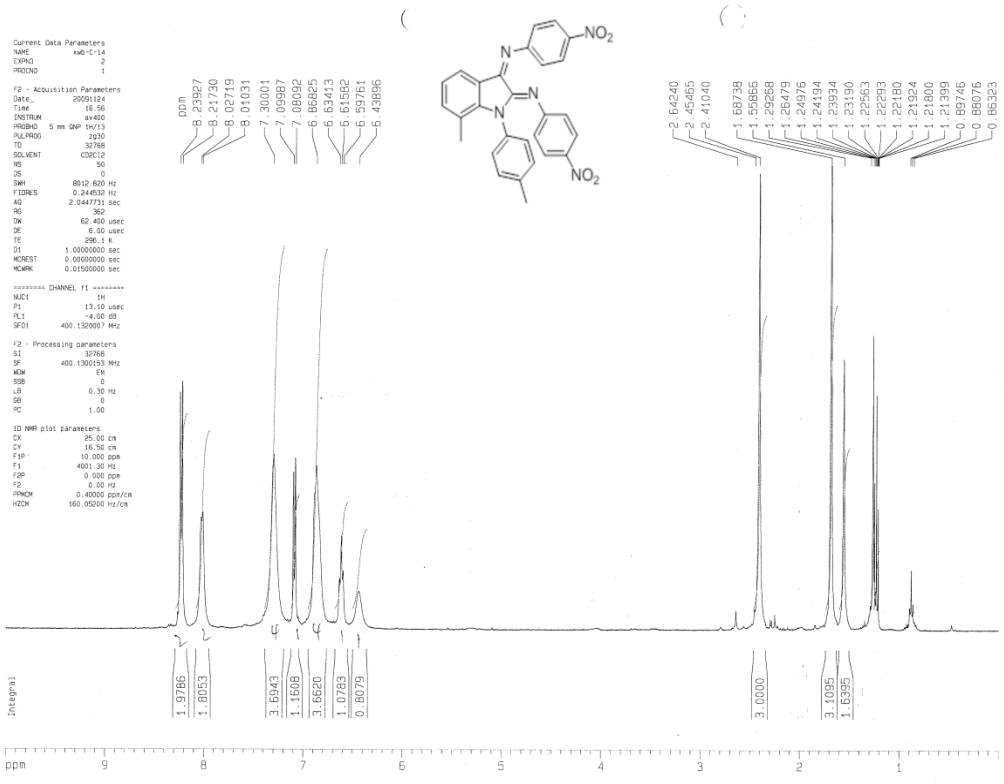


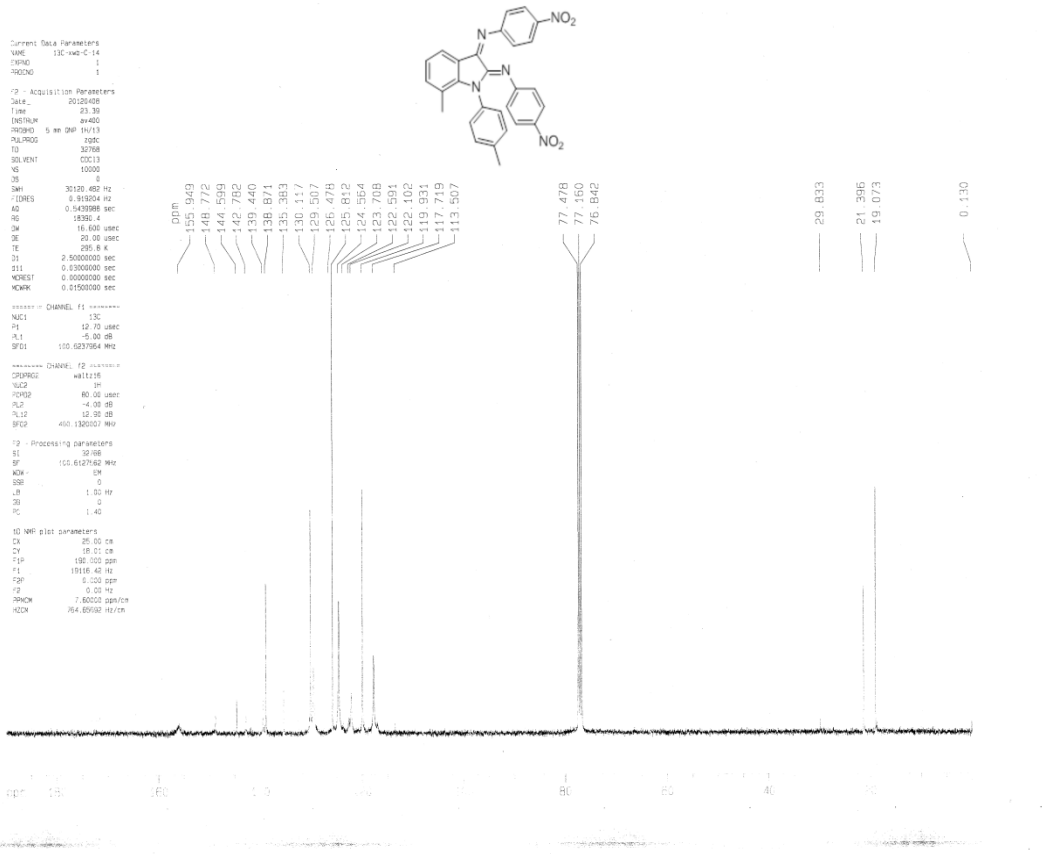
N-(5-methoxy-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine(4k)



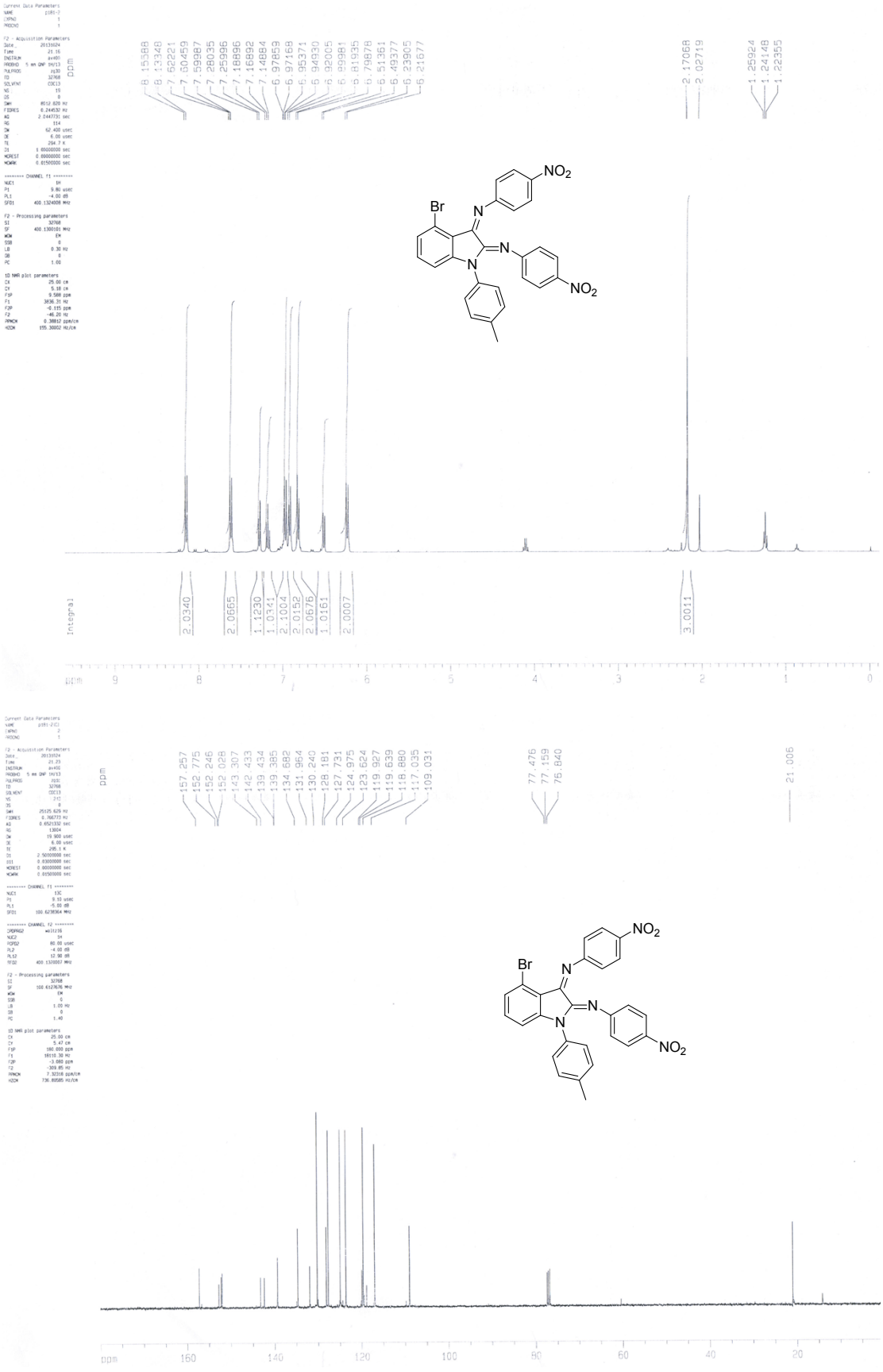


7-Methyl-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine(4l)

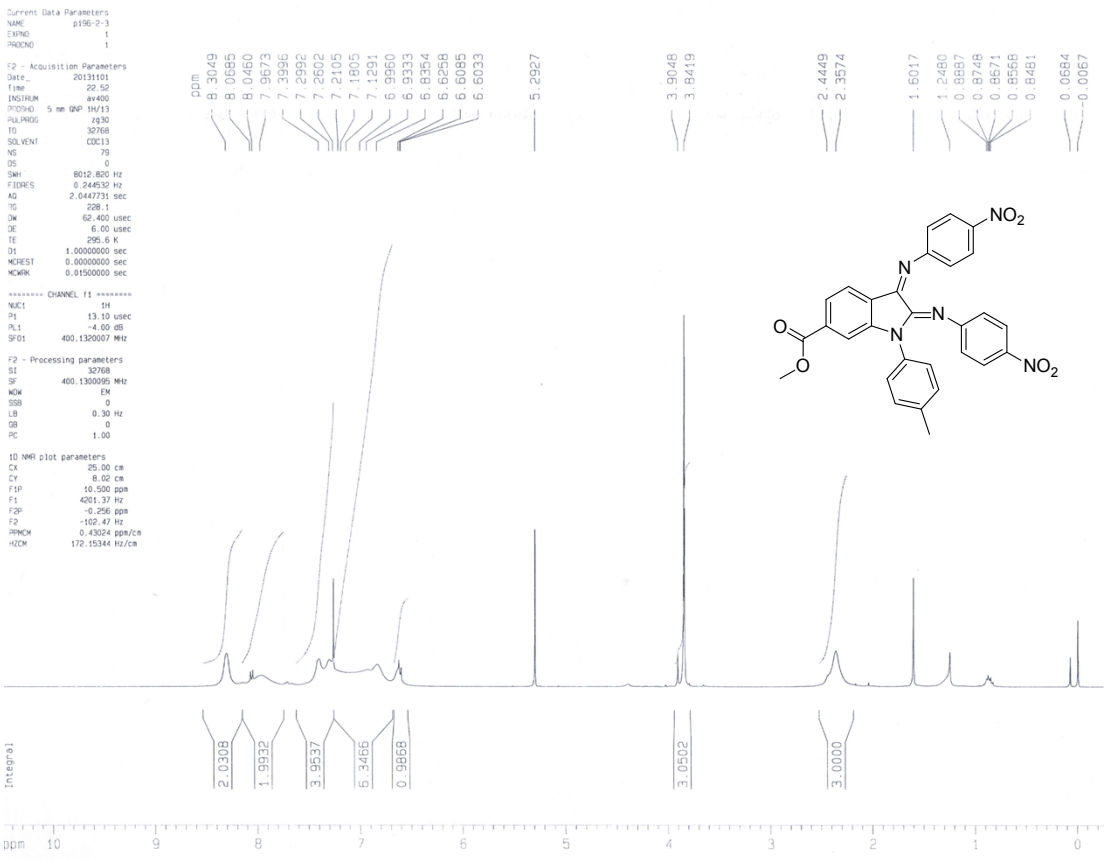




4-Bromo-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine (4m)



Methyl 1-methyl-2,3-bis(4-nitrophenylimino) indoline-6-carboxylate(4n)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6.9960
6.9333
6.8354
6.6258
6.6085
6.6033
5.2927
3.9048
3.8419
2.4449
2.3574
1.6017
1.2480
0.8887
0.8748
0.8671
0.8568
0.8481
0.0684
-0.0067
NO2
N
N
O
O
N
NO2
Integral
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0.9868
3.0502
3.0000
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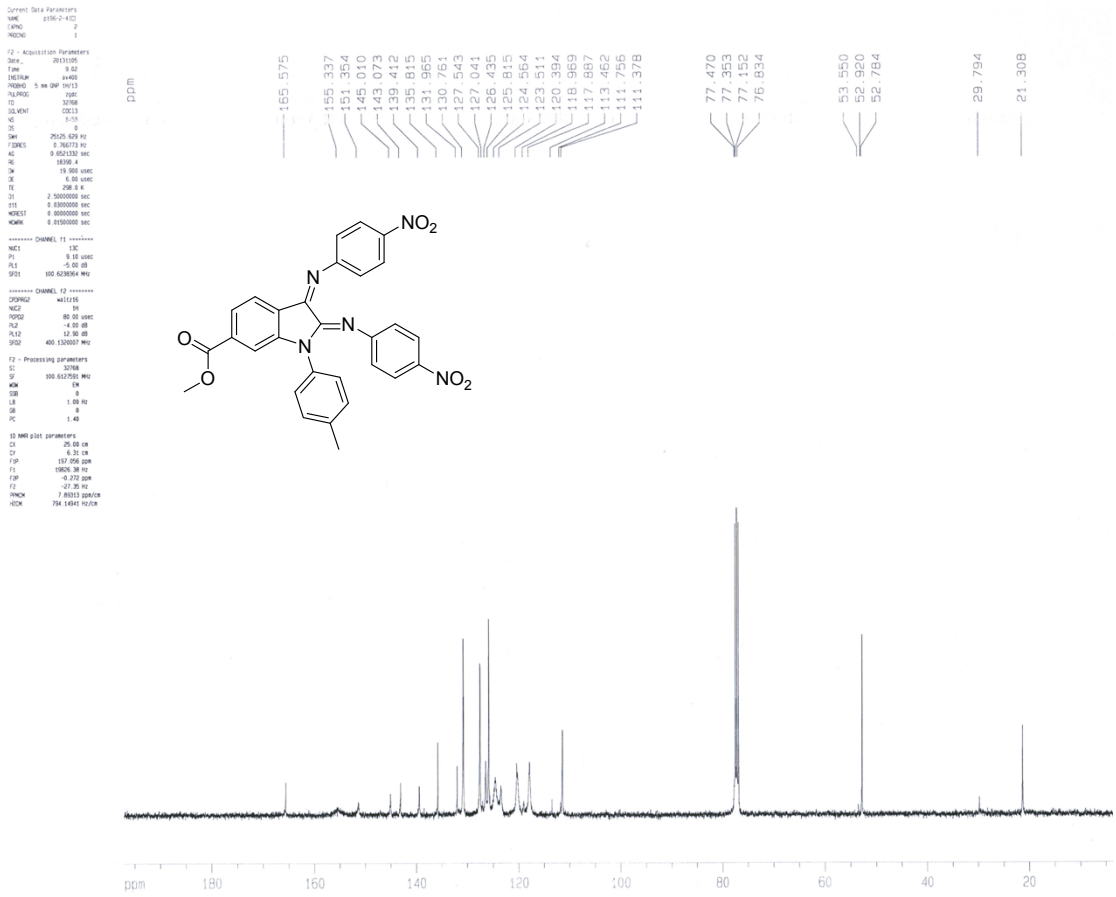
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124.564
123.511
120.394
118.969
117.887
113.462
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111.378
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77.353
77.152
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52.784
29.794
21.308
NO2
N
N
O
O
N
NO2
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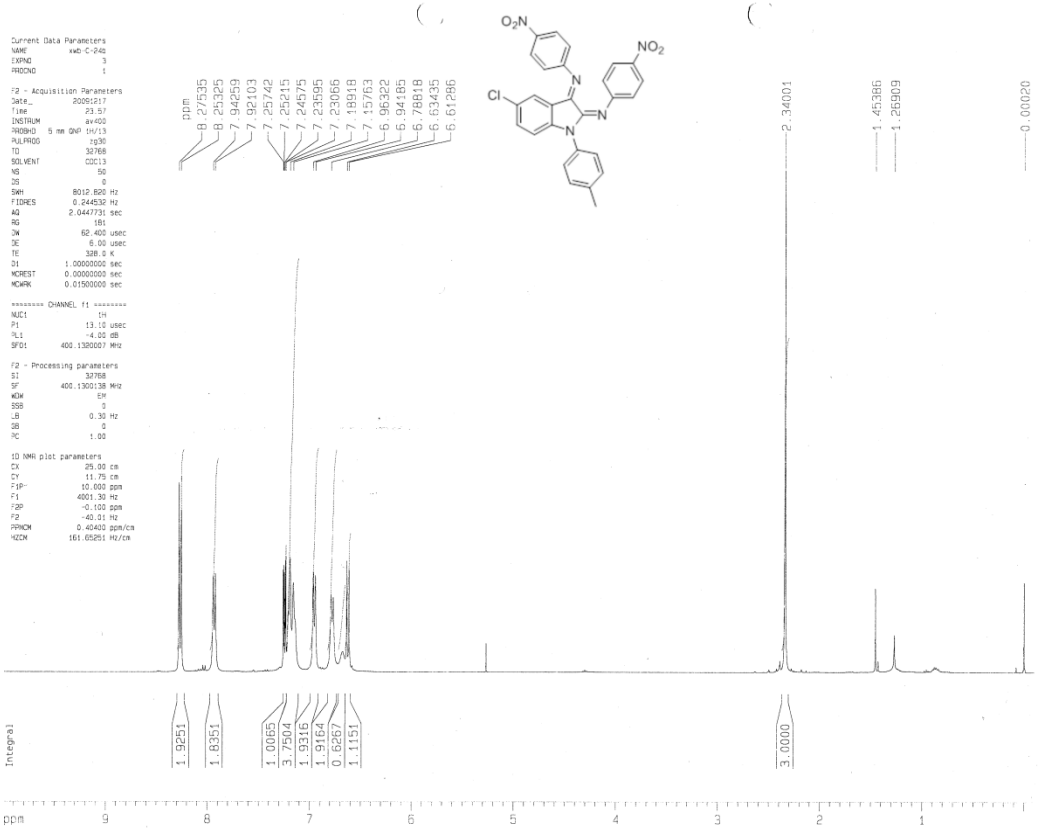
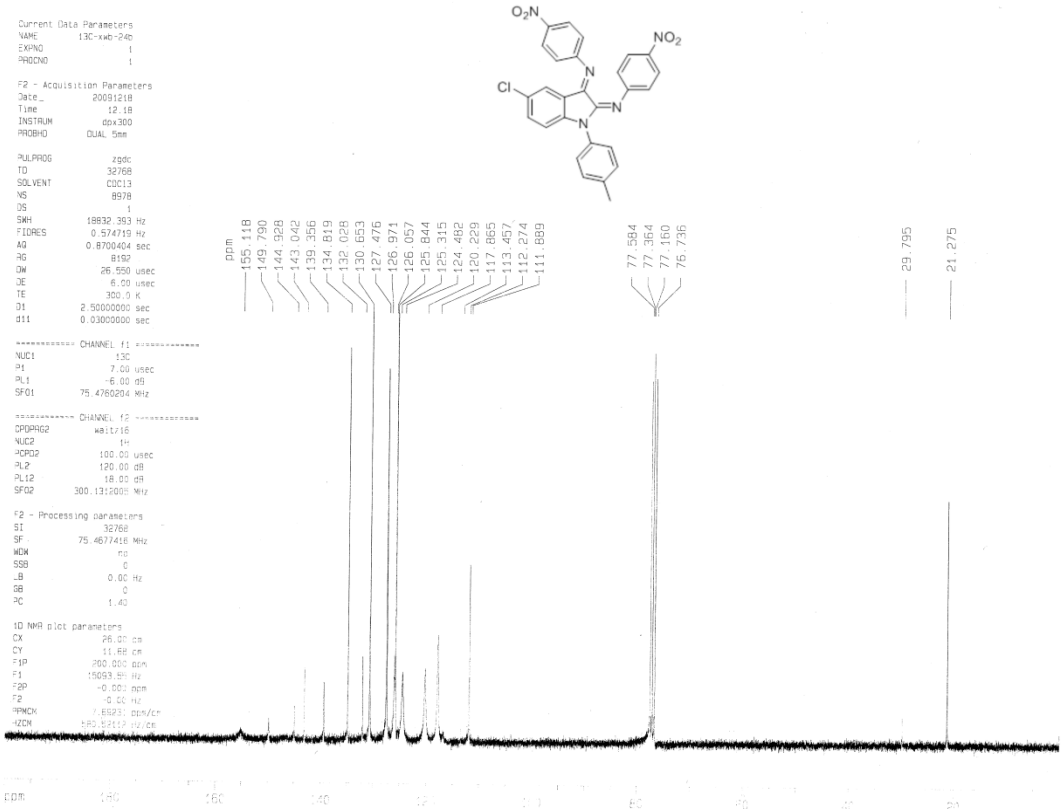
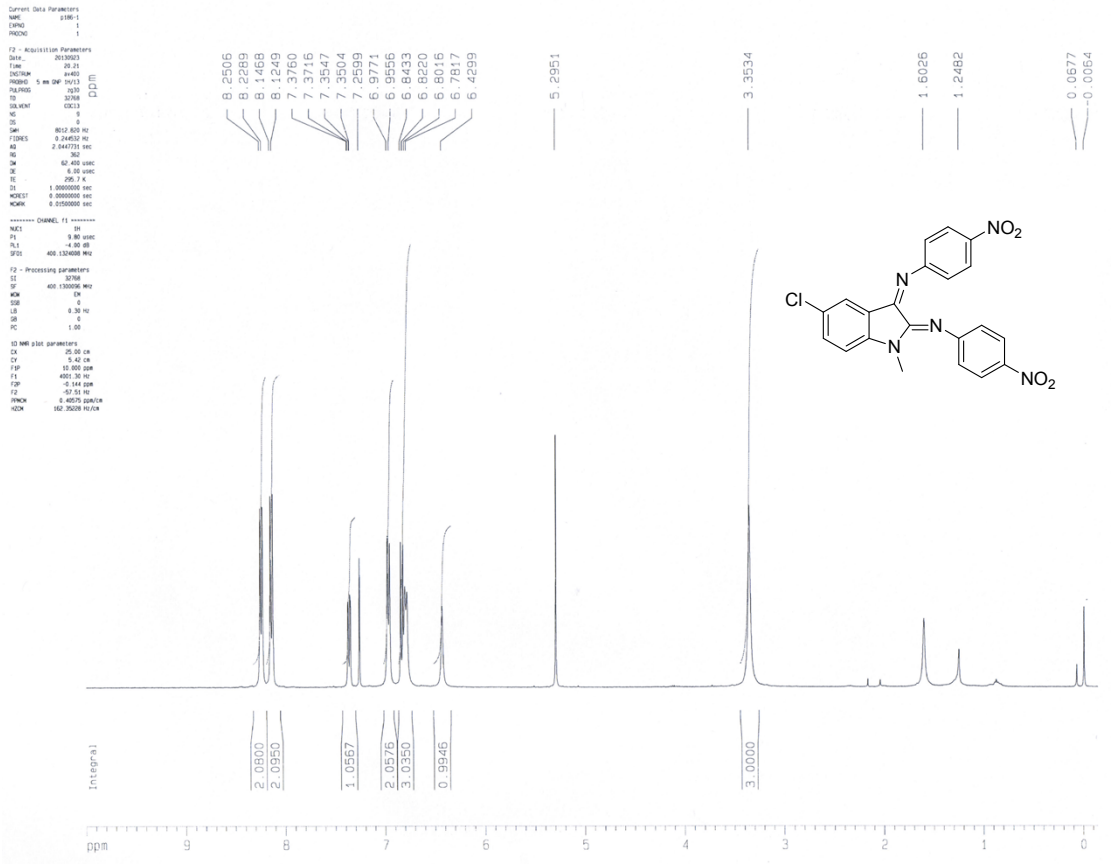
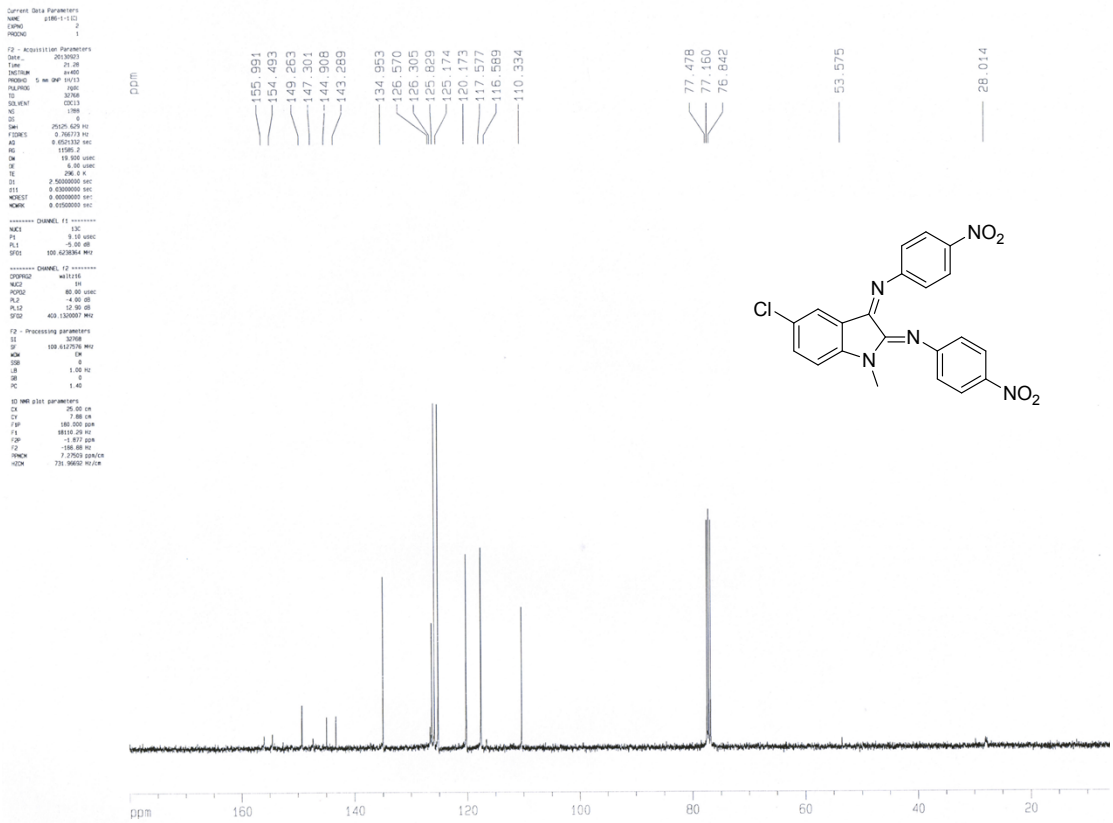
5-Chloro-3-(4-nitrophenylimino)-1-p-tolylindolin-2-ylidene)-4-nitrobenzenamine(4o)



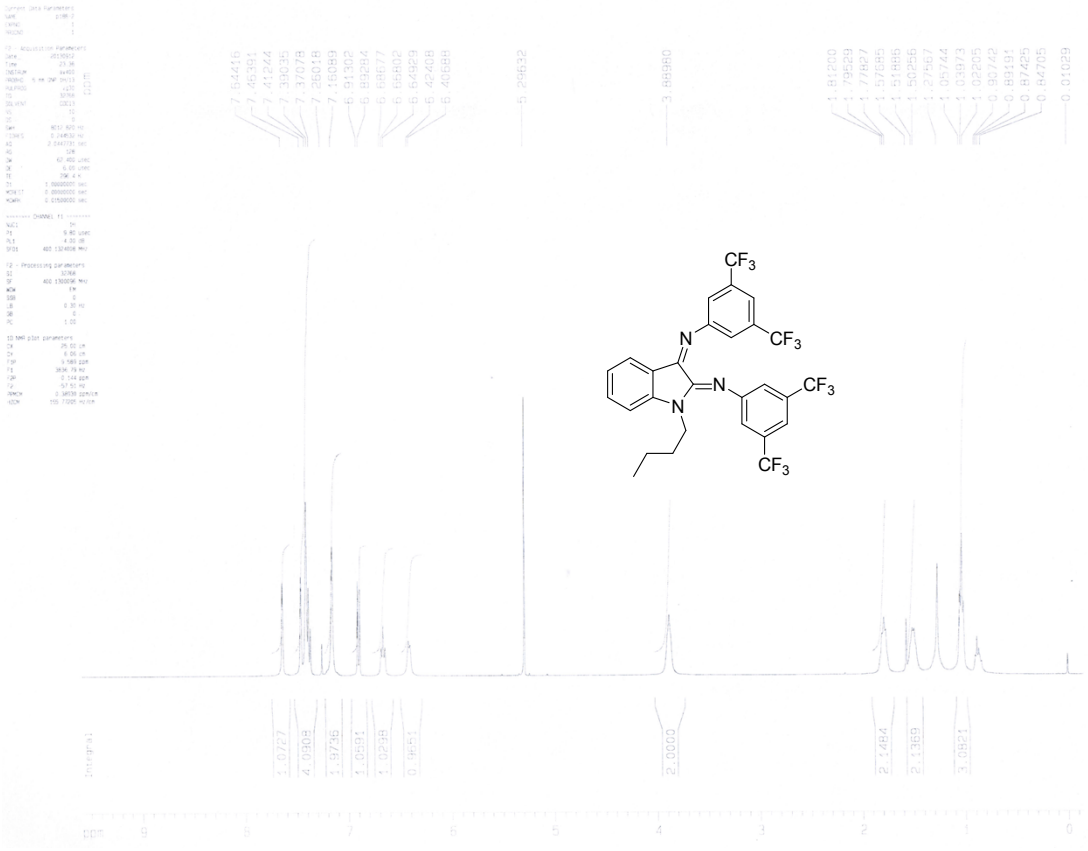


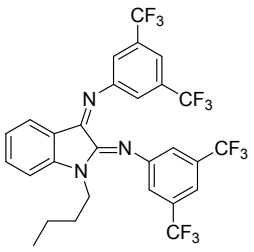
N-(5-chloro-1-methyl-3-(4-nitrophenylimino)indolin-2-ylidene)-4-nitrobenzenamine(4p)

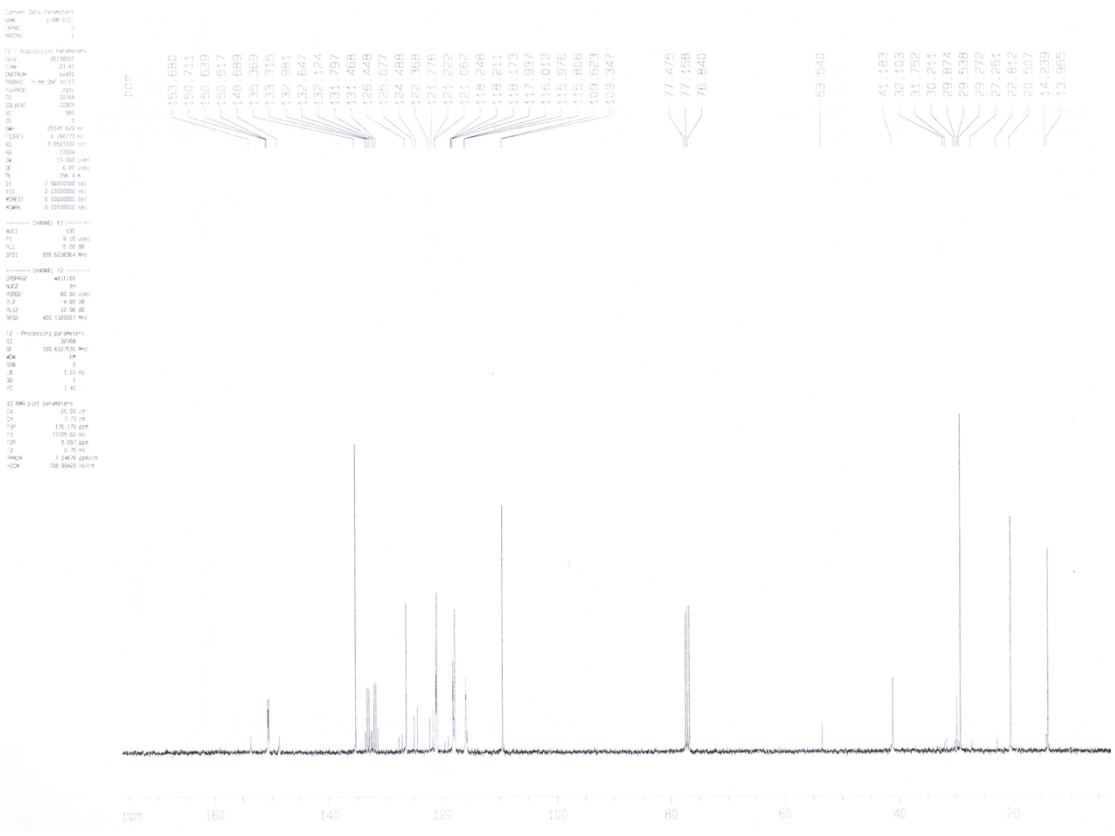




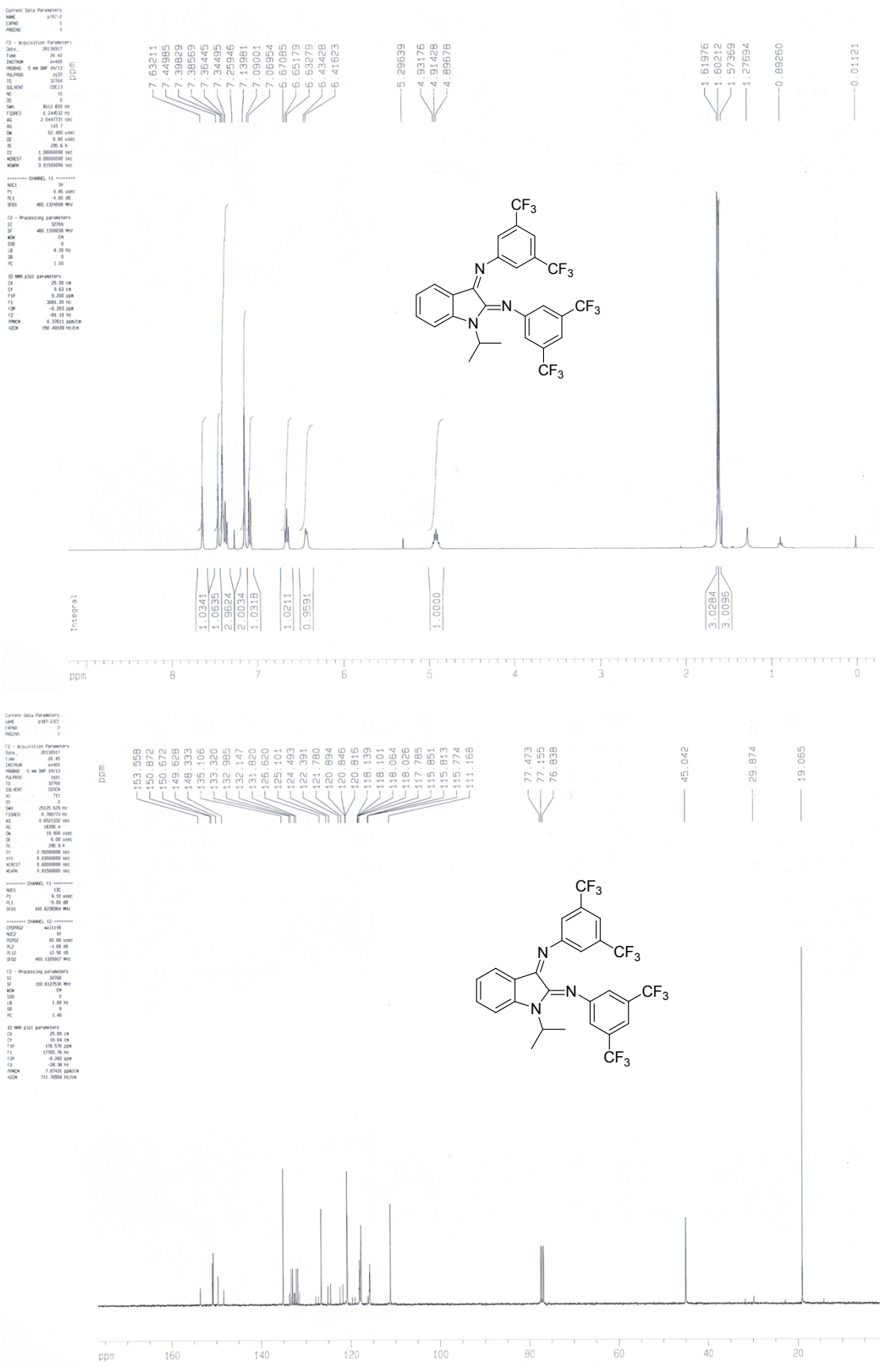
3-(3,5-Bis(trifluoromethyl)phenylimino)-1-butylindolin-2-ylidene)-3,5-bis(trifluoromethyl)benzenamine(4q)





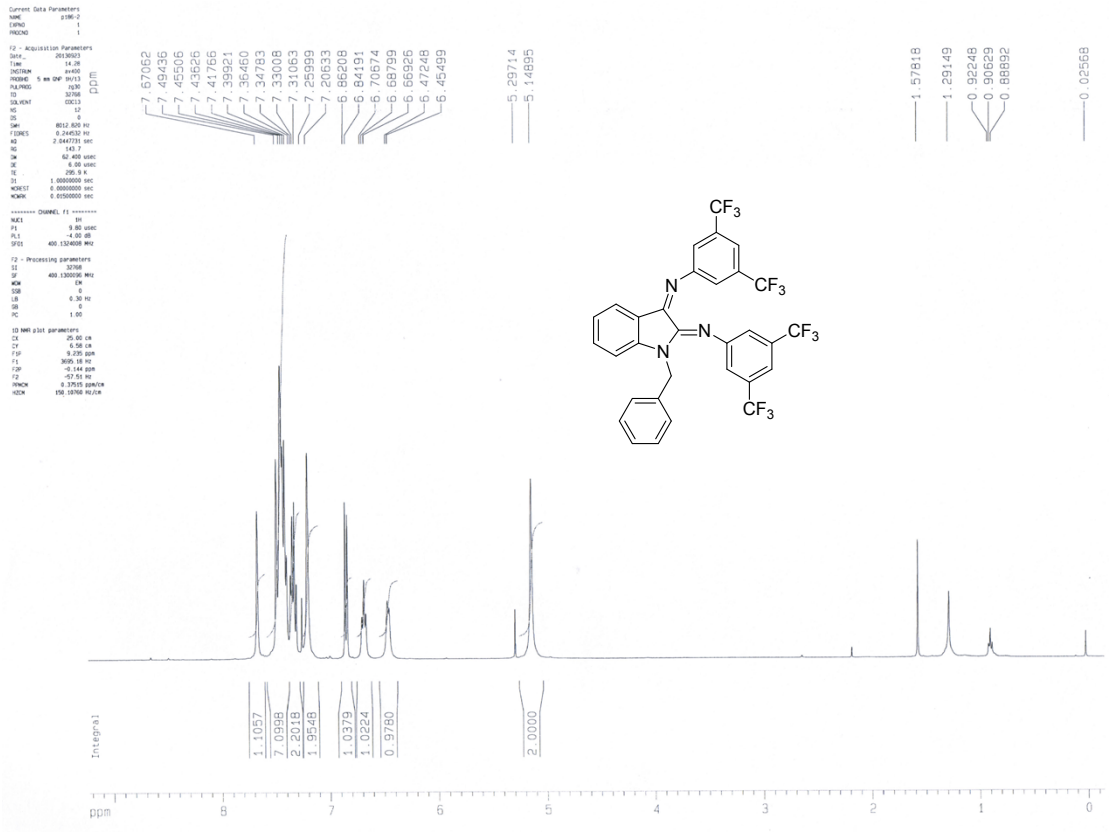


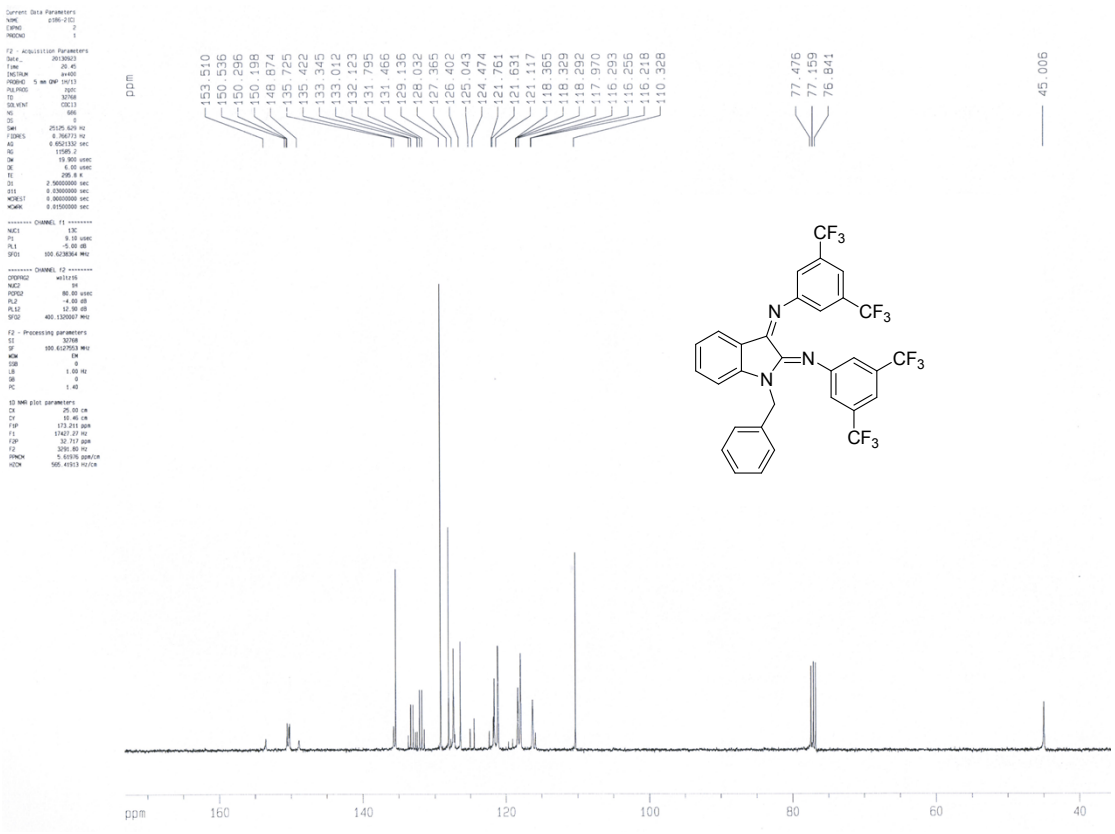
3-(3,5-Bis(trifluoromethyl)phenylimino)-1-isopropylindolin-2-ylidene)-3,5-bis(trifluoromethyl)benzenamine(4r)



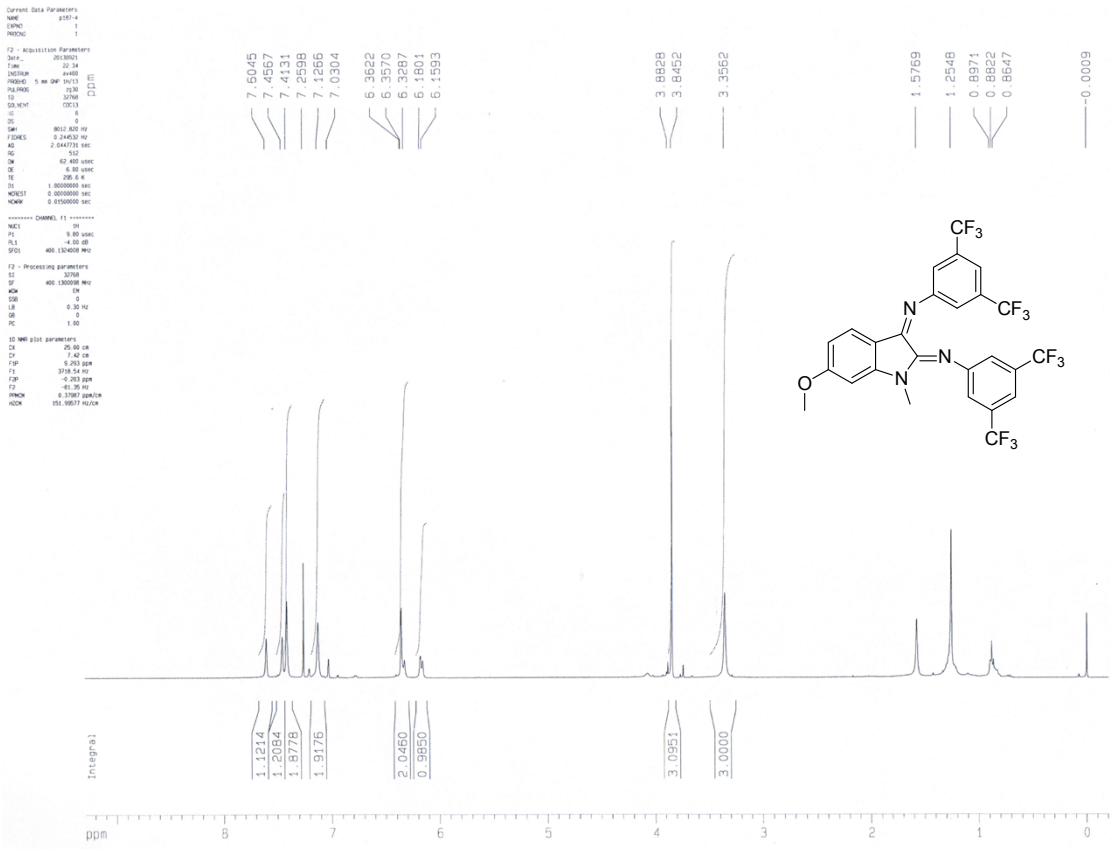
3-(3,5-Bis(trifluoromethyl)phenylimino)-1-benzylindolin-2-ylidene)-3,5-

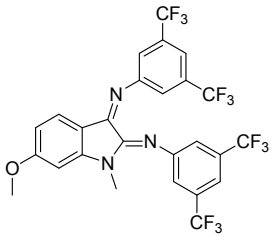
bis(trifluoromethyl)benzenamine(4s)

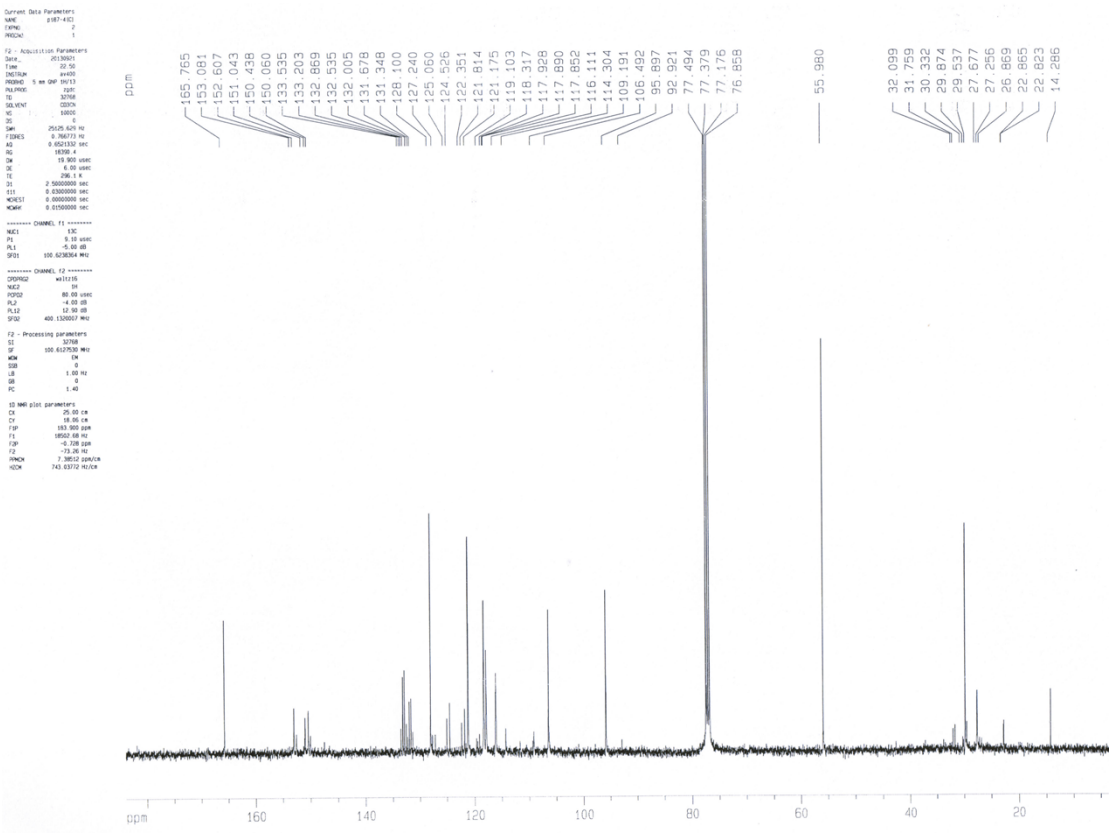




3-(3,5-Bis(trifluoromethyl)phenylimino)-6-methoxy-1-methylindolin-2-ylidene)-3,5-bis(trifluoromethyl)benzenamine(4t)



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