Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Radical Perfluoroalkylation – Easy Access to 2-Perfluoroalkylindol-3-imines *via* Electron Catalysis

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1. General

All reaction were carried out in oven-dried glassware under argon atmosphere using standard *Schlenk* technique.

For thin layer chromatography (**TLC**) *Merck* silica gel 60 F_{254} plates were used. Detection was done by UV light (254 nm/366 nm). Flash chromatography (**FC**) was performed on *Merck* silica gel 60 (40–63 µm) or *Acros Organics* silica gel (35-70 µm) with an excess argon pressure up to 0.5 bar.

Phosphoryl chloride (99%), trimethylamine (99%), acetic anhydride (99%+), formic acid (99%) and ethyl acetate (99.9%, Extra Dry over Molecular Sieve, AcroSeal) were purchased by *Acros Organics*, 2,2′-azobis(2-methylpropionitrile) (98%) and 1,1′-azobis(cyclohexanecarbonitrile) (98%) were purchased by *Sigma Aldrich* and were used as received. All other chemicals were purchased by *ABCR*, *Acros Organics*, *Alfa Aesar*, *Fluka*, *Sigma Aldrich* and *TCI* and used as received. Solvents for flash chromatography and extraction were distilled. Tetrahydrofuran (THF) was dried over sodium and potassium.

^{1}H-NMR (300 MHz, 400 MHz, 600 MHz), **^{13}C-NMR** (75 MHz, 101 MHz, 151 MHz) and **^{19}F-NMR** (282 MHz, 564 MHz) were carried out on a *Bruker DPX 300*, *Bruker AV 300*, *Bruker AV 400* or *Agilent DD2 600* spectrometer. Chemical shifts (δ in ppm) were referenced to the residual peak of $CDCl_3$ (^{1}H-NMR: δ = 7.26; ^{13}C-NMR: δ = 77.0) or CD_2Cl_2 (^{1}H-NMR: δ = 5.32; ^{13}C-NMR: δ = 54.0) or to an external standard (^{19}F-NMR: $CFCl_3$: δ = 0.0). The multiplicity of all signals was described by s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Melting points (**MP**) were determined by *Stuart SMP10* and are uncorrected. Infrared spectra (**IR**) were recorded on a *Digilab 3100 FT-IR Excalibur Series* spectrometer. *w* (weak), *m* (medium), *s* (strong) were used to describe the intensity of the signals. **HRMS ESI** (*m/z*) spectra were measured on a *Bruker MicroTof* or *Thermo-Fisher Scientific LTQ XL Orbitrap*.

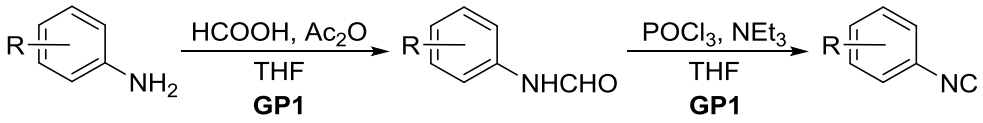
GC/MS (EI, 70 eV) was carried out on an *Agilent 6890N* chromatograph using a *HP-5* column combined with a *Waters-Micromass Quatro Micro* spectrometer. As carrier gas (~ 1 bar) helium was used. *MassLinx 4.0 of Water-Micromass* was used for data analysis. **UV/vis** spectra were recorded by a *Jasco V-650 UV/vis double beam spectrometer* with a *PAC-743* 6-position peltier cell changer using a quartz-glass cuvette in CH_2Cl_2 as solvent.

Absorption spectra were measured on a *Varian Cary 5000* double-beam **UV-Vis-NIR** spectrometer and baseline corrected. Steady-state emission spectra were recorded on a

FluoTime300 spectrometer from *PicoQuant* equipped with a 300 W ozone-free Xe lamp (250-900 nm), a 10 W Xe flash-lamp (250-900 nm, pulse width < 10 µs) with repetition rates of 0.1 – 300 Hz, an excitation monochromator (*Czerny-Turner* 2.7 nm/mm dispersion, 1200 grooves/mm, blazed at 300 nm), diode lasers (pulse width < 80 ps) operated by a computer-controlled laser driver *PDL-820* (repetition rate up to 80 MHz, burst mode for slow and weak decays), two emission monochromators (*Czerny-Turner*, selectable gratings blazed at 500 nm with 2.7 nm/mm dispersion and 1200 grooves/mm, or blazed at 1250 nm with 5.4 nm/mm dispersion and 600 grooves/mm), *Glan-Thompson* polarizers for excitation (Xe-lamps) and emission, a *Peltier*-thermostatized sample holder from *Quantum Northwest* (-40°C –105°C), and two detectors, namely a *PMA Hybrid 40* (transit time spread FWHM < 120 ps, 300 – 720 nm). Steady-state and fluorescence lifetimes were recorded in TCSPC mode by a *PicoHarp 300* (minimum base resolution 4 ps). Emission and excitation spectra were corrected for source intensity (lamp and grating) by standard correction curves. Phosphorescence lifetimes were recorded by a *NanoHarp 250* (minimum base resolution 32 ns) in MCS mode. Lifetime analysis was performed using the commercial *FluoFit* software. The quality of the fit was assessed by minimizing the reduced chi squared function ($\chi 2$) and visual inspection of the weighted residuals and their autocorrelation. Luminescence quantum yields were measured with a *Hamamatsu Photonics* absolute PL quantum yield measurement system (*C9920-02*) equipped with a *L9799-01 CW* Xenon light source (150 W), monochromator, *C7473* photonic multi-channel analyzer, integrating sphere and employing *U6039-05 PLQY* measurement software (*Hamamatsu Photonics*, Ltd., Shizuoka, Japan). All solvents used were of spectrometric grade.

2. General procedures

1-Trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one (**2a**),[1] 1-(perfluoroethyl)-1λ^3-benzo[d][1,2]iodaoxol-3(1*H*)-one (**2b**),[1] 1-(perfluoropropyl)-1λ^3-benzo[d][1,2]iodaoxol-3(1*H*)-one (**2c**)[1] and *N*-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)formamide[2] were synthesized according to a literature procedure. For the synthesis of isocyanoaryls **4** a literature procedure by *Chatani et al.*[3] was used. Starting from commercially available aniline derivatives isocyanoaryls **4** were synthesized in a two-step route (see scheme below).



*2.1. General procedure for the synthesis of isocyanoaryls **4** (**GP1**)*

1. Acetic formic anhydride was formed *in situ* by stirring an equimolar mixture of acetic anhydride and formic acid at 55 °C for two hours. This mixture (about 2.0 equiv.) was cooled to room temperature and was added to a solution of aniline (1.0 equiv.) in THF (0.6-0.8 M) at 0 °C. After stirring the reaction mixture at room temperature for two hours a saturated aq. solution of $NaHCO_3$ was added. After extraction with diethyl ether or ethyl acetate (three times) the combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*.

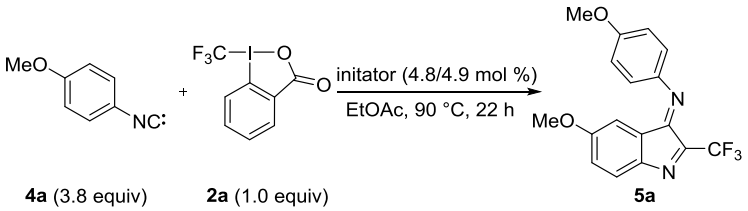
2. The residue was used without further purification. It was dissolved in THF (0.6 M) and triethylamine (6.0 equiv.) was added. To this reaction mixture phosphoryl chloride (1.5 equiv.) was added slowly at 0 °C. After stirring for 2 h at this temperature a saturated aq. solution of Na_2CO_3 was added. The reaction mixture was stirred at room temperature for 1 h. After phase separation the aqueous phase was extracted with CH_2Cl_2 (three times). The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by FC (P/EtOAc) to afford the desired isocyanoaryl **4**.

*2.2. General procedure for the synthesis of 3H-indol-3-imine **5** (**GP2**)*

To a solution of isocyanoaryls **4** (1.00 mmol, 3.8 equiv.) and lithium iodide (13 µmol, 4.9 mol%) in ethyl acetate (0.26 M) *Togni*-reagent **2** (0.261 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at 90 °C for 22 h. After removal of the solvent *in vacuo* FC (P/EtOAc or P/DEE) afforded the desired 3*H*-indol-3-imine **5**.

3. Optimization

Table S1 Optimization of the initiator



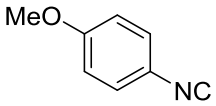
4a (3.8 equiv) **2a** (1.0 equiv) **5a**

entry	init.	conc. (mmol/L)	yield[a] (%)
1	TBAI	0.52	42
2	TBAI	0.09	49
3	TBAI	0.26	54
4	LiI	0.26	60
5	NaI	0.26	51
6	KI	0.26	53
7	CsI	0.26	53
8	MgI_2	0.26	56
9	CaI_2	0.26	57

[a] isolated yields

4. Synthesis of isocyanoaryls 4 and diazene 6c

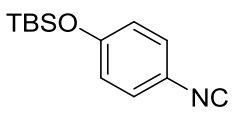
1-Isocyano-4-methoxybenzene (4a)



According to ***GP1*** with *p*-anisidine (6.168 g, 50.06 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (13 mL), triethylamine (42 mL, 0.30 mol, 6.0 equiv.) and phosphoryl chloride (7.0 mL, 77 mmol, 1.5 equiv.). FC (P/EtOAc = 20/1) afforded the desired isocyanoaryl **4a** (4.788 g, 35.95 mmol, 72%) as a yellow solid.

MP: 31 °C. **IR** (neat): 3072*w*, 3010*w*, 2966*w*, 2840*w*, 2125*m*, 1607*m*, 1585*w*, 1505*s*, 1465*w*, 1443*w*, 1302*m*, 1254*s*, 1193*w*, 1164*w*, 1108*w*, 1029*m*, 833*m*, 699*w*, 515*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 (d, *J* = 8.9 Hz, 2H, $C_{arom}H$), 6.90 – 6.82 (m, 2H, $C_{arom}H$), 3.82 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.8 (t, *J* = 8.9 Hz, C), 159.9 (C), 127.7 (2 × CH), 119.5 (t, *J* = 14.9 Hz, C), 114.6 (2 × CH), 55.5 (CH_3). **HRMS** (ESI) *m/z* = 156.0420 calcd. for C_8H_7NONa $[M+Na]^+$, found: 156.0417.

tert-Butyl(4-isocyanophenoxy)dimethylsilane (4b)

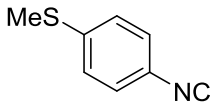


According to ***GP1-2*** with *N*-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)formamide (921 mg, 3.66 mmol, 1.0 equiv.), triethylamine (3.0 mL, 22 mol, 5.9 equiv.) and phosphoryl chloride (0.50 mL, 5.1 mmol, 1.4 equiv.). FC (P/EtOAc = 15/1) afforded the desired isocyanoaryl **4b** (579 mg, 2.48 mmol, 68%) as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.26 (d, *J* = 8.7 Hz, 2H, $C_{arom}H$), 6.85 – 6.78 (m, 2H, $C_{arom}H$), 0.99 (s, 9H, CH_3), 0.21 (s, 6H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.8 (C), 156.4 (C), 127.7 (2 × CH), 120.7 (2 × CH), 120.3 – 119.8 (m, C), 25.5 (3 × CH_3), 18.2 (C), -4.5 (2 × CH_3). **MS** (EI) *m/z* (relative intensity %) = 233.2 (13), 176.2 (100), 75.0 (12).

Spectroscopic data are in accordance with those described in the literature.[4]

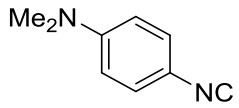
(4-Isocyanophenyl)(methyl)sulfane (4c)



According to ***GP1*** with 4-(methylthio)aniline (1.392 g, 10.00 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (2.7 mL), triethylamine (8.3 mL, 60 mol, 6.0 equiv.) and phosphoryl chloride (1.4 mL, 15 mmol, 1.5 equiv.). FC (P/EtOAc = 30/1) afforded the desired isocyanoaryl **4c** (1.066 g, 7.145 mmol, 71%) as a green solid.

MP: 42 °C. **IR** (neat): 3067*w*, 2988*w*, 2921*w*, 2123*s*, 1593*w*, 1488*s*, 1436*w*, 1404*w*, 1323*w*, 1302*w*, 1200*w*, 1118*w*, 1092*m*, 1015*w*, 968*w*, 822*s*, 590*w*, 509*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 (d, *J* = 8.7 Hz, 2H, $C_{arom}H$), 7.22 (d, *J* = 8.7 Hz, 2H, $C_{arom}H$), 2.51 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 164.1 (C), 141.2 (C), 126.5 (2 × CH), 126.3 (2 × CH), 123.0 (t, *J* = 14.0 Hz, C), 15.2 (CH_3). **HRMS** (ESI) *m/z* = 172.0192 calcd. for C_8H_7NSNa $[M+Na]^+$, found: 172.0188.

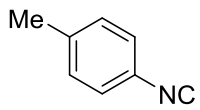
4-Isocyano-*N*,*N*-dimethylaniline (4d)



According to ***GP1*** with N^1,N^1-dimethylbenzene-1,4-diamine (1.362 g, 10.00 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (2.7 mL), triethylamine (8.3 mL, 60 mol, 6.0 equiv.) and phosphoryl chloride (1.4 mL, 15 mmol, 1.5 equiv.). FC (P/EtOAc = 10/1) afforded the desired isocyanoaryl **4d** (903 mg, 6.18 mmol, 62%) as a white solid.

MP: 62 °C. **IR** (neat): 2901*w*, 2818*w*, 2118*m*, 1883*w*, 1609*s*, 1524*s*, 1447*w*, 1368*m*, 1228*m*, 1172*w*, 1123*w*, 1068*w*, 941*w*, 817*s*, 519*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.21 (d, *J* = 8.9 Hz, 2H, $C_{arom}H$), 6.63 – 6.54 (m, 2H, $C_{arom}H$), 2.98 (s, 6H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 161.3 (t, *J* = 6.3 Hz, C), 150.3 (C), 127.2 (2 × CH), 115.0 (t, *J* = 14.4 Hz, C), 111.7 (2 × CH), 40.2 (2 × CH_3). **HRMS** (ESI) *m/z* = 169.0736 calcd. for $C_9H_{10}N_2Na$ $[M+Na]^+$, found: 169.0739.

1-Isocyano-4-methylbenzene (4e)

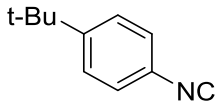


According to ***GP1*** with *p*-toluidine (5.381 g, 50.20 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (13 mL), triethylamine (42 mL, 0.30 mol, 6.0 equiv.) and phosphoryl chloride (7.0 mL, 77 mmol, 1.5 equiv.). Distillation at reduced pressure (b.p. 68 °C, 8.0 mbar) afforded the desired isocyanoaryl **4e** (3.130 g, 26.71 mmol, 53%) as a yellow liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.28 (d, *J* = 8.1 Hz, 2H, $C_{arom}H$), 7.20 (d, *J* = 8.2 Hz, 2H, $C_{arom}H$), 2.40 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.4 (t, *J* = 5.8 Hz, C), 139.6 (C), 129.9 (2 × CH), 126.1 (2 × CH), 124.1 (t, *J* = 13.6 Hz, C), 21.2 (CH_3). **MS** (EI) *m/z* (relative intensity %) = 117.1 (100), 90.1 (66), 63.1 (21), 51.1 (10), 39.1 (22).

Spectroscopic data are in accordance with those described in the literature.[5]

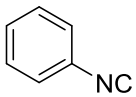
1-(*tert*-Butyl)-4-isocyanobenzene (4f)



According to ***GP1*** with 4-(*tert*-butyl)aniline (1.194 g, 8.003 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (2.1 mL), triethylamine (7.0 mL, 50 mol, 6.3 equiv.) and phosphoryl chloride (1.1 mL, 12 mmol, 1.5 equiv.). FC (P/EtOAc = 40/1) afforded the desired isocyanoaryl **4f** (1.006 g, 6.319 mmol, 79%) as a green liquid.

IR (neat): 2965*s*, 2907*w*, 2871*w*, 2123*s*, 1693*w*, 1605*w*, 1510*m*, 1499*m*, 1480*w*, 1464*w*, 1408*w*, 1396*w*, 1366*m*, 1270*w*, 1205*w*, 1172*w*, 1113*w*, 1016*w*, 838*s*, 783*w*, 730*w*, 553*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.42 – 7.37 (m, 2H, $C_{arom}H$), 7.30 (d, *J* = 8.6 Hz, 2H, $C_{arom}H$), 1.31 (s, 9H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.3 (t, *J* = 5.7 Hz, C), 152.8 (C), 126.3 (2 × CH), 126.0 (2 × CH), 124.0 (t, *J* = 13.9 Hz, C), 34.9 (C), 31.1 (3 × CH_3). **HRMS** (ESI) *m/z* = 182.0940 calcd. for $C_{11}H_{13}NNa$ $[M+Na]^+$, found: 182.0944.

Isocyanobenzene (4g)

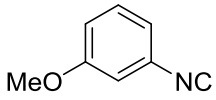


According to ***GP1-2*** with phenylformanilide (1.817 g, 15.00 mmol, 1.0 equiv.), triethylamine (13 mL, 92 mol, 6.2 equiv.) and phosphoryl chloride (2.1 mL, 23 mmol, 1.5 equiv.). Destillation at reduced pressure (b.p. 75 °C, 13 mbar) afforded the desired isocyanoaryl **4g** (598 mg, 5.80 mmol, 39%) as a colorless liquid which changes color after few seconds to light blue.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.45 – 7.32 (m, 5H, $C_{arom}H$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.1 (t, *J* = 3.8 Hz, C), 106.3 (2 × CH), 106.3 (CH), 103.6 (t, *J* = 13.5 Hz, C), 103.3 (2 × CH). **MS** (EI) *m/z* (relative intensity %) = 103.2 (100), 76.1 (27).

Spectroscopic data are in accordance with those described in the literature.[6]

1-Isocyano-3-methoxybenzene (4h)

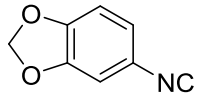


According to ***GP1*** with 3-methoxyaniline (1.1 mL, 9.8 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (2.7 mL), triethylamine (8.3 mL, 60 mol, 6.1 equiv.) and phosphoryl chloride (1.4 mL, 15 mmol, 1.5 equiv.). FC (P/EtOAc = 20/1) afforded the desired isocyanoaryl **4h** (896 mg, 6.73 mmol, 67%) as a green liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.28 (t, *J* = 8.1 Hz, 1H, $C_{arom}H$), 7.00 – 6.86 (m, 3H, $C_{arom}H$), 3.81 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.8 (t, *J* = 5.4 Hz, C), 160.0 (C), 130.2 (C), 127.4 (t, *J* = 13.2 Hz, C), 118.6 (CH), 115.6 (CH), 111.8 (CH), 55.5 (CH_3). **MS** (EI) *m/z* (relative intensity %) = 133.2 (100), 118.2 (10), 103.2 (98), 90.2 (29).

Spectroscopic data are in accordance with those described in the literature.[7]

5-Isocyanobenzo[*d*][1,3]dioxole (4i)

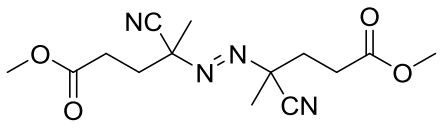


According to ***GP1*** with benzo[d][1,3]dioxol-5-amine (1.371 g, 10.00 mmol, 1.0 equiv.), the *in situ* formed acetic formic anhydride (2.7 mL), triethylamine (8.3 mL, 60 mol, 6.0 equiv.) and phosphoryl chloride (1.4 mL, 15 mmol, 1.5 equiv.). FC (P/EtOAc = 50/1) afforded the desired isocyanoaryl **4i** (796 mg, 5.41 mmol, 54%) as a yellow solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.90 (dd, *J* = 8.2 Hz, *J* = 2.0 Hz, 1H, $C_{arom}H$), 6.82 (d, *J* = 2.0 Hz, 1H, $C_{arom}H$), 6.76 (d, *J* = 8.2 Hz, 1H, $C_{arom}H$), 6.03 (s, 2H, CH_2). **^{13}C-NMR** (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.8 (C), 148.3 (C), 148.0 (C), 120.8 (CH), 120.2 (t, *J* = 14.1 Hz, C), 108.4 (CH), 107.2 (CH), 102.1 (CH_2). **HRMS** (ESI) *m/z* = 170.0212 calcd. for $C_8H_5NO_2Na$ $[M+Na]^+$, found: 170.0216.

Spectroscopic data are in accordance with those described in the literature.[8]

Dimethyl 4,4'-(diazene-1,2-diyl)(*E*)-bis(4-cyanopentanoate) (6c)



According to a literature procedure by *Baudoin et al.*[9] $TMSCHN_2$ (2.0 M in hexane, 5.0 mL, 10 mmol, 6.7 equiv.) was added slowly to a solution of 4,4'-azobis(4-cyanovaleric

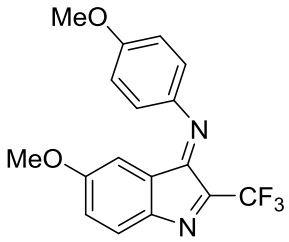
acid) (420 mg, 1.50 mmol, 1.0 equiv.) in MeOH (8.0 mL, 0.19 M) at 0 °C. After 30 min stirring at 0 °C, acetic acid (1.0 mL) was added. The reaction mixture was concentrated *in vacuo*. FC afforded the desired ester **6c** (412.5 mg, 1.338 mmol, 89%) as a colorless solid.

^{1}H-NMR (300 MHz, CD_3Cl, 300 K): δ (ppm) = 3.71 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 2.63 – 2.24 (m, 8H, CH_2), 1.72 (s, 3H, CH_3), 1.67 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, CD_3Cl, 300 K): δ (ppm) = 171.7 (C), 171.7 (C), 117.5 (C), 117.4 (C), 71.9 (C), 71.8 (C), 52.0 (2 × CH_3), 33.2 (CH_2), 33.2 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 23.9 (CH_3), 23.7 (CH_3). **HRMS** (ESI) *m/z* = 331.1382 calcd. for $C_{14}H_{20}N_4O_4Na$ $[M+Na]^+$, found: 331.1372.

Spectroscopic data are in accordance with those described in the literature.[10]

5. Synthesis of 3*H*-indol-3-imines 5 and 7

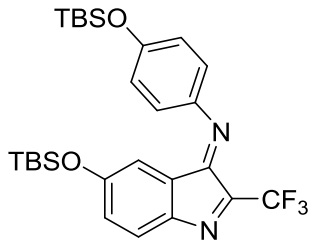
(*E*)-5-Methoxy-*N*-(4-methoxyphenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5a)



According to ***GP2*** with isocyanoaryl **4a** (133.7 mg, 1.004 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/EtOAc = 10/1 → P/EtOAc = 5/1) afforded the desired 3*H*-indol-3-imine **5a** (52.2 mg, 0.156 mmol, 60%) as a red solid.

MP: 127 °C. **IR** (neat): 3006*w*, 2964*w*, 2839*w*, 1593*w*, 1561*m*, 1501*m*, 1469*m*, 1435*m*, 1382*w*, 1323*m*, 1290*m*, 1245*s*, 1232*m*, 1199*m*, 1174*s*, 1151*s*, 1135*s*, 1104*s*, 1081*w*, 1028*s*, 940*w*, 885*w*, 860*m*, 833*m*, 769*m*, 730*m*, 694*w*, 590*w*, 550*w*, 530*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.51 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 7.18 – 7.09 (m, 2H, $C_{arom}H$), 7.07 – 6.99 (m, 2H, $C_{arom}H$), 6.93 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H, $C_{arom}H$), 6.78 (d, *J* = 2.5 Hz, 1H, $C_{arom}H$), 3.88 (s, 3H, CH_3), 3.68 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 161.6 (C), 159.9 (C), 158.8 (C), 157.4 (q, *J* = 35.3 Hz, C), 149.0 (C), 142.4 (C), 124.8 (CH), 122.8 (q, *J* = 1.5 Hz, C), 122.0 (2 × CH), 120.6 (q, *J* = 273.4 Hz, CF_3), 116.8 (CH), 115.2 (2 × CH), 112.9 (CH), 56.3 (CH_3), 56.2 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -65.1. **HRMS** (ESI) *m/z* = 357.08213 calcd. for $C_{17}H_{13}F_3N_2O_2Na$ $[M+Na]^+$, found: 357.08182.

(*E*)-5-((*tert*-Butyldimethylsilyl)oxy)-*N*-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5b)

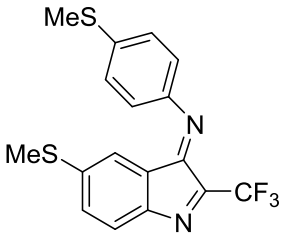


According to ***GP2*** with isocyanoaryl **4b** (233.4 mg, 1.000 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/DEE = 100/1 → P/DEE = 50/1) afforded the desired 3*H*-indol-3-imine **5b** (57.4 mg, 0.107 mmol, 41%) as a red solid.

MP: 38 °C. **IR** (neat): 2956*w*, 2931*w*, 2898*w*, 2887*w*, 2860*w*, 1591*w*, 1568*w*, 1498*m*, 1462*m*, 1435*w*, 1381*w*, 1363*w*, 1031*m*, 1255*s*, 1235*m*, 1195*m*, 1176*m*, 1145*s*, 1105*m*, 1008*w*, 968*w*, 910*m*, 891*s*, 883*s*, 837*s*, 802*m*, 780*s*, 732*w*, 718*w*, 705*w*, 687*w*, 660*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.46 (d, *J* = 8.3 Hz, 1H, $C_{arom}H$), 7.07 – 7.01 (m, 2H, $C_{arom}H$), 6.99 – 6.92 (m, 2H, $C_{arom}H$), 6.90 (dd, *J* = 8.3 Hz, *J* = 2.4 Hz, 1H, $C_{arom}H$), 6.69 (d, *J* = 2.4 Hz, 1H, $C_{arom}H$), 1.03 (s, 9H, CH_3), 0.91 (s, 9H, CH_3), 0.27 (s, 6H, CH_3), 0.10 (s, 6H, CH_3). **^{13}C-NMR**

(75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 159.1 (C), 157.9 (C), 157.7 (q, *J* = 35.5 Hz, C), 155.9 (C), 149.6 (C), 143.0 (C), 124.9 (CH), 124.3 (CH), 122.6 (q, *J* = 1.7 Hz, C), 121.6 (2 × CH), 121.3 (2 × CH), 120.6 (q, *J* = 273.5 Hz, CF_3), 117.9 (CH), 26.0 (3 × CH_3), 25.9 (3 × CH_3), 18.7 (C), 18.7 (C), -4.0 (2 × CH_3), -4.2 (2 × CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -65.1. **HRMS** (ESI) *m/z* = 535.24184 calcd. for $C_{27}H_{38}F_3N_2O_2Si_2$ $[M+H]^+$, found: 535.24191.

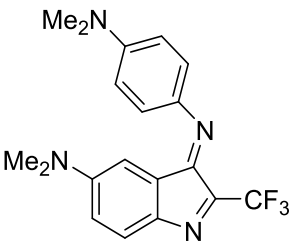
(*E*)-5-(Methylthio)-*N*-(4-(methylthio)phenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5c)



According to ***GP2*** with isocyanoaryl **4c** (149.4 mg, 1.001 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/EtOAc = 30/1 → P/EtOAc = 20/1) afforded the desired 3*H*-indol-3-imine **5c** (13.5 mg, 36.8 µmol, 14%) as a dark red solid.

MP: 132 °C. **IR** (neat): 3094*w*, 3066*w*, 2921*w*, 1564*m*, 1484*w*, 1436*w*, 1415*m*, 1381*m*, 1299*w*, 1204*m*, 1184*s*, 1134*s*, 1116*s*, 1092*m*, 1012*w*, 954*w*, 923*w*, 856*w*, 830*m*, 731*w*, 523*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.51 (d, *J* = 8.1 Hz, 1H, $C_{arom}H$), 7.38 (d, *J* = 8.5 Hz, 2H, $C_{arom}H$), 7.29 (dd, *J* = 8.1 Hz, *J* = 1.9 Hz, 1H, $C_{arom}H$), 7.06 (d, *J* = 8.5 Hz, 2H, $C_{arom}H$), 6.88 (d, *J* = 1.9 Hz, 1H, $C_{arom}H$), 2.54 (s, 3H, CH_3), 2.29 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 159.2 (C), 157.4 (q, *J* = 35.8 Hz, C), 152.4 (C), 146.4 (C), 142.2 (C), 138.6 (C), 130.2 (CH), 127.7 (2 × CH), 124.0 (CH), 123.1 (CH), 121.7 (q, *J* = 1.5 Hz, C), 120.3 (q, *J* = 273.6 Hz, CF_3), 120.1 (2 × CH), 16.2 (CH_3), 15.7 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -65.2. **HRMS** (ESI) *m/z* = 367.05450 calcd. for $C_{17}H_{14}F_3N_2S_2$ $[M+H]^+$, found: 367.05415.

(*E*)-3-((4-(Dimethylamino)phenyl)imino)-*N*,*N*-dimethyl-2-(trifluoromethyl)-3*H*-indol-5-amine (5d)

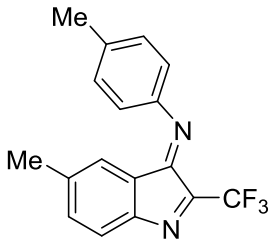


According to ***GP2*** with isocyanoaryl **4d** (147.0 mg, 1.005 mmol, 3.9 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/DEE = 15/1 → P/DEE = 4/1) afforded the desired 3*H*-indol-3-imine **5d** (36.7 mg, 0.102 mmol, 39%) as a violet solid.

MP: 125 °C. **IR** (neat): 2898*w*, 2812*w*, 1611*m*, 1583*m*, 1529*s*, 1437*m*, 1356*s*, 1284*w*, 1253*w*, 1214*w*, 1178*s*, 1147*s*, 1130*s*, 1099*s*, 1069*m*, 945*w*, 911*w*, 850*w*, 823*m*, 809*w*, 761*w*, 724*w*, 687*w*.

^{1}H-NMR (600 MHz, CD_2Cl_2, 300 K): 7.38 (d, *J* = 8.6 Hz, 1H, $C_{arom}H$), 7.29 – 7.24 (m, 2H, $C_{arom}H$), 7.10 (d, *J* = 2.6 Hz, 1H, $C_{arom}H$), 6.80 – 6.75 (m, 2H, $C_{arom}H$), 6.62 (dd, *J* = 8.6 Hz, *J* = 2.6 Hz, 1H, $C_{arom}H$), 3.05 (s, 6H, CH_3), 2.87 (s, 6H, CH_3). **^{13}C-NMR** (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 156.3 (C), 154.3 (q, *J* = 34.5 Hz, C), 152.1 (C), 151.3 (C), 144.8 (C), 138.1 (C), 124.4 (2 × CH), 124.2 (CH), 123.6 (q, *J* = 2.0 Hz, C), 121.3 (q, *J* = 272.7 Hz, CF_3), 113.7 (CH), 112.4 (2 × CH), 108.9 (CH), 40.9 (2 × CH_3), 40.8 (2 × CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -64.3. **HRMS** (ESI) *m/z* = 361.16346 calcd. for $C_{19}H_{20}F_3N_4$ $[M+H]^+$, found: 361.16331.

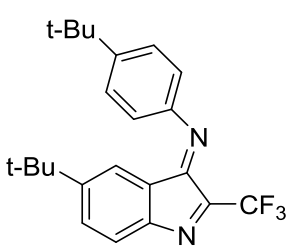
(*E*)-5-Methyl-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5e)



According to ***GP2*** with isocyanoaryl **4e** (117.6 mg, 1.003 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/DEE = 150/1) afforded the desired 3*H*-indol-3-imine **5e** (25.6 mg, 84.7 µmol, 32%) as an orange solid.

MP: 106 °C. **IR** (neat): 3058*w*, 2987*w*, 2920*w*, 2861*w*, 2733*w*, 1928*w*, 1646*w*, 1612*w*, 1574*m*, 1500*m*, 1470*w*, 1453*w*, 1420*w*, 1378*s*, 1306*w*, 1284*w*, 1230*w*, 1195*w*, 1174*m*, 1151*s*, 1133*s*, 1118*s*, 1110*s*, 1079*m*, 1041*w*, 1017*m*, 942*m*, 895*w*, 860*m*, 833*m*, 823*s*, 795*m*, 775*w*, 766*w*, 729*m*, 575*w*, 521*m*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.48 (d, *J* = 7.8 Hz, 1H, $C_{arom}H$), 7.35 – 7.21 (m, 3H, $C_{arom}H$), 7.03 – 6.96 (m, 2H, $C_{arom}H$), 6.86 – 6.83 (m, 1H, $C_{arom}H$), 2.44 (s, 3H, CH_3), 2.20 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 159.6 (C), 158.4 (q, *J* = 35.4 Hz, C), 153.7 (C), 147.1 (C), 140.9 (C), 137.5 (C), 134.2 (CH), 130.5 (2 × CH), 126.8 (CH), 123.7 (CH), 121.6 (q, *J* = 1.7 Hz, C), 120.6 (q, *J* = 273.7 Hz, CF_3), 119.4 (2 × CH), 21.9 (CH_3), 21.4 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -65.3. **HRMS** (ESI) *m/z* = 303.11036 calcd. for $C_{17}H_{14}F_3N_2$ $[M+H]^+$, found: 303.11025.

(*E*)-5-(*tert*-Butyl)-*N*-(4-(*tert*-butyl)phenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5f)

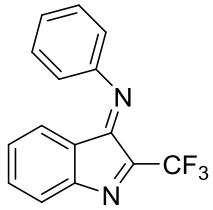


According to ***GP2*** with isocyanoaryl **4f** (159.9 mg, 1.004 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/DEE = 150/1 → P/DEE = 50/1) afforded the desired 3*H*-indol-3-imine **5f** (22.4 mg,

58.0 µmol, 22%) as an orange solid.

MP: 124 °C. **IR** (neat): 2964*m*, 2906*w*, 2871*w*, 1639*w*, 1615*w*, 1575*w*, 1503*w*, 1477*w*, 1382*m*, 1311*w*, 1287*w*, 1267*w*, 1178*s*, 1147*s*, 1123*s*, 1015*w*, 936*w*, 865*m*, 837*m*, 739*w*, 724*m*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.56 – 7.48 (m, 3H, $C_{arom}H$), 7.45 (dd, *J* = 8.1 Hz, *J* = 1.8 Hz, 1H, $C_{arom}H$), 7.02 – 6.94 (m, 2H, $C_{arom}H$), 6.72 (d, *J* = 1.8 Hz, 1H, $C_{arom}H$), 1.39 (s, 9H, CH_3), 1.08 (s, 9H, CH_3). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 161.0 (C), 158.6 (q, *J* = 35.7 Hz, C), 154.1 (C), 153.2 (C), 150.4 (C), 148.0 (C), 130.6 (CH), 126.8 (2 × CH), 124.1 (CH), 123.3 (CH), 121.3 (q, *J* = 1.6 Hz, C), 120.5 (q, *J* = 273.9 Hz, CF_3), 118.3 (2 × CH), 35.5 (C), 35.1 (C), 31.8 (3 × CH_3), 31.2 (3 × CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -65.4. **HRMS** (ESI) *m/z* = 387.20426 calcd. for $C_{23}H_{25}F_3N_2$ $[M+H]^+$, found: 387.20389.

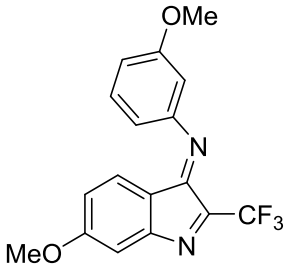
(*E*)-*N*-Phenyl-2-(trifluoromethyl)-3*H*-indol-3-imine (5g)



According to ***GP2*** with isocyanoaryl **4g** (103.0 mg, 0.9990 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/EtOAc = 40/1 → P/EtOAc = 20/1) afforded the desired 3*H*-indol-3-imine **5g** (9.9 mg, 36 µmol, 14%) as an orange solid.

MP: 64 °C. **IR** (neat): 3068*w*, 1669*w*, 1642*w*, 1614*w*, 1594*w*, 1578*w*, 1483*w*, 1468*w*, 1449*w*, 1380*m*, 1332*w*, 1286*w*, 1197*s*, 1179*s*, 1144*s*, 1113*s*, 1072*w*, 1024*w*, 917*w*, 893*w*, 773*m*, 765*m*, 730*w*, 719*m*, 695*m*, 605*w*, 557*w*. **^{1}H-NMR** (600 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.62 (d, *J* = 7.7 Hz, 1H, $C_{arom}H$), 7.51 – 7.45 (m, 3H, $C_{arom}H$), 7.35 – 7.31 (m, 1H, $C_{arom}H$), 7.13 (td, *J* = 7.6 Hz, *J* = 0.9 Hz, 1H, $C_{arom}H$), 7.07 – 7.02 (m, 2H, $C_{arom}H$), 6.82 (ddd, *J* = 7.6 Hz, *J* = 1.2 Hz, *J* = 0.6 Hz, 1H, $C_{arom}H$). **^{13}C-NMR {^{19}F}** (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 159.9 (C), 159.1 (C), 155.7 (C), 149.8 (C), 134.1 (CH), 130.3 (CH), 130.0 (2 × CH), 127.0 (CH), 126.3 (CH), 124.2 (CH), 121.3 (C), 120.4 (CF_3), 118.7 (2 × CH). **^{19}F-NMR** (564 MHz, CD_2Cl_2, 300 K): δ (ppm) = -65.5. **HRMS** (ESI) *m/z* = 275.07906 calcd. for $C_{15}H_{10}F_3N_2$ $[M+H]^+$, found: 275.07893.

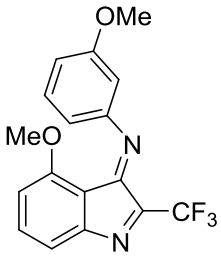
(*E*)-6-Methoxy-*N*-(3-methoxyphenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5h)



According to ***GP2*** with isocyanoaryl **4h** (133.2 mg, 1.000 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/DEE = 14/1) afforded the desired 3*H*-indol-3-imine **5h** (22.2 mg, 66.4 µmol, 25%) as an orange oil.

IR (neat): 2968*w*, 2943*w*, 2840*w*, 1617*m*, 1594*m*, 1580*m*, 1485*m*, 1466*w*, 1439*w*, 1367*m*, 1344*w*, 1287*m*, 1267*w*, 1254*w*, 1235*w*, 1182*m*, 1147*s*, 1120*w*, 1091*m*, 1081*w*, 1044*w*, 1023*w*, 946*w*, 899*w*, 869*w*, 777*w*, 732*w*, 686*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.40 – 7.32 (m, 1H, $C_{arom}H$), 7.17 (d, *J* = 2.4 Hz, 1H, $C_{arom}H$), 6.86 – 6.82 (m, 1H, $C_{arom}H$), 6.80 (d, *J* = 8.6 Hz, 1H, $C_{arom}H$), 6.62 – 6.56 (m, 3H, $C_{arom}H$), 3.85 (s, 3H, CH_3), 3.81 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 164.8 (C), 161.3 (C), 160.6 (q, *J* = 35.8 Hz, C), 159.3 (C), 158.0 (C), 151.3 (C), 130.9 (CH), 127.9 (CH), 120.4 (q, *J* = 274.0 Hz, CF_3), 114.3 (CH), 114.1 (q, *J* = 1.8 Hz, C), 112.4 (CH), 110.9 (CH), 110.7 (CH), 104.4 (CH), 56.6 (CH_3), 56.0 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -65.5. **HRMS** (ESI) *m/z* = 335.10019 calcd. for $C_{17}H_{14}F_3N_2O_2$ $[M+H]^+$, found: 335.10010.

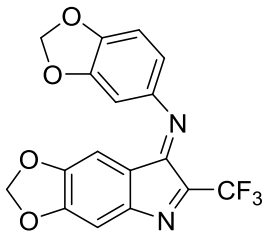
(*E*)-4-Methoxy-*N*-(3-methoxyphenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5h′)



According to ***GP2*** with isocyanoaryl **4h** (133.2 mg, 1.000 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/DEE = 14/1) afforded the desired 3*H*-indol-3-imine **5h′** (10.0 mg, 29.9 µmol, 11%) as an orange solid.

MP: 60-67 °C. **IR** (neat): 3007*w*, 2943*w*, 2840*w*, 1710*w*, 1654*w*, 1600*s*, 1496*m*, 1486*m*, 1379*w*, 1332*w*, 1283*m*, 1265*m*, 1181*m*, 1148*s*, 1108*m*, 1041*w*, 947*w*, 896*w*, 845*w*, 783*w*, 720*w*, 689*w*, 546*s*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.58 – 7.46 (m, 1H, $C_{arom}H$), 7.29 – 7.21 (m, 2H, $C_{arom}H$), 6.85 (d, *J* = 8.6 Hz, 1H, $C_{arom}H$), 6.79 (dd, *J* = 8.3 Hz, *J* = 2.6 Hz, 1H, $C_{arom}H$), 6.45 (t, *J* = 2.2 Hz, 1H, $C_{arom}H$), 6.43 – 6.39 (m, 1H, $C_{arom}H$), 3.80 (s, 3H, CH_3), 3.37 (s, 3H, CH_3). **^{13}C-NMR {^{19}F}** (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 159.9 (C), 159.7 (C), 157.7 (C), 156.5 (C), 156.2 (C), 153.1 (C), 135.7 (CH), 128.8 (CH), 120.5 (CF_3), 117.1 (CH), 114.3 (CH), 113.1 (CH), 111.9 (CH), 108.9 (C), 106.1 (CH), 56.3 (CH_3), 55.9 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -65.1. **HRMS** (ESI) *m/z* = 373.05607 calcd. for $C_{17}H_{13}F_3N_2O_2K$ $[M+K]^+$, found: 373.05604.

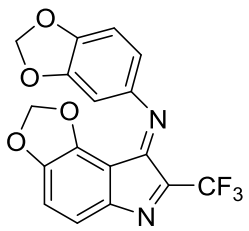
(*E*)-*N*-(Benzo[*d*][1,3]dioxol-5-yl)-6-(trifluoromethyl)-7*H*-[1,3]dioxolo[4,5-*f*]indol-7-imine (5i)



According to ***GP2*** with isocyanoaryl **4i** (147.6 mg, 1.003 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/EtOAc = 20/1 → P/EtOAc = 10/1) afforded the desired indol-3-imine **5i** (37.8 mg, 0.104 mmol, 40%) as a dark red solid.

MP: 146 °C. **IR** (neat): 2923*w*, 2855*w*, 2362*w*, 2337*w*, 1698*w*, 1616*w*, 1568*w*, 1503*m*, 1468*s*, 1377*w*, 1341*w*, 1294*s*, 1247*m*, 1182*s*, 1151*s*, 1091*m*, 1036*s*, 932*m*, 896*w*, 858*w*, 814*w*, 737*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.08 (s, 1H, $C_{arom}H$), 6.90 (d, *J* = 8.2 Hz, 1H, $C_{arom}H$ H), 6.66 (s, 1H, $C_{arom}H$), 6.65 (d, *J* = 2.1 Hz, 1H, $C_{arom}H$), 6.57 (dd, *J* = 8.2 Hz, *J* = 2.1 Hz, 1H, $C_{arom}H$), 6.06 (s, 2H, CH_2), 6.02 (s, 2H, CH_2). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 158.7 (C), 158.5 (q, *J* = 35.5 Hz, C), 152.6 (C), 152.2 (C), 149.4 (C), 148.9 (C), 147.5 (C), 143.7 (C), 120.3 (q, *J* = 273.6 Hz, CF_3), 114.6 (q, *J* = 1.8 Hz, C), 113.2 (CH), 109.2 (CH), 106.2 (CH), 105.8 (CH), 103.4 (CH_2), 102.6 (CH_2), 101.9 (CH). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -65.0. **HRMS** (ESI) *m/z* = 363.05872 calcd. for $C_{17}H_{10}F_3N_2O_4$ $[M+H]^+$, found: 363.05852.

(*E*)-*N*-(Benzo[*d*][1,3]dioxol-5-yl)-7-(trifluoromethyl)-6*H*-[1,3]dioxolo[4,5-*g*]indol-6-imine (5i′)

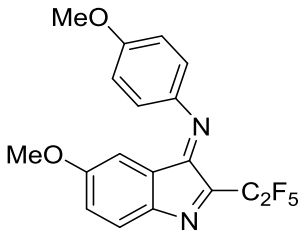


According to ***GP2*** with isocyanoaryl **4i** (147.6 mg, 1.003 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2a** (82.5 mg, 0.261 mmol, 1.0 equiv.). FC (P/DEE = 14/1) afforded the desired indol-3-imine **5i′** (4.9 mg, 13.5 µmol, 5%) as a dark red solid.

MP: 185 °C. **IR** (neat): 2915*w*, 1628*w*, 1563*w*, 1503*m*, 1481*s*, 1460*s*, 1443*m*, 1424*m*, 1351*m*, 1249*s*, 1222*w*, 1172*s*, 1142*s*, 1092*w*, 1038*m*, 1003*m*, 927*m*, 873*w*, 817*w*, 716*w*, 659*w*, 545*m*, 508*m*. **^{1}H-NMR** (600 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.17 (d, *J* = 7.8 Hz, 1H, $C_{arom}H$), 6.86 (d, *J* = 7.8 Hz, 1H, $C_{arom}H$), 6.84 (d, *J* = 8.2 Hz, 1H, $C_{arom}H$), 6.61 (d, *J* = 2.1 Hz, 1H, $C_{arom}H$), 6.47 (dd, *J* = 8.2, *J* = 2.1 Hz, 1H, $C_{arom}H$), 6.03 (s, 2H, CH_2), 5.90 (s, 2H, CH_2). **^{13}C-NMR {^{19}F}** (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 156.8 (C), 154.3 (C), 151.4 (C), 149.7 (C), 148.5 (C), 147.6 (C), 145.0 (C), 144.2 (C), 120.6 (CF_3), 118.7 (CH), 116.3 (CH), 109.9 (CH), 108.1 (CH), 104.2 (CH), 103.5 (C), 103.4 (CH_2), 102.4 (CH_2). **^{19}F-NMR** (282 MHz,

CD_2Cl_2, 300 K): δ (ppm) = -65.0. **HRMS** (ESI) *m/z* = 363.05872 calcd. for $C_{17}H_{10}F_3N_2O_4$ $[M+H]^+$, found: 363.05865.

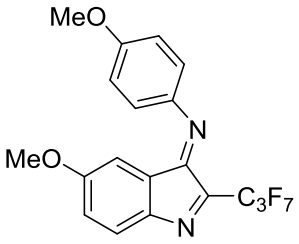
(*E*)-5-Methoxy-*N*-(4-methoxyphenyl)-2-(perfluoroethyl)-3*H*-indol-3-imine (5j)



According to ***GP2*** with isocyanoaryl **4a** (133.7 mg, 1.004 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2b** (95.4 mg, 0.261 mmol, 1.0 equiv.). FC (P/EtOAc = 14/1 → P/EtOAc = 5/1) afforded the desired 3*H*-indol-3-imine **4j** (53.6 mg, 0.139 mol, 53%) as a red solid.

MP: 129 °C. **IR** (neat): 3093*w*, 3018*w*, 2950*w*, 2843*w*, 1591*w*, 1561*w*, 1503*m*, 1467*m*, 1436*m*, 1392, 1295*s*, 1254*m*, 1217*s*, 1203*s*, 1188*s*, 1168*m*, 1156*m*, 1111*s*, 1089*m*, 1030*m*, 1019*m*, 910, 886, 849*m*, 828*w*, 769*w*, 739*m*, 613*w*, 533*w*. **^{1}H-NMR** (600 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.52 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 7.12 – 7.09 (m, 2H, $C_{arom}H$), 7.04 – 7.01 (m, 2H, $C_{arom}H$), 6.93 (dd, *J* = 8.5 Hz, *J* = 2.6 Hz, 1H, $C_{arom}H$), 6.76 (d, *J* = 2.5 Hz, 1H, $C_{arom}H$), 3.87 (s, 3H, CH_3), 3.67 (s, 3H, CH_3). **^{13}C-NMR** (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 161.7 (C), 159.8 (C), 159.5 (C), 156.9 (t, *J* = 26.3 Hz, C), 149.2 (C), 142.5 (C), 124.8 (CH), 122.6 (C), 121.8 (2 × CH), 119.2 (qt, *J* = 286.8 Hz, *J* = 35.3 Hz, CF_3), 116.8 (CH), 115.2 (2 × CH), 112.9 (CH), 111.4 (tq, *J* = 254.4 Hz, *J* = 38.9 Hz, CF_2), 56.3 (CH_3), 56.1 (CH_3). **^{19}F-NMR** (564 MHz, CD_2Cl_2, 300 K): δ (ppm) = -82.4 – -82.6 (m, 3F, CF_3), -113.5 – -113.7 (m, 2F CF_2). **HRMS** (ESI) *m/z* = 385.09700 calcd. for $C_{18}H_{14}F_5N_2O_2$ $[M+H]^+$, found: 385.09685.

(*E*)-5-Methoxy-*N*-(4-methoxyphenyl)-2-(perfluoropropyl)-3*H*-indol-3-imine (5k)

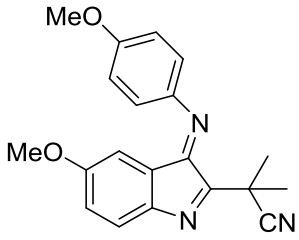


According to ***GP2*** with isocyanoaryl **4a** (133.1 mg, 0.9992 mmol, 3.8 equiv.), LiI (1.7 mg, 13 µmol, 4.9 mol%) and *Togni*-reagent **2c** (108.3 mg, 0.260 mmol, 1.0 equiv.). FC (P/EtOAc = 10/1 → P/EtOAc = 5/1) afforded the desired 3*H*-indol-3-imine **5k** (65.4 mg, 0.151 mol, 58%) as a red solid

MP: 71 °C. **IR** (neat): 3009*w*, 2948*w*, 2841*w*, 1593*w*, 1548*w*, 1502*m*, 1469*m*, 1437*w*, 1340*w*, 1289*m*, 1228*s*, 1210*s*, 1119*s*, 1083*w*, 1031*m*, 970*w*, 904*w*, 843*m*, 819*w*, 766*w*, 744*w*, 697*w*. **^{1}H-NMR** (600 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.54 (d, *J* = 8.5 Hz, 1H, $C_{arom}H$), 7.12 – 7.06 (m, 2H, $C_{arom}H$), 7.05 – 6.99 (m, 2H, $C_{arom}H$), 6.93 (dd, *J* = 8.5 Hz, *J* = 2.6 Hz, 1H, $C_{arom}H$), 6.75 (d, *J* = 2.7 Hz, 1H, $C_{arom}H$), 3.87 (s, 3H, CH_3), 3.67 (s, 3H, CH_3). **^{13}C-NMR {^{19}F}** (151 MHz,

CD_2Cl_2, 300 K): δ (ppm) = 161.7 (C), 159.8 (C), 159.6 (C), 157.2 (C), 149.3 (C), 142.6 (C), 124.8 (CH), 122.7 (C), 121.7 (2 × CH), 118.6 (CF_3), 116.8 (CH), 115.2 (2 × CH), 113.2 (CF_2), 112.9 (CH), 109.5 (CF_2), 56.3 (CH_3), 56.1 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -80.5 (t, *J* = 9.4 Hz, 3F, CF_3), -111.7 – -111.9 (m, 2F, CF_2), -125.5 – -125.7 (m, 2F, CF_2). **HRMS** (ESI) *m/z* = 435.09380 calcd. for $C_{19}H_{14}F_7N_2O_2$ $[M+H]^+$, found: 435.09366.

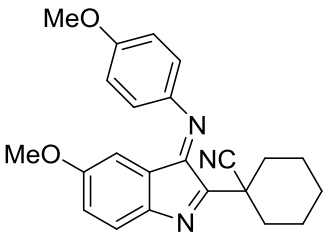
(*E*)-2-(5-Methoxy-3-((4-methoxyphenyl)imino)-3*H*-indol-2-yl)-2-methylpropanenitrile (7a)



To a solution of isocyanoaryl **4a** (133.2 mg, 1.000 mmol, 3.8 equiv.) in benzene (1.0 mL, 1.0 M) a solution of 2,2'-azobis(2-methyl-propionitrile) (42.7 mg, 0.260 mmol, 1.0 equiv.) in benzene (1.0 mL, 0.26 M) was added over one hour at 100 °C and stirring was continued for 21 h at this temperature. After concentration *in vacuo* FC (P/DEE = 5/1) afforded the desired 3*H*-indol-3-imine **7a** (52.5 mg, 0.157 mmol, 60%, corrected[11]: 81%) as a red solid.

MP: 129 °C. **IR** (neat): 2997*w*, 2941*w*, 2836*w*, 1636*w*, 1595*m*, 1560*w*, 1501*s*, 1470*s*, 1437*m*, 1387*w*, 1354*w*, 1295*m*, 1245*s*, 1230*m*, 1217*m*, 1182*w*, 1160*m*, 1107*w*, 1086*w*, 1030*m*, 968*w*, 883*w*, 839*m*, 770*w*, 762*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.34 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 7.09 – 6.98 (m, 4H, $C_{arom}H$), 6.85 (dd, *J* = 8.4 Hz, *J* = 2.6 Hz, 1H, $C_{arom}H$), 6.60 (d, *J* = 2.6 Hz, 1H, $C_{arom}H$), 3.86 (s, 3H, CH_3), 3.63 (s, 3H, CH_3), 1.89 (s, 6H, CH_3). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 169.2 (C), 160.9 (C), 159.9 (C), 159.2 (C), 150.4 (C), 142.4 (C), 123.4 (C), 123.3 (C), 122.7 (CH), 121.2 (2 × CH), 116.7 (CH), 115.1 (2 × CH), 113.0 (CH), 56.2 (CH_3), 56.1 (CH_3), 35.9 (C), 27.0 (2 × CH_3). **HRMS** (ESI) *m/z* = 334.15500 calcd. for $C_{20}H_{20}N_3O_2$ $[M+H]^+$, found: 334.15493.

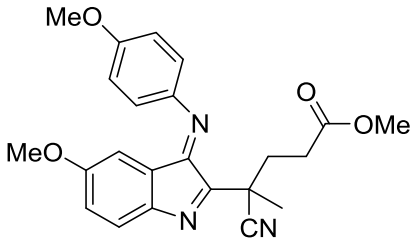
(*E*)-1-(5-Methoxy-3-((4-methoxyphenyl)imino)-3*H*-indol-2-yl)cyclohexane-1-carbonitrile (7b)



To a solution of isocyanoaryl **4a** (133.2 mg, 1.000 mmol, 3.8 equiv.) in benzene (1.0 mL, 1.0 M) a solution of 1,1'-azobis(cyclohexancarbonitril) (63.5 mg, 0.260 mmol, 1.0 equiv.) in benzene (1.0 mL, 0.26 M) was added over one hour at 100 °C and stirring was continued for 21 h at this temperature. After concentration *in vacuo* FC (P/DEE = 10/1) afforded the desired 3*H*-indol-3-imine **7b** (56.9 mg, 0.152 mmol, 59%, corrected[11]: 78%) as a red solid.

MP: 130 °C. **IR** (neat): 3001*w*, 2935*w*, 2860*w*, 2837*w*, 1634*w*, 1594*w*, 1558*w*, 1501*m*, 1468*m*, 1440*m*, 1350*w*, 1288*m*, 1245*s*, 1182*w*, 1164*w*, 1106*w*, 1030*m*, 966*w*, 840*m*, 762*w*, 735*w*, 577*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.34 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 7.09 – 6.97 (m, 4H, $C_{arom}H$), 6.85 (dd, *J* = 8.4 Hz, *J* = 2.6 Hz, 1H, $C_{arom}H$), 6.57 (d, *J* = 2.6 Hz, 1H, $C_{arom}H$), 3.86 (s, 3H, CH_3), 3.62 (s, 3H, CH_3), 2.41 (d, *J* = 13.6 Hz, 2H, CH_2), 2.20 – 2.07 (m, 2H, CH_2), 1.92 – 1.71 (m, 5H, CHH), 1.43 – 1.26 (m, 1H, CHH). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 169.2 (C), 161.2 (C), 159.8 (C), 159.1 (C), 150.6 (C), 142.5 (C), 123.3 (C), 122.6 (CH), 121.3 (C), 121.1 (2 × CH), 116.7 (CH), 115.1 (2 × CH), 113.0 (CH), 56.2 (CH_3), 56.1 (CH_3), 42.4 (C), 35.0 (2 × CH_2), 25.6 (CH_2), 23.4 (2 × CH_2). **HRMS** (ESI) *m/z* = 374.18630 calcd. for $C_{23}H_{24}N_3O_2$ $[M+H]^+$, found: 374.18625.

Methyl (*E*)-4-cyano-4-(5-methoxy-3-((4-methoxyphenyl)imino)-3*H*-indol-2-yl)pentanoate (7c)



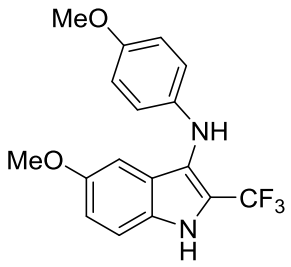
To a solution of isocyanoaryl **4a** (133.2 mg, 1.000 mmol, 3.8 equiv.) in benzene (1.0 mL, 1.0 M) a solution of **6c** (80.2 mg, 0.260 mmol, 1.0 equiv.) in benzene (1.0 mL, 0.26 M) was added over one hour at 100 °C and stirring was continued for 21 h at this temperature. After concentration *in vacuo* FC (P/DEE = 4/1 → P/DEE = 2/1) afforded the desired 3*H*-indol-3-imine **7c** (72.7 mg, 0.179 mmol, 69%, corrected[11]: 92%) as a red oil.

IR (neat): 2998*w*, 2949*w*, 2838*w*, 1736*m*, 1595*w*, 1559*w*, 1501*m*, 1468*m*, 1437*m*, 1374*w*, 1289*m*, 1245*s*, 1198*m*, 1180*m*, 1107*w*, 1029*m*, 958*w*, 842*m*, 765*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.36 (d, *J* = 8.4 Hz, 1H, $C_{arom}H$), 7.13 – 6.95 (m, 4H, $C_{arom}H$), 6.86 (dd, *J* = 8.4 Hz,

J = 2.6 Hz, 1H, $C_{arom}H$), 6.61 (d, *J* = 2.5 Hz, 1H, $C_{arom}H$), 3.86 (s, 3H, CH_3), 3.63 (s, 3H, CH_3), 3.60 (s, 3H, CH_3), 2.85 – 2.73 (m, 1H, CHH), 2.66 – 2.53 (m, 2H, CHH), 2.47 – 2.34 (m, 1H, CHH), 1.92 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 173.0 (C), 167.8 (C), 161.0 (C), 160.0 (C), 159.3 (C), 150.2 (C), 142.3 (C), 123.3 (C), 122.8 (CH), 121.8 (CH), 121.3 (2 × CH), 116.8 (CH), 115.2 (2 × CH), 113.0 (CH), 56.2 (CH_3), 56.1 (CH_3), 52.2 (CH_3), 41.0 (C), 34.4 (CH_2), 30.8 (CH_2), 25.4 (CH_3). **HRMS** (ESI) *m/z* = 406.17613 calcd. for $C_{23}H_{24}N_3O_4$ $[M+H]^+$, found: 406.17612.

6. Synthesis of indoles 8, indolin-2-ols 9 and indoline-3-ones 10 and 11

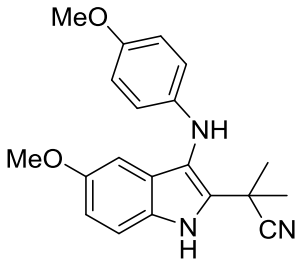
5-Methoxy-*N*-(4-methoxyphenyl)-2-(trifluoromethyl)-1*H*-indol-3-amine (8a)



3*H*-Indol-3-imine **5a** (33.4 mg, 0.100 mmol, 1.0 equiv.) was stirred with palladium activated on charcoal (10%, 8.0 mg) in EtOAc (1.0 mL, 0.10 M) in a hydrogen atmosphere (atmospheric pressure) for 24 h at room temperature. The reaction mixture was filtered through a short pad of silica with a mixture of water and CH_2Cl_2. After extraction with CH_2Cl_2 (three times) the combined organic phases were dried over $MgSO_4$ and filtered. Removal of all volatile compounds *in vacuo* afforded the desired 1*H*-indol-3-amine **8a** (27.0 mg, 80.3 µmol, 80%) as a red solid.

MP: 37 °C. **IR** (neat): 3347*w*, 2951*w*, 2838*w*, 1716*w*, 1652*w*, 1594*w*, 1491*s*, 1388*w*, 1285*m*, 1242*s*, 1162*s*, 1107*m*, 1032*m*, 950*w*, 834*w*, 767*w*, 730*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 8.28 (s, 1H, NH), 7.32 (d, *J* = 8.9 Hz, 1H, $C_{arom}H$), 6.98 (dd, *J* = 8.9 Hz, *J* = 2.5 Hz, 1H, $C_{arom}H$), 6.82 – 6.66 (m, 5H, $C_{arom}H$), 5.34 (s, 1H, NH), 3.74 (s, 3H, CH_3), 3.70 (s, 3H, CH_3). **^{13}C-NMR** (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 155.2 (C), 154.0 (C), 140.6 (C), 130.5 (C), 125.0 (C) 122.5 (q, *J* = 268.0 Hz, CF_3), 121.8 (q, *J* = 2.6 Hz, C), 118.5 (q, *J* = 36.3 Hz, C), 116.9 (CH), 116.7 (2 × CH), 115.2 (2 × CH), 113.7 (CH), 101.8 (CH), 56.2 (2 × CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -59.4. **HRMS** (ESI) *m/z* = 359.0978 calcd. for $C_{17}H_{15}F_3N_2O_2Na$ $[M+Na]^+$, found: 359.0972.

2-(5-Methoxy-3-((4-methoxyphenyl)amino)-1H-indol-2-yl)-2-methylpropanenitrile (8b)

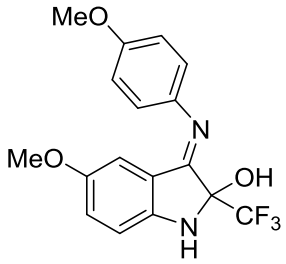


3*H*-Indol-3-imine **7a** (33.4 mg, 0.100 mmol, 1.0 equiv.) was stirred with palladium activated on charcoal (10%, 8.0 mg) in EtOAc (1.0 mL, 0.10 M) in a hydrogen atmosphere (atmospheric pressure) for 24 h at room temperature. The reaction mixture was filtered through a short pad of silica with a mixture of water and CH_2Cl_2. After extraction with CH_2Cl_2 (three times) the combined organic phases were dried over $MgSO_4$ and filtered. Removal of all volatile compounds *in vacuo* afforded the desired 1*H*-indol-3-amine **8b** (27.8 mg, 82.9 µmol, 83%) as a red solid.

^{1}H-NMR (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 8.14 (s, 1H, NH), 7.28 (d, *J* = 8.8 Hz, 1H, $C_{arom}H$), 6.84 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H, $C_{arom}H$), 6.77 – 6.71 (m, 2H, $C_{arom}H$), 6.70 (d,

J = 2.4 Hz, 1H, $C_{arom}H$), 6.62 – 6.50 (m, 2H, $C_{arom}H$), 4.96 (s, 1H, NH), 3.72 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 1.81 (s, 6H, CH_3). **^{13}C-NMR** (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 155.1 (C), 153.1 (C), 142.2 (C), 133.4 (C), 129.4 (C), 127.9 (C), 123.6 (C), 116.1 (C), 115.3 (2 × CH), 115.0 (2 × CH), 113.5 (CH), 112.8 (CH), 100.8 (CH), 56.2 (CH_3), 56.2 (CH_3), 33.0 (C), 27.4 (2 × CH_3). **HRMS** (ESI) *m/z* = 358.1526 calcd. for $C_{20}H_{21}N_3O_2Na$ $[M+Na]^+$, found: 358.1518.

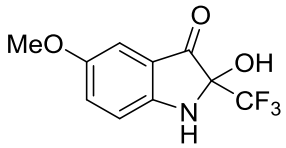
(*E*)-5-Methoxy-3-((4-methoxyphenyl)imino)-2-(trifluoromethyl)indolin-2-ol (9a)



A solution of 3*H*-indol-3-imine **5a** (33.4 mg, 0.100 mmol, 1.0 equiv.) and 4-toluenesulfonic acid monohydrate (19.2 mg, 0.101 mmol, 1.0 equiv.) in DEE (1.5 mL, 67 µM) was stirred one hour at 65 °C. After cooling down to room temperature the reaction mixture was diluted with water and DEE. After extraction with DEE (three times) the combined organic phases were dried over $MgSO_4$ and filtered. Removal of the all volatile compounds *in vacuo* afforded the desired indolin-2-ol **9a** (35.3 mg, 0.100 mmol, 99%) as a yellow solid.

MP: 50°C (decomposition). **IR** (neat): 3343*w*, 3004*w*, 2949*w*, 2837*w*, 1651*m*, 1490*s*, 1441*m*, 1284*m*, 1240*s*, 1179*s*, 1161*s*, 1104*m*, 1032*m*, 950*w*, 874*w*, 837*m*, 767*w*, 729*w*, 561*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.02 – 6.84 (m, 5H, $C_{arom}H$), 6.78 (d, *J* = 8.7 Hz, 1H, $C_{arom}H$), 6.20 (d, *J* = 2.6 Hz, 1H, $C_{arom}H$), 4.98 (s, 1H, NH), 3.82 (s, 3H, CH_3), 3.45 (s, 3H, CH_3). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 165.7 (C), 157.7 (C), 153.7 (C), 149.9 (C), 142.7 (C), 123.6 (q, *J* = 287.1 Hz, CF_3), 123.2 (CH), 120.4 (2 × CH), 117.7 (q, *J* = 1.2 Hz, C), 115.0 (2 × CH), 113.2 (CH), 110.2 (CH), 87.9 (q, *J* = 31.3 Hz, C), 55.9 (CH_3), 55.8 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -83.4. **HRMS** (ESI) *m/z* = 353.1108 calcd. for $C_{17}H_{16}F_3N_2O_3$ $[M+H]^+$, found: 353.1101.

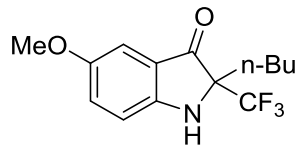
2-Hydroxy-5-methoxy-2-(trifluoromethyl)indolin-3-one (10a)



Aq. HCl (10%, 1.0 mL) was added to a solution of 3*H*-indol-3-imine **5a** (33.4 mg, 0.100 mmol, 1.0 equiv.) in DEE (1.0 mL, 0.10 M) and the reaction mixture was stirred for one hour at 65 °C. After diluting with a DEE/water mixture and extraction with DEE (three times) the combined organic phases were dried over $MgSO_4$ and filtered. Removal of the all volatile compounds *in vacuo* afforded the desired indolin-3-one **10a** (24.4 mg, 98.7 µmol, 99%) as a yellow solid.

MP: 113 °C. **IR** (neat): 3347*m*, 2950*w*, 2841*w*, 1704*s*, 1628*w*, 1594, 1496*s*, 1457*w*, 1442*w*, 1267*m*, 1228*m*, 1179*s*, 1160*s*, 1096*w*, 1025*m*, 950*w*, 826*w*, 788*w*, 771*w*, 740*m*, 716*w*, 691*w*, 672*w*, 529*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.22 (dd, *J* = 8.8 Hz, *J* = 2.7 Hz, 1H, $C_{arom}H$), 7.03 (d, *J* = 2.7 Hz, 1H, $C_{arom}H$), 6.91 (d, *J* = 8.8 Hz, 1H, $C_{arom}H$), 5.10 (s, 1H, NH), 4.14 (s, 1H, OH), 3.78 (s, 3H, CH_3). **^{13}C-NMR** (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 194.5 (C), 155.9 (C), 155.4 (C), 129.6 (CH), 122.9 (q, *J* = 286.0 Hz, CF_3), 119.3 (q, *J* = 1.6 Hz, C), 114.8 (CH), 106.4 (CH), 85.3 (d, *J* = 32.4 Hz, C), 56.4 (CH_3). **^{19}F-NMR** (564 MHz, CD_2Cl_2, 300 K): δ (ppm) = -82.1 (CF_3). **HRMS** (ESI) *m/z* = 246.03835 calcd. for $C_{10}H_7F_3NO_3$ $[M-H]^-$, found: 246.3829.

2-Butyl-5-methoxy-2-(trifluoromethyl)indolin-3-one (11a)

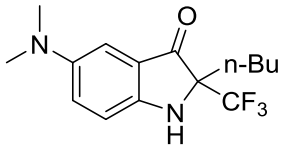


A solution of n-BuLi (1.6 M in hexane, 64 µL, 0.10 mmol, 1.0 equiv.) was added dropwise at -78 °C to a solution of 3*H*-indol-3-imine **5a** (33.4 mg, 0.100 mmol, 1.0 equiv.) in THF (1.5 mL, 67 mM). After stirring for one hour at this temperature stirring was continued for one hour at room temperature. HCl (aq, 10 %, 1.0 mL) was added and the reaction mixture was stirred at 90 °C for 19 h. After cooling to room temperature a saturated aq. solution of $NaHCO_3$ was added. After extracting with CH_2Cl_2 (three times) the combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. FC (P/CH_2Cl_2 = 5/1 → P/CH_2Cl_2 = 1/1) afforded the desired indolin-3-one **11a** (17.2 mg, 59.9 µmol, 60%) as a yellow solid.

MP: 82 °C. **IR** (neat): 3351*w*, 2960*w*, 2933*w*, 2872*w*, 2840*w*, 1692*s*, 1630*w*, 1593*w*, 1498*s*, 1458*w*, 1441*w*, 1350*w*, 1279*m*, 1255*m*, 1220*m*, 1177*s*, 1161*s*, 1030*w*, 950*w*, 825*w*, 787*w*, 725*w*, 670*w*, 545*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.20 (dd, *J* = 8.9 Hz, *J* = 2.7 Hz, 1H, $C_{arom}H$), 7.02 (d, *J* = 2.7 Hz, 1H, $C_{arom}H$), 6.94 (d, *J* = 8.9 Hz, 1H, $C_{arom}H$), 4.60 (s, 1H, NH), 3.78 (s, 3H, CH_3), 2.17 – 2.04 (m, 1H, CHH), 1.91 (ddd, *J* = 13.6 Hz, *J* = 12.1 Hz, *J* = 4.1 Hz,

1H, CHH), 1.37 – 1.14 (m, 3H, CH_2, CHH), 1.14 – 0.97 (m, 1H, CHH), 0.84 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C-NMR** (75 MHz, CD_2Cl_2, 300 K): δ (ppm) = 196.1 (C), 157.2 (C), 154.9 (C), 128.9 (CH), 125.0 (q, *J* = 283.8 Hz, CF_3), 121.9 (q, *J* = 1.6 Hz, C), 114.7 (CH), 105.3 (CH), 71.3 (q, *J* = 26.7 Hz, C), 56.4 (CH_3), 31.6 (q, *J* = 1.4 Hz, CH_2), 24.9 (CH_2), 23.3 (CH_2), 14.1 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -76.6. **HRMS** (ESI) *m/z* = 288.12059 calcd. for $C_{14}H_{17}F_3NO_2$ $[M+H]^+$, found: 288.12052.

2-Butyl-5-(dimethylamino)-2-(trifluoromethyl)indolin-3-one (11d)

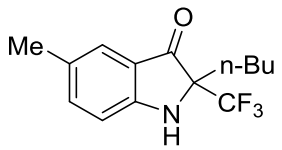


A solution of n-BuLi (1.6 M in hexane, 36 µL, 58 mmol, 1.0 equiv.) was added dropwise at -78 °C to a solution of 3*H*-indol-3-imine **5d** (20.7 mg, 57.4 µmol, 1.0 equiv.) in THF (2.0 mL, 29 mM). After stirring for one hour at this temperature stirring was continued for one hour at room temperature. HCl (aq, 10 %, 1.0 mL) was added and the reaction mixture was stirred at 90 °C for 19 h. After cooling to room temperature a saturated aq. solution of $NaHCO_3$ was added. After extracting with CH_2Cl_2 (three times) the combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. FC (P/EtOAc = 5/1) afforded the desired indolin-3-one **11d** (5.9 mg, 20 µmol, 34%) as an orange oil.

IR (neat): 3343*w*, 2959*w*, 2931*w*, 2870*w*, 2805*w*, 1688*s*, 1585*w*, 1505*s*, 1443*w*, 1353*w*, 1289*m*, 1254*m*, 1176*s*, 1147*m*, 1038*w*, 930*w*, 910*w*, 817*w*, 719*w*, 669*w*, 575*w*, 535*w*. **^{1}H-NMR** (300 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.18 (dd, *J* = 8.9, *J* = 2.7 Hz, 1H, $C_{arom}H$), 6.94 (dd, *J* = 8.9 Hz, *J* = 0.6 Hz, 1H, $C_{arom}H$), 6.85 (d, *J* = 2.7 Hz, 1H, $C_{arom}H$), 4.44 (s, 1H, NH), 2.89 (s, 6H, CH_3), 2.17 – 2.03 (m, 1H, CHH), 1.90 (ddd, *J* = 13.5 Hz, *J* = 12.1 Hz, *J* = 4.0 Hz, 1H, CHH), 1.34 – 1.15 (m, 3H, CH_2, CHH), 1.13 – 0.97 (m, 1H, CHH), 0.84 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C-NMR (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 196.6 (C), 154.8 (C), 146.8 (C), 126.8 (CH), 125.1 (q, *J* = 283.5 Hz, CF_3), 122.5 – 122.4 (m, C), 114.3 (CH), 106.2 (CH), 70.9 (q, *J* = 26.6 Hz, C), 41.9 (2 × CH_3), 31.6 (CH_2), 24.9 (CH_2), 23.3 (CH_2), 14.1 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -76.6. **HRMS** (ESI) *m/z* = 301.15222 calcd. for $C_{15}H_{20}F_3N_2O$ $[M+H]^+$, found: 301.15235.

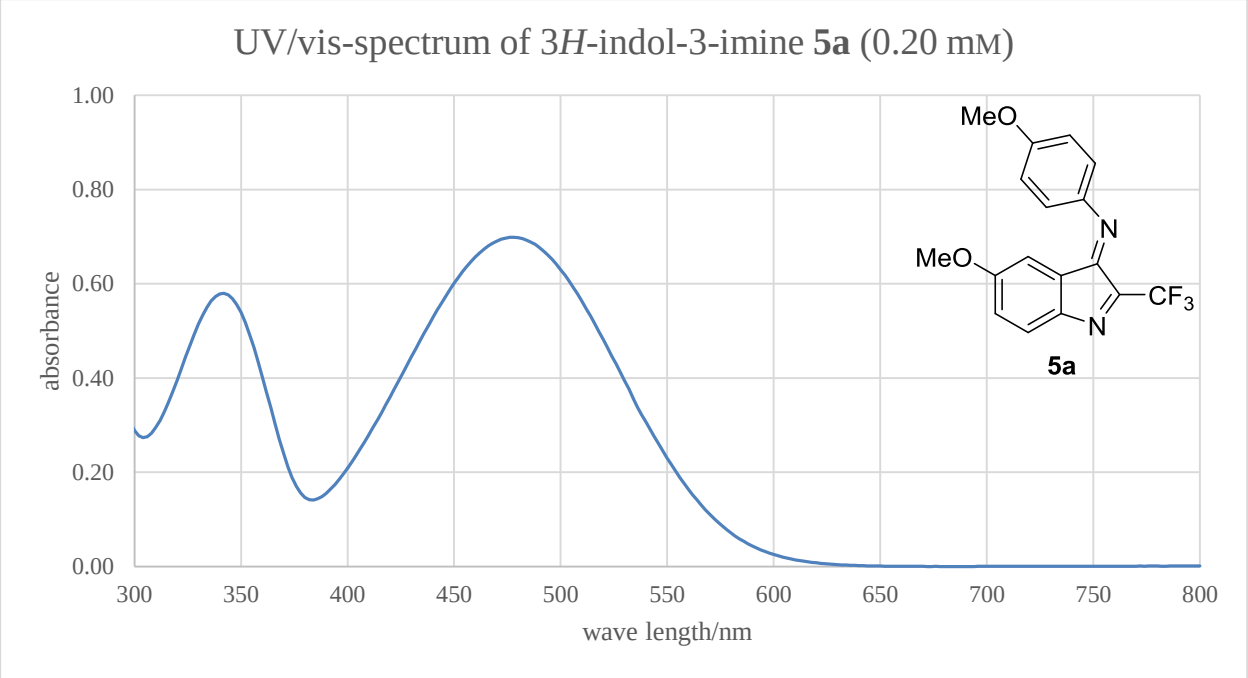
2-Butyl-5-methyl-2-(trifluoromethyl)indolin-3-one (11e)



A solution of n-BuLi (1.6 M in hexane, 48 µL, 77 mmol, 1.0 equiv.) was added dropwise at -78 °C to a solution of 3*H*-indol-3-imine **5e** (22.8 mg, 75.4 mmol, 1.0 equiv.) in THF (2.0 mL, 38 mM). After stirring for one hour at this temperature stirring was continued for one hour at room temperature. HCl (aq, 10 %, 1.0 mL) was added and the reaction mixture was stirred at 90 °C for 19 h. After cooling to room temperature a saturated aq. solution of $NaHCO_3$ was added. After extracting with CH_2Cl_2 (three times) the combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. FC (P/DEE = 30/1) afforded the desired indolin-3-one **11e** (9.2 mg, 34 µmol, 45%) as a yellow solid.

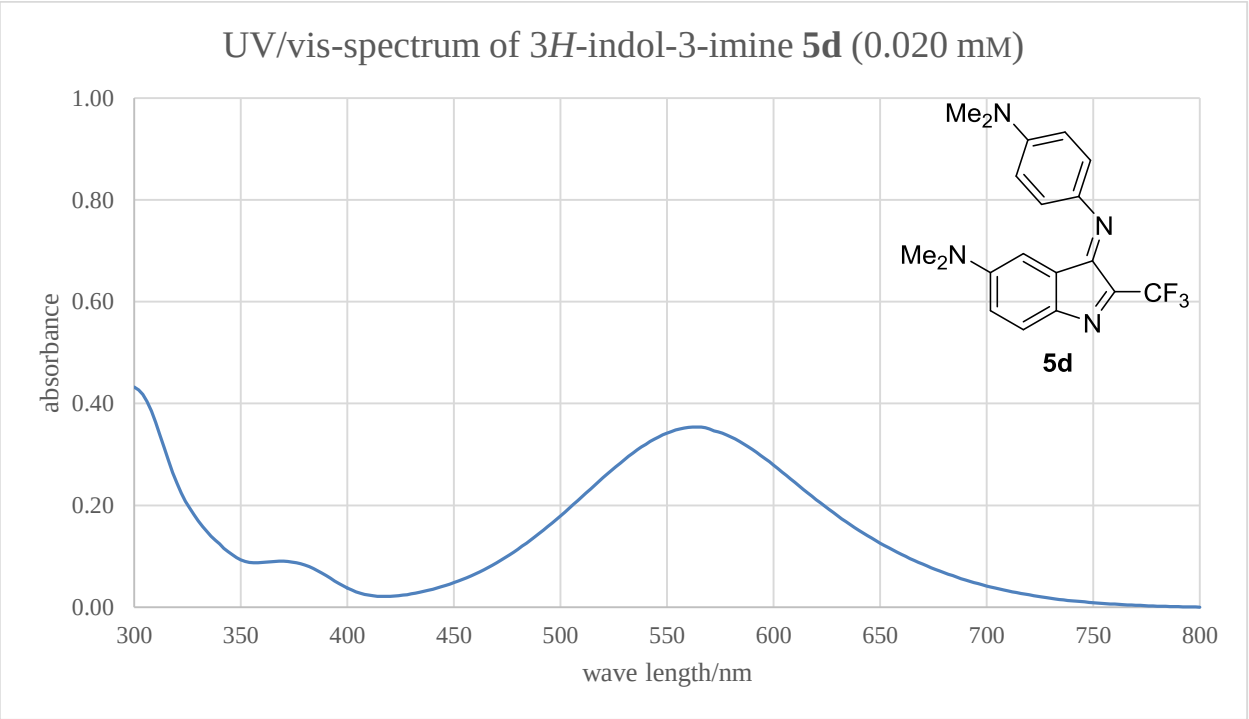
MP: 47 °C. **IR** (neat): 3352*w*, 2960*w*, 2931*w*, 2868*w*, 1694*s*, 1629*m*, 1590*w*, 1501*m*, 1436*w*, 1288*m*, 1255*m*, 1177*s*, 1158*s*, 1121*m*, 1037*w*, 945*w*, 817*w*, 776*w*, 726*w*, 669*w*, 527*w*. **^{1}H-NMR** (600 MHz, CD_2Cl_2, 300 K): δ (ppm) = 7.39 – 7.36 (m, 2H, $C_{arom}H$), 6.91 – 6.88 (m, 1H, $C_{arom}H$), 4.74 (s, 1H, NH), 2.30 (s, 3H, CH_3), 2.13 – 2.07 (m, 1H, CHH), 1.91 (ddd, *J* = 13.7 Hz, *J* = 12.4 Hz, *J* = 4.2 Hz, 1H, CHH), 1.34 – 1.18 (m, 3H, CHH), 1.09 – 1.01 (m, 1H, CHH), 0.84 (t, *J* = 7.3 Hz, 3H, CH_3). **^{13}C-NMR** (151 MHz, CD_2Cl_2, 300 K): δ (ppm) = 195.8 (C), 159.9 (C), 140.0 (CH), 130.5 (C), 124.9 (q, *J* = 283.6 Hz, CF_3), 124.5 (CH), 121.5 (q, *J* = 1.4 Hz, C), 113.0 (CH), 70.7 (q, *J* = 26.7 Hz, C), 31.5 (CH_2), 24.9 (CH_2), 23.3 (CH_2), 20.7 (CH_3), 14.1 (CH_3). **^{19}F-NMR** (282 MHz, CD_2Cl_2, 300 K): δ (ppm) = -76.7. **HRMS** (ESI) *m/z* = 272.12568 calcd. for $C_{14}H_{17}F_3NO$ $[M+H]^+$, found: 272.12552.

7. UV/vis-spectra of 3*H*-indol-3-imine 5a and 5d



wave length /nm	absorbance						
800	0.0012	758	0.0007	716	0.0004	674	0.0002
798	0.0012	756	0.0006	714	0.0003	672	0.0002
796	0.0012	754	0.0006	712	0.0004	670	0.0003
794	0.0012	752	0.0007	710	0.0003	668	0.0004
792	0.0012	750	0.0007	708	0.0003	666	0.0004
790	0.0013	748	0.0007	706	0.0003	664	0.0003
788	0.0011	746	0.0007	704	0.0003	662	0.0004
786	0.0010	744	0.0006	702	0.0004	660	0.0004
784	0.0009	742	0.0006	700	0.0003	658	0.0004
782	0.0009	740	0.0006	698	0.0003	656	0.0005
780	0.0009	738	0.0006	696	0.0003	654	0.0007
778	0.0009	736	0.0007	694	0.0001	652	0.0008
776	0.0010	734	0.0005	692	0.0001	650	0.0010
774	0.0009	732	0.0005	690	0.0001	648	0.0011
772	0.0009	730	0.0004	688	0.0000	646	0.0013
770	0.0009	728	0.0005	686	0.0001	644	0.0016
768	0.0008	726	0.0004	684	0.0000	642	0.0018
766	0.0009	724	0.0004	682	0.0001	640	0.0020
764	0.0009	722	0.0004	680	0.0001	638	0.0023
762	0.0008	720	0.0004	678	0.0002	636	0.0028
760	0.0008	718	0.0004	676	0.0003	634	0.0032

632	0.0036	548	0.2448	464	0.6734	380	0.1468
630	0.0041	546	0.2600	462	0.6657	378	0.1560
628	0.0048	544	0.2754	460	0.6571	376	0.1699
626	0.0054	542	0.2910	458	0.6476	374	0.1887
624	0.0062	540	0.3067	456	0.6373	372	0.2120
622	0.0070	538	0.3225	454	0.6259	370	0.2399
620	0.0079	536	0.3389	452	0.6138	368	0.2706
618	0.0089	534	0.3570	450	0.6008	366	0.3031
616	0.0101	532	0.3767	448	0.5872	364	0.3365
614	0.0114	530	0.3944	446	0.5733	362	0.3699
612	0.0129	528	0.4120	444	0.5589	360	0.4027
610	0.0145	526	0.4296	442	0.5439	358	0.4349
608	0.0163	524	0.4471	440	0.5282	356	0.4649
606	0.0184	522	0.4644	438	0.5122	354	0.4932
604	0.0206	520	0.4816	436	0.4960	352	0.5180
602	0.0230	518	0.4986	434	0.4796	350	0.5390
600	0.0257	516	0.5153	432	0.4627	348	0.5563
598	0.0288	514	0.5316	430	0.4457	346	0.5686
596	0.0320	512	0.5476	428	0.4285	344	0.5767
594	0.0355	510	0.5628	426	0.4113	342	0.5801
592	0.0393	508	0.5777	424	0.3942	340	0.5786
590	0.0436	506	0.5920	422	0.3772	338	0.5735
588	0.0482	504	0.6055	420	0.3603	336	0.5638
586	0.0532	502	0.6183	418	0.3435	334	0.5503
584	0.0586	500	0.6305	416	0.3269	332	0.5335
582	0.0645	498	0.6417	414	0.3108	330	0.5142
580	0.0710	496	0.6519	412	0.2951	328	0.4921
578	0.0780	494	0.6613	410	0.2798	326	0.4691
576	0.0855	492	0.6698	408	0.2648	324	0.4447
574	0.0934	490	0.6773	406	0.2501	322	0.4198
572	0.1019	488	0.6836	404	0.2357	320	0.3953
570	0.1110	486	0.6888	402	0.2220	318	0.3711
568	0.1204	484	0.6929	400	0.2088	316	0.3487
566	0.1304	482	0.6961	398	0.1962	314	0.3285
564	0.1410	480	0.6981	396	0.1847	312	0.3106
562	0.1522	478	0.6989	394	0.1739	310	0.2952
560	0.1637	476	0.6985	392	0.1643	308	0.2833
558	0.1759	474	0.6971	390	0.1557	306	0.2757
556	0.1887	472	0.6946	388	0.1488	304	0.2734
554	0.2020	470	0.6909	386	0.1439	302	0.2776
552	0.2158	468	0.6861	384	0.1415	300	0.2885
550	0.2301	466	0.6802	382	0.1421		



wave length /nm	absorbance						
800	0.0000	754	0.0074	708	0.0337	662	0.0996
798	0.0002	752	0.0080	706	0.0355	660	0.1036
796	0.0004	750	0.0085	704	0.0374	658	0.1077
794	0.0005	748	0.0093	702	0.0394	656	0.1120
792	0.0005	746	0.0101	700	0.0415	654	0.1165
790	0.0007	744	0.0109	698	0.0437	652	0.1210
788	0.0009	742	0.0117	696	0.0460	650	0.1256
786	0.0012	740	0.0123	694	0.0483	648	0.1304
784	0.0014	738	0.0132	692	0.0508	646	0.1354
782	0.0016	736	0.0142	690	0.0533	644	0.1404
780	0.0019	734	0.0151	688	0.0560	642	0.1456
778	0.0022	732	0.0163	686	0.0588	640	0.1509
776	0.0026	730	0.0174	684	0.0617	638	0.1563
774	0.0029	728	0.0186	682	0.0646	636	0.1618
772	0.0032	726	0.0198	680	0.0676	634	0.1675
770	0.0036	724	0.0212	678	0.0708	632	0.1734
768	0.0039	722	0.0224	676	0.0740	630	0.1795
766	0.0044	720	0.0240	674	0.0773	628	0.1856
764	0.0049	718	0.0255	672	0.0809	626	0.1919
762	0.0051	716	0.0270	670	0.0843	624	0.1983
760	0.0057	714	0.0286	668	0.0880	622	0.2047
758	0.0061	712	0.0302	666	0.0918	620	0.2112
756	0.0067	710	0.0319	664	0.0956	618	0.2178

616	0.2245	536	0.3090	456	0.0579	376	0.0871
614	0.2314	534	0.3030	454	0.0544	374	0.0887
612	0.2383	532	0.2966	452	0.0511	372	0.0896
610	0.2450	530	0.2899	450	0.0481	370	0.0904
608	0.2518	528	0.2830	448	0.0452	368	0.0904
606	0.2587	526	0.2760	446	0.0425	366	0.0899
604	0.2654	524	0.2690	444	0.0400	364	0.0892
602	0.2720	522	0.2617	442	0.0375	362	0.0881
600	0.2790	520	0.2542	440	0.0351	360	0.0875
598	0.2855	518	0.2468	438	0.0331	358	0.0869
596	0.2918	516	0.2392	436	0.0311	356	0.0871
594	0.2979	514	0.2317	434	0.0293	354	0.0880
592	0.3039	512	0.2242	432	0.0276	352	0.0898
590	0.3098	510	0.2166	430	0.0259	350	0.0930
588	0.3154	508	0.2090	428	0.0245	348	0.0972
586	0.3207	506	0.2014	426	0.0233	346	0.1026
584	0.3256	504	0.1940	424	0.0225	344	0.1089
582	0.3302	502	0.1865	422	0.0219	342	0.1152
580	0.3345	500	0.1792	420	0.0213	340	0.1241
578	0.3383	498	0.1722	418	0.0210	338	0.1312
576	0.3416	496	0.1652	416	0.0210	336	0.1396
574	0.3443	494	0.1583	414	0.0214	334	0.1486
572	0.3463	492	0.1514	412	0.0221	332	0.1585
570	0.3500	490	0.1448	410	0.0233	330	0.1693
568	0.3527	488	0.1383	408	0.0249	328	0.1812
566	0.3536	486	0.1319	406	0.0271	326	0.1939
564	0.3539	484	0.1258	404	0.0300	324	0.2079
562	0.3537	482	0.1196	402	0.0335	322	0.2243
560	0.3530	480	0.1138	400	0.0374	320	0.2433
558	0.3518	478	0.1081	398	0.0416	318	0.2646
556	0.3501	476	0.1025	396	0.0465	316	0.2880
554	0.3478	474	0.0971	394	0.0516	314	0.3130
552	0.3451	472	0.0919	392	0.0568	312	0.3385
550	0.3420	470	0.0870	390	0.0621	310	0.3633
548	0.3384	468	0.0823	388	0.0669	308	0.3854
546	0.3344	466	0.0776	386	0.0713	306	0.4039
544	0.3301	464	0.0733	384	0.0755	304	0.4178
542	0.3252	462	0.0691	382	0.0793	302	0.4270
540	0.3201	460	0.0652	380	0.0825	300	0.4321
538	0.3147	458	0.0614	378	0.0852		

8. Absorption spectra simulation

In the following, we provide computational details and additional results for the calculation of the absorption spectra for compounds **5a** and **5d** with the goal of reproducing and rationalizing their difference in color.

8.1 Computational details

Both structures have been optimized with the ORCA program[12] using the meta-GGA exchange-correlation functional TPSS[13], the valence triple-ζ basis with polarization functions dubbed TZVP[14] for all atoms and the D3 dispersion correction by *Grimme*[15] with *Becke–Johnson* damping. The structures obtained in this way have been consistently used for further excitation energy calculations as described below. In order to perform calculations of excitation energies and oscillator strengths, we have applied three different theoretical methods: time-dependent density functional theory (TDDFT)[16] as implemented in ADF[17], the second-order algebraic-diagrammatic construction scheme [ADC(2)][18] and the approximate linear-response (LR) coupled cluster model CC2[19] as implemented in the TURBOMOLE quantum chemical program[20]. Calculations of the first type have been carried out using the long range-corrected or Coulomb-attenuation method versions of the BLYP (LC-BLYP) and B3LYP (CAMY-B3LYP) exchange-correlation functionals with a *Yukawa*-type range-separation[21] in combination with the triple-ζ basis sets including one set of polarization functions (TZP) from the ADF basis set library. The full exchange-correlation kernel has been evaluated[22]. The CC2 and ADC(2) results have been obtained with the `ricc2` module using the valence triple-ζ polarized def2-TZVP[23] basis set and the resolution-of-the-identity (RI) approximation. To check the convergence of our results we performed calculations for the lowest 20 excitations in case of TDDFT and the lowest 5 in case of CC2 and ADC(2). However, for the simulation of absorption spectra, it is sufficient to consider only the two lowest-energy singlet–singlet transitions from these calculations.

For the actual spectra plots, we have converted the calculated oscillator strengths to extinction coefficients $\varepsilon_k(\nu)$ [for absorption band k] assuming a Gaussian band shape of the absorption bands when represented as a function of the frequency (ν). The full width at half maximum (denoted as δ in the following) has been estimated separately from the corresponding experimental spectra of the **5a** and **5d** compounds (δ=0.606 and 0.526 eV, respectively). Finally, the extinction coefficients have been converted to the corresponding coefficients as a function of

the wavelengths, $\varepsilon_k(\lambda)$, which is the quantity plotted in the spectra in the following. The reported λ_{max}-values correspond to the peak maxima from the superimposed bands in the spectra. Calculated vertical excitation energies are listed separately.

8.2 Results

8.2.1 Structures

In order to assess the quality of the optimized structures, we compare the results of the DFT geometry optimization with the available crystal structure data for compound **5a**. In Tab. S2, we present a comparison of some important structural parameters for this compound (see Fig. S1 for atom labels).

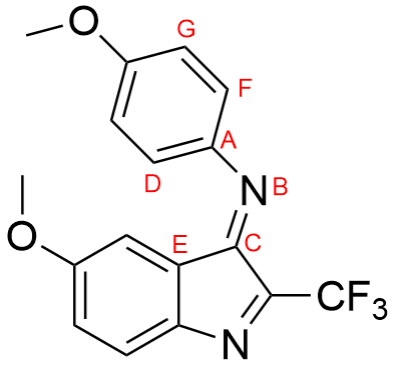


Fig. S1 Lewis structure and atom labelling scheme of compound **5a**.

As one can see from Tab. S2, KS-DFT calculations reproduce the experimental structure for compound **5a** very well. The errors are about 0.01 Å in case of bond distances, and 0.5° and 3° for bond and dihedral angles, respectively.

Table S2 Calculated and experimental geometrical parameters of compound **5a**. Bond distances *R* are presented in units of Å, bond (∟) and dihedral (ω) angles in degrees.

Parameter	Our results	Exp.
R_{AB}	1.3938	1.4073(18)
R_{BC}	1.2917	1.2856(17)
∟*ABC*	122.9	123.53(12)
ω (*ABCE*)	−13.0	−10.1(2)
ω (*BAFG*)	178.9	178.1(9)
ω (*CBAD*)	−43.7	−46.2(14)

8.2.2 Vertical excitations

Results of the excitation energy and oscillator strength calculations are listed in Tab. S3. Our calculations show that the absorption spectra of the compounds **5a** and **5d** in the visible range could be described considering only the two lowest singlet–singlet excitations, which predominantly have HOMO→LUMO and (HOMO−1)→LUMO character. The third lowest excitations for both compounds are out of the visible range and do not produce any notable contributions to the bands studied here. The orbitals involved in the transitions are presented in Figs. S2 and S3.

Table S3 Vertical excitation energies and oscillator strengths (in parentheses) of the two lowest singlet–singlet transitions of compounds **5a** and **5d** in the visible range. Energies are given in units of eV.

Method	Main character	**5a**	**5d**
LC-BLYP	HOMO→LUMO	2.15 (0.170)	1.65 (0.038)
	(HOMO−1)→LUMO	1.99 (0.017)	2.09 (0.279)
CAMY-B3LYP	HOMO→LUMO	2.39 (0.080)	2.03 (0.060)
	(HOMO−1)→LUMO	2.46 (0.146)	2.33 (0.322)
CC2	HOMO→LUMO	2.59 (0.183)	2.37 (0.345)
	(HOMO−1)→LUMO	2.75 (0.049)	2.20 (0.115)
ADC(2)	HOMO→LUMO	2.55 (0.150)	2.16 (0.097)
	(HOMO−1)→LUMO	2.74 (0.044)	2.30 (0.228)

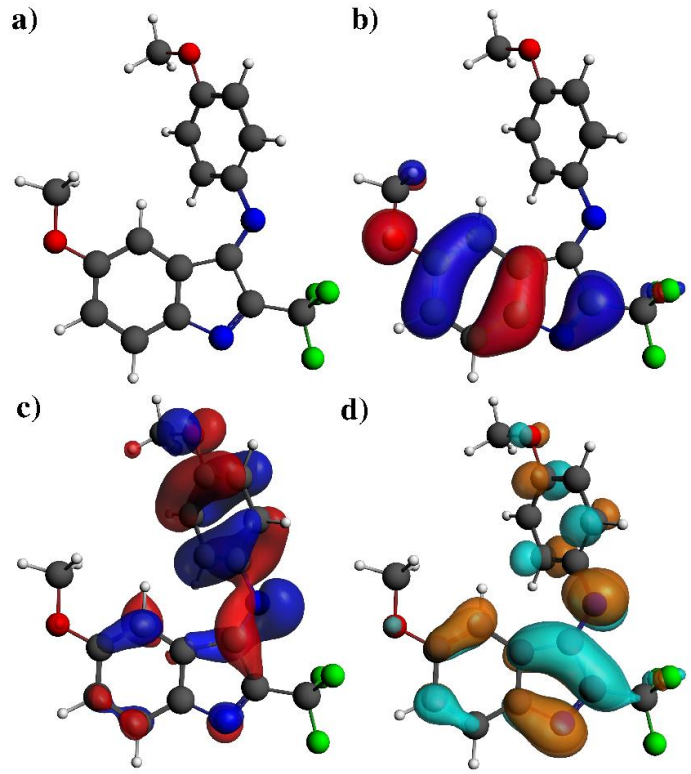


Figure S2 Compound **5a**: a) optimized (TPSS-D3/TZVP) structure, b) – d) isosurface plots (isosurface value ±0.03 a.u.) of the molecular orbitals involved in the two lowest singlet–singlet transitions: b) (HOMO−1), c) HOMO, and d) LUMO. Results have been obtained with CAMY-B3LYP/TZP.

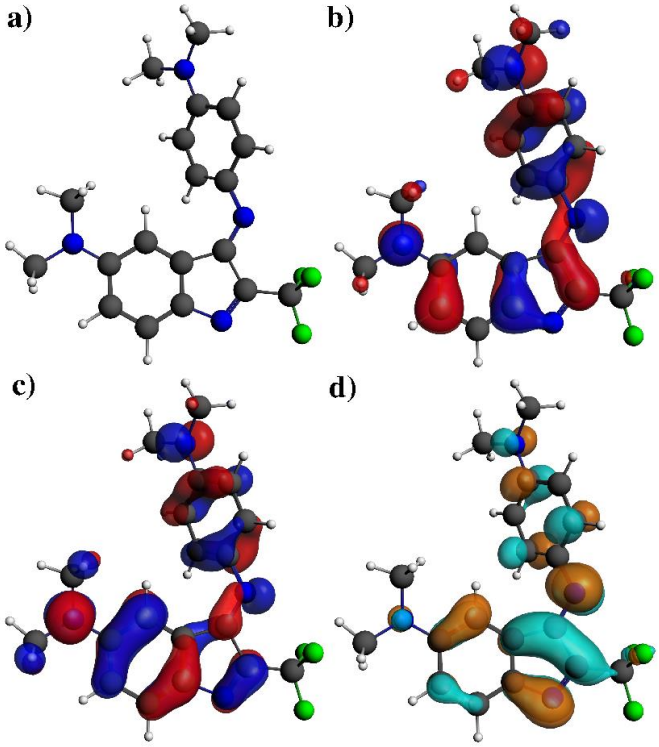


Figure S3 Compound **5d**: a) optimized (TPSS-D3/TZVP) structure, b) – d) isosurface plots (isosurface value ±0.03 a.u.) of the molecular orbitals involved in the two lowest singlet–singlet transitions: b) (HOMO−1), c) HOMO, and d) LUMO. Results have been obtained with CAMY-B3LYP/TZP.

The wavefunction-based reference methods CC2 and ADC(2) agree quite well for compound **5a**, and also for compound **5d** we observe a similar set of results: A less intense transition at 2.20 [CC2] or 2.16 eV [ADC(2)] and a more intense one at 2.37 [CC2] or 2.30 [ADC(2)], respectively. However, the main character of these transitions is inverted in the two calculations. TDDFT calculations with CAMY-B3LYP lead to lower excitation energies. Moreover, the (HOMO−1)→LUMO excitations are the most intense transitions for both compounds. The LC-BLYP functional produces a larger deviation in comparison with the wavefunction-based methods.

8.2.3 Spectra simulations

Since the two lowest transitions contribute to one spectral band, the direct comparison of the calculated vertical excitations and experimental band maxima does not allow to assess the quality of the calculations directly. Instead, the comparison of the experimental and theoretical band maxima seems to be a more promising approach. In order to do so, we simulated the spectra using the broadening of the calculated transitions as described in Sec. 1.1. The resulting spectra are shown in Figs. S4 and S5.

As one can see, the CC2 and ADC(2) methods provide a very good agreement with the experimental spectrum for compound **5a**, and also for **5d** the ADC(2) results are quite good, while CC2 underestimates λ_{max} a bit more in this case. The total shift in the position of the band maximum is in reasonable agreement for ADC(2) [0.33 eV], and only slightly worse for CC2 [0.29 eV, see Tab. S4]. Qualitatively, both methods are in line with experiment. The CAMY-B3LYP band almost coincides with CC2 for compound **5d**, but is somewhat red-shifted for **5a**. The predicted total shift between **5a** and **5d** is significantly smaller than the experimental one.

The best calculated results [obtained with ADC(2)] are compared to the experimental ones in Fig. S6 for both compounds together, again highlighting the rather good agreement.

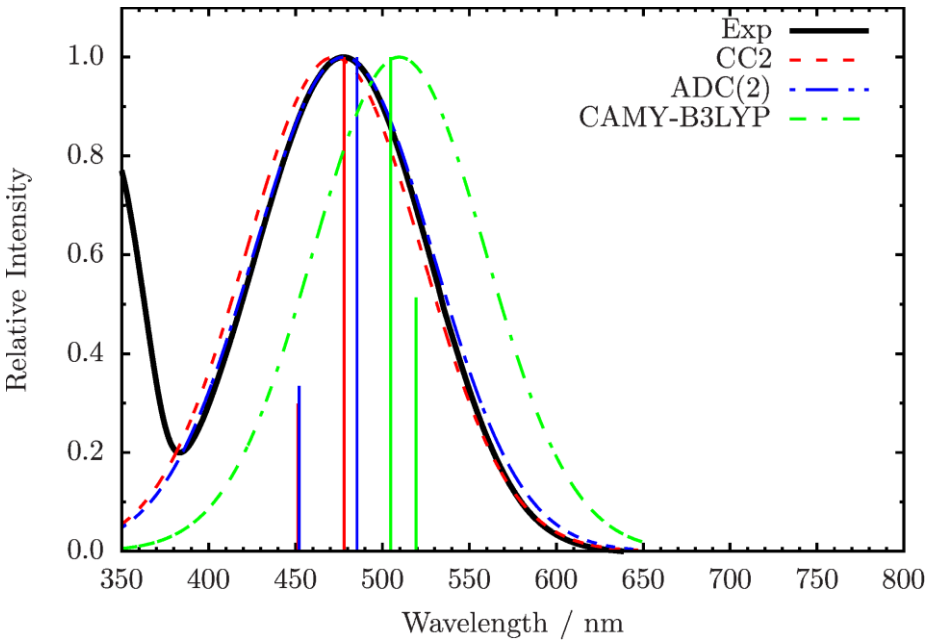


Figure S4 Theoretical and experimental absorption spectra of compound **5a** in the visible range. The straight lines indicate the two lowest electronic singlet–singlet transitions.

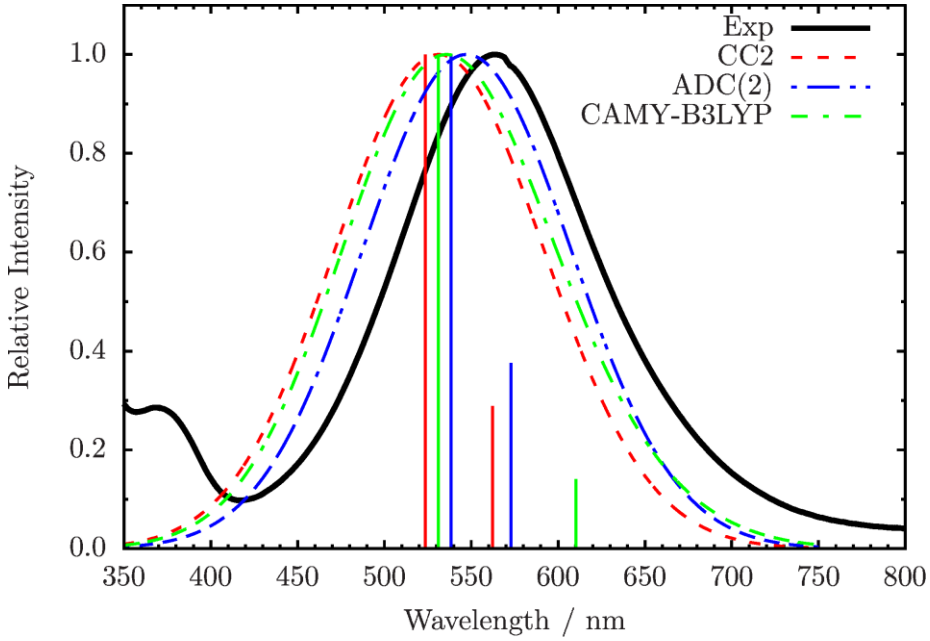


Figure S5 Theoretical and experimental absorption spectra of compound **5d** in the visible range. The straight lines indicate the two lowest electronic singlet–singlet transitions.

Table S4 Absorption maxima of compounds **5a** and **5d** in units of nm (λ_{max}) and eV (E_{max}). The substitution-induced shifts are given separately in eV.

Method	**5a**		**5d**		Shift
	λ_{max}	E_{max}	λ_{max}	E_{max}	
CAMY-B3LYP	510.2	2.43	536.7	2.31	0.12
CC2	473.2	2.62	532.1	2.33	0.29
ADC(2)	478.7	2.59	548.6	2.26	0.33
Exp.	477.6	2.60	563.8	2.20	0.40

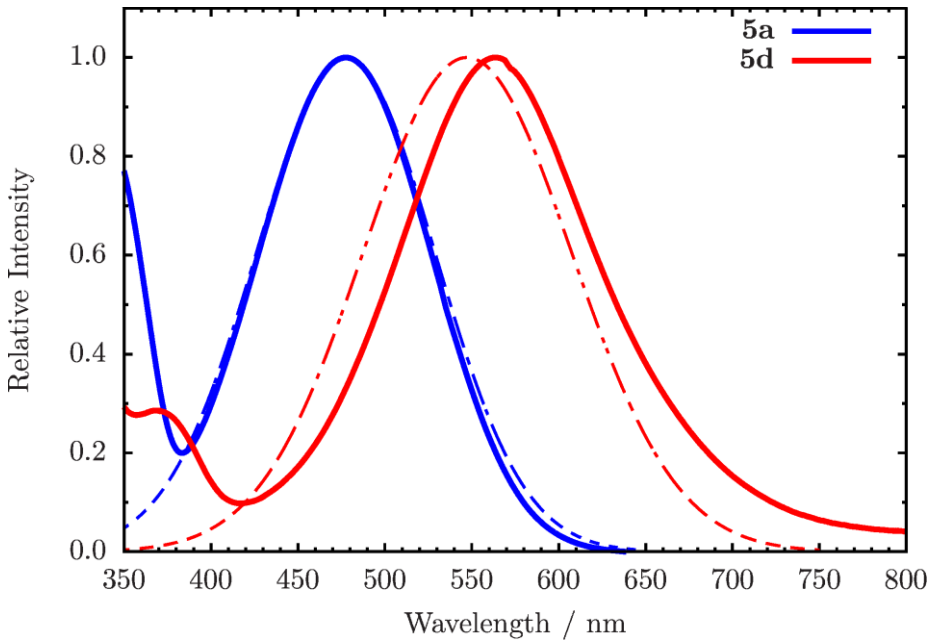


Figure S6 The experimental (solid lines) and simulated ADC(2) (dashed) absorption spectra of compounds **5a** and **5d** in the visible range.

In a zero-order approximation, we can try to rationalize excitation energies in terms of orbital-energy differences between occupied and unoccupied orbitals involved in the corresponding excitations. At the same time, orbital energies are influenced by the electronic effects of the substituents. Thus, a direct connection between the nature of a substituent and the position of a spectral band can be established. Orbital energy diagrams for chromophores **5a** and **5d** are shown in Fig. S7. As one can see, DFT calculations predict an upshift of the HOMO and (HOMO−1) for **5d** relative to **5a**. The LUMO is also shifted, but to a smaller extent. Thus, the HOMO/LUMO and (HOMO−1)/LUMO gaps are reduced by about 0.4 eV, which causes the red shift of the spectral band for **5d**. The substitution of the methoxy by dimethylamino groups apparently destabilizes the orbitals in the π-system, but the upshift is larger for the occupied than for the virtual orbitals. As a result, the occupied–virtual gap decreases.

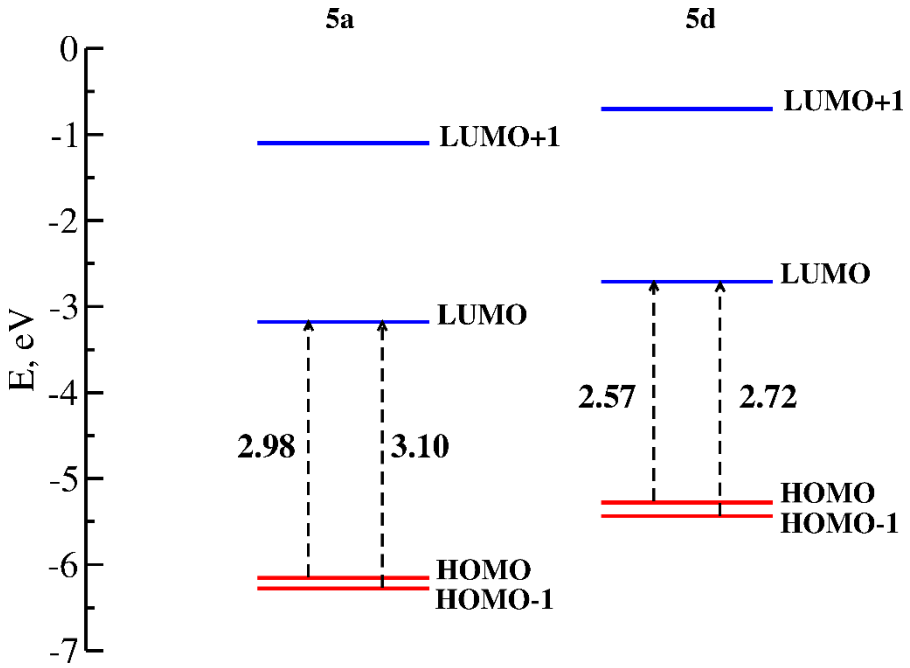
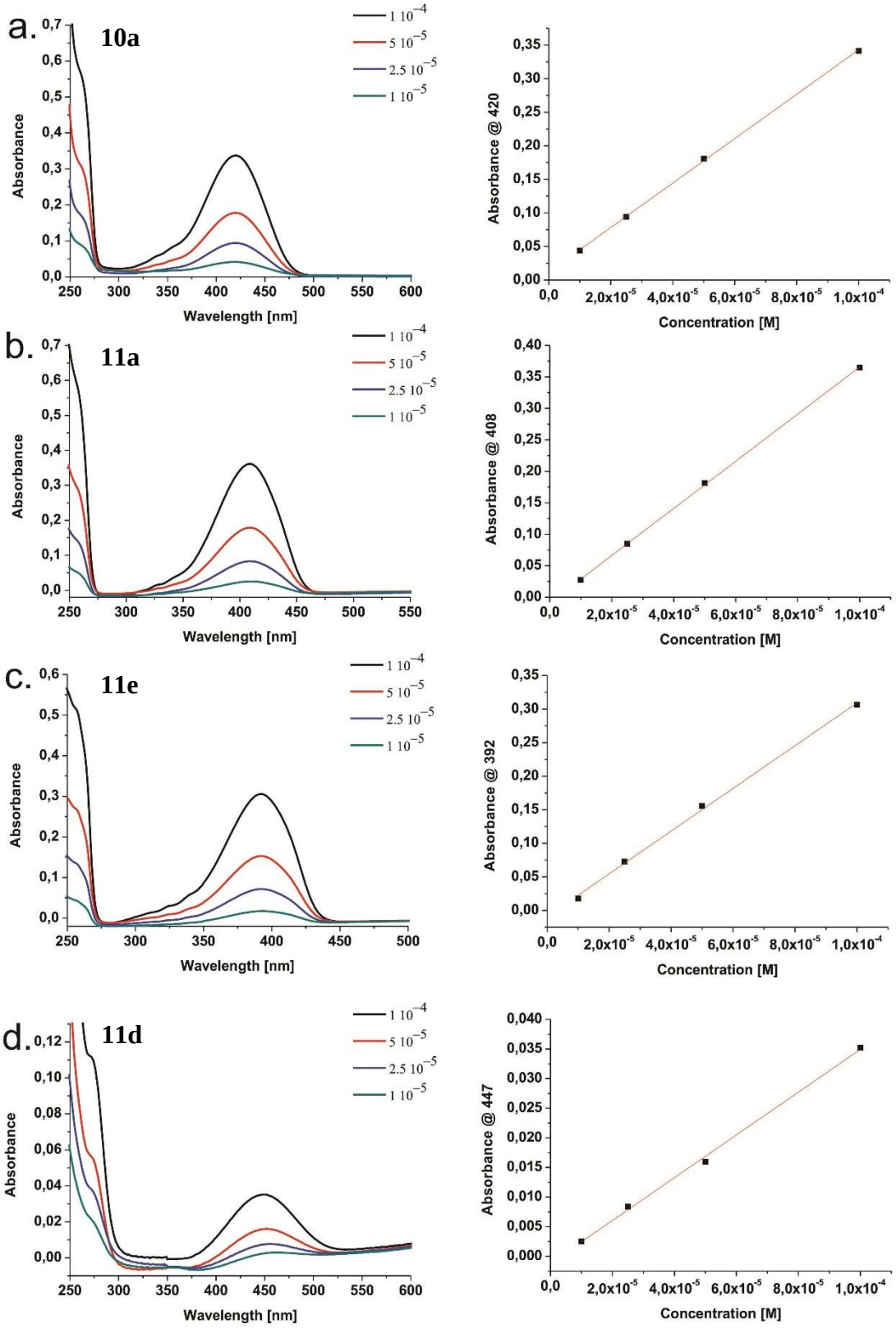
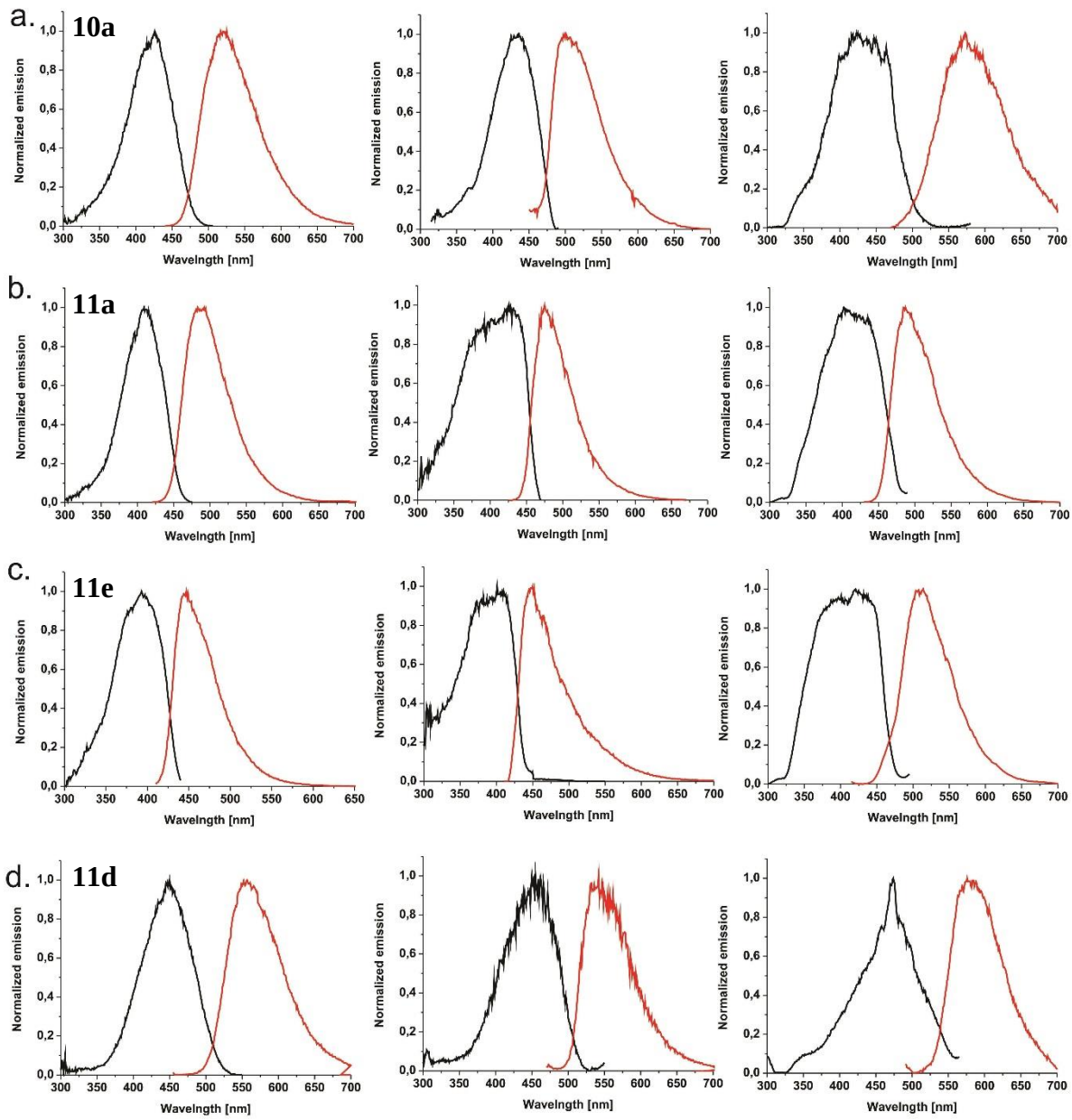


Figure S7 Orbital energy diagram of compounds **5a** and **5d**. Arrows indicate the two lowest singlet−singlet excitations producing the largest contribution to the spectral bands in the visible range. Values in eV refer to HOMO/LUMO and (HOMO−1)/LUMO gaps. The present data have been obtained with CAMY-B3LYP/TZP.

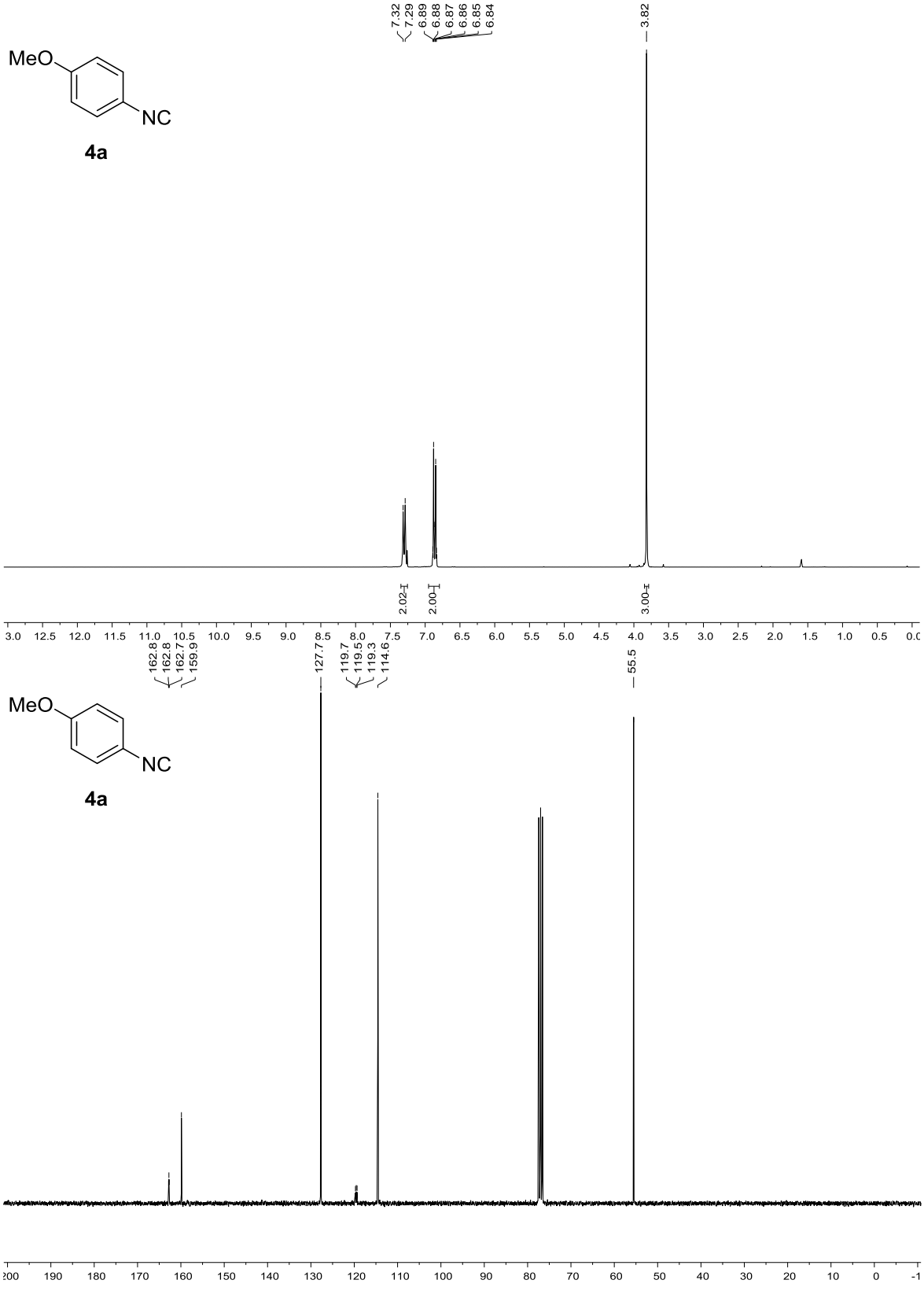
9. Fluorescence data of 3-oxindoles 10a, 11



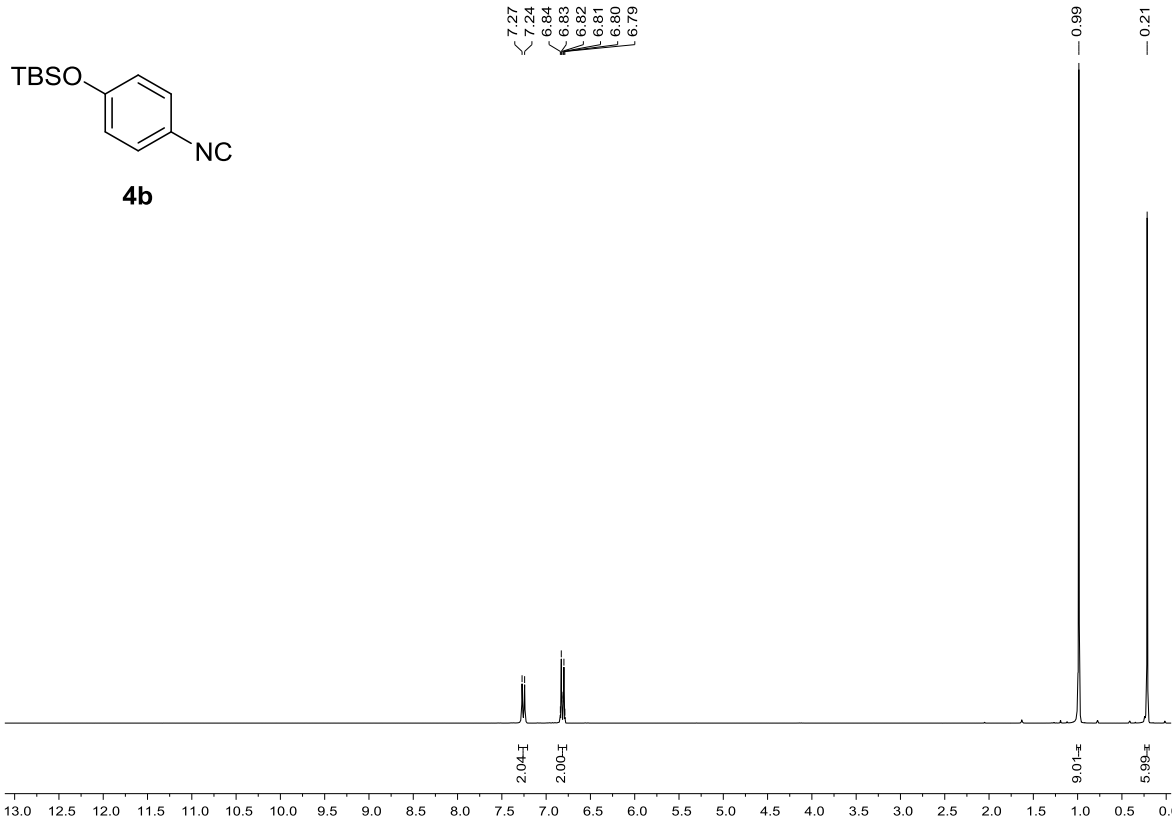

solution, rt
solid, 77K
solid, rt
a.
10a
b.
11a
c.
11e
d.
11d
Normalized emission
Wavelngth [nm]

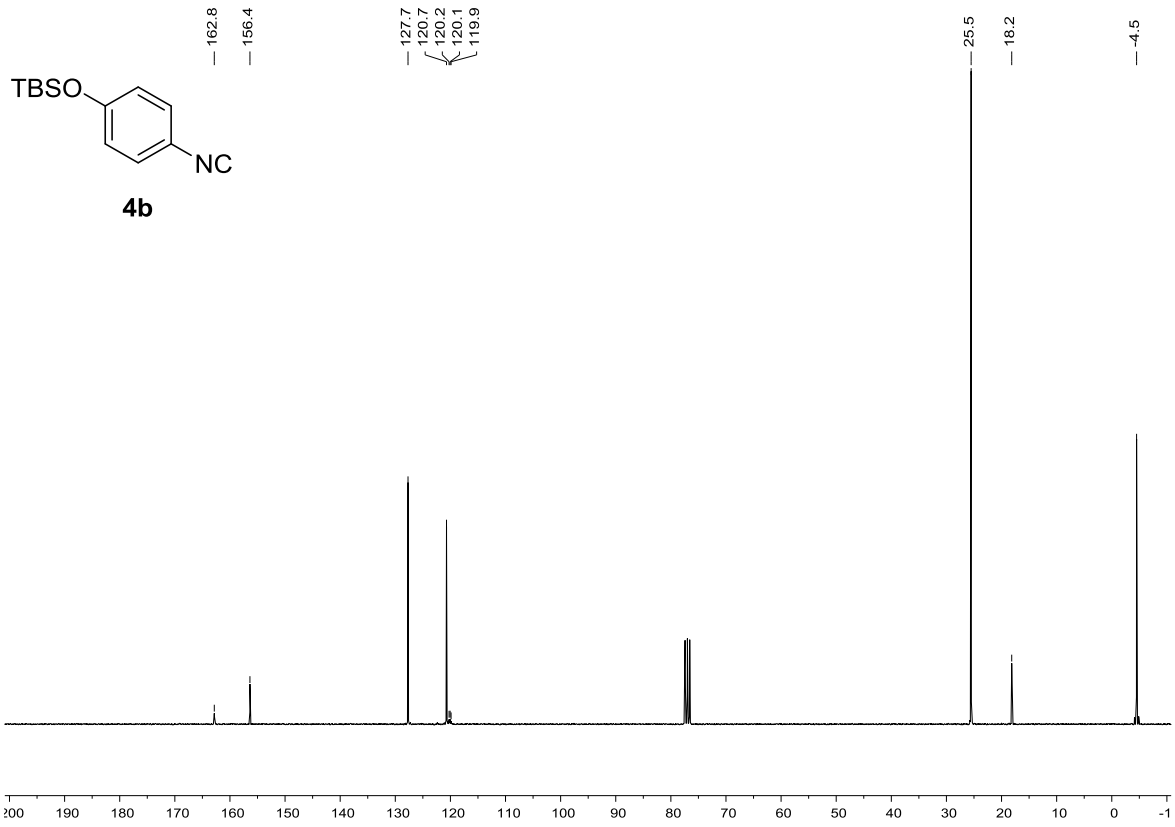
10. Spectra if isocyanoaryls 4 and diazene 6c

1-Isocyano-4-methoxybenzene (4a)

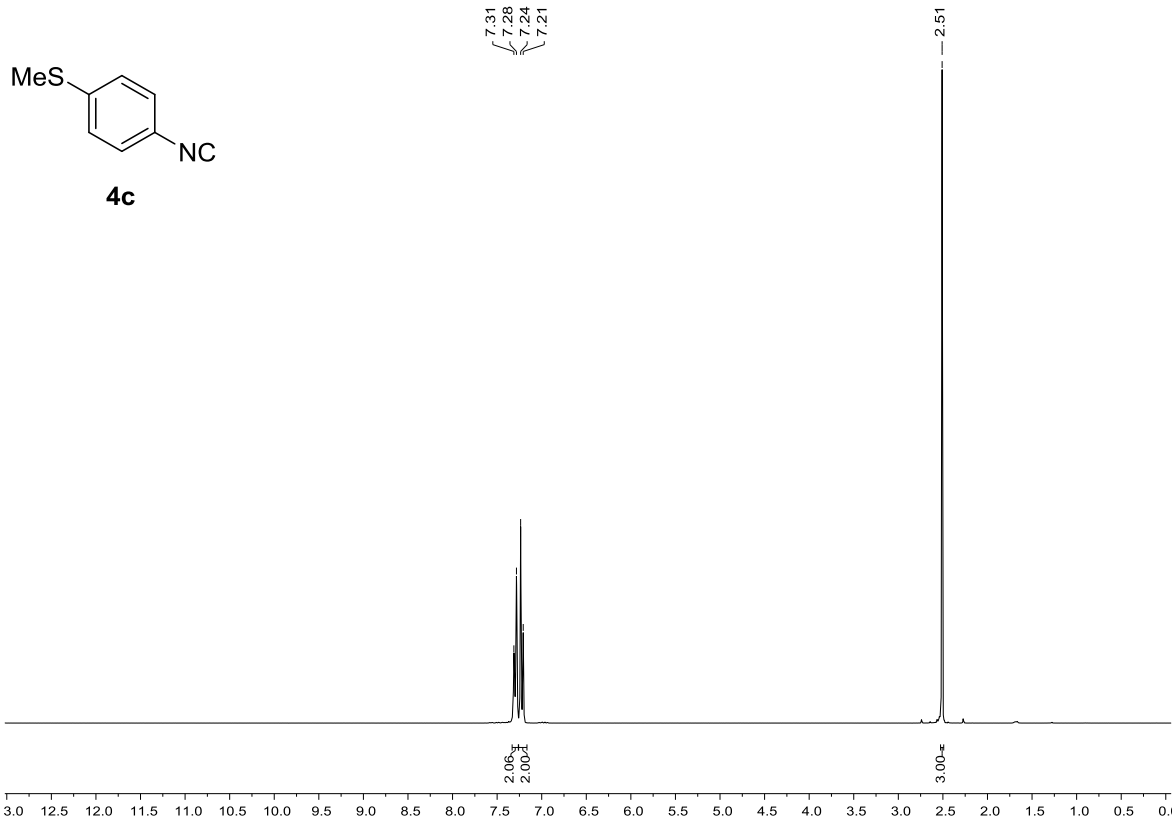


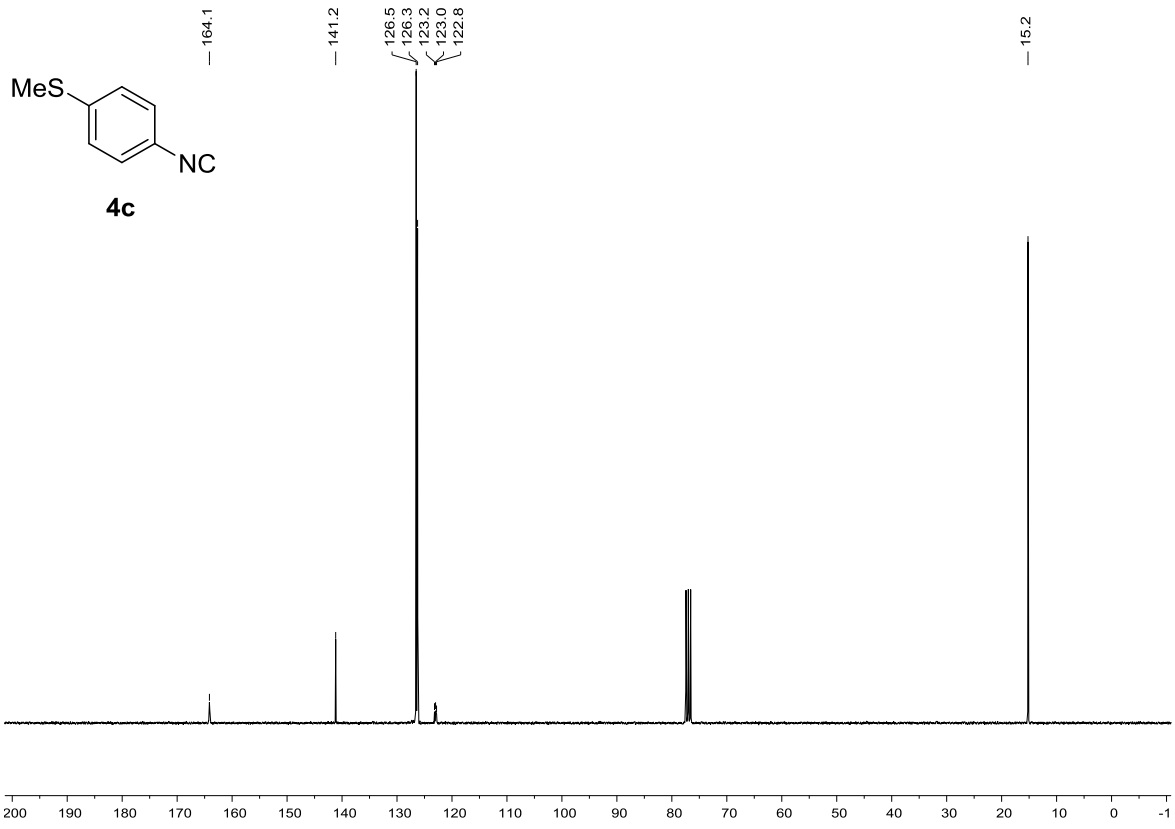
tert-Butyl(4-isocyanophenoxy)dimethylsilane (4b)



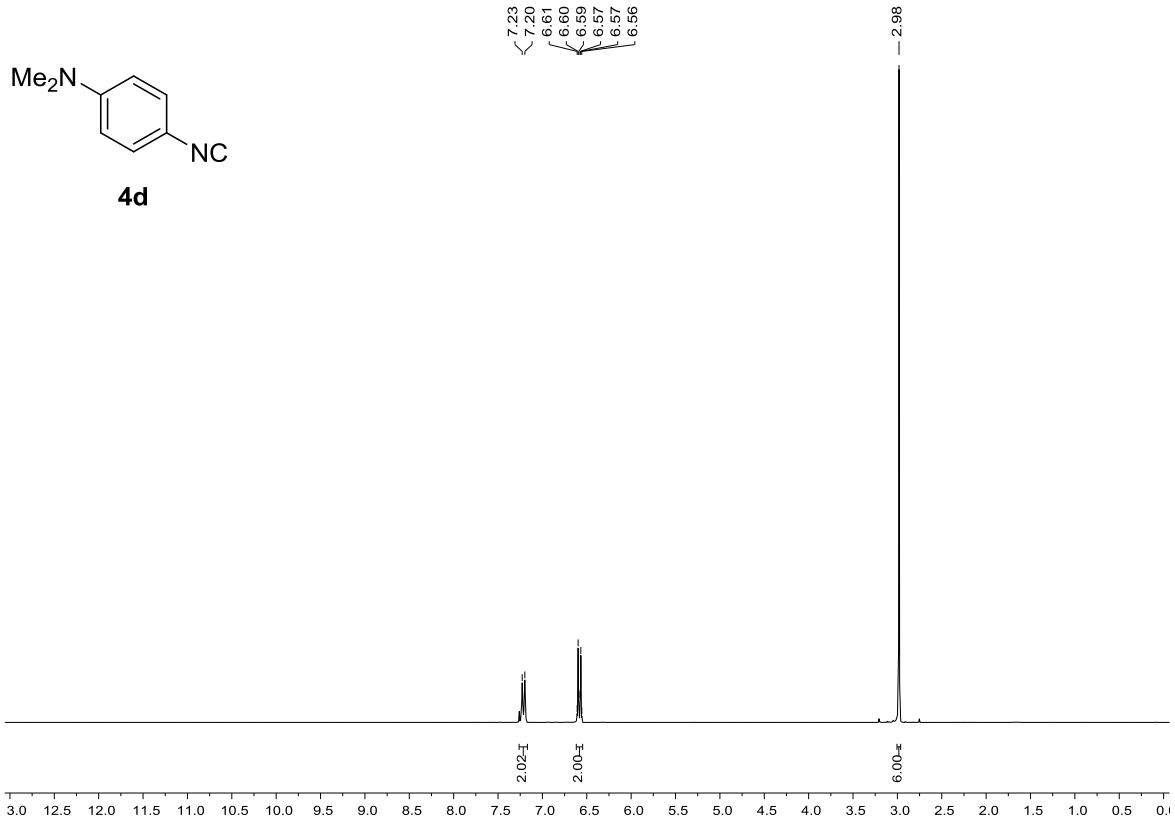


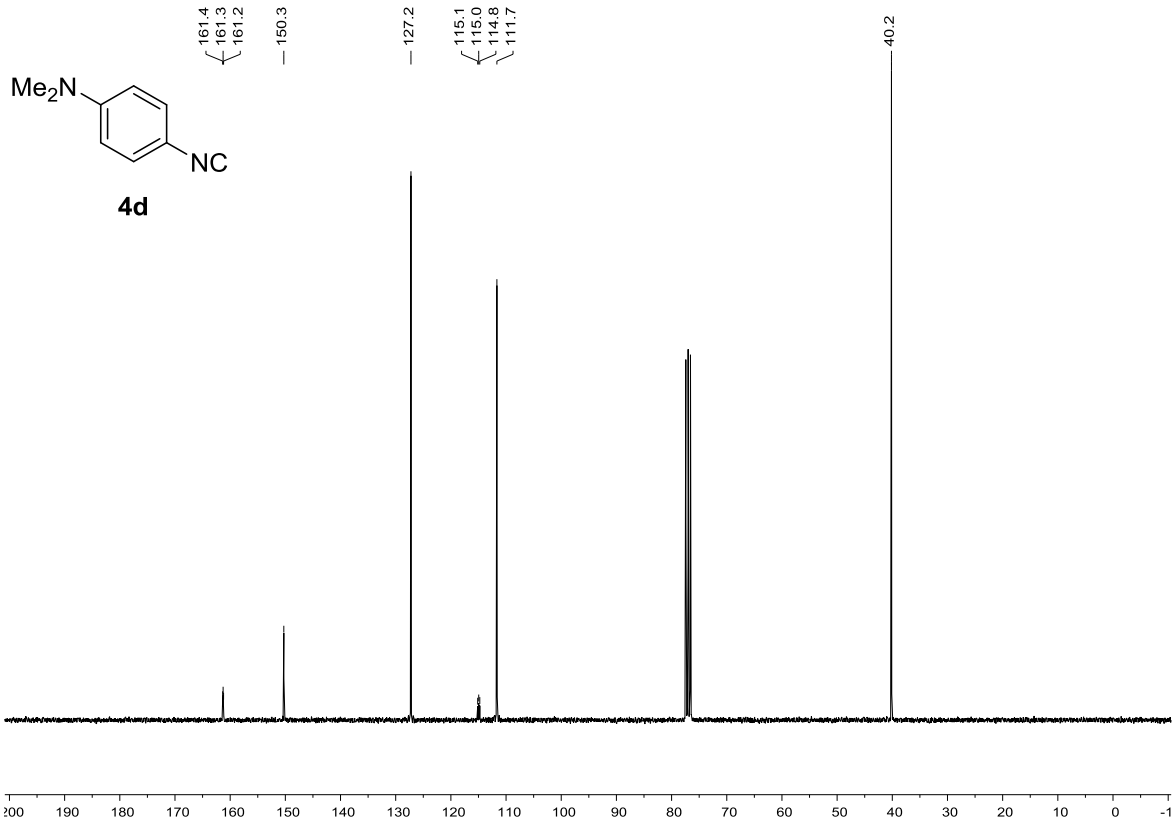
(4-Isocyanophenyl)(methyl)sulfane (4c)



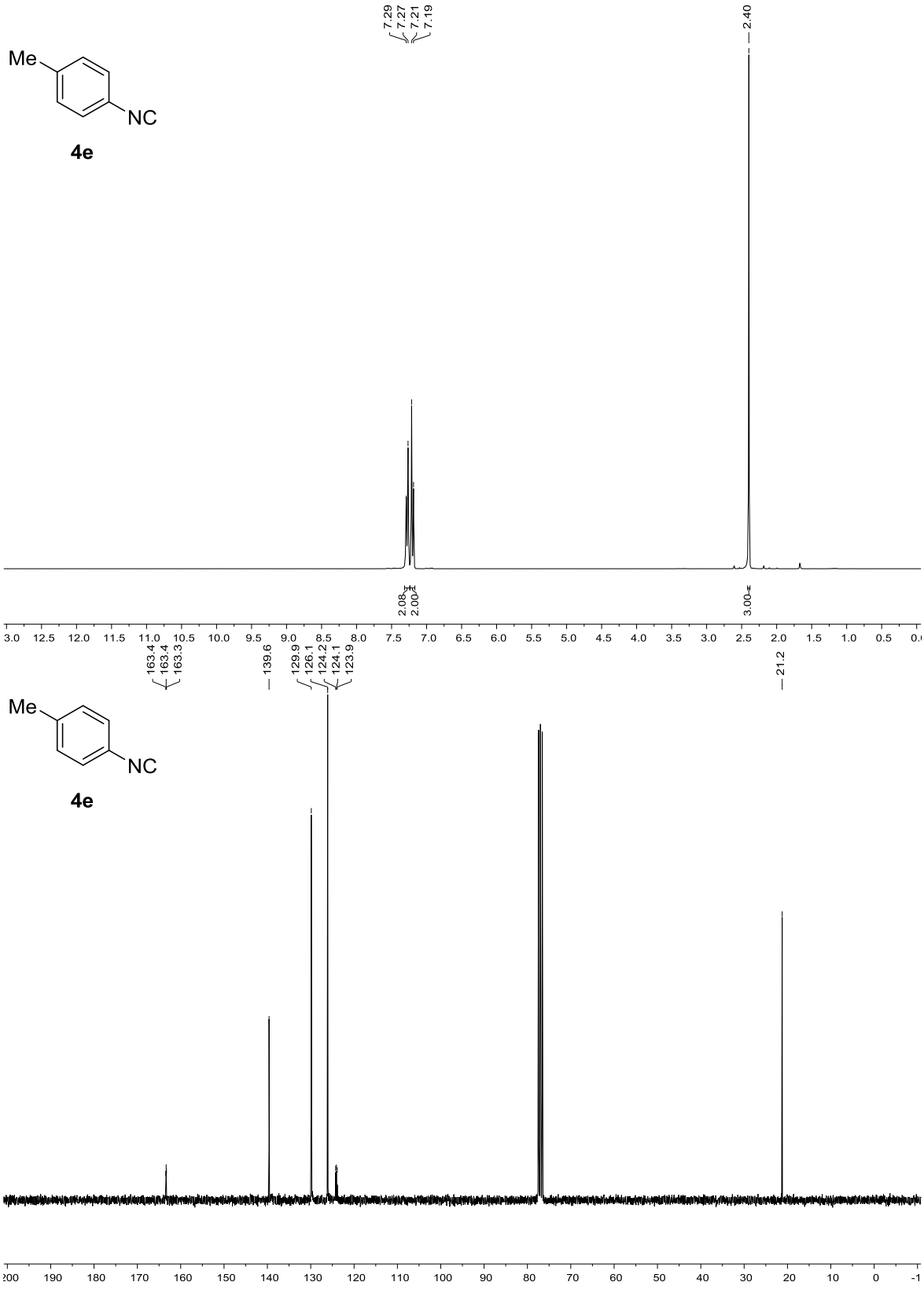


4-Isocyano-*N*,*N*-dimethylaniline (4d)

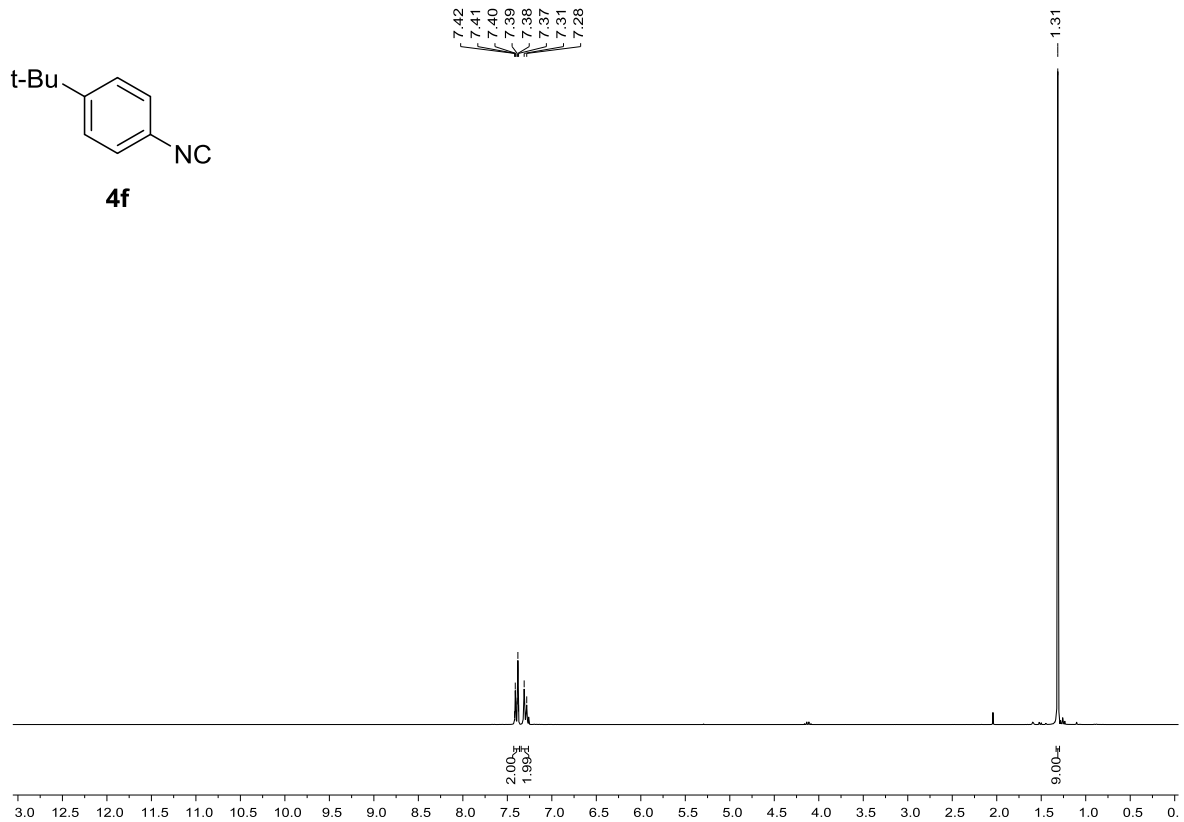


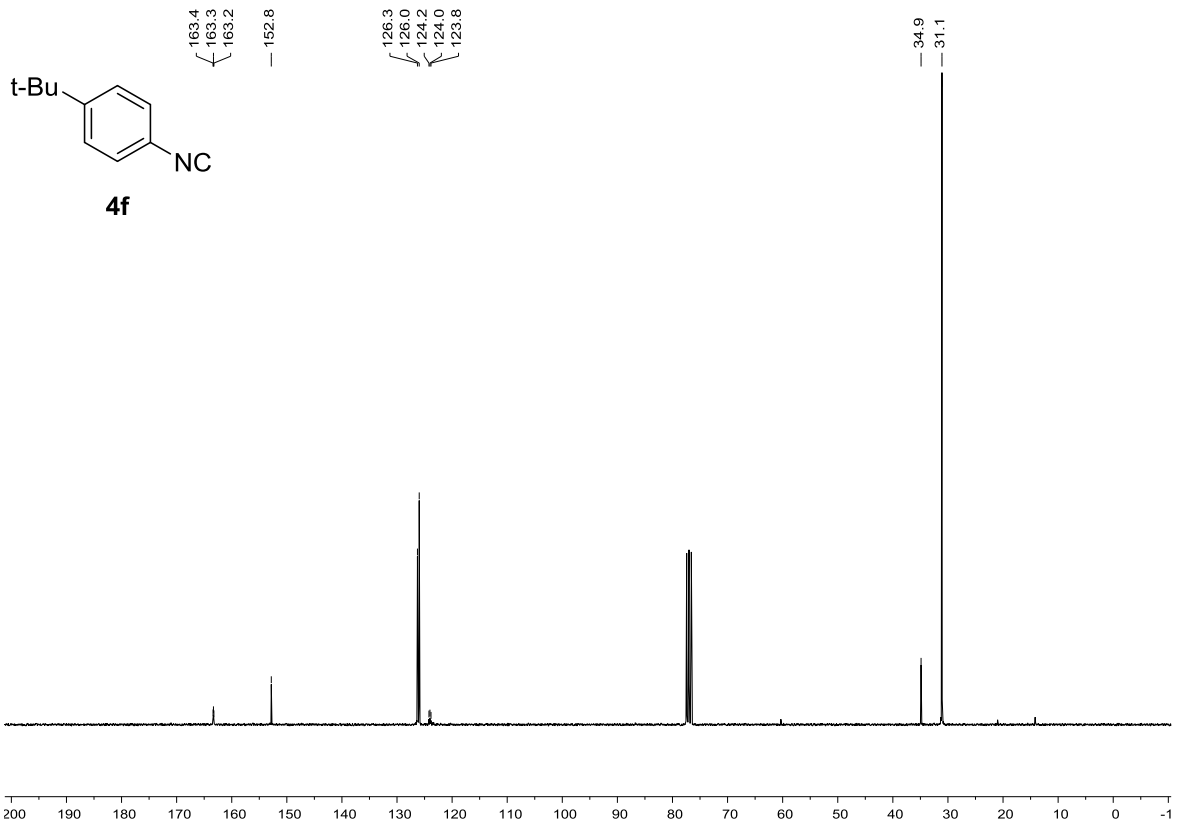


1-Isocyano-4-methylbenzene (4e)

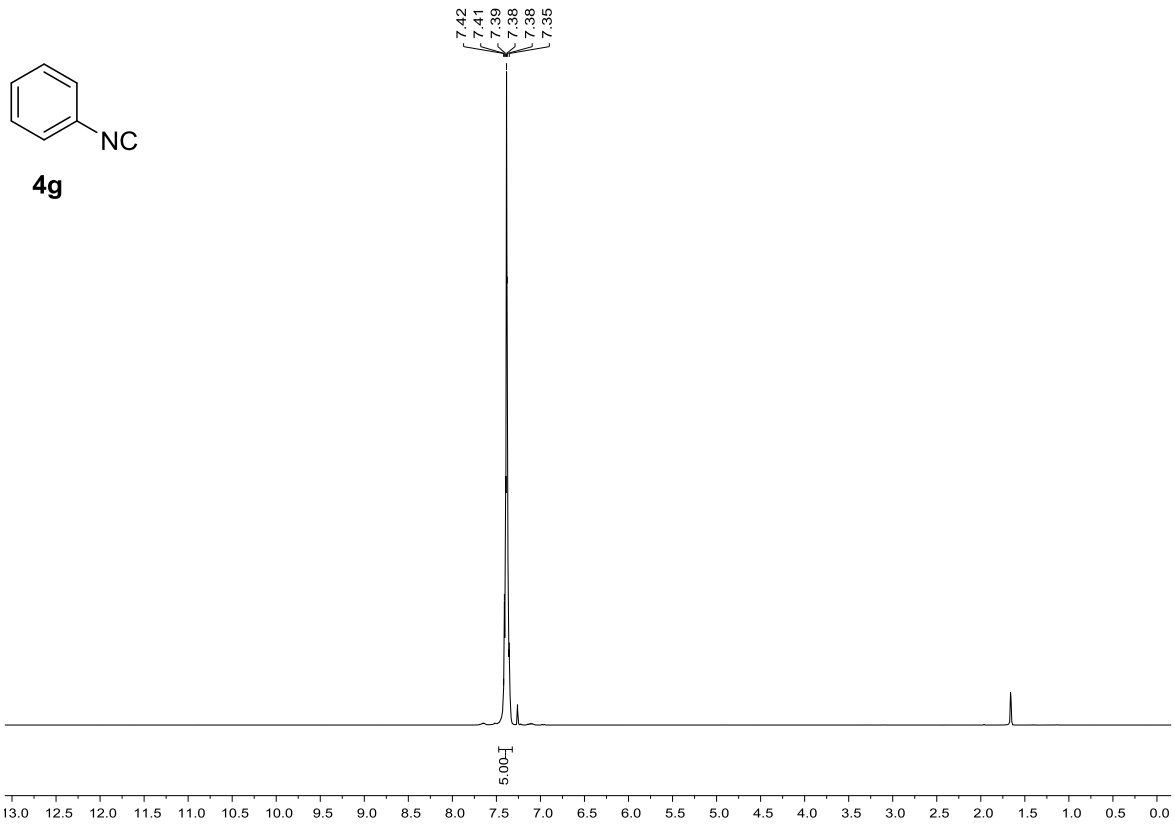


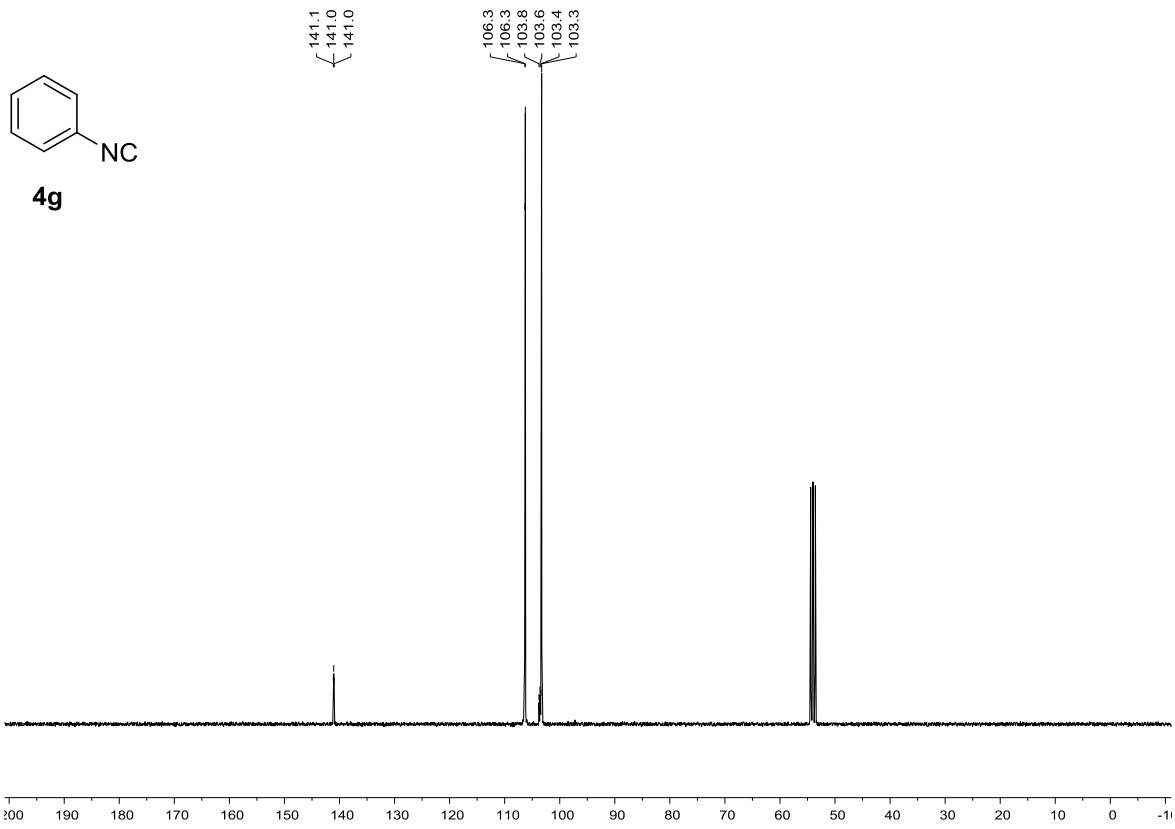
1-(*tert*-Butyl)-4-isocyanobenzene (4f)



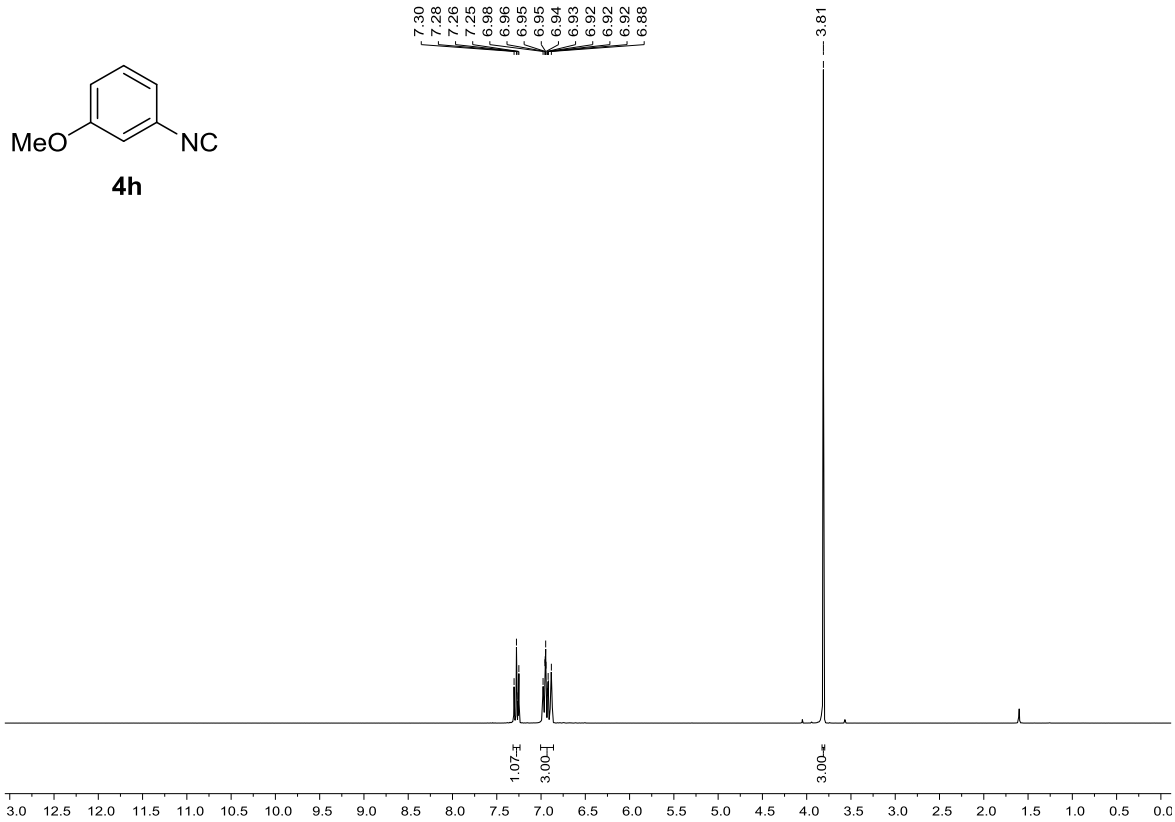


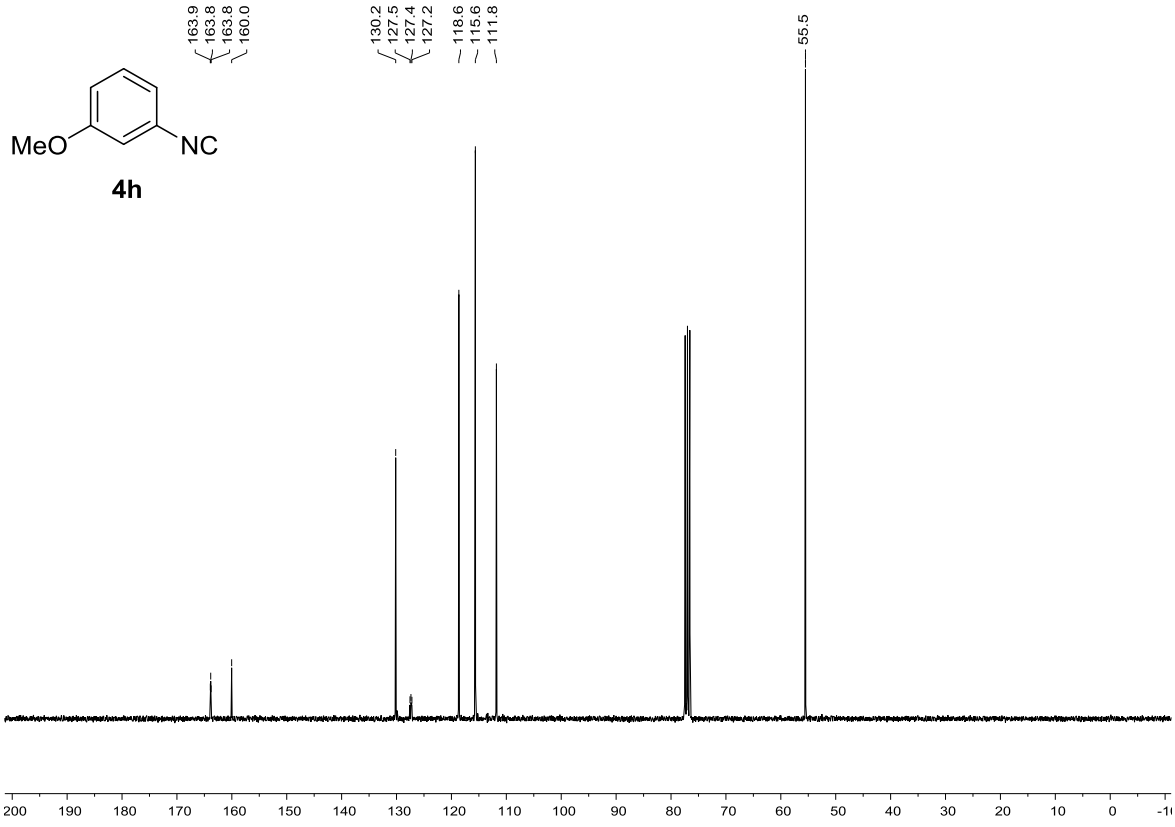
Isocyanobenzene (4g)



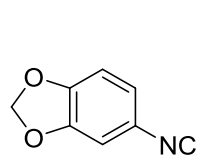


1-Isocyano-3-methoxybenzene (4h)

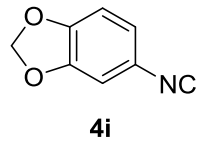




5-Isocyanobenzo[*d*][1,3]dioxole (4i)

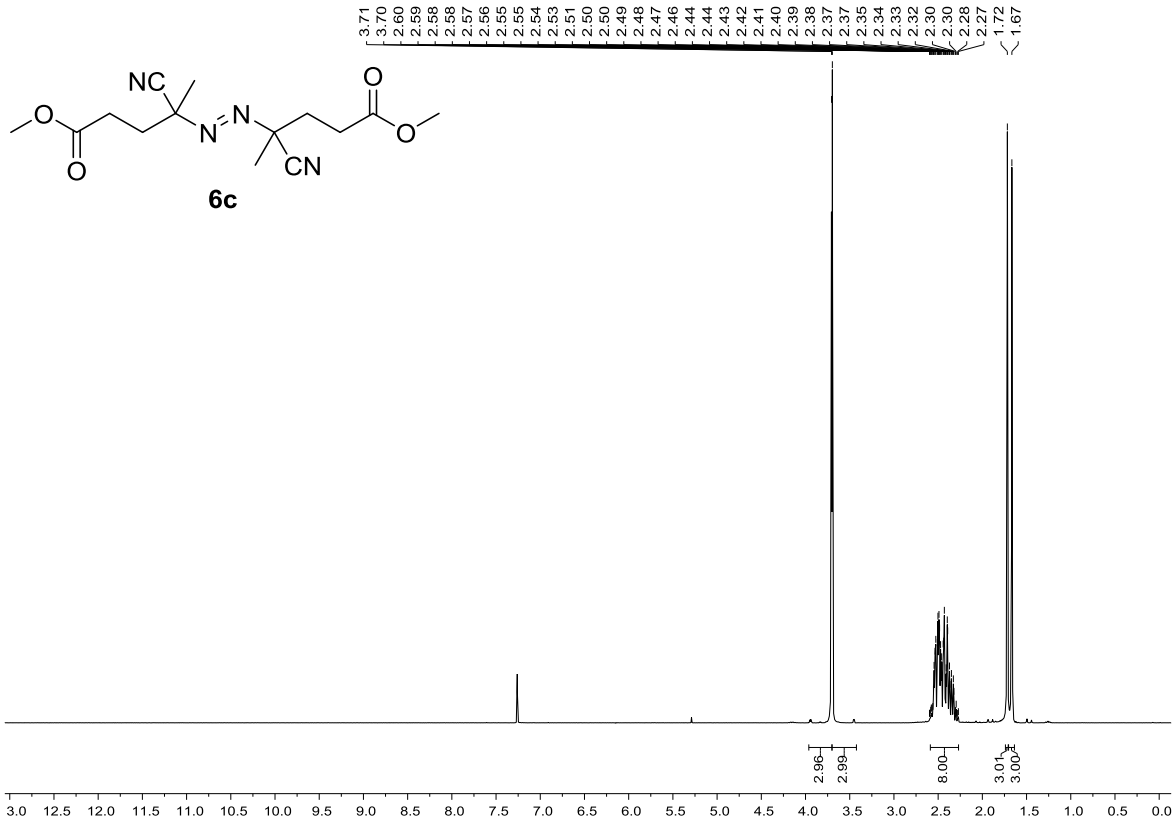


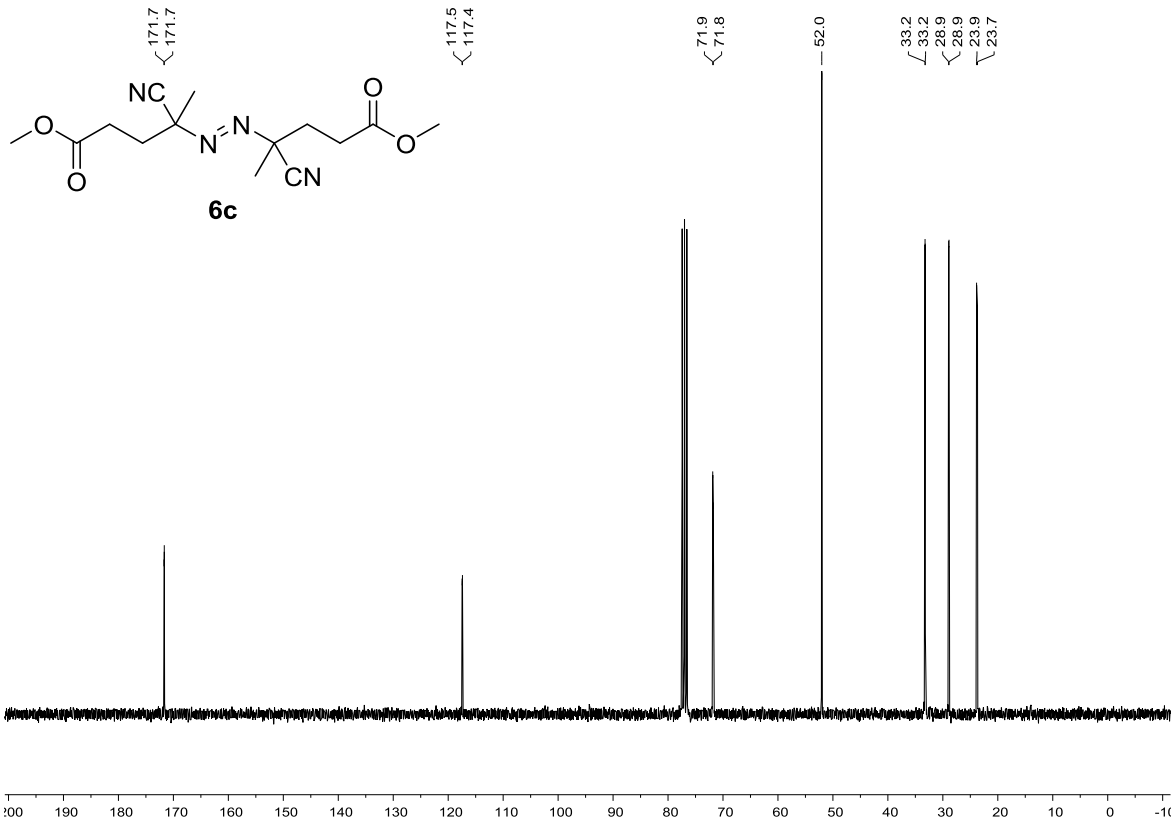
4i



4i

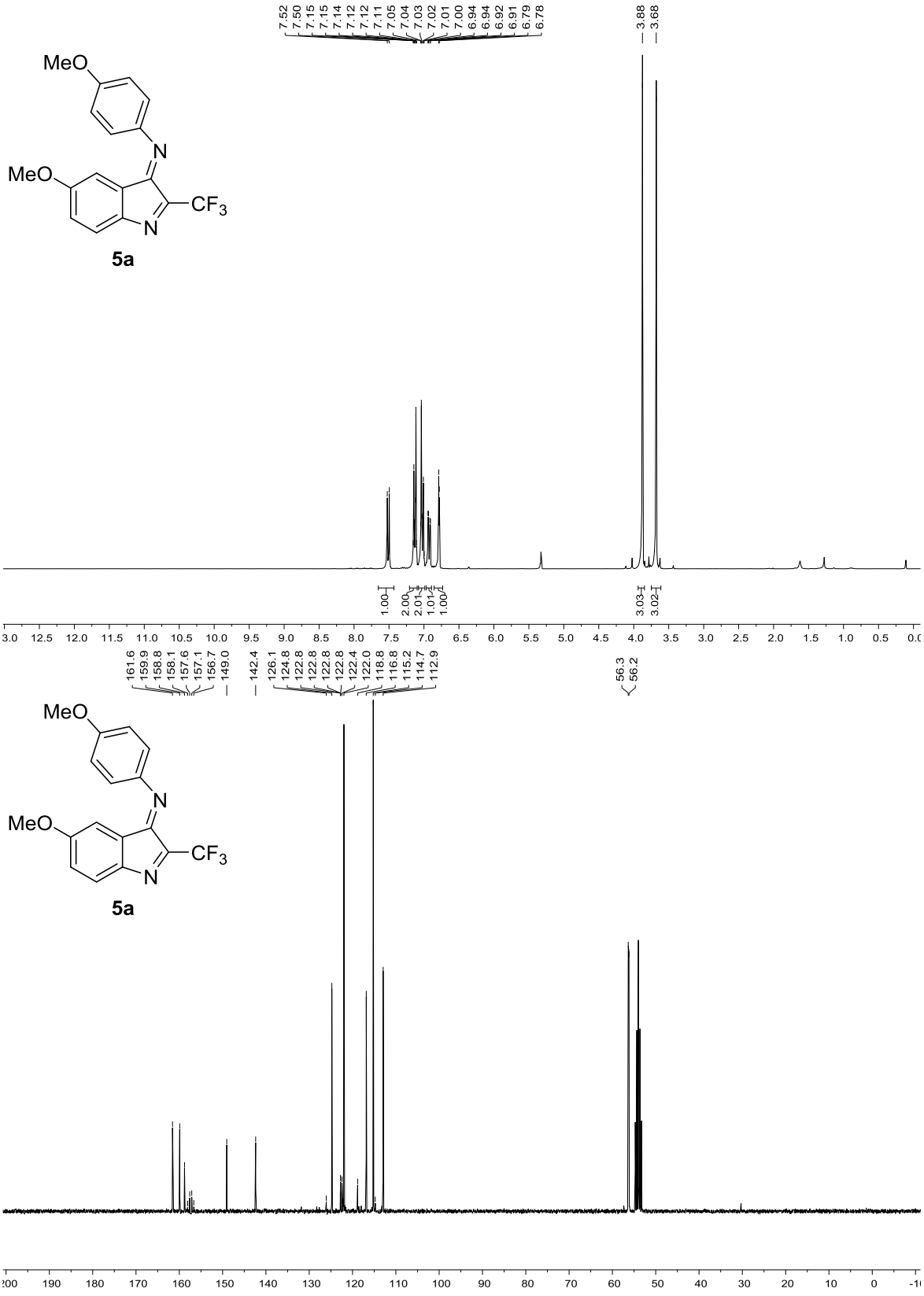
Dimethyl 4,4'-(diazene-1,2-diyl)(*E*)-bis(4-cyanopentanoate) (6c)

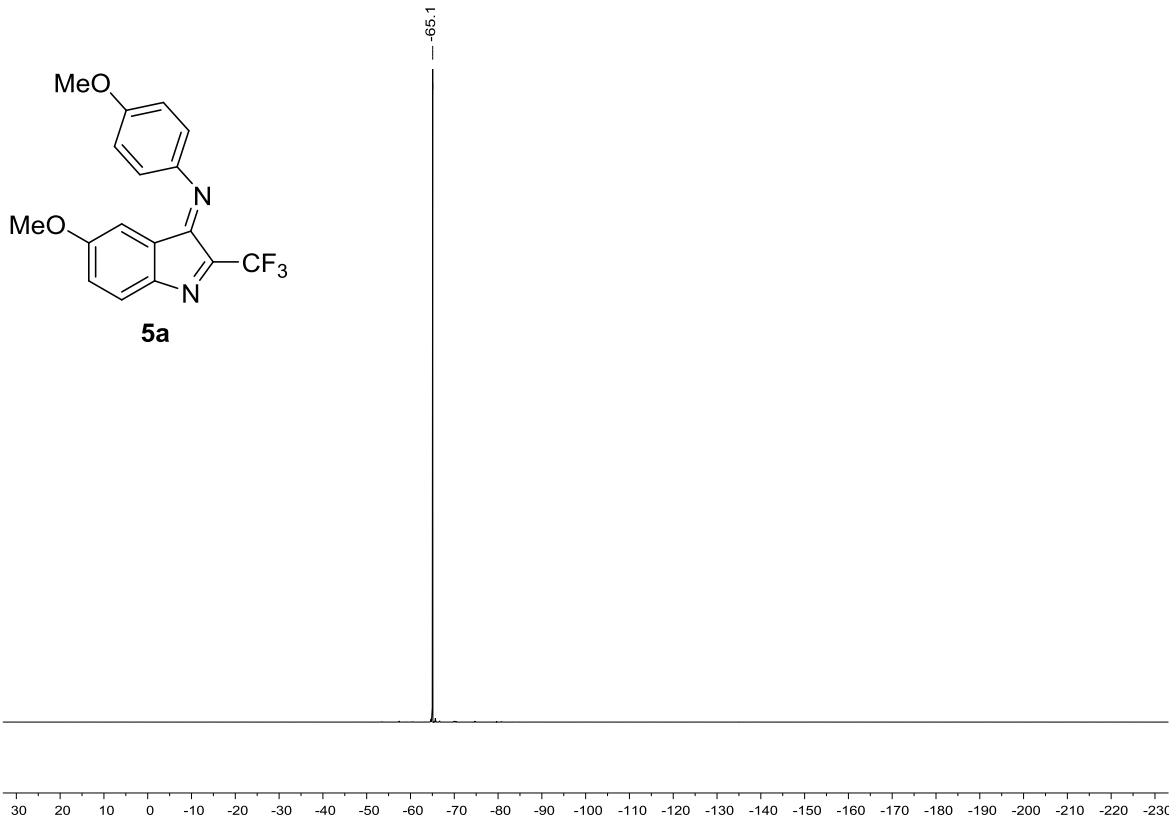




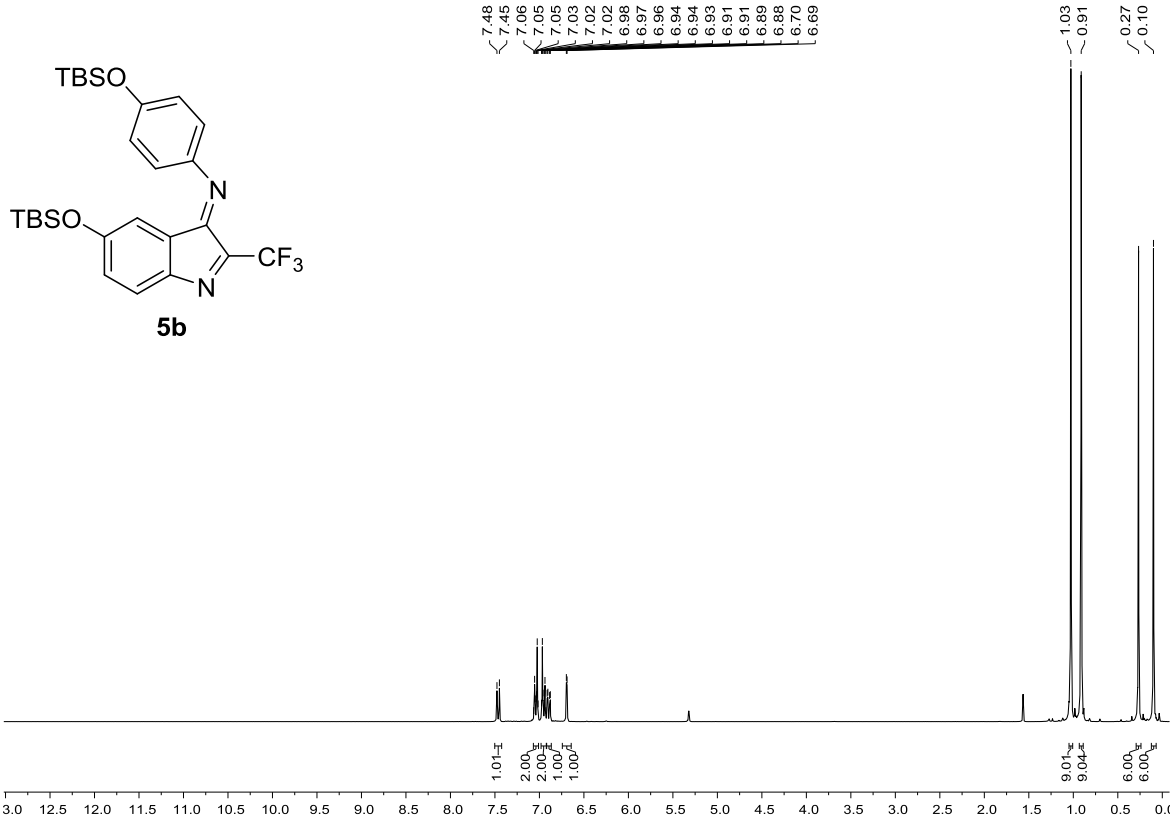
11. Spectra of 3*H*-indol-3-imine 5 and 7

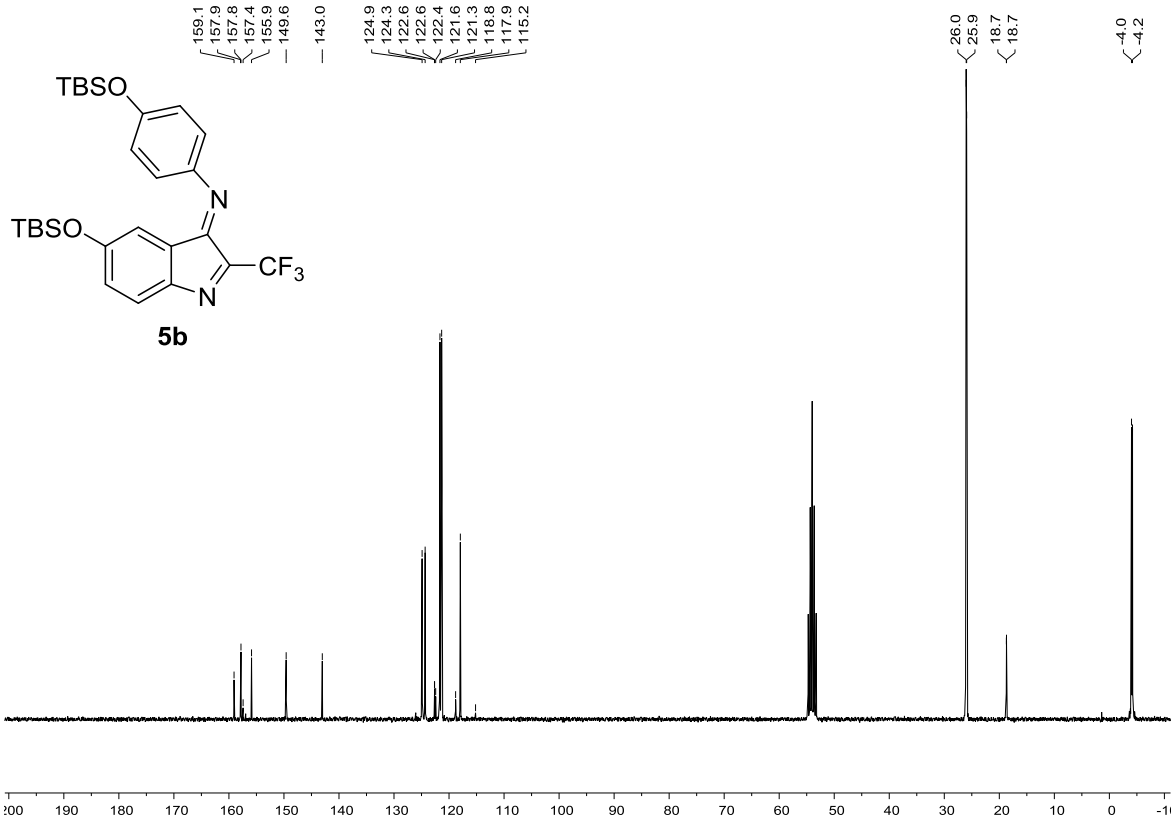
(*E*)-5-Methoxy-*N*-(4-methoxyphenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5a)

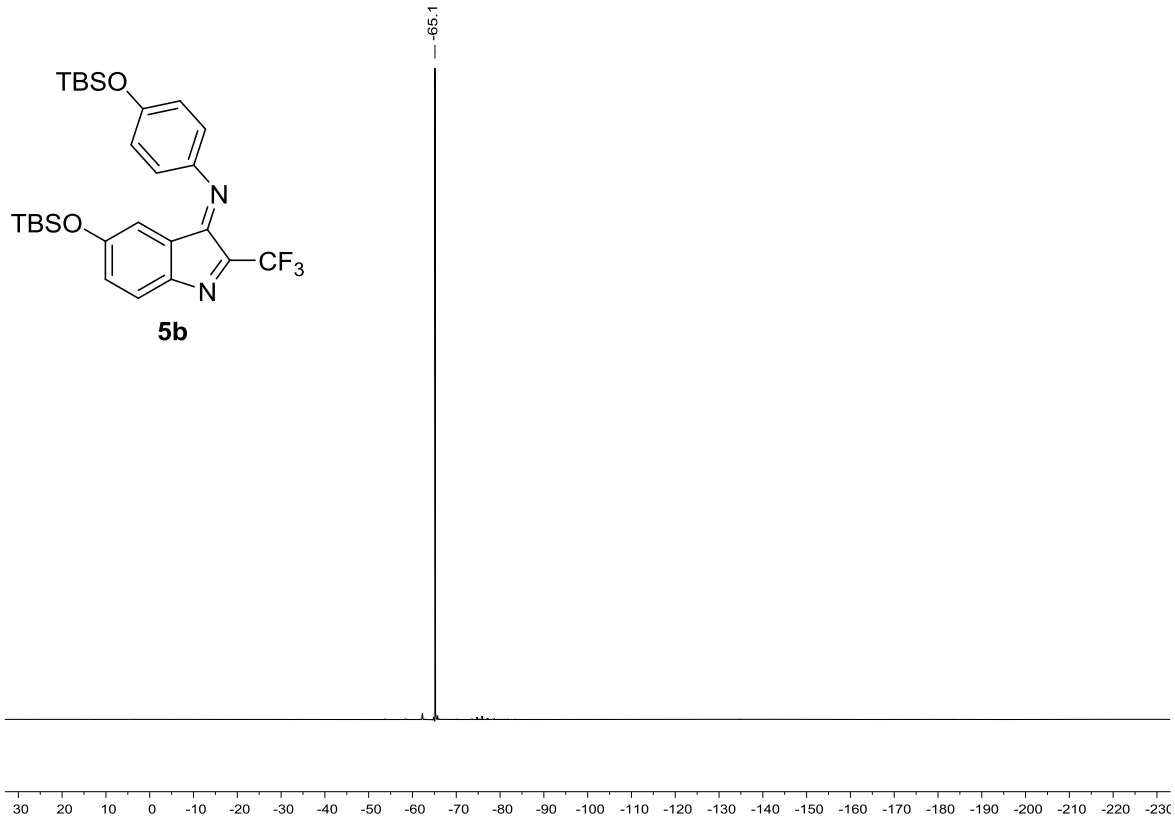




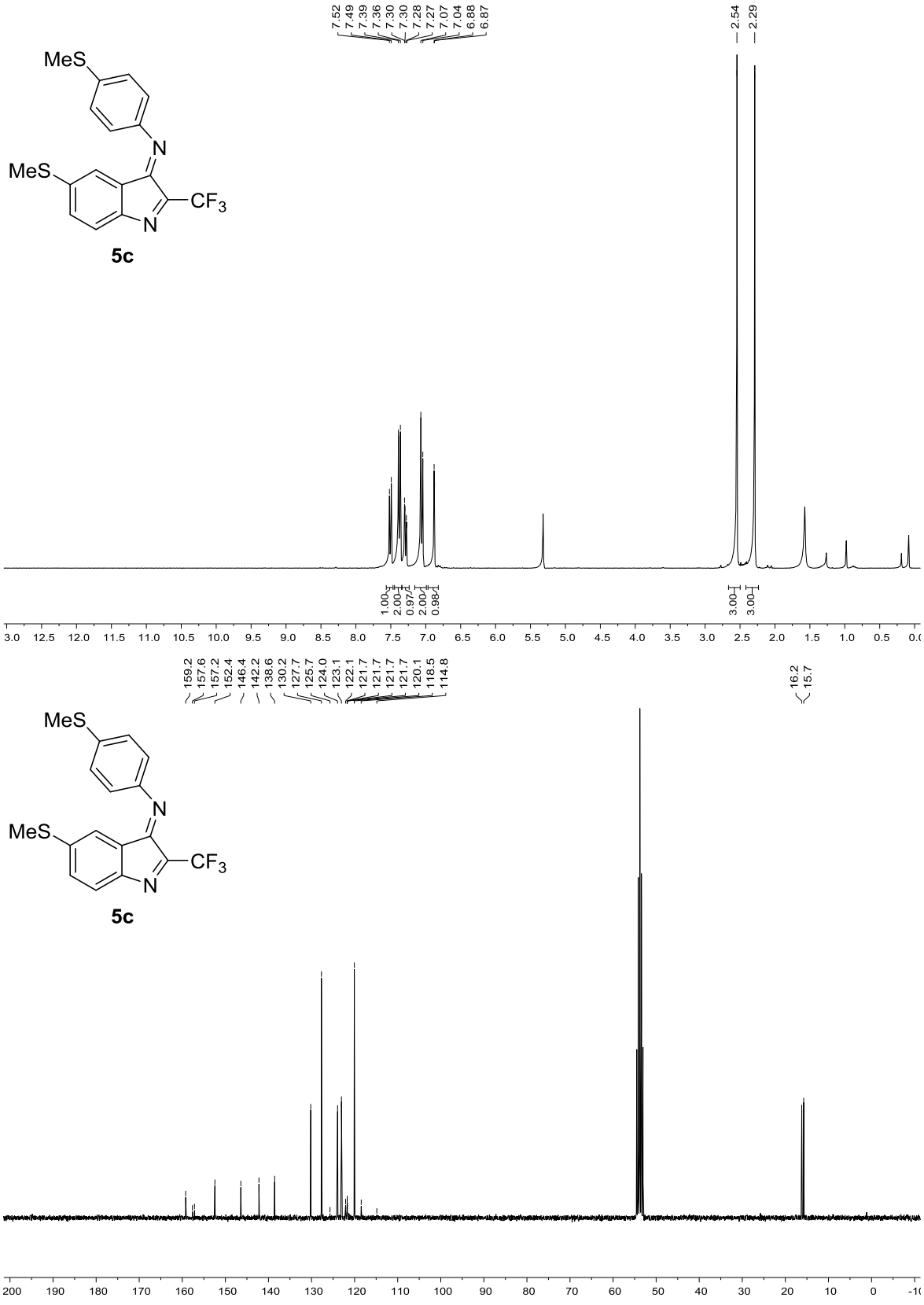
(*E*)-5-((*tert*-Butyldimethylsilyl)oxy)-*N*-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-(trifluoro-methyl)-3*H*-indol-3-imine (5b)

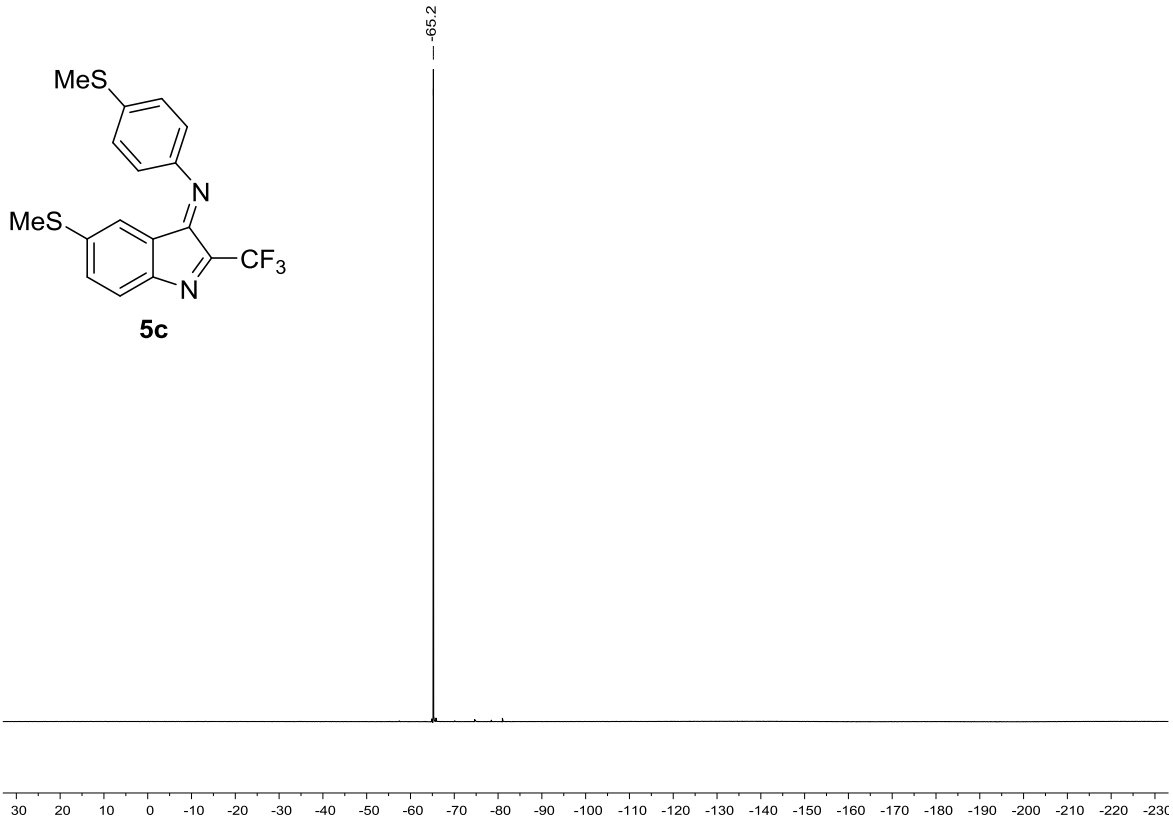



159.1
157.9
157.8
157.4
155.9
149.6
143.0
124.9
124.3
122.6
122.6
122.4
121.6
121.3
118.8
117.9
115.2
26.0
25.9
18.7
18.7
-4.0
-4.2
TBSO
TBSO
N
N
CF3
5b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

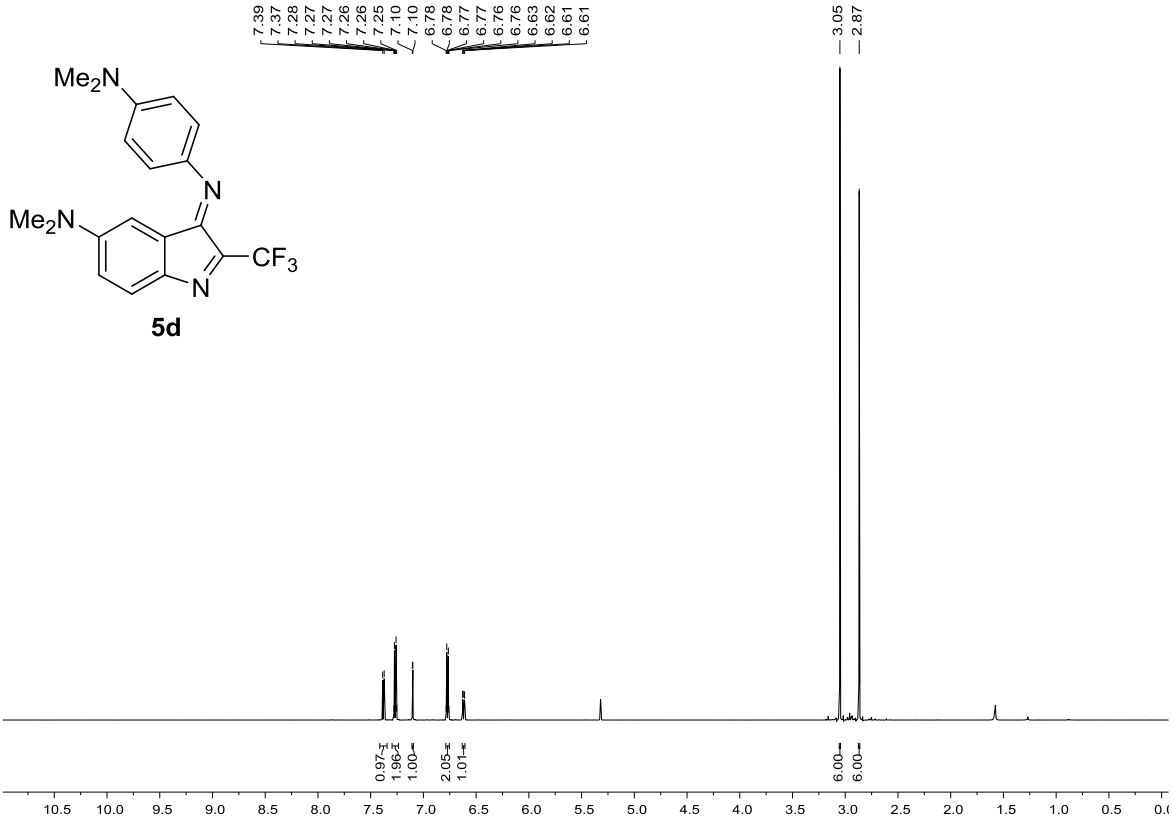

-65.1
TBSO
TBSO
N
N
CF3
5b
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230

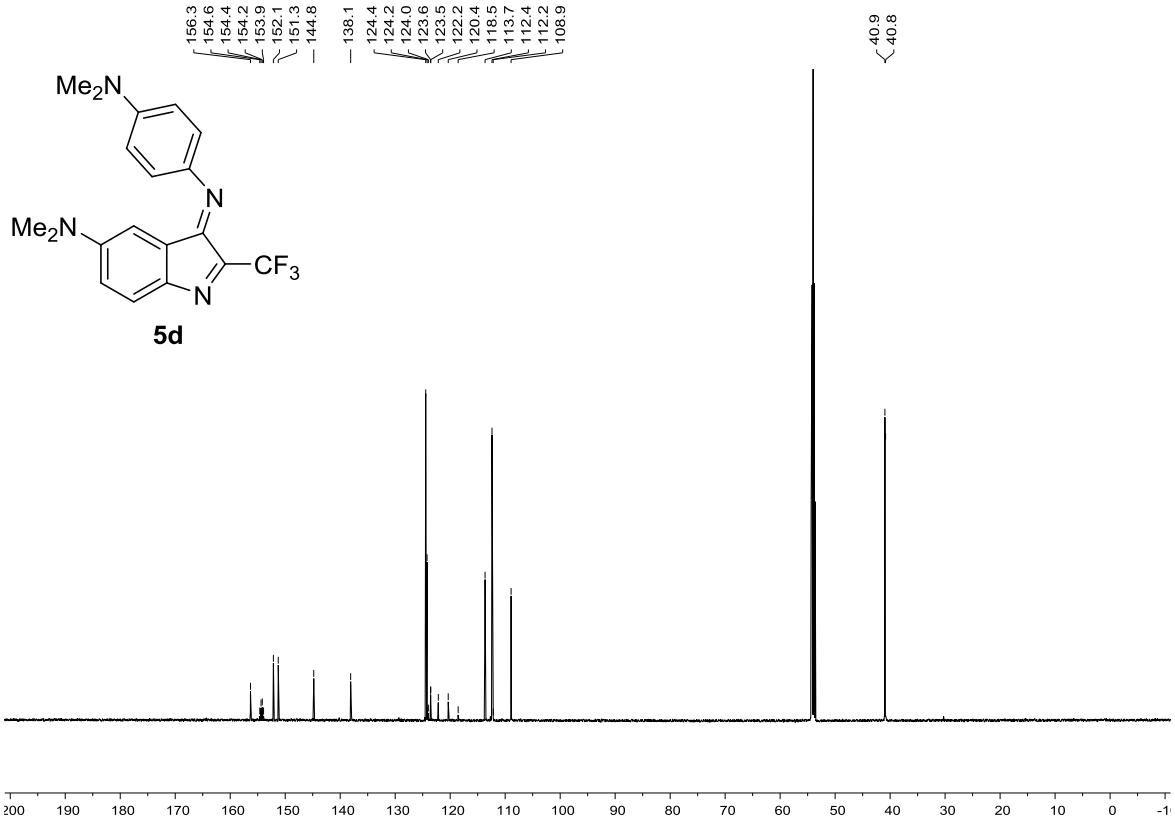
(*E*)-5-(Methylthio)-*N*-(4-(methylthio)phenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5c)

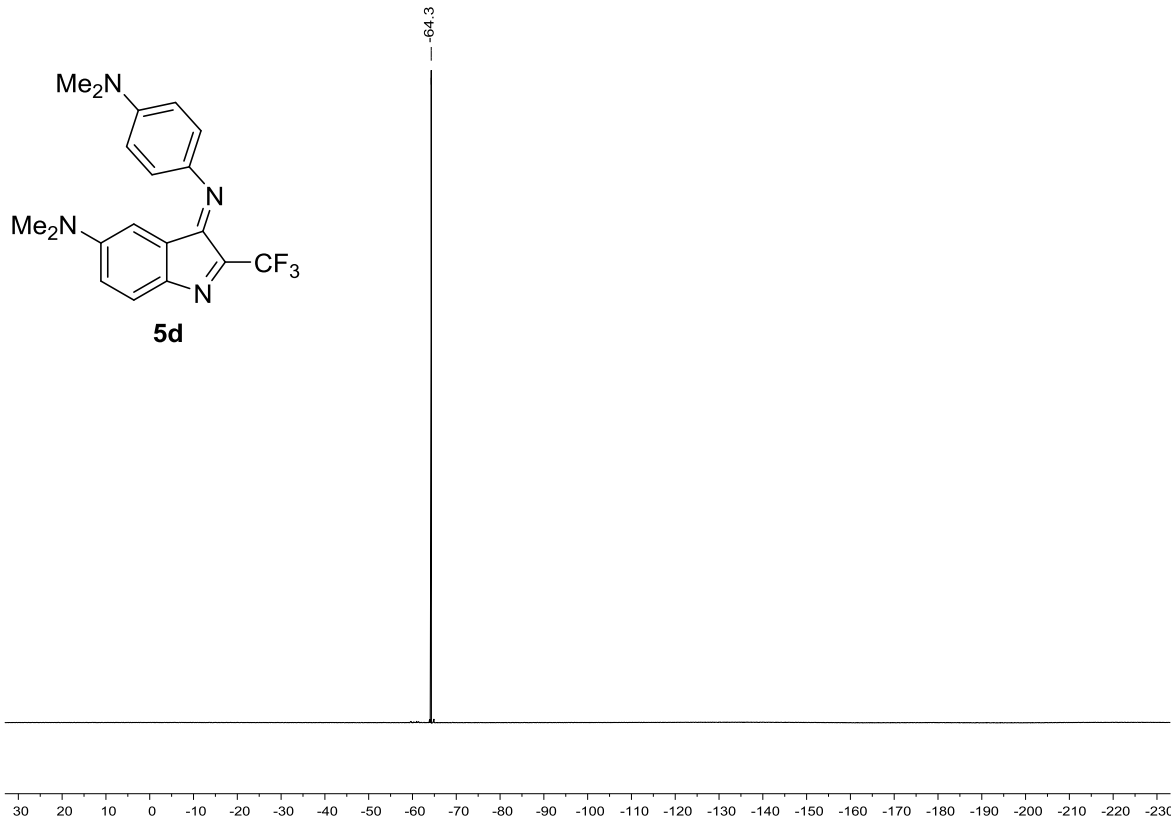




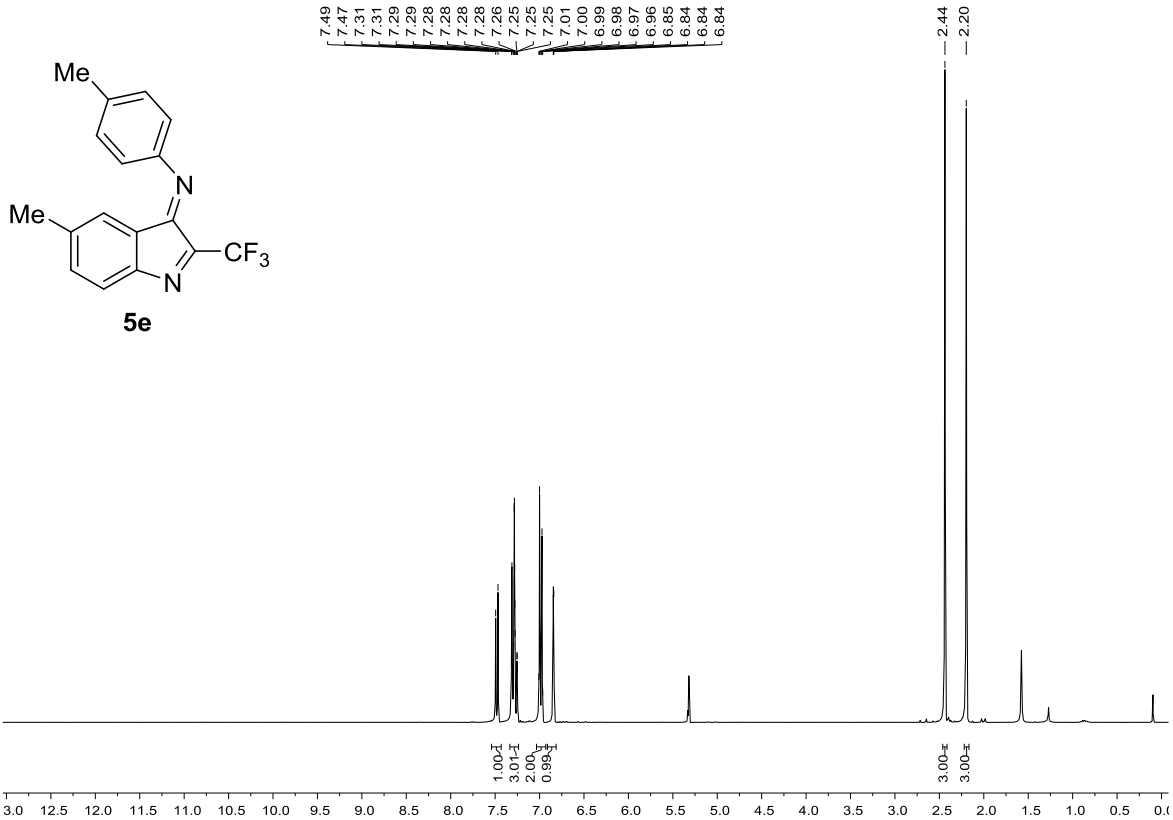
(*E*)-3-((4-(Dimethylamino)phenyl)imino)-*N*,*N*-dimethyl-2-(trifluoromethyl)-3*H*-indol-5-amine (5d)

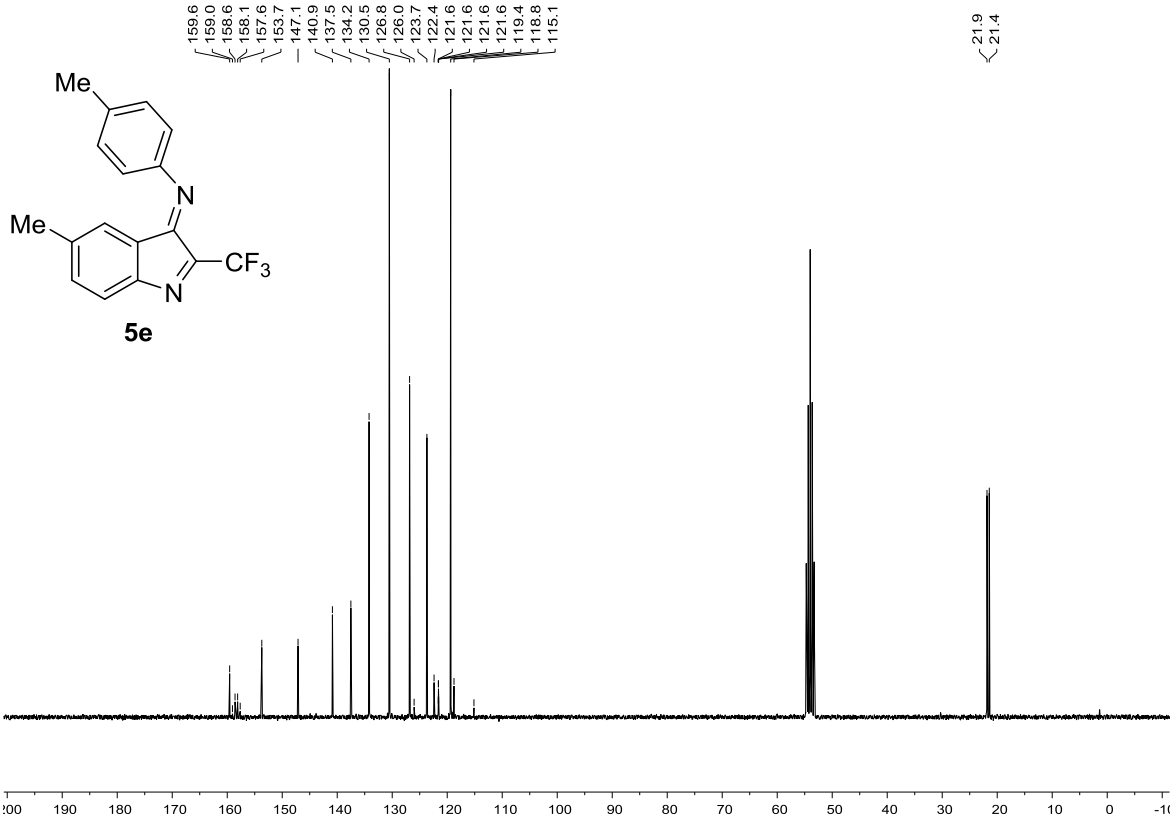


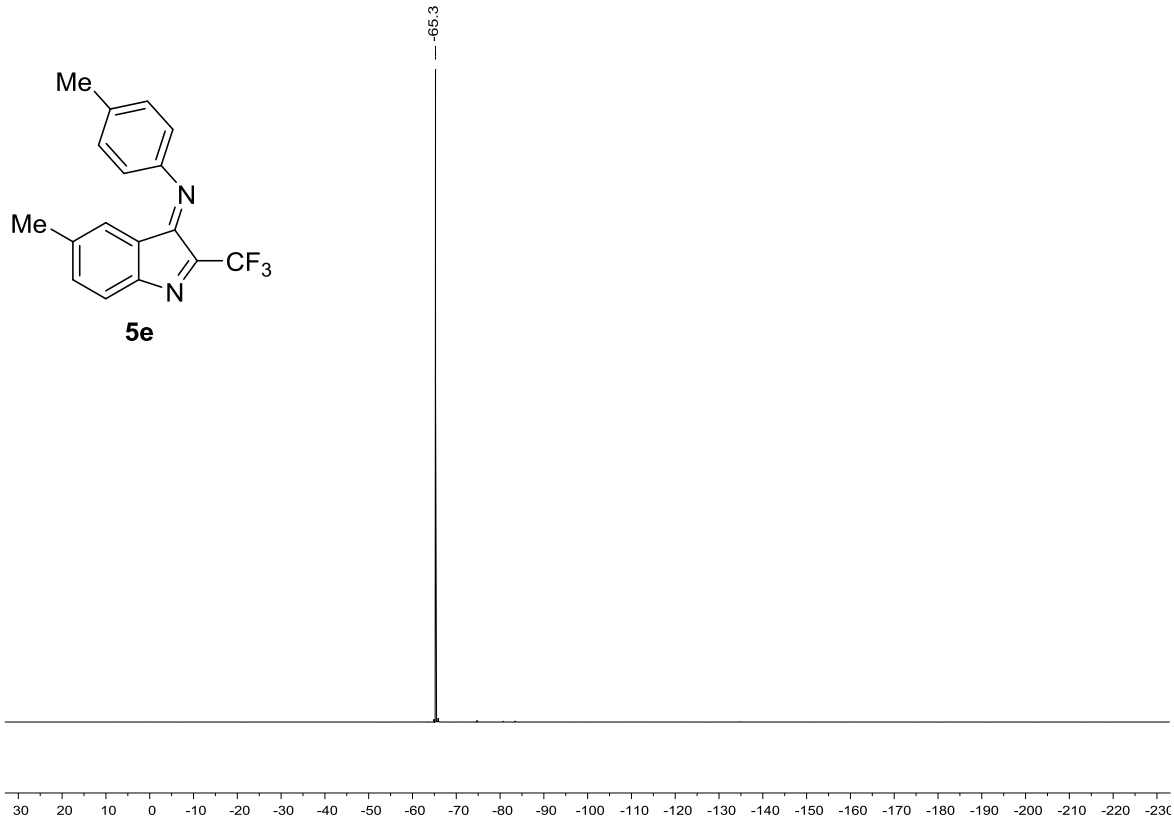

156.3
154.6
154.4
154.2
153.9
152.1
151.3
144.8
138.1
124.4
124.2
124.0
123.6
123.5
122.2
120.4
118.5
113.7
112.4
112.2
108.9
40.9
40.8
Me2N
N
Me2N
CF3
N
5d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


-64.3
Me2N
N
Me2N
CF3
N
5d
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230

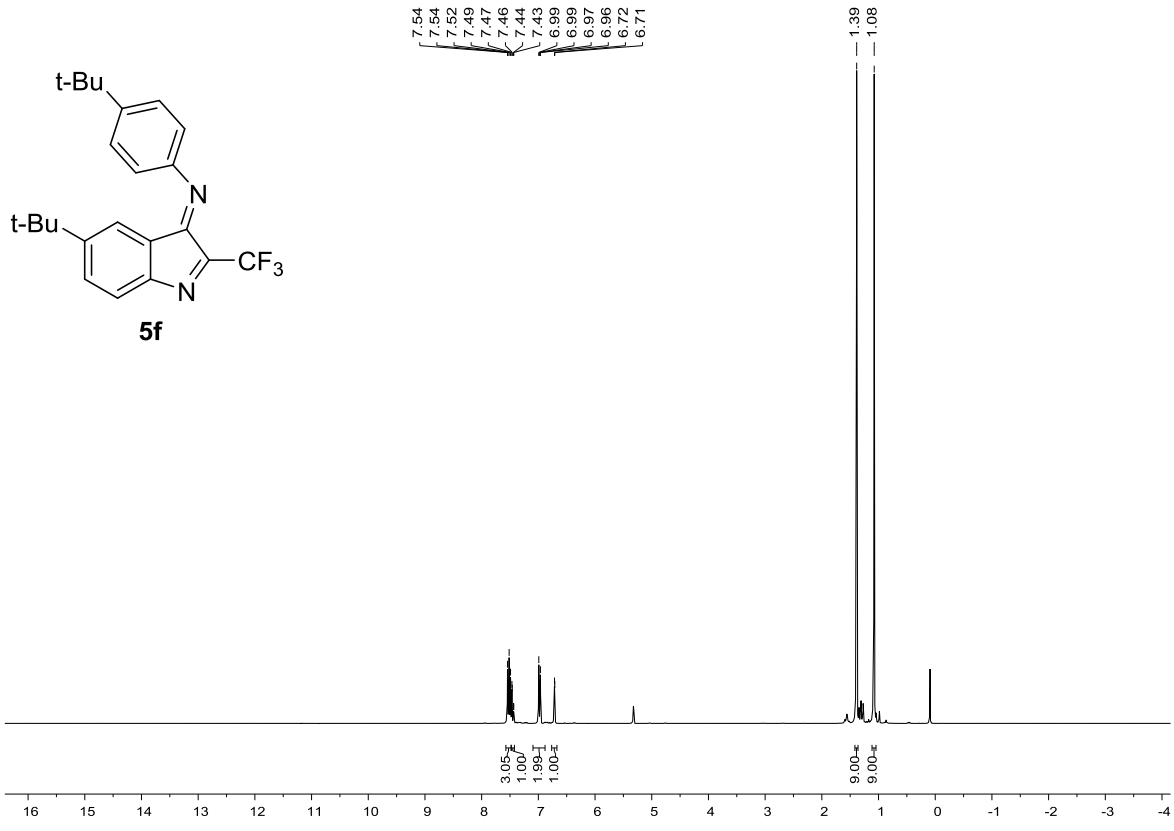
(*E*)-5-Methyl-*N*-(*p*-tolyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5e)

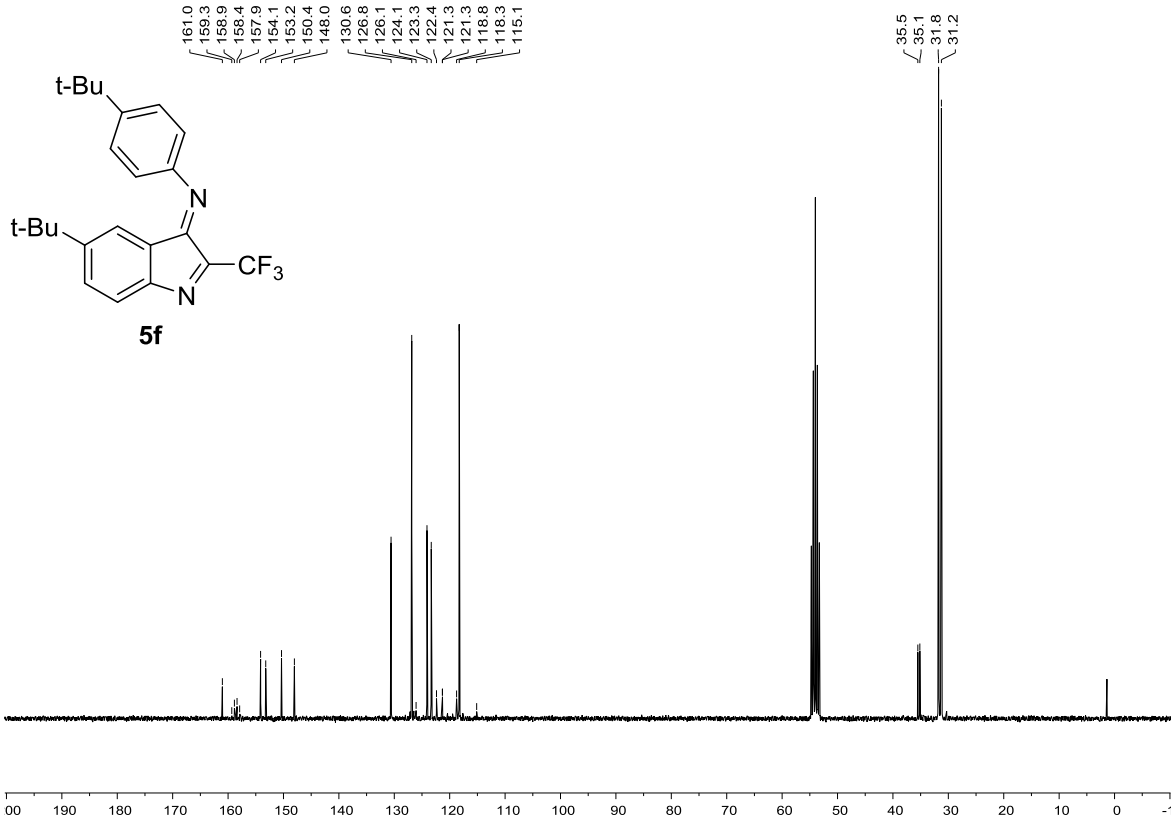


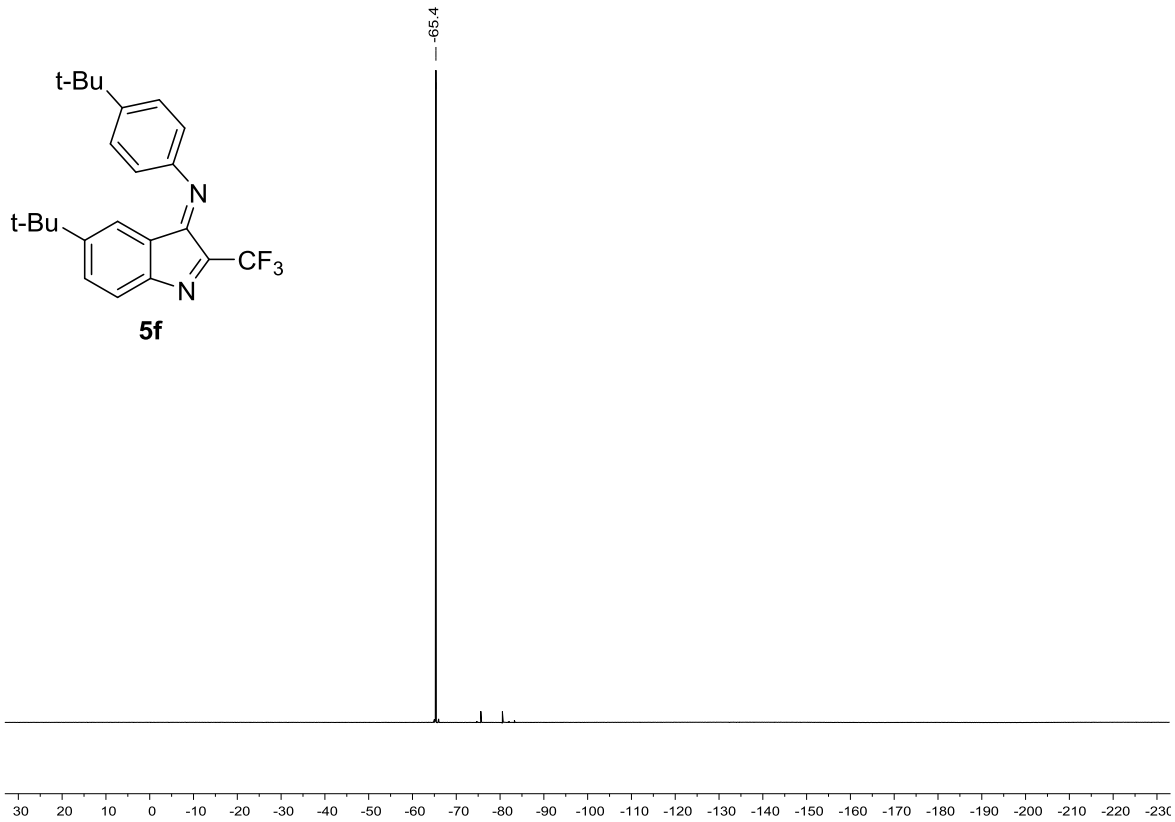




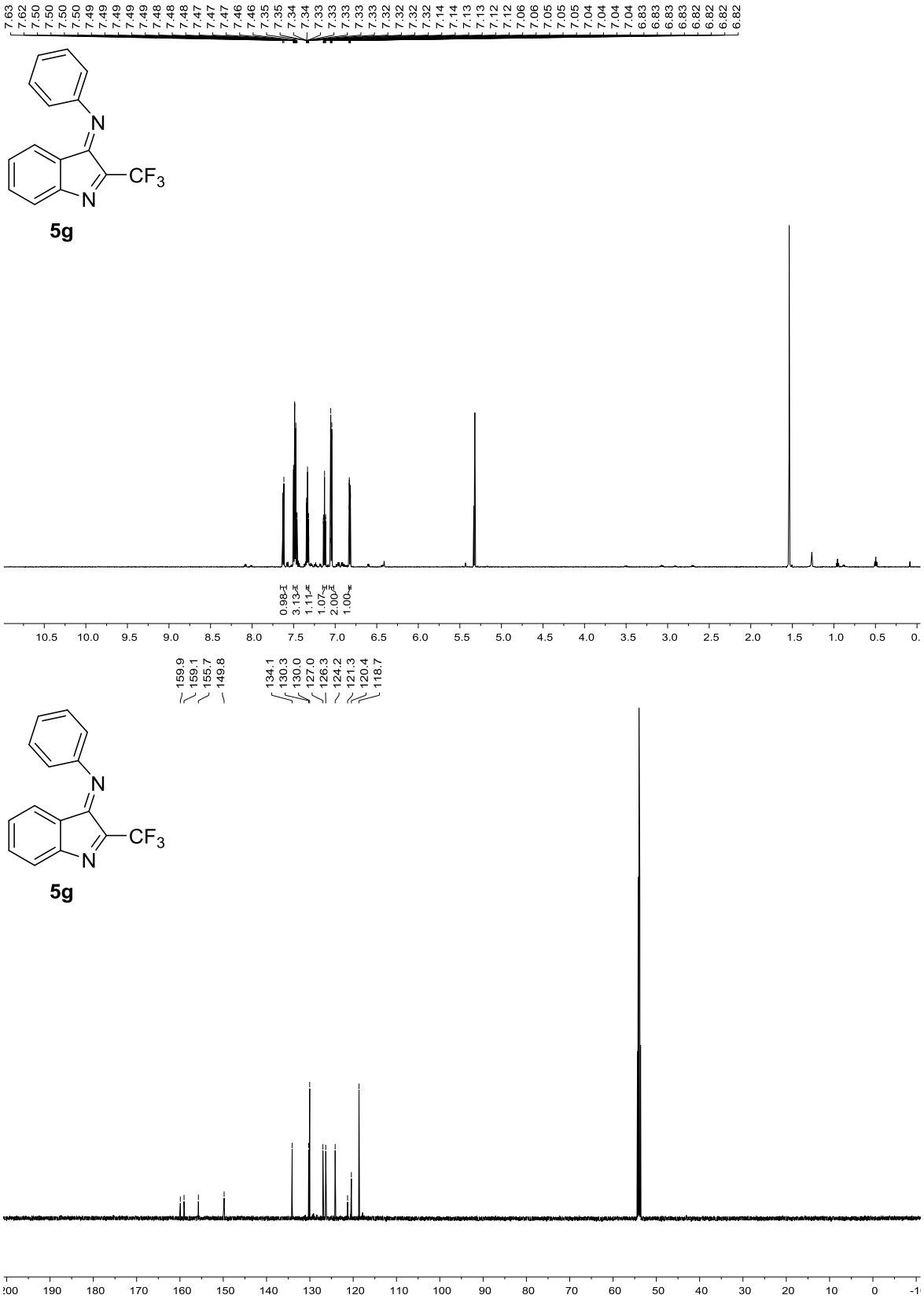
(*E*)-5-(*tert*-Butyl)-*N*-(4-(*tert*-butyl)phenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5f)

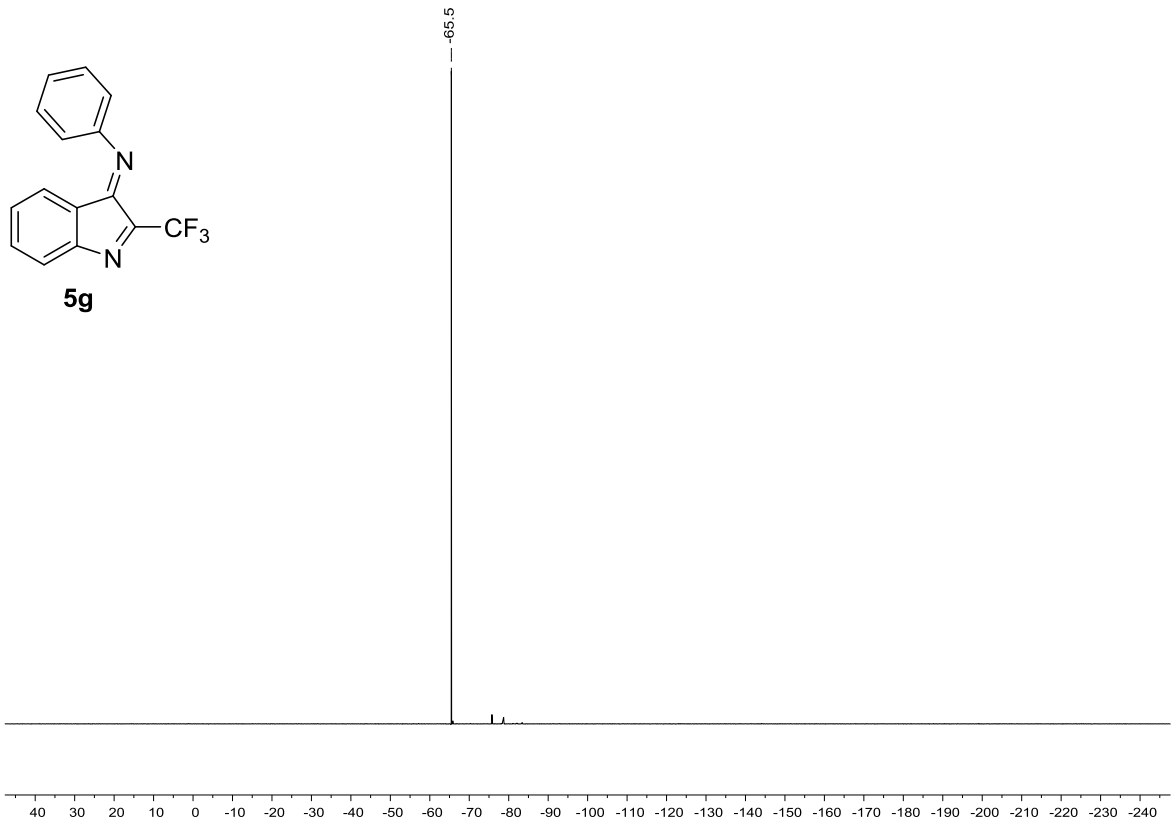



161.0
159.3
158.9
158.4
157.9
154.1
153.2
150.4
148.0
130.6
126.8
126.1
124.1
123.3
122.4
121.3
121.3
118.8
118.3
115.1
35.5
35.1
31.8
31.2
t-Bu
t-Bu
N
N
CF3
5f
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

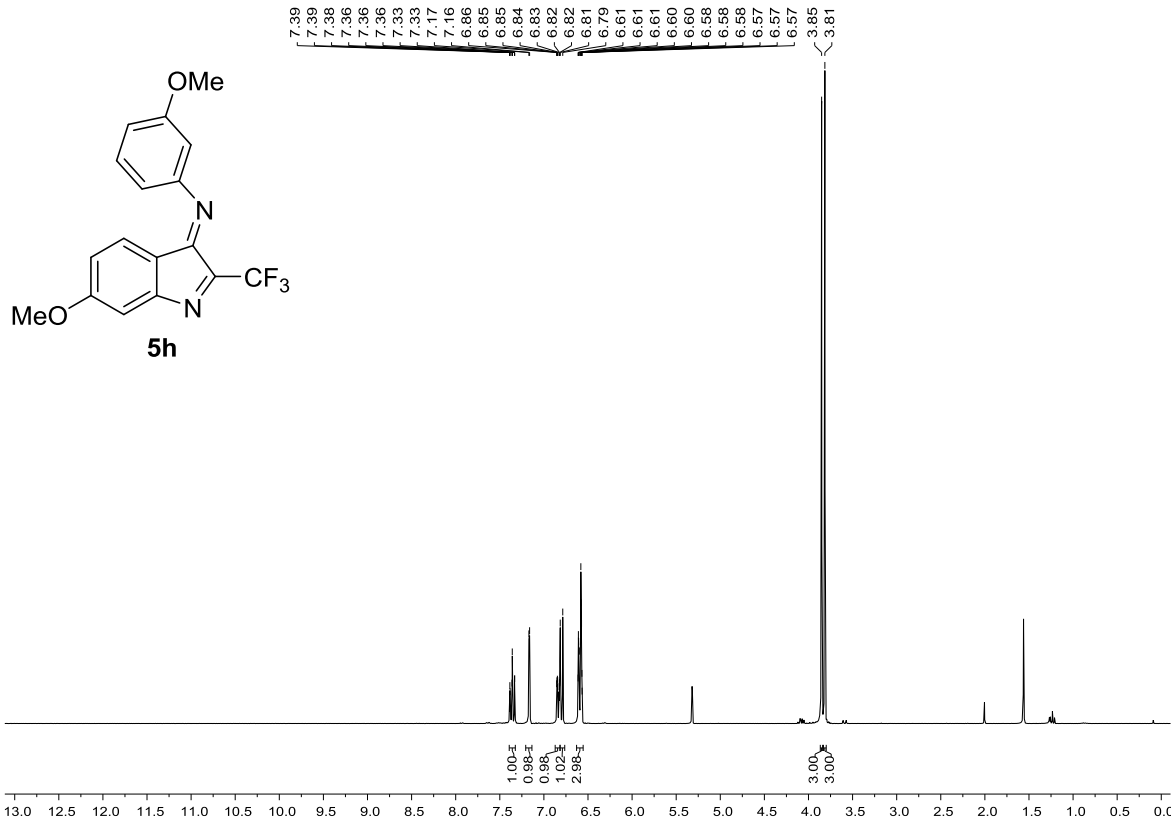

-65.4
t-Bu
t-Bu
N
N
CF3
5f
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230

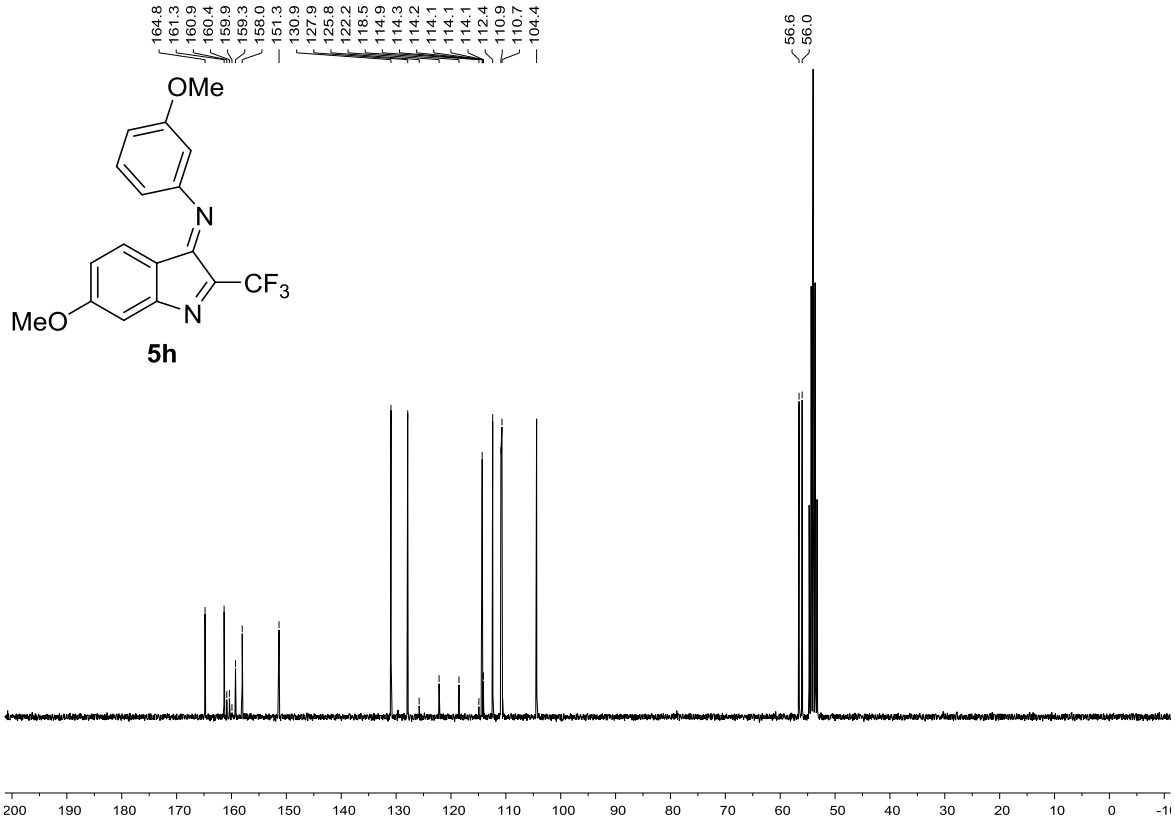
(*E*)-*N*-Phenyl-2-(trifluoromethyl)-3*H*-indol-3-imine (5g)

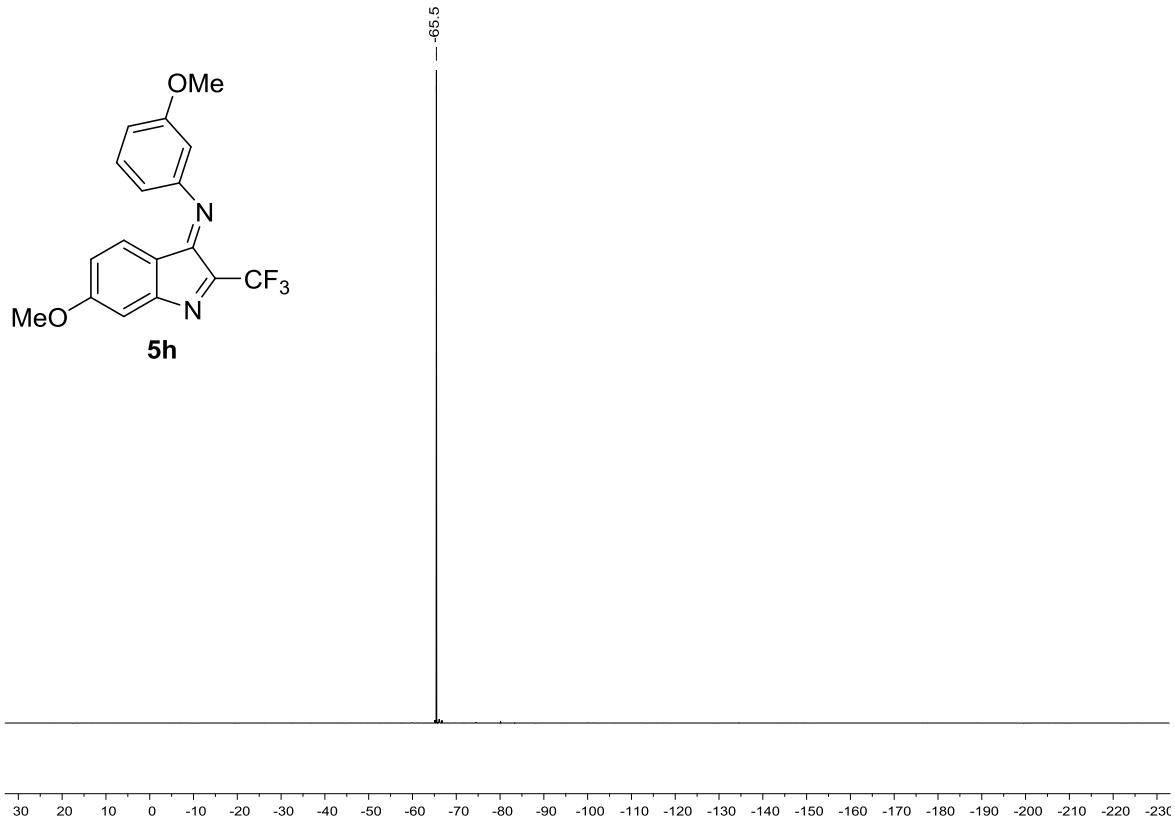




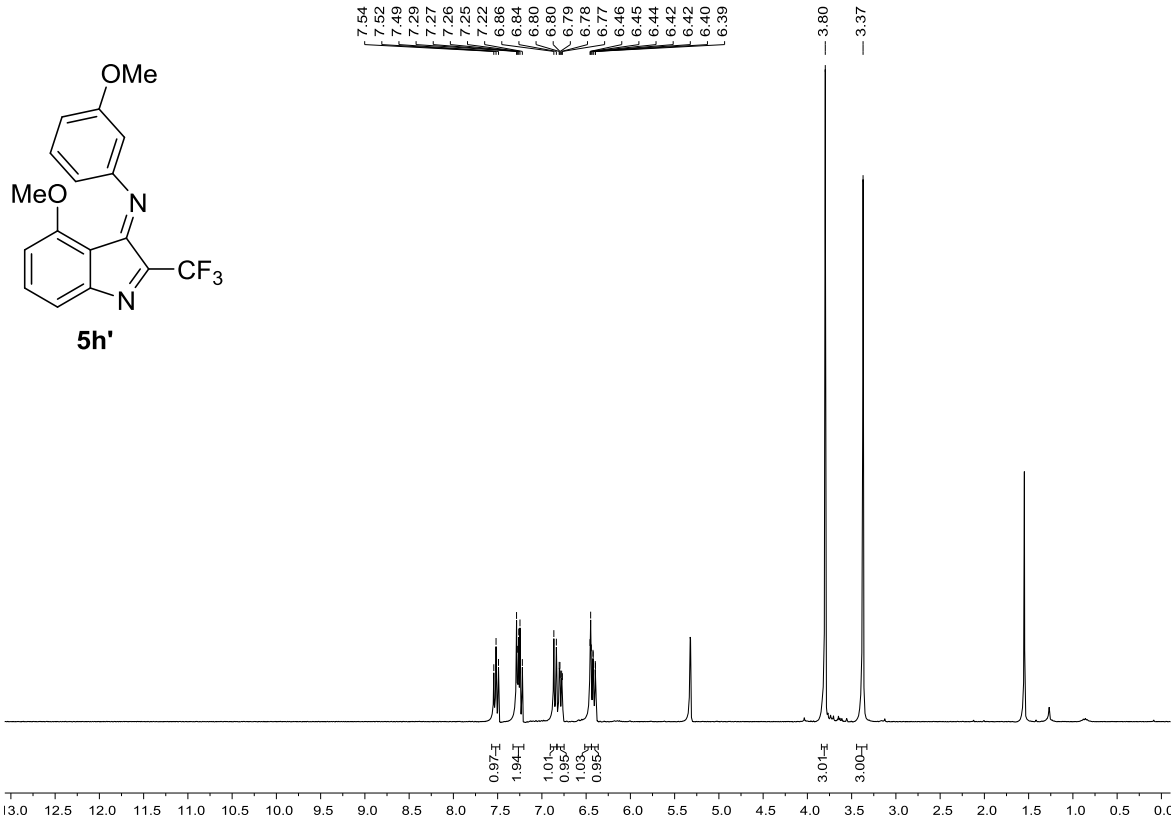
(*E*)-6-Methoxy-*N*-(3-methoxyphenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5h)

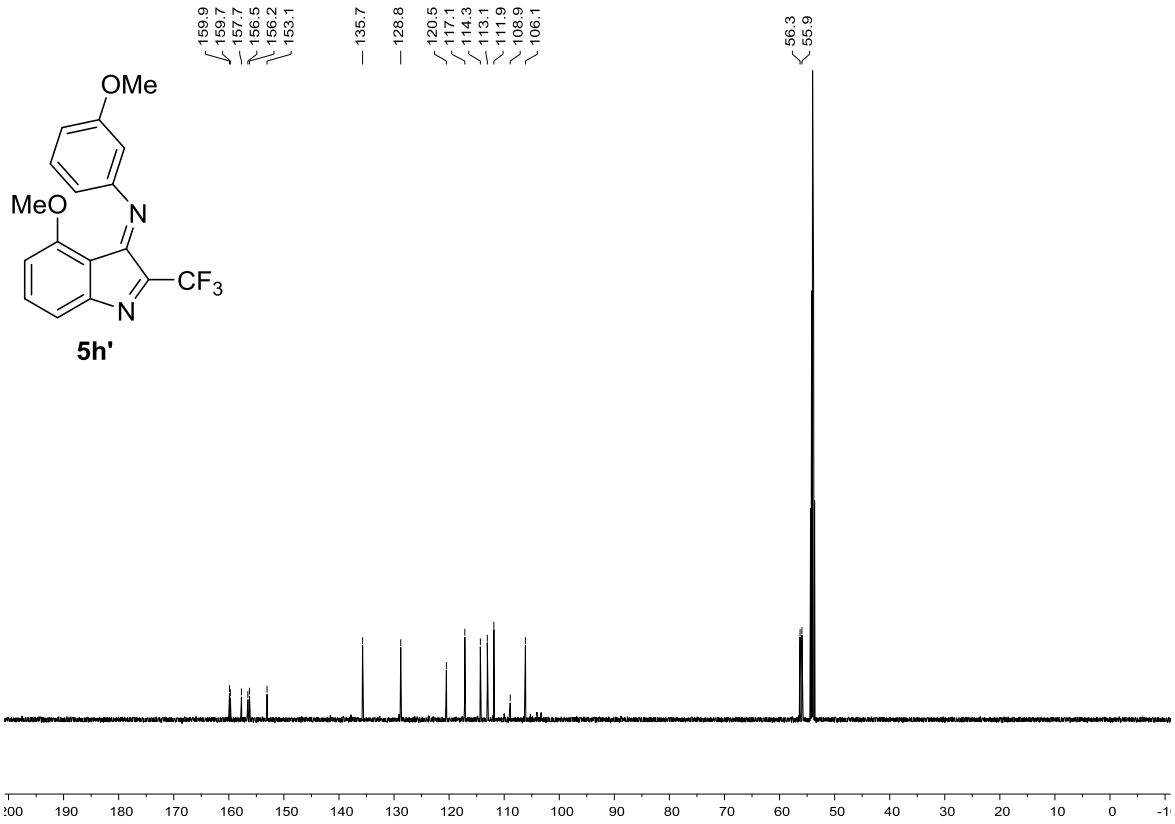


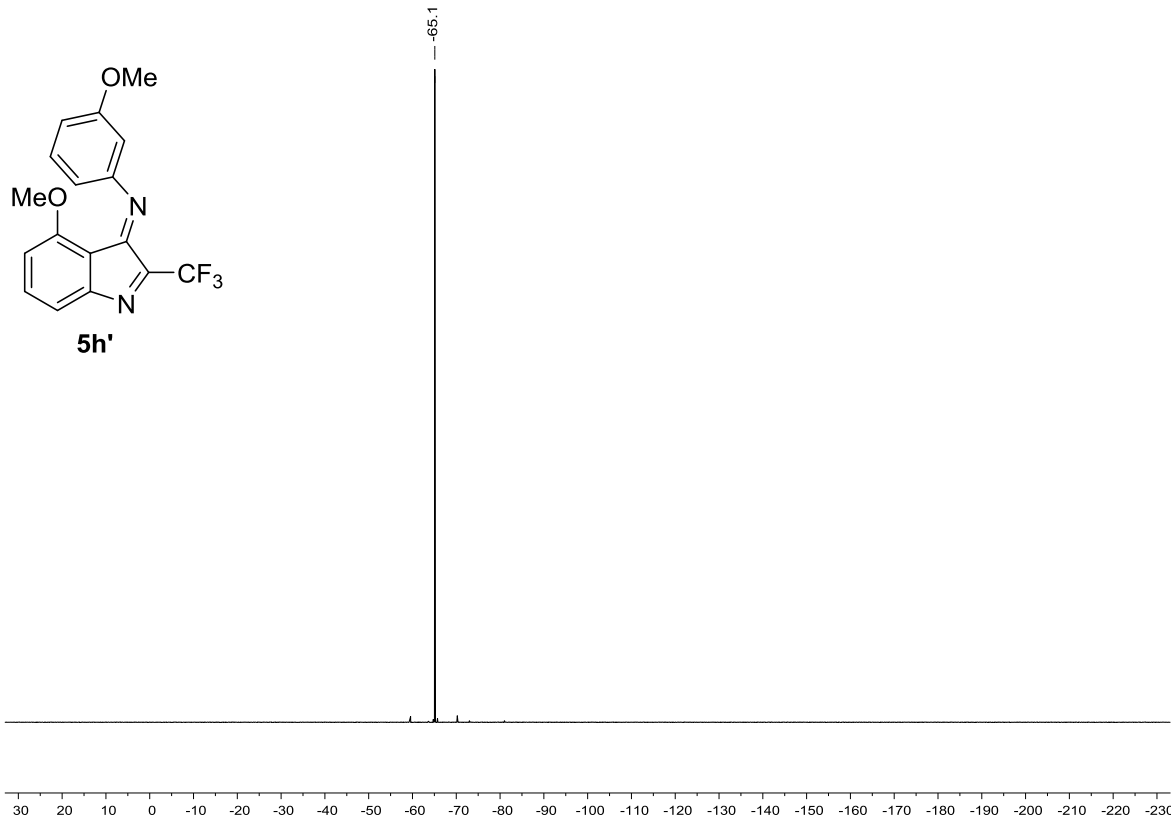

164.8
161.3
160.9
160.4
159.9
159.3
158.0
151.3
130.9
127.9
125.8
122.2
118.5
114.9
114.3
114.2
114.1
114.1
112.4
110.9
110.7
104.4
56.6
56.0
OMe
N
CF3
MeO
N
5h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


-65.5
OMe
N
CF3
MeO
N
5h
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220

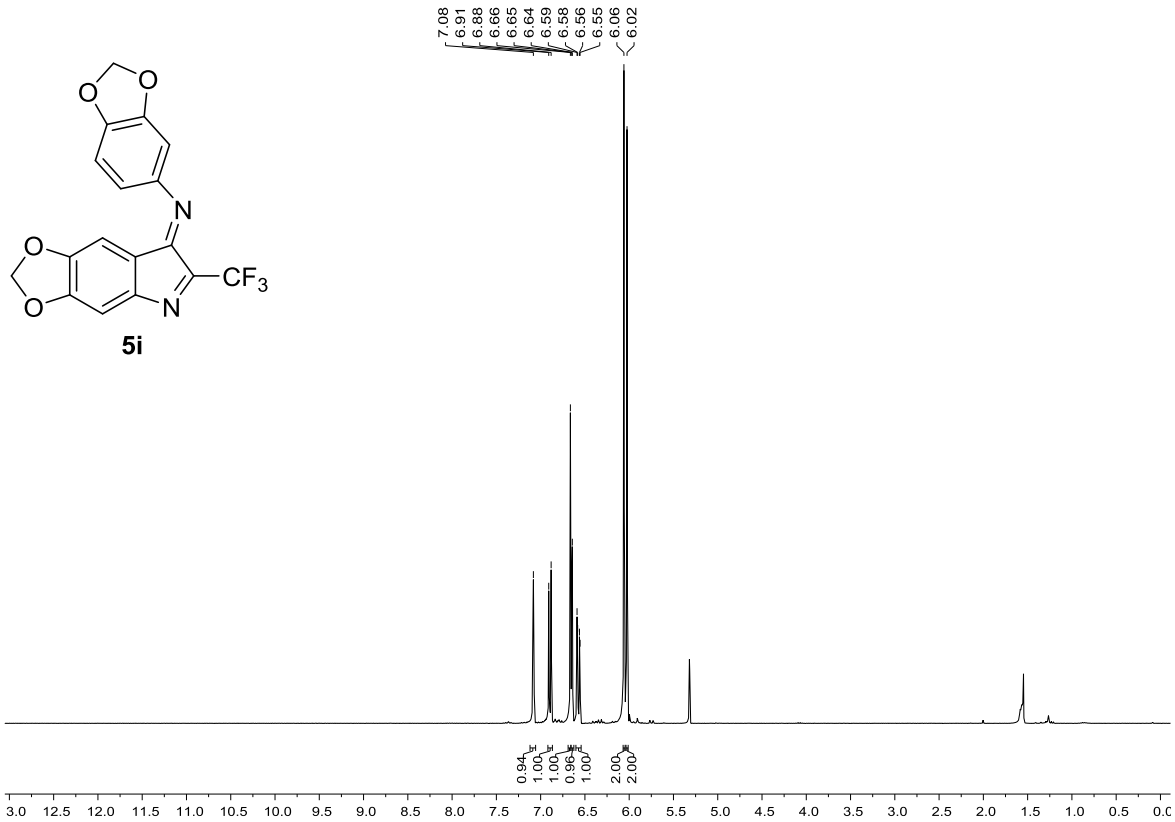
(*E*)-4-Methoxy-*N*-(3-methoxyphenyl)-2-(trifluoromethyl)-3*H*-indol-3-imine (5h′)

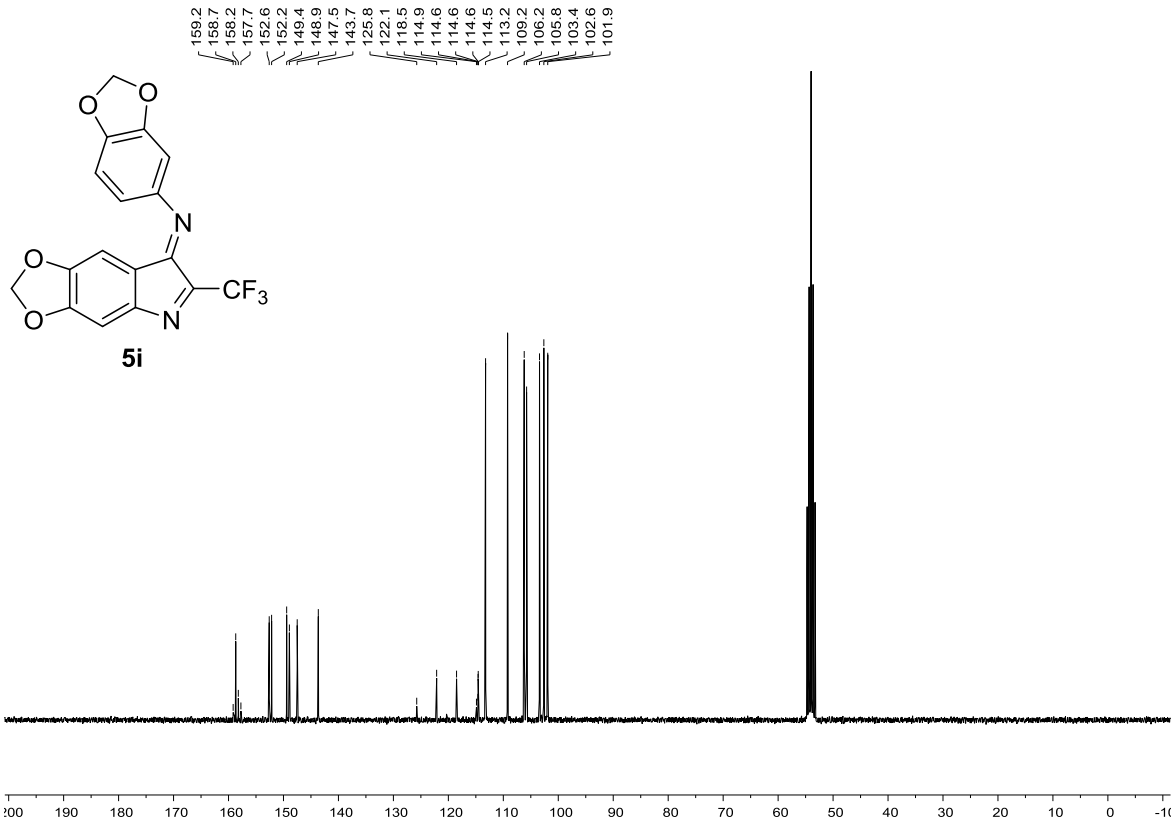


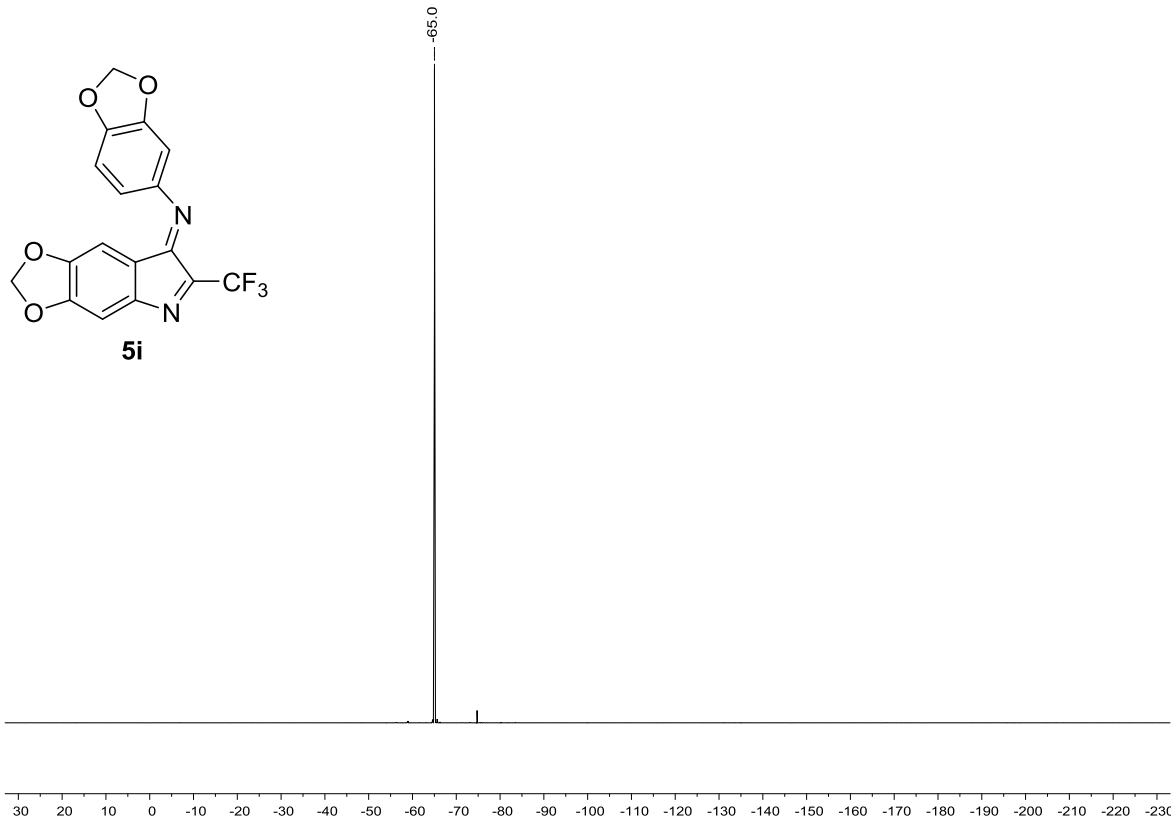




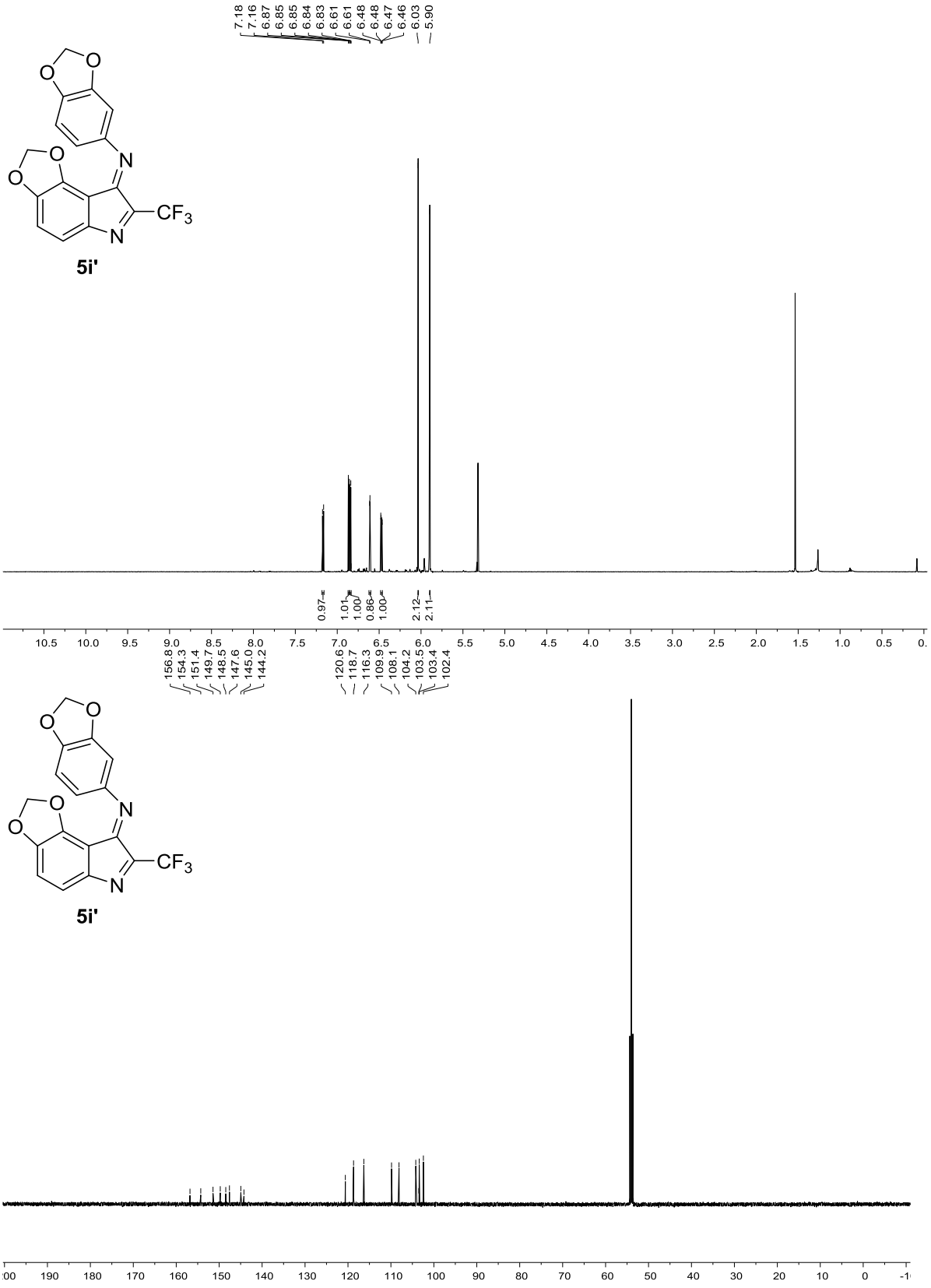
(*E*)-*N*-(Benzo[*d*][1,3]dioxol-5-yl)-6-(trifluoromethyl)-7*H*-[1,3]dioxolo[4,5-*f*]indol-7-imine (5i)

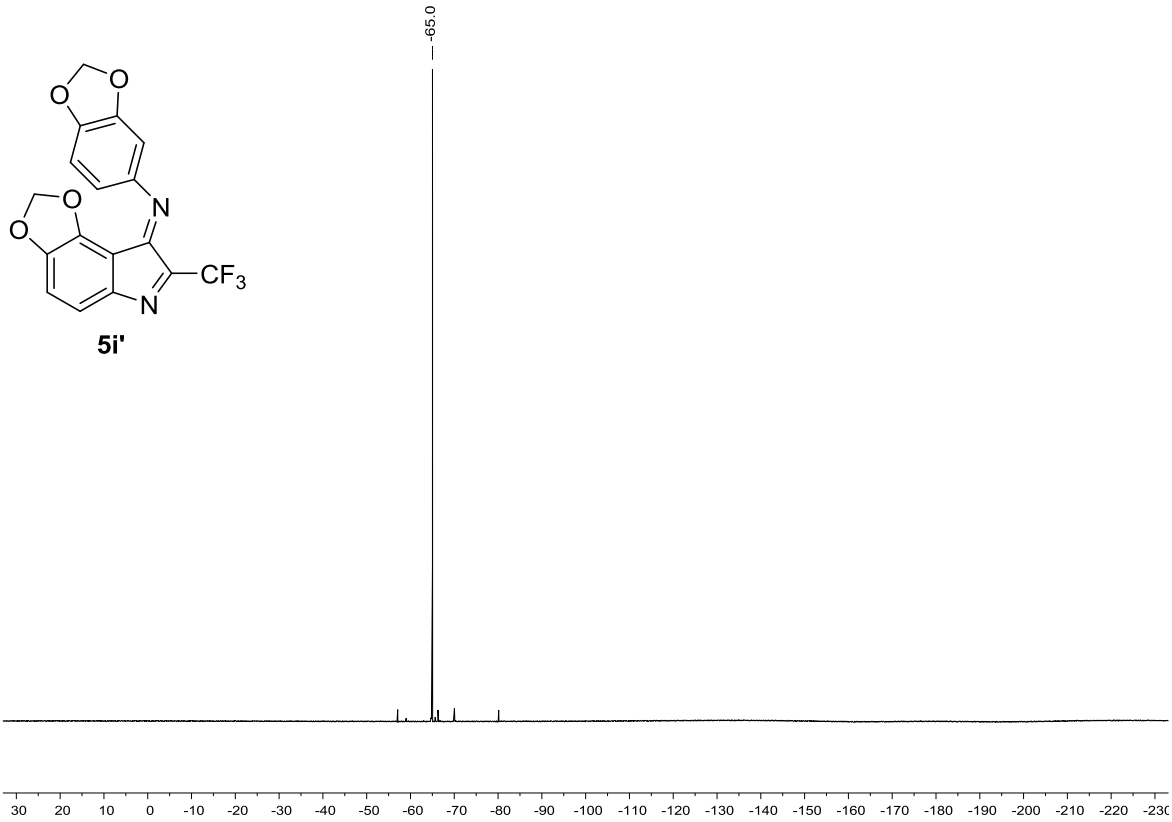



159.2
158.7
158.2
157.7
152.6
152.2
149.4
148.9
147.5
143.7
125.8
122.1
118.5
114.9
114.6
114.6
114.6
114.5
113.2
109.2
106.2
105.8
103.4
102.6
101.9
O
O
N
O
O
N
CF3
5i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


-65.0
O
O
N
O
O
N
CF3
5i
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230

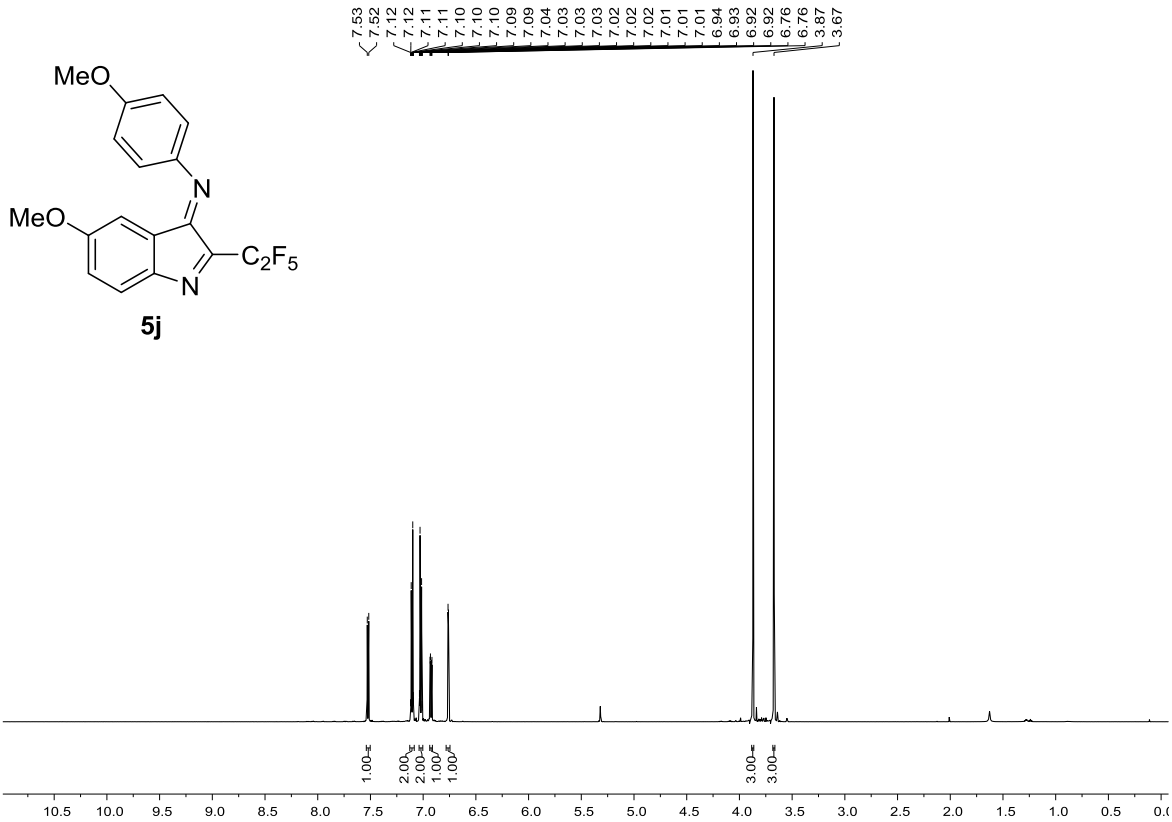
(*E*)-*N*-(Benzo[*d*][1,3]dioxol-5-yl)-7-(trifluoromethyl)-6*H*-[1,3]dioxolo[4,5-*g*]indol-6-imine (5i′)



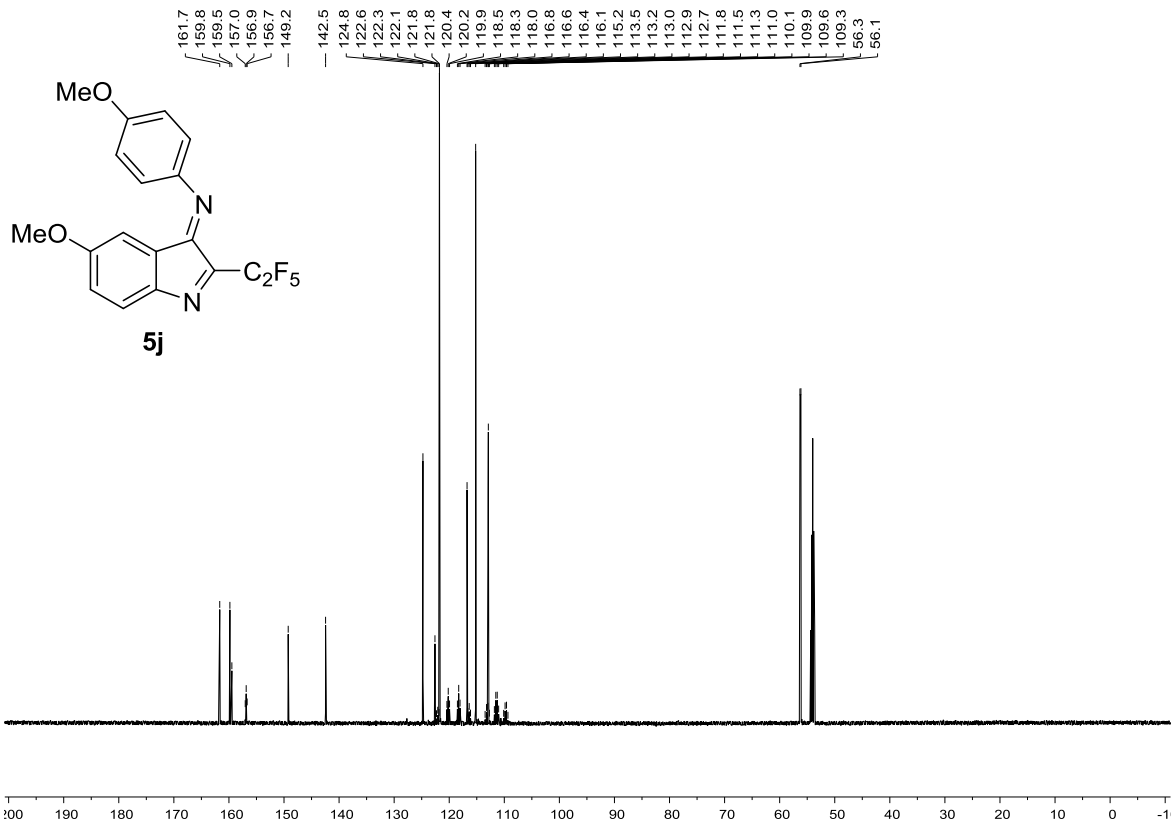


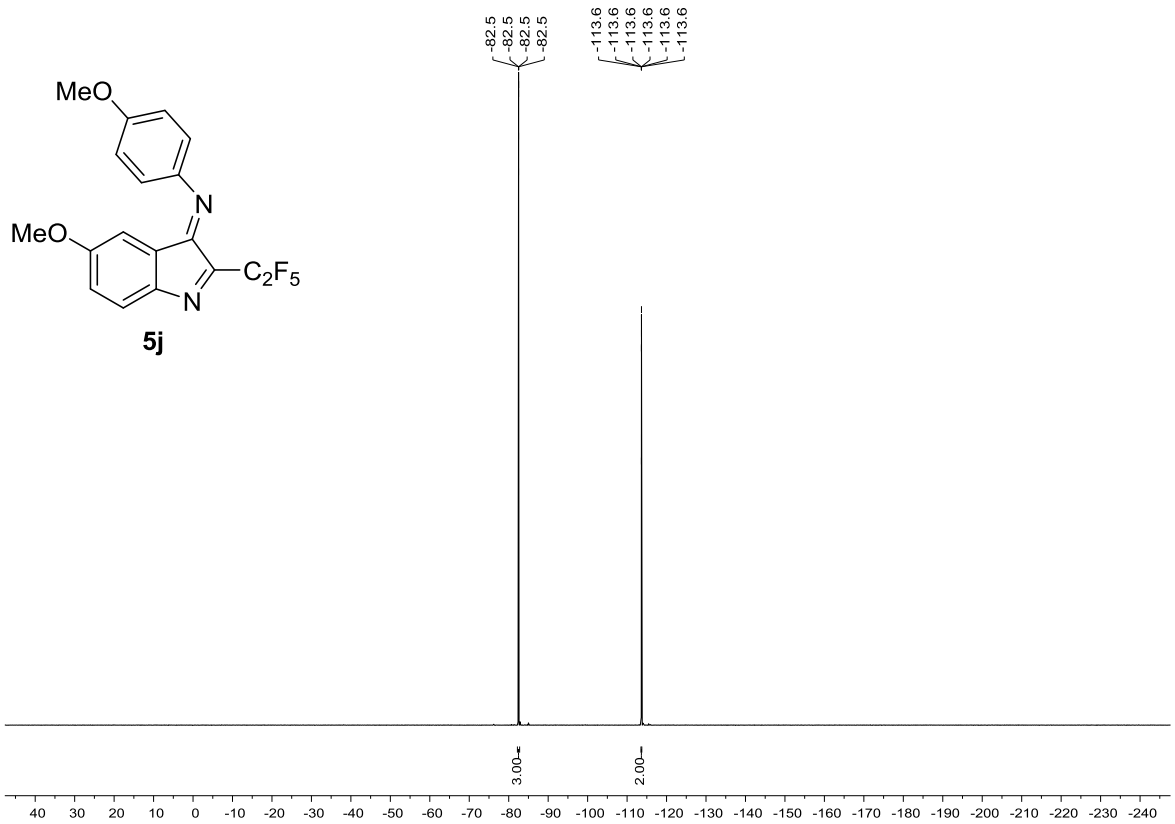
5i'

(*E*)-5-Methoxy-*N*-(4-methoxyphenyl)-2-(perfluoroethyl)-3*H*-indol-3-imine (5j)

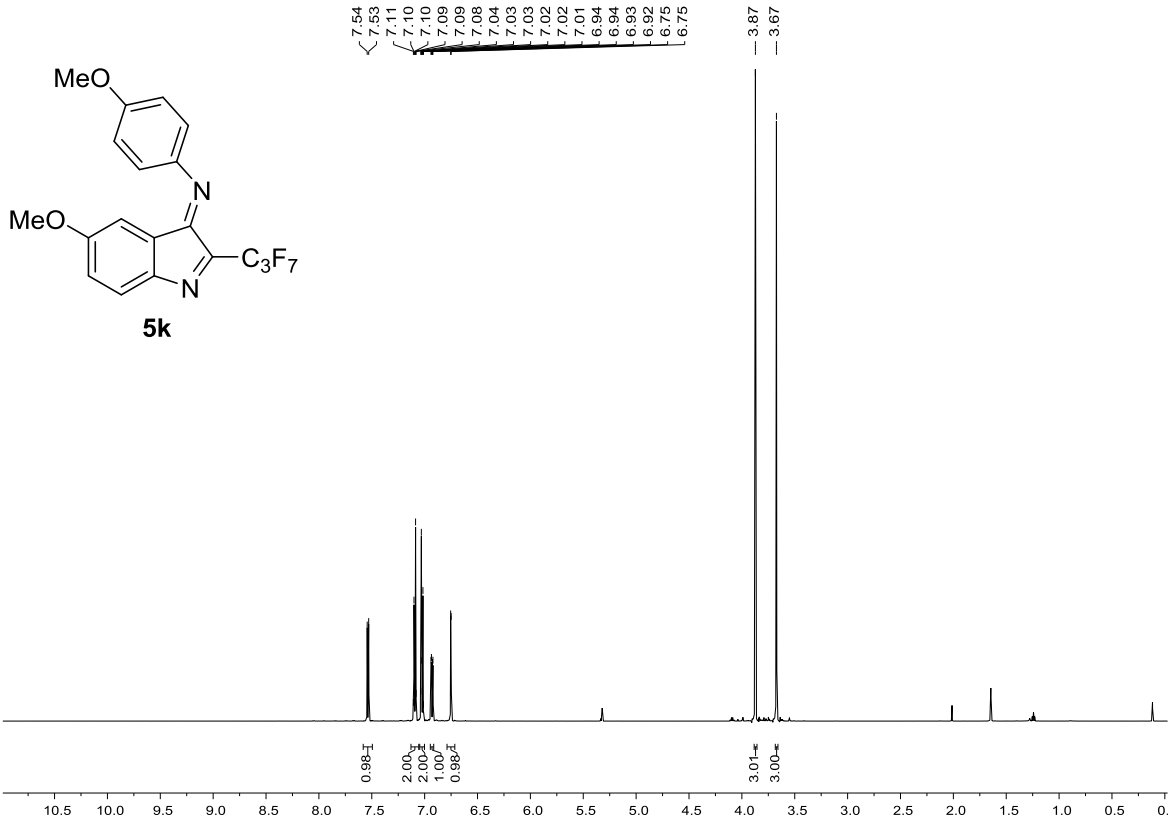


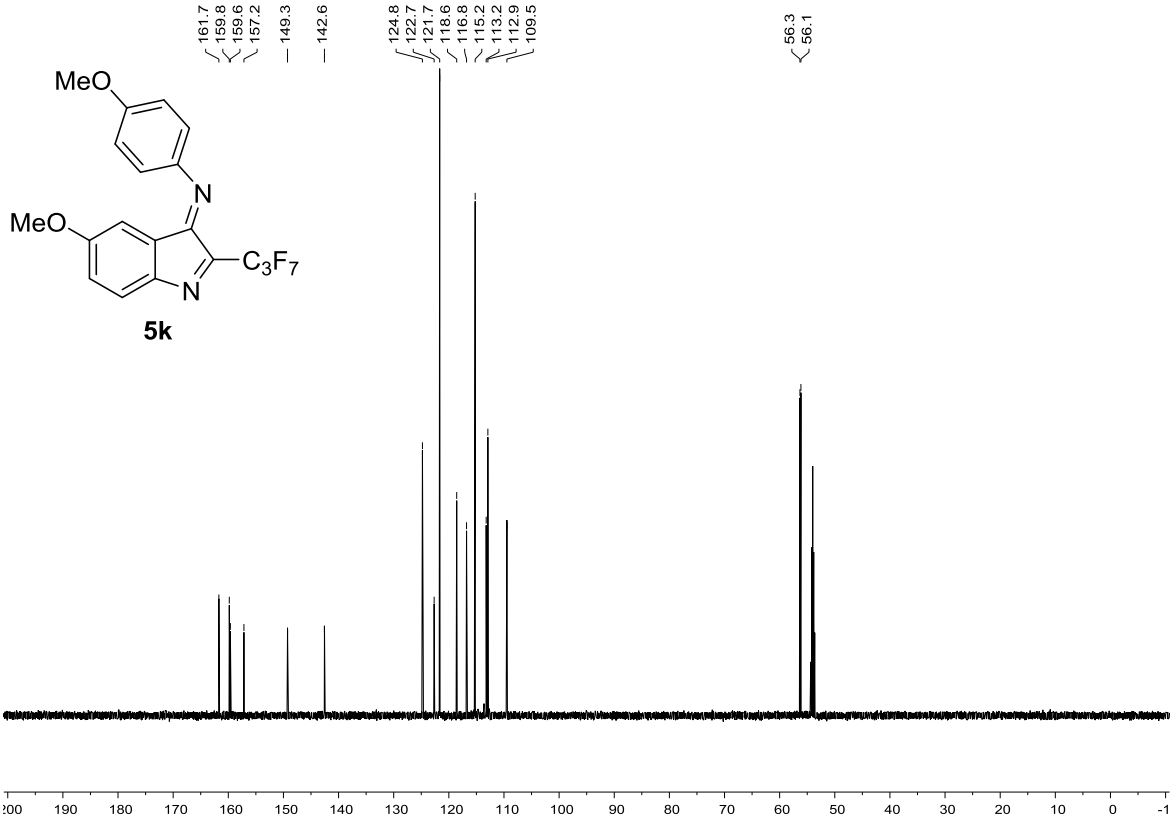
5j

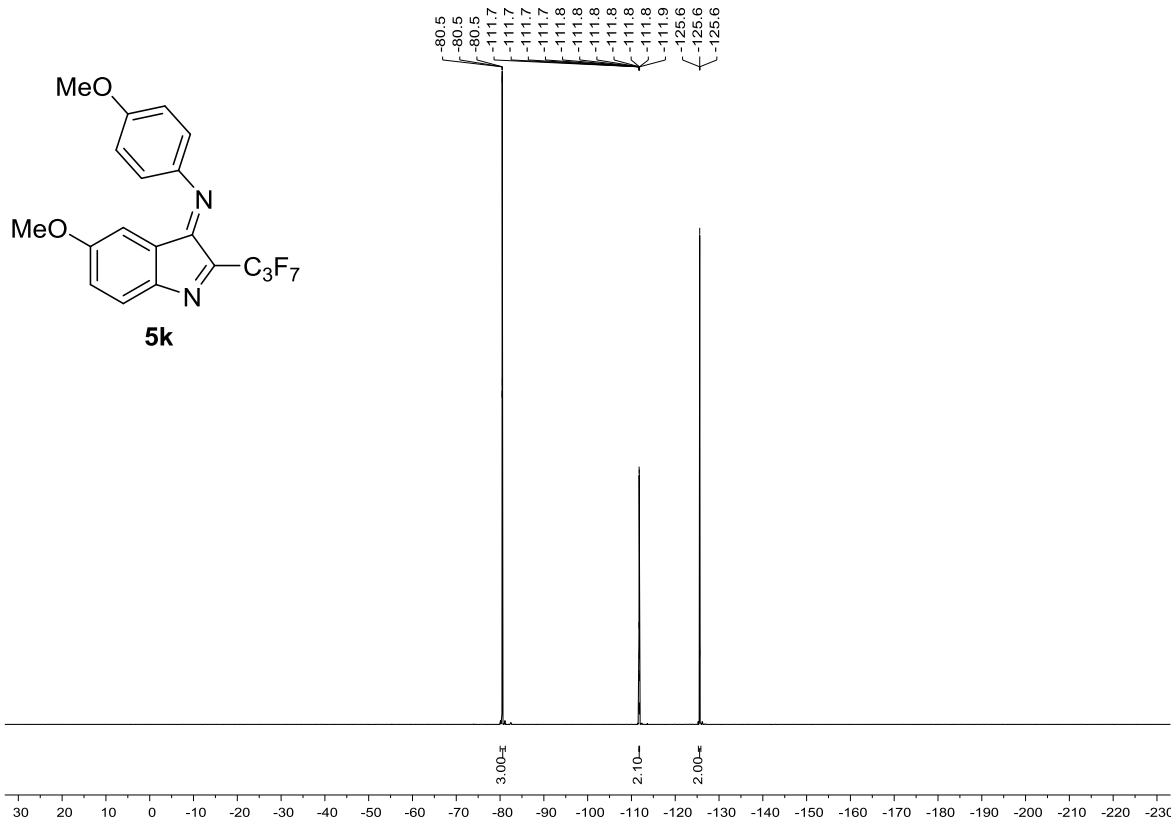

161.7
159.8
159.5
157.0
156.9
156.7
149.2
142.5
124.8
122.6
122.3
122.1
121.8
121.8
120.4
120.2
119.9
118.5
118.3
118.0
116.8
116.6
116.4
116.1
115.2
113.5
113.2
113.0
112.9
112.7
111.8
111.5
111.3
111.0
110.1
109.9
109.6
109.3
56.3
56.1
MeO
N
MeO
C_2F_5
N
5j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1


-82.5
-82.5
-82.5
-82.5
-113.6
-113.6
-113.6
-113.6
-113.6
-113.6
MeO
N
MeO
C_2F_5
N
5j
3.00
2.00
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240

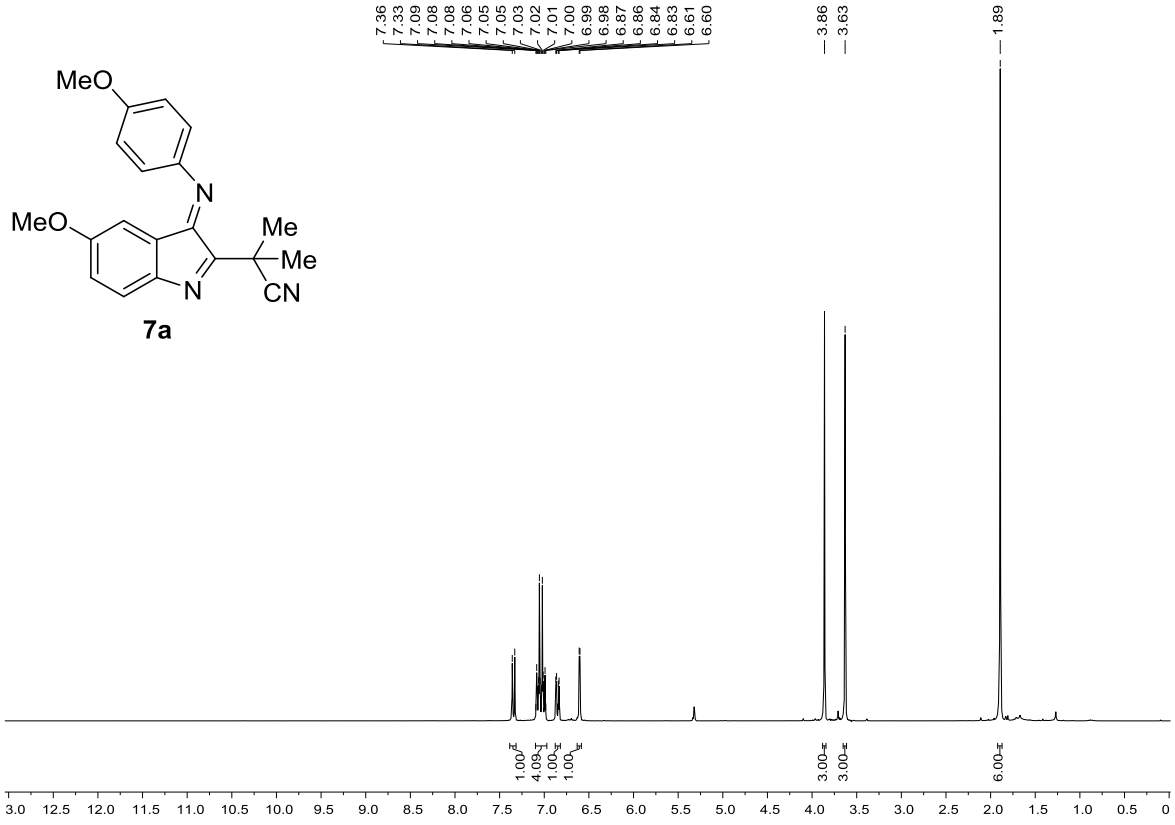
(*E*)-5-Methoxy-*N*-(4-methoxyphenyl)-2-(perfluoropropyl)-3*H*-indol-3-imine (5k)

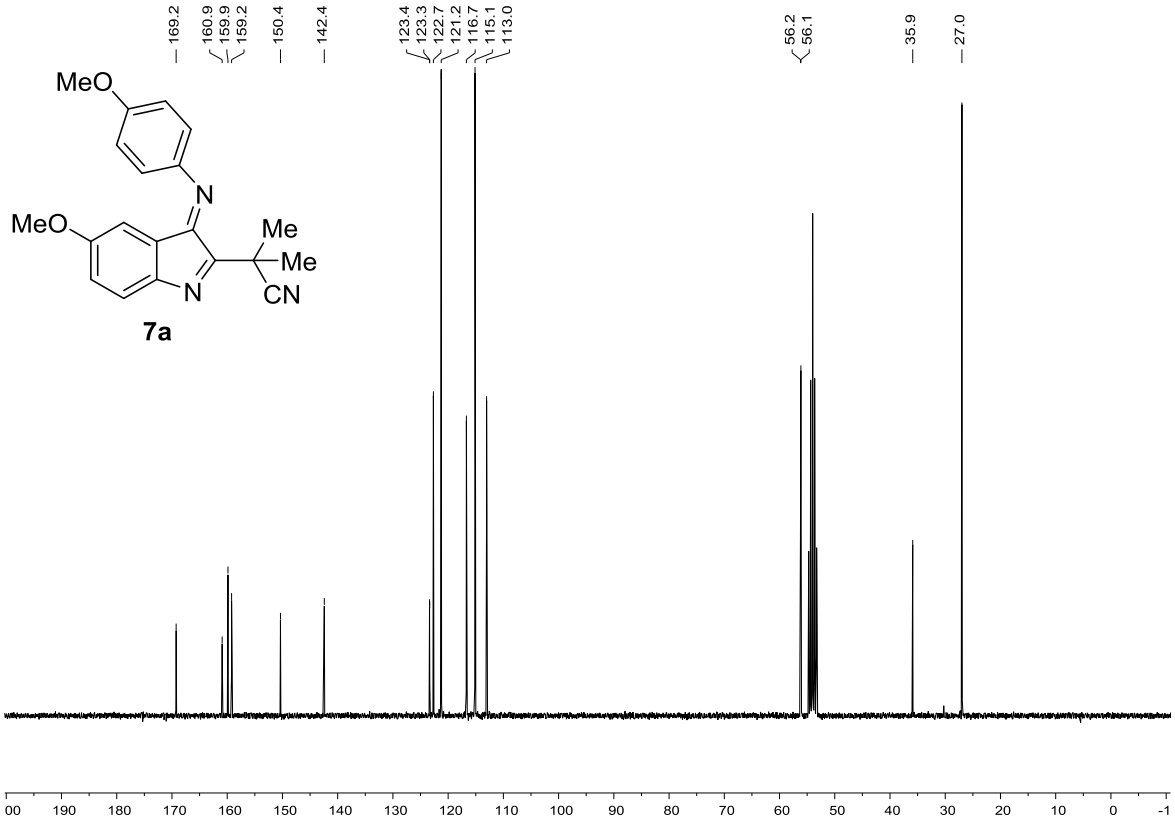




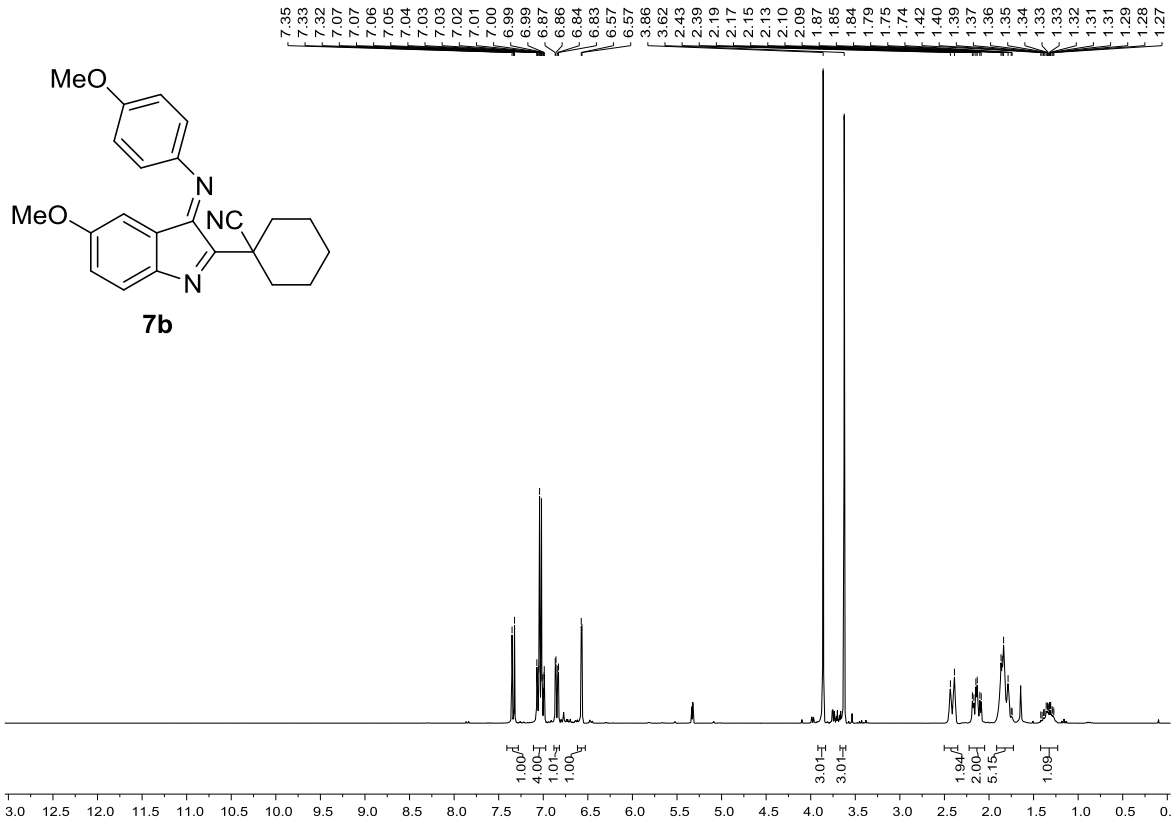


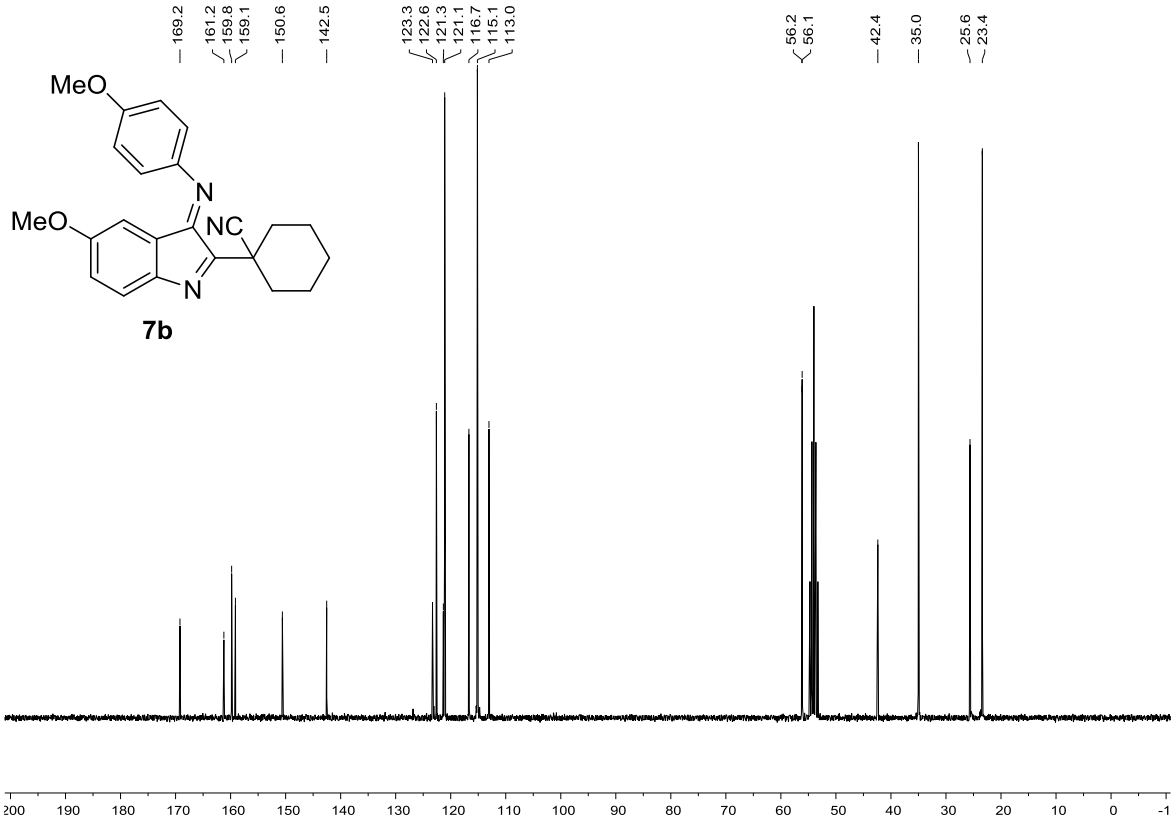
(*E*)-2-(5-Methoxy-3-((4-methoxyphenyl)imino)-3*H*-indol-2-yl)-2-methylpropanenitrile (7a)



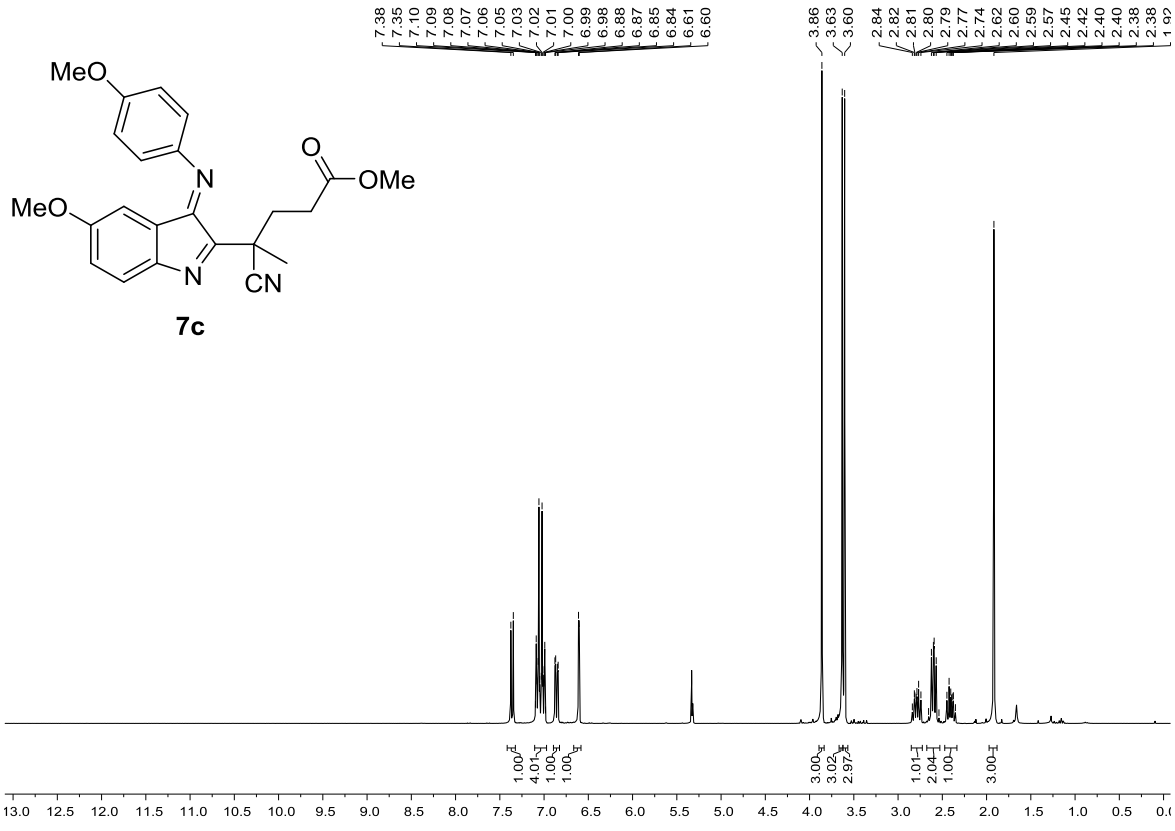


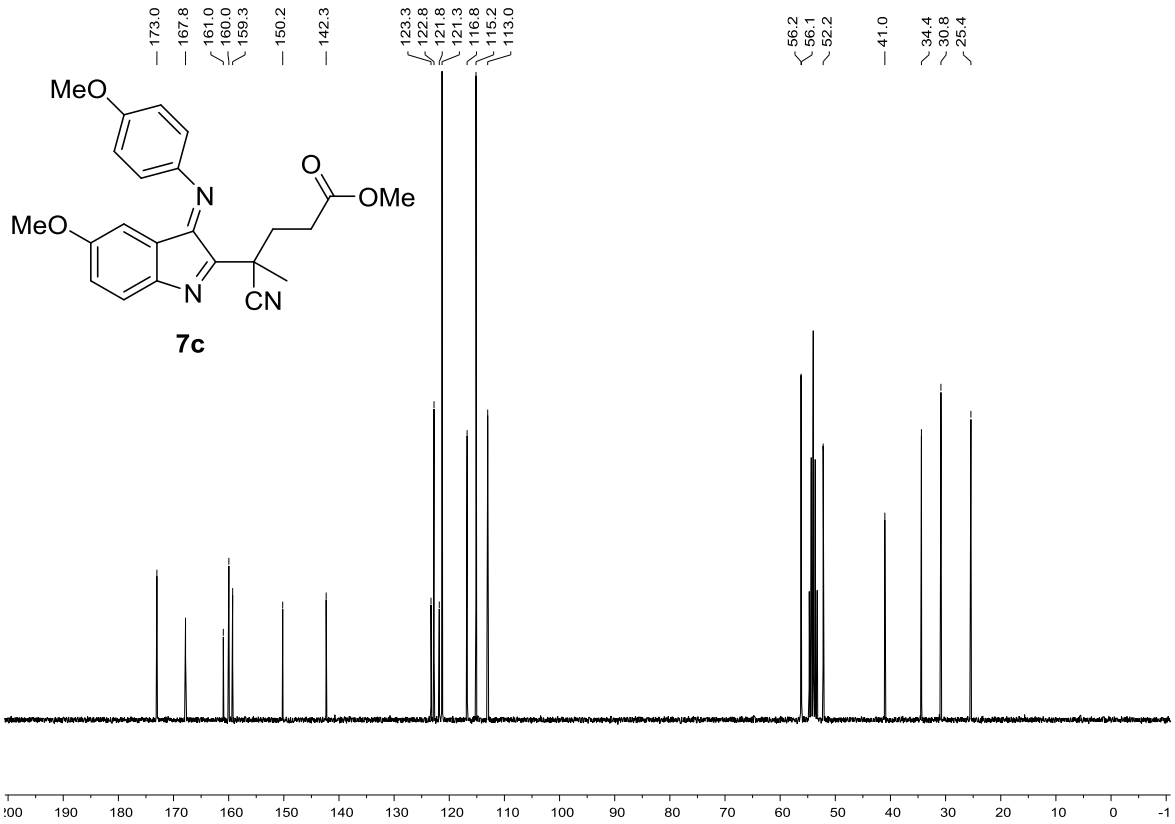
(*E*)-1-(5-Methoxy-3-((4-methoxyphenyl)imino)-3*H*-indol-2-yl)cyclohexane-1-carbonitrile (7b)





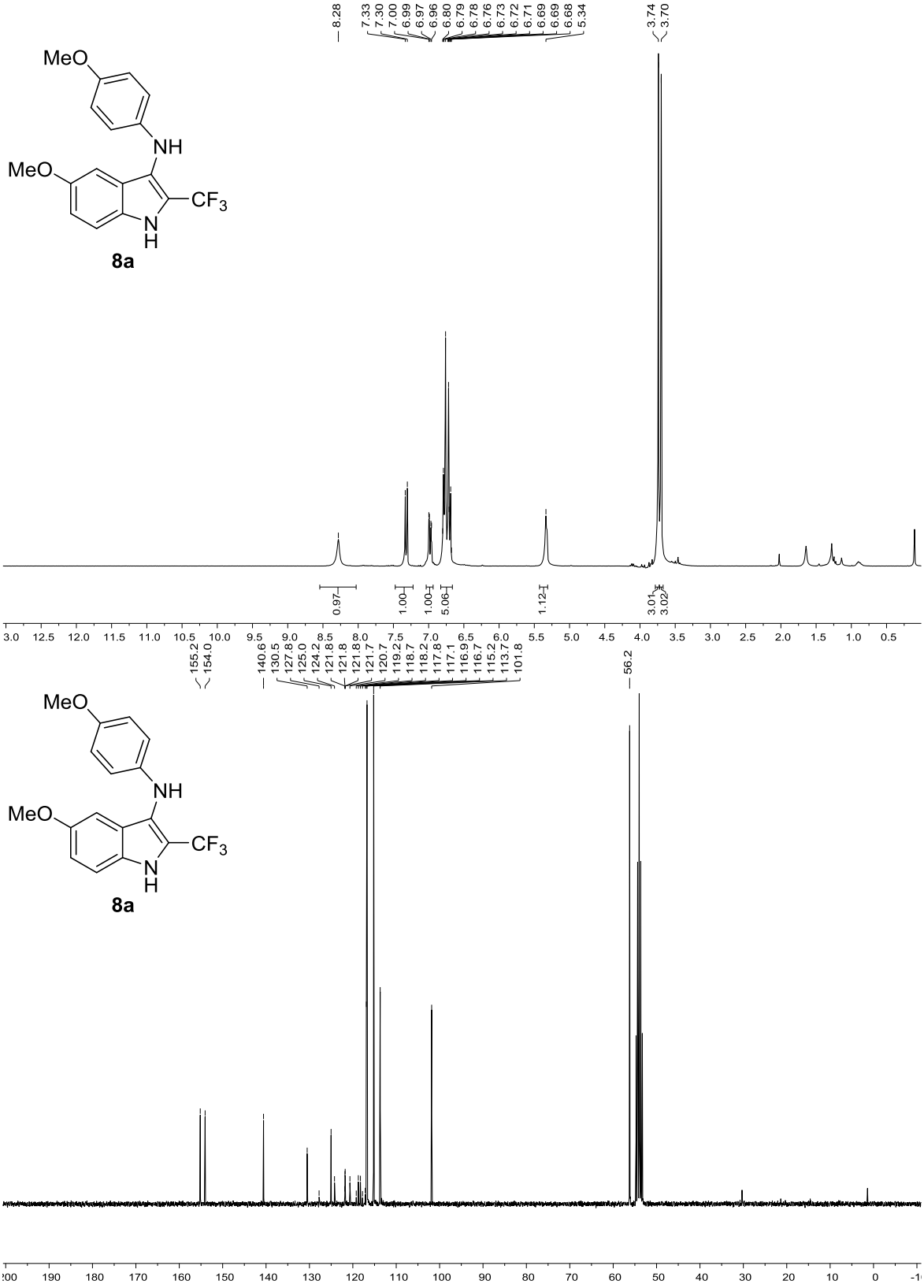
Methyl (*E*)-4-cyano-4-(5-methoxy-3-((4-methoxyphenyl)imino)-3*H*-indol-2-yl)pentanoate (7c)

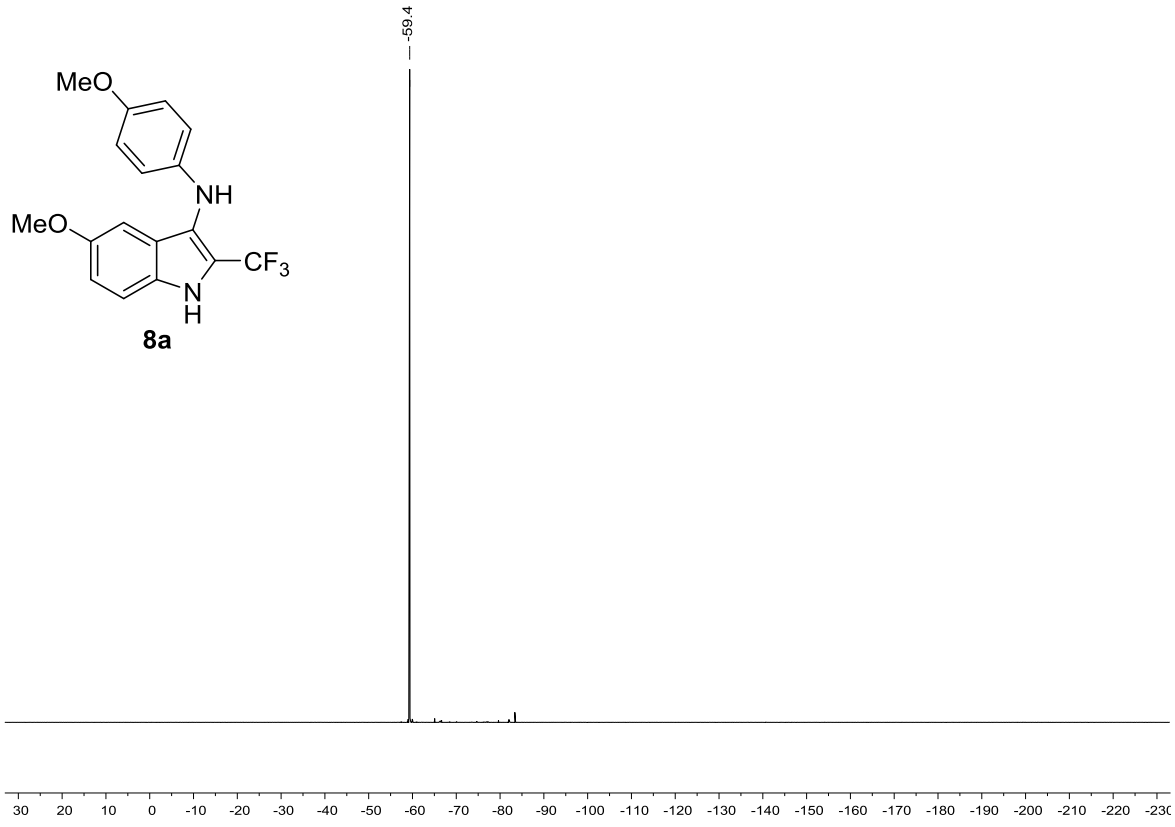



173.0
167.8
161.0
160.0
159.3
150.2
142.3
123.3
122.8
121.8
121.3
116.8
115.2
113.0
56.2
56.1
52.2
41.0
34.4
30.8
25.4
MeO
N
O
OMe
MeO
N
CN
7c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

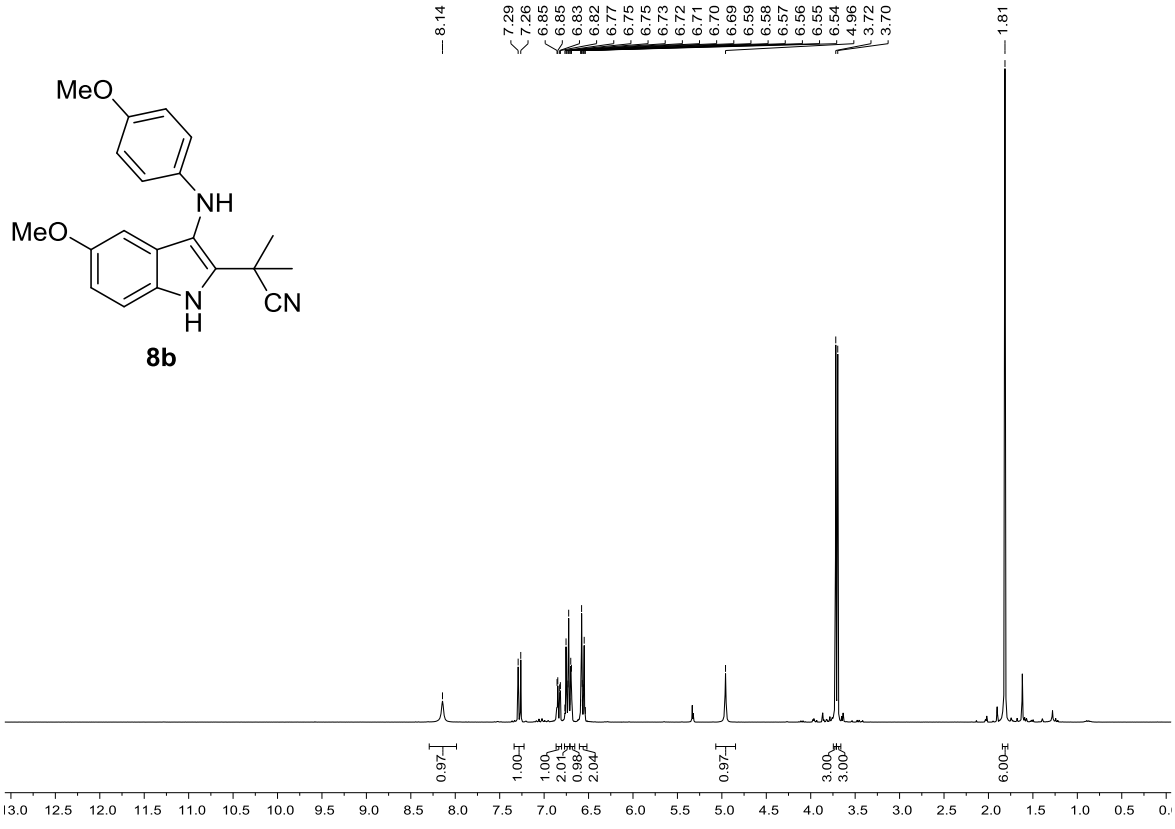
12. Spectra of indoles 8, indolin-2-ols 9 and indoline-3-ones 10 and 11

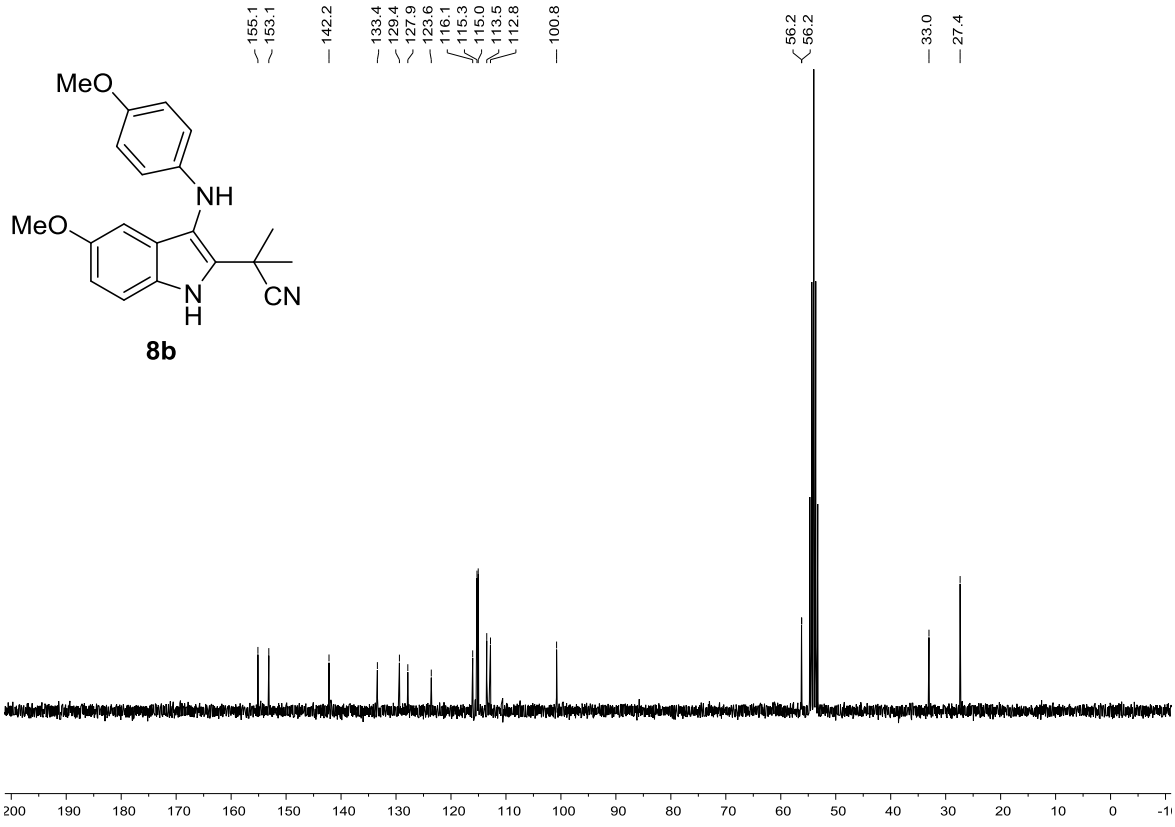
5-Methoxy-*N*-(4-methoxyphenyl)-2-(trifluoromethyl)-1*H*-indol-3-amine (8a)



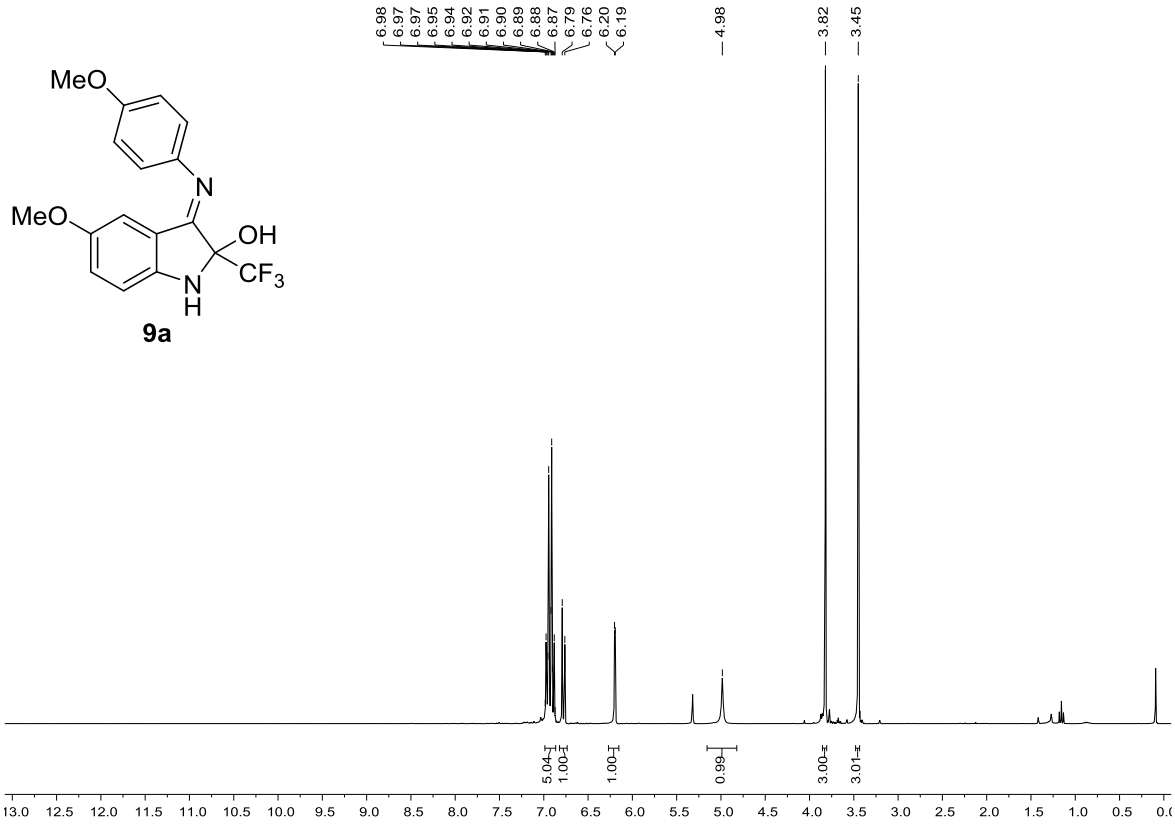


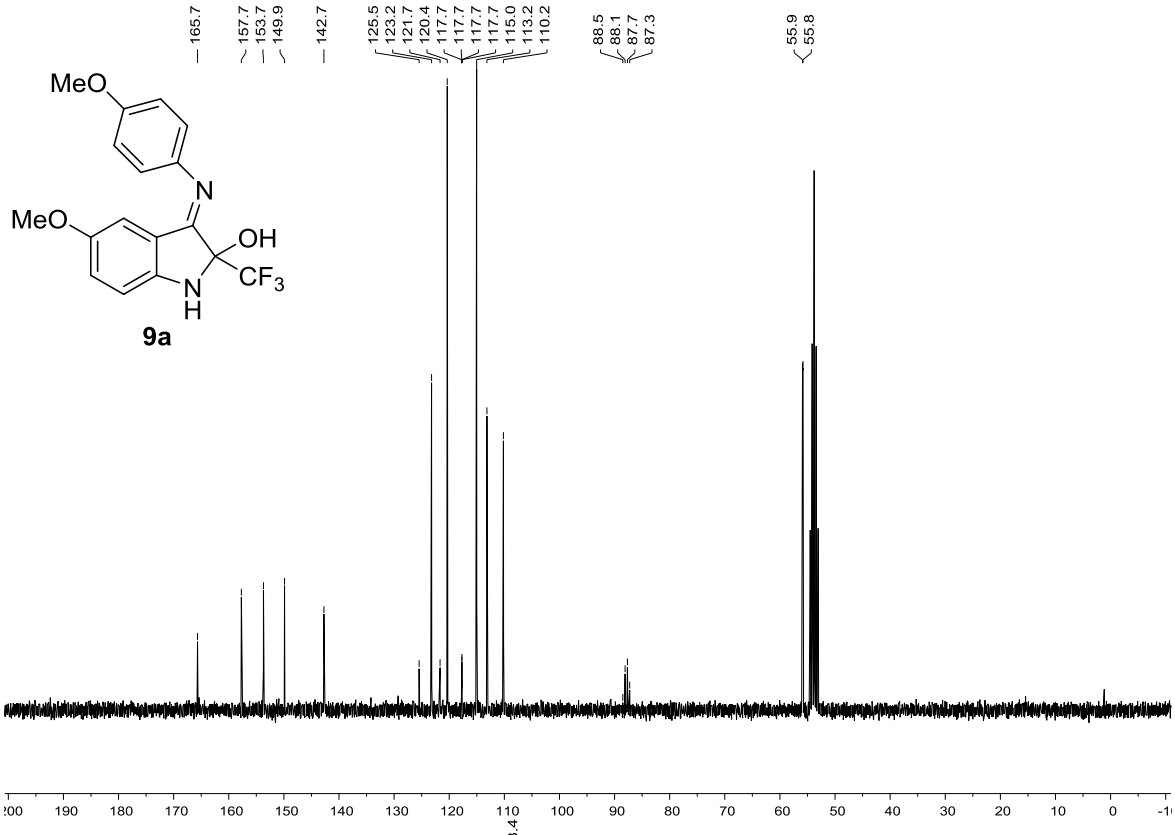
2-(5-Methoxy-3-((4-methoxyphenyl)amino)-1H-indol-2-yl)-2-methylpropanenitrile (8b)

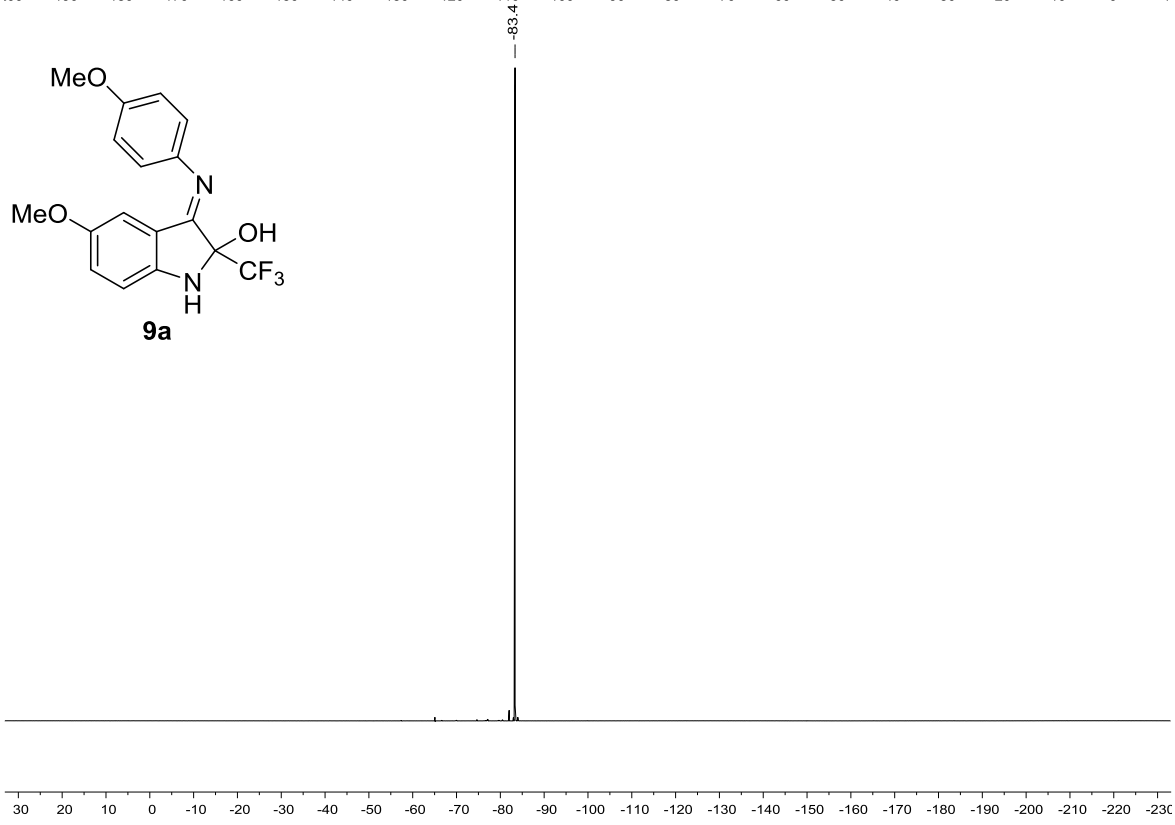




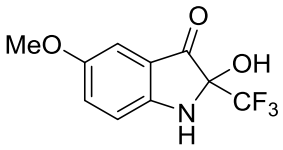
(*E*)-5-Methoxy-3-((4-methoxyphenyl)imino)-2-(trifluoromethyl)indolin-2-ol (9a)




165.7
157.7
153.7
149.9
142.7
125.5
123.2
121.7
120.4
117.7
117.7
117.7
117.7
115.0
113.2
110.2
88.5
88.1
87.7
87.3
55.9
55.8
MeO
N
MeO
OH
CF3
N
H
9a

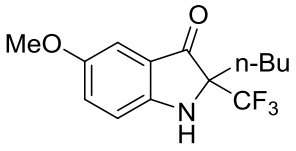

-83.4
MeO
N
MeO
OH
CF3
N
H
9a

2-Hydroxy-5-methoxy-2-(trifluoromethyl)indolin-3-one (10a)

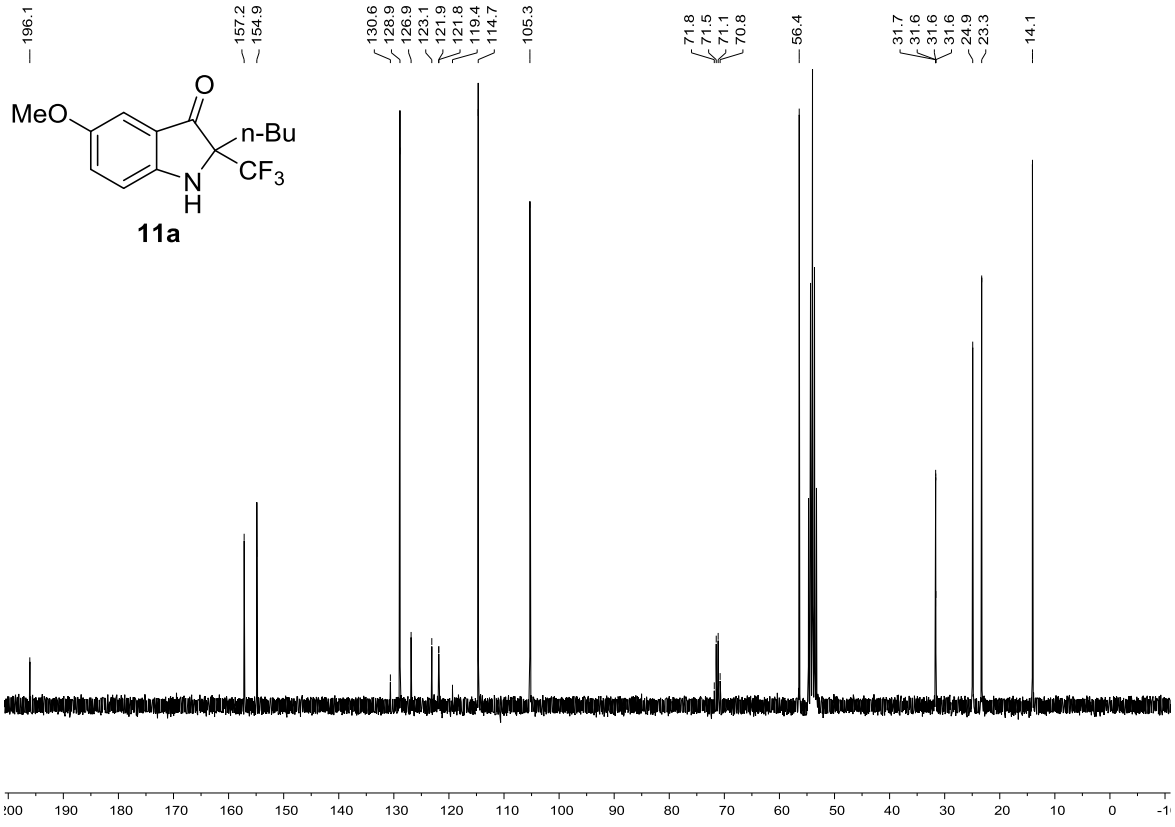


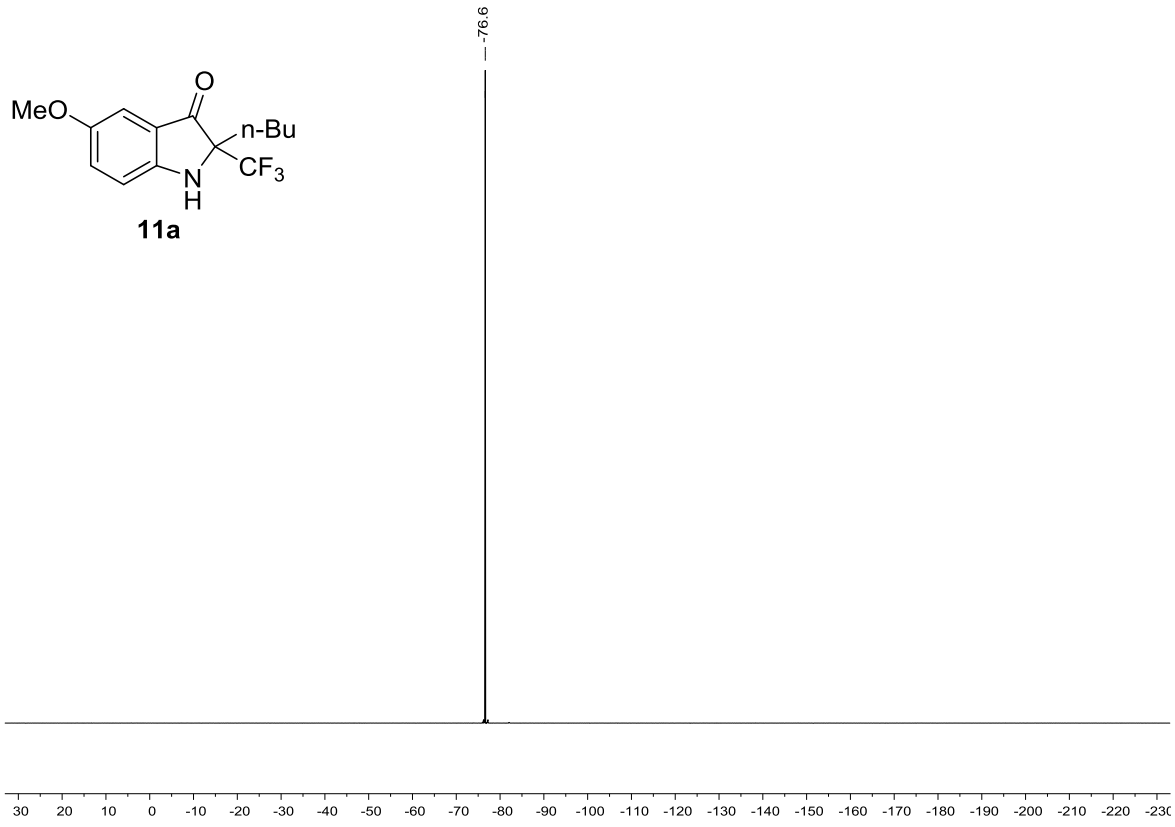
10a

2-Butyl-5-methoxy-2-(trifluoromethyl)indolin-3-one (11a)

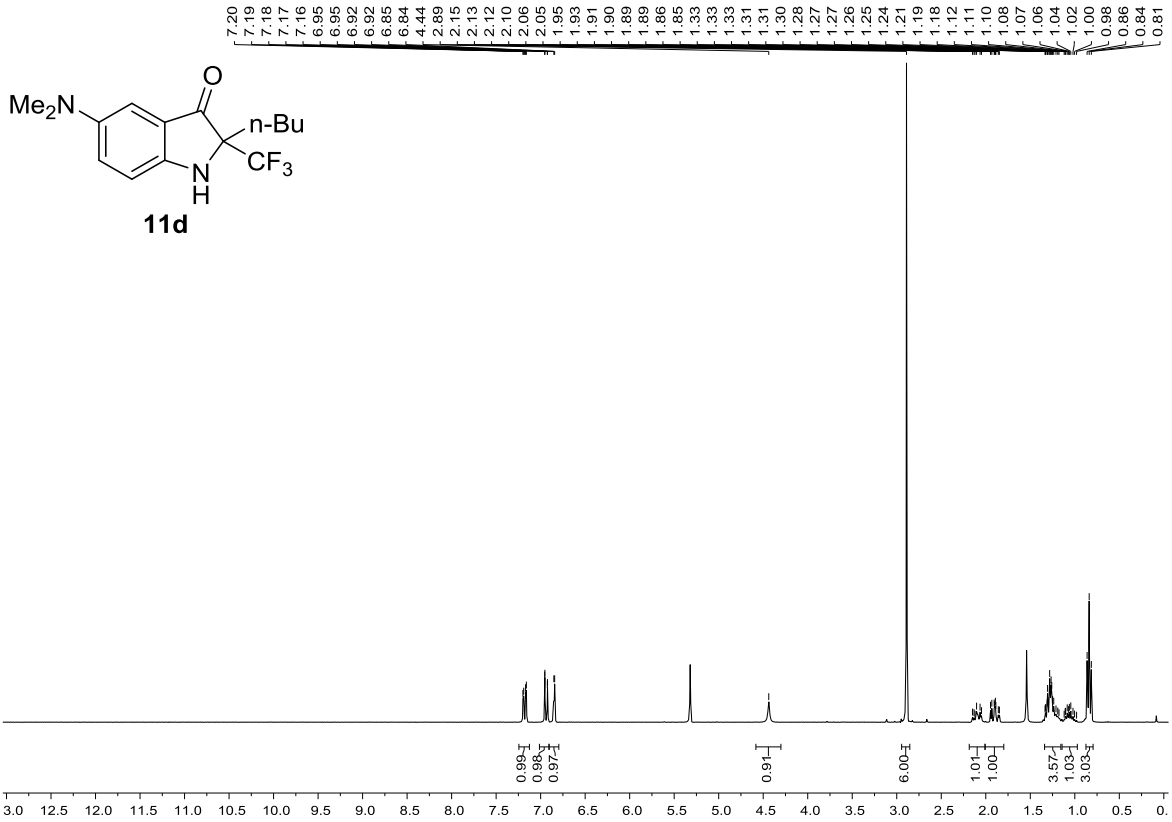


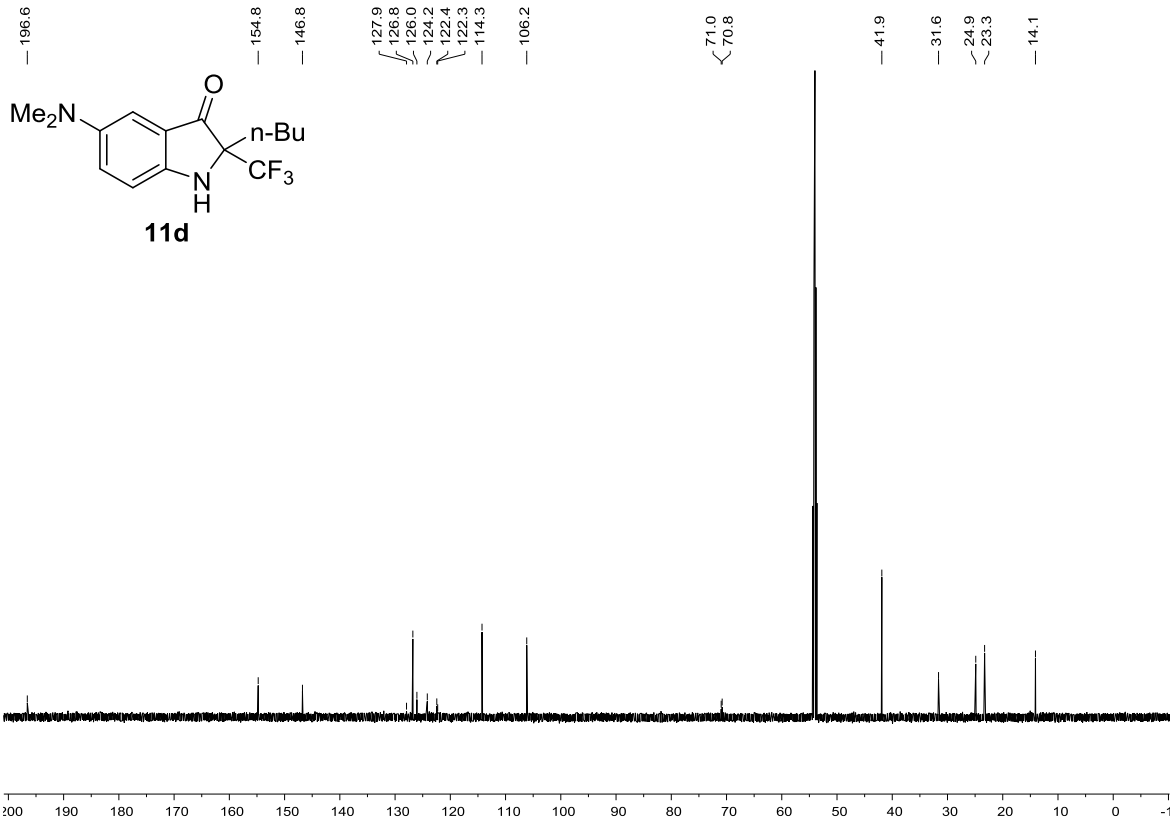
11a

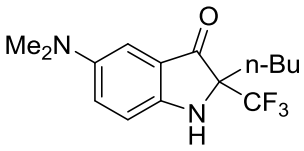

196.1
157.2
154.9
130.6
128.9
126.9
123.1
121.9
121.8
119.4
114.7
105.3
71.8
71.5
71.1
70.8
56.4
31.7
31.6
31.6
31.6
24.9
23.3
14.1
MeO
O
n-Bu
CF3
N
H
11a


-76.6
MeO
O
n-Bu
CF3
N
H
11a

2-Butyl-5-(dimethylamino)-2-(trifluoromethyl)indolin-3-one (11d)

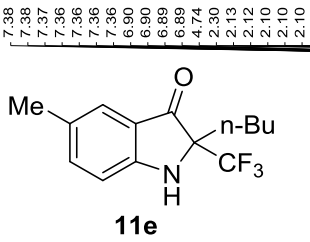




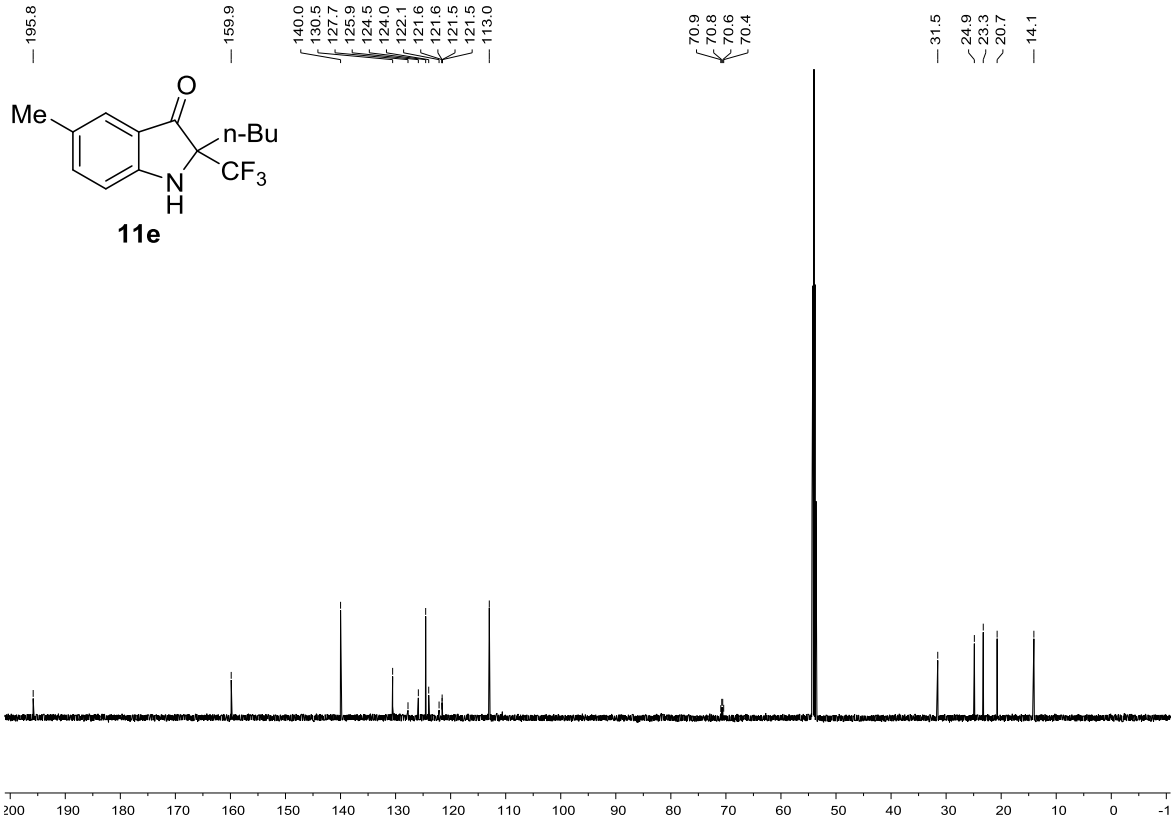


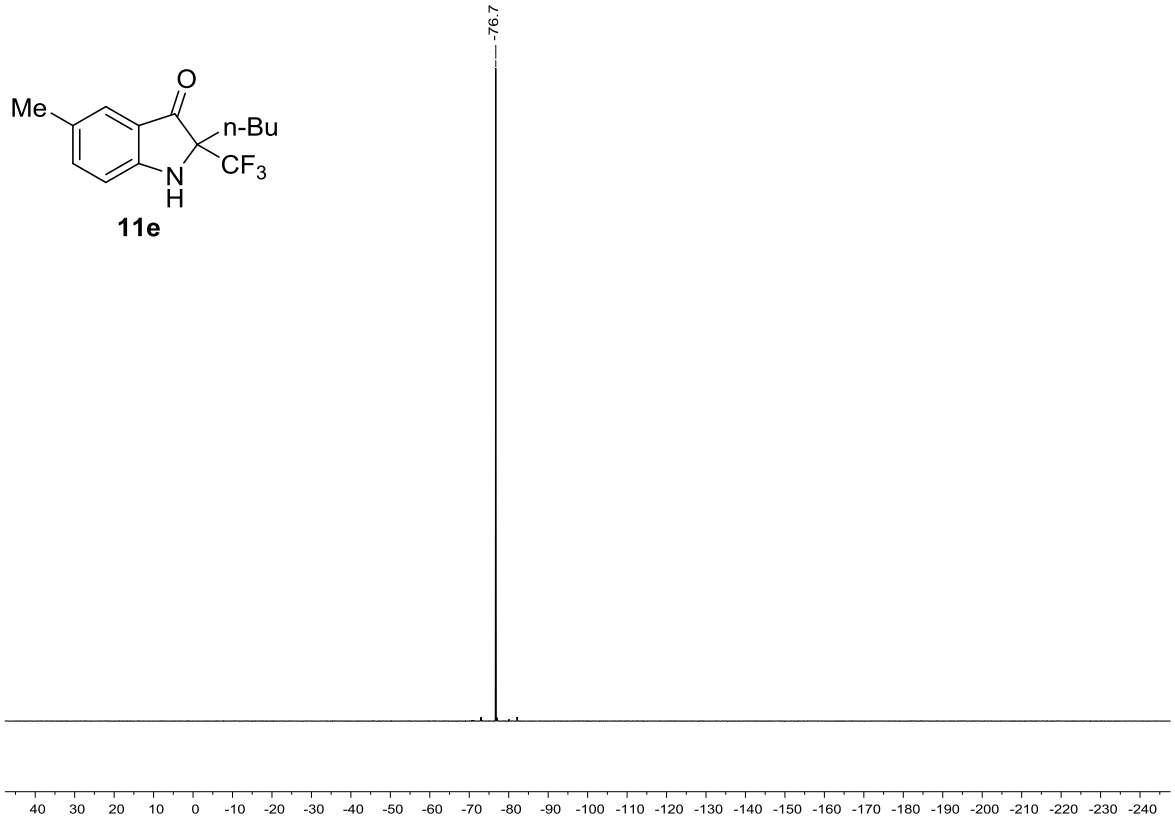
11d

2-Butyl-5-methyl-2-(trifluoromethyl)indolin-3-one (11e)



11e


195.8
159.9
140.0
130.5
127.7
125.9
124.5
124.0
122.1
121.6
121.6
121.5
121.5
113.0
70.9
70.8
70.6
70.4
31.5
24.9
23.3
20.7
14.1
Me
O
n-Bu
CF3
N
H
11e


-76.7
Me
O
n-Bu
CF3
N
H
11e

13. Literature

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