Supporting Information

Rhodium-Catalyzed Annulation of Tertiary Aniline *N*-Oxides to *N*-Alkylindoles: Regioselective C-H Activation, Oxygen-Atom Transfer, and *N*-Dealkylative Cyclization

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General Experimental Section

Analytic methods. All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz), ^{19}F (376 MHz) and ^{13}C NMR (100 MHz) were recorded on Bruker AV400 NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H, ^{19}F, and $^{13}C\{^{1}H\}$ NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200-300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). HRMS were done on Agilent 6520 Q-TOF LC/MS or Varian 7.0T FTMS.

General preparation for chemicals. $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3{\cdot}3H_2O$ following a literature procedure.[1] Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Tertiary anilines[2], tertiary aniline *N*-oxides[3], and *N,N*-Dimethylaniline-2,3,4,5,6-d_5 *N*-oxide ([D_5]-**1a**)[4] were prepared according to the literature procedures.

Single crystal X-ray structure of complex 3p and 3r

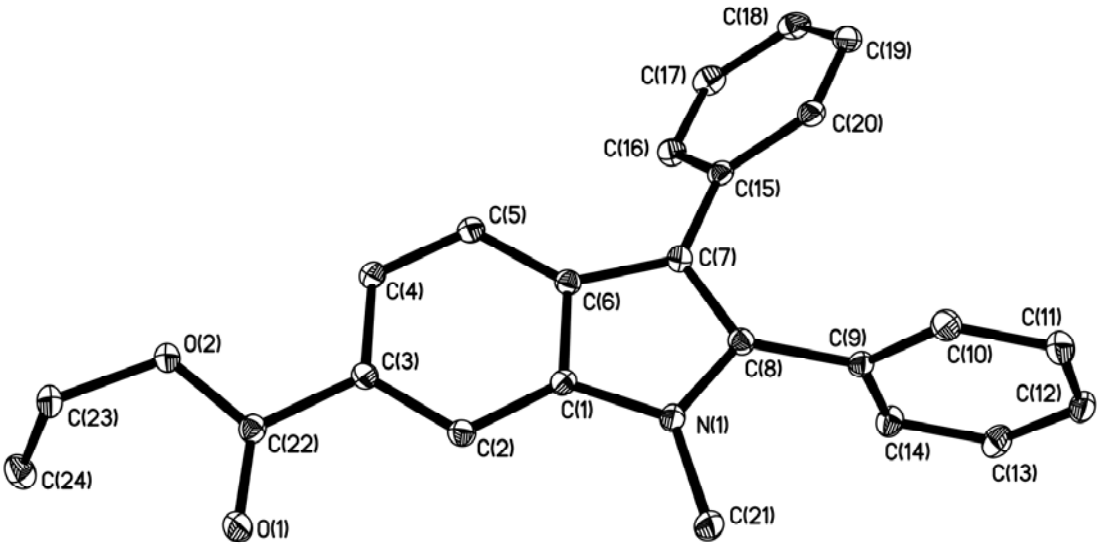


Figure S1. ORTEP diagram of complex **3p**

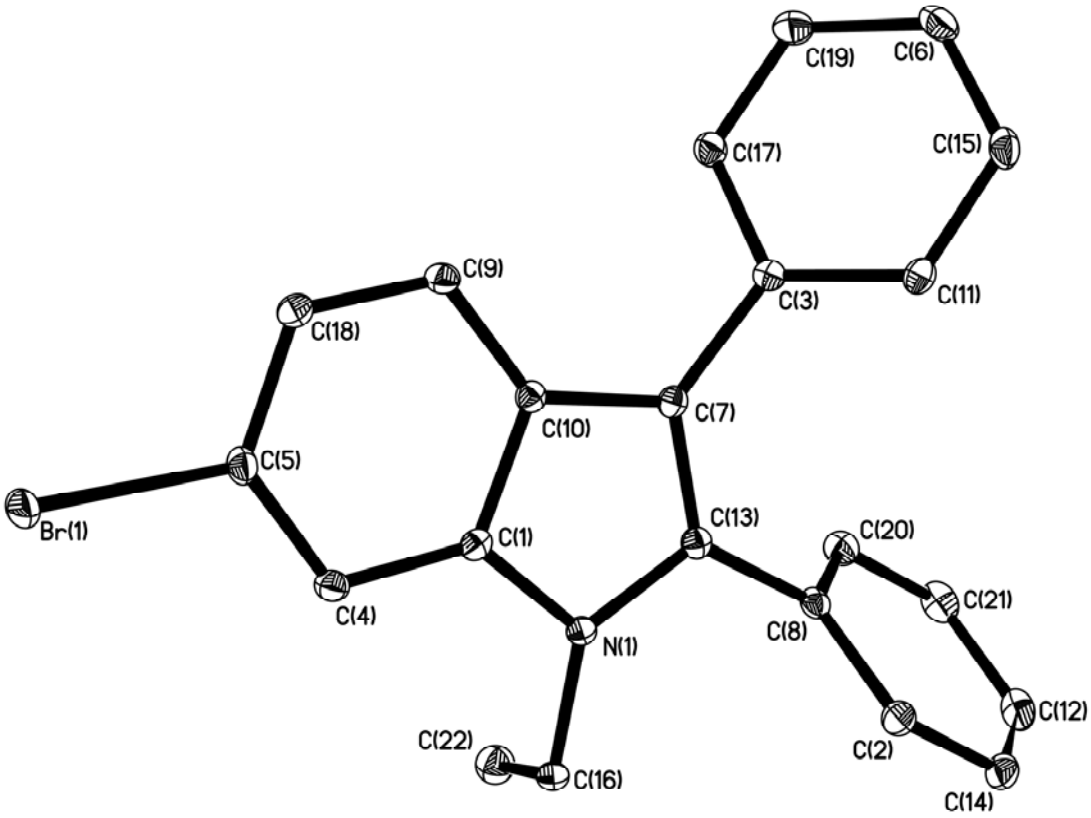


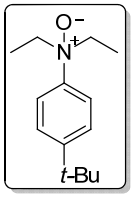
Figure S2. ORTEP diagram of complex **3r**

Table S1. Crystal Data and Summary of X-ray Data Collection for 3p and 3r.

	3p	**3r**
formula	$C_{24}H_{21}NO_2$	$C_{22}H_{18}BrN$
fw	355.42	376.28
crystal system	Monoclinic	Monoclinic
space group	P2(1)/c	P2(1)/n
a (Å)	12.787(2)	9.6700(18)
b (Å)	12.7131(18)	19.620(3)
c (Å)	12.427(2)	9.9545(18)
α (deg)	90	90
β (deg)	114.445(3)	112.567(3)
γ (deg)	90	90
V (Å^3)	1839.2(5)	1744.0(5)
Z	4	4
D_{calcd} (g cm^{-3})	1.284	1.433
μ (mm^{-1})	0.081	2.359
F(000)	752	768
cryst size (mm)	0.20×0.18× 0.12	0.20×0.18×0.12
max. 2θ (deg)	55.14	55.08
no. of reflns collected	18357	17655
no. of indep reflns/R_{int}	4215 / 0.0286	4008 / 0.0259
no. of params	246	213
goodness-of-fit on F^2	1.074	1.072
R1, wR2 ($I > 2\sigma(I)$)	0.0365, 0.1046	0.0221, 0.0574
R1, wR2 (all data)	0.0399, 0.1068	0.0260, 0.0584

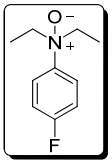
Analytical data of substrates 1

4-tert-butyl-*N*,*N*-diethylaniline oxide (1e)



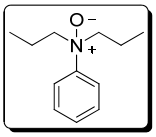
The title compound was isolated by column chromatography (eluent: EtOAc to CH_3OH) as an off-white solid in 95% yield. M.p.: 86-88 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.67 (2H, d, *J* = 8.8 Hz), 7.41 (2H, d, *J* = 8.8 Hz), 3.71-3.58 (1H, m), 1.31 (9H, s), 1.13 (6H, t, *J* = 7.0 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 151.4, 146.1, 125.7, 121.3, 66.7, 34.5, 31.2, 8.3; **HRMS (ESI):** Calcd for $C_{14}H_{24}NO$ $[M+H]^+$ 222.1852, Found: 222.1853.

N,*N*-diethyl-4-fluoroaniline oxide (1h)



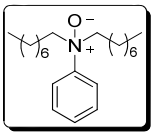
The title compound was isolated by column chromatography (eluent: EtOAc to CH_3OH) as an off-white solid in 97% yield. M.p.: 102-104 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.85-7.76 (2H, m), 7.14-7.04 (2H, m), 3.72-3.51 (4H, m), 1.16-1.06 (6H, m); **^{13}C{^{1}H} NMR (CDCl3, 100 MHz):** δ 161.9 (d, *J* = 248.4 Hz), 145.3, 123.9 (d, *J* = 8.6 Hz), 115.4 (d, *J* = 22.8 Hz), 67.1, 8.3; **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -113.8 (s); **HRMS (ESI):** Calcd for $C_{14}H_{23}NNaO$ $[M+Na]^+$ 244.1672, Found: 244.1670.

N,*N*-dipropylaniline oxide (1u)



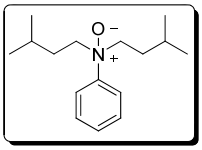
The title compound was isolated by column chromatography (eluent: EtOAc to CH_3OH) as an off-white solid in 83% yield. M.p.: 66-68 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.79 (2H, d, *J* = 8.1 Hz), 7.40 (2H, t, *J* = 7.7 Hz), 7.32 (1H, t, *J* = 7.2 Hz), 3.59-3.45 (4H, m), 2.04-1.89 (2H, m), 1.30-1.15 (2H, m), 0.80 (6H, t, *J* = 7.5 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 150.2, 128.7, 128.3, 121.6, 74.0, 16.2, 10.8; **HRMS (ESI):** Calcd for $C_{12}H_{20}NO$ $[M+H]^+$ 194.1539, Found: 194.1543.

N,N-dioctylaniline oxide (1v)



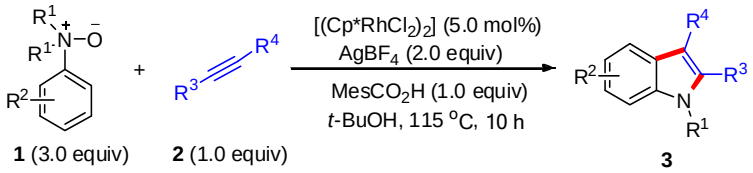
The title compound was isolated by column chromatography (eluent: EtOAc to CH_3OH) as an off-white solid in 78% yield. M.p.: 57-59 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.82 (2H, d, *J* = 8.1 Hz), 7.44 (2H, t, *J* = 7.7 Hz), 7.36 (1H, t, *J* = 7.3 Hz), 3.68-3.49 (4H, m), 2.03-1.89 (2H, m), 1.25-1.10 (22H, m), 0.83 (6H, t, *J* = 6.9 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 150.0, 128.8, 128.3, 121.6, 72.6, 31.6, 29.2, 29.0, 26.6, 22.8, 22.5, 14.0; **HRMS (ESI):** Calcd for $C_{22}H_{40}NO$ $[M+H]^+$ 334.3104, Found: 334.3108.

N,N-diisopentylaniline oxide (1w)



The title compound was isolated by column chromatography (eluent: EtOAc to CH_3OH) as an off-white solid in 92% yield. M.p.: 89-91 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.81 (2H, d, *J* = 8.0 Hz), 7.44 (2H, t, *J* = 7.7 Hz), 7.36 (1H, t, *J* = 7.2 Hz), 3.71-3.50 (4H, m), 1.95-1.87 (2H, m), 1.57-1.47 (2H, m), 1.10-1.01 (2H, m), 0.85 (6H, d, *J* = 6.6 Hz), 0.80 (6H, d, *J* = 6.6 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 149.9, 128.8, 128.3, 121.6, 71.5, 31.2, 26.2, 22.6, 22.4; **HRMS (ESI):** Calcd for $C_{16}H_{28}NO$ $[M+H]^+$ 250.2165, Found: 250.2163.

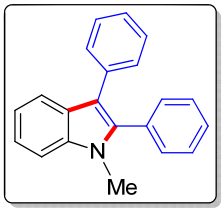
General Procedure for the Rhodium(III)-Catalyzed C-H Annulation of Tertiary Anilines N-Oxides with Alkynes



A mixture of tertiary aniline *N*-oxide (0.6 mmol, 3.0 equiv), alkyne (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mol, 5.0 mol %), $AgBF_4$ (78 mg, 0.4 mmol, 2.0 equiv), and $MesCO_2H$ (33 mg,1.0 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 10 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/CH_2Cl_2.

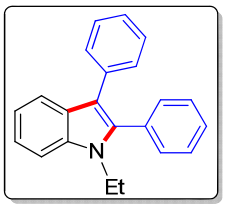
Characterization of Products 3 and Products 4

1-methyl-2,3-diphenyl-1*H*-indole (3a).[5]



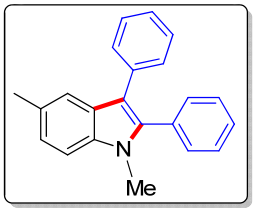
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 80% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.82 (1H, d, *J* = 7.9 Hz), 7.43 (1H, d, *J* = 8.2 Hz), 7.42-7.37 (3H, m), 7.36-7.30 (5H, m), 7.27 (2H, d, *J* = 7.7 Hz), 7.22 (1H, d, *J* = 7.9 Hz), 7.18 (1H, d, *J* = 7.6 Hz), 3.70 (3H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.7, 137.3, 135.2, 131.9, 131.1, 129.9, 128.4, 128.2, 128.0, 126.9, 125.5, 122.2, 120.2, 119.6, 115.1, 109.6, 30.9; **MS (EI):** Calcd for $C_{21}H_{17}N$ [M^+] 283.14, Found: 283.

1-ethyl-2,3-diphenyl-1*H*-indole (3b).[5]



The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 91% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.82 (1H, d, *J* = 7.9 Hz), 7.46 (1H, d, *J* = 8.2 Hz), 7.42-7.38 (3H, m), 7.37-7.36 (2H, m), 7.32-7.26 (4H, m), 7.26-7.24 (1H, m), 7.21-7.15 (2H, m), 4.15 (2H, q, *J* = 7.2 Hz), 1.30 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.3, 136.0, 135.2, 132.2, 131.0, 129.8, 128.4, 128.1, 127.2, 125.4, 122.0, 120.1, 119.7, 115.3, 109.8, 38.6, 15.4 (one signal missing due to overlap); **MS (EI):** Calcd for $C_{22}H_{19}N$ [M^+] 297.15, Found: 297.

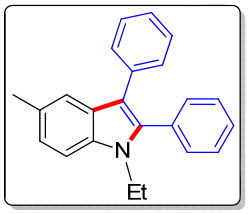
1,5-dimethyl-2,3-diphenyl-1*H*-indole (3c).[5]



The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 55% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.61 (1H, s), 7.42-7.38 (3H, m), 7.37-7.34 (3H, m), 7.33-7.28 (4H, m), 7.22-7.15 (2H, m), 3.68 (3H, s), 2.51 (3H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.8, 135.8, 135.4, 132.0, 131.1, 129.9, 129.5, 128.3, 128.1, 127.9, 127.1, 125.4, 123.7, 119.1, 114.6, 109.3,

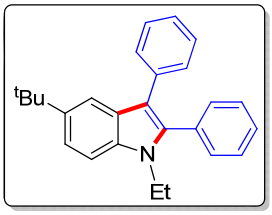
30.9, 21.5; **MS (EI):** Calcd for $C_{22}H_{19}N$ [M^+] 297.15, Found: 297.

1-ethyl-5-methyl-2,3-diphenyl-1*H*-indole (3d).



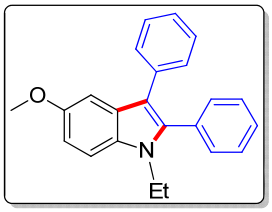
The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 93% yield; M.p.: 126-128 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.59 (1H, s), 7.40-7.36 (3H, m), 7.36-7.31 (3H, m), 7.31-7.24 (4H, m), 7.17 (1H, d, *J* = 6.9 Hz), 7.12 (1H, d, *J* = 8.6 Hz), 4.12 (2H, q, *J* = 7.2 Hz), 2.48 (3H, s), 1.28 (3H, t, *J* = 7.1 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.4, 135.4, 134.5, 132.3, 131.0, 129.8, 129.4, 128.4, 128.1, 128.0, 127.4, 125.3, 123.5, 119.3, 114.8, 109.5, 38.6, 21.5, 15.4; **HRMS (ESI):** Calcd for $C_{23}H_{22}N$ $[M+H]^+$ 312.1747, Found: 312.1751.

5-tert-butyl-1-ethyl-2,3-diphenyl-1*H*-indole (3e).



The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 92% yield; M.p.: 188-190 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.81 (1H, s), 7.40-7.37 (5H, m), 7.33-7.30 (5H, m), 7.28 (1H, br s), 7.19-7.15 (1H, m), 4.12 (2H, q, *J* = 7.2 Hz), 1.41 (9H, s), 1.30 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 143.1, 137.5, 135.4, 134.2, 132.4, 131.0, 129.8, 128.4, 128.1, 128.0, 126.8, 125.3, 120.3, 115.4, 115.3, 109.3, 38.6, 34.7, 32.0, 15.5; **HRMS (ESI):** Calcd for $C_{26}H_{28}N$ $[M+H]^+$ 354.2216, Found: 354.2224.

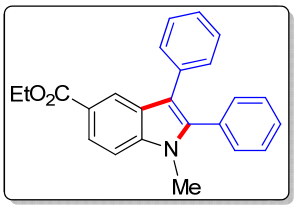
1-ethyl-5-methoxy-2,3-diphenyl-1*H*-indole (3f).



The title compound was isolated by column chromatography (eluent:EtOAc/petroleum ether = 1/20 to 1/10) as an yellow solid in 46% yield; M.p.: 156-158 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.40-7.37 (3H, m), 7.35-7.31 (3H, m), 7.30-7.24 (5H, m), 7.18-7.14 (1H, m), 6.96 (1H, dd, *J* = 8.8, 2.4 Hz), 4.11 (2H, q, *J* = 7.2 Hz), 3.86 (3H, s), 1.28 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 154.7, 137.9, 135.3,

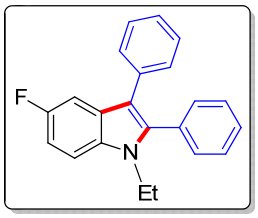
132.2, 131.3, 131.0, 129.7, 128.4, 128.2, 128.0, 127.5, 125.3, 115.0, 112.3, 110.6, 101.3, 56.0, 38.7, 15.5; **HRMS (ESI):** Calcd for $C_{23}H_{22}NO$ $[M+H]^+$ 328.1696, Found: 328.1699.

ethyl 1-methyl-2,3-diphenyl-1*H*-indole-5-carboxylate (3g).



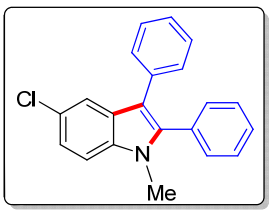
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as an off-white solid in 88% yield; M.p.: 156-158 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.53 (1H, dd, *J* = 1.5, 0.4 Hz), 8.02 (1H, dd, *J* = 8.6, 1.6 Hz), 7.42 (1H, d, *J* = 6.2 Hz), 7.41-7.38 (3H, m), 7.35-7.32 (2H, m), 7.32-7.29 (4H, m), 7.24-7.19 (1H, m), 4.40 (2H, q, *J* = 7.1 Hz), 3.71 (3H, s), 1.41 (3H, t, *J* = 7.1 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 167.7, 139.6, 138.9, 134.4, 131.3, 131.0, 129.9, 128.5, 128.3, 126.6, 125.9, 123.5, 122.6, 122.5, 116.4, 109.1, 60.6, 31.2, 14.5 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{24}H_{22}NO_2$ $[M+H]^+$ 356.1645, Found: 356.1649.

1-ethyl-5-fluoro-2,3-diphenyl-1*H*-indole (3h).



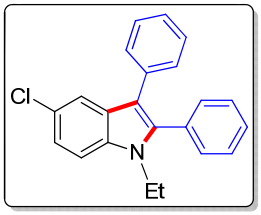
The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 95% yield; M.p.: 102-104 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.46 (1H, dd, *J* = 9.9, 2.2 Hz), 7.44-7.38 (3H, m), 7.37-7.32 (3H, m), 7.29-7.24 (4H, m), 7.21-7.15 (1H, m), 7.04 (1H, td, *J* = 8.9, 2.2 Hz), 4.13 (2H, q, *J* = 7.1 Hz), 1.29 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 158.4 (d, *J* = 234.5 Hz), 138.8, 134.8, 132.6, 131.9, 130.9, 129.5, 128.5, 128.3, 128.2, 127.5 (d, *J* = 9.9 Hz), 125.6, 115.3 (d, *J* = 4.5 Hz), 110.4 (d, *J* = 9.3 Hz), 110.3 (d, *J* = 26.3 Hz), 104.6 (d, *J* = 23.9 Hz), 38.9, 15.4; **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -124.3 (s); **HRMS (ESI):** Calcd for $C_{22}H_{19}FN$ $[M+H]^+$ 316.1496, Found: 316.1495.

5-chloro-1-methyl-2,3-diphenyl-1*H*-indole (3i).



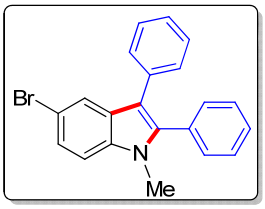
The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 85% yield; M.p.: 153-155 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.74 (1H, d, *J* = 1.6 Hz), 7.41-7.37 (3H, m), 7.33-7.30 (3H, m), 7.29-7.26 (3H, m), 7.25-7.23 (1H, m), 7.22-7.17 (1H, m), 3.67 (3H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 138.9, 135.7, 134.5, 131.4, 131.0, 129.7, 128.5, 128.3, 128.0, 125.9, 125.8, 122.3, 119.0, 114.8, 110.6, 31.1 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{21}H_{17}ClN$ $[M+H]^+$ 318.1044, Found: 318.1044.

5-chloro-1-ethyl-2,3-diphenyl-1*H*-indole (3j).



The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 87% yield; M.p.: 141-143 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.76 (1H, d, *J* = 1.9 Hz), 7.43-7.39 (3H, m), 7.37-7.33 (3H, m), 7.30-7.26 (3H, m), 7.26-7.22 (2H, m), 7.20-7.16 (1H, m), 4.12 (2H, q, *J* = 7.2 Hz), 1.28 (3H, t, *J* = 7.1 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 138.5, 134.5, 134.4, 131.7, 130.9, 129.6, 128.5, 128.3, 128.2, 125.8, 125.7, 122.2, 119.1, 115.0, 110.8, 38.8, 15.3 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{22}H_{18}ClN$ 332.1201 $[M+H]^+$ Found: 332.1197.

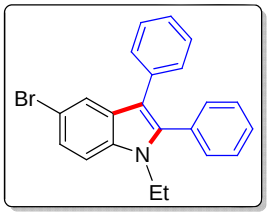
5-bromo-1-methyl-2,3-diphenyl-1*H*-indole (3k).



The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 73% yield; M.p.: 156-158 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.90 (1H, t, *J* = 1.7 Hz), 7.41-7.37 (4H, m), 7.33-7.31 (2H, m), 7.30-7.24 (5H, m), 7.22-7.18 (1H, m), 3.67 (3H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 138.8, 136.0, 134.5, 131.3, 131.0, 129.7, 128.6, 128.5, 128.3, 125.8, 124.9, 122.0, 114.8, 113.5, 111.0, 31.1 (one signal missing due to overlap); **HRMS (ESI):** Calcd for

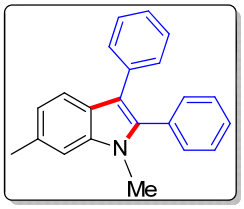
$C_{21}H_{17}BrN$ $[M+H]^+$ 362.0539, Found: 362.0540.

5-bromo-1-ethyl-2,3-diphenyl-1*H*-indole (3l).



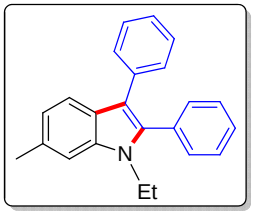
The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 82% yield; M.p.: 160-162 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.93 (1H, d, *J* = 1.7 Hz), 7.44-7.40 (3H, m), 7.37-7.32 (4H, m), 7.31-7.27 (4H, m), 7.23-7.17 (1H, m), 4.13 (2H, q, *J* = 7.2 Hz), 1.29 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 138.3, 134.7, 134.4, 131.6, 130.9, 129.7, 128.9, 128.5, 128.3, 128.2, 125.7, 124.7, 122.2, 114.9, 113.4, 111.2, 38.8, 15.3; **HRMS (ESI):** Calcd for $C_{22}H_{19}BrN$ $[M+H]^+$ 376.0695, Found: 376.0695.

1,6-dimethyl-2,3-diphenyl-1*H*-indole (3m).[5]



The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 73% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.68 (1H, d, *J* = 8.1 Hz), 7.41-7.36 (3H, m), 7.34-7.25 (6H, m), 7.22 (1H, s), 7.20-7.15 (1H, m), 7.04 (1H, d, *J* = 8.1 Hz), 3.65 (3H, s), 2.55 (3H, s).**^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.7, 137.1, 135.4, 132.0, 131.1, 129.8, 128.3, 128.1, 127.9, 125.4, 124.8, 121.9, 119.3, 114.9, 109.6, 30.8, 21.9; **MS (EI):** Calcd for $C_{22}H_{19}N$ $[M^+]$ 297.15, Found: 297.

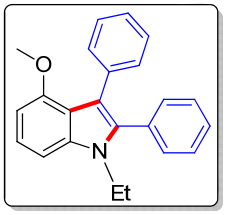
1-ethyl-6-methyl-2,3-diphenyl-1*H*-indole (3n).



The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 86% yield; M.p.: 114-116 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.69 (1H, d, *J* = 8.1 Hz), 7.40-7.37 (3H, m), 7.35-7.32 (2H, m), 7.30-7.21 (5H, m), 7.17-7.12 (1H, m), 7.03 (1H, d, *J* = 8.1 Hz), 4.10 (2H, q, *J* = 7.2 Hz), 2.55 (3H, s), 1.28 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 136.6, 136.4, 135.4, 132.4, 131.8, 131.1, 129.7, 128.4, 128.0, 127.9, 125.3, 125.1, 121.8, 119.4,

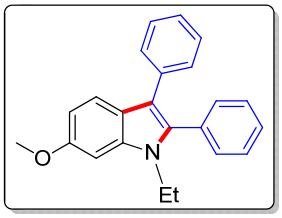
115.1, 109.7, 38.5, 21.9, 15.4; **HRMS (ESI):** Calcd for $C_{23}H_{22}N$ $[M+H]^+$ 312.1747, Found: 312.1752.

1-ethyl-4-methoxy-2,3-diphenyl-1*H*-indole (3o).



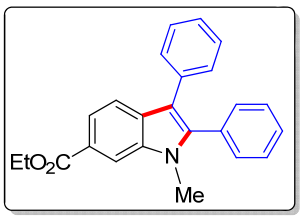
The title compound was isolated by column chromatography (eluent:EtOAc/petroleum ether = 1/20) as an yellow solid in 49% yield; M.p.: 131-133 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.35-7.32 (3H, m), 7.29-7.24 (4H, m), 7.21 (1H, d, *J* = 8.0 Hz), 7.20-7.15 (2H, m), 7.15-7.12 (1H, m), 7.09 (1H, d, *J* = 7.9 Hz), 6.60 (1H, d, *J* = 7.7 Hz), 4.11 (2H, q, *J* = 7.2 Hz), 3.76 (3H, s), 1.29 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 154.7, 137.4, 136.7, 135.8, 132.2, 131.6, 131.2, 128.1, 127.7, 126.7, 125.1, 122.5, 116.8, 115.3, 103.1, 100.6, 55.3, 38.9, 15.3; **HRMS (ESI):** Calcd for $C_{23}H_{22}NO$ $[M+H]^+$ 328.1696, Found: 328.1701.

1-ethyl-6-methoxy-2,3-diphenyl-1*H*-indole (3o').



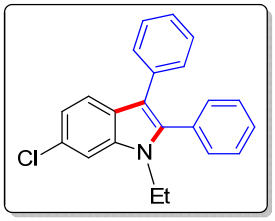
The title compound was isolated by column chromatography (eluent:EtOAc/petroleum ether = 1/20) as an yellow solid in 49% yield; M.p.: 139-141 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.69 (1H, d, *J* = 8.7 Hz), 7.40-7.36 (3H, m), 7.34-7.32 (2H, m), 7.30-7.23 (4H, m), 7.17-7.13 (1H, m), 6.90 (1H, d, *J* = 2.1 Hz), 6.86 (1H, dd, *J* = 8.7, 2.2 Hz), 4.09 (2H, q, *J* = 7.1 Hz), 3.93 (3H, s), 1.28 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 156.5, 136.8, 136.2, 135.3, 132.4, 131.1, 129.7, 128.4, 128.1, 127.9, 125.3, 121.7, 120.5, 115.1, 109.6, 93.6, 55.9, 38.6, 15.1; **HRMS (ESI):** Calcd for $C_{23}H_{22}NO$ $[M+H]^+$ 328.1696, Found: 328.1701.

ethyl 1-methyl-2,3-diphenyl-1*H*-indole-6-carboxylate (3p).



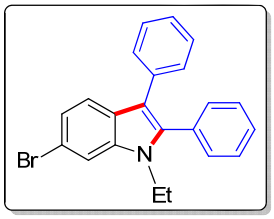
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as an off-white solid in 89% yield; M.p.: 147-149 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.19 (1H, d, *J* = 0.8 Hz), 7.88 (1H, dd, *J* = 8.4, 1.4 Hz), 7.78 (1H, dd, *J* = 8.4, 0.5 Hz), 7.42-7.39 (3H, m), 7.36-7.32 (2H, m), 7.29-7.28 (4H, m), 7.23-7.18 (1H, m), 4.44 (2H, q, *J* = 7.1 Hz), 3.75 (3H, s), 1.45 (3H, t, *J* = 7.1 Hz); **^{13}C{^{1}H} NMR (CDCl3, 100 MHz):** δ 167.7, 140.9, 136.7, 134.5, 131.2, 131.0, 130.4, 129.8, 128.5, 128.4, 128.3, 125.8, 123.9, 121.2, 119.0, 115.5, 112.0, 60.8, 31.1, 14.5; **HRMS (ESI):** Calcd for $C_{24}H_{22}NO_2$ $[M+H]^+$ 356.1645, Found: 356.1652.

6-chloro-1-ethyl-2,3-diphenyl-1*H*-indole (3q).



The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 58% yield; M.p.: 116-118 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.70 (1H, d, *J* = 8.4 Hz), 7.43-7.40 (4H, m), 7.37-7.31 (2H, m), 7.30-7.24 (4H, m), 7.22-7.18 (1H, m), 7.15 (1H, d, *J* = 8.7 Hz), 4.10 (2H, q, *J* = 7.1 Hz), 1.29 (3H, t, *J* = 7.1 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.8, 136.5, 134.6, 131.7, 130.9, 129.7, 128.5, 128.3, 128.2, 127.8, 125.8, 125.7, 120.6, 115.4, 109.7, 38.7, 15.3 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{22}H_{19}ClN$ $[M+H]^+$ 332.1201, Found: 332.1195.

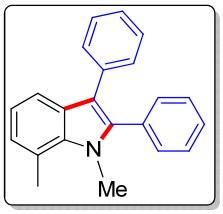
6-bromo-1-ethyl-2,3-diphenyl-1*H*-indole (3r).



The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 71% yield; M.p.: 148-150 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.65 (1H, d, *J* = 8.5 Hz), 7.59 (1H, d, *J* = 1.6 Hz), 7.43-7.38 (3H, m), 7.35-7.32 (2H, m), 7.28-7.24 (5H, m), 7.21-7.15 (1H, m), 4.09 (2H, q, *J* = 7.2 Hz),

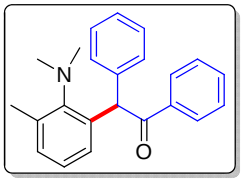
1.28 (3H, t, *J* = 7.2 Hz); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 137.7, 136.9, 134.6, 131.7, 130.9, 129.7, 128.5, 128.3, 128.2, 126.1, 125.7, 123.2, 121.0, 115.4, 112.7, 38.7, 15.3 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{22}H_{19}BrN$ $[M+H]^+$ 376.0695, Found: 376.0686.

1,7-dimethyl-2,3-diphenyl-1*H*-indole (3s).[5]



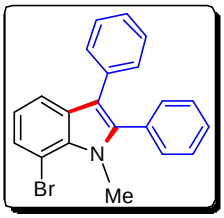
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 49% yield; **^1H NMR ($CDCl_3$, 400 MHz):** δ 7.61 (1H, d, *J* = 7.6 Hz), 7.37 (3H, m), 7.32-7.31 (2H, m), 7.29-7.25 (4H, m), 7.20-7.15 (1H, m), 7.07-7.03 (1H, m), 7.01 (1H, d, *J* = 6.8 Hz), 3.90 (3H, s), 2.86 (3H, s); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 138.9, 136.5, 135.3, 132.1, 131.3, 130.0, 128.3, 128.1, 128.0, 127.9, 125.5, 125.2, 121.4, 120.3, 117.7, 115.6, 34.3, 20.4; **MS (EI):** Calcd for $C_{22}H_{19}N$ $[M^+]$ 297.15, Found: 297.

(2-(dimethylamino)-3-methylphenyl)-1,2-diphenylethanone (3s*).



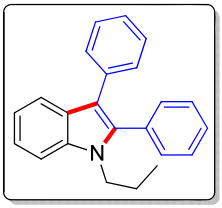
The title compound was isolated by column chromatography (eluent:EtOAc/petroleum ether = 1/20) as an yellow solid in 24% yield; M.p.: 62-64 °C; **^1H NMR ($CDCl_3$, 400 MHz):** δ 8.08 (1H, br s), 8.06 (1H, m), 7.52-7.47 (1H, m), 7.45-7.41 (4H, m), 7.38-7.34 (2H, m), 7.29 (dt, *J* = 4.4, 1.7 Hz), 7.04-7.00 (1H, m), 6.97 (1H, t, *J* = 7.5 Hz), 6.60 (1H, d, *J* = 7.1 Hz), 6.19 (1H, s), 2.48 (3H, s), 2.44 (3H, s), 2.32 (3H, s); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 196.0, 146.8, 143.2, 137.6, 137.5, 137.1, 132.0, 130.9, 130.1, 128.8, 128.3, 128.1, 127.9, 127.2, 127.0, 125.7, 54.6, 41.6, 40.9, 19.0; **HRMS (MALDI):** Calcd for $C_{23}H_{24}NO$ $[M+H]^+$ 330.1852, Found: 330.1855.

7-bromo-1-methyl-2,3-diphenyl-1H-indole (3t).



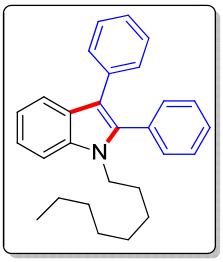
The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 24% yield;M.p.: 152-154 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.67 (1H, dd, *J* = 7.9, 0.9 Hz), 7.43 (1H, dd, *J* = 7.6, 0.9 Hz), 7.40-7.36 (3H, m), 7.32-7.29 (2H, m), 7.27 (1H, m), 7.25-7.22 (3H, m), 7.21-7.17 (1H, m), 6.98 (1H, t, *J* = 7.8 Hz), 4.01 (3H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 140.1, 134.5, 134.1, 131.4, 131.3, 130.4, 130.0, 128.4, 128.3, 128.2, 127.5, 125.9, 121.1, 118.9, 115.8, 104.2, 34.4; **HRMS (ESI):** Calcd for $C_{21}H_{17}BrN$ $[M+H]^+$ 362.0539, Found: 362.0534.

2,3-diphenyl-1-propyl-1*H*-indole (3u).



The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 90% yield; M.p.: 113-115 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.81 (1H, d, *J* = 7.9 Hz), 7.44 (1H, d, *J* = 8.2 Hz), 7.40-7.36 (3H, m), 7.35-7.32 (2H, m), 7.31-7.24 (5H, m), 7.21-7.14 (2H, m), 4.06 (2H, t, *J* = 7.5 Hz), 1.77-1.68 (2H, m), 0.79 (3H, t, *J* = 7.4 Hz) ; **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.6, 136.4, 135.2, 132.3, 131.1, 129.8, 128.4, 128.1, 128.0, 127.1, 125.4, 121.9, 120.0, 119.7, 115.2, 110.0, 45.5, 23.3, 11.4; **HRMS (ESI):** Calcd for $C_{23}H_{22}N$ $[M+H]^+$ 312.1747, Found: 312.1749.

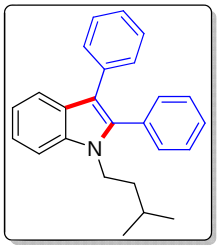
1-octyl-2,3-diphenyl-1*H*-indole (3v).



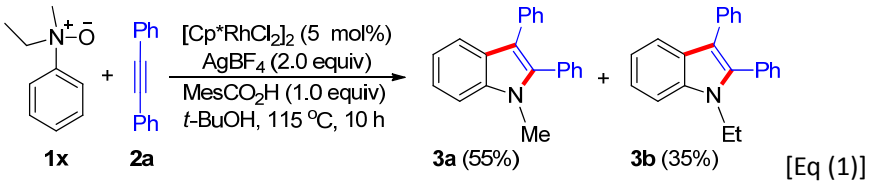
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 60% yield; M.p.: 51-53 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.85 (1H, d, *J* = 7.9 Hz), 7.47 (1H, d, *J* = 8.2 Hz), 7.42-7.39 (3H, m), 7.39-7.27 (7H, m), 7.23 (1H, d, *J* = 7.7 Hz), 7.21-7.17 (1H, m), 4.11 (2H, t, *J* = 7.6 Hz), 1.71 (2H, m), 1.30-1.25 (2H, m), 1.19 (8H, br s), 0.89 (3H, t, *J* = 7.0 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.5, 136.3, 135.2, 132.3, 131.1, 129.8, 128.3, 128.1, 128.0, 127.1, 125.3, 121.9, 120.0, 119.7, 115.1, 109.9, 43.8, 31.7, 29.9, 29.03, 28.97,

26.8, 22.6, 14.1; **HRMS (ESI):** Calcd for $C_{28}H_{32}N$ $[M+H]^+$ 382.2529, Found: 382.2535.

1-isopentyl-2,3-diphenyl-1*H*-indole (3w).

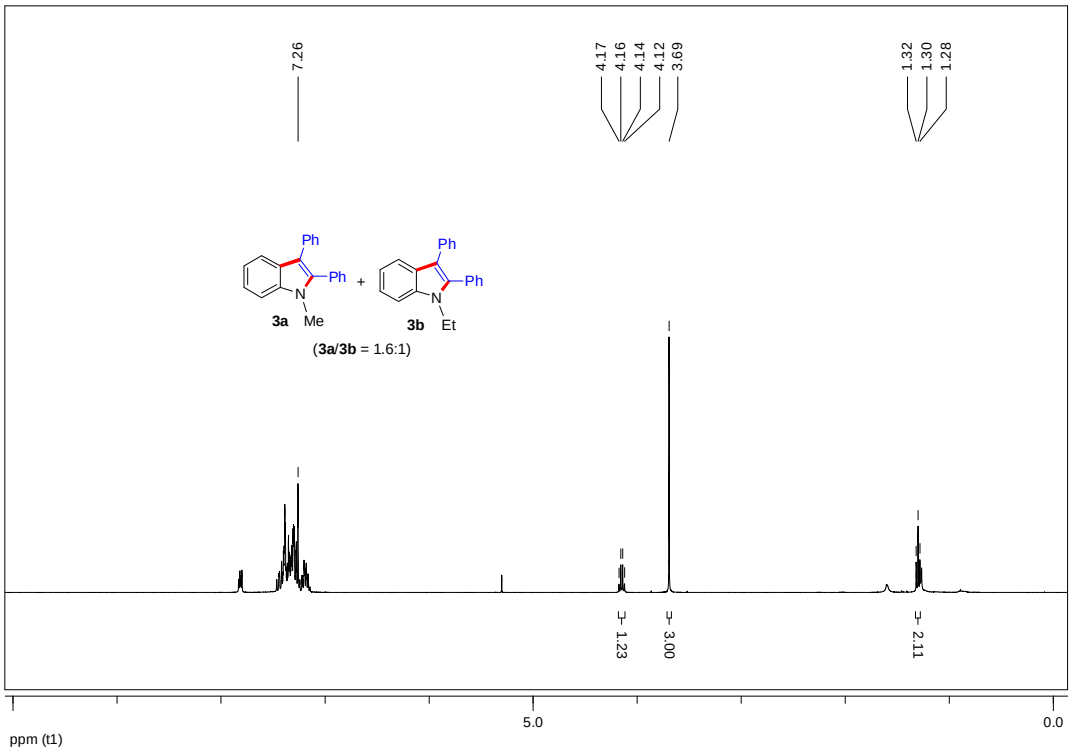


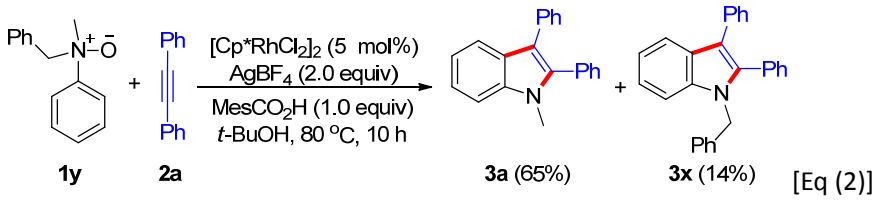
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 90% yield; M.p.: 133-135 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.81 (1H, d, *J* = 7.9 Hz), 7.43 (1H, d, *J* = 8.2 Hz), 7.41-7.36 (3H, m), 7.35-7.31 (3H, m), 7.29-7.24 (4H, m), 7.20-7.14 (2H, m), 4.11-4.07 (2H, m), 1.61-1.55 (2H, m), 1.52-1.46 (1H, m), 0.79 (6H, d, *J* = 6.5 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.4, 136.3, 135.2, 132.2, 131.1, 129.8, 128.4, 128.1, 128.0, 127.1, 125.3, 121.9, 120.0, 119.7, 115.1, 109.8, 42.2, 38.8, 25.9, 22.3; **HRMS (ESI):** Calcd for $C_{25}H_{26}N$ $[M+H]^+$ 340.2060, Found: 340.2064.



[Eq (1)]

A mixture of **3a** and **3b** was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) in total 90% yield. The ratio of **3a**/**3b** was determined to be **1.6:1** by ^{1}H NMR.

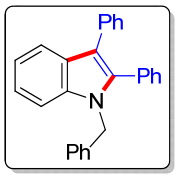




[Eq (2)]

A mixture of **3a** and **3x** was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) in 65% and 14% yields, respectively.

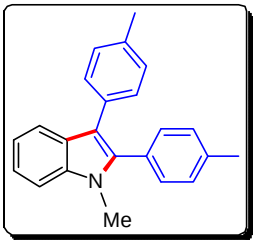
1-benzyl-2,3-diphenyl-1H-indole (3x).[5]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.89 (1H, m), 7.42-7.23 (16H, m), 7.08 (2H, d, *J* = 6.9 Hz), 5.35 (2H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ

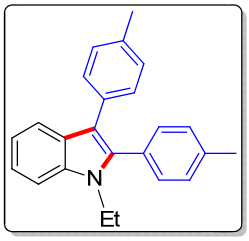
138.1, 137.9, 137.0, 135.1, 131.8, 131.1, 129.9, 128.6, 128.4, 128.2, 128.1, 127.4, 127.1, 126.1, 125.6, 122.3, 120.4, 119.7, 115.6, 110.5, 47.6; **MS (EI):** Calcd for $C_{27}H_{21}N$ [M^+] 359.46, Found: 359.

2,3-bis(4-methylphenyl)-1-methyl-1H-indole (4a).[5]



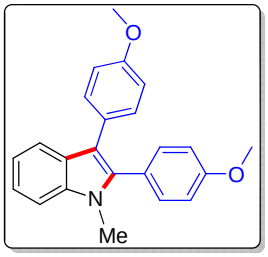
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 60% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.79 (1H, d, *J* = 7.8 Hz), 7.41 (1H, d, *J* = 8.1 Hz), 7.30 (1H, t, *J* = 7.5 Hz), 7.25-7.17 (7H, m), 7.10 (2H, d, *J* = 7.7 Hz), 3.67 (3H, s), 2.41 (3H, s), 2.34 (3H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.7, 137.6, 137.2, 134.9, 132.3, 131.0, 129.7, 129.1, 129.0, 128.9, 127.1, 121.9, 120.0, 119.6, 114.7, 109. 5, 30.9, 21.4, 21.2; **MS (EI):** Calcd for $C_{23}H_{21}N$ [M^+] 311.17, Found: 311.

2,3-bis(4-methylphenyl)-1-ethyl-1*H*-indole (4b).



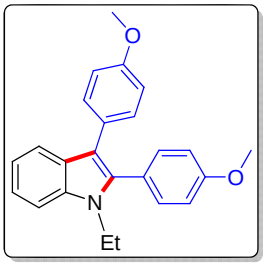
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 80% yield; M.p.: 153-155 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.79 (1H, d, *J* = 7.9 Hz), 7.43 (1H, d, *J* = 8.2 Hz), 7.30-7.28 (1H, m), 7.24-7.22 (3H, m), 7.20-7.15 (4H, m), 7.08 (2H, d, *J* = 7.9 Hz), 4.12 (2H, q, *J* = 7.2 Hz), 2.40 (3H, s), 2.32 (3H, s), 1.29 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.8, 137.2, 136.0, 134.7, 132.3, 130.9, 129.6, 129.3, 129.1, 128.8, 127.3, 121.8, 119.9, 119.7, 114.9, 109.7, 38.5, 21.4, 21.2, 15.4; **HRMS (ESI):** Calcd for $C_{22}H_{24}N$ [M+H]$^+$ 326.1903, Found: 326.1907.

2,3-bis(4-methoxyphenyl)-1-methyl-1*H*-indole (4c).[5]



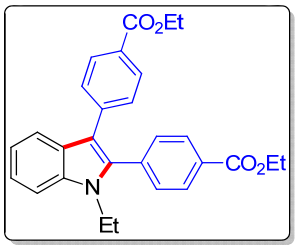
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as an off-white solid in 50% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.76 (1H, d, *J* = 7.9 Hz), 7.40 (1H, d, *J* = 8.2 Hz), 7.32-7.27 (1H, m), 7.26-7.23 (4H, m), 7.20-7.16 (1H, m), 6.95-6.92 (2H, m), 6.87-6.83 (2H, m), 3.85 (3H, s), 3.81 (3H, s), 3.67 (3H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 159.3, 157.5, 137.2, 137.1, 132.3, 130.8, 127.8, 127.1, 124.2, 121.9, 119.9, 119.4, 114.4, 113.9, 113.7, 109.4, 55.23, 55.15, 30.8; **MS (EI):** Calcd for $C_{23}H_{21}NO_2$ [M$^+$] 343.16, Found: 343.

1-ethyl-2,3-bis(4-methoxyphenyl)-1*H*-indole (4d).[6]



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as an yellow solid in 75% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.76 (1H, d, *J* = 7.9 Hz), 7.42 (1H, d, *J* = 8.1 Hz), 7.29-7.21 (4H, m), 7.16 (1H, t, *J* = 7.5 Hz), 6.92 (2H, d, *J* = 8.5 Hz), 6.83 (1H, d, *J* = 8.6 Hz), 4.12 (2H, q, *J* = 7.1 Hz), 3.85 (3H, s), 3.79 (3H, s), 1.28 (3H, t, *J* = 7.1 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 159.3, 157.3, 136.7, 135.8, 132.2, 130.7, 127.7, 127.3, 124.4, 121.7, 119.8, 119.5, 114.6, 113.8, 113.6, 109.6, 55.14, 55.06, 38.5, 15.4; **MS (EI):** Calcd for $C_{24}H_{23}NO_2$ [M$^+$] 357.17, Found: 357.

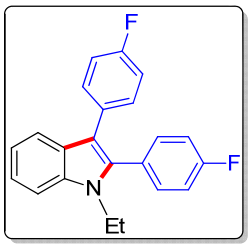
diethyl 4,4'-(1-ethyl-1*H*-indole-2,3-diyl)dibenzoate (4e).



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20 to 1/10) as an yellow solid in 45% yield; M.p.: 88-90 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.10-8.08 (2H, m), 7.96-7.93 (2H, m), 7.81 (1H, d, *J* = 7.9 Hz), 7.47 (1H, d, *J* = 8.2 Hz), 7.43-7.40 (2H, m), 7.36-7.31 (3H, m), 7.23 (1H, td, *J* = 7.9, 0.9 H), 4.42 (2H, q, *J* = 7.1 Hz), 4.36

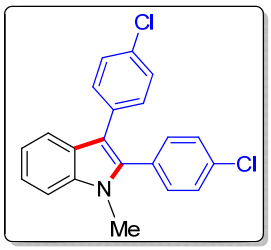
(2H, q, *J* = 7.1 Hz), 4.16 (2H, q, *J* = 7.1 Hz), 1.42 (3H, t, *J* = 7.1 Hz), 1.38 (3H, t, *J* = 7.1 Hz), 1.29 (3H, t, *J* = 7.2 Hz); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 166.7, 166.2, 139.8, 136.7, 136.4, 130.9, 130.3, 129.8, 129.6, 129.5, 128.8, 127.5, 126.8, 122.8, 120.7, 119.7, 115.2, 110.1, 61.2, 60.8, 38.8, 15.3, 14.34, 14.32; **HRMS (ESI):** Calcd for $C_{28}H_{28}NO_4$ $[M+H]^+$ 442.2013, Found: 442.2021.

1-ethyl-2,3-bis(4-fluorophenyl)-1*H*-indole (4f).



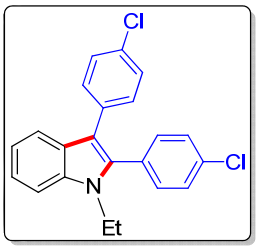
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 67% yield; M.p.: 152-154 °C; **^1H NMR ($CDCl_3$, 400 MHz):** δ 7.73 (1H, d, *J* = 7.9 Hz), 7.44 (1H, d, *J* = 8.2 Hz), 7.32-7.28 (3H, m), 7.24-7.17 (3H, m), 7.12-7.08 (2H, m), 6.99-6.95 (2H, t, *J* = 8.8 Hz), 4.12 (2H, q, *J* = 7.2 Hz), 1.29 (3H, t, *J* = 7.2 Hz); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 162.6 (d, *J* = 248.9 Hz), 161.1 (d, *J* = 244.8 Hz), 136.0, 135.9, 132.7 (d, *J* = 8.3 Hz), 131.1 (d, *J* = 7.6 Hz), 130.9 (d, *J* = 2.4 Hz), 128.0 (d, *J* = 2.9 Hz), 127.1, 122.3, 120.3, 119.5, 115.7 (d, *J* = 21.8 Hz), 115.1 (d, *J* = 21.1 Hz), 114.6, 109.8, 38.6, 15.4; **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -112.9 (s), -117.2 (s); **HRMS (ESI):** Calcd for $C_{22}H_{18}F_2N$ $[M+H]^+$ 334.1402, Found: 334.1399.

2,3-bis(4-chlorophenyl)-1-methyl-1*H*-indole (4g). [5]



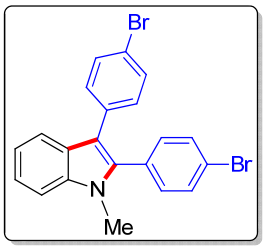
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 54% yield; **^1H NMR ($CDCl_3$, 400 MHz):** δ 7.73 (1H, d, *J* = 8.0 Hz), 7.42 (1H, d, *J* = 8.2 Hz), 7.40-7.38 (2H, m), 7.35-7.31 (1H, m), 7.28-7.25 (2H, m), 7.24-7.20 (4H, m) 3.68 (3H, s); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 137.4, 136.5, 134.4, 133.4, 132.3, 131.5, 131.0, 130.0, 128.9, 128.5, 126.7, 122.6, 120.5, 119.4, 114.3, 109.7, 31.0; **MS (EI):** Calcd for $C_{21}H_{15}Cl_2N$ $[M^+]$ 351.06, Found: 351.

2,3-bis(4-chlorophenyl)-1-ethyl-1*H*-indole (4h).



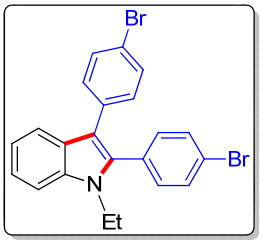
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 88% yield; M.p.: 200-202 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.66 (1H, d, *J* = 7.9 Hz), 7.37 (1H, d, *J* = 8.2 Hz), 7.32 (2H, d, *J* = 8.2 Hz), 7.23 (1H, d, *J* = 7.9 Hz), 7.20-7.00 (7H, m) 4.05 (2H, q, J = 7.1 Hz), 1.21 (3H, t, *J* = 7.1 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 136.1, 136.0, 134.4, 133.4, 132.2, 131.4, 130.9, 130.3, 128.9, 128.5, 126.9, 122.5, 120.4, 119.5, 114.6, 109.9, 38.7, 15.4; **HRMS (ESI):** Calcd for $C_{22}H_{18}Cl_2N$ $[M+H]^+$ 366.0811, Found: 366.0814.

2,3-bis(4-bromophenyl)-1-methyl-1H-indole (4i).[7]



The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 44% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.72 (1H, d, *J* = 8.0 Hz), 7.54 (2H, d, *J* = 7.8 Hz), 7.42-7.39 (3H, m), 7.35-7.30 (1H, m), 7.22-7.13 (5H, m), 3.67 (3H, s); **^{13}C{^{1}H} NMR (CDCl3, 100 MHz):** δ 137.4, 136.4, 133.9, 132.6, 131.8, 131.5, 131.3, 130.4, 126.6, 122.7, 120.6, 119.6, 119.3, 114.3, 109.7, 31.0; **MS (EI):** Calcd for $C_{21}H_{15}Br_2N$ $[M^+]$ 438.96, Found: 439.

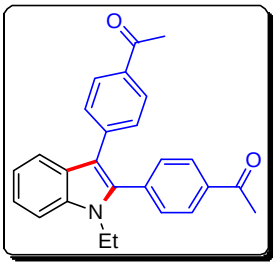
2,3-bis(4-bromophenyl)-1-ethyl-1H-indole (4j).



The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 73% yield; M.p.: 203-205 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.73 (1H, d, *J* = 7.9 Hz), 7.54 (1H, d, *J* = 8.3 Hz), 7.44 (1H, d, *J* = 8.3 Hz), 7.40 (2H, d, *J* = 8.4 Hz), 7.31 (1H, t, *J* = 7.6 Hz), 7.23-7.17 (3H, m), 7.13 (2H, d, *J* = 8.4 Hz), 4.12 (2H, q, *J* = 7.1 Hz), 1.28 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 136.2, 136.0, 133.8, 132.5, 131.9, 131.4, 131.3, 130.8, 126.8, 122.7, 122.5, 120.5, 119.5, 114.5, 109.9, 38.7, 15.4 (one signal missing due to

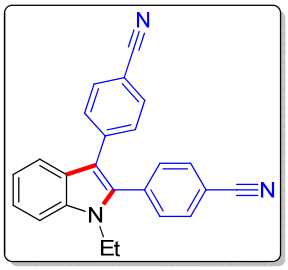
overlap); **HRMS (ESI):** Calcd for $C_{22}H_{18}Br_2N$ $[M+H]^+$ 453.9805, Found: 453.9819.

1-ethyl-2,3-bis(4-acetylphenyl)-1*H*-indole (4k).



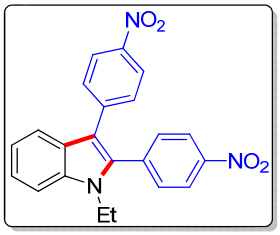
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/10) as an yellow solid in 91% yield; M.p.: 147-149 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.00 (2H, d, *J* = 8.3 Hz), 7.86 (2H, d, *J* = 8.4 Hz), 7.81 (1H, d, *J* = 8.0 Hz), 7.48 (1H, d, *J* = 8.2 Hz), 7.44 (2H, d, *J* = 8.3 Hz), 7.37-7.33 (3H, m), 7.24 (1H, t, *J* = 7.8 Hz), 4.17 (2H, q, *J* = 7.2 Hz), 2.65 (3H, s), 2.58 (3H, s), 1.30 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 197.8, 197.6, 140.2, 136.69, 136.66, 136.5, 134.3, 131.1, 129.6, 128.6, 128.5, 126.8, 122.9, 120.9, 119.7, 115.2, 110.1, 38.9, 26.7, 26.5, 15.3 (one signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{26}H_{24}NO_2$ $[M+H]^+$ 382.1802, Found: 382.1808.

4,4'-(1-ethyl-1*H*-indole-2,3-diyl)dibenzonitrile (4l).



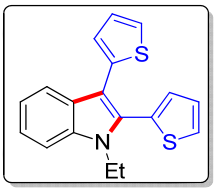
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/10) as an yellow solid in 57% yield; M.p.: 256-258 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.76-7.72 (3H, m), 7.56 (2H, d, *J* = 8.3 Hz), 7.49 (1H, d, *J* = 8.3 Hz), 7.45 (2H, d, *J* = 8.2 Hz), 7.37 (1H, t, *J* = 7.6 Hz), 7.32 (2H, d, *J* = 8.3 Hz), 7.26 (1H, t, *J* = 7.5 Hz), 4.16 (2H, q, *J* = 7.1 Hz), 1.30 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 139.6, 136.5, 136.3, 135.7, 132.5, 132.2, 131.5, 130.1, 126.5, 123.4, 121.2, 119.5, 119.1, 118.3, 115.0, 112.4, 110.3, 109.2, 39.0, 15.3; **HRMS (ESI):** Calcd for $C_{24}H_{18}N_3$ $[M+H]^+$ 348.1495, Found: 348.1501.

1-ethyl-2,3-bis(4-nitrophenyl)-1*H*-indole(4m).



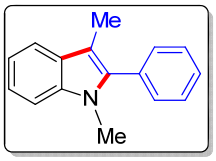
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/10) as an orange solid in 40% yield; M.p.: 258-260 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.31 (2H, d, *J* = 8.6 Hz), 8.15 (2H, d, *J* = 8.7 Hz), 7.78 (1H, d, *J* = 8.0 Hz), 7.54-7.50 (3H, m), 7.41-7.37 (3H, m), 7.30-7.26 (1H, m), 4.19 (2H, q, *J* = 7.1 Hz), 1.32 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 147.8, 145.7, 141.7, 138.2, 136.7, 135.7, 131.8, 130.0, 126.5, 124.1, 123.9, 123.6, 121.5, 119.5, 115.0, 110.4, 39.1, 15.4; **HRMS (ESI):** Calcd for $C_{22}H_{18}N_3O_4$ $[M+H]^+$ 388.1292, Found: 388.1291.

1-ethyl-2,3-di(thiophen-2-yl)-1*H*-indole (4n).



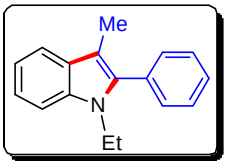
The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as a pale yellow solid in 37% yield; M.p.: 93-95 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.96 (1H, d, *J* = 8.0 Hz), 7.53 (1H, dd, *J* = 3.9, 2.4 Hz), 7.43 (1H, d, *J* = 8.2 Hz), 7.35-7.31 (1H, m), 7.26-7.16 (4H, m), 7.06-7.01 (2H, m), 4.17 (2H, q, *J* = 7.2 Hz), 1.37 (3H, t, *J* = 7.2 Hz); **^{13}C NMR (CDCl3, 100 MHz):** δ 136.8, 136.0, 131.8, 130.6, 129.4, 128.3, 127.3, 126.8, 126.5, 124.8, 123.7, 122.8, 120.4, 120.2, 111.2, 109.7, 38.8, 15.6; **HRMS (ESI):** Calcd for $C_{18}H_{16}NS_2$ $[M+H]^+$ 310.0719, Found: 310.0713.

1,3-dimethyl-2-phenyl-1*H*-indole (4o).[5]



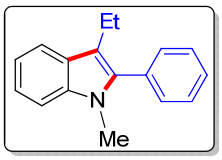
The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 50% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.64 (1H, d, *J* = 7.8 Hz), 7.54-7.50 (2H, m), 7.46-7.42 (3H, m), 7.36 (1H, d, *J* = 8.1 Hz), 7.31-7.27 (1H, m), 7.21-7.17 (1H, m), 3.64 (3H, s), 2.32 (3H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.6, 137.2, 132.1, 130.6, 128.4, 128.3, 127.7, 121.7, 119.1, 118.8, 109.2, 108.5, 30.9, 9.3; **MS (EI):** Calcd for $C_{16}H_{15}N$ $[M^+]$ 221.12, Found: 221.

1-ethyl-3-methyl-2-phenyl-1*H*-indole (4p).[8]



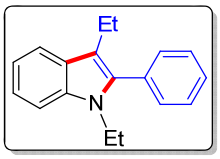
The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 45% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.62 (1H, d, *J* = 7.8 Hz), 7.53-7.47 (2H, m), 7.47-7.37 (4H, m), 7.28-7.24 (1H, m), 7.18-7.14 (1H, m), 4.09 (2H, q, *J* = 7.2 Hz), 2.26 (3H, s), 1.23 (3H, t, *J* = 7.2 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.1, 135.9, 132.4, 130.5, 128.7, 128.3, 127.8, 121.5, 119.0, 118.9, 109.5, 108.8, 38.6, 15.3, 9.2; **MS (EI):** Calcd for $C_{17}H_{17}N$ [M$^+$] 235.14, Found: 235.

3-ethyl-1-methyl-2-phenyl-1*H*-indole (4q).[9]



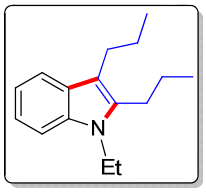
The title compound was isolated by column chromatography (eluent: CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 54% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.71 (1H, d, *J* = 7.9 Hz), 7.55-7.50 (2H, m), 7.49-7.46 (1H, m), 7.45-7.42 (2H, m), 7.38 (1H, d, *J* = 8.2 Hz), 7.32-7.28 (1H, m), 7.23-7.18 (1H, m), 3.62 (3H, s), 2.77 (2H, q, *J* = 7.5 Hz), 1.28 (3H, t, *J* = 7.5 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.22, 137.19, 132.2, 130.6, 128.3, 127.9, 127.4, 121.6, 119.0, 115.3, 109.3, 30.8, 17.9, 16.0 (one signal missing due to overlap); **MS (EI):** Calcd for $C_{17}H_{17}N$ [M$^+$] 235.14, Found: 235.

1,3-diethyl-2-phenyl-1*H*-indole (4r).[8]



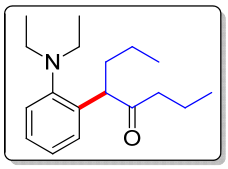
The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an off-white solid in 44% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.66 (1H, d, *J* = 7.8 Hz), 7.51-7.44 (3H, m), 7.41-7.36 (3H, m), 7.24 (1H, t, *J* = 7.2 Hz), 7.15 (1H, t, *J* = 7.4 Hz), 4.04 (2H, q, *J* = 7.1 Hz), 2.68 (2H, q, *J* = 7.5 Hz), 1.22 (3H, t, *J* = 7.1 Hz), 1.20 (3H, t, *J* = 7.4 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 136.7, 135.9, 132.6, 130.6, 128.3, 127.9, 127.7, 121.4, 119.1, 118.9, 115.5, 109.6, 38.5, 17.8, 16.0, 15.4; **MS (EI):** Calcd for $C_{18}H_{19}N$ [M$^+$] 249.15, Found: 249.

1-ethyl-2,3-dipropyl-1*H*-indole (4s).[10]



The title compound was isolated by column chromatography (eluent:CH_2Cl_2/petroleum ether = 1/10) as an colourless oil in 22% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.53 (1H, dt, *J* = 7.8, 0.8 Hz), 7.27-7.25 (1H, m), 7.13 (1H, ddd, *J* = 8.2, 7.0, 1.2 Hz), 7.05 (1H, ddd, *J* = 8.0, 7.1, 1.1 Hz), 4.12 (2H, q, *J* = 7.2 Hz), 2.72-2.66 (4H, m), 1.70-1.58 (4H, m), 1.34 (3H, t, *J* = 7.2 Hz), 1.02 (3H, t, *J* = 7.4 Hz), 0.98 (3H, t, *J* = 7.4 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 136.2, 135.4, 128.2, 120.3, 118.43, 118.35, 111.7, 108.8, 37.7, 26.8, 26.6, 24.4, 23.9, 15.4, 14.4, 14.2; **MS (EI):** Calcd for $C_{16}H_{23}N$ [M$^+$] 229.18, Found: 229.

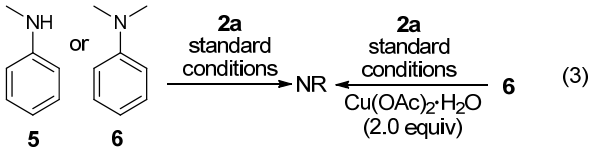
(2-(diethylamino)phenyl)octan-4-one (4s*).



The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/20) as an yellow solid in 35% yield; M.p.: 60-62 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.21-7.17 (1H, m), 7.16-7.11 (2H, m), 7.04 (1H, td, *J* = 7.2, 1.6 Hz), 4.53 (1H, dd, *J* = 9.1, 4.7 Hz), 3.04-2.91 (4H, m), 2.32-2.27 (2H, m), 2.17-2.08 (1H, m), 1.57-1.32 (4H, m), 1.24-1.17 (1H, m), 1.03 (6H, t, *J* = 7.1 Hz), 0.91 (3H, t, *J* = 7.1 Hz), 0.79 (3H, t, *J* = 7.4 Hz); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** 211.4, 149.8, 137.4, 128.1, 127.0, 124.4, 123.4, 50.6, 48.3, 44.1, 34.6, 21.6, 17.3, 14.3, 13.6, 12.7; **HRMS (MALDI):** Calcd for $C_{18}H_{30}NO$ [M+H]$^+$ 276.2322, Found: 276.2326;

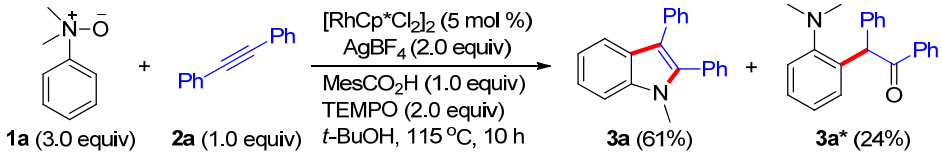
Mechanistic Study

(1) Rhodium-catalyzed Annulation of *N*-methylaniline (5) or *N*,*N*-dimethylaniline (6) with 2a---[Eq (3)]



A mixture of *N*-methylaniline (**5**) or *N*,*N*-dimethylaniline (**6**) (0.6 mmol, 3.0 equiv), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mol, 5.0 mol %), $AgBF_4$ (78 mg, 0.4 mmol, 2.0 equiv), [or with additional oxidant 2.0 equiv of $Cu(OAc)_2 \bullet H_2O$ for **6**] and $MesCO_2H$ (33 mg,1.0 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 10 h under vigorous stirring. The reaction was cooled to room temperature and diluted with 3 mL of CH_2Cl_2. *No desired products was detected by TLC and* ^{1}*H NMR.*

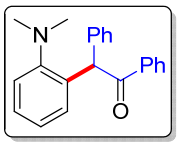
(2) Free radical trapping experiments---[Eq (4)]



A mixture of **1a** (82 mg, 0.6 mmol, 3.0 equiv), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mol, 5.0 mol %), $AgBF_4$ (78 mg, 0.4 mmol, 2.0 equiv), TEMPO (62 mg, 0.4 mmol, 2.0 equiv), and $MesCO_2H$ (33 mg,1.0 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 10 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (CH_2Cl_2/petroleum ether =

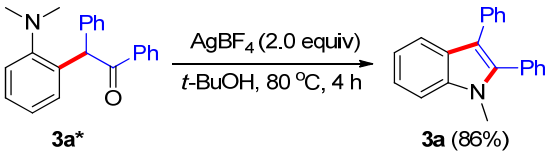
1/10 , then EtOAc/ petroleum ether = 1/20) to provide **3a** and **3a*** in 61% and 24% yields, respectively.

2-(2-(dimethylamino)phenyl)-1,2-diphenylethanone (3a*).

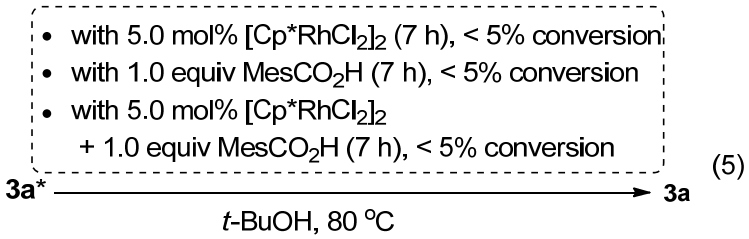


M.p.: 50-52 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.06 (2H, d, *J* = 7.6 Hz), 7.48 (1H, t, *J* = 7.3 Hz), 7.41 (2H, d, *J* = 7.8 Hz), 7.31-7.33 (4H, m), 7.30-7.25 (3H, m), 7.06-7.02 (2H, m), 6.49 (1H, s), 2.51 (6H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 198.0, 151.7, 138.2, 137.6, 137.2, 132.3, 129.9, 129.8, 128.6, 128.3, 128.2, 128.0, 127.0, 124.6, 121.6, 53.6, 44.7; **HRMS (MALDI):** Calcd for $C_{22}H_{21}NO$ $[M+H]^+$ 316.1696 Found: 316.1699.

(3) Conversion of 3a* to 3a---[Eq (5)]



A mixture of **3a*** (12.5 mg, 0.04 mmol, 1.0 equiv) and $AgBF_4$ (16mg, 0.08 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (1.5 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 80 °C for 4 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1/10) to provide **3a** in 86% yields.

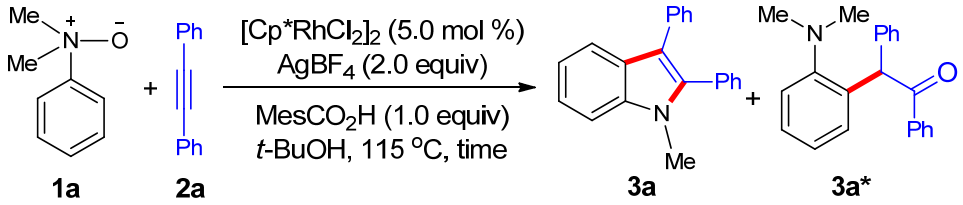


(5)

A mixture of **3a*** (12.5 mg, 0.04 mmol, 1.0 equiv) and $[Cp^*RhCl_2]_2$ (5 mol %) or $MesCO_2H$ (1.0 equiv) or $[Cp^*RhCl_2]_2$ (5 mol %) with $MesCO_2H$ (1.0 equiv) were

weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (1.5 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 80 °C for 7 h under vigorous stirring. The reaction was cooled to room temperature and diluted with 3 mL of CH_2Cl_2. The reaction mixture was detected by ^{1}H NMR.

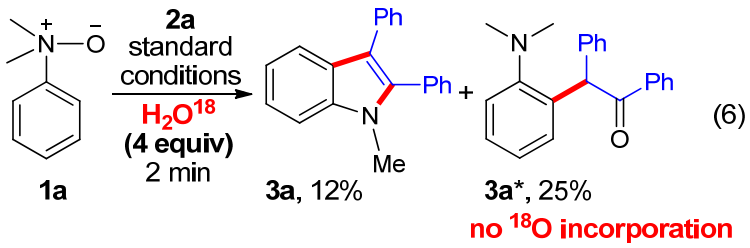
(4) Reactions at control time



time	**3a**/**3a*** (by ^{1}H NMR)
1 min	27%/14%
3 min	41%/14%
5 min	47%/10%
7 min	49%/10%

A mixture of **1a** (82 mg, 0.6 mmol, 3.0 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (7.8 mg, 0.04 mmol, 20 mol%), and $MesCO_2H$ (33 mg, 0.2 mmol, 1 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for indicated time under vigorous stirring. The reaction was cooled to room temperature by ice water transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. Unreacted **2a** was removed by petroleum ether and then the reaction mixture was washed by petroleum ether /EA (10:1 to 5:1). The crude mixtures are determined by ^{1}H NMR.

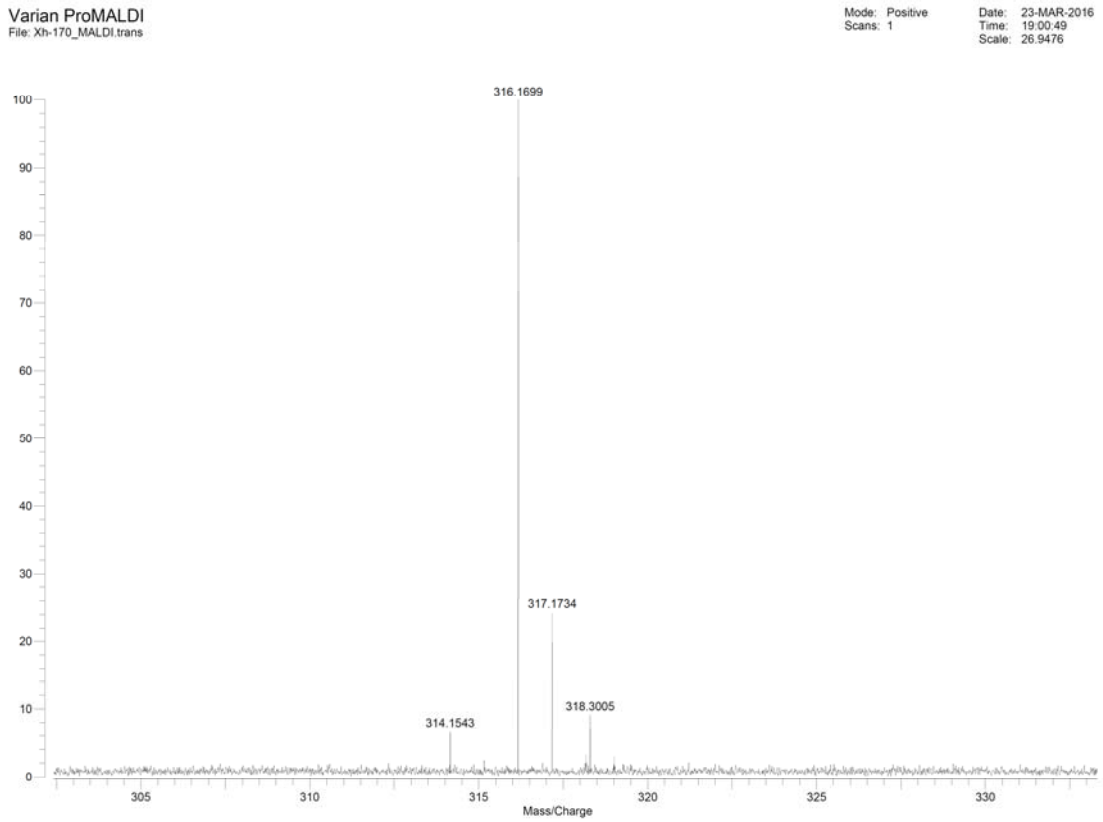
(5) ^{18}O labeling experiment---[Eq (6)]



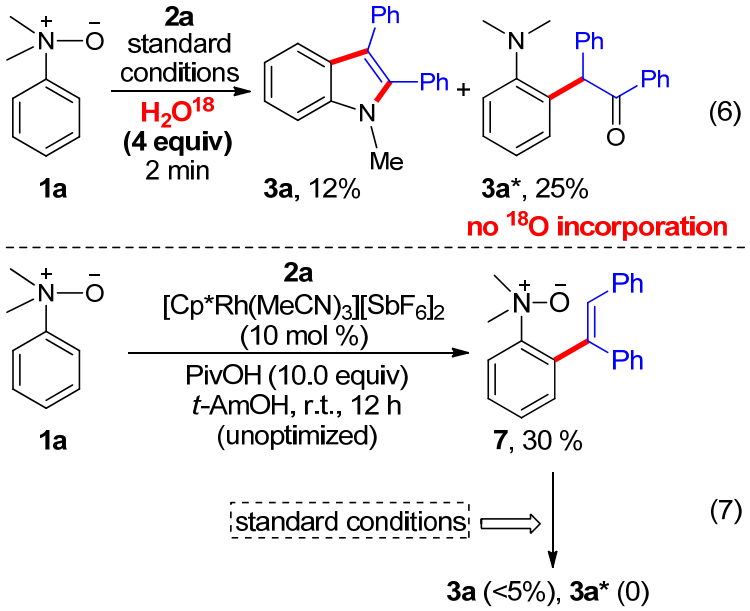
(6)

A mixture of **1a** (0.6 mmol, 3.0 equiv), **2a** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mol, 5.0 mol %), $AgBF_4$ (78 mg, 0.4 mmol, 2.0 equiv), and $MesCO_2H$ (33 mg,1.0 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. H_2O^{18} (14.4mg, 4.0 equiv) and dry *t*-BuOH (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 2 minutes under vigorous stirring. The reaction was quenched and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/CH_2Cl_2. HRMS(MALDI) demonstrates that there are no ^{18}O was detected in the isolated **3a***, indicating that water is not involved in the OAT step and an intramolecular OAT is most likely to occur.

[**Note**: HRMS: Calcd for $C_{22}H_{21}NO$ $[3a^*]^+$ 315.1618; Calcd for $C_{22}H_{22}NO$ $[3a^*+H]^+$ 316.1696; Calcd for $C_{22}H_{21}N^{18}O$ $[3a^*(^{18}O)]^+$ 317.1660; Calcd for $C_{22}H_{22}N^{18}O$ $[3a^*(^{18}O)+H]^+$ 318.1738.]


Varian ProMALDI
File: Xh-170_MALDI.trans
Mode: Positive
Scans: 1
Date: 23-MAR-2016
Time: 19:00:49
Scale: 26.9476
316.1699
317.1734
318.3005
314.1543
Mass/Charge

(6) Preparation of *N,N*-dimethylaniline *N*-oxide 7 and its transformation---[Eq (7)]



A mixture of **1a** (0.5 mmol, 1.0 equiv), **2a** (0.75 mmol, 1.5 equiv), [Cp*Rh(MeCN)3][SbF6]2 (10 mol %), and PivOH (10.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-AmOH (5.0 mL) was added and the resulting mixture was stirred at room temperature for 12 hours. Then solid NaOH (15.0 equiv) was added and the reaction mixture was stirred for 1 hour ,the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/MeOH (4:1 to 1:1) to give **7** in 30 % yield.

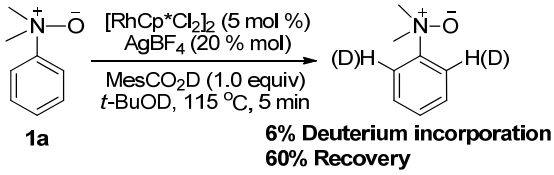
(*E*)-2-(1,2-diphenylvinyl)-*N,N*-dimethylaniline oxide (7)

The title compound was isolated by column chromatography (eluent: EtOAc/MeOH = 1/1) as an colorless oil; **^{1}H NMR (CDCl$_3$, 400 MHz):** δ 8.87 (1H, d, *J* = 7.8 Hz), 7.54 (1H, td, *J* = 7.3, 1.1 Hz), 7.46 (1H, td, *J* = 7.3, 1.1 Hz), 7.40 (1H, dd, *J* = 7.4, 1.7 Hz), 7.25-7.19 (6H, m), 7.18-7.16 (2H, m), 7.14-7.12 (2H, m), 6.73 (1H, s), 3.80-3.00 (6H, br s) ; **^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz):** δ 152.2, 141.0, 138.1, 136.2, 134.8, 134.1, 132.3, 129.8, 129.4, 129.1, 129.0, 128.6, 128.3, 127.6, 123.8, 62.42 (one signal missing due to overlap); **HRMS (MALDI):** Calcd for $C_{22}H_{22}NO$ $[M+H]^+$ 316.1696, Found:

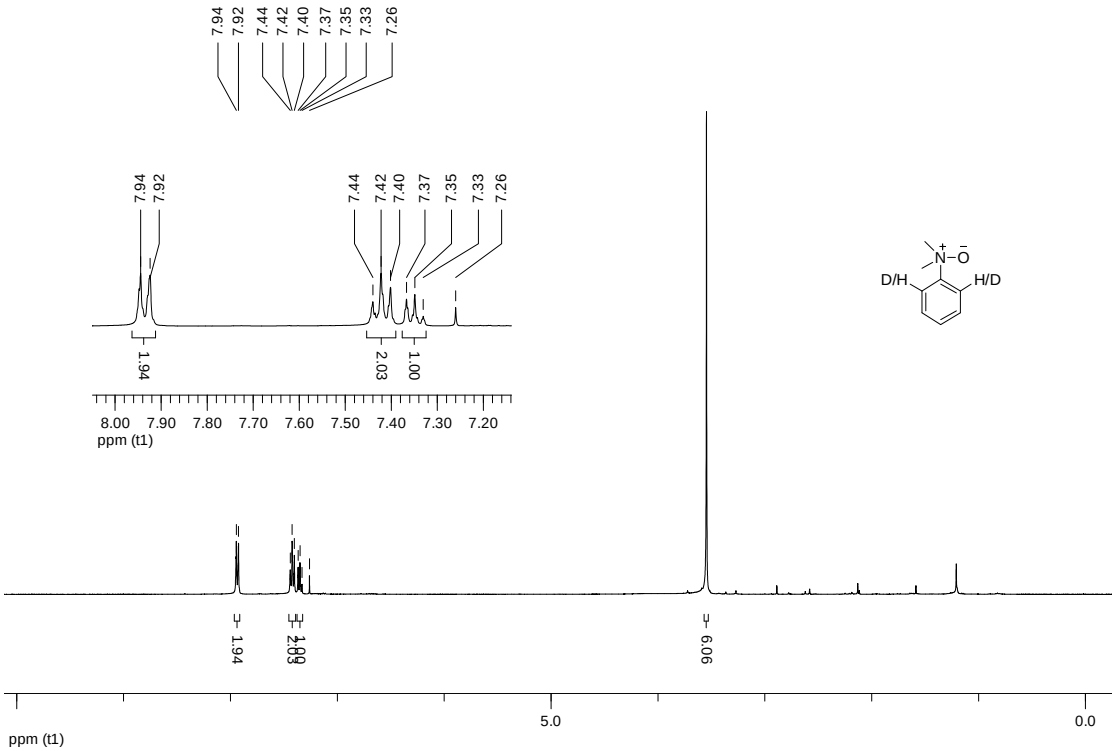
316.1699.

Transformation: Olefin **7** as then subjected to the standard conditions, very low transformation from **7** to **3a*** was observed. Therefore, the *ortho*-olefination intermediate can be ruled out.

(7) Hydrogen-deuterium exchange experiment---[Eq (8)]

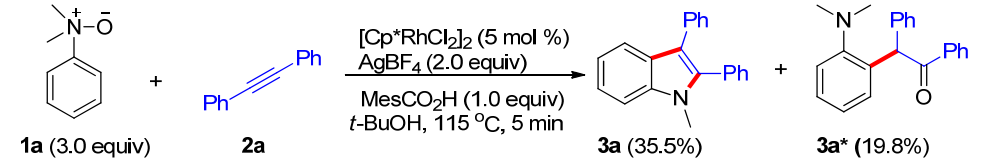


A mixture of **1a** (82 mg, 0.6 mmol, 3.0 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (7.8 mg, 0.04 mmol, 20 mol%), and $MesCO_2D$ (33 mg, 0.2 mmol, 1 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOD (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 5 min under vigorous stirring. The reaction was cooled to room temperature by ice water and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on alumina (CH_2Cl_2/MeOH = 5/1, v/v) to provide $[D_n]$-**1a** (49.2 mg, 60% recovery). ^{1}H NMR analysis showed that 6% hydrogen at the *ortho* position of phenyl ring of **1a** was deuterated.

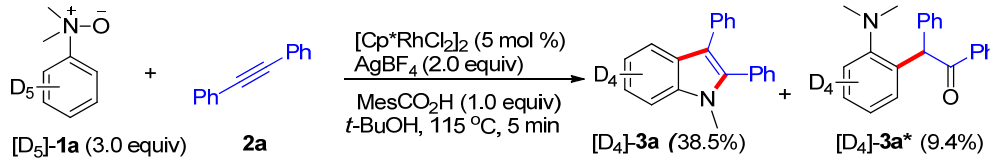

7.94
7.92
7.44
7.42
7.40
7.37
7.35
7.33
7.26
1.94
2.03
1.00
8.00 7.90 7.80 7.70 7.60 7.50 7.40 7.30 7.20
ppm (t1)
1.94
2.09
6.06
5.0
0.0
ppm (t1)
D/H
H/D
N
O

(8) Kinetic isotope effect---[Eq (9)]

(i)



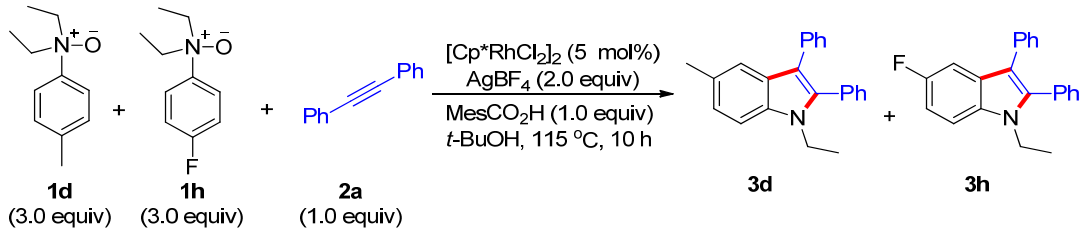
(ii)



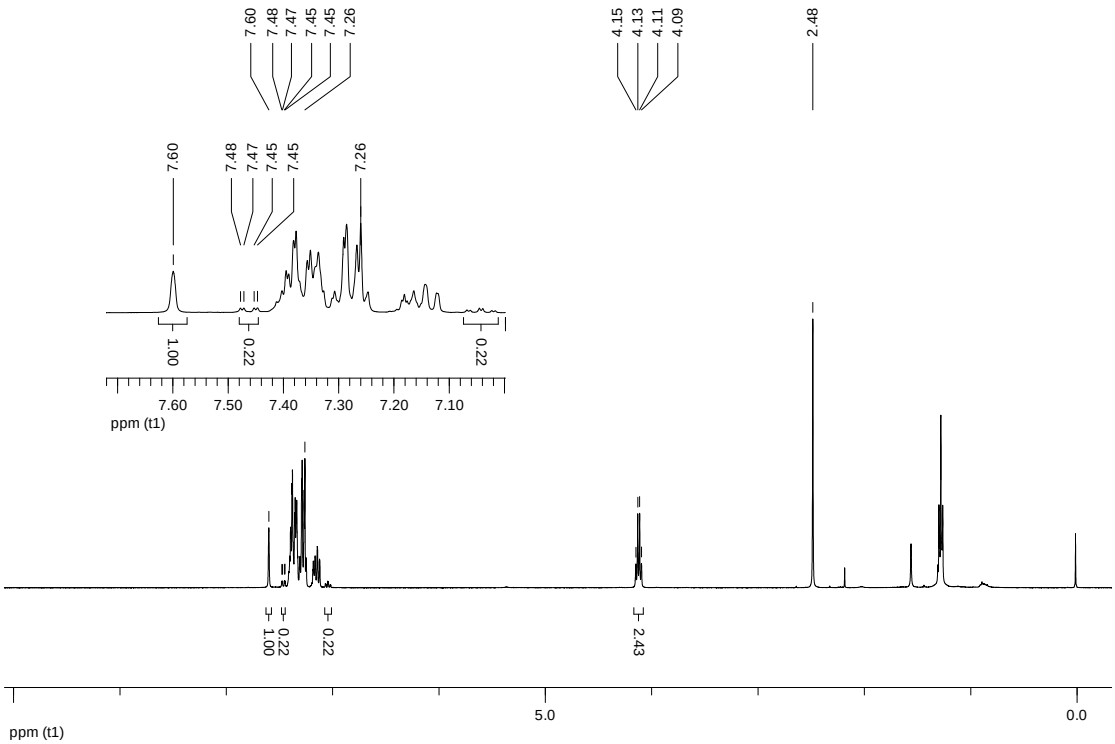
A mixture of **1a** (82 mg, 0.6 mmol, 3.0 equiv) or **1a-*d*$_5$** (85 mg, 0.6 mmol, 3.0 equiv), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), [RhCp*Cl_2]$_2$ (6.2 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (7.8 mg, 0.04 mmol, 20 mol%), and $MesCO_2D$ (33 mg, 0.2 mmol, 1 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOD (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 5 min under vigorous stirring. The reaction was cooled to room temperature by ice water and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1/10 to get **3a** or [D$_4$]-**3a**, EtOAc/petroleum ether = 1/20 to get **3a*** or [D$_4$]-**3a***). A kinetic isotope effect (KIE) of k_H/k_D = 1.14 [(35.5 + 19.8)/(38.5 + 9.8)] in the intermolecular isotopic study of two parallel competition reactions was observed.

[D$_4$]-**3a:** **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.44-7.37 (3H, m), 7.37-7.31 (3H, m), 7.31-7.27 (3H, m), 7.21-7.16 (1H, m), 3.69 (3H, s); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 137.7, 137.2, 135.2, 131.9, 131.1, 129.8, 128.6, 128.1, 128.0, 126.8, 125.5, 121.6 (t, *J* = 24 Hz), 119.9, 119.3 (q, *J* = 25 Hz), 115.0, 109.2 (t, *J* = 25 Hz), 30.9.

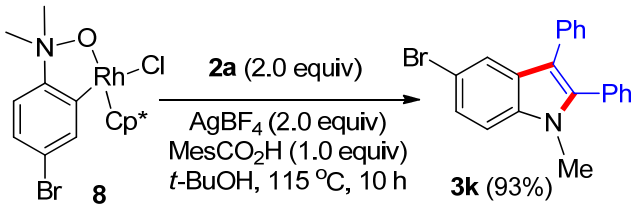
(9) Competition experiments between electronically differentiated aniline *N*-oxides---[Eq (10)]



A mixture of **1d** (107 mg, 0.6 mmol, 3.0 equiv), **1h** (110 mg, 0.6 mmol, 3.0 equiv), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (7.8 mg, 0.04 mmol, 20 mol %), and $MesCO_2H$ (33 mg, 0.2 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 10 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1/10). The ratio of **3d**/**3h** was determined to be **4.5:1** by ^{1}H NMR.

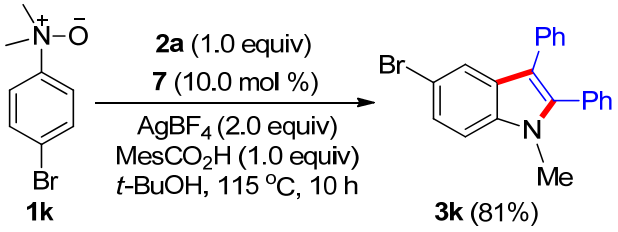


(10) The reaction of stoichiometric amounts of complex 8 with alkyne 2a ---[Eq (11)]



A mixture of **8** (48.9 mg, 0.1 mmol, 1.0 equiv), **2a** (35.6 mg, 0.2 mmol, 2.0 equiv), $AgBF_4$ (39 mg, 0.2 mmol, 2.0 equiv), and $MesCO_2H$ (16.4 mg,0.1 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 10 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1/10) to provide **3k** (34.0 mg, 93%).

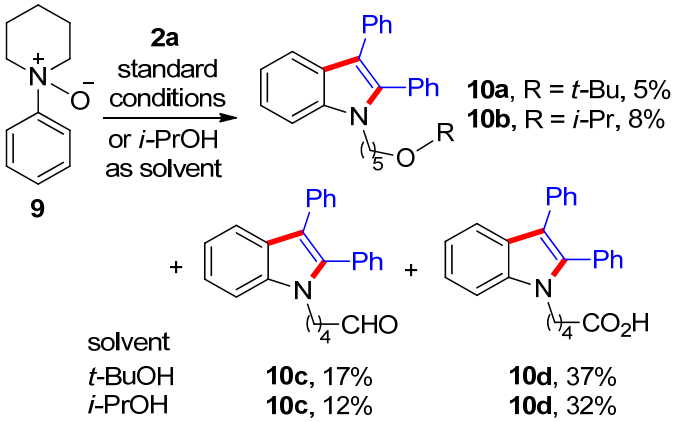
(11) Complex 8-catalyzed annulation of aniline *N*-oxide 1k with 2a---[Eq (12)]



A mixture of **1k** (130 mg, 0.6 mmol, 3.0 equiv), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), **8** (9.8 mg, 0.02 mol, 10 mol %), $AgBF_4$ (78 mg, 0.4 mmol, 2.0 equiv), and $MesCO_2H$ (33 mg,0.2 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 10 h under vigorous stirring. The reaction was

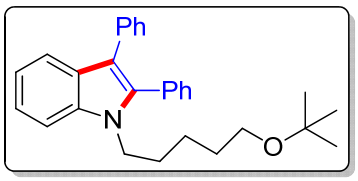
cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1/10) to provide **3k** (58.9 mg, 81%).

(12) 1-phenylpiperidine *N*-oxide experiments---[Eq (13)]



A mixture of **9** (106 mg, 0.6 mmol, 3.0 equiv), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %), $AgBF_4$ (7.8 mg, 0.04 mmol, 20 mol %), and $MesCO_2H$ (33 mg, 0.2 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Solvent (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 10 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (EtOAc/petroleum ether = 1/50-1/1) to provide the resulting products.

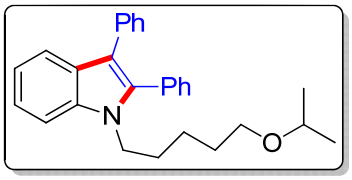
1-(5-(tert-butoxy)pentyl)-2,3-diphenyl-1H-indole (10a)



The title compound was isolated by column chromatography (eluent:EtOAc/petroleum ether = 1/50) as an yellow oil in 5% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.80 (1H, d, *J* = 7.9 Hz), 7.43 (1H, d, *J* = 8.2 Hz), 7.40-7.36 (3H, m), 7.34-7.31 (2H, m), 7.30-7.26 (4H, m), 7.25-7.23 (1H, m), 7.20-7.13 (2H, m), 4.09 (2H, t, *J* = 7.7 Hz), 3.22 (2H, t, *J* = 6.4 Hz), 1.74-1.66 (2H, m), 1.45-1.38

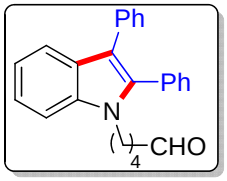
(2H, m), 1.27-1.21 (2H, m), 1.13 (9H, s); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 137.5, 136.3, 135.2, 132.2, 131.1, 129.8, 128.4, 128.1, 127.1, 125.4, 121.9, 120.0, 119.7, 115.2, 109.9, 72.4, 61.1, 43.9, 30.0, 29.8, 27.5, 23.6 (one carbon signal missing due to overlap); **HRMS (ESI):** Calcd for $C_{29}H_{34}NO$ $[M+H]^+$ 412.2635, Found: 412.2641.

1-(5-isopropoxypentyl)-2,3-diphenyl-1H-indole (10b)



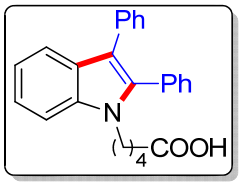
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as an yellow oil in 8% yield; **^1H NMR ($CDCl_3$, 400 MHz):** δ 7.81 (1H, d, *J* = 7.9 Hz), 7.43 (1H, d, *J* = 8.2 Hz), 7.41-7.36 (3H, m), 7.34-7.31 (3H, m), 7.29-7.26 (3H, m), 7.26-7.23 (1H, m), 7.21-7.13 (2H, m), 4.09 (2H, t, *J* = 7.6 Hz), 3.47 (1H, dt, *J* = 12.1, 6.1 Hz), 3.29 (2H, t, *J* = 6.4 Hz), 1.76-1.66 (m), 1.49-1.40 (2H, m), 1.30-1.20 (2H, m), 1.11 (6H, d, *J* = 6.1 Hz); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 137.5, 136.3, 135.2, 132.2, 131.1, 129.8, 128.4, 128.1, 127.1, 125.4, 122.0, 120.0, 119.7, 115.2, 109.9, 71.3, 67.7, 43.8, 29.8, 29.6, 23.6, 22.1; **HRMS (ESI):** Calcd for $C_{28}H_{32}NO$ $[M+H]^+$ 398.2478, Found: 398.2481.

5-(2,3-diphenyl-1H-indol-1-yl)pentanal (10c)



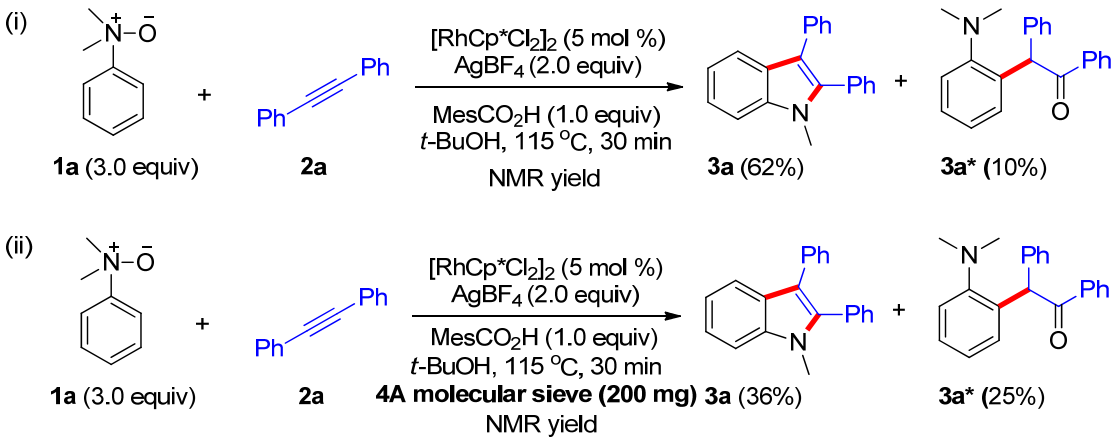
The title compound was isolated by column chromatography (eluent:EtOAc/petroleum ether = 1/10 to 1/5) as an orange oil in 20% yield; **^1H NMR ($CDCl_3$, 400 MHz):** δ 9.63 (1H, t, *J* = 1.4 Hz), 7.81 (1H, d, *J* = 7.9 Hz), 7.42 (1H, d, *J* = 8.2 Hz), 7.40-7.38 (3H, m), 7.34-7.27 (6H, m), 7.26-7.24 (1H, m), 7.21-7.14 (2H, m), 4.14 (2H, t, *J* = 7.3Hz), 2.25 (2H, td, *J* = 7.3, 1.4 Hz), 1.74-1.67 (2H, m), 1.50-1.43 (2H, m); **$^{13}C\{^1H\}$ NMR (CDCl3, 100 MHz):** δ 201.7, 137.4, 136.3, 135.0, 132.1, 131.1, 129.8, 128.5, 128.2, 128.1, 127.2, 125.5, 122.1, 120.2, 119.8, 115.5, 109.8, 43.2, 43.1, 29.2, 19.1; **HRMS (ESI):** Calcd for $C_{25}H_{24}NO$ $[M+H]^+$ 354.1852, Found: 354.1848.

5-(2,3-diphenyl-1H-indol-1-yl)pentanoic acid (10d)



The title compound was isolated by column chromatography (eluent:EtOAc/petroleum ether = 1/2 to 1/1) as an off-white solid in 37% yield; M.p.: 85-87 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.81 (1H, d, *J* = 7.9 Hz), 7.42 (1H, d, *J* = 8.2 Hz), 7.40-7.36 (3H, m), 7.34-7.28 (6H, m), 7.26-7.24 (1H, m), 7.21-7.15 (2H, m), 4.13 (2H, t, *J* = 7.4 Hz), 2.19 (2H, t, *J* = 7.3 Hz), 1.77-1.69 (2H, m), 1.53-1.45 (2H, m); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 179.2, 137.3, 136.3, 135.0, 132.1, 131.1, 129.8, 128.5, 128.14, 128.07, 127.2, 125.4, 122.1, 120.1, 119.8, 115.4, 109.8, 43.2, 33.2, 29.2, 21.7; **HRMS (ESI):** Calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$ 370.1802, Found: 370.1809.

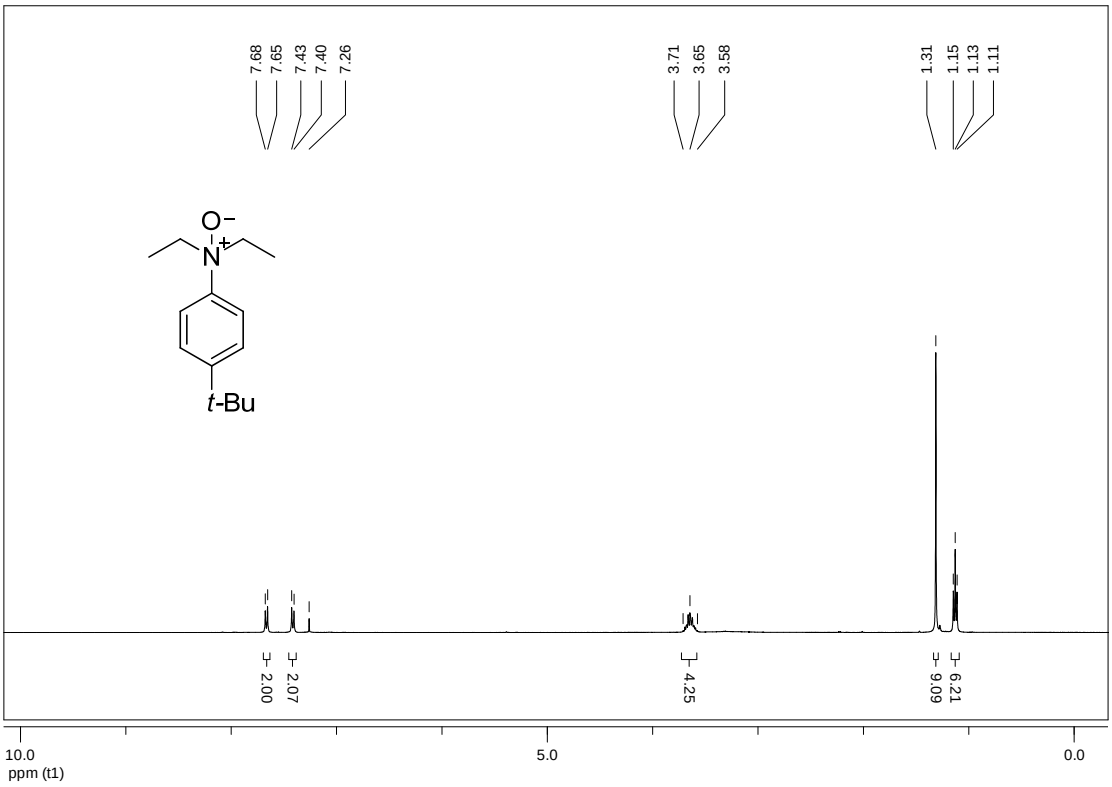
(13) Control experiments by adding 4Å molecular sieve

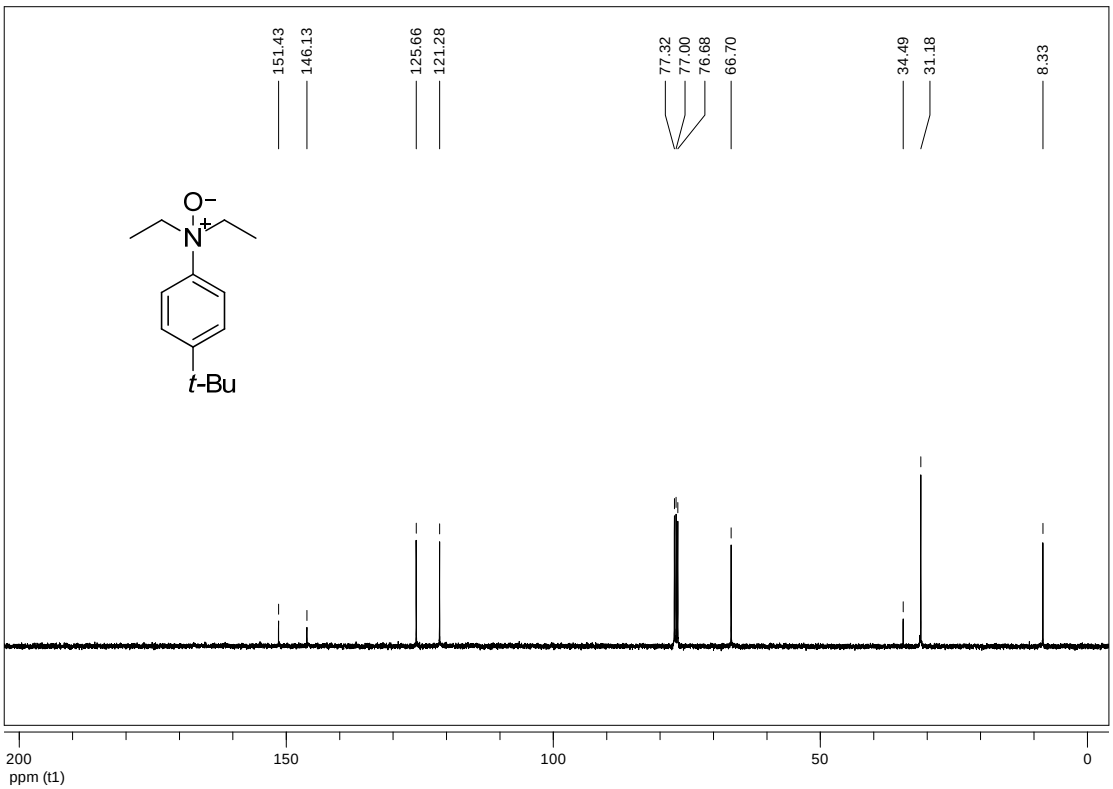


A mixture of **1a** (82 mg, 0.6 mmol, 3.0 equiv), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mol, 5.0 mol %), $AgBF_4$ (78 mg, 0.4 mmol, 2.0 equiv), [4Å molecular sieve (200 mg) was added in experiment (ii)], and $MesCO_2H$ (33 mg,1.0 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry *t*-BuOH (2.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 115 °C for 30 min under vigorous stirring. The reaction was cooled to room temperature, filtered through a pad of celite and then washed with CH_2Cl_2 (10 mL x 3). The solvents were removed under reduced pressure. The yields were determined by integration of ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

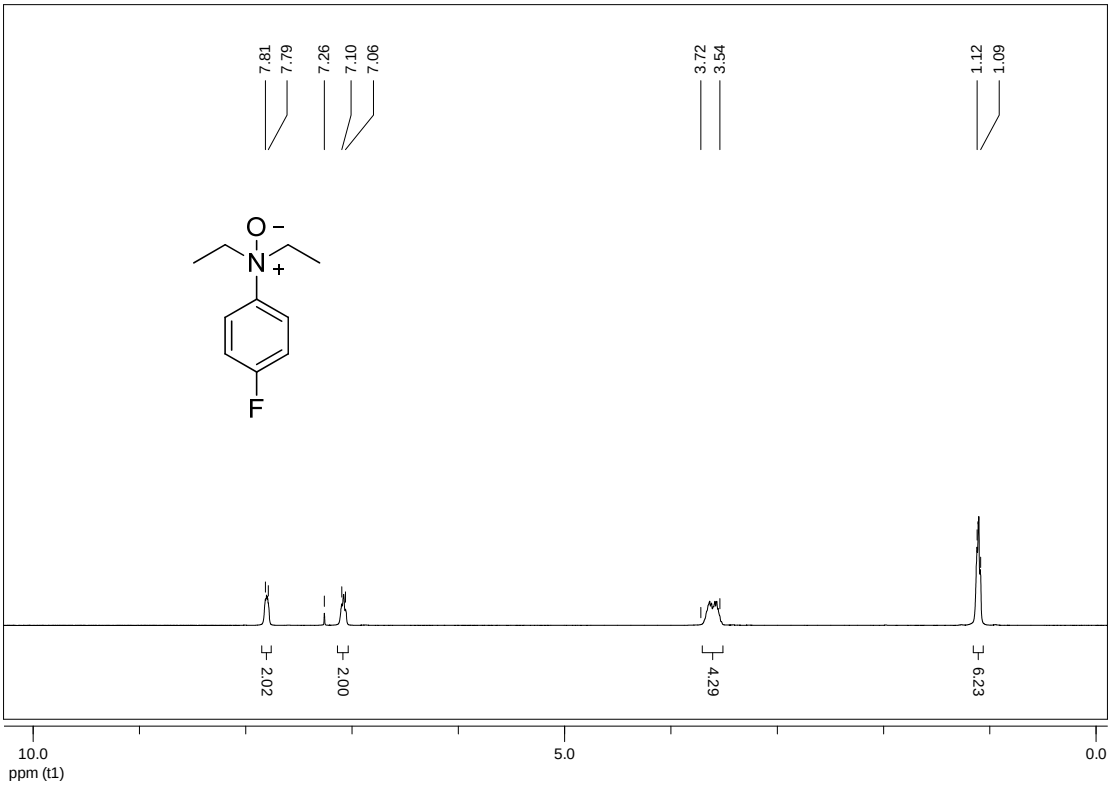
Spectral Copies of ^{1}H, ^{19}F and ^{13}C NMR of Compounds Obtained in this Study

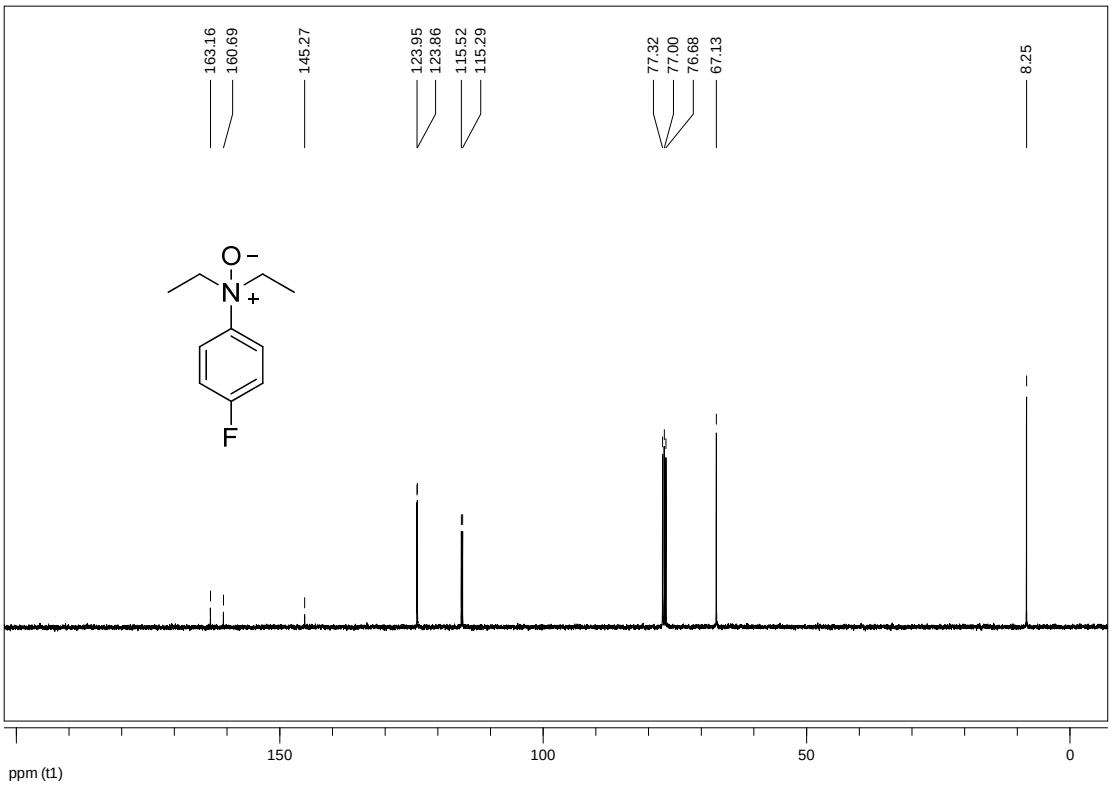
4-tert-butyl-*N*,*N*-diethylaniline oxide (1e)

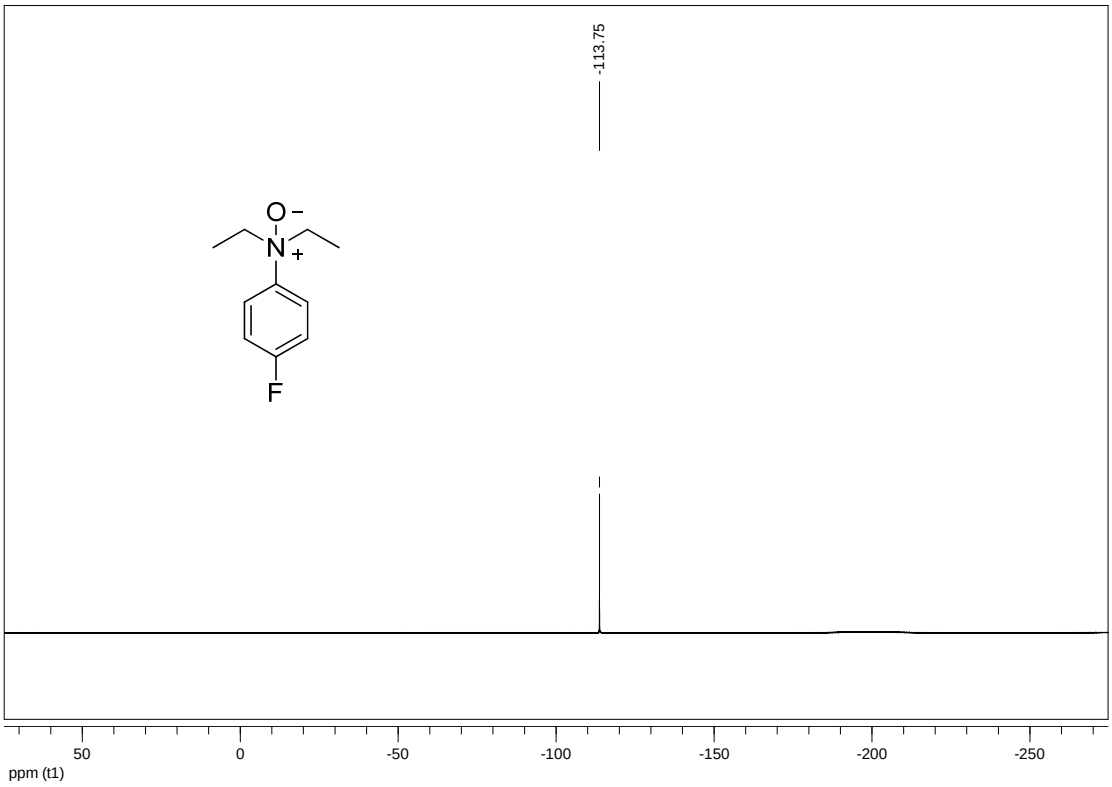




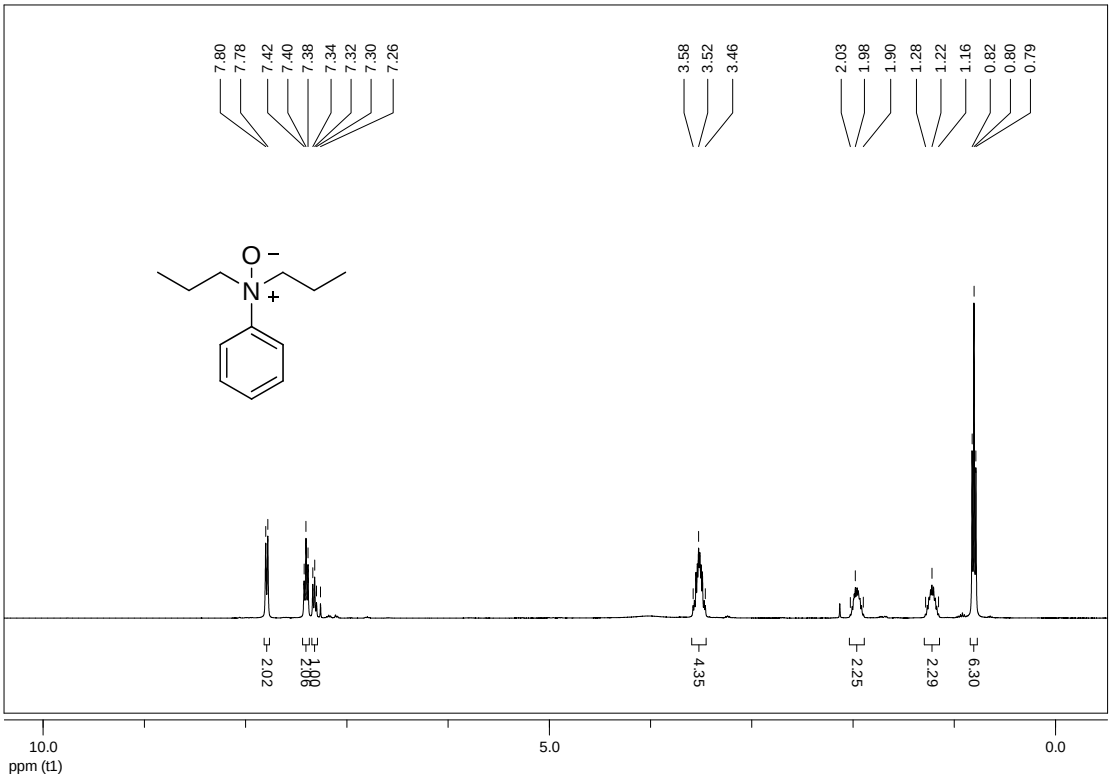
N,*N*-diethyl-4-fluoroaniline oxide (1h)

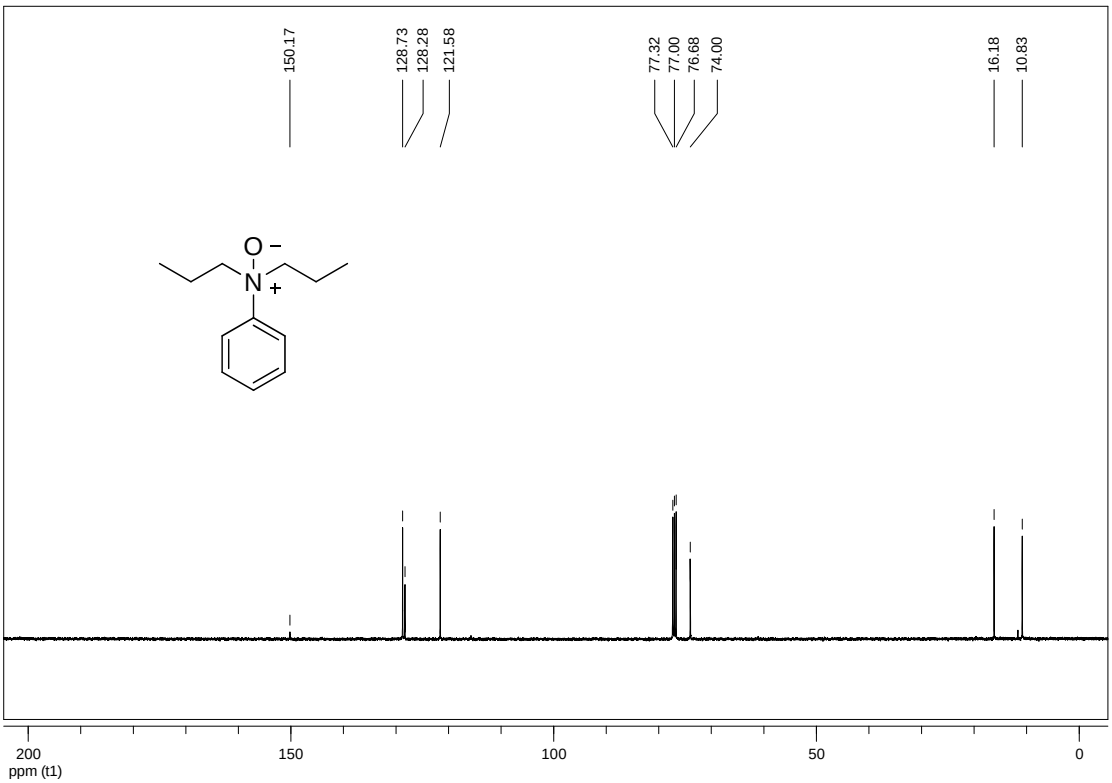




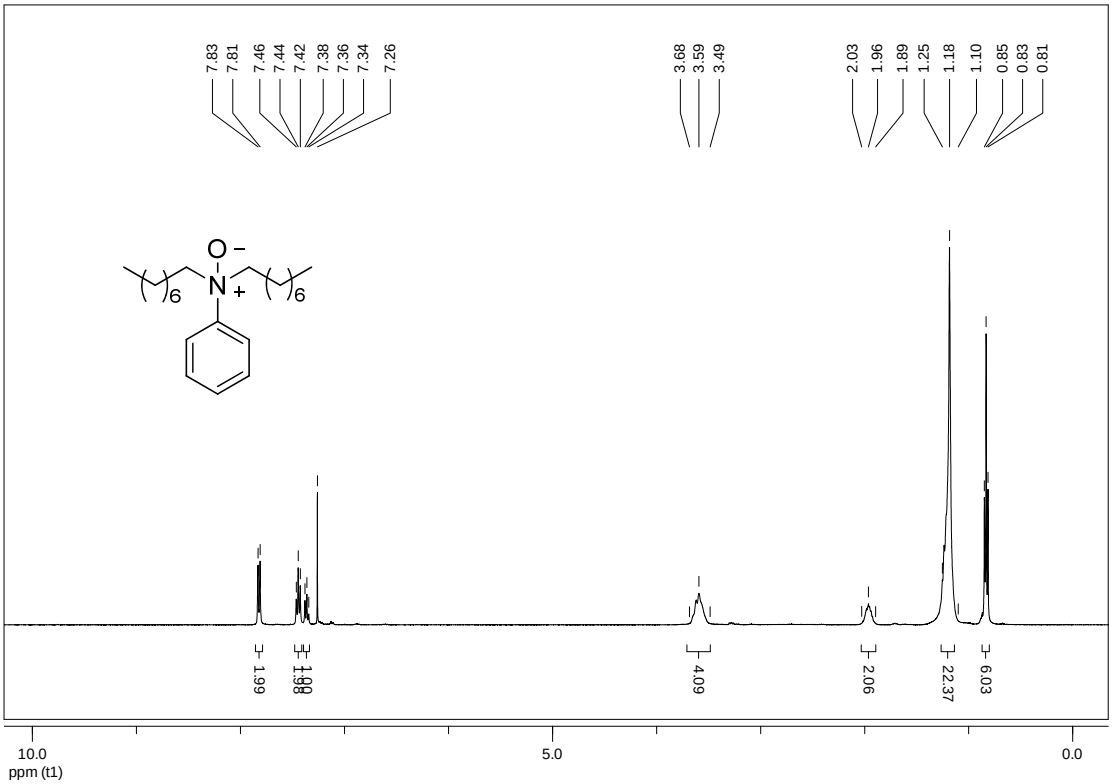

-113.75
O
N
F
50
0
-50
-100
-150
-200
-250
ppm (t1)

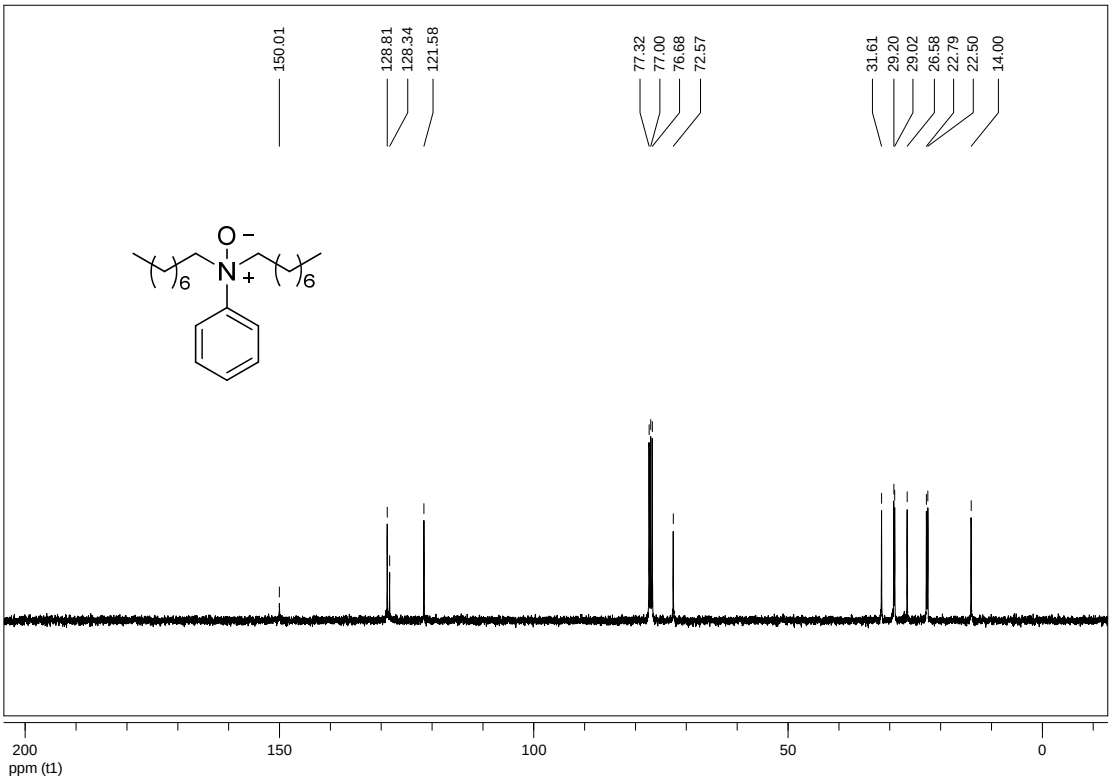
N,N-dipropylaniline oxide (1u)



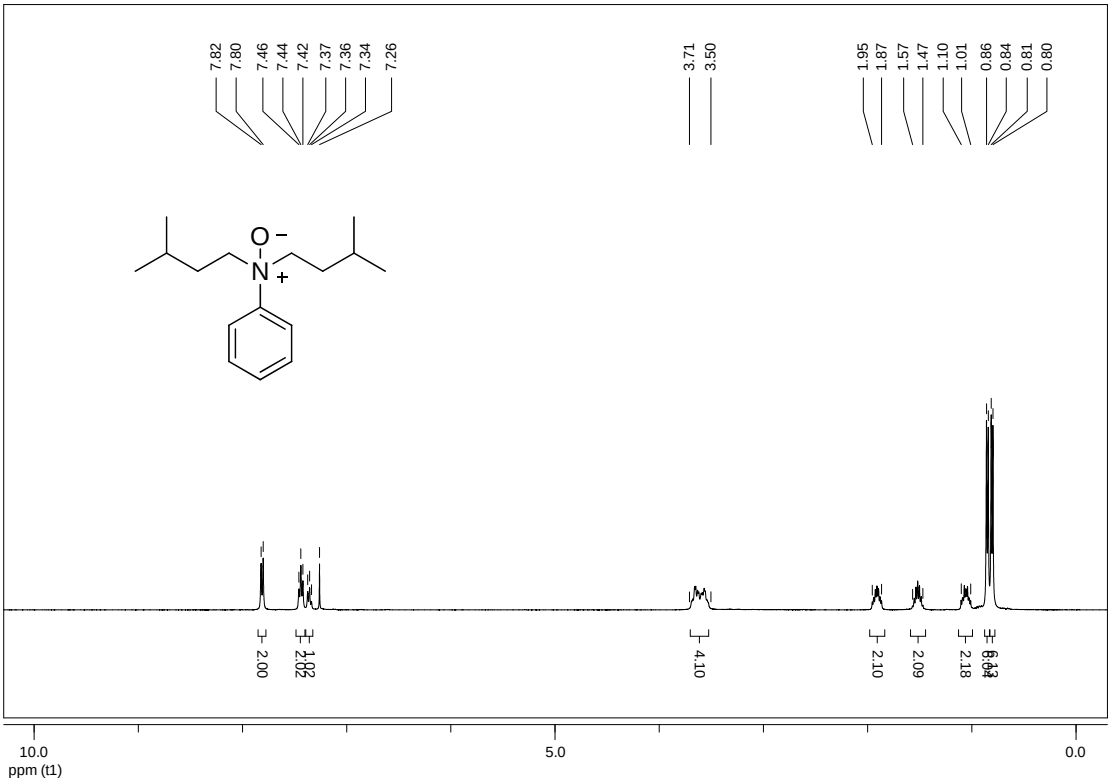


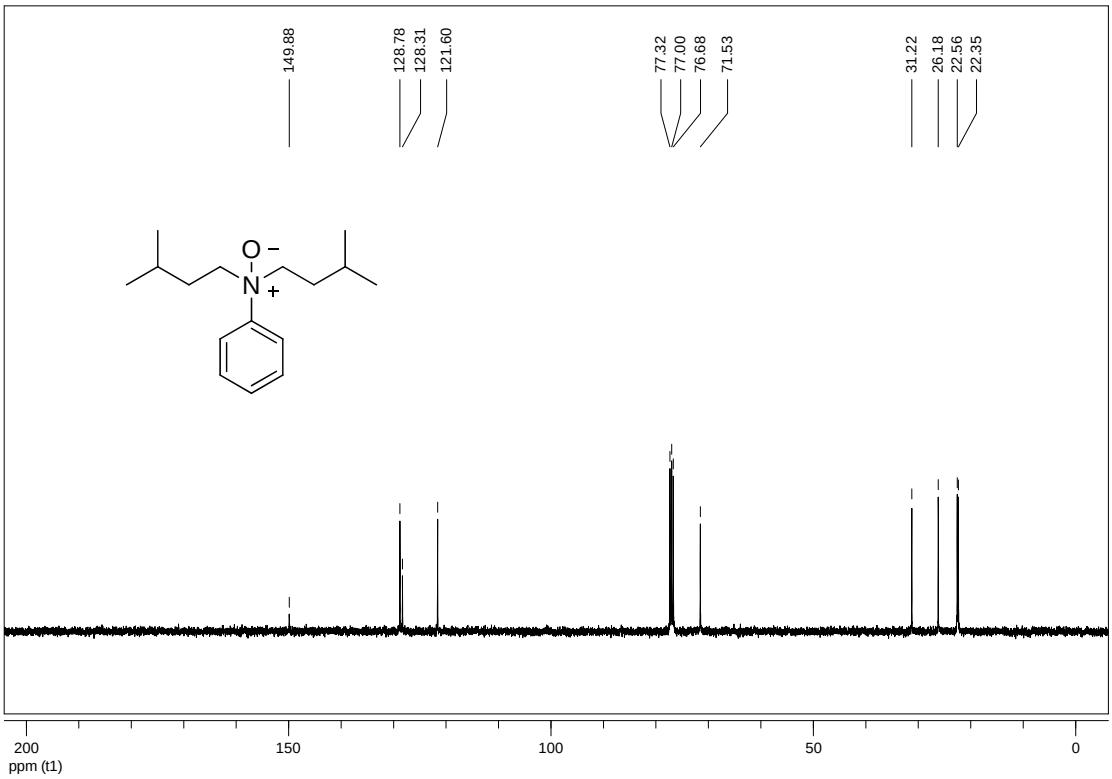
N,N-dioctylaniline oxide (1v)



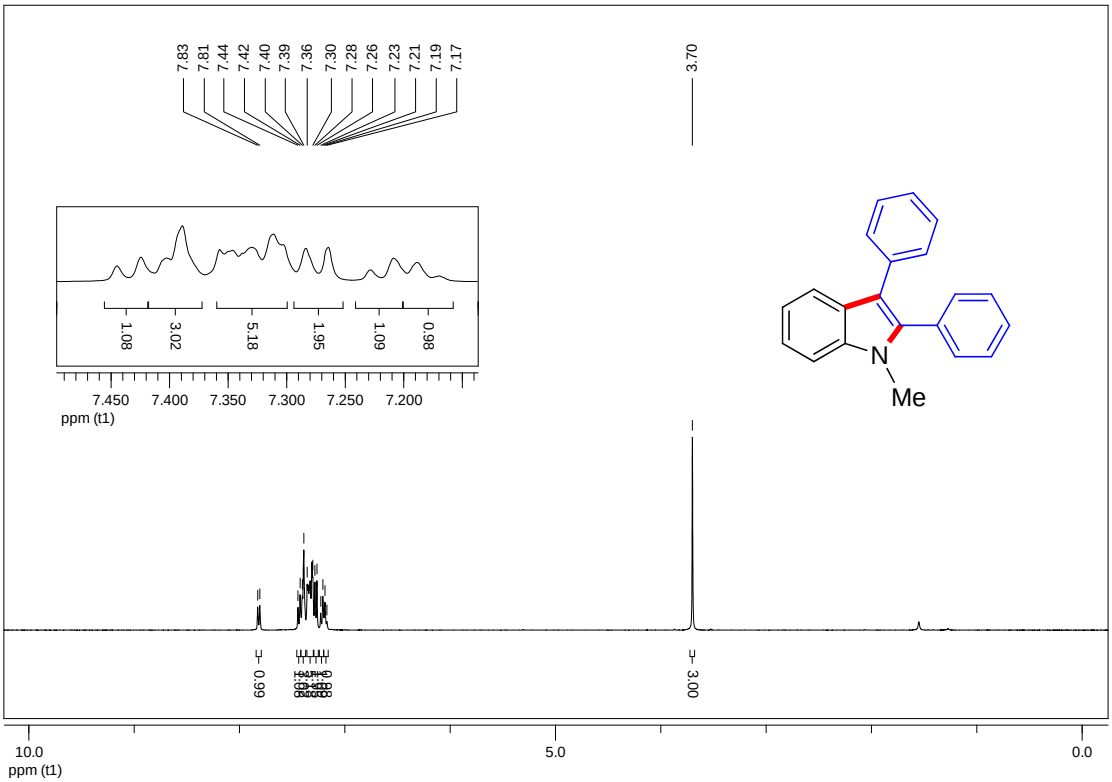


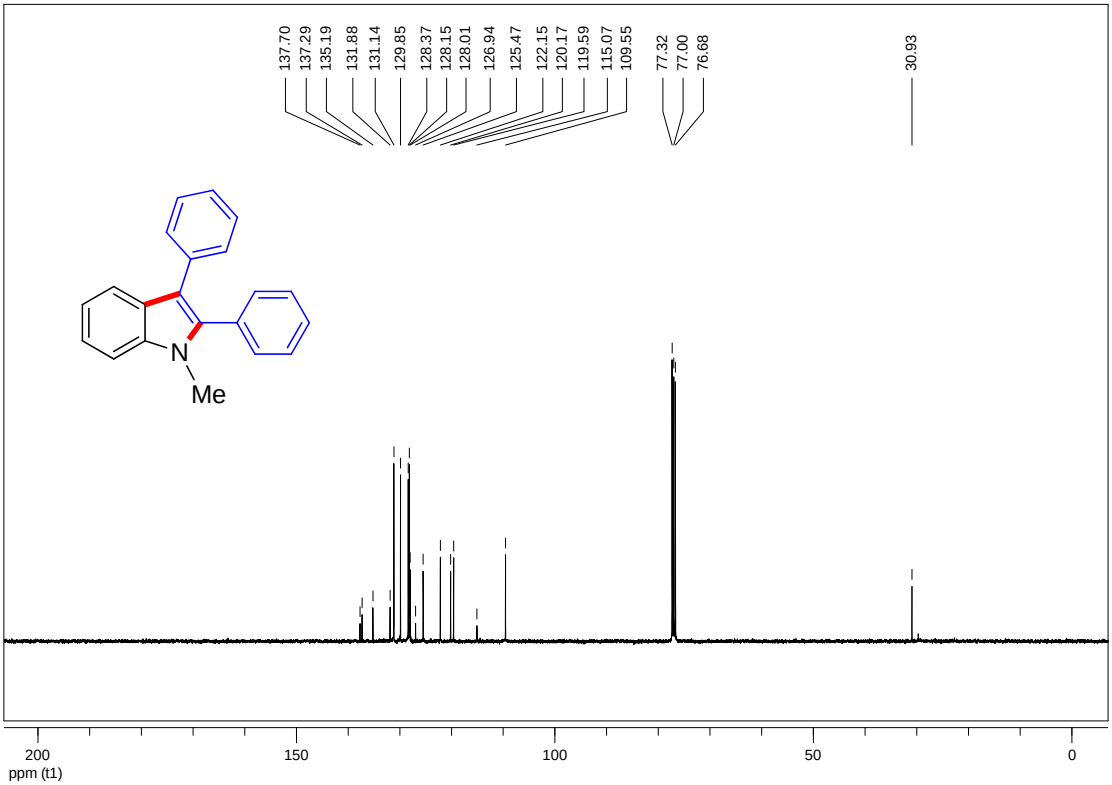
N,N-diisopentylaniline oxide (1w)



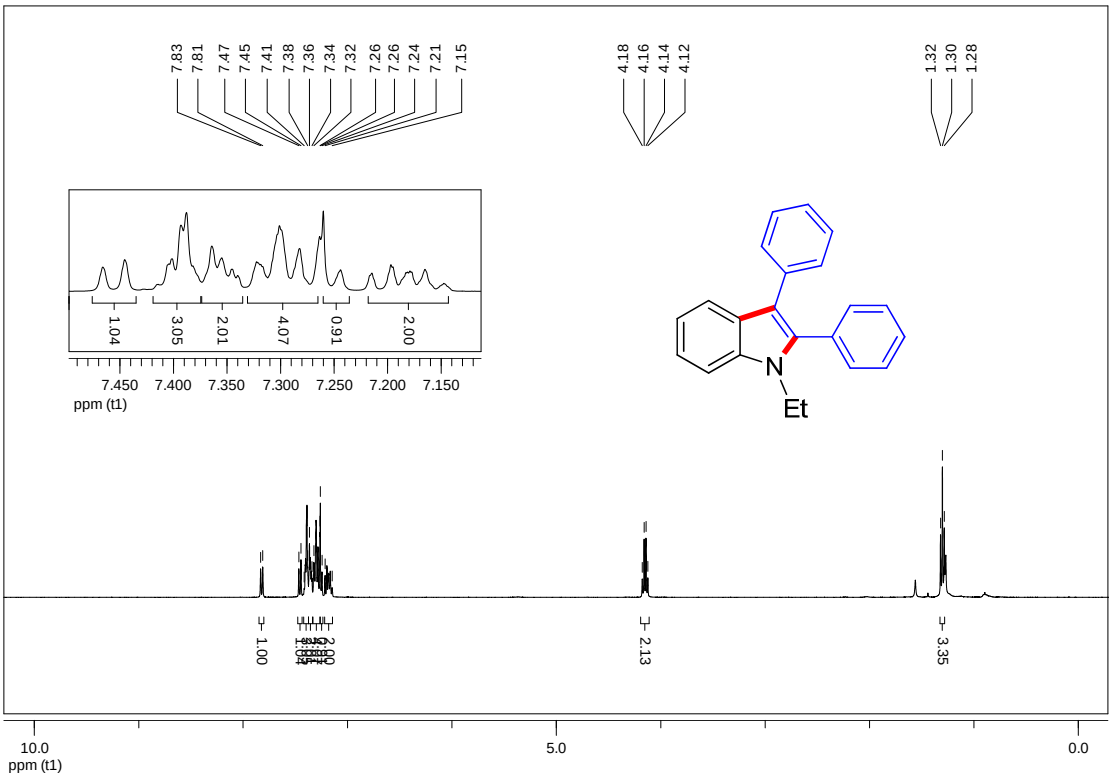


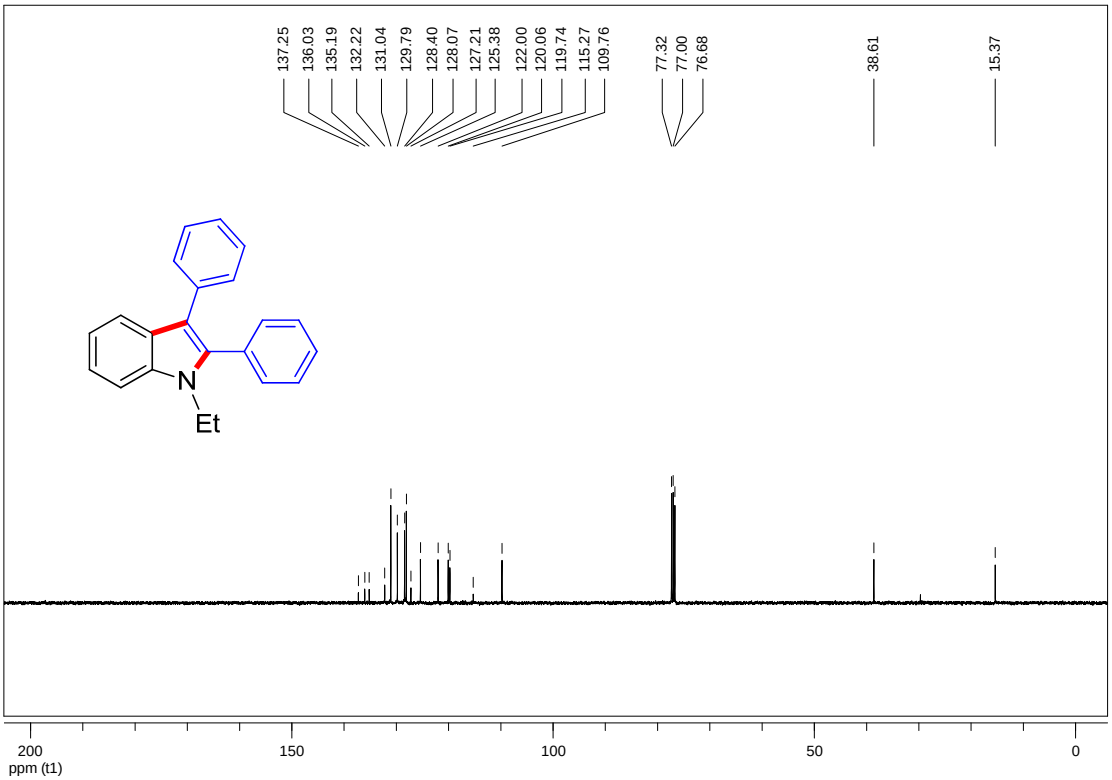
1-methyl-2,3-diphenyl-1*H*-indole (3a)



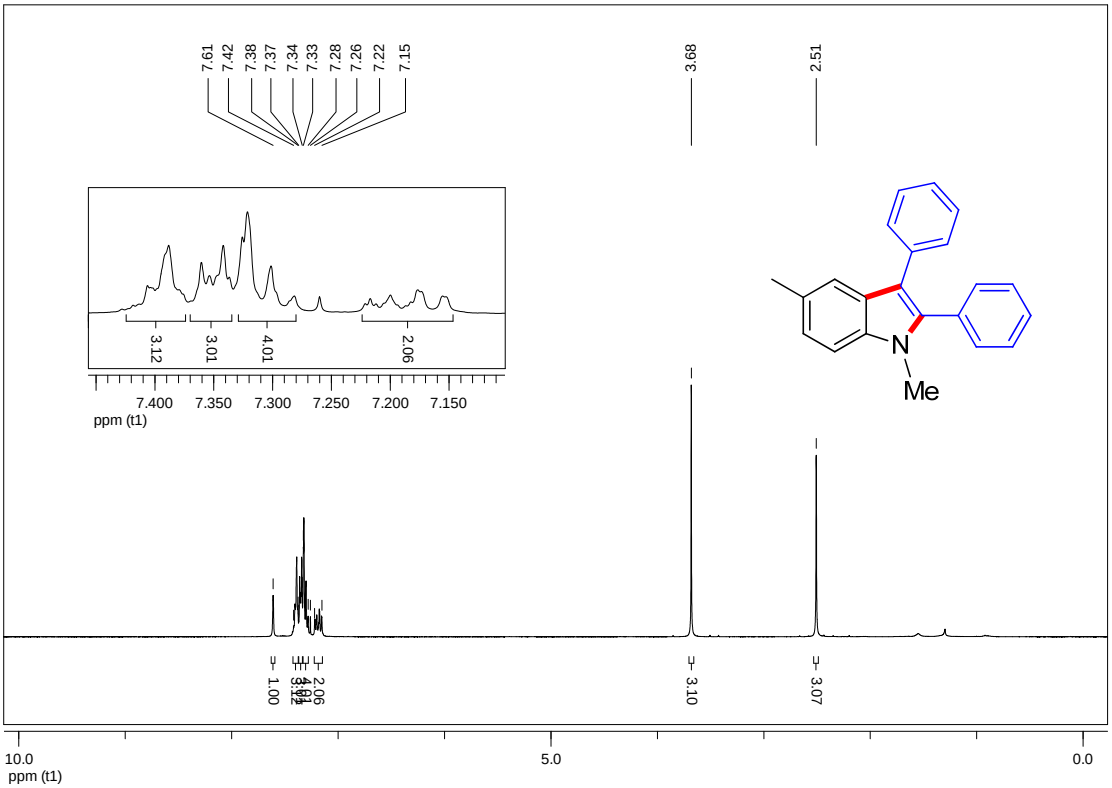


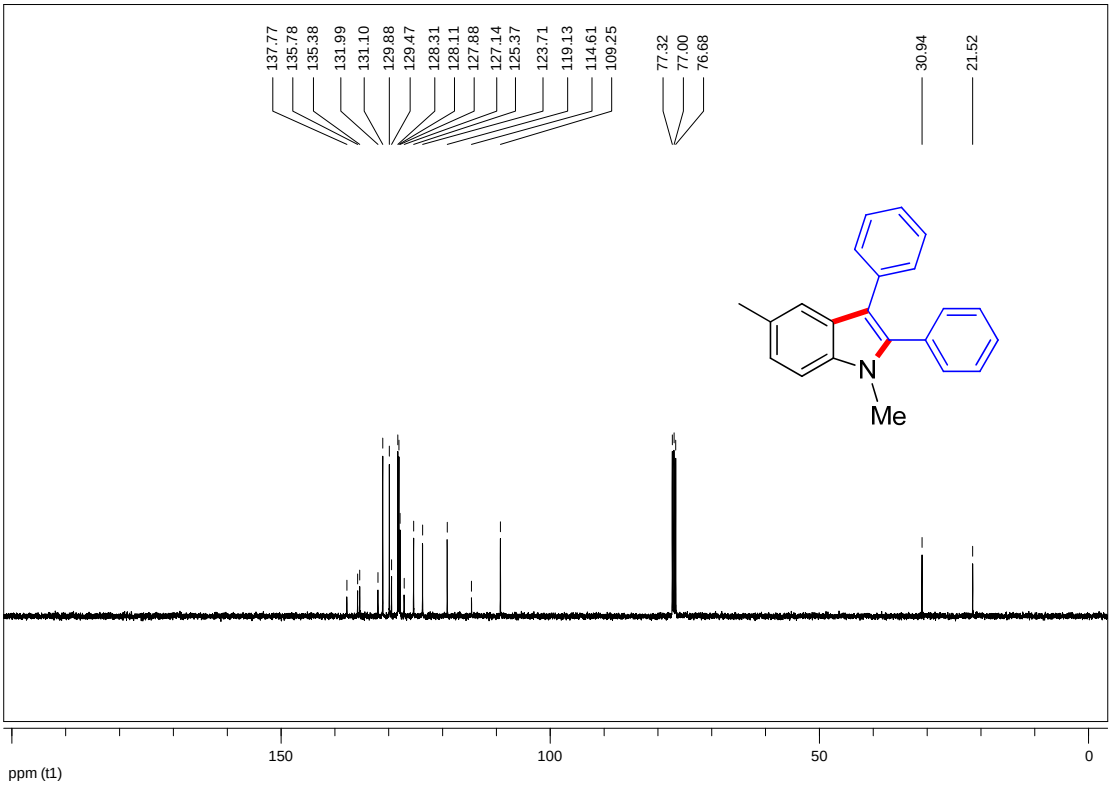
1-ethyl-2,3-diphenyl-1*H*-indole (3b)



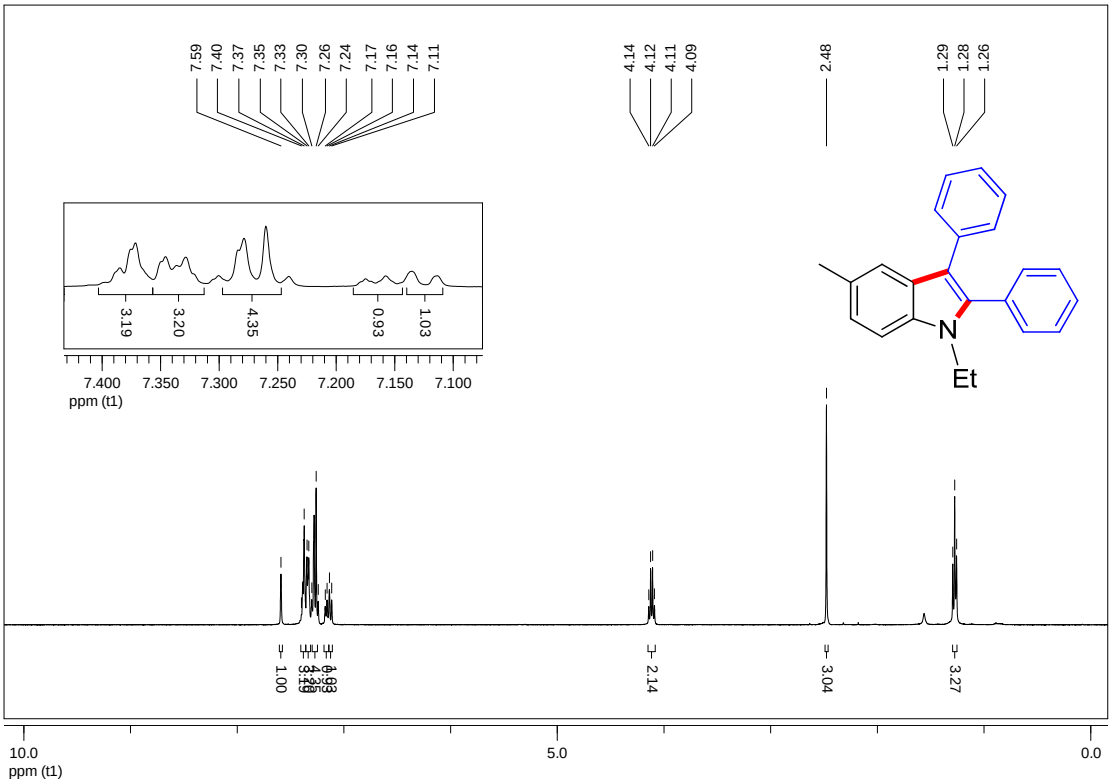


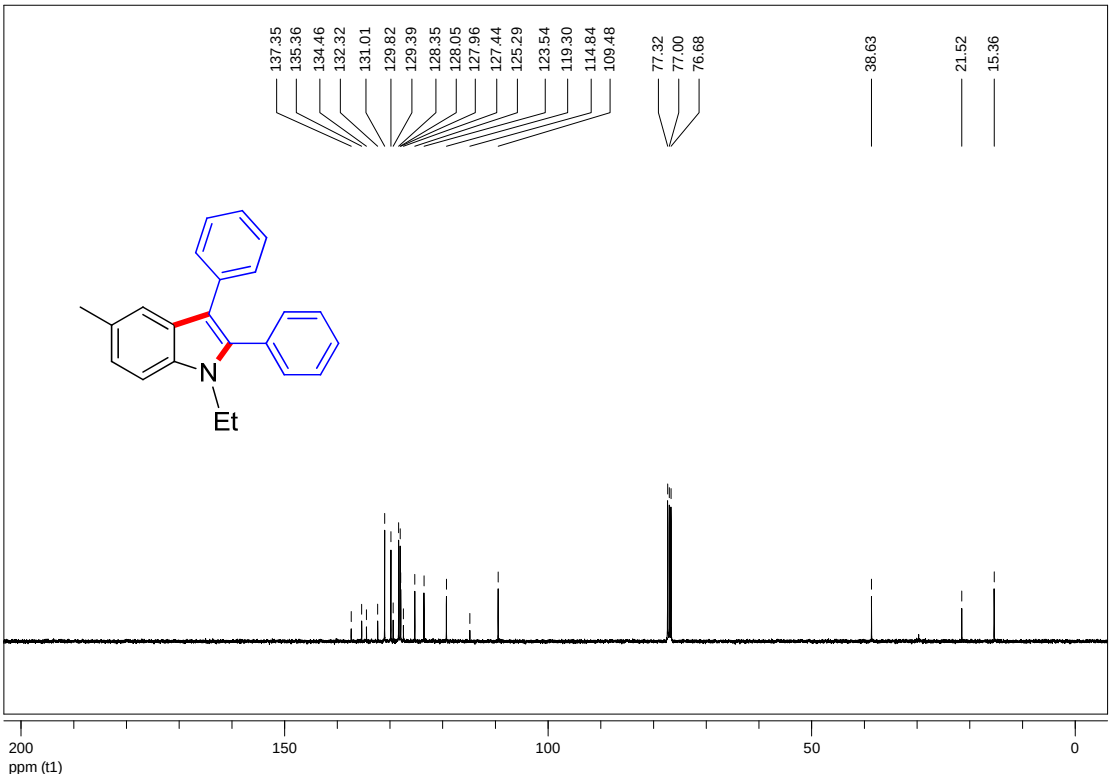
1,5-dimethyl-2,3-diphenyl-1*H*-indole (3c)



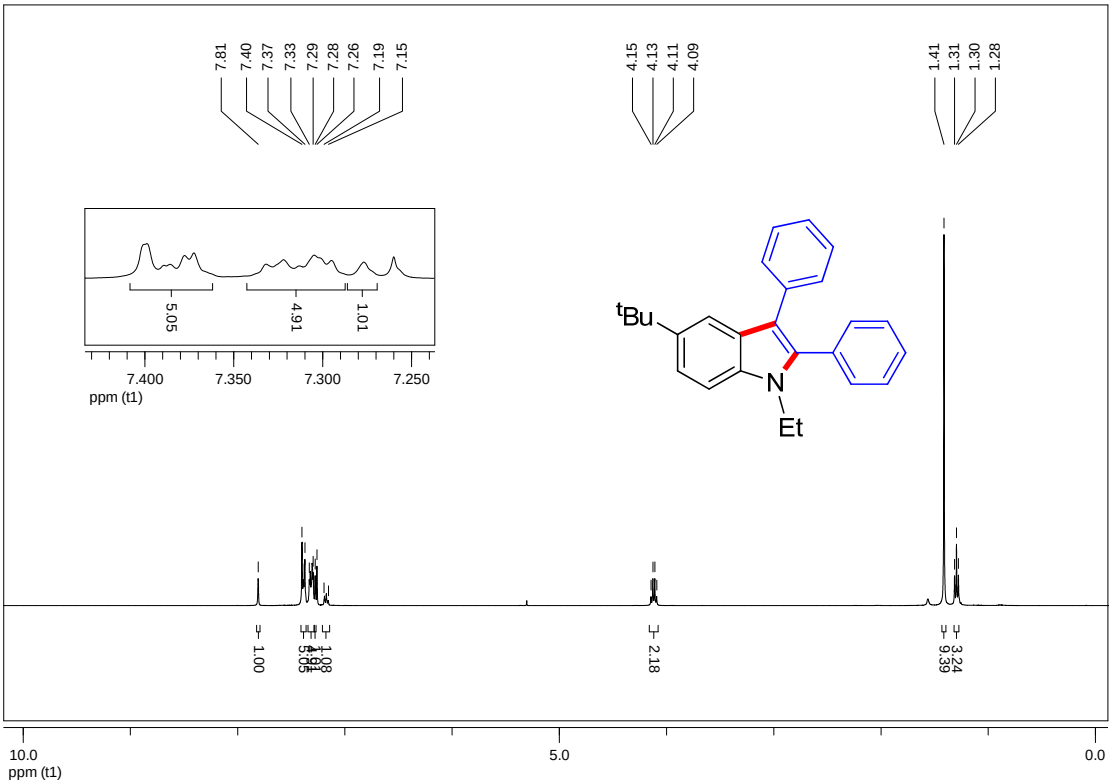


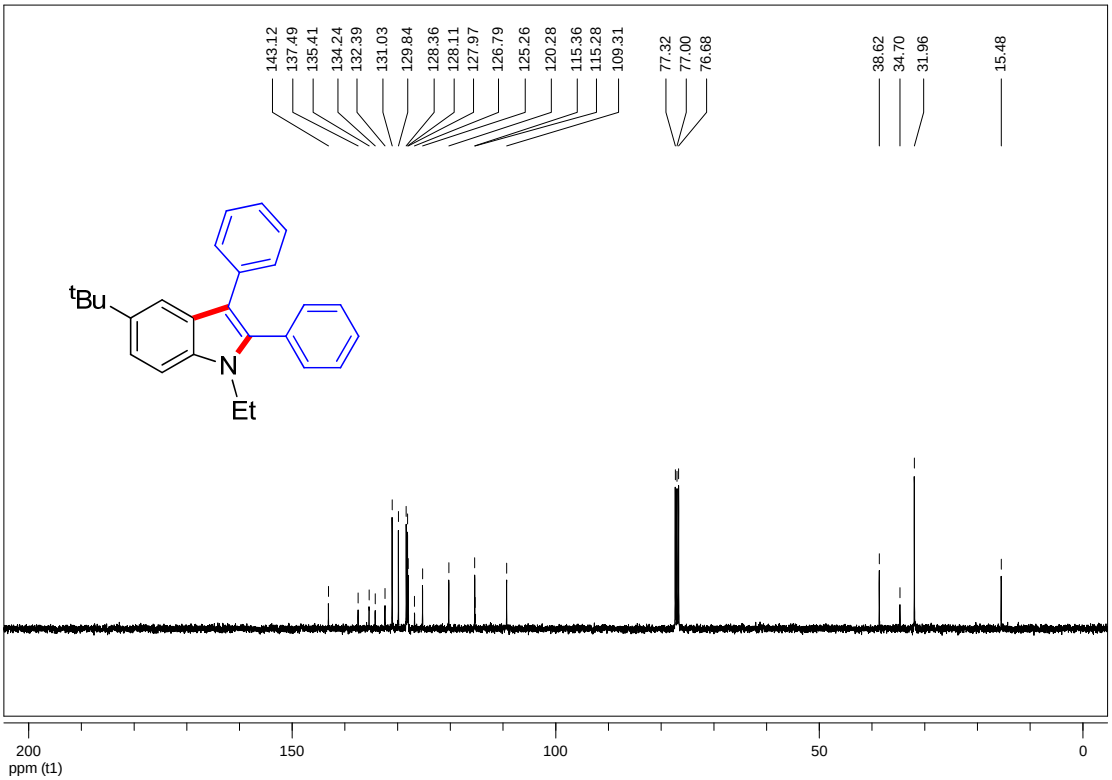
1-ethyl-5-methyl-2,3-diphenyl-1*H*-indole (3d)



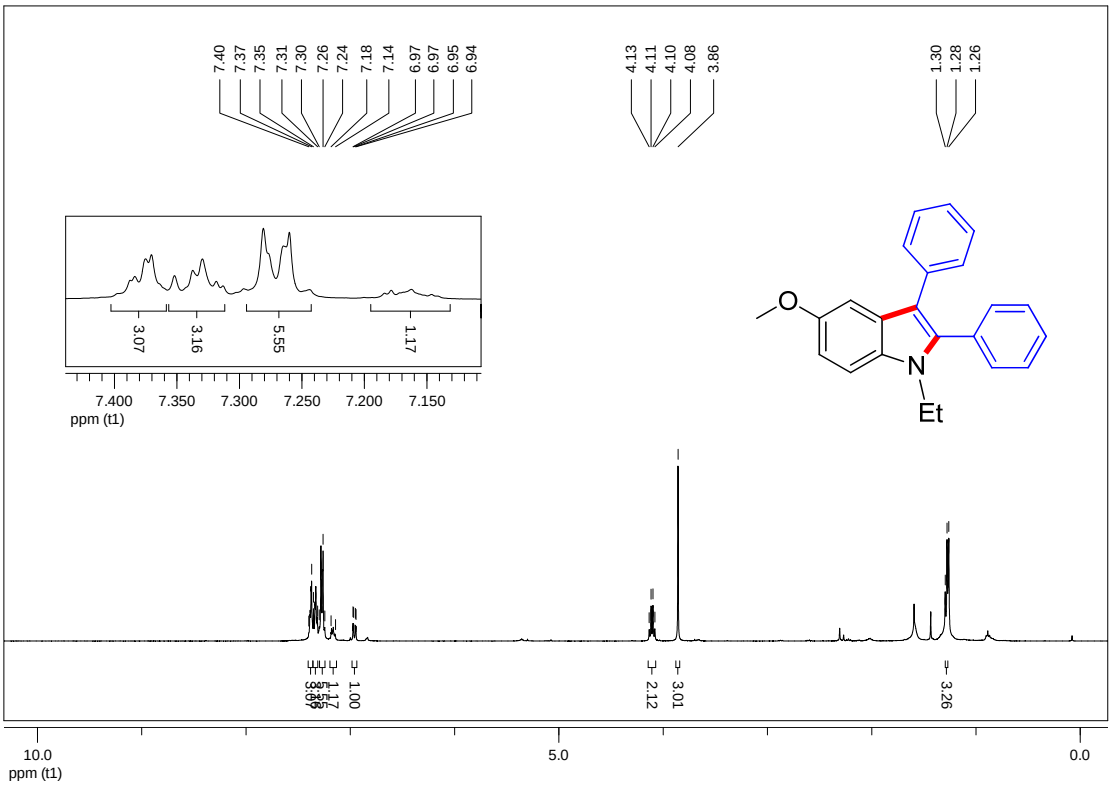


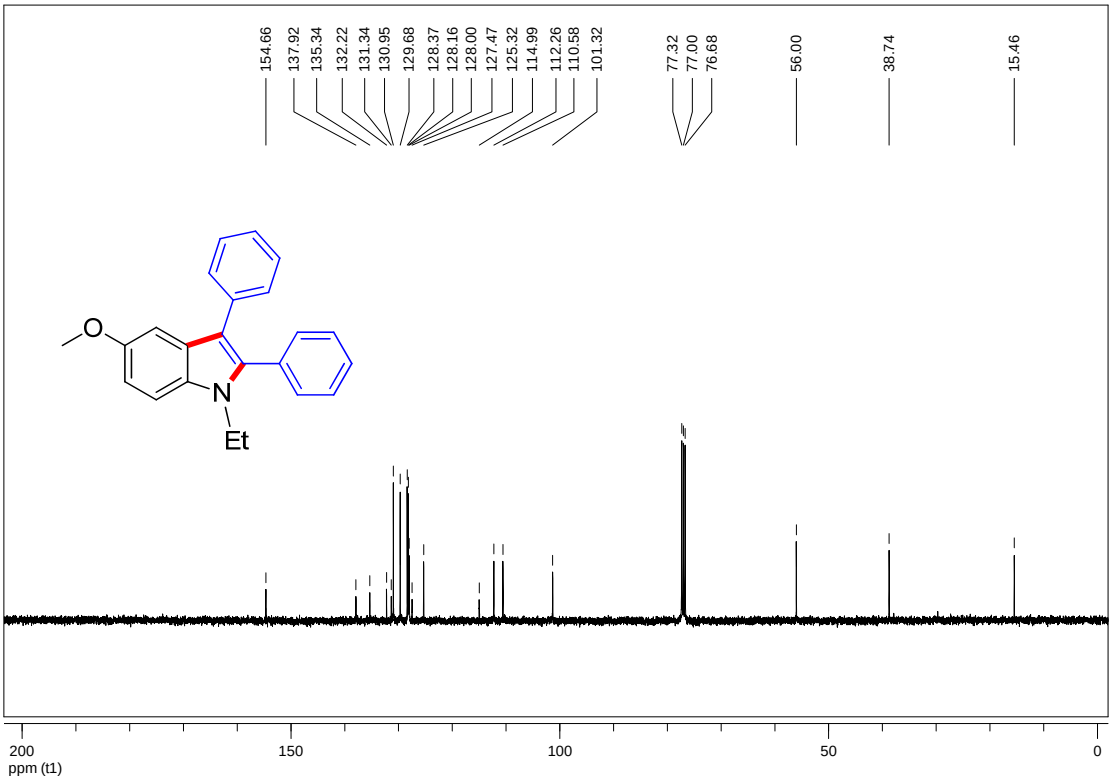
5-tert-butyl-1-ethyl-2,3-diphenyl-1*H*-indole (3e)



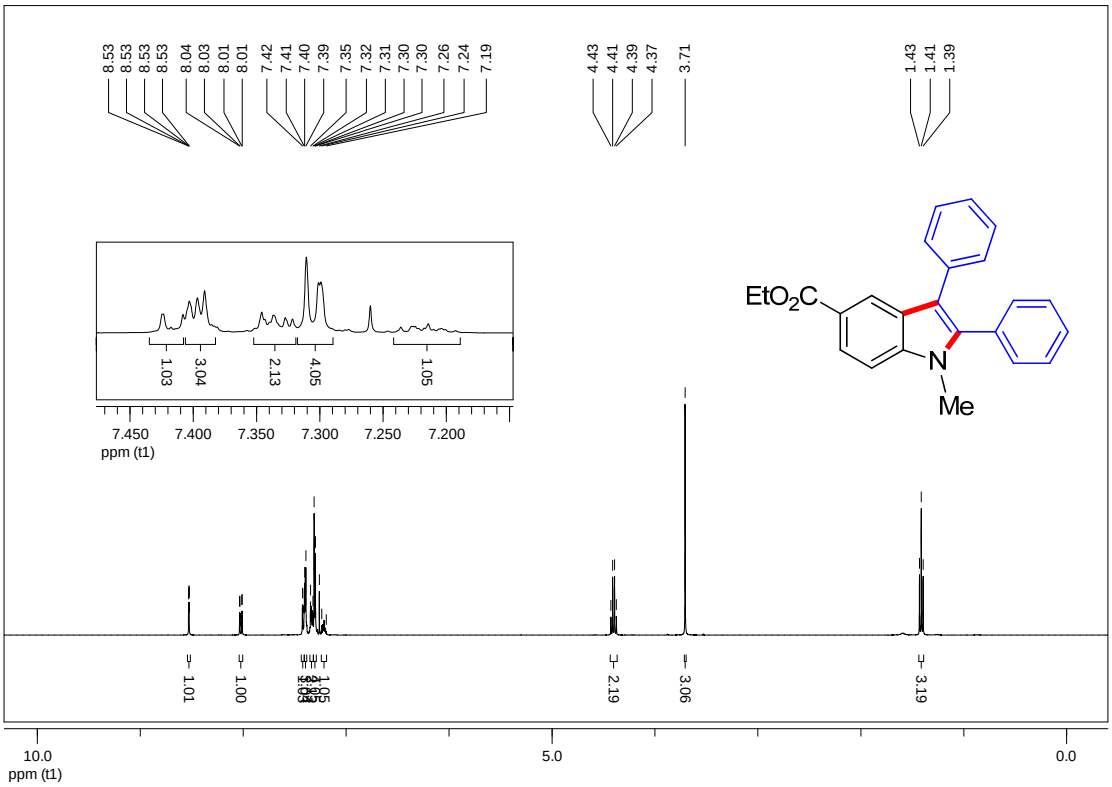


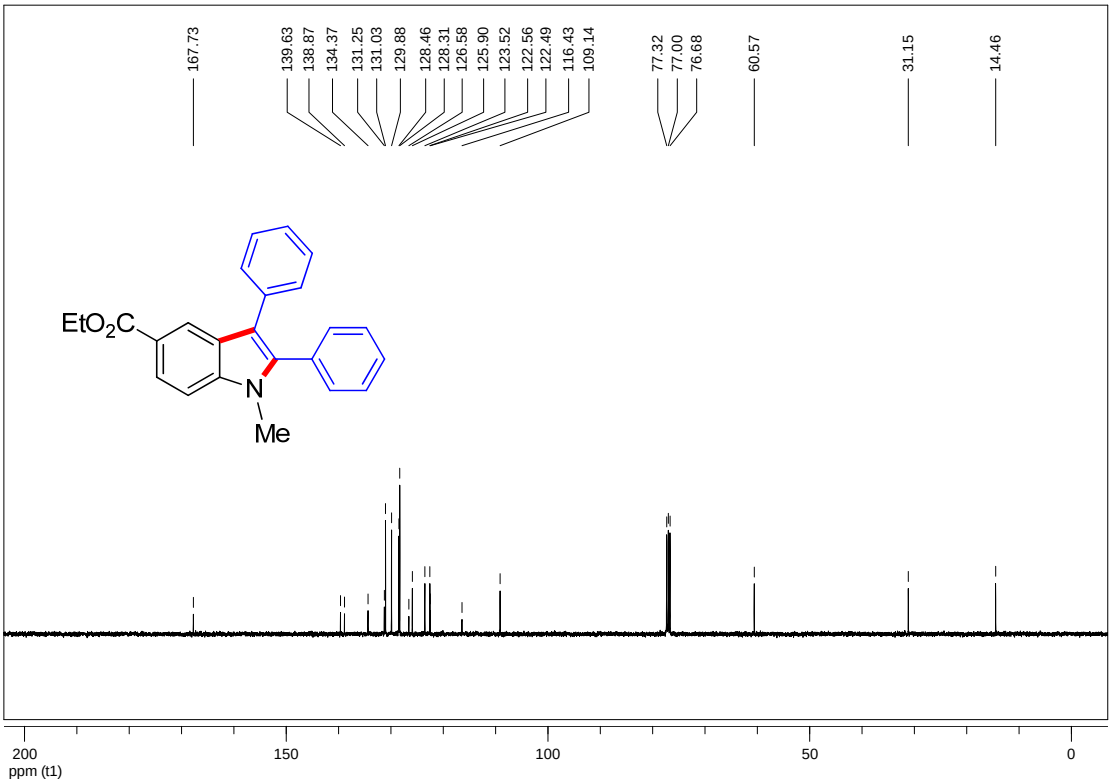
1-ethyl-5-methoxy-2,3-diphenyl-1*H*-indole (3f)



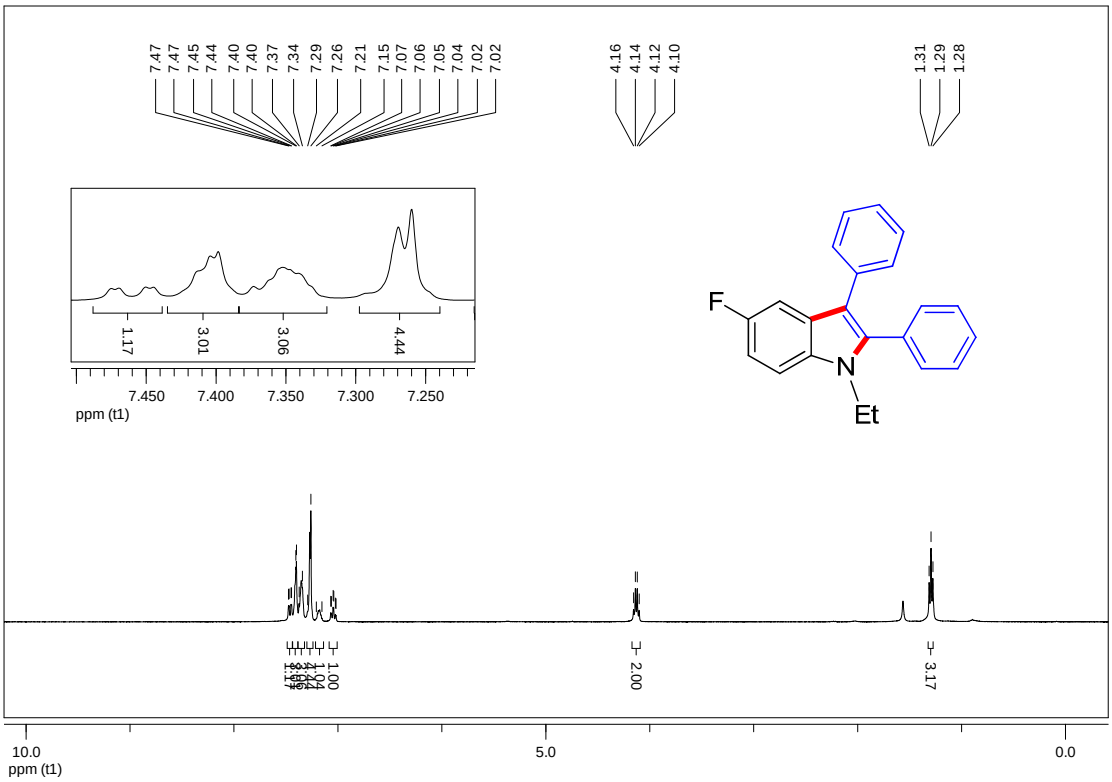


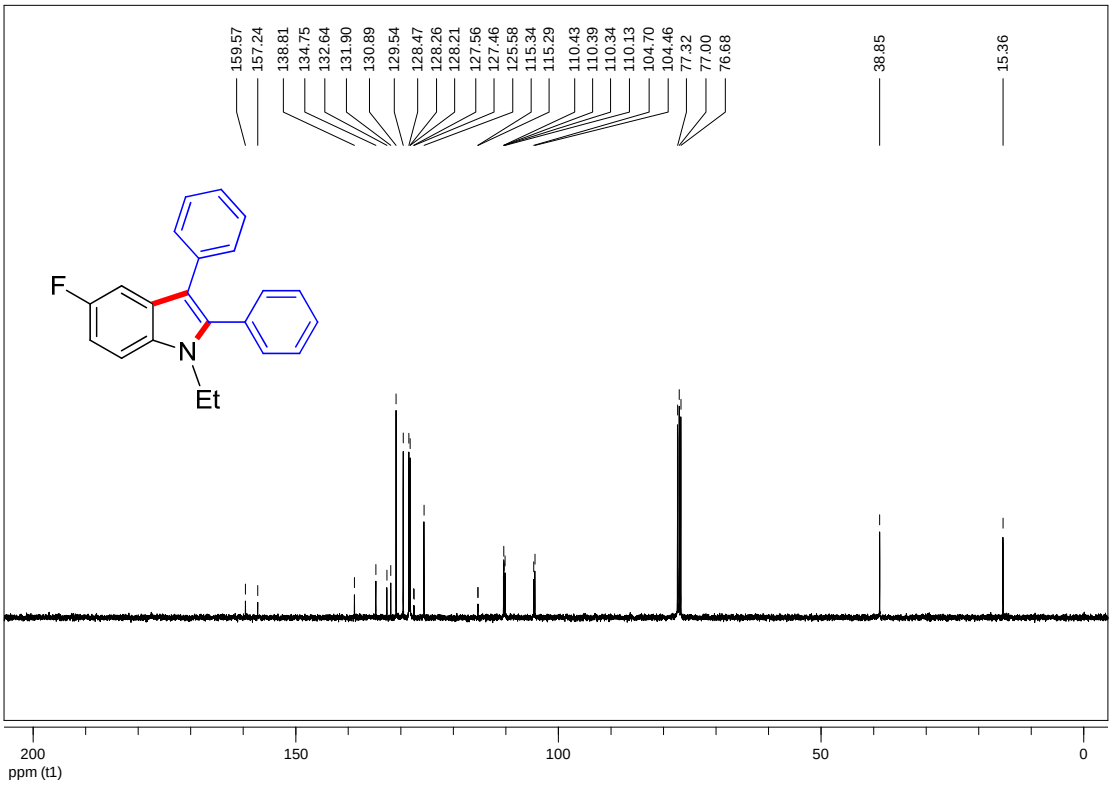
ethyl 1-methyl-2,3-diphenyl-1*H*-indole-5-carboxylate (3g)

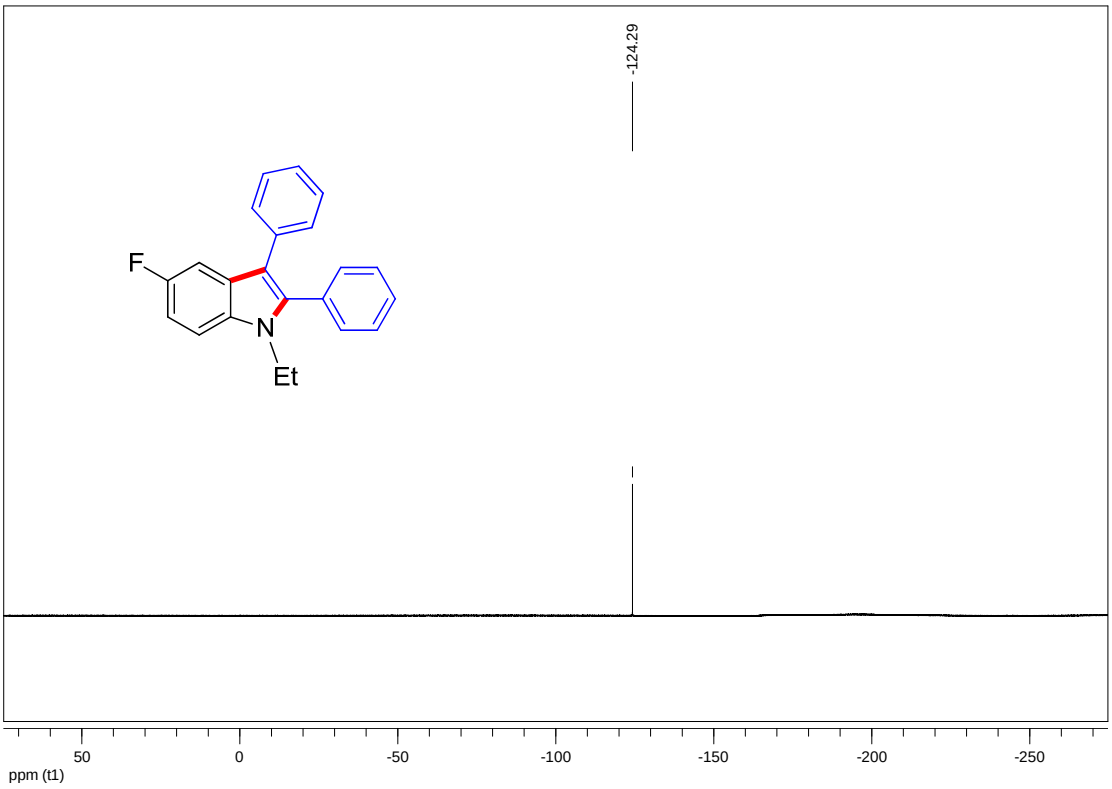




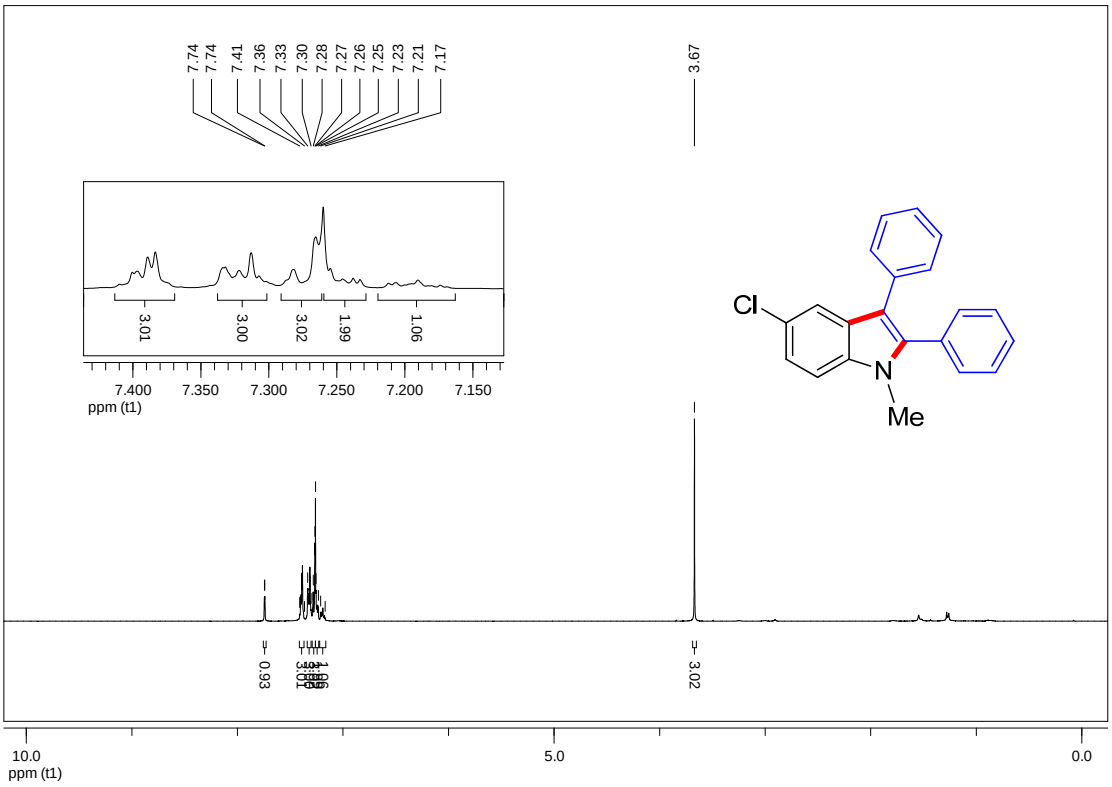
1-ethyl-5-fluoro-2,3-diphenyl-1*H*-indole (3h)

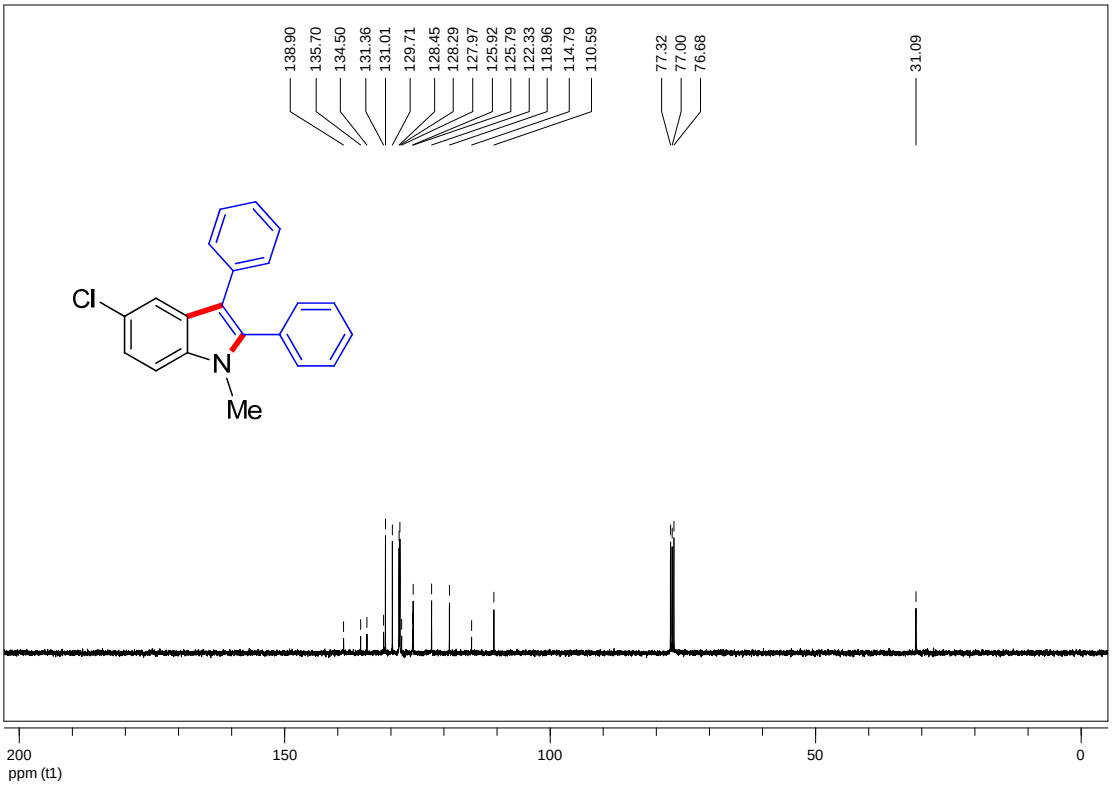




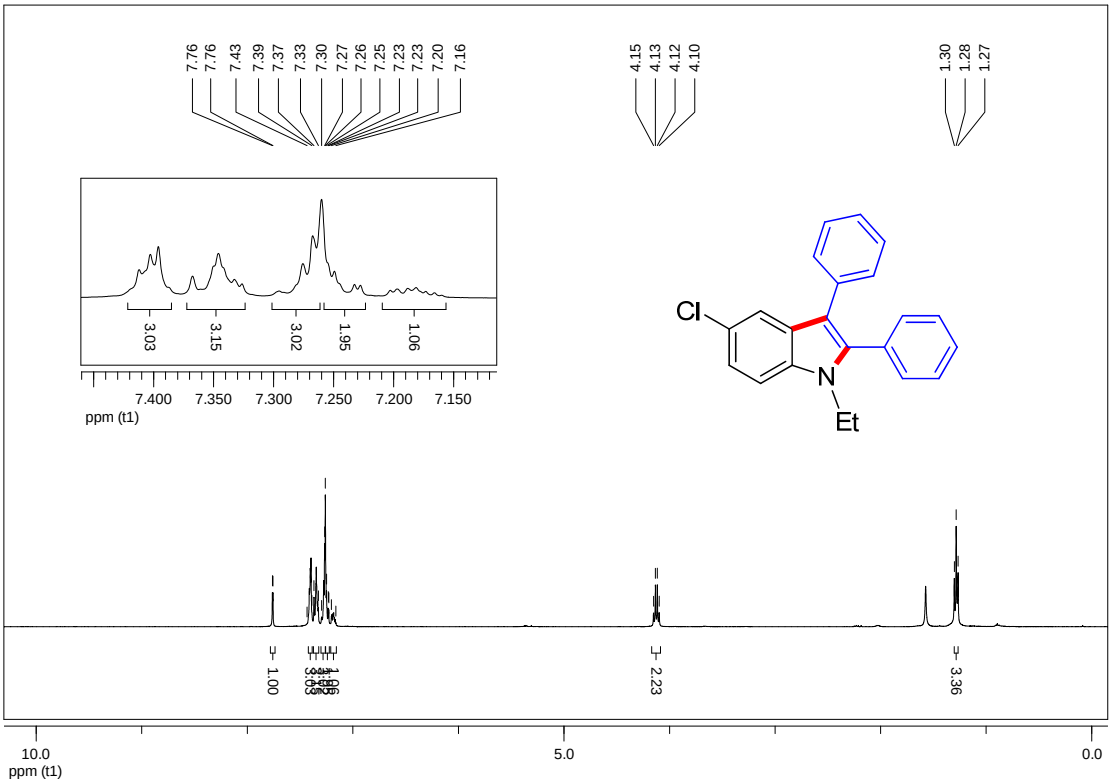

-124.29
F
N
Et
50
0
-50
-100
-150
-200
-250
ppm (t1)

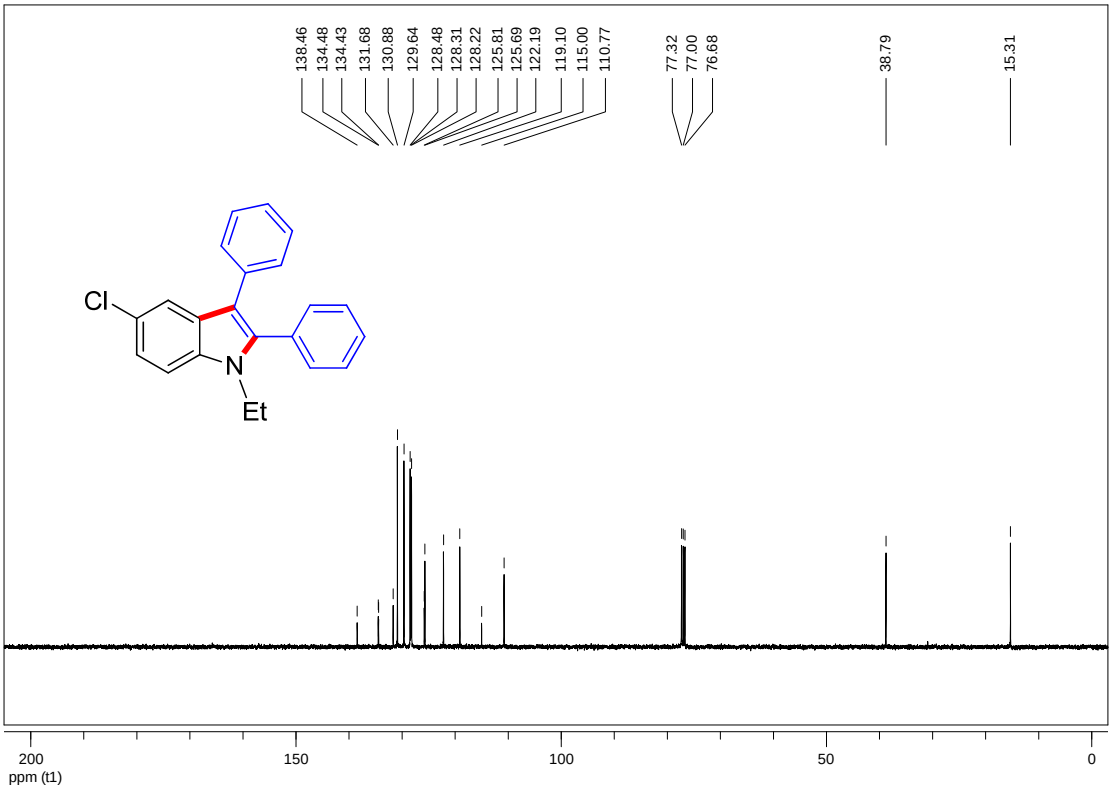
5-chloro-1-methyl-2,3-diphenyl-1*H*-indole (3i)



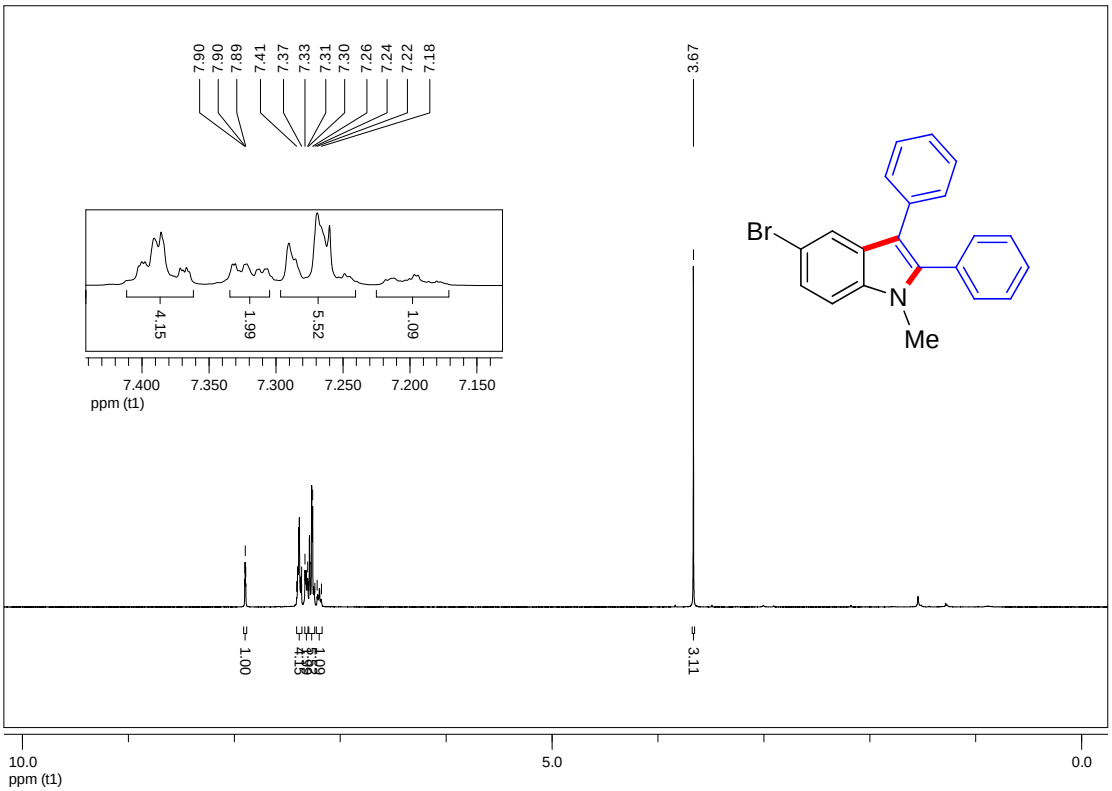


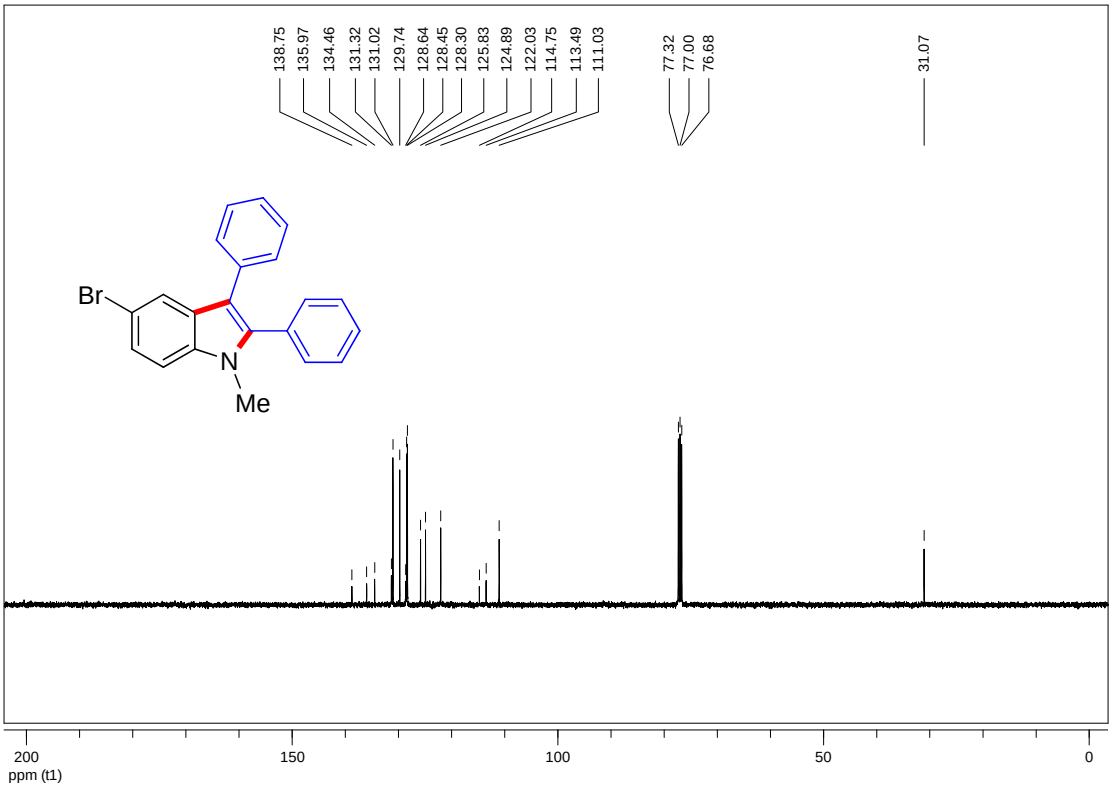
5-chloro-1-ethyl-2,3-diphenyl-1*H*-indole (3j)



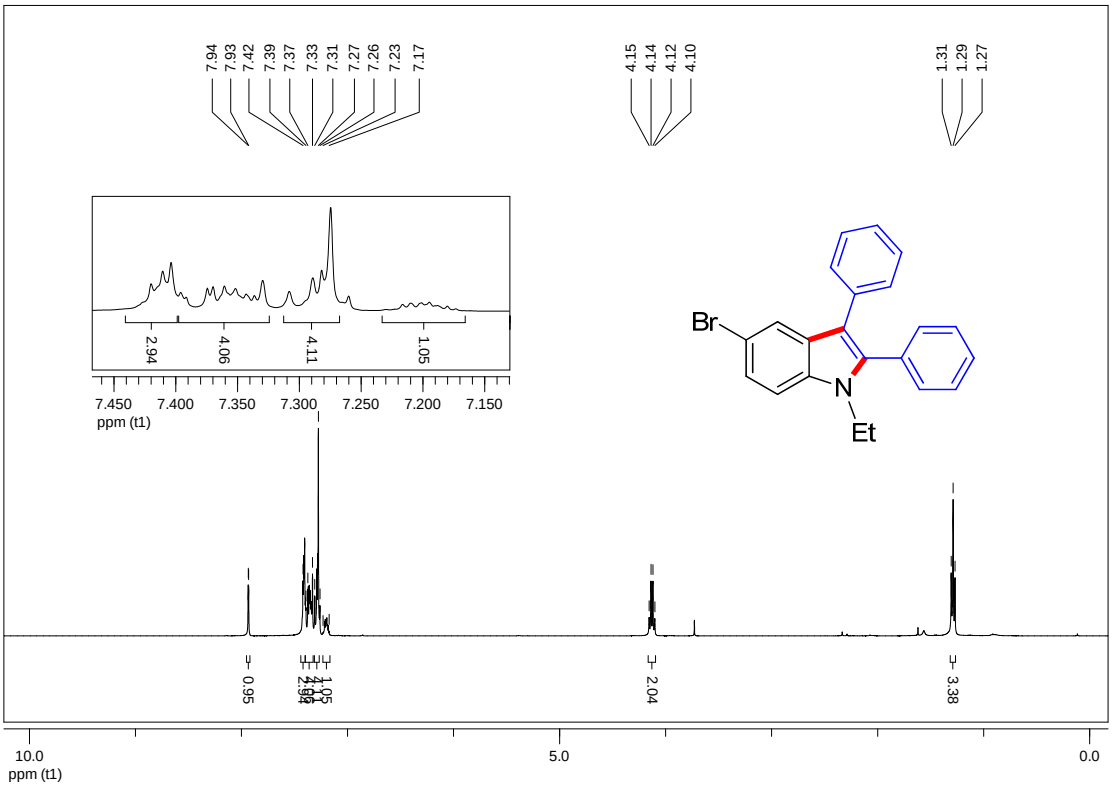


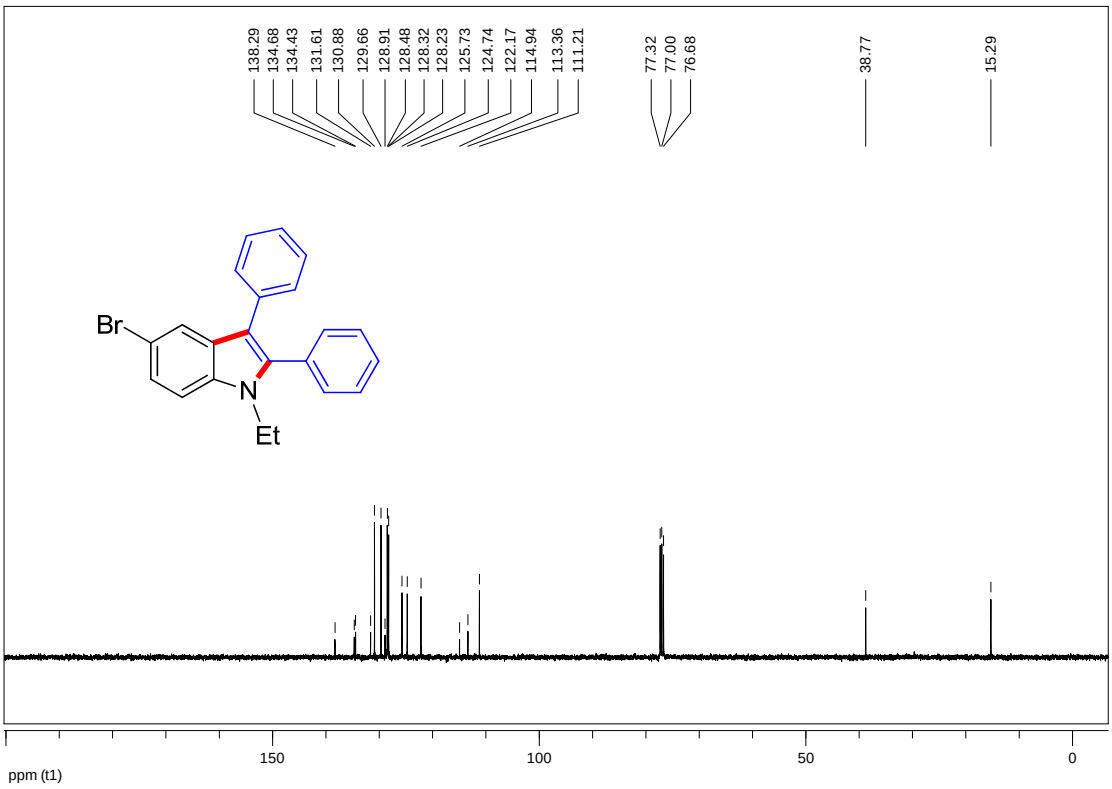
5-bromo-1-methyl-2,3-diphenyl-1*H*-indole (3k)



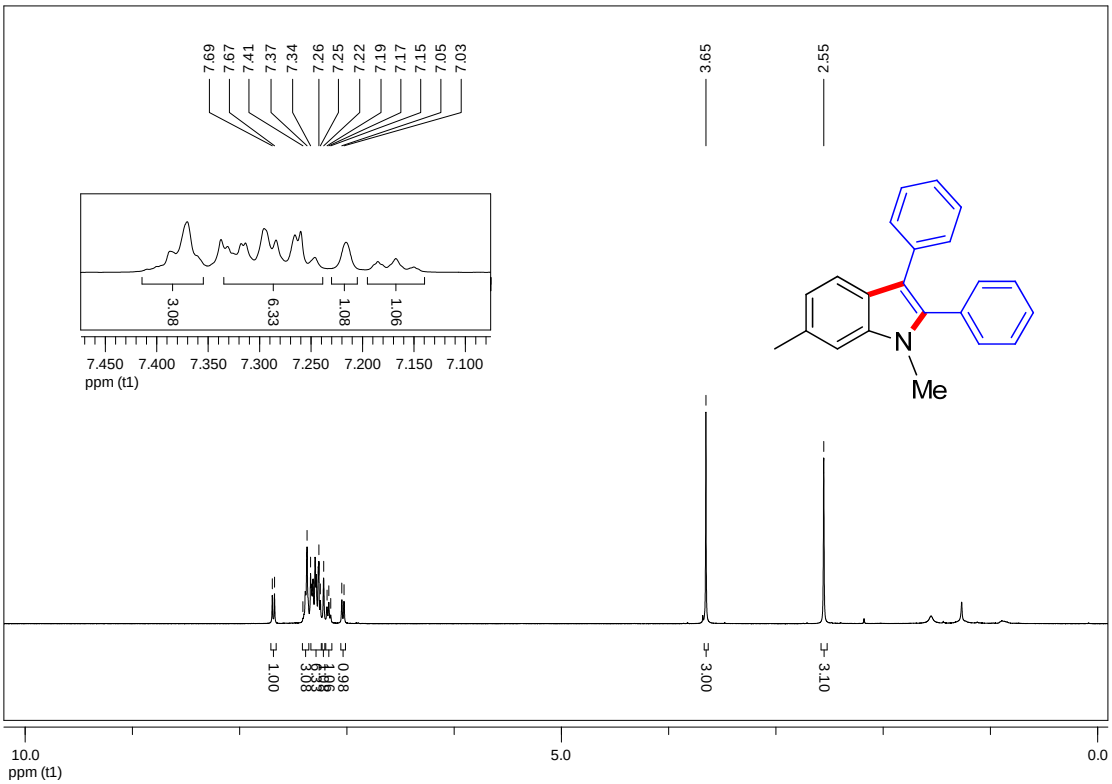


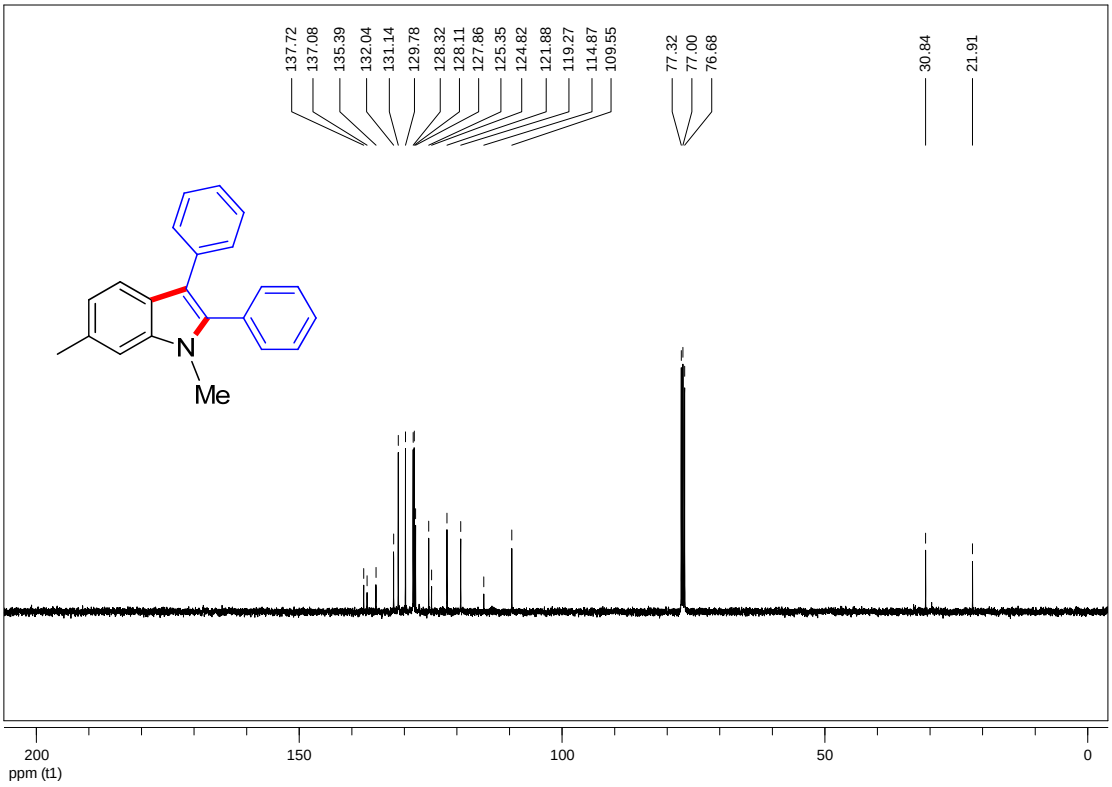
5-bromo-1-ethyl-2,3-diphenyl-1*H*-indole (3l)



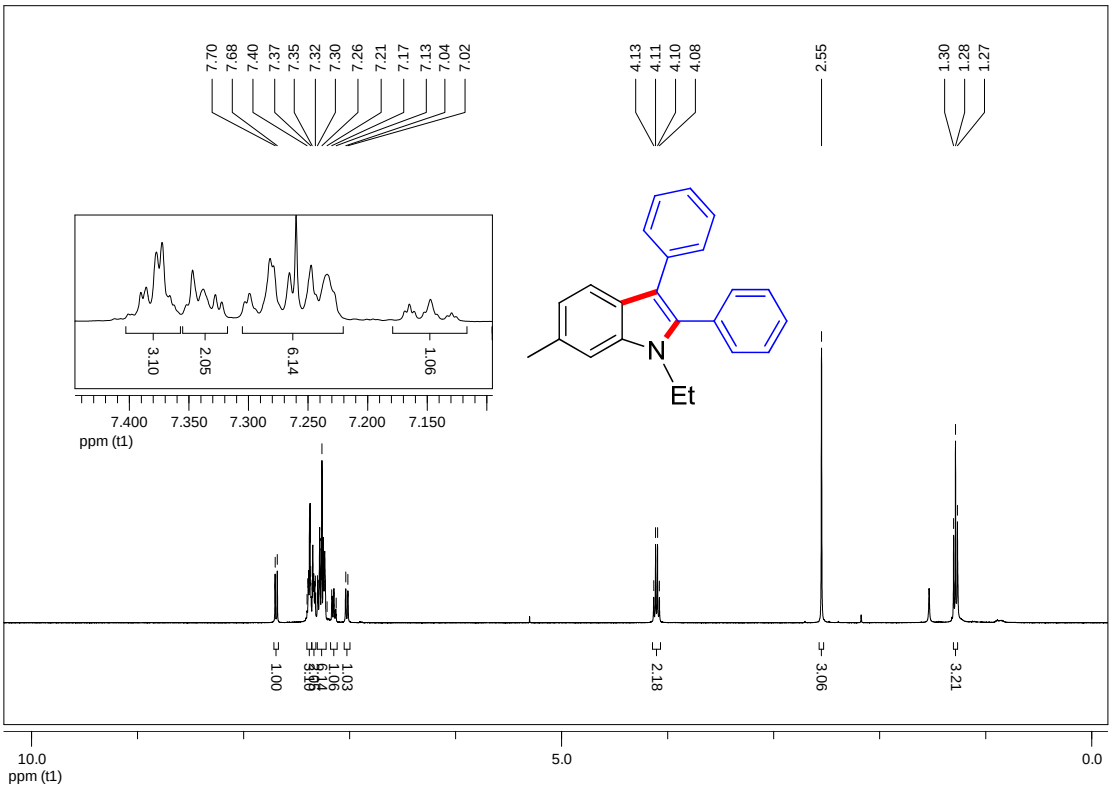


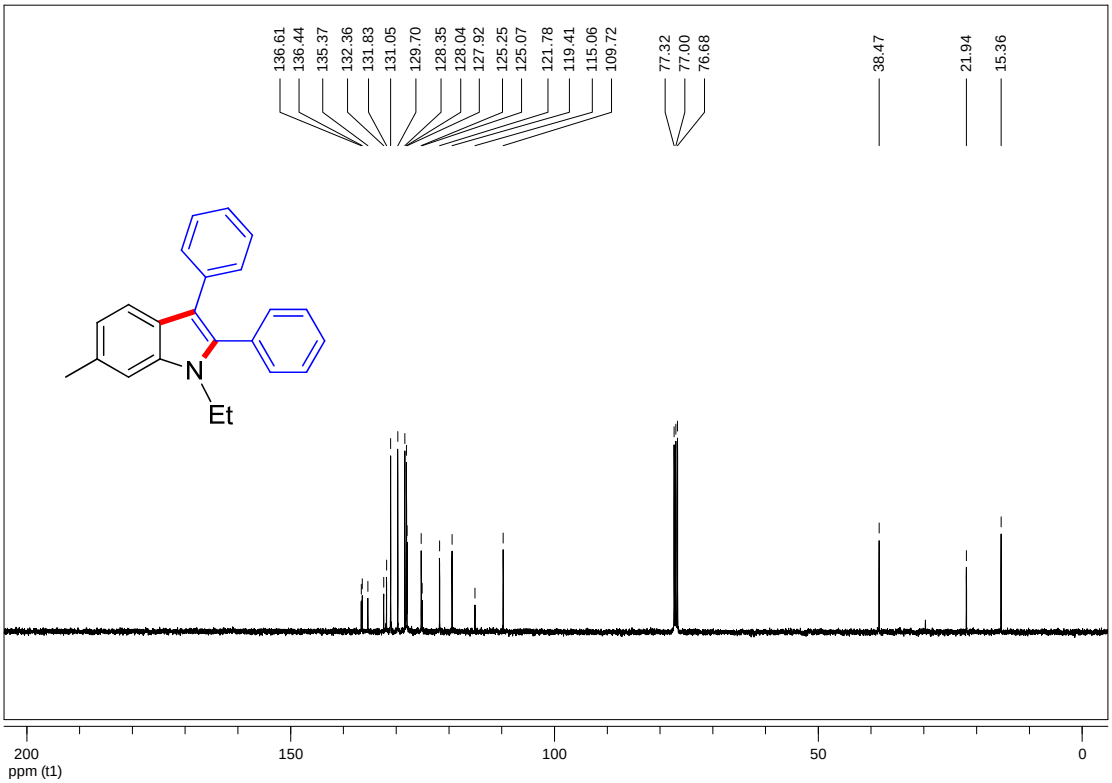
1,6-dimethyl-2,3-diphenyl-1*H*-indole (3m)



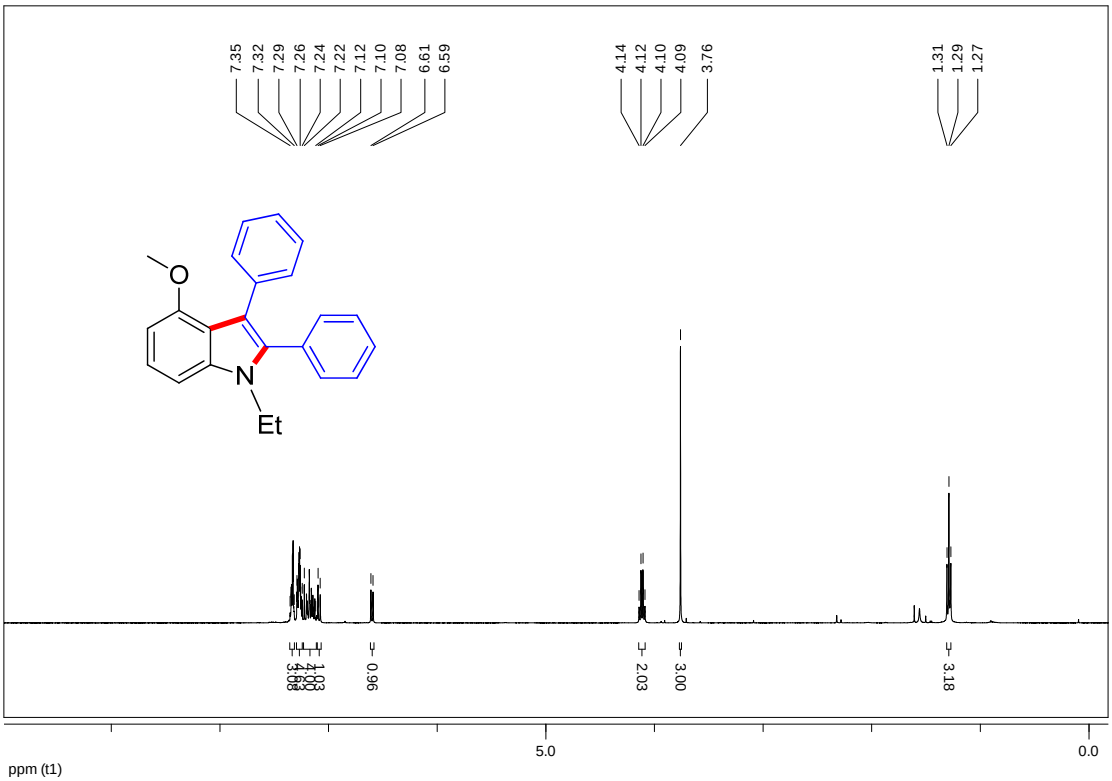


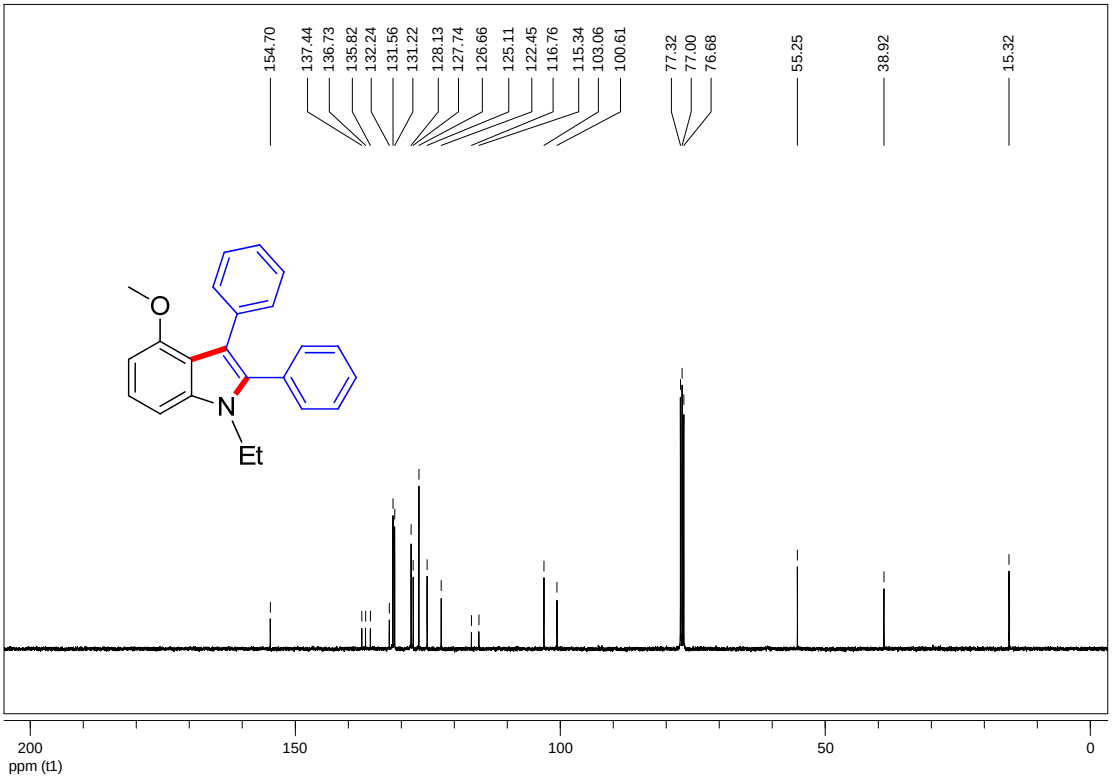
1-ethyl-6-methyl-2,3-diphenyl-1*H*-indole (3n)



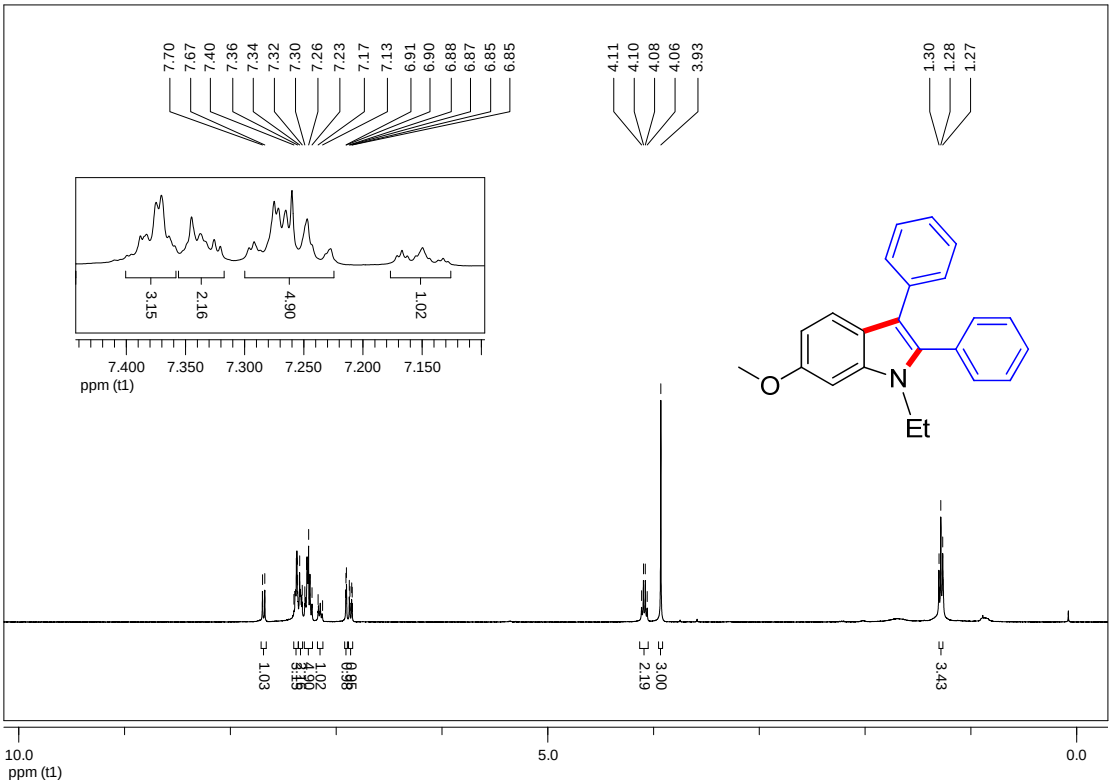


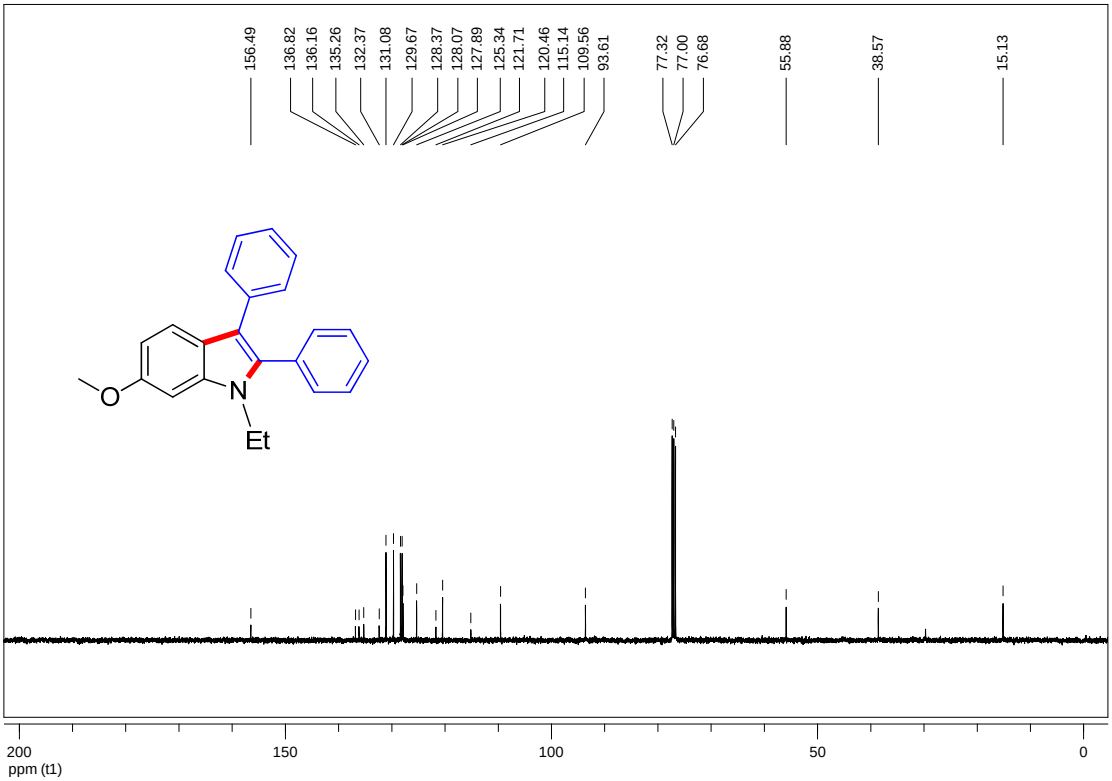
1-ethyl-4-methoxy-2,3-diphenyl-1*H*-indole (3o)



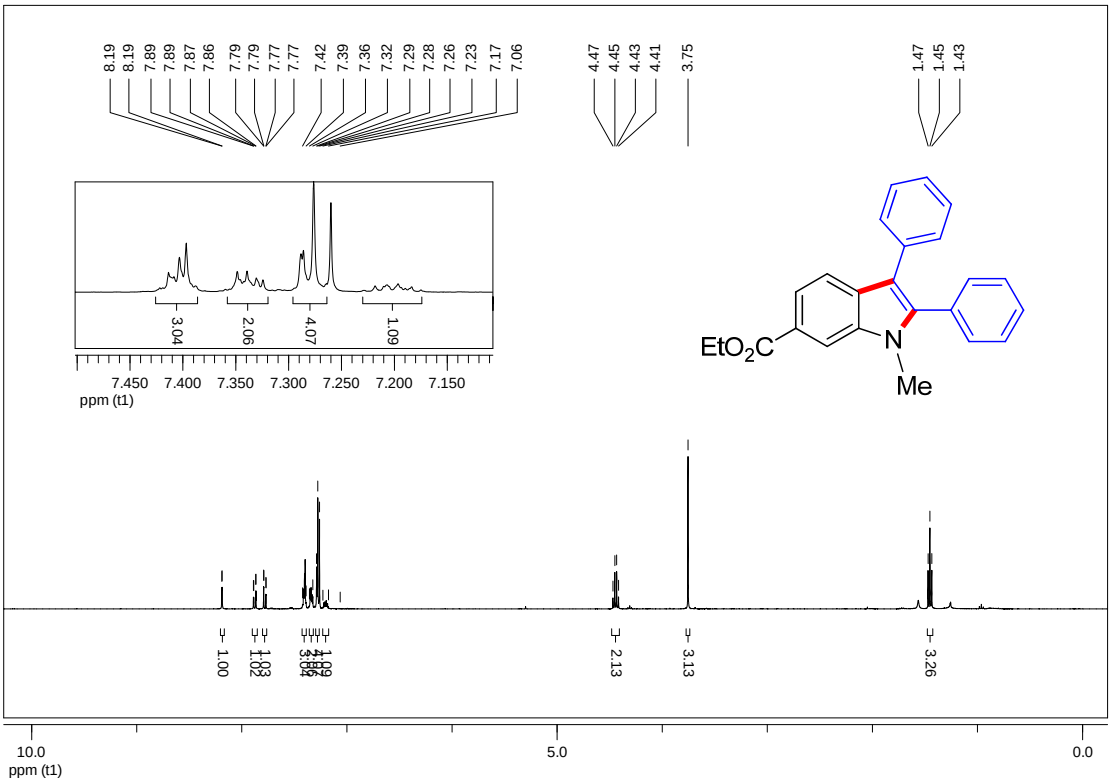


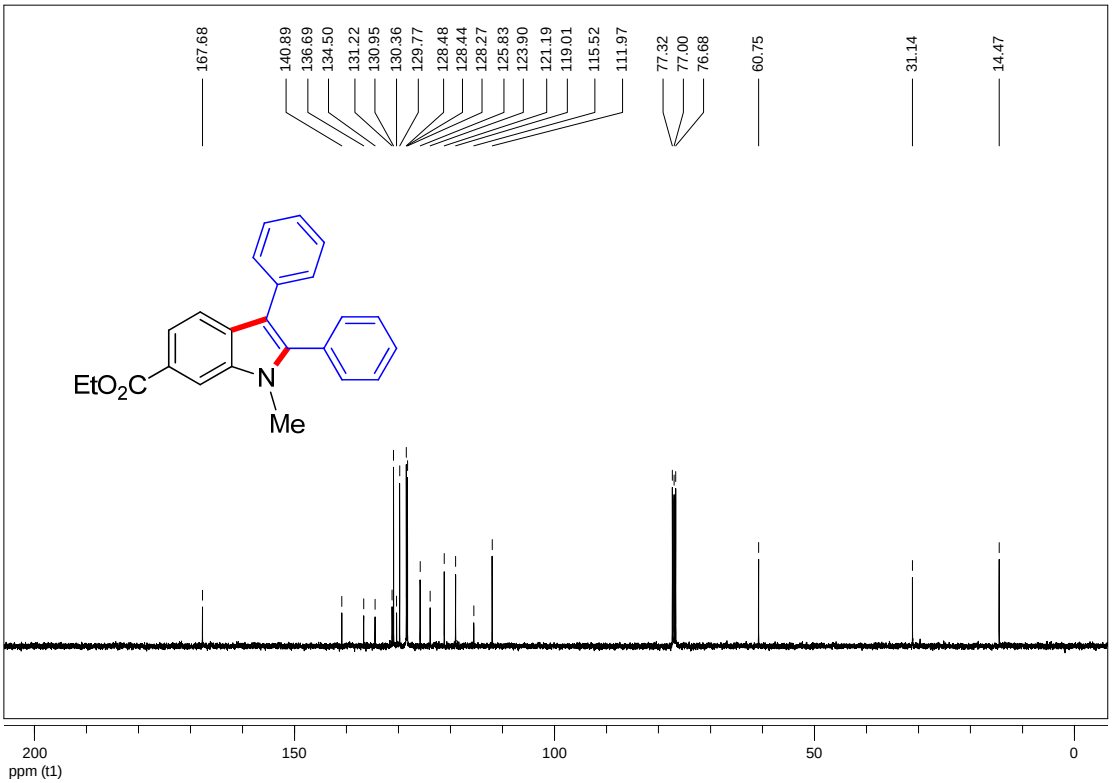
1-ethyl-6-methoxy-2,3-diphenyl-1*H*-indole (3o')



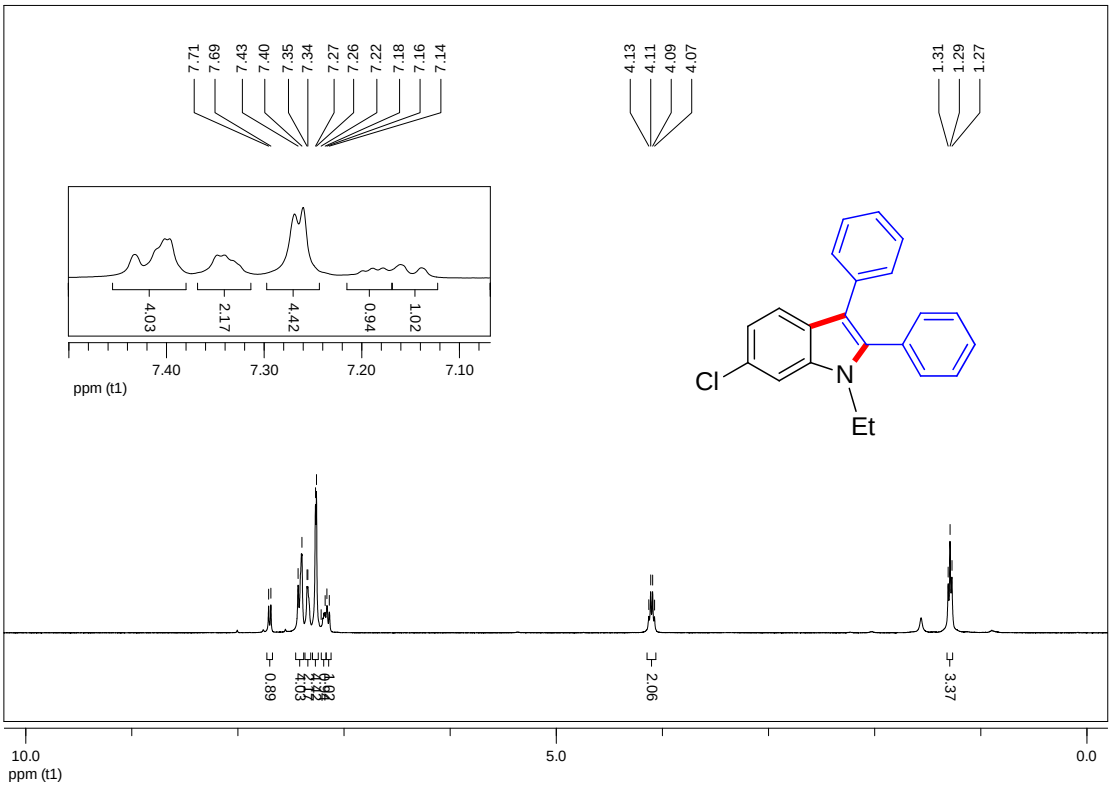


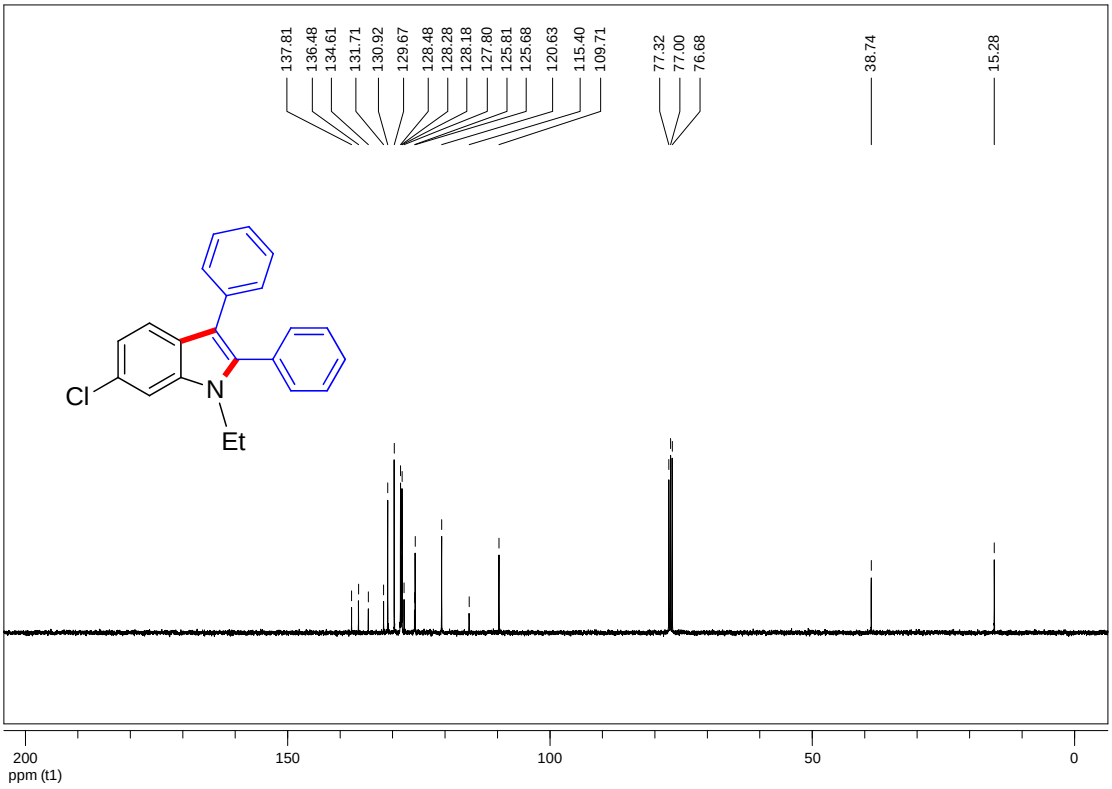
ethyl 1-methyl-2,3-diphenyl-1*H*-indole-6-carboxylate (3p)



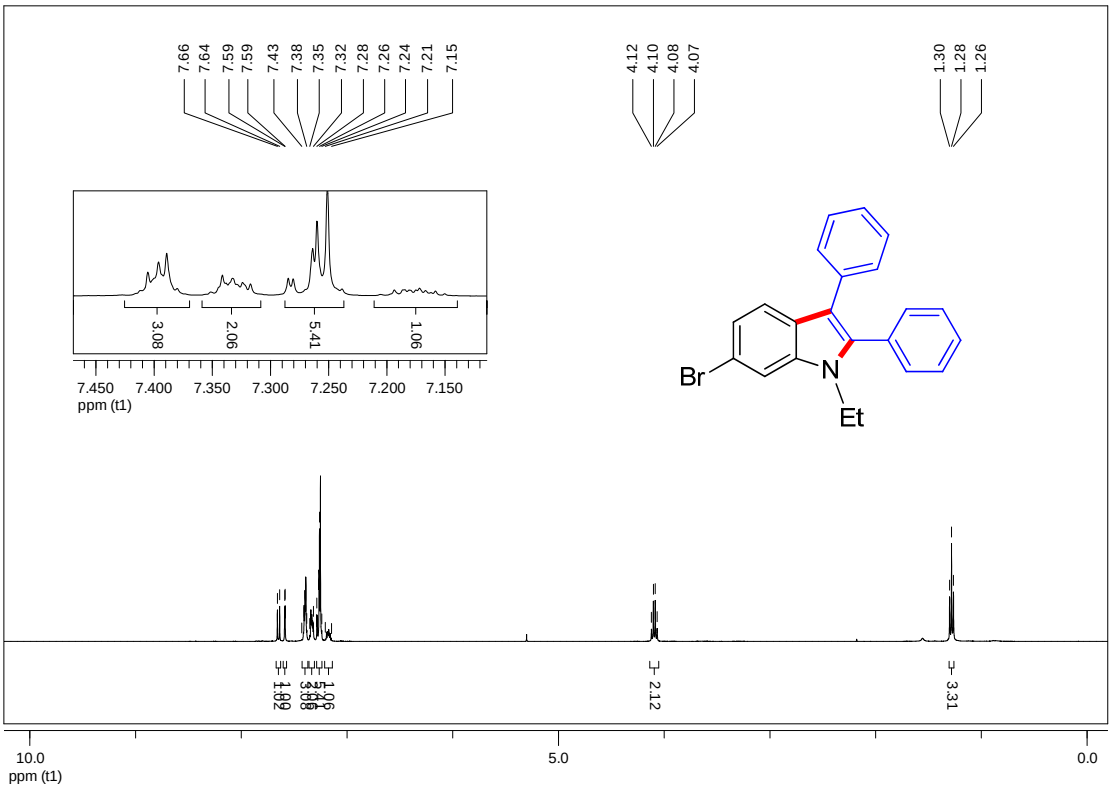


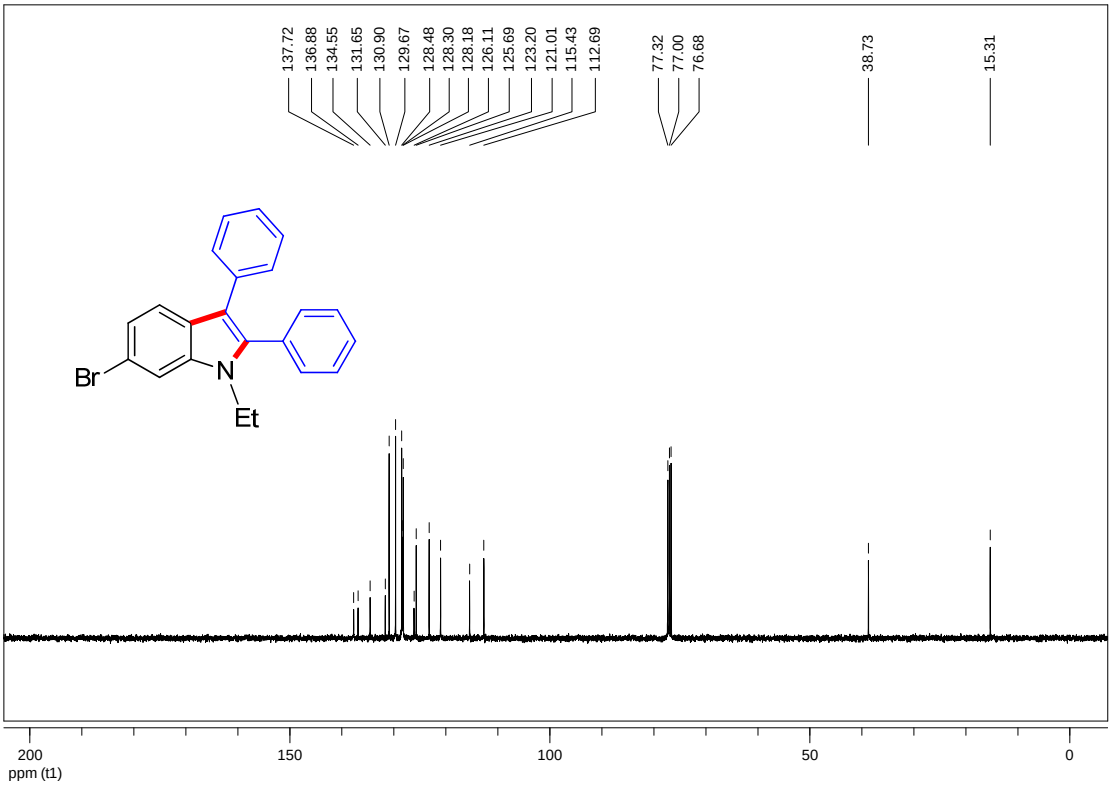
6-chloro-1-ethyl-2,3-diphenyl-1*H*-indole (3q)



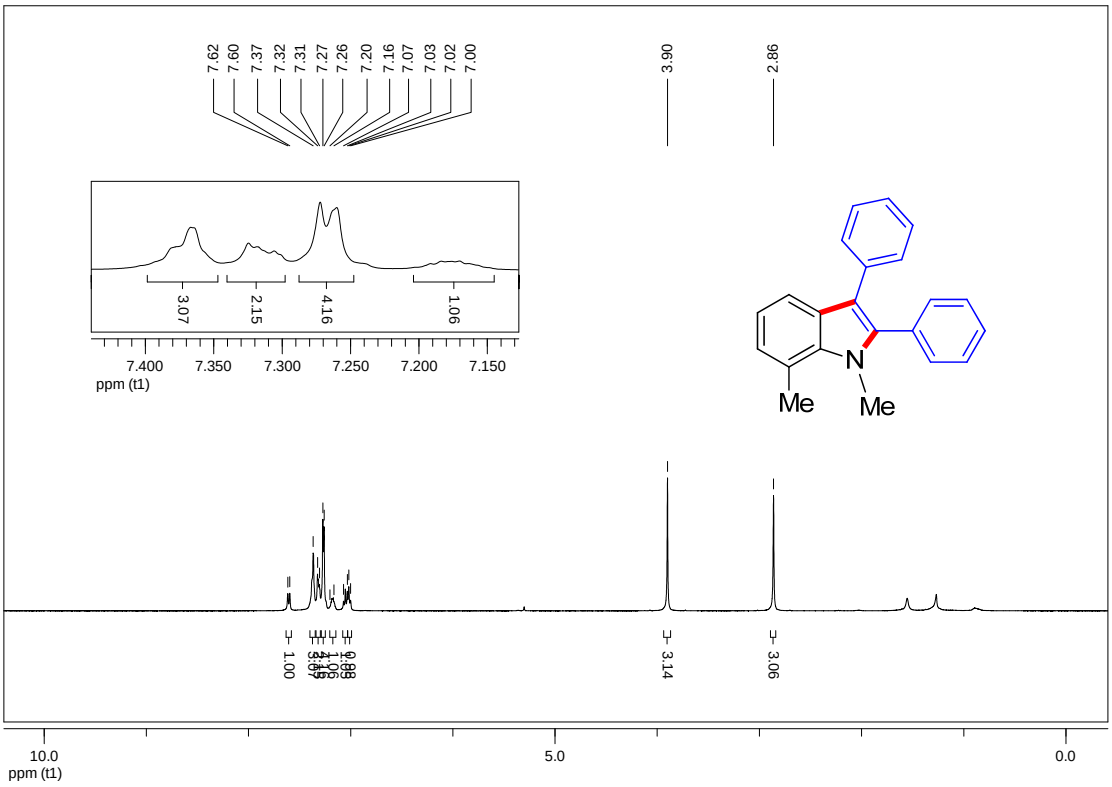


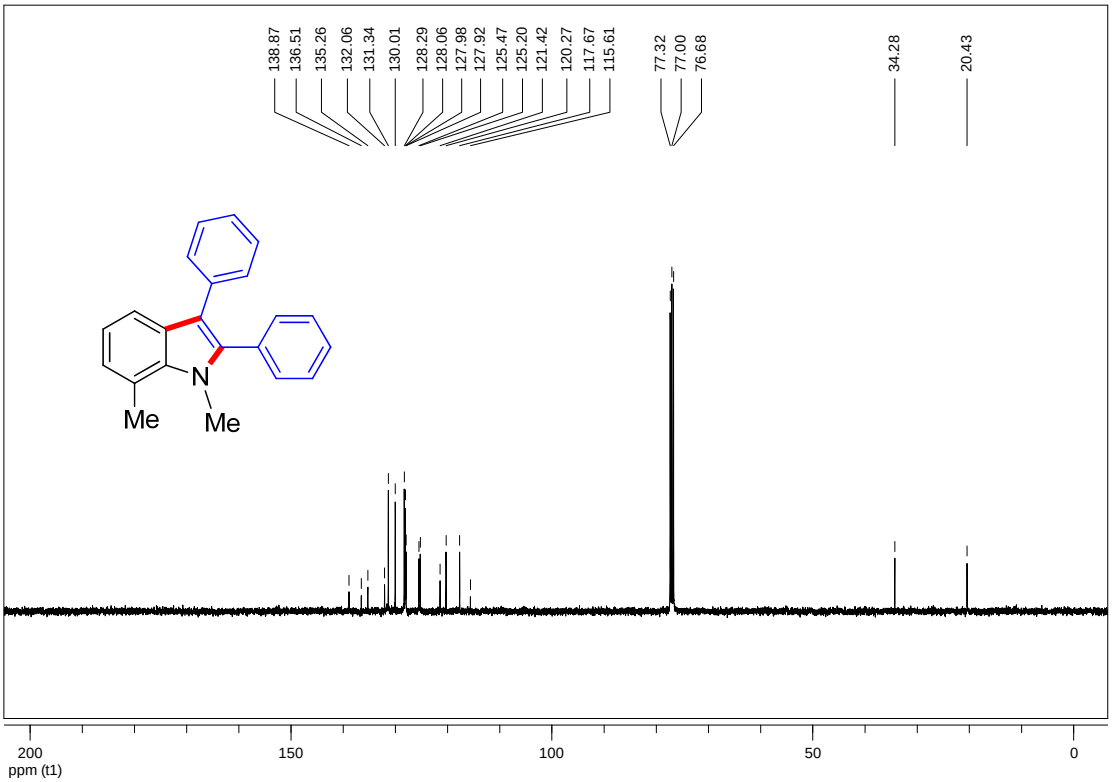
6-bromo-1-ethyl-2,3-diphenyl-1*H*-indole (3r)



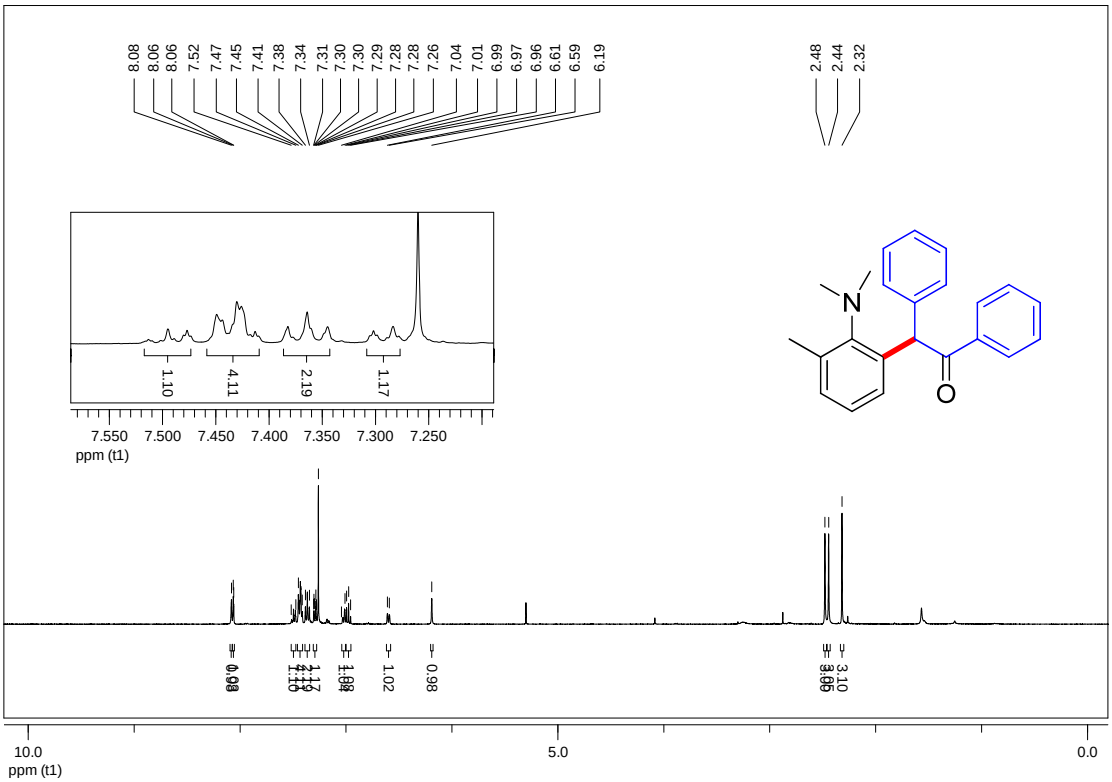


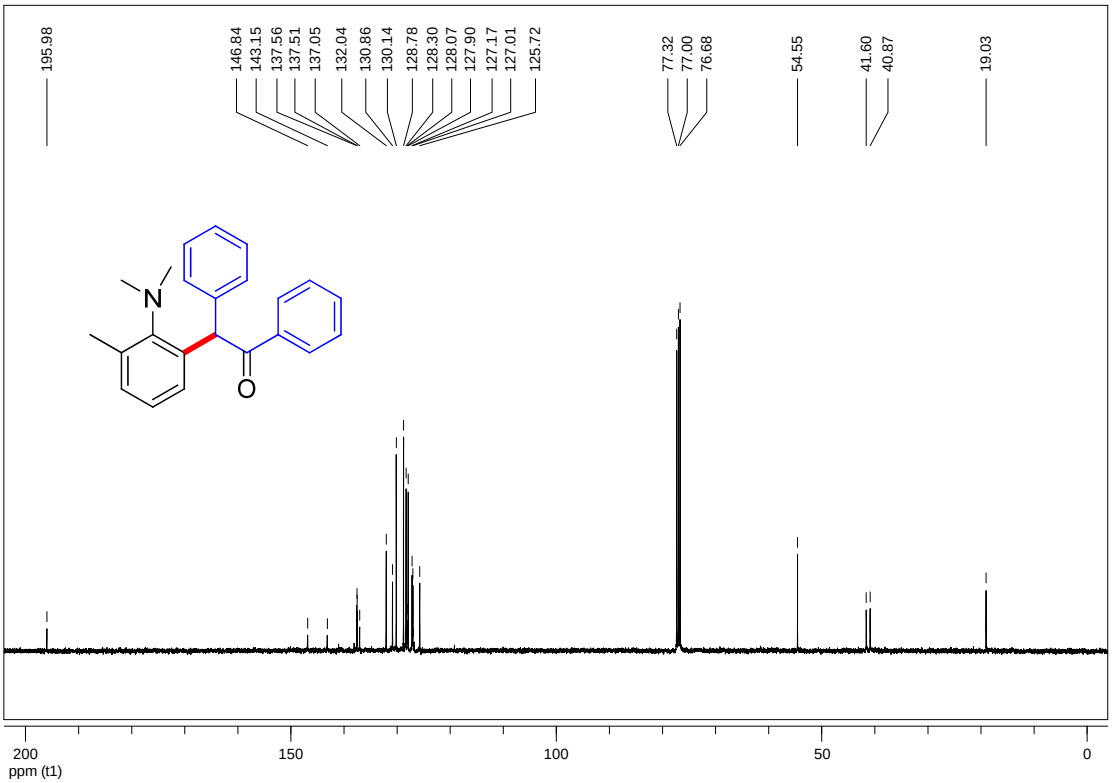
1,7-dimethyl-2,3-diphenyl-1*H*-indole (3s)



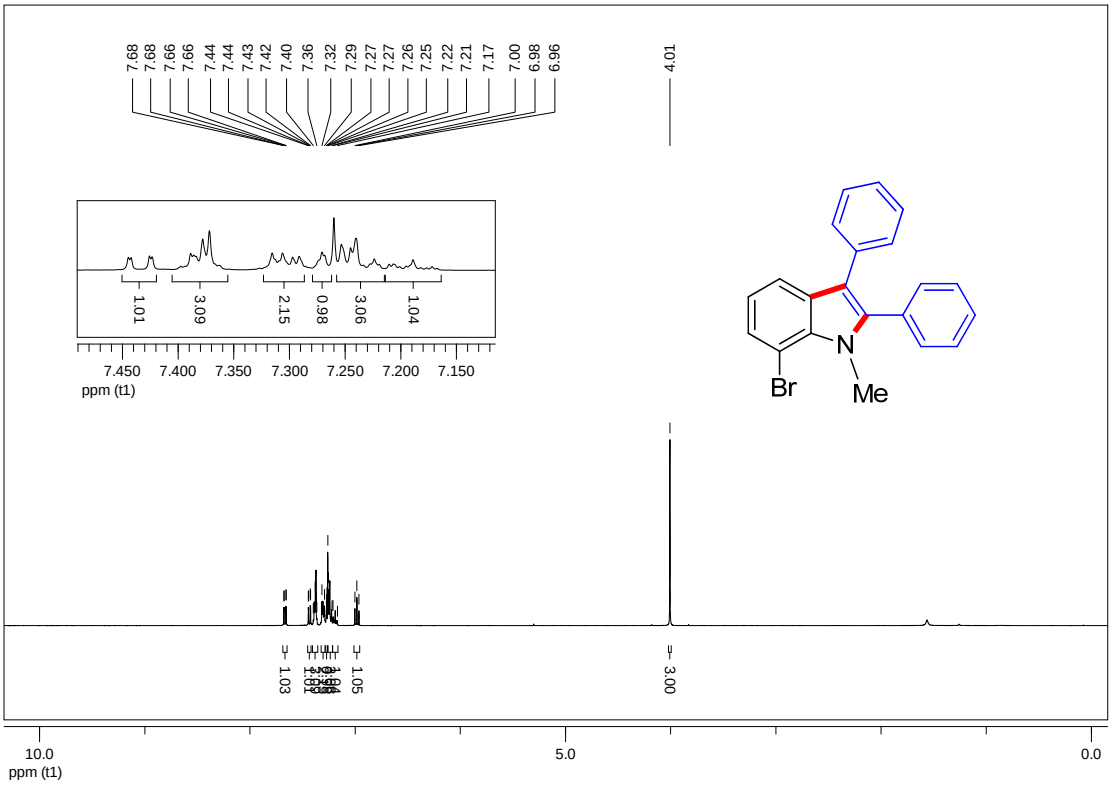


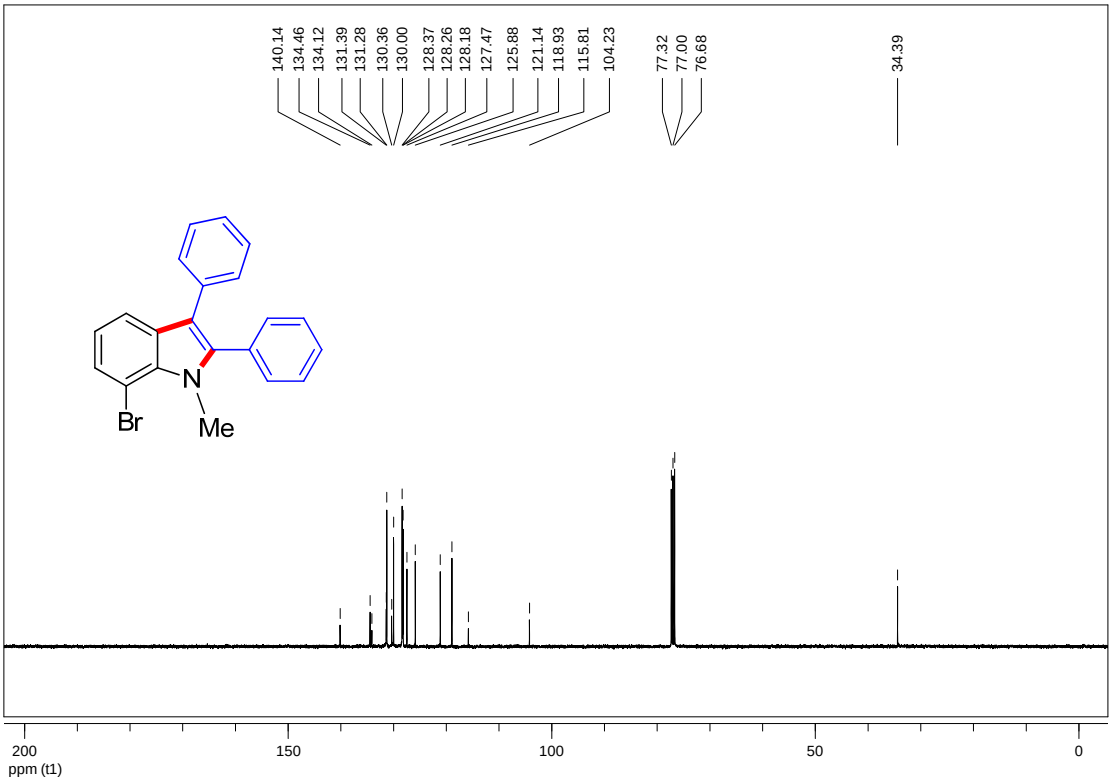
(2-(dimethylamino)-3-methylphenyl)-1,2-diphenylethanone (3s*)



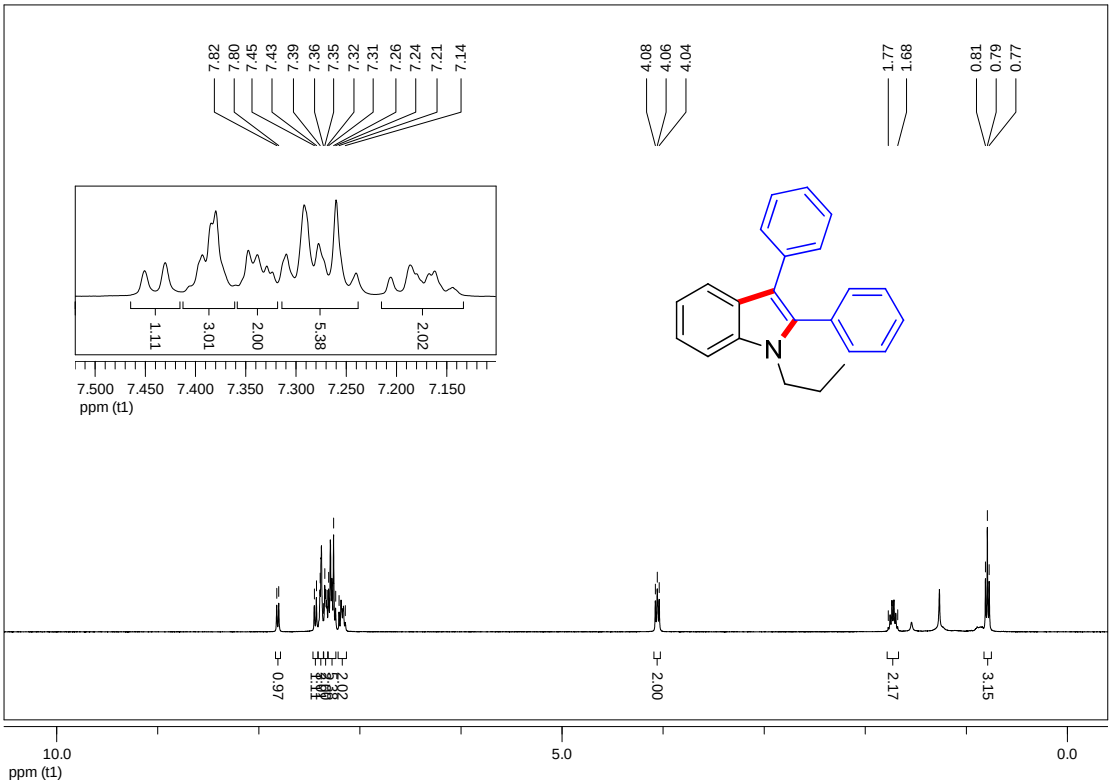


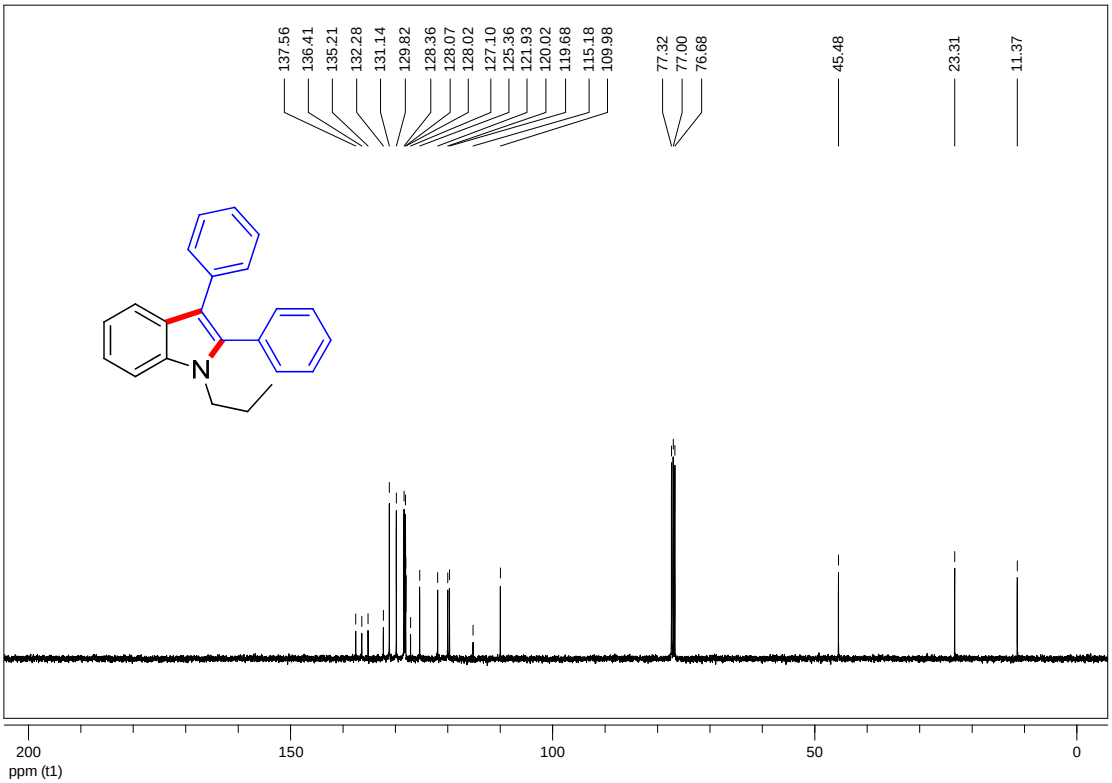
7-bromo-1-methyl-2,3-diphenyl-1H-indole (3t)



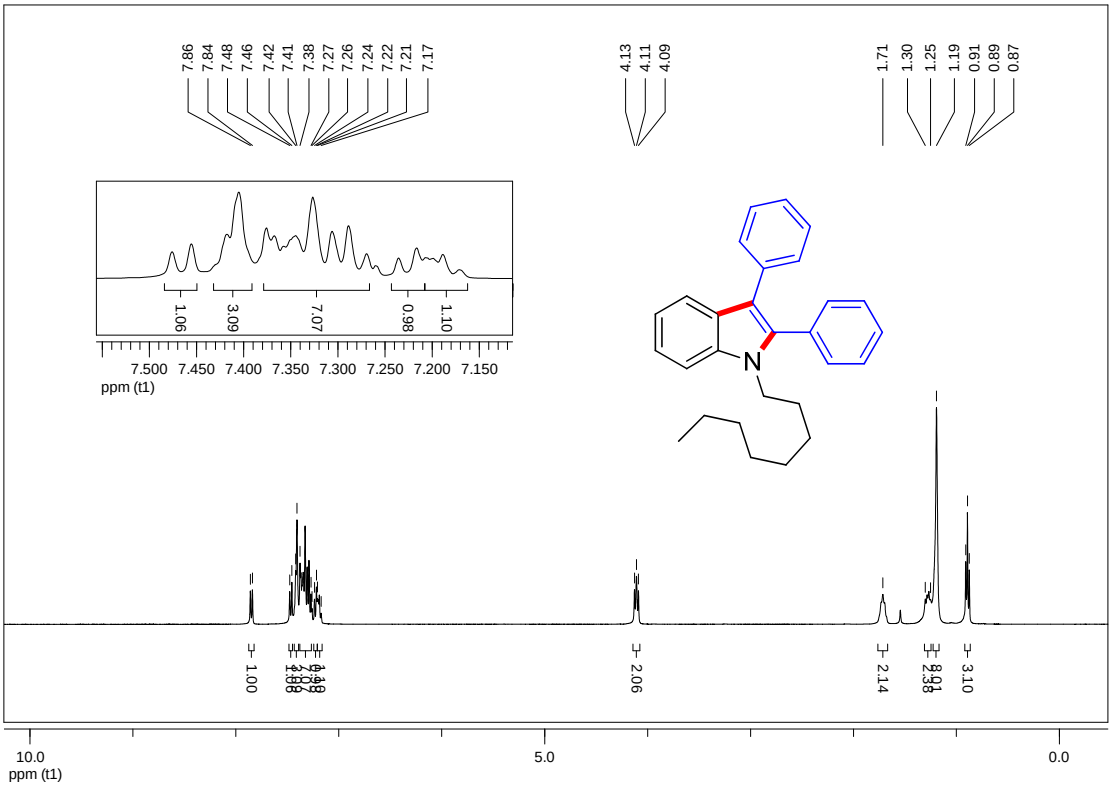


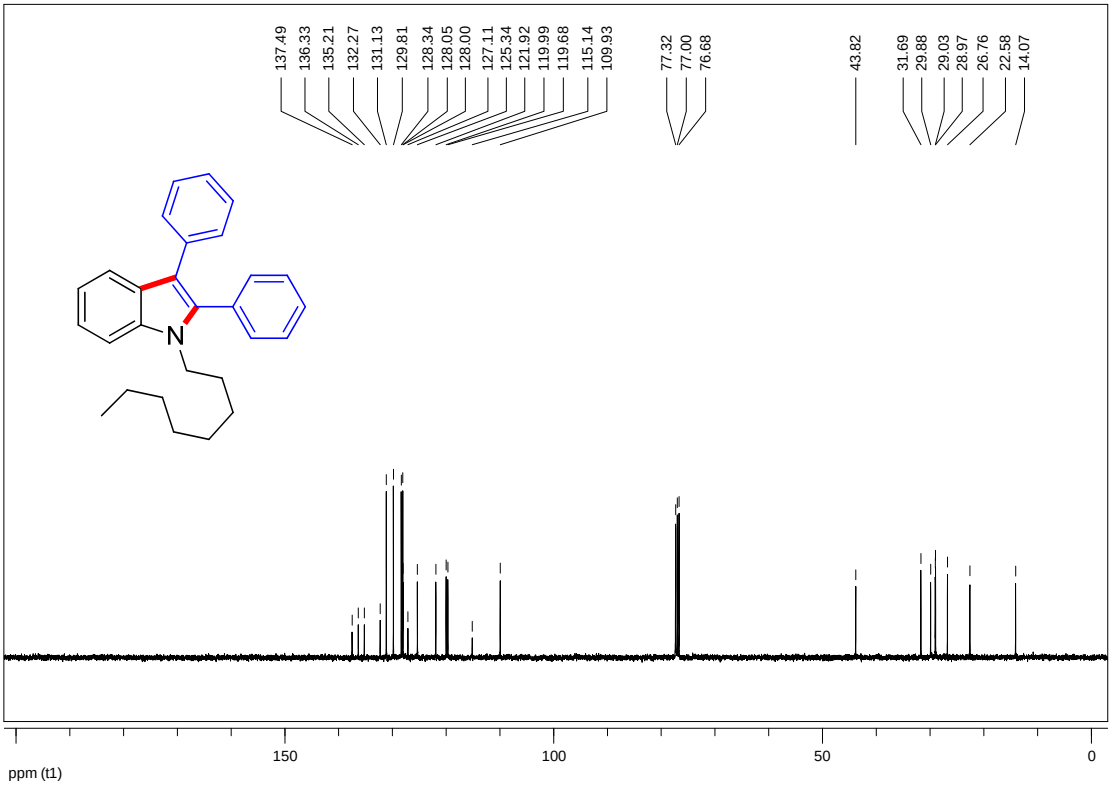
2,3-diphenyl-1-propyl-1*H*-indole (3u)



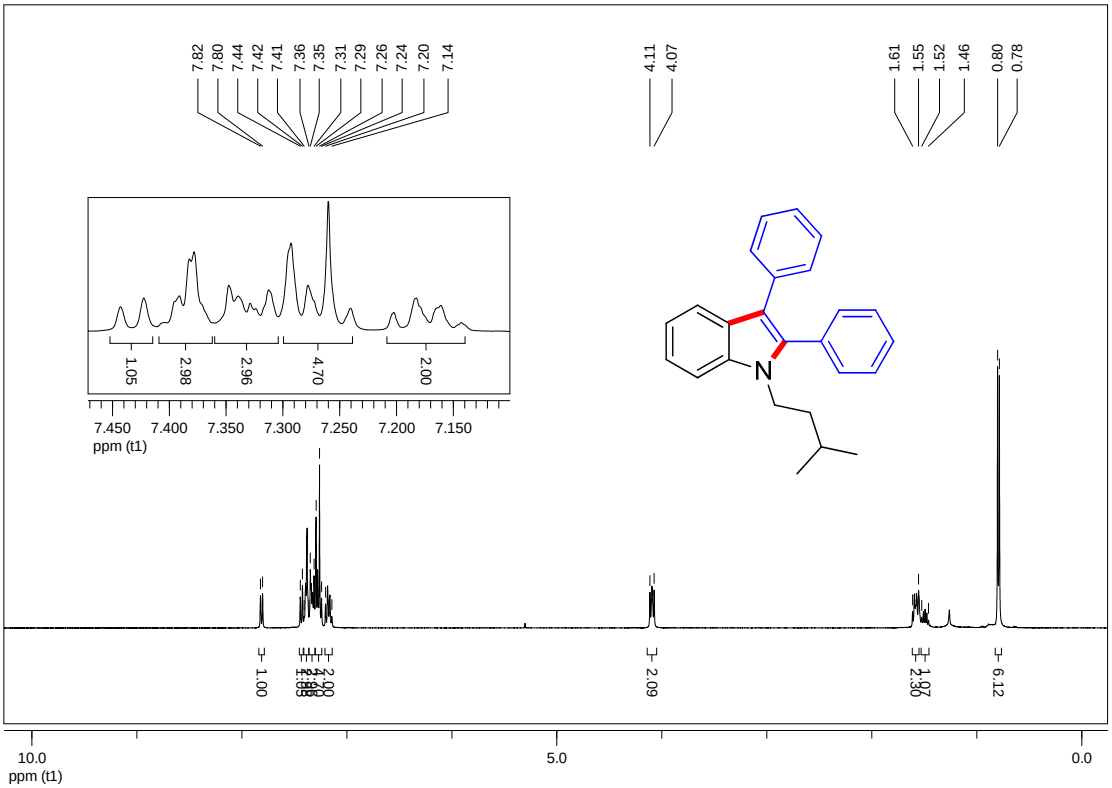


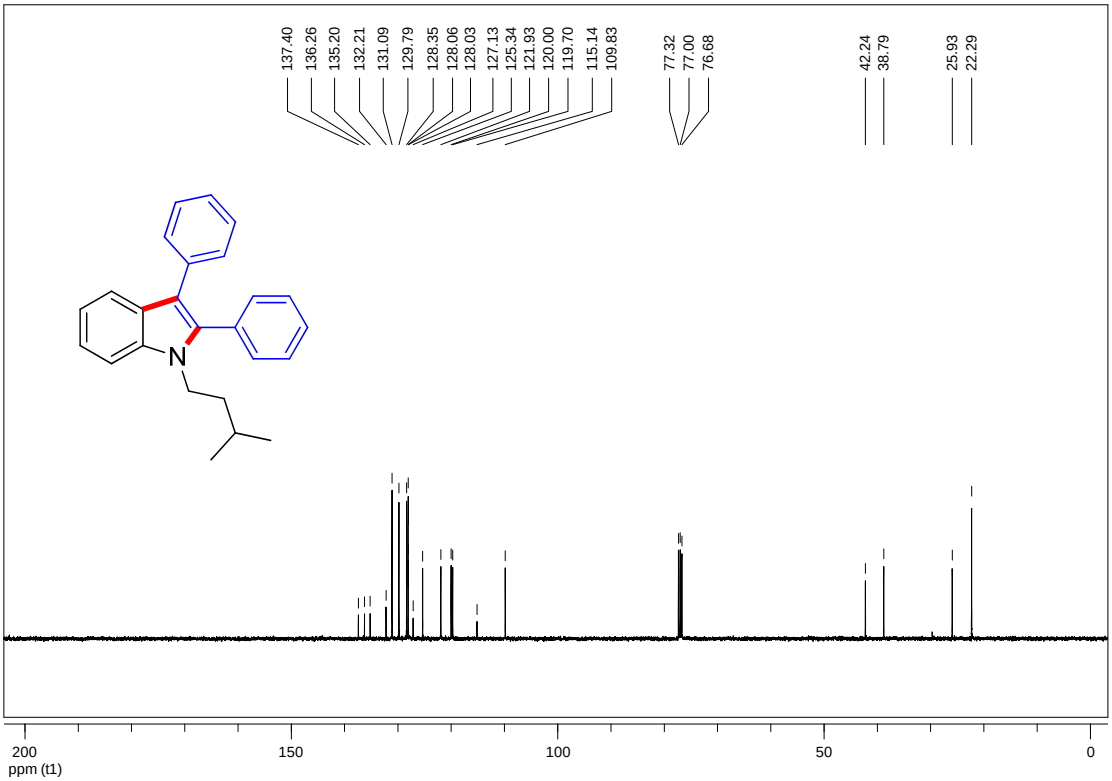
1-octyl-2,3-diphenyl-1*H*-indole (3v)



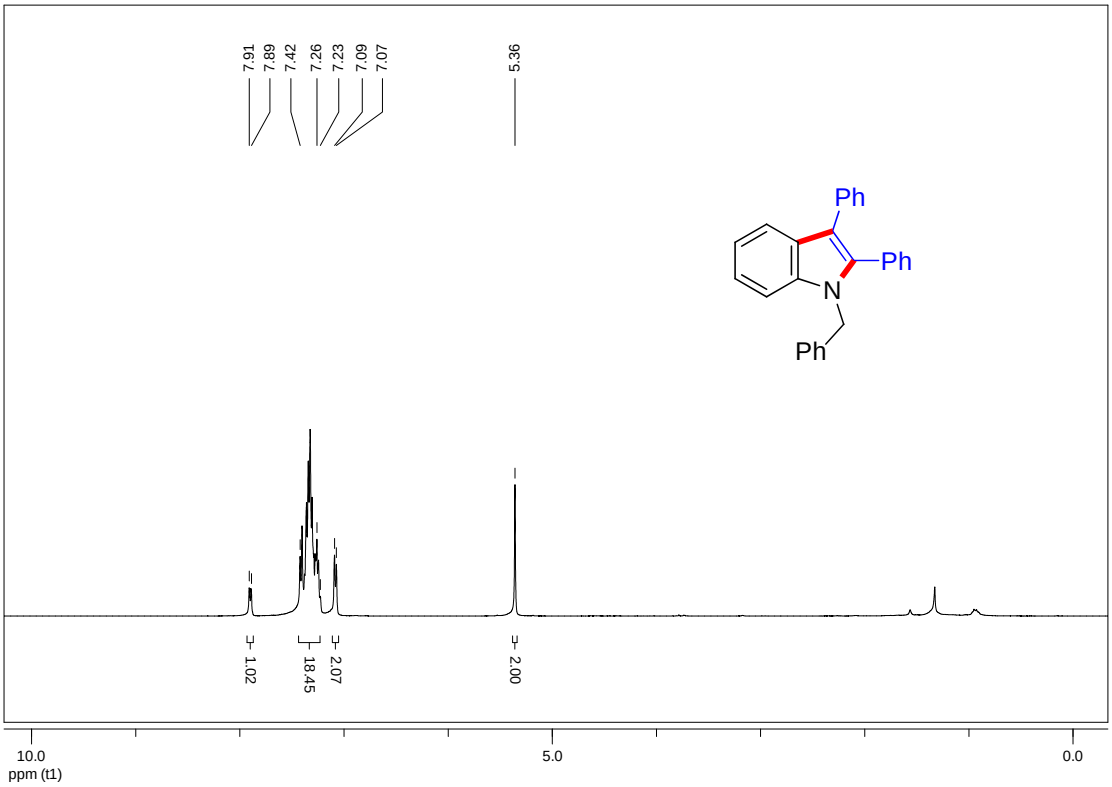


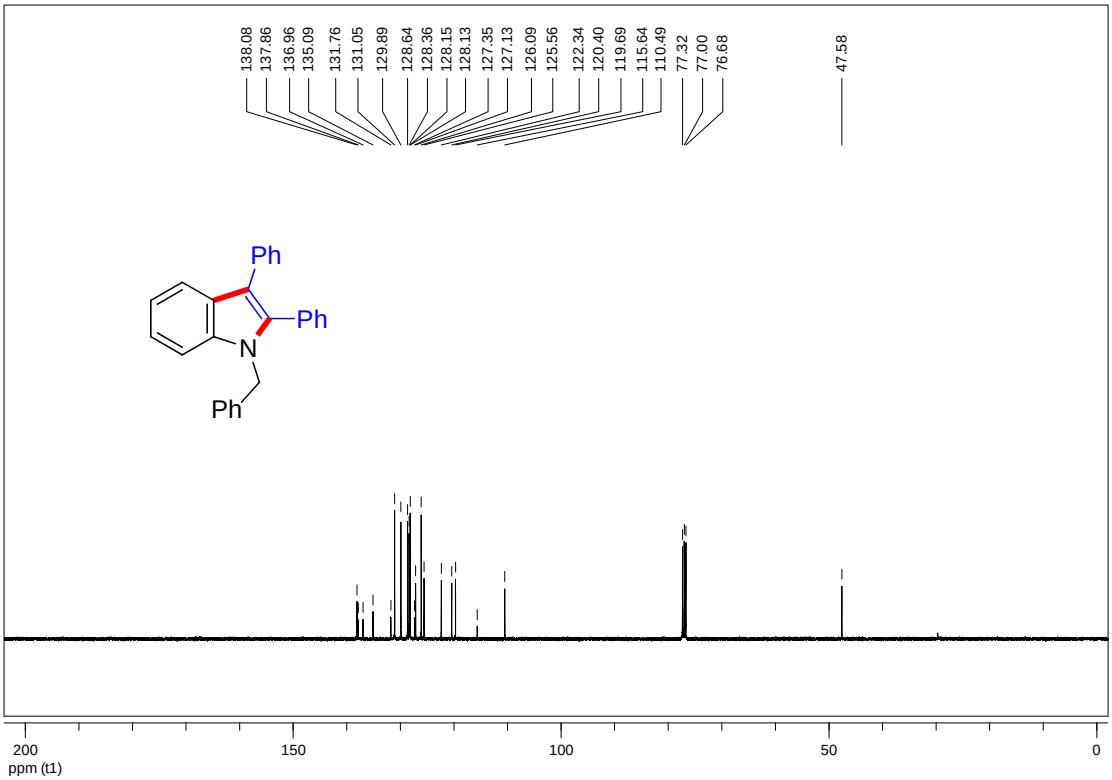
1-isopentyl-2,3-diphenyl-1*H*-indole (3w)



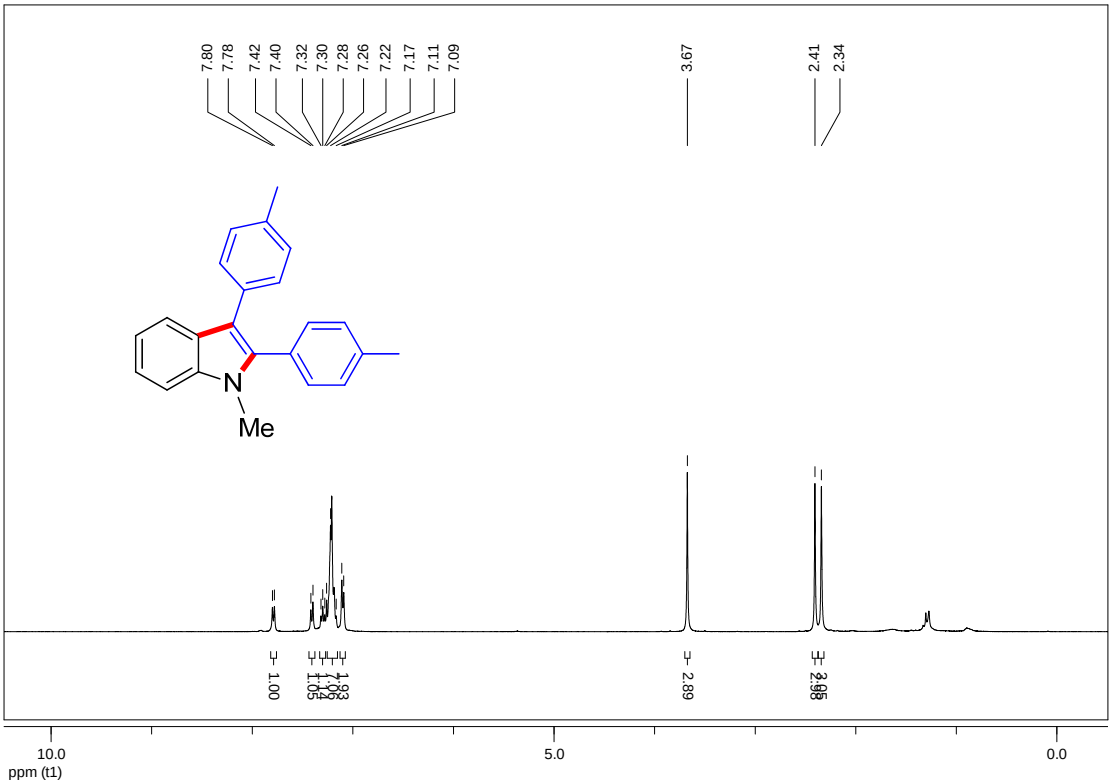


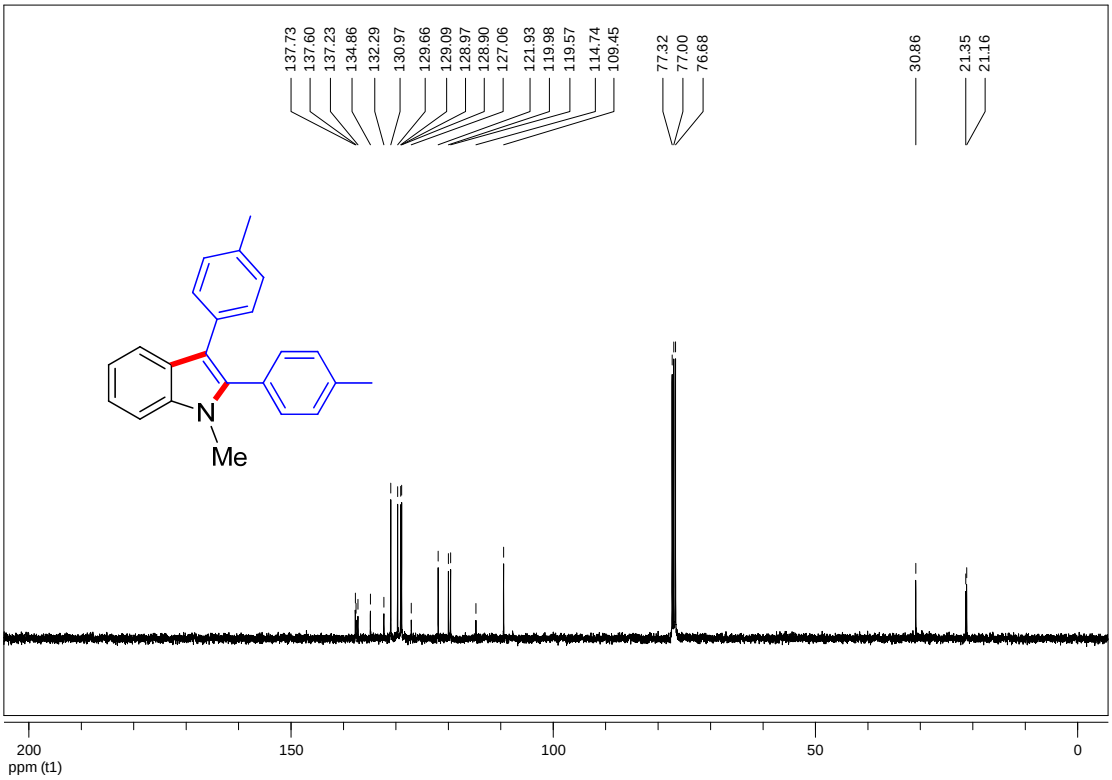
1-benzyl-2,3-diphenyl-1H-indole (3x)



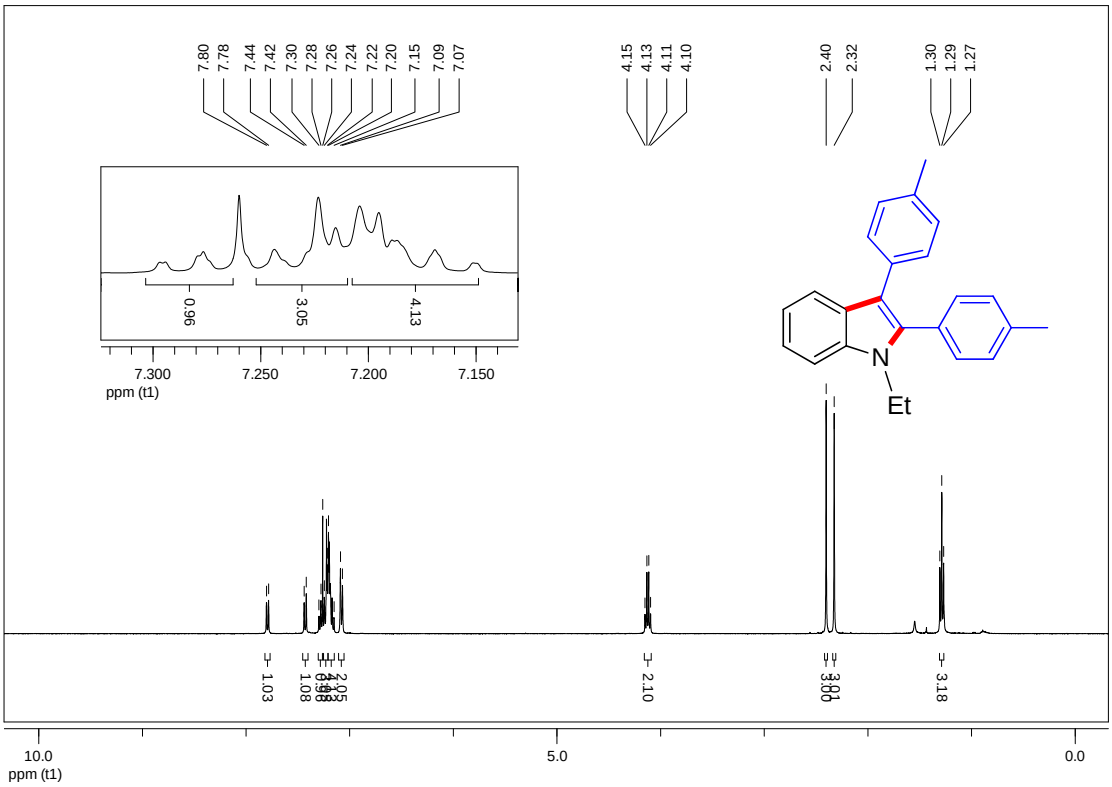


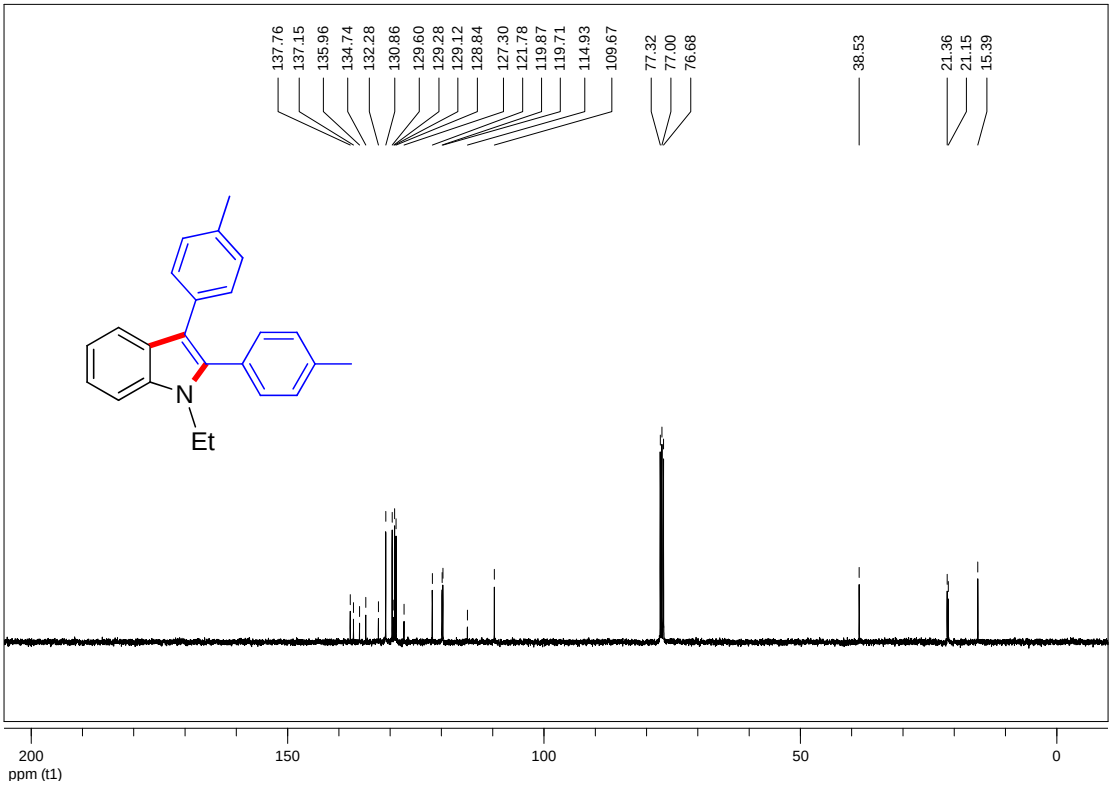
2,3-bis(4-methylphenyl)-1-methyl-1H-indole (4a)



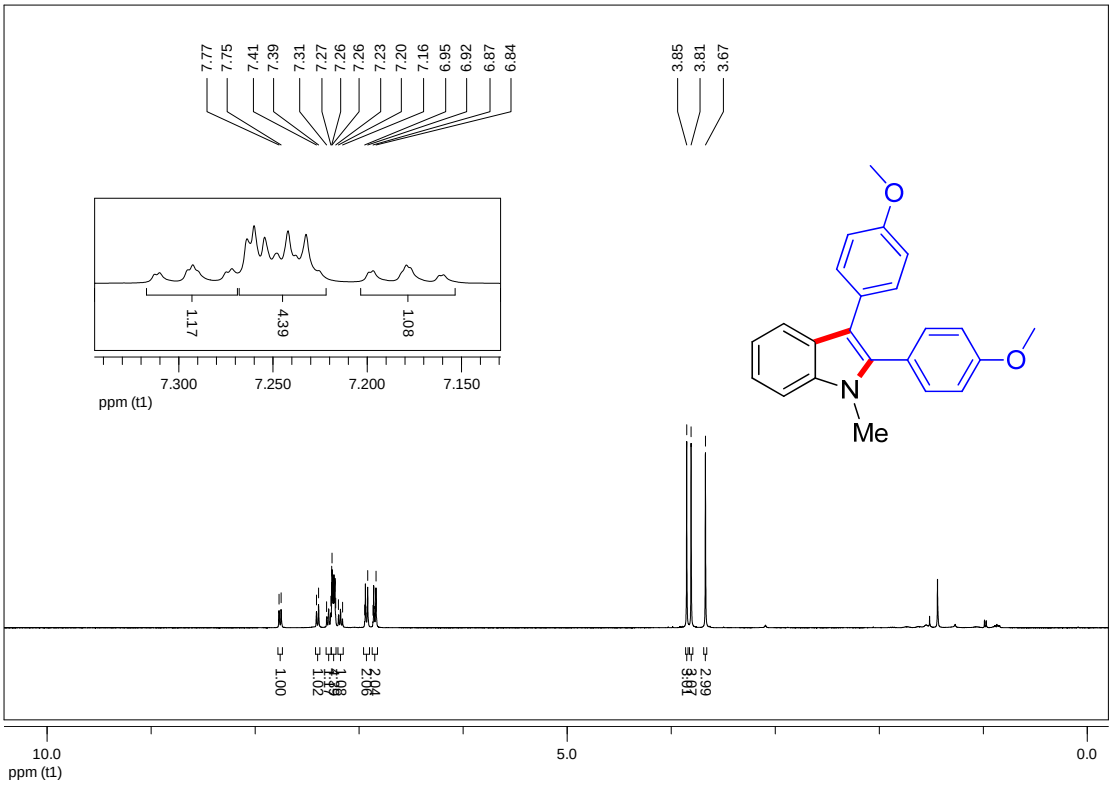


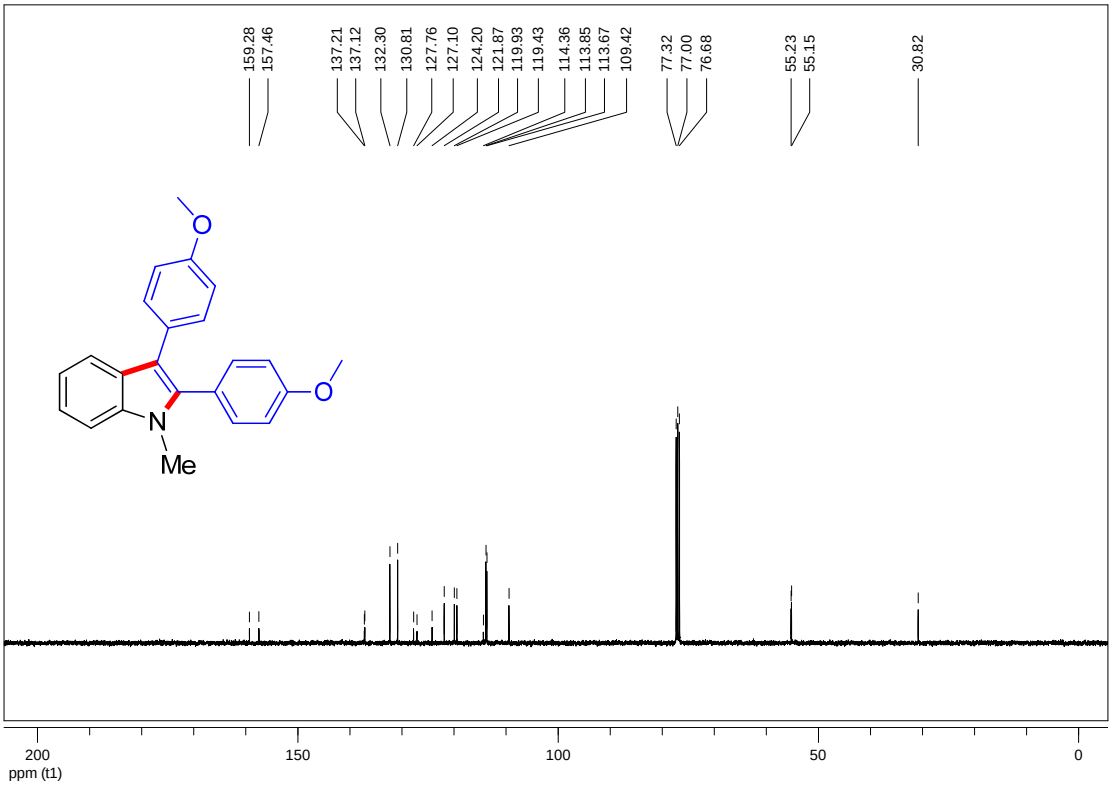
2,3-bis(4-methylphenyl)-1-ethyl-1*H*-indole (4b)



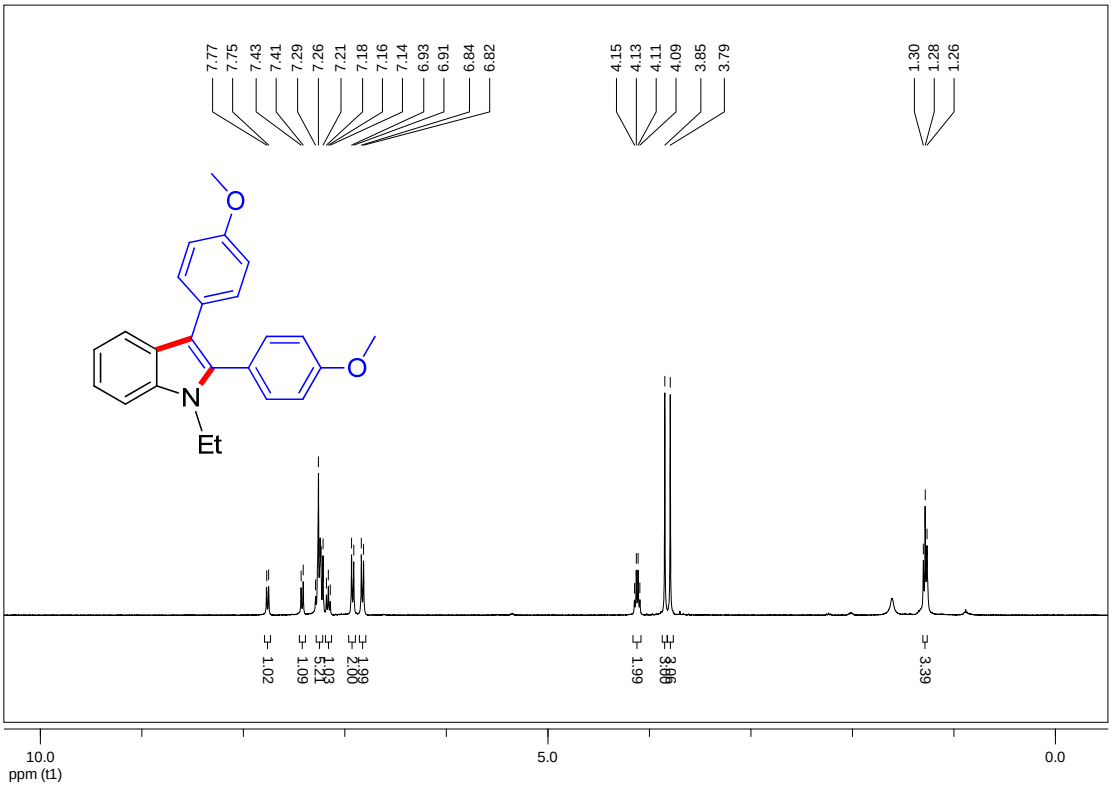


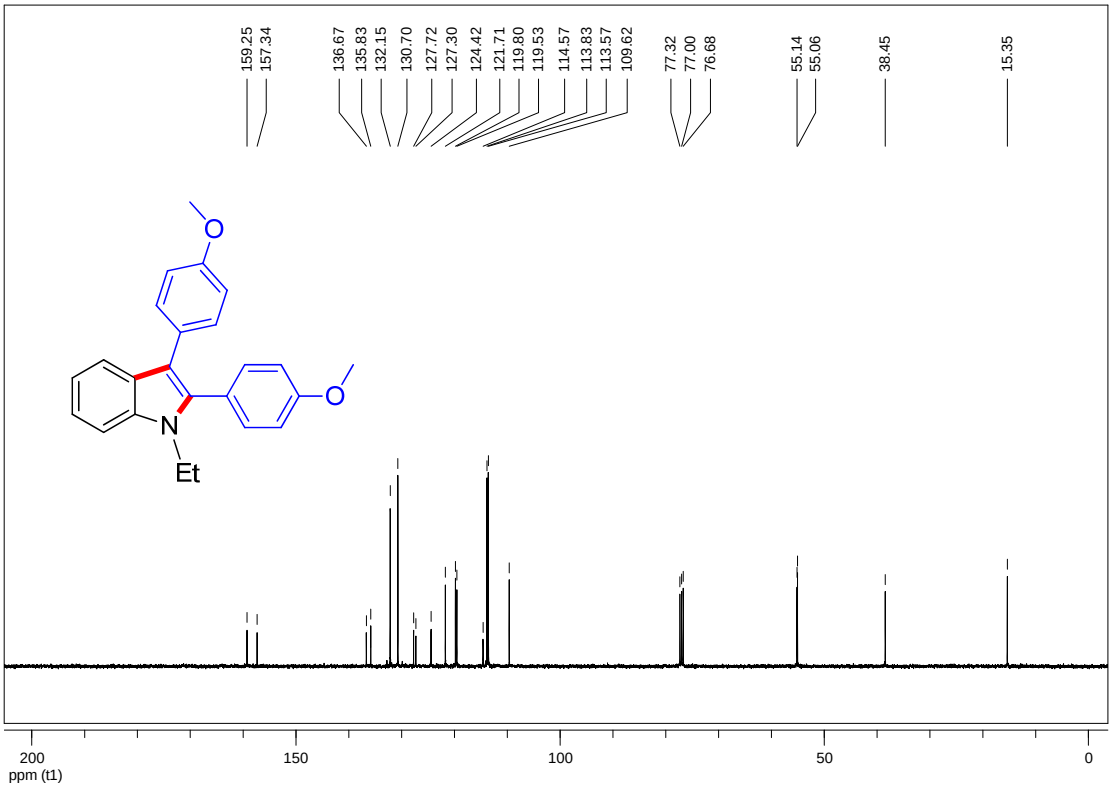
2,3-bis(4-methoxyphenyl)-1-methyl-1*H*-indole (4c)



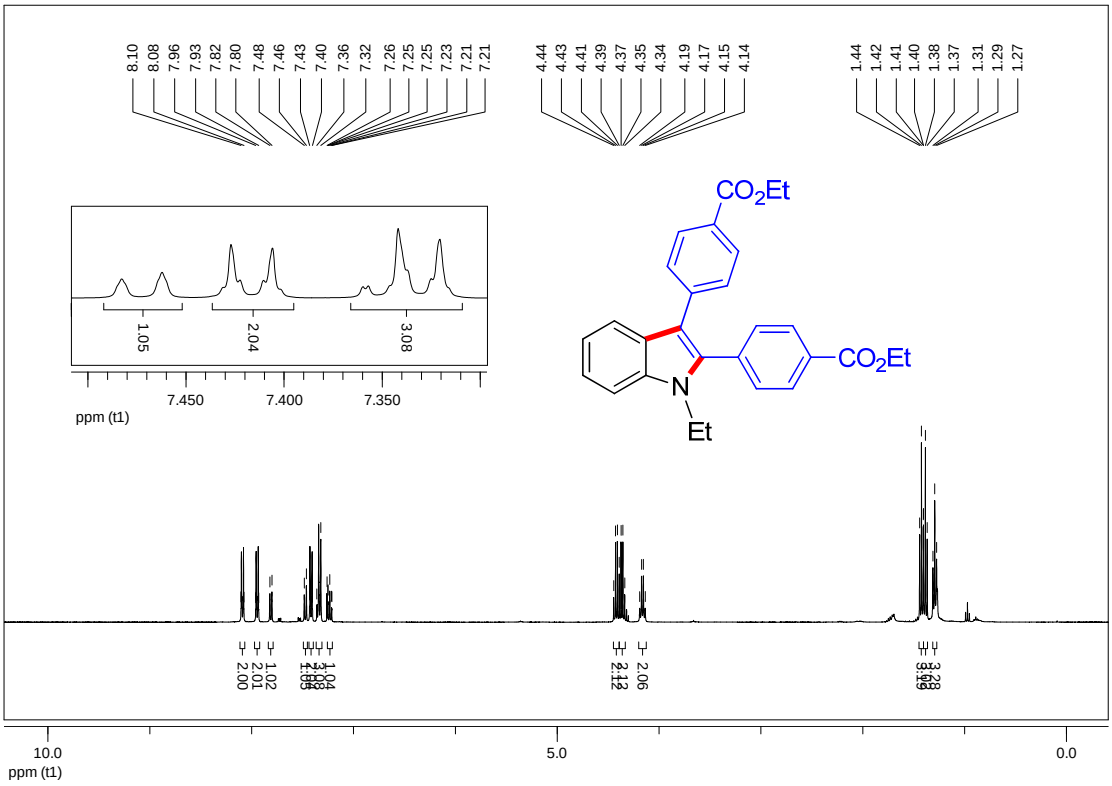


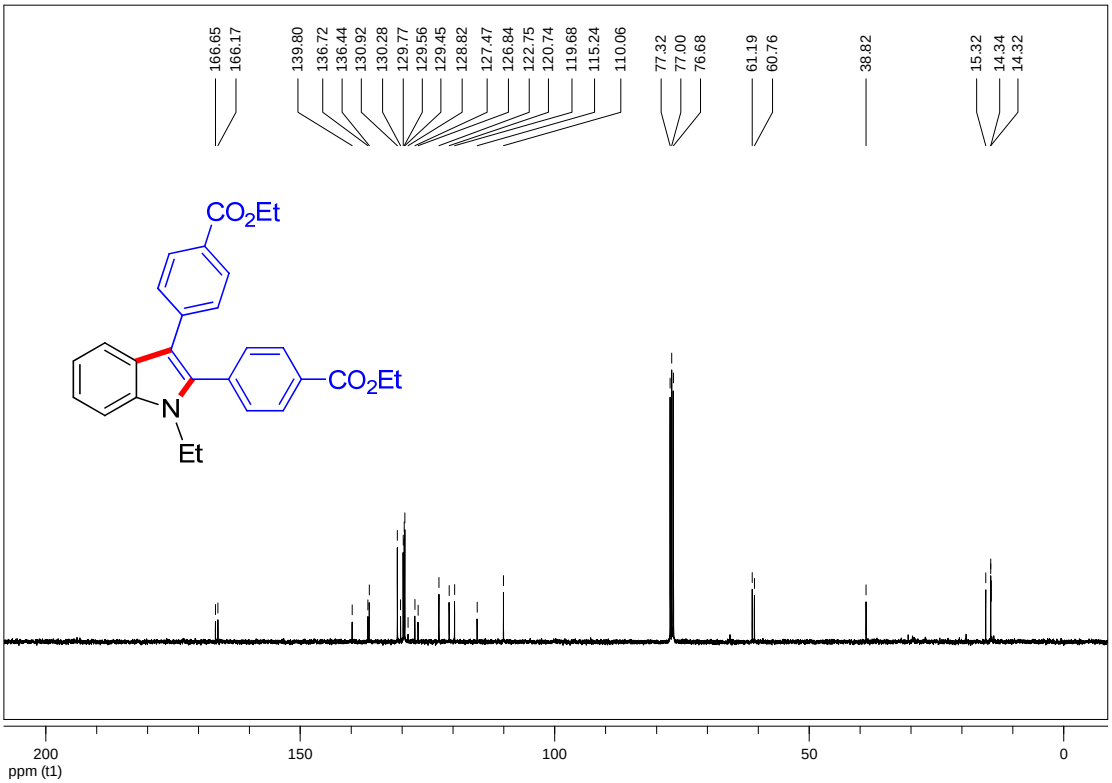
1-ethyl-2,3-bis(4-methoxyphenyl)-1*H*-indole (4d)



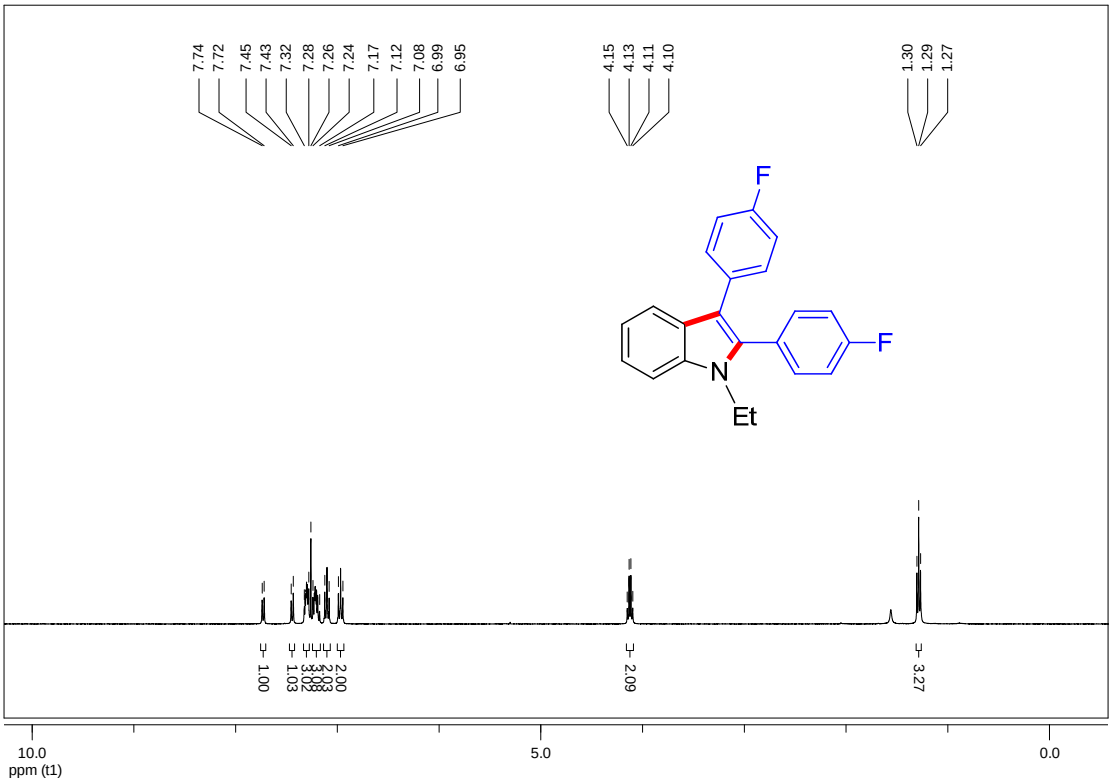


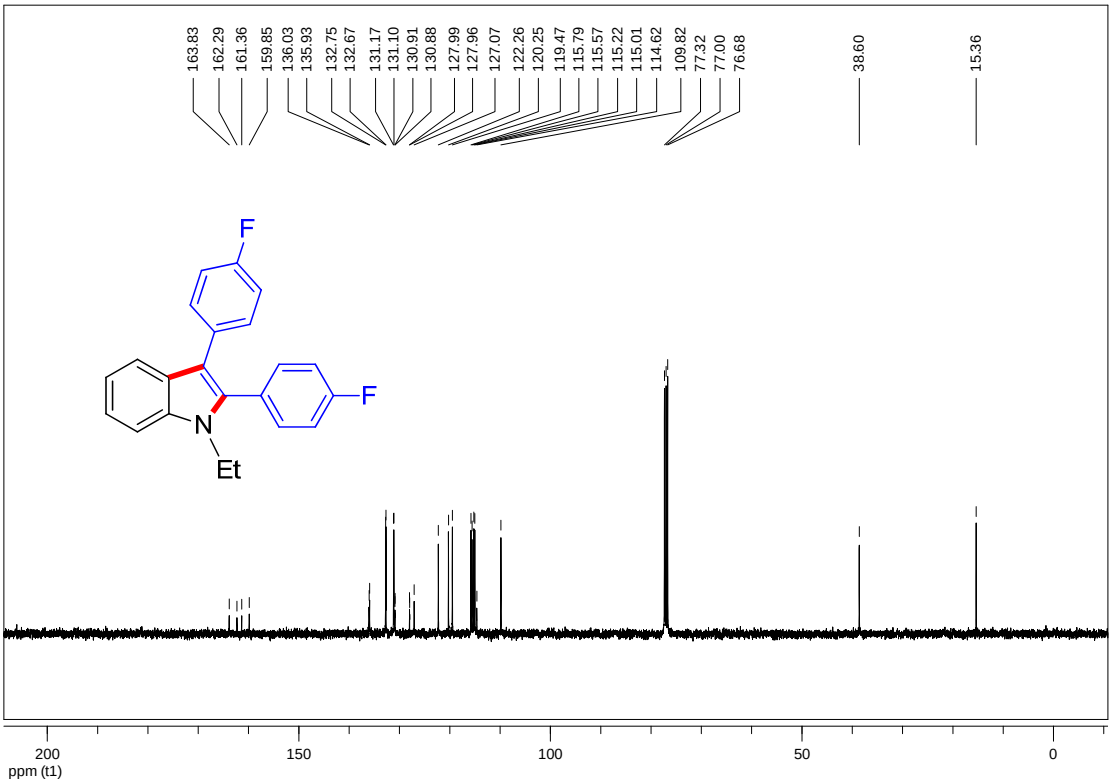
diethyl 4,4'-(1-ethyl-1*H*-indole-2,3-diyl)dibenzoate (4e)

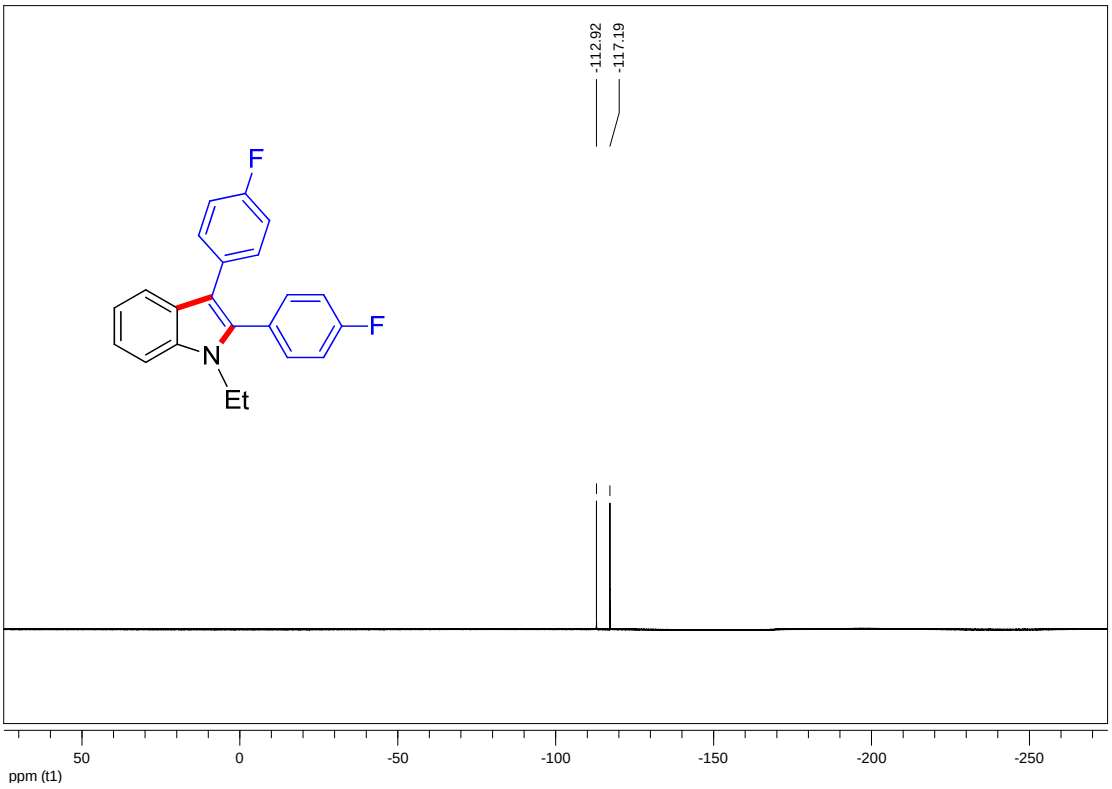




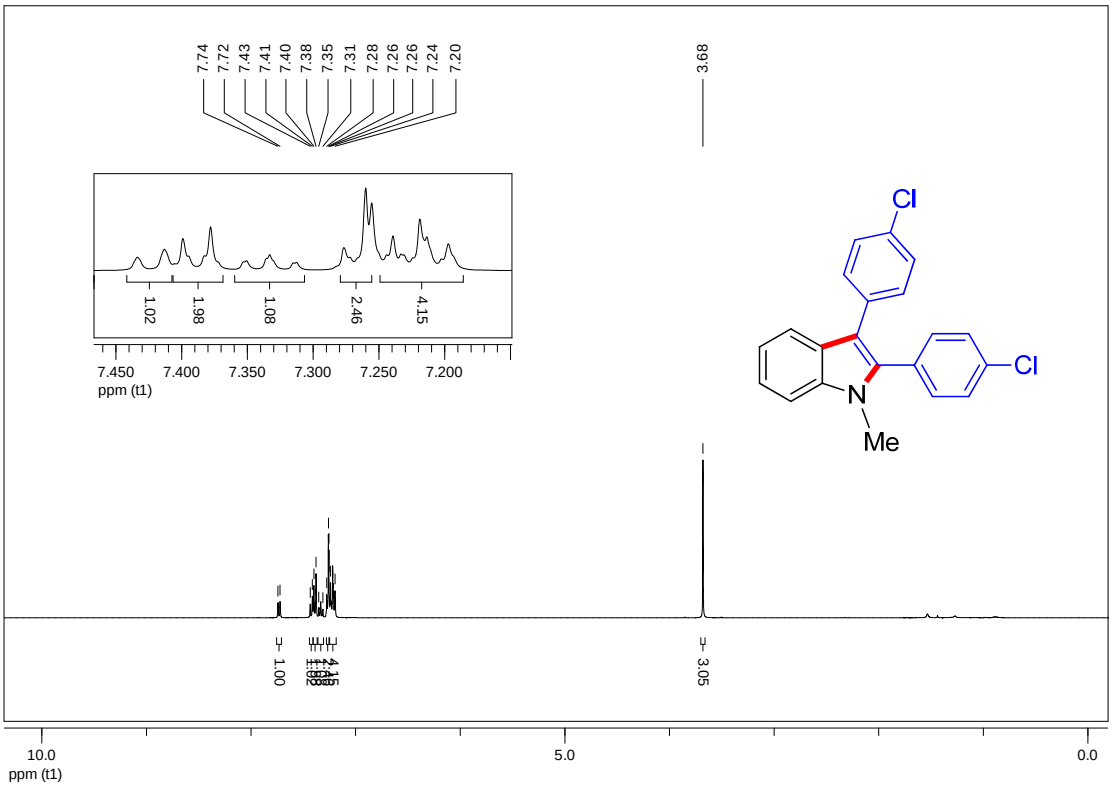
1-ethyl-2,3-bis(4-fluorophenyl)-1*H*-indole (4f)

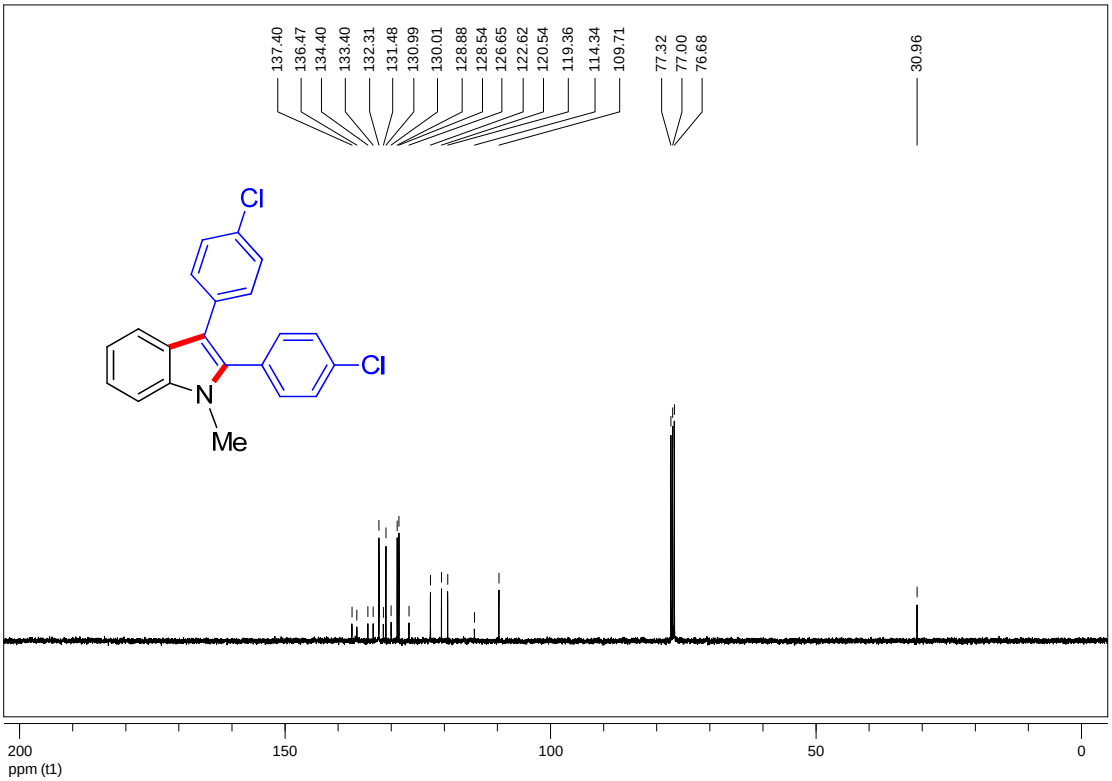




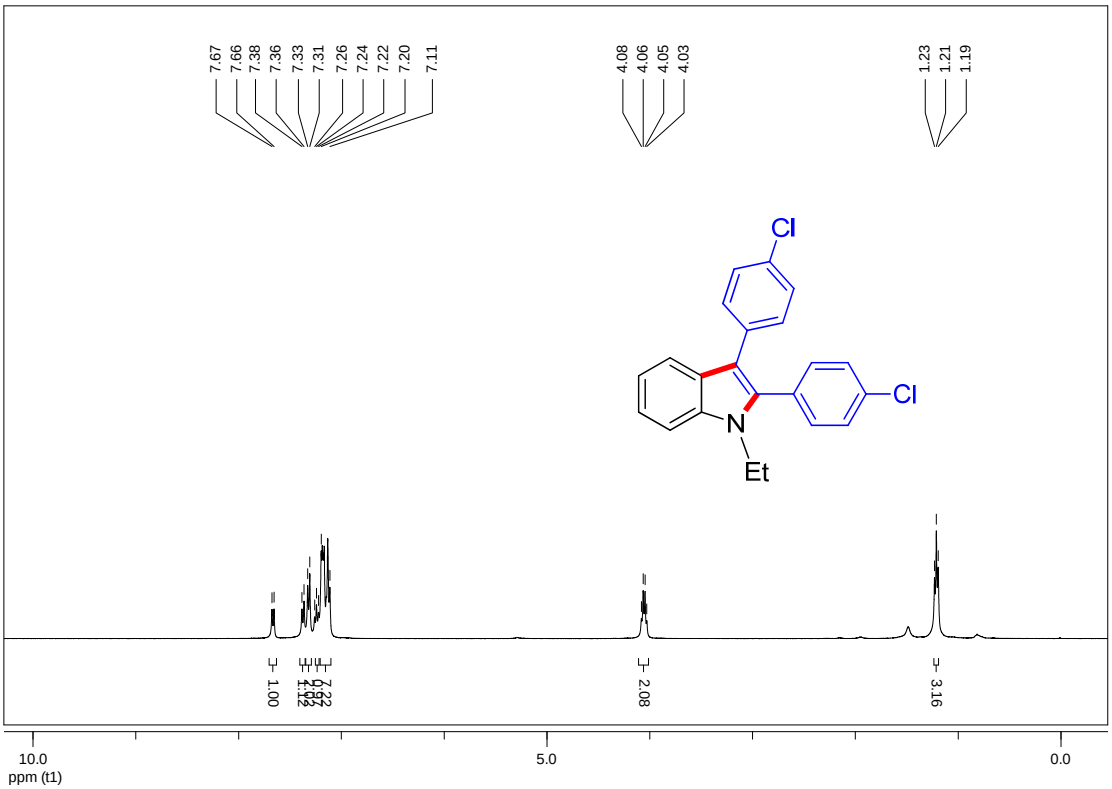

-112.92
-117.19
F
F
N
Et
50
0
-50
-100
-150
-200
-250
ppm (t1)

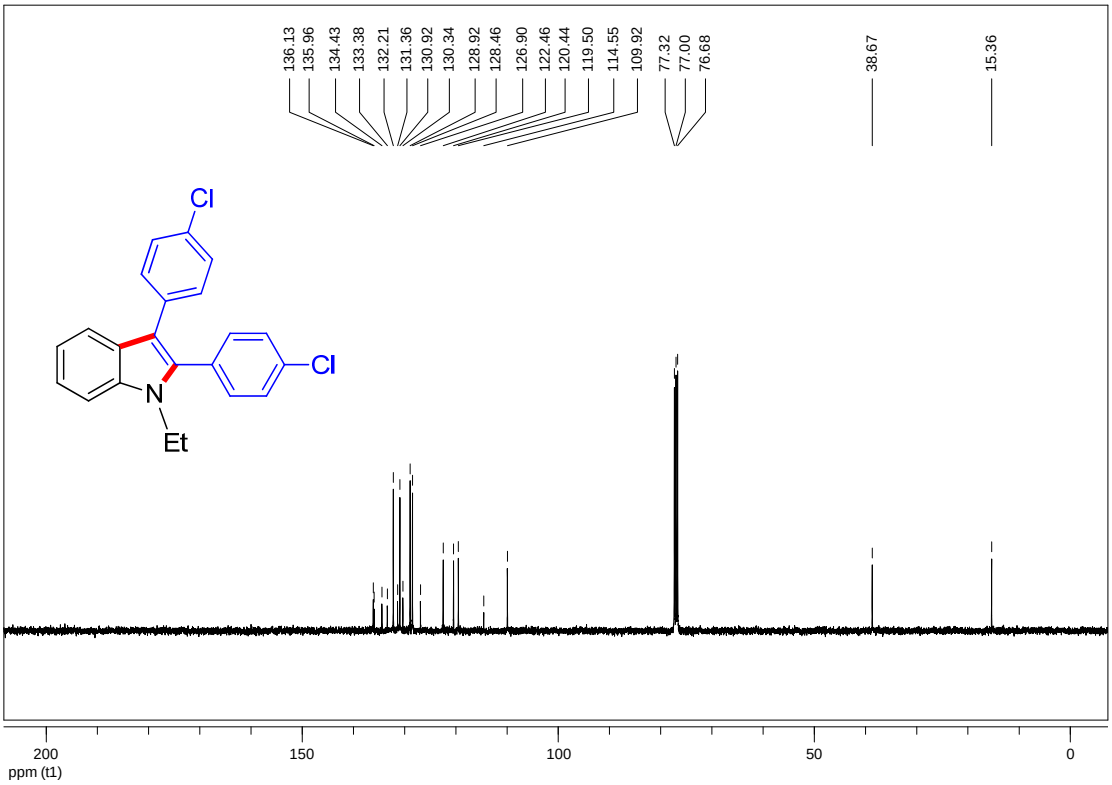
2,3-bis(4-chlorophenyl)-1-methyl-1*H*-indole (4g)



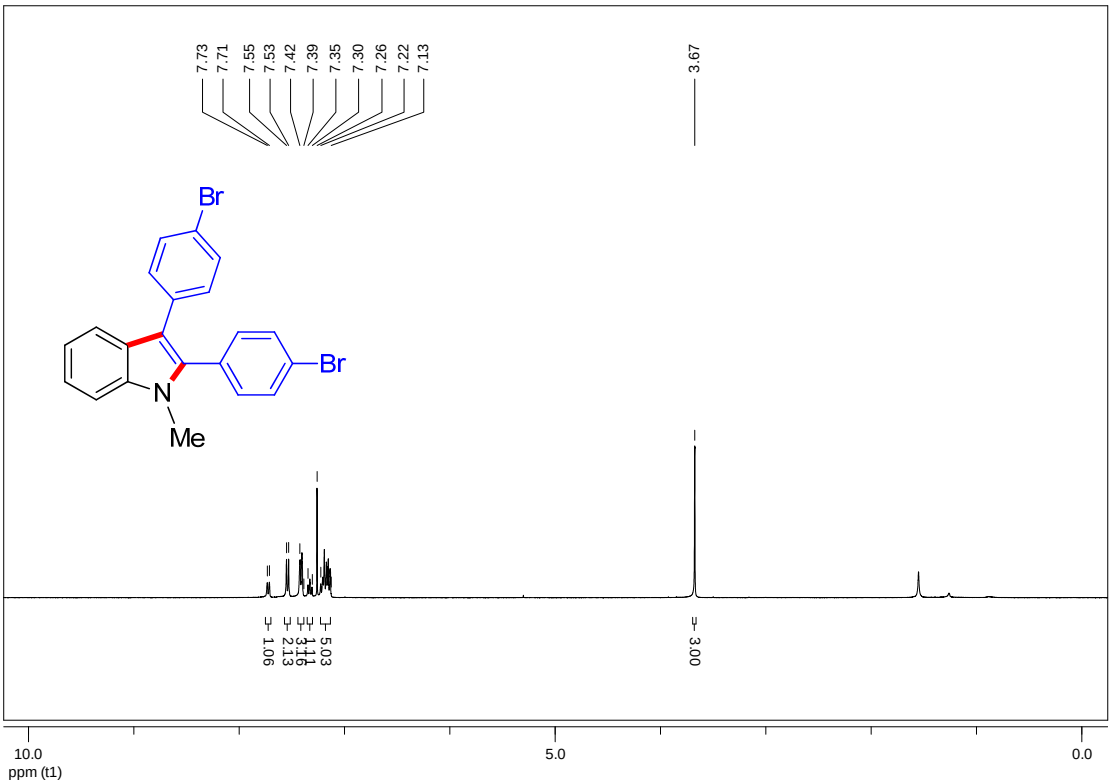


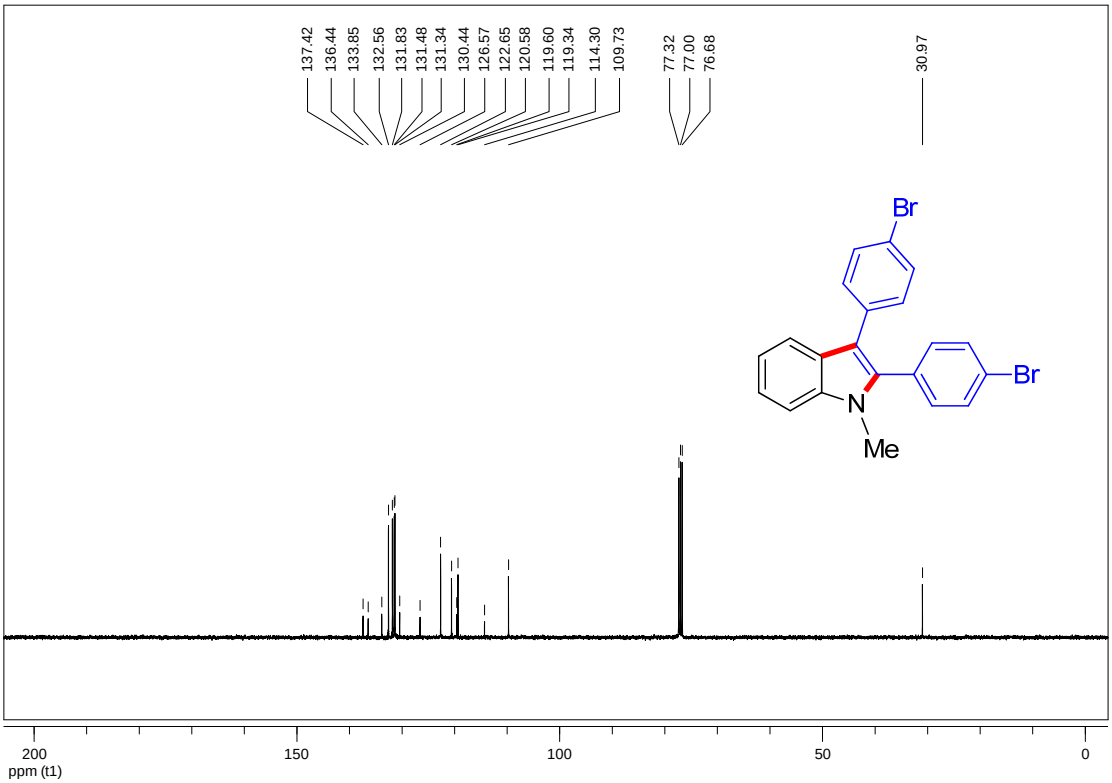
2,3-bis(4-chlorophenyl)-1-ethyl-1*H*-indole (4h)



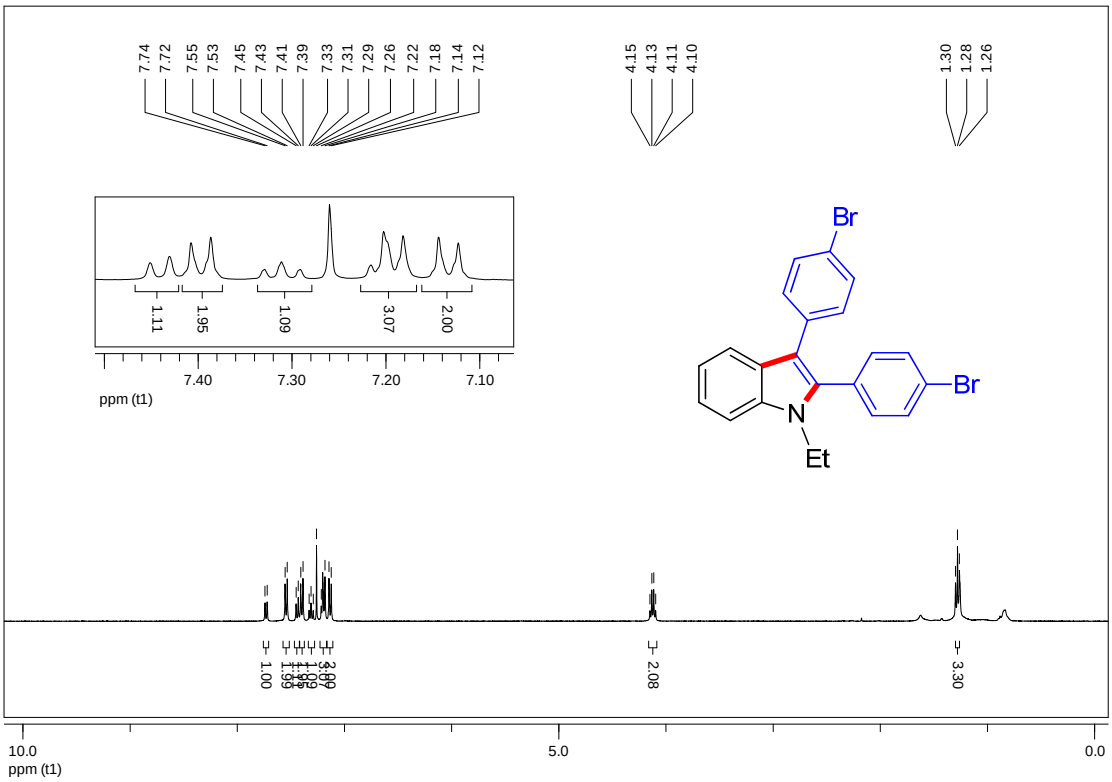


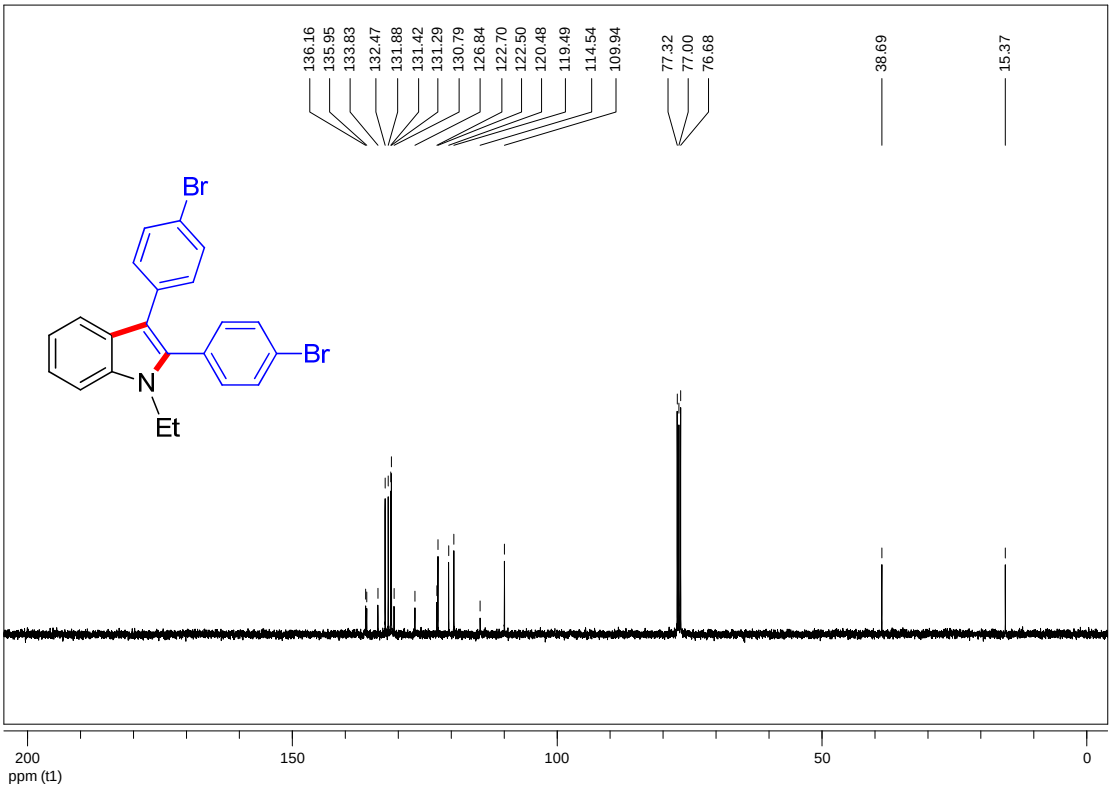
2,3-bis(4-bromophenyl)-1-methyl-1H-indole (4i)



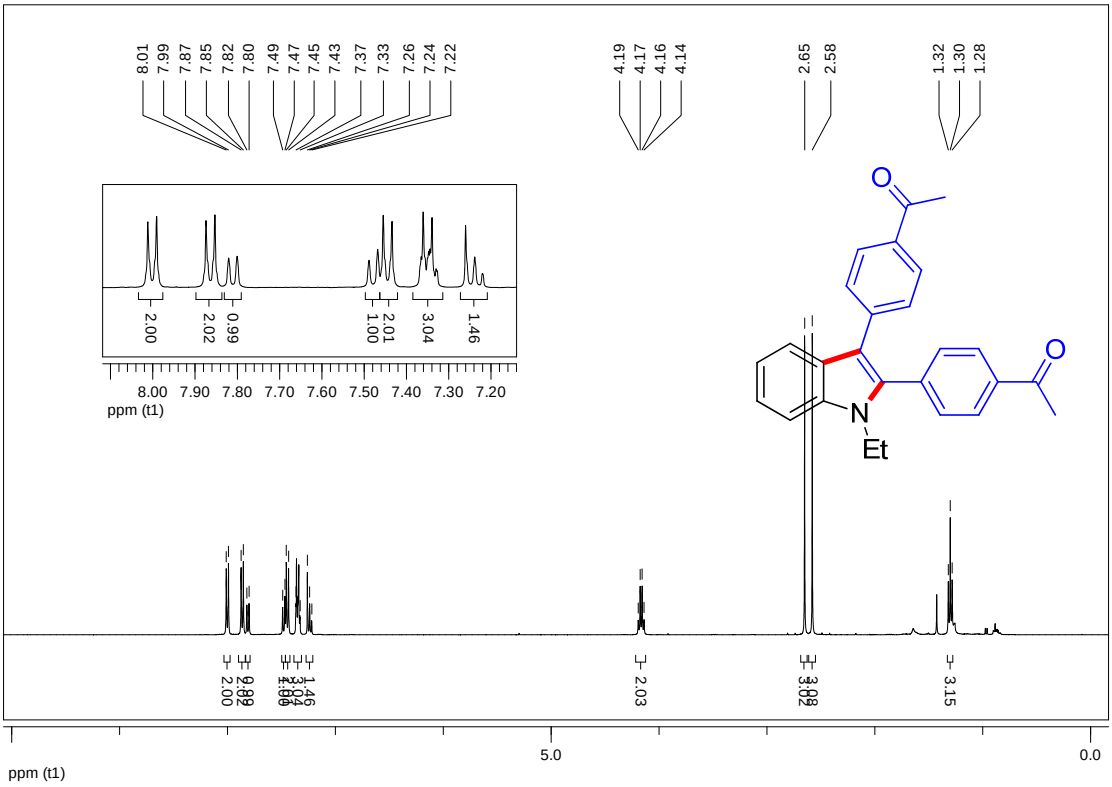


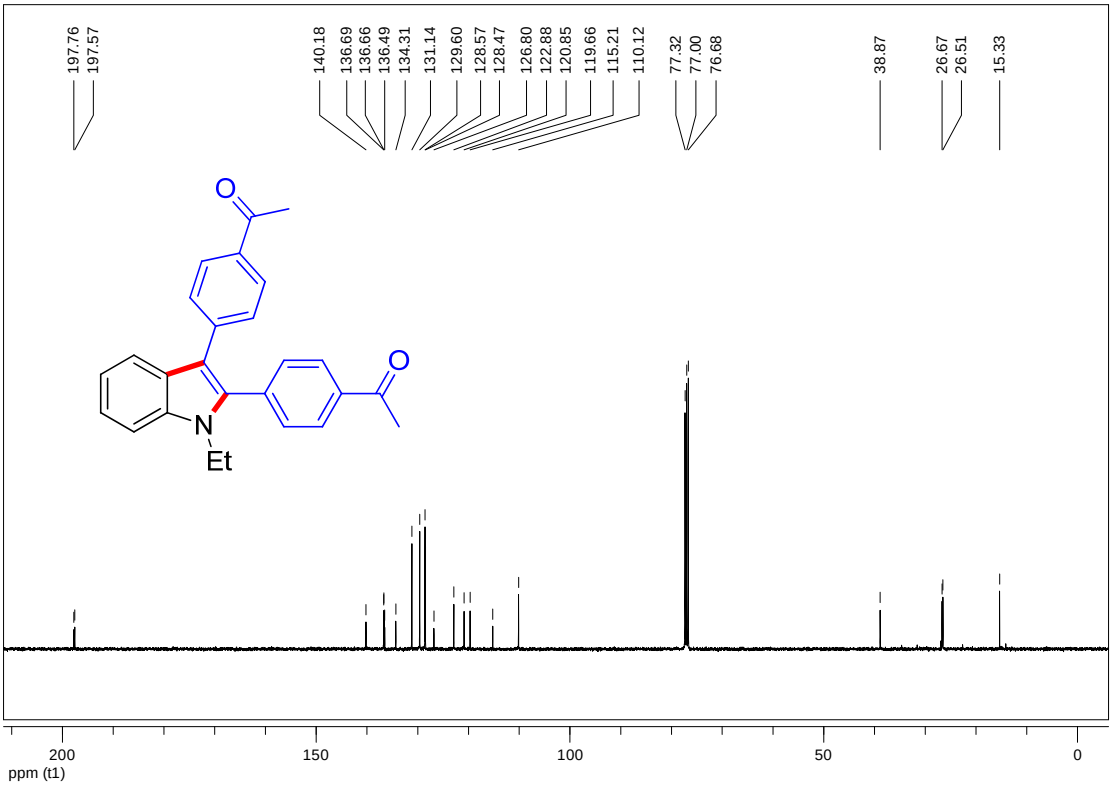
2,3-bis(4-bromophenyl)-1-ethyl-1H-indole (4j)



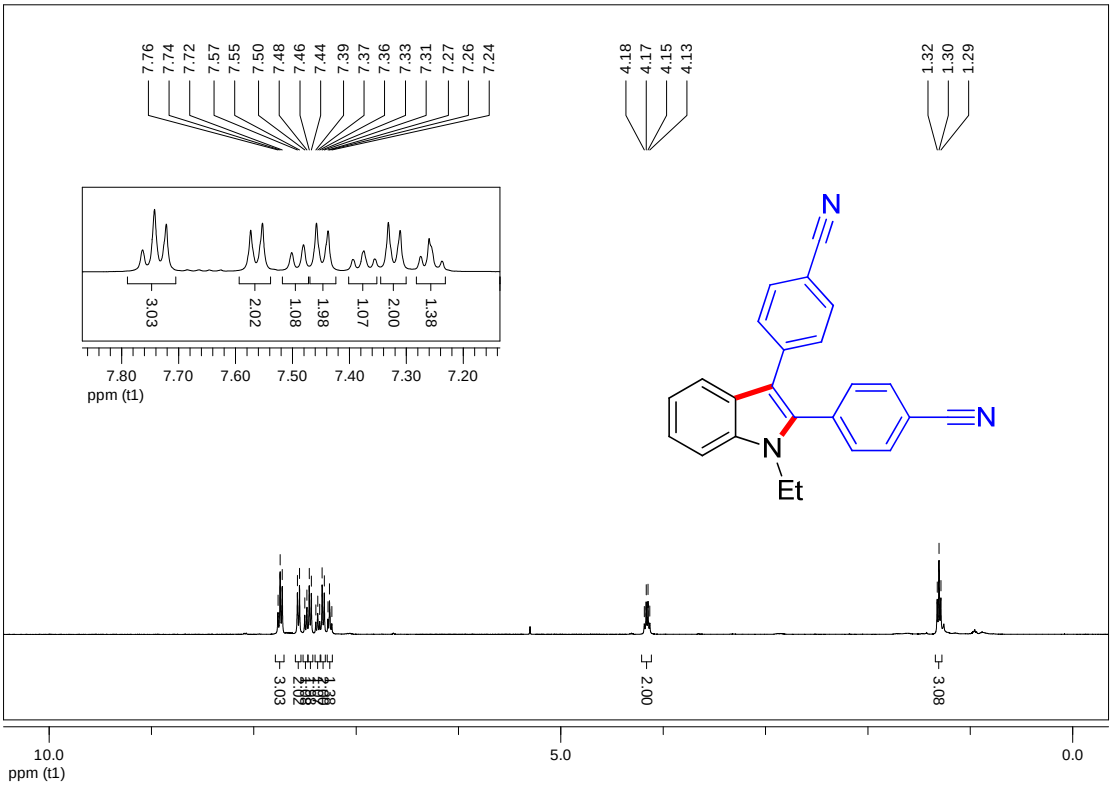


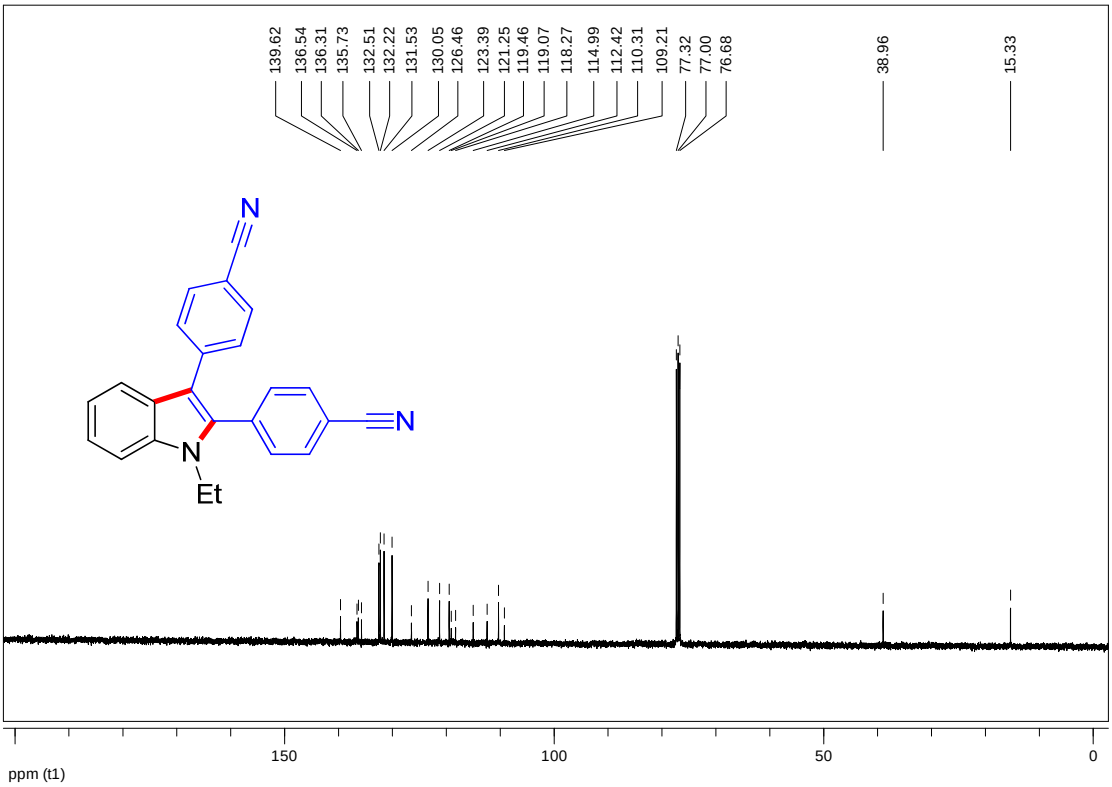
1-ethyl-2,3-bis(4-acetylphenyl)-1*H*-indole (4k)



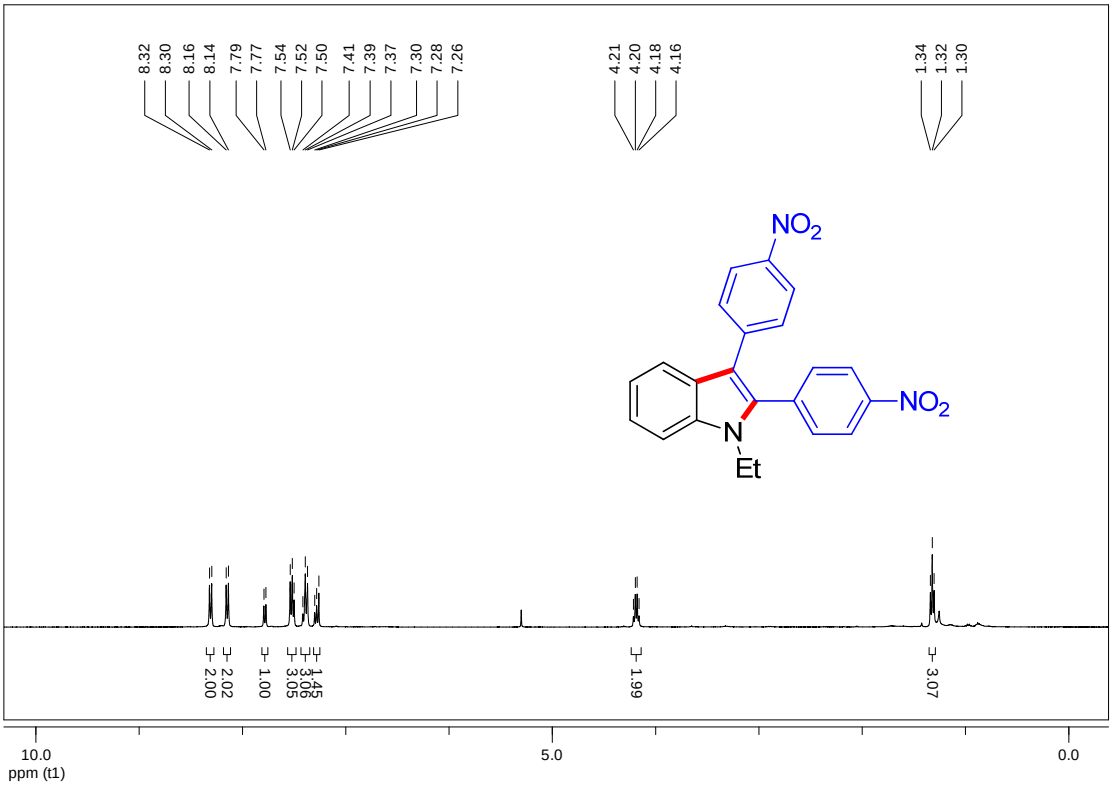


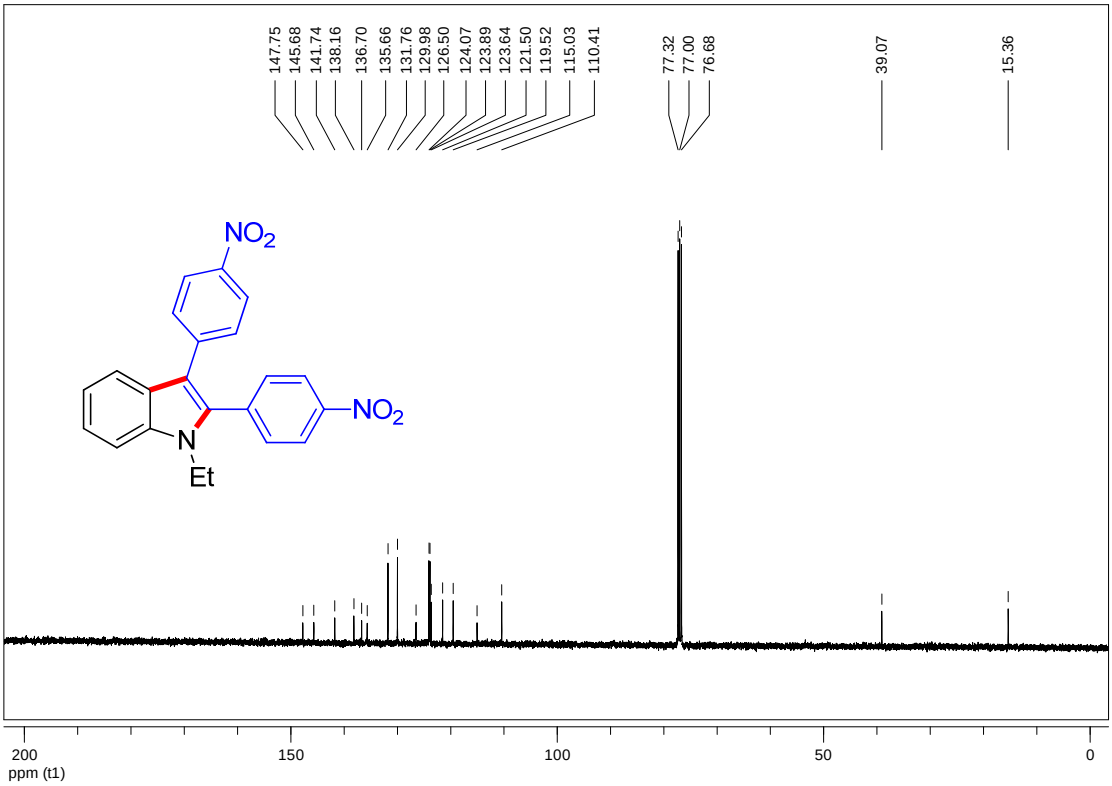
4,4'-(1-ethyl-1*H*-indole-2,3-diyl)dibenzonitrile (4l)



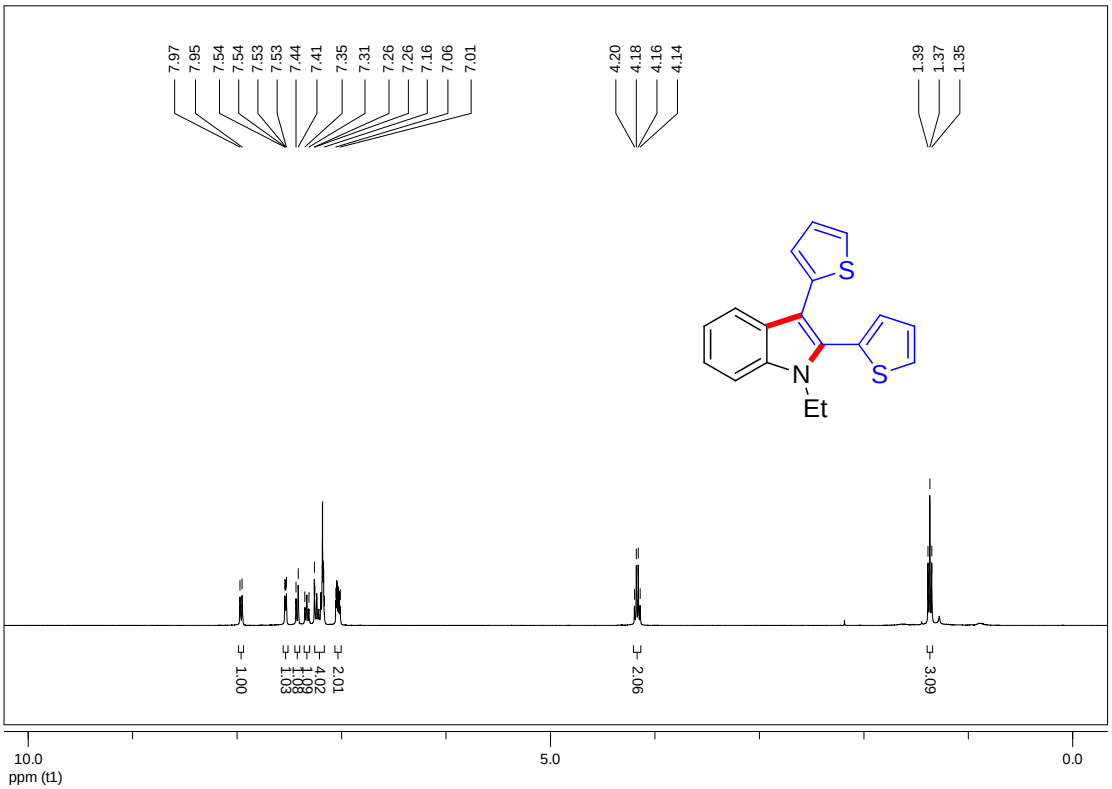


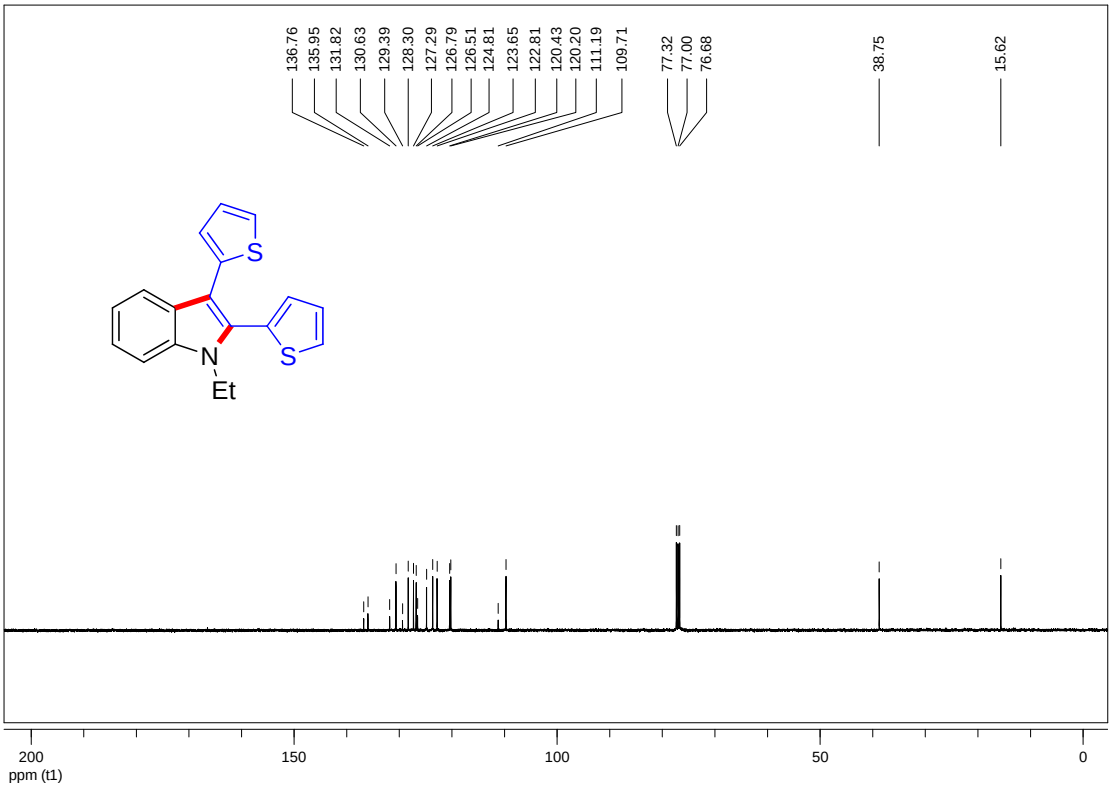
1-ethyl-2,3-bis(4-nitrophenyl)-1*H*-indole(4m)



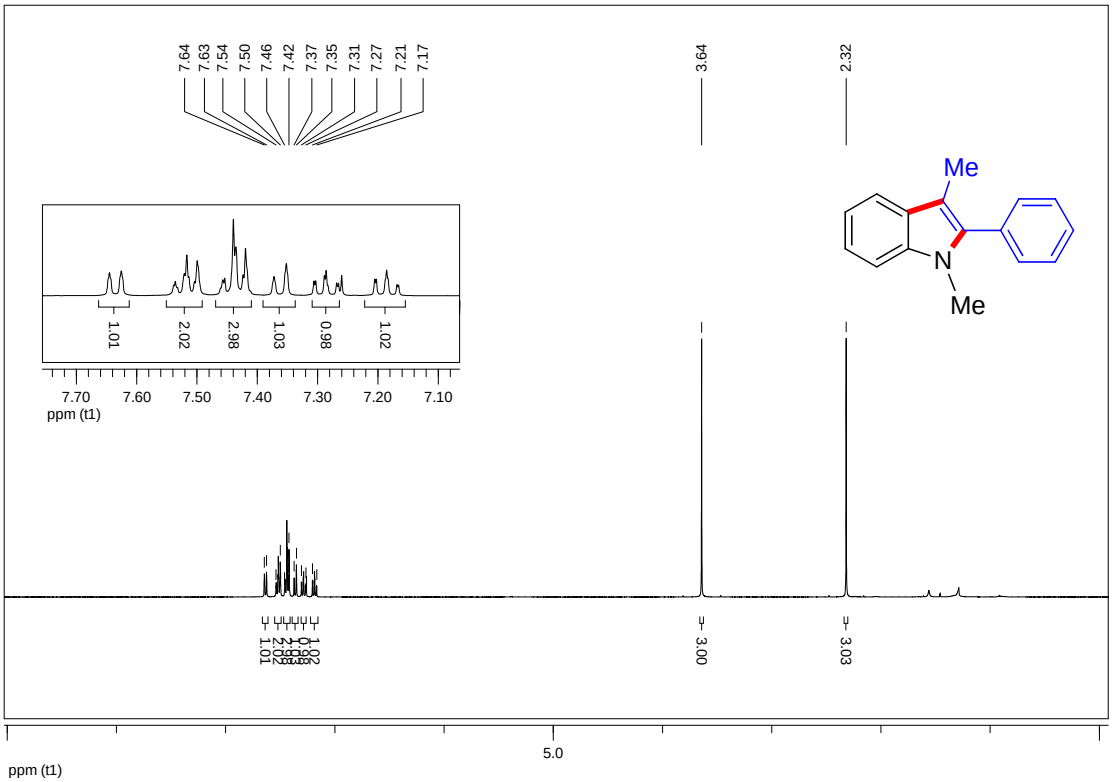


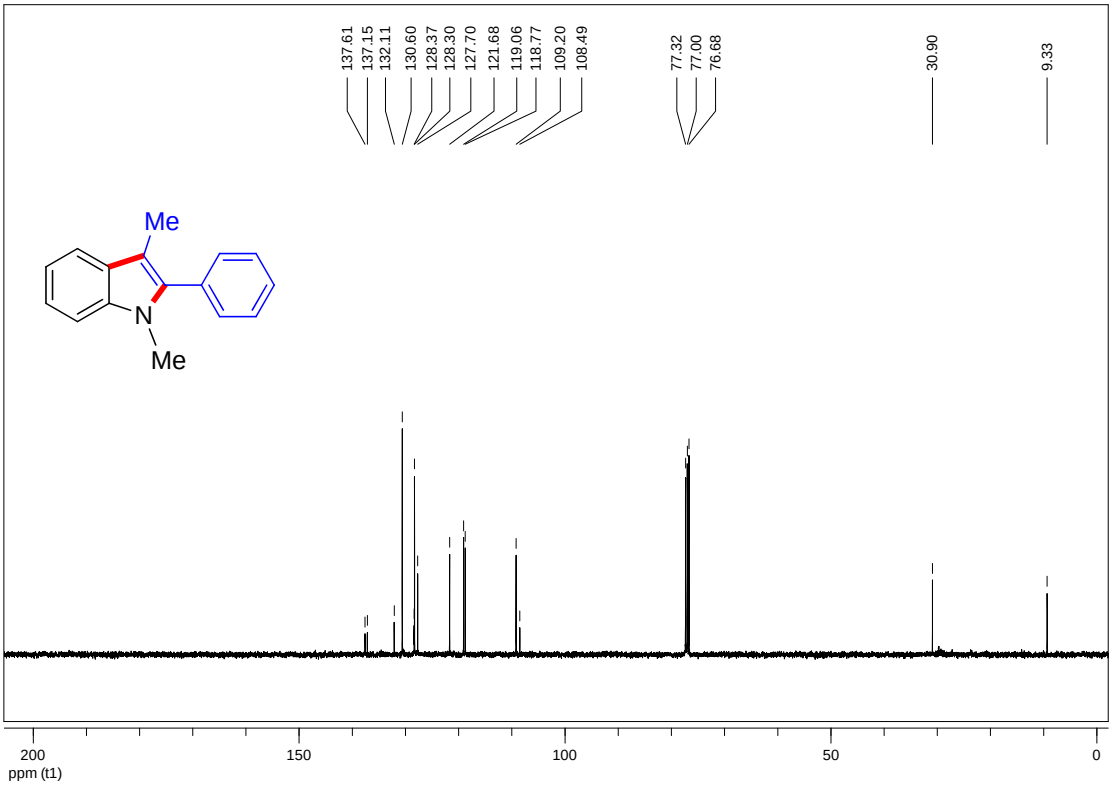
1-ethyl-2,3-di(thiophen-2-yl)-1*H*-indole (4n)



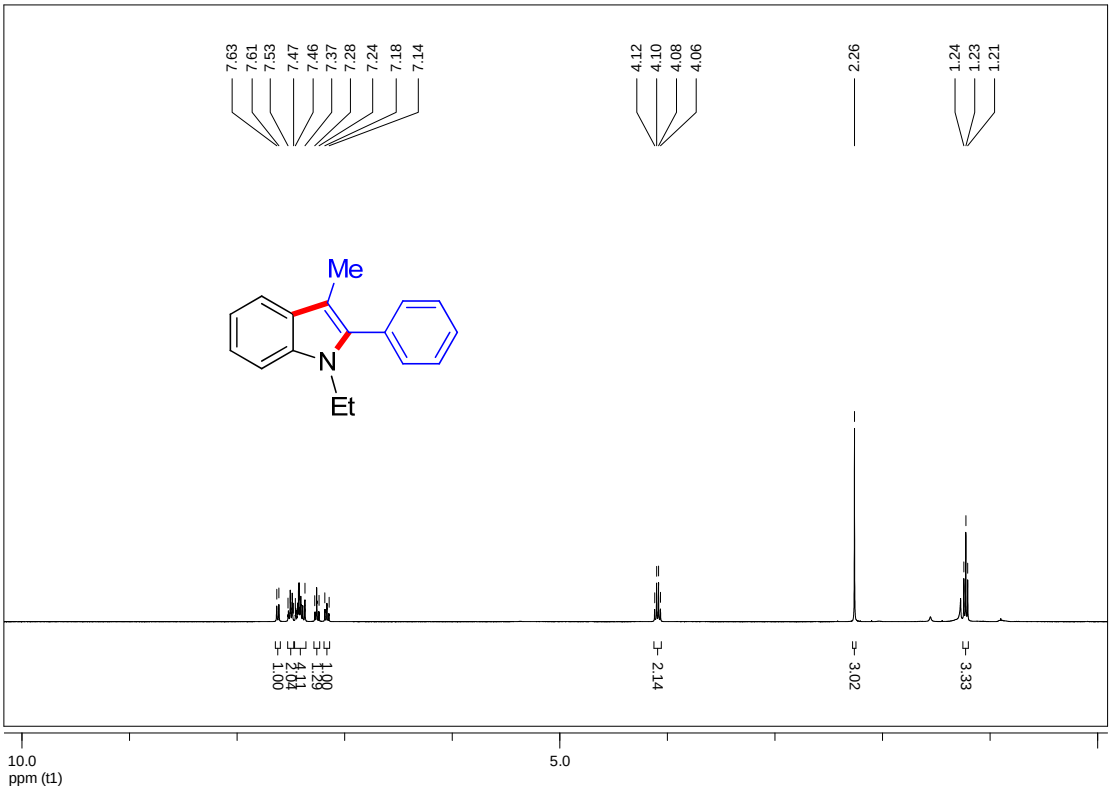


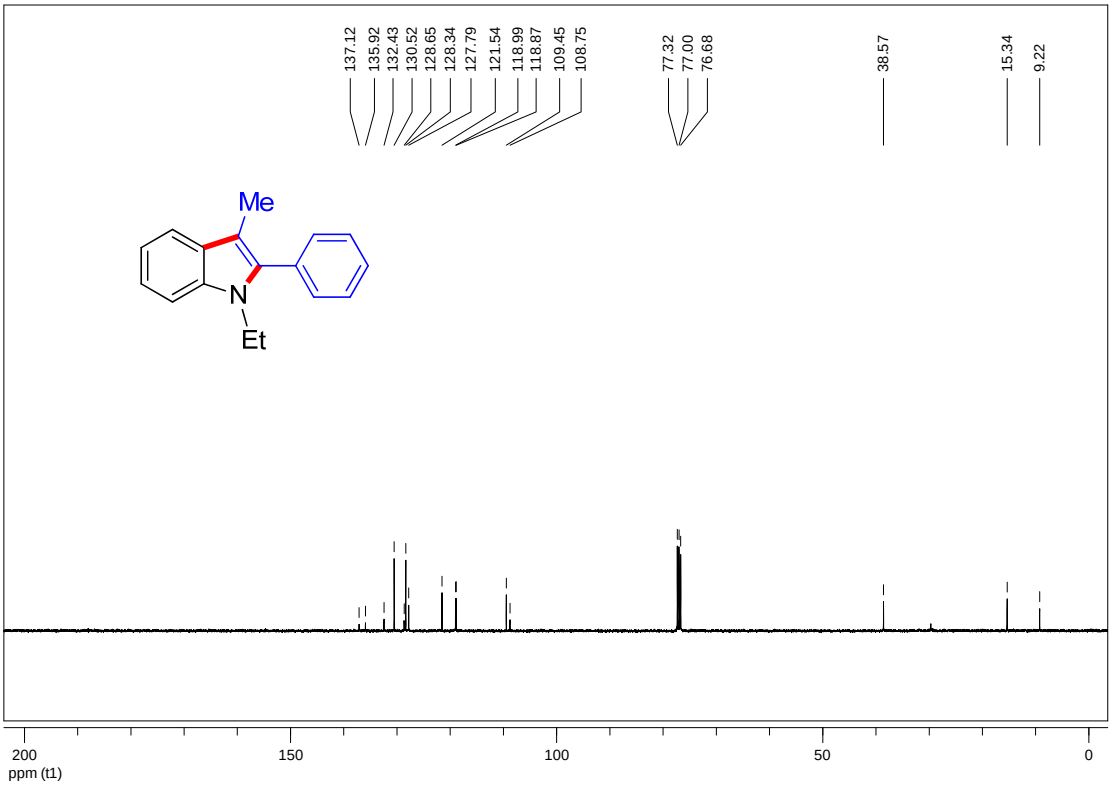
1,3-dimethyl-2-phenyl-1*H*-indole (4o)



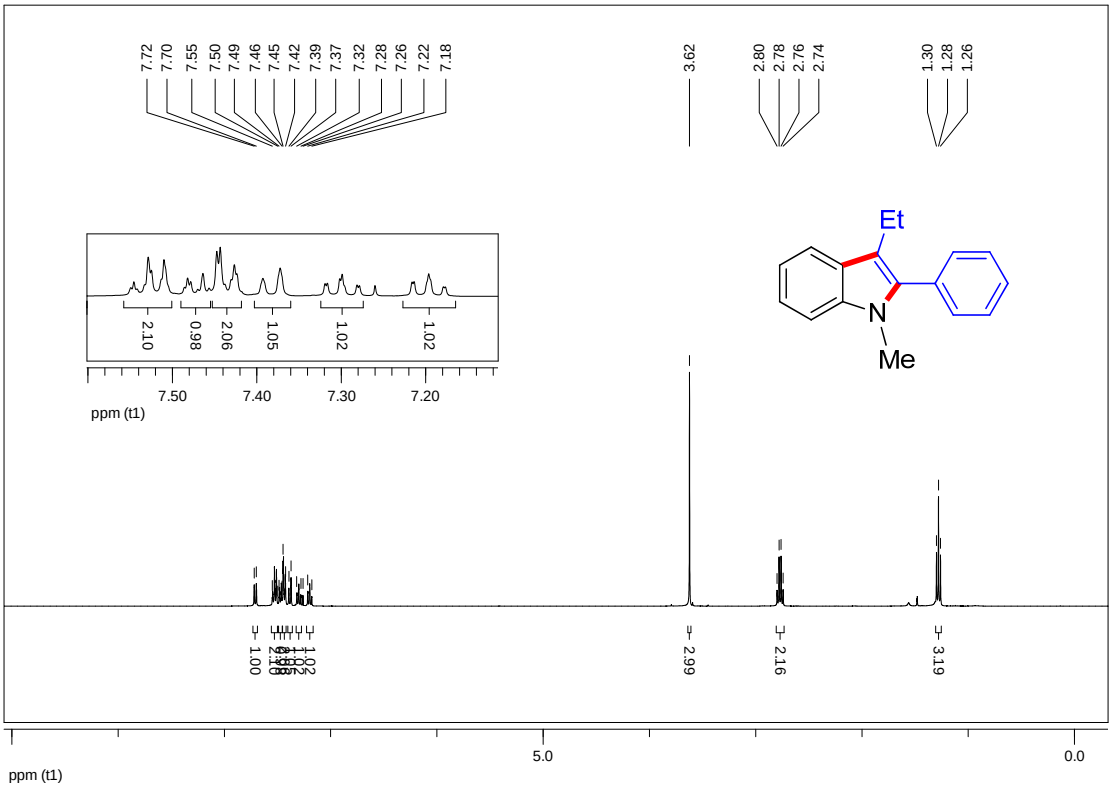


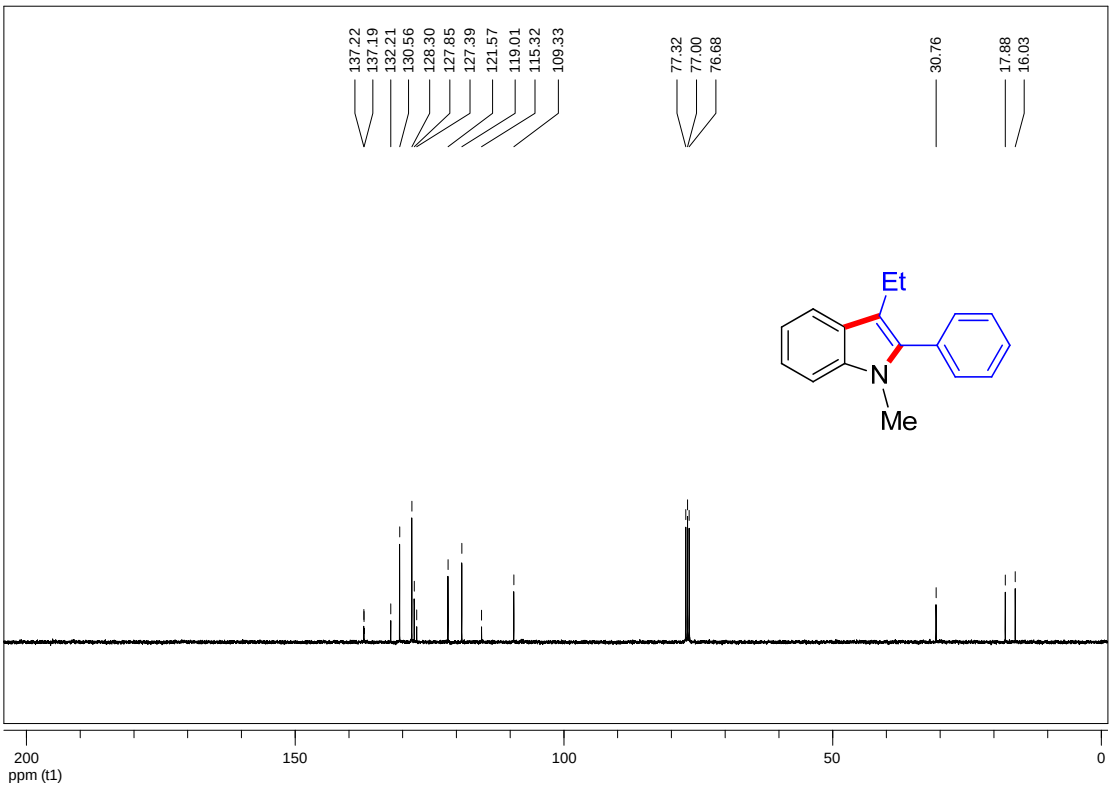
1-ethyl-3-methyl-2-phenyl-1*H*-indole (4p)



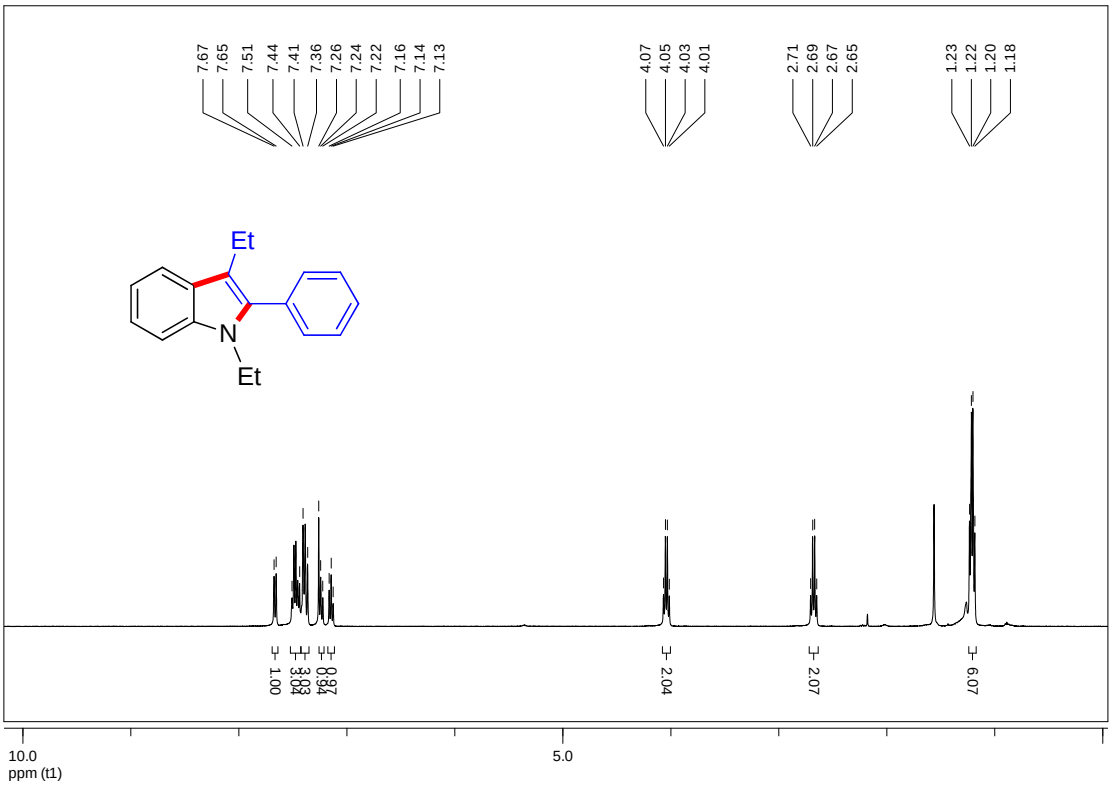


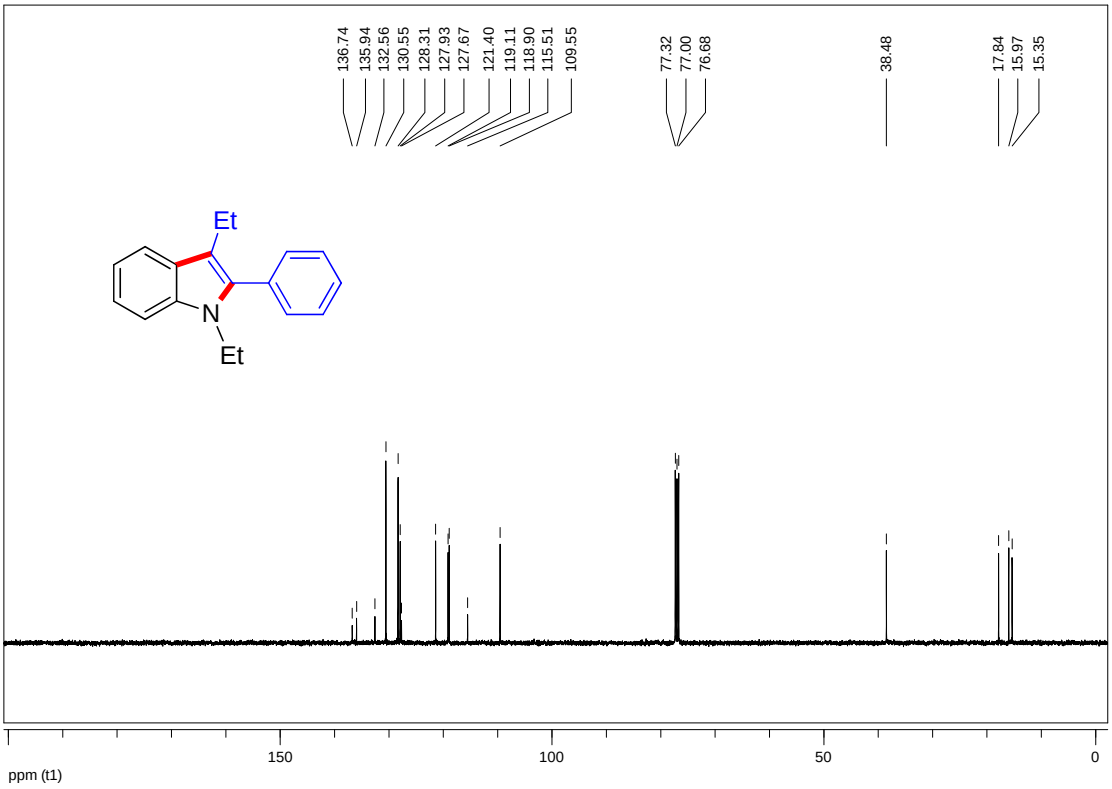
3-ethyl-1-methyl-2-phenyl-1*H*-indole (4q)



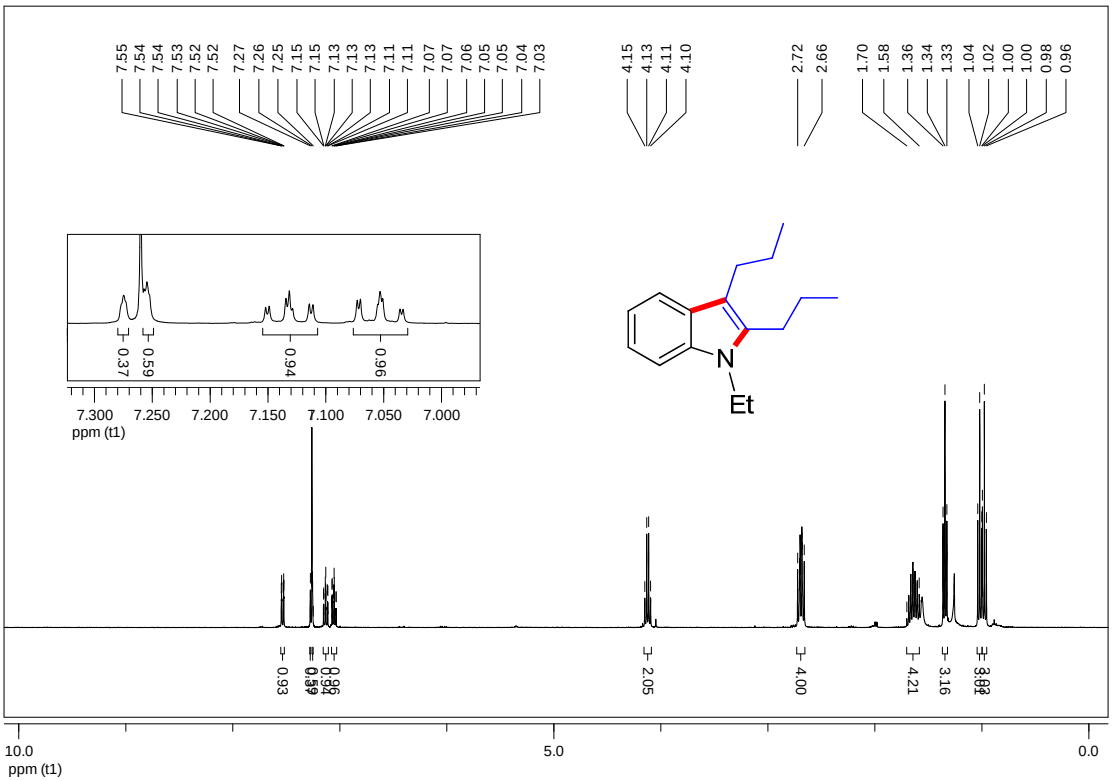


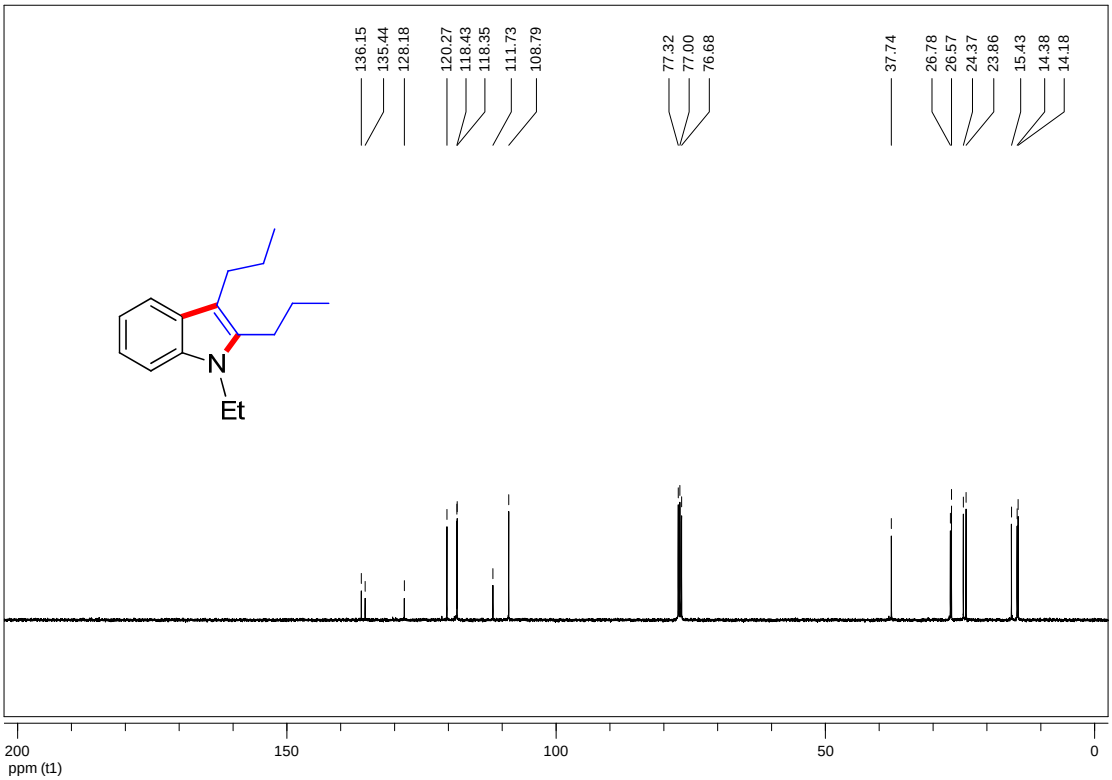
1,3-diethyl-2-phenyl-1*H*-indole (4r)



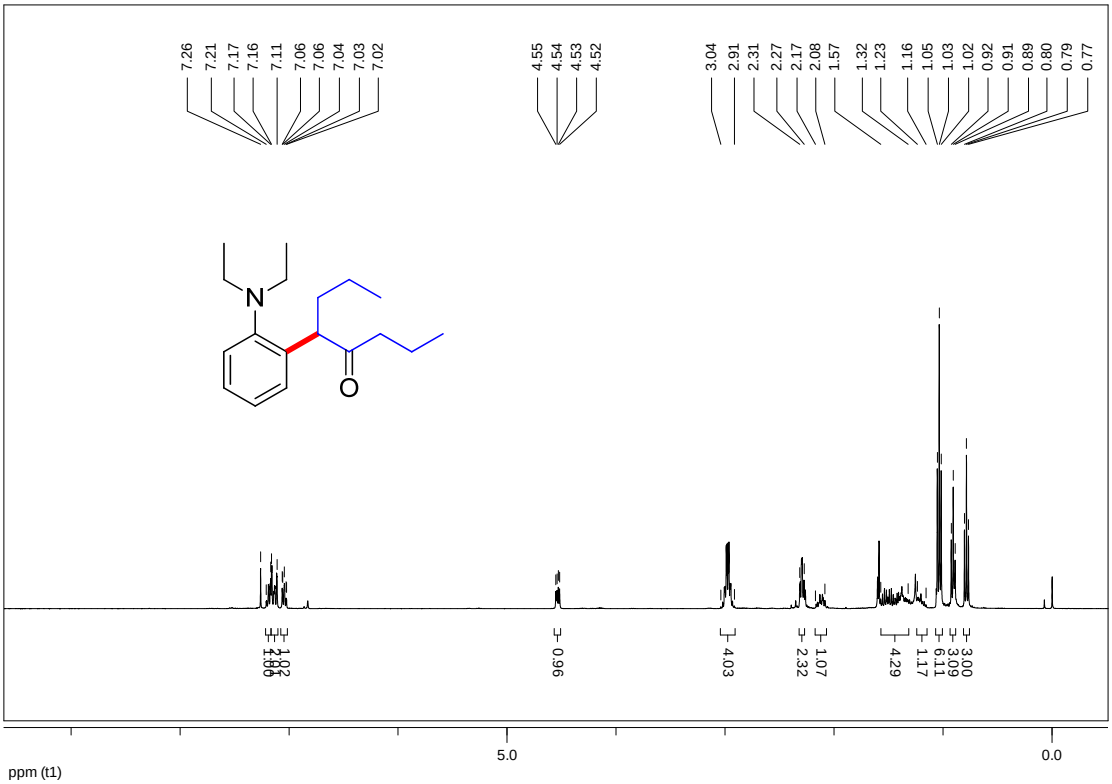


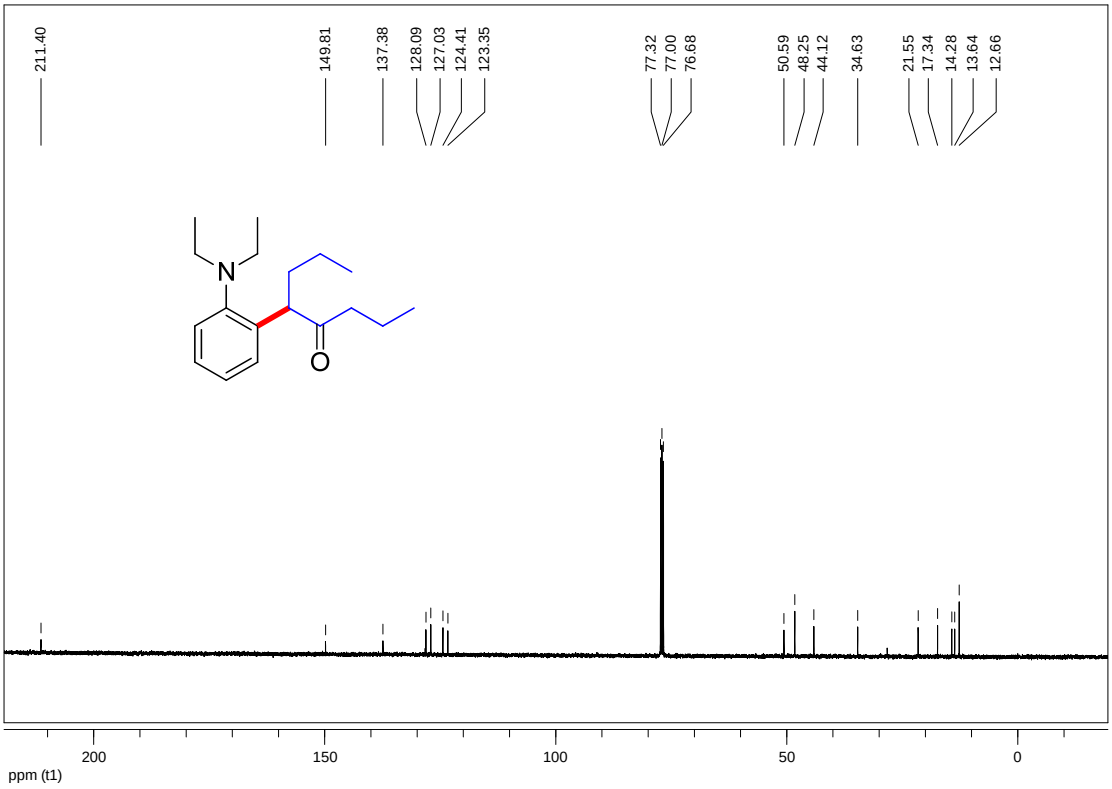
1-ethyl-2,3-dipropyl-1*H*-indole (4s)



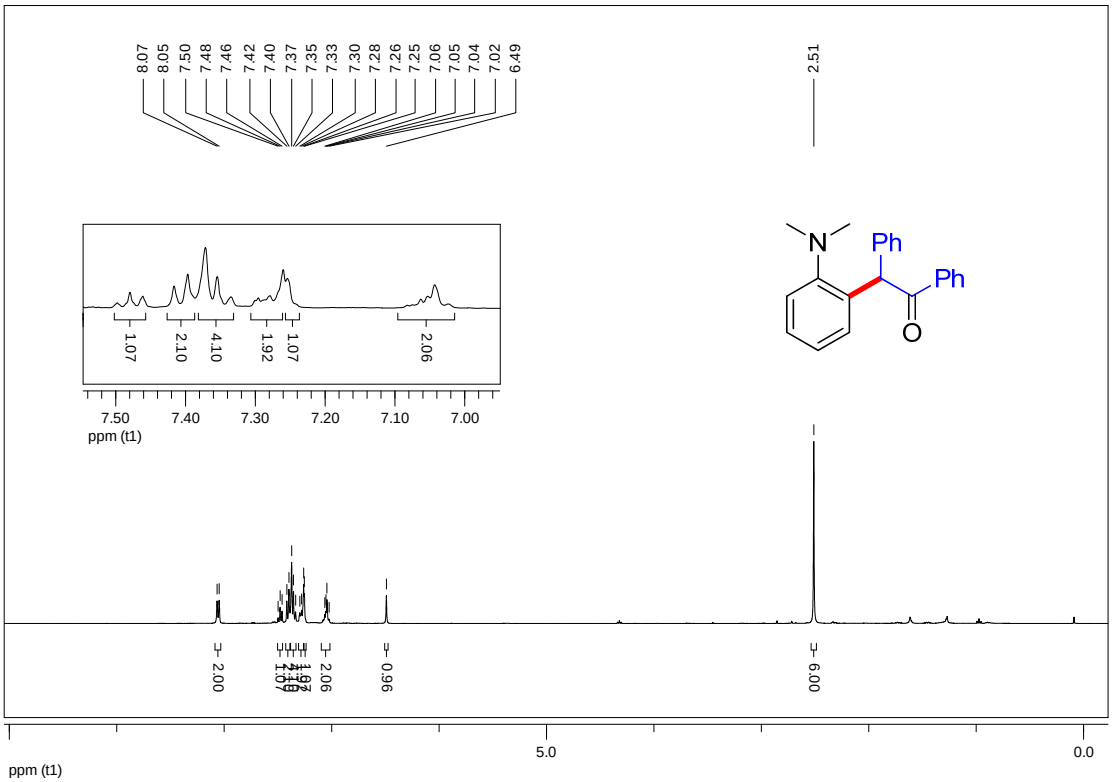


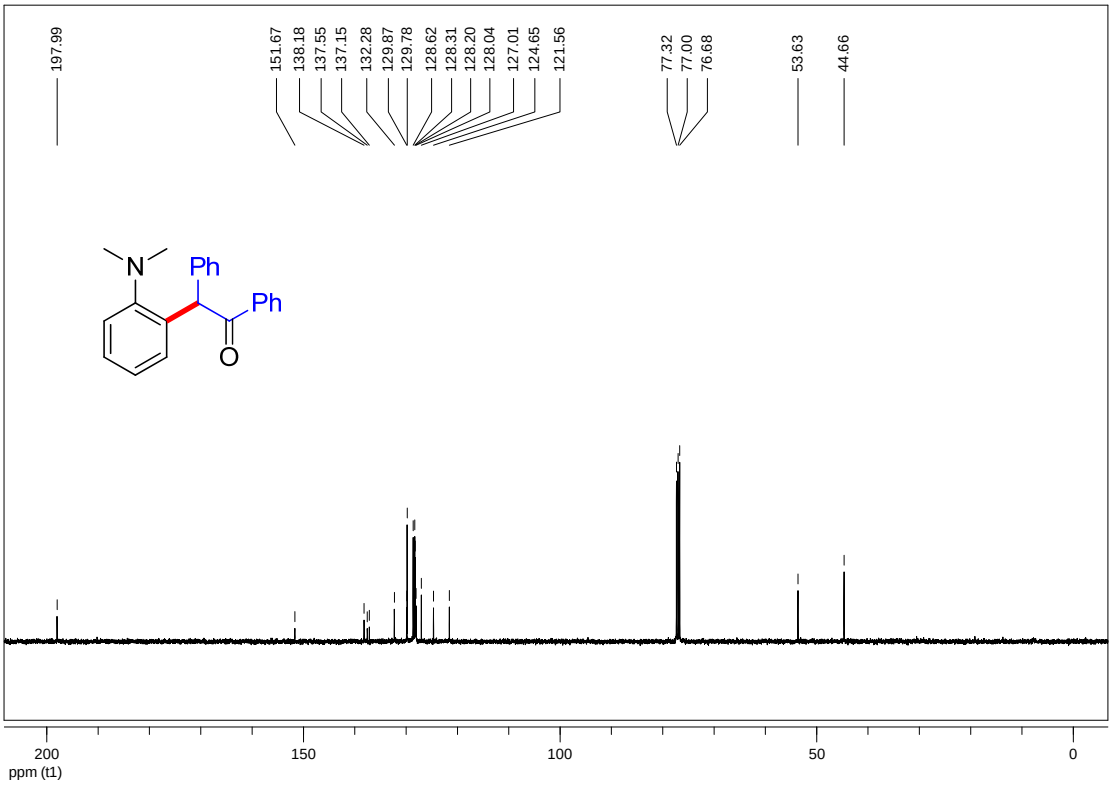
(2-(diethylamino)phenyl)octan-4-one (4s*)



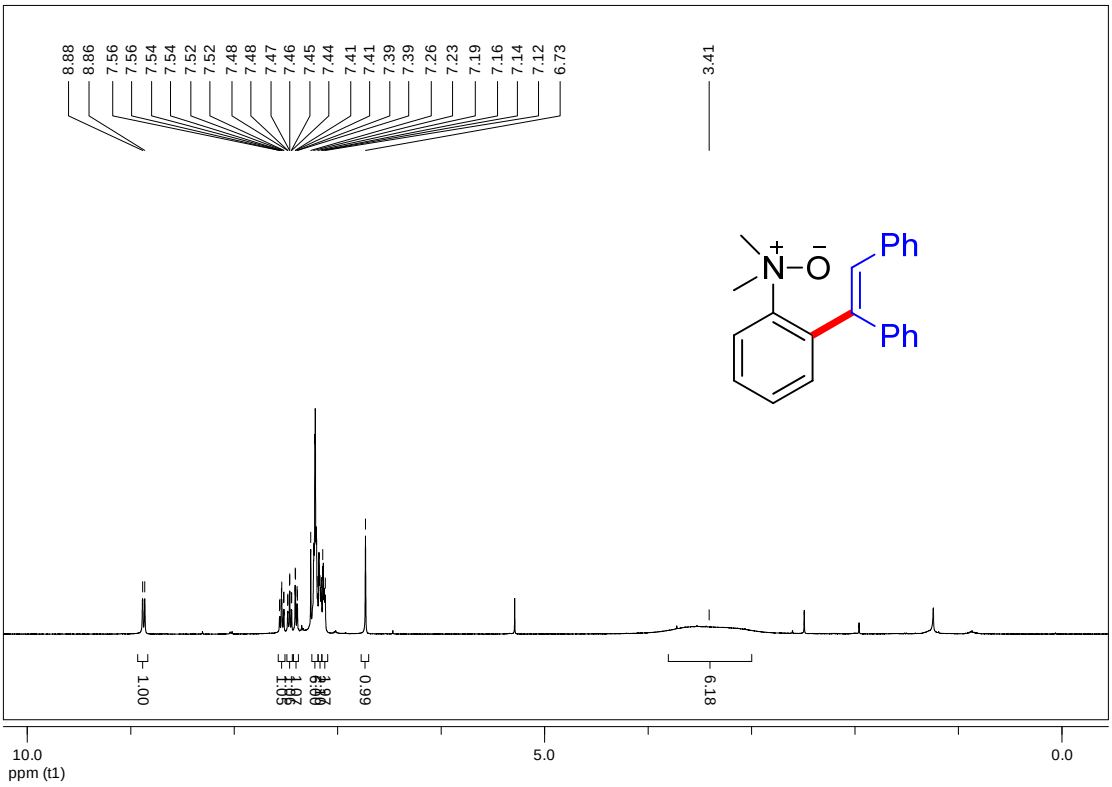


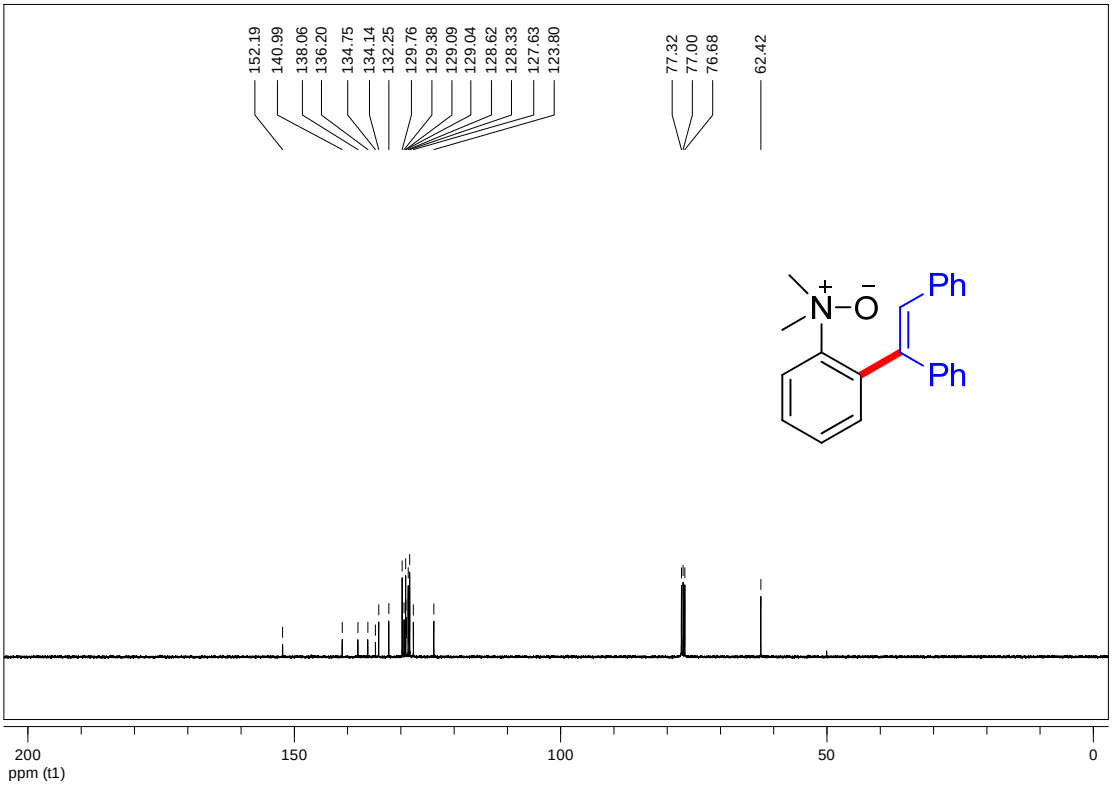
2-(2-(dimethylamino)phenyl)-1,2-diphenylethanone (3a*)



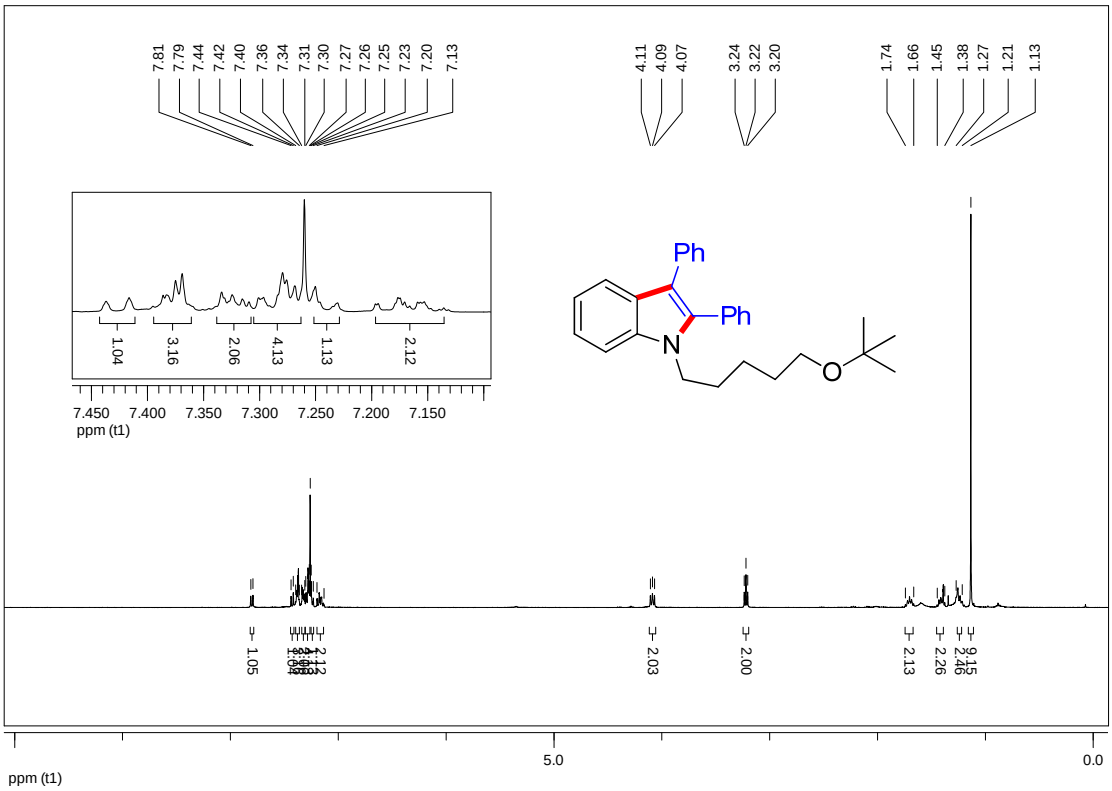


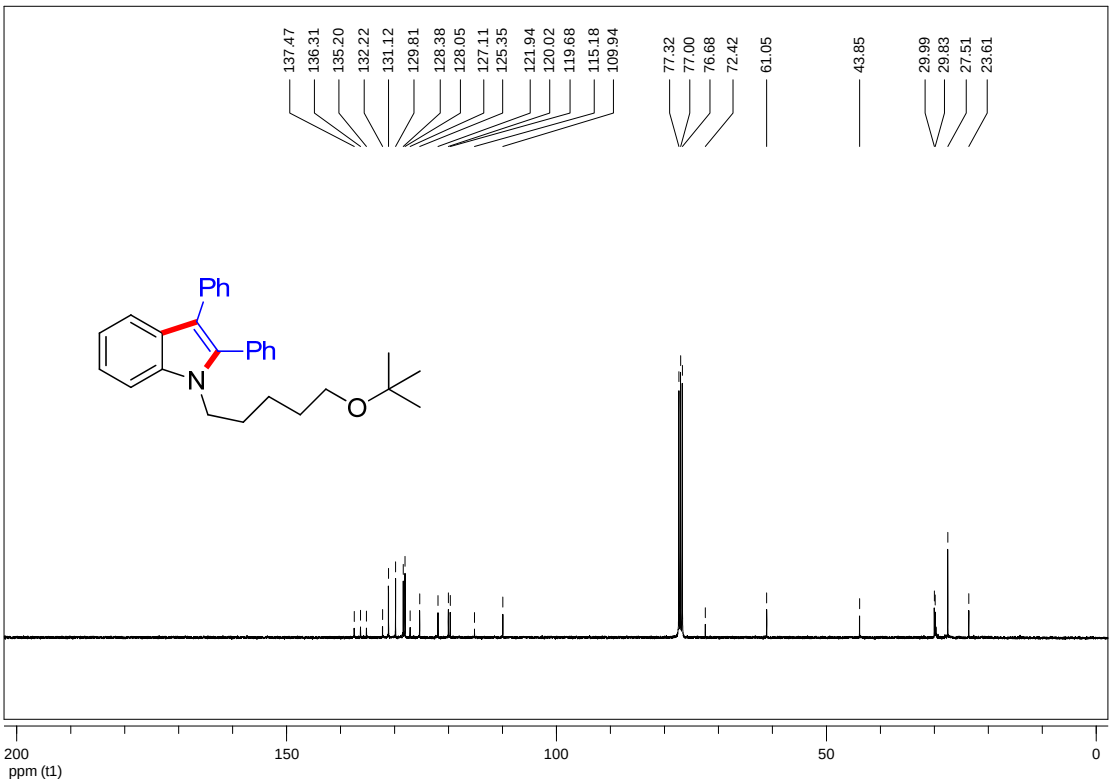
(*E*)-2-(1,2-diphenylvinyl)-*N,N*-dimethylaniline oxide (7)



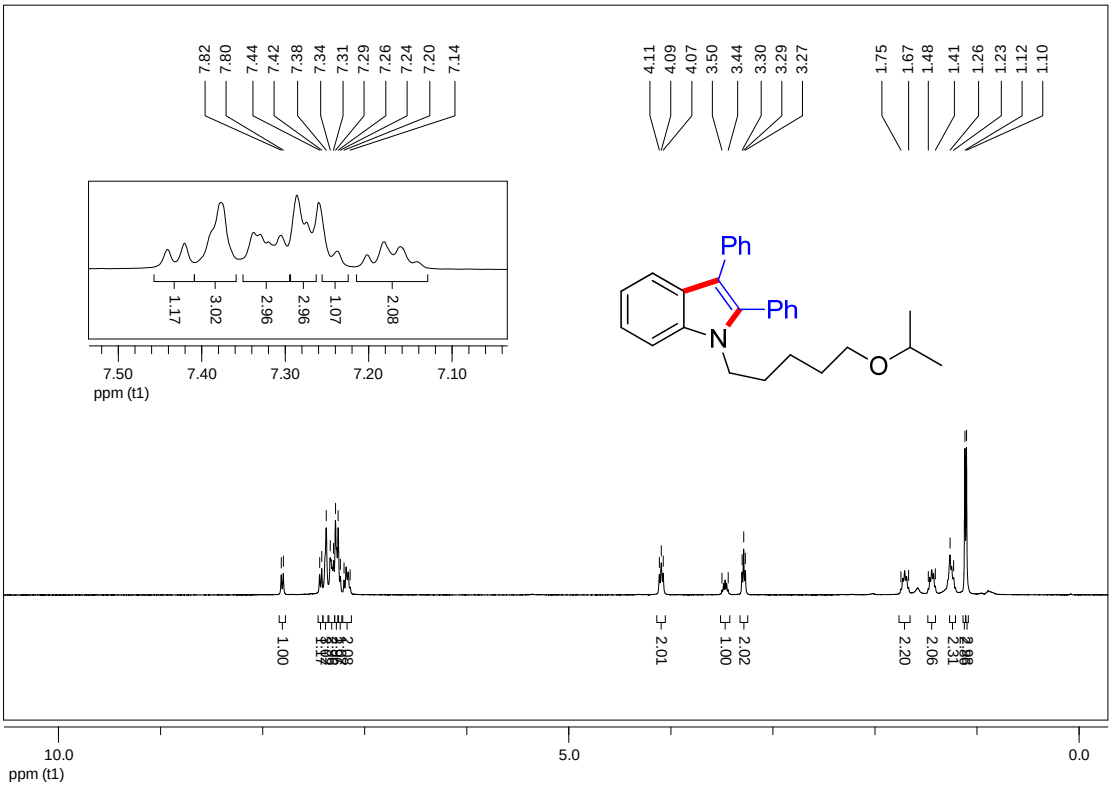


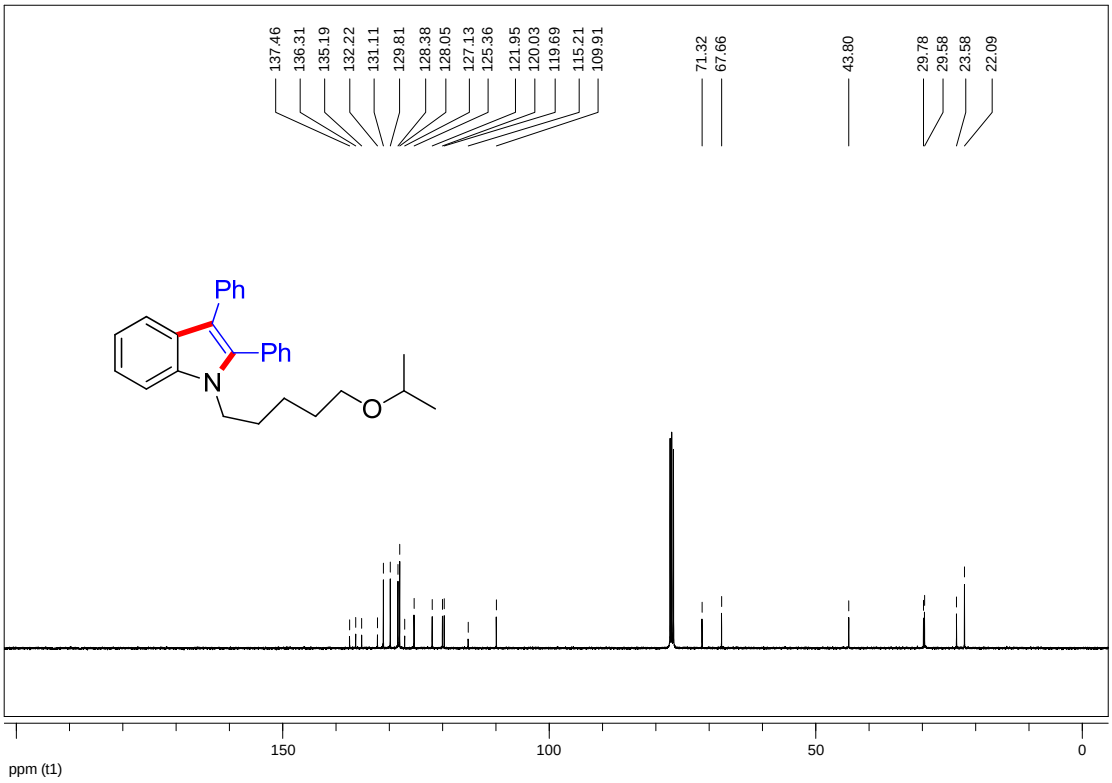
1-(5-(tert-butoxy)pentyl)-2,3-diphenyl-1H-indole (10a)



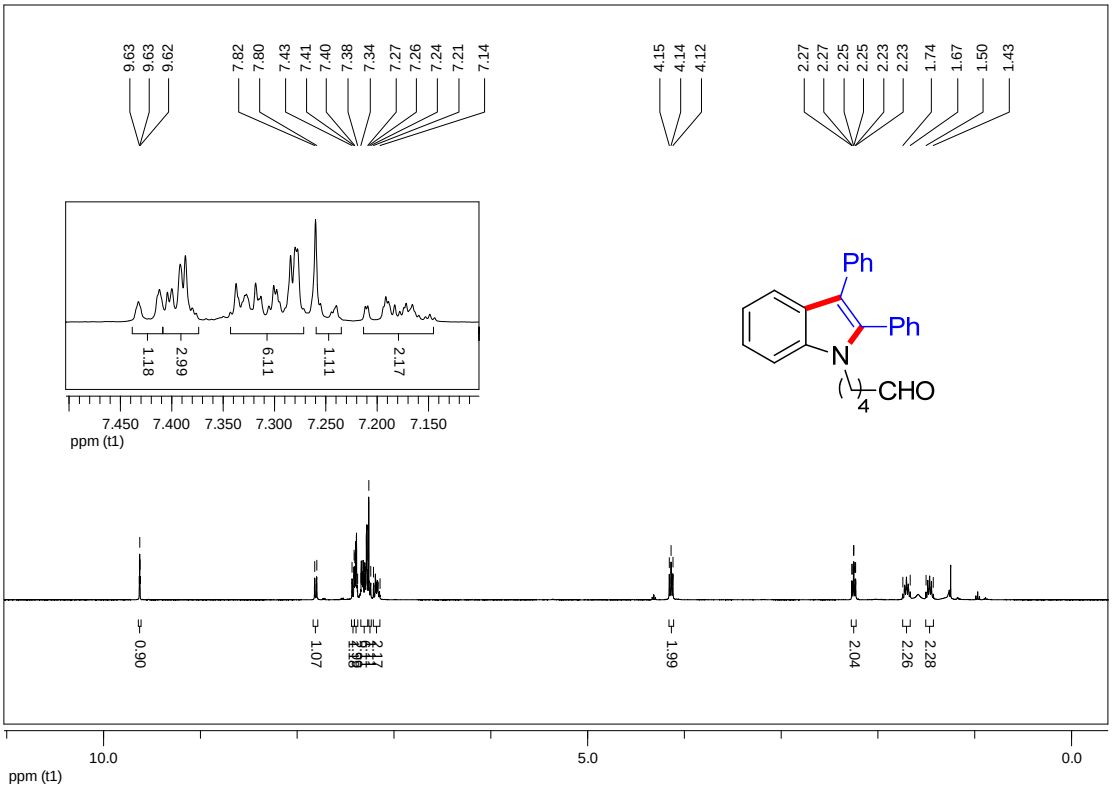


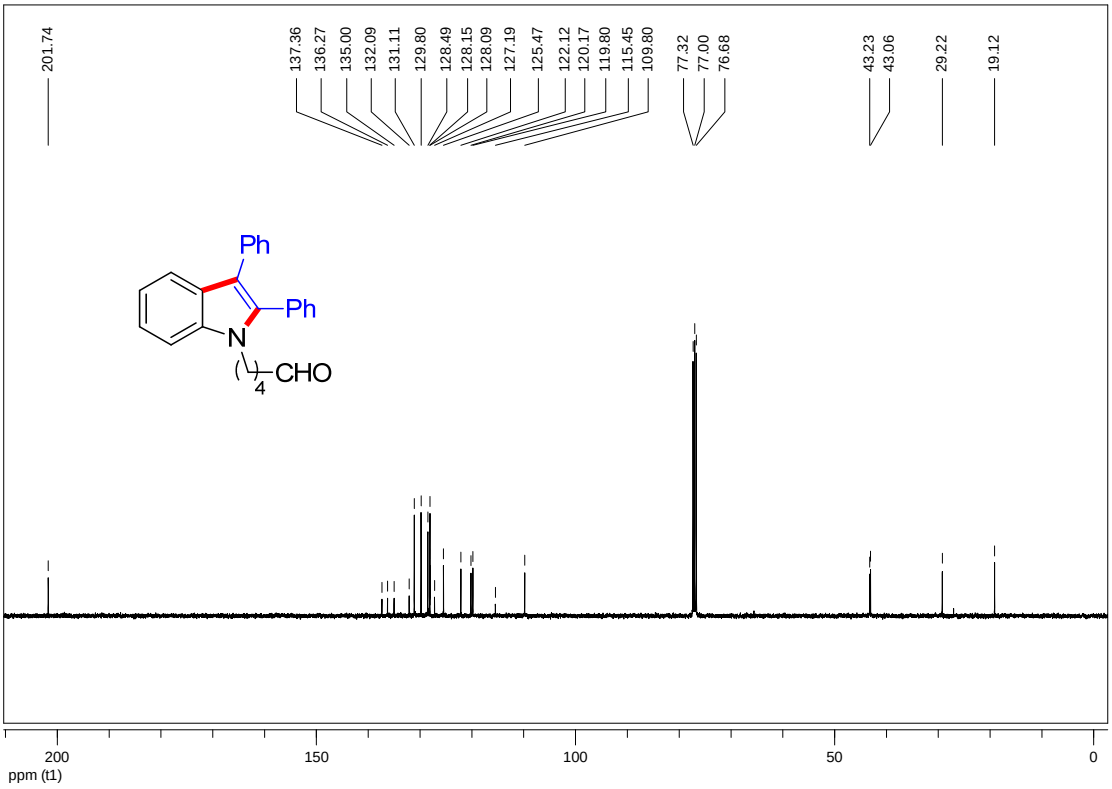
1-(5-isopropoxypentyl)-2,3-diphenyl-1H-indole (10b)



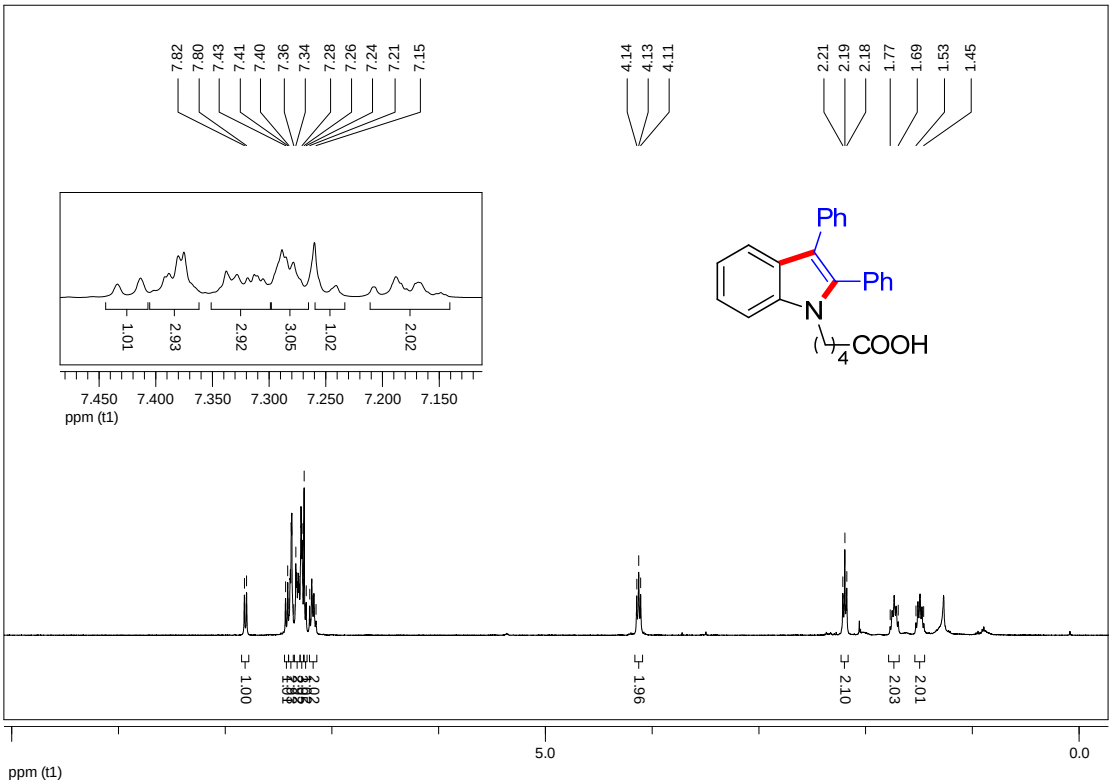


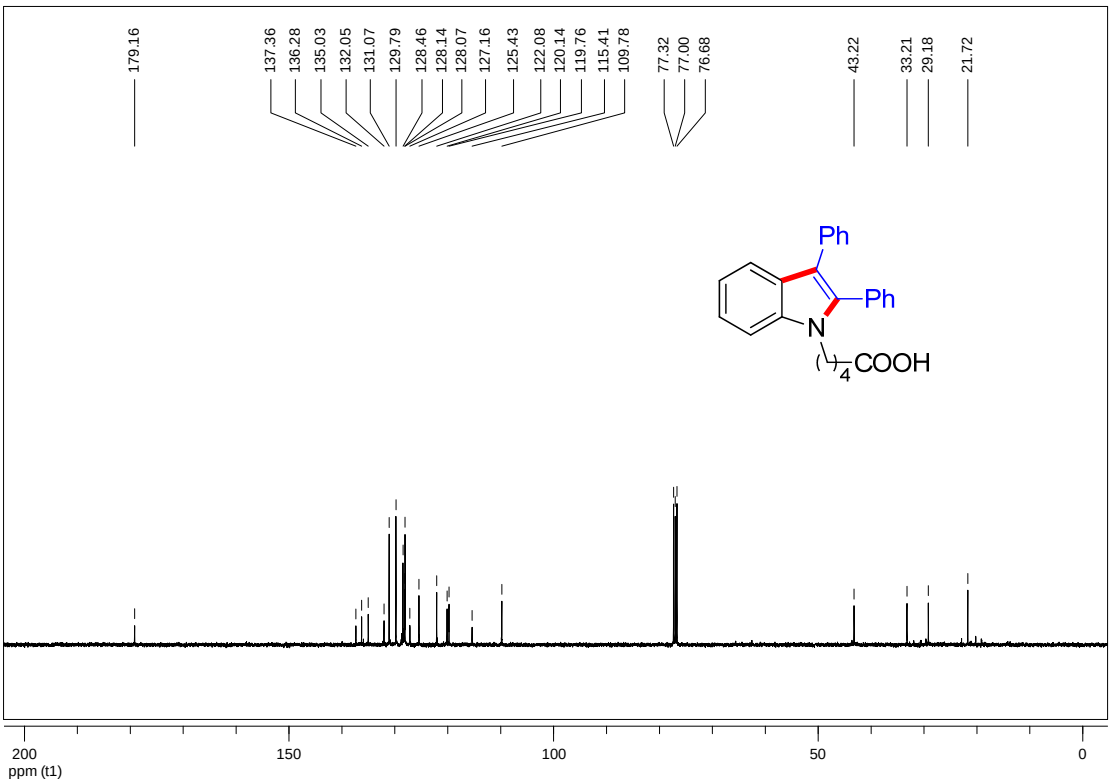
5-(2,3-diphenyl-1H-indol-1-yl)pentanal (10c)





5-(2,3-diphenyl-1H-indol-1-yl)pentanoic acid (10d)





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