Supporting Information

Palladium-catalyzed alkyne insertion and rearrangements to synthesize oxindoles from *o*-iodonitroheteroarenes and alkynes

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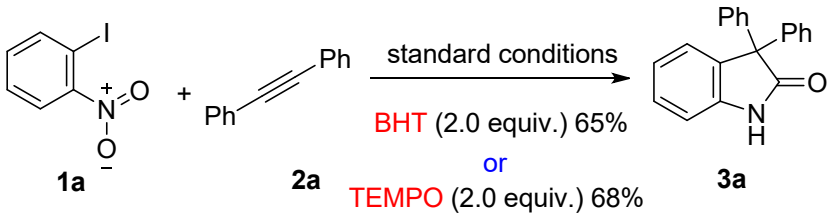
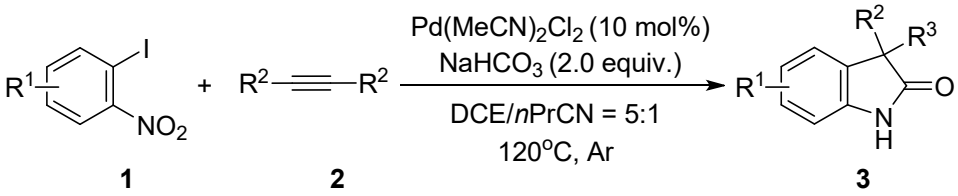
1 General remark

^{1}H NMR and ^{13}C NMR spectra were recorded on 400MHz and 100MHz in $CDCl_3$ (BRUKER 400M or JNM-ECS 400M). All chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS (HRMS were recorded on an Agilent 6210 TOF-MASS spectrometer at a 170 V fragmentor voltage); copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. Unless otherwise noted, commercially available reagents and solvents were used without further purification.

2 Control experiments

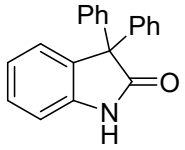


3 General procedure for 3,3-disubstituted oxindoles



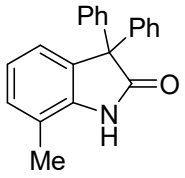
To a solution of *o*-nitroiodobenzenes **1** (0.2 mmol, 1.0 equiv.) in DCE (2.5 mL), 10 mol% of $Pd(MeCN)Cl_2$ was added. The reaction vial was then sealed and flushed with Ar. Then, 40 mol% of $NaHCO_3$ and alkyne **2** (0.26 mmol, 1.3 equiv.) were added to the reaction mixture. The reaction was then stirred at 120 °C for 12 hours (monitored by TLC). After completion, the reaction mixture was then allowed to cool and diluted with H_2O and extracted with EtOAc (3 X10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate (4/1) as eluent to afford pure products 3,3-disubstituted oxindoles **3**.

4 The data of products



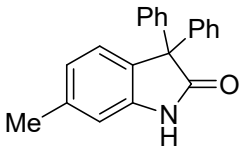
3,3-Diphenylindolin-2-one (3a)

According to the general procedure, 3,3-diphenylindolin-2-one **3a** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 71% yield; eluent: PE/EtOAc = 4:1), mp 284-286 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.47 (s, 1H), 7.52-7.41 (m, 10H), 7.39-7.32 (m, 2H), 7.28-7.22 (m, 1H), 7.15-7.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.3, 141.8, 140.4, 133.7, 128.6, 128.5, 128.4, 127.5, 126.4, 122.9, 110.5, 63.2； HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}NO^+$ 286.1226; Found 286.1225.



7-Methyl-3,3-diphenylindolin-2-one (3b)

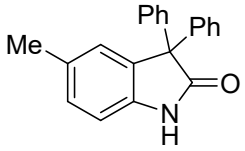
According to the general procedure, 7-methyl-3,3-diphenylindolin-2-one **3b** was obtained from 1-iodo-3-methyl-2-nitrobenzene **1b** (52.6 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 19% yield; eluent: PE/EtOAc = 4:1), mp 308-310 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.59 (s, 1H), 7.86 (dd, J = 7.4, 1.6 Hz, 1H), 7.80-7.68 (m, 4H), 7.55-7.39 (m, 7H), 7.38-7.24 (m, 1H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.5, 141.3, 139.6, 136.1, 133.4, 129.8, 128.6, 127.1, 124.0, 123.1, 111.8, 63.8, 23.2； HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO^+$ 300.1383; Found 300.1380.



6-Methyl-3,3-diphenylindolin-2-one (3c)

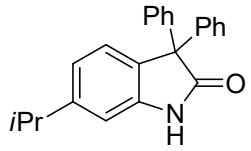
According to the general procedure, 6-methyl-3,3-diphenylindolin-2-one **3c** was obtained from 1-iodo-4-methyl-2-nitrobenzene **1c** (52.6 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 67% yield; eluent: PE/EtOAc = 4:1), mp 311-313 ℃. ^{1}H NMR

(400 MHz, $CDCl_3$, ppm): δ 9.44 (s, 1H), 7.54-7.35 (m, 9H), 7.33-7.25 (m, 2H), 7.20 (s, 1H), 7.17-7.12 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 143.4, 139.6, 136.4, 132.6, 128.6, 128.6, 127.1, 126.4, 124.7, 110.1, 64.7, 23.7； HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO^+$ 300.1383; Found 300.1380.



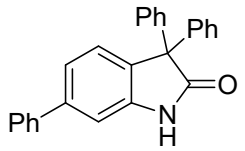
5-Methyl-3,3-diphenylindolin-2-one (3d)

According to the general procedure, 5-methyl-3,3-diphenylindolin-2-one **3d** was obtained from 2-iodo-4-methyl-1-nitrobenzene **1d** (52.6 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 54% yield; eluent: PE/EtOAc = 4:1), mp 309-311 ℃. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.40 (s, 1H), 7.56-7.42 (m, 10H), 7.41-7.33 (m, 2H), 7.30-7.24 (m, 1H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.3, 141.8, 140.4, 133.7, 128.5, 128.3, 128.1, 127.7, 126.4, 122.8, 110.6, 63.4, 26.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO^+$ 300.1383; Found 300.1380.



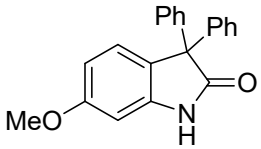
6-Isopropyl-3,3-diphenylindolin-2-one (3e)

According to the general procedure, 6-isopropyl-3,3-diphenylindolin-2-one **3e** was obtained from 1-iodo-4-isopropyl-2-nitrobenzene **1e** (58.2 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 62% yield; eluent: PE/EtOAc = 4:1), mp 317-319 ℃. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.42-9.24 (m, 1H), 7.96 (d, J = 7.4 Hz, 1H), 7.83-7.69 (m, 4H), 7.62 (dd, J = 7.5, 1.5 Hz, 1H), 7.54-7.38 (m, 7H), 3.41-2.94 (m, 1H), 1.31 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.6, 146.7, 145.8, 141.0, 139.6, 133.9, 130.8, 128.6, 127.1, 122.8, 111.2, 63.5, 35.4, 25.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}NO^+$ 328.1696; Found 328.1699.



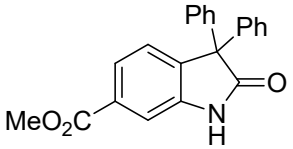
3,3,6-Triphenylindolin-2-one (3f)

According to the general procedure, 3,3,6-triphenylindolin-2-one **3f** was obtained from 4-iodo-3-nitro-1,1'-biphenyl **1f** (65.0 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 53% yield; eluent: PE/EtOAc = 4:1), mp 373-375 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.22 (s, 1H), 8.17-8.13 (m, 2H), 7.92-7.87 (m, 1H), 7.79-7.76 (m, 4H), 7.67 (dd, J = 7.6, 1.5 Hz, 1H), 7.64-7.52 (m, 4H), 7.51-7.45 (m, 5H), 7.28-7.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.9, 144.9, 140.8, 139.6, 138.9, 137.7, 134.2, 132.2, 128.8, 127.7, 127.1, 126.9, 125.6, 114.4, 63.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{20}NO^+$ 362.1539; Found 362.1535.



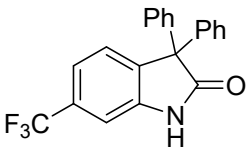
6-Methoxy-3,3-diphenylindolin-2-one (3g)

According to the general procedure, 6-methoxy-3,3-diphenylindolin-2-one **3g** was obtained from 1-iodo-4-methoxy-2-nitrobenzene **1g** (55.8 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 51% yield; eluent: PE/EtOAc = 4:1), mp 336-338 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.25 (s, 1H), 7.93 (d, J = 7.4 Hz, 1H), 7.76 (pd, J = 4.6, 1.8 Hz, 4H), 7.49-7.45 (m, 6H), 7.29-7.20 (m, 1H), 7.01 (s, 1H), 4.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.9, 162.0, 146.7, 141.9, 139.6, 138.4, 130.2, 127.7, 127.1, 111.4, 104.2, 64.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO_2^+$ 316.1332; Found 316.1330.



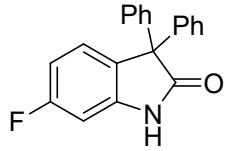
Methyl 2-oxo-3,3-diphenylindoline-6-carboxylate (3h)

According to the general procedure, methyl 2-oxo-3,3-diphenylindoline-6-carboxylate **3h** was obtained from methyl 4-iodo-3-nitrobenzoate **1h** (61.4 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 70% yield; eluent: PE/EtOAc = 4:1), mp 366-368 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.22 (s, 1H), 8.15 (d, J = 7.6 Hz, 1H), 8.02 (dd, J = 7.5, 1.5 Hz, 1H), 7.88-7.69 (m, 5H), 7.62-7.21 (m, 6H), 4.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.8, 165.8, 144.1, 143.4, 139.6, 135.2, 131.7, 130.6, 128.6, 127.1, 122.8, 110.5, 63.7,52.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}NO_3^+$ 344.1281; Found 344.1285.



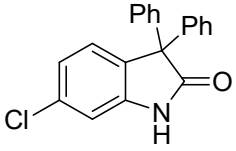
3,3-Diphenyl-6-(trifluoromethyl)indolin-2-one (3i)

According to the general procedure, 3,3-diphenyl-6-(trifluoromethyl)indolin-2-one **3i** was obtained from 1-iodo-2-nitro-4-(trifluoromethyl)benzene **1i** (63.4 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 73% yield; eluent: PE/EtOAc = 4:1), mp 316-318 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.28 (s, 1H), 8.02 (d, J = 7.4 Hz, 1H), 7.89 (s, 1H), 7.67 (dd, J = 7.5, 1.5 Hz, 1H), 7.55-7.39 (m, 4H), 7.39-7.30 (m, 1H), 7.30-7.07 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.5, 142.9, 142.5, 139.6, 134.3, 129.5 (q, J = 32.0 Hz, 1C), 128.6, 127.1, 125.8, 123.1, 122.7 (q, J = 4.0 Hz, 1C), 110.4 (q, J = 4.0 Hz, 1C), 63.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}F_3NO^+$ 354.1100; Found 354.1105.



6-Fluoro-3,3-diphenylindolin-2-one (3j)

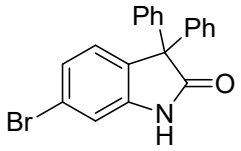
According to the general procedure, 6-fluoro-3,3-diphenylindolin-2-one **3j** was obtained from 4-fluoro-1-iodo-2-nitrobenzene **1j** (53.4 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 69% yield; eluent: PE/EtOAc = 4:1), mp 295-297 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.11-8.99 (m, 1H), 7.87-7.65 (m, 2H), 7.55-7.52 (m, 1H), 7.31-6.94 (m, 8H), 6.89-6.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.5, 162.7 (d, J = 252.0 Hz, 1C), 143.4 (d, J = 8.0 Hz, 1C), 139.6, 135.8 (d, J = 8.0 Hz, 1C), 133.9, 131.2 (d, J = 4.0 Hz, 1C), 128.6, 127.1, 110.7 (d, J = 19.0 Hz, 1C), 95.5 (d, J = 20.0 Hz, 1C), 63.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}FNO^+$ 304.1132; Found 304.1133.



6-Chloro-3,3-diphenylindolin-2-one (3k)

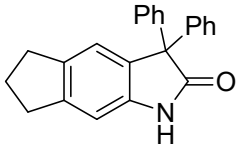
According to the general procedure, 6-chloro-3,3-diphenylindolin-2-one **3k** was obtained from 4-chloro-1-iodo-2-nitrobenzene **1k** (56.6 mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 64% yield; eluent: PE/EtOAc = 4:1), mp 331-333 ℃. ^{1}H NMR

(400 MHz, $CDCl_3$, ppm): δ 9.43 (s, 1H), 8.05-7.87 (m, 2H), 7.81-7.65 (m, 2H), 7.50-7.39 (m, 1H), 7.44-7.35 (m, 3H), 7.35-7.17 (m, 3H), 7.09-6.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.6, 143.6, 139.6, 135.9, 134.5, 133.2, 131.5, 128.6, 127.1, 125.3, 111.0, 63.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}ClNO^+$ 320.0837; Found 320.0834.



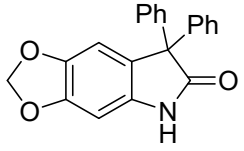
6-Bromo-3,3-diphenylindolin-2-one (3l)

According to the general procedure, 6-bromo-3,3-diphenylindolin-2-one **3l** was obtained from 4-bromo-1-iodo-2-nitrobenzene **1l** (65.4mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 49% yield; eluent: PE/EtOAc = 4:1), mp 360-362 ℃. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.29 (s, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.82-7.69 (m, 4H), 7.61 (dd, J = 7.5, 1.5 Hz, 1H), 7.53-7.42 (m, 3H), 7.36 (s, 1H), 7.33-7.22 (m, 2H), 7.20-7.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 143.0, 139.6, 138.2, 133.2, 130.6, 128.6, 127.1, 126.3, 122.3, 113.3, 63.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}BrNO^+$ 364.0332; Found 364.0330.



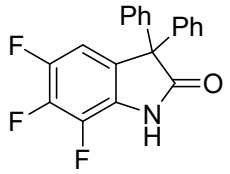
3,3-Diphenyl-3,5,6,7-tetrahydrocyclopenta[*f*]indol-2(1*H*)-one (3m)

According to the general procedure, 3,3-diphenyl-3,5,6,7-tetrahydrocyclopenta[*f*]indol-2(1*H*)-one **3m** was obtained from 5-iodo-6-nitro-2,3-dihydro-1H-indene **1m** (57.8mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 62% yield; eluent: PE/EtOAc = 4:1), mp 360-362 ℃. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.14 (s, 1H), 7.85 (s, 1H), 7.81-7.72 (m, 3H), 7.72-7.59 (m, 2H), 7.57-7.43 (m, 3H), 7.39 (s, 1H), 7.37-7.25 (m, 2H), 3.10-2.91 (m, 4H), 2.25-2.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.5, 148.4, 140.4, 139.6, 139.5, 135.1, 131.0, 127.7, 127.1, 121.6, 110.7, 63.3, 34.6, 28.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}BrNO^+$ 405.0723; Found 405.0720.



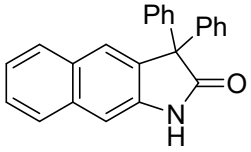
7,7-Diphenyl-5*H*-[1,3]dioxolo[4,5-*f*]indol-6(7*H*)-one (3n)

According to the general procedure, 7,7-diphenyl-5*H*-[1,3]dioxolo[4,5-*f*]indol-6(7*H*)-one **3n** was obtained from 5-iodo-6-nitrobenzo[*d*][1,3]dioxole **1n** (58.6mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 44% yield; eluent: PE/EtOAc = 4:1), mp 380-382 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.63-7.60 (m, 2H), 7.51-7.49 (m, 2H), 7.38-7.13 (m, 7H), 6.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.0, 147.9, 143.6, 141.2, 139.6, 134.8, 128.6, 127.1, 126.5, 110.7, 102.7, 96.0, 63.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}NO_3^+$ 329.1046; Found 329.1044.



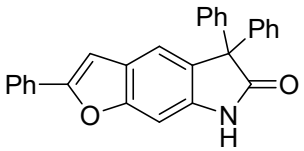
5,6,7-Trifluoro-3,3-diphenylindolin-2-one (3o)

According to the general procedure, 5,6,7-trifluoro-3,3-diphenylindolin-2-one **3o** was obtained from 1,2,3-trifluoro-5-iodo-4-nitrobenzene **1o** (60.6mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 67% yield; eluent: PE/EtOAc = 4:1), mp 320-322 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.20 (s, 1H), 7.78-7.72 (m, 3H), 7.64-7.38 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 151.1 (ddd, J = 252.0, 20.0, 8.0 Hz, 1C), 142.6 (ddd, J = 252.0, 20.0, 8.0 Hz, 1C), 139.6, 134.3 (ddd, J = 252.0, 20.0, 8.0 Hz, 1C), 131.7, 131.0 (dd, J = 20.0, 8.0 Hz, 1C), 129.1 (dd, J = 20.0, 8.0 Hz, 1C), 128.6, 127.1, 112.7 (dd, J = 20.0, 8.0 Hz, 1C), 63.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{13}F_3NO^+$ 340.0944; Found 340.0947.



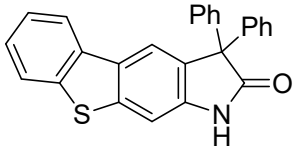
3,3-Diphenyl-1*H*-benzo[*f*]indol-2(3*H*)-one (3p)

According to the general procedure, 3,3-diphenyl-1*H*-benzo[*f*]indol-2(3*H*)-one **3p** was obtained from 2-iodo-3-nitronaphthalene **1p** (59.8mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 48% yield; eluent: PE/EtOAc = 4:1), mp 372-374 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.99 (s, 1H), 8.36 (s, 1H), 7.96-7.93 (m, 1H), 7.91-7.88 (m, 1H), 7.86-7.66 (m, 5H), 7.61-7.30 (m, 6H), 7.30-7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.3, 142.3, 140.9, 139.6, 137.3, 134.1, 130.5, 128.6, 128.4, 128.1, 127.1, 127.0, 126.8, 123.5, 109.5, 63.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}NO^+$ 336.1383; Found 336.1388.



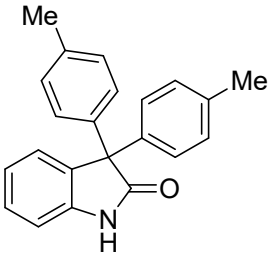
2,5,5-Triphenyl-5*H*-furo[3,2-*f*]indol-6(7*H*)-one (3q)

According to the general procedure, 2,5,5-triphenyl-5*H*-furo[3,2-*f*]indol-6(7*H*)-one **3q** was obtained from 5-iodo-6-nitro-2-phenylbenzofuran **1q** (73.0mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 46% yield; eluent: PE/EtOAc = 4:1), mp 400-402 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.98 (s, 1H), 8.40 (s, 1H), 8.23 (s, 1H), 8.09-8.06 (m, 1H), 7.95-7.92 (m, 1H), 7.8i-7.78 (m, 2H), 7.67-7.54 (m, 2H), 7.54-7.40 (m, 7H), 7.37-7.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.6, 158.5, 157.7, 142.4, 139.6, 135.3, 132.9, 131.0, 130.4, 129.1, 128.6, 127.1, 124.9, 121.6, 117.3, 101.8, 97.2, 63.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{20}NO_2^+$ 402.1489; Found 402.1488.



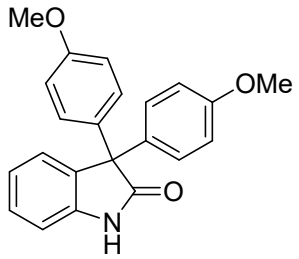
3,3-Diphenyl-1*H*-benzo[4,5]thieno[3,2-*f*]indol-2(3*H*)-one (3r)

According to the general procedure, 3,3-diphenyl-1*H*-benzo[4,5]thieno[3,2-*f*]indol-2(3*H*)-one **3r** was obtained from 2-iodo-3-nitrodibenzo[*b,d*]thiophene **1r** (71.0mg, 0.2 mmol) and 1,2-diphenylethyne **2a** (46.3 mg, 0.26 mmol) as white solid (40.5 mg, 40% yield; eluent: PE/EtOAc = 4:1), mp 410-412 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.09 (s, 1H), 8.60 (s, 1H), 8.49 (dd, J = 7.5, 1.5 Hz, 1H), 8.31-8.07 (m, 3H), 7.88-7.83 (m, 3H), 7.74-7.70 m, 1H), 7.59-7.42 (m, 4H), 7.39-7.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.3, 141.7, 139.6, 138.4, 138.4, 137.0, 135.1, 131.1, 129.8, 128.6, 127.1, 127.0, 125.2, 124.2, 120.2, 111.1, 63.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{18}NOS^+$ 392.1104; Found 392.1106.



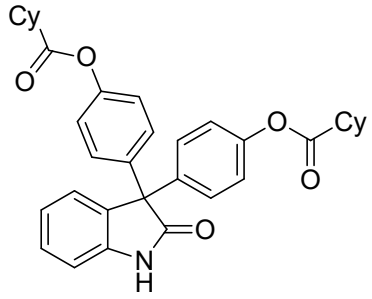
3,3-Di-p-tolylindolin-2-one (3s)

According to the general procedure, 3,3-di-p-tolylindolin-2-one **3s** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-di-p-tolylethyne **2b** (41.2 mg, 0.26 mmol) as white solid (40.5 mg, 52% yield; eluent: PE/EtOAc = 4:1), mp 322-324 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.23 (s, 1H), 7.80-7.96 (m, 2H), 7.74-7.64 (m, 3H), 7.57-7.52 (m, 1H), 7.44-7.19 (m, 6H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 142.9, 138.3, 137.6, 135.4, 130.6, 128.2, 127.2, 125.5, 122.4, 109.0, 63.8, 25.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO^+$ 314.1464; Found 314.1464.



3,3-Bis(4-methoxyphenyl)indolin-2-one (3t)

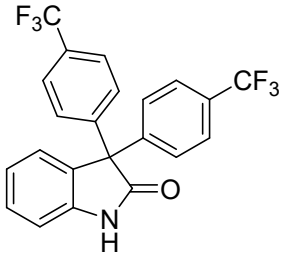
According to the general procedure, 3,3-bis(4-methoxyphenyl)indolin-2-one **3t** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-bis(4-methoxyphenyl)ethyne **2c** (47.6 mg, 0.26 mmol) as white solid (40.5 mg, 48% yield; eluent: PE/EtOAc = 4:1), mp 366-368 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.44 (s, 1H), 8.00 (dd, J = 7.4, 1.5 Hz, 1H), 7.95-7.70 (m, 5H), 7.44-7.20 (m, 2H), 7.18-6.94 (m, 4H), 3.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.0, 161.4, 145.2, 136.9, 135.7, 132.0, 128.2, 127.9, 125.5, 123.4, 110.6, 62.1, 57.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO_3^+$ 346.1359; Found 346.1360.



(2-Oxoindoline-3,3-diyl)bis(4,1-phenylene) dicyclohexanecarboxylate (3u)

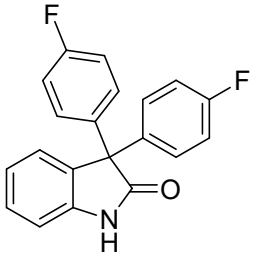
According to the general procedure, (2-oxoindoline-3,3-diyl)bis(4,1-phenylene) dicyclohexanecarboxylate **3u** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and ethyne-1,2-diylbis(4,1-phenylene) dicyclohexanecarboxylate **2d** (86.0 mg, 0.26 mmol) as white solid (40.5 mg, 42% yield; eluent: PE/EtOAc = 4:1), mp 401-413 ℃. ^{1}H NMR (400 MHz,

$CDCl_3$, ppm): δ 9.30 (s, 1H), 8.14-7.84 (m, 4H), 7.77-7.49 (m, 2H), 7.49-7.21 (m, 2H), 7.11-7.03 (m, 4H), 2.63-2.47 (m, 2H), 2.37-2.16 (m, 6H), 2.02-1.79 (m, 7H), 1.72-0.85 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.8, 177.2, 153.9, 142.9, 142.0, 138.6, 135.4, 128.2, 125.5, 123.5, 122.4, 109.0, 63.5, 43.3, 33.5, 28.4, 26.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{36}NO_5^+$ 538.2510; Found 538.2515.



3,3-Bis(4-(trifluoromethyl)phenyl)indolin-2-one (3v)

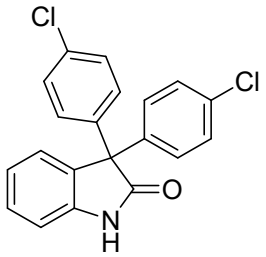
According to the general procedure, 3,3-bis(4-(trifluoromethyl)phenyl)indolin-2-one **3v** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-bis(4-(trifluoromethyl)phenyl)ethyne **2e** (62.8 mg, 0.26 mmol) as white solid (40.5 mg, 55% yield; eluent: PE/EtOAc = 4:1), mp 338-340 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.50 (s, 1H), 8.16-8.10 (m, 2H), 8.00 (dd, J = 7.5, 1.5 Hz, 1H), 7.76-7.72 (m, 3H), 7.71-7.04 (m, 2H), 7.62-7.49 (m, 2H), 7.35-7.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 142.9, 141.7, 138.4 (q, J = 4.0 Hz, 1C), 135.4, 132.8, 130.5 (q, J = 320.0 Hz, 1C), 128.2, 127.8, 125.2 (q, J = 4.0 Hz, 1C), 122.9, 122.4, 63.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{14}F_6NO^+$ 422.0896; Found 422.0899.



3,3-Bis(4-fluorophenyl)indolin-2-one (3w)

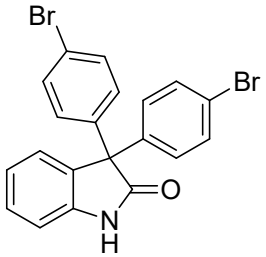
According to the general procedure, 3,3-bis(4-fluorophenyl)indolin-2-one **3w** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-bis(4-fluorophenyl)ethyne **2f** (42.8 mg, 0.26 mmol) as white solid (40.5 mg, 67% yield; eluent: PE/EtOAc = 4:1), mp 308-310 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.29 (s, 1H), 8.07-7.88 (m, 2H), 7.82-7.72 (m, 2H), 7.60-7.54 (m, 2H), 7.41-7.37 (m, 2H), 7.29-7.16 (m, 1H), 7.10-6.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,

ppm): δ 180.9, 162,3 (d, J = 252.0 Hz, 1C), 142.9, 138.1(d, J = 3.0 Hz, 1C), 135.4, 128.2, 127.2 (d, J = 8.0 Hz, 1C), 125.5, 122.4, 114.2 (d, J = 20.0 Hz, 1C), 110.3, 63.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}F_2NO^+$ 322.0960; Found 322.0965.



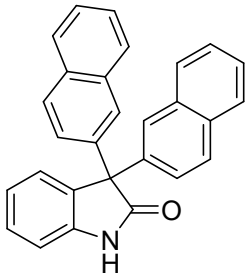
3,3-Bis(4-chlorophenyl)indolin-2-one (3x)

According to the general procedure, 3,3-bis(4-chlorophenyl)indolin-2-one **3x** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-bis(4-chlorophenyl)ethyne **2g** (49.2 mg, 0.26 mmol) as white solid (40.5 mg, 72% yield; eluent: PE/EtOAc = 4:1), mp 367-369 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.49 (s, 1H), 8.22-8.07 (m, 1H), 7.96 (dd, J = 7.5, 2.0 Hz, 1H), 7.86 (ddd, J = 7.2, 4.9, 2.1 Hz, 2H), 7.72 (ddd, J = 13.4, 7.6, 2.0 Hz, 2H), 7.53 (ddd, J = 21.4, 7.5, 1.8 Hz, 3H), 7.39 (ddd, J = 9.3, 7.8, 1.6 Hz, 2H), 7.35-7.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.9, 145.4, 139.1, 135.4, 132.6, 131.2, 128.2, 128.0, 125.5, 123.4, 111.4, 64.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}Cl_2NO^+$ 354.0369; Found 354.0371.



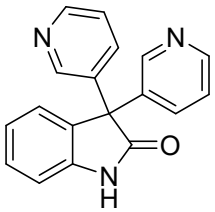
3,3-Bis(4-bromophenyl)indolin-2-one (3y)

According to the general procedure, 3,3-bis(4-bromophenyl)indolin-2-one **3y** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-bis(4-bromophenyl)ethyne **2h** (66.8 mg, 0.26 mmol) as white solid (40.5 mg, 70% yield; eluent: PE/EtOAc = 4:1), mp 419-421 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.78 (s, 1H), 7.97 (dd, J = 7.6, 1.5 Hz, 1H), 7.77-7.65 (m, 4H), 7.63-7.60 (m, 2H), 7.58-7.49 (m, 2H), 7.35-7.31 (m, 1H), 7.28-7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.8, 142.9, 139.9, 137.3, 135.4, 132.3, 129.6, 128.2, 123.7, 122.5, 111.0, 63.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{14}Br_2NO^+$ 441.9358; Found 441.9360.



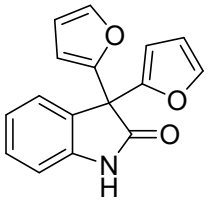
3,3-Di(naphthalen-2-yl)indolin-2-one (3z)

According to the general procedure, 3,3-di(naphthalen-2-yl)indolin-2-one **3z** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-di(naphthalen-2-yl)ethyne **2i** (55.6 mg, 0.26 mmol) as white solid (40.5 mg, 48% yield; eluent: PE/EtOAc = 4:1), mp 413-415℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.18 (s, 1H), 7.33 (dd, J = 7.5, 1.4 Hz, 1H), 7.16 (s, 1H), 7.02-6.91 (m, 2H), 6.81 (dd, J = 7.8, 1.6 Hz, 1H), 6.75-6.55 (m, 5H), 6.48 (dd, J = 7.4, 1.5 Hz, 1H), 6.35-6.26 (m, 4H), 6.20-6.10 (m, 2H), 6.06-5.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.5, 144.2, 142.9, 138.9, 135.4, 133.7, 133.2, 130.6, 128.5, 128.4, 128.2, 127.5, 127.4, 126.4, 125.5, 123.1, 110.4, 63.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{20}NO^+$ 386.1461; Found 386.1466.



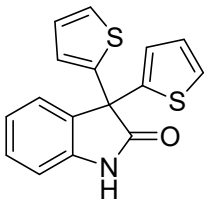
3,3-Di(pyridin-3-yl)indolin-2-one (3aa)

According to the general procedure, 3,3-di(pyridin-3-yl)indolin-2-one **3aa** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-di(pyridin-3-yl)ethyne **2j** (36.0 mg, 0.26 mmol) as white solid (40.5 mg, 36% yield; eluent: PE/EtOAc = 4:1), mp 306-308 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.31 (s, 1H), 8.89 (dd, J = 5.0, 1.2 Hz, 1H), 8.67-8.50 (m, 3H), 8.46-8.43 (m, 1H), 8.08-8.06 (m, 1H), 7.98 (dd, J = 7.4, 1.5 Hz, 1H), 7.65 (dd, J = 8.0, 5.0 Hz, 1H), 7.58-7.53 (m, 1H), 7.45-7.32 (m, 2H), 7.28-7.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 149.8, 149.0, 144.2, 139.6, 137.9, 134.9, 128.2, 125.5, 122.9, 122.4, 110.7, 63.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}N_3O^+$ 2881053; Found 288.1055.



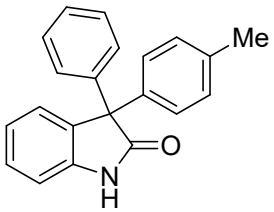
3,3-Di(furan-2-yl)indolin-2-one (3ab)

According to the general procedure, 3,3-di(furan-2-yl)indolin-2-one **3ab** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-di(furan-2-yl)ethyne **2k** (31.6 mg, 0.26 mmol) as white solid (40.5 mg, 44% yield; eluent: PE/EtOAc = 4:1), mp 289-291 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.44 (s, 1H), 8.23-7.98 (m, 1H), 7.85 (dd, J = 7.5, 1.5 Hz, 1H), 7.69 (dd, J = 7.5, 1.5 Hz, 1H), 7.48-7.21 (m, 3H), 7.00-6.84 (m, 2H), 6.62 (dd, J = 7.5, 1.5 Hz, 1H), 6.46-6.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 149.9, 142.0, 139.6, 134.0, 128.2, 123.9, 121.8, 110.7, 109.2, 104.1, 69.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{12}NO_3^+$ 266.0733; Found 266.0736.



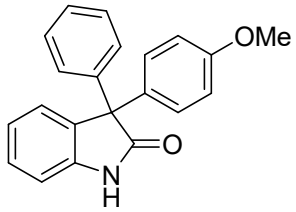
3,3-Di(thiophen-2-yl)indolin-2-one (3ac)

According to the general procedure, 3,3-di(thiophen-2-yl)indolin-2-one **3ac** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1,2-di(thiophen-2-yl)ethyne **2l** (38.0 mg, 0.26 mmol) as white solid (40.5 mg, 44% yield; eluent: PE/EtOAc = 4:1), mp 378-380 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.29 (s, 1H), 8.02 (dd, J = 7.4, 1.6 Hz, 1H), 7.76-7.60 (m, 2H), 7.50-7.44 (m, 1H), 7.39-7.26 (m, 2H), 7.24-7.16 (m, 2H), 7.08 (t, J = 7.4 Hz, 1H), 6.95-6.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 158.1, 147.7, 141.6, 138.1, 131.8, 129.7, 128.2, 126.3, 122.5, 110.0, 63.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{12}S_2NO^+$ 298.0277; Found 298.0280.



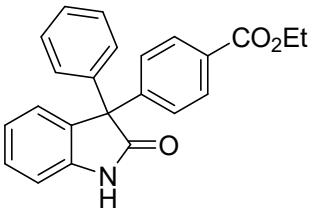
3-Phenyl-3-(p-tolyl)indolin-2-one (3ad)

According to the general procedure, 3-phenyl-3-(p-tolyl)indolin-2-one **3ad** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1-methyl-4-(phenylethynyl)benzene **2m** (38.4 mg, 0.26 mmol) as white solid (40.5 mg, 63% yield; eluent: PE/EtOAc = 4:1), mp 307-309 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.28 (s, 1H), 8.22-8.12 (m, 1H), 7.97-7.83 (m, 2H), 7.79-7.65 (m, 2H), 7.60-7.43 (m, 3H), 7.41-7.23 (m, 4H), 7.15-7.04 (m, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 181.2, 142.9, 141.4, 139.6, 138.3, 137.6, 135.4, 133.9, 131.2, 130.5, 128.2, 127.1, 125.5, 123.1, 111.0, 63.5, 26.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO^+$ 300.1305; Found 300.1307.



3-(4-Methoxyphenyl)-3-phenylindolin-2-one (3ae)

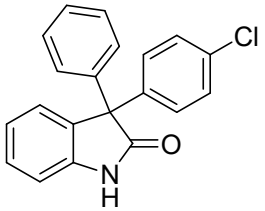
According to the general procedure, 3-(4-methoxyphenyl)-3-phenylindolin-2-one **3ae** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1-methoxy-4-(phenylethynyl)benzene **2n** (41.6 mg, 0.26 mmol) as white solid (40.5 mg, 57% yield; eluent: PE/EtOAc = 4:1), mp 335-337 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.43 (s, 1H), 8.01-7.95 (m, 1H), 7.79-7.77 (m, 2H), 7.75-7.71 (m, 2H), 7.59-7.52 (m, 1H), 7.51-7.43 (m, 2H), 7.42-7.24 (m, 3H), 7.07-6.99 (m, 2H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 160.4, 142.9, 141.7, 138.4, 135.7, 135.4, 133.9, 131.1, 128.4, 128.2, 127.1, 123.4, 112.8, 110.3, 63.0, 57.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO_2^+$ 316.1254; Found 316.1257.



Ethyl 4-(2-oxo-3-phenylindolin-3-yl)benzoate (3af)

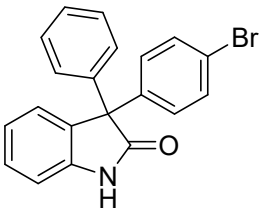
According to the general procedure, ethyl 4-(2-oxo-3-phenylindolin-3-yl)benzoate **3af** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and ethyl 4-(phenylethynyl)benzoate **2o** (50.0 mg, 0.26 mmol) as white solid (40.5 mg, 59% yield; eluent: PE/EtOAc = 4:1), mp 382-384 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.41 (s, 1H), 8.31 (dd, J = 7.5, 2.0 Hz, 1H), 8.20-

8.17 (m, 2H), 8.07-7.99 (m, 2H), 7.80-7.76 (m, 1H), 7.72-7.61 (m, 2H), 7.56-7.48 (m, 2H), 7.41-7.36 (m, 2H), 7.28-7.19 (m, 1H), 4.61-4.53 (m, 1H), 4.26-4.18 (m, 1H), 1.99 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.6, 167.0, 142.9, 141.78, 139.6, 137.8, 135.4, 131.7, 129.0, 128.8, 128.6, 128.4, 128.2, 127.1, 122.4, 109.0, 63.4, 61.1, 20.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}NO_3^+$ 358.1359; Found 358.1362.



3-(4-Chlorophenyl)-3-phenylindolin-2-one (3ag)

According to the general procedure, 3-(4-chlorophenyl)-3-phenylindolin-2-one **3ag** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1-chloro-4-(phenylethynyl)benzene **2p** (42.4 mg, 0.26 mmol) as white solid (40.5 mg, 65% yield; eluent: PE/EtOAc = 4:1), mp 326-328 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.45 (s, 1H), 7.99 (dd, J = 7.3, 1.6 Hz, 1H), 7.88 (dd, J = 7.5, 2.1 Hz, 1H), 7.80-7.73 (m, 2H), 7.69 (dd, J = 7.5, 2.0 Hz, 1H), 7.59-7.44 (m, 4H), 7.40-7.36 (m, 2H), 7.28-7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.8, 142.9, 140.4, 139.6, 139.1, 136.4, 135.4, 133.8, 131.2, 128.6, 128.4, 128.2, 127.1, 122.9, 110.7, 62.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}ClNO^+$ 320.0758; Found 320.0760.

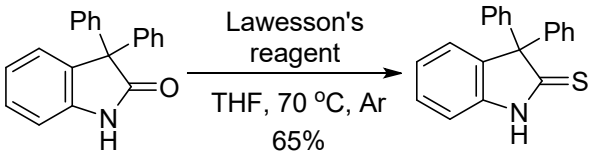


3-(4-Bromophenyl)-3-phenylindolin-2-one (3ah)

According to the general procedure, 3-(4-bromophenyl)-3-phenylindolin-2-one **3ah** was obtained from 1-iodo-2-nitrobenzene **1a** (49.8mg, 0.2 mmol) and 1-bromo-4-(phenylethynyl)benzene **2q** (51.2 mg, 0.26 mmol) as white solid (40.5 mg, 61% yield; eluent: PE/EtOAc = 4:1), mp 357-359 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.57 (s, 1H), 8.35-8.28 (m, 1H), 8.07-8.03 (m, 1H), 7.94-7.91 (m, 1H), 7.84-7.73 (m, 3H), 7.65-7.63 (m, 1H), 7.59-7.43 (m, 2H), 7.40-7.36 (m, 2H), 7.31-7.22 (m, 1H), 7.17 (dd, J = 7.5, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 180.2, 142.9,

139.9, 139.6, 138.7, 135.4, 133.7, 131.5, 128.6, 128.4, 128.2, 127.1, 123.2, 122.4, 110.0, 63.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}BrNO^+$ 364.0253; Found 364.0256.

5. Procedures and data for compounds 4-7

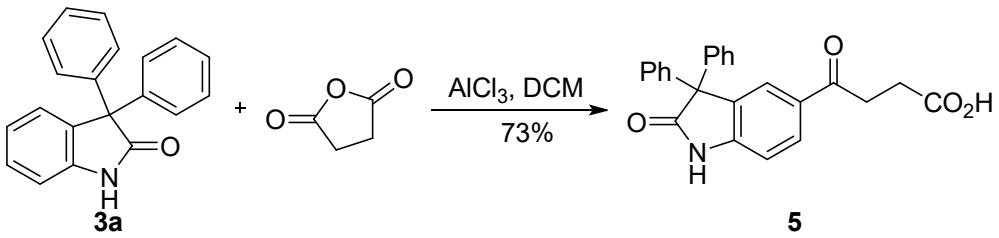


3a **4**

Into oven-dried 25 mL schlenk tube was added oxindole derivative **3a** (0.2 mmol, 1.0 equiv.) and Lawesson's reagent (0.26 mmol, 1.3 equiv.). The resulting mixture was added 3 mL THF and stirred overnight under Ar atmosphere at 70 °C. The reaction mixture was cooled to room temperature, quenched with H_2O (10 mL), extracted with EtOAc (3 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to give the desired product **4**.[2]

3,3-Diphenylindoline-2-thione (4)

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 10.93 (s, 1H), 8.06-7.76 (m, 5H), 7.76-7.51 (m, 5H), 7.36 (dd, J = 7.5, 1.4 Hz, 1H), 7.33-7.15 (m,3H)；^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 208.9, 142.2, 140.9, 138.4, 128.4, 127.7, 127.6, 126.7, 125.6, 123.6, 109.6, 72.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}NS^+$ 302.0998; Found 302.0994.



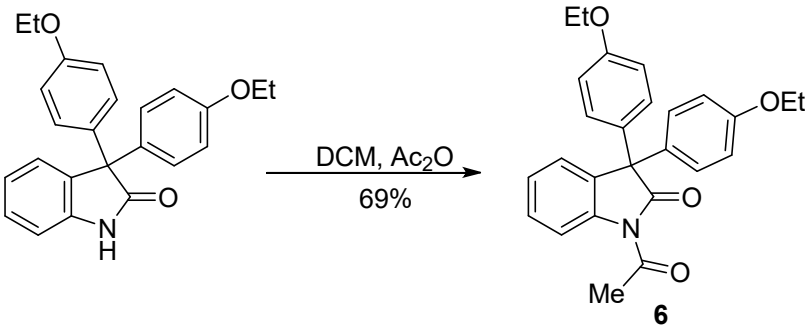
3a **5**

Into oven-dried 25 mL schlenk tube was added oxindole derivative **3a** (0.2 mmol, 1.0 equiv.) and succinic anhydride (0.25 mmol, 1.25 equiv.). The resulting mixture was added 2 mL DCM. This solution was cooled to 0°C in an ice bath. Slowly over a period of approximately fifteen minutes 10 mol% of $AlCl_3$ was added. The reaction was allowed to proceed for 6 h. The reaction was allowed to slowly rise to ambient temperature and the reaction vessel was fitted with a drying tube to maintain anhydrous conditions. The reaction was quenched by pouring over an ice-water slurry. The reaction mixture was quenched with H_2O (10 mL), extracted with EtOAc (3 x 10 mL),

dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to give the desired product **5**.[3]

4-Oxo-4-(2-oxo-3,3-diphenylindolin-5-yl)butanoic acid (5)

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 10.98 (s, 1H), 9.38 (s, 1H), 8.35 (d, J = 1.6 Hz, 1H), 8.15-8.11 (m, 1H), 8.06-7.83 (m, 2H), 7.83-7.72 (m, 3H), 7.72-7.54 (m, 3H), 7.54-7.42 (m, 2H), 7.25 (s, 1H), 3.53 (t, J = 8.5 Hz, 2H), 2.94 (t, J = 8.5 Hz, 2H)；^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 206.6, 177.5, 173.8, 144.4, 140.6, 138.9, 136.3, 133.6, 132.1, 130.4, 129.7, 128.6, 113.9, 63.0, 37.4, 29.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}NO_4^+$ 386.1387; Found 386.1385.

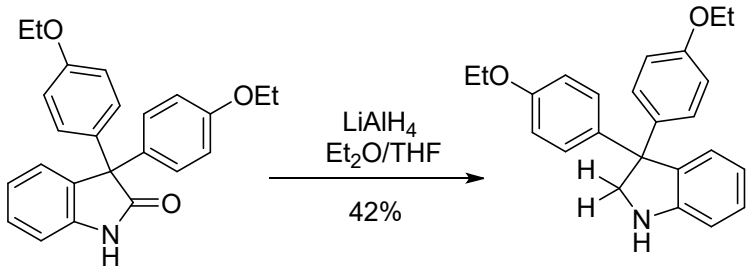


6

To a solution of indole derivative (0.2 mmol, 1.0 equiv.) in DCM (20 mL), acetic anhydride (0.4 mmol, 2.0 equiv.), Et_3N (0.3 mmol, 1.5 equiv.) and 4-dimethylaminopyridine (DMAP) 2 mol% were added, and the mixture was stirred at room temperature for 24 h. After completion of the reaction as monitored by TLC, the residue was washed with a saturated solution of NH_4Cl (10 mL) and extracted with DCM (3 X 20 mL). The combined organic extracts were died over Na_2SO_4 and concentrated under vacuum. Purification using silica gel column chromatography (elution with petroleum ether (PE):ethyl acetate (EtOAc) = 9:1) afforded the pure product **6** in 69% yield.[4]

1-Acetyl-3,3-bis(4-ethoxyphenyl)indolin-2-one (6)

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.53-8.46 (m, 1H), 7.53-7.40 (m, 3H), 7.36 (dd, J = 7.5, 1.9 Hz, 1H), 7.34-7.28 (m, 2H), 7.25 (d, J = 6.9 Hz, 1H), 7.20-7.01 (m, 4H), 4.42-4.35 (m, 4H), 2.94 (s, 3H), 1.49 (t, J = 6.0 Hz, 6H)；^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 178.3, 170.8, 157.6, 140.7, 138.9, 137.9, 128.9, 127.9, 125.2, 124.5, 122.4, 116.1, 65.7, 62.2, 23.4, 14.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}NO_4^+$ 416.1856; Found 416.1852.



7

To a solution of indole derivative (0.2 mmol, 1.0 equiv.) in Et_2O (2 mL) was added $LiAlH_4$ (1.0 M in THF, 5.0 mL, 5.0 mmol). The reaction mixture was stirred at rt for 4 h and then at reflux for 2 h. The mixture was cooled to rt and carefully quenched with H_2O (2 mL), 6 N NaOH (2 mL) and H_2O (2 mL). The resulting slurry was extracted with EtOAc (20 mL x 3) and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated 7 (42%) as a yellowish powder.[5]

3,3-Bis(4-ethoxyphenyl)indoline (7)

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.84 (s, 1H), 6.29-6.05 (m, 11H), 5.88-5.74 (m, 3H), 5.68-5.43 (m, 2H), 2.84 (s, 2H), 2.70-2.30 (m, 6H)；^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 157.7, 150.0, 145.9, 128.1, 127.6, 127.5, 126.6, 125.9, 125.6, 119.4, 112.4, 65.7, 24.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{26}NO_2^+$ 360.1958; Found 360.1963.

6. X-Ray crystallographic data of compounds 3u

Compound **3u** was dissolved in MeOH and cold *n*hexane was added, leaving to slow evaporation overnight to yield colorless needle. A suitable crystal was selected and mounted on a X-ray with Mo radiation (a=11.0218(12), b=11.6603(13), c=12.6999(14)) for cell determination and subsequent data collection at 296 K. Using SHELXL-2014, the structurwas solved with the ShelXT11 structure solution program using Intrinsic Phasing and refined with the ShelXL12 refinemee package using Least Squares minimisation. The solved structures of **3u** has been deposited in The Cambridge Crystallographic Data Centre (CCDC 2294000). The single crystal analysis was carried out using Bruker Smart instrument.

Table S1 Crystal data and structure refinement for 3u

Identification code	**3u**
Empirical formula	$C_{34}H_{35}NO_5$
Formula weight	537.63

Temperature/K	298.15
Crystal system	triclinic
Space group	P-1
a/Å	11.0218(12)
b/Å	11.6603(13)
c/Å	12.6999(14)
α/°	71.954(2)
β/°	81.725(3)
γ/°	81.160(3)
Volume/Å^3	1525.4(3)
Z	2
ρ_{calc}g/cm^3	1.171
μ/mm^{-1}	0.078
F(000)	572.0
Crystal size/mm^3	0.35 × 0.27 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.22 to 50.04
Index ranges	-13 ≤ h ≤ 12, -10 ≤ k ≤ 13, -14 ≤ l ≤ 15
Reflections collected	7396
Independent reflections	5277 [R_{int} = 0.0366, R_{sigma} = 0.0647]
Data/restraints/parameters	5277/0/361
Goodness-of-fit on F^2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0644, wR_2 = 0.1414
Final R indexes [all data]	R_1 = 0.1173, wR_2 = 0.1573
Largest diff. peak/hole / e Å^{-3}	0.24/-0.25

7. Refrences

(1) M. Peng, C.-S. Wang, P.-P. Chen, T. Roisnel, H. Doucet, K. N. Houk, J.-F. Soule, Merging C-H Bond Activation, Alkyne Insertion, and Rearrangements by Rh(III)-Catalysis: Oxindole Synthesis from Nitroarenesand Alkynes, *J. Am. Chem. Soc.*, 2023, **145**, 4508−4516.

(2) A. Saputra, R. Fan, T. L. Yao, J. Chen, J. J. Tan, Synthesis of 2-(Arylthio)indolenines via Chemoselective Arylation of Thio-Oxindoles with Arynes, *Adv. Synth.Catal.,* 2020, **362**, 2683-2688.

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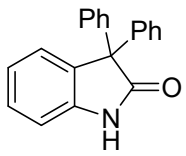
(4) S. Pandit, V. K. Pandey, A. S. Adhikari, S. Kumar, A. K. Maurya, R. Kant, and N. Majumdar, Palladium-Catalyzed Dearomative [4 + 2]-Cycloaddition toward Hydrocarbazoles, *J. Org.Chem*., 2023, **88**, 97−105.

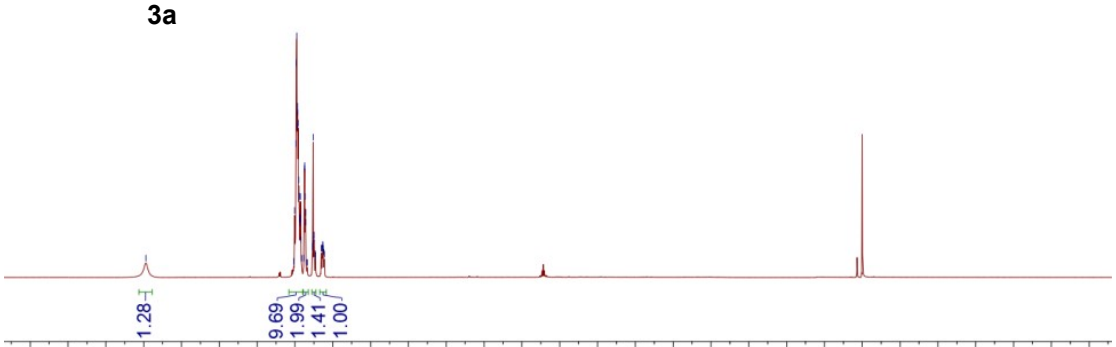
(5) J. X. Qiao, T. C. Wang, R. Ruel, C. Thibeault, A. Heureux, W. A. Schumacher, S. A. Spronk, S. Hiebert, G. Bouthillier, J. Lloyd, Z. Pi, D. M. Schnur, L. M. Abell, J. Hua, L. A. Price, E. Liu, Q. Wu, T. E. Steinbacher, J. S. Bostwick, M. Chang, J. Zheng, Q. Gao, B. Ma, P. A. McDonnell, C. S. Huang, R. Rehfuss, R. R. Wexler, and P. Y. S. Lam, Conformationally Constrained ortho-Anilino Diaryl Ureas: Discovery of 1-(2-(1′-Neopentylspiro[indoline-3,4′-piperidine]-1-yl)phenyl)-3-(4-(trifluoromethoxy)phenyl)urea, a Potent, Selective, and Bioavailable P2Y1 Antagonist, *J. Med. Chem*., 2013, **56**, 9275–9295.

8. Copies of NMR Spectra

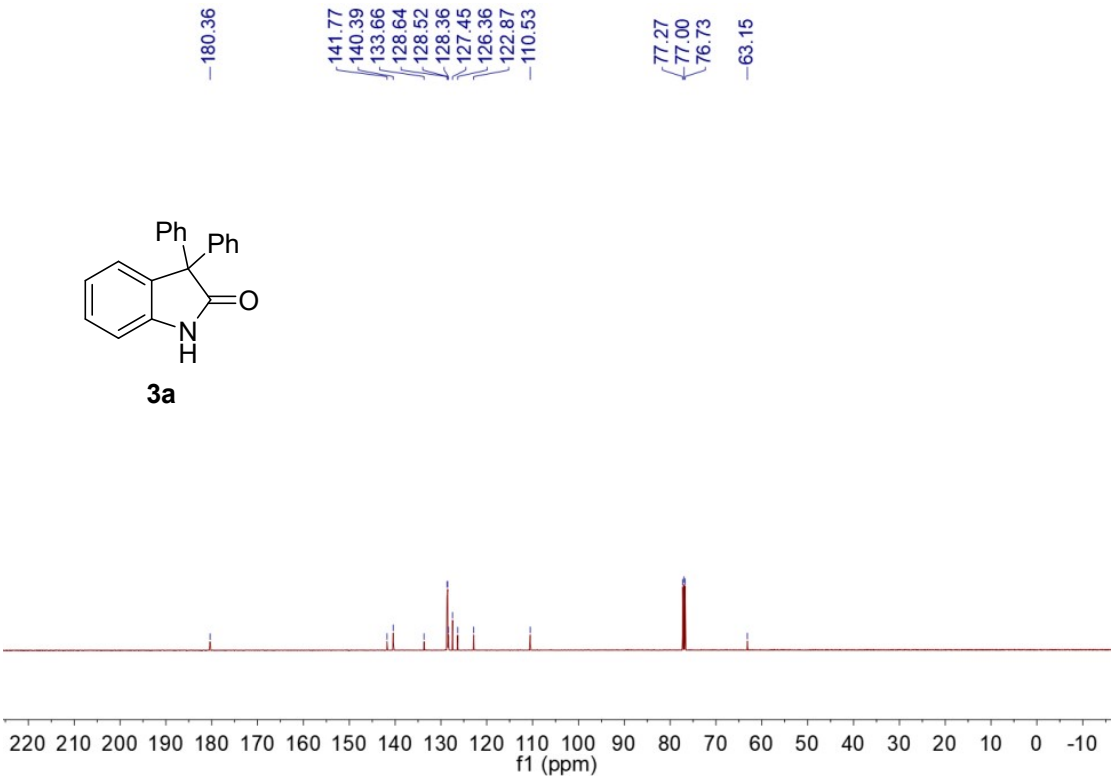
^{1}H NMR of **3a** (400 MHz, $CDCl_3$, ppm):



3a

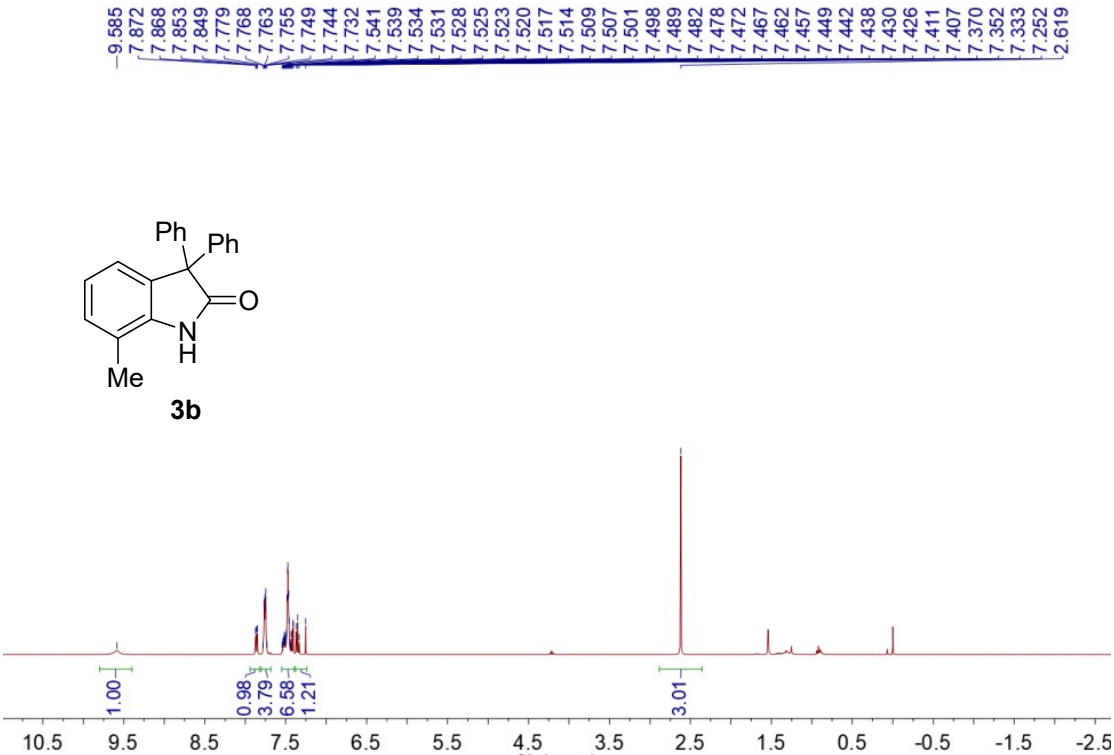


^{13}C NMR of **3a** (100 MHz, $CDCl_3$, ppm):



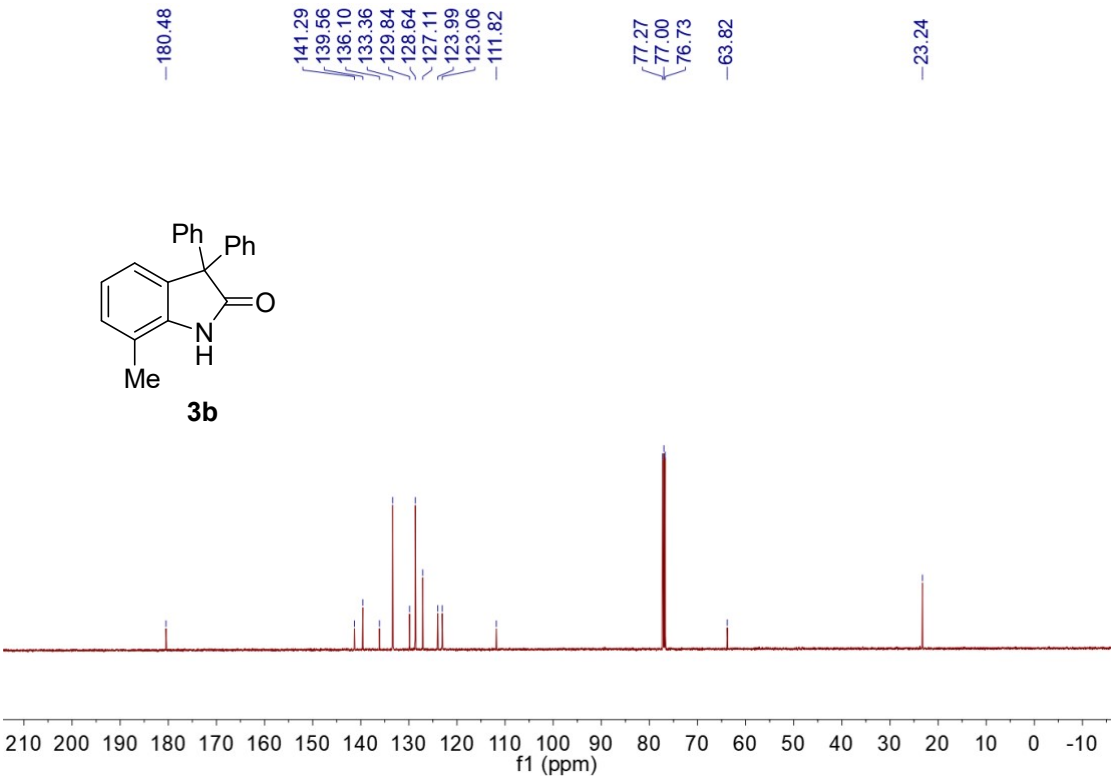
3a

^{1}H NMR of **3b** (400 MHz, $CDCl_3$, ppm):

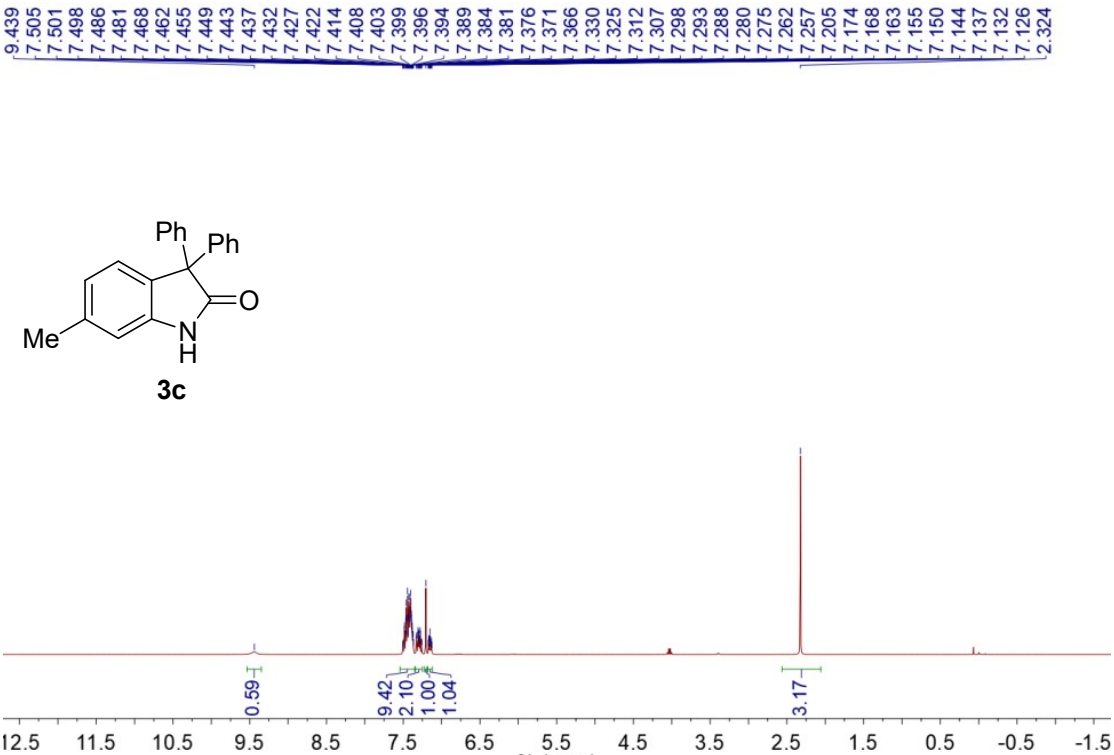


3b

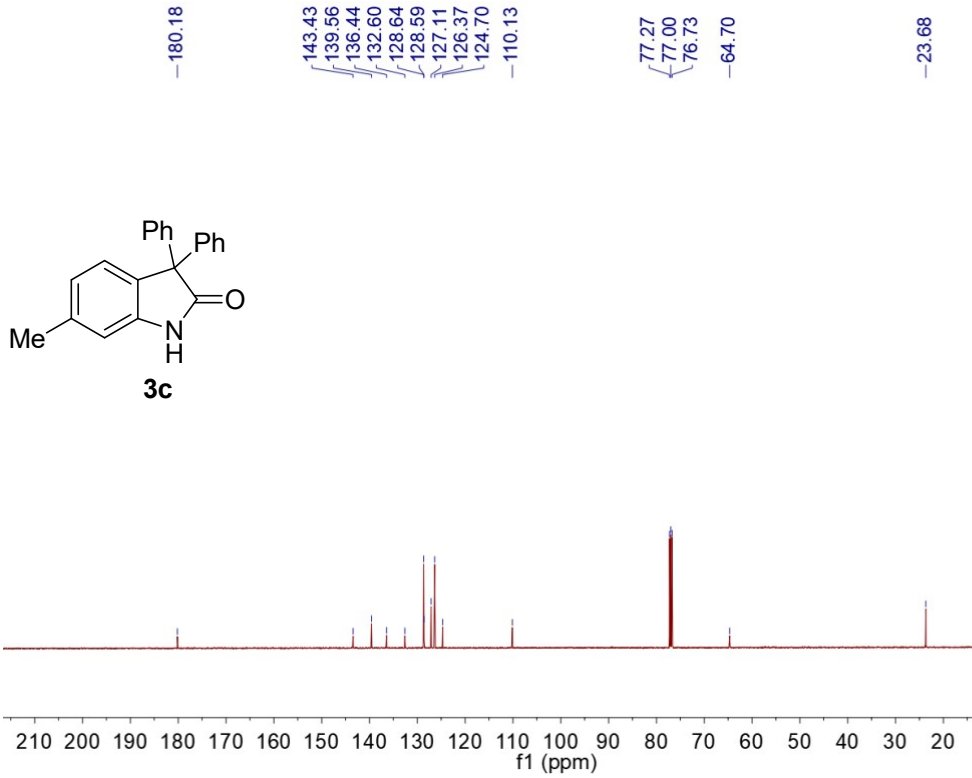
^{13}C NMR of **3b** (100 MHz, $CDCl_3$, ppm):



^{1}H NMR of **3c** (400 MHz, $CDCl_3$, ppm):

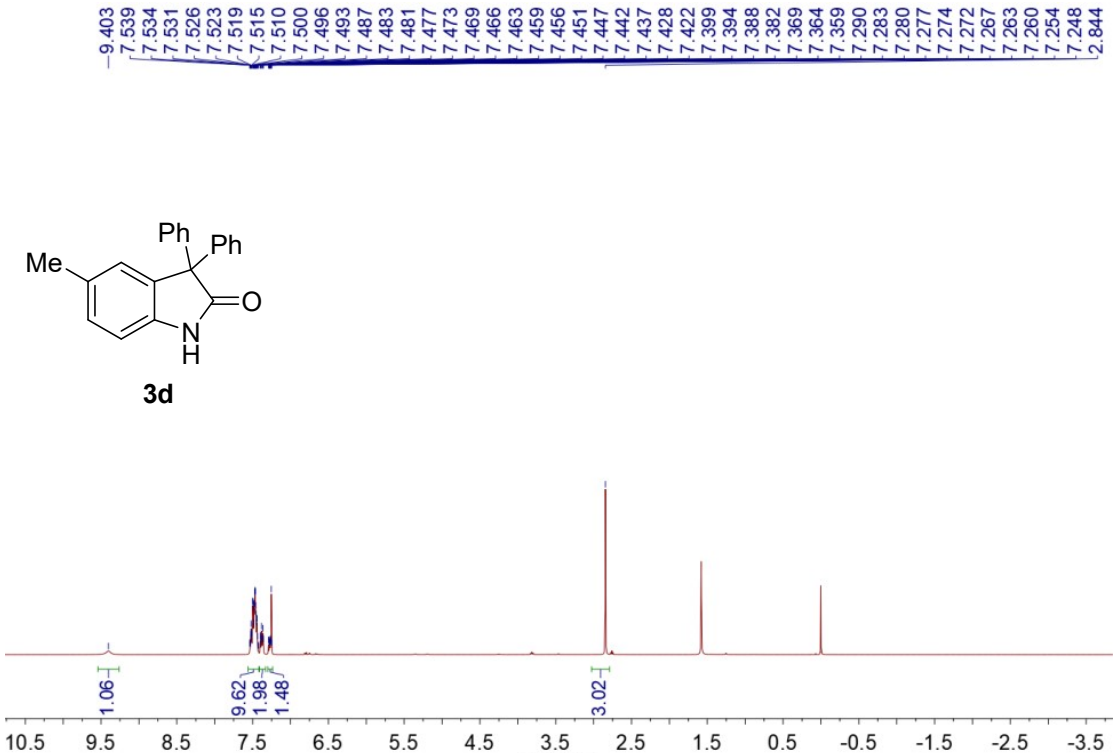


^{13}C NMR of **3c** (100 MHz, $CDCl_3$, ppm):



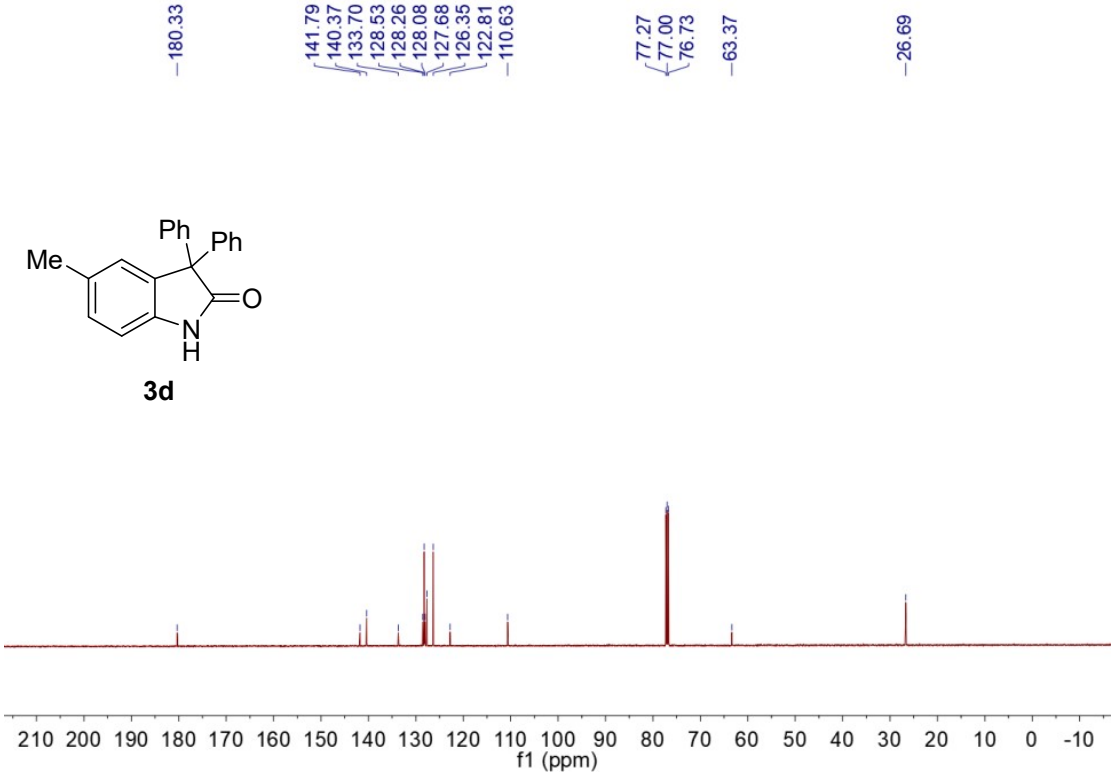
3c

^{1}H NMR of **3d** (400 MHz, $CDCl_3$, ppm):

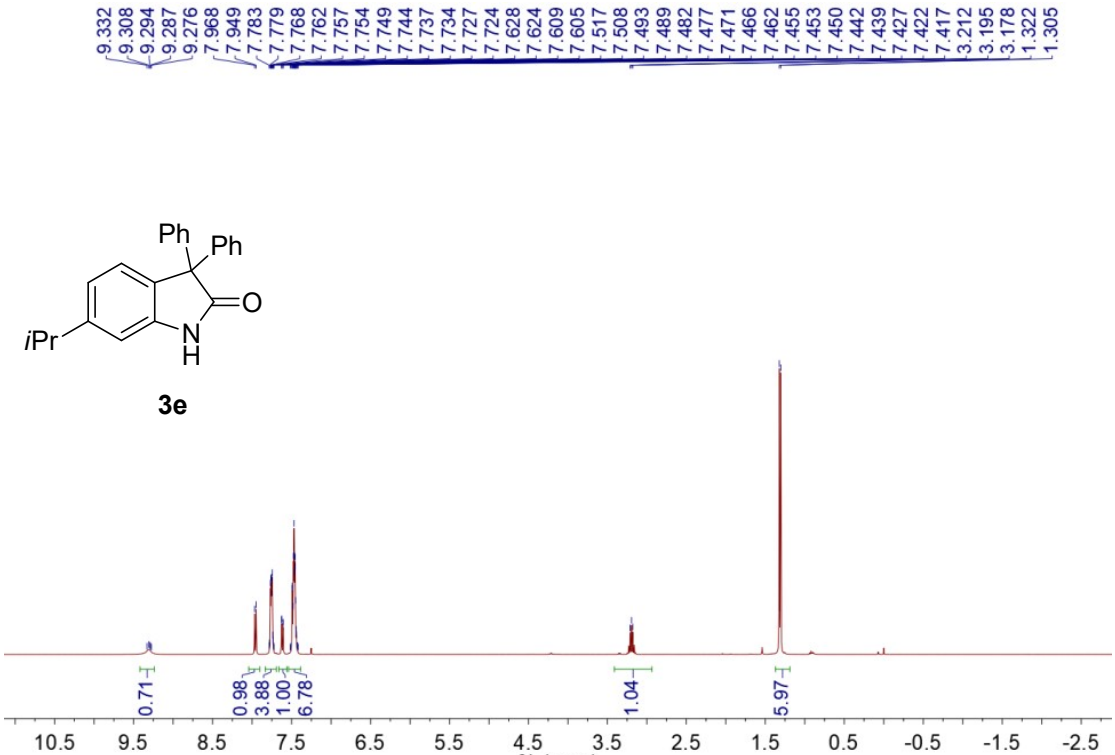


3d

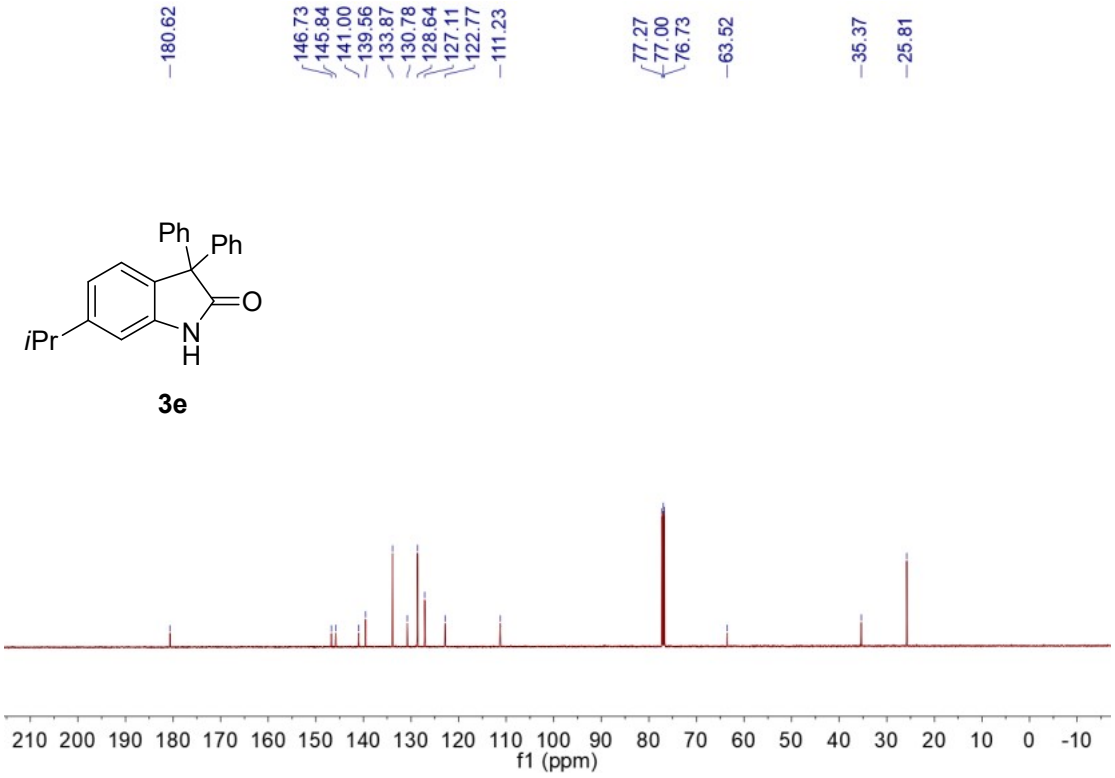
^{13}C NMR of **3d** (100 MHz, $CDCl_3$, ppm):



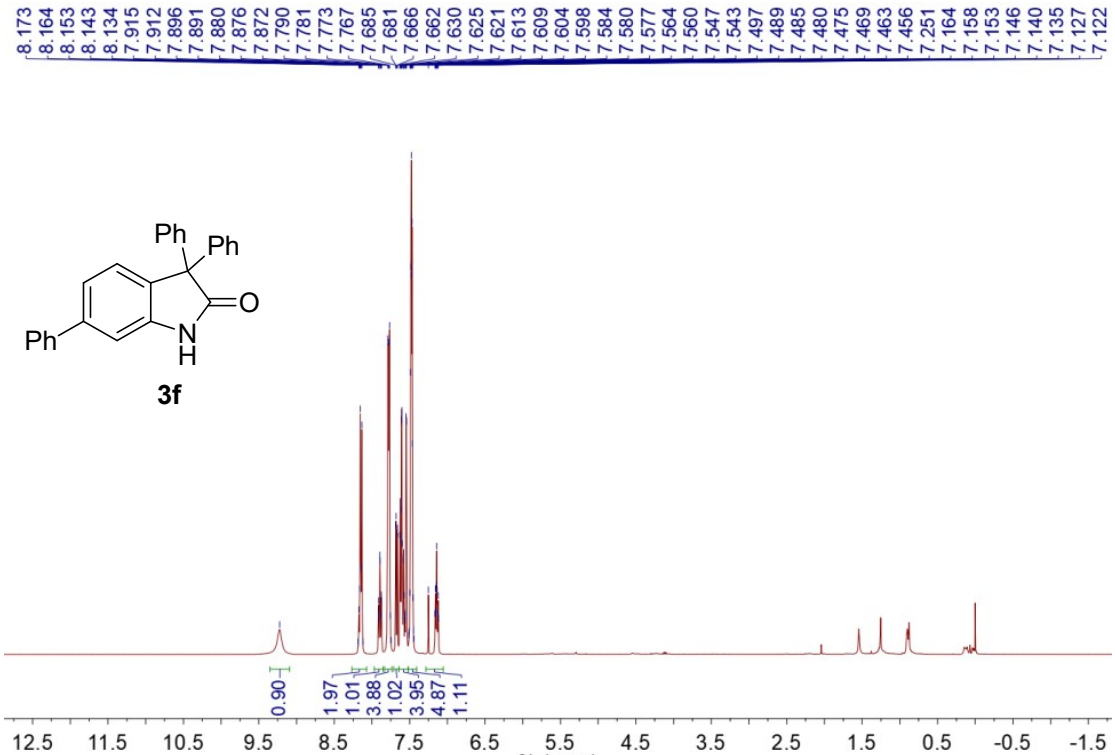
^{1}H NMR of **3e** (400 MHz, $CDCl_3$, ppm):



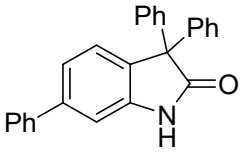
^{13}C NMR of **3e** (100 MHz, $CDCl_3$, ppm):



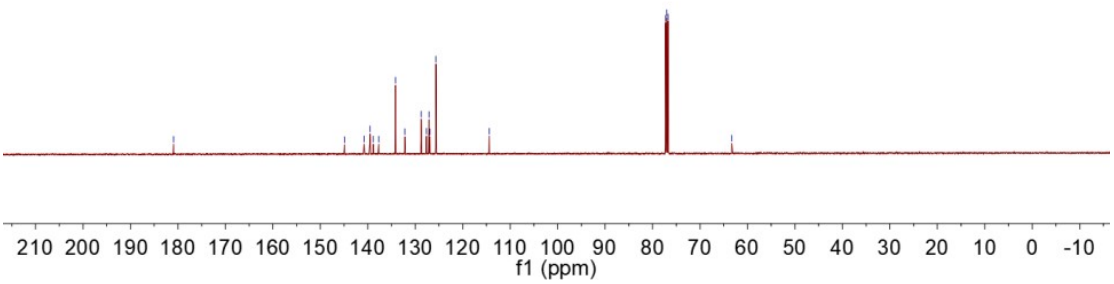
^{1}H NMR of **3f** (400 MHz, $CDCl_3$, ppm):



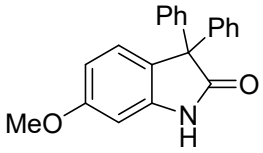
^{13}C NMR of **3f** (100 MHz, $CDCl_3$, ppm):



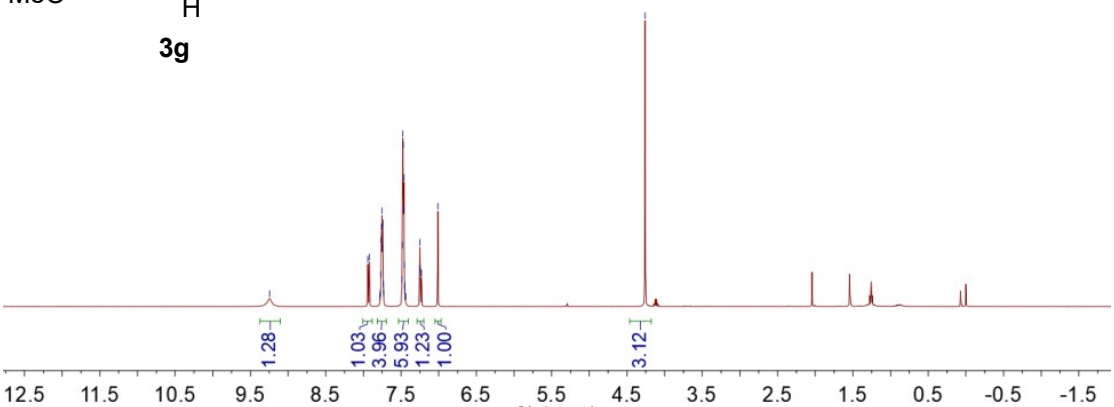
3f



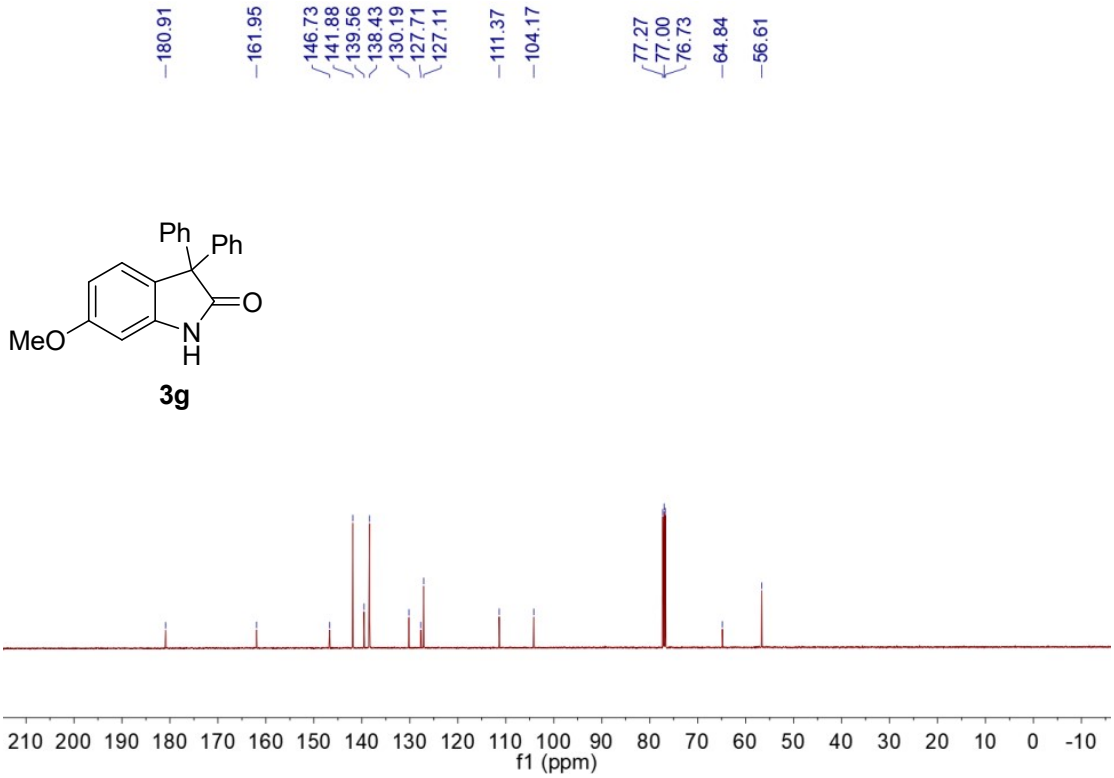
^{1}H NMR of **3g** (400 MHz, $CDCl_3$, ppm):



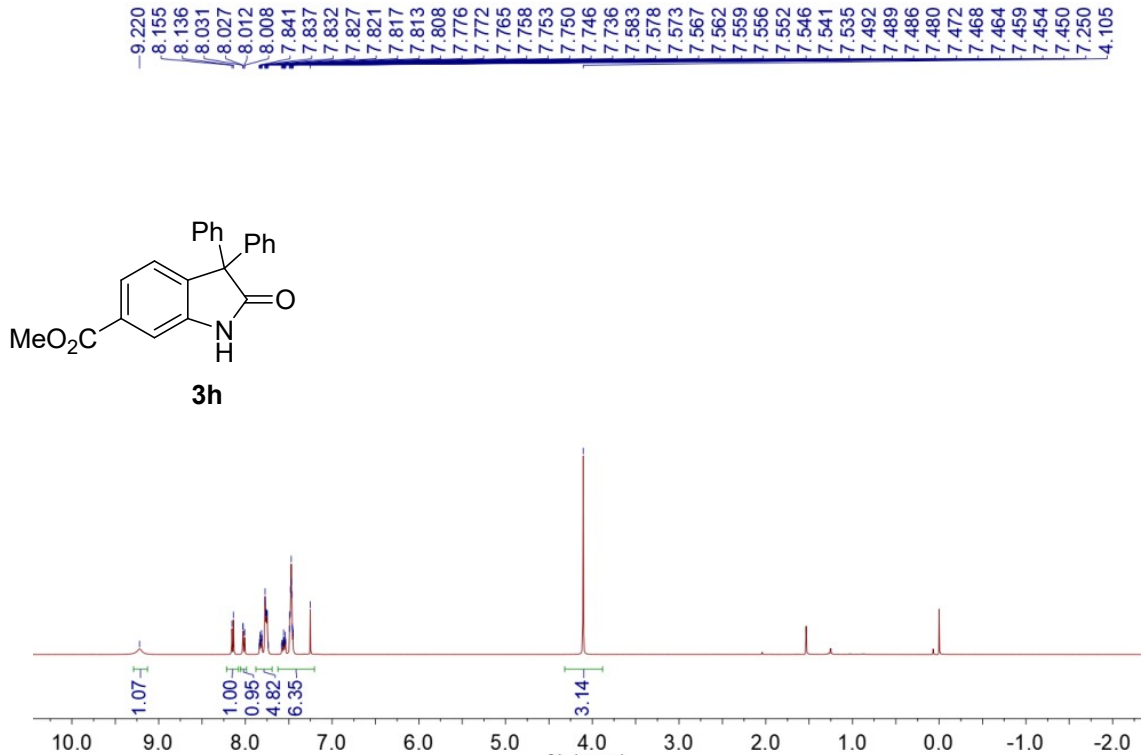
3g



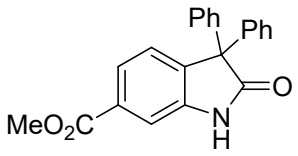
^{13}C NMR of **3g** (100 MHz, $CDCl_3$, ppm):



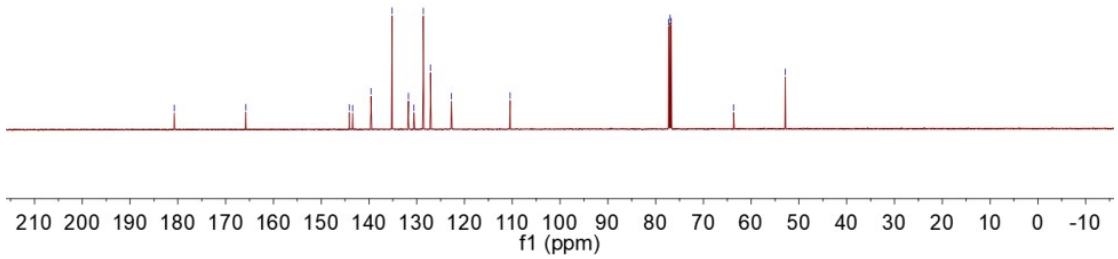
^{1}H NMR of **3h** (400 MHz, $CDCl_3$, ppm):



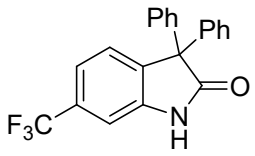
^{13}C NMR of **3h** (100 MHz, $CDCl_3$,ppm):



3h

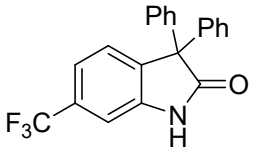


^{1}H NMR of **3i** (400 MHz, $CDCl_3$, ppm):

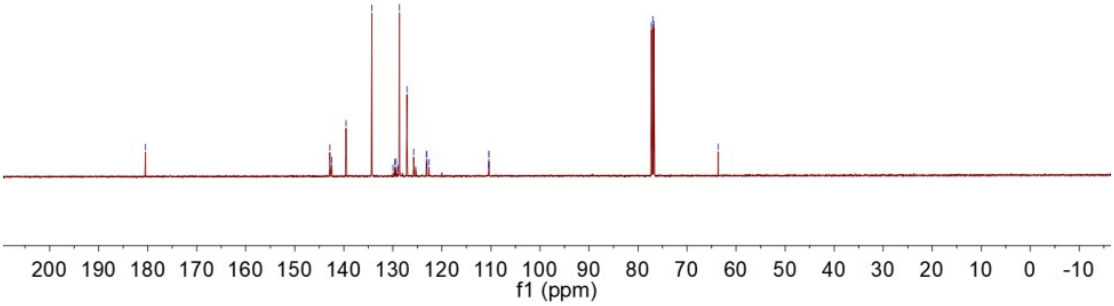


3i

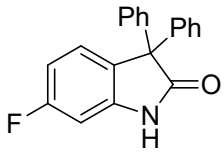
^{13}C NMR of **3i** (100 MHz, $CDCl_3$, ppm):



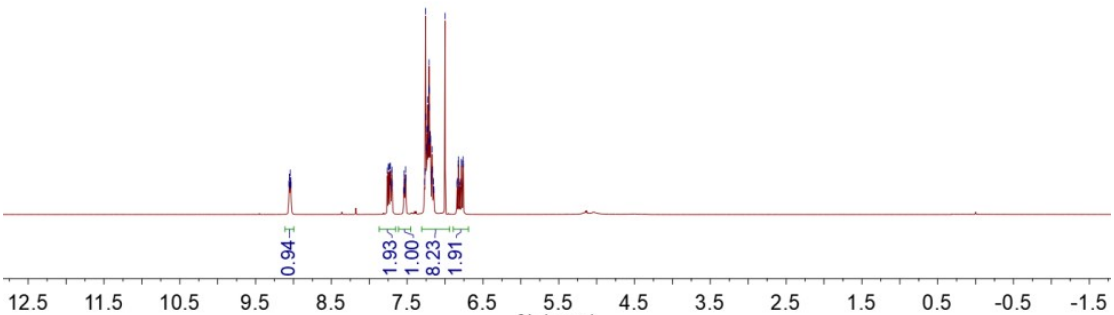
3i



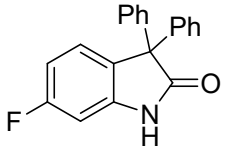
^{1}H NMR of **3j** (400 MHz, $CDCl_3$, ppm):



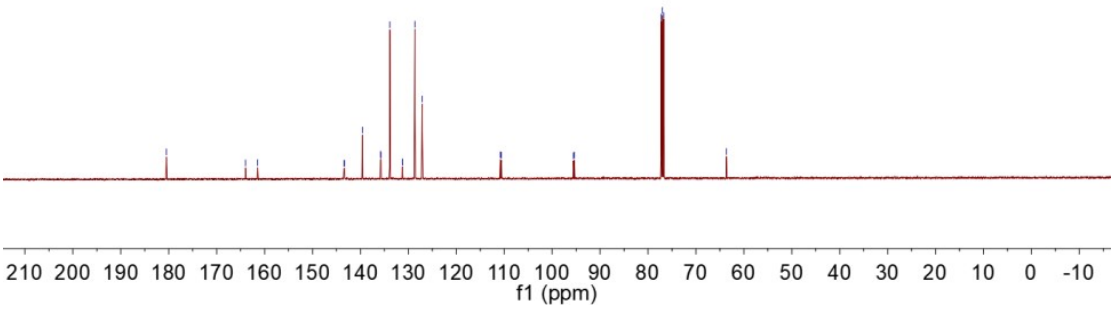
3j



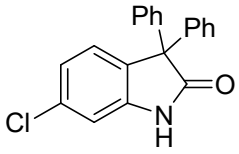
^{13}C NMR of **3j** (100 MHz, $CDCl_3$, ppm):



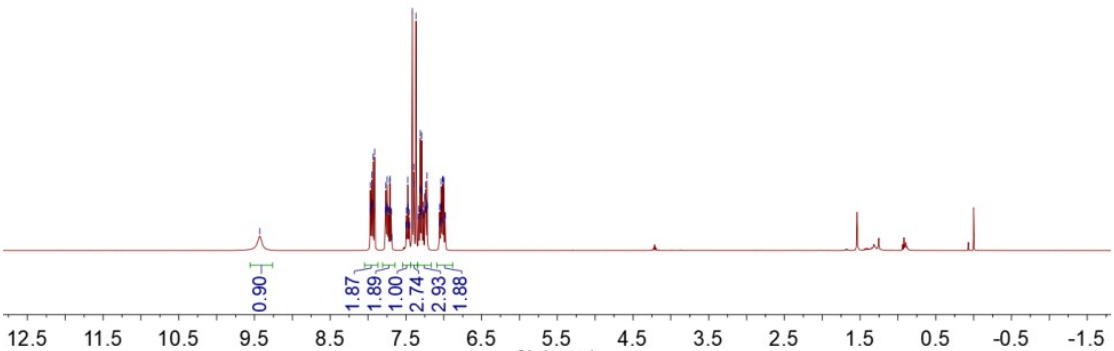
3j



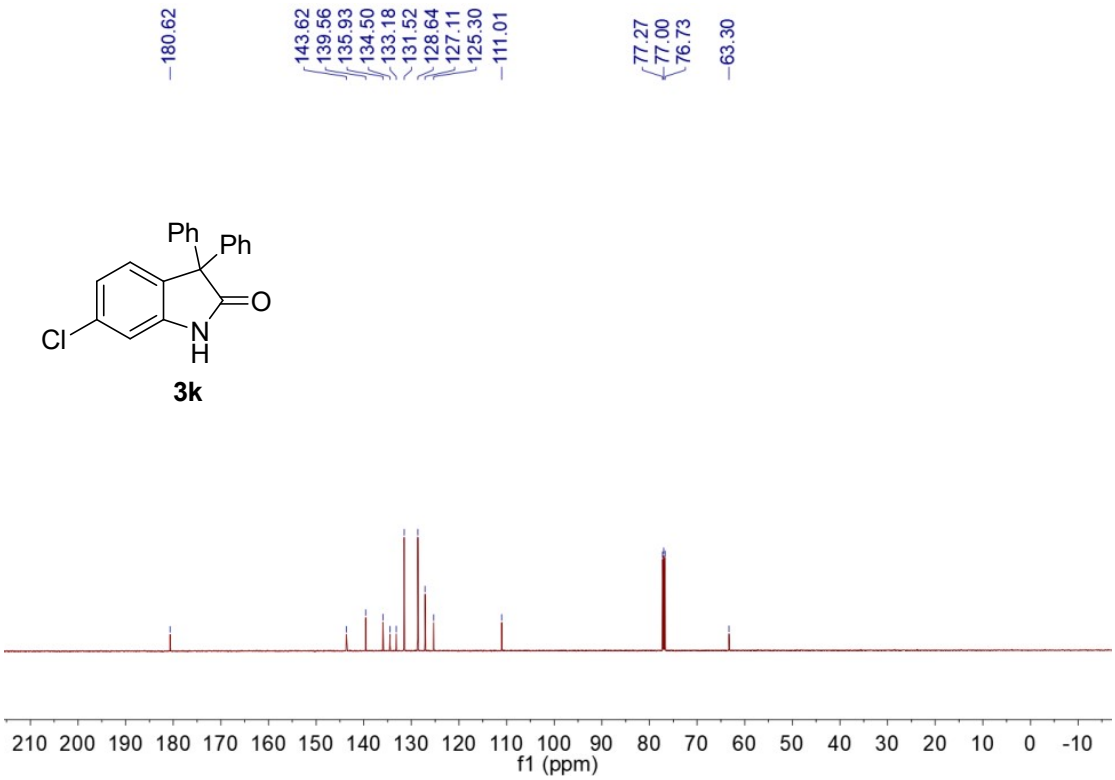
^{1}H NMR of **3k** (400 MHz, $CDCl_3$, ppm):



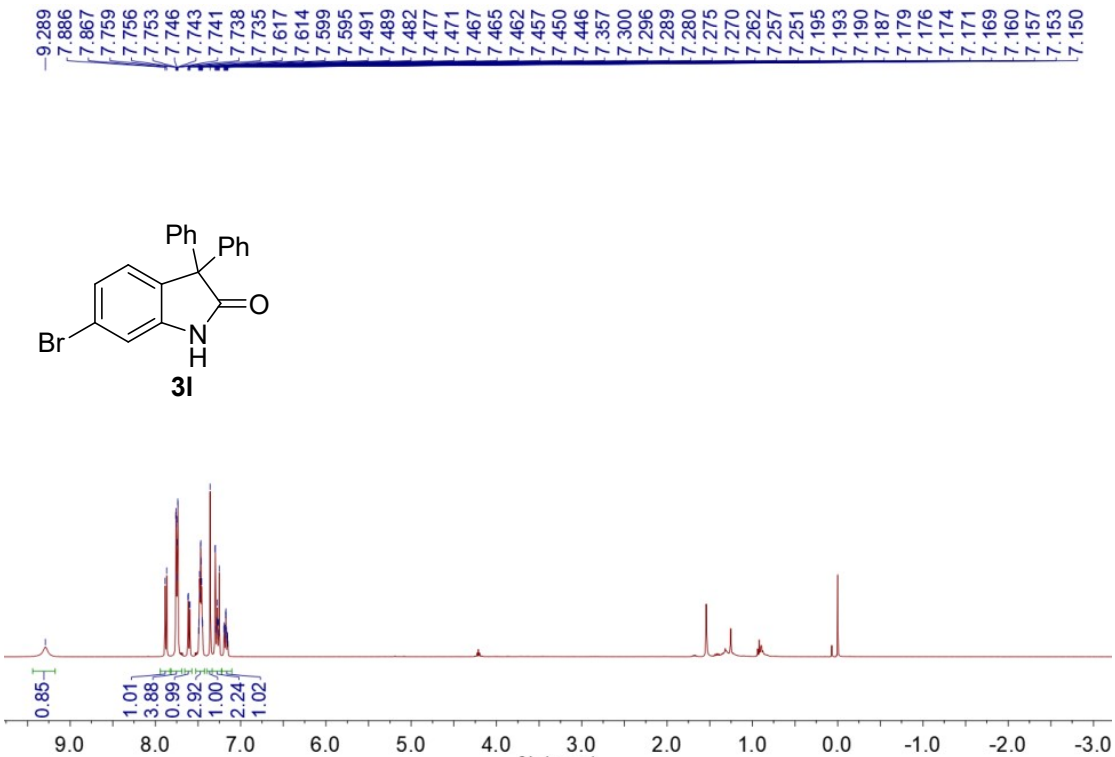
3k



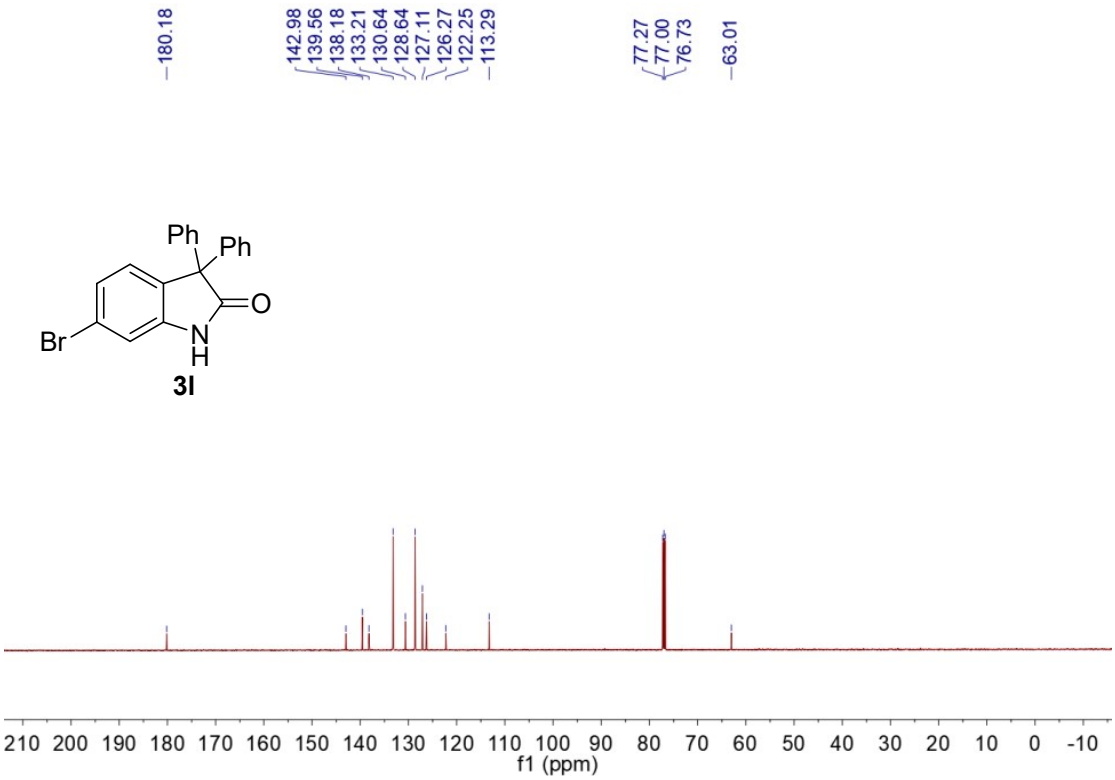
^{13}C NMR of **3k** (100 MHz, $CDCl_3$, ppm):



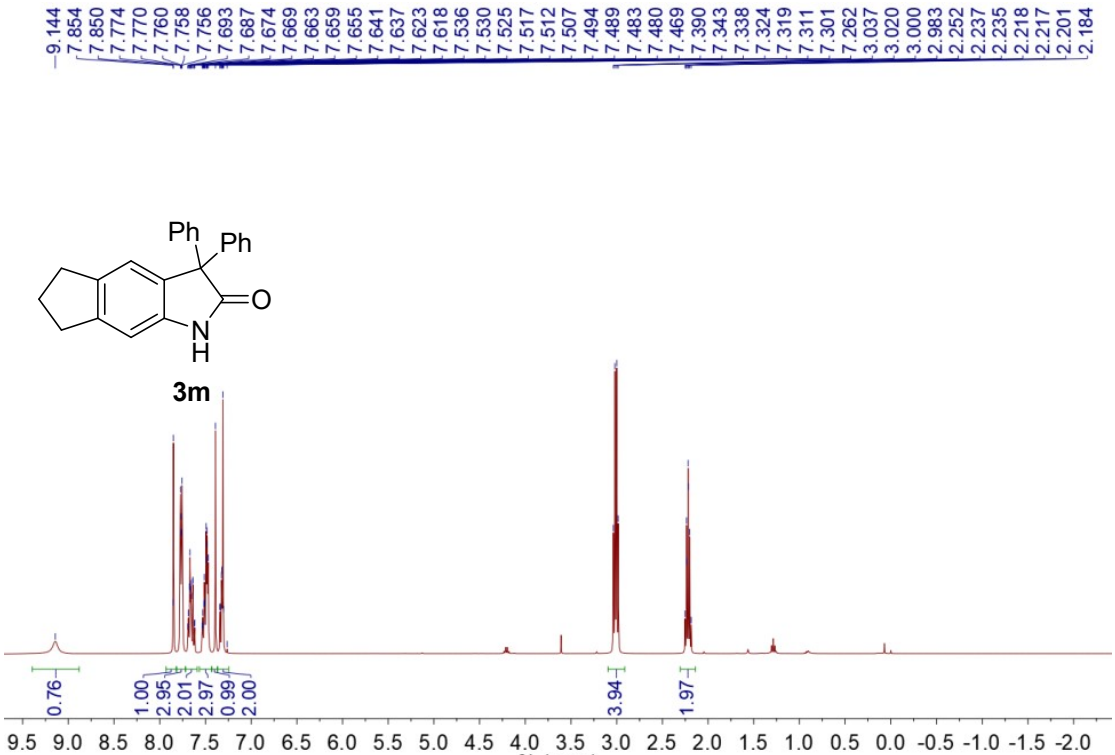
^{1}H NMR of **3l** (400 MHz, $CDCl_3$, ppm):



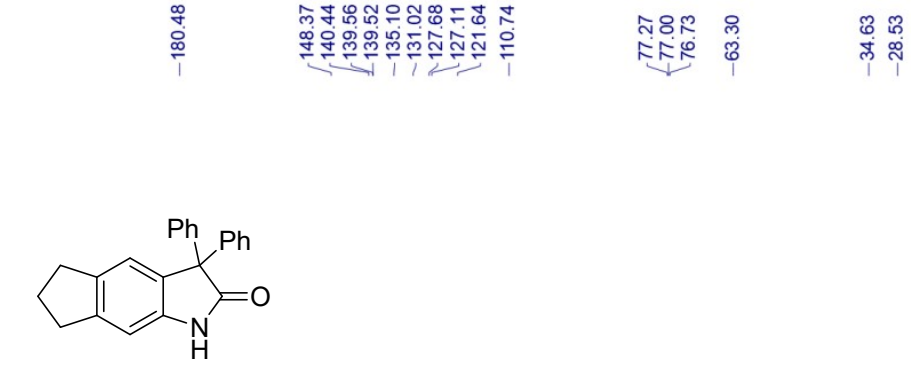
^{13}C NMR of **3l** (100 MHz, $CDCl_3$, ppm):



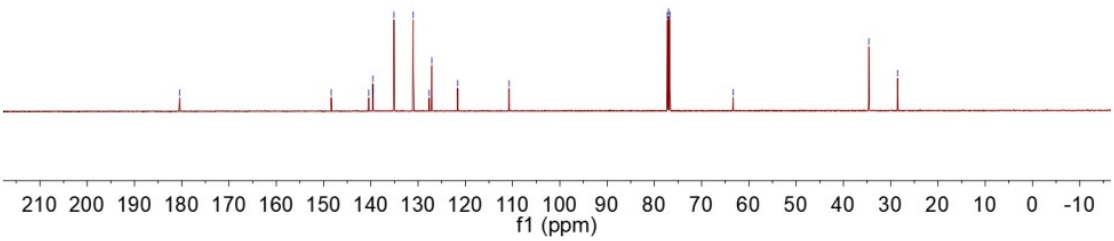
^{1}H NMR of **3m** (400 MHz, $CDCl_3$, ppm):



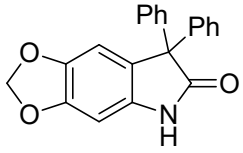
^{13}C NMR of **3m** (100 MHz, $CDCl_3$, ppm):



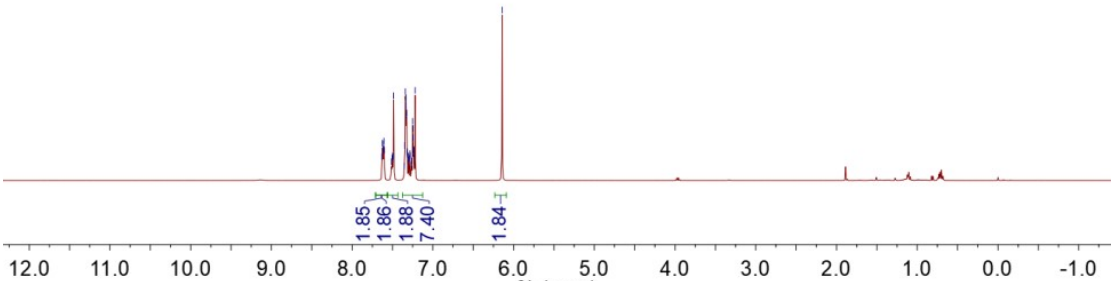
3m



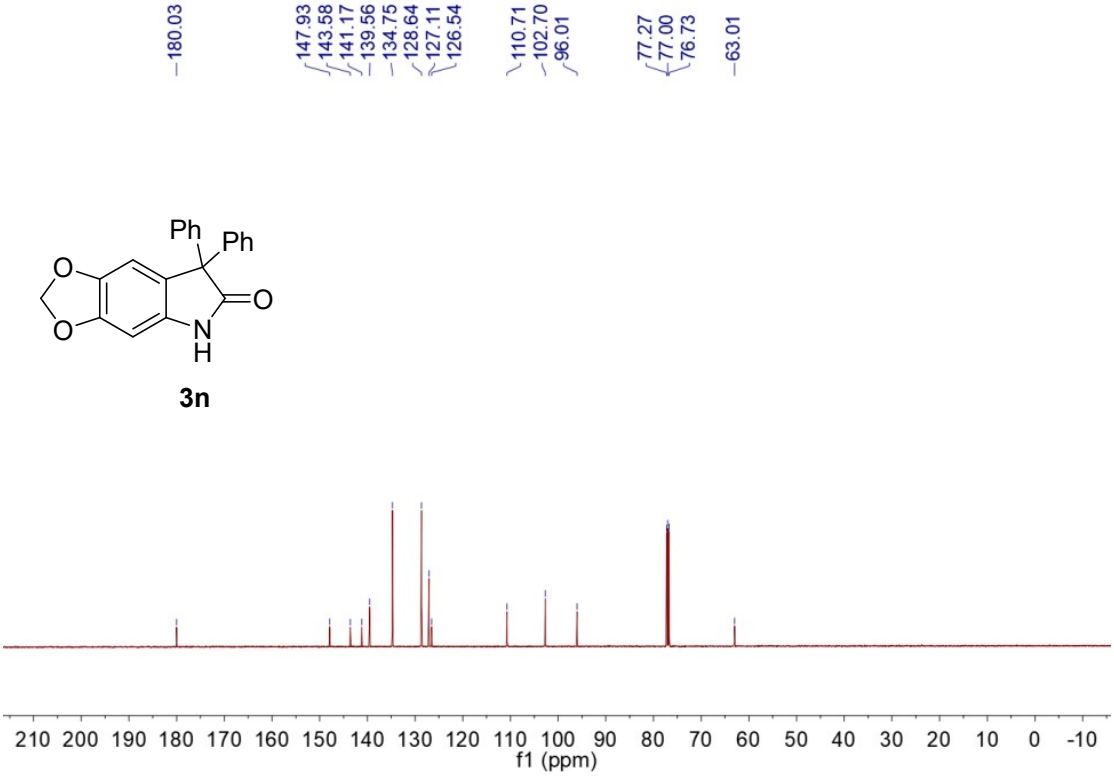
^{1}H NMR of **3n** (400 MHz, $CDCl_3$, ppm):



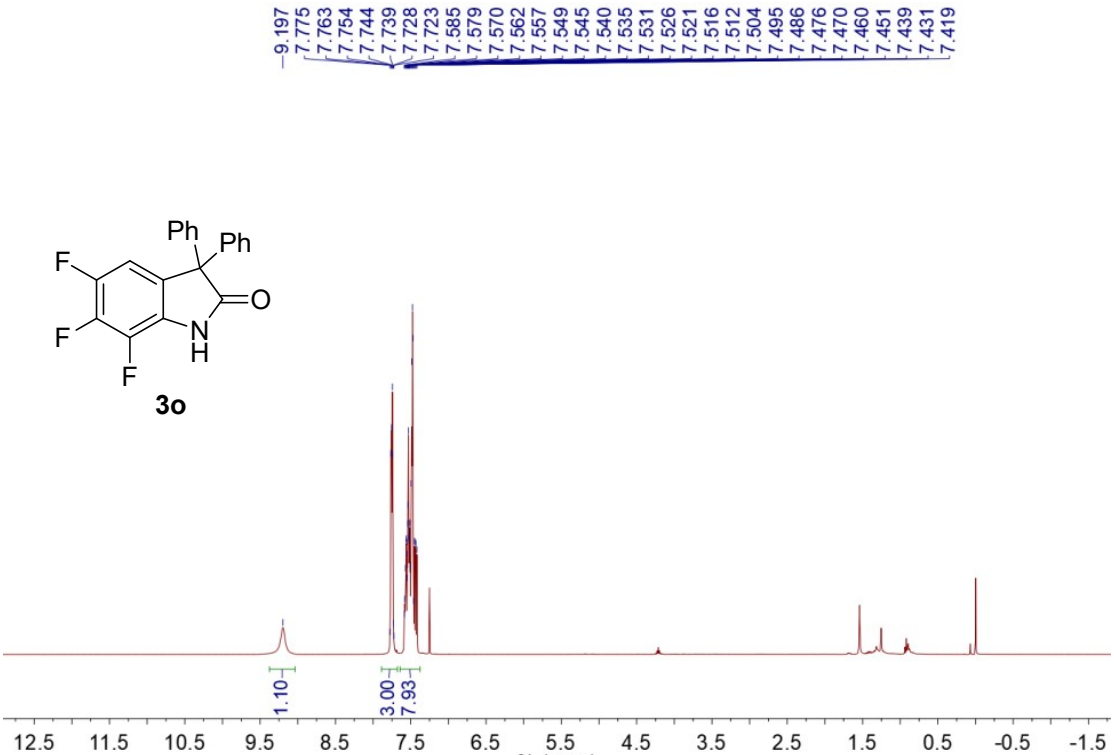
3n



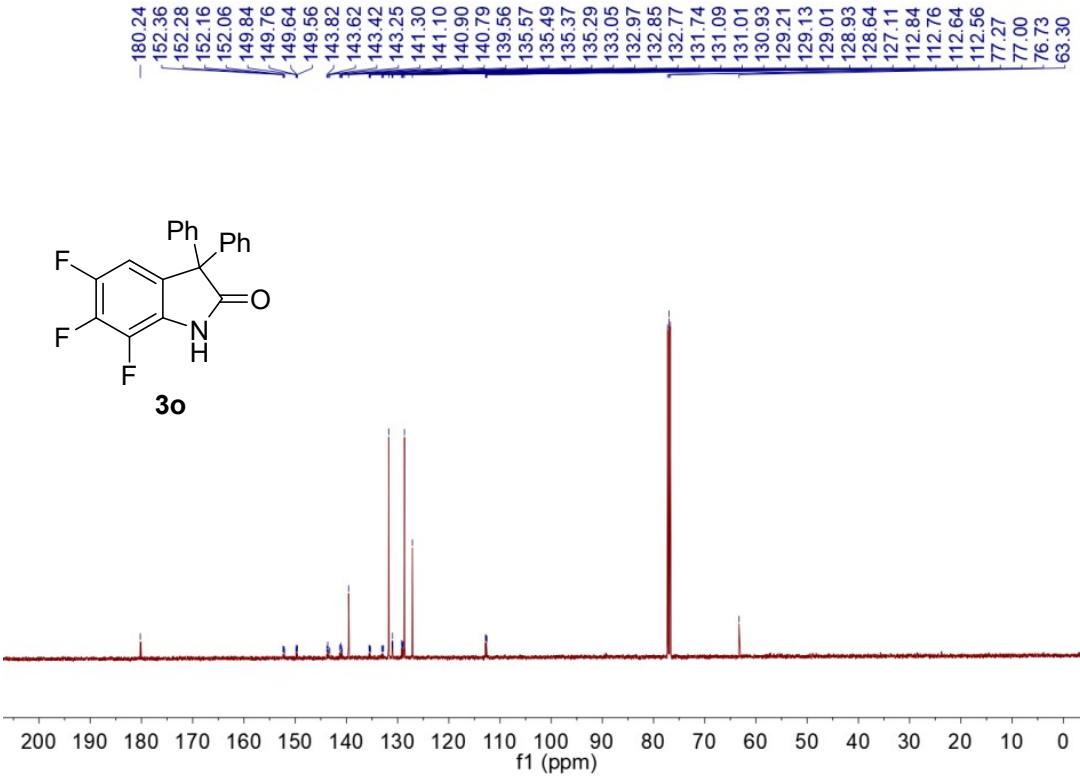
^{13}C NMR of **3n** (100 MHz, $CDCl_3$, ppm):



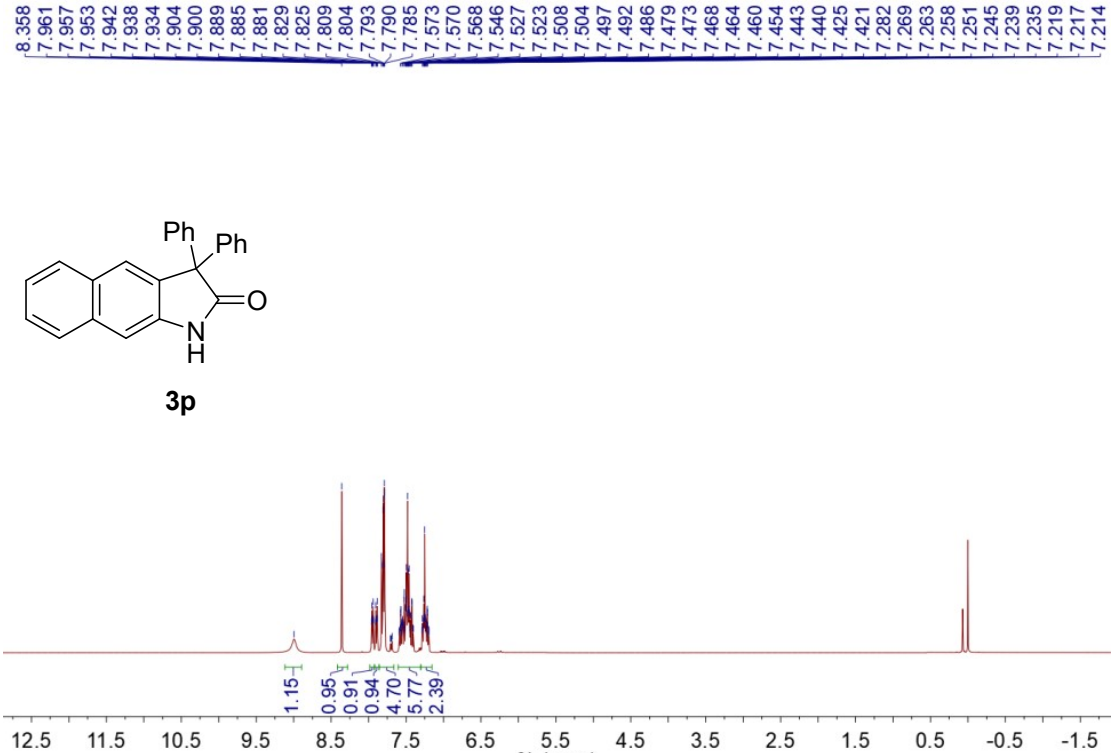
^{1}H NMR of **3o** (400 MHz, $CDCl_3$, ppm):



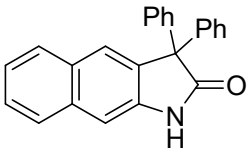
^{13}C NMR of **3o** (100 MHz, $CDCl_3$, ppm):



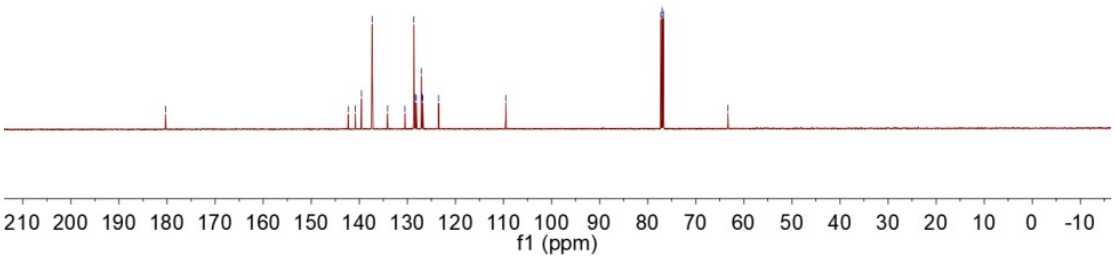
^{1}H NMR of **3p** (400 MHz, $CDCl_3$, ppm):



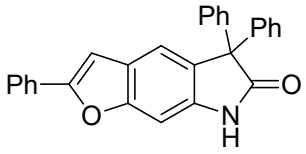
^{13}C NMR of **3p** (100 MHz, $CDCl_3$, ppm):



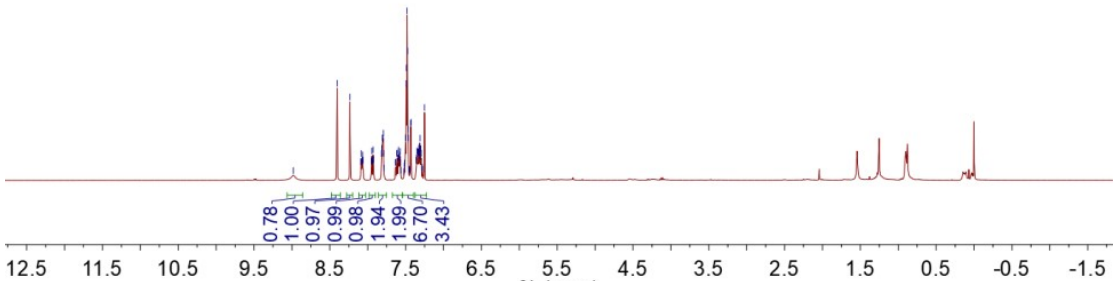
3p



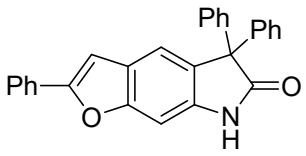
^{1}H NMR of **3q** (400 MHz, $CDCl_3$, ppm):



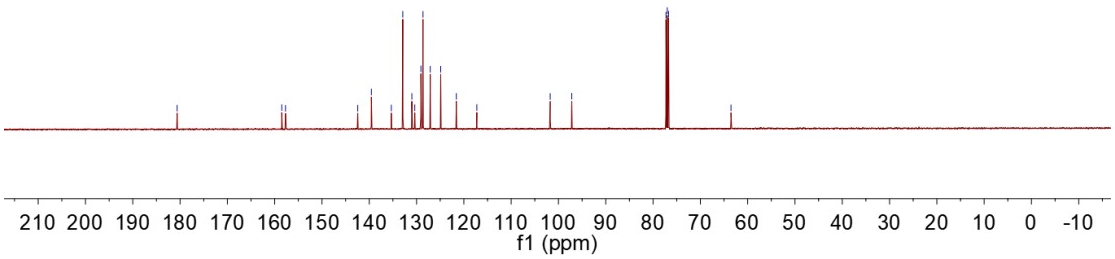
3q



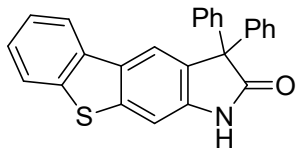
^{13}C NMR of **3q** (100 MHz, $CDCl_3$, ppm):



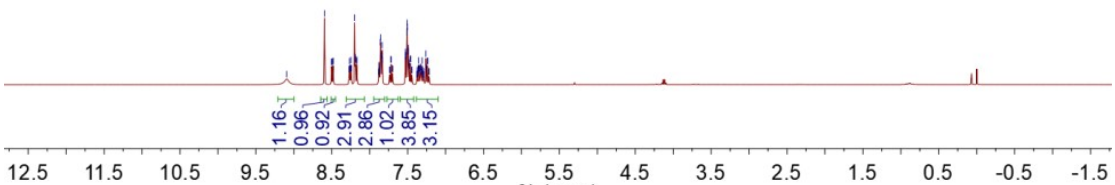
3q



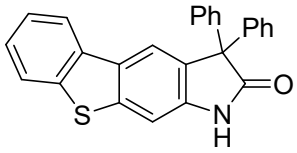
^{1}H NMR of **3r** (400 MHz, $CDCl_3$, ppm):



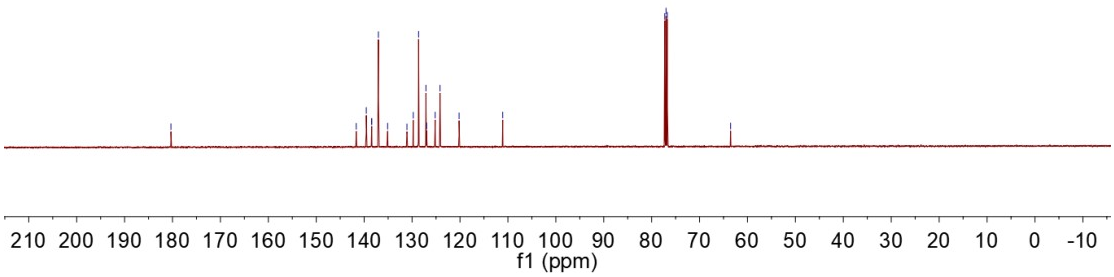
3r



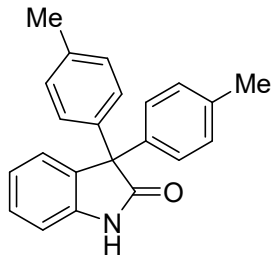
^{13}C NMR of **3r** (100 MHz, $CDCl_3$, ppm):



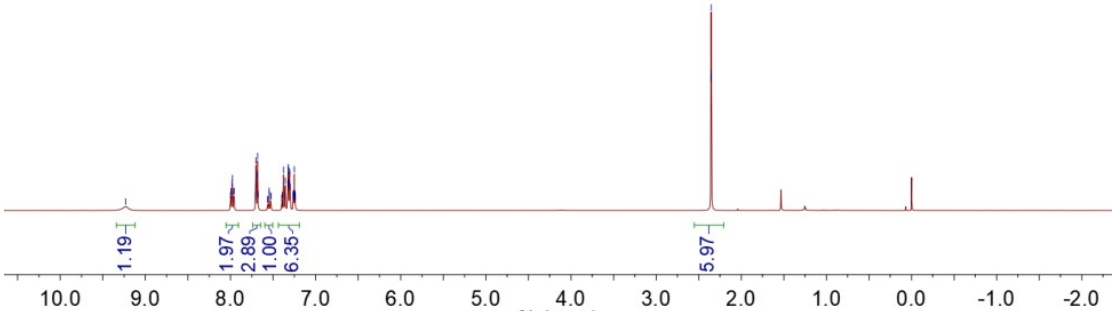
3r



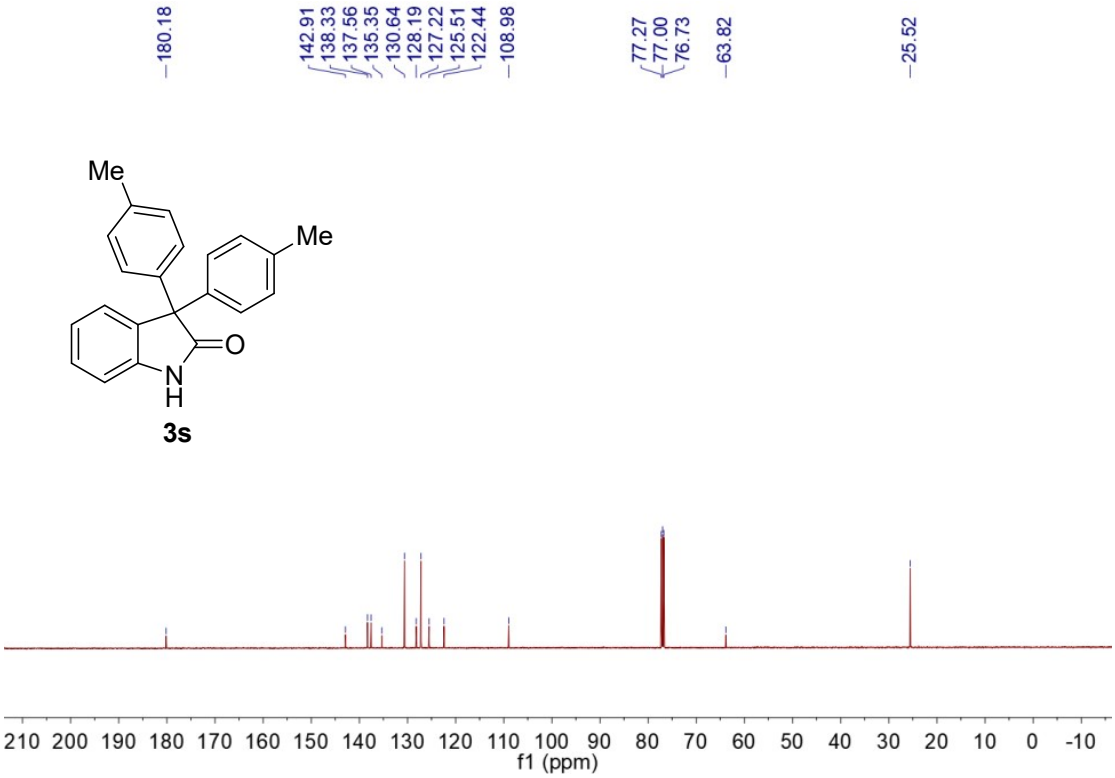
^{1}H NMR of **3s** (400 MHz, $CDCl_3$, ppm):



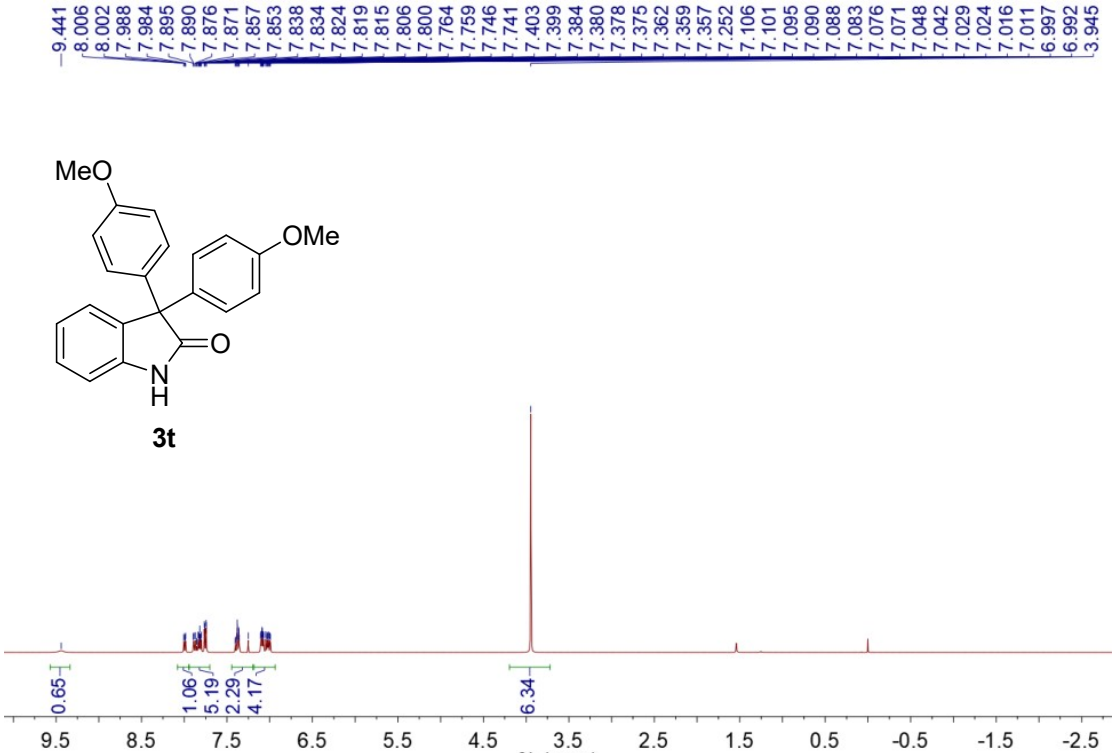
3s



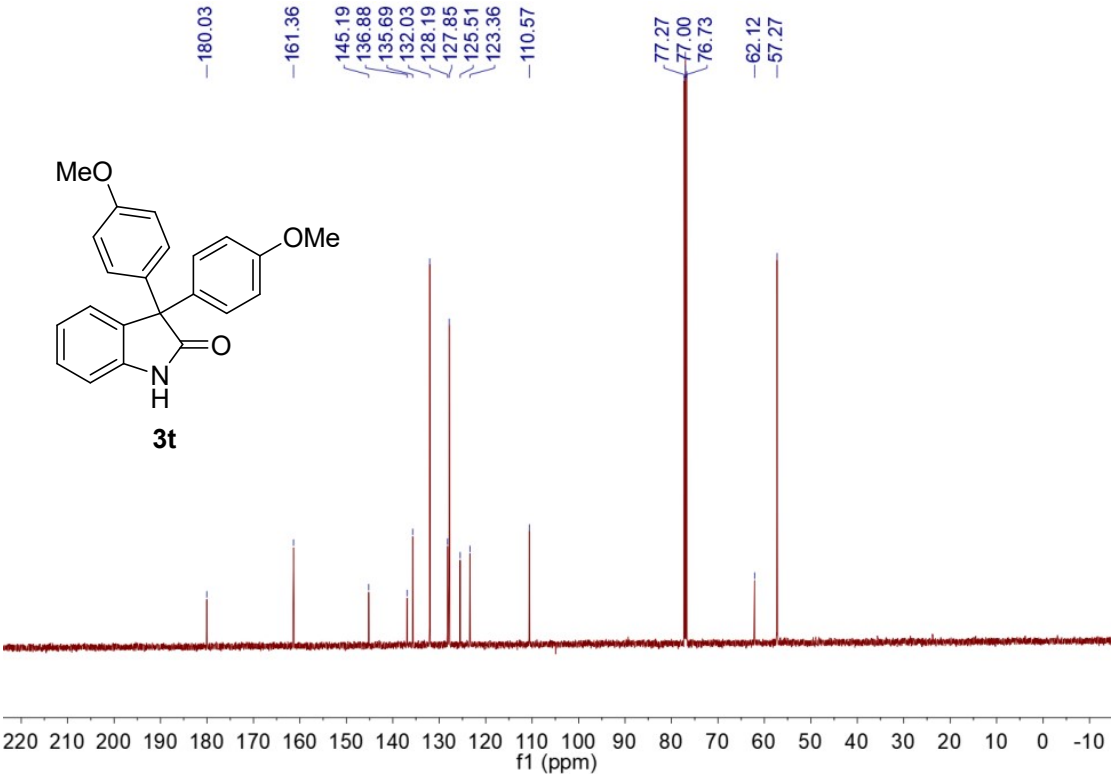
^{13}C NMR of **3s** (100 MHz, $CDCl_3$, ppm):



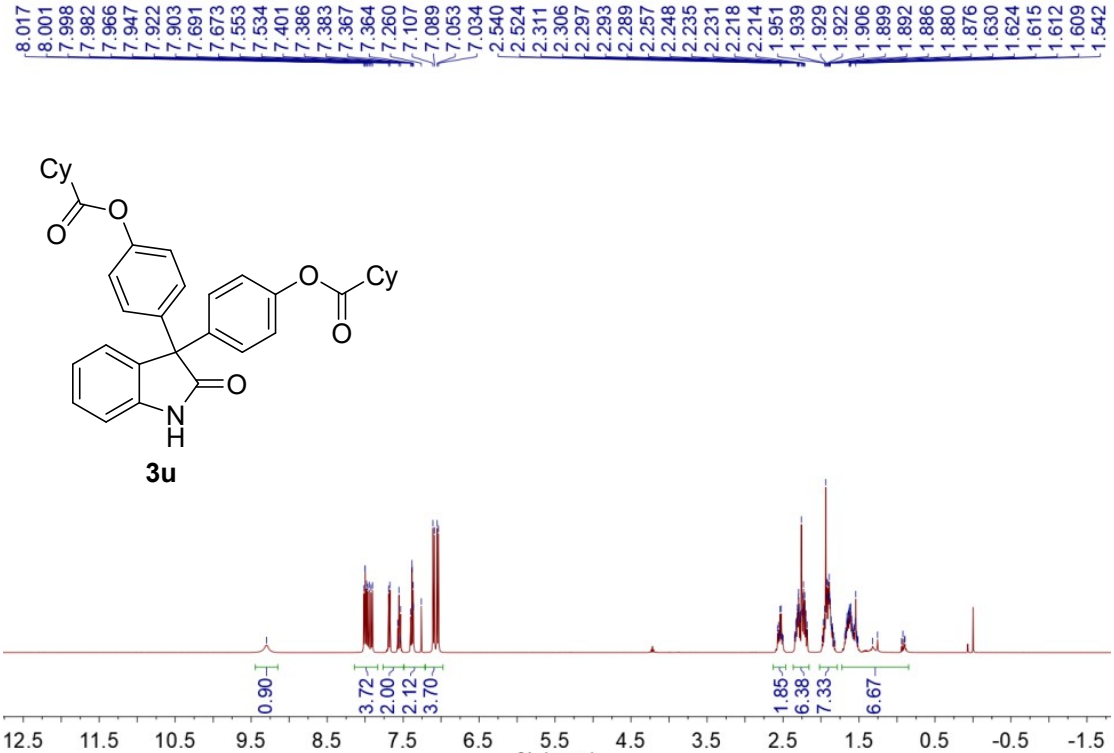
^{1}H NMR of **3t** (400 MHz, $CDCl_3$, ppm):



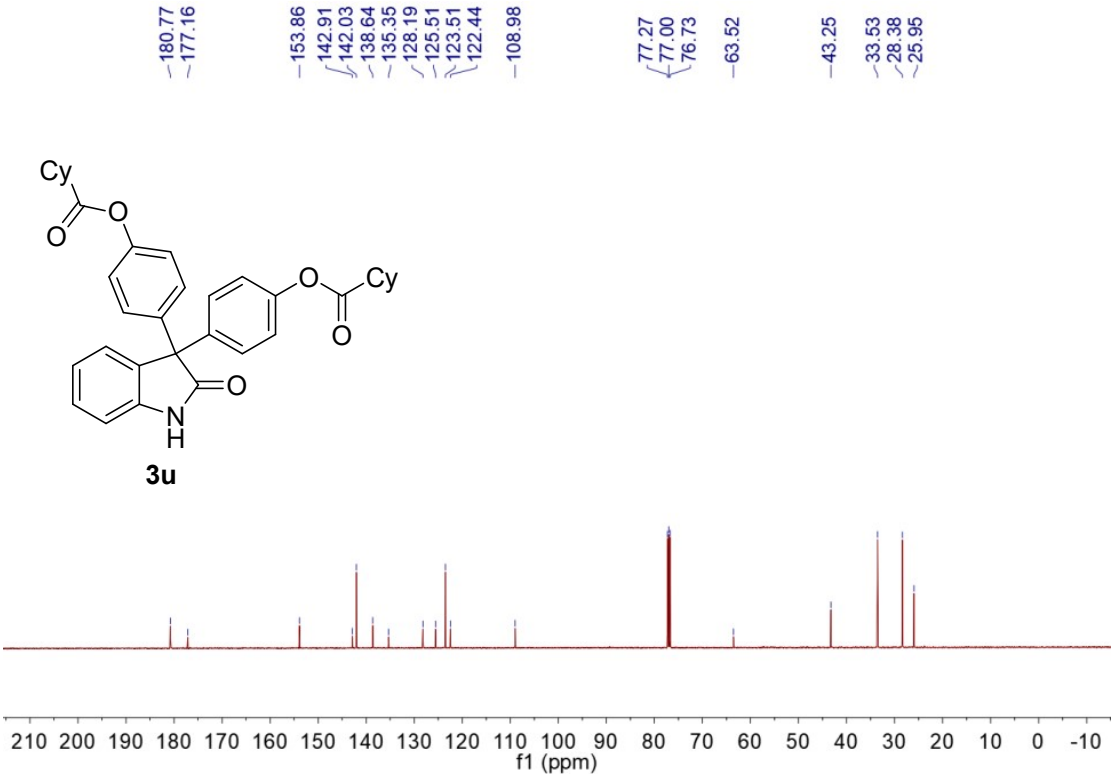
^{13}C NMR of **3t** (100 MHz, $CDCl_3$, ppm):



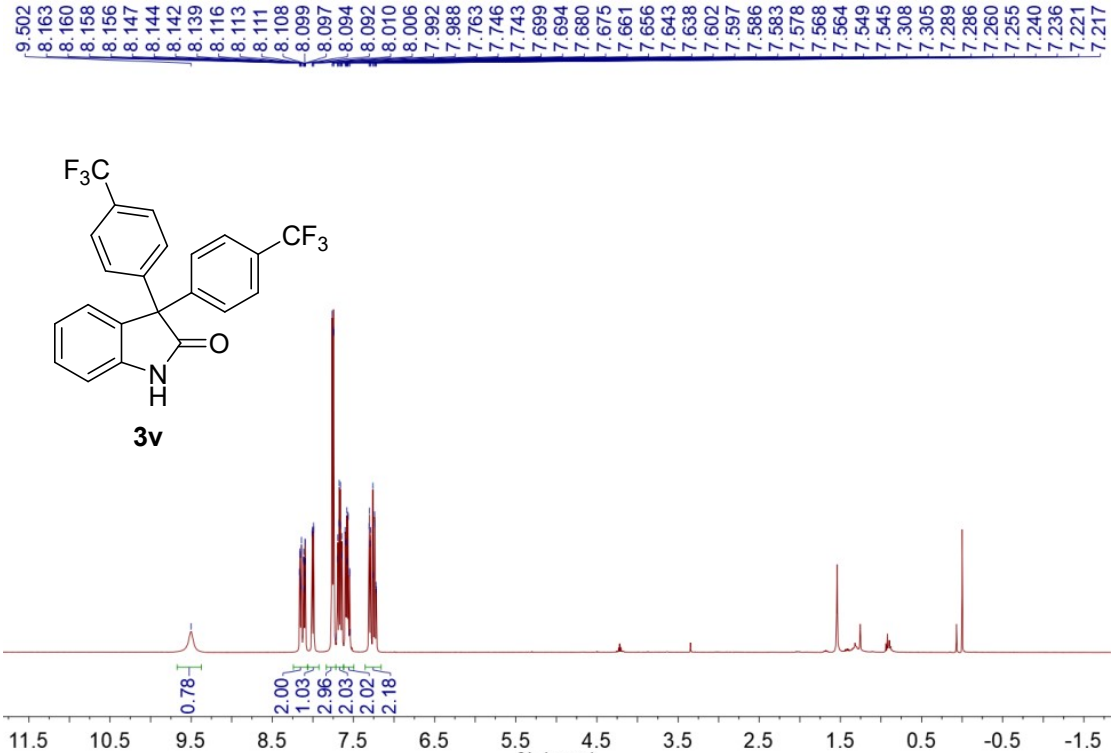
^{1}H NMR of **3u** (400 MHz, $CDCl_3$, ppm):



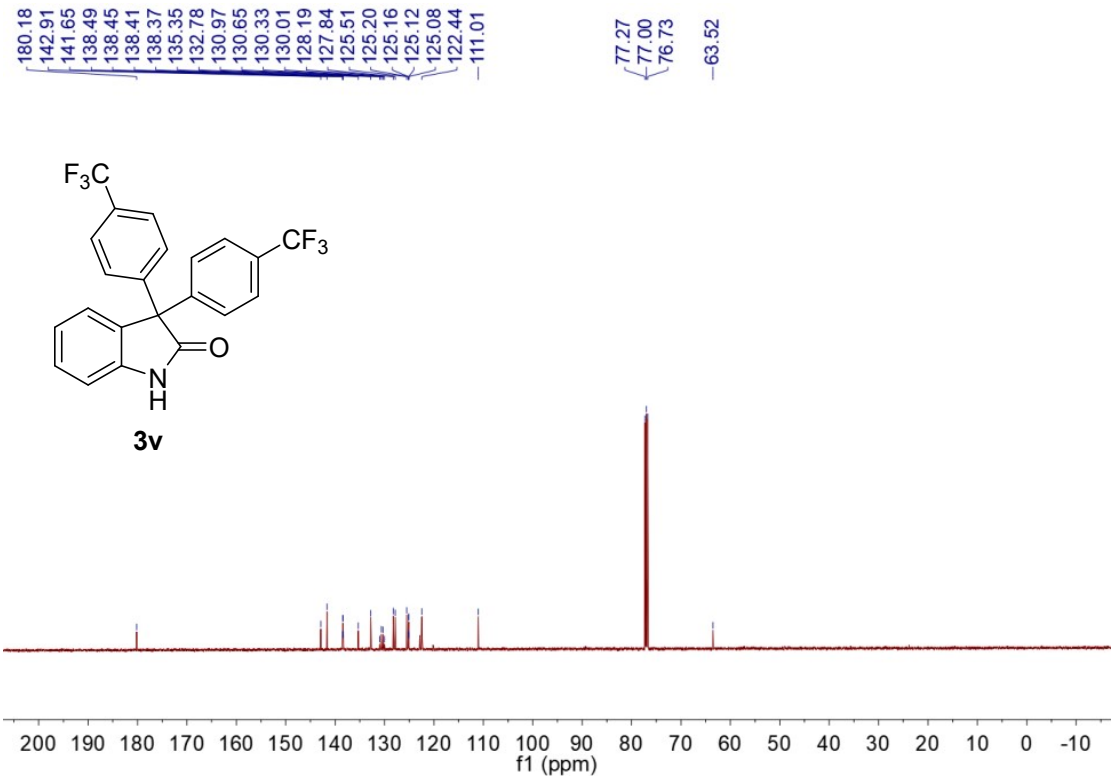
^{13}C NMR of **3u** (100 MHz, $CDCl_3$, ppm):



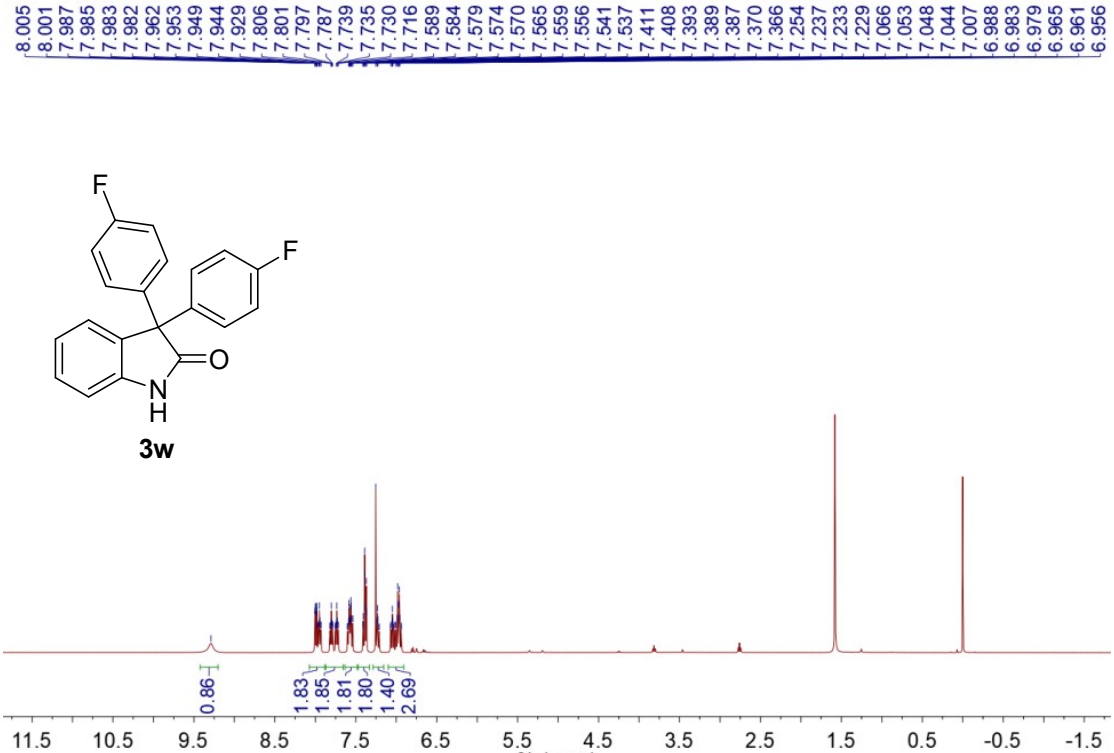
^{1}H NMR of **3v** (400 MHz, $CDCl_3$, ppm):



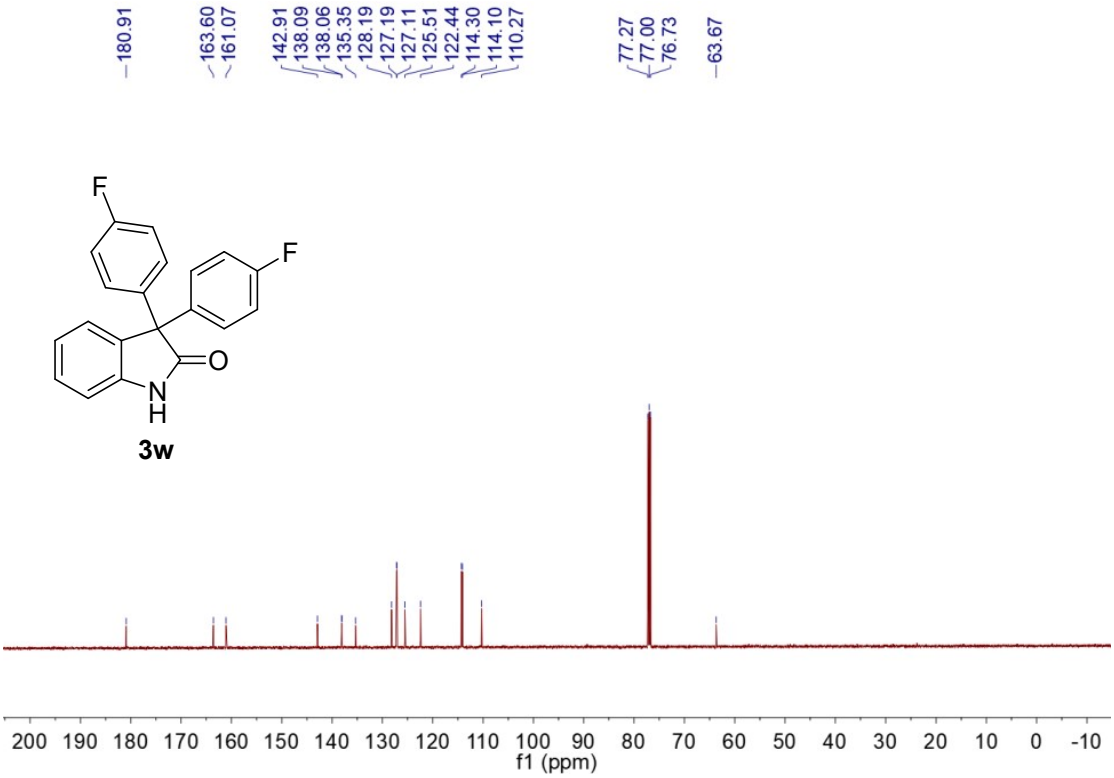
^{13}C NMR of **3v** (100 MHz, $CDCl_3$, ppm):



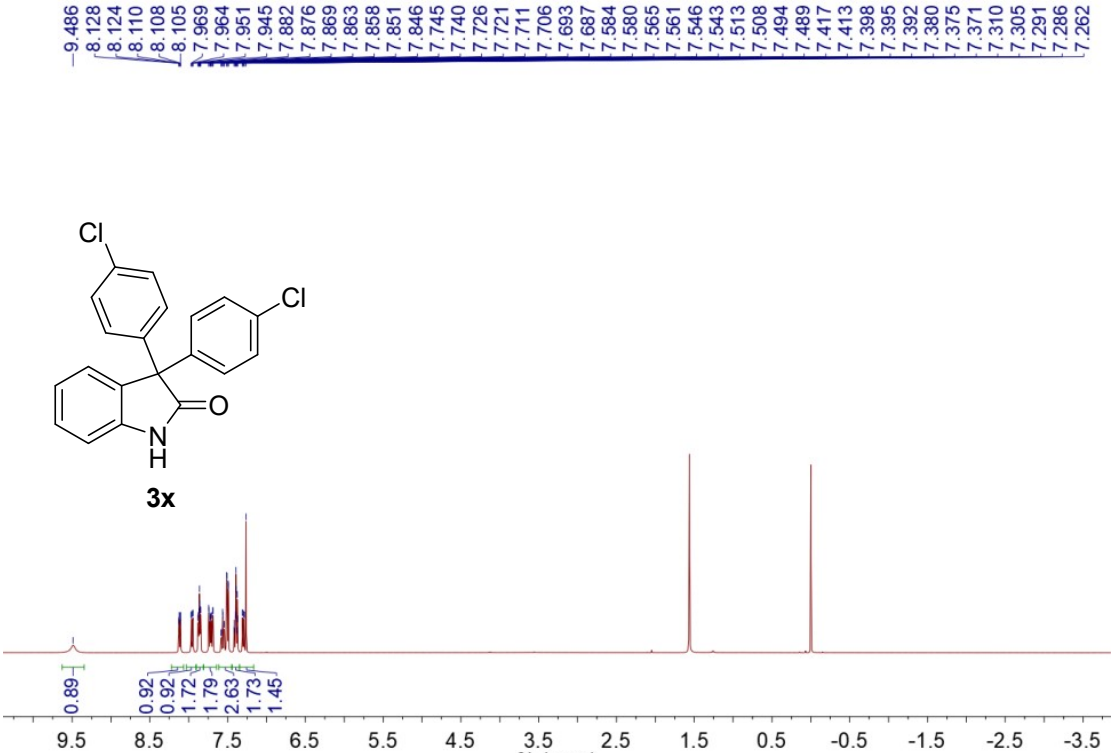
^{1}H NMR of **3w** (400 MHz, $CDCl_3$, ppm):



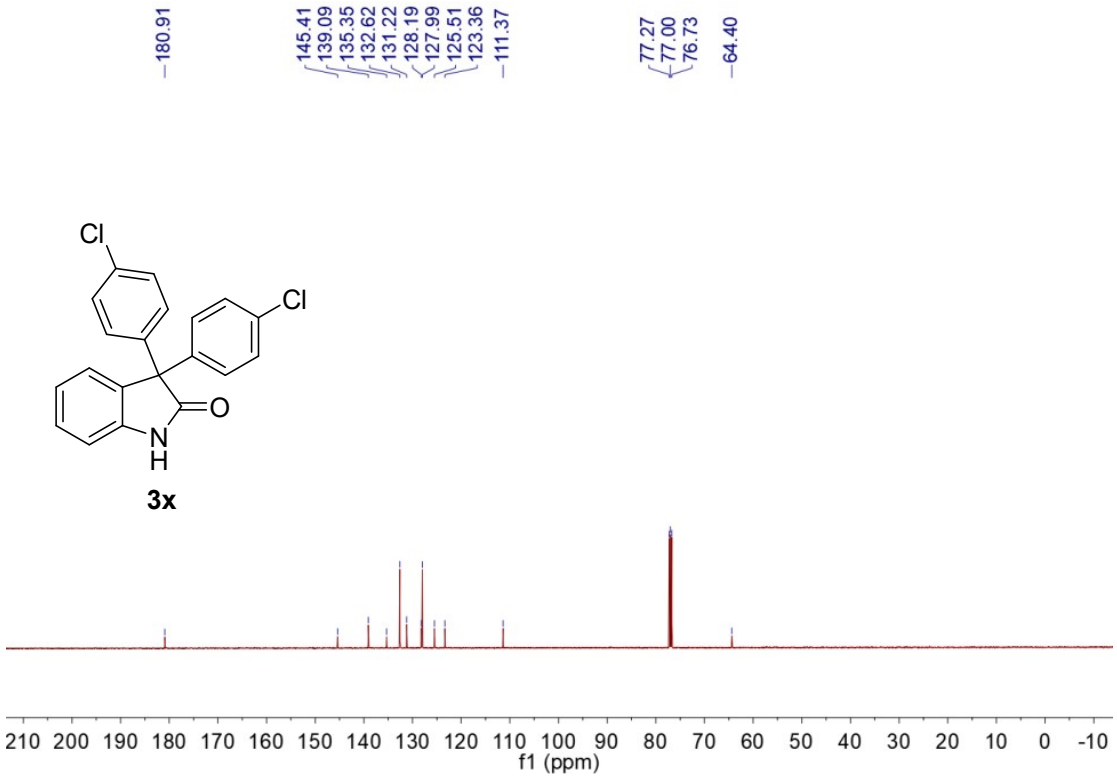
^{13}C NMR of **3w** (100 MHz, $CDCl_3$, ppm):



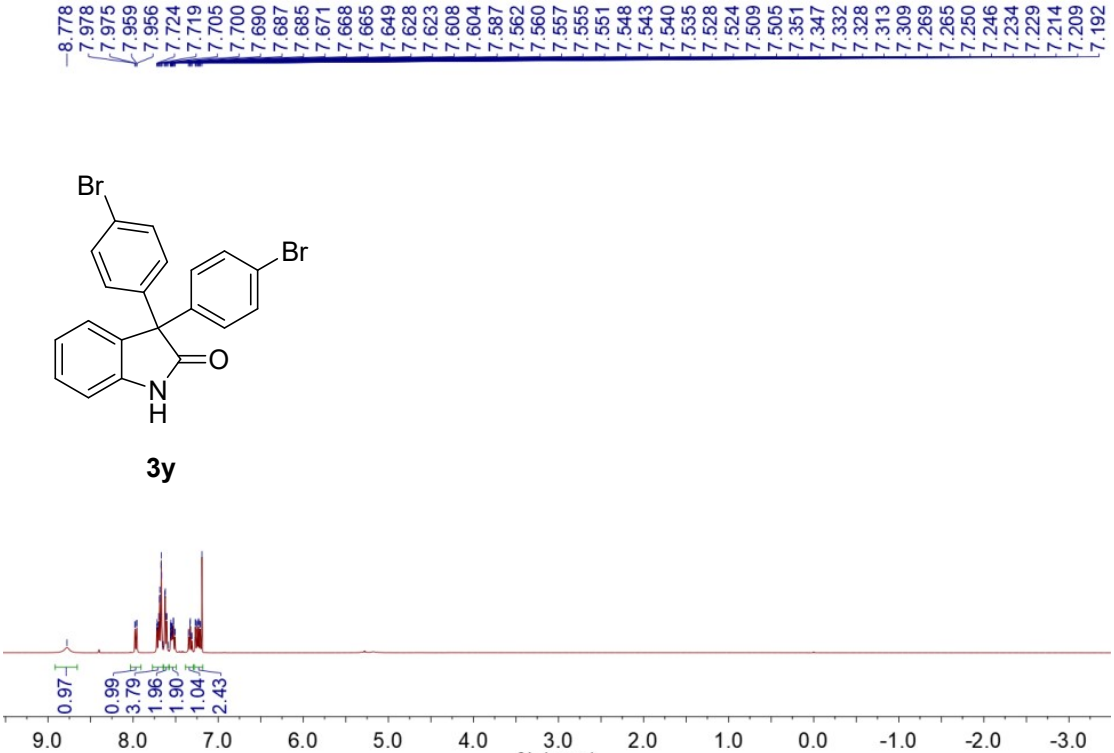
^{1}H NMR of **3x** (400 MHz, $CDCl_3$, ppm):



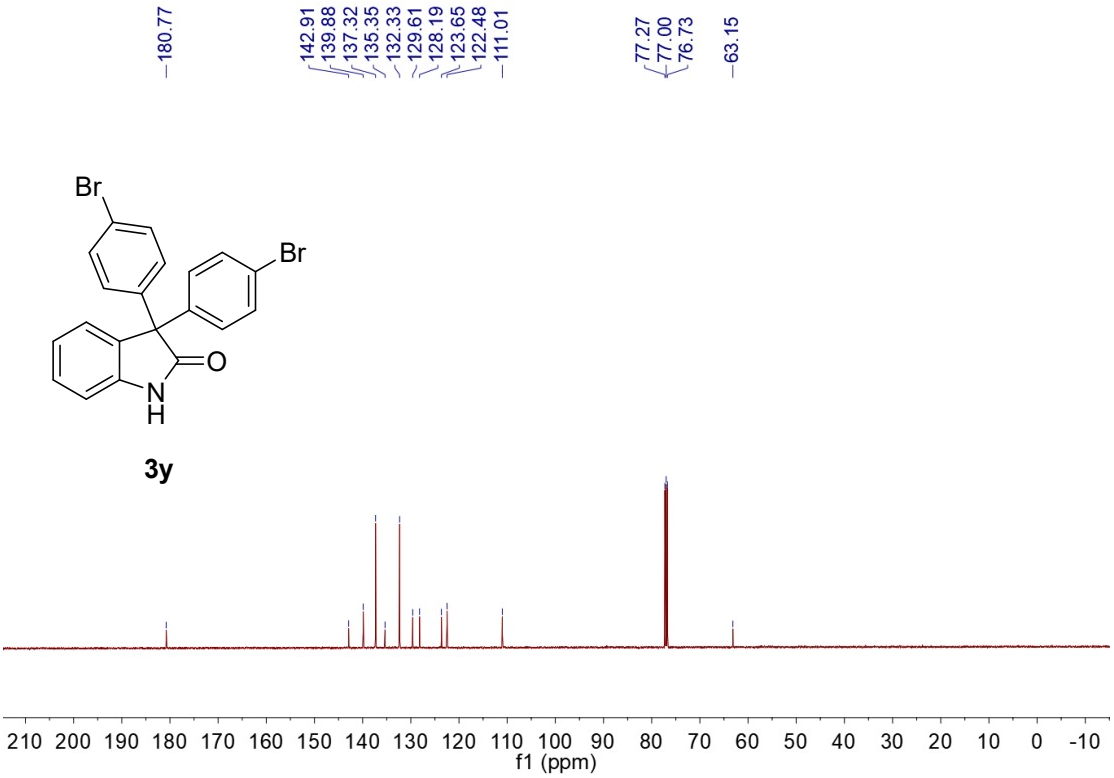
^{13}C NMR of **3x** (100 MHz, $CDCl_3$, ppm):



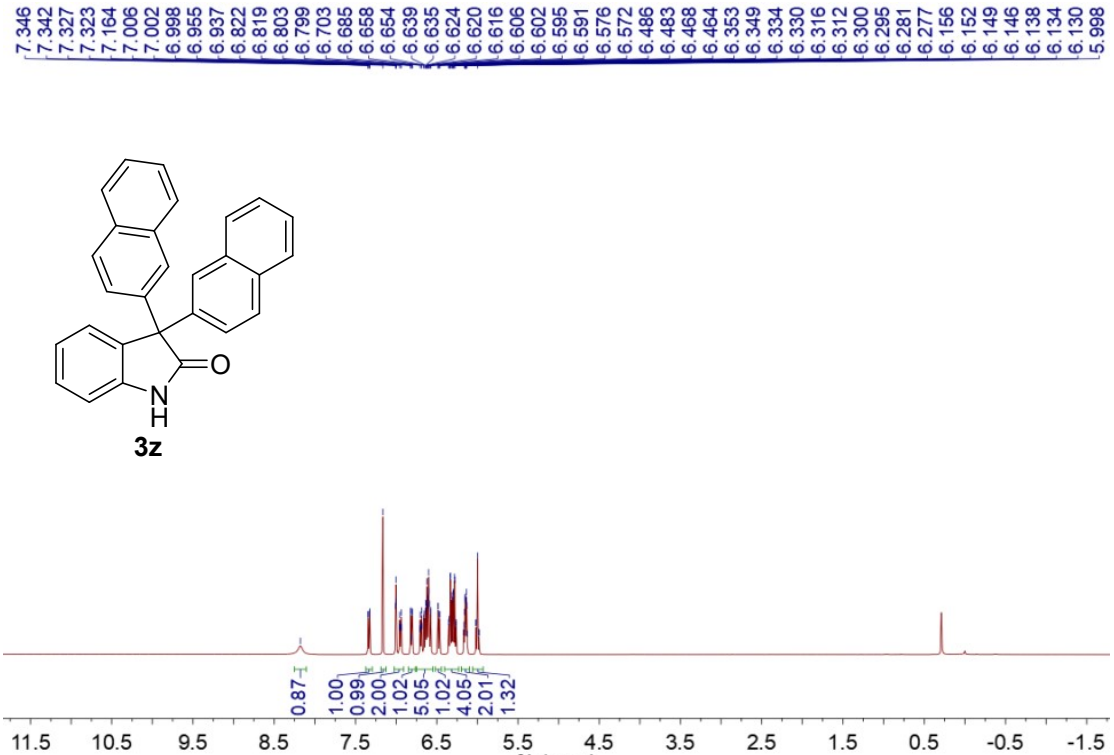
^{1}H NMR of **3y** (400 MHz, $CDCl_3$, ppm):



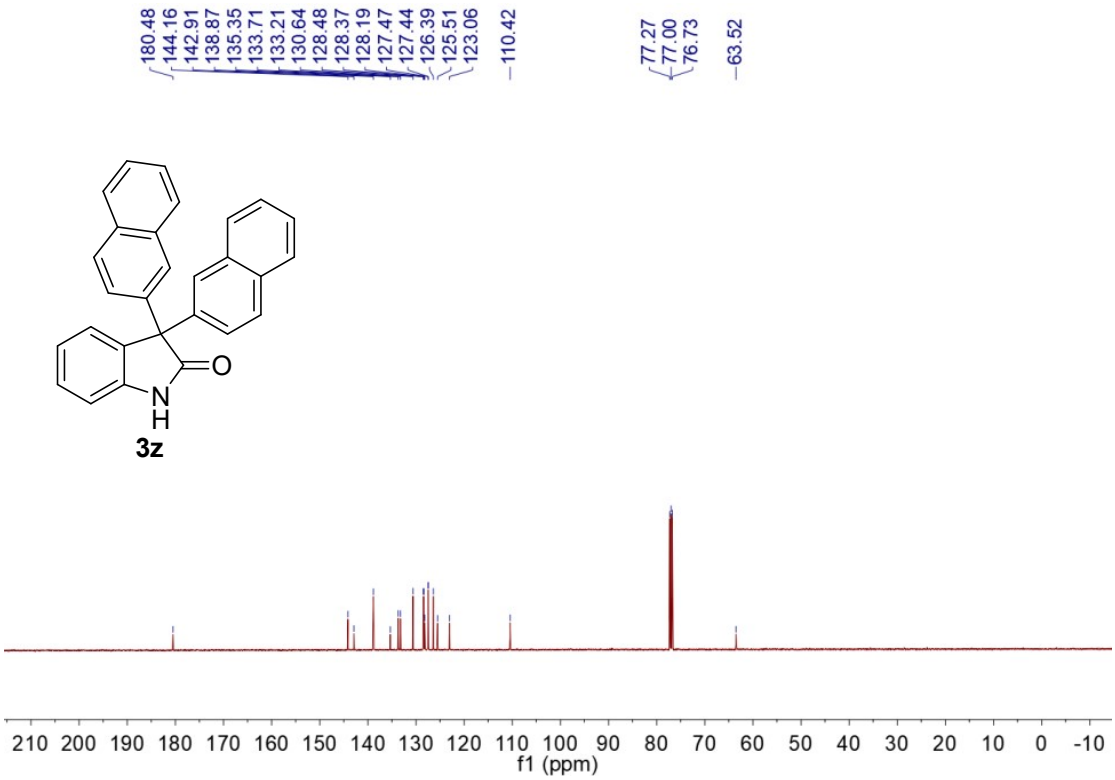
^{13}C NMR of **3y** (100 MHz, $CDCl_3$, ppm):



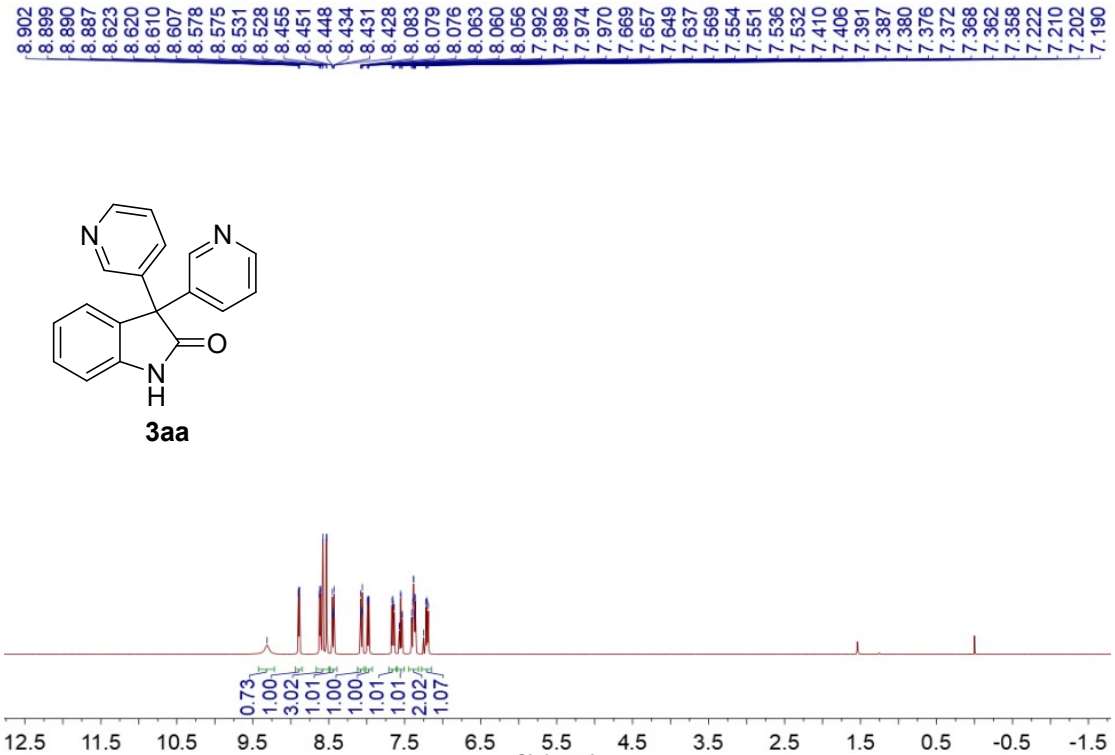
^{1}H NMR of **3z** (400 MHz, $CDCl_3$, ppm):



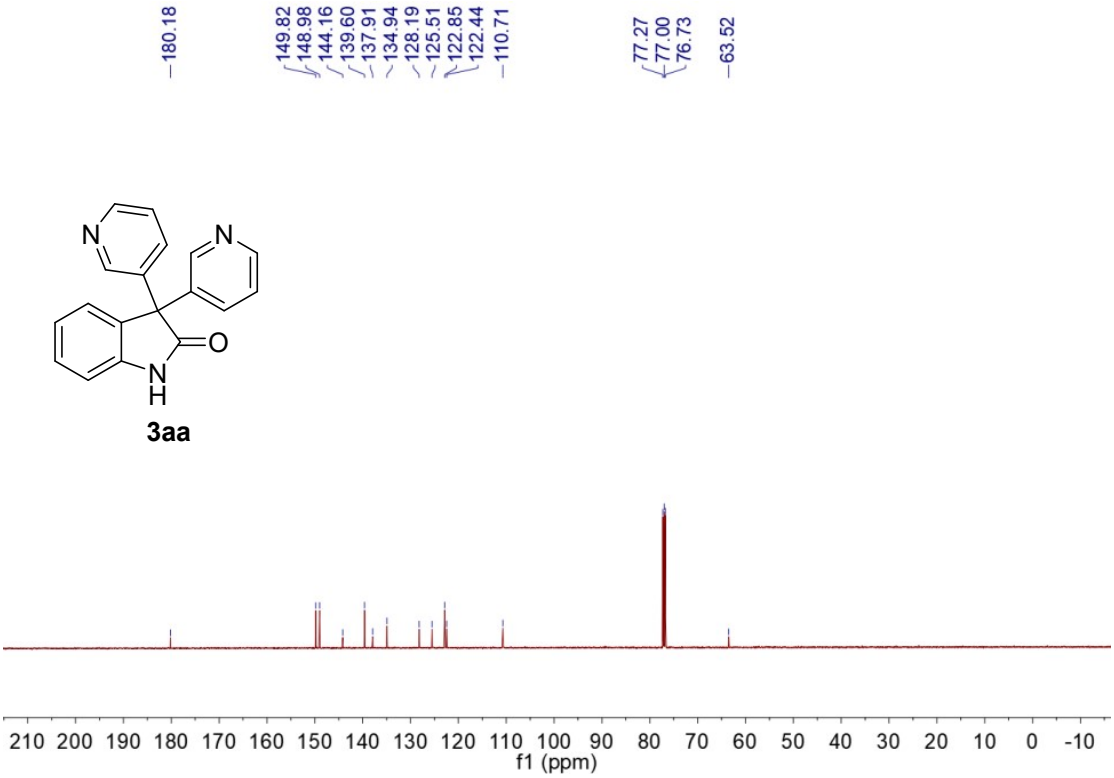
^{13}C NMR of **3z** (100 MHz, $CDCl_3$, ppm):



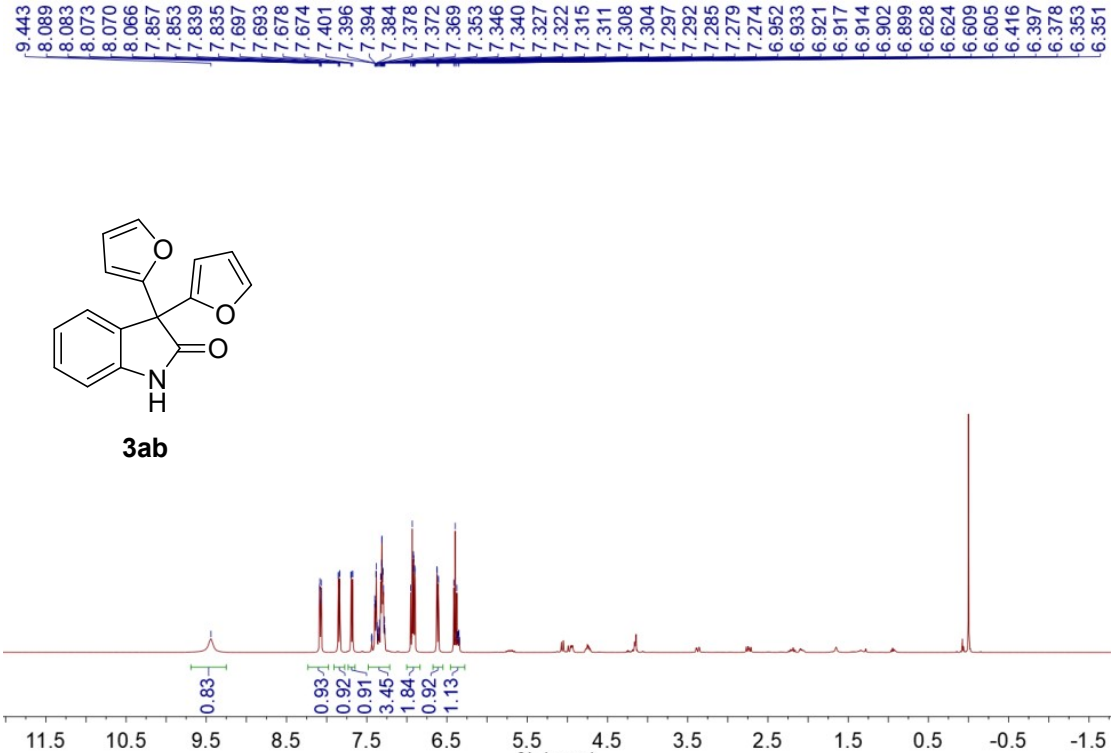
^{1}H NMR of **3aa** (400 MHz, $CDCl_3$, ppm):



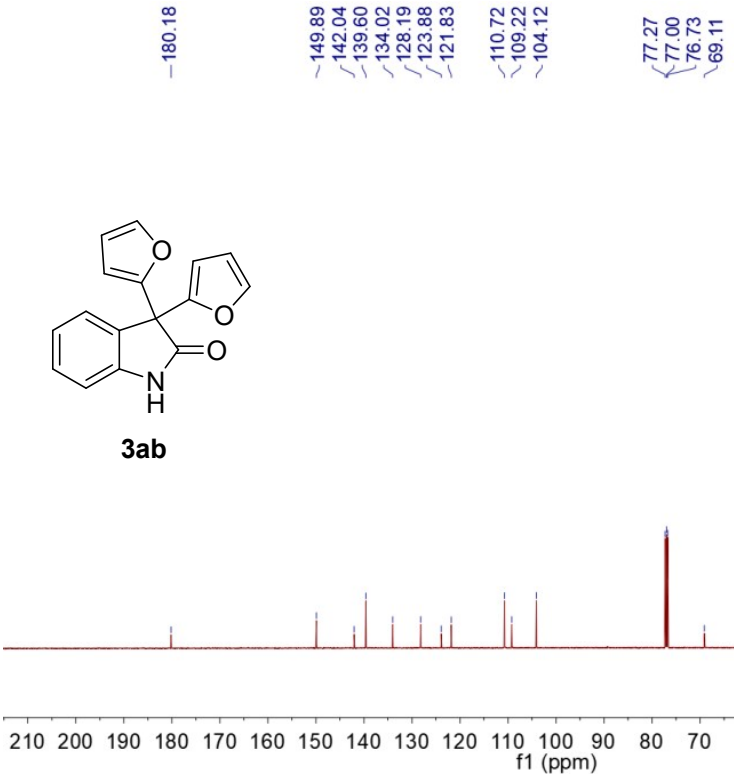
^{13}C NMR of **3aa** (100 MHz, $CDCl_3$, ppm):



^{1}H NMR of **3ab** (400 MHz, $CDCl_3$, ppm):

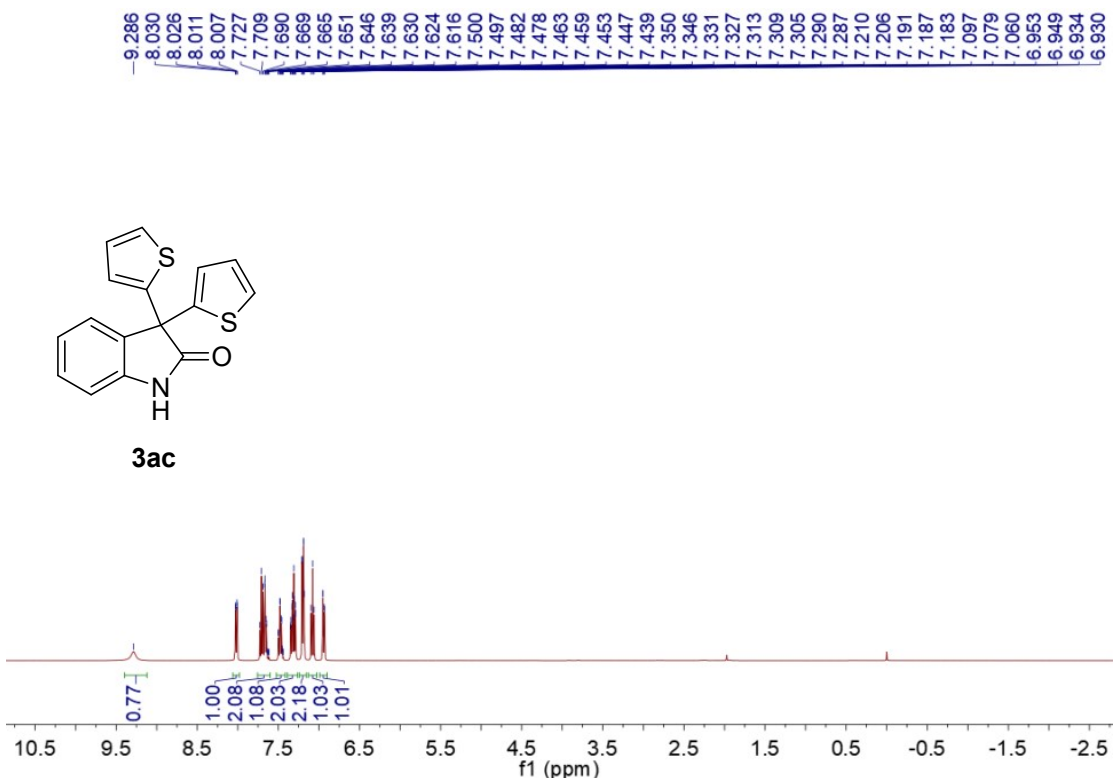


^{13}C NMR of **3ab** (100 MHz, $CDCl_3$, ppm):



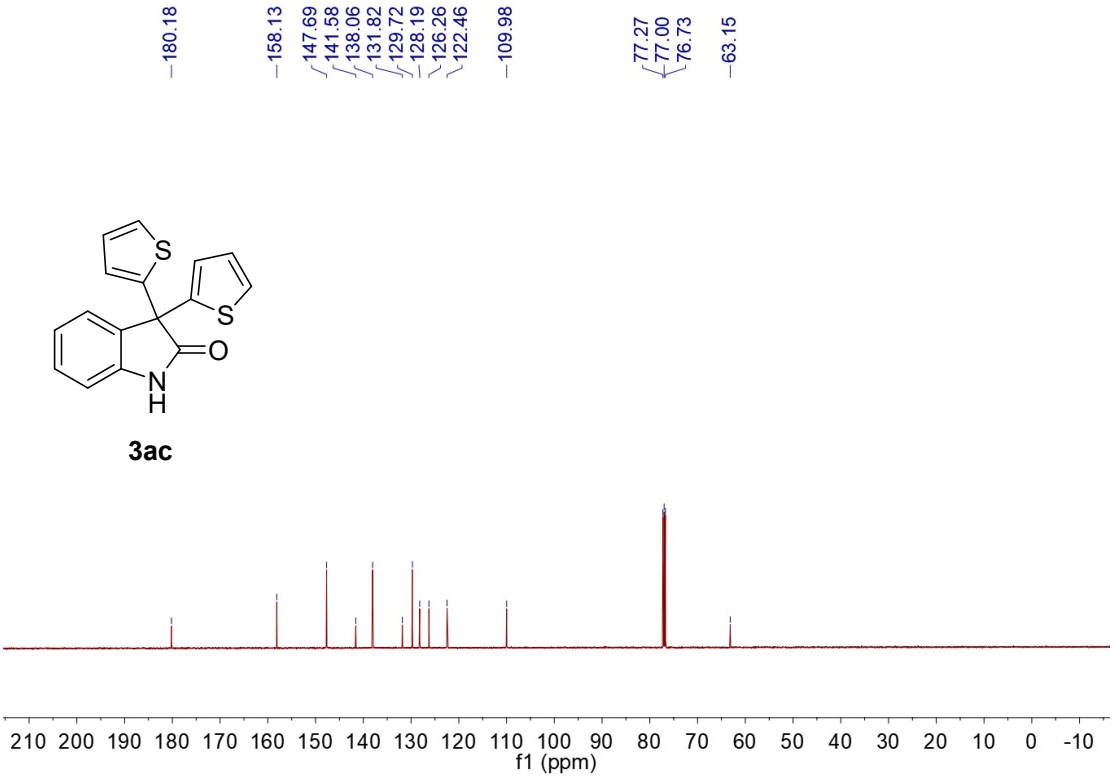
3ab

^{1}H NMR of **3ac** (400 MHz, $CDCl_3$, ppm):

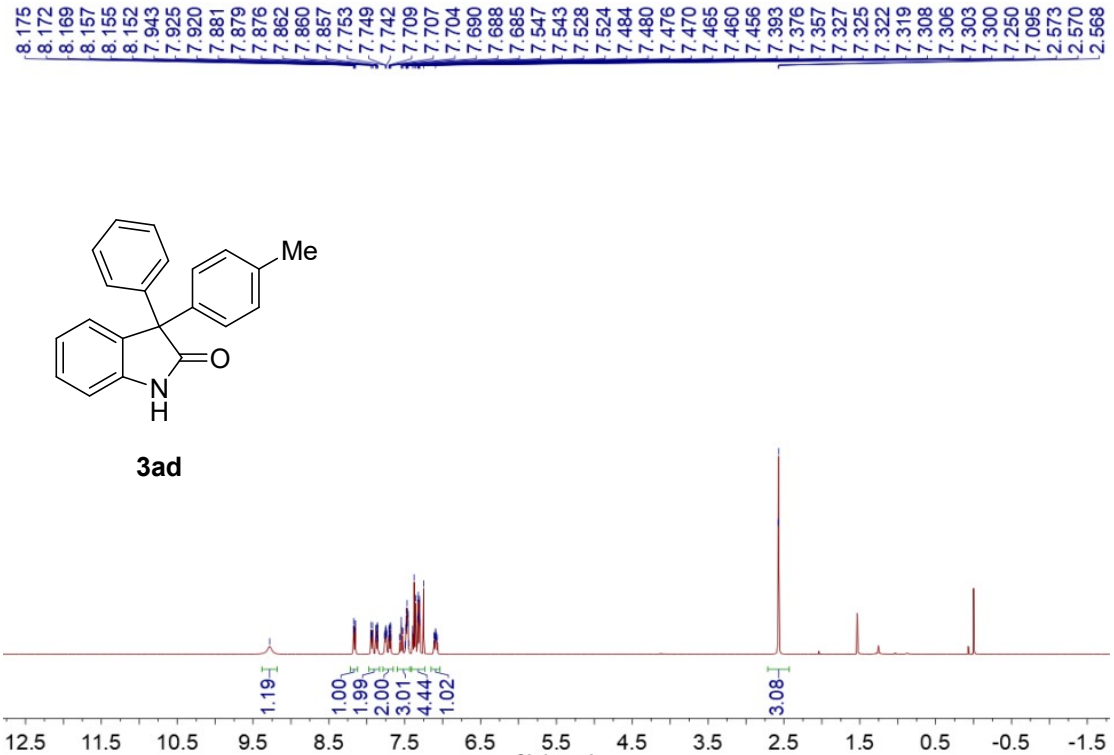


3ac

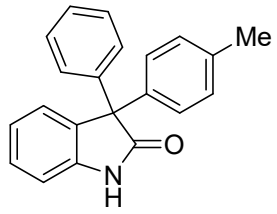
^{13}C NMR of **3ac** (100 MHz, $CDCl_3$, ppm):



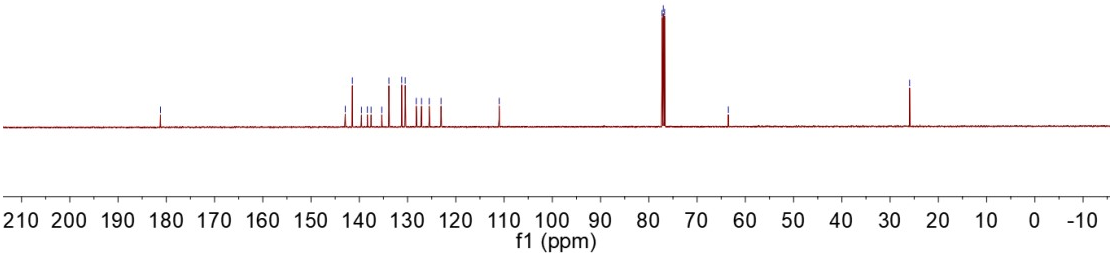
^{1}H NMR of **3ad** (400 MHz, $CDCl_3$, ppm):



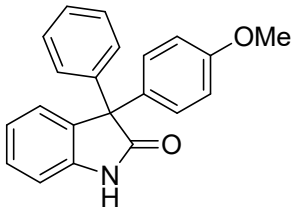
^{13}C NMR of **3ad** (100 MHz, $CDCl_3$, ppm):



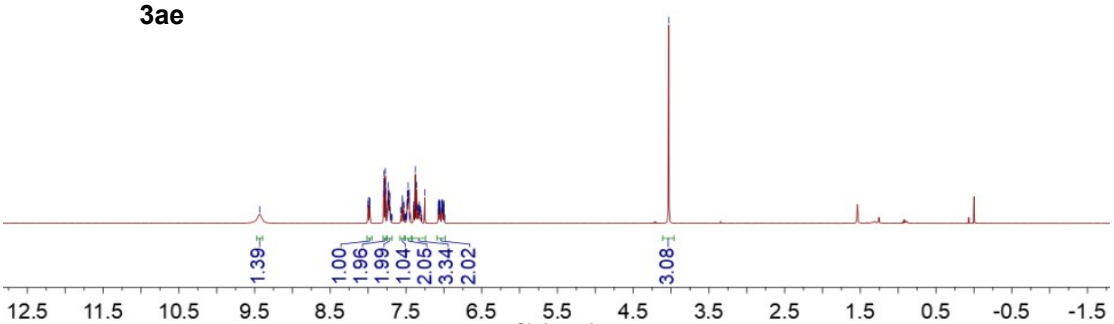
3ad



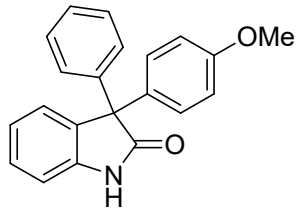
^{1}H NMR of **3ae** (400 MHz, $CDCl_3$, ppm):



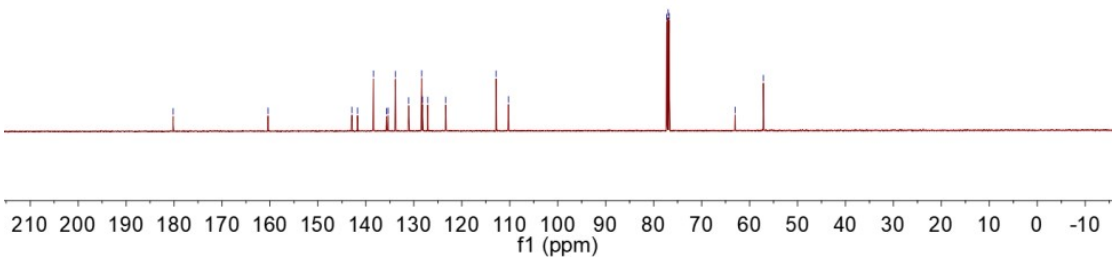
3ae



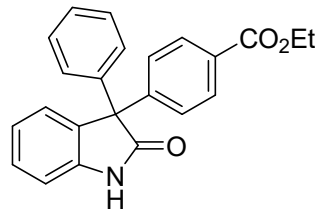
^{13}C NMR of **3ae** (100 MHz, $CDCl_3$, ppm):



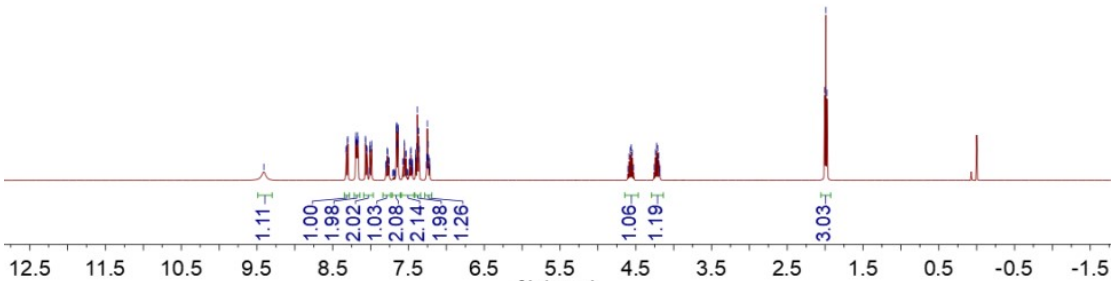
3ae



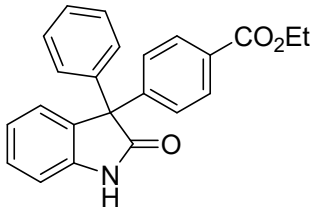
^{1}H NMR of **3af** (400 MHz, $CDCl_3$, ppm):



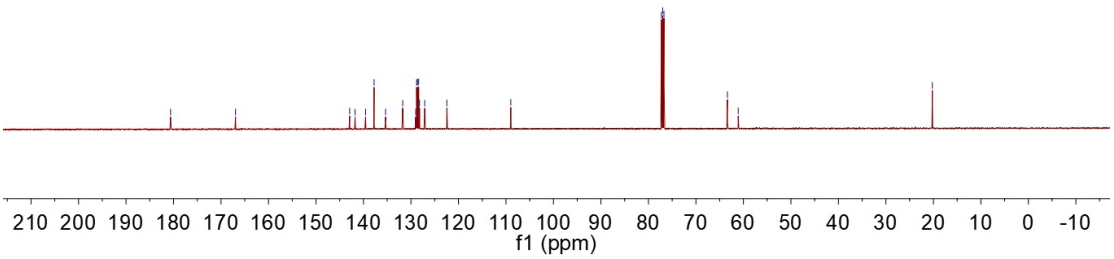
3af



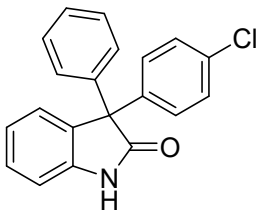
^{13}C NMR of **3af** (100 MHz, $CDCl_3$, ppm):



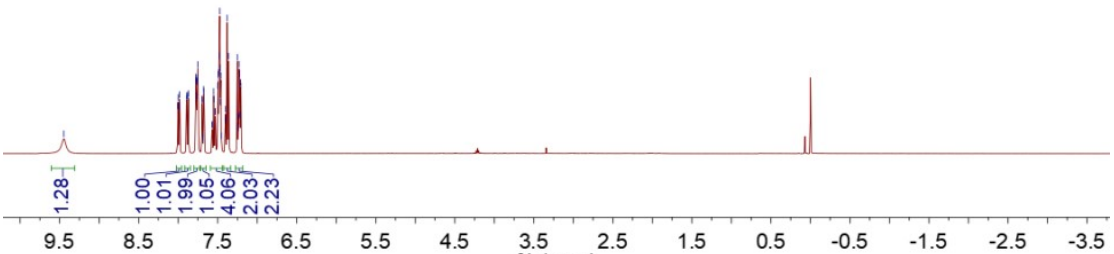
3af



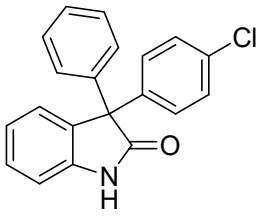
^{1}H NMR of **3ag** (400 MHz, $CDCl_3$, ppm):



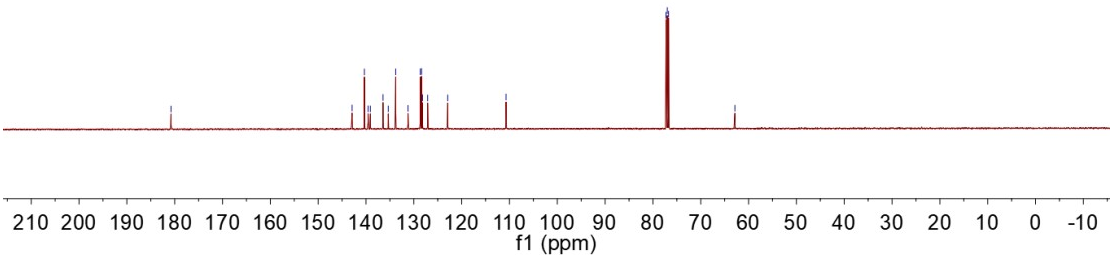
3ag



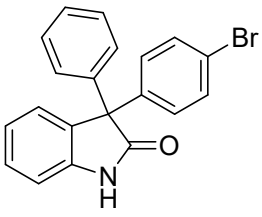
^{13}C NMR of **3ag** (100 MHz, $CDCl_3$, ppm):



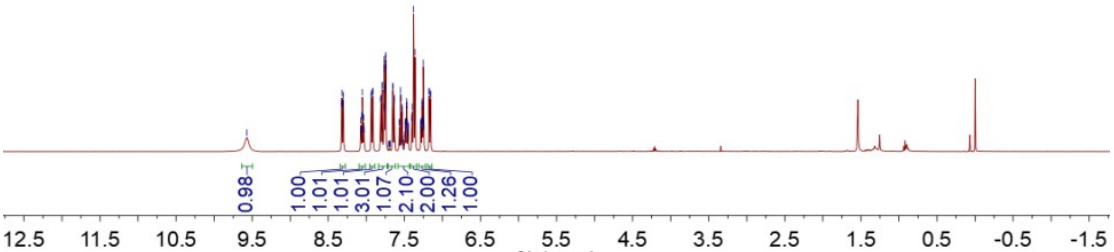
3ag



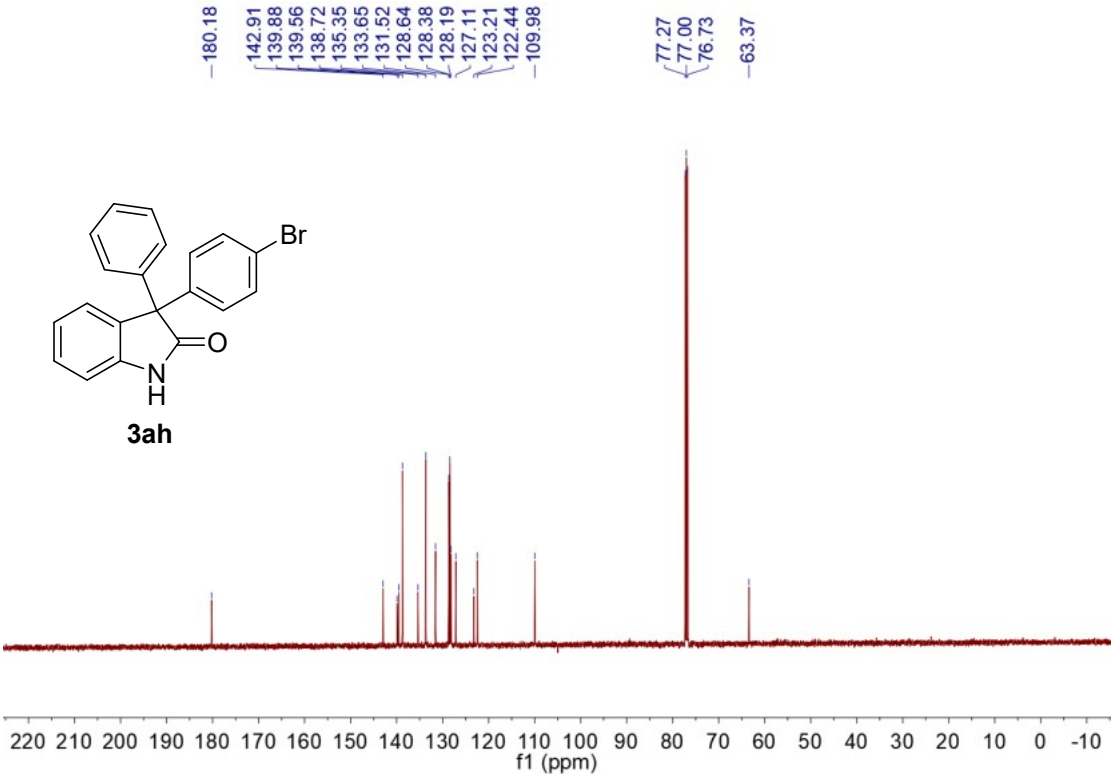
^{1}H NMR of **3ah** (400 MHz, $CDCl_3$, ppm):



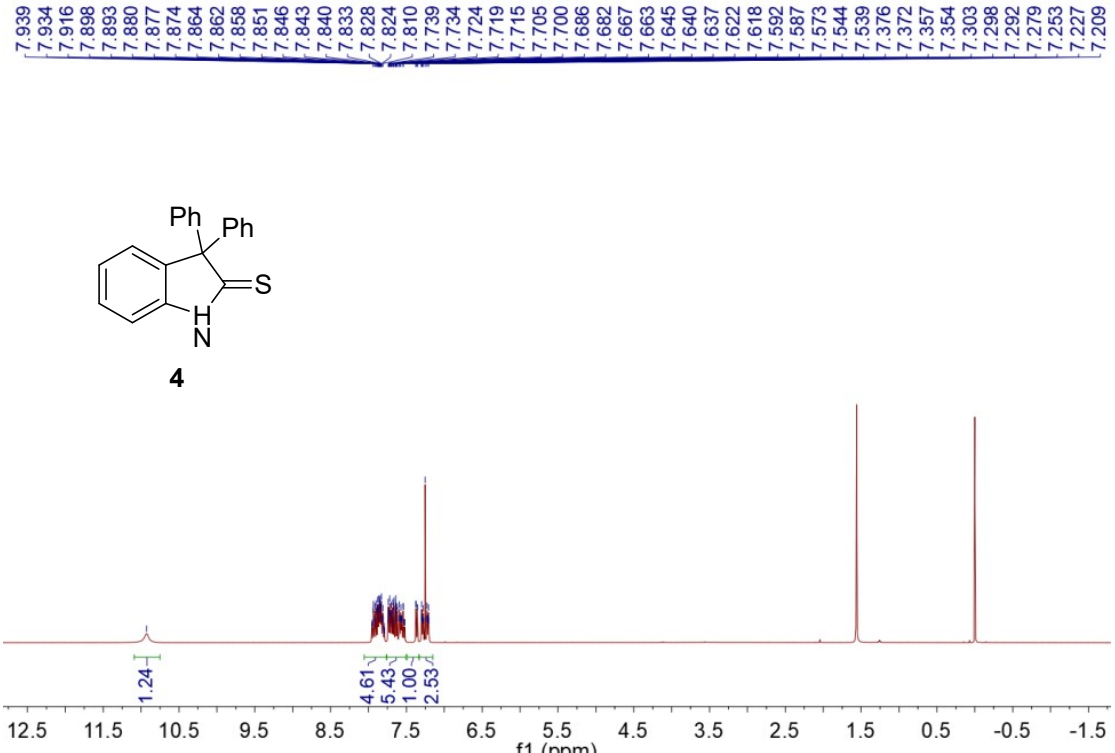
3ah



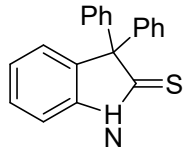
^{13}C NMR of **3ah** (100 MHz, $CDCl_3$, ppm):



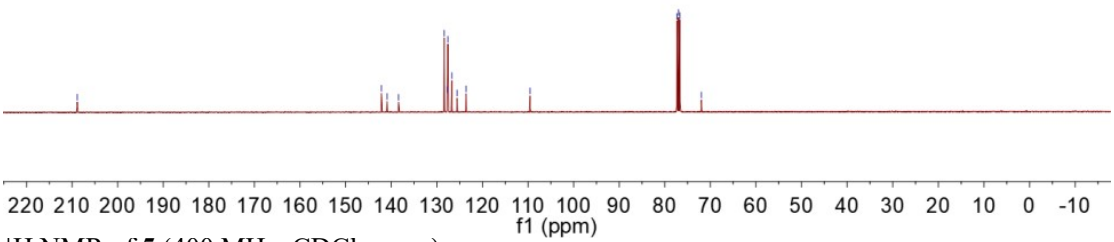
^{1}H NMR of **4** (400 MHz, $CDCl_3$, ppm):



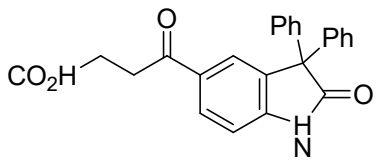
^{13}C NMR of **4** (100 MHz, $CDCl_3$, ppm):



4



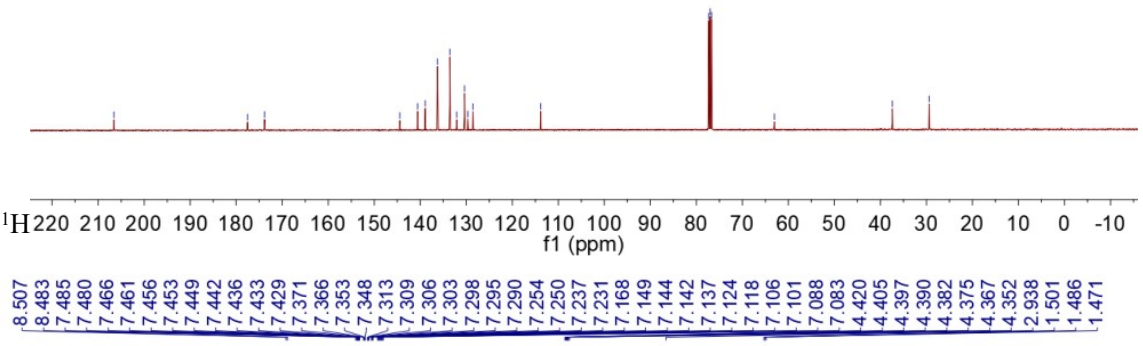
^{1}H NMR of **5** (400 MHz, $CDCl_3$, ppm):

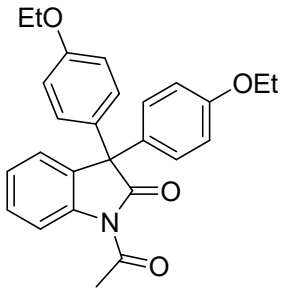


5

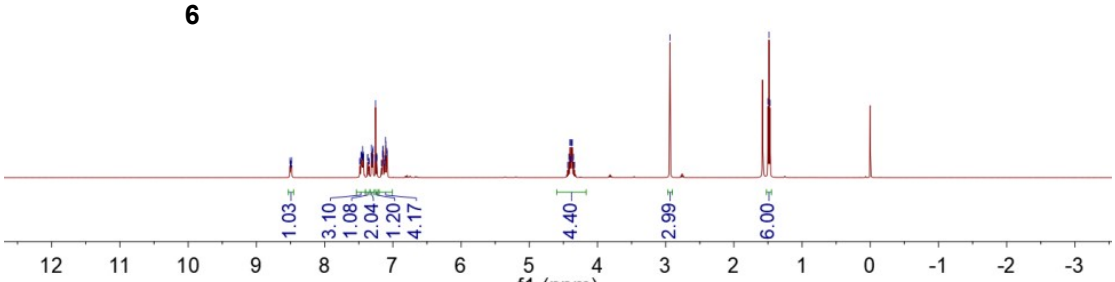
^{13}C NMR of **5** (100 MHz, $CDCl_3$, ppm):

5

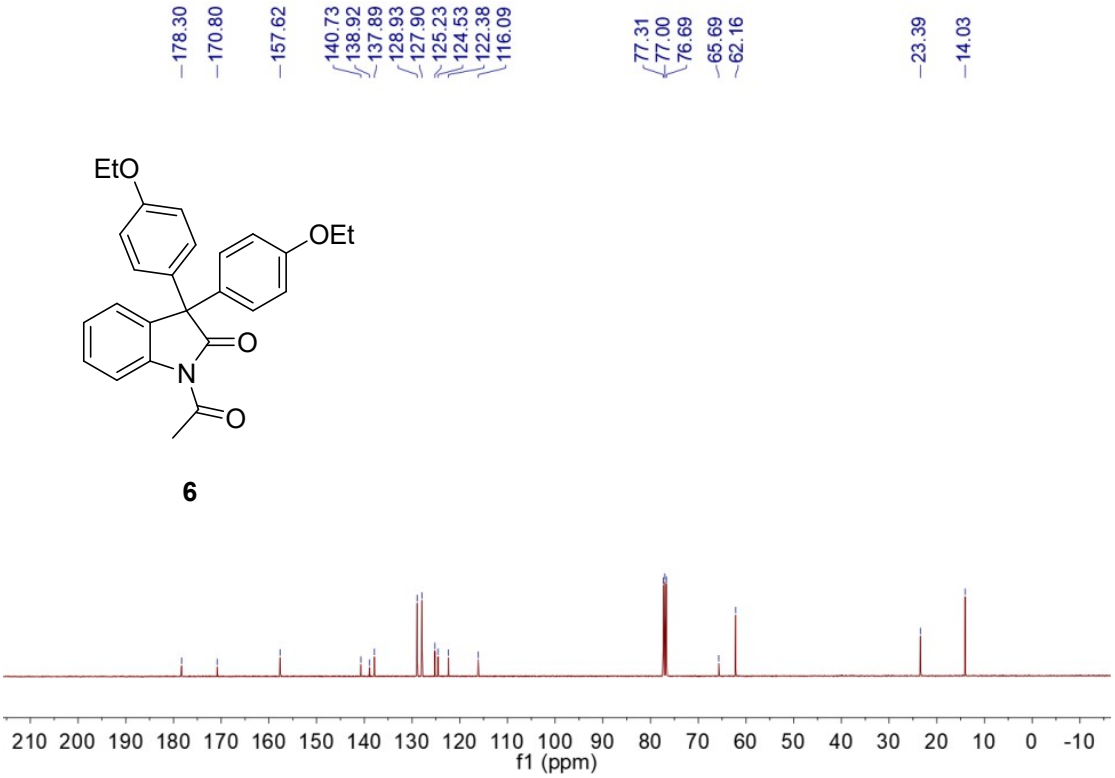




6

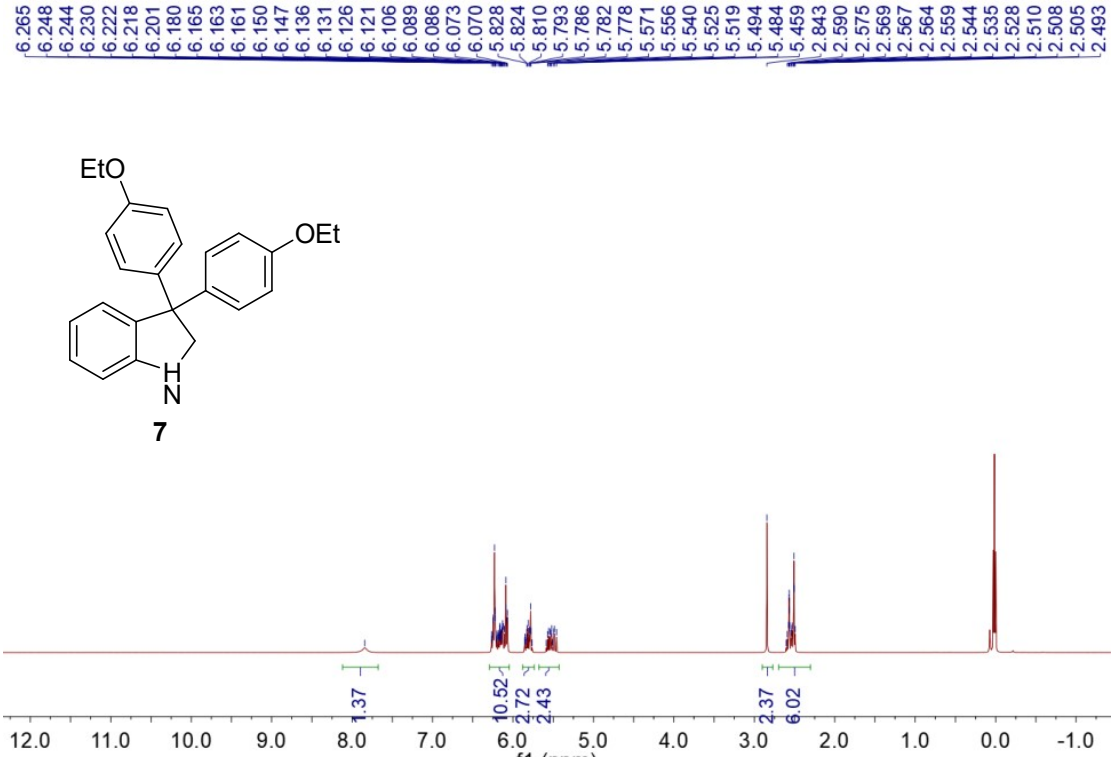


^{13}C NMR of **6** (100 MHz, $CDCl_3$, ppm):



6

^{1}H NMR of **7** (400 MHz, $CDCl_3$, ppm):



7

^{13}C NMR of **7** (100 MHz, $CDCl_3$, ppm):