

Supporting Information

Synthesis of 3-Spirooxindole 3*H*-Indoles through Rh(III)-Catalyzed [4 + 1] Redox-Neutral

Spirocyclization of *N*-Aryl Amidines with Diazo Oxindoles

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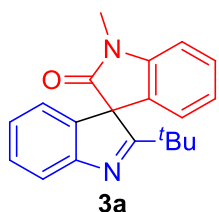
I. General experimental information

Commercial reagents were used without further purification. Amidines (**1**),^[1] diazooxindoles (**2**),^[2] and $[\text{RhCp}^*\text{Cl}_2]_2$ ^[3] were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet), br s (broad singlet), etc. The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

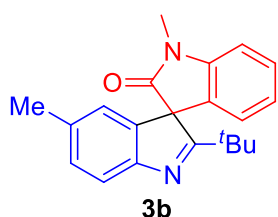
1. Typical procedures for the synthesis of **3a** and spectroscopic data of **3a-3jj**

To a reaction tube equipped with a stir bar were charged with *N*-phenylpivalimidamide (**1a**, 35.2 mg, 0.2 mmol), DCE (2.0 mL), [RhCp*Cl₂]₂ (2.5 mg, 0.004 mmol), 1-AdCO₂H (72.1 mg, 0.4 mmol), CsOAc (1.9 mg, 0.01 mmol) and 3-diazo-1-methylindolin-2-one (**2a**, 52.0 mg, 0.3 mmol). The tube was sealed, and the mixture was stirred at 60 °C (oil bath) under air for 4 h. Upon completion, it was cooled to room temperature, quenched with saturated aqueous solution of NaHCO₃, and then extracted with dichloromethane (10 mL × 3). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3a** (44 mg, 72%). **3b-3jj** were obtained in a similar manner.



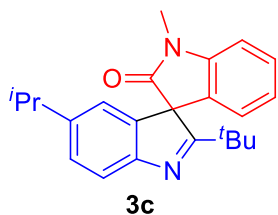
2-(*tert*-Butyl)-1'-methylspiro[indole-3,3'-indolin]-2'-one (**3a**)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (44 mg, 72%), mp 134-135 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.39-7.32 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.01-6.97 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.77-6.75 (m, 1H), 3.35 (s, 3H), 1.17 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 187.0, 172.3, 156.2, 144.7, 139.8, 129.2, 128.9, 127.0, 126.2, 124.1, 123.2, 121.3, 120.6, 108.9, 70.1, 38.5, 29.4, 27.1. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₂₀N₂NaO 327.1468; Found 327.1456.



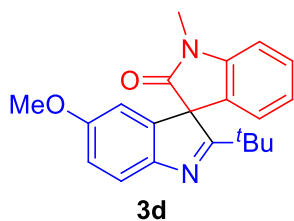
2-(*tert*-Butyl)-1',5-dimethylspiro[indole-3,3'-indolin]-2'-one (**3b**)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (45 mg, 71%), mp 139-140 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.53 (d, $J = 8.0$ Hz, 1H), 7.37 (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.13 (d, $J = 7.6$ Hz, 1H), 7.02-6.98 (m, 2H), 6.78-6.76 (m, 1H), 6.60 (s, 1H), 3.35 (s, 3H), 2.24 (s, 3H), 1.16 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 185.9, 172.6, 153.9, 144.7, 139.9, 136.1, 129.5, 129.1, 127.3, 124.2, 123.1, 121.9, 120.2, 108.9, 69.9, 38.4, 29.4, 27.1, 21.3. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}$ 319.1805; Found 319.1798.



2-(*tert*-Butyl)-5-isopropyl-1'-methylspiro[indole-3,3'-indolin]-2'-one (3c)

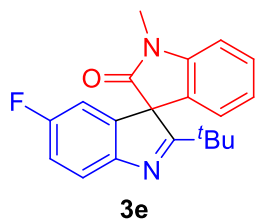
Eluent: petroleum ether/ethyl acetate (10:1). White solid (51 mg, 74%), mp 161-162 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.37 (td, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 7.21 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.01-6.98 (m, 2H), 6.78-6.76 (m, 1H), 6.62 (d, $J = 1.2$ Hz, 1H), 3.36 (s, 3H), 2.82-2.75 (m, 1H), 1.15-1.12 (m, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 186.1, 172.6, 154.3, 147.3, 144.7, 139.8, 129.1, 127.3, 126.8, 124.2, 123.1, 120.3, 119.6, 108.9, 70.0, 38.4, 34.1, 29.4, 27.1, 24.2, 24.1. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}$ 347.2118; Found 347.2105.



2-(*tert*-Butyl)-5-methoxy-1'-methylspiro[indole-3,3'-indolin]-2'-one (3d)

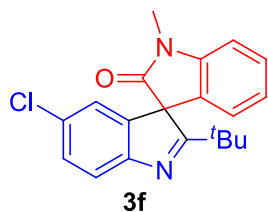
Eluent: petroleum ether/ethyl acetate (10:1). White solid (38 mg, 57%), mp 184-185 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.56 (d, $J = 8.4$ Hz, 1H), 7.37 (td, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.00 (t, $J = 7.8$ Hz, 2H), 6.86 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 6.78 (d, $J = 7.2$ Hz, 1H), 6.34 (d, $J = 2.4$ Hz, 1H), 3.69 (s, 3H), 3.34 (s, 3H), 1.15 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 184.8, 172.4, 158.5, 149.7, 144.6, 141.3, 129.2, 127.2, 124.2,

123.2, 121.0, 113.7, 108.9, 107.9, 70.2, 55.7, 38.3, 29.4, 27.1. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{21}H_{23}N_2O_2$ 335.1754; Found 335.1741.



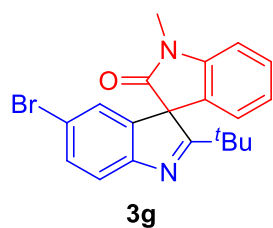
2-(*tert*-Butyl)-5-fluoro-1'-methylspiro[indole-3,3'-indolin]-2'-one (3e)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (45 mg, 70%), mp 148-149 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 7.59 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.4$ Hz, 1H), 7.41-7.37 (m, 1H), 7.05-6.99 (m, 3H), 6.77 (d, $J = 7.2$ Hz, 1H), 6.52 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.8$ Hz, 1H), 3.35 (s, 3H), 1.15 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 186.9 (d, $^5J_{C-F} = 3.3$ Hz), 171.7, 161.4 (d, $^1J_{C-F} = 243.9$ Hz), 152.3 (d, $^4J_{C-F} = 2.3$ Hz), 144.6, 141.4 (d, $^3J_{C-F} = 8.7$ Hz), 129.5, 126.4, 124.2, 123.4, 121.4 (d, $^3J_{C-F} = 8.7$ Hz), 115.6 (d, $^2J_{C-F} = 23.0$ Hz), 109.3 (d, $^2J_{C-F} = 25.2$ Hz), 109.1, 70.3 (d, $^4J_{C-F} = 2.1$ Hz), 38.5, 29.3, 27.1. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -115.7 (td, $J_1 = 8.3$ Hz, $J_2 = 4.1$ Hz). HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{19}FN_2NaO$ 345.1374; Found 345.1359.



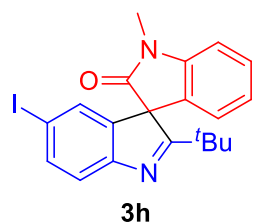
2-(*tert*-Butyl)-5-chloro-1'-methylspiro[indole-3,3'-indolin]-2'-one (3f)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (52 mg, 77%), mp 159-160 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.39 (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.31 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.04-6.99 (m, 2H), 6.77-6.76 (m, 2H), 3.35 (s, 3H), 1.15 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 187.6, 171.5, 154.8, 144.6, 141.3, 131.7, 129.5, 129.1, 126.2, 124.2, 123.4, 121.9, 121.5, 109.1, 70.2, 38.5, 29.3, 27.2. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{20}H_{19}ClN_2NaO$ 361.1078; Found 361.1067.



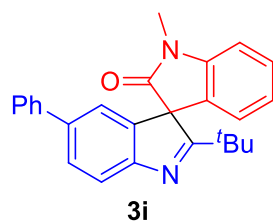
5-Bromo-2-(*tert*-butyl)-1'-methylspiro[indole-3,3'-indolin]-2'-one (3g)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (58 mg, 76%), mp 182-183 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.46 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H), 7.39 (td, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 7.04-6.99 (m, 2H), 6.91 (d, *J* = 1.6 Hz, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 3.35 (s, 3H), 1.15 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 187.7, 171.5, 155.2, 144.6, 141.7, 132.0, 129.6, 126.1, 124.7, 124.2, 123.4, 122.0, 119.5, 109.2, 70.2, 38.5, 29.3, 27.2. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₀H₂₀BrN₂O 383.0754; Found 383.0739.



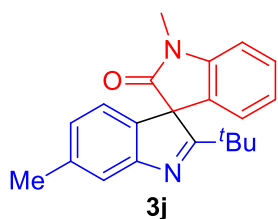
2-(*tert*-Butyl)-5-iodo-1'-methylspiro[indole-3,3'-indolin]-2'-one (3h)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (58 mg, 67%), mp 207-208 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.67 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 7.42-7.37 (m, 2H), 7.09 (s, 1H), 7.04-6.99 (m, 2H), 6.76 (d, *J* = 7.2 Hz, 1H), 3.35 (s, 3H), 1.15 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 187.6, 171.5, 155.9, 144.6, 141.9, 138.0, 130.4, 129.5, 126.1, 124.2, 123.4, 122.5, 109.1, 90.5, 70.0, 38.5, 29.3, 27.2. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₀H₂₀IN₂O 431.0615; Found 431.0614.



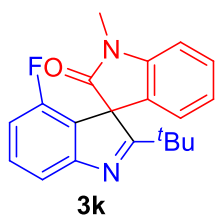
2-(*tert*-Butyl)-1'-methyl-5-phenylspiro[indole-3,3'-indolin]-2'-one (3i)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (26 mg, 34%), mp 189-190 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.72 (d, $J = 8.4$ Hz, 1H), 7.57 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H), 7.44 (d, $J = 7.2$ Hz, 2H), 7.40-7.33 (m, 3H), 7.28 (d, $J = 7.6$ Hz, 1H), 7.02-6.97 (m, 3H), 6.81 (d, $J = 7.2$ Hz, 1H), 3.37 (s, 3H), 1.19 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 187.3, 172.2, 155.6, 144.7, 140.9, 140.5, 139.6, 129.3, 128.7, 128.1, 127.2, 127.0, 124.2, 123.3, 120.8, 120.3, 109.0, 70.2, 38.6, 29.4, 27.1. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}$ 381.1961; Found 381.1958.



2-(*tert*-Butyl)-1',6-dimethylspiro[indole-3,3'-indolin]-2'-one (3j)

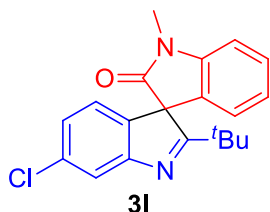
Eluent: petroleum ether/ethyl acetate (10:1). White solid (48 mg, 75%), mp 179-180 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.48 (s, 1H), 7.35 (td, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 6.99-6.97 (m, 2H), 6.90 (dd, $J_1 = 7.8$ Hz, $J_2 = 0.6$ Hz, 1H), 6.76 (dd, $J_1 = 7.8$ Hz, $J_2 = 0.6$ Hz, 1H), 6.68 (d, $J = 7.8$ Hz, 1H), 3.33 (s, 3H), 2.38 (s, 3H), 1.16 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 187.2, 172.5, 156.4, 144.7, 139.0, 136.9, 129.1, 127.2, 126.8, 124.1, 123.1, 121.4, 120.9, 108.9, 69.8, 38.5, 29.4, 27.0, 21.6. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}$ 319.1805; Found 319.1801.



2-(*tert*-Butyl)-4-fluoro-1'-methylspiro[indole-3,3'-indolin]-2'-one (3k)

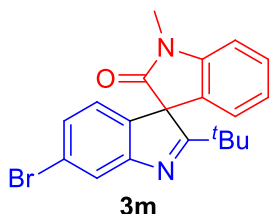
Eluent: petroleum ether/ethyl acetate (10:1). White solid (47 mg, 73%), mp 105-106 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.46 (d, $J = 7.8$ Hz, 1H), 7.38 (td, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.34-7.31 (m, 1H), 7.01-6.98 (m, 2H), 6.79-6.76 (m, 2H), 3.37 (s, 3H), 1.16 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 187.9, 170.9, 158.7 (d,

$^3J_{\text{C-F}} = 4.3$ Hz), 156.9 (d, $^1J_{\text{C-F}} = 250.7$ Hz), 144.8, 130.7 (d, $^3J_{\text{C-F}} = 7.9$ Hz), 129.5, 125.3 (d, $^2J_{\text{C-F}} = 14.4$ Hz), 124.6, 123.7, 123.1, 116.6 (d, $^4J_{\text{C-F}} = 3.6$ Hz), 113.5 (d, $^2J_{\text{C-F}} = 19.5$ Hz), 109.0, 68.7 (d, $^3J_{\text{C-F}} = 3.6$ Hz), 38.7, 29.4, 27.1. ^{19}F NMR (CDCl_3 , 376 MHz): δ -120.1 (dd, $J_1 = 8.3$ Hz, $J_2 = 5.6$ Hz). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{FN}_2\text{NaO}$ 345.1374; Found 345.1368.



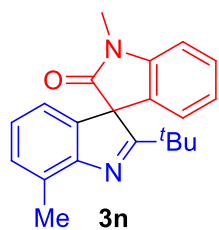
2-(*tert*-Butyl)-6-chloro-1'-methylspiro[indole-3,3'-indolin]-2'-one (**3l**)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (53 mg, 78%), mp 177-178 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.64 (d, $J = 1.6$ Hz, 1H), 7.38 (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.06 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.02-6.98 (m, 2H), 6.75-6.71 (m, 2H), 3.33 (s, 3H), 1.15 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 189.1, 171.6, 157.4, 144.7, 138.2, 134.6, 129.5, 126.3, 126.1, 124.1, 123.4, 122.1, 121.2, 109.1, 69.8, 38.7, 29.3, 27.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{ClN}_2\text{NaO}$ 361.1078; Found 361.1070.



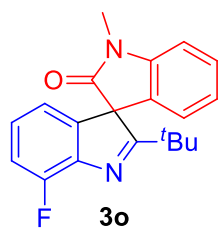
6-Bromo-2-(*tert*-butyl)-1'-methylspiro[indole-3,3'-indolin]-2'-one (**3m**)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (53 mg, 69%), mp 168-169 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.81 (d, $J = 1.2$ Hz, 1H), 7.38 (td, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.22 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 1H), 7.02-6.99 (m, 2H), 6.75 (d, $J = 6.6$ Hz, 1H), 6.67 (d, $J = 7.8$ Hz, 1H), 3.34 (s, 3H), 1.15 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 189.0, 171.5, 157.6, 144.7, 138.7, 129.5, 129.0, 126.2, 124.15, 124.12, 123.4, 122.5, 122.4, 109.1, 69.9, 38.6, 29.3, 27.1. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{BrN}_2\text{NaO}$ 405.0573; Found 405.0563.



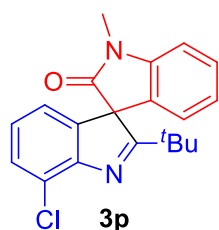
2-(*tert*-Butyl)-1',7-dimethylspiro[indole-3,3'-indolin]-2'-one (3n)

Eluent: petroleum ether/ethyl acetate (30:1). White solid (35 mg, 55%), mp 135-136 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.35 (td, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.13 (d, $J = 7.8$ Hz, 1H), 6.99-6.95 (m, 3H), 6.76 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 1H), 6.60 (d, $J = 7.2$ Hz, 1H), 3.34 (s, 3H), 2.63 (s, 3H), 1.16 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 185.0, 172.7, 155.0, 144.7, 139.7, 130.6, 130.3, 129.0, 127.4, 125.9, 124.1, 123.1, 118.6, 108.8, 70.3, 38.5, 29.5, 27.0, 17.1. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}$ 319.1805; Found 319.1801.



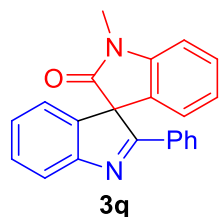
2-(*tert*-Butyl)-7-fluoro-1'-methylspiro[indole-3,3'-indolin]-2'-one (3o)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (27 mg, 42%), mp 129-130 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.39 (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.08-6.99 (m, 4H), 6.78-6.76 (m, 1H), 6.60-6.58 (m, 1H), 3.35 (s, 3H), 1.18 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 187.6, 171.6, 153.6 (d, $^1J_{\text{C-F}} = 253.8$ Hz), 144.7, 143.1 (d, $^2J_{\text{C-F}} = 11.0$ Hz), 142.9 (d, $^3J_{\text{C-F}} = 3.3$ Hz), 129.5, 127.6 (d, $^3J_{\text{C-F}} = 6.5$ Hz), 126.4, 124.1, 123.4, 117.1 (d, $^4J_{\text{C-F}} = 3.3$ Hz), 116.3 (d, $^2J_{\text{C-F}} = 18.6$ Hz), 109.1, 70.5, 38.7, 29.3, 27.1. ^{19}F NMR (CDCl_3 , 376 MHz): δ -125.19 – -125.23 (m). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{FN}_2\text{NaO}$ 345.1374; Found 345.1366.



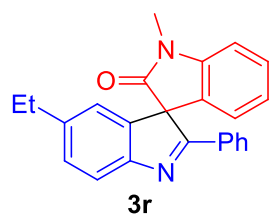
2-(*tert*-Butyl)-7-chloro-1'-methylspiro[indole-3,3'-indolin]-2'-one (3p)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (35 mg, 52%), mp 160-161 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.38 (td, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1H), 7.31 (d, $J = 7.8$ Hz, 1H), 7.02-6.99 (m, 3H), 6.77-6.76 (m, 1H), 6.68 (dd, $J_1 = 7.2$ Hz, $J_2 = 0.6$ Hz, 1H), 3.34 (s, 3H), 1.18 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 188.1, 171.6, 153.2, 144.6, 141.6, 129.54, 129.50, 127.2, 126.3, 125.6, 124.2, 123.4, 119.7, 109.1, 71.1, 38.8, 29.4, 27.2. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{ClN}_2\text{NaO}$ 361.1078; Found 361.1062.



1'-Methyl-2-phenylspiro[indole-3,3'-indolin]-2'-one (3q)

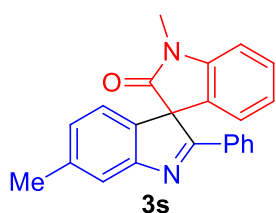
Eluent: petroleum ether/ethyl acetate (30:1). White solid (37 mg, 57%), mp 176-177 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.78 (d, $J = 8.0$ Hz, 1H), 7.60-7.58 (m, 2H), 7.43-7.33 (m, 3H), 7.28-7.24 (m, 2H), 7.17-7.13 (m, 1H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.98-6.93 (m, 2H), 6.74 (d, $J = 7.2$ Hz, 1H), 3.40 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 174.2, 172.4, 156.4, 144.4, 140.1, 132.2, 131.2, 129.4, 129.3, 128.8, 128.0, 127.8, 126.7, 123.9, 123.8, 121.7, 121.4, 109.2, 69.0, 27.3. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}$ 325.1335; Found 325.1337.



5-Ethyl-1'-methyl-2-phenylspiro[indole-3,3'-indolin]-2'-one (3r)

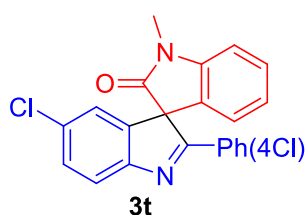
Eluent: petroleum ether/ethyl acetate (30:1). White solid (26 mg, 37%), mp 172-173 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.61 (d, $J = 7.6$ Hz, 1H), 7.51-7.48 (m, 2H), 7.32 (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.20-7.16 (m, 3H), 7.02 (d, $J = 8.0$ Hz, 1H), 6.90 (t, $J = 7.6$ Hz, 1H), 6.70-6.68 (m, 2H), 3.35 (s, 3H), 2.51 (q, $J = 7.6$ Hz, 2H), 1.09 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 173.3, 172.6, 154.3, 144.4, 143.3, 140.2, 132.4, 131.0, 129.3, 128.8, 128.2, 127.6, 123.9, 123.8, 121.2, 121.1, 109.1, 68.9, 28.9,

27.3, 15.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}N_2O$ 353.1648; Found 353.1644.



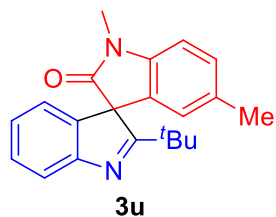
1',6-Dimethyl-2-phenylspiro[indole-3,3'-indolin]-2'-one (3s)

Eluent: petroleum ether/ethyl acetate (30:1). White solid (30 mg, 44%), mp 205-206 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.57 (m, 3H), 7.41-7.33 (m, 2H), 7.28-7.24 (m, 2H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 2H), 6.82 (d, $J = 7.6$ Hz, 1H), 6.75 (d, $J = 7.2$ Hz, 1H), 3.41 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 174.3, 172.6, 156.7, 144.3, 139.5, 137.1, 132.3, 131.1, 129.3, 128.8, 128.2, 127.7, 127.4, 123.9, 123.7, 122.2, 121.3, 109.1, 68.7, 27.3, 21.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}N_2O$ 339.1492; Found 339.1494.



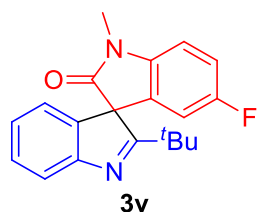
5-Chloro-2-(4-chlorophenyl)-1'-methylspiro[indole-3,3'-indolin]-2'-one (3t)

Eluent: petroleum ether/ethyl acetate (30:1). White solid (30 mg, 38%), mp 217-218 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, $J = 8.4$ Hz, 1H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.44 (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.39 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.27-7.25 (m, 2H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 1.6$ Hz, 1H), 6.75 (d, $J = 7.2$ Hz, 1H), 3.42 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 173.4, 171.4, 154.7, 144.2, 141.4, 137.8, 132.5, 130.3, 130.0, 129.7, 129.2, 129.0, 126.8, 124.1, 124.0, 122.4, 122.3, 109.4, 68.9, 27.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{14}Cl_2N_2NaO$ 415.0375; Found 415.0362.



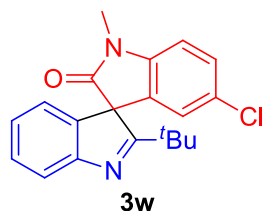
2-(*tert*-Butyl)-1',5'-dimethylspiro[indole-3,3'-indolin]-2'-one (3u)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (37 mg, 58%), mp 148-149 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.66 (d, $J = 7.6$ Hz, 1H), 7.36-7.32 (m, 1H), 7.16 (d, $J = 7.6$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 6.80 (d, $J = 7.6$ Hz, 1H), 6.57 (s, 1H), 3.32 (s, 3H), 2.23 (s, 3H), 1.17 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 187.3, 172.2, 156.1, 142.4, 139.9, 132.9, 129.5, 128.9, 126.9, 126.2, 124.7, 121.4, 120.6, 108.7, 70.2, 38.5, 29.4, 27.1, 21.0. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}$ 319.1805; Found 319.1795.



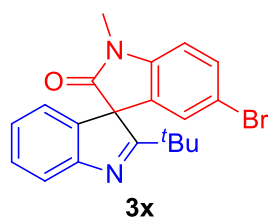
2-(*tert*-Butyl)-5'-fluoro-1'-methylspiro[indole-3,3'-indolin]-2'-one (3v)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (40 mg, 62%), mp 130-131 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.66 (d, $J = 7.6$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.12-7.05 (m, 2H), 6.92 (dd, $J_1 = 8.8$ Hz, $J_2 = 4.0$ Hz, 1H), 6.79 (d, $J = 7.2$ Hz, 1H), 6.52 (dd, $J_1 = 7.6$ Hz, $J_2 = 2.4$ Hz, 1H), 3.33 (s, 3H), 1.18 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 186.4, 171.9, 159.3 (d, $^1J_{\text{C-F}} = 241.2$ Hz), 156.2, 140.7, 139.3, 129.2, 128.6 (d, $^3J_{\text{C-F}} = 8.7$ Hz), 126.3, 121.3, 120.8, 115.6 (d, $^2J_{\text{C-F}} = 23.1$ Hz), 112.1 (d, $^2J_{\text{C-F}} = 24.6$ Hz), 109.5 (d, $^3J_{\text{C-F}} = 8.0$ Hz), 70.1, 38.5, 29.4, 27.2. ^{19}F NMR (CDCl_3 , 376 MHz): δ -119.1 (td, $J_1 = 8.6$ Hz, $J_2 = 4.5$ Hz). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{FN}_2\text{NaO}$ 345.1374; Found 345.1364.



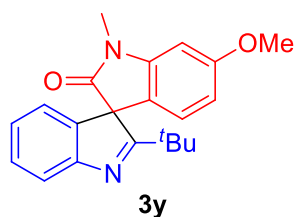
2-(*tert*-Butyl)-5'-chloro-1'-methylspiro[indole-3,3'-indolin]-2'-one (3w)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (43 mg, 63%), mp 167-168 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.38-7.33 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 3.33 (s, 3H), 1.18 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 186.3, 171.8, 156.2, 143.2, 139.2, 129.3, 129.2, 128.7, 128.6, 126.3, 124.3, 121.3, 120.9, 109.8, 69.8, 38.5, 29.4, 27.2. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₁₉ClN₂NaO 361.1078; Found 361.1068.



5'-Bromo-2-(*tert*-butyl)-1'-methylspiro[indole-3,3'-indolin]-2'-one (3x)

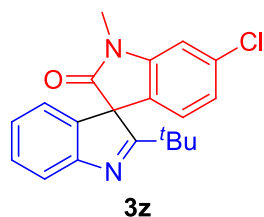
Eluent: petroleum ether/ethyl acetate (10:1). White solid (39 mg, 51%), mp 194-195 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.49 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.6 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.88-6.86 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 3.33 (s, 3H), 1.18 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 186.3, 171.7, 156.2, 143.7, 139.2, 132.1, 129.3, 129.1, 127.1, 126.4, 121.3, 120.9, 115.7, 110.3, 69.7, 38.5, 29.4, 27.2. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₀H₂₀BrN₂O 383.0754; Found 383.0750.



2-(*tert*-Butyl)-6'-methoxy-1'-methylspiro[indole-3,3'-indolin]-2'-one (3y)

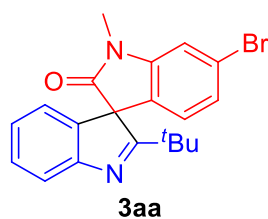
Eluent: petroleum ether/ethyl acetate (10:1). White solid (38 mg, 57%), mp 183-184 °C. ¹H NMR (CDCl₃, 400

MHz): δ 7.65 (d, $J = 8.0$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.08 (t, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 7.6$ Hz, 1H), 6.66 (d, $J = 8.4$ Hz, 1H), 6.57 (d, $J = 2.4$ Hz, 1H), 6.49 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 1H), 3.85 (s, 3H), 3.31 (s, 3H), 1.17 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 187.4, 172.8, 161.0, 155.9, 146.0, 140.0, 128.9, 126.2, 124.8, 121.3, 120.6, 118.3, 107.0, 97.0, 69.6, 55.6, 38.4, 29.3, 27.1. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_2$ 335.1754; Found 335.1740.



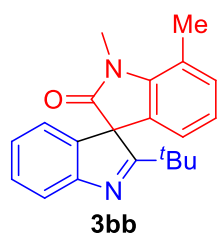
2-(*tert*-Butyl)-6'-chloro-1'-methylspiro[indole-3,3'-indolin]-2'-one (3z)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (46 mg, 68%), mp 195-196 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.66 (d, $J = 7.6$ Hz, 1H), 7.35 (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.10 (t, $J = 7.6$ Hz, 1H), 7.01-6.97 (m, 2H), 6.79 (d, $J = 7.2$ Hz, 1H), 6.68 (d, $J = 7.6$ Hz, 1H), 3.33 (s, 3H), 1.17 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 186.5, 172.2, 156.2, 145.8, 139.3, 135.0, 129.2, 126.3, 125.4, 125.0, 123.1, 121.2, 120.8, 109.7, 69.5, 38.5, 29.4, 27.2. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{ClN}_2\text{O}$ 339.1259; Found 339.1254.



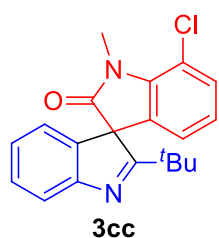
6'-Bromo-2-(*tert*-butyl)-1'-methylspiro[indole-3,3'-indolin]-2'-one (3aa)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (50 mg, 65%), mp 191-192 °C. ^1H NMR (CDCl_3 , 600 MHz): δ 7.65 (d, $J = 7.8$ Hz, 1H), 7.35 (td, $J_1 = 7.8$ Hz, $J_2 = 0.6$ Hz, 1H), 7.15-7.13 (m, 2H), 7.09 (t, $J = 7.8$ Hz, 1H), 6.78 (d, $J = 7.2$ Hz, 1H), 6.62 (d, $J = 7.8$ Hz, 1H), 3.32 (s, 3H), 1.17 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 186.4, 172.0, 156.1, 146.0, 139.2, 129.2, 126.3, 126.1, 125.9, 125.3, 122.8, 121.3, 120.8, 112.5, 69.5, 38.5, 29.4, 27.2. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{20}\text{BrN}_2\text{O}$ 383.0754; Found 383.0740.



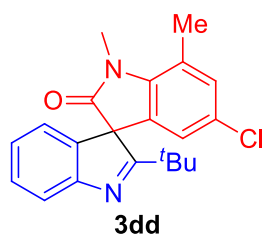
2-(*tert*-Butyl)-1',7'-dimethylspiro[indole-3,3'-indolin]-2'-one (3bb)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (40 mg, 63%), mp 186-187 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.33 (td, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 7.10-7.07 (m, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 7.2 Hz, 1H), 3.61 (s, 3H), 2.67 (s, 3H), 1.18 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 187.3, 173.0, 156.1, 142.5, 140.3, 132.9, 128.8, 127.3, 126.1, 123.0, 122.0, 121.3, 120.6, 120.5, 69.9, 38.5, 30.4, 29.4, 19.1. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₁H₂₃N₂O 319.1805; Found 319.1796.



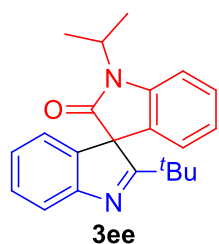
2-(*tert*-Butyl)-7'-chloro-1'-methylspiro[indole-3,3'-indolin]-2'-one (3cc)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (42 mg, 62%), mp 158-159 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.35 (td, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 1H), 7.29 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.2 Hz, 1H), 7.11 (td, *J*₁ = 7.6 Hz, *J*₂ = 0.8 Hz, 1H), 6.89 (t, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.61 (dd, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1H), 3.71 (s, 3H), 1.18 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 186.6, 172.4, 156.0, 140.6, 139.6, 131.5, 129.5, 129.2, 126.4, 123.9, 122.6, 121.3, 120.8, 116.1, 69.7, 38.6, 30.5, 29.5. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₀H₂₀ClN₂O 339.1259; Found 339.1246.



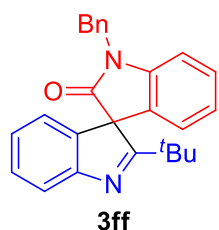
2-(*tert*-Butyl)-5'-chloro-1',7'-dimethylspiro[indole-3,3'-indolin]-2'-one (3dd)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (40 mg, 57%), mp 223-224 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.12-7.08 (m, 2H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 3.59 (s, 3H), 2.64 (s, 3H), 1.18 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 186.5, 172.6, 156.1, 141.1, 139.7, 132.4, 129.14, 129.09, 128.0, 126.3, 122.0, 121.3, 120.8, 69.7, 38.5, 30.4, 29.5, 18.9. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₁H₂₂ClN₂O 353.1415; Found 353.1405.



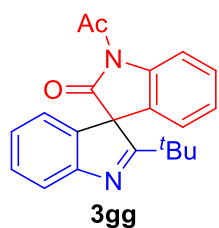
2-(*tert*-Butyl)-1'-isopropylspiro[indole-3,3'-indolin]-2'-one (3ee)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (38 mg, 57%), mp 169-170 °C. ¹H NMR (CDCl₃, 600 MHz): δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.35-7.31 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.08 (td, *J*₁ = 7.8 Hz, *J*₂ = 1.2 Hz, 1H), 6.95 (td, *J*₁ = 7.8 Hz, *J*₂ = 0.6 Hz, 1H), 6.77-6.74 (m, 2H), 4.74-4.69 (m, 1H), 1.58 (d, *J* = 6.6 Hz, 3H), 1.54 (d, *J* = 7.2 Hz, 3H), 1.20 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 150 MHz): δ 187.3, 171.6, 156.1, 143.4, 140.3, 128.83, 128.80, 127.4, 126.1, 124.4, 122.5, 121.0, 120.6, 110.5, 70.3, 44.5, 38.4, 29.4, 19.5, 18.8. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₂H₂₅N₂O 333.1961; Found 333.1959.



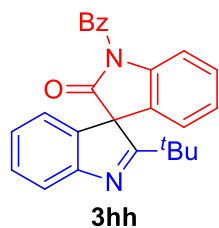
1'-Benzyl-2-(*tert*-butyl)spiro[indole-3,3'-indolin]-2'-one (3ff)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (41 mg, 54%), mp 181-182 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.67 (d, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 2H), 7.38-7.31 (m, 4H), 7.27-7.23 (m, 1H), 7.11-7.08 (m, 1H), 6.96-6.93 (m, 2H), 6.76 (t, $J = 8.4$ Hz, 2H), 5.18 (d, $J = 15.2$ Hz, 1H), 4.84 (d, $J = 15.2$ Hz, 1H), 1.18 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 187.1, 172.3, 156.1, 143.8, 140.1, 135.6, 129.0, 128.97, 128.91, 128.0, 127.9, 127.1, 126.2, 124.2, 123.1, 121.2, 120.7, 110.0, 70.1, 44.7, 38.5, 29.5. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}$ 381.1961; Found 381.1951.



1'-Acetyl-2-(*tert*-butyl)spiro[indole-3,3'-indolin]-2'-one (3gg)

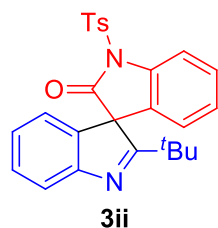
Eluent: petroleum ether/ethyl acetate (30:1). White solid (16 mg, 24%), mp 146-147 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 8.37 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.43-7.37 (m, 2H), 7.13 (t, $J = 7.6$ Hz, 2H), 6.84 (d, $J = 7.6$ Hz, 1H), 6.77 (dd, $J_1 = 7.6$ Hz, $J_2 = 0.8$ Hz, 1H), 2.68 (s, 3H), 1.20 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 186.6, 173.1, 170.8, 155.8, 141.0, 140.5, 129.5, 126.6, 126.3, 125.7, 123.8, 121.4, 120.9, 117.5, 70.5, 38.6, 29.6, 26.7. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{NaO}_2$ 355.1417; Found 355.1409.



1'-Benzoyl-2-(*tert*-butyl)spiro[indole-3,3'-indolin]-2'-one (3hh)

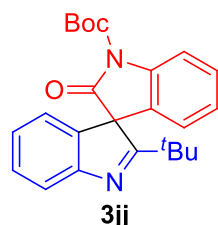
Eluent: petroleum ether/ethyl acetate (30:1). White solid (30 mg, 38%), mp 182-183 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.96 (d, $J = 8.4$ Hz, 1H), 7.75-7.72 (m, 2H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.46-7.38 (m, 4H), 7.21-7.14 (m, 2H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.85-6.83 (m, 1H), 1.23 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 186.8, 171.8, 169.0, 155.8, 141.1, 140.3, 133.5, 133.3, 129.52, 129.46, 129.44,

128.4, 126.8, 126.6, 125.5, 124.1, 121.13, 121.05, 116.0, 70.6, 38.5, 29.6. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{26}H_{22}N_2NaO_2$ 417.1573; Found 417.1567.



2-(*tert*-Butyl)-1'-tosylspiro[indole-3,3'-indolin]-2'-one (**3ii**)

Eluent: petroleum ether/ethyl acetate (30:1). White solid (40 mg, 45%), mp 241-242 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 8.12 (d, $J = 8.4$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 2H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.34-7.29 (m, 3H), 7.08 (t, $J = 7.6$ Hz, 1H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.69 (d, $J = 7.6$ Hz, 1H), 6.48 (d, $J = 7.2$ Hz, 1H), 2.44 (s, 3H), 0.98 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 186.2, 170.2, 155.6, 146.1, 140.1, 139.9, 134.5, 129.81, 129.77, 129.4, 128.2, 126.4, 126.2, 125.3, 124.3, 121.3, 120.8, 114.7, 69.9, 38.2, 29.4, 21.8. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{26}H_{24}N_2NaO_3S$ 467.1400; Found 467.1385.

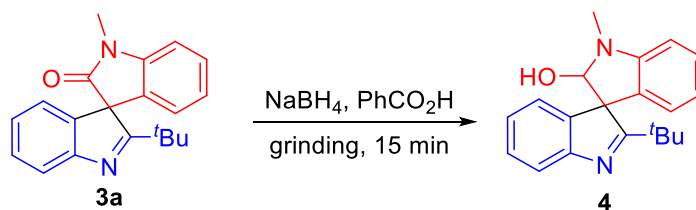


tert-Butyl 2-(*tert*-butyl)-2'-oxospiro[indole-3,3'-indoline]-1'-carboxylate (**3jj**)

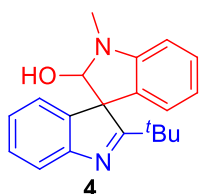
Eluent: petroleum ether/ethyl acetate (30:1). White solid (25 mg, 32%), mp 115-116 °C. 1H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.40-7.34 (m, 2H), 7.13-7.06 (m, 2H), 6.87 (d, $J = 7.2$ Hz, 1H), 6.74 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 1.64 (s, 9H), 1.20 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 186.9, 170.0, 155.8, 149.1, 140.7, 140.6, 129.33, 129.26, 126.4, 126.0, 124.9, 124.0, 121.6, 120.7, 115.8, 85.0, 70.5, 38.5, 29.5, 28.1. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{24}H_{27}N_2O_3$ 391.2016; Found 391.2010.

2. Structural elaborations of **3a**

2.1. Synthesis of **4**^[4]



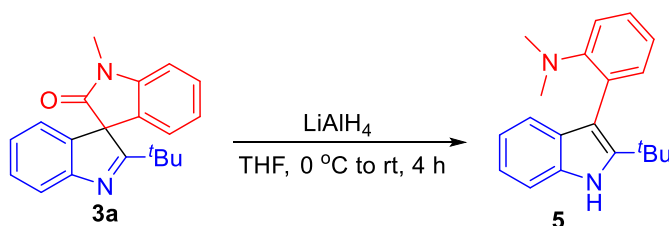
A mixture of **3a** (60.9 mg, 0.2 mmol), sodium borohydride (15.1 mg, 0.4 mmol) and benzoic acid (48.8 mg, 0.4 mmol) was ground with an agate mortar and pestle at room temperature for 15 min. It was then quenched with saturated aqueous solution of NaHCO₃ and extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were washed with water and dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to give **4** (36 mg, 59%).



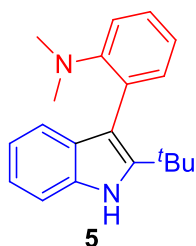
2-(*tert*-Butyl)-1'-methylspiro[indole-3,3'-indolin]-2'-ol (**4**)

Eluent: petroleum ether/ethyl acetate (20:1). Yellow solid (36 mg, 59%), mp 187-188 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.32 (td, *J*₁ = 7.6 Hz, *J*₂ = 0.8 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.11-7.06 (m, 2H), 6.87-6.84 (m, 2H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 1H), 4.13 (s, 1H), 4.02 (s, 1H), 3.24 (s, 3H), 0.88 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 176.2, 151.1, 144.2, 133.6, 132.0, 128.8, 128.4, 124.0, 123.1, 122.7, 119.8, 111.1, 107.8, 80.5, 59.3, 34.2, 28.0, 26.4. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₀H₂₃N₂O 307.1805; Found 307.1800.

2.2. Synthesis of **5**^[5]



Under an argon atmosphere, a solution of LiAlH_4 (75.9 mg, 2.0 mmol) in anhydrous THF (2 mL) was added dropwise to a solution of **3a** (60.9 mg, 0.2 mmol) in anhydrous THF (2 mL) at 0 °C. The resulting mixture was then stirred at room temperature for 4 h. Upon completion, it was quenched with saturated aqueous solution of NaHCO_3 , filtered and extracted with ethyl acetate (10 mL \times 3). The combined organic layers were washed with water and dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (30:1) as the eluent to give **5** (27 mg, 46%).

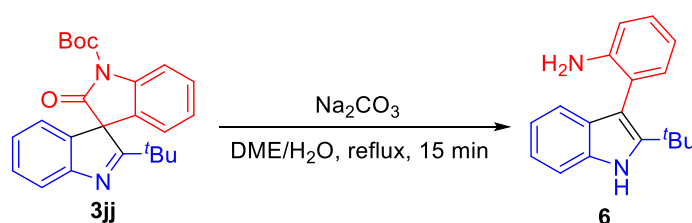


2-(2-(*tert*-Butyl)-1*H*-indol-3-yl)-*N,N*-dimethylaniline (**5**)

Eluent: petroleum ether/ethyl acetate (30:1). White solid (27 mg, 46%), mp 67-68 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.95 (s, 1H), 7.30-7.25 (m, 2H), 7.22-7.17 (m, 2H), 7.13 (td, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.03-6.98 (m, 2H), 6.93 (td, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 2.48 (s, 6H), 1.27 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 153.4, 141.8, 134.5, 133.9, 130.4, 129.3, 127.7, 121.3, 120.3, 119.38, 119.36, 117.2, 112.0, 109.8, 42.9, 33.5, 30.1. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{25}\text{N}_2$ 293.2012; Found 293.2011.

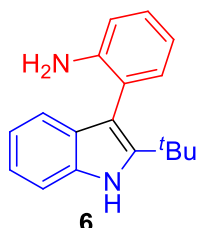
3. Structural elaborations of **3jj**

3.1. Synthesis of **6**^[6]



A solution of Na_2CO_3 (12.7 mg, 0.12 mmol) in H_2O (2 mL) was added to a solution of **3jj** (39 mg, 0.1 mmol) in DME (2 mL), and the resulting mixture was stirred under reflux for 15 min. Upon completion, it was

cooled to room temperature, and extracted with CH_2Cl_2 (10 mL \times 3). The combined organic layers were washed with water and dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (30:1) as the eluent to give **6** (20 mg, 76%).

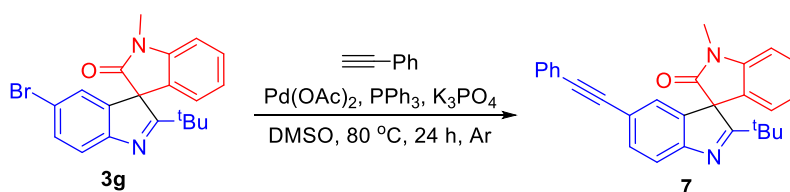


2-(2-(*tert*-Butyl)-1*H*-indol-3-yl)aniline (**6**)

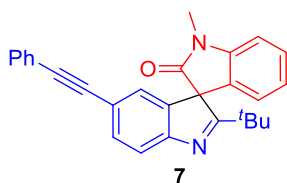
Eluent: petroleum ether/ethyl acetate (30:1). White solid (20 mg, 76%), mp 134-135 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 8.11 (s, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.22-7.14 (m, 4H), 7.03 (t, $J = 7.6$ Hz, 1H), 6.82-6.78 (m, 2H), 3.57 (s, 2H), 1.34 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 MHz): δ 145.7, 143.9, 134.3, 132.9, 129.5, 128.3, 121.8, 121.6, 119.7, 119.0, 117.9, 114.7, 110.2, 108.8, 33.3, 30.4. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2$ 265.1699; Found 265.1685.

4. Structural elaborations of **3g**

4.1. Synthesis of **7**^[7]



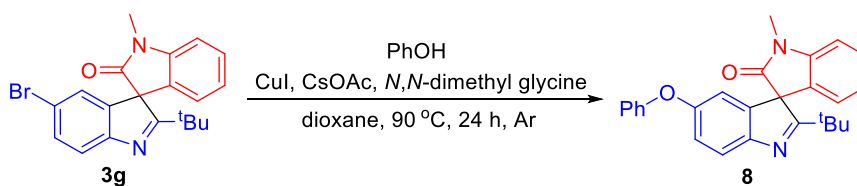
To a reaction tube equipped with a stir bar were added **3g** (38.3 mg, 0.1 mmol), ethynylbenzene (16.5 μL , 0.15 mmol), PPh_3 (5.2 mg, 0.02 mmol), K_3PO_4 (25.5 mg, 0.12 mmol), $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.005 mmol) and DMSO (1 mL), and the resulting mixture was stirred at 80 °C for 24 h under an argon atmosphere. Upon completion, it was diluted with ethyl acetate (20 mL) and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **7** (23 mg, 57%).



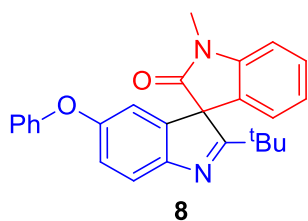
2-(*tert*-Butyl)-1'-methyl-5-(phenylethynyl)spiro[indole-3,3'-indolin]-2'-one (**7**)

Eluent: petroleum ether/ethyl acetate (10:1). Brown solid (23 mg, 57%), mp 150-151 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.53 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz, 1H), 7.45-7.42 (m, 2H), 7.38 (td, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 7.31-7.28 (m, 3H), 7.03-6.97 (m, 3H), 6.78 (d, *J* = 7.2 Hz, 1H), 3.36 (s, 3H), 1.18 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 188.3, 171.8, 156.1, 144.7, 140.1, 132.8, 131.5, 129.4, 128.33, 128.26, 126.5, 124.6, 124.2, 123.3, 123.1, 121.0, 120.6, 109.1, 89.7, 89.4, 70.0, 38.6, 29.3, 27.1. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₂₅N₂O 405.1961; Found 405.1953.

4.2. Synthesis of **8**^[7]



To a reaction tube equipped with a stir bar were added **3g** (38.3 mg, 0.1 mmol), phenol (14.1 mg, 0.15 mmol), *N,N*-dimethyl glycine hydrochloride (4.2 mg, 0.03 mmol), Cs₂CO₃ (65.2 mg, 0.2 mmol), CuI (1.9 mg, 0.01 mmol) and dioxane (1 mL), and the resulting mixture was stirred at 90 °C for 24 h under an argon atmosphere. Upon completion, it was diluted with ethyl acetate (20 mL) and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **8** (16 mg, 40%).



2-(*tert*-Butyl)-1'-methyl-5-phenoxySpiro[indole-3,3'-indolin]-2'-one (**8**)

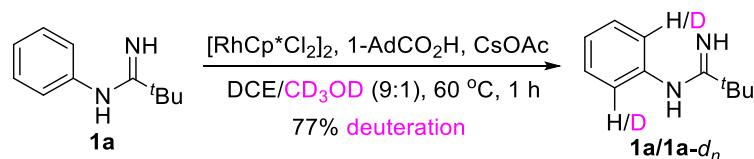
Eluent: petroleum ether/ethyl acetate (10:1). White solid (16 mg, 40%), mp > 300 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.35 (td, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 7.29-7.25 (m, 2H), 7.06-6.98 (m, 2H), 6.97-6.94 (m, 2H), 6.91-6.89 (m, 2H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 3.32 (s, 3H), 1.16 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 186.4, 172.0, 157.5, 155.4, 152.0, 144.6, 141.6, 129.7, 129.3, 126.8, 124.1, 123.3, 123.0, 121.3, 119.3, 118.3, 113.2, 109.0, 70.3, 38.5, 29.4, 27.1. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₆H₂₅N₂O₂ 397.1911; Found 397.1892.

5. Gram-Scale Synthesis of **3a**

To a reaction tube equipped with a stir bar were charged with *N*-phenylpivalimidamide (**1a**, 0.881 g, 5 mmol), DCE (50 mL), [RhCp*Cl₂]₂ (61.8 mg, 0.1 mmol), 1-AdCO₂H (1.803 g, 10.0 mmol), CsOAc (48.0 mg, 0.25 mmol), and 3-diazo-1-methylindolin-2-one (**2a**, 1.298 g, 7.5 mmol). The tube was sealed, and the resulting mixture was stirred at 60 °C (oil bath) under air for 4 h. Upon completion, it was cooled to room temperature, quenched with saturated aqueous solution of NaHCO₃, and then extracted with dichloromethane (75 mL × 3). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3a** (0.897 g, 59%).

III. Mechanism studies

1. Studies on the reversibility of C–H bond activation



To a reaction tube equipped with a stir bar were charged with **1a** (35.2 mg, 0.2 mmol), CD₃OD (0.2 mL), DCE (1.8 mL), $[\text{RhCp}^*\text{Cl}_2]_2$ (2.5 mg, 0.004 mmol), 1-AdCO₂H (72.1 mg, 0.4 mmol) and CsOAc (1.9 mg, 0.01 mmol). The resulting mixture was stirred at 60 °C (oil bath) under air for 1 h. It was then cooled to room temperature, quenched with saturated aqueous solution of NaHCO₃, and then extracted with dichloromethane (10 mL × 3). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1) as eluent to give a mixture of **1a** and **1a-d_n**. Upon analyzing the ¹H NMR spectrum of the mixture as shown in Fig. S1, the deuteration ratio was determined to be 77%.

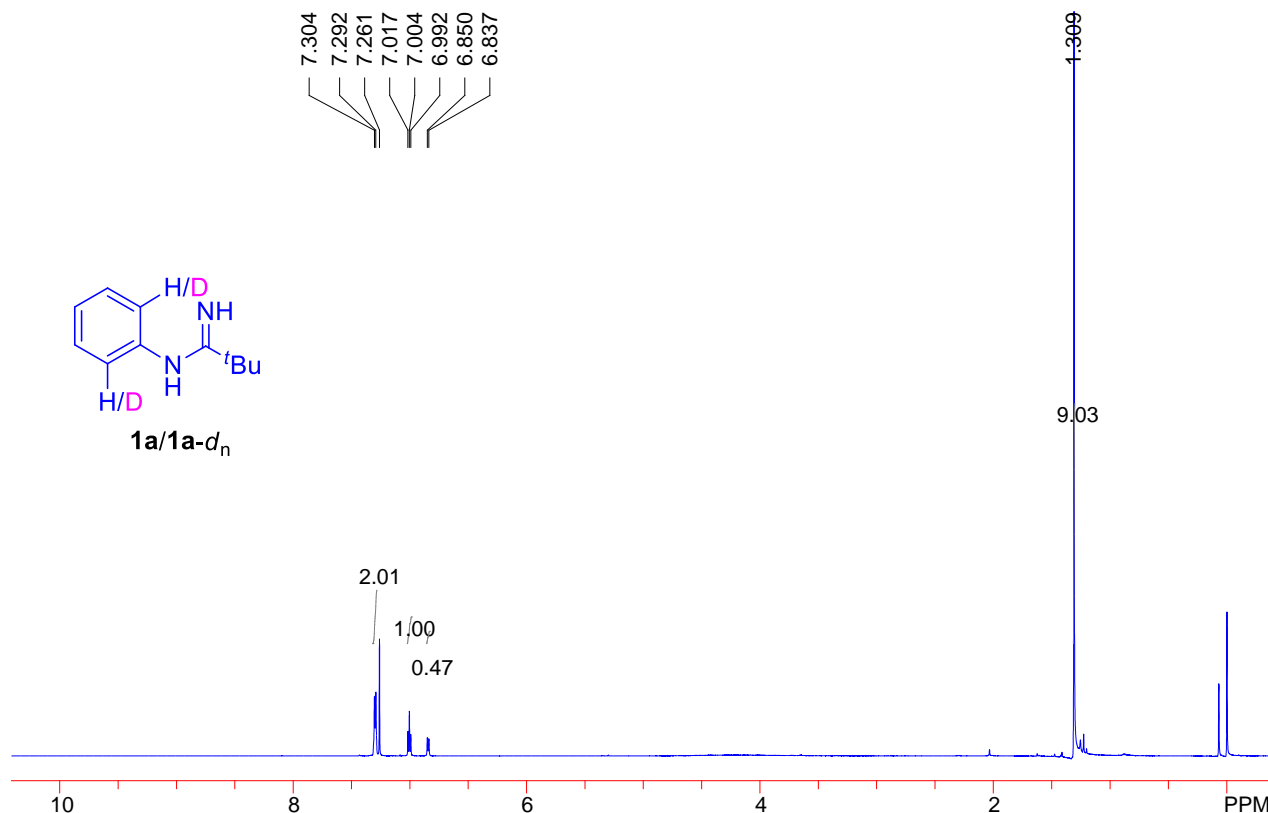
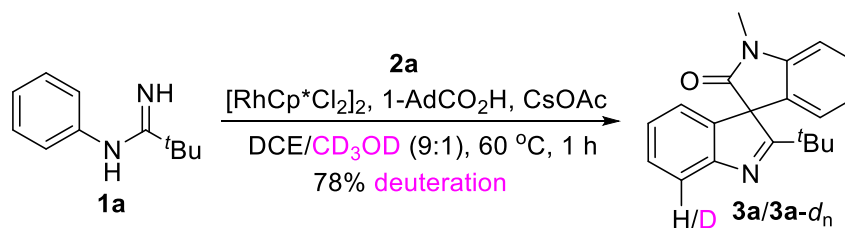


Fig. S1 The ¹H NMR spectrum of products obtained from H/D exchange experiment (I)



To a reaction tube equipped with a stir bar were charged with **1a** (35.2 mg, 0.2 mmol), CD₃OD (0.2 mL), DCE (1.8 mL), [RhCp*Cl₂]₂ (2.5 mg, 0.004 mmol), 1-AdCO₂H (72.1 mg, 0.4 mmol), CsOAc (1.9 mg, 0.01 mmol) and **2a** (52.0 mg, 0.3 mmol). The resulting mixture was stirred at 60 °C (oil bath) under air for 1 h. It was then cooled to room temperature, quenched with saturated aqueous solution of NaHCO₃ and extracted with dichloromethane (10 mL × 3). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to give a mixture of **3a** and **3a-d_n**. Upon analyzing the ¹H NMR spectrum of the mixture as shown in Fig. S2, the deuteration ratio was determined to be 78%.

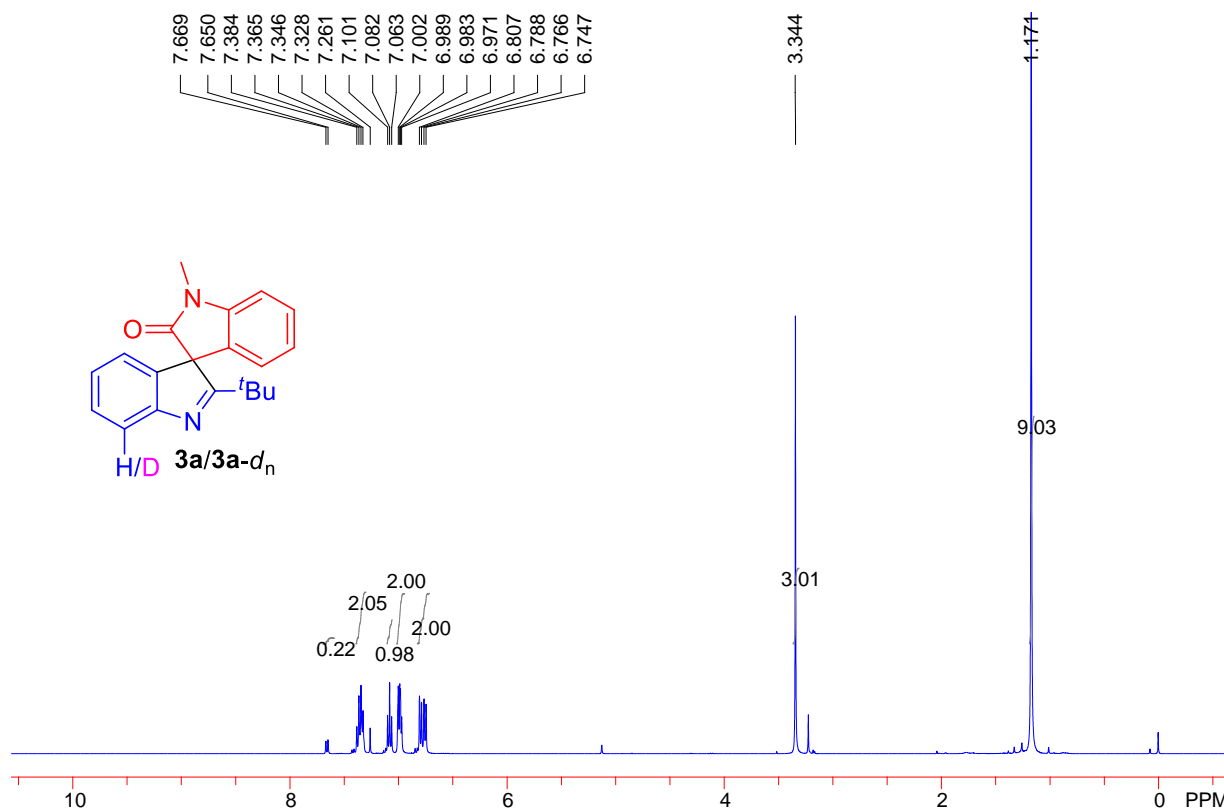
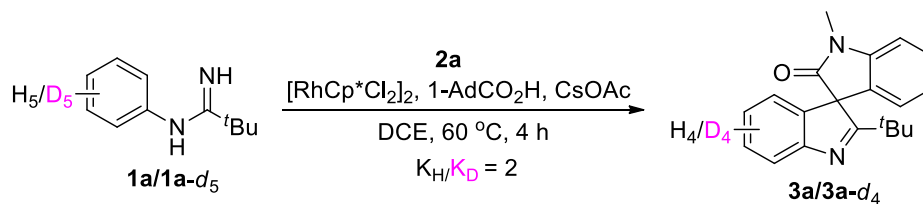


Fig. S2 The ¹H NMR spectrum of products obtained from H/D exchange experiment (II)

2. Kinetic isotope effect study



To a reaction tube equipped with a stir bar were added **1a** (17.6 mg, 0.1 mmol), **1a-d₅** (18.1 mg, 0.1 mmol), DCE (1.0 mL), **2a** (26.0 mg, 0.15 mmol), [RhCp*Cl₂]₂ (1.2 mg, 0.002 mmol), 1-AdCO₂H (36.0 mg, 0.2 mmol) and CsOAc (1.0 mg, 0.005 mmol) with stirring. The tube was sealed, and the resulting mixture was stirred at 60 °C (oil bath) under air for 4 h. Upon completion, it was cooled to room temperature, quenched with saturated aqueous solution of NaHCO₃, and then extracted with dichloromethane (10 mL × 3). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford a mixture of **3a** and **3a-d₄**. Upon analyzing the ¹H NMR spectrum of the mixture as shown in Fig. S3, the ratio of **3a** to **3a-d₄** was determined to be 0.67:0.33. Accordingly, the intermolecular KIE ($k_{\text{H}}/k_{\text{D}}$) was calculated to be 2.

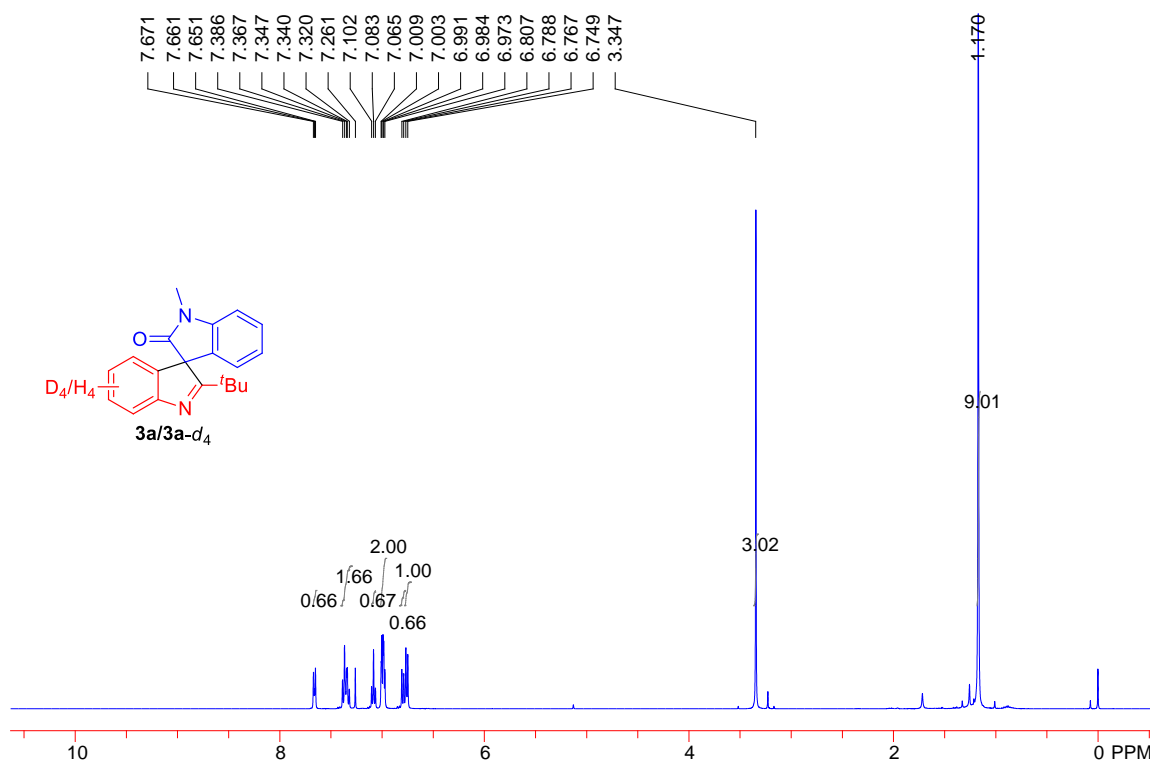
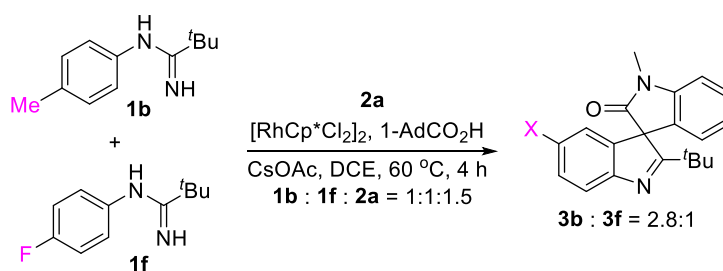


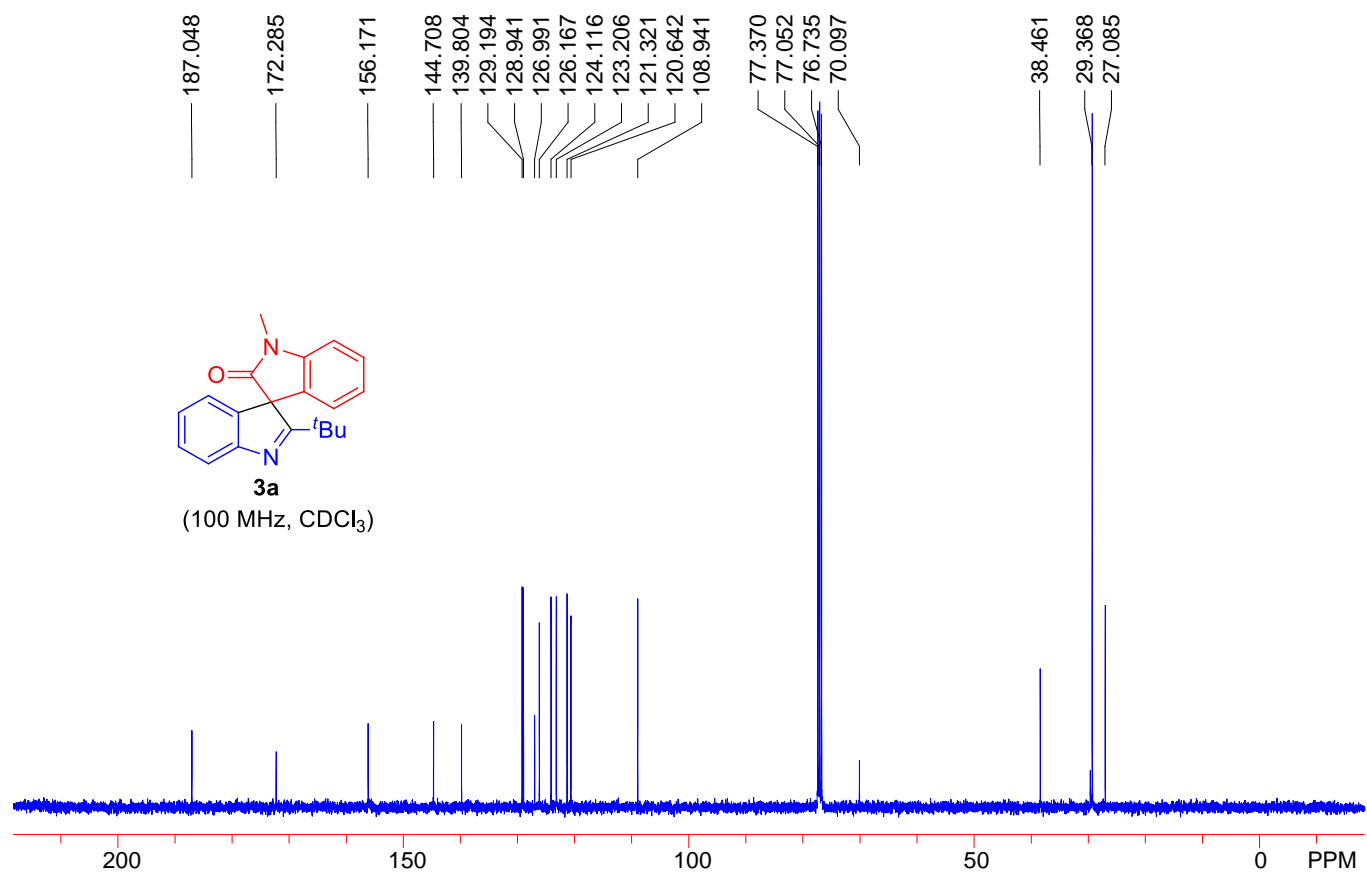
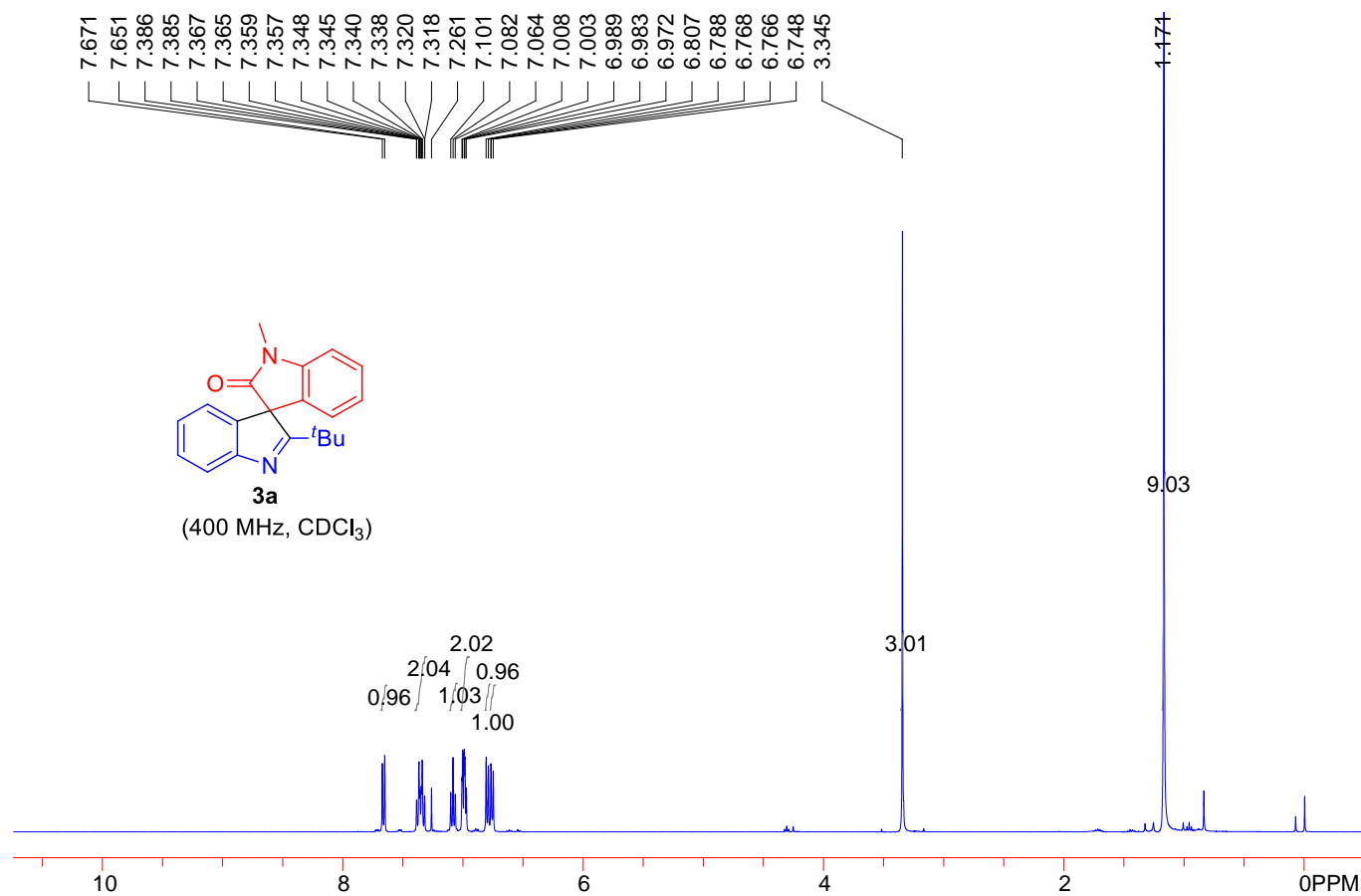
Fig. S3 The ¹H NMR spectrum of products obtained from the intermolecular KIE experiment

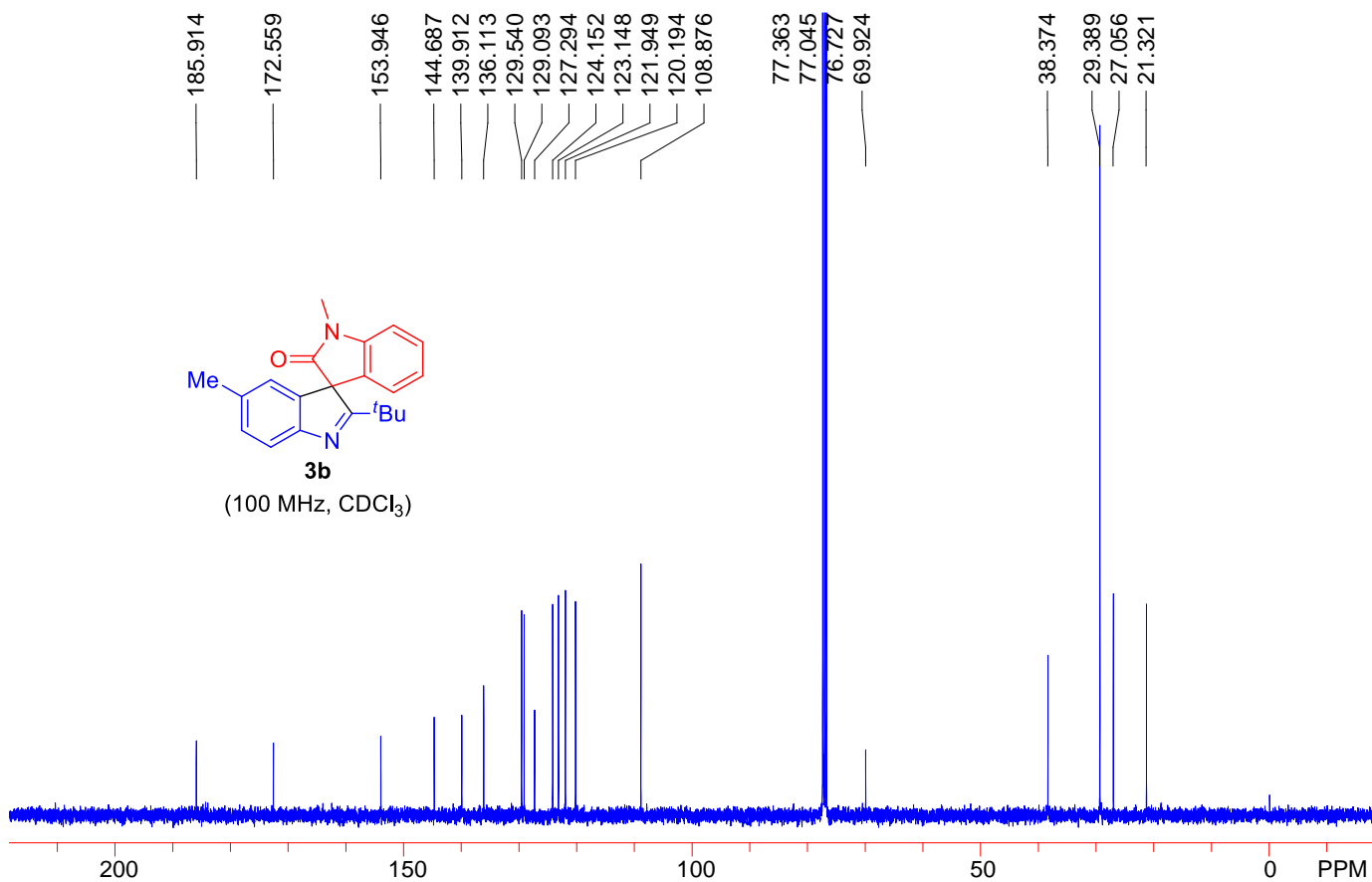
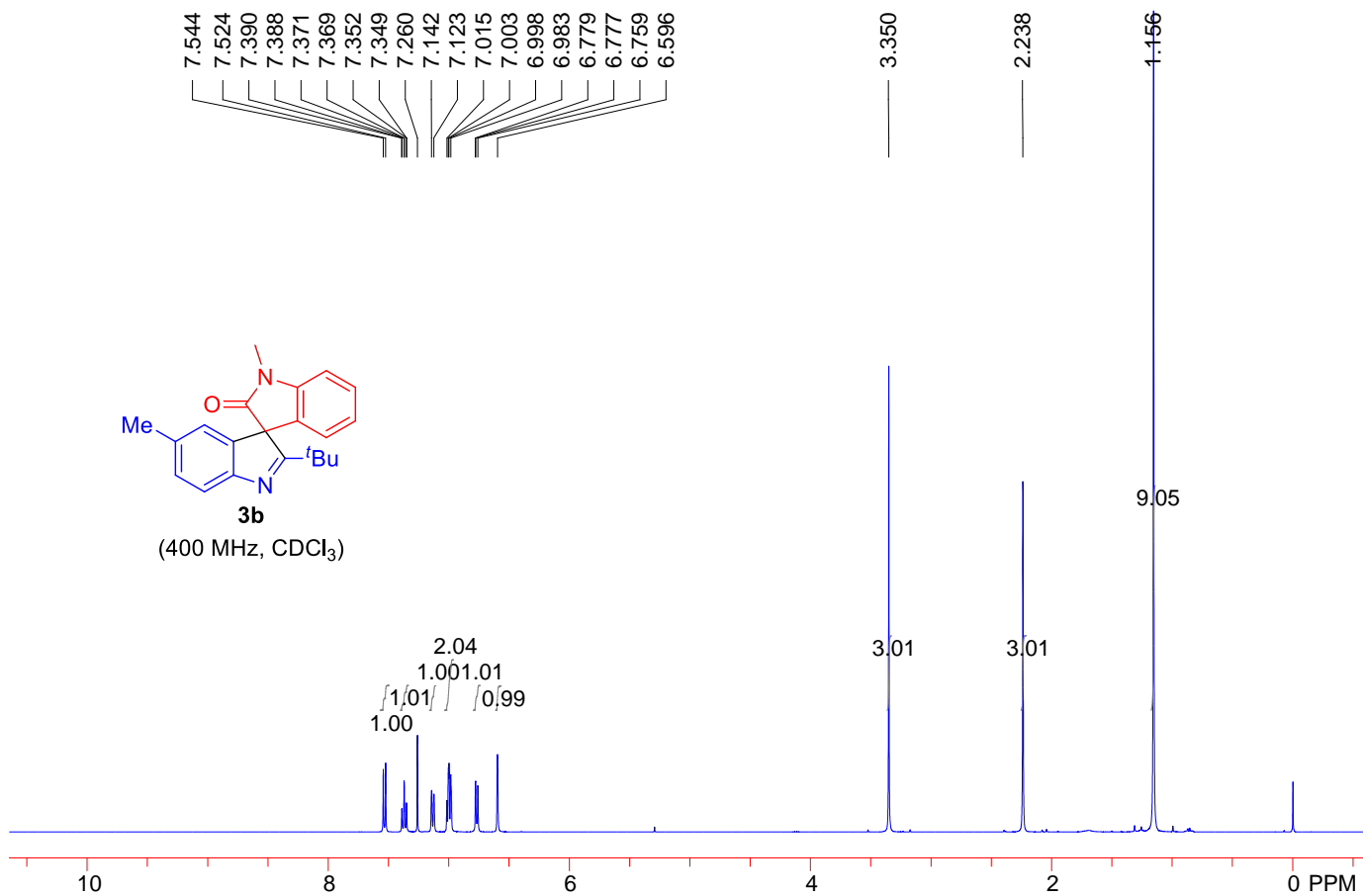
3. Competition experiment between **1b** and **1f**



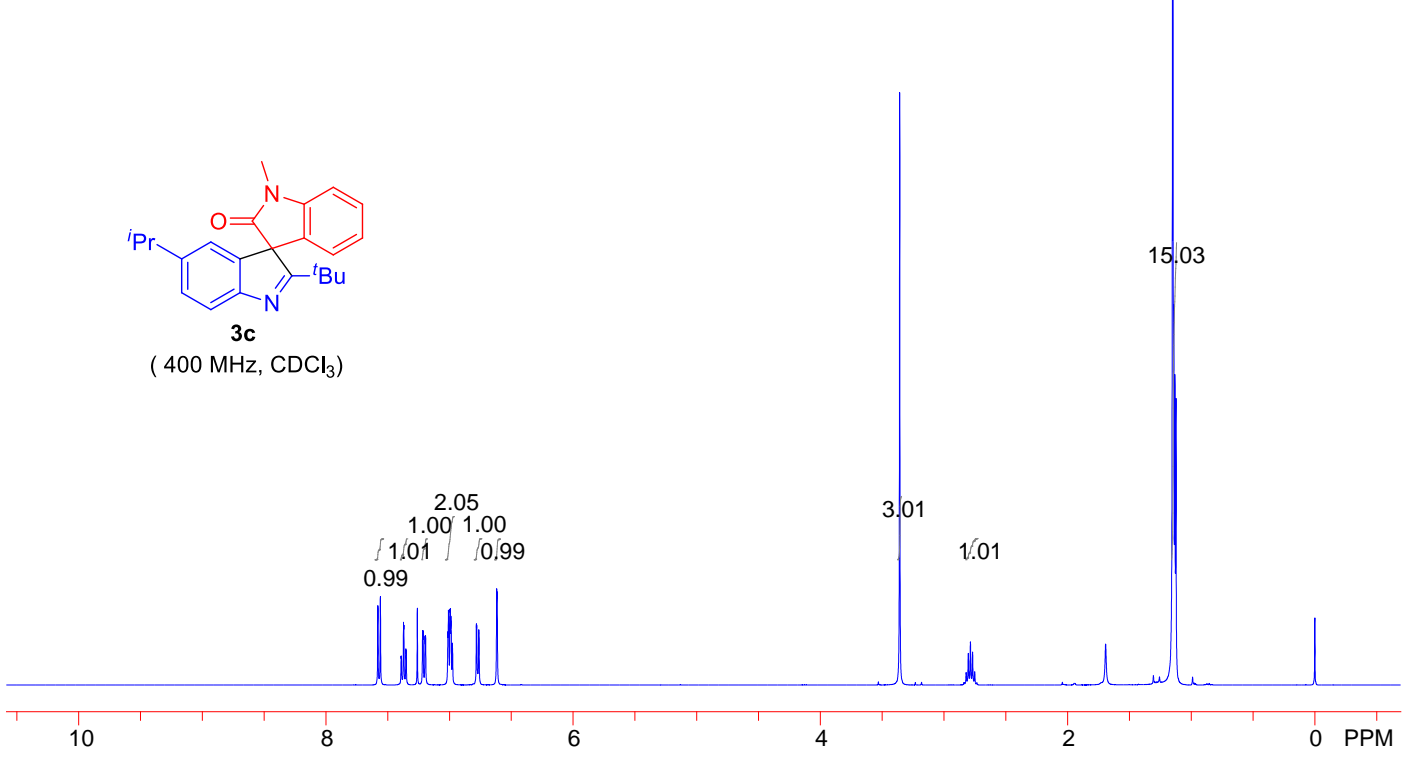
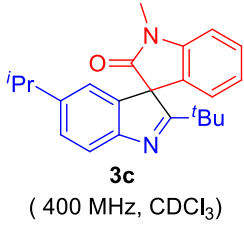
To a reaction tube equipped with a stir bar were charged with *N*-(*p*-tolyl)pivalimidamide (**1b**, 38.1 mg, 0.2 mmol), *N*-(4-fluorophenyl)pivalimidamide (**1f**, 38.8 mg, 0.2 mmol), 3-diazo-1-methylindolin-2-one (**2a**, 52.0 mg, 0.3 mmol), [Cp*RhCl₂]₂ (2.5 mg, 0.004 mmol), 1-AdCO₂H (72.1 mg, 0.4 mmol), CsOAc (1.9 mg, 0.01 mmol) and DCE (2.0 mL). The mixture was stirred at 60 °C (oil bath) for 4 h. Upon completion, it was cooled to room temperature, quenched with saturated aqueous solution of NaHCO₃, and then extracted with dichloromethane (10 mL × 3). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3b** (36 mg, 57%) and **3f** (13 mg, 20%).

IV. Copies of NMR spectra of 3a-3jj

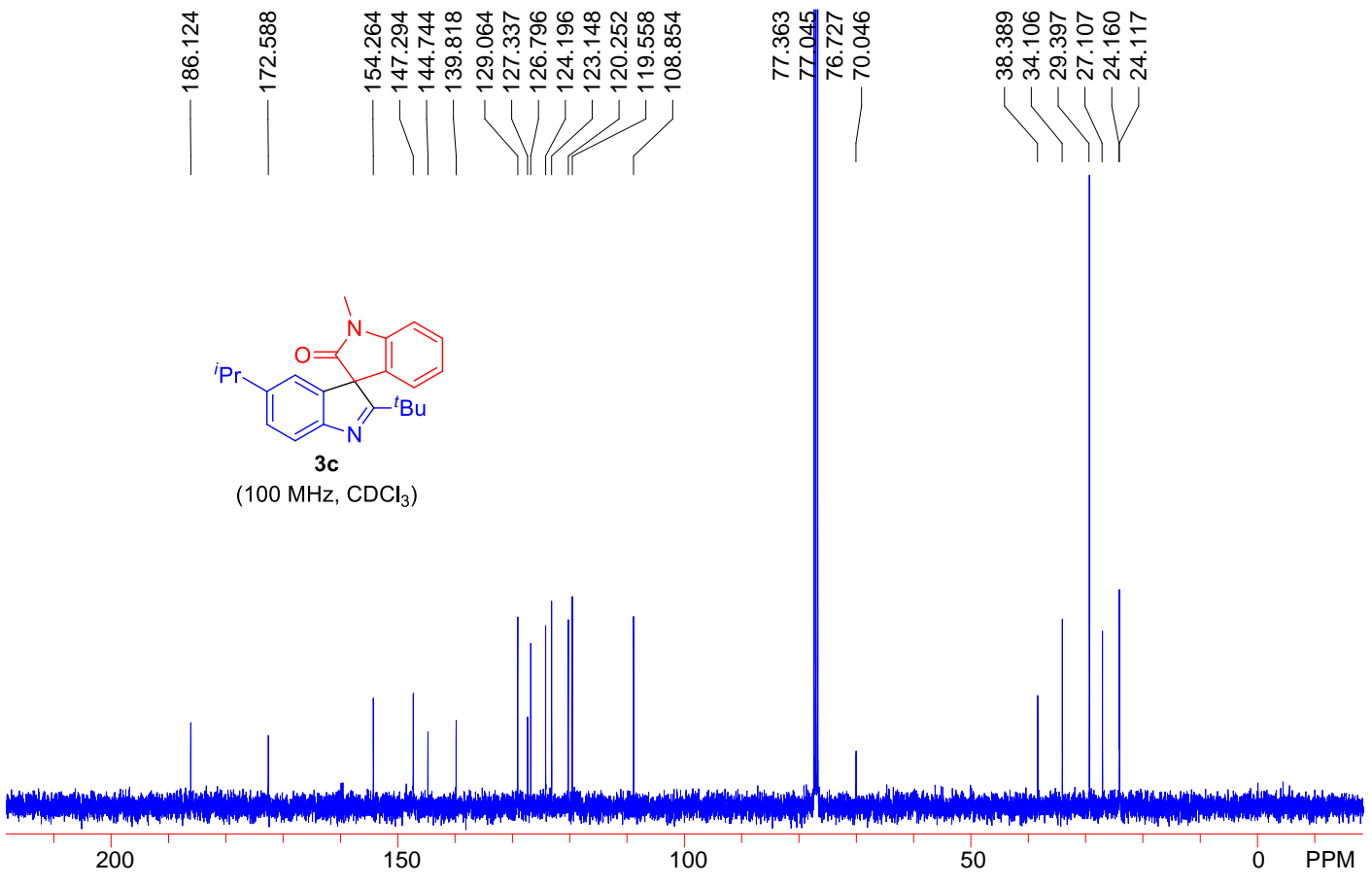
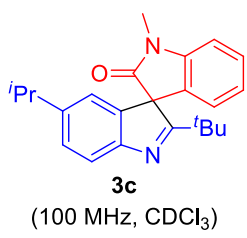


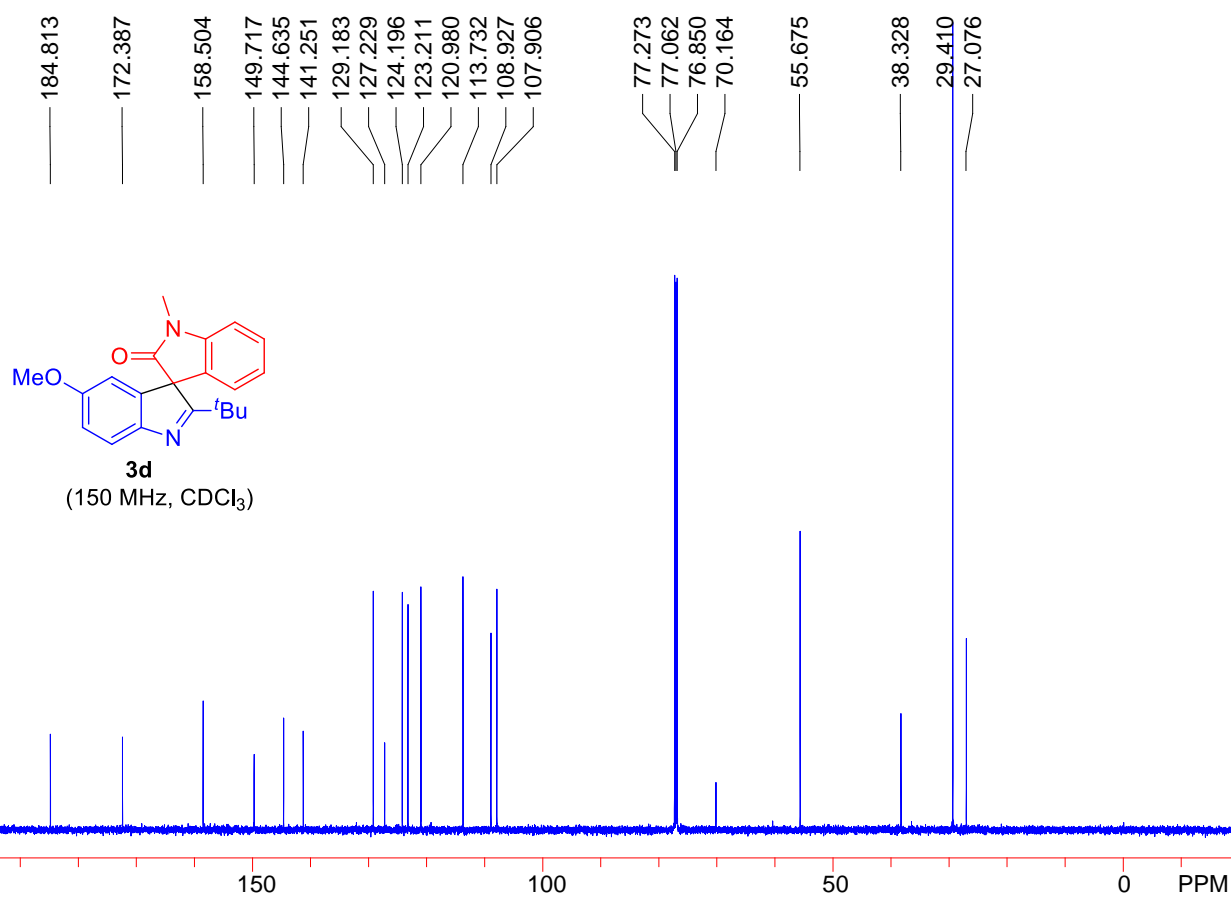
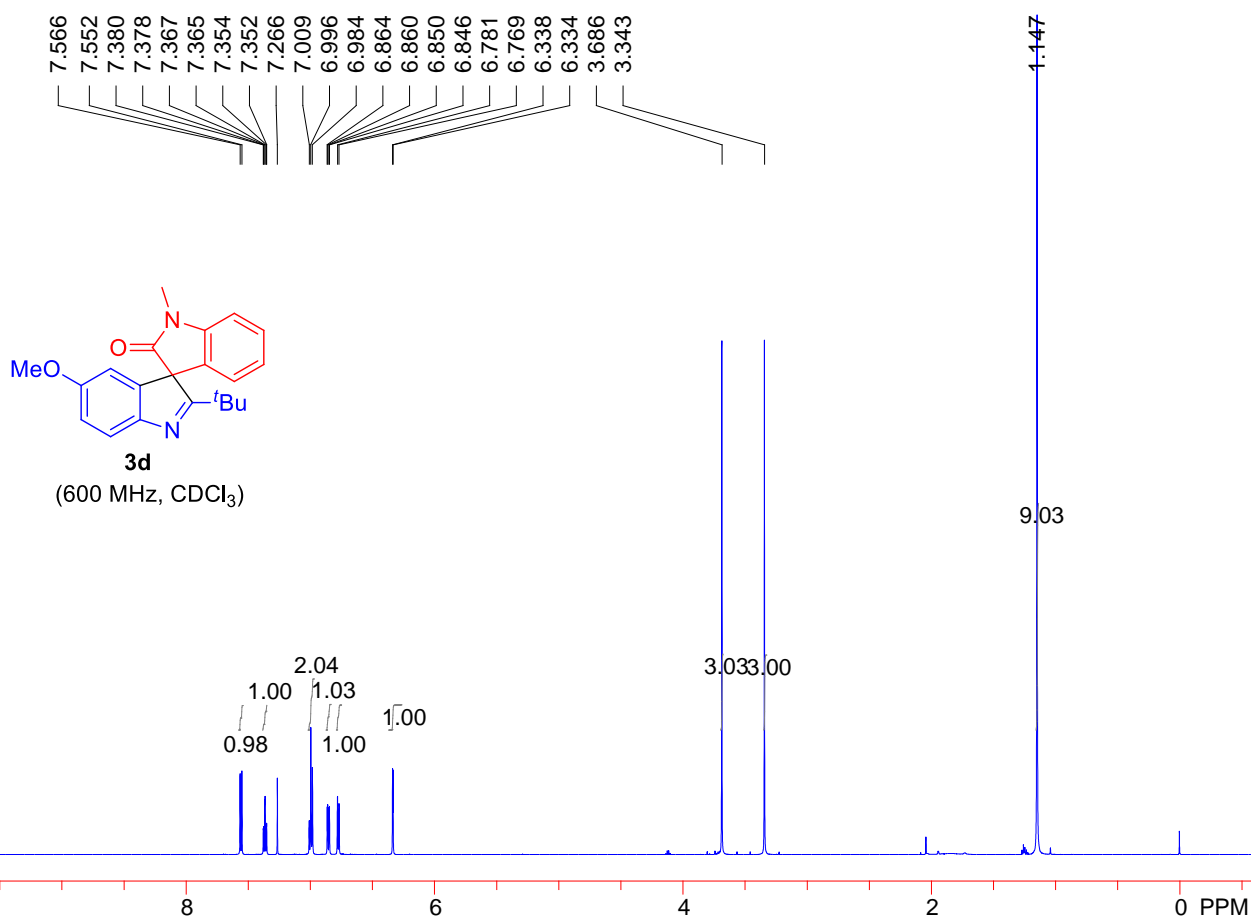


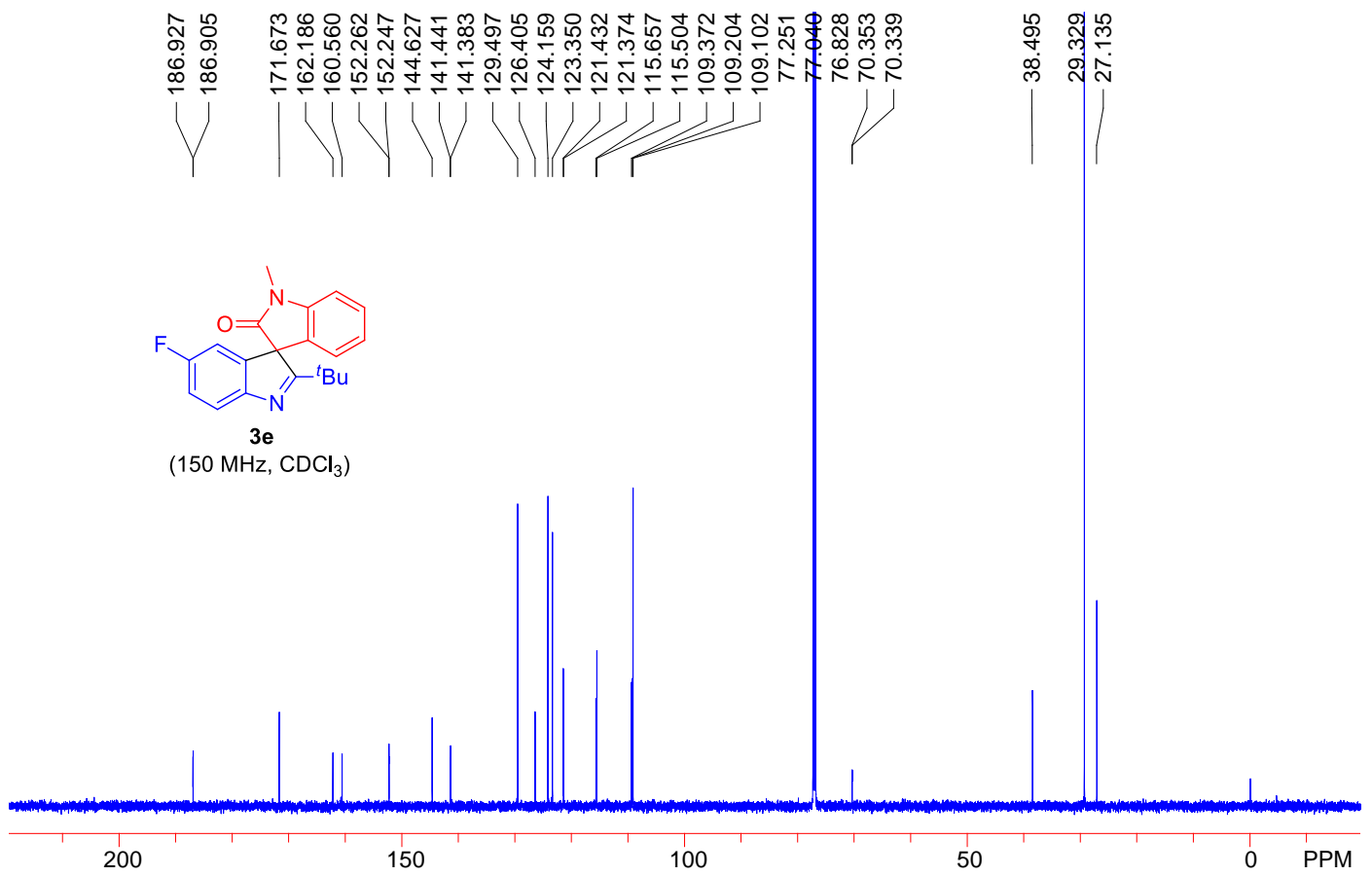
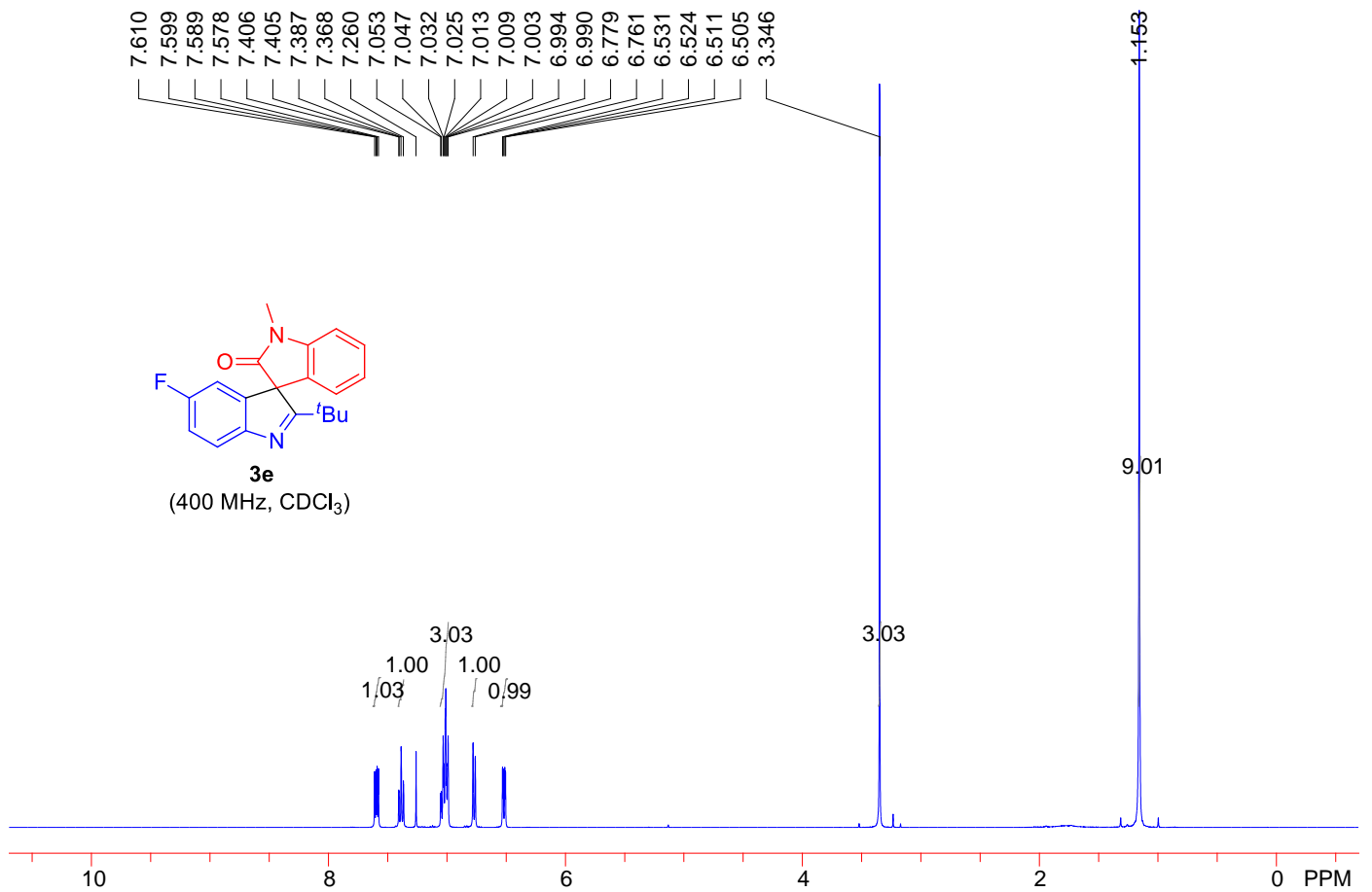
7.579
7.559
7.391
7.388
7.372
7.369
7.353
7.350
7.260
7.217
7.213
7.197
7.193
7.012
7.008
6.995
6.993
6.988
6.976
6.782
6.779
6.770
6.762
6.761
6.617
6.614
6.614
3.357
2.819
2.802
2.784
2.767
2.750
1.147
1.139
1.130
1.122



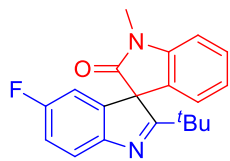
186.124
172.588
154.264
147.294
144.744
139.818
129.064
127.337
126.796
124.196
123.148
120.252
119.558
108.854
77.363
77.045
76.727
70.046
38.389
34.106
29.397
27.107
24.160
24.117



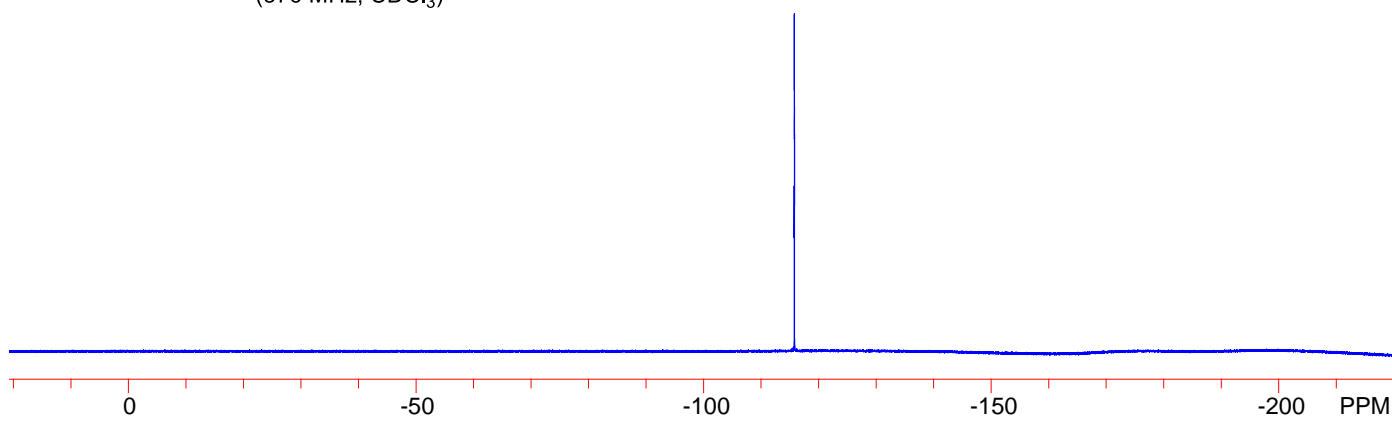


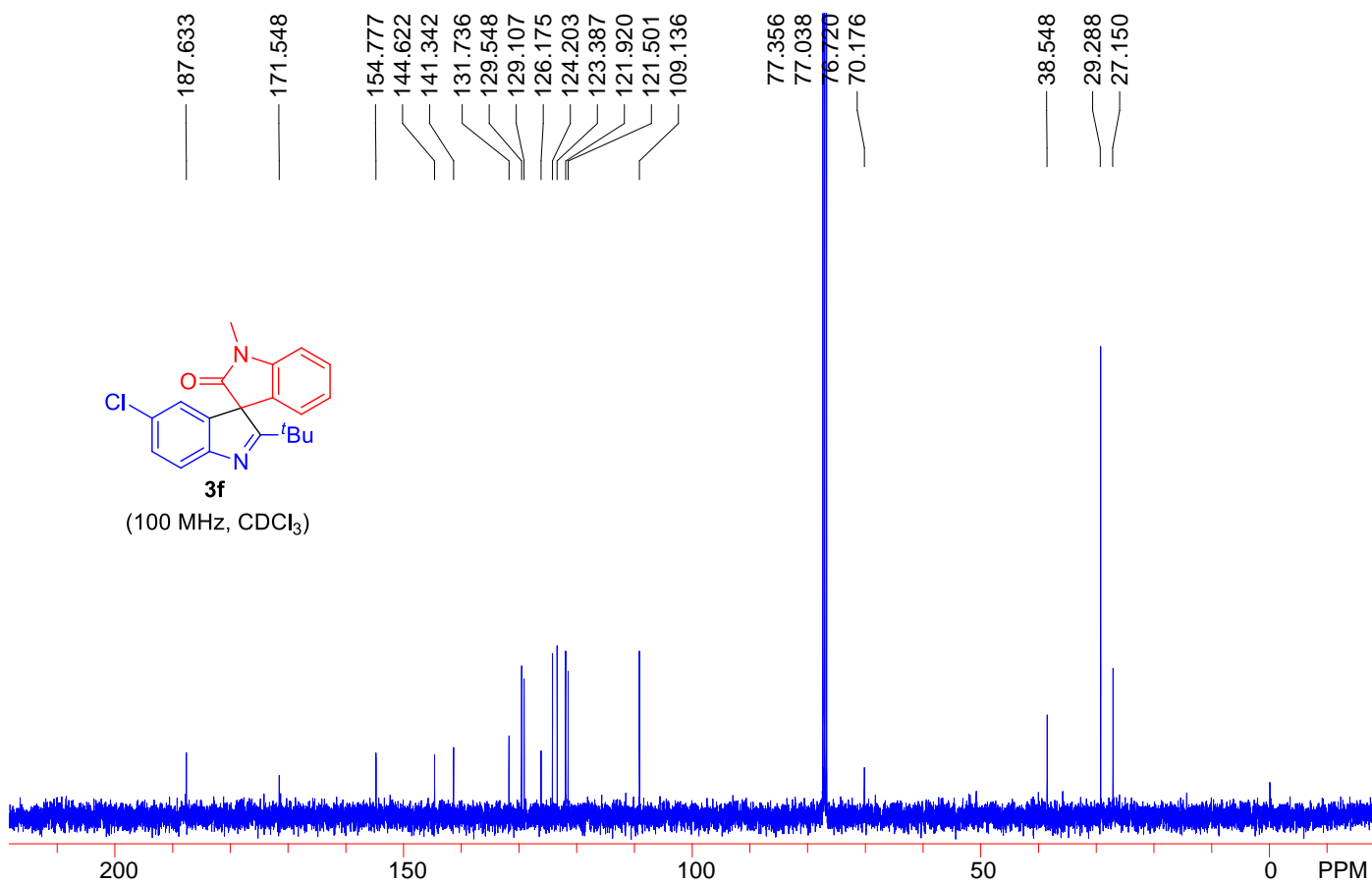
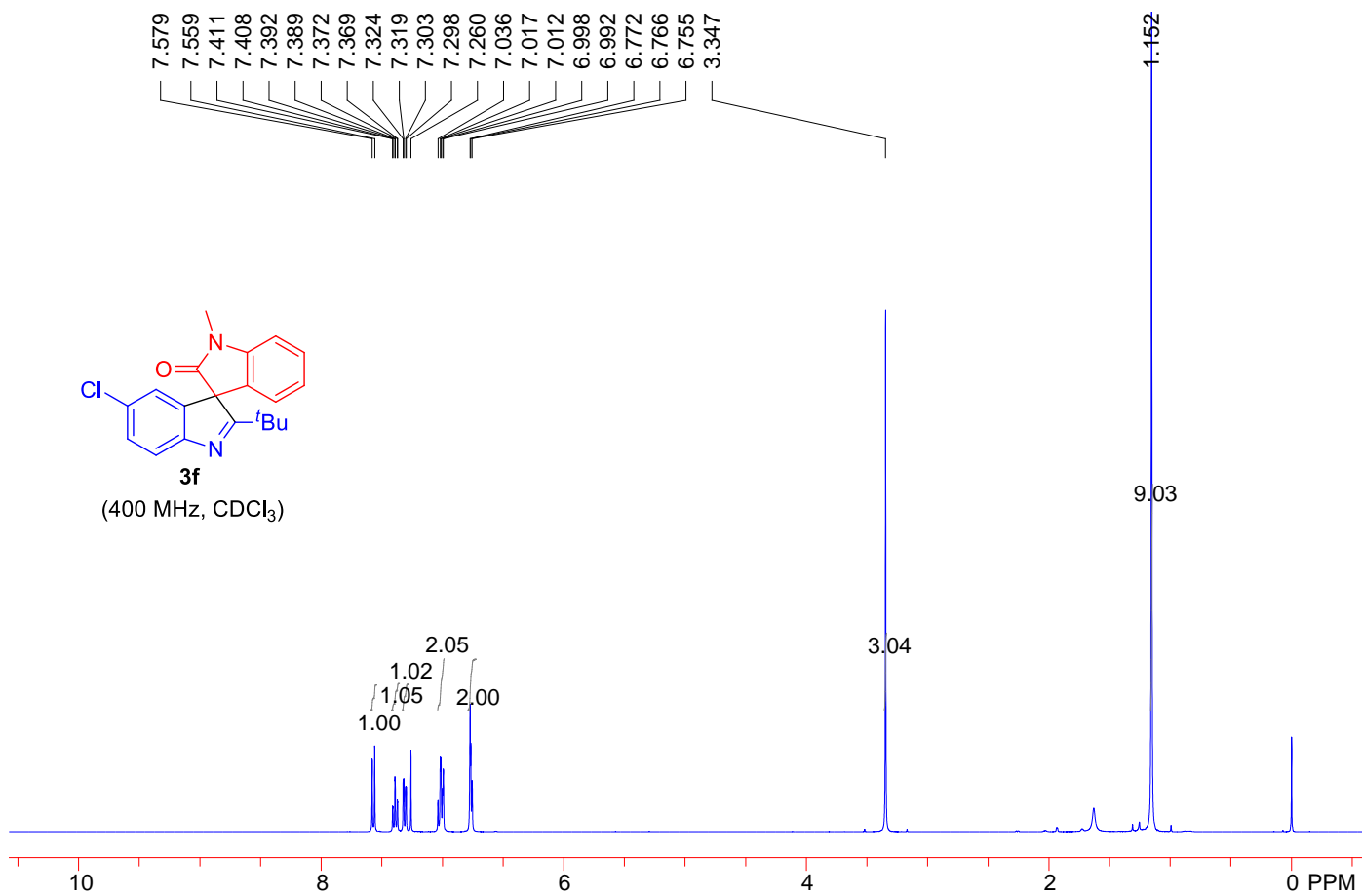


115.690
115.701
115.712
115.723
115.734
115.745

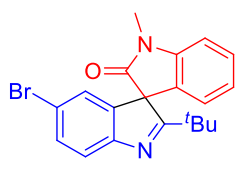


3e
(376 MHz, CDCl₃)

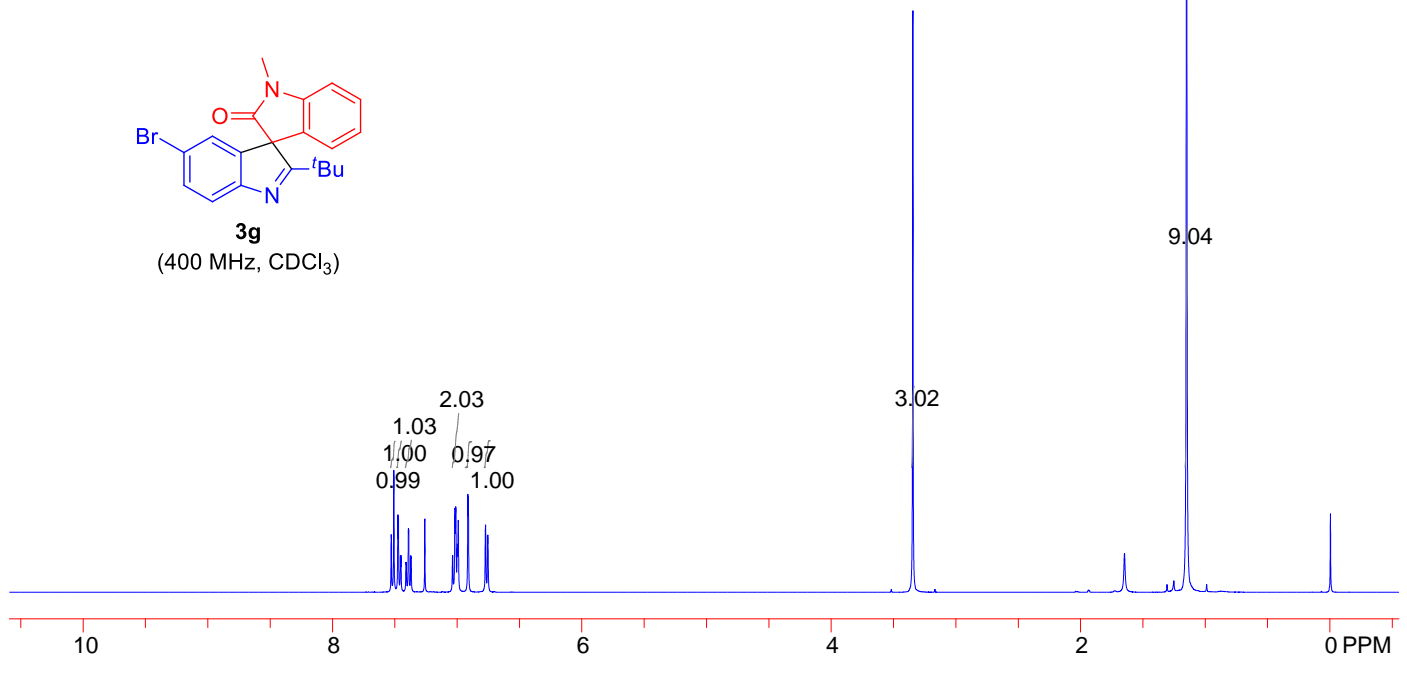




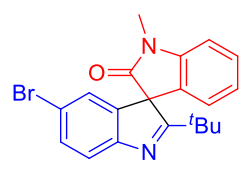
7.529
7.508
7.476
7.471
7.455
7.451
7.411
7.408
7.391
7.389
7.372
7.370
7.260
7.036
7.017
7.011
6.998
6.991
6.914
6.910
6.772
6.754
3.346



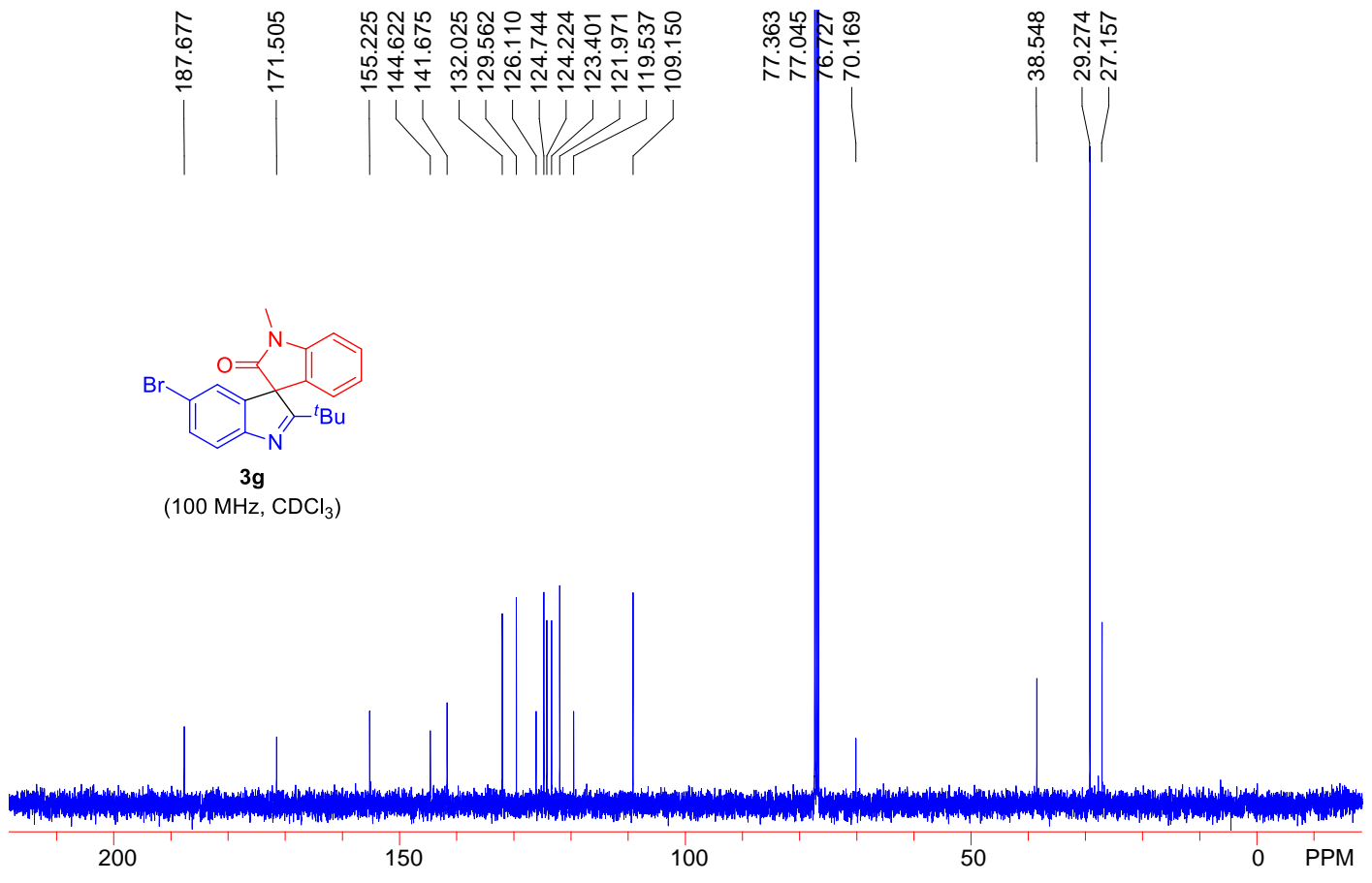
3g
(400 MHz, CDCl₃)

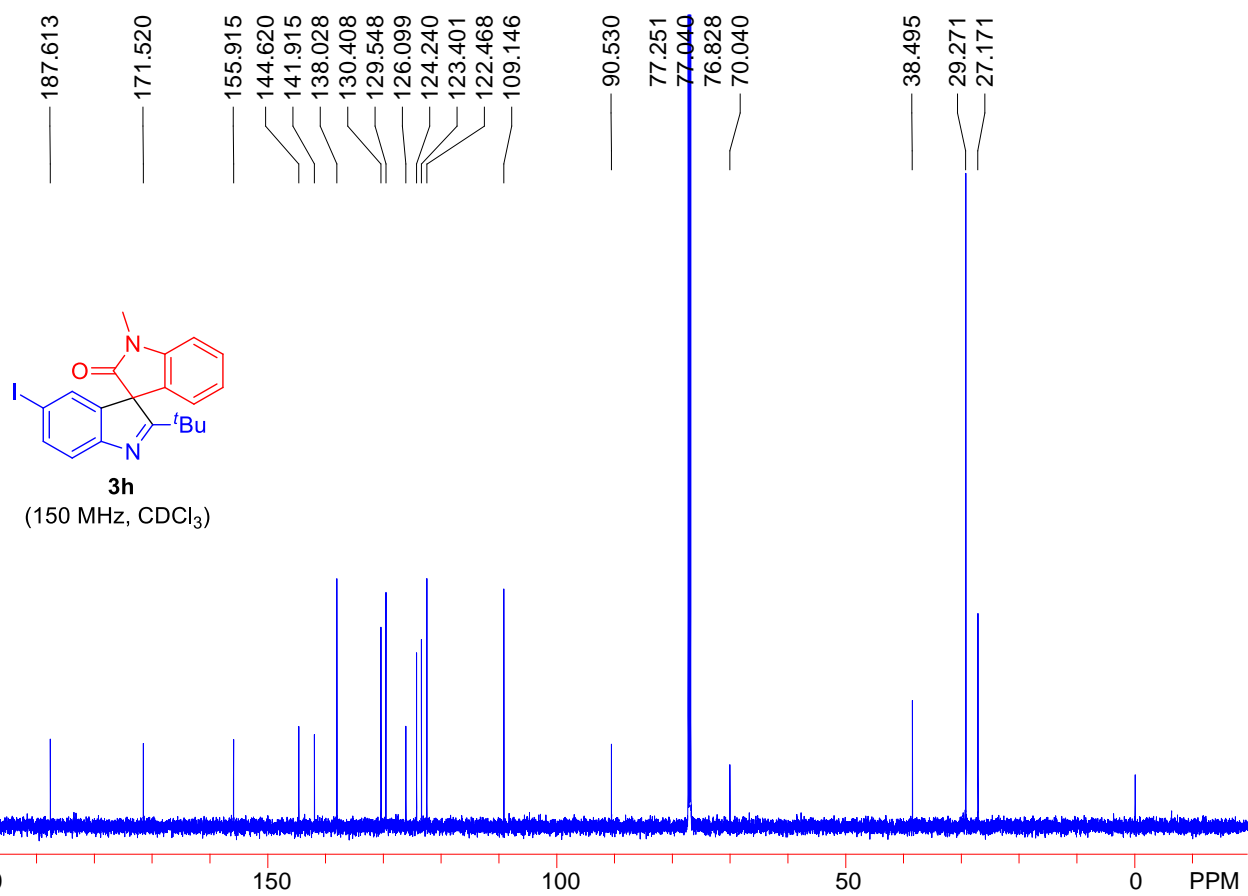
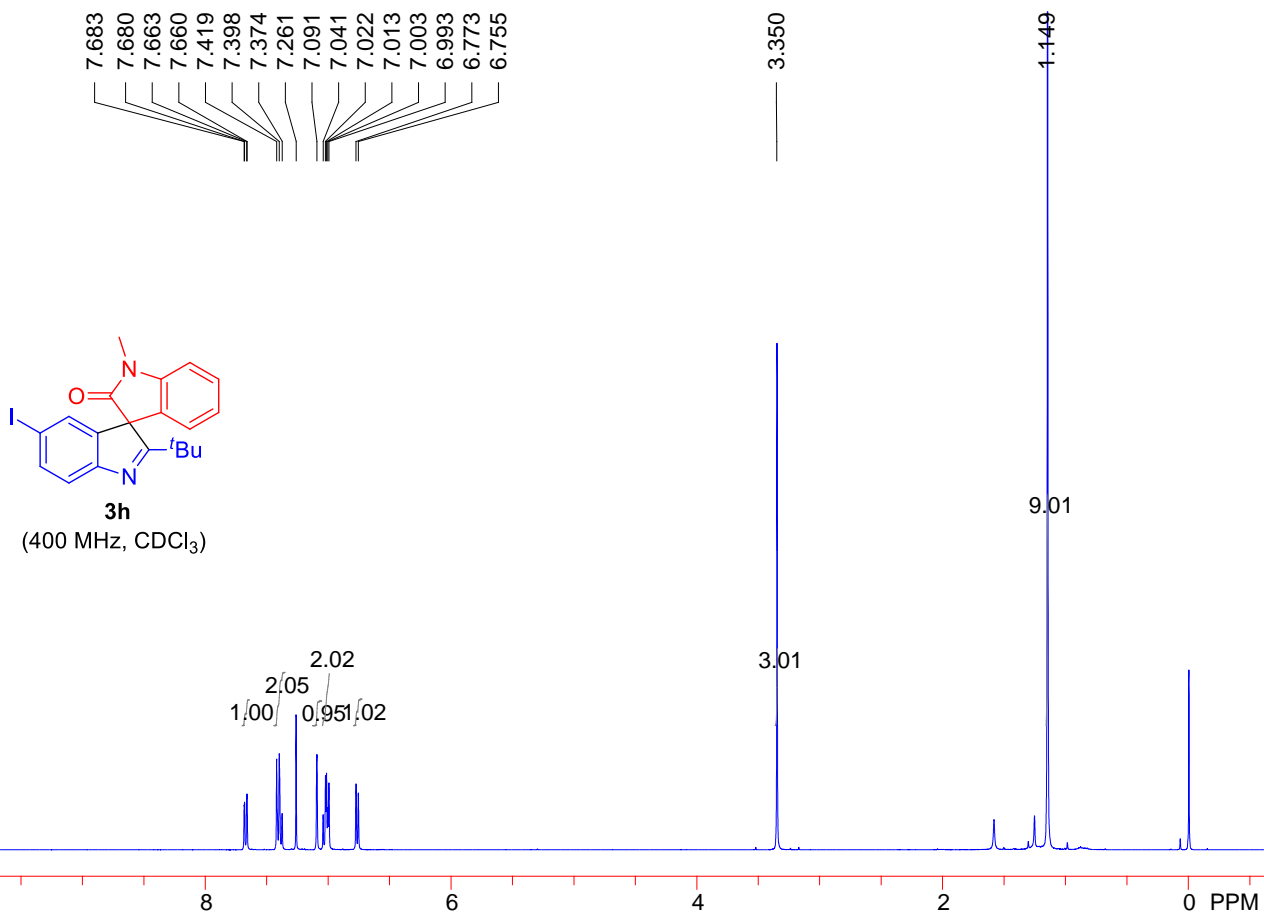


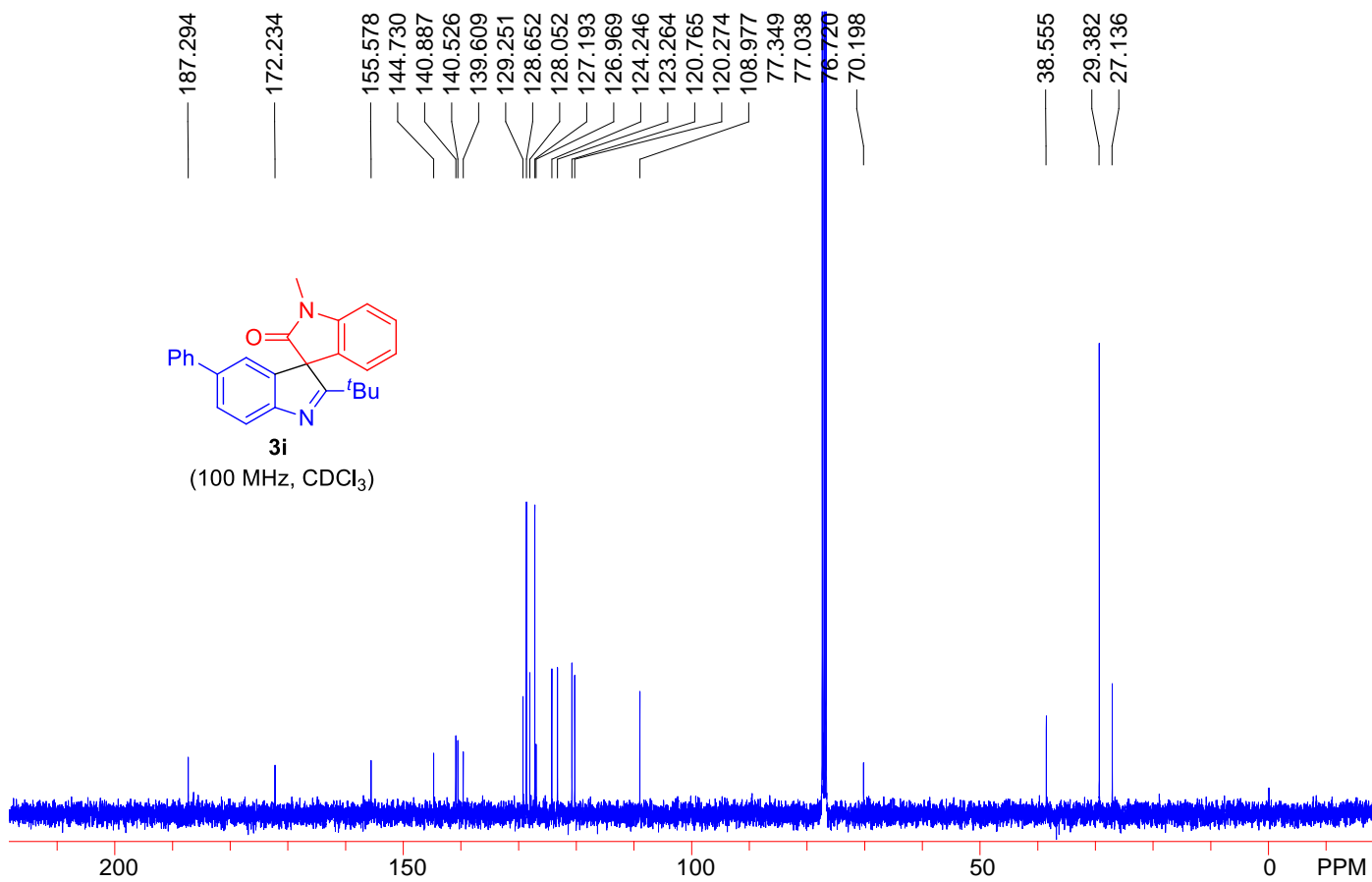
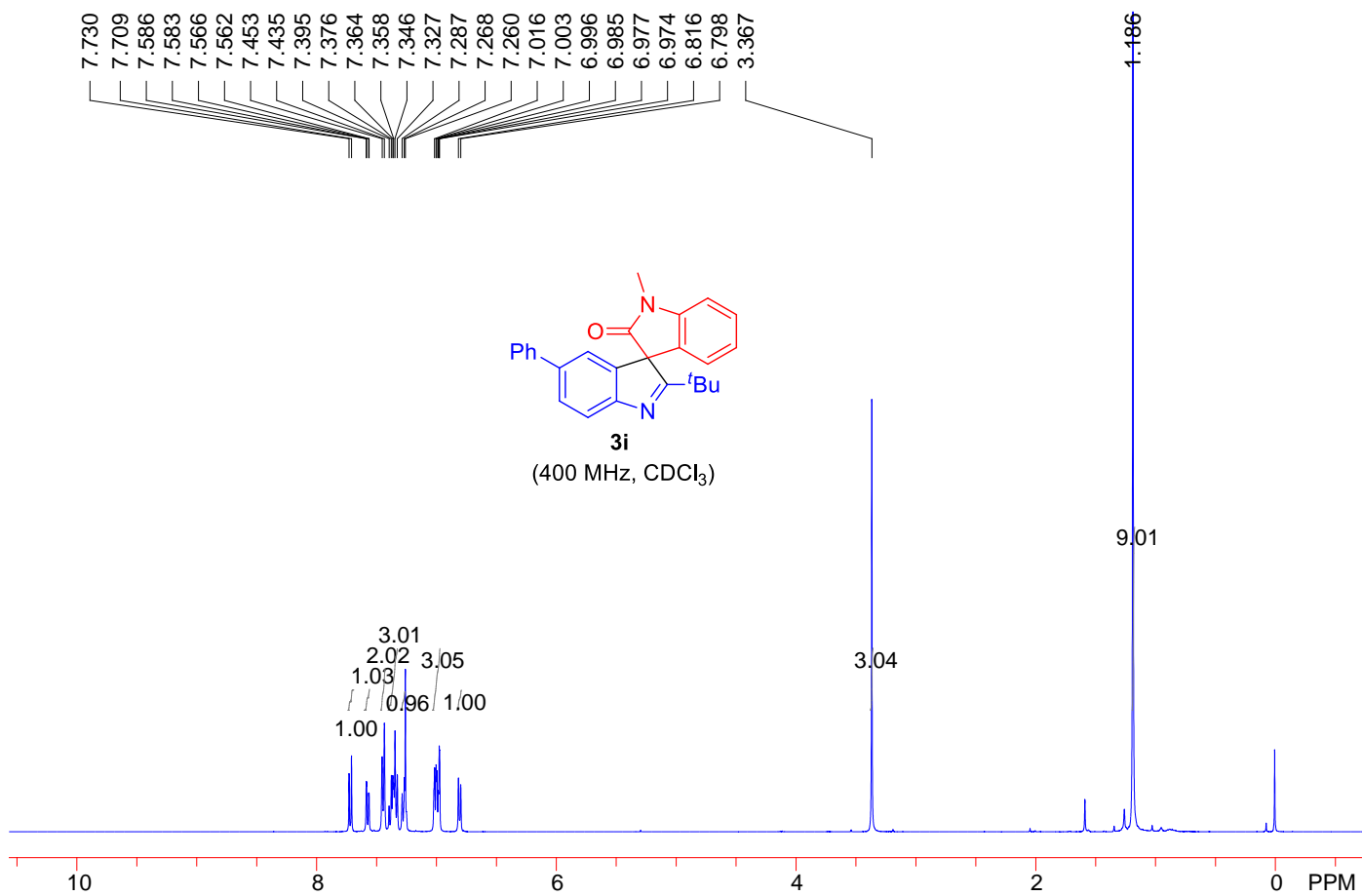
187.677
171.505
155.225
144.622
141.675
132.025
129.562
126.110
124.744
124.224
123.401
121.971
119.537
109.150

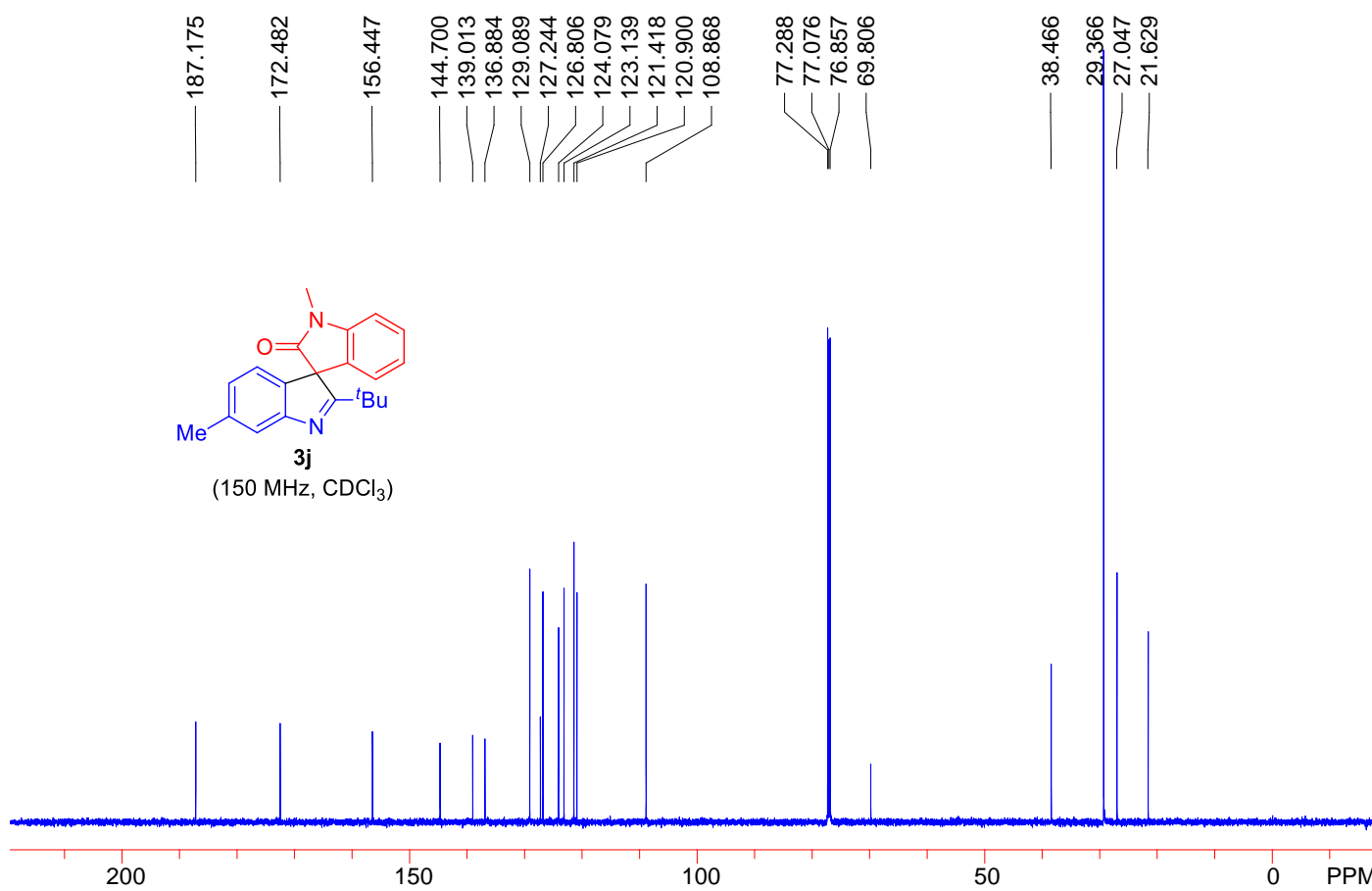
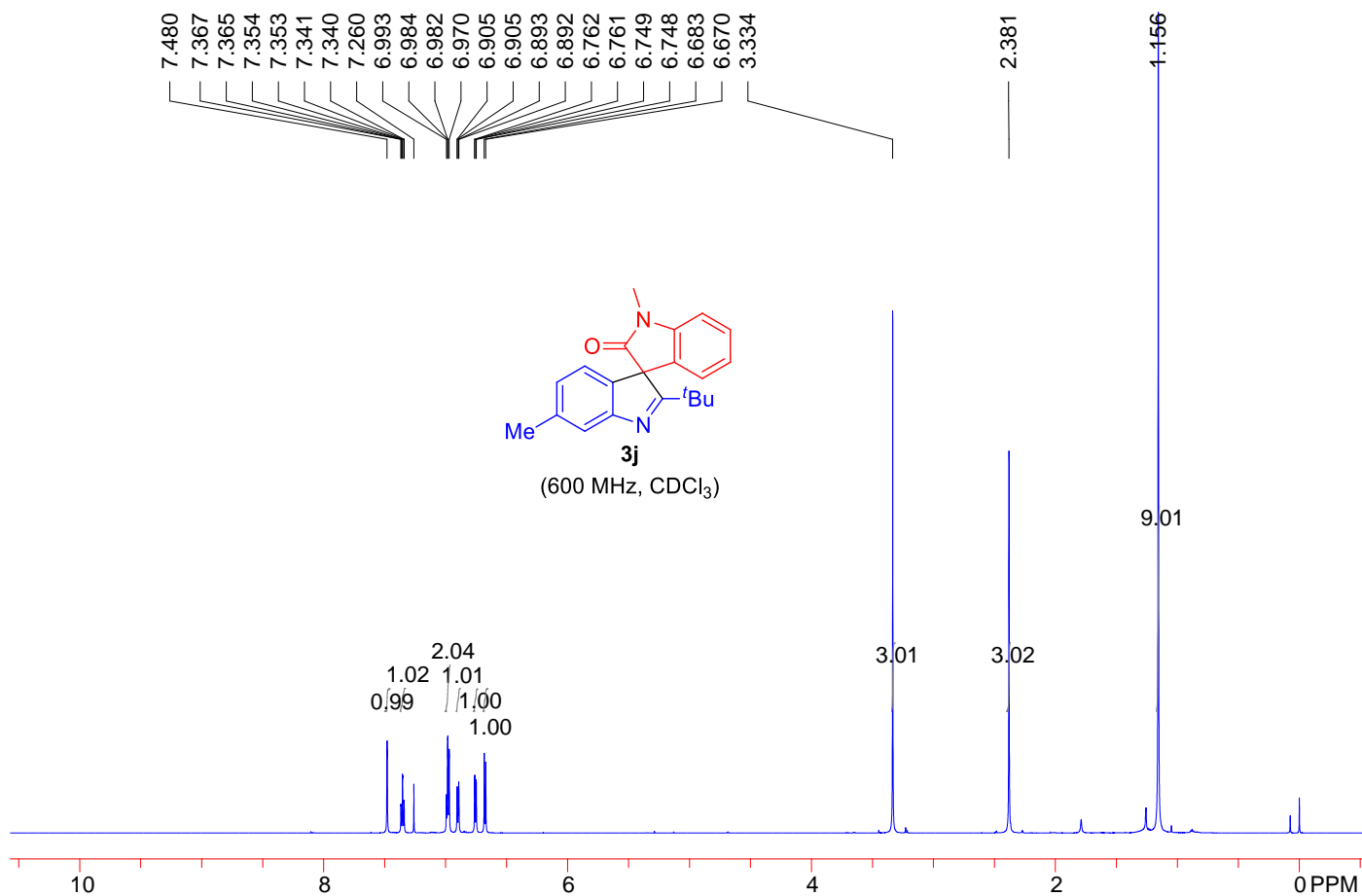


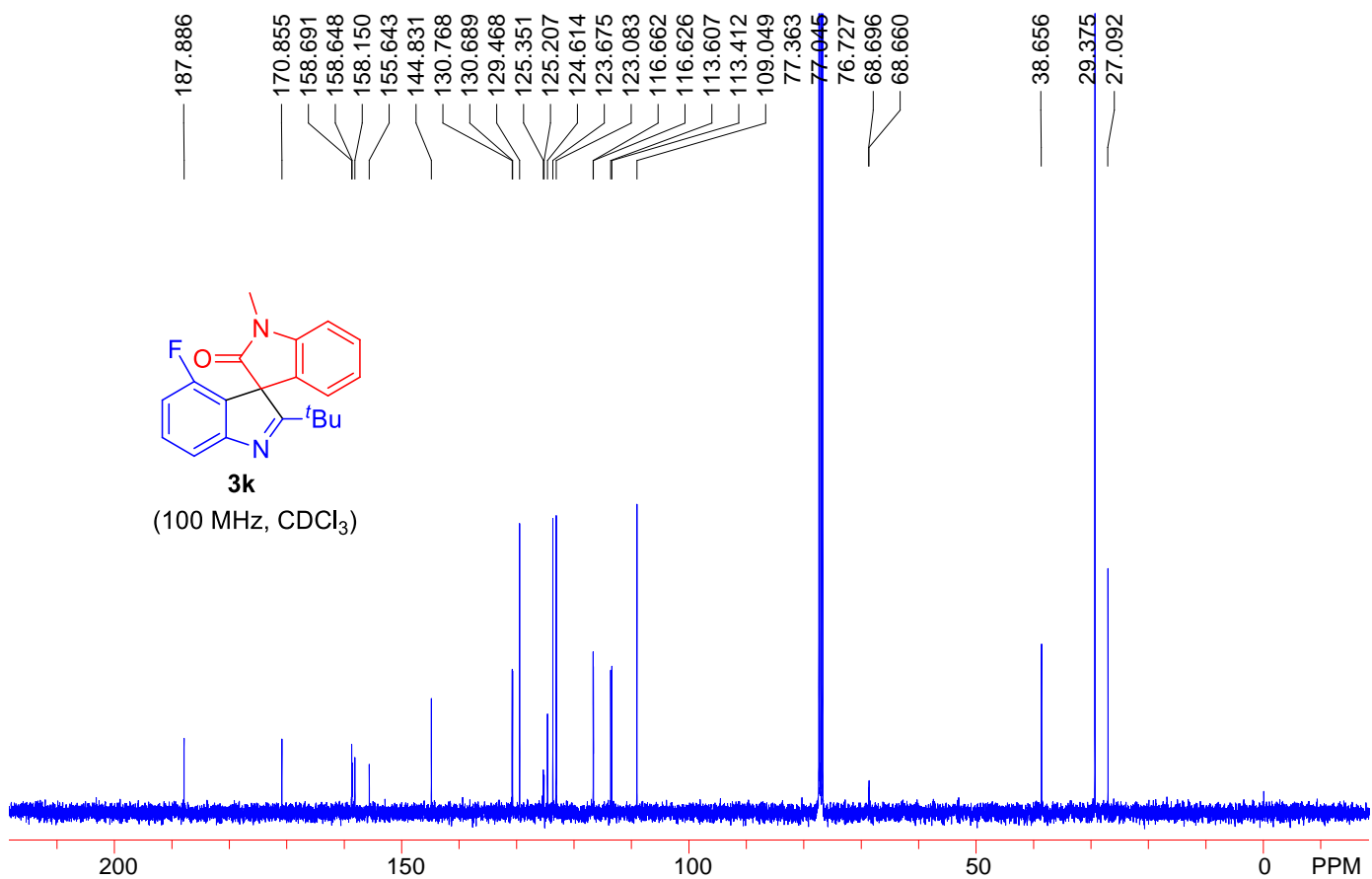
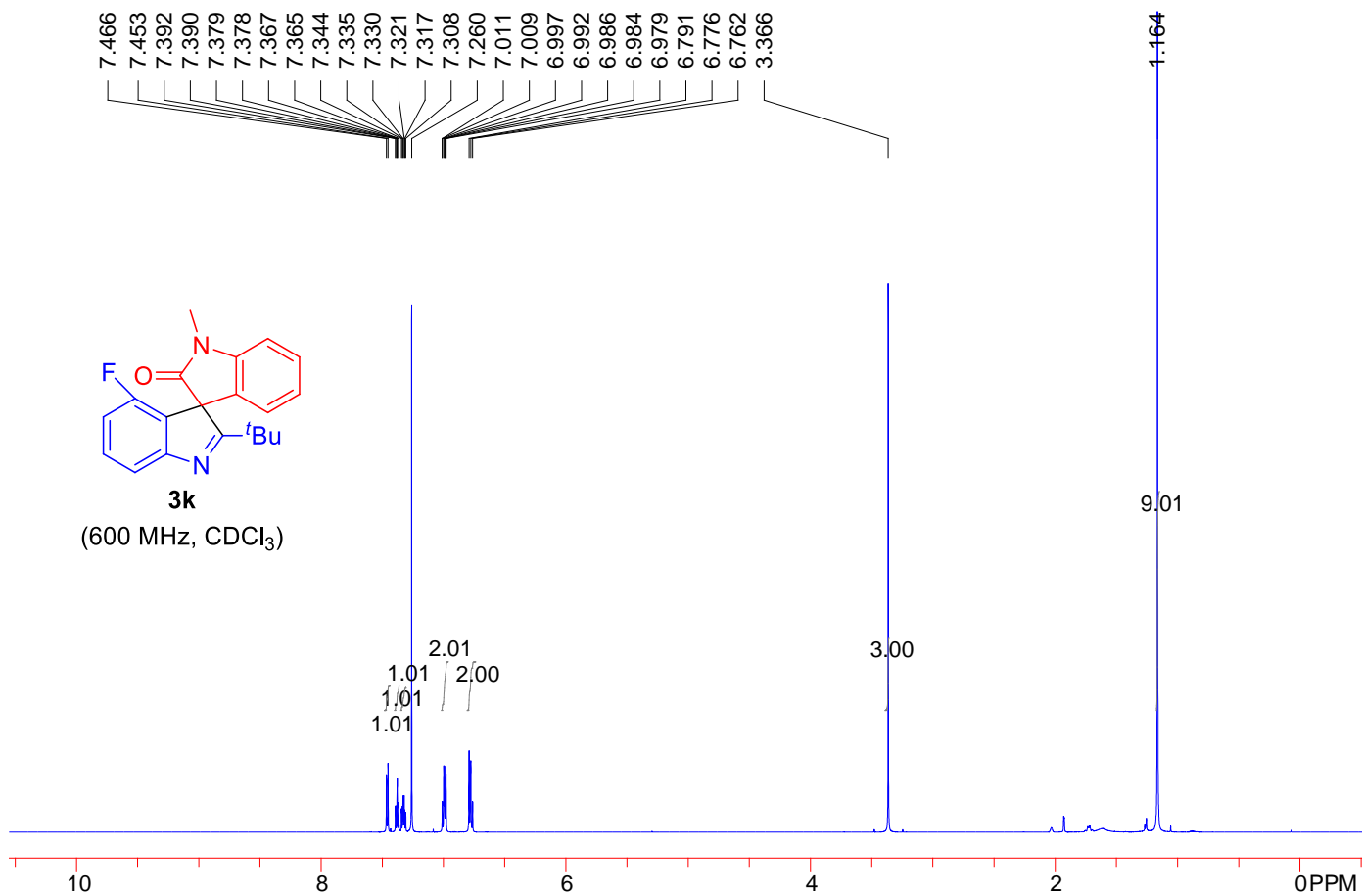
3g
(100 MHz, CDCl₃)



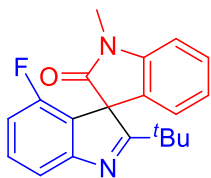






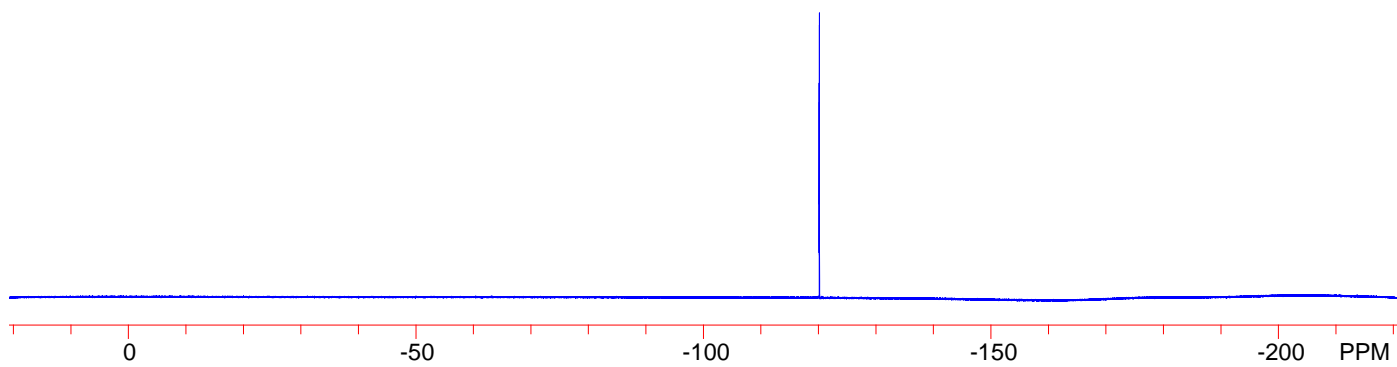


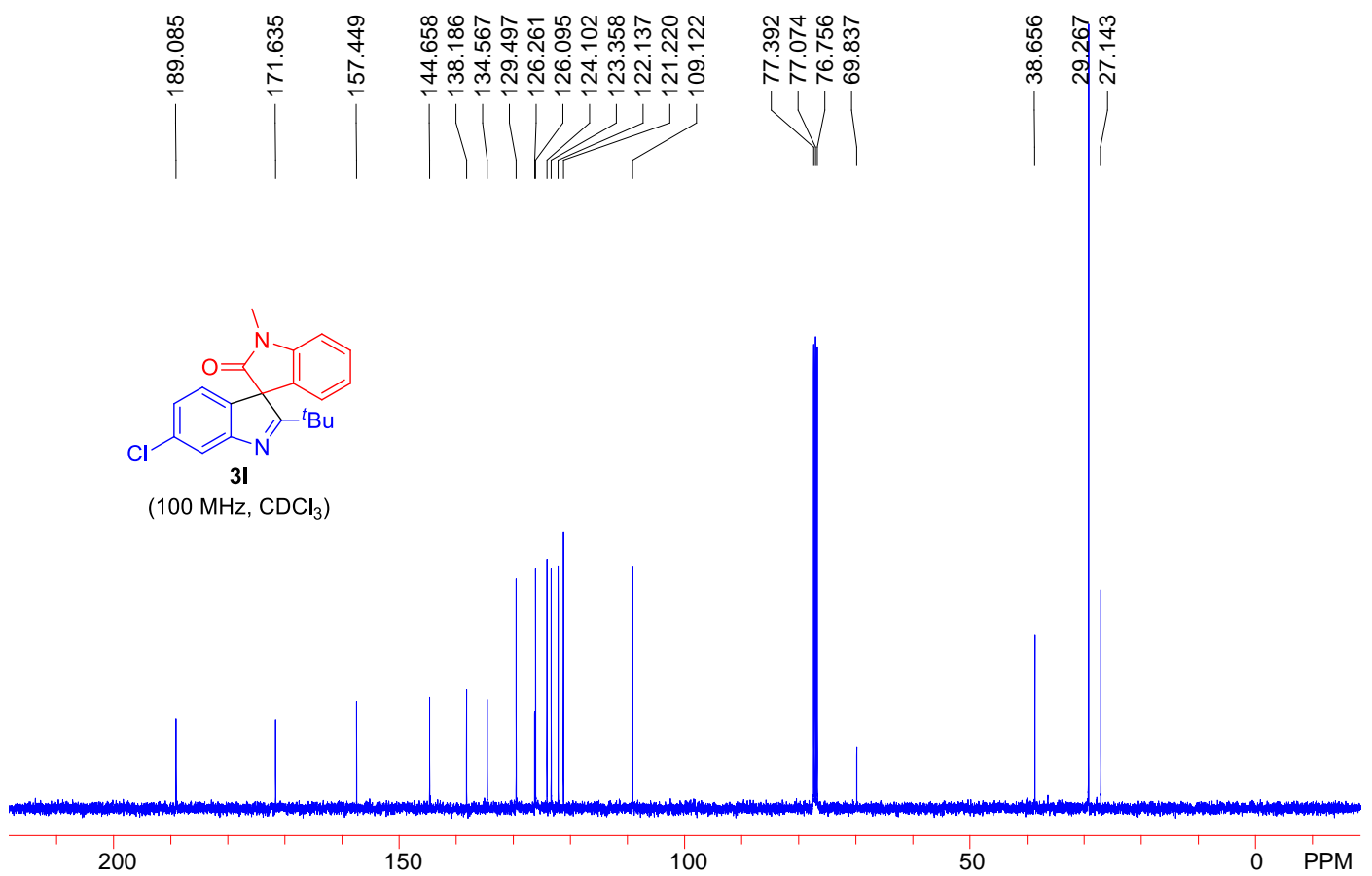
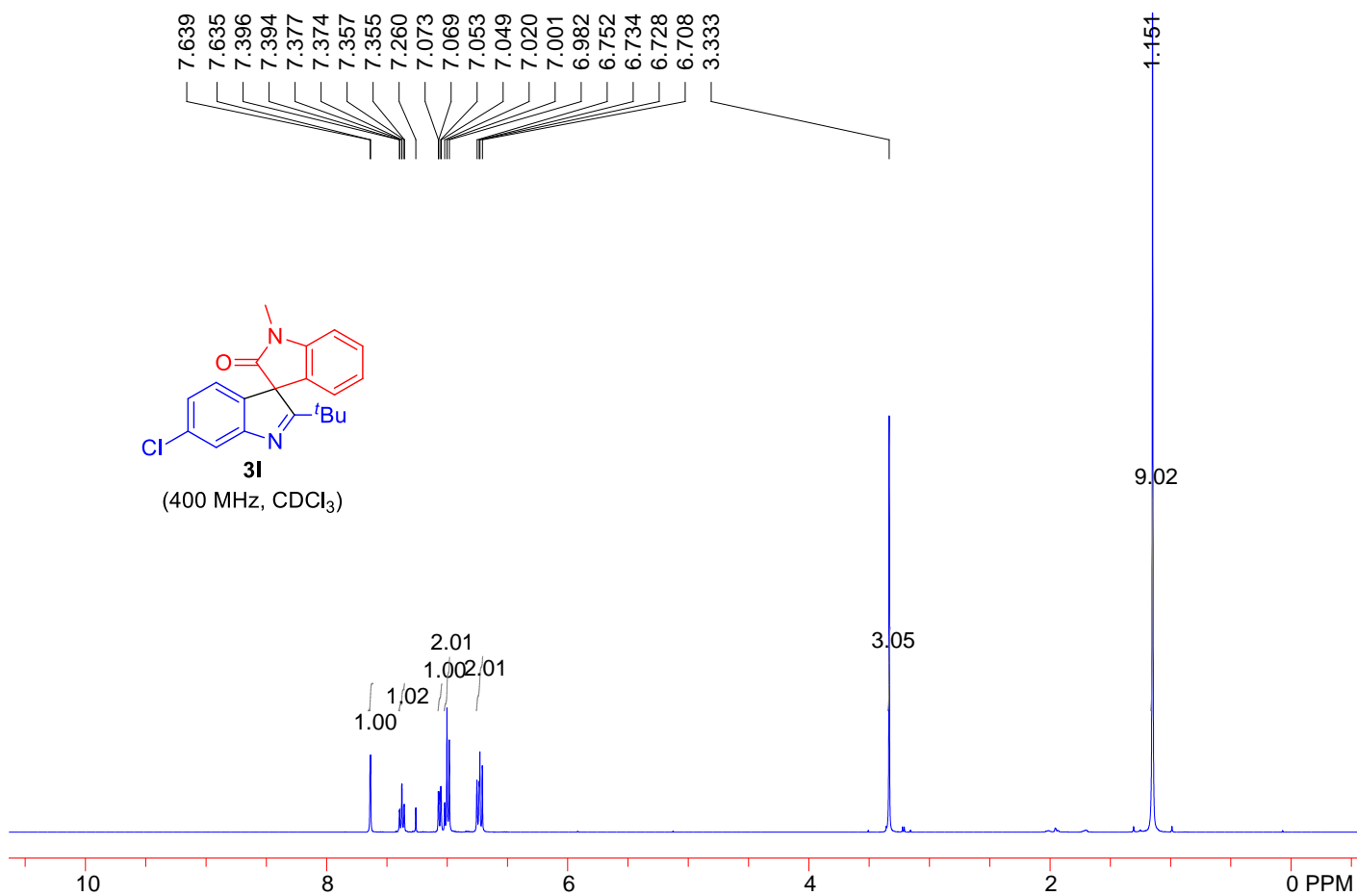
120.070
120.085
120.092
120.107

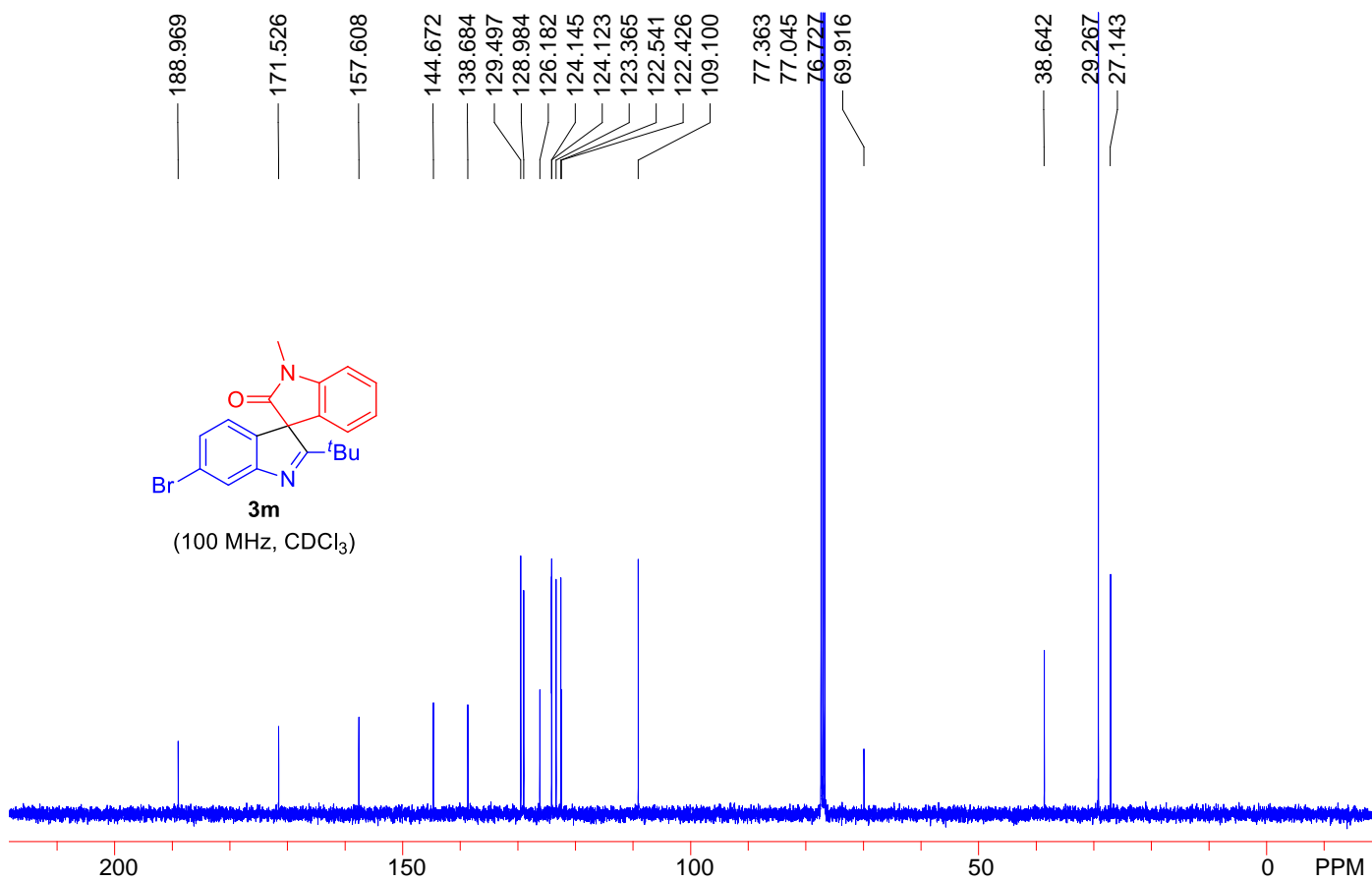
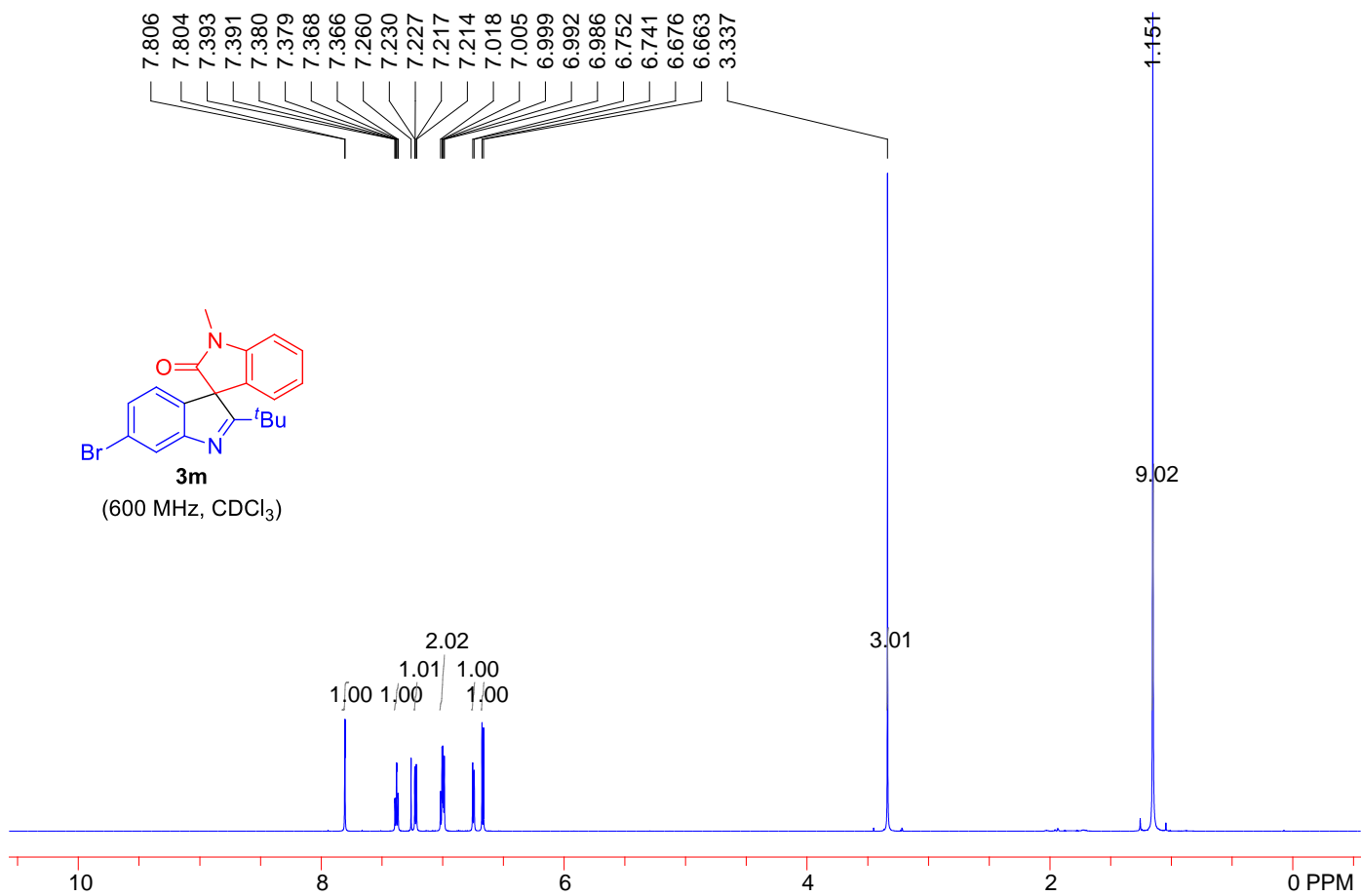


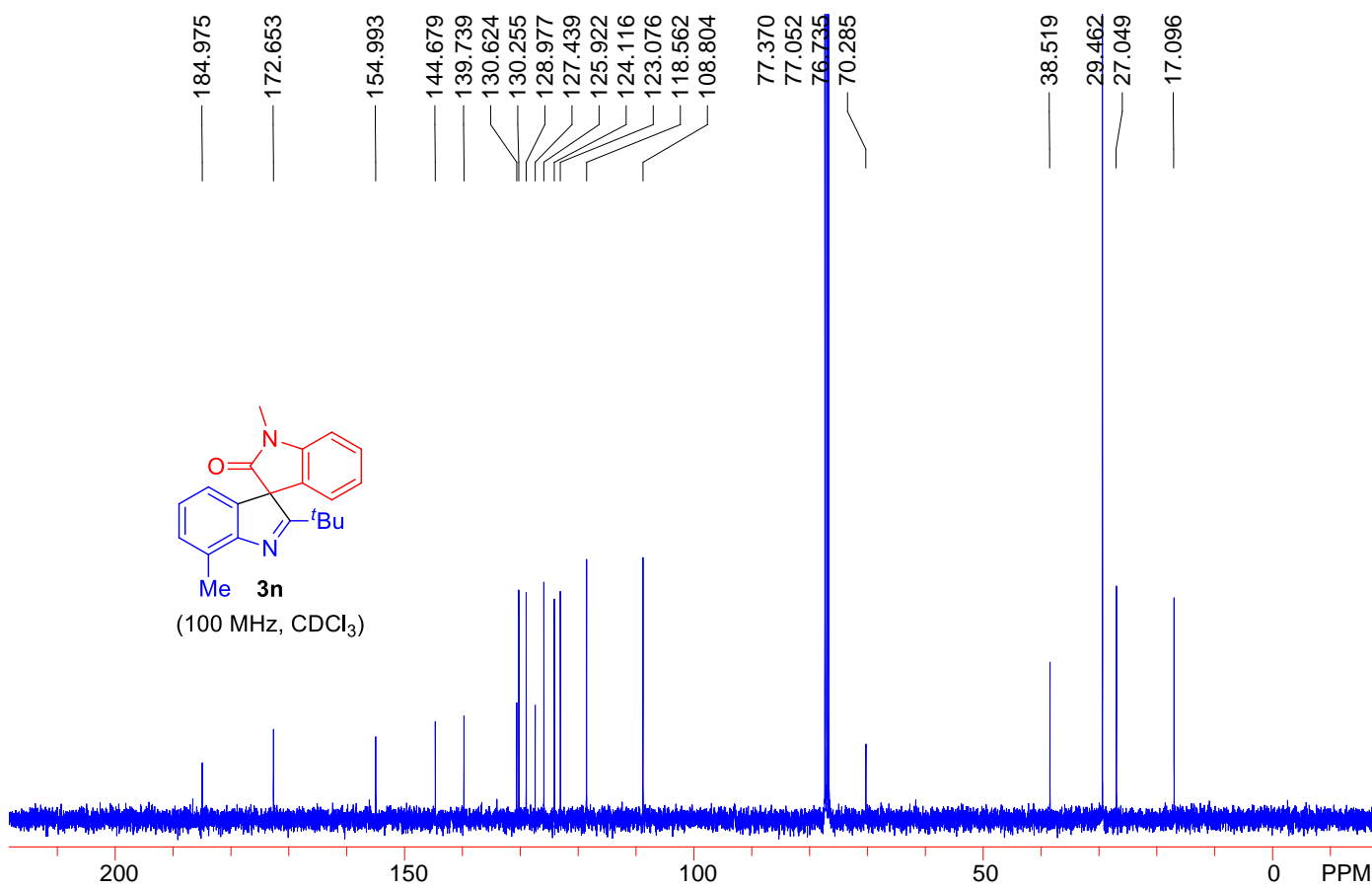
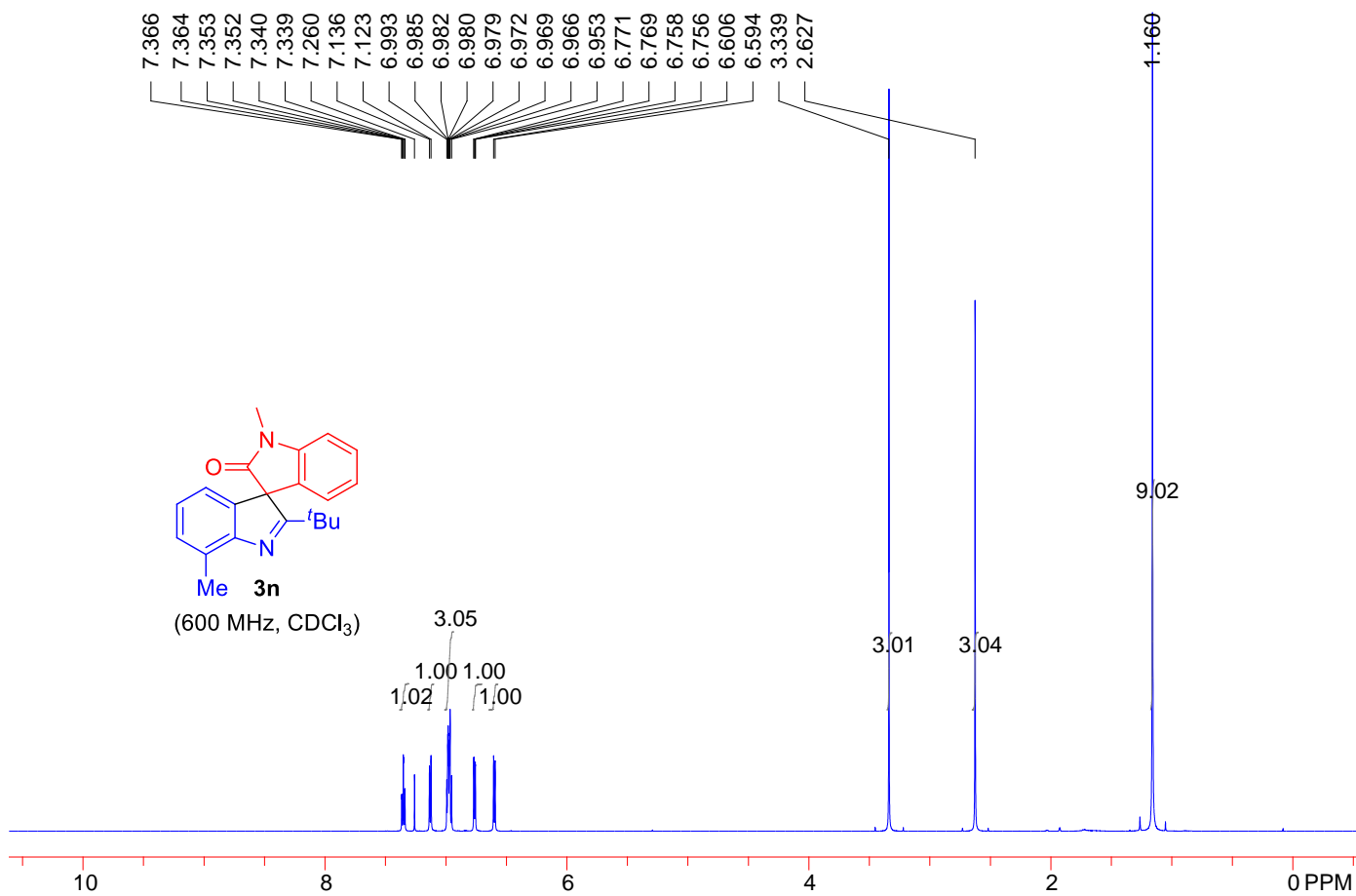
3k

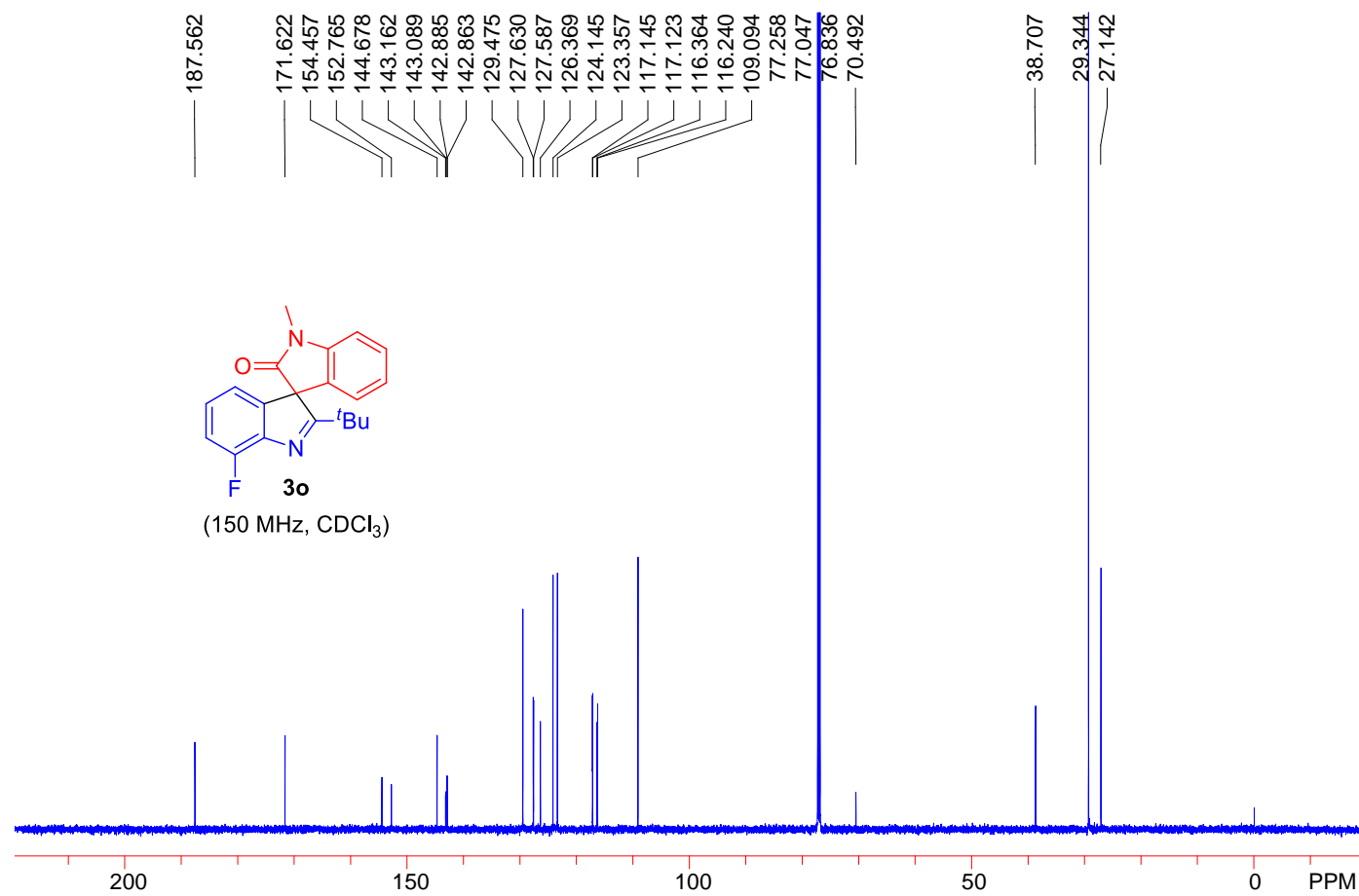
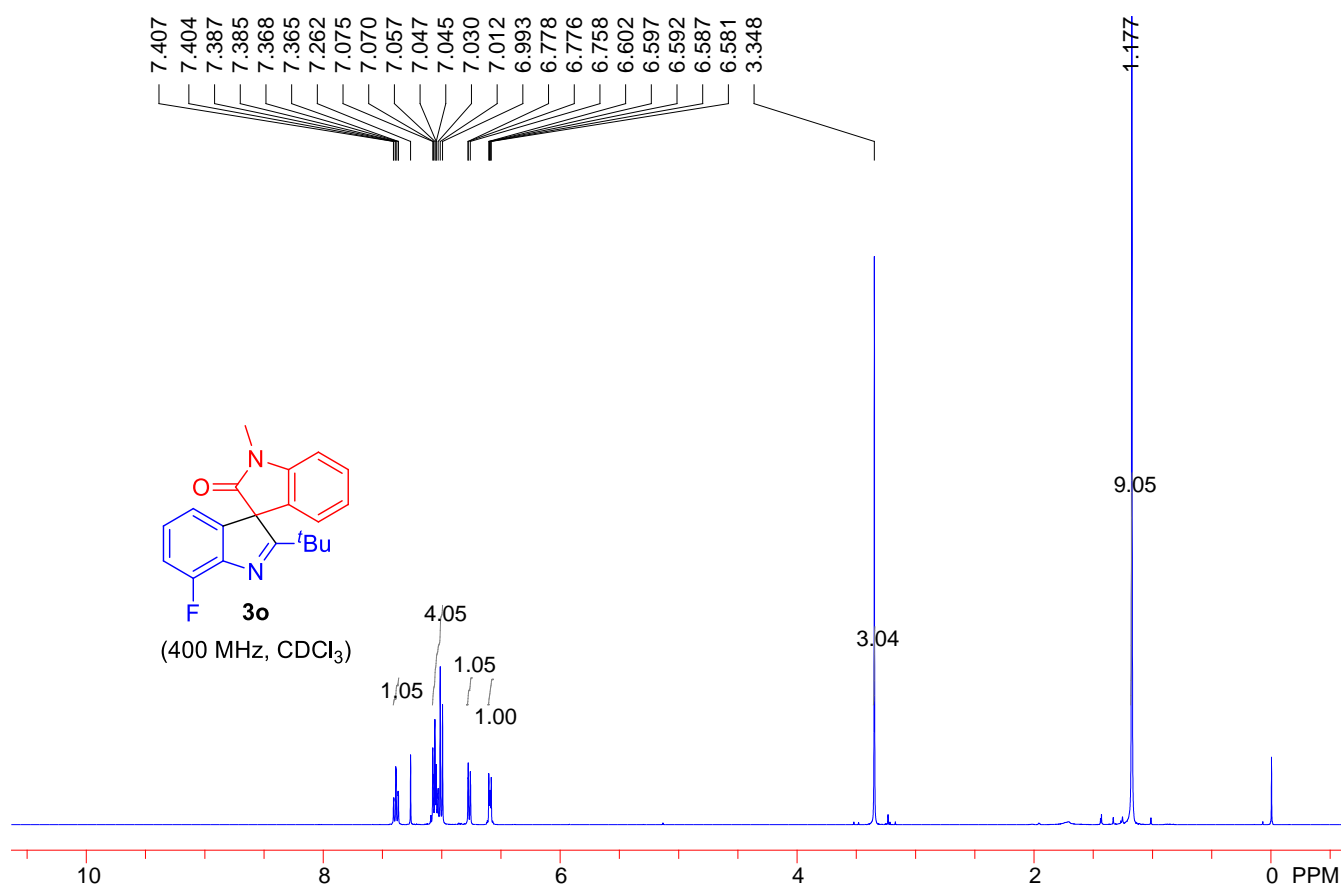
(376 MHz, CDCl₃)



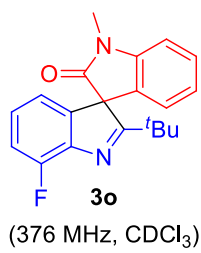


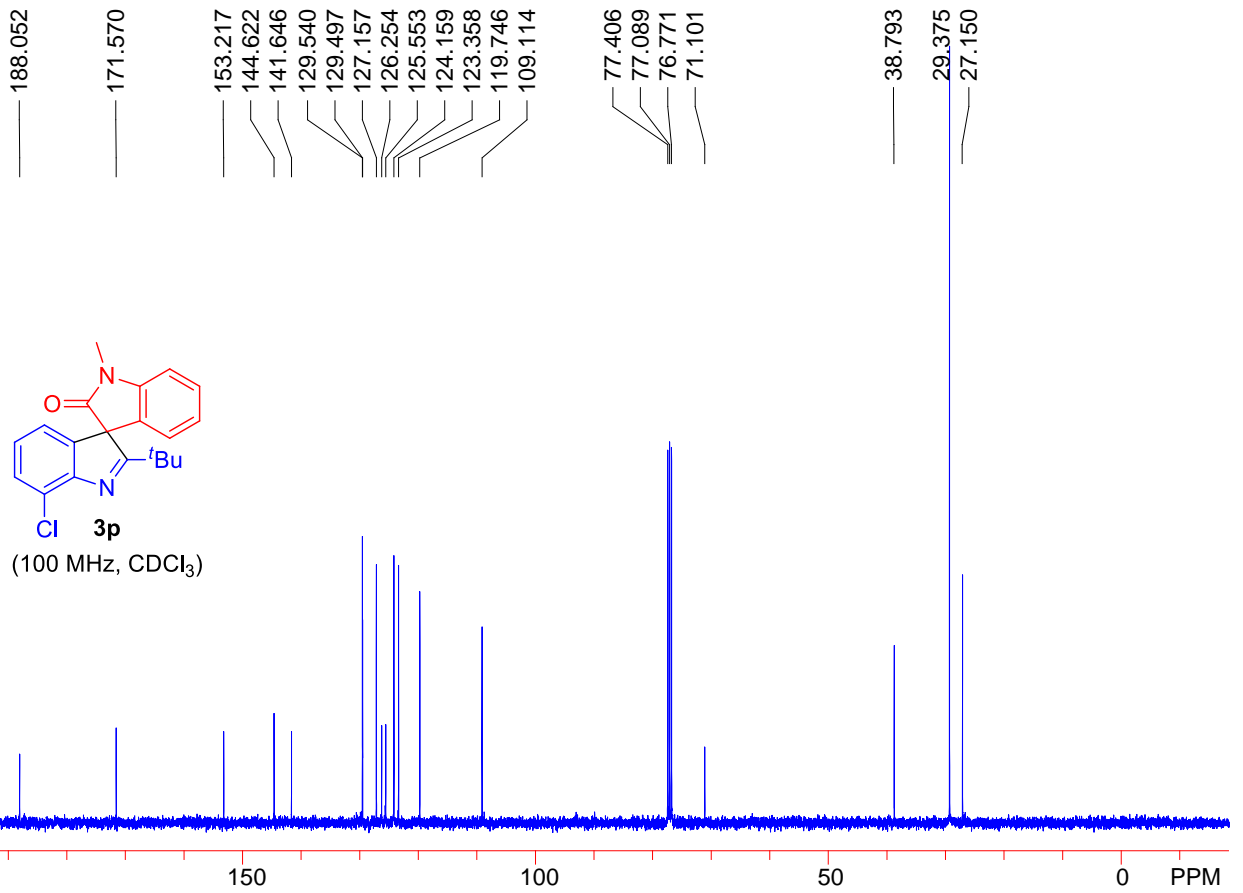
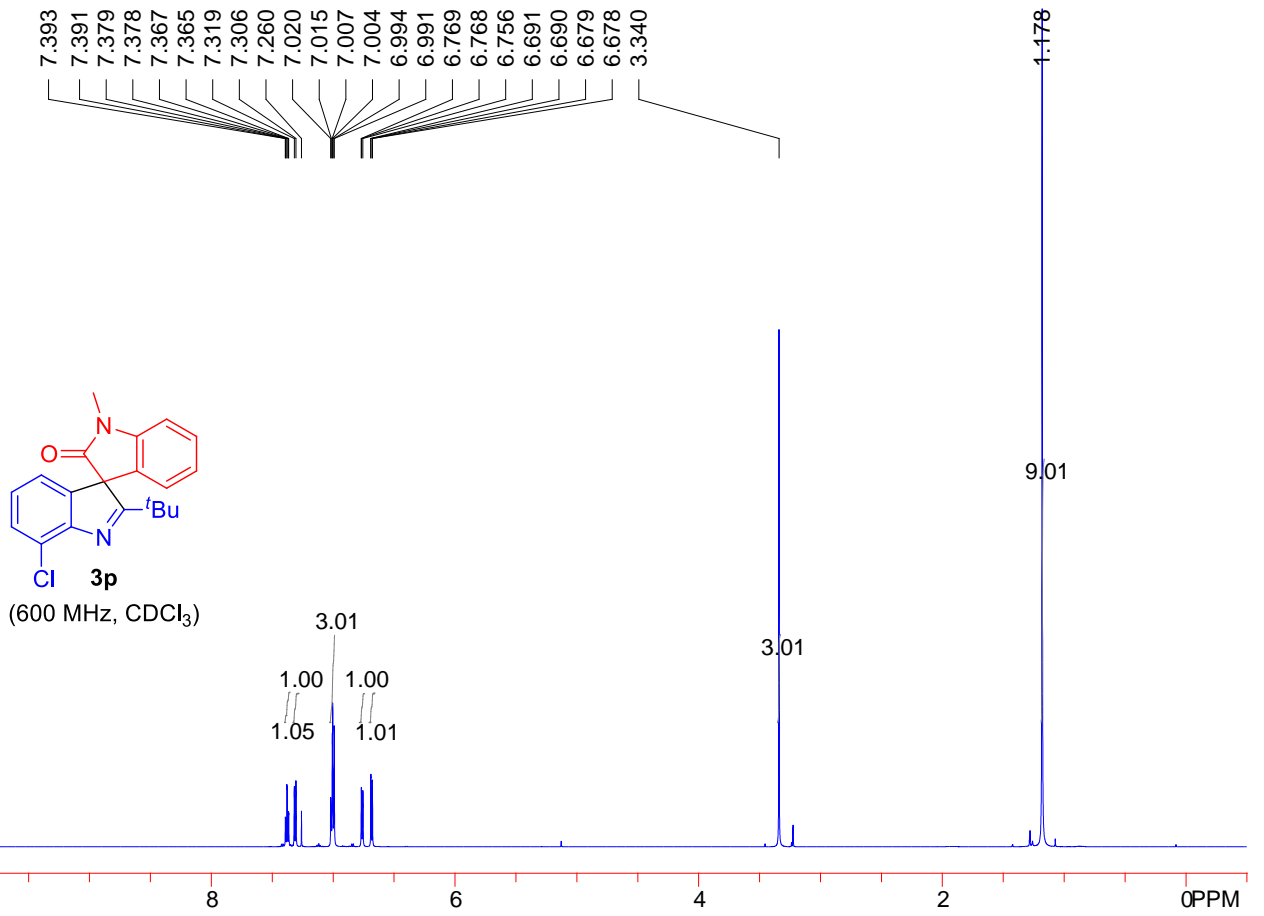




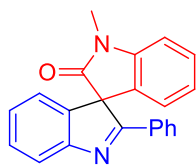


125.191
125.209
125.228

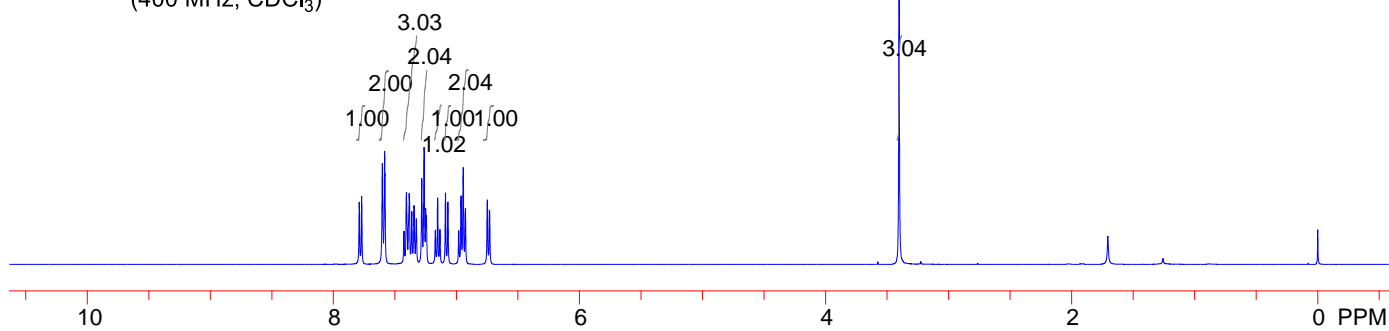




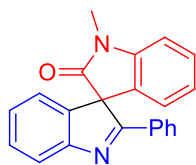
7.790
7.770
7.602
7.584
7.580
7.428
7.425
7.406
7.384
7.381
7.363
7.345
7.326
7.282
7.262
7.250
7.244
7.170
7.153
7.152
7.134
7.133
7.089
7.069
6.980
6.963
6.945
6.927
6.749
6.731
3.402



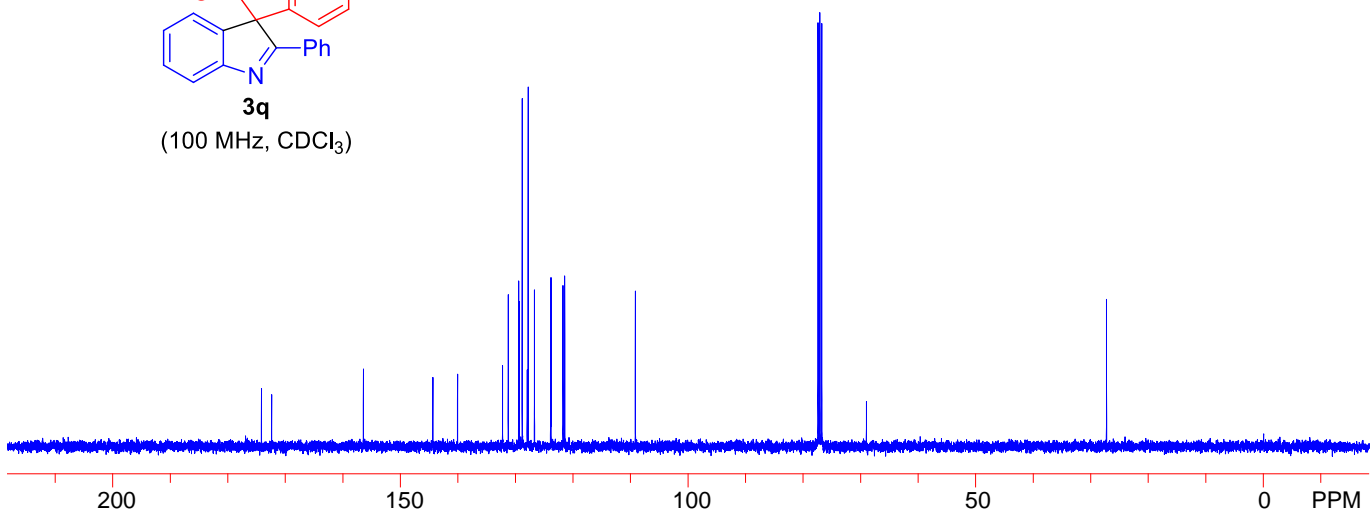
3q
(400 MHz, CDCl₃)



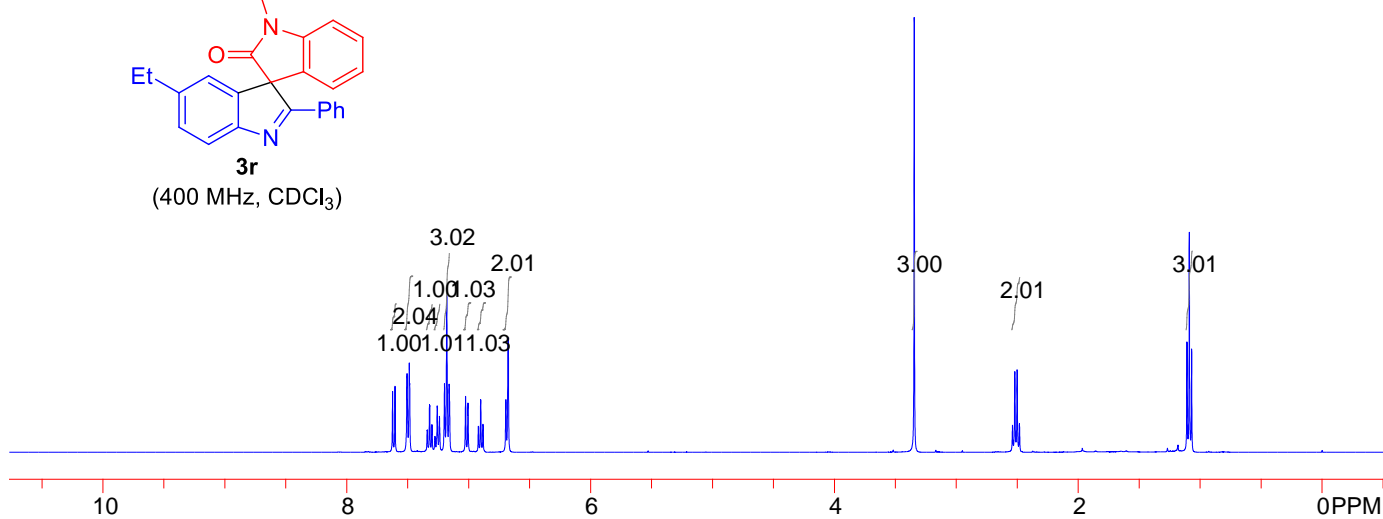
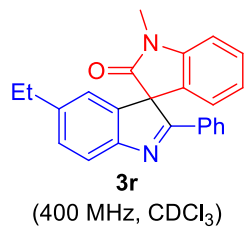
174.155
172.386
144.354
156.431
140.064
132.242
131.245
129.432
129.324
128.818
127.951
127.785
126.695
123.878
123.805
121.725
121.444
109.158
77.399
77.081
76.764
68.999
27.309



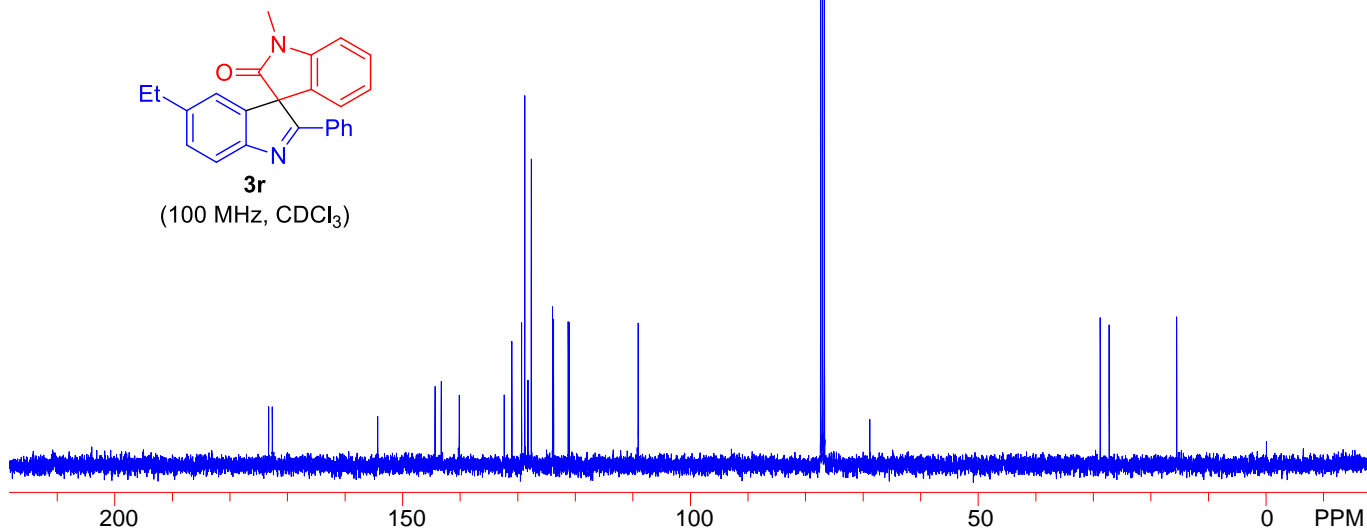
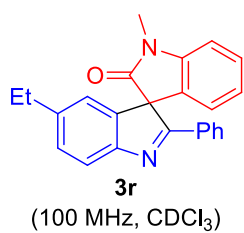
3q
(100 MHz, CDCl₃)



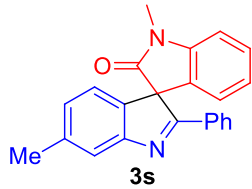
7.624
7.605
7.506
7.487
7.484
7.341
7.339
7.322
7.319
7.303
7.300
7.277
7.258
7.240
7.199
7.180
7.161
7.026
7.006
6.921
6.902
6.883
6.695
6.677
3.346
2.539
2.520
2.502
2.483
1.108
1.089
1.070



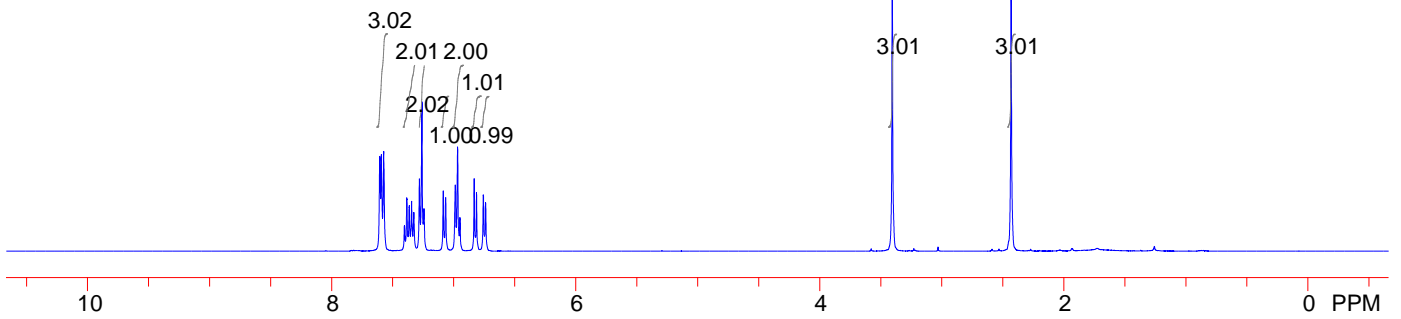
173.282
172.639
154.336
144.362
143.285
140.158
132.350
131.021
129.324
128.775
128.219
127.648
123.943
123.777
121.234
121.075
109.078
77.370
77.052
76.735
68.862
28.862
27.309
15.594



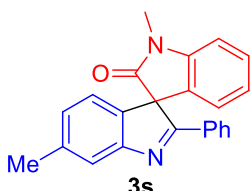
7.605
7.593
7.574
7.405
7.403
7.385
7.383
7.366
7.363
7.345
7.327
7.281
7.260
7.243
7.086
7.066
6.987
6.968
6.949
6.832
6.813
6.757
6.739
3.406
2.433



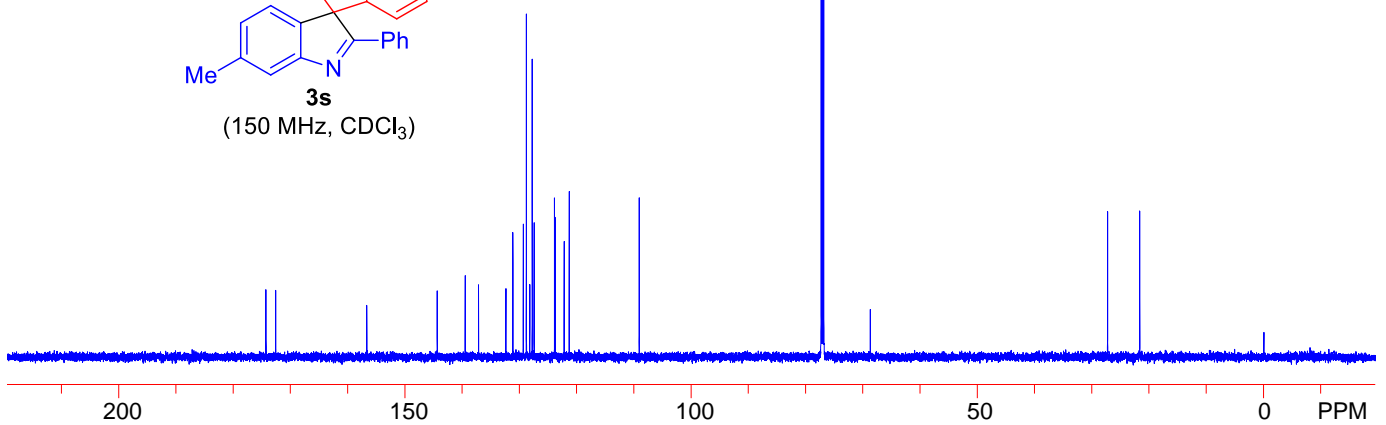
(400 MHz, CDCl₃)

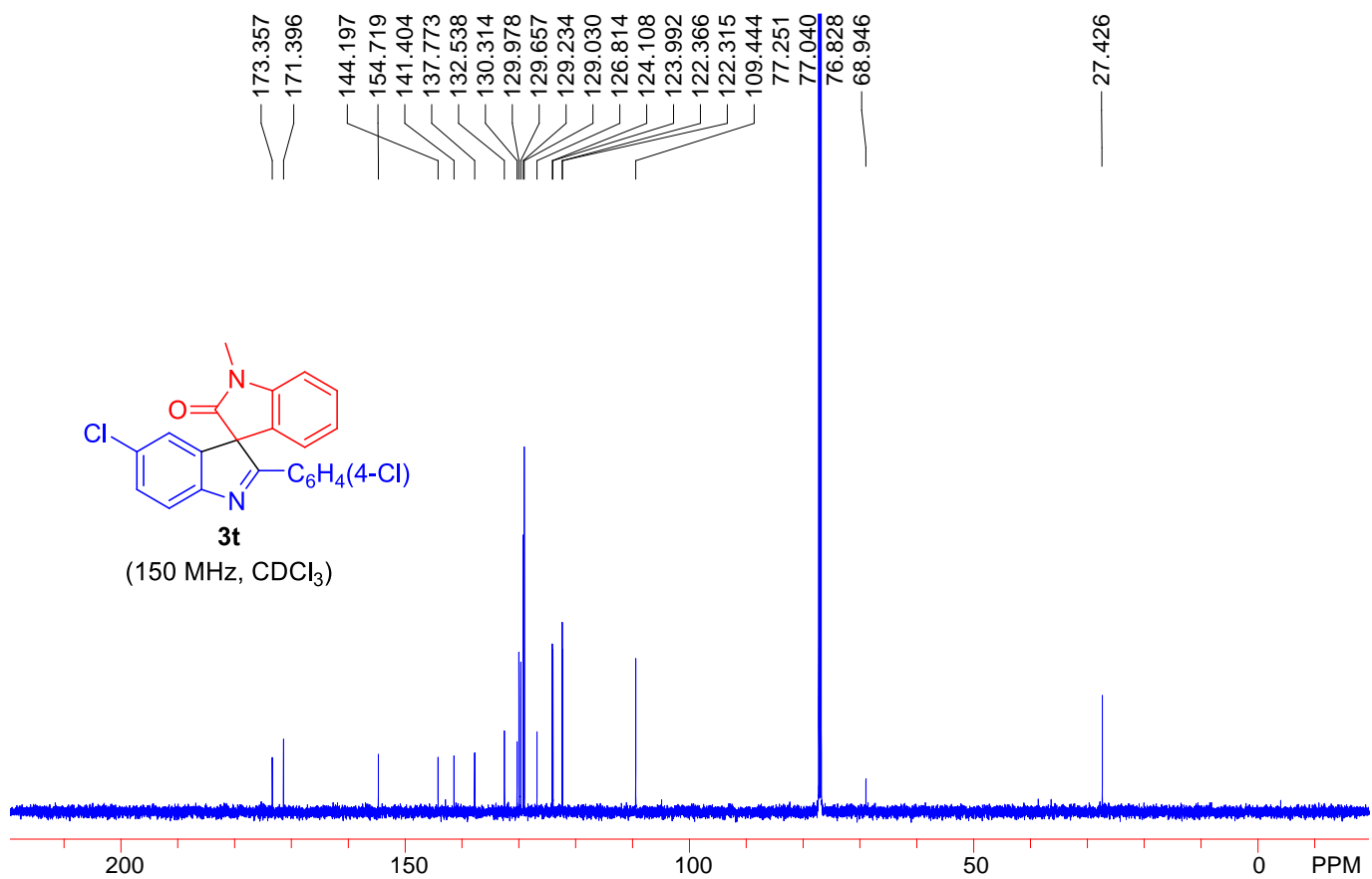
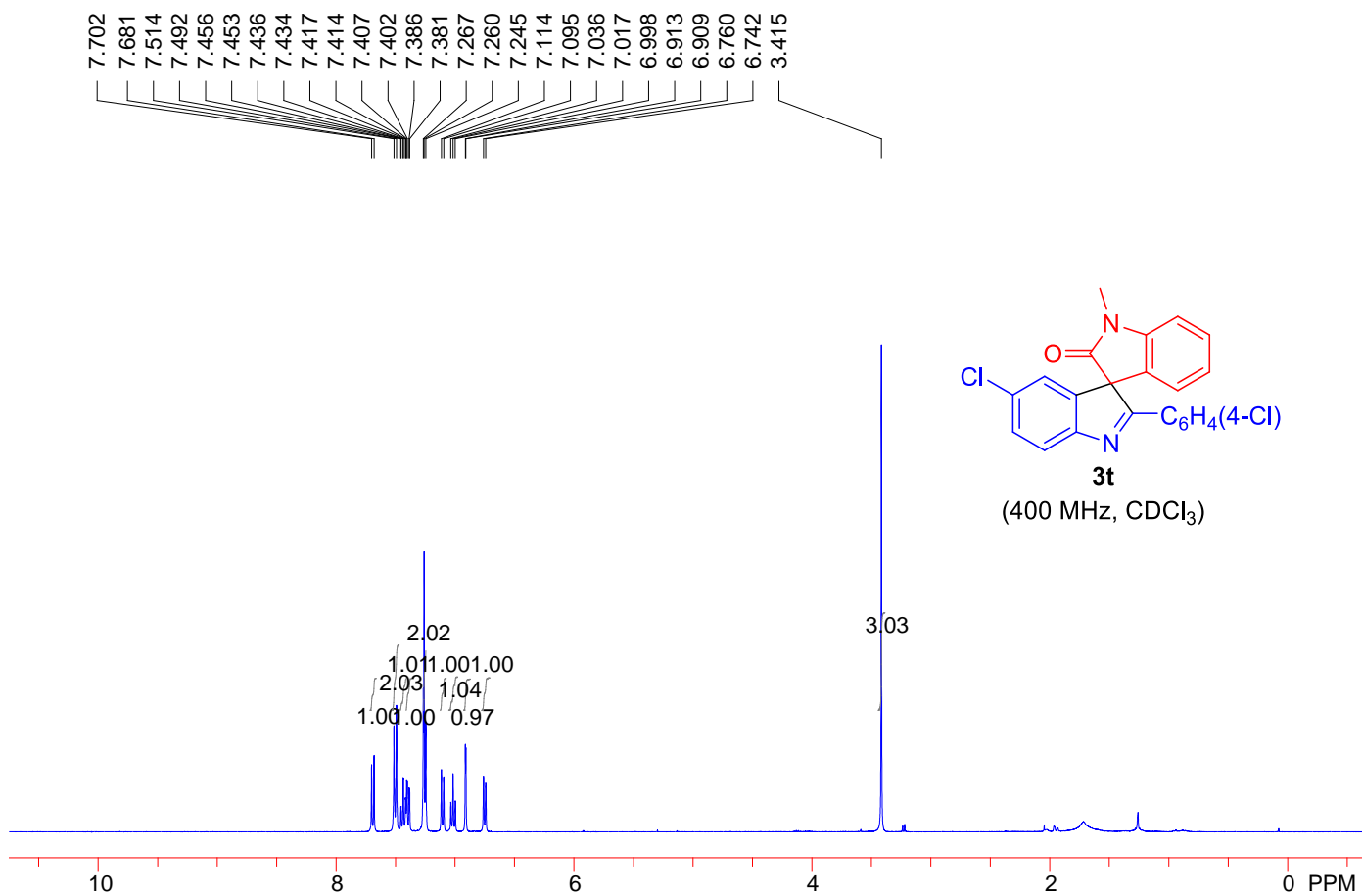


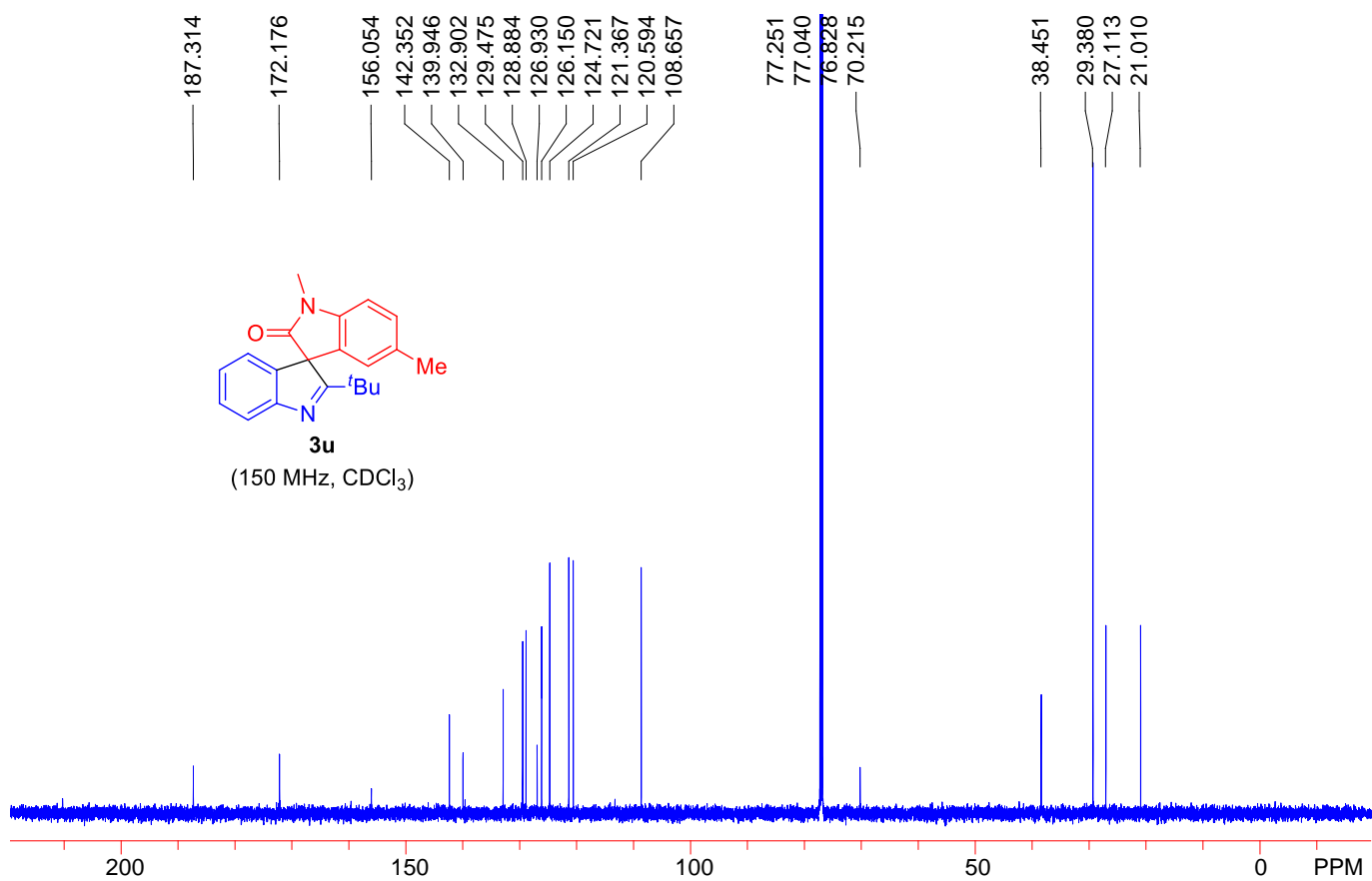
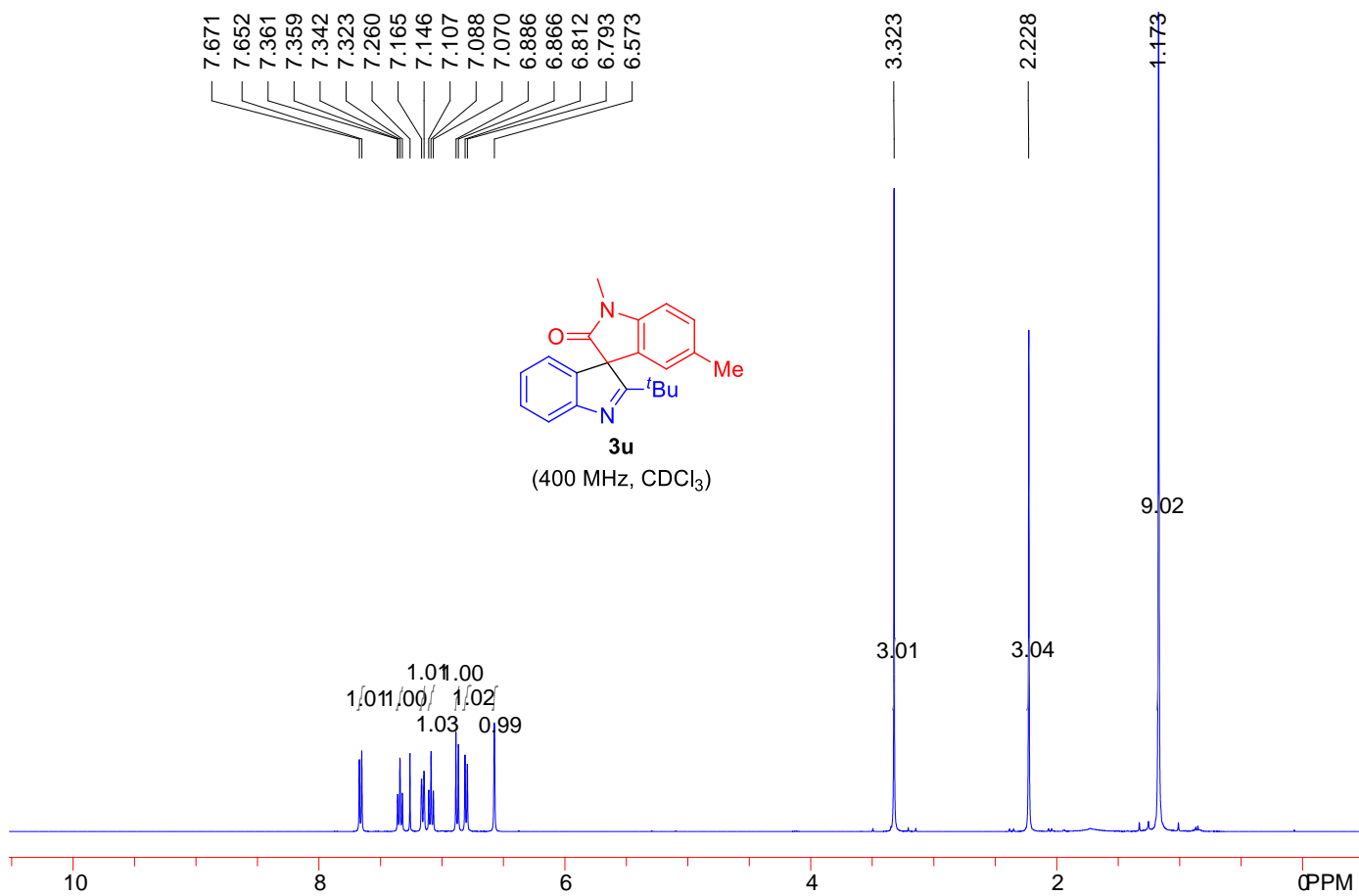
174.276
172.570
156.659
139.458
137.124
144.343
132.348
131.130
129.307
128.775
128.177
127.747
127.412
123.853
123.744
122.161
121.286
109.051
77.258
77.047
76.836
68.691
27.280
21.680

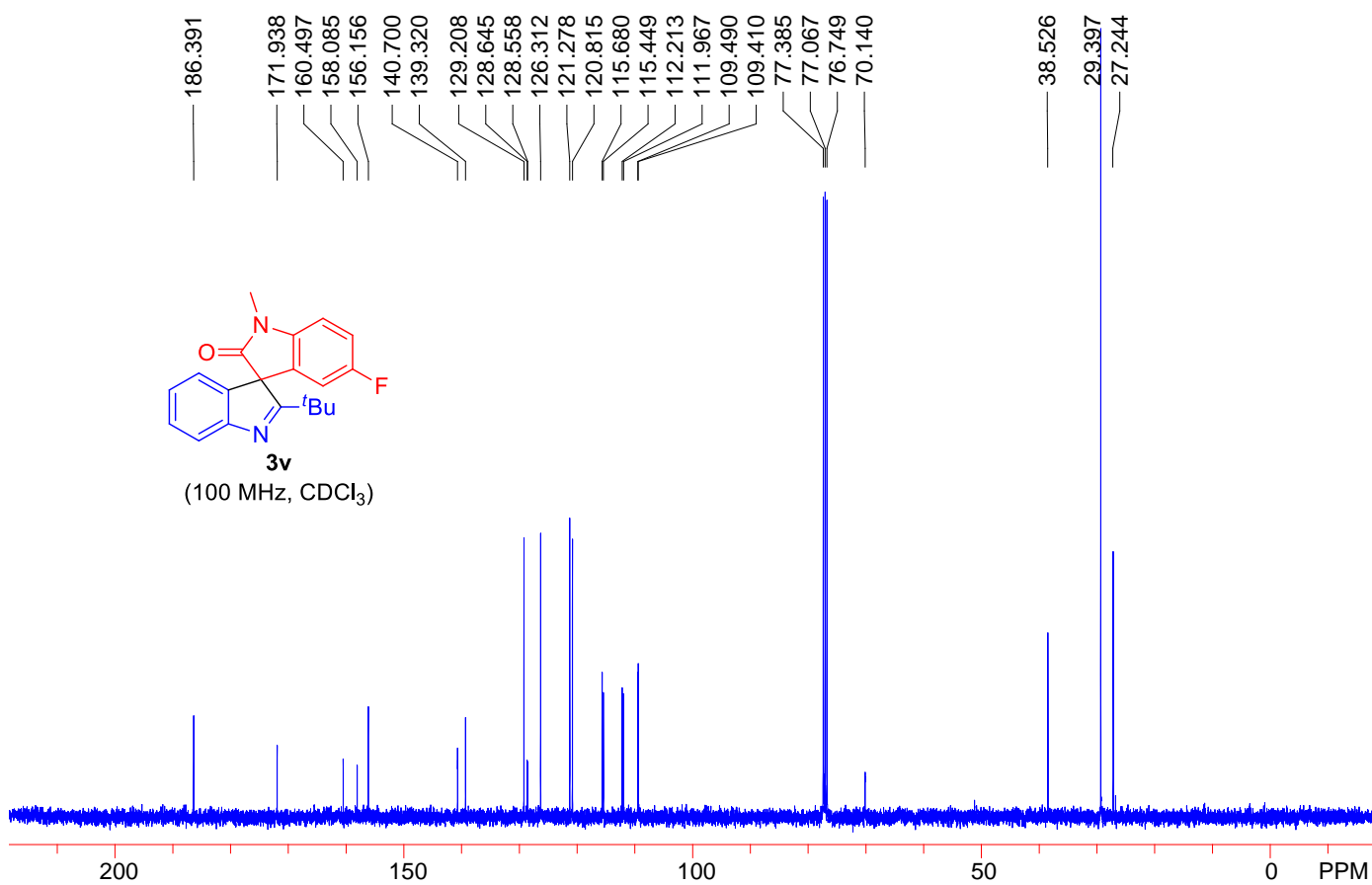
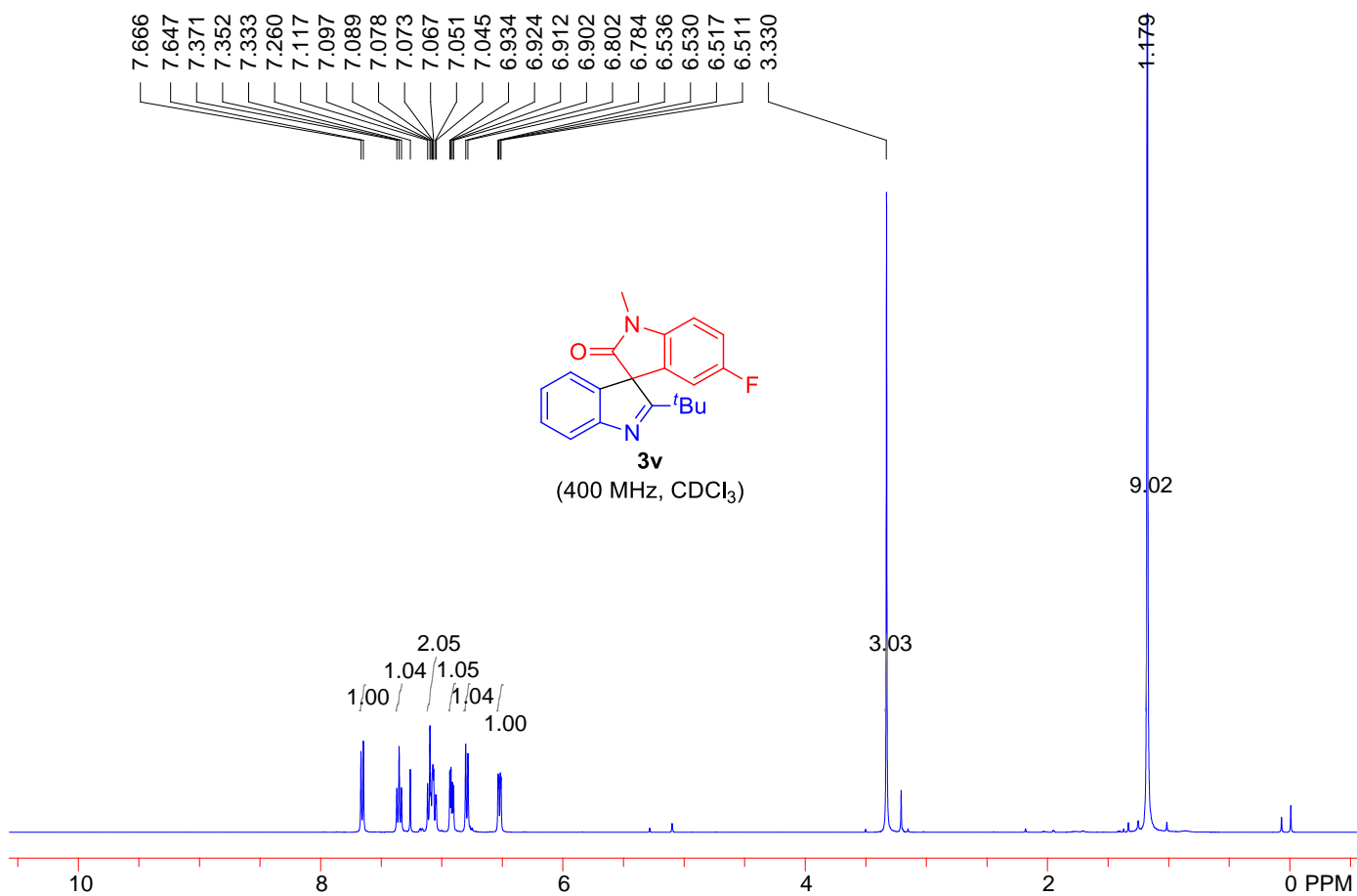


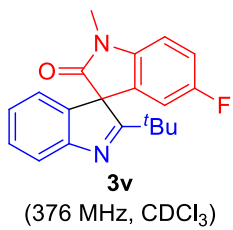
(150 MHz, CDCl₃)



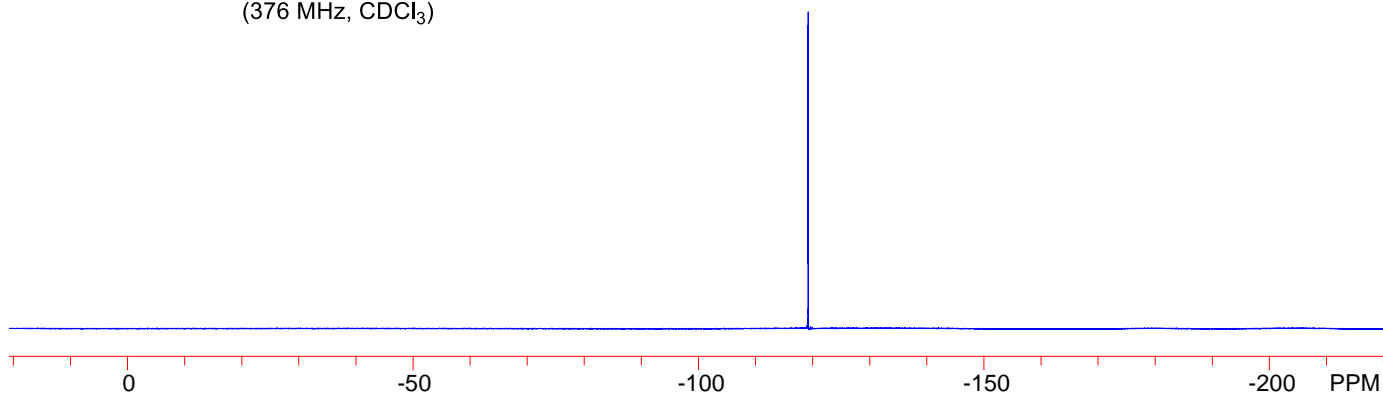


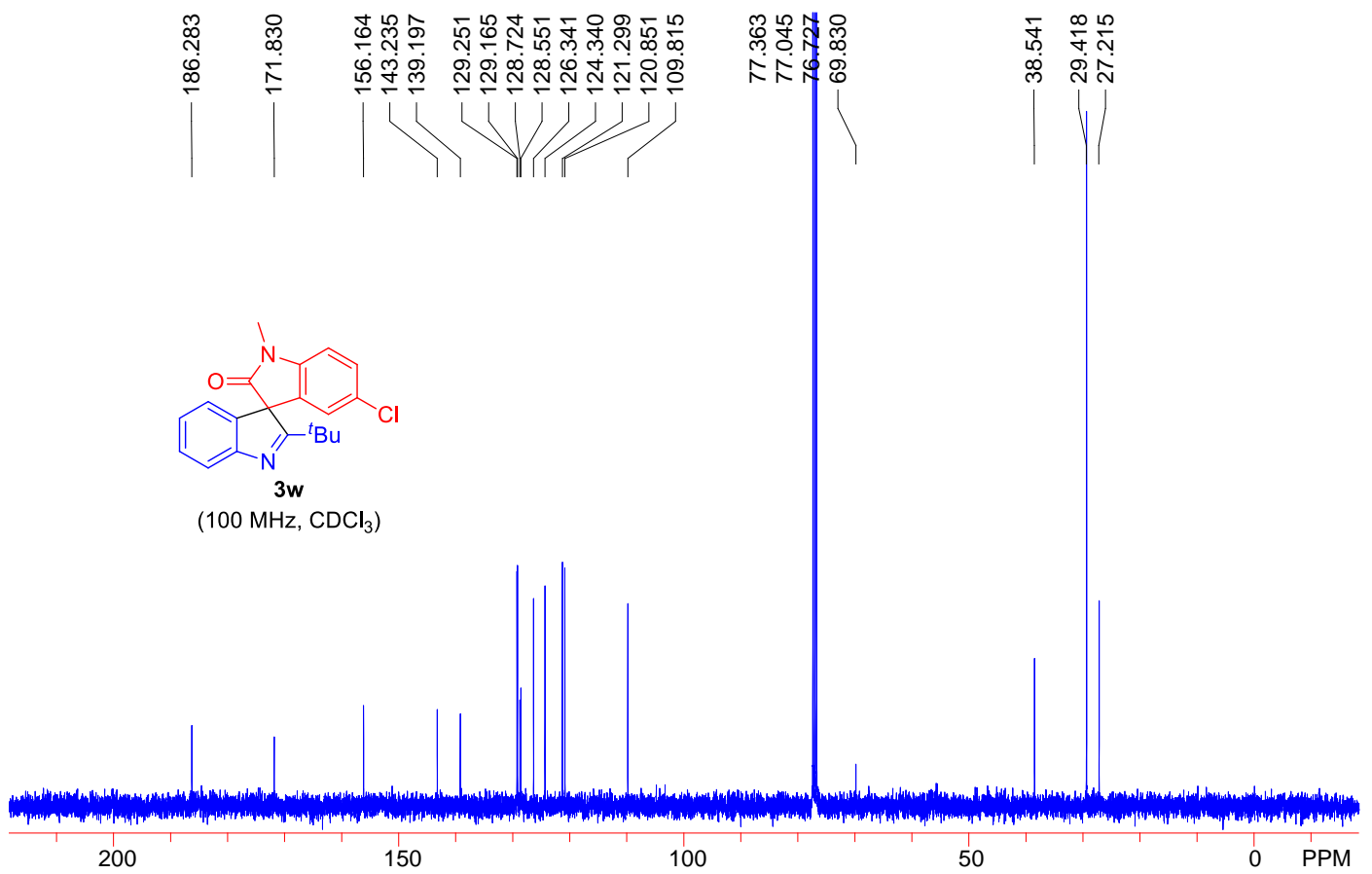
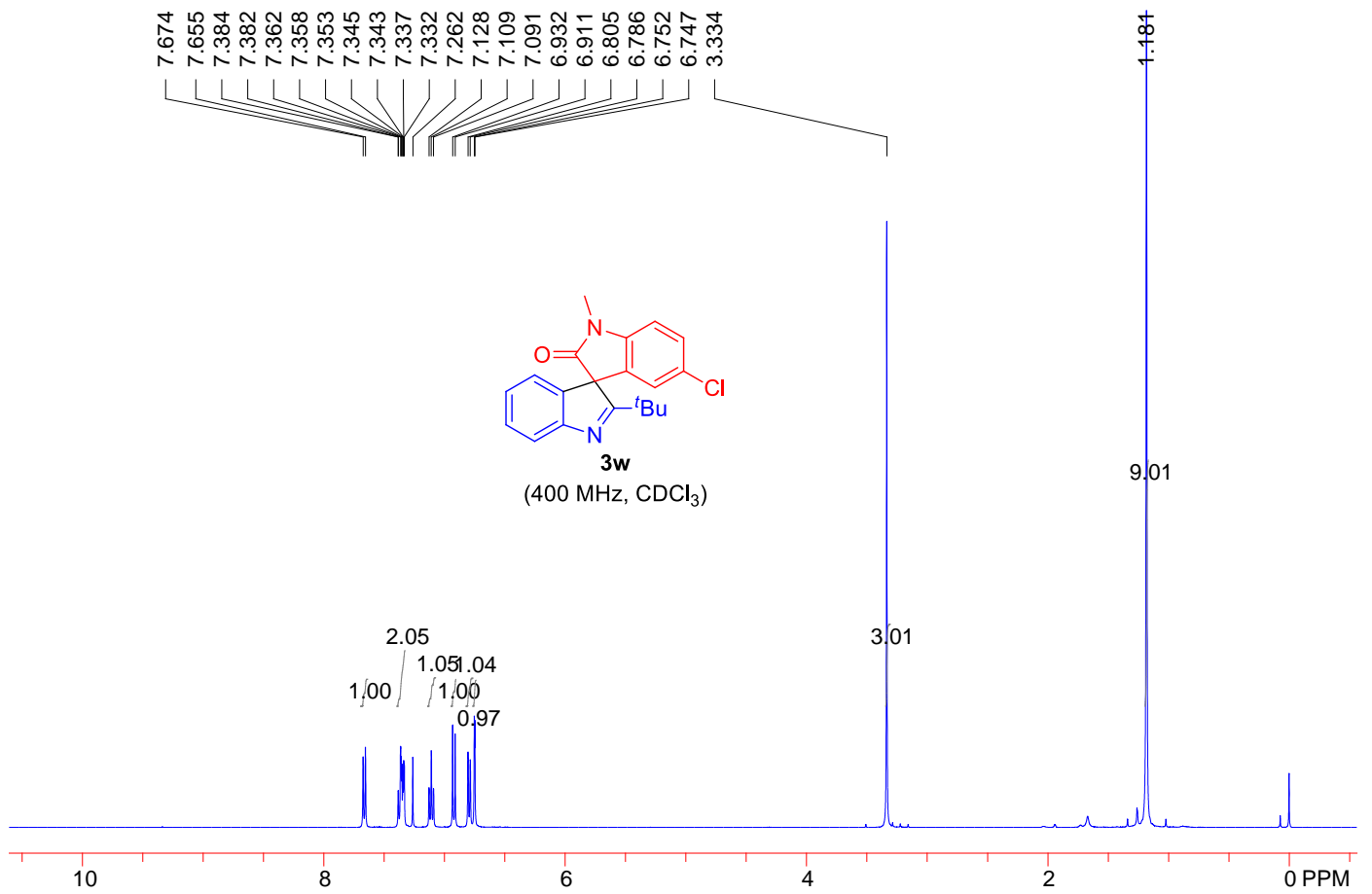


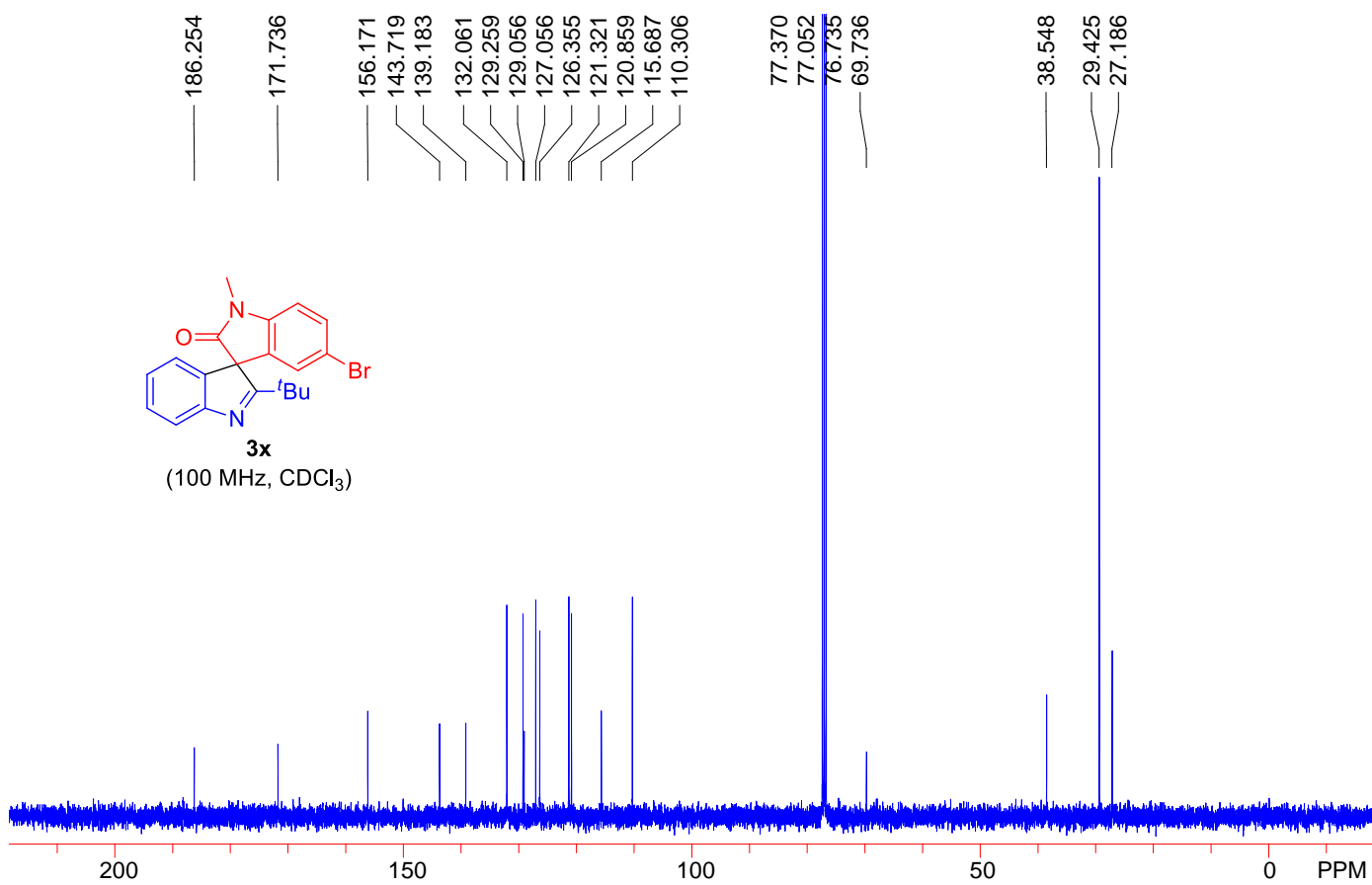
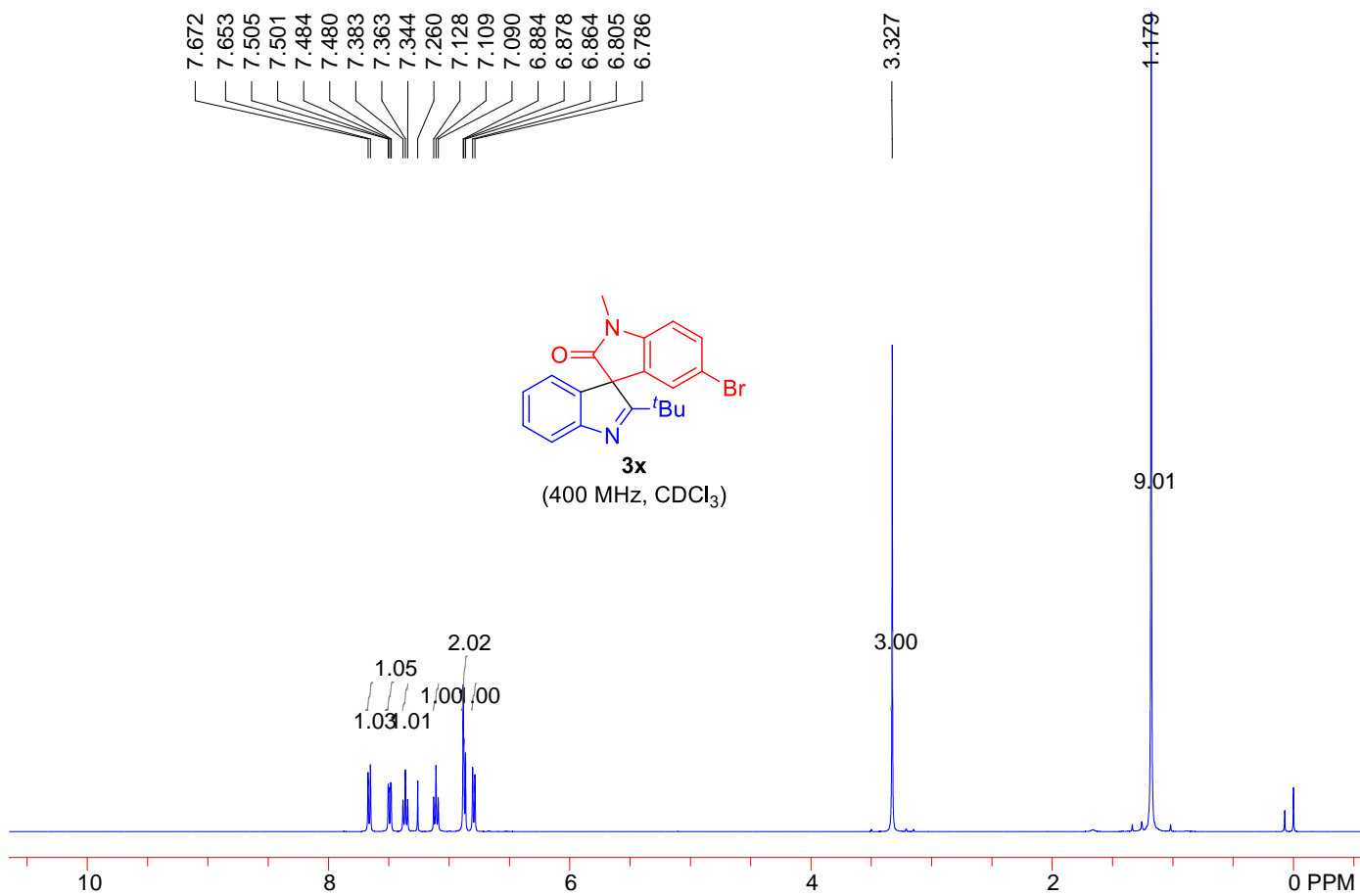


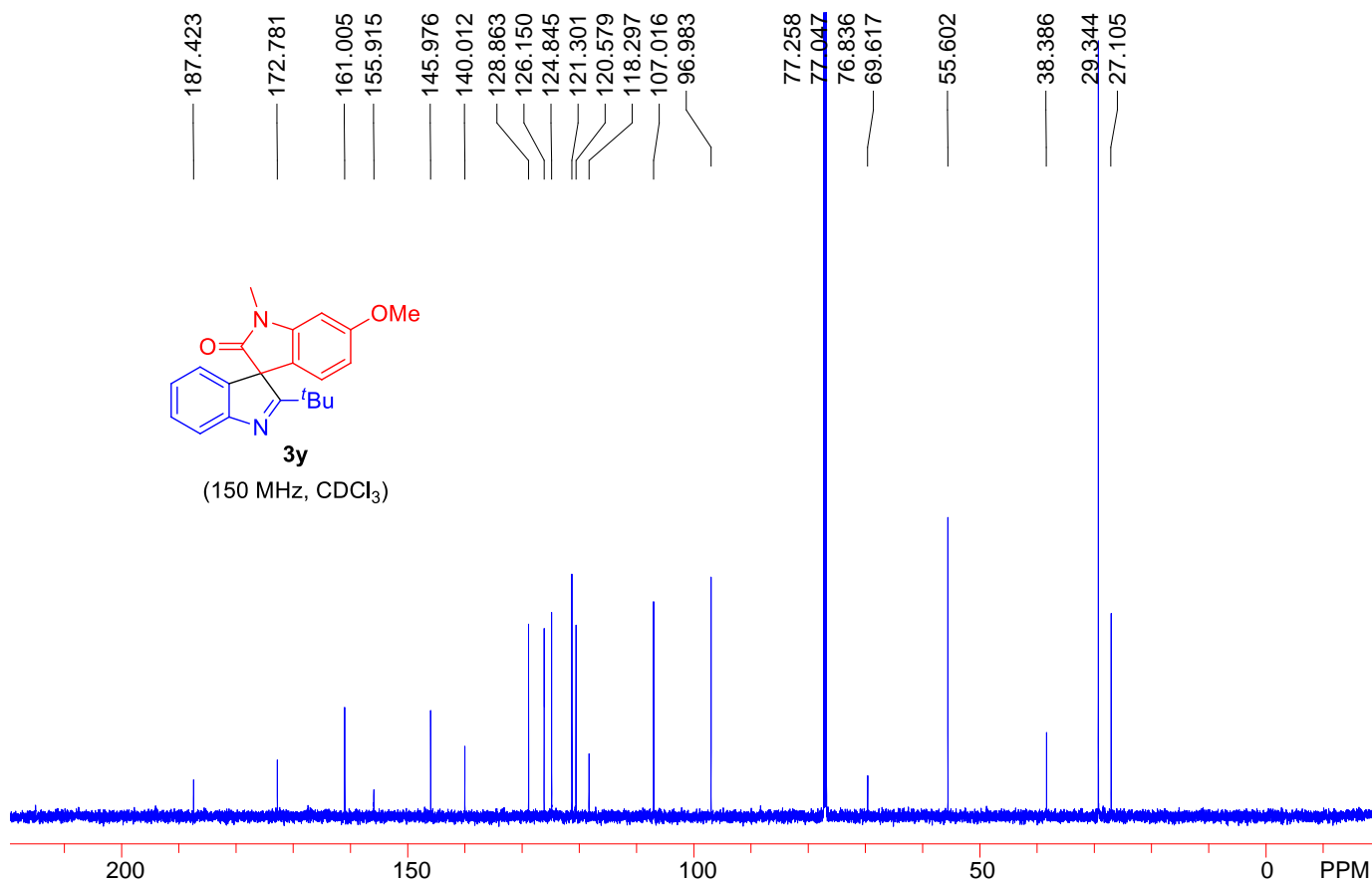
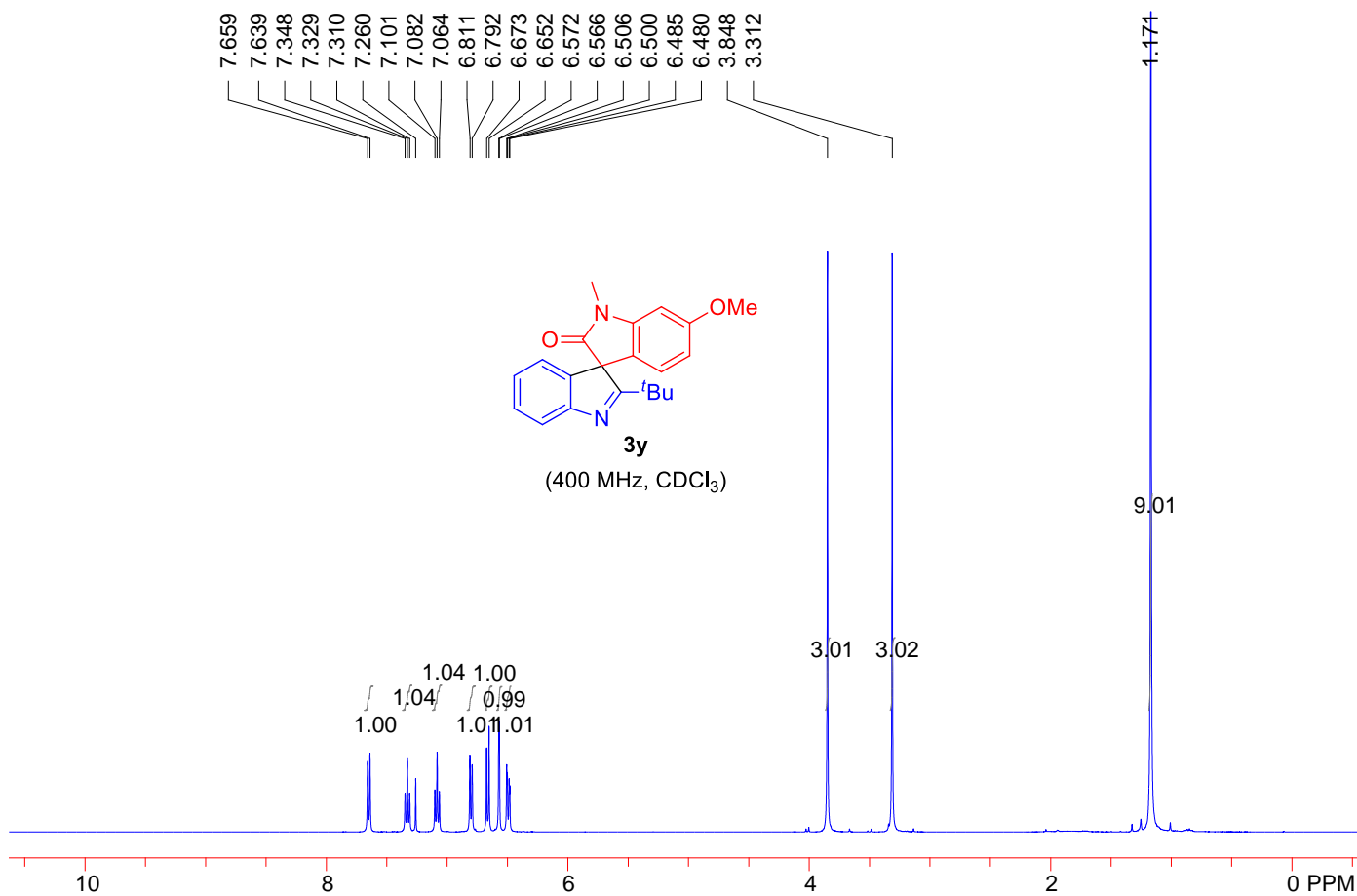


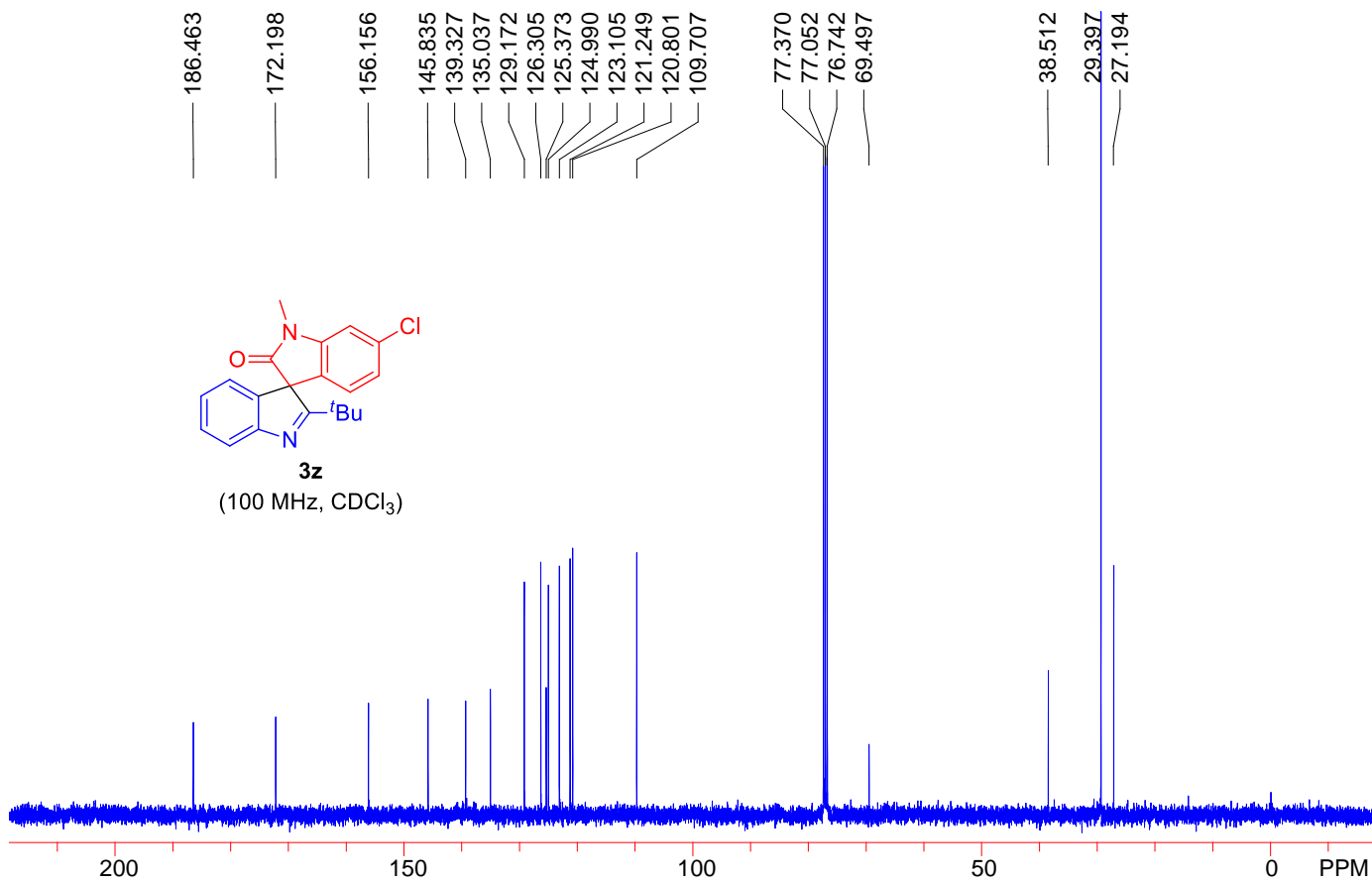
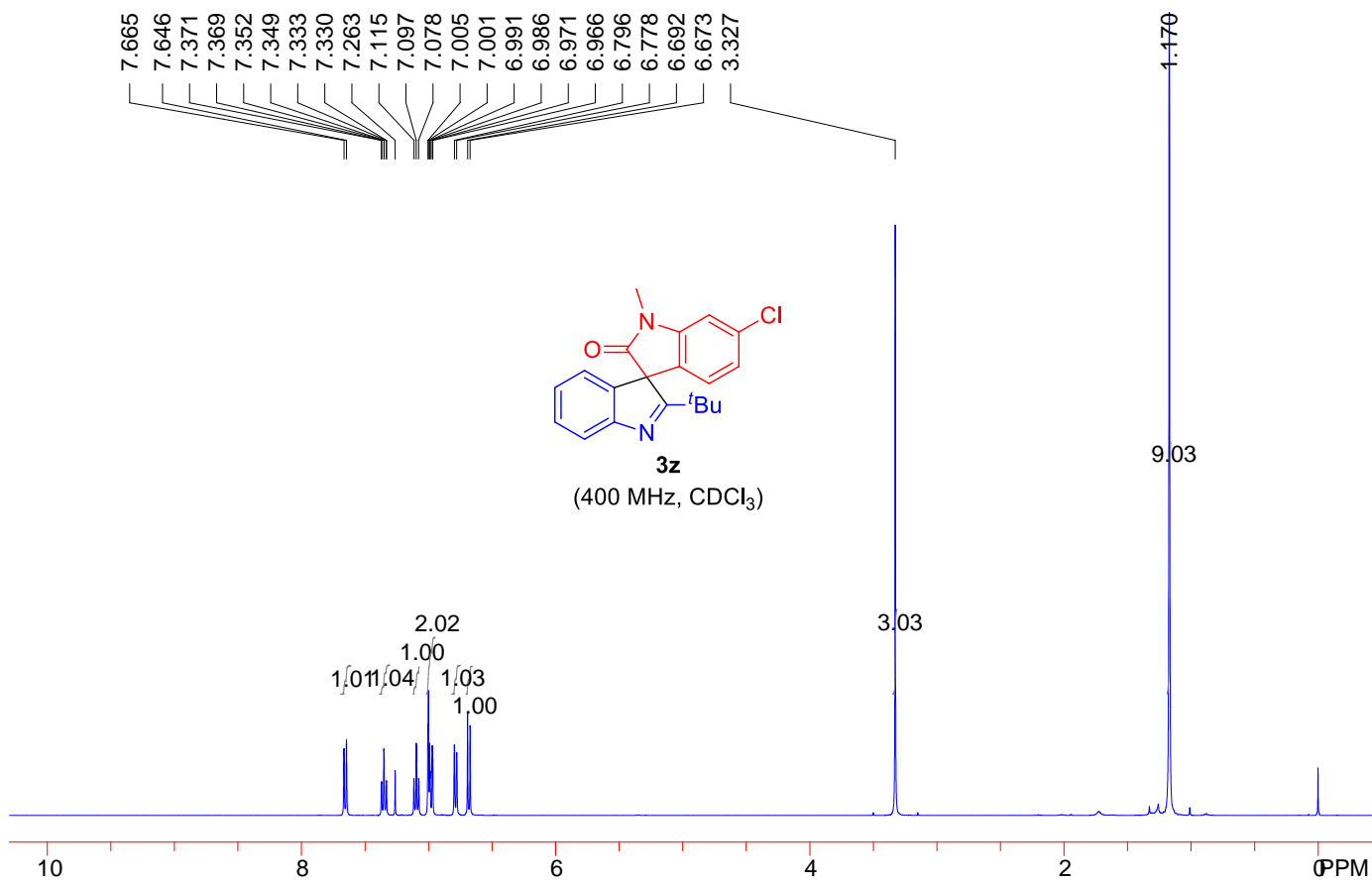
119.108
119.120
119.131
119.142
119.153
119.164

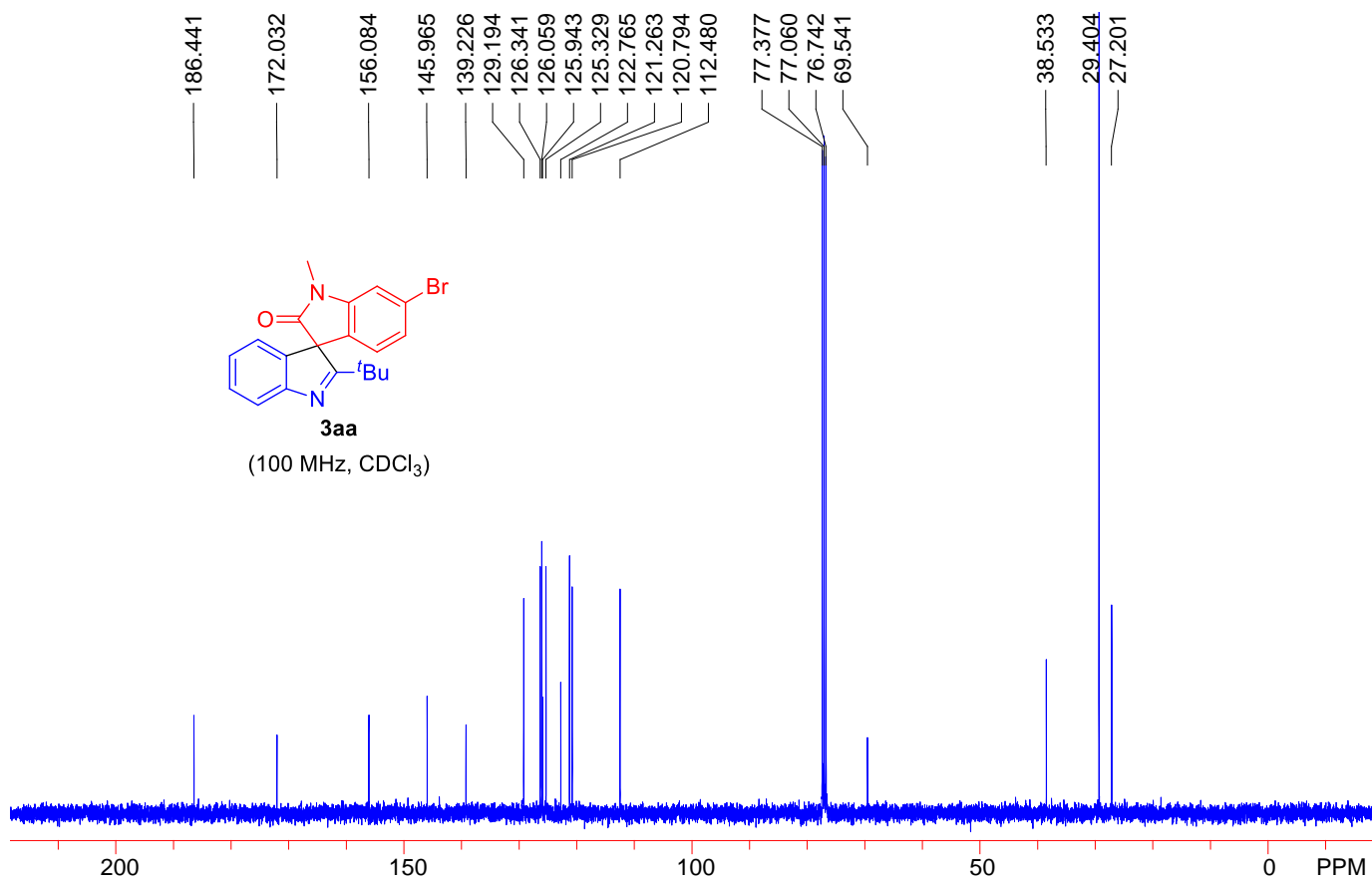
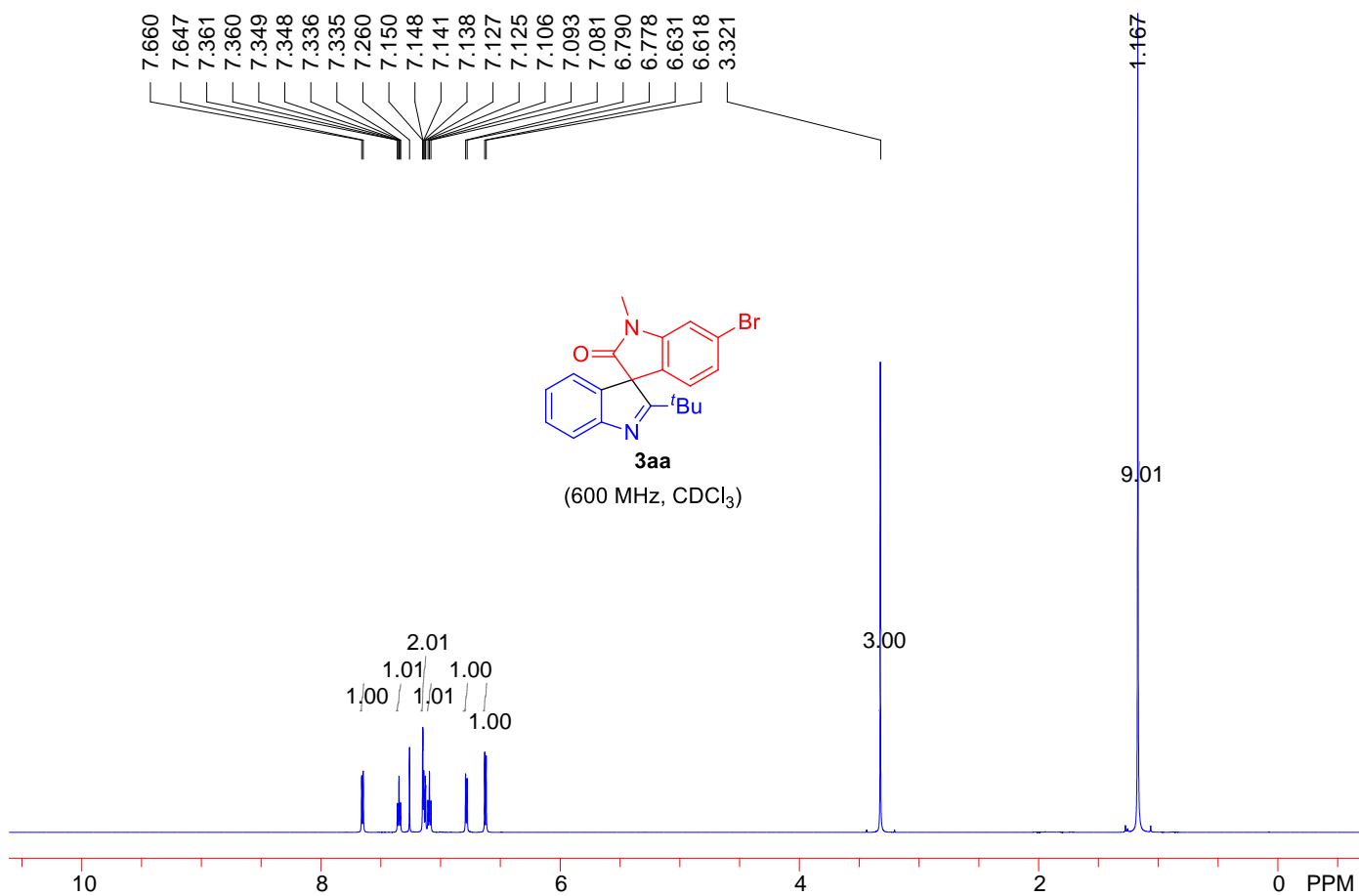


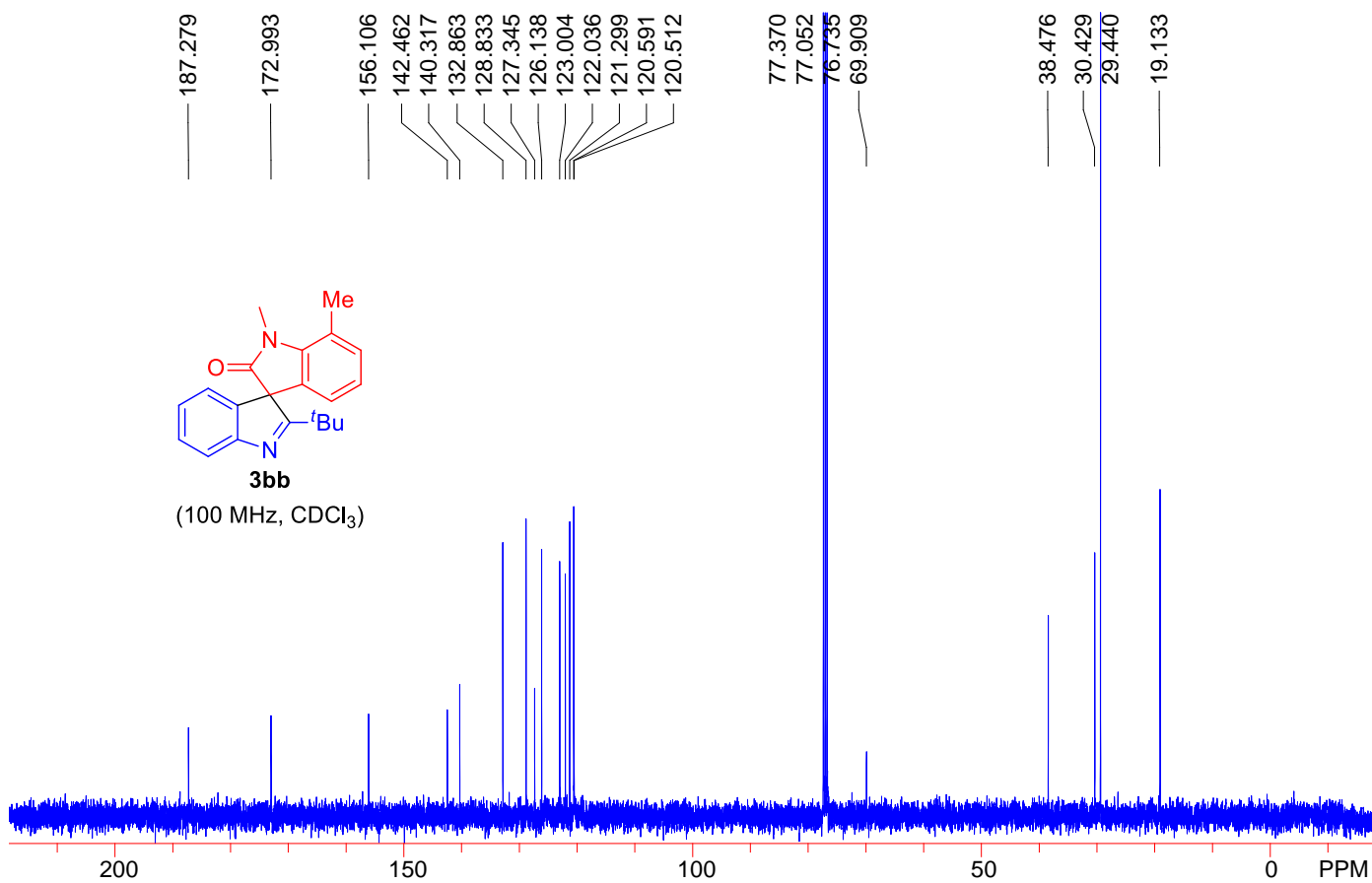
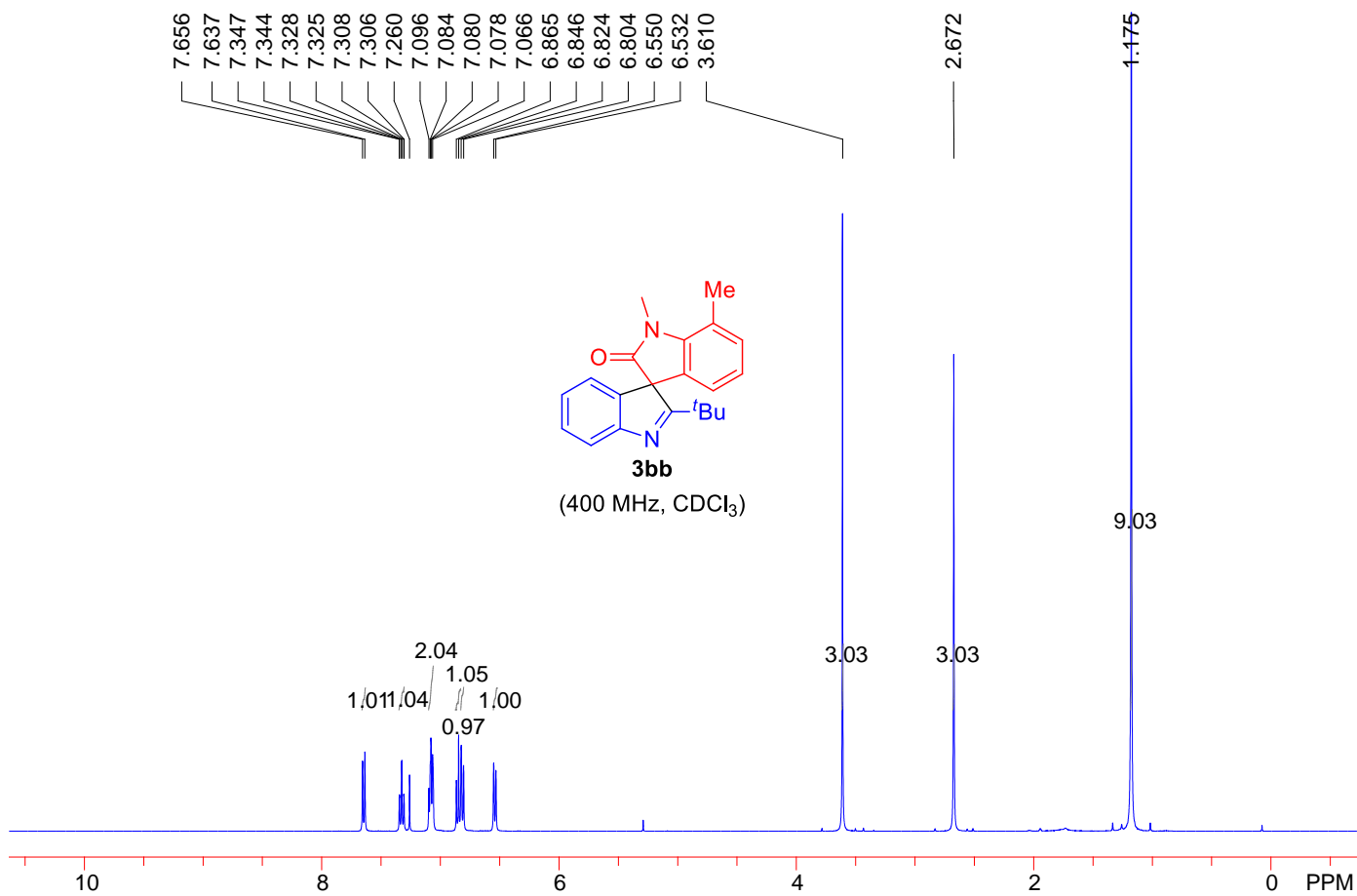


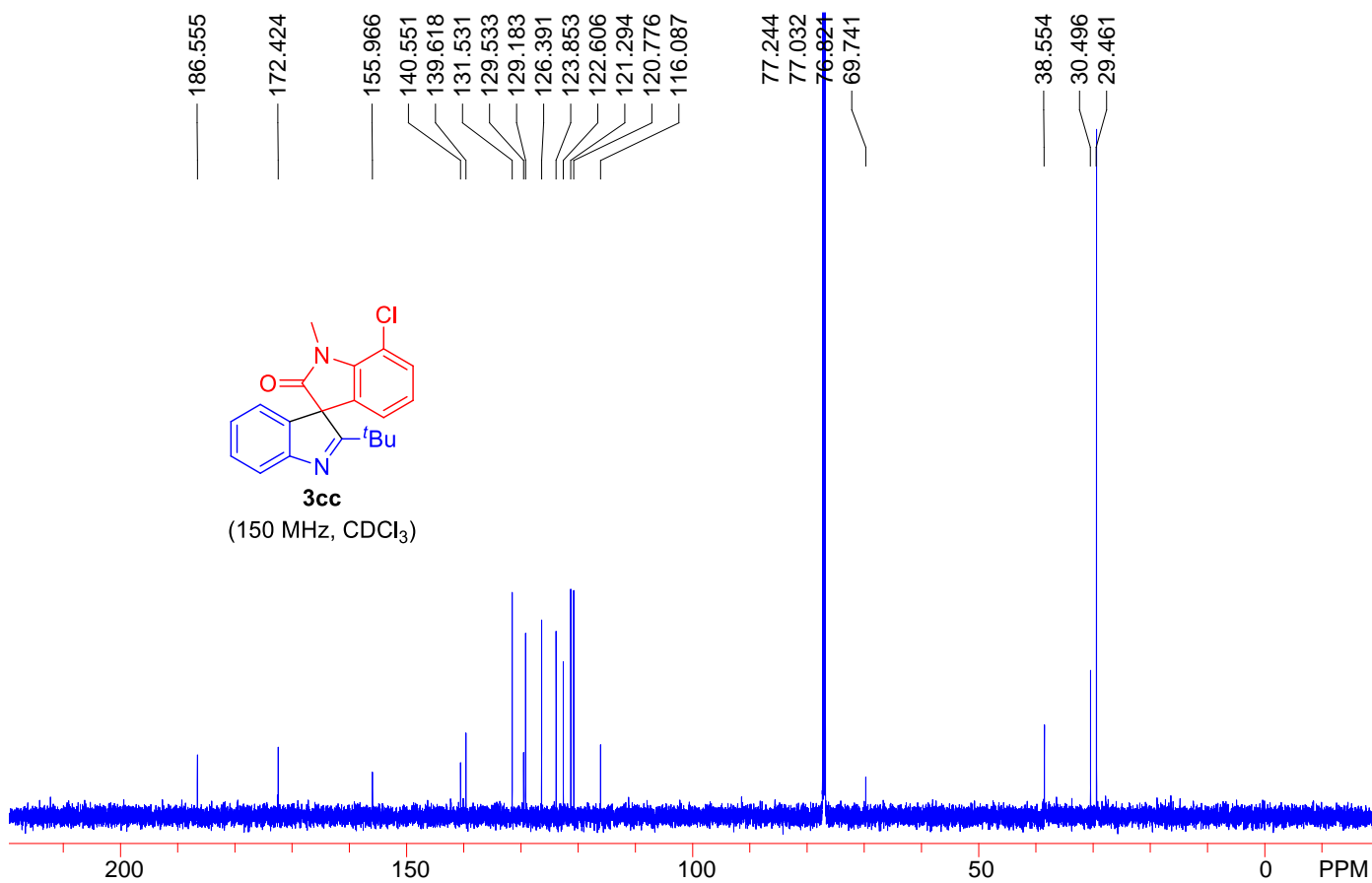
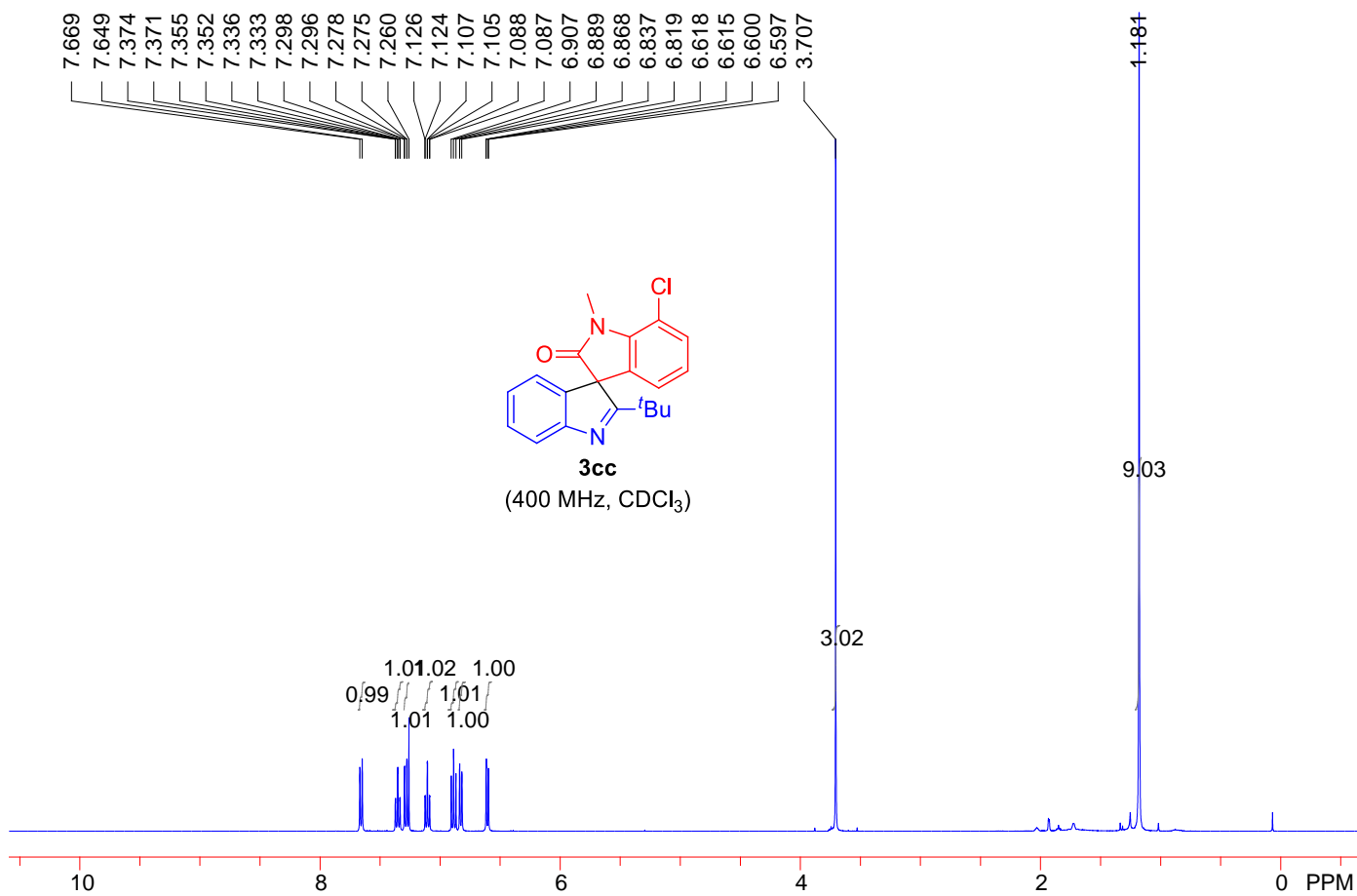


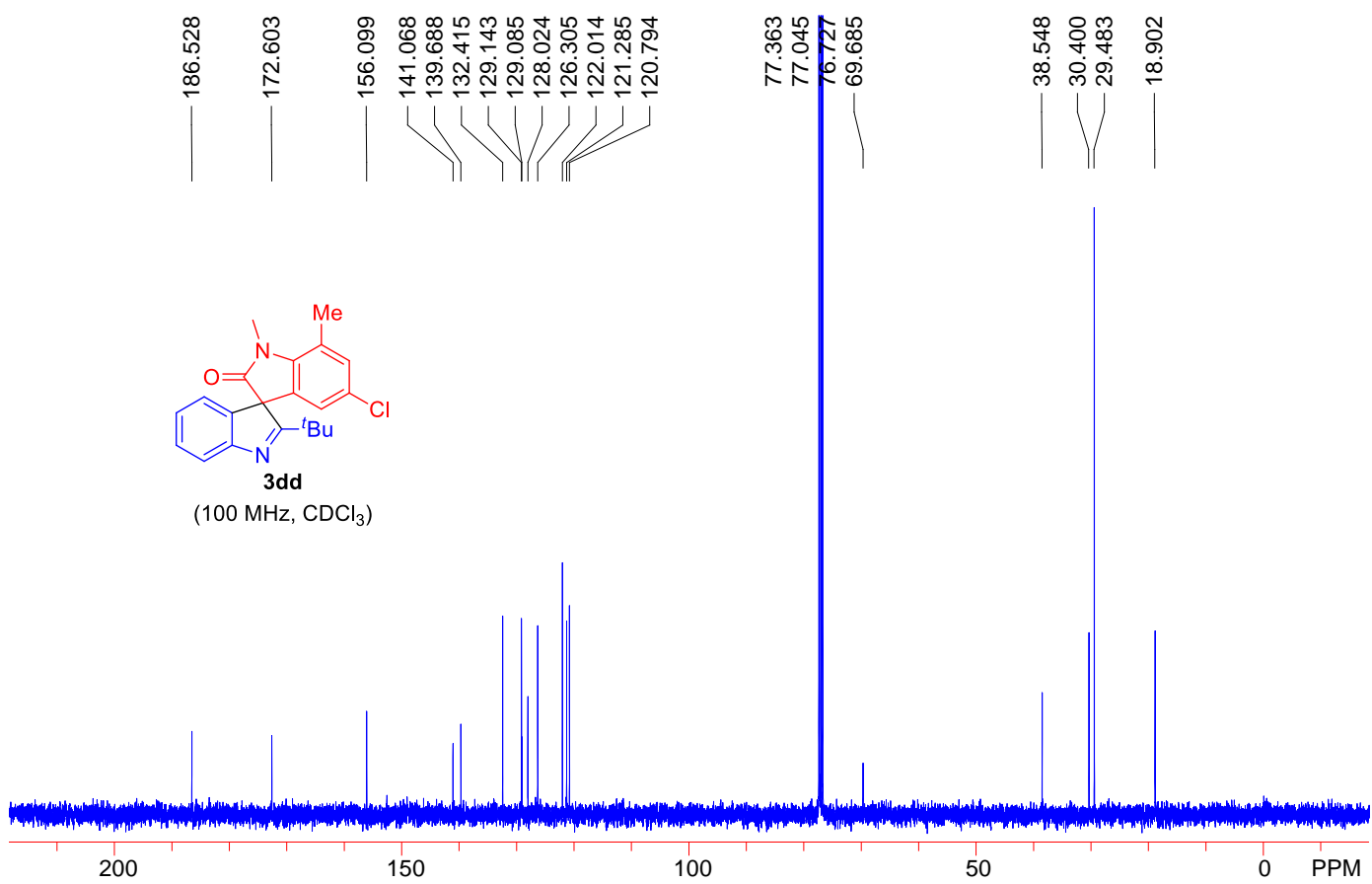
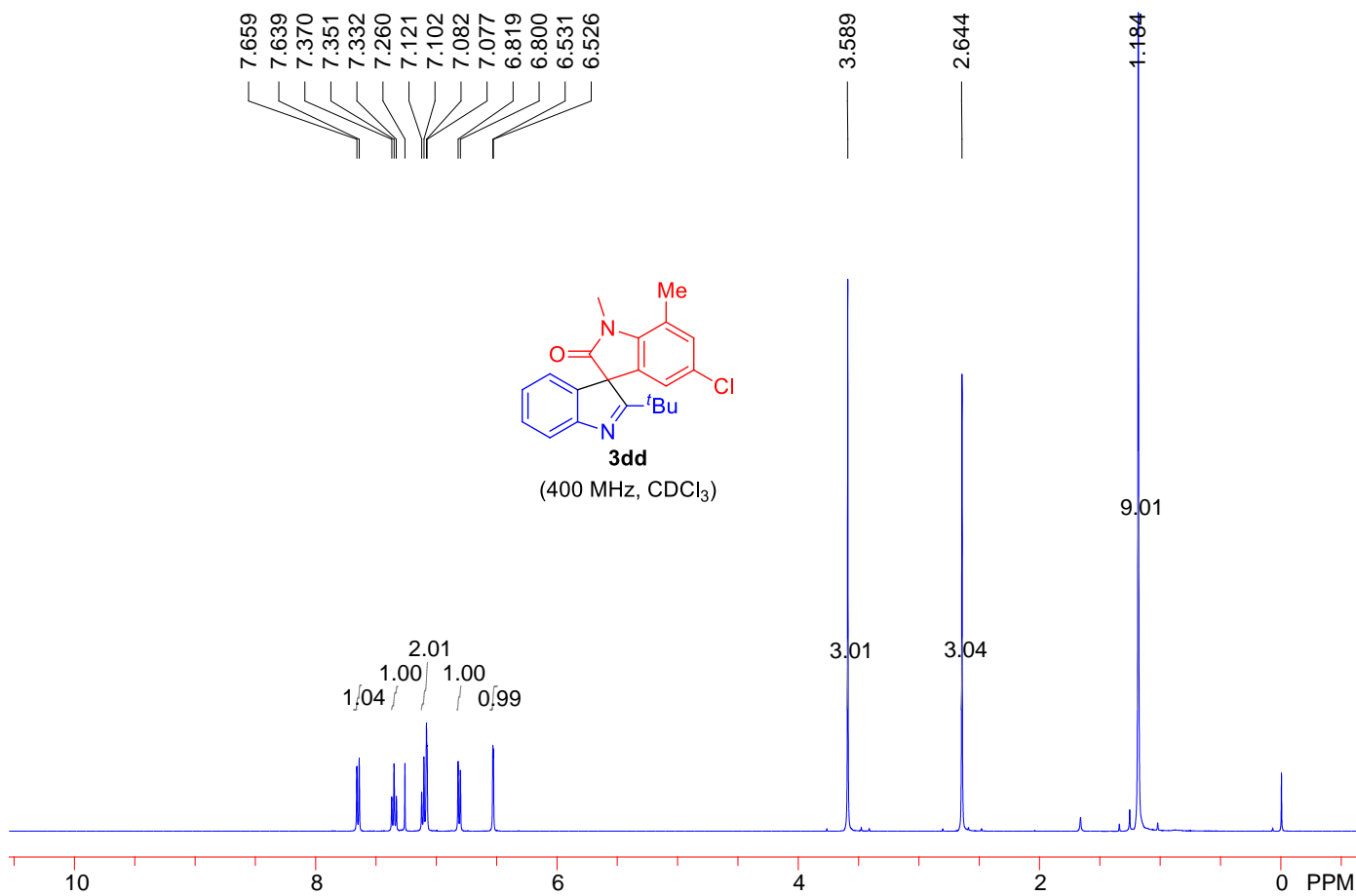


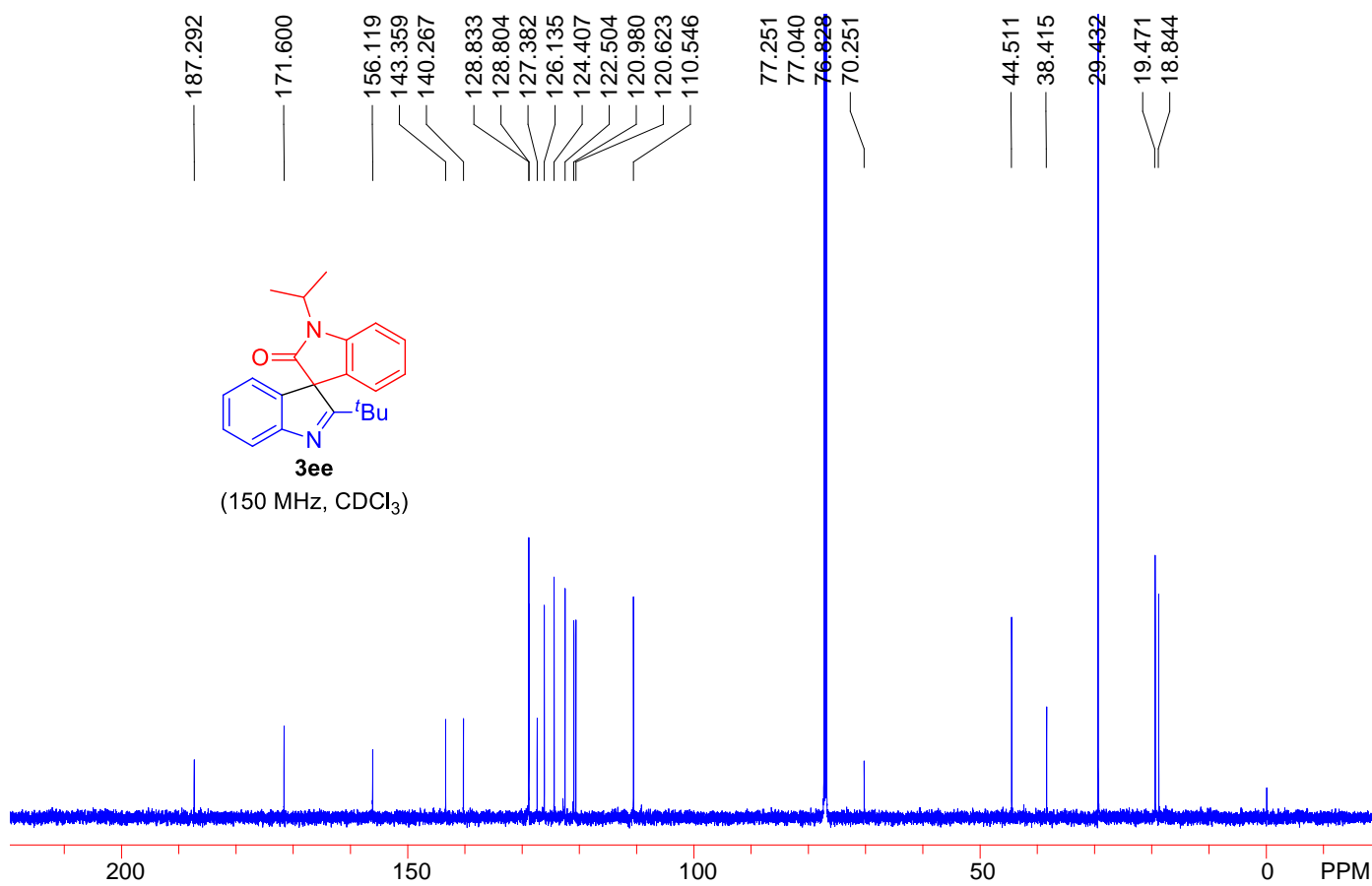
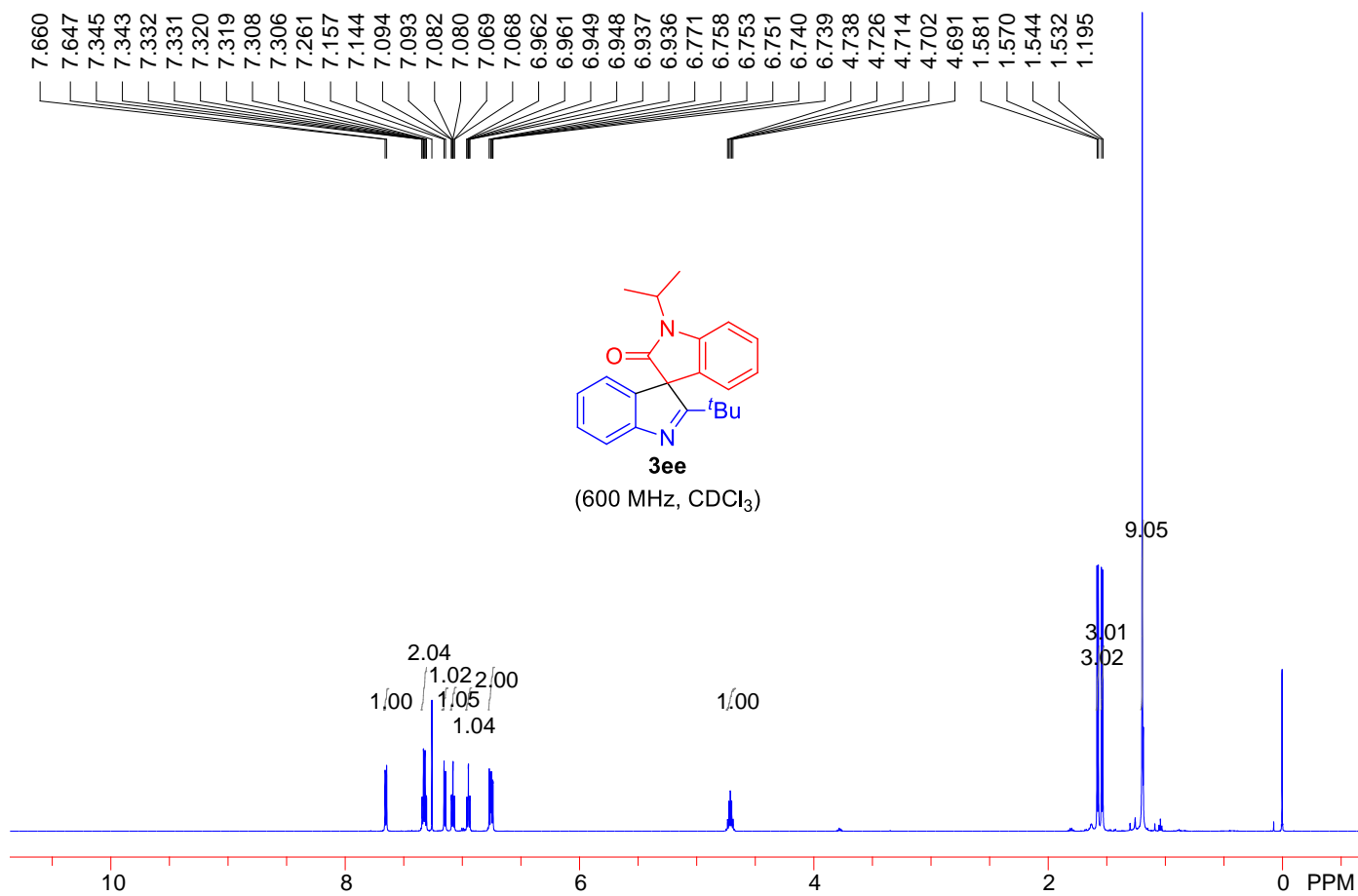


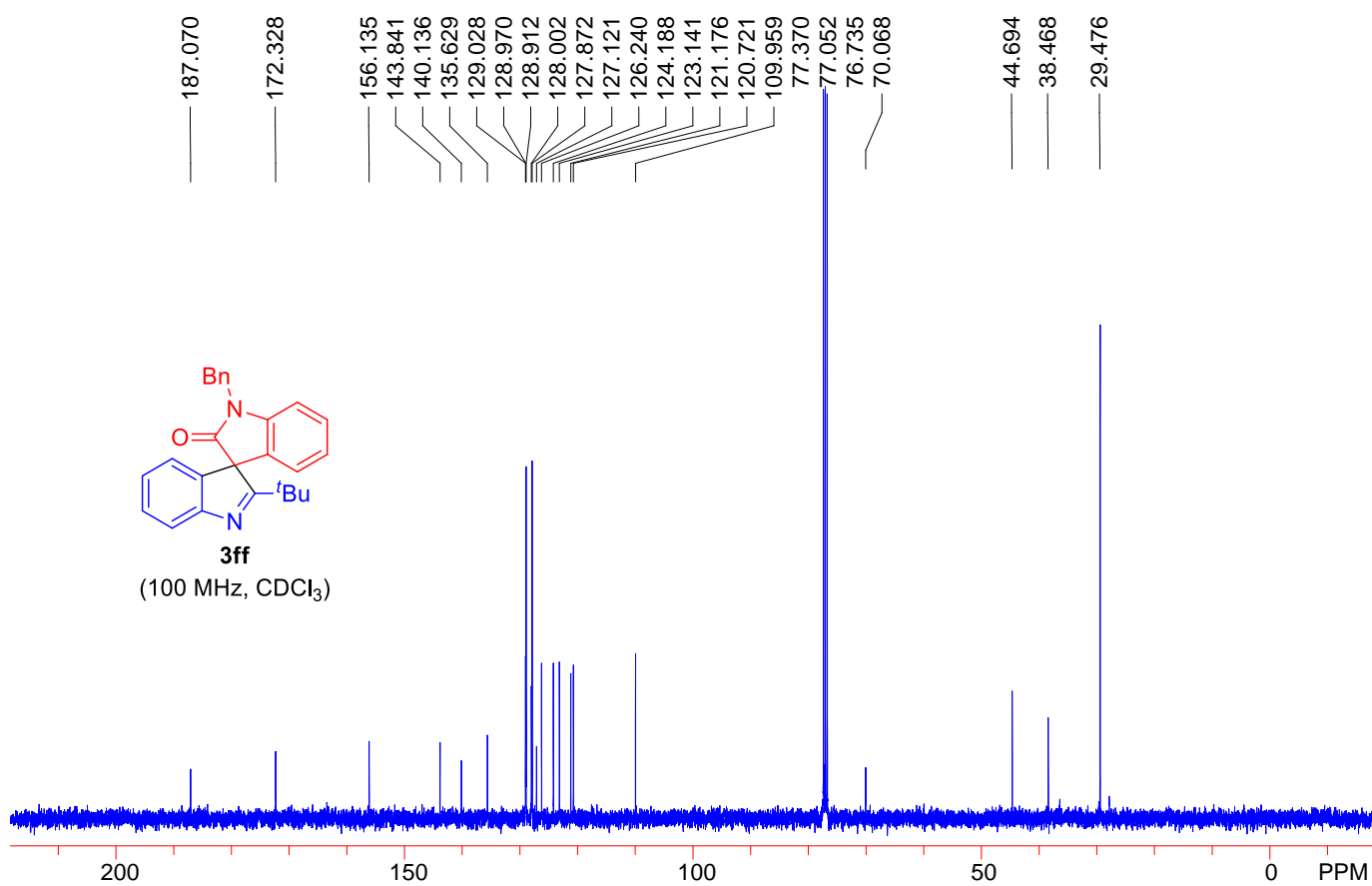
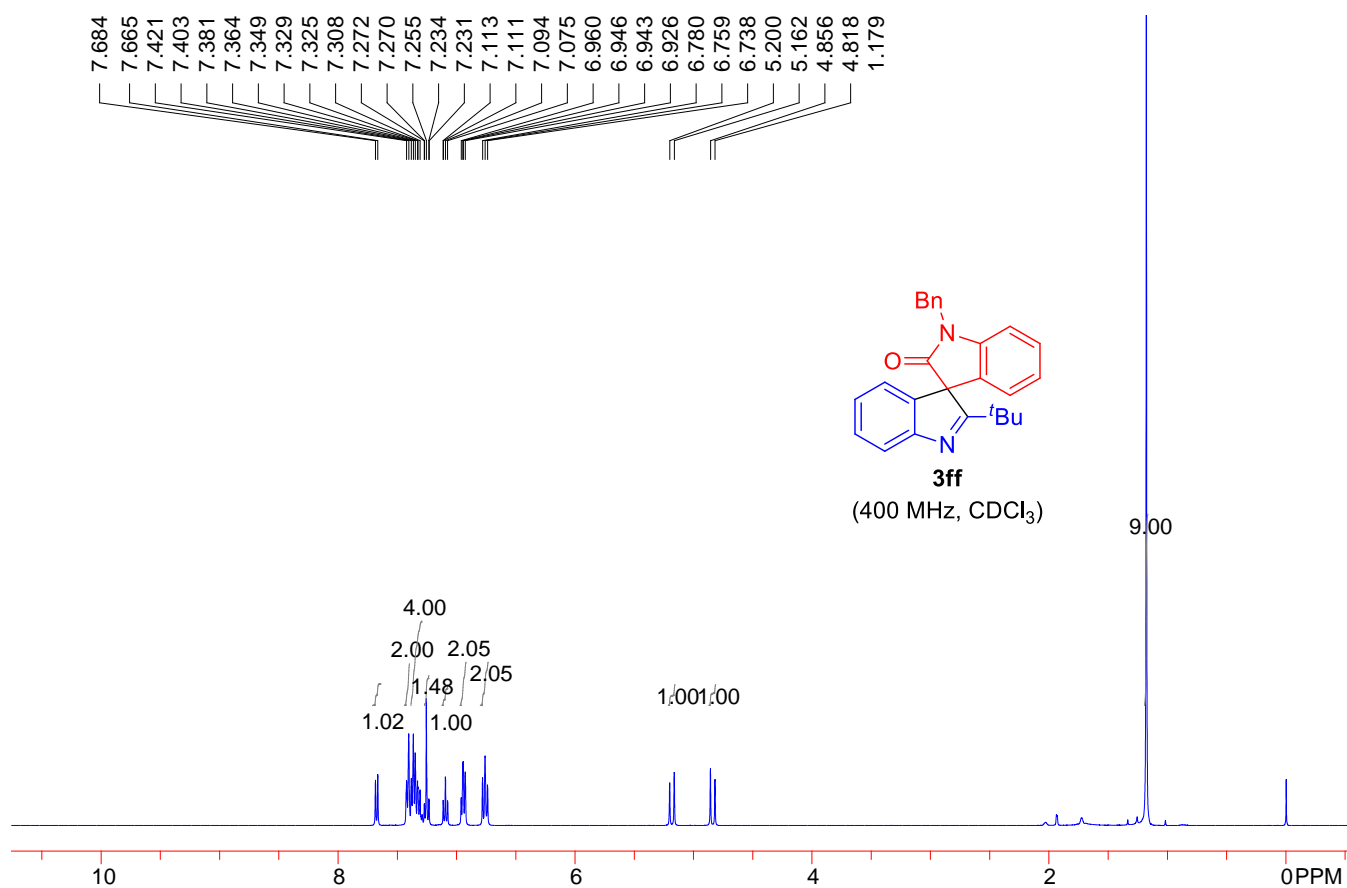


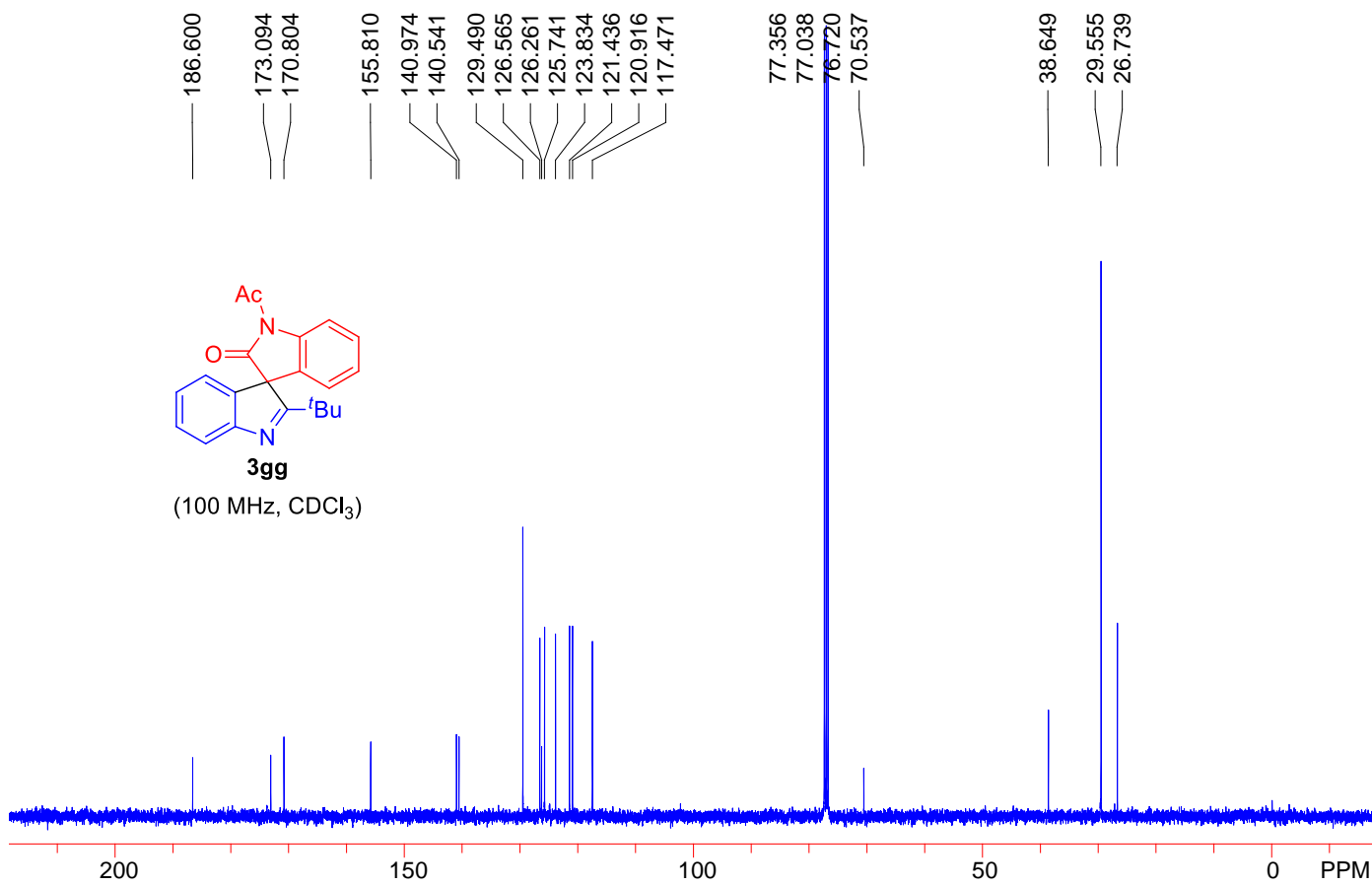
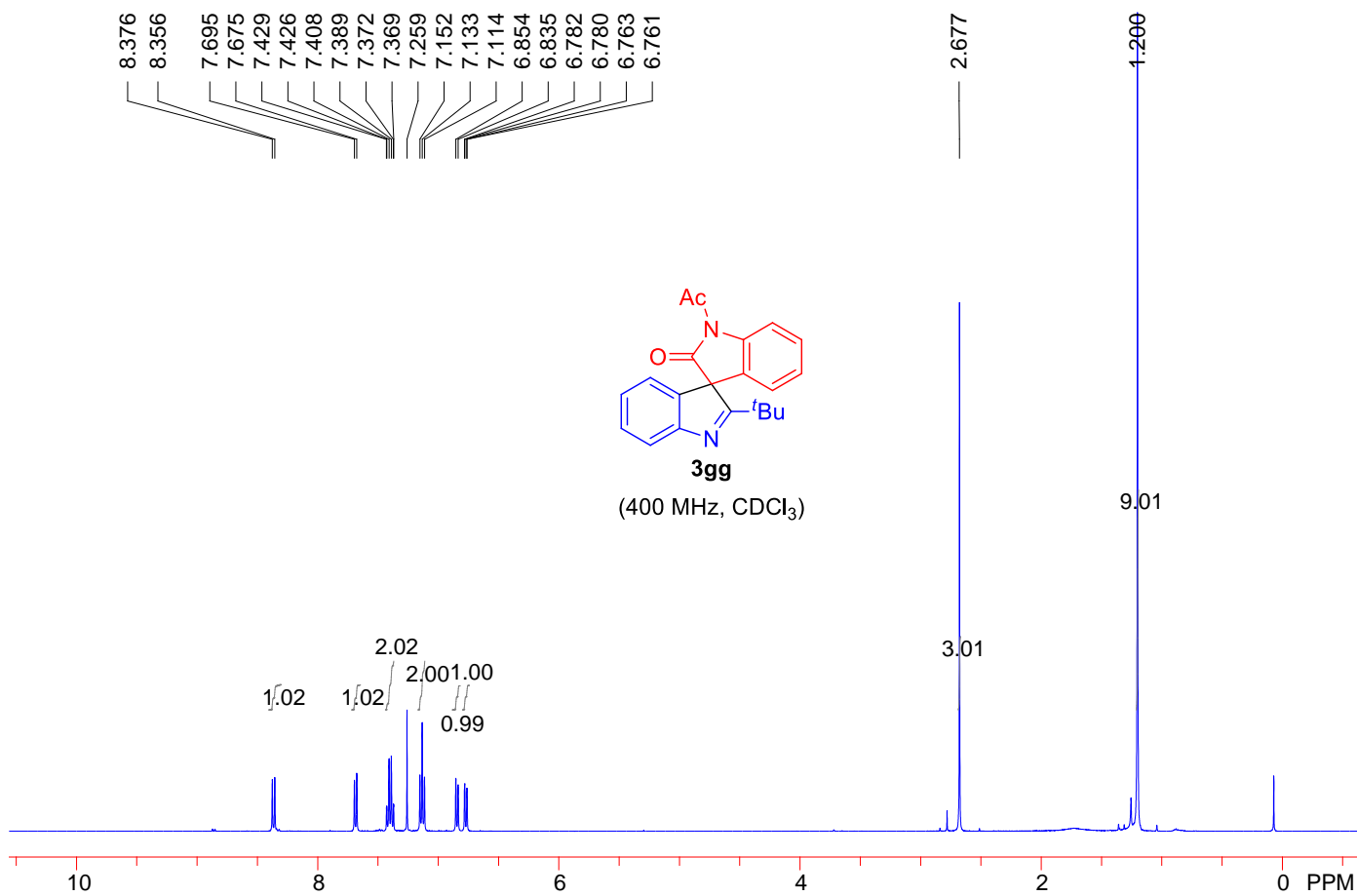


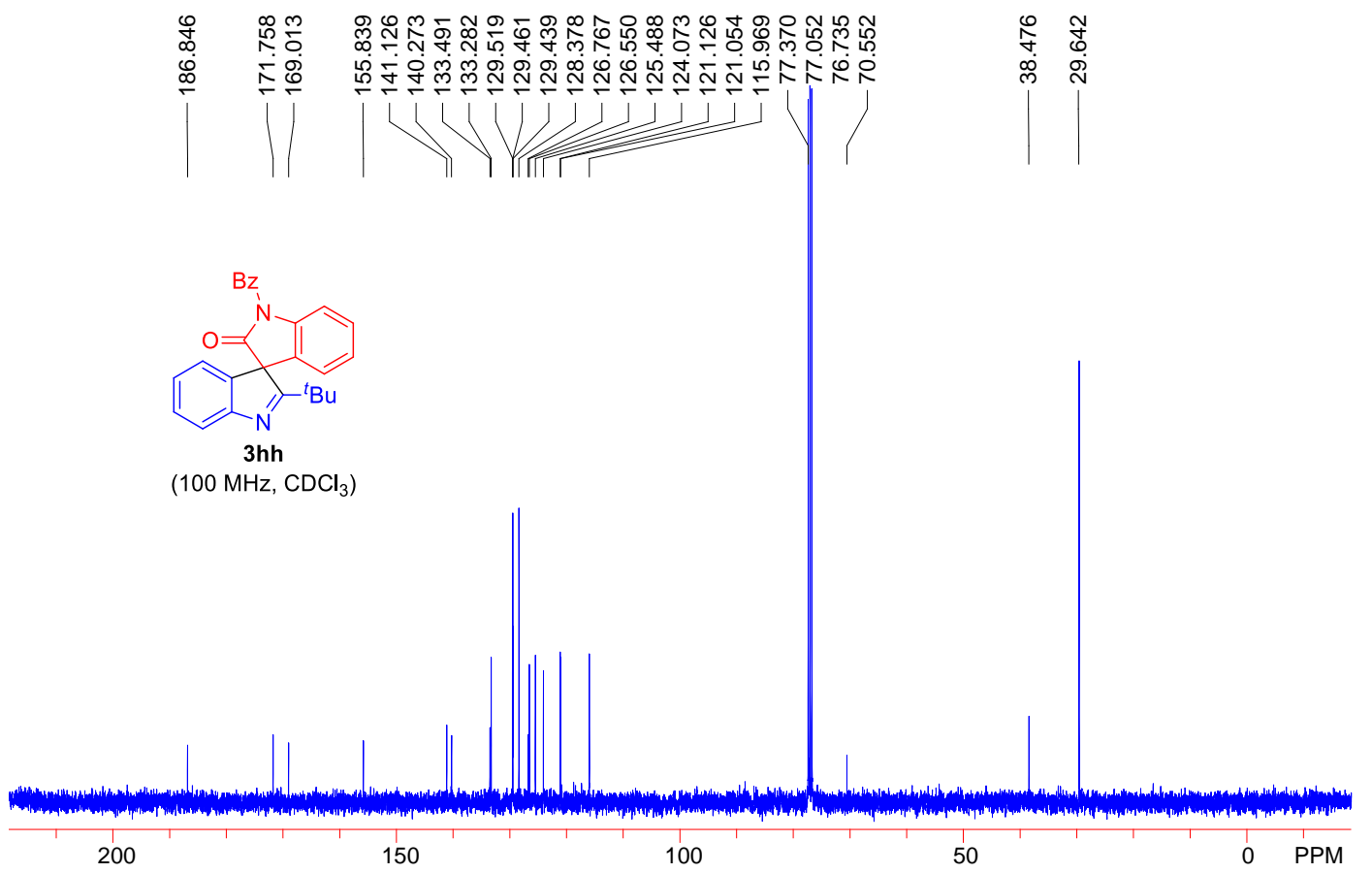
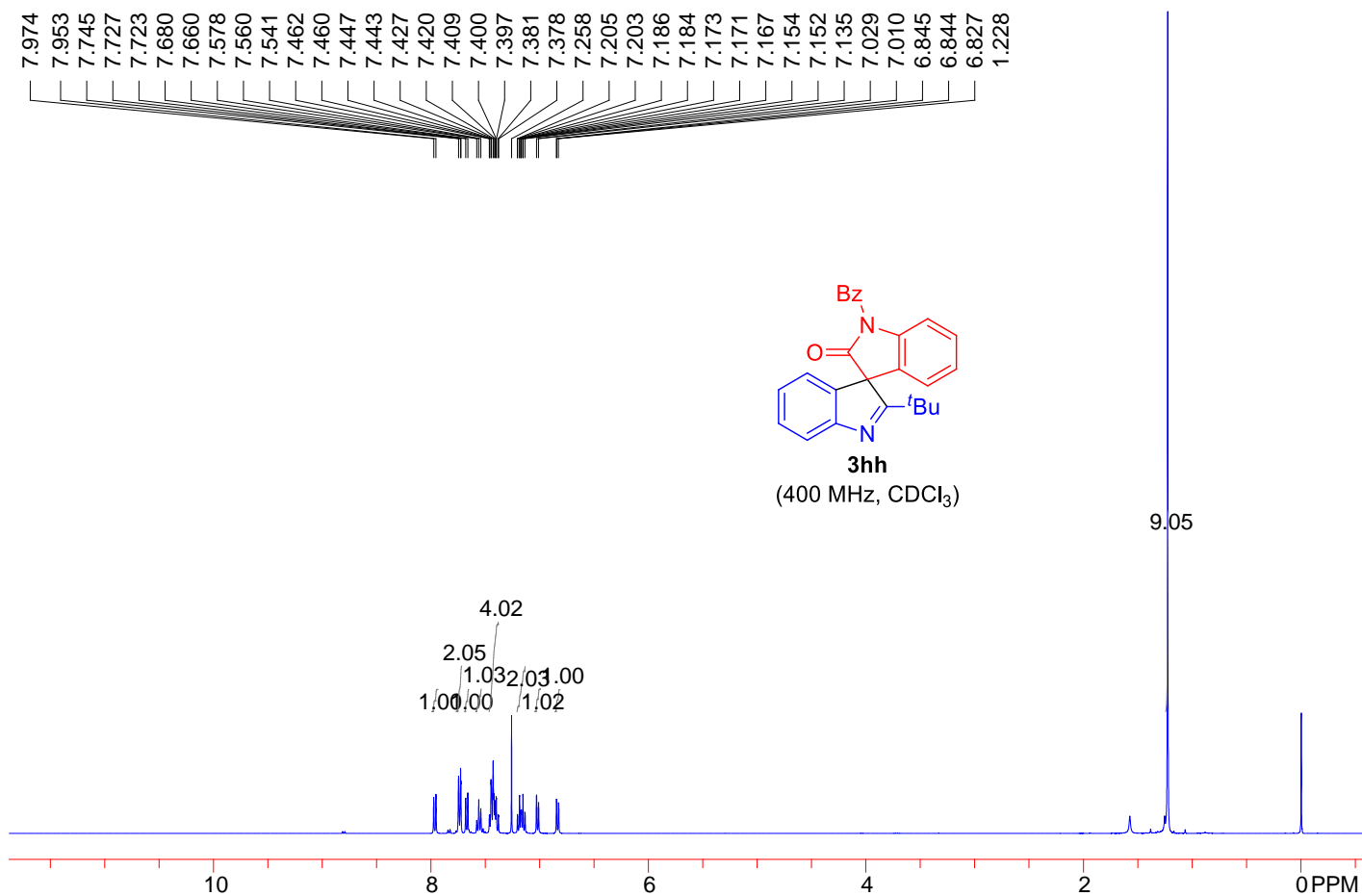




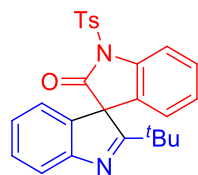




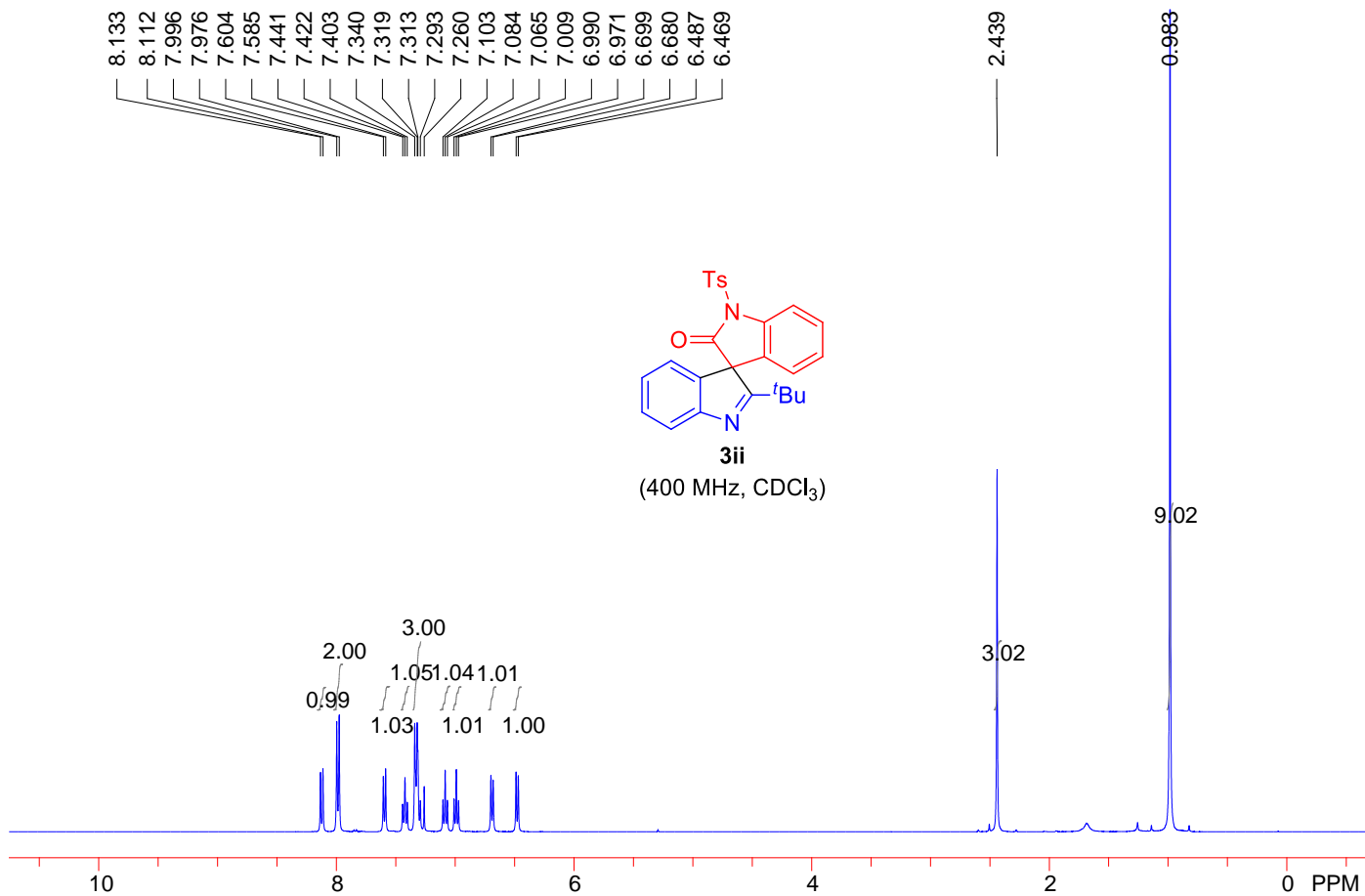




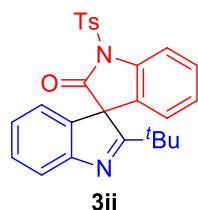
8.133
8.112
7.996
7.976
7.604
7.585
7.441
7.422
7.403
7.340
7.319
7.313
7.293
7.260
7.103
7.084
7.065
7.009
6.990
6.971
6.699
6.680
6.487
6.469



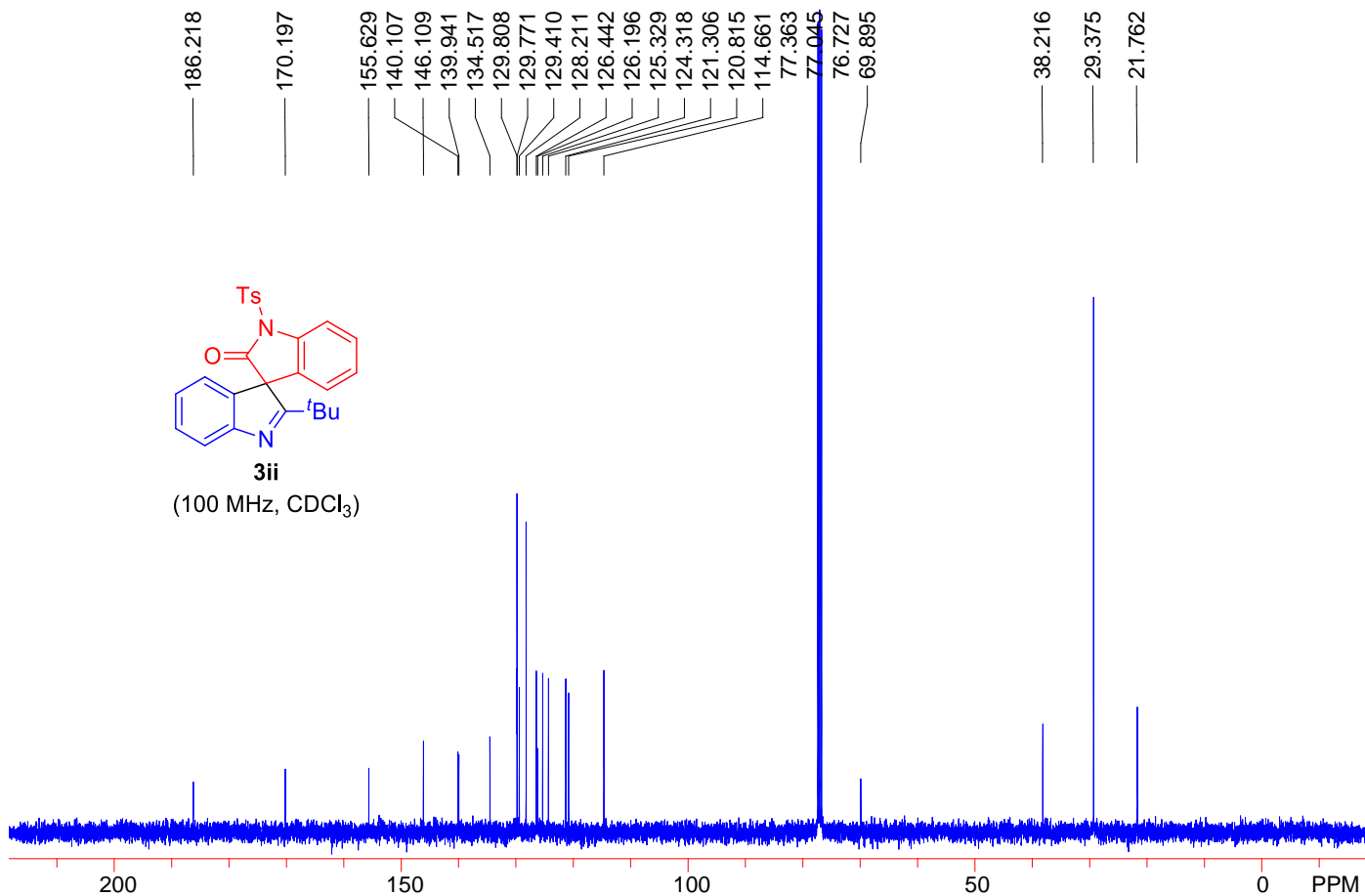
3ii
(400 MHz, CDCl₃)

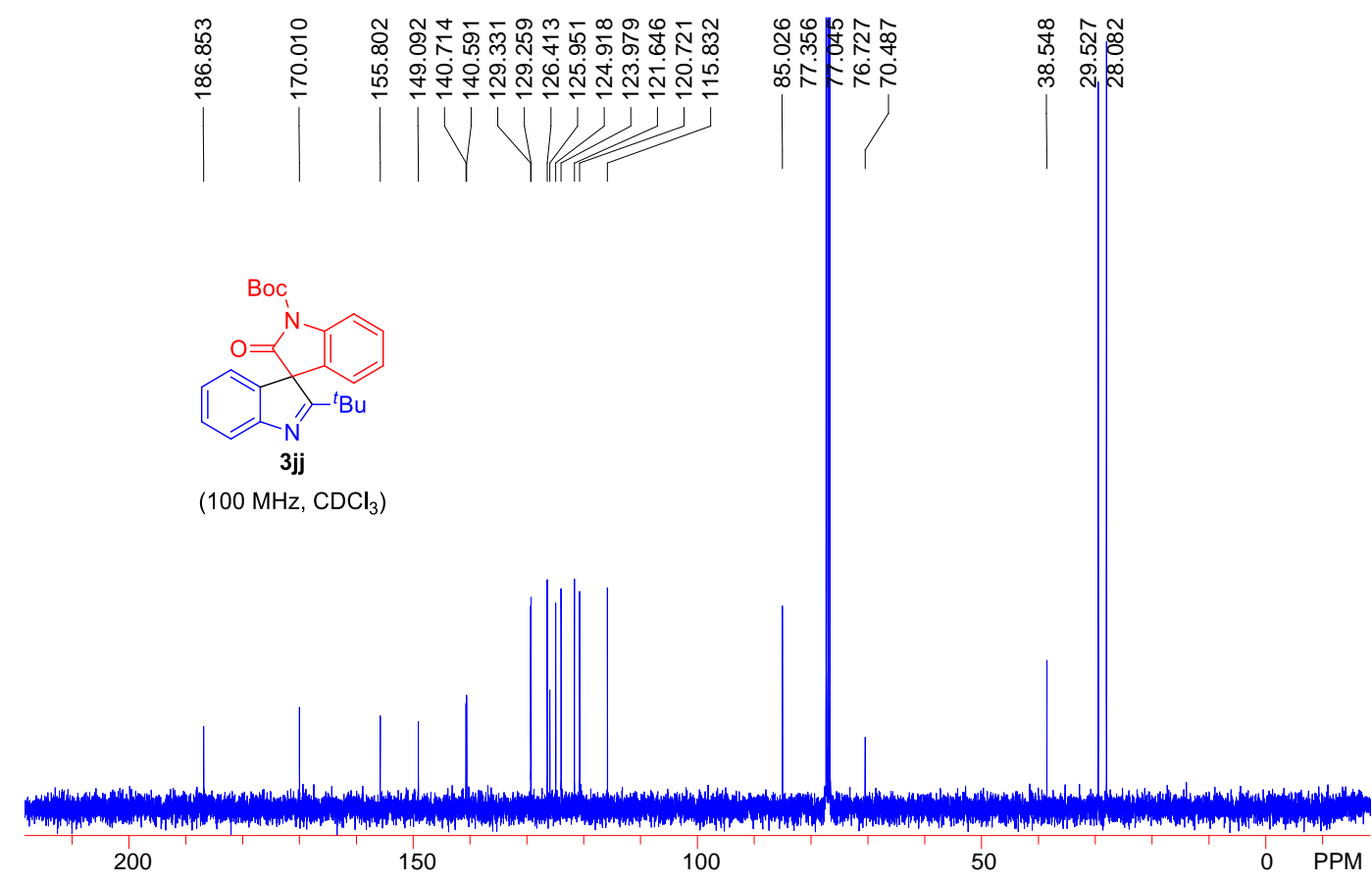
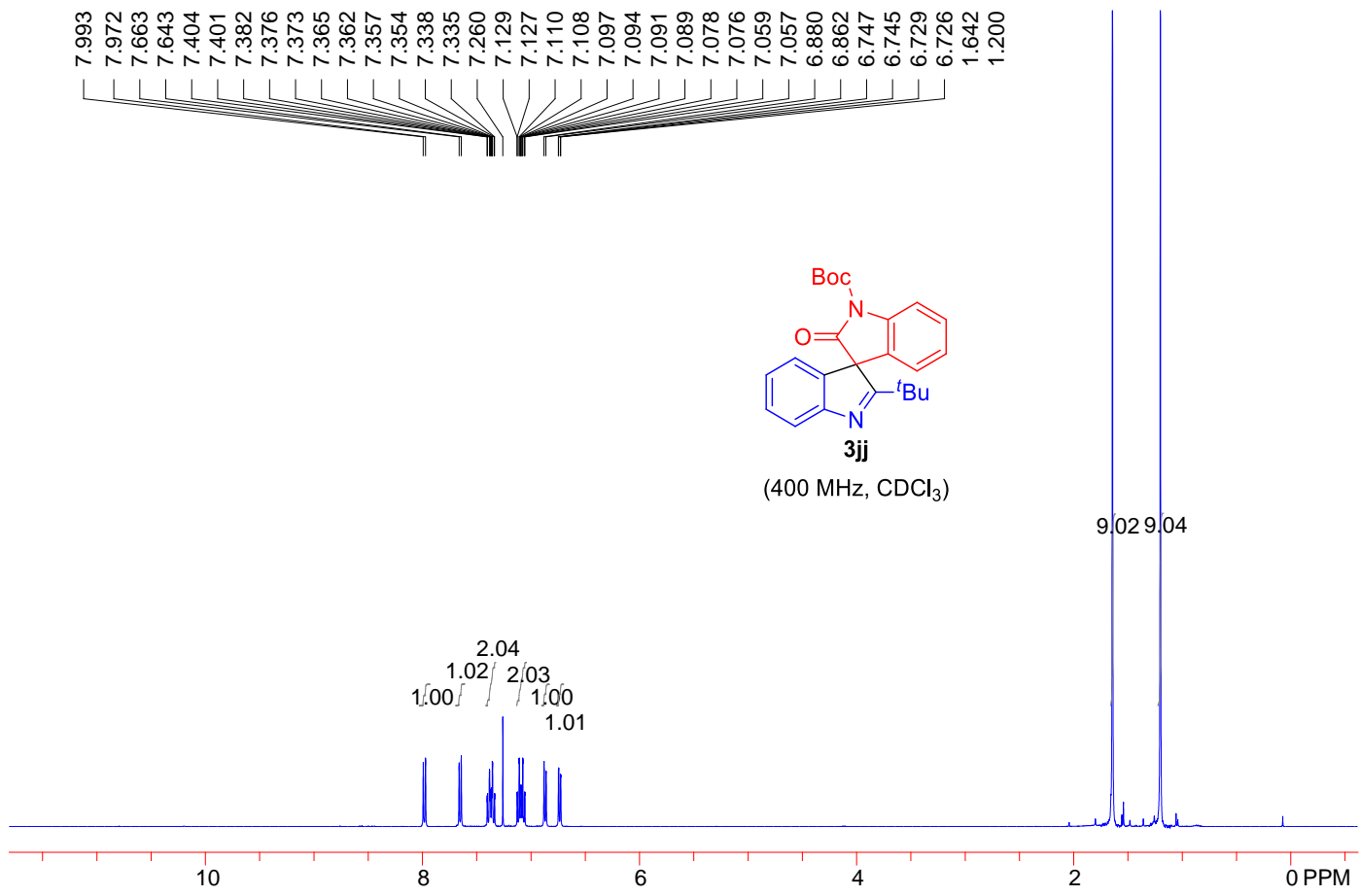


186.218
170.197
155.629
140.107
146.109
139.941
134.517
129.808
129.771
129.410
128.211
126.442
126.196
125.329
124.318
121.306
120.815
114.661
77.363
77.045
76.727
69.895
38.216
29.375
21.762

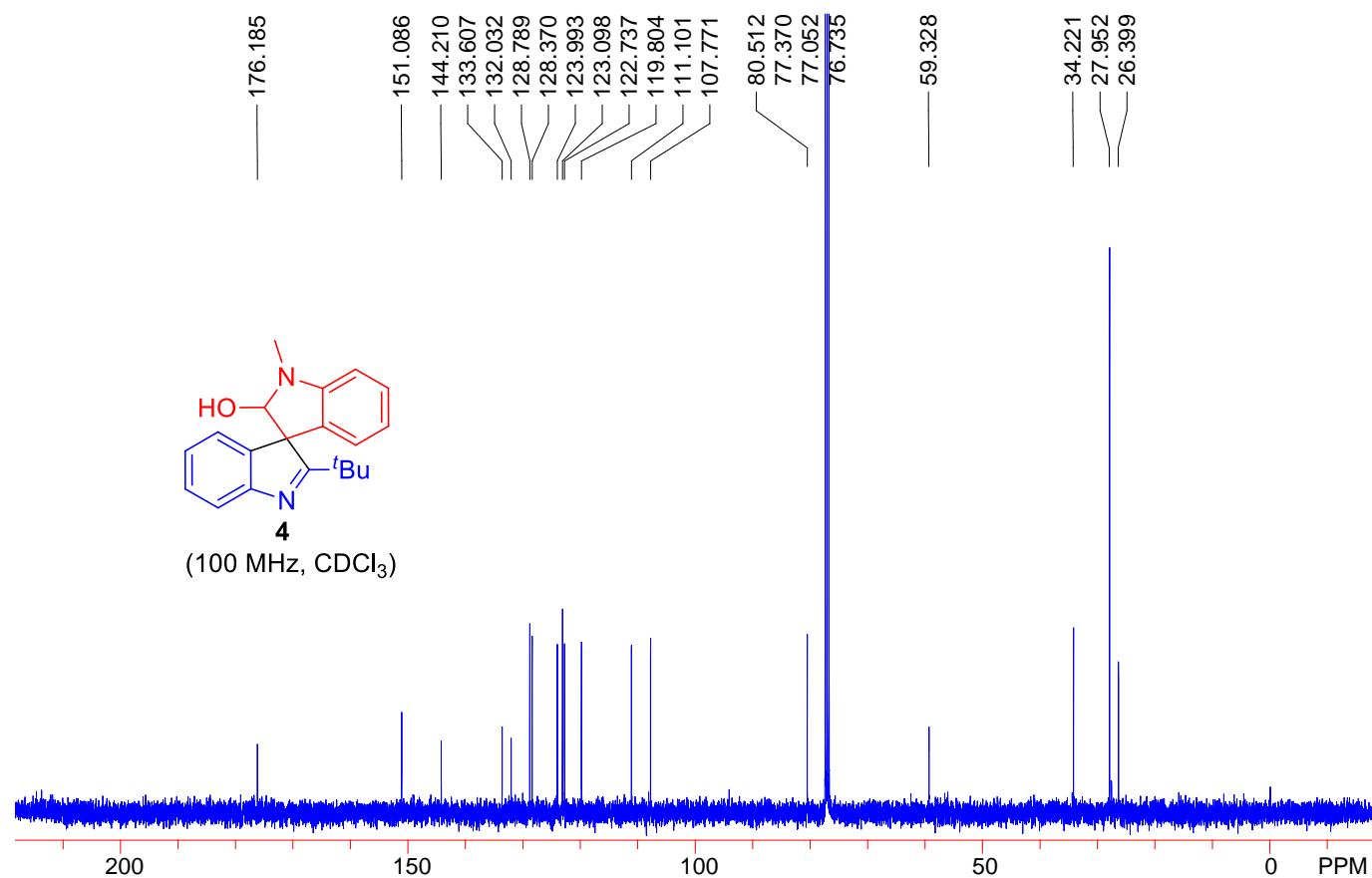
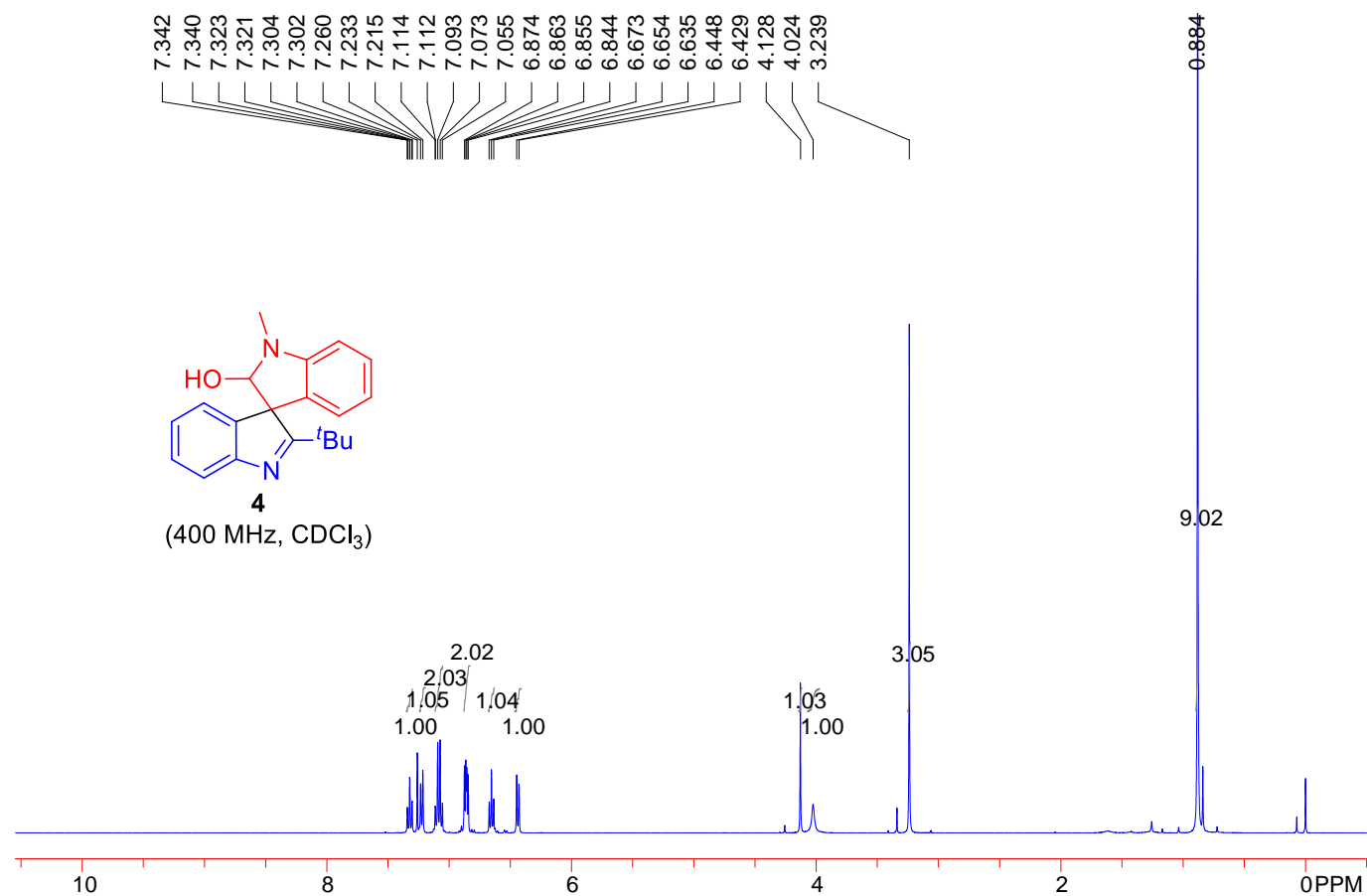


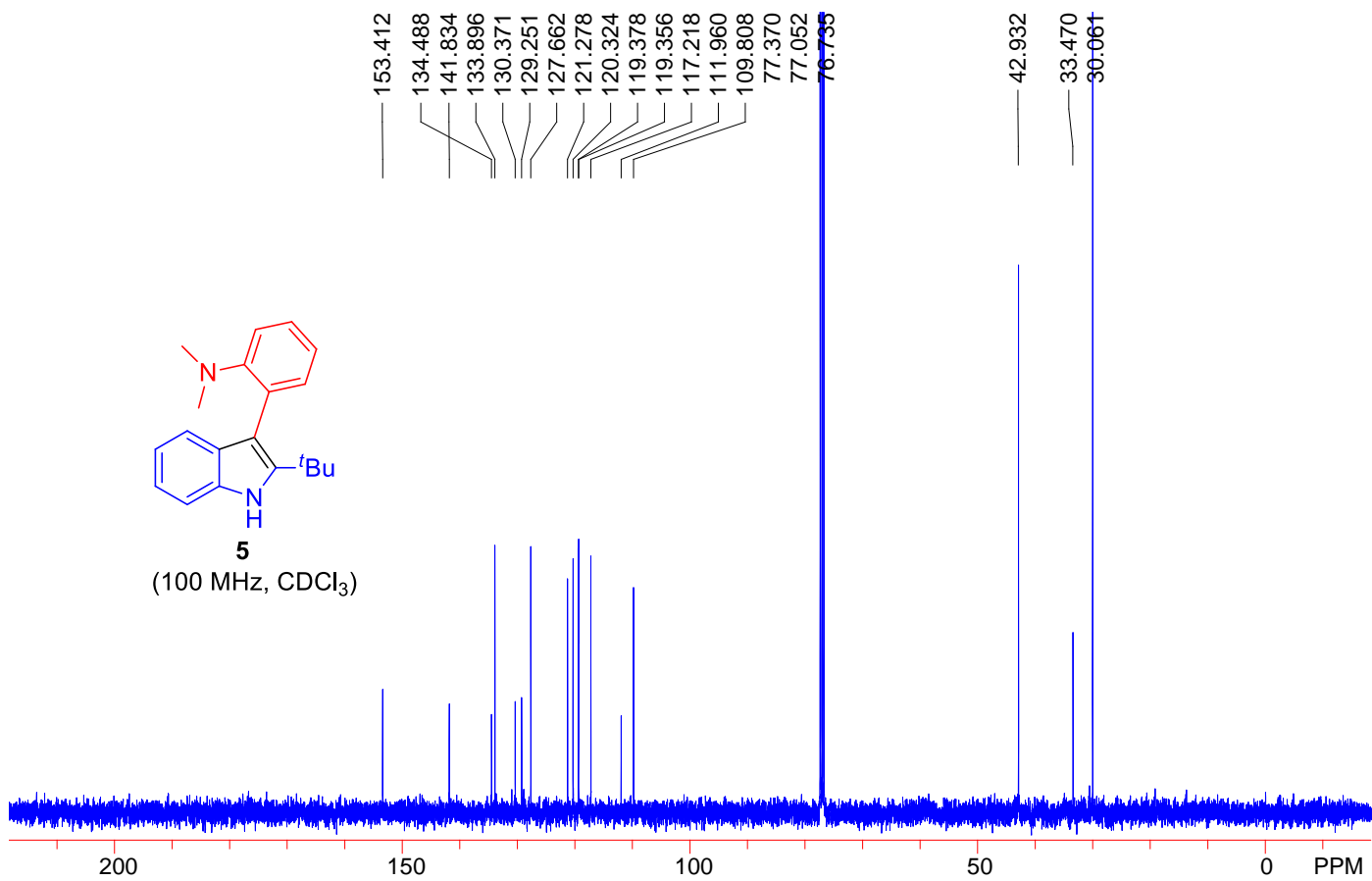
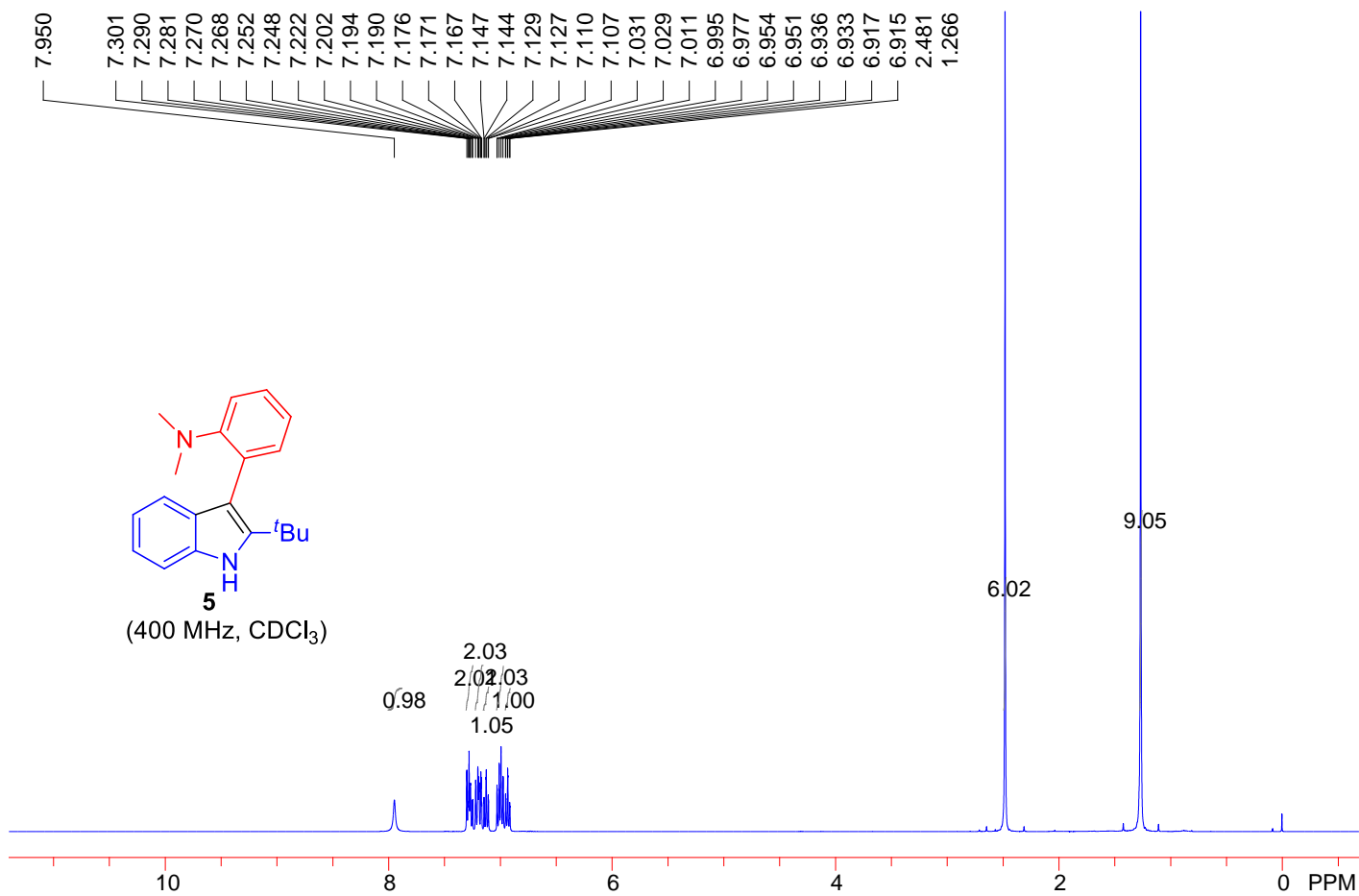
3ii
(100 MHz, CDCl₃)

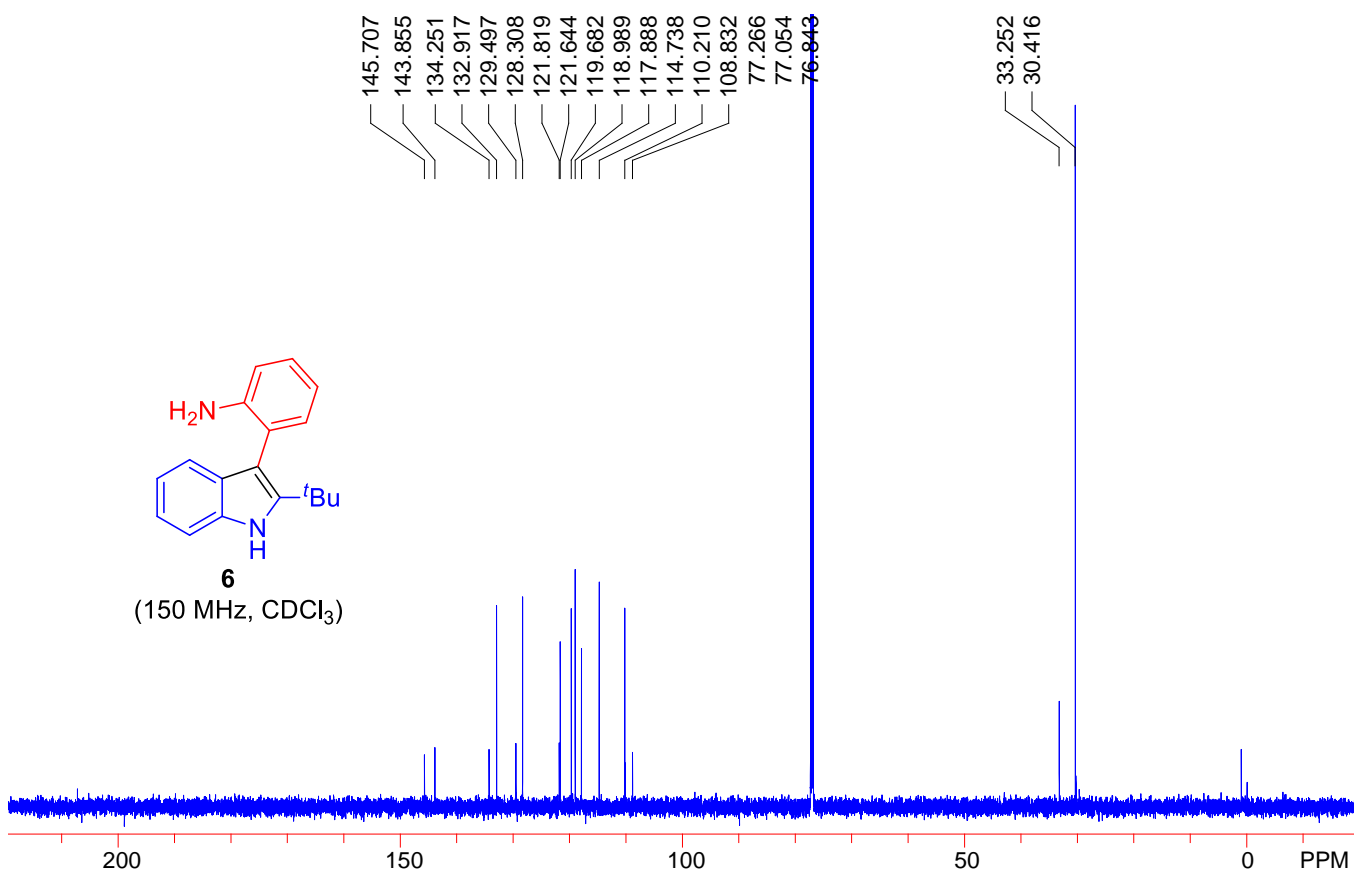
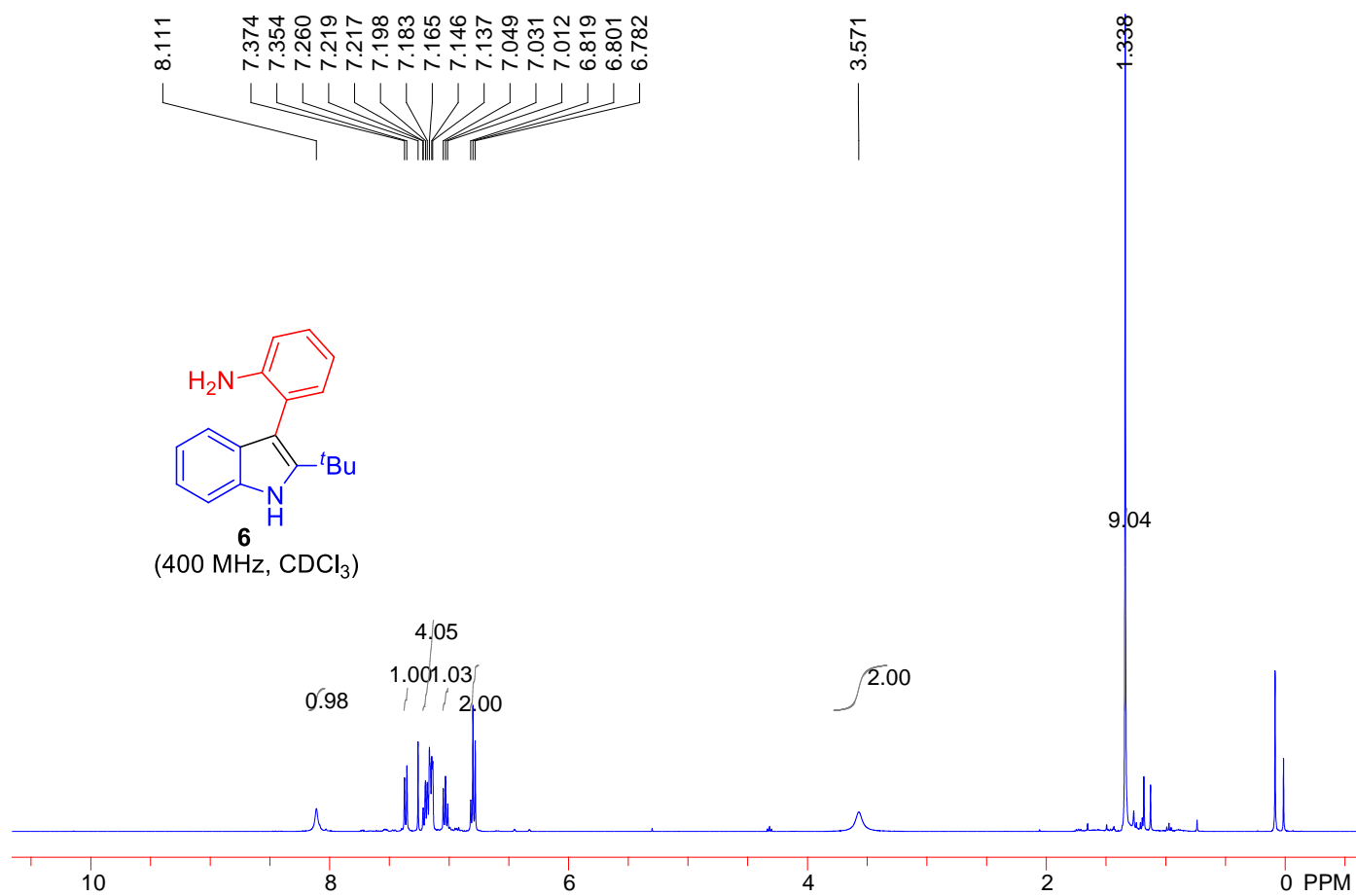




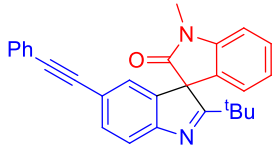
V. Copies of NMR spectra of 4, 5, 6, 7, 8



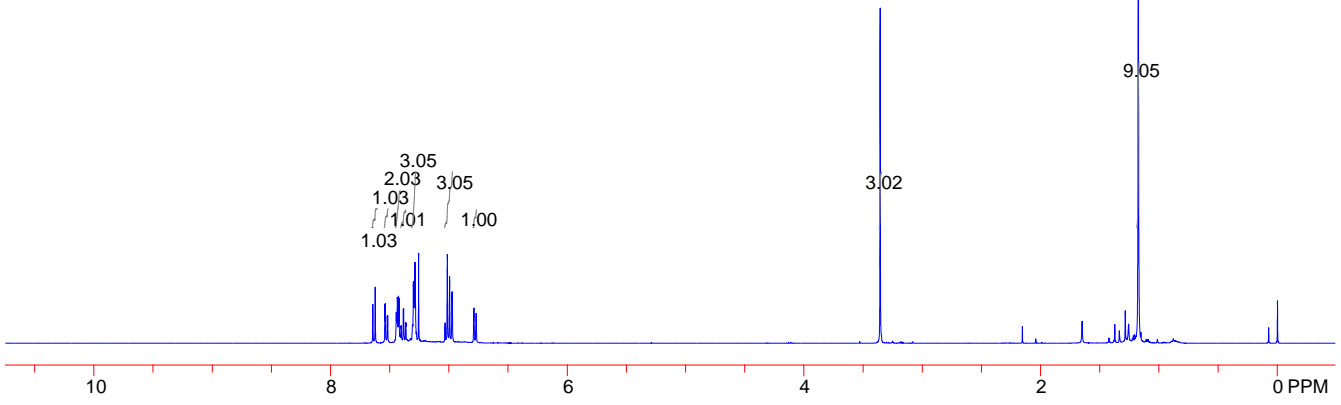




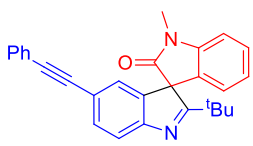
7.643
7.623
7.541
7.537
7.521
7.517
7.446
7.442
7.440
7.436
7.427
7.421
7.405
7.402
7.385
7.382
7.366
7.363
7.308
7.301
7.298
7.296
7.291
7.284
7.256
7.032
7.013
6.994
6.974
6.972
6.788
6.770
3.355



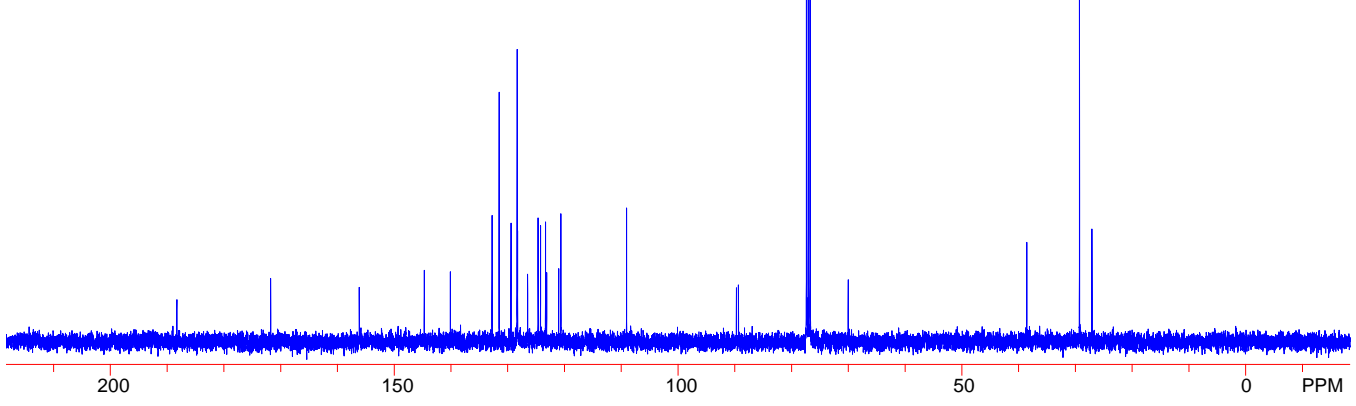
7
(CDCl₃, 400 MHz)

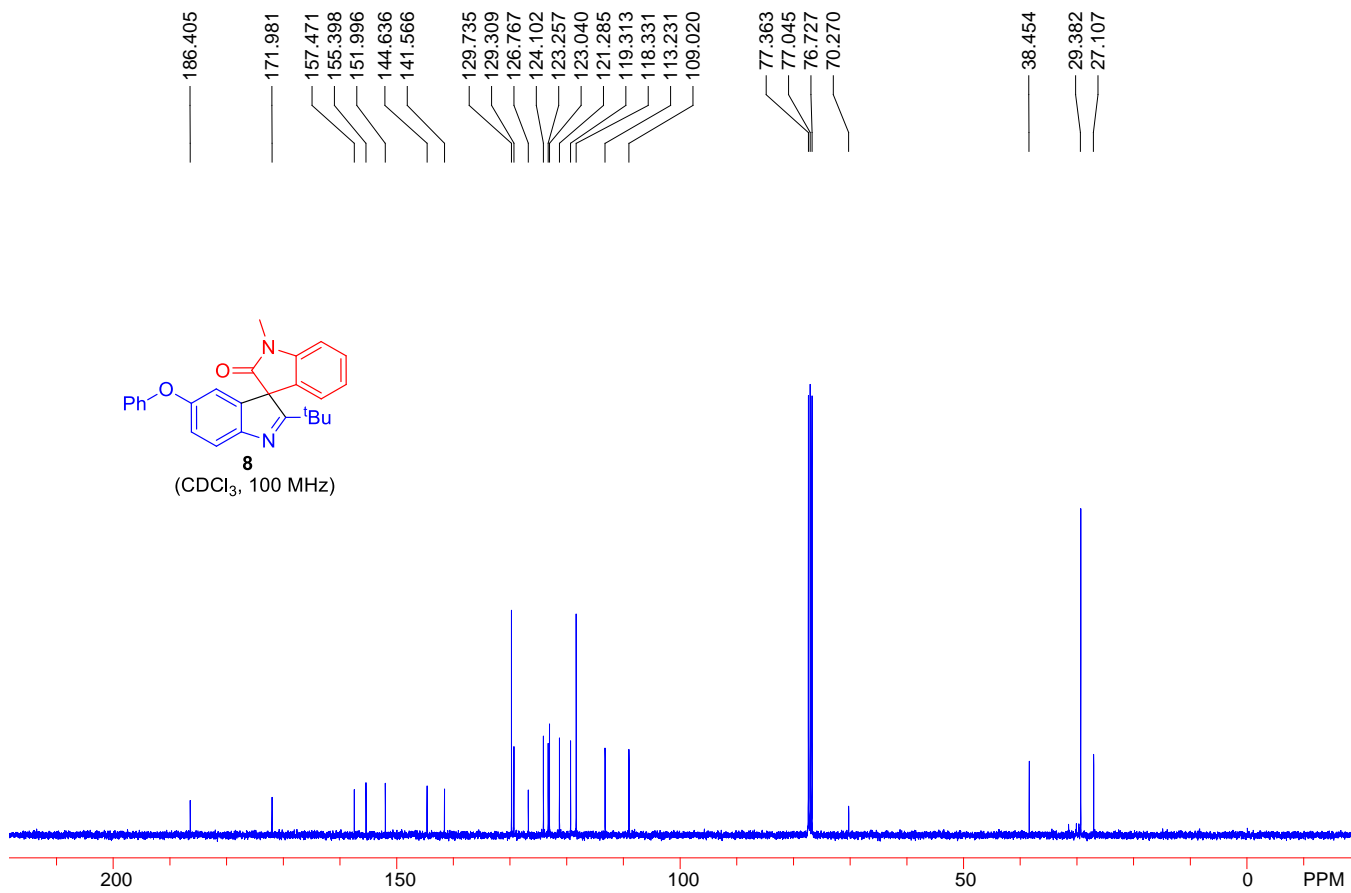
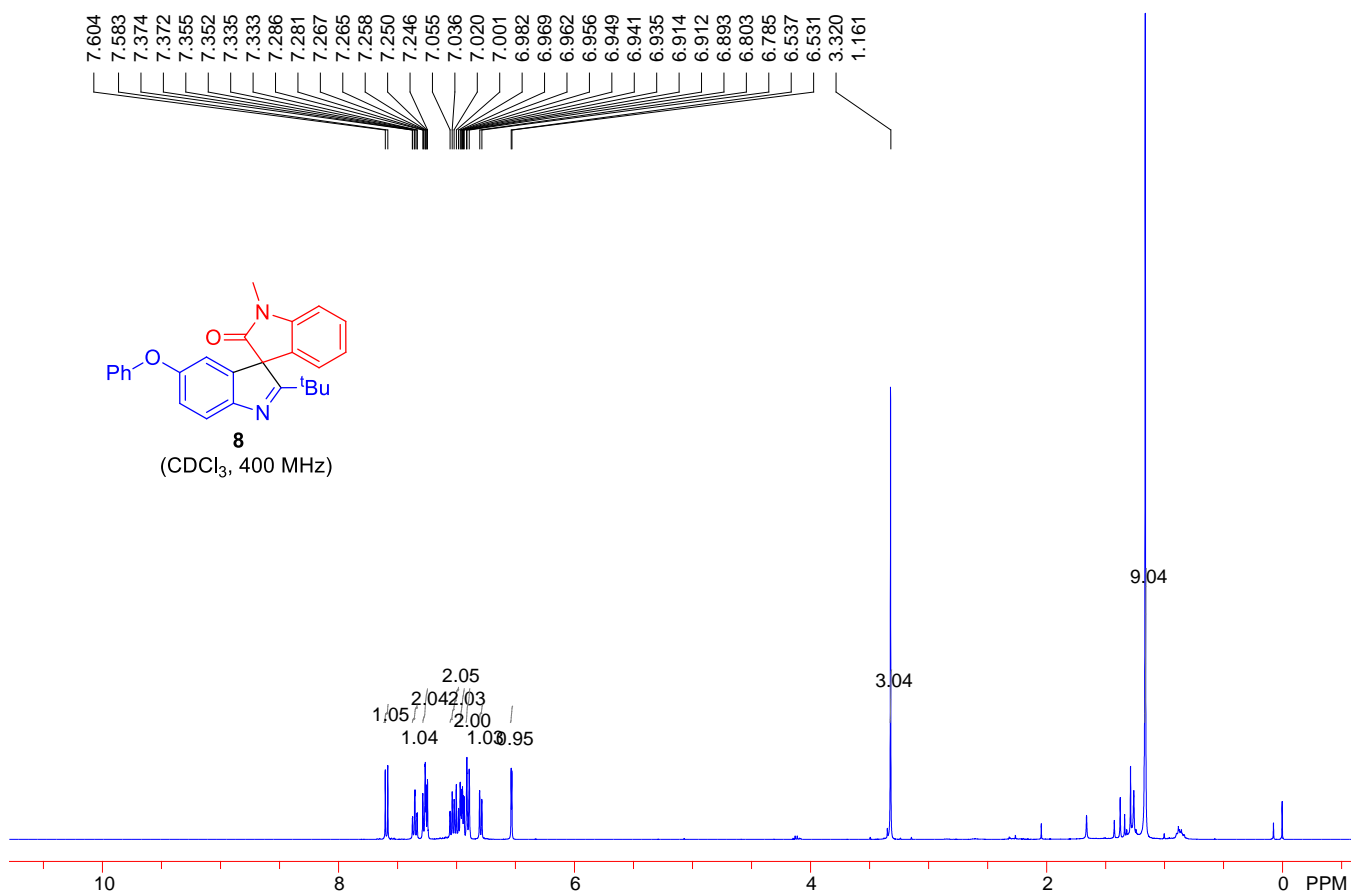


188.283
171.765
156.149
144.694
140.100
132.755
131.512
129.410
128.334
128.255
126.492
124.643
124.210
123.329
123.134
121.017
120.627
109.064
89.714
89.353
77.370
77.052
76.735
70.025
38.613
29.339
27.136



7
(CDCl₃, 100 MHz)





VI. X-ray crystal structure and data of **3a**

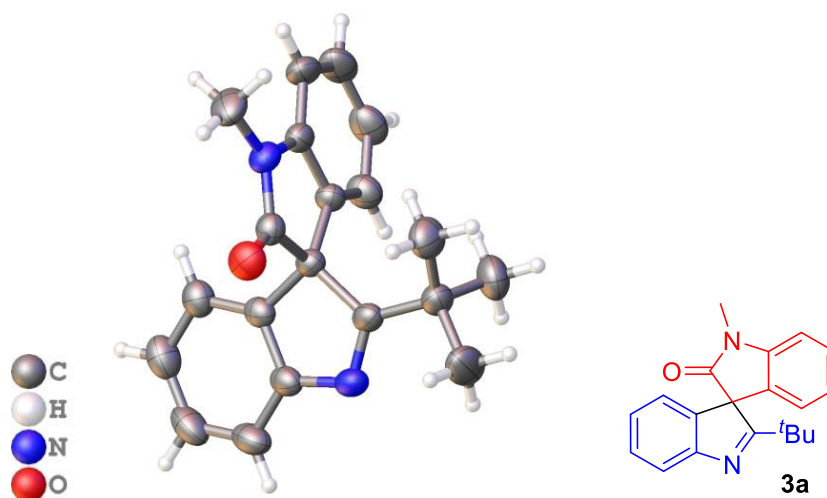


Fig. S4 X-ray crystal structure of **3a** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a methanol solution of **3a**. Crystal data collection and refinement parameters of **3a** are summarized in Table S1. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu K α radiation, $\lambda = 1.54184$ Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **3a**

Empirical formula	2(C ₂₀ H ₂₀ N ₂ O)
Formula weight	608.76
Temp, K	293 (2)
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> , Å	16.8519(3)
<i>b</i> , Å	8.94750(10)

c , Å	22.5301(4)
α (°)	90
β (°)	98.216(2)
γ (°)	90
Volume, Å ³	3362.27(9)
Z	4
d_{calc} , g cm ⁻³	1.203
λ , Å	1.54184
μ , mm ⁻¹	0.586
No. of data collected	15329
No. of unique data	6400
R_{int}	0.0245
Goodness-of-fit on F^2	1.044
R_1 , wR_2 ($I > 2\sigma(I)$)	0.0531, 0.1408
R_1 , wR_2 (all data)	0.0608, 0.1486

VII. X-ray crystal structure and data of **3k**

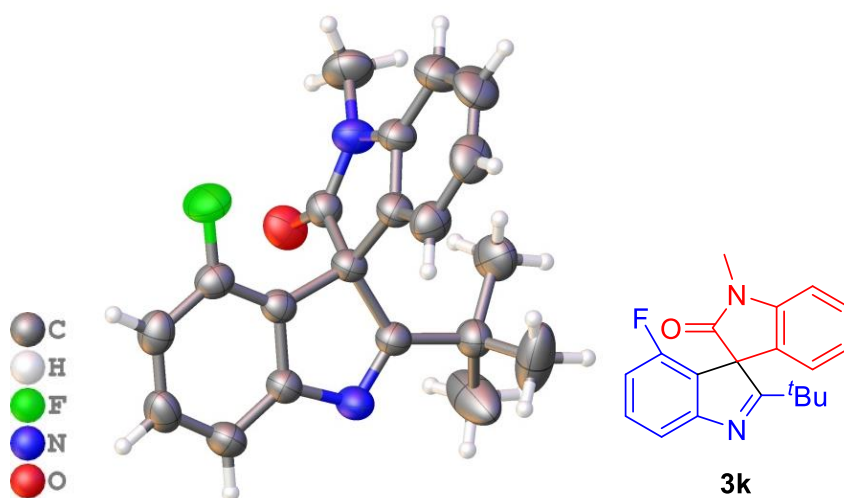


Fig. S5 X-ray crystal structure of **3k** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a petroleum ether/dichloromethane (1:1) solution of **3k**. Crystal data collection and refinement parameters of **3k** are summarized in Table S1. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Cu K α radiation, $\lambda = 1.54184$ Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S2 Crystallographic data and structure refinement results of **3k**

Empirical formula	C ₂₀ H ₁₉ FN ₂ O
Formula weight	322.37
Temp, K	293 (2)
Crystal system	monoclinic
Space group	P2 ₁ /n
<i>a</i> , Å	11.2828(2)
<i>b</i> , Å	12.1461(3)

c , Å	12.2864(2)
α (°)	90
β (°)	95.877(2)
γ (°)	90
Volume, Å ³	1674.90(6)
Z	4
d_{calc} , g cm ⁻³	1.278
λ , Å	1.54184
μ , mm ⁻¹	0.707
No. of data collected	6680
No. of unique data	3184
R_{int}	0.0200
Goodness-of-fit on F^2	1.073
R_1 , wR_2 ($I > 2\sigma(I)$)	0.0550, 0.1578
R_1 , wR_2 (all data)	0.0643, 0.1661

VIII. X-ray crystal structure and data of **6**

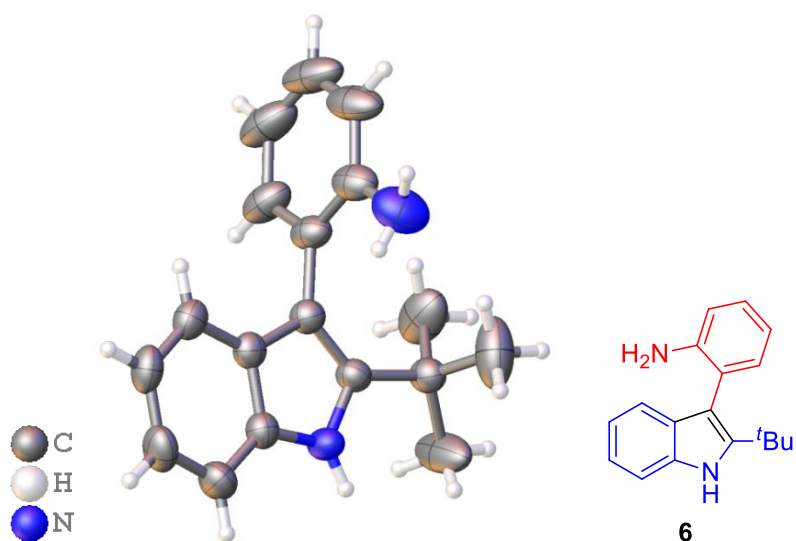


Fig. S6 X-ray crystal structure of **6** with 50% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from an dichloromethane solution of **6**. Crystal data collection and refinement parameters of **6** are summarized in Table S2. Intensity data were collected at 293 K on a SuperNova Dual diffractometer using mirror-monochromated Mo K α radiation, $\lambda = 0.71073$ Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S3 Crystallographic data and structure refinement results of **6**

Empirical formula	C ₁₈ H ₂₀ N ₂
Formula weight	264.36
Temp, K	293 (2)
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> , Å	9.3300(8)

b , Å	9.9923(6)
c , Å	16.3551(9)
α (°)	90
β (°)	103.250(7)
γ (°)	90
Volume, Å ³	1484.17(18)
Z	4
d_{calc} , g cm ⁻³	1.183
λ , Å	0.71073
μ , mm ⁻¹	0.070
No. of data collected	9252
No. of unique data	3472
R_{int}	0.0228
Goodness-of-fit on F^2	1.083
R_1 , wR_2 ($I > 2\sigma(I)$)	0.0657, 0.1756
R_1 , wR_2 (all data)	0.0926, 0.1935

IX. References

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