Supporting Information for

Nickel-Catalyzed *β*-Regioselective Amination/Cyclization of Ynamide-Nitriles with Amines: Synthesis of Functionalized 3-Aminoindoles and 4-Aminoisoquinolines

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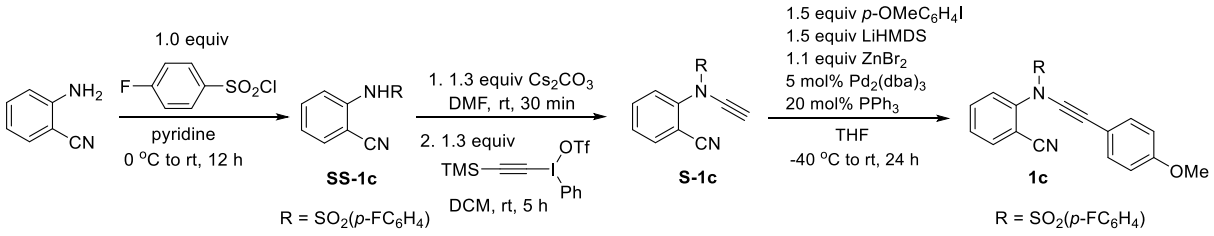
Contents:

General Methods. Unless noted, all reactions were carried out using standard Schlenk technique under an argon atmosphere or a dry box technique under a nitrogen atmosphere. Tetrahydrofuran and 1, 4-dioxane were distilled from sodium and benzophenone. Toluene was distilled from sodium. Acetonitrile was dried using Innovative Technology Solvent Purifier. Dimethyl formamide was purchased from J & K. Zinc powder (99.8% metals basis, -100 mesh) was purchased from Alfa Aesar Organics. Zinc powder (98%, -325 mesh) was purchased from

Adamas. Before using, zinc powder was stirred with 1 M HCl, filtered and washed thoroughly with water, acetone and diethyl ether and dried under vacuum. $NiCl_2$(DME) was purchased from Sigma Aldrich. $Ni(COD)_2$ and NiI_2 were purchased from Strem Chemicals Inc. $NiCl_2$(dppp) was purchased from TCI. 4-Fluoroaniline was purified by distillation before use. Unless noted, all commercial reagents were used without further purification. ^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ or d_6-DMSO (containing 0.03% TMS) on Varian or Agilent XL-400 MHz spectrometer. ^1H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) or solvent residual peak ($CDCl_3$: 7.26 ppm; d_6-DMSO: 2.50 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (77.00 ppm) or d_6-DMSO (39.52 ppm) as internal reference. ^{19}F NMR spectra was recorded with $CFCl_3$ (0.00 ppm) as outside reference. High-resolution mass spectra were obtained by using AccuTOF 4G LC-plus and Waters Premier GC-TOF MS. The IR spectra were measured on a ThermoFisher Nicolet FT-IR spectrometer. Single crystal X-ray diffraction data were collected at Single crystal X-ray diffraction data were collected at 293(2) K for **3g**, **5**, **6**, **7** and at 193(2) K for **4**, **S-5** on a Bruker SMART diffractometer or a Bruker APEX-II diffractometer. The X-ray crystal structure of **4** has been reported previously.[1]

Ynamides **1a-1b**, **1e-1m** were synthesized according to the published methods,[2] if needed, which were recrystallized before using. For the characterization of the new compounds, see following:

Synthesis of *N*-(2-Cyanophenyl)-4-fluoro-*N*-((4-methoxyphenyl)ethynyl)benzenesulfonamide (1c).



To solution of 2-aminobenzonitrile (4.96 g, 42 mmol) in pyridine (30 mL) was cooled to 0 °C and 4-fluorobenzenesulfonyl chloride (7.78 g, 40 mmol) was added under argon. The

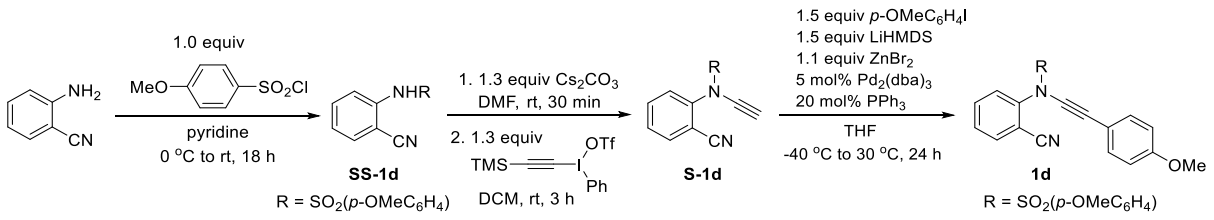
reaction mixture was warmed up to room temperature and stirred for 12 h until the reaction was completed as monitored by TLC. The reaction mixture was quenched by water and extracted with ethyl acetate, washed with water and brine, and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure, then the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford the crude and recrystallization (petroleum ether/ethyl acetate = 5/1) to afford **SS-1c** in 63% yield (6.99 g) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.84 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.53-7.51 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5 (d, $^1J_{C\text{-}F}$ = 255.1 Hz), 138.8, 134.4 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 134.2, 132.9, 130.1 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 125.7, 122.8, 116.5 (d, $^2J_{C\text{-}F}$ = 22.6 Hz), 115.6, 105.1. ^{13}F NMR (376 MHz, $CDCl_3$): δ -103.2--102.3 (m). IR (neat): 3196, 2237, 1590, 1493, 1457, 1414, 1342, 1291, 1240, 1231, 1166, 1151, 1098, 1088, 1011, 912, 837, 821, 772, 746, 708, 692 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{15}H_9O_2N_2FS$ 300.0363, found 300.0360.

To a solution of **SS-1c** (2.76 g, 10 mmol) in *N*,*N*-dimethylformamide (25 mL) was added Cs_2CO_3 (4.24 g, 13 mmol). The solution was stirred at room temperature for 30 min, then phenyl((trimethylsilyl)ethynyl)iodonium triflate (5.85 g, 13 mmol) in dichloromethane (10 mL) was added to the mixture and stirred 5 h until the reaction was completed as monitored by TLC. The reaction mixture was quenched by water. The resulting mixture was extracted with EA, washed with brine and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure, then the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford the desired product **S-1c** in 58% yield (1.74 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.88 (m, 2H), 7.71 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.66 (td, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.53 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.28-7.24 (m, 2H), 2.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4 (d, $^1J_{C\text{-}F}$ = 257.1 Hz), 139.4, 134.2, 133.8, 131.7, 131.6, 131.5, 129.8 (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 116.8 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 114.9, 112.8, 74.6, 60.3. ^{13}F NMR (376 MHz, $CDCl_3$): δ -101.2--101.3 (m). IR (neat): 3310, 3100, 2236, 2136, 1588, 1490, 1483, 1447, 1380, 1293, 1230, 1182, 1155, 1118, 1083, 920, 885, 843, 816, 771, 737, 708, 678, 665, 656 cm^{-1}. HRMS

(EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_9O_2N_2FS$ 276.0363, found 276.0362.

To solution of **S-1c** (901.0mg, 3 mmol) in THF (15 mL) was cooled to -40 °C and LiHMDS (3.5 mL, 4.5 mmol, 1.3 M in THF) was added dropwise under argon. After stirring at the same temperature for 40 min, $ZnBr_2$ (743.1 mg, 3.3 mol) in THF (3 mL) was added and stirred for another 20 min at -40 °C. Then the mixture of $Pd_2(dba)_3$ (137.4 mg, 0.15 mmol), PPh_3 (157.4 mg, 0.6 mmol) and 4-methoxyiodobenzene (1.05 g, 4.5 mmol) in THF (2 mL) was added dropwise. The reaction mixture was warmed up to 30 °C and stirred for 24 h until the reaction was completed as monitored by TLC, then quenched by brine and extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford the desired product **1c** in 57% yield (699 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.69-7.63 (m, 2H), 7.52-7.47 (m, 2H), 7.38-7.34 (m, 2H), 7.27-7.23 (m, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2 (d, $^1J_{C\text{-}F}$ = 256.3 Hz), 160.0, 140.3, 134.1, 134.0, 133.6, 131.5 (d, $^4J_{C\text{-}F}$ = 2.4 Hz), 131.4, 131.3, 129.5 (d, $^3J_{C\text{-}F}$ = 6.9 Hz), 116.6 (d, $^2J_{C\text{-}F}$ = 22.6 Hz), 115.1, 113.9, 113.4, 112.4, 79.8, 71.4, 55.2. ^{13}F NMR (376 MHz, $CDCl_3$): δ -101.5--101.6 (m). IR (neat): 3108, 2843, 2235, 1604, 1590, 1511, 1491, 1447, 1407, 1378, 1336, 1291, 1247, 1177, 1155, 1106, 1086, 1026, 959, 913, 832, 771, 711, 698, 670 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{15}O_3N_2FSNa$ 429.0680, found 429.0675.

Synthesis of *N*-(2-cyanophenyl)-4-methoxy-*N*-((4-methoxyphenyl)ethynyl)benzenesulfonamide (1d).



To solution of 2-aminobenzonitrile (2.36 g, 20 mmol) in pyridine (20 mL) was cooled to 0 °C and 4-methoxybenzenesulfonyl chloride (4.12 g, 20 mmol) was added under argon. The

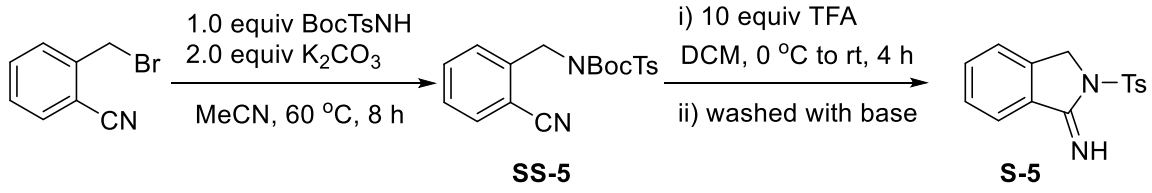
reaction mixture was warmed up to room temperature and stirred for 18 h until the reaction was completed as monitored by TLC. The reaction mixture was quenched by saturated NH_4Cl solution and extracted with DCM, washed with brine, and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure, then the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/DCM = 10/2/1) to afford **SS-1d** in 67% yield (3.89 g) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.57-7.53 (m, 1H), 7.49 ((dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.20-7.16 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 139.3, 134.1, 132.7, 129.7, 129.5, 125.1, 121.7, 115.7, 114.4, 104.3, 55.6. IR (neat): 3202, 2838, 2233, 1596, 1577, 1495, 1457, 1425, 1330, 1315, 1267, 1155, 1093, 1029, 912, 833, 755, 716, 664 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{12}O_3N_2SNa$ 311.0461, found 311.0453.

To a solution of **SS-1d** (1.44 g, 5 mmol) in *N*,*N*-dimethylformamide (10 mL) was added Cs_2CO_3 (2.12 g, 6.5 mmol). The solution was stirred at room temperature for 30 min, then phenyl((trimethylsilyl)ethynyl)iodonium triflate (2.92 g, 6.5 mmol) in dichloromethane (5 mL) was added to the mixture and stirred 3 h until the reaction was completed as monitored by TLC. The reaction mixture was quenched by water and extracted with ethyl acetate, washed with brine, and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure, then the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford the desired product **S-1d** in 66% yield (1.03 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.77 (m, 2H), 7.70 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.64 (td, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.52 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.39 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 7.04-7.01 (m, 2H), 3.91 (s, 3H), 2.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 139.8, 134.1, 133.6, 130.9, 129.6, 129.4, 126.8, 115.2, 114.5, 113.0, 75.1, 59.9, 55.7. IR (neat): 3275, 2838, 2228, 2128, 1593, 1577, 1497, 1488, 1443, 1369, 1311, 1263, 1192, 1163, 1115, 1087, 1026, 923, 882, 829, 804, 779, 756, 714, 678, 655 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{12}O_3N_2SNa$ 335.0461, found 335.0452.

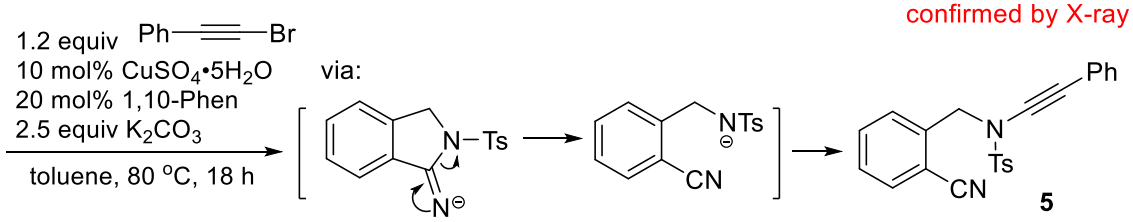
To solution of **S-1d** (1.25 g, 4 mmol) in THF (15 mL) was cooled to -40 °C and LiHMDS

(4.62 mL, 6 mmol, 1.3 M in THF) was added dropwise under argon. After stirring at the same temperature for 40 min, $ZnBr_2$ (990.9 mg, 4.4 mol) in THF (4 mL) was added and stirred for another 20 min at -40 °C. Then the mixture of $Pd_2(dba)_3$ (183.1 mg, 0.2 mmol), PPh_3 (209.8 mg, 0.8 mmol) and 4-iodoanisole (1.40 g, 6 mmol) in THF (3 mL) was added dropwise. The reaction mixture was warmed up to 30 °C (oil bath) and stirred for 24 h until the reaction was completed as monitored by TLC, then quenched by brine and extracted with ethyl acetate. The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1 to 4/1) to afford the desired product **1d** in 42% yield (695 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.80 (m, 2H), 7.68 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.63 (td, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.51-7.45 (m, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.03-7.01 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 159.9, 140.9, 134.1, 134.0, 133.5, 131.0, 129.7, 129.1, 127.1, 115.3, 114.4, 113.9, 112.7, 80.4, 71.2, 55.7, 55.3. IR (neat): 3079, 2995, 2841, 2231, 1605, 1593, 1574, 1513, 1497, 1488, 1443, 1363, 1329, 1249, 1164, 1089, 1030, 1016, 895, 845, 836, 814, 804, 782, 763, 697, 671 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}O_4N_2SNa$ 441.0880, found 441.0869.

Synthesis the *N*-(2-Cyanobenzyl)-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (5).



confirmed by X-ray



confirmed by X-ray

To a 100 mL Schlenk tube was added 2-(bromomethyl)benzonitrile (1.96 g, 10 mmol), BocTsNH (2.71 g, 10 mmol), K_2CO_3 (2.76 g, 20 mmol) and MeCN (50 mL) under argon. The

mixture was heated at 60 ºC (oil bath) for 8 h, then removed the solvent under the reduced pressure. The residue was extracted with ethyl acetate and the combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford the desired product **SS-5** in 89% yield (3.43 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.66-7.58 (m, 3H), 7.39 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 2H), 2.46 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 144.7, 141.5, 136.4, 133.2, 132.6, 129.3, 128.0, 127.6, 126.9, 117.1, 110.6, 85.0, 48.6, 27.7, 21.6. IR (neat): 3001, 2967, 2925, 1719, 1664, 1597, 1462, 1337, 1283, 1219, 1163, 1086, 1027, 880, 812, 777, 734, 705, 673 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+NH_4]^+$ Calcd for $C_{20}H_{26}N_3O_4S$ 404.1639; Found 404.1637.

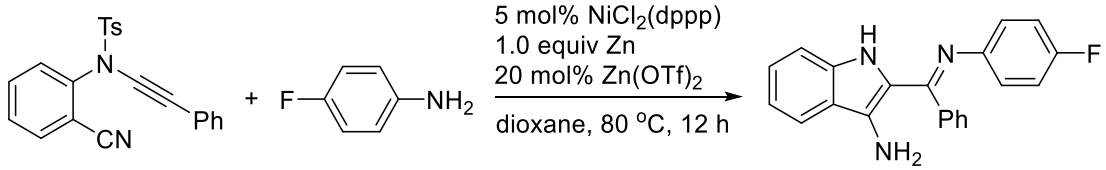
To a solution of **SS-5** (3.43 g, 8.9 mmol) in DCM (89 mL) was cooled to 0 ºC and TFA (10.1 g, 89 mmol) was added dropwise under air. The reaction mixture was warmed up to room temperature and stirred 4 h, then removed the solvent under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1 to MeOH) to afford the crude product. The residue was dissolved with DCM and washed with saturated Na_2CO_3 solution for three times, then dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1 to petroleum ether/ethyl acetate/dichloromethane = 2/1/1) to afford the desired product **S-5** in 59% yield with two steps (1.68 g) as a white solid. Alternatively, the following work-up procedure is also suitable for isolation of **S-5**: after the reaction was complete, the solvent was removed under the reduced pressure. The residue was dissolved in DCM and washed with saturated Na_2CO_3 solution, then dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel. M.p. 120-122 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (br, 1H), 7.84 (d, *J* = 6.8 Hz, 3H), 7.51 (td, *J* = 7.2 Hz, 0.8 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.35-7.27 (m, 3H), 4.78 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8 (m), 145.0, 138.1,

134.8, 132.4, 132.1, 130.0, 128.5, 127.1, 123.6, 122.7, 51.9, 21.5. IR (neat): 3318, 1659, 1597, 1468, 1439, 1350, 1304, 1241, 1209, 1169, 1158, 1150, 1107, 1086, 1062, 1017, 947, 875, 814, 807, 779, 741, 726, 703, 665 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}O_2N_2S$ 287.0849; Found 287.0853.

To a solution of $CuSO_4•5H_2O$ (50.0 mg, 0.2 mmol), 1,10-Phen (72.1 mg, 0.4 mmol), K_2CO_3 (691.1 mg, 5 mmol), **S-5** (572.7 mg, 2 mmol) and toluene (6 mL) was added (bromoethynyl)benzene (434.5 mg, 2.4 mmol). The reaction mixture was heated to 80 °C (oil bath) for 18 h until the reaction was completed as monitored by TLC. Then petroleum ether was added and stirred for 10 min. The mixture was filtered over a celite pad, and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford the desired product **5** in 93% yield (716.2 mg) as a yellow solid. M.p. 96-98 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.65-7.60 (m, 2H), 7.44-7.37 (m, 3H), 7.30-7.24 (m, 5H), 4.80 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 138.3, 134.0, 133.2, 132.7, 131.2, 130.0, 129.5, 128.7, 128.2, 127.9, 127.7, 122.2, 117.0, 112.2, 81.8, 71.5, 53.2, 21.6. IR (neat): 3016, 2242, 1594, 1365, 1327, 1230, 1187, 1172, 1110, 1086, 1044, 1021, 1012, 936, 814, 799, 785, 758, 738, 705, 692, 682 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{18}O_2N_2SNa$ 409.0981; Found 409.0978.

Optimization studies for the formation of 3a.

General procedure for optimization studies.

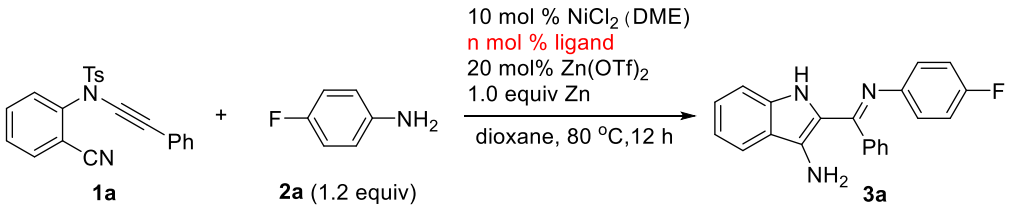


1a **2a** (1.2 equiv) **3a**

The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $NiCl_2$(dppp) (5.4 mg, 0.01 mmol) [or other Ni(II) salts], Zn powder (13.1 mg, 0.2 mmol) [or other reductants], $Zn(OTf)_2$ (14.5 mg, 0.04 mmol) [or other Lewis acid], ynamide **1a** (74.5 mg, 0.2 mmol), 1,4-dioxane (2 mL) or

other solvents and 4-fluoroaniline (26.7 mg, 0.24 mmol) were added sequentially to a screw-cap vial (If the aniline was solid, it was added before dioxane). The vial cap was securely fitted and taken outside the glove box, and sealed with electrical tape. After the reaction mixture was stirred in an oil bath preheated at 80 °C for 12 h, the mixture was quenched with brine and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent to afford the crude product mainly containing **3a** and the starting material **1a**. The solvent was evaporated under the reduced pressure and the residue was dissolved in d_6-DMSO. The NMR yields were obtained by ^{1}H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) as an internal standard.

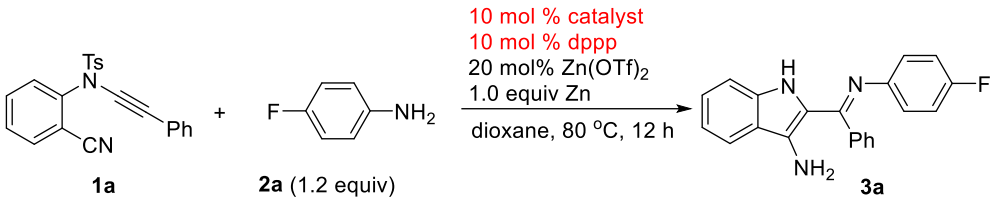
Table S1. The effect of the ligands



entry	catalyst (mol%)	ligand (mol%)	Lewis acid (mol%)	solvent	yield[a] (%)
1	$NiCl_2$(DME)	dppp (10)	$Zn(OTf)_2$	dioxane	77[b]
2	$NiCl_2$(DME)	dppp (10)	-	dioxane	38 (6)
3	$NiCl_2$(DME)	$PMePh_2$(20)	$Zn(OTf)_2$	dioxane	20 (7)
4	$NiCl_2$(DME)	Pcy_3(20)	$Zn(OTf)_2$	dioxane	3 (54)
5	$NiCl_2$(DME)	dppe (10)	$Zn(OTf)_2$	dioxane	4 (73)
6	$NiCl_2$(DME)	Xantphos (10)	$Zn(OTf)_2$	dioxane	- (72)
7	$NiCl_2$(DME)	dtbbpy (10)	$Zn(OTf)_2$	dioxane	- (85)

[a]Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The yields of the unreacted **1a** are shown in parentheses. [b]Isolated yield.

Table S2. The effect of the catalysts

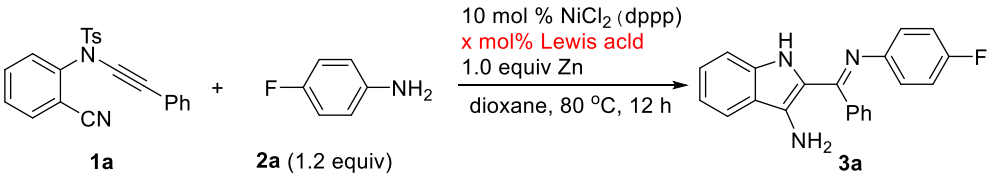


1a **2a** (1.2 equiv) **3a**

entry	catalyst (mol%)	ligand (mol%)	Lewis acid (mol%)	solvent	yield[a] (%)
1	$NiBr_2$(DME)	dppp	$Zn(OTf)_2$	dioxane	11 (50)
2	NiI_2	dppp	$Zn(OTf)_2$	dioxane	77 (-)
3	$NiCl_2 \cdot 6H_2O$	dppp	$Zn(OTf)_2$	dioxane	38 (6)
4	**$NiCl_2$(dppp)**	**-**	**$Zn(OTf)_2$**	**dioxane**	**78, 77[b]**

[a]Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The yields of the unreacted **1a** are shown in parentheses. [b]Isolated yield.

Table S3. The effect of the additives

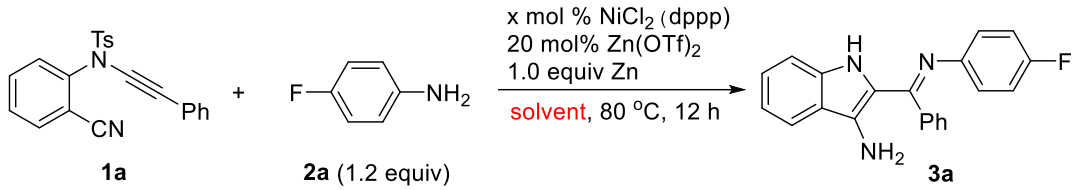


1a **2a** (1.2 equiv) **3a**

entry	catalyst (mol%)	Lewis acid (mol%)	solvent	temp. (°C)	time (h)	yield[a] (%)
1	$NiCl_2$(dppp)	$Sc(OTf)_3$ (20)	dioxane	80	12	63 (3)
2	$NiCl_2$(dppp)	$Al(OTf)_3$ (20)	dioxane	80	12	48 (7)
3	$NiCl_2$(dppp)	$Fe(OTf)_3$ (20)	dioxane	80	12	7 (54)
4	$NiCl_2$(dppp)	$ZnCl_2$ (20)	dioxane	80	12	73 (2)
5	$NiCl_2$(dppp)	BPh_3 (20)	dioxane	80	12	16 (11)
6	$NiCl_2$(dppp)	$Zn(OTf)_2$ (50)	dioxane	80	12	73 (2)
7	$NiCl_2$(dppp)	$Zn(OTf)_2$ (100)	dioxane	80	12	78 (-)

[a]Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The yields of the unreacted **1a** are shown in parentheses.

Table S4. The effect of the solvent



entry	catalyst (mol%)	Lewis acid (mol%)	solvent	temp. (°C)	time (h)	yield[a] (%)
1	$NiCl_2$(dppp) (10)	$Zn(OTf)_2$	dioxane	80	12	**78, 77**[b]
2	$NiCl_2$(dppp) (5)	$Zn(OTf)_2$	dioxane	80	12	**81, 77**[b]
3	$NiCl_2$(dppp) (5)	$Zn(OTf)_2$	THF	80	12	71
4	$NiCl_2$(dppp) (5)	$Zn(OTf)_2$	CH_3CN	80	12	33 (32)
5	$NiCl_2$(dppp) (5)	$Zn(OTf)_2$	toluene	80	12	57 (6)
6	$NiCl_2$(dppp) (5)	$Zn(OTf)_2$	DMF	80	12	22 (13)

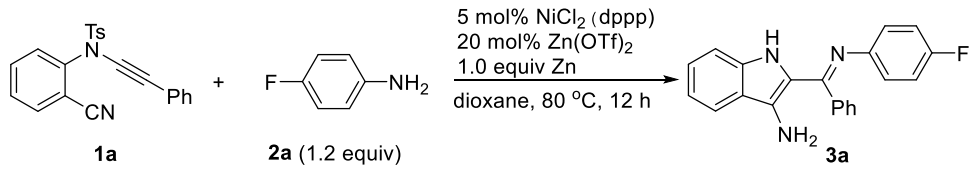
[a]Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The yields of the unreacted **1a** are shown in parentheses. [b]Isolated yield.

Table S5. The effect of the temperature and the amount of Zn powder

entry	catalyst (mol%)	Lewis acid (mol%)	solvent	temp. (°C)	time (h)	yield[a] (%)
1	$NiCl_2$(dppp)	$Zn(OTf)_2$	dioxane	50	12	68 (12)
2	$NiCl_2$(dppp)	$Zn(OTf)_2$	dioxane	rt	12	40 (29)
3[b]	$NiCl_2$(dppp)	$Zn(OTf)_2$	dioxane	80	12	35 (37)
4[c]	$NiCl_2$(dppp)	$Zn(OTf)_2$	dioxane	80	12	7 (38)

[a]Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The yields of the unreacted **1a** are shown in parentheses. [b]50 mol% Zn powder was used (Alfa 100 mesh). [c]20 mol% Zn powder was used (Alfa 100 mesh).

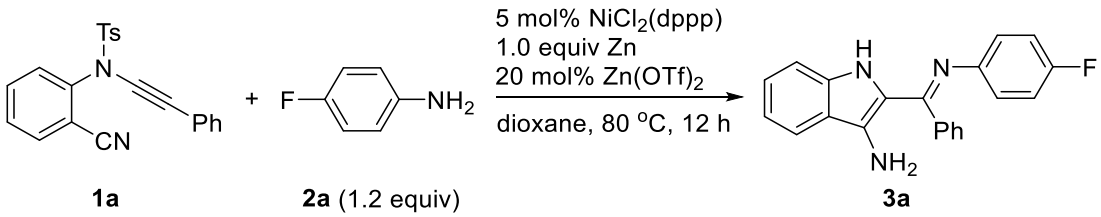
Table S6. Control experiments



entry	catalyst (mol%)	ligand (mol%)	Lewis acid (mol%)	solvent	temp. (°C)	time (h)	yield[a] (%)
1	-	dppp (5)	$Zn(OTf)_2$ (20)	dioxane	80	12	- (70)
2	$NiCl_2$(DME) (5)	-	$Zn(OTf)_2$ (20)	dioxane	80	12	- (81)
3	$NiCl_2$(dppp) (5)	-	-	dioxane	80	12	25 (35)
4[b]	$NiCl_2$(dppp) (5)	-	$Zn(OTf)_2$ (20)	dioxane	80	12	- (61)
5[c]	$NiCl_2$(dppp) (10)	-	$Zn(OTf)_2$ (20)	dioxane	80	12	31 (25)
6[c]	$NiCl_2$(dppp) (10)	-	$Zn(OTf)_2$ (100)	dioxane	80	12	78

[a]Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The yields of the unreacted **1a** are shown in parentheses. [b]Without Zn powder (Alfa 100 mesh). [c]1.0 equiv Zinc powder (Adamas 325 mesh) was used.

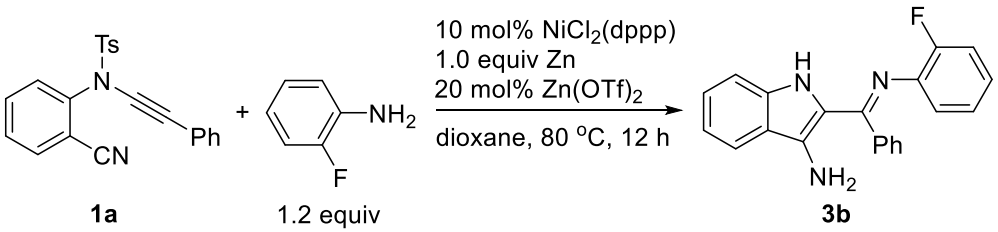
Synthesis of (*E*)-2-(((4-Fluorophenyl)imino)(phenyl)methyl)-1*H*-indol-3-amine (3a).



The reaction was conducted in an oven-dried screw-cap vial (volume: 8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $NiCl_2$(dppp) (8.1 mg, 0.015 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 1,4-dioxane (3 mL) and 4-fluoroaniline (40.0 mg, 0.36 mmol) were added sequentially to a screw-cap vial. The vial cap was securely fitted and taken outside the glove box, and sealed with electrical tape. After the reaction mixture was stirred in an oil bath preheated at 80 °C for 12 h, the mixture was quenched with brine and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent to afford the desired product **3a** in 77% yield (75.6 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 1H), 7.52-7.35 (br, 1H), 7.35-7.34 (m, 3H), 7.22-7.21

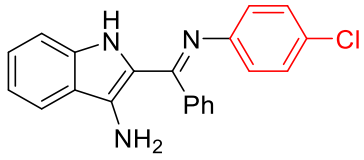
(m, 3H), 7.13-7.11 (m, 1H), 7.02 (t, J = 7.2 Hz, 1H), 6.79 (t, J = 8.4 Hz, 2H), 6.67-6.63 (m, 2H), 5.05 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9 (m), 158.9 (d, $^1J_{C\text{-}F}$ = 239.9 Hz), 146.5 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 136.0, 135.5, 132.0, 129.0, 128.8, 128.6, 125.7, 123.3 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 120.5, 118.9, 118.7, 117.3, 114.9 (d, $^2J_{C\text{-}F}$ = 22.8 Hz), 111.4. ^{13}F NMR (376 MHz, $CDCl_3$): δ -121.3. IR (neat): 3405, 3382, 3257, 3058, 1604, 1593, 1569, 1519, 1494, 1446, 1361, 1327, 1289, 1269, 1214, 1197, 1152, 1091, 1008, 981, 923, 890, 837, 805, 785, 757, 739, 702 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}N_3F$ 330.1401; Found 330.1394. Note: high purity of the starting material is important for reproducibility.

Typical procedure for the synthesis of (*E*)-2-(((2-Fluorophenyl)imino)(phenyl)methyl)-1*H*-indol-3-amine (3b).



$NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 1,4-dioxane (3 mL) and 2-fluoroaniline (40.4 mg, 0.36 mmol) were added sequentially to a 8 mL screw-cap vial. The vial cap was securely fitted and taken outside the glove box, and sealed with electrical tape. After the reaction mixture was stirred at 80 °C (oil bath) for 12 h, the mixture was quenched with brine and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent to afford the desired product **3b** in 50% yield (49.7 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 1H), 7.54-7.32 (br, 1H), 7.32-7.30 (m, 5H), 7.25-7.21 (m, 1H), 7.14-7.12 (m, 1H), 7.02 (t, J = 7.2 Hz, 1H), 6.90-6.82 (m, 3H), 6.73-6.70 (m, 1H), 5.10 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 153.3 (d, $^1J_{C\text{-}F}$ = 242.6 Hz), 138.8 (d, $^2J_{C\text{-}F}$ = 12.5 Hz), 136.2, 135.7, 132.7, 129.1, 128.6, 128.0,

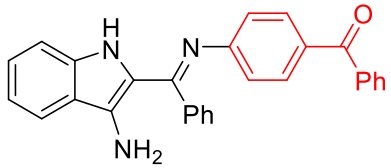
125.9, 123.8 (d, $^{3}J_{C\text{-}F}$ = 7.3 Hz), 123.7, 123.6 (d, $^{4}J_{C\text{-}F}$ = 3.7 Hz), 120.4, 119.0, 118.6, 117.1, 115.4 (d, $^{2}J_{C\text{-}F}$ = 20.2 Hz), 111.5. ^{13}F NMR (376 MHz, $CDCl_3$): δ -124.7. IR (neat): 3396, 3241, 3058, 3045, 2222, 1604, 1568, 1513, 1490, 1444, 1357, 1328, 1287, 1271, 1248, 1208, 1172, 1152, 1103, 1008, 980, 890, 858, 843, 791, 779, 734, 703 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}N_3F$ 330.1401; Found 330.1401.



3c

(*E*)-2-(((4-Chlorophenyl)imino)(phenyl)methyl)-1*H*-indol-3-amine (3c).

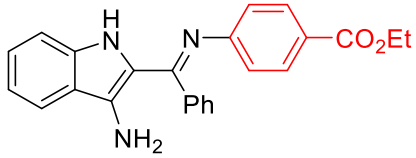
$NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 4-chloroaniline (45.9 mg, 0.36 mmol) and 1,4-dioxane (3 mL) were stirred at 80 ºC (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3c** in 35% yield (35.9 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.53-7.36 (br, 1H), 7.36 (s, 3H), 7.24 (s, 3H), 7.15-7.13 (m, 1H), 7.06-7.01 (m, 3H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.08 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 149.0, 136.1, 135.3, 132.4, 129.1, 128.8, 128.6, 128.3, 127.9, 125.9, 123.4, 120.4, 118.9, 118.7, 117.2, 111.4. IR (neat): 3414, 3390, 3267, 3058, 3021, 1615, 1602, 1594, 1568, 1514, 1486, 1475, 1445, 1359, 1325, 1287, 1262, 1246, 1197, 1154, 1091, 1009, 981, 889, 842, 831, 788, 744, 734, 716, 699 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}N_3Cl$ 346.1106; Found 346.1105.



3d

(*E*)-(4-(((3-Amino-1*H*-indol-2-yl)(phenyl)methylene)amino)phenyl)(phenyl)methanone

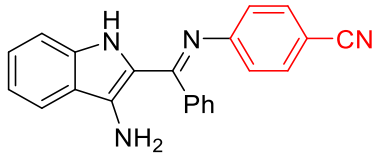
(3d). $NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 4-aminobenzophenone (71.0 mg, 0.36 mmol) and 1,4-dioxane (3 mL) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3d** in 54% yield (67.3 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.13 (m, 16H), 7.03 (t, J = 7.2 Hz, 1H), 6.79 (d, J = 7.6 Hz, 2H), 5.24 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 161.8 (m), 155.1, 138.2, 136.4, 135.1, 133.1, 131.8, 131.5, 131.1, 129.7, 129.2, 128.8, 128.5, 128.0, 126.1, 121.9, 120.2, 119.0, 118.7, 117.1, 111.5. IR (neat): 3427, 3368, 3241, 3055, 2239, 1635, 1593, 1567, 1508, 1444, 1412, 1359, 1329, 1315, 1307, 1296, 1270, 1208, 1172, 1160, 1141, 1103, 979, 937, 917, 890, 861, 850, 788, 749, 741, 726, 699 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{22}N_3O$ 416.1757; Found 416.1753.



3e

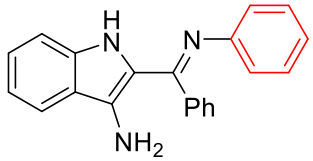
Ethyl (*E*)-4-(((3-amino-1*H*-indol-2-yl)(phenyl)methylene)amino)benzoate (3e). $NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), ethyl aminobenzoate (59.5 mg, 0.36 mmol) and 1,4-dioxane (3 mL) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3e** in 49% yield (55.8 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.56-7.34 (br, 1H), 7.34-7.32 (m, 3H), 7.26-7.23 (m, 3H), 7.15-7.13 (m, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 8.4 Hz, 2H), 5.18 (br, 2H), 4.29 (q, J = 6.8 Hz, 2H), 1.33 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 161.8 (m), 155.1, 136.3, 135.1, 132.9, 130.0, 129.1, 128.8, 128.5, 126.1, 124.5, 121.9, 120.2, 119.0, 118.7, 117.1, 111.5, 60.6, 14.3. IR (neat): 3443, 3335, 3055, 2979, 2956, 1673, 1606, 1567, 1505, 1485, 1444, 1363, 1326, 1308, 1290, 1270, 1252, 1164, 1146, 1103, 1010, 977, 896, 867, 792, 780, 757,

744, 712, 702, 687 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}N_3O_2$ 384.1707; Found 384.1701.



3f

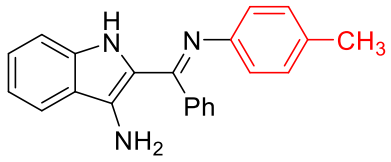
(*E*)-4-(((3-Amino-1*H*-indol-2-yl)(phenyl)methylene)amino)benzonitrile (3f). $NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 4-aminobenzonitrile (42.5 mg, 0.36 mmol) and 1,4-dioxane (3 mL) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3f** in 38% yield (38.5 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.55-7.37 (br, 1H), 7.37-7.36 (m, 5H), 7.28-7.23 (m, 3H), 7.16-7.14 (m, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 5.29 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 155.0, 136.6, 134.8, 132.5, 129.4, 128.9, 128.5, 126.4, 122.8, 120.0, 119.5, 119.1, 118.8, 111.5, 105.4. IR (neat): 3388, 3257, 3207, 3058, 2958, 2919, 2851, 1615, 1595, 1577, 1569, 1518, 1489, 1444, 1363, 1325, 1290, 1248, 1226, 1189, 1161, 1101, 1030, 983, 919, 890, 847, 804, 781, 760, 735, 714, 699 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}N_4$ 337.1448; Found 337.1440.



3g

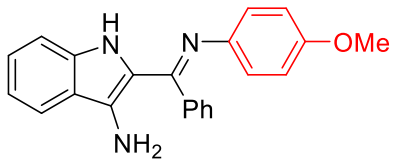
(*E*)-2-(Phenyl(phenylimino)methyl)-1*H*-indol-3-amine (3g). $NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 1,4-dioxane (3 mL) and aniline (33.5 mg, 0.36 mmol) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum

ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3g** in 76% yield (71.0 mg) as a yellow solid. m.p. = 189-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.6 Hz, 1H), 7.53-7.32 (br, 1H), 7.32-7.31 (m, 3H), 7.26-7.20 (m, 3H), 7.13-7.07 (m, 3H), 7.02 (t, J = 7.6 Hz, 1H), 6.87 (t, J = 7.2 Hz, 1H), 6.72 (d, J = 7.6 Hz, 2H), 4.98 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 150.5, 136.0, 135.6, 131.9, 128.8, 128.7, 128.6, 128.2, 125.6, 122.7, 122.1, 120.6, 118.8, 118.6, 117.4, 111.4. IR (neat): 3386, 3254, 3202, 3060, 3011, 1615, 1604, 1595, 1570, 1522, 1488, 1445, 1363, 1324, 1290, 1272, 1247, 1201, 1157, 1070, 984, 901, 847, 806, 785, 772, 755, 740, 728, 695 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}N_3$ 312.1495; Found 312.1493.



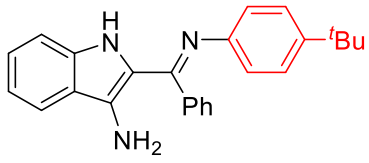
3h

(*E*)-2-(Phenyl(*p*-tolylimino)methyl)-1*H*-indol-3-amine (3h). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (14.5 mg, 0.04 mmol), ynamide **1a** (74.5 mg, 0.2 mmol), *p*-toluidine (25.7 mg, 0.24 mmol) and 1,4-dioxane (2 mL) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3h** in 77% yield (50.2 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.0 Hz, 1H), 7.54-7.34 (br, 1H), 7.34-7.33 (m, 3H), 7.27-7.19 (m, 3H), 7.13-7.11 (m, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.2 Hz, 2H), 6.62 (d, J = 8.0 Hz, 2H), 5.02 (br, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2 (m), 147.7, 135.80, 135.78, 132.1, 131.5, 128.9, 128.8, 128.7, 128.6, 125.4, 122.0, 120.6, 118.8, 118.6, 117.6, 111.3, 20.8. IR (neat): 3394, 3249, 3220, 3058, 3016, 2917, 2854, 1615, 1606, 1596, 1571, 1522, 1505, 1444, 1359, 1325, 1287, 1270, 1248, 1156, 1100, 983, 917, 888, 827, 816, 779, 756, 735, 700 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3$ 326.1652; Found 326.1655.



3i

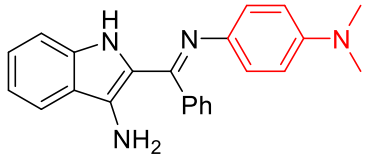
(*E*)-2-(((4-Methoxyphenyl)imino)(phenyl)methyl)-1*H*-indol-3-amine (3i). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (14.5 mg, 0.04 mmol), ynamide **1a** (74.5 mg, 0.2 mmol), *p*-anisidine (29.6 mg, 0.24 mmol) and 1,4-dioxane (2 mL) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 2/1 as the eluent afforded the desired product **3i** in 76% yield (51.8 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.54-7.36 (br, 1H), 7.36-7.34 (m, 3H), 7.27-7.19 (m, 3H), 7.13-7.11 (m, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.66 (s, 4H), 5.03 (br, 2H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 155.4, 143.5, 135.9, 135.8, 131.4, 128.8, 128.7, 125.4, 123.3, 120.6, 118.8, 118.5, 117.7, 113.6, 111.3, 55.2. IR (neat): 3419, 3370, 3291, 3055, 2992, 2958, 2833, 1608, 1596, 1560, 1513, 1505, 1494, 1465, 1452, 1440, 1355, 1321, 1276, 1247, 1230, 1179, 1170, 1104, 1025, 982, 888, 828, 811, 777, 740, 724, 702 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3O$ 342.1601; Found 342.1596.



3j

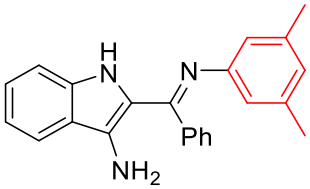
(*E*)-2-(((4-(*tert*-Butyl)phenyl)imino)(phenyl)methyl)-1*H*-indol-3-amine (3j). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (14.5 mg, 0.04 mmol), ynamide **1a** (74.5 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-tert-butylaniline (35.8 mg, 0.24 mmol) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3j**

in 81% yield (59.6 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 1H), 7.52-7.33 (br, 1H), 7.33-7.18 (m, 6H), 7.12-7.09 (m, 3H), 7.00 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 8.4 Hz, 2H), 5.04 (br, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0 (m), 147.5, 145.5, 135.77, 135.76, 131.6, 128.8, 128.7, 128.6, 125.4, 125.1, 121.8, 120.6, 118.8, 118.5, 117.6, 111.3, 34.1, 31.3. IR (neat): 3443, 3055, 2960, 2901, 2862, 1606, 1568, 1507, 1492, 1444, 1360, 1322, 1283, 1267, 1246, 1200, 1150, 1106, 980, 888, 838, 787, 741, 703 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}N_3$ 368.2121; Found 368.2115.



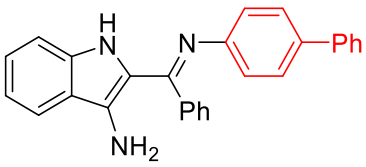
3k

(*E*)-2-(((4-(Dimethylamino)phenyl)imino)(phenyl)methyl)-1*H*-indol-3-amine (3k). $NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), *N*,*N*-dimethyl-1,4-phenylenediamine (49.0 mg, 0.36 mmol) and 1,4-dioxane (3 mL) were stirred at 80 °C (oil bath) for 12 h. Twice column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3k** in 28% yield (29.3 mg) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.4 Hz, 1H), 7.52-7.39 (br, 1H), 7.39-7.30 (m, 5H), 7.24-7.13 (m, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.68 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 4.96 (br, 2H), 2.84 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 147.0, 139.9, 136.4, 135.6, 130.9, 128.9, 128.7, 125.1, 123.7, 120.9, 118.6, 118.5, 118.1, 112.7, 111.3, 40.9. IR (neat): 3424, 3259, 3205, 3053, 2791, 1606, 1593, 1569, 1509, 1441, 1324, 1284, 1272, 1245, 1222, 1164, 1058, 980, 948, 920, 889, 819, 789, 756, 740, 718, 699 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}N_4$ 355.1917; Found 355.1908.



3l

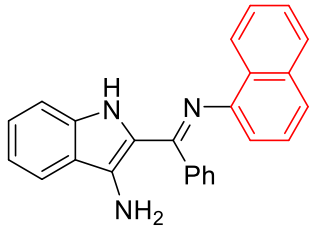
(*E*)-2-(((3,5-Dimethylphenyl)imino)(phenyl)methyl)-1*H*-indol-3-amine (3l). $NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 3,5-dimethylaniline (43.6 mg, 0.36 mmol) and 1,4-dioxane (3 mL) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3l** in 40% yield (40.6 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.54-7.35 (br, 1H), 7.35-7.22 (m, 6H), 7.14-7.12 (m, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.53 (s, 1H), 6.35 (s, 2H), 4.96 (br, 2H), 2.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1 (m), 150.3, 137.7, 135.83, 135.75, 131.6, 128.7, 128.6, 125.4, 124.5, 120.6, 119.9, 118.8, 118.6, 117.5, 111.4, 21.2. IR (neat): 3416, 3267, 3202, 2911, 2859, 1618, 1604, 1576, 1522, 1448, 1363, 1328, 1292, 1245, 1173, 1138, 1105, 1019, 979, 943, 891, 842, 739, 714, 698, 684 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3$ 340.1808; Found 340.1806.



3m

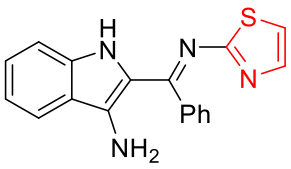
(*E*)-2-(([1,1'-Biphenyl]-4-ylimino)(phenyl)methyl)-1*H*-indol-3-amine (3m). $NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 4-aminobiphenyl (60.9 mg, 0.36 mmol) and 1,4-dioxane (3 mL) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3m** in 45% yield (52.0 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (m, 4H), 7.37-7.21

(m, 11H), 7.14-7.12 (m, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 8.0 Hz, 2H), 5.13 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 149.7, 140.7, 136.0, 135.6, 135.4, 132.1, 128.9, 128.8, 128.7, 128.6, 126.9, 126.7, 126.6, 125.7, 122.6, 120.5, 118.9, 118.6, 117.5, 111.4. IR (neat): 3427, 3283, 3160, 3079, 3053, 3024, 1602, 1592, 1567, 1513, 1480, 1445, 1326, 1290, 1259, 1248, 1154, 979, 922, 889, 840, 817, 789, 767, 734, 723, 697 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{27}H_{22}N_3$ 388.1808; Found 388.1808.



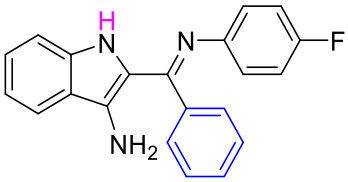
3n

(*E*)-2-((Naphthalen-1-ylimino)(phenyl)methyl)-1*H*-indol-3-amine (3h). $NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 1-naphthylamine (51.5 mg, 0.36 mmol) and 1,4-dioxane (3 mL) were stirred at 80 ºC (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3n** in 34% yield (37.2 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32-8.24 (m, 1H), 7.77-7.75 (m, 1H), 7.57(d, J = 8.0 Hz, 1H), 7.47-7.45 (m, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.27-7.03 (m, 10H), 6.45 (d, J = 7.6 Hz, 1H), 5.26 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9 (m), 147.1, 136.0, 135.5, 133.8, 132.2, 128.9, 128.6, 128.4, 128.0, 127.7, 125.9, 125.7, 125.5, 125.3, 124.1, 122.7, 120.5, 118.9, 118.7, 117.5, 115.8, 111.5. IR (neat): 3421, 3293, 3053, 1615, 1604, 1595, 1563, 1510, 1488, 1443, 1389, 1362, 1323, 1281, 1248, 1140, 1107, 1071, 1038, 1012, 1001, 982, 912, 885, 806, 791, 774, 735, 725, 714, 699 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{20}N_3$ 362.1652; Found 362.1650.



3o

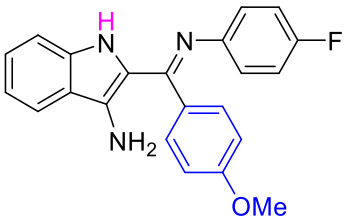
(*E*)-2-(Phenyl(thiazol-2-ylimino)methyl)-1*H*-indol-3-amine (3o). $NiCl_2$(dppp) (16.3 mg, 0.03 mmol), Zn powder (19.6 mg, 0.3 mmol), $Zn(OTf)_2$ (21.8 mg, 0.06 mmol), ynamide **1a** (111.7 mg, 0.3 mmol), 2-aminothiazole (36.1 mg, 0.36 mmol) and 1,4-dioxane (3 mL) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate/acetone = 1/3/1 as the eluent afforded the desired product **3o** in 54% yield (51.9 mg) as a red solid. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.57 (br, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.56 (s, 3H), 7.39-7.37 (m, 3H), 7.20-7.19 (m, 2H), 7.103-7.095 (m, 1H), 6.92-6.90 (m, 1H), 3.39 (br, 1H). ^{13}C NMR (100 MHz, d_6-DMSO): δ 170.0, 163.6 (m), 139.4, 139.1, 138.2, 134.8, 130.2, 129.8, 128.6, 127.3, 121.1, 118.5, 118.0, 116.8, 116.6, 112.6. IR (neat): 3385, 3358, 3263, 2252, 1612, 1560, 1521, 1502, 1473, 1433, 1356, 1329, 1312, 1293, 1248, 1128, 1114, 1101, 1046, 1023, 995, 883, 821, 789, 753, 708, 695 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}N_4S$ 319.1012; Found 319.1014.



3a, EWG = Ms

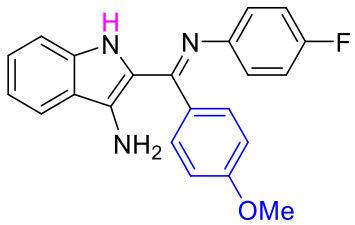
(*E*)-2-(((4-Fluorophenyl)imino)(phenyl)methyl)-1*H*-indol-3-amine (3a). This compound was synthesized from ynamide **1b**. $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1b** (59.3 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3a** in 58% yield (38.4 mg) as a yellow solid. The

spectroscopic data are in agreement with that obtained from **1a**.



3p, EWG = $SO_2(p\text{-}FC_6H_4)$

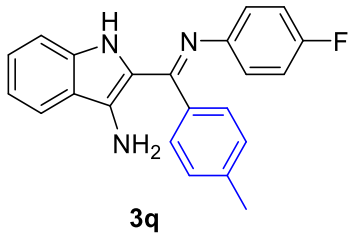
(*E*)-2-(((4-Fluorophenyl)imino)(4-methoxyphenyl)methyl)-1*H*-indol-3-amine (3p). $NiCl_2(dppp)$ (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1c** (81.3 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 ºC (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3p** in 59% yield (42.3 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.0 Hz, 1H), 7.55-7.27 (br, 1H), 7.27-7.23 (m, 1H), 7.19-7.16 (m, 3H), 7.05 (t, J = 7.2 Hz, 1H), 6.89-6.81 (m, 4H), 6.70-6.66 (m, 2H), 5.02 (br, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (m), 159.8, 158.8 (d, $^1J_{C\text{-}F}$ = 240.3 Hz), 146.7 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 135.9, 131.8, 130.2, 127.5, 125.6, 123.3 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 120.6, 118.8, 118.6, 117.7, 115.0 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 114.1, 111.4, 55.2. ^{13}F NMR (376 MHz, $CDCl_3$): δ -121.4. IR (neat): 3440, 3381, 1607, 1569, 1512, 1500, 1488, 1444, 1354, 1323, 1281, 1250, 1215, 1199, 1176, 1155, 1089, 1027, 983, 888, 838, 811, 789, 749, 735 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{19}N_3OF$ $[M+H]^+$: 360.1507, found 360.1504.



3p, EWG = $SO_2(p\text{-}OMeC_6H_4)$

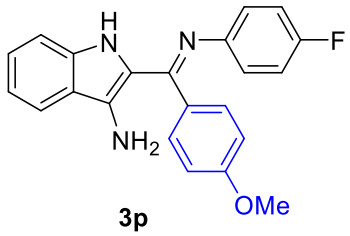
(*E*)-2-(((4-Fluorophenyl)imino)(4-methoxyphenyl)methyl)-1*H*-indol-3-amine (3p). This compound was synthesized from ynamide **1d**. $NiCl_2(dppp)$ (10.8 mg, 0.02 mmol), Zn powder

(13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1d** (83.7 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3p** in 58% yield (41.9 mg) as a yellow solid. The spectroscopic data are in agreement with that obtained from **1c**.



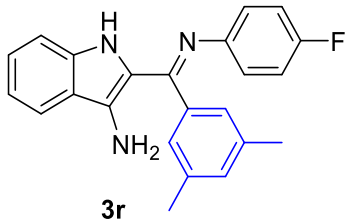
3q

(*E*)-2-(((4-Fluorophenyl)imino)(*p*-tolyl)methyl)-1*H*-indol-3-amine (3q). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1e** (77.3 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3q** in 66% yield (45.5 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.0 Hz, 1H), 7.53-7.25 (br, 1H), 7.25-7.21 (m, 2H), 7.17-7.12 (m, 5H), 7.03 (t, J = 7.6 Hz, 1H), 6.80 (t, J = 8.8 Hz, 2H), 6.68-6.65 (m, 2H), 5.02 (br, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (m), 158.9 (d, $^1J_{C\text{-}F}$ = 239.8 Hz), 146.7 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 139.0, 135.9, 132.5, 131.8, 129.5, 128.6, 125.6, 123.3 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 120.6, 118.8, 118.6, 117.5, 114.9 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 111.4, 21.3. ^{13}F NMR (376 MHz, $CDCl_3$): δ -121.4. IR (neat): 3453, 3304, 3249, 3058, 3021, 2917, 1598, 1570, 1514, 1493, 1446, 1357, 1328, 1285, 1266, 1221, 1213, 1194, 1181, 1151, 1088, 980, 834, 825, 789, 761, 742, 735, 703 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}N_3F$ 344.1558; Found 344.1565.



3p

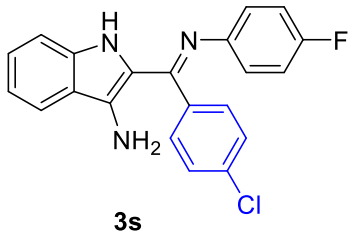
(*E*)-2-(((4-Fluorophenyl)imino)(4-methoxyphenyl)methyl)-1*H*-indol-3-amine (3p). This compound was synthesized from ynamide **1f**. $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1f** (80.5 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3p** in 58% yield (41.8 mg) as a yellow solid. The spectroscopic data are in agreement with that obtained from **1c**.



3r

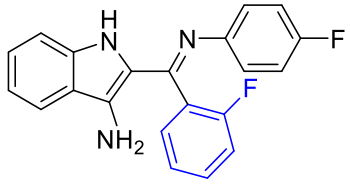
(*E*)-2-((3,5-Dimethylphenyl)((4-fluorophenyl)imino)methyl)-1*H*-indol-3-amine (3r). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1g** (80.1 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3r** in 67% yield (48.1 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.4 Hz, 1H), 7.51-7.23 (br, 1H), 7.23-7.20 (m, 1H), 7.14-7.12 (m, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.97 (s, 1H), 6.83-6.77 (m, 4H), 6.69-6.65 (m, 2H), 4.99 (br, 2H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (m), 158.9 (d, $^1J_{C\text{-}F}$ = 239.8 Hz), 146.6 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 138.4, 135.9, 135.4, 131.7, 130.6, 126.1, 125.5, 123.3 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 120.6,

118.8, 118.6, 117.6, 114.8 (d, $^{2}J_{C\text{-}F}$ = 22.2 Hz), 111.4, 21.2. ^{13}F NMR (376 MHz, $CDCl_3$): δ -121.4. IR (neat): 3432, 3286, 3199, 2914, 2856, 1731, 1615, 1592, 1570, 1518, 1496, 1447, 1359, 1326, 1305, 1223, 1192, 1149, 1090, 1035, 1006, 919, 850, 824, 789, 759, 741, 730, 697 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}N_3F$ 358.1714; Found 358.1710.



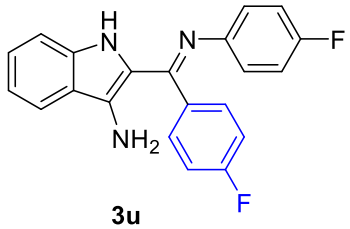
3s

(*E*)-2-((4-Chlorophenyl)((4-fluorophenyl)imino)methyl)-1*H*-indol-3-amine (3s). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1h** (81.4 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3s** in 39% yield (28.4 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.54-7.36 (br, 1H), 7.36-7.33 (m, 2H), 7.25 (td, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.20-7.15 (m, 3H), 7.07-7.03 (m, 1H), 6.84-6.80 (m, 2H), 6.66-6.63 (m, 2H), 5.14 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7 (m), 159.0 (d, $^{1}J_{C\text{-}F}$ = 240.6 Hz), 146.3 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 136.2, 135.1, 133.8, 132.4, 130.1, 129.1, 126.0, 123.2 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 120.4, 118.94, 118.85, 116.9, 115.1 (d, $^{2}J_{C\text{-}F}$ = 22.2 Hz), 111.5. ^{13}F NMR (376 MHz, $CDCl_3$): δ -120.85--120.86 (m). IR (neat): 3424, 3259, 3045, 2919, 1599, 1572, 1517, 1493, 1447, 1328, 1285, 1261, 1216, 1196, 1152, 1085, 1015, 982, 832, 805, 754, 744, 731 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}N_3FCl$ 364.1011; Found 364.1006.



3t

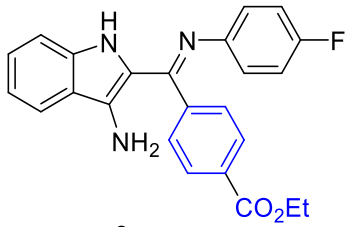
(*E*)-2-((2-Fluorophenyl)((4-fluorophenyl)imino)methyl)-1*H*-indol-3-amine (3t). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1i** (78.1 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3t** in 56% yield (38.6 mg) as a yellow solid. The product contains small amount of ethyl acetate and NEt_3. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.54-7.39 (br, 1H), 7.39-7.33 (m, 1H), 7.27-7.22 (m, 2H), 7.18-7.14 (m, 2H), 7.08-7.02 (m, 2H), 6.83-6.79 (m, 2H), 6.73-6.70 (m, 2H), 5.09 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2 (d, $^1J_{C\text{-}F}$ = 240.3 Hz), 158.6 (d, $^1J_{C\text{-}F}$ = 247.5 Hz), 156.4 (m), 146.7 (d, $^4J_{C\text{-}F}$ = 2.4 Hz), 136.3, 132.3, 131.2 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 130.1 (d, $^4J_{C\text{-}F}$ = 4.0 Hz), 125.9, 124.6 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 123.3 (d, $^2J_{C\text{-}F}$ = 18.1 Hz), 122.4 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 120.5, 118.9, 118.8, 117.1, 116.2 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 114.9 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 111.5. ^{13}F NMR (376 MHz, $CDCl_3$): δ -111.4--111.5 (m), -120.9. IR (neat): 3396, 3207, 3058, 1616, 1597, 1572, 1524, 1495, 1448, 1362, 1325, 1293, 1248, 1223, 1195, 1161, 1149, 1088, 1011, 987, 892, 839, 822, 800, 766, 753, 733, 704 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}N_3F_2$ 348.1307; Found 348.1304.



3u

(*E*)-2-((4-Fluorophenyl)((4-fluorophenyl)imino)methyl)-1*H*-indol-3-amine (3u). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1j** (78.1 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3u** in 68% yield (46.9 mg) as a yellow solid. ^{1}H NMR (400

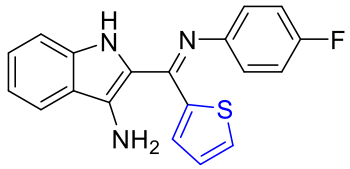
MHz, $CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 1H), 7.42 (br, 1H), 7.26-7.20 (m, 3H), 7.16-7.14 (m, 1H), 7.07-7.03 (m, 3H), 6.81 (t, J = 8.8 Hz, 2H), 6.65-6.61 (m, 2H), 5.08 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, $^1J_{C\text{-}F}$ = 248.7 Hz), 160.9 (m), 158.9 (d, $^1J_{C\text{-}F}$ = 240.3 Hz), 146.4 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 136.1, 132.3, 131.3 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 130.7 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 125.9, 123.2 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 120.4, 118.9, 118.8, 117.1, 116.0 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 111.5. ^{13}F NMR (376 MHz, $CDCl_3$): δ -110.8, -121.0. IR (neat): 3430, 3416, 3257, 3058, 1603, 1571, 1518, 1494, 1449, 1362, 1330, 1285, 1268, 1226, 1212, 1198, 1153, 1093, 1008, 985, 922, 836, 816, 797, 743, 735, 704 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}N_3F_2$ 348.1307; Found 348.1301.



3v

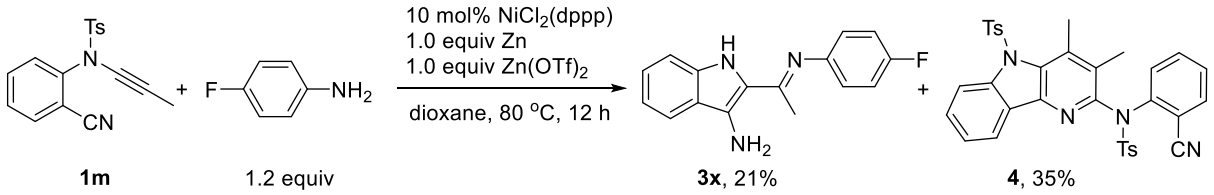
Ethyl (*E*)-4-((3-amino-1*H*-indol-2-yl)((4-fluorophenyl)imino)methyl)benzoate (3v). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1k** (88.9 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 ºC (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3v** in 61% yield (48.8 mg) as a yellow solid.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.56-7.32 (br, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.2 Hz, 1H), 7.15-7.13 (m, 1H), 7.04 (t, J = 7.2 Hz, 1H), 6.79 (t, J = 8.8 Hz, 2H), 6.65-6.62 (m, 2H), 5.19 (br, 2H), 4.36 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 161.0 (m), 159.0 (d, $^1J_{C\text{-}F}$ = 240.6 Hz), 146.3 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 140.0, 136.3, 132.6, 130.8, 129.9, 128.7, 125.9, 123.2 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 120.3, 118.9, 118.8, 116.8, 115.1 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 111.5, 61.3, 14.2. ^{13}F NMR (376 MHz, $CDCl_3$): δ -120.82--120.83 (m). IR (neat): 3458, 3440, 3357, 3060, 2987, 1712, 1703, 1695, 1617, 1601, 1572, 1513, 1499, 1490, 1448, 1403, 1365, 1327, 1289, 1278, 1216, 1179, 1152, 1131, 1104,

1090, 1021, 983, 856, 840, 804, 782, 740, 727, 706 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}N_3O_2F$ 402.1612; Found 402.1613.



3w

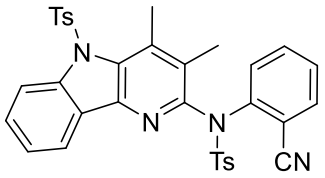
(*Z*)-2-((Phenylimino)(thiophen-2-yl)methyl)-1*H*-indol-3-amine (3w). $NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1l** (75.7 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) in 4 mL screw-cap vial were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3w** in 58% yield (39.1 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (bs, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.40-7.39 (m, 1H), 7.27-7.23 (m, 1H), 7.18-7.16 (m, 1H), 7.10-7.09 (m, 1H), 7.06-7.02 (m, 2H), 6.88-6.84 (m, 2H), 6.74-6.70 (m, 2H), 5.17 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2 (d, $^1J_{C\text{-}F}$ = 240.6 Hz), 154.8, 146.9 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 136.0, 134.8, 132.4, 129.6, 128.3, 126.9, 125.9, 122.7 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 120.4, 119.0, 118.8, 117.3, 115.1 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 111.5. ^{13}F NMR (376 MHz, $CDCl_3$): δ -120.8--120.9 (m). IR (neat): 3398, 3207, 3063, 1590, 1569, 1519, 1495, 1447, 1424, 1362, 1346, 1325, 1281, 1270, 1249, 1223, 1192, 1145, 1089, 1040, 965, 888, 853, 828, 800, 736, 699 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}N_3FS$ 336.0965; Found 336.0956.



1m 1.2 equiv **3x**, 21% **4**, 35%

(*E*)-2-(1-((4-Fluorophenyl)imino)ethyl)-1*H*-indol-3-amine (3x). $NiCl_2$(dppp) (27.1 mg, 0.05 mmol), Zn powder (32.7 mg, 0.5 mmol), $Zn(OTf)_2$ (181.8 mg, 0.5 mmol), ynamide **1m** 310.37 (155.2 mg, 0.5 mmol), 1,4-dioxane (5 mL) and 4-fluoroaniline (66.7 mg, 0.6 mmol) in 12 mL

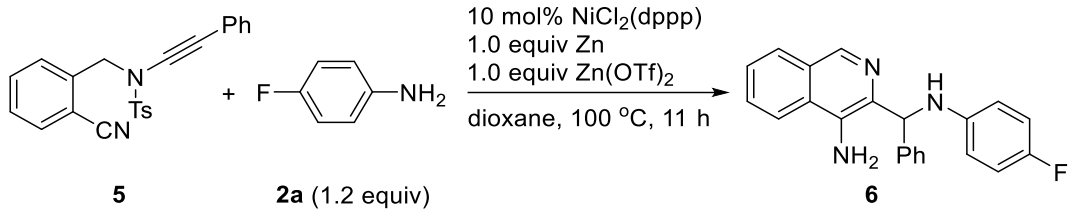
screw-cap vial were stirred at 80 ºC (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3x** in 21% yield (28.0 mg) as a yellow solid, and product **4** in 35% yield (54.8 mg). ^{1}H NMR (400 MHz, d_6-DMSO): δ 10.34 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.18-7.13 (m, 3H), 6.92-6.85 (m, 3H), 6.17 (br, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, d_6-DMSO): δ 161.1, 158.3 (d, $^1J_{C\text{-}F}$ = 236.5 Hz), 147.6 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 136.1, 132.0, 124.6, 122.5 (d, $^3J_{C\text{-}F}$ = 7.4 Hz), 120.0, 119.6, 117.3, 117.0, 115.4 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 111.6, 17.4. ^{13}F NMR (376 MHz, d_6-DMSO): δ -121.9--122.0 (m). IR (neat): 3427, 3398, 3327, 3246, 3173, 3058, 1600, 1574, 1533, 1496, 1370, 1317, 1246, 1223, 1210, 1194, 1092, 1006, 853, 760, 743, 714 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_3F$ 268.1245; Found 268.1247.



4

***N*-(2-Cyanophenyl)-*N*-(3,4-dimethyl-5-tosyl-5*H*-pyrido[3,2-*b*]indol-2-yl)-4-methylbenzenesulfonamide (4).** M.p. 182-184 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.4 Hz, 1H), 7.78-7.76 (m, 1H), 7.64-7.61 (m, 1H), 7.50 (t, J = 7.6Hz, 1H), 7.44-7.41 (m, 3H), 7.33 (d, J = 7.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 2.80 (s, 3H), 2.77 (s, 3H), 2.46 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 145.5, 144.6, 144.0, 142.9, 141.8, 141.6, 135.3, 134.5, 134.1, 132.8, 132.7, 131.5, 130.9, 129.6, 129.0, 128.8, 128.65, 128.56, 128.5, 127.0, 126.0, 120.0, 119.6, 117.5, 115.8, 21.7, 21.4, 19.5, 15.8. IR (neat): 2959, 2920, 2852, 2234, 1730, 1595, 1448, 1362, 1187, 1165, 1097, 1088, 1070, 875, 816, 790, 761, 719, 700, 681, 664 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{29}N_4O_4S_2$ 621.1625; Found 621.1625.

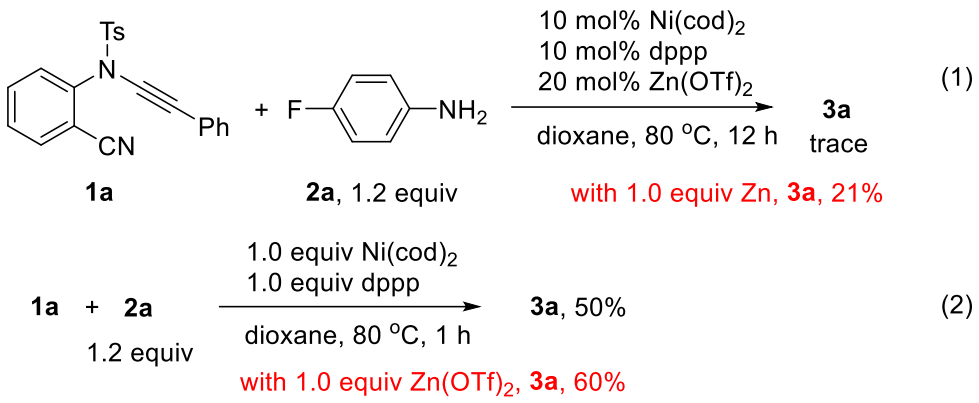
Typical procedure for the synthesis of 3-(((4-Fluorophenyl)amino)(phenyl)methyl)isoquinolin-4-amine (6).



5 **2a** (1.2 equiv) **6**

$NiCl_2$(dppp) (10.8 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **5** (77.3 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) were added sequentially to a 4 mL screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 100 °C (oil bath) for 11 h, the mixture was quenched with brine and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent to afford the desired product **6** in 57% yield (39.3 mg) as a yellow solid. M.p. = 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.63-7.59 (m, 1H), 7.54-7.50 (m, 3H), 7.30 (t, J = 7.2 Hz, 2H), 7.24-7.20 (m, 1H), 6.82 (t, J = 8.8 Hz, 2H), 6.66-6.63 (m, 2H), 5.75 (s, 1H), 5.29 (br, 1H), 4.58 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (d, $^1J_{C\text{-}F}$ = 234.0 Hz), 143.6 (d, $^4J_{C\text{-}F}$ = 1.7 Hz), 142.1, 141.4, 135.7, 134.0, 129.2, 128.8, 128.1, 127.9, 127.6, 127.5, 126.8, 126.7, 119.7, 115.5 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 114.9 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 61.8. ^{13}F NMR (376 MHz, $CDCl_3$): δ -127.27--127.3 (m). IR (neat): 3474, 3399, 3358, 3076, 3055, 2919, 2846, 1843, 1622, 1507, 1470, 1443, 1401, 1309, 1219, 1188, 1091, 951, 894, 817, 784, 770, 750, 736, 699 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}N_3F$ 344.1558; Found 344.1549.

Mechanistic studies.

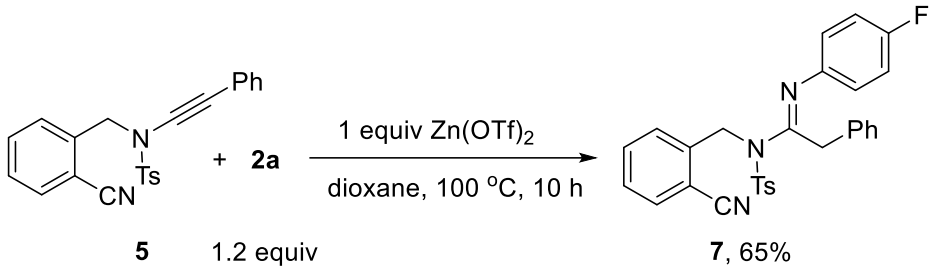


The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $Ni(cod)_2$ (5.5 mg, 0.02 mmol), dppp (8.2 mg, 0.02 mmol), $Zn(OTf)_2$ (14.5 mg, 0.04 mmol), ynamide **1a** (74.5 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 80 °C (oil bath) for 12 h, trace amount of **3a** was observed according to TLC analysis.

When $Ni(cod)_2$ (5.5 mg, 0.02 mmol), dppp (8.2 mg, 0.02 mmol), Zn powder (13.1 mg, 0.2 mmol), $Zn(OTf)_2$ (14.5 mg, 0.04 mmol), ynamide **1a** (74.5 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) were stirred at 80 °C (oil bath) for 12 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent to afford the main product **3a** and starting material **1a** mixture. The solvent was evaporated under the reduced pressure and the residue was dissolved in d_6-DMSO. The NMR yields were obtained by ^1H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) as an internal standard. The NMR yield of **3a** was 21% and the NMR yield of the unreacted **1a** was 24%.

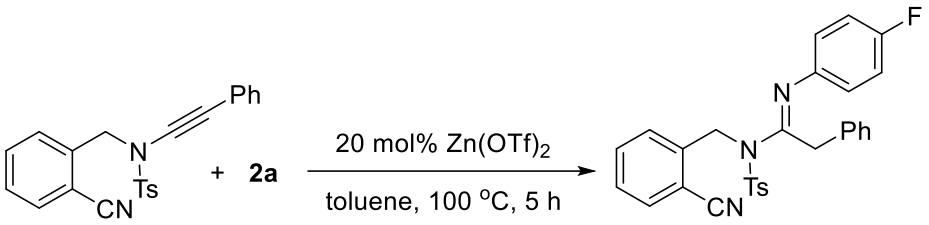
When $Ni(cod)_2$ (55.0 mg, 0.2 mmol), dppp (82.5 mg, 0.2 mmol), ynamide **1a** (74.5 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) were stirred at 80 °C (oil bath) for 1 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3a** in 50% yield (33.1 mg) as a yellow solid.

When $Ni(cod)_2$ (55.0 mg, 0.2 mmol), dppp (82.5 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), ynamide **1a** (74.5 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) were stirred at 80 °C (oil bath) for 1 h. Column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 3/1 as the eluent afforded the desired product **3a** in 60% yield (39.8 mg) as a yellow solid.



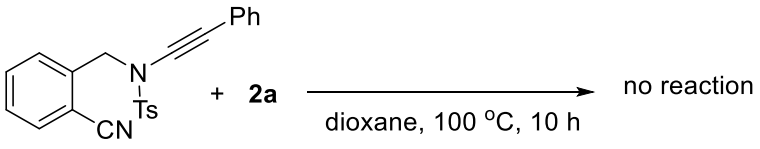
5 1.2 equiv **7**, 65%

The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, ynamide **5** (77.3 mg, 0.2 mmol), $Zn(OTf)_2$ (72.7 mg, 0.2 mmol), dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 100 °C (oil bath) for 10 h, the mixture was filter with a silica pad and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford the desired product **7** in 65% yield (64.9 mg) as a white solid. M.p. 119-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.4 Hz, 2H), 7.52-7.50 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.28-7.25 (m, 2H), 7.18-7.08 (m, 4H), 6.93 (t, J = 8.4 Hz, 2H), 6.84 (d, J = 7.2 Hz, 2H), 6.41-6.38 (m, 2H), 4.93 (s, 2H), 4.00 (s, 2H), 2.46 (s, 3H). m.p. = 119-121 °C. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4 (d, $^1J_{C\text{-}F}$ = 240.4 Hz), 156.2, 144.7, 143.5 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 139.9, 134.7, 134.3, 132.5, 132.3, 129.8, 129.1, 129.0, 128.5, 127.7, 127.5, 126.7, 120.9 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 117.2, 115.7 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 111.9, 49.2, 37.1, 21.6. ^{13}F NMR (376 MHz, $CDCl_3$): δ -120.1. IR (neat): 3061, 3030, 2954, 2922, 2852, 2223, 1660, 1594, 1498, 1453, 1365, 1351, 1226, 1206, 1184, 1170, 1144, 1087, 1019, 881, 854, 844, 811, 771, 761, 737, 720, 707, 700, 692, 657 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{25}N_3O_2FS$ 498.1646; Found 498.1646.



5 1.2 equiv **7**, 88%

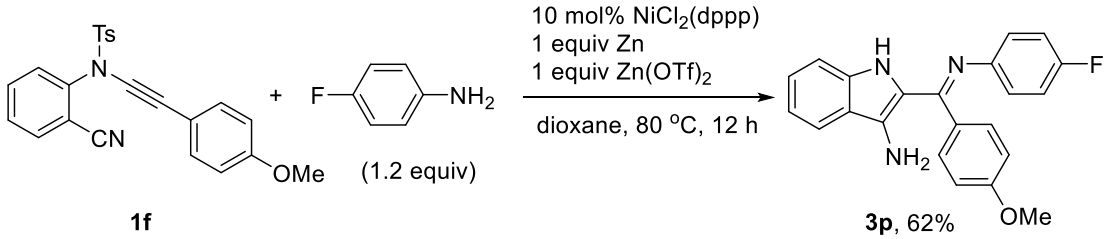
The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, ynamide **5** (77.3 mg, 0.2 mmol), $Zn(OTf)_2$ (14.5 mg, 0.04 mmol), toluene (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 100 °C (oil bath) for 5h, the mixture was filter with a silica pad and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford the desired product **7** in 88% yield (87.5 mg) as a white solid.



5 1.2 equiv

The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, ynamide **5** (77.3 mg, 0.2 mmol), 1,4-dioxane (2 mL) and 4-fluoroaniline (26.7 mg, 0.24 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 100 °C (oil bath) for 10 h. The mixture was filter with a silica pad and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the NMR yields were obtained by ^1H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) as an internal standard. No desired product was formed. The NMR yield of **5** was 96%.

1 mmol scale reaction of 1f.



(*E*)-2-(((4-Fluorophenyl)imino)(4-methoxyphenyl)methyl)-1*H*-indol-3-amine (3p). This compound was synthesized from ynamide **1f**. To an oven dried Schlenk tube (25 mL) were added $NiCl_2$(dppp) (54.2 mg, 0.1 mmol), Zn powder (65.4 mg, 1 mmol), $Zn(OTf)_2$ (363.5 mg, 1 mmol), ynamide **1f** (402.5 mg, 1 mmol), 1,4-dioxane (10 mL) and 4-fluoroaniline (133.3 mg, 1.2 mmol) in the glovebox. The Schlenk tube was capped with a rubber septum and take out of the golvebox. The tube cap was then securely fitted and sealed with electrical tape, and the stopcock valve on the sidearm of the Schlenk tube was closed. After the reaction mixture was stirred at 80 °C (oil bath) for 12 h, the mixture was quenched with brine and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (which was treated with NEt_3:petroleum ether = 1:20 and then petroleum ether before loading the sample) using petroleum ether/ethyl acetate = 5/1 as the eluent afforded the desired product **3p** in 62% yield (222.8 mg) as a yellow solid.

References:

(1) Zhang, J.; Guo, M.; Chen, Y.; Zhang, S.; Wang, X.-N.; Chang, J. *Org. Lett.* **2019**, *21*, 1331.

(2) (a) Wang, G.; You, X.; Gan, Y.; Liu, Y. *Org. Lett.* **2017**, *19*, 110. (b) Kloeckner, U.; Nachtsheim, B. J. *Chem. Commun.* **2014**, *50*, 10485.

The single crystal of **3g** was prepared by slow diffusion of its solution in ethyl acetate/hexane. The structure of **3g** was established by X-ray analysis of its crystal (Figure S1). Thermal ellipsoids are set at 30% probability.

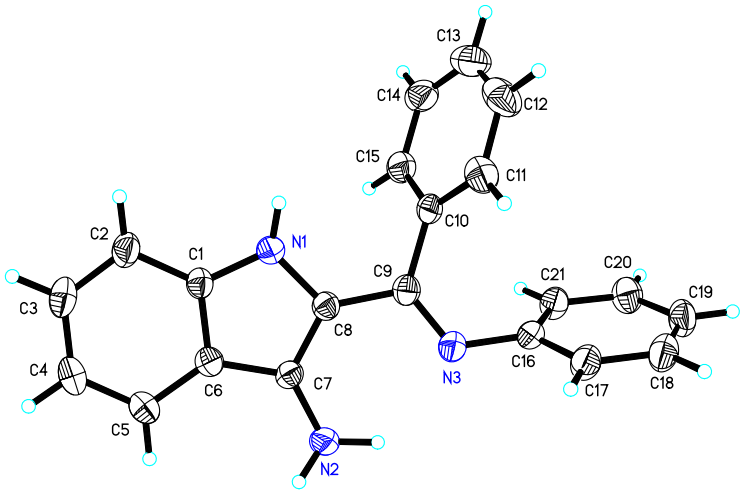


Figure S1. X-ray crystal structure of compound **3g**

Crystal data and structure refinement for cd17034 (compound **3g**).

Identification code	cd17034	
Empirical formula	C21 H17 N3	
Formula weight	311.38	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.5511(18) Å	α= 90°.
	b = 15.281(3) Å	β= 103.866(4)°.
	c = 9.5714(16) Å	γ = 90°.
Volume	1640.2(5) $Å^3$	
Z	4	
Density (calculated)	1.261 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	656	
Crystal size	0.180 x 0.140 x 0.100 mm^3	
Theta range for data collection	1.816 to 24.996°.	
Index ranges	-13<=h<=13, -18<=k<=13, -11<=l<=11	
Reflections collected	8935	
Independent reflections	2886 [R(int) = 0.0405]	
Completeness to theta = 25.242°	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6486	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2886 / 0 / 229
Goodness-of-fit on F^2	1.151
Final R indices [I>2sigma(I)]	R1 = 0.0651, wR2 = 0.1398
R indices (all data)	R1 = 0.0904, wR2 = 0.1513
Extinction coefficient	n/a
Largest diff. peak and hole	0.186 and -0.139 e.Å^{-3}

The single crystal of **4** was prepared by slow diffusion of its solution in dichloromethane/ethyl acetate/hexane. The structure of **4** was established by X-ray analysis of its crystal (Figure S2). Thermal ellipsoids are set at 30% probability.

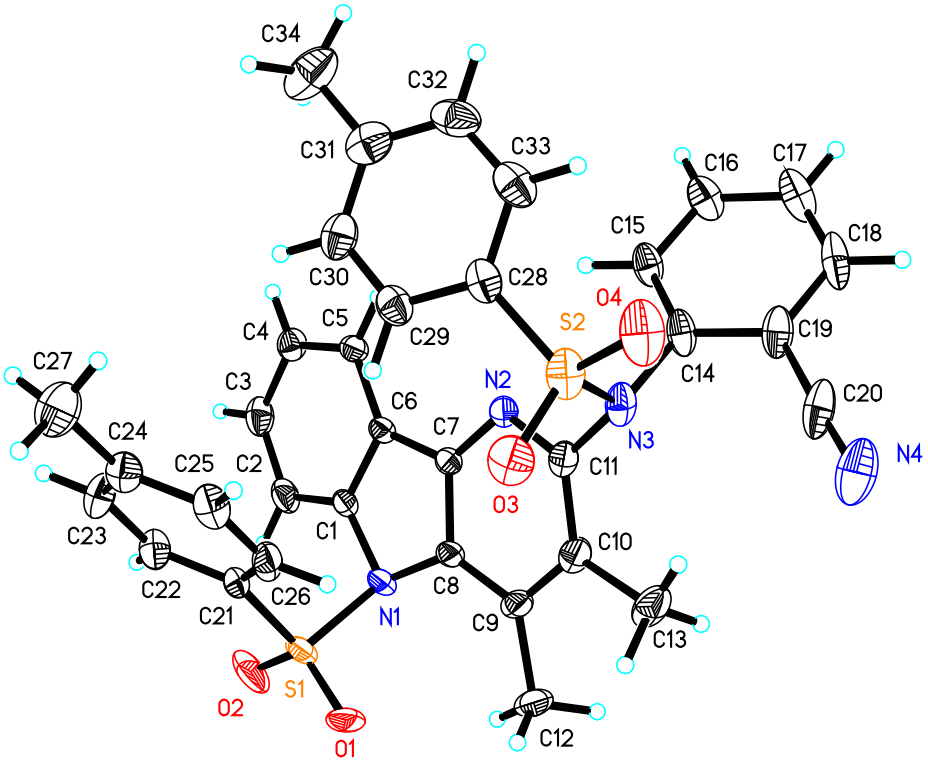


Figure S2. X-ray crystal structure of compound **4**

Crystal data and structure refinement for mo_d8v21043_0m_4. (compound **4**)

Identification code	mo_d8v21043_0m_4
Empirical formula	C34 H28 N4 O4 S2
Formula weight	620.72
Temperature	193(2) K

Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.4151(8) Å	α= 90.241(3)°.
	b = 13.3841(12) Å	β= 94.199(3)°.
	c = 14.0084(13) Å	γ = 104.514(3)°.
Volume	1703.8(3) $Å^3$	
Z	2	
Density (calculated)	1.210 Mg/m^3	
Absorption coefficient	0.197 mm^{-1}	
F(000)	648	
Crystal size	0.200 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.766 to 24.996°.	
Index ranges	-16<=h<=16, -17<=k<=17, -22<=l<=20	
Reflections collected	48588	
Independent reflections	5918 [R(int) = 0.0583]	
Completeness to theta = 25.242°	96.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6630	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5918 / 0 / 401	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2sigma(I)]	R1 = 0.0802, wR2 = 0.2022	
R indices (all data)	R1 = 0.0916, wR2 = 0.2086	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.444 and -0.723 $e.Å^{-3}$	

The single crystal of **S-5** was prepared by slow evaporation of its solution in methyl acetate/petroleum ether. The structure of **S-5** was established by X-ray analysis of its crystal (Figure S3). Thermal ellipsoids are set at 30% probability.

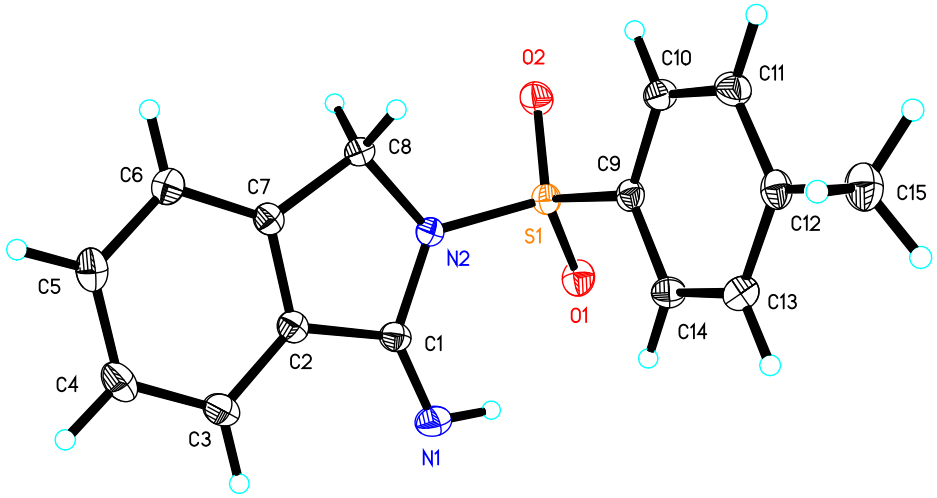


Figure S3. X-ray crystal structure of compound **S-5**

Crystal data and structure refinement for mo_d8v21055_0m (compound **S-5**).

Identification code	mo_d8v21055_0m	
Empirical formula	C15 H14 N2 O2 S	
Formula weight	286.34	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.4834(5) Å	α= 90°.
	b = 5.1425(2) Å	β= 94.4310(10)°.
	c = 20.4041(6) Å	γ = 90°.
Volume	1305.94(8) $Å^3$	
Z	4	
Density (calculated)	1.456 Mg/m^3	
Absorption coefficient	0.250 mm^{-1}	
F(000)	600	
Crystal size	0.200 x 0.120 x 0.100 mm^3	
Theta range for data collection	2.486 to 25.998°.	
Index ranges	-15<=h<=12, -6<=k<=6, -25<=l<=25	
Reflections collected	10279	
Independent reflections	2560 [R(int) = 0.0286]	
Completeness to theta = 25.242°	99.6 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6605
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2560 / 0 / 186
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0843
R indices (all data)	R1 = 0.0453, wR2 = 0.0916
Extinction coefficient	n/a
Largest diff. peak and hole	0.286 and -0.389 e.$Å^{-3}$

The single crystal of **5** was prepared by slow evaporation of its solution in dichloromethane/hexane. The structure of **5** was established by X-ray analysis of its crystal (Figure S4). Thermal ellipsoids are set at 30% probability.

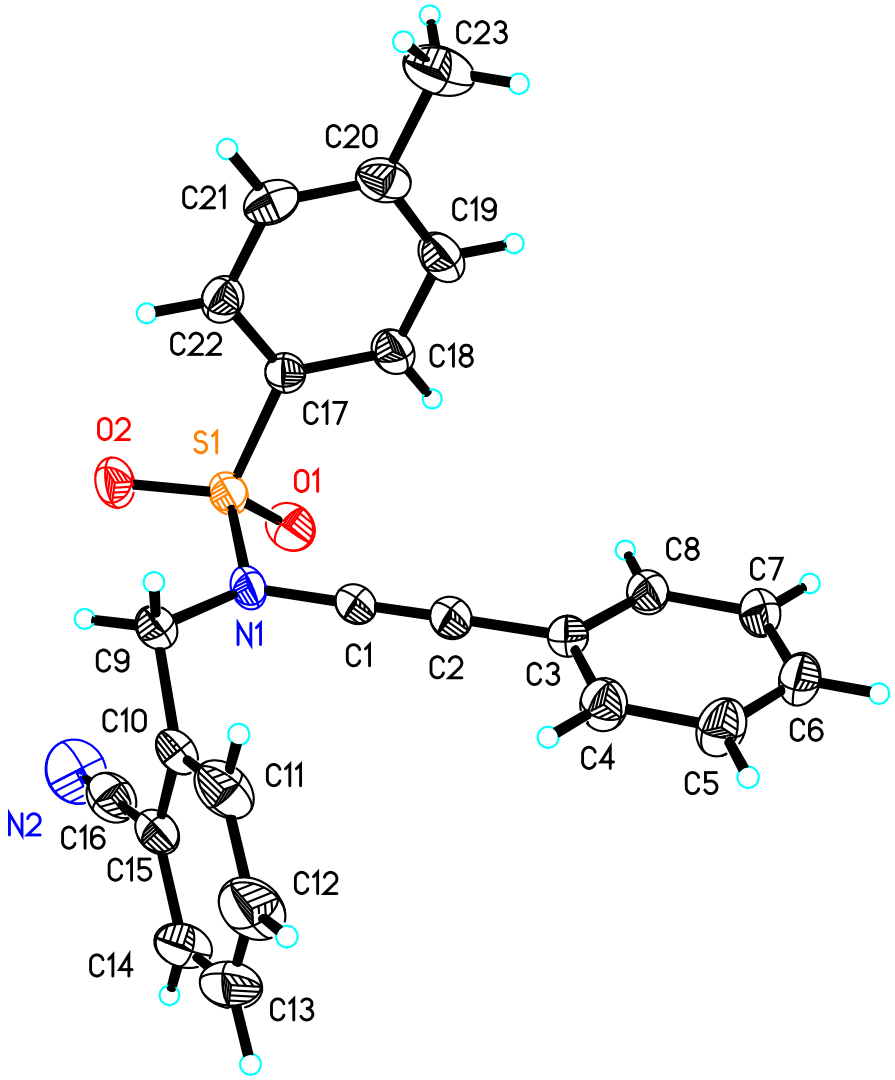


Figure S4. X-ray crystal structure of compound **5**

Crystal data and structure refinement for d8v21050 (compound **5**).

Identification code	d8v21050	
Empirical formula	C23 H18 N2 O2 S	
Formula weight	386.45	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.2238(4) Å	α= 90°.

	b = 22.1909(10) Å	β= 117.9640(10)°.
	c = 10.0711(4) Å	γ = 90°.
Volume	2018.11(15) Å^3	
Z	4	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.181 mm^{-1}	
F(000)	808	
Crystal size	0.180 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.255 to 25.999°.	
Index ranges	-12<=h<=11, -23<=k<=27, -12<=l<=12	
Reflections collected	10038	
Independent reflections	3941 [R(int) = 0.0283]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6763	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3941 / 0 / 255	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1013	
R indices (all data)	R1 = 0.0665, wR2 = 0.1157	
Extinction coefficient	0.018(3)	
Largest diff. peak and hole	0.183 and -0.277 e.Å^{-3}	

The single crystal of **6** was prepared by slow evaporation of its solution in dichloromethane/petroleum ether. The structure of **6** was established by X-ray analysis of its crystal (Figure S5). Thermal ellipsoids are set at 30% probability.

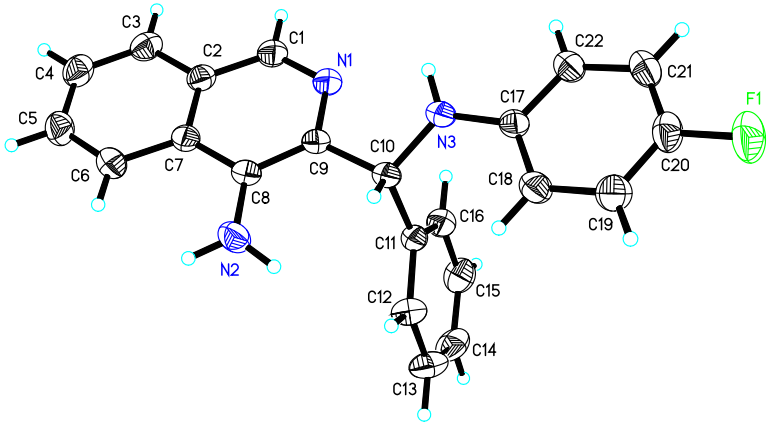


Figure S5. X-ray crystal structure of compound **6**

Crystal data and structure refinement for mo_d8v20253_0m (compound **6**).

Identification code	mo_d8v20253_0m	
Empirical formula	C22 H18 F N3	
Formula weight	343.39	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 18.6906(6) Å	α= 90°.
	b = 8.6187(3) Å	β= 92.8330(10)°.
	c = 21.8032(9) Å	γ = 90°.
Volume	3508.0(2) $Å^3$	
Z	8	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	1440	
Crystal size	0.200 x 0.160 x 0.140 mm^3	
Theta range for data collection	2.603 to 25.998°.	
Index ranges	-22<=h<=22, -10<=k<=10, -26<=l<=21	
Reflections collected	17267	
Independent reflections	3440 [R(int) = 0.0324]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6494	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3440 / 0 / 244	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.1010	
R indices (all data)	R1 = 0.0599, wR2 = 0.1151	
Extinction coefficient	0.0048(10)	
Largest diff. peak and hole	0.301 and -0.287 $e.Å^{-3}$	

The single crystal of **7** was prepared by slow evaporation of its solution in dichloromethane/hexane. The structure of **7** was established by X-ray analysis of its crystal (Figure S6). Thermal ellipsoids are set at 30% probability.

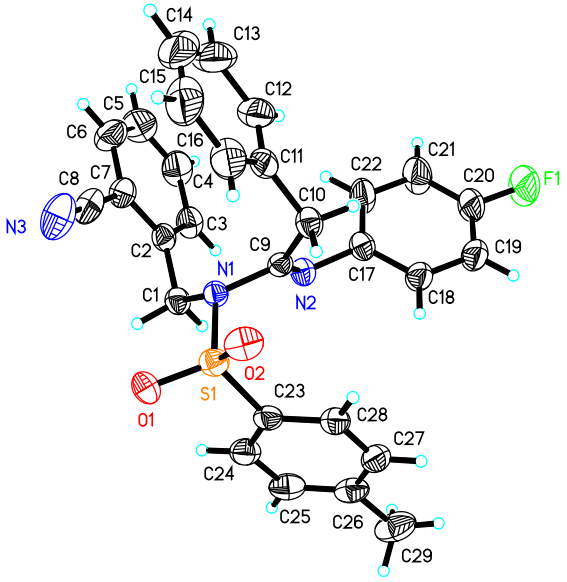
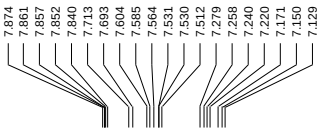


Figure S6. X-ray crystal structure of compound **7**

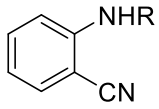
Crystal data and structure refinement for mo_d8v20727_0m (compound **7**).

Identification code	mo_d8v20727_0m	
Empirical formula	C29 H24 F N3 O2 S	
Formula weight	497.57	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 30.093(2) Å	α= 90°.
	b = 8.4008(5) Å	β= 103.592(2)°.
	c = 21.1075(15) Å	γ = 90°.
Volume	5186.7(6) $Å^3$	
Z	8	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.163 mm^{-1}	
F(000)	2080	
Crystal size	0.180 x 0.130 x 0.100 mm^3	
Theta range for data collection	2.522 to 25.999°.	
Index ranges	-34<=h<=36, -10<=k<=10, -26<=l<=26	
Reflections collected	38089	

Independent reflections	5092 [R(int) = 0.0659]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6034
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5092 / 0 / 326
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1178
R indices (all data)	R1 = 0.0931, wR2 = 0.1415
Extinction coefficient	n/a
Largest diff. peak and hole	0.270 and -0.274 e.$Å^{-3}$

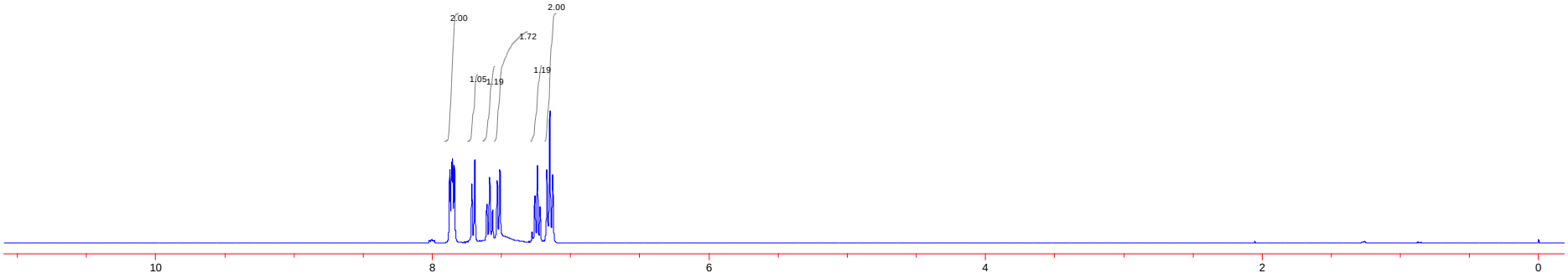


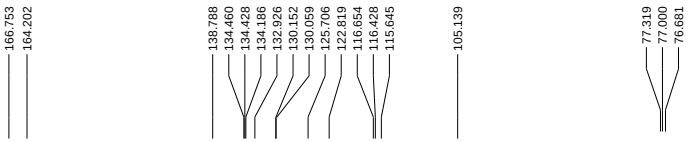
^{1}H NMR (400 MHz, $CDCl_3$)



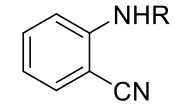
SS-1c

R = SO_2(*p*-FC_6H_4)



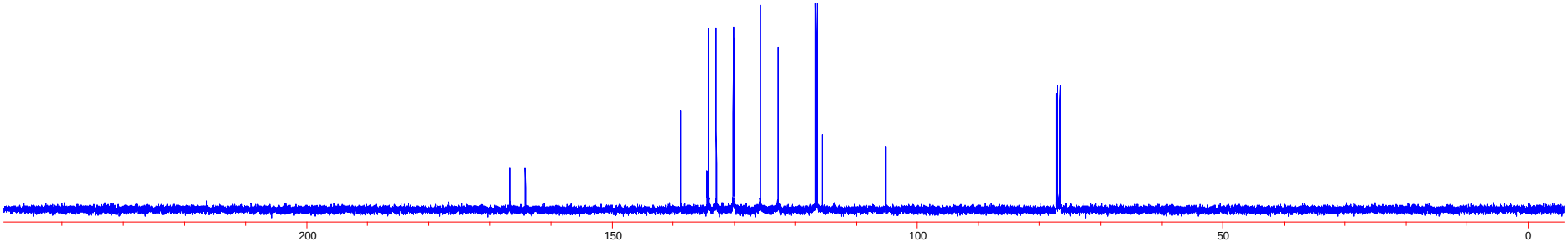


^{13}C NMR (100 MHz, $CDCl_3$)

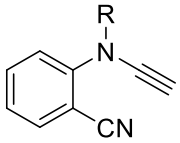


SS-1c

R = SO_2(*p*-FC_6H_4)

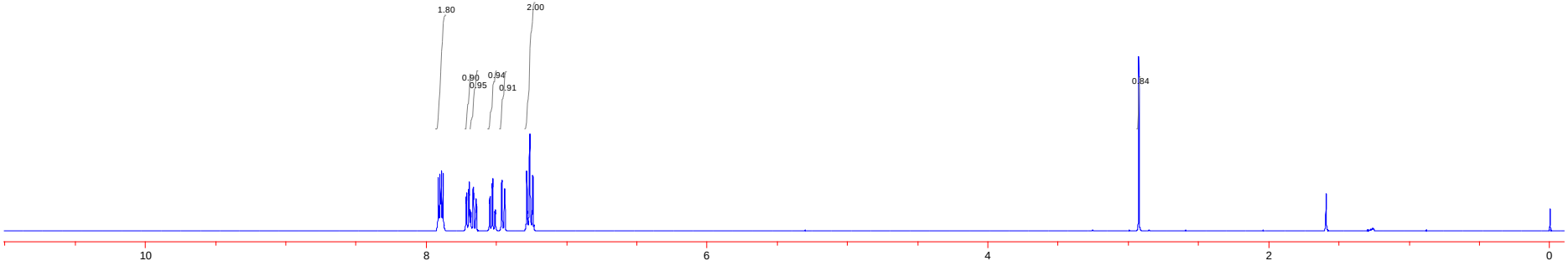


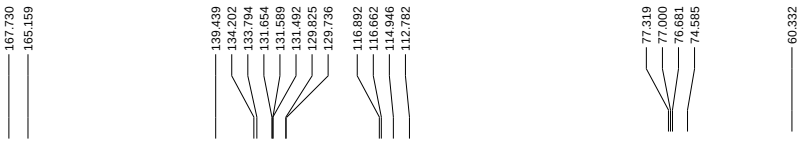
^{1}H NMR (400 MHz, $CDCl_3$)



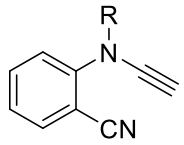
S-1c

R = SO_2(*p*-FC_6H_4)



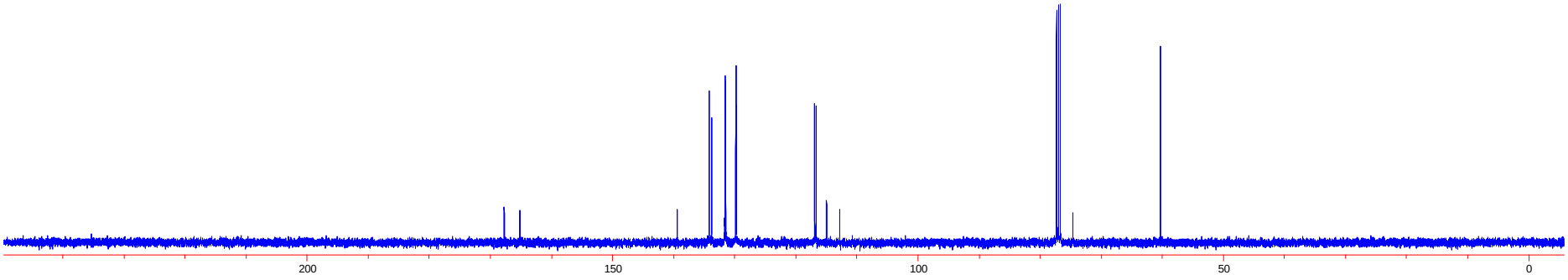


^{13}C NMR (100 MHz, $CDCl_3$)

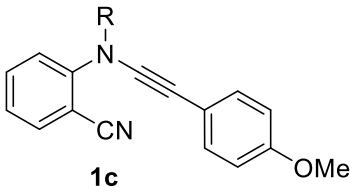


S-1c

R = SO_2(*p*-FC_6H_4)

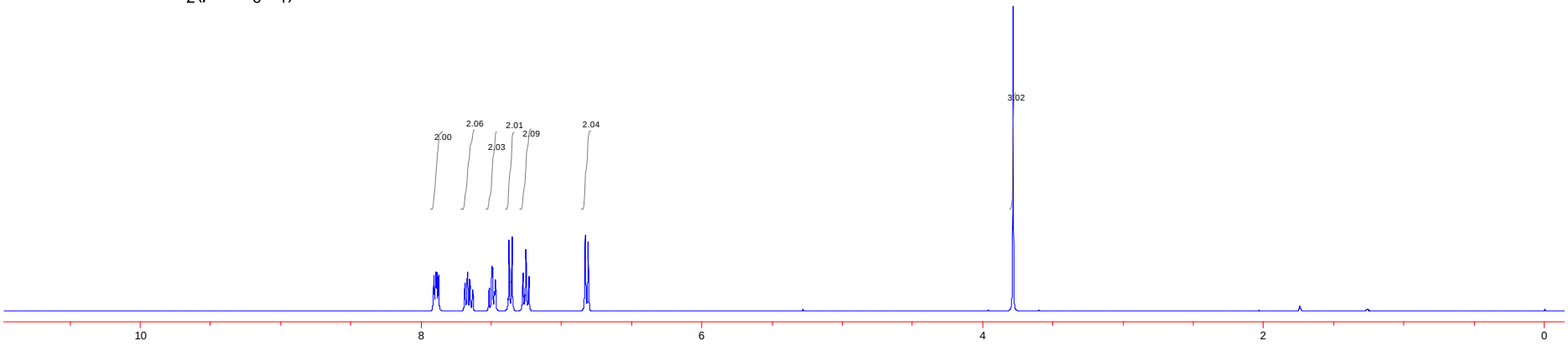


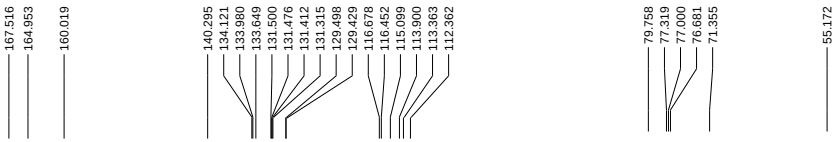
^{1}H NMR (400 MHz, $CDCl_3$)



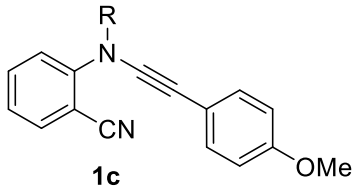
1c

R = SO_2(*p*-FC_6H_4)



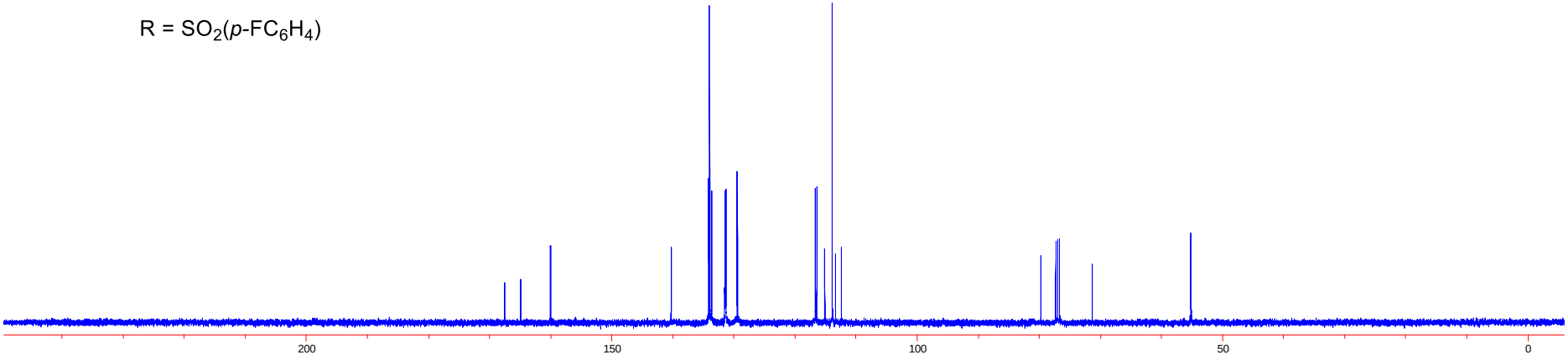


^{13}C NMR (100 MHz, $CDCl_3$)

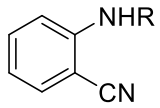


1c

R = SO_2(*p*-FC_6H_4)

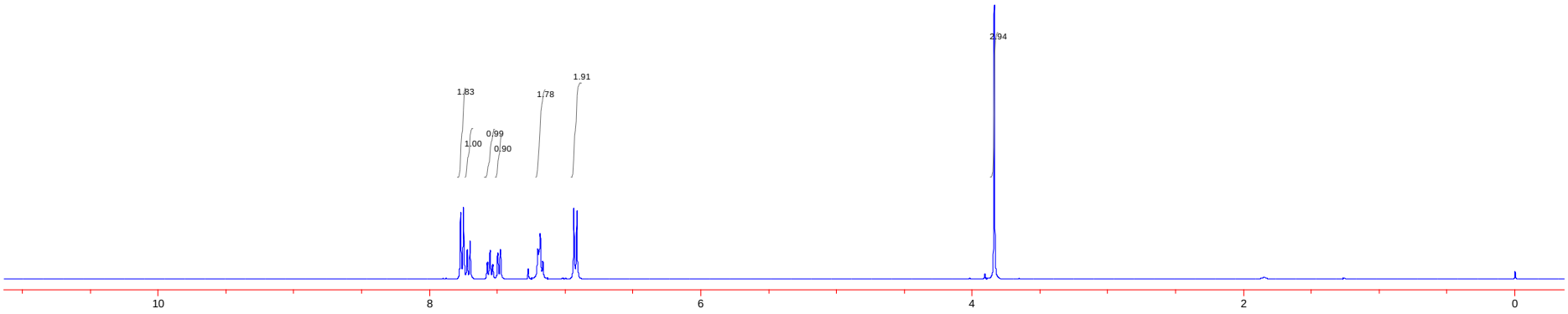


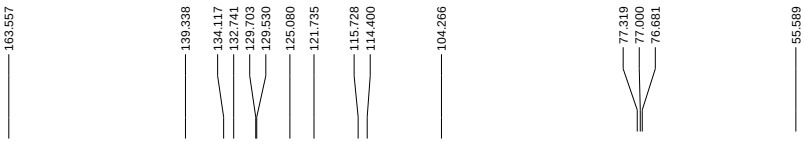
^{1}H NMR (400 MHz, $CDCl_3$)



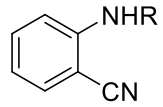
SS-1d

R = SO_2(*p*-$OMeC_6H_4$)



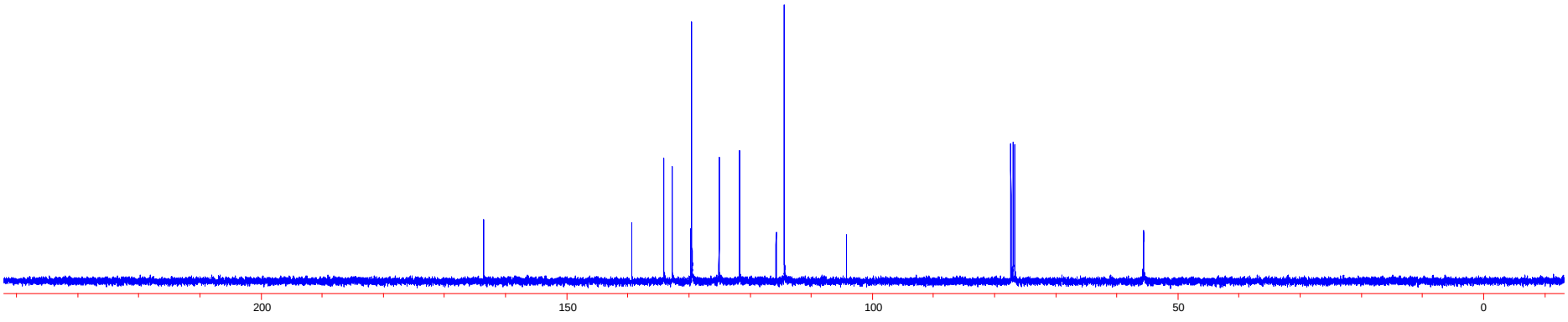


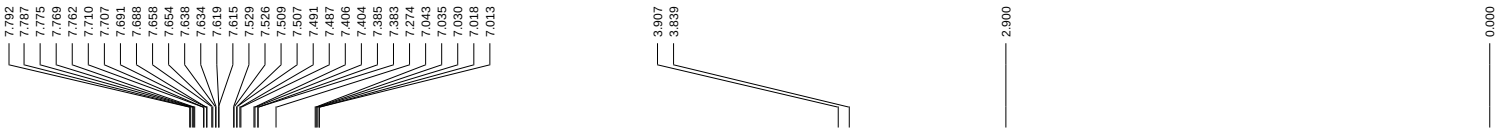
^{13}C NMR (100 MHz, $CDCl_3$)



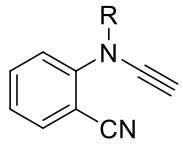
SS-1d

R = SO_2(*p*-$OMeC_6H_4$)



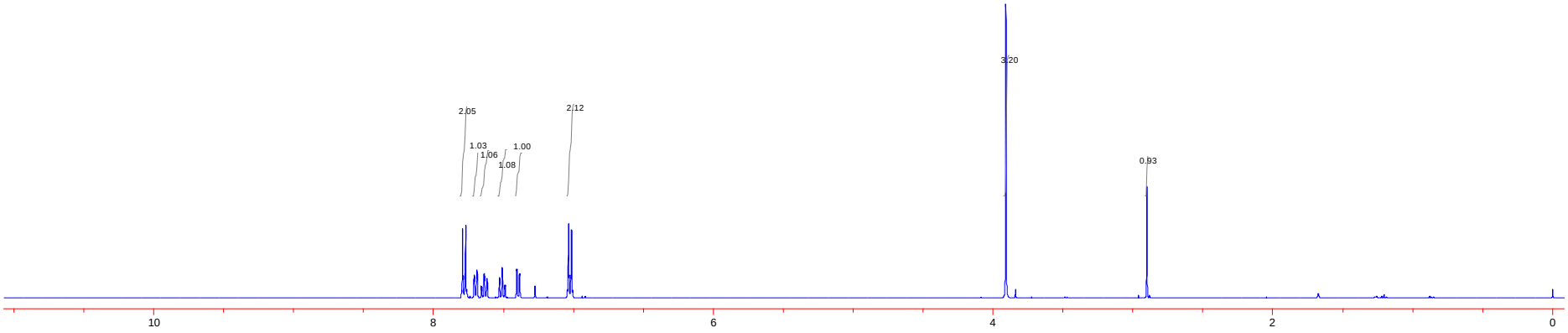


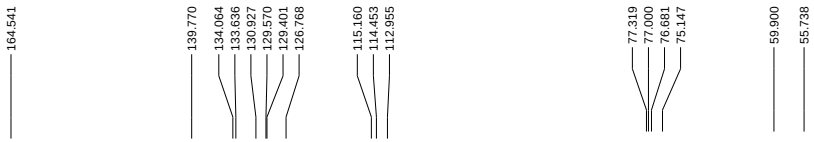
^{1}H NMR (400 MHz, $CDCl_3$)



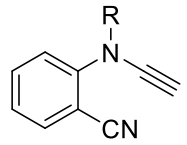
R = SO_2(*p*-$OMeC_6H_4$)

S-1d



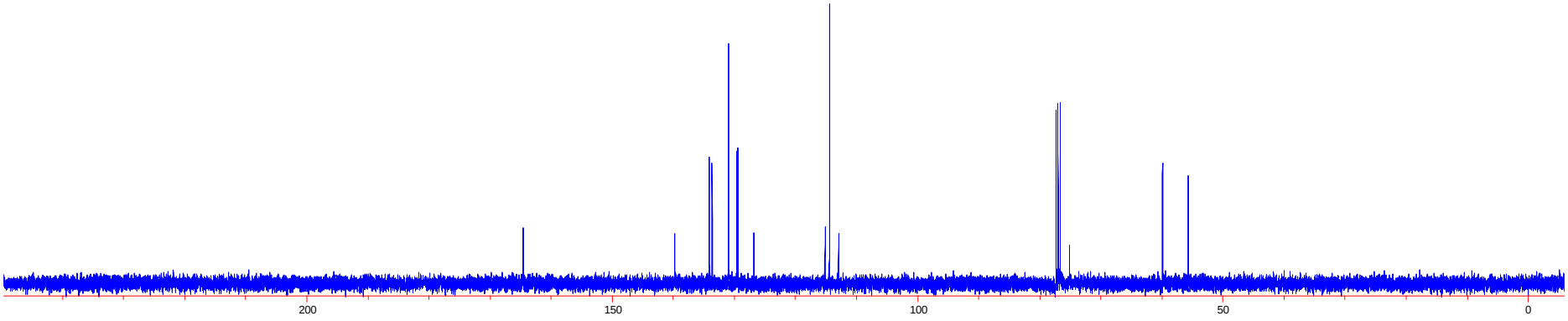


^{13}C NMR (100 MHz, $CDCl_3$)

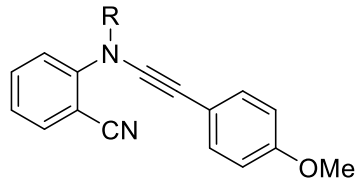


R = SO_2(*p*-$OMeC_6H_4$)

S-1d

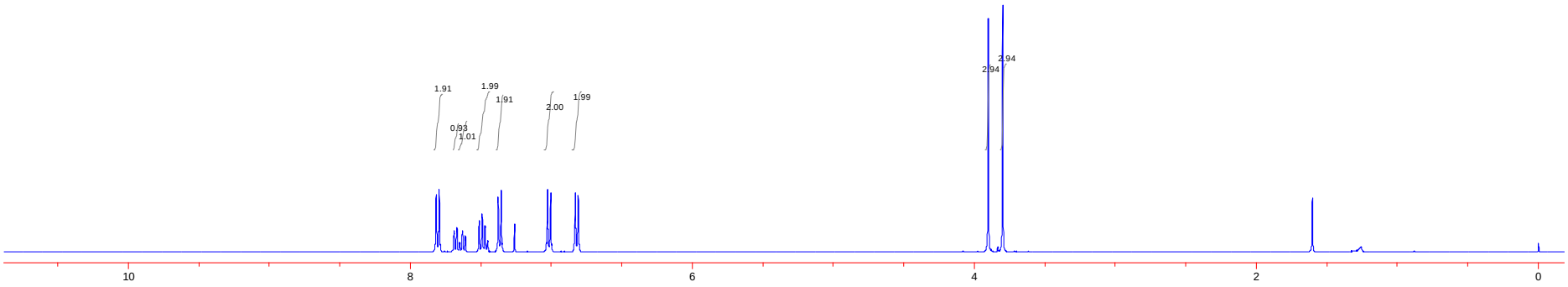


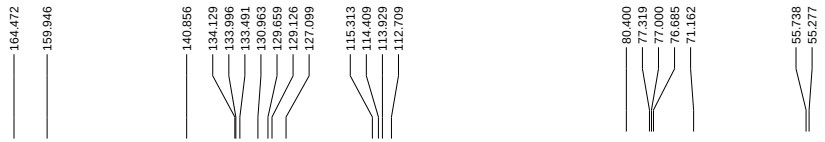
^{1}H NMR (400 MHz, $CDCl_3$)



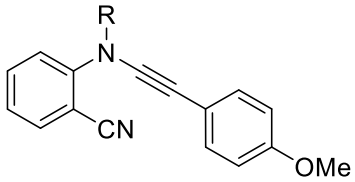
R = SO_2(*p*-$OMeC_6H_4$)

1d



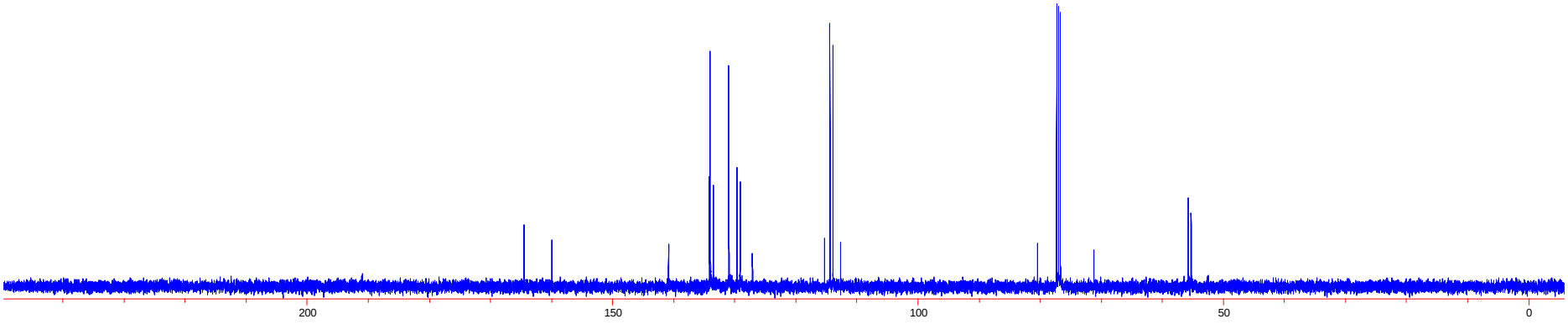


^{13}C NMR (100 MHz, $CDCl_3$)

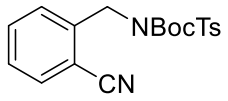


R = SO_2(*p*-$OMeC_6H_4$)

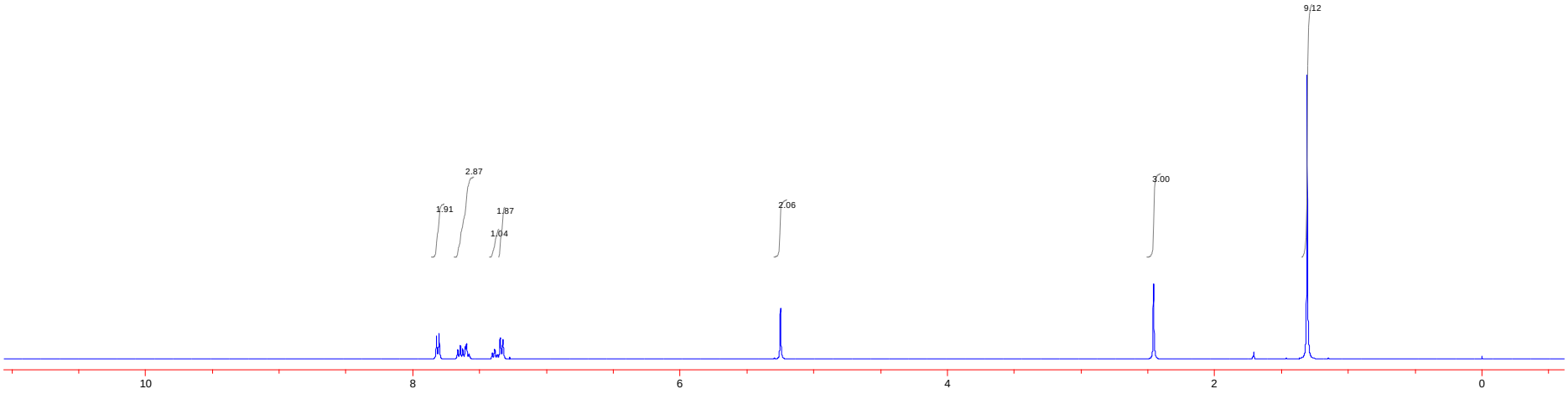
1d

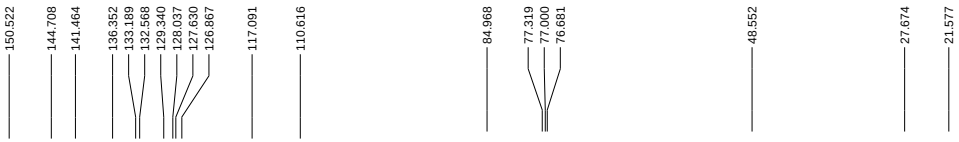


^{1}H NMR (400 MHz, $CDCl_3$)

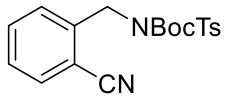


SS-5

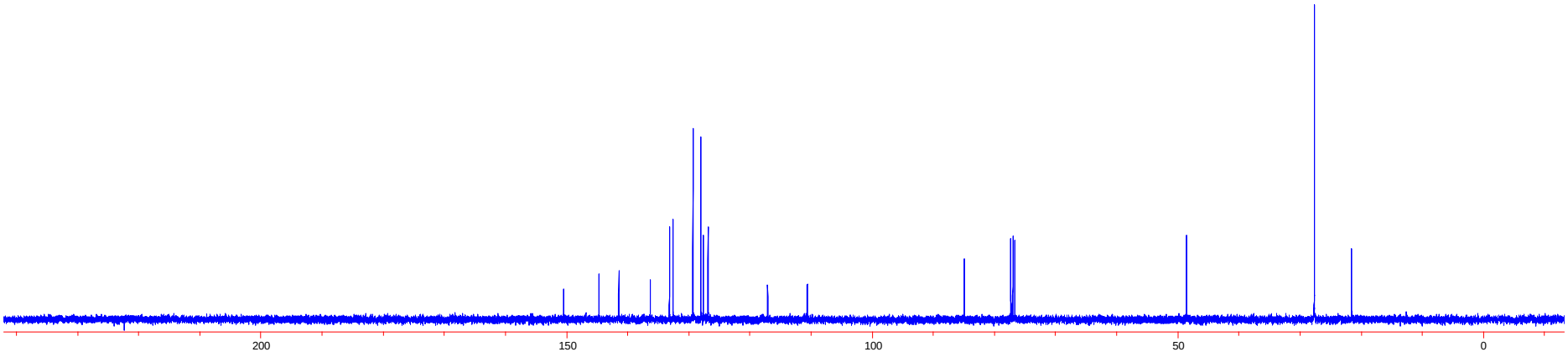




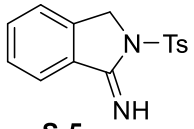
^{13}C NMR (100 MHz, $CDCl_3$)



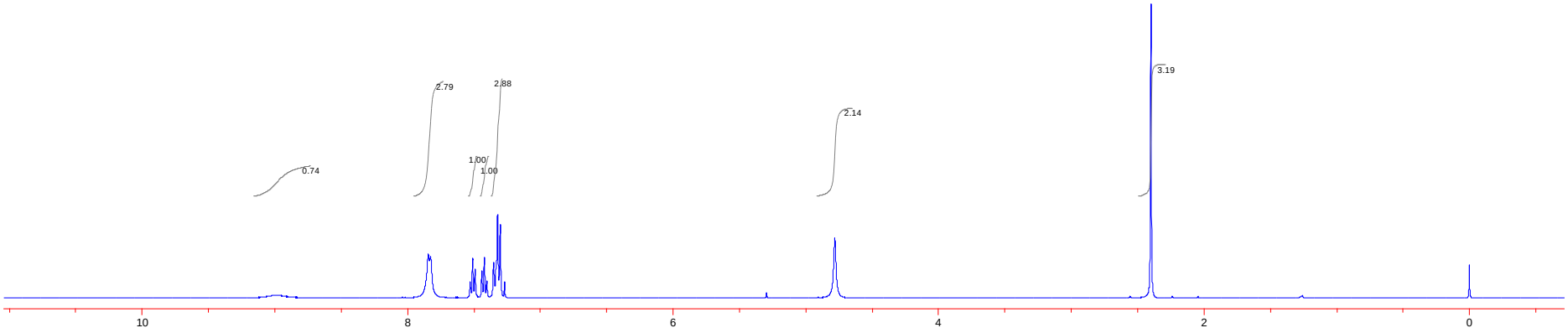
SS-5

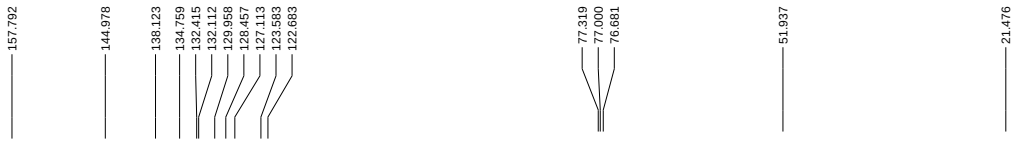


^{1}H NMR (400 MHz, $CDCl_3$)

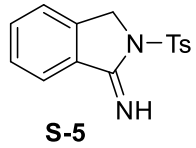


S-5

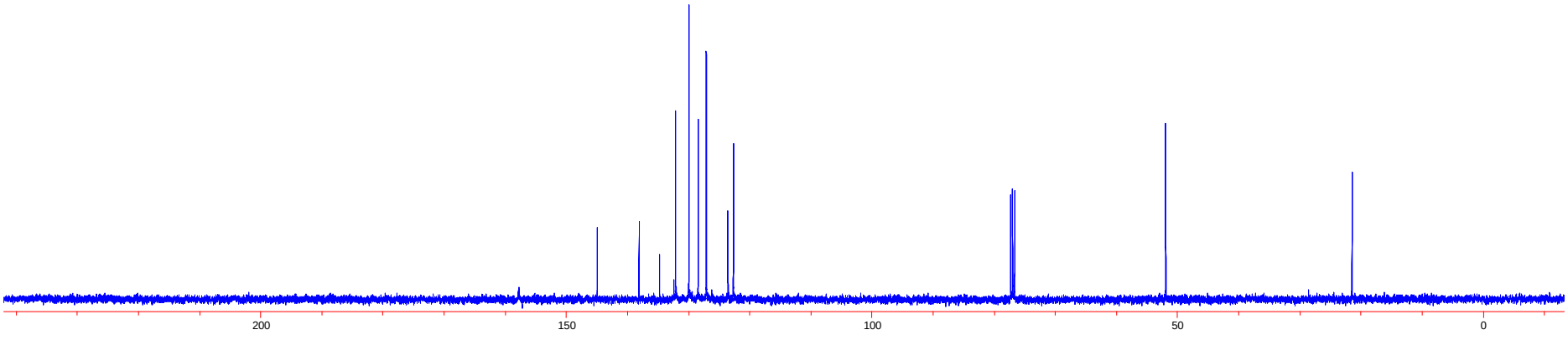


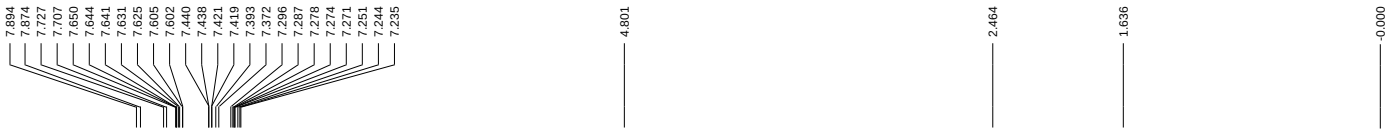


^{13}C NMR (100 MHz, $CDCl_3$)

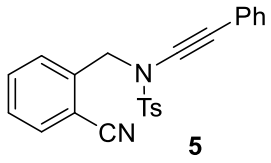


S-5





^{1}H NMR (400 MHz, $CDCl_3$)



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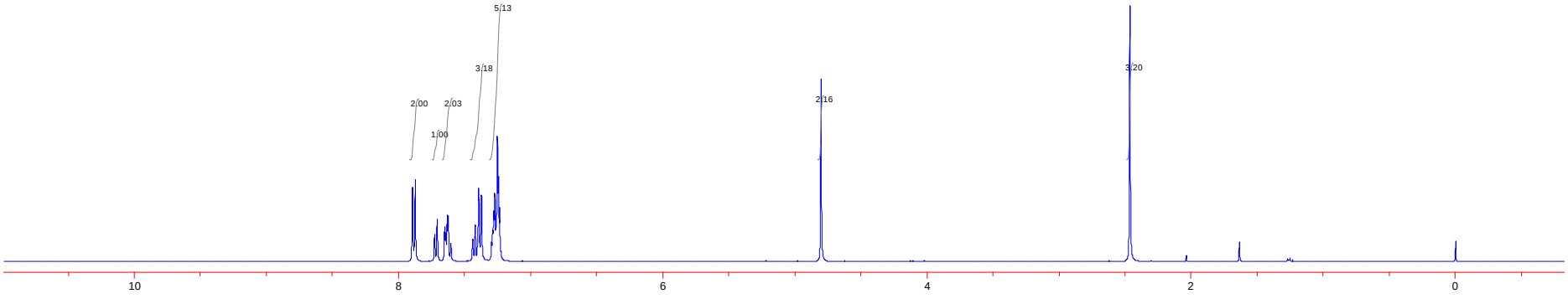
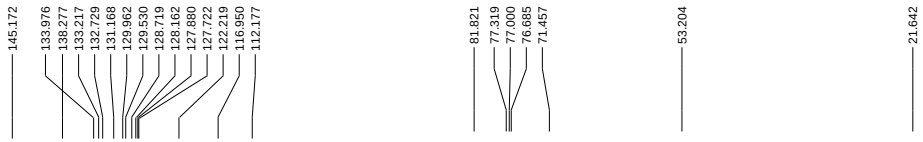
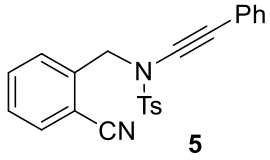




^{13}C NMR (100 MHz, $CDCl_3$)



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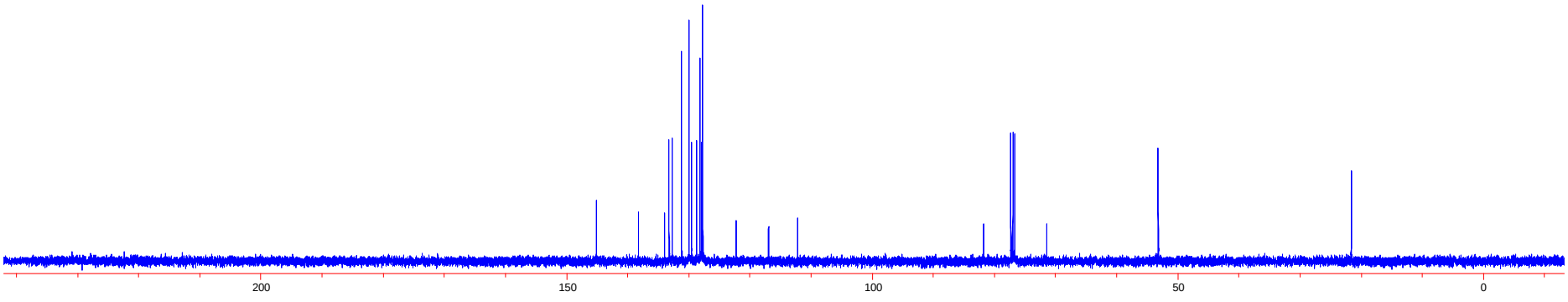
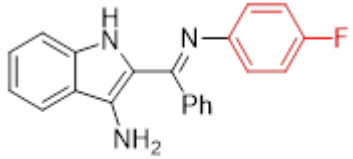
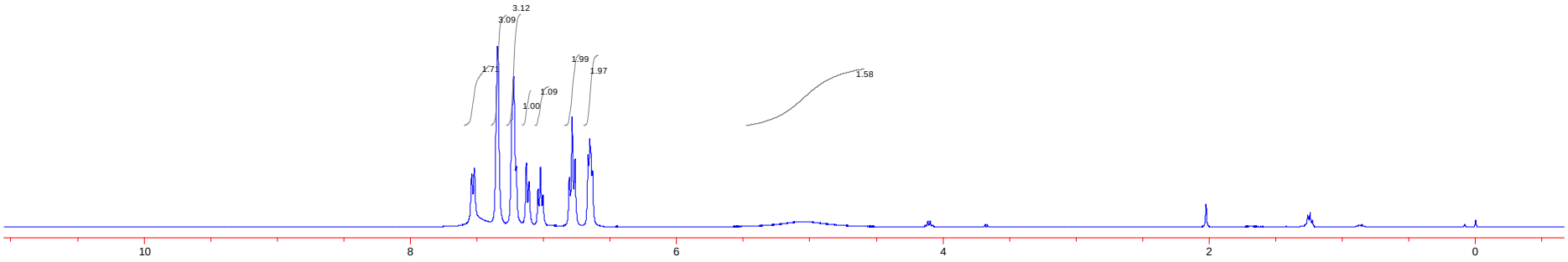
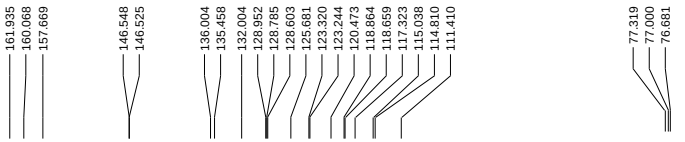


^{1}H NMR (400 MHz, $CDCl_3$)

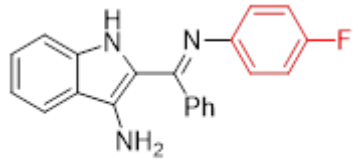


3a

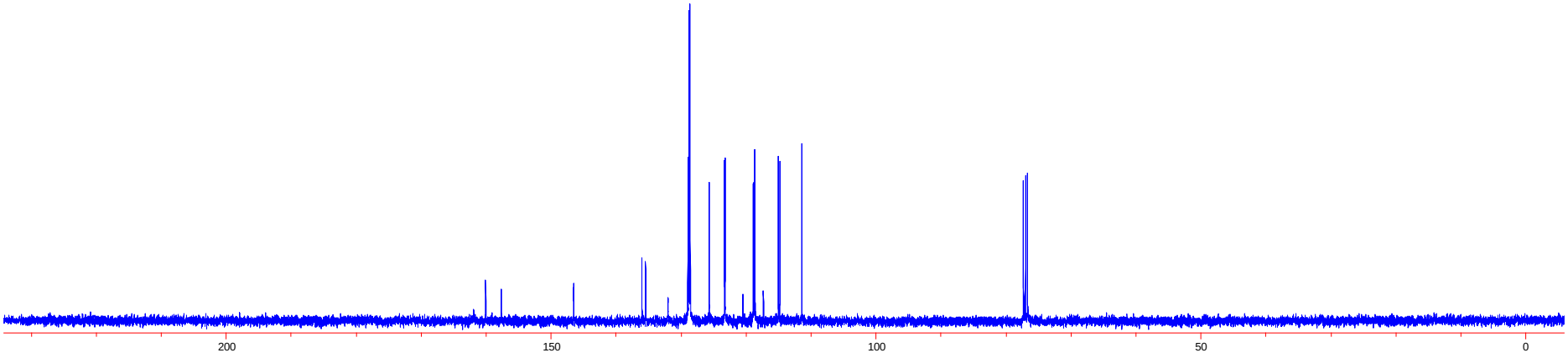


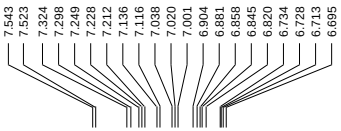


^{13}C NMR (100 MHz, $CDCl_3$)

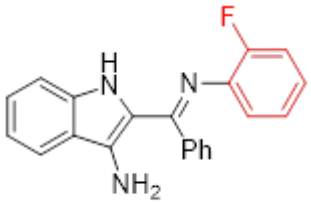


3a





^{1}H NMR (400 MHz, $CDCl_3$)



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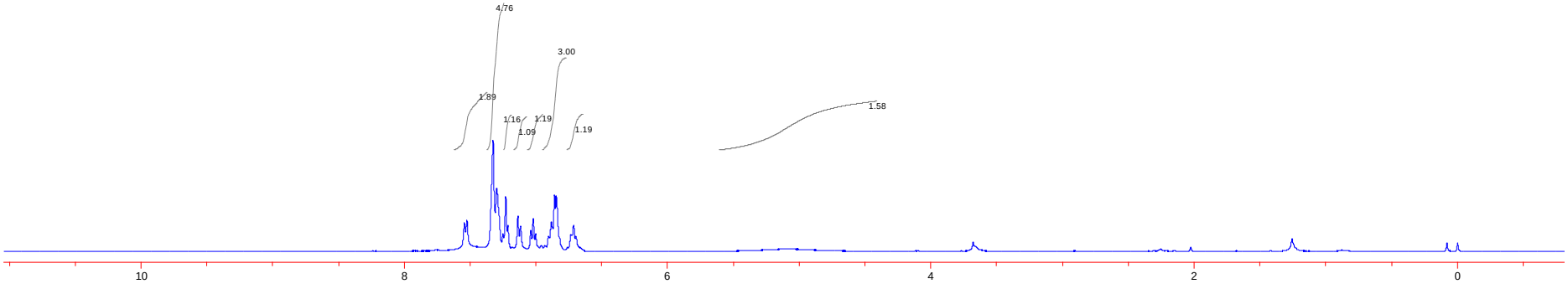
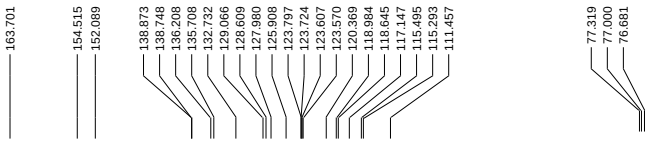
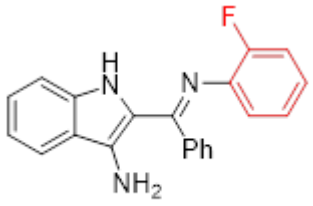




^{13}C NMR (100 MHz, $CDCl_3$)



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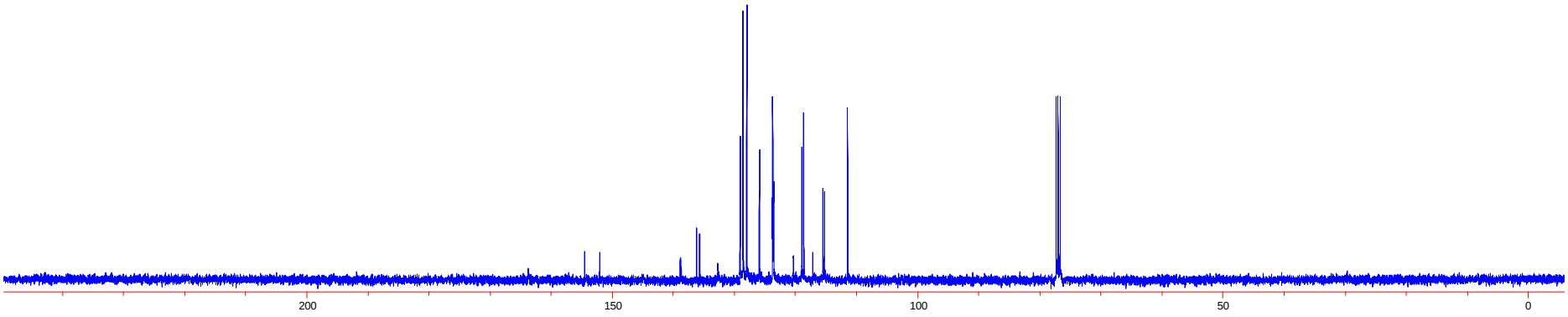
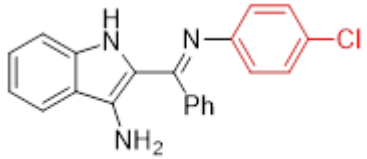


^{1}H NMR (400 MHz, $CDCl_3$)



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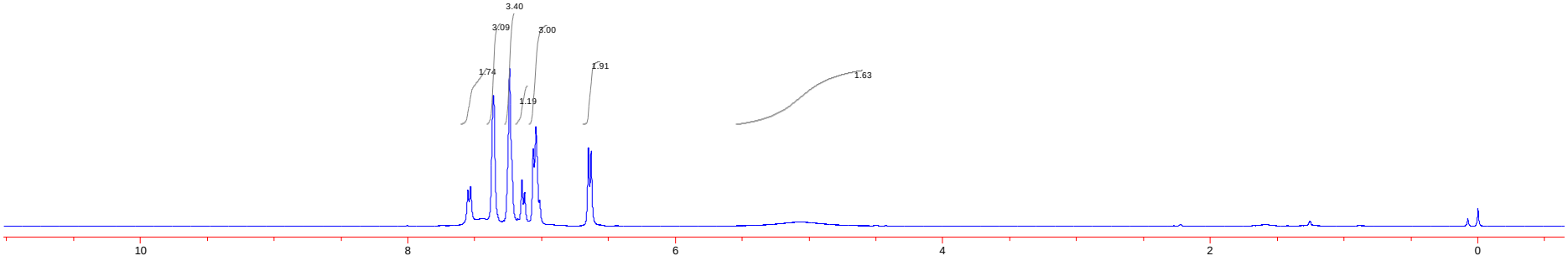
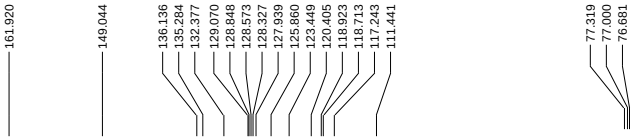
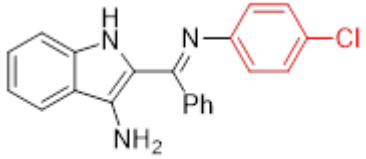




^{13}C NMR (100 MHz, $CDCl_3$)



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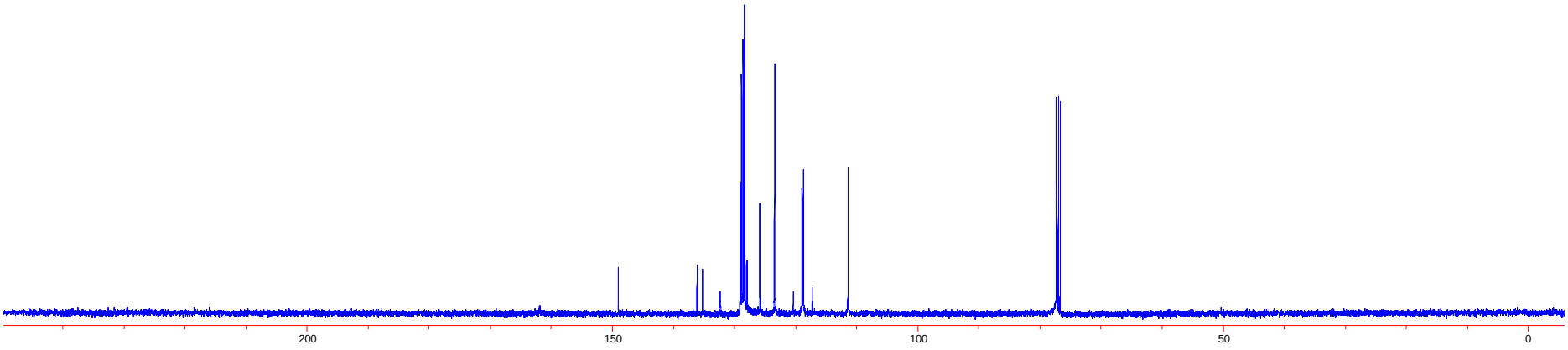
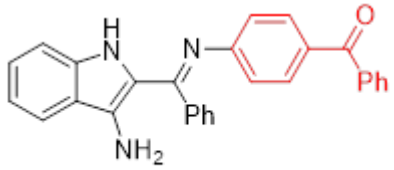


^{1}H NMR (400 MHz, $CDCl_3$)



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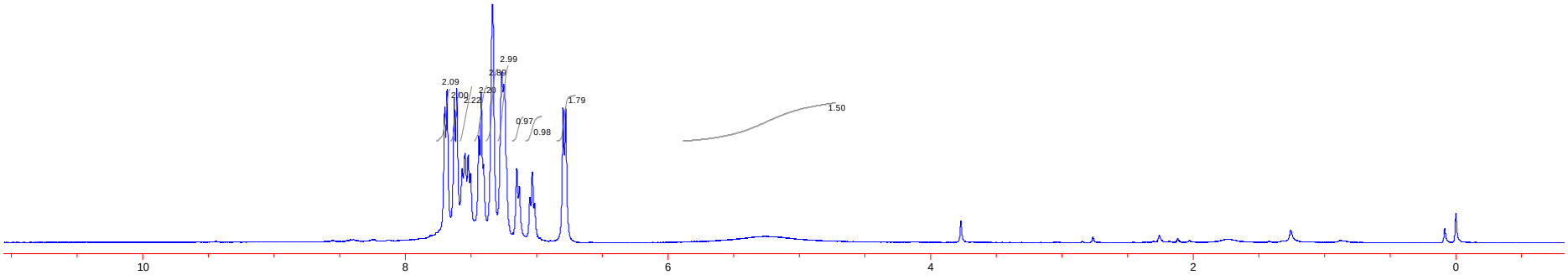
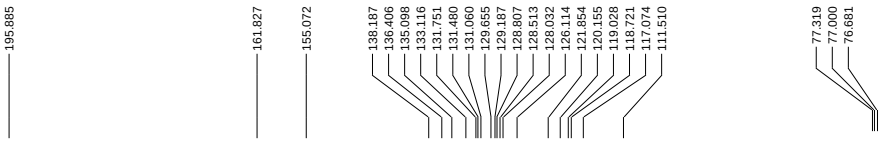
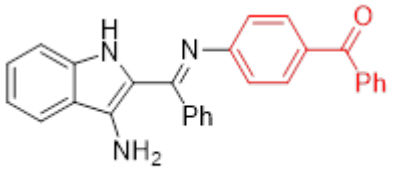




^{13}C NMR (100 MHz, $CDCl_3$)



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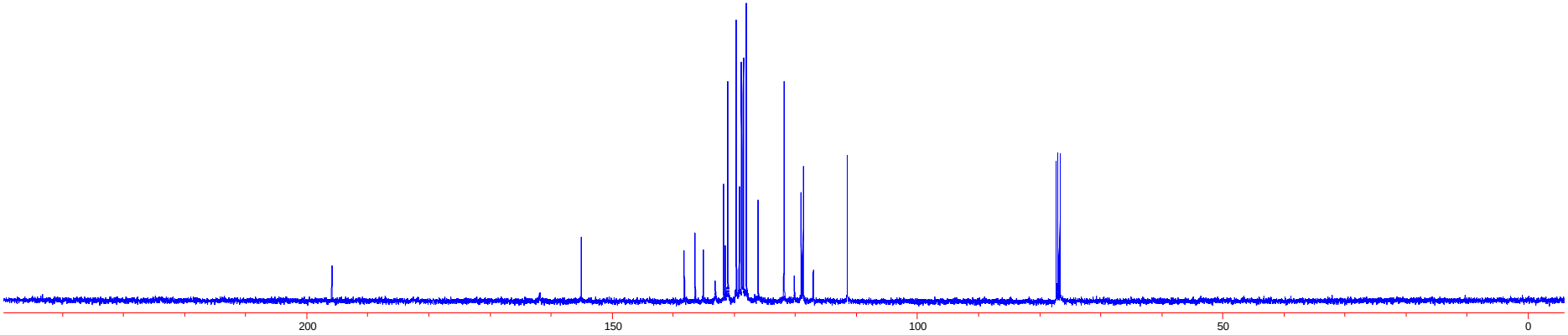
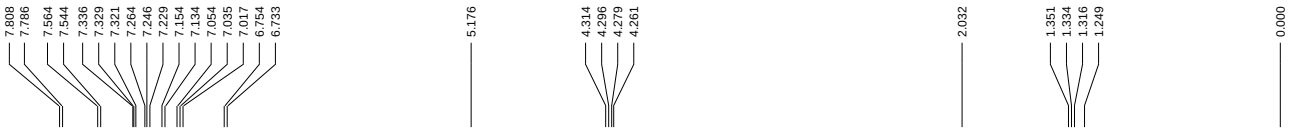
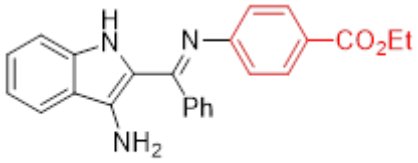




^{1}H NMR (400 MHz, $CDCl_3$)



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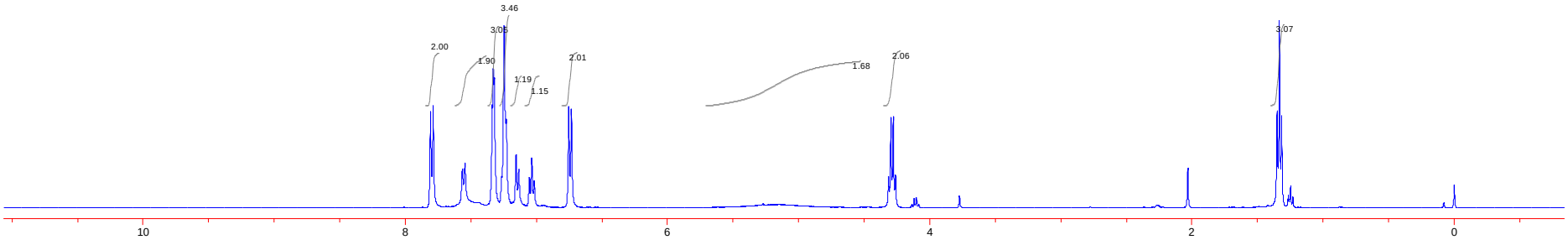
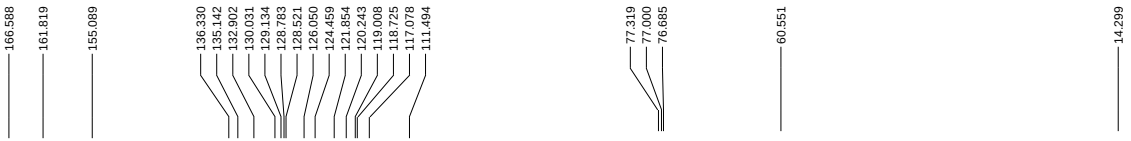
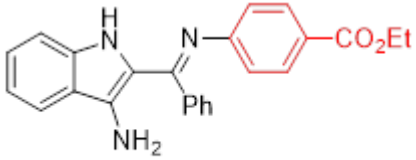




^{13}C NMR (100 MHz, $CDCl_3$)



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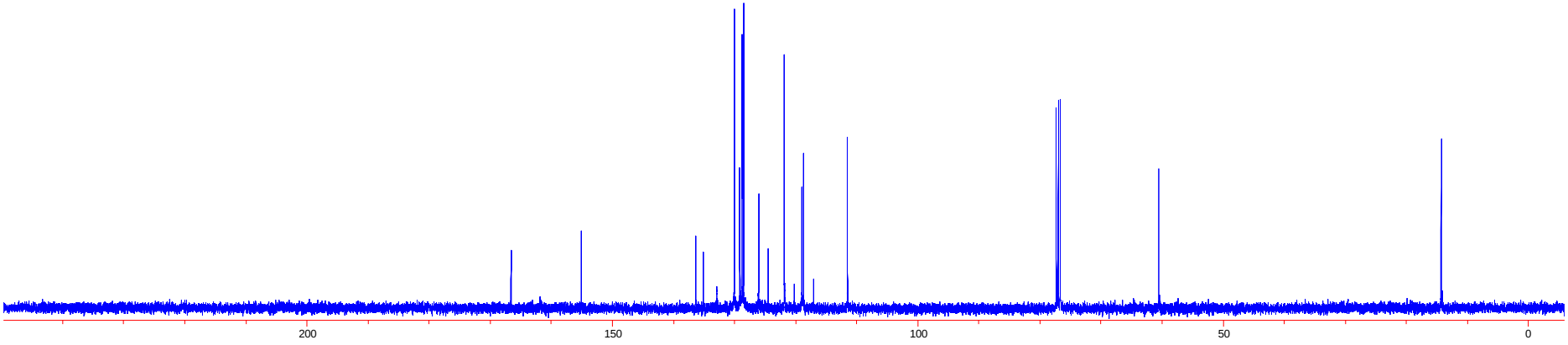
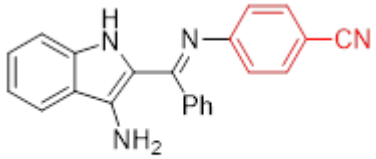


^{1}H NMR (400 MHz, $CDCl_3$)



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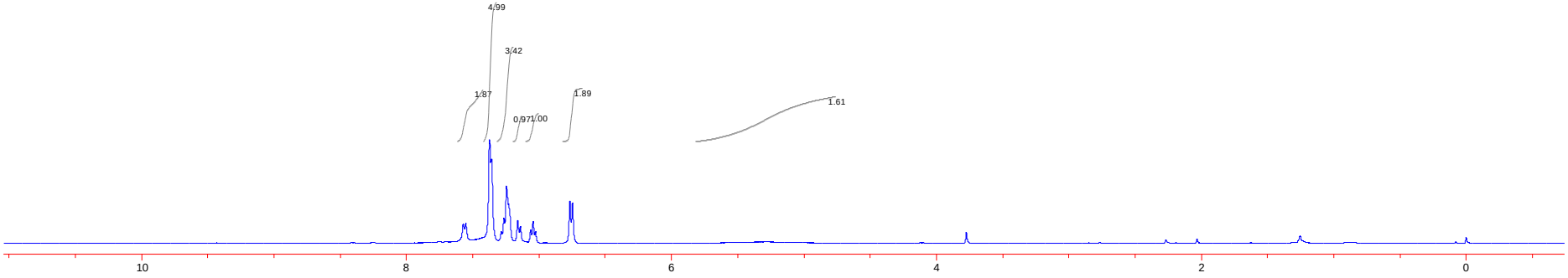
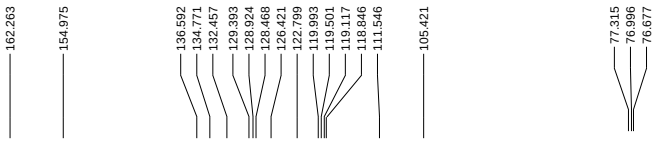
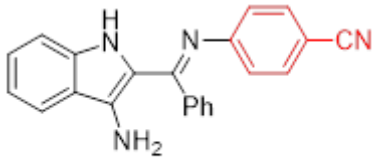




^{13}C NMR (100 MHz, $CDCl_3$)



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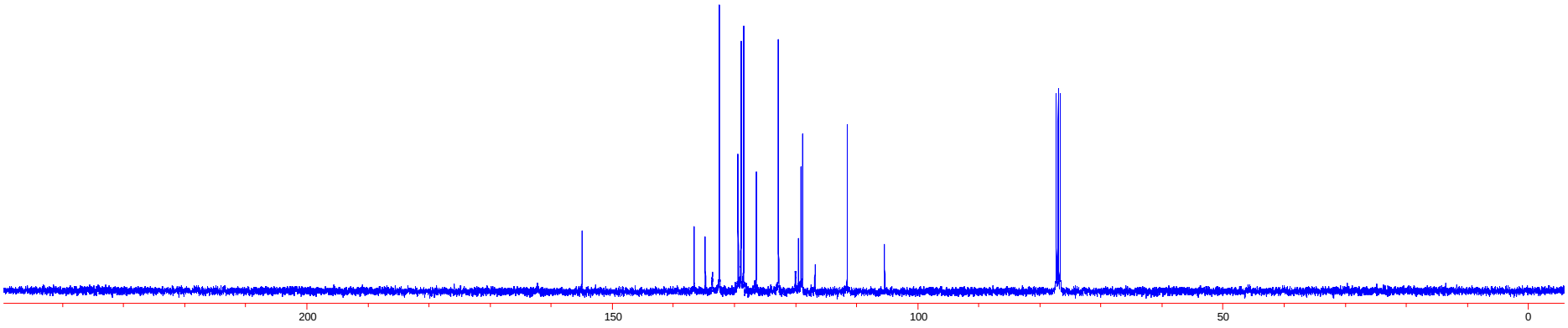
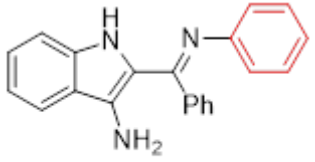


^{1}H NMR (400 MHz, $CDCl_3$)



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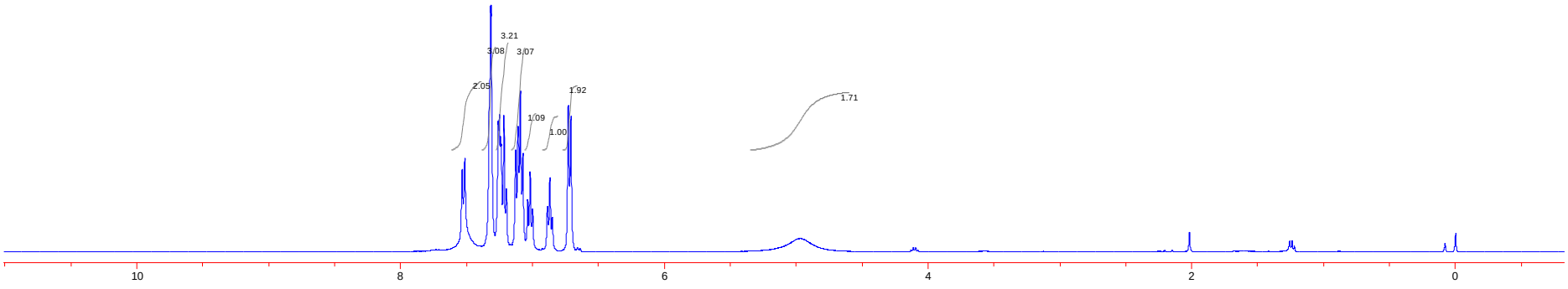
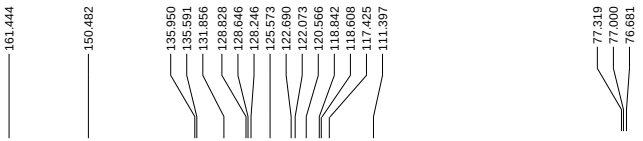
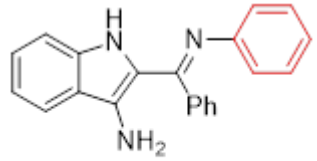




^{13}C NMR (100 MHz, $CDCl_3$)



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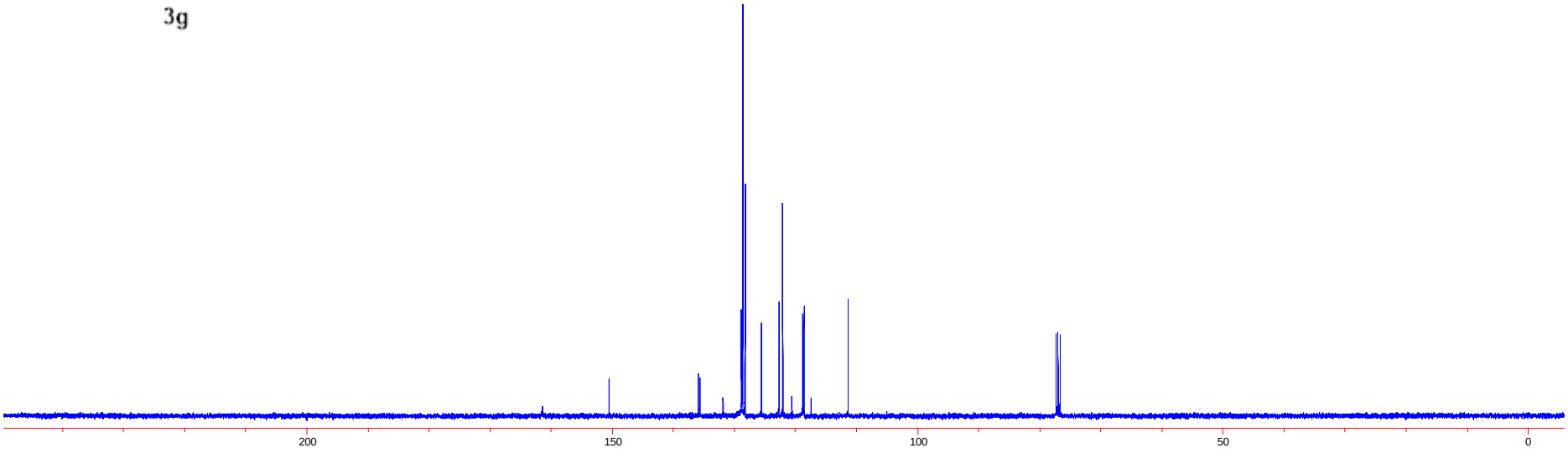
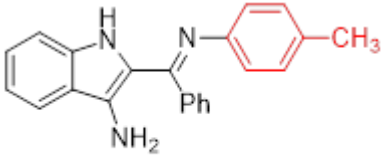


^{1}H NMR (400 MHz, $CDCl_3$)



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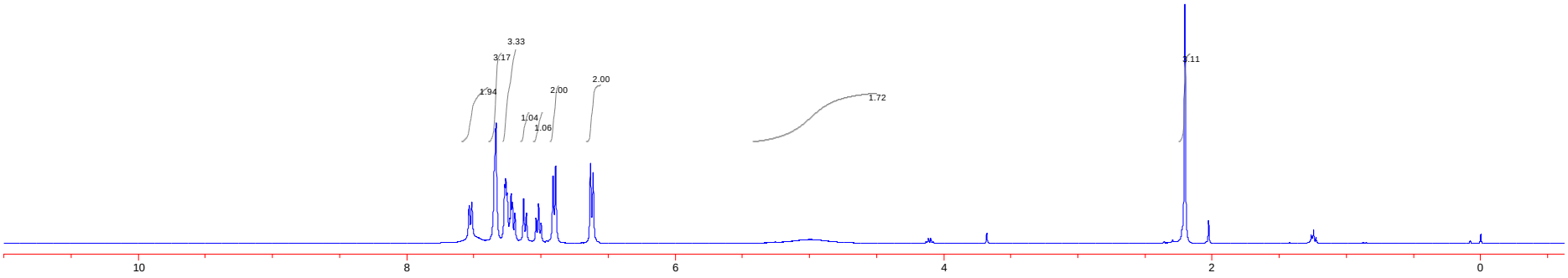
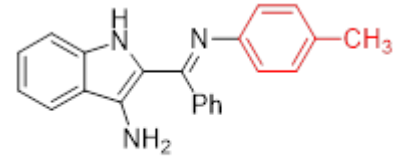


^{13}C NMR (100 MHz, $CDCl_3$)



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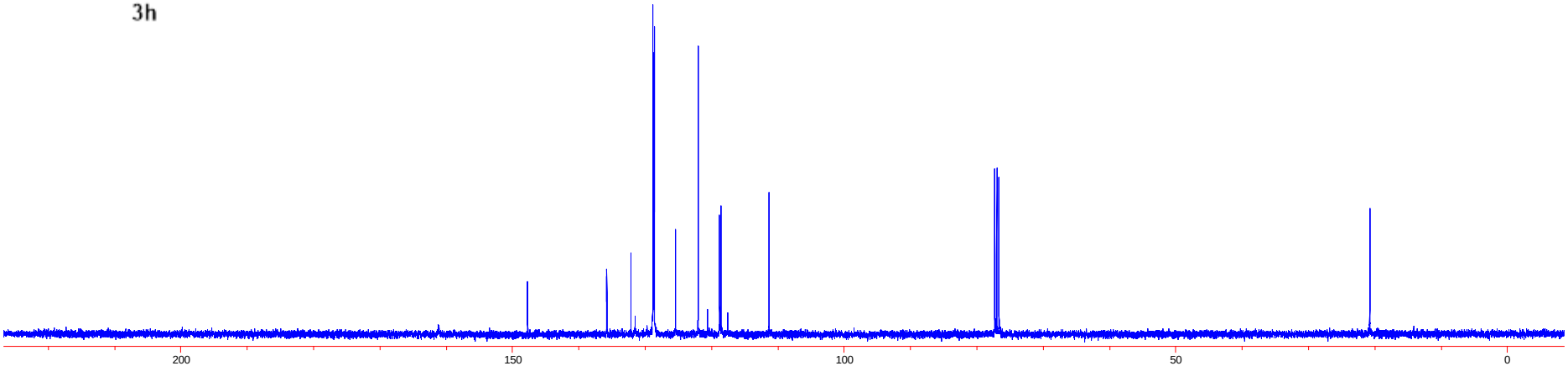
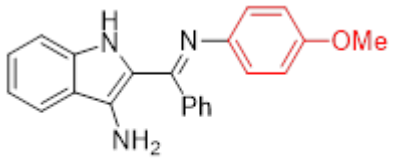


^{1}H NMR (400 MHz, $CDCl_3$)



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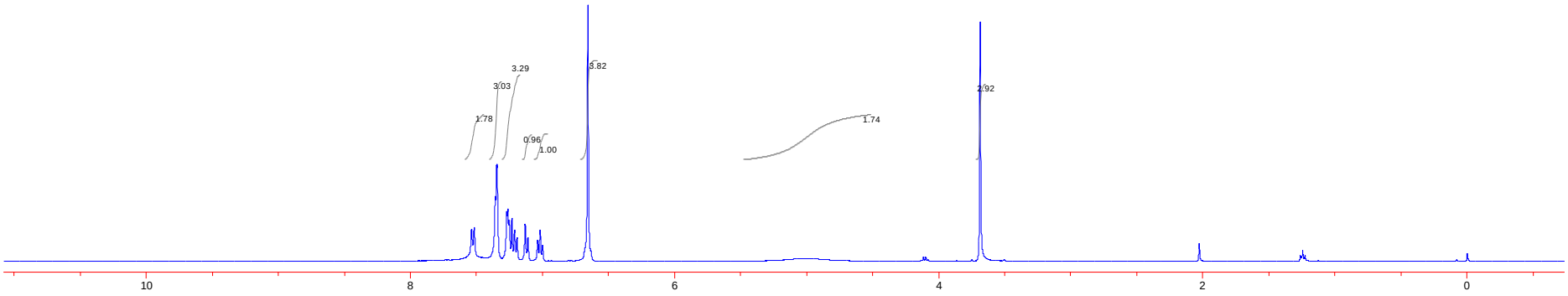
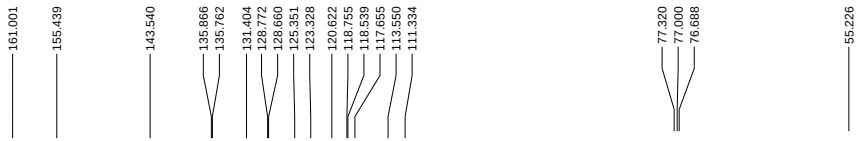
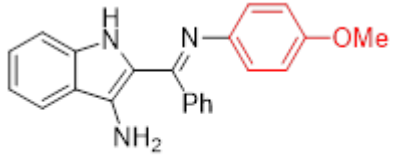




^{13}C NMR (100 MHz, $CDCl_3$)



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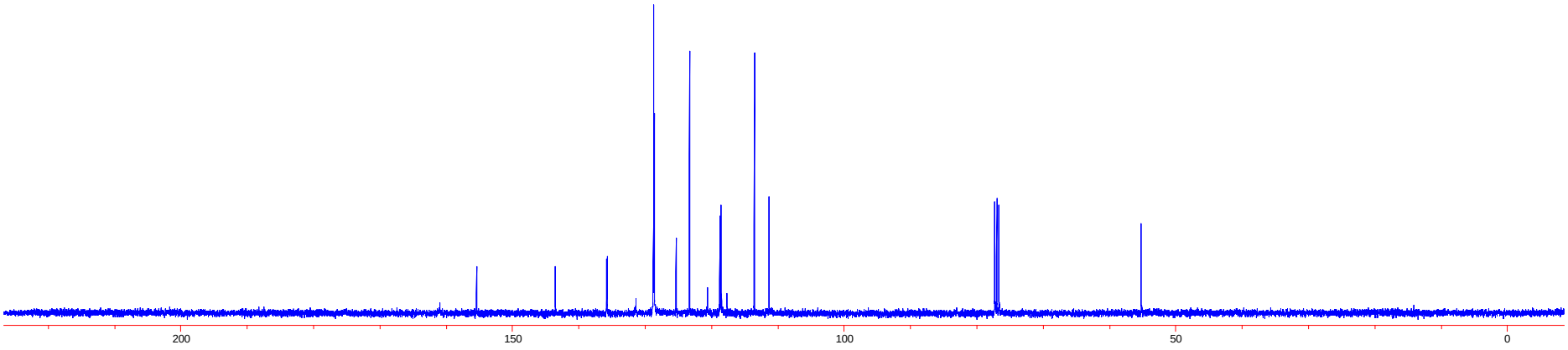
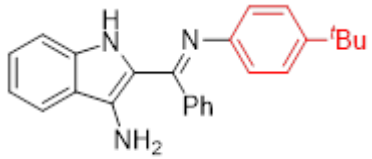


^{1}H NMR (400 MHz, $CDCl_3$)



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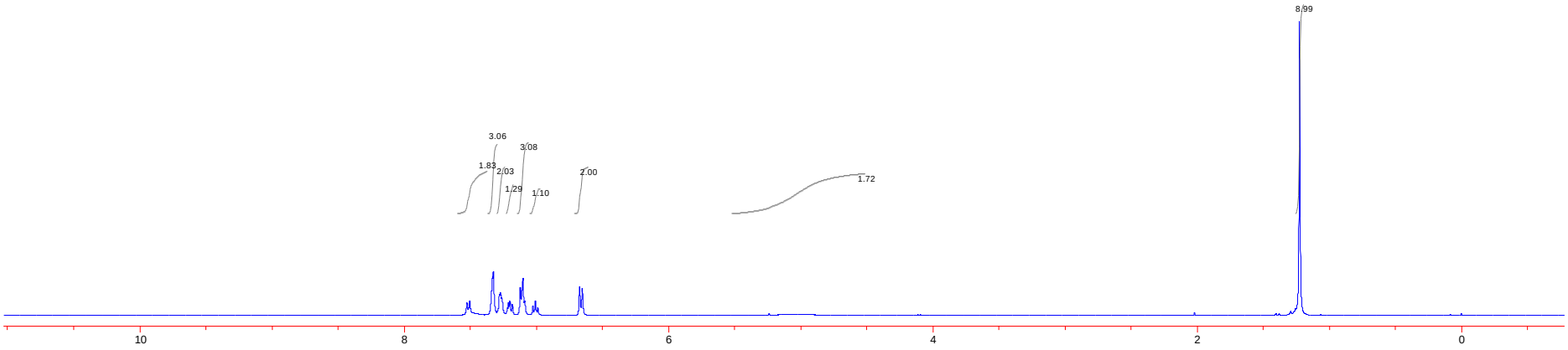
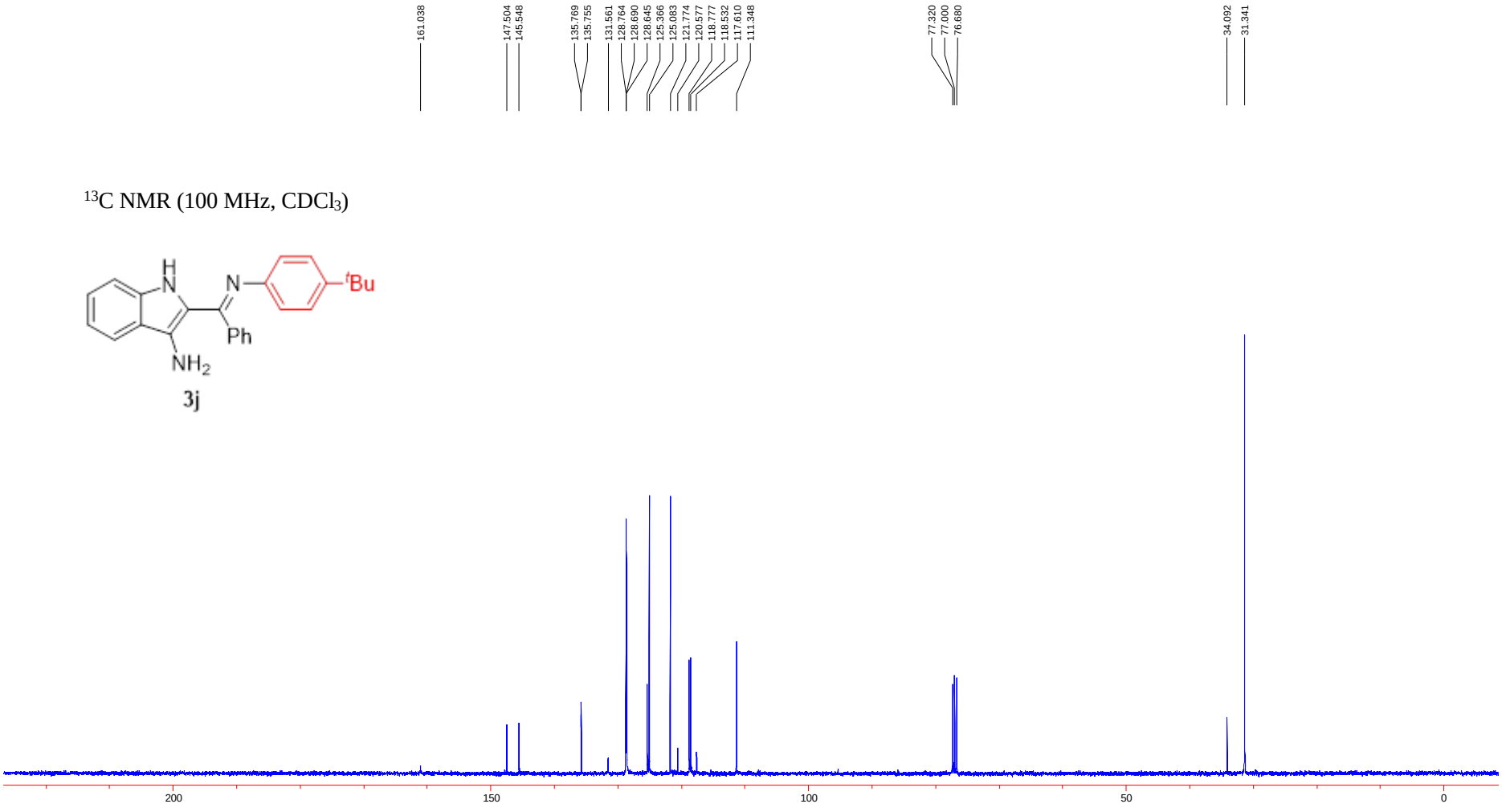
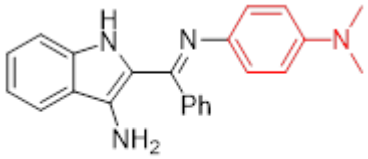




^{13}C NMR (100 MHz, $CDCl_3$)

3j

^{1}H NMR (400 MHz, $CDCl_3$)



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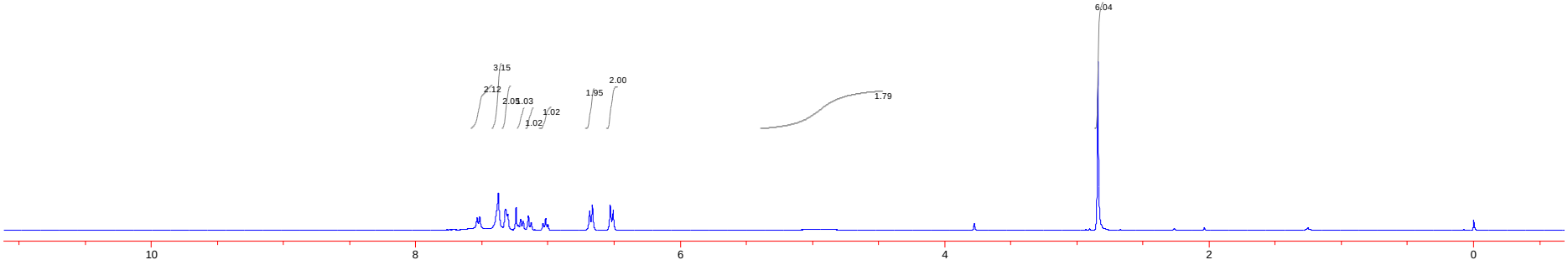
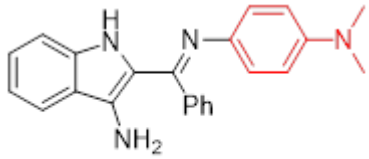


^{13}C NMR (100 MHz, $CDCl_3$)



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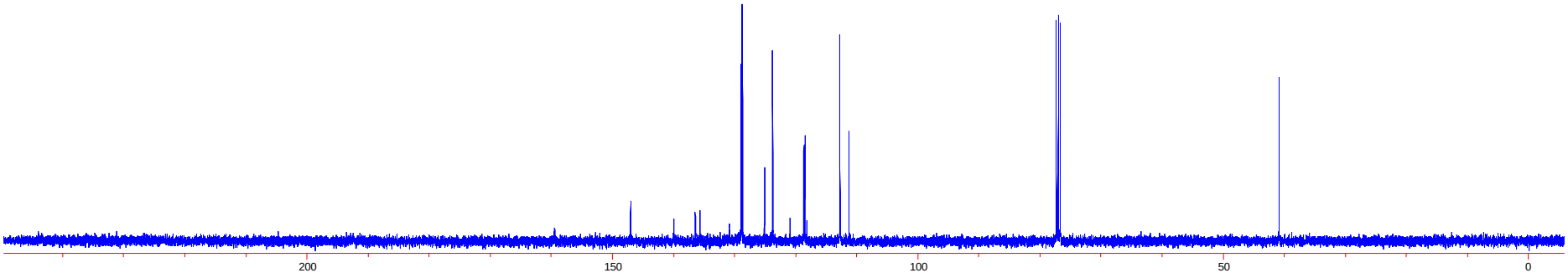
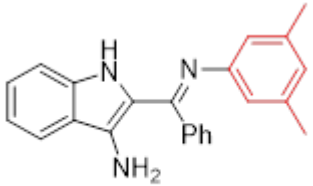


^{1}H NMR (400 MHz, $CDCl_3$)



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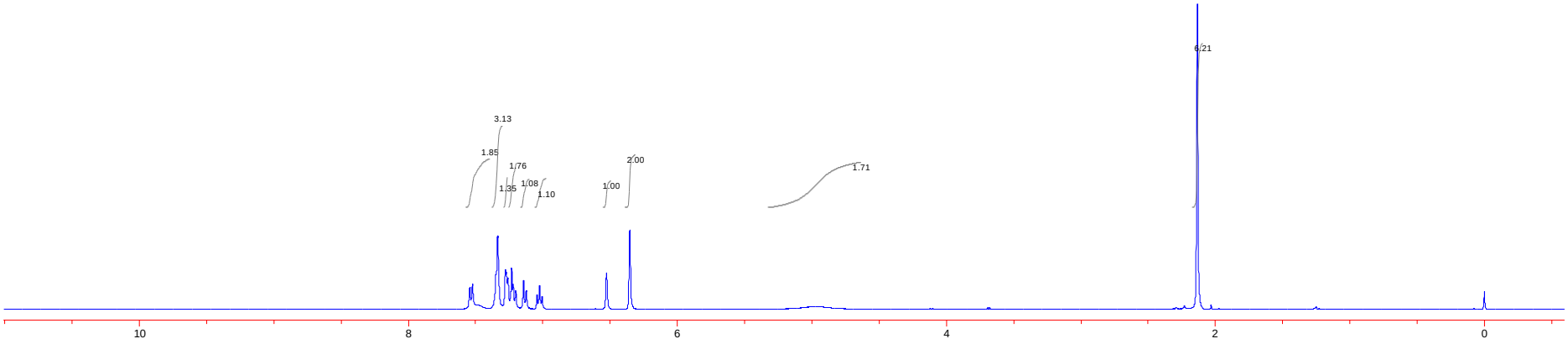
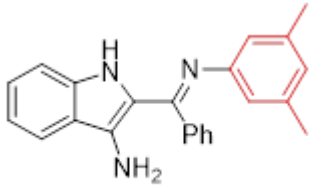


^{13}C NMR (100 MHz, $CDCl_3$)



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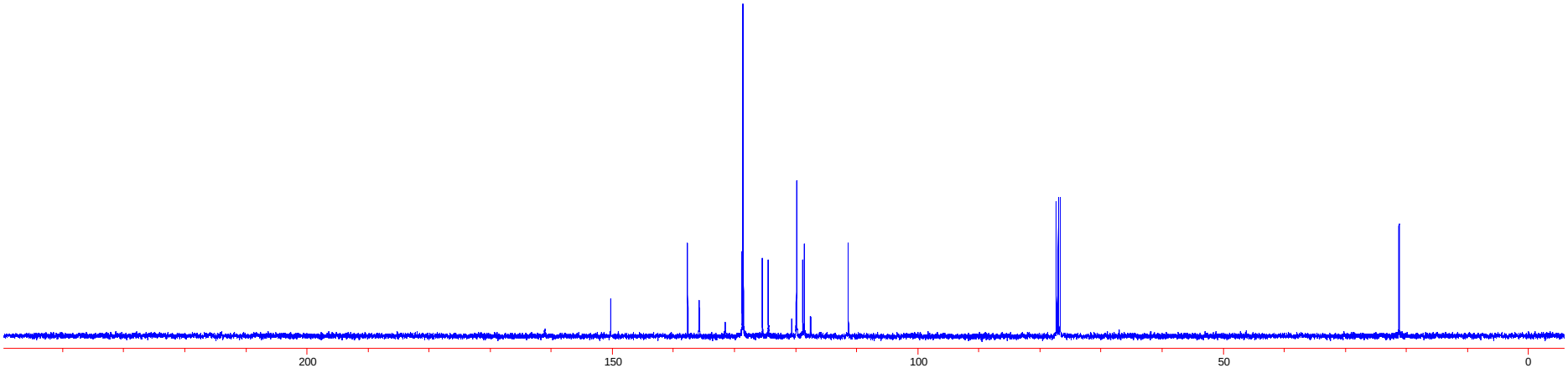
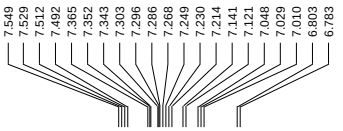
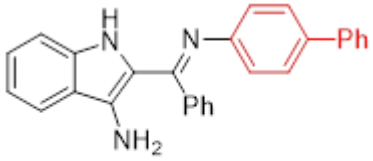




^{1}H NMR (400 MHz, $CDCl_3$)



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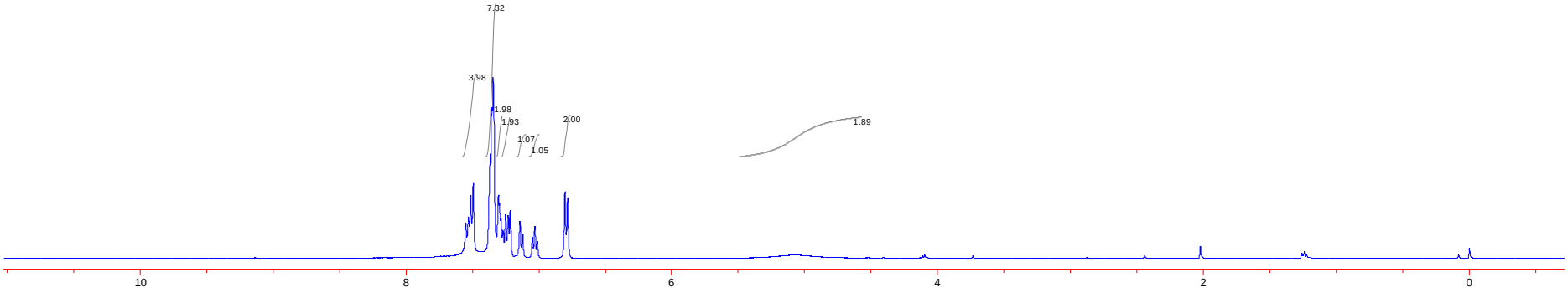
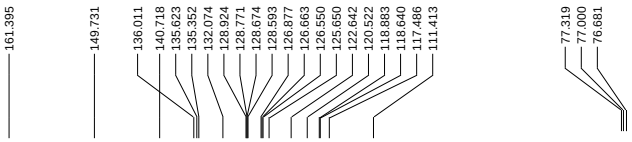
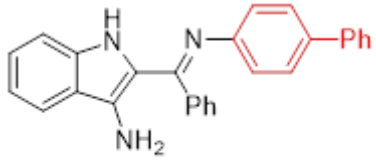
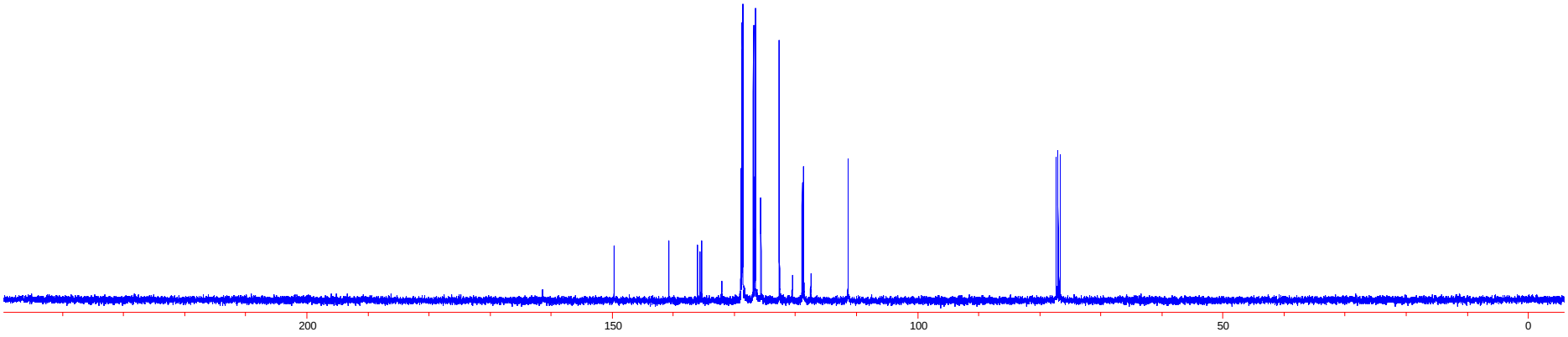




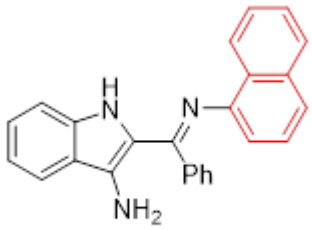
^{13}C NMR (100 MHz, $CDCl_3$)



3m



^{1}H NMR (400 MHz, $CDCl_3$)



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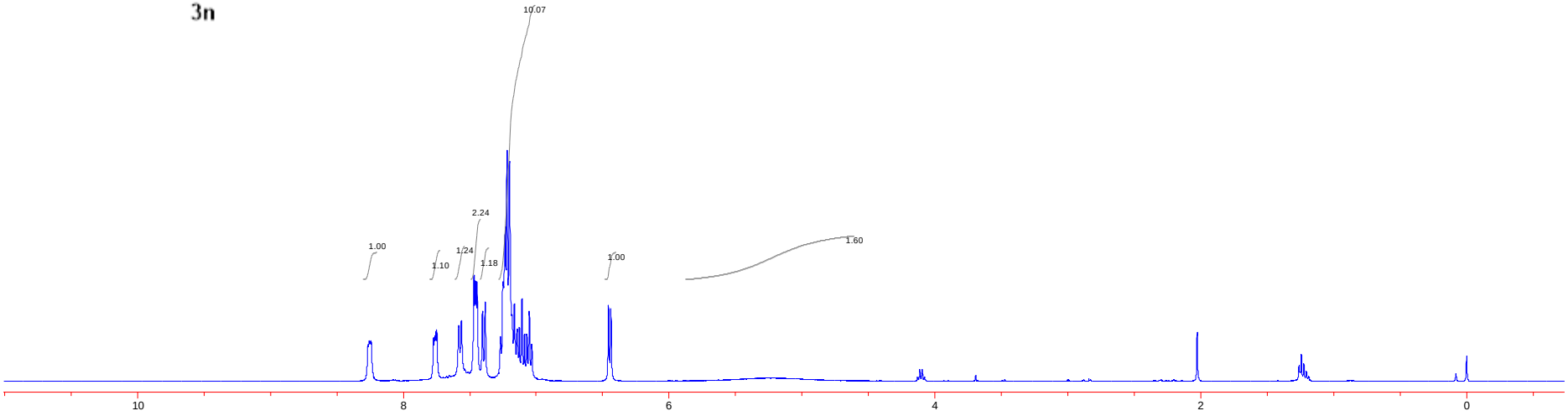
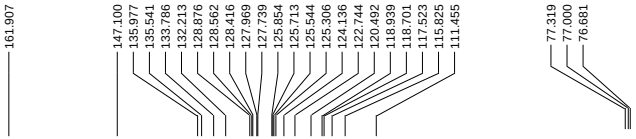
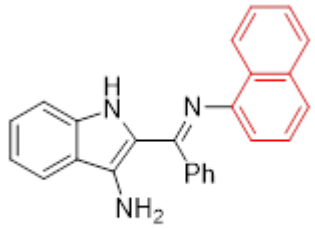




^{13}C NMR (100 MHz, $CDCl_3$)



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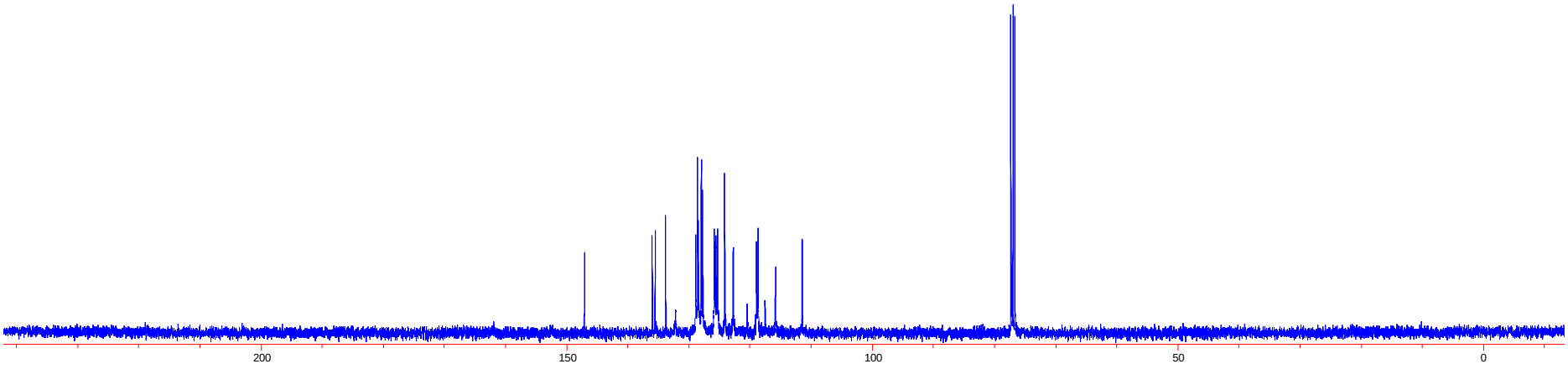
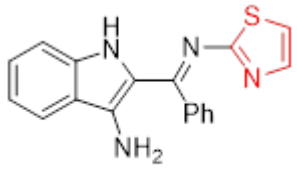


^{1}H NMR (400 MHz, DMSO-d_6)



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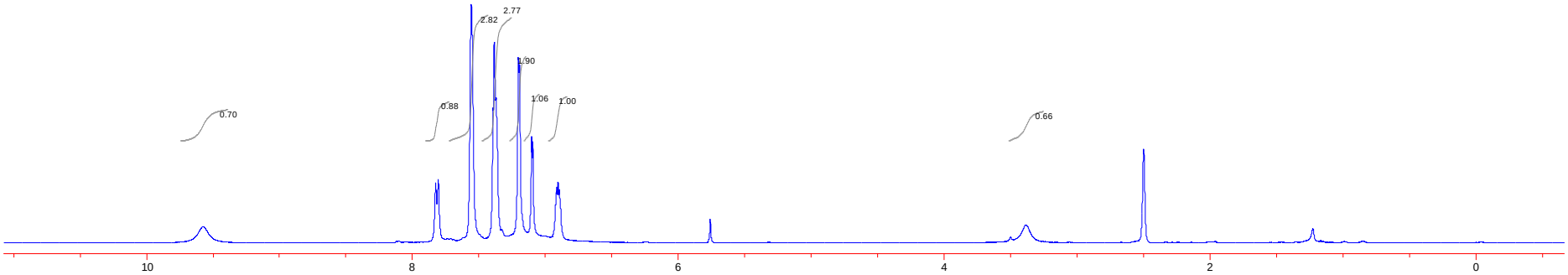
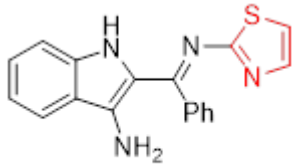


^{3}C NMR (400 MHz, DMSO-d_6)



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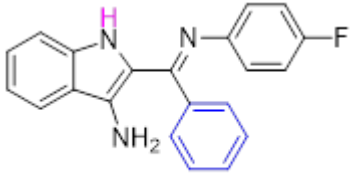
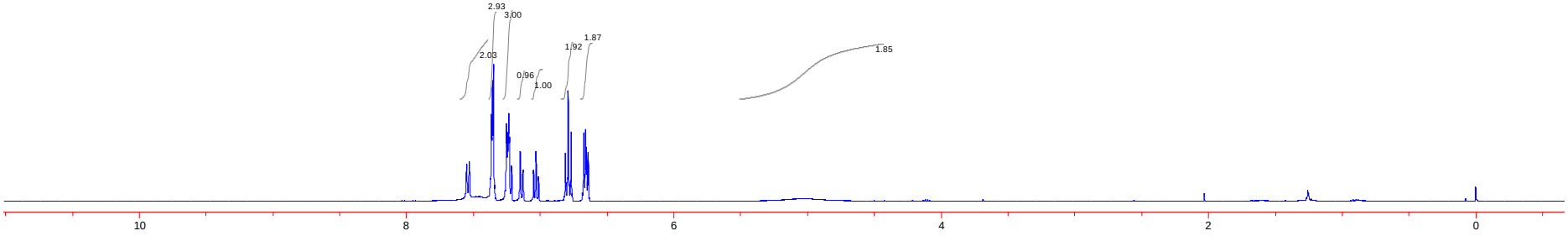
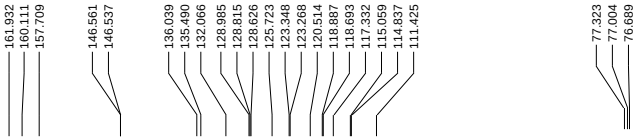
^{1}H NMR (400 MHz, $CDCl_3$)

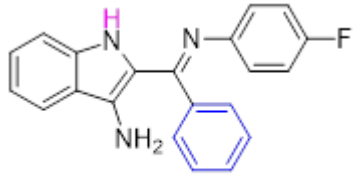


3a, EWG = Ms





^{13}C NMR (100 MHz, $CDCl_3$)



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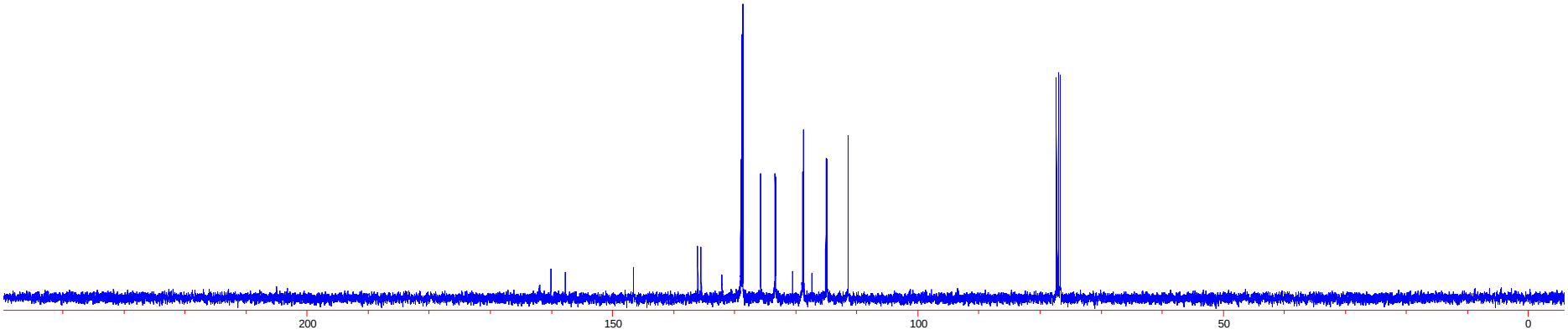
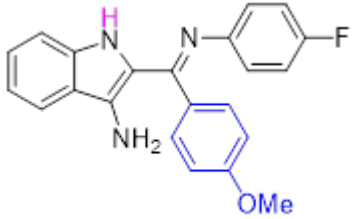
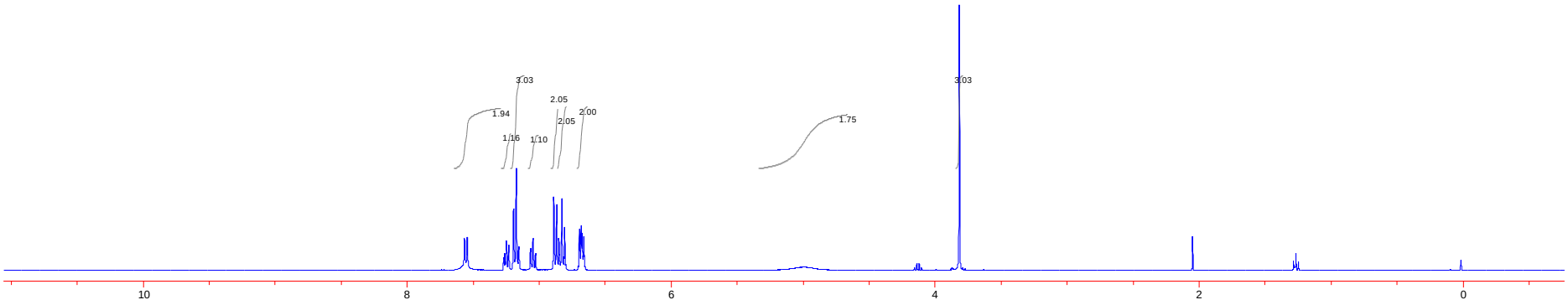
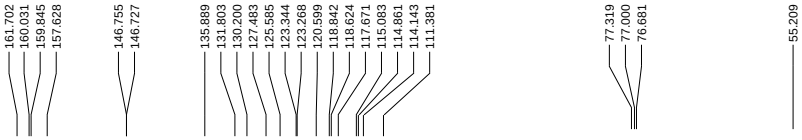


^{1}H NMR (400 MHz, $CDCl_3$)

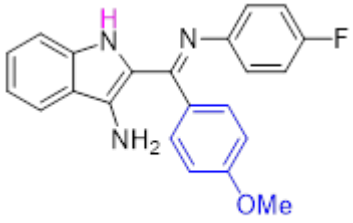


3p, EWG = $SO_2(p\text{-F})C_6H_4$

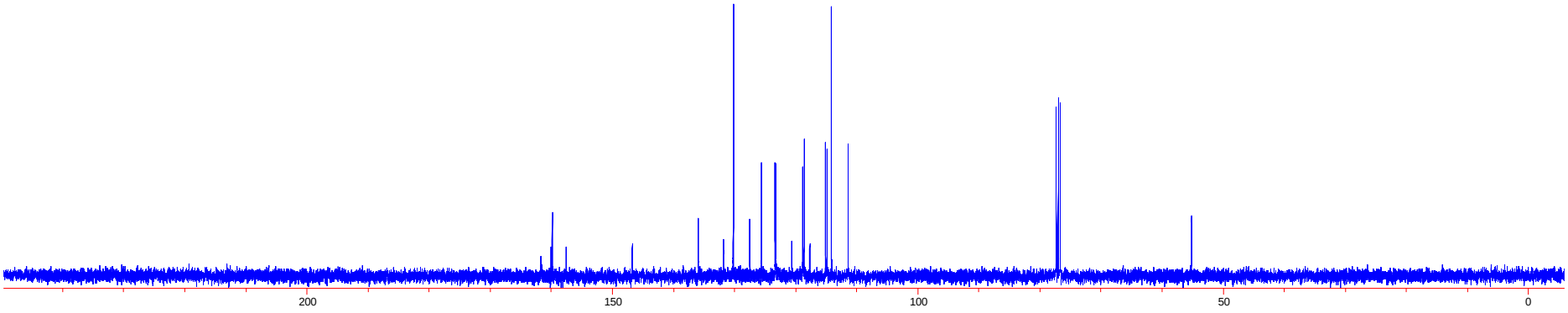




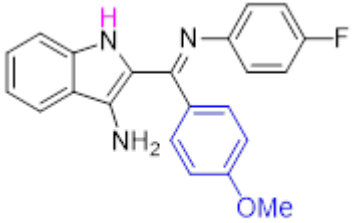
^{13}C NMR (100 MHz, $CDCl_3$)



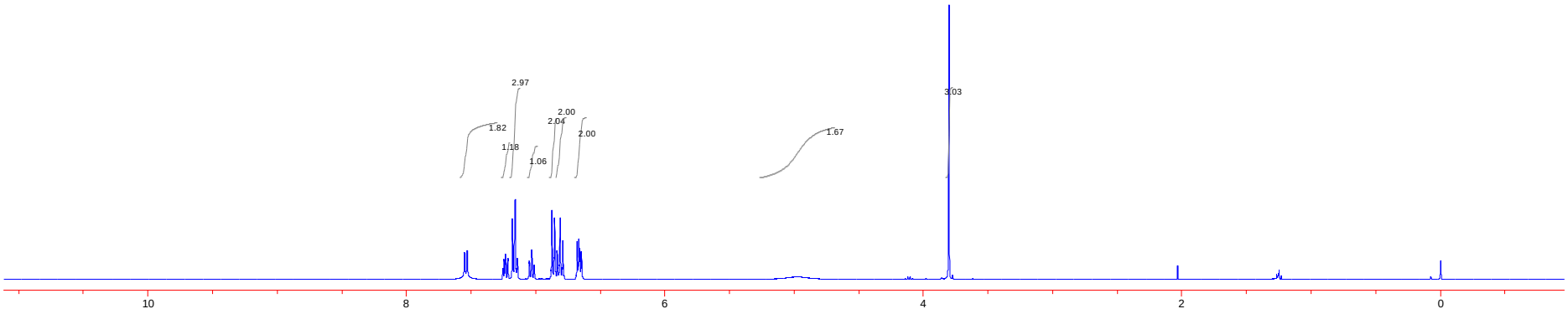
3p, EWG = SO_2(*p*-F)C_6H_4

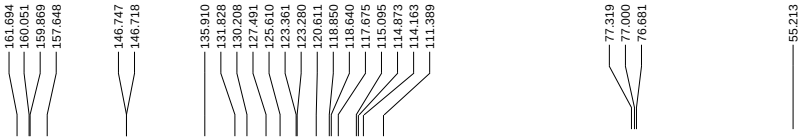


^{1}H NMR (400 MHz, $CDCl_3$)

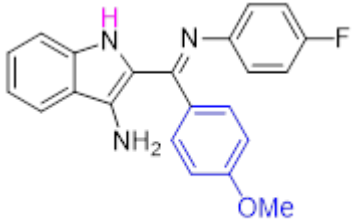


3p, EWG = SO_2(*p*-OMe)C_6H_4

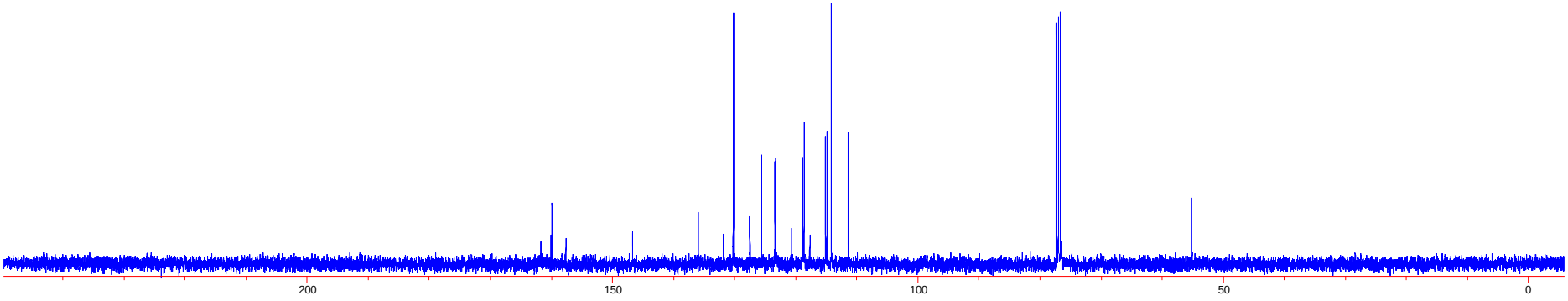




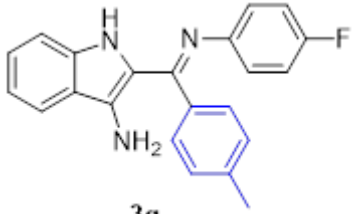
^{13}C NMR (100 MHz, $CDCl_3$)



3p, EWG = SO_2(*p*-OMe)C_6H_4



^{1}H NMR (400 MHz, $CDCl_3$)



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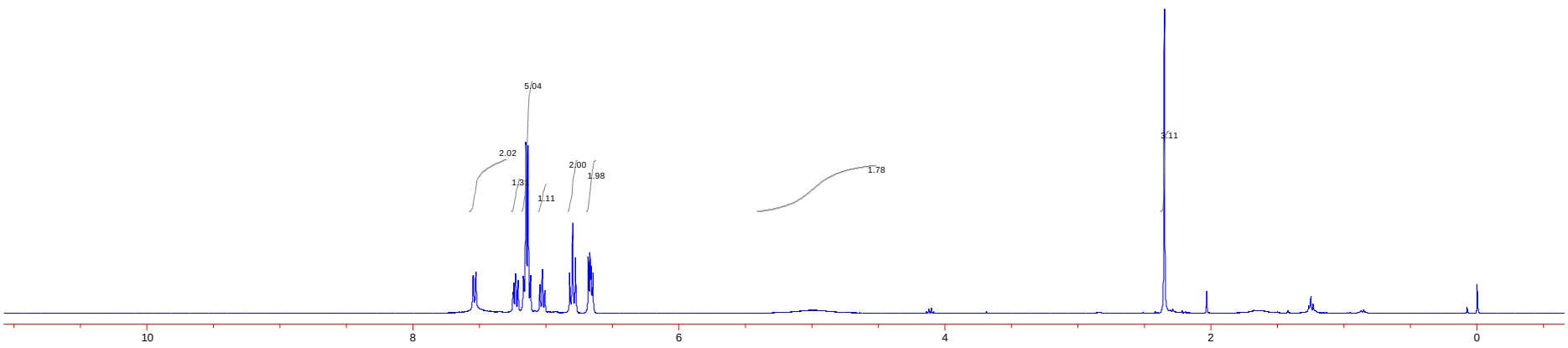
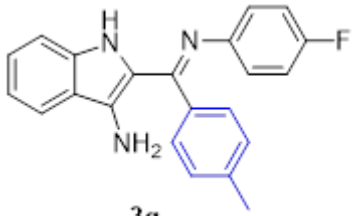


^{13}C NMR (100 MHz, $CDCl_3$)



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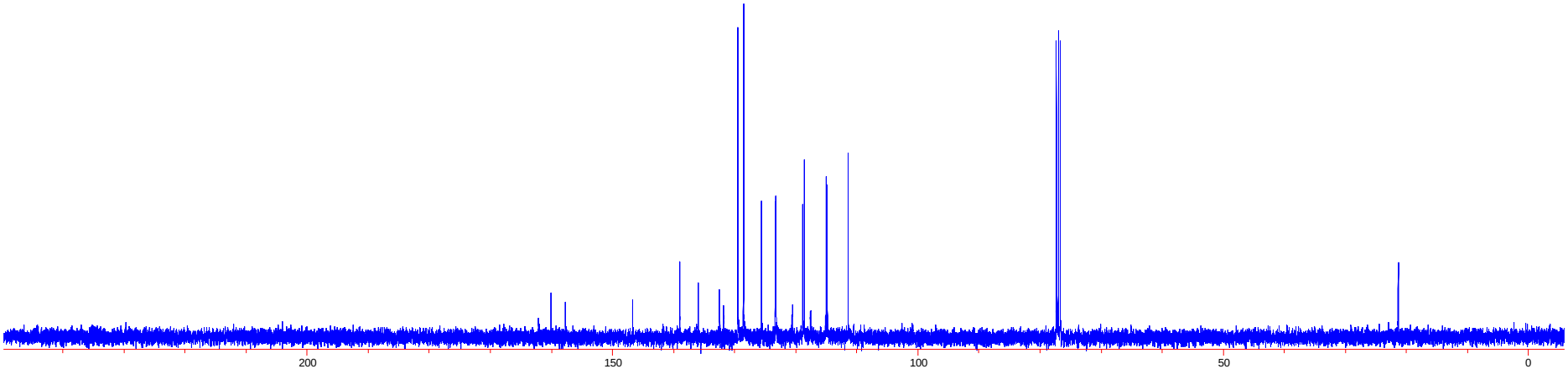
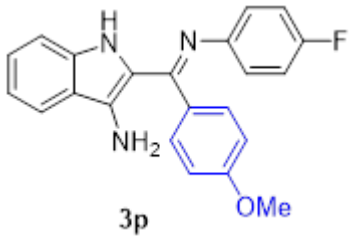


^{1}H NMR (400 MHz, $CDCl_3$)



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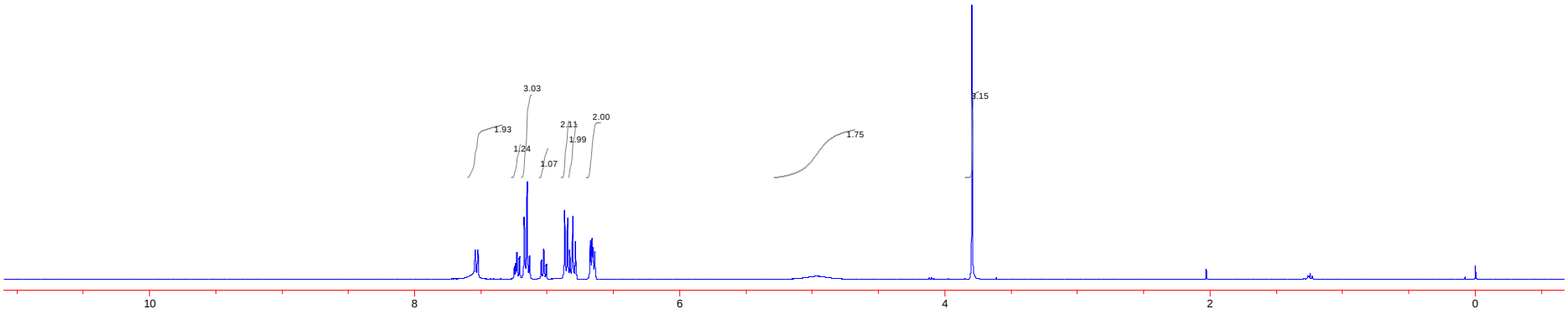
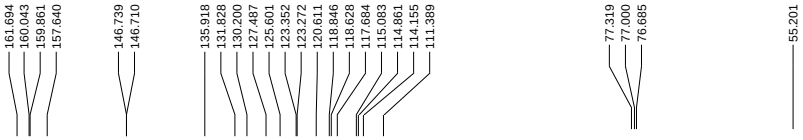
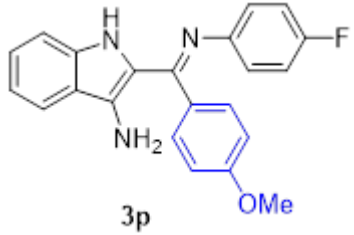




^{13}C NMR (100 MHz, $CDCl_3$)



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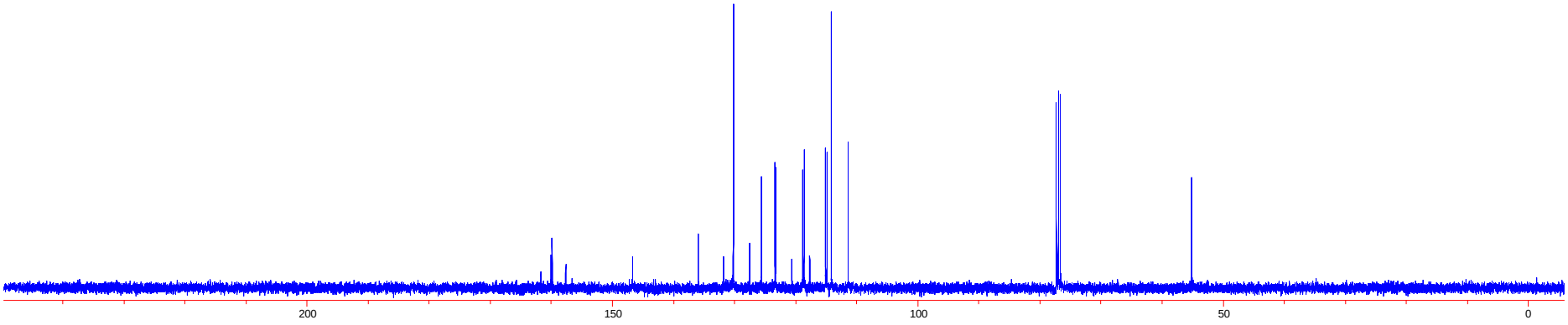
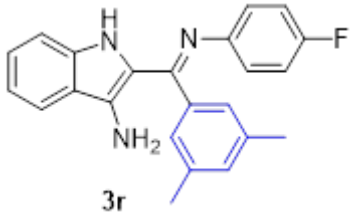


^{1}H NMR (400 MHz, $CDCl_3$)



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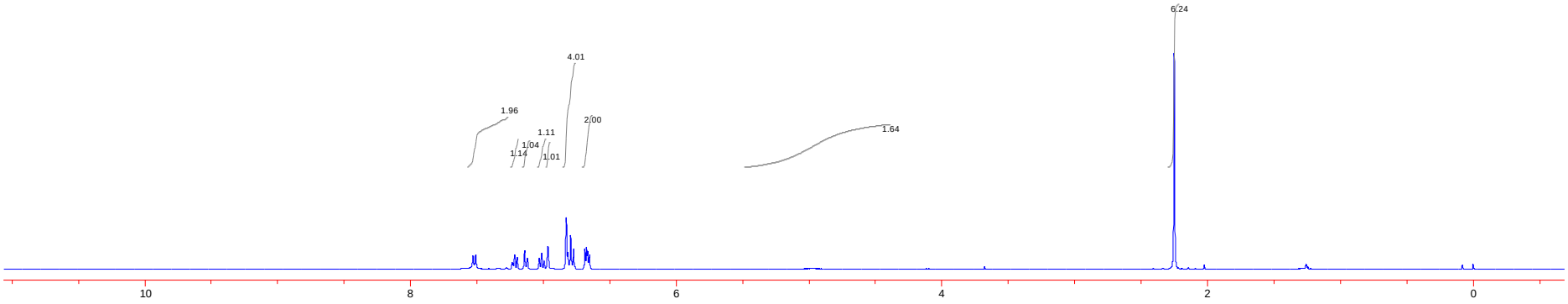
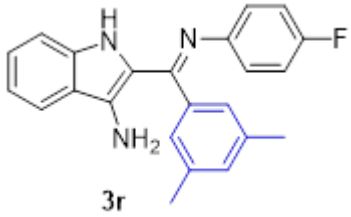


^{13}C NMR (100 MHz, $CDCl_3$)



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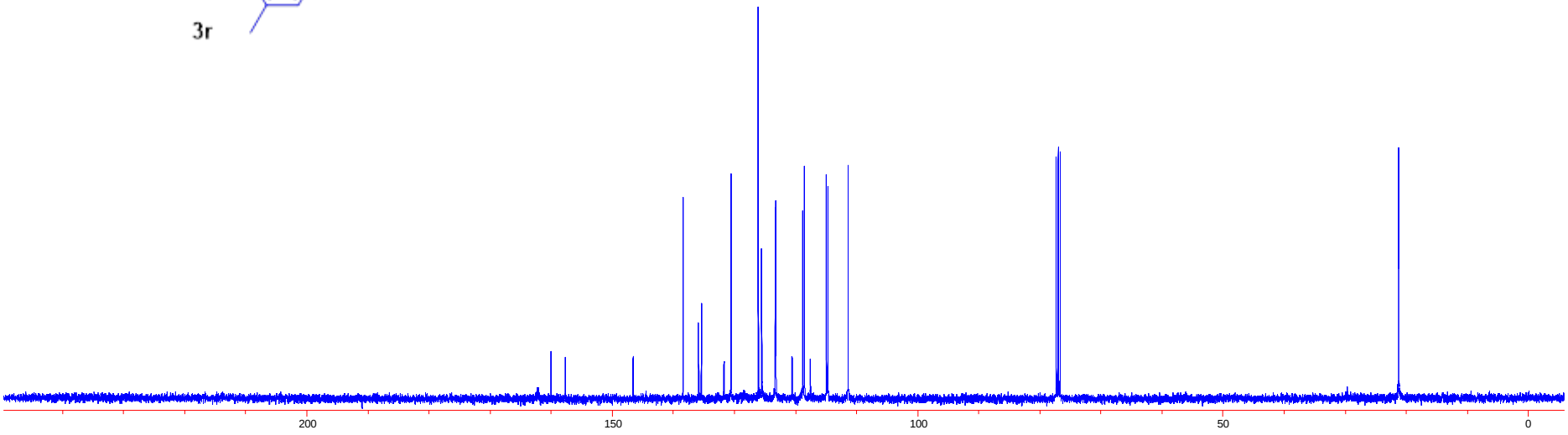
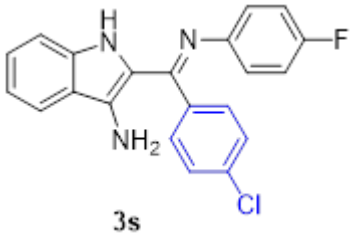


^{1}H NMR (400 MHz, $CDCl_3$)



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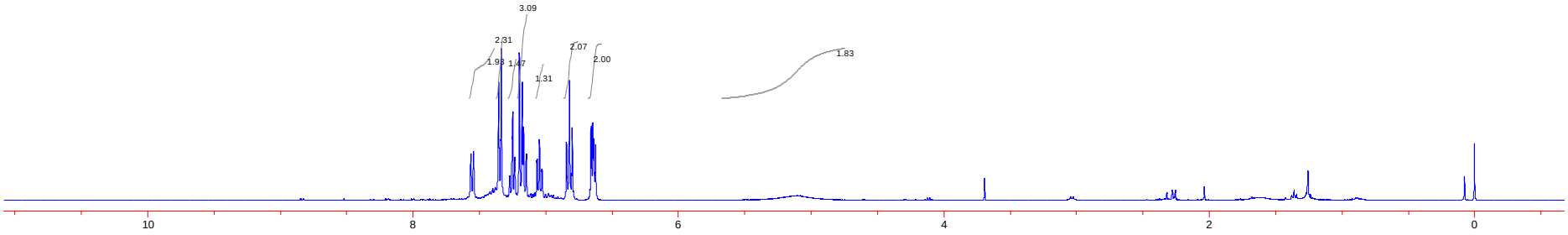
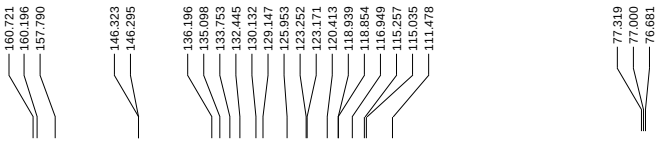
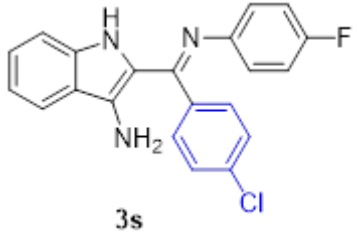




^{13}C NMR (100 MHz, $CDCl_3$)



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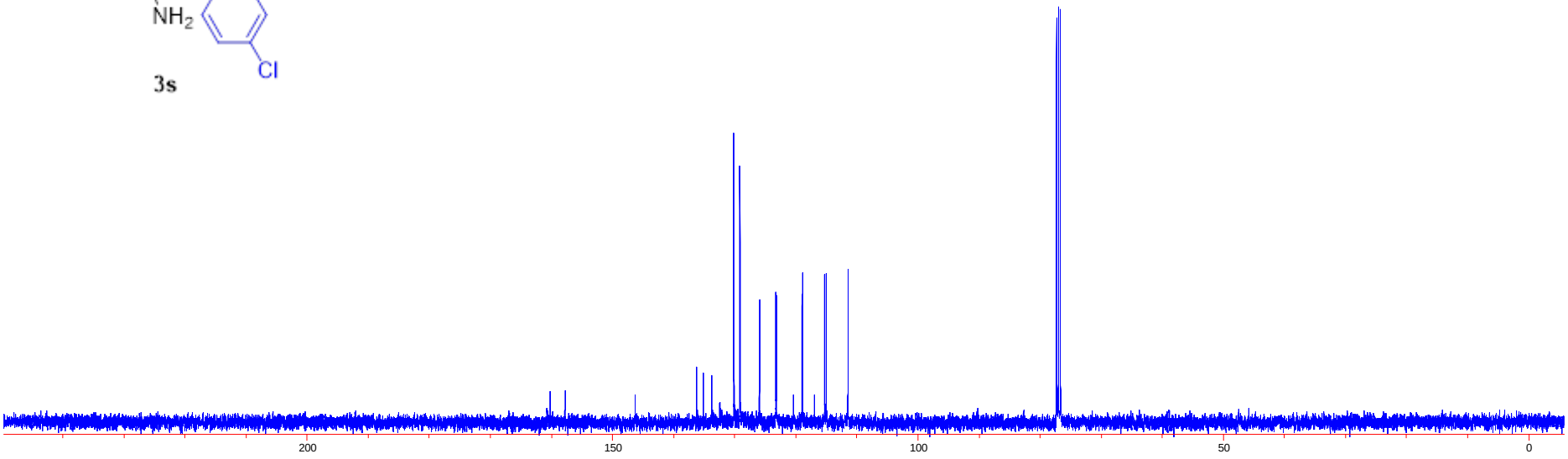
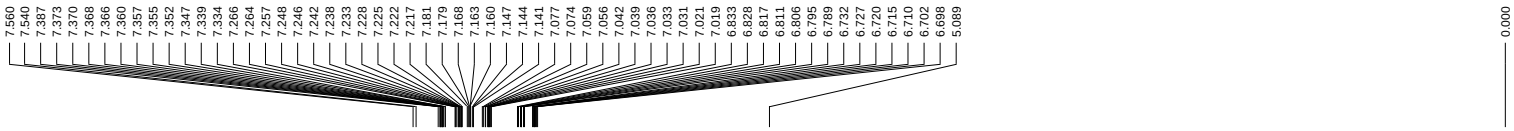
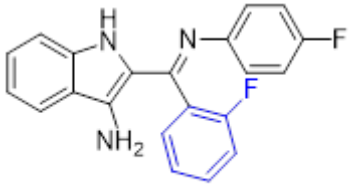




^{1}H NMR (400 MHz, $CDCl_3$)



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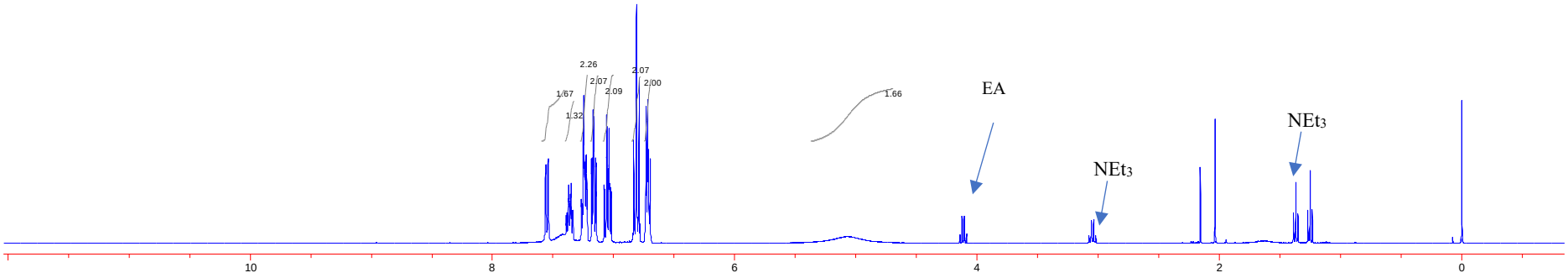
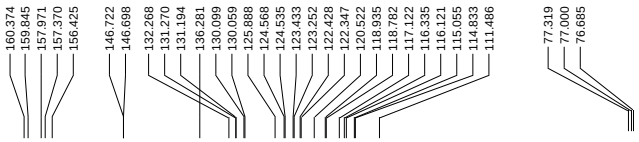
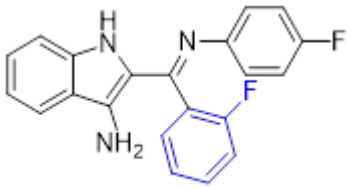




^{13}C NMR (100 MHz, $CDCl_3$)



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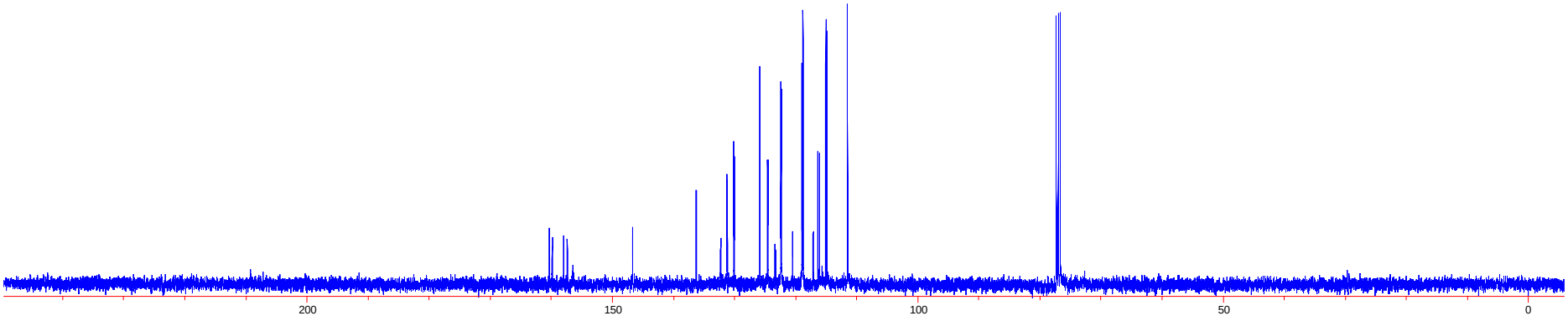
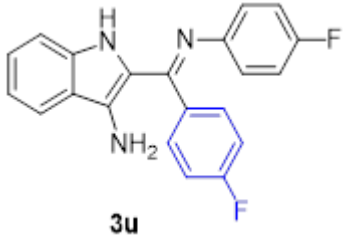


^{1}H NMR (400 MHz, $CDCl_3$)



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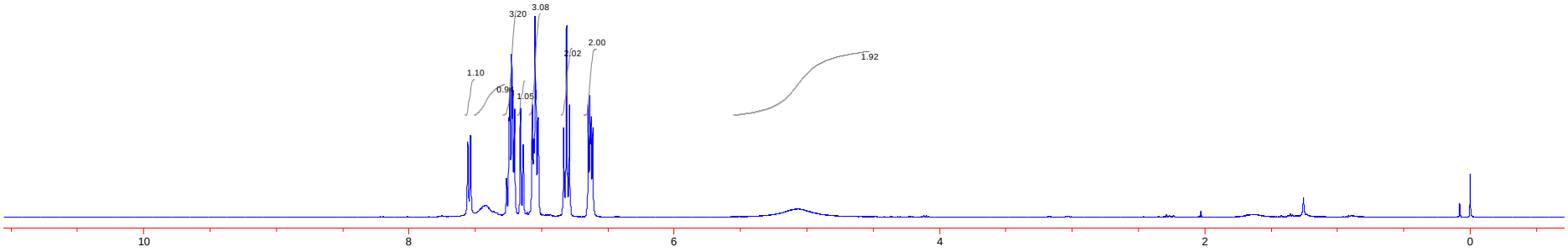
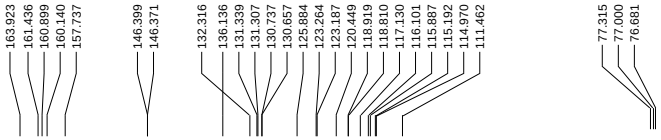
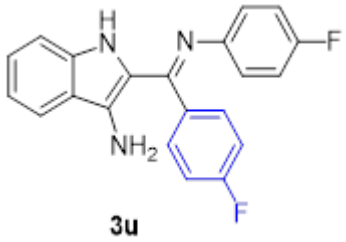




^{13}C NMR (100 MHz, $CDCl_3$)



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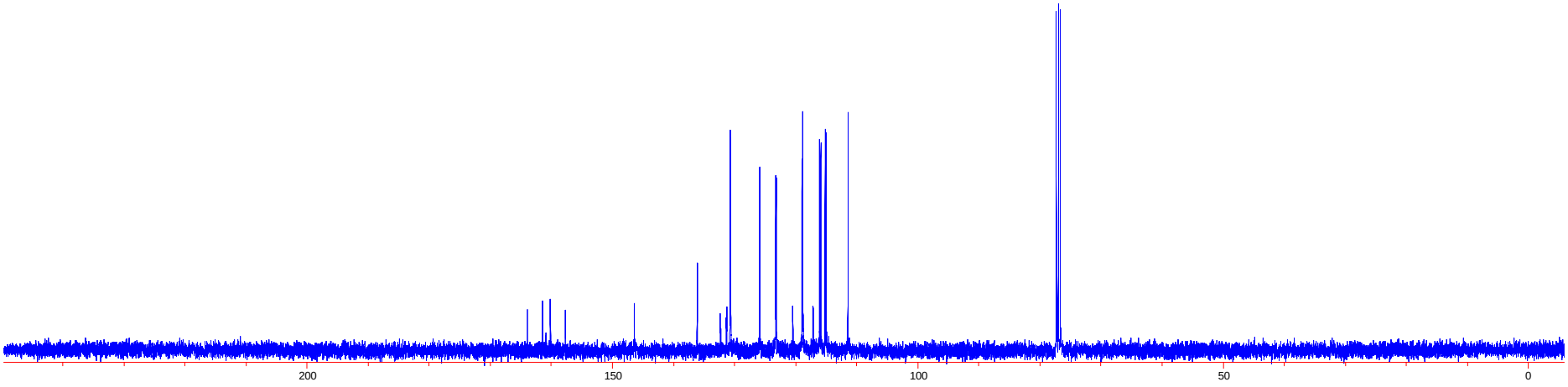
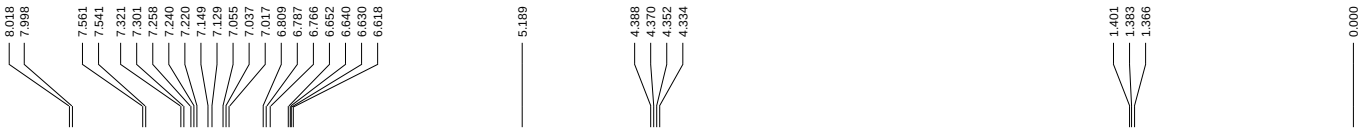
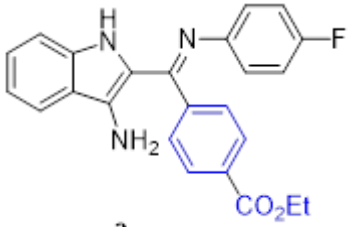




^{1}H NMR (400 MHz, $CDCl_3$)



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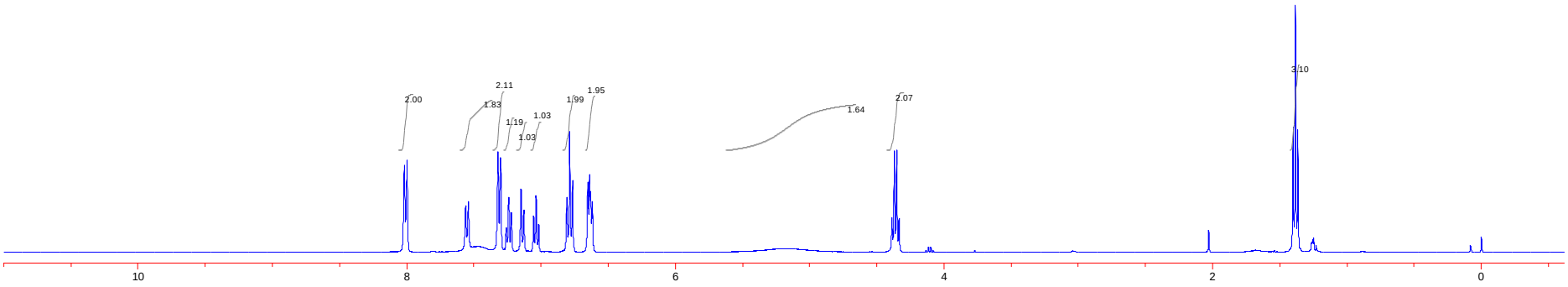
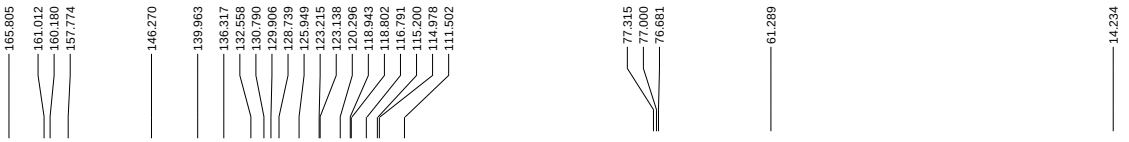
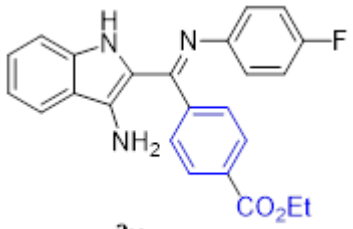
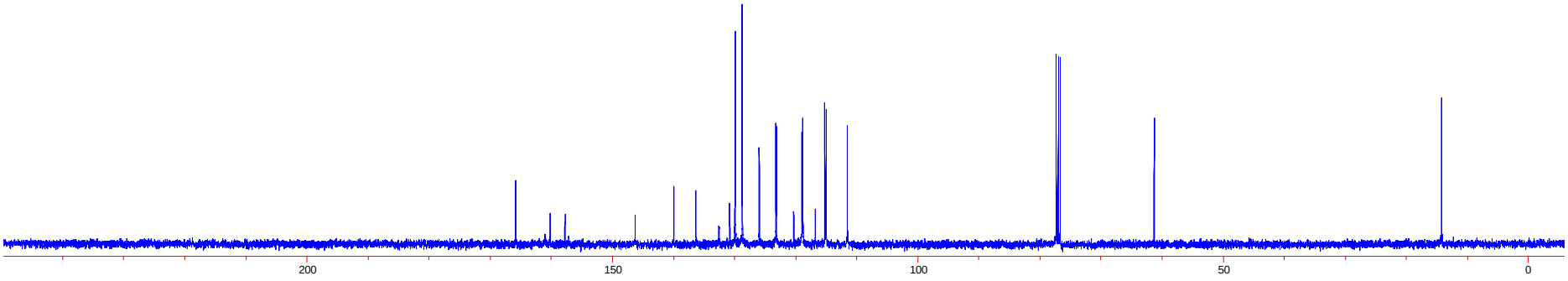




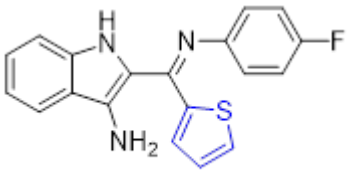
^{13}C NMR (100 MHz, $CDCl_3$)



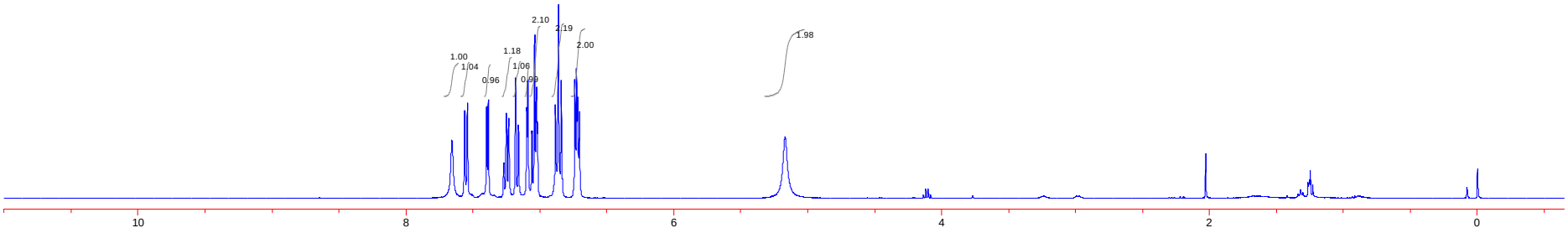
3v

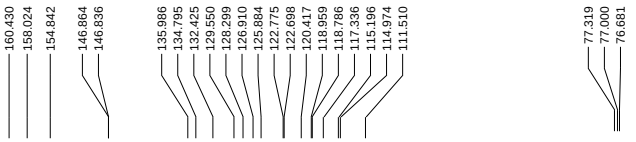


^{1}H NMR (400 MHz, $CDCl_3$)

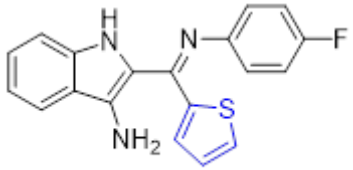


3w

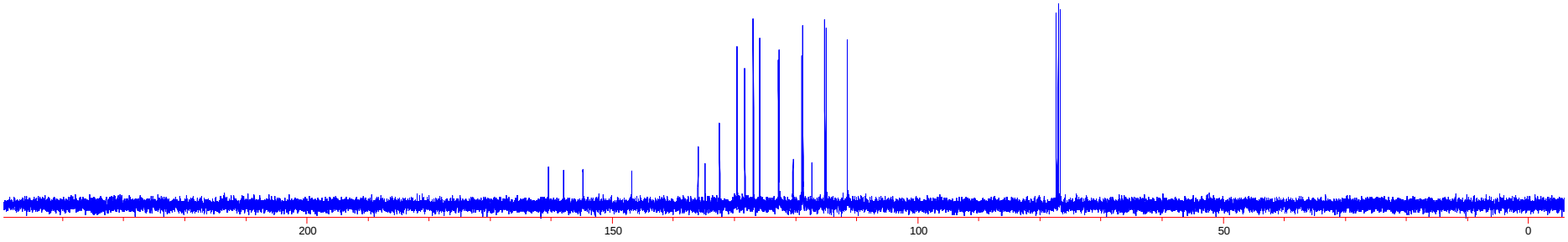


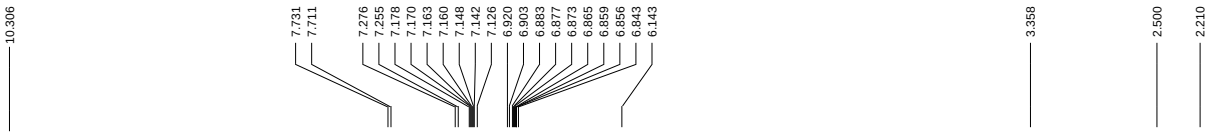


^{13}C NMR (100 MHz, $CDCl_3$)

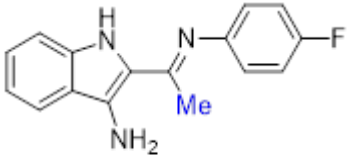


3w

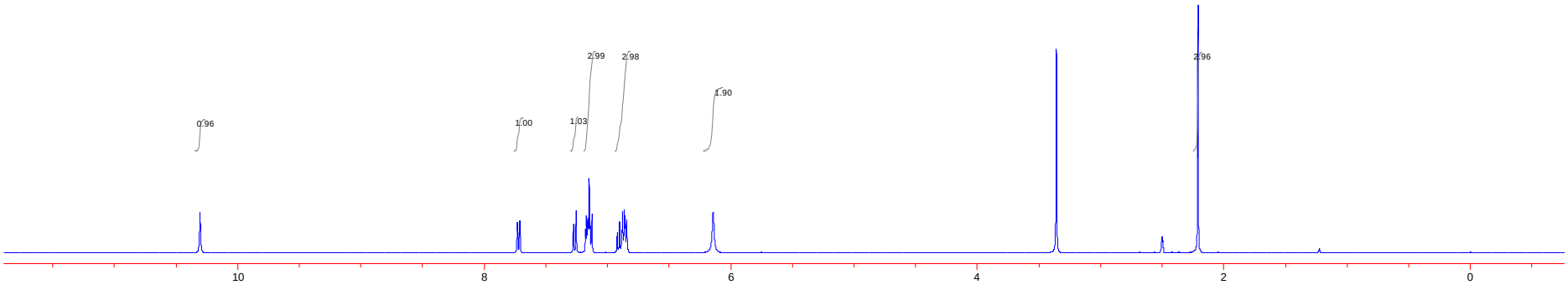




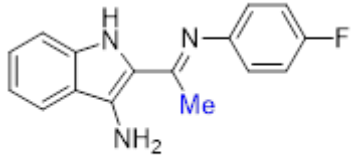
^{1}H NMR (400 MHz, DMSO-d_6)



3x

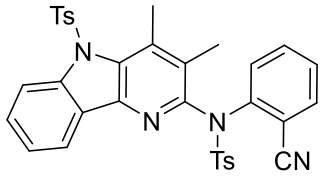


^{3}C NMR (400 MHz, DMSO-d_6)



3x

^{1}H NMR (400 MHz, $CDCl_3$)



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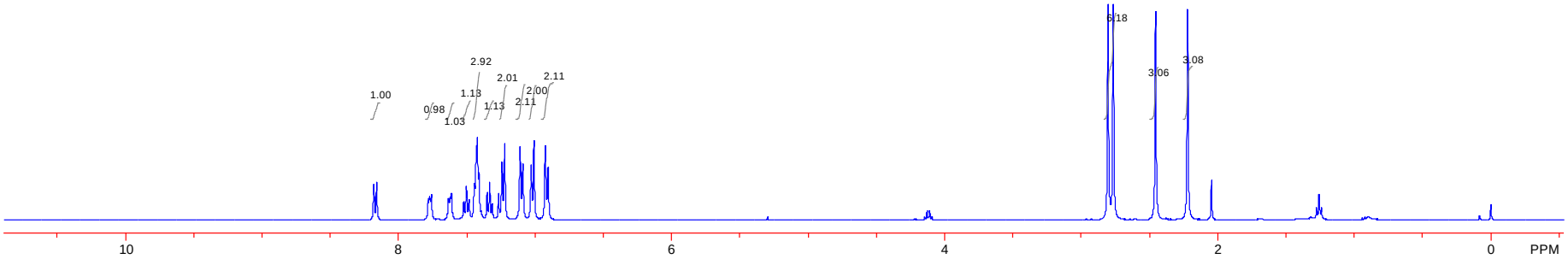
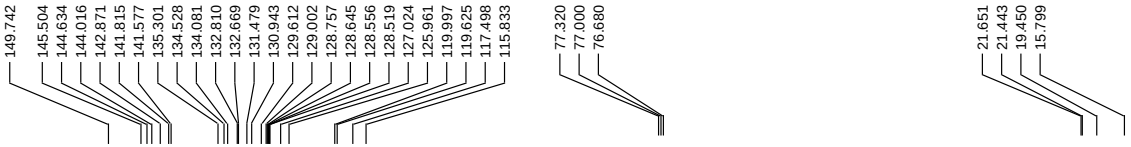
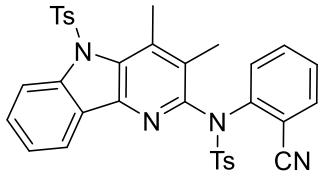




^{13}C NMR (100 MHz, $CDCl_3$)



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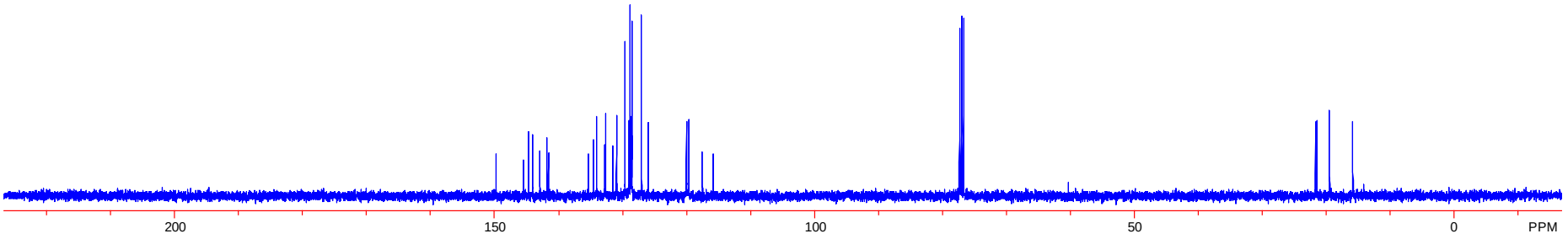
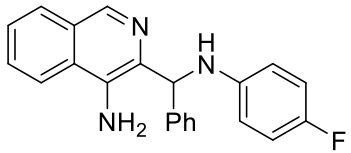


^{1}H NMR (400 MHz, $CDCl_3$)



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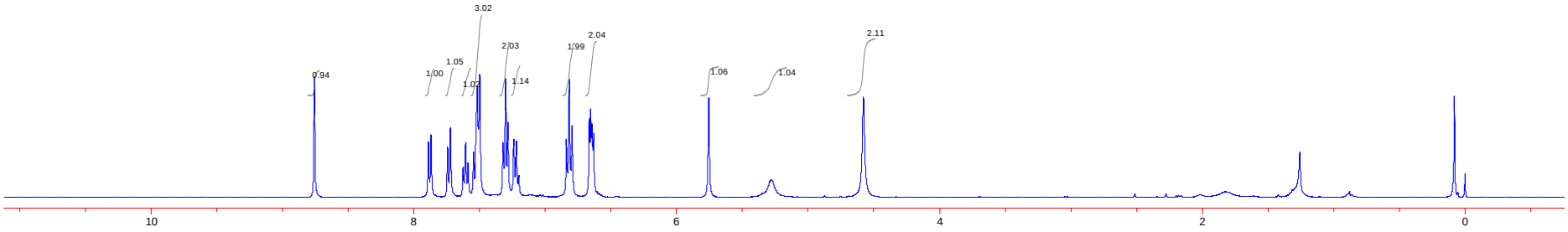
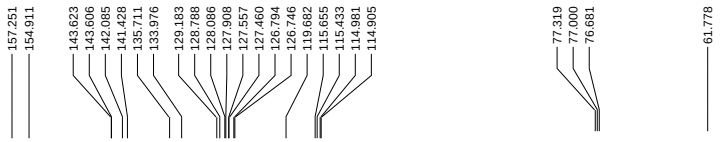
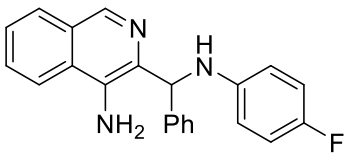




^{13}C NMR (100 MHz, $CDCl_3$)



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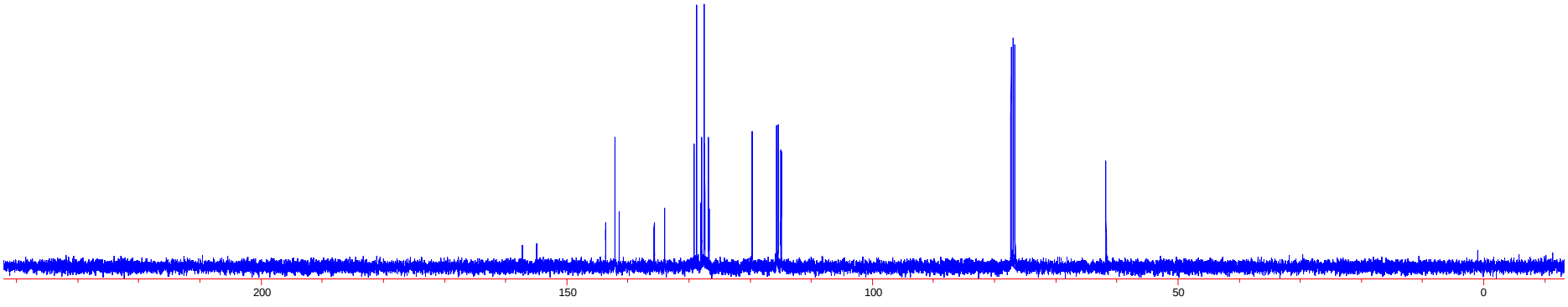
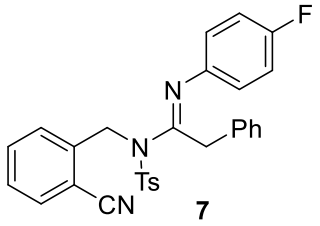


^{1}H NMR (400 MHz, $CDCl_3$)



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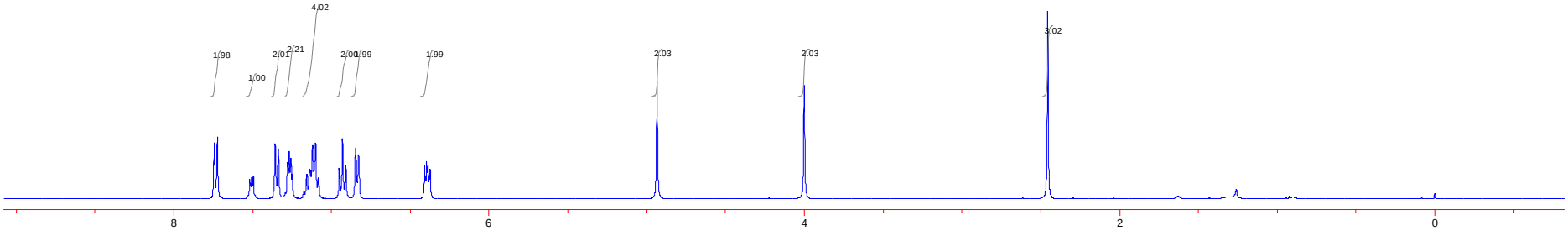
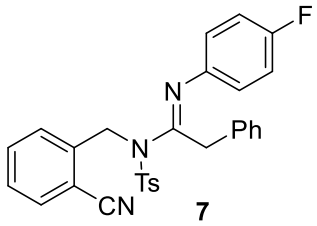


^{13}C NMR (100 MHz, $CDCl_3$)



7