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Access to 2-Subtituted 1-Pyridin-3-yl-β-Carboline Derivatives by an Intramolecular Radical Cyclization-Ring Opening-S_NAr Substitution

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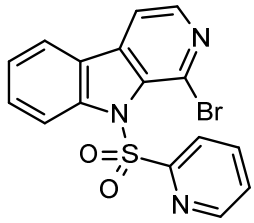
General Information

Reagents of the highest commercial quality were purchased and used without further purification, unless stated otherwise. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60FS-254) using UV light for visualization. Column chromatography was performed using silica gel (60 F254, 70−200 mm) as the stationary phase. All melting points were determined in open capillary tubes, on a Stuart Scientific SMP3 melting point apparatus. IR spectra were obtained on a Perkin−Elmer FTIR spectrum 2000 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with either a Varian Mercury VX-300, Varian Unity 300, or Varian Unity 500 MHz spectrometer at room temperature. Chemical shifts are given in ppm (δ) downfield from TMS. Coupling constants (J) are in hertz (Hz), and signals are described as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; br, broad; ap, apparent. Samples were analyzed by high pressure liquid chromatography (HP 1260 series) coupled to a mass spectrometer Quadrupole (6120 series) from Agilent Tecnhologies. The chromatographic separation was carried out with a Luna C18 column (100 mm x 4,6 mm x 3 µm) (supplied by Phenomenex). LC conditions were: flow rate, 1 mL/min; mobile phases, water containing 0,1 % formic acid (A) and methanol containing 0.1 % formic acid (solvent B); elution gradient: 10-100 % B in 20 minutes, 100-10% for 1 min, and 10% for 5 min in order to re-equilibrate the column at the initial conditions; injected volumen, 5 µL; temperature 50ºC. High-resolution analyses (HRMS) were performed on an Agilent 6210 time-of-flight LC/MS. Compounds **1**,[9] **3a**[10] and **3b**[18] have been previously described.

Preparation of compounds 2a and 2b

1-Bromo-9-(2-pyridylsulfonyl)pyrido[3,4-*b*]indole 2a



2a

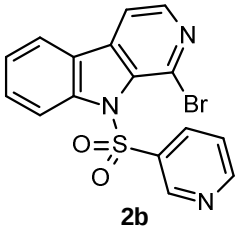
Method A: To a stirred solution of 1-bromo-9*H*-pyrido[3,4-*b*]indole **1** (247 mg, 1 mmol) and TEBACl (57 mg, 0.25 mmol) in CH_2Cl_2 (10 mL), a solution of KOH (35% in H_2O, 10 mL) was added, at 0 °C. The reaction mixture was allowed to room temperature and pyridine-2-sulfonyl chloride **3a** (887 mg, 5 mmol) was portionwise added during 1 h. The reaction mixture was vigorously stirred at 35 ºC for an additional period of 5 h. Then, at room temperature, the reaction mixture was neutralized with aq HCl 1M solution and EtOAc (20 mL) were added. The two layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under

[9] (*a*) G. La Regina, V. Famiglini, S. Passacantilli, S. Pelliccia, P. Punzi and R. Silvestri, *Synthesis*, 2014, **46**, 2093; (*b*) F. Bracher and D. Hildebrand, *Tetrahedron*, 1994, **50**, 12329.
[10] E. Dupont-Passelaigue, I. Le Roy and C. Pignier, *PCT. Int. Appl.*, WO 2012069503 A1, 2012.
[18] M. Birch, G. E. M. Sibley, D. Law and J. D. Oliver, *PCT. Int. Appl.*, WO 2009144473 A1, 2009.

reduced pressure. The crude product was purified by flash column chromatography on silica gel (2:8 EtOAc/ hexanes) to supply **2a** as a white solid (194 mg, 0.50 mmol, 50%).

Method B: To a stirred solution of 1-bromo-9*H*-pyrido[3,4-*b*]indole **1** (247 mg, 1 mmol) in dry THF (3 mL) NaH 99.9% (24 mg, 1 mmol) was added. The reaction mixture was stirred for 10 min at 35 ºC and then pyridine-2-sulfonyl chloride **3a** (177 mg, 1 mmol) was added in portions during 10 min and the reaction mixture was vigorously stirred at the same temperature for 10 additional min. The process was repeated, at 35º C, until a total of 4 equiv of NaH and 4 equiv **3a**. Then, at room temperature, the reaction mixture was neutralized with aq HCl 1M solution and EtOAc (20 mL) was added. The two layers were separated, and the aqueous one was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (2:8 EtOAc/ hexanes) to supply **2a** as a white solid (20−87%). Mp: 196−197º C. IR (KBr) υ_{max} (cm^{-1}) 3092, 1547, 1426, 1399, 1369, 1186, 1118, 1149, 958, 751, 585. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.66 (td, *J* = 4.8, 0.9 Hz, 1H), 8.39−8.35 (m, 2H), 8.22 (d, *J* = 7.9 Hz, 1H), 8.00−7.92 (m, 2H), 7.80 (d, *J* = 5.0 Hz, 1H), 7.64 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.55 (ddd, *J* = 7.7, 4.8, 0.9 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 156.7, 150.1, 144.2, 141.9, 138.0, 137.8, 136.2, 130.2, 128.7, 127.6, 125.0, 124.8, 122.7, 121.0, 118.9, 113.6. HPLC-Ms (ES-API) 388.0, 390.0 $[M + H]^+$, t_R 14.375 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{16}H_{11}{}^{79}BrN_3O_2S$ $[M + H]^+$ 387.9749, found: 387.9750.

1-Bromo-9-(3-pyridylsulfonyl)pyrido[3,4-*b*]indole 2b

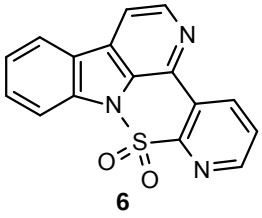


2b

Method A: To a stirred solution of 1-bromo-9*H*-pyrido[3,4-*b*]indole **1** (247 mg, 1 mmol) and TEBACl (57 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) was added, at 0 °C, a solution of KOH (35% in H_2O, 10 mL). The reaction mixture was warmed to room temperature and pyridine-3-sulfonyl chloride **3b** (887 mg, 5 mmol) was added in portions during 1 h. The reaction mixture was vigorously stirred at 35 ºC for additional 5 h. Then, at room temperature, the reaction mixture was neutralized with aq HCl 1M solution and EtOAc (20 mL) were added. The two layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (2:8 EtOAc/ hexanes) to supply **2b** as a white solid (217 mg, 0.56 mmol, 56%). Mp: 181−182 ºC. IR (KBr) υ_{max} (cm^{-1}) 3124, 3036, 2974, 1612, 1571, 1543, 1421, 1393, 1183, 1104, 1045, 921, 776. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.71 (brs, 1H), 8.66 (d, *J* = 4.8 Hz, 1H), 8.39 (d, *J* = 4.9 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 7.84−7.80 (m, 2H), 7.68−7.62 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.24 (dd, *J* = 8.1, 4.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 154.1, 147.5, 145.6, 141.6, 139.2, 134.4, 133.6, 131.0, 130.7, 126.3, 126.0, 125.8, 123.1,

121.1, 119.1, 113.5. HPLC-Ms (ES-API) 388.0, 390.0 $[M + H]^+$, t_R 14.332 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{16}H_{11}{}^{79}BrN_3O_2S$ $[M + H]^+$ 387.9749, found: 387.9751.

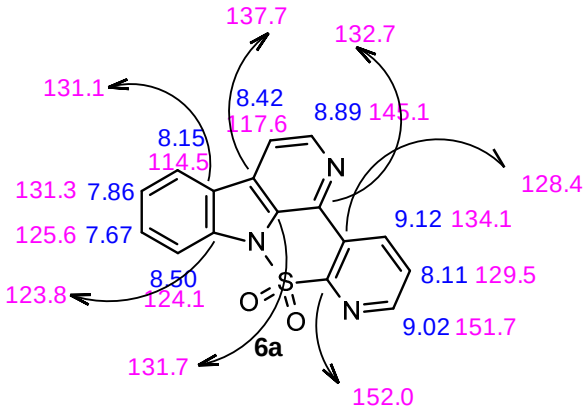
8-Thia-6,7b,9-triazabenzo[e]acephenanthrylene-8,8-dioxide 6



6

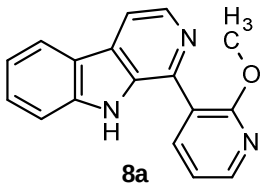
A solution of TTMSS (620 mg, 2.5 mmol) and AIBN (328 mg, 2 mmol) in *m*-xylene (10 mL) was added dropwise, by using a syringe pump during 24 h, to a stirred solution of **2a** (194 mg, 0.5 mmol) in *m*-xylene/acetonitrile(9:1), (1.5 mL) at 80 °C (bath temperature), under an atmosphere of dry argon. When the addition was finished, the reaction mixture was stirred for an additional 24 h period, at the same temperature, until full consumption of **2a** (TLC analysis). The resulting solution was concentrated and the crude mixture was separated of the by product **7 (**β-carboline, norharmane)[26] by flash chromatography on silica gel (hexane/EtOAc (95:5)). The resulting pale yellow solid was triturated in CH_2Cl_2 to furnish **6a** as a white solid (89 mg, 0.13 mmol, 58%). Mp: 231−232º C. IR (KBr) υ_{max} (cm^{-1}) 3057, 1622, 1418, 1353, 1215, 1176, 1118, 986, 745, 601. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 9.12 (dd, *J* = 8.1, 1.6 Hz, 1H), 9.02 (dd, *J* = 4.5, 1.6 Hz, 1H), 8.89 (d, *J* = 5.1 Hz, 1H), 8.50 (brd, *J* = 7.4 Hz, 1H), 8.42 (d, *J* = 5.1 Hz, 1H), 8.15 (brd, *J* = 8.0 Hz, 1H), 8.11 (dd, *J* = 8.1, 4.5 Hz, 1H), 7.86 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.67 (dt, *J* = 7.4, 0.9 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) 152.0, 151.7, 145.1, 137.7, 134.1, 132.7, 131.7, 131.3, 131.1, 129.5, 128.4, 125.6, 124.1, 123.8, 117.6, 114.5. HPLC-Ms (ES-API) 308.0 $[M + H]^+$, t_R 14.828 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{16}H_{10}N_3O_2S$ $[M + H]^+$ 308.0488, found: 308.0492. Compound **7** was identical in all respects to an authentic sample obtained from Aldrich (13 mg, 0.077 mmol, 15%).

Full assignation of **6**, in basis of ^{1}H, ^{13}C, COSY, HSQZ, HMBC and TOCSY spectra.



[26] S. Li, B. Yang, Q. Zhang, J. Zhang, J. Wang and W. Wu, *Nat. Prod. Communications*, 2010, **5**, 1591.

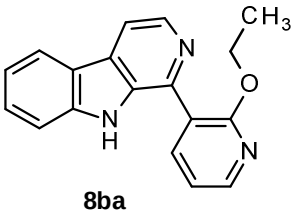
1-(2-Methoxy-3-pyridyl)-9*H*-pyrido[3,4-*b*]indole 8a



8a

A mixture of **6** (154 mg, 0.5 mmol) and Cs_2CO_3 (815 mg, 2.5 mmol) in dry THF: MeOH (2:1) (30 mL), under dry argon atmosphere was stirred at 60 °C for 2 h, until full consumption of **6** (TLC analysis). The reaction mixture was allowed to room temperature and concentrated, and then filtered through a pad of Celite, eluting with MeOH. The resulting filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (hexane/ EtOAc (7:3)) to give **8a** as a white solid (100 mg, 0.36 mmol, 72%). Mp: 195−196º C. IR (KBr) υ_{max} (cm^{-1}) 3061, 2920, 1626, 1583, 1463, 1402, 1235, 1018, 745. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.73 (brs, 1H), 8.59 (d, *J* = 5.2, 1H), 8.33 (dd, *J* = 4.9, 1.9 Hz, 1H), 8.21−8.15 (m, 2H), 8.02 (d, *J* = 5.2 Hz, 1H), 7.58 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.32 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.14 (dd, *J* = 7.4, 4.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 160.1, 147.5, 141.2, 140.4, 139.0 (2C), 138.7, 134.5, 129.9, 128.6, 121.7, 121.6, 120.1, 117.9, 114.1, 111.6, 53.8. HPLC-Ms (ES-API) 276.2 $[M + H]^+$, t_R 7.205 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{17}H_{14}N_3O$ $[M + H]^+$ 276.1131, found: 276.1143.

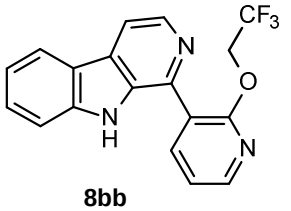
1-(2-Ethoxy-3-pyridyl)-9*H*-pyrido[3,4-*b*]indole 8ba



8ba

A mixture of **6** (154 mg, 0.5 mmol) and Cs_2CO_3 (815 mg, 2.5 mmol) in dry THF: EtOH (2:1) (30 mL), and under an atmosphere of dry argon was stirred at 60 °C for 3 h, until full consumption of **6** (TLC analysis). The reaction mixture was warmed to room temperature and concentrated, and then filtered through a pad of Celite, eluting with MeOH. The resulting filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (hexane/EtOAc (7:3)) to give **8ba** as a white solid (113 mg, 0.39 mmol, 78%). Mp: 128−129º C. IR (KBr) υ_{max} (cm^{-1}) 3153, 3060, 2981, 2926, 2858, 1796, 1628, 1580, 1437, 1383, 321, 1234, 1032, 745. ^{1}H NMR (500 MHz, CD_3OD) δ (ppm) 8.39 (d, *J* = 5.5, 1H), 8.36 (dd, *J* = 5.0, 1.9 Hz, 1H), 8.26 (brd, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 5.5 Hz, 1H), 7.99 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.61−7.57 (m, 2H), 7.32 (dt, *J* = 8.0, 2.3 Hz, 1H), 7.20 (dd, *J* = 7.3, 5.0 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CD_3OD) δ (ppm) 161.1, 149.3, 143.2, 141.6, 139.3, 136.4, 135.6, 131.8, 130.4, 122.9, 121.8, 121.1, 120.5, 118.1, 115.8, 112.9, 63.5, 15.1. HPLC-Ms (ES-API) 290.0 $[M + H]^+$, t_R 8.609 min (94%). HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}N_3O$ $[M + H]^+$ 290.1287, found: 290.1288.

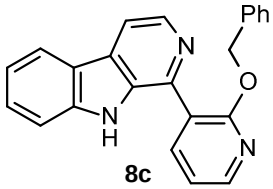
1-[2-(2,2,2-Trifluoroethoxy)-3-pyridyl]-9*H*-pyrido[3,4-*b*]indole 8bb



8bb

A mixture of **6** (154 mg, 0.5 mmol) and Cs_2CO_3 (815 mg, 2.5 mmol) in dry THF: trifluoroethanol (2:1) (30 mL), and under an atmosphere of dry argon was stirred at 80 °C for 24 h, until full consumption of **6** (TLC analysis). The reaction mixture was warmed to room temperature and concentrated, and then filtered through a pad of Celite, eluting with MeOH. The resulting filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (CH_2Cl_2/MeCN (9:1)) to give **8bb** as a white solid (120 mg, 0.35 mmol, 70%). Mp: 162−164º C. IR (KBr) υ_{max} (cm^{-1}) 3229, 1627, 1422, 1324, 1163, 796, 743. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.67−8.56 (m, 2H), 8.35−8.28 (m, 2H), 8.17 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 5.2 Hz, 1H), 7.57 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.31 (dt, *J* = 7.3, 1.0 Hz, 1H), 7.28−7.24 (m, 1H), 4.98 (q, $^4J_{H\text{-}F}$ = 8.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 157.4, 147.0, 142.5, 140.4, 139.5, 137.6, 134.4, 130.1, 128.7, 123.8 (q, $^1J_{C\text{-}F}$ = 278.0 Hz, CF_3), 122.1, 121.6, 121.4, 120.2, 119.6, 114.5, 111.6, 62.3 (q, $^2J_{C\text{-}F}$ = 35.6.0 Hz, CH_2). HRMS (ESI-TOF) m/z calcd for $C_{18}H_{13}F_3N_3O$ $[M + H]^+$ 344.1005, found: 344.1006.

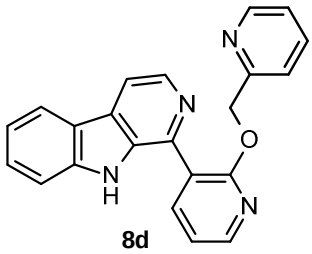
1-(2-Benzyloxy-3-pyridyl)-9*H*-pyrido[3,4-*b*]indole 8c



8c

A mixture of **6** (154 mg, 0.5 mmol), Cs_2CO_3 (815 mg, 2.5 mmol) and benzyl alcohol (270 mg, 2.5 mmol, 0.26 mL) in dry THF (10 mL), under dry argon atmosphere was stirred at 60 °C for 3 h, until full consumption of **6** (TLC analysis). The reaction mixture was allowed to reach room temperature and concentrated, and then filtered through a pad of Celite, eluting with MeOH. The resulting filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (hexane/EtOAc (8:2)) to give **8c** as a white solid (154 mg, 0.44 mmol, 88%). Mp: 130−131º C. IR (KBr) υ_{max} (cm^{-1}) 3060, 2922, 2851, 1626, 1581, 1454, 1420, 1320, 1233, 1019, 743. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.57−8.53 (m, 2H), 8.34 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.25 (dd, *J* = 7.7, 1.8 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 5.1 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.42−7.39 (m, 2H), 7.31−7.29 (m, 3H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.15 (dd, *J* = 7.3, 4.9 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 5.62 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 159.4, 147.2, 141.9, 140.2, 139.4, 138.8, 136.8, 134.5, 130.0, 129.9, 128.9 (2C), 128.5 (2C), 128.3 (2C), 122.3, 121.5, 119.9, 118.2, 114.1, 111.5, 67.6. HPLC-Ms (ES-API) 352.2 $[M + H]^+$, t_R 11.289 min (98%). HRMS (ESI-TOF) m/z calcd for $C_{23}H_{18}N_3O$ $[M + H]^+$ 352.1443, found: 352.1440.

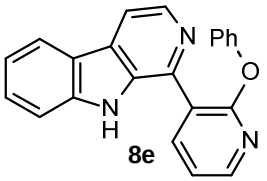
1-(2-Pyridylmethoxy-3-pyridyl)-9*H*-pyrido[3,4-*b*]indole 8d



8d

A mixture of **6** (154 mg, 0.5 mmol), Cs_2CO_3 (815 mg, 2.5 mmol) and 2-pyridinemethanol (1.635 g, 15 mmol, 1.5 mL) in dry THF (25 mL), under dry argon atmosphere, was stirred at 60 °C for 3 h, until full consumption of **6** (TLC analysis). The reaction mixture was allowed to reach room temperature and concentrated, and then filtered through a pad of Celite, eluting with MeOH. The resulting filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (EtOAc/CH_2Cl_2 (7:4)) to give **8d** as a white solid (140 mg, 0.40 mmol, 81%). Mp: 155−156º C. IR (KBr) υ_{max} (cm^{-1}) 3238, 3058, 2983, 2946, 1625, 1578, 1450, 1413, 1321, 1234, 1032, 743. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 12.66 (s, 1H), 8.80 (d, *J* = 4.8 Hz, 1H), 8.59 (d, *J* = 5.2 Hz, 1H), 8.20 (dd, *J* = 7.3, 1.9 Hz, 1H), 8.18 (d, *J* = 6.8 Hz, 1H), 8.10 (dd, *J* = 4.9, 1.9 Hz, 1H), 8.03 (d, *J* = 5.2 Hz, 1H), 7.81 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.52−7.51 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 7.2, 5.2 Hz, 1H), 7.29−7.28 (m, 1H), 7.07 (dd, *J* = 7.4, 4.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 158.7, 157.6, 148.3, 146.9, 141.5, 141.4, 139.0, 138.6, 137.5, 137.3, 135.0, 129.5, 128.0, 122.8, 121.7, 121.6, 121.3, 119.1, 117.9, 114.1, 111.7, 65.8. HPLC-Ms (ES-API) 353.2 $[M + H]^+$, t_R 9.385 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{22}H_{17}N_4O$ $[M + H]^+$ 353.1395, found: 353.1404.

1-(2-Phenoxy-3-pyridyl)-9*H*-pyrido[3,4-*b*]indole 8e

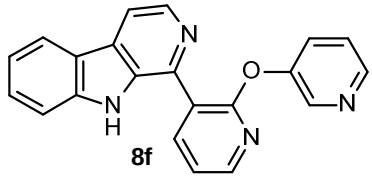


8e

A mixture of **6** (154 mg, 0.5 mmol), Cs_2CO_3 (815 mg, 2.5 mmol) and phenol (376 mg, 4 mmol, 0.37 mL) in dry THF (20 mL), under dry argon atmosphere, was stirred at 60 °C for 20 h, until full consumption of **6** (TLC analysis). The reaction mixture was allowed to reach room temperature and concentrated, and then filtered through a pad of Celite, eluting with MeOH. The resulting filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (hexane/EtOAc (8:2)) to give **8e** as a white solid (98 mg, 0.29 mmol, 58%). Mp: 222−224º C. IR (KBr) υ_{max} (cm^{-1}) 3167, 3060, 1623, 1577, 1493, 1420, 1320, 1232, 1070, 753. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.90 (brs, 1H), 8.63 (d, *J* = 5.1 Hz, 1H), 8.35−8.32 (m, 2H), 8.17 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 5.1 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.37−7.28 (m, 4H), 7.16 (t, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 159.6, 153.9, 148.1, 142.4, 140.4, 139.6, 138.4, 134.6, 130.0, 129.7 (2C), 128.7, 124.7,

122.6, 121.7, 121.6, 120.6, 120.2 (2C), 120.0, 114.4, 111.6. HPLC-Ms (ES-API) 338.0 $[M + H]^+$, t_R 10.739 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{22}H_{16}N_3O$ $[M + H]^+$ 338.1287, found: 338.1293.

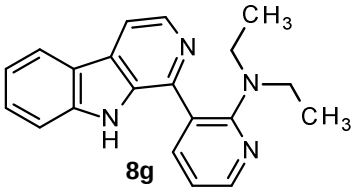
1-[2-(3-Pyridyloxy)-3-pyridyl]-9*H*-pyrido[3,4-*b*]indole 8f



8f

A mixture of **6** (154 mg, 0.5 mmol), Cs_2CO_3 (815 mg, 2.5 mmol) and 3-pyridinol (1.187 g, 12.5 mmol) in dry THF (15 mL), under dry argon atmosphere, was stirred at 60 °C for 24 h, until full consumption of **6** (TLC analysis). The reaction mixture was warmed to room temperature and concentrated, and then filtered through a pad of Celite, eluting with MeOH. The resulting filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (CH_2Cl_2/EtOH (9:1)) to give **8f** as a white solid (120 mg, 0.36 mmol, 71%). Mp: 207−210º C. IR (KBr) υ_{max} (cm^{-1}) 3214, 3165, 3088, 1626, 1569, 1475, 1412, 1237, 1023, 749. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.81 (brs, 1H), 8.60 (d, *J* = 5.2 Hz, 1H), 8.46 (brd, *J* = 2.6 Hz, 1H), 8.38 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.29 (s, 1H), 8.27 (dd, *J* = 3.9, 2.0 Hz, 1H), 8.16 (brd, *J* = 7.8 Hz, 1H), 8.03 (dd, *J* = 5.2, 0.6 Hz, 1H), 7.60−7.49 (m, 2H), 7.45 (ddd, *J* = 8.0, 2.7, 1.4 Hz, 1H), 7.34−7.24 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 159.2, 150.5, 148.1, 145.9, 143.2, 142.6, 140.6, 139.6, 138.0, 134.7, 130.3, 129.1, 128.6, 124.1, 123.3, 122.0, 121.7, 120.6 (2C), 114.8, 111.7. HPLC-Ms (ES-API) 339.2 $[M + H]^+$, t_R 8.166 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{21}H_{15}N_4O$ $[M + H]^+$ 339.1239, found: 338.1240.

***N*,*N*-Diethyl-3-(9*H*-pyrido[3,4-*b*]indole-1-yl)pyridin-2-amine 8g**

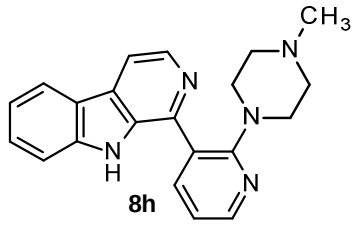


8g

A solution of *i*PrMgCl·LiCl (1.3 M in THF, 3.84 mL, 5 mmol) was added to a stirred solution of diethylamine (365 mg, 5 mmol, 0.5 mL) in dry THF (15 mL), at 0 °C and under dry argon atmosphere. The solution was stirred at 0 °C for 15 min and then 15 min at 25 °C before being added to a solution of **6** (154 mg, 0.5 mmol) in THF (6 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 1 h, until full consumption of **6** was observed (TLC analysis). The reaction mixture was warmed to room temperature, quenched with water and extracted with EtOAc. The organic phase was dried (Na_2SO_4), concentrated under reduced pressure and purified by flash chromatography on silica gel (hexane/EtOAc (8:2)) to give **8g** as a yellow solid (136 mg, 0.43 mmol, 86%). Mp: 228−230º C. IR (KBr) υ_{max} (cm^{-1}) 3141, 3054, 2976, 1623, 1588, 1560, 1488, 1434, 1359, 1236, 1013, 755. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.61 (brs, 1H), 8.62

(d, *J* = 5.2 Hz, 1H), 8.42 (dd, *J* = 4.6, 1.8 Hz, 1H), 8.18 (dd, *J* = 7.5, 1.7 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 5.2 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.08 (dd, *J* = 7.5, 4.6 Hz, 1H), 3.19 (q, *J* = 7.0 Hz, 4H), 0.99 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 157.9, 147.6, 142.1, 141.5, 140.5, 139.7, 139.5, 133.7, 129.7, 128.6, 122.0, 121.8, 120.2, 117.2, 113.6, 111.8, 44.6 (2C), 12.5 (2C). HPLC-Ms (ES-API) 317.2 $[M + H]^+$, t_R 9.213 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{20}H_{21}N_4$ $[M + H]^+$ 317.1758, found: 317.1766.

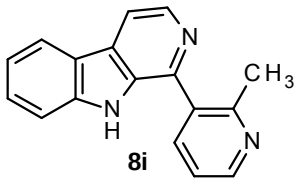
1-[2-(4-Methylpiperazin-1-yl)-3-pyridyl]-(9*H*-pyrido[3,4-*b*]indole-1-yl)pyridin-2-amine 8h



8h

A solution of *i*PrMgCl·LiCl (1.3 M in THF, 3.8 mL, 5 mmol) was added to a stirred solution of 1 methylpiperazine (500 mg, 5 mmol, 0.5 mL) in dry THF (15 mL), at 0 °C and under an atmosphere of dry argon. The solution was stirred at 0 °C for 15 min and then 15 min at 25 °C before being added to a solution of **6** (154 mg, 0.5 mmol) in THF (6 mL) at 0 °C. The reaction mixture was stirred 1 h at 25 °C until full consumption of **6** (TLC analysis). The reaction mixture was warmed to room temperature, quenched with water and extracted with EtOAc. The organic phase was dried (Na_2SO_4), concentrated under reduced pressure and purified by flash chromatography on silica gel (CH_2Cl_2/EtOH (9:1)) to give **8h** as a yellow oil (106 mg, 0.31 mmol, 62%). IR (NaCl) υ_{max} (cm^{-1}) 3270, 3058, 2938, 2846, 1667, 1625, 1433, 1140, 1007, 938, 781, 745. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.61 (brs, 1H), 8.60 (d, *J* = 5.2 Hz, 1H), 8.42 (dd, *J* = 4.7, 1.9 Hz, 1H), 8.21 (dd, *J* = 7.6, 1.9 Hz, 1H), 8.17 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 5.2 Hz, 1H), 7.58 (t, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 7.6, 4.7 Hz, 1H), 3.28−3.14 (m, 4H), 2.30−2.17 (m, 4H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 158.1, 147.8, 142.2, 140.9, 140.3, 139.7, 133.4, 129.9, 128.8, 125.3, 121.9, 121.8, 120.3, 118.1, 114.0, 111.8, 54.8 (2C), 49.5 (2C), 45.9. HPLC-Ms (ES-API) 344.2 $[M + H]^+$, t_R 3.371 min (98%). HRMS (ESI-TOF) m/z calcd for $C_{21}H_{22}N_5$ $[M + H]^+$ 344.1870, found: 344.1874

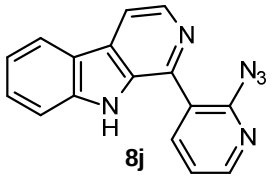
1-(2-Methyl-3-pyridyl]-(9*H*-pyrido[3,4-*b*]indole 8i



8i

A solution of CH_3MgBr (1.0 M in dibutyl ether, 2.0 mL, 2 mmol) was added to a stirred solution of **6** (154 mg, 0.5 mmol) in THF (6 mL) at 0 °C and under an atmosphere of dry argon. The solution was stirred at 0 °C for 15 min and then at 25 °C 24 h, until full consumption of **6** (TLC analysis). The reaction mixture was warmed to room temperature, quenched with water and extracted with EtOAc. The organic phase was dried (Na_2SO_4), concentrated under reduced pressure and purified by flash chromatography on silica gel (CH_2Cl_2/EtOH (99:1)) to give **8i** as a yellow semisolid (62 mg, 0.24 mmol, 48%). IR (KBr) υmax (cm−1) 3391, 2922, 2852, 1644, 1428, 1365, 1319, 1239, 1102, 746. ^{1}H NMR (300 MHz, CD_3OD) δ (ppm) 8.62 (dd, *J* = 5.0, 1.4 Hz, 1H), 8.42 (d, *J* = 5.4 Hz, 1H), 8.25 (d, *J* = 7.9 Hz, 1H), 8.22 (d, *J* = 5.4 Hz, 1H), 7.95 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.61−7.50 (m, 3H), 7.31 (ddd *J* = 7.9, 6.1, 2.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, CD_3OD) δ (ppm) 157.6, 149.7, 142.9, 142.1, 139.5, 138.3, 135.6, 134.3, 131.3, 129.9, 122.9, 122.7, 122.1, 121.0, 115.8, 112.9, 22.3. HPLC-Ms (ES-API) 260.1 $[M + H]^+$, t_R 6.559 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{17}H_{14}N_3$ $[M + H]^+$ 260.1182, found: 260.1190.

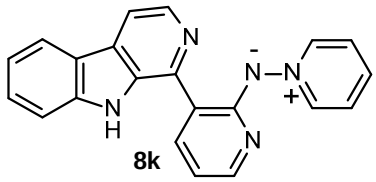
1-(2-Azido-3-pyridyl]-(9*H*-pyrido[3,4-*b*]indole 8j



8j

NaN_3 (163 mg, 2.5 mmol) was added to a stirred solution of **6** (154 mg, 0.5 mmol) in DMF (6 mL) at 0 °C and under an atmosphere of dry argon. The solution was stirred at 0 °C for 15 min and then at 50 °C 24 h, until full consumption of **6** (TLC analysis). The reaction mixture was warmed to room temperature, quenched with water and extracted with EtOAc. The organic phase was dried (Na_2SO_4), concentrated under reduced pressure to supply a yellow solid, purified by washing and filtration from MeCN. Yellow solid (86 mg, 0.23 mmol, 60%). Mp: 177−180º C. IR (KBr) υ_{max} (cm^{-1}) 3102, 3056, 2922, 2853, 1525, 1499, 1402, 1294, 1212, 1136, 1108. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 12.49 (brs, 1H), 9.08 (d, *J* = 7.5 Hz, 1H), 8.91 (d, *J* = 6.7 Hz, 1H), 8.59 (d, *J* = 5.0 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 5.0 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.32 (at, *J* = 7.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 147.4, 140.9, 138.9, 134.8, 133.5, 131.1, 132.1, 129.0, 127.4, 124.5, 121.4, 121.1, 120.1, 117.7, 115.9, 112.5. HPLC-Ms (ES-API) 257.2 $[M - N_2]^+$, t_R 9.423 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{16}H_{11}N_6$ $[M + H]^+$ 287.1038, found: 287.1040.

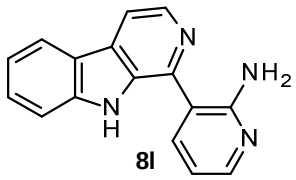
***N*-[3-(9*H*-Pyrido[3,4-*b*]indol-1-yl)pyridin-2-yl]pyridinium aminide 8k**



8k

A suspension of *N*-aminopyridinium iodide (167 mg, 0.75 mmol) and K_2CO_3 (207 mg, 1.5 mmol) in MeCN (4 mL) at 25 °C and under an atmosphere of dry argon was stirred for 45 min. Then, a solution of **6** (154 mg, 0.5 mmol) in MeCN (2 mL) was added and the mixture was stirred at 80 °C for 18 h, until full consumption of **6** (TLC analysis). The reaction mixture was warmed to room temperature and concentrated under reduced pressure. The resulting solid was dissolved in ethyl acetate (10 mL), vigorously stirred and treated again with an excess of solid K_2CO_3. The inorganic salts were filtered and the filtrate evaporated to dryness. Purification by flash chromatography on silica gel (hexane/ethyl acetate (1:1)) supply **8k** as a brown semisolid (89 mg, 0.26 mmol, 53%). IR (KBr) υ_{max} (cm^{-1}) 3433, 2918, 2850, 1623, 1454, 1401, 1229, 748. ^{1}H NMR (500 MHz, CD_3OD) δ (ppm) 8.86 (d, *J* = 6.0 Hz, 2H), 8.42 (d, *J* = 5.2 Hz, 1H), 8.23 (t, *J* = 7.8 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 5.3 Hz, 1H), 7.93−7.90 (m, 3H), 7.83 (d, *J* = 7.1 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 6.82 (dd, *J* = 7.0, 5.3 Hz, 1H). ^{13}C NMR (126 MHz, CD_3OD) δ (ppm) 161.0, 148.2, 146.7, 142.8, 142.1, 141.2, 140.6, 138.5, 135.9, 131.3, 129.7 (2C), 128.8 (2C), 122.6, 122.5, 120.9, 120.4, 115.3, 114.2, 113.0. HPLC-Ms (ES-API) 338.2 $[M + H]^+$, t_R 4.207 min (96%). HRMS (ESI-TOF) m/z calcd for $C_{21}H_{16}N_5$ $[M + H]^+$ 338.1198, found: 338.1400.

3-(9*H*-Pyrido[3,4-*b*]indol-1-yl)pyridin-2-amine 8l



8l

A suspension of *N*-aminopyridinium iodide (833 mg, 3.75 mmol) and K_2CO_3 (345 mg, 2.5 mmol) in MeCN (4 mL) at 25 °C and under an atmosphere of dry argon was stirred for 1 h, and CH_3I (156 µL, 355 mg, 2.5 mmol) was added and the mixture was stirred at 25 °C for 30 min. Then, K_2CO_3 (207 mg, 1.5 mmol) was added and after stirring 30 min at the same temperature, a solution of **6** (154 mg, 0.5 mmol) in MeCN (2 mL) was added and the mixture was stirred at 80 °C for 18 h, until full consumption of **6** (TLC analysis). The reaction was warmed to room temperature and concentrated under reduced pressure. The resulting crude product was dissolved glacial acetic acid (10 mL), vigorously stirred and treated with zinc dust (1.44 g, 22.1 mmol) for 2 h at 25°C. When almost all the zinc had disappeared, another portion of zinc (504 mg,

7.75 mmol) was added and the mixture was kept stirring, at the same temperature, 16 h more. The resulting suspension was passed through a cellite column, and eluted with acetic acid. The eluate was dissolved in EtOAc, neutralized with solid $NaHCO_3$, the inorganic salts were filtered and the filtrate evaporated to dryness. Purification by flash chromatography on silica gel (hexane/ethyl acetate (1:1)) supply **8k** as a white solid (77 mg, 0.30 mmol, 59%). IR (KBr) υ_{max} (cm^{-1}) 3464, 1624, 1606, 1565, 1454, 1230, 744. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.96 (brs, 1H), 8.51 (d, *J* = 5.2 Hz, 1H), 8.17−8.11 (m, 2H), 7.95−7.91 (m, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.81 (dd, *J* = 7.3, 5.0 Hz, 1H), 5.72 (brs, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 156.5, 148.0, 140.3, 140.2, 138.6, 137.4, 133.6, 130.2, 128.6, 121.6 (2C), 120.3, 117.1, 114.0, 113.9, 111.7. HPLC-Ms (ES-API) 261.2 $[M + H]^+$, t_R 5.462 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{16}H_{13}N_4$ $[M + H]^+$ 261.1134, found: 261.1135.

X-ray crystallographic data for 2b and 6

Colourless crystals of **2b** and **6** were obtained from recrystallization processes in acetone and dichloromethane respectively. The crystals were covered with a layer of a viscous perfluoropolyether (FomblinY). Suitable crystals were selected with the aid of a microscope, mounted on a cryoloop, and placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data are presented in Table S1. The structures were solved, using the WINGX package,[27] by intrinsic phasing methods (SHELXT),[28] and refined by least-squares against F^2 (SHELXL-2014/7).[29] In the crystallographic study of **2b** and **6** all non-hydrogen atoms were anisotropically refined, whereas hydrogen atoms were included, positioned geometrically and refined by using a riding model.

Table S1. Experimental Data for the X-ray Diffraction Study on **2b** and **6**.

	2b	**6**
CCDC[a] code	1897908	1897274
Formula	$C_{16}H_{10}BrN_3O_2S$	$C_{16}H_9N_3O_2S$
M_r	388.24	307.32
T [K]	200(2)	200(2)
λ [Å]	0.71073	0.71073
crystal system	Triclinic	Orthorhombic
space group	P-1	$P2_12_12_1$
a [Å]; α [º]	8.325(1); 65.08(1)	5.168(1)
b [Å]; β [º]	9.840(1); 71.70(1)	15.659(1)
c [Å]; γ [º]	11.187(1); 67.23(1)	15.934(1)
V [Å^3]	753.7(2)	1289.5(2)
Z	2	4
ρ_{calcd} [g cm^{-3}]	1.711	1.583
$\mu_{MoK\alpha}$ [mm^{-1}]	2.878	0.262
F(000)	388	632
crystal size [mm^3]	0.30×0.30×0.31	0.15×0.18×0.27
θ range (deg)	3.03 to 27.50	3.65 to 27.50
index ranges	-10 to 10, -12 to 12, -14 to 14	-6 to 6, -20 to 20, -20 to 20
Reflections collected	24452	18859
Unique data	3451 [R_{int} = 0.107]	2968 [R_{int} = 0.074]
obsd data [I>2σ(I)]	2972	2401
Goodness-of-fit on F^2	1.087	1.087
final R^a indices [I>2σ(I)]	$R1$ = 0.036, w$R2$ = 0.082	$R1$ = 0.044, w$R2$ = 0.084
R^b indices (all data)	$R1$ = 0.047, w$R2$ = 0.088	$R1$ = 0.069, w$R2$ = 0.094
largest diff. peak/hole[e.Å^{-3}]	0.859/-0.798	0.231/-0.277

[a]Cambridge Crystallographic Data Centre. [b]$R1 = \Sigma||F_0|-|F_c|| / [\Sigma|F_0|]$, w$R2 = \{[\Sigma w(F_0^2-F_c^2)^2] / [\Sigma w(F_0^2)^2]\}^{1/2}$

[27] L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849.
[28] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **71**, 3.
[29] G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3.

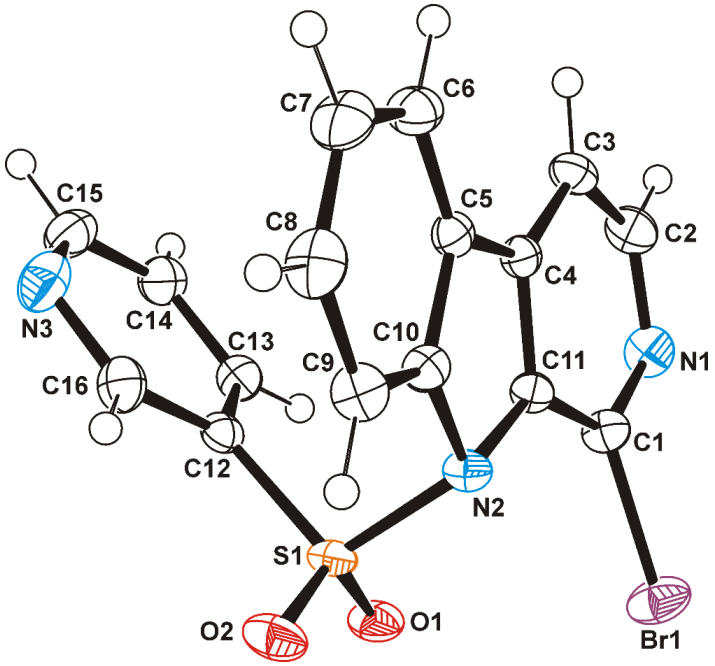
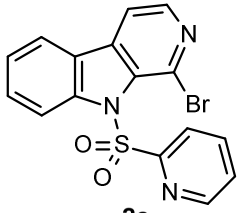


Figure S1. ORTEP diagram for compound **2b**. Thermal ellipsoids are drawn at the 50% probability level.

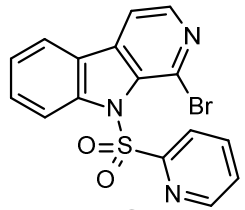
Copies of ^{1}H and ^{13}C-NMR spectra for compounds **2a,b, 6**, and **8a–l**

^{1}H-NMR 300 MHz, $CDCl_3$



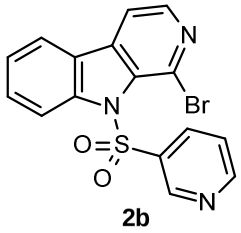
2a

^{13}C-NMR 75 MHz, $CDCl_3$



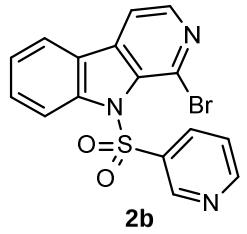
2a

^{1}H-NMR 300 MHz, $CDCl_3$



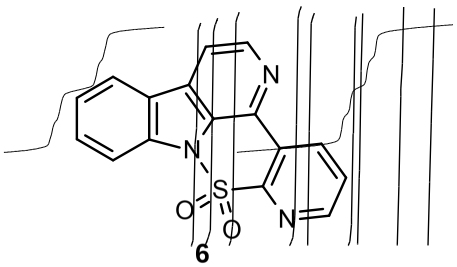
2b

^{13}C-NMR 75 MHz, $CDCl_3$



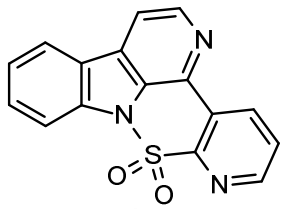
2b

^{1}H-NMR 500 MHz, DMSO-d_6



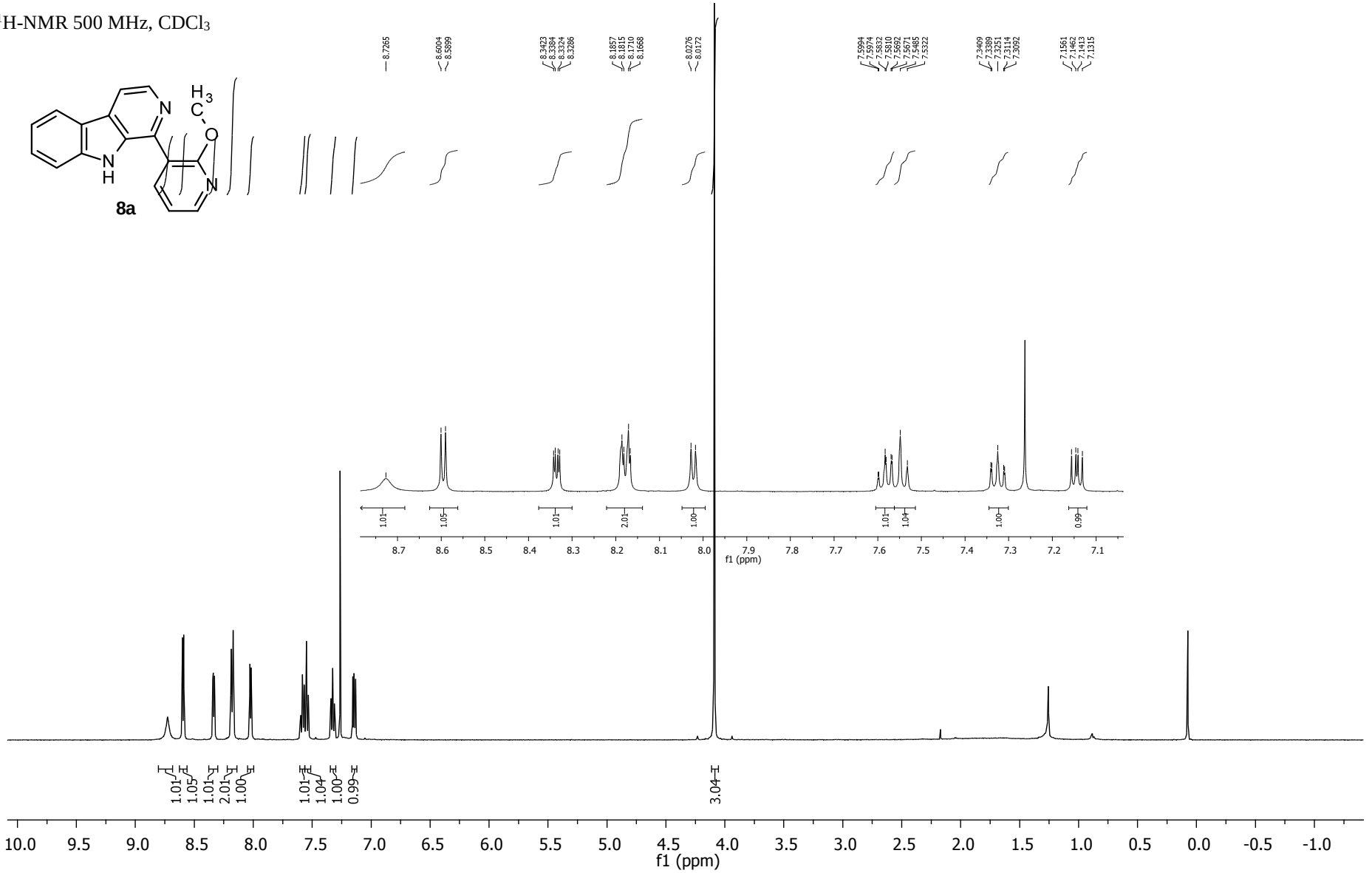
6

^{13}C-NMR 126 MHz, DMSO-*d*$_6$



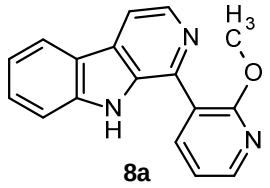
6

^{1}H-NMR 500 MHz, $CDCl_3$



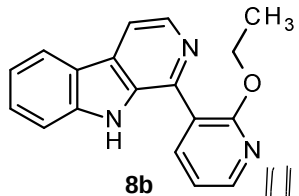
8a

^{1}H-NMR 75 MHz, $CDCl_3$



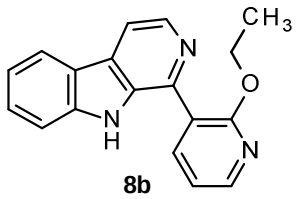
8a

^{1}H-NMR 500 MHz, CD_3OD



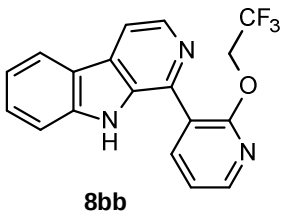
8b

^{13}C-NMR 75 MHz, CD_3OD

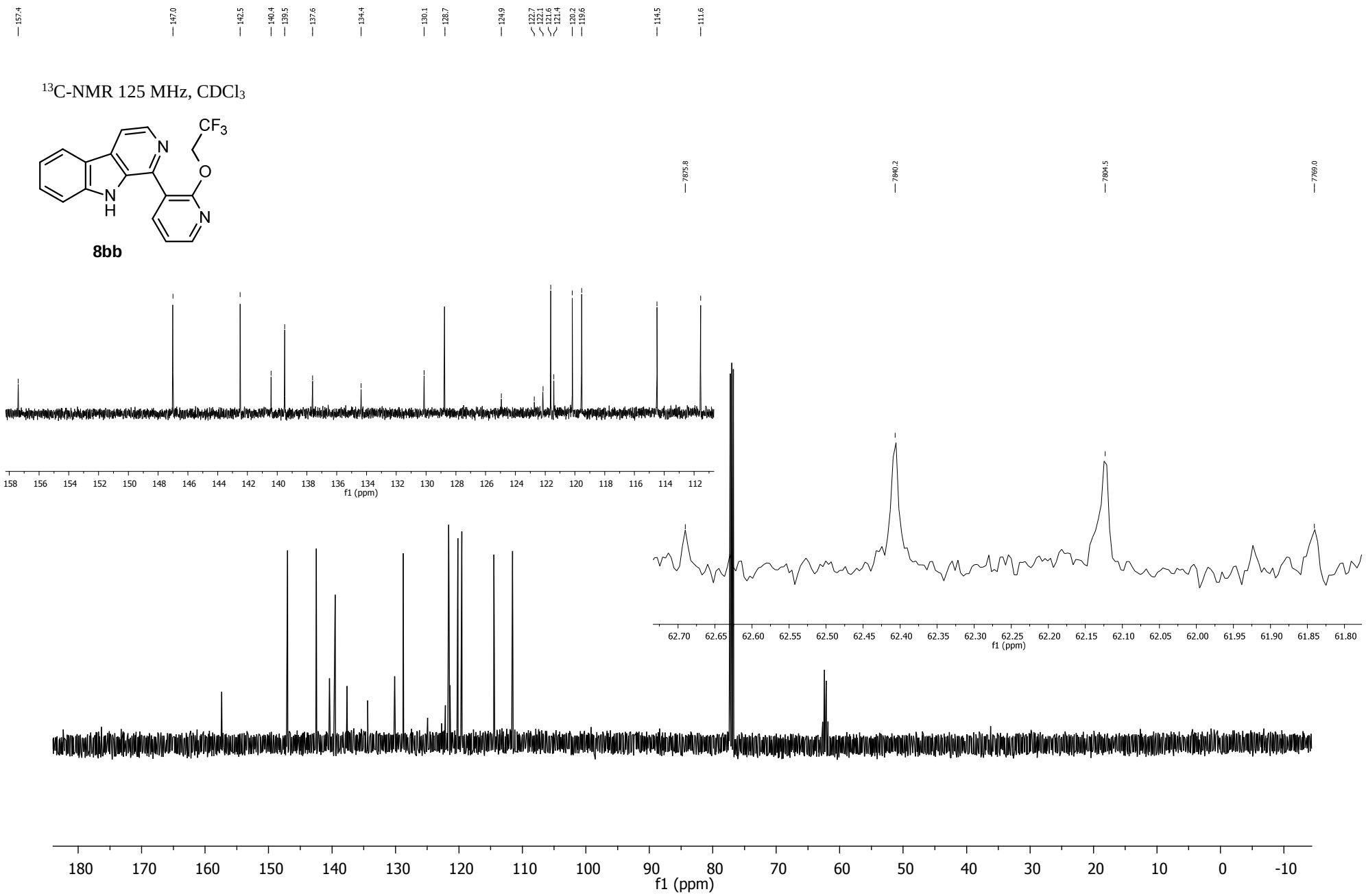


8b

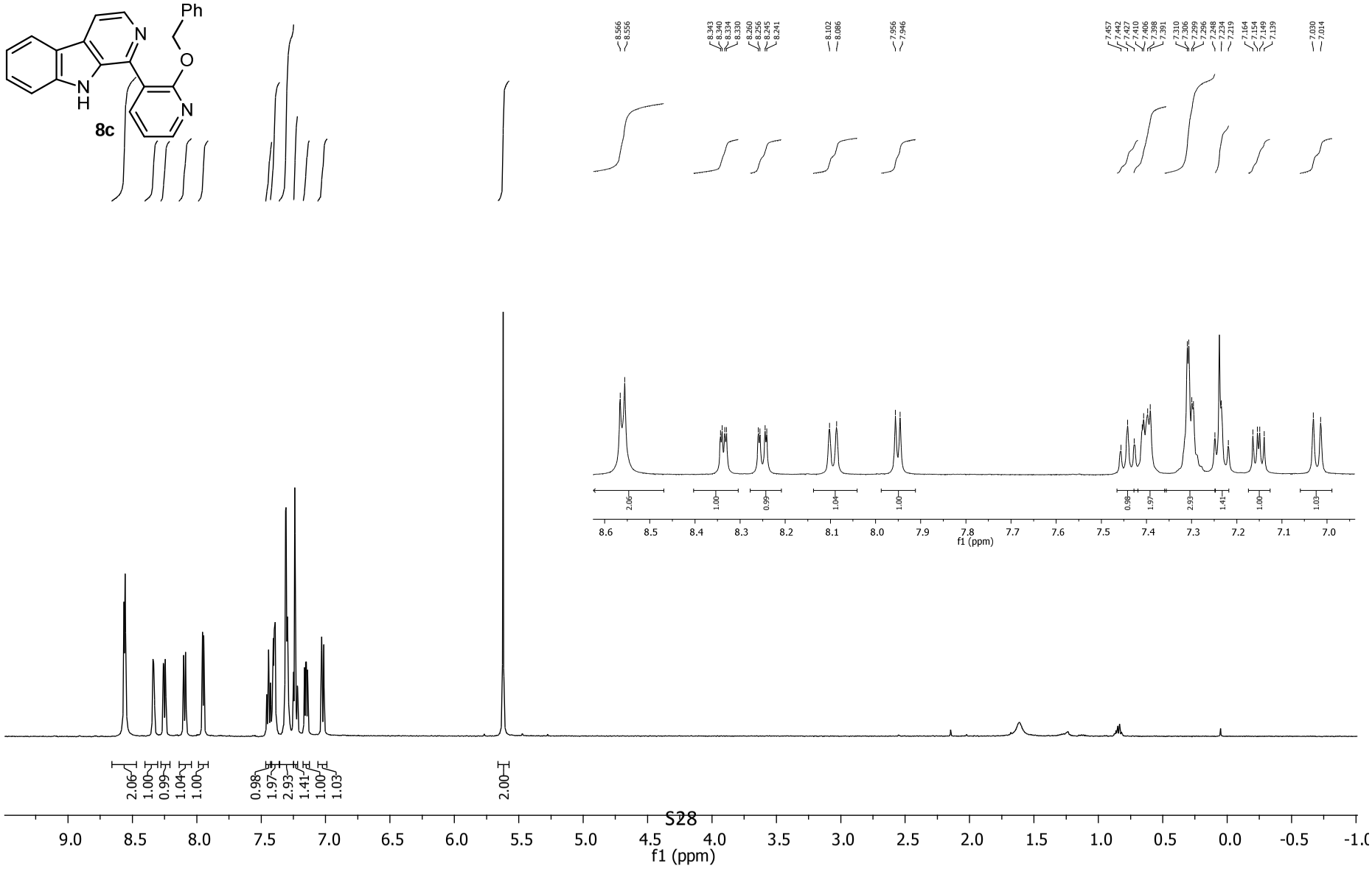
^{1}H-NMR 300 MHz, $CDCl_3$



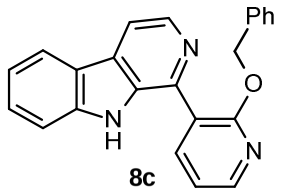
8bb


157.4
147.0
142.5
140.4
139.5
137.6
134.4
130.1
128.7
124.9
122.7
122.1
121.6
121.4
120.2
119.6
114.5
111.6
^{13}C-NMR 125 MHz, $CDCl_3$
CF3
N
O
N
H
N
8bb
78/5.8
7840.2
7804.5
7769.0
158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112
f1 (ppm)
62.70 62.65 62.60 62.55 62.50 62.45 62.40 62.35 62.30 62.25 62.20 62.15 62.10 62.05 62.00 61.95 61.90 61.85 61.80
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H-NMR 500 MHz, $CDCl_3$

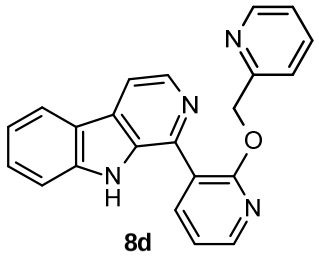


^{13}C-NMR 126 MHz, $CDCl_3$



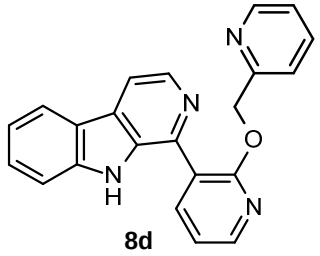
8c

^{1}H-NMR 500 MHz, $CDCl_3$



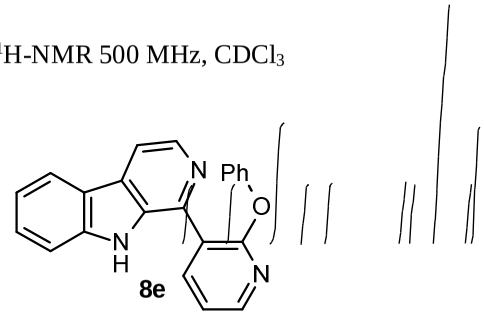
8d

^{13}C-NMR 75 MHz, $CDCl_3$



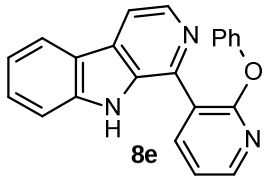
8d

^{1}H-NMR 500 MHz, $CDCl_3$



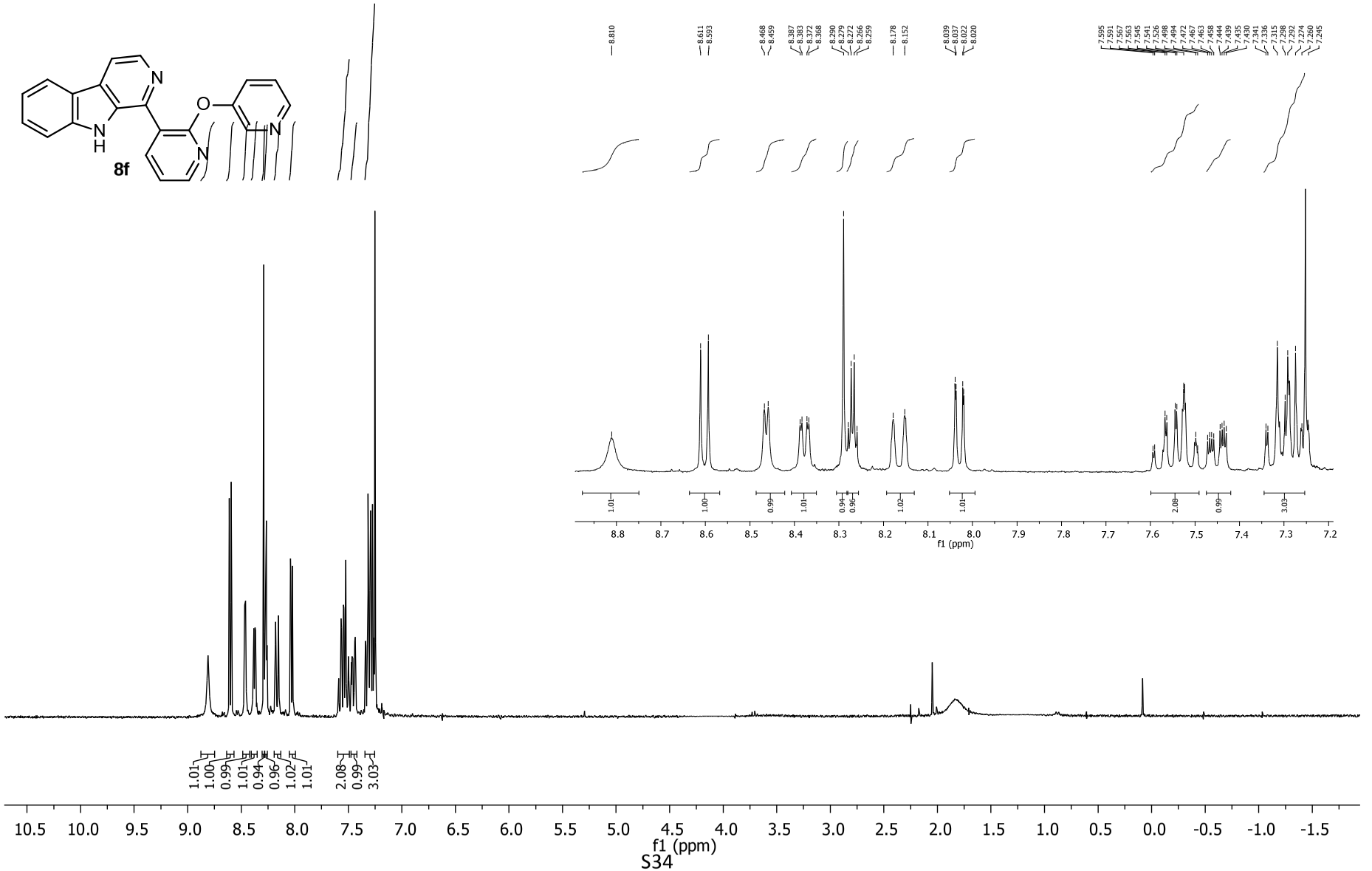
8e

^{13}C-NMR 126 MHz, $CDCl_3$

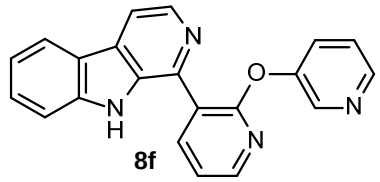


8e

^{1}H-NMR 300 MHz, $CDCl_3$

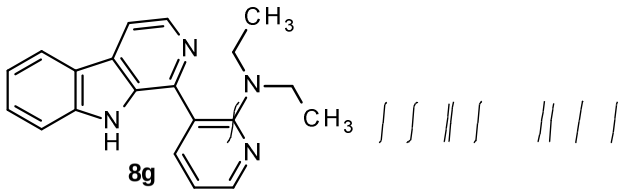


^{13}C-NMR 75 MHz, $CDCl_3$



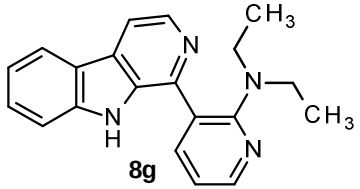
8f

^{1}H-NMR 500 MHz, $CDCl_3$



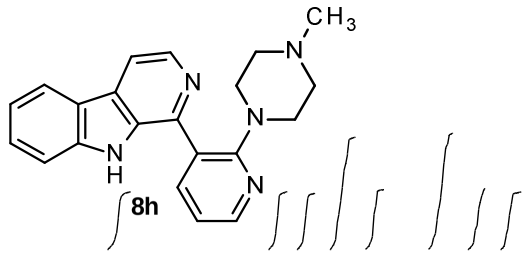
8g

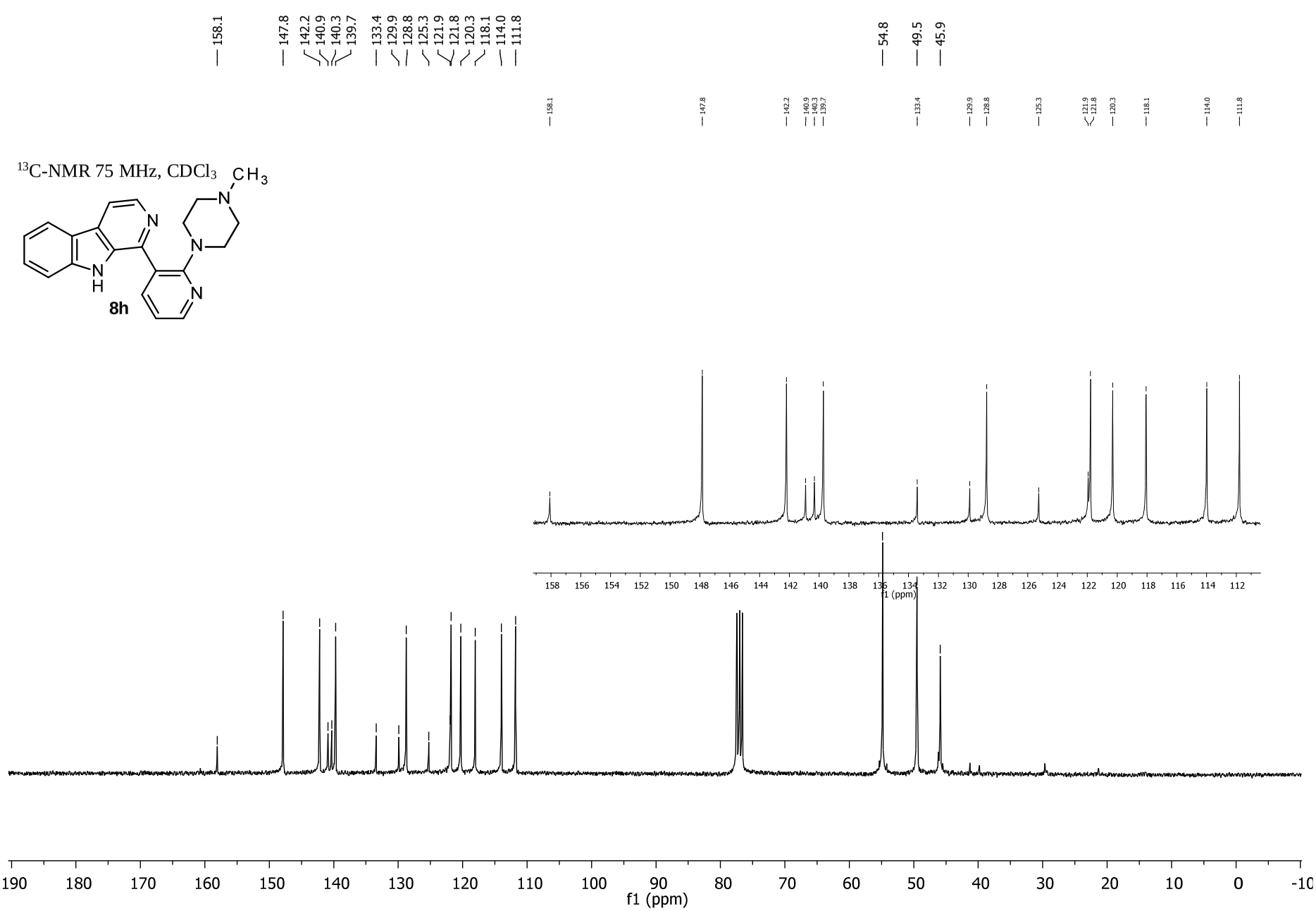
^{13}C-NMR 75 MHz, $CDCl_3$



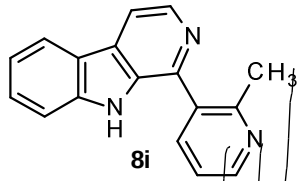
8g

^{1}H-NMR 500 MHz, $CDCl_3$

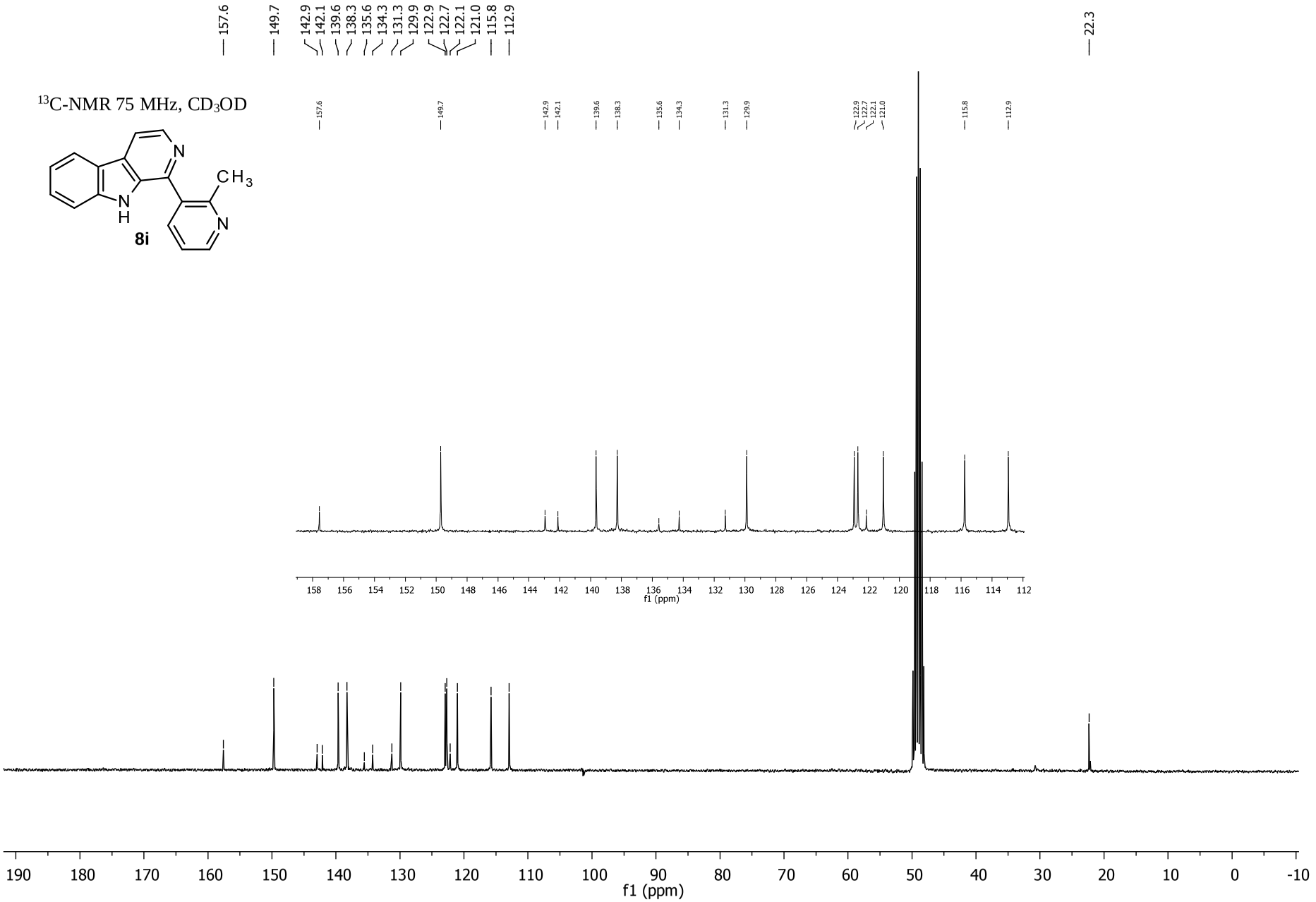



158.1
147.8
142.2
140.9
140.3
139.7
133.4
129.9
128.8
125.3
121.9
121.8
120.3
118.1
114.0
111.8
54.8
49.5
45.9
13C-NMR 75 MHz, CDCl3
CH3
N
N
N
N
H
8h
f1 (ppm)

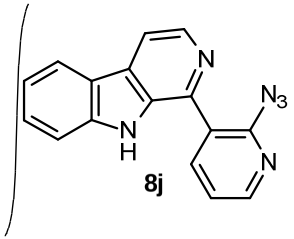
^{1}H-NMR 300 MHz, CD_3OD



8i


157.6
149.7
142.9
142.1
139.6
138.3
135.6
134.3
131.3
129.9
122.9
122.7
122.1
121.0
115.8
112.9
22.3
^{13}C-NMR 75 MHz, CD_3OD
N
CH_3
N
H
N
8i
f1 (ppm)

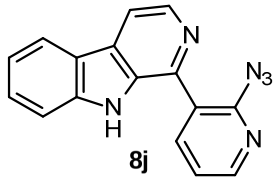
^{1}H-NMR 300 MHz, $CDCl_3$



8j

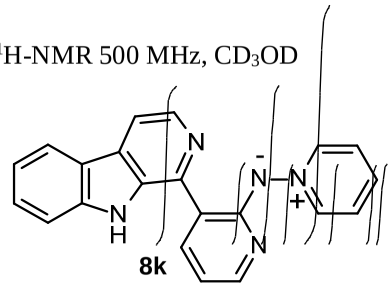
147.4
140.9
138.9
134.8
133.5
133.1
132.1
129.0
127.4
124.5
121.4
121.1
120.1
117.7
115.9
112.5

^{13}C-NMR 75 MHz, $CDCl_3$



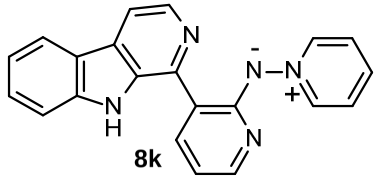
8j

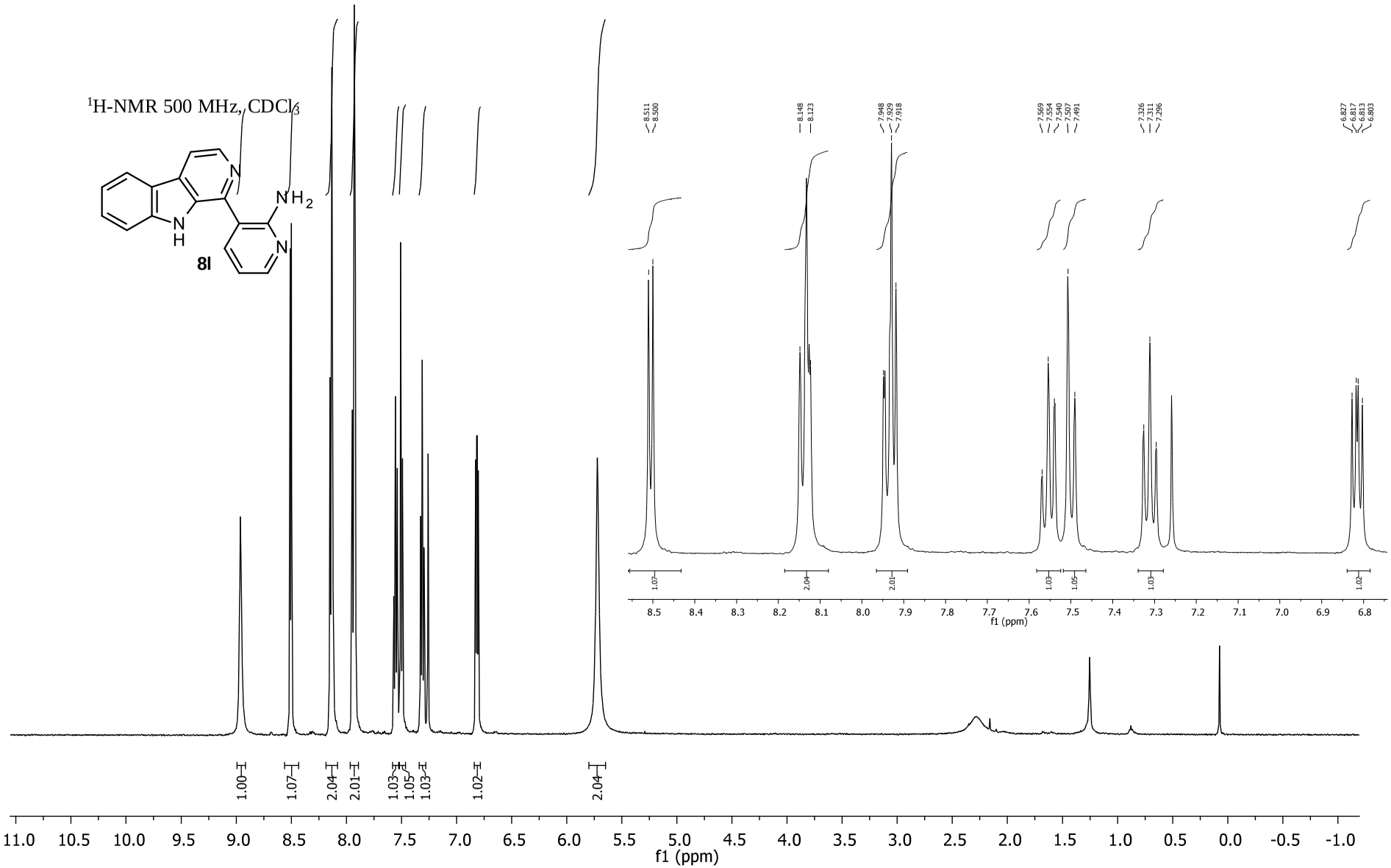
^{1}H-NMR 500 MHz, CD_3OD



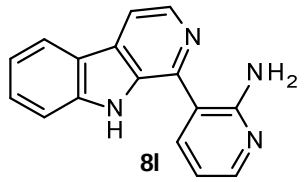
8k

^{13}C-NMR 126 MHz, CD_3OD




^{1}H-NMR 500 MHz, $CDCl_3$
8l
8.511
8.500
8.148
8.123
7.948
7.939
7.929
7.918
7.569
7.554
7.540
7.507
7.491
7.326
7.311
7.296
6.827
6.817
6.813
6.803
1.00
1.07
2.04
2.01
1.03
1.05
1.03
1.02
2.04
f1 (ppm)

^{13}C-NMR 75 MHz, $CDCl_3$



8l

156.5 148.0 140.3 140.3 138.6 137.4 133.6 130.2 128.6 121.6 120.3 117.1 114.0 113.9 111.7