Supporting Information

Rhodium-Catalyzed Selective C–H Functionalization of NNN Tridentate Chelating Compounds via a Rollover Pathway

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I. General Methods

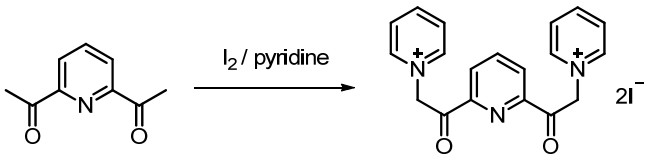
Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates, aluminium oxide 60 F_{254} neutral sheets, or aluminium oxide 60 F_{254} basic plates. Visualization on TLC was achieved by the use of UV light (254 nm), treatment with acidic anisaldehyde, 10% ninhydrin in ethanol, 5% phosphormolybdic acid in ethanol, or ceric ammonium molybdate stain followed by heating. Flash column chromatography was undertaken on silica gel (400-630 mesh) or aluminium oxide 90 active basic (0.063-0.200 mm) using a proper eluent system. The purity of argon gas is 99.99999%. Reactions of ethylene gas were performed by using Q-Tube-Purging-35 (QLabTech). Air sensitive liquid and solutions were transferred via syringe or cannula by using degassed solvents. Concentration of solution was carried out by using a rotary evaporator and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 torr. Unless otherwise stated, all commercial reagents were used without additional purification. Terpyridine substrates, olefins, rhodium complexes, bases, and NHC (N-heterocyclic carbene) ligands were purchased from Aldrich chemical company, TCI, or Strem.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Brucker Avance 400MHz or Agilent Technologies DD2 600MHz. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak ($CHCl_3$ in $CDCl_3$: 7.26 ppm) or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz). Carbon 13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded on Brucker Avance (100MHz) or Agilent Technologies DD2 (150MHz) and was fully decoupled by broad band decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded on Bruker Alpha FT-IR Spectrometer. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using FAB or ESI from KAIST Research Analysis Center (Daejeon). Melting points were measured with Buchi Melting Point M-565. The diffraction data of **4e** and **6a** were collected on a Bruker D8 QUEST. A suitable size and quality of crystal was coated with Paratone-N oil and mounted on a DualThickness MicroLoops LD purchased from MiTeGen. The data were collected with graphite mono-chromated Mo Kα radiation (λ = 0.71073 Å) at 120 K. Cell parameters were determined and refined by SMART program. Data reduction was performed using SAINT software.4 An empirical absorption correction was applied using the SADABS program.

II. Procedures for the Preparation of Starting Materials

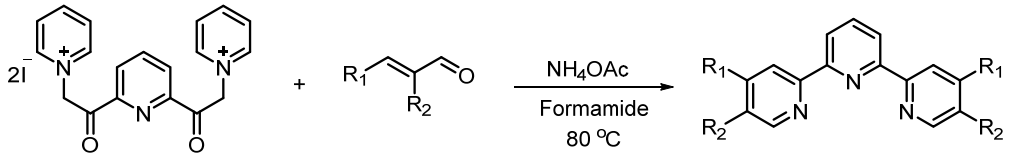
1. Preparation of 2,2':6',2''-Terpyridine Derivatives[S1]

1-1. Synthesis of Bispyridinium Iodide Salt



To a solution of 2,6-diacetylpyridine (1.6 mg, 9.8 mmol) in pyridine (12.5 mL) were added dropwise iodine (5.0 g, 20.0 mmol) in pyridine (12.5 mL). The mixture was stirred for 3 h at 110 ˚C. After cooling at room temperature, the reaction mixture started to give precipitates which were collected by filtration, washed with cold ethanol, and then dried under reduced pressure to afford the desired bispyridinium iodide salt (4.2 g, 73%) which were used for the next step without further purification.

1-2. Synthesis of 2,2':6',2''-Terpyridine Derivatives



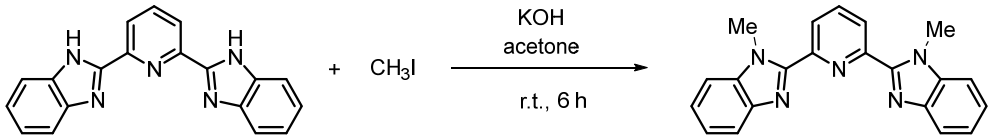
To a solution of bispyridinium iodide salt (1.7 g, 3.0 mmol) and ammonium acetate (3.6 g) in formamide (18 mL), α,β-unsaturated aldehyde (6.0 mmol) was added. Heating the reaction mixture was maintained overnight at 80 °C. After cooling to room temperature, pale beige precipitate was formed that was filtered, washed with H_2O to afford the crude product, which was purified by flash chromatography on basic alumina oxide with *n*-hexane/EtOAc.

2. Preparation of 2,6-Bis(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)pyridine[S2]

2-1. Synthesis of 2,6-Bis(1*H*-benzo[*d*]imidazol-2-yl)pyridine

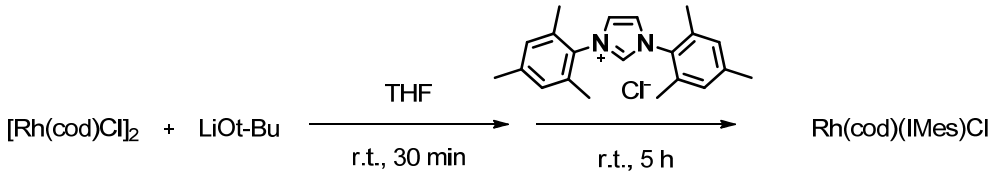
In a 100 mL round-bottom flask, 2,6-pyridinedicarboxylic acid (1.7 g, 10 mmol), 1,2-diaminobenzene (2.4 g, 22 mmol), and 10 mL of PPA (polyphosphoric acid) were added and the reaction mixture was heated at 230 ˚C under nitrogen for 4 h. The dark solution mixture was poured into 325 mL of distilled water, and pH of the mixture was adjusted to 11 by adding ammonium hydroxide. Slightly purple precipitate was filtered, washed with water and recrystallized from methanol to give the desired product (2.8 g, 90%) which was used for the next step without further purification.

2-2. Synthesis of 2,6-Bis(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)pyridine



To a suspension of 2,6-bis(1*H*-benzo[*d*]imidazol-2-yl)pyridine (622 mg, 2.0 mmol) in acetone (10 mL), powdered KOH (560 mg, 10 mmol) was added. The mixture was stirred for 15 min at room temperature, followed by the addition of methyl iodide (32 mmol) with vigorous stirring. Reaction continued for another 6 h at room temperature. The reaction mixture was poured into water. The precipitate was filtered and recrystallized from methanol to afford crude mixture. The crude mixture was purified by flash chromatography on silica gel with *n*-hexane/EtOAc (6:1) to afford desired product (463 mg, 68%).

3. Preparation of Rh(cod)(IMes)Cl[S3]

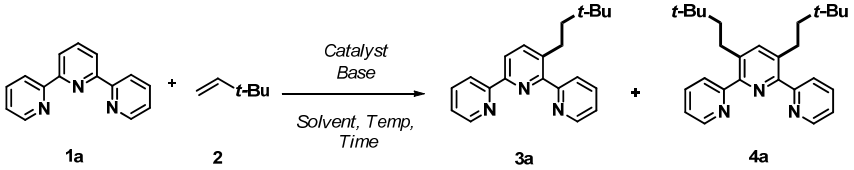


A suspension of $[Rh(cod)Cl]_2$ (250 mg, 0.5 mmol) and LiO*t*-Bu (104 mg, 1.3 mmol) in THF (8.5 mL) was stirred at room temperature. After 30 min, to this mixture, a solution of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (340 mg, 1.0 mmol) in THF(2.0 mL) was added with vigorous stirring. The reaction continued for another 3 h at room temperature. The resulting yellowish suspension was concentrated under the reduced pressure. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 4:1) to give the desired product (240 mg, 44%).

III. Procedure of the Optimization Study (Table S1)

To an oven-dried screwed vial were added 2,2':6',2"-terpyridine (**1a**, 46.6 mg, 0.2 mmol), ligand, metal catalyst, base, and solvent (0.4 mL) in a glove box. The mixture was taken outside the box. 3,3-Dimethyl-1-butene (0.13 mL, 1.0 mmol) was added to the reaction mixture, and then vigorously stirred at 150 ^{0}C. The reaction mixture was diluted with ethyl acetate, and filtered through a pad of basic alumina oxide, and then organic solvents were removed under the reduced pressure. Crude yield of each product was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

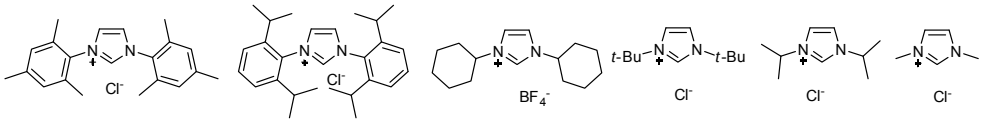
Table S1. Optimization of Reaction Conditions



1a 2 3a 4a

Entry	Catalytic system (mol %)	Base (equiv)	Temp (^{o}C)	Time (h)	**3a** (%)	**4a** (%)
1[a]	Rh(cod)(IMes)Cl (3)	*t*-BuONa (0.3)	130	24	24	16
2[a]	Rh(cod)(IMes)Cl (10)	*t*-BuONa (1.5)	130	24	20	55
3[a]	Rh(cod)(IMes)Cl (10)	*t*-BuONa (3.0)	130	24	24	74
4	Rh(cod)(IMes)Cl (5)	*t*-BuONa (1.5)	150	24	<5	95
5	Rh(cod)(IMes)Cl (3)	*t*-BuONa (1.5)	150	24	39	51
6	**Rh(cod)(IMes)Cl (5)**	***t*-BuONa (0.3)**	**150**	**24**	<5	**99 (95)**
7[b]	Rh(cod)(IMes)Cl (5)	*t*-BuONa (0.3)	150	24	13	87
8	Rh(cod)(IMes)Cl (5)	*t*-BuONa (0.3)	150	20	13	84
9	Rh(cod)(IMes)Cl (5)	*t*-BuONa (0.3)	150	12	22	77
10	$[Rh(cod)Cl]_2$ (2.5) + **L1** (5)	*t*-BuONa (0.35)	150	24	<5	95
11	$[Rh(coe)_2Cl]_2$ (2.5) + **L1** (5)	*t*-BuONa (0.35)	150	24	<5	97
12	Rh(cod)(IMes)Cl (5)	Cs_2CO_3 (0.3)	150	24	<5	95
13	$[Rh(cod)Cl]_2$ (2.5) + **L2** (5)	*t*-BuONa (0.35)	150	24	11	-
14	$[Rh(cod)Cl]_2$ (2.5) + **L3** (5)	*t*-BuONa (0.35)	150	24	-	-
15	$[Rh(cod)Cl]_2$ (2.5) + **L4** (5)	*t*-BuONa (0.35)	150	24	-	-
16	$[Rh(cod)Cl]_2$ (2.5) + **L5** (5)	*t*-BuONa (0.35)	150	24	<5	-
17	$[Rh(cod)Cl]_2$ (2.5) + **L6** (5)	*t*-BuONa (0.35)	150	24	<5	-
18	Rh(cod)(IMes)Cl (5)	-	150	24	<5	<5
19	-	*t*-BuONa (0.3)	150	24	-	-
20	$[Rh(cod)Cl]_2$ (2.5)	*t*-BuONa (0.3)	150	24	-	-

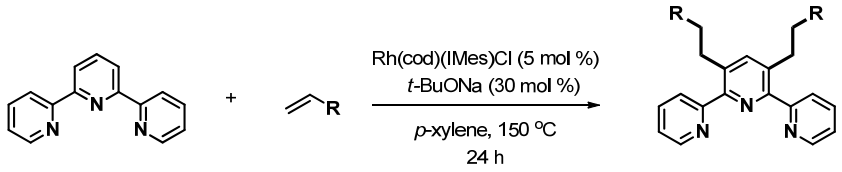
[a] Toluene as solvent. [b] Weighed in air.



L1 (IMes·HCl) L2 (IPr·HCl) L3 (ICy·HBF$_4$) L4 (I*t*Bu·HCl) L5 (I*i*Pr·HCl) L6 (IMe·HCl)

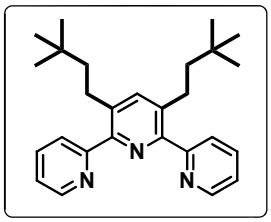
IV. Rh-Catalyzed Bis-alkylation of Tridentate Compounds

1. Rh-Catalyzed Bis-alkylation of 2,2′:6′,2″-Terpyridine with Various Alkenes (Table 2)



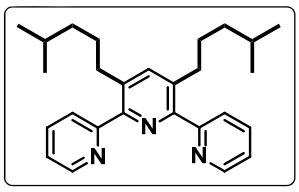
In an Ar charged glove box with oxygen and water levels ≤2 ppm, to an oven-dried screwed vial were added 2,2′:6′,2″-terpyridine (46.6 mg, 0.2 mmol), Rh(cod)(IMes)Cl (5.5 mg, 5.0 mol %), sodium *tert*-butoxide (5.8 mg, 30 mol %), and *p*-xylene (0.4 mL, 0.5 M). The mixture was taken outside the box and olefin (1.0 mmol, 5.0 equiv) was added to the reaction mixture. The reaction mixture was vigorously stirred at 150 ˚C for the indicated time, cooled to room temperature, and diluted with ethyl acetate. The crude product was filtered through a pad of basic alumina oxide, and organic solvents were removed under reduced pressure. Desired product was obtained by basic alumina oxide chromatography (*n*-hexane/ EtOAc, 6:1~4:1).

3',5'-Bis(3,3-dimethylbutyl)-2,2':6',2''-terpyridine (4a, Table 2**)**



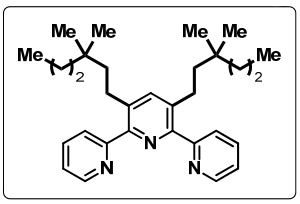
White solid (76 mg, 95%); **m.p.** 102–104 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (2H, d, *J* = 4.7 Hz), 7.84–7.82 (2H, m), 7.77 (2H, td, *J* = 7.7, 1.7 Hz), 7.50 (1H, s), 7.27–7.24 (2H, m), 2.91–2.88 (4H, m), 1.42–1.39 (4H, m), 0.85 (18H, s); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.1, 153.0, 148.2, 140.9, 137.4, 136.4, 124.3, 122.4, 45.8, 30.6, 29.2, 27.8; **IR** (cm^{-1}) 3059, 2950, 2901, 1585, 1448, 1245, 1038, 993, 801, 742; **HRMS** (EI) m/z calcd. for $C_{27}H_{35}N_3$ $[M]^+$: 401.2831, found: 401.2832.

3',5'-Bis(4-methylpentyl)-2,2':6',2''-terpyridine (4b, Table 2**)**



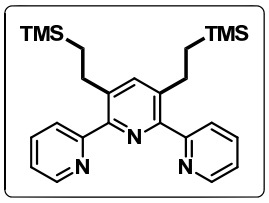
White solid (69 mg, 89%); **m.p.** 62–64 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.3 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.76 (t, *J* = 7.7 Hz, 2H), 7.54 (s, 1H), 7.28–7.22 (m, 2H), 2.90 (t, *J* = 7.9 Hz, 4H), 1.49 (m, 6H), 1.14 (q, *J* = 7.2 Hz, 4H), 0.80 (d, *J* = 6.6 Hz, 12H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.1, 153.0, 148.2, 140.6, 136.6, 136.6, 124.4, 122.4, 38.7, 32.4, 28.6, 27.6, 22.5; **IR** (cm^{-1}) 2951, 2864, 1585, 1561, 1446, 1418, 1037, 990, 912, 797, 748; **HRMS** (EI) m/z calcd. for $C_{27}H_{35}N_3$ $[M]^+$: 401.2831, found: 401.2829.

3',5'-Bis(3,3-dimethylhexyl)-2,2':6',2''-terpyridine (4c, Table 2**)**



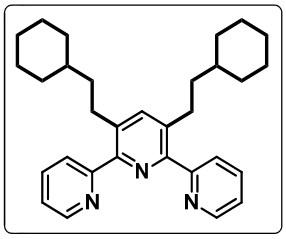
Colorless resin (76 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.8 Hz, 2H), 7.81–7.72 (m, 4H), 7.45 (s, 1H), 7.24 (td, *J* = 5.7, 4.8, 1.7 Hz, 2H), 2.87–2.78 (m, 4H), 1.38–1.30 (m, 4H), 1.10-1.08 (m, 8H), 0.81 (t, *J* = 6.2 Hz, 6H), 0.77 (s, 12H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.1, 153.0, 148.2, 140.9, 137.5, 136.5, 124.4, 122.4, 44.2, 43.7, 33.0, 27.3, 27.1, 17.0, 15.1; **IR** (cm^{-1}) 2953, 2928, 2868, 1585, 1469, 1384, 1091, 1038, 991, 741; **HRMS** (EI) m/z calcd. for $C_{31}H_{43}N_3$ $[M]^+$: 457.3457, found: 457.3458.

3',5'-Bis[2-(trimethylsilyl)ethyl]-2,2':6',2''-terpyridine (4d, Table 2**)**



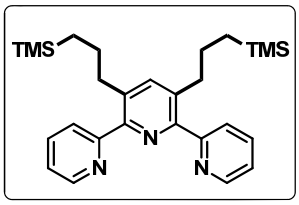
White solid (66 mg, 76%); **m.p.** 88–90 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 2H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.77 (td, *J* = 7.8, 1.8 Hz, 2H), 7.56 (s, 1H), 7.29–7.22 (m, 2H), 2.96–2.82 (m, 4H), 0.80–0.67 (m, 4H), -0.05 (s, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.2, 152.3, 148.2, 139.7, 139.6, 136.4, 124.4, 122.3, 26.8, 18.9, -1.9; **IR** (cm^{-1}) 3050, 2951, 1584, 1445, 1258, 1173, 1088, 903, 742; **HRMS** (EI) m/z calcd. for $C_{25}H_{35}N_3Si_2$ $[M]^+$:, 433.2370, found: 433.2368.

3',5'-Bis(2-cyclohexylethyl)-2,2':6',2''-terpyridine (4e, Table 2**)**



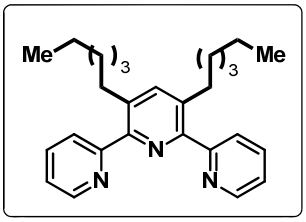
White solid (84 mg, 93%); **m.p.** 91–93 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.0 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.77–7.72 (m, 2H), 7.51 (s, 1H), 7.28–7.17 (m, 2H), 2.96–2.88 (m, 4H), 1.63–1.59 (m, 10H), 1.38 (q, *J* = 7.3Hz, 4H), 1.16–1.08 (m, 8H), 0.81 (q, *J* = 11.1Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.2, 153.0, 148.2, 140.6, 137.0, 136.4, 124.4, 122.3, 38.9, 37.5, 33.1, 29.6, 26.6, 26.3; **IR** (cm^{-1}) 2916, 2843, 1583, 1561, 1444, 1417, 1261, 1206, 1162, 996, 887, 748; **HRMS** (EI) m/z calcd. for $C_{31}H_{39}N_3$ $[M]^+$: 453.3144, found: 453.3145.

3',5'-Bis[3-(trimethylsilyl)propyl]-2,2':6',2''-terpyridine (4f, Table 2**)**



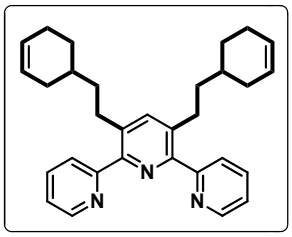
Colorless resin (66 mg, 72%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.75 (t, *J* = 7.8 Hz, 2H), 7.52 (s, 1H), 7.27–7.23 (m, 2H), 2.94 (t, *J* = 7.7 Hz, 4H), 1.54–1.48 (m, 4H), 0.48–0.42 (m, 4H), -0.10 (s, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.2, 153.2, 148.3, 140.7, 136.4, 136.2, 124.4, 122.7, 36.0, 25.3, 16.7, -1.8; **IR** (cm^{-1}) 3059, 2950, 1586, 1418, 1245, 1113, 1038, 992, 831, 758; **HRMS** (EI) m/z calcd. for $C_{27}H_{39}N_3Si_2$ $[M]^+$: 461.2683, found: 461.2684.

3',5'-Dihexyl-2,2':6',2''-terpyridine (4g, Table 2**)**



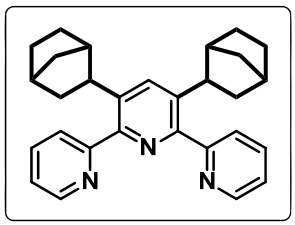
Colorless resin (59 mg, 73%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.7 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.77 (t, *J* = 7.7 Hz, 2H), 7.54 (s, 1H), 7.26 (t, *J* = 6.1 Hz, 2H), 2.92 (t, *J* = 7.9 Hz, 4H), 1.53–1.48 (m, 4H), 1.28–1.14 (m, 12H), 0.83 (t, *J* = 6.8 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.1, 153.0, 148.2, 140.6, 136.6, 136.5, 124.5, 122.4, 32.1, 31.5, 30.8, 29.1, 22.5, 14.0; **IR** (cm^{-1}) 2953, 2922, 2852, 1585, 1562, 1449, 1418, 1145, 1091, 1038, 991, 741; **HRMS** (EI) m/z calcd. for $C_{27}H_{35}N_3$ $[M]^+$: 401.2831, found: 401.2833.

3',5'-Bis[2-(cyclohex-3-en-1-yl)ethyl]-2,2':6',2''-terpyridine (4h, Table 2**)**



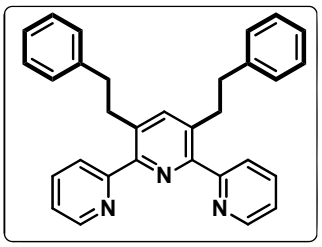
White solid (79 mg, 88%); **m.p.** 72–74 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.8 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.74 (t, *J* = 7.7 Hz, 2H), 7.53 (s, 1H), 7.24 (t, *J* = 6.1 Hz, 2H), 5.64–5.54 (m, 4H), 2.96 (t, *J* = 7.3 Hz, 4H), 2.05–1.86 (m, 6H), 1.70–1.41 (m, 10H), 1.20–1.04 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.1, 153.0, 148.2, 140.7, 136.9, 136.5, 127.0, 126.5, 124.4, 122.4, 38.0, 33.5, 31.7, 29.7, 28.6, 25.1; **IR** (cm^{-1}) 3058, 2911, 2850, 1585, 1562, 1418, 1143, 1091, 1038, 871, 743; **HRMS** (EI) m/z calcd. for $C_{31}H_{35}N_3$ $[M]^+$: 449.2831, found: 449.2829.

3',5'-Di(bicyclo[2.2.1]heptan-2-yl)-2,2':6',2''-terpyridine (4i, Table 2**)**



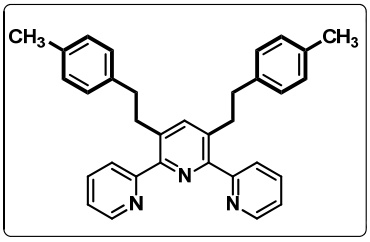
White solid (67 mg, 80%); **m.p.** 184–186 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.8 Hz, 2H), 7.79 (s, 1H), 7.75 (t, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.27–7.23 (m, 2H), 3.31 (t, *J* = 7.2 Hz, 2H), 2.45–2.40 (m, 2H), 2.34–2.28 (m, 2H), 1.58–1.46 (m, 10H), 1.27–1.20 (m, 4H), 1.18–1.11 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.6, 153.1, 148.4, 140.4, 136.4, 132.1, 124.7, 122.2, 42.5, 42.2, 39.7, 37.1, 36.5, 30.3, 28.7; **IR** (cm^{-1}) 2946, 2866, 1586, 1561, 1419, 1096, 1066, 1038, 898, 770, 745; **HRMS** (EI) m/z calcd. for $C_{29}H_{31}N_3$ $[M]^+$: 421.2518, found: 421.2516.

3',5'-Bis(2-phenylethyl)-2,2':6',2''-terpyridine (4j, Table 2**)**



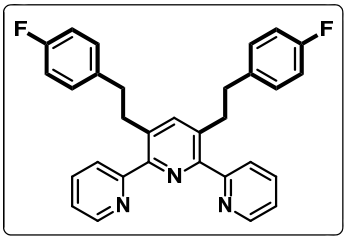
White solid (44 mg, 50%); **m.p.** 162–164 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 4.8, 1.8, 2H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.77 (td, *J* = 7.9, 1.8 Hz, 2H), 7.39 (s, 1H), 7.28 (dd, *J* = 7.9, 4.8, 2H), 7.24 (t, *J* = 7.3 Hz, 4H), 7.20–7.11 (m, 2H), 7.10 (d, *J* = 7.0 Hz, 4H), 3.28–3.19 (m, 4H), 2.89–2.80 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.9, 153.1, 148.2, 141.8, 141.6, 136.6, 135.6, 128.5, 128.3, 128.1, 127.6, 125.8, 124.4, 122.6, 37.4, 34.7; **IR** (cm^{-1}) 3059, 2922, 2856, 1586, 1563, 1419, 1179, 1074, 1038, 743, 698; **HRMS (EI)** m/z calcd. for $C_{31}H_{27}N_3$ $[M]^+$: 441.2205, found: 441.2203.

3',5'-Bis[2-(4-methylphenyl)ethyl]-2,2':6',2''-terpyridine (4k, Table 2**)**



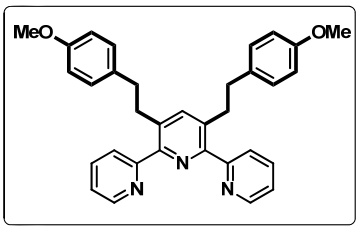
Yellow resin (45 mg, 48%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 4.8, 1.8 Hz 2H), 7.87 (dt, *J* = 7.8, 1.2 Hz, 2H), 7.77 (td, *J* = 7.8, 1.8 Hz, 2H), 7.42 (s, 1H), 7.28 (dd, *J* = 7.8, 4.8, 1.2 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 4H), 7.01 (d, *J* = 7.9 Hz, 4H), 3.28–3.20 (m, 4H), 2.86–2.78 (m, 4H), 2.31 (s, 6H);**^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.0, 153.1, 148.2, 141.6, 138.8, 136.5, 135.7, 135.3, 129.0, 128.4, 124.4, 122.5, 37.0, 34.8, 21.0; **IR** (cm^{-1}) 3046, 2918, 2857, 1586, 1512, 1418, 1140, 1091, 1038, 809, 737; **HRMS** (EI) m/z calcd. for $C_{33}H_{31}N_3$ $[M]^+$: 469.2518, found: 469.2515.

3',5'-Bis[2-(4-fluorophenyl)ethyl]-2,2':6',2''-terpyridine (4l, Table 2**)**



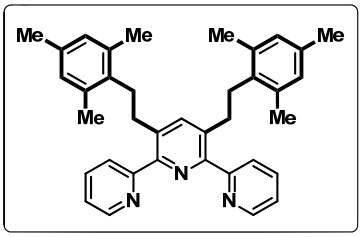
White solid (47 mg, 49%); **m.p.** 164–166 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 4.9, 1.3 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.79 (td, *J* = 7.8, 1.8 Hz, 2H), 7.36 (s, 1H), 7.32–7.29 (m, 2H), 7.04 (dd, *J* = 8.5, 5.6 Hz, 4H), 6.92 (t, *J* = 8.5 Hz, 4H), 3.28–3.22 (m, 4H), 2.87–2.82 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.2 (d, *J* = 243.4 Hz), 158.8, 153.1, 148.1, 141.8, 137.3 (d, *J* = 3.2 Hz), 136.6, 135.4, 129.8 (d, *J* = 7.8 Hz), 124.4, 122.6, 115.0 (d, *J* = 21.1 Hz), 36.6, 34.8; **^{19}F NMR** (564 MHz, $CDCl_3$) δ -117.7 (m); **IR** (cm^{-1}) 3022, 2921, 2852, 1585, 1450, 1418, 1037, 990, 807, 741; **HRMS** (ESI) m/z calcd. for $C_{31}H_{25}F_2N_3$ $[M+H]^+$: 478.2089, found: 478.2088.

3',5'-Bis[2-(4-methoxyphenyl)ethyl]-2,2':6',2''-terpyridine (4m, Table 2**)**



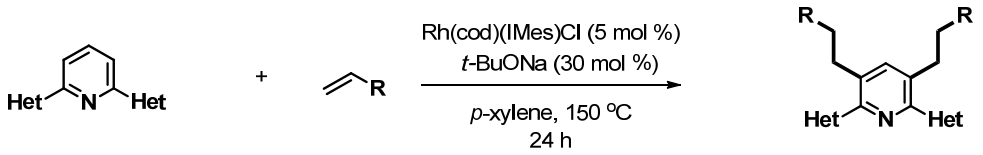
White solid (39 mg, 39%); **m.p.** 108–109 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.5 Hz, 2H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.78 (t, *J* = 7.7 Hz, 2H), 7.39 (s, 1H), 7.35–7.27 (m, 2H), 7.02 (d, *J* = 8.3 Hz, 4H), 6.79 (d, *J* = 8.3 Hz, 4H), 3.77 (s, 6H), 3.22 (t, *J* = 8.0 Hz, 4H), 2.80 (t, *J* = 8.0 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.0, 157.8, 153.1, 148.2, 141.6, 136.4, 135.6, 133.9, 129.4, 124.4, 122.5, 113.7, 55.2, 36.5, 34.9; **IR** (cm^{-1}) 3004, 2925, 2828, 1582, 1509, 1420, 1242, 1036, 848, 750; **HRMS** (EI) m/z calcd. for $C_{33}H_{31}N_3O_2$ $[M]^+$: 501.2416, found: 501.2415.

3',5'-Bis[2-(2,4,6-trimethylphenyl)ethyl]-2,2':6',2''-terpyridine (4n, Table 2**)**



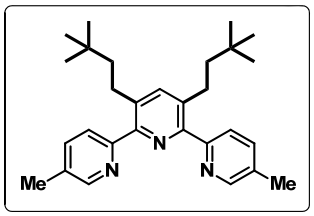
White solid (82 mg, 78%); **m.p.** 146–147 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.0 Hz, 2H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.79 (td, *J* = 7.7, 1.7 Hz, 2H), 7.50 (s, 1H), 7.32–7.28 (m, 2H), 6.81 (s, 4H), 3.13–3.08 (m, 4H), 2.87–2.83 (m, 4H), 2.24 (s, 6H), 2.19 (s, 12H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.0, 153.3, 148.4, 141.5, 136.6, 136.2, 136.1, 135.3, 135.1, 128.9, 124.4, 122.6, 31.9, 31.3, 20.8, 19.5; **IR** (cm^{-1}) 2907, 2852, 1582, 1416, 1137, 1036, 991, 848, 748; **HRMS (EI)** m/z calcd. for $C_{37}H_{39}N_3$ $[M]^+$: 525.3144, found: 525.3141.

2. Rh-Catalyzed Bis-alkylation of NNN Tridentate Heteroarene Compounds (Table 3)



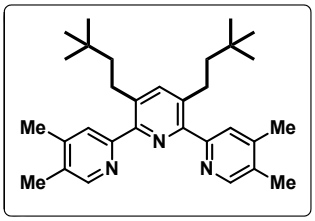
In an Archarged glove box with oxygen and water levels ≤2 ppm, to an oven-dried screwed vial were added NNN tridentate heteroarene compound (0.2 mmol), Rh(cod)(IMes)Cl (5.5 mg, 5.0 mol %), sodium *tert*-butoxide (5.8 mg, 30 mol %), and *p*-xylene (0.4 mL). The mixture was taken outside the box and olefin (1.0 mmol, 5.0 equiv) was added to the reaction mixture. The reaction mixture was vigorously stirred at 150 ˚C for the indicated time, cooled to room temperature, and diluted with ethyl acetate. The crude product was filtered through a pad of basic alumina oxide, and organic solvents were removed under reduced pressure. Desired product was obtained by basic alumina oxide chromatography or silica chromatography (*n*-hexane/ EtOAc, 6:1~4:1).

3',5'-Bis(3,3-dimethylbutyl)-5,5''-dimethyl-2,2':6',2''-terpyridine (5a, Table 3**)**



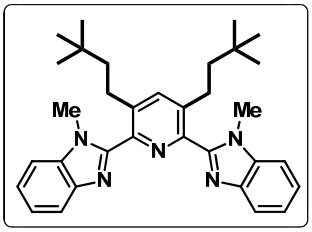
White solid (69 mg, 80 %); **m.p.** 149–151 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.8 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.57 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.46 (s, 1H), 2.96–2.87 (m, 4H), 2.36 (s, 6H), 1.46–1.37 (m, 4H), 0.86 (s, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.4, 152.7, 148.3, 140.8, 137.1, 137.0, 131.7, 123.8, 45.7, 30.6, 29.1, 27.8, 18.3; **IR** (cm^{-1}) 2948, 2861, 1438, 1360, 1243, 1130, 1029, 843, 798; **HRMS** (EI) m/z calcd. for $C_{29}H_{39}N_3$ $[M]^+$: 429.3144, found: 429.3144.

3',5'-Bis(3,3-dimethylbutyl)-4,4'',5,5''-tetramethyl-2,2':6',2''-terpyridine (5b, Table 3**)**



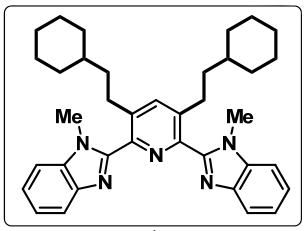
Slightly yellow solid (87 mg, 95 %); **m.p.** 152–153 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.33 (s, 2H), 7.55 (s, 2H), 7.44 (s, 1H), 2.88–2.80 (m, 4H), 2.29 (s, 6H), 2.26 (s, 6H), 1.42–1.37 (m, 4H), 0.84 (s, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.9, 153.2, 148.5, 145.8, 140.6, 136.9, 130.9, 125.0, 45.7, 30.6, 29.2, 27.8, 19.3, 16.2; **IR** (cm^{-1}) 2946, 2859, 1597, 1440, 1359, 1243, 1023, 986, 888; **HRMS** (EI) m/z calcd. for $C_{31}H_{43}N_3$ $[M]^+$: 457.3457, found: 457.3459.

2,2'-[3,5-Bis(3,3-dimethylbutyl)pyridine-2,6-diyl]-bis(1-methyl-1*H*-benzo[*d*]imidazole) (5c, Table 3**)**



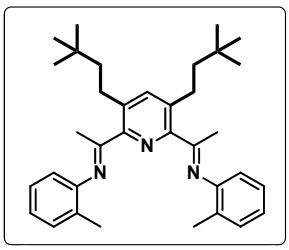
White solid (98 mg, 96%); **m.p.** 235–237 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.72 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.37–7.32 (m, 4H), 3.78 (s, 6H), 3.07–2.83 (m, 4H), 1.52–1.41 (m, 4H), 0.84 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.4, 145.3, 142.5, 141.1, 140.5, 135.7, 122.9, 122.2, 120.0, 109.6, 45.8, 31.3, 30.7, 29.1, 28.0; **IR** (cm^{-1}) 2953, 2864, 1460, 1417, 1390, 1376, 1264, 731; **HRMS** (ESI) m/z calcd. for $C_{33}H_{41}N_5$ $[M+H]^+$: 508.3435, found: 508.3438.

2,2'-[3,5-Bis(2-cyclohexylethyl)pyridine-2,6-diyl]-bis(1-methyl-1*H*-benzo[*d*]imidazole) (5d, Table 3**)**



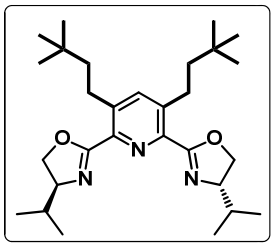
White solid (97 mg, 87%); **m.p.** 57–58 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.72 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.36–7.31 (m, 4H), 3.76 (s, 6H), 3.04–2.99 (m, 4H), 1.58 (m, 10H), 1.42 (q, *J* = 6.9 Hz, 4H), 1.09 (m, 8H), 0.80 (q, *J* = 10.7 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.6, 145.4, 142.5, 140.7, 140.3, 135.7, 123.0, 122.2, 120.0, 109.7, 38.7, 37.1, 33.1, 31.3, 29.5, 26.5, 26.2; **IR** (cm^{-1}) 2918, 2847, 1460, 1445, 1326, 1058, 1031, 1005, 739; **HRMS** (EI) m/z calcd. for $C_{37}H_{45}N_5$ $[M]^+$: 559.3675, found: 559.3672.

3,5-Bis(3,3-dimethylbutyl)-2,6-bis[1-(2-methylphenylimino)ethyl]pyridine (5e, Table 3**)**



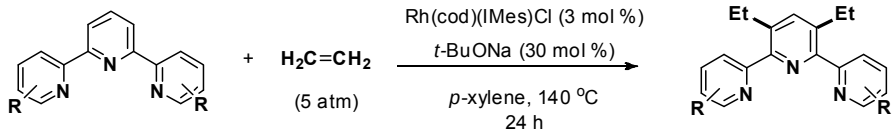
Yellow solid (91 mg, 90%); **m.p.** 94–96 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.22–7.15 (m, 4H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 2H), 3.09–2.97 (m, 4H), 2.23 (s, 6H), 2.14 (s, 6H), 1.61–1.54 (m, 4H), 0.94 (s, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.3, 151.4, 150.2, 141.5, 138.4, 130.3, 126.6, 126.3, 123.1, 118.1, 45.8, 30.8, 29.4, 28.2, 19.3, 18.0; **IR** (cm^{-1}) 2951, 2864, 1641, 1481, 1220, 1176, 1089, 1041, 785, 734; **HRMS** (EI) m/z calcd. for $C_{35}H_{47}N_3$ $[M]^+$: 509.3770, found: 509.3769.

(4*S*,4'*S*)-2,2'-[3,5-Bis(3,3-dimethylbutyl)pyridine-2,6-diyl]-bis(4-isopropyl-4,5-dihydrooxazole) (5f, Table 3**)**



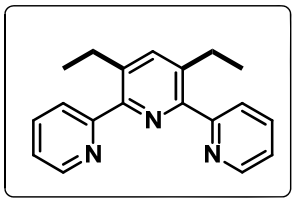
White solid (33 mg, 35%); **m.p.** 97–99 °C; **^{1}H NMR** (600Hz, $CDCl_3$) δ 7.44 (s, 1H), 4.50–4.43 (m, 2H), 4.15–4.05 (m, 4H), 3.09–2.99 (m, 4H), 1.87–1.80 (m, 2H), 1.49–1.44 (m, 4H), 1.06 (d, J = 6.7 Hz, 6H), 0.97 (s, 18H), 0.95 (d, J = 6.7 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.6, 142.7, 141.7, 140.6, 73.8, 69.9, 45.3, 33.1, 30.8, 29.3, 28.4, 19.3, 18.7; **IR** (cm^{-1}) 2952, 2903, 2868, 1638, 1466, 1362, 1247, 1079; **HRMS** (ESI) m/z calcd. for $C_{29}H_{47}N_3O_2$ $[M+H]^+$: 470.3741, found: 470.3733.

3. Rh-Catalyzed Bis-alkylation with Ethylene Gas (Table 4)



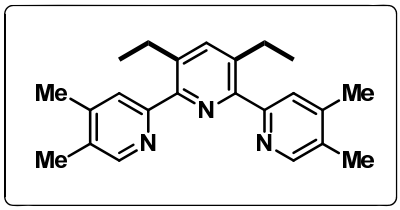
High-pressure reaction was performed by using Q-Tube-Purging-35 (QLabTech). In an Ar charged glove box with oxygen and water levels ≤2 ppm, to an oven-dried pressure tube were added 2,2′:6′,2″-terpyridine derivatives (2.0 mmol), Rh(cod)(IMes)Cl (33 mg, 3.0 mol %), sodium *tert*-butoxide (57.7 mg, 30 mol %), and *p*-xylene (4 mL). The mixture was taken outside the box. Pressure tube was fitted into regulator, then evacuated and backfilled with ethylene twice. Internal pressure was adjusted to 5 atm, and heated to 140 °C. After 24 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate. The crude product was filtered through a pad basic alumina oxide, and organic solvents were removed under reduced pressure, and purified by a basic alumina oxide column chromatography (*n*-hexane/ EtOAc, 6:1~4:1).

3',5'-Diethyl-2,2':6',2''-terpyridine (6a, Table 4**)**



White solid (440 mg, 76%); **m.p.** 136–137 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.7 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.79–7.74 (m, 2H), 7.59 (s, 1H), 7.26 (t, *J* = 6.2 Hz, 2H), 2.95 (q, *J* = 7.5 Hz, 4H), 1.16 (t, *J* = 7.5 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.1, 152.9, 148.3, 139.2, 137.9, 136.4, 124.4, 122.4, 25.4, 15.2; **IR** (cm^{-1}) 2968, 2922, 2861, 1585, 1560, 1451, 1419, 795, 771, 749; **HRMS** (EI) m/z calcd. for $C_{19}H_{19}N_3$ $[M]^+$: 289.1579, found: 289.1578.

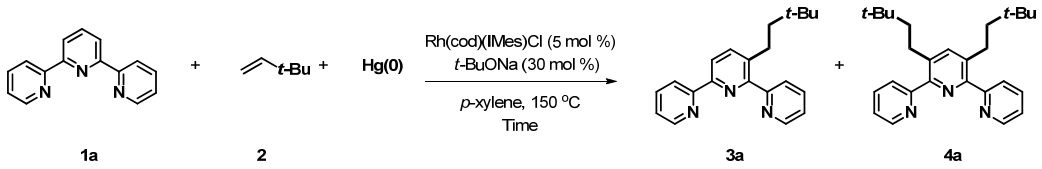
3',5'-Diethyl-4,4'',5,5''-tetramethyl-2,2':6',2''-terpyridine (6b, Table 4**)**



White solid (160 mg, 93%); **m.p**. 107–108 °C**; ^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.36 (s, 2H), 7.54 (s, 1H), 7.53 (s, 2H), 2.91 (q, *J* = 7.5 Hz, 4H), 2.30 (s, 6H), 2.28 (s, 6H), 1.13 (t, *J* = 7.5 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.9, 153.3, 148.6, 146.0, 138.7, 137.4, 131.0, 125.1, 25.3, 19.3, 16.2, 15.1; **IR** (cm^{-1}) 2963, 2922, 2869, 1598, 1540, 1487, 1376, 1292, 1065, 881, 784; **HRMS** (EI) m/z calcd. for $C_{23}H_{27}N_3$ $[M]^+$: 345.2205, found: 345.2203.

V. Preliminary Mechanism Study

1. Hg(0) poisoning experiments (Ref 15)



1a 2 3a 4a

In an Ar charged glove box with oxygen and water levels ≤2 ppm, to an oven-dried screwed vial were added 2,2′:6′,2″-terpyridine (46.6 mg, 0.2 mmol), Rh(cod)(IMes)Cl (5.5 mg, 5.0 mol %), sodium *tert*-butoxide (5.8 mg, 30 mol %), and *p*-xylene (0.4 mL, 0.5 M). The mixture was taken outside the box and 3,3-dimethyl-1-butene (1.0 mmol, 0.13 ml) and 1–2 drops of Hg(0) were added. The reaction mixture was stirred at 150 ˚C for the indicated time, cooled to room temperature, and quenched with sulfur to remove remain Hg(0). The crude product was filtered through a pad of celite, and organic solvents were removed under the reduced pressure.

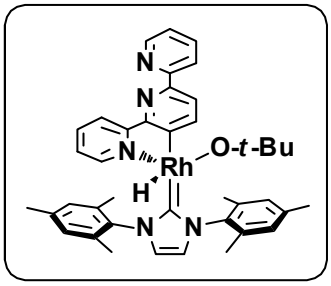
The same reaction was repeated in the absence of Hg(0).

Crude yield of each run was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

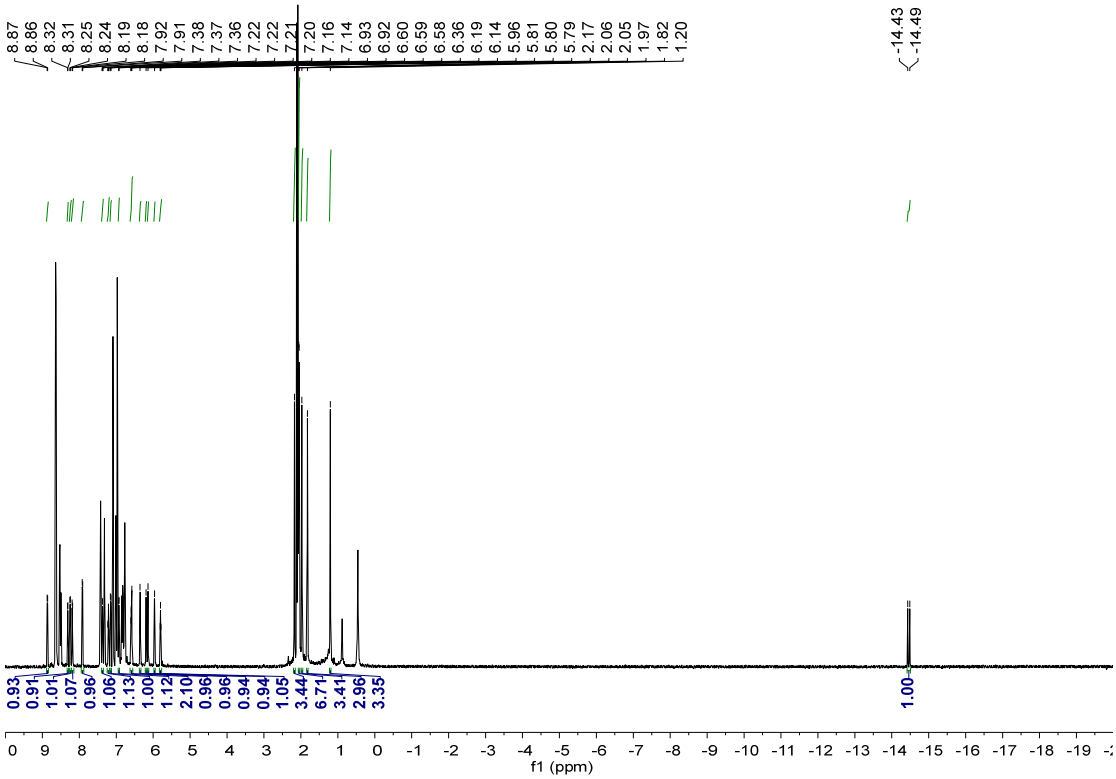
Table S2. Hg(0) poisoning experiments

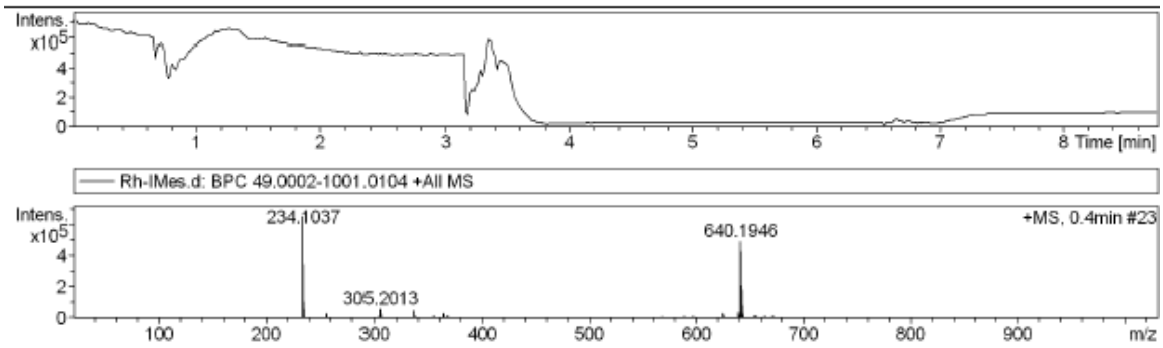
	Time	**3a** (%)	**4a** (%)
without Hg(0)	12 h	22	77
	24 h	<5	99
with Hg(0)	12 h	12	83
	24 h	<5	98

2. Detection of a Reaction Intermediate (Ref 16)



In Ar-charged glove box with oxygen and water levels ≤2 ppm, to an oven-dried screwed vial were added 2,2':6',2"- terpyridine (93.2 mg, 0.4 mmol), $[Rh(coe)_2Cl]_2$ (72.0 mg, 0.1 mmol), 1,3-dimesitylimidazol-2-ylidene (IMes, 60.0 mg, 0.2 mmol) and sodium *tert*-butoxide (19.2 mg, 0.2 mmol) in toluene (1 mL). The mixture was stirred at room temperature for 6 h. The crude product was filtered through a pad of basic alumina oxide washing with acetonitrile. The organic solvent was removed under the reduced pressure, and the resulting precipitate was collected by filtration, washed with n-hexane to afford green solid that was taken by ^{1}H-NMR (shown below): **HRMS** (ESI) m/z calcd. for $C_{36}H_{35}N_5Rh^+$ $[M\text{-}O\text{-}t\text{-}Bu]^+$: 640.1942, found: 640.1946.





VI. References

(S1) I. Sasaki, J. C. Daran and G. G. A. Balavoine, *Synthesis,* 1999, ***5***, 815.

(S2) I. Mathew and W. Sun, *Dalton Trans*., 2010, **39**, 5885.

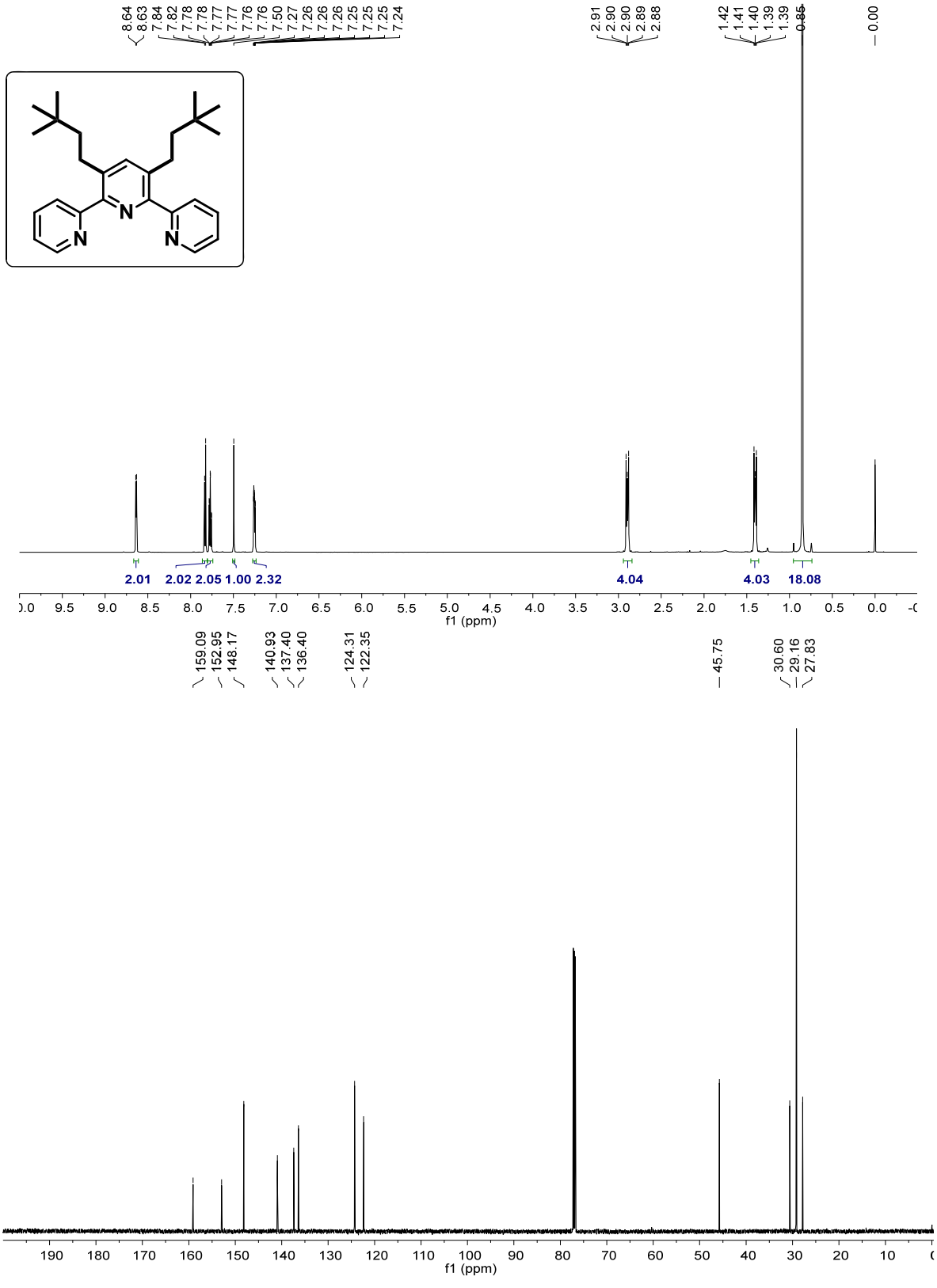
(S3) X. -Y. Yu, B. O. Patrick and B. R. James, *Organometallics,* 2006, **25,** 2359.

(S4) J. Peng and Y. Kishi, *Org. Lett.*, 2012, **14**, 86.

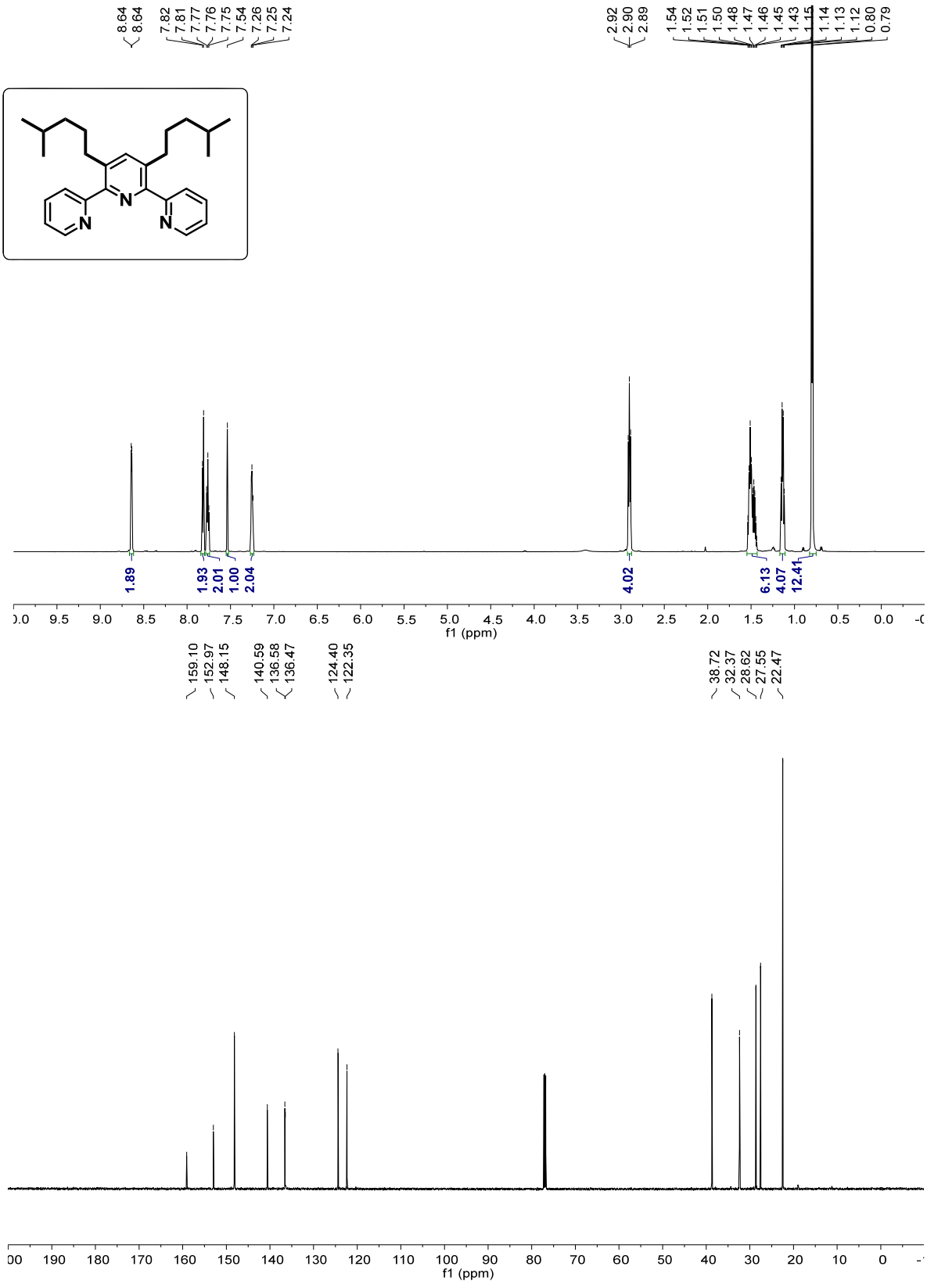
Appendix I

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

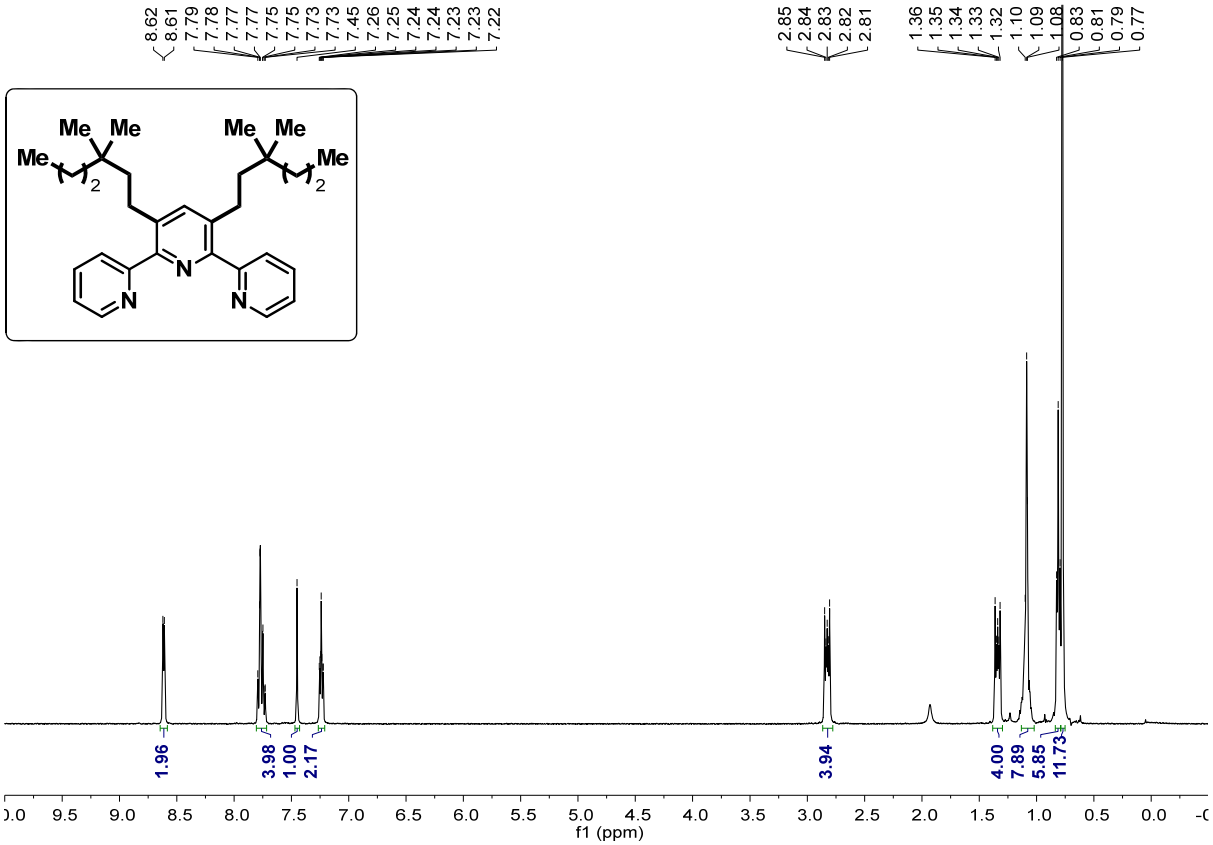
3',5'-Bis(3,3-dimethylbutyl)-2,2':6',2''-terpyridine (4a, Table 2**)**

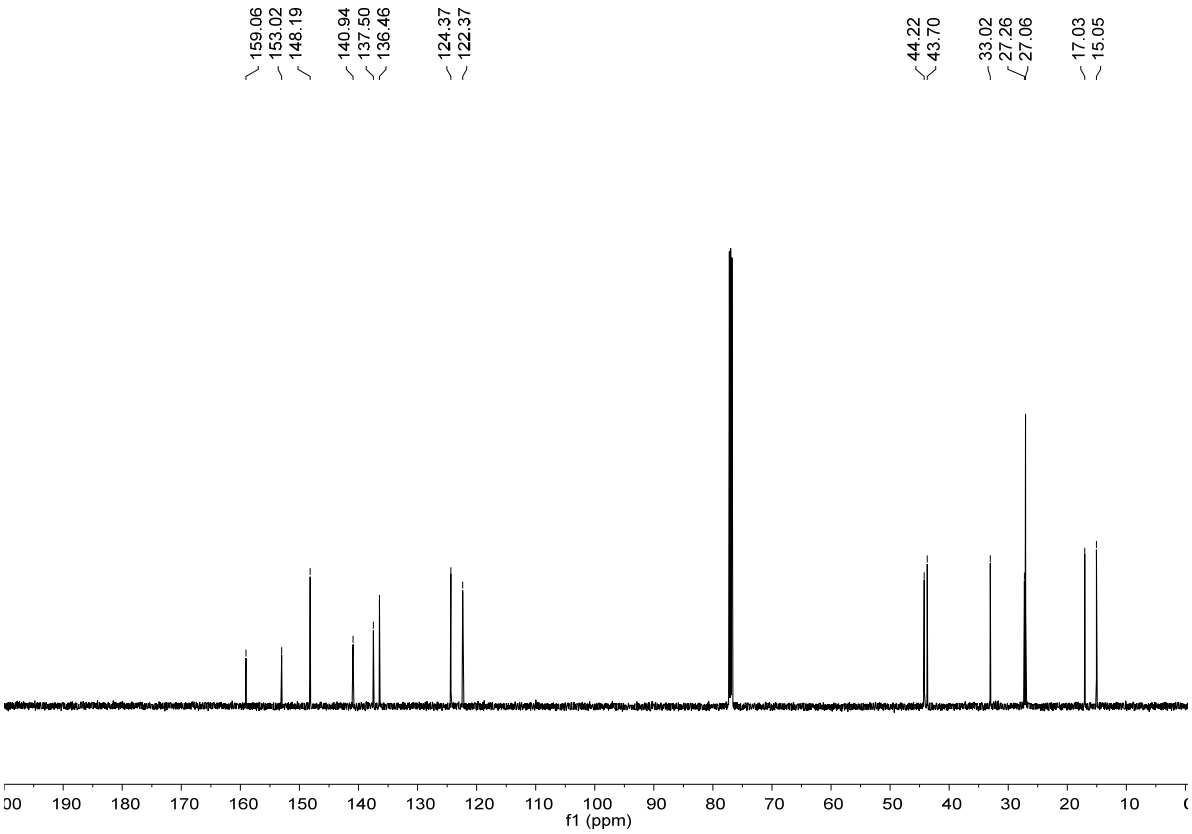


3',5'-Bis(4-methylpentyl)-2,2':6',2''-terpyridine (4b, Table 2**)**

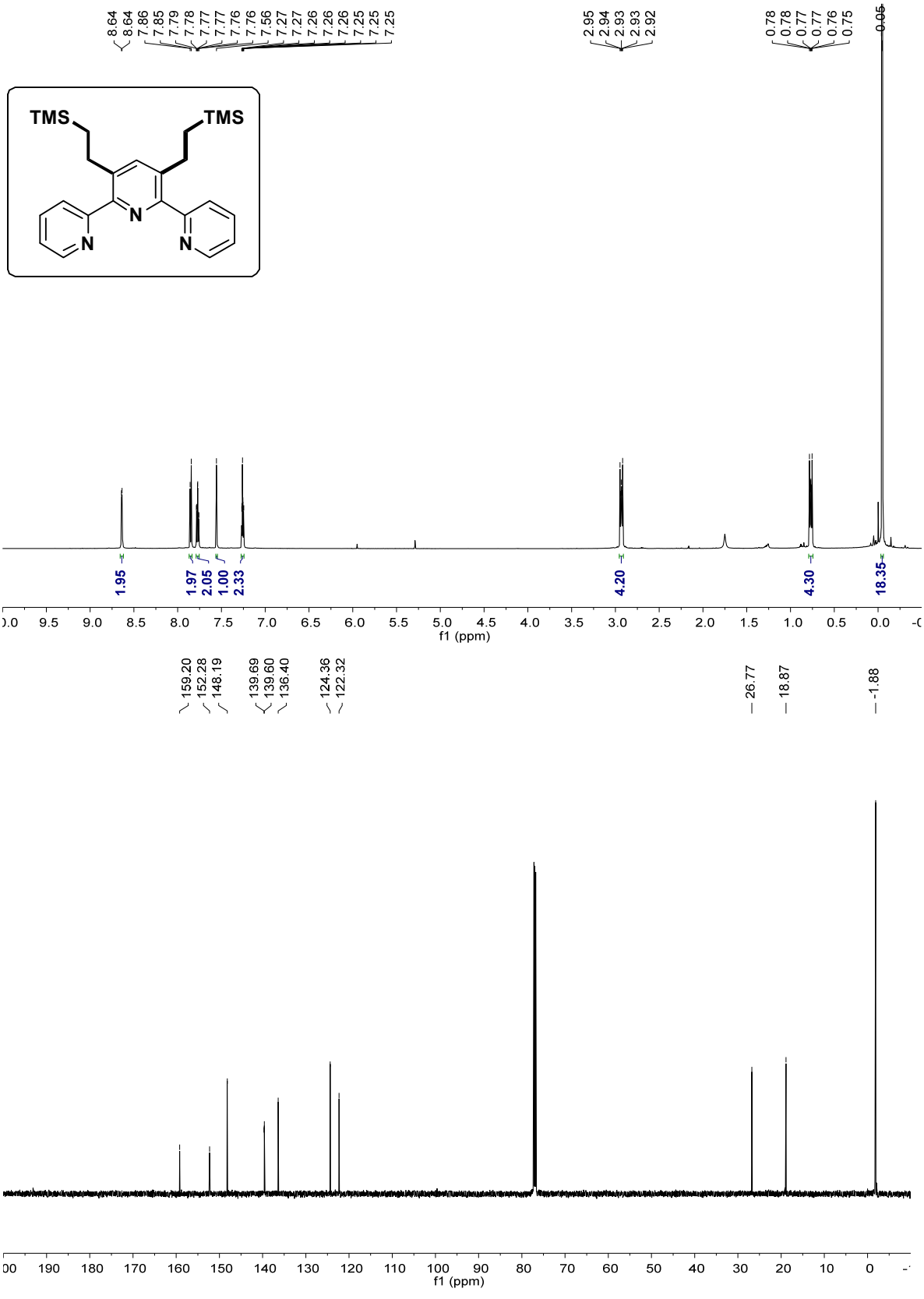


3',5'-Bis(3,3-dimethylhexyl)-2,2':6',2''-terpyridine (4c, Table 2**)**

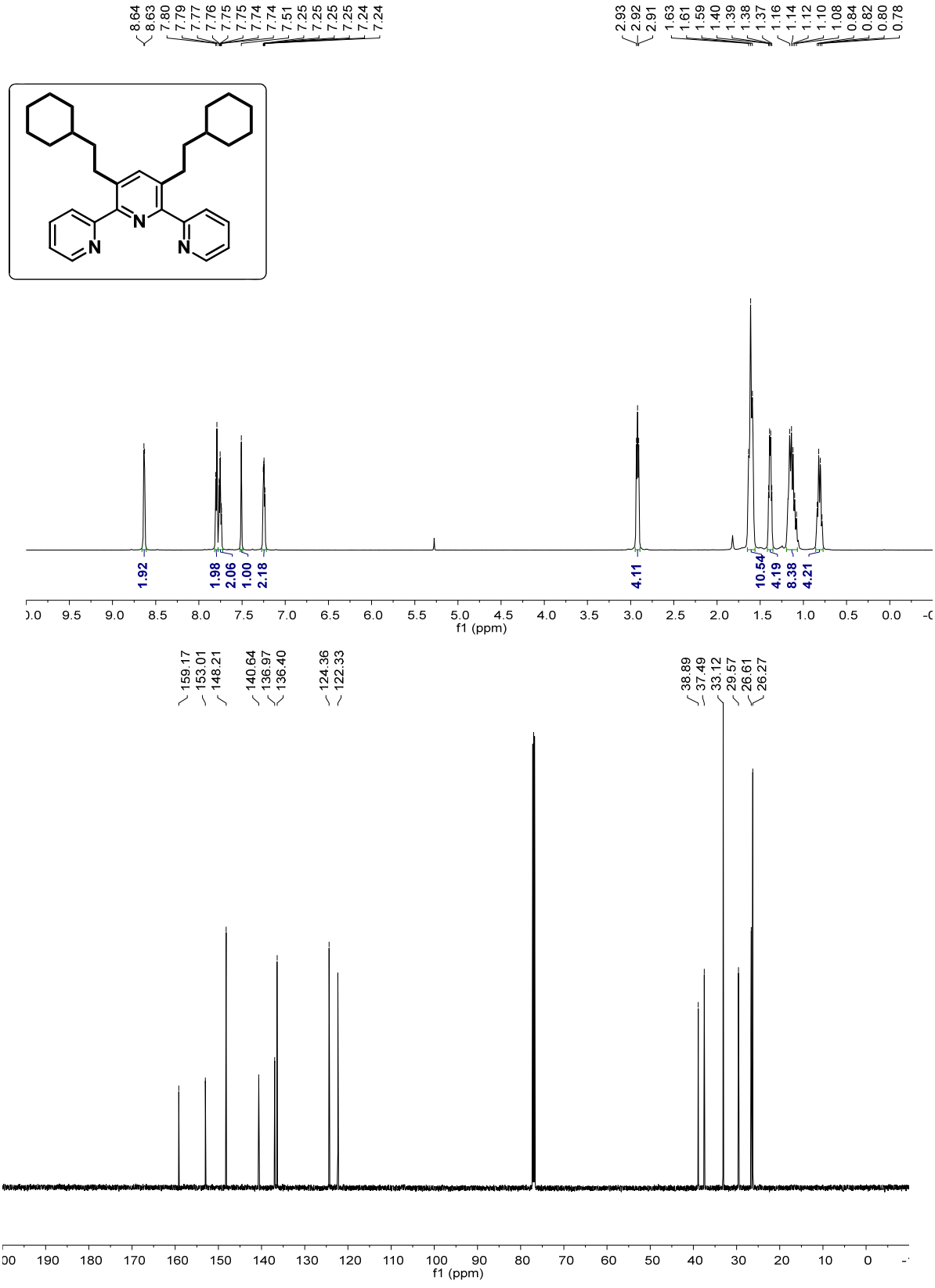




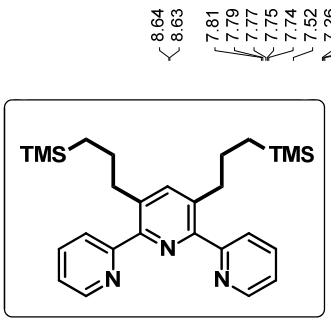
3',5'-Bis[2-(trimethylsilyl)ethyl]-2,2':6',2''-terpyridine (4d, Table 2**)**

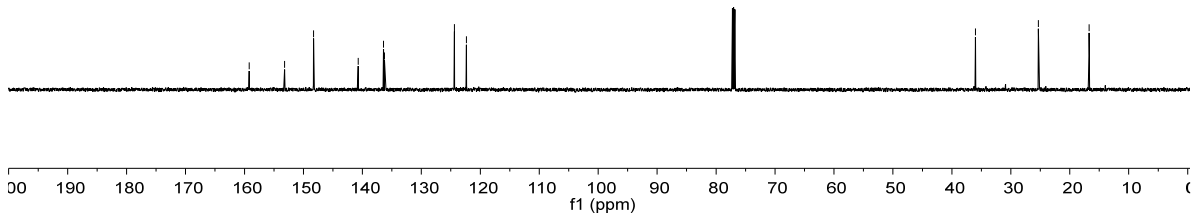


3',5'-Bis(2-cyclohexylethyl)-2,2':6',2''-terpyridine (4e, Table 2**)**

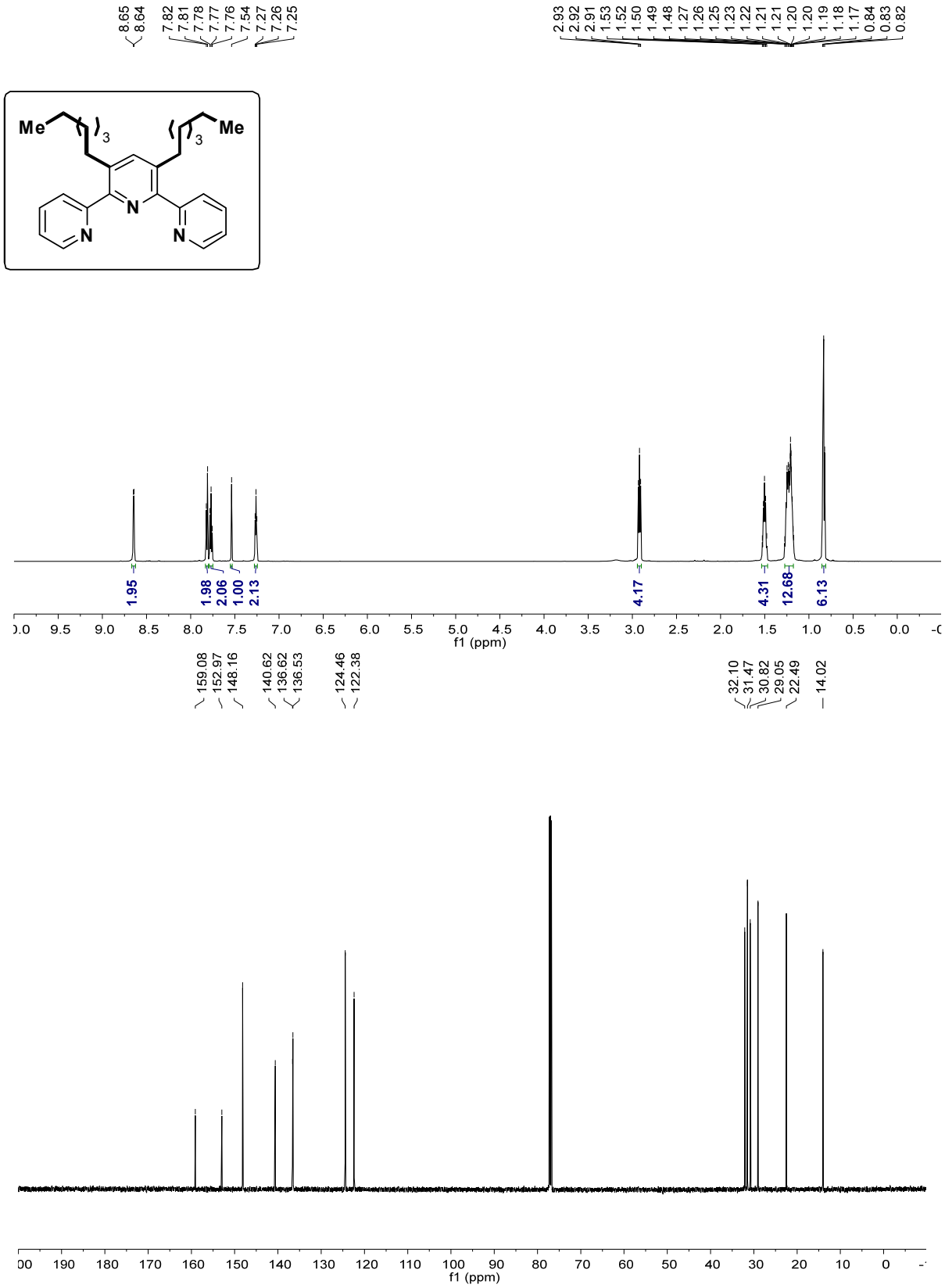


3',5'-Bis[3-(trimethylsilyl)propyl]-2,2':6',2''-terpyridine (4f, Table 2**)**

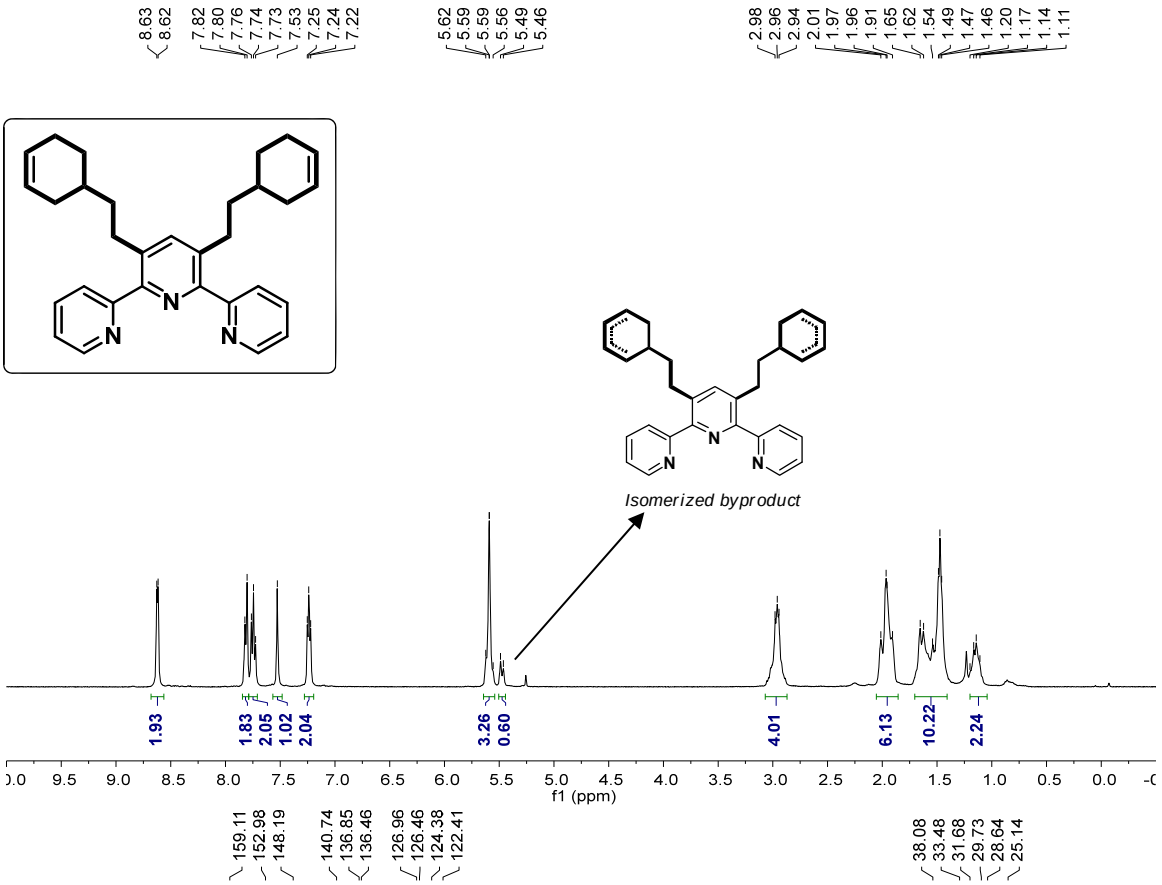


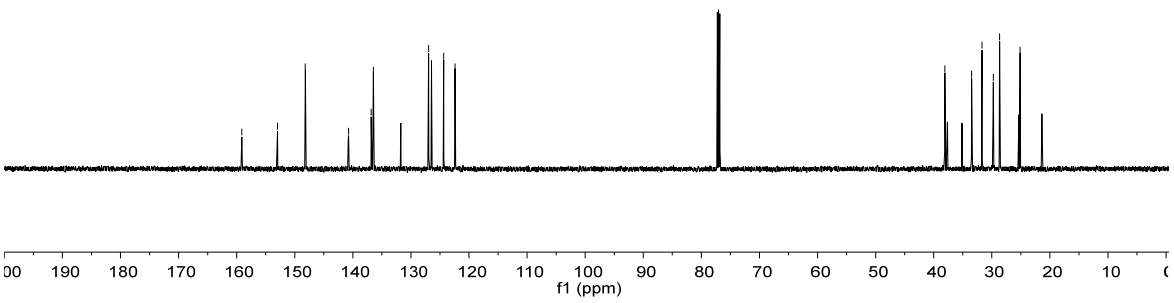


3',5'-Dihexyl-2,2':6',2''-terpyridine (4g, Table 2**)**

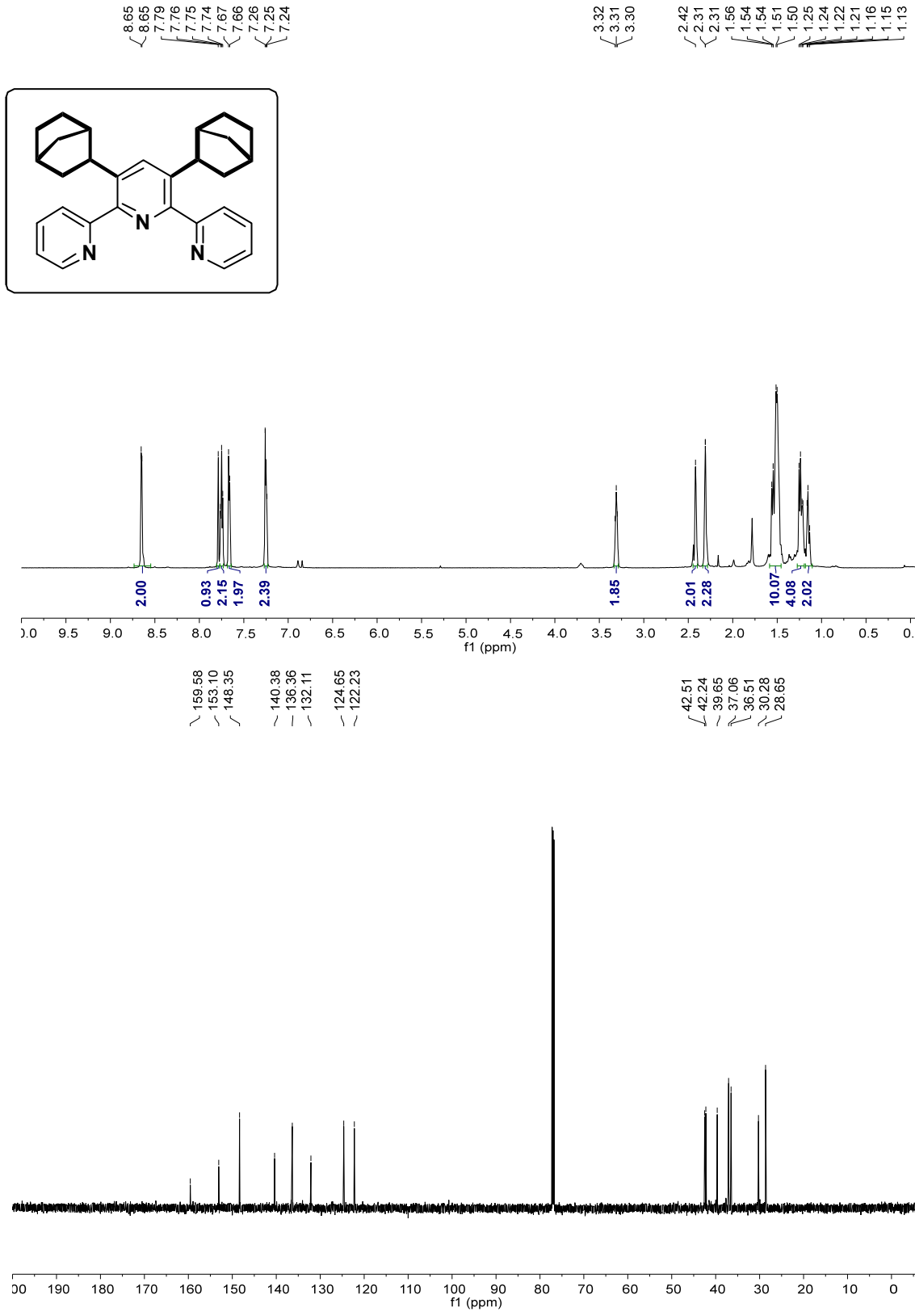


3',5'-Bis[2-(cyclohex-3-en-1-yl)ethyl]-2,2':6',2''-terpyridine (4h, Table 2**)**

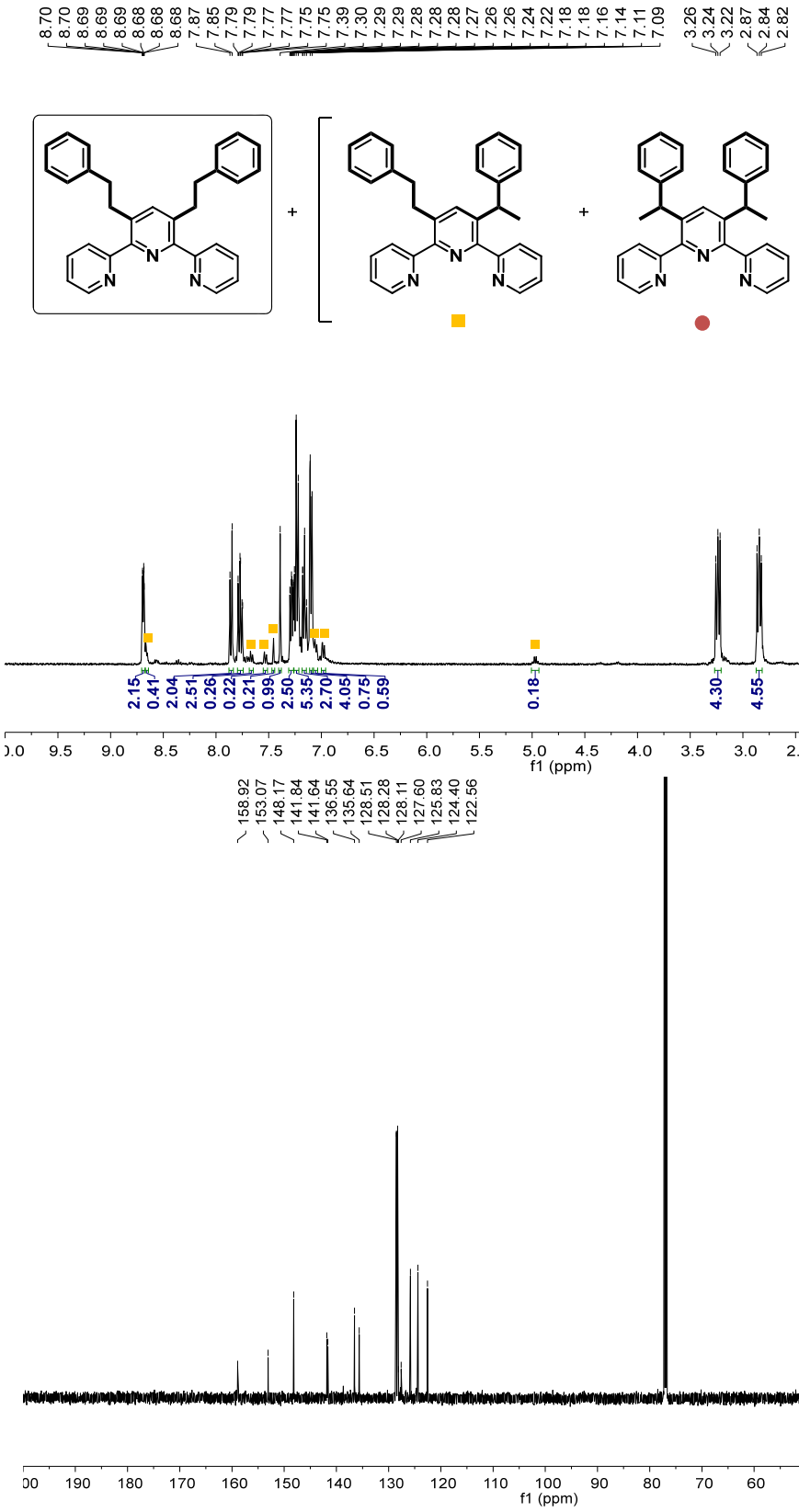




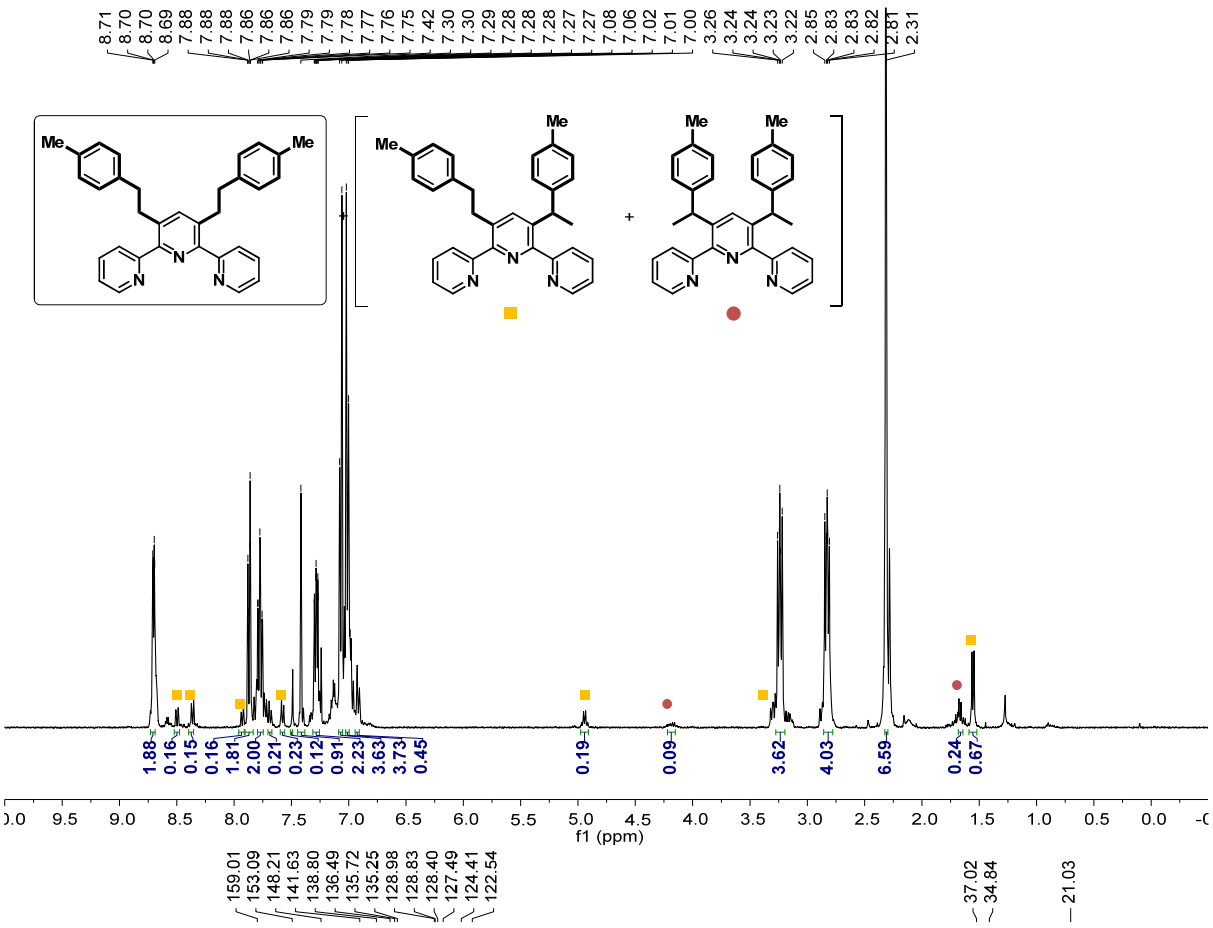
3',5'-Di(bicyclo[2.2.1]heptan-2-yl)-2,2':6',2''-terpyridine (4i, Table 2**)**

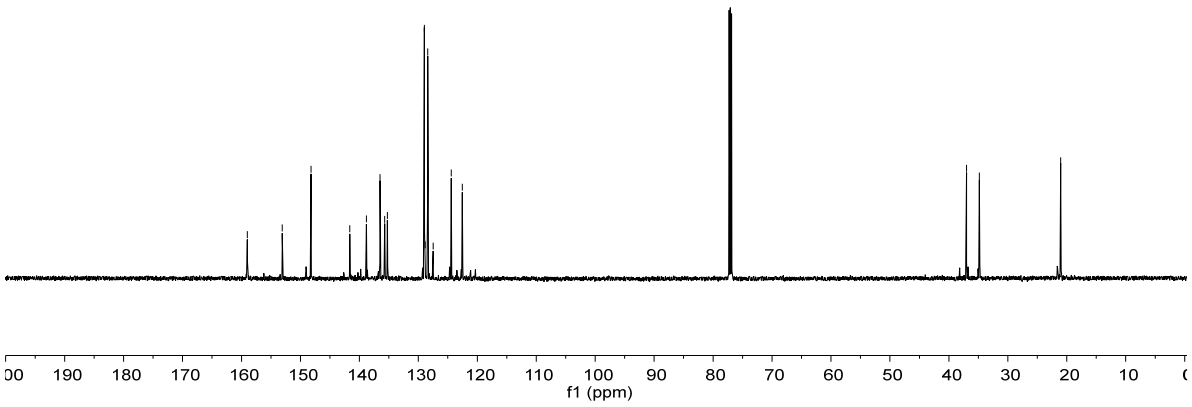


3',5'-Bis(2-phenylethyl)-2,2':6',2''-terpyridine (4j, Table 2**)**

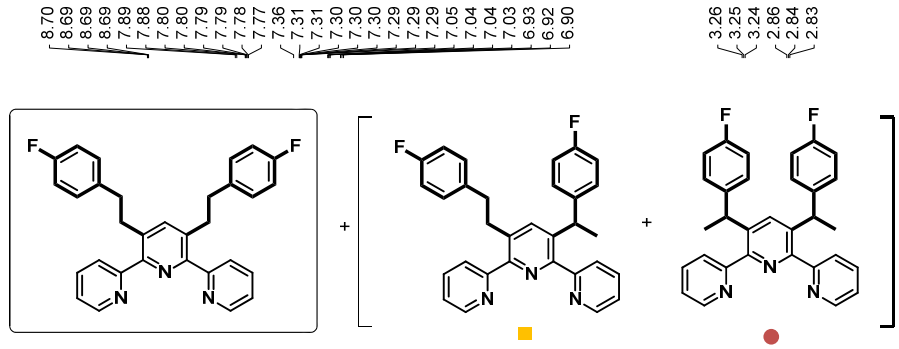


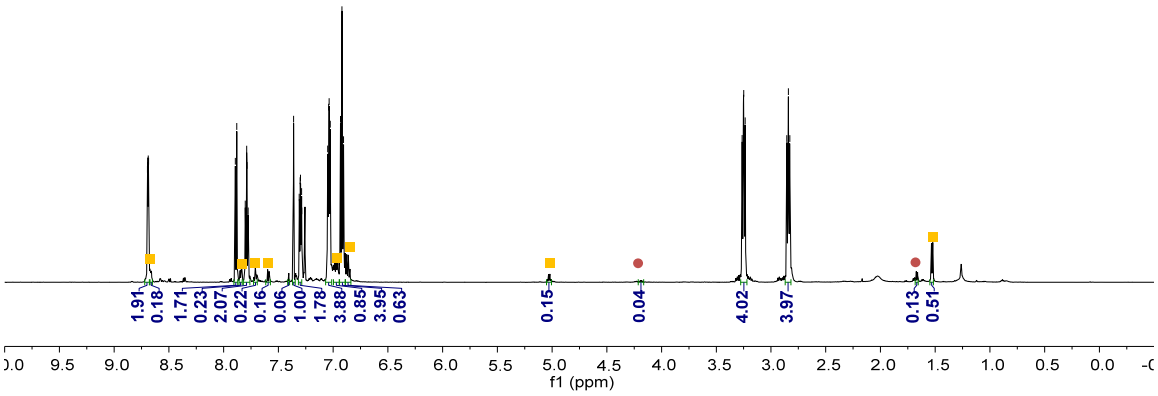
3',5'-Bis[2-(4-methylphenyl)ethyl]-2,2':6',2''-terpyridine (4k, Table 2**)**

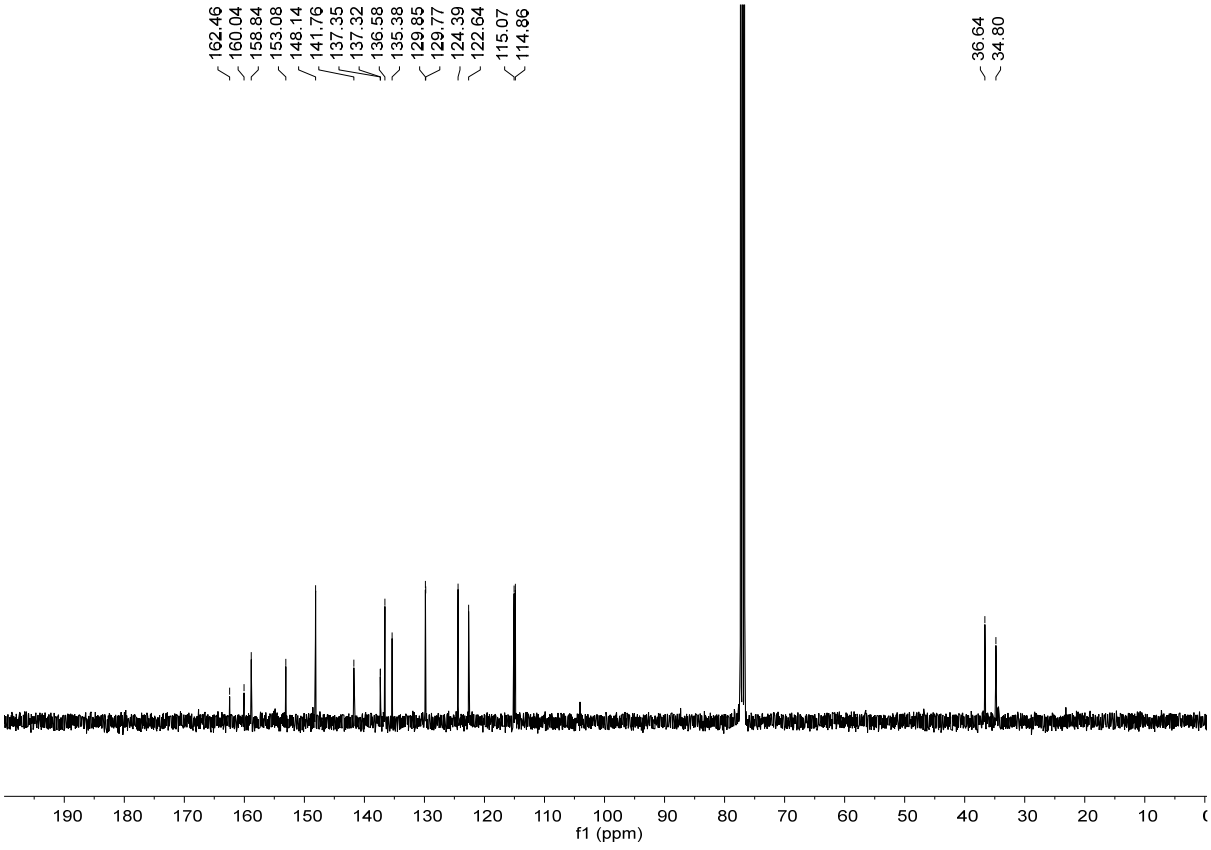


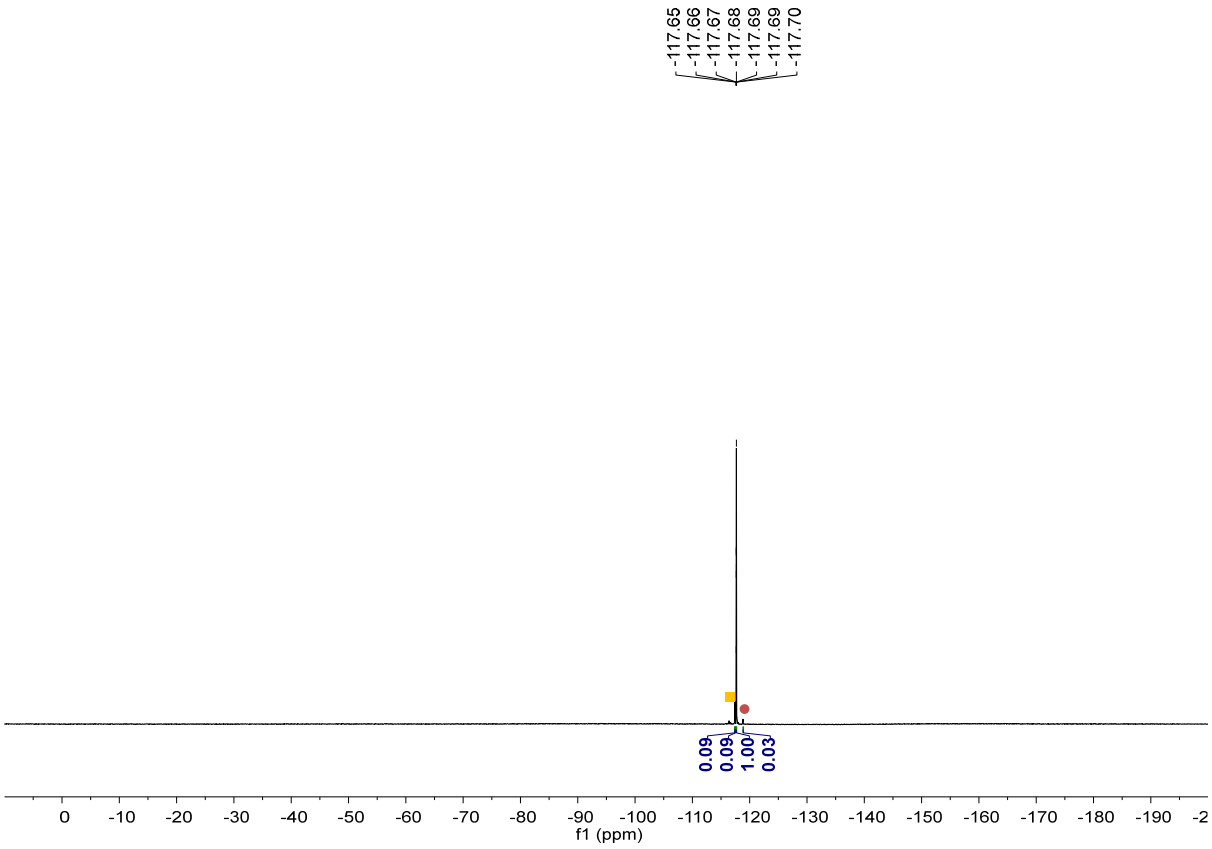


3',5'-Bis[2-(4-fluorophenyl)ethyl]-2,2':6',2''-terpyridine (4l, Table 2**)**

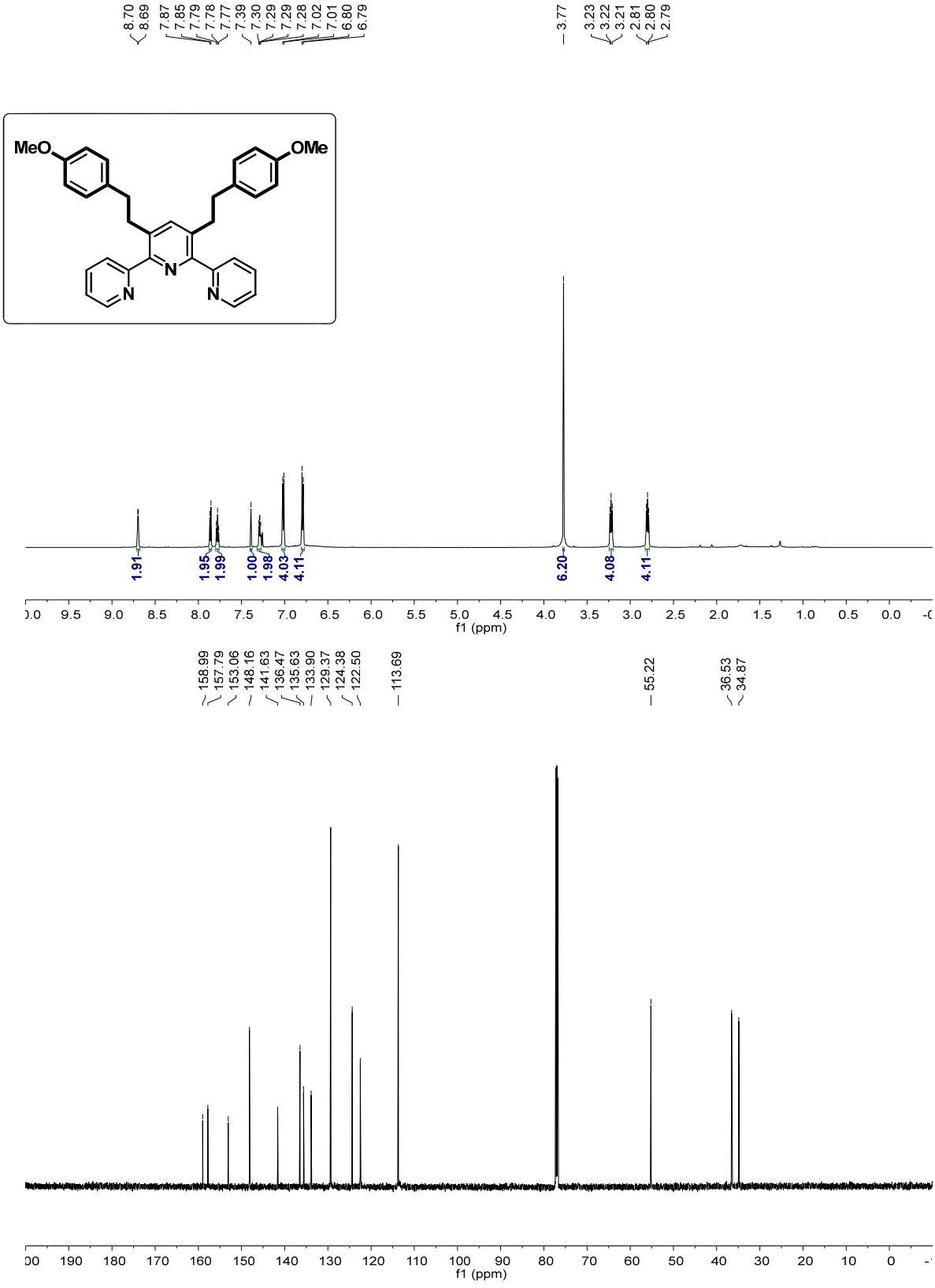




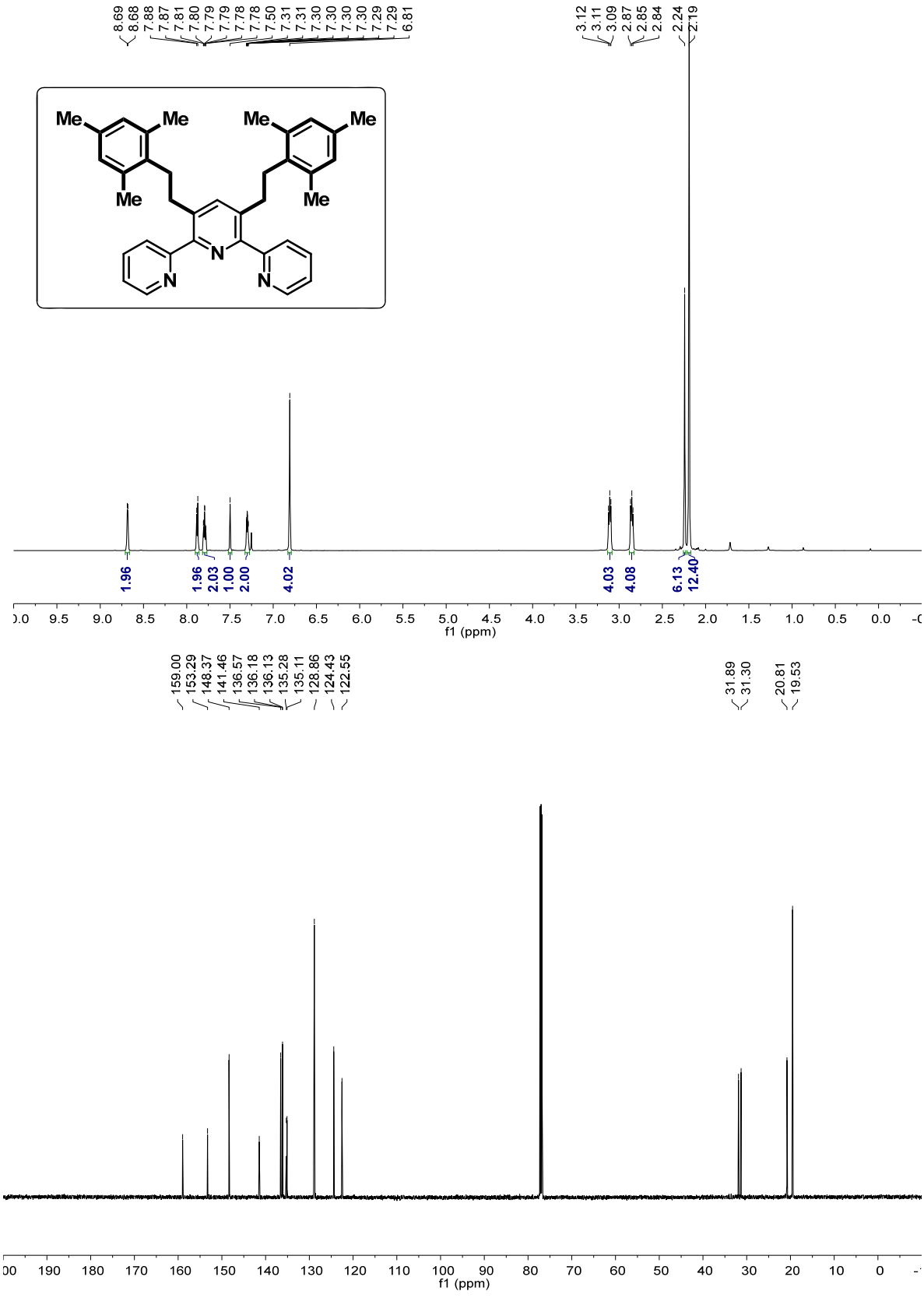



-117.65
-117.66
-117.67
-117.68
-117.69
-117.69
-117.70
0.09
0.09
1.00
0.03
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

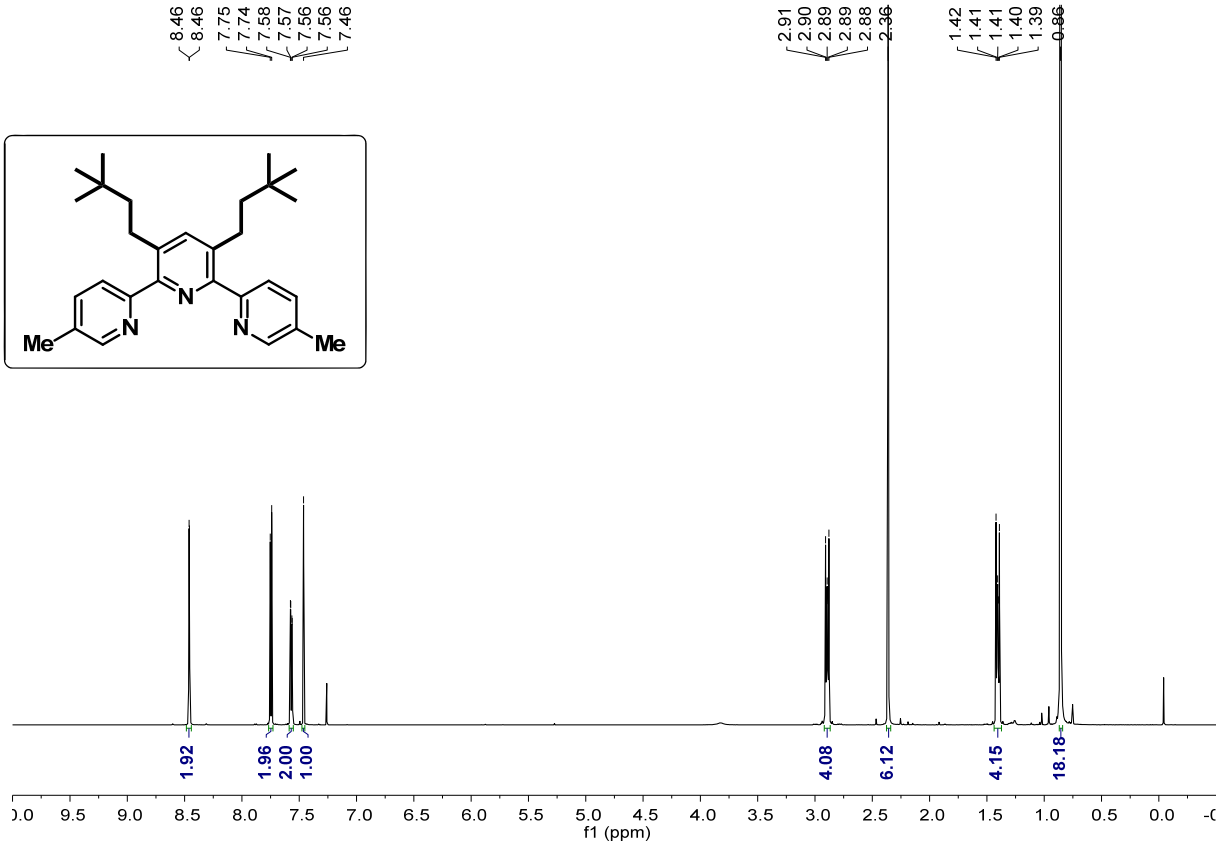
3',5'-Bis[2-(4-methoxy phenyl)ethyl]-2,2':6',2''-terpyridine (4m, Table 2**)**

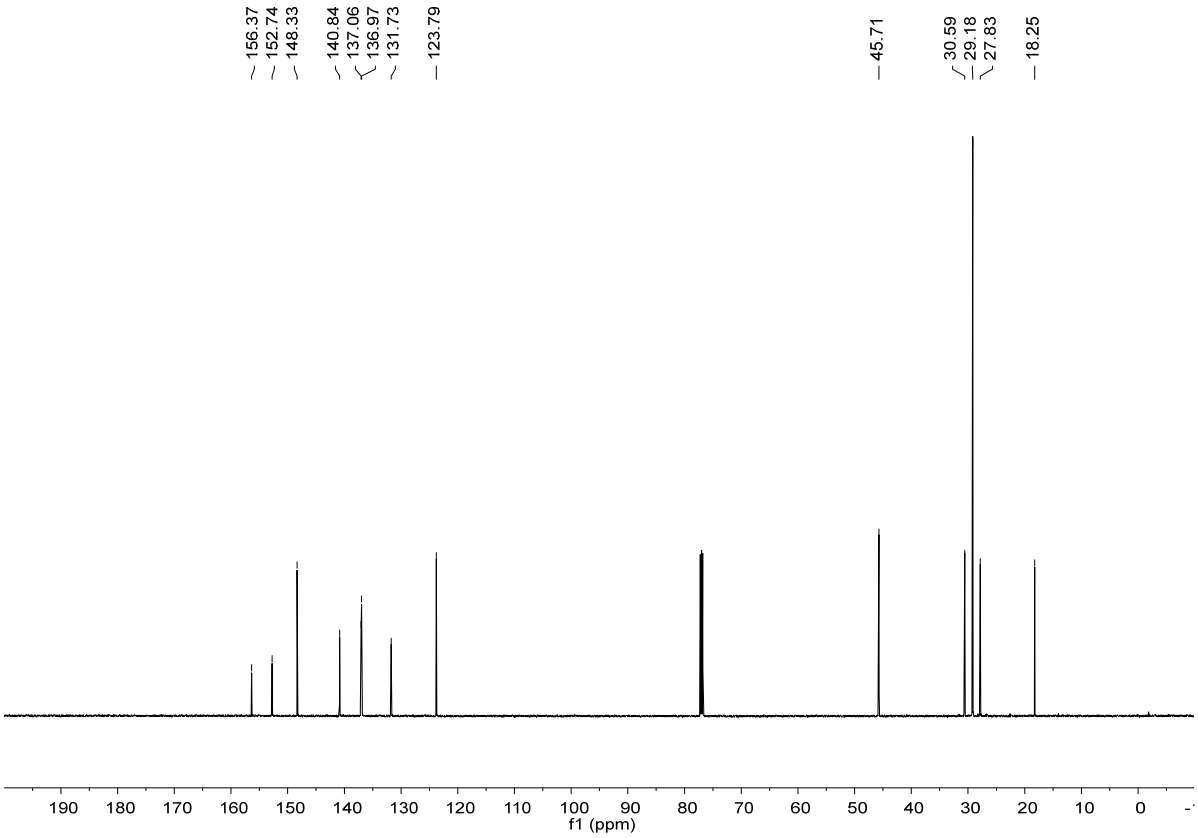


3',5'-Bis[2-(2,4,6-trimethylphenyl)ethyl]-2,2':6',2''-terpyridine (4n, Table 2**)**

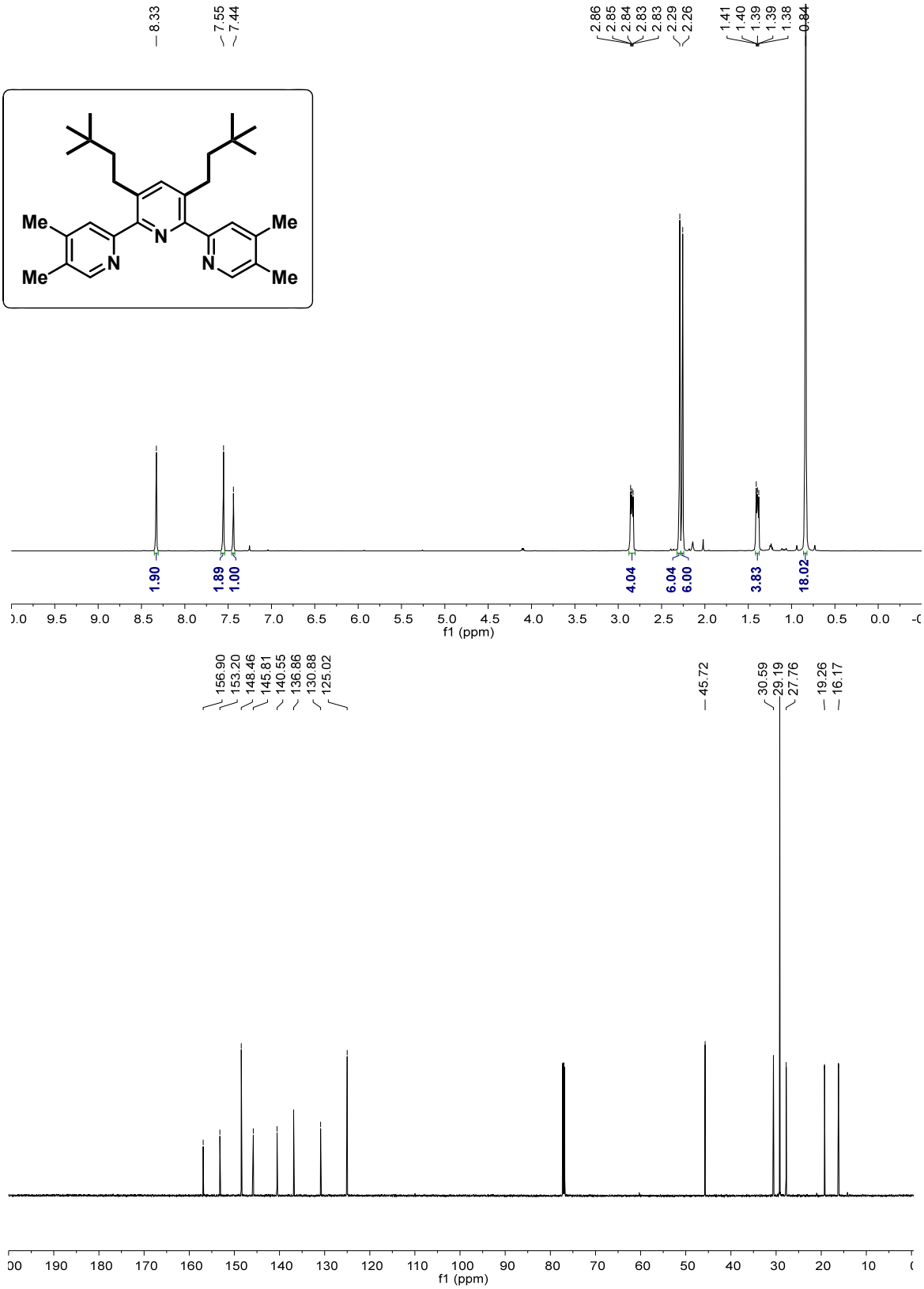


3',5'-Bis(3,3-dimethylbutyl)-5,5''-dimethyl-2,2':6',2''-terpyridine (5a, Table 3**)**

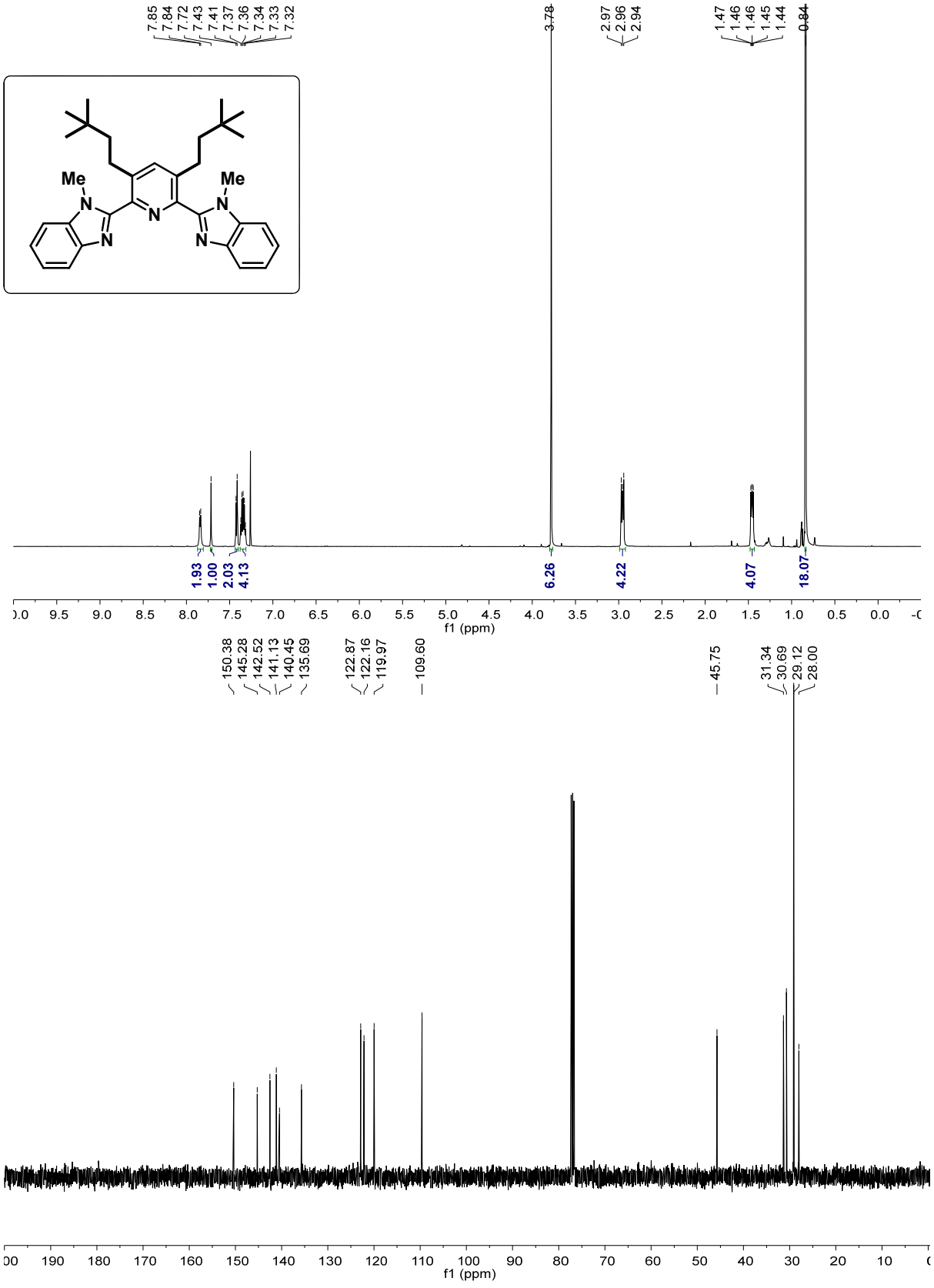




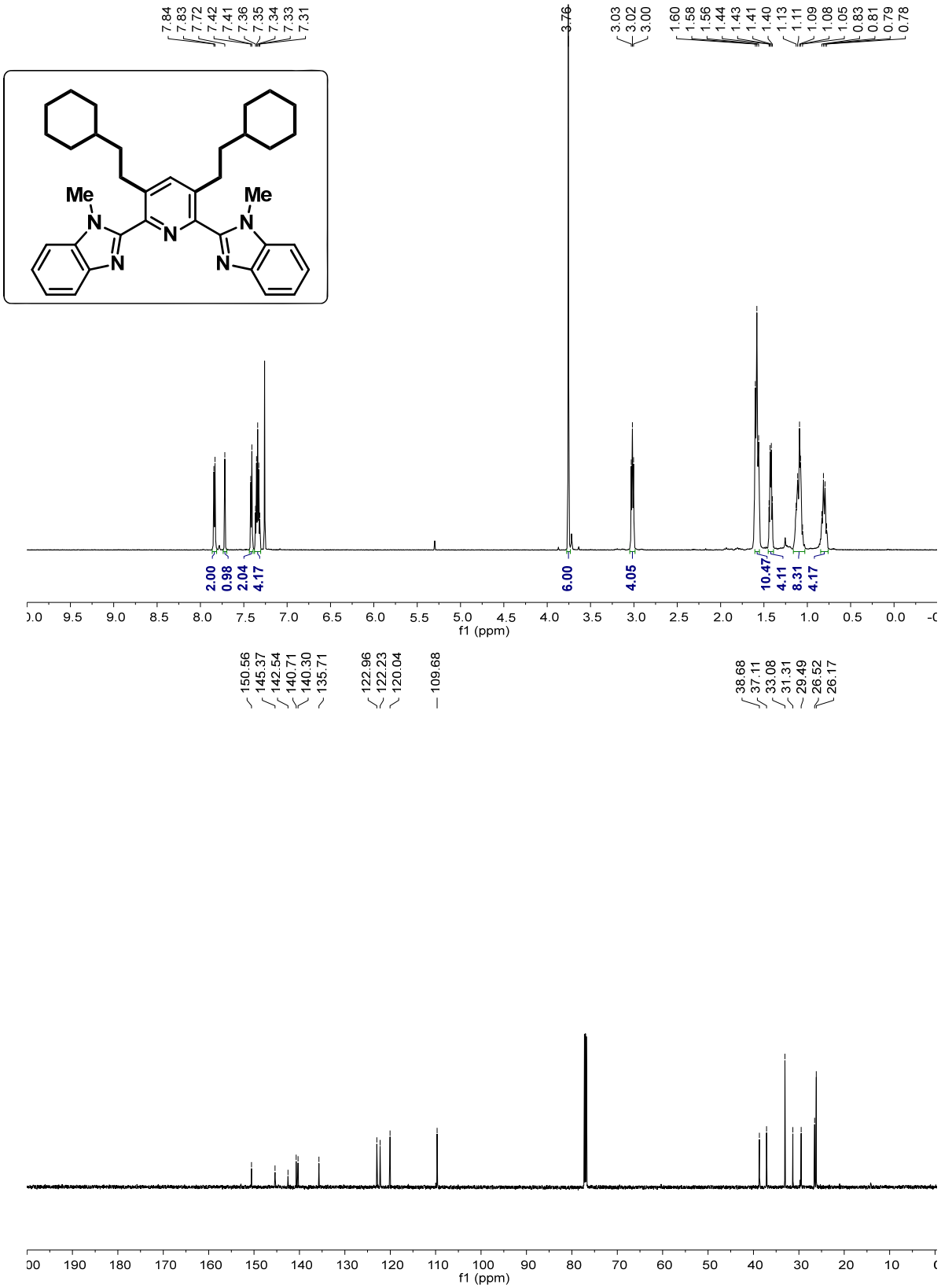
3',5'-Bis(3,3-dimethylbutyl)-4,4'',5,5''-tetramethyl-2,2':6',2''-terpyridine (5b, Table 3**)**



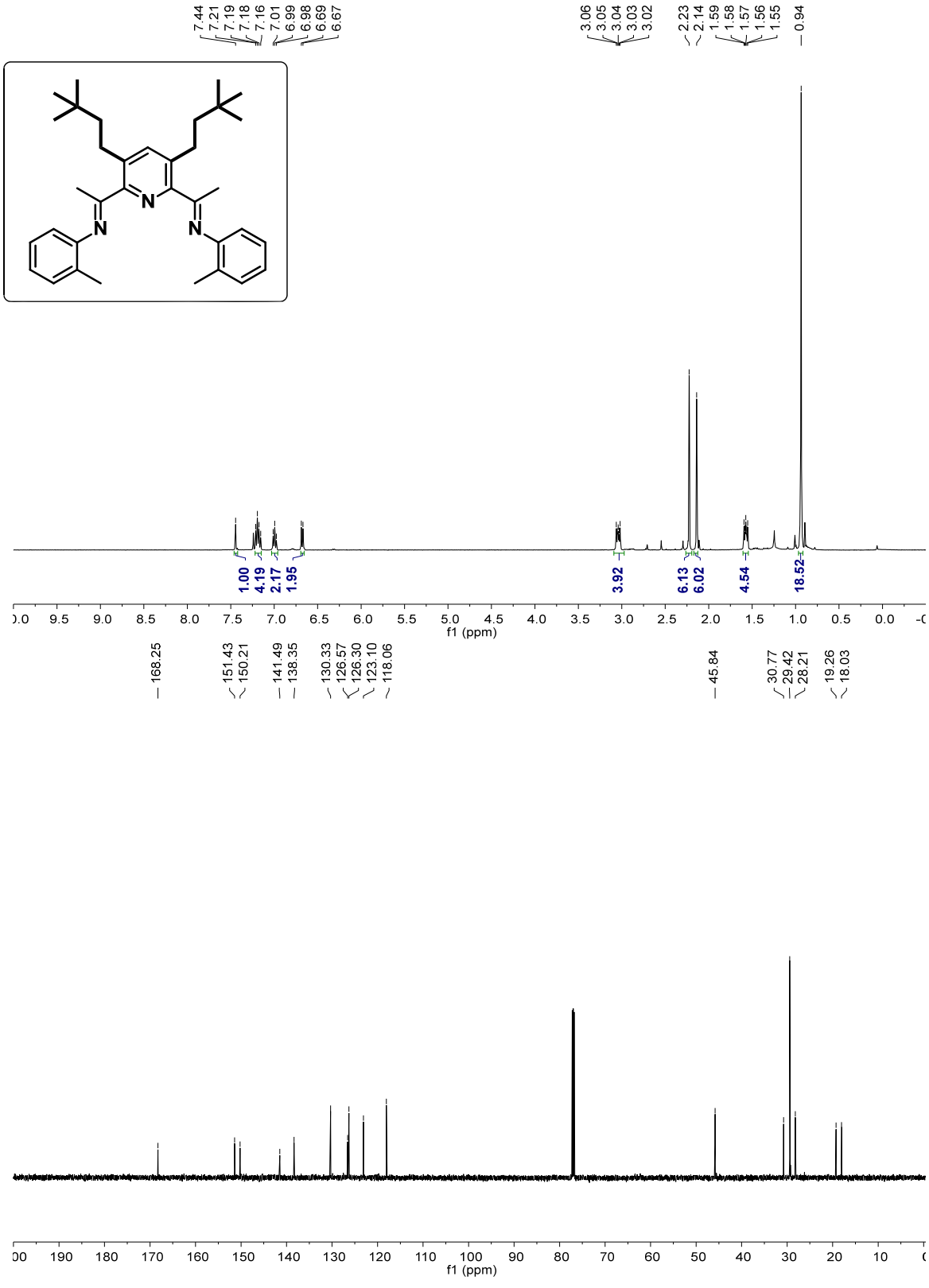
2,2'-[3,5-Bis(3,3-dimethylbutyl)pyridine-2,6-diyl]-bis(1-methyl-1*H*-benzo[*d*]imidazole) (5c, Table 3**)**



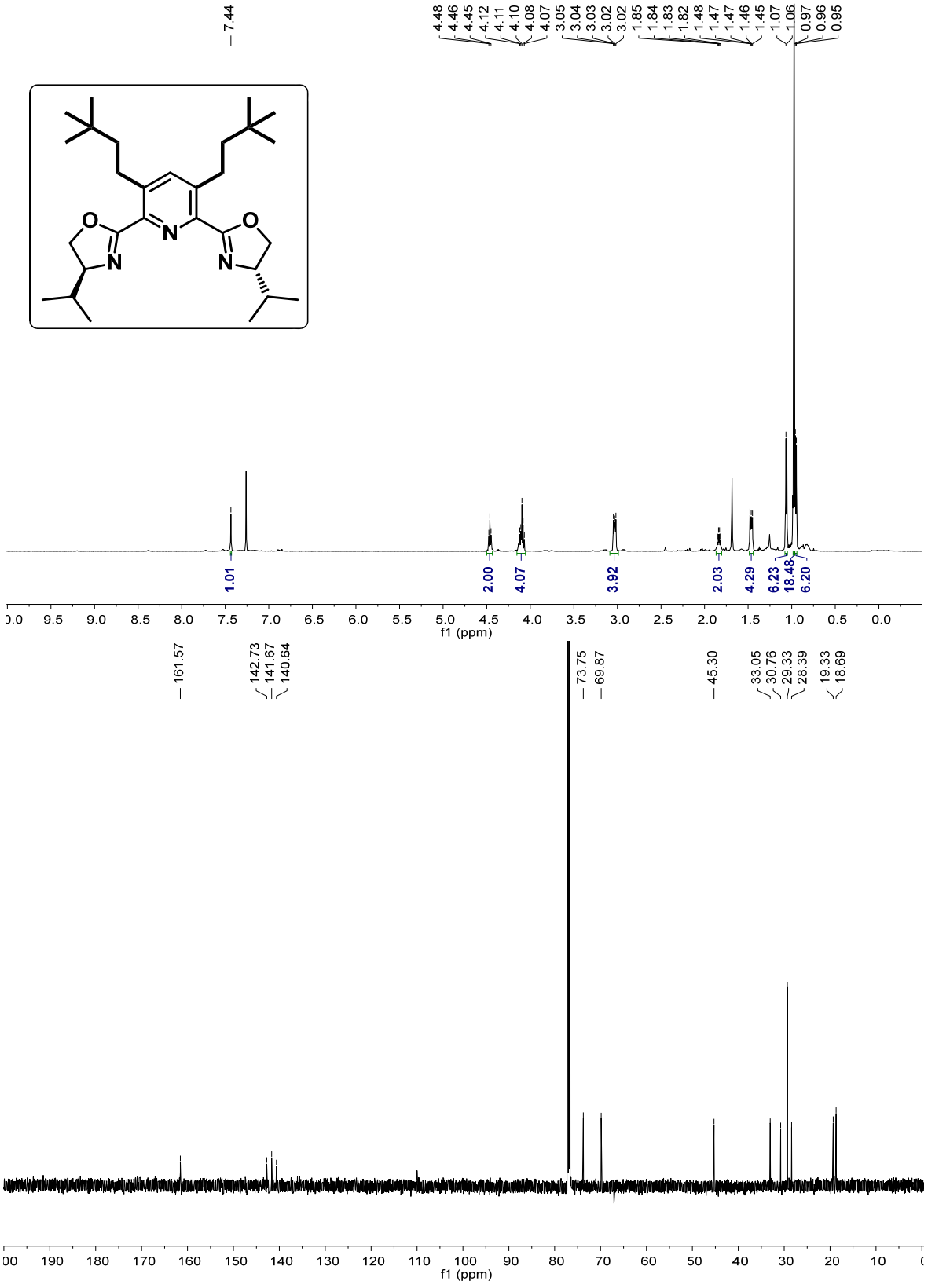
2,2'-[3,5-Bis(2-cyclohexylethyl)pyridine-2,6-diyl]-bis(1-methyl-1*H*-benzo[*d*]imidazole) (5d, Table 3**)**



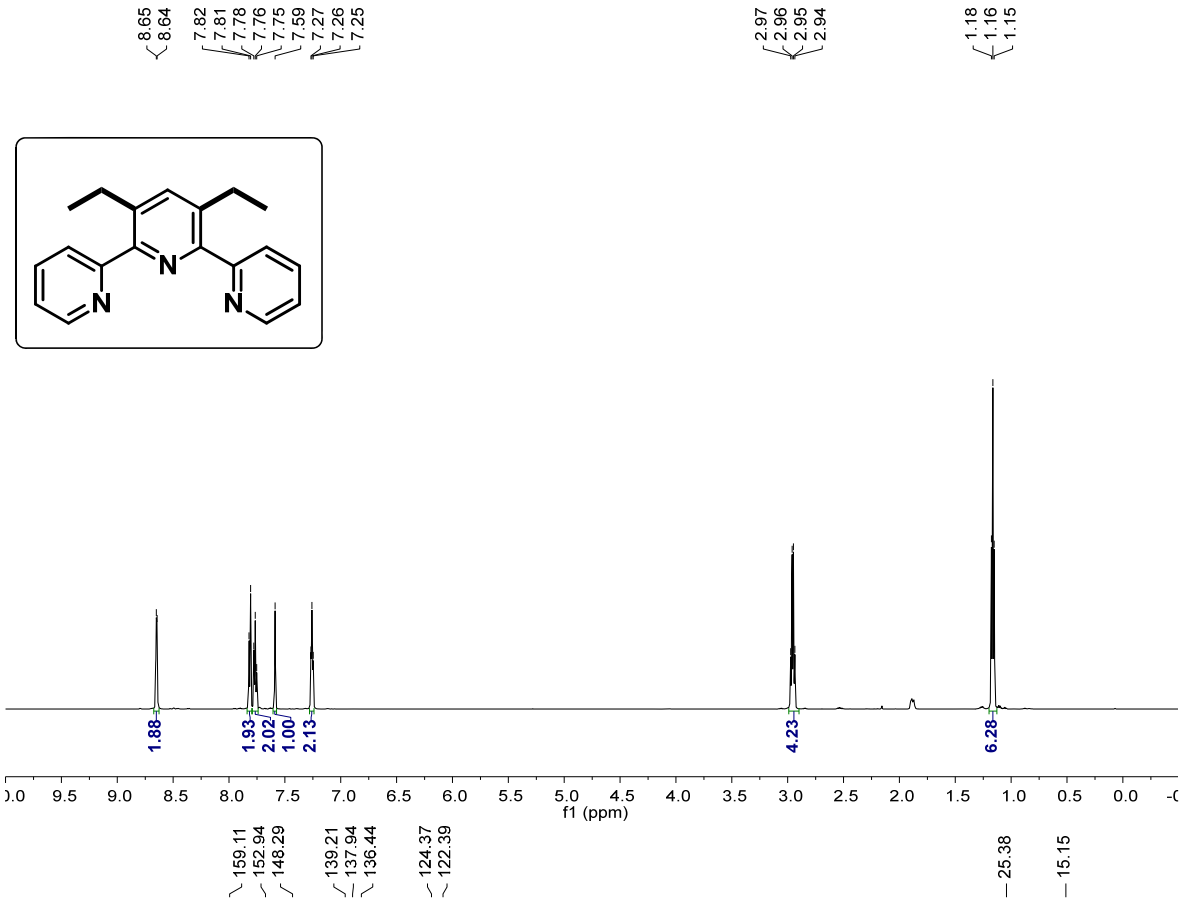
3,5-Bis(3,3-dimethylbutyl)-2,6-bis[1-(2-methylphenylimino)ethyl]pyridine (5e, Table 3**)**



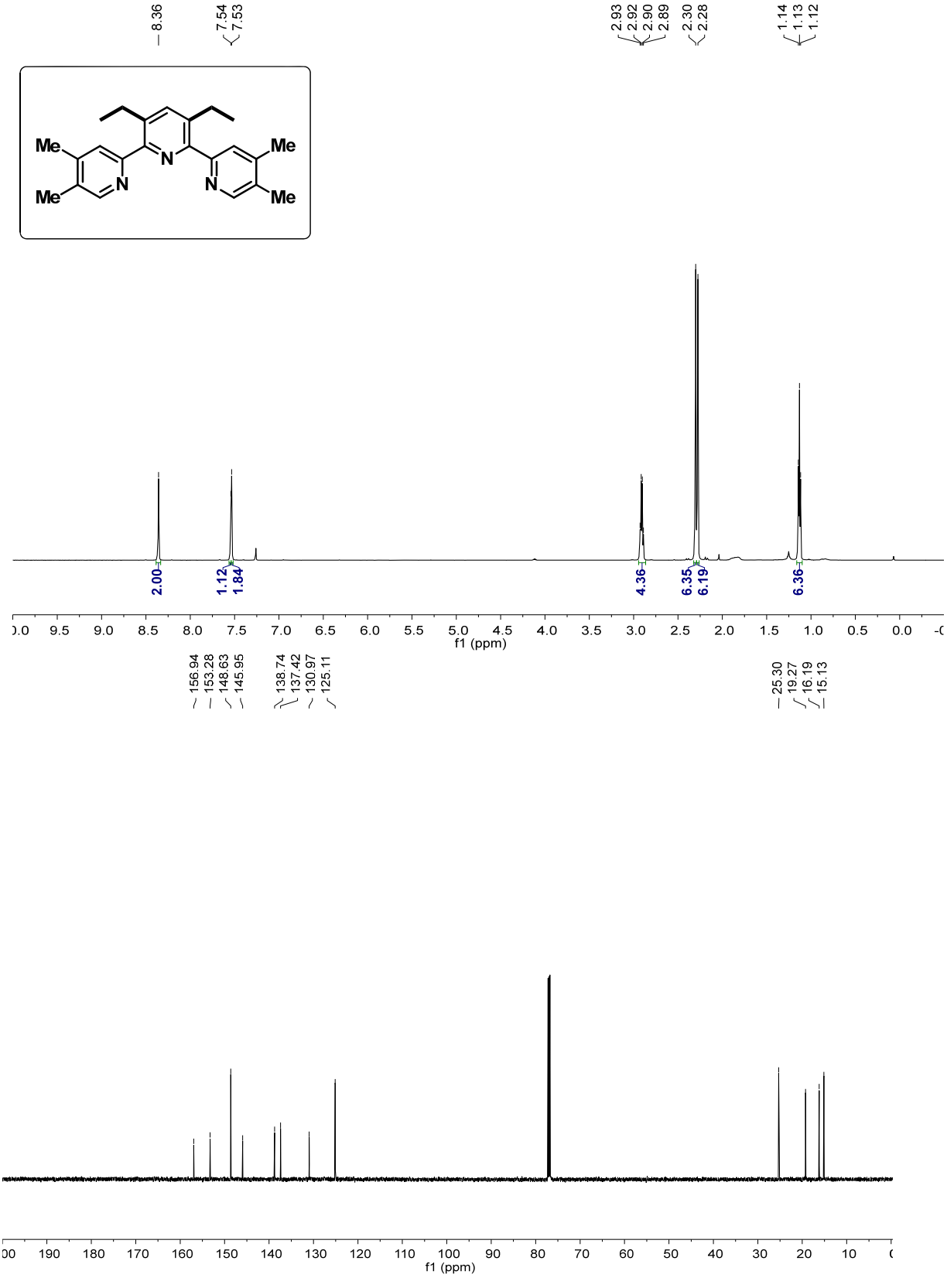
(4*S*,4'*S*)-2,2'-[3,5-Bis(3,3-dimethylbutyl)pyridine-2,6-diyl]-bis(4-isopropyl-4,5-dihydrooxazole) (5f, Table 3**)**



3',5'-Diethyl-2,2':6',2''-terpyridine (6a, Table 4**)**



3',5'-Diethyl-4,4'',5,5''-tetramethyl-2,2':6',2''-terpyridine (6b, Table 4**)**



Appendix II

Crystallographic Data for **4e** and **6a**

Crystallographic data of 4e (Table 2)

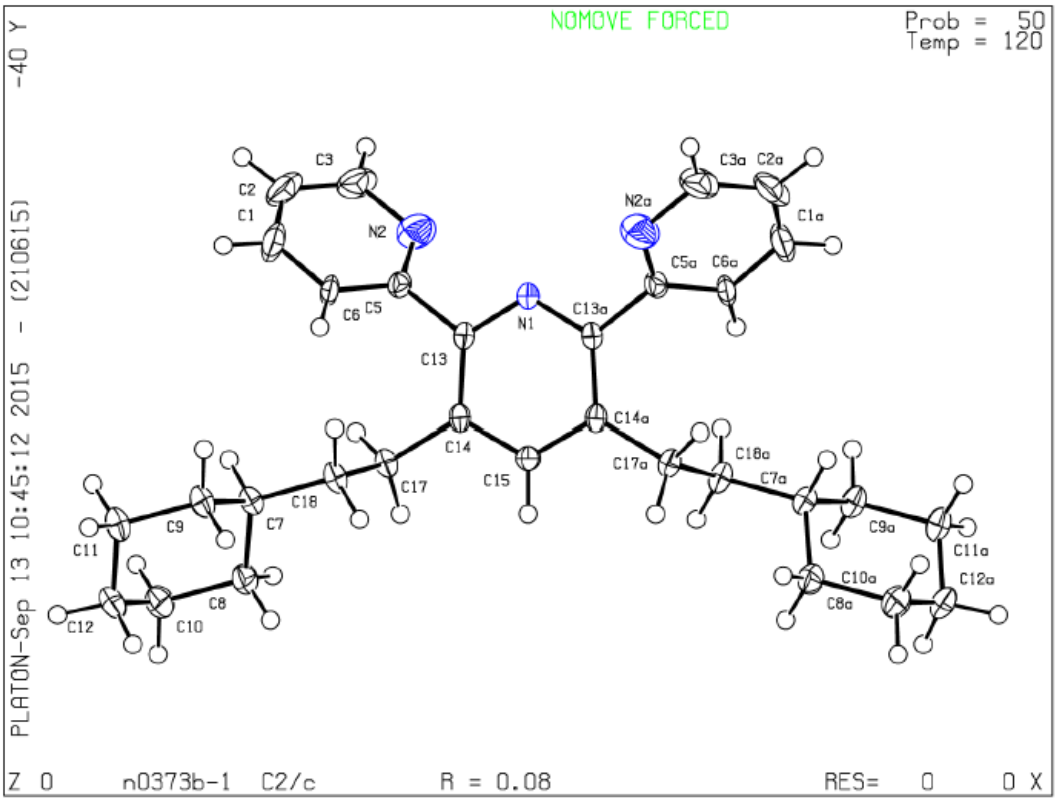


Table S3. Crystal data and structure refinement for **4e**

Identification code	**4e**	
Empirical formula	C31 H39 N3	
Formula weight	453.65	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 30.5673(18) Å	a= 90°.
	b = 9.9939(5) Å	b= 106.271(2)°.
	c = 8.7408(6) Å	g = 90°.
Volume	2563.2(3) $Å^3$	
Z	4	
Density (calculated)	1.176 Mg/m^3	
Absorption coefficient	0.069 mm^{-1}	
F(000)	984	
Crystal size	0.40 x 0.35 x 0.28 mm^3	
Theta range for data collection	2.78 to 30.41°	
Index ranges	-39<=h<=43, -14<=k<=13, -9<=l<=12	
Reflections collected	17425	
Independent reflections	3858 [R(int) = 0.0525]	
Completeness to theta = 30.41°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9810 and 0.9731	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3858 / 0 / 155	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0750, wR2 = 0.2059	
R indices (all data)	R1 = 0.1235, wR2 = 0.2414	
Largest diff. peak and hole	0.802 and -0.661 $e.Å^{-3}$	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(5)	4428(1)	7651(2)	10031(2)	21(1)
C(6)	3975(1)	7548(2)	9640(2)	23(1)
C(3)	4396(1)	9386(3)	8108(3)	42(1)
N(2)	4653(1)	8560(2)	9305(3)	46(1)
C(1)	3733(1)	8372(3)	8492(3)	42(1)
C(2)	3928(1)	9284(3)	7702(3)	45(1)
C(7)	3482(1)	3972(2)	9109(2)	21(1)
C(9)	3048(1)	3953(2)	9650(3)	26(1)
C(8)	3546(1)	2632(2)	8363(3)	29(1)
C(10)	3122(1)	2239(3)	7018(3)	35(1)
C(12)	2697(1)	2225(3)	7588(3)	37(1)
C(11)	2628(1)	3564(2)	8298(3)	32(1)
N(1)	5000	7451(2)	12500	20(1)
C(15)	5000	4697(3)	12500	17(1)
C(14)	4681(1)	5372(2)	11288(2)	17(1)
C(13)	4707(1)	6770(2)	11325(2)	18(1)
C(17)	4332(1)	4615(2)	10023(2)	20(1)
C(18)	3891(1)	4371(2)	10506(2)	22(1)

Table S5. Bond lengths [Å] and angles [°] for **4e**

C(5)-C(6)	1.335(3)
C(5)-N(2)	1.395(3)
C(5)-C(13)	1.496(3)
C(6)-C(1)	1.347(3)
C(3)-C(2)	1.379(4)
C(3)-N(2)	1.390(3)
C(1)-C(2)	1.375(4)
C(7)-C(8)	1.526(3)
C(7)-C(9)	1.529(3)
C(7)-C(18)	1.534(3)
C(9)-C(11)	1.530(3)
C(8)-C(10)	1.536(3)
C(10)-C(12)	1.518(4)
C(12)-C(11)	1.514(4)
N(1)-C(13)#1	1.344(2)
N(1)-C(13)	1.344(2)
C(15)-C(14)	1.397(2)
C(15)-C(14)#1	1.397(2)
C(14)-C(13)	1.399(3)
C(14)-C(17)	1.508(3)
C(17)-C(18)	1.540(3)
C(6)-C(5)-N(2)	122.9(2)
C(6)-C(5)-C(13)	118.51(19)
N(2)-C(5)-C(13)	118.61(19)
C(5)-C(6)-C(1)	117.1(2)
C(2)-C(3)-N(2)	118.5(3)
C(3)-N(2)-C(5)	118.8(2)
C(6)-C(1)-C(2)	123.8(2)
C(1)-C(2)-C(3)	118.9(2)
C(8)-C(7)-C(9)	110.37(18)
C(8)-C(7)-C(18)	113.26(17)
C(9)-C(7)-C(18)	109.92(16)
C(7)-C(9)-C(11)	112.11(19)
C(7)-C(8)-C(10)	111.68(18)

C(12)-C(10)-C(8)	111.6(2)
C(11)-C(12)-C(10)	110.8(2)
C(12)-C(11)-C(9)	111.08(19)
C(13)#1-N(1)-C(13)	119.1(2)
C(14)-C(15)-C(14)#1	122.3(3)
C(15)-C(14)-C(13)	116.19(18)
C(15)-C(14)-C(17)	120.97(18)
C(13)-C(14)-C(17)	122.84(17)
N(1)-C(13)-C(14)	123.01(18)
N(1)-C(13)-C(5)	113.31(18)
C(14)-C(13)-C(5)	123.62(17)
C(14)-C(17)-C(18)	111.85(16)
C(7)-C(18)-C(17)	113.74(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+5/2

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4e.** The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	
C(5)	22(1)	22(1)	17(1)	-3(1)	-1(1)	4(1)
C(6)	13(1)	28(1)	22(1)	2(1)	-3(1)	4(1)
C(3)	60(2)	28(1)	33(1)	9(1)	5(1)	6(1)
N(2)	55(2)	36(1)	42(1)	8(1)	6(1)	3(1)
C(1)	29(1)	47(2)	37(1)	-4(1)	-12(1)	16(1)
C(2)	60(2)	34(1)	29(1)	2(1)	-6(1)	23(1)
C(7)	19(1)	23(1)	19(1)	-2(1)	4(1)	-5(1)
C(9)	18(1)	31(1)	28(1)	-3(1)	4(1)	-6(1)
C(8)	25(1)	28(1)	29(1)	-7(1)	-1(1)	1(1)
C(10)	36(1)	31(1)	30(1)	-10(1)	-4(1)	0(1)
C(12)	31(1)	29(1)	39(1)	-3(1)	-8(1)	-10(1)
C(11)	18(1)	35(1)	37(1)	-2(1)	1(1)	-6(1)
N(1)	17(1)	21(1)	20(1)	0	1(1)	0
C(15)	16(1)	17(1)	20(1)	0	7(1)	0
C(14)	13(1)	24(1)	16(1)	-1(1)	5(1)	0(1)
C(13)	13(1)	23(1)	16(1)	0(1)	3(1)	1(1)
C(17)	16(1)	24(1)	18(1)	-4(1)	4(1)	-3(1)
C(18)	18(1)	29(1)	17(1)	-2(1)	4(1)	-6(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4e**

x	y	z	U(eq)	
H(6A)	3829	6921	10150	27
H(3A)	4540	10007	7582	50
H(1A)	3410	8320	8212	50
H(2B)	3742	9834	6889	54
H(7A)	3444	4674	8268	25
H(9A)	2999	4851	10053	32
H(9B)	3086	3308	10538	32
H(8A)	3609	1929	9195	35
H(8B)	3812	2688	7931	35
H(10A)	3081	2883	6128	42
H(10B)	3169	1341	6613	42
H(12A)	2428	2019	6680	44
H(12B)	2724	1514	8399	44
H(11A)	2359	3516	8713	38
H(11B)	2570	4258	7458	38
H(15)	5000	3747	12500	21
H(17A)	4461	3744	9833	24
H(17B)	4258	5128	9014	24
H(18A)	3947	3654	11320	26
H(18B)	3813	5196	11000	26

Table S8. Torsion angles [°] for **4e**

N(2)-C(5)-C(6)-C(1)	-0.1(3)
C(13)-C(5)-C(6)-C(1)	178.8(2)
C(2)-C(3)-N(2)-C(5)	0.8(4)
C(6)-C(5)-N(2)-C(3)	-0.8(4)
C(13)-C(5)-N(2)-C(3)	-179.7(2)
C(5)-C(6)-C(1)-C(2)	1.0(4)
C(6)-C(1)-C(2)-C(3)	-0.9(4)
N(2)-C(3)-C(2)-C(1)	0.0(4)
C(8)-C(7)-C(9)-C(11)	-54.5(2)
C(18)-C(7)-C(9)-C(11)	179.85(19)
C(9)-C(7)-C(8)-C(10)	53.8(3)
C(18)-C(7)-C(8)-C(10)	177.55(19)
C(7)-C(8)-C(10)-C(12)	-55.3(3)
C(8)-C(10)-C(12)-C(11)	55.9(3)
C(10)-C(12)-C(11)-C(9)	-56.1(3)
C(7)-C(9)-C(11)-C(12)	56.0(3)
C(14)#1-C(15)-C(14)-C(13)	1.89(12)
C(14)#1-C(15)-C(14)-C(17)	-178.23(19)
C(13)#1-N(1)-C(13)-C(14)	2.14(14)
C(13)#1-N(1)-C(13)-C(5)	-175.16(18)
C(15)-C(14)-C(13)-N(1)	-4.1(3)
C(17)-C(14)-C(13)-N(1)	176.07(15)
C(15)-C(14)-C(13)-C(5)	172.97(16)
C(17)-C(14)-C(13)-C(5)	-6.9(3)
C(6)-C(5)-C(13)-N(1)	-125.46(19)
N(2)-C(5)-C(13)-N(1)	53.5(2)
C(6)-C(5)-C(13)-C(14)	57.3(3)
N(2)-C(5)-C(13)-C(14)	-123.8(2)
C(15)-C(14)-C(17)-C(18)	90.2(2)
C(13)-C(14)-C(17)-C(18)	-89.9(2)
C(8)-C(7)-C(18)-C(17)	64.3(2)
C(9)-C(7)-C(18)-C(17)	-171.68(18)
C(14)-C(17)-C(18)-C(7)	163.62(17)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+5/2

Crystallographic data of 6a (Table 4)

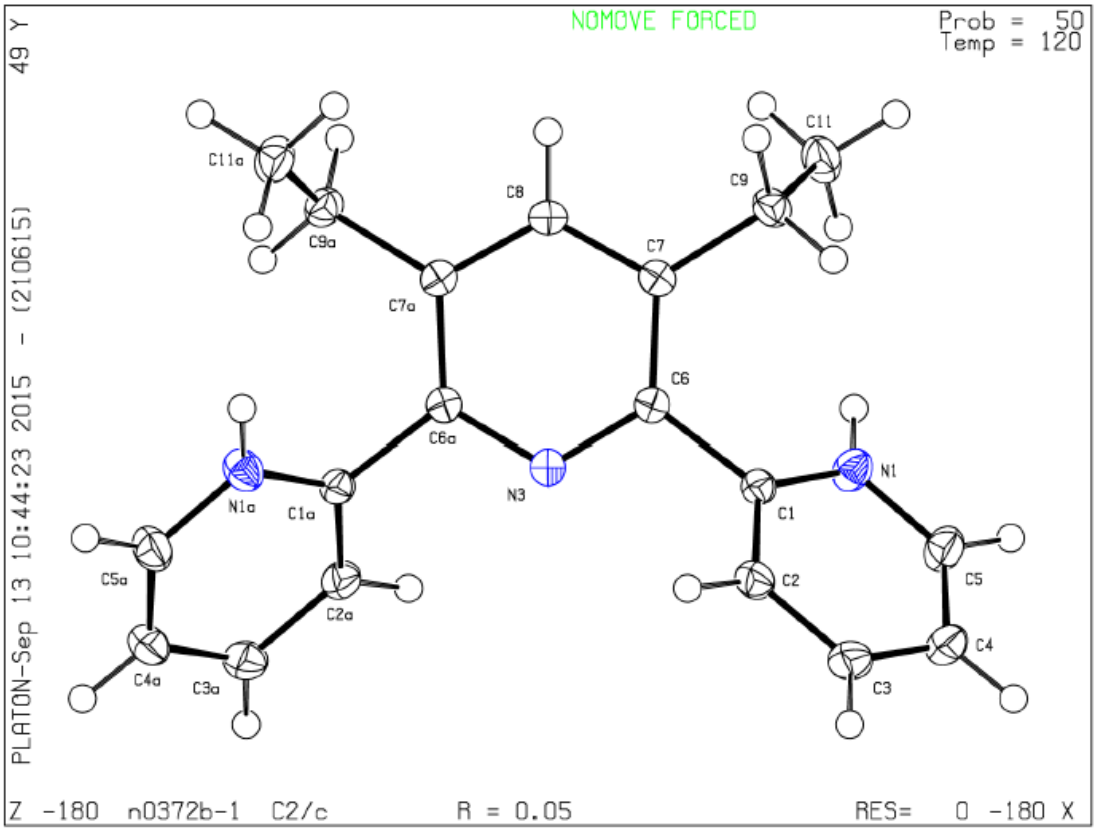


Table S9. Crystal data and structure refinement for **6a**

Identifiation code	**6a**	
Empirical formula	C19 H21 N3	
Formula weight	291.39	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 21.0859(12) Å	= 90°.
	b = 8.8941(5) Å	= 110.4477(18)°.
	c = 8.6908(5) Å	= 90°.
Volume	1527.18(15) $Å^3$	
Z	4	
Density (calculated)	1.267 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	624	
Crystal size	0.20 x 0.16 x 0.14 mm^3	
Theta range for data collection	3.28 to 34.48°	
Index ranges	-33<=h<=33, -14<=k<=14, -13<=l<=13	
Reflections collected	30990	
Independent reflections	3224 [R(int) = 0.0284]	
Completeness to theta = 34.48°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9894 and 0.9849	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3224 / 0 / 101	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1442	
R indices (all data)	R1 = 0.0611, wR2 = 0.1534	
Largest diff. peak and hole	0.546 and -0.832 $e.Å^{-3}$	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9026(1)	7351(1)	104(1)	17(1)
N(1)	8365(1)	7558(1)	-194(1)	21(1)
C(2)	9270(1)	6192(1)	-618(1)	22(1)
C(5)	7933(1)	6579(1)	-1203(1)	25(1)
C(3)	8816(1)	5191(1)	-1664(1)	26(1)
C(4)	8130(1)	5385(1)	-1954(1)	26(1)
C(6)	9518(1)	8352(1)	1323(1)	16(1)
N(3)	10000	7590(1)	2500	17(1)
C(8)	10000	10682(1)	2500	17(1)
C(7)	9495(1)	9927(1)	1255(1)	16(1)
C(9)	8969(1)	10811(1)	-65(1)	20(1)
C(11)	8408(1)	11408(1)	500(1)	26(1)

Table S11. Bond lengths [Å] and angles [°] for **6a**

C(1)-N(1)	1.3399(11)
C(1)-C(2)	1.3944(12)
C(1)-C(6)	1.4907(11)
N(1)-C(5)	1.3415(12)
C(2)-C(3)	1.3887(13)
C(5)-C(4)	1.3846(14)
C(3)-C(4)	1.3886(15)
C(6)-N(3)	1.3464(9)
C(6)-C(7)	1.4015(12)
N(3)-C(6)#1	1.3463(9)
C(8)-C(7)#1	1.3963(10)
C(8)-C(7)	1.3963(10)
C(7)-C(9)	1.5091(11)
C(9)-C(11)	1.5269(13)

N(1)-C(1)-C(2)	122.47(8)
N(1)-C(1)-C(6)	118.24(7)
C(2)-C(1)-C(6)	119.20(7)
C(1)-N(1)-C(5)	117.41(8)
C(3)-C(2)-C(1)	119.38(8)
N(1)-C(5)-C(4)	123.99(9)
C(4)-C(3)-C(2)	118.37(9)
C(5)-C(4)-C(3)	118.35(8)
N(3)-C(6)-C(7)	122.70(8)
N(3)-C(6)-C(1)	113.08(7)
C(7)-C(6)-C(1)	124.21(7)
C(6)#1-N(3)-C(6)	119.56(10)
C(7)#1-C(8)-C(7)	122.48(11)
C(8)-C(7)-C(6)	116.27(8)
C(8)-C(7)-C(9)	119.82(8)
C(6)-C(7)-C(9)	123.90(7)
C(7)-C(9)-C(11)	112.53(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+1/2

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	18(1)	16(1)	15(1)	1(1)	5(1)	0(1)
N(1)	18(1)	23(1)	24(1)	-5(1)	8(1)	-2(1)
C(2)	22(1)	19(1)	22(1)	-2(1)	4(1)	5(1)
C(5)	20(1)	26(1)	27(1)	-4(1)	6(1)	-4(1)
C(3)	32(1)	19(1)	25(1)	-5(1)	5(1)	3(1)
C(4)	29(1)	21(1)	24(1)	-3(1)	3(1)	-4(1)
C(6)	16(1)	16(1)	16(1)	0(1)	6(1)	0(1)
N(3)	16(1)	17(1)	17(1)	0	5(1)	0
C(8)	20(1)	15(1)	19(1)	0	8(1)	0
C(7)	17(1)	17(1)	16(1)	1(1)	7(1)	1(1)
C(9)	22(1)	19(1)	18(1)	3(1)	6(1)	2(1)
C(11)	22(1)	29(1)	24(1)	-1(1)	4(1)	7(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6a**

x	y	z	U(eq)	
H(1A)	8219	8308	256	26
H(2A)	9742	6089	-397	26
H(5A)	7463	6714	-1416	30
H(3A)	8970	4393	-2169	32
H(4A)	7804	4715	-2650	31
H(8)	10000	11750	2500	21
H(9A)	8767	10160	-1038	24
H(9B)	9191	11668	-400	24
H(11A)	8079	11970	-397	39
H(11B)	8603	12073	1447	39
H(11C)	8180	10563	814	39

Table S14. Torsion angles [°] for **6a**

C(2)-C(1)-N(1)-C(5)	1.37(13)
C(6)-C(1)-N(1)-C(5)	-175.29(8)
N(1)-C(1)-C(2)-C(3)	-1.21(14)
C(6)-C(1)-C(2)-C(3)	175.42(8)
C(1)-N(1)-C(5)-C(4)	-0.39(15)
C(1)-C(2)-C(3)-C(4)	0.03(14)
N(1)-C(5)-C(4)-C(3)	-0.73(16)
C(2)-C(3)-C(4)-C(5)	0.87(15)
N(1)-C(1)-C(6)-N(3)	127.16(7)
C(2)-C(1)-C(6)-N(3)	-49.61(10)
N(1)-C(1)-C(6)-C(7)	-53.88(11)
C(2)-C(1)-C(6)-C(7)	129.34(9)
C(7)-C(6)-N(3)-C(6)#1	0.44(6)
C(1)-C(6)-N(3)-C(6)#1	179.42(7)
C(7)#1-C(8)-C(7)-C(6)	0.39(5)
C(7)#1-C(8)-C(7)-C(9)	-179.29(8)
N(3)-C(6)-C(7)-C(8)	-0.84(10)
C(1)-C(6)-C(7)-C(8)	-179.70(6)
N(3)-C(6)-C(7)-C(9)	178.83(6)
C(1)-C(6)-C(7)-C(9)	-0.03(12)
C(8)-C(7)-C(9)-C(11)	-79.93(9)
C(6)-C(7)-C(9)-C(11)	100.41(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+1/2