Supporting Information

Photocatalytic three-component 1, 2-boroarylation and carbopyridylation of alkene

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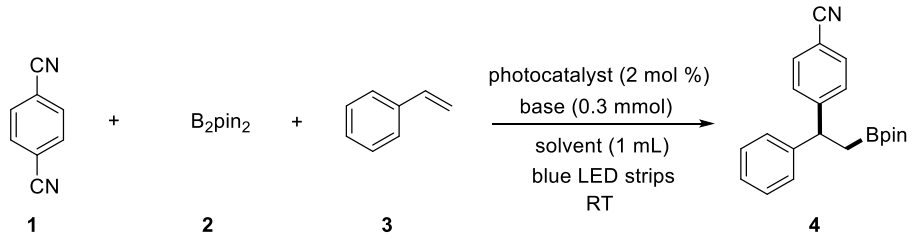
1. General Information

All reactions were carried out with standard Schlenk techniques under argon or in an argon-filled glove-box. Photocatalysts, bis(pinacolato)diboron, (hetero)aryl nitriles, alkylboronic pinacol esters, base, unactivited alkenes and substituted styrene were purchased from TCI and used without purification. Other commercial chemicals were purchased from Acros, Sigma-Aldrich, J&K, and Alfa Aesar Chemical Companies and used as received. Anhydrous THF was purchased from J&K and used as received (water < 30 ppm, J&KSeal). Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum sheets from Qingdao Haiyang Chemical Co., Ltd. Flash chromatography was performed on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd). ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE Avance III 400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for $^{13}C\{^{1}H$ NMR). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet), coupling constants (Hz) and integration. Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using a neat thin-film technique. High-resolution mass spectra (HRMS) were recorded on the Thermo Quest Finnigan LCQDECA system equipped with an ESI ionization source and a TOF detector mass spectrometer.

2. Experimental Details for the Arylboration of Alkene

2.1 Reaction Conditions Optimization Studies



Experimental procedure: In an argon-filled glovebox, in an oven-dried reaction vial (10 ml) containing a magnetic stir bar was charged with 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), Bis(pinacolato)diboron [$B_2(pin)_2$, 76 mg, 0.3 mmol, 1.5 equiv.], styrene (0.4 mmol, 2.0 equiv.), and base (0.3 mmol, 1.5 equiv.), photocatalyst (2 mol%) and anhydrous THF (1 mL) in an argon-filled glove box. The vial was tightly sealed, then removed from the glovebox. After stirring under blue LED irradiation (λ=450 nm, 8 W or 2×40 W) at room temperature for 24 h (The temperature of the reaction was maintained at room temperature via a fan). Then, the reaction mixture was diluted by diethyl ether, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under

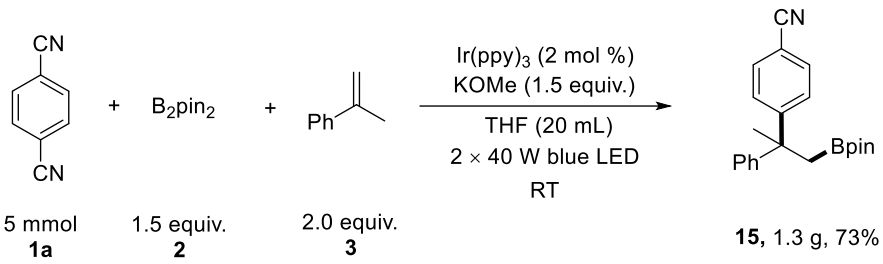
reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding arylboration of alkenes product.

2.2 Experimental Procedure for the arylboration of alkene

2.2.1 General procedure

In an oven-dried reaction vial (10 ml) containing a magnetic stir bar was charged with (hetero)aryl nitriles (0.2 mmol, 1.0 equiv.), bis(pinacolato)diboron [$B_2(pin)_2$] or alkylboronic pinacol esters (0.3 mmol, 1.5 equiv.], alkene (0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL) in an argon-filled glove box or standard Schlenk techniques under argon. The vial was tightly sealed, then removed from the glovebox. After stirring under 2×40 W blue LED irradiation (λ = 450 nm) at room temperature for 24 h (The temperature of the reaction was maintained at room temperature via a fan). Upon completion, the reaction mixture was quenched by NH_4Cl solution and extracted by ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding arylboration of alkenes product.

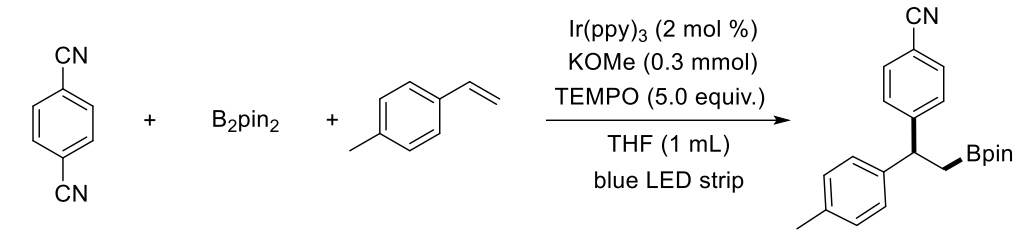
2.2.2 Gram scale experiment



Experimental procedure: according to the general procedure, in an oven-dried reaction vial (100 ml) containing a magnetic stir bar was charged with 1.4-dicyanobenzene (640 mg, 5 mmol, 1.0 equiv.), Bis(pinacolato)diboron [$B_2(pin)_2$] (1.9 g, 7.5 mmol, 1.5 equiv.], 2-phenyl-1-propene (1.18 g, 10 mmol, 2.0 equiv.), and KOMe (525 mg, 7.5 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (20 mL) in an argon-filled glove box. The vial was tightly sealed, then removed from the glovebox. After stirring under blue LED irradiation (λ = 450 nm, 2× 40 W) at room temperature for 24 h (The temperature of the reaction was maintained at room temperature via a fan). Upon completion, the reaction mixture was quenched by saturated NH_4Cl solution and extracted by ethyl acetate. After the solvent was removed under reduced pressure, and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 10: 1) to afford the desired product **15** in 73% yield.

2.3 Experimental Studies on the Reaction Mechanism

2.3.1 Radical trapping experiments

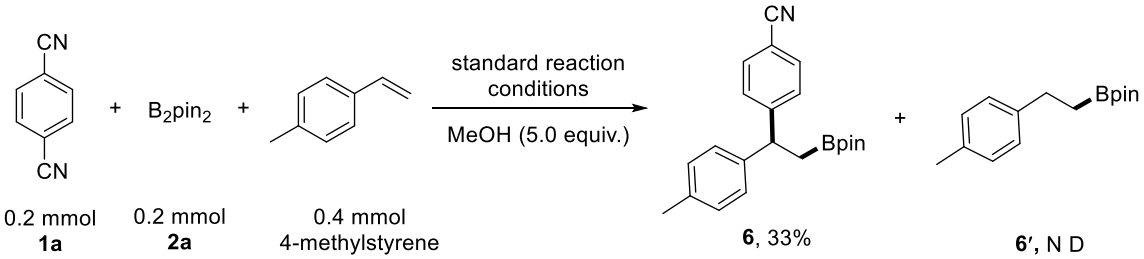


1a (0.2 mmol) **2a** (0.3 mmol) **3** (0.4 mmol) **6**, N D

When adding the 2,2,6,6-Tetramethyl-1-piperinedinyloxy (TEMPO) into the reaction of 4-methylstyrene, 1,4-dicyanobenzene and $B_2(pin)_2$ under standard condition, the desired product **6** was inhibited, indicating a radical mechanism.

Experimental procedure: according to the general procedure, in an oven-dried reaction vial (10 ml) containing a magnetic stir bar was charged with 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), Bis(pinacolato)diboron [$B_2(pin)_2$, 76 mg, 0.3 mmol, 1.5 equiv.], 4-methylstyrene (0.4 mmol, 2.0 equiv.), 2,2,6,6-tetramethylpiperidinyl-1-oxide (TEMPO, 10 mmol, 5.0 equiv.) and KOMe (0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL) in an argon-filled glove box. The vial was tightly sealed, then removed from the glovebox. After stirring under blue LED irradiation (λ = 450 nm, 2× 40 W) at room temperature for 24 h (The temperature of the reaction was maintained at room temperature via a fan). Then, the reaction mixture was detected by GC-MS analysis.

2.3.2 Carbanion trapping experiment



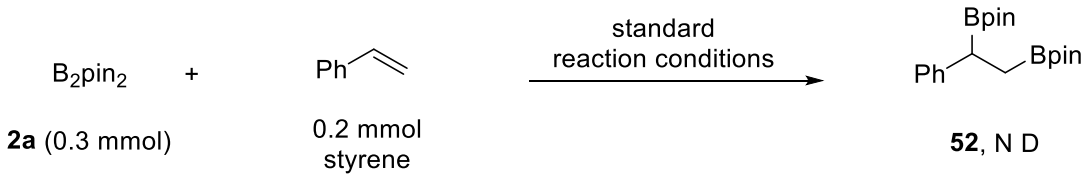
0.2 mmol **1a** 0.2 mmol **2a** 0.4 mmol 4-methylstyrene **6**, 33% **6′**, N D

When MeOH was added in the reaction mixture, the corre-sponding product **6** was obtained in 33% yield and protoboration adduct **6**‘ was not detected.

Experimental procedure: according to the general procedure, in an argon-filled glovebox, in an oven-dried reaction vial (10 ml) containing a magnetic stir bar was charged with 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), Bis(pinacolato)diboron [$B_2(pin)_2$, 76 mg, 0.3 mmol, 1.5 equiv.], 4-methylstyrene (0.4 mmol, 2.0 equiv.), MeOH (10 mmol, 5.0 equiv.) and KOMe (0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL) in an argon-filled glove box. The vial was tightly sealed, then removed from the glovebox. After stirring under blue LED irradiation (λ = 450 nm, 2× 40 W) at room temperature for 24 h (The temperature of the reaction was maintained at room temperature via a fan). Then, the reaction mixture was detected by GC-MS analysis. Upon completion, the reaction mixture was

quenched by saturated NH_4Cl solution and extracted by ethyl acetate. After the solvent was removed under reduced pressure, and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 10: 1) to afford the desired product **6** in 33% yield.

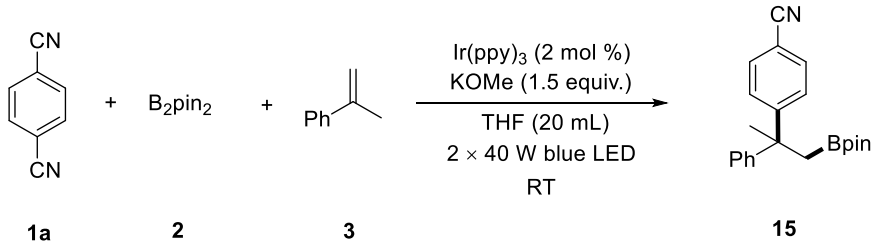
2.3.3 Control experiment



We also performed the reaction of B_2pin_2 with styrene un-der standard conditions and observed that boration product **52** and other possible by-products were not detected.

Experimental procedure: according to the general procedure, in an argon-filled glovebox, in an oven-dried reaction vial (10 ml) containing a magnetic stir bar was charged with styrene (0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (0.3 mmol, 1.5 equiv.), and KOMe (0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL) in an argon-filled glove box. The vial was tightly sealed, then removed from the glovebox. After stirring under blue LED irradiation (λ = 450 nm, 2× 40 W) at room temperature for 24 h (The temperature of the reaction was maintained at room temperature via a fan). Then, the reaction mixture was detected by GC-MS analysis.

2.3.4 Light on-off experiment



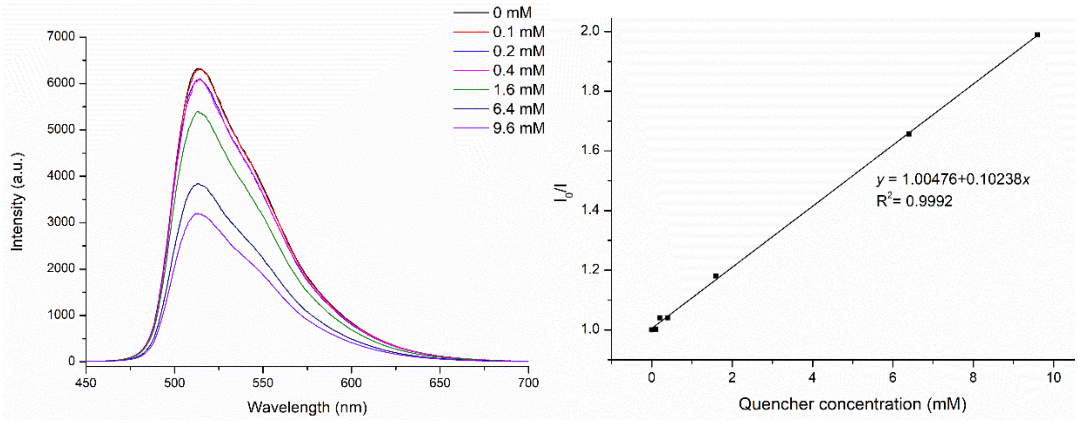
Light on-off experiments were performed implying a con-tinuous visible light irradiation is essential for this protocol

Experimental procedure: according to the general procedure, six oven-dried reaction vials were charged respectively 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76 mg, 0.3 mmol, 1.5 equiv.), α-methylstyrene (0.4 mmol, 2.0 equiv.), KOMe (0.3 mmol, 1.5 equiv.) and $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL) in an argon-filled glove box. The vial was tightly sealed, then removed from the glovebox. After stirring under blue LED irradiation (λ = 450 nm, 2× 40 W) at room temperature for 24 h (The temperature of the reaction was maintained at room temperature via a fan). After 2 hours, the lamps were turned off, and one vial was removed from the irradiation setup for analysis. The

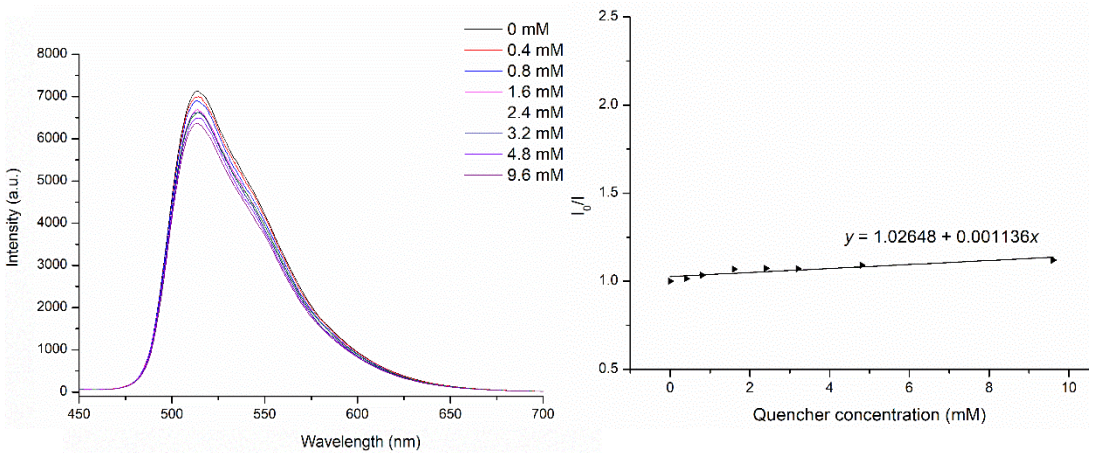
remaining three vials were stirred in the absence of light for an additional 2 hours. Then, one vial was removed for analysis, and the other lamps were turned back on to irradiate. After an additional 2 hours irradiation, the lamps were turned off, and one vial was removed for analysis. The remaining vial was stirred in the absence of light for an additional 2 hours. Then, the lamps were turned off, and the last vial was removed for analysis. The reaction mixtures were diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding product **15**.

2.3.5 Stern-Volmer luminescence quenching experiments

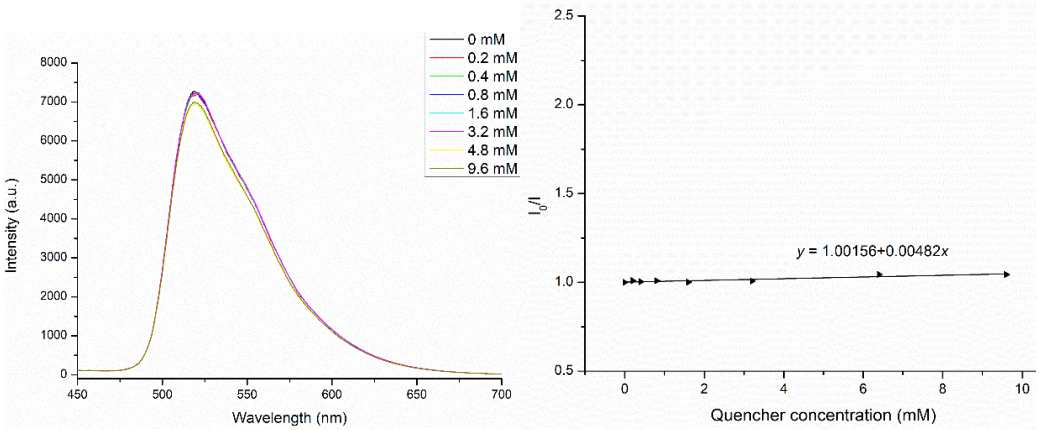
Stern-Volmer luminescence quenching analysis was conducted using a HITACHI F-7000 spectrofluorometer. All the mixed degassed anhydrous THF solutions were excited at 375 nm. All samples used in the luminescence quenching experiments were freshly prepared in a glovebox and placed in a 4 mL screw-top quartz cuvette at room temperature. I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; I = observed emission intensity of the photocatalyst with added quencher.



(a) Stern–Volmer plot for the spectrum of $Ir(ppy)_3$ with the change of the concentration of 1,4-dicyanobenzene in anhydrous tetrahydrofuran with excitation at 375 nm and the emission intensity at 516 nm was observed, $[Ir(ppy)_3] = 3\times10^{-5}$ M.



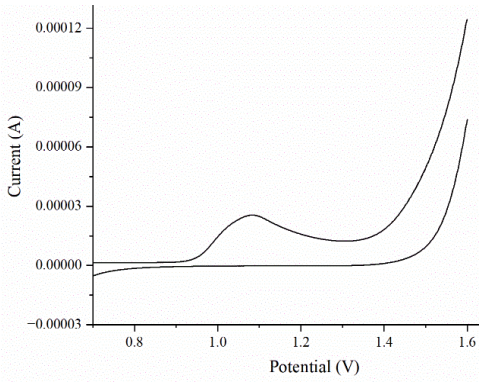
(b) Stern–Volmer plot for the spectrum of $Ir(ppy)_3$ with the change of the concentration of KOMe and $B_2(pin)_2$ in anhydrous tetrahydrofuran with excitation at 375 nm and the emission intensity at 516 nm was observed, $[Ir(ppy)_3] = 3\times10^{-5}$ M.



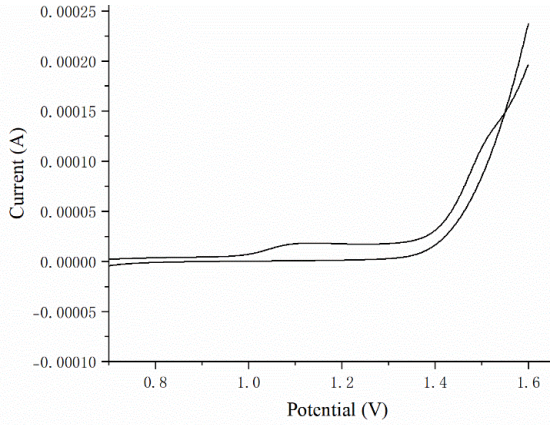
(c) Stern–Volmer plot for the spectrum of $Ir(ppy)_3$ with the change of the concentration of styrene in Anhydrous tetrahydrofuran with excitation at 375 nm and the emission intensity at 516 nm was observed, $[Ir(ppy)_3] = 3\times10^{-5}$ M.

2.3.6 Cyclic Voltammetry studies

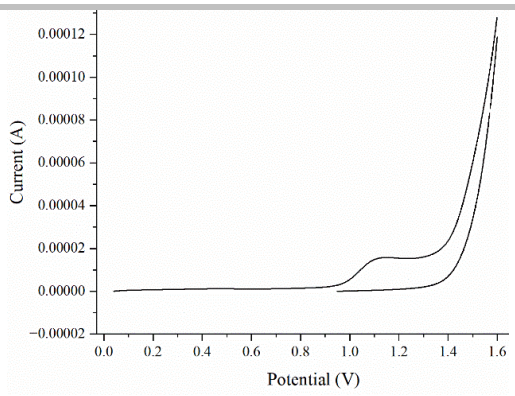
Cyclic voltammograms experiment were recorded on a CHI 630E instrument by using a three-electrode system, in which glassy carbon electrode was used as the working electrode, platinum wire was used as the counter electrode, and a SCE electrode was used as the reference electrode. The experiments were conducted with a scan rate of 100 $mV\cdot s^{-1}$, employing anhydrous THF as the solvent and NaAc-HAc (PH=7) as the supporting electrolyte.



(a) Cyclic voltammogram of $B_2(pin)_2$ with KOMe (10 mM) in an electrolyte of NaAc-HAc in THF (10 mL). $E_{p/2}$ = 1.08 V.

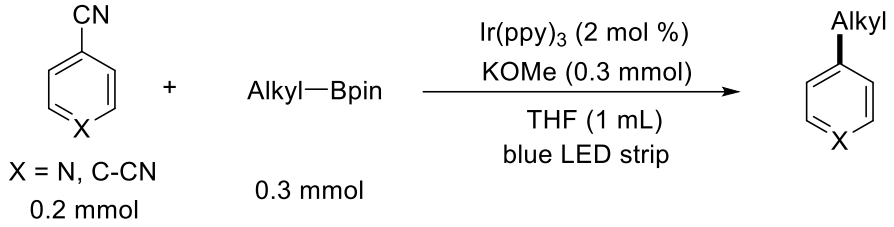


(b) Cyclic voltammogram of $B_2(pin)_2$ with KO^{t}Bu (10 mM) in an electrolyte of NaAc-HAc in THF (10 mL). $E_{p/2}$ = 1.14 V.



(c) Cyclic voltammogram of $Ir(ppy)_3$ in an electrolyte of NaAc-HAc in THF (10 mL). $E_{p/2}$ = 1.13 V.

2.3.7 Experimental Procedure for the Direct Coupling of Alkyl Boronic Pinacol Esters with (Hetero)aryl nitriles

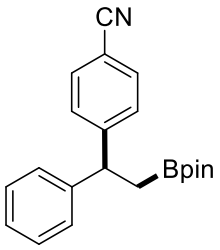


Cross-coupling of alkylboronic pinacol esters and (het-ero)aryl nitriles gave the various aryl derivatives, suggesting the involvement of alkyl radical during this process.

Experimental procedure: in an oven-dried reaction vial (10 mL) containing a magnetic stir bar was charged with (hetero)aryl nitriles (0.2 mmol, 1.0 equiv.), alkylboronic pinacol esters (0.3 mmol, 1.5 equiv.], KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL) in an argon-filled glove box or standard Schlenk techniques under argon. The vial was tightly sealed, then removed from the glovebox. After stirring under 2×40 W blue LED irradiation (λ = 450 nm, 2× 40 W) at room temperature for 24 h (The temperature of the reaction was maintained at room temperature via a fan). Upon completion, the reaction mixture was quenched by NH_4Cl solution and extracted by ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding coupling products.

2.4 Characterization Data of the Arylborated Products

2.4.1 4-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (**4**)



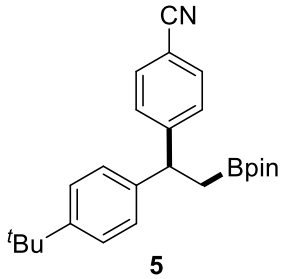
4

$C_{21}H_{24}BNO_2$

M = 333.23 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), styrene (41.7 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **4** as colorless oil (44 mg, 66% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 – 7.48 (m, 2H), 7.36 – 7.32 (m, 2H), 7.26 – 7.13 (m, 5H), 4.30 (t, *J* = 8.4 Hz, 1H), 1.56 (dd, *J* = 8.4, 3.6 Hz, 2H), 1.04 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 152.3, 145.0, 132.2, 128.6, 128.6, 127.7, 126.6, 119.1, 109.8, 83.4, 46.7, 24.6, 18.9 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.8 ppm. **IR** (film): 3061, 2977, 2931, 2227, 1606, 1367, 1325, 1142, 967, 846 cm^{-1}. **HRMS** (ESI): calculated for $C_{21}H_{25}BNO_2^+$ $[M+H]^+$ 334.1973; found 334.1969.

2.4.2 4-(1-(4-(tert-butyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (**5**)



5

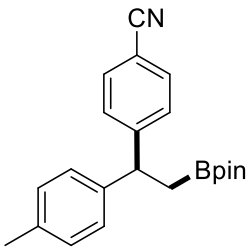
$C_{25}H_{32}BNO_2$

M = 389.34 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 4-tert-Butylstyrene (64.1 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **5** as colorless oil (47.5 mg, 61% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 – 7.50 (m, 2H), 7.40 – 7.36 (m, 2H), 7.30 – 7.26 (m, 2H), 7.16 – 7.12 (m, 2H), 4.28 (t, *J* = 8.5 Hz, 1H), 1.60 – 1.55 (d, *J* = 7.8 Hz, 2H), 1.27 (s, 9H), 1.05 (s, 6H), 1.03

(s, 6H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 152.5, 149.4, 142.0, 132.2, 128.6, 127.3, 125.4, 119.2, 109.7, 83.4, 46.3, 34.4, 31.4, 24.7, 24.6, 19.0 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.8 ppm. **IR** (film): 2964, 2904, 2868, 2227, 1605, 1466, 1364, 1326, 1143, 967, 848 cm^{-1}. **HRMS** (ESI): calculated for $C_{25}H_{33}BNO_2^+$ $[M+H]^+$ 390.2599; found 390.2595.

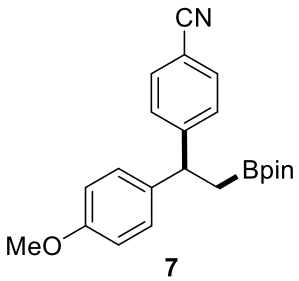
2.4.3 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)ethyl)benzonitrile (**6**)



6
$C_{22}H_{26}BNO_2$
M = 347.26 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **6** as colorless oil (41.7 mg, 60% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.49 (m, 2H), 7.37 – 7.34 (m, 2H), 7.12 – 7.05 (m, 4H), 4.28 (t, *J* = 8.4 Hz, 1H), 2.28 (s, 3H), 1.58 – 1.54 (m, 2H), 1.06 (s, 12H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 152.6, 142.1, 136.1, 132.2, 129.3, 128.5, 127.5, 119.2, 109.7, 83.4, 46.3, 24.7, 21.0, 19.0 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.6 ppm. **IR** (film): 2977, 2928, 2226, 1605, 1512, 1369, 1325, 1165, 1143, 967, 846 cm^{-1}. **HRMS** (ESI): calculated for $[M+H]^+$ $C_{22}H_{27}BNO_2^+$ 348.2129; found 348.2123.

2.4.4 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)ethyl)benzonitrile (**7**)

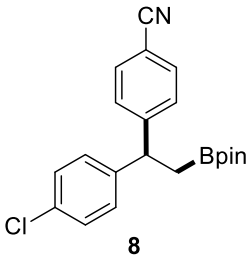


7
$C_{22}H_{26}BNO_3$
M = 363.26 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 4-methoxystyrene (53.7 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by

preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **7** as colorless oil (40.0 mg, 55% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 – 7.50 (m, 2H), 7.36 – 7.33 (m, 2H), 7.15 – 7.11 (m, 2H), 6.83 – 6.79 (m, 2H), 4.28 (t, *J* = 8.4 Hz, 1H), 3.76 (s, 3H), 1.58 – 1.51 (m, 2H), 1.07 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 158.2, 152.8, 137.2, 132.2, 128.6, 128.4, 119.2, 113.9, 109.7, 83.4, 55.3, 45.8, 24.6, 19.1 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.5 ppm. **IR** (film): 2977, 2933, 2836, 2226, 16808, 1510, 1369, 1326, 1247, 1143, 1036, 847, 575 cm^{-1}. **HRMS** (ESI): calculated for $[M+H]^+$ $C_{22}H_{27}BNO_3^+$ 364.2079; found 364.2072.

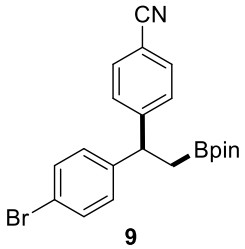
2.4.5 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)ethyl)benzonitrile (**8**)



8
$C_{21}H_{23}BClNO_2$
M = 367.68 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 4-chlorostyrene (55.4 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **8** as colorless oil (46.3 mg, 63% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.51 (m, 2H), 7.34 – 7.31 (m, 2H), 7.26 – 7.21 (m, 2H), 7.16 – 7.13 (m, 2H), 4.29 (t, *J* = 8.3 Hz, 1H), 1.56 – 1.52 (m, 2H), 1.07 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 151.7, 143.5, 132.3, 129.1, 129.0, 128.7, 128.5, 119.0, 110.1, 83.5, 46.0, 24.7, 18.9 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.1 ppm. **IR** (film): 2977, 2931, 2227, 1606, 1490, 1368, 1325, 1142, 1092, 1013, 966, 846 cm^{-1}. **HRMS** (ESI): calculated for $C_{21}H_{24}BClNO_2^+$ $[M+H]^+$ 368.1583; found 368.1575.

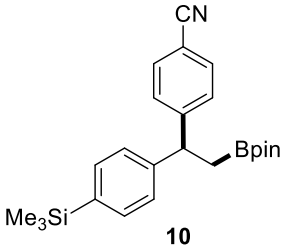
2.4.6 4-(1-(4-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (**9**)



9
$C_{21}H_{23}BBrNO_2$
M = 412.13 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 4-bromostyrene (73.2 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **9** as colorless oil (45.3 mg, 55% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 – 7.51 (m, 2H), 7.45 – 7.37 (m, 2H), 7.35 – 7.31 (m, 2H), 7.12 – 7.07 (m, 2H), 4.28 (t, *J* = 8.3 Hz, 1H), 1.57 – 1.51 (m, 2H), 1.07 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 151.6, 144.1, 132.3, 131.7, 129.5, 128.5, 120.4, 119.0, 110.1, 83.6, 46.1, 24.7, 18.9 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.8 ppm. **IR** (film): 2977, 2930, 2227, 1606, 1487, 1402, 1370, 1326, 1142, 1009, 846, 554 cm^{-1}. **HRMS** (ESI): calculated for $C_{21}H_{24}BBrNO_2^+$ $[M+H]^+$ 412.1078; found 412.1076.

2.4.7 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trimethylsilyl)phenyl)ethyl)benzonitrile (**10**)



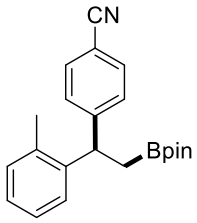
10

$C_{24}H_{32}BNO_2Si$

M = 405.42 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 4-trimethylsilylstyrene (70.5 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **10** as colorless oil (40.5 mg, 50% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 – 7.24 (m, 2H), 7.16 – 7.10 (m, 4H), 6.95 – 6.92 (m, 2H), 4.03 (t, J = 8.4 Hz, 1H), 1.32 (d, *J* = 8.4 Hz, 2H), 0.79 (s, 6H), 0.77 (s, 6H), 0.05 (s, 9H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 152.1, 145.6, 138.5, 133.6, 132.2, 128.6, 127.1, 119.2, 109.8, 83.4, 46.7, 24.7, 18.8, -1.0 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.8 ppm. **IR** (film): 3067, 2977, 2895, 2227, 1597, 1501, 1366, 1324, 1248, 1143, 1109, 845, 752 cm^{-1}. **HRMS** (ESI): calculated for $C_{24}H_{33}BNO_2Si^+$ $[M+H]^+$ 406.2368; found 406.2361.

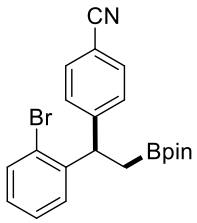
2.4.8 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(o-tolyl)ethyl)benzonitrile (**11**)



11
$C_{22}H_{26}BNO_2$
M = 347.26 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 2-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **11** as colorless oil (41.7 mg, 60% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 – 7.47 (m, 2H), 7.32 – 7.29 (m, 3H), 7.21 – 7.16 (m, 1H), 7.13 – 7.07 (m, 2H), 4.50 (t, *J* = 8.3 Hz, 1H), 2.25 (s, 3H), 1.59 – 1.50 (m, 2H), 1.08 (s, 6H), 1.04 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 152.3, 142.6, 136.1, 132.1, 130.6, 128.7, 126.8, 126.6, 126.3, 119.2, 109.6, 83.4, 42.6, 24.6, 19.9, 19.6 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.1 ppm. **IR** (film): 2977, 2931, 2226, 1605, 1462, 1367, 1324, 1143, 967, 848, 738 cm^{-1}. **HRMS** (ESI): calculated for $[M+H]^+$ $C_{22}H_{27}BNO_2^+$ 348.2129; found 348.2127.

2.4.9 4-(1-(2-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (**12**)

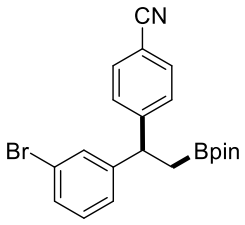


12
$C_{21}H_{23}BBrNO_2$
M = 412.13 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 2-bromostyrene (73.2 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **12** as colorless oil (41.2 mg, 50% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 – 7.60 (m, 3H), 7.48 – 7.45 (m, 2H), 7.41 – 7.31 (m, 2H), 7.18 – 7.13 (m, 1H), 4.88 (t, J = 8.4 Hz, 1H), 1.69 – 1.60 (m, 2H), 1.16 (s, 6H), 1.14 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 151.0, 143.8, 133.2, 132.2, 128.9, 128.7, 128.2, 127.8, 125.1, 119.1, 109.9, 83.5, 45.3, 24.7, 19.2 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.8 ppm. **IR** (film): 3063, 2977, 2931, 2227,

1606, 1467, 1369, 1327, 1142, 1021, 967, 745 cm^{-1}. **HRMS** (ESI): calculated for $C_{21}H_{24}BBrNO_2^+$ $[M+H]^+$ 412.1078; found 412.1073.

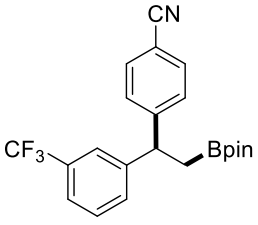
2.4.10 4-(1-(3-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (**13**)



13
$C_{21}H_{23}BBrNO_2$
M = 412.13 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 3-bromostyrene (73.2 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **13** as colorless oil (47.8 mg, 58% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 – 7.43 (m, 2H), 7.35 – 7.19 (m, 4H), 7.11 – 7.00 (m, 2H), 4.22 (t, J = 8.3 Hz, 1H), 1.50 – 1.44 (m, 2H), 1.01 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 151.4, 147.4, 132.4, 130.9, 130.2, 129.7, 128.6, 126.4, 122.7, 119.0, 110.2, 83.6, 46.3, 24.7, 18.9 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.7 ppm. **IR** (film): 2977, 2931, 2227, 1974, 1606, 1591, 1473, 1369, 1327, 1142, 966, 846, 692 cm^{-1}. **HRMS** (ESI): calculated for $C_{21}H_{24}BBrNO_2^+$ $[M+H]^+$ 412.1078; found 412.1075.

2.4.11 (R)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3-(trifluoromethyl)phenyl) ethyl) benzonitrile (**14**)

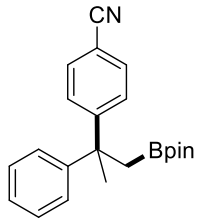


14
$C_{21}H_{23}BF_3NO_2$
M = 401.23 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 4-(Trifluoromethyl)styrene (0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **14** as colorless oil (40.1 mg, 50% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.54 (m, 2H), 7.52 (s, 1H), 7.47 – 7.42 (m, 1H), 7.41 – 7.33

(m, 4H), 4.39 (t, J = 8.3 Hz, 1H), 1.59 (dd, J = 8.4, 2.0 Hz, 2H), 1.06 (s, 12H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 151.2, 146.0, 132.4, 132.1, 131.2, 130.8 (q, J = 32 Hz), 129.1, 128.5, 128.1, 124.1 (q, J = 100 Hz), 119.0, 110.3, 83.6, 46.4, 24.6, 19.3 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.5 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.4 ppm. **IR** (film): 2967, 2908, 2197, 2008, 1945, 1600, 1372, 977, 853 cm^{-1}. **HRMS** (ESI): calculated for $[M+H]^+$ 402.1847; found 402.1859.

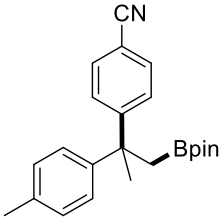
2.4.12 4-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**15**)



15
$C_{22}H_{26}BNO_2$
M = 347.26 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), α-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **15** as colorless oil (54.1 mg, 78% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 – 7.51 (m, 2H), 7.38 – 7.35 (m, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 1.81 (s, 3H), 1.75 – 1.70 (m, 2H), 1.03 (s, 12H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 157.0, 149.8, 131.7, 128.1, 128.0, 127.0, 126.1, 119.2, 109.3, 83.1, 45.0, 29.7, 26.0, 24.6 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.4 ppm. **IR** (film): 3056, 2977, 2932, 2226, 1605, 1355, 1328, 1143, 968, 846, 699 cm^{-1}. **HRMS** (ESI): calculated for $C_{22}H_{27}BNO_2^+$ $[M+H]^+$ 348.2129; found 348.2127.

2.4.13 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(p-tolyl)propan-2-yl)benzonitrile (**16**)

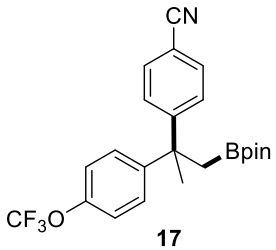


16
$C_{23}H_{28}BNO_2$
M = 361.29 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 2-(*p*-Methylphenyl)propene (52.8 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL).

Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **16** as colorless oil (52.0 mg, 72% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.48 (m, 2H), 7.36 – 7.33 (m, 2H), 7.07 (s, 4H), 2.30 (s, 3H), 1.78 (s, 3H), 1.69 (s, 1H), 1.01 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 157.1, 147.0, 135.5, 131.7, 128.8, 128.0, 126.8, 119.2, 109.2, 83.0, 44.6, 29.7, 26.1, 24.6, 20.9 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.8 ppm. **IR** (film): 2976, 2928, 2226, 1605, 1502, 1465, 1353, 1327, 1142, 968, 845, 734, 573 cm^{-1}. **HRMS** (ESI): calculated for $C_{23}H_{29}BNO_2^+$ $[M+H]^+$ 362.2286; found 362.2281.

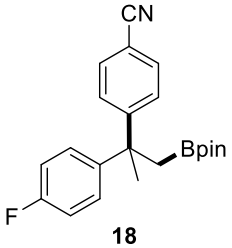
2.4.14 4-(2-(4-trifluoromethoxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**17**)



17
$C_{22}H_{25}BF_3NO_3$
M = 431.26 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 1-(1-Methylethenyl)-4-(trifluoromethoxy)benzene (40.4 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **17** as colorless oil (53.4 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 – 7.51 (m, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.10 (d, J = 8.8 Hz, 2H), 1.77 (s, 3H), 1.69 (d, J = 2.8 Hz, 2H), 1.03 – 0.94 (m, 12H).**^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): 156.4, 148.4, 147.4, 131.9, 128.5, 127.9, 121.8, 120.6, 119.1, 109.7, 83.2, 44.7, 29.8, 26.2, 24.6 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.8 ppm. **IR** (film): 2988, 2901, 1734, 1493, 1301, 992, 745 cm^{-1}. **HRMS** (ESI): calculated for $[M+H]^+$ 432.1952; found 432.1961.

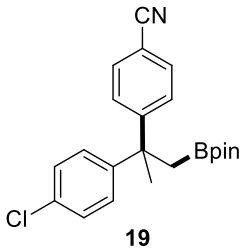
2.4.15 4-(2-(4-fluorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**18**)



18
$C_{22}H_{25}BFNO_2$
M = 365.25 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 4-fluoro-alpha-methylstyrene (54.5 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **18** as colorless oil (58.4 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.49 (m, 2H), 7.33 – 7.30 (m, 2H), 7.16 – 7.12 (m, 2H), 6.97 – 6.89 (m, 2H), 1.76 (s, 3H), 1.68 (d, J = 1.8 Hz, 2H), 1.01 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 161.2 (d, J = 245.0 Hz), 156.8, 145.5 (d, J = 3.5 Hz), 131.8, 128.6 (d, J = 8.0 Hz), 127.9, 119.1, 114.8 (d, J = 21.0 Hz), 109.5, 83.1, 44.5, 29.9, 26.3, 24.7 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.4 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.2 ppm. **IR** (film): 2977, 2933, 2227, 2026, 1605, 1508, 1355, 1329, 1232, 1143, 1060, 1015, 968, 845, 574 cm^{-1}. **HRMS** (ESI): calculated for $C_{22}H_{26}BFNO_2^+$ $[M+H]^+$ 366.2035; found 366.2028.

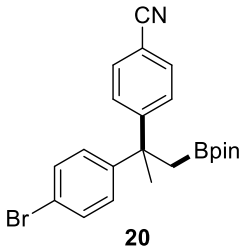
2.4.16 4-(2-(4-chlorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**19**)



19
$C_{22}H_{25}BClNO_2$
M = 381.70 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 4-chloro-alpha-methylstyrene (61.0 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **19** as colorless oil (65.6 mg, 86% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.49 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.17 (m, 2H), 7.13 – 7.09 (m, 2H), 1.76 (s, 3H), 1.67 (s, 2H), 1.01 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 156.4, 148.4, 131.9, 131.8, 128.5, 128.2, 127.9, 119.0, 109.6, 83.1, 44.7, 29.7, 26.1, 24.6 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.1 ppm. **IR** (film): 2977, 2933, 2227, 1606, 1491, 1354, 1328, 1142, 1095, 1011, 968, 845, 733 cm^{-1}. **HRMS** (ESI): calculated for $C_{22}H_{26}BClNO_2^+$ $[M+H]^+$ 382.1740; found 382.1731.

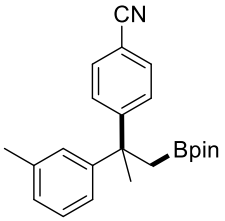
2.4.17 4-(2-(4-bromophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**20**)



20
$C_{22}H_{25}BBrNO_2$
M = 426.16 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 1-bromo-4-(prop-1-en-2-yl)benzene (78.8 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **20** as colorless oil (58.8 mg, 69% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.50 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.29 (m, 2H), 7.07 – 7.03 (m, 2H), 1.75 (s, 3H), 1.68 – 1.63 (s, 2H), 1.02 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 156.3, 148.9, 131.9, 131.2, 128.9, 128.0, 120.0, 119.1, 109.6, 83.2, 44.8, 29.6, 26.0, 24.7 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.7 ppm. **IR** (film): 1976, 2932, 2226, 1605, 1488, 1354, 1328, 1272, 1142, 1007, 968, 845, 735, 554 cm^{-1}. **HRMS** (ESI): calculated for $C_{22}H_{26}BBrNO_2^+$ $[M+H]^+$ 426.1234; found 426.1227.

2.4.18 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(m-tolyl)propan-2-yl)benzonitrile (**21**)

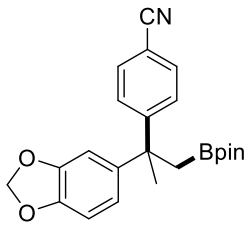


21
$C_{23}H_{28}BNO_2$
M = 361.29 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), m, alpha-dimethylstyrene (52.8 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **21** as colorless oil (52.0 mg, 72% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.49 (m, 2H), 7.36 – 7.33 (m, 2H), 7.14 (t, J = 7.6 Hz, 1H), 7.01 – 6.94 (m, 3H), 2.29 (s, 3H), 1.78 (s, 3H), 1.69 (d, J = 3.5 Hz, 2H), 1.01 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 157.0, 149.7, 137.4, 131.6, 127.9, 127.8, 127.6, 126.7, 124.1, 119.2, 109.2, 82.9, 44.8, 29.6, 25.8, 24.5, 21.6 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.7 ppm. **IR** (film): 2976,

2931, 2226, 1604, 1354, 1328, 1142, 968, 848, 706 cm^{-1}. **HRMS** (ESI): calculated for $[M+H]^+$ $C_{23}H_{29}BNO_2^+$ 362.2286; found 362.2280.

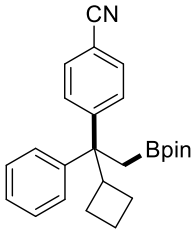
2.4.19 4-(2-(benzo[d][1,3]dioxol-5-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**22**)



22
$C_{23}H_{26}BNO_4$
M = 391.27 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 5-(prop-1-en-2-yl)benzo[d][1,3]dioxole (64.8 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **22** as colorless oil (59.4 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 – 7.49 (m, 2H), 7.36 – 7.33 (m, 2H), 6.72 – 6.66 (m, 2H), 6.63 – 6.61 (m, 1H), 5.90 (s, 2H), 1.75 (s, 3H), 1.65 (s, 2H), 1.03 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 157.0, 147.5, 145.7, 144.1, 131.8, 127.9, 119.9, 119.2, 109.4, 108.1, 107.6, 101.0, 83.1, 44.8, 29.9, 26.5, 24.7 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.4 ppm. **IR** (film): 2977, 2933, 2886, 2226, 1605, 1503, 1485, 1432, 1356, 1327, 1227, 1143, 1038, 934, 846, 730, 517 cm^{-1}. **HRMS** (ESI): calculated for $C_{23}H_{27}BNO_4^+$ $[M+H]^+$ 392.2028; found 392.2024.

2.4.20 4-(1-cyclobutyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (**24**)

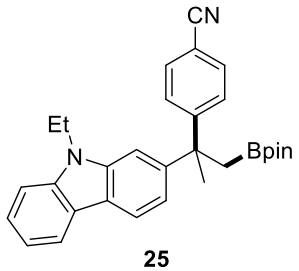


24
$C_{25}H_{30}BNO_2$
M = 387.33 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), (1-cyclobutylvinyl)benzene (63.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **24** as colorless oil (56.5

mg, 73% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 – 7.46 (m, 2H), 7.25 – 7.19 (m, 4H), 7.17 – 7.13 (m, 1H), 7.07 – 7.04 (m, 2H), 3.55 – 3.48 (m, 1H), 1.96 – 1.89 (m, 2H), 1.77 – 1.61 (m, 2H), 1.59 – 1.50 (m, 3H), 1.34 – 1.25 (m, 1H), 0.94 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 154.7, 147.2, 131.1, 129.8, 128.9, 127.6, 126.0, 119.3, 109.3, 82.9, 51.0, 42.3, 24.8, 24.6, 22.0, 17.4 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.2 ppm. **IR** (film): 3055, 2977, 2865, 2226, 2033, 1982, 1604, 1501, 1444, 1358, 1273, 1213, 1143, 967, 847, 702, 566 cm^{-1}. **HRMS** (ESI): calculated for $C_{25}H_{31}BNO_2^+$ $[M+H]^+$ 388.2442; found 399.2434.

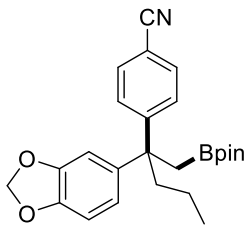
2.4.21 4-(2-(9-ethyl-9H-carbazol-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**25**)



25
$C_{30}H_{33}BN_2O_2$
M = 464.41 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 9-ethyl-2-(prop-1-en-2-yl)-9H-carbazole (94.0 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **4b** as colorless oil (63.1 mg, 68% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 – 8.05 (m, 2H), 7.78 (s, 1H), 7.55 – 7.52 (m, 2H), 7.43 – 7.39 (m, 4H), 7.23 – 7.17 (m, 2H), 4.34 (d, J = 7.2 Hz, 2H), 1.93 (s, 3H), 1.85 (d, J = 9.6 Hz, 2H), 1.42 (d, J = 7.2 Hz, 3H), 0.99 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 158.0, 140.5, 138.3, 132.8, 131.7, 128.1, 125.8, 125.6, 123.1, 122.4, 120.3, 119.4, 118.8, 118.1, 109.1, 108.6, 108.3, 83.0, 45.0, 37.6, 30.3, 27.0, 24.7, 13.9 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.0 ppm. **IR** (film): 3049, 2976, 2933, 2226, 2158, 2033, 1982, 1604, 1490, 1355, 1330, 1234, 1143, 846, 748 cm^{-1}. **HRMS** (ESI): calculated for $C_{30}H_{33}BNaN_2O_2^+$ $[M+Na]^+$ 487.2527; found 487.2526.

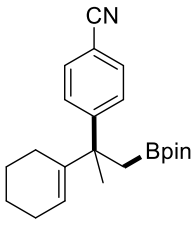
2.4.22 4-(2-(benzo[d][1,3]dioxol-5-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)benzonitrile (**26**)



26
$C_{25}H_{30}BNO_4$
M = 419.32 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 5-(pent-1-en-2-yl)benzo[d][1,3]dioxole (76.0 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **26** as colorless oil (41.9 mg, 50% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 – 7.49 (m, 2H), 7.32 (d, J = 8.5 Hz, 2H), 6.77 – 6.61 (m, 2H), 6.60 – 6.53 (m, 1H), 5.91 – 5.88 (m, 2H), 2.24 – 2.11 (m, 2H), 1.65 – 1.59 (m, 3H), 1.03 (s, 12H), 0.92 – 0.81 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 156.3, 147.4, 145.6, 143.1, 131.6, 128.6, 120.6, 119.3, 109.2, 108.6, 107.5, 100.9, 83.0, 48.2, 42.2, 24.7, 23.0, 17.8, 14.8 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.4 ppm. **IR** (film): 2976, 2958, 2872, 2248, 2167, 1973, 1940, 1605. 1487, 1433, 1360, 1235, 1144, 1039, 934. 847 cm^{-1}. **HRMS** (ESI): calculated for $C_{25}H_{31}BNO_4^+$ $[M+H]^+$ 420.2341; found 420.2339.

2.4.23 4-(2-(cyclohex-1-en-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**27**)

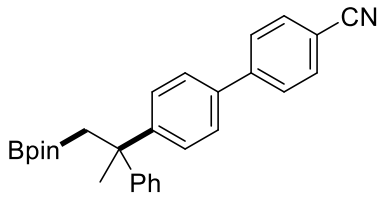


27
$C_{22}H_{30}BNO_2$
M = 351.29 g/mol

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), 1-(prop-1-en-2-yl)cyclohex-1-ene (48.8 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **27** as colorless oil (35.1 mg, 50% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.50 (m, 2H), 7.42 – 7.36 (m, 2H), 5.75 – 5.70 (m,

1H), 2.15 – 2.05 (m, 2H), 1.64 – 1.51 (m, 4H), 1.46 (s, 3H), 1.41 – 1.32 (m, 2H), 1.30 – 1.21 (m, 2H), 1.15 (s, 12H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 156.2, 143.4, 131.8, 127.3, 121.0, 119.4, 109.2, 83.0, 46.0, 27.6, 25.8, 25.6, 25.0, 24.8, 23.2, 22.5 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 36.2 ppm. **IR** (film): 3402, 2977, 2930, 2227, 1670, 1605, 1501, 1448, 1351, 1327, 1142, 968, 731 cm^{-1}. **HRMS** (ESI): calculated for $C_{25}H_{31}BNO_2^+$ $[M+H]^+$ 352.2442; found 352.2442.

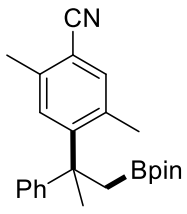
2.4.24 4-(2-(cyclohex-1-en-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**33**)



33
$C_{28}H_{30}BNO_2$
M = 423.36 g/mol

Prepared according to general procedure from 4,4′ -Biphenyldicarbonitrile (40.8 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), α-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **33** as colorless oil (50.8 mg, 60% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): 7.69 (t, J = 8.2 Hz, 4H), 7.49 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.29 – 7.26 (m, 4H), 7.17 (dq, J = 5.2, 2.8 Hz, 1H), 1.85 (s, 3H), 1.77 (s, 2H), 1.02 (s, 12H). **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 152.3, 150.7, 145.5, 136.1, 132.6, 128.0, 127.9, 127.5, 127.1, 126.7, 125.7, 119.1, 110.5, 82.9, 44.4, 29.9, 26.2, 24.6 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.9 ppm. **IR** (film): 3023, 2959, 2243, 1598, 1347, 1138, 869, 753 cm^{-1}. **HRMS** (ESI): calculated for $C_{28}H_{31}BNO_2^+$ $[M+H]^+$ 424.2442; found 424.2454.

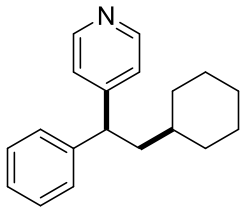
2.4.25 4-(2-(cyclohex-1-en-1-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)benzonitrile (**34**)



34
$C_{24}H_{30}BNO_2$
M = 375.31 g/mol

Prepared according to general procedure from 2,5-DiMethylterephthalonitrile (31.2 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (76.2 mg, 0.3 mmol, 1.5 equiv.), α-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **34** as colorless oil (33.8 mg, 45% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 1H), 7.36 – 7.30 (m, 3H), 7.25 – 7.16 (m, 3H), 2.64 (s, 3H), 2.02 – 1.92 (m, 1H), 1.85 (d, J = 6.5 Hz, 6H), 1.71 (d, J = 14.8 Hz, 1H), 1.08 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 150.8, 138.4, 136.0, 135.8, 129.4, 128.4, 125.8, 125.7, 118.7, 110.2, 82.9, 76.8, 45.4, 31.8, 24.7, 24.7, 21.2, 20.3 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.8 ppm. **HRMS** (ESI): calculated for $C_{24}H_{31}BNO_2^+$ $[M+H]^+$ 376.2442; found 376.2438.

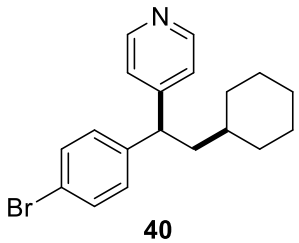
2.4.26 4-(2-cyclohexyl-1-phenylethyl)pyridine (**39**)



39
$C_{19}H_{23}N$
M = 265.40

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), styrene (41.7 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **39** as colorless oil (27 mg, 51% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.44 (d, J = 5.1 Hz, 2H), 7.30 – 7.22 (m, 2H), 7.21 – 7.13 (m, 3H), 7.12 – 7.06 (m, 2H), 3.99 (t, J = 7.9 Hz, 1H), 1.90 – 1.83 (m, 2H), 1.75 – 1.67 (m, 2H), 1.64 – 1.53 (m, 3H), 1.13 – 1.02 (m, 4H), 0.95 – 0.86 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 154.5, 149.8, 143.5, 128.7, 128.0, 126.7, 123.4, 47.6, 42.9, 34.9, 33.5, 33.3, 26.6, 26.2, 26.1 ppm. **IR** (film): 3063, 3025, 2919, 2849, 1594, 1493, 1448, 1413, 1070, 993, 812, 698, 574 cm^{-1}. **HRMS** (ESI): calculated for $C_{19}H_{24}N^+$ $[M+H]^+$ 266.1903; found 266.1898.

2.4.27 4-(1-(4-bromophenyl)-2-cyclohexylethyl)pyridine (**40**)



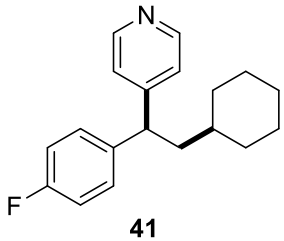
40

$C_{19}H_{22}NBr$

M = 344.29

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), 4-bromostyrene (73.2 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 5:1) to afford **40** as colorless oil (34.4 mg, 50% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.56 – 8.40 (s, 2H), 7.43 – 7.38 (m, 2H), 7.14 – 7.04 (m, 4H), 3.99 (t, J = 8.0 Hz, 1H), 1.90 – 1.83 (m, 2H), 1.80 – 1.69 (m, 2H), 1.68 – 1.59 (m, 3H), 1.15 – 1.05 (m, 4H), 0.97 – 0.88 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 153.9, 149.9, 142.4, 131.8, 129.7, 123.3, 120.5, 47.0, 42.7, 34.8, 33.5, 33.2, 26.5, 26.1, 26.1 ppm. **IR** (film): 3023, 2920, 2849, 1596, 1557, 1486, 1447, 1414, 1072, 1009, 810 cm^{-1}. **HRMS** (ESI): calculated for $C_{19}H_{23}BrN^+$ $[M+H]^+$ 344.1008; found 344.1008.

2.4.28 4-(2-cyclohexyl-1-(4-fluorophenyl)ethyl)pyridine (**41**)



41

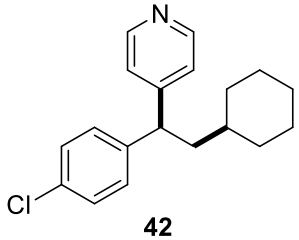
$C_{19}H_{22}NF$

M = 283.39

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), 4-fluorostyrene (48.8 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 5:1) to afford **41** as colorless oil (25.5 mg, 45% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (d, J = 5.1 Hz, 2H), 7.21 – 7.08 (m, 4H), 7.03 – 6.94 (m, 2H), 4.02 (t, J = 8.0 Hz, 1H), 1.91 – 1.84 (m, 2H), 1.75 – 1.59 (m, 5H), 1.17 – 1.04 (m, 4H), 0.99 – 0.90 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 161.6 (d, J = 245.2 Hz), 154.3, 149.9, 139.1, 129.4 (d, J = 7.9 Hz), 123.2, 115.5 (d, J = 21.3 Hz), 46.8, 43.0, 34.9, 33.5, 33.2, 26.6, 26.1, 26.1

ppm. **^{19}F NMR** (376 MHz, Chloroform-d) δ -116.3 ppm. **IR** (film): 3024, 2921, 2850, 2172, 2034, 2022, 1595, 1507, 1448, 1413, 1223, 1158, 818 cm^{-1}. **HRMS** (ESI): calculated for $C_{19}H_{23}FN^+$ $[M+H]^+$ 284.1809; found 284.1804.

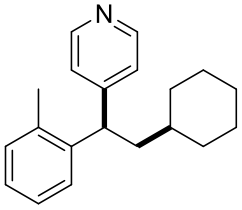
2.4.29 4-(1-(4-chlorophenyl)-2-cyclohexylethyl)pyridine (**42**)



42
$C_{19}H_{22}NCl$
M = 299.84

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), 4-chlorostyrene (55.4 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 5:1) to afford **42** as colorless oil (25.1 mg, 42% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.55 – 8.41 (m, 2H), 7.29 – 7.24 (m, 2H), 7.15 – 7.09 (m, 4H), 4.01 (t, J = 8.0 Hz, 1H), 1.91 – 1.83 (m, 2H), 1.76 – 1.61 (m, 5H), 1.14 – 1.06 (m, 4H), 0.98 – 0.90 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 153.9, 149.9, 141.9, 132.5, 129.3, 128.9, 123.3, 46.9, 42.8, 34.9, 33.5, 33.2, 26.6, 26.1, 26.1 ppm. **IR** (film): 3025, 2921, 2850, 2160, 2027, 1597, 1489, 1448, 1413, 1093, 1013, 811 cm^{-1}. **HRMS** (ESI): calculated for $C_{19}H_{22}ClN^+$ $[M+H]^+$ 300.1514; found 300.1512.

2.4.30 4-(2-cyclohexyl-1-(o-tolyl)ethyl)pyridine (**43**)

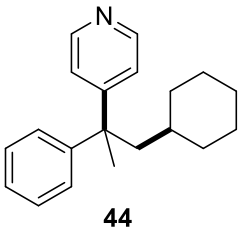


43
$C_{20}H_{25}N$
M = 279.42

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), 2-methylstyrene (47.2 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **43** as colorless oil

(24.5 mg, 44% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.46 (d, J = 5.1 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.23 – 7.17 (m, 1H), 7.16 – 7.06 (m, 4H), 4.25 (t, J = 7.8 Hz, 1H), 2.26 (s, 3H), 1.92 – 1.78 (m, 3H), 1.71 – 1.59 (m, 4H), 1.22 – 1.09 (m, 4H), 1.00 – 0.90 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 154.3, 149.7, 141.1, 136.2, 130.8, 126.9, 126.6, 126.3, 123.7, 43.4, 43.1, 35.0, 33.6, 33.5, 26.6, 26.2, 26.1, 19.9 ppm. **IR** (film): 3019, 2920, 2850, 1593, 1556, 1489, 1448, 1413, 818, 747, 585 cm^{-1}. **HRMS** (ESI): calculated for $C_{20}H_{26}N^+$ $[M+H]^+$ 280.2060; found 280.2054.

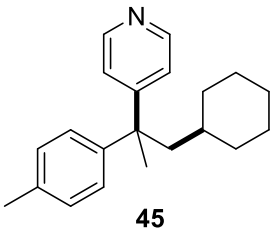
2.4.31 4-(1-cyclohexyl-2-phenylpropan-2-yl)pyridine (**44**)



44
$C_{20}H_{25}N$
M = 279.42

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), 2-phenyl-1-propene (47.2 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **44** as colorless oil (30.7 mg, 55% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.44 (d, J = 5.3 Hz, 2H), 7.31 – 7.19 (m, 2H), 7.18 – 7.04 (m, 5H), 1.98 (t, J = 4.4 Hz, 2H), 1.61 (s, 3H), 1.56 – 1.47 (m, 3H), 1.36 – 1.27 (m, 2H), 1.18 – 1.09 (m, 1H), 1.07 – 0.98 (m, 3H), 0.93 – 0.83 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 159.4, 149.5, 148.2, 128.1, 127.4, 126.2, 122.9, 48.2, 46.6, 35.7, 35.6, 34.1, 27.4, 26.5, 26.5, 26.2 ppm. **IR** (film): 3024, 2920, 2849, 1593, 1549, 1495, 1410, 1377, 821, 763, 700 cm^{-1}. **HRMS** (ESI): calculated for $C_{20}H_{26}N^+$ $[M+H]^+$ 280.2060; found 280.2055.

2.4.32 4-(1-cyclohexyl-2-(p-tolyl)propan-2-yl)pyridine (**45**)

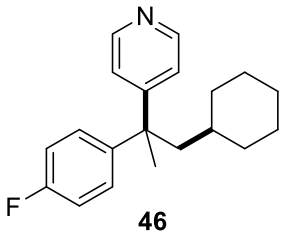


45
$C_{20}H_{27}N$
M = 293.45

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), 2-(p-Methylphenyl)propene (52.8

mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **45** as colorless oil (25.2 mg, 43% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.45 (d, J = 4.9 Hz, 2H), 7.13 – 7.10 (m, 2H), 7.09 – 7.02 (m, 4H), 2.31 (s, 3H), 2.00 – 1.95 (m, 2H), 1.62 (s, 3H), 1.56 – 1.50 (m, 3H), 1.39 – 1.32 (m, 2H), 1.17 – 1.01 (m, 4H), 0.94 – 0.85 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 13C NMR (101 MHz, Chloroform-d) δ 159.6, 149.4, 145.3, 135.7, 128.9, 127.3, 122.9, 48.3, 46.3, 35.7, 35.6, 34.1, 27.4, 26.6, 26.5, 26.2, 21.0 ppm. **IR** (film): 3021, 2920, 2849, 1592, 1512, 1447, 1409, 1376, 994, 816 cm^{-1}. **HRMS** (ESI): calculated for $C_{21}H_{28}N^+$ $[M+H]^+$ 294.2216; found 294.2210.

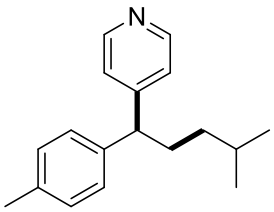
2.4.33 4-(1-cyclohexyl-2-(4-fluorophenyl)propan-2-yl)pyridine (**46**)



46
$C_{20}H_{24}NF$
M = 297.41

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), 1-fluoro-4-(1-methylethenyl)benzene (54.4 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **46** as colorless oil (27.9 mg, 47% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (d, J = 5.4 Hz, 2H), 7.13 – 7.08 (m, 4H), 7.01 – 6.90 (m, 2H), 1.98 – 1.95 (m, 2H), 1.62 (s, 3H), 1.56 – 1.50 (m, 3H), 1.40 – 1.26 (m, 3H), 1.08 – 1.00 (m, 3H), 0.93 – 0.83 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 161.2 (d, J = 245.6 Hz), 159.4, 149.4, 143.8, 129.0 (d, J = 7.7 Hz), 122.8, 114.9 (d, J = 20.9 Hz), 48.4, 46.3, 35.7, 35.6, 34.1, 27.6, 26.5, 26.5, 26.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.98 ppm. **IR** (film): 3024, 2921, 2850, 2033, 2005, 1981, 1964, 1594, 1508, 1448, 1409, 1233, 1163, 832, 818 cm^{-1}. **HRMS** (ESI): calculated for $C_{20}H_{25}FN^+$ $[M+H]^+$ 298.1966; found 298.1960.

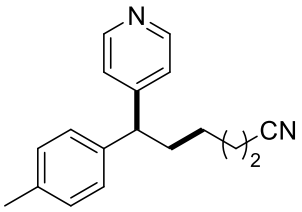
2.4.34 4-(4-methyl-1-(p-tolyl)pentyl)pyridine (**47**)



47
$C_{18}H_{23}N$
M = 253.38

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), Isobutylboronic acid pinacol ester (55.2 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **47** as colorless oil (20.3 mg, 40% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (d, J = 2.8 Hz, 2H), 7.17 – 7.13 (m, 2H), 7.10 (s, 4H), 3.78 (t, J = 7.8 Hz, 1H), 2.31 (s, 3H), 2.04 – 1.98 (m, 2H), 1.60 – 1.50 (m, 1H), 1.17 – 1.10 (m, 2H), 0.87 (s, 3H), 0.85 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 154.7, 149.8, 140.5, 136.3, 129.4, 127.8, 123.3, 50.8, 37.1, 33.0, 28.1, 22.6, 22.6, 21.1 ppm. **IR** (film): 3020, 2952, 2927, 2868, 1594, 1912, 1466, 1412, 1384, 1219, 1070, 993, 813, 570 cm^{-1}. **HRMS** (ESI): calculated for $C_{18}H_{24}N^+$ $[M+H]^+$ 254.1903; found 254.1899.

2.4.35 6-(pyridin-4-yl)-6-(p-tolyl)hexanenitrile (**48**)

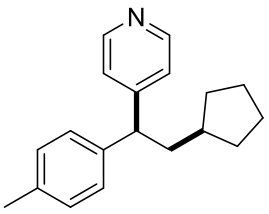


48
$C_{18}H_{20}N_2$
M = 264.37

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), 3-cyano-1-propylboronic acid pinacol ester (58.5 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **48** as colorless oil (26.4 mg, 50% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (d, J = 5.0 Hz, 2H), 7.16 (d, J = 6.1 Hz, 2H), 3.84 (t, J = 7.8 Hz, 1H), 2.32 – 2.28 (m, 5H), 2.09 – 2.02 (m, 2H), 1.72 – 1.64 (m, 2H), 1.46 – 1.37 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 154.2, 149.7, 139.5, 136.7, 129.6, 127.7, 123.2, 119.5,

50.3, 34.2, 27.1, 25.4, 21.1, 17.1 ppm. **IR** (film): 3021, 2930, 2863, 2246, 2179, 2034, 1595, 1557, 1512, 1413, 808 cm^{-1}. **HRMS** (ESI): calculated for $C_{18}H_{21}N_2^+$ $[M+H]^+$ 265.1699; found 265.1694.

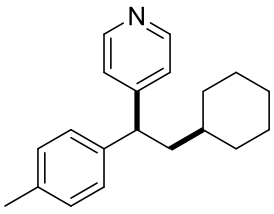
2.4.36 4-(2-cyclopentyl-1-(p-tolyl)ethyl)pyridine (**49**)



49
$C_{19}H_{23}N$
M = 265.40

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclopentylboronic acid pinacol ester (58.8 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **49** as colorless oil (23.8 mg, 45% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.46 (d, J = 5.4 Hz, 2H), 7.16 (d, J = 6.1 Hz, 2H), 7.11 (s, 4H), 3.89 (t, J = 7.9 Hz, 1H), 2.31 (s, 3H), 2.08 – 1.96 (m, 2H), 1.78 – 1.70 (m, 2H), 1.64 – 1.56 (m, 3H), 1.49 – 1.39 (m, 2H), 1.18 – 1.10 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 154.8, 149.7, 140.4, 136.3, 129.4, 127.8, 123.3, 49.5, 41.7, 37.7, 32.8, 32.6, 25.2, 25.2, 21.1 ppm. **IR** (film): 3020, 2945, 2862, 1594, 1557, 1511, 1450, 1412, 807 cm^{-1}. **HRMS** (ESI): calculated for $C_{19}H_{24}N^+$ $[M+H]^+$ 266.1903; found 266.1898.

2.4.37 4-(2-cyclohexyl-1-(p-tolyl)ethyl)pyridine (**50**)

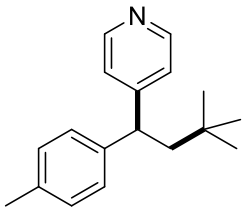


50
$C_{20}H_{25}N$
M = 279.42

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **50** as colorless oil (36.3 mg, 65% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (d, J = 5.3 Hz, 2H), 7.14 (d, J = 6.1 Hz, 2H),

7.10 (s, 4H), 4.00 (t, J = 7.9 Hz, 1H), 2.31 (s, 3H), 1.96 – 1.87 (m, 2H), 1.79 – 1.71 (m, 2H), 1.67 – 1.59 (m, 3H), 1.18 – 1.03 (m, 4H), 0.98 – 0.89 (m, 2H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 154.8, 149.8, 140.5, 136.2, 129.4, 127.8, 123.3, 47.2, 42.9, 34.9, 33.5, 33.3, 26.6, 26.2, 26.1, 21.1 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ ppm. **IR** (film): 3020, 2919, 2850, 1594, 1557, 1511, 1492, 1412, 810 cm^{-1}. **HRMS** (ESI): calculated for $C_{20}H_{26}N^+$ $[M+H]^+$ 280.2060; found 280.2056.

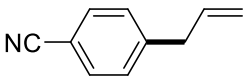
2.4.38 4-(3,3-dimethyl-1-(p-tolyl)butyl)pyridinetert-Butylboronic acid pinacol ester (**51**)



51
$C_{18}H_{23}N$
M = 253.38

Prepared according to general procedure from 4-cyanopyridine (20.8 mg, 0.2 mmol, 1.0 equiv.), tert-Butylboronic acid pinacol ester (55.2 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene (47.3 mg, 0.4 mmol, 2.0 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **51** as colorless oil (27.8 mg, 55% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.50 – 8.42 (m, 2H), 7.23 – 7.18 (m, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 3.98 (t, J = 6.6 Hz, 1H), 2.29 (s, 3H), 2.07 (dd, J = 6.6, 3.9 Hz, 2H), 0.84 (s, 9H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 156.0, 149.8, 141.9, 136.1, 129.4, 127.7, 123.2, 48.9, 47.5, 31.6, 30.2, 21.0 ppm. **^{11}B NMR** (128 MHz, $CDCl_3$) δ ppm. **IR** (film): 3019, 2952, 2864, 1593, 1557, 1511, 1474, 1413, 1364, 805, 620 cm^{-1}. **HRMS** (ESI): calculated for $C_{18}H_{24}N^+$ $[M+H]^+$ 254.1903; found 254.1899.

2.4.39 4-allylbenzonitrile (**53**)

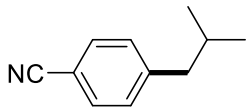


53
$C_{10}H_9N$
M = 143.18

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), Allylboronic acid pinacol ester (50.4 mg, 0.3 mmol, 1.5 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **53** as colorless oil (18.3 mg, 64% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 – 7.52 (m, 2H), 7.31 – 7.27 (m, 2H), 5.98 – 5.86 (m, 1H), 5.16 – 5.08 (m, 2H), 3.46 –

3.43 (m, 2H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 145.7, 135.7, 132.3, 129.5, 119.1, 117.3, 110.1, 40.2 ppm. **IR** (film): 2918, 2227, 1638, 1606, 1503, 1414, 1176, 918, 550 cm^{-1}. **HRMS** (ESI): calculated for $C_{10}H_{13}N_2^+$ $[M+NH_4]^+$ 161.1073; found 161.1070.

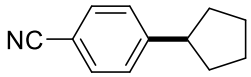
2.4.40 4-isobutylbenzonitrile (**54**)



54
$C_{11}H_{13}N$
M = 159.23

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), Isobutylboronic acid pinacol ester (55.2 mg, 0.3 mmol, 1.5 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **54** as colorless oil (14.3 mg, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.53 (m, 2H), 7.26 – 7.23 (m, 2H), 2.56 – 2.49 (m, 2H), 1.92 – 1.83 (m, 1H), 0.90 (s, 6H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 147.5, 132.0, 129.9, 119.3, 109.7, 45.6, 30.1, 22.3 ppm. **IR** (film): 3036, 2957, 2927, 2227, 2022, 1687, 1607, 1505, 1465, 1385, 1117, 851, 559 cm^{-1}. **HRMS** (ESI): calculated for $C_{11}H_{14}N^+$ $[M+H]^+$ 161.1121; found 160.1119. All recorded spectroscopic data were in line with those previously reported values in the literature.

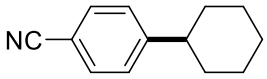
2.4.41 4-cyclopentylbenzonitrile (**55**)



55
$C_{12}H_{13}N$
M = 171.24

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), cyclopentylboronic acid pinacol ester (58.8 mg, 0.3 mmol, 1.5 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **55** as colorless oil (17.1 mg, 50% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.53 (m, 2H), 7.34 – 7.31 (m, 2H), 3.09 – 2.98 (m, 1H), 2.13 – 2.05 (m, 2H), 1.87 – 1.78 (m, 2H), 1.76 – 1.69 (m, 2H), 1.63 – 1.56 (m, 2H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 152.4, 132.2, 128.0, 119.3, 109.5, 46.1, 34.5, 25.6 ppm. **IR** (film): 2905, 2867, 2226, 2197, 2153, 2034, 1983, 1606, 1430, 830, 520 cm^{-1}. **HRMS** (ESI): calculated for $C_{12}H_{14}N^+$ $[M+H]^+$ 172.1121; found 172.1119.

2.4.42 4-cyclohexylbenzonitrile (**56**)



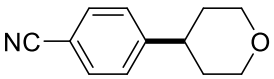
56

$C_{13}H_{15}N$

M = 185.27

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), cyclohexylboronic acid pinacol ester (63.0 mg, 0.3 mmol, 1.5 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **56** as colorless oil (21.4 mg, 58% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 – 7.53 (m, 2H), 7.31 – 7.28 (m, 2H), 2.60 – 2.50 (m, 1H), 1.92 – 1.81 (m, 4H), 1.43 – 1.37 (m, 4H), 1.35 – 1.20 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 153.6, 132.3, 127.8, 119.3, 109.6, 44.8, 34.1, 26.7, 26.0 ppm. **IR** (film): 2924, 2851, 2226, 2006, 1606, 1504, 1448, 827, 564 cm^{-1}. **HRMS** (ESI): calculated for $C_{13}H_{16}N^+$ $[M+H]^+$ 182.1277; found 182.1276.

2.4.43 4-(tetrahydro-2H-pyran-4-yl)benzonitrile (**57**)



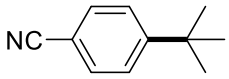
57

$C_{12}H_{13}NO$

M = 187.24

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), tetrahydropyran-4-boronic acid pinacol ester (63.6 mg, 0.3 mmol, 1.5 equiv.), and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **57** as colorless oil (20.2 mg, 54% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 – 7.57 (m, 2H), 7.34 – 7.31 (m, 2H), 4.12 – 4.07 (m, 2H), 3.56 – 3.47 (m, 2H), 2.85 – 2.78 (m, 1H), 1.83 – 1.73 (m, 4H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 151.2, 132.5, 127.7, 119.0, 110.3, 68.1, 41.8, 33.5 ppm. **IR** (film): 2938, 2844, 2226, 2179, 2022, 2006, 1992, 1607, 1505, 1416, 1386, 1238, 1124, 1099, 1018, 894, 838, 561 cm^{-1}. **HRMS** (ESI): calculated for $C_{12}H_{14}NO^+$ $[M+H]^+$ 188.1070; found 188.1069.

2.4.44 4-(tert-butyl)benzonitrile (**58**)



58

$C_{11}H_{13}N$

M = 159.23

Prepared according to general procedure from 1.4-dicyanobenzene (25.6 mg, 0.2 mmol, 1.0 equiv.), tert-Butylboronic acid pinacol ester (55.2 mg, 0.3 mmol, 1.5 equiv.], and KOMe (21 mg, 0.3 mmol, 1.5 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous THF (1 mL). Purification by preparative TLC (petroleum ether/ethyl acetate = 20:1) to afford **60** as colorless oil (15.9 mg, 50% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 2H), 7.50 – 7.46 (m, 2H), 1.33 (s, 9H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 156.7, 132.1, 126.3, 119.2, 109.4, 35.4, 31.0 ppm. **IR** (film): 3020, 2952, 2865, 2179, 2033, 1593, 1511, 1413, 1365, 1244, 1112, 993, 817, 619 cm^{-1}. **HRMS** (ESI): calculated for $C_{11}H_{17}N_2^+$ $[M+H]^+$ 177.1386; found 177.1382.

3. Computational Investigations

3.1 Computational Details

All calculations were performed with the Gaussian 16 package.[1] Geometry optimizations and frequencies calculations were performed at the B3LYP-D3[2] level of theory. The def2sVP basis set is employed for the Iridium atom,[3] and the 6-31+G(2d,p) basis set is used for all the other atoms. Intrinsic reaction coordinate calculations are performed to confirm that each transition state connects with the desired reactants and products.[4] To obtain more accurate energies, single-point energy calculations were done with the M06-2X functional.[5] The def2TZVPP basis set is employed for the Iridium atom, and the 6-311+G(3df,2p) basis set is used for all the other atoms in conjugation with the polarizable continuum model (SMD) solvation model for tetrahydrofuran.[6] The 3D structures of the optimized species were generated using CYLview.[7] Activation free energy barriers here are defined as the free energy difference between the transition state and the lowest-energy stationary point before it along the reaction pathways.

3.2 Macus theory calculations

The barrier heights of single electron transfer steps were calcualted by using Marcus-Hush theory.[8] The free energy barrier of a single electron transfer process of outer-sphere electron transfer can be applied according to the following equation:

$$\Delta G_{ET}^{\dagger} = \frac{(\Delta G_r + \lambda)^2}{4\lambda}$$

Where ΔG_r is the Gibbs free energy change of the studied single electron transfer step, λ is the reorganization energy which includes two components, inner reorganization energy (λ_i) and outer reorganization energy (λ_0). The outer-sphere electron transfer model is applicable and the activation barrier may be estimated from the outer-sphere Marcus-Hush model. Since the inner reorganization energies are usually small and could be neglected. Thus, the total reorganization energy $\lambda \approx \lambda_0$.

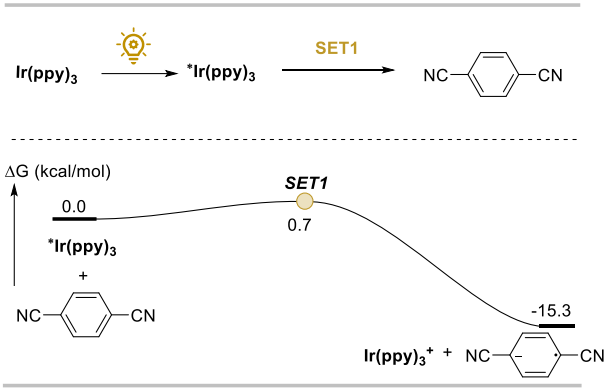
$$\lambda = \lambda_o = 332(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R})(\frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon})$$

Where, a_1 and a_2 are the radii of donor and acceptor, R is the sum of a_1 and a_2, ε_{opt} and ε is the optical dielectric constant and static dielectric constant of solvent respectively (for tetrahydrofuran ε_{opt} = 1.97, ε = 7.43). a_1 and a_2 are calculated by using Multiwfn package.[9]

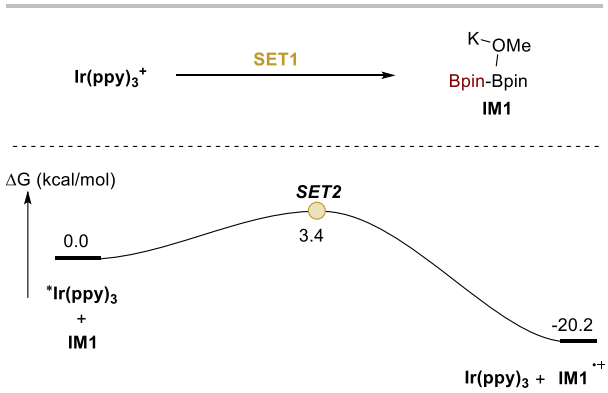
Table S2. Calculated free energy barriers ($\Delta G_{ET}^{\dagger}$, kcal/mol) of single electron transfer steps and their relevant parameters.

entry	a_1 (Å)	a_2 (Å)	R (Å)	λ	ΔG_r	$\Delta G_{ET}^{\dagger}$
SET1	7.16	5.54	12.70	10.04	-15.3	0.7
SET2	6.20	7.65	13.85	9.10	-20.2	3.4

3.3 Single electron transfer from the excited state of $Ir(ppy)_3$ to 1,4-dicyanobenzene (SET1)



3.4 Single electron transfer from **IM1** to $Ir(ppy)_3^+$ (**SET2**)



3.5 Computational reaction mechanism of the Bpin radical, and styrene and 1,4-dicyanobenzene radical anion

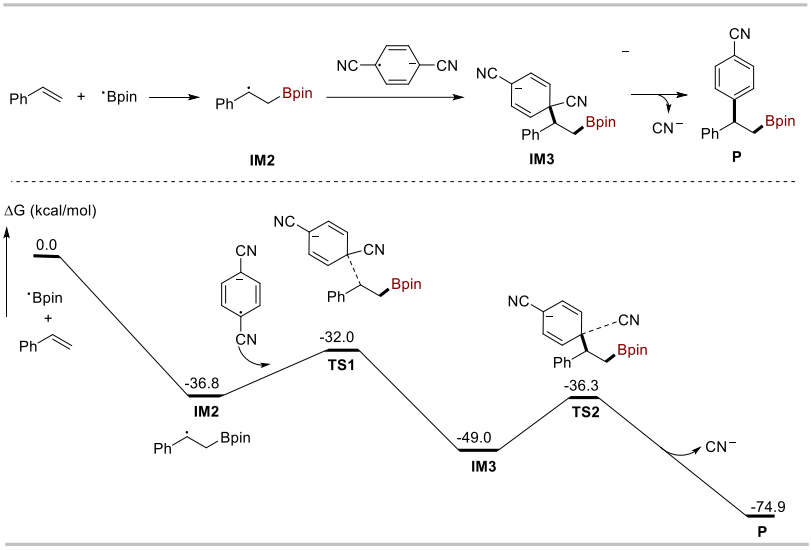
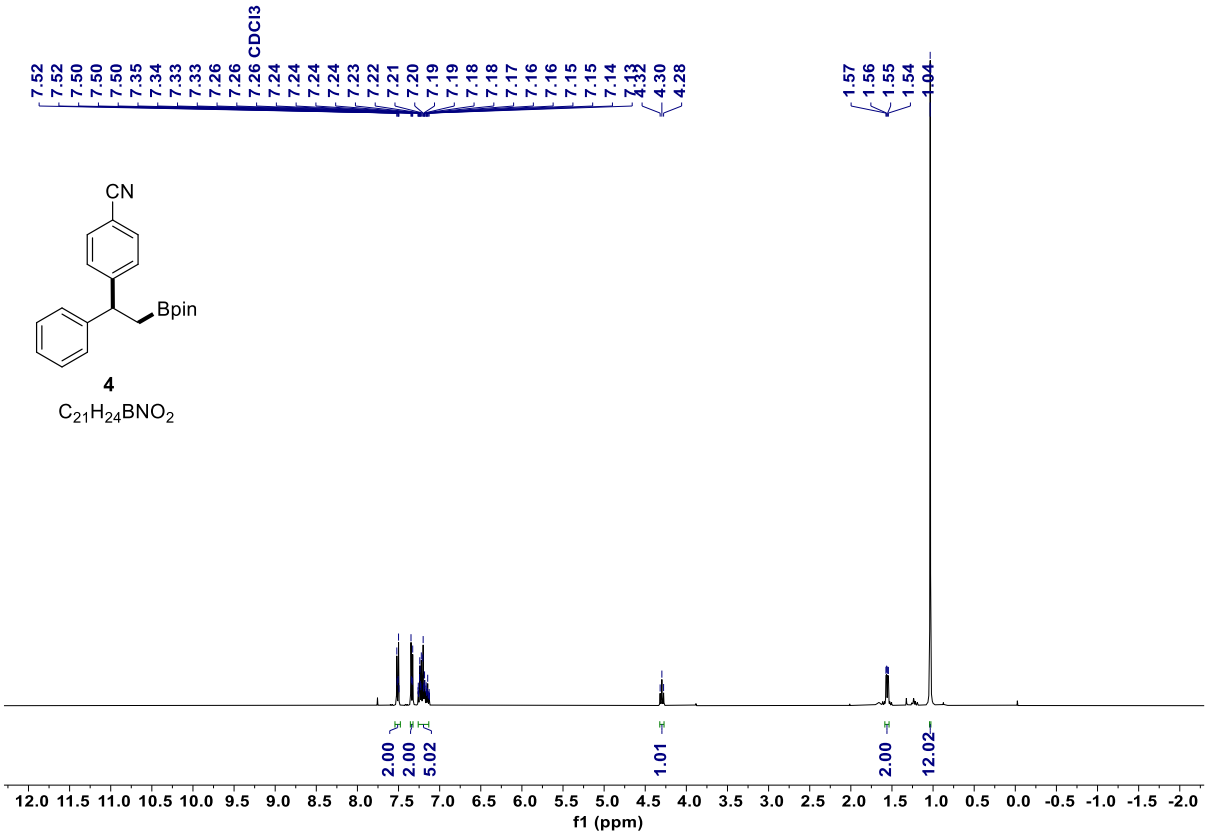
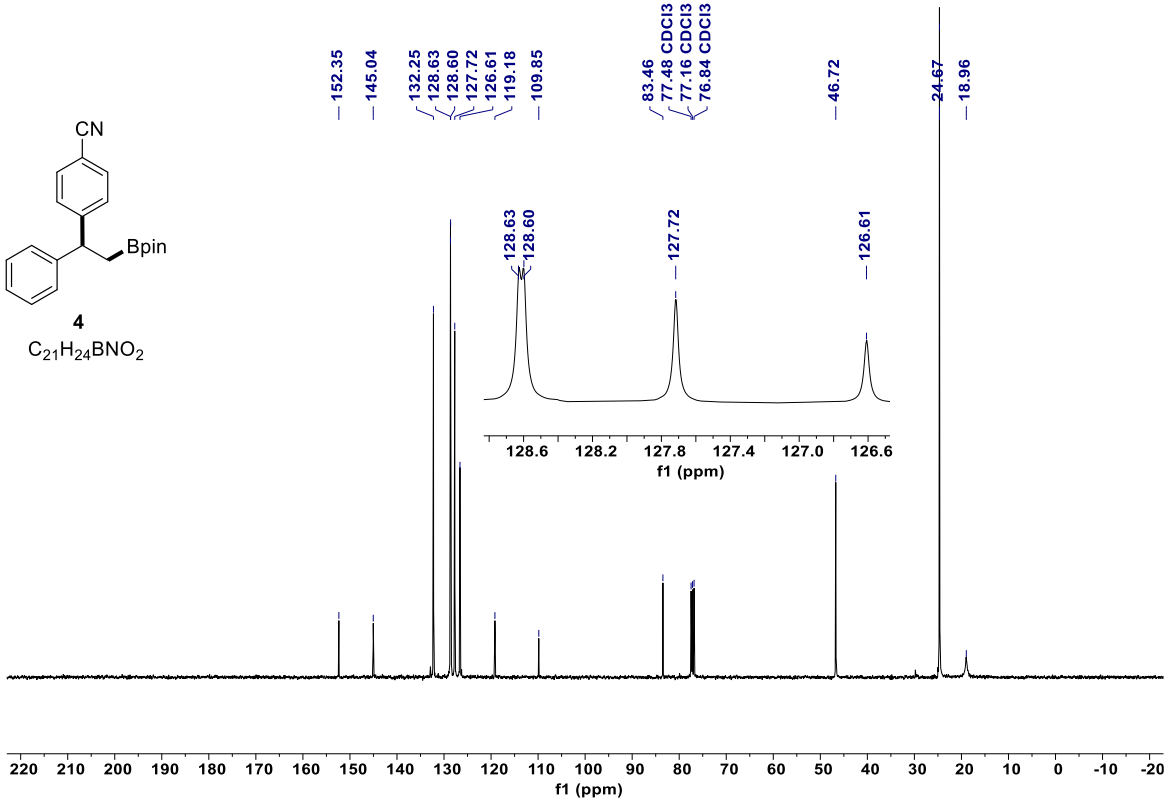


Figure S1. calculated Gibbs energy profile for the reaction mechanism of the Bpin radical, and styrene and 1,4-dicyanobenzene radical anion.

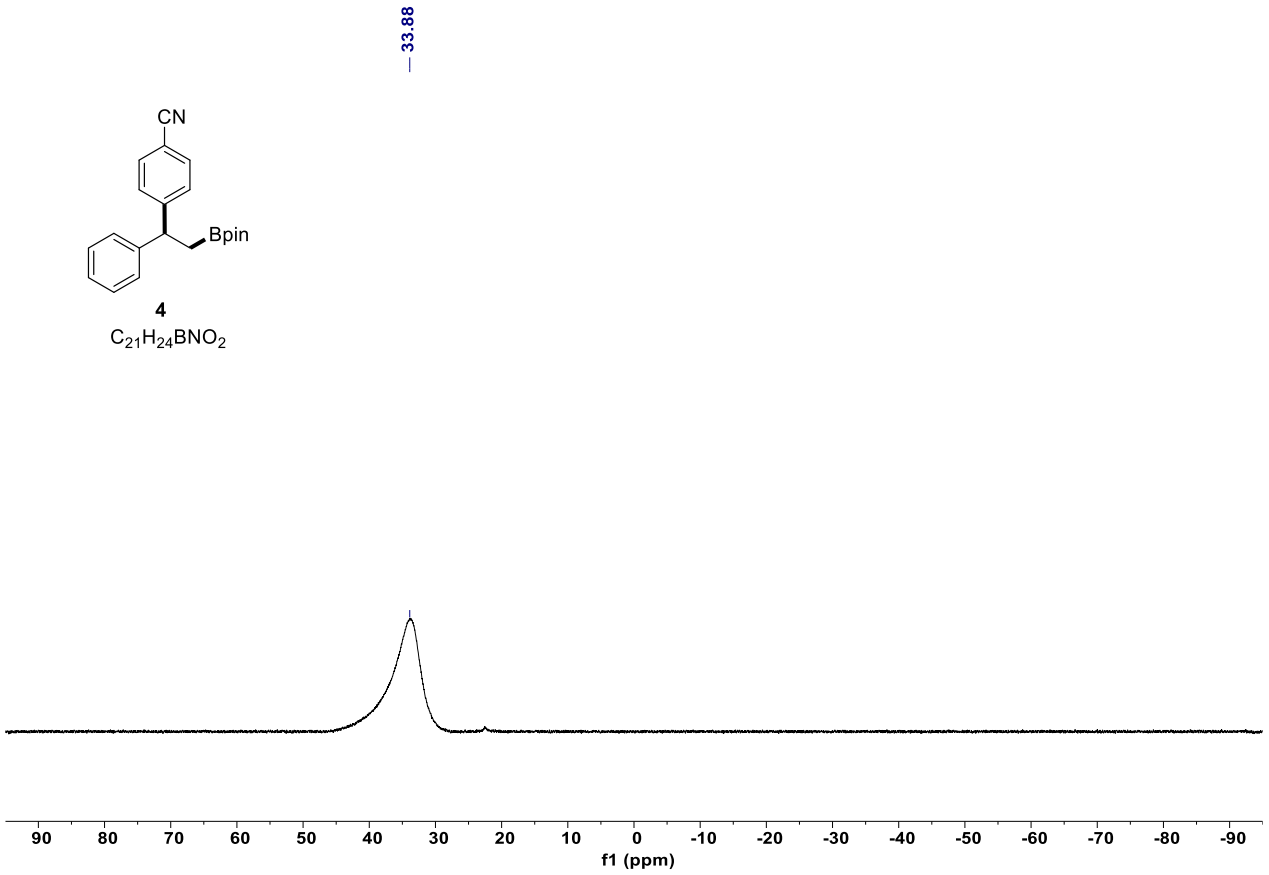
4. NMR Spectra



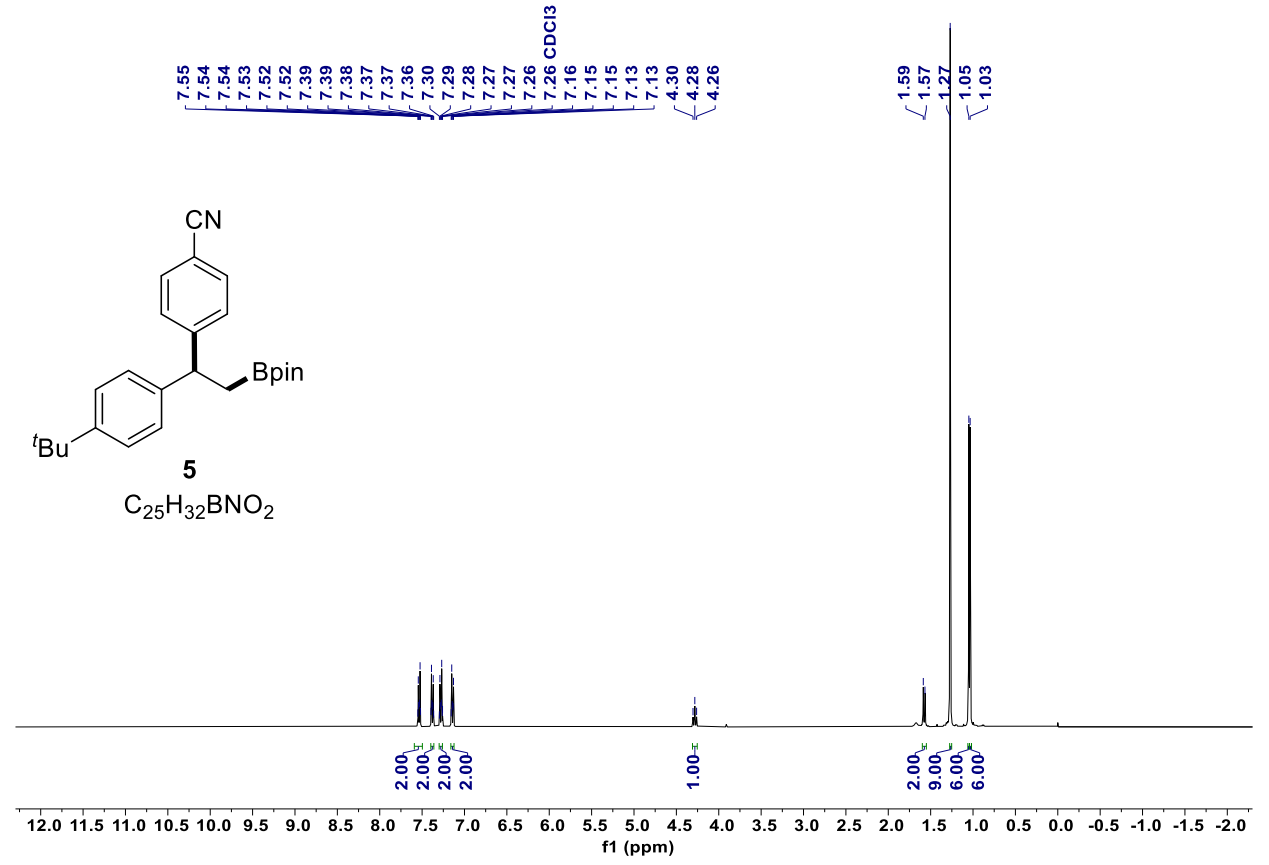
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4**.



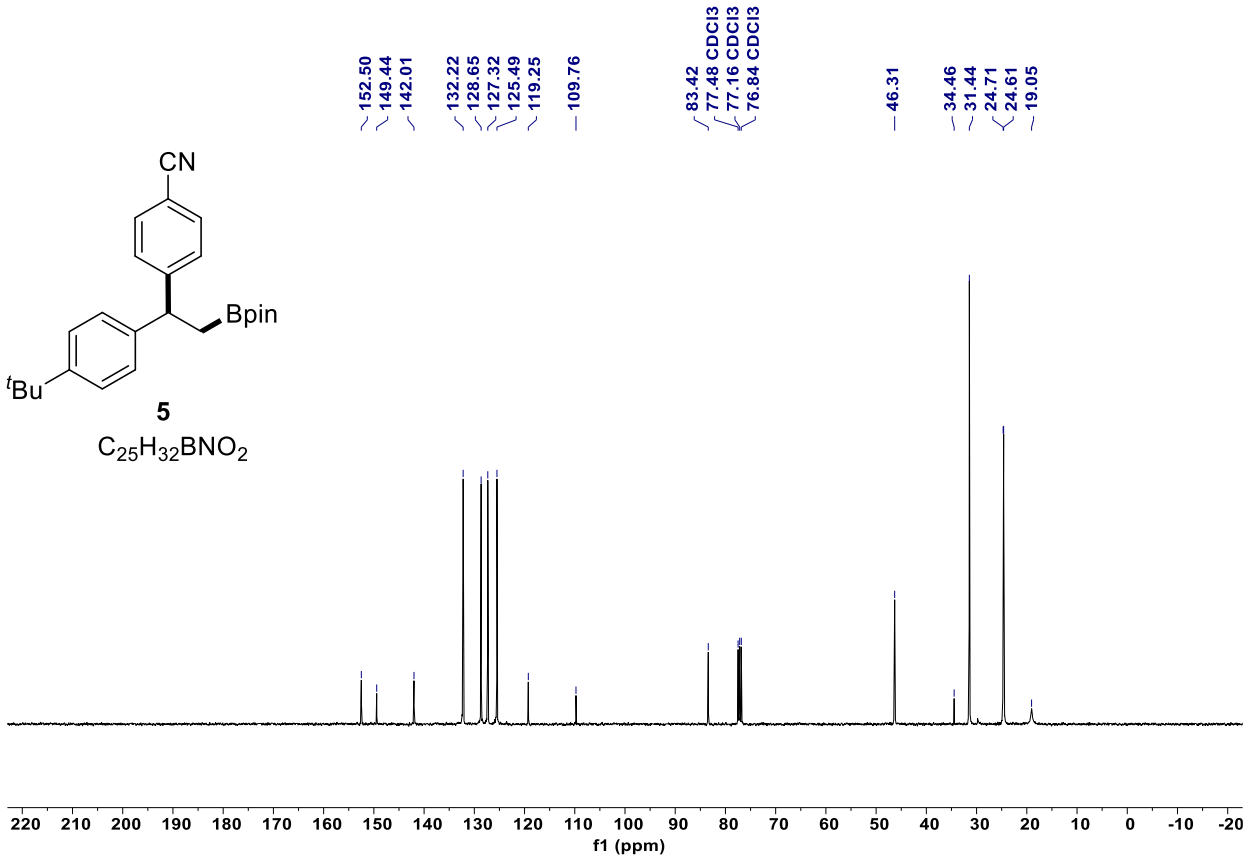
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4**.



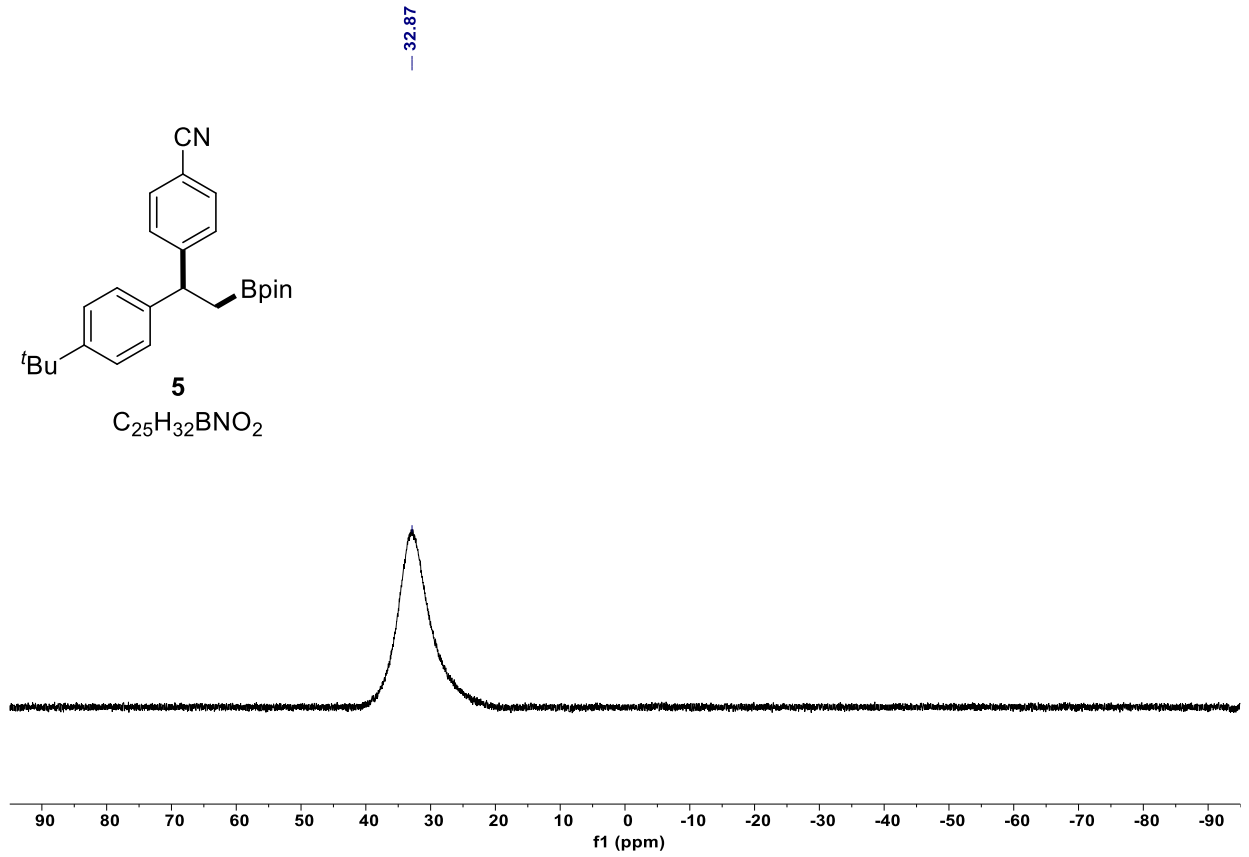
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **4**.



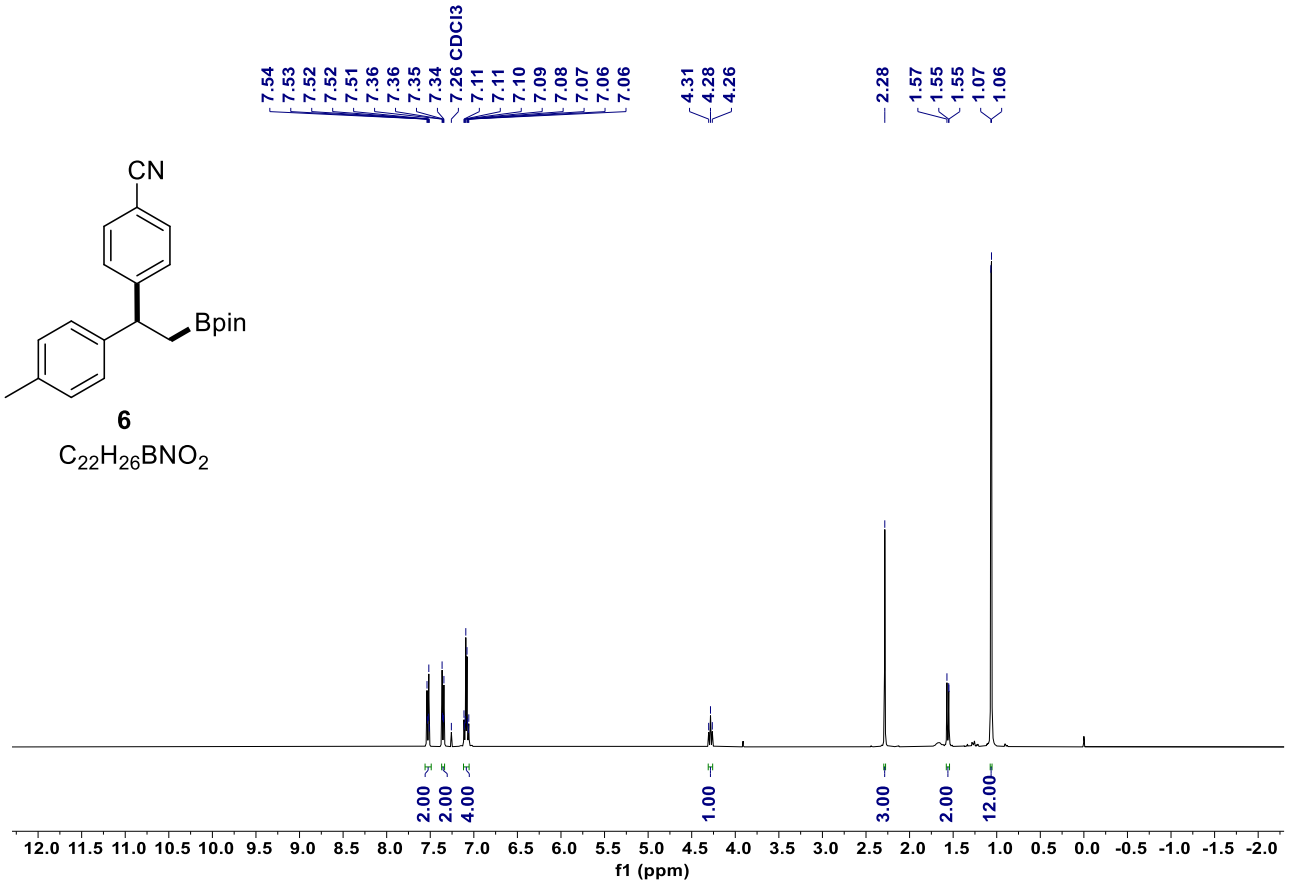
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **5**.



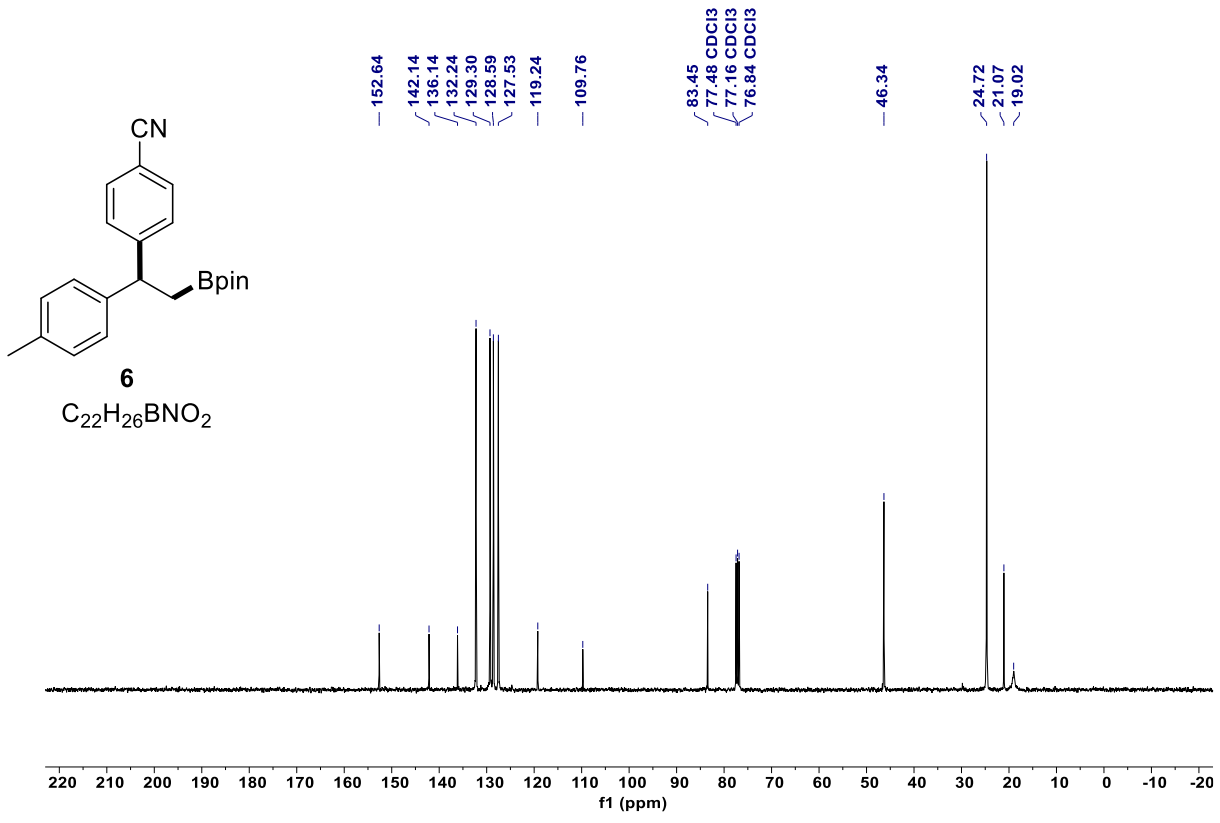
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5**.



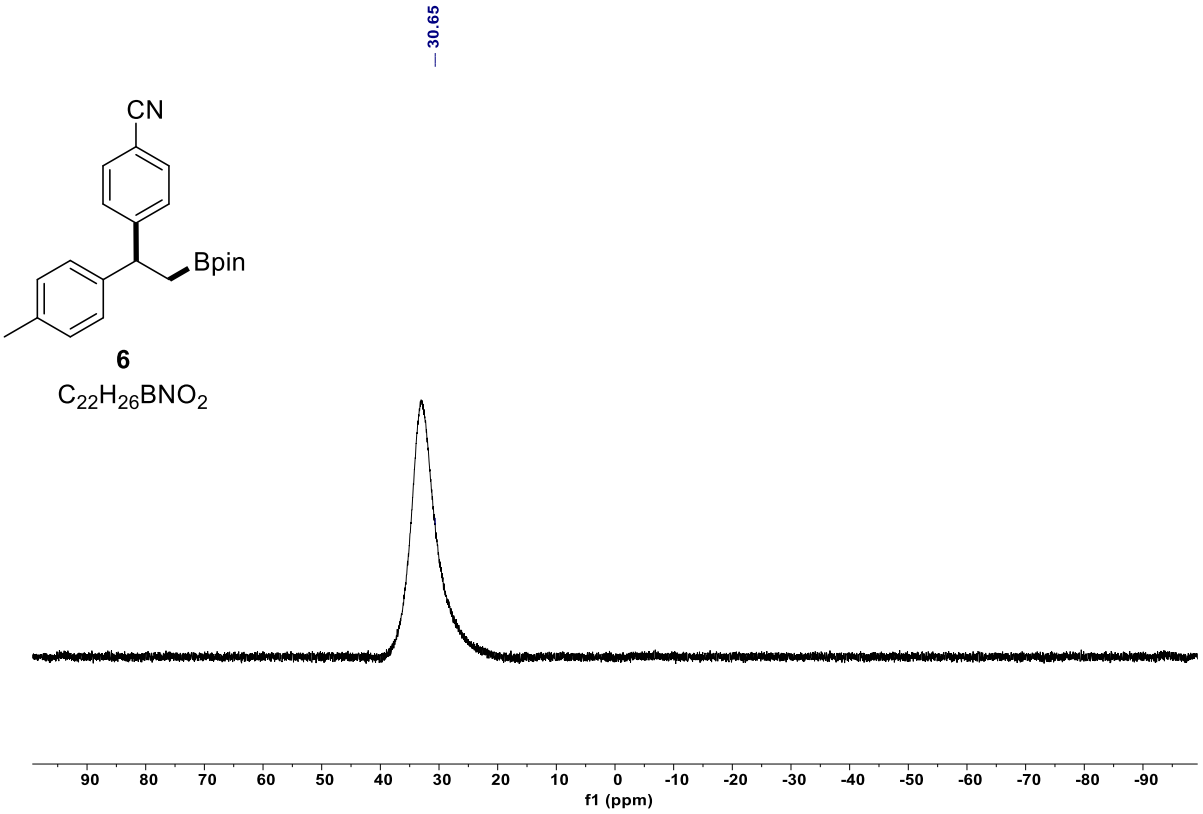
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **5**.



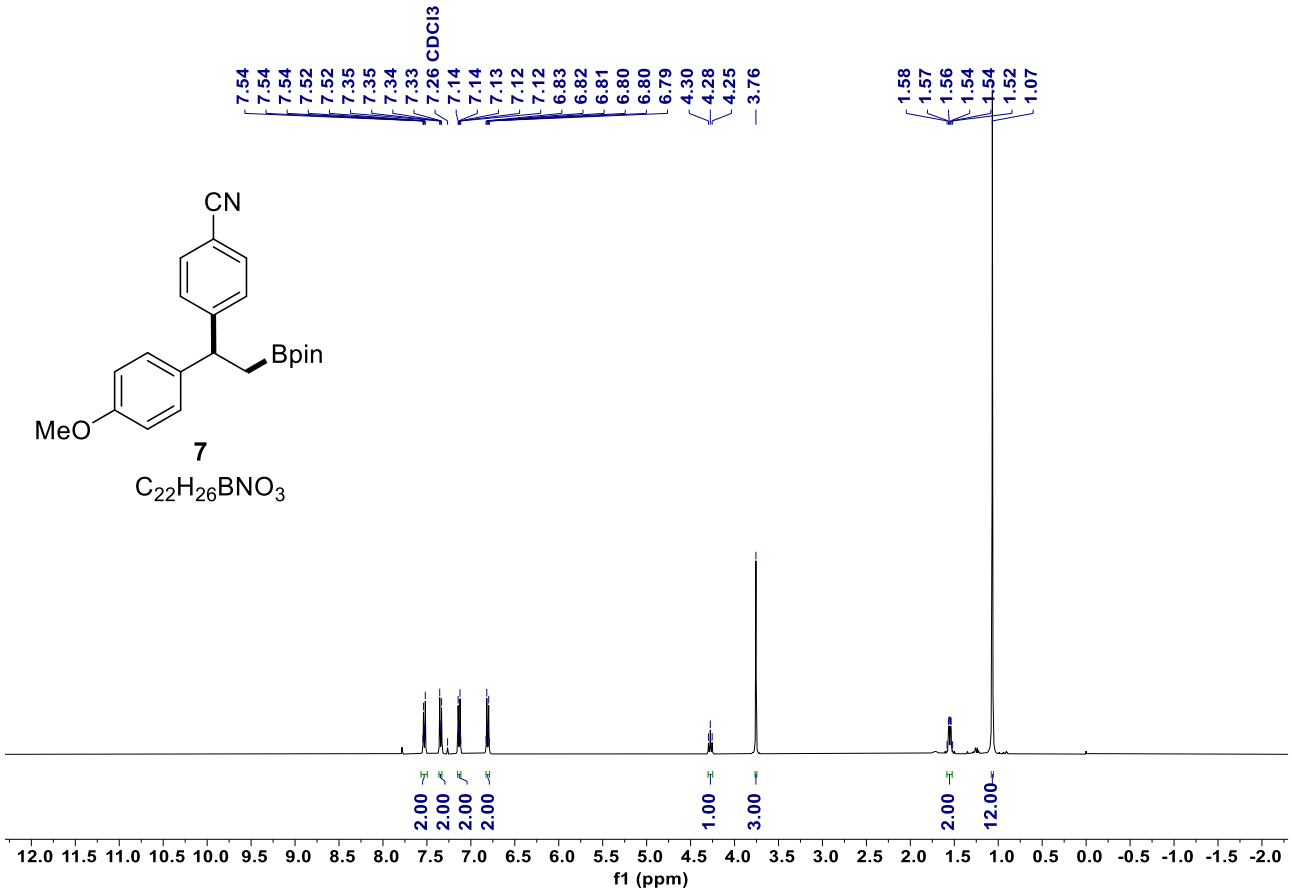
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **6**.



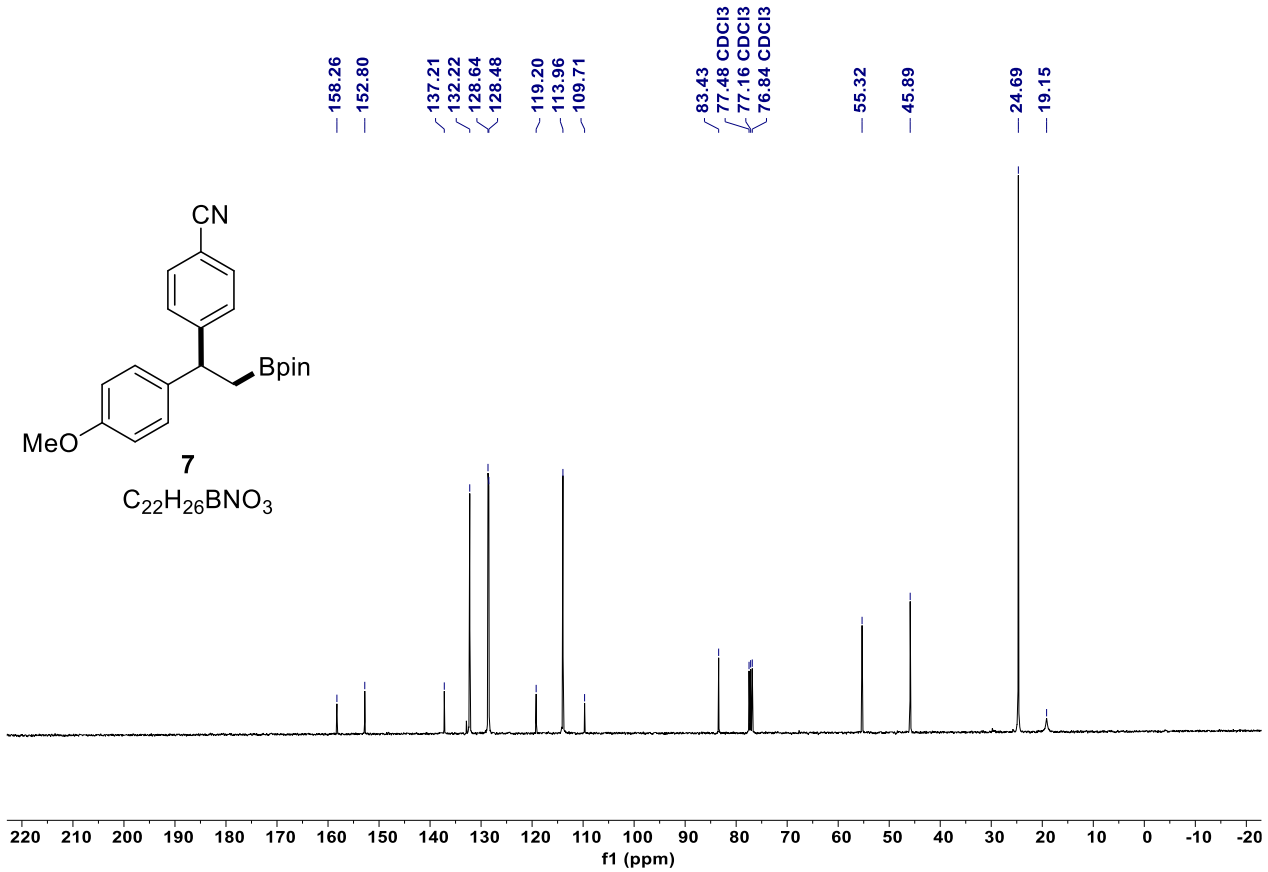
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **6**.



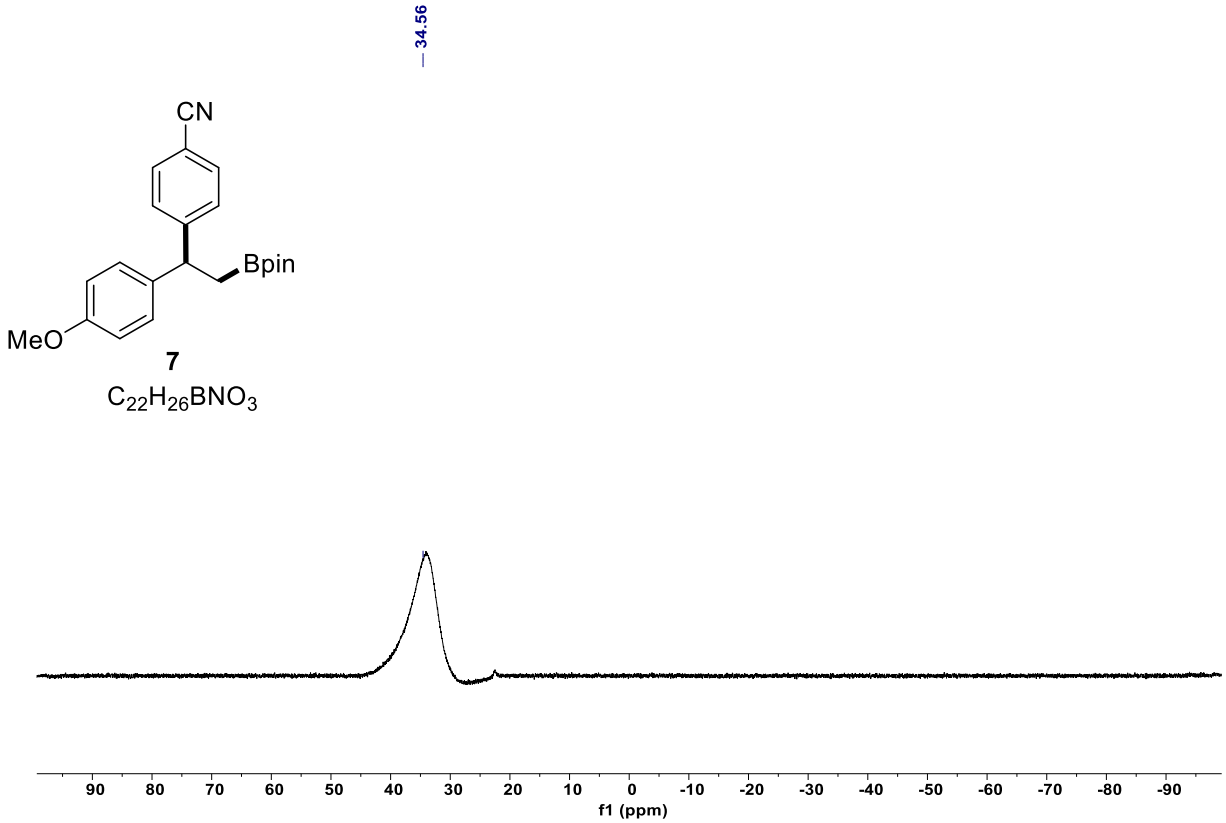
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **6**.



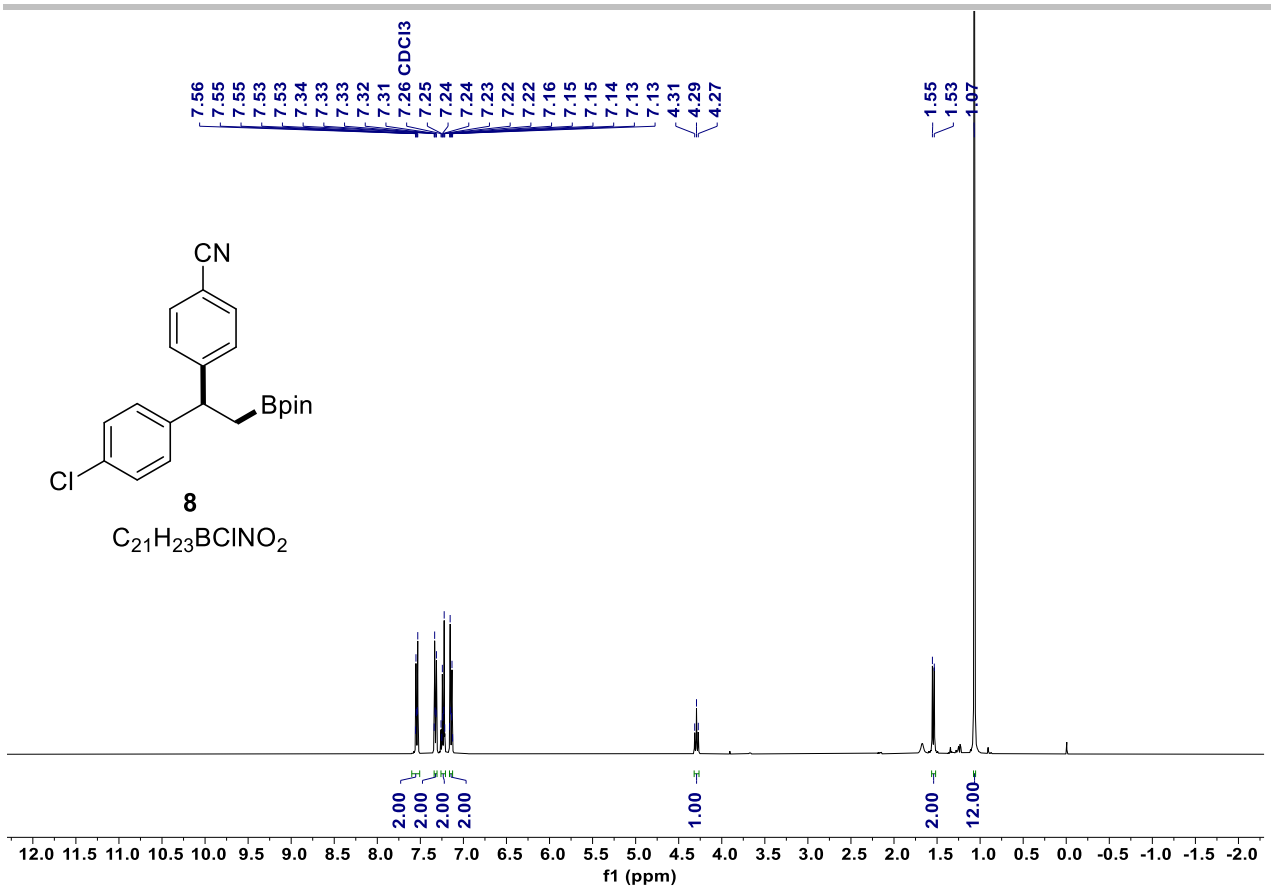
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **7**.



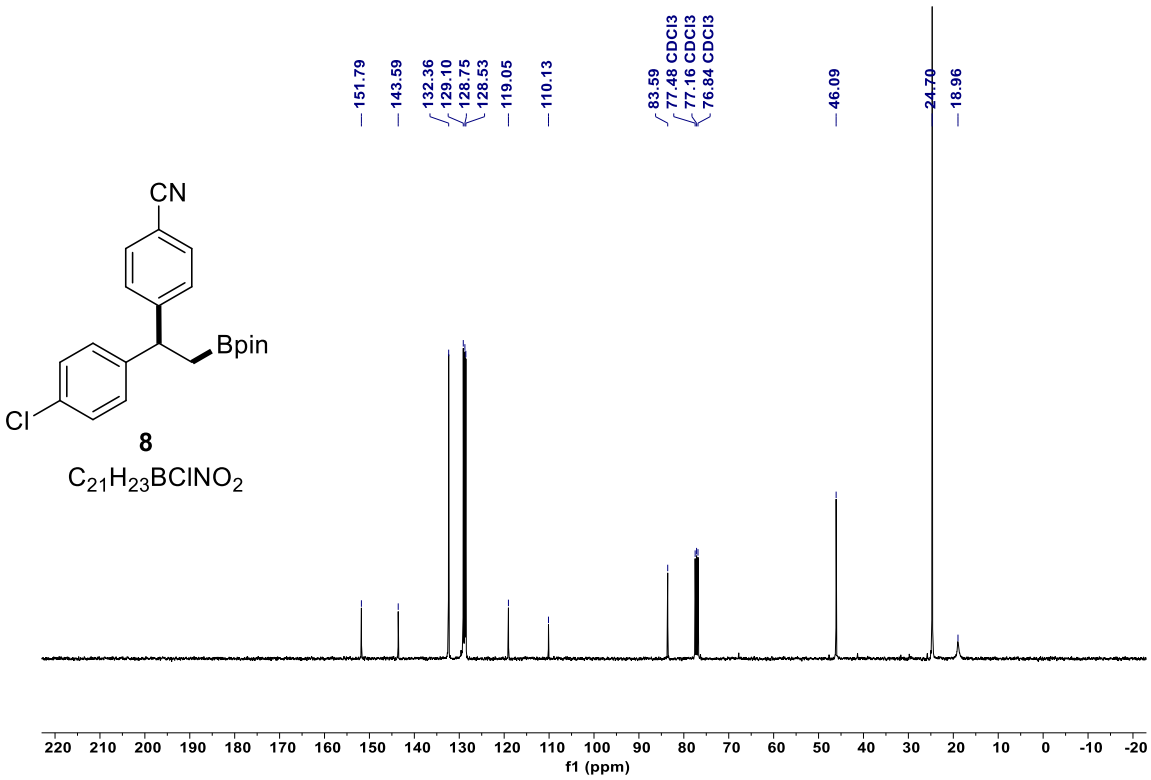
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **7**.



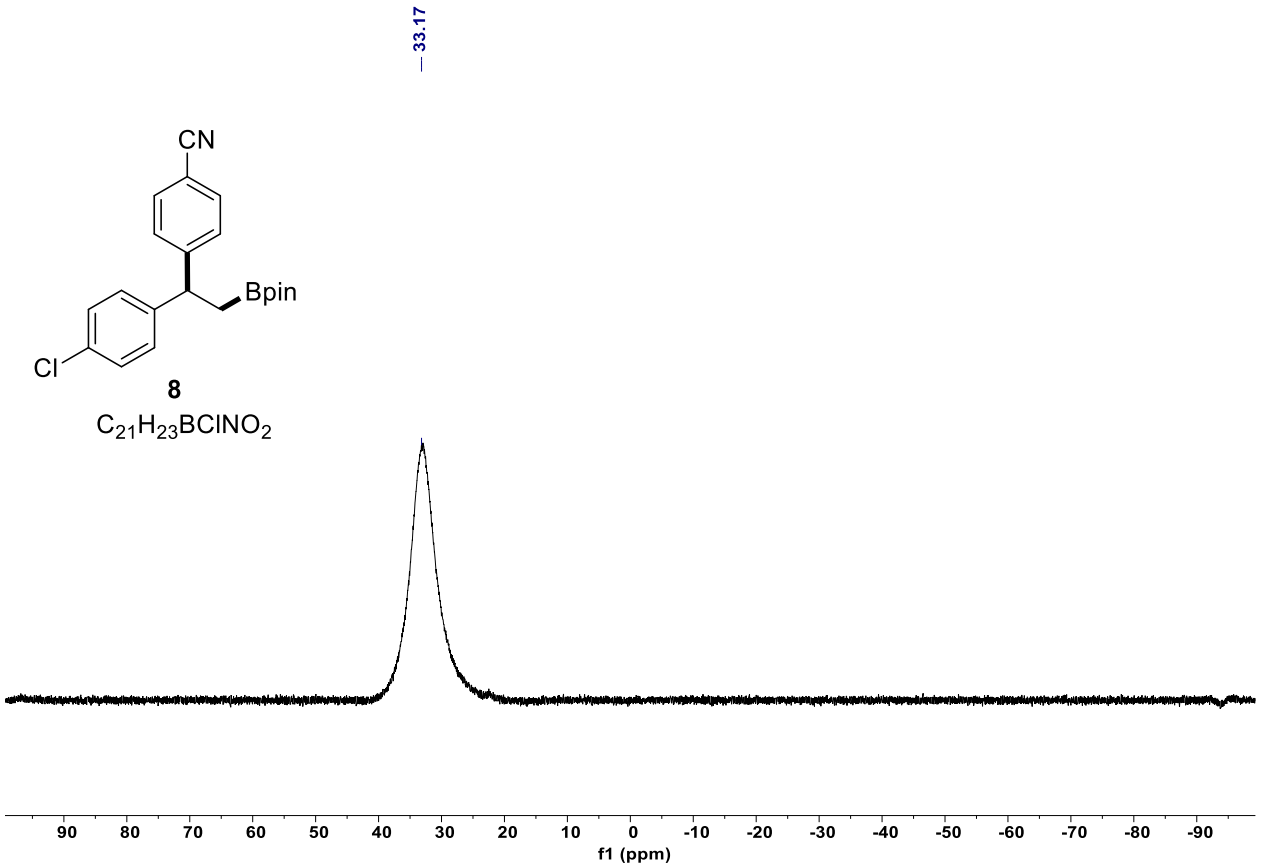
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **7**.



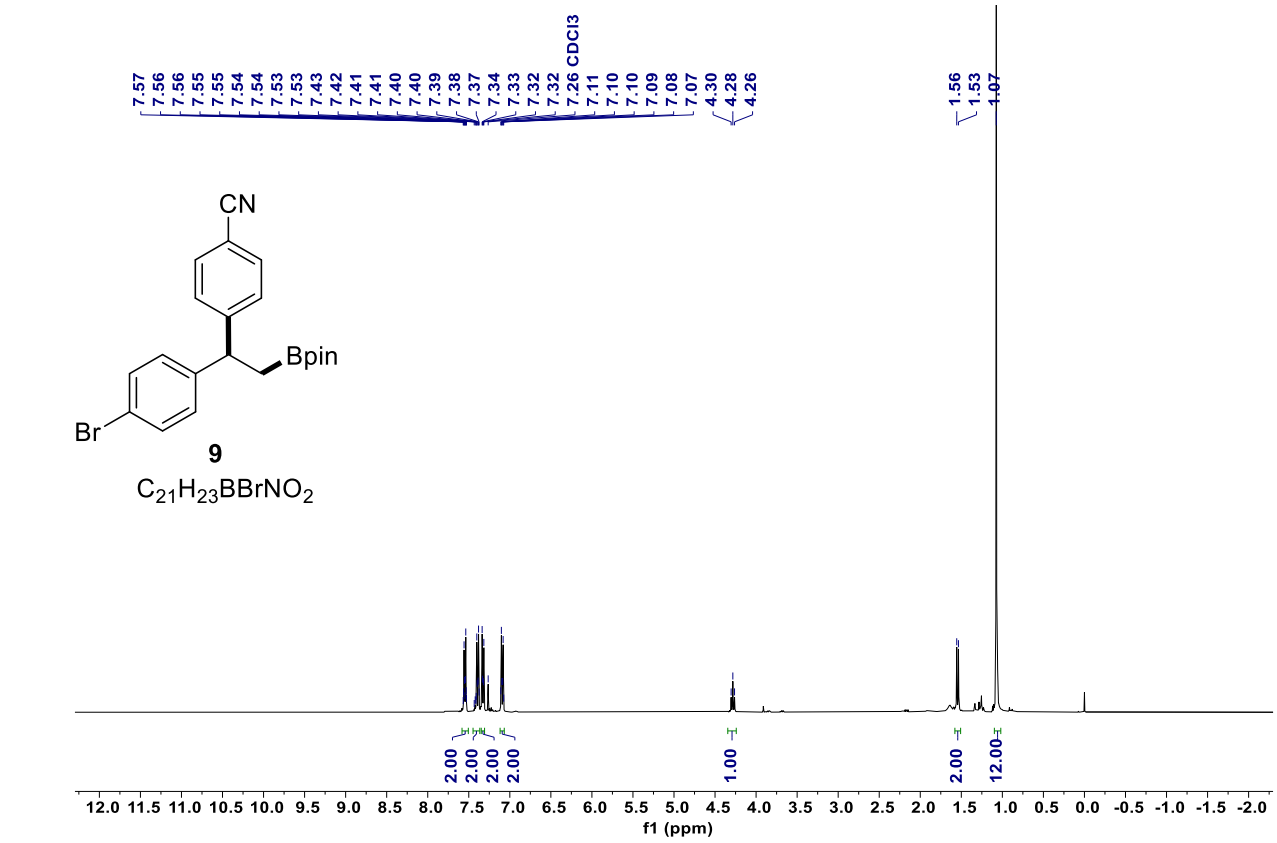
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **8**.



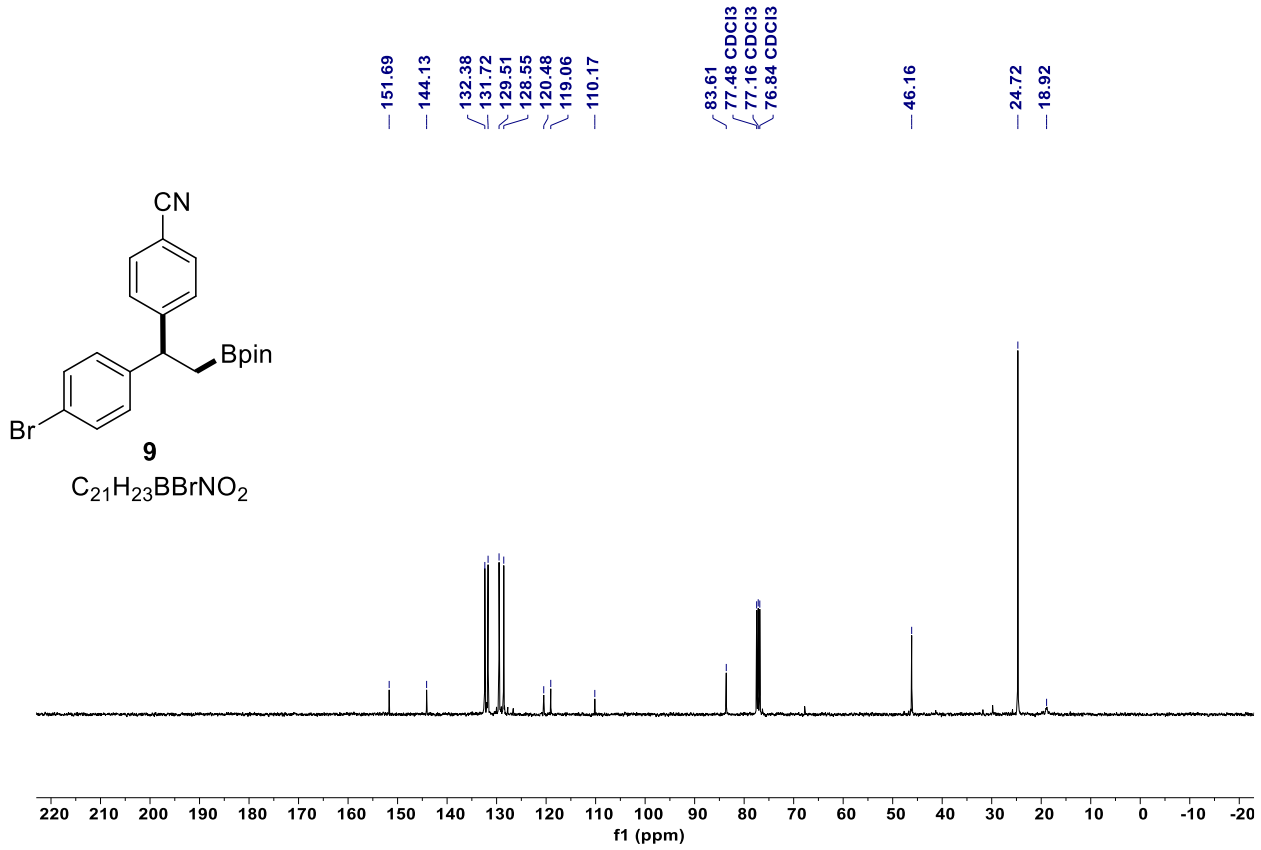
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **8**.



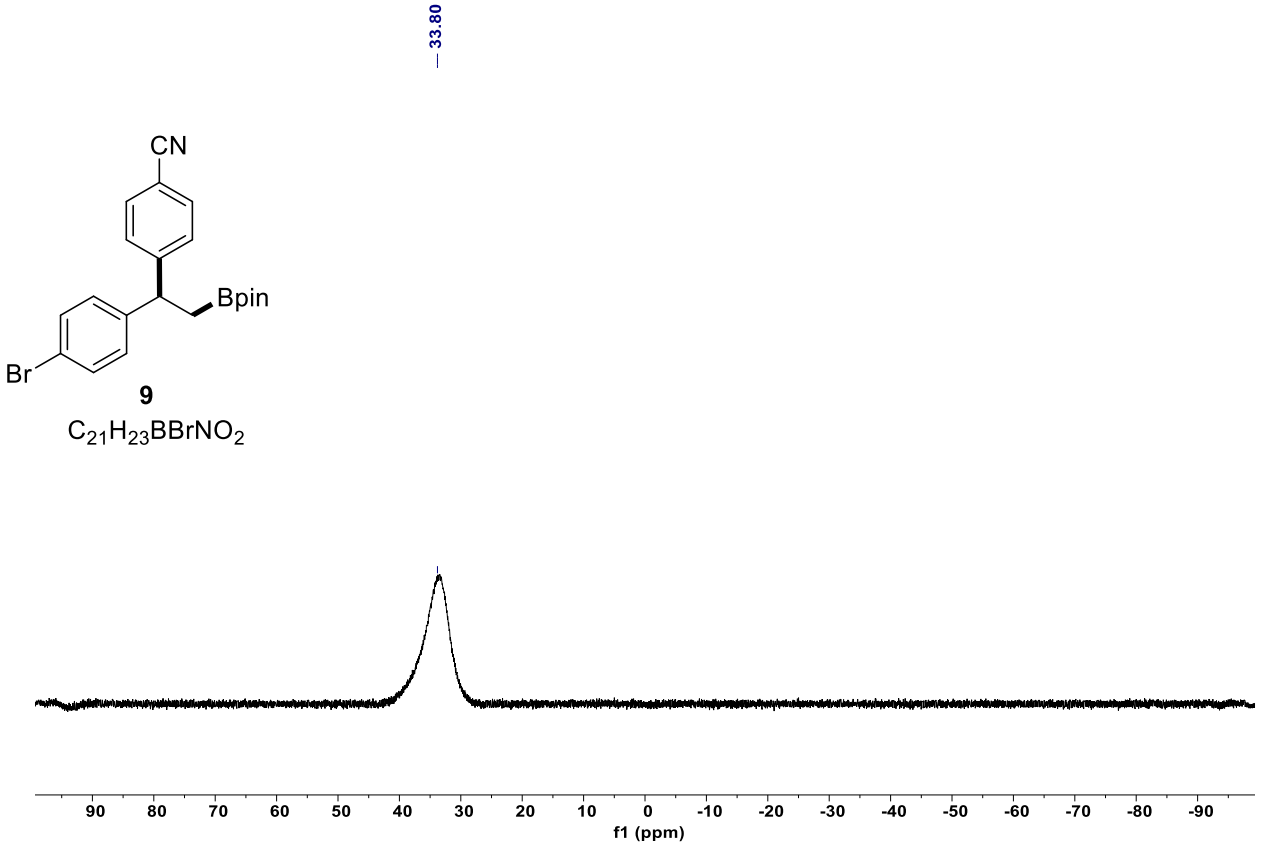
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **8**.



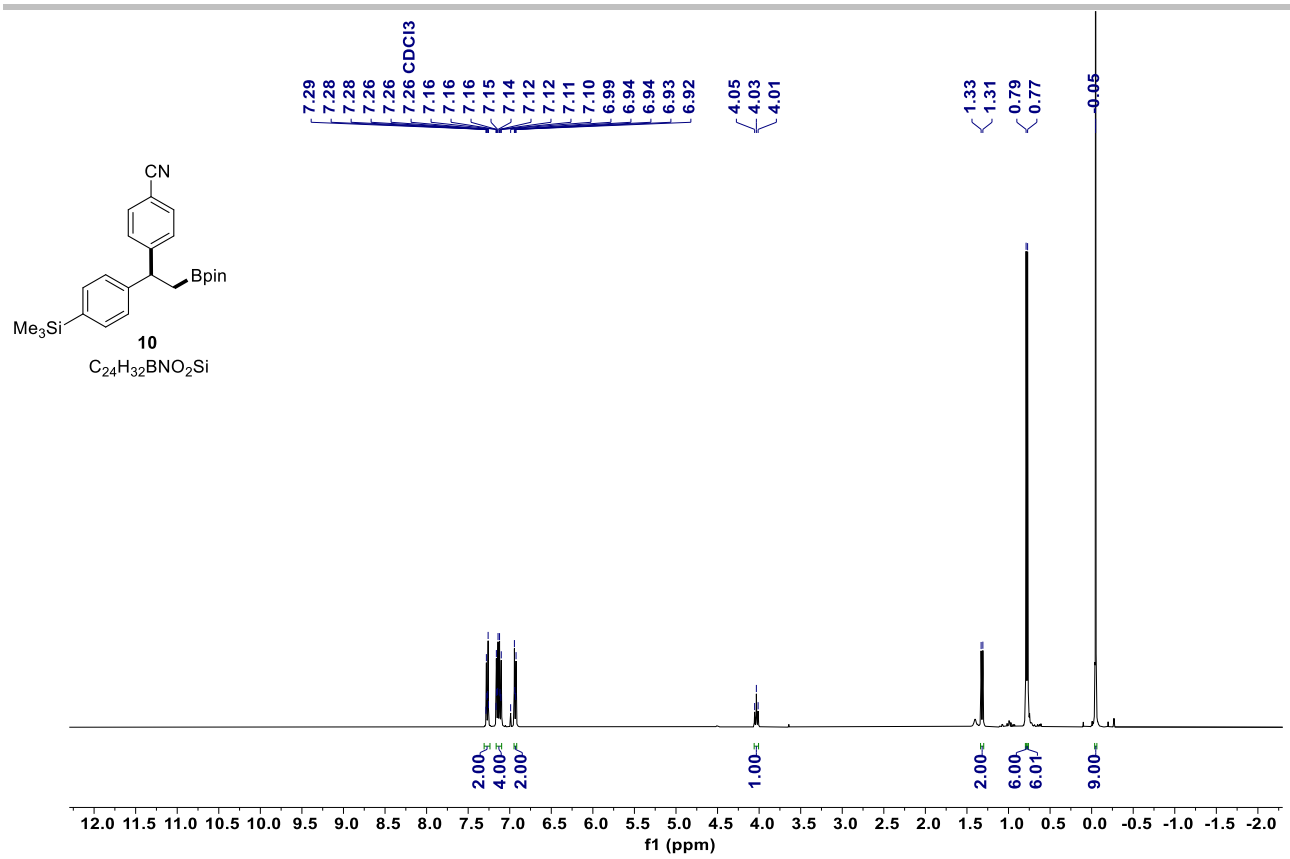
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **9**.



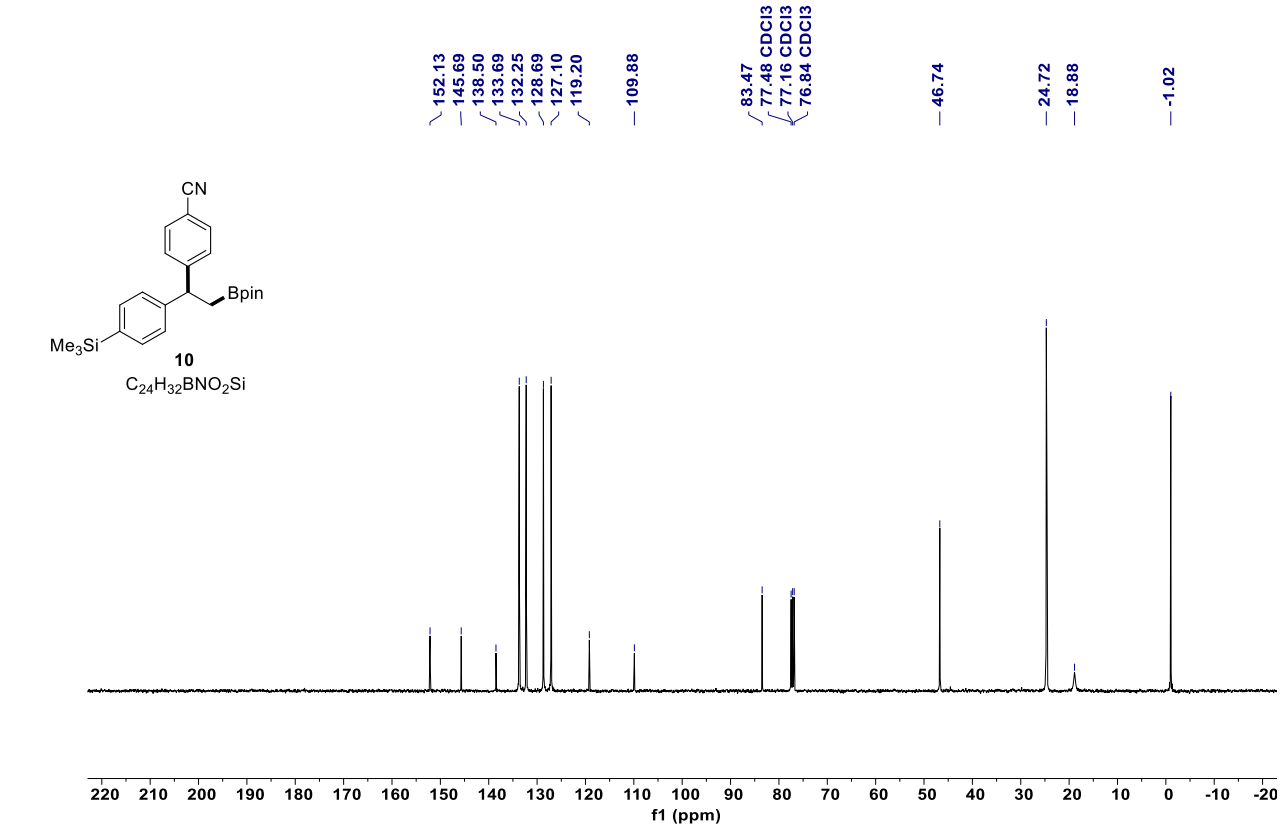
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **9**.



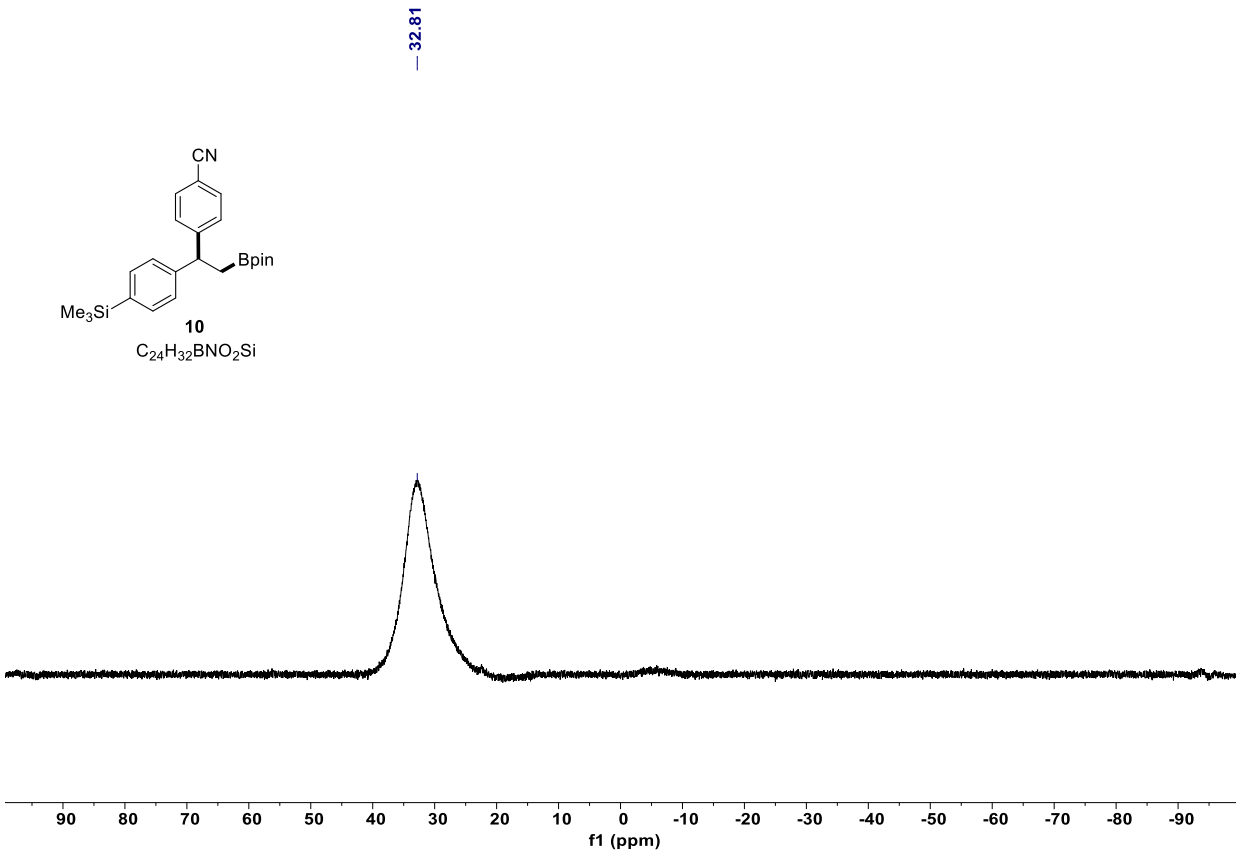
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **9**.



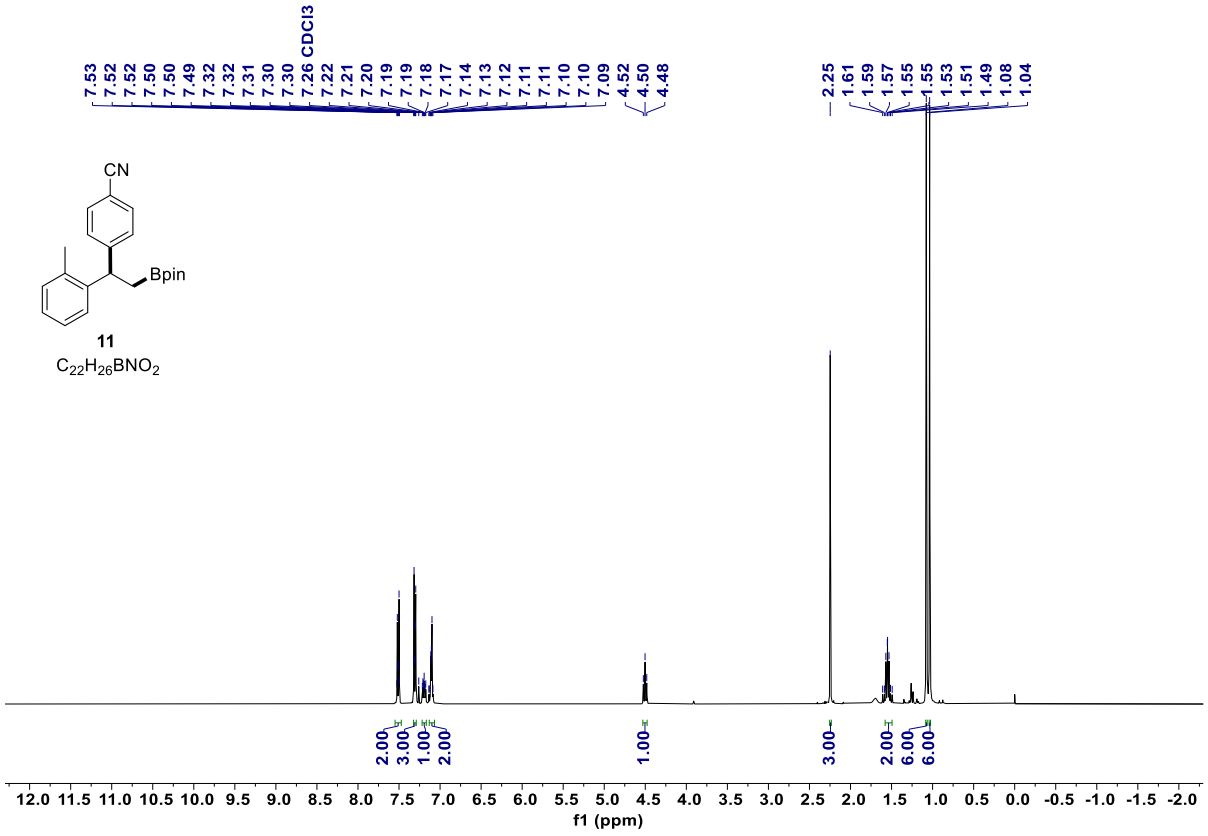
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **10**.



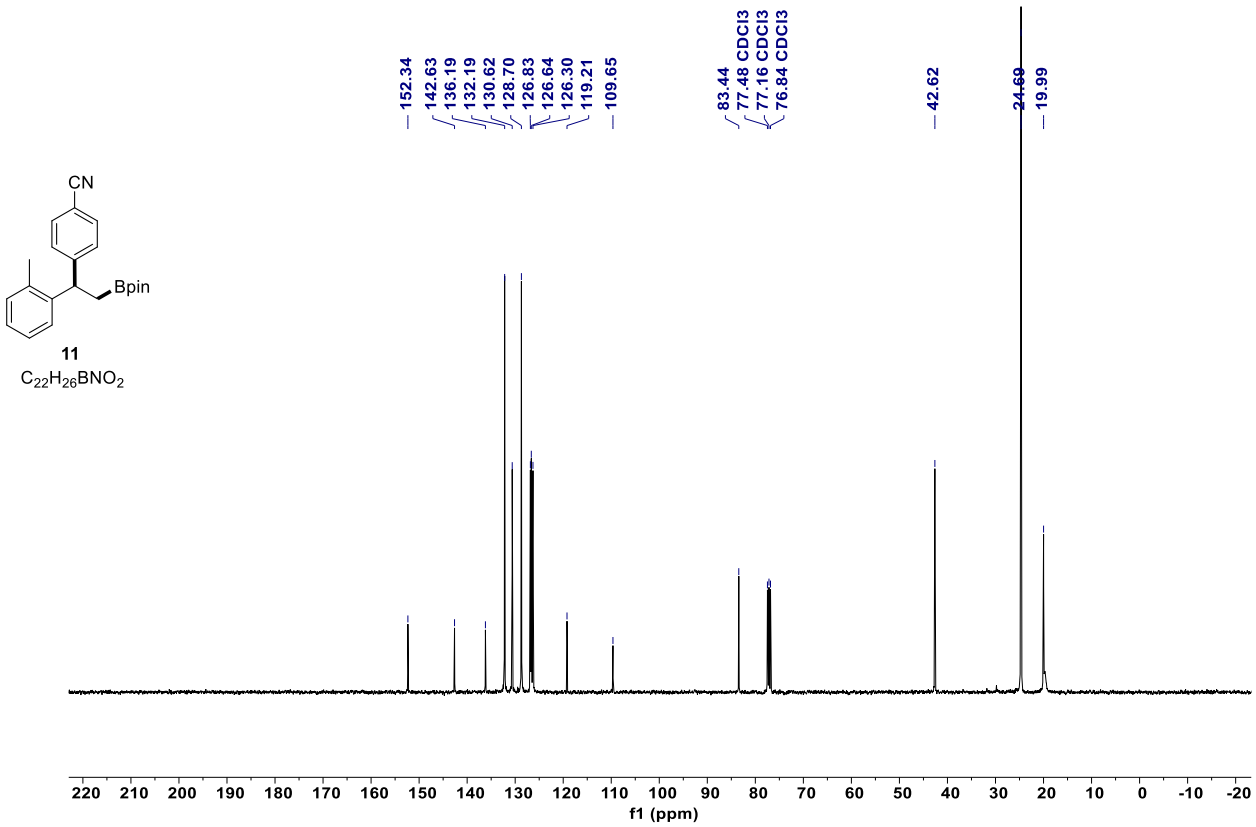
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **10**.



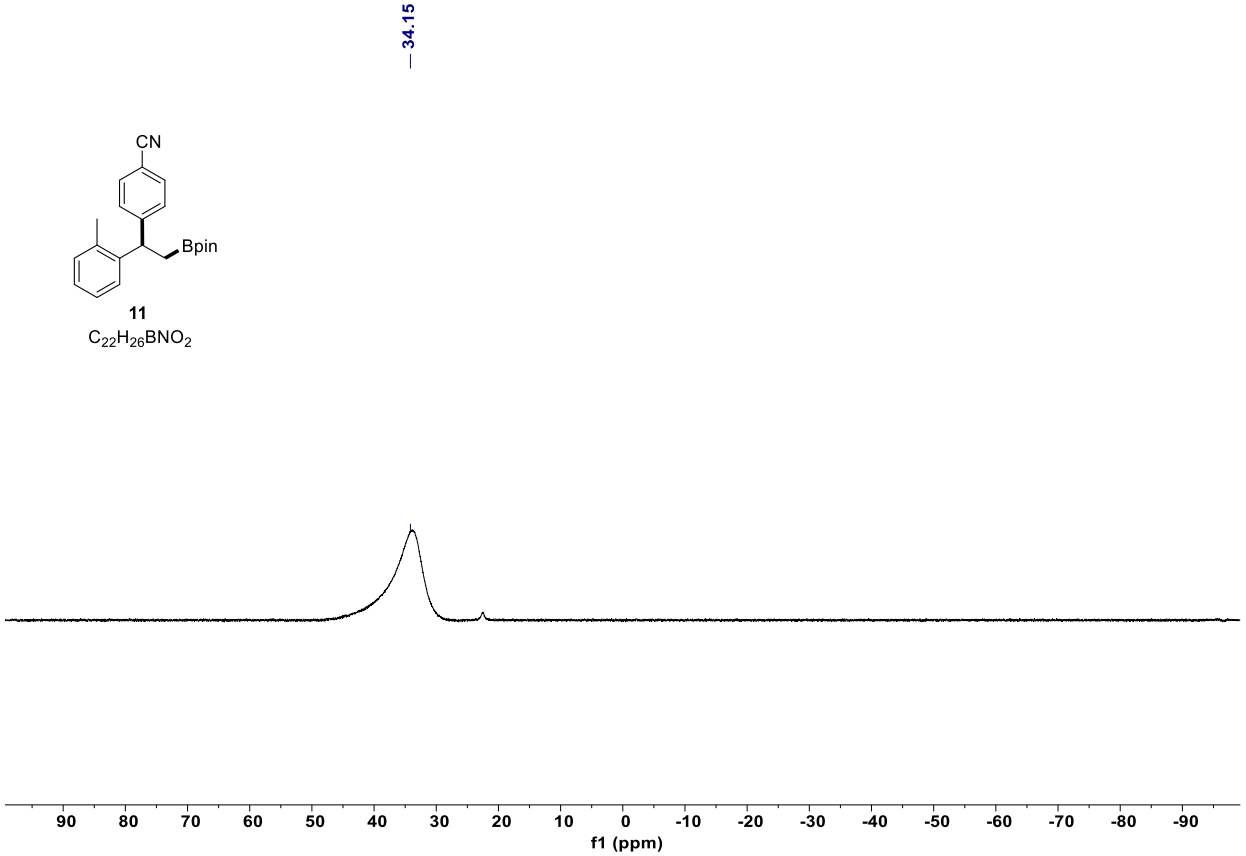
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **10**.



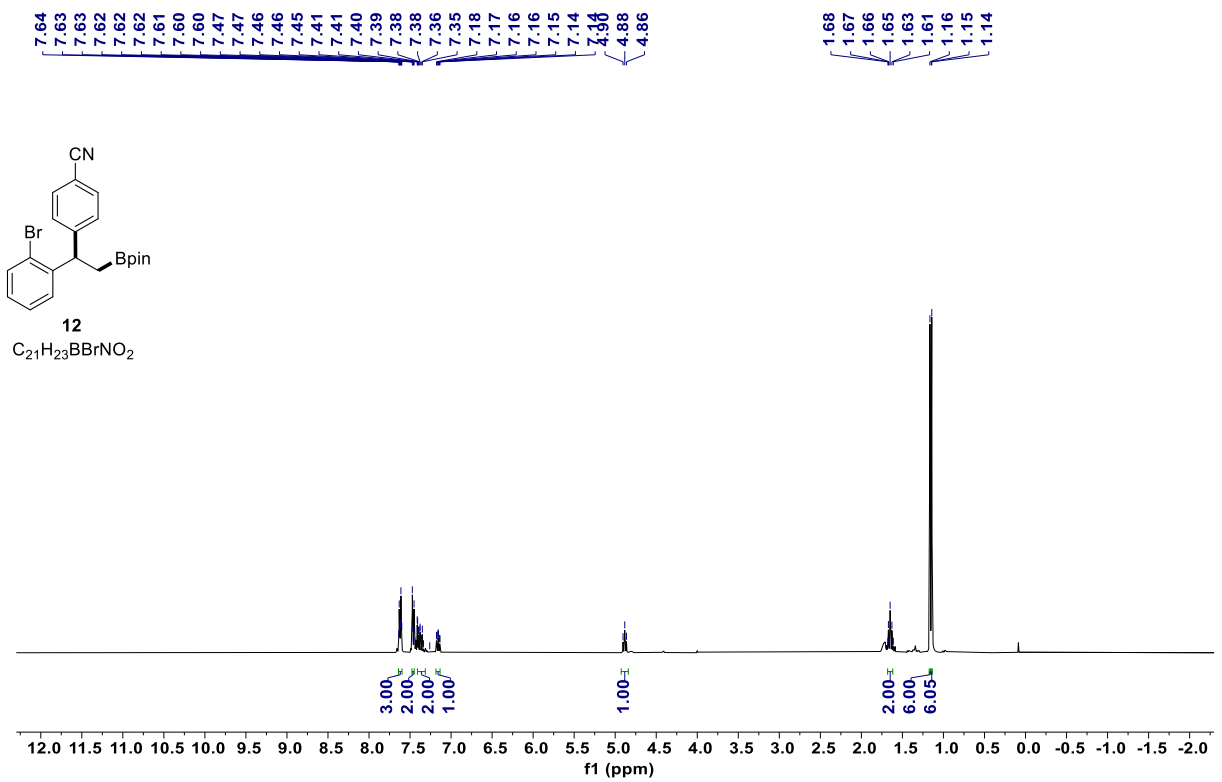
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **11**.



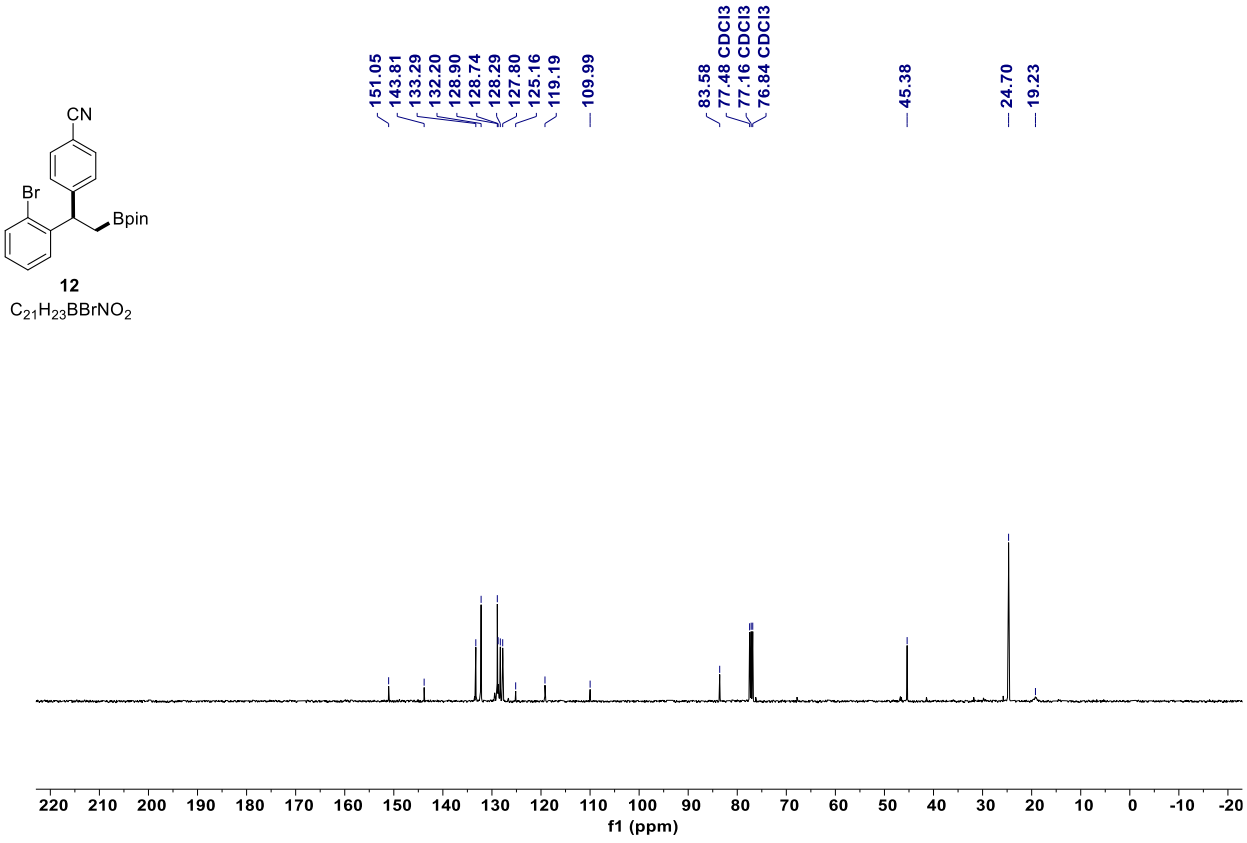
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **11**.



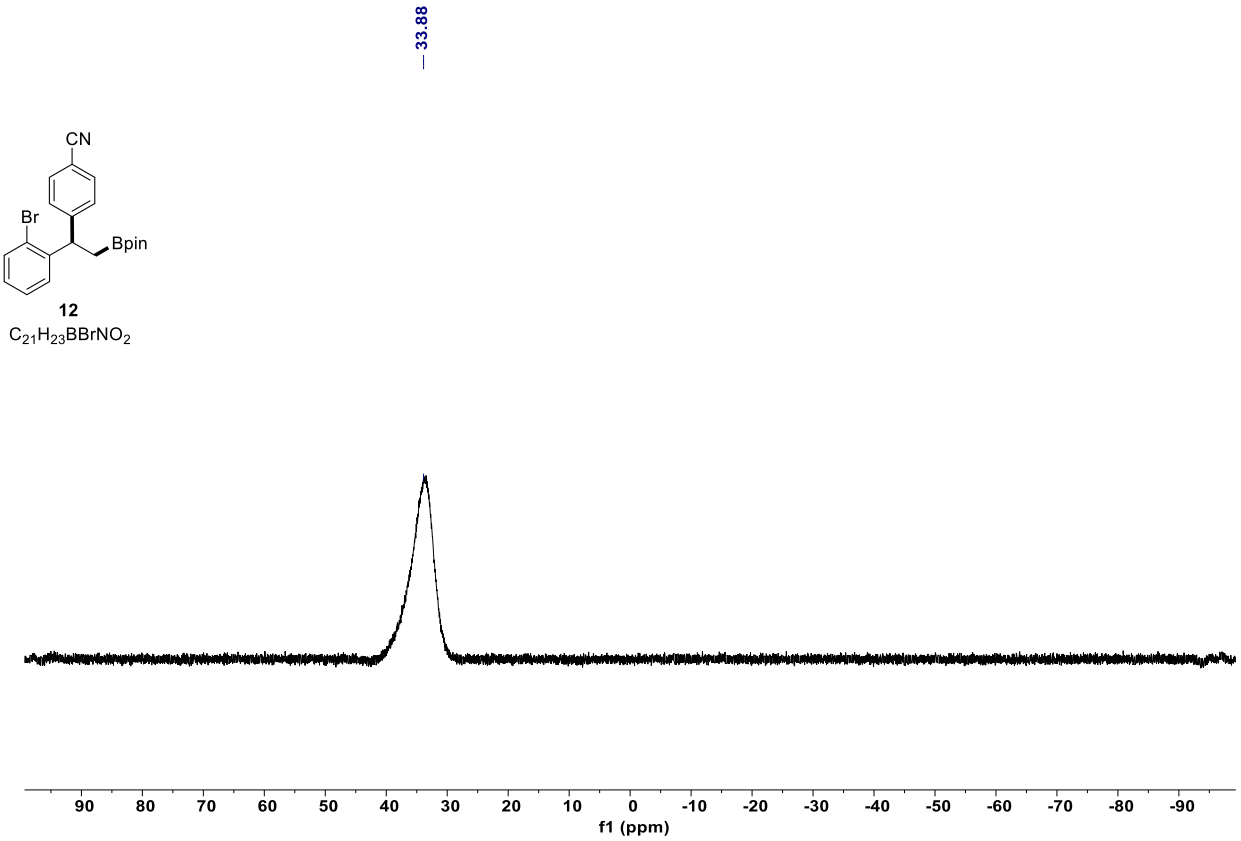
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **11**.



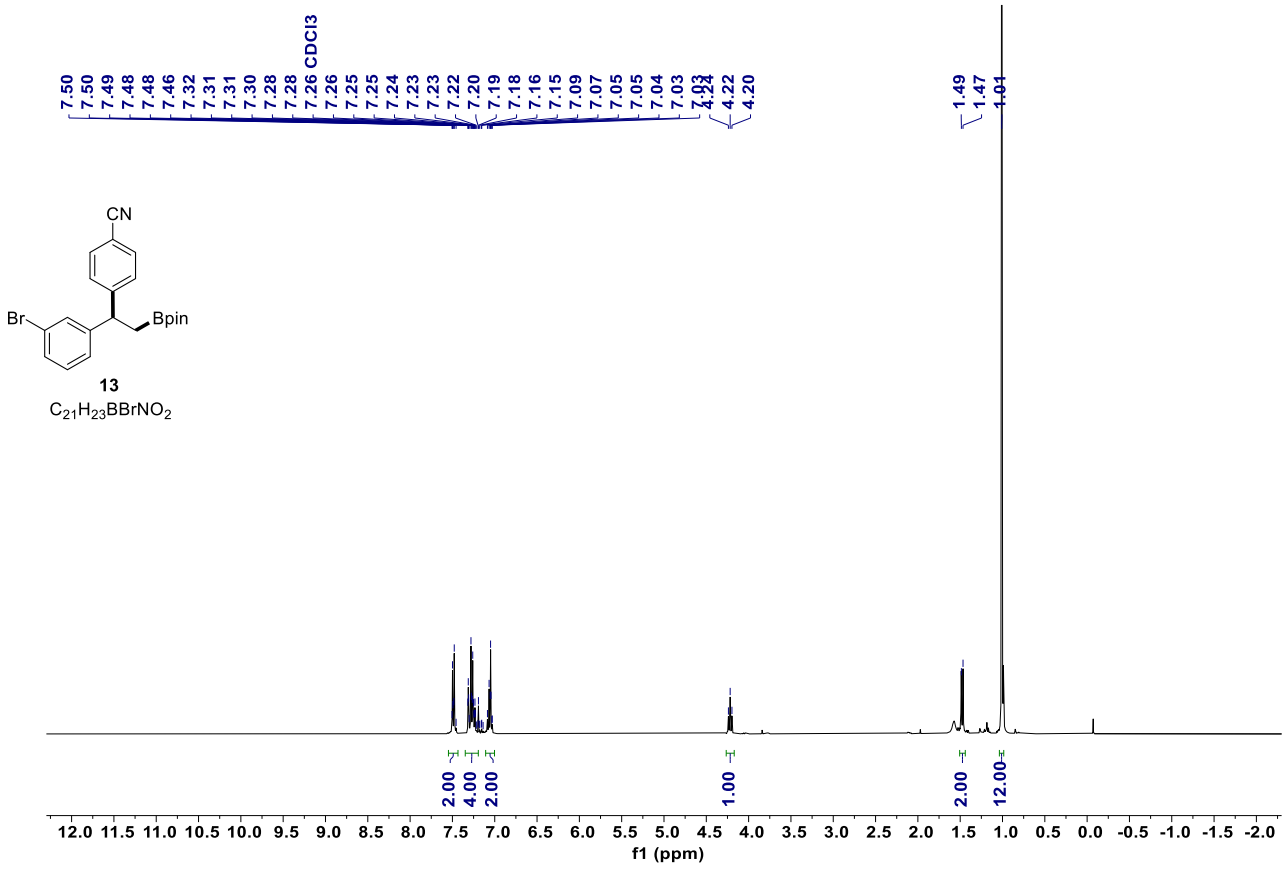
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **12**.



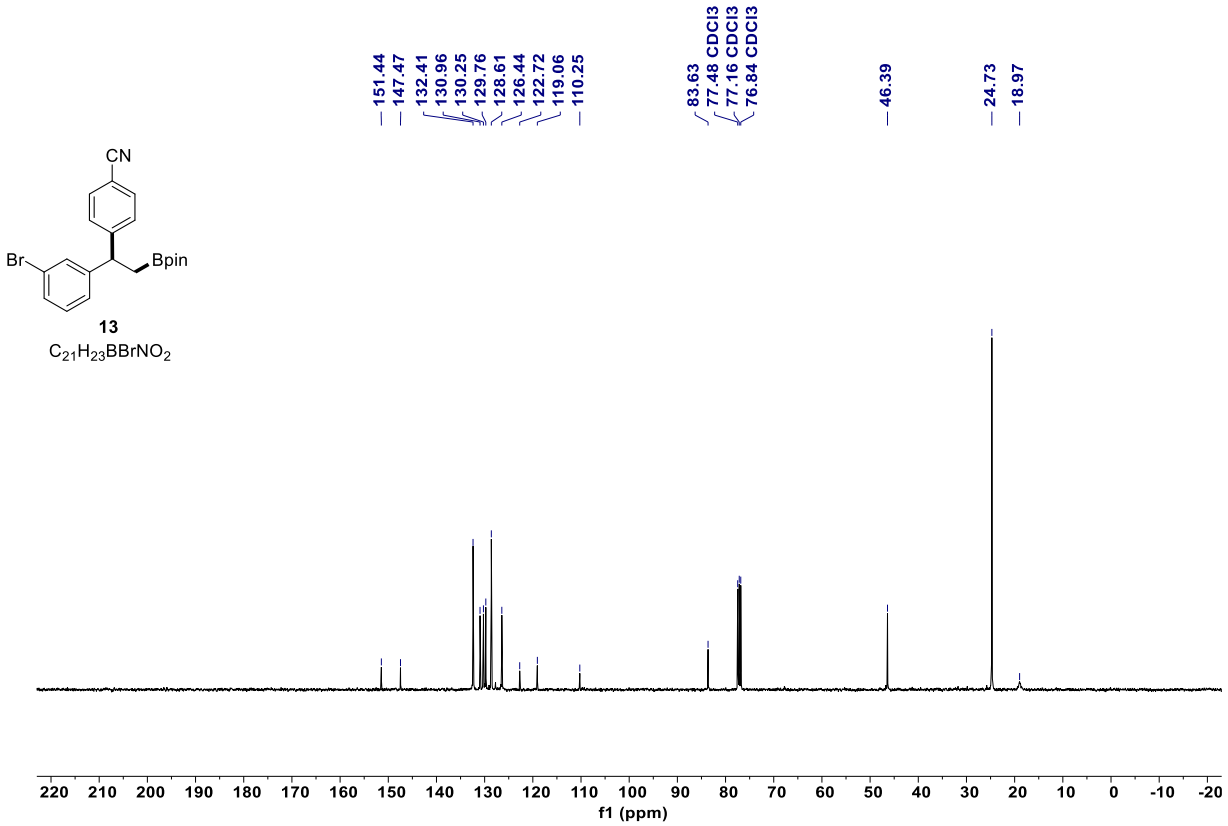
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **12**.



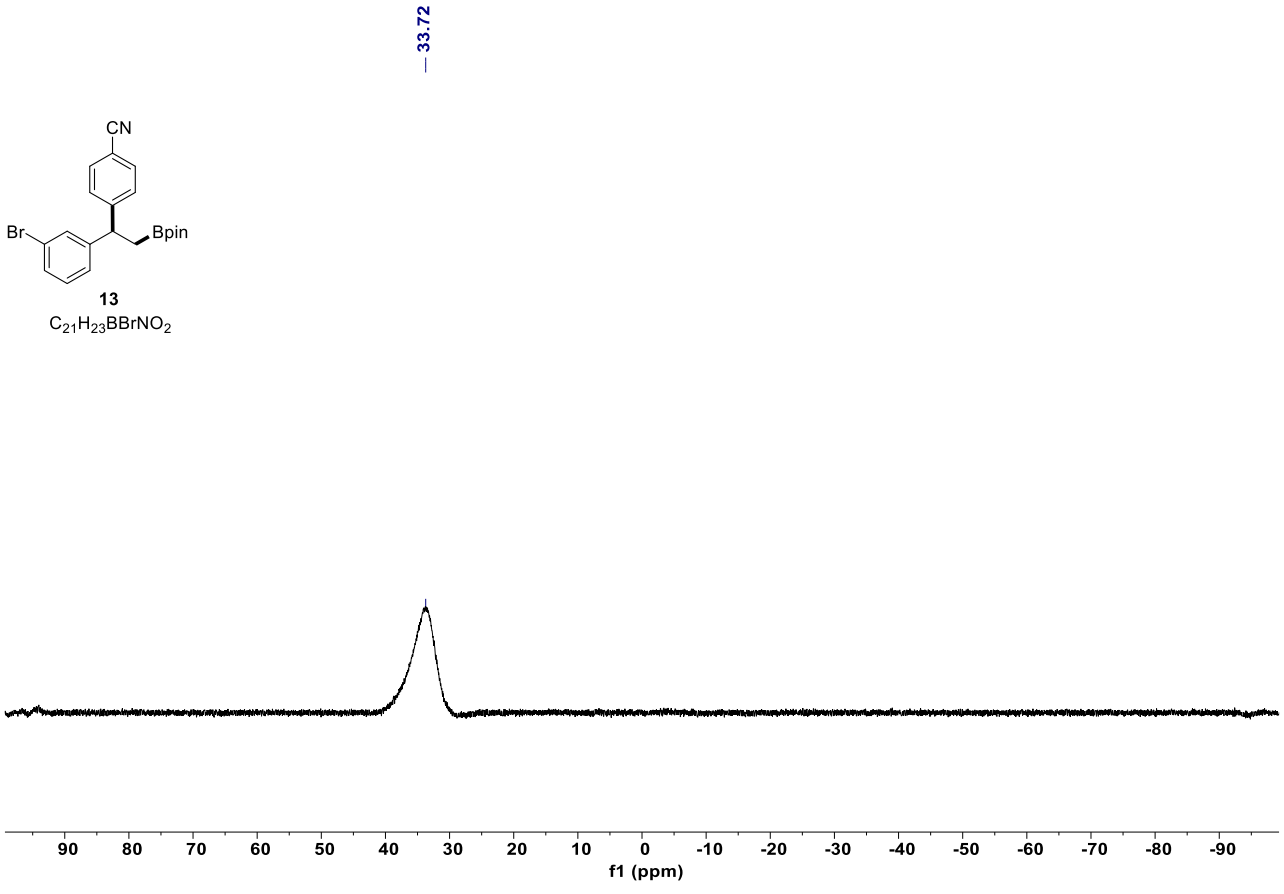
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **12**.



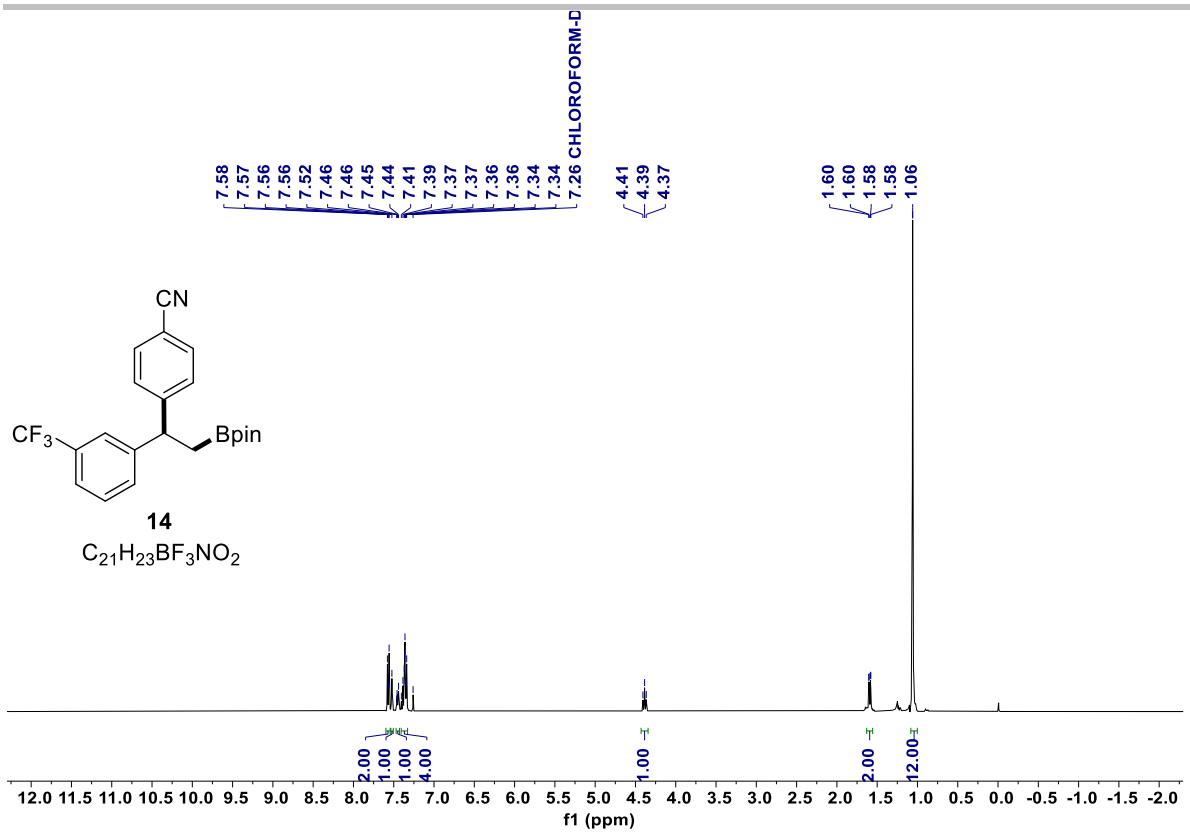
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **13**.



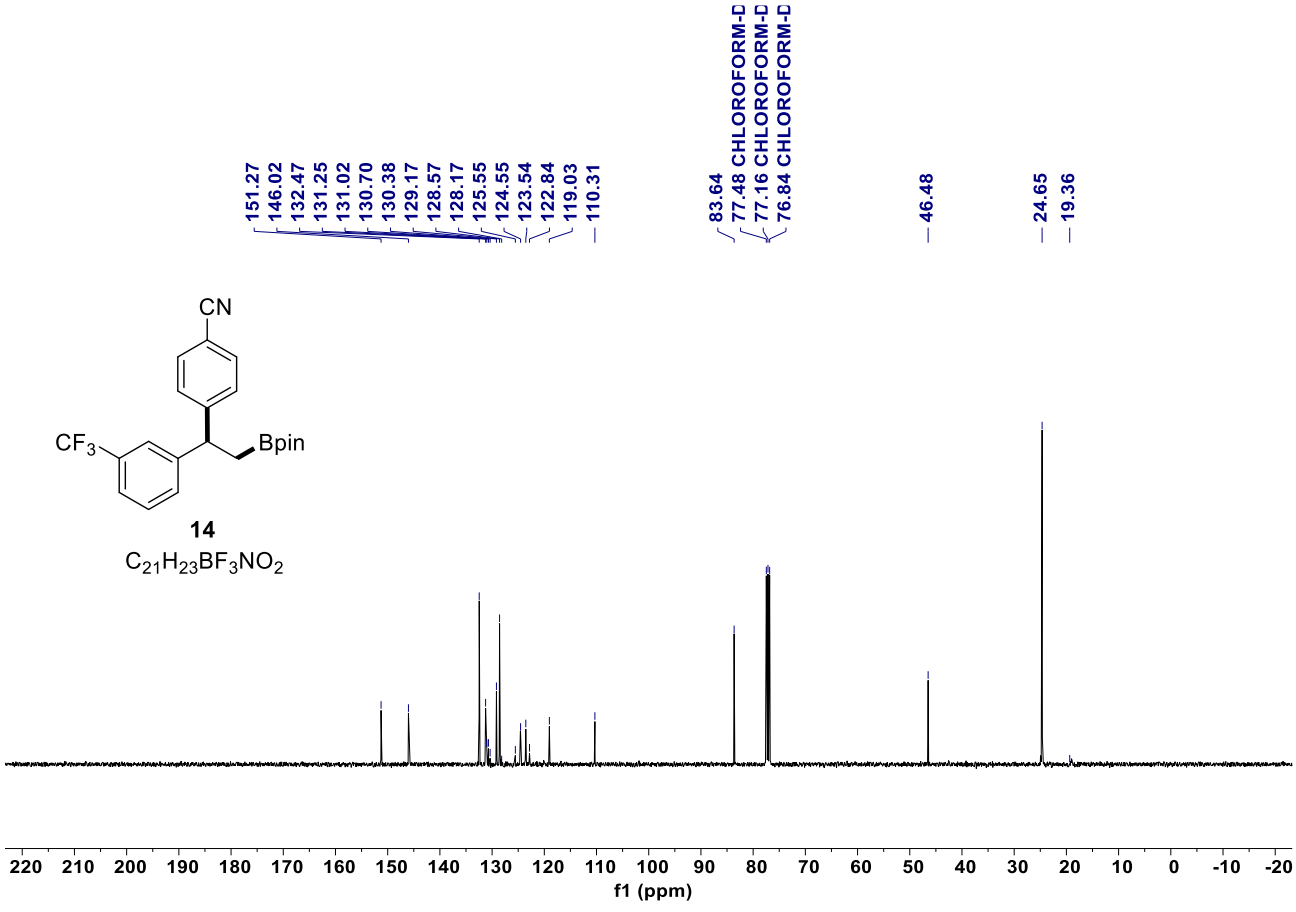
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **13**.



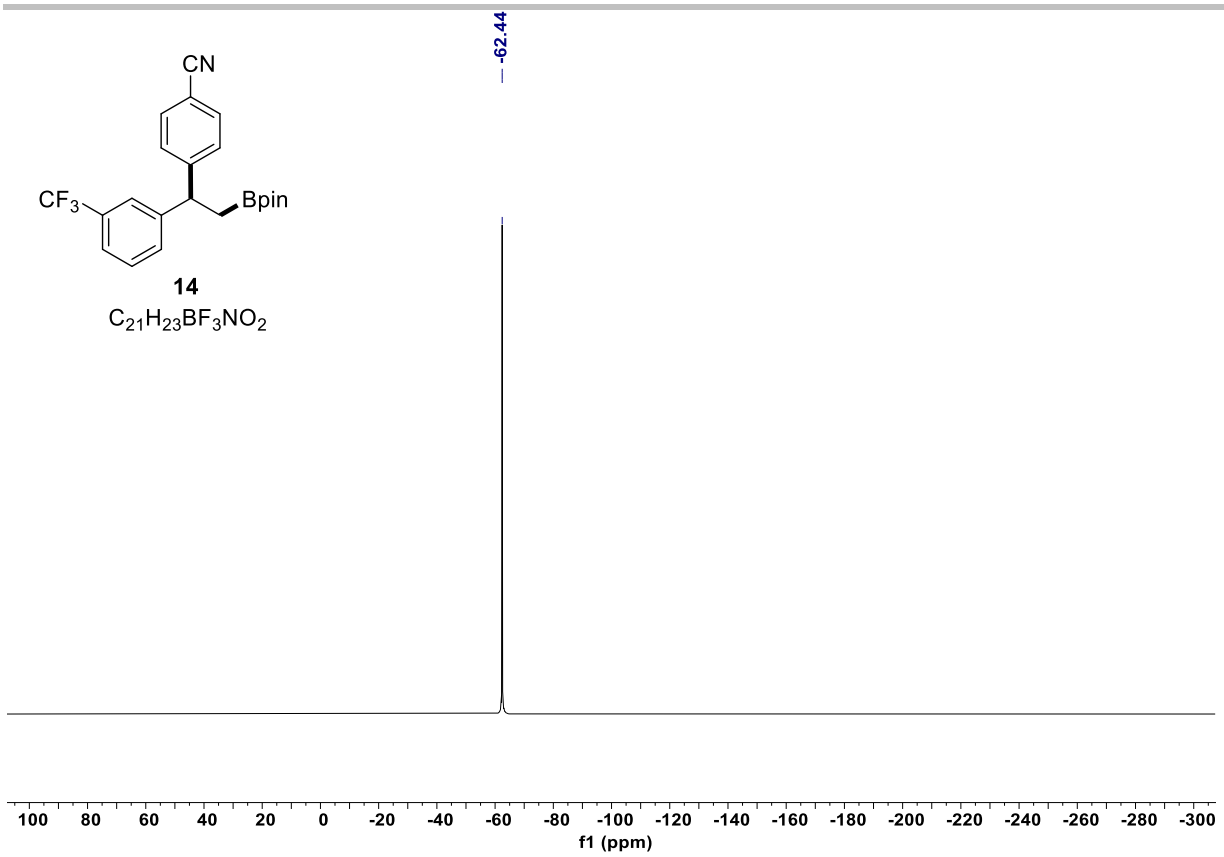
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **13**.



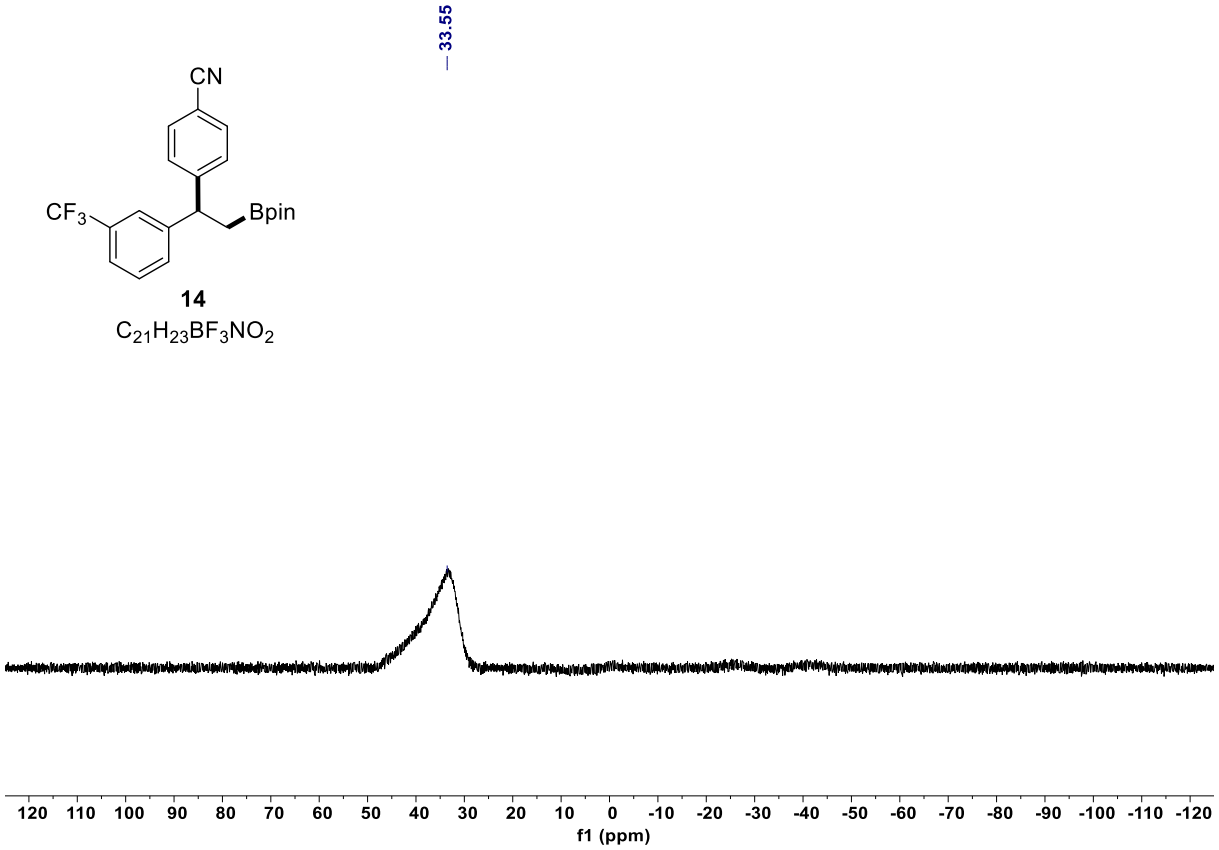
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **14**.



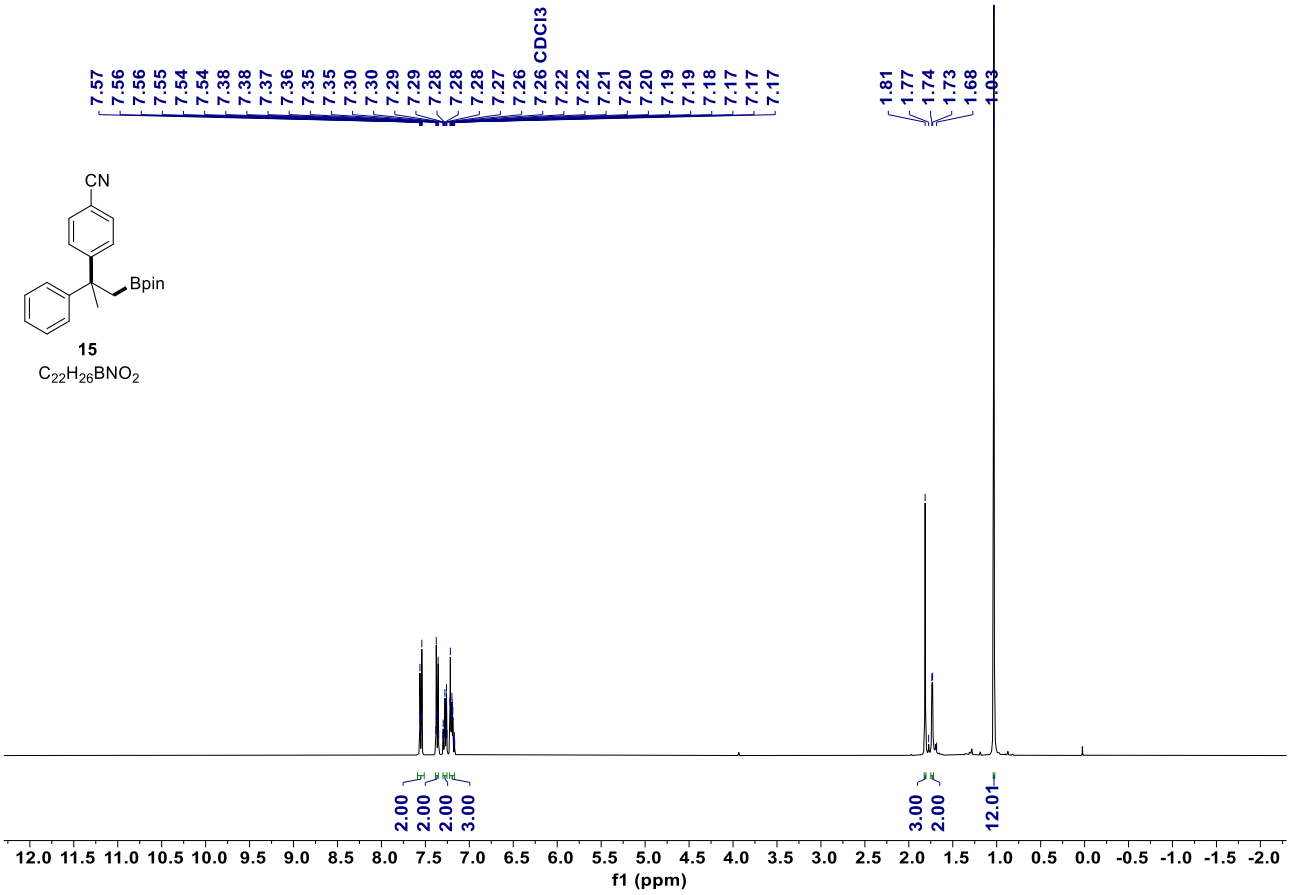
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **14**.



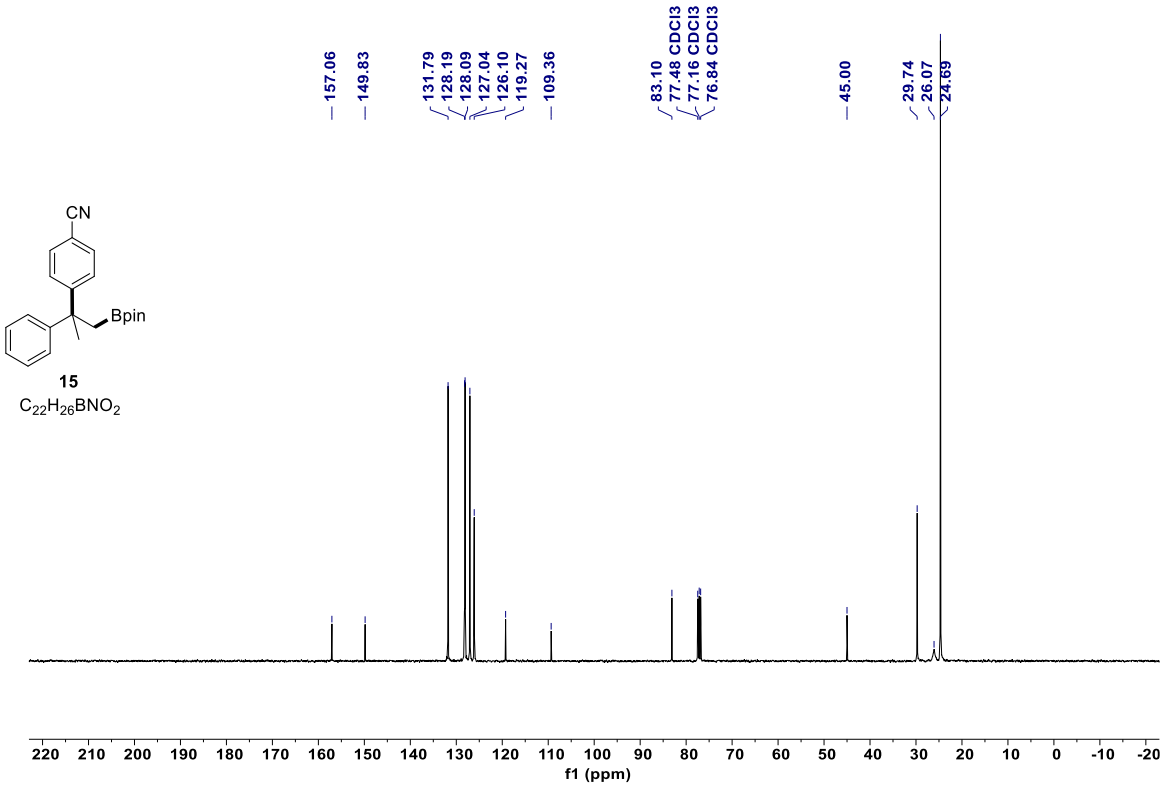
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **14**



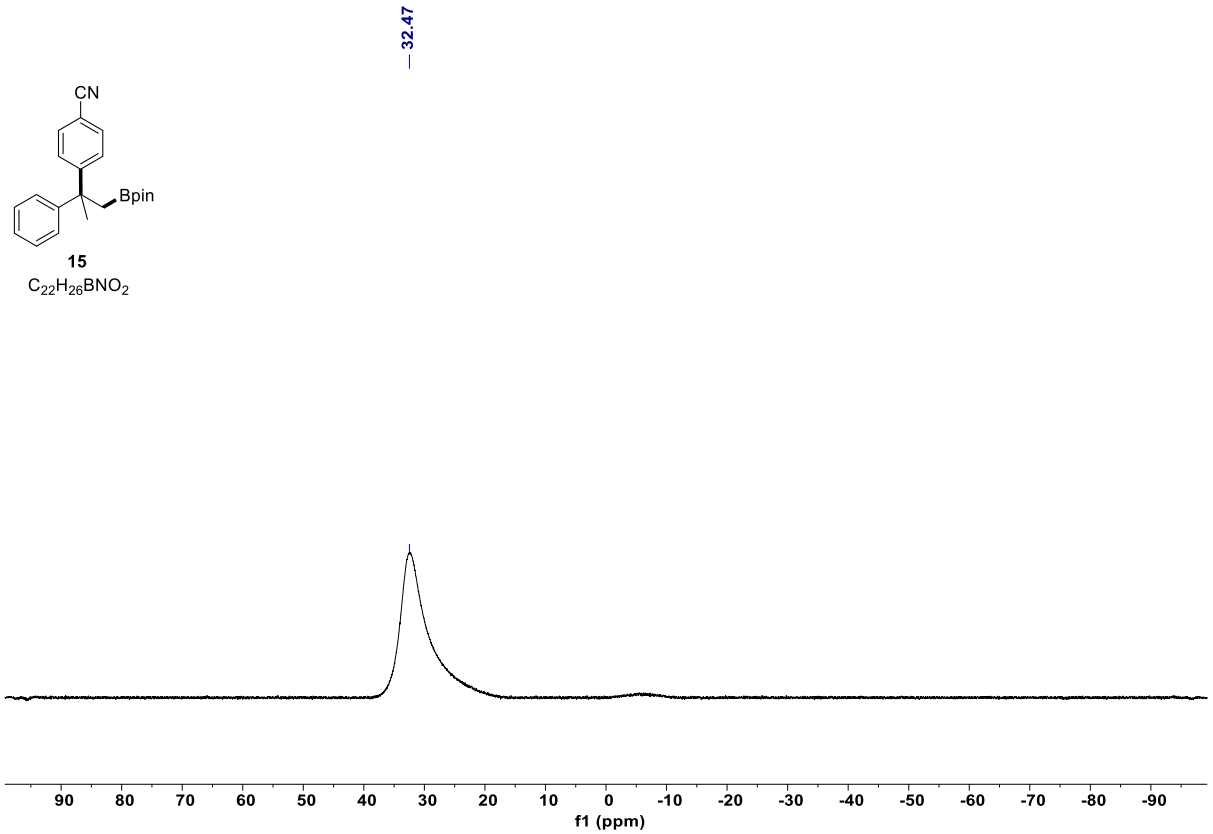
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **14**.



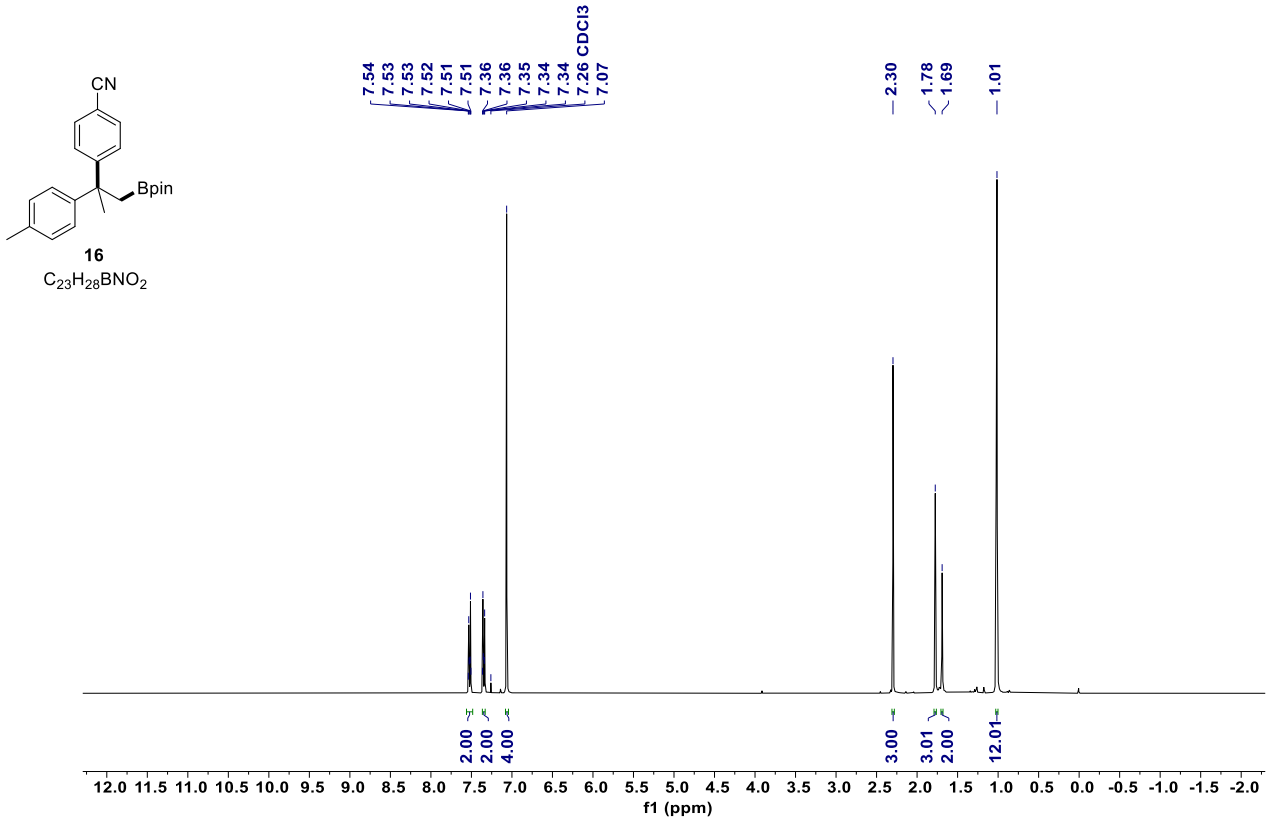
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **15**.



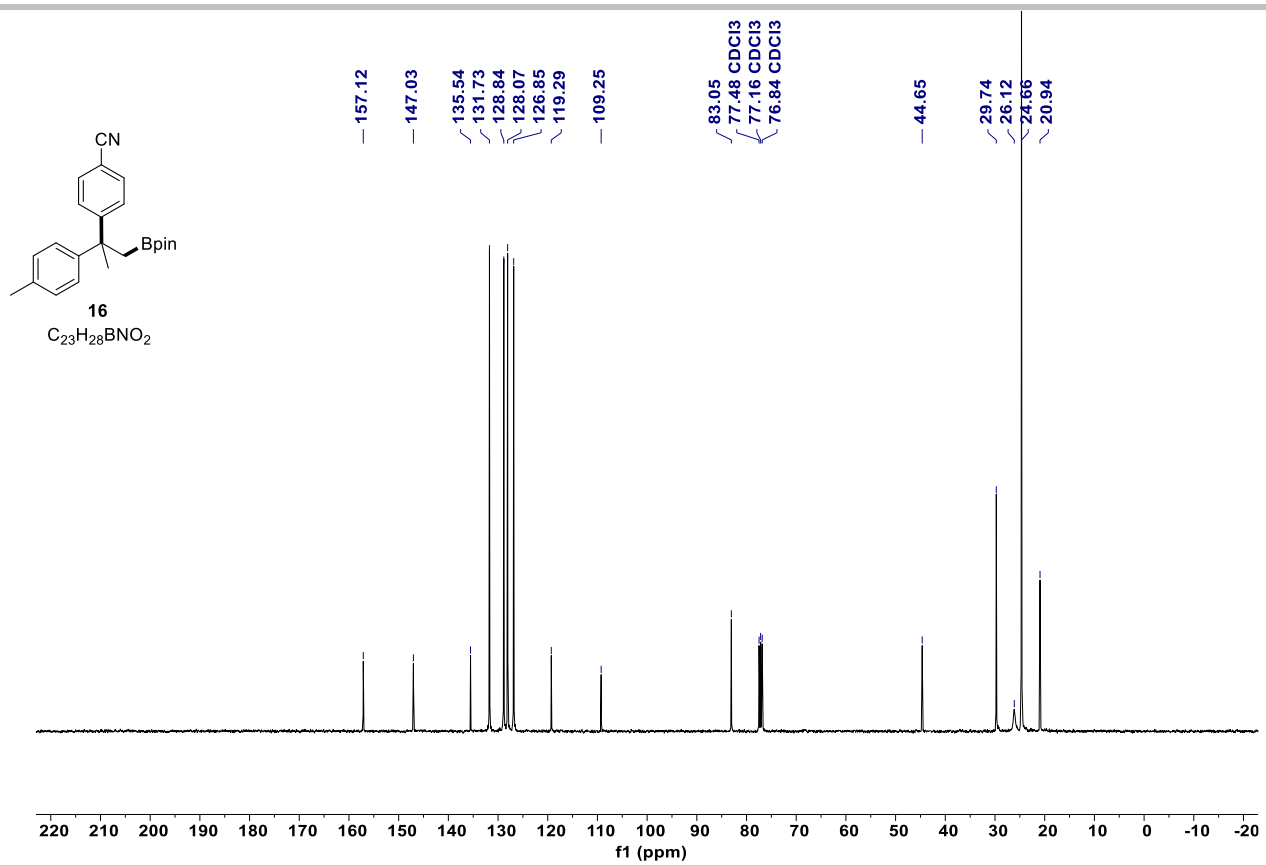
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **15**.



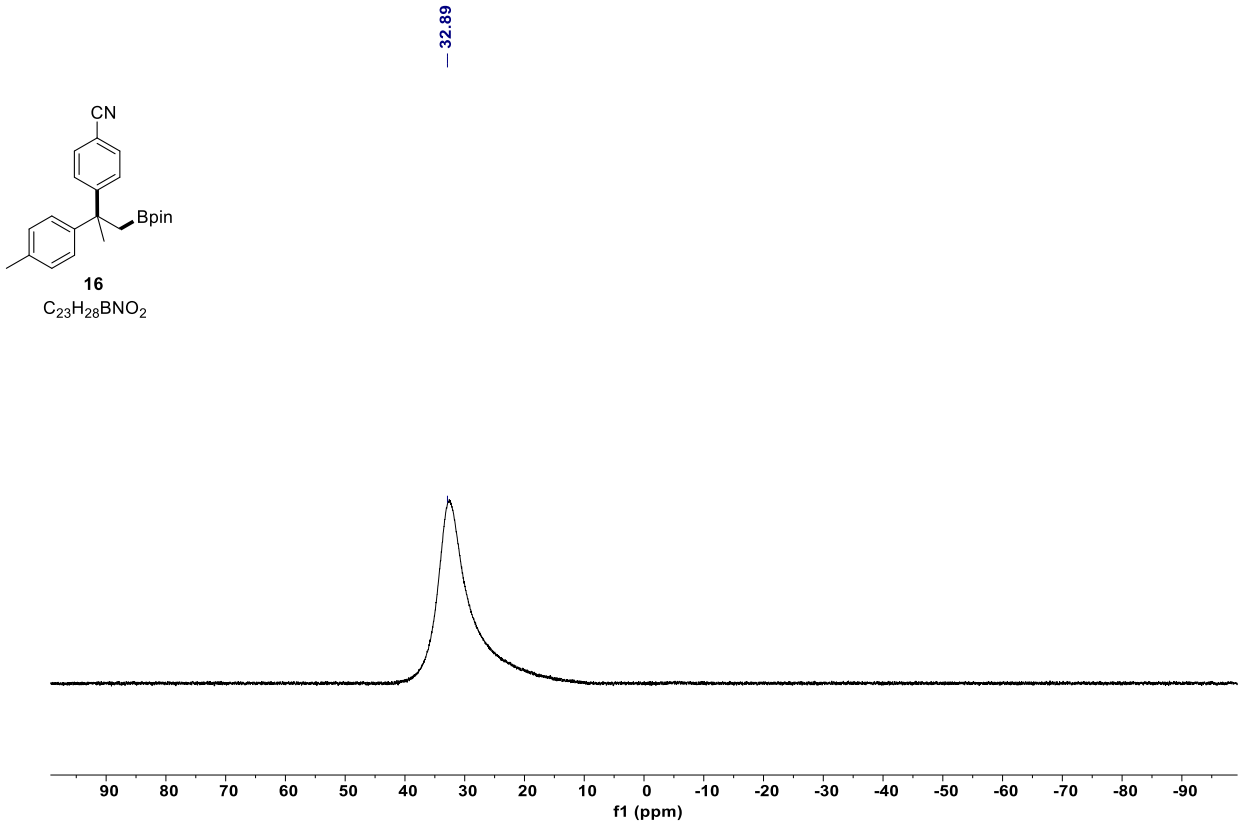
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **15**.



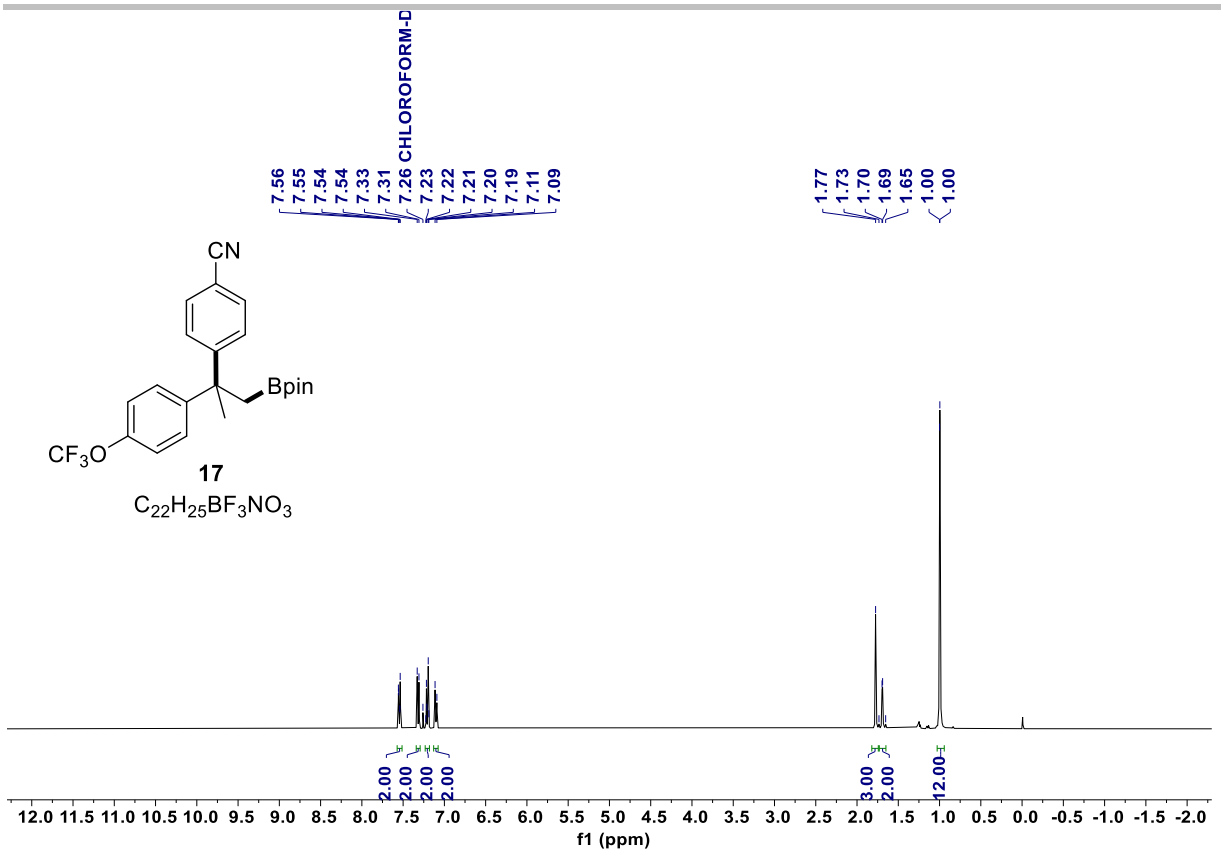
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **16**.



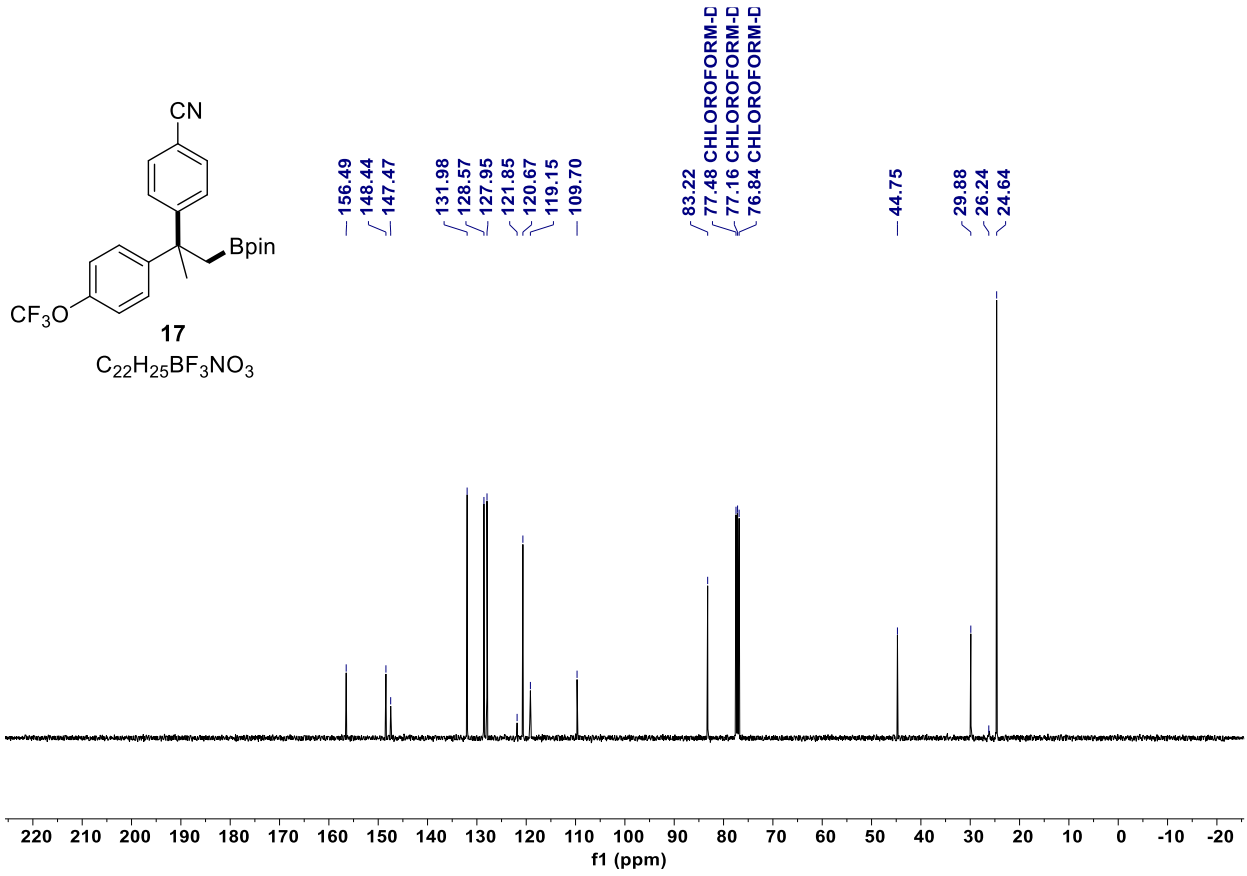
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **16**.



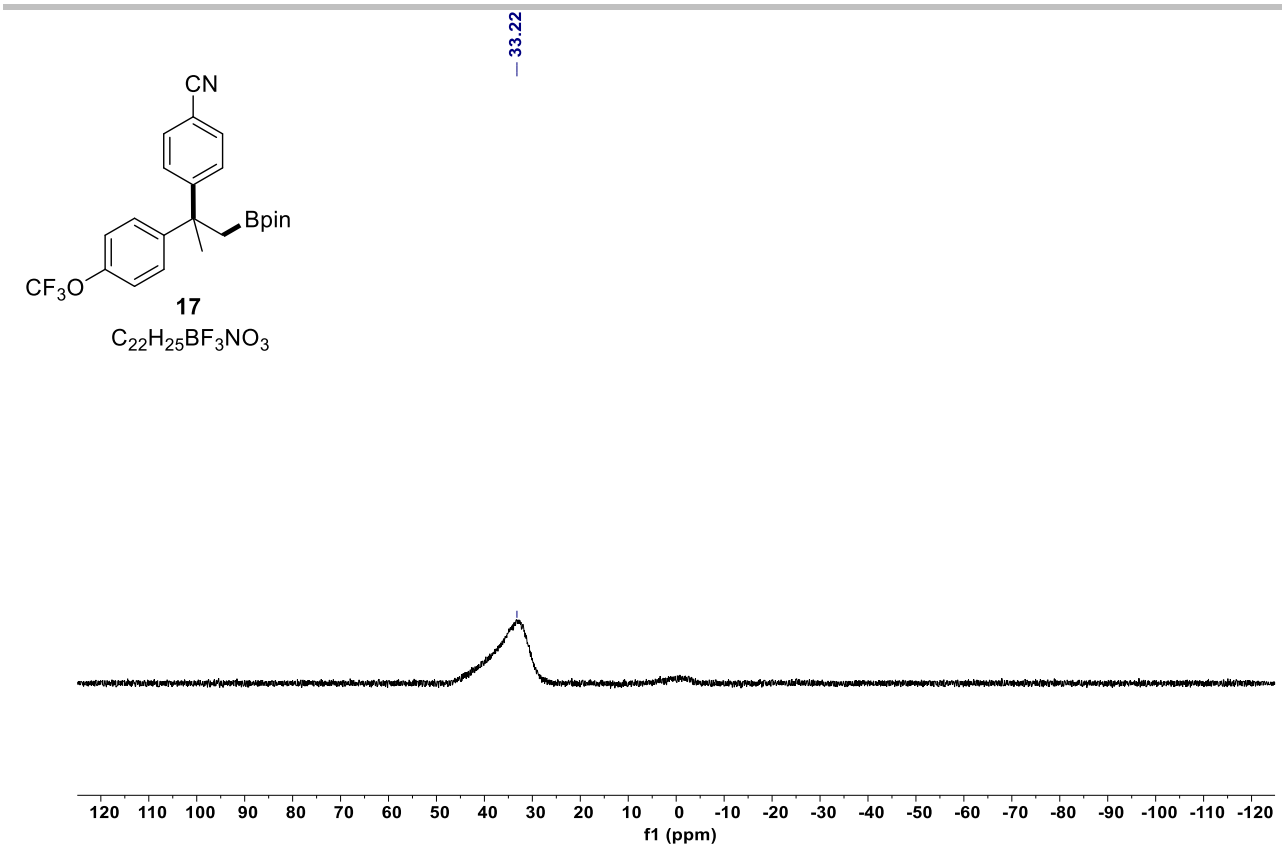
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **16**.



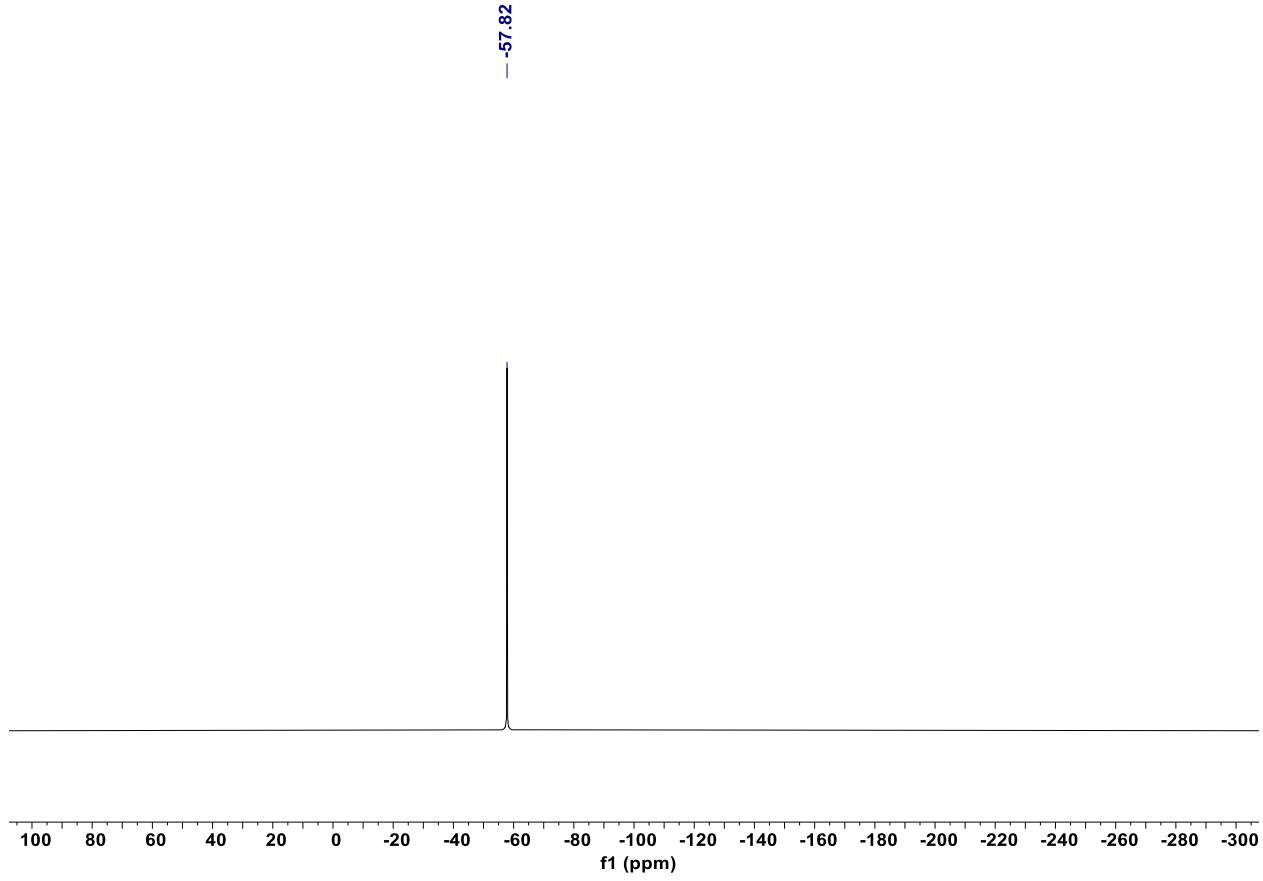
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **17**.



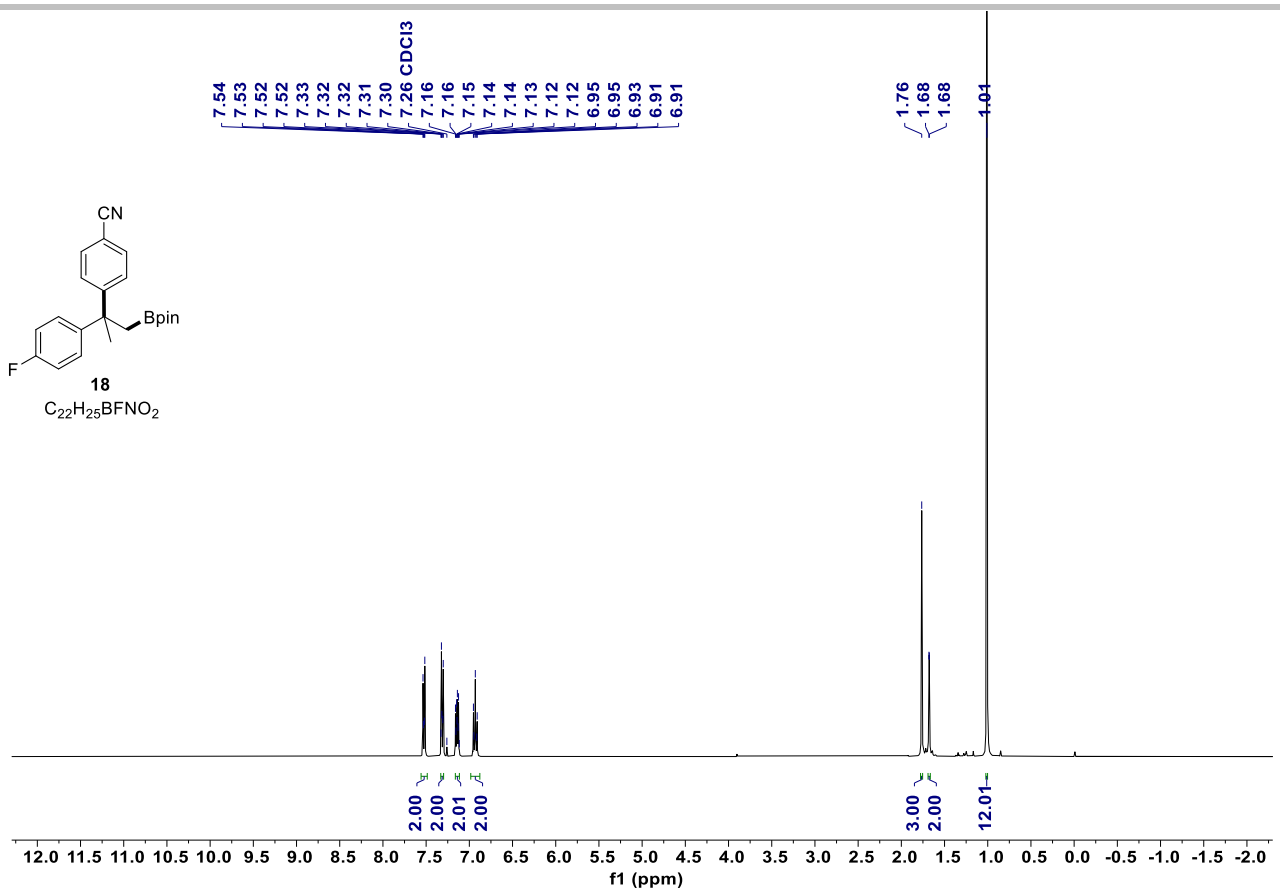
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **17**.



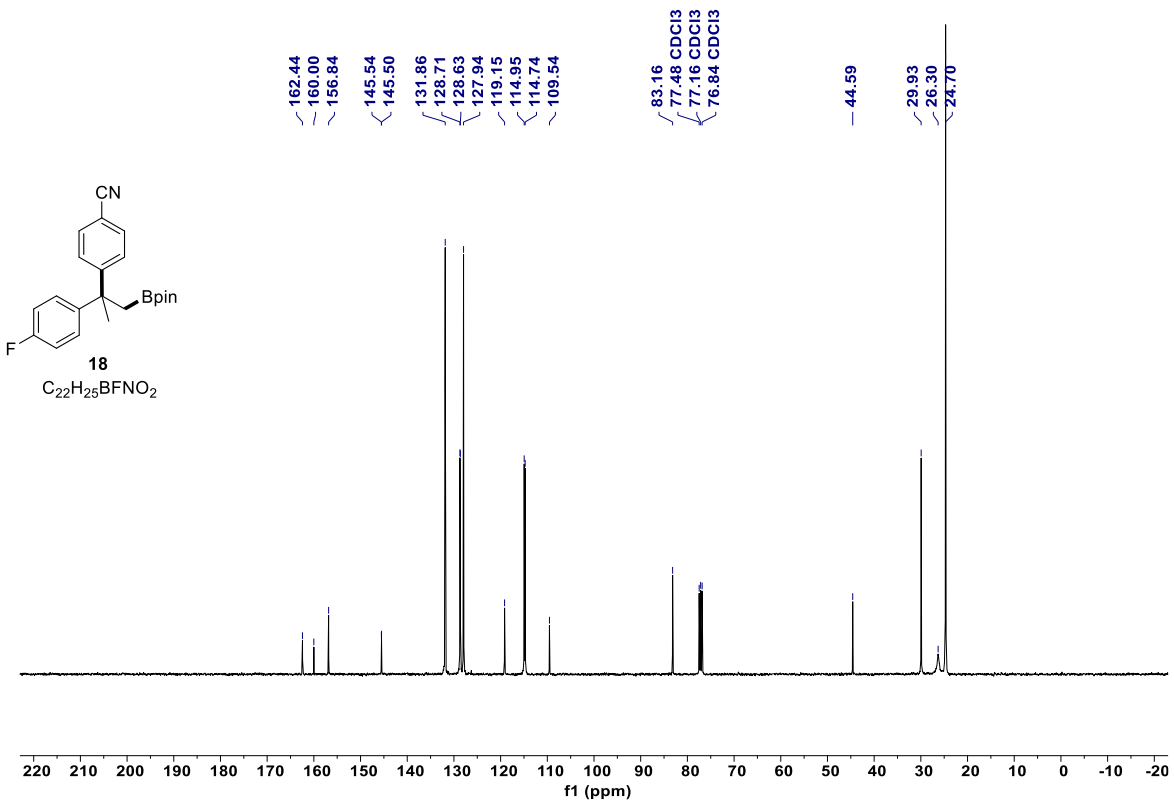
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **17**.



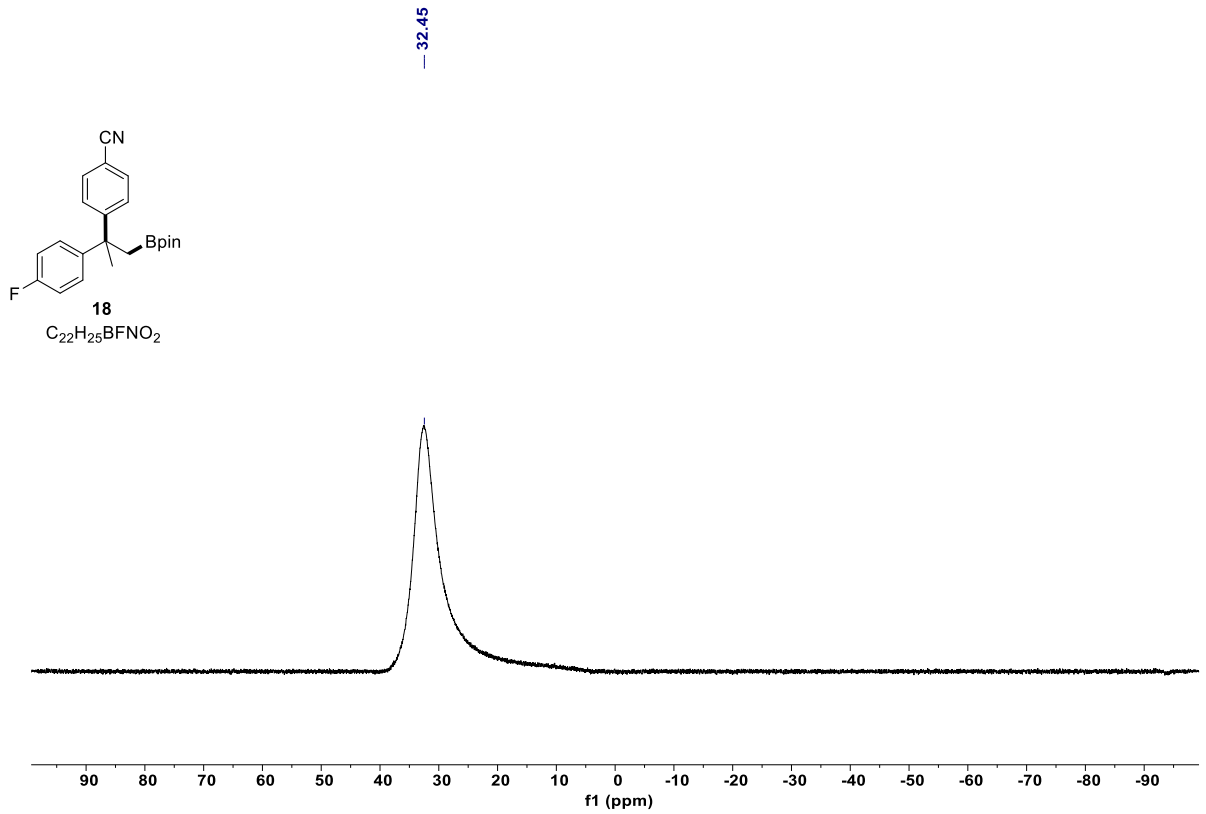
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **17**



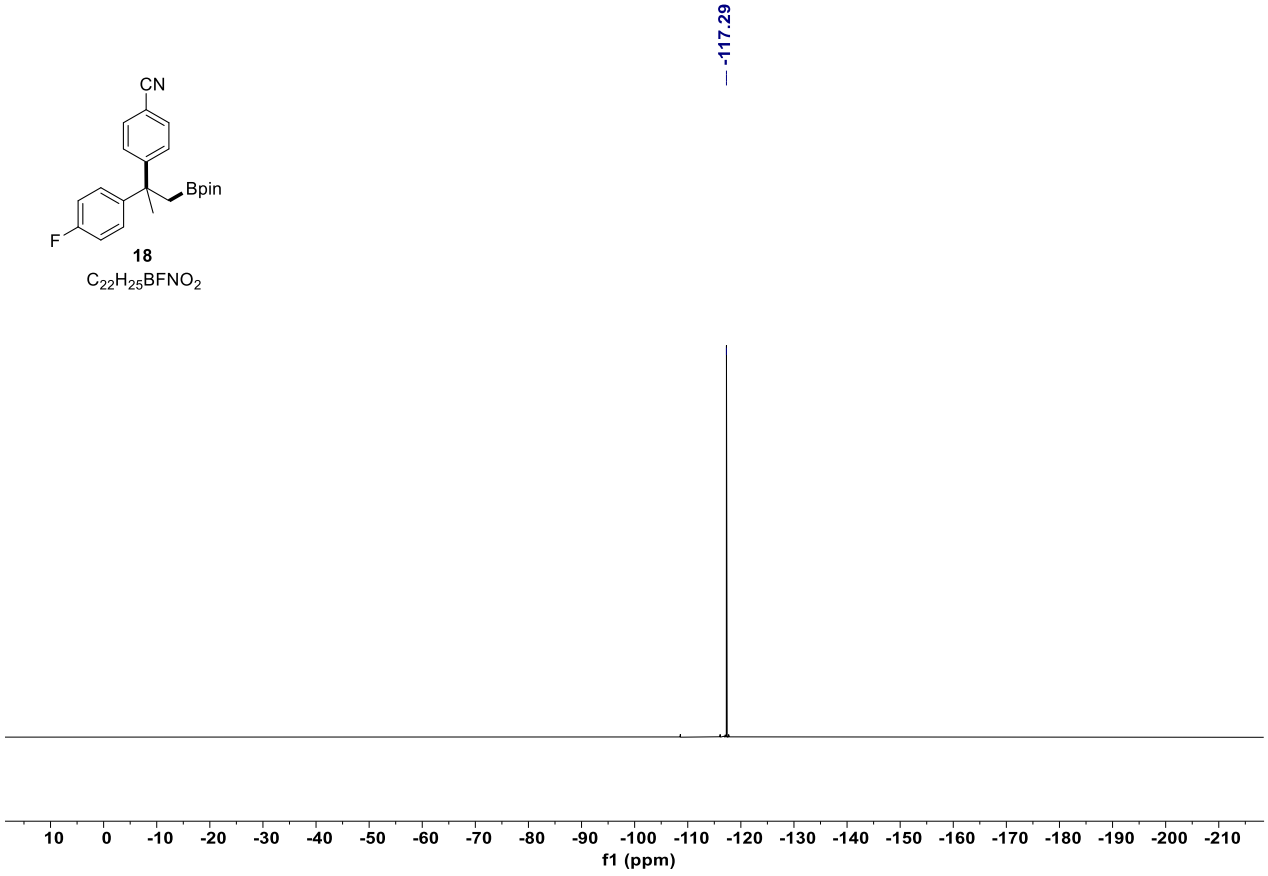
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **18**.



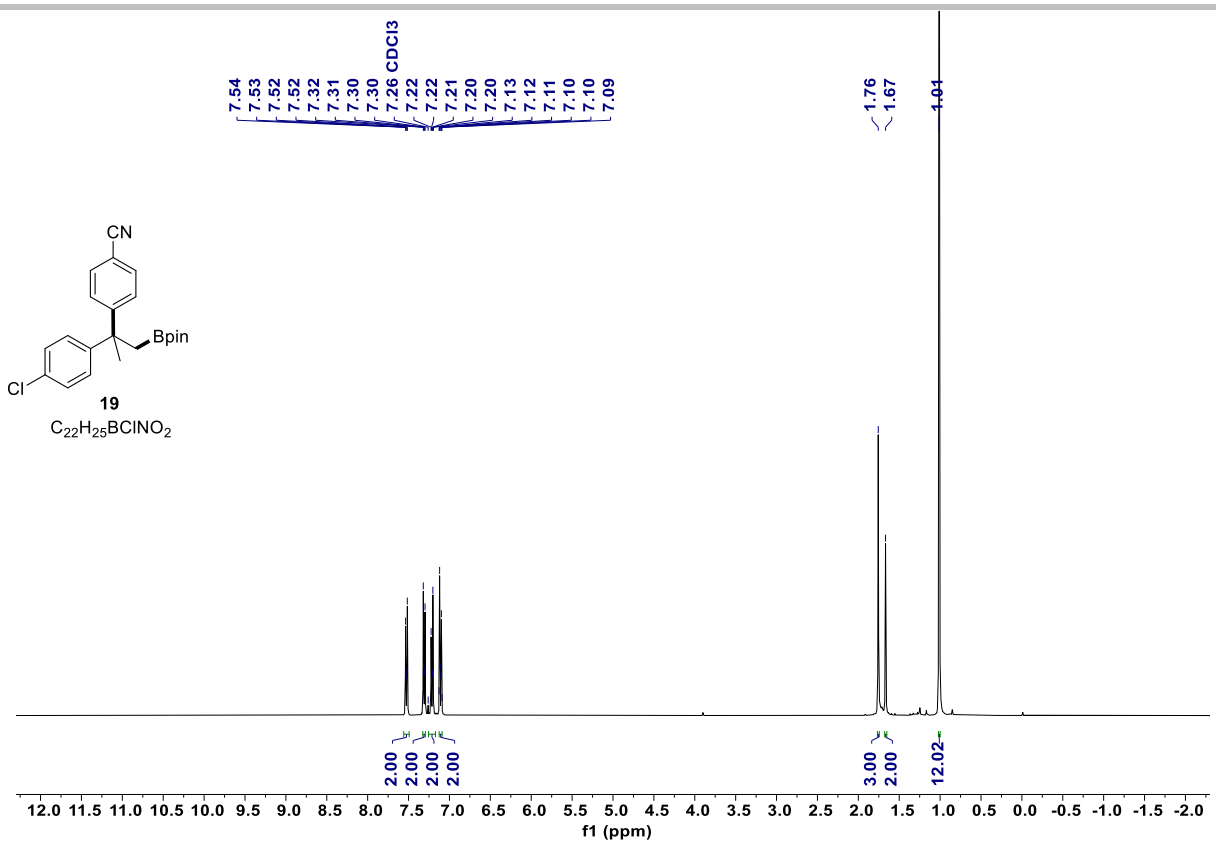
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **18**.



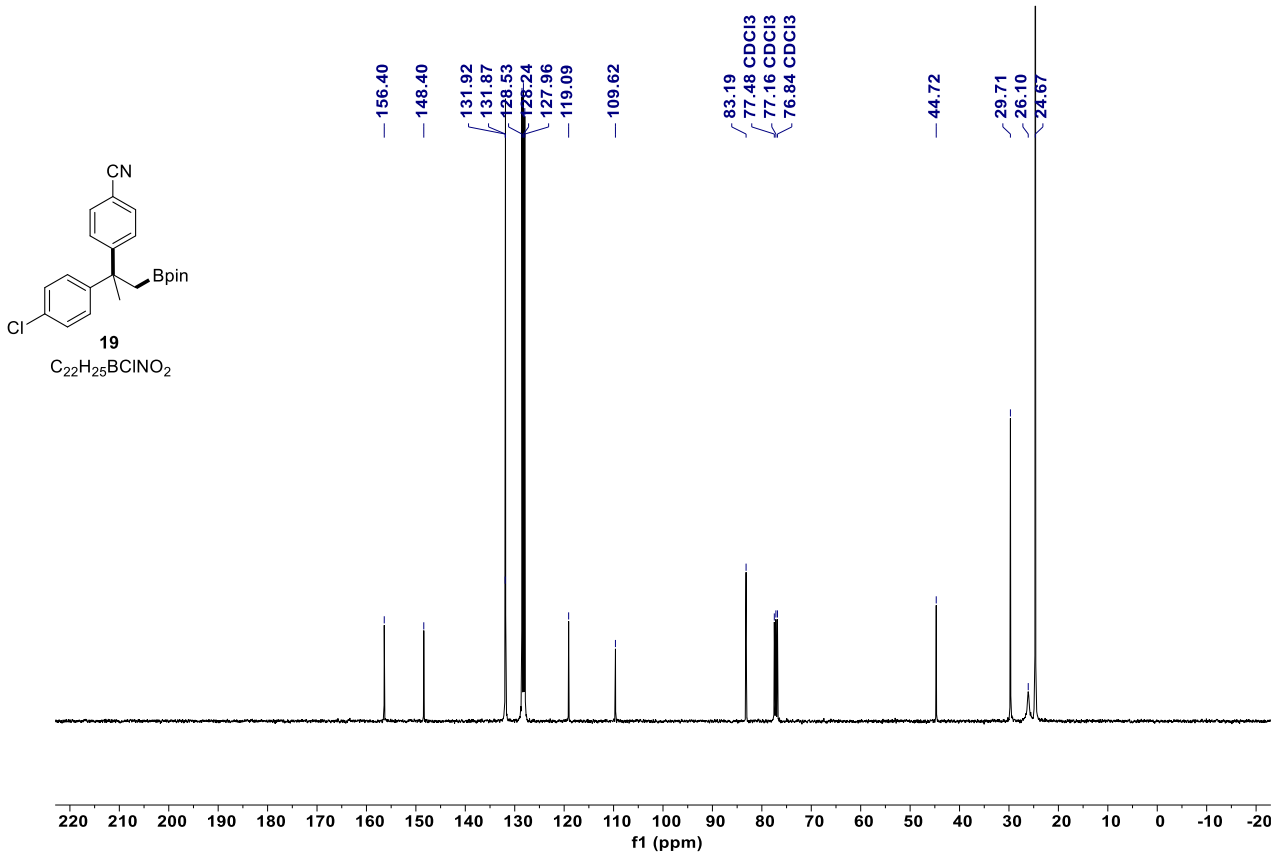
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **18**.



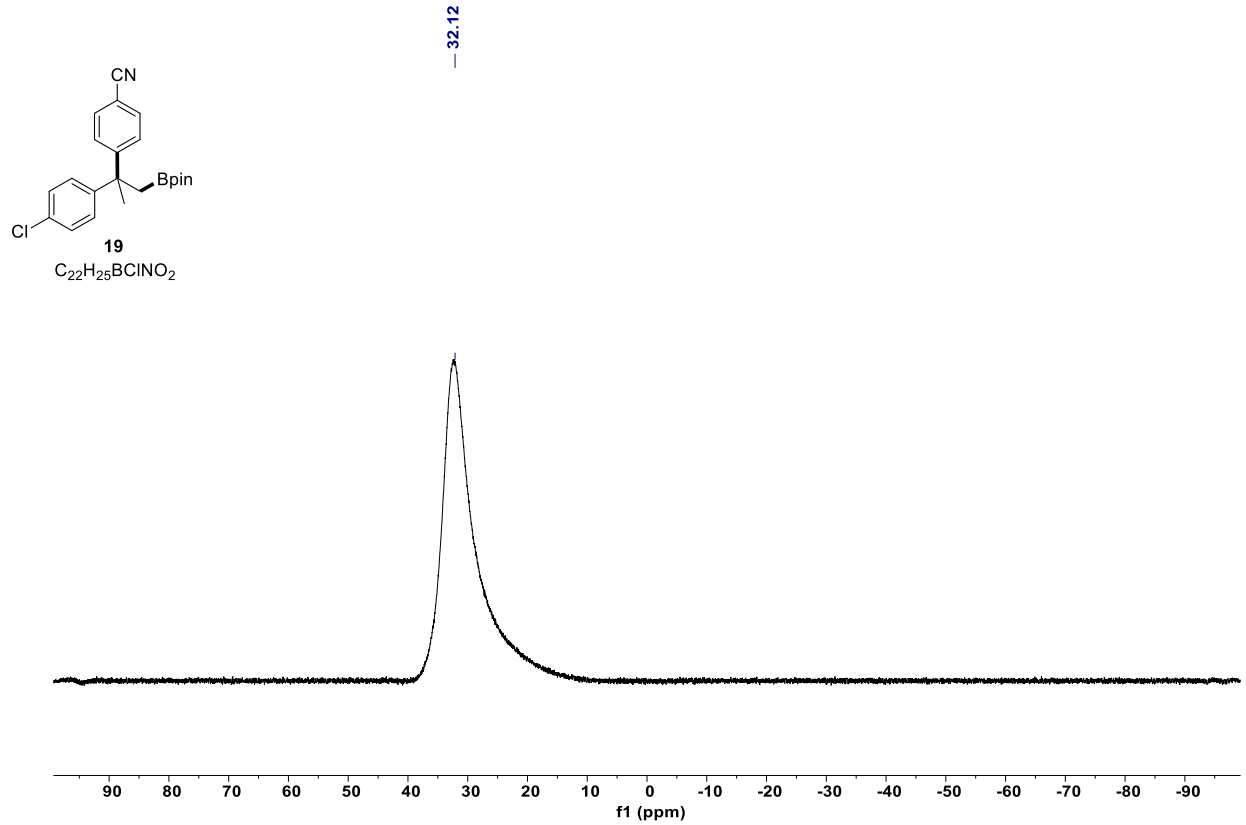
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **18**.



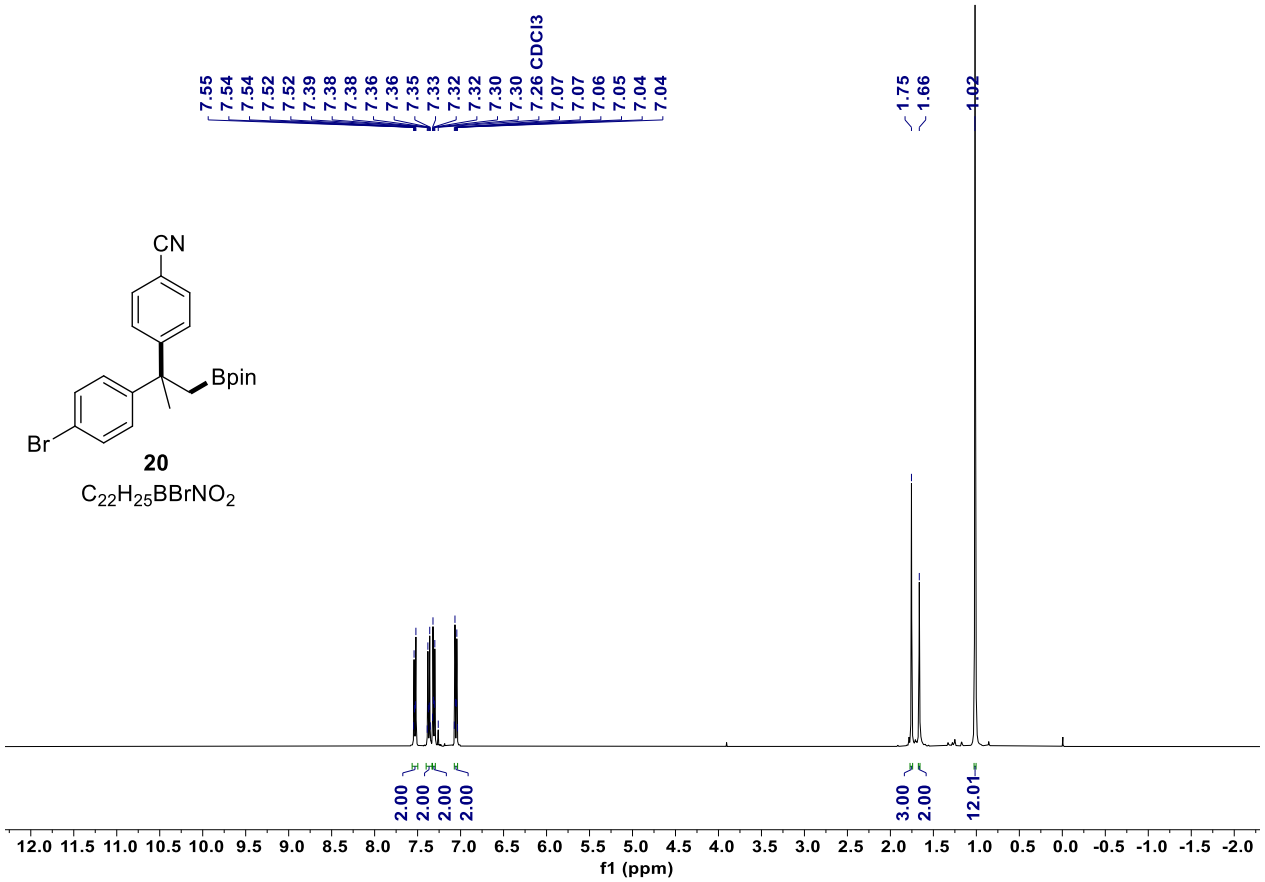
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **19**.



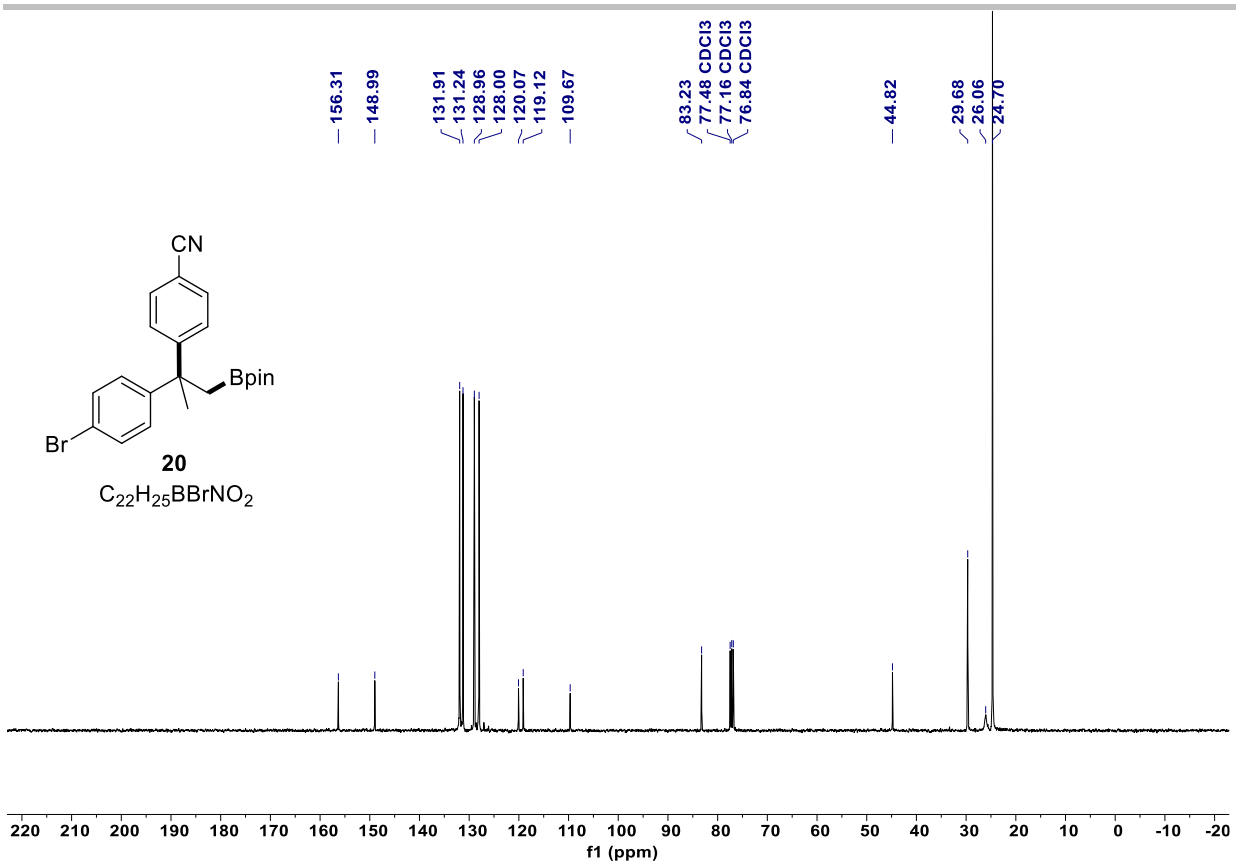
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **19**.



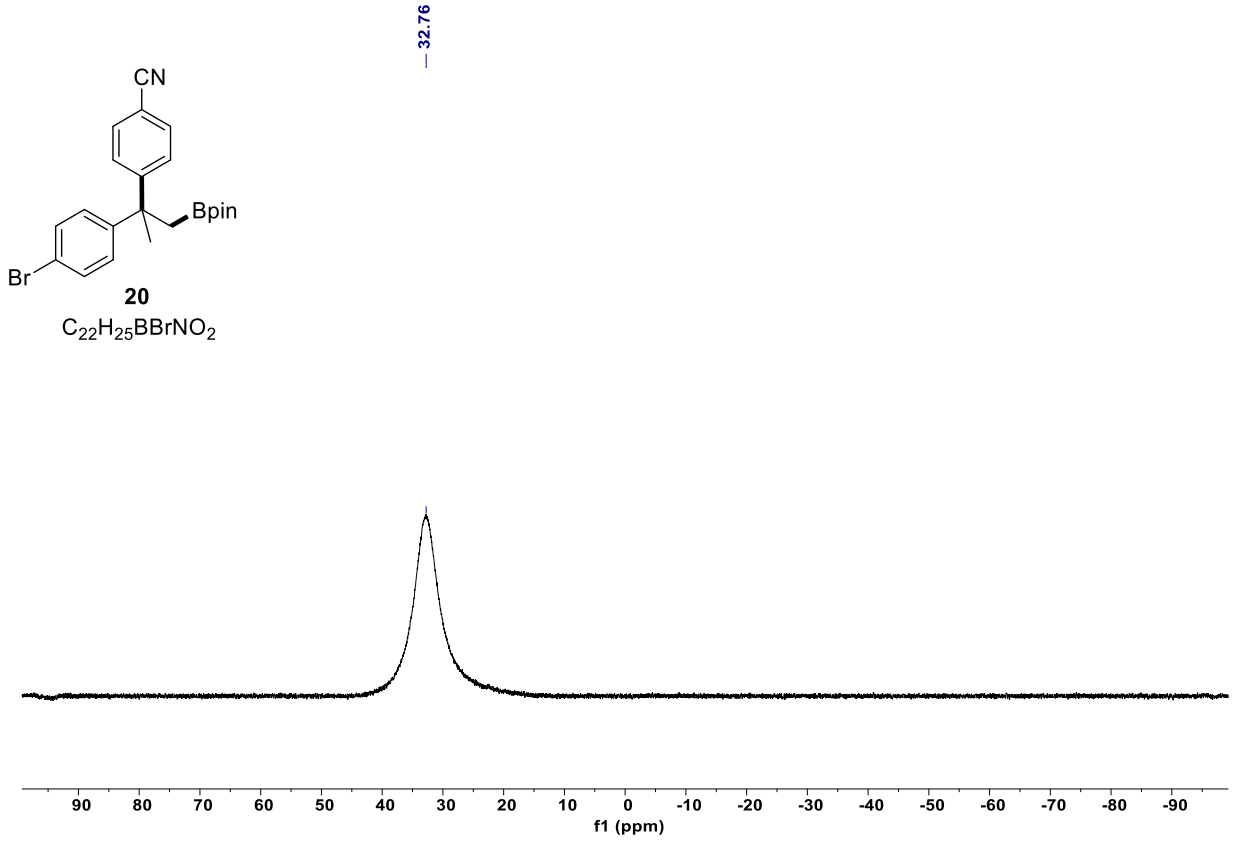
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **19**.



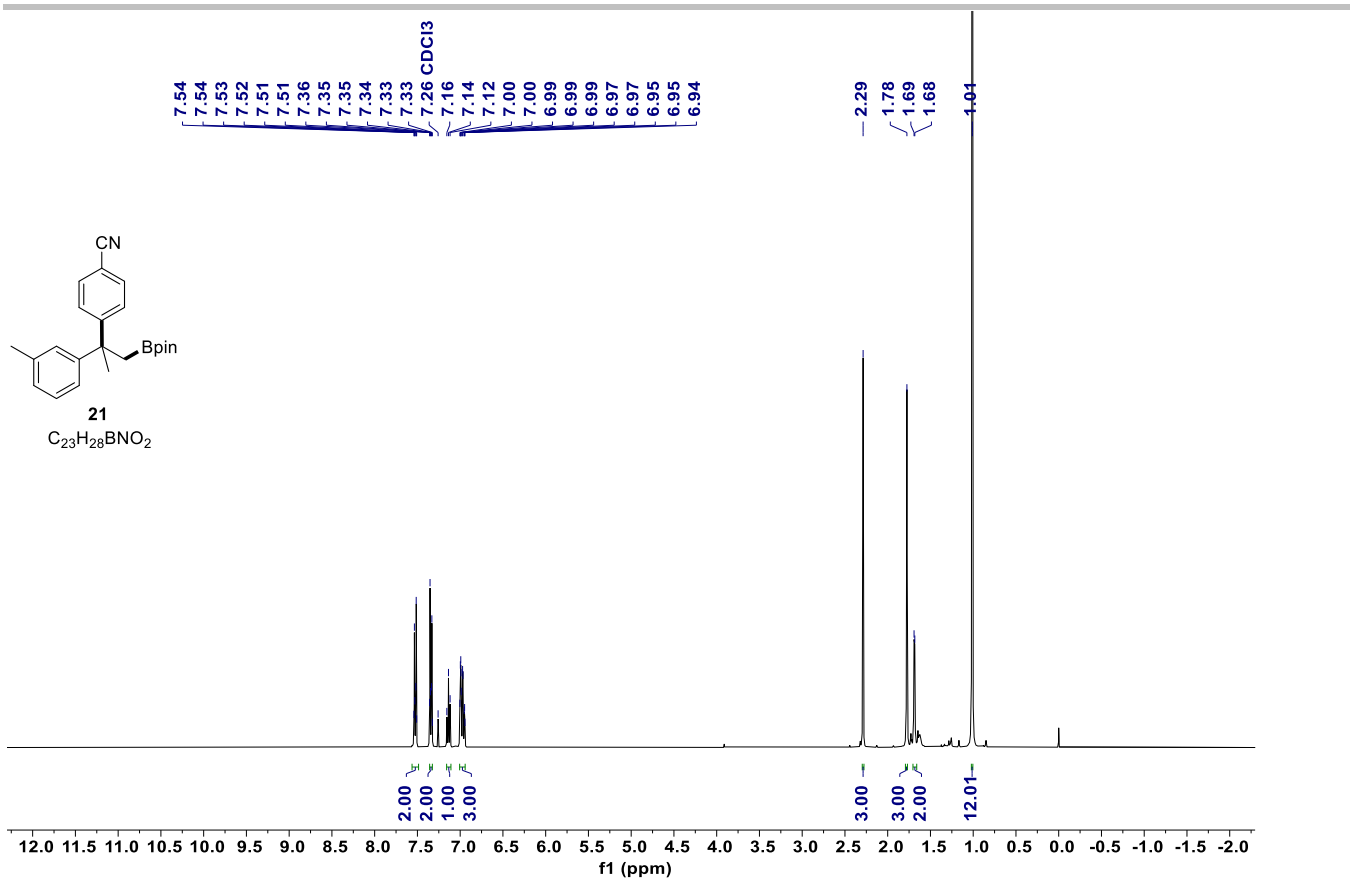
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **20**.



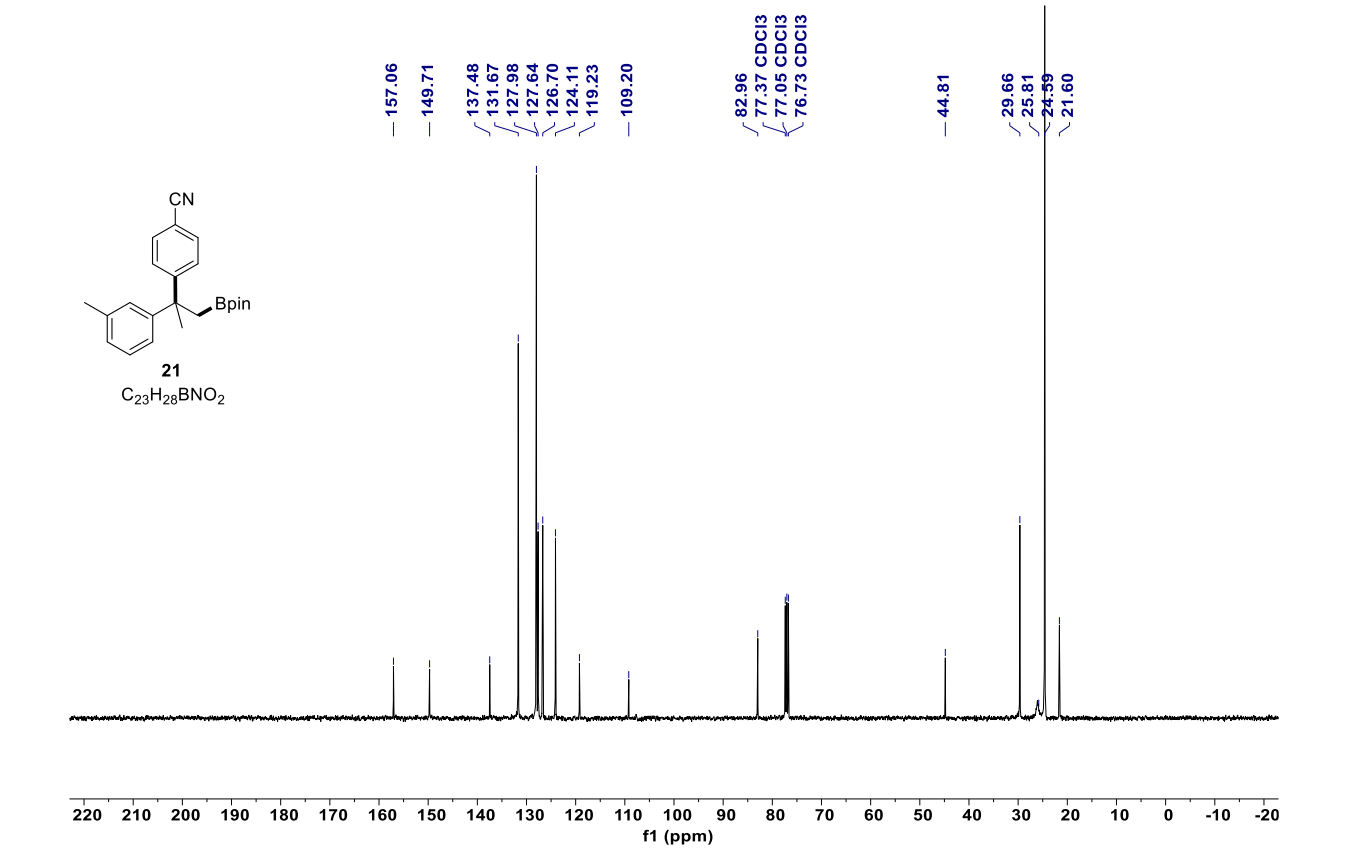
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **20**.



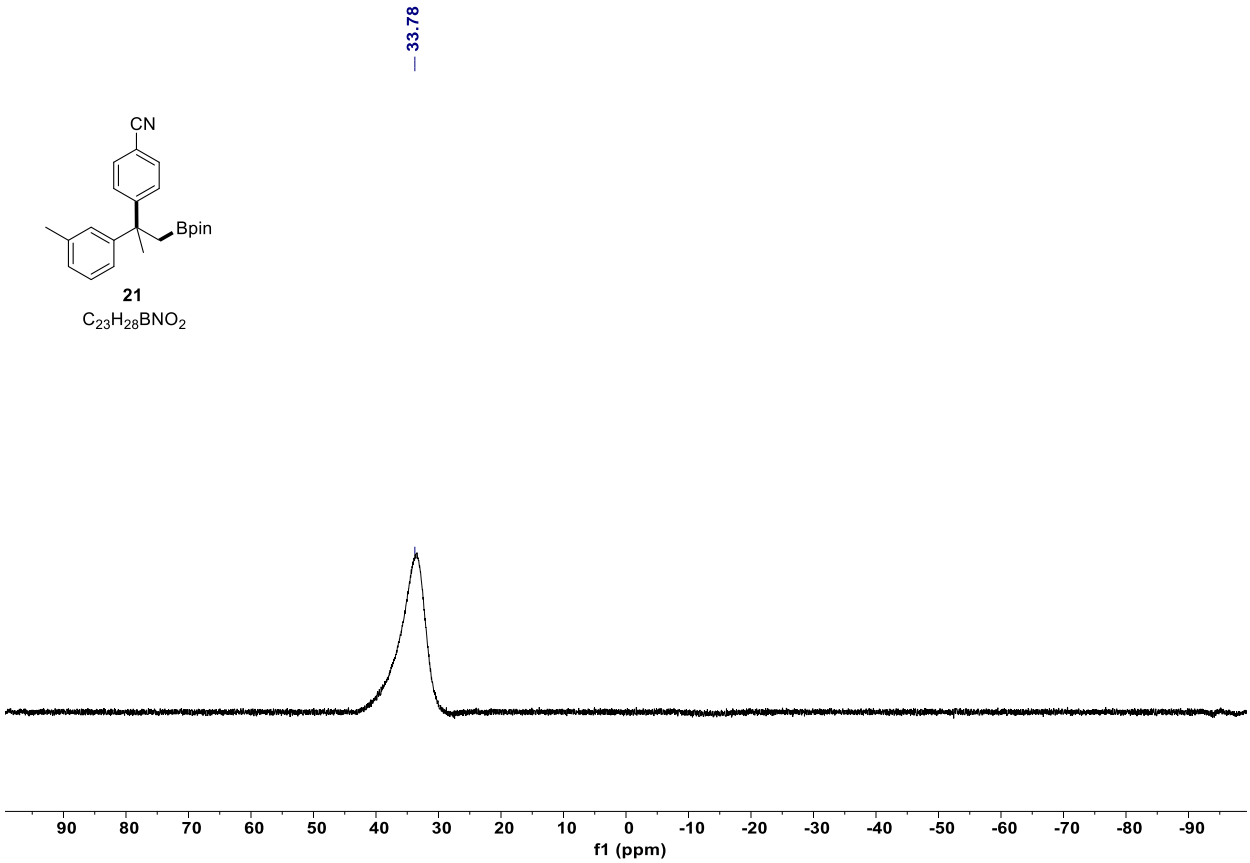
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **20**.



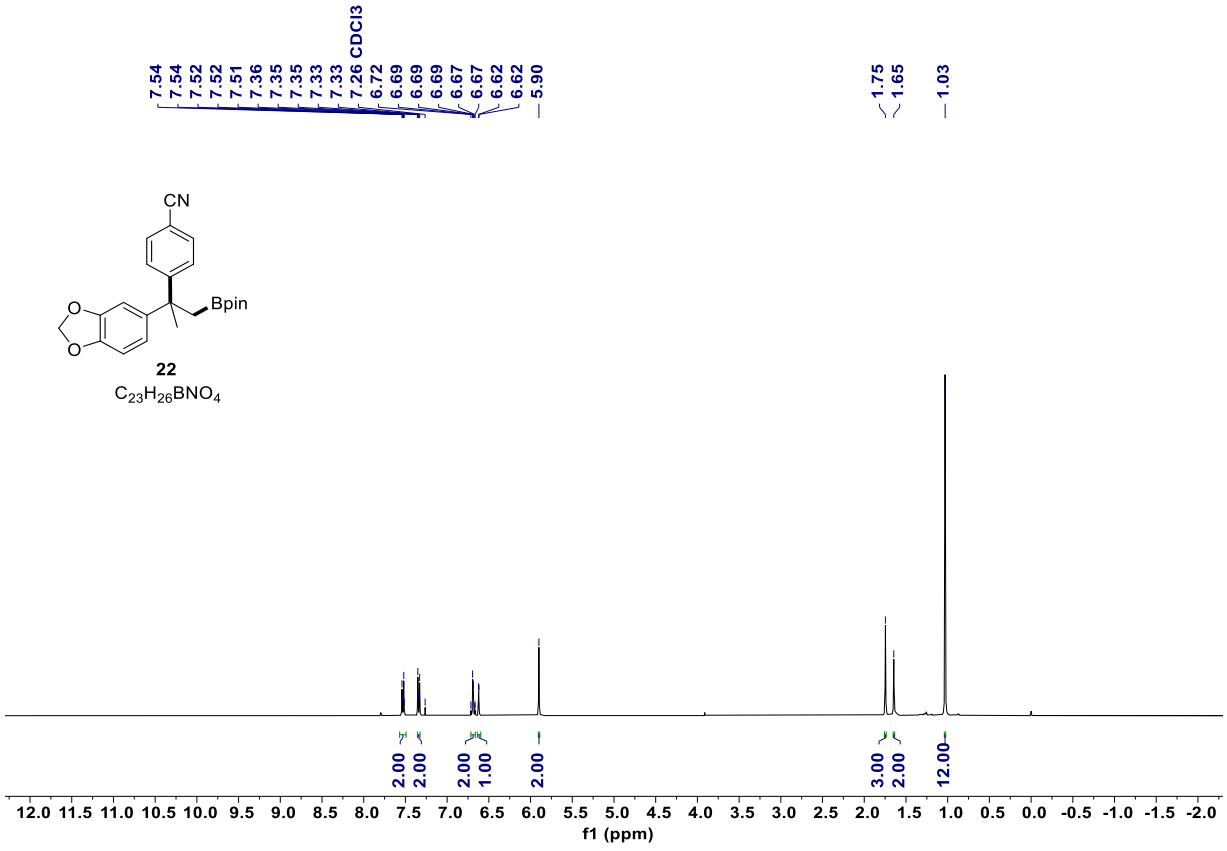
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **21**.



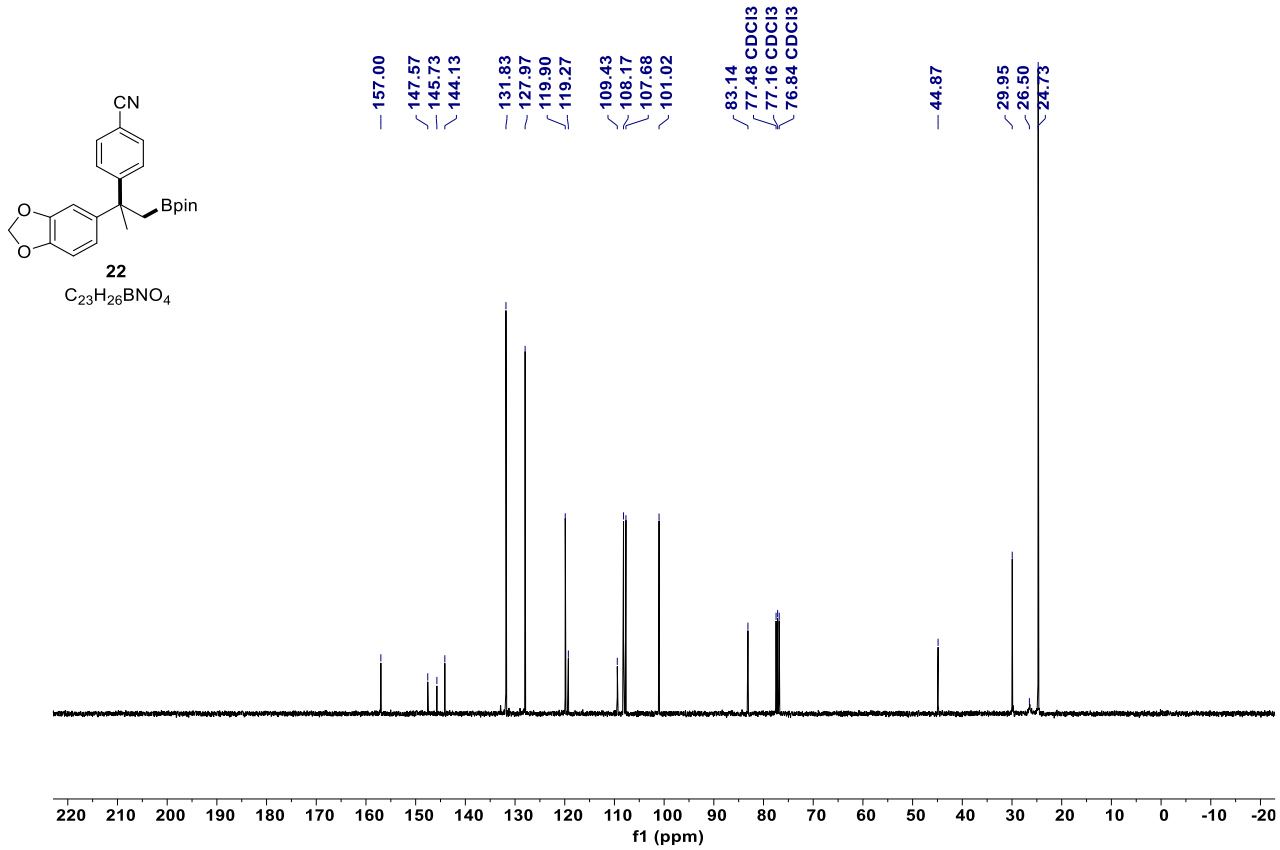
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **21**.



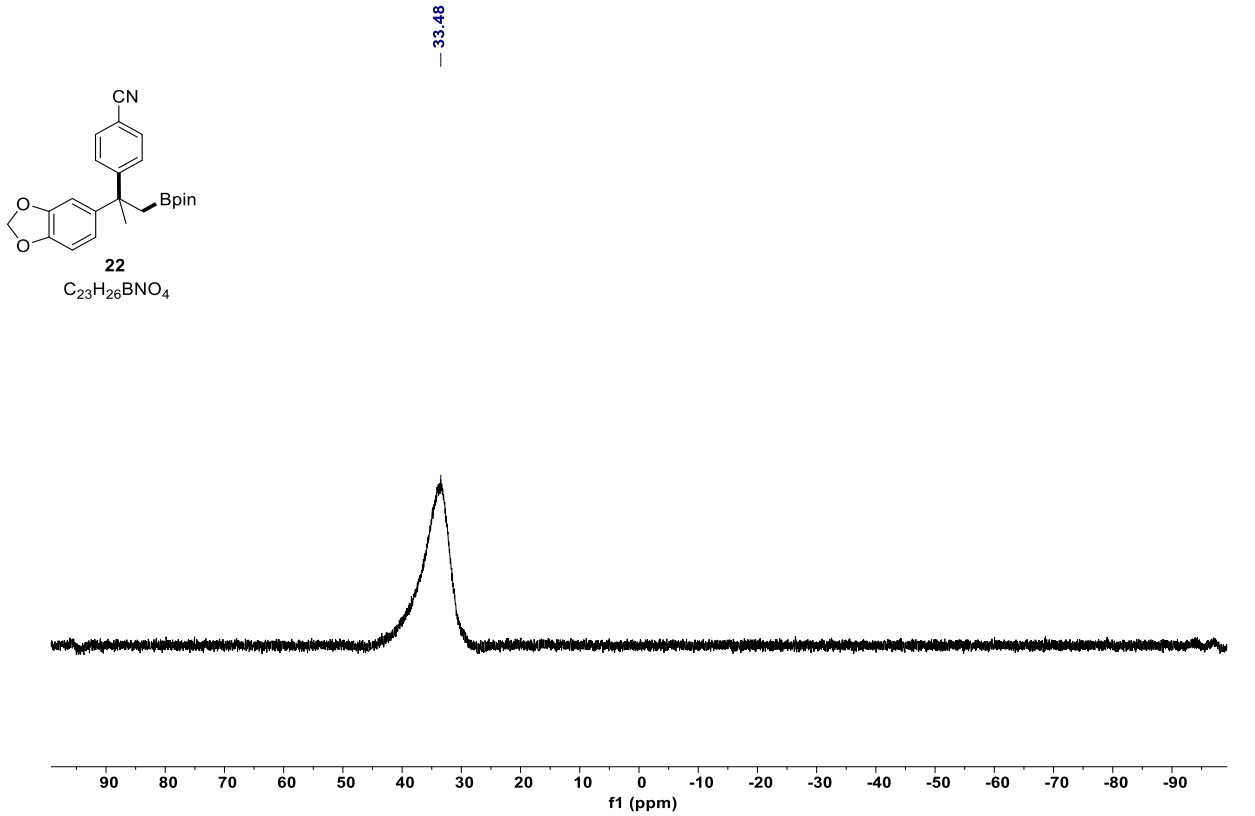
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **21**.



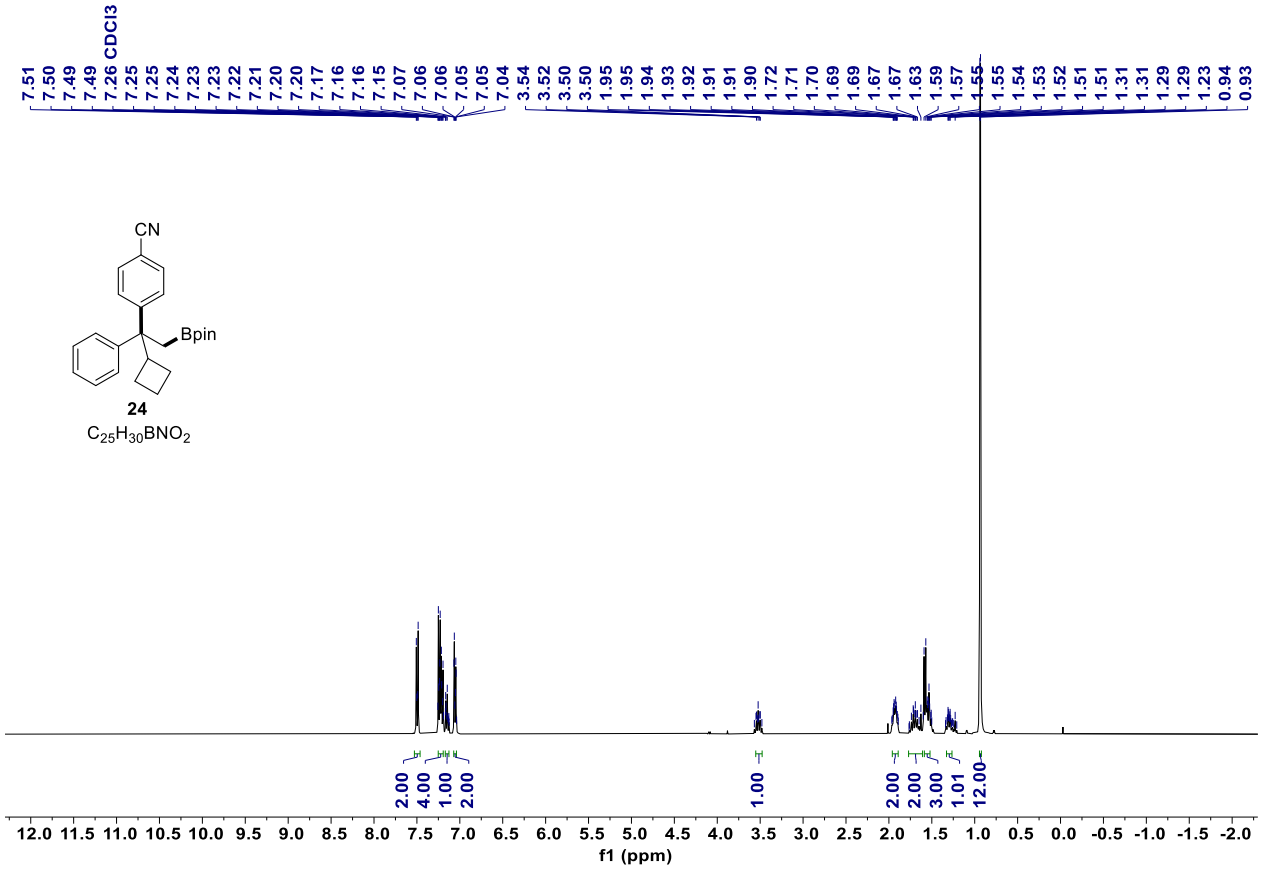
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **22**.



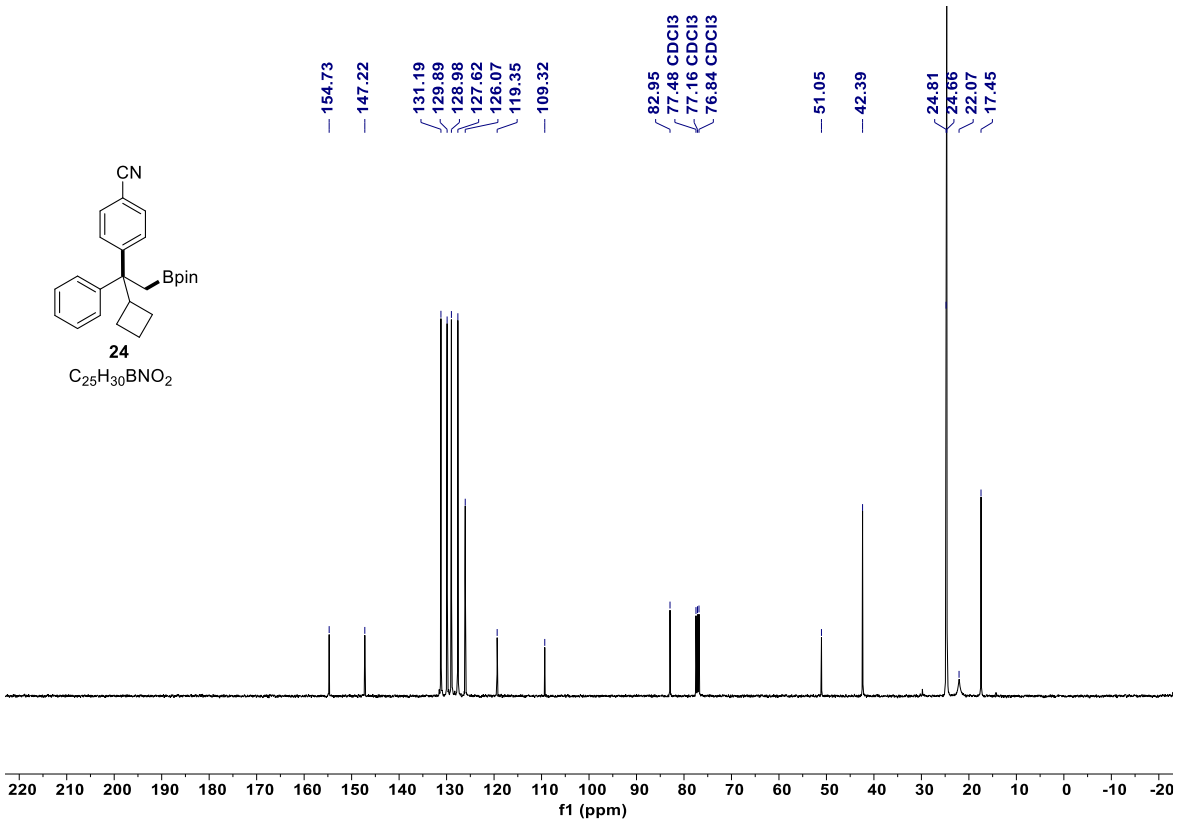
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **22**.



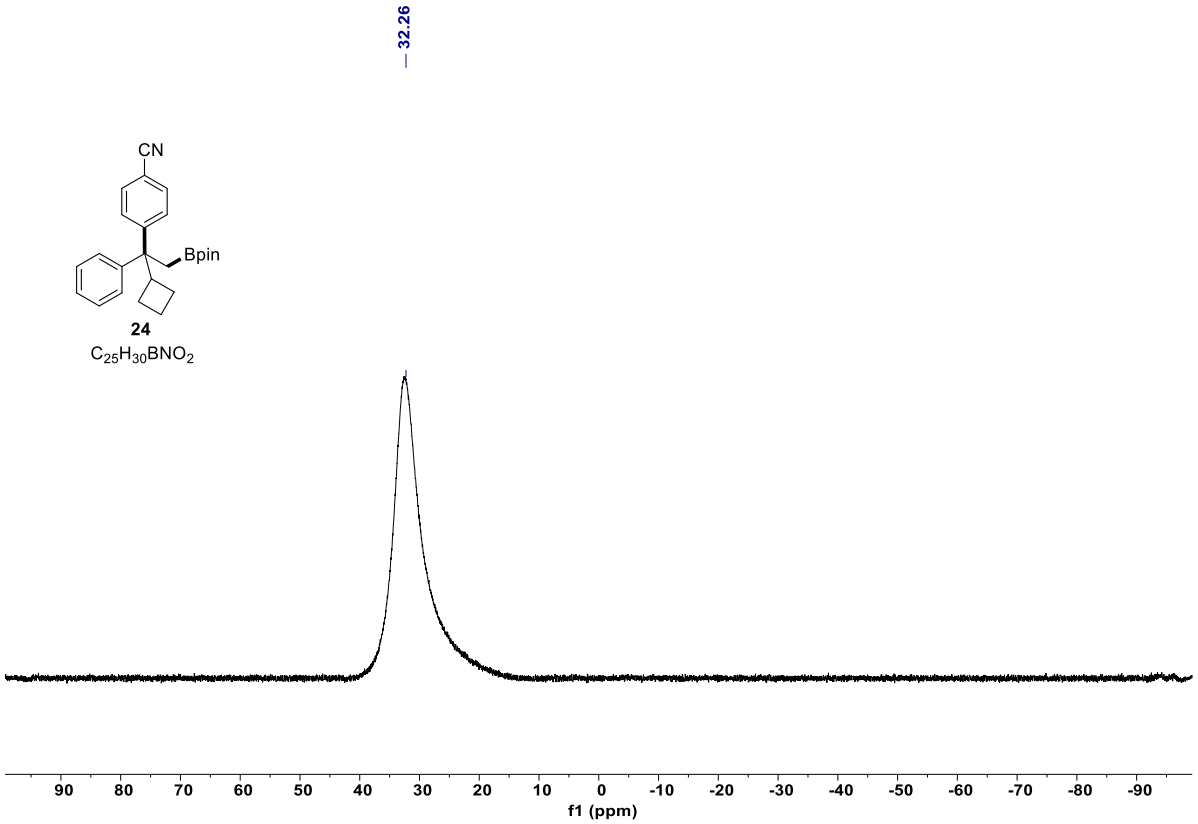
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **22**.



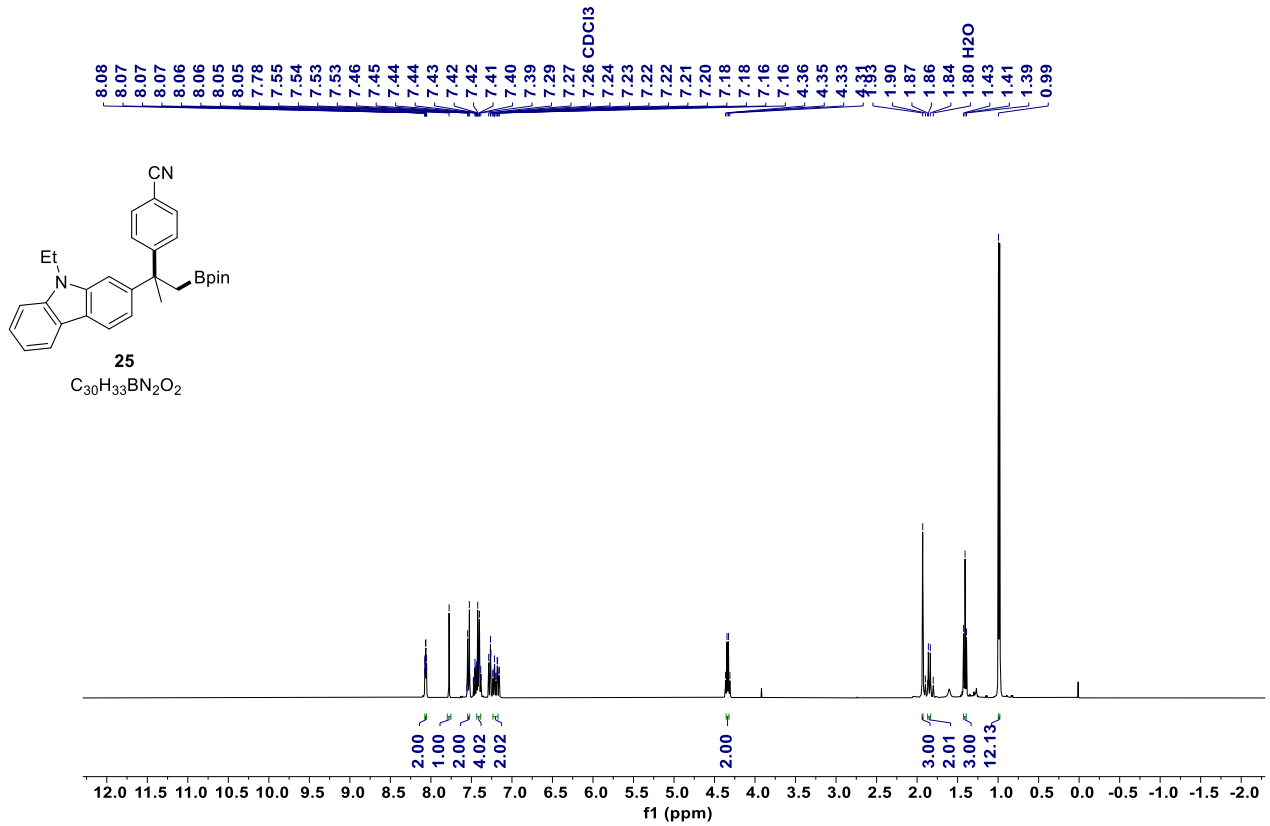
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **24**.



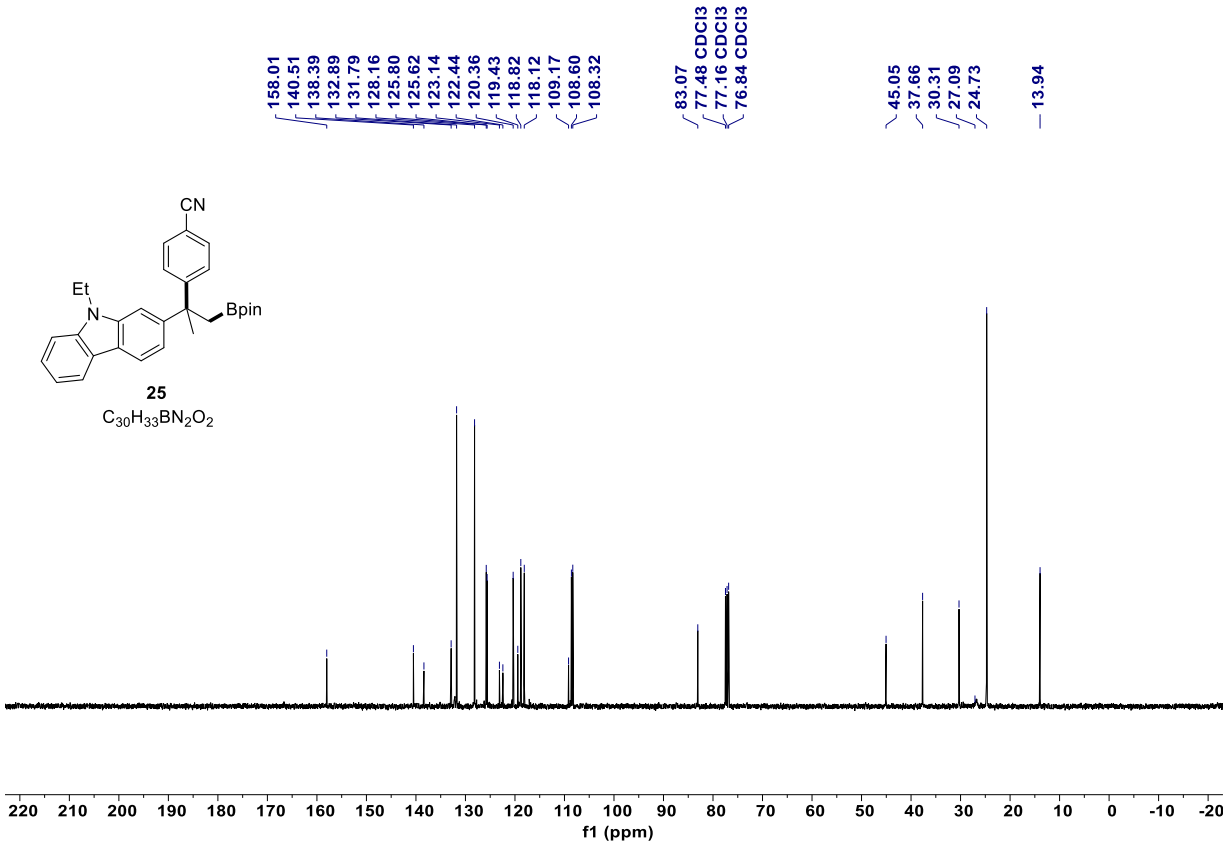
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **24**.



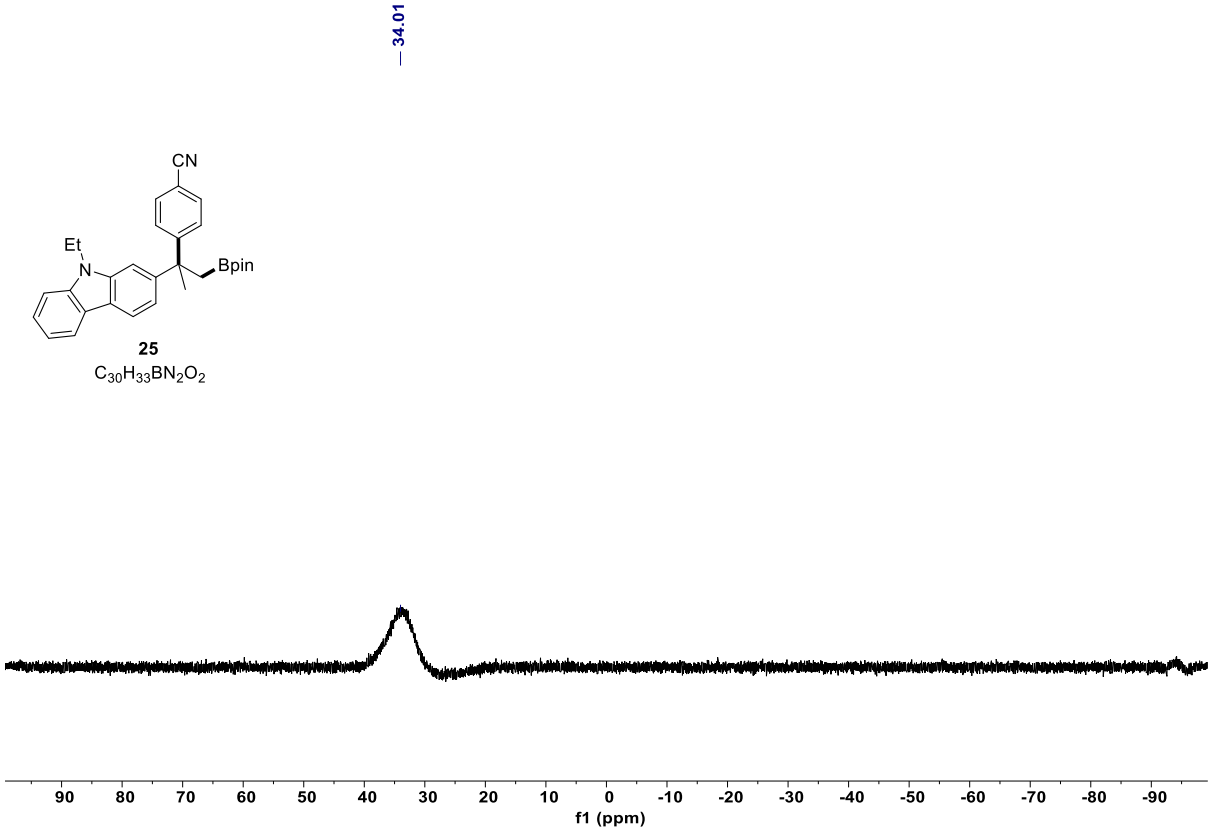
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **24**.



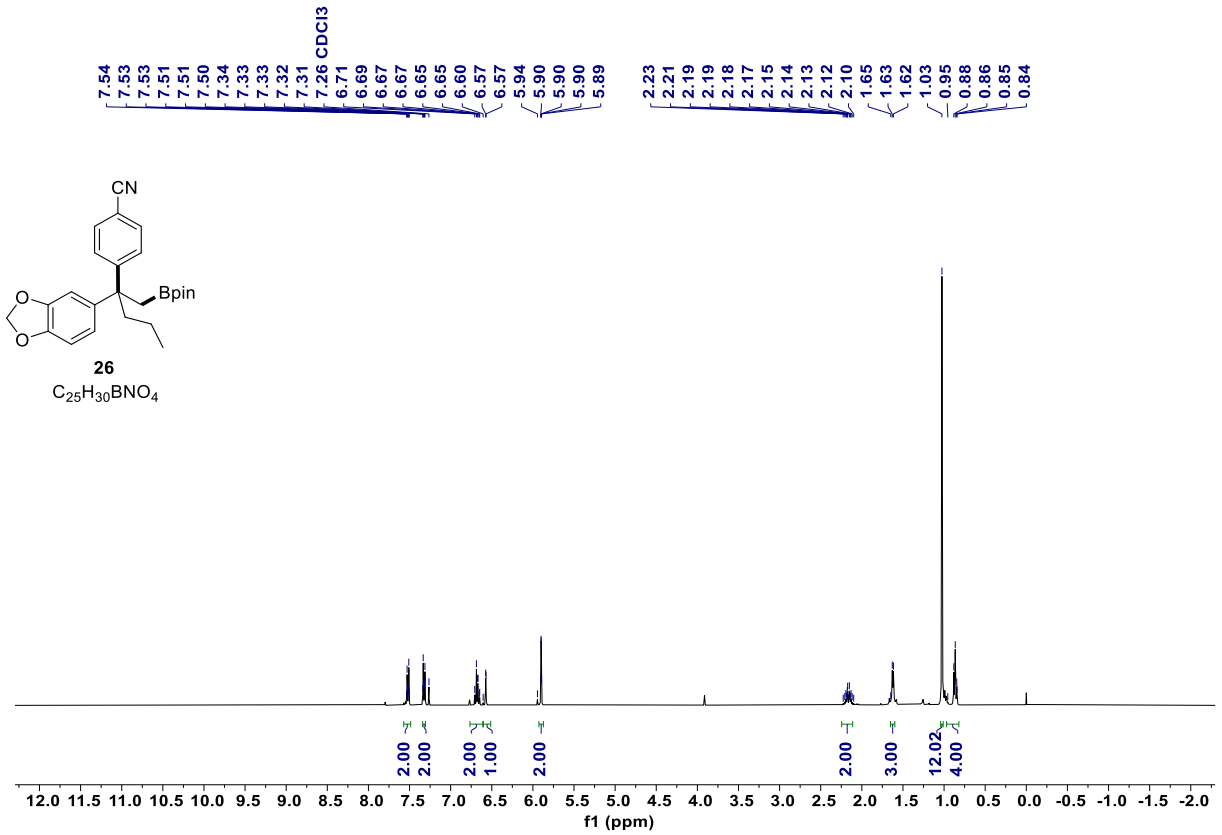
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **25**.



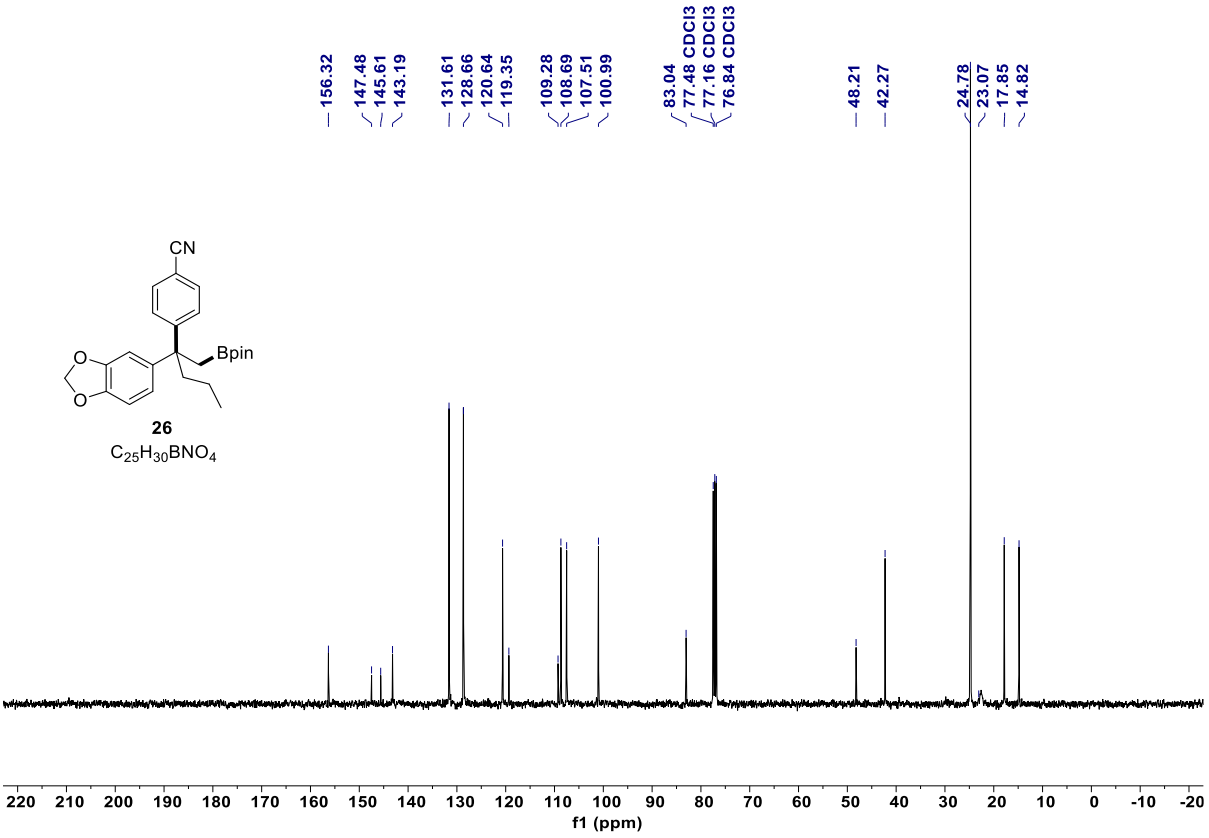
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **25**.



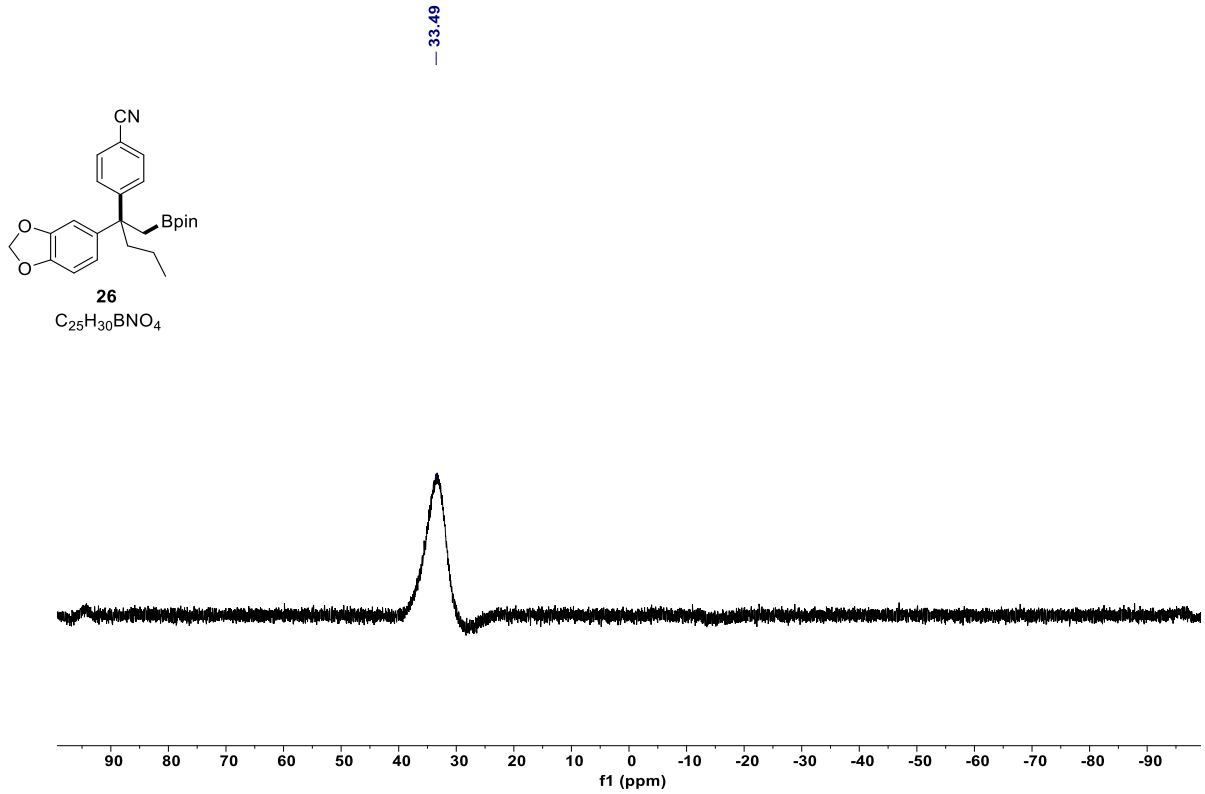
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **25**.



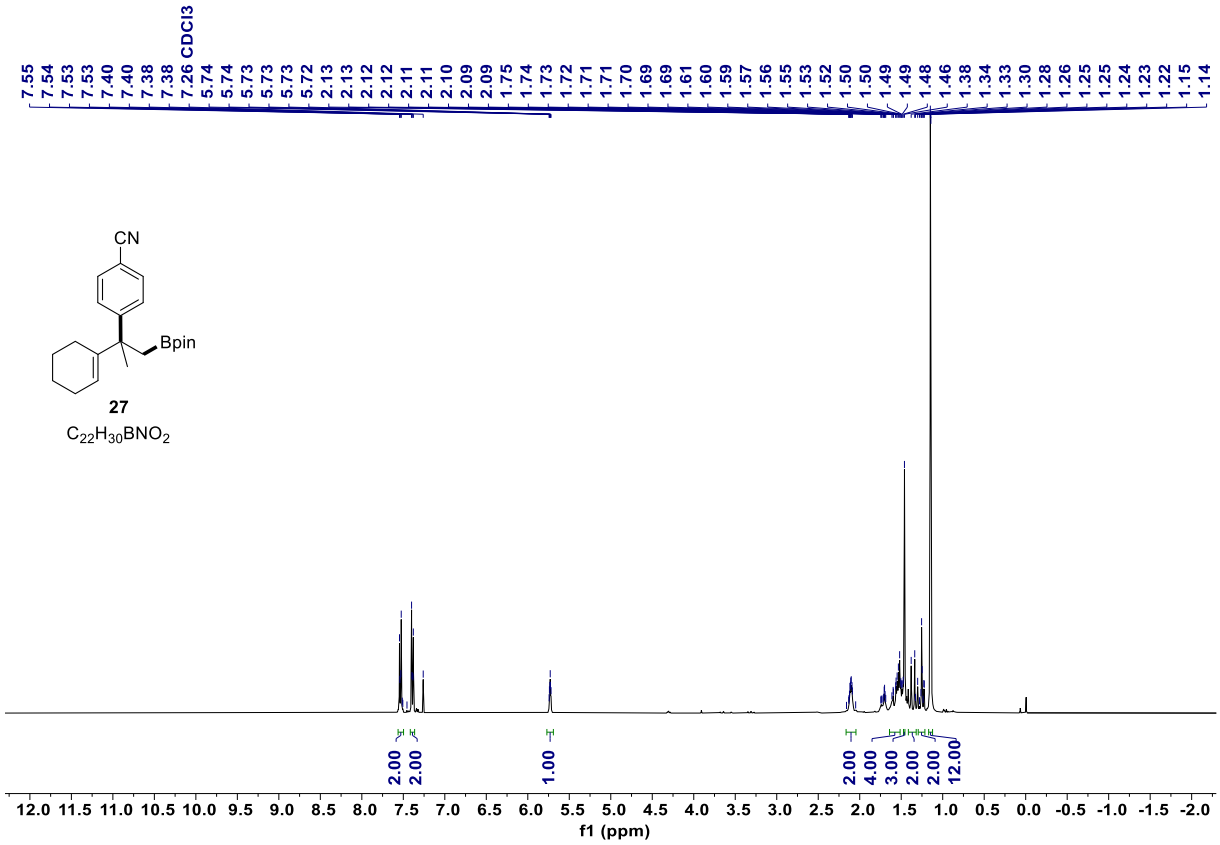
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **26**.



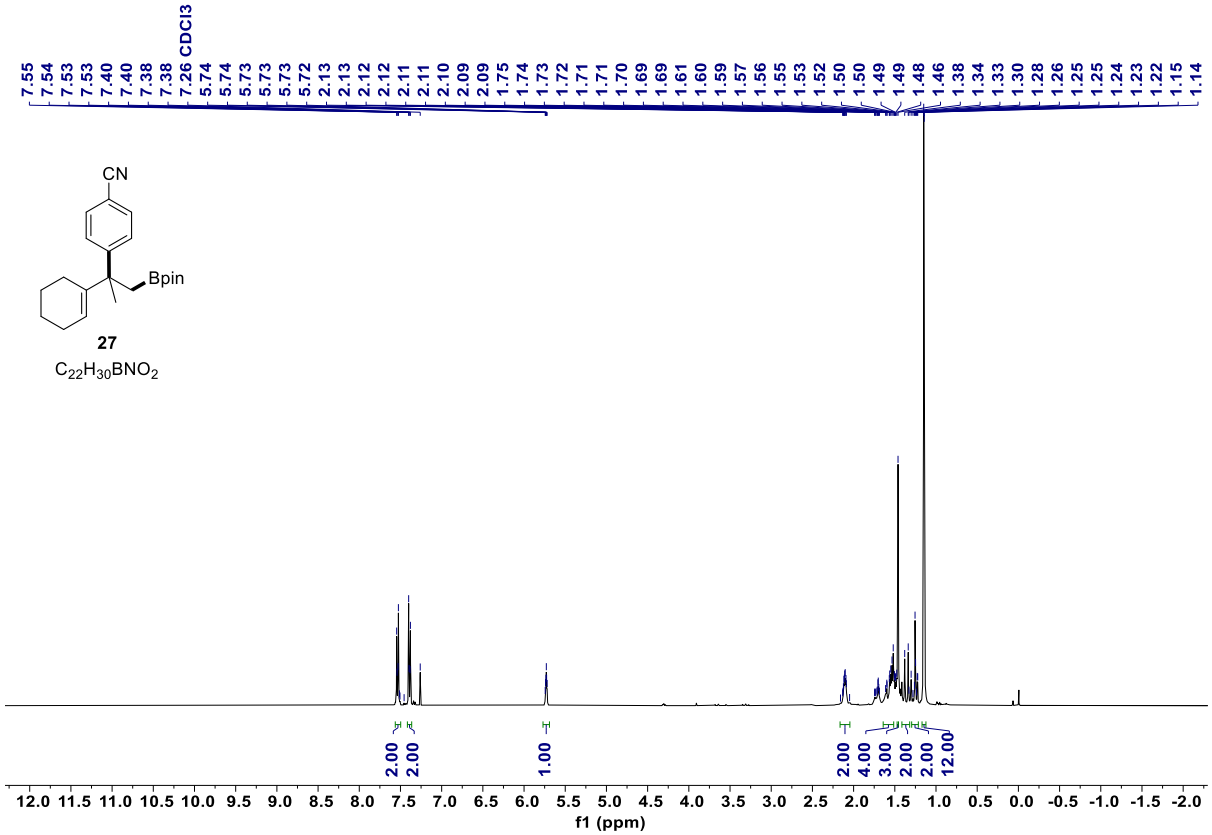
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **26**.



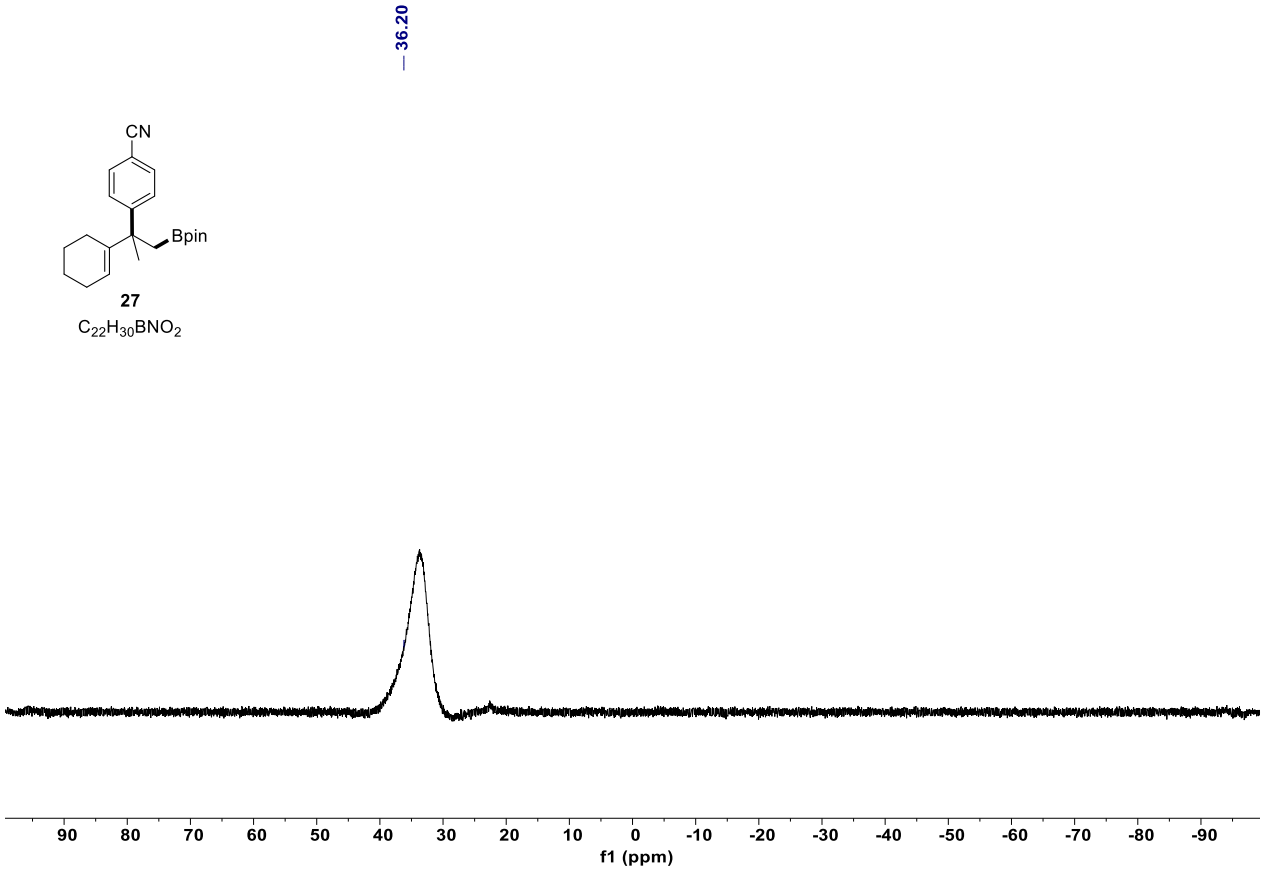
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **26**.



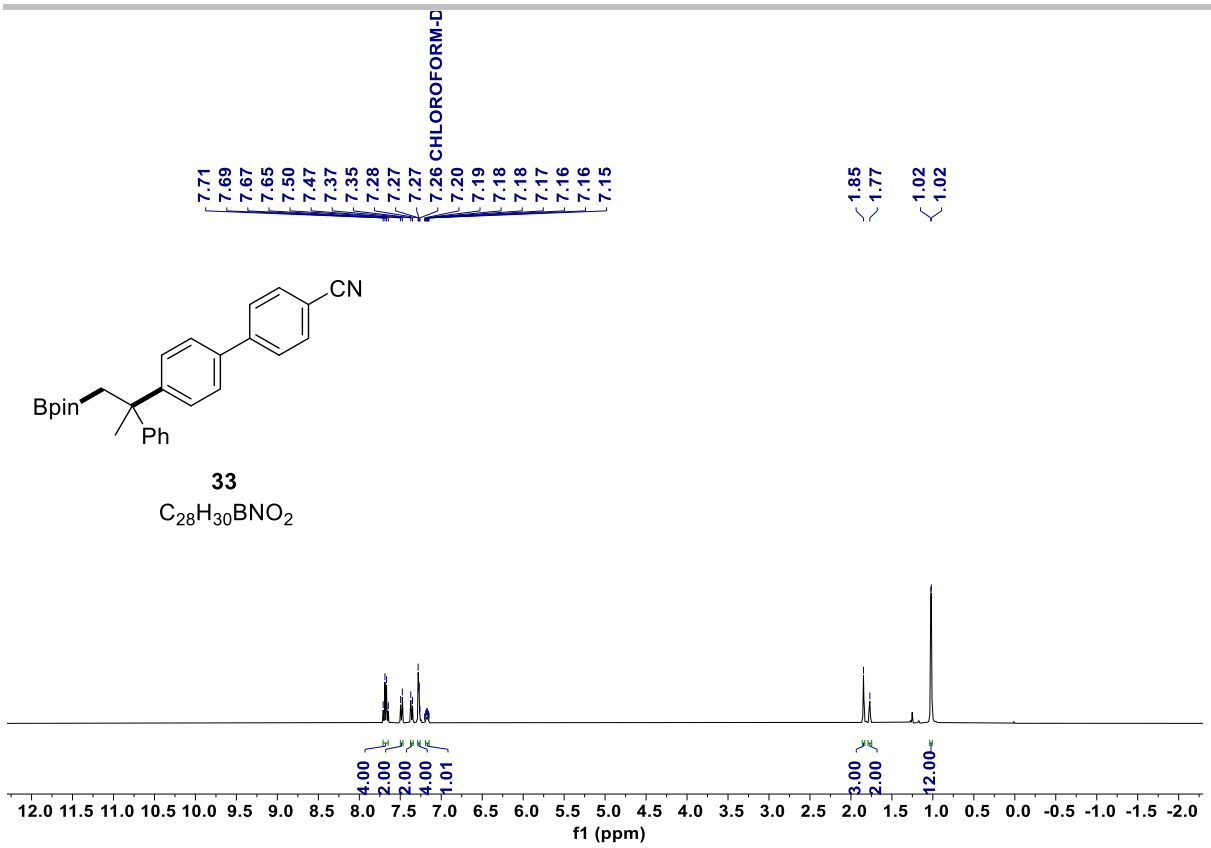
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **27**.



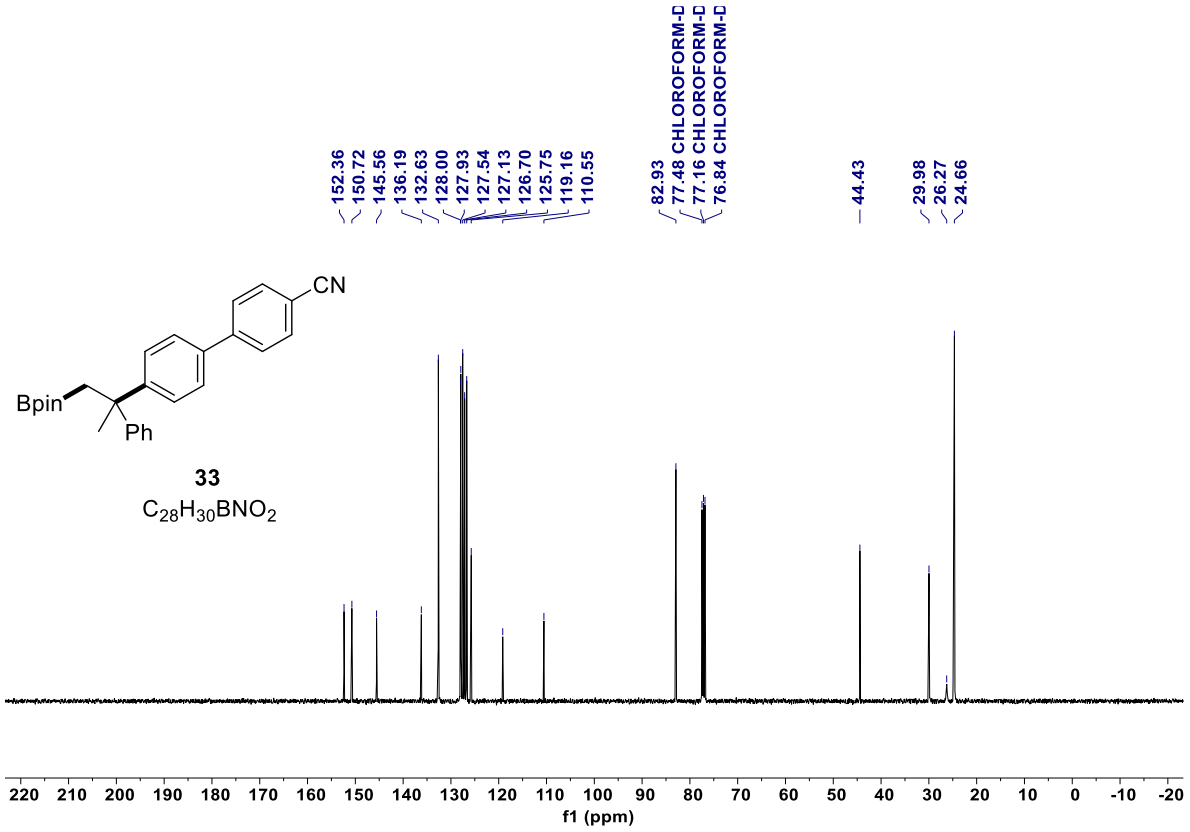
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **27**.



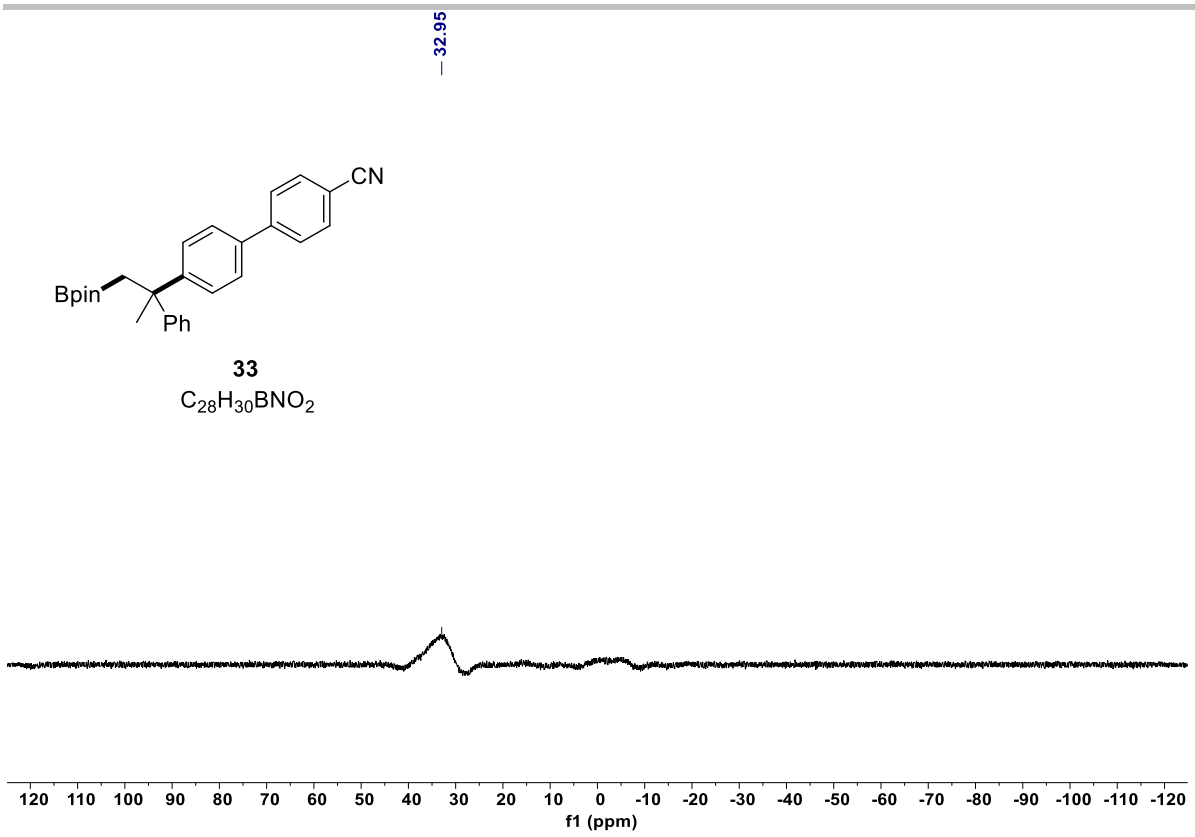
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **27**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **33**.



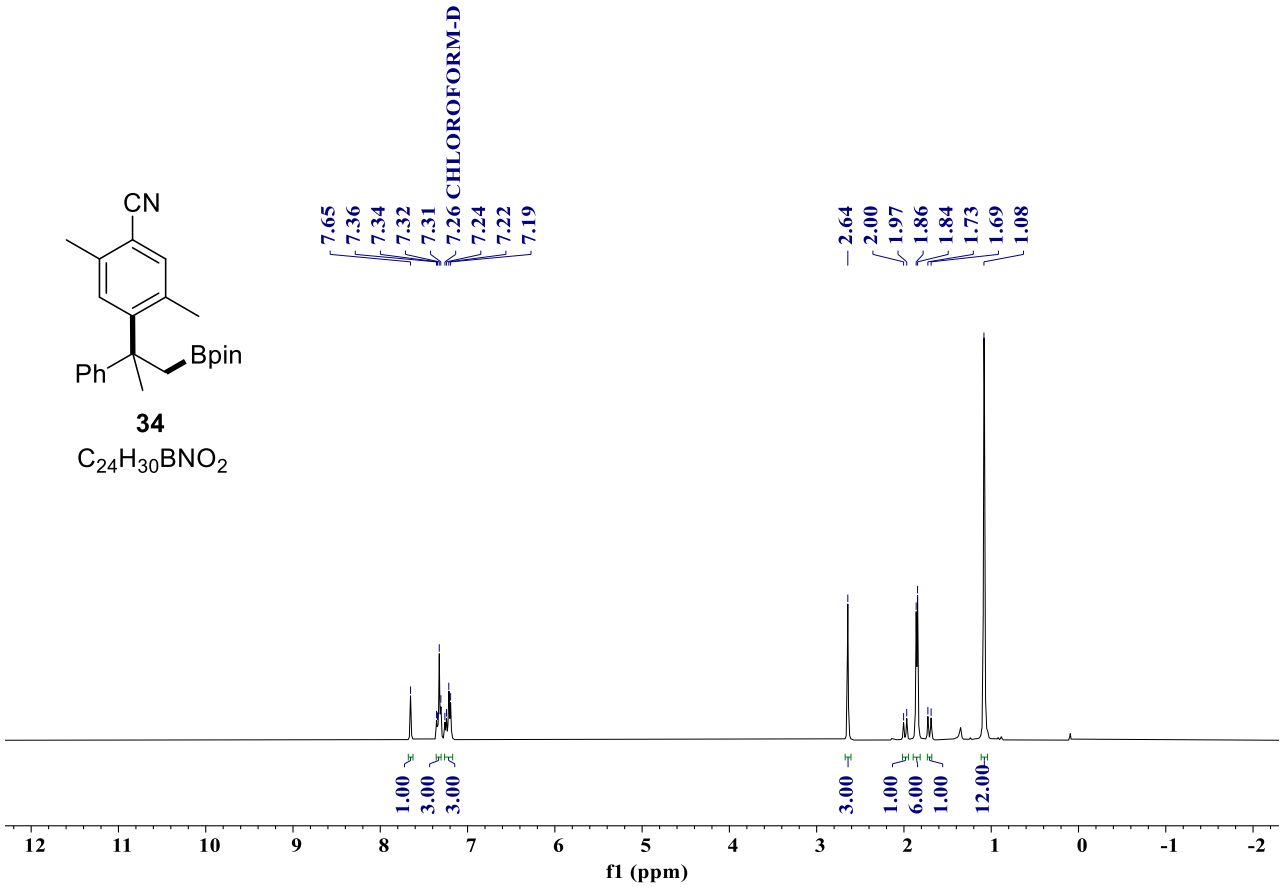
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **33**.



33

$C_{28}H_{30}BNO_2$

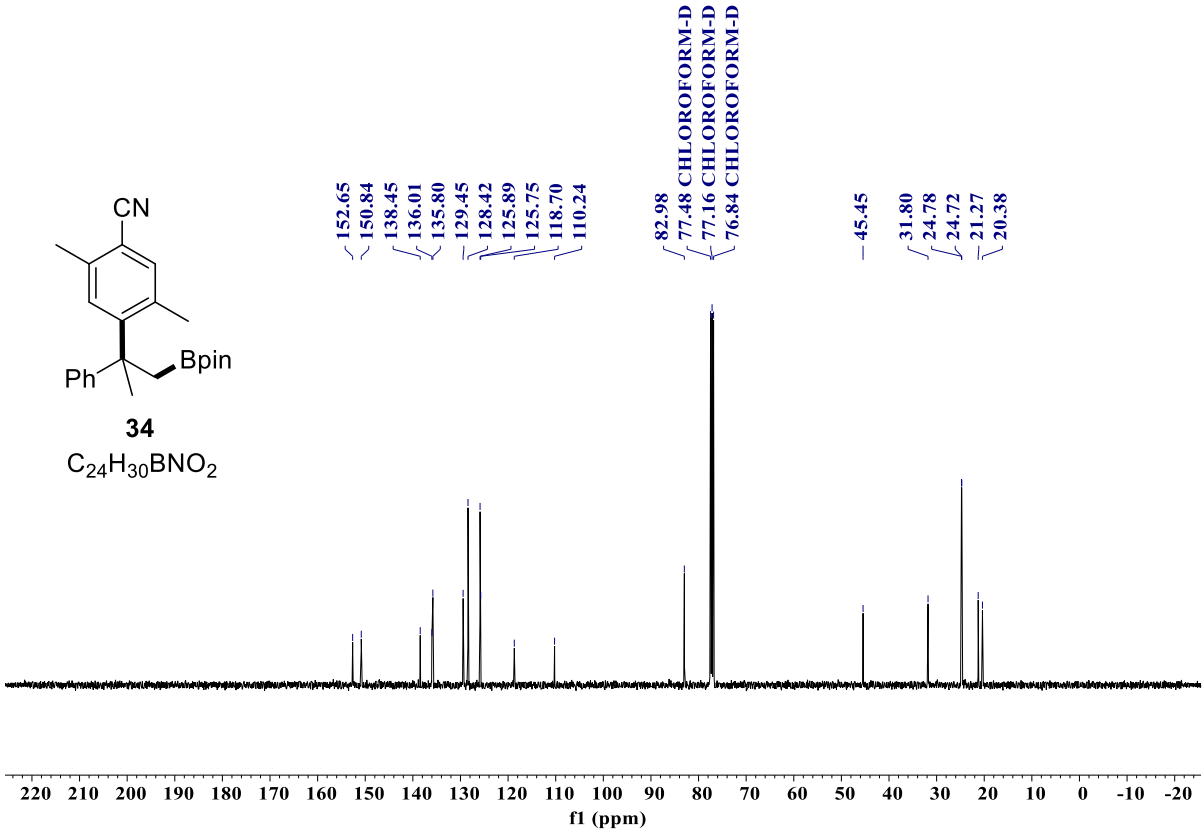
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **33**.



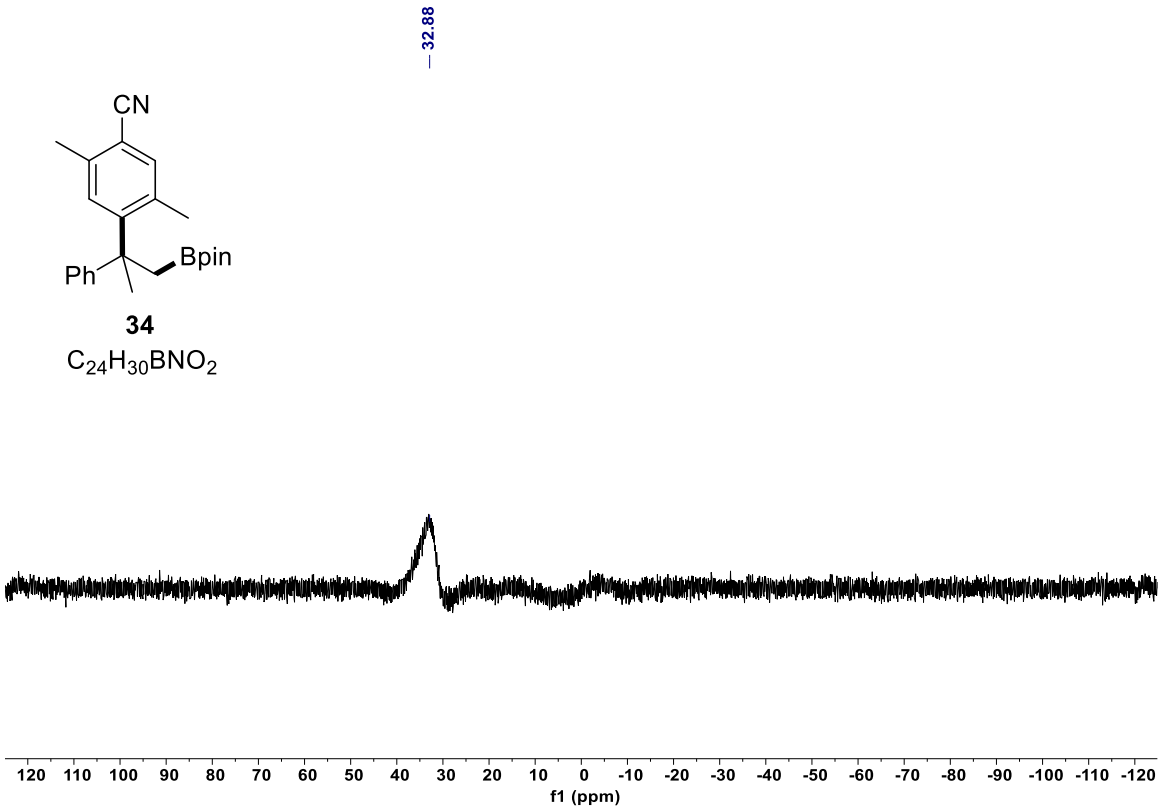
34

$C_{24}H_{30}BNO_2$

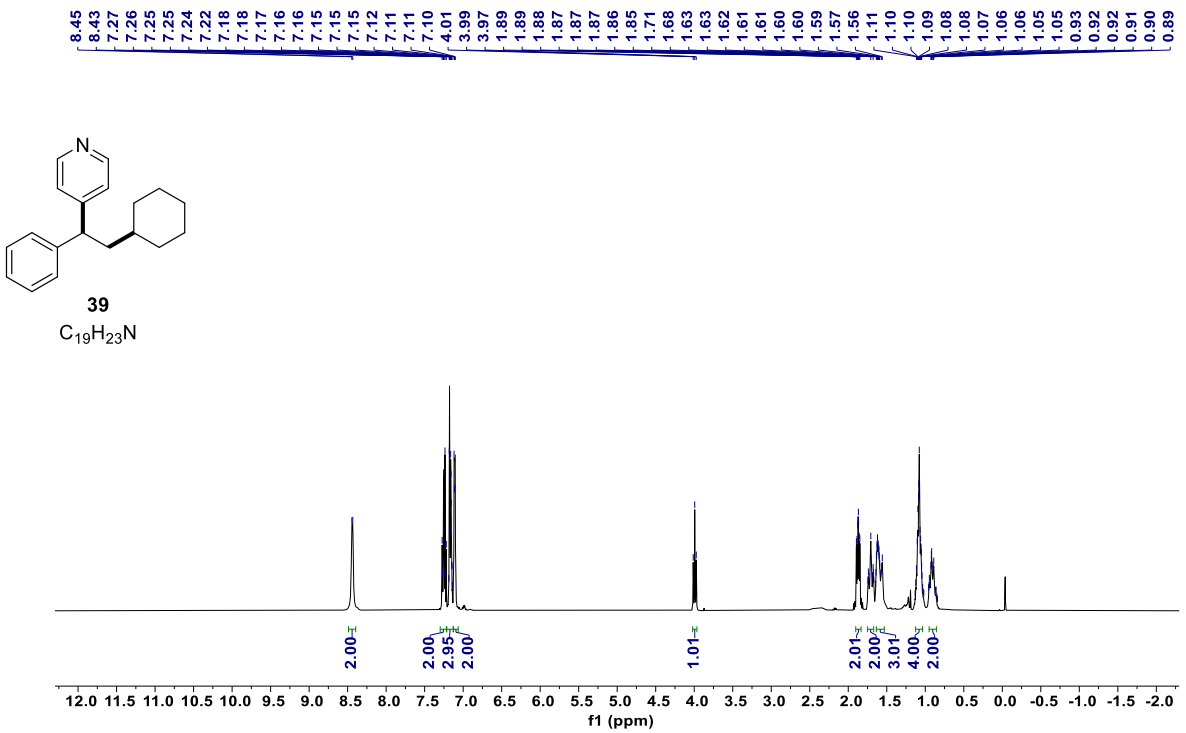
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **34**.



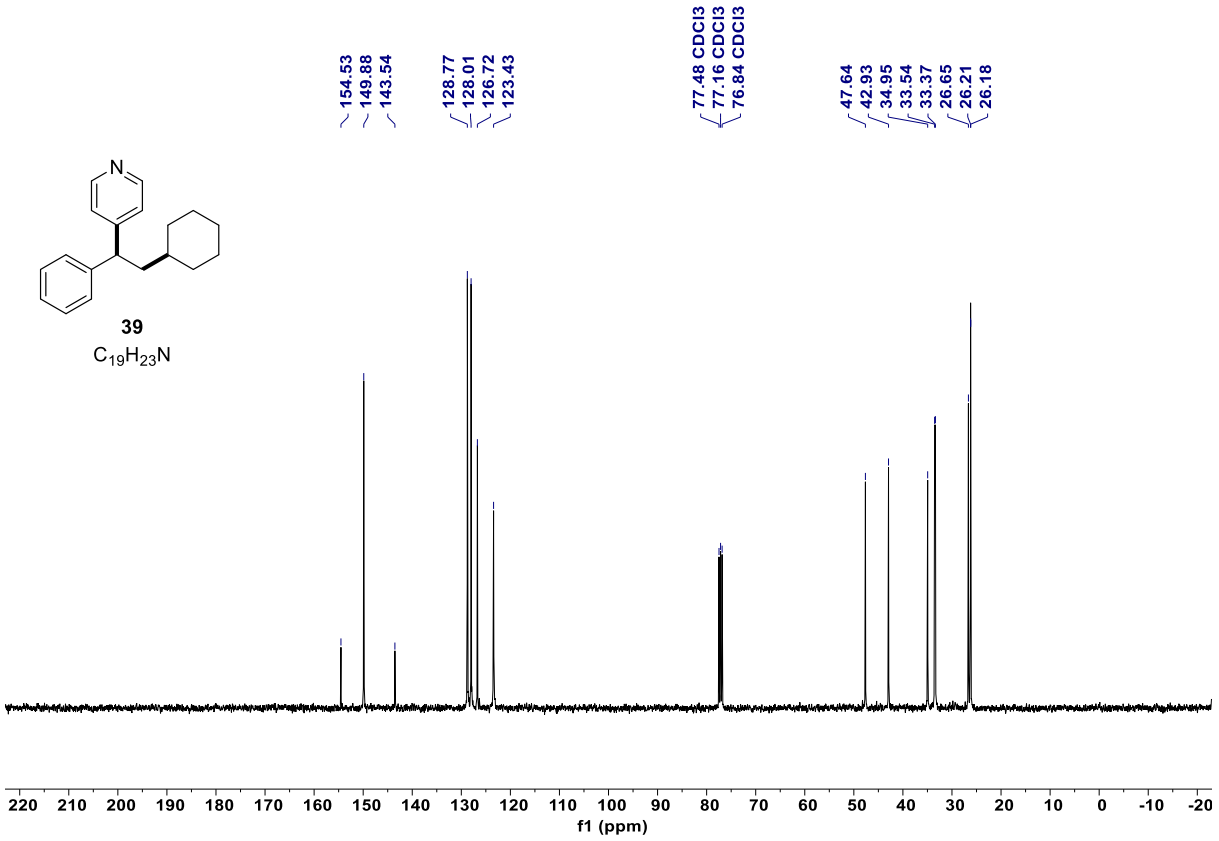
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **34**.



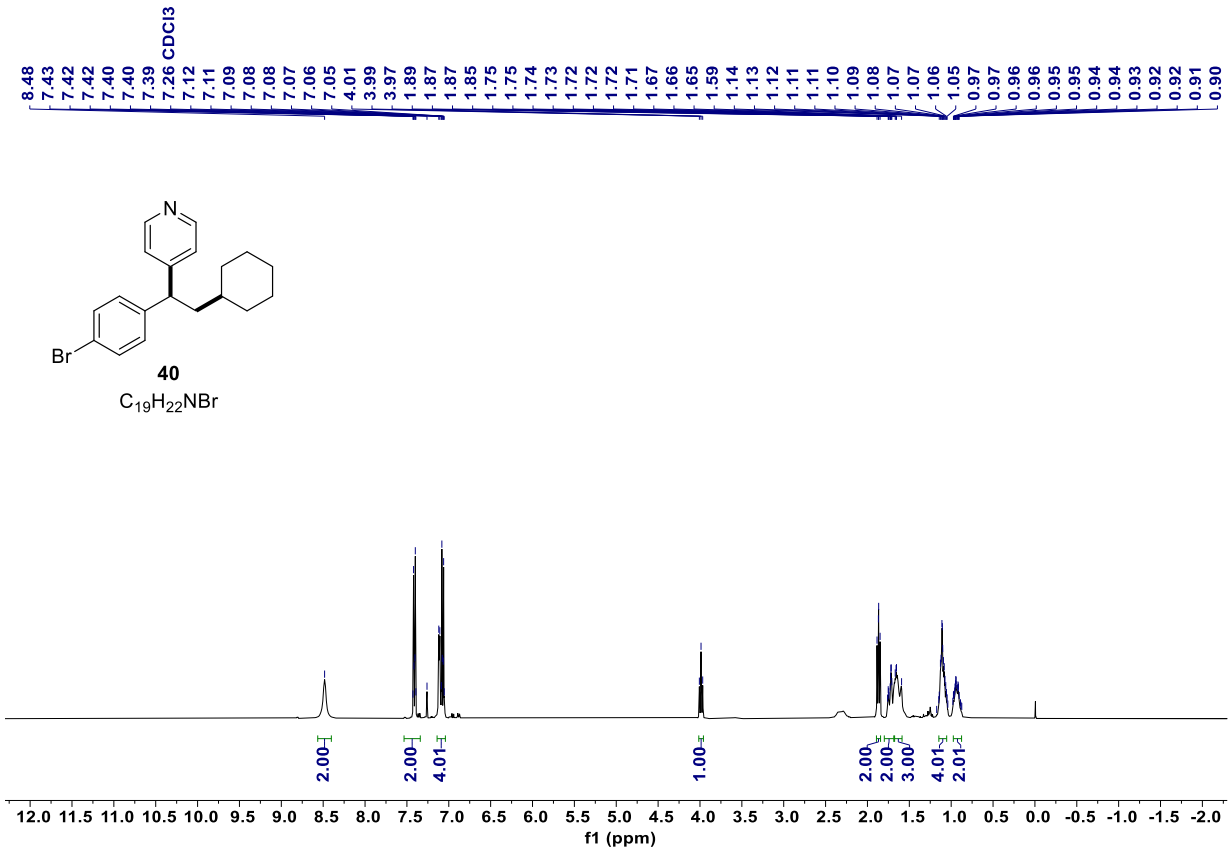
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **34**.



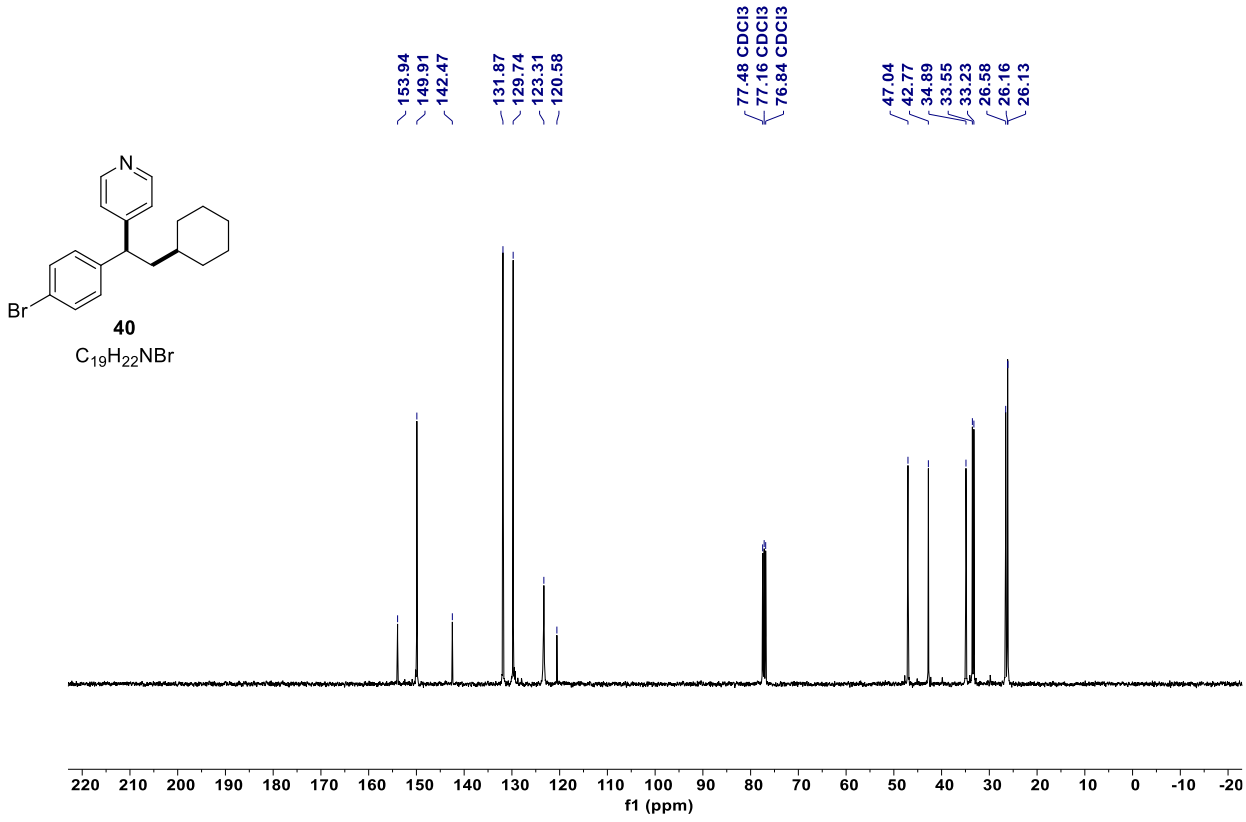
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **39**.



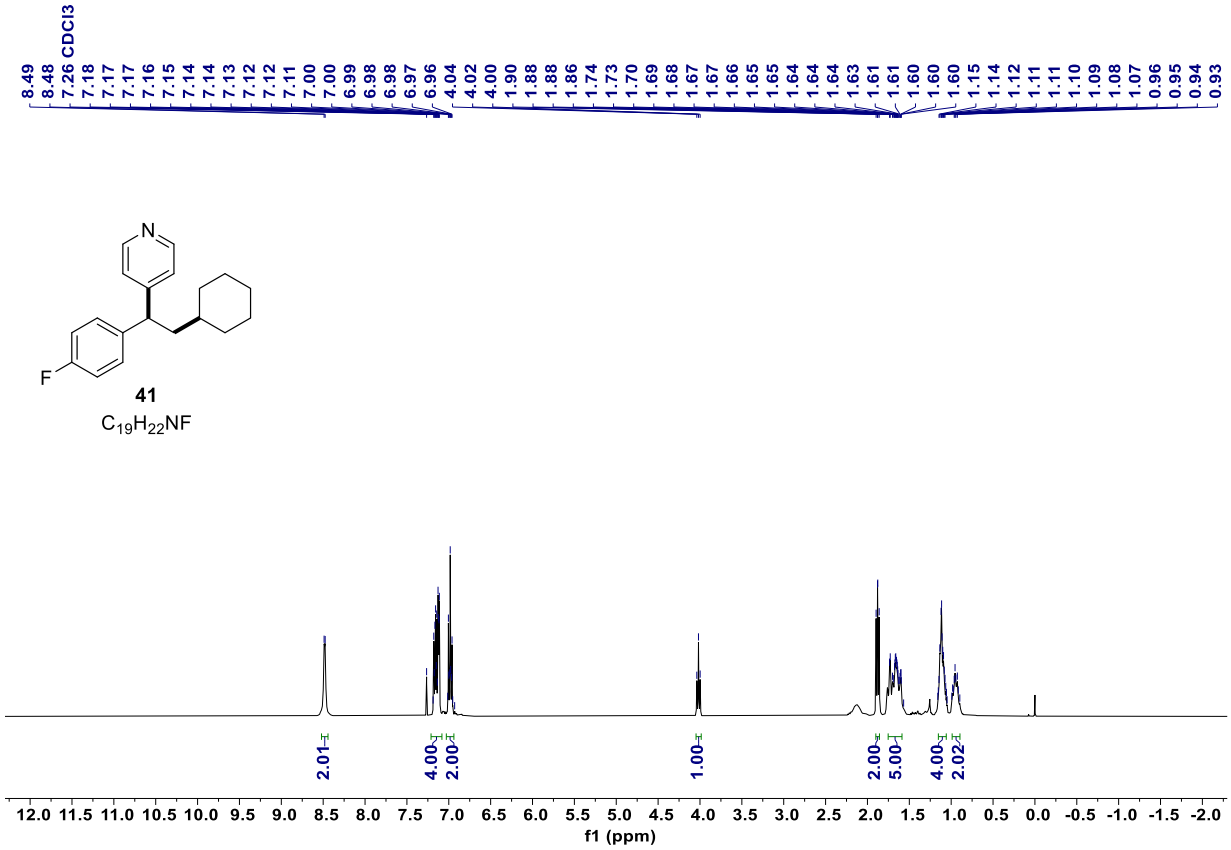
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **39**.



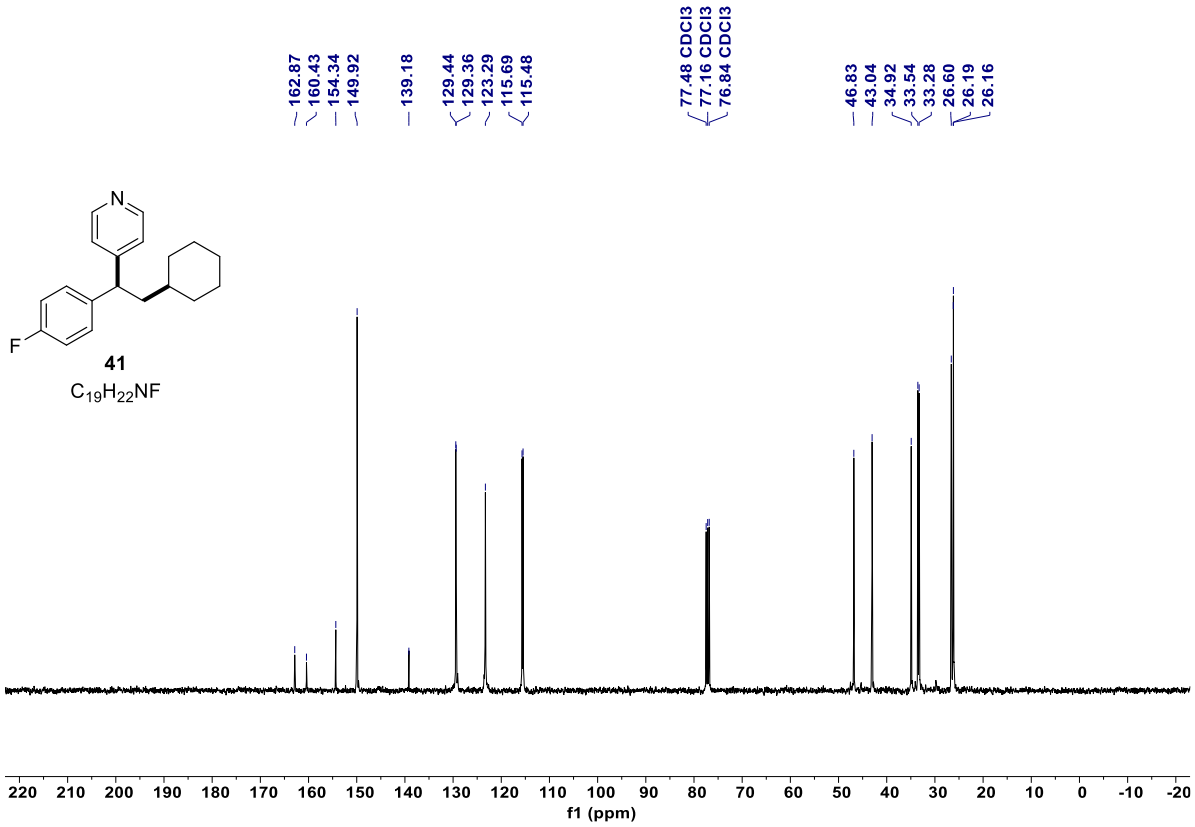
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **40**.



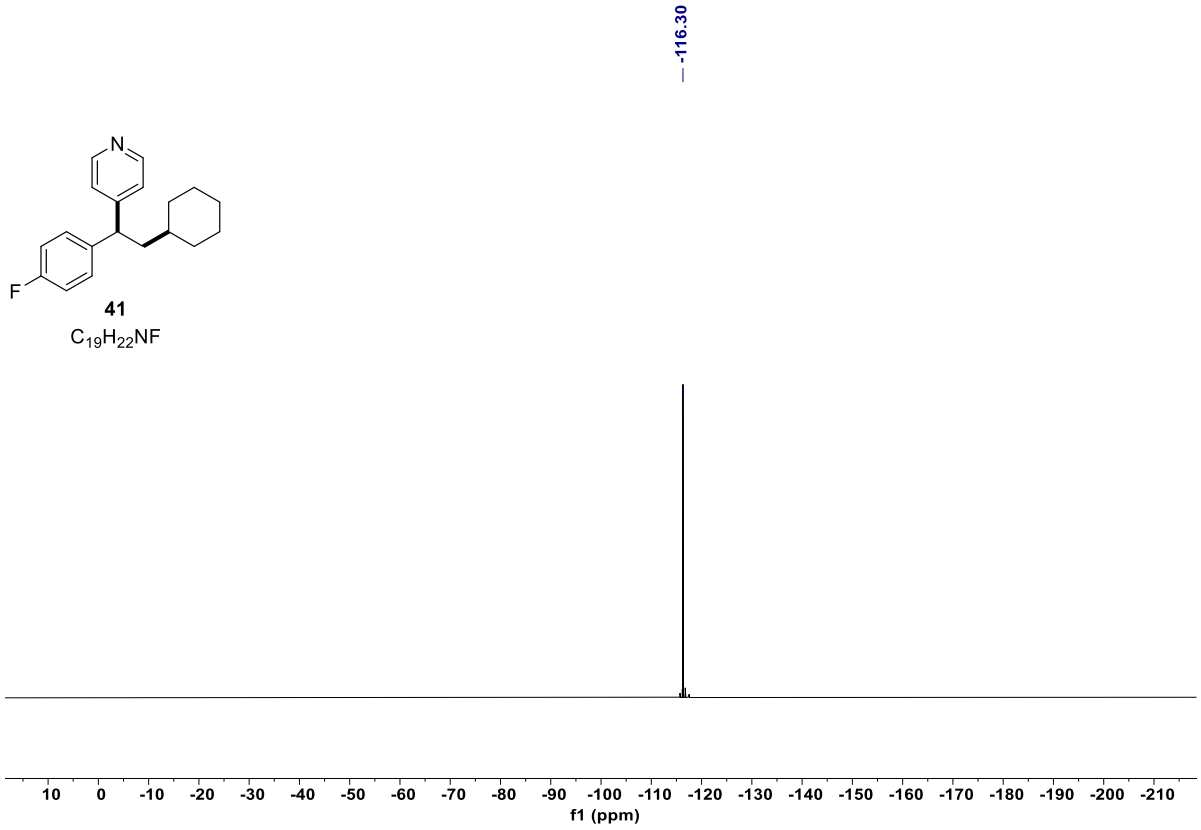
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **40**.



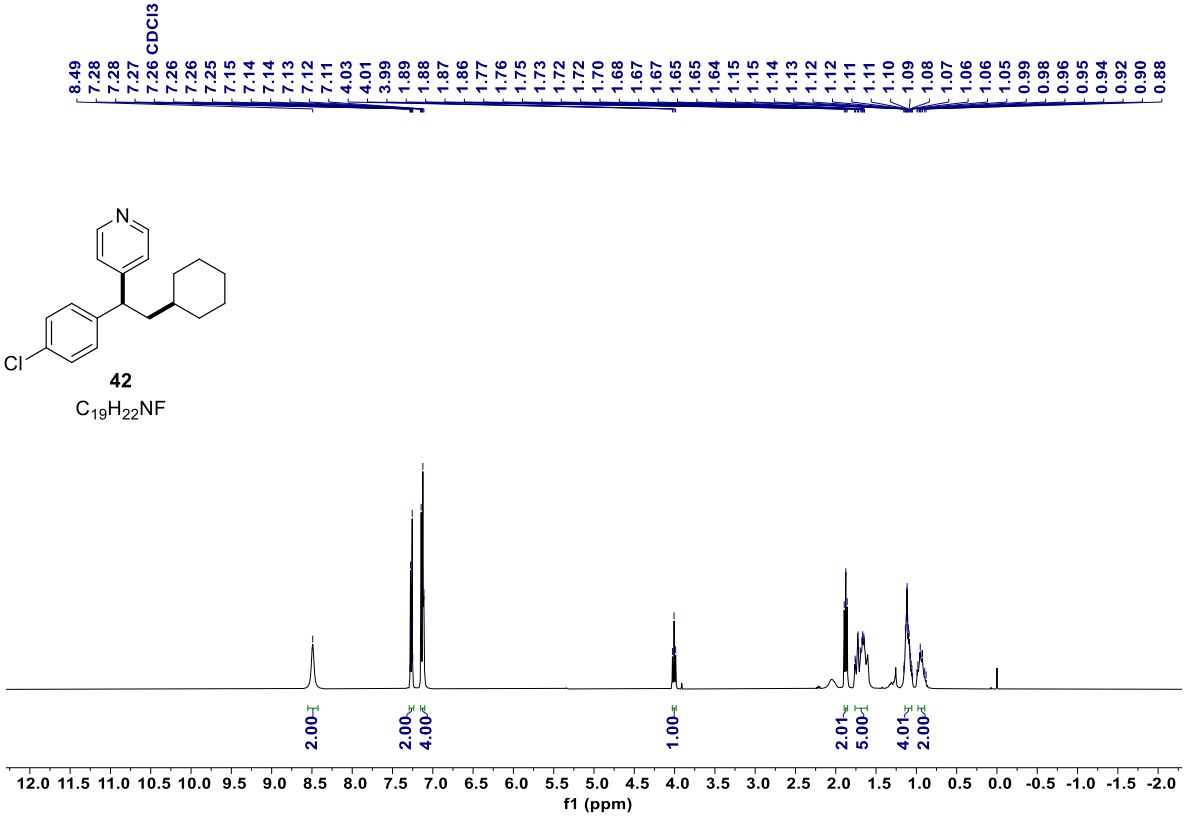
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **41**.



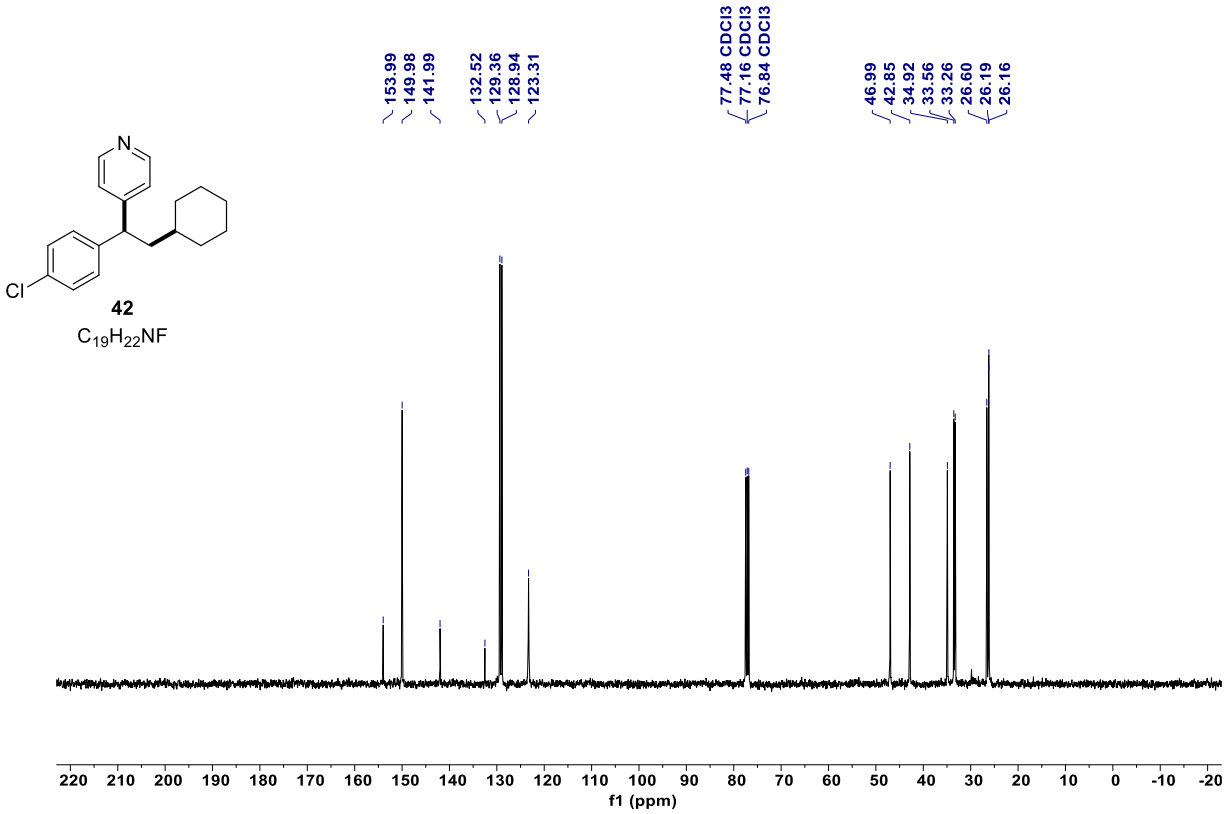
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **41**.



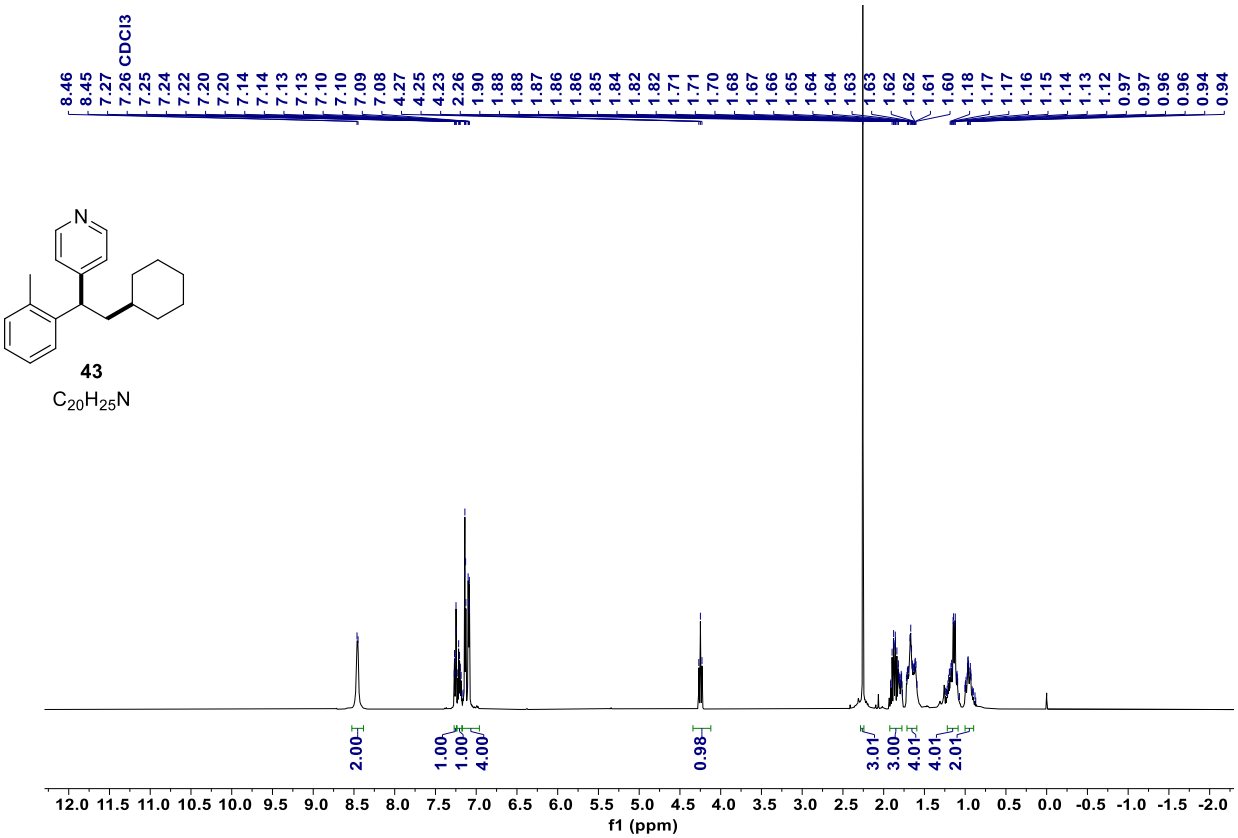
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of the compound **41**.



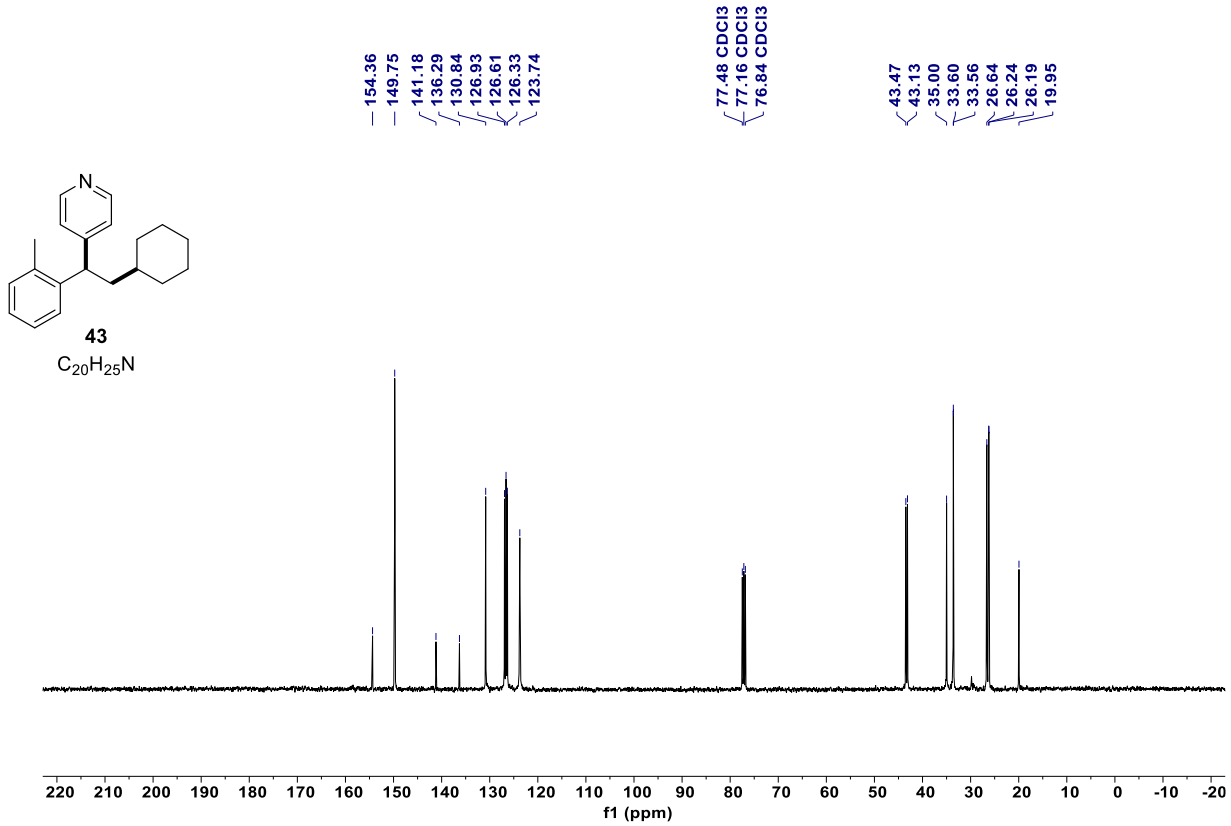
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **42**.



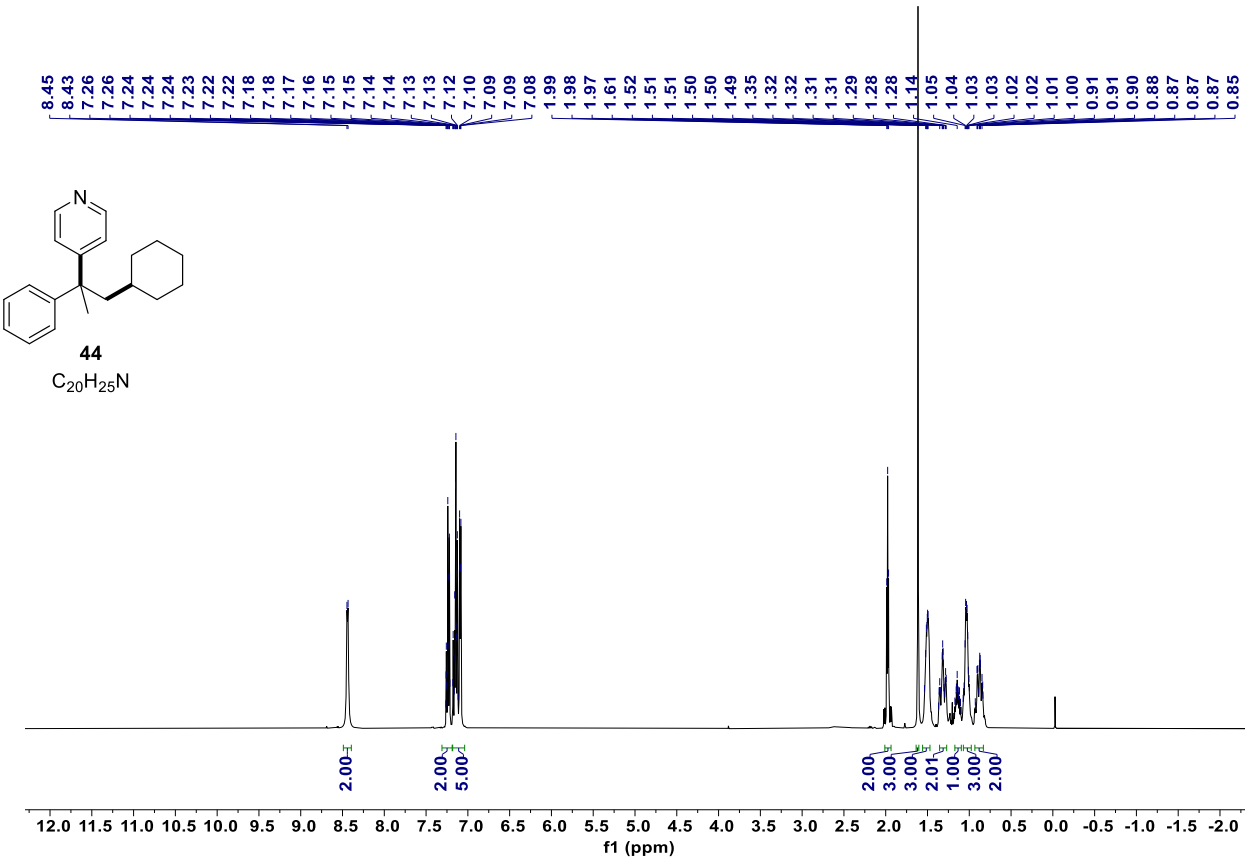
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **42**.



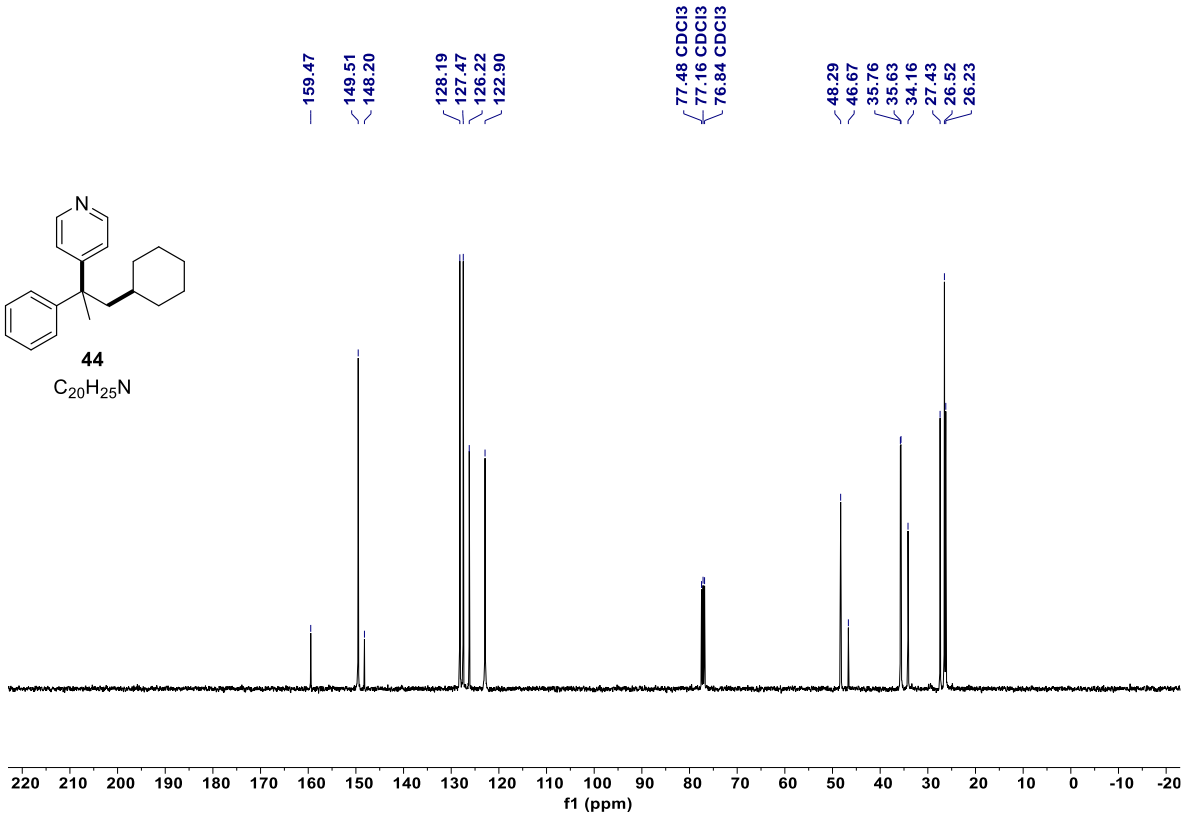
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **43**.



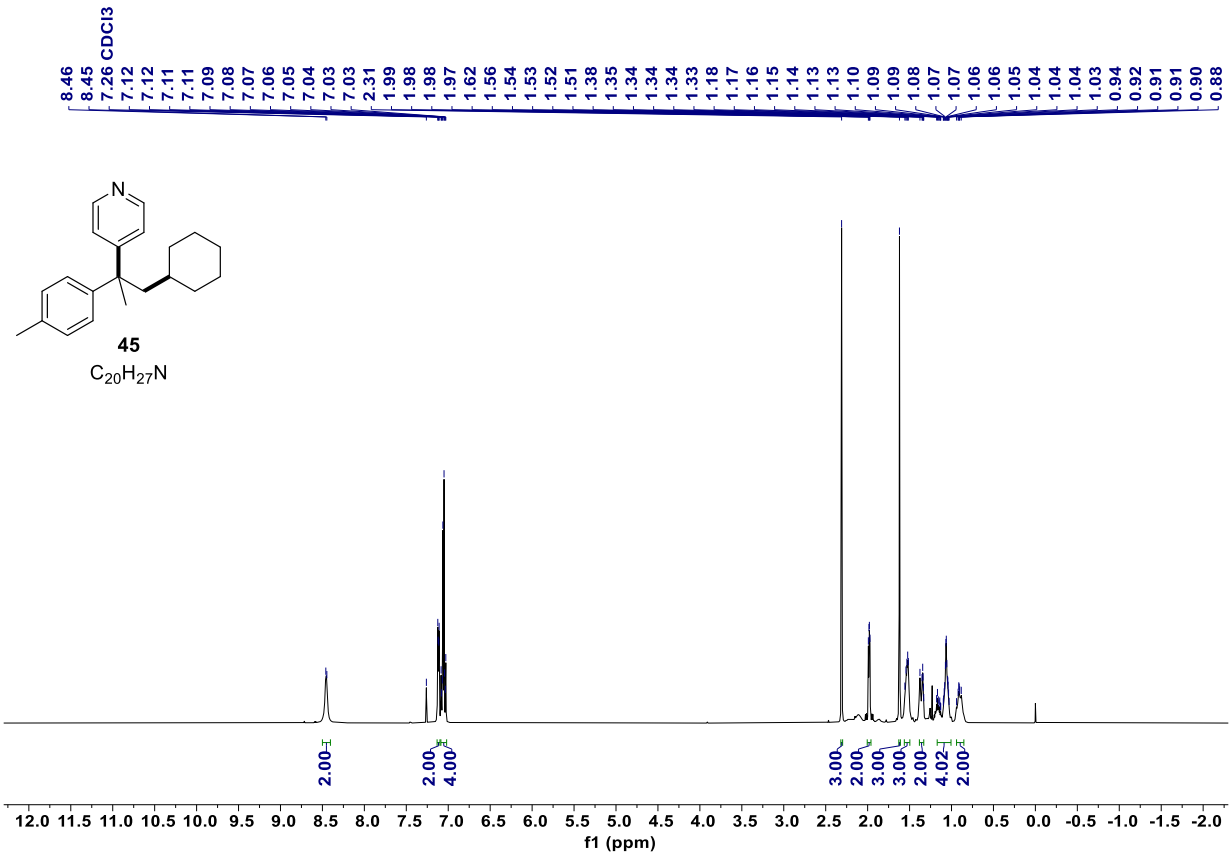
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **43**.



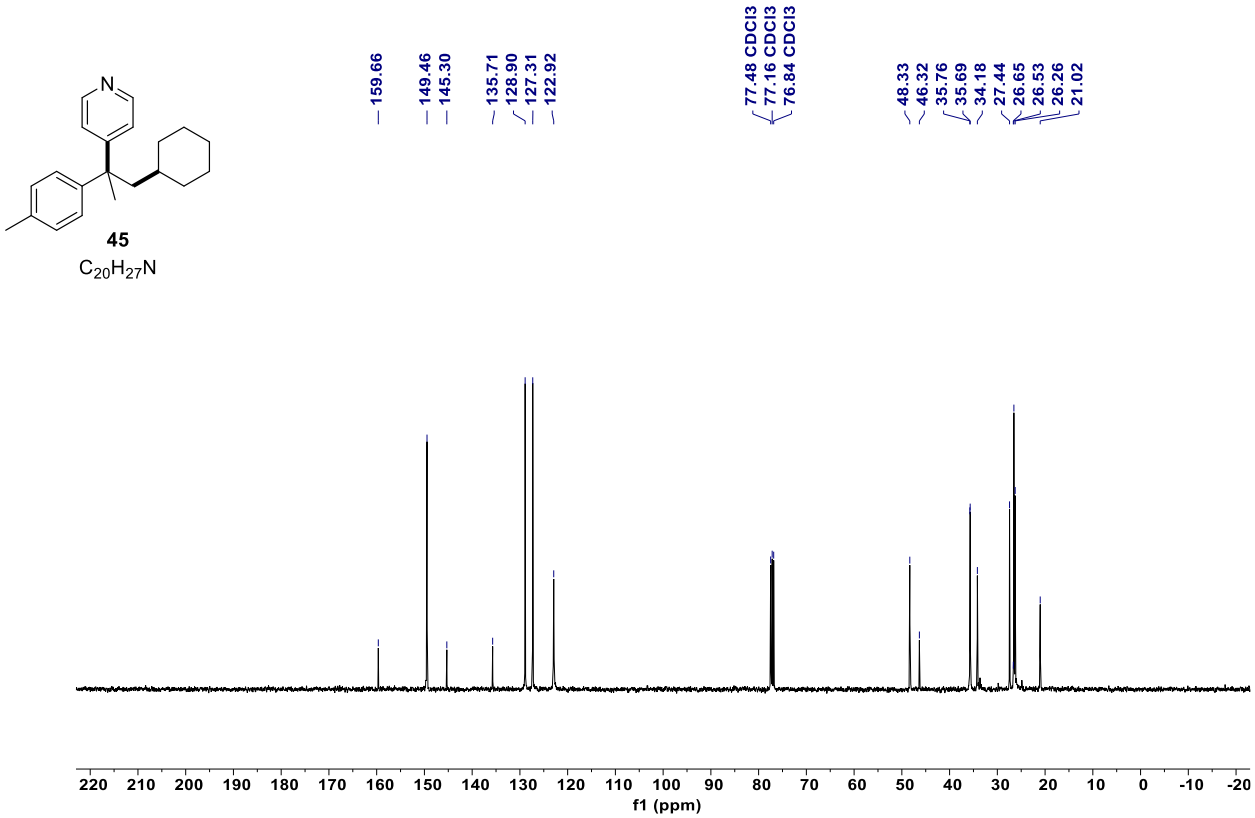
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **44**.



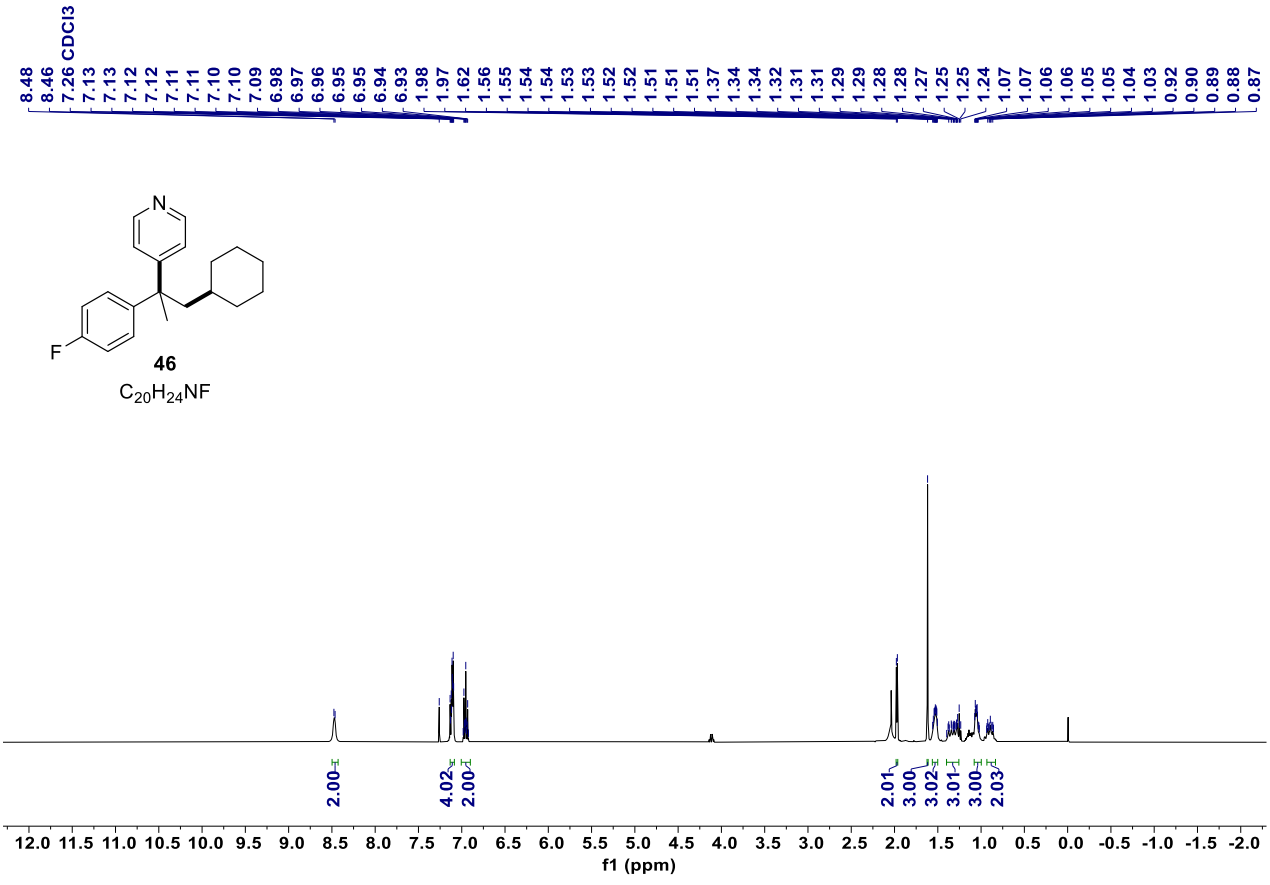
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **44**.



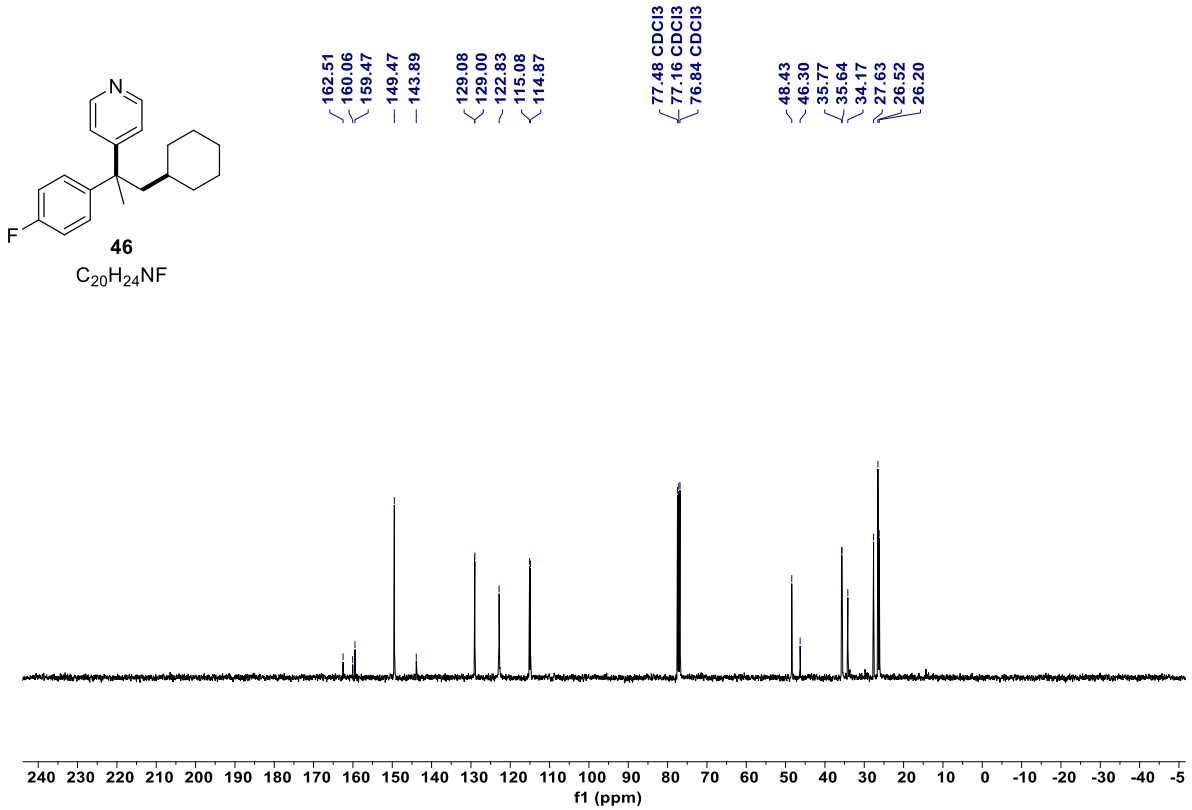
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **45**.



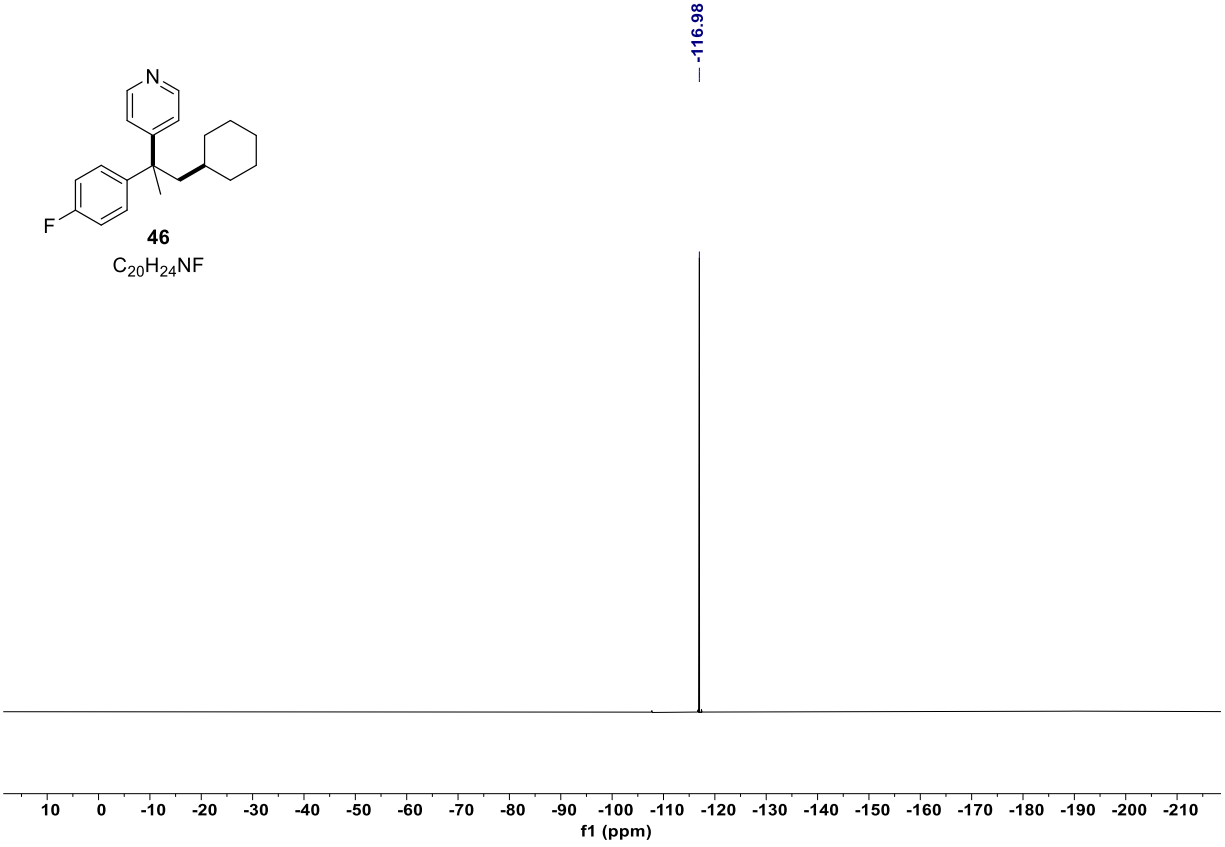
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **45**.



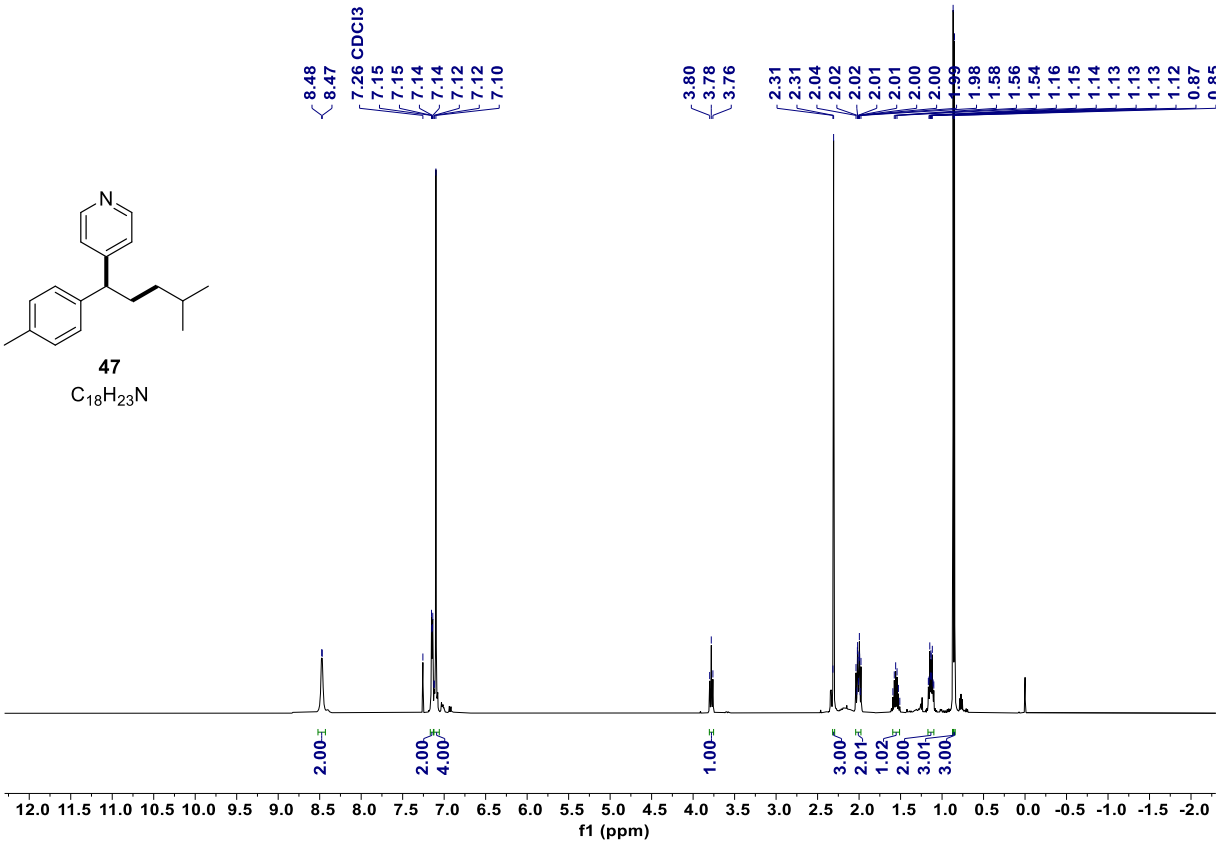
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **46**.



$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **46**.



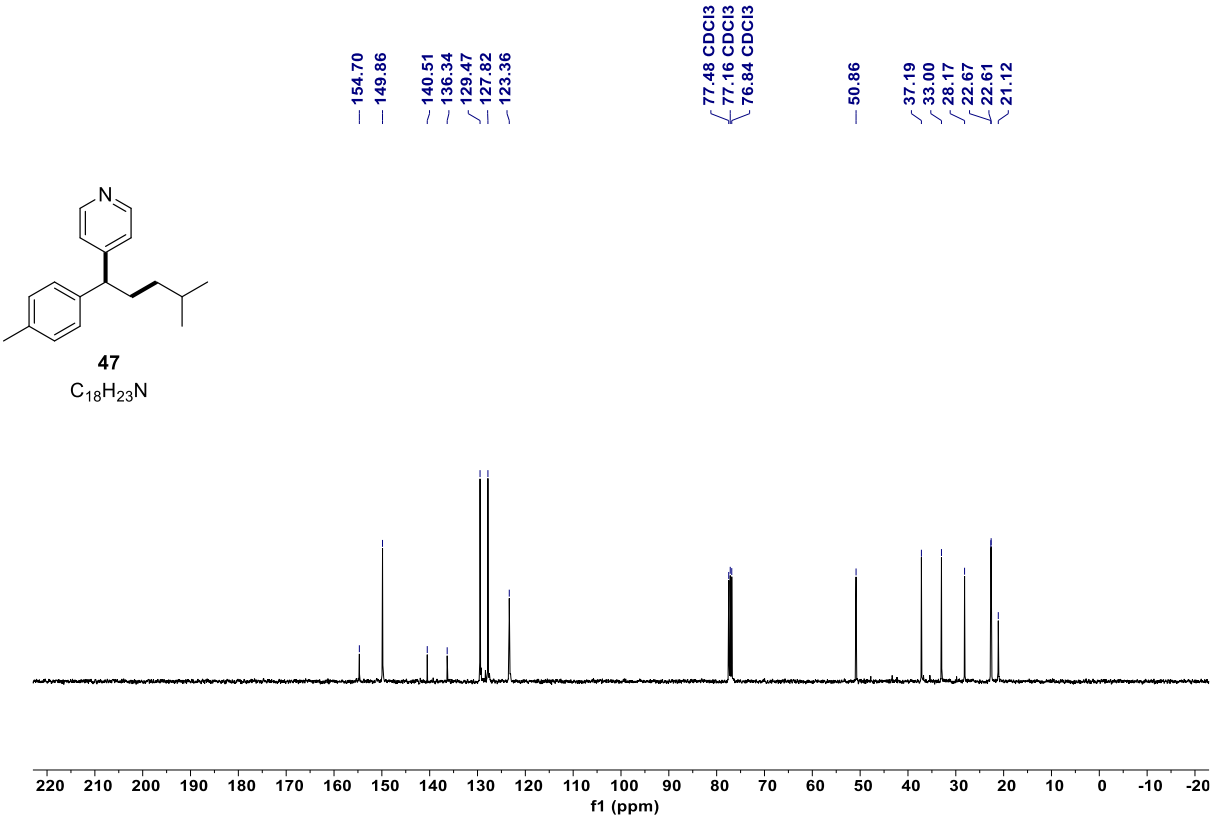
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of the compound **46**.



47

$C_{18}H_{23}N$

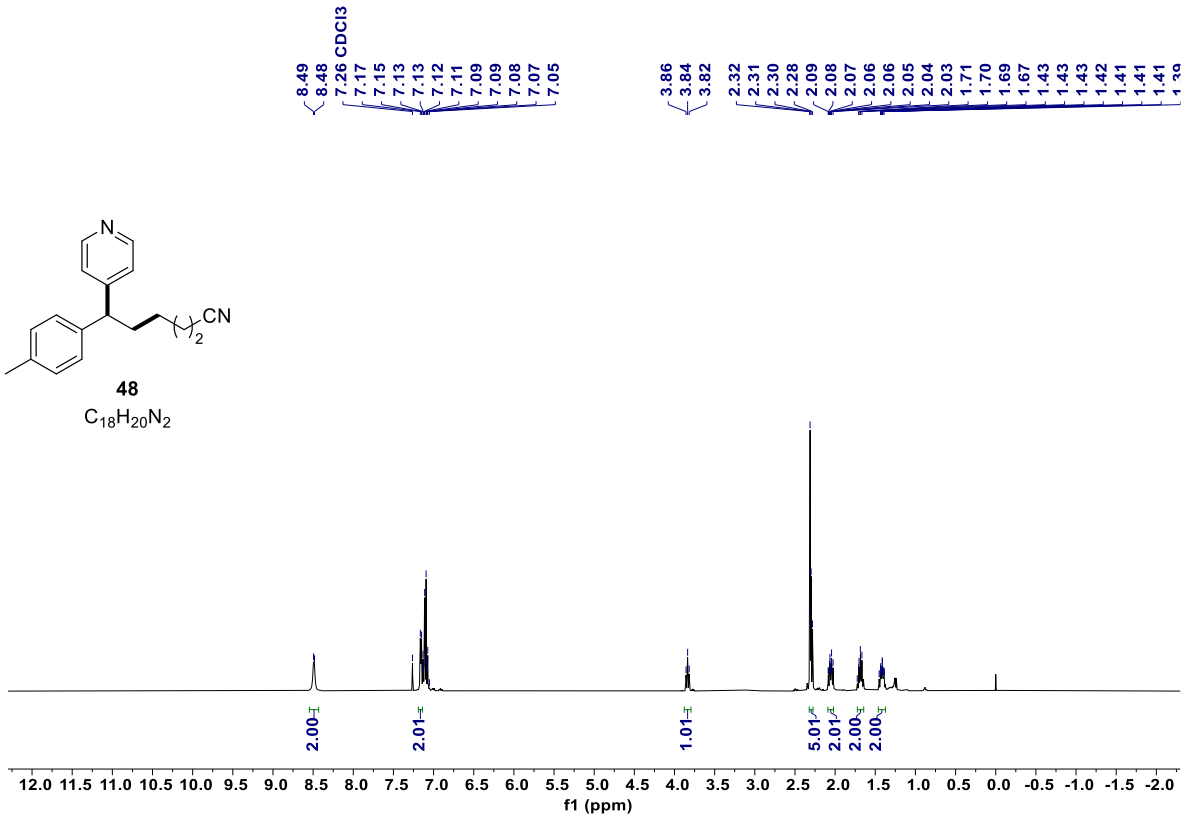
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **47**.



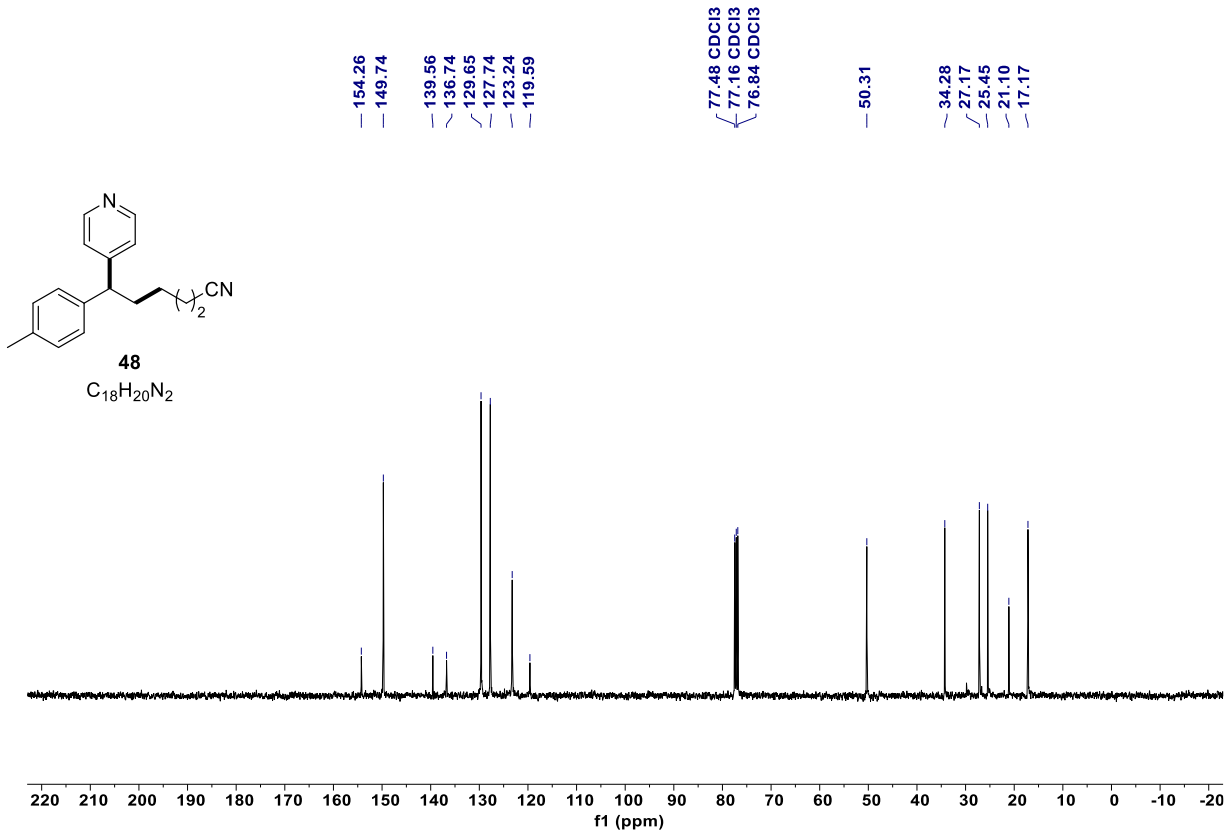
47

$C_{18}H_{23}N$

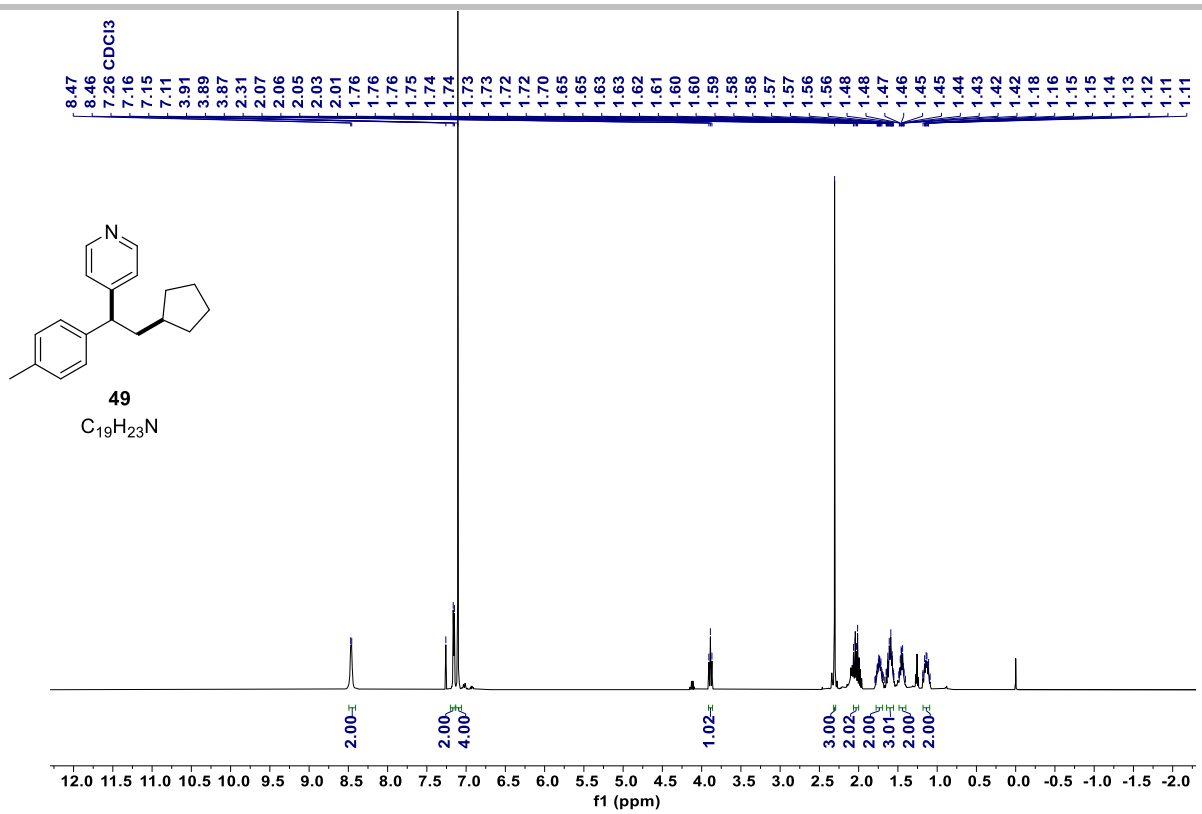
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **47**.



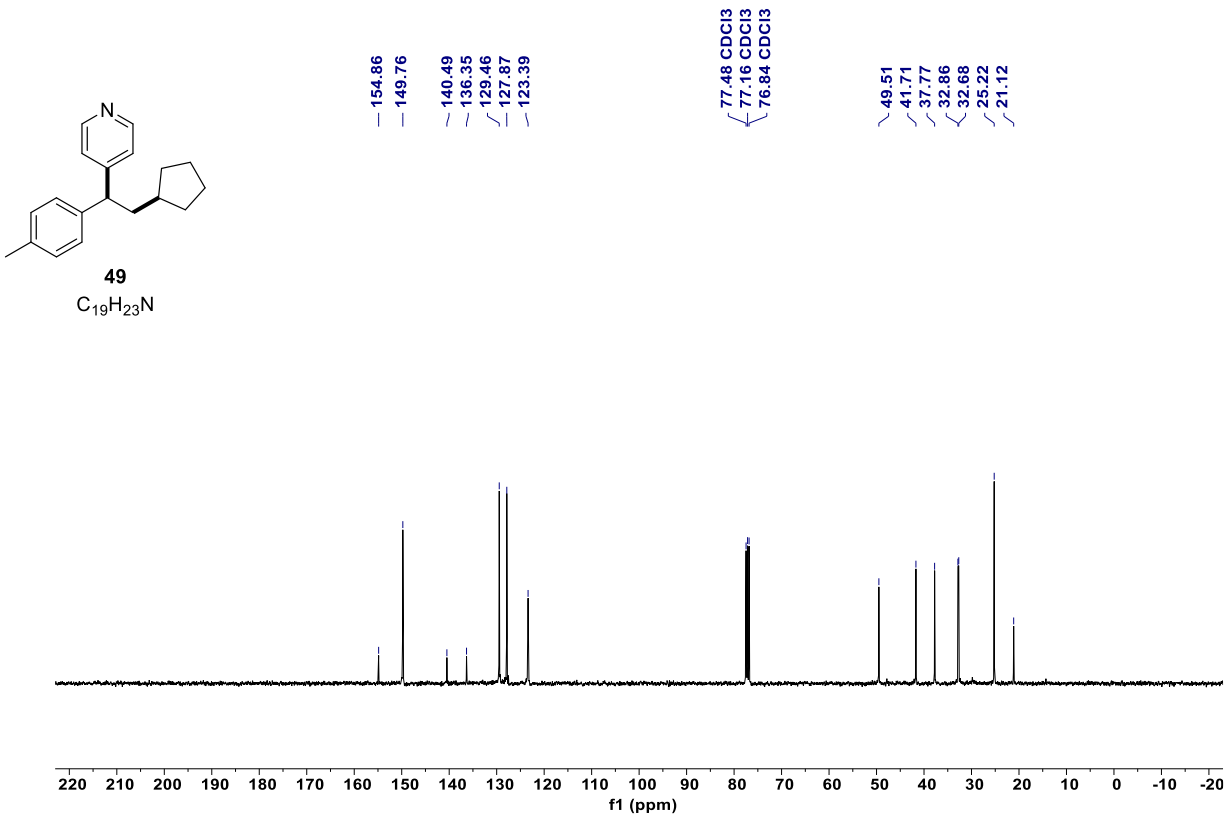
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **48**.



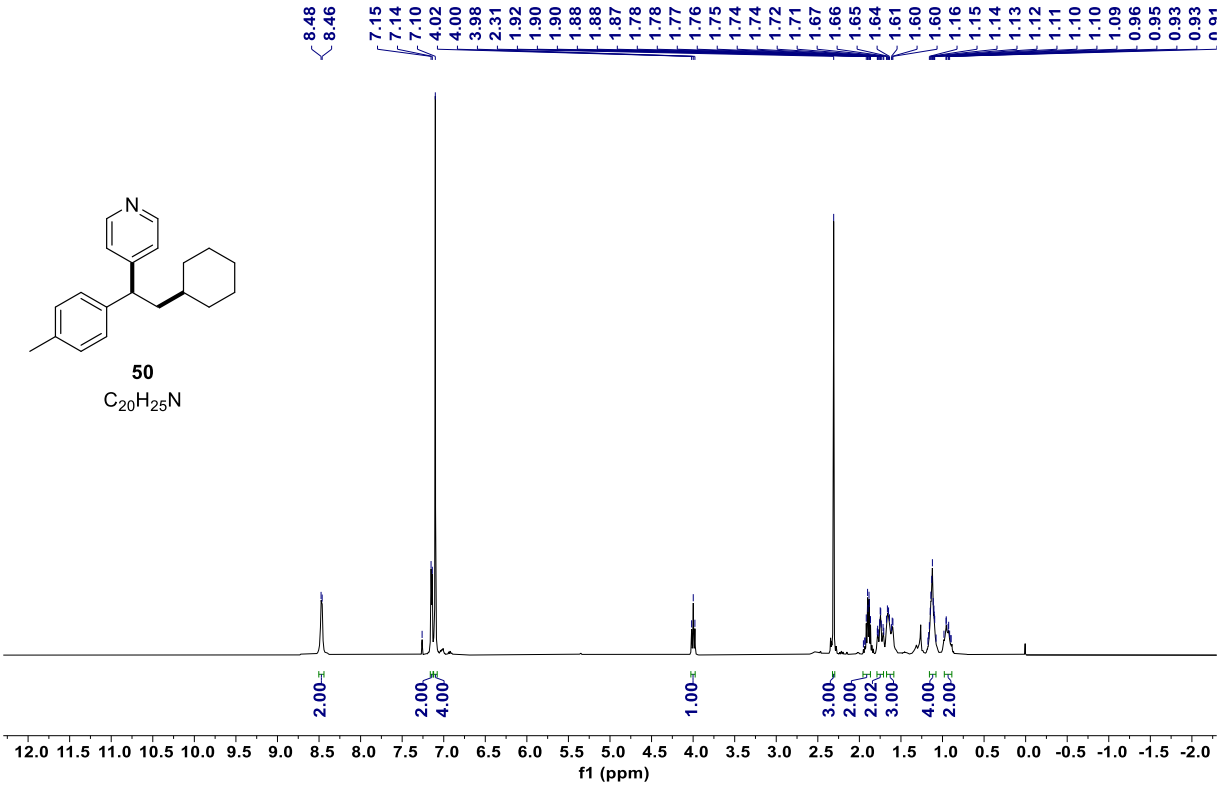
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **48**.



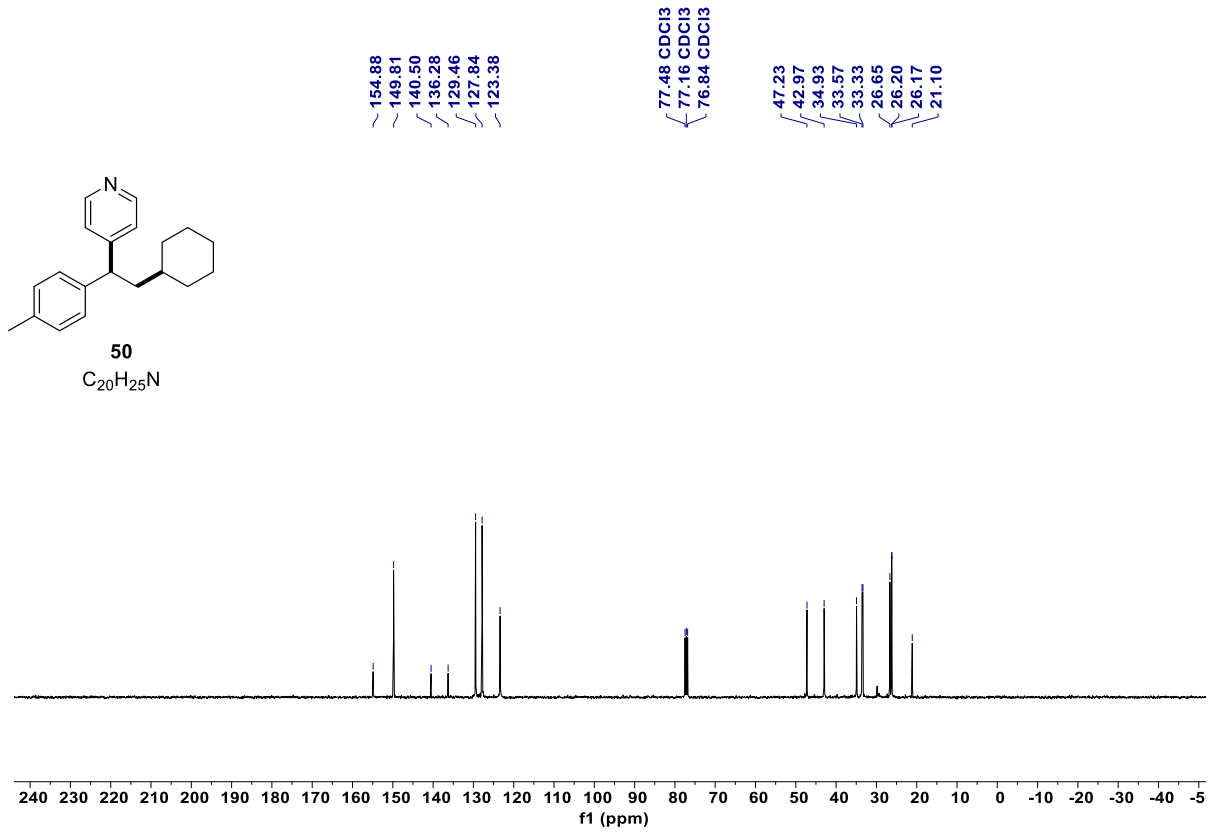
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **49**.



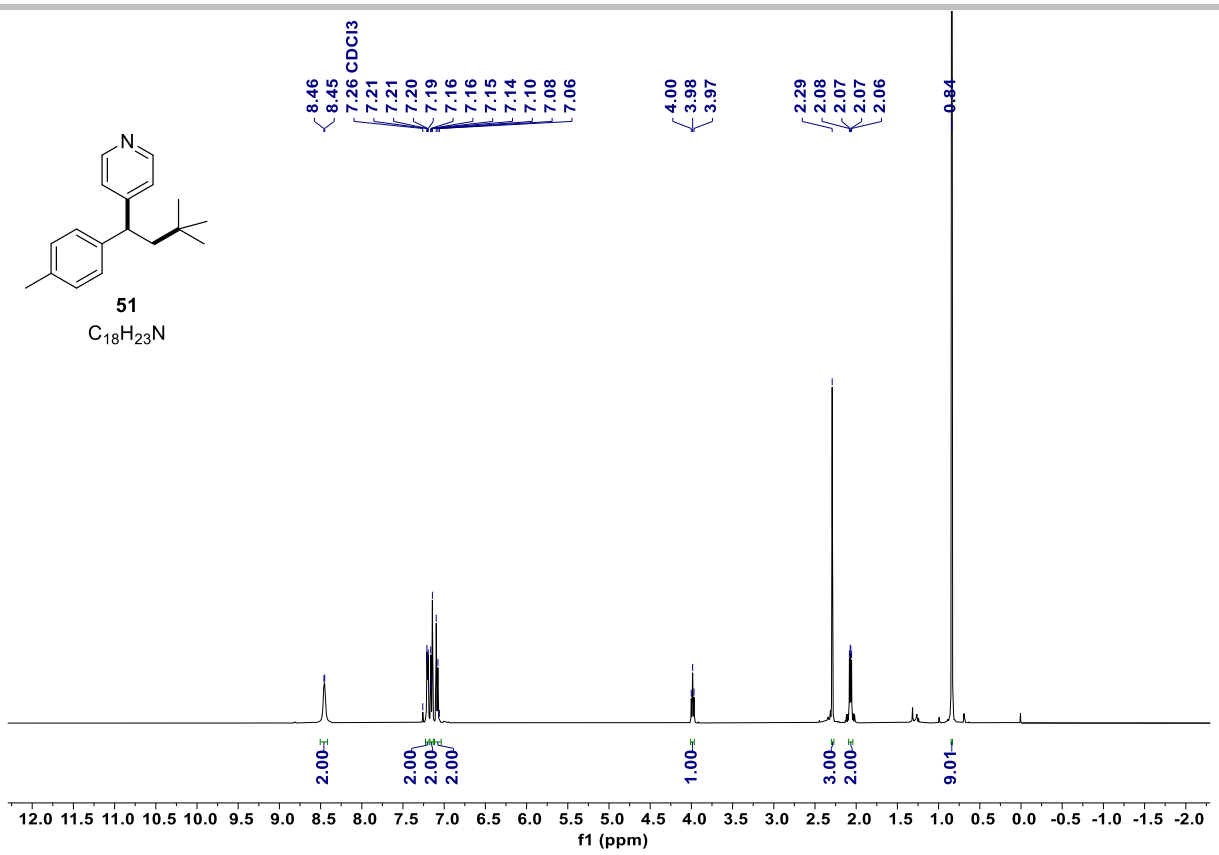
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **49**.



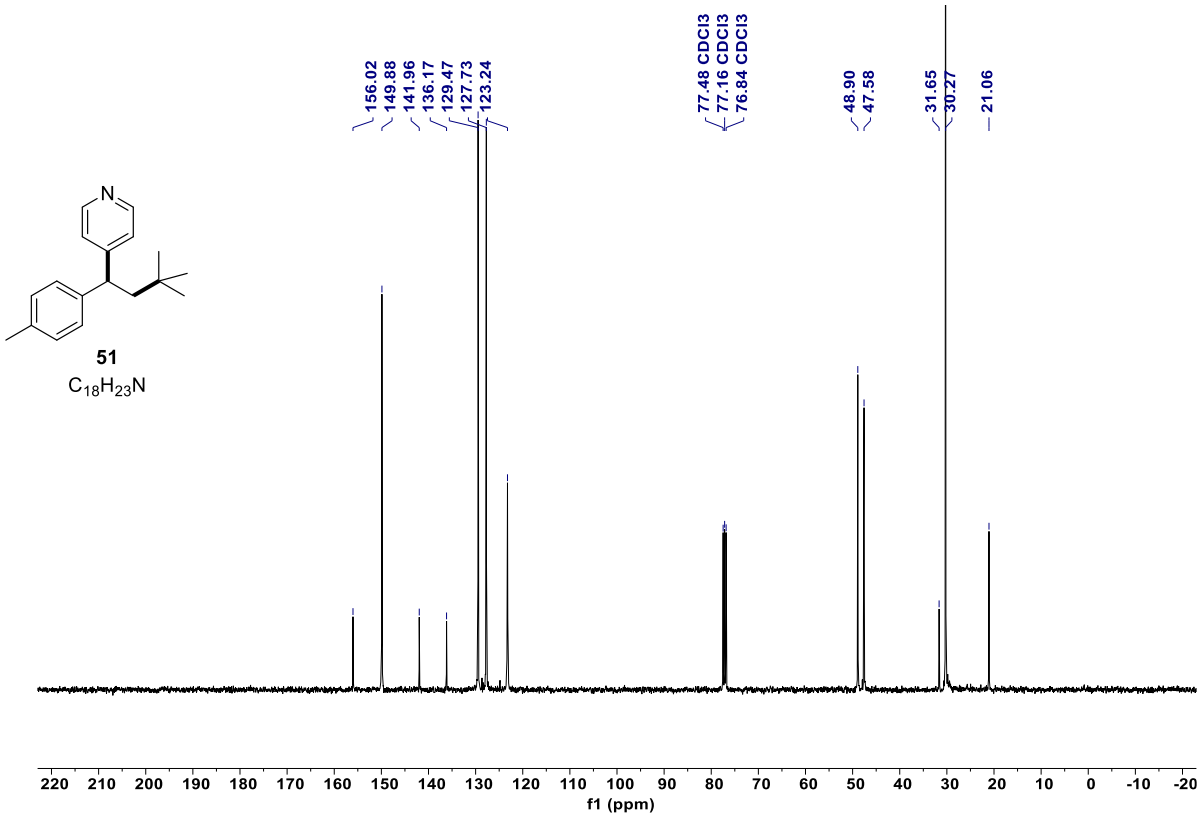
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **50**.



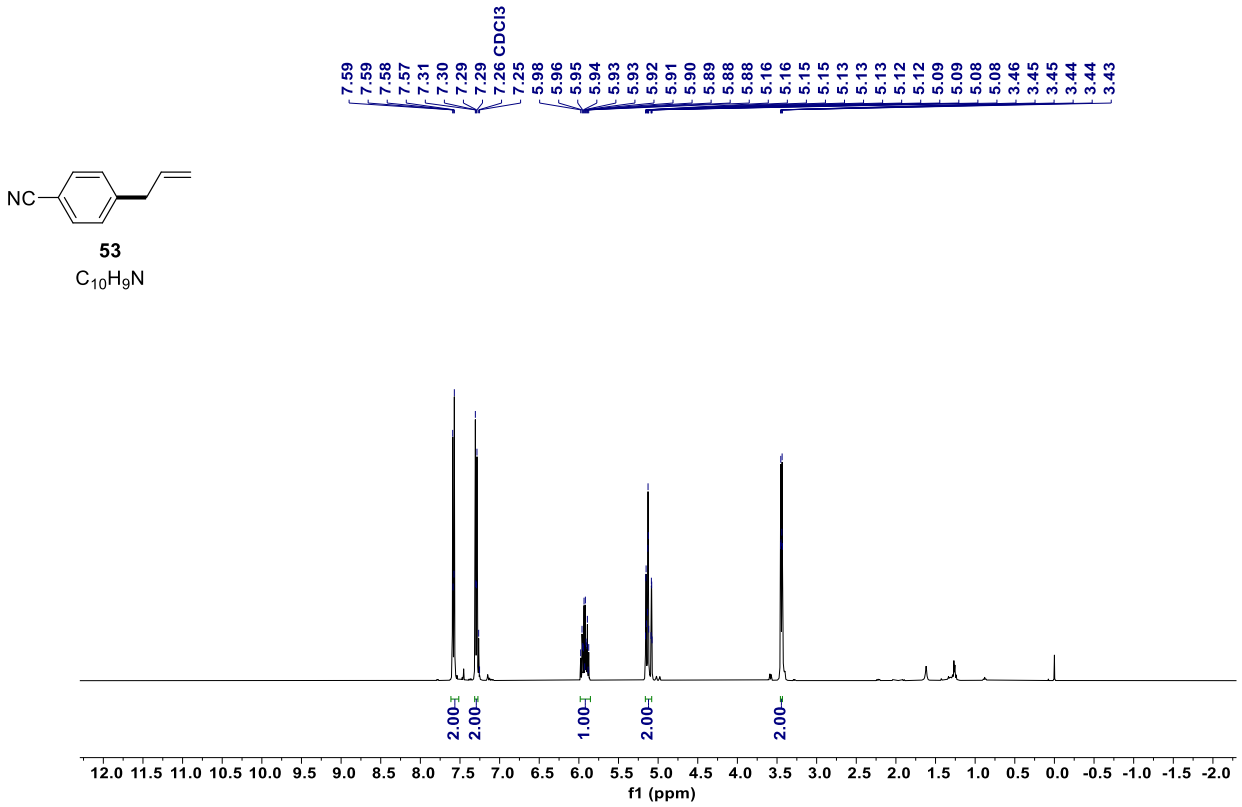
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **50**.



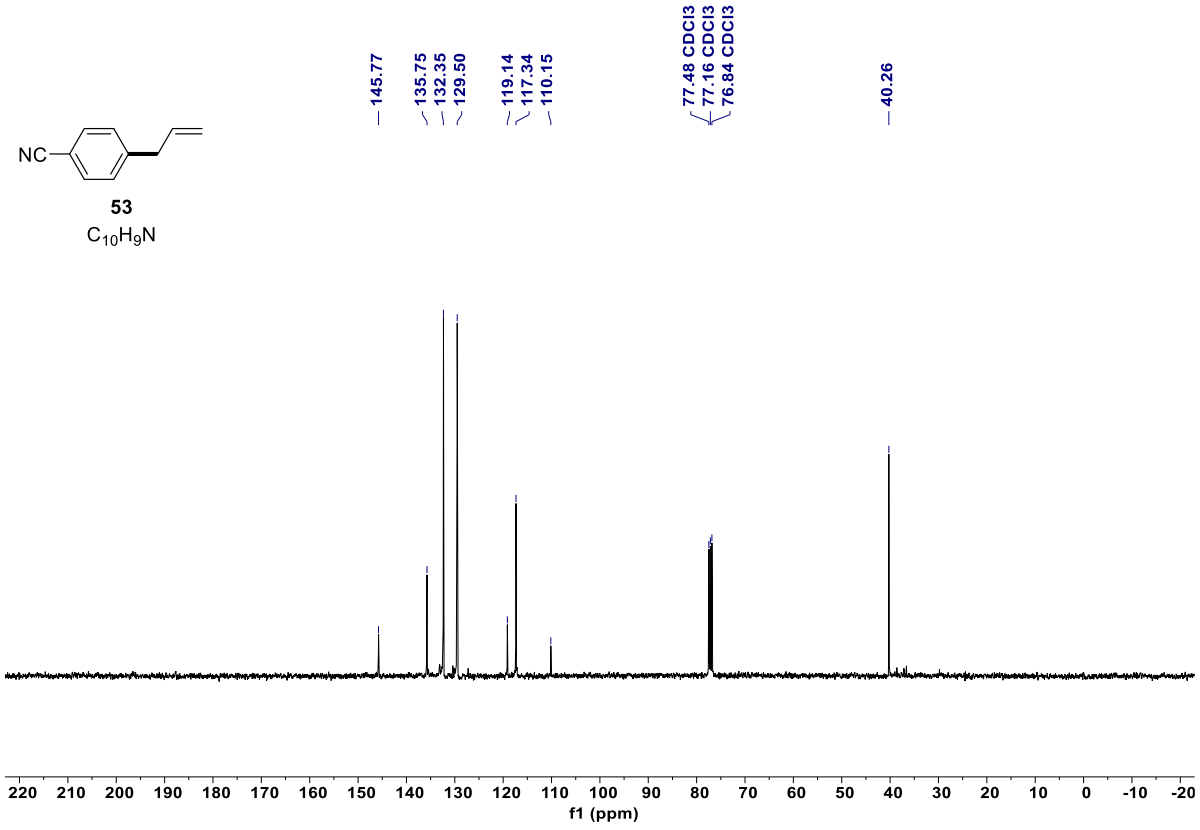
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **51**.



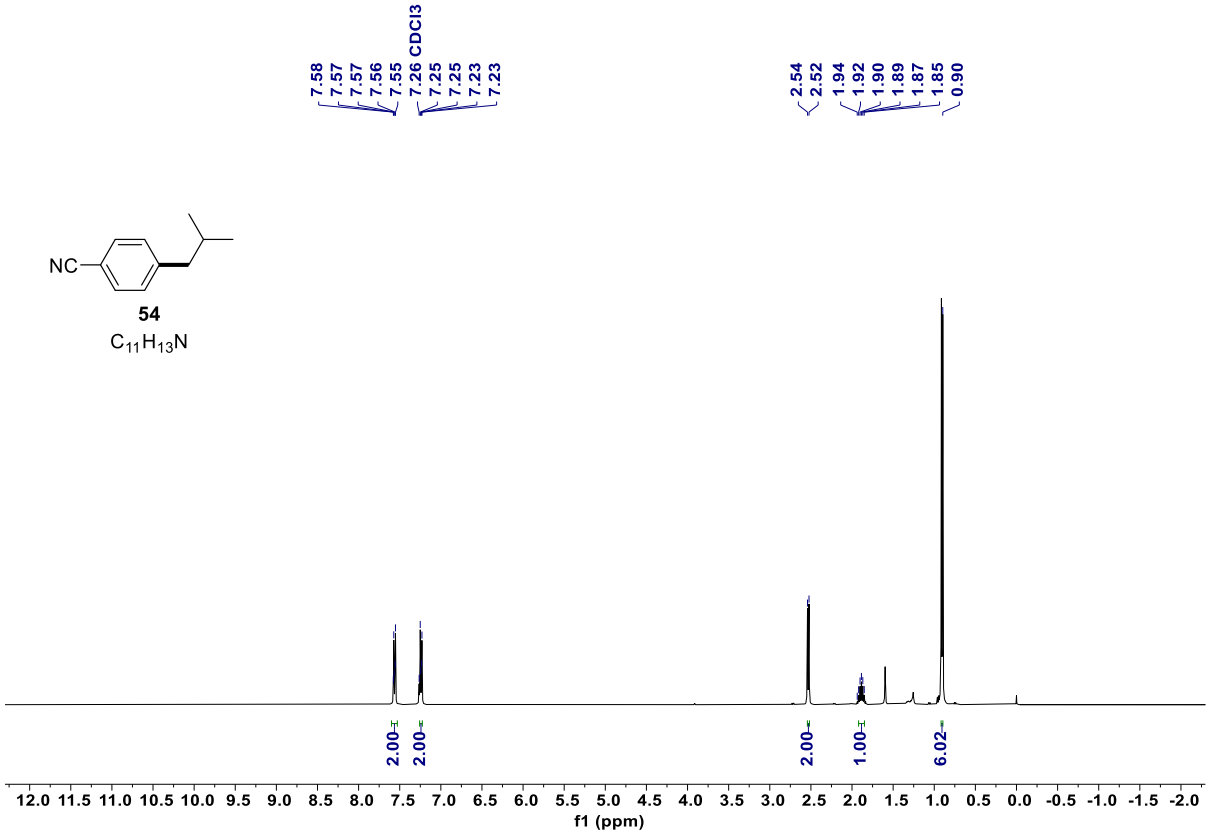
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **51**.



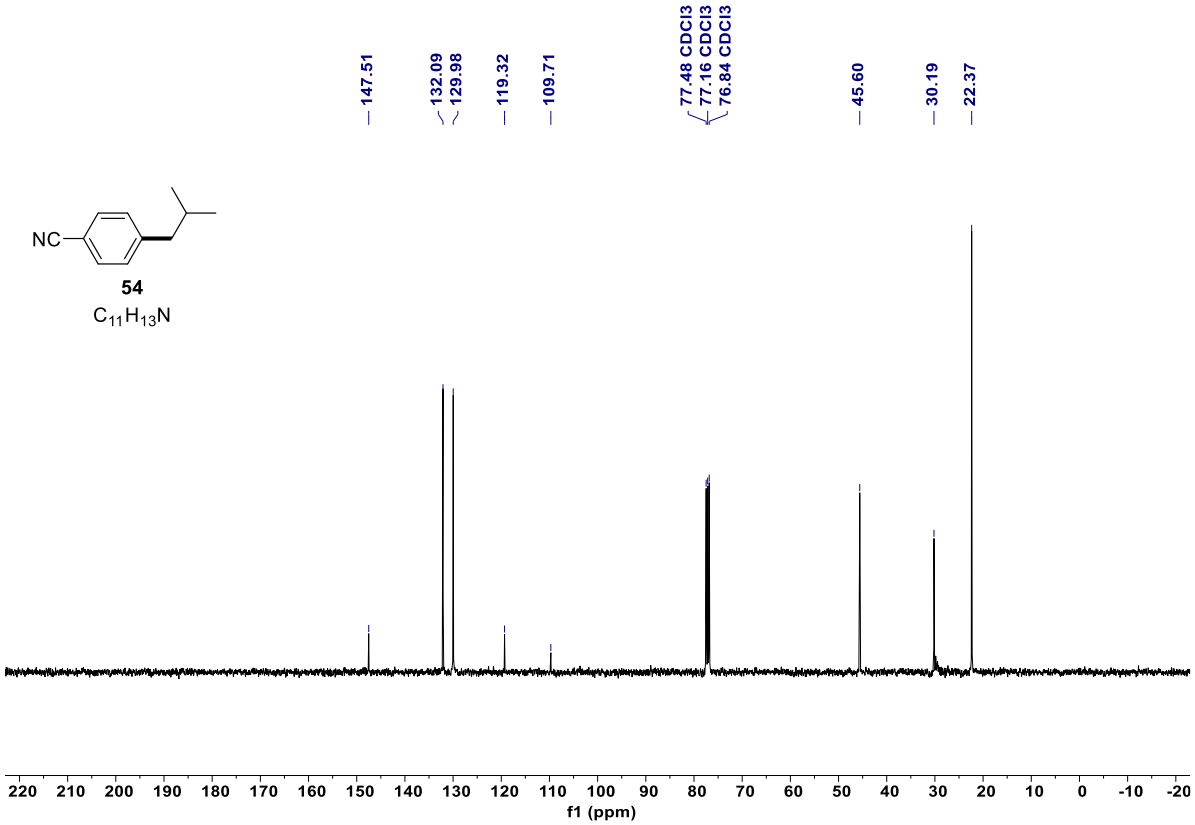
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **53**.



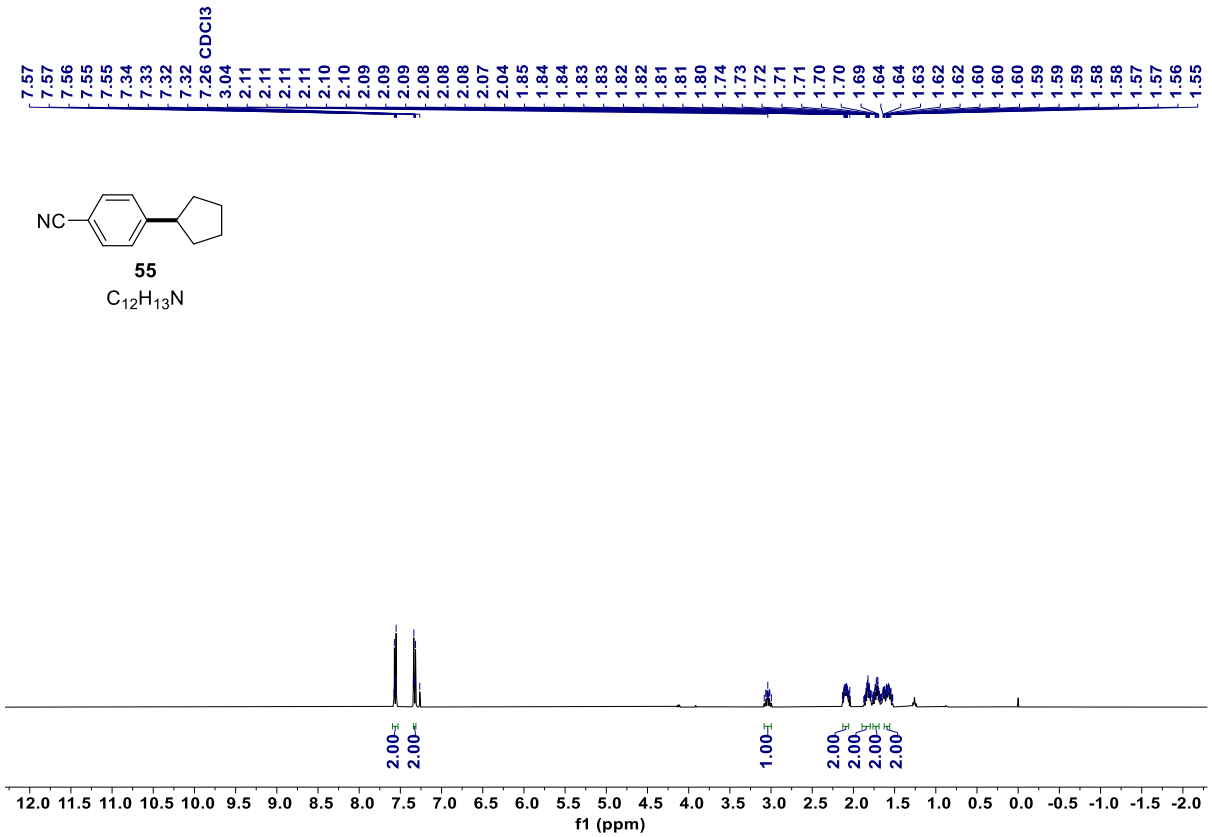
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **53**.



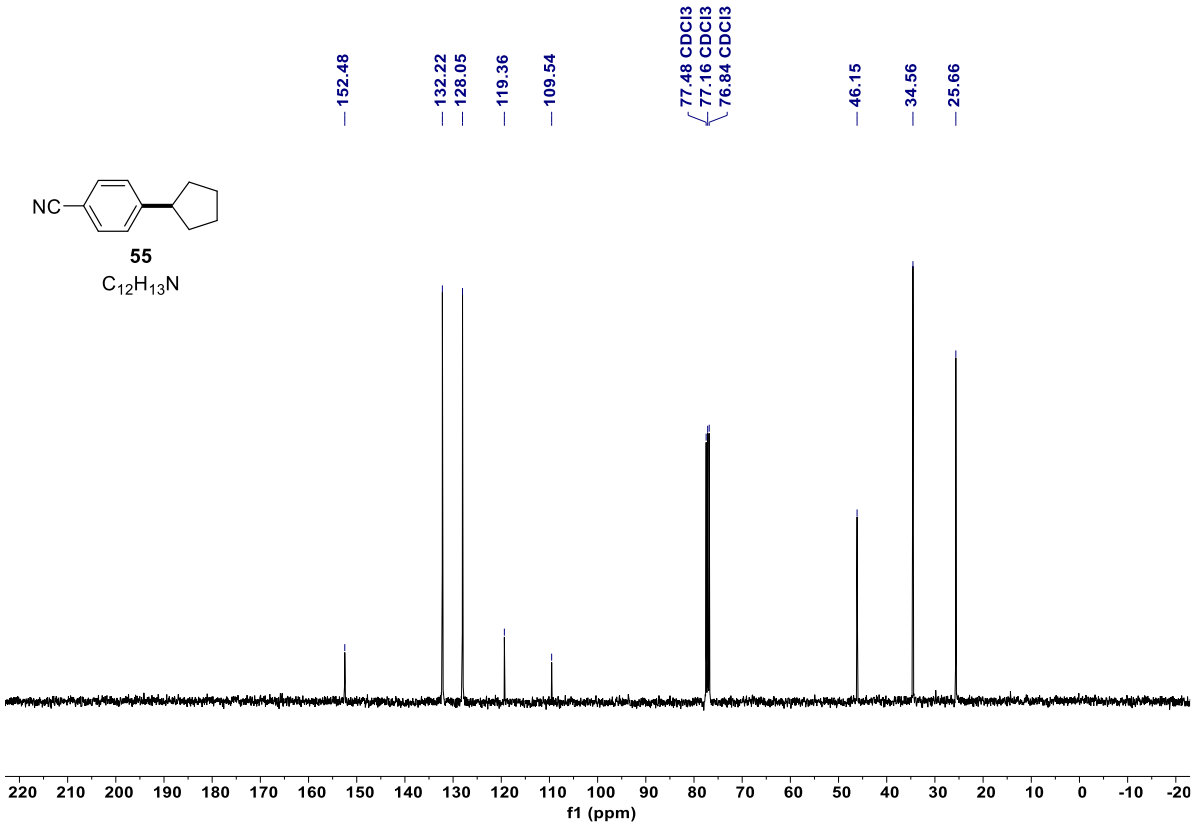
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **54**.



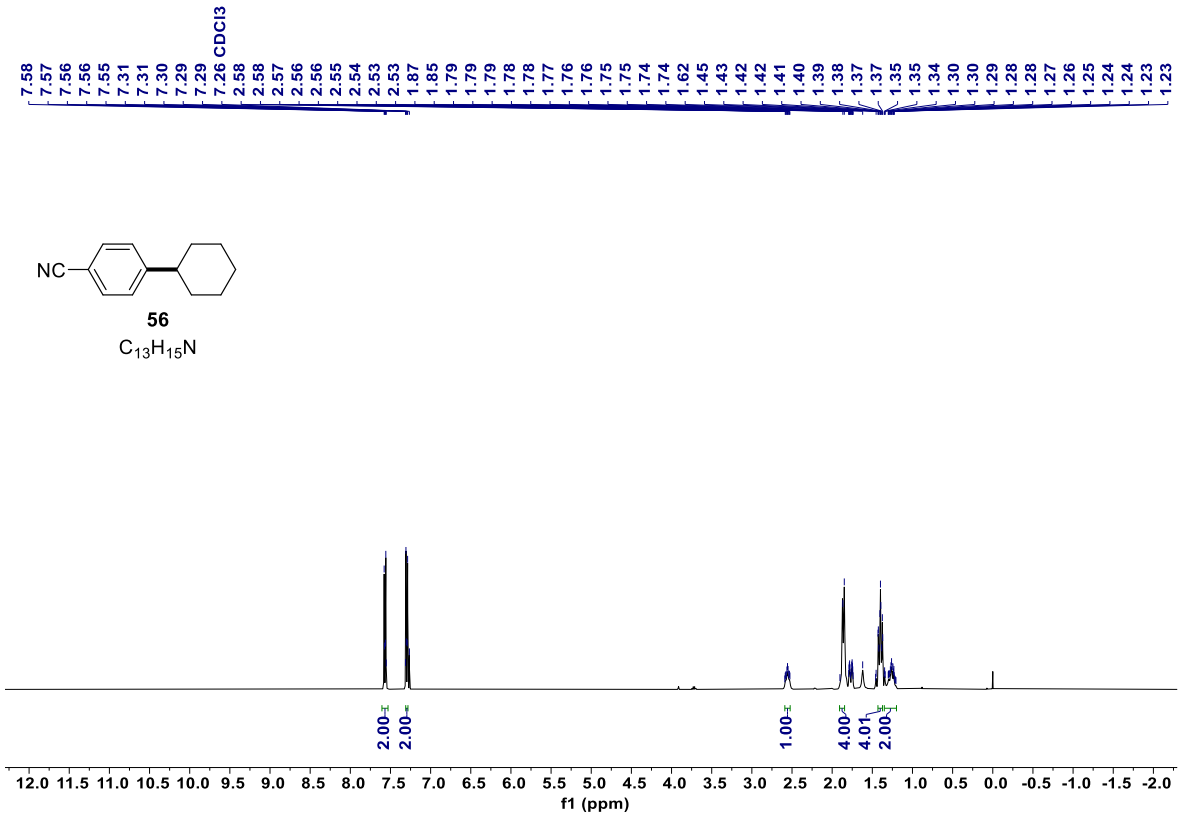
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **54**.



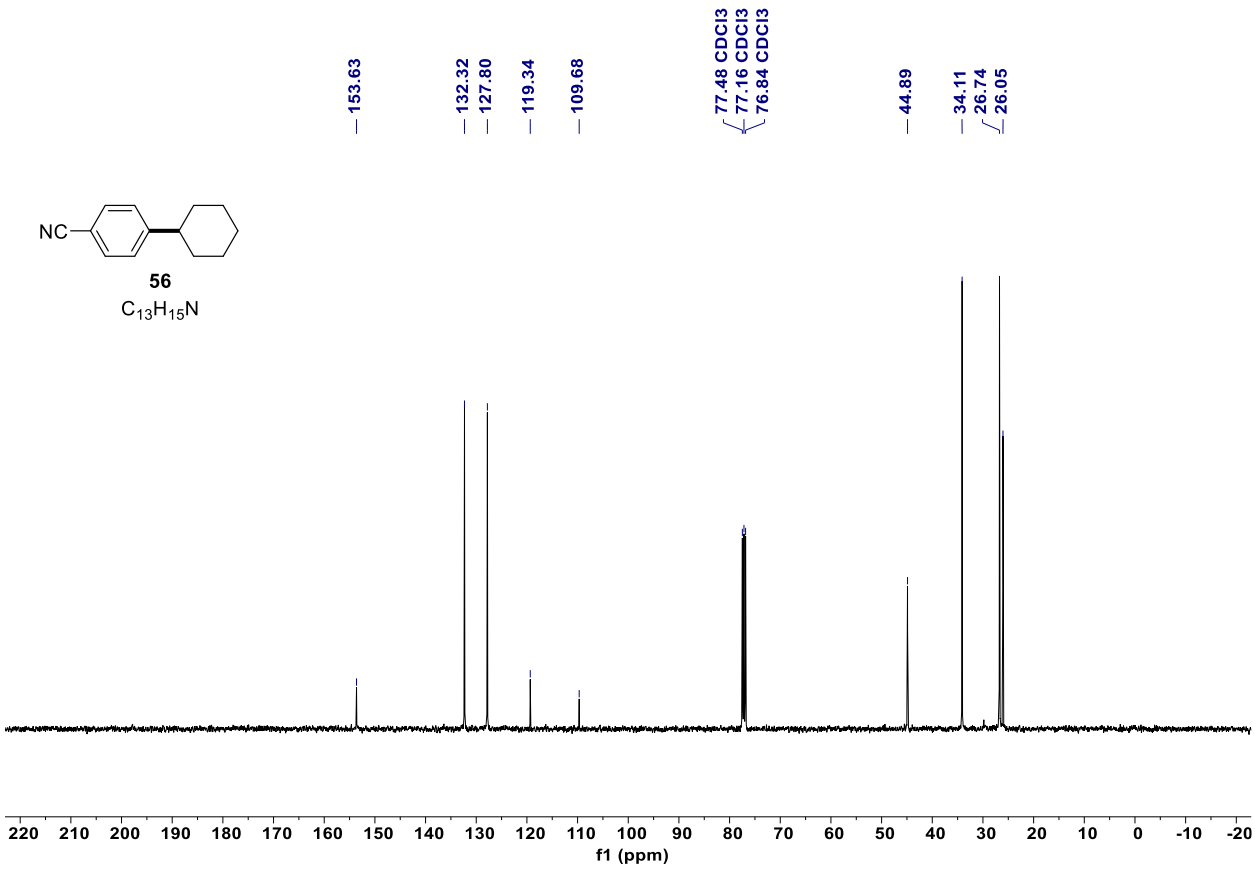
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **55**.



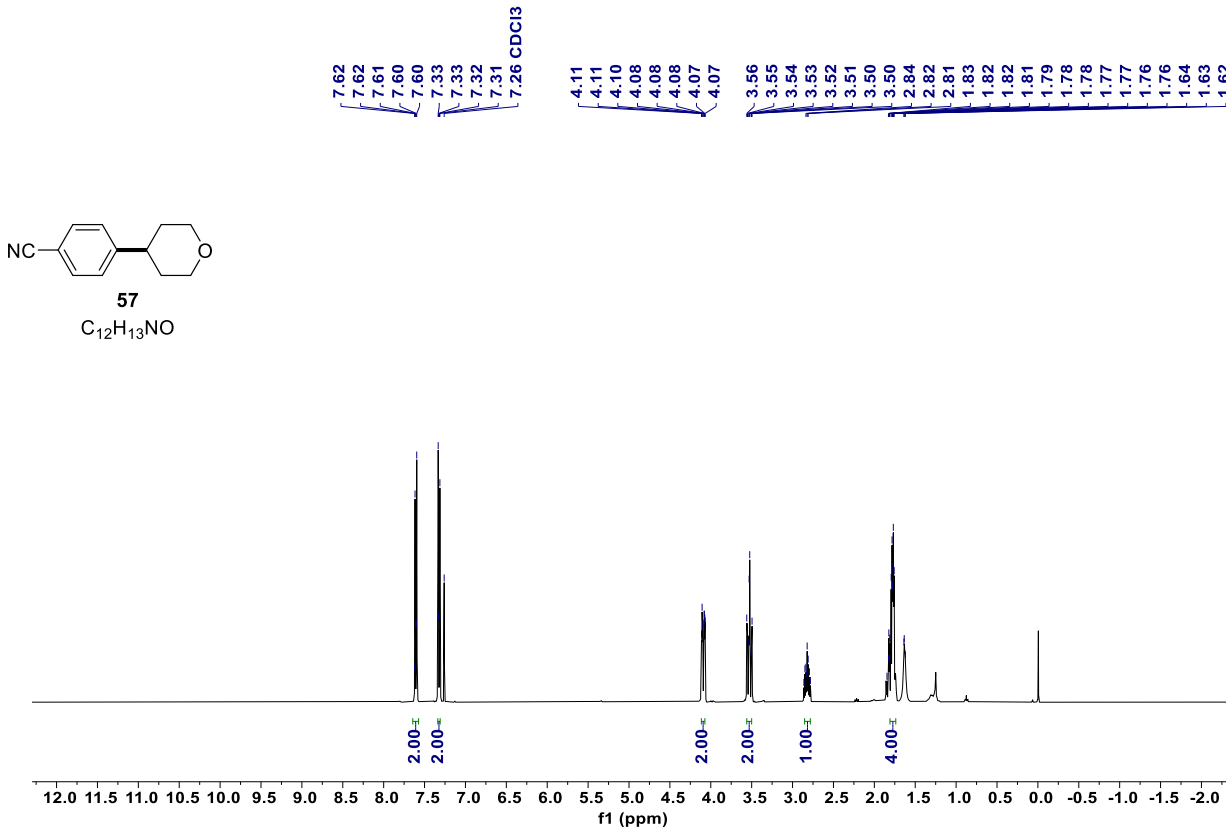
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **55**.



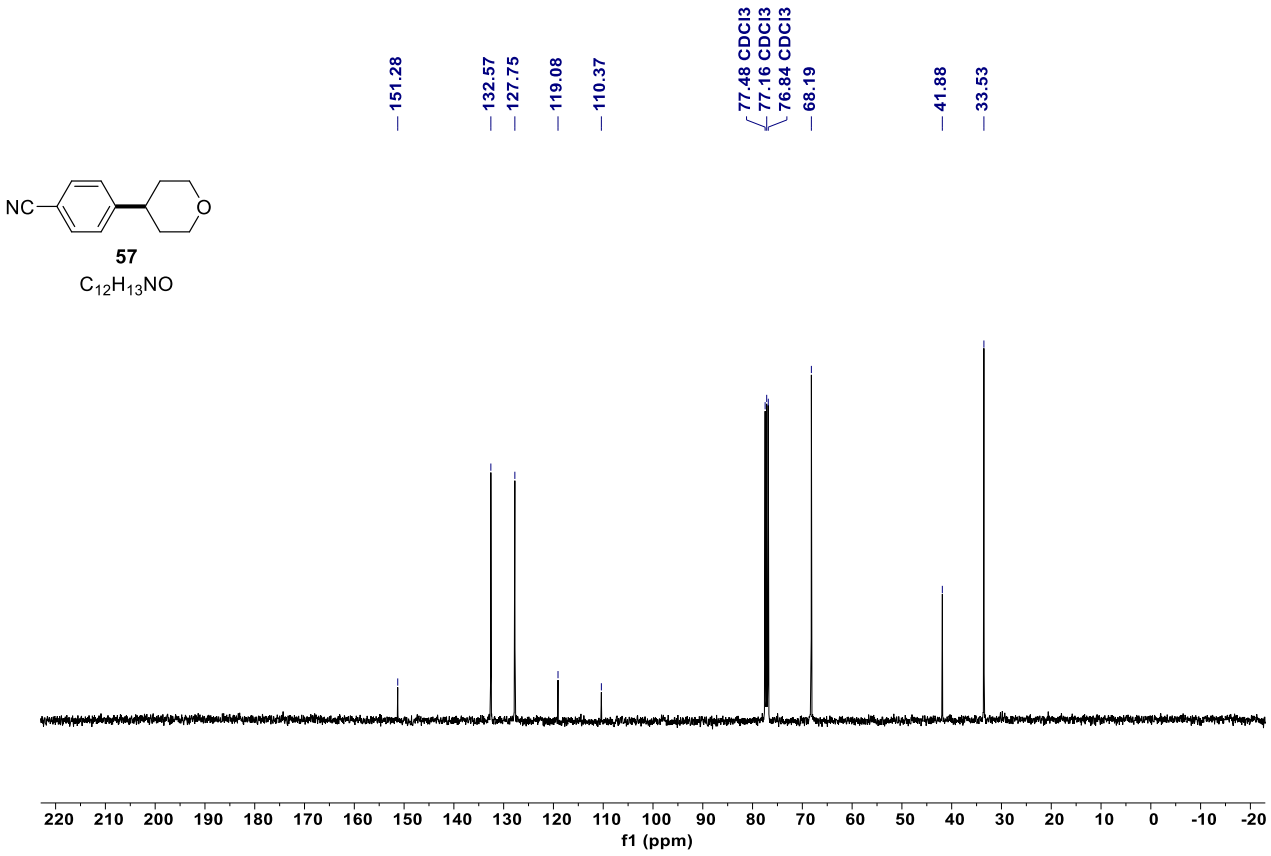
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **56**.



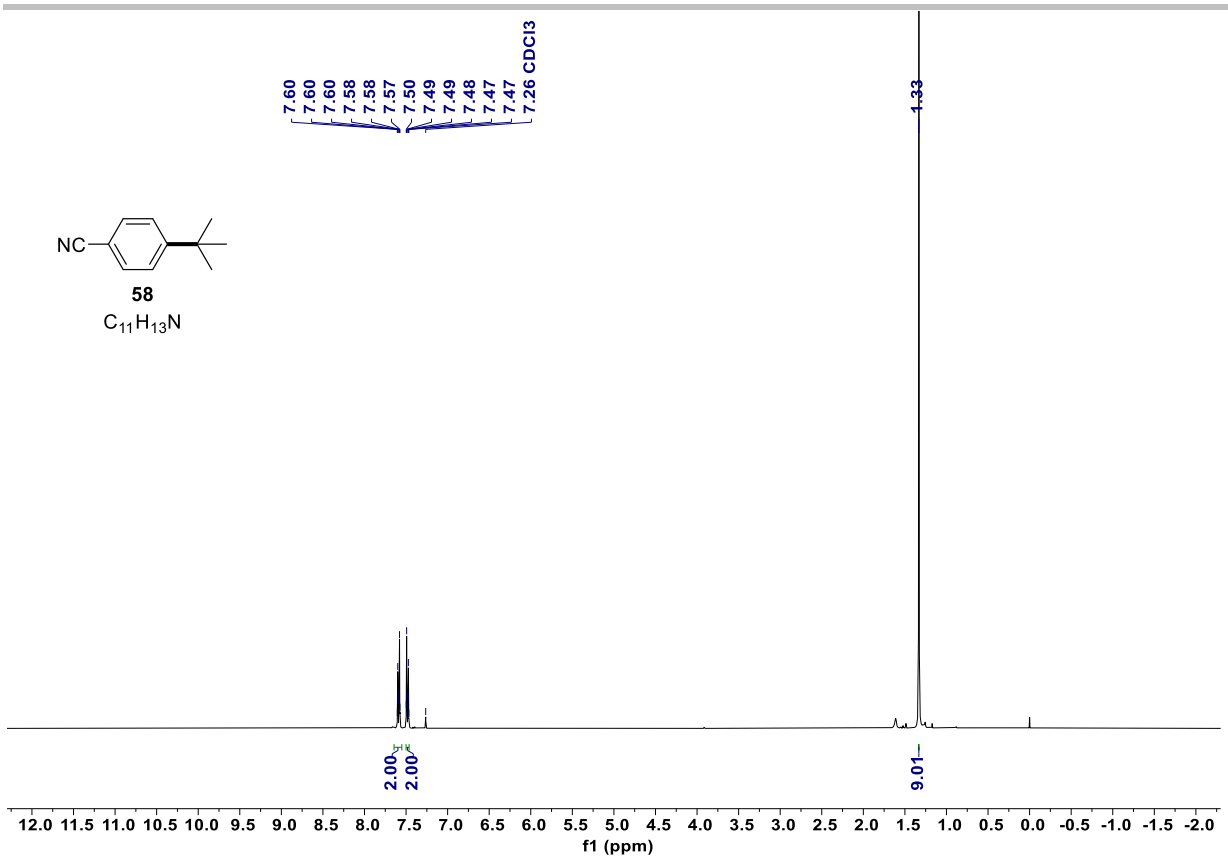
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **56**.



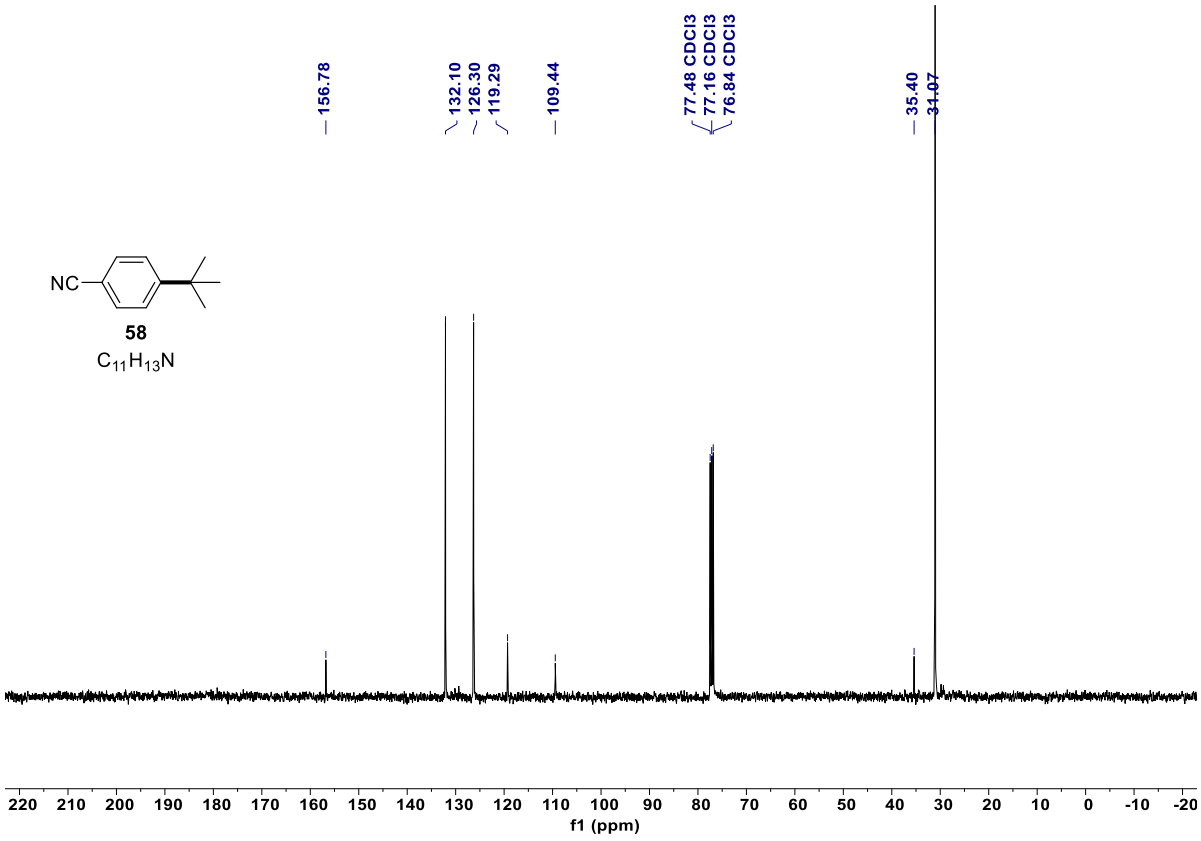
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **57**.



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **57**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the compound **58**.



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **58**.

5. Energies and Cartesian Coordinates of the Optimized Structures

$Ir(ppy)_3$

B3LYP-D3 Electronic Energy: -1540.8756292 a.u.

B3LYP-D3 Gibbs free Energy: -1540.456313 a.u.

M06-2X Electronic Energy: -1540.4824677 a.u.

M06-2X E(TD-HF/TD-DFT): -1540.36748706

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.001161	-0.000768	0.036650
2	6	0	0.995294	-1.434853	1.070672
3	6	0	0.849189	-2.764546	0.578610
4	6	0	1.811743	-1.262606	2.204234
5	6	0	1.493304	-3.847151	1.205629
6	6	0	-0.014224	-2.934922	-0.593932
7	6	0	2.446800	-2.338798	2.821708
8	1	0	1.942865	-0.265079	2.611325
9	6	0	2.290824	-3.639489	2.324240
10	1	0	1.374058	-4.857856	0.825821
11	6	0	-0.310569	-4.156695	-1.222849
12	1	0	3.067597	-2.167600	3.697925
13	1	0	2.784919	-4.477569	2.806245
14	6	0	-1.378024	-1.817917	-2.136646
15	6	0	-1.153587	-4.187991	-2.324979
16	1	0	0.117179	-5.075418	-0.840921
17	6	0	-1.704881	-2.993186	-2.798156
18	1	0	-1.779714	-0.859710	-2.449184
19	1	0	-1.383850	-5.132237	-2.809152
20	1	0	-2.374467	-2.969932	-3.650375
21	6	0	0.749002	1.576632	1.069534
22	6	0	1.970204	2.117762	0.572116
23	6	0	0.195821	2.195779	2.206186
24	6	0	2.586090	3.218233	1.196397
25	6	0	2.545717	1.456608	-0.603029
26	6	0	0.810813	3.285000	2.821113
27	1	0	-0.730958	1.808681	2.617561
28	6	0	2.011497	3.803407	2.317924
29	1	0	3.518171	3.622701	0.812178
30	6	0	3.748412	1.813508	-1.237245
31	1	0	0.355349	3.735601	3.699727

32	1	0	2.490497	4.651408	2.797810
33	6	0	2.257812	-0.284136	-2.143970
34	6	0	4.194017	1.099788	-2.341042
35	1	0	4.329807	2.644828	-0.858075
36	6	0	3.435552	0.022923	-2.810560
37	1	0	1.629482	-1.112731	-2.453455
38	1	0	5.124138	1.374593	-2.829309
39	1	0	3.748054	-0.568229	-3.663816
40	6	0	-1.735002	-0.142493	1.075993
41	6	0	-2.815617	0.646058	0.584123
42	6	0	-1.990134	-0.931866	2.213108
43	6	0	-4.073699	0.629999	1.214251
44	6	0	-2.535264	1.475887	-0.591507
45	6	0	-3.238081	-0.943128	2.833802
46	1	0	-1.189946	-1.541577	2.620445
47	6	0	-4.288830	-0.160947	2.336102
48	1	0	-4.891100	1.236286	0.834432
49	6	0	-3.447867	2.340280	-1.220837
50	1	0	-3.397151	-1.563351	3.712707
51	1	0	-5.260475	-0.169421	2.820531
52	6	0	-0.890170	2.097100	-2.139186
53	6	0	-3.056882	3.083852	-2.325630
54	1	0	-4.456763	2.428488	-0.837128
55	6	0	-1.747255	2.964845	-2.801102
56	1	0	0.140108	1.966816	-2.453426
57	1	0	-3.761570	3.752987	-2.810110
58	1	0	-1.394938	3.531584	-3.655413
59	7	0	-1.267356	1.371184	-1.076853
60	7	0	1.820383	0.408782	-1.082692
61	7	0	-0.557360	-1.783452	-1.076865

Ir(ppy)$_3^+$

B3LYP-D3 Electronic Energy: -1540.6482171 a.u.

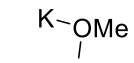
B3LYP-D3 Gibbs free Energy: -1540.230421 a.u.

M06-2X Electronic Energy: -1540.2905532 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.000634	0.001900	0.096175
2	6	0	1.038652	-1.433207	1.063608
3	6	0	0.845606	-2.762738	0.584649
4	6	0	1.928491	-1.234388	2.133717
5	6	0	1.505866	-3.838435	1.198033

6	6	0	-0.037652	-2.924288	-0.574752
7	6	0	2.568537	-2.312148	2.741598
8	1	0	2.094530	-0.231481	2.511403
9	6	0	2.357861	-3.616335	2.275558
10	1	0	1.363417	-4.853310	0.841671
11	6	0	-0.352728	-4.144043	-1.194571
12	1	0	3.232435	-2.140235	3.583748
13	1	0	2.860085	-4.453385	2.749268
14	6	0	-1.419024	-1.793700	-2.097667
15	6	0	-1.216913	-4.167382	-2.280230
16	1	0	0.076260	-5.065788	-0.822499
17	6	0	-1.766734	-2.968534	-2.746018
18	1	0	-1.818372	-0.834075	-2.407037
19	1	0	-1.464911	-5.109228	-2.758956
20	1	0	-2.450943	-2.943683	-3.585971
21	6	0	0.726483	1.615684	1.064064
22	6	0	1.973500	2.114908	0.583033
23	6	0	0.111834	2.284728	2.137490
24	6	0	2.575896	3.223368	1.197125
25	6	0	2.552735	1.432791	-0.578718
26	6	0	0.726351	3.376590	2.746070
27	1	0	-0.838523	1.925853	2.516984
28	6	0	1.959836	3.847612	2.277631
29	1	0	3.524934	3.608752	0.839293
30	6	0	3.765439	1.770563	-1.200277
31	1	0	0.247735	3.863681	3.590562
32	1	0	2.434508	4.700304	2.751874
33	6	0	2.261858	-0.327780	-2.101919
34	6	0	4.216124	1.034371	-2.287047
35	1	0	4.349705	2.602821	-0.828695
36	6	0	3.452267	-0.041145	-2.751947
37	1	0	1.630007	-1.153408	-2.410426
38	1	0	5.154977	1.290855	-2.767168
39	1	0	3.771725	-0.645874	-3.592506
40	6	0	-1.755584	-0.177984	1.073062
41	6	0	-2.814974	0.648436	0.593738
42	6	0	-2.021044	-1.041235	2.150590
43	6	0	-4.073815	0.615012	1.212891
44	6	0	-2.520146	1.488780	-0.571235
45	6	0	-3.271628	-1.056089	2.764088
46	1	0	-1.232011	-1.681718	2.529049
47	6	0	-4.300232	-0.227574	2.296948
48	1	0	-4.884760	1.241521	0.856364
49	6	0	-3.424220	2.364507	-1.193381

50	1	0	-3.449169	-1.711805	3.611458
51	1	0	-5.274082	-0.243590	2.775125
52	6	0	-0.856824	2.118596	-2.101906
53	6	0	-3.018177	3.120615	-2.283994
54	1	0	-4.436474	2.451423	-0.819381
55	6	0	-1.705657	3.000473	-2.752490
56	1	0	0.173740	1.987030	-2.412981
57	1	0	-3.713902	3.800879	-2.764581
58	1	0	-1.346577	3.577952	-3.596211
59	7	0	-1.251130	1.380218	-1.052667
60	7	0	1.820581	0.389245	-1.056721
61	7	0	-0.576281	-1.768936	-1.053260



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IM1

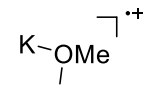
B3LYP-D3 Electronic Energy: -1537.7950786 a.u.

B3LYP-D3 Gibbs free Energy: -1537.444054 a.u.

M06-2X Electronic Energy: -1537.6301131 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.735913	1.324299	0.549274
2	6	0	-2.728630	-0.222574	0.824729
3	5	0	-0.873961	0.732401	1.896990
4	8	0	-1.380732	1.682127	0.837256
5	8	0	-1.855348	-0.338900	1.937056
6	6	0	-4.092135	-0.803761	1.198608
7	1	0	-4.829343	-0.625464	0.406599
8	1	0	-4.001439	-1.885038	1.343206
9	1	0	-4.460525	-0.371470	2.131205
10	6	0	-3.663702	2.080343	1.514846
11	1	0	-3.483021	3.157144	1.409764
12	1	0	-4.721218	1.896313	1.296693
13	1	0	-3.448784	1.795712	2.546742
14	6	0	-3.054598	1.717387	-0.891820
15	1	0	-4.040086	1.342413	-1.190652
16	1	0	-3.067440	2.809321	-0.989576
17	1	0	-2.305669	1.324520	-1.582574
18	6	0	-2.136587	-1.016357	-0.354525
19	1	0	-1.947824	-2.040072	-0.019174

20	1	0	-2.814483	-1.047900	-1.214892
21	1	0	-1.181307	-0.588403	-0.669534
22	6	0	2.889572	0.806514	0.628771
23	6	0	2.726518	-0.736754	0.852697
24	5	0	0.763011	0.325552	1.447713
25	8	0	1.751432	1.331763	1.364364
26	8	0	1.295547	-0.870835	1.034397
27	6	0	3.155584	-1.606461	-0.323978
28	1	0	4.217240	-1.457397	-0.550917
29	1	0	3.004304	-2.660121	-0.072953
30	1	0	2.568824	-1.388552	-1.218007
31	6	0	2.702916	1.225939	-0.833793
32	1	0	2.642185	2.318056	-0.887907
33	1	0	3.540775	0.901625	-1.458264
34	1	0	1.776329	0.814354	-1.242336
35	6	0	4.169426	1.411436	1.193747
36	1	0	5.050241	0.957348	0.727050
37	1	0	4.198112	2.486528	0.985959
38	1	0	4.236222	1.271801	2.274089
39	6	0	3.387472	-1.230994	2.144912
40	1	0	3.054619	-2.254339	2.337650
41	1	0	4.479605	-1.227693	2.068798
42	1	0	3.089146	-0.615018	2.997763
43	8	0	-0.869460	1.514547	3.191183
44	6	0	-0.597456	0.752706	4.343248
45	1	0	-0.616951	1.408143	5.223346
46	1	0	-1.342755	-0.042714	4.480281
47	1	0	0.397625	0.273325	4.294687
48	19	0	0.151902	3.471697	1.845669



Bpin-Bpin

B3LYP-D3 Electronic Energy: -1537.5854264 a.u.

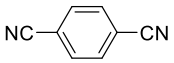
B3LYP-D3 Gibbs free Energy: -1537.239127 a.u.

M06-2X Electronic Energy: -1537.4672864 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.284780	1.492383	0.763670
2	6	0	-3.397696	-0.035970	1.142820

3	5	0	-1.634019	0.891547	2.221135
4	8	0	-1.933191	1.827200	1.250658
5	8	0	-2.513589	-0.132904	2.312582
6	6	0	-4.791656	-0.487222	1.551272
7	1	0	-5.496256	-0.336811	0.727297
8	1	0	-4.775690	-1.552918	1.793070
9	1	0	-5.153471	0.053479	2.426906
10	6	0	-4.255881	2.383466	1.536868
11	1	0	-3.996053	3.432437	1.367983
12	1	0	-5.284244	2.230479	1.199964
13	1	0	-4.210549	2.186407	2.611452
14	6	0	-3.344639	1.787374	-0.726993
15	1	0	-4.300105	1.451468	-1.140832
16	1	0	-3.269557	2.865485	-0.898734
17	1	0	-2.538553	1.291334	-1.270111
18	6	0	-2.812150	-0.968538	0.081814
19	1	0	-2.751932	-1.978519	0.494608
20	1	0	-3.441883	-0.998674	-0.811393
21	1	0	-1.802222	-0.661189	-0.207122
22	6	0	3.289943	0.735983	0.253572
23	6	0	3.236605	-0.769660	0.707489
24	5	0	1.134542	-0.034554	0.250547
25	8	0	1.843148	1.130742	0.342514
26	8	0	1.851447	-1.160293	0.331292
27	6	0	4.202244	-1.691060	-0.019902
28	1	0	5.235570	-1.379050	0.164026
29	1	0	4.084718	-2.711681	0.352210
30	1	0	4.023635	-1.700284	-1.095644
31	6	0	3.690129	0.928465	-1.206095
32	1	0	3.517404	1.968419	-1.496605
33	1	0	4.750783	0.706538	-1.351530
34	1	0	3.106205	0.286283	-1.869755
35	6	0	4.085290	1.656768	1.164543
36	1	0	5.132515	1.340649	1.198051
37	1	0	4.066925	2.679655	0.775017
38	1	0	3.699912	1.658608	2.186135
39	6	0	3.333554	-0.959284	2.220229
40	1	0	3.084987	-1.994918	2.463701
41	1	0	4.346007	-0.755214	2.579690
42	1	0	2.633770	-0.308771	2.751863
43	8	0	-0.510680	1.074833	2.972374
44	6	0	-0.131932	0.059238	3.922034
45	1	0	0.724788	0.440681	4.479448
46	1	0	-0.955658	-0.146481	4.609936

47	1	0	0.143726	-0.860984	3.399473
48	19	0	0.367776	3.167556	1.316865

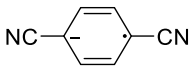


B3LYP-D3 Electronic Energy: -416.7702385 a.u.

B3LYP-D3 Gibbs free Energy: -416.705657 a.u.

M06-2X Electronic Energy: -416.7157343 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.919463	5.057291	5.089390
2	6	0	0.994817	4.071084	5.465348
3	6	0	1.331814	2.728638	5.355901
4	6	0	2.596020	2.362213	4.869659
5	6	0	3.520675	3.348430	4.493693
6	6	0	3.183682	4.690862	4.603139
7	1	0	0.020308	4.361373	5.840057
8	1	0	0.622720	1.961633	5.644396
9	1	0	4.495178	3.058121	4.118984
10	1	0	3.892761	5.457884	4.314647
11	6	0	2.944050	0.976000	4.756600
12	7	0	3.225542	-0.144730	4.665138
13	6	0	1.571474	6.443516	5.202429
14	7	0	1.290151	7.564293	5.293822



B3LYP-D3 Electronic Energy: -416.8159462 a.u.

B3LYP-D3 Gibbs free Energy: -416.755372 a.u.

M06-2X Electronic Energy: -416.811571 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.909709	5.096286	5.092538
2	6	0	0.987145	4.060474	5.468514
3	6	0	1.319949	2.733975	5.360456
4	6	0	2.605417	2.323131	4.866646
5	6	0	3.528210	3.359083	4.490612
6	6	0	3.195398	4.685472	4.598674

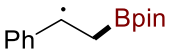
7	1	0	0.008087	4.341890	5.845156
8	1	0	0.602509	1.972522	5.652140
9	1	0	4.507204	3.077394	4.114041
10	1	0	3.912708	5.447086	4.307081
11	6	0	2.946811	0.966049	4.755643
12	7	0	3.232774	-0.169843	4.662648
13	6	0	1.569004	6.453508	5.203195
14	7	0	1.283729	7.589582	5.295858

B3LYP-D3 Electronic Energy: -309.6866649 a.u.

B3LYP-D3 Gibbs free Energy: -309.585058 a.u.

M06-2X Electronic Energy: -309.6123139 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.917244	5.067511	5.089967
2	6	0	0.997081	4.083407	5.464223
3	6	0	1.324944	2.735807	5.358526
4	6	0	2.583021	2.334320	4.875171
5	6	0	3.495347	3.335433	4.503992
6	6	0	3.169288	4.687084	4.608874
7	1	0	1.658172	6.118053	5.173765
8	1	0	0.019756	4.369946	5.840225
9	1	0	0.595476	1.989744	5.655090
10	1	0	4.473254	3.047244	4.128037
11	1	0	3.893227	5.440617	4.314863
12	6	0	2.982640	0.924639	4.742122
13	6	0	2.257123	-0.161840	5.036882
14	1	0	3.990483	0.775546	4.356410
15	1	0	2.665318	-1.156625	4.894434
16	1	0	1.244859	-0.106411	5.425022



IM2

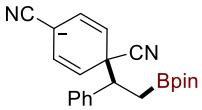
B3LYP-D3 Electronic Energy: -721.0221299 a.u.

B3LYP-D3 Gibbs free Energy: -720.752471 a.u.

M06-2X Electronic Energy: -720.8605504 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-1.823214	-1.757354	-1.142387
2	6	0	-1.933988	-2.578459	-0.012940
3	6	0	-2.922368	-2.355621	0.934729
4	6	0	-3.851243	-1.284499	0.786809
5	6	0	-3.719549	-0.466803	-0.374068
6	6	0	-2.728198	-0.699680	-1.313011
7	1	0	-1.046904	-1.938615	-1.878446
8	1	0	-1.241087	-3.403669	0.123474
9	1	0	-3.005428	-3.021416	1.785220
10	1	0	-4.415396	0.355955	-0.514089
11	1	0	-2.652644	-0.057922	-2.185750
12	6	0	-4.871249	-1.014059	1.729641
13	6	0	-5.132679	-1.800725	2.981764
14	1	0	-5.568850	-0.215490	1.492106
15	1	0	-5.750994	-1.212481	3.666602
16	1	0	-4.198968	-2.057530	3.496794
17	6	0	-7.552735	-4.569785	1.987780
18	6	0	-6.150520	-5.169552	1.598640
19	5	0	-5.883896	-3.122615	2.559047
20	8	0	-7.221202	-3.180029	2.274636
21	8	0	-5.238459	-4.310936	2.343486
22	6	0	-5.925393	-6.613921	2.025474
23	1	0	-6.660196	-7.272373	1.550076
24	1	0	-4.927370	-6.937255	1.715968
25	1	0	-5.998048	-6.730086	3.108068
26	6	0	-8.127176	-5.160679	3.278544
27	1	0	-8.985991	-4.559792	3.590187
28	1	0	-8.459650	-6.192767	3.132704
29	1	0	-7.388025	-5.140938	4.084312
30	6	0	-8.595899	-4.603217	0.877949
31	1	0	-8.796258	-5.635527	0.571752
32	1	0	-9.531473	-4.166134	1.238617
33	1	0	-8.271289	-4.034384	0.005271
34	6	0	-5.803302	-4.986626	0.117875
35	1	0	-4.748574	-5.232541	-0.030417
36	1	0	-6.408184	-5.639230	-0.518582
37	1	0	-5.949948	-3.949990	-0.197372



IM3

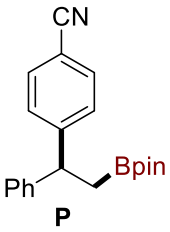
B3LYP-D3 Electronic Energy: -1137.8750744 a.u.

B3LYP-D3 Gibbs free Energy: -1137.516574 a.u.

M06-2X Electronic Energy: -1137.7199268 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.450244	-2.050945	-1.311594
2	6	0	-2.789737	-2.602673	-0.211939
3	6	0	-3.065007	-2.147804	1.076963
4	6	0	-4.002231	-1.127939	1.299273
5	6	0	-4.648243	-0.575048	0.184219
6	6	0	-4.382133	-1.031784	-1.106982
7	1	0	-3.239539	-2.409161	-2.315243
8	1	0	-2.059096	-3.393546	-0.356010
9	1	0	-2.542300	-2.588071	1.917874
10	1	0	-5.368307	0.221881	0.340384
11	1	0	-4.899883	-0.587547	-1.952623
12	6	0	-4.315252	-0.609407	2.685736
13	6	0	-4.606015	-1.750744	3.692097
14	1	0	-5.216536	0.006015	2.612969
15	1	0	-4.950431	-1.291531	4.626688
16	1	0	-3.693622	-2.311594	3.922595
17	6	0	-7.706023	-3.375234	2.231169
18	6	0	-6.595974	-4.457308	1.954511
19	5	0	-5.696753	-2.694286	3.092470
20	8	0	-6.925297	-2.241100	2.671105
21	8	0	-5.532485	-4.039238	2.847486
22	6	0	-6.991548	-5.889329	2.297930
23	1	0	-7.852585	-6.205091	1.698073
24	1	0	-6.156511	-6.561509	2.078172
25	1	0	-7.241175	-5.995627	3.355339
26	6	0	-8.641810	-3.746829	3.387181
27	1	0	-9.243841	-2.871136	3.646090
28	1	0	-9.314795	-4.566457	3.114981
29	1	0	-8.071051	-4.038419	4.273436
30	6	0	-8.515994	-2.960248	1.007132
31	1	0	-9.048500	-3.820177	0.585261
32	1	0	-9.253944	-2.205506	1.295185

33	1	0	-7.874496	-2.527578	0.237795
34	6	0	-6.029309	-4.389268	0.531688
35	1	0	-5.139773	-5.022502	0.477651
36	1	0	-6.757226	-4.743831	-0.205410
37	1	0	-5.723775	-3.373418	0.270700
38	6	0	-4.432363	2.207799	4.545249
39	6	0	-3.701870	1.057997	4.537668
40	6	0	-3.227328	0.452155	3.225198
41	6	0	-3.032894	1.557549	2.199566
42	6	0	-3.776198	2.695307	2.259312
43	1	0	-4.857077	2.552889	5.485488
44	1	0	-3.511833	0.509099	5.453013
45	1	0	-2.373970	1.360536	1.361845
46	1	0	-3.703666	3.412179	1.444303
47	6	0	-1.957724	-0.267070	3.448943
48	7	0	-0.975422	-0.856588	3.629511
49	6	0	-4.597944	3.024182	3.384075
50	6	0	-5.371733	4.197865	3.412392
51	7	0	-6.024594	5.171795	3.431904



P

B3LYP-D3 Electronic Energy: -1044.9985264 a.u.

B3LYP-D3 Gibbs free Energy: -1044.644725 a.u.

M06-2X Electronic Energy: -1044.7926357 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.371116	-1.840870	-1.119706
2	6	0	-2.619344	-1.685450	0.047308
3	6	0	-3.209113	-1.159502	1.194883
4	6	0	-4.558495	-0.785947	1.200764
5	6	0	-5.301863	-0.943658	0.027218
6	6	0	-4.714068	-1.465235	-1.127019
7	1	0	-2.911887	-2.247850	-2.014868
8	1	0	-1.572164	-1.970936	0.061846
9	1	0	-2.615431	-1.032346	2.095395
10	1	0	-6.353405	-0.674187	0.024396

11	1	0	-5.307527	-1.579551	-2.029006
12	6	0	-5.215045	-0.260613	2.475585
13	6	0	-5.346388	-1.395317	3.519534
14	1	0	-6.231979	0.046899	2.205298
15	1	0	-5.857592	-1.008454	4.411620
16	1	0	-4.358207	-1.741711	3.840605
17	6	0	-7.819560	-3.796119	1.921641
18	6	0	-6.542979	-4.701444	2.104100
19	5	0	-6.142437	-2.615006	2.927845
20	8	0	-7.297486	-2.466978	2.207876
21	8	0	-5.739165	-3.916419	3.032927
22	6	0	-6.806835	-6.070183	2.718519
23	1	0	-7.479008	-6.653252	2.080021
24	1	0	-5.864702	-6.617806	2.811438
25	1	0	-7.249522	-5.988769	3.712589
26	6	0	-8.913816	-4.070073	2.956698
27	1	0	-9.669393	-3.282399	2.889262
28	1	0	-9.400132	-5.033925	2.779939
29	1	0	-8.506836	-4.063783	3.971702
30	6	0	-8.405853	-3.791076	0.515031
31	1	0	-8.725956	-4.798247	0.228189
32	1	0	-9.279356	-3.133374	0.483122
33	1	0	-7.681713	-3.430500	-0.217247
34	6	0	-5.709056	-4.840090	0.826309
35	1	0	-4.755676	-5.311753	1.079085
36	1	0	-6.217574	-5.461680	0.083189
37	1	0	-5.493195	-3.864259	0.383692
38	6	0	-3.117935	2.204190	4.562501
39	6	0	-3.770493	1.039210	4.163686
40	6	0	-4.499037	0.991087	2.971481
41	6	0	-4.558642	2.152153	2.184262
42	6	0	-3.918959	3.321485	2.568042
43	1	0	-2.556252	2.226146	5.489819
44	1	0	-3.707353	0.164758	4.799879
45	1	0	-5.111602	2.129330	1.249908
46	1	0	-3.977288	4.210288	1.949728
47	6	0	-3.187764	3.354102	3.767189
48	6	0	-2.521412	4.555654	4.173776
49	7	0	-1.982303	5.528823	4.502311

CN^-

B3LYP-D3 Electronic Energy: -92.8668412 a.u.

B3LYP-D3 Gibbs free Energy: -92.881064 a.u.

M06-2X Electronic Energy: -92.9495295 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.978587	1.514960	-0.355930
2	7	0	-0.479380	2.576933	-0.483221

TS1

B3LYP-D3 Electronic Energy: -1137.8625839 a.u.

B3LYP-D3 Gibbs free Energy: -1137.506976 a.u.

M06-2X Electronic Energy: -1137.6899165 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.805934	-1.908531	-1.229525
2	6	0	-2.565605	-2.708655	-0.103289
3	6	0	-3.129828	-2.401591	1.127310
4	6	0	-3.968958	-1.267610	1.292446
5	6	0	-4.191860	-0.466151	0.140157
6	6	0	-3.624037	-0.782701	-1.089945
7	1	0	-2.366172	-2.158539	-2.190519
8	1	0	-1.928419	-3.585501	-0.190263
9	1	0	-2.930546	-3.042524	1.977097
10	1	0	-4.832238	0.405752	0.230972
11	1	0	-3.824467	-0.147079	-1.949278
12	6	0	-4.503126	-0.857355	2.562486
13	6	0	-4.723482	-1.839605	3.703313
14	1	0	-5.276319	-0.094845	2.495793
15	1	0	-5.038729	-1.281682	4.593406
16	1	0	-3.802587	-2.381009	3.948685
17	6	0	-7.893808	-3.595079	2.561479
18	6	0	-6.750826	-4.383148	1.821852
19	5	0	-5.837975	-2.801561	3.186056
20	8	0	-7.177482	-2.471086	3.121135
21	8	0	-5.588734	-4.029389	2.608556
22	6	0	-6.905947	-5.899918	1.824684
23	1	0	-7.830990	-6.193872	1.315563
24	1	0	-6.063718	-6.352983	1.293035
25	1	0	-6.919503	-6.300828	2.840192

26	6	0	-8.498342	-4.371313	3.738005
27	1	0	-9.126120	-3.691291	4.321445
28	1	0	-9.114620	-5.209458	3.396117
29	1	0	-7.712732	-4.755671	4.394704
30	6	0	-9.000271	-3.067700	1.653889
31	1	0	-9.501169	-3.893237	1.135287
32	1	0	-9.745356	-2.535047	2.253029
33	1	0	-8.604960	-2.372508	0.911660
34	6	0	-6.493213	-3.877181	0.396993
35	1	0	-5.559292	-4.312090	0.032202
36	1	0	-7.306050	-4.157642	-0.281218
37	1	0	-6.367769	-2.791792	0.377948
38	6	0	-4.551133	2.459078	4.265588
39	6	0	-3.843371	1.296045	4.431534
40	6	0	-3.107909	0.716166	3.325841
41	6	0	-2.874624	1.585293	2.191525
42	6	0	-3.586917	2.749056	2.048691
43	1	0	-5.154458	2.841471	5.083641
44	1	0	-3.878700	0.762334	5.374397
45	1	0	-2.187126	1.263676	1.419261
46	1	0	-3.450126	3.352113	1.155892
47	6	0	-2.109690	-0.265263	3.638274
48	7	0	-1.322156	-1.079979	3.900289
49	6	0	-4.482078	3.202482	3.054987
50	6	0	-5.210587	4.404436	2.895839
51	7	0	-5.815992	5.395220	2.763602

TS2

B3LYP-D3 Electronic Energy: -1137.8553098 a.u.

B3LYP-D3 Gibbs free Energy: -1137.498701 a.u.

M06-2X Electronic Energy: -1137.6977962 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.703370	-2.012289	-1.305755
2	6	0	-2.921886	-2.326833	-0.192771
3	6	0	-3.250309	-1.829270	1.068177
4	6	0	-4.363564	-0.995111	1.244796
5	6	0	-5.139000	-0.688578	0.118586
6	6	0	-4.818819	-1.188983	-1.144172
7	1	0	-3.447381	-2.404345	-2.285962

8	1	0	-2.050082	-2.965274	-0.302815
9	1	0	-2.630526	-2.077494	1.920590
10	1	0	-6.008675	-0.049162	0.238312
11	1	0	-5.438696	-0.933137	-1.999071
12	6	0	-4.769330	-0.451557	2.608267
13	6	0	-4.974747	-1.604925	3.625756
14	1	0	-5.750009	0.018155	2.464953
15	1	0	-5.451001	-1.201632	4.527788
16	1	0	-4.005808	-2.011212	3.929882
17	6	0	-7.726604	-3.711128	2.078081
18	6	0	-6.475934	-4.662311	1.969004
19	5	0	-5.883436	-2.717428	3.008074
20	8	0	-7.125300	-2.456786	2.474005
21	8	0	-5.538940	-4.042491	2.885088
22	6	0	-6.718580	-6.100695	2.413256
23	1	0	-7.487542	-6.571672	1.790526
24	1	0	-5.793533	-6.675445	2.308026
25	1	0	-7.030528	-6.152824	3.458055
26	6	0	-8.698198	-4.110266	3.194505
27	1	0	-9.421902	-3.302247	3.335885
28	1	0	-9.242276	-5.027777	2.947885
29	1	0	-8.167939	-4.258088	4.139525
30	6	0	-8.482263	-3.494390	0.770838
31	1	0	-8.871717	-4.443782	0.386389
32	1	0	-9.327450	-2.820989	0.943543
33	1	0	-7.838993	-3.042221	0.014260
34	6	0	-5.818289	-4.637019	0.584960
35	1	0	-4.856009	-5.152356	0.644961
36	1	0	-6.439778	-5.140880	-0.162614
37	1	0	-5.622666	-3.614649	0.254396
38	6	0	-4.081186	2.645905	4.670492
39	6	0	-4.303377	1.324062	4.377601
40	6	0	-3.886657	0.722601	3.118986
41	6	0	-3.500427	1.704694	2.116591
42	6	0	-3.281359	3.023377	2.424018
43	1	0	-4.356818	3.025795	5.650772
44	1	0	-4.712650	0.681604	5.148951
45	1	0	-3.296337	1.356511	1.110362
46	1	0	-2.932876	3.698745	1.647053
47	6	0	-2.243425	-0.244130	3.568147
48	7	0	-1.167882	-0.467684	3.971091
49	6	0	-3.532680	3.541064	3.719104
50	6	0	-3.330617	4.908027	4.021832
51	7	0	-3.168685	6.038230	4.270609

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