

Supplementary Information

Dual Role Tertiary Amines in Photocatalytic Cyclizations: Towards Sustainable Syntheses of 1,3-Dinitrogen Heterocycles

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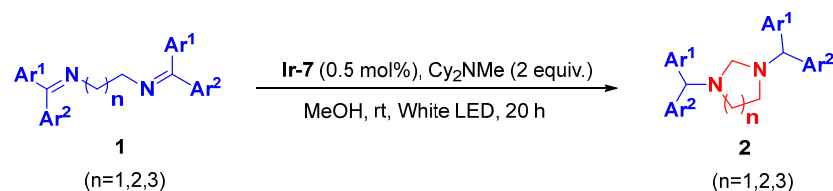
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General methods

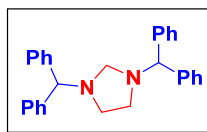
All chemicals were purchased from J&K Scientific or Energy Chemical unless otherwise specified. All reactions were conducted under a nitrogen atmosphere with oven-dried glassware by using standard Schlenk or vacuum line techniques. All solutions were handled under nitrogen and transferred via syringe. Solvents were purchased from Sigma-Aldrich and directly used. Unless otherwise stated, reagents were commercially available and used as purchased. The progress of the reactions was monitored by thin-layer chromatography using TLC plates purchased from commercial suppliers and visualized by short-wave ultraviolet light or by treatment with ninhydrin. Flash chromatography was performed with silica gel (200–300 mesh) or basic aluminum oxide (100–200 mesh). The infrared spectra were obtained with KBr plates by using an IS10 FT-IR Spectrometer (ThermoFisher Corporation). High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QToF) using electrospray ionization (ESI) in positive or negative mode. Melting points were measured using a SGW X-4 Melt-Temp apparatus and were uncorrected. NMR spectra were recorded on a Bruker 400 MHz Fourier transform spectrometer at Nanjing Tech University NMR facility. Chemical shifts in ^1H spectra were referenced to TMS, and in ^{13}C NMR spectra were referenced to residual solvent. UPLC-MS analysis was performed on an ACQUITY UPLC I-Class SQD 2 (Waters) system equipped with electrospray ionization (ESI) and a BEH C18 Acquity column (1.7 μm , 2.1 \times 50 mm).

General experimental procedure



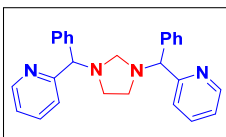
Diimine **1** (0.1 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol %), Cy_2NMe (42.8 μL , 0.2 mmol, 2 equiv.) were dissolved in MeOH (1 mL) in a 5 mL ordinary glass Schlenk tube under nitrogen. A magnetic stirring bar was added and then the vial was sealed with a septum. The mixture was placed under a 23 W white LED light source (0.5 cm distance from the reaction tube) and stirred at ambient temperature (20 – 30 $^\circ\text{C}$). The reaction progress was monitored using TLC. Upon completion of the reaction, the vessel was opened to air and the volatile materials were removed using a rotary evaporator under reduced pressure. The crude residue was purified by flash chromatography on silica gel using ethyl acetate and petroleum ether as eluents.

Compound characterization:



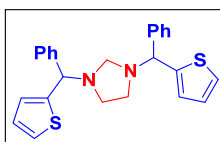
1,3-dibenzhydrylimidazolidine (2a)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1,1-diphenylmethanimine) (38.8 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (39.99 mg, 99% yield) as a white solid. M.p. 156.4 – 157.3 °C R_f = 0.45 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.46 - 7.44 (m, 8H), 7.24 - 7.20 (m, 8H), 7.15 – 7.10 (m, 4H), 4.47 (s, 2H), 3.32 (s, 2H), 2.73 (s, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 143.72, 128.43, 127.41, 126.95, 74.94, 74.55, 51.91 ppm. FTIR (neat, cm^{-1}) ν : 3022.96, 3002.89, 2919.60, 2799.21, 2714.70, 1490.63, 1451.17, 1338.31, 1192.78, 1161.60, 761.28, 743.55, 05.02, 695.67, 630.67, 524.52 cm^{-1} ; HRMS calcd for $\text{C}_{29}\text{H}_{28}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 427.2150, found 427.2145.



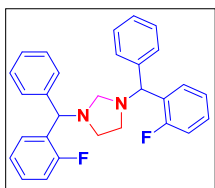
1,3-bis(phenyl(pyridin-2-yl)methyl)imidazolidine (2b)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-phenyl-1-(pyridin-2-yl)methanimine) (39.0 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (34.6 mg, 85% yield) as a white solid. M.p. 158.4 – 160.1 °C R_f = 0.67 (petroleum ether/EtOAc = 1/1). ^1H NMR (400 MHz, CDCl_3) δ : 8.42 – 8.40 (m, 2H), 7.61 – 7.50 (m, 8H), 7.25 – 7.21 (m, 4H), 7.14 – 7.11 (m, 2H), 7.02 – 6.99 (m, 2H), 4.71 (d, J = 2.6 Hz, 2H), 3.40 – 3.30 (m, 2H), 2.77 (s, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 162.68, 149.03, 142.11, 136.86, 128.56, 127.91, 127.41, 122.16, 121.90, 76.12, 74.50, 51.61 ppm. FTIR (neat, cm^{-1}) ν : 3058.93, 3029.33, 2974.60, 2929.57, 2815.71, 1663.34, 1589.56, 1452.66, 1433.60, 1279.38, 1163.02, 1073.06, 995.07, 929.61, 896.69, 771.17, 622.23, 525.24 cm^{-1} ; HRMS calcd for $\text{C}_{27}\text{H}_{26}\text{N}_4\text{Na}$ $[\text{M}+\text{Na}]$ 429.2055, found 429.2046.



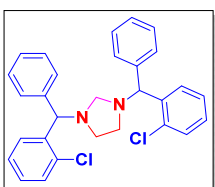
1,3-bis(phenyl(thiophen-2-yl)methyl)imidazolidine (2c)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-phenyl-1-(thiophen-2-yl)methanimine) (40.0 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (16.7 mg, 40% yield) as a white solid. M.p. 120.9 – 123.7 °C R_f = 0.56 (petroleum ether/EtOAc = 5/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.48 – 7.44 (m, 4H), 7.28 – 7.23 (m, 4H), 7.20 – 7.15 (m, 2H), 7.14 – 7.11 (m, 2H), 6.97 – 6.92 (m, 2H), 6.82 – 6.79 (m, 2H), 4.80 (s, 2H), 3.40 (s, 2H), 2.79 – 2.75 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 148.14, 143.12, 128.60, 127.63, 127.43, 126.23, 125.00, 124.23, 74.62, 69.40, 51.81 ppm. FTIR (neat, cm^{-1}) ν : 2974.30, 2798.37, 2310.20, 2113.80, 1640.03, 1491.65, 747.55, 699.64, 638.98, 615.67, 502.89, 416.02 cm^{-1} ; HRMS calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$ 417.1459, found 417.1462.



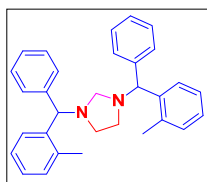
1,3-bis((2-fluorophenyl)(phenyl)methyl)imidazolidine (2d)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-(2-fluorophenyl)-1-phenylmethanimine) (42.4 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (37.4 mg, 85% yield) as a white solid. M.p. 145.4 – 146.9 °C R_f = 0.46 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.78 – 7.73 (m, 2H), 7.50 (d, J = 7.6 Hz, 4H), 7.27 – 7.23 (m, 4H), 7.18 – 7.06 (m, 6H), 6.95 – 6.90 (m, 2H), 4.97 (s, 2H), 3.45 – 3.29 (m, 2H), 2.82 – 2.75 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 160.03 (d, J = 245.6 Hz), 158.81, 142.60, 128.70, 128.57, 128.27 (d, J = 8.3 Hz), 127.81, 127.29, 124.48, 115.45 (d, J = 22.2 Hz), 74.78, 65.33, 51.83 ppm. ^{19}F NMR (375 MHz, CDCl_3) δ : - 118.67 (s) ppm. FTIR (neat, cm^{-1}) ν : 3028.06, 3006.20, 2989.70, 1636.80, 1484.96, 1454.90, 1275.24, 1260.87, 764.00, 750.74, 699.07 cm^{-1} ; HRMS calcd for $\text{C}_{29}\text{H}_{26}\text{F}_2\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 463.1962, found 463.1961.



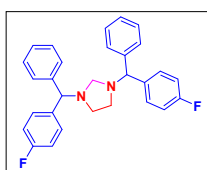
1,3-bis((2-chlorophenyl)(phenyl)methyl)imidazolidine (2e)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-(2-chlorophenyl)-1-phenylmethanimine) (45.7 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (42.1 mg, 89% yield) as a white solid. M.p. 133.6 – 136.5 °C R_f = 0.46 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.92 – 7.87 (m, 2H), 7.54 – 7.49 (m, 4H), 7.26 – 7.21 (m, 8H), 7.18 – 7.12 (m, 2H), 7.08 – 7.03 (m, 2H), 5.10 (s, 2H), 3.40 – 3.19 (m, 2H), 2.82 – 2.65 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 142.00, 140.74, 132.93, 129.64, 129.20, 128.45, 128.20, 128.15, 128.00, 127.35, 74.64, 68.72, 51.73 ppm. FTIR (neat, cm^{-1}) ν : 3064.08, 3029.18, 2928.71, 2849.14, 1636.60, 1452.70, 1275.29, 1261.56, 1032.97, 751.09, 698.59 cm^{-1} ; HRMS calcd for $\text{C}_{29}\text{H}_{26}\text{Cl}_2\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 495.1371, found 495.1381.



1,3-bis(phenyl(o-tolyl)methyl)imidazolidine (2f)

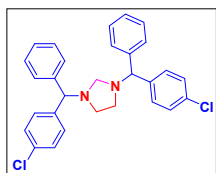
The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-phenyl-1-(o-tolyl)methanimine) (41.7 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (35.0 mg, 81% yield) as a colorless oil. R_f = 0.49 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.90 – 7.87 (m, 2H), 7.45 – 7.42 (m, 4H), 7.25 – 7.14 (m, 8H), 7.09 – 7.02 (m, 4H), 4.72 (s, 2H), 3.54 – 3.11 (m, 2H), 2.85 – 2.63 (m, 4H), 2.36 (d, J = 2.8 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 142.35, 141.47, 135.23, 130.56, 128.52, 128.40, 127.41, 127.11, 126.66, 126.32, 75.18, 69.64, 52.11, 20.04 ppm. FTIR (neat, cm^{-1}) ν : 3083.82, 3062.16, 3025.53, 2970.61, 2807.66, 1644.04, 1492.27, 1485.41, 1460.69, 1265.45, 791.16, 737.60, 699.9 cm^{-1} ; HRMS calcd for $\text{C}_{31}\text{H}_{33}\text{N}_2$ $[\text{M}+\text{H}]^+$ 433.2644, found 433.2651.



1,3-bis((4-fluorophenyl)(phenyl)methyl)imidazolidine (2g)

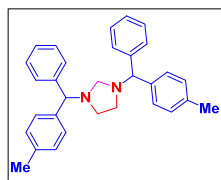
The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-(4-fluorophenyl)-1-phenylmethanimine) (42.4 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (37.4 mg, 85% yield) as a white solid. M.p. 145.4 – 146.9 °C R_f = 0.46 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.78 – 7.73 (m, 2H), 7.50 (d, J = 7.6 Hz, 4H), 7.27 – 7.23 (m, 4H), 7.18 – 7.06 (m, 6H), 6.95 – 6.90 (m, 2H), 4.97 (s, 2H), 3.45 – 3.29 (m, 2H), 2.82 – 2.75 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 160.03 (d, J = 245.6 Hz), 158.81, 142.60, 128.70, 128.57, 128.27 (d, J = 8.3 Hz), 127.81, 127.29, 124.48, 115.45 (d, J = 22.2 Hz), 74.78, 65.33, 51.83 ppm. ^{19}F NMR (375 MHz, CDCl_3) δ : - 118.67 (s) ppm. FTIR (neat, cm^{-1}) ν : 3028.06, 3006.20, 2989.70, 1636.80, 1484.96, 1454.90, 1275.24, 1260.87, 764.00, 750.74, 699.07 cm^{-1} ; HRMS calcd for $\text{C}_{29}\text{H}_{26}\text{F}_2\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 463.1962, found 463.1961.

and CH₃OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (30.0 mg, 68% yield) as a white solid. M.p. 113.3 – 115.9 °C *R_f* = 0.48 (petroleum ether/EtOAc = 10/1). ¹H NMR (400 MHz, CDCl₃) δ: 7.42 – 7.37 (m, 8H), 7.26 – 7.19 (m, 4H), 7.17 – 7.11 (m, 2H), 6.92 – 6.87 (m, 4H), 4.44 (s, 2H), 3.25 (s, 2H), 2.75 – 2.66 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 161.88 (d, *J* = 245.1 Hz), 143.54, 139.52, 130.61, 128.90 (d, *J* = 7.8 Hz), 128.66, 127.34, 115.41 (d, *J* = 21.2 Hz), 74.92, 73.81, 51.98 ppm. ¹⁹F NMR (375 MHz, CDCl₃) δ: - 115.70 (s) ppm. FTIR (neat, cm⁻¹) v: 3027.64, 2927.39, 2803.11, 2736.33, 1603.25, 1506.87, 1452.93, 1222.42, 1155.36, 818.97, 798.65, 739.59, 719.41 cm⁻¹; HRMS calcd for C₂₇H₂₆F₂N₂Na [M+Na]⁺ 463.1962, found 463.1956.



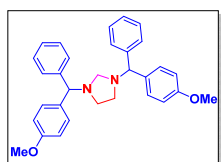
1,3-bis((4-chlorophenyl)(phenyl)methyl)imidazolidine (2h)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-(4-chlorophenyl)-1-phenylmethanimine) (45.7 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy₂NMe (42.8 μL, 0.2 mmol), and CH₃OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (27.9 mg, 59% yield) as a white solid. M.p. 125.3 – 127.9 °C *R_f* = 0.47 (petroleum ether/EtOAc = 10/1). ¹H NMR (400 MHz, CDCl₃) δ: 7.41 – 7.36 (m, 8H), 7.24 – 7.17 (m, 8H), 7.17 – 7.13 (m, 2H), 4.44 (s, 2H), 3.28 (q, *J* = 5.8, 5.2 Hz, 2H), 2.71 (s, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 143.15, 142.26, 132.75, 130.24, 128.79, 128.73, 127.61, 127.36, 74.83, 73.88, 51.87 ppm. FTIR (neat, cm⁻¹) v: 3062.47, 3027.12, 2976.31, 2801.21, 1643.62, 1488.83, 1275.20, 1262.27, 1089.68, 1013.97, 805.15, 752.43, 698.70, 493.24 cm⁻¹; HRMS calcd for C₂₉H₂₇Cl₂N₂ [M+H]⁺ 473.1551, found 473.1552.



1,3-bis(phenyl(p-tolyl)methyl)imidazolidine (2i)

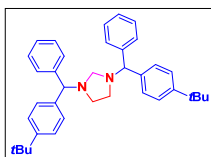
The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-phenyl-1-(p-tolyl)methanimine) (41.7 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy₂NMe (42.8 μL, 0.2 mmol), and CH₃OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (38.9mg, 90% yield) as a white solid. M.p. 135.3 – 138.4 °C *R_f* = 0.49 (petroleum ether/EtOAc = 10/1). ¹H NMR (400 MHz, CDCl₃) δ: 7.49 – 7.42 (m, 4H), 7.39 – 7.32 (m, 4H), 7.25 – 7.21 (m, 4H), 7.16 – 7.09 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 4H), 4.47 (s, 2H), 3.36 (d, *J* = 2.0 Hz, 2H), 2.75 (s, 4H), 2.26 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 144.13, 140.96, 136.58, 129.26, 128.54, 127.44, 127.39, 126.96, 75.14, 74.43, 52.04, 21.15 ppm. FTIR (neat, cm⁻¹) v: 3084.40, 3024.20, 2970.61, 2807.66, 1644.04, 1492.27, 1460.69, 1265.45, 791.16, 737.60, 699.76, 623.67, 570.40 cm⁻¹; HRMS calcd for C₃₁H₃₂N₂Na [M+Na]⁺ 455.2463, found 455.2460.



1,3-bis((4-methoxyphenyl)(phenyl)methyl)imidazolidine (2j)

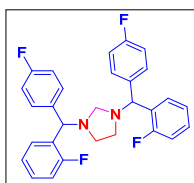
The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-(4-methoxyphenyl)-1-phenylmethanimine) (44.9 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy₂NMe (42.8 μL, 0.2 mmol), and CH₃OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (44.1mg, 95% yield) as a white solid. M.p. 137.8 – 139.3 °C *R_f* = 0.46 (petroleum ether/EtOAc = 10/1). ¹H NMR (400 MHz, CDCl₃) δ: 7.47 – 7.42 (m, 4H), 7.39 – 7.33 (m, 4H), 7.25 – 7.21 (m, 4H), 7.16 – 7.10 (m, 2H), 6.78 – 6.76 (m, 4H), 4.43 (s, 2H), 3.72 (s, 6H), 3.32 (t, *J* = 1.6 Hz, 2H), 2.78 –

2.69 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 158.57, 144.20, 136.14, 128.53, 128.51, 127.37, 126.94, 113.89, 75.15, 74.01, 55.25, 52.03 ppm. FTIR (neat, cm^{-1}) ν : 3082.85, 3059.63, 2931.27, 2833.67, 2798.33, 1609.95, 1509.77, 1452.32, 1246.94, 1173.99, 1033.58, 816.95, 726.00, 699.76, 623.67, 570.40 cm^{-1} ; HRMS calcd for $\text{C}_{31}\text{H}_{32}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 487.2361, found 487.2357.



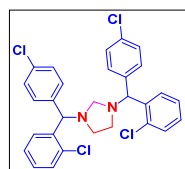
1,3-bis((4-*tert*-butylphenyl)(phenyl)methyl)imidazolidine (2k)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-(4-*tert*-butylphenyl)-1-phenylmethanimine) (50.1 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (44.4 mg, 86% yield) as a white solid. M.p. 130.9 –134.4 $^\circ\text{C}$ R_f = 0.50 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.47 – 7.44 (m, 4H), 7.38 – 7.32 (m, 4H), 7.25 – 7.19 (m, 8H), 7.15 – 7.09 (m, 2H), 4.45 (d, J = 7.0 Hz, 2H), 3.32 – 3.26 (m, 2H), 2.73 (d, J = 1.9 Hz, 4H), 1.24 (s, 18H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 149.65, 144.19, 140.77, 128.45, 127.57, 127.07, 126.90, 125.37, 75.17, 74.31, 52.02, 34.46, 31.44 ppm. FTIR (neat, cm^{-1}) ν : 3083.62, 3060.74, 2961.34, 2903.88, 2867.73, 1658.70, 1620.75, 1605.87, 1445.67, 1405.55, 1277.76, 1102.20, 938.03, 831.63, 794.67, 698.50, 664.88, 562.41 cm^{-1} ; HRMS calcd for $\text{C}_{37}\text{H}_{44}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 539.3402, found 539.3396.



1,3-bis((2-fluorophenyl)(4-fluorophenyl)methyl)imidazolidine (2l)

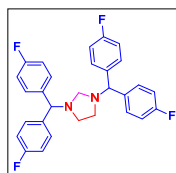
The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-(2-fluorophenyl)-1-(4-fluorophenyl)methanimine) (46.0 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (37.6 mg, 79% yield) as a colorless oil. R_f = 0.43 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.75 – 7.62 (m, 2H), 7.45 – 7.42 (m, 4H), 7.15 – 7.05 (m, 4H), 6.96 – 6.89 (m, 6H), 4.92 (s, 2H), 3.42 – 3.20 (m, 2H), 2.80 – 2.69 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 161.95 (d, J = 246.4 Hz), 159.95 (d, J = 246.4 Hz), 158.73, 138.30, 130.45 (d, J = 11.1 Hz), 129.25 (d, J = 8.1 Hz), 128.43 (d, J = 2.02 Hz), 124.54, 115.53 (d, J = 22.2 Hz), 115.42 (d, J = 21.2 Hz), 74.61, 64.58, 51.76 ppm. ^{19}F NMR (375 MHz, CDCl_3) δ : -115.21 (s), -118.77 (s) ppm. FTIR (neat, cm^{-1}) ν : 2980.58, 2932.72, 2847.95, 2821.62, 1640.13, 1604.82, 1507.39, 1485.10, 1455.82, 1223.32, 1155.14, 827.38, 794.51, 757.65, 616.41, 566.29, 536.26 cm^{-1} ; HRMS calcd for $\text{C}_{29}\text{H}_{24}\text{F}_4\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 499.1773, found 499.1772.



1,3-bis((2-chlorophenyl)(4-chlorophenyl)methyl)imidazolidine (2m)

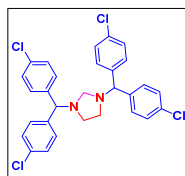
The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1-(2-chlorophenyl)-1-(4-chlorophenyl)methanimine) (52.6 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (3.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (29.8 mg, 55% yield) as a colorless oil. R_f = 0.47 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.83 – 7.79 (m, 2H), 7.46 – 7.41 (m, 4H), 7.24 – 7.18 (m, 8H), 7.11 – 7.05 (m, 2H), 5.06 (s, 2H), 3.34 – 3.16 (m, 2H), 2.79 – 2.65 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 140.50, 140.24, 133.04, 132.81, 129.78, 129.38, 128.95, 128.69, 128.26, 127.38, 74.45, 67.97, 51.64. ppm. FTIR (neat, cm^{-1}) ν : 2969.11, 2928.20, 2848.21, 2810.79, 1651.28, 1644.00, 1489.17, 1439.70, 1262.94,

1090.15, 1014.57, 808.36, 755.57, 738.74, 615.83, 502.90 cm^{-1} ; HRMS calcd for $\text{C}_{29}\text{H}_{24}\text{Cl}_4\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 563.0591, found 563.0596.



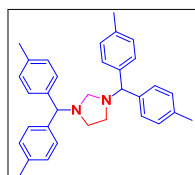
1,3-bis(bis(4-fluorophenyl)methyl)imidazolidine (2n)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1,1-bis(4-fluorophenyl)methanimine) (46.1 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (42.9 mg, 90% yield) as a white solid. M.p. 102.1– 104.8 $^\circ\text{C}$ R_f = 0.46 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.38 – 7.35 (m, 8H), 6.94 – 6.90 (m, 8H), 4.43 (s, 2H), 3.22 (s, 2H), 2.70 (s, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 161.92 (d, J = 245.5 Hz), 139.27, 128.80, 115.61, 74.79, 72.97, 51.87 ppm. ^{19}F NMR (375 MHz, CDCl_3) δ : -115.30 (s) ppm. FTIR (neat, cm^{-1}) ν : 2975.01, 2928.96, 2804.19, 1641.66, 1603.39, 1505.24, 1221.87, 1152.97, 826.53, 786.91, 740.45, 576.52, 545.21, 527.78 cm^{-1} ; HRMS calcd for $\text{C}_{29}\text{H}_{25}\text{F}_4\text{N}_2$ $[\text{M}+\text{H}]^+$ 477.1954, found 477.1956.



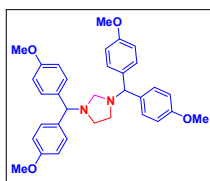
1,3-bis(bis(4-chlorophenyl)methyl)imidazolidine (2o)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1,1-bis(4-chlorophenyl)methanimine) (52.6 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (44.5 mg, 82% yield) as a white solid. M.p. 136.8– 138.3 $^\circ\text{C}$ R_f = 0.46 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.35 – 7.30 (m, 8H), 7.23 – 7.18 (m, 8H), 4.41 (s, 2H), 3.24 (s, 2H), 2.69 (s, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 141.71, 133.05, 128.94, 128.59, 74.72, 73.15, 51.82 ppm. FTIR (neat, cm^{-1}) ν : 2975.47, 2928.04, 2800.89, 1641.37, 1488.72, 1408.84, 1090.26, 1030.68, 811.88, 740.77, 530.33, 484.77, 461.86 cm^{-1} ; HRMS calcd for $\text{C}_{29}\text{H}_{25}\text{Cl}_4\text{N}_2$ $[\text{M}+\text{H}]^+$ 541.0772, found 541.0775.



1,3-bis(di-p-tolylmethyl)imidazolidine (2p)

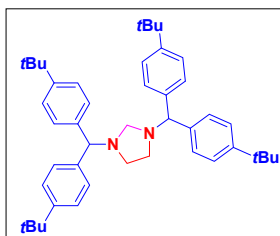
The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1,1-di-p-tolylmethanimine) (44.5 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (42.8 mg, 93% yield) as a white solid. M.p. 143.9– 145.1 $^\circ\text{C}$ R_f = 0.47 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.37 – 7.32 (m, 8H), 7.04 (d, J = 7.9 Hz, 8H), 4.43 (s, 2H), 3.37 (s, 2H), 2.74 (s, 4H), 2.26 (s, 12H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 141.26, 136.44, 129.25, 127.30, 75.27, 74.21, 52.07, 21.14 ppm. FTIR (neat, cm^{-1}) ν : 3046.43, 3020.31, 2973.02, 2921.11, 1643.40, 1508.77, 1450.65, 1264.84, 1178.02, 807.58, 771.36, 734.31, 578.86 cm^{-1} ; HRMS calcd for $\text{C}_{33}\text{H}_{36}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 483.2776, found 483.2773.



1,3-bis(bis(4-methoxyphenyl)methyl)imidazolidine (2q)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1,1-bis(4-methoxyphenyl)methanimine) (50.9 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (47.2 mg, 90%

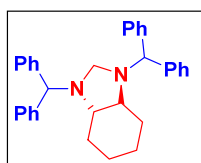
yield) as a white solid. M.p. 100.9 – 102.1 °C R_f = 0.47 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.34 – 7.28 (m, 8H), 6.78 – 6.72 (m, 8H), 4.34 (s, 2H), 3.71 (s, 12H), 3.26 (s, 2H), 2.68 (s, 4H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 158.47, 136.44, 128.34, 113.87, 75.19, 73.34, 55.25, 52.00 ppm. FTIR (neat, cm^{-1}) ν : 3001.71, 2954.32, 2834.08, 1643.62, 1609.46, 1508.25, 1245.46, 1172.16, 1033.10, 819.57, 770.45, 587.63 cm^{-1} ; HRMS calcd for $\text{C}_{33}\text{H}_{36}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 547.2573, found 547.2589.



1,3-bis(bis(4-*tert*-butylphenyl)methyl)imidazolidine (2r)

The reaction was performed following the general experimental procedure with *N,N'*-(ethane-1,2-diyl)bis(1,1-bis(4-*tert*-butylphenyl)methylmethanimine) (61.3 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (3.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (53.5 mg, 85%

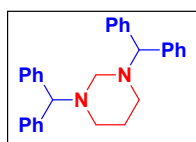
yield) as a white solid. M.p. 211.5 – 212.7 °C R_f = 0.52 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.38 – 7.34 (m, 8H), 7.21 (d, J = 8.1 Hz, 8H), 4.41 (s, 2H), 3.23 (s, 2H), 2.70 (s, 4H), 1.22 (s, 36H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 149.52, 140.96, 127.15, 125.27, 75.03, 73.87, 51.98, 34.44, 31.44 ppm. FTIR (neat, cm^{-1}) ν : 2963.46, 2868.13, 2784.65, 1747.68, 1634.72, 1506.82, 1264.79, 1161.02, 1110.94, 811.11, 732.73, 580.64 cm^{-1} ; HRMS calcd for $\text{C}_{45}\text{H}_{60}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 651.4654, found 651.4663.



(3a*R*,7a*S*)-1,3-dibenzhydryloctahydro-1*H*-benzo[*d*]imidazole (2s)

The reaction was performed following the general experimental procedure with *N,N'*-((1*R*,2*S*)-cyclohexane-1,2-diyl)bis(1,1-diphenylmethanimine) (44.3 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (20.2 mg, 44%

yield) as a white solid. M.p. 183.2– 184.6 °C R_f = 0.47 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.37 (d, J = 7.5 Hz, 4H), 7.30 (d, J = 7.5 Hz, 4H), 7.23 – 7.17 (m, 8H), 7.17 – 7.09 (m, 4H), 4.63 (s, 2H), 3.47 (s, 2H), 2.4 (s, 2H), 1.40 – 1.38 (m, 2H), 0.98 – 0.90 (m, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 143.80, 128.53, 128.28, 127.02, 74.74, 73.08, 69.91, 31.59, 24.75 ppm. FTIR (neat, cm^{-1}) ν : 3025.39, 2931.70, 2852.24, 2789.11, 1493.38, 1451.84, 1191.33, 1080.33, 1027.77, 764.01, 745.47, 703.96, 696.20, 618.86 cm^{-1} ; HRMS calcd for $\text{C}_{33}\text{H}_{34}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 481.2620, found 481.2635.

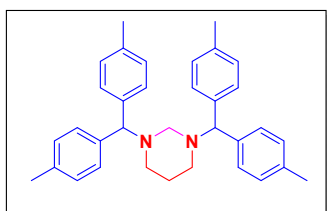


1,3-dibenzhydrylhexahydropyrimidine (2t)

The reaction was performed following the general experimental procedure with *N,N'*-(propane-1,3-diyl)bis(1,1-diphenylmethanimine) (40.3 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (36.0 mg, 86% yield) as a yellow solid. M.p. 190.6

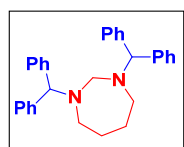
– 191.3 °C R_f = 0.48 (petroleum ether/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ : 7.37 – 7.33 (m, 8H), 7.18 – 7.13 (m, 8H), 7.11 – 7.04 (m, 4H), 4.54 (s, 2H), 3.25 (s, 2H), 2.53 (t, J = 5.5 Hz, 4H), 1.68 – 1.60 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ : 142.88, 128.44, 127.80, 126.77, 72.82, 72.39, 51.19, 22.44 ppm. FTIR (neat, cm^{-1}) ν : 3081.99, 3025.10, 2932.92, 2914.04, 2810.91, 2779.87, 1491.17, 1451.54, 1265.63, 1073.35, 1027.61, 757.66, 744.88, 703.86, 653.44 cm^{-1} ;

HRMS calcd for $C_{30}H_{31}N_2 [M+H]^+$ 419.2487, found 419.2473.



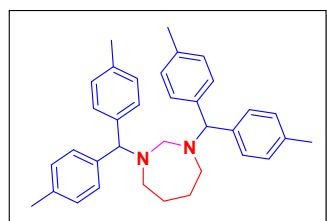
1,3-bis(di-*p*-tolylmethyl)hexahydropyrimidine (2u)

The reaction was performed following the general experimental procedure with *N,N'*-(propane-1,3-diyl)bis(1,1-di-*p*-tolylmethanimine) (45.9 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (37.5 mg, 79% yield) as a white solid. M.p. 150.7 – 151.8 °C R_f = 0.47 (petroleum ether/EtOAc = 10/1). 1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 7.9 Hz, 8H), 6.95 (d, J = 7.7 Hz, 8H), 4.42 (s, 2H), 3.17 (s, 2H), 2.49 (s, 4H), 2.22 (s, 12H), 1.64 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ : 140.13, 136.08, 129.08, 127.58, 72.86, 71.81, 51.15, 22.47, 21.11 ppm. FTIR (neat, cm^{-1}) ν : 3020.78, 2966.22, 2920.55, 2858.40, 2797.37, 2731.40, 2069.94, 1639.81, 1508.83, 1451.04, 1265.06, 1185.92, 1019.94, 977.39, 805.99, 769.86, 577.25, 479.98 cm^{-1} ; HRMS calcd for $C_{34}H_{38}N_2Na [M+Na]^+$ 497.2933, found 497.2932.



1,3-dibenzhydryl-1,3-diazepane (2v)

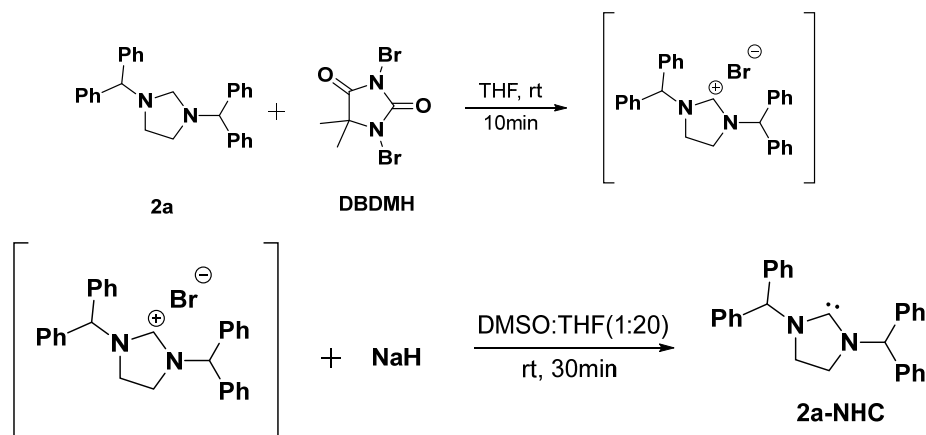
The reaction was performed following the general experimental procedure with *N,N'*-(butane-1,4-diyl)bis(1,1-diphenylmethanimine) (41.7 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (38.1 mg, 88% yield) as a white solid. M.p. 92.2–93.8 °C R_f = 0.48 (petroleum ether/EtOAc = 10/1). 1H NMR (400 MHz, $CDCl_3$) δ : 7.31 – 7.26 (m, 8H), 7.26 – 7.21 (m, 8H), 7.20 – 7.14 (m, 4H), 4.79 (s, 2H), 3.67 (s, 2H), 2.71 (t, J = 4 Hz, 4H), 1.71 – 1.68 (m, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ : 142.29, 127.70, 127.61, 126.09, 72.33, 70.97, 50.76, 26.58 ppm. FTIR (neat, cm^{-1}) ν : 3082.53, 3059.06, 3024.27, 2925.63, 2853.70, 1597.38, 1490.85, 1451.38, 1302.00, 1144.30, 966.20, 924.10, 744.07, 704.07 cm^{-1} ; HRMS calcd for $C_{31}H_{32}N_2Na [M+Na]^+$ 455.2463, found 455.2466.



1,3-bis(di-*p*-tolylmethyl)-1,3-diazepane (2w)

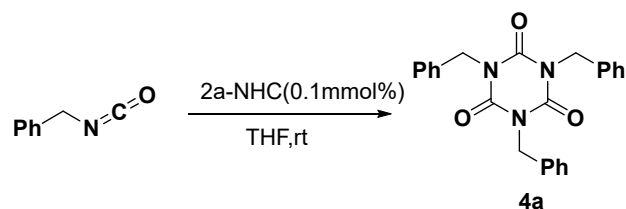
The reaction was performed following the general experimental procedure with *N,N'*-(butane-1,4-diyl)bis(1,1-di-*p*-tolylmethanimine) (47.3 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), Cy_2NMe (42.8 μL , 0.2 mmol), and CH_3OH (1.0 mL). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (39.1 mg, 80% yield) as a white solid. M.p. 99.9 – 102.4 °C R_f = 0.44 (petroleum ether/EtOAc = 10/1). 1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 7.9 Hz, 8H), 6.95 (d, J = 7.7 Hz, 8H), 4.42 (s, 2H), 3.17 (s, 2H), 2.49 (s, 4H), 2.22 (s, 12H), 1.64 (s, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ : 140.22, 136.14, 129.01, 128.19, 73.03, 70.96, 51.34, 27.27, 21.25 ppm. FTIR (neat, cm^{-1}) ν : 3049.79, 3020.56, 2921.76, 2857.62, 1640.17, 1508.88, 1452.11, 1409.94, 1299.60, 1180.53, 1144.55, 1056.84, 965.19, 943.81, 807.46, 774.58, 673.54, 671.64, 487.62 cm^{-1} ; HRMS calcd for $C_{35}H_{41}N_2 [M+H]^+$ 489.3270, found 489.3267.

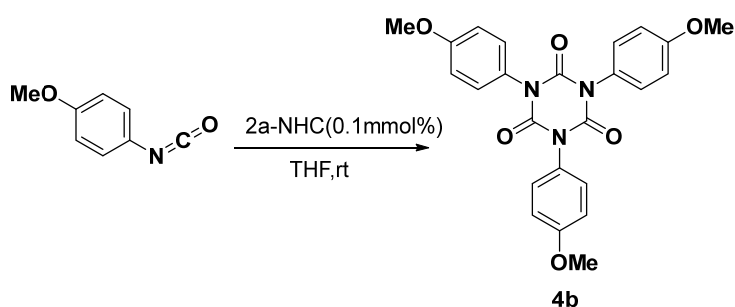
Synthesis of nitrogen heterocyclic carbene (NHC)



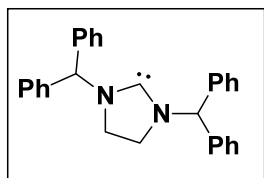
1,3-dibenzhydrylimidazolidine **2a** (1.2140 g, 3 mmol), 1,3-Dibromo-5,5-dimethylhydantoin (**DBDMH**) (1.0290 g, 3.6 mmol, 1.2 equiv.) were dissolved in anhydrous THF (40 mL) in an oven-dried round bottom flask. A magnetic stirring bar was added and then the vial was sealed with a septum. The mixture was stirred at ambient temperature (20 – 30 °C). The reaction progress was monitored using TLC. After the reaction is complete, diethyl ether is added to the flask and the solid is separated out and a small amount of diethyl ether is filtered to get the solid crude product. The crude product was recrystallized with methanol to obtain intermediate. Then, the intermediate (486 mg, 1 mmol) were dissolved in anhydrous THF (20 mL) in an oven-dried round bottom flask under nitrogen. A magnetic stirring bar was added and then the vial was sealed with a septum. NaH (36 mg, 1.5 mmol, 1.5 equiv.) was dissolved in anhydrous THF (5 mL) and add it to the solution drop by drop, and finally add DMSO (5 mL). The reaction progress was monitored using TLC. Upon completion of the reaction, the vessel was opened to air and the volatile materials were removed using a rotary evaporator under reduced pressure. The crude residue was purified by flash chromatography on silica gel using ethyl acetate and petroleum ether as eluents. The product is a white solid **2a-NHC** (0.3236 g, yield: 80%).

Tri-polymerization of isocyanates catalyzed by NHC



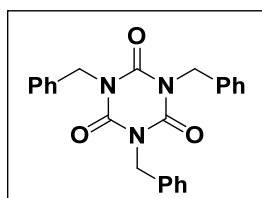


Isocyanate and THF are added to the **2a-NHC** in the form of 1:1 volume ratio, in a nitrogen atmosphere. The solution was stirred at ambient temperature (20 – 30 °C) for 30 min. Upon completion of the reaction, the vessel was opened to air and the volatile materials were removed using a rotary evaporator under reduced pressure. The crude residue was purified by flash chromatography on silica gel using ethyl acetate and petroleum ether as eluents.



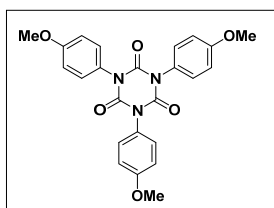
Nitrogen heterocyclic carbene (**2a-NHC**)

¹H NMR (400 MHz, CDCl₃) δ 7.37 (t, *J* = 1.9 Hz, 1H), 7.35 – 7.33 (m, 7H), 7.32 – 7.30 (m, 4H), 7.24 – 7.21 (m, 8H), δ 6.55 (s, 2H), δ 3.16 (s, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 160.53, 139.33, 128.73, 128.51, 127.46, 59.82, 39.51 ppm. FTIR (neat, cm⁻¹) v: 3028.91, 2084.92, 1689.61, 1639.84, 1493.85, 1447.06, 1421.01, 1250.78, 1250.78, 1180.46, 1156.94, 1075.57, 1030.49, 739.58, 700.48, 604.08, 590.30, 460.82 cm⁻¹; HRMS calcd for C₂₉H₂₇N₂ [M+H]⁺ 403.2174, found 403.2179. M.p. 150.6 – 151.7 °C



1,3,5-tribenzyl-1,3,5-triazinane-2,4,6-trione (**4a**)

Isocyanate 1 (0.618 mL, 5 mmol) and THF (0.618 mL) are added to the **2a-NHC** (2 mg, 0.005 mmol) in a nitrogen atmosphere. The solution was stirred at ambient temperature (20 – 30 °C) for 30 min. Upon completion of the reaction, the vessel was opened to air and the volatile materials were removed using a rotary evaporator under reduced pressure. The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc =20/1) to give the desired product (313 mg, 47% yield) as a white solid. M.p. 94.9 – 96.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.25 (m, 15H), 4.34 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 156.97, 135.36, 129.04, 128.28, 127.99, 44.52 ppm. FTIR (neat, cm⁻¹) v: 3088.80, 3034.82, 2970.09, 2932.82, 2186.20, 2157.59, 1770.98, 1740.01, 1627.15, 1456.15, 1375.02, 1344.19, 1320.76, 1159.61, 1035.74, 988.84, 868.77, 791.09, 738.55, 696.98, 586.94, 477.65 cm⁻¹; HRMS calcd for C₂₄H₂₁N₃O₃Na [M+Na]⁺ 422.1481, found 422.1496.

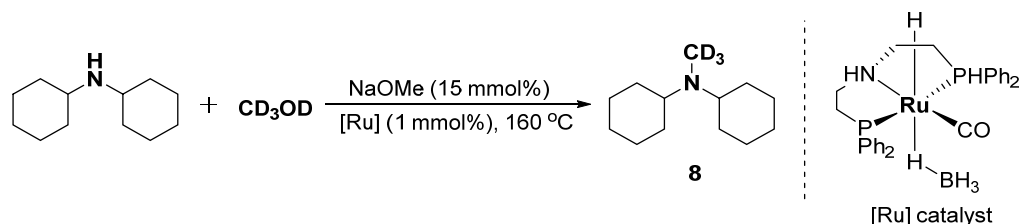


1,3,5-tris(4-methoxyphenyl)-1,3,5-triazinane-2,4,6-trione (**4b**)

Isocyanate 2 (0.648 mL, 5 mmol) and THF (0.648 mL) are added to the **2a-NHC** (2 mg, 0.005 mmol) in a nitrogen atmosphere. The solution was stirred at ambient temperature (20 – 30 °C) for 30 min. Upon completion of the reaction, the vessel was opened to air and the volatile materials were removed using a rotary evaporator under reduced pressure. The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (387.8 mg, 52% yield) as a white solid. M.p. 235.2 – 237.7 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.34 (d, *J* = 8.9 Hz, 6H), 6.85 (d, *J* = 8.9 Hz, 6H), 3.71 (s, 9H) ppm. ¹³C NMR (101 MHz, DMSO-*d*₆) δ 154.77, 153.42, 133.43, 120.35, 114.41, 55.62 ppm. FTIR (neat, cm⁻¹) ν: 3041.27, 2836.96, 2084.32, 1769.81, 1738.15, 1674.52, 1565.44, 1513.93, 1450.90, 1416.68, 1315.00, 1244.25, 1183.70, 1056.20, 825.36, 525.98, 437.40 cm⁻¹; HRMS calcd for C₂₄H₂₁N₃O₆Na [M+Na]⁺ 470.1328, found 470.1333.

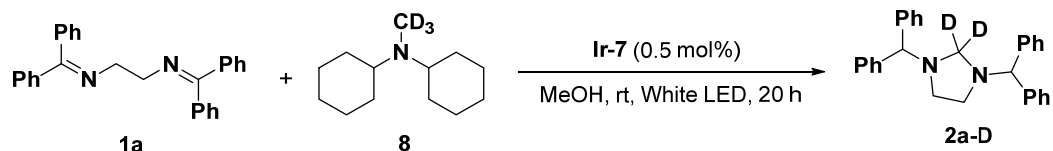
Methyl source investigation

Preparation of Cy₂NCD₃ (**8**)



Dicyclohexylamine (0.398 mL, 2.0 mmol), methanol-*d*₄ (4 mL), [Ru] catalyst (12 mg, 1.0 mmol%), and NaOMe (16 mg, 15 mmol %) at 160 °C in an oil bath for 24 h in a closed autoclave. Upon completion of the reaction, the vessel was opened to air and the volatile materials were removed using a rotary evaporator under reduced pressure to get the crude product **8**, which was directly used for subsequent synthesis.

Reaction with deuterated methylamine **8** (Cy₂NCD₃)



N,N'-(ethane-1,2-diyl)bis(1,1-diphenylmethanimine) (**1a**, 38.8 mg, 0.10 mmol), catalyst **Ir-7** (0.5 mg, 0.5 mol%), **8** (39.7 mg, 0.2 mmol), and CH₃OH (3.0 mL) in an oven-dried Shrek Tube under nitrogen. A magnetic stirring bar was added and then the vial was sealed with a septum. The mixture was placed under a 20 W white LED light source and stirred at ambient temperature (20 – 30 °C). The reaction progress was monitored using TLC. Upon completion of the reaction, the vessel was opened to air and the volatile materials were removed using a rotary evaporator under reduced

pressure. The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 30/1) to give the desired product (35.4 mg, 87% yield) as a white solid.

Detection of reaction intermediates

Under the general experimental procedure, after the reaction had proceeded for 4 hours, a 10 μ L aliquot of the reaction mixture was taken and diluted to a total volume of 1 mL with acetonitrile. The reaction intermediates were then analyzed by UPLC-MS.

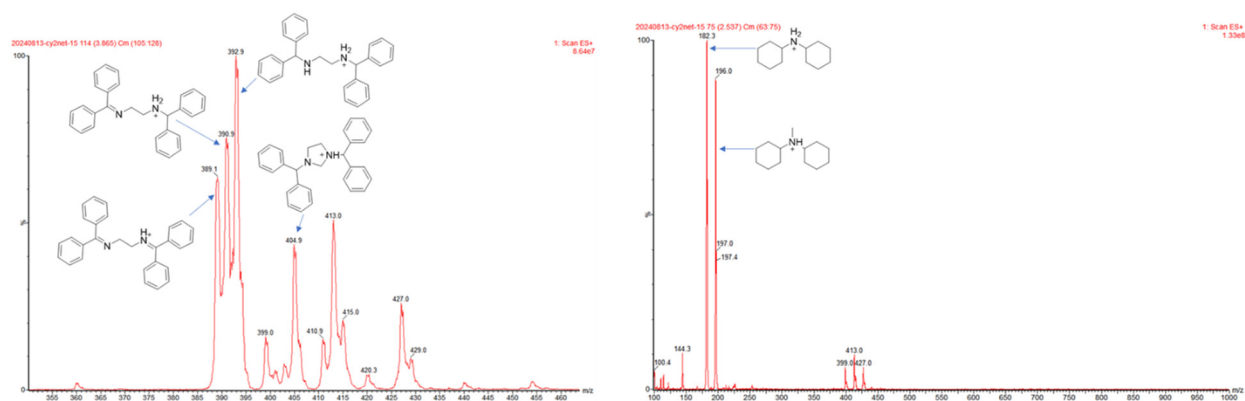
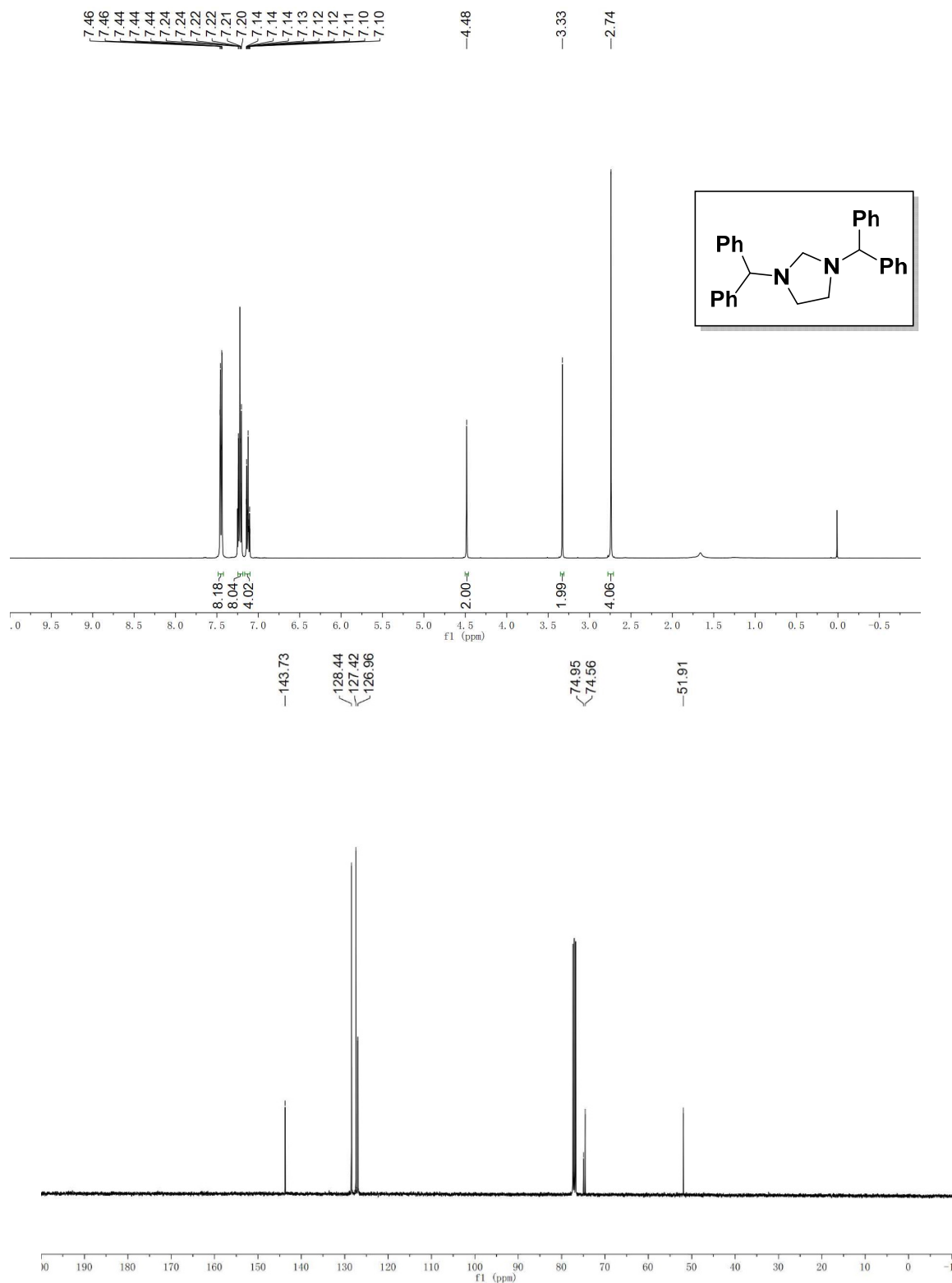


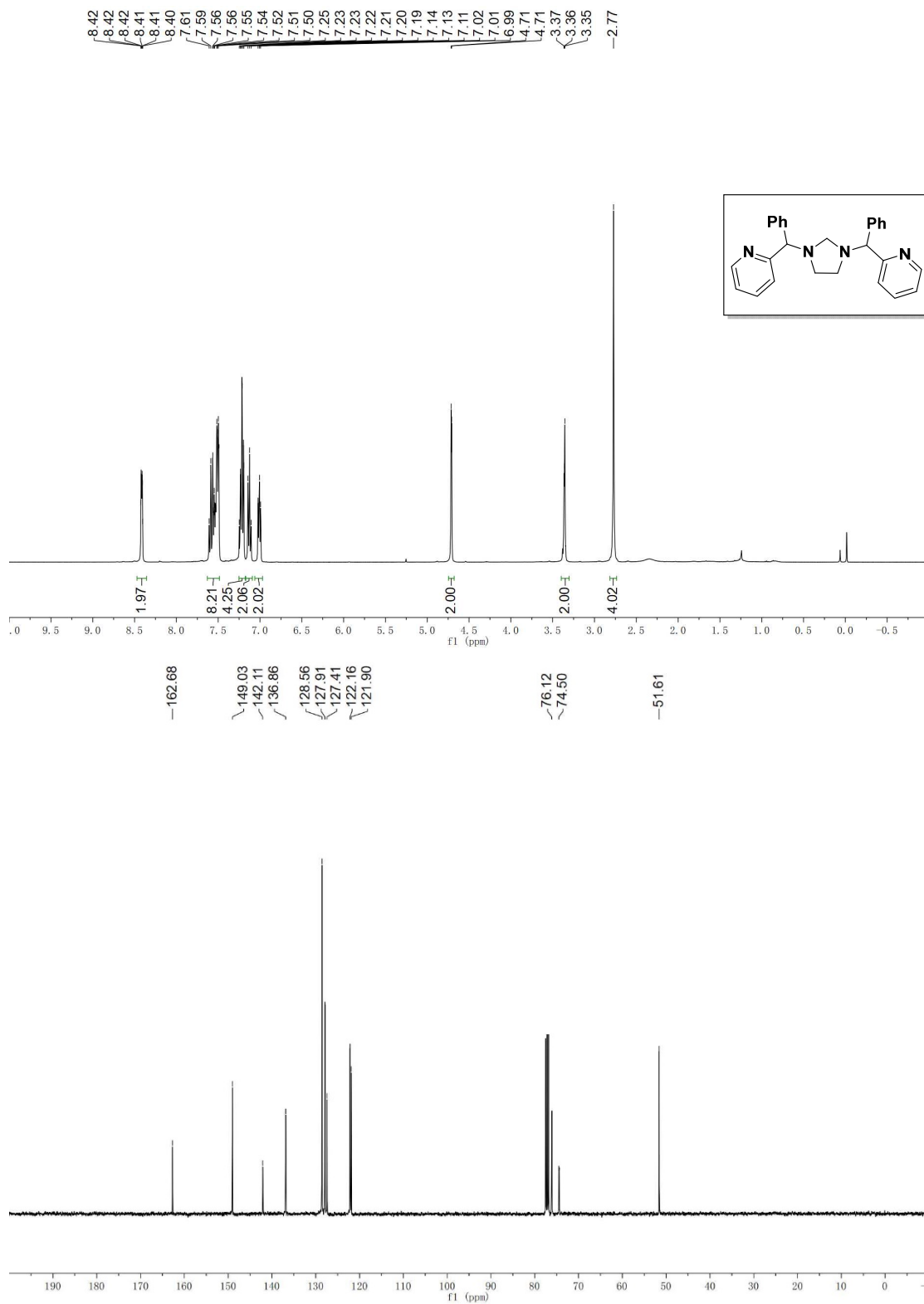
Fig. S1 MS spectra of the detected reaction intermediates

NMR spectra

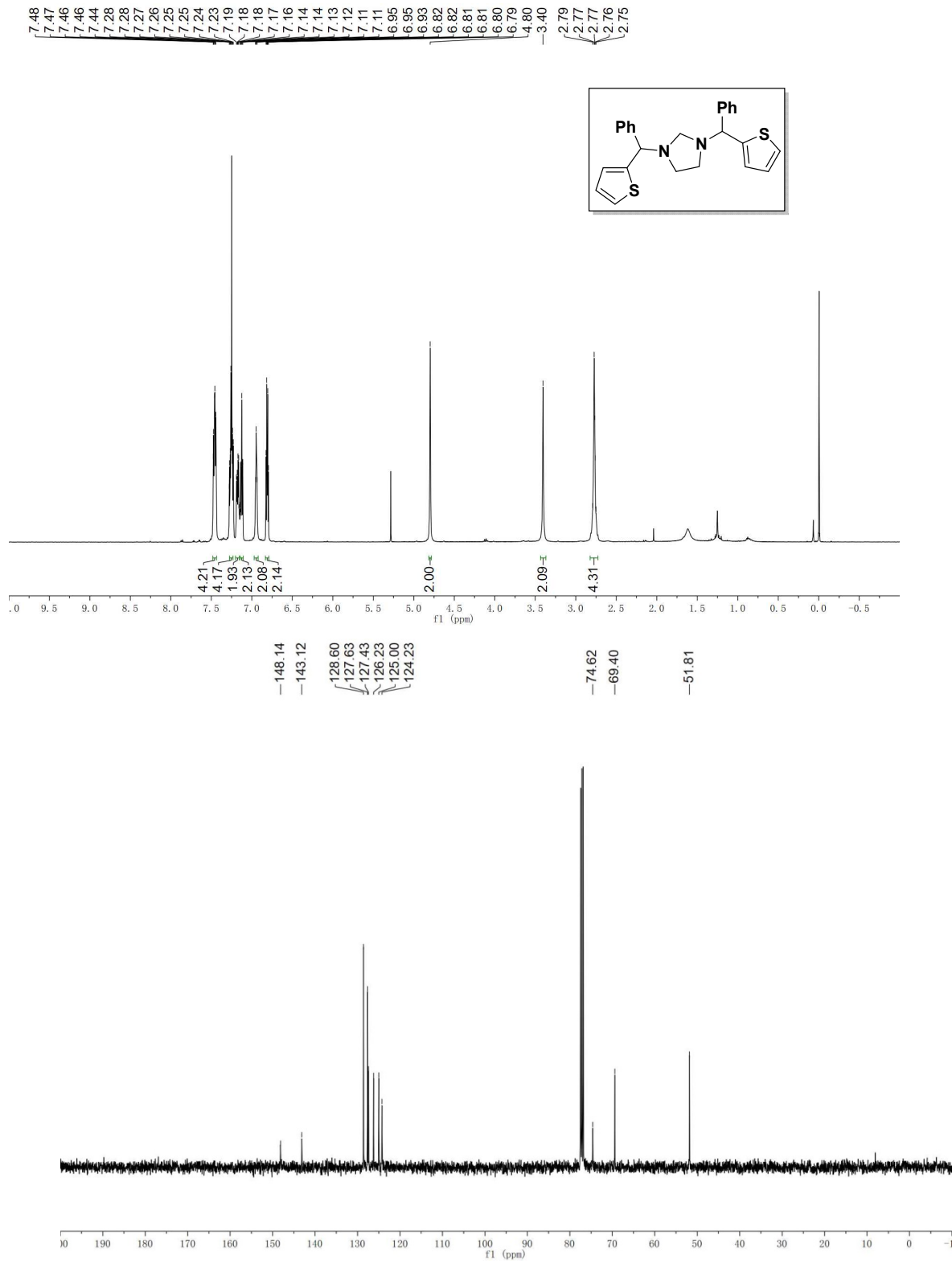
^1H and ^{13}C -NMR spectra of compound **2a** in CDCl_3



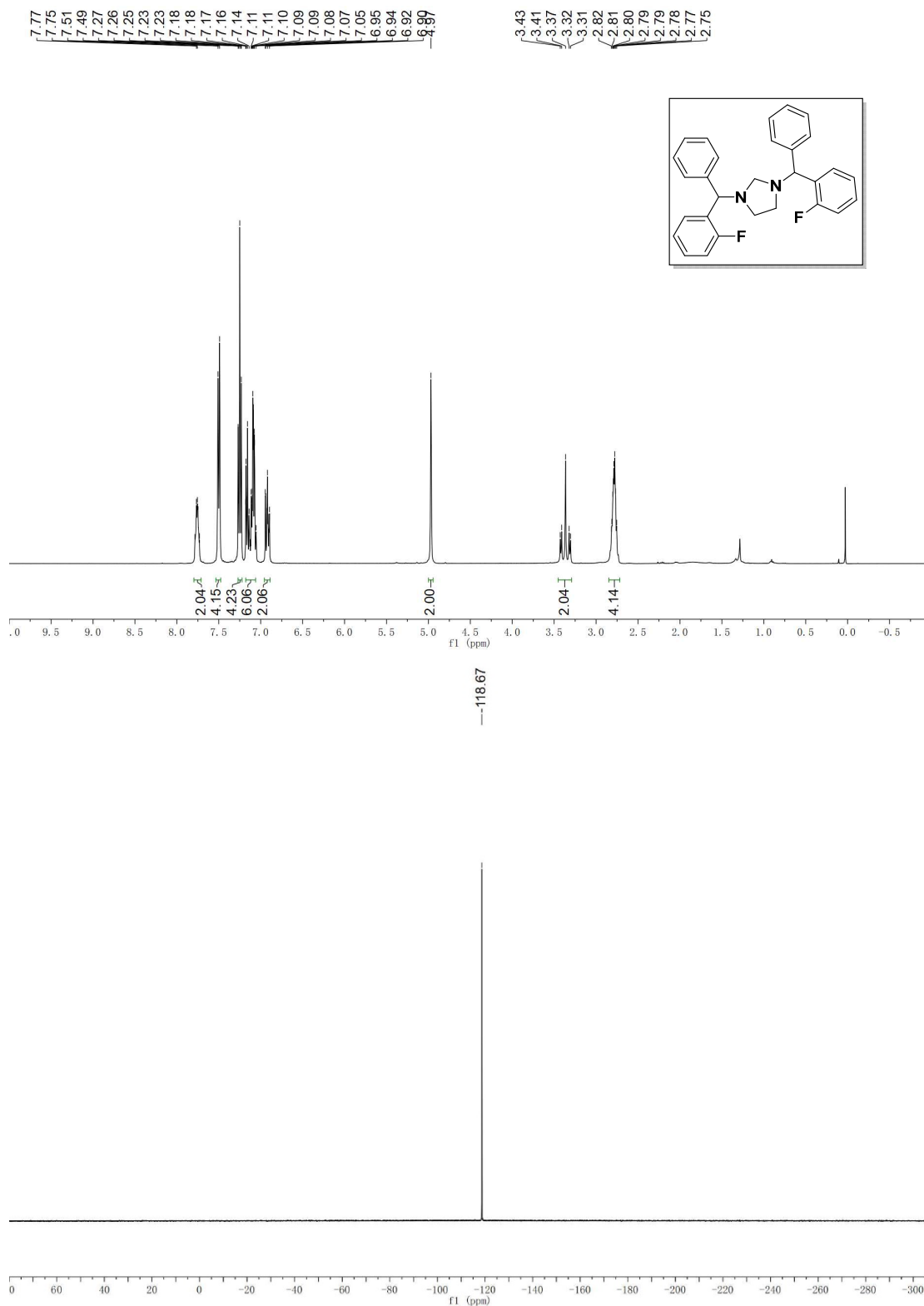
^1H and ^{13}C -NMR spectra of compound **2b** in CDCl_3

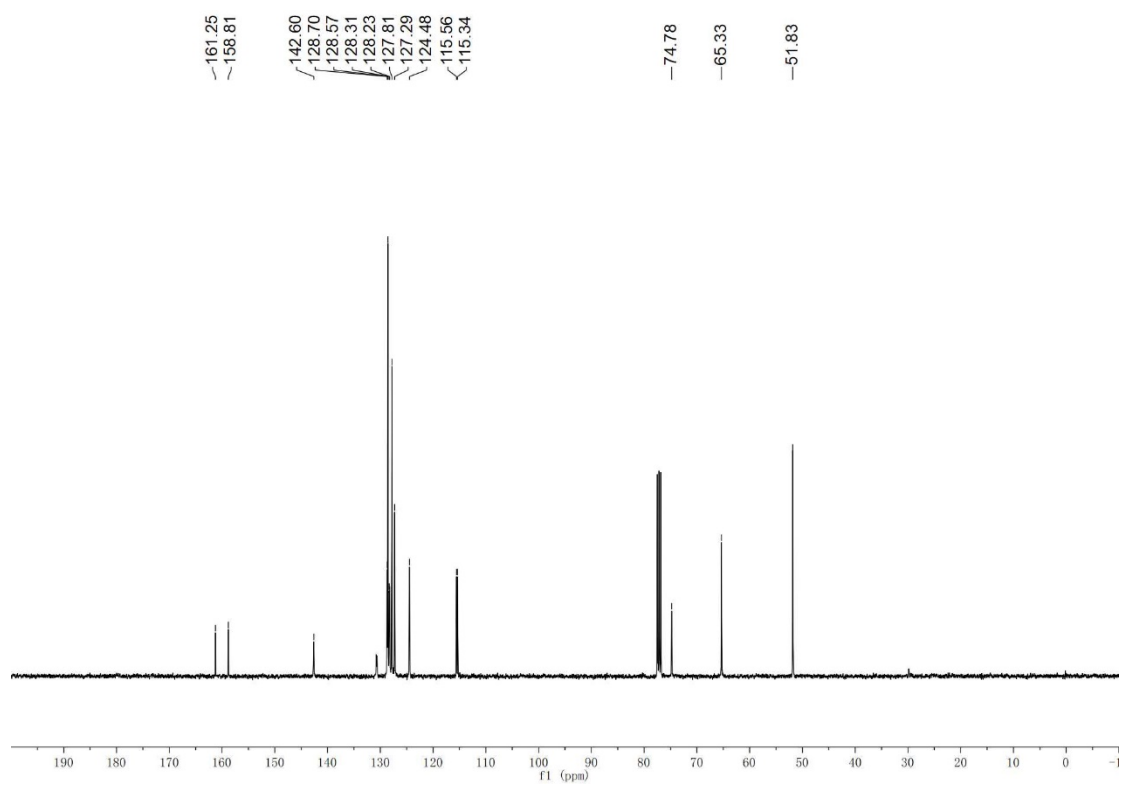


^1H and ^{13}C -NMR spectra of compound **2c** in CDCl_3

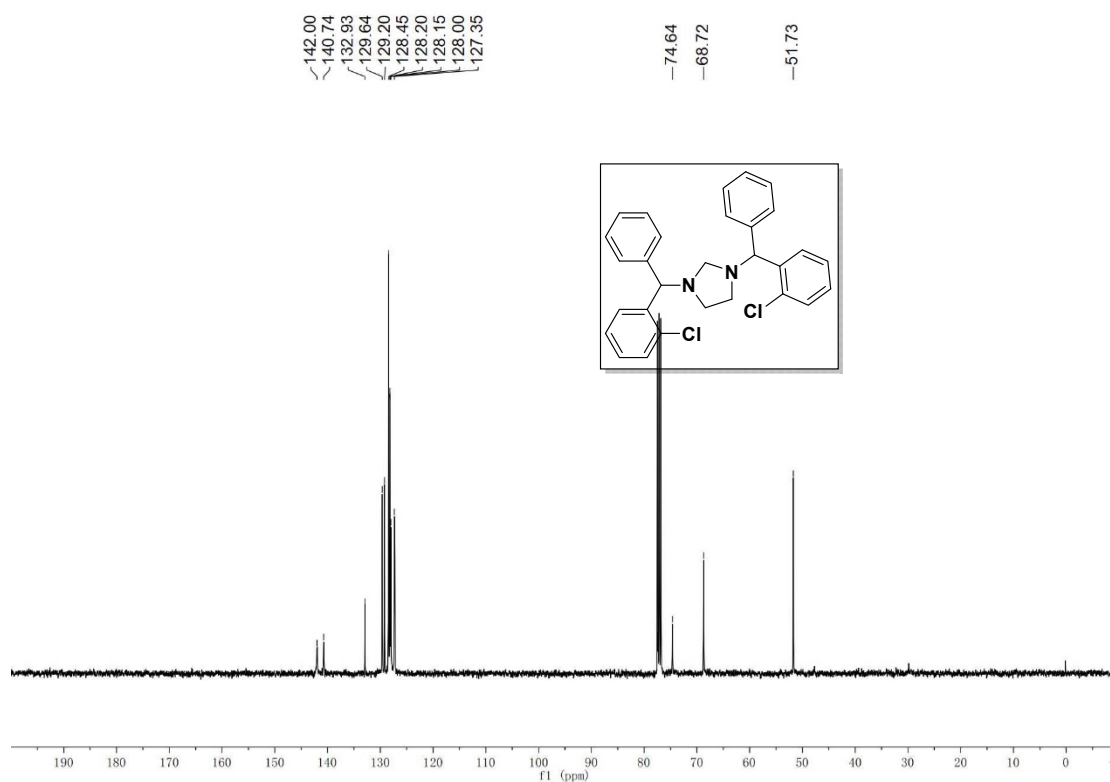
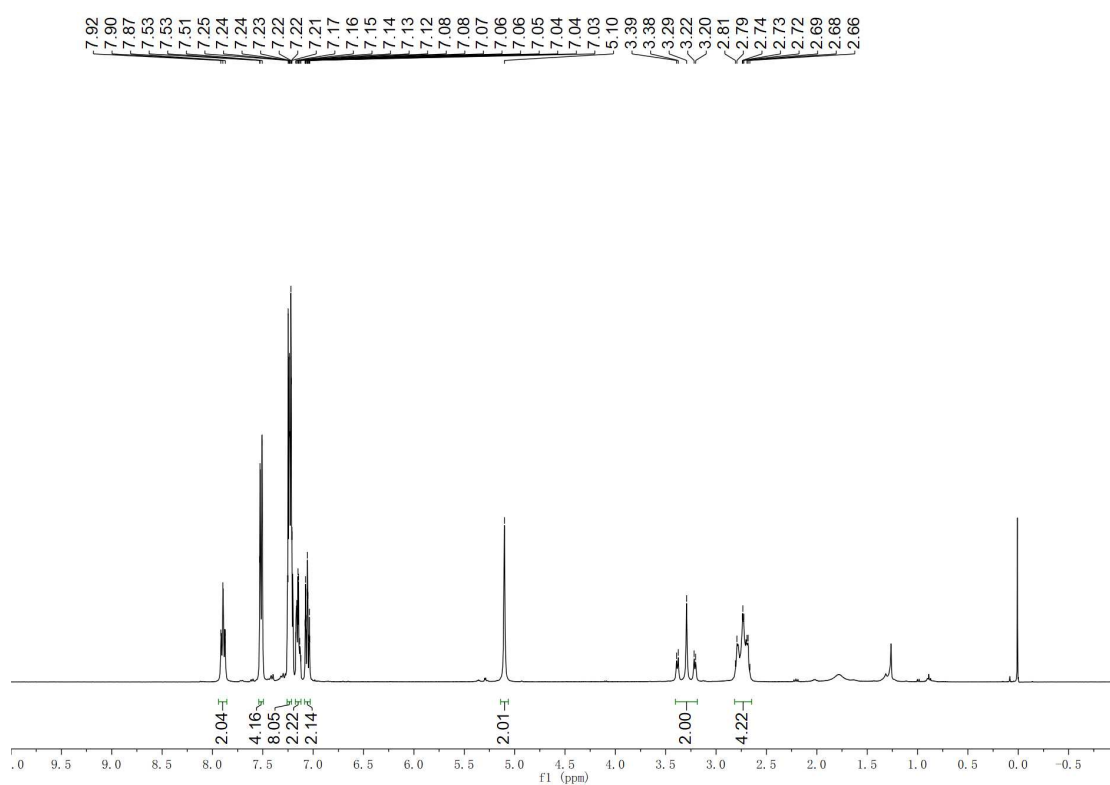


^1H , ^{19}F and ^{13}C -NMR spectra of compound **2d** in CDCl_3

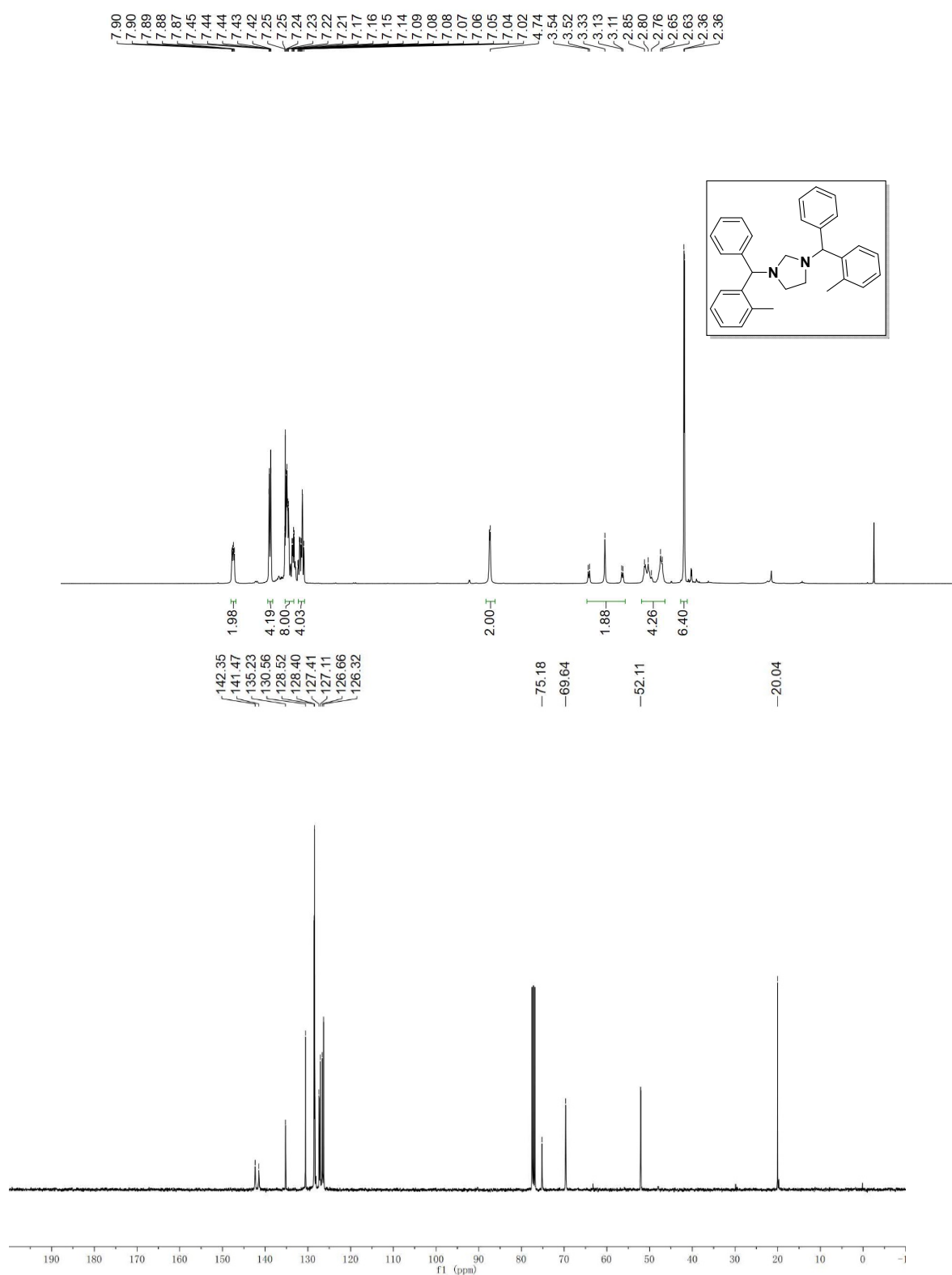




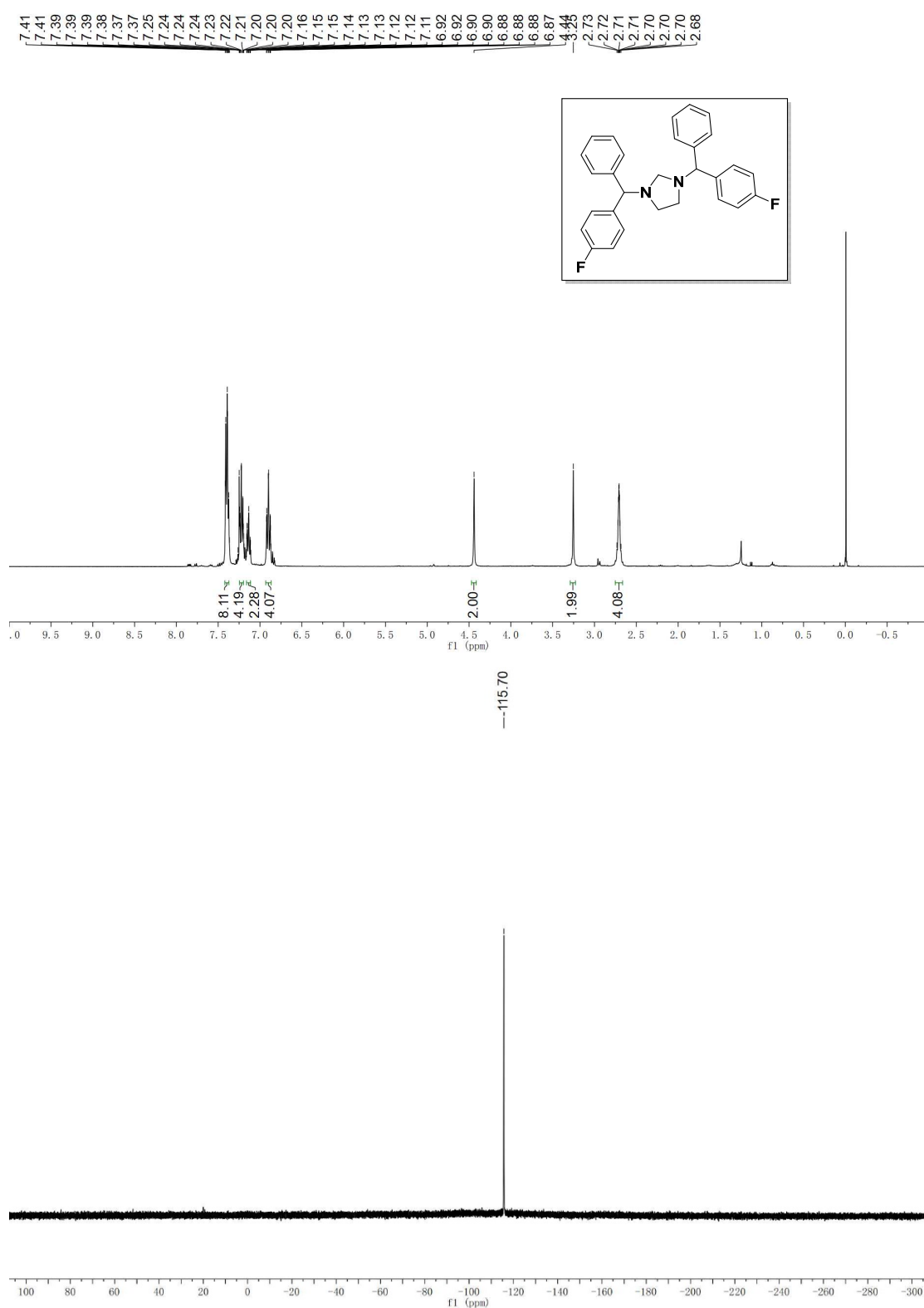
¹H and ¹³C-NMR spectra of compound **2e** in CDCl₃

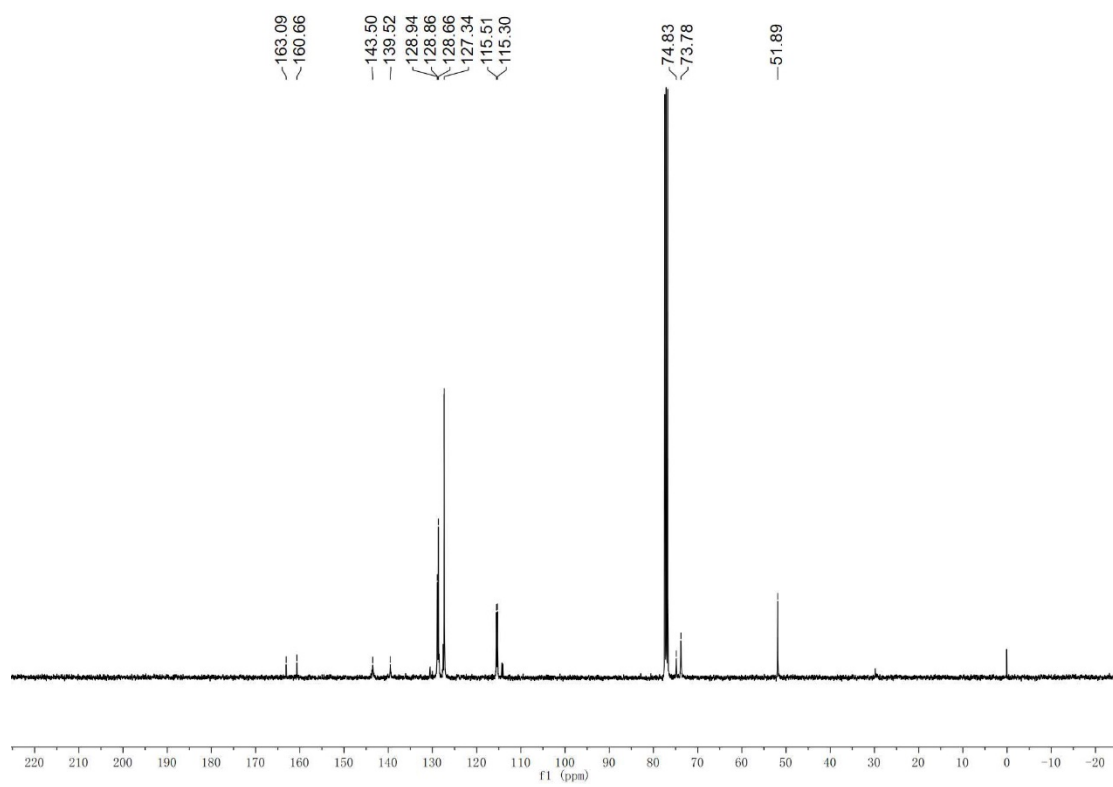


^1H and ^{13}C -NMR spectra of compound **2f** in CDCl_3

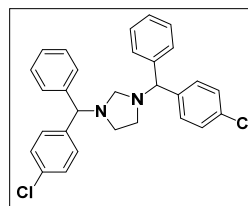
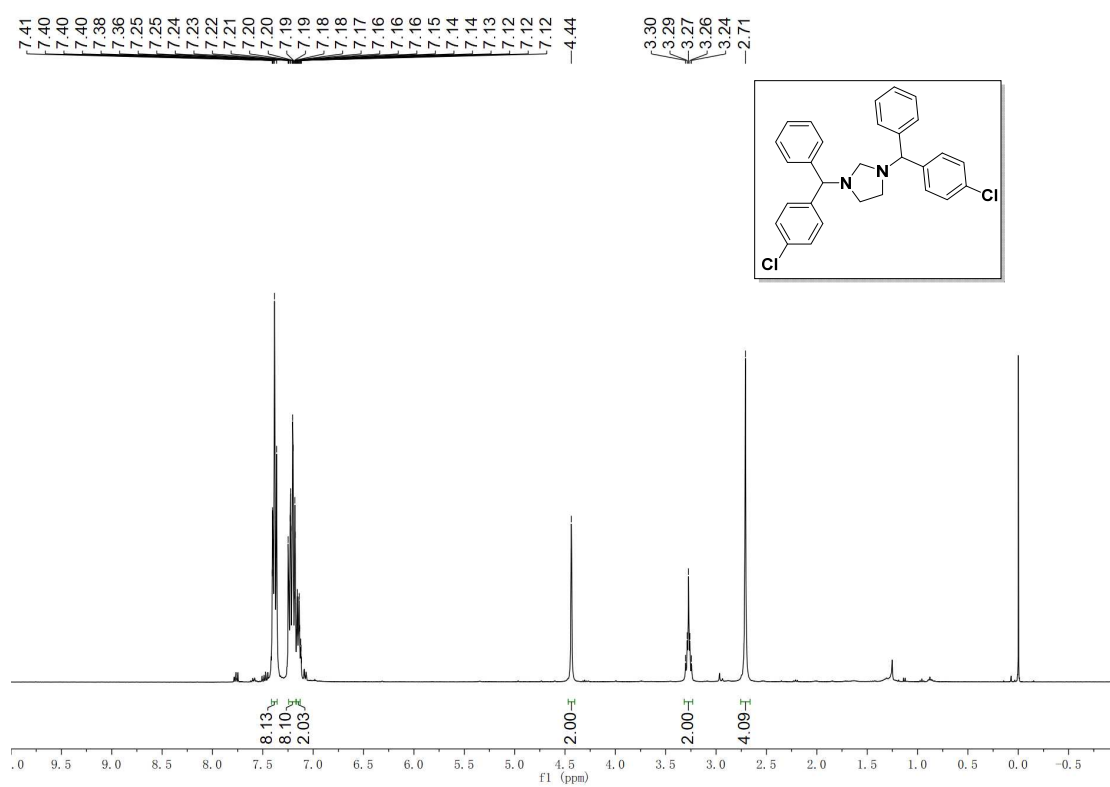


^1H , ^{19}F and ^{13}C -NMR spectra of compound **2g** in CDCl_3

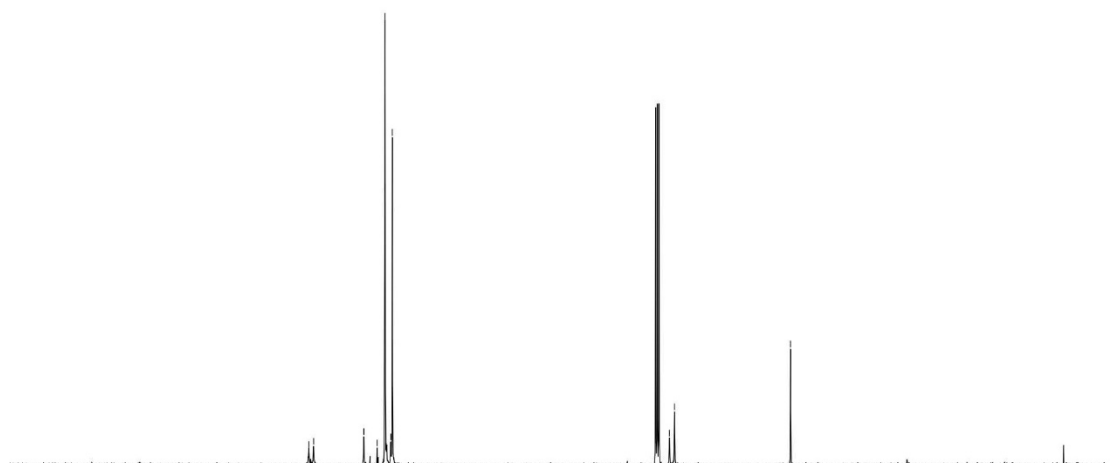




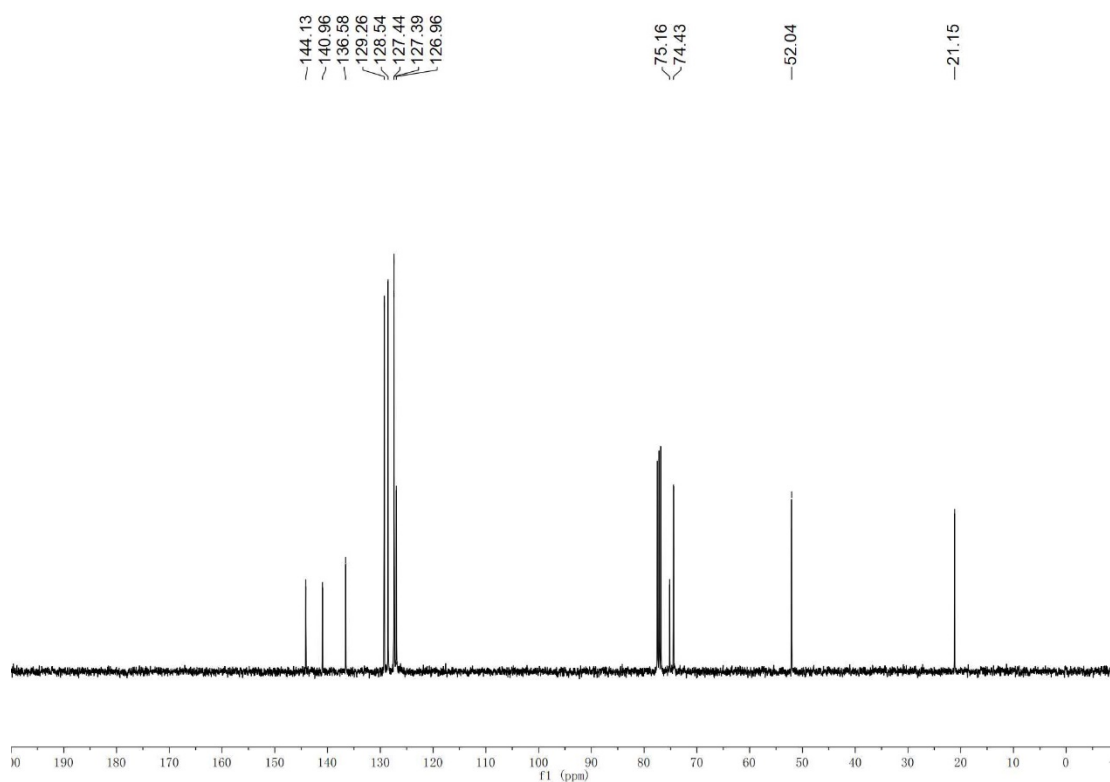
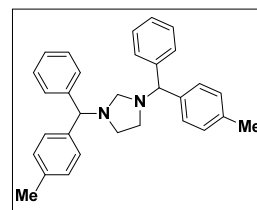
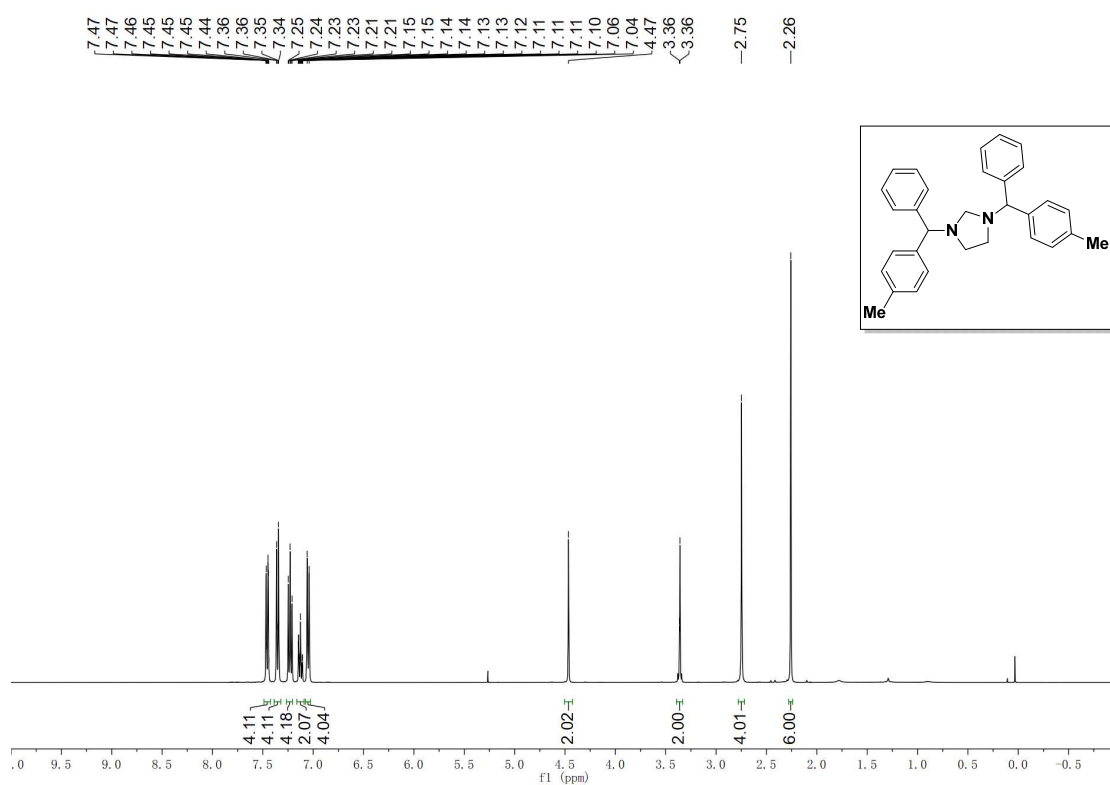
^1H and ^{13}C -NMR spectra of compound **2h** in CDCl_3



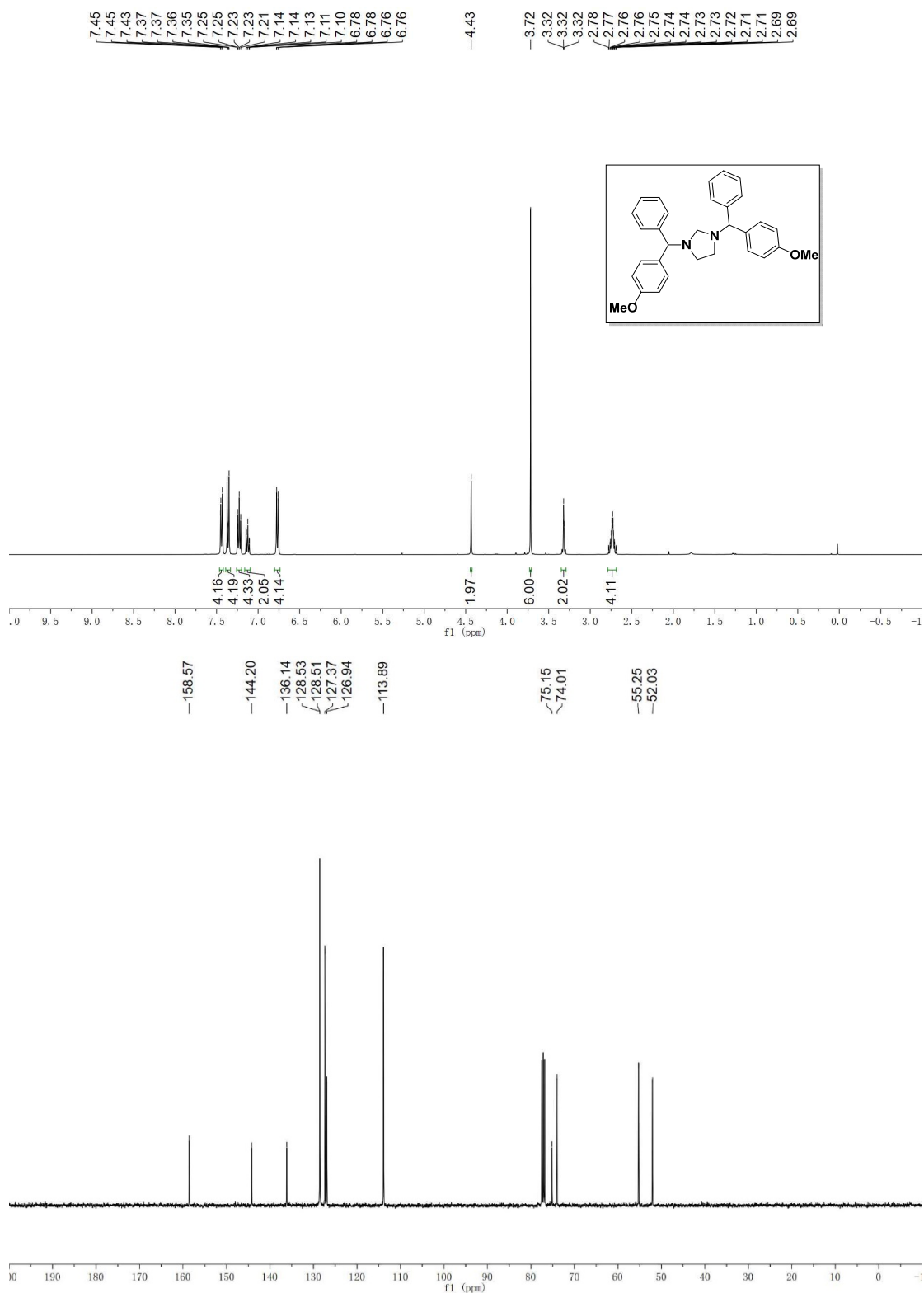
Chemical shifts (ppm): 143.15, 142.26, 132.75, 130.24, 128.79, 128.73, 127.61, 127.36, 74.83, 73.88, 51.87.



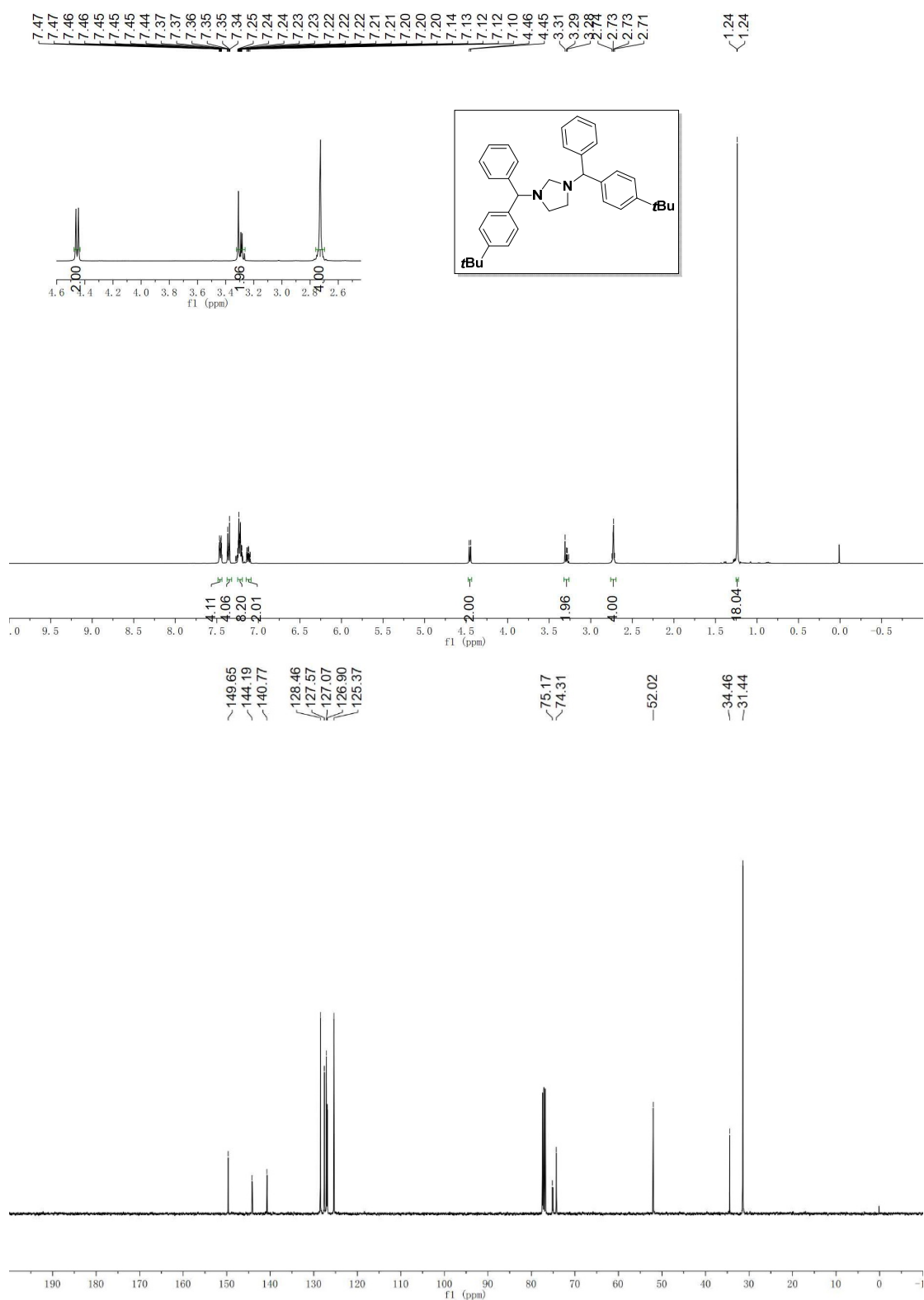
¹H and ¹³C-NMR spectra of compound **2i** in CDCl₃



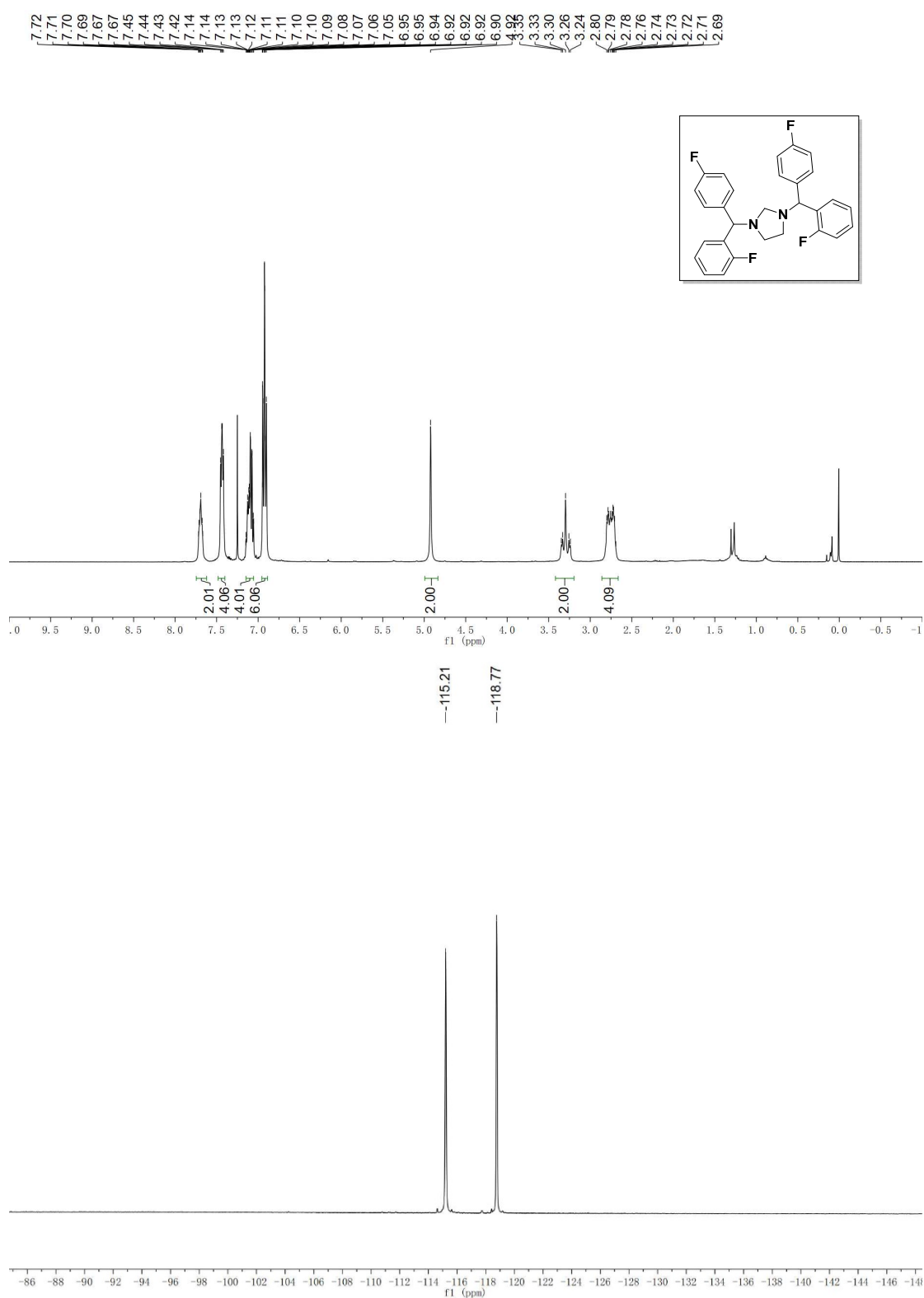
^1H and ^{13}C -NMR spectra of compound **2j** in CDCl_3

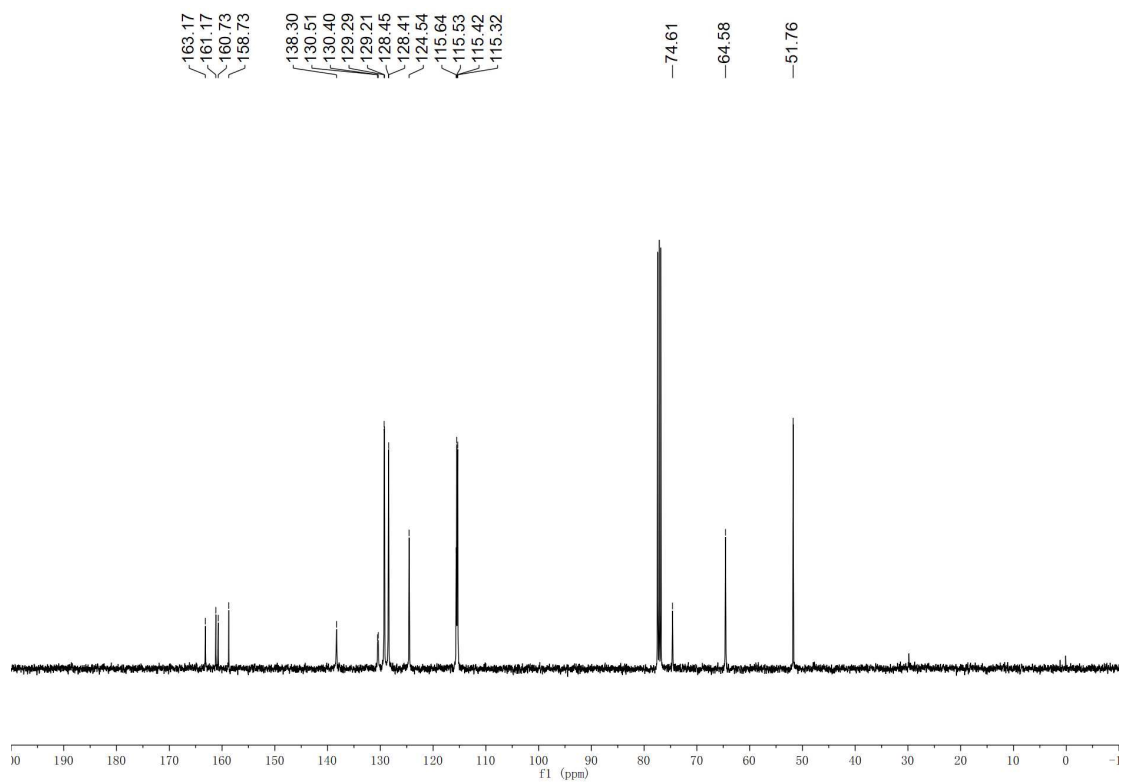


¹H and ¹³C-NMR spectra of compound **2k** in CDCl₃

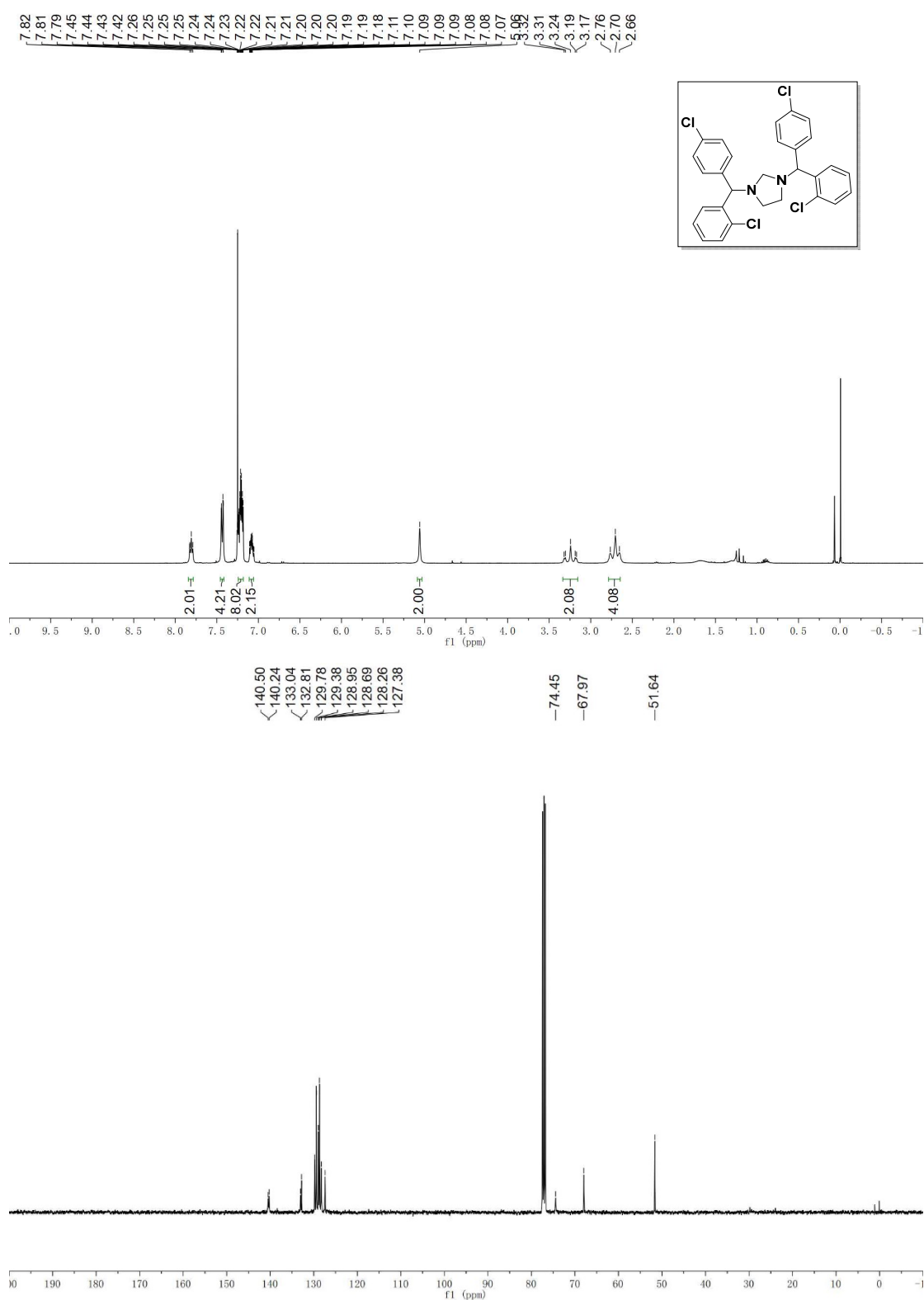


^1H , ^{19}F and ^{13}C -NMR spectra of compound **2I** in CDCl_3

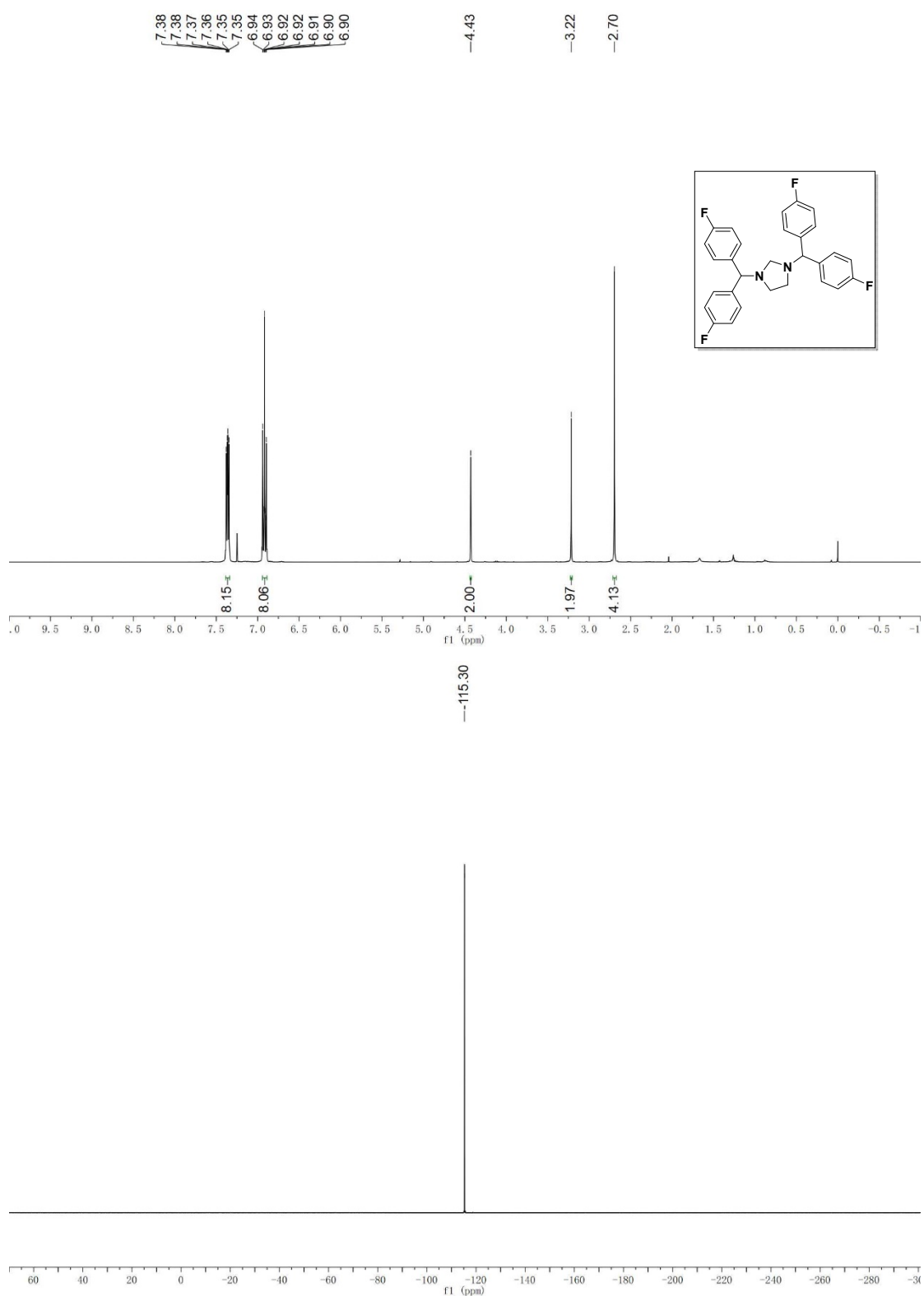


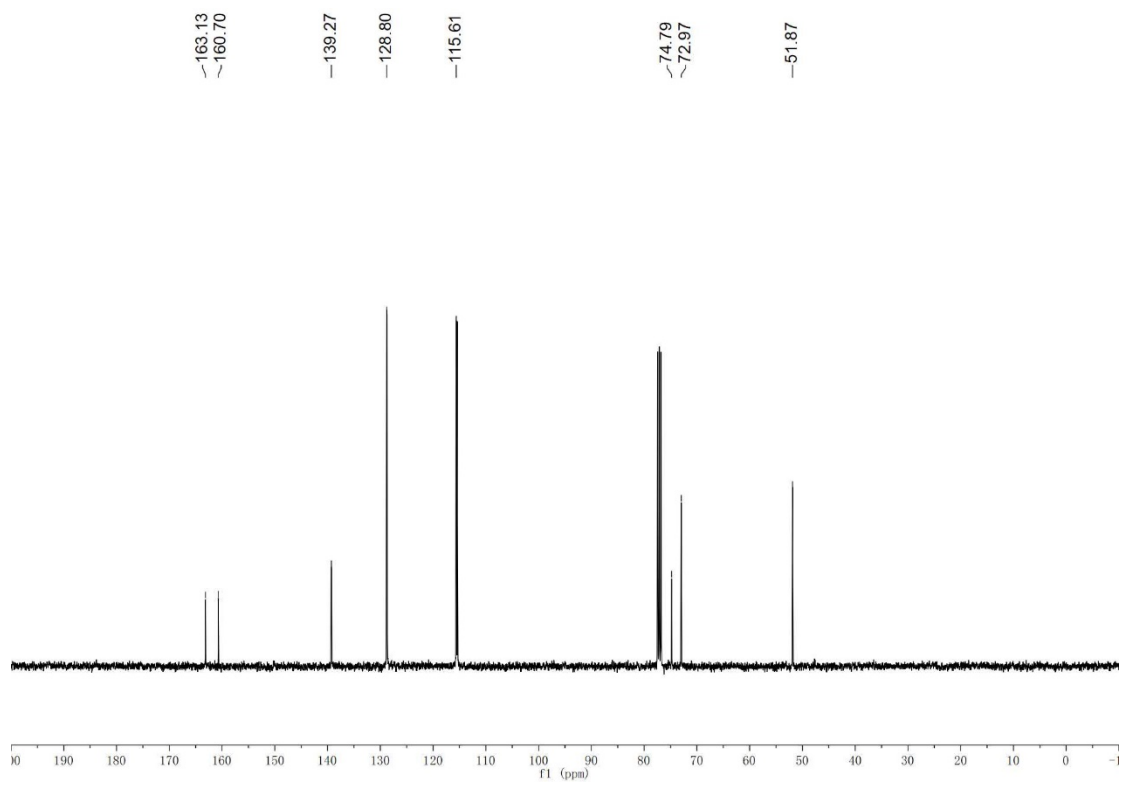


^1H and ^{13}C -NMR spectra of compound **2m** in CDCl_3

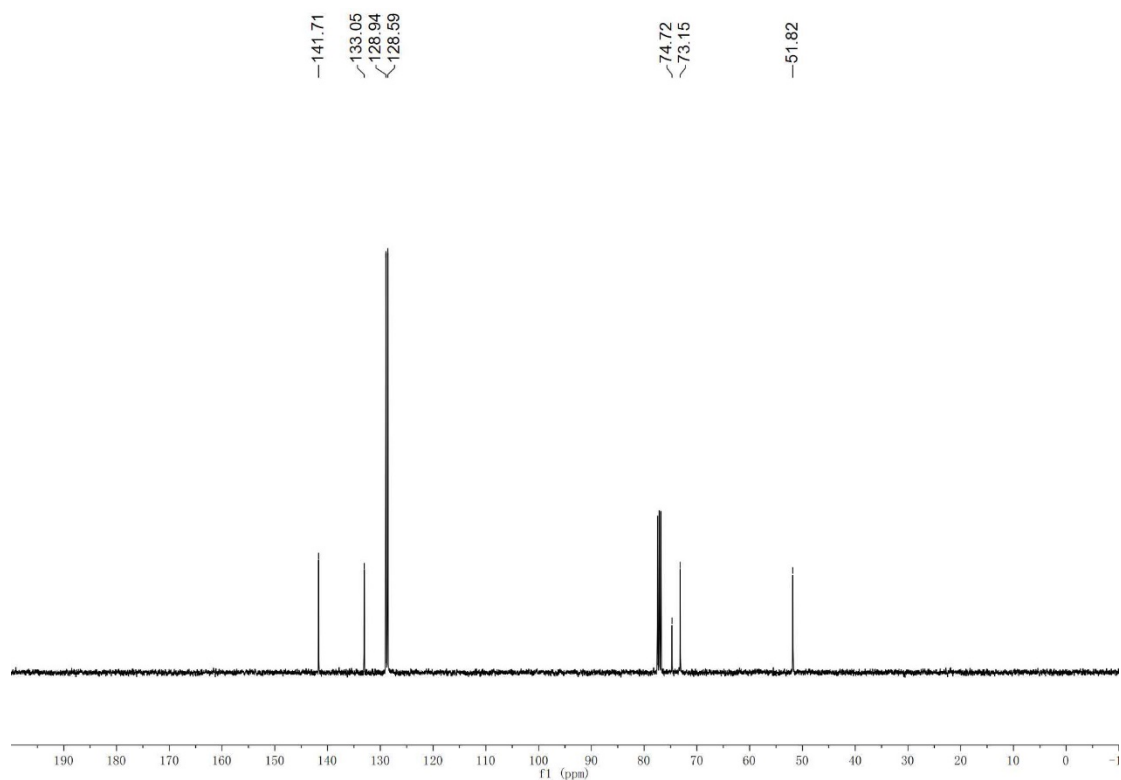
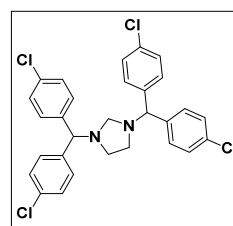
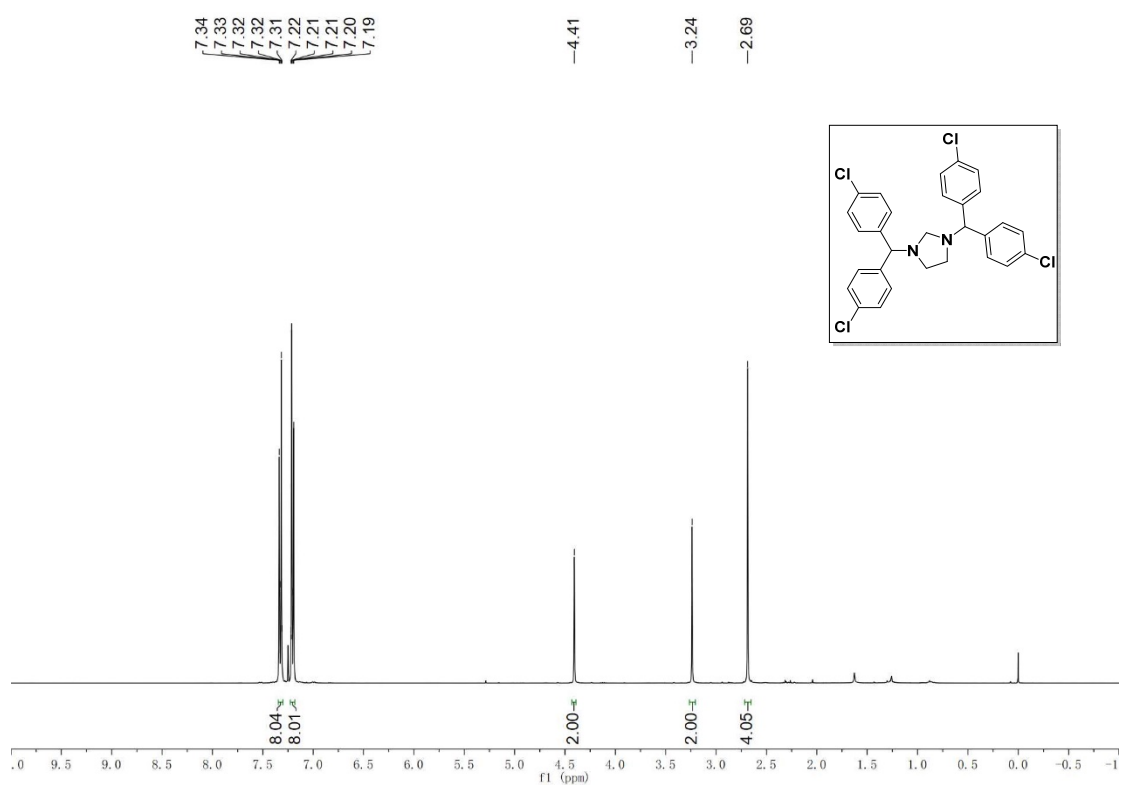


^1H , ^{19}F and ^{13}C -NMR spectra of compound **2n** in CDCl_3

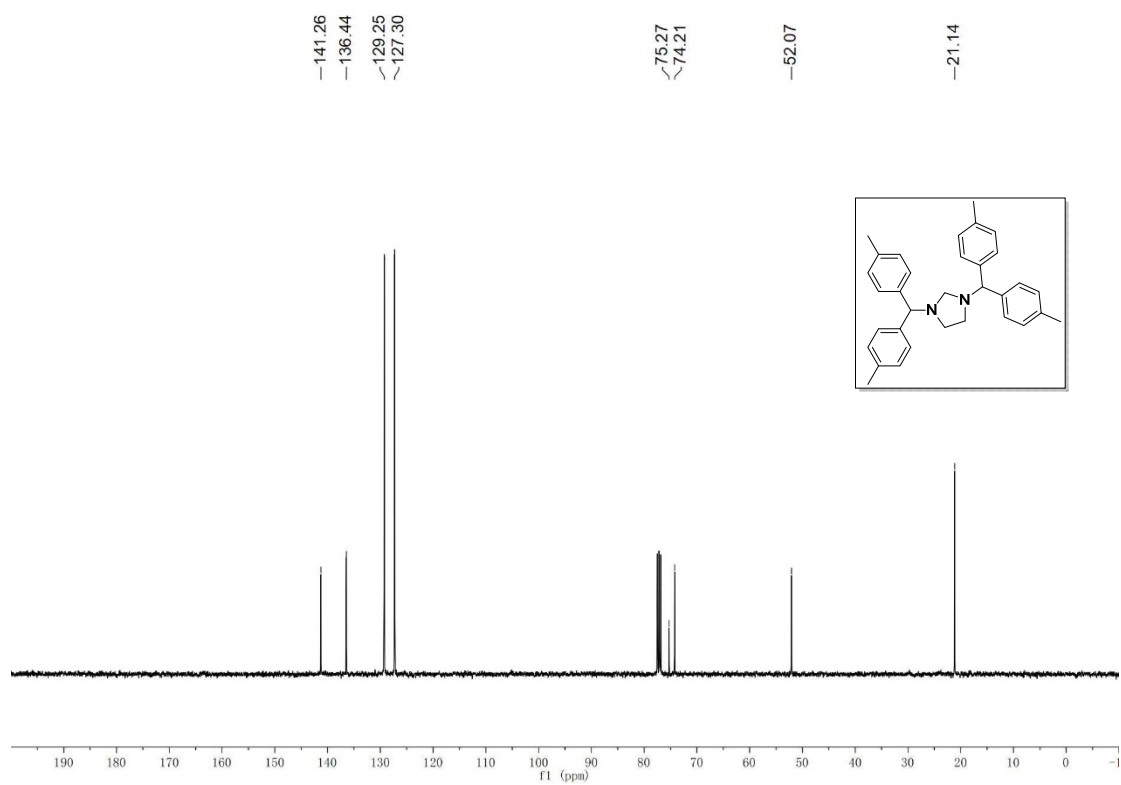
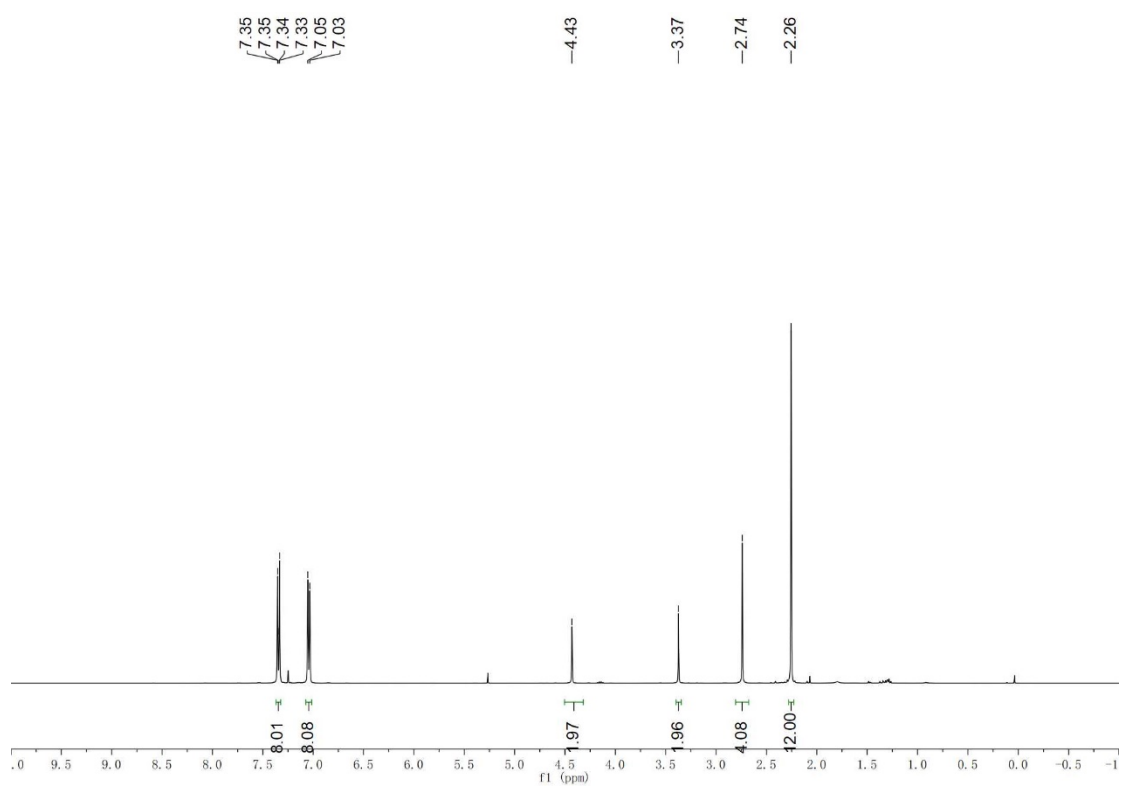




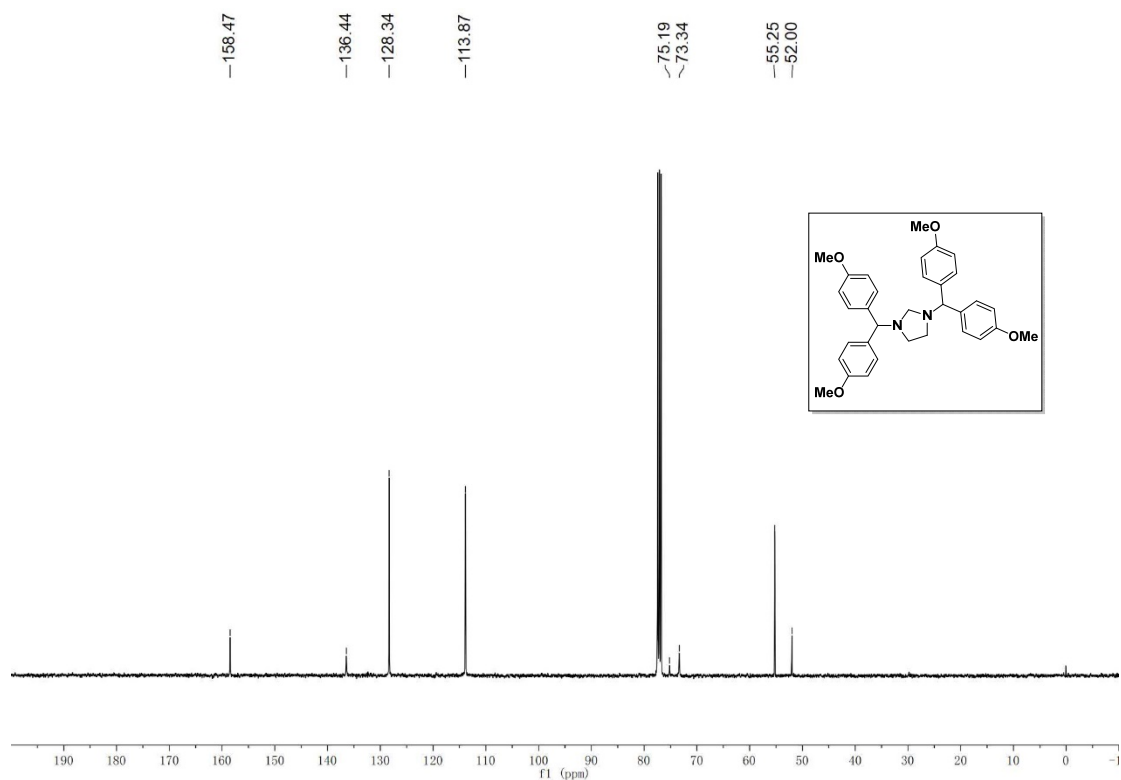
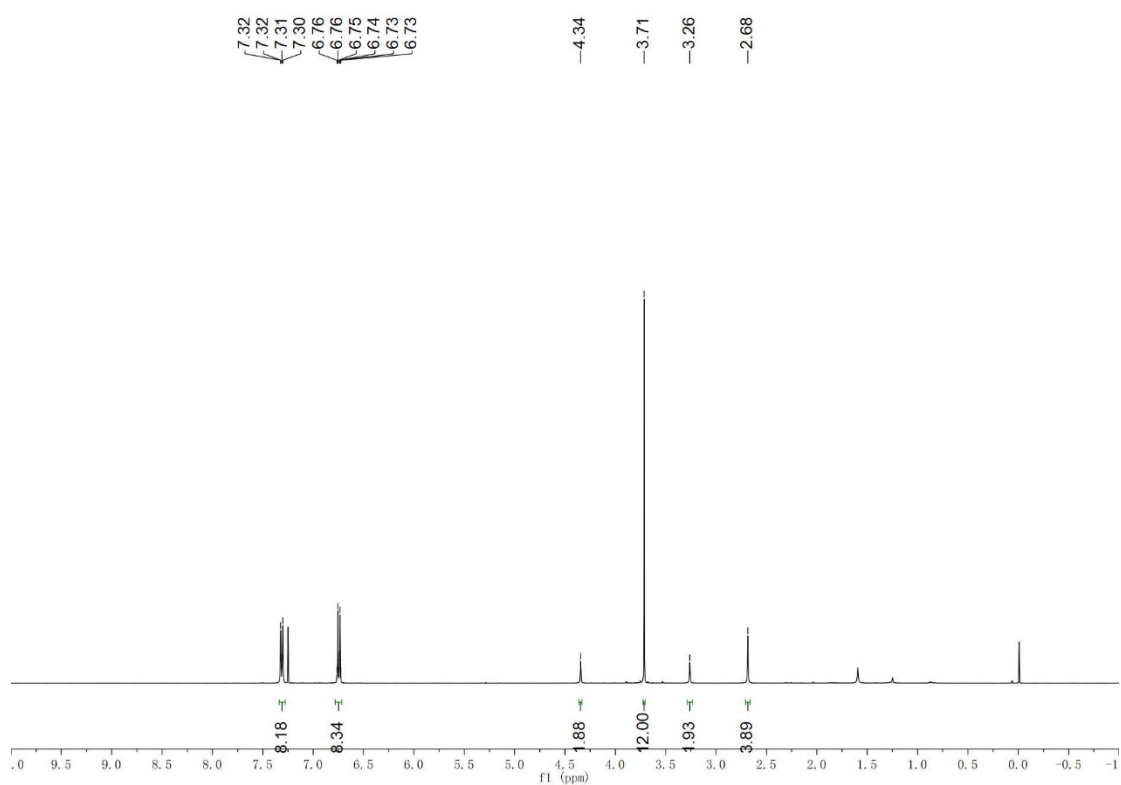
^1H and ^{13}C -NMR spectra of compound **2o** in CDCl_3



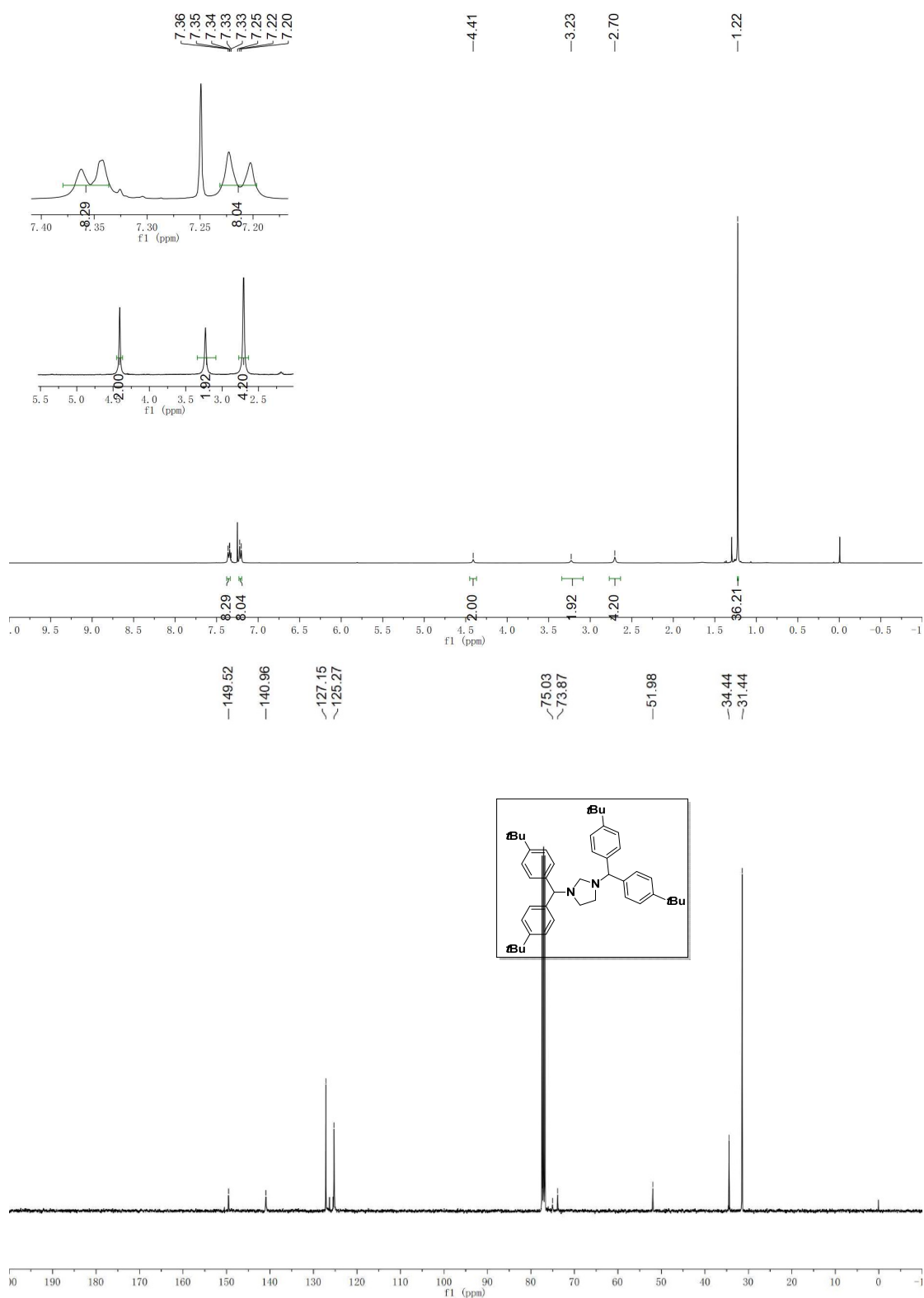
^1H and ^{13}C -NMR spectra of compound **2p** in CDCl_3



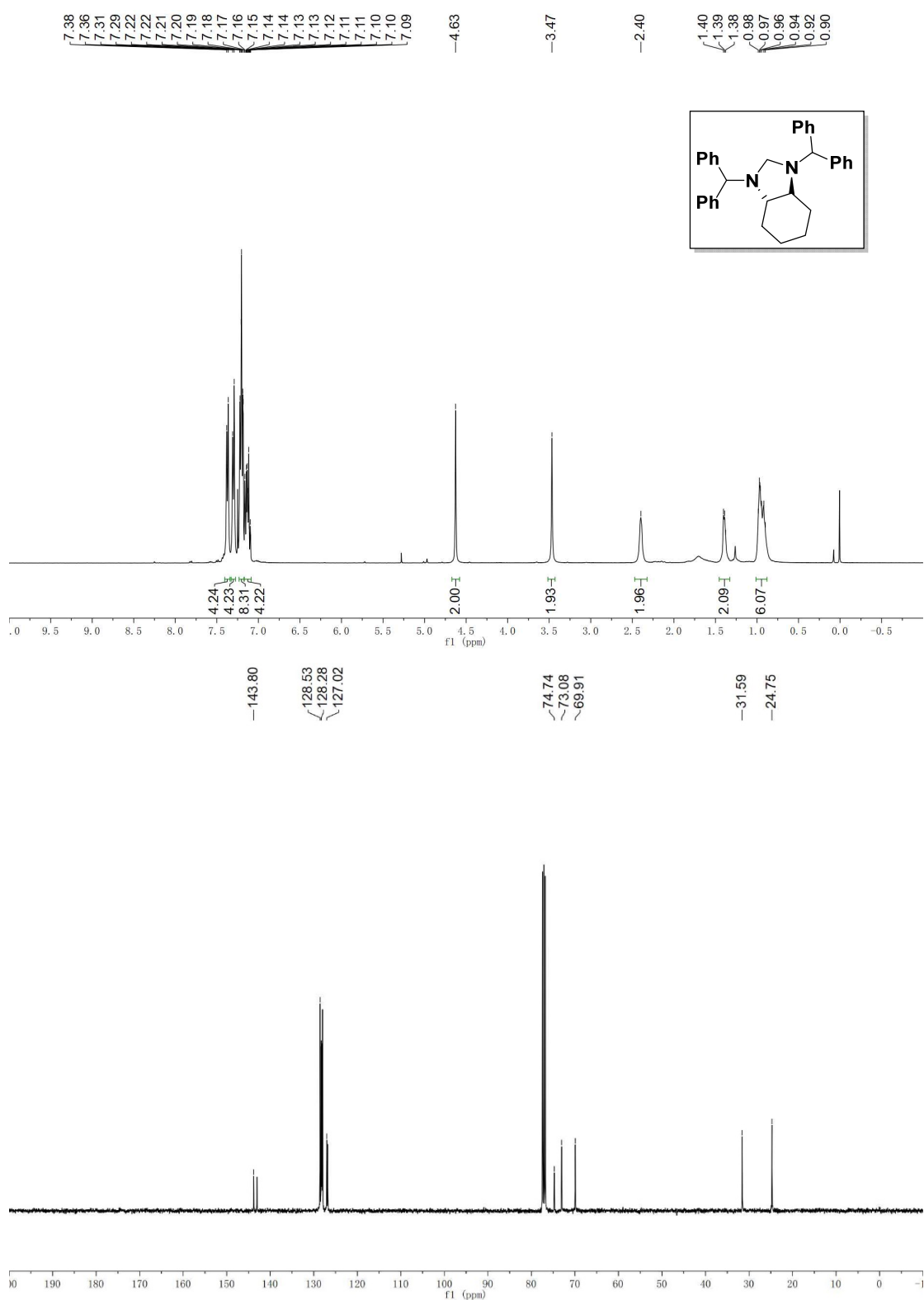
^1H and ^{13}C -NMR spectra of compound **2q** in CDCl_3



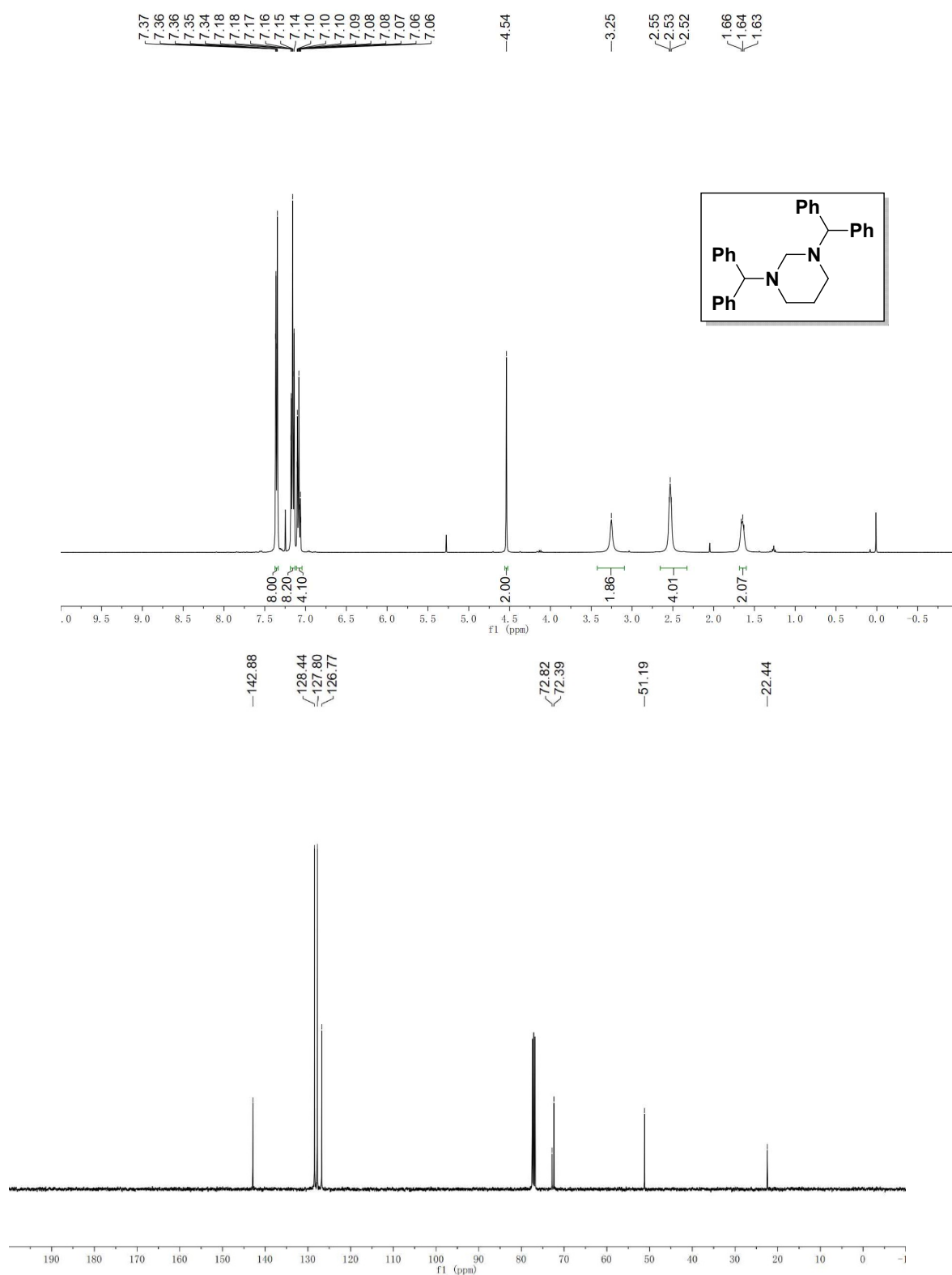
^1H and ^{13}C -NMR spectra of compound **2r** in CDCl_3



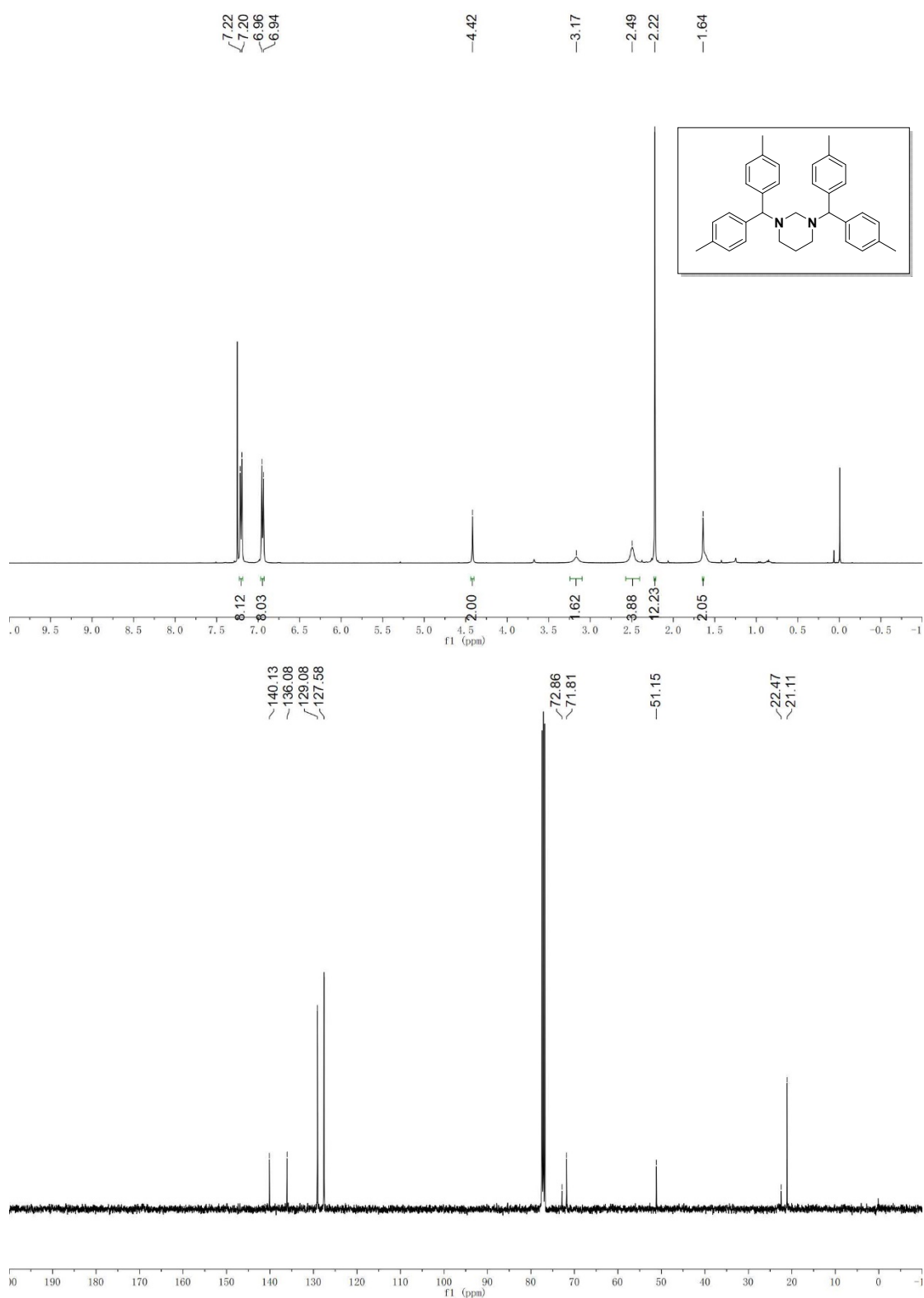
^1H and ^{13}C -NMR spectra of compound **2s** in CDCl_3



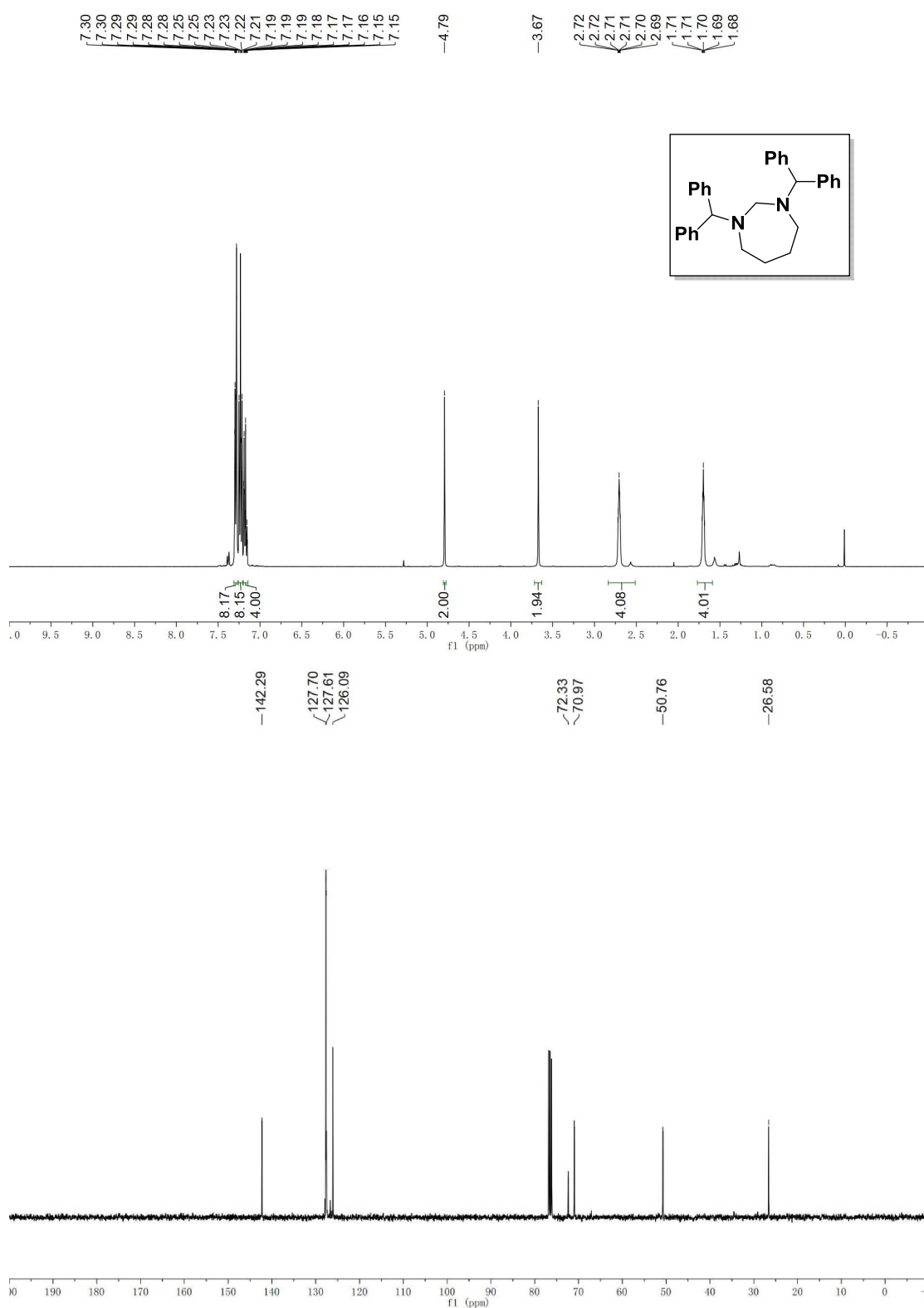
^1H and ^{13}C -NMR spectra of compound **2t** in CDCl_3



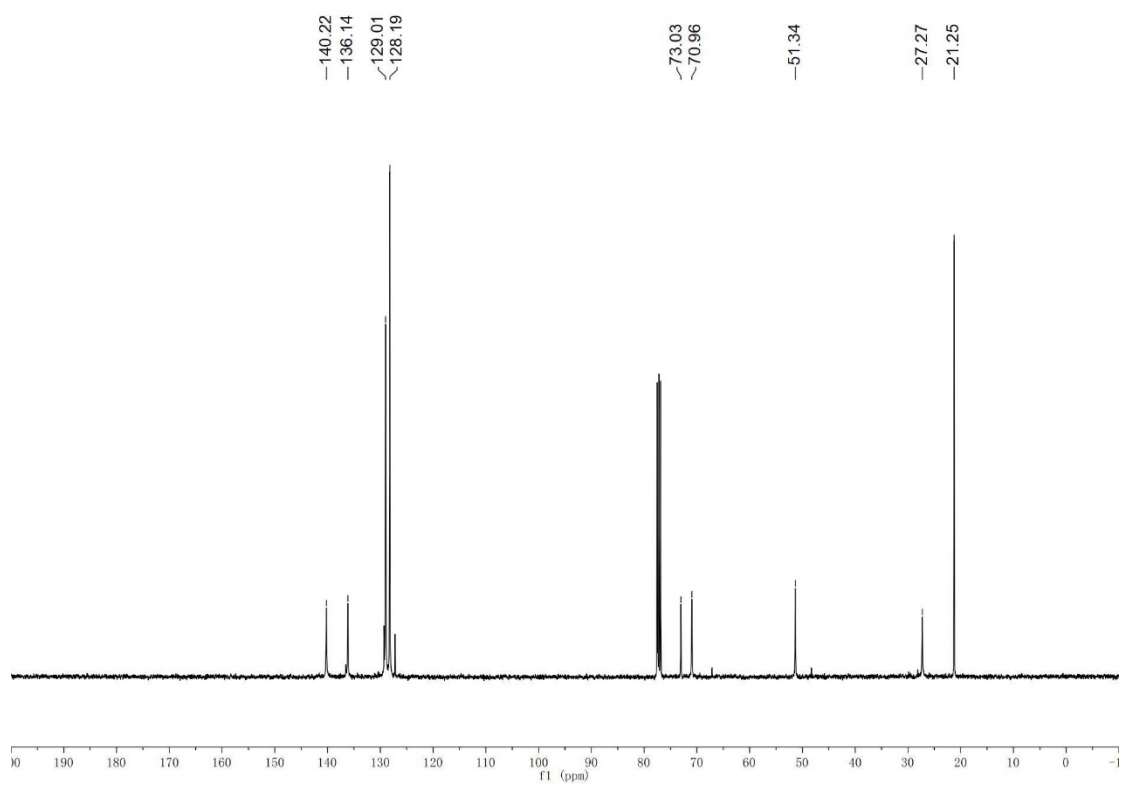
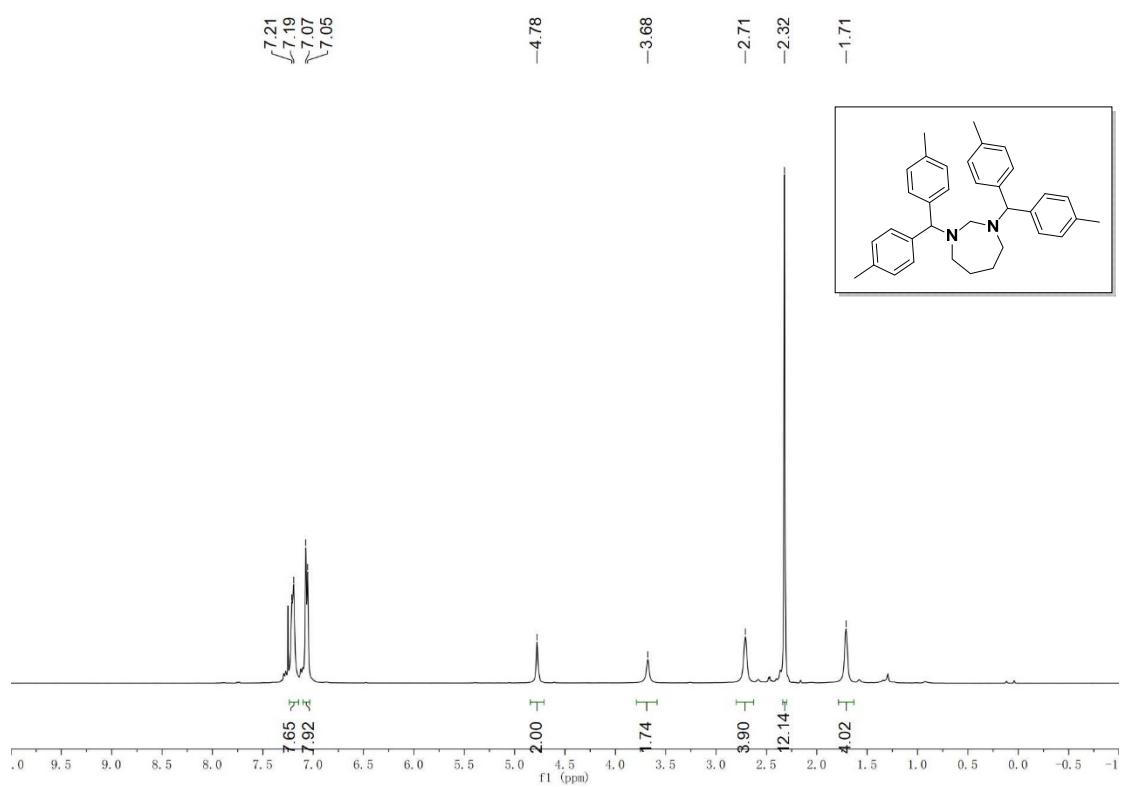
^1H and ^{13}C -NMR spectra of compound **2u** in CDCl_3



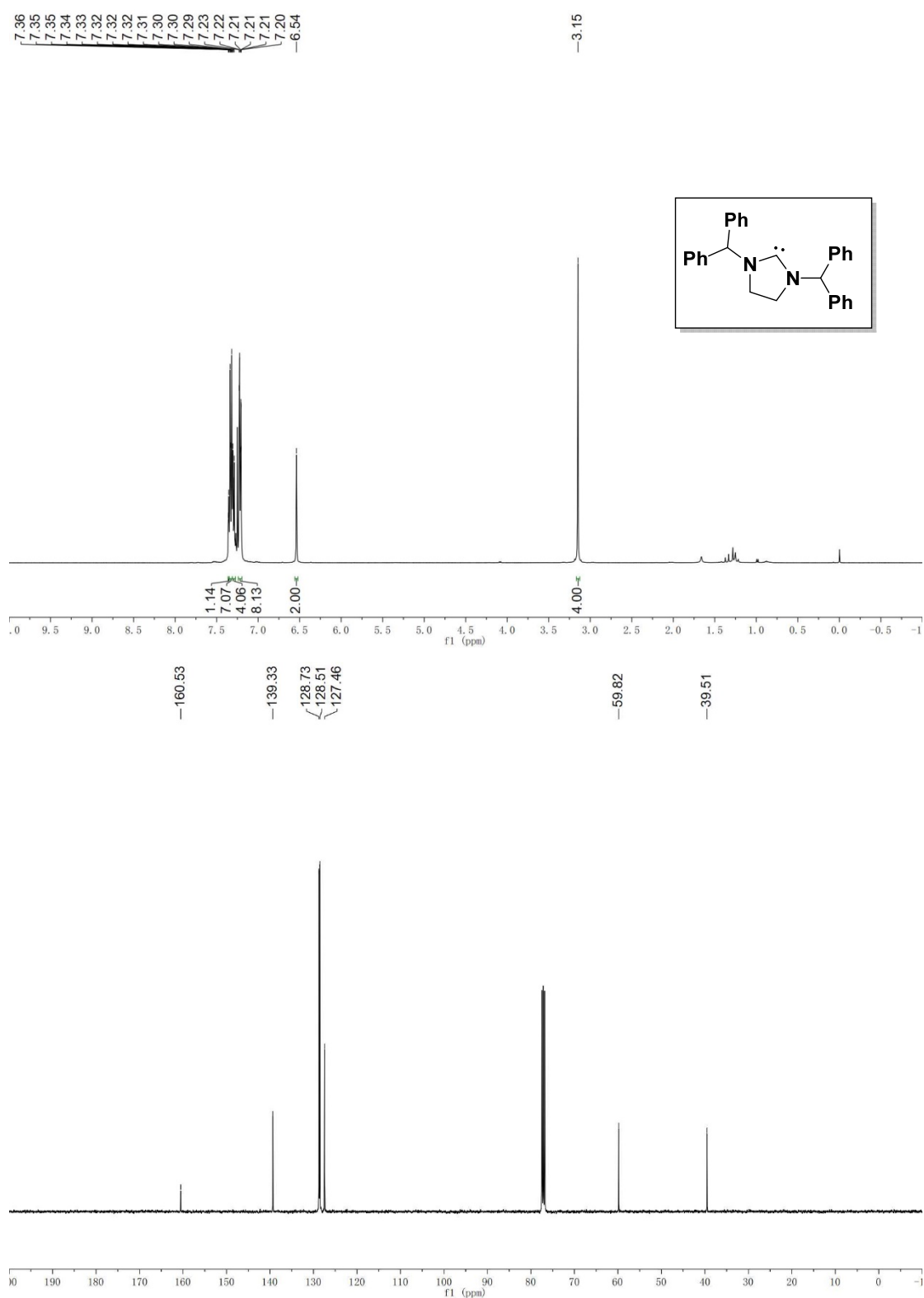
^1H and ^{13}C -NMR spectra of compound **2v** in CDCl_3



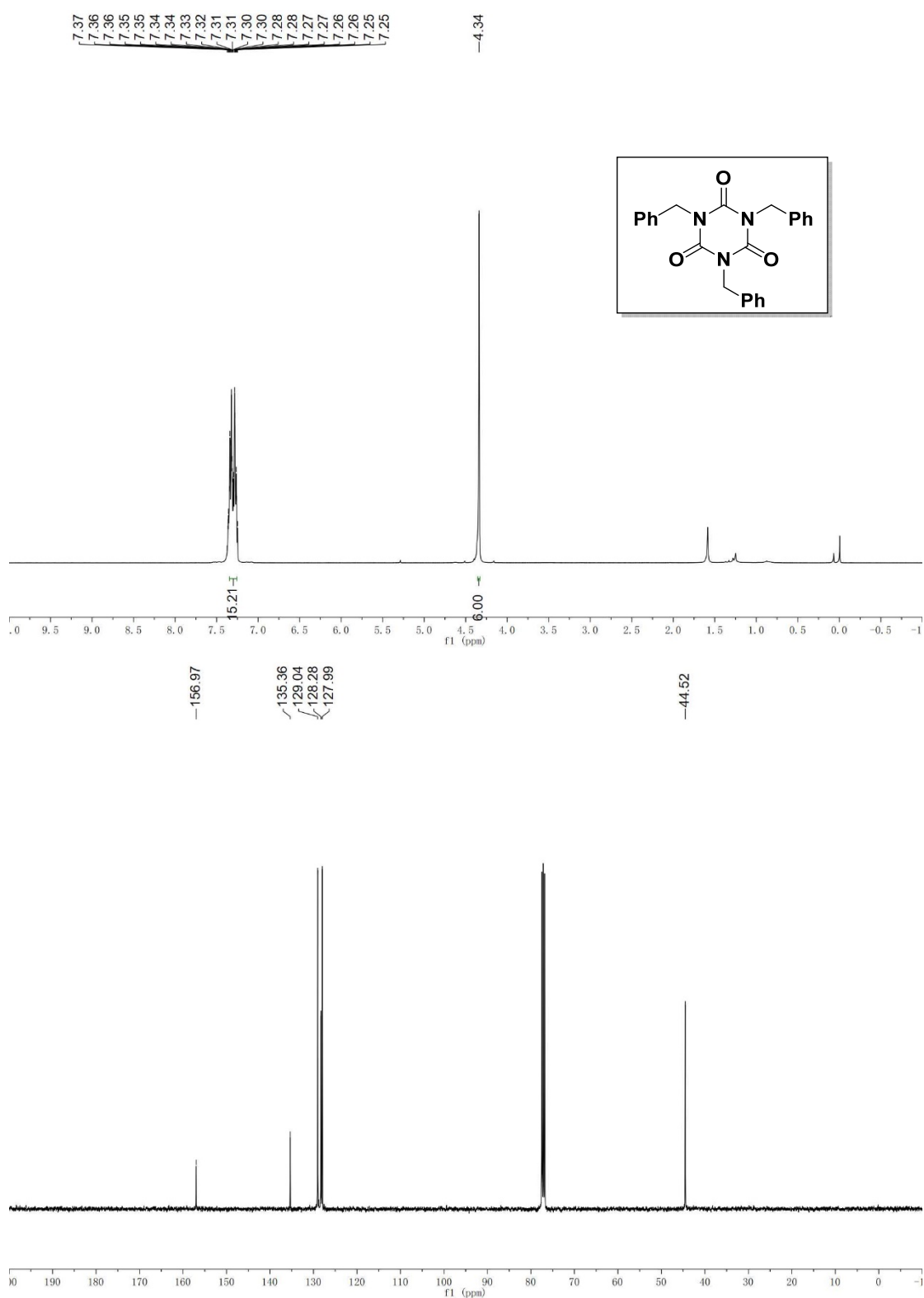
^1H and ^{13}C -NMR spectra of compound **2w** in CDCl_3



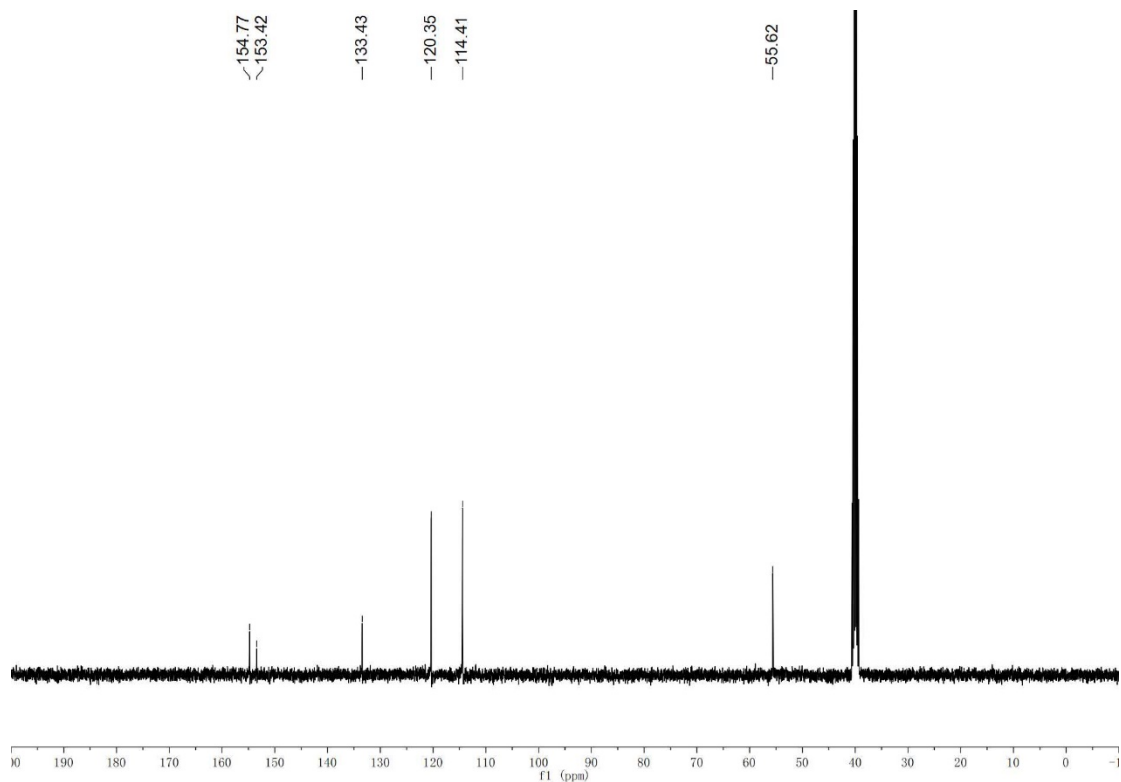
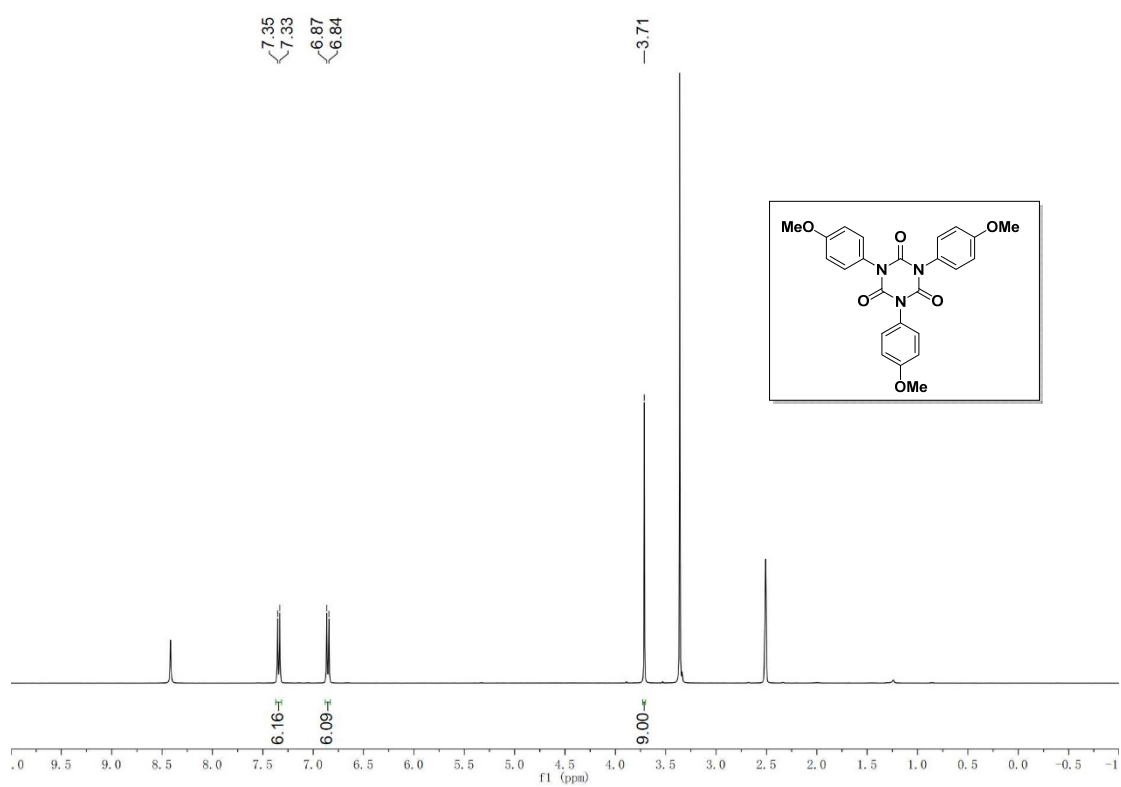
^1H and ^{13}C -NMR spectra of compound **2a-NHC** in CDCl_3



^1H and ^{13}C -NMR spectra of compound **4a** in CDCl_3



^1H and ^{13}C -NMR spectra of compound **4b** in $\text{DMSO}-d_6$



^1H and ^{13}C -NMR spectra of compound **2a-D** in CDCl_3

