Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

for

Visible Light-Mediated Cross-Coupling of Electrophiles: Synthesis of α-Amino Amides from Isocyanates and Ketimines

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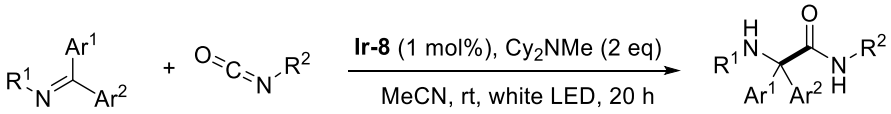
General Methods

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. Anhydrous 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 Brüker 400 MHz Fourier transform spectrometer. Chemical shifts in ^{1}H spectra were referenced to TMS, and in $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual solvent. All coupling constants are reported in hertz.

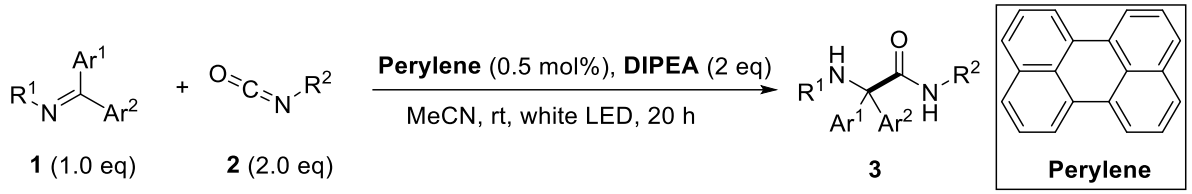
General Procedure A: Photoredox iridium catalyzed cross couplings between ketimines and isocyanates



1 **2** **3**

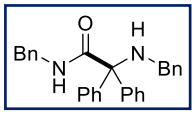
Ketimine **1** (0.1 mmol), Ir-8 (1.0 mg, 1 mol %), Cy_2NMe (42.8 µL, 0.2 mmol, 2 equiv) and isocyanate **2** (0.2 mmol, 2 equiv) were dissolved in anhydrous MeCN (1 mL) in an oven-dried 2 mL vial under nitrogen. A magnetic stirring bar was added and then the vial was sealed with a septum. The mixture was placed under a 20 W white LED light source and stirred at ambient temperature (20 – 30 ^{o}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.

General Procedure B: Photoredox perylene catalyzed cross couplings between ketimines and isocyanates



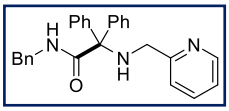
Ketimine **1** (0.1 mmol), perylene (0.13 mg, 0.5 mol%), DIPEA (33 µL, 0.2 mmol, 2 equiv) and isocyanate **2** (0.2 mmol, 2 equiv) were dissolved in anhydrous MeCN (1 mL) in an oven-dried 2 mL vial under nitrogen. A magnetic stirring bar was added and then the vial was sealed with a septum. The mixture was placed under a 20 W white LED light source1 and stirred at ambient temperature (20 – 30 ^{o}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



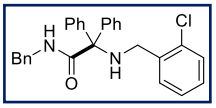
N-benzyl-2-(benzylamino)-2,2-diphenylacetamide (3aa)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and benzyl isocyanate (27 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 32.9 mg, 81% yield; General Procedure B: 31.3 mg, 77% yield) as light yellow solid. M.p. 129.5 – 130.4 °C. R_f = 0.42 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.32 – 7.24 (m, 5H), 7.24 – 7.19 (m, 5H), 7.19 – 7.16 (m, 3H), 7.15 – 7.14 (m, 3H), 6.98 – 6.89 (m, 4H), 6.75 (s, 1H), 4.68 (t, *J* = 5.3 Hz, 1H), 4.56 (s, 2H), 4.34 (d, *J* = 5.4 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.68, 139.92, 139.28, 138.04, 129.08, 128.76, 128.68, 128.58, 127.73, 127.37, 127.31, 127.14, 127.11, 63.31, 49.11, 45.15 ppm. IR (thin film): 3053, 1648, 1516, 1496, 1454, 1265, 738, 704 cm^{-1}; HRMS calcd for $C_{28}H_{27}N_2O^+$ 407.2123, observed 407.2122 $[M+H]^+$.



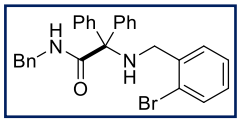
N-benzyl-2,2-diphenyl-2-((pyridin-2-ylmethyl)amino)acetamide (3ba)

The reaction was performed following the General Procedures using 1,1-diphenyl-N-(pyridin-2-ylmethyl)methanimine (27.2 mg, 0.10 mmol) and benzyl isocyanate (27 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 33.8 mg, 83% yield; General Procedure B: 35.8 mg, 88% yield) as a white solid. M.p. 123.6 – 125.0 °C. R_f = 0.70 (petroleum ether/EtOAc = 1/1). ^{1}H NMR (400 MHz, chloroform-d) δ 8.27 (d, *J* = 4.2 Hz, 1H), 7.84 (s, 1H), 7.34 – 7.22 (m, 12H), 7.22 – 7.16 (m, 4H), 7.05 – 7.01 (m, 1H), 6.93 (s, 1H), 5.89 (d, *J* = 7.8 Hz, 1H), 4.53 (s, 2H), 4.50 (d, *J* = 5.3 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 159.99, 158.04, 148.25, 140.63, 139.98, 136.69, 129.23, 128.53, 128.50, 127.66, 127.36, 126.93, 122.62, 122.34, 62.90, 50.56, 45.24 ppm. IR (thin film): 3440, 3054, 1637, 1265, 896, 777, 733, 706 cm^{-1}; HRMS calcd for $C_{27}H_{26}N_3O^+$ 408.2076, observed 408.2073 $[M+H]^+$.



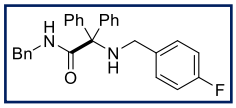
N-benzyl-2-((2-chlorobenzyl)amino)-2,2-diphenylacetamide (3ca)

The reaction was performed following the General Procedures using N-(2-chlorobenzyl)-1,1-diphenylmethanimine (35.6 mg, 0.10 mmol) and benzyl isocyanate (27 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 34.8 mg, 79% yield; General Procedure B: 34.8 mg, 79% yield) as a light yellow solid. M.p. 123.2 – 125.3 °C. R_f = 0.42 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.27 – 7.16 (m, 13H), 7.15 – 7.11 (m, 1H), 7.07 – 6.96 (m, 5H), 6.76 (s, 1H), 4.74 (t, *J* = 4.8 Hz, 1H), 4.66 (s, 2H), 4.38 (d, *J* = 5.5 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.42, 139.49, 139.28, 134.68, 132.24, 129.16, 128.92, 128.66, 128.59, 128.55, 128.23, 127.69, 127.38, 127.20, 126.64, 63.37, 46.40, 45.09 ppm. IR (thin film): 3031, 1650, 1514, 1454, 1239, 867, 760, 739 cm^{-1}; HRMS calcd for $C_{28}H_{26}ClN_2O^+$ 441.1734, observed 441.1730 $[M+H]^+$.



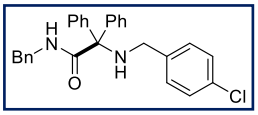
N-benzyl-2-((2-bromobenzyl)amino)-2,2-diphenylacetamide (3da)

The reaction was performed following the General Procedures using N-(2-bromobenzyl)-1,1-diphenylmethanimine (35 mg, 0.10 mmol) and benzyl isocyanate (27 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 42.7 mg, 88% yield; General Procedure B: 38.8 mg, 80% yield) as a light yellow solid. M.p. 129.2 – 130.4 °C. R_f = 0.45 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.37 – 7.31 (m, 1H), 7.29 – 7.16 (m, 13H), 7.10 – 7.02 (m, 3H), 7.01 – 6.94 (m, 2H), 6.76 (s, 1H), 4.68 (t, *J* = 5.5 Hz, 1H), 4.62 (s, 2H), 4.40 (d, *J* = 5.5 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.36, 139.48, 139.23, 136.16, 132.42, 128.89, 128.72, 128.62, 128.55, 128.50, 127.65, 127.37, 127.21, 127.17, 122.28, 63.40, 49.03, 45.11 ppm. IR (thin film): 3446, 3054, 1649, 1515, 1265, 777, 738, 705 cm^{-1}; HRMS calcd for $C_{28}H_{26}BrN_2O^+$ 485.1229, observed 485.1226 $[M+H]^+$.



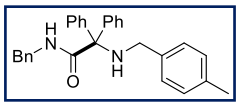
N-benzyl-2-((4-fluorobenzyl)amino)-2,2-diphenylacetamide (3ea)

The reaction was performed following the General Procedures using N-(4-fluorobenzyl)-1,1-diphenylmethanimine (28.9 mg, 0.10 mmol) and benzyl isocyanate (27 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 36.9 mg, 87% yield; General Procedure B: 39 mg, 92% yield) as a light yellow solid. M.p. 122.0 – 123.5 °C. R_f = 0.45 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.29 – 7.24 (m, 6H), 7.23 – 7.14 (m, 7H), 6.96 – 6.94 (m, 2H), 6.92 – 6.85 (m, 2H), 6.81 (t, *J* = 8.7 Hz, 2H), 6.61 (s, 1H), 4.65 (t, *J* = 5.3 Hz, 1H), 4.54 (s, 2H), 4.35 (d, *J* = 5.4 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 161.90 (d, *J* =246.4Hz), 158.42, 139.50, 139.07, 133.92, 128.85, 128.75, 128.66, 128.45, 127.71, 127.18, 127.07, 115.21 (d, *J* = 21.4 Hz), 63.38, 48.37, 45.04 ppm. ^{19}F NMR (375 MHz, chloroform-d) δ -115.57 ppm. IR (thin film): 3443, 1645, 1509, 1239, 818, 747, 739, 728 cm^{-1}; HRMS calcd for $C_{28}H_{26}FN_2O^+$ 425.2029, observed 425.2023 $[M+H]^+$.



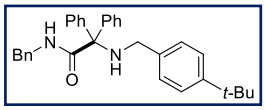
N-benzyl-2-((4-chlorobenzyl)amino)-2,2-diphenylacetamide (3fa)

The reaction was performed following the General Procedures using N-(4-chlorobenzyl)-1,1-diphenylmethanimine (30.6 mg, 0.10 mmol) and benzyl isocyanate (27 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 39.2 mg, 89% yield; General Procedure B: 35.2 mg, 80% yield) as a light yellow solid. M.p. 114.2 – 115.8 °C. R_f = 0.42 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.31 – 7.23 (m, 6H), 7.23 – 7.14 (m, 7H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.96 – 6.93 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.60 (s, 1H), 4.65 (t, *J* = 5.4 Hz, 1H), 4.53 (s, 2H), 4.34 (d, *J* = 5.4 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.37, 139.44, 139.04, 136.82, 132.79, 128.85, 128.69, 128.47 (x2), 127.75, 127.18 (x2), 127.09, 63.45, 48.43, 45.05 ppm. IR (thin film): 3447, 1648, 1516, 1256, 758, 738, 701, 601 cm^{-1}; HRMS calcd for $C_{28}H_{26}ClN_2O^+$ 441.1734, observed 441.1730 $[M+H]^+$.



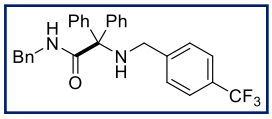
N-benzyl-2-((4-methylbenzyl)amino)-2,2-diphenylacetamide (3ga)

The reaction was performed following the General Procedures using N-(4-methylbenzyl)-1,1-diphenylmethanimine (28.5 mg, 0.10 mmol) and benzyl isocyanate (27 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 37 mg, 88% yield; General Procedure B: 37.8 mg, 90% yield) as a light yellow solid. M.p. 106.5 – 108.0 °C. R_f = 0.45 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.30 – 7.21 (m, 10H), 7.19 – 7.16 (m, 3H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.93 – 6.89 (m, 2H), 6.82 (s, 1H), 6.80 (s, 2H), 4.69 (t, *J* = 4.9 Hz, 1H), 4.51 (s, 2H), 4.32 (d, *J* = 5.4 Hz, 2H), 2.25 (s, 3H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.75, 140.10, 139.37, 137.11, 134.91, 129.46, 129.13, 128.79, 128.55, 127.71, 127.31, 127.09 (x2), 63.22, 48.89, 45.12, 21.25 ppm. IR (thin film): 3442, 3031, 1647, 1515, 1257, 801, 765, 714 cm^{-1}; HRMS calcd for $C_{29}H_{29}N_2O^+$ 421.2280, observed 421.2276 $[M+H]^+$.



N-benzyl-2-((4-(tert-butyl)benzyl)amino)-2,2-diphenylacetamide (3ha)

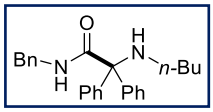
The reaction was performed following the General Procedures using N-(4-(tert-butyl)benzyl)-1,1-diphenylmethanimine (32.7 mg, 0.10 mmol) and benzyl isocyanate (27 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 40.3 mg, 87% yield; General Procedure B: 37.5 mg, 81% yield) as a white solid. M.p. 119.0 – 120.5 °C. R_f = 0.55 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.33 – 7.20 (m, 10H), 7.19 – 7.12 (m, 5H), 6.91 – 6.87 (m, 2H), 6.85 (s, 1H), 6.83 (s, 2H), 4.69 (t, *J* = 5.3 Hz, 1H), 4.51 (s, 2H), 4.33 (d, *J* = 5.4 Hz, 2H), 1.25 (s, 9H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.76, 150.47, 140.16, 139.31, 134.97, 129.16, 128.77, 128.56, 127.68, 127.33, 127.13, 126.93, 125.70, 63.22, 48.82, 45.18, 34.64, 31.54 ppm. IR (thin film): 3443, 3055, 1644, 1265, 781, 735, 705, 560 cm^{-1}; HRMS calcd for $C_{32}H_{35}N_2O^+$ 463.2749, observed 463.2745 $[M+H]^+$.



N-benzyl-2,2-diphenyl-2-((4-(trifluoromethyl)benzyl)amino) acetamide (3ia)

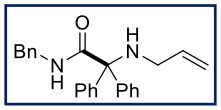
The reaction was performed following the General Procedures using 1,1-diphenyl-N-(4-(trifluoromethyl)benzyl)methanimine (33.9 mg, 0.10 mmol) and benzyl isocyanate (27 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 37 mg, 78% yield; General Procedure B: 38.4 mg, 81% yield) as a white solid. M.p. 104.2 – 105.5 °C. R_f = 0.44 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.22 (m, 6H), 7.22 – 7.12 (m, 7H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.90 (m, 2H), 6.56 (s, 1H), 4.68 (t, *J* = 5.3 Hz, 1H), 4.62 (s, 2H), 4.36 (d, *J* = 5.4 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.34, 142.67, 139.24, 138.97, 128.83, 128.81 (q, *J* = 32.3 Hz), 128.71, 128.49, 127.86, 127.31, 127.16 (x2), 125.18 (q, *J* = 3.7 Hz), 124.13 (q, *J* = 273.7 Hz), 63.68, 48.67, 45.08 ppm. ^{19}F NMR (375 MHz, chloroform-

d) δ – 62.40 ppm. IR (thin film): 3443, 3055, 1640, 1265, 896, 776, 738, 705 cm^{-1}; HRMS calcd for $C_{29}H_{26}F_3N_2O^+$ 475.1997, observed 475.1992 $[M+H]^+$.



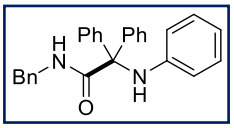
N-benzyl-2-(butylamino)-2,2-diphenylacetamide (3ja)

The reaction was performed following the General Procedures using N-butyl-1,1-diphenylmethanimine (23.7 mg, 0.10 mmol) and benzyl isocyanate (27 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 32.8 mg, 88% yield; General Procedure B: 32 mg, 86% yield) as a light yellow solid. M.p. 119.7 – 120.3 °C. R_f = 0.45 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.34 – 7.26 (m, 8H), 7.21 (d, *J* = 6.9 Hz, 5H), 7.17 (d, *J* = 7.0 Hz, 2H), 6.58 (s, 1H), 4.73 (t, *J* = 5.3 Hz, 1H), 4.43 (d, *J* = 5.4 Hz, 2H), 3.31 – 3.13 (m, 2H), 1.i13 – 0.92 (m, 4H), 0.64 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.04, 140.17, 139.71, 128.94, 128.65, 128.60, 127.60, 127.49, 127.20, 63.08, 45.58, 45.08, 31.24, 20.21, 13.66 ppm. IR (thin film): 3440, 3055, 1640, 1510, 1265, 781, 735, 704, cm^{-1}; HRMS calcd for $C_{25}H_{29}N_2O^+$ 373.2280, observed 373.2278 $[M+H]^+$.



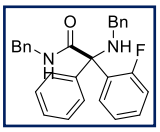
2-(allylamino)-N-benzyl-2,2-diphenylacetamide (3ka)

The reaction was performed following the General Procedures using N-allyl-1,1-diphenylmethanimine (22.1 mg, 0.10 mmol) and benzyl isocyanate (27 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 27.4 mg, 77% yield; General Procedure B: 26.3 mg, 74% yield) as a light yellow solid. M.p. 112.0 – 114.1 °C. R_f = 0.45 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.36 – 7.26 (m, 8H), 7.26 – 7.17 (m, 7H), 6.86 (s, 1H), 5.37 – 5.27 (m, 1H), 5.03 – 4.88 (m, 3H), 4.44 (d, *J* = 5.4 Hz, 2H), 3.89 (d, *J* = 5.5 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.52, 140.04, 139.40, 135.31, 128.85, 128.55, 128.49, 127.44, 127.41, 127.14, 117.15, 62.43, 47.92, 45.06 ppm. IR (thin film): 3443, 3054, 1643, 1265, 779, 737, 705, 591 cm^{-1}; HRMS calcd for $C_{24}H_{25}N_2O$+ 357.1967, observed 357.1964 $[M+H]^+$.



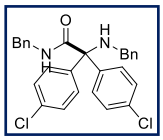
N-benzyl-2,2-diphenyl-2-(phenylamino)acetamide (3la)

The reaction was performed following the General Procedures using N,1,1-triphenylmethanimine (25.7 mg, 0.10 mmol) and benzyl isocyanate (27 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 30.2 mg, 77% yield; General Procedure B: 27.5 mg, 70% yield) as a colorless oil. R_f = 0.48 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.38 – 7.18 (m, 16H), 7.18 – 7.11 (m, 4H), 6.94 (brs, 1H), 6.93 – 6.86 (m, 1H), 4.61 (t, *J* = 5.4 Hz, 1H), 4.45 (d, *J* = 5.8 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 157.39, 140.11, 139.65, 139.32, 130.87, 129.47, 129.33, 128.53, 128.04, 128.00, 127.23, 127.12, 127.11, 64.49, 44.80 ppm. IR (thin film): 3446, 3054, 1656, 1507, 1265, 895, 738, 705, cm^{-1}; HRMS calcd for $C_{27}H_{25}N_2O^+$ 393.1967, observed 393.1963 $[M+H]^+$.



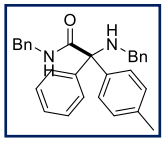
N-benzyl-2-(benzylamino)-2-(2-fluorophenyl)-2-phenylacetamide (3ma)

The reaction was performed following the General Procedures using N-benzyl-1-(2-fluorophenyl)-1-phenylmethanimine (28.9 mg, 0.10 mmol) and benzyl isocyanate (27 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 39.1 mg, 92% yield; General Procedure B: 34 mg, 80% yield) as a light yellow solid. M.p. 140.2 – 142.0 °C. R_f = 0.39 (petroleum ether/EtOAc = 5/1)/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.32 – 7.11 (m, 13H), 7.07 – 7.02 (m, 1H), 7.02 – 6.95 (m, 4H), 6.95 – 6.90 (m, 2H), 4.81 – 4.71 (m, 2H), 4.42 (d, *J* = 9.6 Hz, 1H), 4.40 – 4.34 (m, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 161.17 (d, *J* = 249.5 Hz), 158.47, 139.25, 139.07, 137.81, 130.33 (d, *J* = 3.3Hz), 129.76 (d, *J* = 8.5 Hz), 128.78, 128.55, 128.15, 127.74, 127.27, 127.20, 127.12, 126.78, 124.22 (d, *J* = 3.4 Hz), 115.76 (d, *J* = 21.9 Hz), 57.70, 49.08, 45.07 ppm. ^{19}F NMR (375 MHz, chloroform-d) δ: -113.70 ppm. IR (thin film): 3443, 3055, 1648, 1516, 1265, 778, 733, 704 cm^{-1}; HRMS calcd for $C_{28}H_{26}FN_2O^+$ 425.2029, observed 425.2023 $[M+H]^+$.



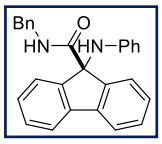
N-benzyl-2-(benzylamino)-2,2-bis(4-chlorophenyl)acetamide (3na)

The reaction was performed following the General Procedures using 1,1-bis(4-chlorophenyl)-N-phenylmethanimine (32.6 mg, 0.10 mmol) and benzyl isocyanate (27 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 38.7 mg, 84% yield; General Procedure B: 40.6 mg, 88% yield) as a light yellow solid. M.p. 140.2 – 142.0 °C. R_f = 0.47 (petroleum ether/EtOAc = 5/1)/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.25 (d, *J* = 8.4 Hz, 4H), 7.23 – 7.15 (m, 6H), 7.13 (d, *J* = 8.6 Hz, 4H), 6.96-6.94 (m, 2H), 6.91 – 6.89 (m, 2H), 6.82 (s, 1H), 4.69 (t, *J* = 5.3 Hz, 1H), 4.49 (s, 2H), 4.34 (d, *J* = 5.3 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.33, 138.98, 138.09, 137.15, 133.67, 130.27, 128.92, 128.82, 128.59, 127.60, 127.27, 127.25, 126.60, 61.94, 48.66, 45.12 ppm. IR (thin film): 3446, 1650, 1492, 1259, 1092, 765, 716, 524 cm^{-1}; HRMS calcd for $C_{28}H_{25}Cl_2N_2O^+$ 475.1344, observed 475.1342 $[M+H]^+$.



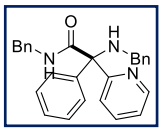
N-benzyl-2-(benzylamino)-2-phenyl-2-(p-tolyl)acetamide (3oa)

The reaction was performed following the General Procedures using N-benzyl-1-phenyl-1-(p-tolyl)methanimine (28.5 mg, 0.10 mmol) and benzyl isocyanate (27 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 37.5 mg, 89% yield; General Procedure B: 36.2 mg, 86% yield) as a white solid. M.p. 136.2 – 137.3 °C. R_f = 0.51 (petroleum ether/EtOAc = 5/1)/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.32 – 7.12 (m, 11H), 7.08 (s, 4H), 7.01 – 6.87 (m, 4H), 6.65 (s, 1H), 4.66 (t, *J* = 5.1 Hz, 1H), 4.56 (d, *J* = 5.5 Hz, 2H), 4.33 (d, *J* = 4.8 Hz, 2H), 2.30 (s, 3H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.63, 140.00, 138.17, 137.38, 136.74, 129.39, 128.95, 128.91, 128.67, 128.60, 128.49, 127.59, 127.27, 127.24 (x2), 127.18, 127.04, 63.08, 49.11, 45.06, 21.21 ppm. IR (thin film): 3432, 3054, 1644, 1265, 896, 777, 737, 705 cm^{-1}; HRMS calcd for $C_{29}H_{29}N_2O^+$ 421.2280, observed 421.2278 $[M+H]^+$.



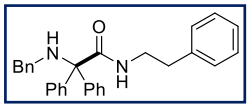
N-benzyl-9-(phenylamino)-9H-fluorene-9-carboxamide (3pa)

The reaction was performed following the General Procedures using N-phenyl-9H-fluoren-9-imine (25.5 mg, 0.10 mmol) and benzyl isocyanate (27 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 34 mg, 87% yield; General Procedure B: 35 mg, 90% yield) as a white solid. M.p. 142.9 – 143.6 °C. R_f = 0.44 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.70 – 7.64 (m, 2H), 7.57 – 7.50 (m, 2H), 7.37 – 7.21 (m, 9H), 7.06 – 6.95 (m, 4H), 6.81 – 6.79 (m, 2H), 4.67 (t, *J* = 5.7 Hz, 1H), 4.52 (d, *J* = 5.8 Hz, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.15, 143.43, 140.80, 139.52, 137.96, 129.53, 129.13, 128.60, 128.19, 127.96, 127.23, 127.17 (x2), 125.78, 119.84, 61.28, 44.94 ppm. IR (thin film): 3442, 1636, 1508, 1265, 779, 737, 704, 526 cm^{-1}; HRMS calcd for $C_{27}H_{23}N_2O^+$ 391.1810, observed 391.1808 $[M+H]^+$.



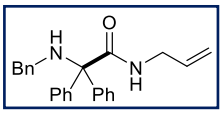
N-benzyl-2-(benzylamino)-2-phenyl-2-(pyridin-2-yl)acetamide (3qa)

The reaction was performed following the General Procedures using N-benzyl-1-phenyl-1-(pyridin-2-yl)methanimine (27.2 mg, 0.10 mmol) and benzyl isocyanate (27 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 35.1 mg, 86% yield; General Procedure B: 35 .9 mg, 88% yield) as a colorless oil. R_f = 0.72 (petroleum ether/EtOAc = 1/1). ^{1}H NMR (400 MHz, chloroform-d) δ 8.55 – 8.40 (m, 1H), 7.62 (td, J = 7.7, 1.8 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.22 – 7.13 (m, 9H), 7.11 – 7.08 (m, 3H), 6.91 – 6.89 (m, 2H), 6.49 (s, 1H), 5.99 (s, 1H), 4.93 – 4.6 (m, 2H), 4.41 – 4.25 (m, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 159.56, 158.83, 149.26, 139.46, 139.20, 138.58, 136.86, 128.67 (x2), 128.59, 128.50, 128.35, 127.53, 127.29, 127.15, 126.79, 124.51, 122.59, 64.29, 50.71, 44.84 ppm. IR (thin film): 3442, 3055, 1637, 1266, 783, 758, 738, 552 cm^{-1}; HRMS calcd for $C_{27}H_{26}N_3O^+$ 408.2076, observed 408.2070 $[M+H]^+$.



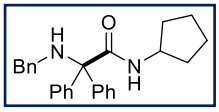
2-(benzylamino)-N-phenethyl-2,2-diphenylacetamide (3ab)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and (2-isocyanatoethyl)benzene (28 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 23.6 mg, 56% yield; General Procedure B: 21.5 mg, 51% yield) as a white solid. M.p. 96.9 – 98.6 °C. R_f = 0.38 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (401 MHz, chloroform-d) δ 7.26 – 7.24 (m, 6H), 7.20 – 7.07 (m, 10H), 6.97 (d, *J* = 6.8 Hz, 2H), 6.88 – 6.77 (m, 2H), 6.68 (s, 1H), 4.45 (s, 2H), 4.33 (s, 1H), 3.43 (q, *J* = 6.0 Hz, 2H), 2.62 (t, *J* = 6.6 Hz, 2H) ppm; ^{13}C NMR (101 MHz, chloroform-d) δ 158.69, 139.87, 139.23, 137.84, 129.00, 128.77, 128.61 (x2), 128.48, 127.57, 127.15, 126.83, 126.29, 63.12, 48.90, 42.13, 36.20 ppm. IR (thin film): 3443, 3054, 1643, 1265, 896, 746, 734, 705 cm^{-1}; HRMS calcd for $C_{29}H_{29}N_2O^+$ 421.2280, observed 421.2281 $[M+H]^+$.



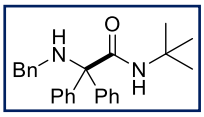
N-allyl-2-(benzylamino)-2,2-diphenylacetamide (3ac)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and 3-isocyanatoprop-1-ene (18 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 31 mg, 87% yield; General Procedure B: 24.6 mg, 69% yield) as a white solid. M.p. 72.5 – 73.4 °C. R_f = 0.34 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.34 – 7.25 (m, 6H), 7.24 – 7.20 (m, 4H), 7.17 – 7.15 (m, 3H), 6.97 – 6.90 (m, 2H), 6.75 (s, 1H), 5.67 (ddt, *J* = 16.9, 10.4, 5.3 Hz, 1H), 4.91 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.80 (dd, *J* = 17.3, 1.4 Hz, 1H), 4.56 (s, 2H), 4.38 (t, *J* = 5.2 Hz, 1H), 3.82 – 3.75 (m, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.56, 139.85, 137.94, 135.26, 129.00, 128.64, 128.55, 127.62, 127.27, 126.97, 114.99, 63.20, 49.04, 43.36 ppm. IR (thin film): 3439, 3054, 2986, 1640, 1265, 776, 734, 705 cm^{-1}; HRMS calcd for $C_{24}H_{25}N_2O^+$ 357.1967, observed 357.1960 $[M+H]^+$.



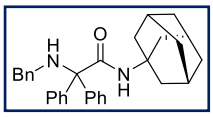
2-(benzylamino)-N-cyclopentyl-2,2-diphenylacetamide (3ad)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and isocyanatocyclopentane (23 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 29.6 mg, 77% yield; General Procedure B: 21.5 mg, 56% yield) as a light yellow solid. M.p. 132.0 – 133.6 °C. R_f = 0.53 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.34 – 7.26 (m, 6H) 7.24 – 7.15 (m, 7H), 7.01 – 6.97 (m, 2H), 6.63 (s, 1H), 4.53 (s, 2H), 4.22 (d, *J* = 7.1 Hz, 1H), 4.11 – 4.03 (m, 1H), 1.75 (m, 2H), 1.48 – 1.35 (m, 2H), 1.33 – 1.16 (m, 2H), 1.04 (m, 2H)ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 158.35, 140.02, 138.41, 128.97, 128.71, 128.65, 127.64, 127.38, 127.28, 63.01, 52.68, 49.28, 33.38, 23.38 ppm. IR (thin film): 3442, 1639, 1516, 1265, 780, 734, 703, 549, cm^{-1}; HRMS calcd for $C_{26}H_{29}N_2O$+ 385.2280, observed 385.2282 $[M+H]^+$.



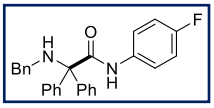
2-(benzylamino)-N-(tert-butyl)-2,2-diphenylacetamide (3ae)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and 2-isocyanato-2-methylpropane (23 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 24.2 mg, 65% yield; General Procedure B: 23.1 mg, 62% yield) as a light yellow solid. M.p. 135.0 – 136.3 °C. R_f = 0.34 (petroleum ether/EtOAc = 20/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.34 – 7.27 (m, 5H), 7.25 – 7.17 (m, 8H), 7.04 – 6.96 (m, 2H), 6.60 (s, 1H), 4.50 (s, 2H), 4.22 (s, 1H), 1.10 (s, 9H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 157.79, 140.22, 138.55, 129.00, 128.71, 128.64, 127.60, 127.40 (x2), 62.75, 50.95, 49.36, 29.26 ppm. IR (thin film): 3440, 3055, 1643, 1265, 896, 746, 733, 706 cm^{-1}; HRMS calcd for $C_{25}H_{29}N_2O^+$ 373.2280, observed 373.2279 $[M+H]^+$.



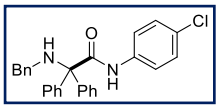
N-(adamantan-1-yl)-2-(benzylamino)-2,2-diphenylacetamide (3af)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and 1-Isocyanatoadamantane (35.4 mg, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 36.9 mg, 82% yield; General Procedure B: 18 mg, 40% yield) as a white solid. M.p. 173.1 – 175.2 °C. R_f = 0.40 (petroleum ether/EtOAc = 20/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.34 – 7.24 (m, 6H), 7.24 – 7.17 (m, 7H), 7.06 – 6.94 (m, 2H), 6.58 (s, 1H), 4.50 (s, 2H), 4.13 (s, 1H), 1.95 (br, 3H), 1.73 – 1.68 (m, 6H), 1.58 (d, *J* = 13.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 157.38, 140.18, 138.51, 128.96, 128.60, 128.52, 127.49, 127.35, 127.24, 62.78, 51.43, 49.36, 42.13, 36.48, 29.58 ppm. IR (thin film): 3435, 3054, 1639, 1265, 896, 776, 737, 705 cm^{-1}; HRMS calcd for $C_{31}H_{35}N_2O^+$ 451.2749, observed 451.2746 $[M+H]^+$.



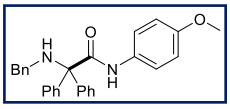
2-(benzylamino)-N-(4-fluorophenyl)-2,2-diphenylacetamide (3ag)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and 1-fluoro-4-isocyanatobenzene (23 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 29.1 mg, 71% yield; General Procedure B: 31.6 mg, 77% yield) as a white solid. M.p. 163.0 – 164.1 °C. R_f = 0.53 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.38 – 7.29 (m, 6H), 7.27 – 7.23 (m, 7H), 7.10 – 7.04 (m, 2H), 6.98 – 6.91 (m, 2H), 6.98 – 6.91 (m, 2H), 6.66 (s, 1H), 6.26 (s, 1H), 4.67 (s, 2H) ppm; ^{13}C NMR (101 MHz, chloroform-d) δ 158.21 (d, *J* = 243.04 Hz) 155.59, 138.66, 136.96, 134.22 (d, *J* = 2.0 Hz), 128.28 (x2), 128.25, 127.36, 127.15, 126.85, 120.92 (d, *J* = 7.8Hz), 114.72 (d, *J* = 22.5 Hz), 62.76, 48.98 ppm. ^{19}F NMR (375 MHz, chloroform-d) δ – 120.04 ppm. IR (thin film): 3421, 3054, 1633, 1509, 1265, 777, 737, 705 cm^{-1}; HRMS calcd for $C_{27}H_{24}FN_2O^+$ 411.1873, observed 411.1875 $[M+H]^+$.



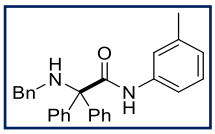
2-(benzylamino)-N-(4-chlorophenyl)-2,2-diphenylacetamide (3ah)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and 1-chloro-4-isocyanatobenzene (30.7 mg, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 17.9 mg, 42% yield; General Procedure B: 19.6 mg, 46% yield) as a white solid. M.p. 158.6 – 159.5 °C. R_f = 0.30 (petroleum ether/EtOAc = 20/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.39 – 7.30 (m, 6H), 7.30 – 7.20 (m, 7H), 7.15 – 7.09 (m, 2H), 7.09 – 7.04 (m, 2H), 6.98 – 6.90 (m, 2H), 6.64 (s, 1H), 6.30 (s, 1H), 4.67 (s, 2H) ppm; ^{13}C NMR (101 MHz, chloroform-d) δ 155.92, 139.20, 137.54, 137.50, 128.97, 128.93, 128.90, 128.76, 128.06, 127.94, 127.86, 127.52, 120.84, 63.44, 49.67 ppm. IR (thin film): 3420, 1632, 1524, 1265, 780, 738, 705, 549 cm^{-1}; HRMS calcd for $C_{27}H_{24}ClN_2O^+$ 427.1577, observed 427.1578 $[M+H]^+$.



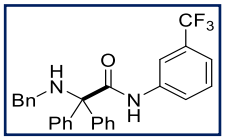
2-(benzylamino)-N-(4-methoxyphenyl)-2,2-diphenylacetamide (3ai)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and 1-isocyanato-4-methoxybenzene (26 µL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 µL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 µL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 38 mg, 90% yield; General Procedure B: 40.5 mg, 96% yield) as a white solid. M.p. 121.2 – 123.1 °C. R_f = 0.38 (petroleum ether/EtOAc = 5/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.36 – 7.30 (m, 5H), 7.29 – 7.18 (m, 8H), 7.09 – 7.03 (m, 2H), 6.97 – 6.87 (m, 2H), 6.77 – 6.70 (m, 2H), 6.68 (s, 1H), 6.17 (s, 1H), 4.66 (s, 2H), 3.72 (s, 3H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 156.48, 155.77, 139.49, 137.78, 132.03, 128.98, 128.87, 128.82, 127.90, 127.67, 127.49, 121.83, 114.05, 63.33, 55.59, 49.56 ppm. IR (thin film): 3415, 3055, 1659, 1513, 1265, 746, 735, 705 cm^{-1}; HRMS calcd for $C_{28}H_{27}N_2O_2^+$ 423.2073, observed 423.2067 $[M+H]^+$.



2-(benzylamino)-2,2-diphenyl-N-(m-tolyl)acetamide (3aj)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and 1-isocyanato-3-methylbenzene (26 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 37.8 mg, 93% yield; General Procedure B: 27.6 mg, 68% yield) as a white solid. M.p. 171.2 – 172.3 °C. R_f = 0.59 (petroleum ether/EtOAc = 10/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.38 – 7.32 (m, 6H), 7.30 – 7.23 (m, 7H), 7.09 – 7.02 (m, 4H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.73 – 6.66 (m, 2H), 6.31 (s, 1H), 4.68 (s, 2H), 2.25 (s, 3H) ppm; ^{13}C NMR (101 MHz, chloroform-d) δ 156.18, 139.43, 138.87, 138.75, 137.73, 128.98, 128.91, 128.86, 128.61, 127.95, 127.72, 127.50, 123.91, 120.46, 116.75, 63.44, 49.64, 21.56 ppm. IR (thin film): 3423, 3054, 1662, 1265, 745, 733, 705, 517 cm^{-1}; HRMS calcd for $C_{28}H_{27}N_2O^+$ 407.2123, observed 407.2118 $[M+H]^+$.

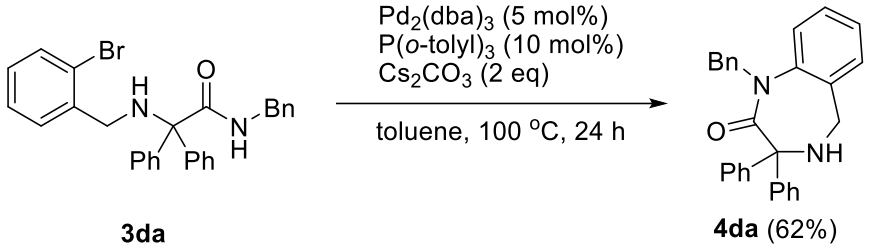


2-(benzylamino)-2,2-diphenyl-N-(3-(trifluoromethyl)phenyl) acetamide (3ak)

The reaction was performed following the General Procedures using N-benzyl-1,1-diphenylmethanimine (27.1 mg, 0.10 mmol) and 1-isocyanato-3-(trifluoromethyl)benzene (27.5 μL, 0.2 mmol) with catalyst **Ir-8** (1 mg, 1 mol%) and Cy_2NMe (42.8 μL, 0.2 mmol) (General Procedure A) or with catalyst **perylene** (0.13 mg, 0.5 mol%) and DIPEA (33 μL, 0.2 mmol) (General Procedure B). The crude product was purified by chromatography on silica gel (eluted with petroleum ether/EtOAc = 10/1) to give the desired product (General Procedure A: 26.7 mg, 58% yield; General Procedure B: 23 mg, 50% yield) as a white solid. M.p. 160.7 – 163.3 °C. R_f = 0.30 (petroleum ether/EtOAc = 20/1). ^{1}H NMR (400 MHz, chloroform-d) δ 7.39 – 7.32 (m, 7H), 7.28 – 7.24 (m, 8H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.09 (m, 3H), 6.63 (s, 1H), 6.43 (s, 1H), 4.69 (s, 2H) ppm; ^{13}C NMR (101 MHz, chloroform-d) δ 155.83, 139.48, 139.07, 137.38, 130.88 (q, *J* = 32.32 Hz), 129.23, 129.03, 128.99, 128.88, 128.15, 127.95, 127.58, 123.97 (q, *J* = 275.73 Hz), 122.60, 119.56, 116.30 (q, *J* = 3.8 Hz), 63.51, 49.77 ppm. ^{19}F NMR (375 MHz, chloroform-d) δ – 62.64 ppm. IR (thin

film): 3420, 3055, 1632, 1268, 1265, 750, 730, 705 cm^{-1}; HRMS calcd for $C_{28}H_{24}F_3N_2O^+$ 461.1841, observed 461.1836 $[M+H]^+$.

Procedure for Sythesis of Compound 4da

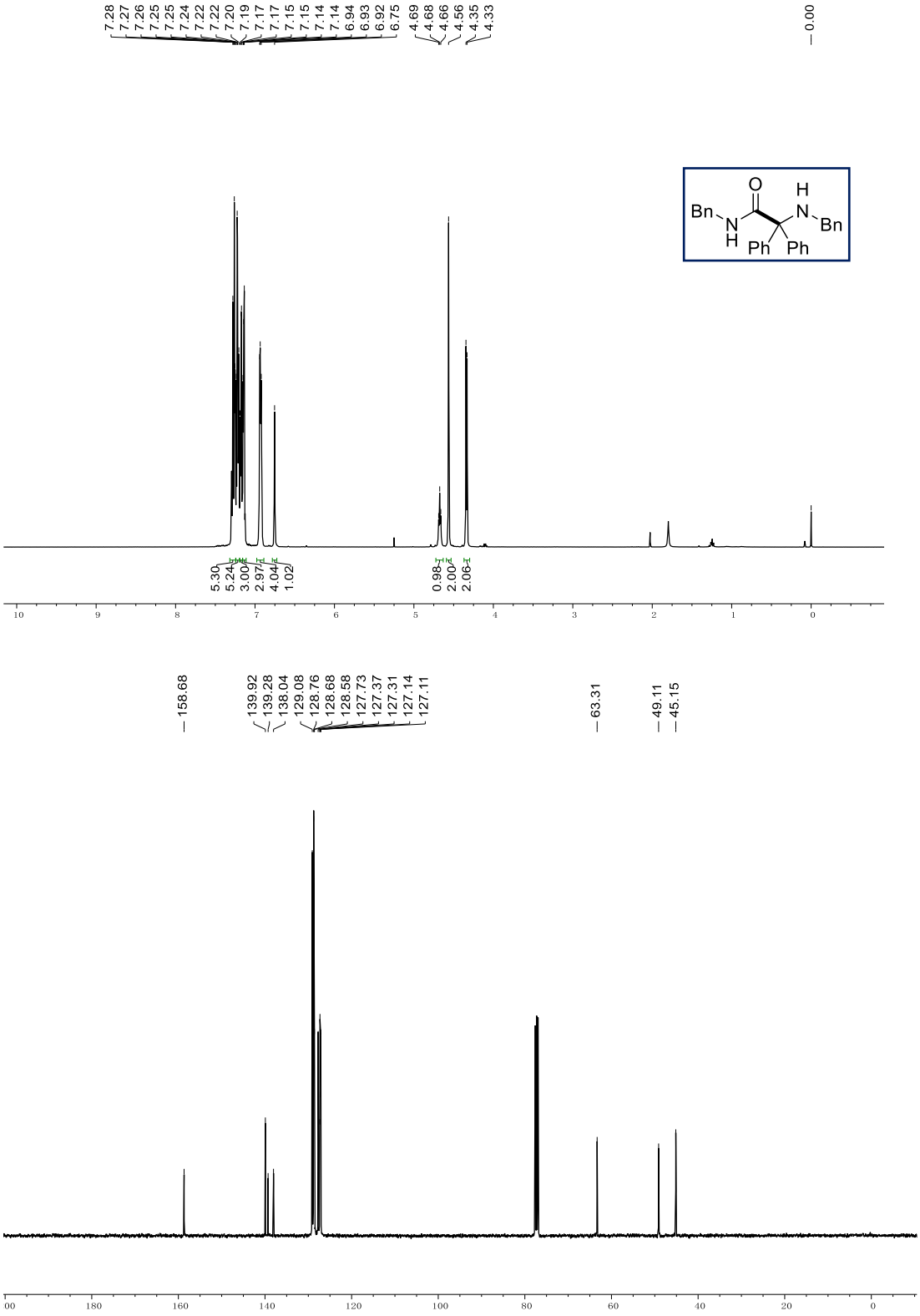


3da **4da** (62%)

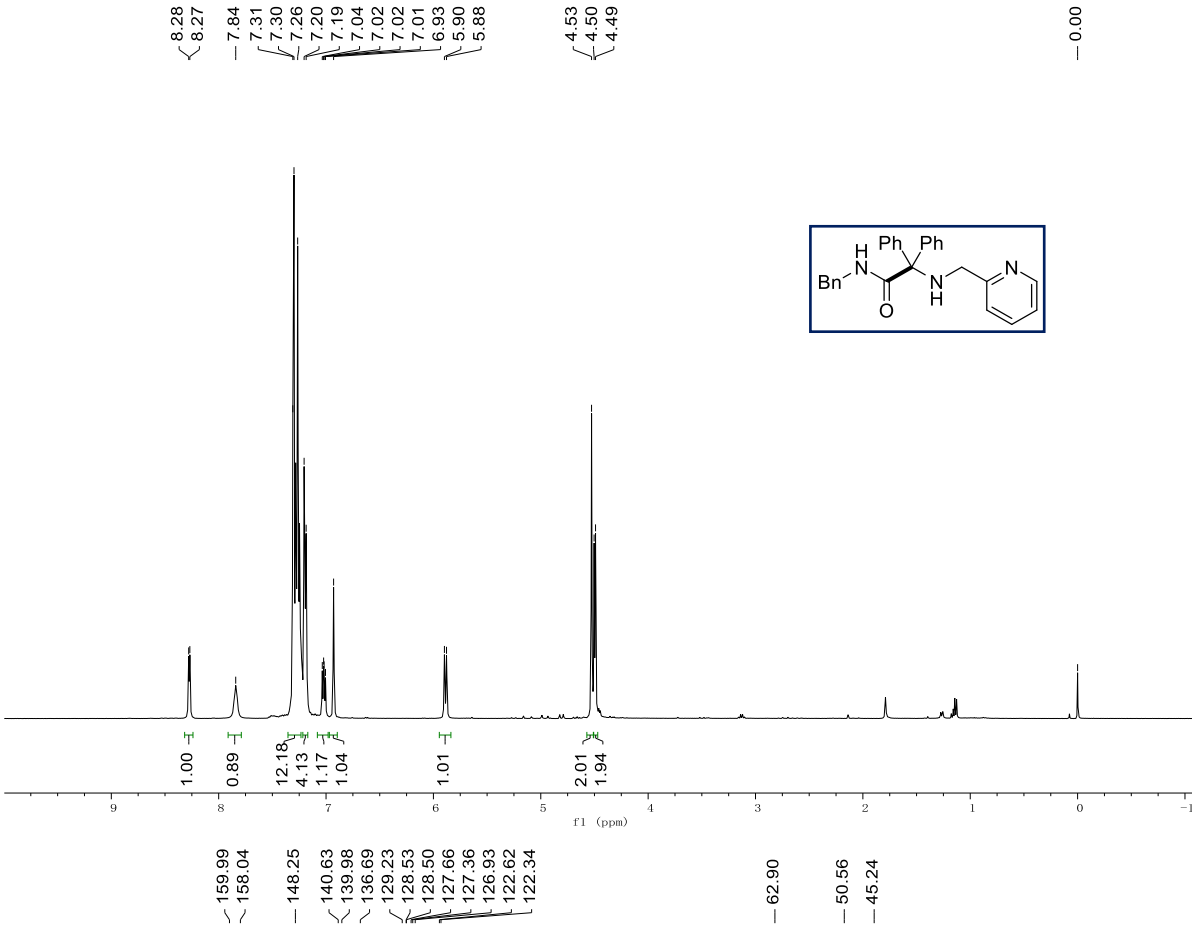
Compound **3da** (48.5 mg, 0.1 mmol, 1 equiv), palladium catalyst $Pd_2(dba)_3$ (4.6 mg, 5 µmol, 5 mol %), phosphorus ligand (3 mg, 10 µmol, 10 mol %), and cesium carbonate (65.2 mg, 0.2 mmol, 2 equiv) were dissolved in toluene (2 mL) under nitrogen atmosphere in an oven-dried 15 mL Schlenk tube. The mixture was heated using a preheated oil bath (100°C) under stirring. The reaction was monitored by thin layer chromatography. After completed, the reaction was cooled to room temperature, diluted with dichloromethane (1 mL), and filtered through a pad of celite. The filtrate was collected and the volatile materials were removed under reduced pressure. The crude residue was purified by flash chromatography on silica gel using ethyl acetate and petroleum ether as eluents, to give the desired product as white solid (25.1 mg, 62% yield). ^{1}H NMR (400 MHz, chloroform-d) δ 7.41 – 7.16 (m, 16H), 7.14 – 7.06 (m, 1H), 6.98 (d, *J* = 6.5 Hz, 1H), 6.95 – 6.88 (m, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 5.18 (s, 2H), 4.13 (s, 2H) ppm. ^{13}C NMR (101 MHz, chloroform-d) δ 154.98, 138.17, 138.03, 137.12, 128.24, 128.11, 127.96, 127.59, 126.95, 126.28, 125.76, 125.07, 121.47, 119.85, 113.31, 60.77, 46.68, 44.03 ppm. IR (thin film): 3435, 3054, 1640, 1265, 895, 737, 705 cm^{-1}; HRMS calcd for $C_{28}H_{25}N_2O^+$ 405.1967, observed 405.1966 $[M+H]^+$.

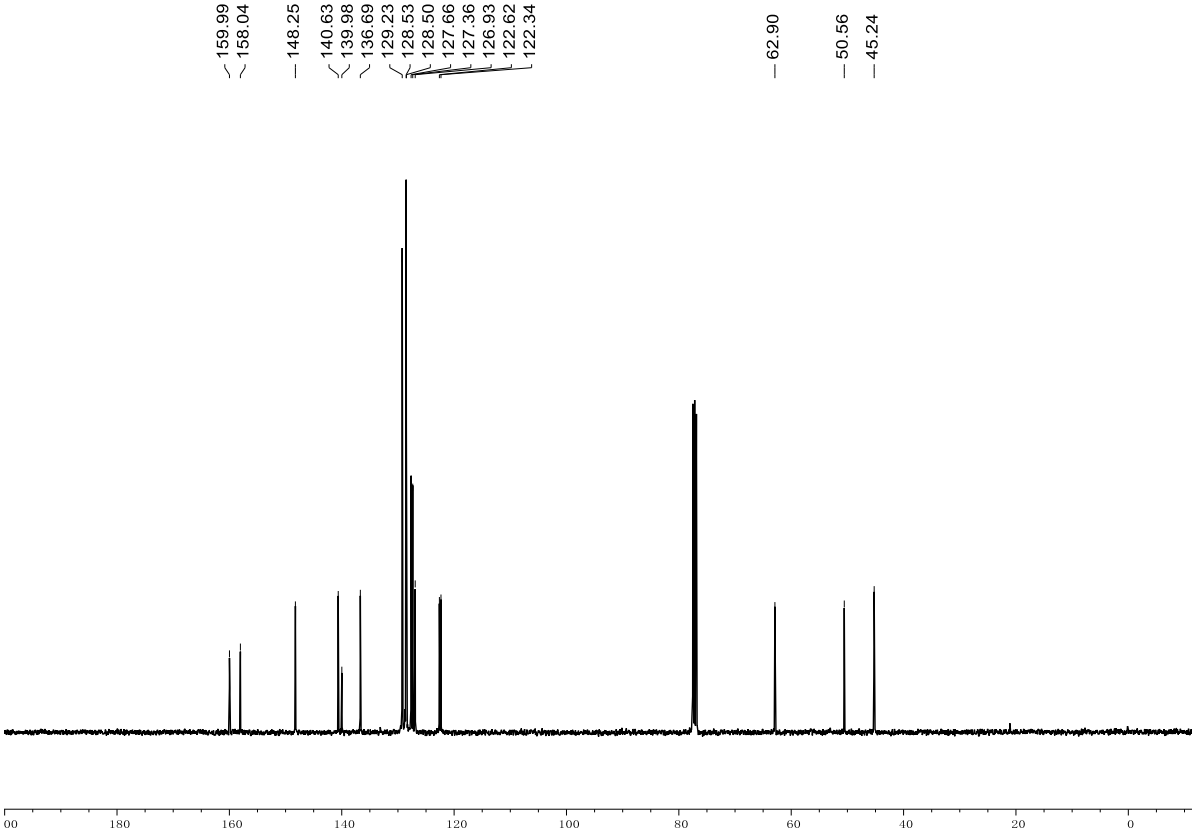
NMR spectra

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3aa** in $CDCl_3$

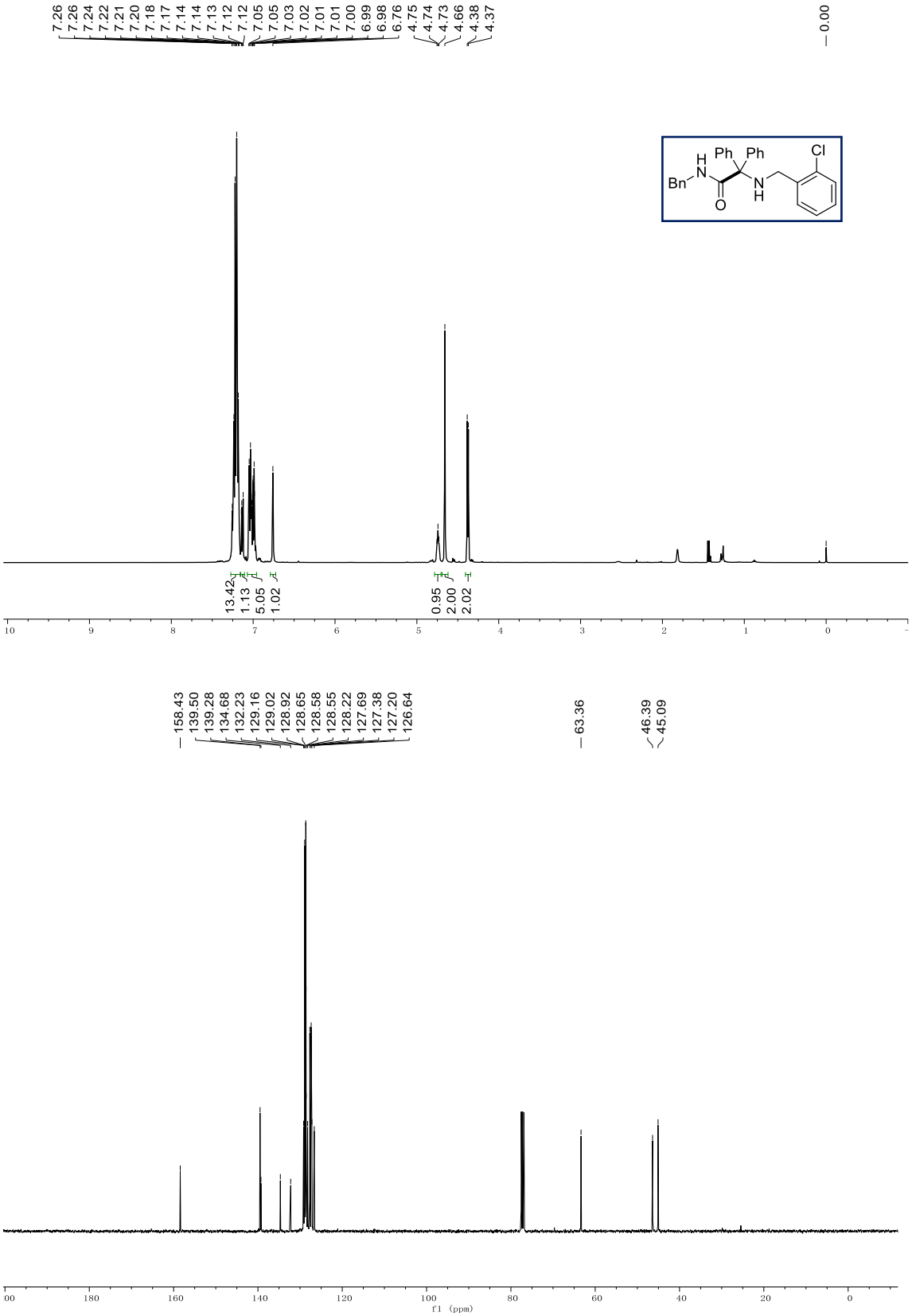


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ba** in $CDCl_3$

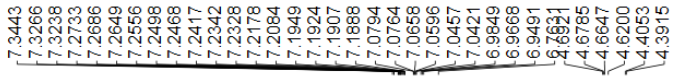


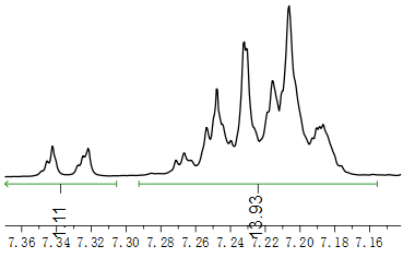


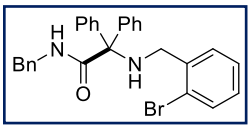
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ca** in $CDCl_3$

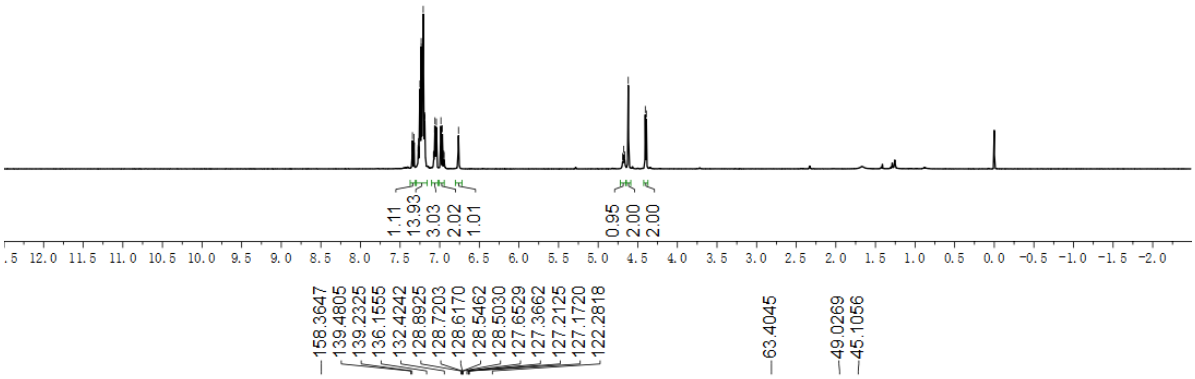


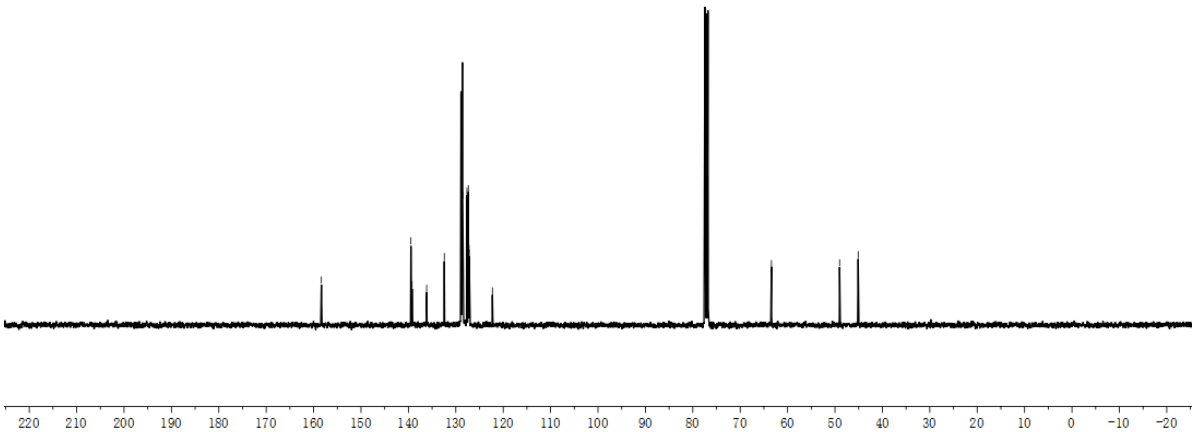
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3da** in $CDCl_3$



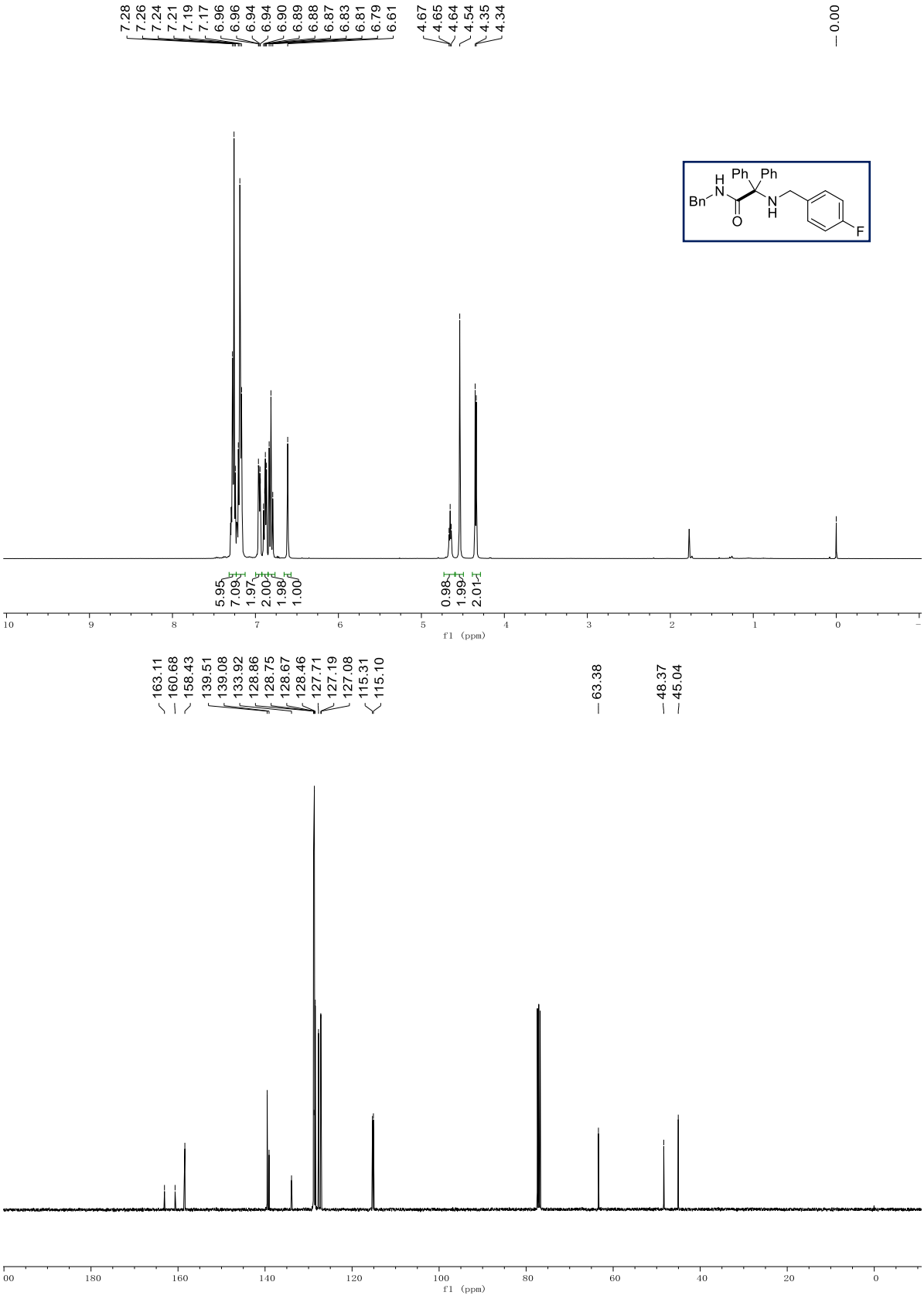


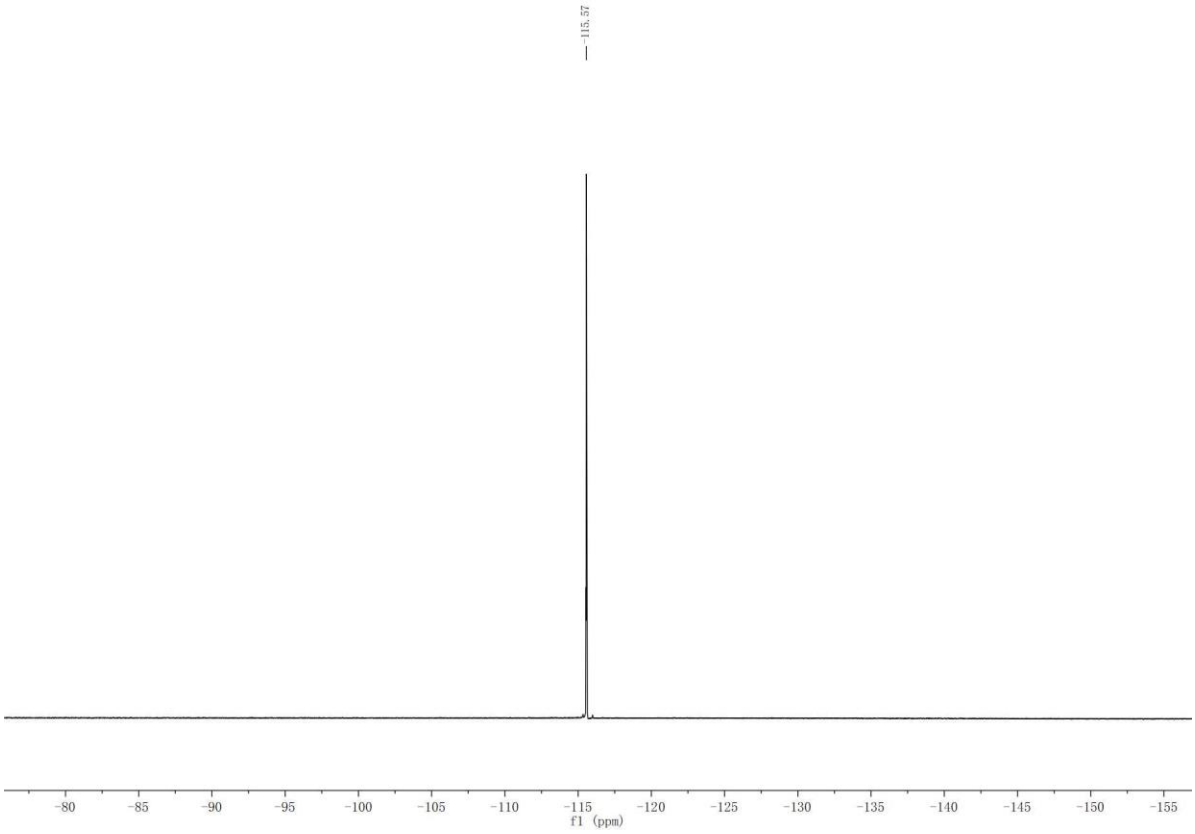




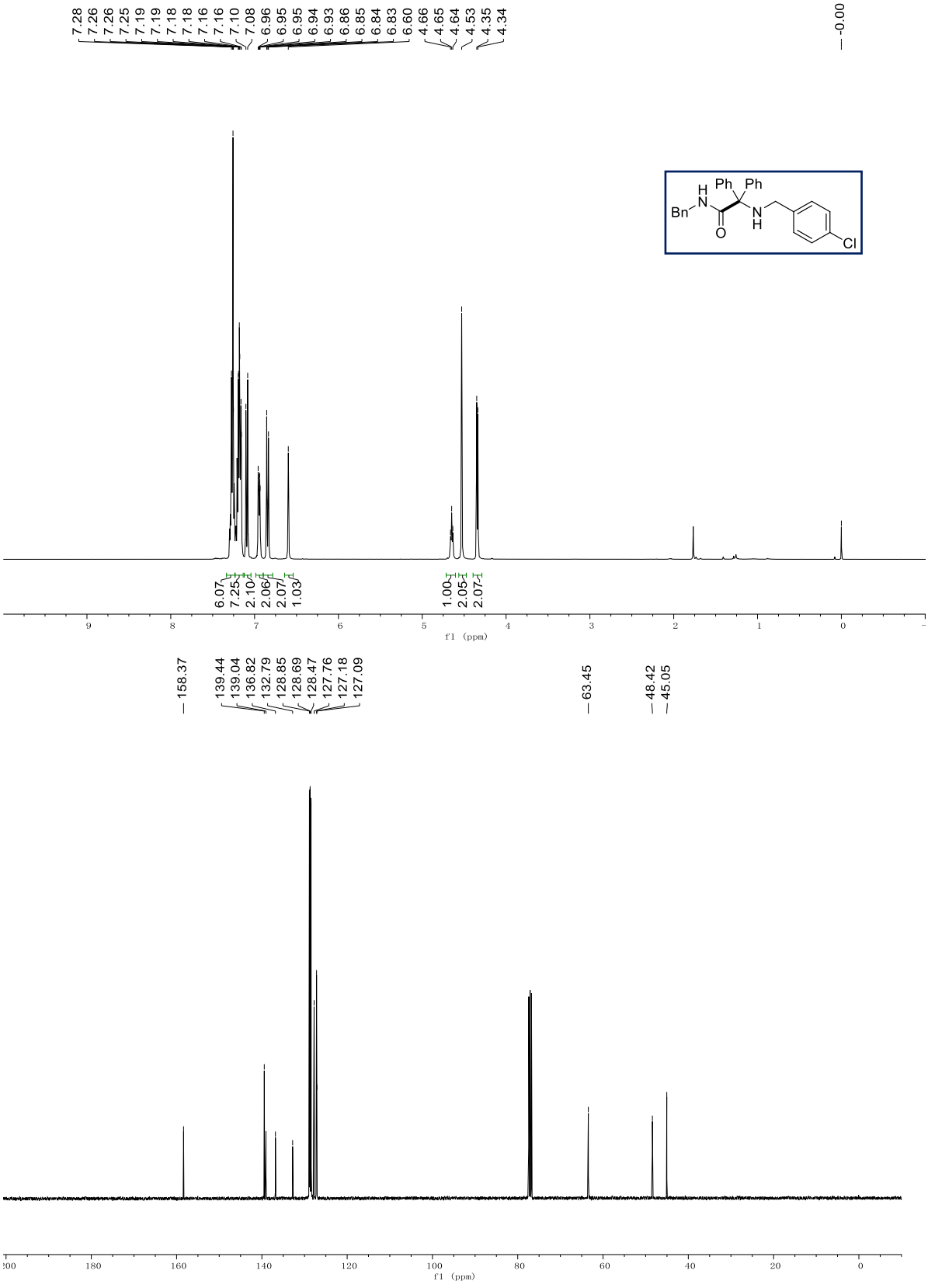


^{1}H,$^{13}C\{^{1}H\}$ and ^{19}F NMR spectra of compound **3ea** in $CDCl_3$

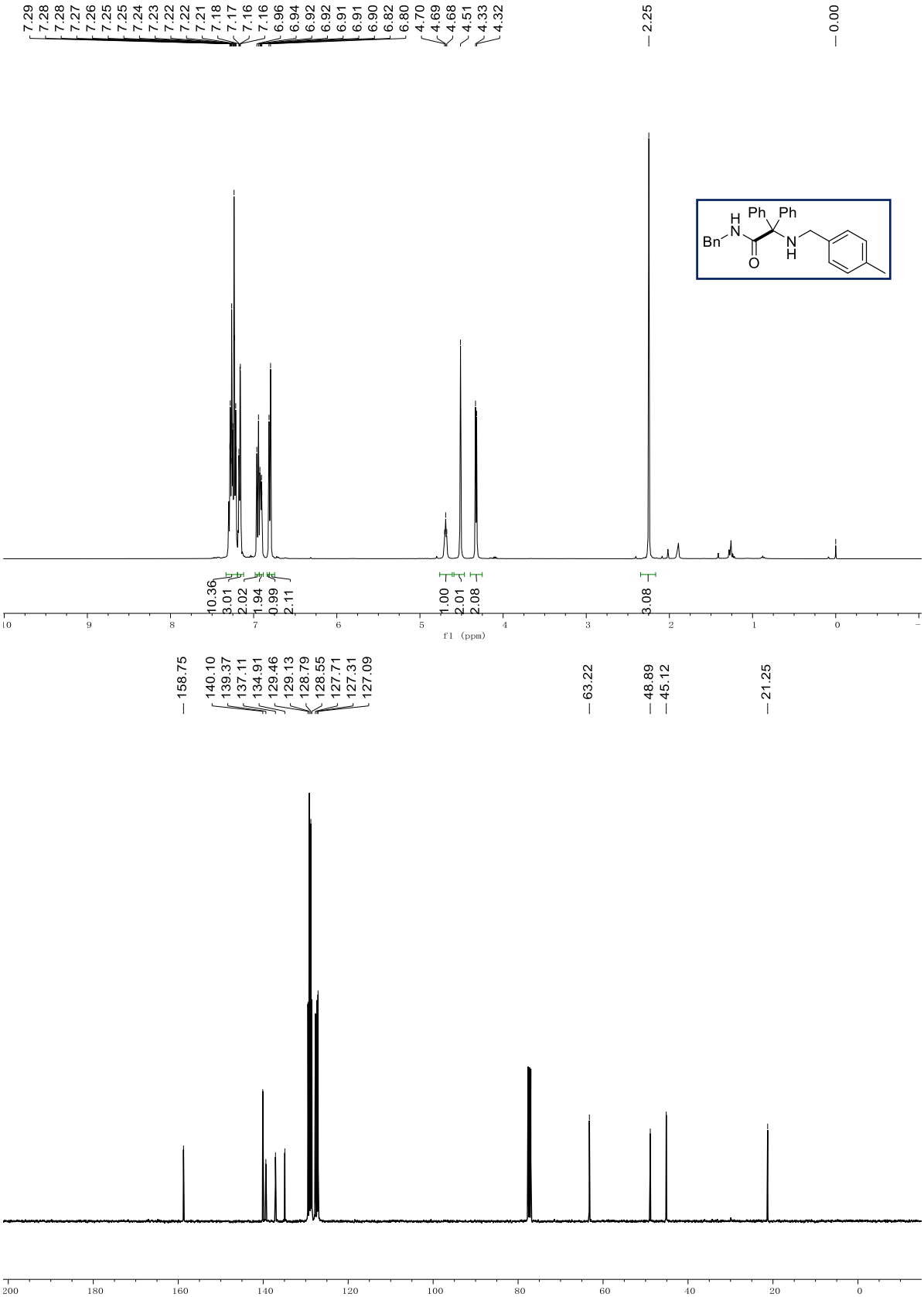



-115.57
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

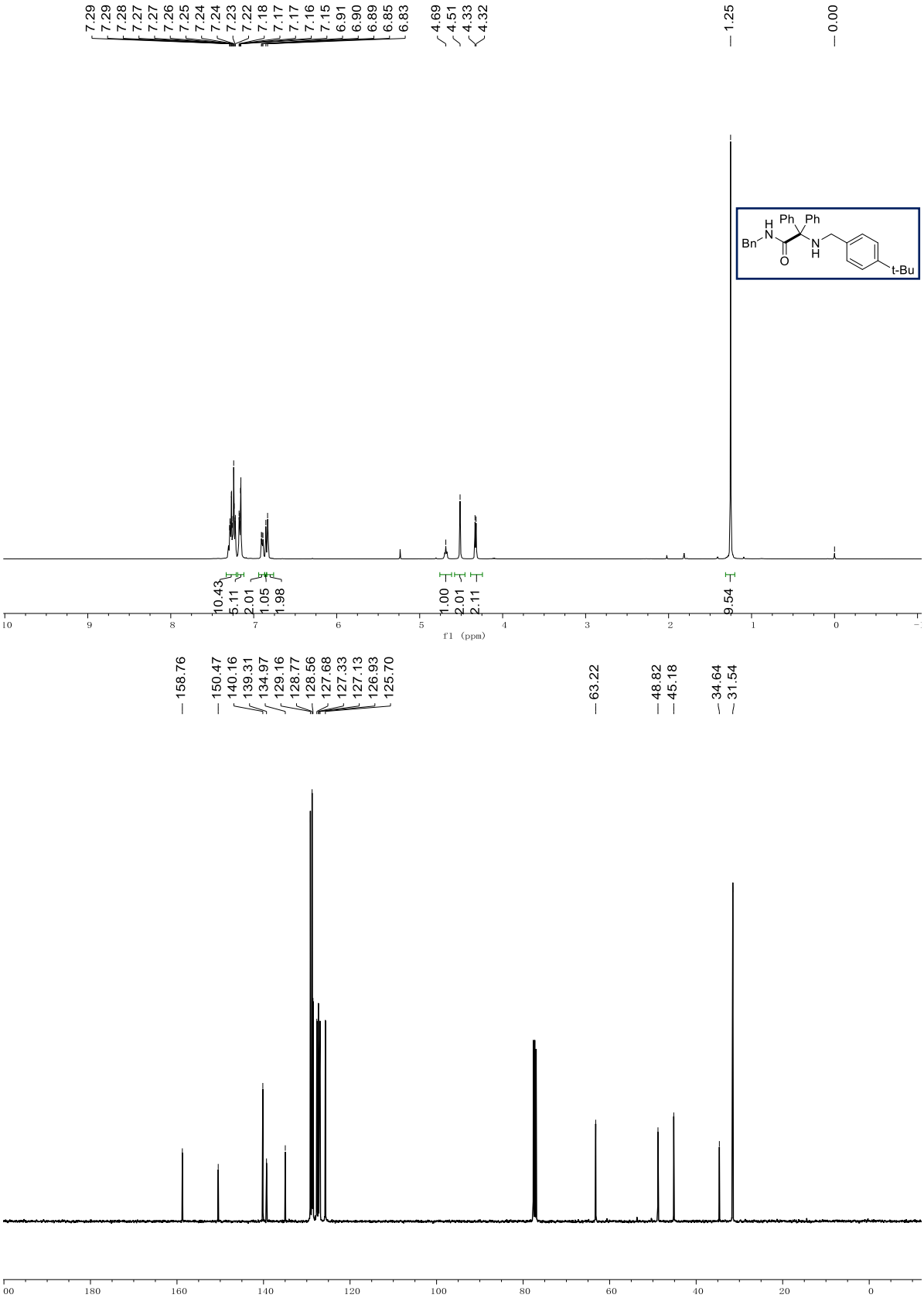
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3fa** in $CDCl_3$



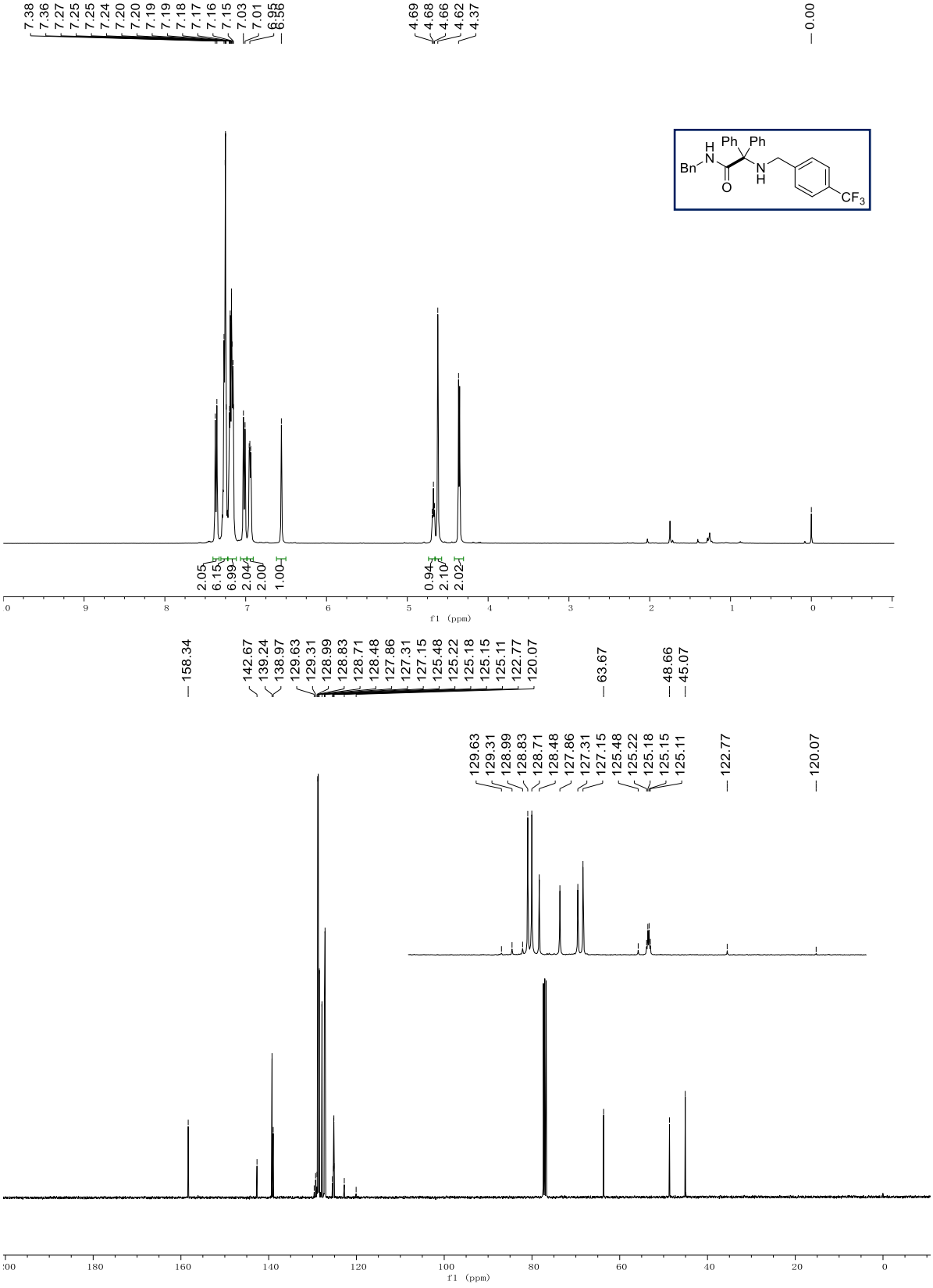
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ga** in $CDCl_3$

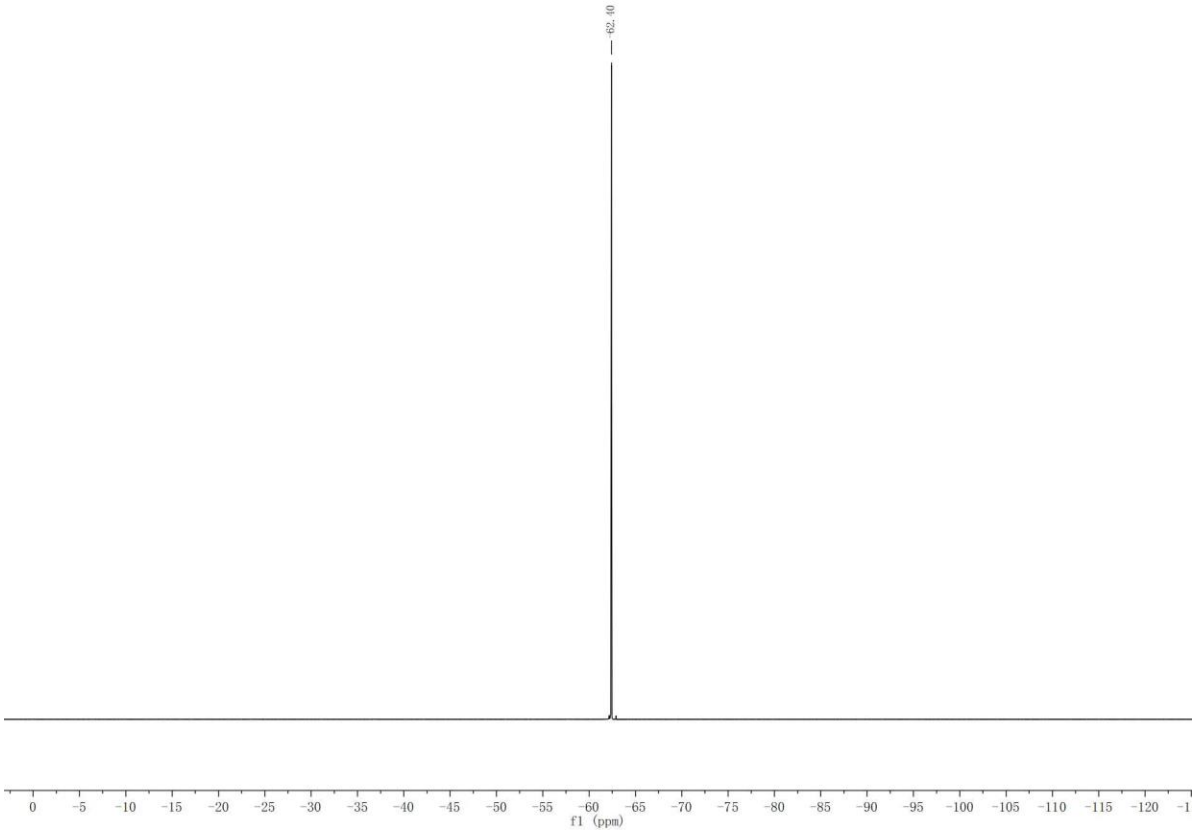


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ha** in $CDCl_3$

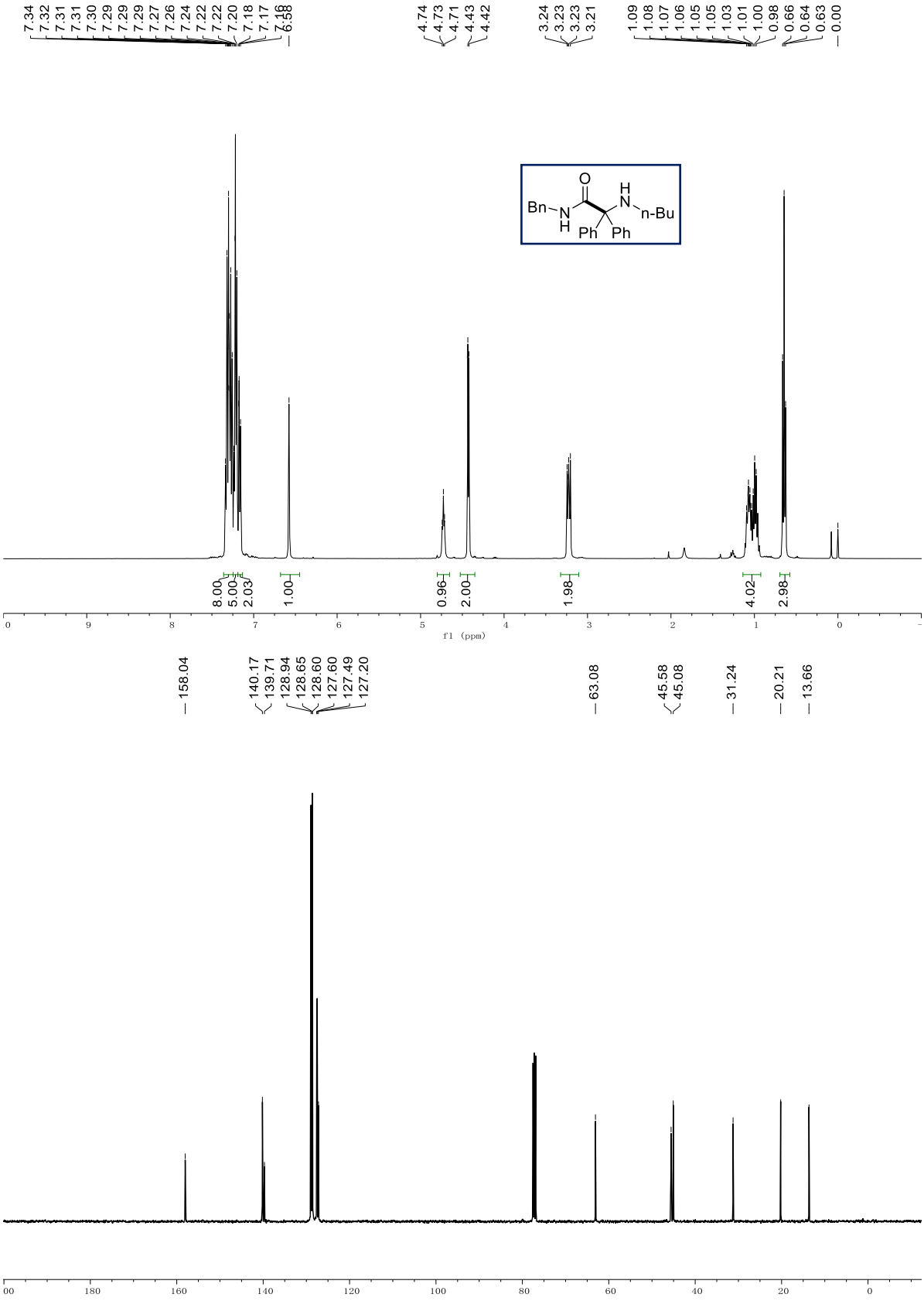


^{1}H ， $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra of compound **3ia** in $CDCl_3$

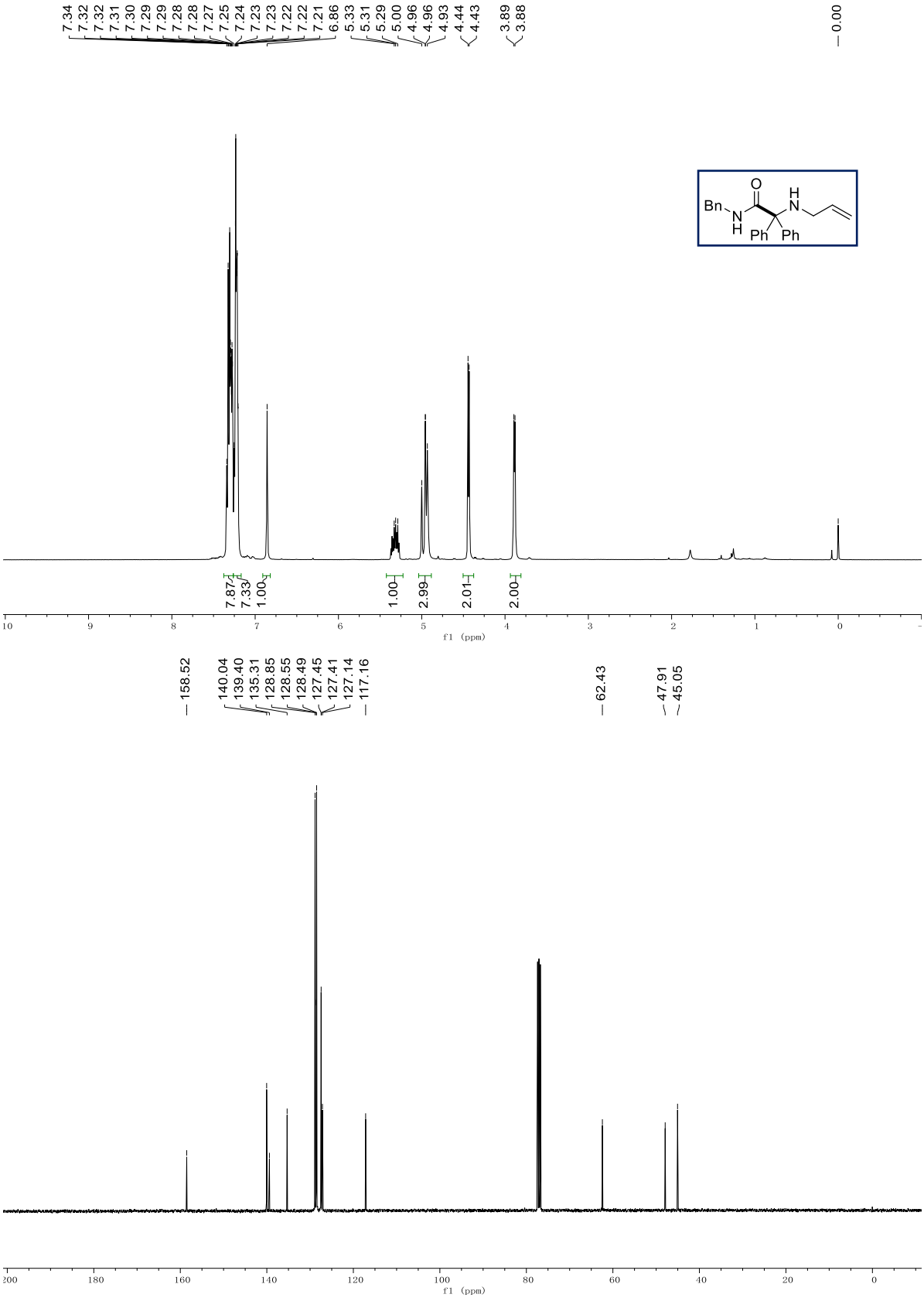



-62.40
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -1
f1 (ppm)

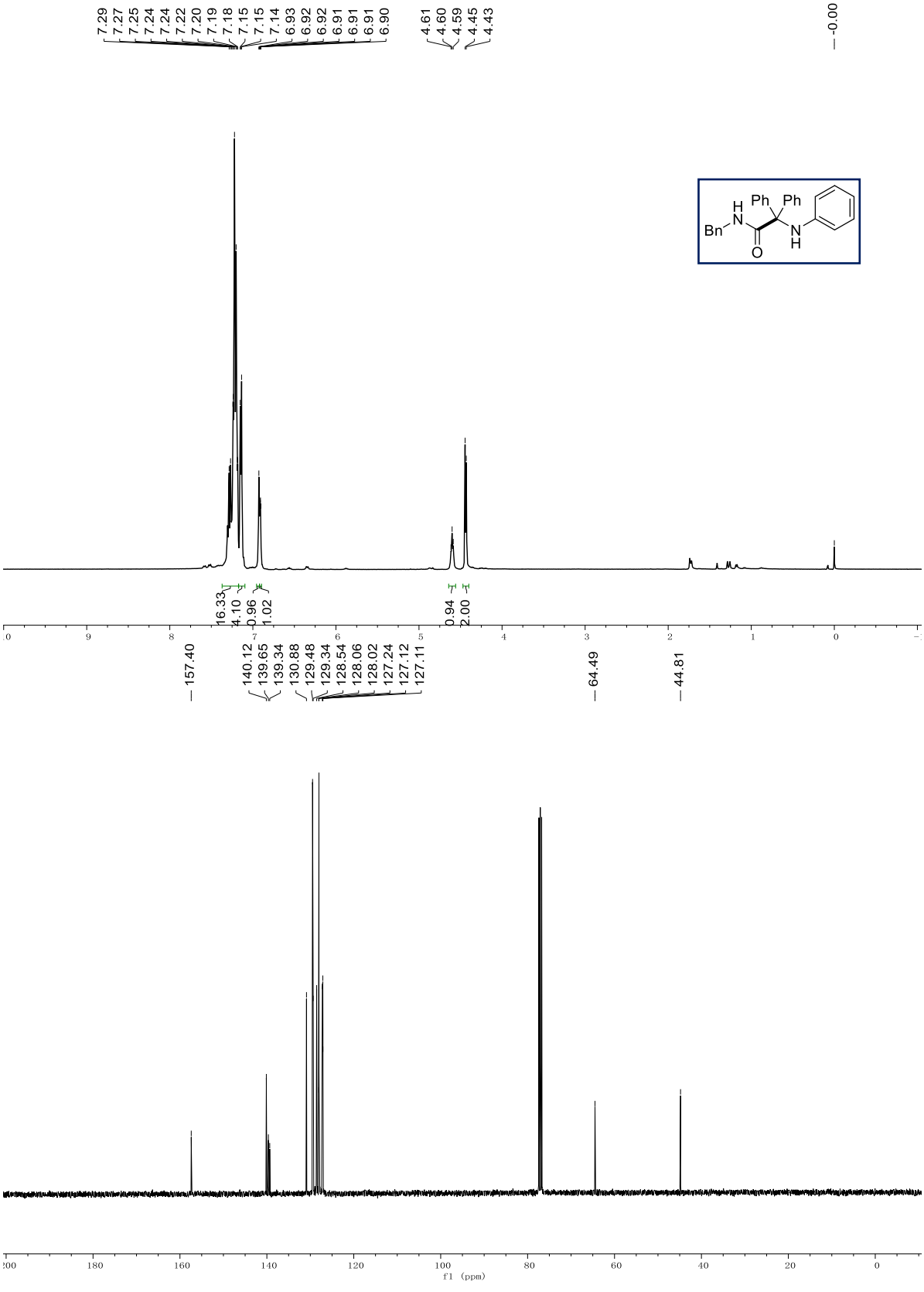
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ja** in $CDCl_3$



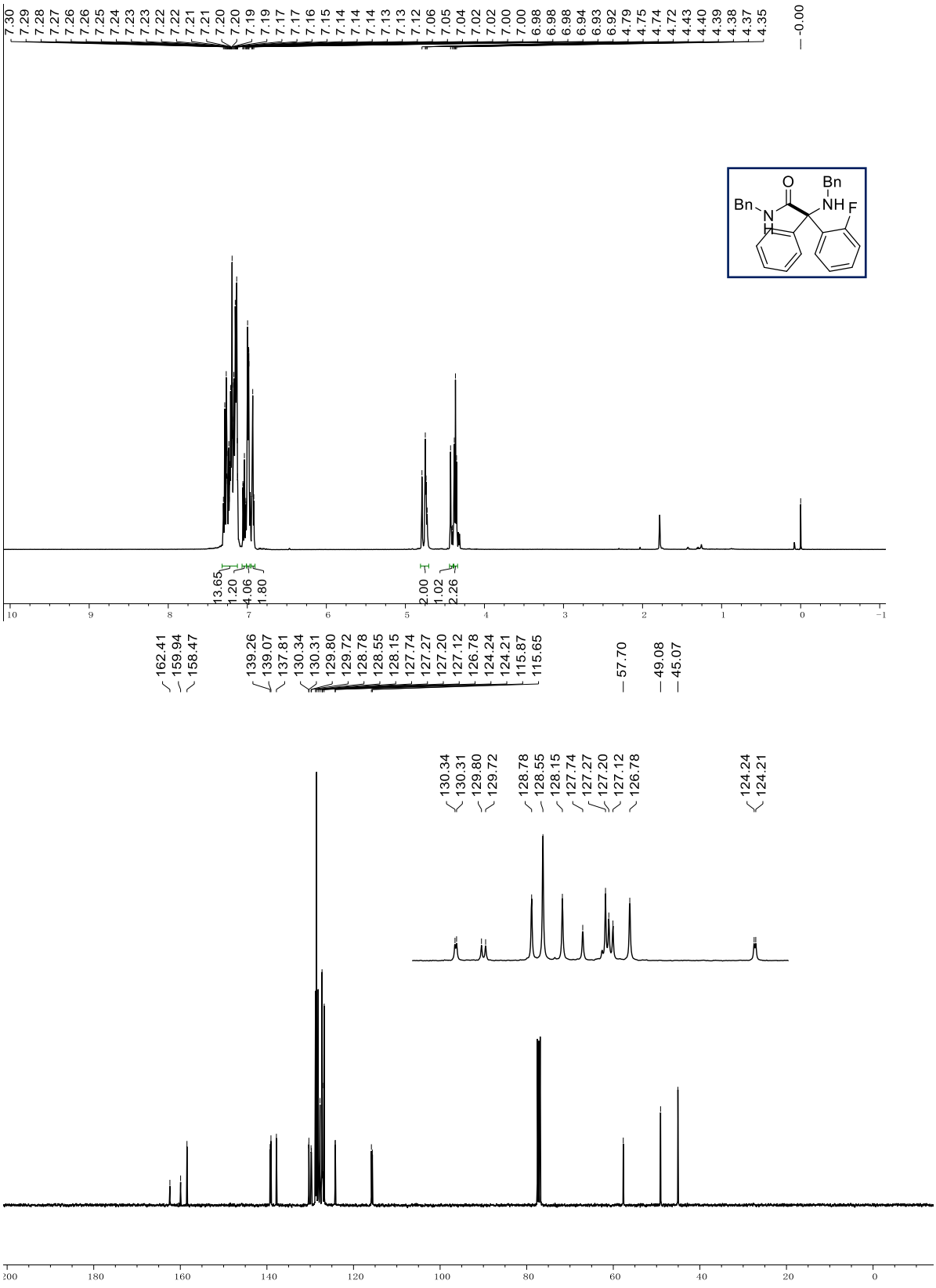
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ka** in $CDCl_3$

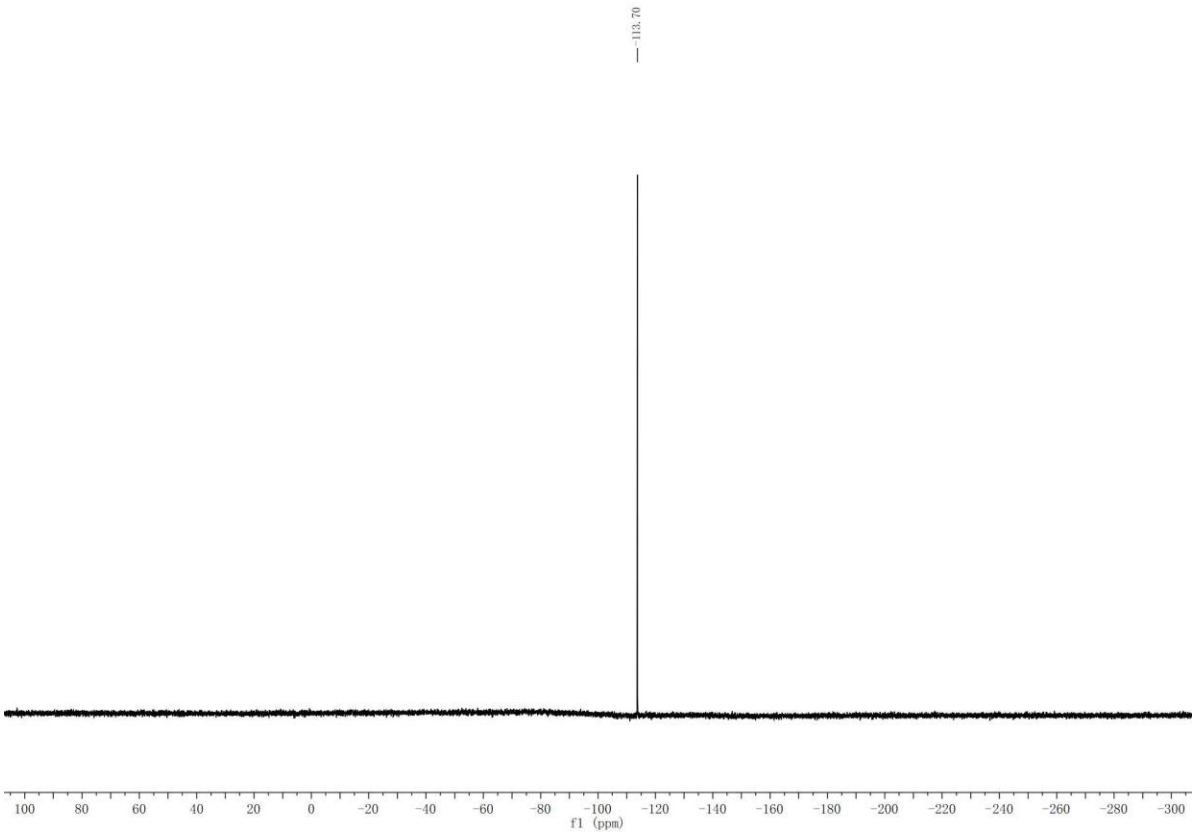


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3la** in $CDCl_3$

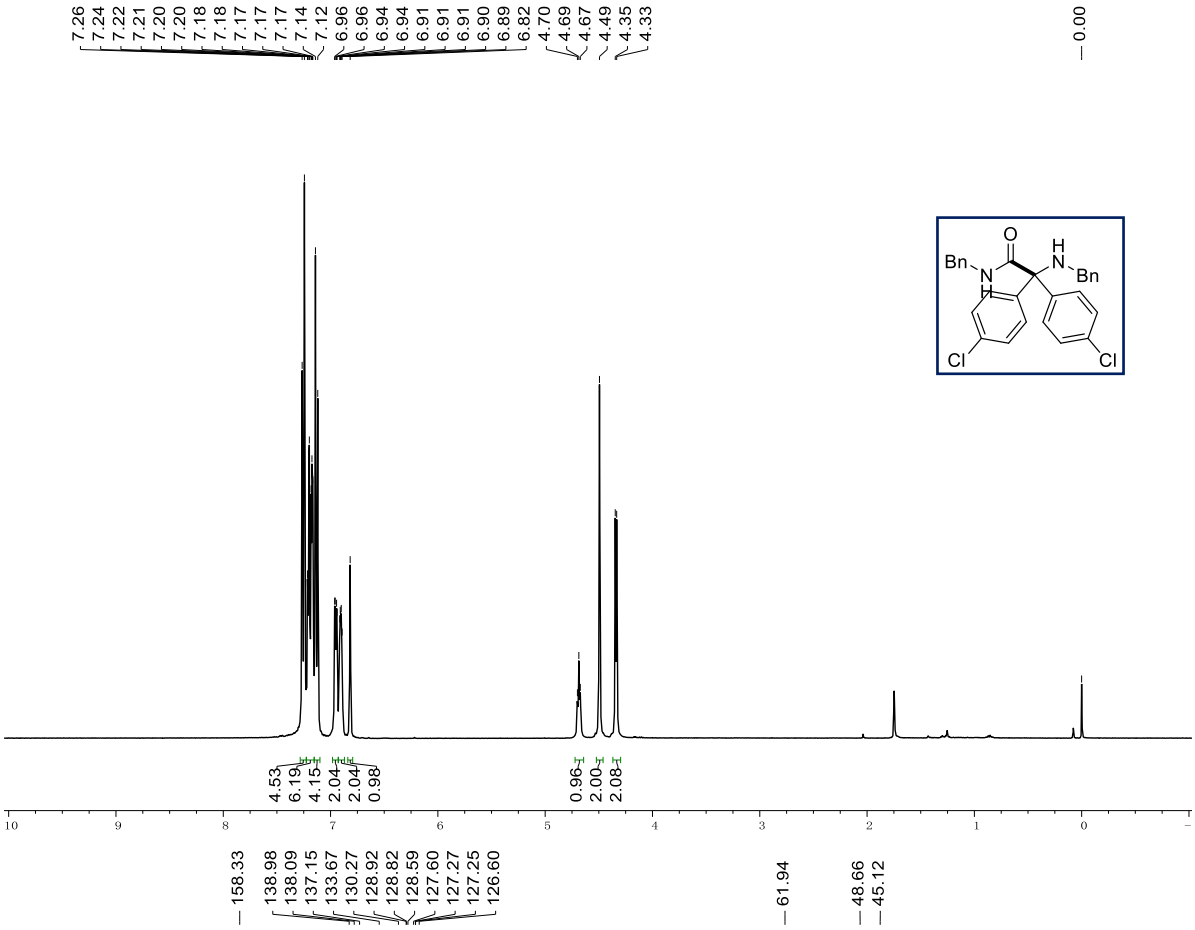


^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra of compound **3ma** in $CDCl_3$

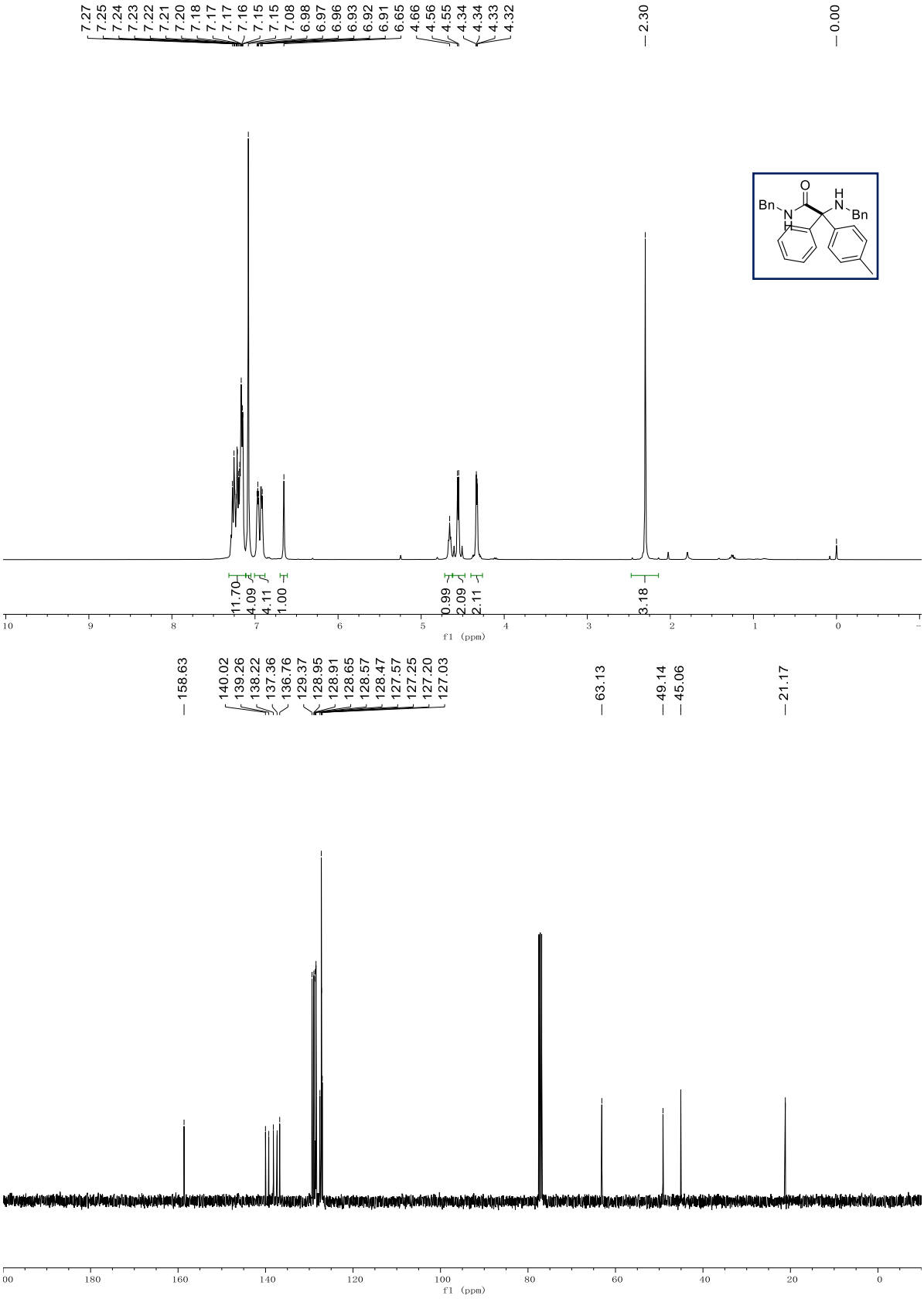



-113.70
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

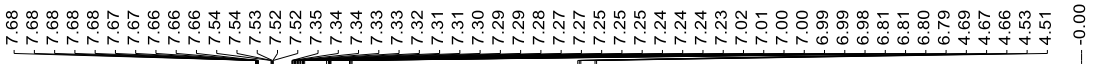
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3na** in $CDCl_3$

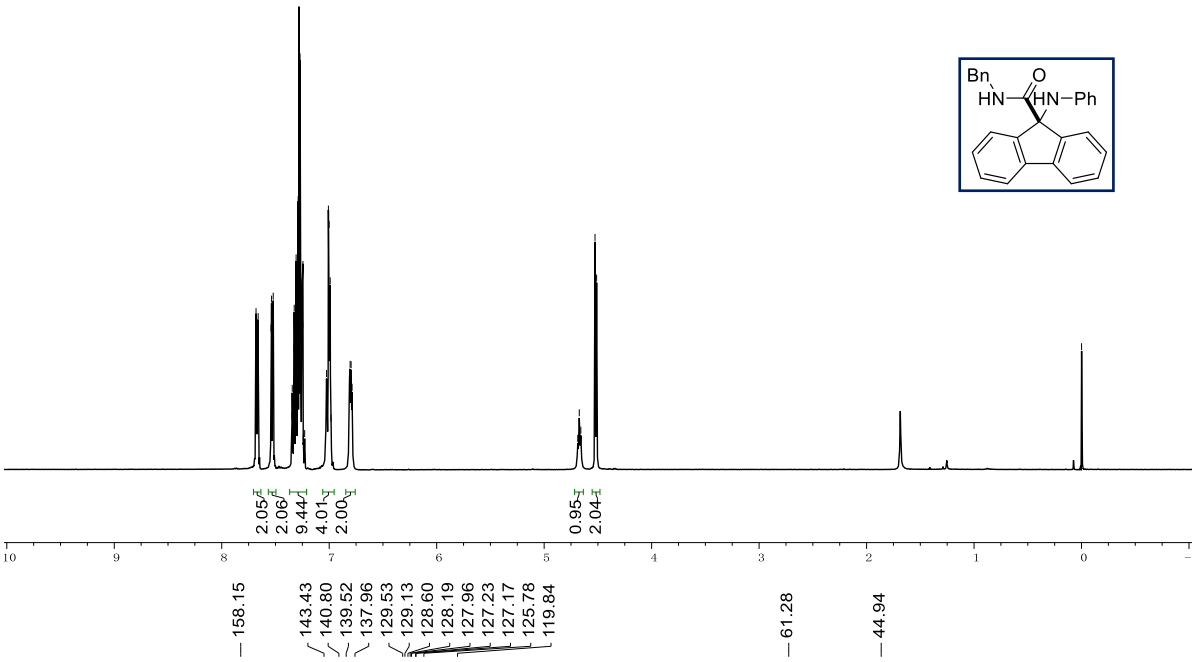


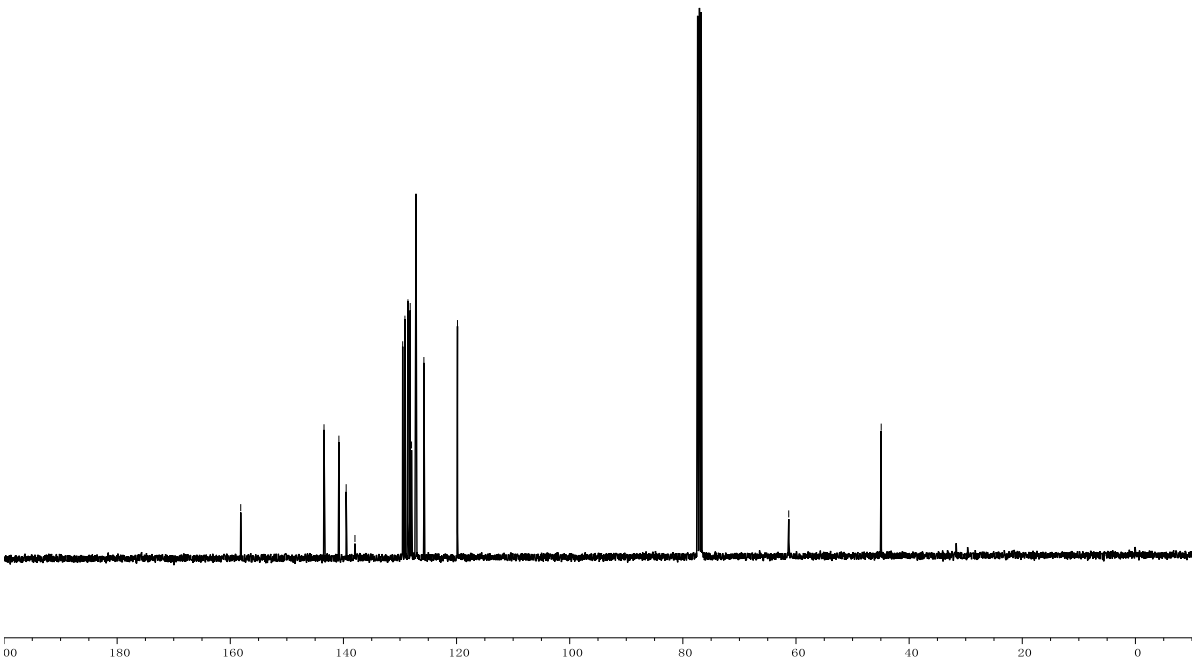
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3oa** in $CDCl_3$



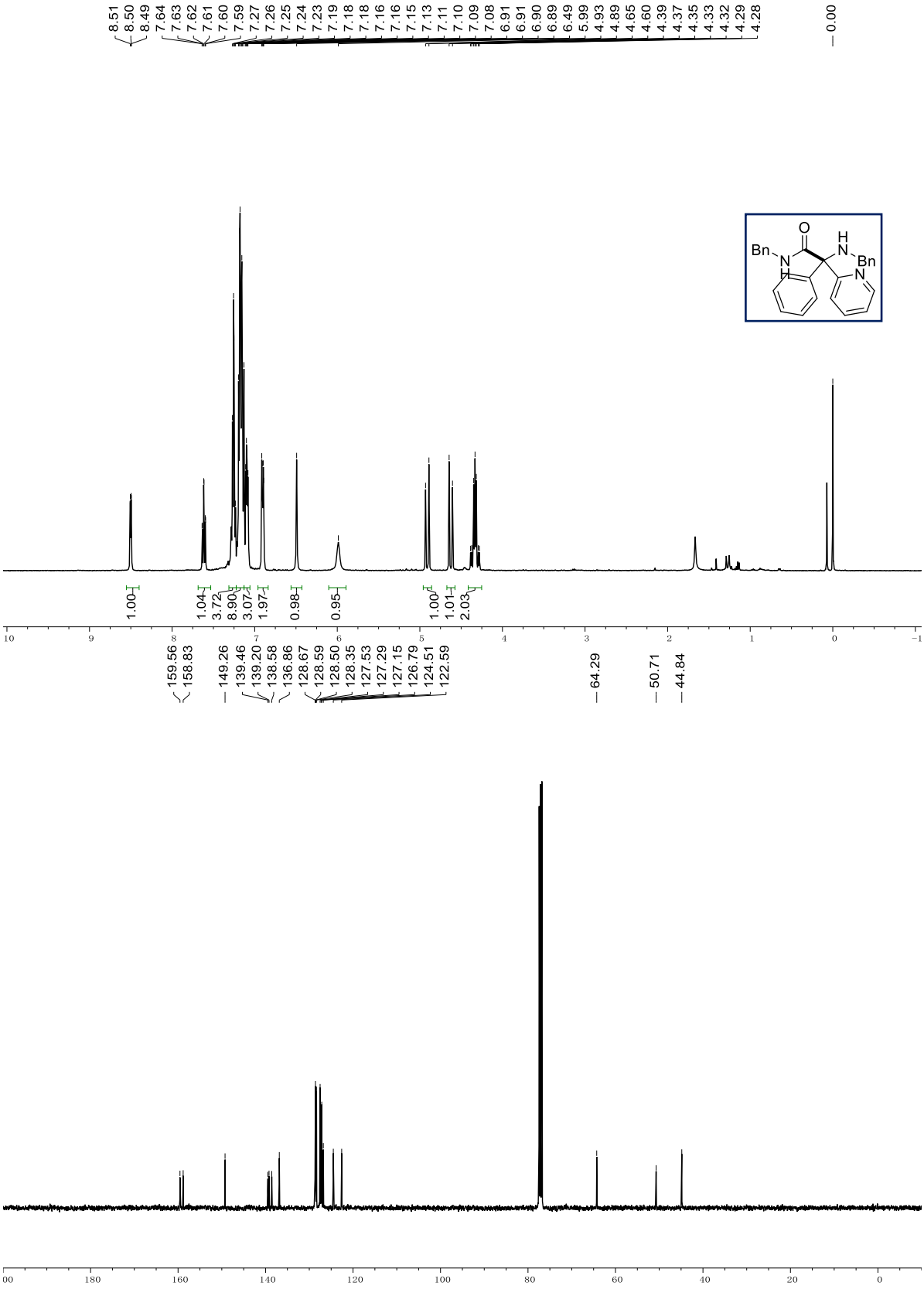
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3pa** in $CDCl_3$



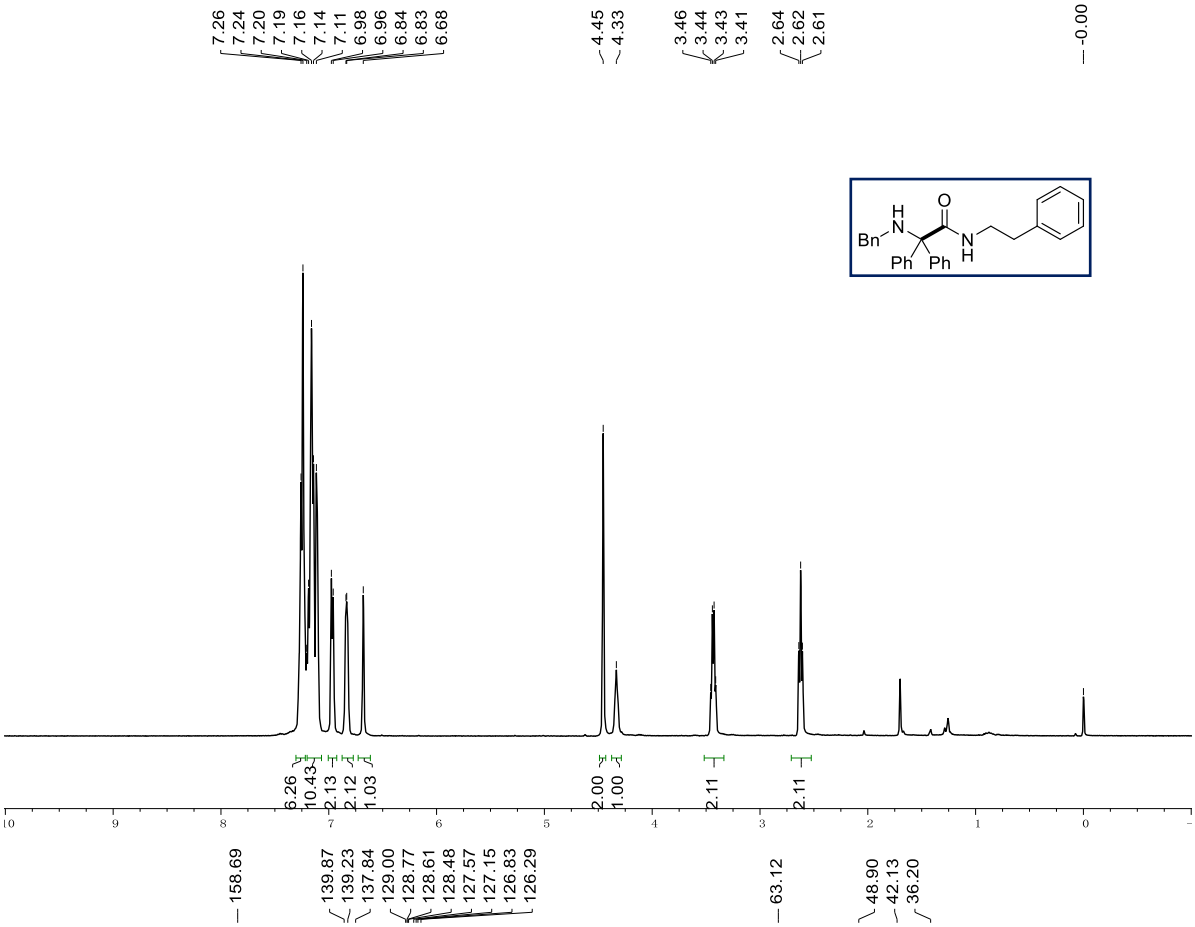


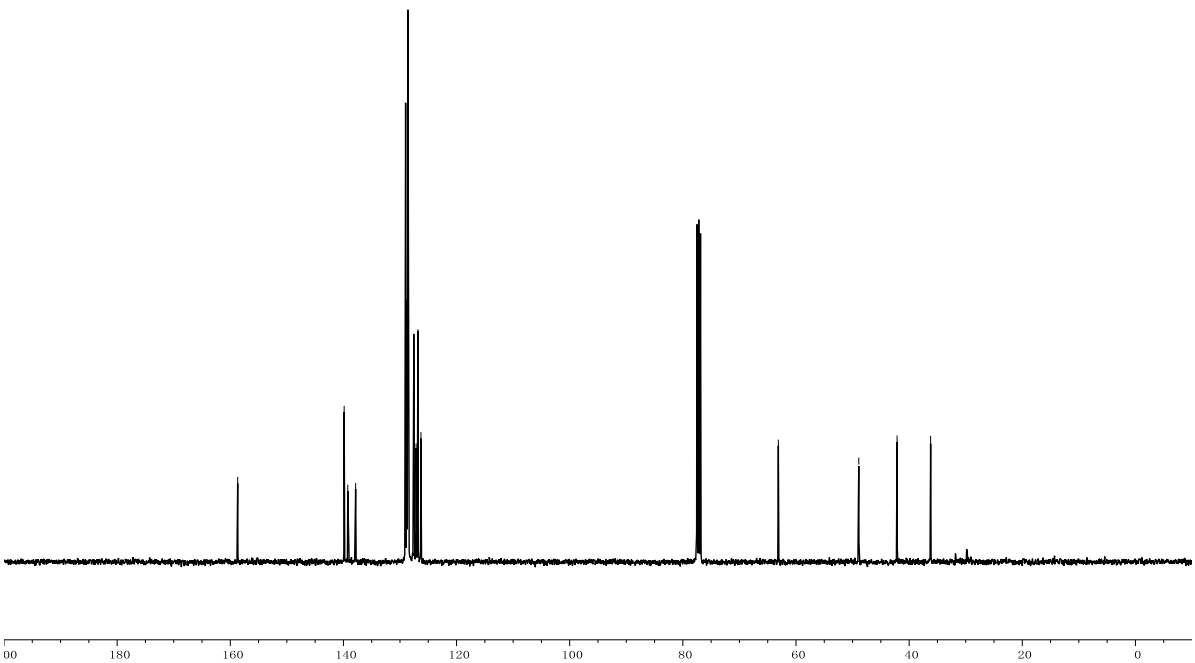


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3qa** in $CDCl_3$

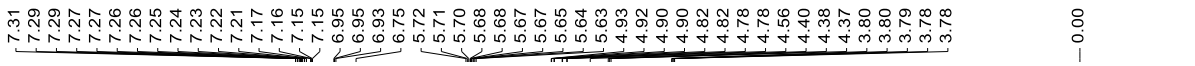


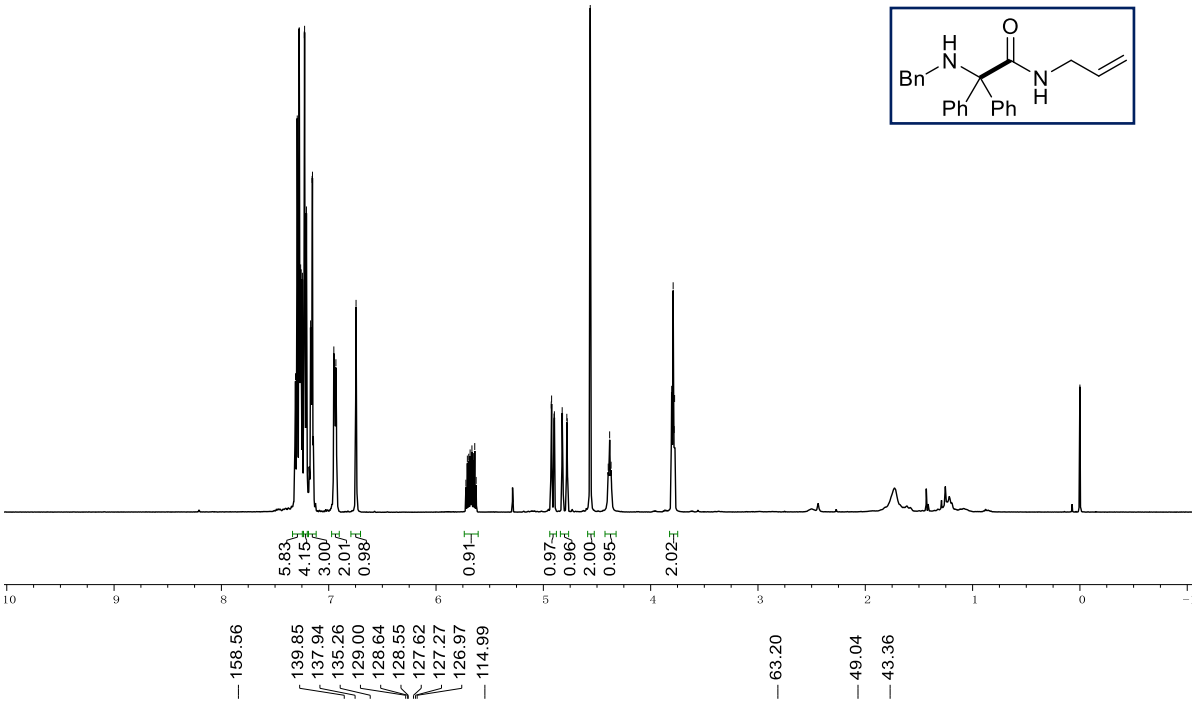
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ab** in $CDCl_3$

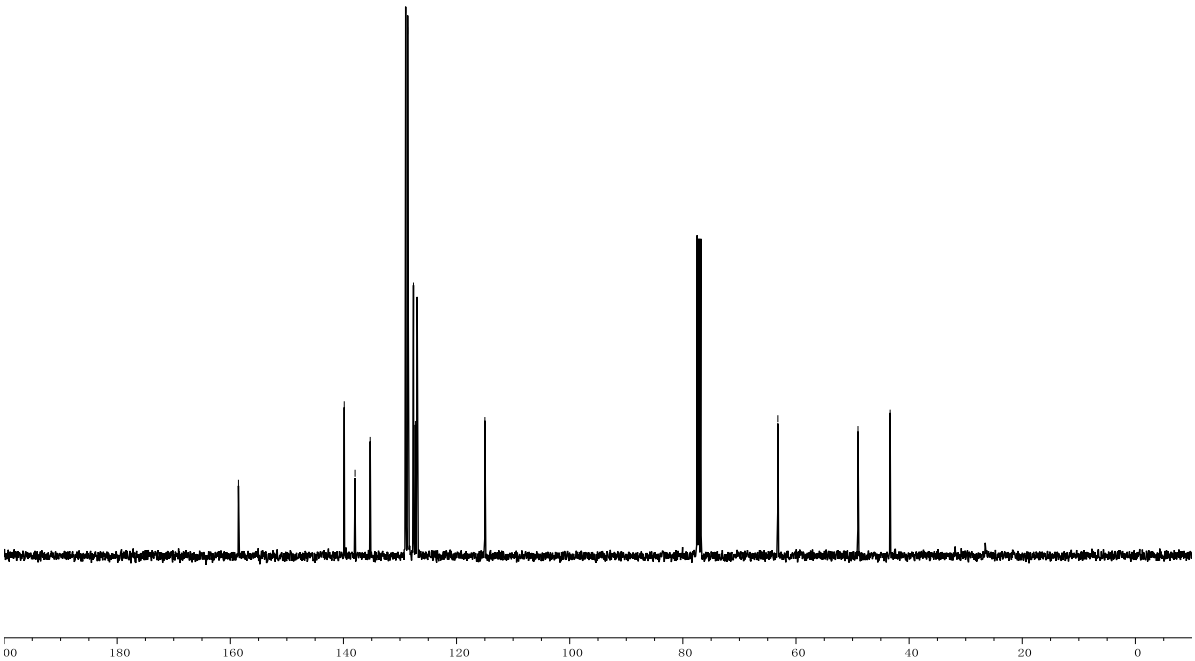




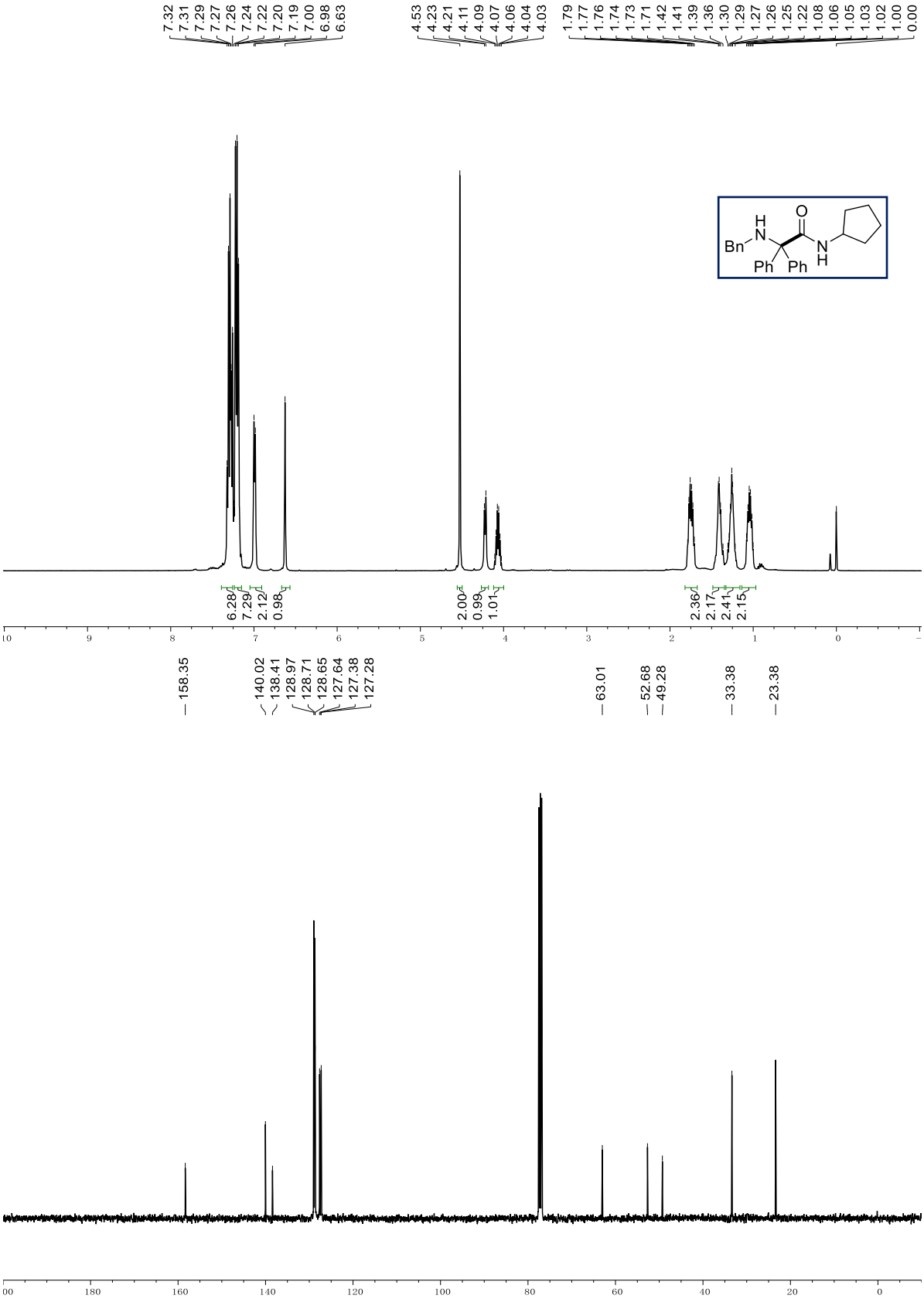
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3ac** in $CDCl_3$



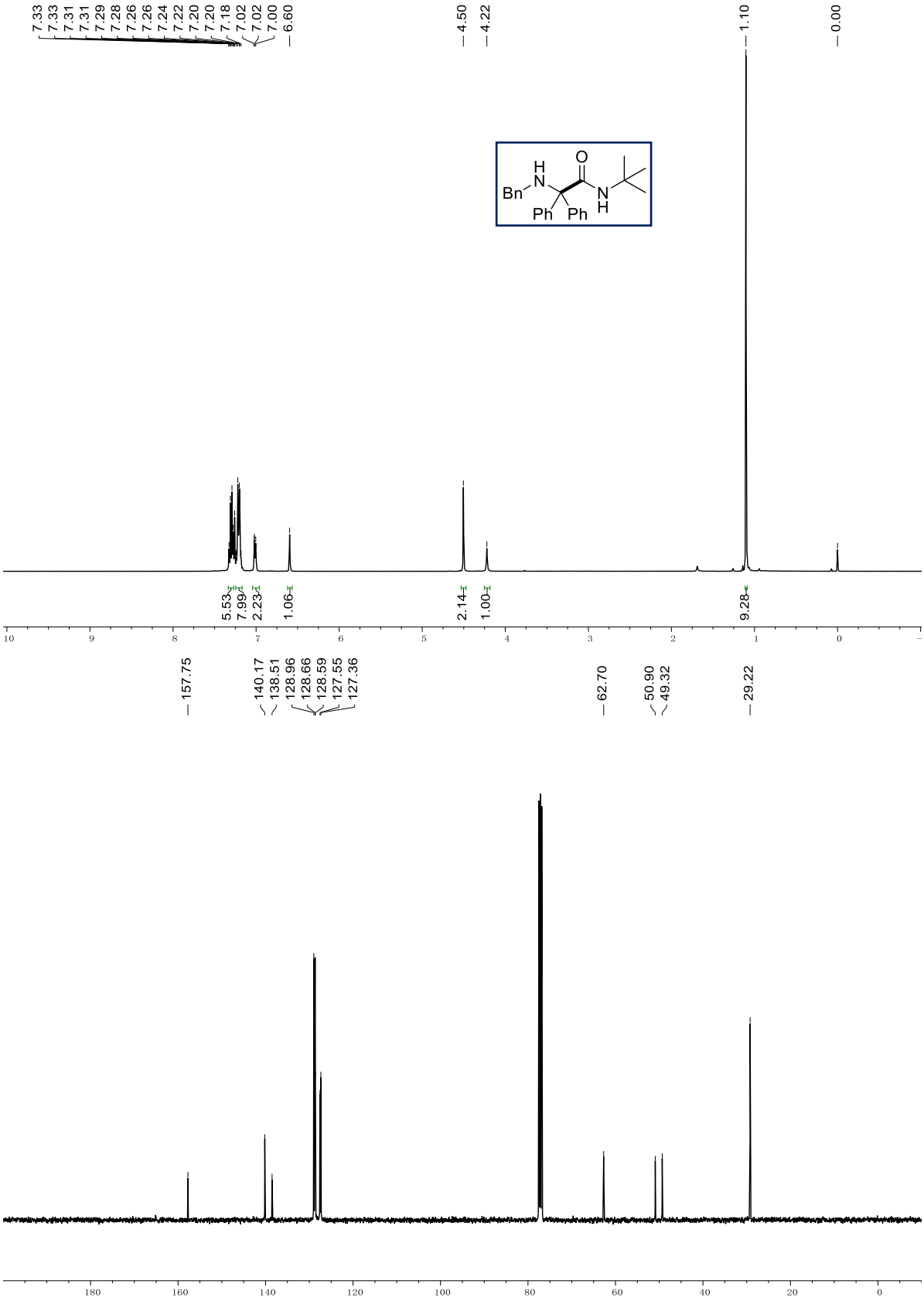




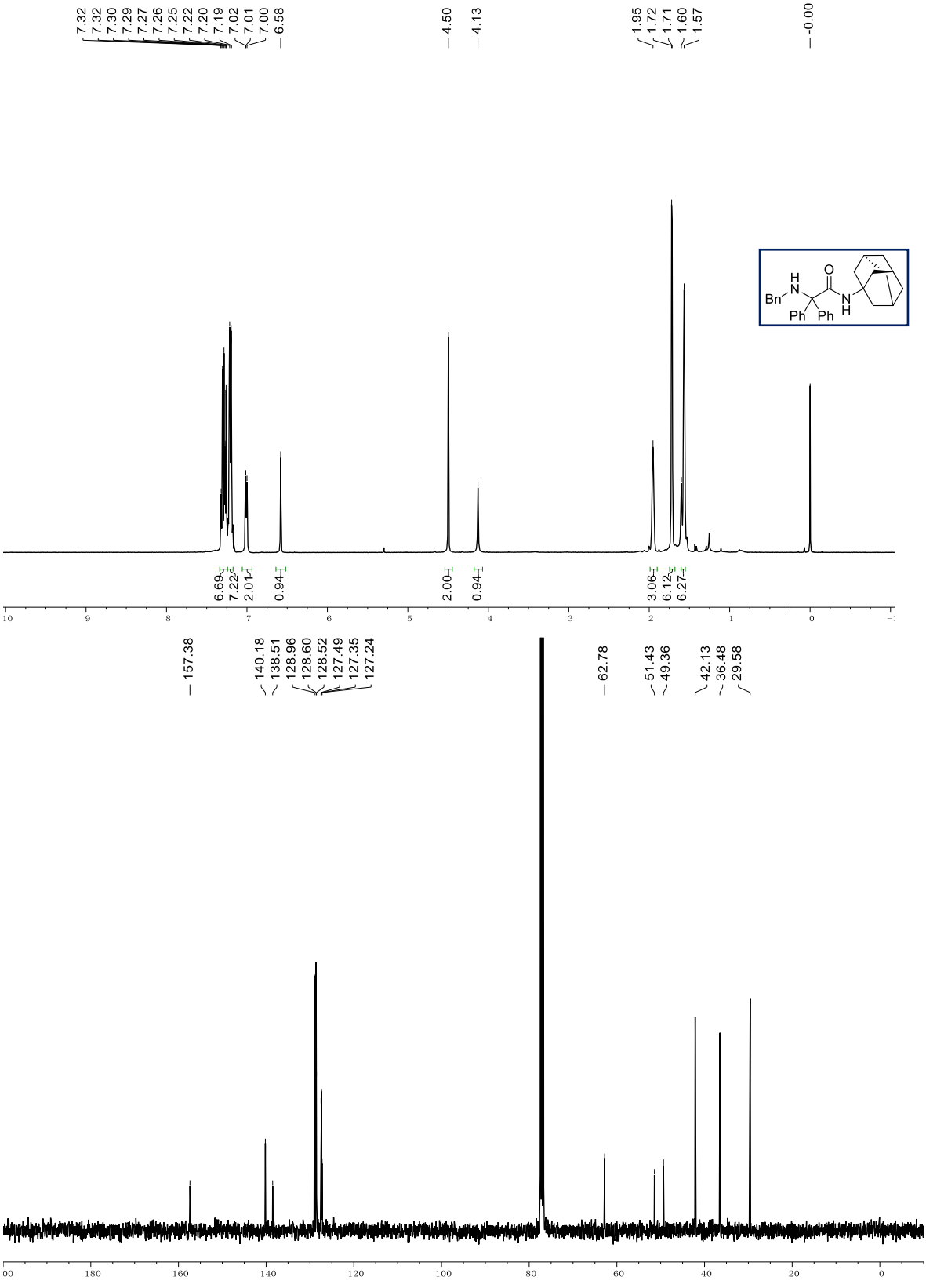
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ad** in $CDCl_3$



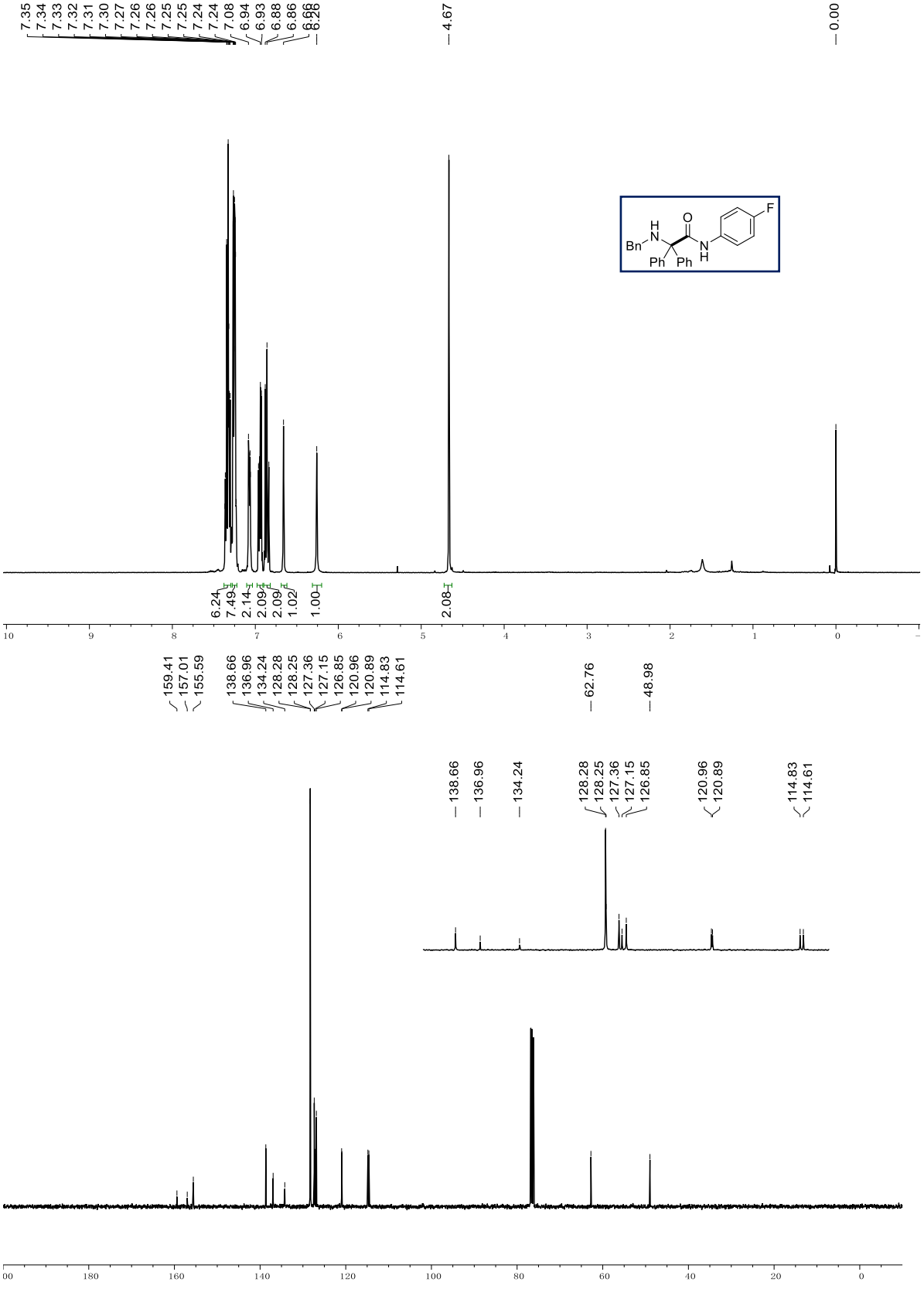
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3ae** in $CDCl_3$

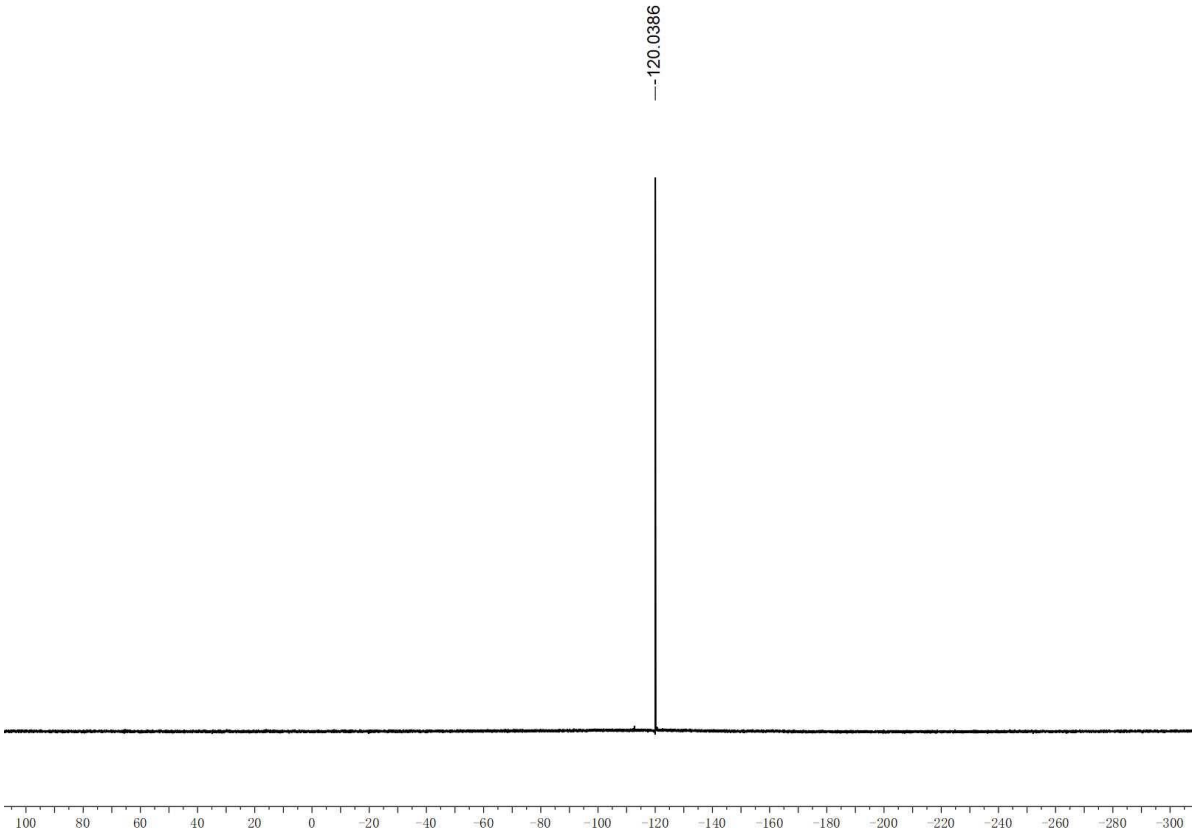


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3af** in $CDCl_3$



^{1}H, $^{13}C\{^{1}H\}$and ^{19}F NMR spectra of **3ag** in $CDCl_3$

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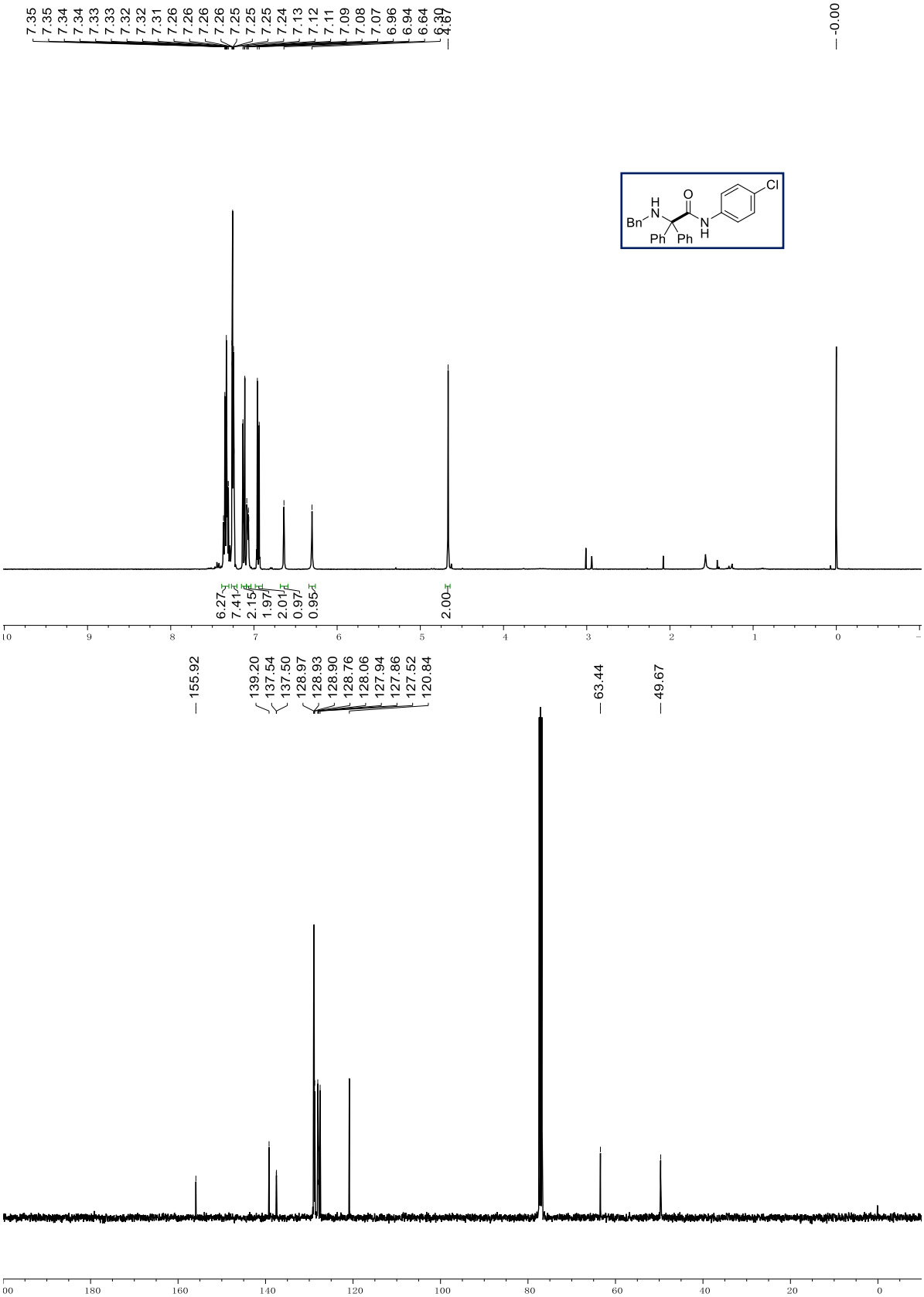
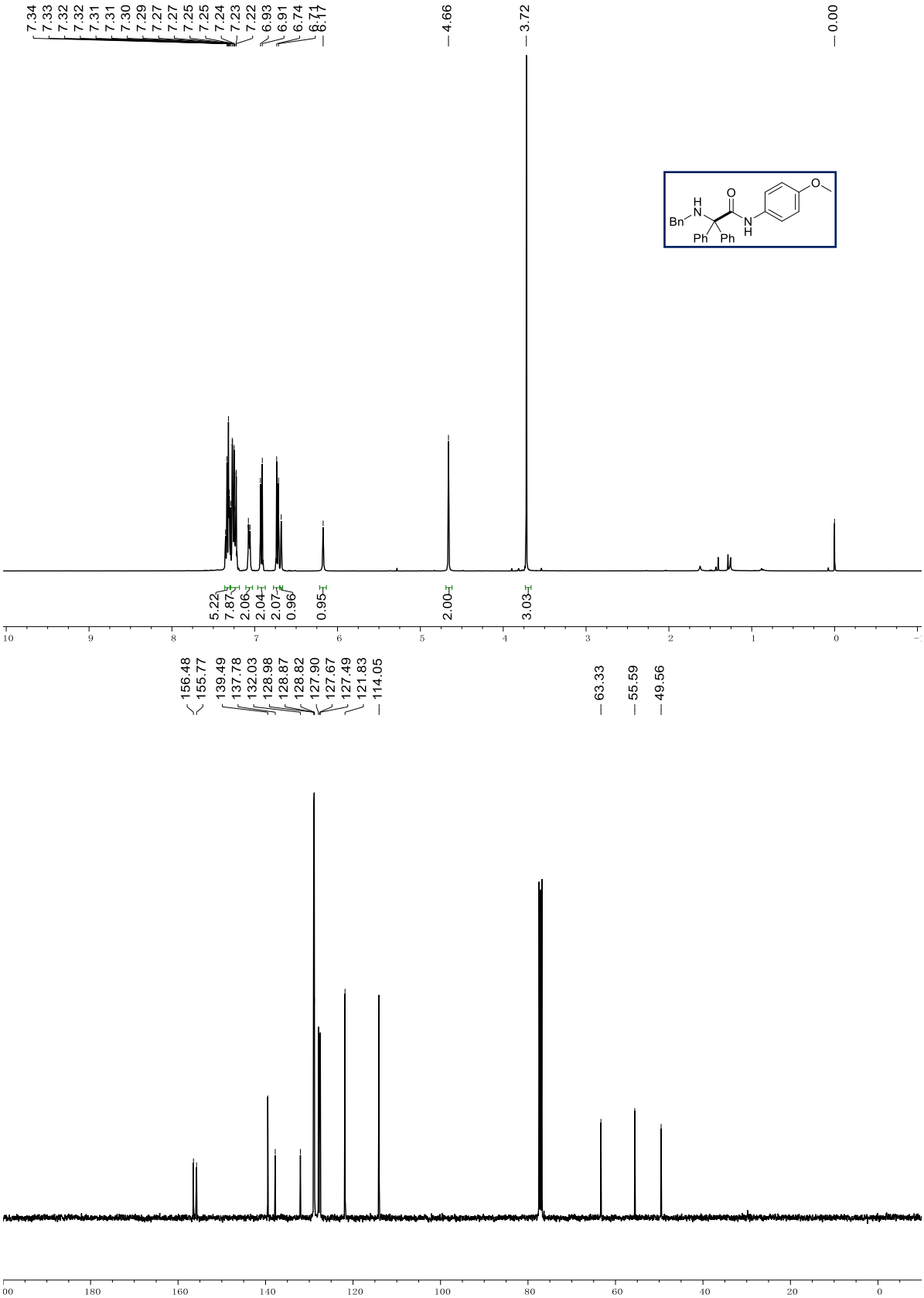
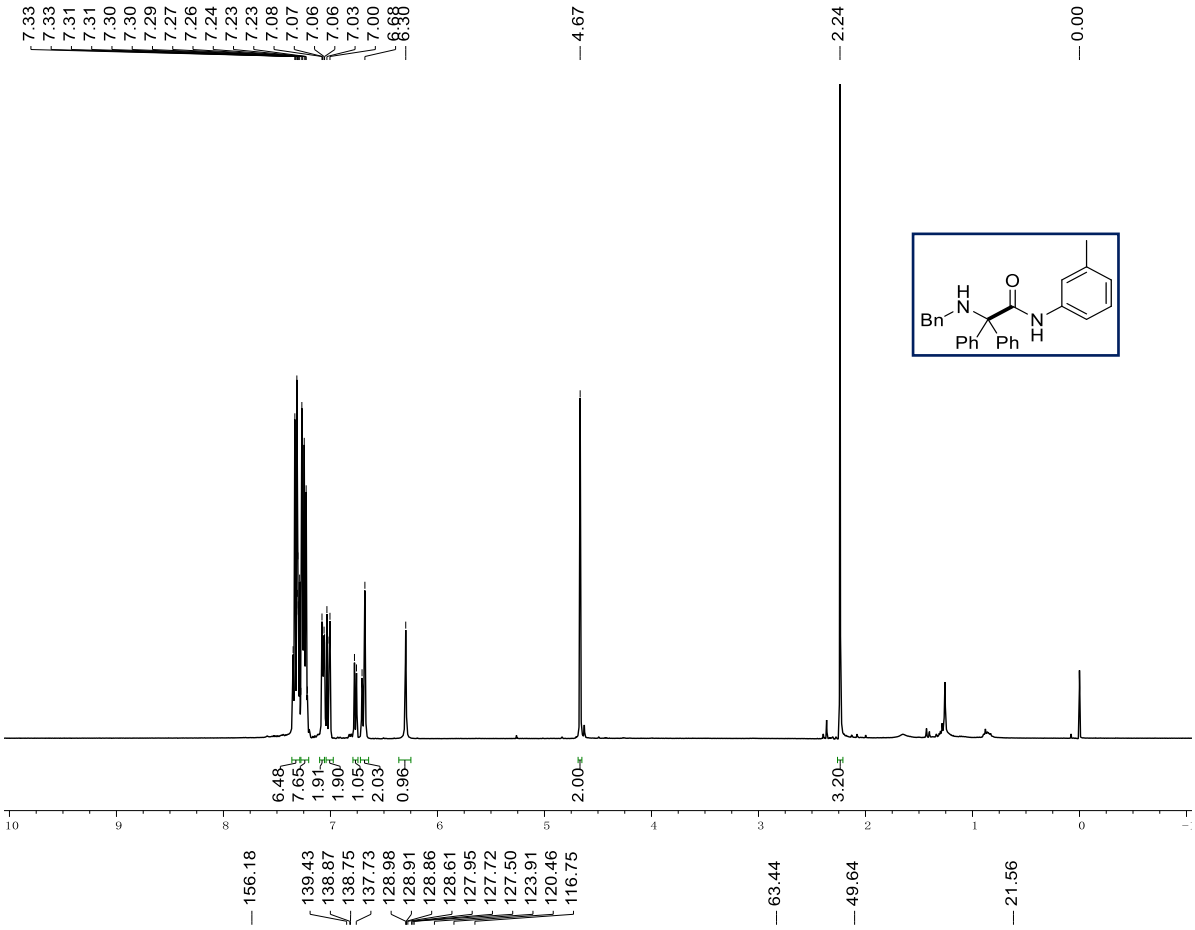
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3ah** in $CDCl_3$

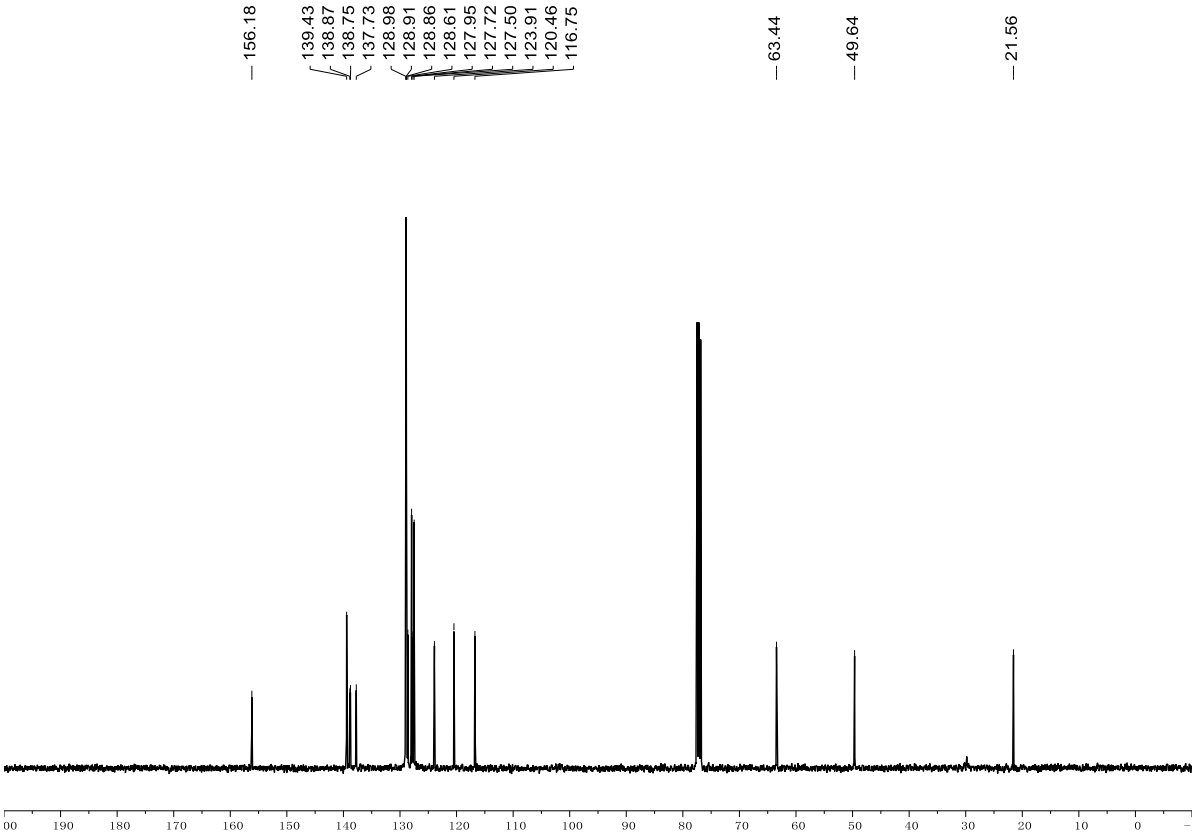


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3ai** in $CDCl_3$

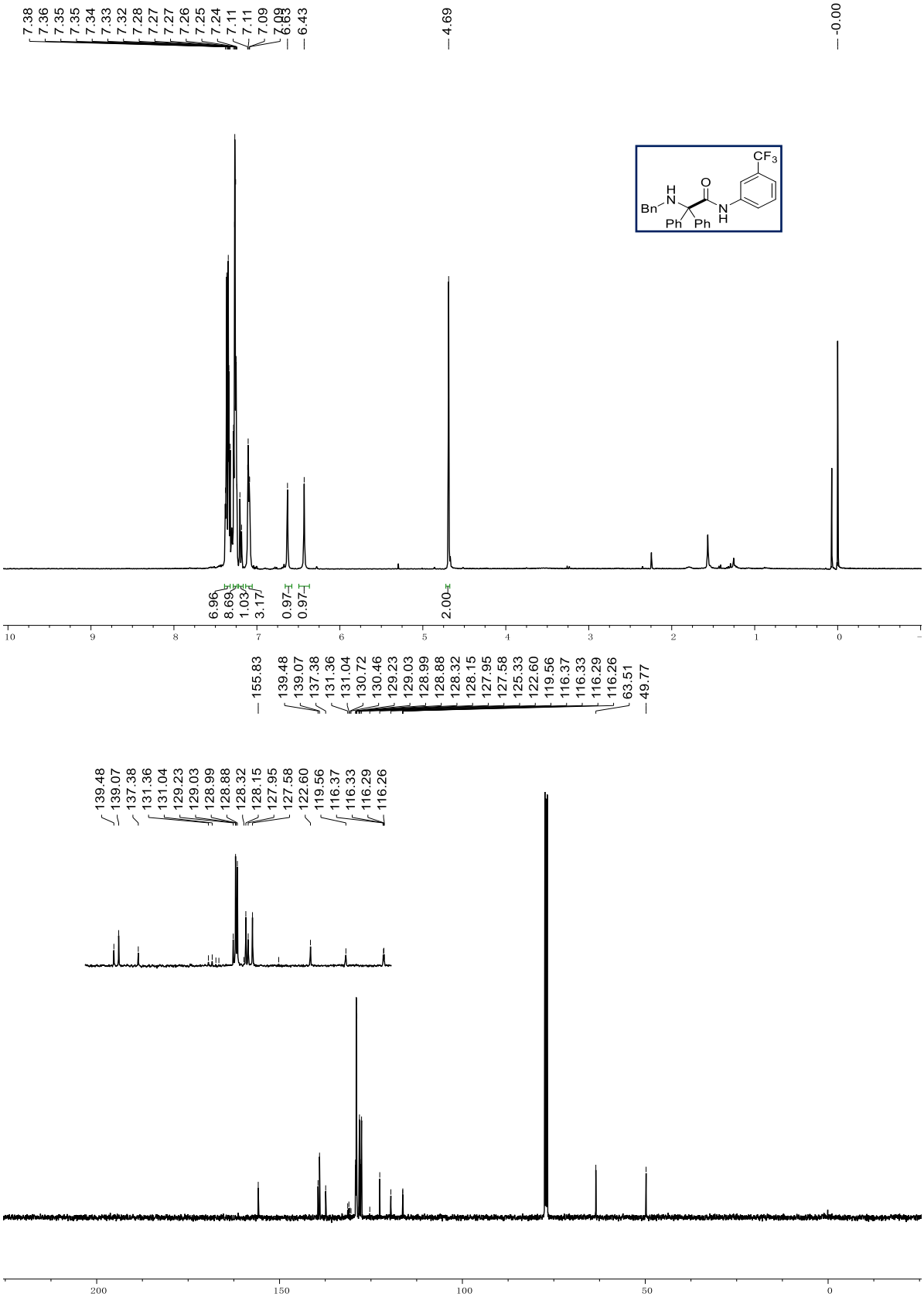


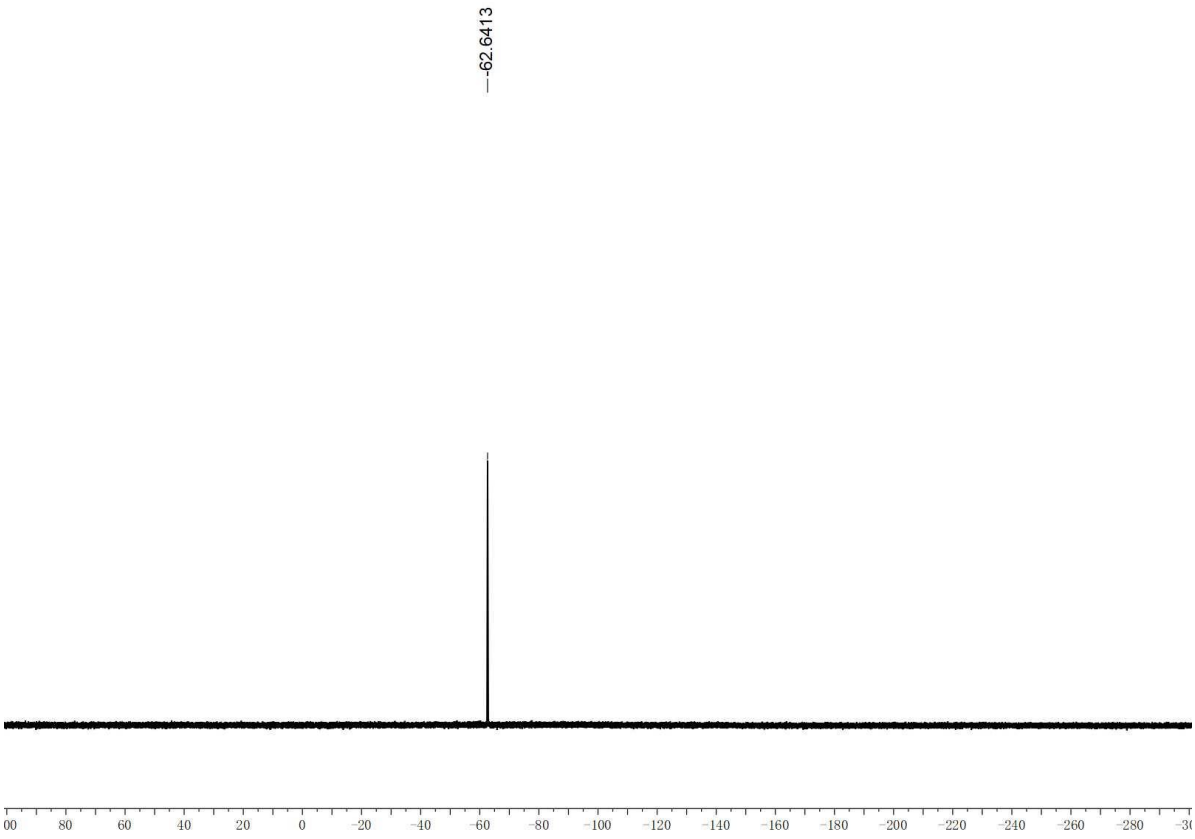
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **3aj** in $CDCl_3$





^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra of **3ak** in $CDCl_3$

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^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **4da** in $CDCl_3$