Supporting information

Green and efficient synthesis dibenzyl cyanamides and ureas with cyanamide as a block

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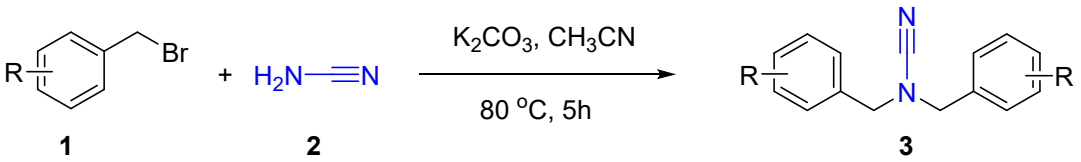
1. General information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker AV-400/500 MHz NMR spectrometers instrument using $CDCl_3$ or DMSO-d_6 as solvent and Me_4Si as internal standard. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and quadrupole Orbitrap Elite (Q-Exactive) mass spectrometer. Cyanamide was purchased from Aladdin Company (China, purity: 95%) and other commercially available reagents were purchased from Tansoole Chemicals, Macklin Biochemical Technology and used as received. Column chromatography was carried out on a flash chromatographic system using silica gel, petroleum ether (60-90 °C) and ethyl acetate as eluent. For thin layer chromatography (TLC), silica gel plates precoated with GF-254 were used.

2. General procedure for synthesis of compound 3, 4, 5:

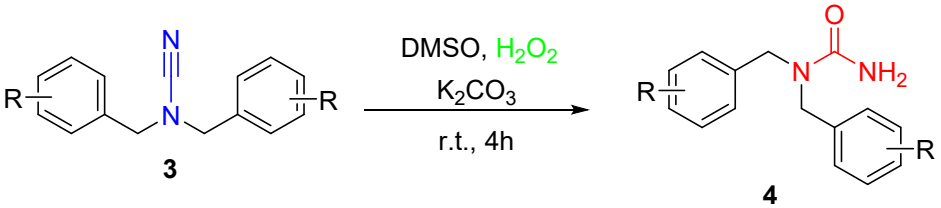
2.1 The General Procedure for the Synthesis of 3



1 **2** **3**

To a 25 mL quartz tube was charged with enzyl bromide compounds **1** (0.44 mmol, 2.2 equiv.), cyanamide compound **2** (0.2 mmol), K_2CO_3 (0.6 mmol, 3.0 equiv.) and CH_3CN (5 mL). Then the mixture was stirred for 5 h under air atmosphere at 80 °C. Perform TLC testing every hour until the reaction is complete. After completion, distilled under reduced pressure to remove acetonitrile. Add water (10 mL) and ethyl acetate (10 mL) to extract and separate the phases. The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried with by Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether (1:20) to give *N,N*-dibenzylcyanamide compounds **3**.

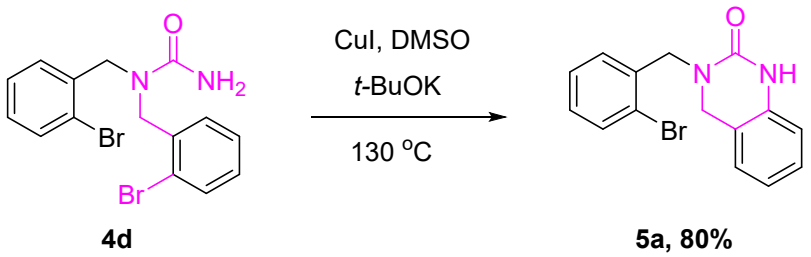
2.2 The General Procedure for the Synthesis of 4



3 **4**

To a 25 mL quartz tube was charged with *N,N*-dibenzylcyanamide compounds **3** (0.2 mmol), hydrogen peroxide (0.24 mmol, 1.2 equiv., 30% aq.) and DMSO (3 mL). Then the mixture was stirred for 4 h under air atmosphere at room temperature. After completion, added water (10 mL) and ethyl acetate (10 mL) to extract and separate the phases. The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried with by Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether (1:10) to give *N,N*-diphenylurea products **4**.

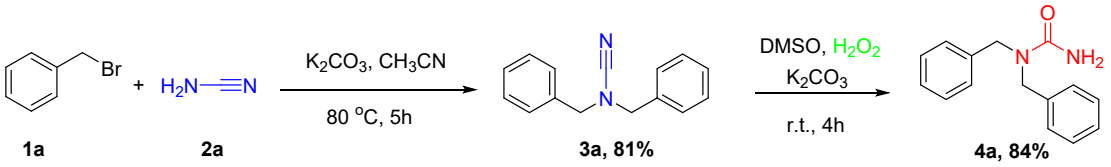
2.3 The General Procedure for the Synthesis of Derivatives 5a



4d **5a, 80%**

To a 25 mL quartz tube was charged with 1,1-bis(2-bromobenzyl)urea compounds **4d** (0.2 mmol), cuprous iodide (0.02 mmol, 0.1 equiv.), potassium *tert*-butoxide (0.6 mmol, 3.0 equiv.) and DMSO (2 mL). Then the mixture was stirred for 8 h under air atmosphere at 130 °C. After completion, added water (10 mL) and ethyl acetate (10 mL) to extract and separate the phases. The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried with by Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether (1:5) to give product **5a**.

2.4 Gram-scale synthesis of 3a, 4a

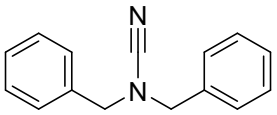


1a **2a** **3a, 81%** **4a, 84%**

To a 100 mL flask was charged with (bromomethyl)benzene **1a** (22.0 mmol, 2.2 equiv., 3.74g), cyanamide **2** (10.0 mmol, 0.42g), K_2CO_3 (30.0 mmol, 3.0 equiv., 4.17g) and MeCN (25mL). Then the mixture was stirred for 5 h under air atmosphere at 80 °C. Perform TLC testing every hour until the reaction is complete. After completion, distilled under reduced pressure to remove acetonitrile. Add water (25 mL) and ethyl acetate (25 mL) to extract and separate the phases. The mixture was extracted with ethyl acetate (25 mL × 3). The combined organic layers were dried with Na_2SO_4, and

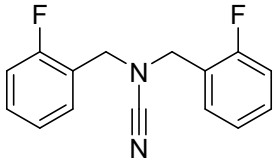
concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether (1:20) to give *N,N*-dibenzylcyanamide **3a** (1.80 g, 8.1 mmol, 81%). To a 100 mL flask was charged with *N,N*-dibenzylcyanamide **3a** (1.80g, 8.1 mmol), hydrogen peroxide (1.1g, 9.7 mmol, 1.2 equiv., 30% aq.) and DMSO (15 mL). Then the mixture was stirred for 4 h under air atmosphere at room temperature. After completion, added water (25 mL) and ethyl acetate (25 mL) to extract and separate the phases. The mixture was extracted with ethyl acetate (25 mL × 3). The combined organic layers were dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether (1:10) to give 1,1-dibenzylurea **4a** (1.63 g, 6.8 mmol, 84%).

3. Spectroscopic data for the products 3-5



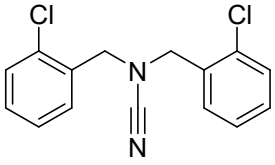
***N,N*-dibenzylcyanamide (3a)**[1]

White solid; 33 mg, 75% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.41 - 7.35 (m, 6H), 7.32 - 7.31 (m, 4H), 4.11 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 134.4, 128.9, 128.6, 128.6, 118.2, 54.4; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}N_2$ $[M + H]^+$: 223.1230, found: 223.1226.



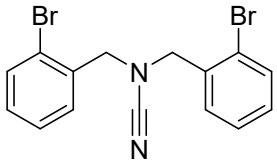
***N,N*-bis(2-fluorobenzyl)cyanamide (3b)**

White solid; 40 mg, 77% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.38 - 7.32 (m, 4H), 7.16 (t, J = 7.5 Hz, 2H), 7.09 (t, J = 9.5 Hz, 2H), 4.23 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 161.2 (d, J = 249.5 Hz), 130.9 (d, J = 3.7 Hz), 130.7 (d, J = 8.8 Hz), 124.6(d, J = 3.7 Hz), 121.7 (d, J = 13.9 Hz), 117.3, 115.8 (d, J = 21.4 Hz), 48.7 (d, J = 3.7 Hz); **^{19}F NMR (376 MHz, Chloroform - *d*)** δ -117.3; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}F_2N_2$ $[M + H]^+$: 259.1041, found: 259.1036.



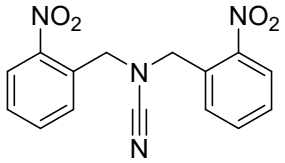
***N,N*-bis(2-chlorobenzyl)cyanamide (3c)**

White solid; 38 mg, 65% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.43 - 7.41 (m, 4H), 7.31 - 7.29 (m, 4H), 4.35 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 134.4, 132.2, 130.8, 130.2, 130.1, 127.4, 117.4, 52.7; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}Cl_2N_2$ $[M + H]^+$: 291.0450, found: 291.0442.



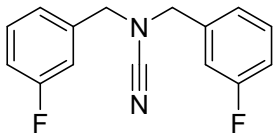
***N,N*-bis(2-bromobenzyl)cyanamide (3d)**

White solid; 56 mg, 74% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.60 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.42 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.36 - 7.33 (m, 2H), 7.23 - 7.20 (m, 2H), 4.35 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 133.8, 133.4, 130.8, 130.4, 128.0, 124.4, 117.3, 55.1; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}Br_2N_2$ $[M - H]^-$: 376.9294, found: 376.9290.



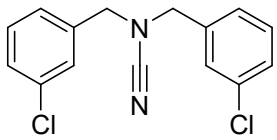
***N,N*-bis(2-nitrobenzyl)cyanamide (3e)** [1]

Brown solid; 39 mg, 62% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.35 - 7.31 (m, 4H), 7.28 - 7.27 (m, 2H), 7.20 - 7.18 (m, 2H), 4.10 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 136.2, 135.0, 130.4, 129.1, 128.7, 126.8, 117.6, 54.2; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}N_4O_4$ $[M + H]^+$: 313.0931, found: 313.0930.



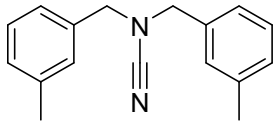
***N,N*-bis(3-fluorobenzyl)cyanamide (3f)**

White solid; 43 mg, 83% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.39 - 7.34 (m, 2H), 7.10 - 7.00 (m, 6H), 4.13 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 163.1 (d, *J* = 248.2 Hz), 136.7 (d, *J* = 7.6 Hz), 130.8 (d, *J* = 7.6 Hz), 124.3 (d, *J* = 2.5 Hz), 117.7 (d, *J* = 20.2 Hz), 115.6 (d, *J* = 22.7 Hz), 54.2 (d, *J* = 2.5 Hz); **^{19}F NMR (376 MHz, Chloroform - *d*)** δ -111.7; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}F_2N_2$ $[M + H]^+$: 259.1041, found: 259.1043.



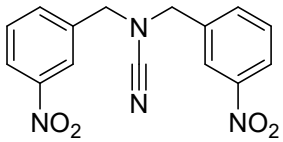
***N,N*-bis(3-chlorobenzyl)cyanamide (3g)**

White solid; 42 mg, 72% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.72 (t, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 2H), 4.69 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 148.4, 134.3, 130.9, 130.0, 129.9, 125.8, 116.7, 53.3; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}Cl_2N_2$ $[M + H]^+$: 291.0450, found: 291.0452.



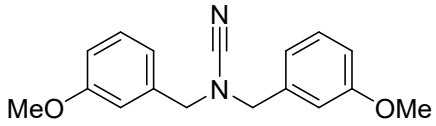
***N,N*-bis(3-methylbenzyl)cyanamide (3h)** [1]

White solid; 42 mg, 84% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13 - 7.10 (m, 4H), 4.09 (s, 4H), 2.39 (s, 6H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 138.7, 134.4, 129.4, 129.4, 128.8, 125.8, 118.5, 54.3, 21.4; **HRMS (ESI)**: m/z calcd for $C_{17}H_{18}N_2$ $[M + H]^+$: 251.1543, found: 251.1540.



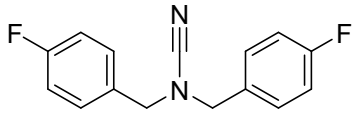
***N,N*-bis(3-nitrobenzyl)cyanamide (3i)**

Brown solid; 32 mg, 52% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 8.23 - 8.21 (m, 2H), 8.16 - 8.15 (m, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 2H), 4.32 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 148.7, 136.2, 134.6, 130.5, 124.1, 123.6, 116.8, 54.6; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}N_4O_4$ $[M + H]^+$: 313.0931, found: 313.0932.



***N,N*-bis(3-methoxybenzyl)cyanamide (3j)**

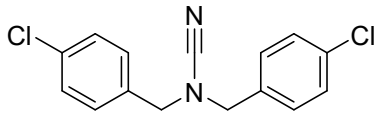
White solid; 44 mg, 78% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.29 (t, *J* = 8.0 Hz, 2H), 6.89 - 6.87 (m, 4H), 6.84 - 6.83 (m, 2H), 4.08 (s, 4H), 3.79 (s, 6H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 160.0, 135.9, 129.9, 120.8, 118.3, 114.1, 114.1, 55.2, 54.3; **HRMS (ESI)**: m/z calcd for $C_{17}H_{18}N_2O_2$ $[M + H]^+$: 283.1441, found: 283.1433.



***N,N*-bis(4-fluorobenzyl)cyanamide (3k)** [1]

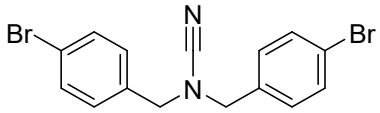
White solid; 44 mg, 85% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.29 - 7.25

(m, 4H), 7.09 - 7.04 (m, 4H), 4.08 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 162.9 (d, *J* = 248.2 Hz), 130.5 (d, *J* = 8.8 Hz), 130.1 (d, *J* = 3.8 Hz), 117.8, 116.0 (d, *J* = 21.4 Hz), 53.8; **^{19}F NMR (376 MHz, Chloroform - *d*)** δ -112.7; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}F_2N_2$ $[M + H]^+$: 259.1041, found: 259.1033.



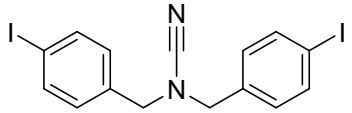
***N,N*-bis(4-chlorobenzyl)cyanamide (3l)** [1]

White solid; 50 mg, 86% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.73 - 7.71 (m, 4H), 7.04 - 7.02 (m, 4H), 4.04 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 138.3, 133.9, 130.6, 117.8, 94.7, 54.1; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}Cl_2N_2$ $[M + H]^+$: 291.0450, found: 291.0440.



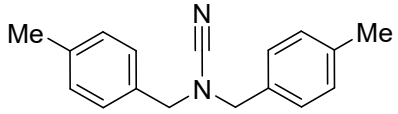
***N,N*-bis(4-bromobenzyl)cyanamide (3m)** [1]

White solid; 63 mg, 83% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.51 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 4H), 4.06 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 133.2, 132.3, 130.4, 123.0, 117.7, 54.0; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}Br_2N_2$ $[M - H]^-$: 376.9294, found: 376.9292.



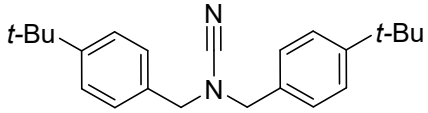
***N,N*-bis(4-iodobenzyl)cyanamide (3n)**

White solid; 59 mg, 62% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.33 (d, *J* = 8.0 Hz, 4H), 7.21 (d, *J* = 8.5 Hz, 4H), 4.05 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 134.7, 132.7, 130.0, 129.2, 117.6, 53.8; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}I_2N_2$ $[M - H^+]$: 472.9017, found: 472.9013.



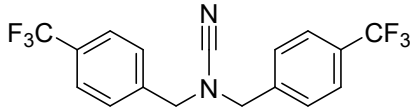
***N,N*-bis(4-methylbenzyl)cyanamide (3o)**[1]

White solid; 40 mg, 80% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.20 (s, 8H), 4.06 (s, 4H), 2.37 (s, 6H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 138.6, 131.5, 129.7, 128.8, 118.6, 54.1, 21.3; **HRMS (ESI)**: m/z calcd for $C_{17}H_{18}N_2$ $[M + H]^+$: 251.1543, found: 251.1540.



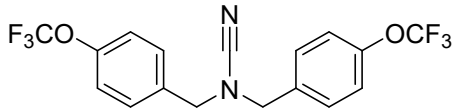
***N,N*-bis(4-(*tert*-butyl)benzyl)cyanamide (3p)**

White solid; 58 mg, 87% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.41 - 7.38 (m, 4H), 7.25 - 7.23 (m, 4H), 4.08 (s, 4H), 1.33 (s, 18H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 151.7, 131.6, 128.5, 125.9, 118.6, 54.0, 34.7, 31.4; **HRMS (ESI)**: m/z calcd for $C_{23}H_{30}N_2$ $[M + H]^+$: 335.2482, found: 335.2474.



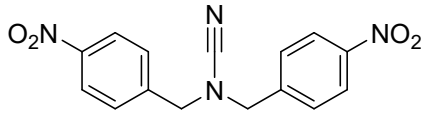
***N,N*-bis(4-(trifluoromethyl)benzyl)cyanamide (3q)**

White solid; 59 mg, 82% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.65 (d, *J* = 8.0 Hz, 4H), 7.43 (d, *J* = 8.0 Hz, 4H), 4.21 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 138.2, 131.2 (q, *J* = 32.8 Hz), 129.0, 126.1 (q, *J* = 3.8 Hz), 122.7 (q, *J* = 272.6 Hz), 117.5, 54.4; **^{19}F NMR (376 MHz, Chloroform - *d*)** δ -62.8; **HRMS (ESI)**: m/z calcd for $C_{17}H_{12}F_6N_2$ $[M + H]^+$: 359.0977, found: 359.0980.



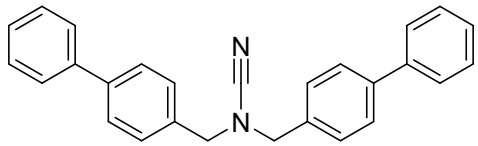
***N,N*-bis(4-(trifluoromethoxy)benzyl)cyanamide (3r)**

White solid; 63 mg, 81% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.35 - 7.32 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 4H), 4.14 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 149.5 (q, *J* = 2.5 Hz), 132.9, 130.1, 121.4, 120.4 (q, *J* = 258.3 Hz), 117.6, 53.9; **^{19}F NMR (376 MHz, Chloroform - *d*)** δ -57.9; **HRMS (ESI)**: m/z calcd for $C_{17}H_{12}F_6N_2O_2$ $[M + H]^+$: 391.0876, found: 391.0865.



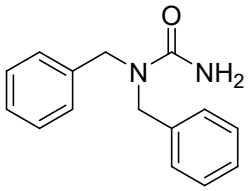
***N,N*-bis(4-nitrobenzyl)cyanamide（3s）**

Brown solid; 50 mg, 76% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 8.26 - 8.24 (m, 4H), 7.52 (d, *J* = 8.5 Hz, 4H), 4.29 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - d)** δ 148.4, 141.0, 129.5, 124.4, 116.8, 54.4; **HRMS (ESI)**: m/z calcd for $C_{15}H_{12}N_4O_4$ $[M + H]^+$: 313.0931, found: 313.0922.



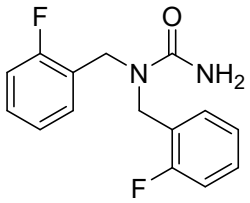
***N,N*-bis([1,1'-biphenyl]-4-ylmethyl)cyanamide (3t)**

White solid; 62 mg, 83% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.66 - 7.62 (m, 8H), 7.50 - 7.47 (m, 4H), 7.44 - 7.38 (m, 6H), 4.22 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 141.7, 140.5, 133.4, 129.2, 128.9, 127.7, 127.7, 127.2, 118.4, 54.2; **HRMS (ESI)**: m/z calcd for $C_{27}H_{22}N_2$ $[M - H]^-$: 373.1710, found: 373.1708.



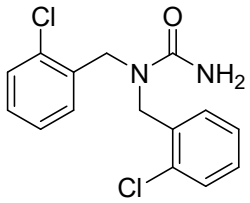
1,1-Dibenzylurea (4a)[2]

White solid; 41 mg, 85% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.31 - 7.28 (m, 4H), 7.25 - 7.19 (m, 6H), 5.07 (s, 2H), 4.23 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.7, 137.3, 128.8, 127.5, 127.2, 50.2; **HRMS (ESI)**: m/z calcd for $C_{15}H_{16}N_2O$ [M + H] $^{+}$: 241.1335, found: 241.1329.



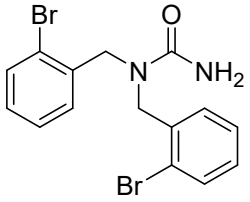
1,1-Bis(2-fluorobenzyl)urea (4b)

White solid; 40 mg, 72% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.32 - 7.29 (m, 2H), 7.25 - 7.20 (m, 2H), 7.10 - 7.07 (m, 2H), 7.02 - 6.98 (m, 2H), 5.17 (s, 2H), 4.52 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 160.8 (d, *J* = 245.7 Hz), 159.5, 129.3 (d, *J* = 3.8 Hz), 129.2 (d, *J* = 8.8 Hz), 124.5 (d, *J* = 3.8 Hz), 124.2 (d, *J* = 15.1 Hz), 115.4 (d, *J* = 21.4 Hz), 44.3 (d, *J* = 5.0 Hz); **^{19}F NMR (376 MHz, Chloroform - *d*)** δ -118.4; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}F_2N_2O$ [M + H] $^{+}$: 277.1147, found: 277.1141.



1,1-Bis(2-chlorobenzyl)urea (4c)

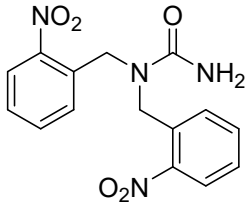
White solid; 48 mg, 78% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.36 - 7.33 (m, 4H), 7.29 - 7.27 (m, 2H), 7.24 - 7.20 (m, 2H), 4.79 (s, 2H), 4.61 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.3, 134.4, 133.2, 129.8, 128.9 128.1, 127.4, 48.8; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}Cl_2N_2O$ [M + H] $^{+}$: 309.0556, found: 309.0547.



1,1-Bis(2-bromobenzyl)urea (4d)

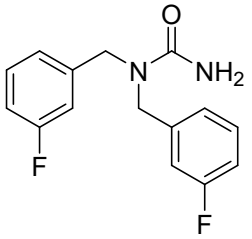
White solid; 59 mg, 75% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 4.5 Hz, 4H), 7.17 - 7.15 (m, 2H), 4.60 (s, 4H), 4.54 (s, 2H);

^{13}C NMR (126 MHz, Chloroform - *d*) δ 158.9, 135.7, 133.1, 129.1, 128.0, 127.9, 123.1, 51.2; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}Br_2N_2O$ [M + H] $^+$: 396.9546, found: 396.9540.



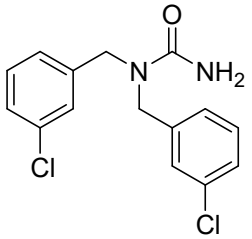
1,1-Bis(2-nitrobenzyl)urea (4e)

Brown solid; 43 mg, 65% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 8.09 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.72 - 7.69 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.50 - 7.47 (m, 2H), 4.92 (s, 4H), 4.77 (s, 2H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.0, 148.3, 134.5, 132.8, 128.7, 128.2, 125.8, 49.1; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}N_4O_5$ [M + H] $^+$: 331.1037, found: 331.1041.



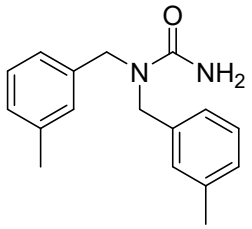
1,1-Bis(3-fluorobenzyl)urea (4f)

White solid; 47 mg, 85% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.30 - 7.25 (m, 2H), 6.99 (d, *J* = 2.0 Hz, 2H), 6.98 - 6.92 (m, 4H), 5.17 (s, 2H), 4.44 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 163.2 (d, *J* = 247.0 Hz), 159.5, 139.9 (d, *J* = 6.3 Hz), 130.4 (d, *J* = 8.8 Hz), 122.8 (d, *J* = 3.8 Hz), 114.5 (d, *J* = 20.2 Hz), 114.1 (d, *J* = 21.4 Hz), 50.0 (d, *J* = 1.3 Hz); **^{19}F NMR (376 MHz, Chloroform - *d*)** δ -122.3; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}F_2N_2O$ [M + H] $^+$:277.1147, found: 277.1141.



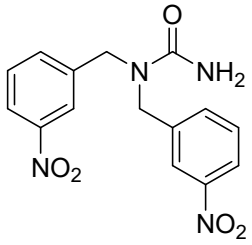
1,1-Bis(3-chlorobenzyl)urea (4g)

White solid; 53 mg, 86% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.24-7.22 (m, 4H), 7.19 (d, *J* = 2.5 Hz, 2H), 7.10 - 7.08 (m, 2H), 5.09 (s, 2H), 4.41 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.4, 139.3, 134.9, 130.2, 127.9, 127.3, 125.4, 50.0; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}Cl_2N_2O$ [M + H] $^+$: 309.0556, found: 309.0550.



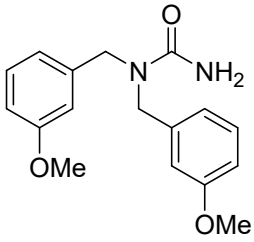
1,1-Bis(3-methylbenzyl)urea (4h)

White solid; 49 mg, 91% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.22 (t, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.06 - 7.03 (m, 4H), 4.86 (s, 2H), 4.45 (s, 4H), 2.34 (s, 6H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.7, 138.6, 137.4, 128.7, 128.3, 127.9, 124.4, 50.4, 21.5; **HRMS (ESI)**: m/z calcd for $C_{17}H_{20}N_2O$ $[M + H]^+$: 269.1648, found: 269.1643.



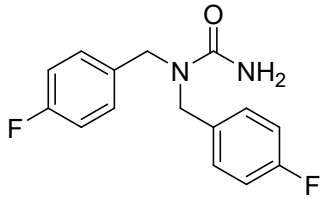
1,1-Bis(3-nitrobenzyl)urea (4i)

Brown solid; 45 mg, 68% yield; **^{1}H NMR (500 MHz, DMSO - d_6)** δ 8.09 - 8.06 (m, 2H), 8.03 - 8.03 (m, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 2H), 6.35 (s, 2H), 4.61 (s, 4H); **^{13}C NMR (126 MHz, DMSO - d_6)** δ 158.5, 147.7, 141.2, 134.1, 129.8, 121.9, 121.8, 49.2; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}N_4O_5$ $[M + H]^+$: 331.1037, found: 331.1030.



1,1-Bis(3-methoxybenzyl)urea (4j)

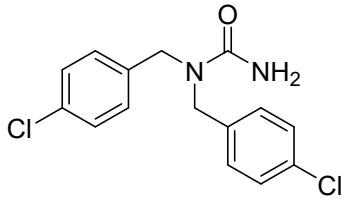
White solid; 53 mg, 88% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.24 (t, *J* = 8.0 Hz, 2H), 6.83 - 6.77 (m, 6H), 4.76 (s, 2H), 4.46 (s, 4H), 3.76 (s, 6H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 160.2, 159.6, 139.1, 130.0, 119.6, 113.2, 112.9, 55.3, 50.6; **HRMS (ESI)**: m/z calcd for $C_{17}H_{20}N_2O_3$ $[M + H]^+$: 301.1547, found: 301.1539.



1,1-Bis(4-fluorobenzyl)urea (4k)

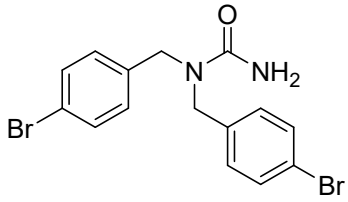
White solid; 45 mg, 81% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.18 - 7.16 (m, 4H), 7.01 - 6.96 (m, 4H), 5.05 (s, 2H), 4.39 (s, 4H); **^{13}C NMR (126 MHz,**

Chloroform - *d*) δ 162.3 (d, *J* = 247.0 Hz), 159.5, 133.0, 132.9, 129.0, 128.9, 115.8, 115.7, 49.7; **^{19}F NMR (376 MHz, Chloroform - *d*)** δ -114.8; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}F_2N_2O$ $[M + H]^+$: 277.1147, found: 277.1140.



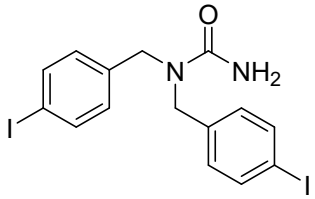
1,1-bis(4-chlorobenzyl)urea (4l)

White solid; 54 mg, 87% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.33 - 7.30 (m, 4H), 7.18 - 7.16 (m, 4H), 4.59 (s, 2H), 4.43 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.1, 135.6, 133.7, 129.2, 128.7, 50.0; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}Cl_2N_2O$ $[M + H]^+$: 309.0556, found: 309.0548.



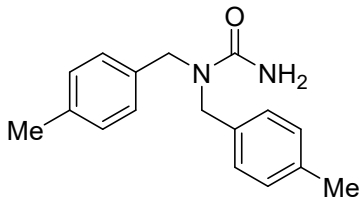
1,1-Bis(4-bromobenzyl)urea (4m)

White solid; 70 mg, 88% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.46 - 7.43 (m, 4H), 7.09 (d, *J* = 8.5 Hz, 4H), 4.89 (s, 2H), 4.38 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.3, 136.1, 132.2, 129.0, 121.7, 49.9; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}Br_2N_2O$ $[M + H]^+$: 396.9546, found: 396.9538.



1,1-Bis(4-iodobenzyl)urea (4n)

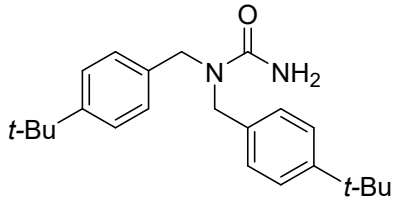
White solid; 83 mg, 84% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.66 (d, *J* = 7.5 Hz, 4H), 7.97 (d, *J* = 8.0 Hz, 4H), 4.63 (s, 2H), 4.39 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.1, 138.1, 136.8, 129.3, 93.2, 50.2; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}I_2N_2O$ $[M + H]^+$: 492.9268, found: 492.9255.



1,1-Bis(4-methylbenzyl)urea (4o)

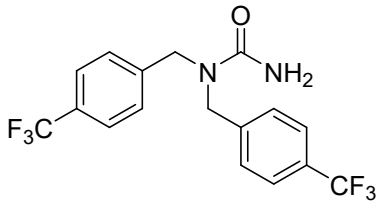
White solid; 45 mg, 84% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.16 - 7.12 (m, 8H), 4.63 (s, 2H), 4.44 (s, 4H), 2.34 (s, 6H); **^{13}C NMR (126 MHz, Chloroform -**

d) δ 159.5, 137.3, 134.4, 129.6, 127.4, 50.2, 21.2; **HRMS (ESI)**: m/z calcd for $C_{17}H_{20}N_2O$ [M + H] $^+$: 269.1648, found: 269.1642.



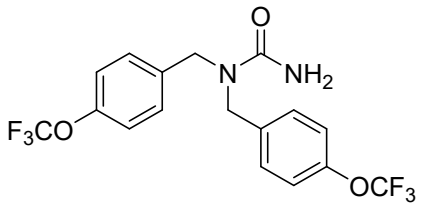
1,1-Bis(4-(*tert*-butyl)benzyl)urea (4p)

White solid; 57 mg, 81% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.38 - 7.35 (m, 4H), 7.19 (d, *J* = 8.5 Hz, 4H), 4.81 (s, 2H), 4.47 (s, 4H), 1.33 (s, 18H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.7, 150.5, 134.4, 127.1, 125.8, 50.2, 34.6, 31.5; **HRMS (ESI)**: m/z calcd for $C_{23}H_{32}N_2O$ [M + H] $^+$: 353.2587, found: 353.2580.



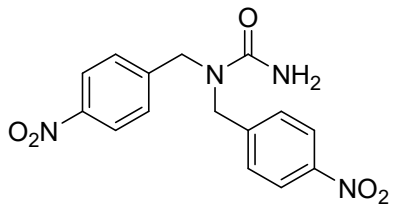
1,1-Bis(4-(trifluoromethyl)benzyl)urea (4q)

White solid; 62 mg, 82% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.59 (d, *J* = 8.0 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 4.91 (s, 2H), 4.53 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.3, 141.2, 130.3 (q, *J* = 32.8 Hz), 127.6, 126.0 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.2 Hz), 50.4; **^{19}F NMR (376 MHz, Chloroform - *d*)** δ -62.6; **HRMS (ESI)**: m/z calcd for $C_{17}H_{14}F_6N_2O$ [M + H] $^+$: 377.1083, found: 377.1075.



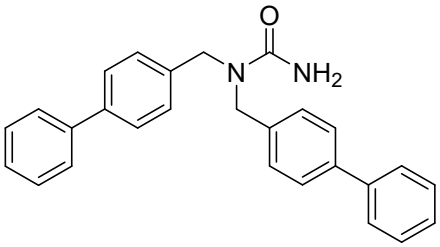
1,1-Bis(4-(trifluoromethoxy)benzyl)urea (4r)

White solid; 65 mg, 80% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.27 (d, *J* = 8.5 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 4H), 4.92 (s, 2H), 4.49 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.3, 148.8 (q, *J* = 2.1 Hz), 135.9, 128.7, 121.5 (q, *J* = 258.3 Hz), 50.0; **^{19}F NMR (126 MHz, Chloroform - *d*)** δ -58.0; **HRMS (ESI)**: m/z calcd for $C_{17}H_{14}F_6N_2O_3$ [M + H] $^+$: 409.0981, found: 409.0972.



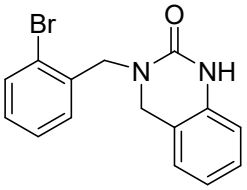
1,1-Bis(4-nitrobenzyl)urea (4s)

Brown solid; 52 mg, 79% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 8.22 - 8.19 (m, 4H), 7.42 (d, *J* = 8.5 Hz, 4H), 4.72 (s, 2H), 4.60 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 158.7, 147.8, 144.3, 128.0, 124.4, 50.5; **HRMS (ESI)**: m/z calcd for $C_{15}H_{14}N_4O_5$ $[M + H]^+$: 331.1037, found: 331.1029.



1,1-Bis([1,1'-biphenyl]-4-ylmethyl)urea (4t)

White solid; 63 mg, 80% yield; **^{1}H NMR (500 MHz, Chloroform - *d*)** δ 7.60 - 7.58 (m, 8H), 7.47 - 7.44 (m, 4H), 7.38 - 7.35 (m, 6H), 4.76 (s, 2H), 4.58 (s, 4H); **^{13}C NMR (126 MHz, Chloroform - *d*)** δ 159.5, 140.8, 140.7, 136.4, 128.9, 127.8, 127.7, 127.5, 127.2, 50.4; **HRMS (ESI)**: m/z calcd for $C_{27}H_{24}N_2O$ $[M + H]^+$: 393.1961, found: 393.1952.

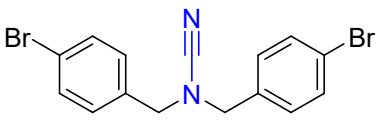


3-(2-Bromobenzyl)-3,4-dihydroquinazolin-2(*1H*)-one (5a)

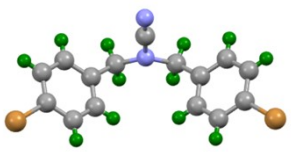
White solid; 51 mg, 80% yield; **^{1}H NMR (500 MHz, DMSO - d_6)** δ 9.41 (s 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.27 - 7.22 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.88 - 6.83 (m, 2H), 4.60 (s, 2H), 4.42 (s, 2H); **^{13}C NMR (126 MHz, DMSO - d_6)** δ 153. 6, 137.5, 136.0, 132.7, 129.1, 128.2, 128.0, 127.9, 125.6, 122.6, 121.1, 117.5, 113.4, 49.8, 48.1; **HRMS (ESI)**: m/z calcd for $C_{15}H_{13}BrN_2O$ $[M + H]^+$: 317.0284, found: 317.0280.

4. X-raySpectra

Single crystal data for compound 3m

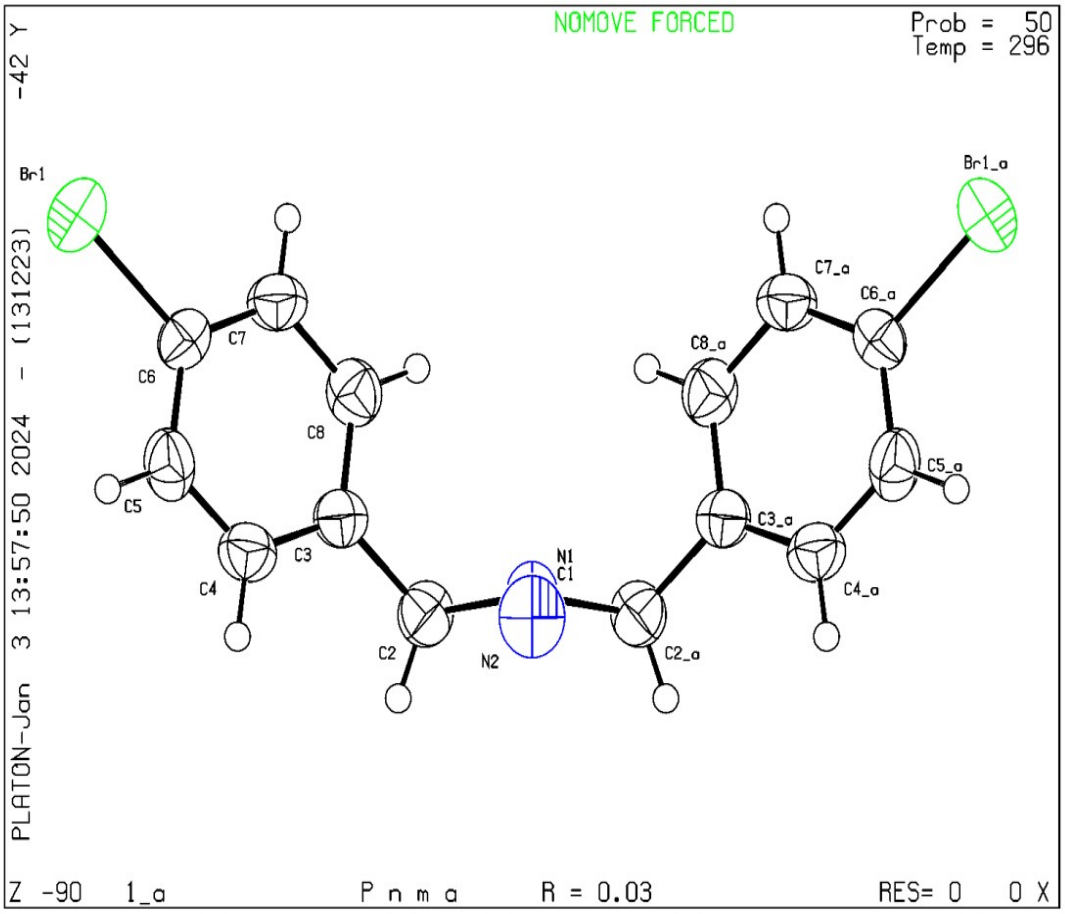


3m



3m X-ray(CCDC 2324482)

Datablock 1_a - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1_a

```
Bond precision:   C-C = 0.0050 A          Wavelength=0.71073

Cell:               a=11.438(12)       b=25.58(3)      c=4.893(5)
                    alpha=90           beta=90         gamma=90
Temperature:        296 K

                 Calculated                Reported
Volume           1432(3)                   1432(3)
Space group      P n m a                   P n m a
Hall group       -P 2ac 2n                 -P 2ac 2n
Moiety formula   C15 H12 Br2 N2            ?
Sum formula      C15 H12 Br2 N2            C15 H12 Br2 N2
Mr               380.07                    380.09
Dx,g cm-3        1.763                     1.763
Z                4                         4
Mu (mm-1)        5.648                     5.649
F000             744.0                     744.0
F000'            742.04
h,k,lmax         13,30,5                   13,30,5
Nref             1275                      1261
Tmin,Tmax        0.513,0.636               0.864,0.864
Tmin'            0.503

Correction method= # Reported T Limits: Tmin=0.864 Tmax=0.864
AbsCorr = MULTI-SCAN

Data completeness= 0.989           Theta(max)= 24.883

R(reflections)= 0.0298( 893)                    wR2(reflections)=
                                                0.0626( 1261)
S = 1.068                  Npar= 91
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The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

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PLAT148_ALERT_3_C s.u. on the      a    - Axis is (Too) Large ....      0.012 Ang.
PLAT148_ALERT_3_C s.u. on the      b    - Axis is (Too) Large ....     0.0300 Ang.
PLAT148_ALERT_3_C s.u. on the      c    - Axis is (Too) Large ....      0.005 Ang.
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Alert level G

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PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          6 Note
                6  1  2,   4  1  3,   3  1  1,   9  1  1,   6  1  0,   3  1  3,
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged     Please Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   3 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

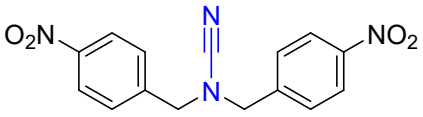
Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

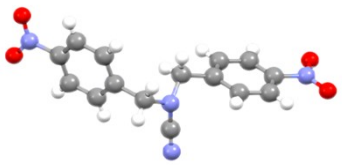
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

Single crystal data for compound 3s

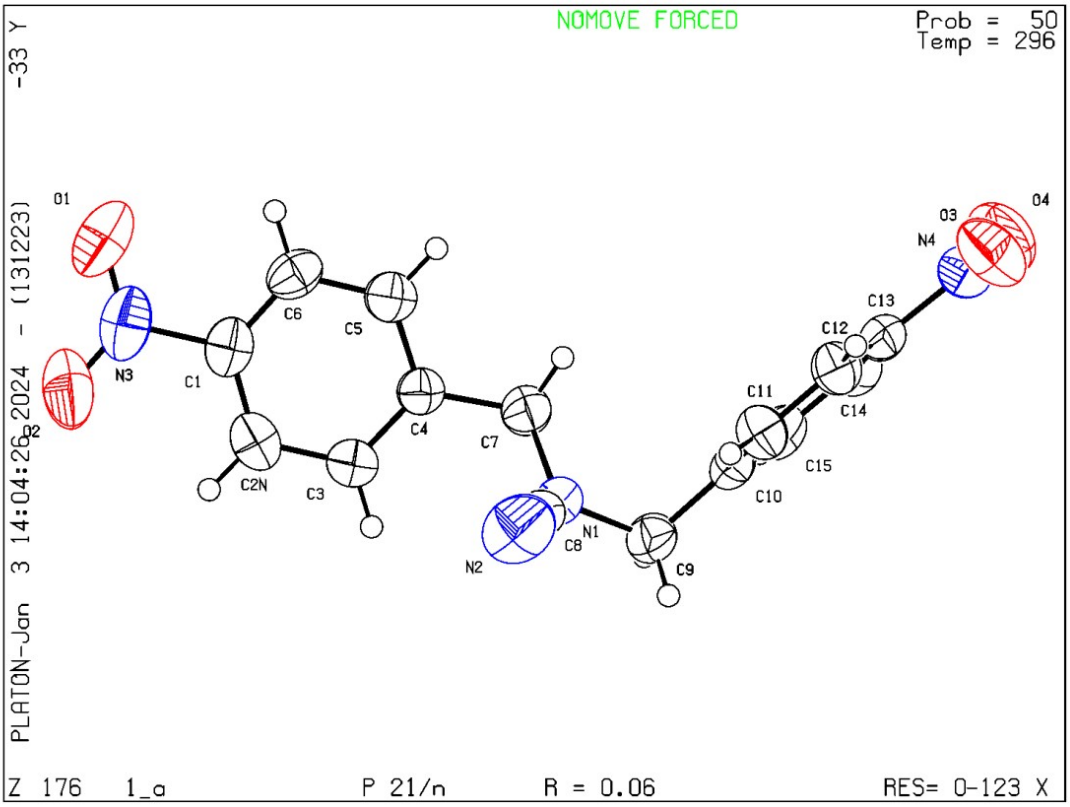


3s



3s X-ray(CCDC 2324486)

Datablock 1_a - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1_a

Bond precision: C-C = 0.0049 A Wavelength=0.71073

Cell:	a=9.0138(8)	b=13.9046(14)	c=11.9428(13)
	alpha=90	beta=100.927(2)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	1469.7(3)	1469.7(3)
Space group	P 21/n	P 21/n

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT026_ALERT_3_C Ratio Observed / Unique Reflections (too) Low .. 47% Check
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00486 Ang.

Alert level G

PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..... 4.9 Low
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged Please Check

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

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Publication of your CIF in other journals

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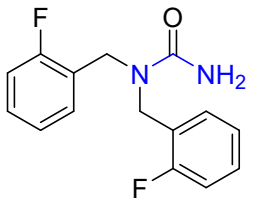
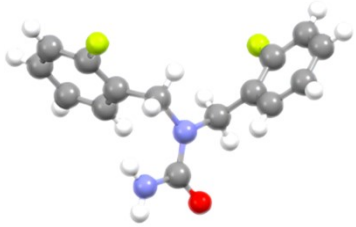
Single crystal data for compound 4b

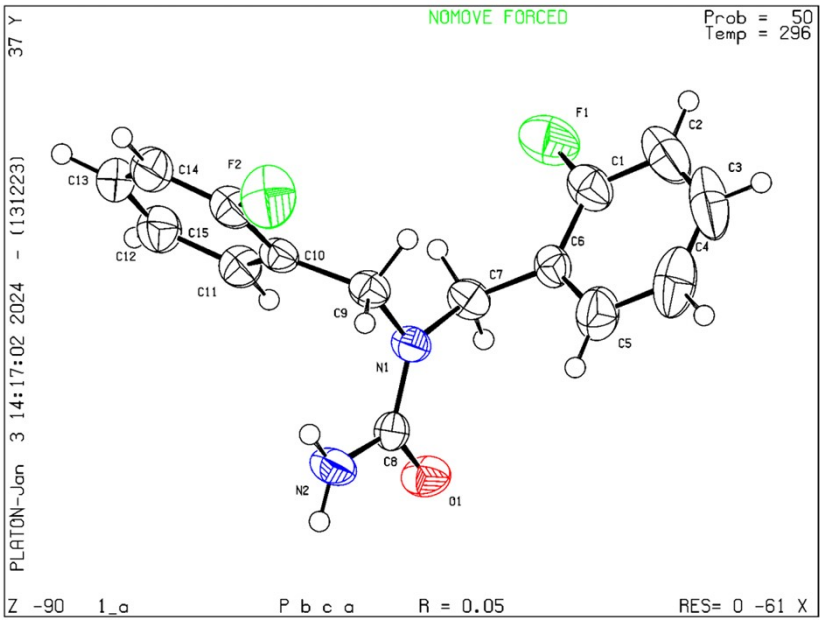


4b



4b X-ray(CCDC 2324490)

Datablock 1_a - ellipsoid plot



checkCIF/PLATON report

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1_a

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Bond precision:   C-C = 0.0035 A          Wavelength=0.71073

Cell:             a=11.6329(6)      b=7.7767(5)      c=29.3752(18)
                  alpha=90          beta=90          gamma=90
Temperature:      296 K

                  Calculated                  Reported
Volume            2657.4(3)                   2657.4(3)
Space group       P b c a                     P b c a
Hall group        -P 2ac 2ab                  -P 2ac 2ab
Moiety formula    C15 H14 F2 N2 O             ?
Sum formula       C15 H14 F2 N2 O             C15 H14 F2 N2 O
Mr                276.28                      276.28
Dx,g cm-3         1.381                       1.381
Z                 8                           8
Mu (mm-1)         0.107                       0.107
F000              1152.0                      1152.0
F000'             1152.65
h,k,lmax          13,9,34                     13,9,34
Nref              2347                        2332
Tmin,Tmax         0.977,0.981                 0.864,0.864
Tmin'             0.977

Correction method= # Reported T Limits: Tmin=0.864 Tmax=0.864
AbsCorr = MULTI-SCAN

Data completeness= 0.994          Theta(max)= 25.036

R(reflections)= 0.0508( 1743)                wR2(reflections)=
                                             0.1202( 2332)
S = 1.033                 Npar= 181
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The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
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Alert level C

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PLAT334_ALERT_2_C Small <C-C> Benzene Dist.   C1       -C6       .       1.37 Ang.
PLAT414_ALERT_2_C Short Intra D-H..H-X       H2B      ..H9B      .       1.96 Ang.
                                                    x,y,z  =      1_555 Check
```

Alert level G

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PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          2 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
              H2A   H2B
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          1 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for First Par     0.0010 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for SecondPar     0.0020 Report
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          1 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
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   3 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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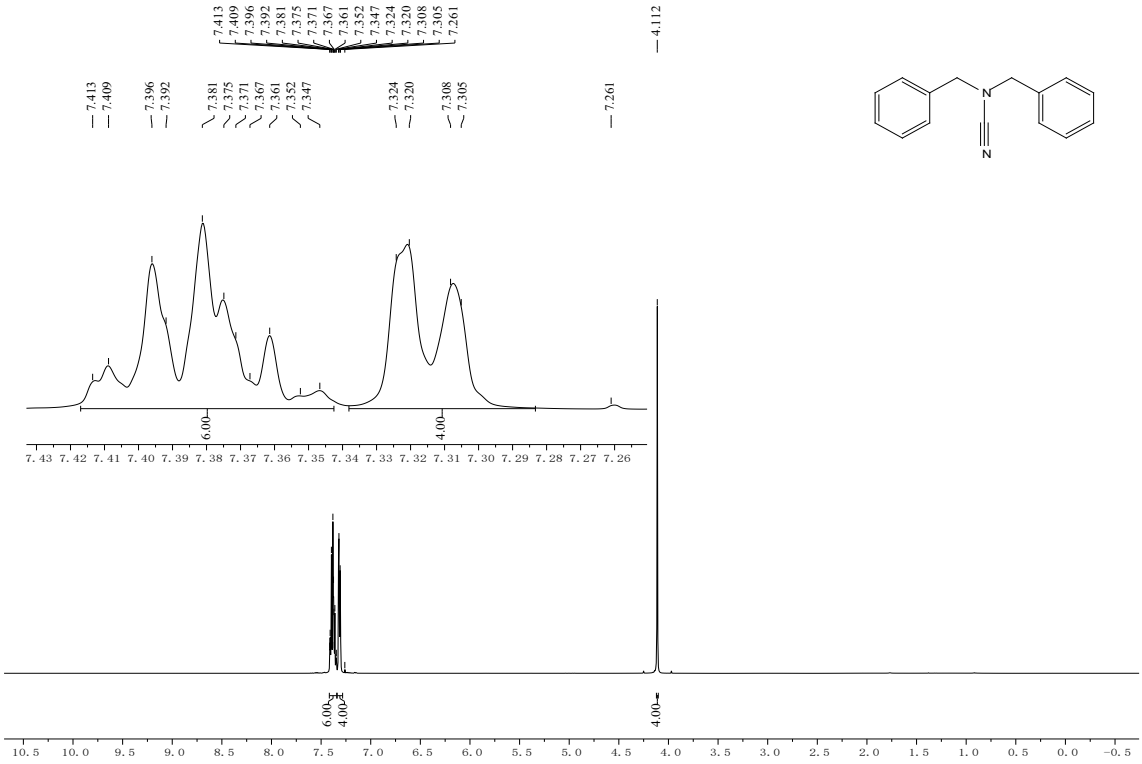
5. References

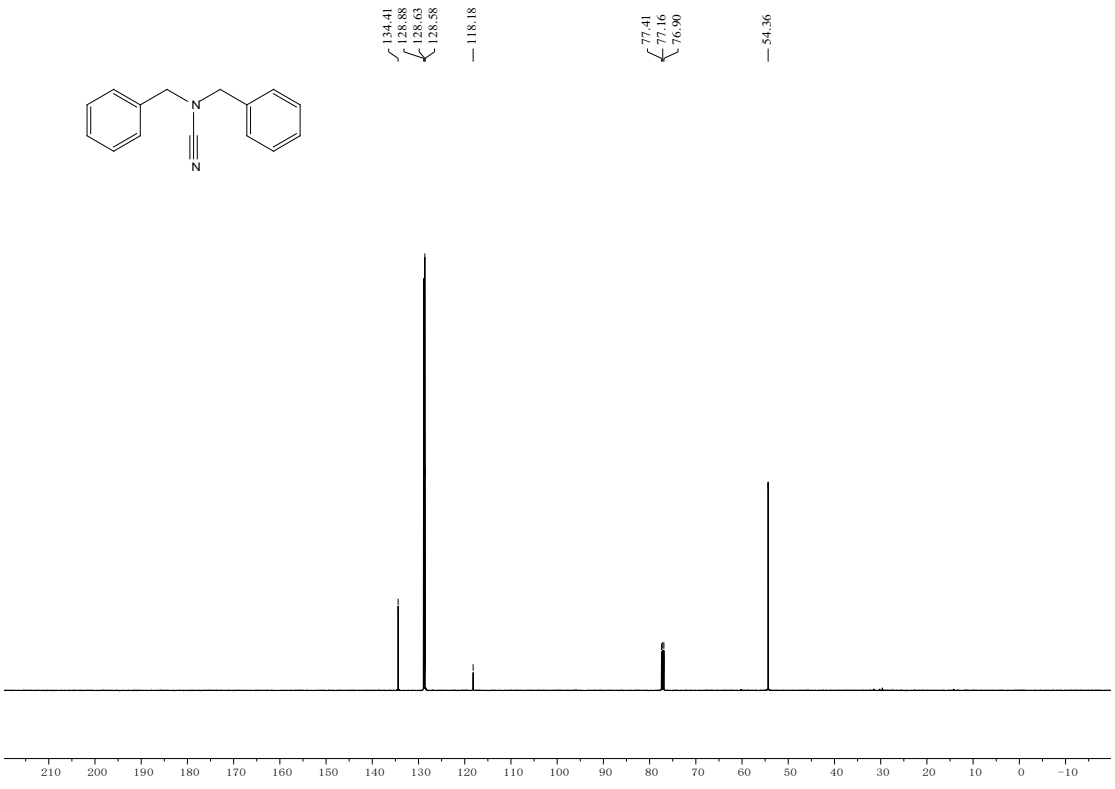
[1] L. J. Wu, Q. R. Wang, J. Guo, J. P. Guo, J. N. Wei, P. Chen and Z. F.Xi, *Angewandte Chem*, 2023, **135**, e202219298;
[2] F, Shi, M. R. Smith and R. E. Maleczka, *Organic Letters,* 2006, **8**, 1411-1414.

6. NMR spectra

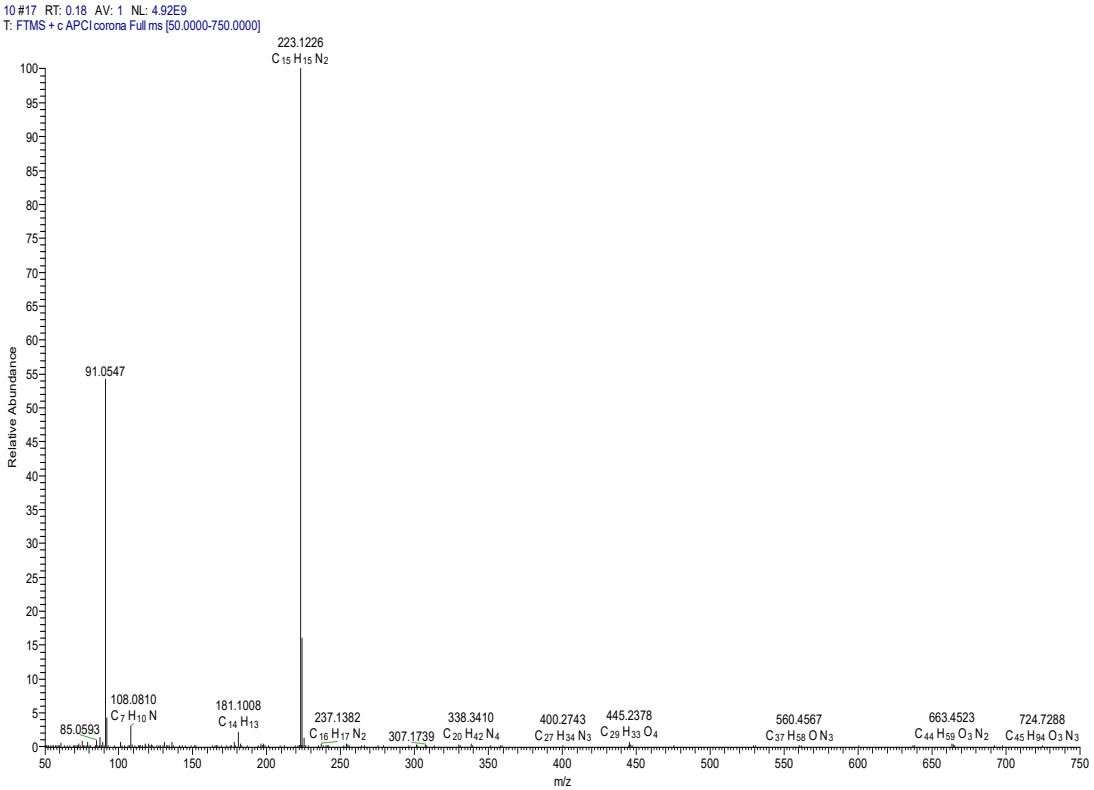
3a ^{1}H NMR (500 MHz, $CDCl_3$)



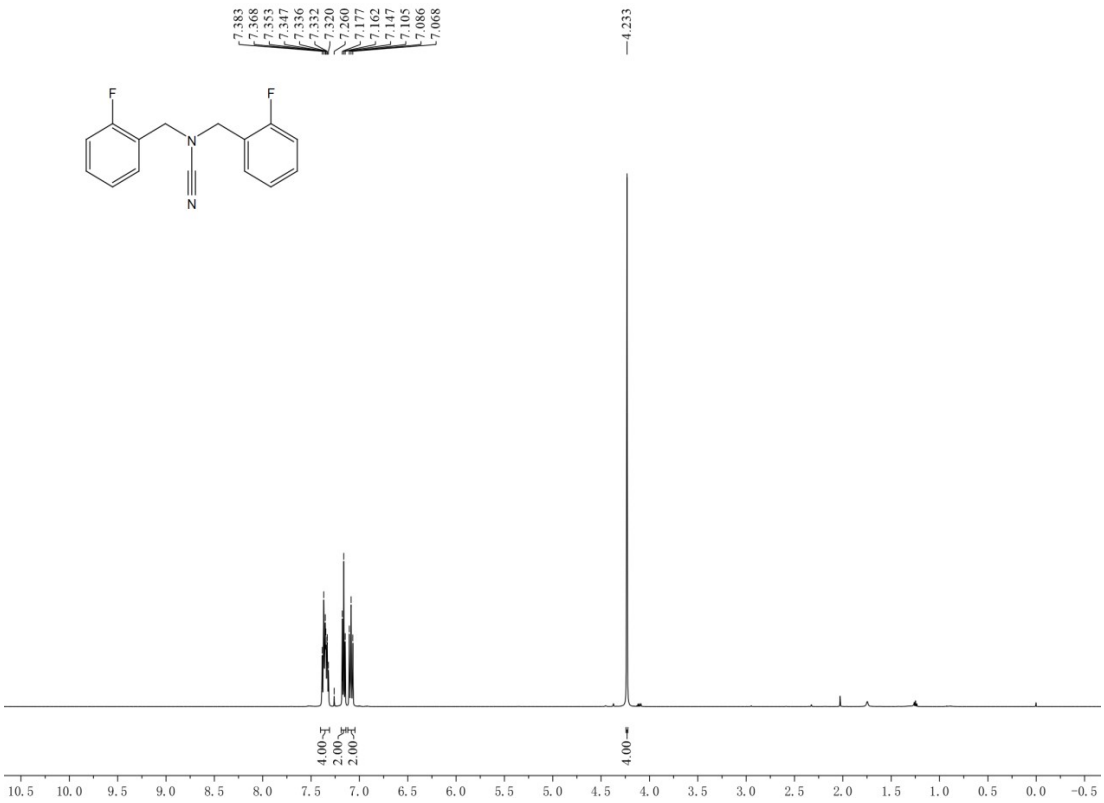
3a ^{13}C NMR (126 MHz, $CDCl_3$)



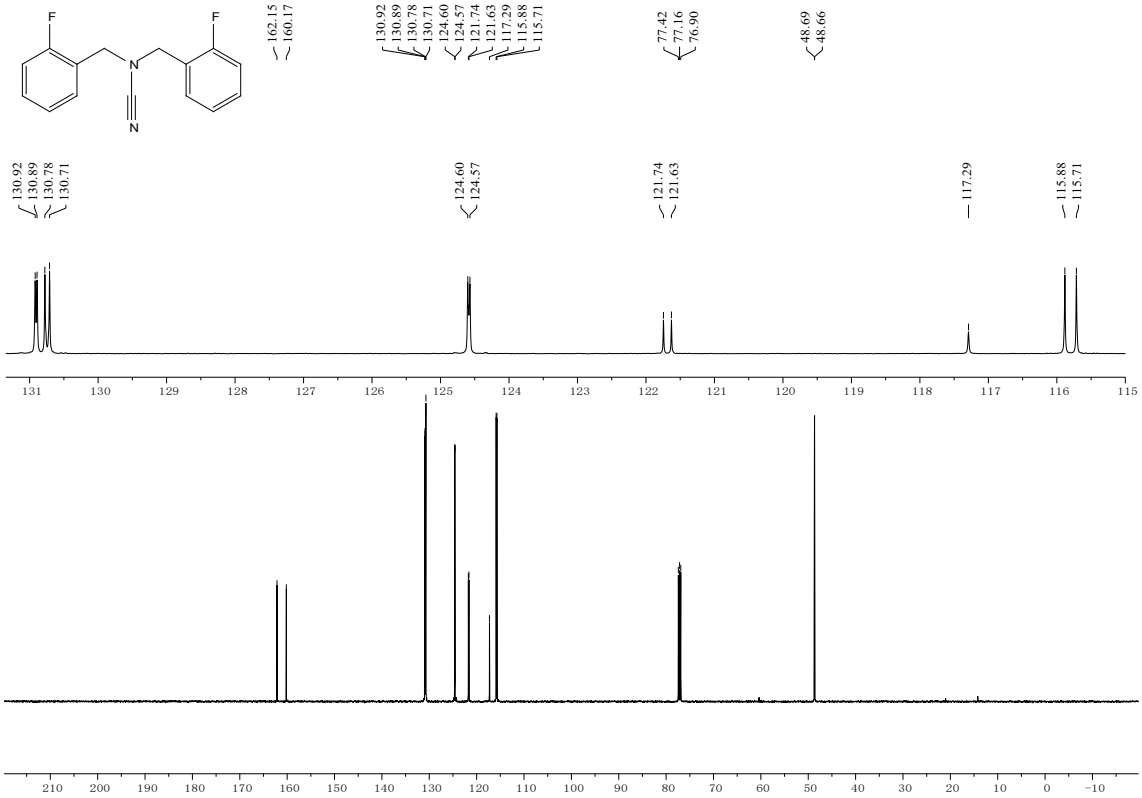
3a High Resolution Mass Spectrometry



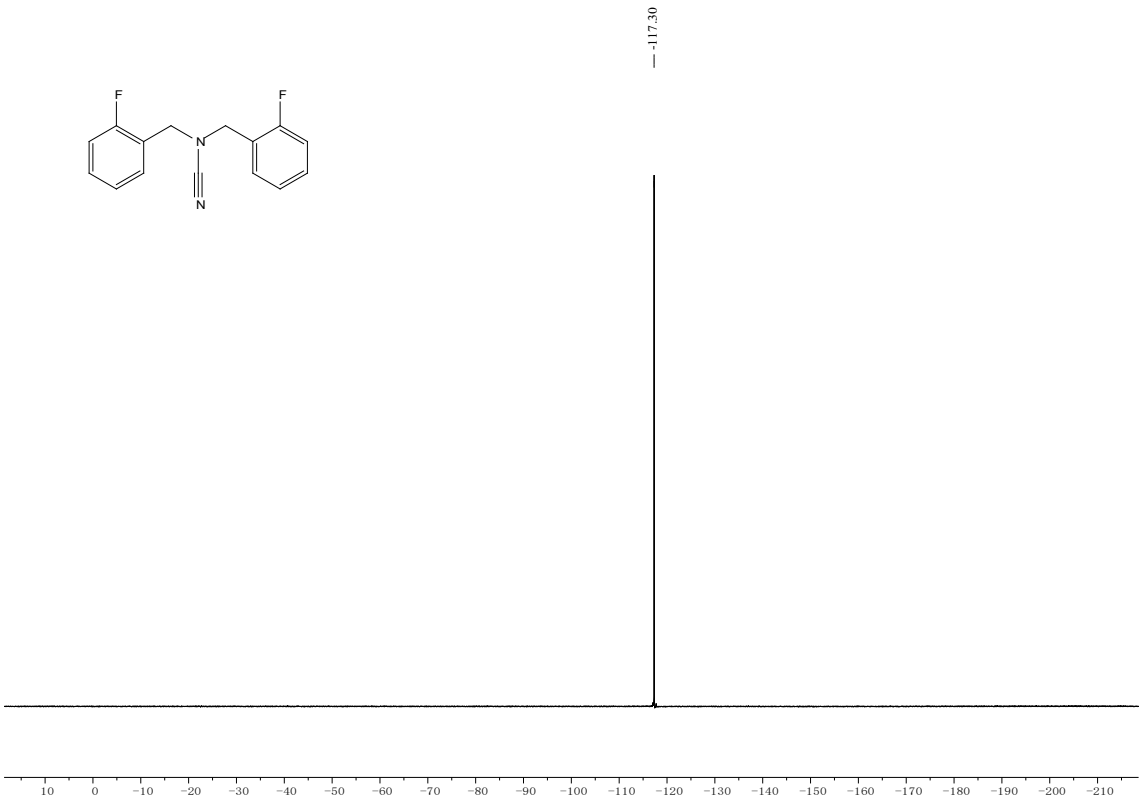
3b ^{1}H NMR (500 MHz, $CDCl_3$)



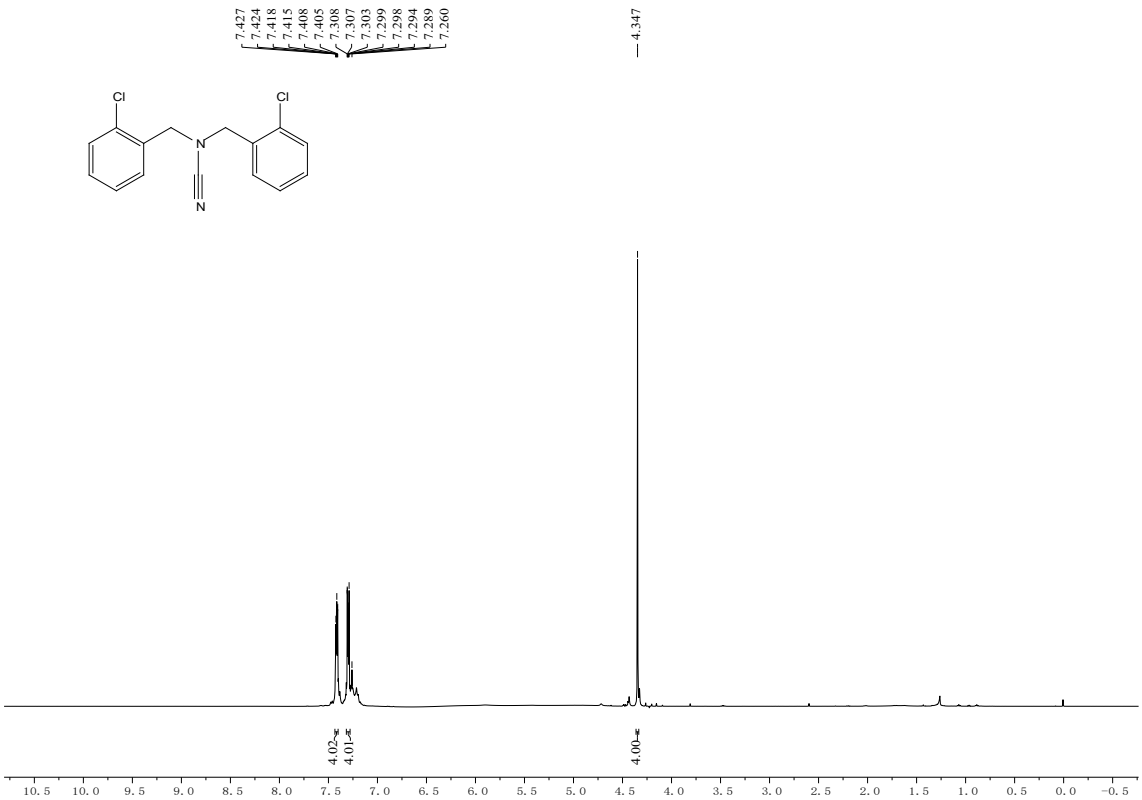
3b ^{13}C NMR (126 MHz, $CDCl_3$)



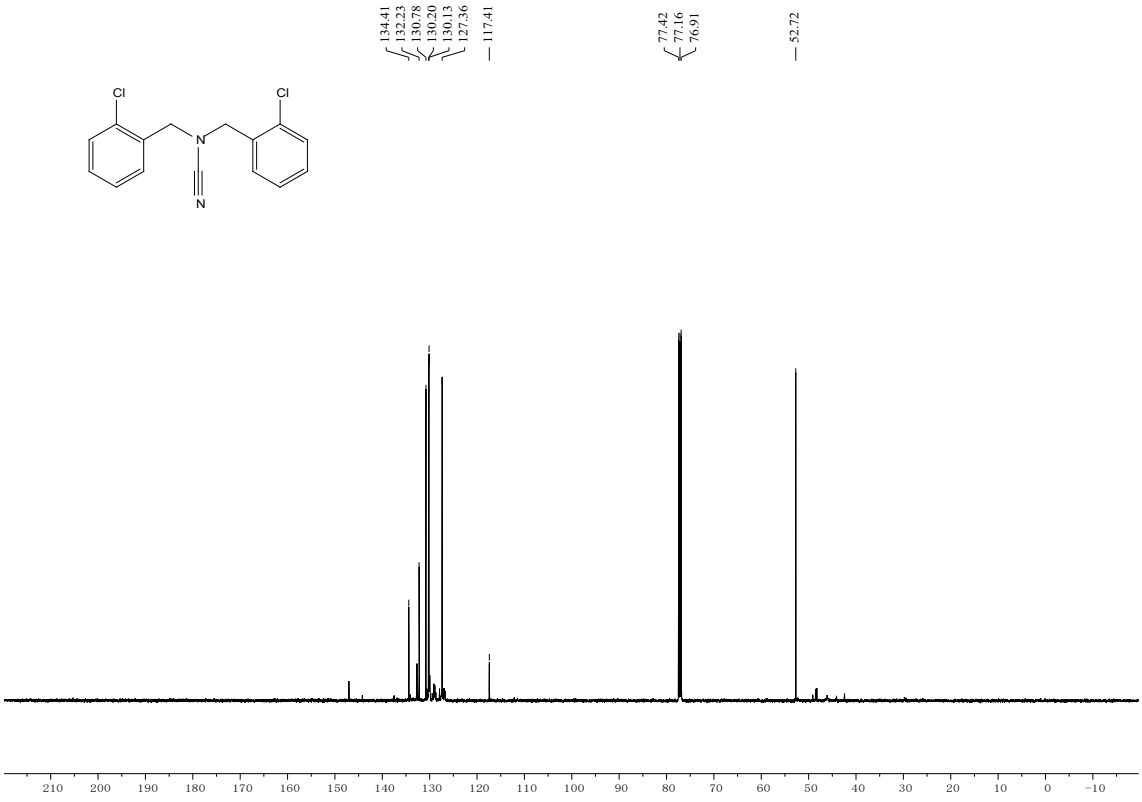
3b ^{19}F NMR (376 MHz, $CDCl_3$)



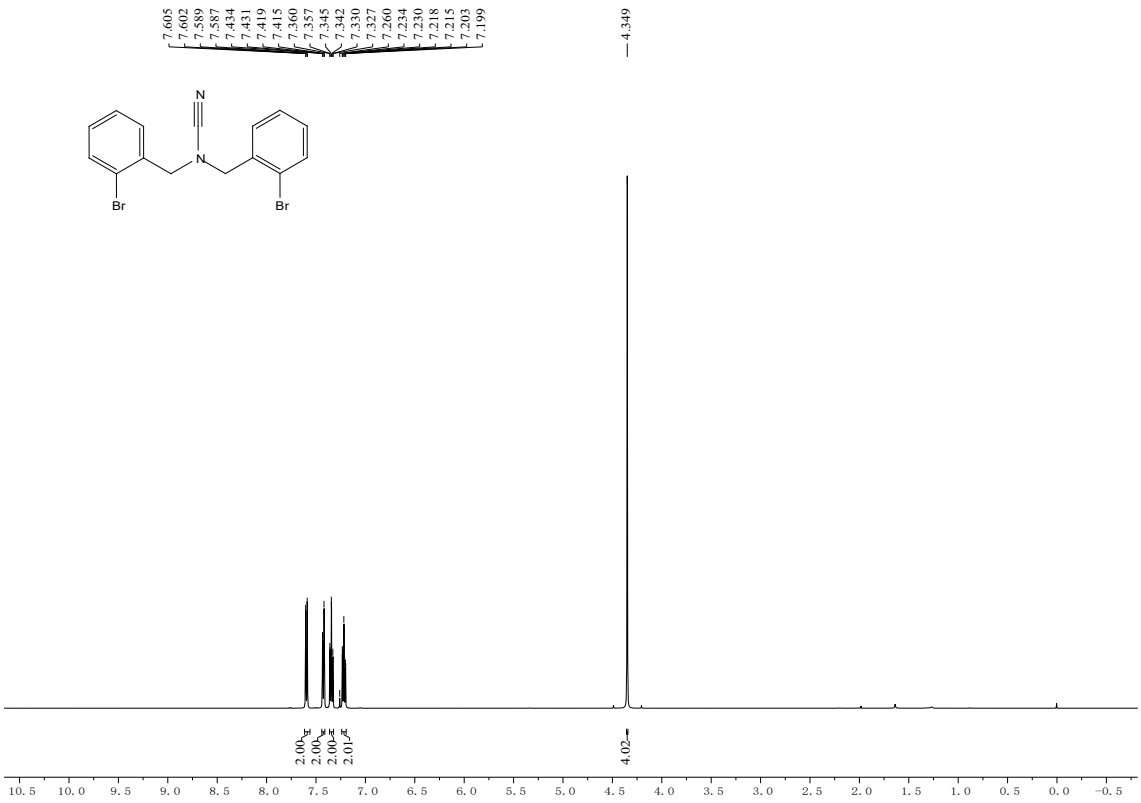
3c ^{1}H NMR (500 MHz, $CDCl_3$)



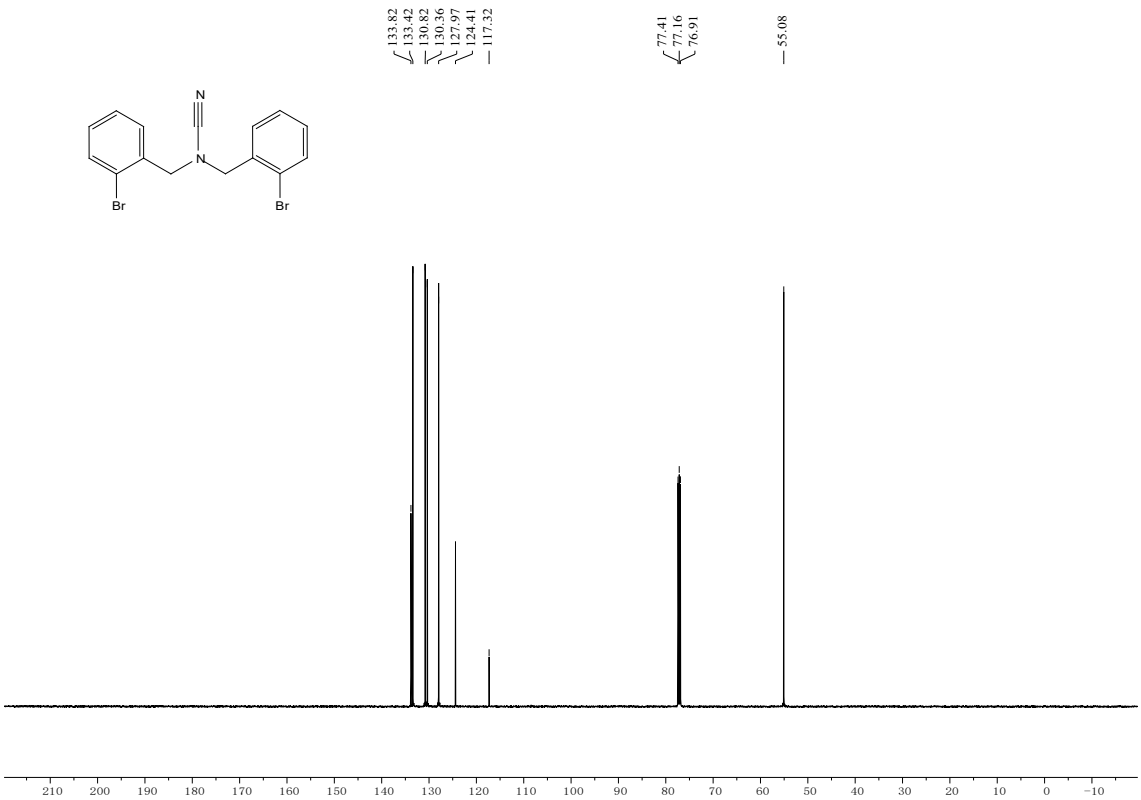
3c ^{13}C NMR (126 MHz, $CDCl_3$)



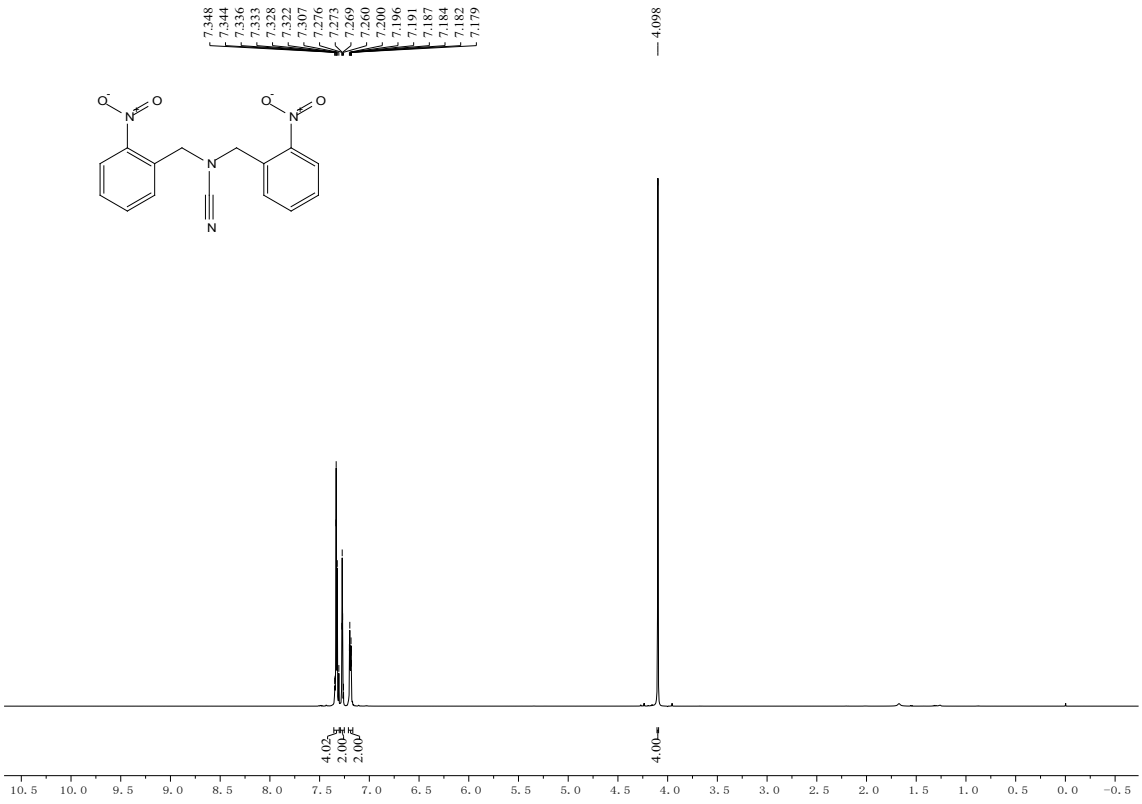
3d ^{1}H NMR (500 MHz, $CDCl_3$)



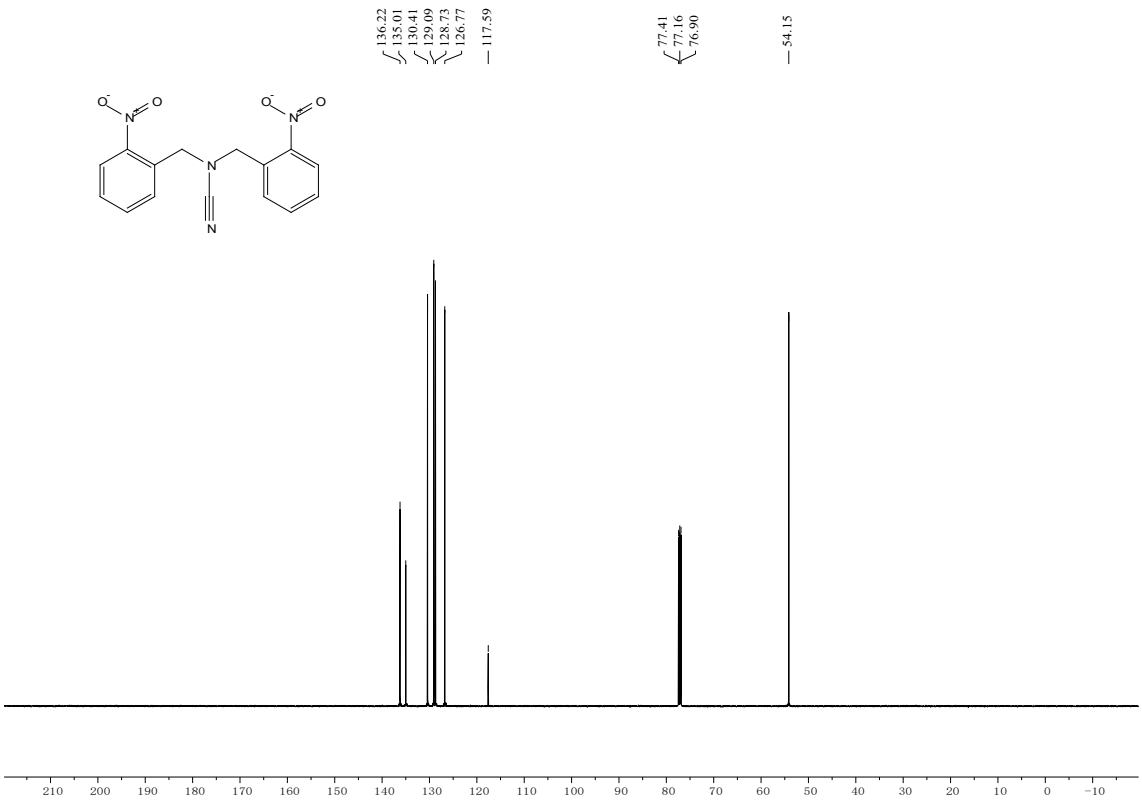
3d ^{13}C NMR (126 MHz, $CDCl_3$)



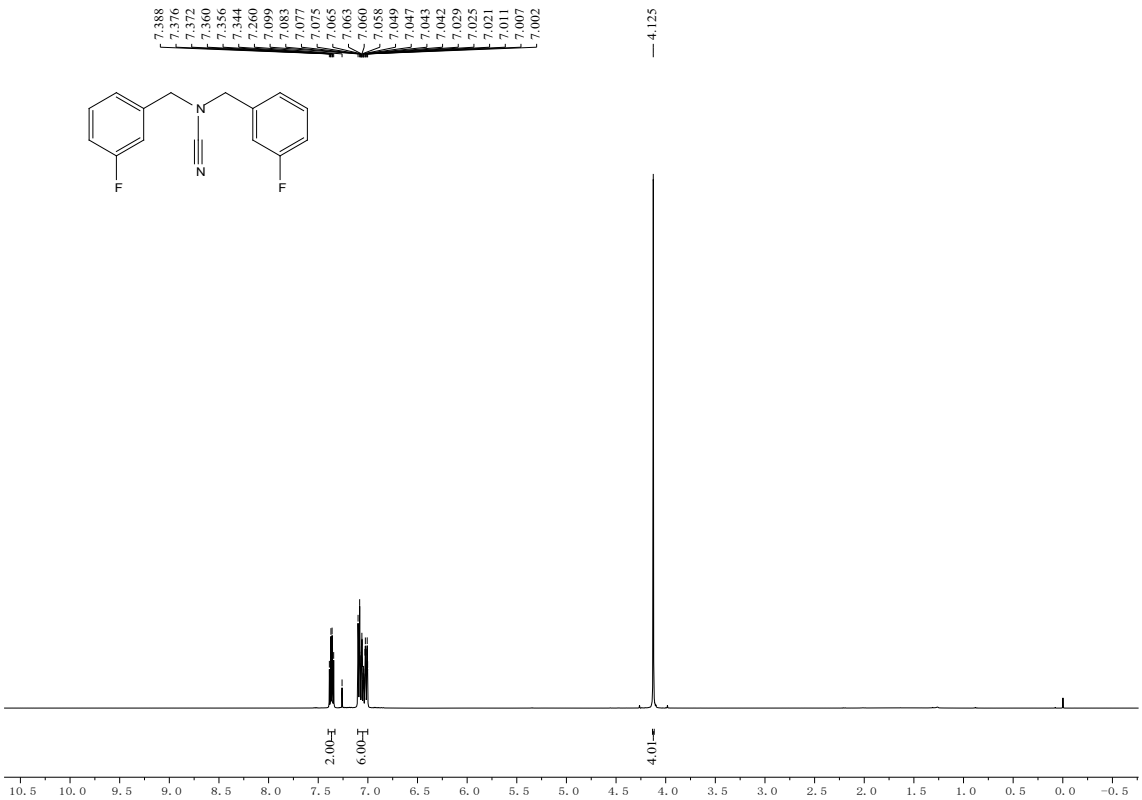
3e ^{1}H NMR (500 MHz, $CDCl_3$)



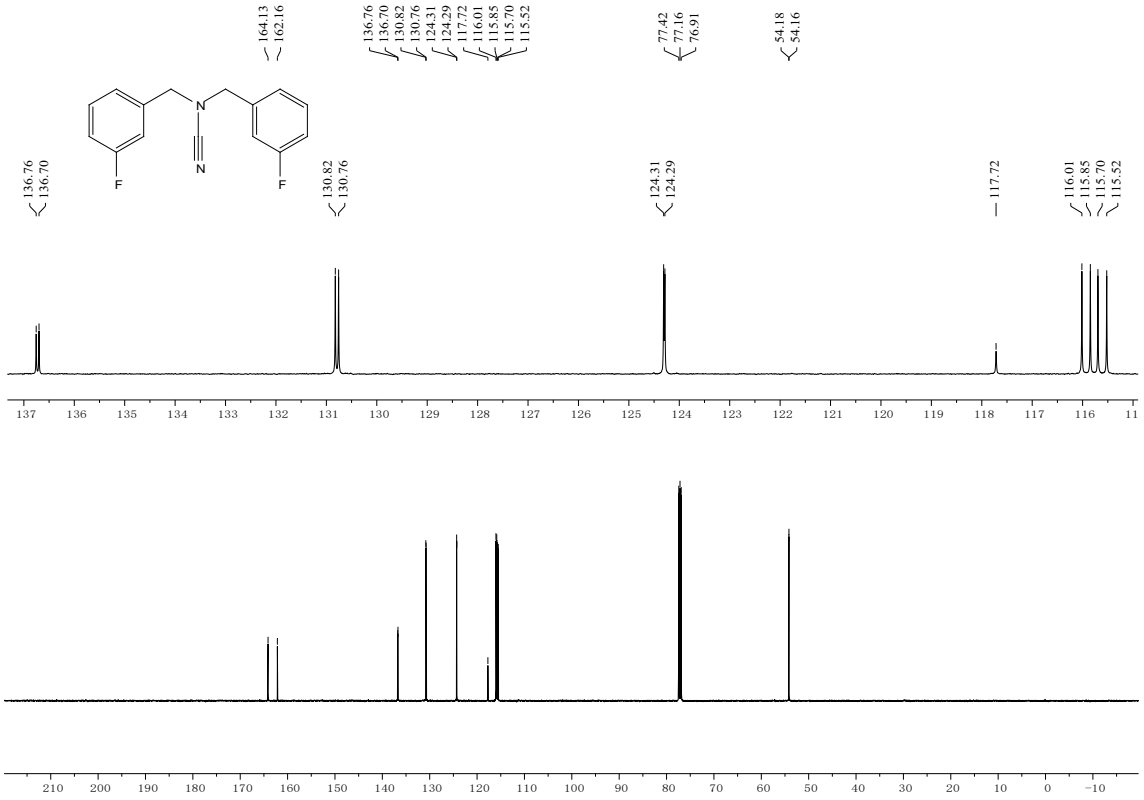
3e ^{13}C NMR (126 MHz, $CDCl_3$)



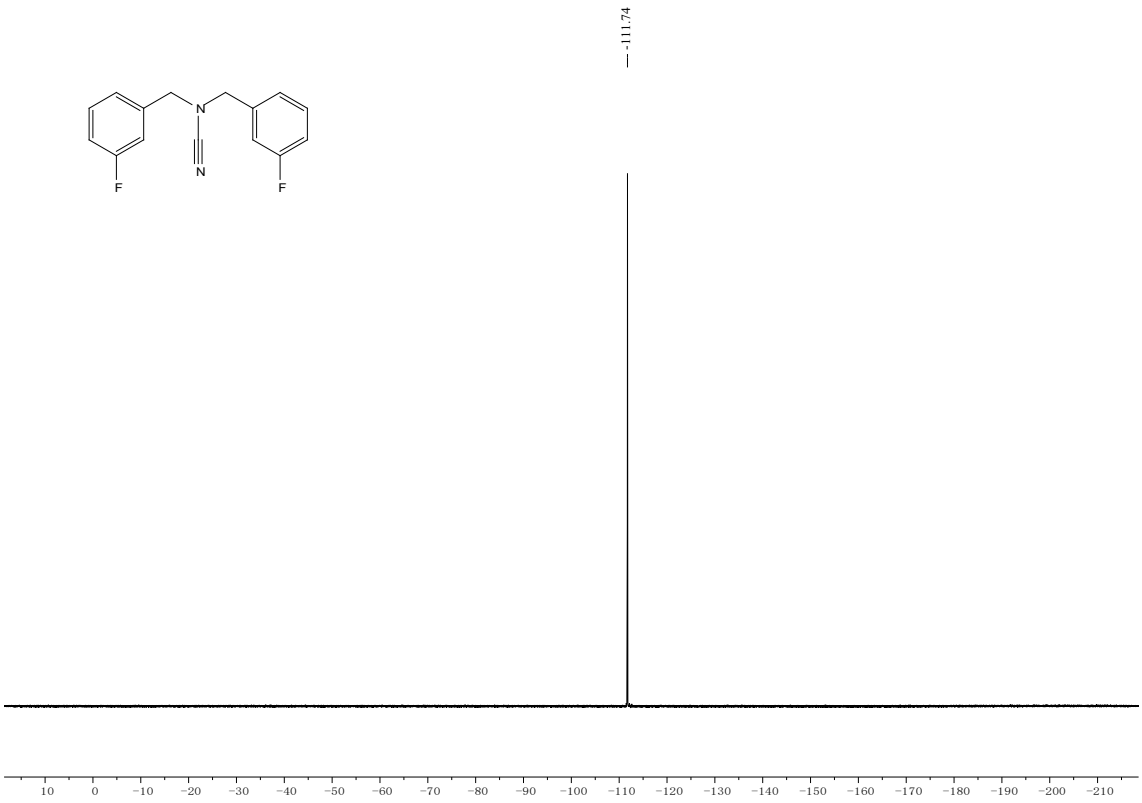
3f ^{1}H NMR (500 MHz, $CDCl_3$)



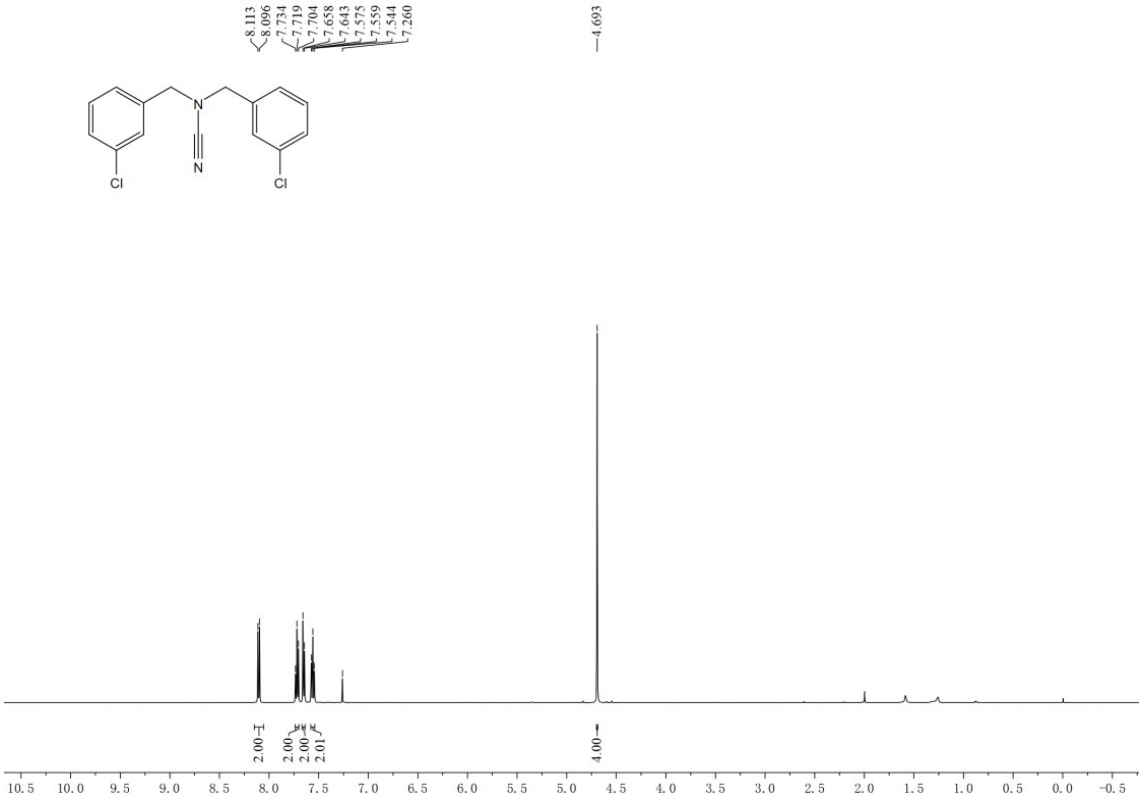
3f ^{13}C NMR (126 MHz, $CDCl_3$)



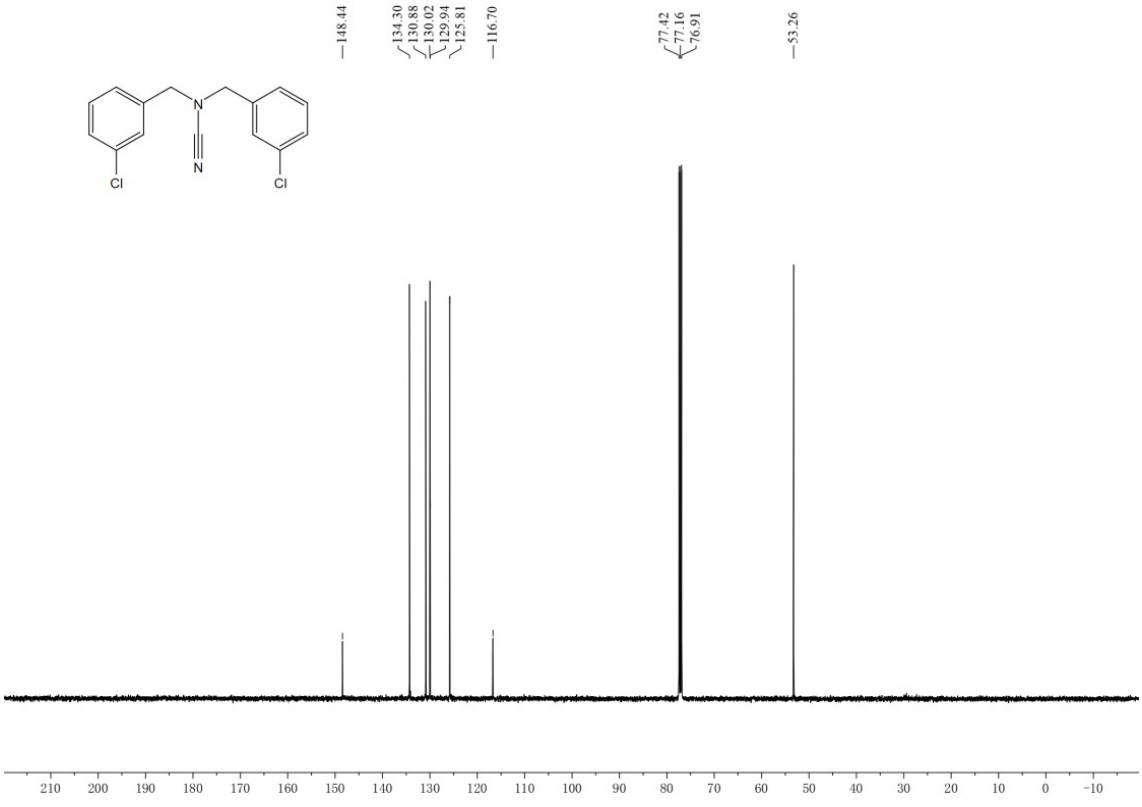
3f ^{13}F NMR (376 MHz, $CDCl_3$)



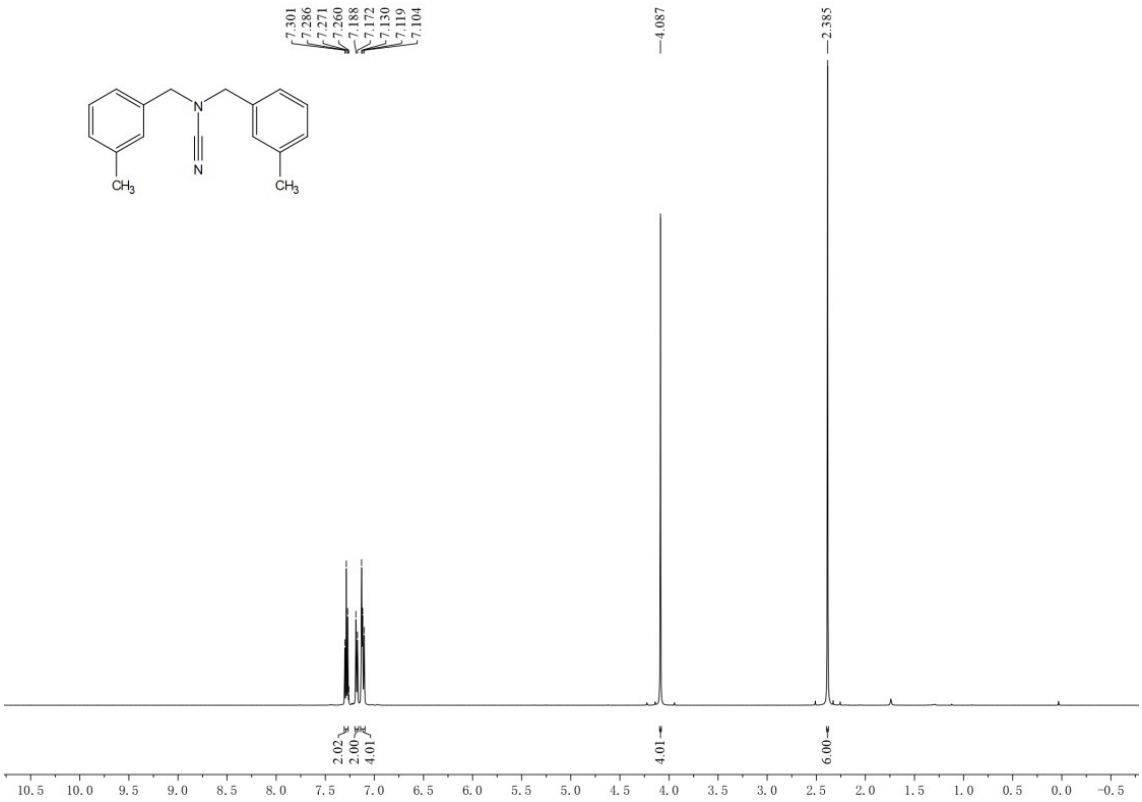
3g ^{1}H NMR (500 MHz, $CDCl_3$)



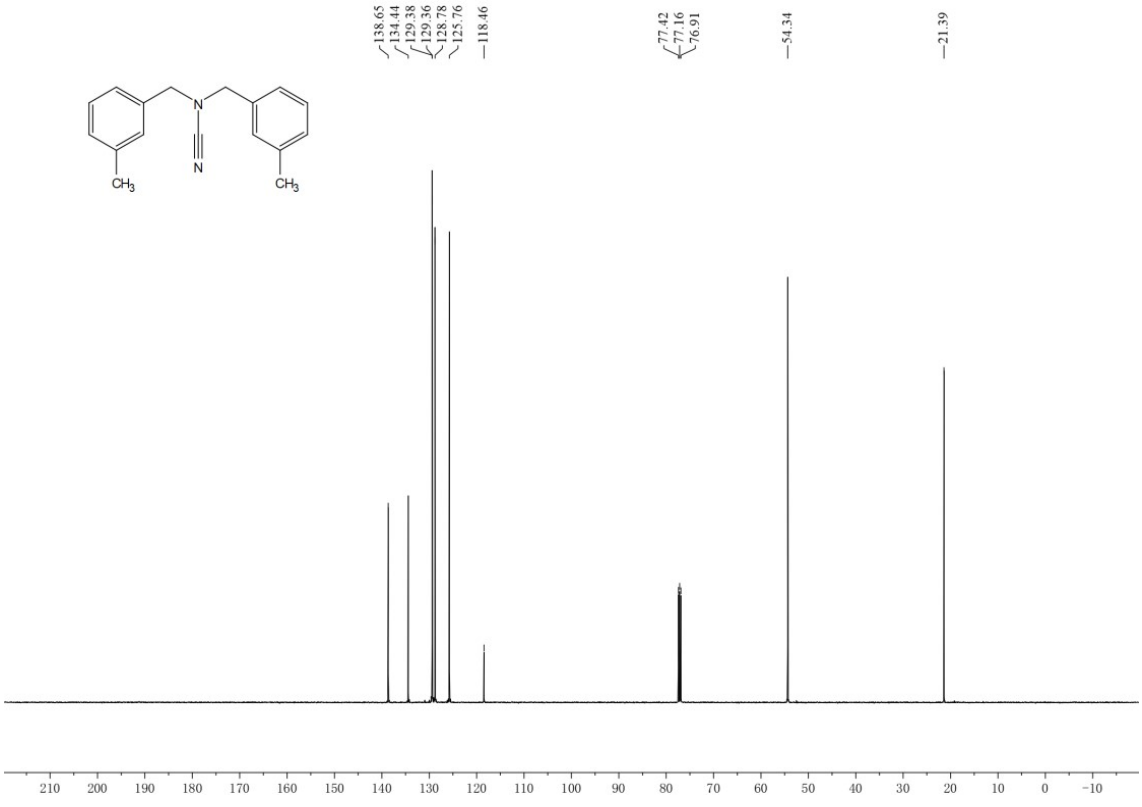
3g ^{13}C NMR (126 MHz, $CDCl_3$)



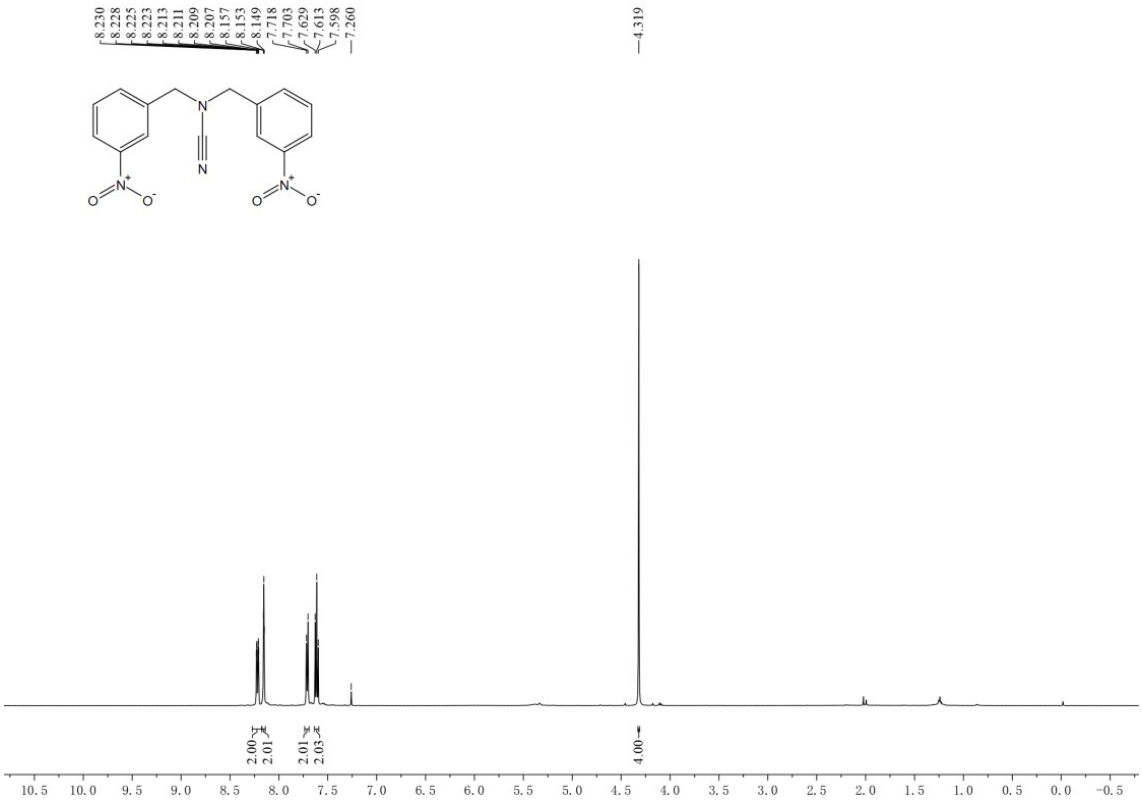
3h ^{1}H NMR (500 MHz, $CDCl_3$)



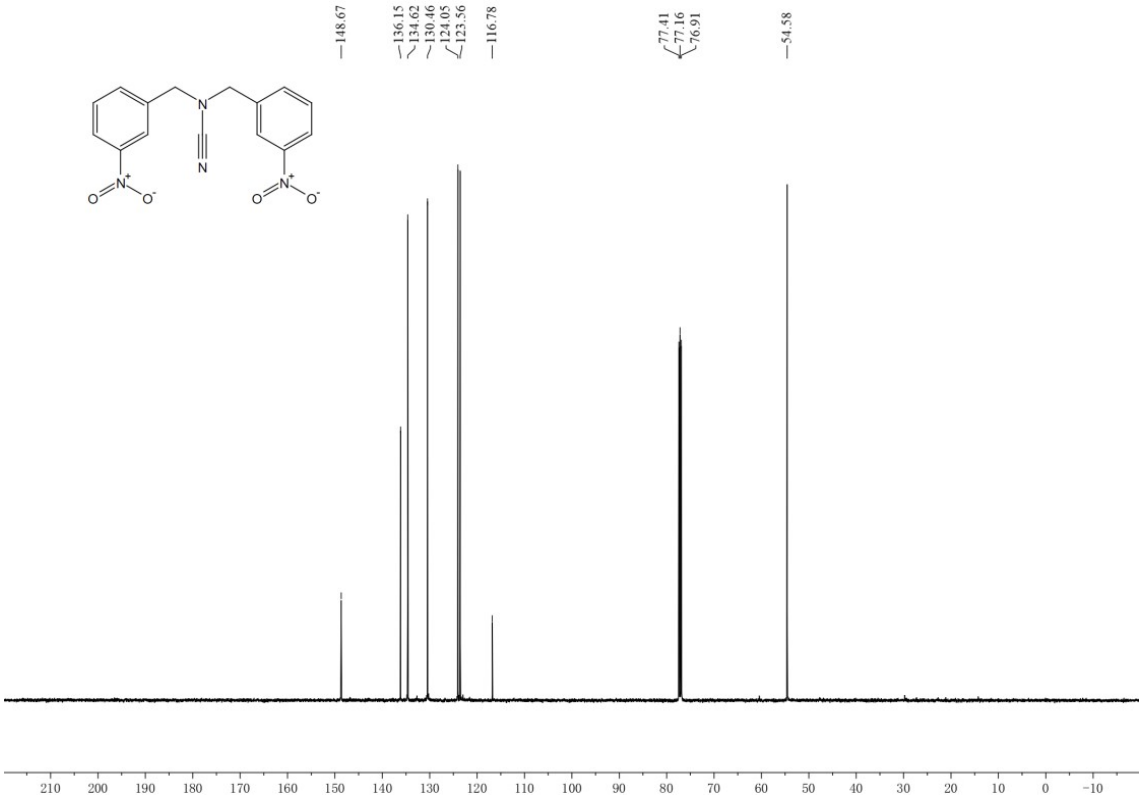
3h ^{13}C NMR (126 MHz, $CDCl_3$)



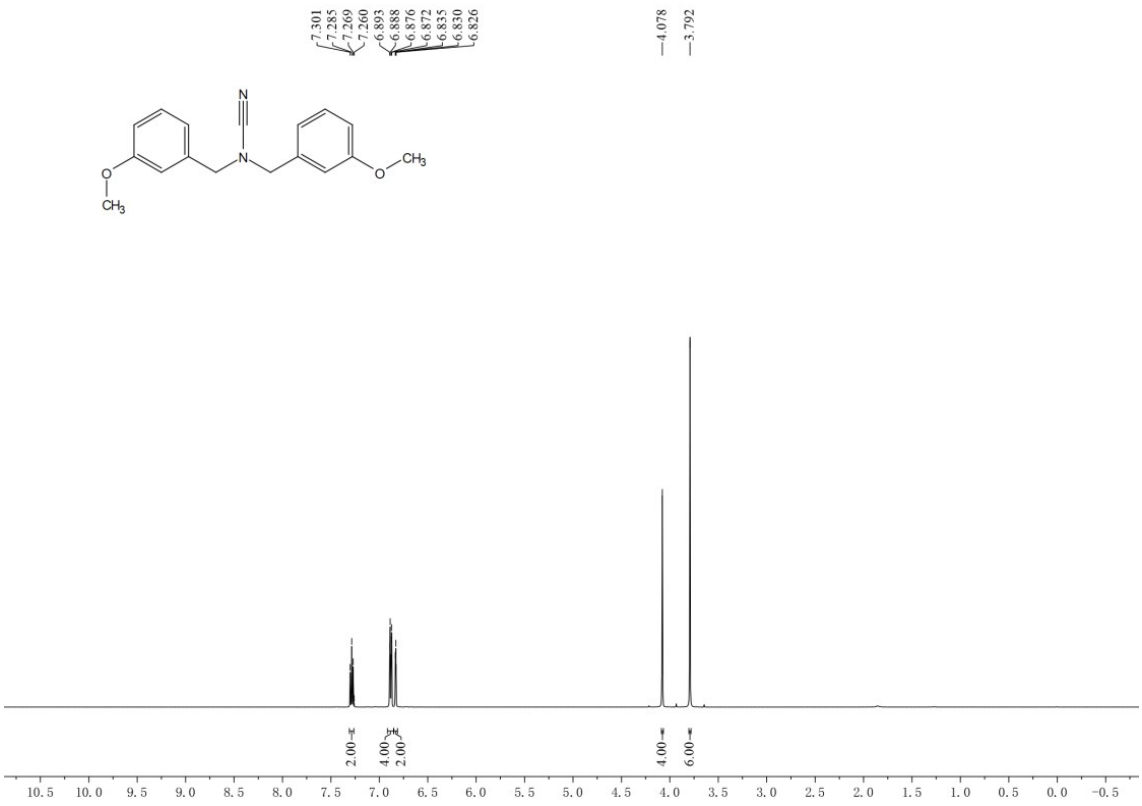
3i ^{1}H NMR (500 MHz, $CDCl_3$)



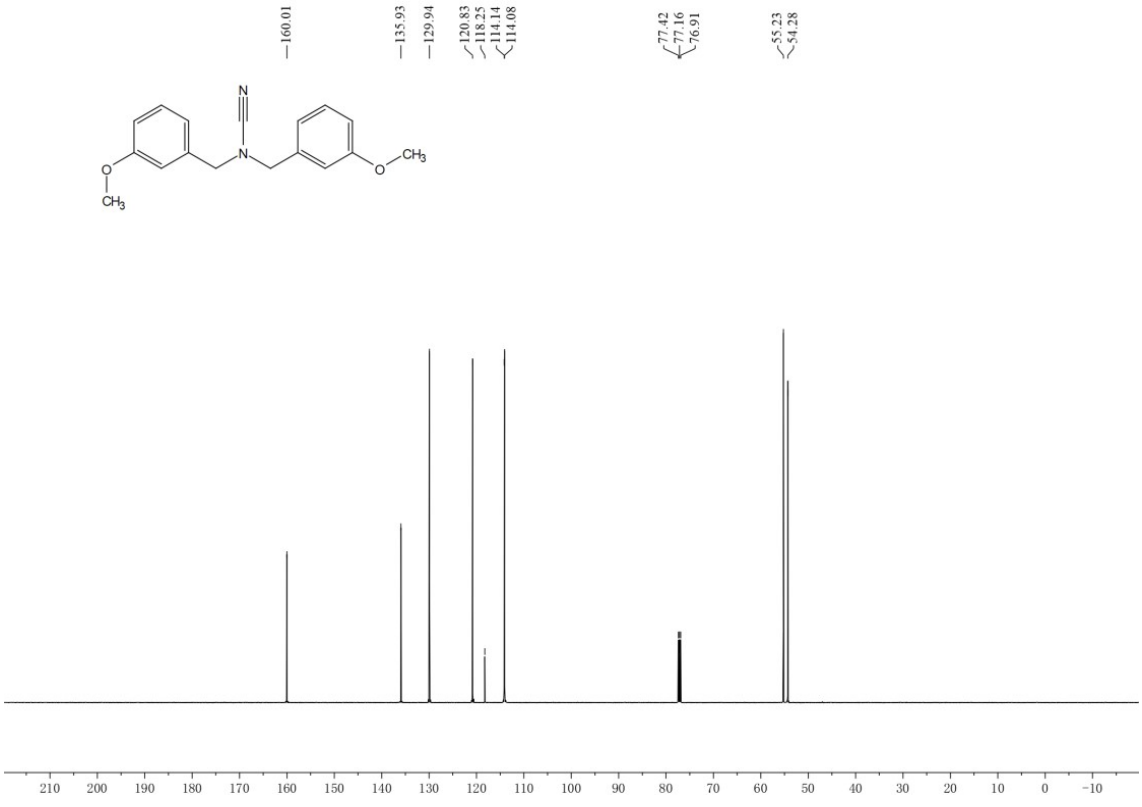
3i ^{13}C NMR (126 MHz, $CDCl_3$)



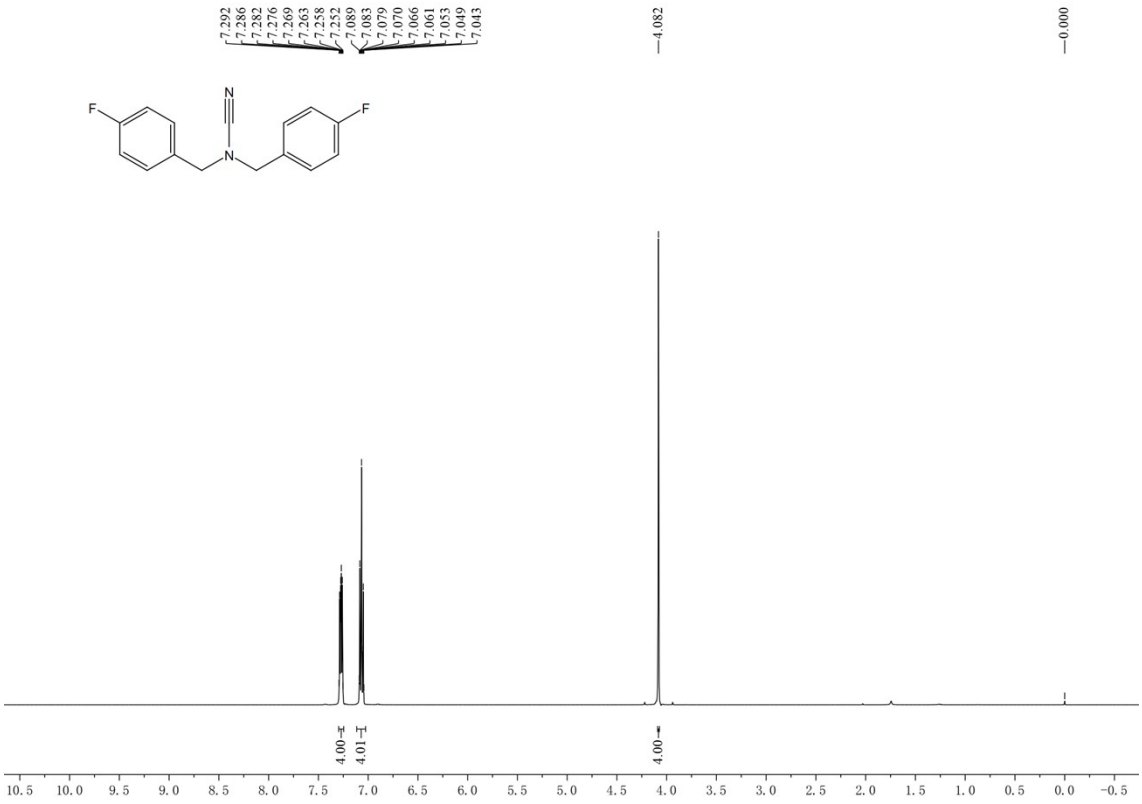
3j ^{1}H NMR (500 MHz, $CDCl_3$)



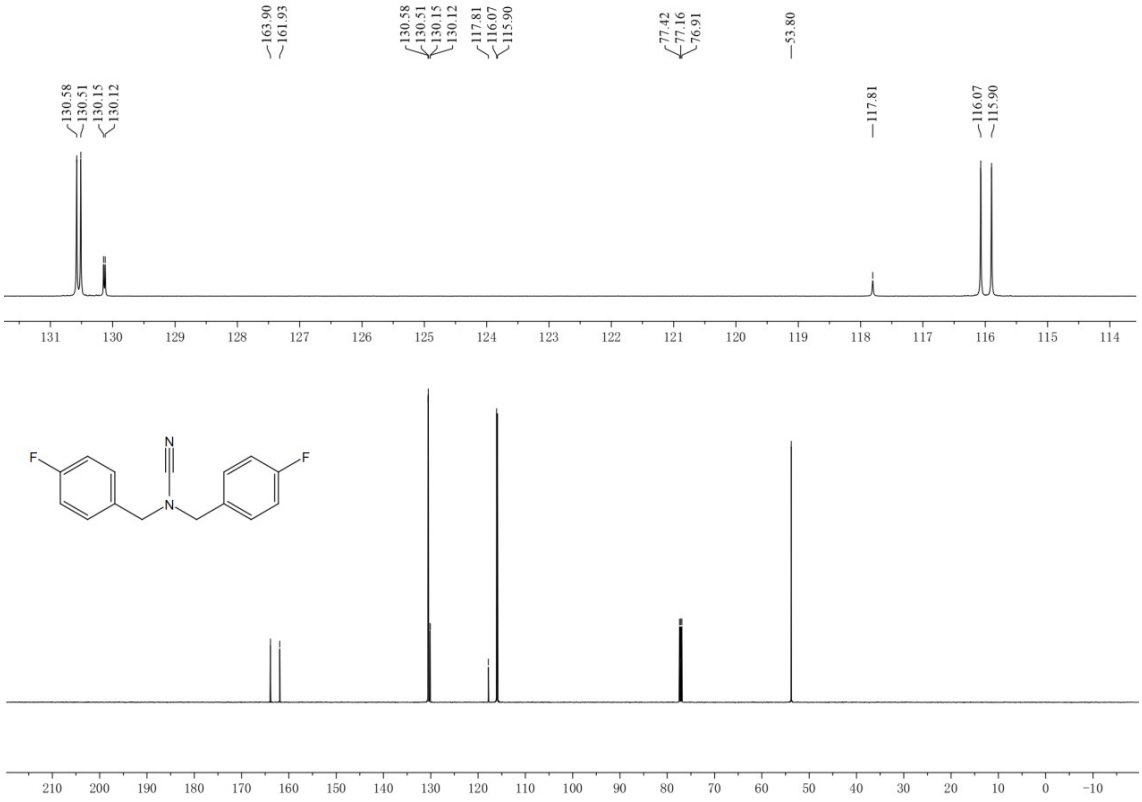
3j ^{13}C NMR (126 MHz, $CDCl_3$)



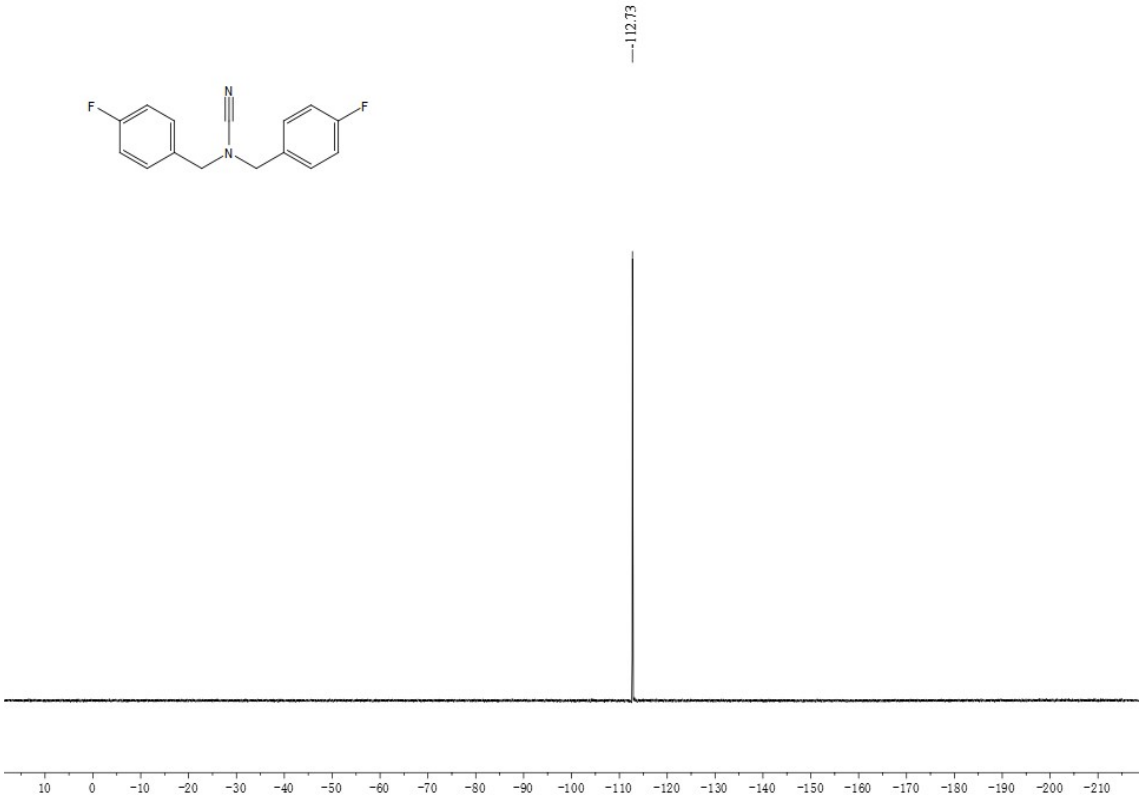
3k ^{1}H NMR (500 MHz, $CDCl_3$)



3k ^{13}C NMR (126 MHz, $CDCl_3$)

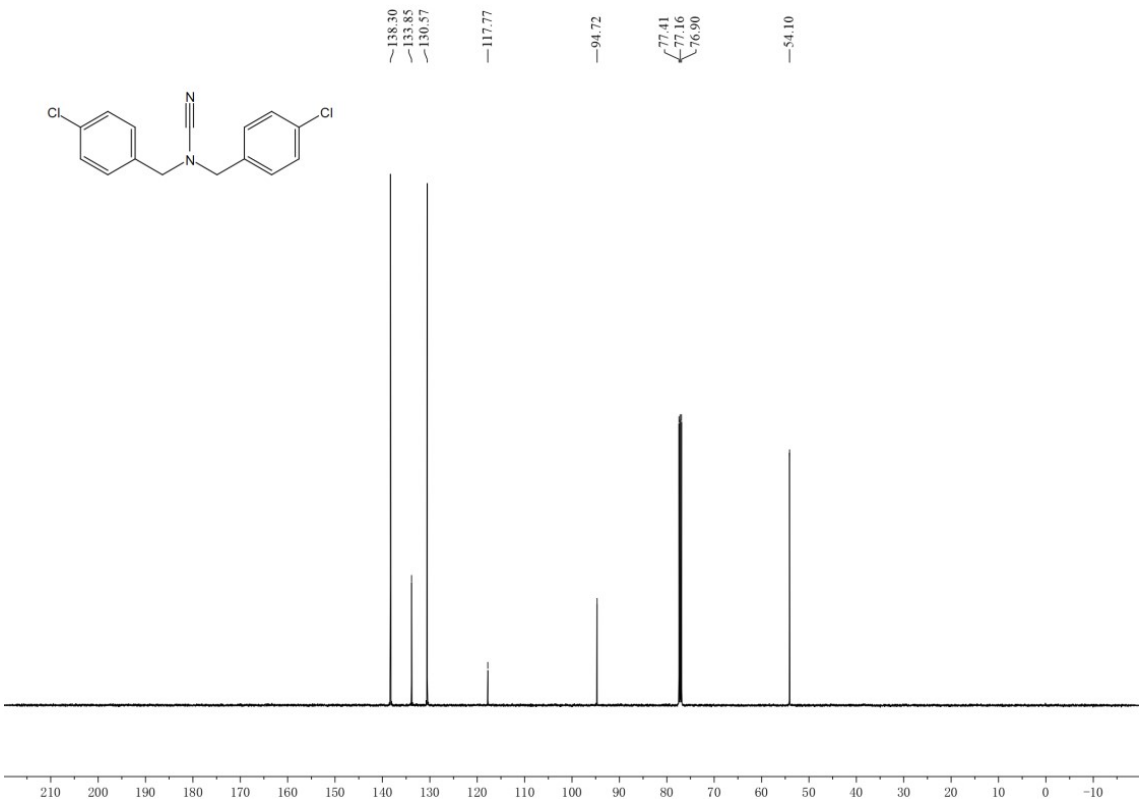


3k ^{19}F NMR (500 MHz, $CDCl_3$)



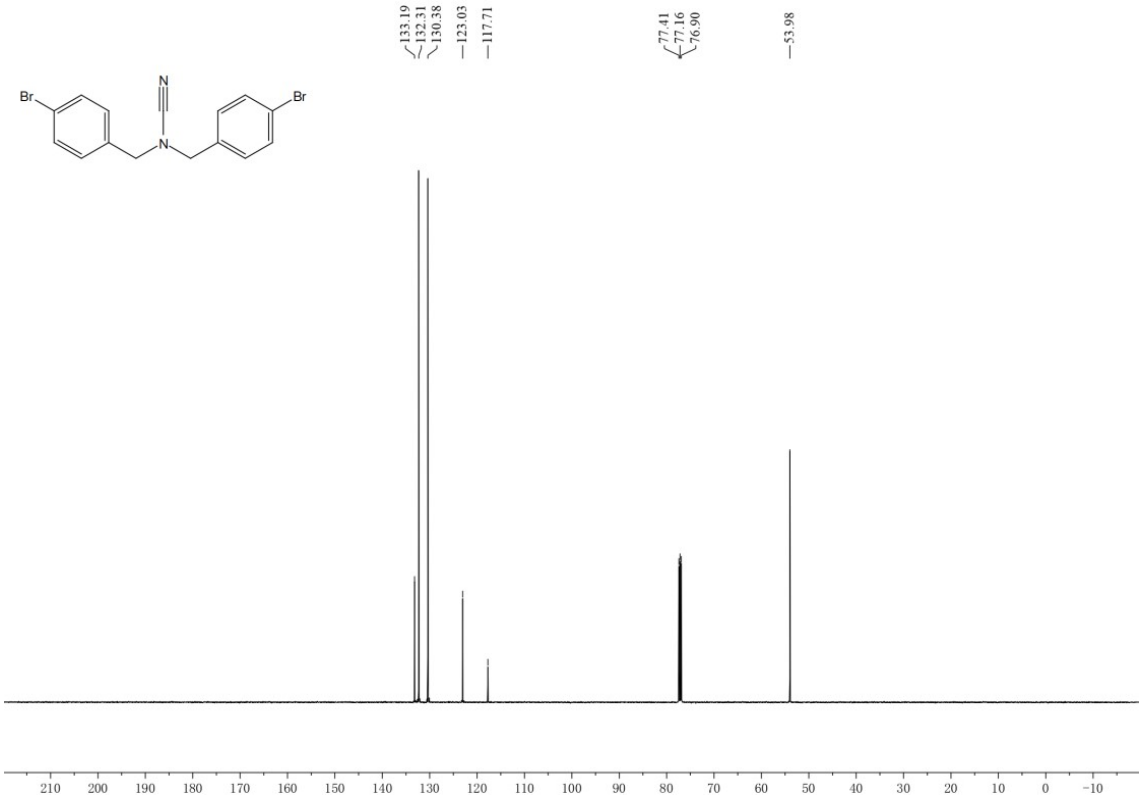
3l ^{1}H NMR (500 MHz, $CDCl_3$)

3l ^{13}C NMR (126 MHz, $CDCl_3$)

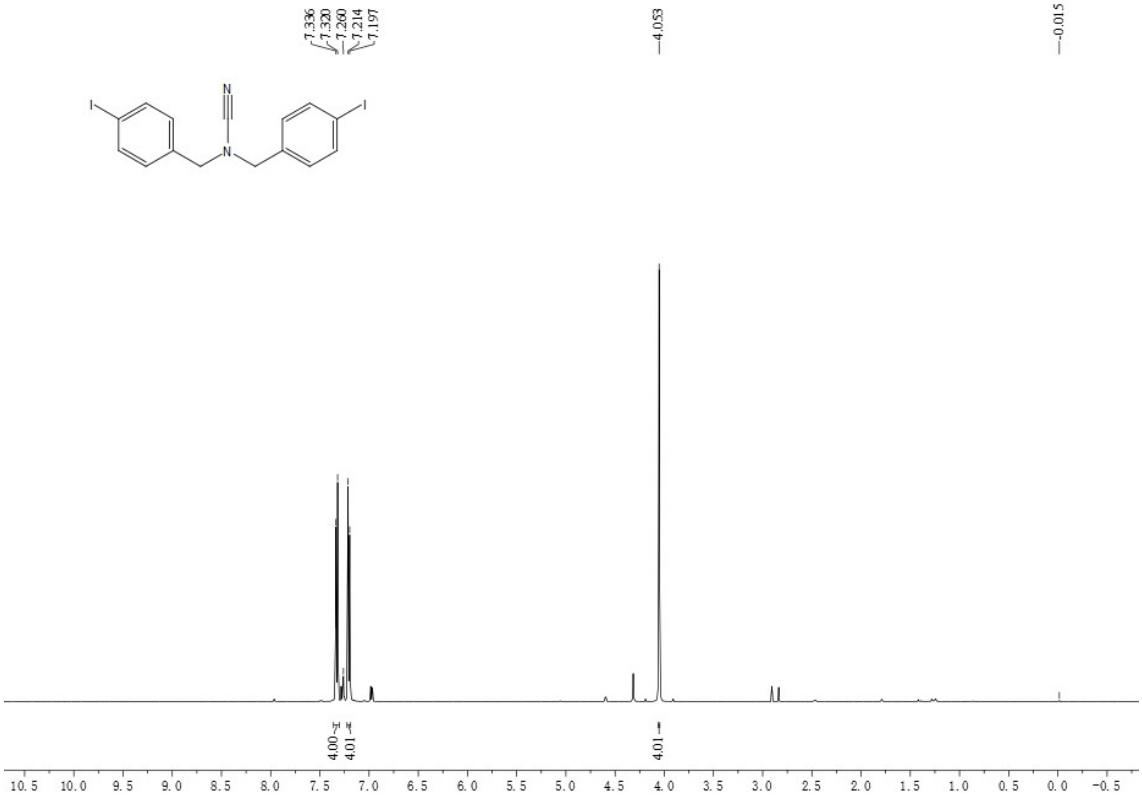


3m ^{1}H NMR (500 MHz, $CDCl_3$)

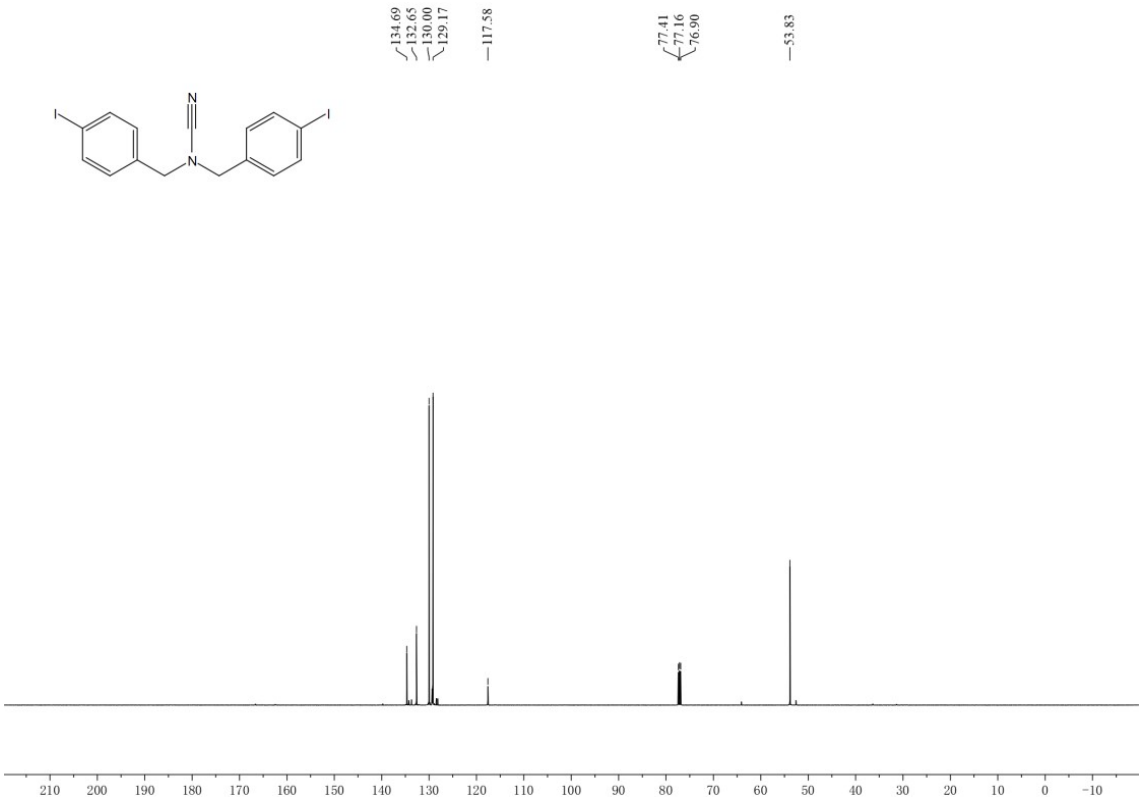
3m ^{13}C NMR (126 MHz, $CDCl_3$)



3n ^{1}H NMR (500 MHz, $CDCl_3$)

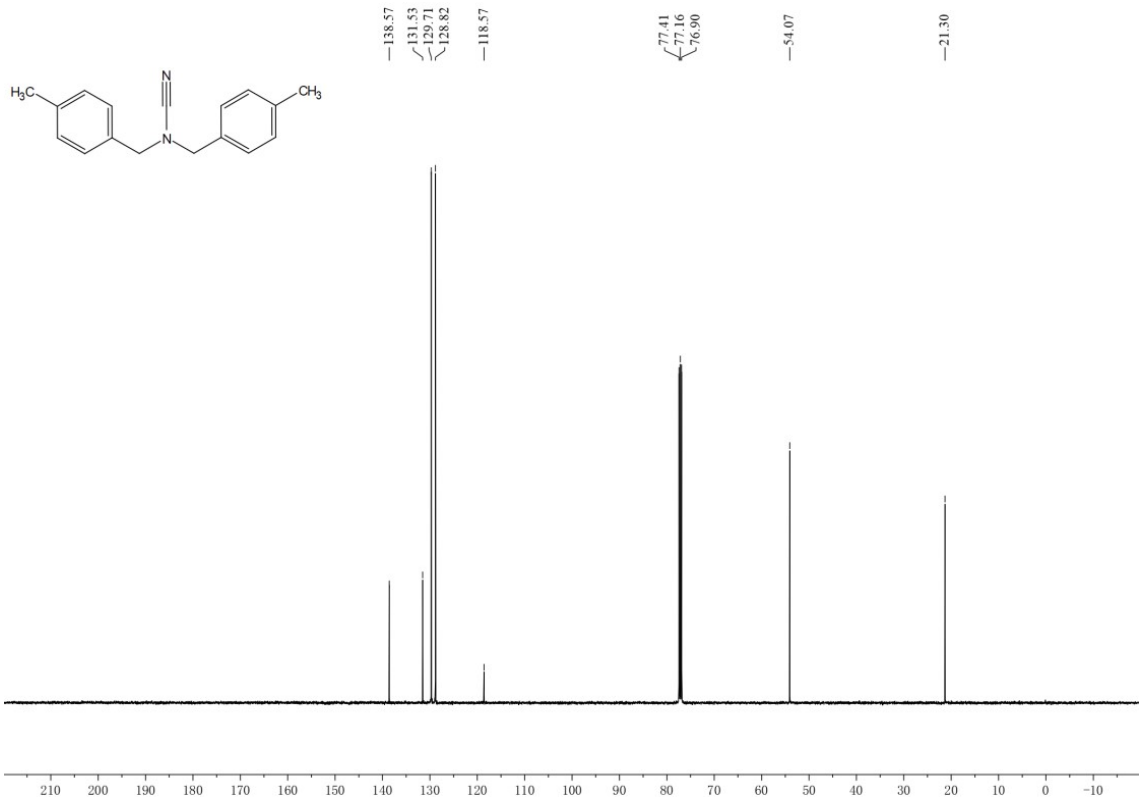


3n ^{13}C NMR (126 MHz, $CDCl_3$)

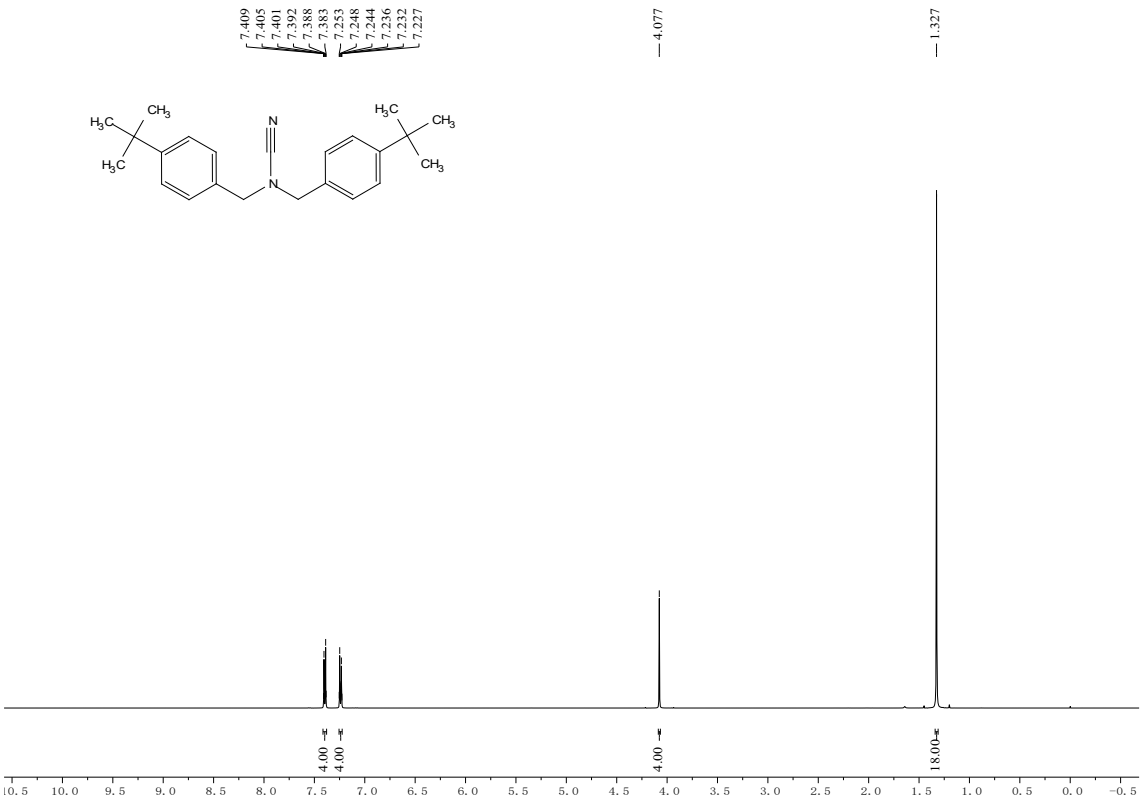


3o ^{1}H NMR (500 MHz, $CDCl_3$)

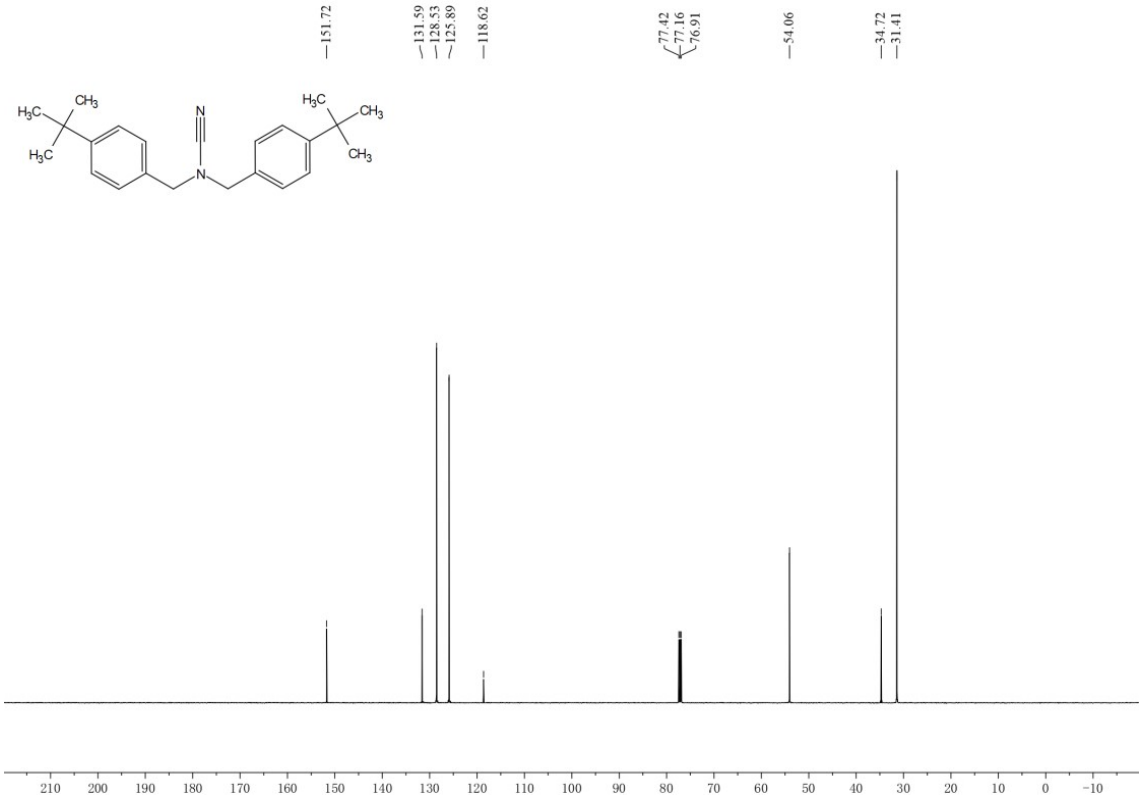
3o ^{13}C NMR (126 MHz, $CDCl_3$)



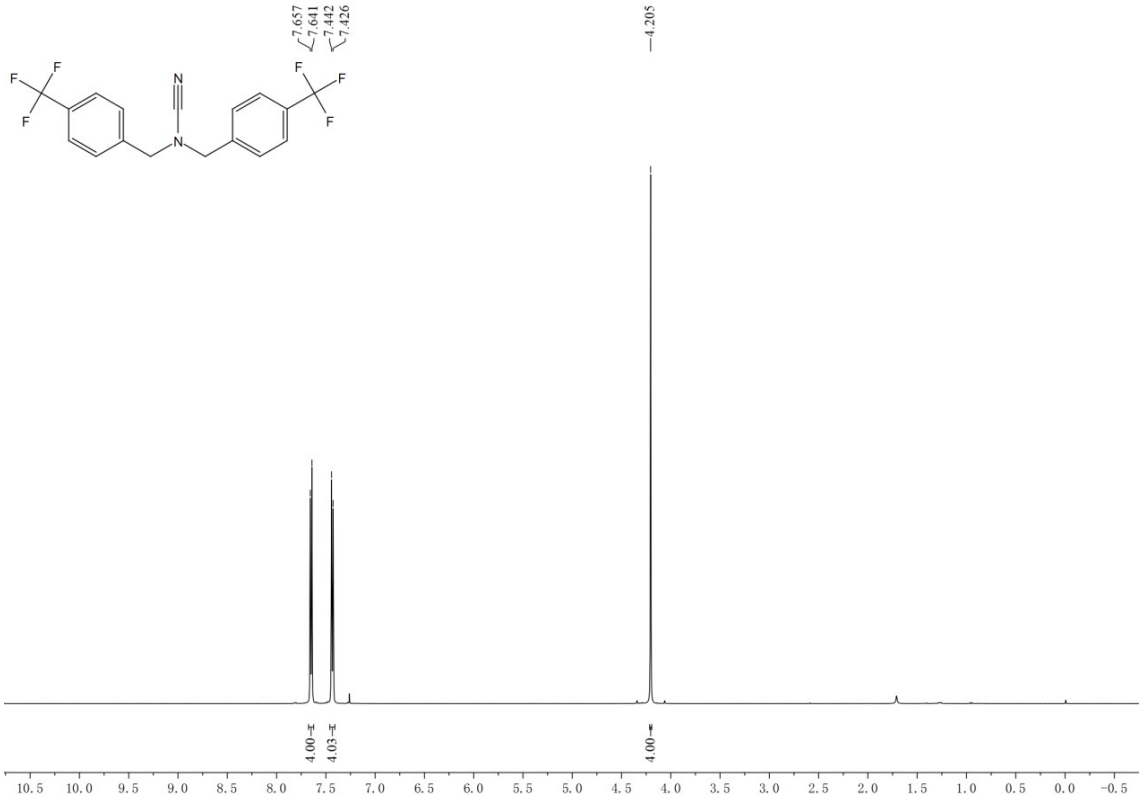
3p ^{1}H NMR (500 MHz, $CDCl_3$)



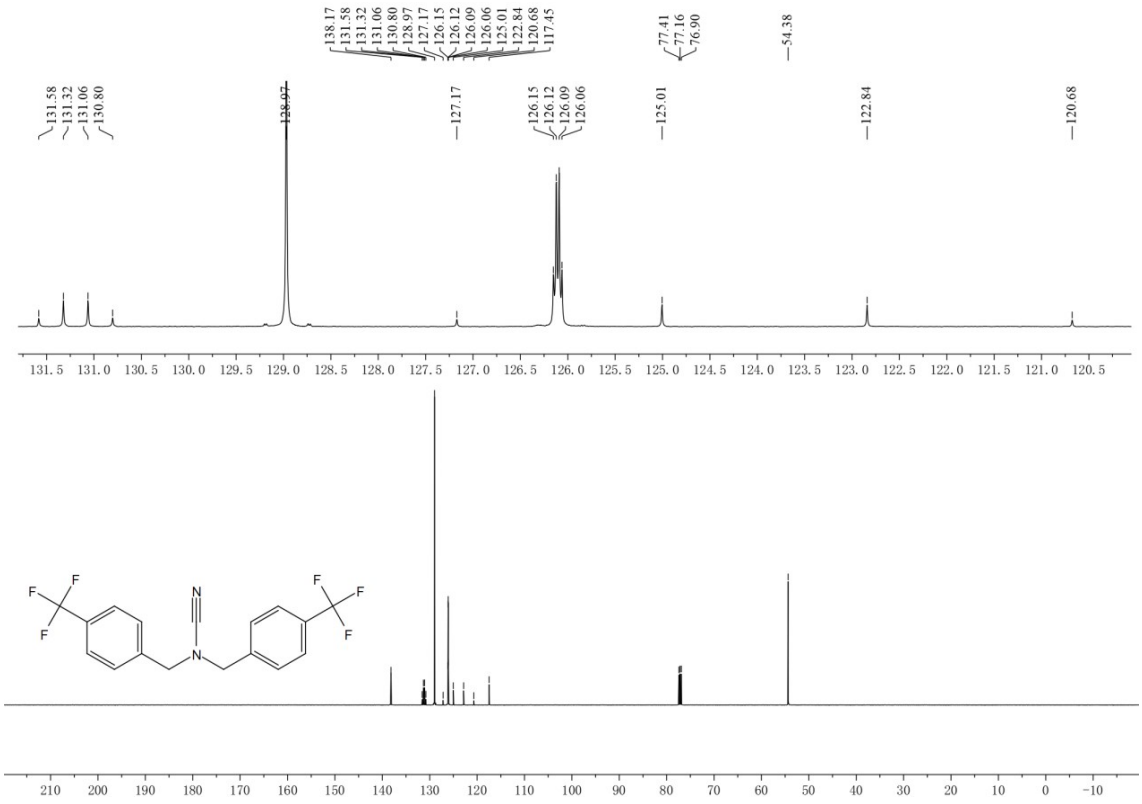
3p 13C NMR (126 MHz, $CDCl_3$)



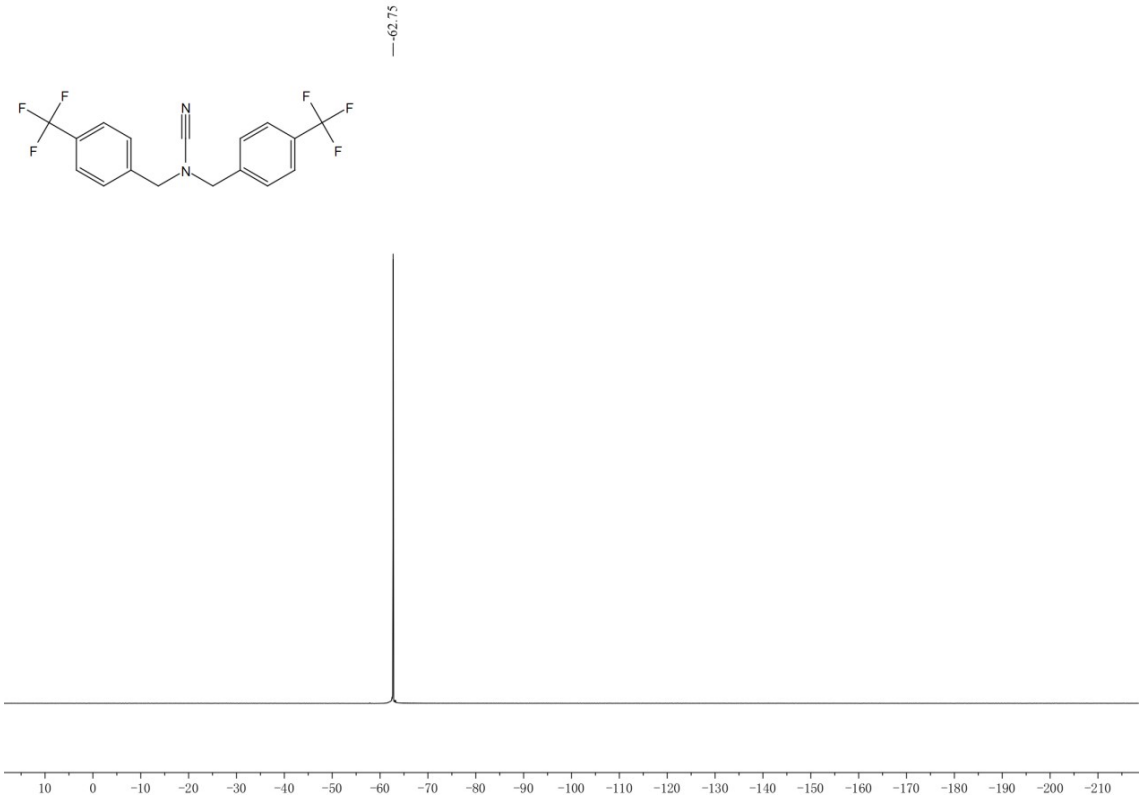
3q ^{1}H NMR (500 MHz, $CDCl_3$)



3q ^{13}C NMR (126 MHz, $CDCl_3$)

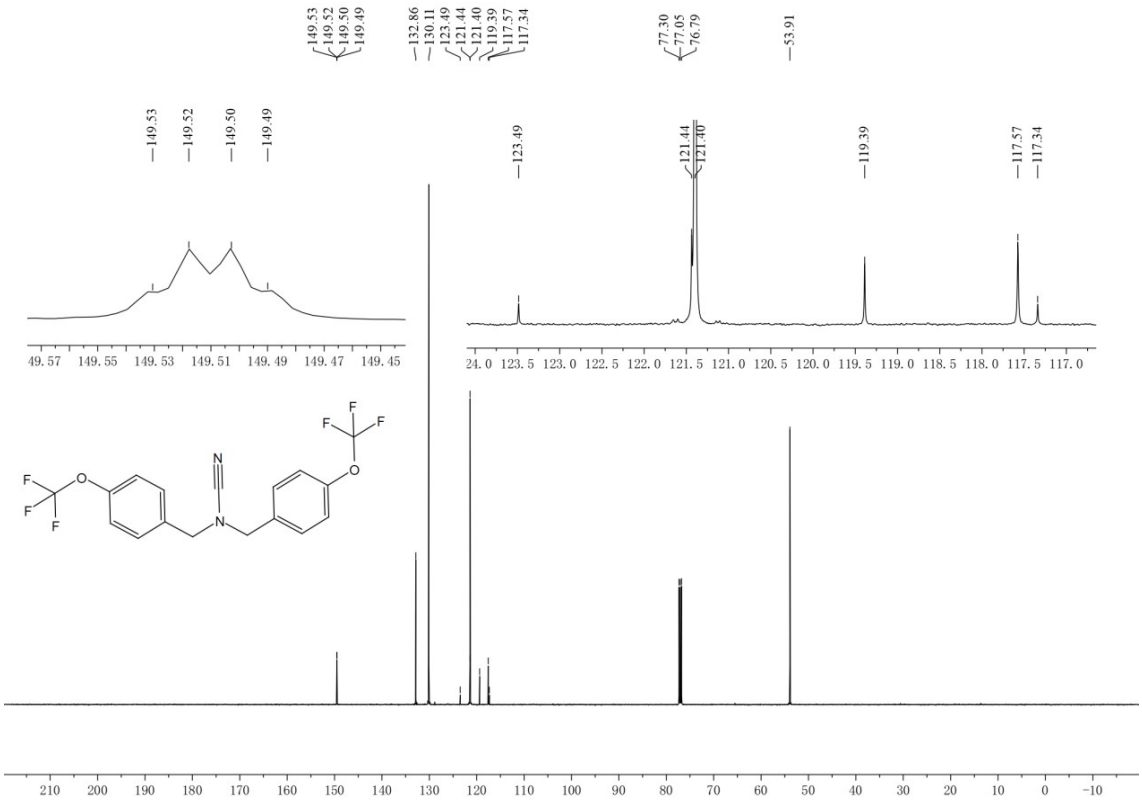


3q ^{19}F NMR (376 MHz, $CDCl_3$)

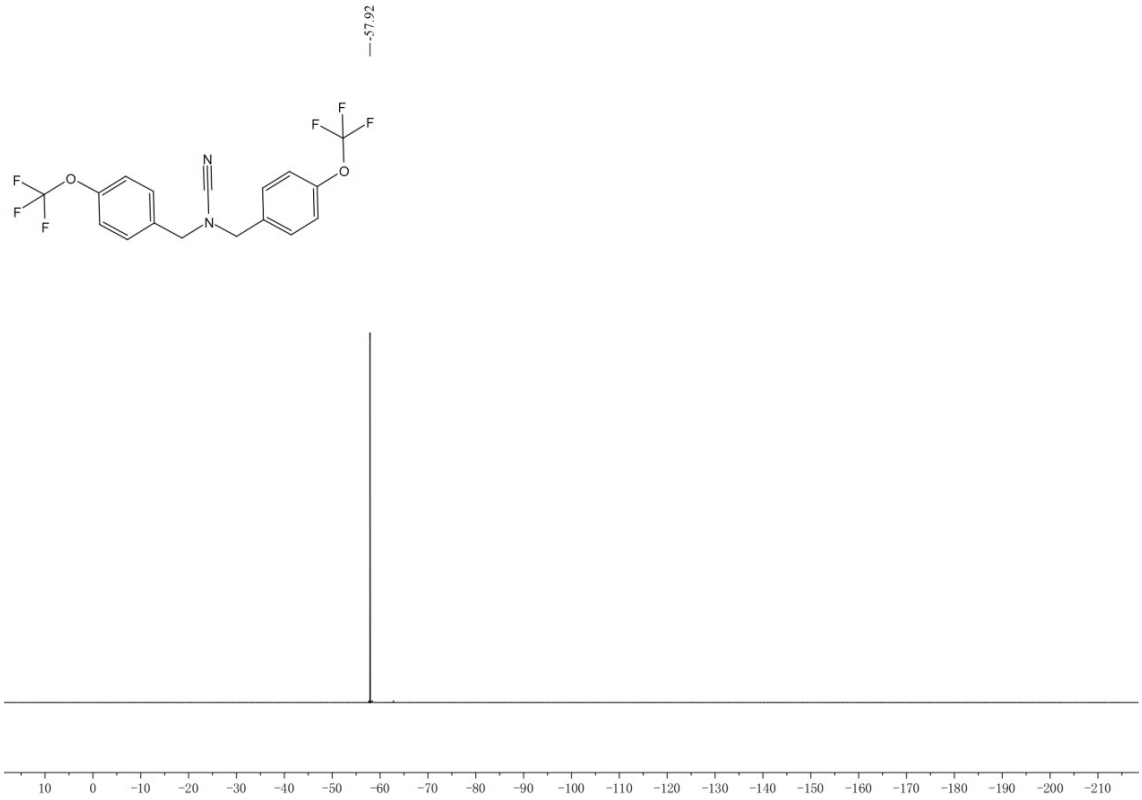


3r ^{1}H NMR (500 MHz, $CDCl_3$)

3r ^{13}C NMR (126 MHz, $CDCl_3$)

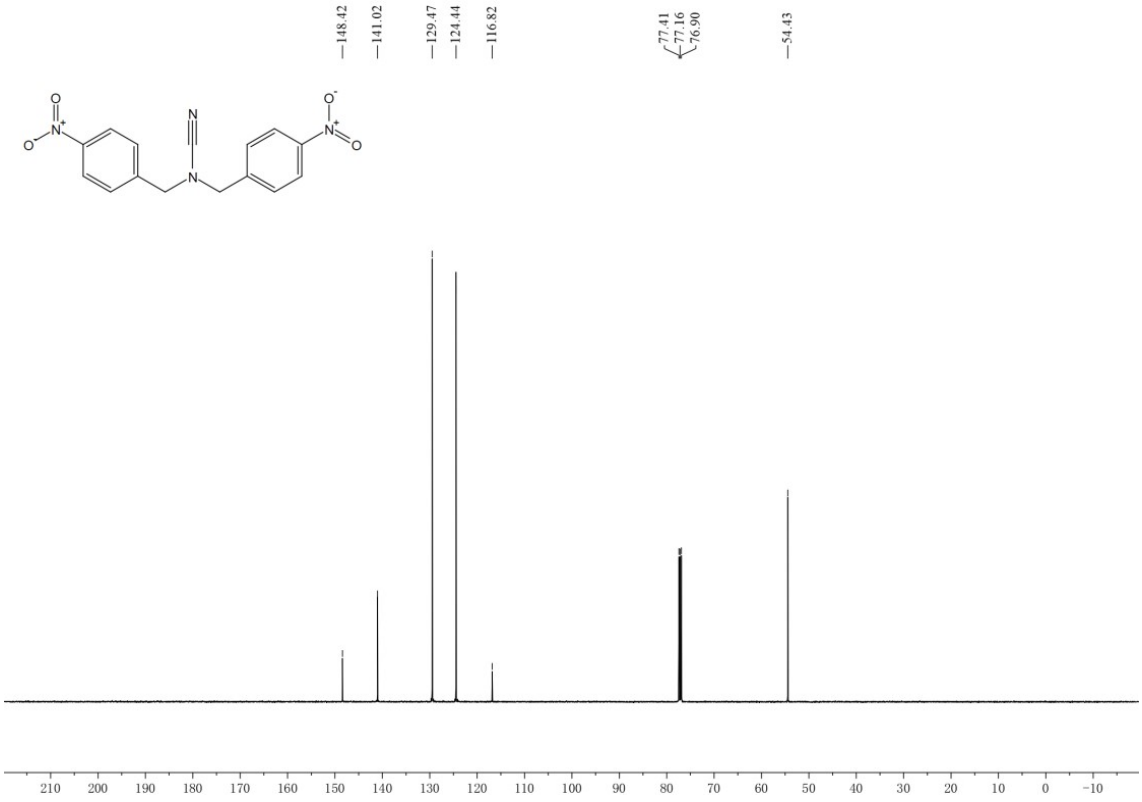


3r ^{19}F NMR (376 MHz, $CDCl_3$)

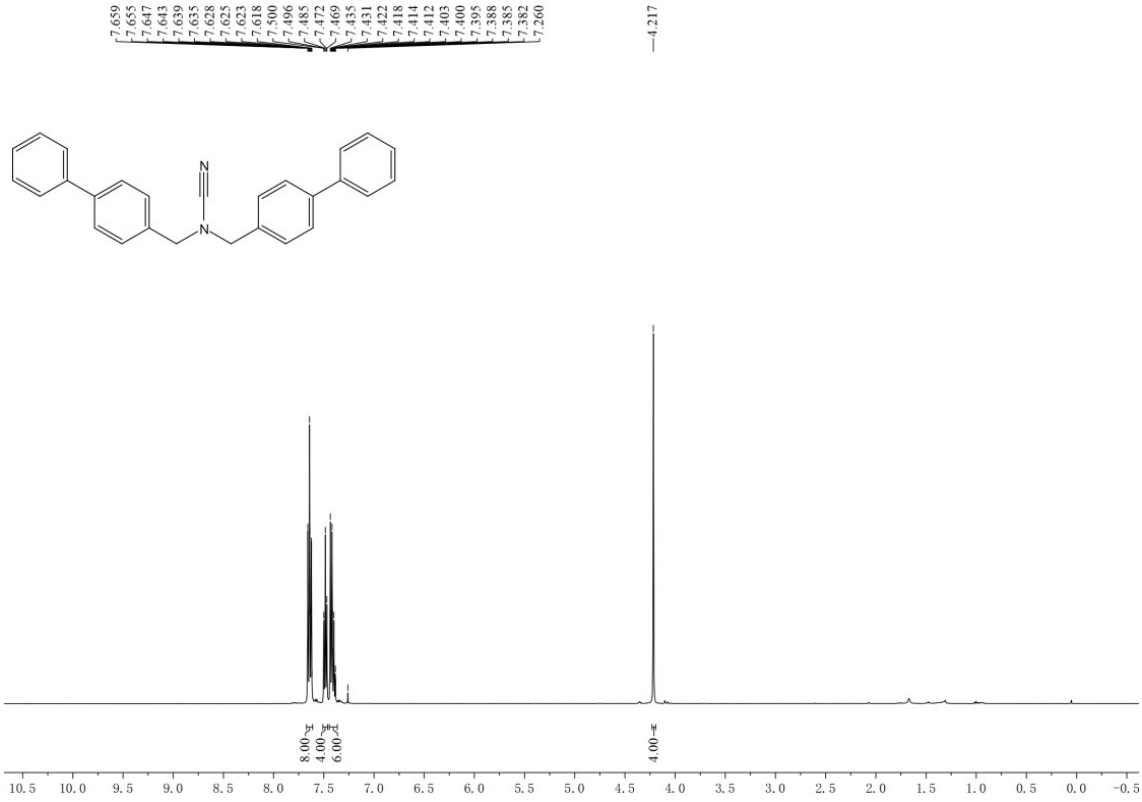


3s ^{1}H NMR (500 MHz, $CDCl_3$)

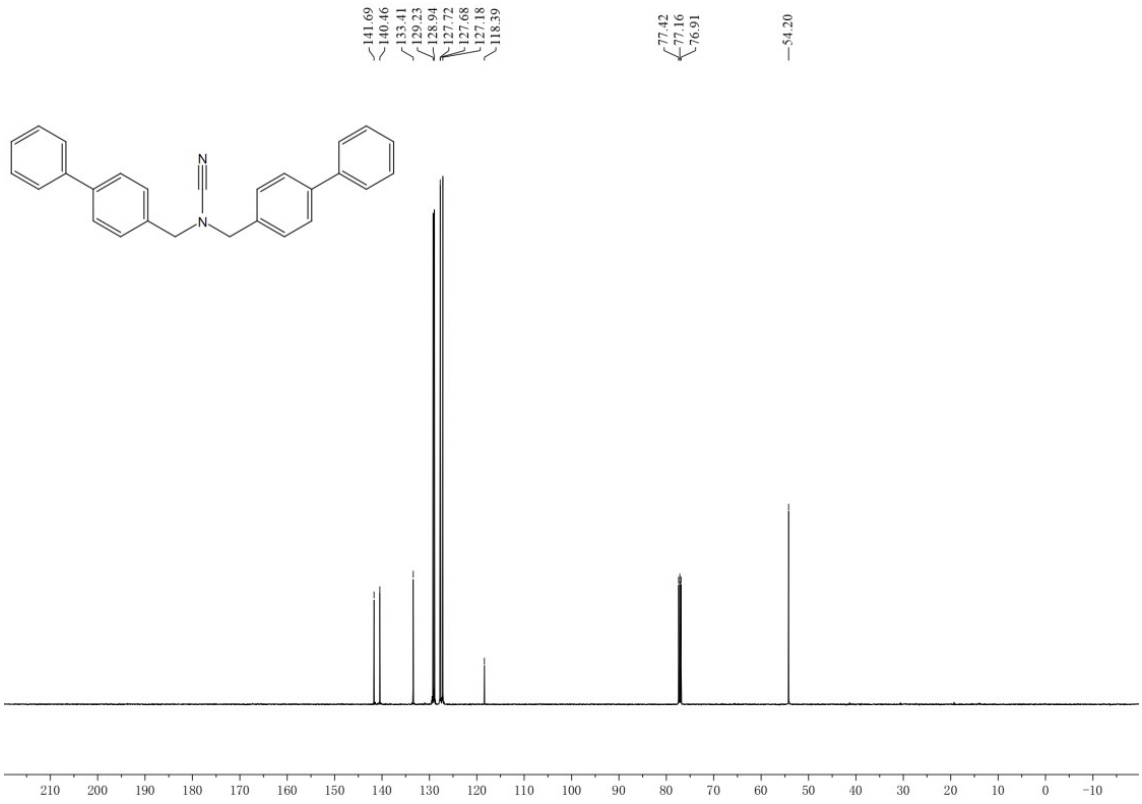
3s ^{13}C NMR (126 MHz, $CDCl_3$)



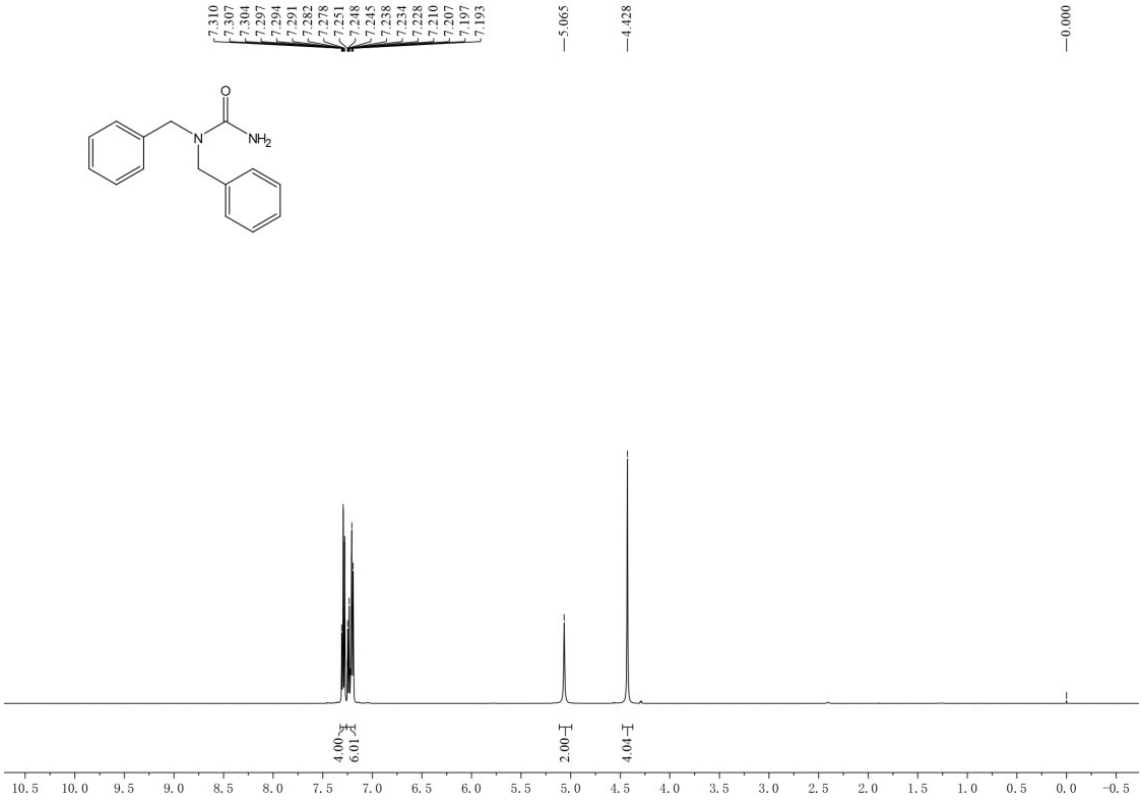
3t ^{1}H NMR (500 MHz, $CDCl_3$)



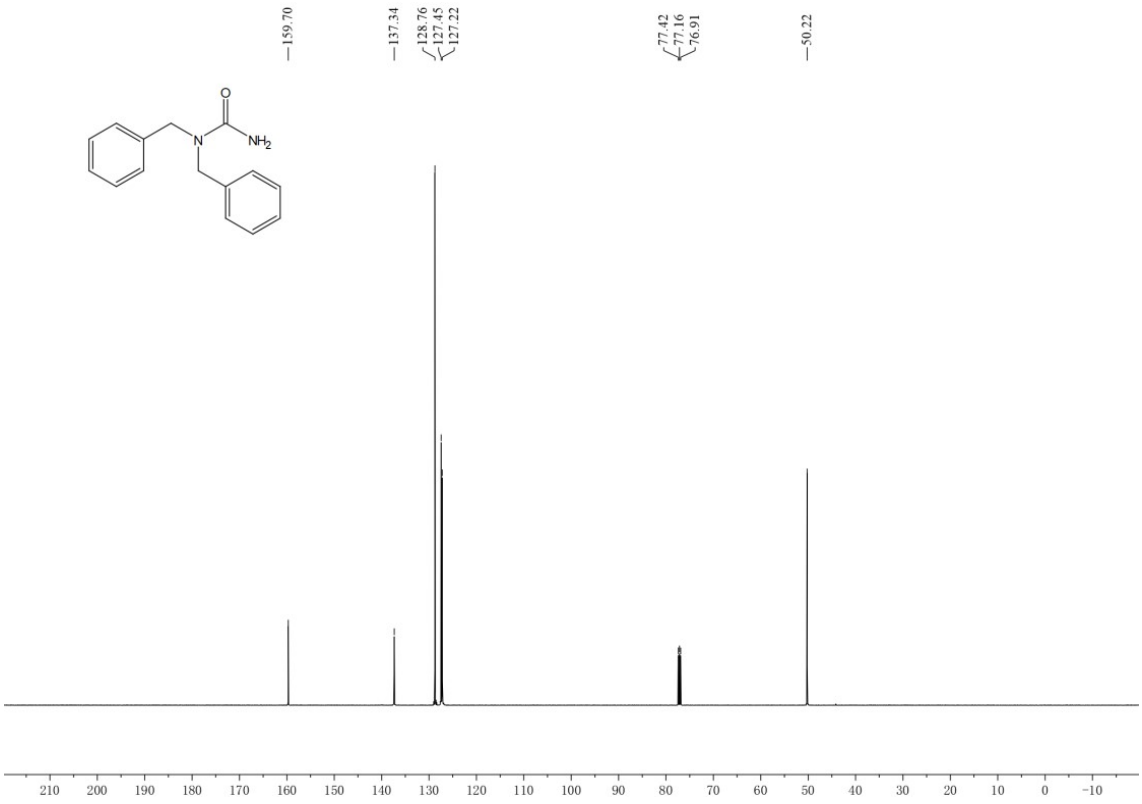
3t ^{13}C NMR (126 MHz, $CDCl_3$)



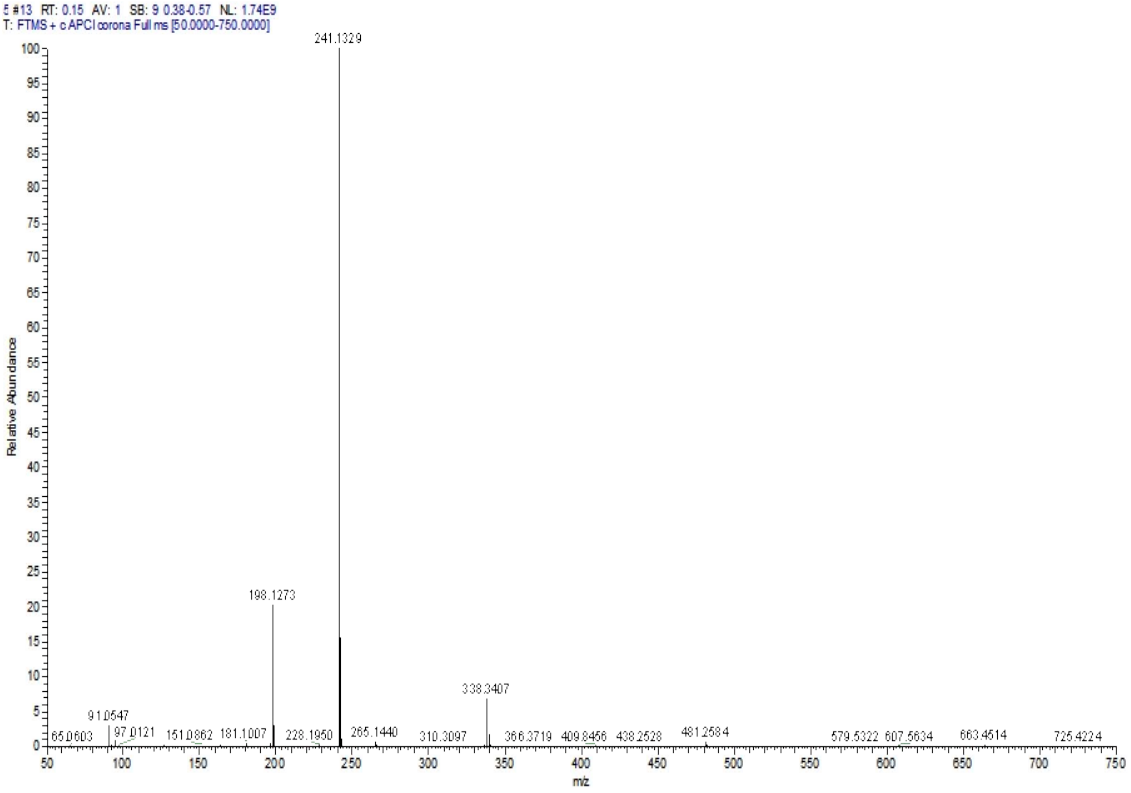
4a ^{1}H NMR (500 MHz, $CDCl_3$)



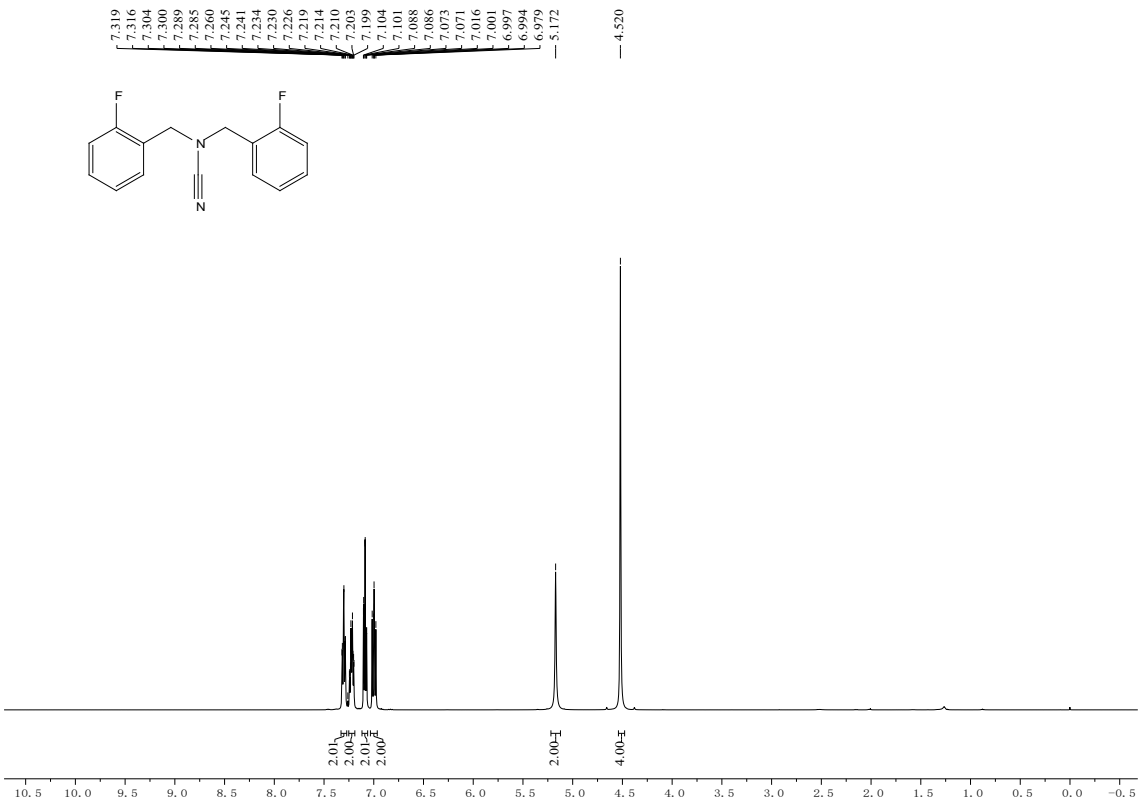
4a ^{13}C NMR (126 MHz, $CDCl_3$)



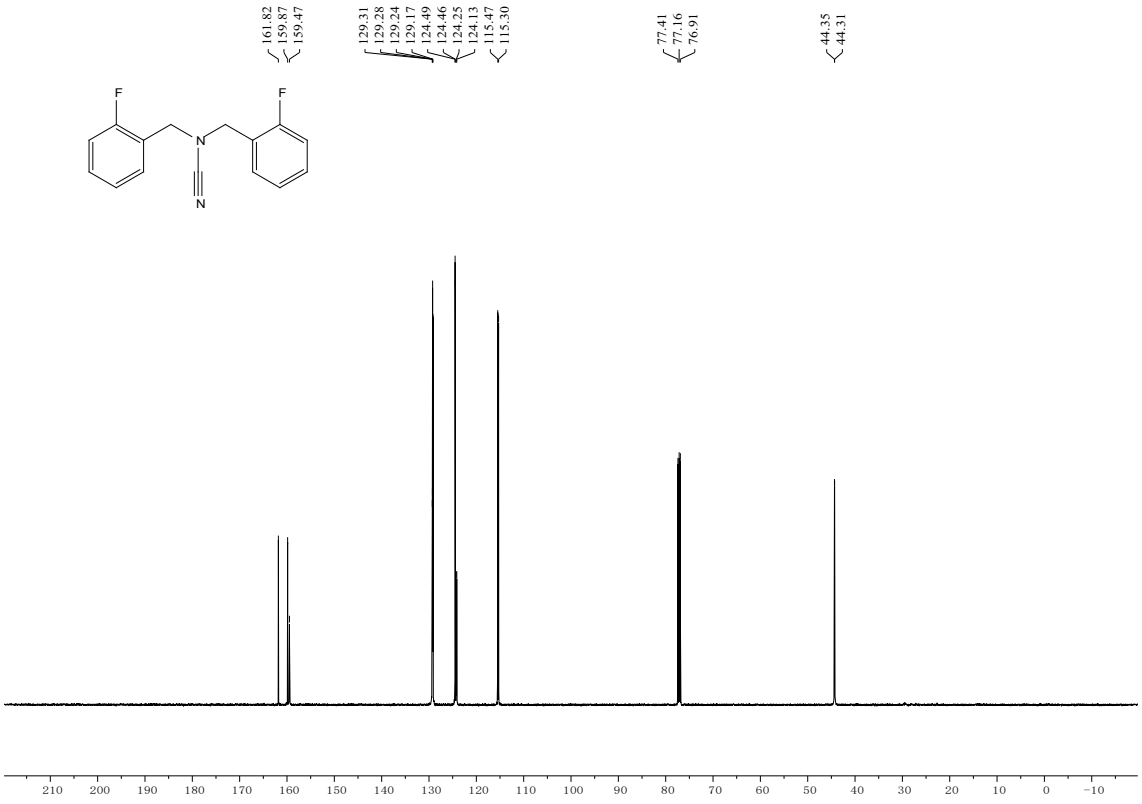
4a High Resolution Mass Spectrometry



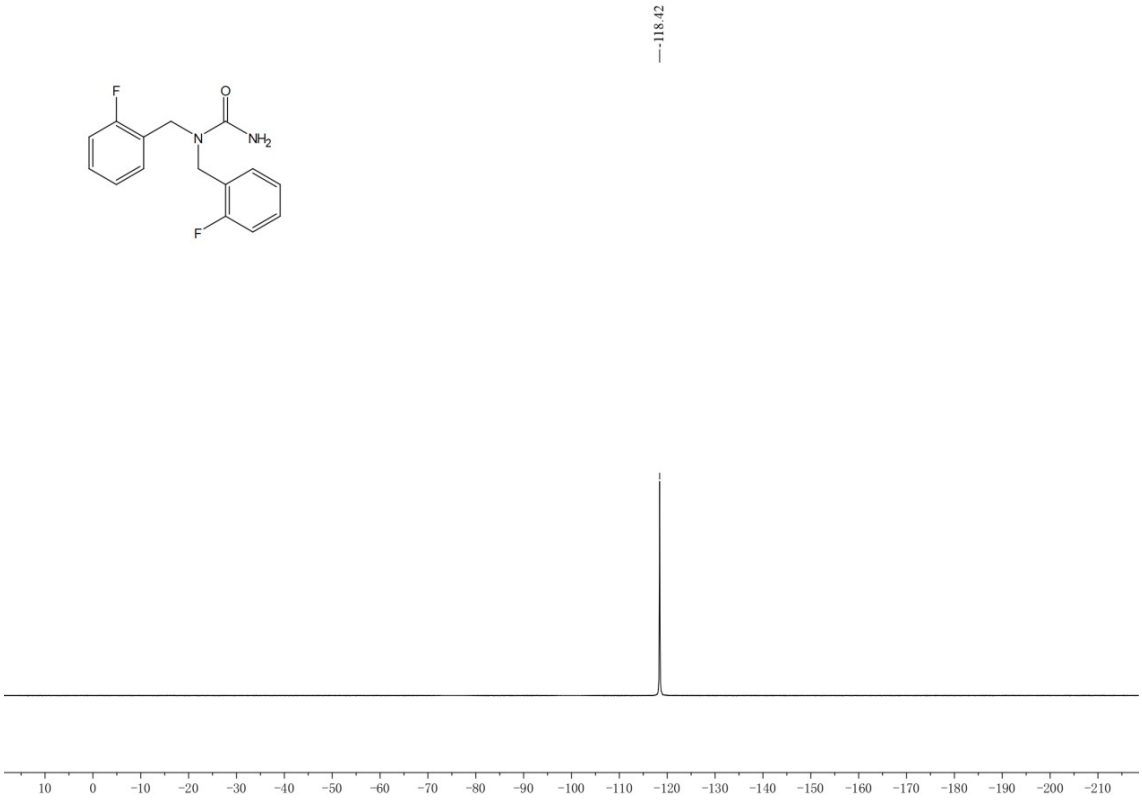
4b ^{1}H NMR (500 MHz, $CDCl_3$)



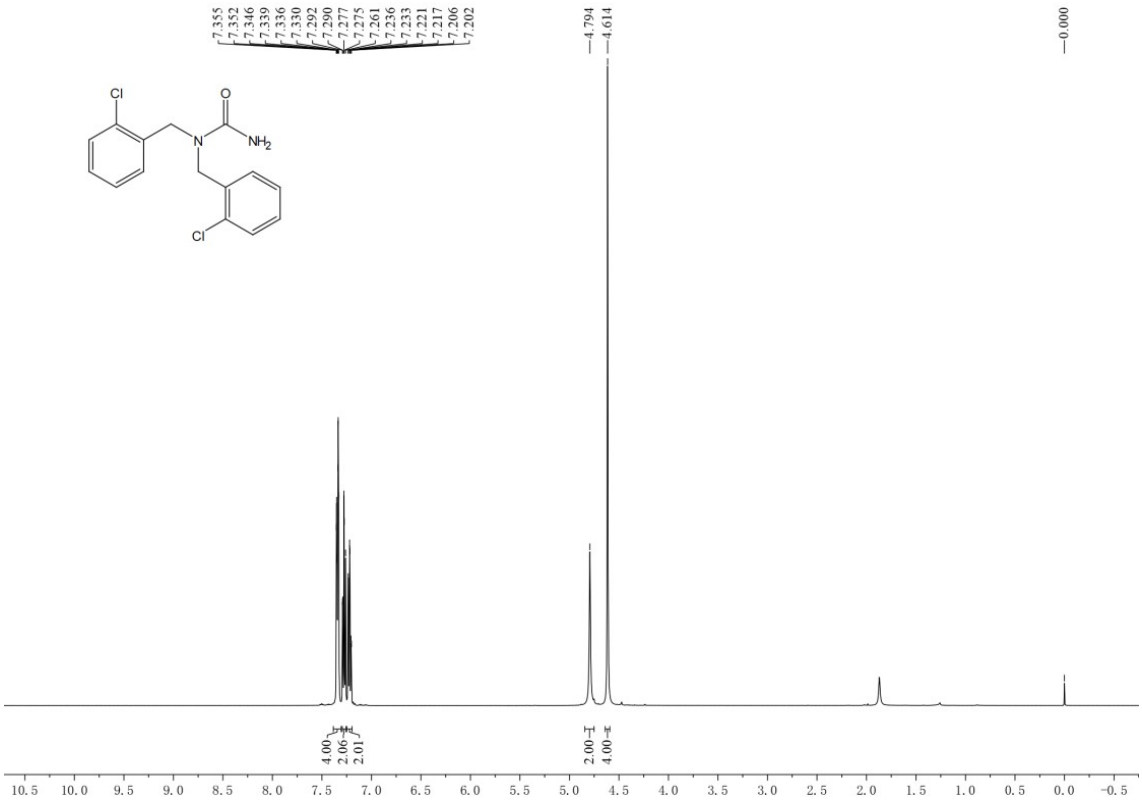
4b ^{13}C NMR (126 MHz, $CDCl_3$)



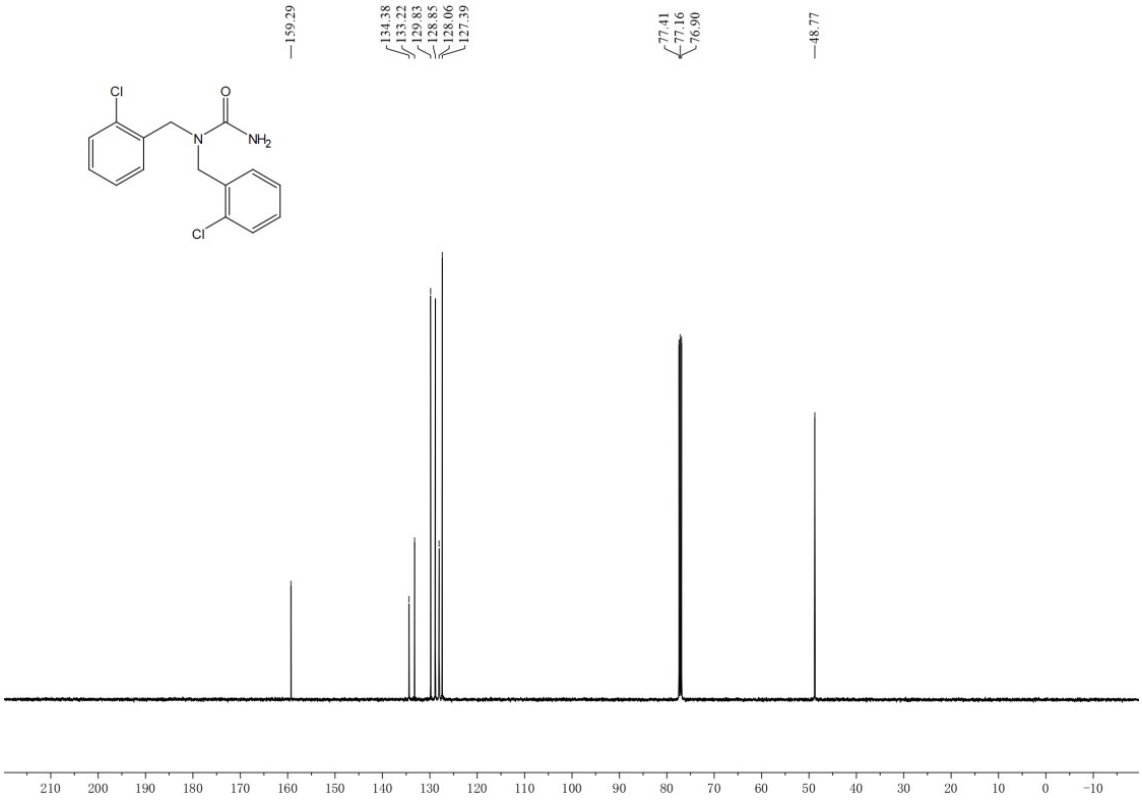
4b ^{19}F NMR (376 MHz, $CDCl_3$)



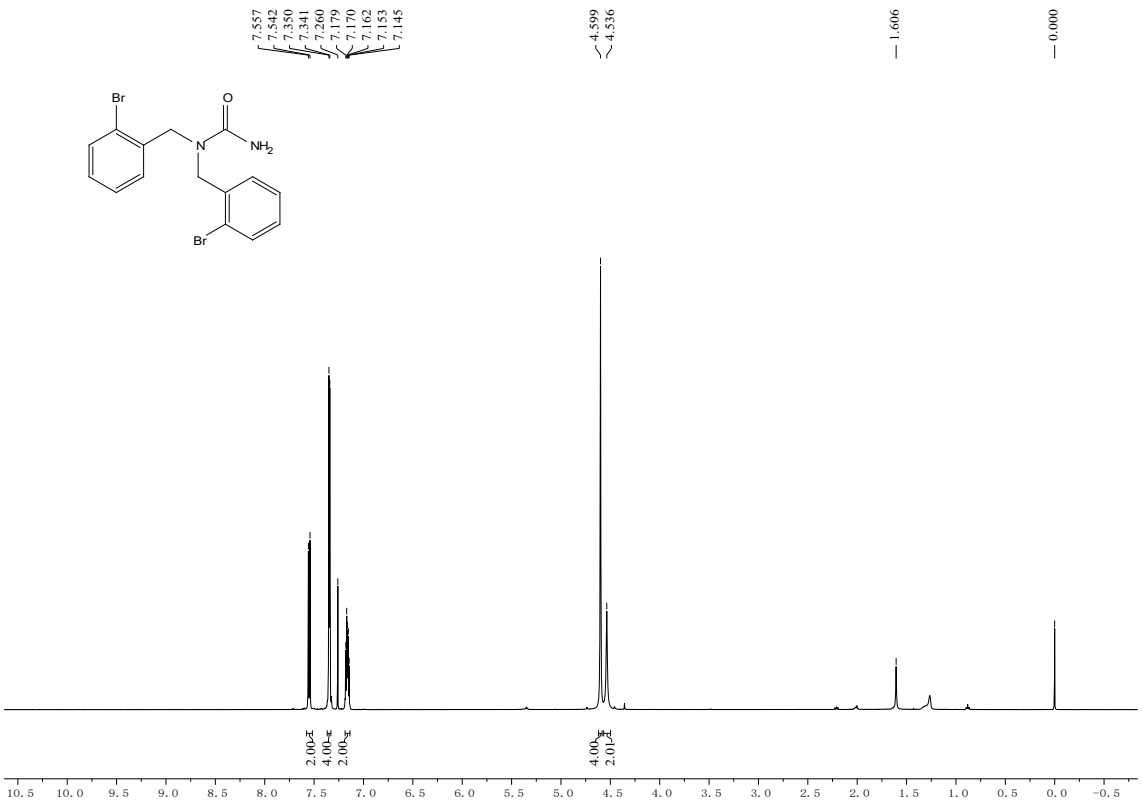
4c ^{1}H NMR (500 MHz, $CDCl_3$)



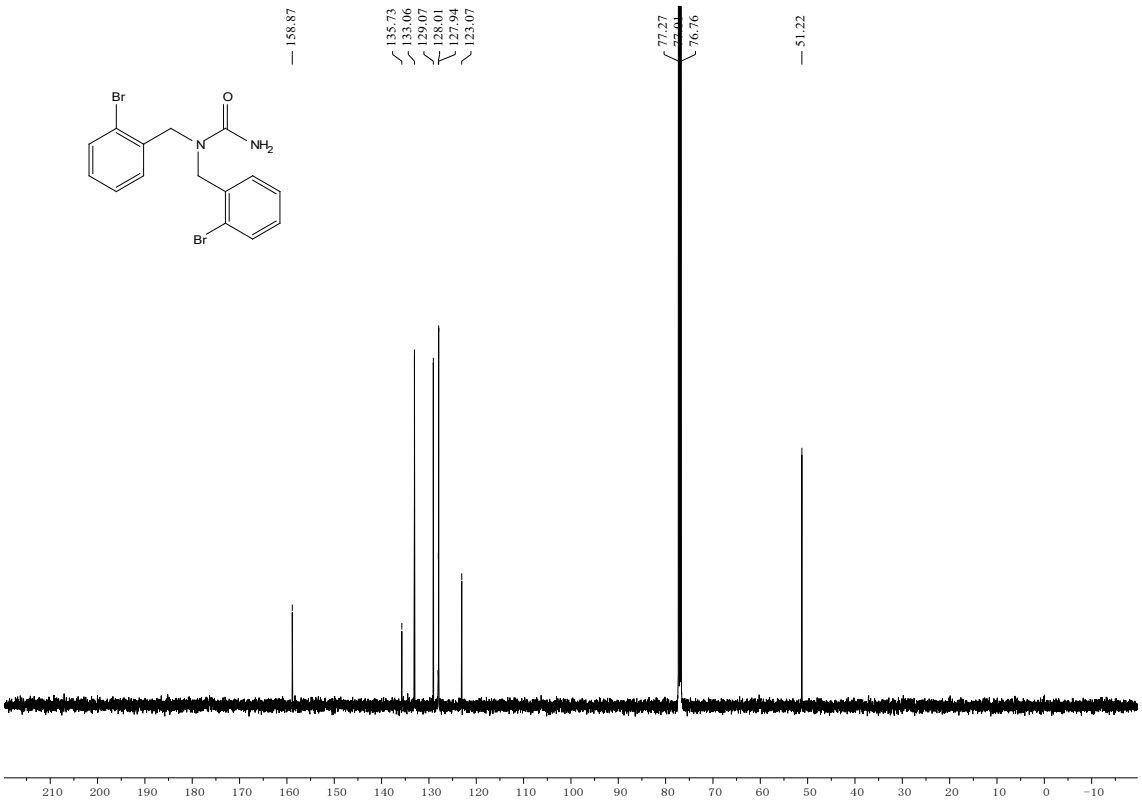
4c ^{13}C NMR (126 MHz, $CDCl_3$)



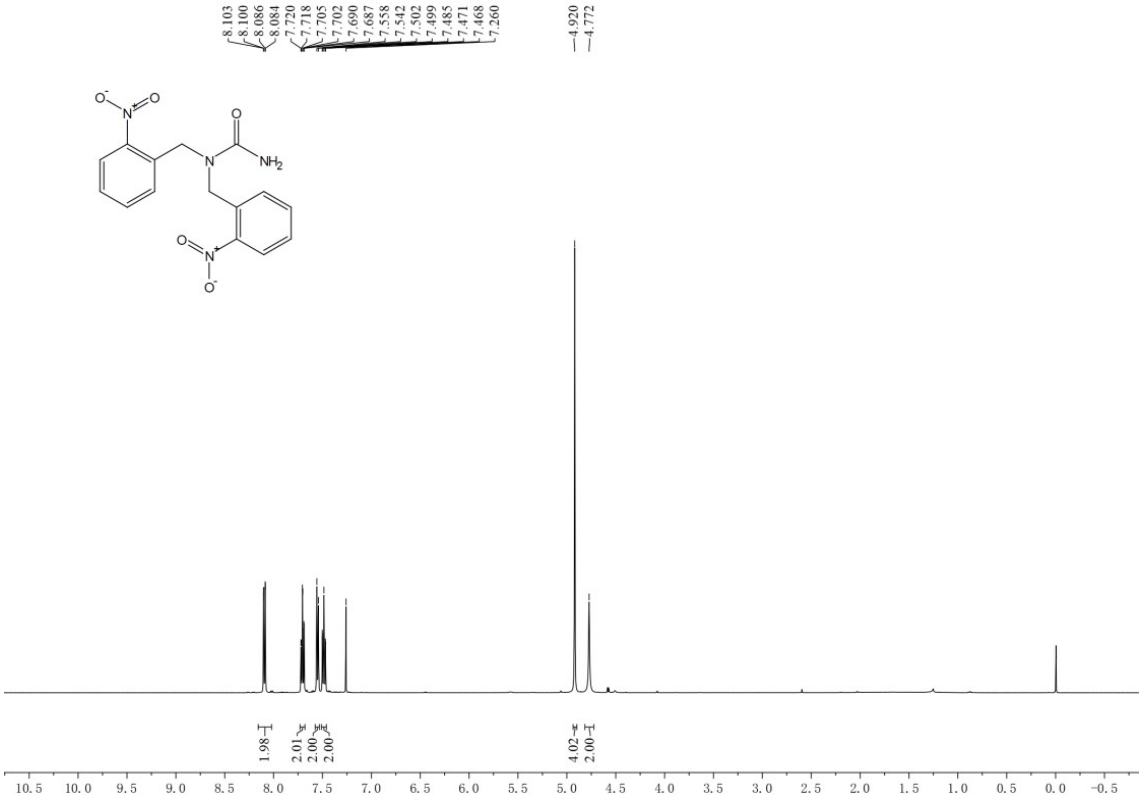
4d ^{1}H NMR (500 MHz, $CDCl_3$)



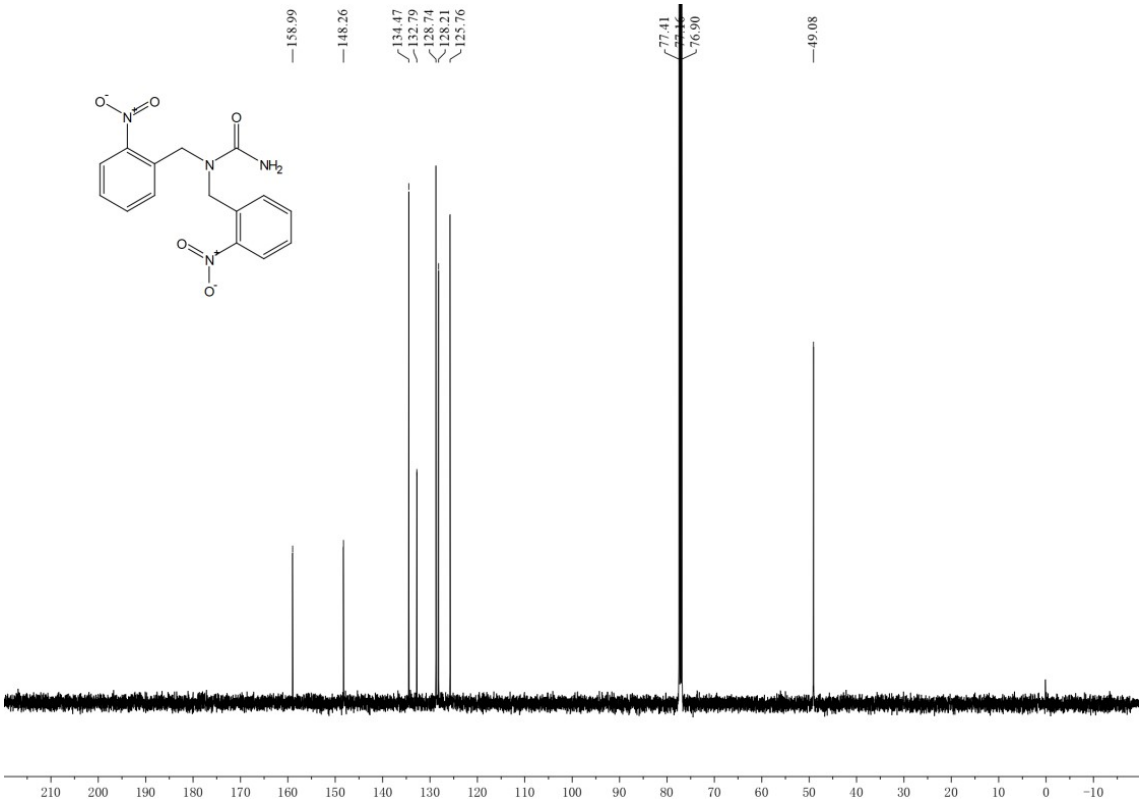
4d ^{13}C NMR (126 MHz, $CDCl_3$)



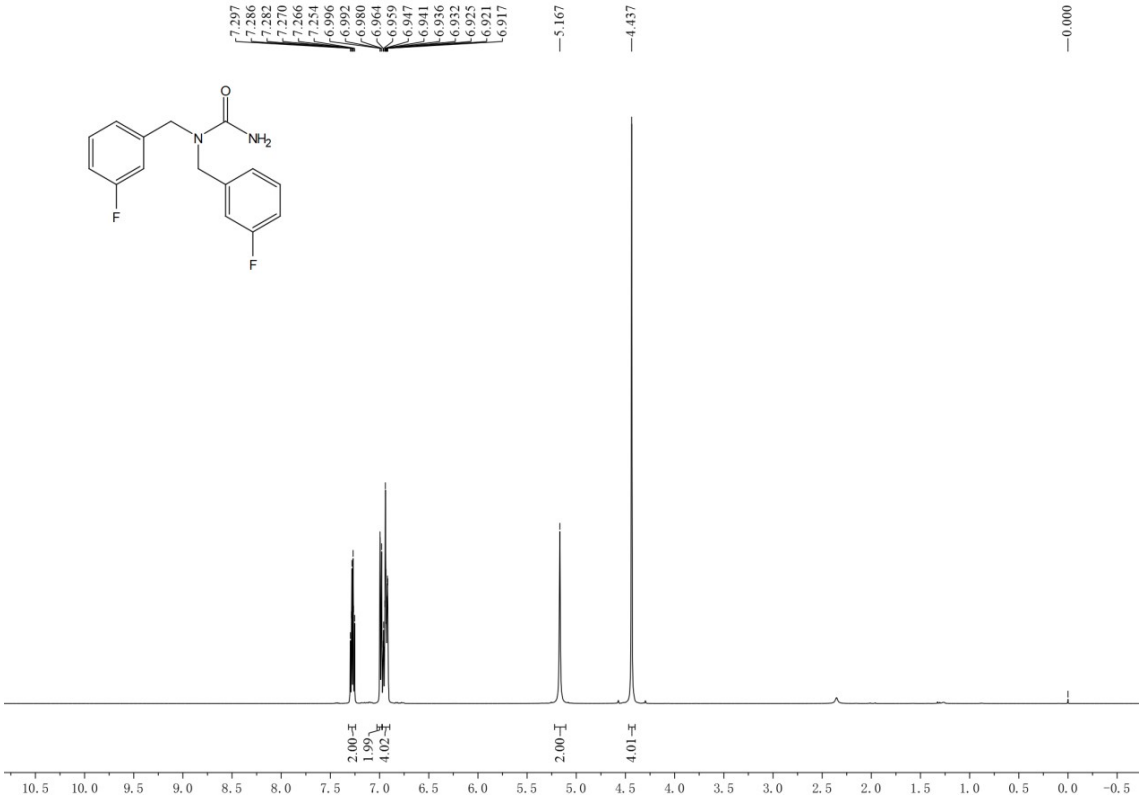
4e ^{1}H NMR (500 MHz, $CDCl_3$)



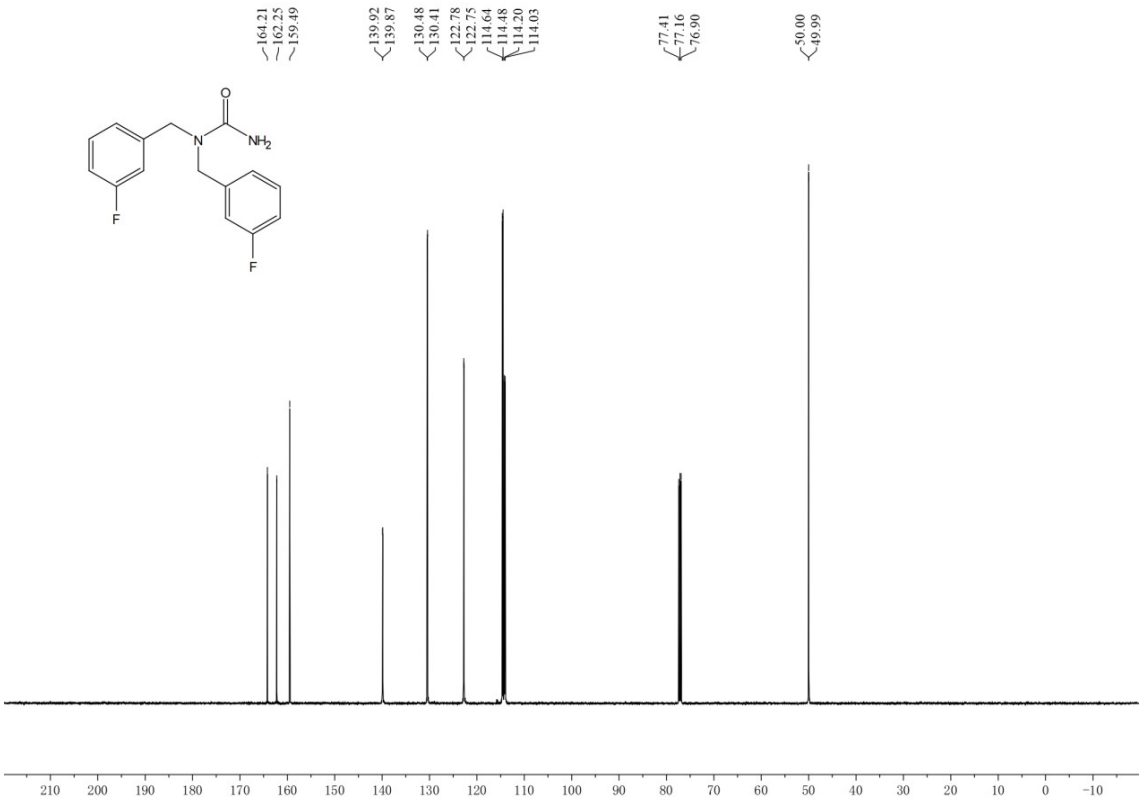
4e ^{13}C NMR (126 MHz, $CDCl_3$)



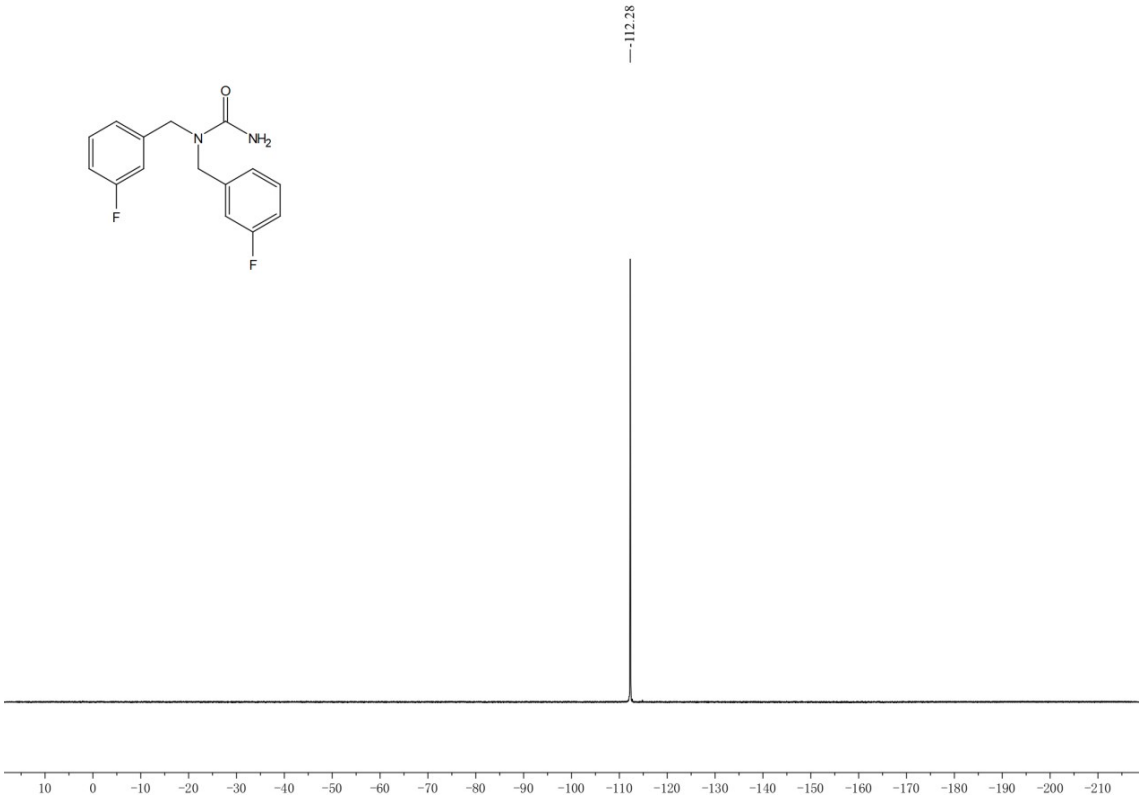
4f ^{1}H NMR (500 MHz, $CDCl_3$)



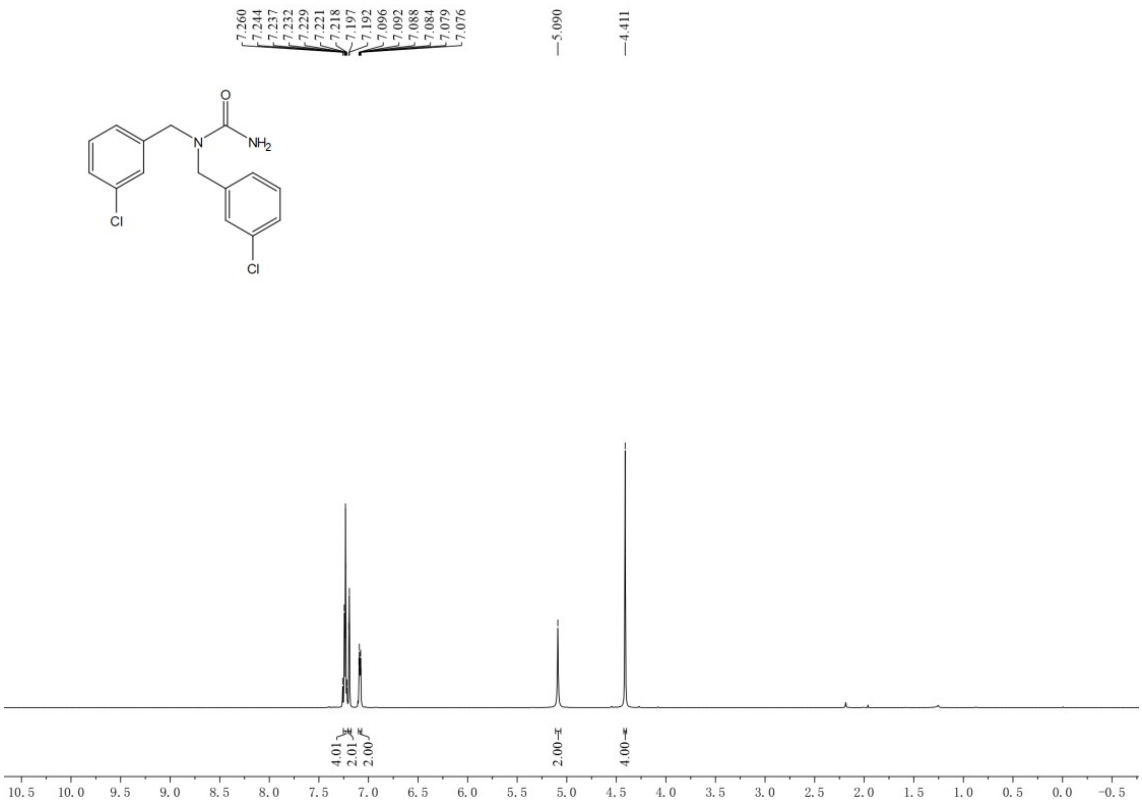
4f ^{13}C NMR (126 MHz, $CDCl_3$)



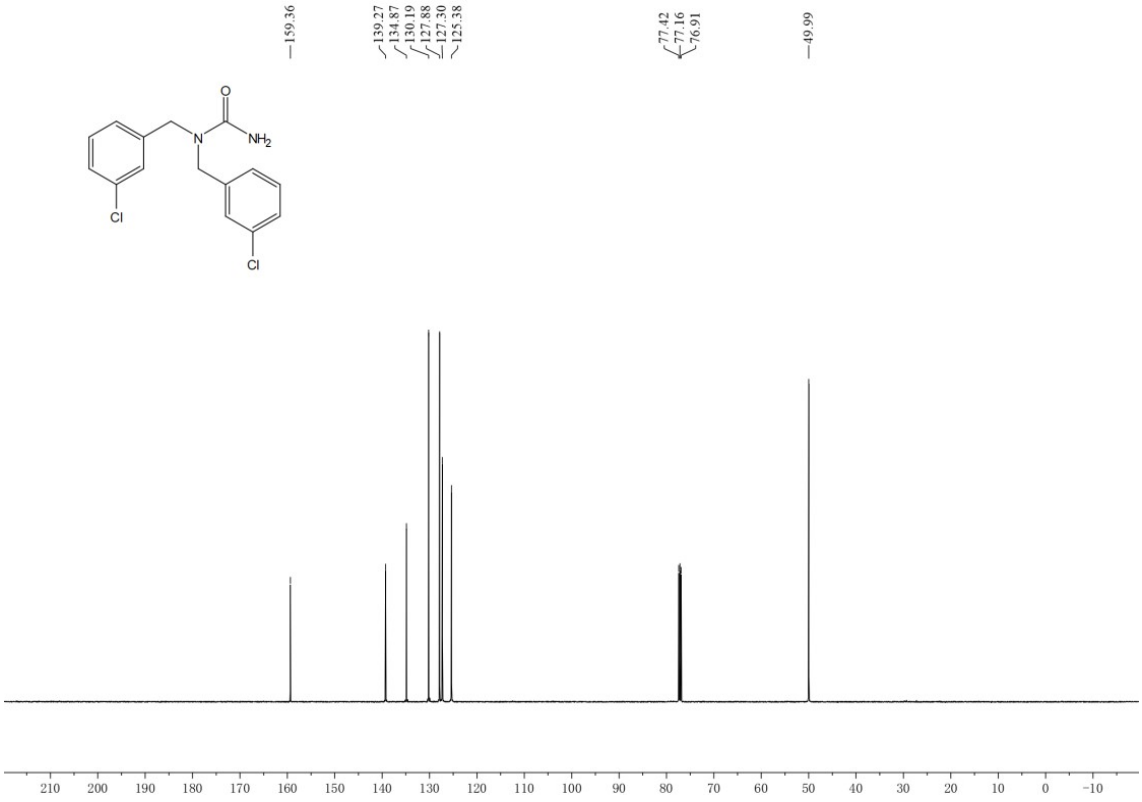
4f ^{19}F NMR (376 MHz, $CDCl_3$)



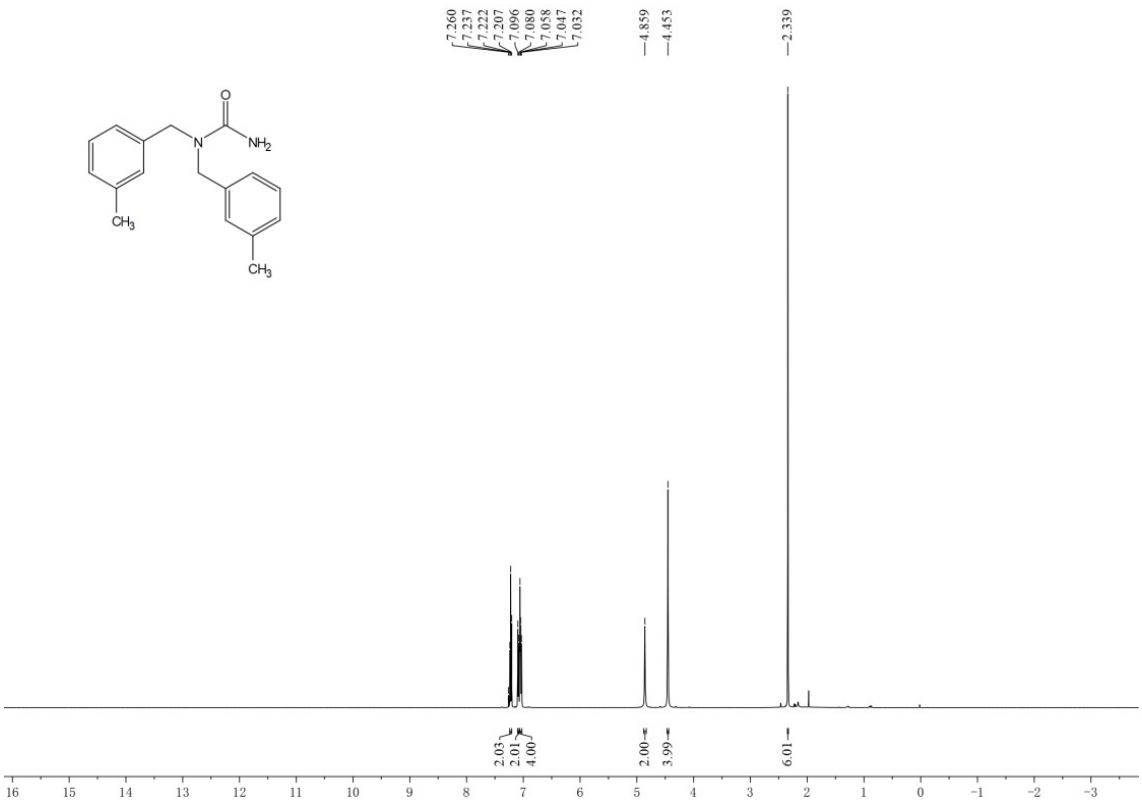
4g ^{1}H NMR (500 MHz, $CDCl_3$)



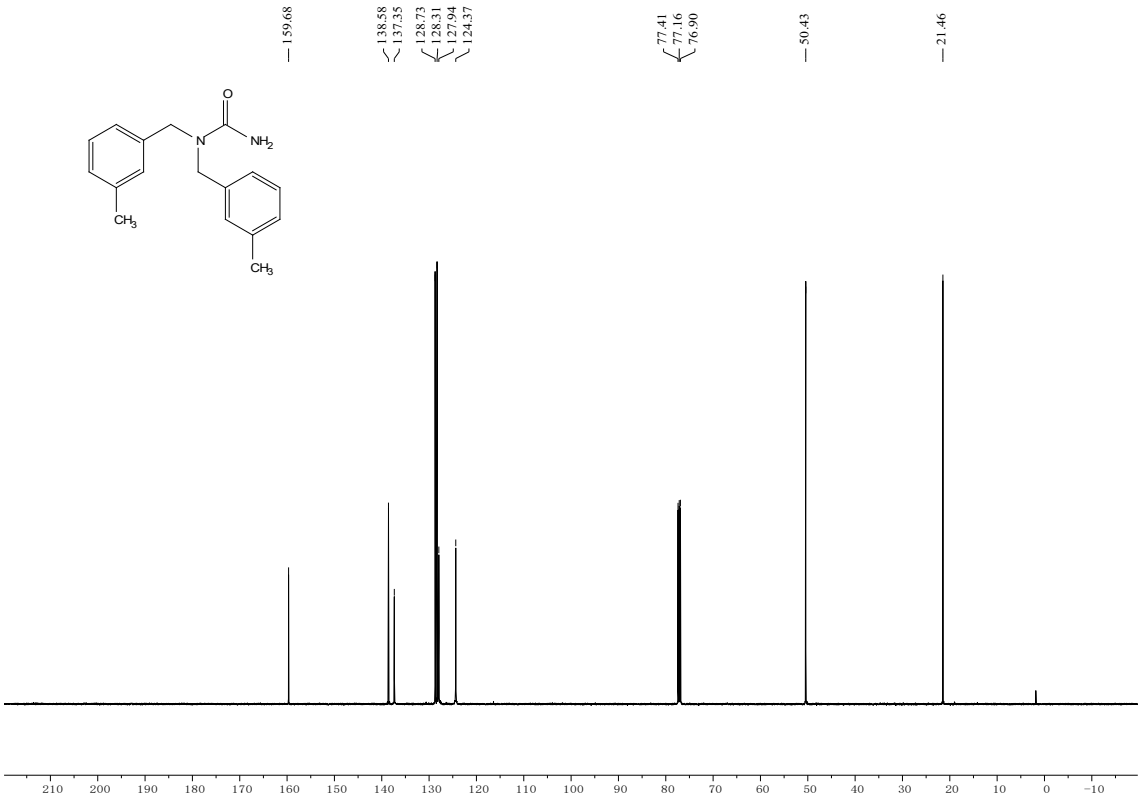
4g ^{13}C NMR (126 MHz, $CDCl_3$)



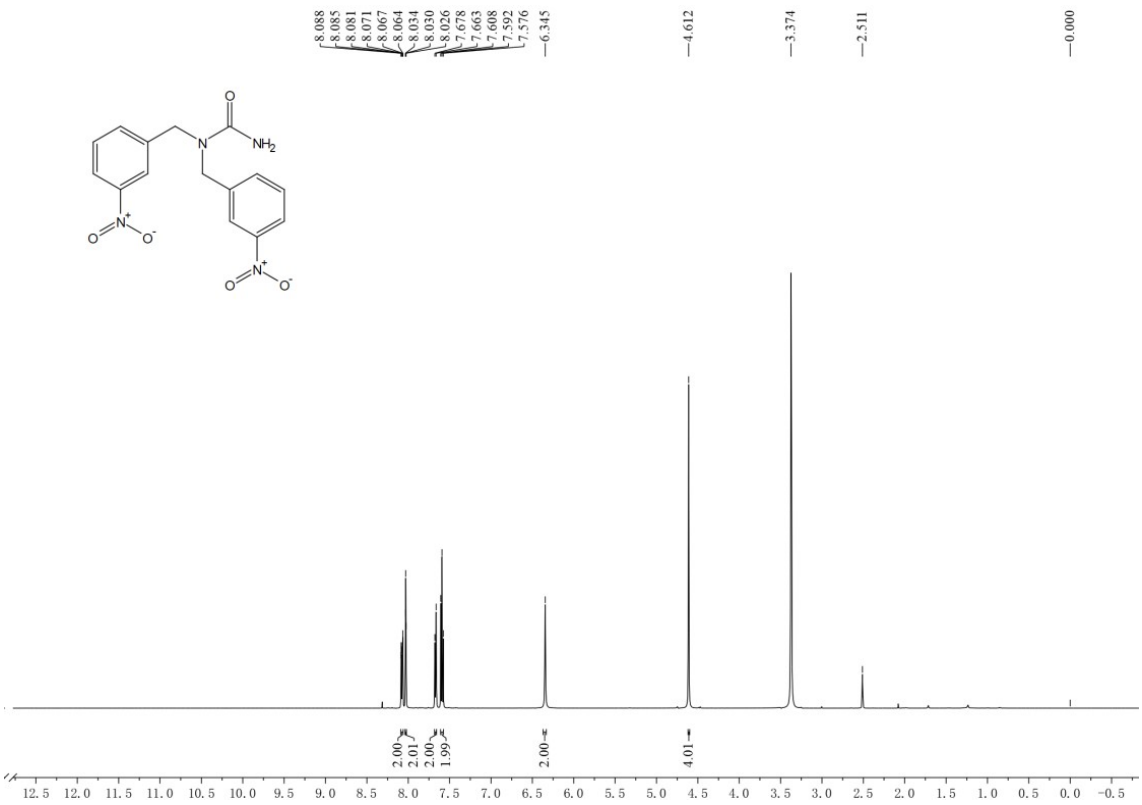
4h ^{1}H NMR (500 MHz, $CDCl_3$)



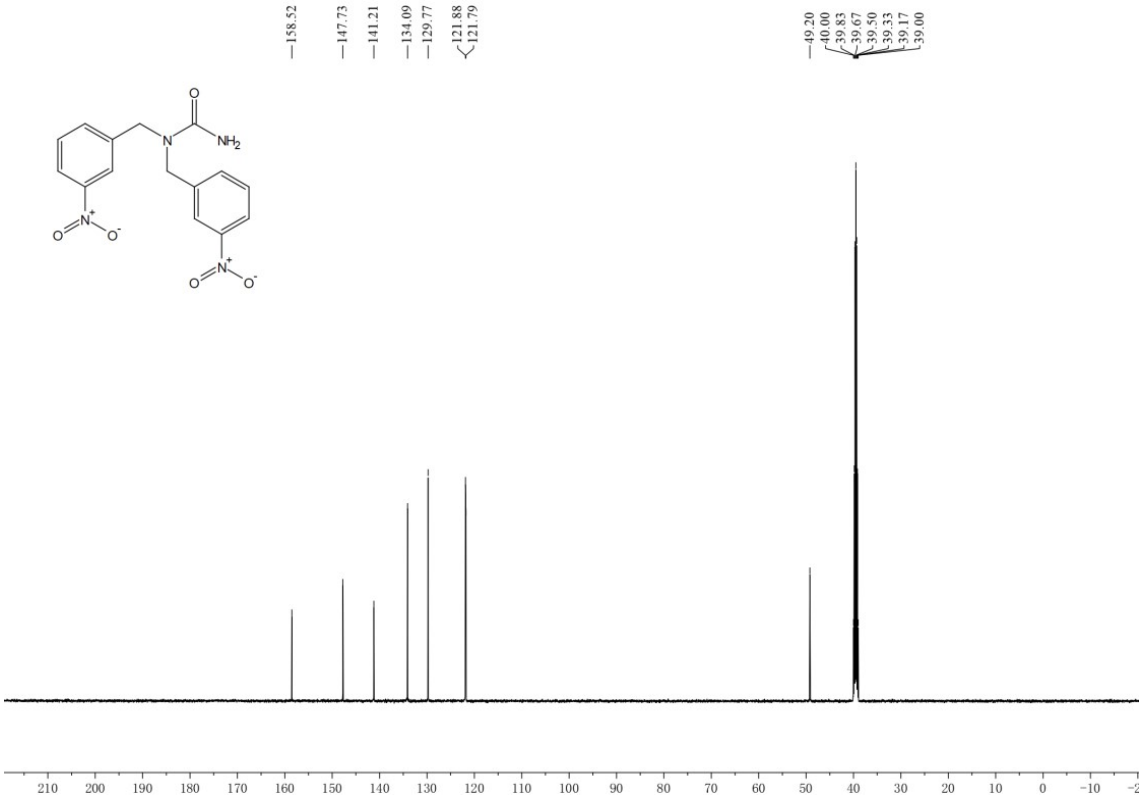
4h ^{13}C NMR (126 MHz, $CDCl_3$)



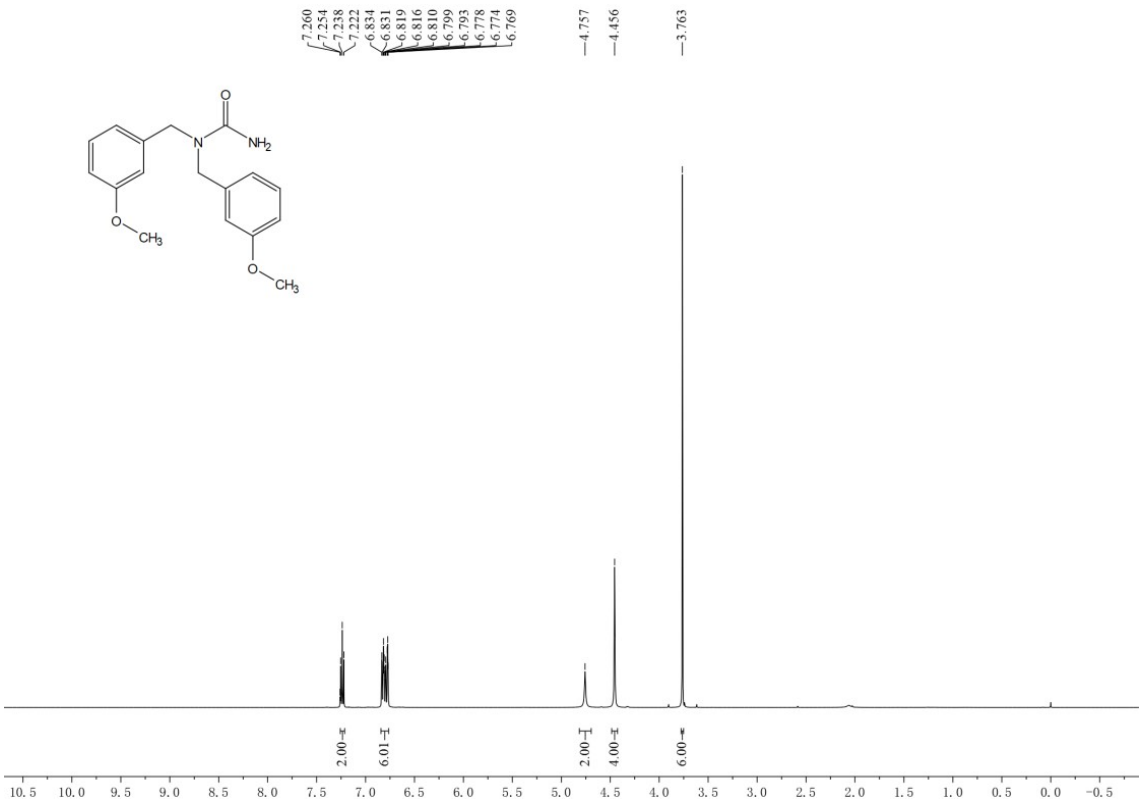
4i ^{1}H NMR (500 MHz, DMSO-d_6)



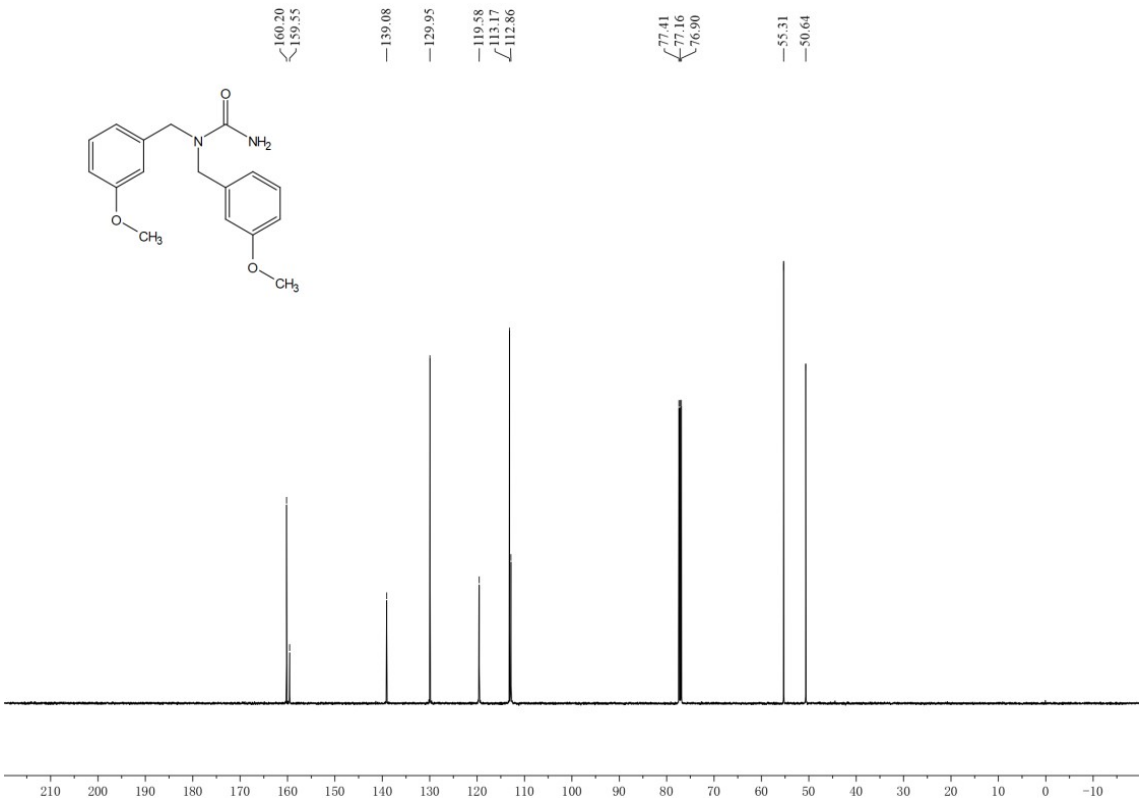
4i ^{13}C NMR (126 MHz, DMSO-d_6)



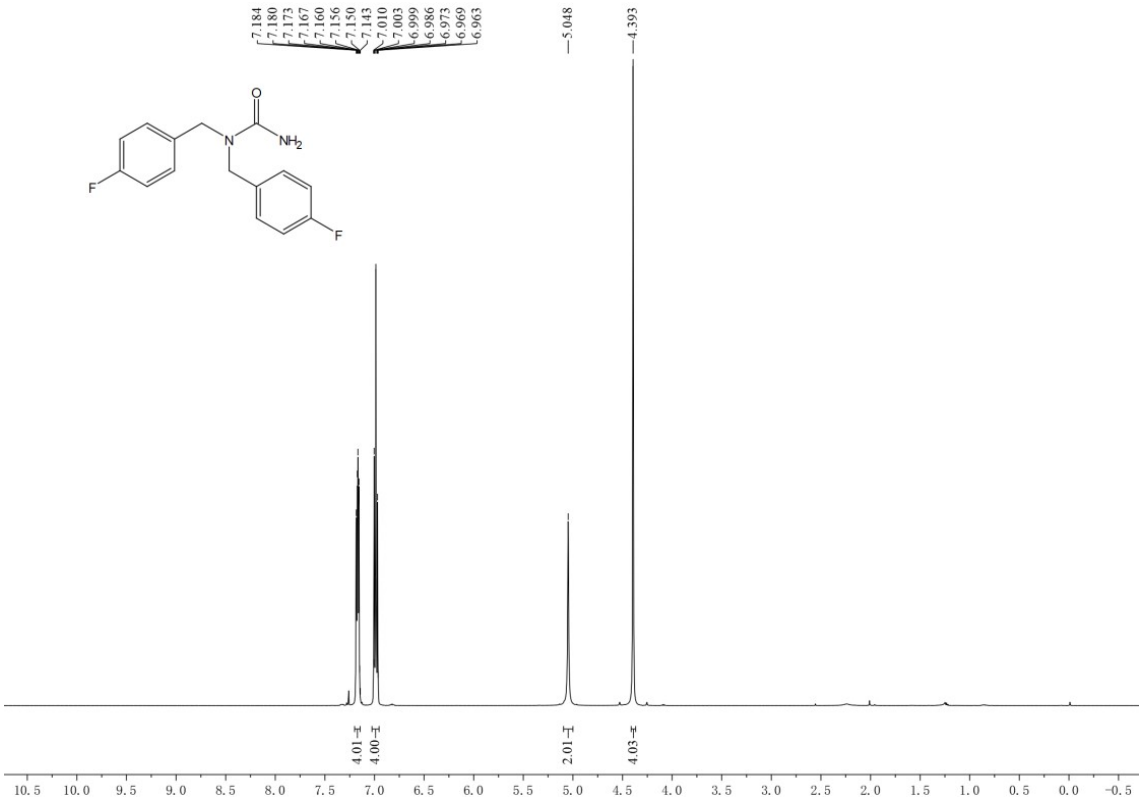
4j ^{1}H NMR (500 MHz, $CDCl_3$)



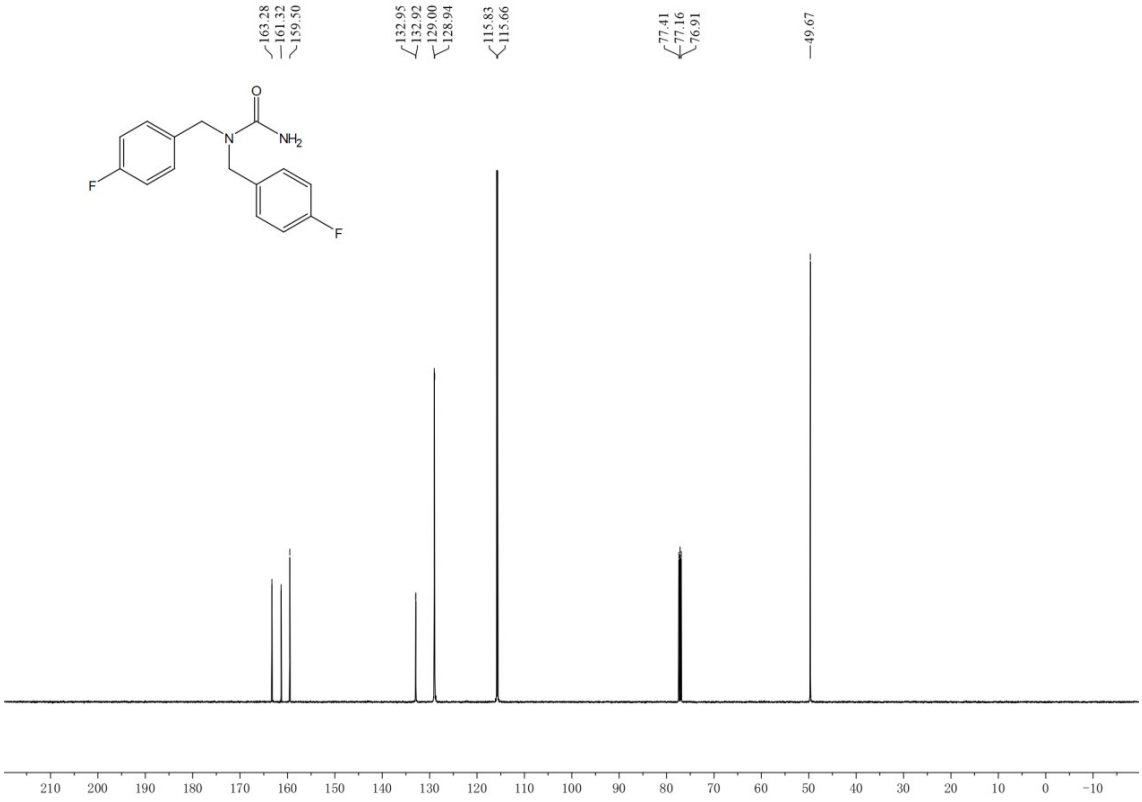
4j ^{13}C NMR (126 MHz, $CDCl_3$)



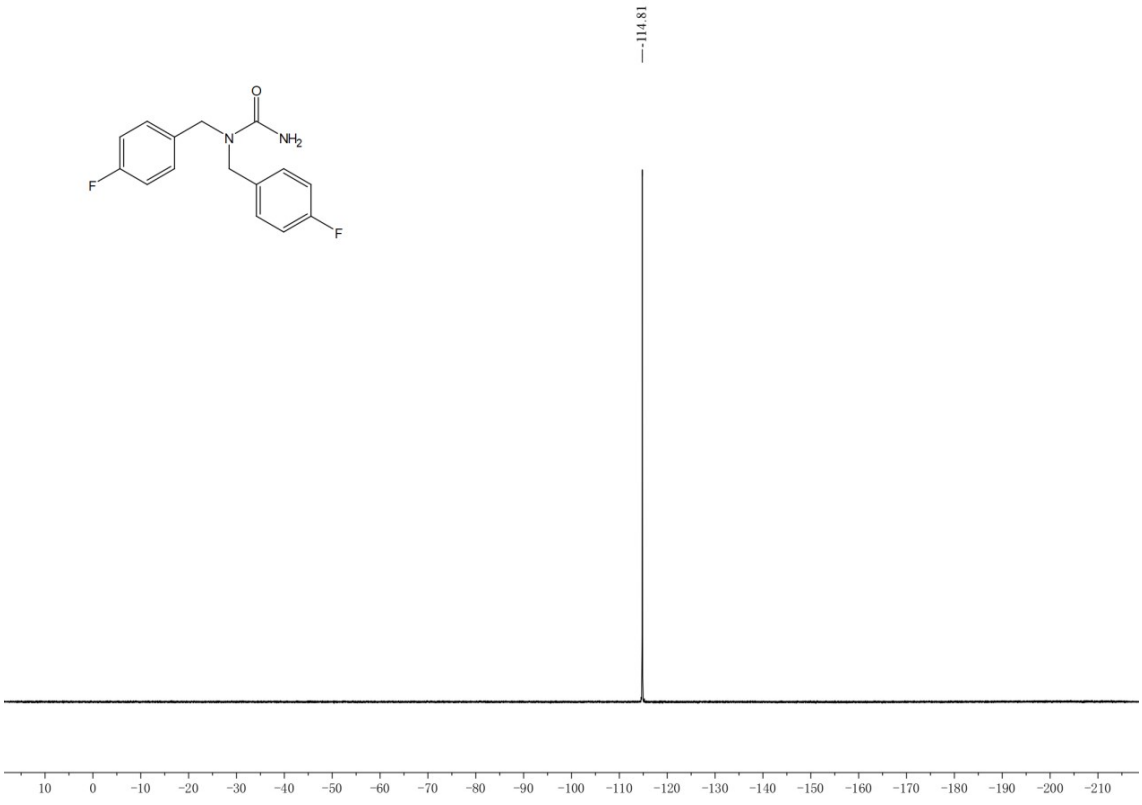
4k ^{1}H NMR (500 MHz, $CDCl_3$)



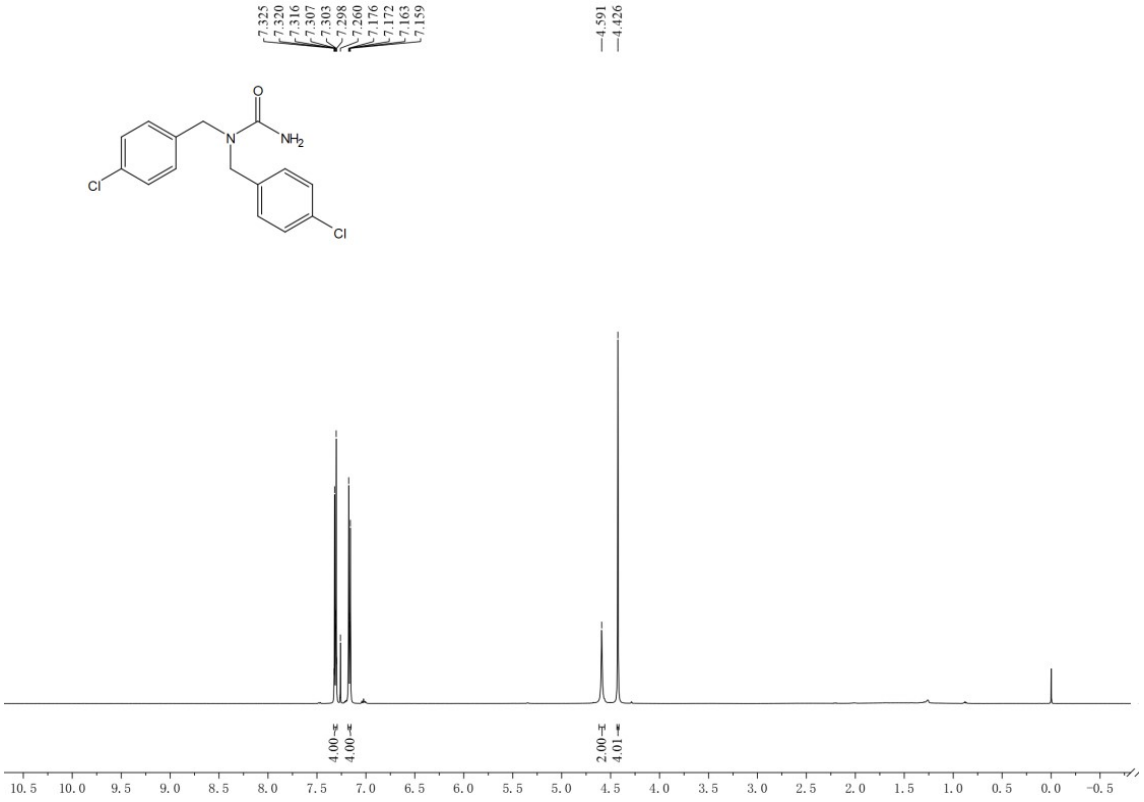
4k ^{13}C NMR (126 MHz, $CDCl_3$)



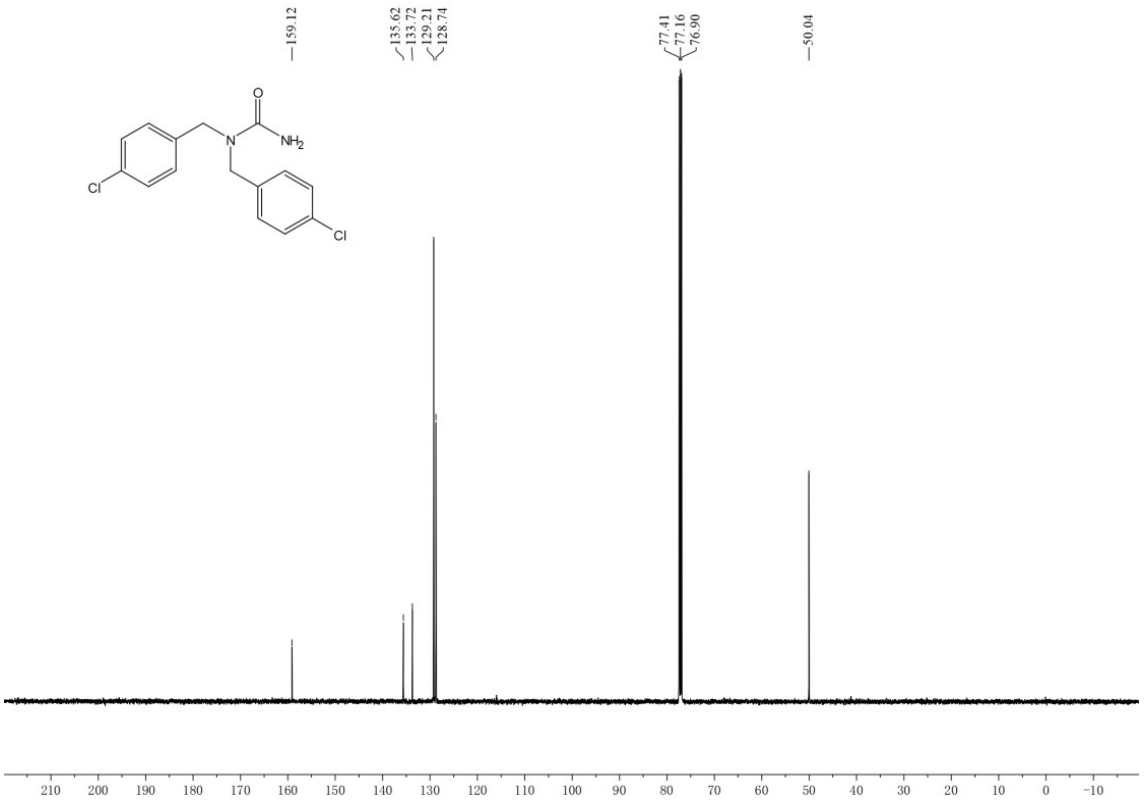
4k ^{19}F NMR (376 MHz, $CDCl_3$)



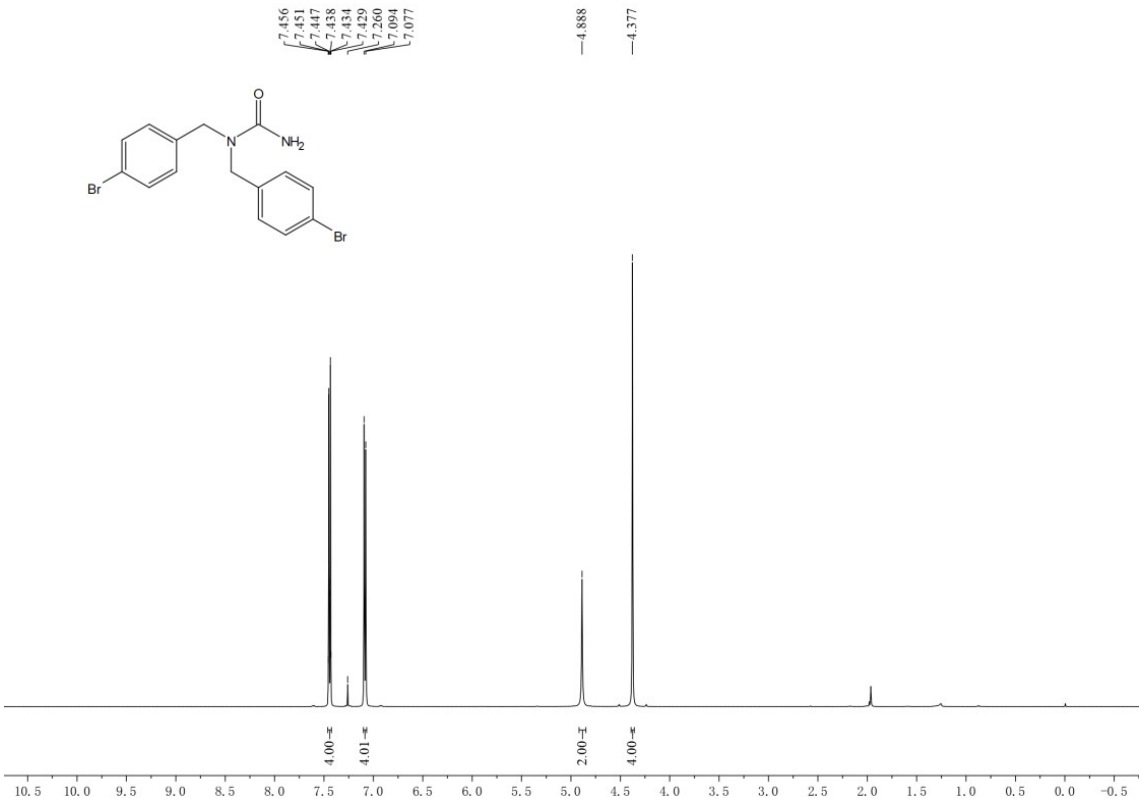
4l ^{1}H NMR (500 MHz, $CDCl_3$)



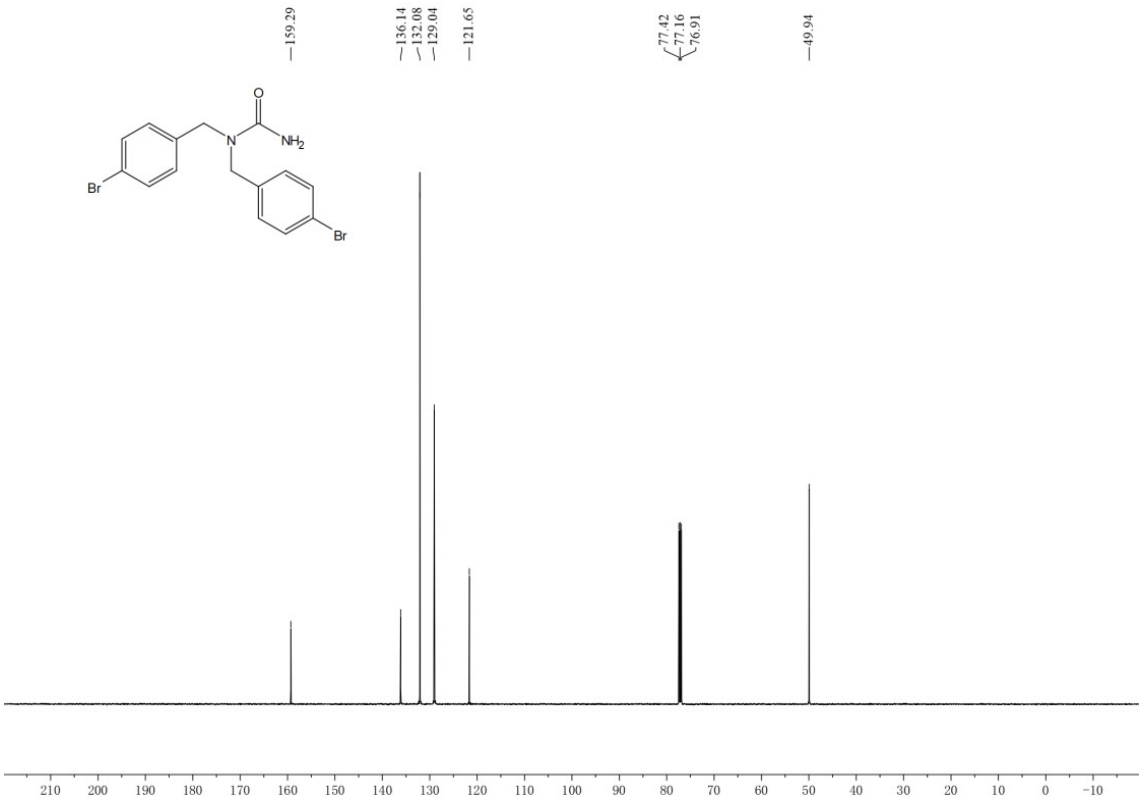
4l ^{13}C NMR (126 MHz, $CDCl_3$)



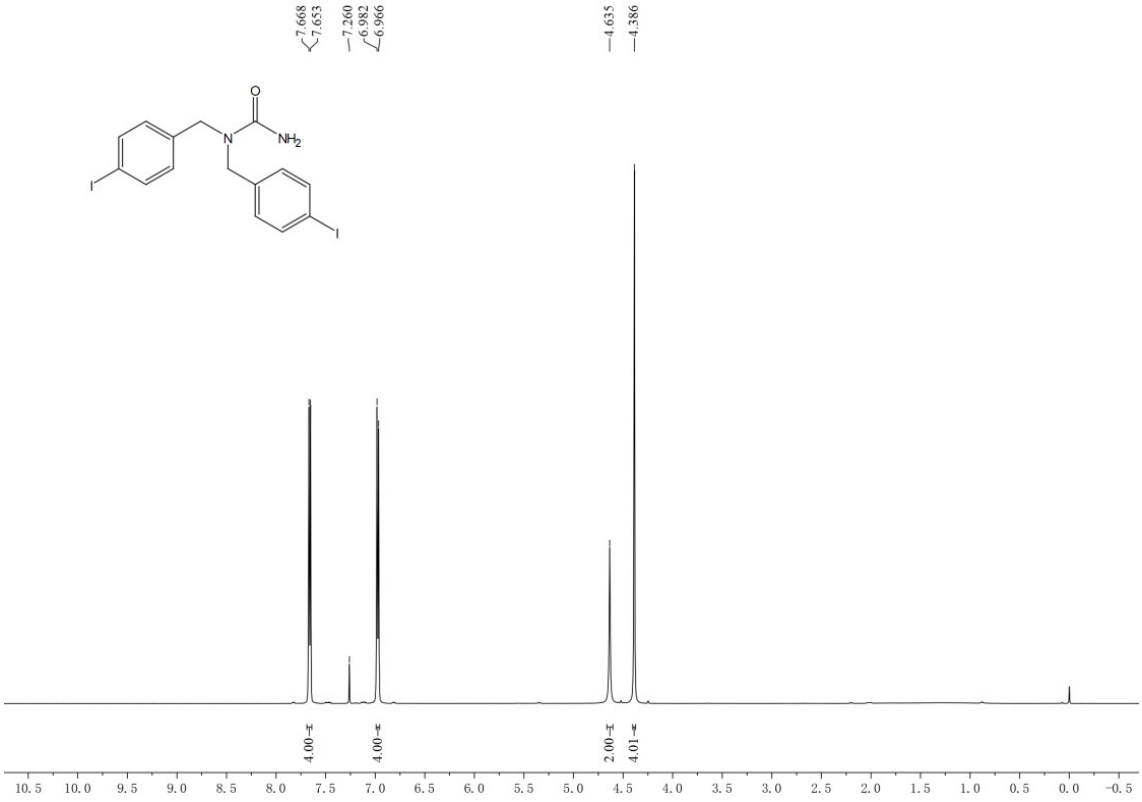
4m ^{1}H NMR (500 MHz, $CDCl_3$)



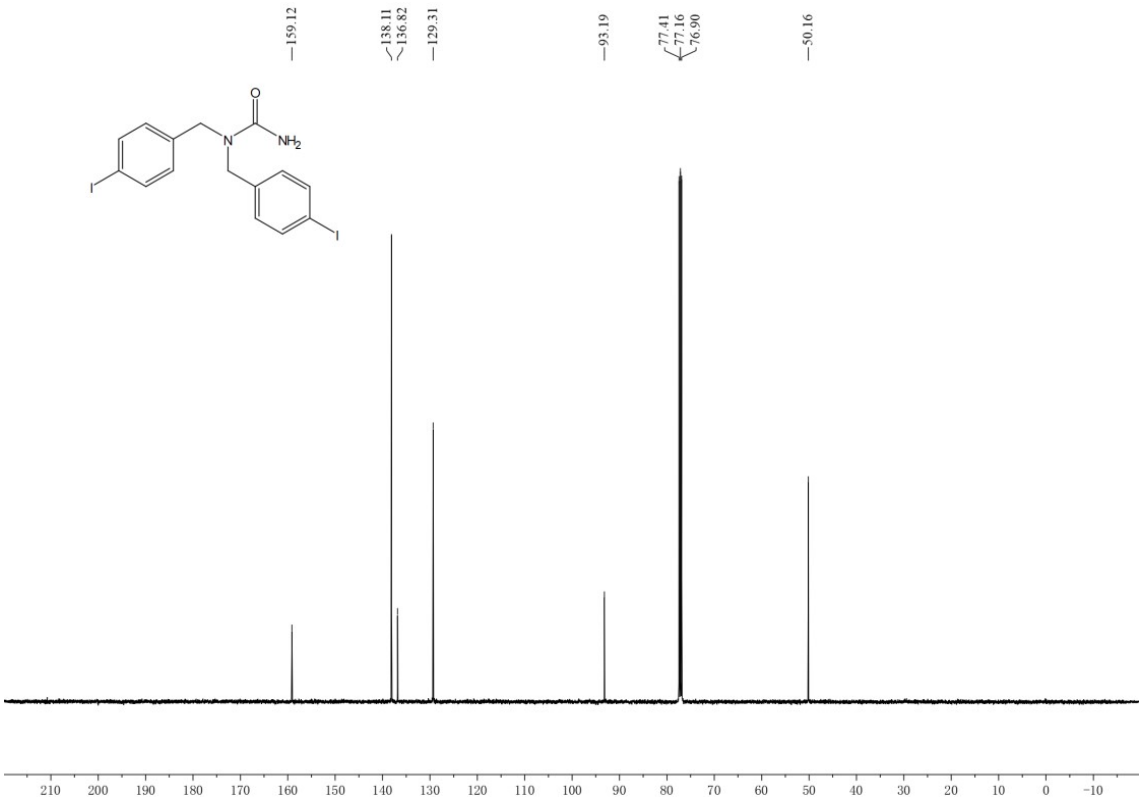
4m ^{13}C NMR (126 MHz, $CDCl_3$)



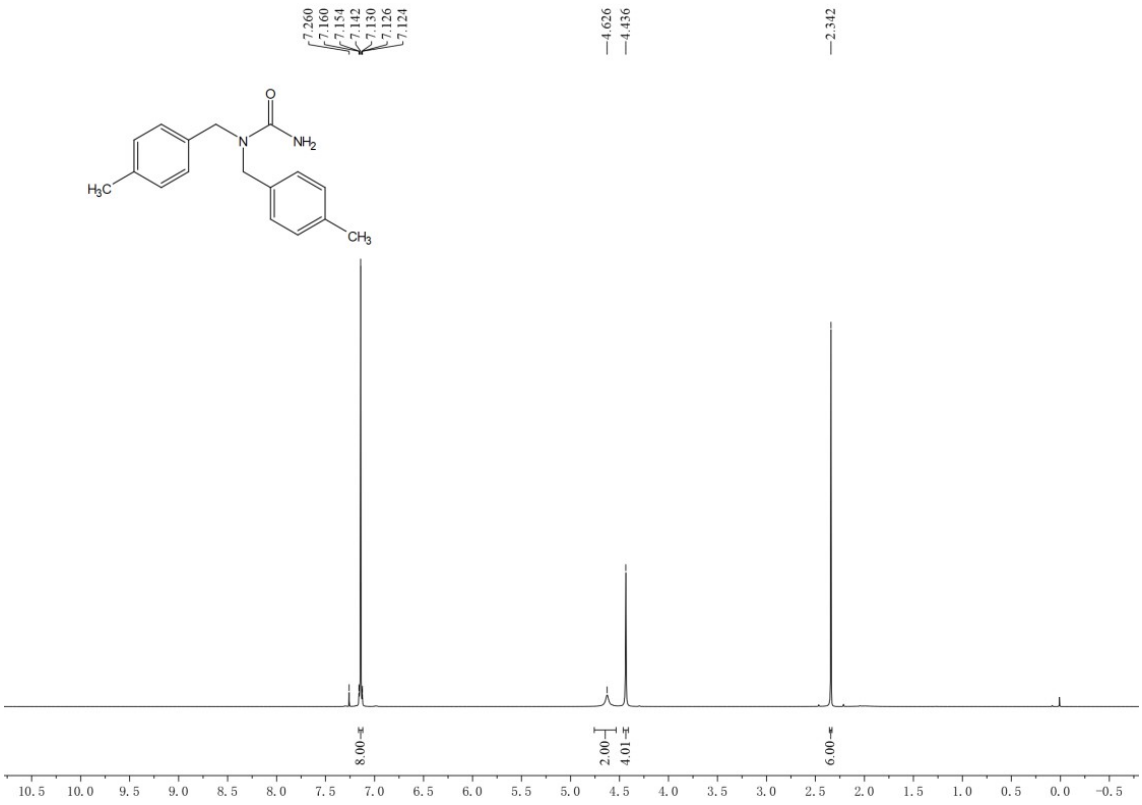
4n ^{1}H NMR (500 MHz, $CDCl_3$)



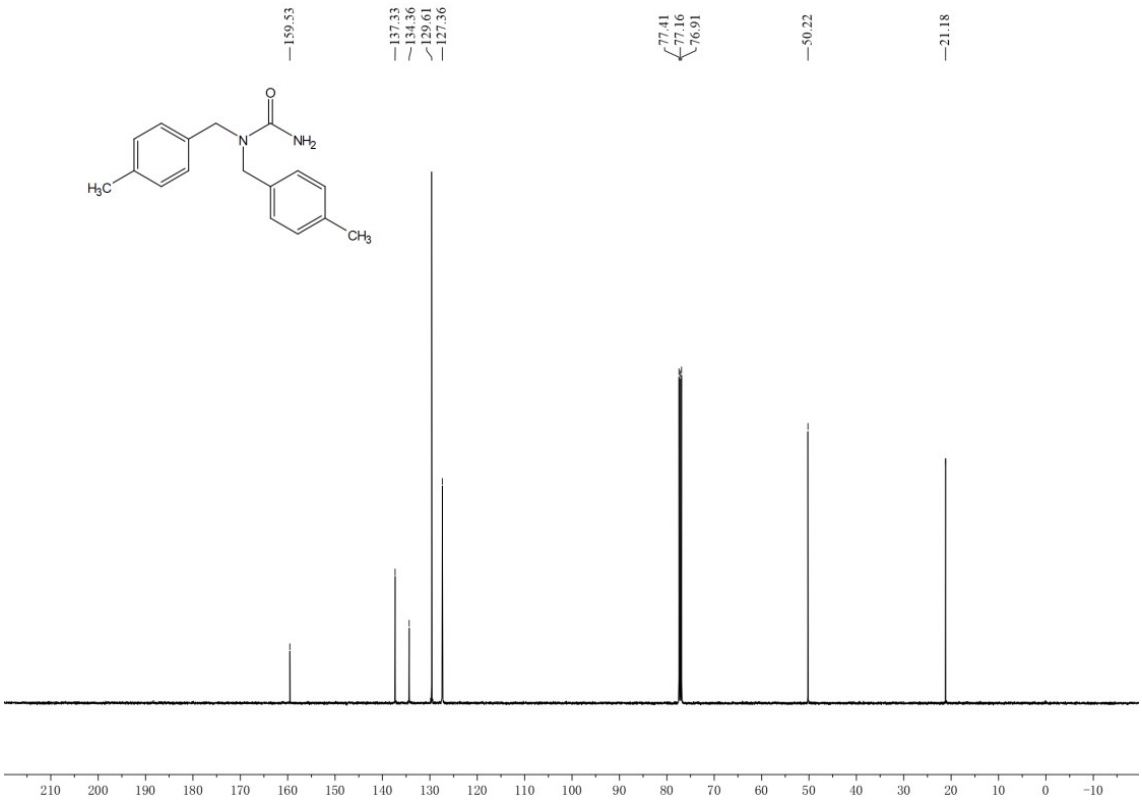
4n ^{13}C NMR (126 MHz, $CDCl_3$)



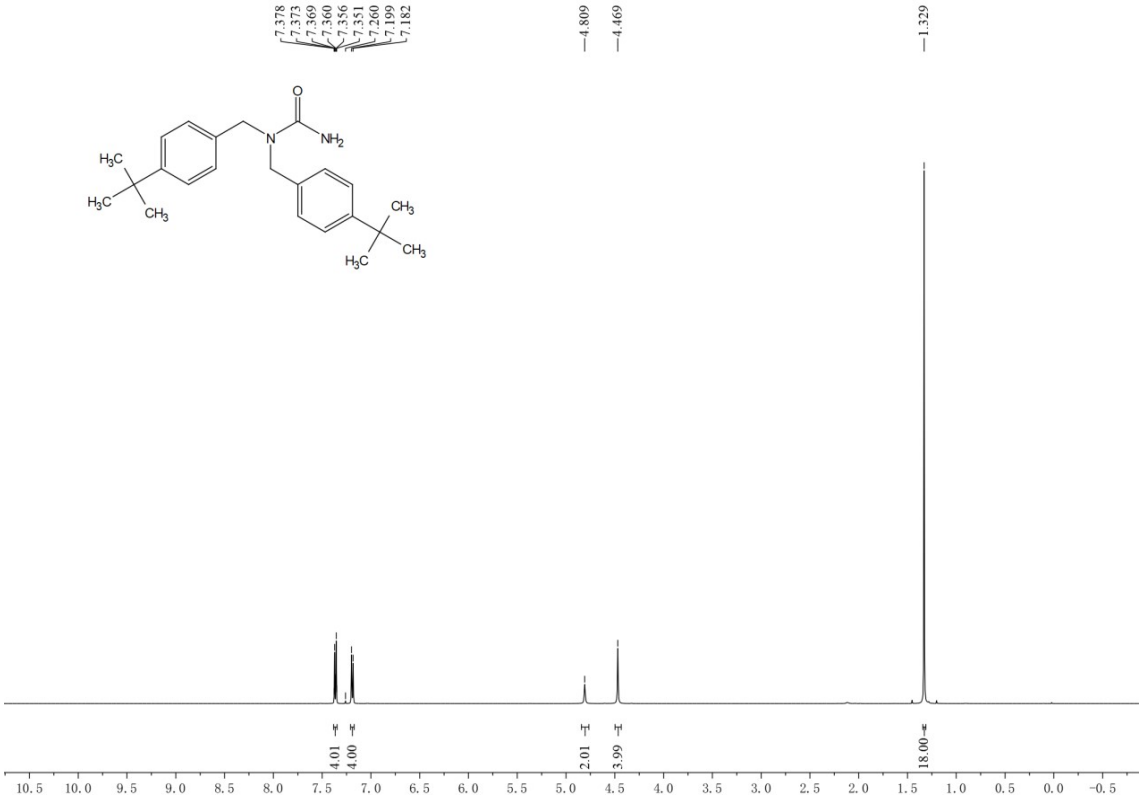
4o ^{1}H NMR (500 MHz, $CDCl_3$)



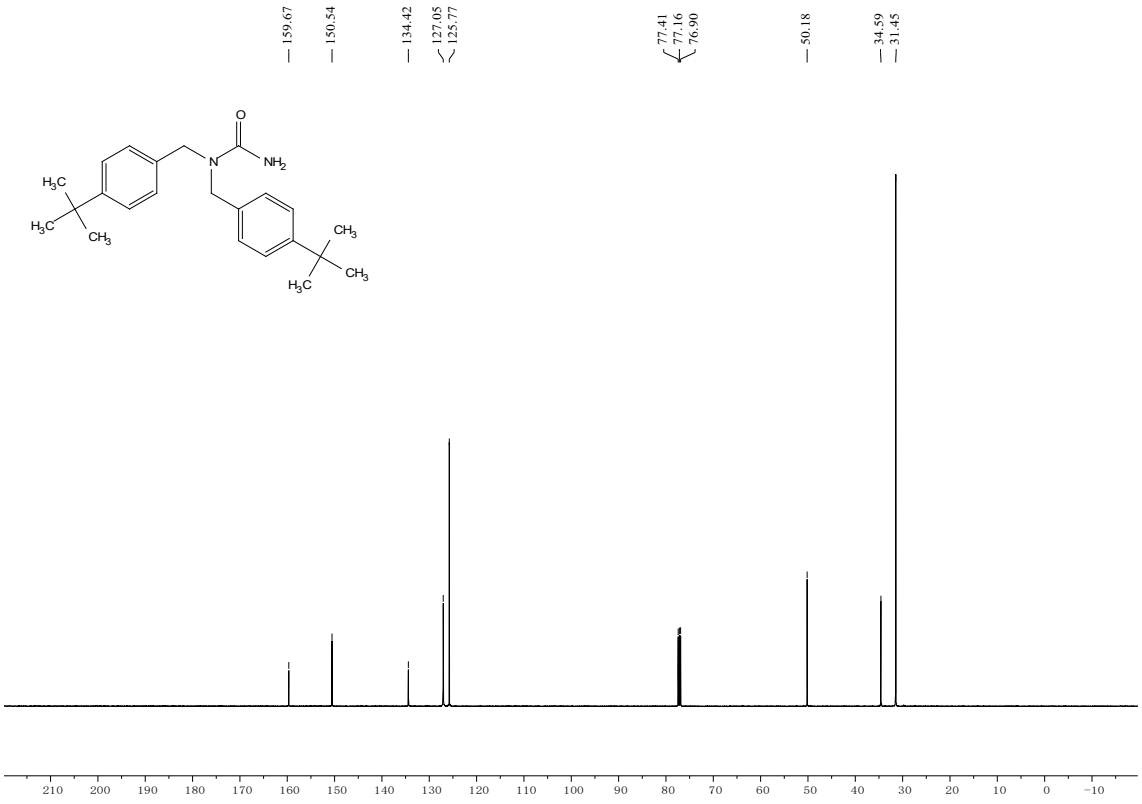
4o ^{13}C NMR (126 MHz, $CDCl_3$)



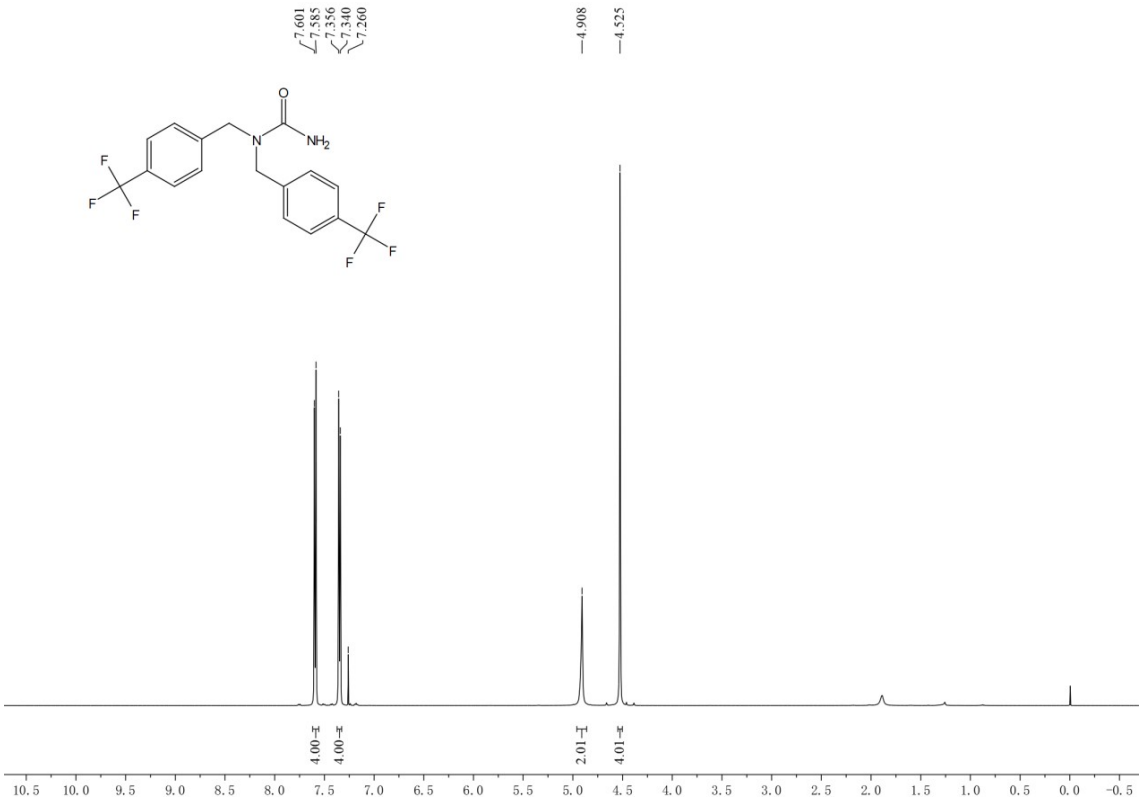
4p ^{1}H NMR (500 MHz, $CDCl_3$)



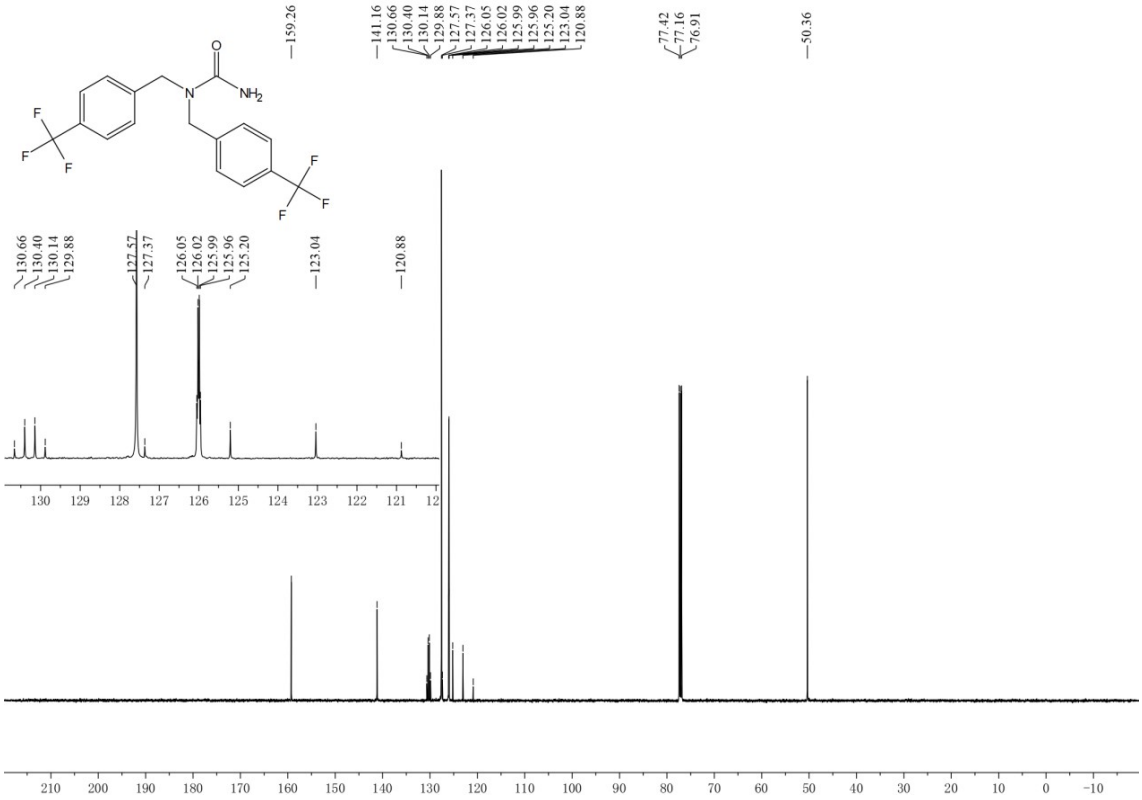
4p ^{13}C NMR (126 MHz, $CDCl_3$)



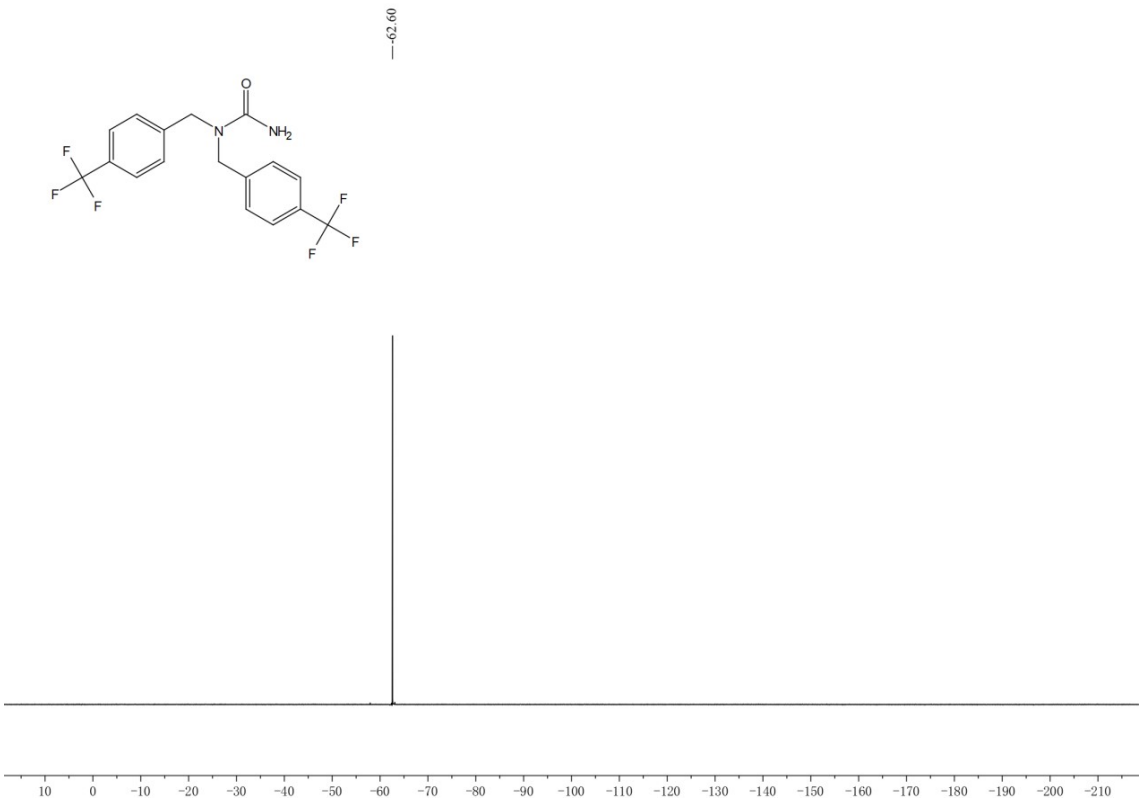
4q ^{1}H NMR (500 MHz, $CDCl_3$)



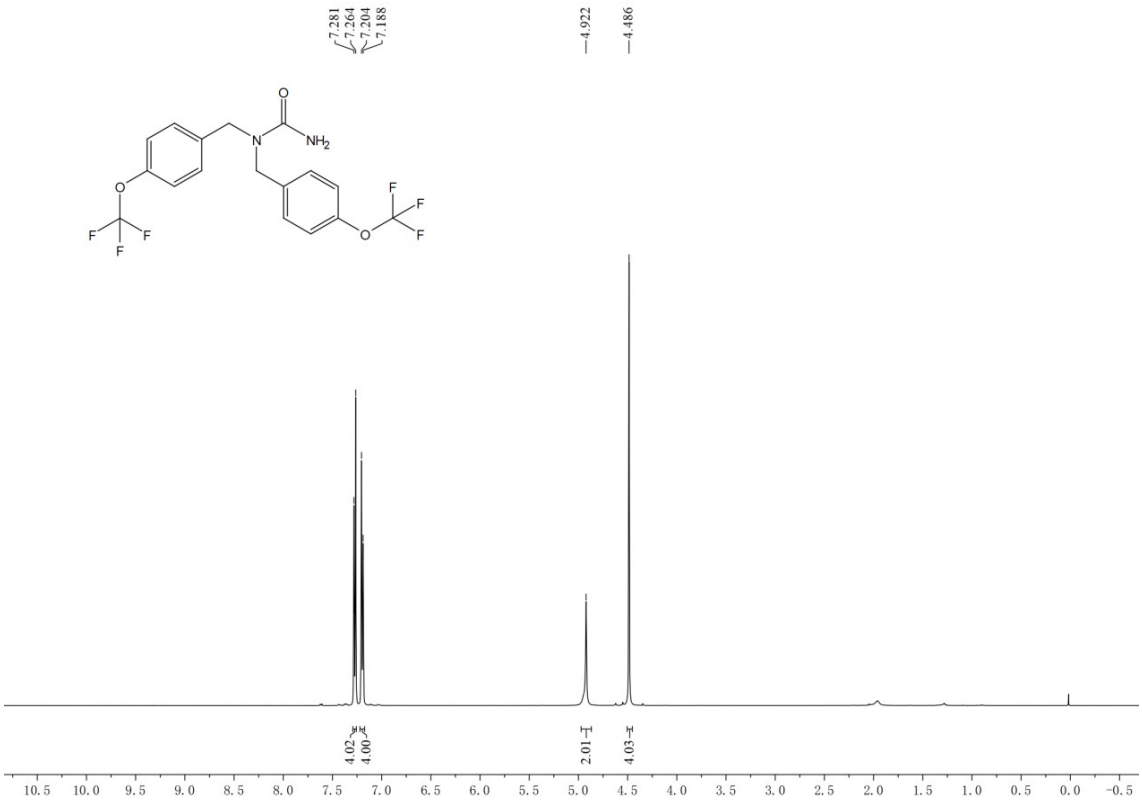
4q ^{13}C NMR (126 MHz, $CDCl_3$)



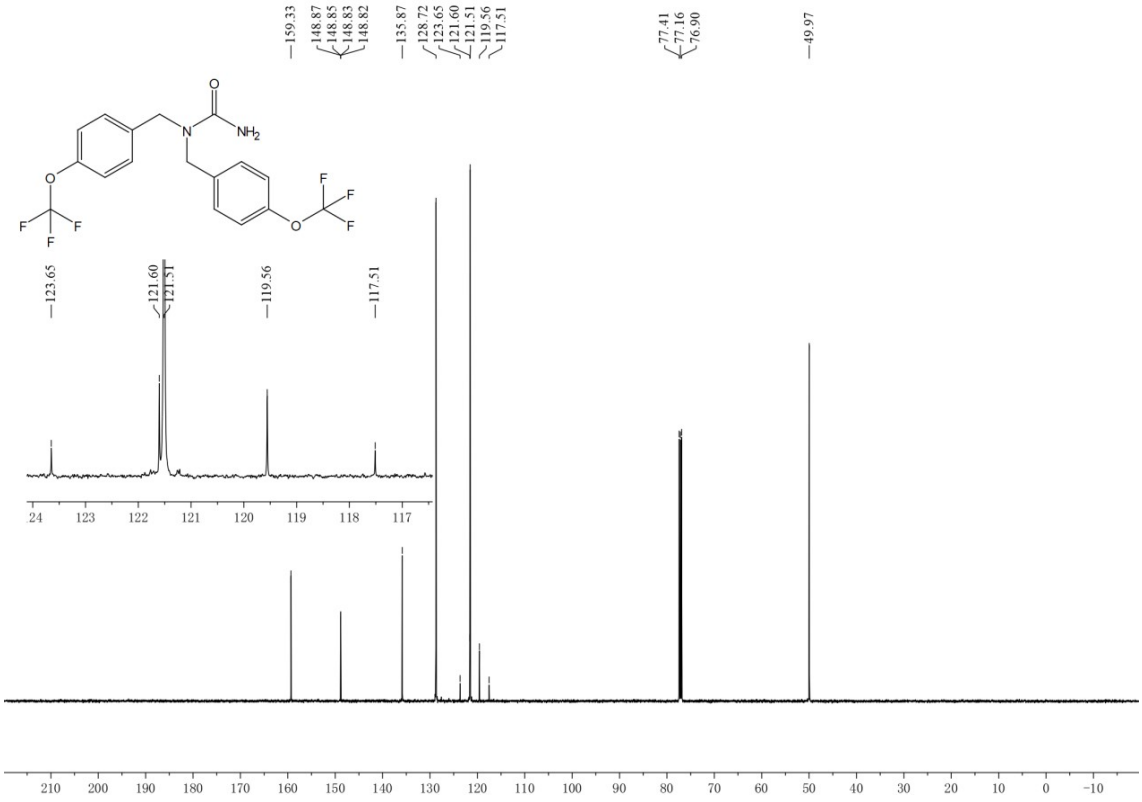
4q ^{19}F NMR (376 MHz, $CDCl_3$)



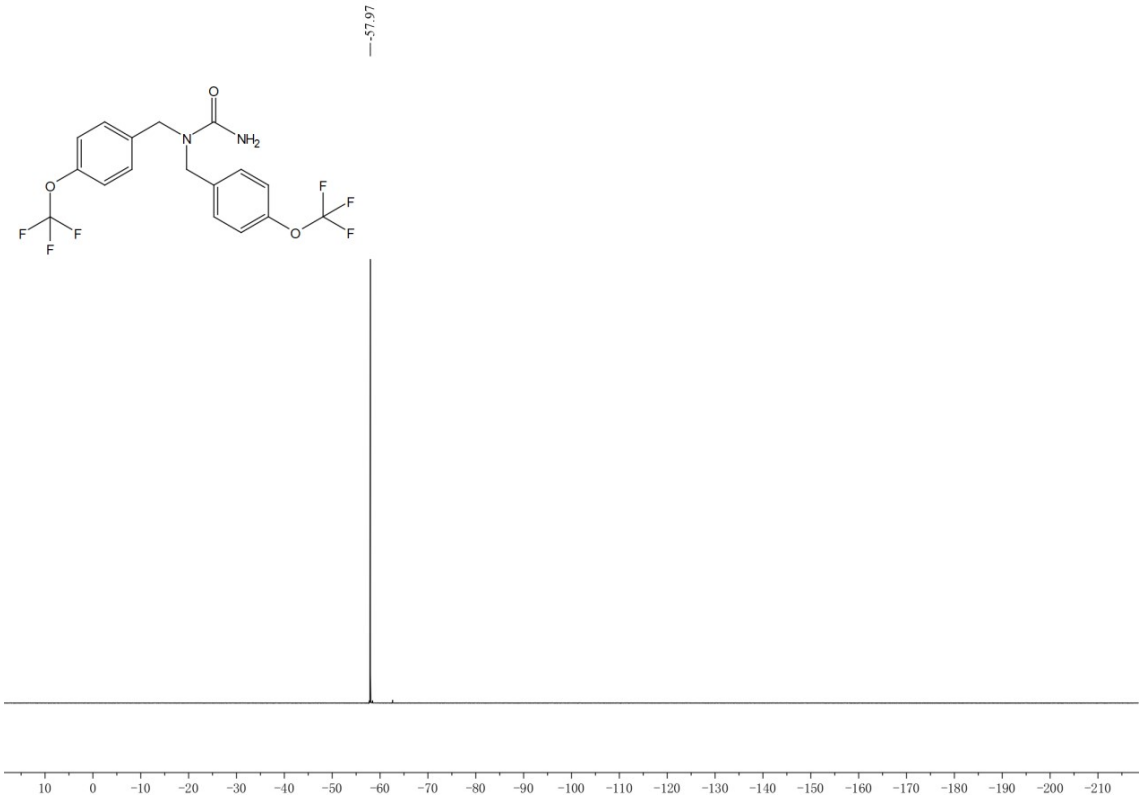
4r ^{1}H NMR (500 MHz, $CDCl_3$)



4r ^{13}C NMR (126 MHz, $CDCl_3$)

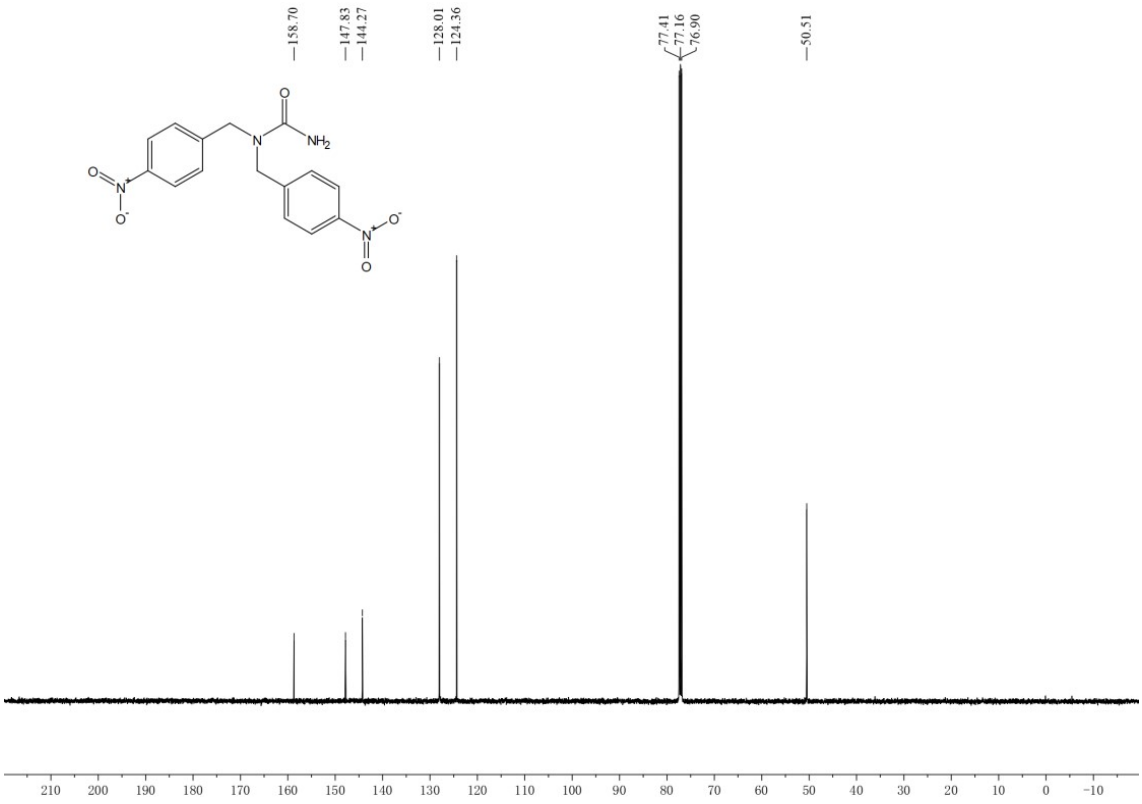


4r ^{19}F NMR (376 MHz, CDCl3)



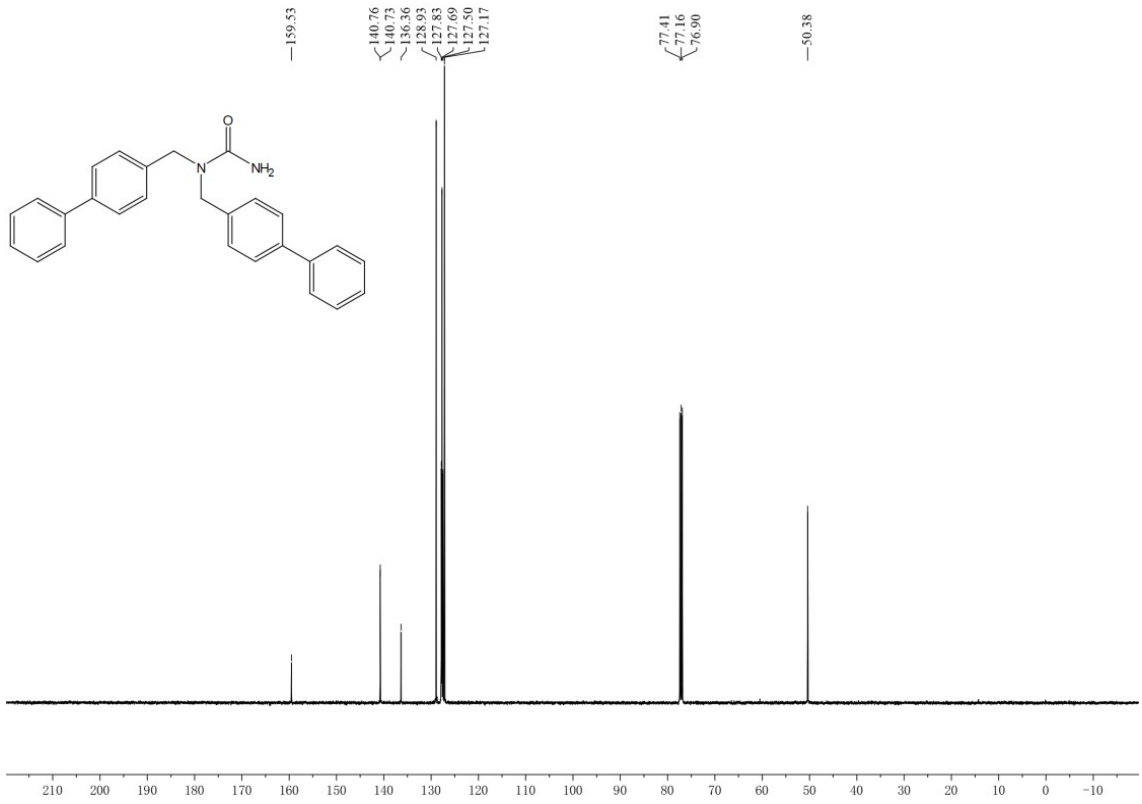
4s ^{1}H NMR (500 MHz, $CDCl_3$)

4s ^{13}C NMR (126 MHz, $CDCl_3$)

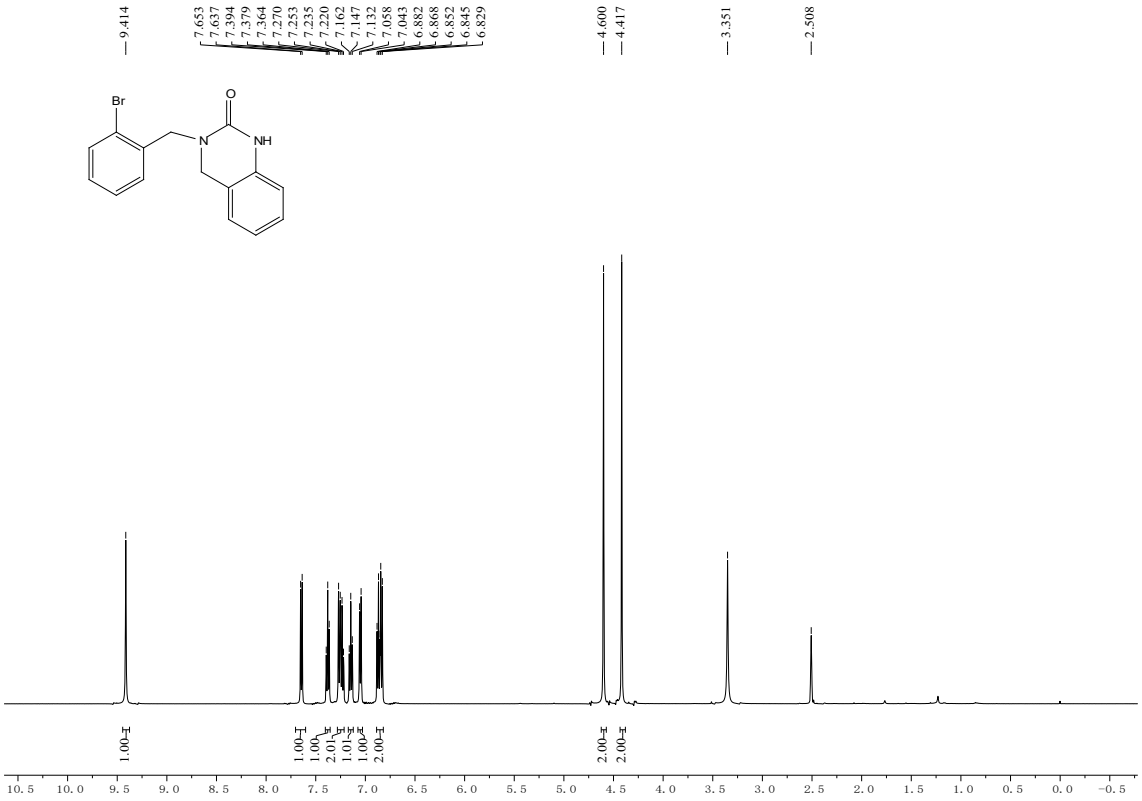


4t ^{1}H NMR (500 MHz, $CDCl_3$)

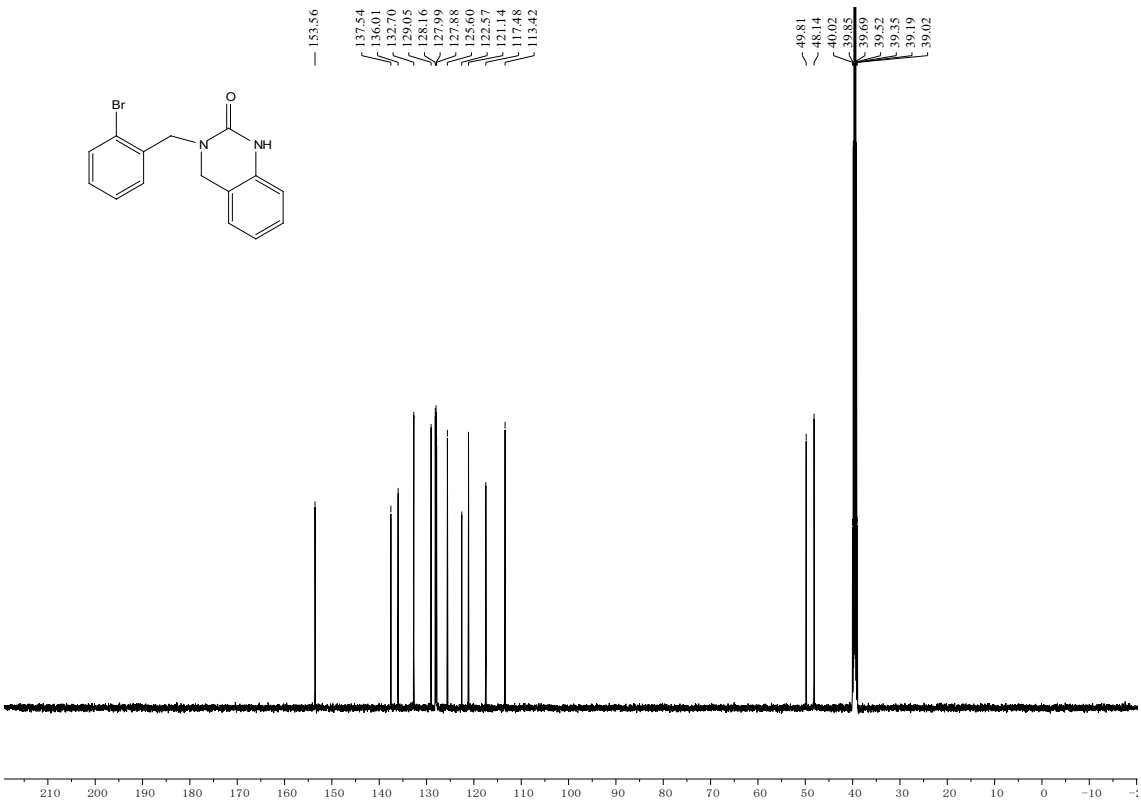
4t ^{13}C NMR (126 MHz, $CDCl_3$)



5a ^{1}H NMR (500 MHz, DMSO - d_6)



5a ^{13}C NMR (126 MHz, DMSO - d_6)



5a HRMS spectra