Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for

Platinum–P(BFPy)$_3$-catalyzed regioselective diboration of terminal alkynes with (pin)B–B(aam)

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1. General Remarks

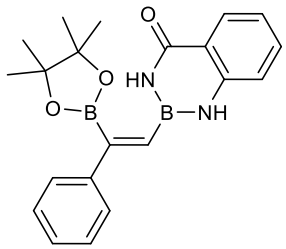
All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 160 MHz) or Varian System 400 (^{1}H, 400 MHz) spectrometer using residual proton in DMSO-*d*$_6$ (^{1}H, δ = 2.50), Acetone-*d*$_6$ (^{1}H, δ = 2.05), residual chloroform (^{1}H, δ = 7.26) or $CDCl_3$ (^{13}C, δ = 77.0) as an internal standard and boron trifluoride diethyl etherate (^{11}B, δ = 0.00) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (toluene as an eluent). Column chromatography was carried out using Merck Kieselgel 60. All microwave reactions (Biotage, Initiator+) were conducted in a sealed tube, and the reaction temperature was maintained by an external infrared sensor. Unless otherwise noted, commercially available reagents were used without purification. All solvents were dried over activated molecular sieves 3Å.

2. Experimental Procedures and Characterization of Products

Pt-Catalyzed Diboration of Alkynes

A reaction tube equipped with a magnetic stirring bar was charged with $Pt(dba)_2$ (4.5 μmol), $P(BFPy)_3$[1] (4.95 μmol), (pin)B–B(aam)[2] (0.15 mmol), an alkyne (0.225 mmol) and toluene (2 mL), and the mixture was stirred at 180 °C for 30 min under microwave irradiation. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by boric acid impregnated silica gel-column chromatography (hexane/ethyl acetate as an eluent) or gel permeation chromatography (toluene as an eluent) gave the product.

(*E*)-2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3a)



A pale yellow solid: mp 190-191 °C (49.4 mg)

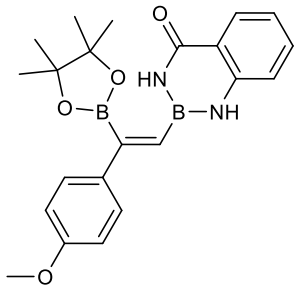
^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.05 (s, 1H), 7.64 (s, 1H), 7.52 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.44 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.60 (s, 1H), 1.40 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 167.79, 144.62, 140.95, 133.79, 129.29, 128.47, 127.85, 127.23, 121.74, 118.86, 117.59, 84.95, 25.08.

^{11}B NMR ($CDCl_3$) δ 29.95, 27.65.

HRMS Calcd for $C_{21}H_{24}B_2N_2O_3$: $[M+Na]^+$, 397.1865. Found: *m*/*z* 397.1867

(*E*)-2-(2-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3b)



A pale yellow solid: mp 82-83 °C (56.3 mg)

^{1}H NMR ($CDCl_3$) δ 8.22 (d, *J* = 7.9 Hz, 1H), 7.98 (s, 1H), 7.56 (s, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.53 (s, 1H), 3.83 (s, 3H), 1.41 (s, 12H).

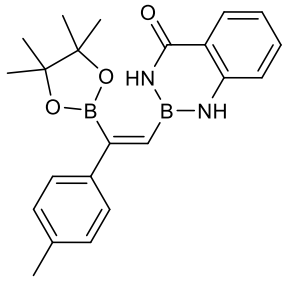
^{13}C NMR ($CDCl_3$) δ 166.76, 159.61, 144.67, 136.68, 133.74, 129.25, 128.46, 121.63, 119.23, 117.55, 113.90, 84.89, 55.43, 25.08.

^{11}B NMR ($CDCl_3$) δ 29.65, 22.19.

HRMS Calcd for $C_{22}H_{26}B_2N_2O_4$: $[M+Na]^+$, 427.1971. Found: *m*/*z* 427.1968

(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*p*-tolyl)vinyl)-2,3-

dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3c)



A pale yellow solid: mp 182-183 ˚C (51.1 mg)

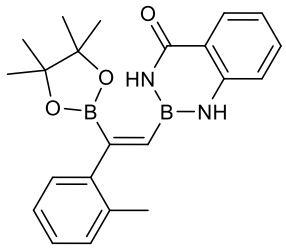
^{1}H NMR ($CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.00 (s, 1H), 7.59 (s, 1H), 7.51 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 18.8, 8.0 Hz, 3H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.57 (s, 1H), 2.36 (s, 3H), 1.40 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.73, 144.65, 141.46, 137.76, 133.74, 129.27, 129.21, 127.13, 121.66, 119.27, 117.57, 84.90, 25.08, 21.32.

^{11}B NMR ($CDCl_3$) δ 31.47.

HRMS Calcd for $C_{22}H_{26}B_2N_2O_3$: $[M+Na]^+$, 411.2022. Found: *m*/*z* 411.2025

(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*o*-tolyl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3d)



A pale yellow solid: mp 142-143 ˚C (52.4 mg)

^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.12 (s, 1H), 7.94 (s, 1H), 7.52 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.21 – 7.06 (m, 5H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.34 (s, 1H), 2.28 (s, 3H), 1.36 (s, 12H).

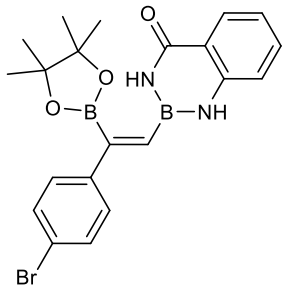
^{13}C NMR ($CDCl_3$) δ 166.86, 146.26, 144.69, 134.37, 133.73, 129.79, 129.23, 128.09, 127.23, 126.13, 121.69, 119.31, 117.67, 84.75, 25.04, 20.42.

^{11}B NMR ($CDCl_3$) δ 29.24.

HRMS Calcd for $C_{22}H_{26}B_2N_2O_3$: $[M+Na]^+$, 411.2022. Found: *m*/*z* 411.2024

(*E*)-2-(2-(4-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-

dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3e)



A pale yellow solid: mp 175-176 °C (62.2 mg)

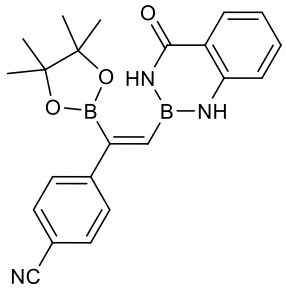
^{1}H NMR ($CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.04 (s, 1H), 7.62 (s, 1H), 7.52 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.17 – 7.11 (m, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.58 (s, 1H), 1.39 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.68, 144.53, 143.39, 133.82, 131.54, 129.29, 128.96, 122.00, 121.84, 119.31, 117.61, 85.07, 25.05.

^{11}B NMR ($CDCl_3$) δ 30.00.

HRMS Calcd for $C_{21}H_{23}B_2BrN_2O_3$: $[M+Na]^+$, 475.0970. Found: *m*/*z* 475.0971

(*E*)-4-(2-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (3f)



A pale yellow solid: mp 229-230 °C (48.7 mg)

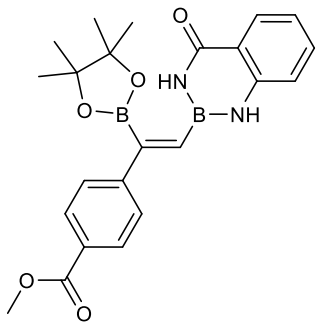
^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.03 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 3H), 7.52 (dd, *J* = 8.7, 3.2 Hz, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.64 (s, 1H), 1.39 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.64, 149.26, 144.41, 133.91, 132.23, 129.30, 128.05, 122.03, 119.35, 119.13, 117.67, 111.16, 85.27, 25.03.

^{11}B NMR ($CDCl_3$) δ 29.95.

HRMS Calcd for $C_{22}H_{23}B_2N_3O_3$: $[M+Na]^+$, 422.1818. Found: *m*/*z* 422.1818

methyl (*E*)-4-(2-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (3g)



A pale yellow solid: mp 159-160 ˚C (50.9 mg)

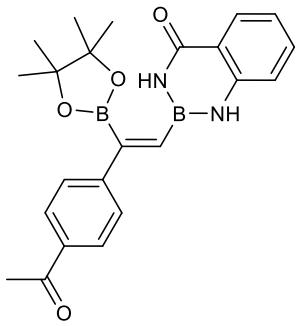
^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.05 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.62 (s, 1H), 7.56 – 7.46 (m, 3H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.66 (s, 1H), 3.92 (s, 3H), 1.39 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 167.37, 166.97, 149.36, 144.76, 134.10, 130.02, 129.55, 127.56, 126.98, 122.15, 119.58, 117.89, 85.38, 52.51, 25.42.

^{11}B NMR ($CDCl_3$) δ 30.07.

HRMS Calcd for $C_{23}H_{26}B_2N_2O_5$: $[M+Na]^+$, 455.1920. Found: *m*/*z* 455.1919

(*E*)-2-(2-(4-acetylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3h)



A pale yellow solid: mp 146-147 ˚C (43.1 mg)

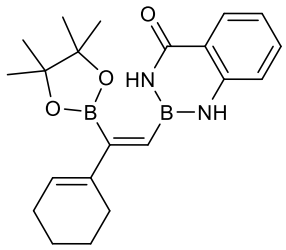
^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.04 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.63 (s, 1H), 7.52 (dd, *J* = 7.6, 4.4 Hz, 3H), 7.18 – 7.12 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.67 (s, 1H), 2.61 (s, 3H), 1.40 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.65, 149.30, 144.50, 136.17, 133.84, 129.29, 128.58, 127.51, 121.90, 119.34, 117.64, 85.14, 26.80, 25.02.

^{11}B NMR ($CDCl_3$) δ 30.77.

HRMS Calcd for $C_{23}H_{26}B_2N_2O_4$: $[M+Na]^+$, 439.1971. Found: *m*/*z* 439.1970

(*E*)-2-(2-(cyclohex-1-en-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3i)



A pale yellow solid: mp 122-123 °C (55.4 mg)

^{1}H NMR ($CDCl_3$) δ 8.19 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78 (s, 1H), 7.49 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.17 (s, 1H), 6.03 (d, *J* = 3.8 Hz, 1H), 2.22 (t, *J* = 5.3 Hz, 4H), 1.71 (dd, *J* = 6.1, 2.5 Hz, 2H), 1.61 (dd, *J* = 6.0, 2.6 Hz, 2H), 1.38 (s, 12H).

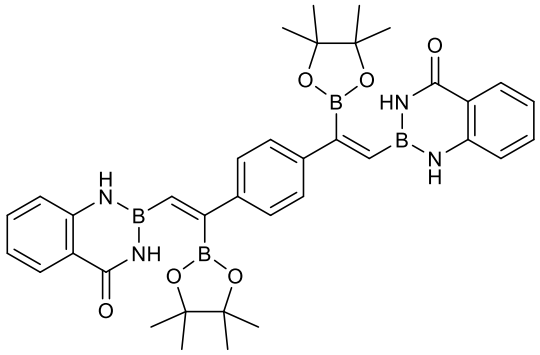
^{13}C NMR ($CDCl_3$) δ 166.65, 144.63, 140.29, 133.72, 132.21, 129.25, 121.54, 119.10, 117.41, 84.78, 26.60, 25.34, 25.20, 22.79, 22.27.

^{11}B NMR ($CDCl_3$) δ 29.77, 23.01.

HRMS Calcd for $C_{21}H_{28}B_2N_2O_3$: $[M+Na]^+$, 401.2178. Found: *m*/*z* 401.2180

2,2'-((1*E*,1'*E*)-1,4-phenylenebis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene-2,1-diyl))bis(2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one) (3j)

A reaction tube equipped with a magnetic stirring bar was charged with $Pt(dba)_2$ (4.5 μmol), $P(BFPy)_3$ (4.95 μmol), (pin)B–B(aam) (0.165 mmol), 1,4-diethynylbenzene (0.075 mmol) and toluene (2 mL), and the mixture was stirred at 180 °C for 30 min under microwave irradiation. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by boric acid impregnated silica gel-column chromatography (hexane/ethyl acetate as an eluent) gave the product **3j**.



A pale yellow solid: mp >300 ˚C (Melting point of **3j** could not be determined, because it is out of the measurable range of the melting point apparatus.) (41.0 mg)

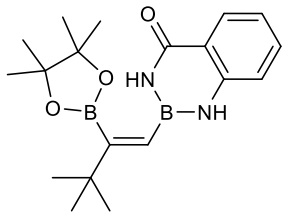
^{1}H NMR (DMSO-d_6) δ 9.12 (s, 2H), 9.01 (s, 2H), 7.98 (dd, J = 7.9, 1.6 Hz, 2H), 7.55 (dd, J = 7.6, 2.1 Hz, 2H), 7.44 (s, 4H), 7.24 (dd, J = 8.3, 1.1 Hz, 2H), 7.08 (ddd, J = 8.1, 7.1, 1.1 Hz, 2H), 6.84 (s, 2H), 1.25 (s, 24H).

^{13}C NMR (DMSO-d_6) δ 165.60, 145.29, 142.37, 133.32, 127.95, 126.78, 120.70, 118.64, 117.96, 84.11, 24.62.

^{11}B NMR (DMSO-d_6) δ 28.59, 21.72.

HRMS Calcd for $C_{36}H_{42}B_4N_4O_6$: $[M+H]^+$, 671.3549. Found: *m*/*z* 671.3563

(*E*)-2-(3,3-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3k)



A pale yellow solid: mp 129-130 ˚C (51.5 mg)

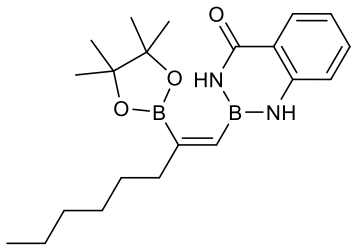
^{1}H NMR ($CDCl_3$) δ 8.19 (dd, J = 7.9, 1.6 Hz, 1H), 7.69 (s, 1H), 7.48 (ddd, J = 8.4, 7.1, 1.6 Hz, 1H), 7.14 – 7.06 (m, 2H), 6.96 (d, J = 8.2 Hz, 1H), 6.15 (s, 1H), 1.33 (s, 12H), 1.15 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 166.62, 144.62, 133.68, 129.22, 121.45, 119.03, 117.38, 84.35, 38.07, 29.74, 25.18.

^{11}B NMR ($CDCl_3$) δ 30.60, 28.56.

HRMS Calcd for $C_{19}H_{28}B_2N_2O_3$: $[M+Na]^+$, 377.2178. Found: *m*/*z* 377.2184

(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3l)



A pale yellow oil (51.7 mg)

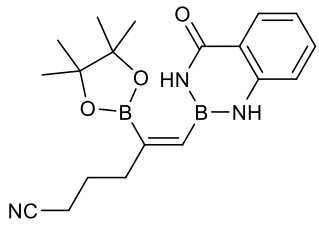
^{1}H NMR ($CDCl_3$) δ 8.19 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.95 (s, 1H), 7.86 (s, 1H), 7.48 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.10 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 6.96 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.19 (s, 1H), 2.33 (td, *J* = 7.5, 1.4 Hz, 2H), 1.37 (s, 12H), 1.29 (d, *J* = 2.8 Hz, 8H), 0.89 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$) δ 166.83, 144.73, 133.50, 129.08, 121.18, 119.02, 117.32, 84.26, 41.65, 31.75, 29.63, 28.99, 24.90, 22.58, 14.11.

^{11}B NMR ($CDCl_3$) δ 30.06.

HRMS Calcd for $C_{21}H_{32}B_2N_2O_3$: $[M+Na]^+$, 405.2491. Found: *m*/*z* 405.2494

(*E*)-6-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enenitrile (3m)



A pale yellow oil (45.3 mg)

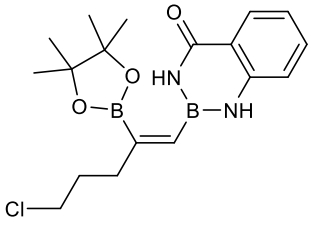
^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.05 (s, 1H), 7.83 (s, 1H), 7.50 (td, *J* = 8.0, 7.2, 1.7 Hz, 1H), 7.16 – 7.08 (m, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.30 (s, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.35 (t, *J* = 7.1 Hz, 2H), 1.85 (t, *J* = 7.4 Hz, 2H), 1.37 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.95, 144.68, 133.74, 129.19, 121.65, 119.82, 119.18, 117.63, 84.70, 40.39, 25.31, 25.02, 16.72.

^{11}B NMR ($CDCl_3$) δ 30.36.

HRMS Calcd for $C_{19}H_{25}B_2N_3O_3$: $[M+Na]^+$, 388.1974. Found: *m*/*z* 388.1975

(*E*)-2-(5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3n)



A pale yellow oil (46.9 mg)

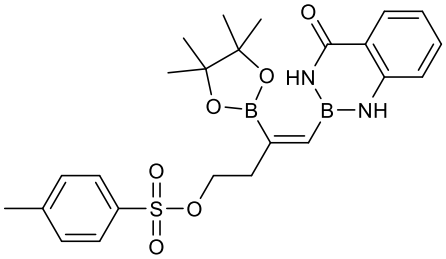
^{1}H NMR ($CDCl_3$) δ 8.20 (d, *J* = 6.8 Hz, 1H), 7.99 (s, 1H), 7.83 (s, 1H), 7.50 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.16 – 7.07 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.28 (s, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 2.48 (t, *J* = 7.8 Hz, 2H), 1.94 (t, *J* = 7.2 Hz, 2H), 1.38 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 167.03, 144.77, 133.76, 129.18, 121.58, 119.09, 117.61, 84.59, 44.57, 38.68, 32.47, 25.03.

^{11}B NMR ($CDCl_3$) δ 29.95, 19.90.

HRMS Calcd for $C_{18}H_{25}B_2ClN_2O_3$: $[M+Na]^+$, 397.1632. Found: *m*/*z* 397.1632

(*E*)-4-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl 4-methylbenzenesulfonate (3o)



A pale yellow solid: mp 116-117 ˚C (53.7 mg)

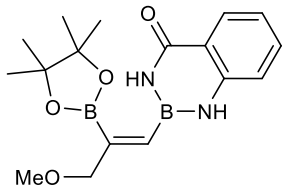
^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.97 (s, 1H), 7.84 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.22 (s, 1H), 4.17 (t, *J* = 6.5 Hz, 2H), 2.65 (t, *J* = 6.5 Hz, 2H), 2.38 (s, 3H), 1.32 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.87, 144.84, 144.65, 133.75, 133.32, 129.89, 129.18, 128.09, 121.67, 119.20, 117.62, 84.71, 70.00, 40.64, 24.97, 21.72.

^{11}B NMR ($CDCl_3$) δ 28.71.

HRMS Calcd for $C_{24}H_{30}B_2N_2O_6S$: $[M+Na]^+$, 519.1903. Found: *m*/*z* 519.1901

(*E*)-2-(3-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3p)



A pale yellow oil (40.3 mg)

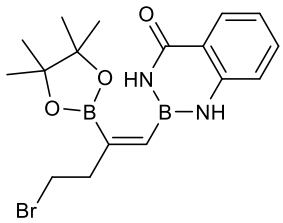
^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.04 (s, 1H), 7.84 (s, 1H), 7.49 (ddd, *J* = 8.2, 7.2, 1.6 Hz, 1H), 7.11 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 6.97 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.53 (t, *J* = 2.0 Hz, 1H), 4.16 (d, *J* = 2.0 Hz, 2H), 3.41 (s, 3H), 1.37 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.86, 144.74, 133.65, 129.21, 128.37, 121.56, 119.29, 117.59, 84.61, 58.58, 25.01.

^{11}B NMR ($CDCl_3$) δ 28.87, 22.47.

HRMS Calcd for $C_{17}H_{24}B_2N_2O_4$: $[M+Na]^+$, 365.1814. Found: *m*/*z* 365.1818

(*E*)-2-(4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3q)



A pale yellow solid: mp 91-92 °C (19.0 mg)

^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.01 (s, 1H), 7.94 (s, 1H), 7.50 (ddd, *J* = 8.3, 7.2, 1.6 Hz, 1H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.98 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.33 (s, 1H), 3.53 (t, *J* = 7.2 Hz, 2H), 2.89 (td, *J* = 7.3, 1.2 Hz, 2H), 1.38 (s, 12H).

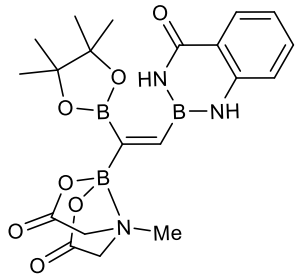
^{13}C NMR ($CDCl_3$) δ 166.87, 144.68, 133.71, 129.20, 121.64, 119.26, 117.62, 84.73, 44.47, 32.75, 25.03.

^{11}B NMR ($CDCl_3$) δ 29.31.

HRMS Calcd for $C_{17}H_{23}B_2BrN_2O_3$: $[M+Na]^+$, 427.0970. Found: *m*/*z* 427.0972

(*E*)-4-methyl-8-(2-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dihydro-4λ^4,8λ^4-

[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (3r)



A pale yellow solid: mp 213-214 °C (28.9 mg)

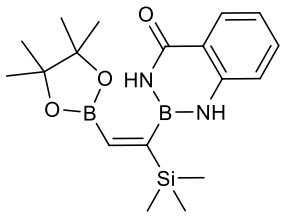
1H NMR (Acetone-*d*6) δ 8.74 (s, 1H), 8.42 (s, 1H), 8.09 (dd, J = 7.9, 1.6 Hz, 1H), 7.54 (ddd, J = 8.2, 7.2, 1.6 Hz, 1H), 7.25 (dd, J = 8.0, 1.0 Hz, 1H), 7.18 (s, 1H), 7.11 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 4.28 (d, J = 16.9 Hz, 2H), 4.12 (d, J = 16.8 Hz, 2H), 2.97 (s, 3H), 1.33 (s, 12H).

^{13}C NMR (Acetone-*d*6) δ 169.29, 166.40, 146.14, 134.13, 129.25, 121.82, 120.34, 118.78, 85.11, 63.78, 48.47, 25.05.

^{11}B NMR (Acetone-*d*6) δ 31.11, 23.49, 21.21.

HRMS Calcd for $C_{20}H_{26}B_3N_3O_7$: $[M+H]^+$, 454.2123. Found: *m*/*z* 454.2120

(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(trimethylsilyl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3's)



A pale yellow solid: mp 121-122 °C (46.8 mg)

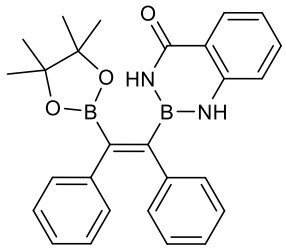
^{1}H NMR ($CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.12 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.92 (s, 1H), 6.70 (s, 1H), 6.30 (s, 1H), 1.12 (s, 13H), 0.13 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 166.42, 144.61, 133.69, 129.26, 121.38, 118.66, 117.30, 83.91, 24.85, -1.18.

^{11}B NMR ($CDCl_3$) δ 31.47, 28.37.

HRMS Calcd for $C_{18}H_{28}B_2N_2O_3Si$: $[M+Na]^+$, 393.1948. Found: *m*/*z* 393.1950

(*Z*)-2-(1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3t)



A pale yellow solid: mp 216-217 °C (57.7 mg)

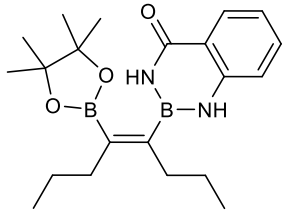
^{1}H NMR ($CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 7.36 (s, 1H), 7.16 – 7.06 (m, 8H), 7.04 – 6.99 (m, 2H), 6.98 – 6.90 (m, 3H), 6.79 (s, 1H), 1.23 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.33, 144.16, 141.32, 140.75, 133.70, 129.46, 129.20, 129.18, 128.20, 127.81, 126.55, 126.32, 121.72, 118.93, 117.47, 84.55, 24.77.

^{11}B NMR ($CDCl_3$) δ 30.39.

HRMS Calcd for $C_{27}H_{28}B_2N_2O_3$: $[M+Na]^+$, 473.2178. Found: *m*/*z* 473.2183

(*Z*)-2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-4-en-4-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3u)



A pale yellow solid: mp 163-164 °C (39.7 mg)

^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H), 7.15 – 7.03 (m, 2H), 6.95 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.50 (s, 1H), 2.32 – 2.20 (m, 4H), 1.44 – 1.31 (m, 4H), 1.11 (s, 12H), 0.92 (dt, *J* = 13.3, 7.3 Hz, 6H).

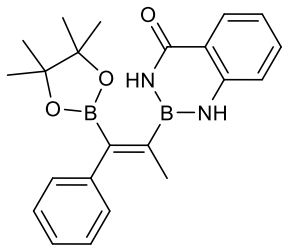
^{13}C NMR ($CDCl_3$) δ 166.65, 144.59, 133.65, 129.22, 121.34, 118.78, 117.36, 83.64, 33.97, 32.78, 24.82, 23.34, 23.06, 14.59, 14.48.

^{11}B NMR ($CDCl_3$) δ 30.41.

HRMS Calcd for $C_{21}H_{32}B_2N_2O_3$: $[M+Na]^+$, 405.2491. Found: *m*/*z* 405.2501

(*Z*)-2-(1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-2,3-

dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3v)



A pale yellow solid: mp 136-137 °C (53.0 mg)

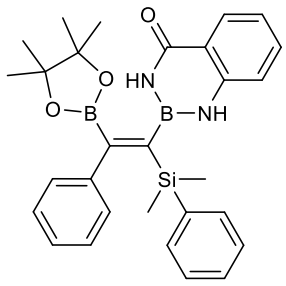
^{1}H NMR ($CDCl_3$) δ 8.24 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57 – 7.42 (m, 2H), 7.38 – 7.32 (m, 2H), 7.25 – 7.17 (m, 1H), 7.19 – 7.10 (m, 3H), 7.02 (dt, *J* = 8.2, 1.5 Hz, 1H), 6.89 (s, 1H), 1.87 (s, 3H), 1.14 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.78, 144.53, 141.23, 133.83, 129.28, 128.51, 128.21, 126.37, 121.64, 118.92, 117.50, 84.21, 24.77, 19.60.

^{11}B NMR ($CDCl_3$) δ 30.39, 22.40.

HRMS Calcd for $C_{22}H_{26}B_2N_2O_3$: $[M+H]^+$, 389.2202. Found: *m*/*z* 389.2201

(*Z*)-2-(1-(dimethyl(phenyl)silyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3w)



A pale yellow solid: mp 177-178 °C (56.2 mg)

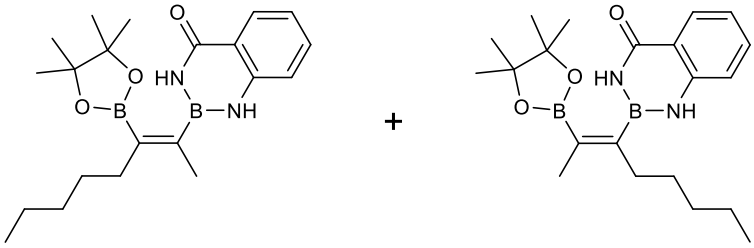
^{1}H NMR ($CDCl_3$) δ 8.18 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.47 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.31 (ddd, *J* = 4.8, 2.0, 0.9 Hz, 3H), 7.26 – 7.20 (m, 3H), 7.14 – 7.07 (m, 3H), 6.95 (s, 1H), 6.82 (ddd, *J* = 8.1, 1.1, 0.5 Hz, 1H), 6.13 (s, 1H), 1.03 (s, 12H), 0.01 (s, 6H).

^{13}C NMR ($CDCl_3$) δ 166.30, 144.67, 144.38, 139.77, 133.83, 133.67, 129.19, 129.15, 128.06, 128.00, 127.66, 126.97, 121.38, 118.51, 117.28, 84.30, 24.70, -0.83.

^{11}B NMR ($CDCl_3$) δ 29.73.

HRMS Calcd for $C_{29}H_{34}B_2N_2O_3Si$: $[M+Na]^+$, 531.2417. Found: *m*/*z* 531.2416

(*Z*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-2-en-2-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (3x + 3'x)



A pale yellow solid: mp 124-125 °C (45.7 mg)

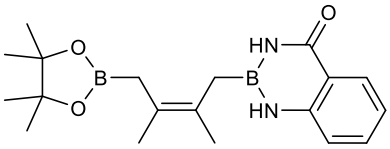
^{1}H NMR ($CDCl_3$) δ 8.24 – 8.17 (m, 2H, **3x + 3'x**), 7.49 (ddt, *J* = 8.1, 7.2, 1.6 Hz, 2H, **3x + 3'x**), 7.24 (d, *J* = 6.8 Hz, 1H), 7.14 – 7.07 (m, 3H, **3x + 3'x**), 6.96 (ddd, *J* = 8.2, 3.2, 1.1 Hz, 2H, **3x + 3'x**), 6.71 (d, *J* = 5.8 Hz, 1H), 6.52 (s, 1H), 2.28 (q, *J* = 8.0 Hz, 4H), 1.92 – 1.78 (m, 6H), 1.38 – 1.25 (m, 14H), 1.16 (s, 13H), 1.12 (s, 11H), 0.92 – 0.85 (m, 6H).

^{13}C NMR ($CDCl_3$) δ 166.79, 166.74, 144.63, 133.68, 133.66, 129.22, 121.37, 121.32, 118.80, 118.77, 117.40, 117.34, 83.78, 83.73, 32.31, 32.20, 32.12, 31.17, 30.12, 29.15, 28.88, 24.86, 24.82, 22.75, 22.66, 17.47, 16.22, 14.18.

^{11}B NMR ($CDCl_3$) δ 30.03.

HRMS Calcd for $C_{21}H_{32}B_2N_2O_3$: $[M+Na]^+$, 405.2491. Found: *m*/*z* 405.2493

(*Z*)-2-(2,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (5)



A pale yellow oil (38.0 mg)

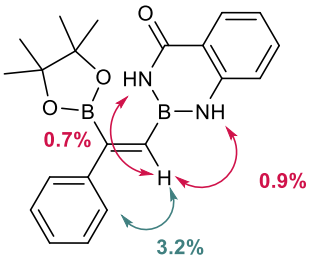
^{1}H NMR ($CDCl_3$) δ 8.18 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.64 (s, 1H), 7.48 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.10 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.00 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.60 (s, 1H), 1.95 (s, 2H), 1.76 – 1.70 (m, 5H), 1.65 (s, 3H), 1.27 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 167.03, 144.77, 133.73, 129.45, 124.84, 123.55, 121.71, 119.38, 117.60, 84.06, 25.09, 20.86, 20.75.

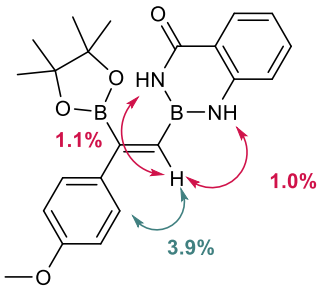
^{11}B NMR ($CDCl_3$) δ 22.24, 18.33.

HRMS Calcd for $C_{19}H_{28}B_2N_2O_3$: $[M+H]^+$, 355.2359. Found: *m*/*z* 355.1994

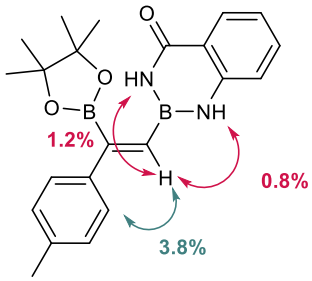
3. NOE Experiments for Determining Stereochemistry



3a



3b



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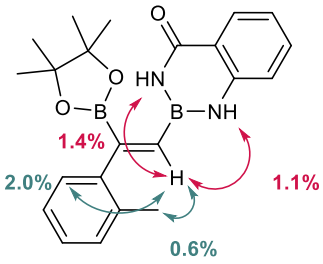
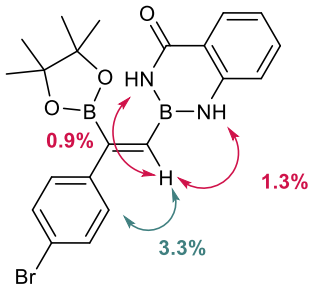
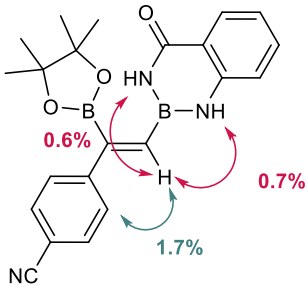


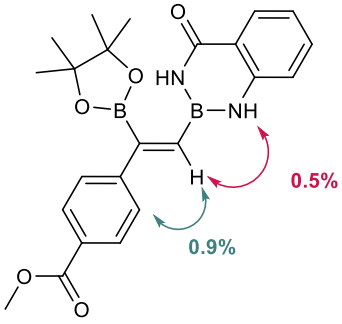
3d



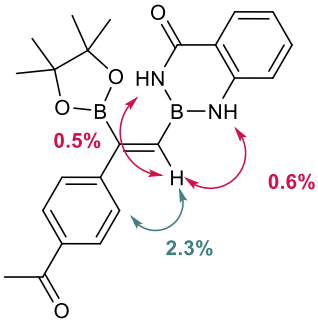
3e



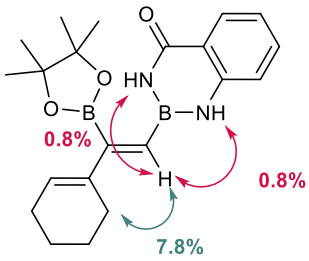
3f



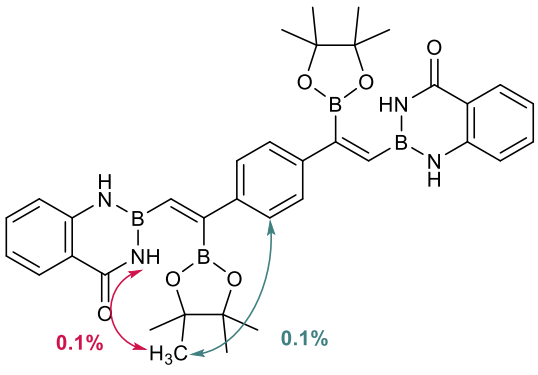
3g



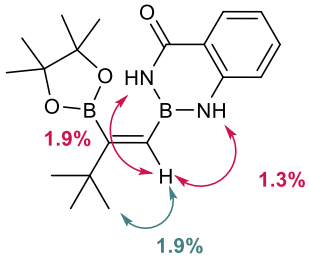
3h



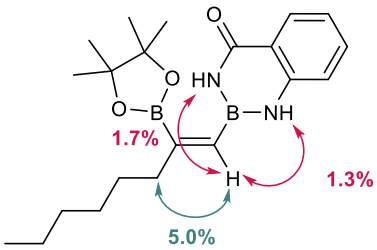
3i



3j



3k



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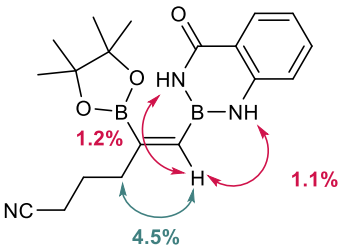

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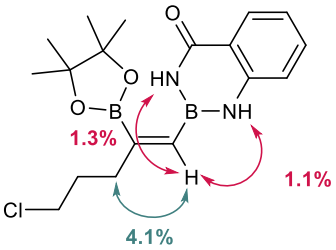
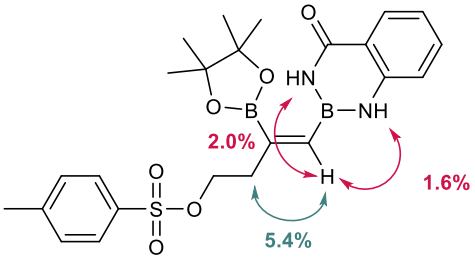
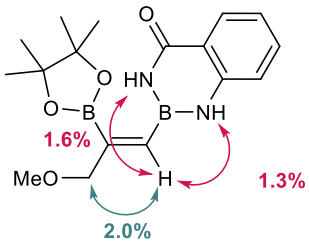


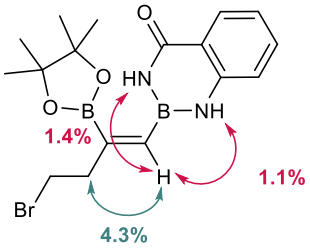
3n



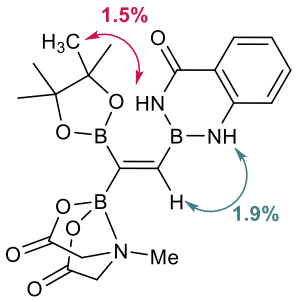
3o



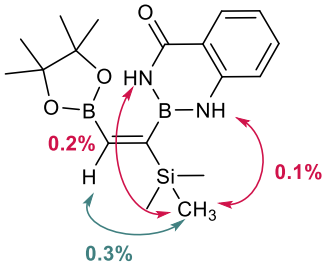
3p



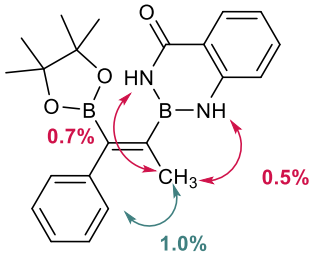
3q



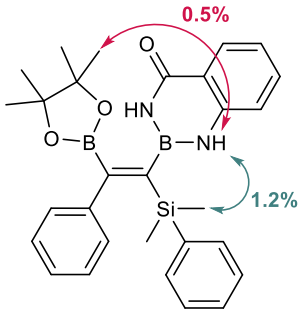
3r



3’s



3v

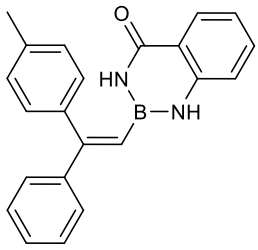


3w

4. Chemoselective Cross-Coupling of 3a

(*Z*)-2-(2-phenyl-2-(p-tolyl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (6)

A Schlenk tube equipped with a magnetic stirring bar was charged with Pd(dppf)•CH_2Cl_2 (2.7 μmol), K_3PO_4 (0.27 mmol), **3a** (0.09 mmol), *p*-bromotoulene (0.135 mmol) and DMF (2 mL), and the mixture was stirred at 80 °C for 18 h. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by boric acid impregnated silica gel-column chromatography (hexane/ethyl acetate as an eluent) gave the product **6**.



A white solid: mp 140-141 ˚C (13.1 mg)

^{1}H NMR ($CDCl_3$) δ 8.12 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.42 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H), 7.39 – 7.30 (m, 6H), 7.28 (s, 1H), 7.22 – 7.17 (m, 2H), 7.06 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 6.81 (s, 1H), 6.63 (dt, *J* = 8.1, 0.7 Hz, 1H), 6.21 (s, 1H), 5.89 (s, 1H), 2.46 (s, 3H).

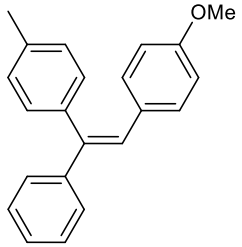
^{13}C NMR ($CDCl_3$) δ 166.81, 160.30, 145.00, 142.78, 138.91, 138.02, 134.48, 129.85, 129.77, 129.37, 129.03, 128.66, 128.03, 121.81, 119.19, 117.75, 22.28.

^{11}B NMR ($CDCl_3$) δ 28.01.

HRMS Calcd for $C_{22}H_{19}BN_2O$: $[M+Na]^+$, 339.1663. Found: *m*/*z* 339.1668

(*Z*)-1-methoxy-4-(2-phenyl-2-(p-tolyl)vinyl)benzene (7)[3]

A reaction tube equipped with a magnetic stirring bar was charged with $Pd(OAc)_2$ (2.7 μmol), PPh_3 (5.4 μmol), **6** (0.09 mmol), *p*-bromoanisole (0.18 mmol), 1,4-dioxane (1 mL) and 6 M KOH aq. (0.54 mmol), and the mixture was stirred at 140 °C for 0.5 h under microwave irradiation. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by gel permeation chromatography (toluene as an eluent) gave the product **7**.



A brown oil (17.2 mg)

^{1}H NMR ($CDCl_3$) δ 7.33 – 7.27 (m, 5H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.88 (s, 1H), 6.69 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 2.39 (s, 3H).

^{13}C NMR ($CDCl_3$) δ 158.44, 144.02, 140.74, 137.70, 137.05, 130.90, 130.54, 130.41, 129.55, 128.26, 127.59, 127.57, 127.27, 113.53, 55.29, 21.48.

5. References

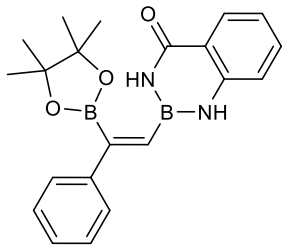
1. T. Korenaga, A. Ko, K. Uotani, Y. Tanaka and T. Sakai, *Angew. Chem. Int. Ed.*, 2011, **50**, 10703.

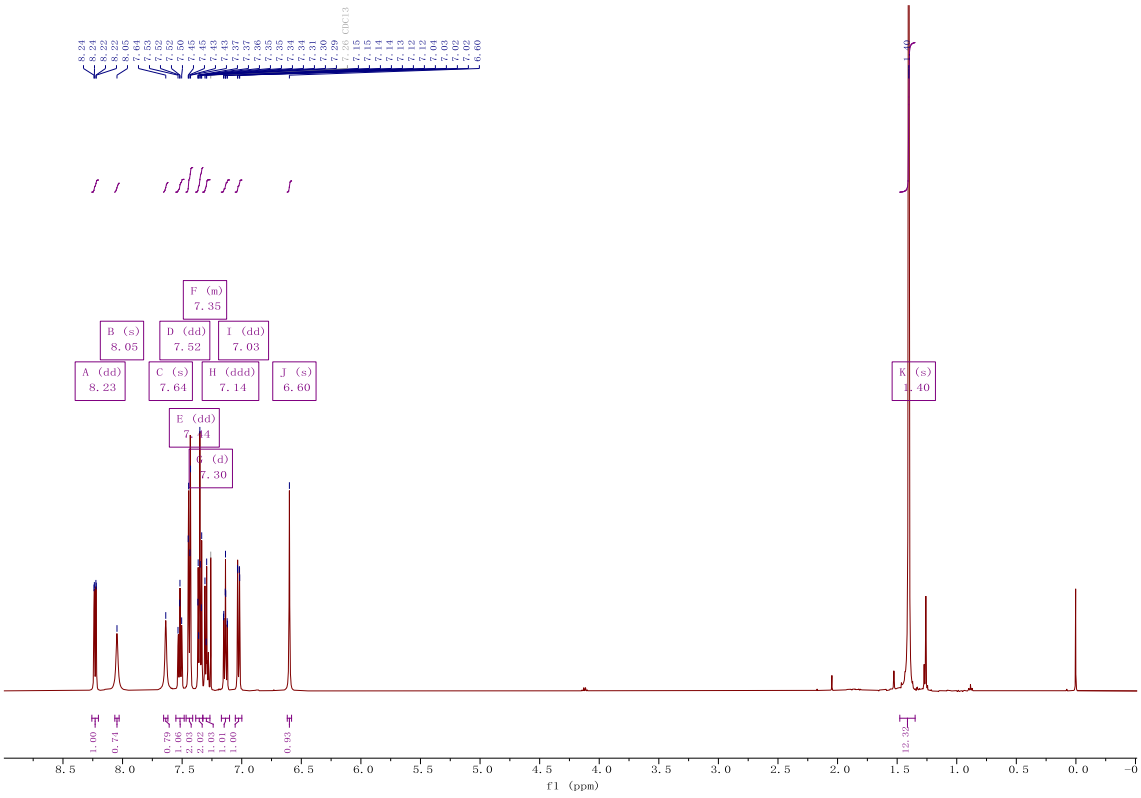
2. S. Kamio, I. Kageyuki, I. Osaka, S. Hatano, A. Abe and H. Yoshida, *Chem. Commun*., 2018, **54**, 9290.

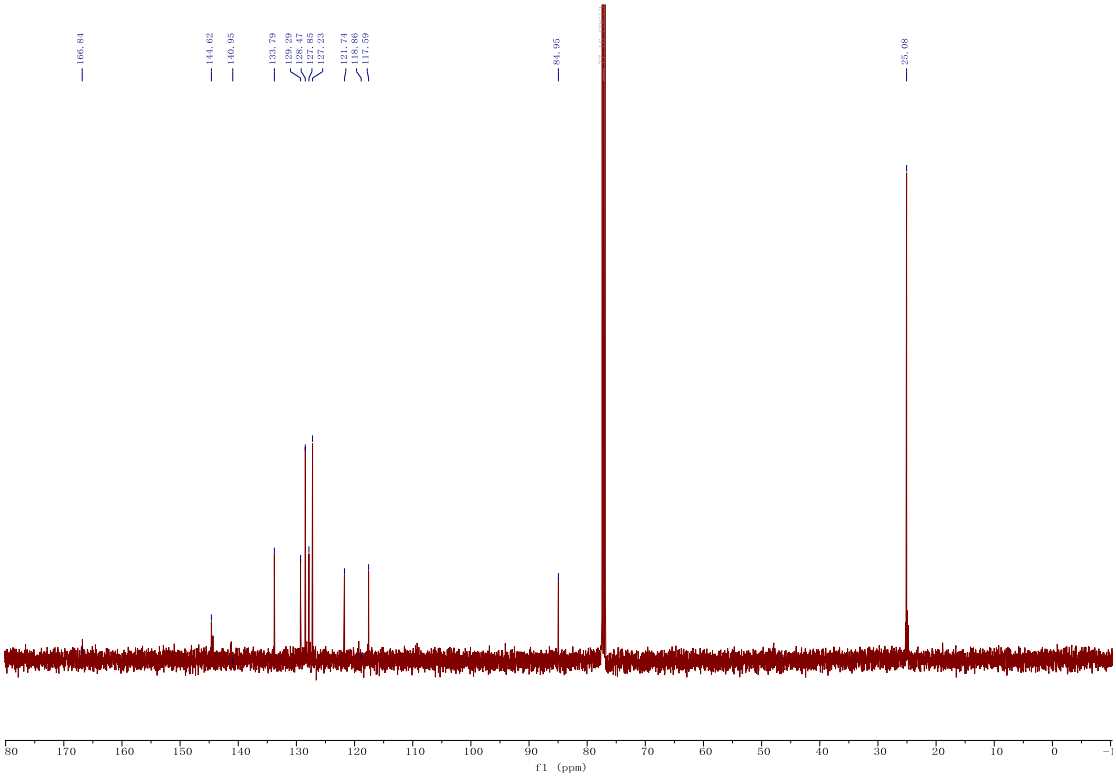
3. W. Dai, J. Xiao, G. Jin, J. Wu and S. Cao, *J. Org. Chem.*, 2014, **79**, 10537.

6. ^{1}H and ^{13}C and ^{11}B and Spectra of Products

3a



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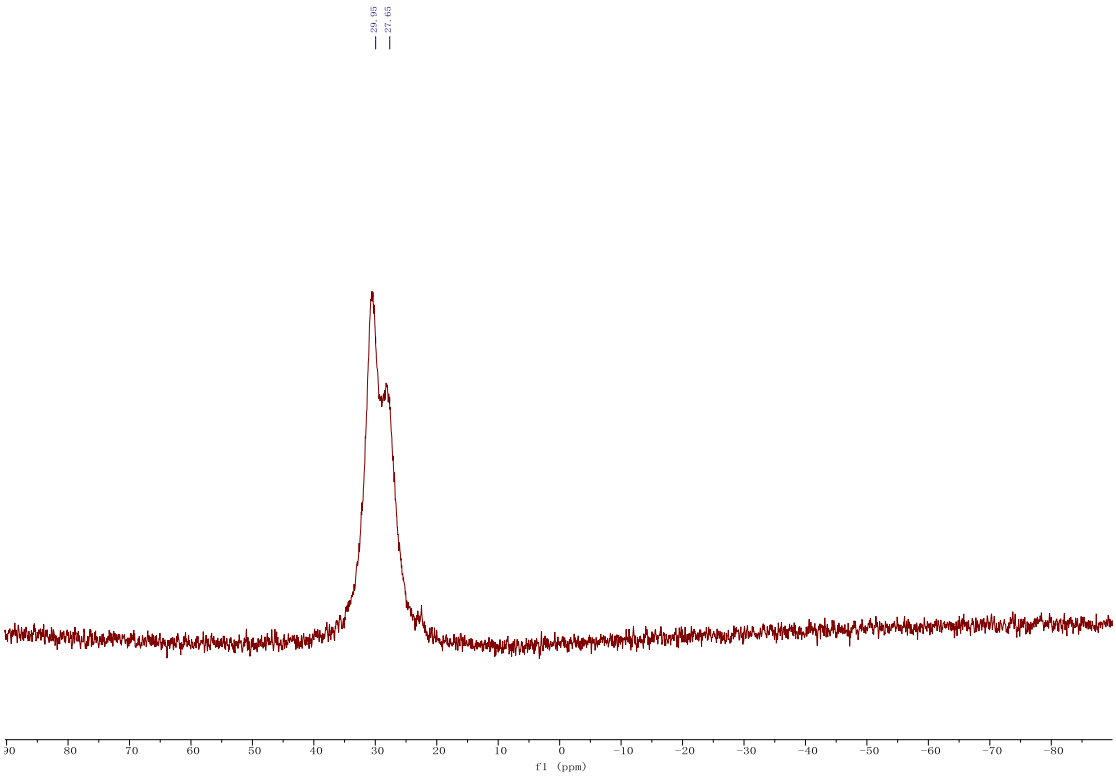
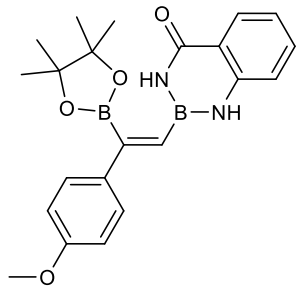
144.62
140.95
133.79
129.29
128.47
127.85
127.23
121.74
118.86
117.89
84.95
25.08
f1 (ppm)


29.95
27.65
f1 (ppm)

3b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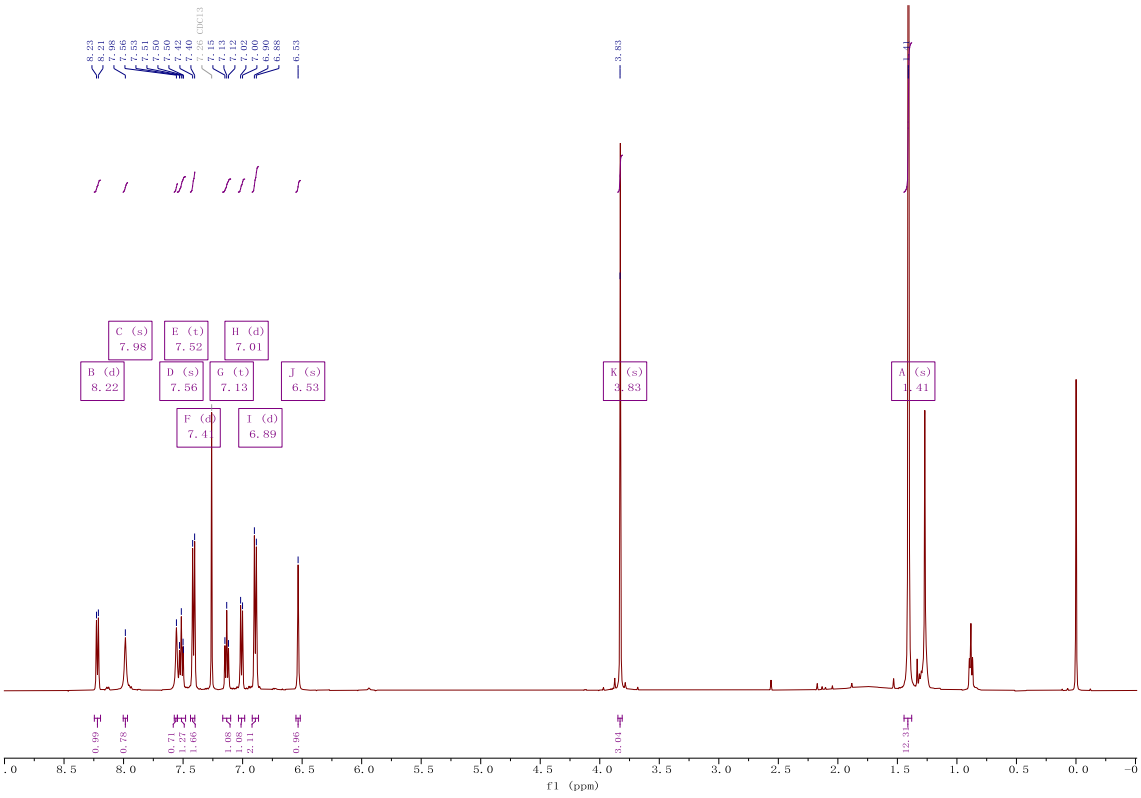
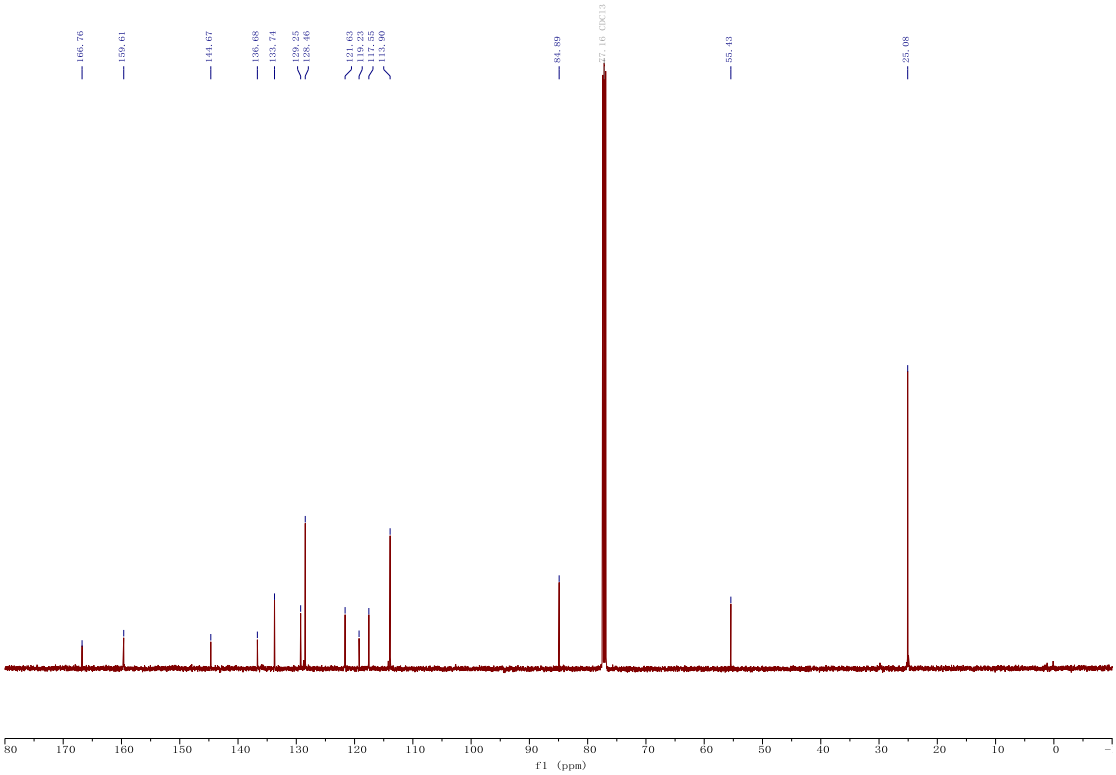
HN
O
O
B
B
NH
O


8.23
8.21
7.98
7.56
7.53
7.51
7.50
7.50
7.42
7.40
7.35
CDCl3
7.15
7.13
7.12
7.02
7.00
6.90
6.88
6.53
3.83
1.41
C (s)
7.98
E (t)
7.52
H (d)
7.01
B (d)
8.22
D (s)
7.56
G (t)
7.13
J (s)
6.53
F (d)
7.41
I (d)
6.89
K (s)
3.83
A (s)
1.41
0.99
0.78
0.71
2.27
1.66
1.08
1.00
2.11
0.96
3.04
12.31
f1 (ppm)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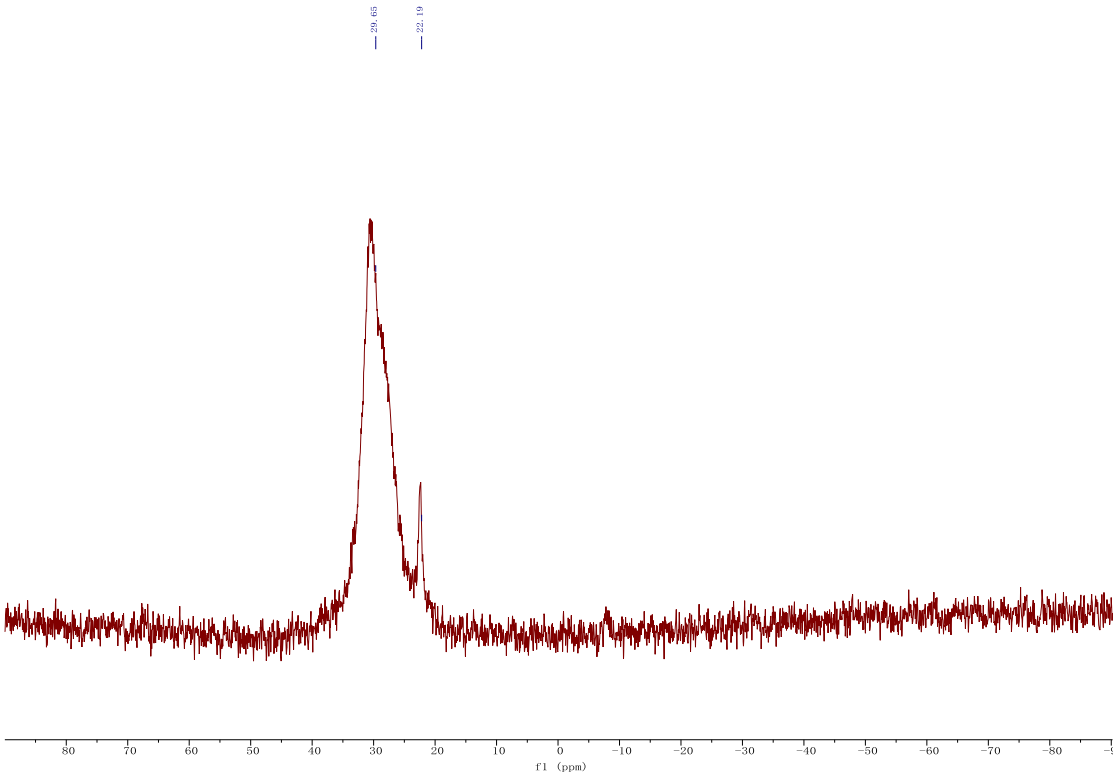
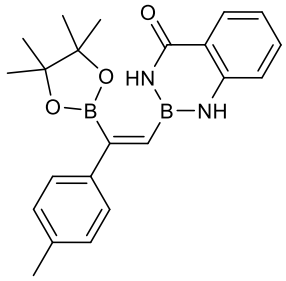
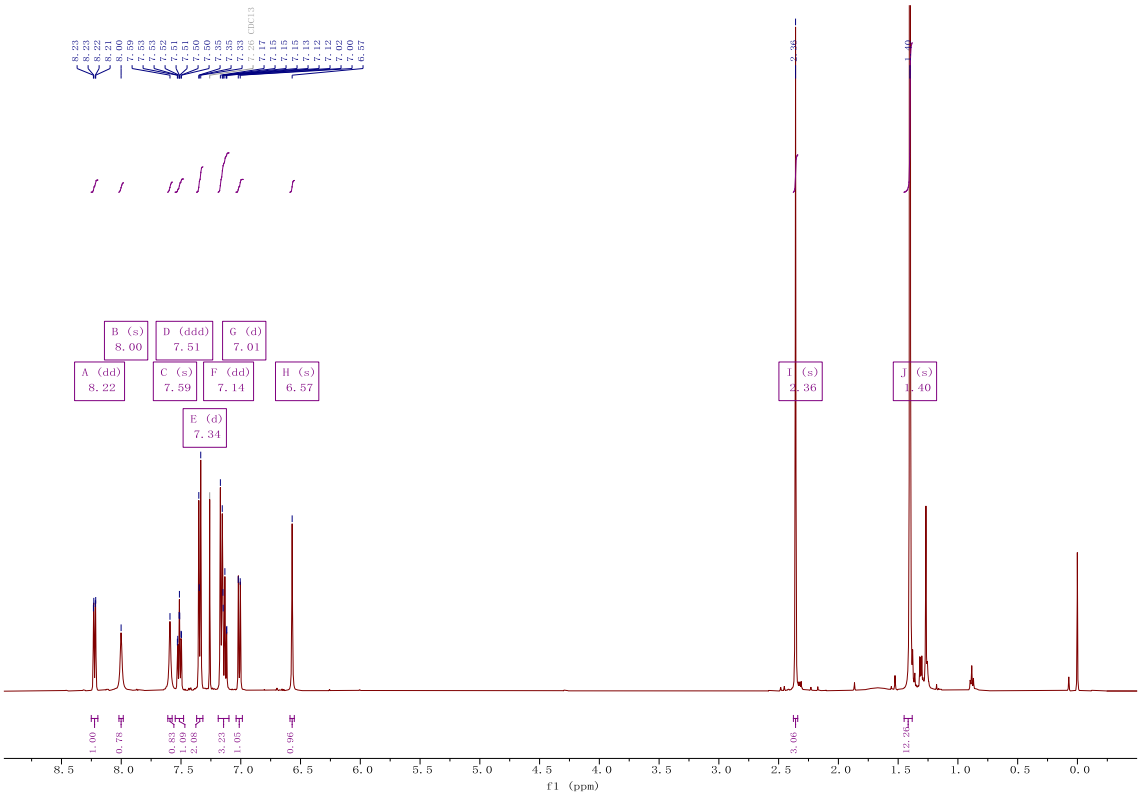
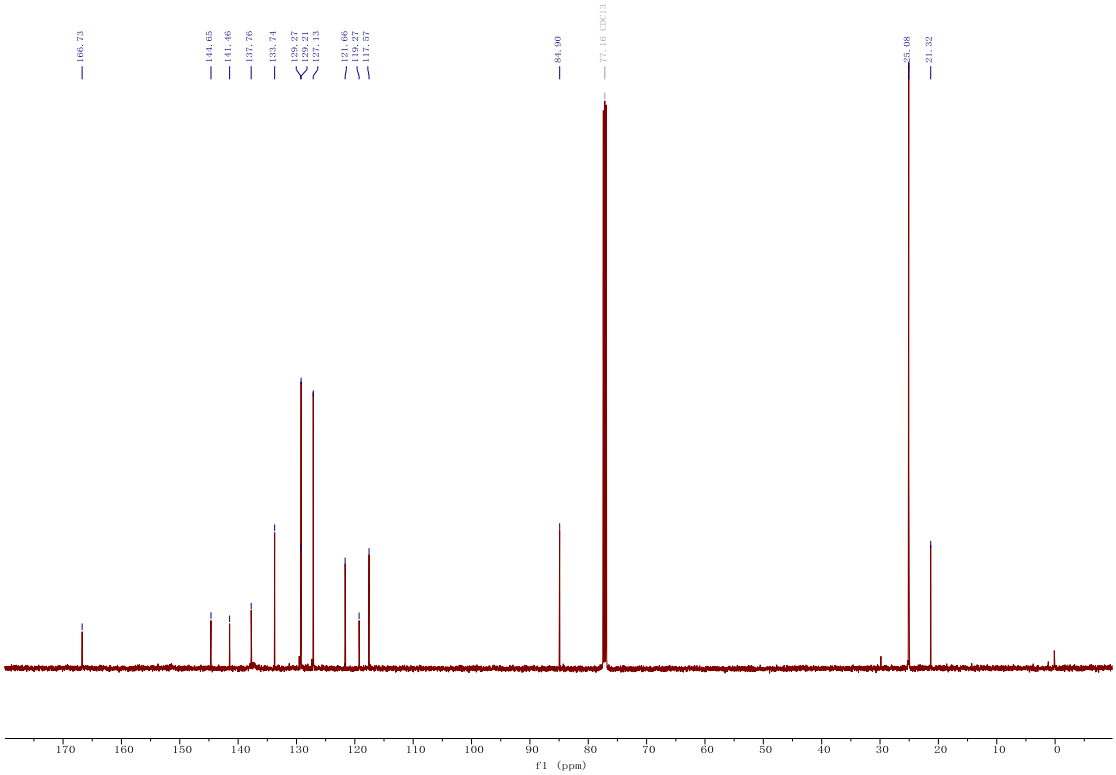
159.61
144.67
136.08
133.74
129.25
128.46
121.63
119.23
117.55
113.90
84.89
77.16 CDCl3
55.43
25.08
f1 (ppm)


29.65
22.19
f1 (ppm)

3c


O
HN
O
O
B
B
NH


B (s) 8.00
D (ddd) 7.51
G (d) 7.01
A (dd) 8.22
C (s) 7.59
F (dd) 7.14
H (s) 6.57
E (d) 7.34
I (s) 2.36
J (s) 1.40
f1 (ppm)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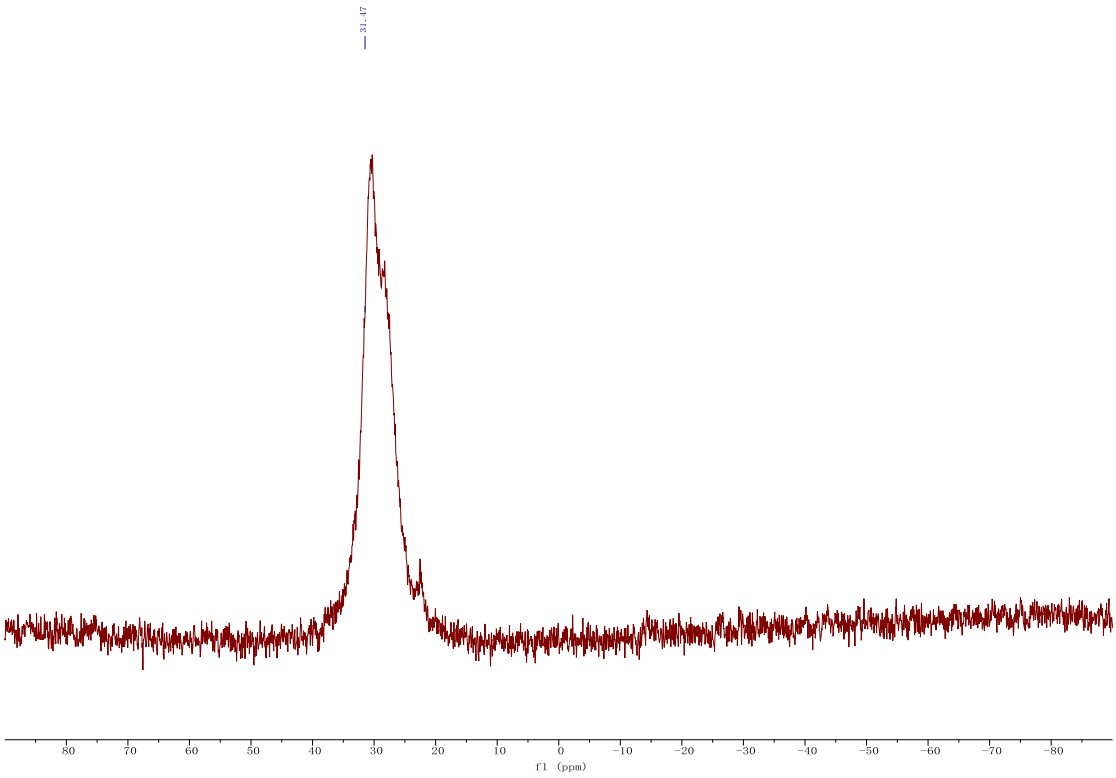
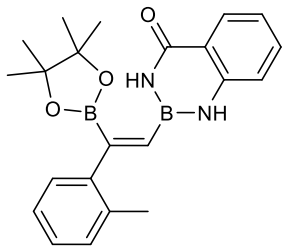
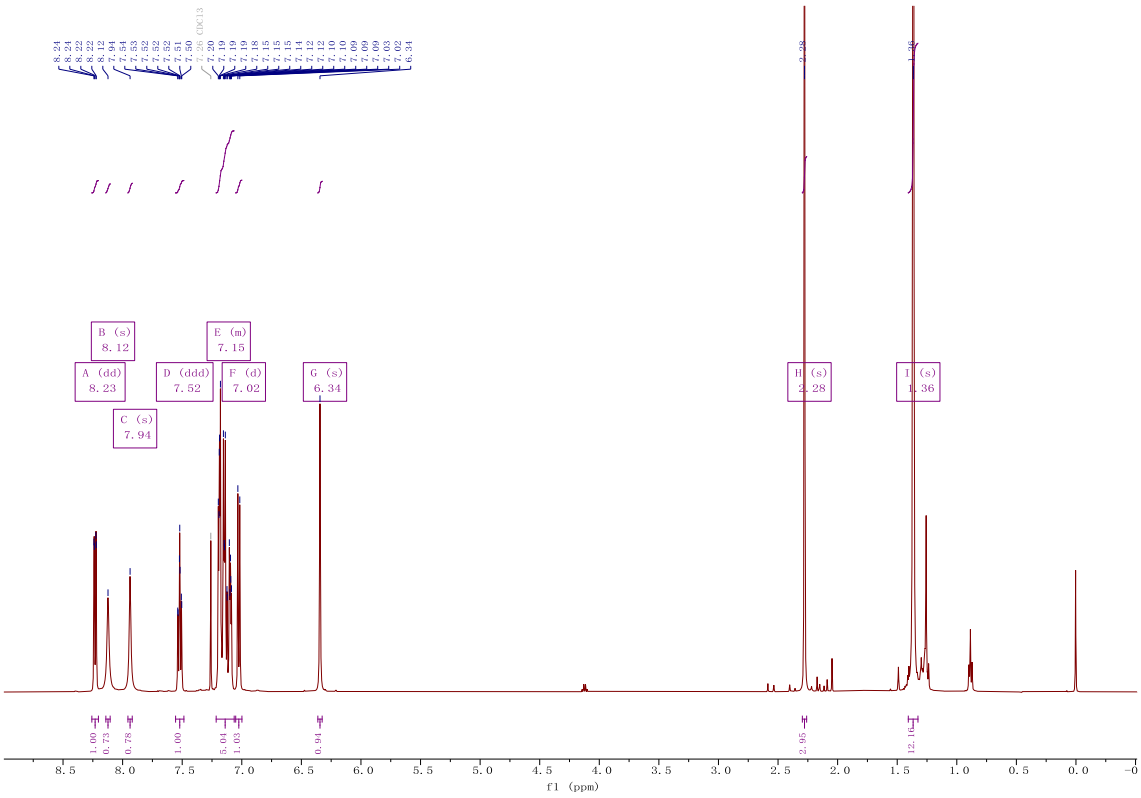
144.65
141.46
137.76
133.74
129.27
129.21
127.13
121.66
119.27
117.57
84.90
77.16 CDCl3
55.08
21.32
f1 (ppm)


31.47
f1 (ppm)

3d


O
HN
O
O
B
B
NH


B (s)
8.12
E (m)
7.15
A (dd)
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D (ddd)
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F (d)
7.02
G (s)
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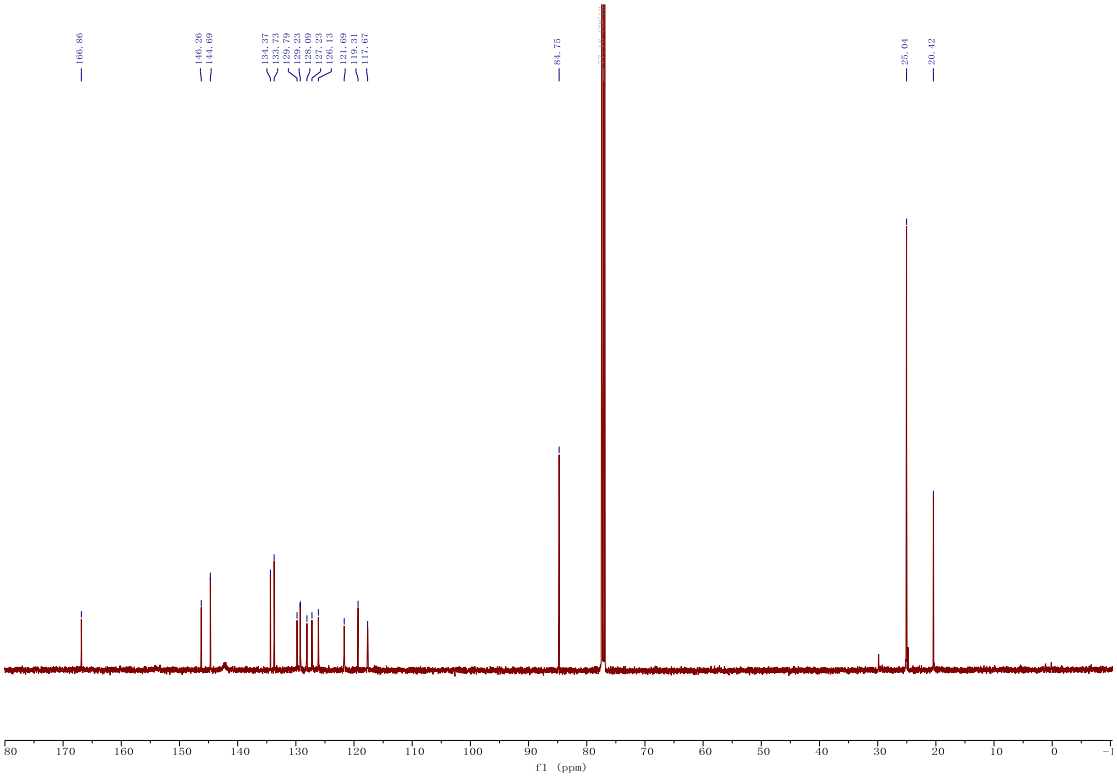
C (s)
7.94
H (s)
2.28
I (s)
1.36
f1 (ppm)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134.37
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119.31
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84.75
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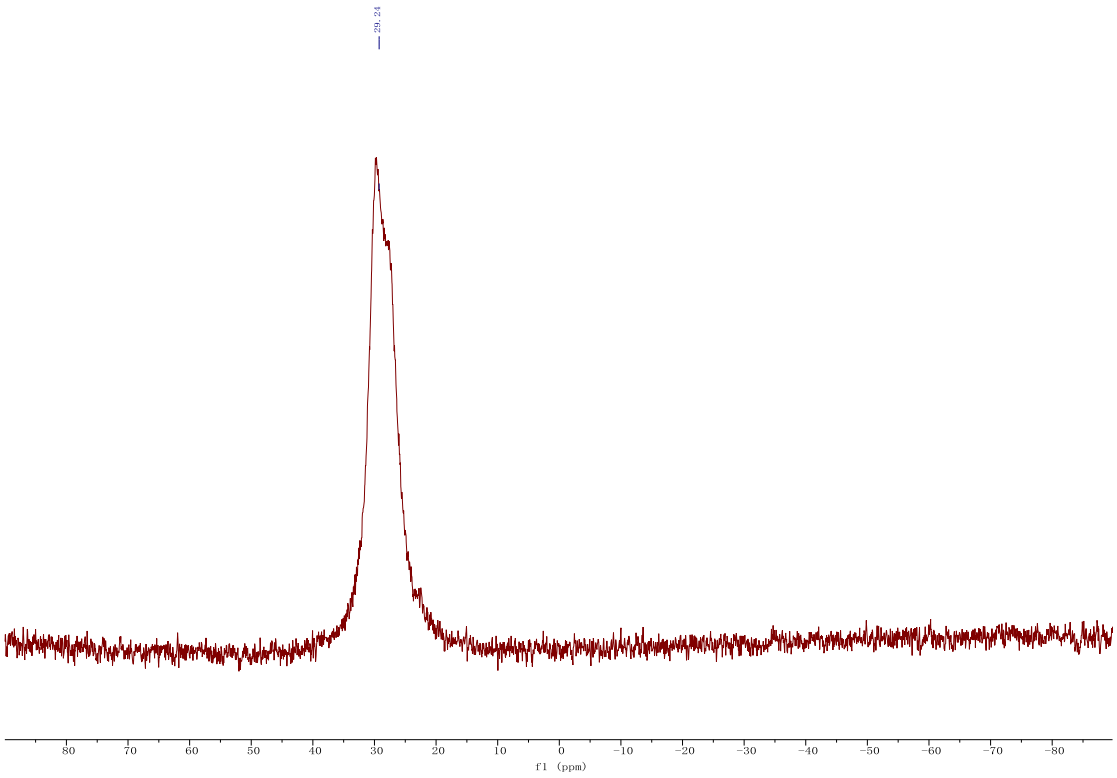
20.42
f1 (ppm)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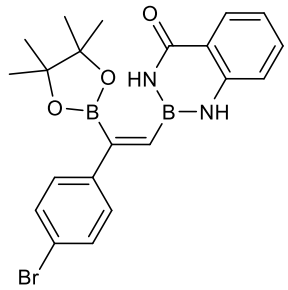
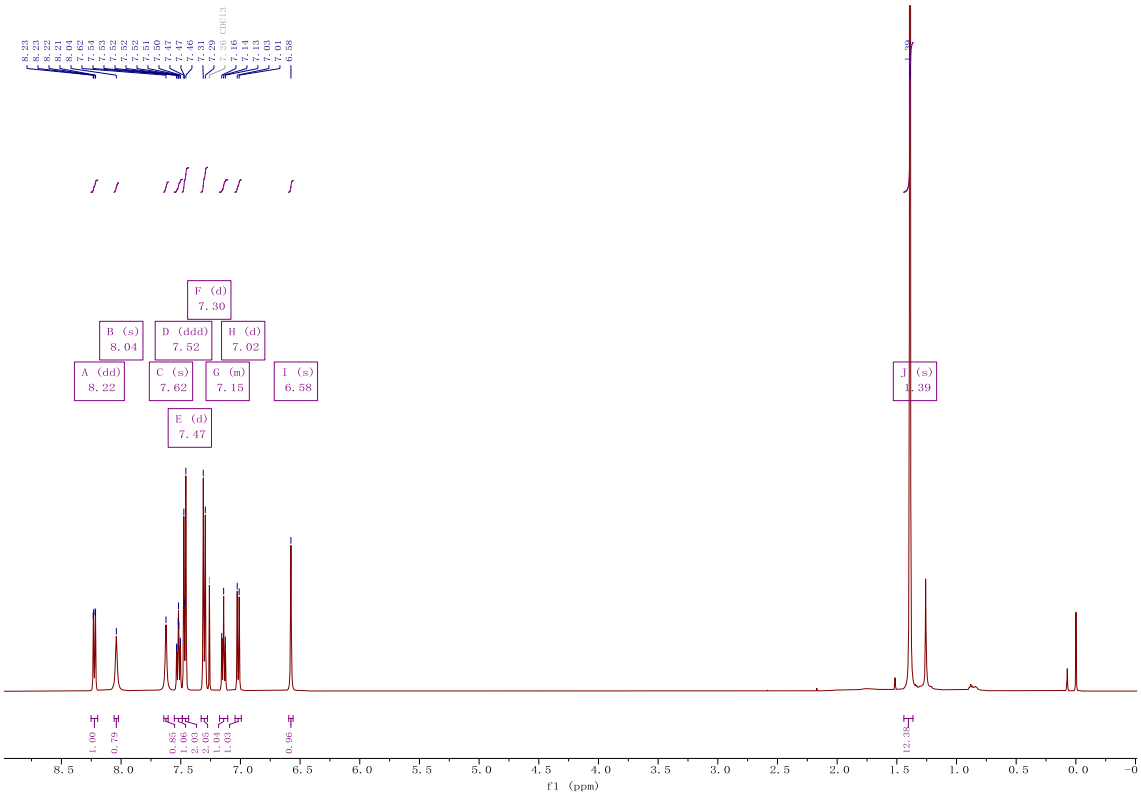
f1 (ppm)

3e


O
HN
O
O
B
B
NH
Br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B (s)
8.04
D (ddd)
7.52
H (d)
7.02
A (dd)
8.22
C (s)
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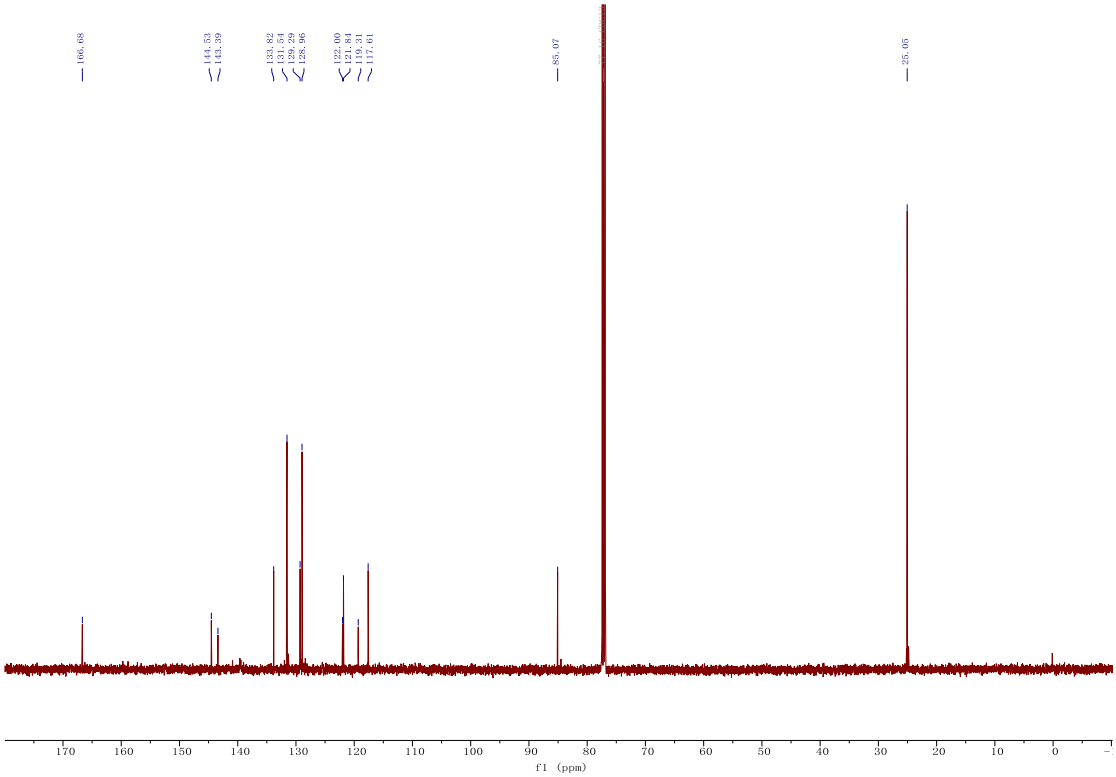
G (m)
7.15
I (s)
6.58
E (d)
7.47
J (s)
1.39
f1 (ppm)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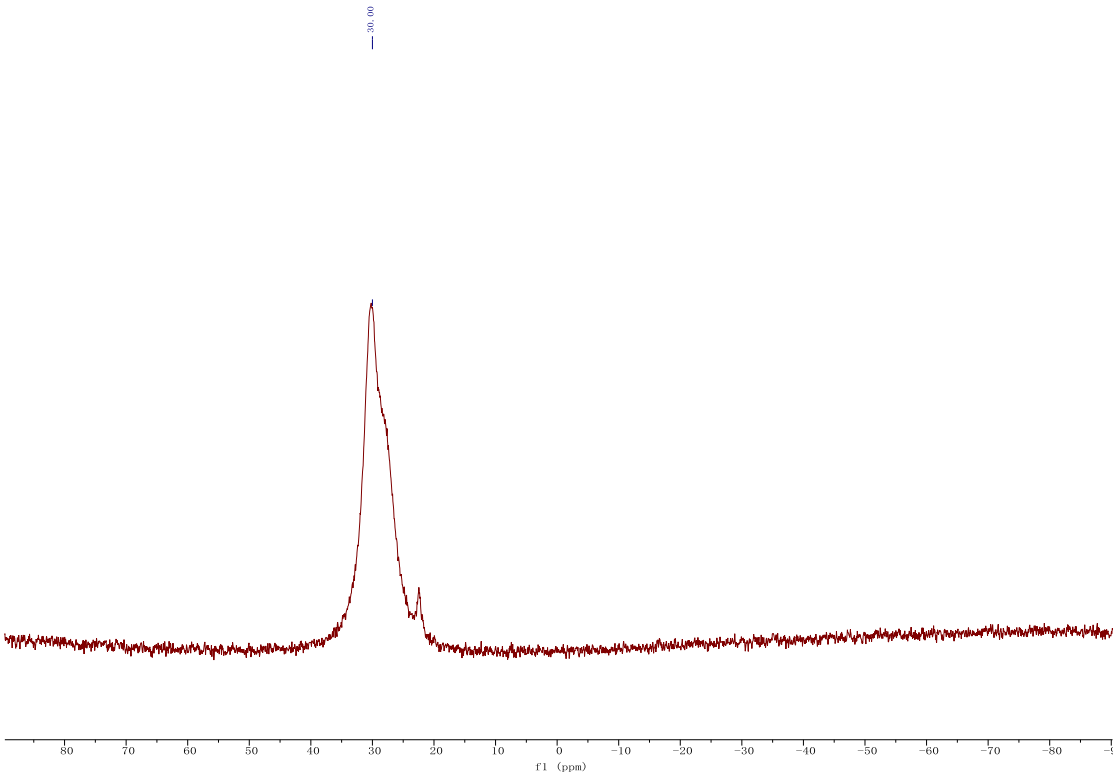
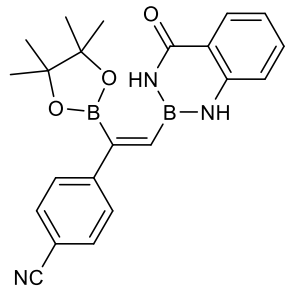
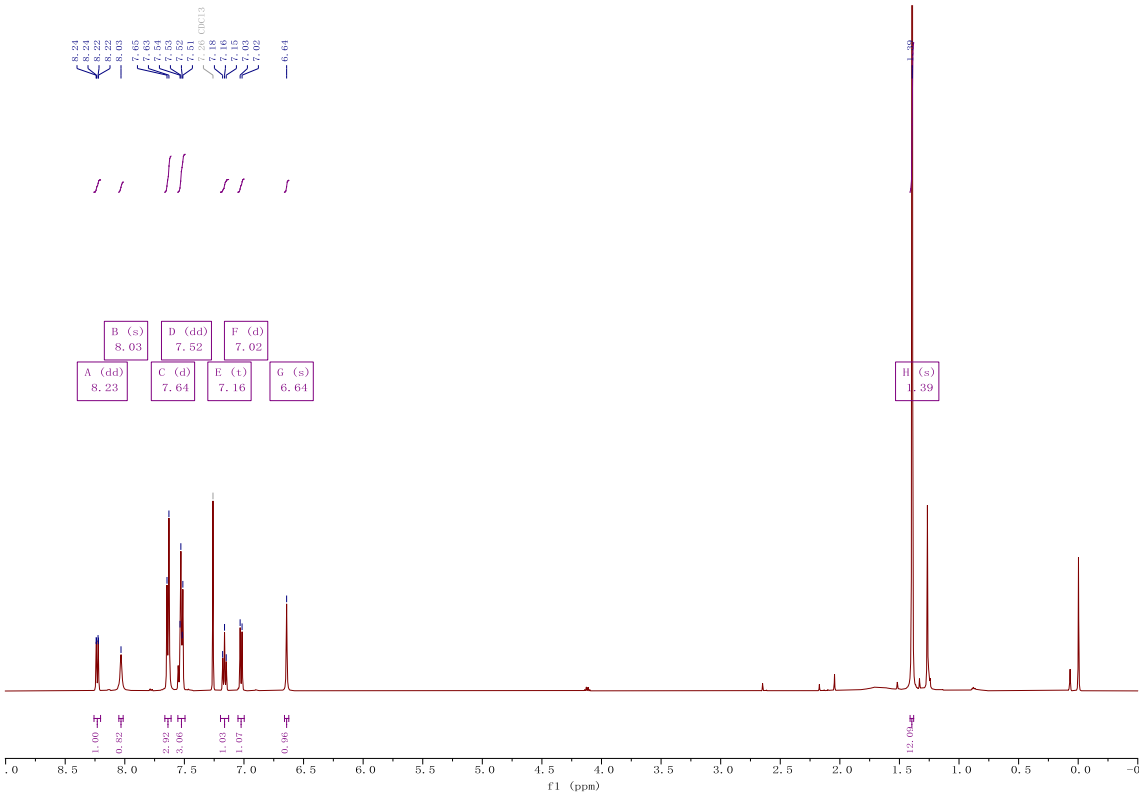
f1 (ppm)


30.00
f1 (ppm)

3f


O
HN
O
O
B
B
NH
NC


8.24
8.24
8.22
8.22
8.03
7.65
7.64
7.64
7.53
7.52
7.51
7.36
CDCl3
7.18
7.16
7.15
7.03
7.02
6.64
1.39
B (s) 8.03
D (dd) 7.52
F (d) 7.02
A (dd) 8.23
C (d) 7.64
E (t) 7.16
G (s) 6.64
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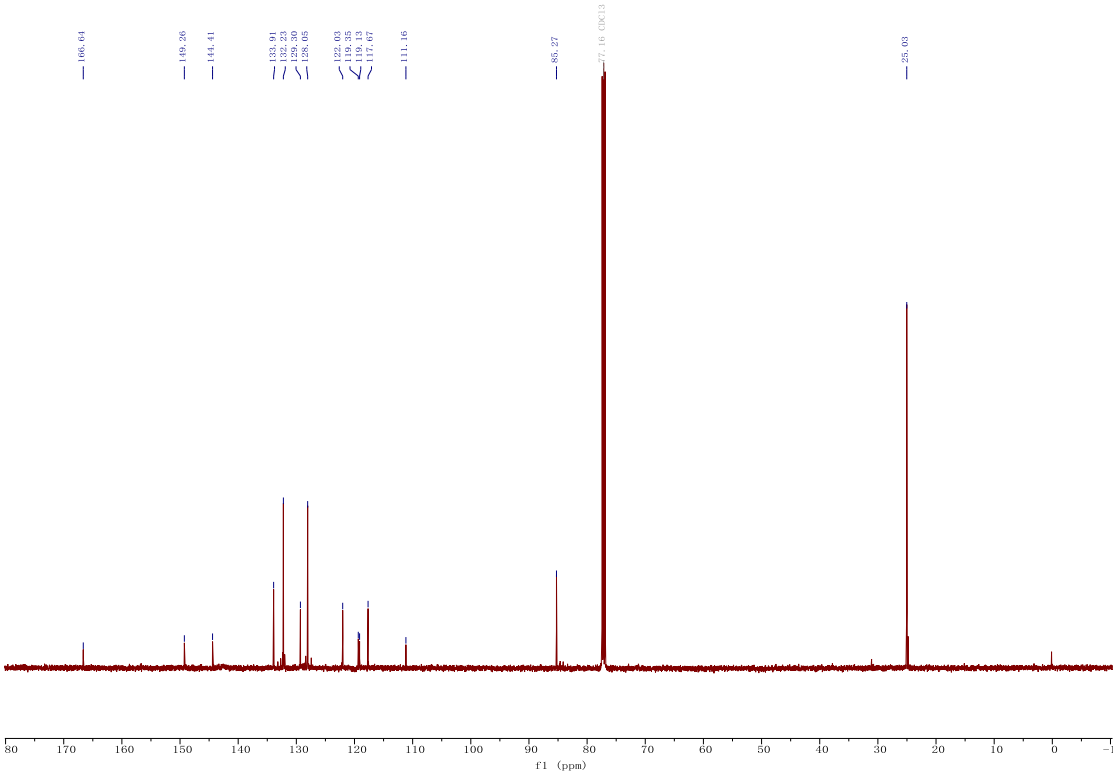
3.06
1.03
1.07
0.96
12.69
f1 (ppm)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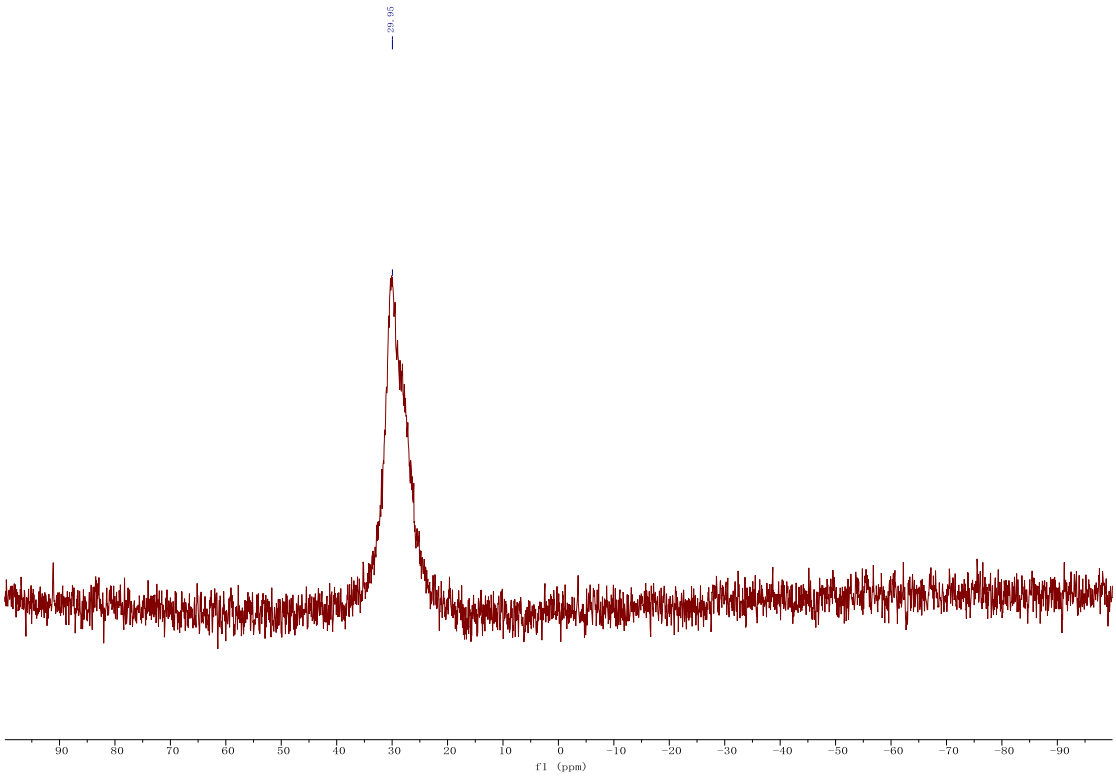
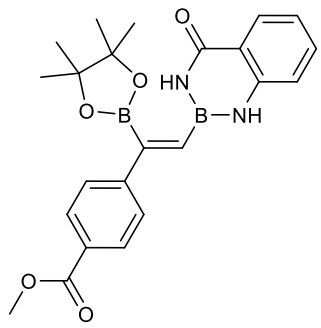
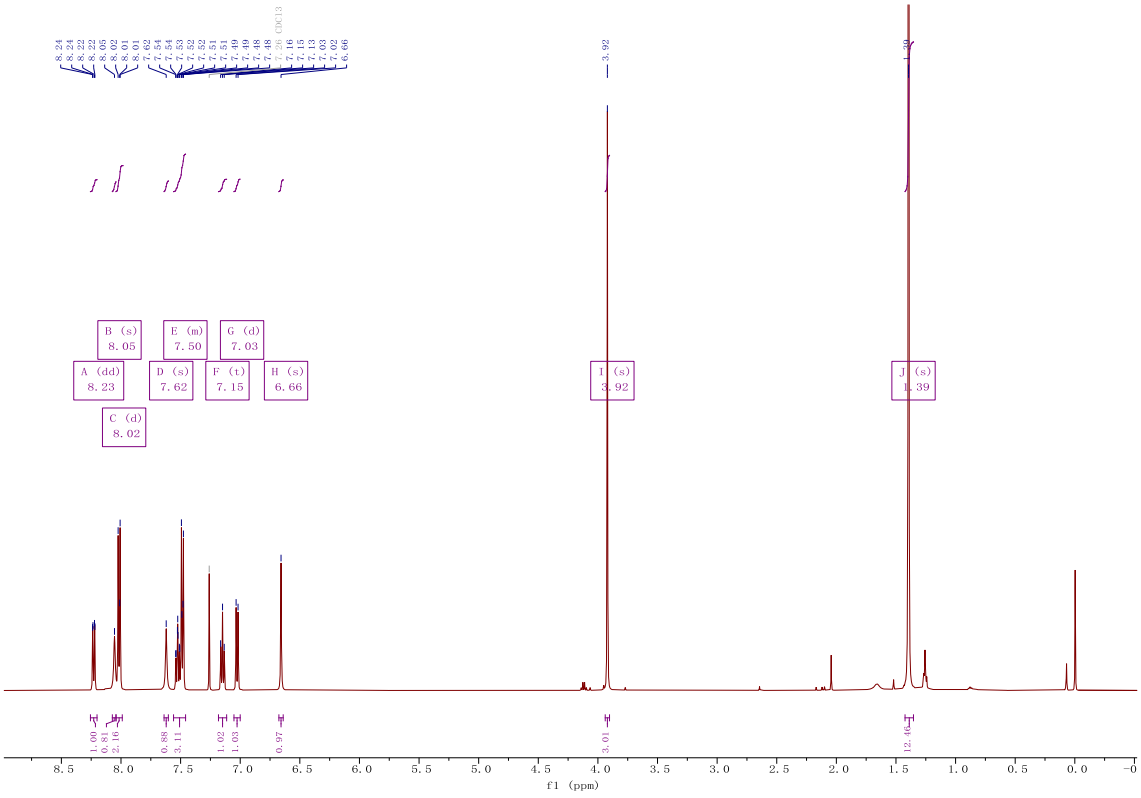
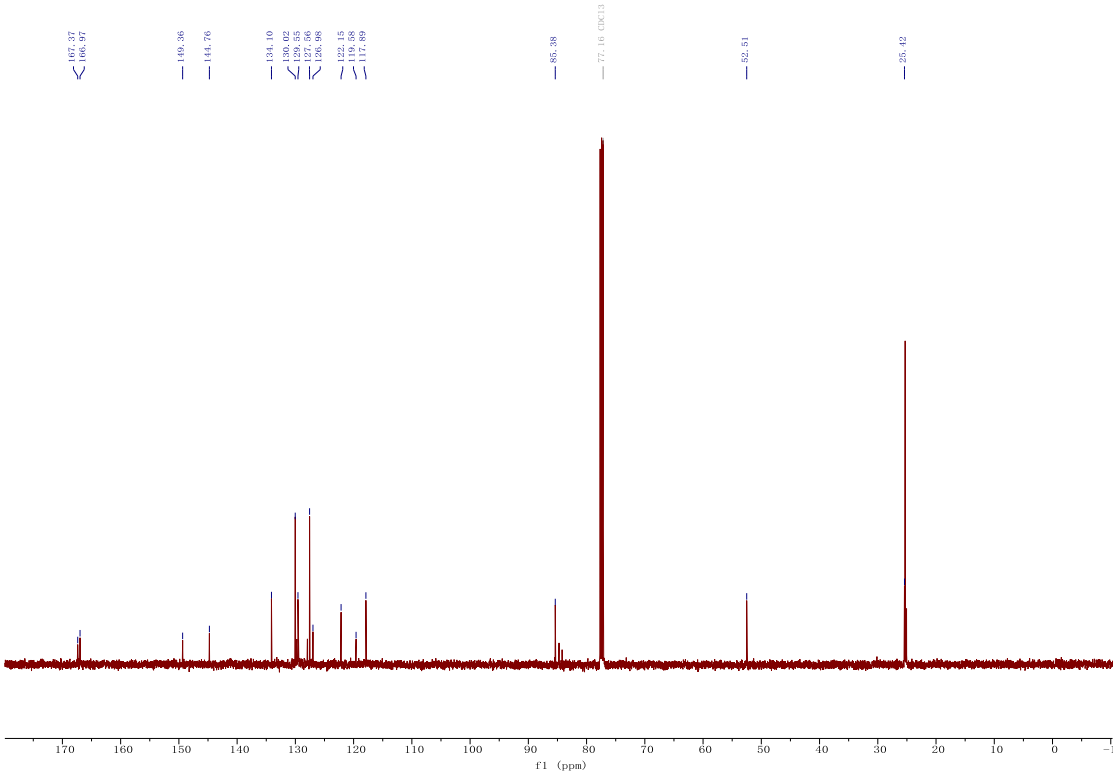
149.26
144.41
133.91
132.23
129.90
128.05
122.03
119.35
119.13
117.67
111.16
85.27
77.16 CDCl3
25.03
f1 (ppm)

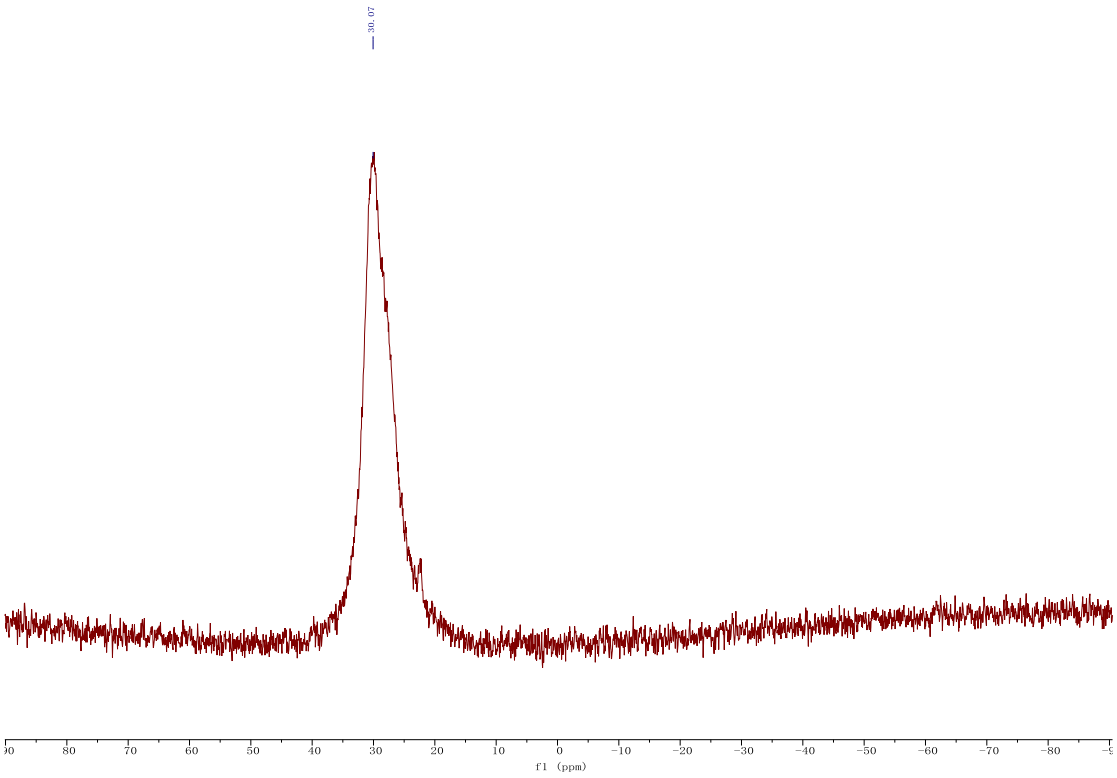

29.95
f1 (ppm)

3g

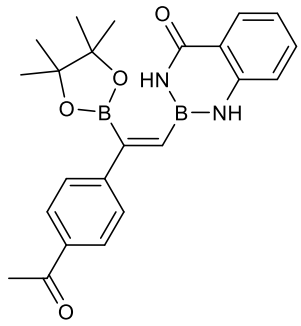

O
HN
O
B
B
NH
O
O

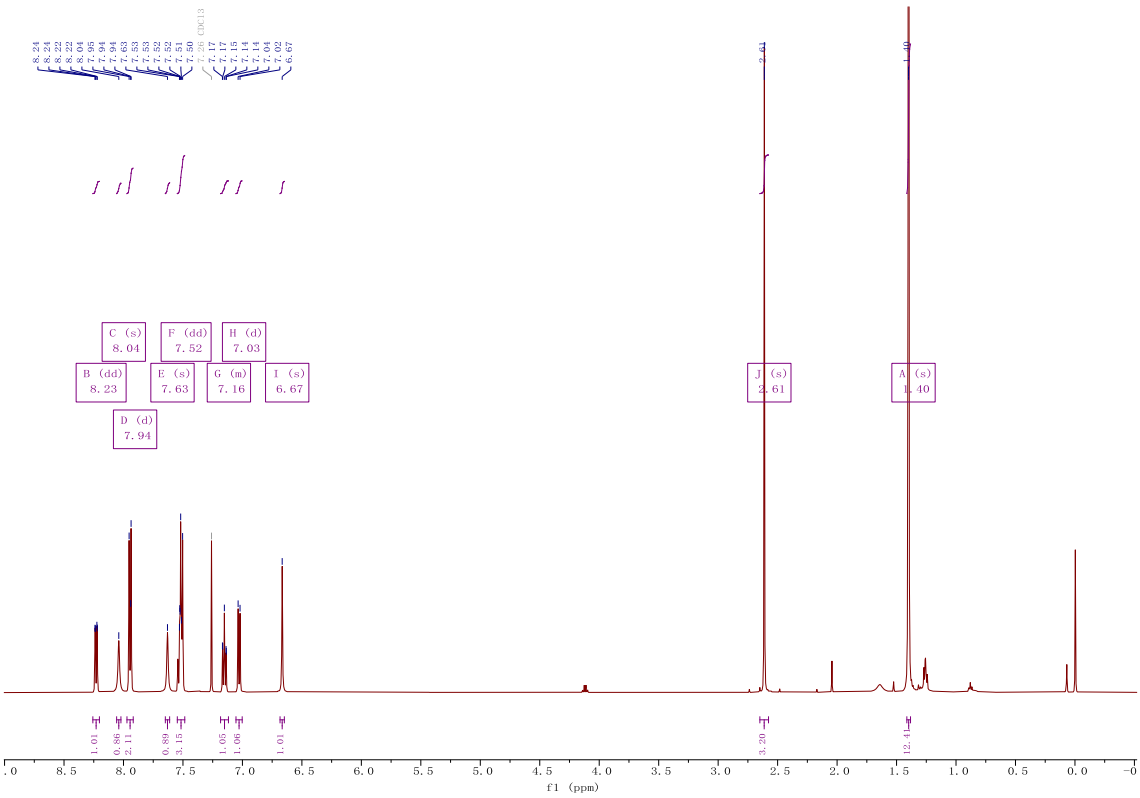

B (s) 8.05
E (m) 7.50
G (d) 7.03
A (dd) 8.23
D (s) 7.62
F (t) 7.15
H (s) 6.66
C (d) 8.02
I (s) 3.92
J (s) 1.39
f1 (ppm)

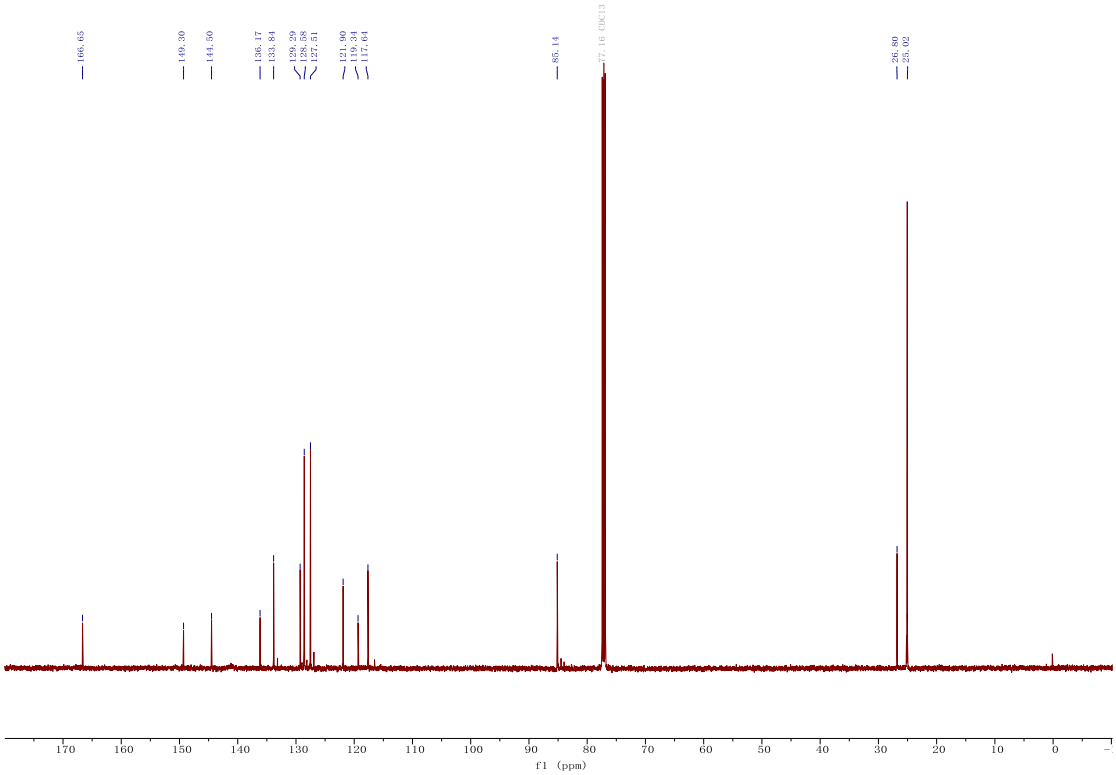

167.27
166.97
149.36
144.76
134.10
130.02
129.55
127.96
126.98
122.15
119.88
117.89
85.38
77.16 CDCl3
52.51
25.42
f1 (ppm)

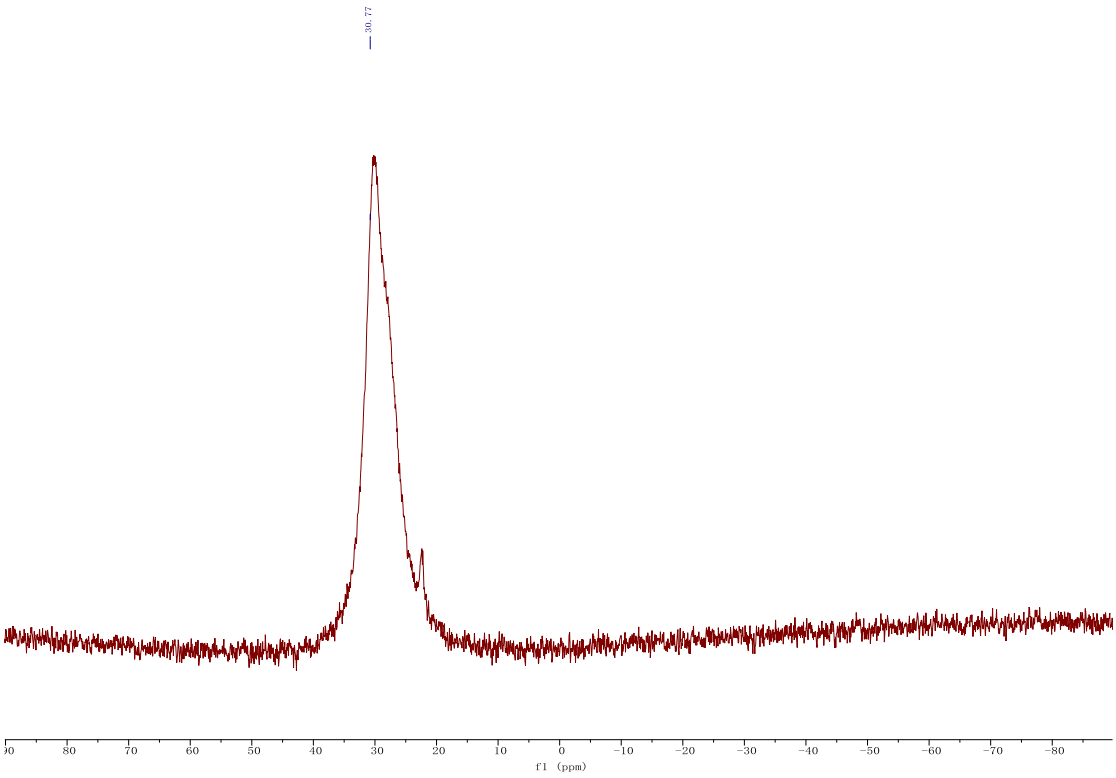

30.07
f1 (ppm)

3h

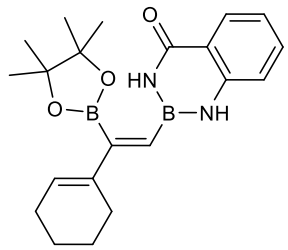

O
HN
O
O
B
B
NH
O

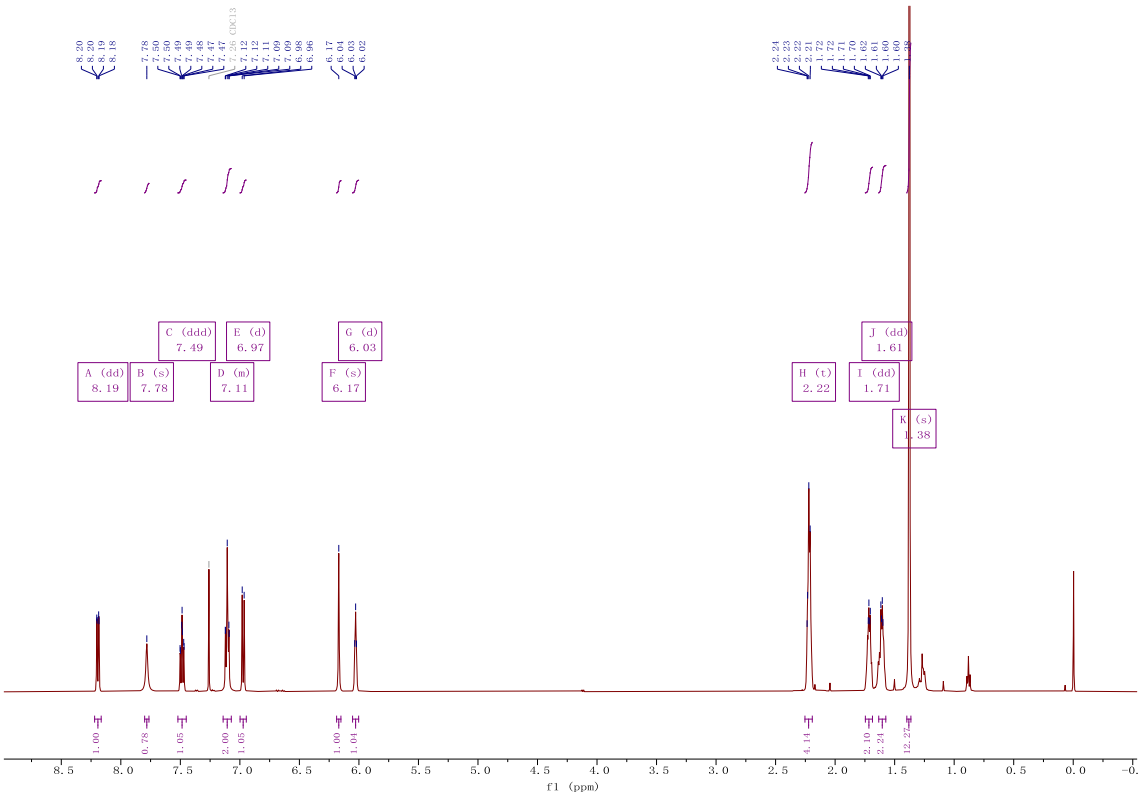

C (s) 8.04
F (dd) 7.52
H (d) 7.03
B (dd) 8.23
E (s) 7.63
G (m) 7.16
I (s) 6.67
D (d) 7.94
J (s) 2.61
A (s) 1.40
f1 (ppm)

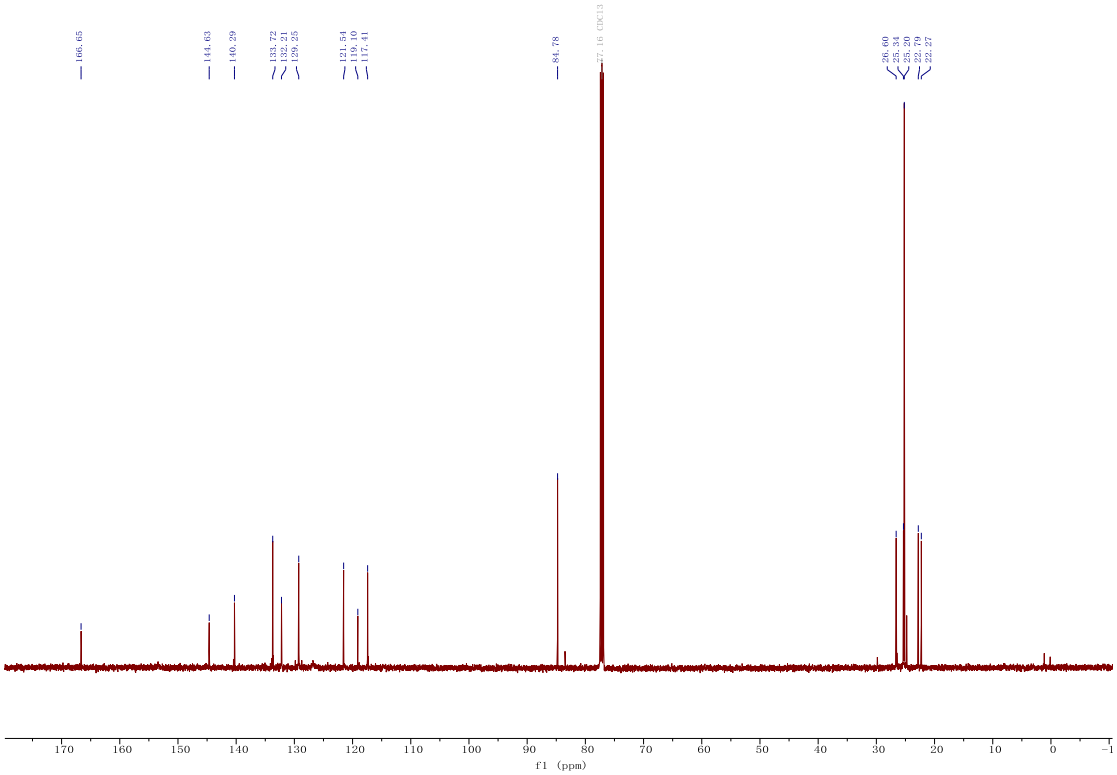

166.65
149.30
144.50
136.17
133.84
129.29
128.58
127.51
121.99
119.34
117.64
85.14
77.16 CDCl3
26.89
25.02
f1 (ppm)

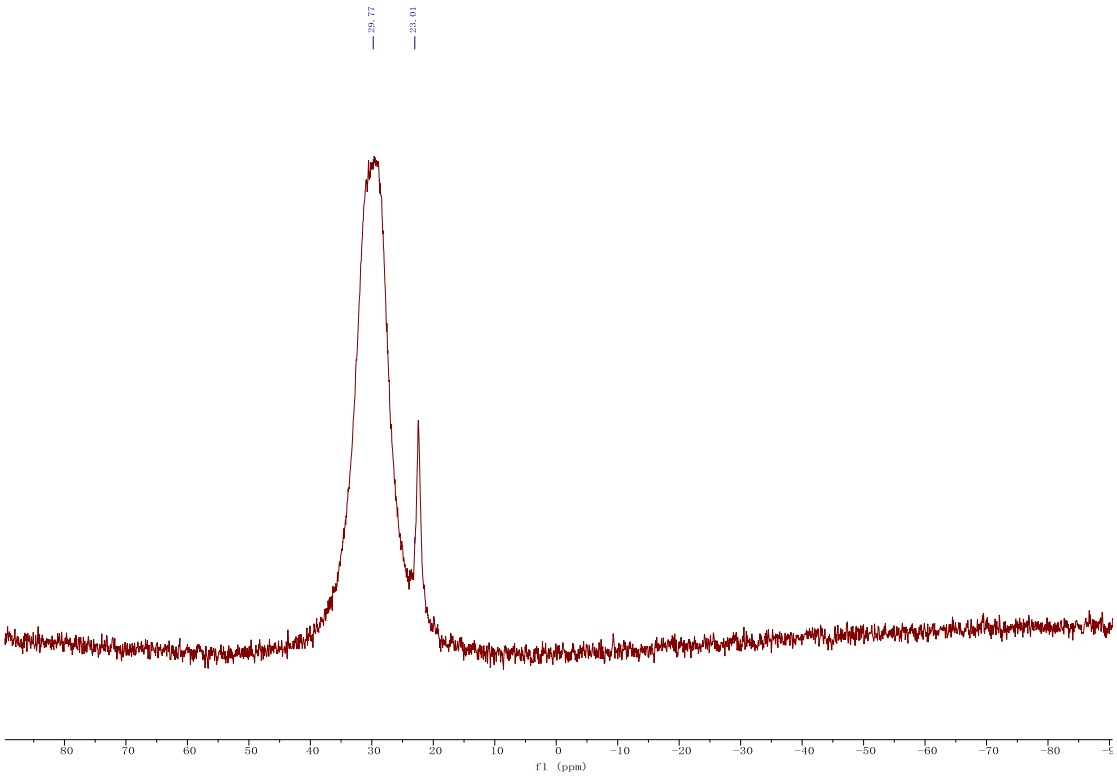

30.77
f1 (ppm)

3i

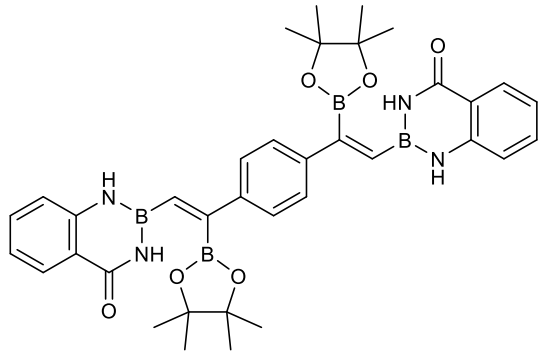

O
HN
O
O
B
B
NH

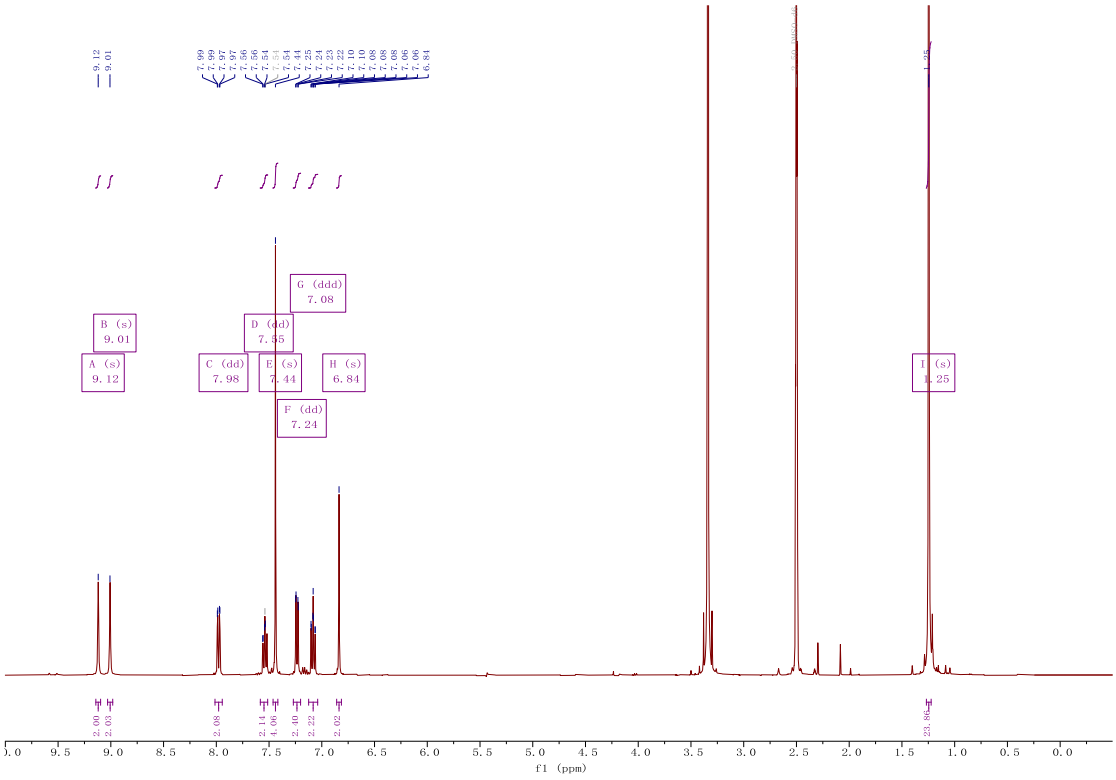

A (dd) 8.19
B (s) 7.78
C (ddd) 7.49
D (m) 7.11
E (d) 6.97
F (s) 6.17
G (d) 6.03
H (t) 2.22
I (dd) 1.71
J (dd) 1.61
K (s) 1.38
f1 (ppm)

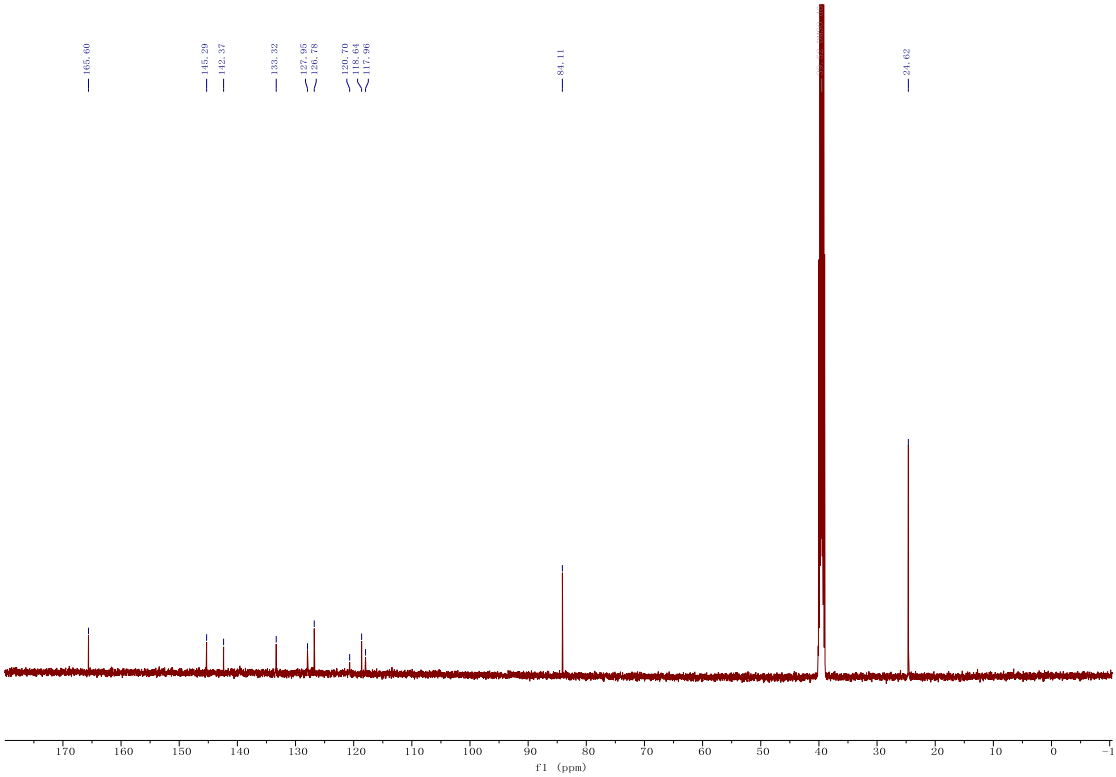

166.65
144.63
140.29
133.72
132.21
129.25
121.54
119.10
117.41
84.78
77.16 CDCl3
26.60
25.34
25.20
22.79
22.27
f1 (ppm)

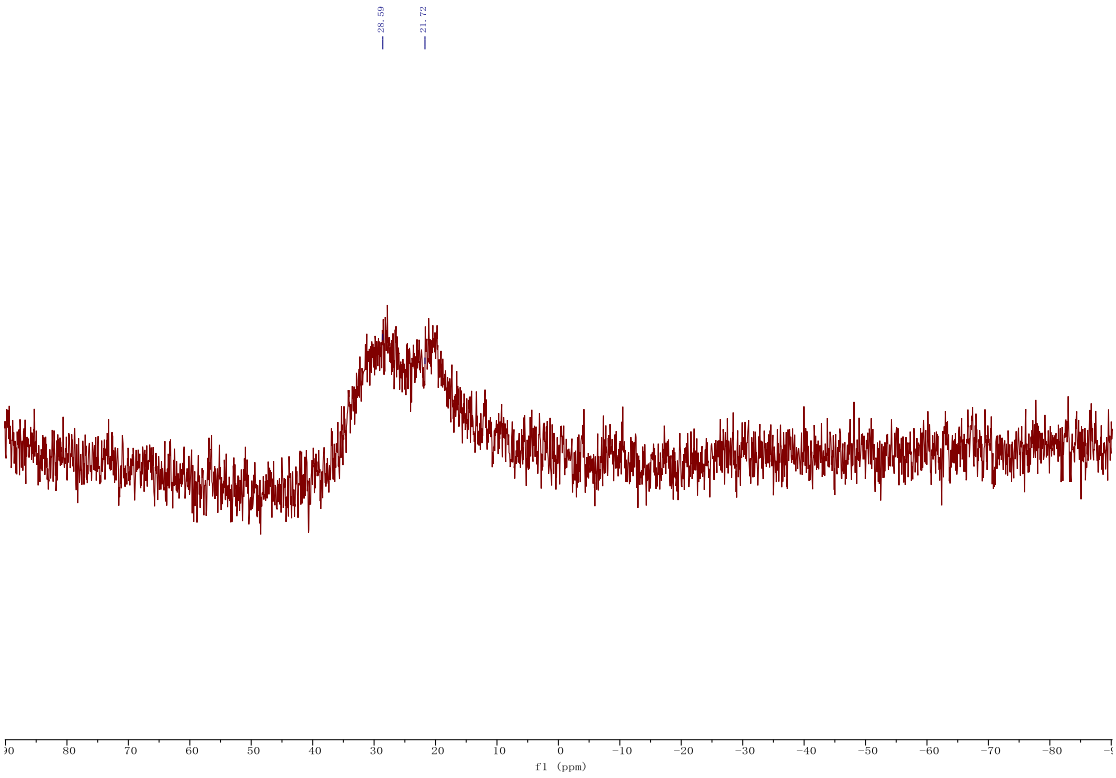

29.77
23.01
f1 (ppm)

3j

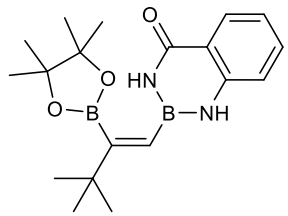


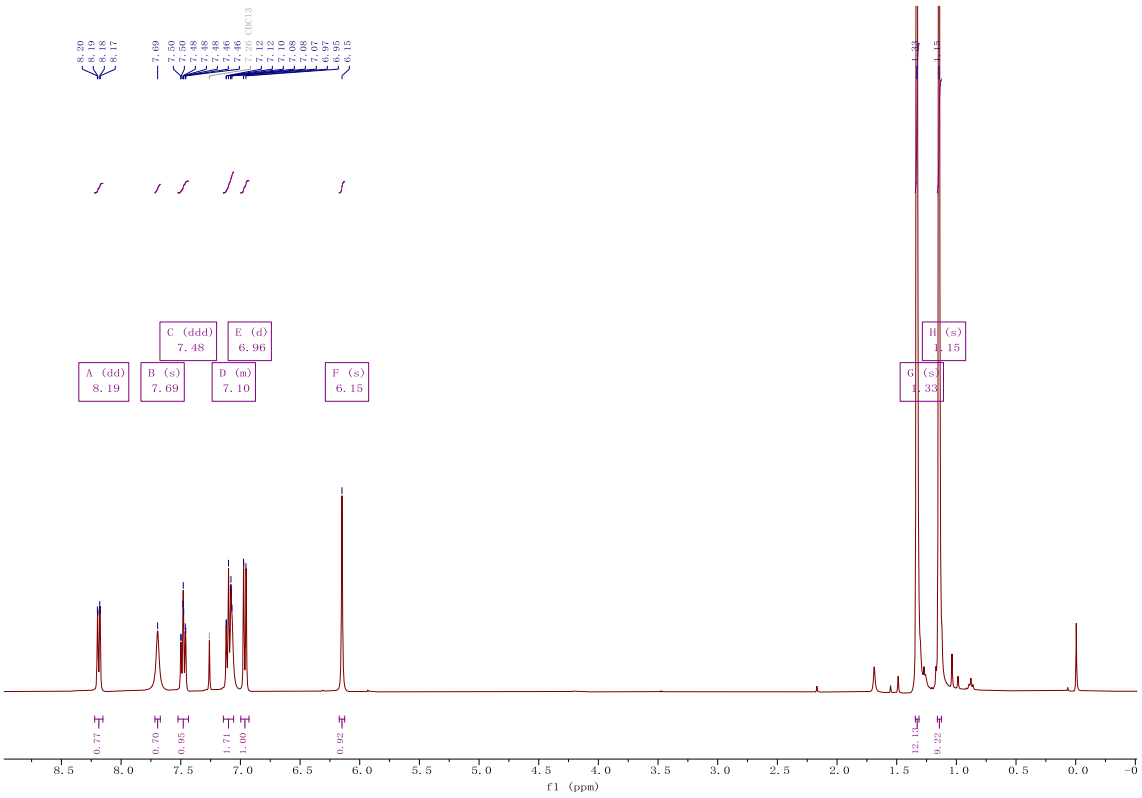

A (s) 9.12
B (s) 9.01
C (dd) 7.98
D (dd) 7.55
E (s) 7.44
F (dd) 7.24
G (ddd) 7.08
H (s) 6.84
I (s) 1.25
f1 (ppm)

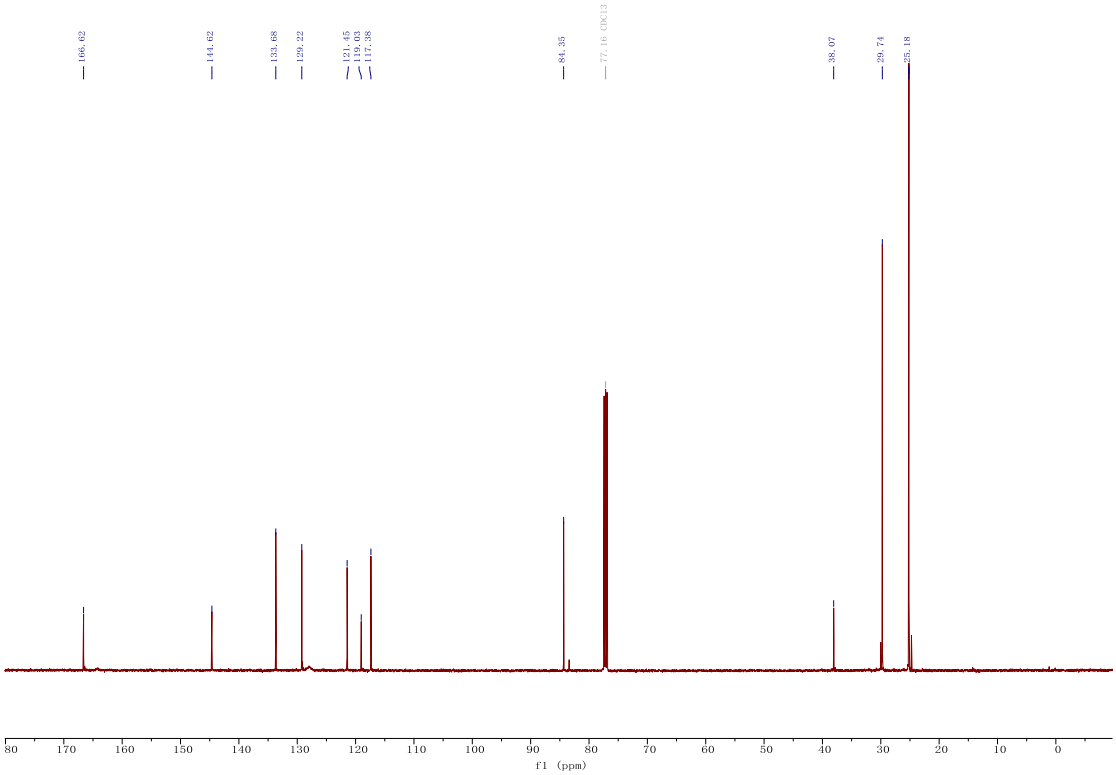

165.60
145.29
142.37
133.32
127.95
126.78
120.70
118.64
117.96
84.11
24.62
f1 (ppm)

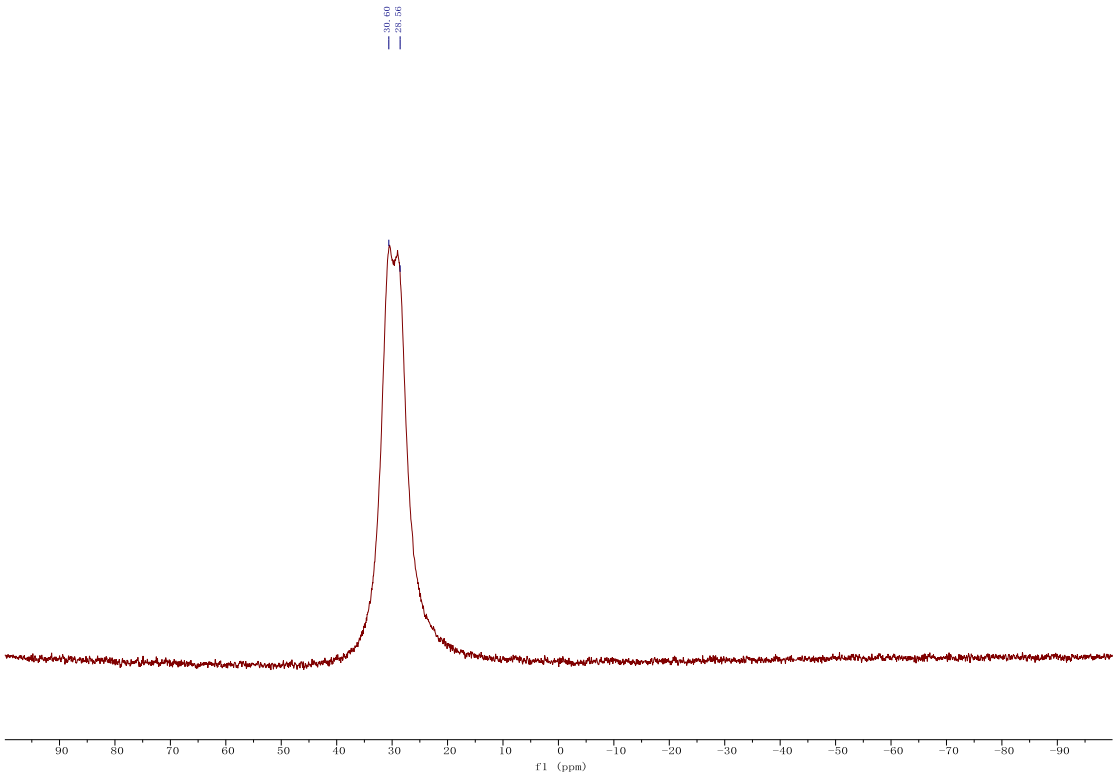

28.59
21.72
f1 (ppm)

3k

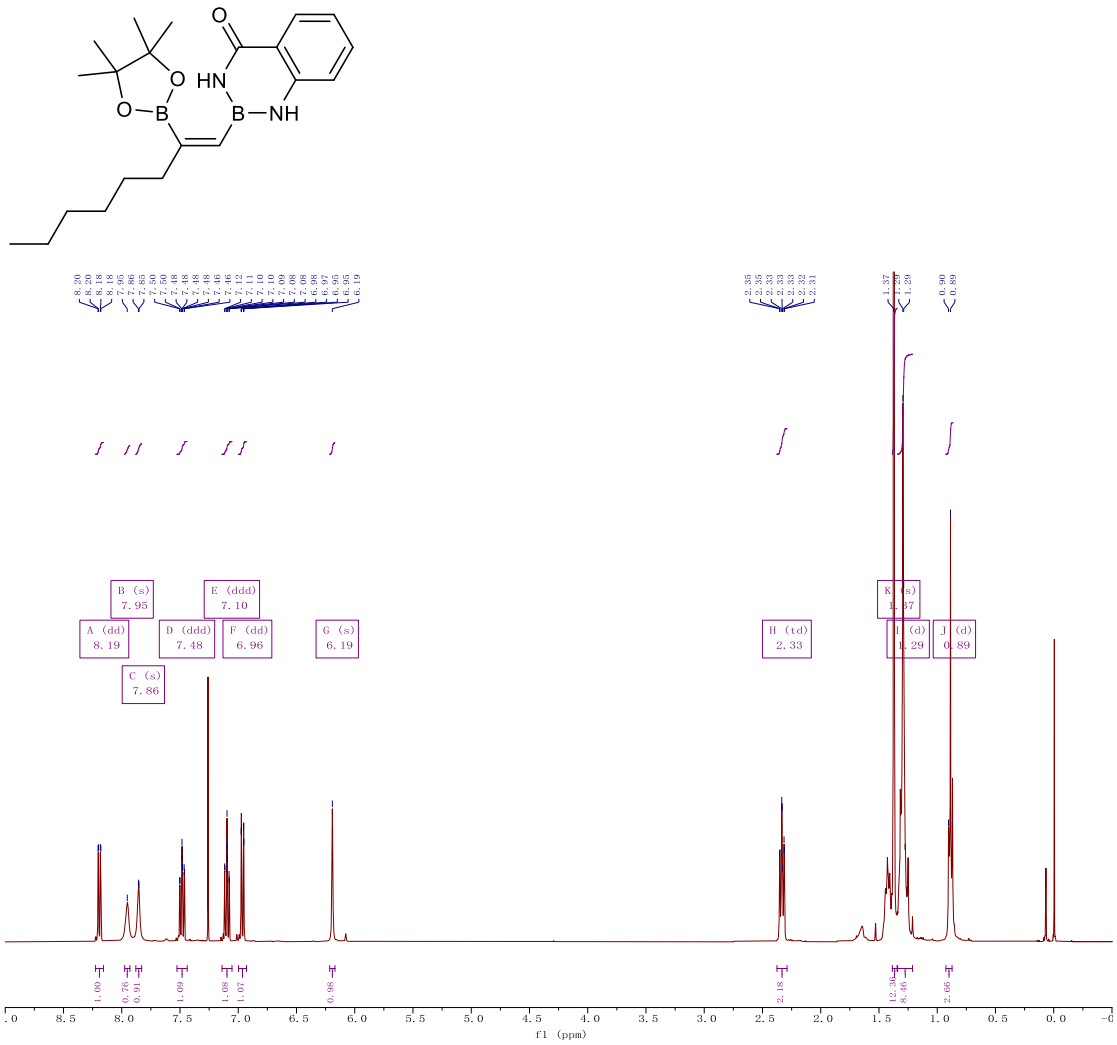

O
HN
O
O
B
B
NH

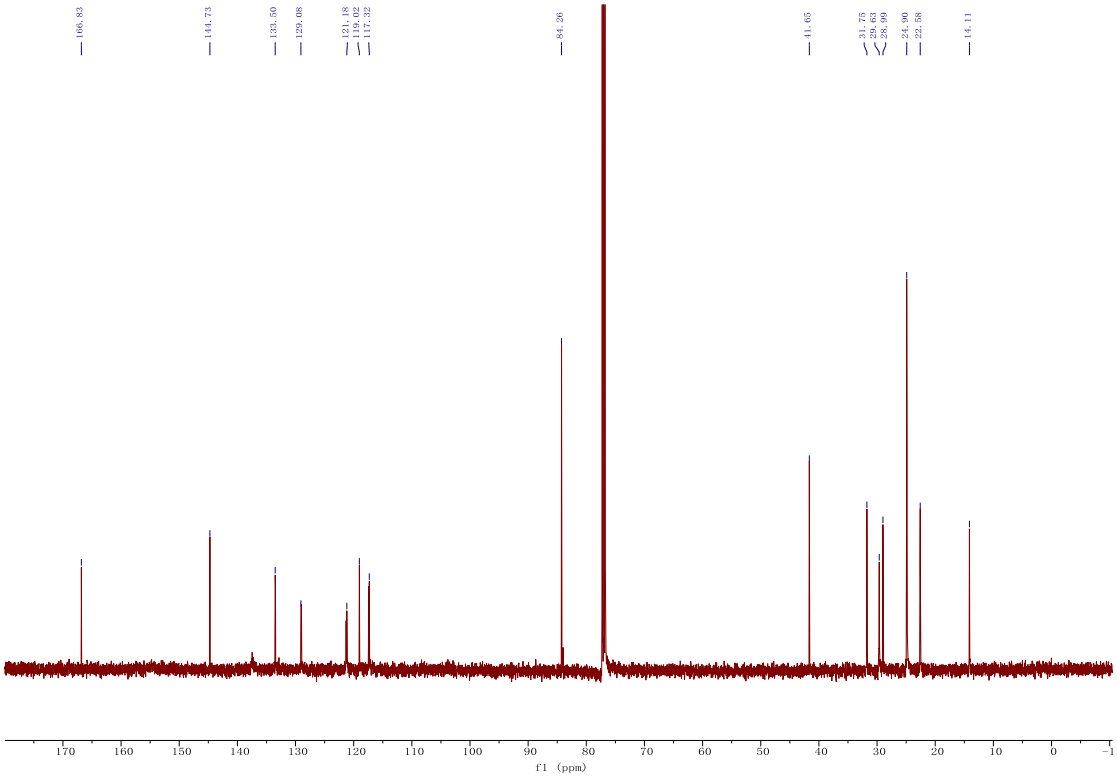

A (dd)
8.19
B (s)
7.69
C (ddd)
7.48
D (m)
7.10
E (d)
6.96
F (s)
6.15
G (s)
1.33
H (s)
1.15
f1 (ppm)

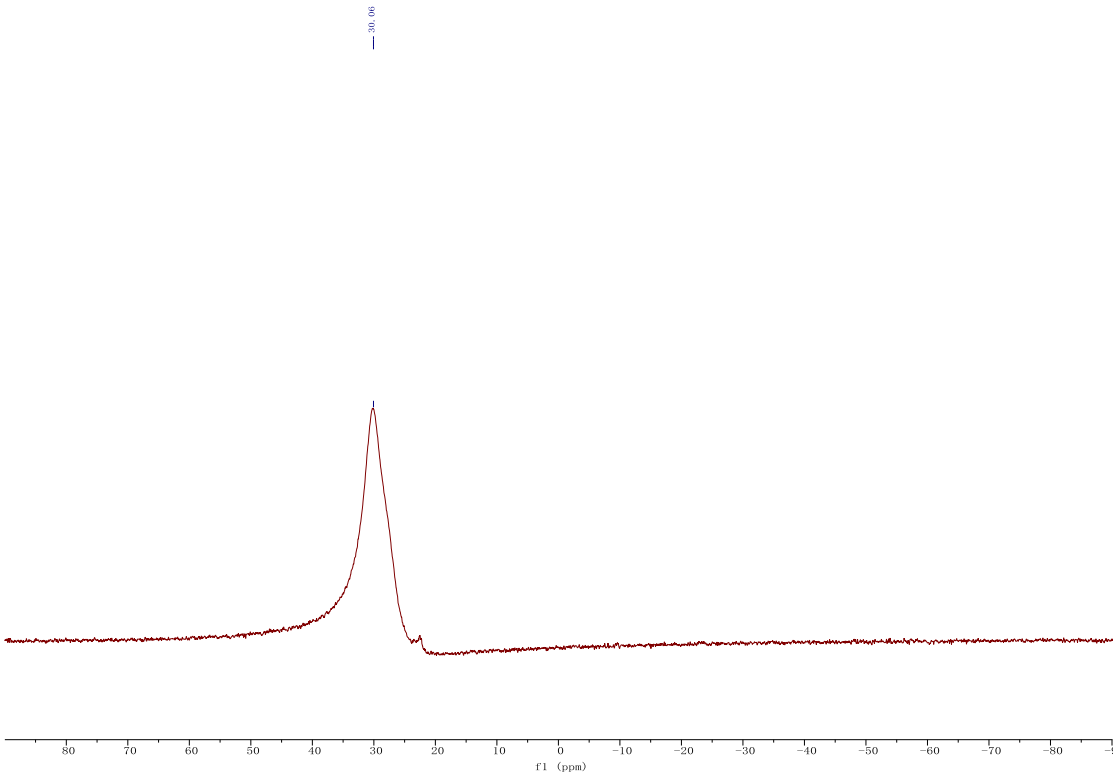

166.62
144.62
133.68
129.22
121.45
119.03
117.38
84.35
77.16 CDCl3
38.07
29.74
25.18
f1 (ppm)


30.60
28.56
f1 (ppm)

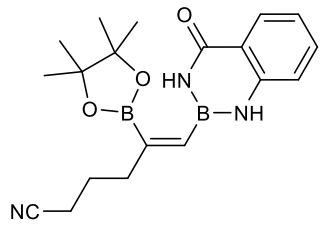
3l

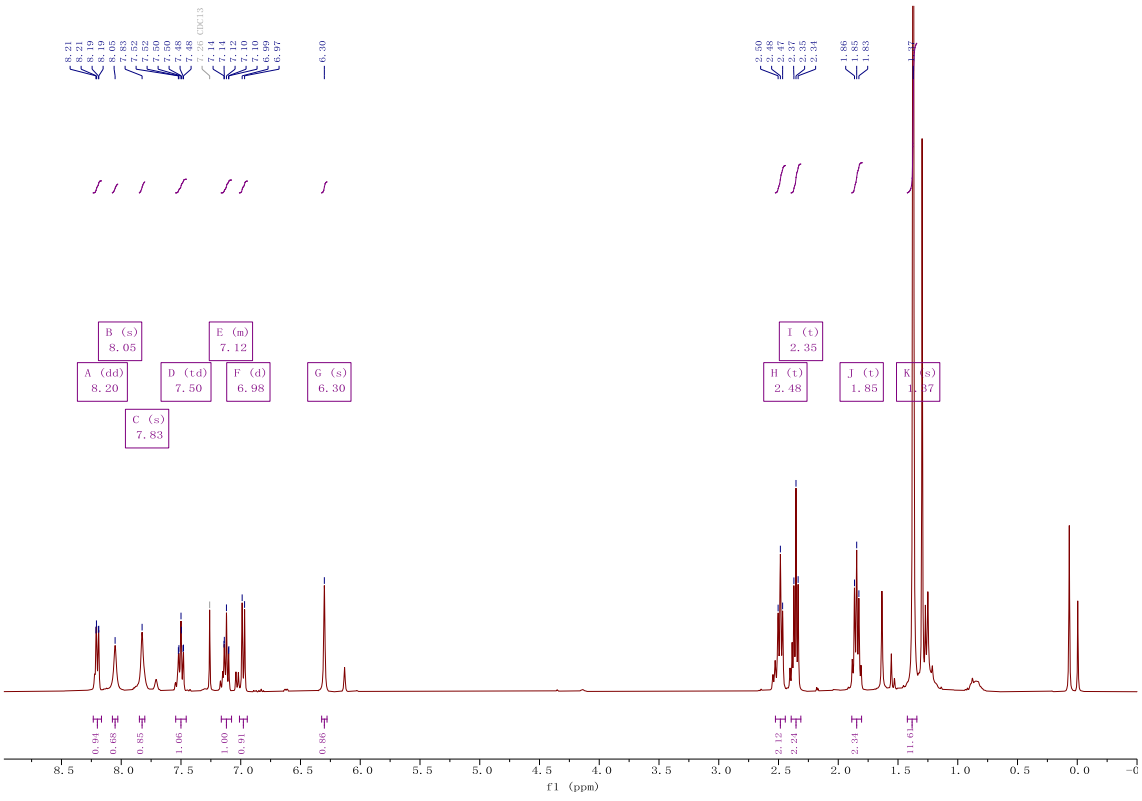

O
HN
O
O
B
B
NH
8.20
8.20
8.18
8.18
7.95
7.86
7.85
7.50
7.50
7.48
7.48
7.48
7.46
7.46
7.22
7.11
7.10
7.09
7.08
7.08
6.98
6.97
6.95
6.19
2.35
2.35
2.33
2.33
2.33
2.32
2.31
1.37
1.29
1.29
0.90
0.89
B (s)
7.95
E (ddd)
7.10
K (s)
1.37
A (dd)
8.19
D (ddd)
7.48
F (dd)
6.96
G (s)
6.19
H (td)
2.33
I (d)
1.29
J (d)
0.89
C (s)
7.86
1.00
0.76
0.91
1.09
1.08
1.07
0.98
2.18
12.36
8.46
2.66
f1 (ppm)

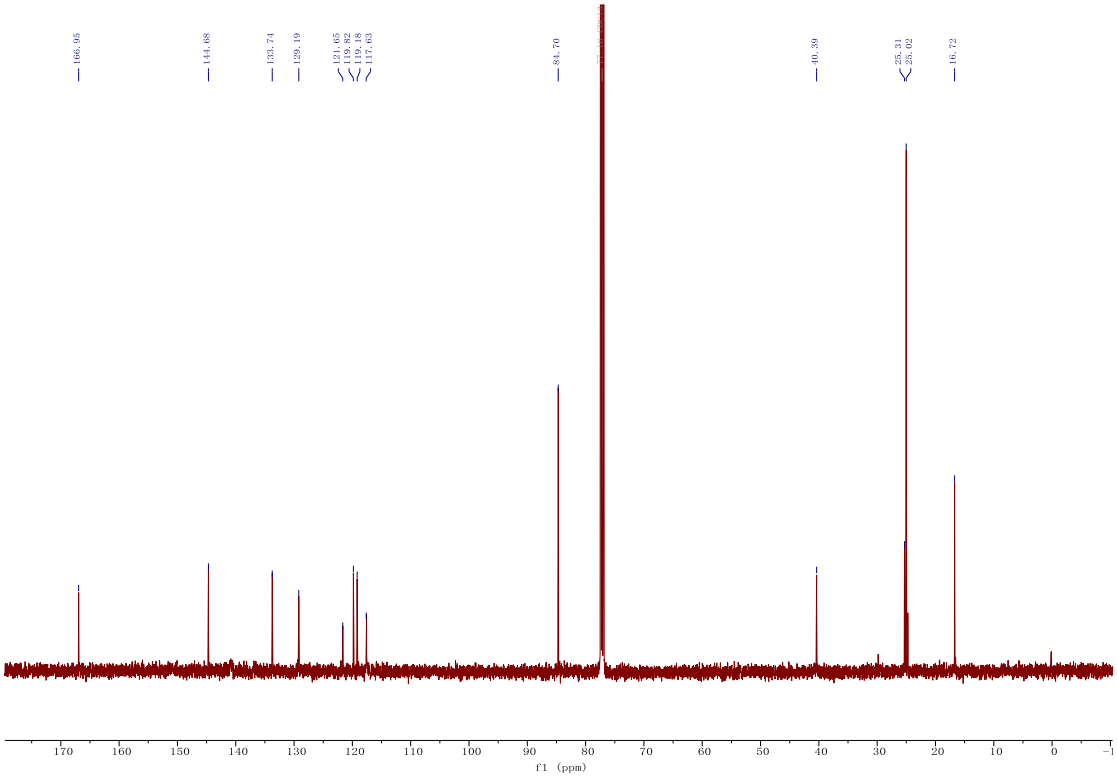

166.83
144.73
133.50
129.08
121.18
119.02
117.32
84.26
41.65
31.75
29.63
28.99
24.90
22.58
14.11
f1 (ppm)

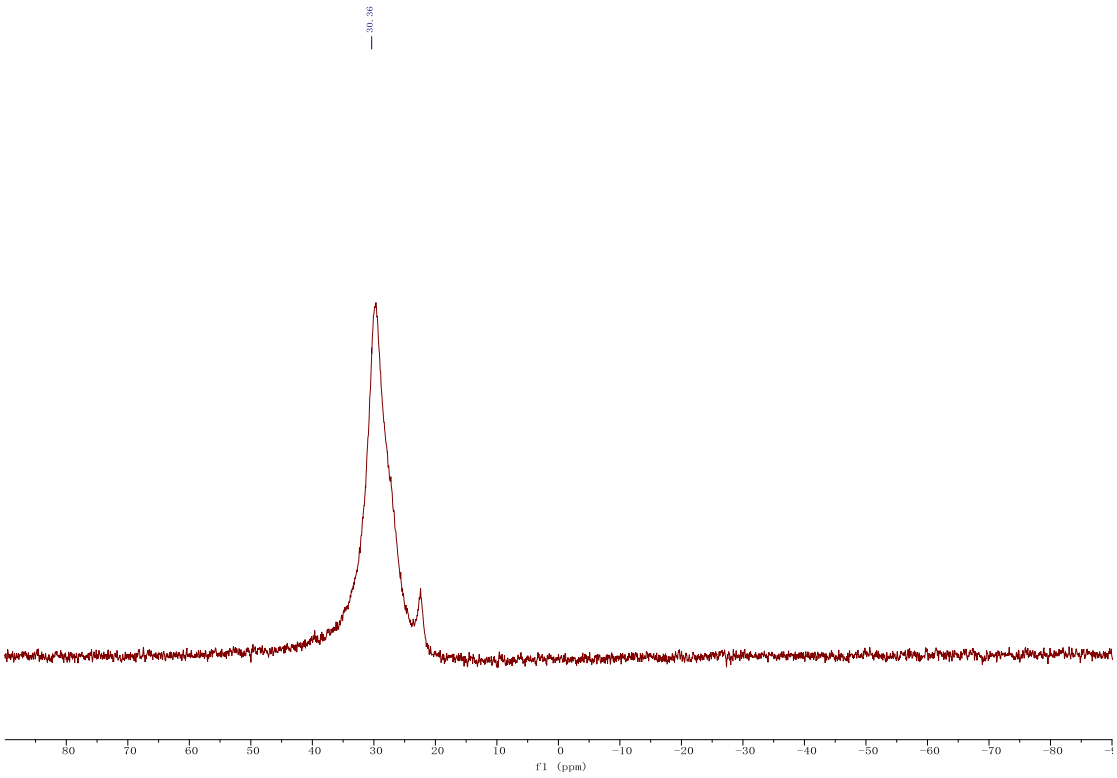

30.06
f1 (ppm)

3m

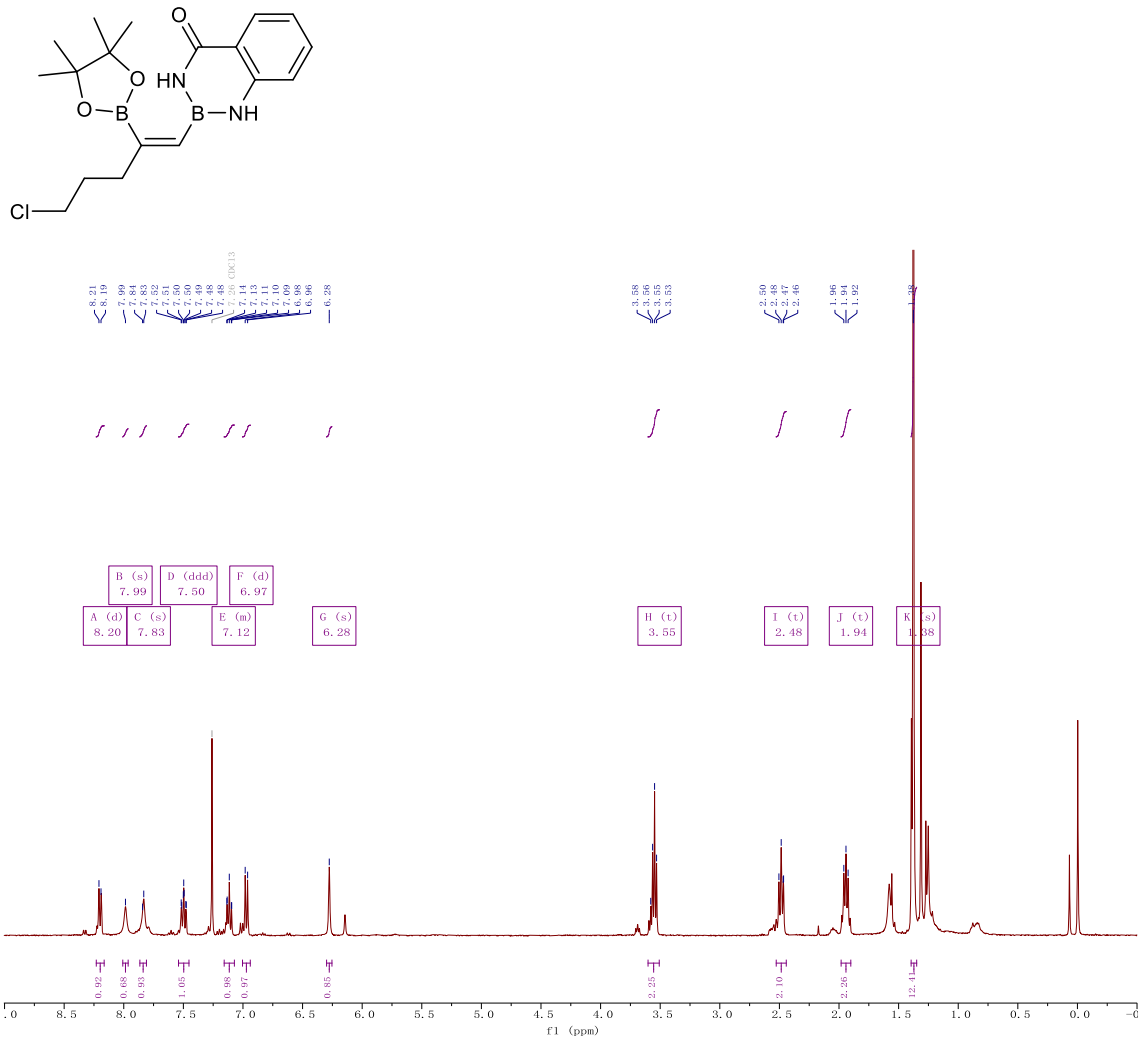

O
HN
O
O
B
B
NH
NC

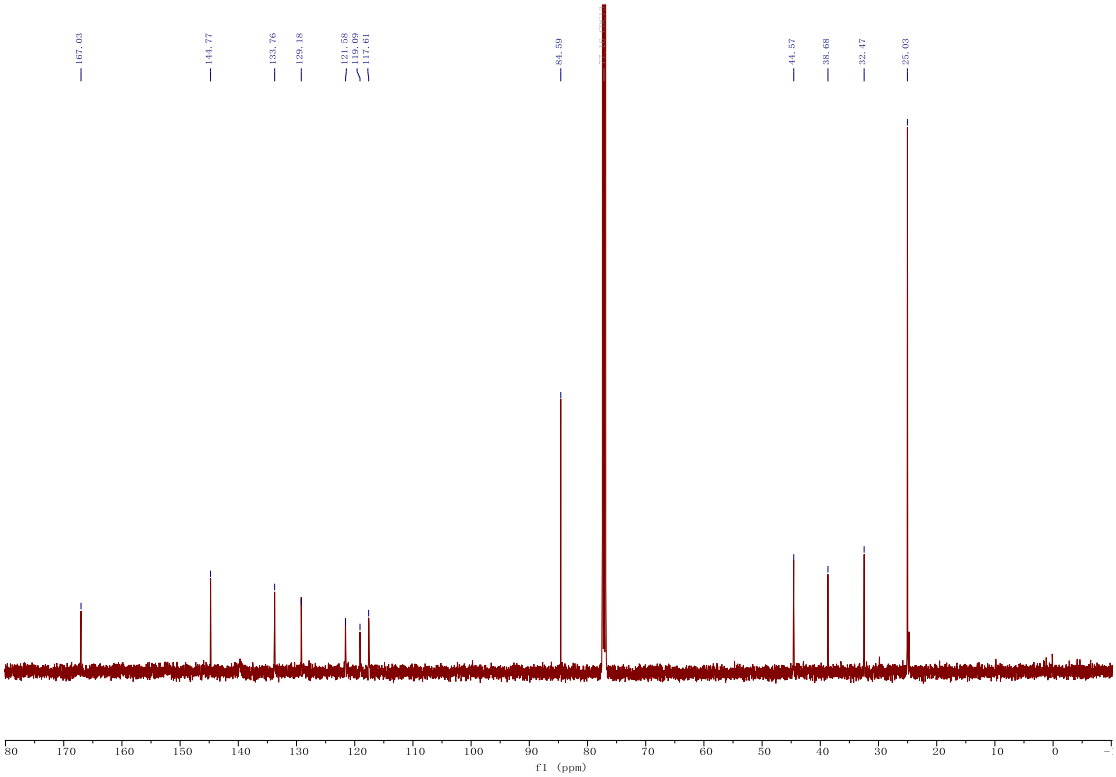

B (s)
8.05
E (m)
7.12
I (t)
2.35
A (dd)
8.20
D (td)
7.50
F (d)
6.98
G (s)
6.30
H (t)
2.48
J (t)
1.85
K (s)
1.37
C (s)
7.83
f1 (ppm)

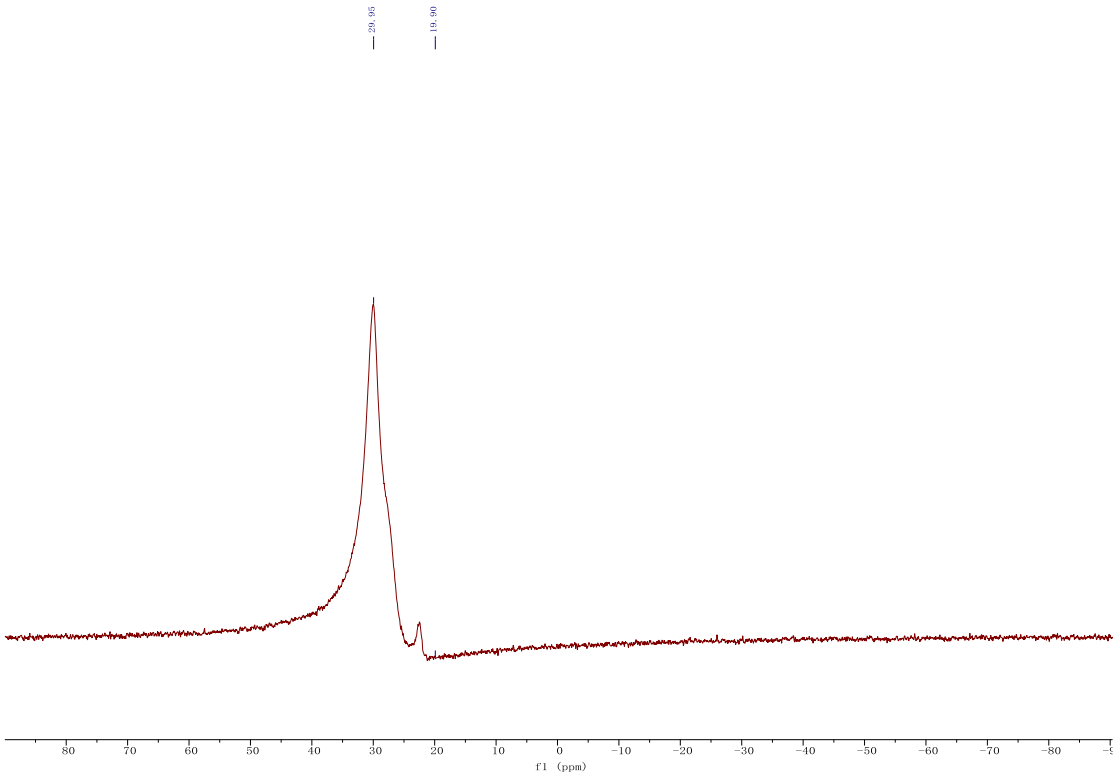

166.95
144.68
133.74
129.19
121.65
119.82
119.18
117.63
84.70
40.39
25.31
25.02
16.72
f1 (ppm)


30.36
f1 (ppm)

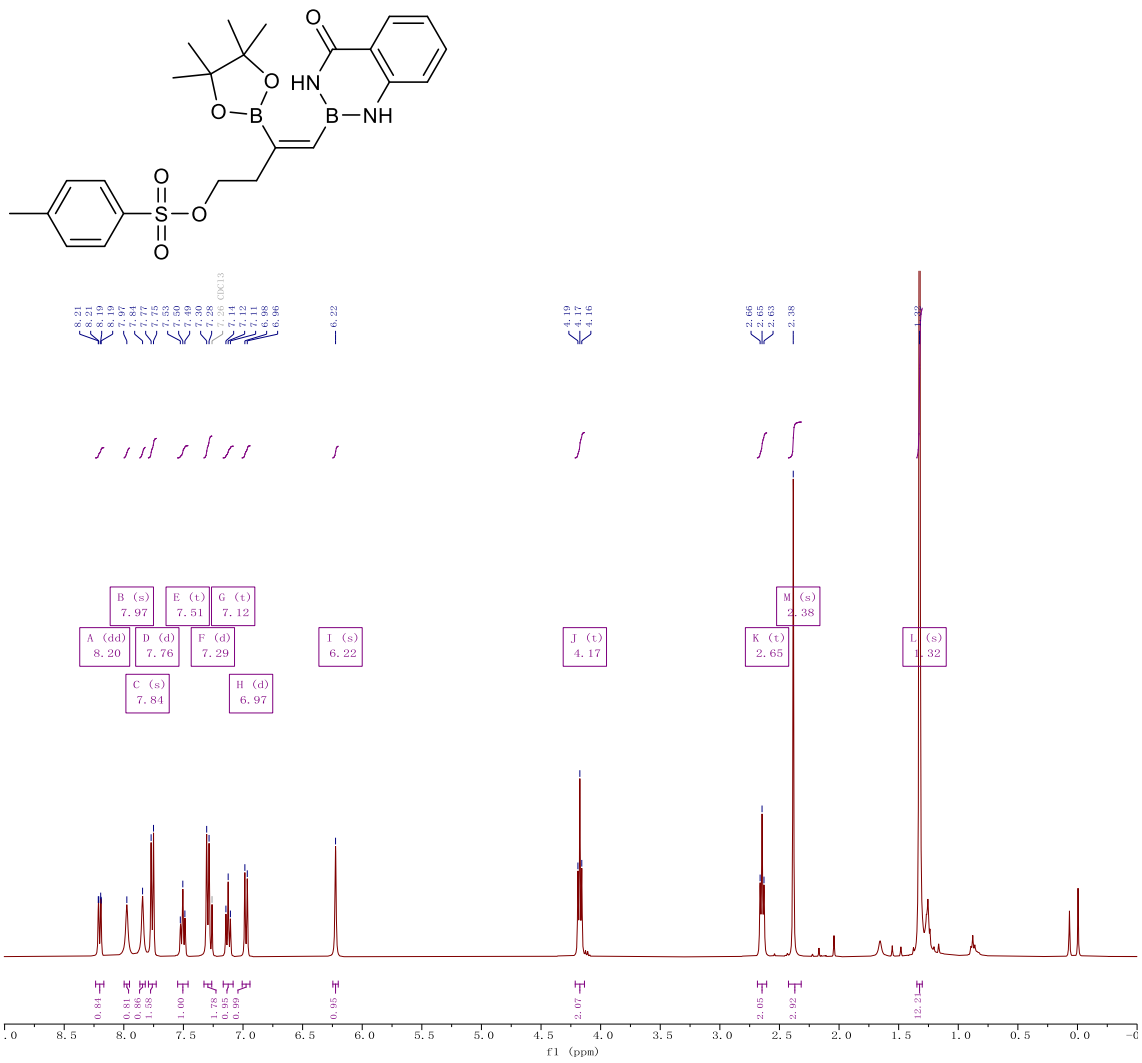
3n

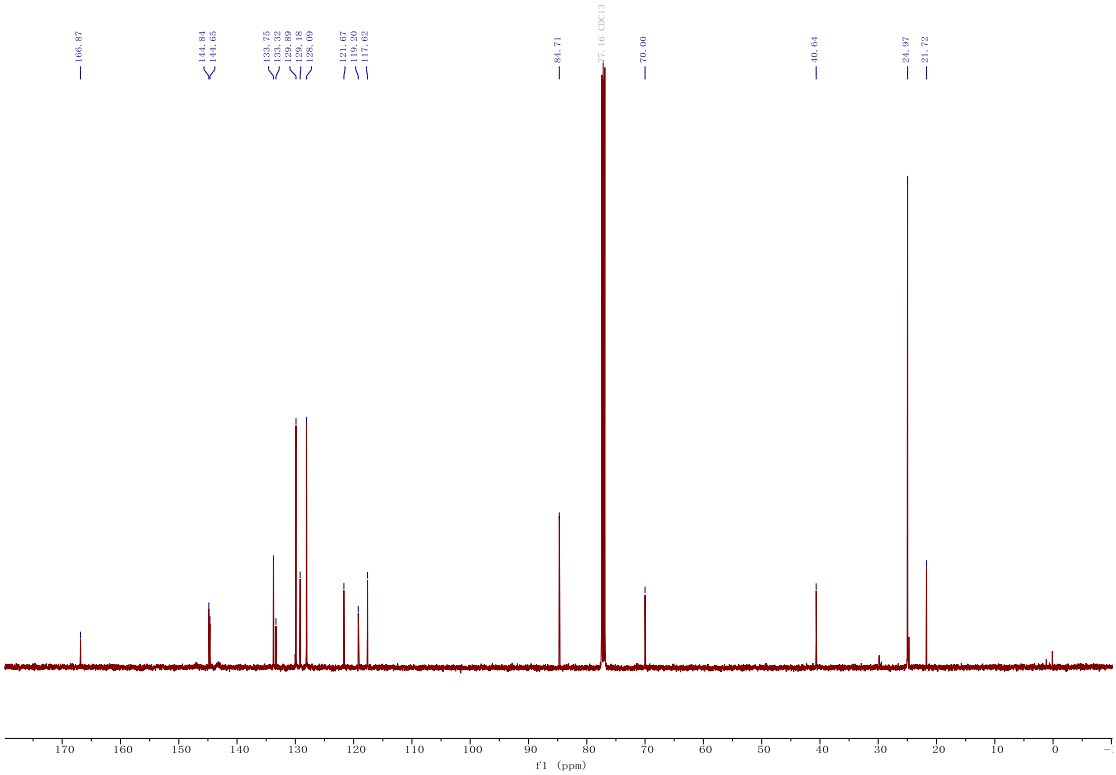

O
HN
O
O
B
B
NH
Cl
B (s) 7.99
D (ddd) 7.50
F (d) 6.97
A (d) 8.20
C (s) 7.83
E (m) 7.12
G (s) 6.28
H (t) 3.55
I (t) 2.48
J (t) 1.94
K (s) 1.38
f1 (ppm)

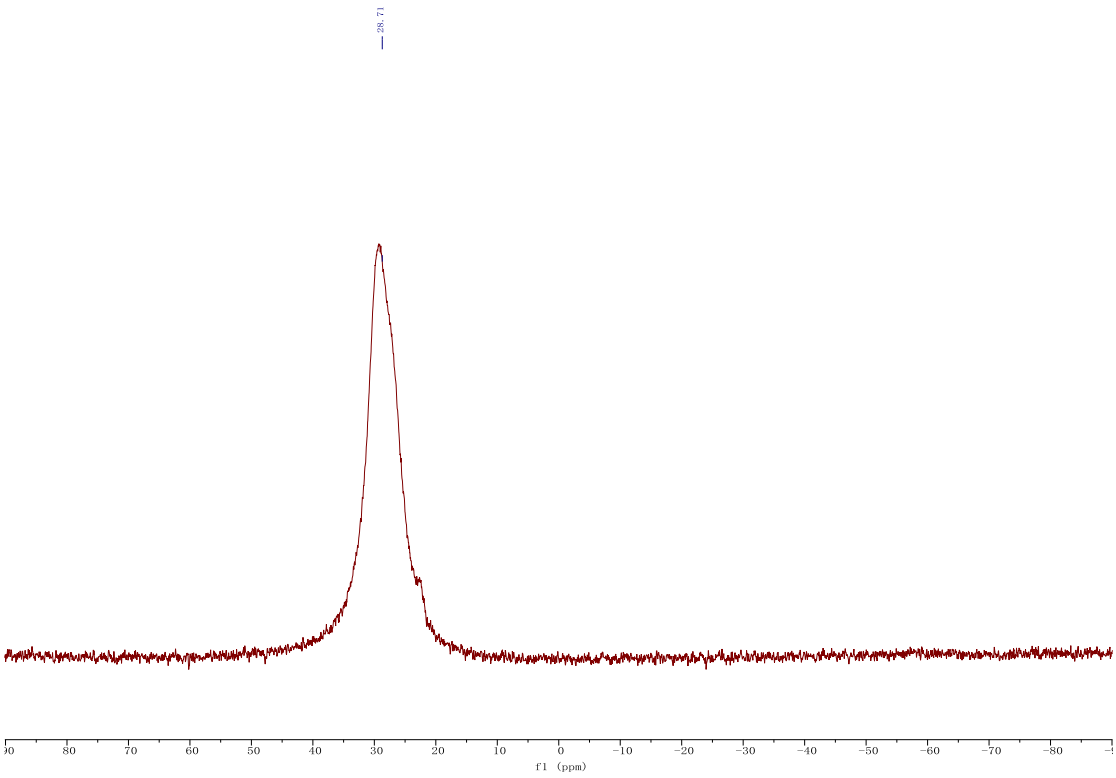

167.03
144.77
133.76
129.18
121.58
119.09
117.61
84.59
44.57
38.68
32.47
25.03
f1 (ppm)


29.95
19.90
f1 (ppm)

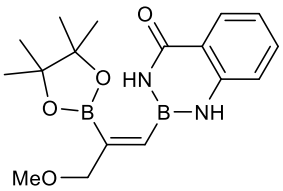
3o

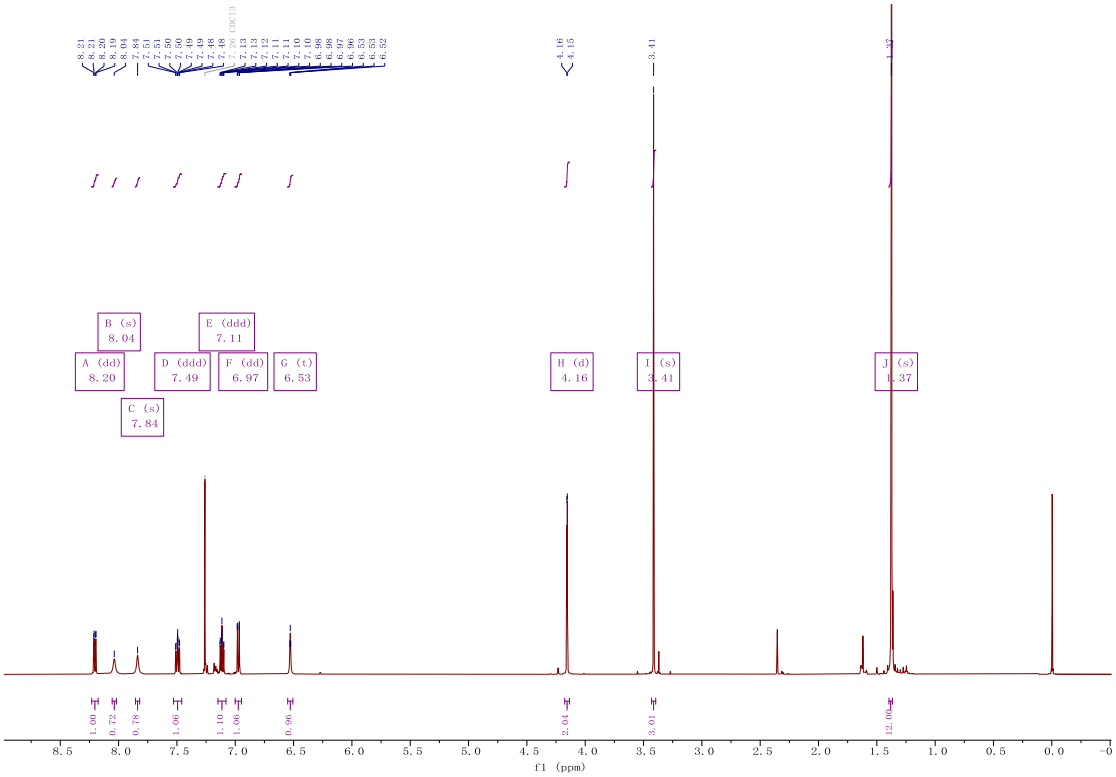

B (s) 7.97
E (t) 7.51
G (t) 7.12
A (dd) 8.20
D (d) 7.76
F (d) 7.29
I (s) 6.22
J (t) 4.17
K (t) 2.65
M (s) 2.38
L (s) 1.32
C (s) 7.84
H (d) 6.97
f1 (ppm)

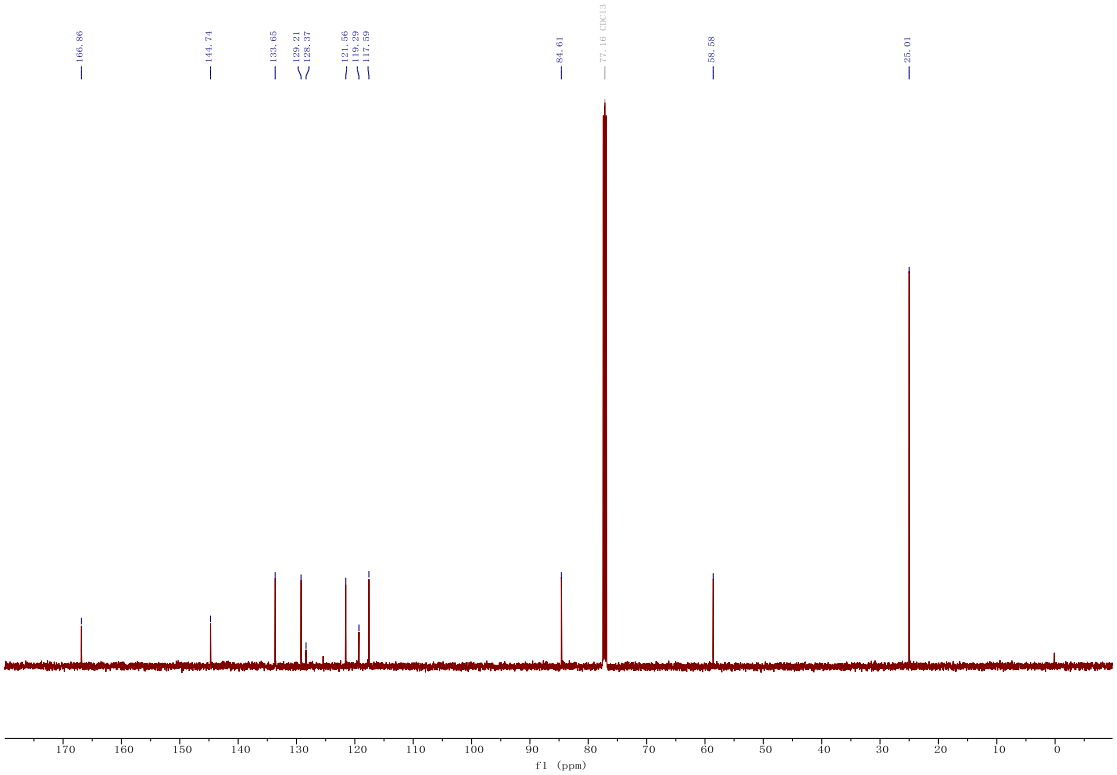

166.87
144.84
144.65
133.75
133.32
129.89
129.18
126.09
121.67
119.20
117.62
84.71
77.16 CDCl3
70.00
40.64
24.97
21.72
f1 (ppm)

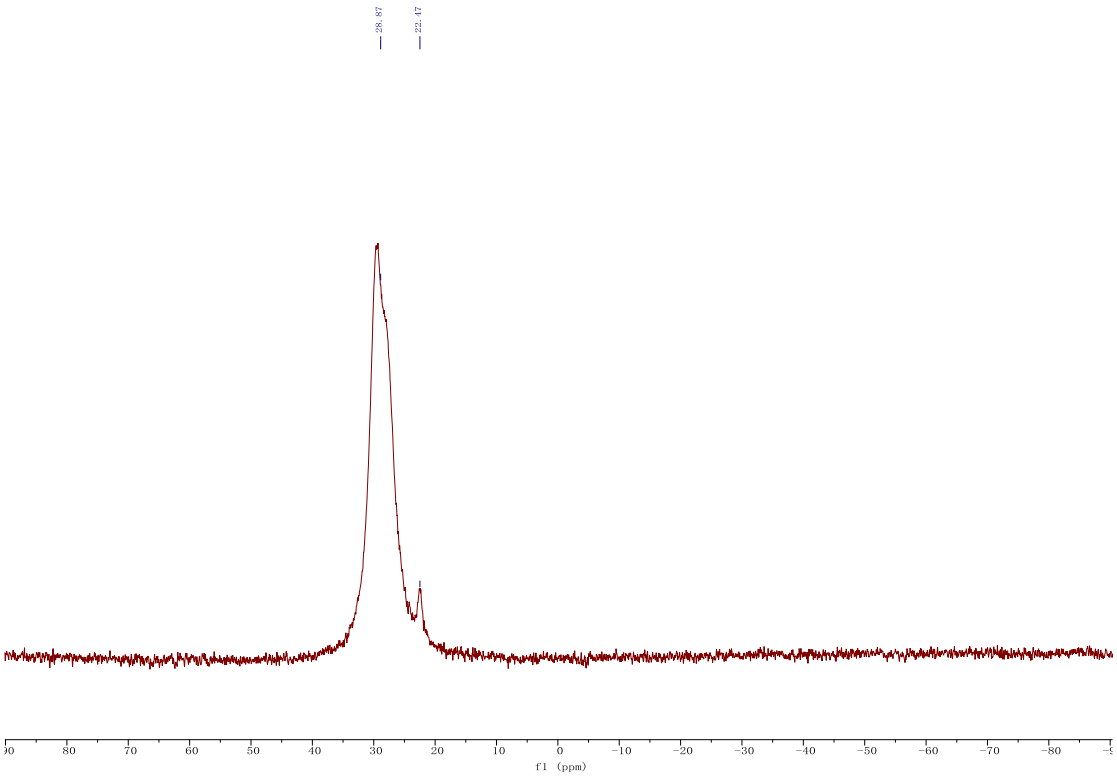

28.71
f1 (ppm)

3p

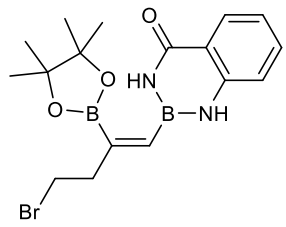

O
HN
O
O
B
B
NH
MeO

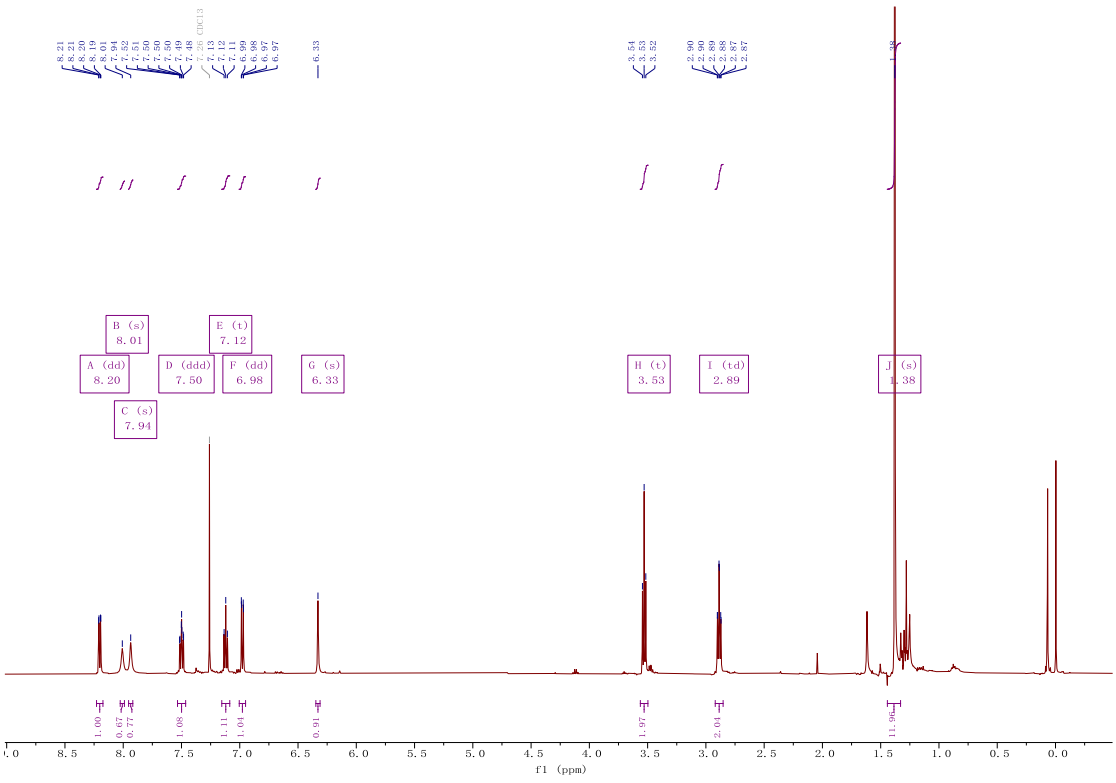

B (s) 8.04
E (ddd) 7.11
A (dd) 8.20
D (ddd) 7.49
F (dd) 6.97
G (t) 6.53
C (s) 7.84
H (d) 4.16
I (s) 3.41
J (s) 1.37
f1 (ppm)

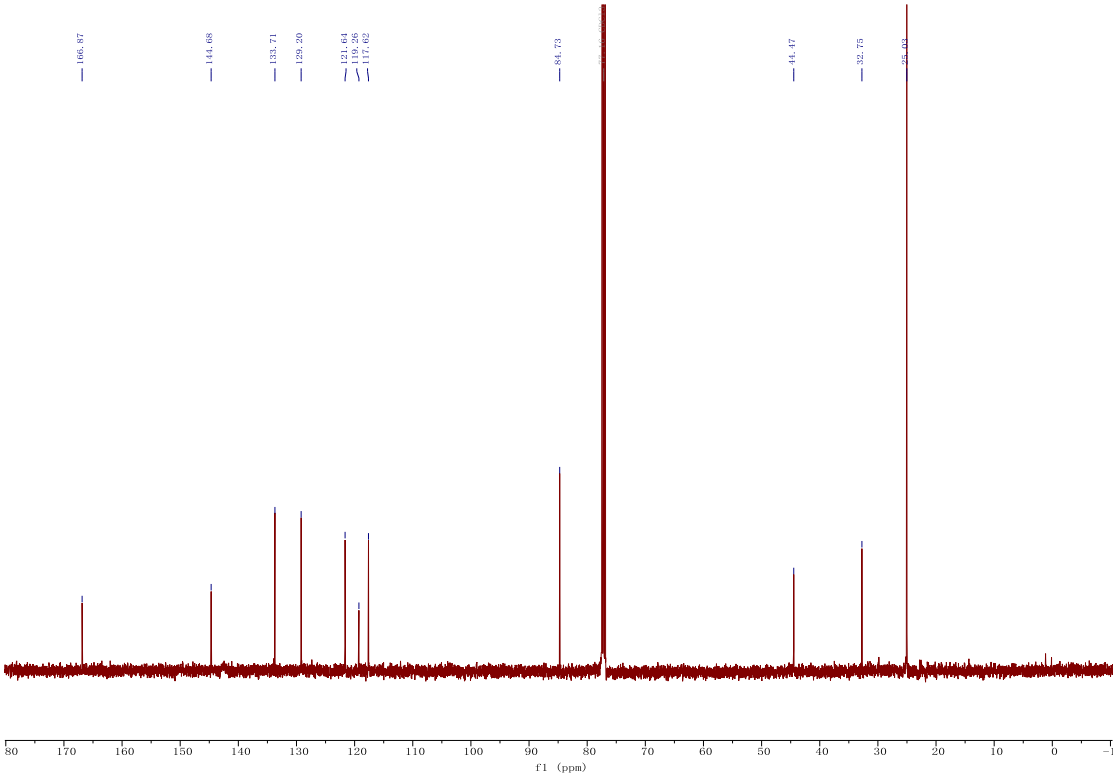

166.86
144.74
133.65
129.21
128.37
121.66
119.29
117.59
84.61
77.16 CDCl3
58.58
25.01
f1 (ppm)

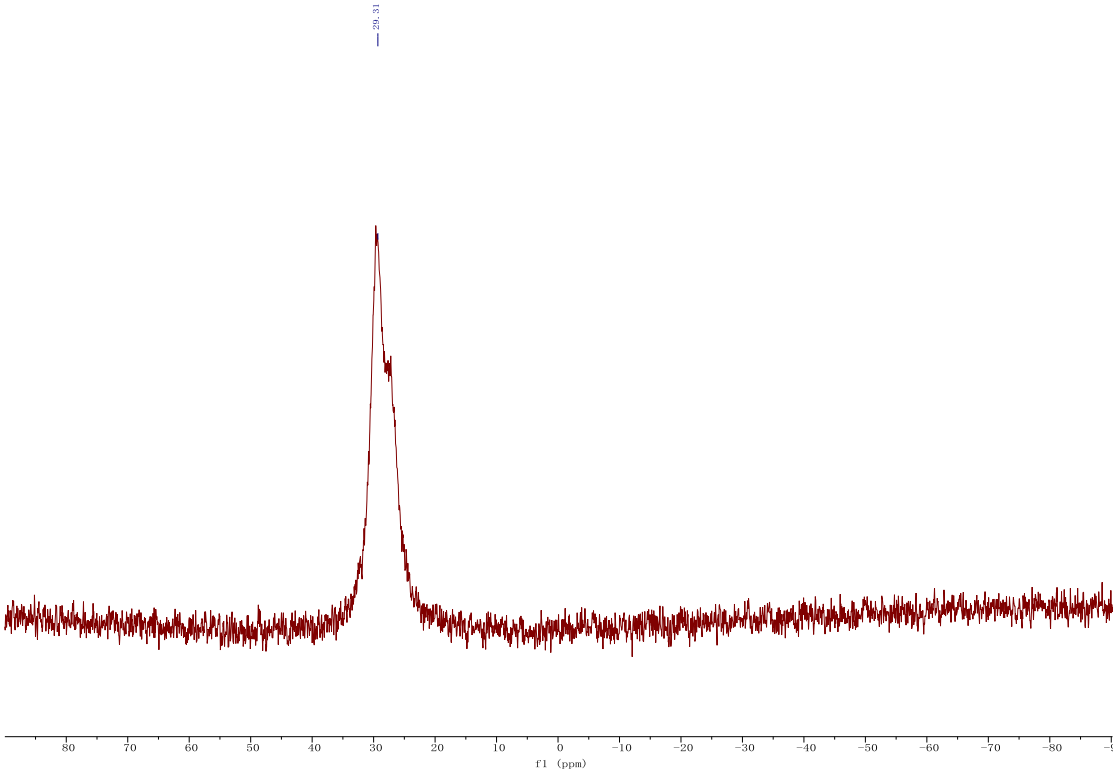

28.87
22.47
f1 (ppm)

3q

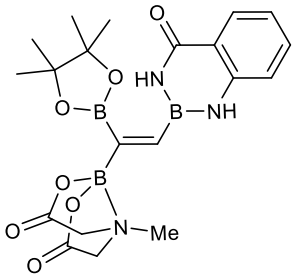

O
HN
O
O
B
B
NH
Br

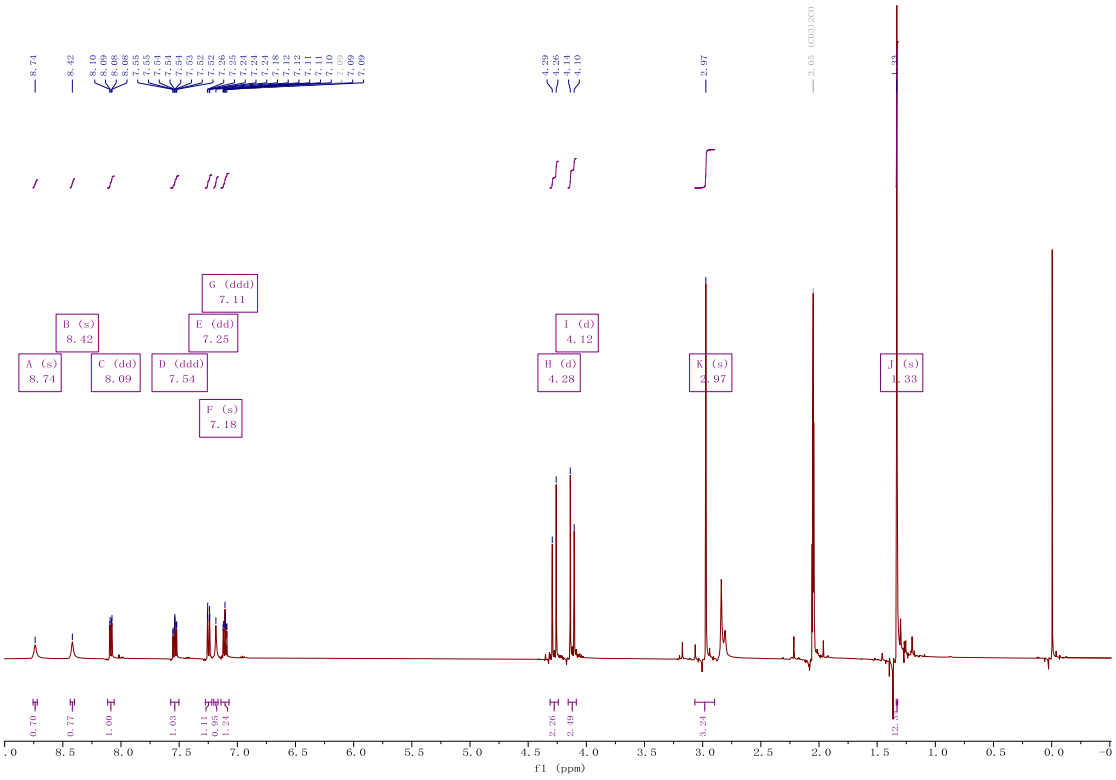

B (s) 8.01
E (t) 7.12
A (dd) 8.20
D (ddd) 7.50
F (dd) 6.98
G (s) 6.33
C (s) 7.94
H (t) 3.53
I (td) 2.89
J (s) 1.38
f1 (ppm)

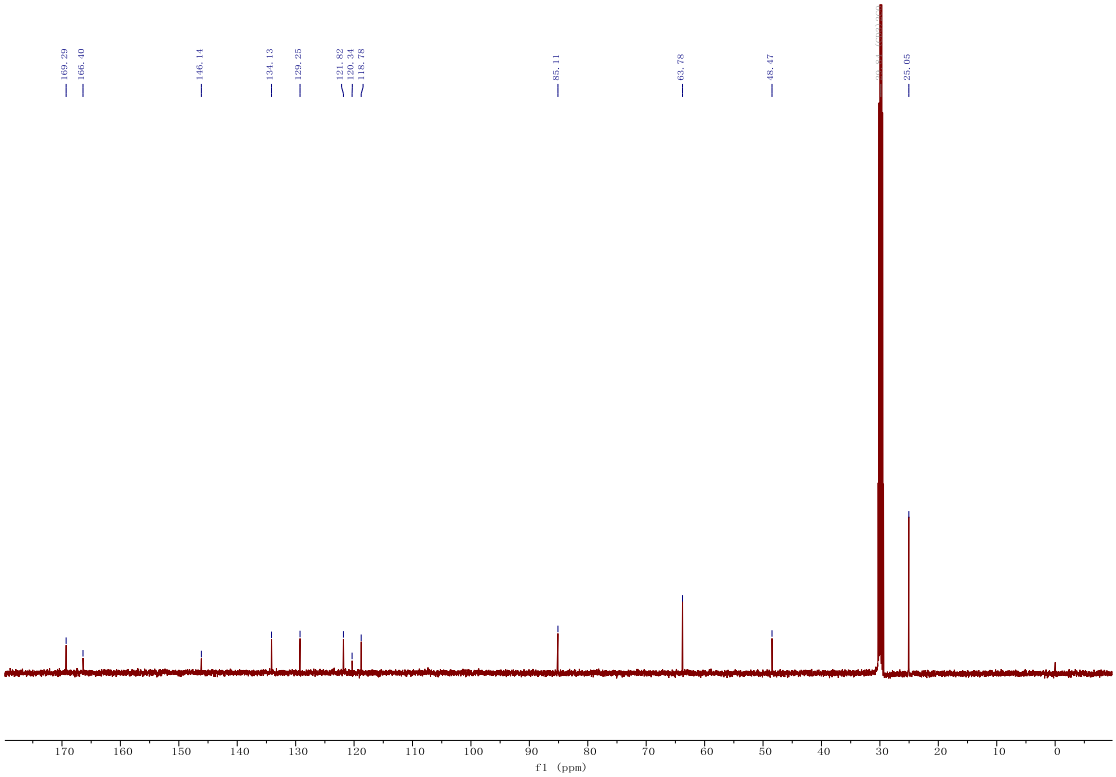

166.87
144.68
133.71
129.20
121.64
119.26
117.62
84.73
44.47
32.75
25.69
f1 (ppm)

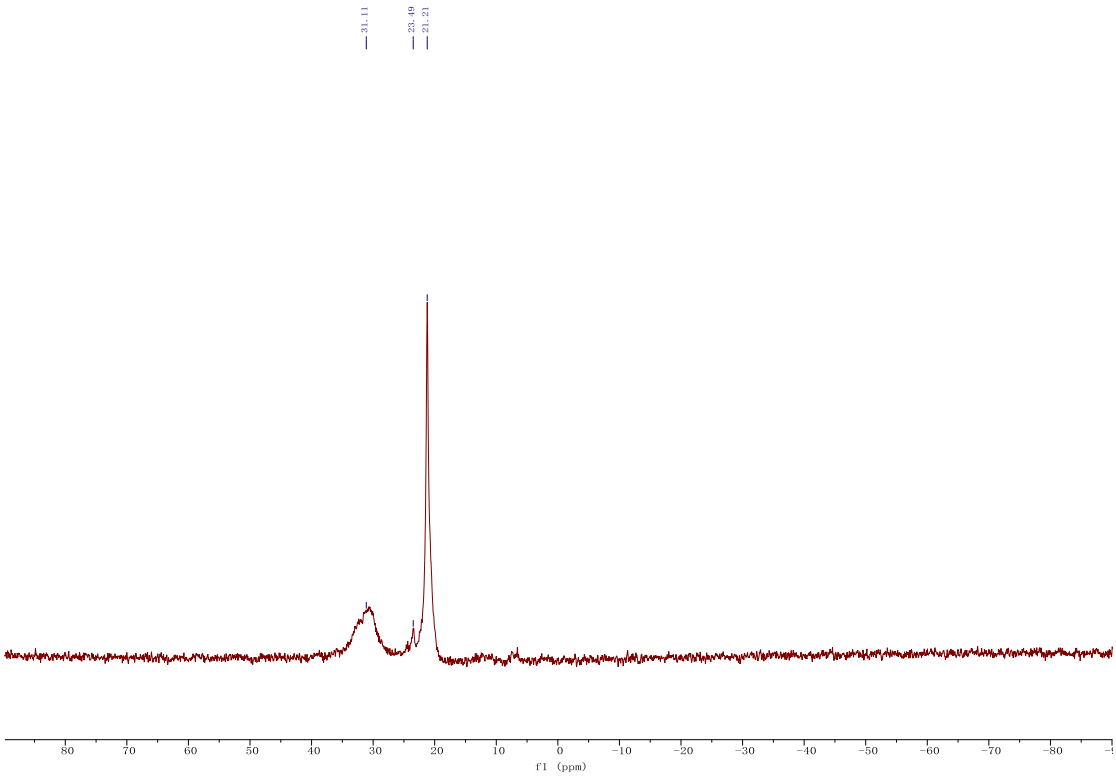

29.31
f1 (ppm)

3r

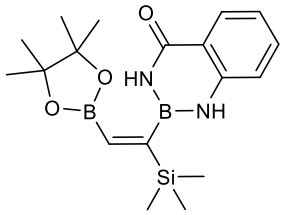

O
HN
O
O
B
B—NH
O
B
O
O
N
Me
O
O

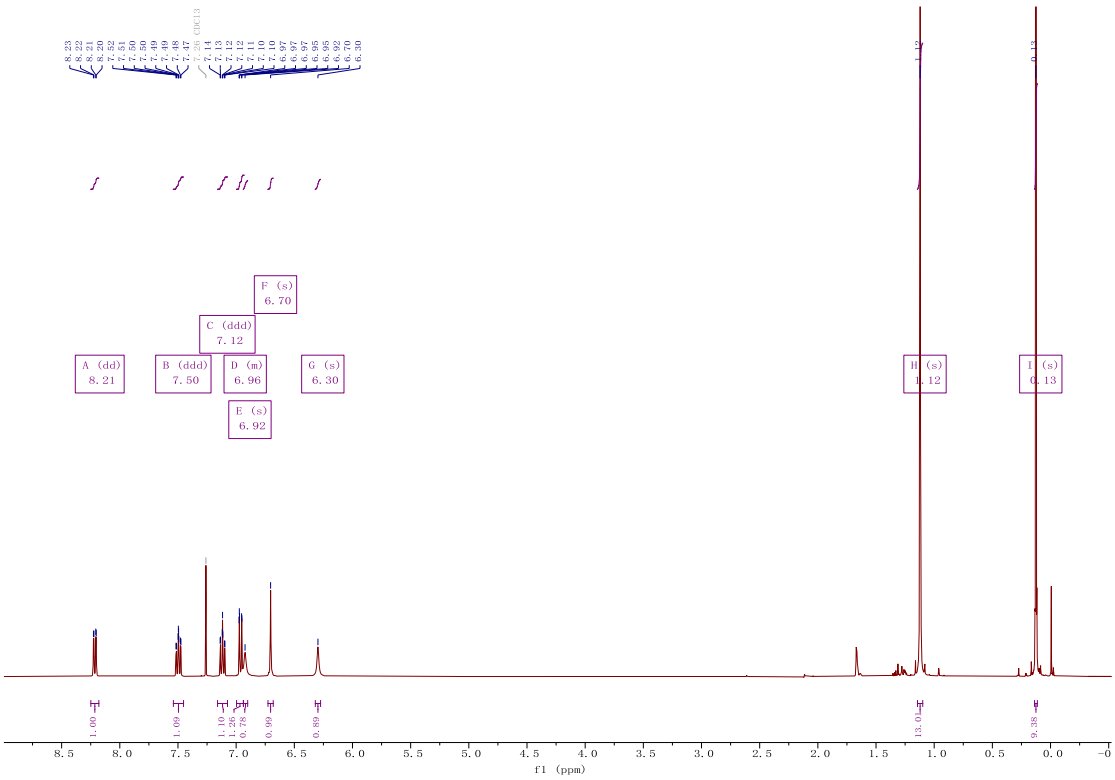

A (s) 8.74
B (s) 8.42
C (dd) 8.09
D (ddd) 7.54
E (dd) 7.25
F (s) 7.18
G (ddd) 7.11
H (d) 4.28
I (d) 4.12
K (s) 2.97
J (s) 1.33
f1 (ppm)

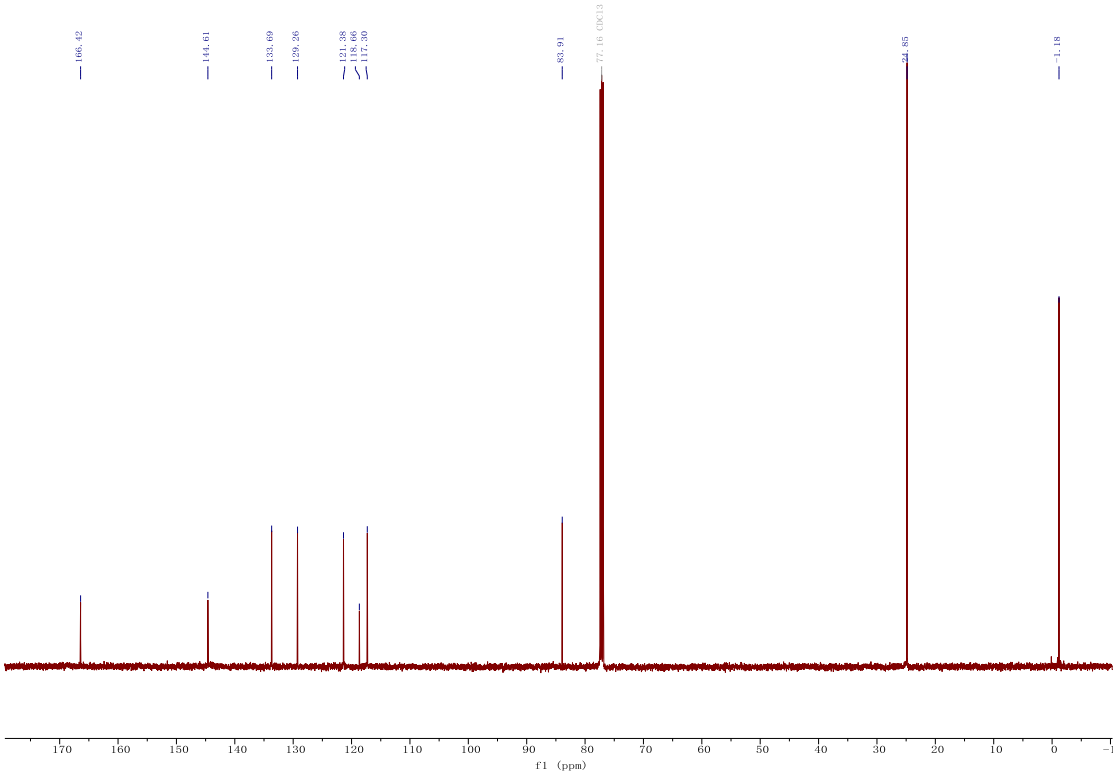

169.29
166.40
146.14
134.13
129.25
121.82
120.34
118.78
85.11
63.78
48.47
30.00
25.05
f1 (ppm)

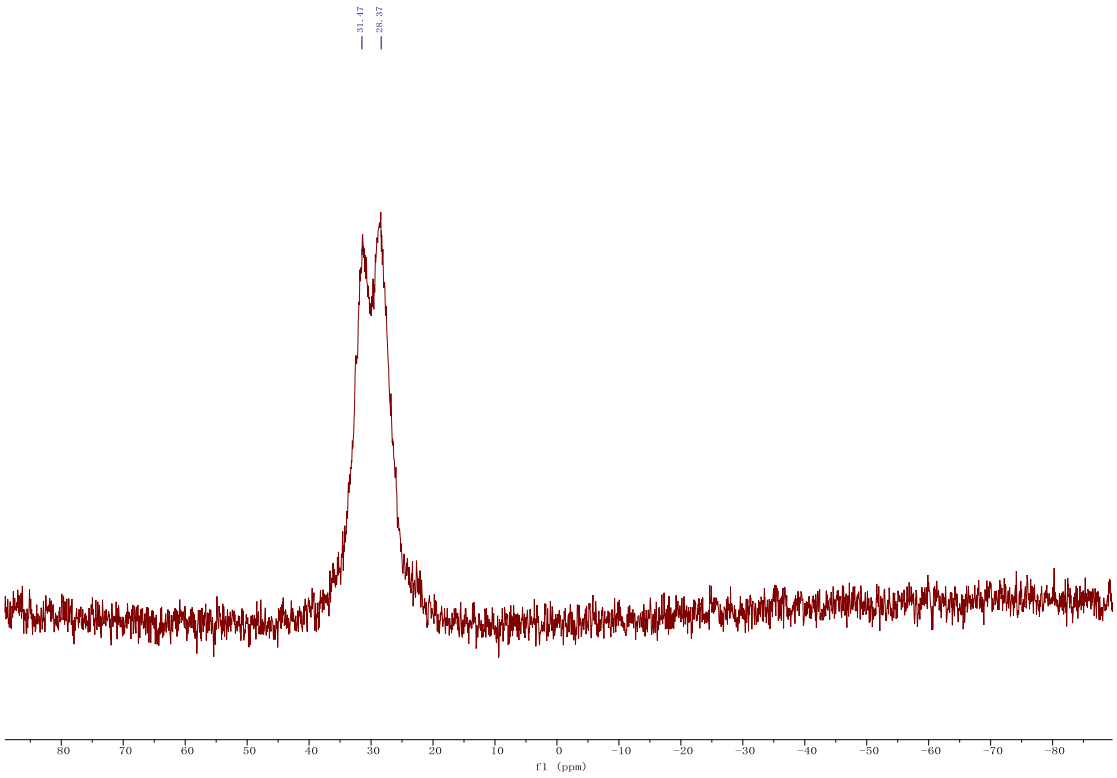

31.11
23.49
21.21
f1 (ppm)

3's

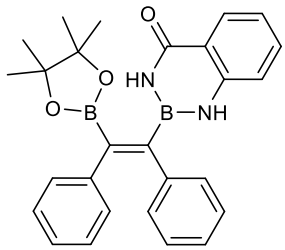

O
HN
O
O
B
B
NH
Si

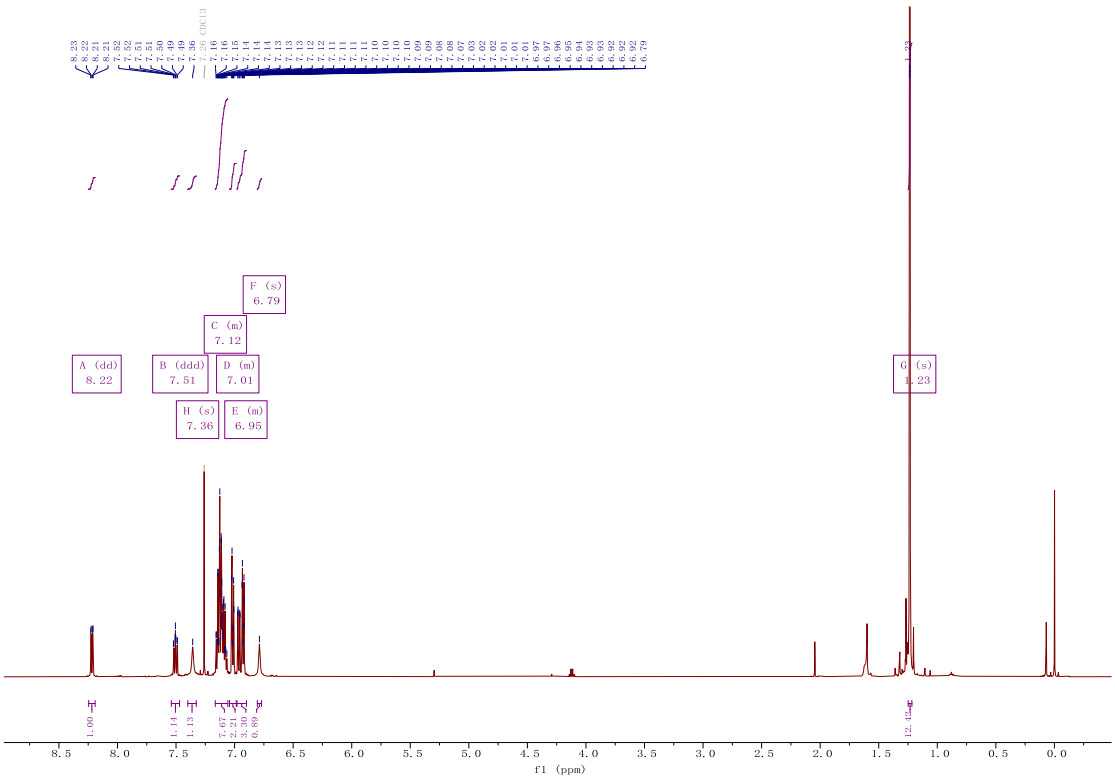

F (s)
6.70
C (ddd)
7.12
A (dd)
8.21
B (ddd)
7.50
D (m)
6.96
G (s)
6.30
E (s)
6.92
H (s)
1.12
I (s)
0.13
f1 (ppm)

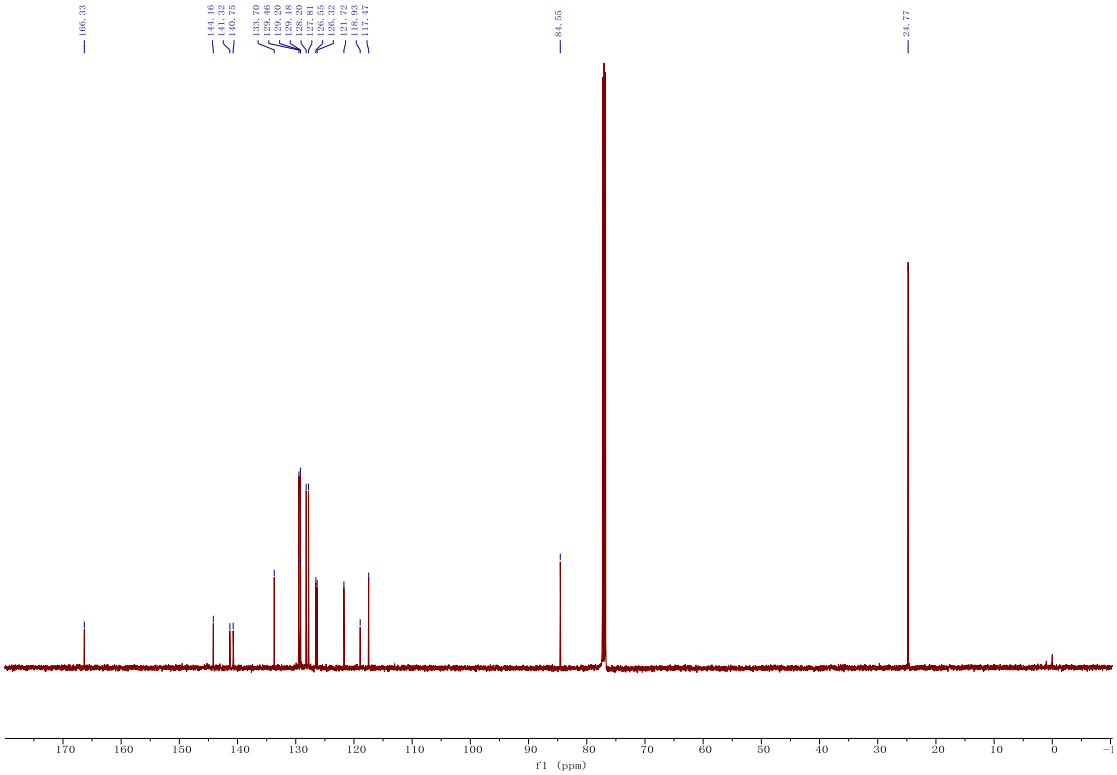

166.42
144.61
133.69
129.26
121.38
118.66
117.00
83.91
77.16 CDCl3
24.85
-1.18
f1 (ppm)

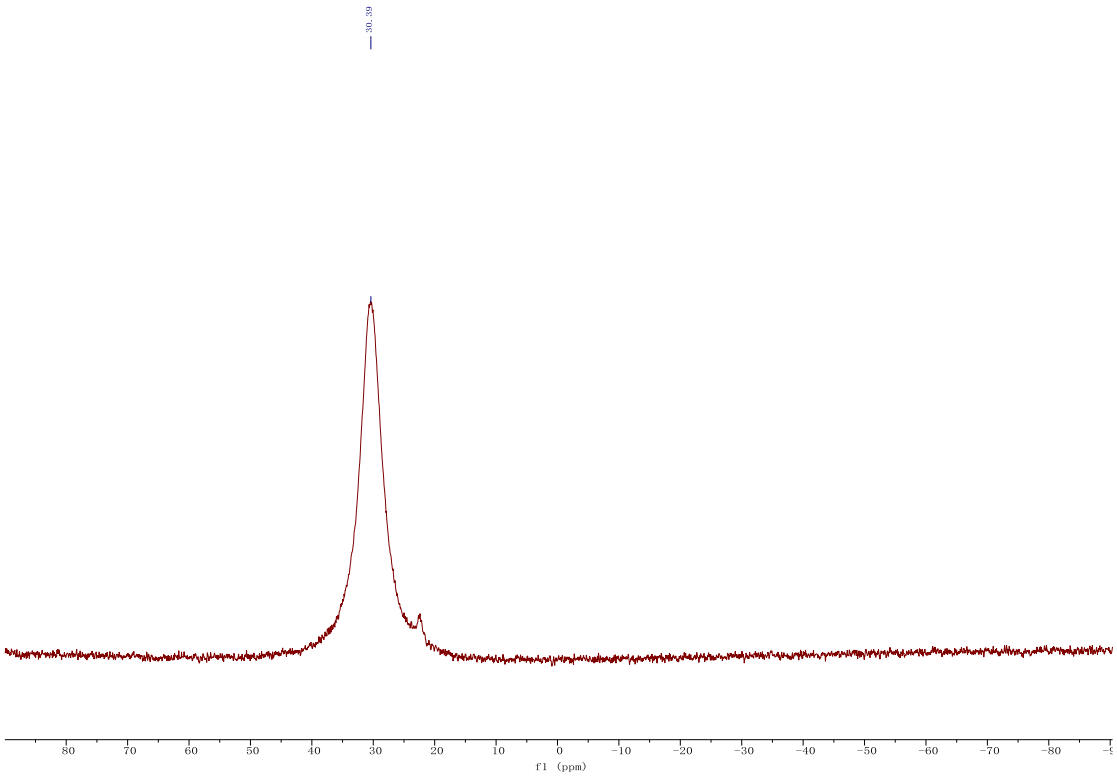

31.47
28.37
f1 (ppm)

3t

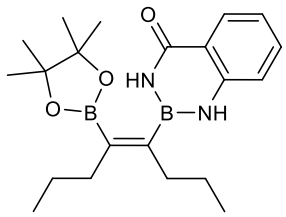

O
HN
O
O
B
B
NH

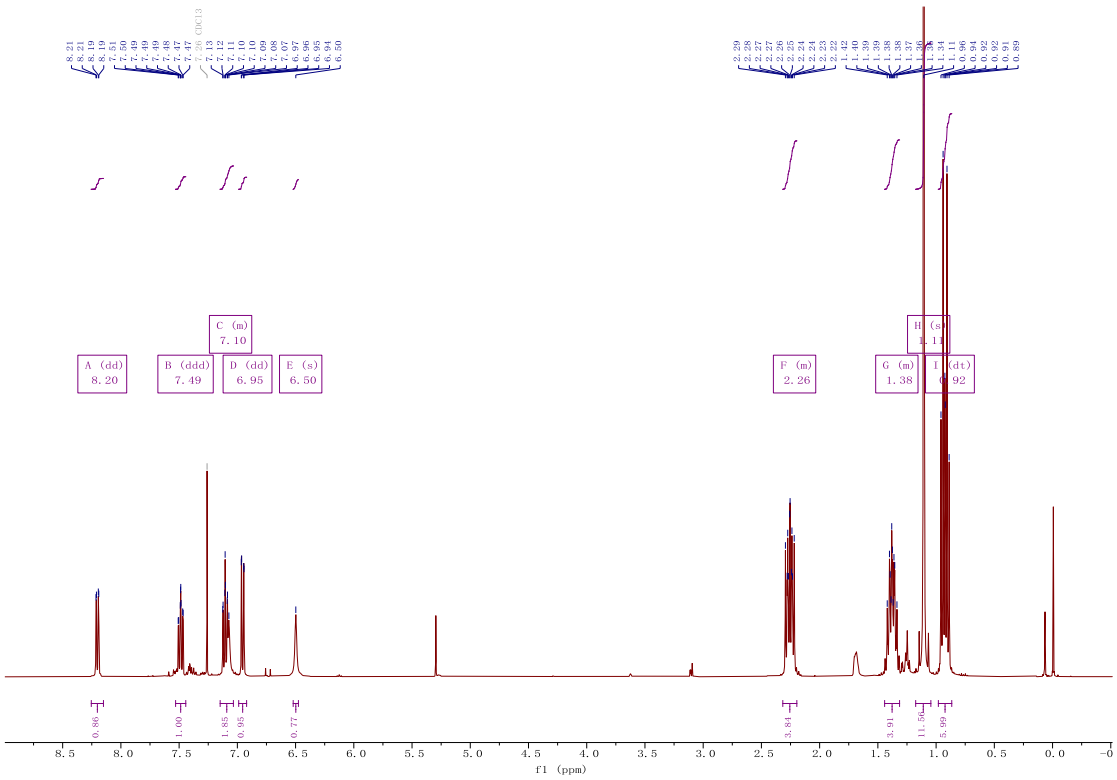

F (s)
6.79
C (m)
7.12
A (dd)
8.22
B (ddd)
7.51
D (m)
7.01
G (s)
1.23
H (s)
7.36
E (m)
6.95
1.00
1.14
1.13
7.67
2.21
3.39
6.89
12.42
f1 (ppm)

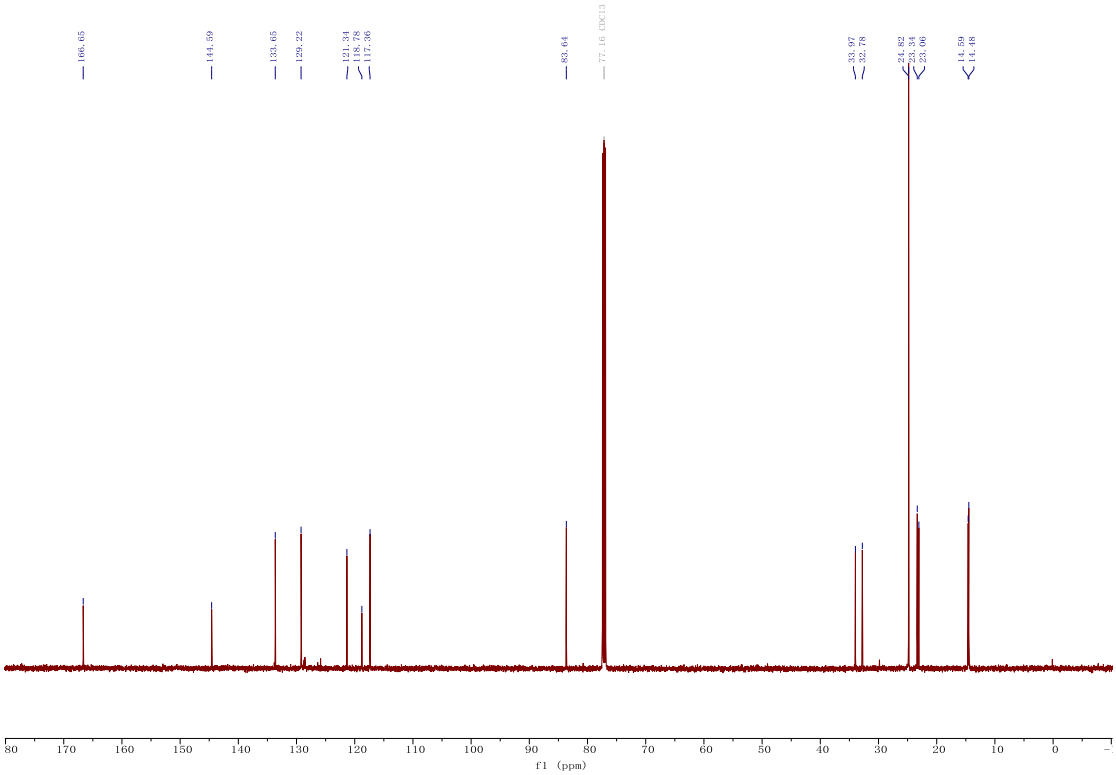

166.33
144.16
141.32
140.75
133.70
130.46
129.20
129.18
128.20
127.81
126.55
126.32
121.72
118.93
117.47
84.55
24.77
f1 (ppm)

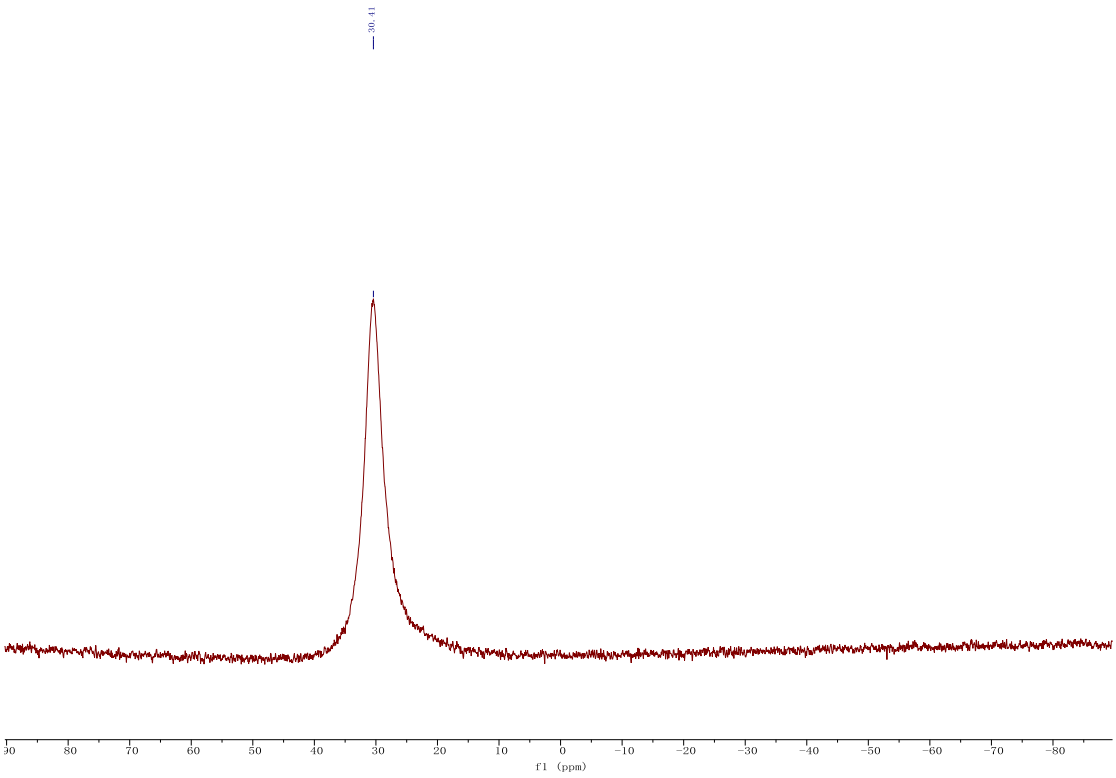

30.39
f1 (ppm)

3u

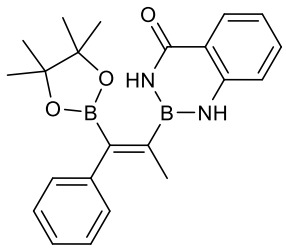

O
HN
O
O
B
B
NH

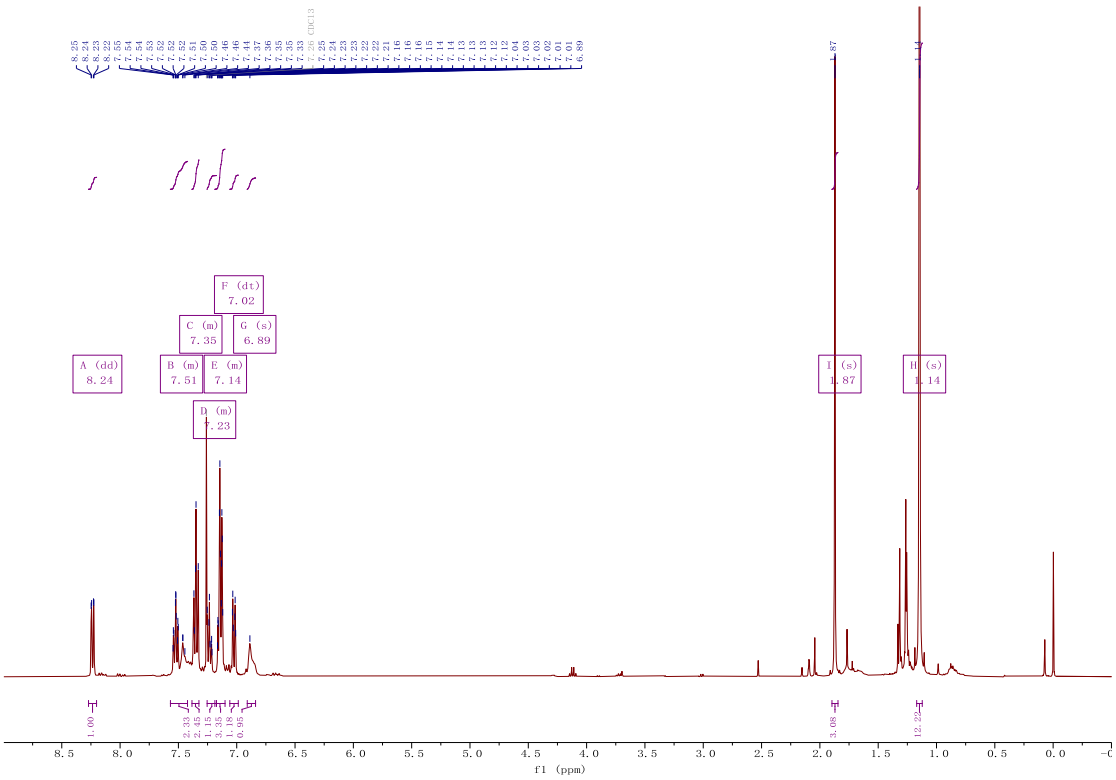

A (dd)
8.20
B (ddd)
7.49
C (m)
7.10
D (dd)
6.95
E (s)
6.50
F (m)
2.26
G (m)
1.38
f1 (ppm)

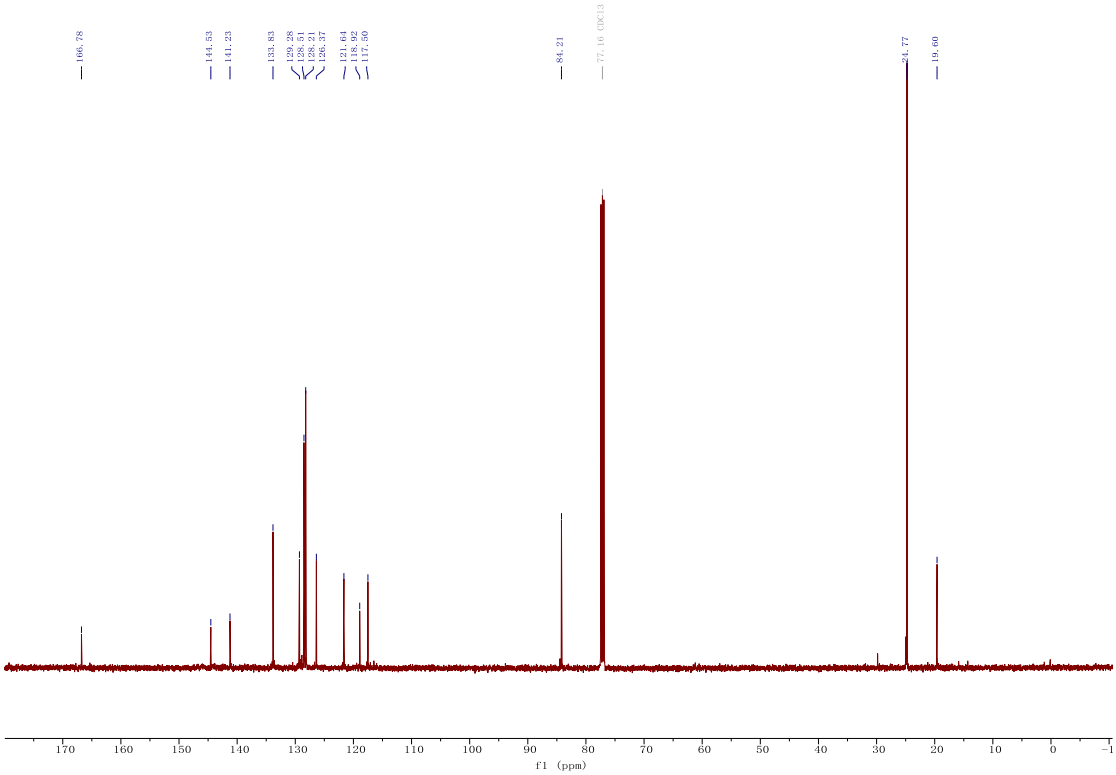

166.65
144.59
133.65
129.22
121.34
118.78
117.36
83.64
77.16 CDCl3
33.97
32.78
24.82
23.84
23.06
14.59
14.48
f1 (ppm)

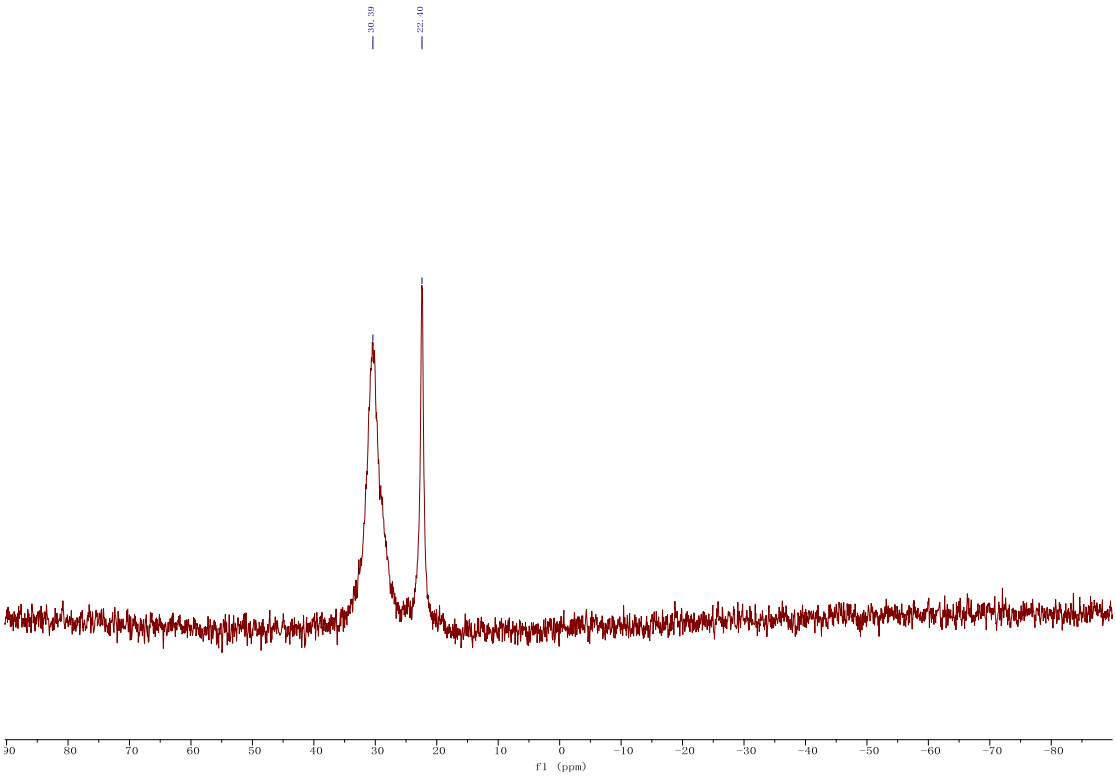

30.41
f1 (ppm)

3v

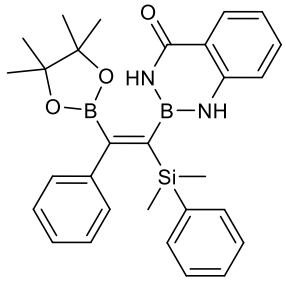

O
HN
O
O
B
B
NH

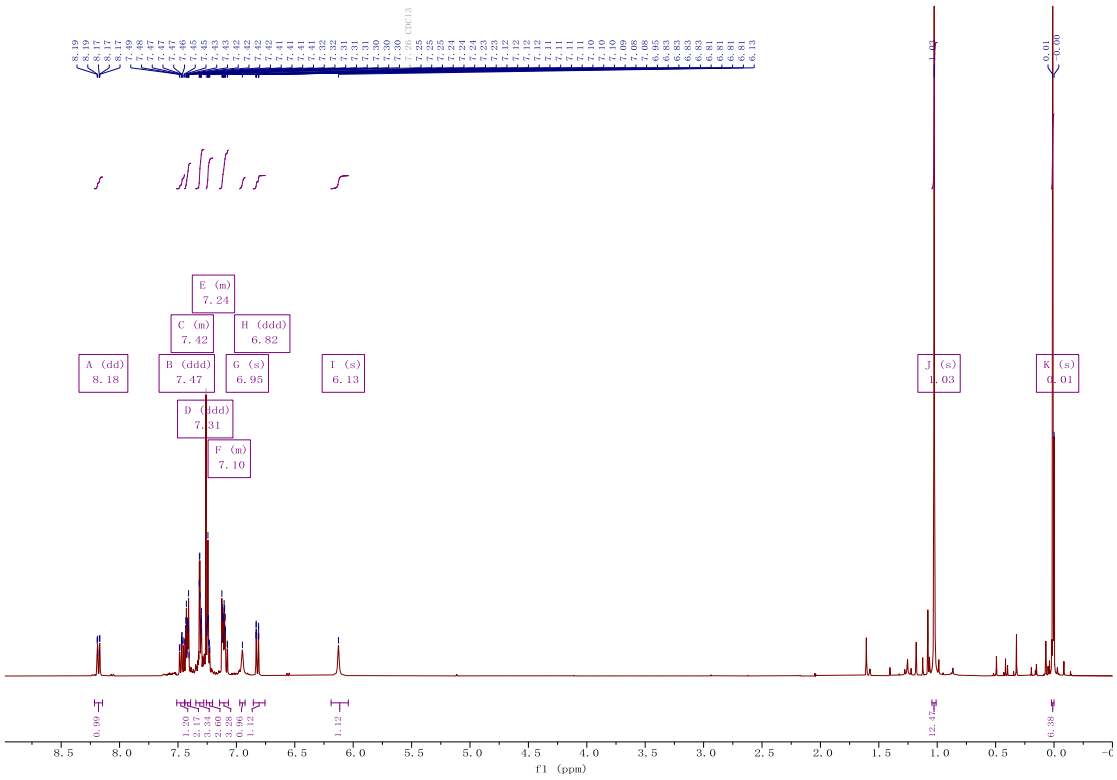

F (dt)
7.02
C (m)
7.35
G (s)
6.89
A (dd)
8.24
B (m)
7.51
E (m)
7.14
D (m)
7.23
I (s)
1.87
H (s)
1.14
f1 (ppm)

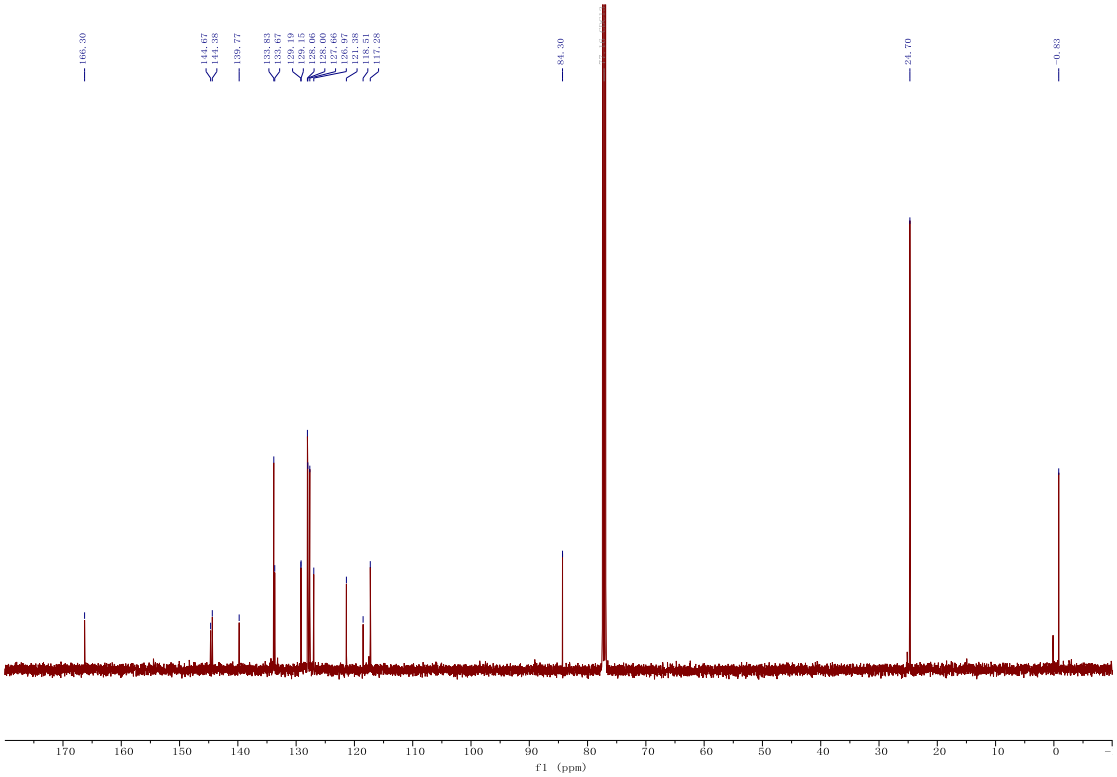

166.78
144.53
141.23
133.83
129.28
128.51
128.21
126.37
121.64
118.92
117.60
84.21
77.16 CDCl3
24.77
19.60
f1 (ppm)

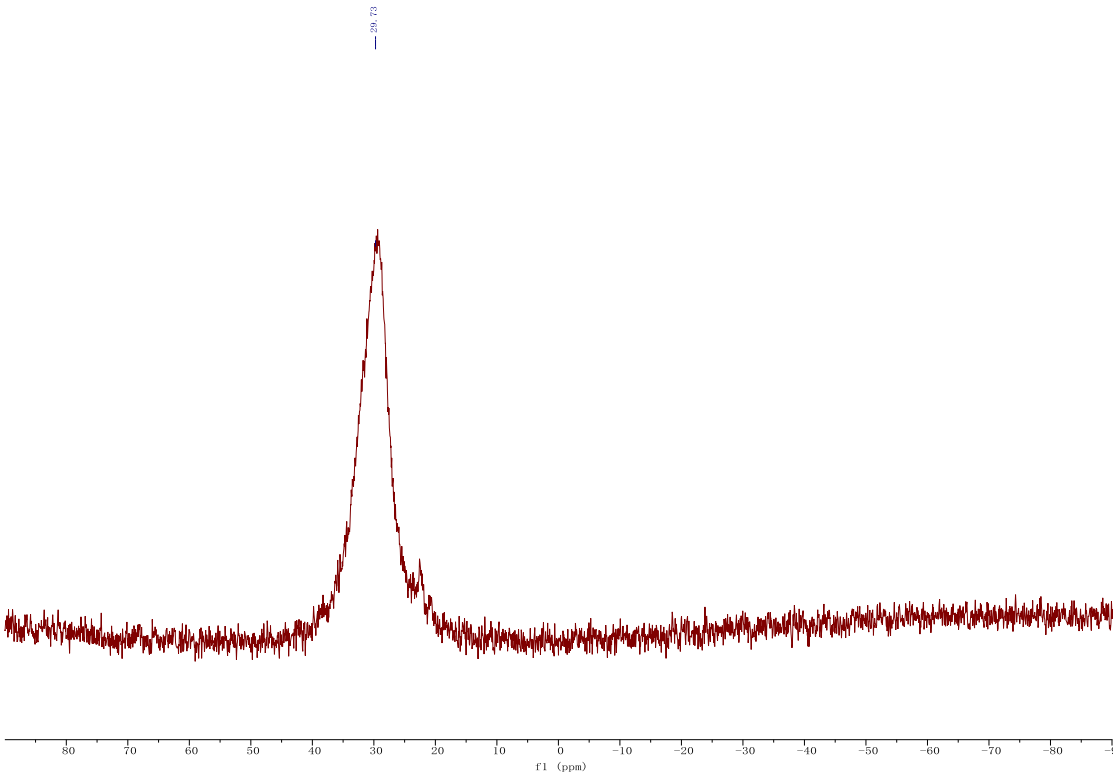

30.39
22.40
f1 (ppm)

3w

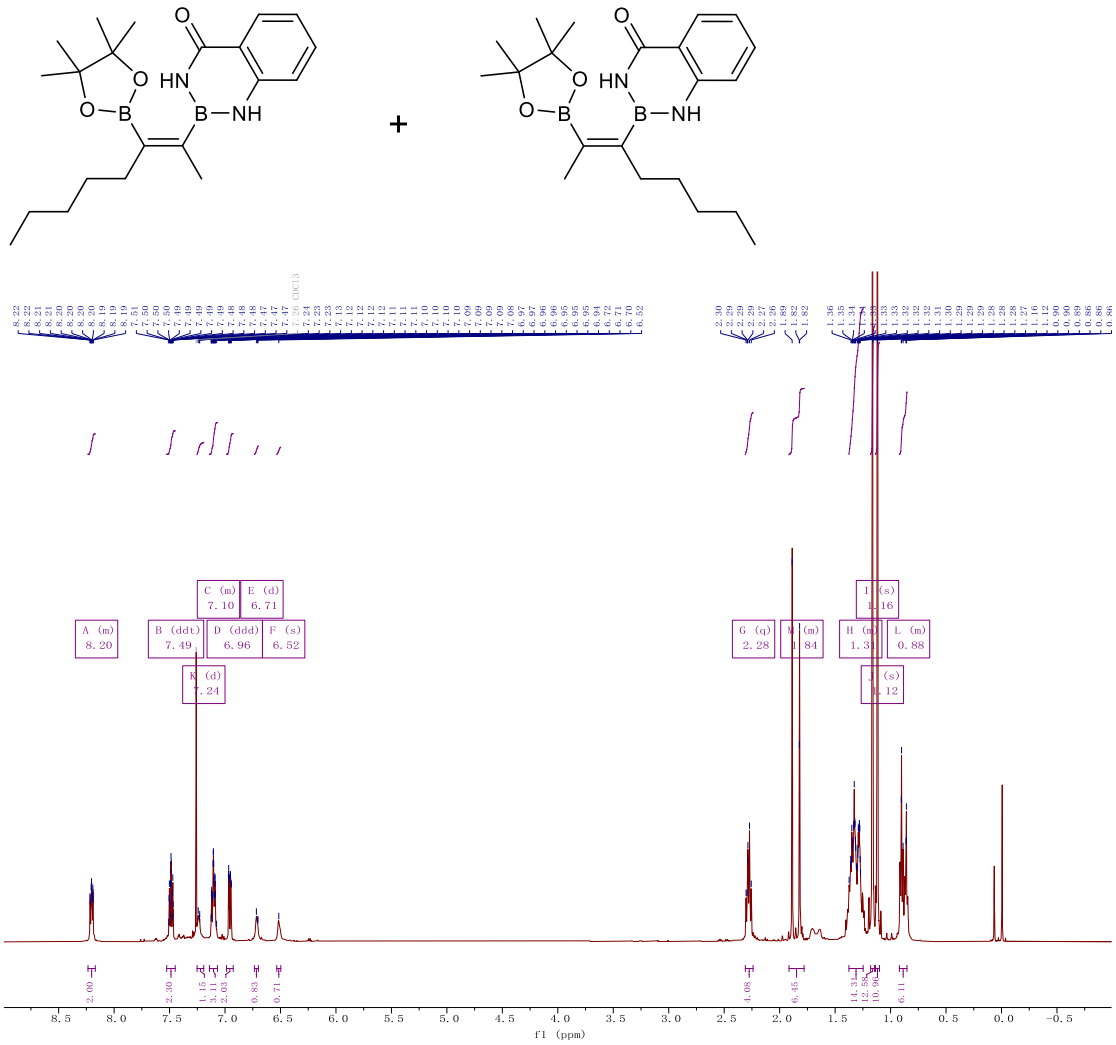

O
HN
O
O
B
B
NH
Si

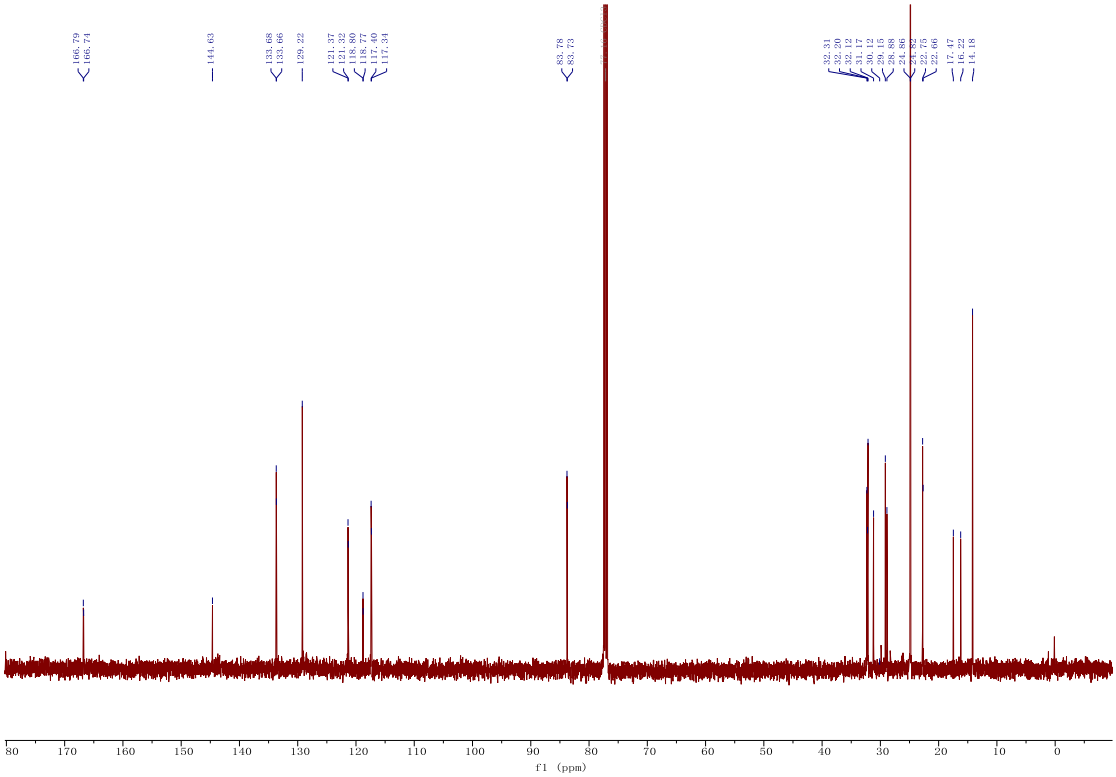

E (m) 7.24
C (m) 7.42
H (ddd) 6.82
A (dd) 8.18
B (ddd) 7.47
G (s) 6.95
I (s) 6.13
J (s) 1.03
K (s) 0.01
D (ddd) 7.31
F (m) 7.10
f1 (ppm)

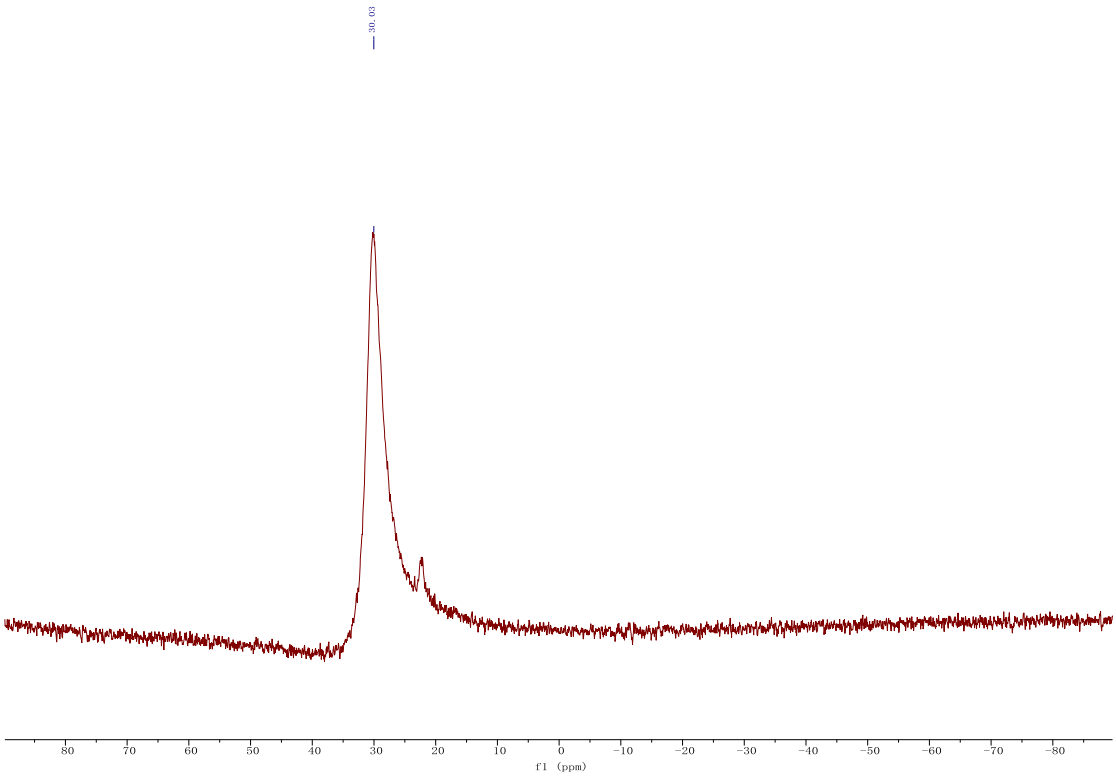

166.30
144.67
144.38
139.77
133.83
133.67
129.19
129.15
128.06
128.00
127.66
126.97
121.38
118.51
117.28
84.30
77.16
24.70
-0.83
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


29.73
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

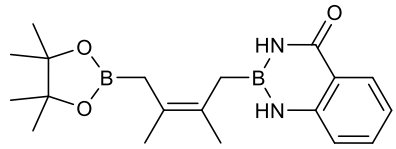
3x + 3'x

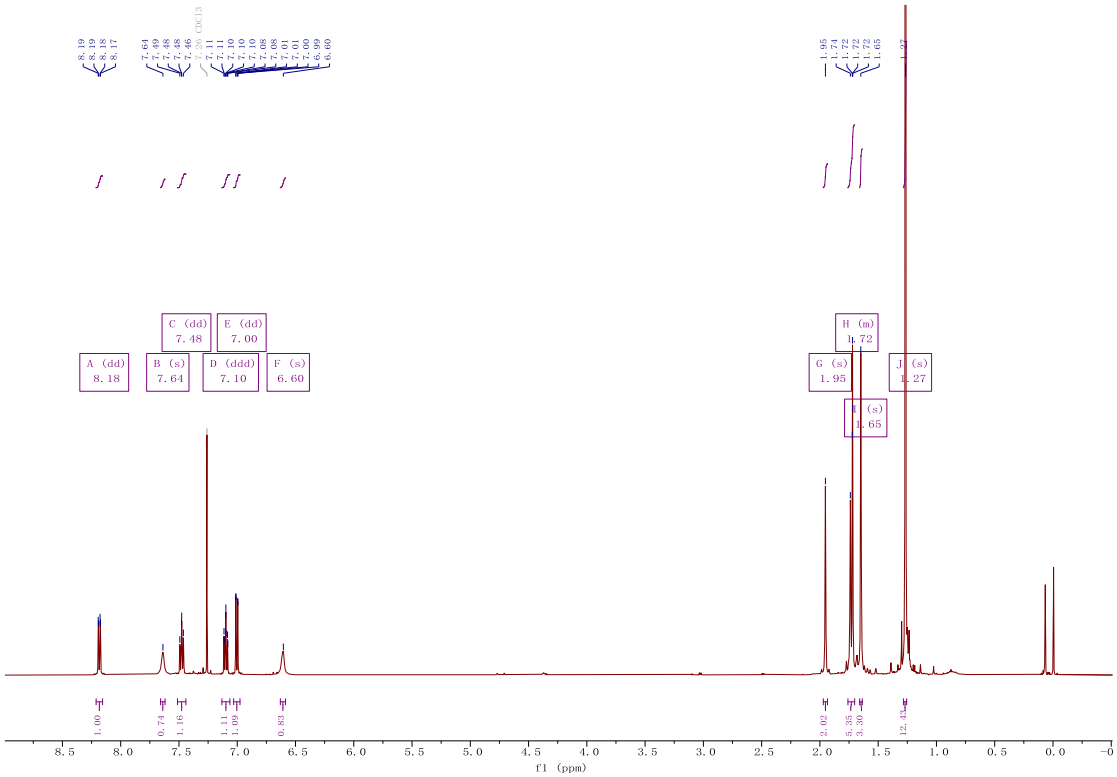


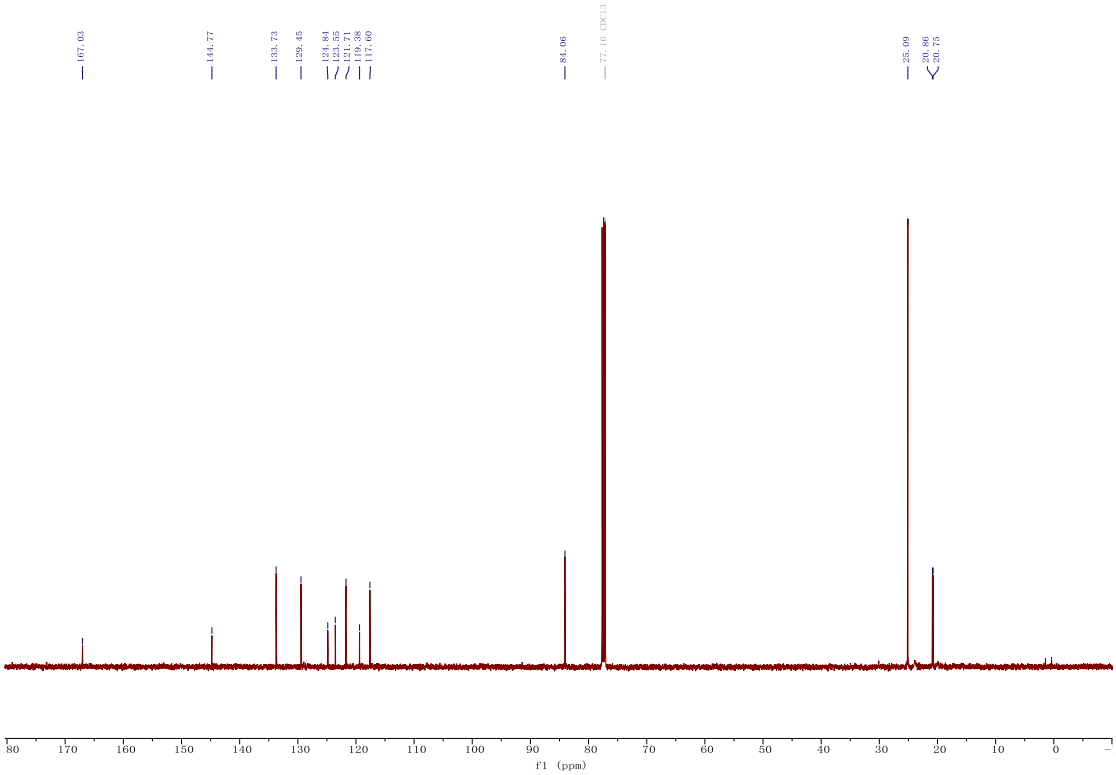

166.79
166.74
144.63
133.68
133.66
129.22
121.37
121.32
118.60
118.57
117.40
117.34
83.78
83.73
32.31
32.20
32.12
31.17
30.12
29.15
28.88
24.86
22.66
17.47
16.22
14.18
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

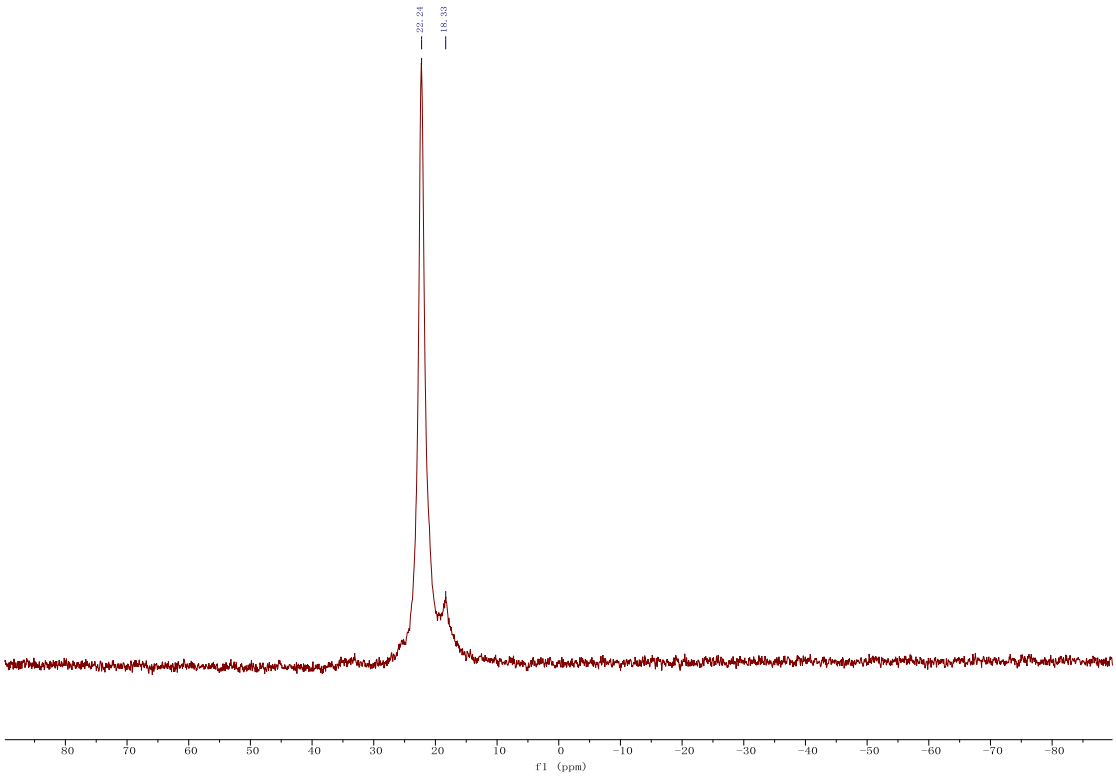

30.03
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80
f1 (ppm)

5

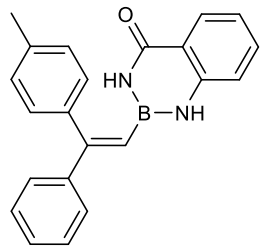

O
HN
B
O
B
O
HN

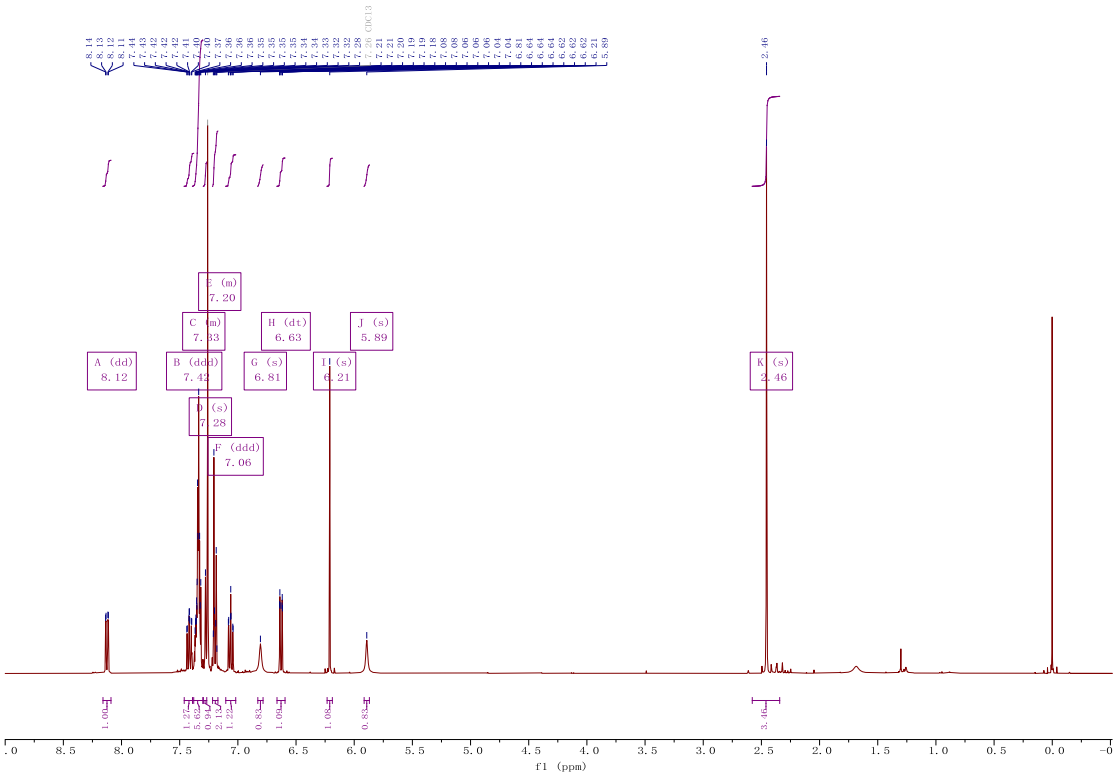

A (dd) 8.18
B (s) 7.64
C (dd) 7.48
D (ddd) 7.10
E (dd) 7.00
F (s) 6.60
G (s) 1.95
H (m) 1.72
I (s) 1.65
J (s) 1.27
f1 (ppm)

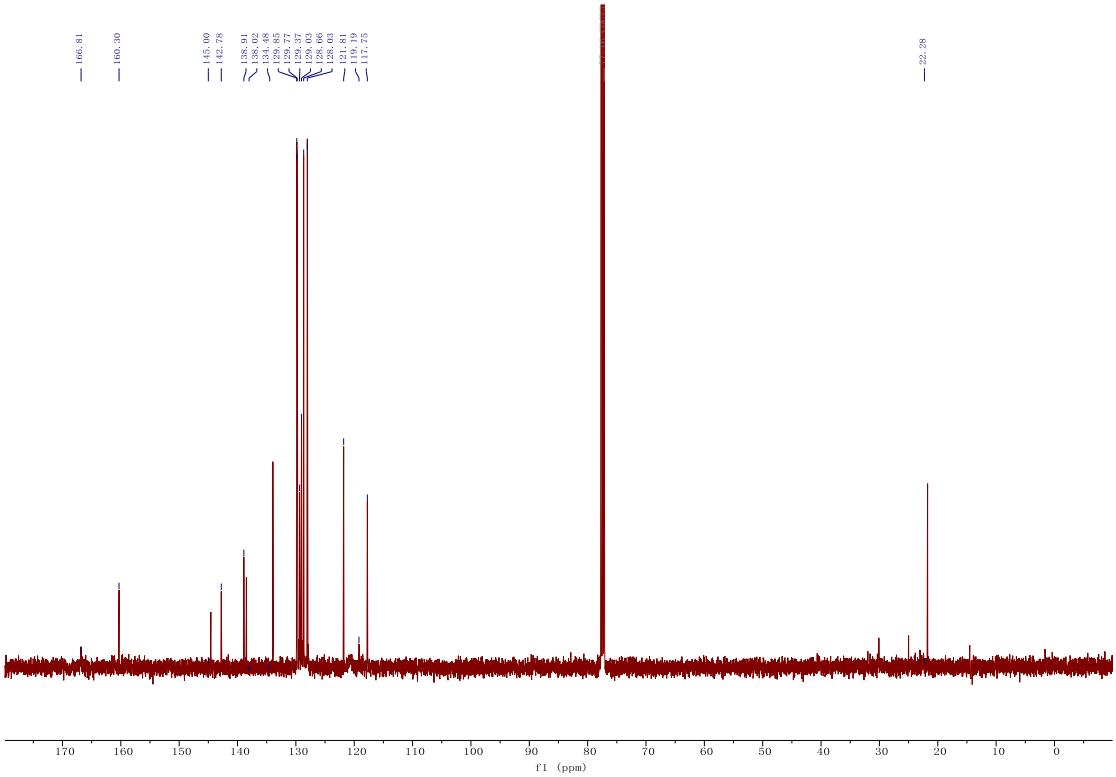

167.03
144.77
133.73
129.45
124.84
123.55
121.71
119.38
117.60
84.06
77.16 CDCl3
25.09
20.86
20.75
f1 (ppm)

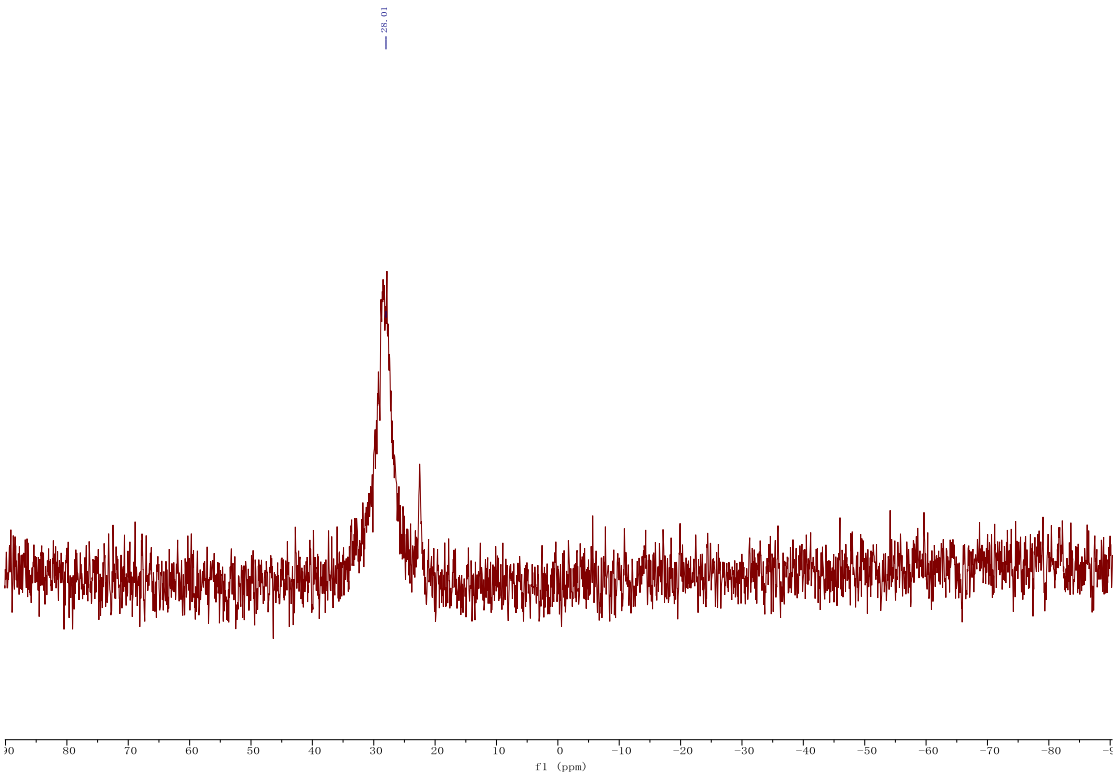

22.24
18.33
f1 (ppm)

6

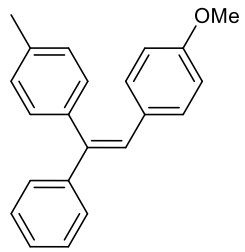

O
HN
B—NH

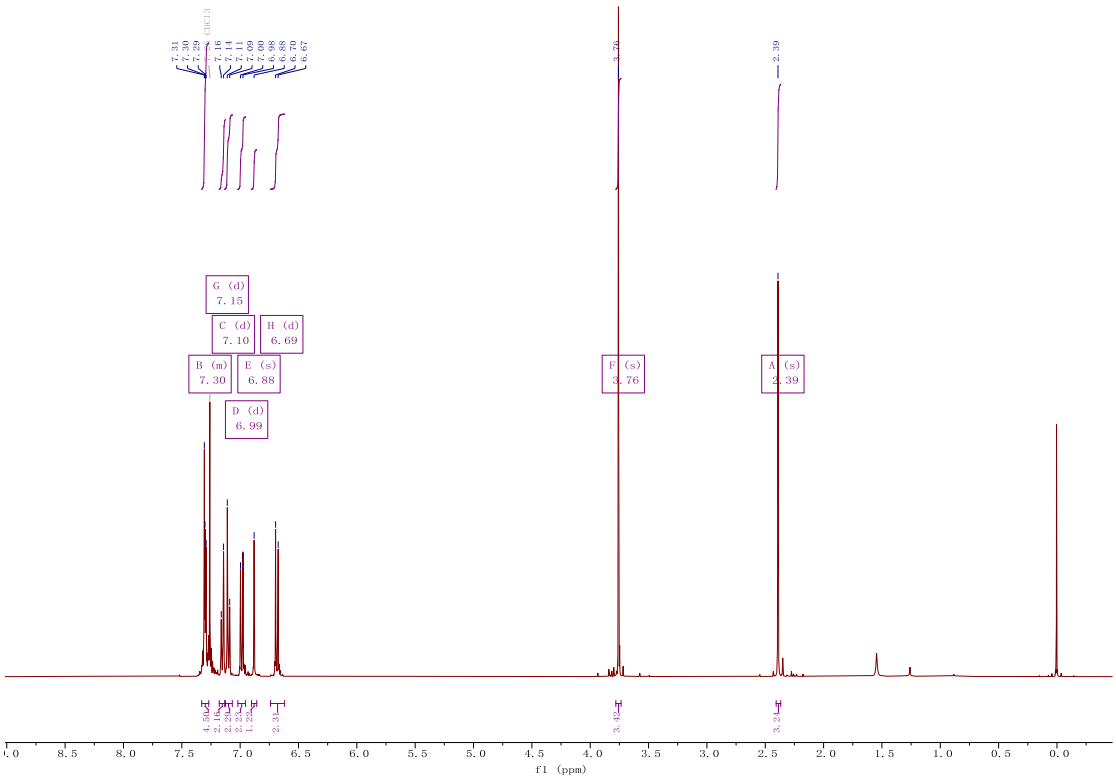

CDCl3
2.46
A (dd) 8.12
B (ddd) 7.42
C (m) 7.33
D (s) 7.28
E (m) 7.20
F (ddd) 7.06
G (s) 6.81
H (dt) 6.63
I (s) 6.21
J (s) 5.89
K (s) 2.46
f1 (ppm)

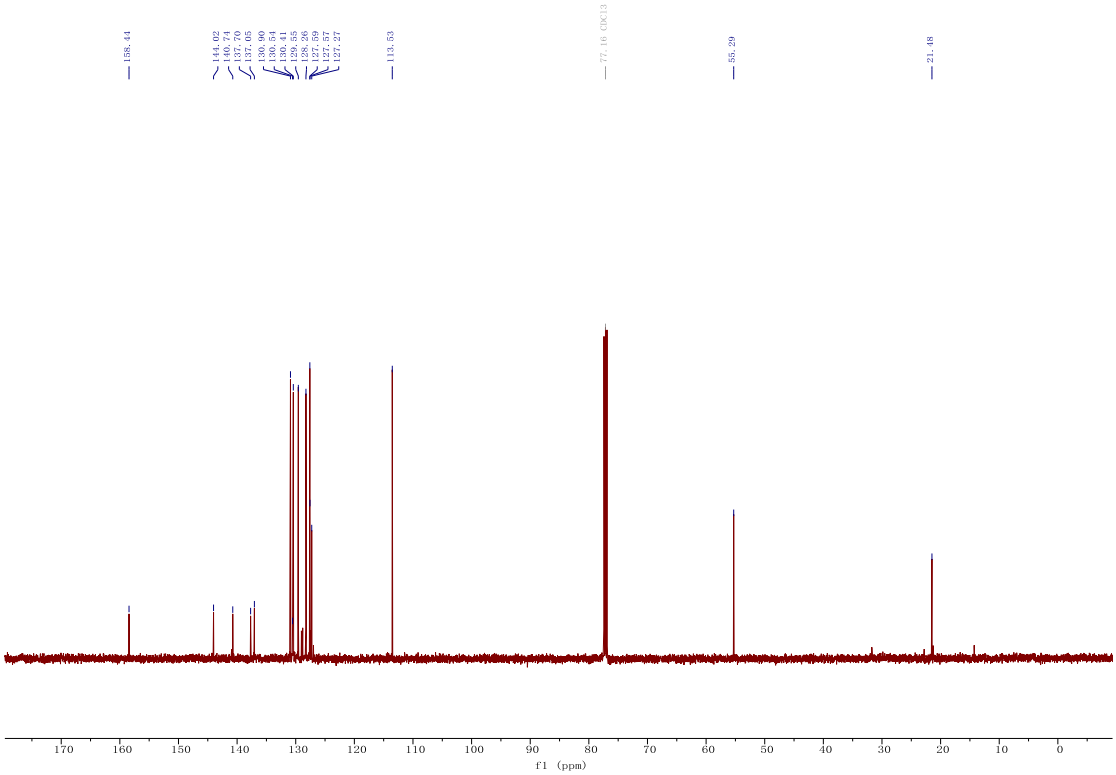

166.81
160.30
145.00
142.78
138.91
138.02
134.86
129.85
129.77
129.37
129.01
128.66
128.03
121.81
119.19
117.75
77.16
77.00
76.84
22.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


28.01
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
f1 (ppm)

7


OMe


7.31
7.30
7.29
7.16
7.14
7.11
7.09
7.00
6.98
6.88
6.70
6.67
3.76
2.39
G (d) 7.15
C (d) 7.10
H (d) 6.69
B (m) 7.30
E (s) 6.88
D (d) 6.99
F (s) 3.76
A (s) 2.39
f1 (ppm)


158.44
144.02
140.74
137.70
137.05
130.90
130.54
130.41
130.15
128.26
127.69
127.57
127.27
113.53
77.16 CDCl3
55.29
21.48
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)