Supporting Information

Scalable Pinacol Coupling Reaction Utilizing Inorganic Electride $[Ca_2N]^+ \cdot e^-$ as an Electron Donor

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Contents

General Methods

Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254. ^{1}H NMR spectra were recorded on a Varian at 500 MHz in $CDCl_3$ (δ 7.26 ppm) or DMSO-d_6 (δ 2.50 ppm), ^{13}C NMR spectral measurements were performed at 125 MHz using $CDCl_3$ (δ 77.16 ppm) or DMSO-d_6 (δ 39.52 ppm). The terms m, s, d, t, q, quint., and sept. represent multiplet, singlet, doublet, triplet, quadruplet, quintuplet, and septet, respectively, and the term br means a broad signal. Commercial grade reagents and solvents were used without further purification.

The measurement of X-ray diffraction patterns for $Ca(OMe)_2$ was made over a 2θ range from 5° to 40° along with a step size of 0.02° and scanning speed was set at 1° at 1°min^{-1} with filtered Cu K_α radiation λ=0.15418 nm (Rigaku Smart Lab, Japan).

Ion chromatography was performed on Metrohm 833 IC plus with conductivity detector (solvent: 1.7mM HNO_3 + 0.7mM PDCA in DI water, temperature: room temperature, fluent speed : 0.9mL/min). Analytic sample was prepared by the following procedure: Each sample was taken from the individual reaction mixture using micro-glass filters. To make more accurate analysis, it diluted with deionized water (200 times less than in the original sample).

Synthesis of dicalcium nitride $[Ca_2N]^+\cdot e^-$ electride

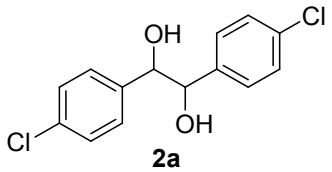
A stoichiometric polycrystalline dicalcium nitride ($[Ca_2N]^+\cdot e^-$) was synthesized by the solid-state reaction of calcium nitride(Ca_3N_2) powders and calcium metals. Mixture of Ca_3N_2 powders and calcium chips at a molar ratio of 1:1 were pressed into a pellet form under pressure (20~30 MPa). The pellet was fully covered with molybdenum foil and annealed at 800 ^{o}C for 48 hrs under vacuum (~10^{-3} Pa). Then, the sample was quenched into water. To improve homogeneity of dicalcium nitride $[Ca_2N]^+\cdot e^-$, the synthesized sample was ground into a powder in an agate mortar in nitrogen-filled glovebox and re-annealed under the same conditions.

Procedure for pinacol coupling reaction of aromatic aldehyde

Dicalcium nitride $[Ca_2N]^+\cdot e^-$ (94 mg, 1 mmol) was added to a suspension of aldehyde (0.5 mmol) in dry THF and MeOH in 1:1 mixture at room temperature. The reaction was stirred until TLC analysis indicated complete consumption of the starting material, and then the reaction mixture was quenched with water and 5% HCl and, extracted with EtOAc or Et_2O (5 mL×3). The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash chromatography on silica gel (EtOAc/ Hexanes) to give the corresponding 1,2-*vic*-diol.

Characterization Data for Products

1,2-Bis(4-chlorophenyl)ethane-1,2-diol (Table 2, Entry 1)

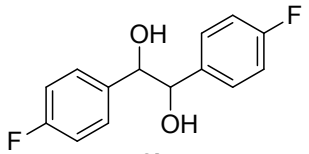


2a

The physical and spectral data were identical to those previously reported for this compound.[1]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 6.95-7.31 (m, 8H), 4.60[4.82] (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.93, 137.78, 133.88, 128.40, 128.36, 128.33, 78.55, 77.16 ppm.

1,2-Bis(4-fluorophenyl)ethane-1,2-diol(Table 2, Entry 2)

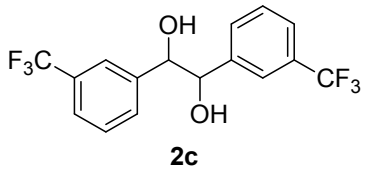


2b

The physical and spectral data were identical to those previously reported for this compound.[3]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 6.85-7.20 (m, 8H), 4.61[4.82] (s, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) *dl* [*meso*] δ: 162.55[162.63] (d, J = 175 Hz), 135.48[135.31] (d, J = 2.5 Hz), 128.76[128.82] (d, J = 6.25 Hz), 115.21[115.20] (d, J = 15 Hz), 78.86[77.39] ppm.

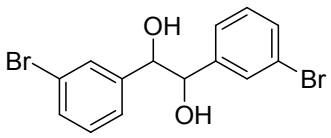
1,2-Bis(3-(trifluorometyl)phenyl)ethane-1,2-diol (Table 2, Entry 3)



2c

^{1}H NMR (500 MHz, DMSO-d_6) *dl* [*meso*] δ: 7.25-7.62 (m, 8H), 5.70[5.63] (s, 2H), 4.85[4.71] (s, 2H) ^{13}C NMR (125 MHz, DMSO-d_6) *dl* [*meso*] δ: 143.32[144.22], 131.11[131.47], 128.13[128.36], 128.05 [128.24] (q, J = 22.5 Hz), 124.38[124.43] (q, J = 193 Hz), 123.53[123.76] (q, J = 2.5 Hz), 123.35(q, J = 2.5Hz), 75.83[76.10] ppm.

1,2-Bis(3-bromophenyl)ethane-1,2diol (Table 2, Entry 4)

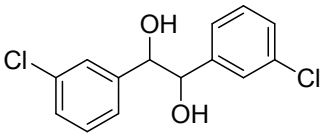


2d

The physical and spectral data were identical to those previously reported for this compound.[3]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 6.89-7.47 (m, 8H), 4.60[4.77] (s, 2H), ^{13}C NMR (125 MHz, $CDCl_3$) *dl* [*meso*] δ: 141.97[141.88], 131.36[131.37], 129.99[130.23], 129.84[129.83], 125.81[125.87], 122.56[122.53], 78.37[77.28] ppm.

1,2-Bis(3-chlorophenyl)ethane-1,2-diol (Table 2, Entry 5)

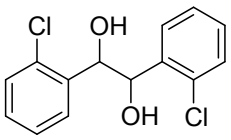


2e

The physical and spectral data were identical to those previously reported for this compound.[4]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 7.08-7.70 (m, 8H), 4.62[4.79] (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) *dl* [*meso*] δ: 141.59[141.49], 134.27[134.24], 129.45[129.42], 128.32, 126.96[127.19], 125.22[125.27], 77.20[78.32] ppm.

1,2-Bis(2-chlorophenyl)ethane-1,2-diol (Table 2, Entry 6)

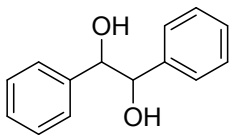


2f

The physical and spectral data were identical to those previously reported for this compound.[3]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 7.08-7.70 (m, 8H), 5.58[5.34] (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) *dl* [*meso*] δ: 137.36[136.51], 132.74[133.50], 129.58[129.00], 129.29[129.25], 128.94[128.88], 73.12[72.21] ppm.

1,2-Diphenylethane-1,2diol (Table 2, Entry 7)

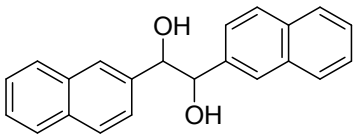


2g

The physical and spectral data were identical to those previously reported for this compound.[1]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 7.11-7.40 (m, 10H), 4.69[4.82] (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) *dl* [*meso*] δ: 139.96[139.88], 128.27[128.38], 128.07[128.25], 127.07[127.22], 79.24[78.23] ppm.

1,2-Di(naphthalene-2-yl)ethane-1,2-diol (Table 2, Entry 8)

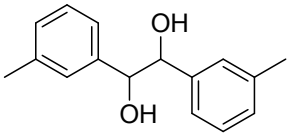


2h

The physical and spectral data were identical to those previously reported for this compound.[1]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 7.26-7.86 (m, 14H), 5.54[5.41] (s, 2H), 4.90[4.83] (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.31, 131.90, 131.70, 126.83, 126.51, 126.19, 124.98, 124.83, 124.61, 124.55, 77.49 ppm.

1,2-Di-*m*-tolyethane-1,2-diol (Table 2, Entry 9)

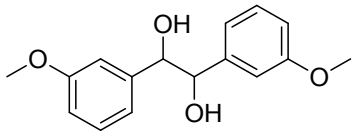


2i

The physical and spectral data were identical to those previously reported for this compound.[3]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 6.86-7.29 (m, 8H), 4.67[4.72] (s, 2H), 2.28[2.34] (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *dl* [*meso*] δ: 140.09[140.07], 137.90[138.17], 128.74[129.11], 128.13[128.37], 127.58[127.92], 124.11[124.40], 78.92[78.38] ppm.

1,2-Bis(3-methoxyphenyl)ethane-1,2-diol (Table 2, Entry 10)

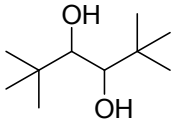


2j

The physical and spectral data were identical to those previously reported for this compound.[1]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 6.64-7.31 (m, 8H), 4.65[4.77] (s, 2H), 3.70[3.73] (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) *dl* [*meso*] δ: 159.52[159.66], 141.64[141.53], 129.28[129.38], 119.37[119.57], 113.80[114.10], 112.33[112.41], 78.98[78.10], 55.31[55.33] ppm.

2,2,5,5-Tetrametylhexane-3,4-diol (Table 2, Entry 11)

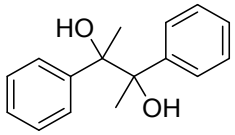


2k

The physical and spectral data were identical to those previously reported for this compound.[5]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 3.33[3.25] (s, 2H), 0.91[1.01] (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) *dl* [*meso*] δ: 75.12[80.57], 35.39[35.84], 25.99[26.73] ppm.

2,3-Diphenylbutane-2,3-diol (Table 2, Entry 12)



2l

The physical and spectral data were identical to those previously reported for this compound.[2]

^{1}H NMR (500 MHz, $CDCl_3$) *dl* [*meso*] δ: 7.14-7.30 (m, 10H), 2.57[2.27] (s, 2H), 1.50[1.58] (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) *dl* [*meso*] δ: 143.54[143.90], 127.50[127.43], 127.29[127.19], 127.05[127.04], 78.98[78.72], 25.09[25.25] ppm.

References

1 N. Takenaka, G. Xia and H. Yamamoto, *J. Am. Chem. Soc.*, 2004, **126**, 13198.

2 M. Uchiyama, Y. Matsumoto, S. Nakamura, T. Ohwada, N. Kobayashi, N. Yamashita, A. Matsumiya and T. Sakamoto, *J. Am. Chem. Soc.*, 2004, **126**, 8755.

3 H. Yang, H. Wang and C. Zhu, *J. Org. Chem*., 2007, **72**, 10029.

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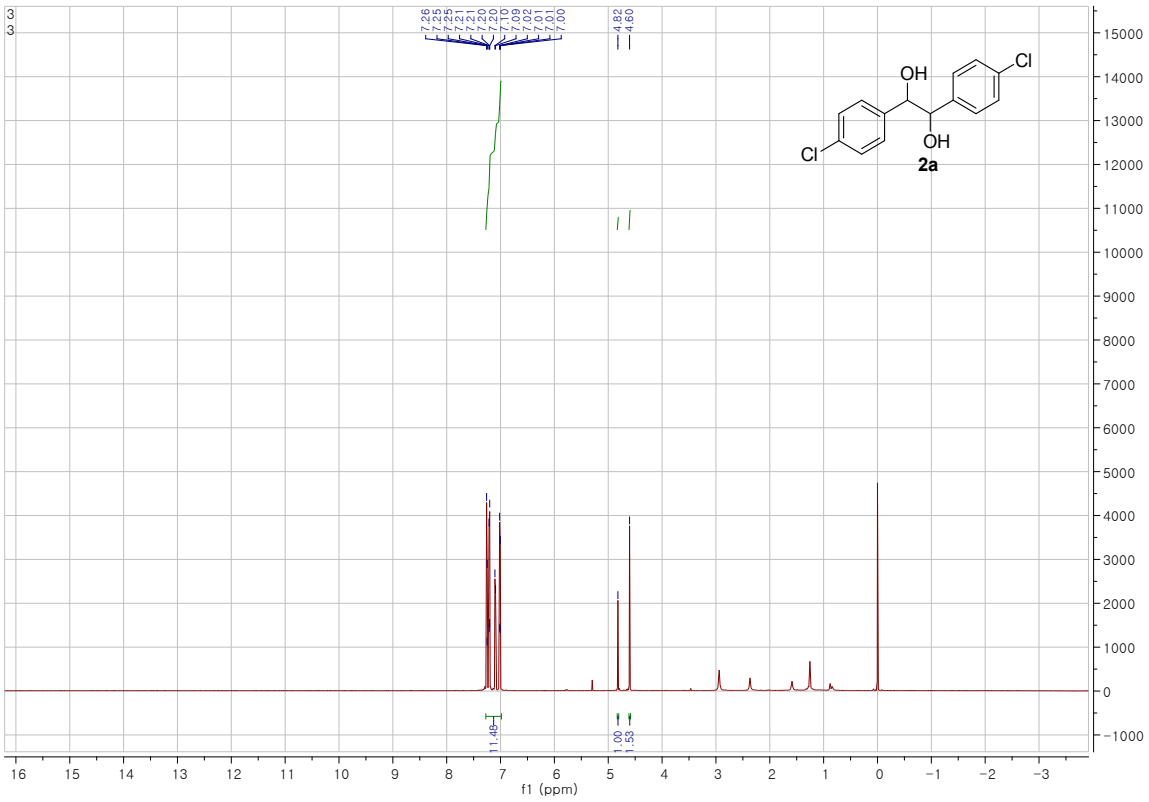
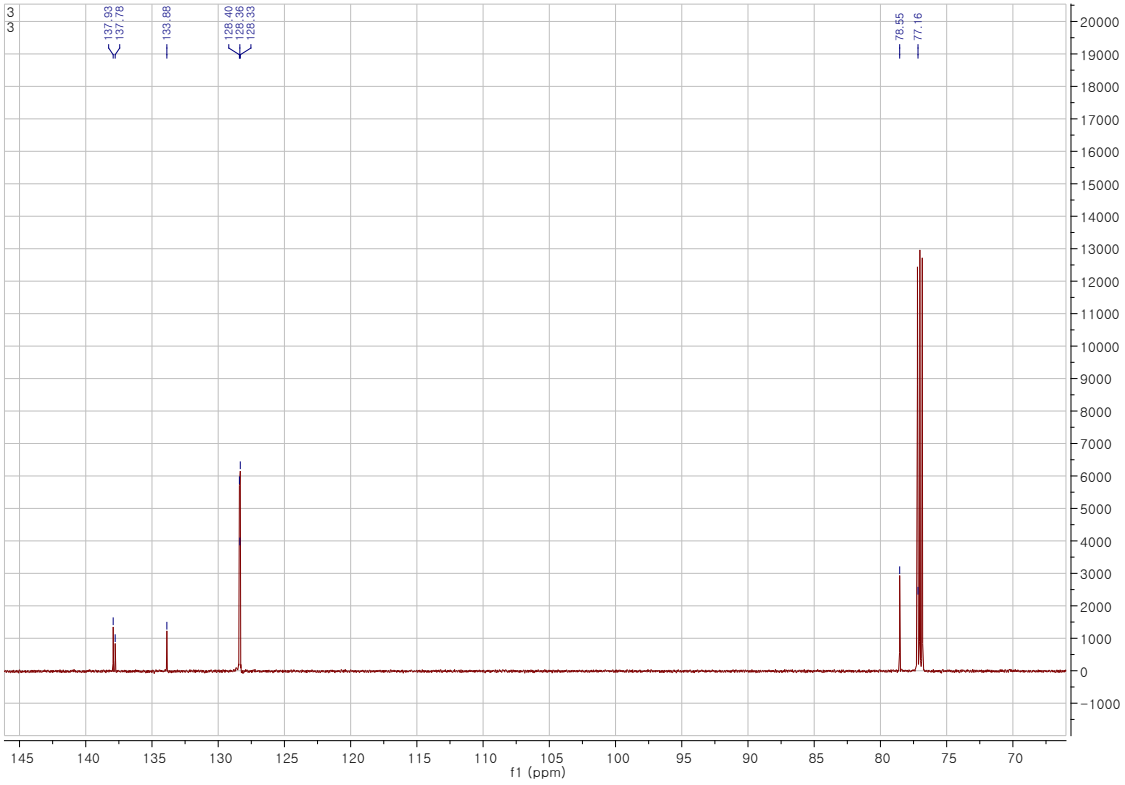
5 M. -I. Lannou, F. Hélion and J. –L. Namy, *Tetrahedron*, 2003, **59**, 10551.

1,2-Bis(4-chlorophenyl)ethane-1,2-diol (Table 2, Entry1)





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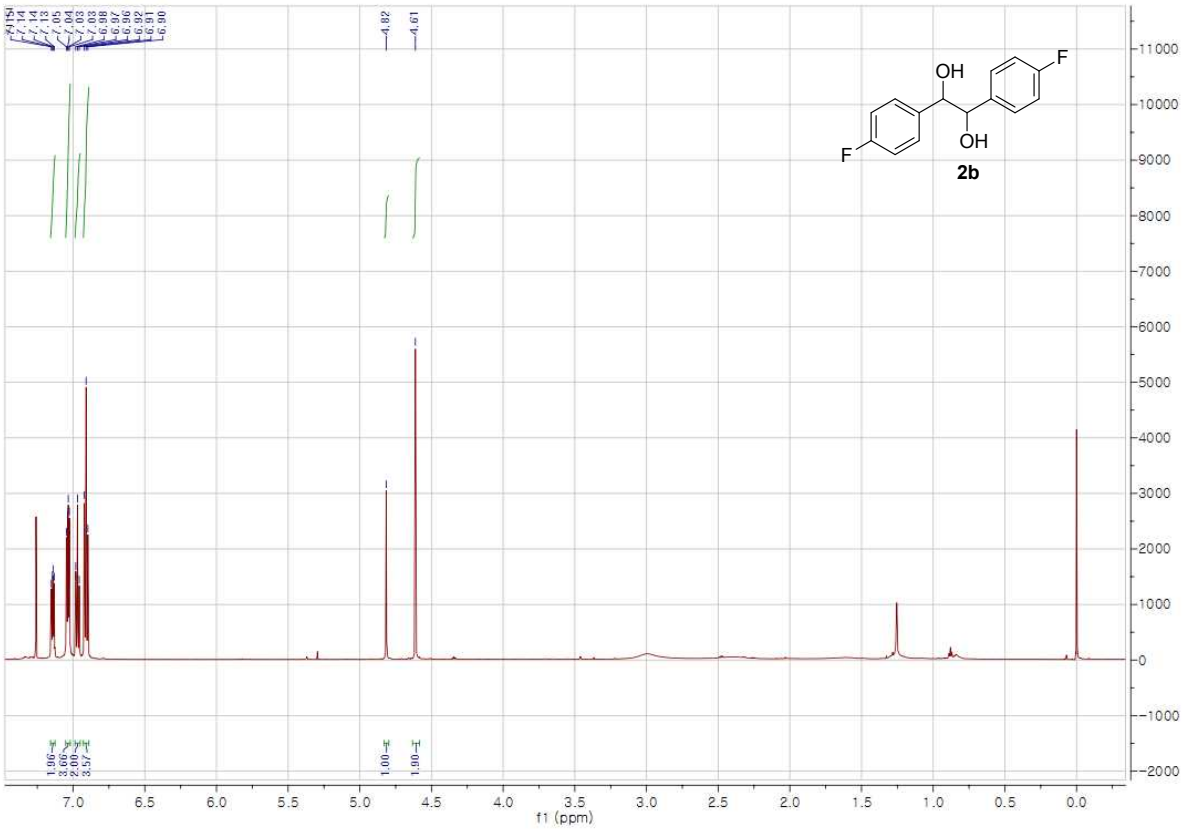
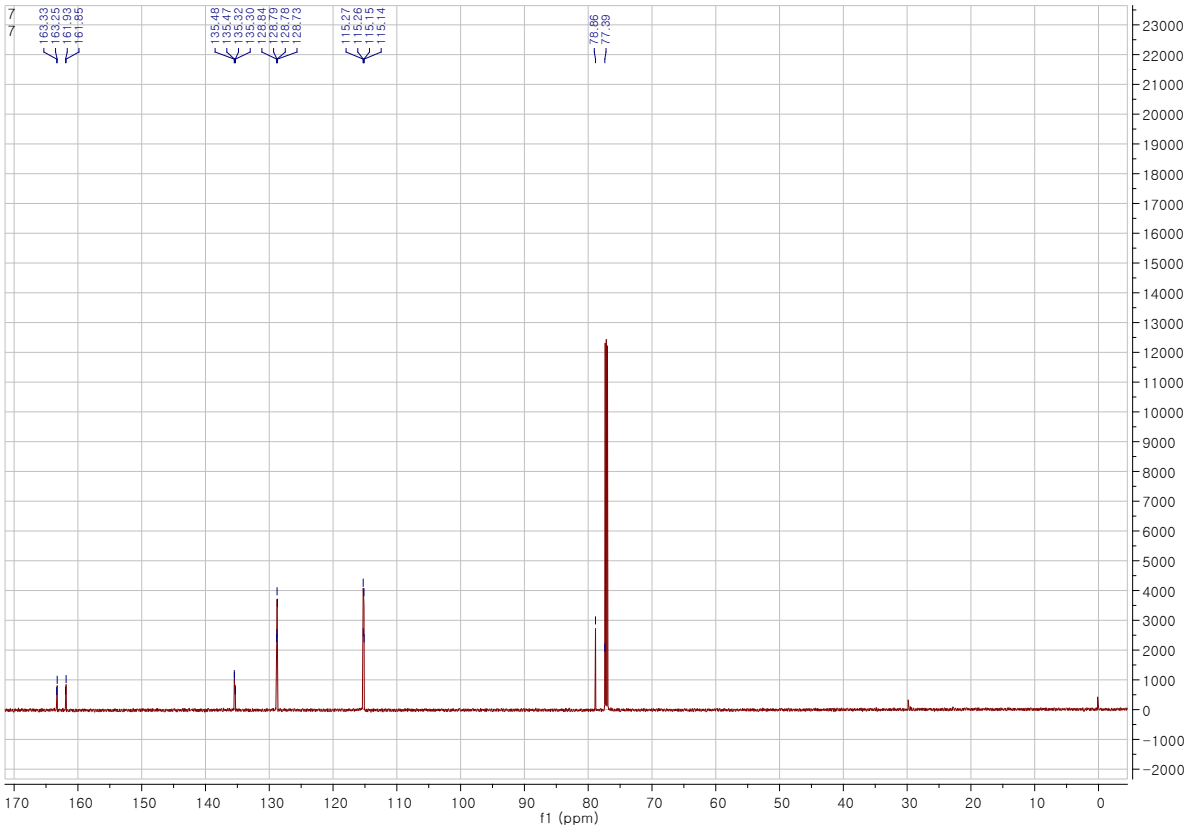
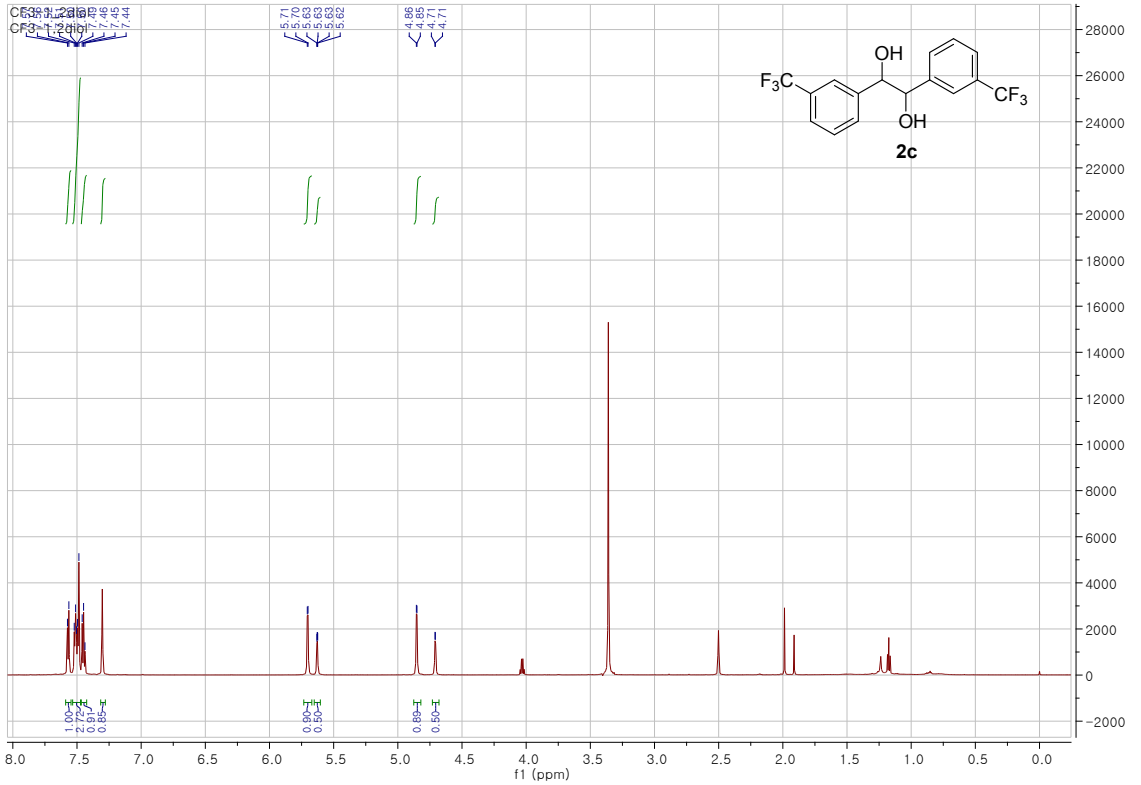
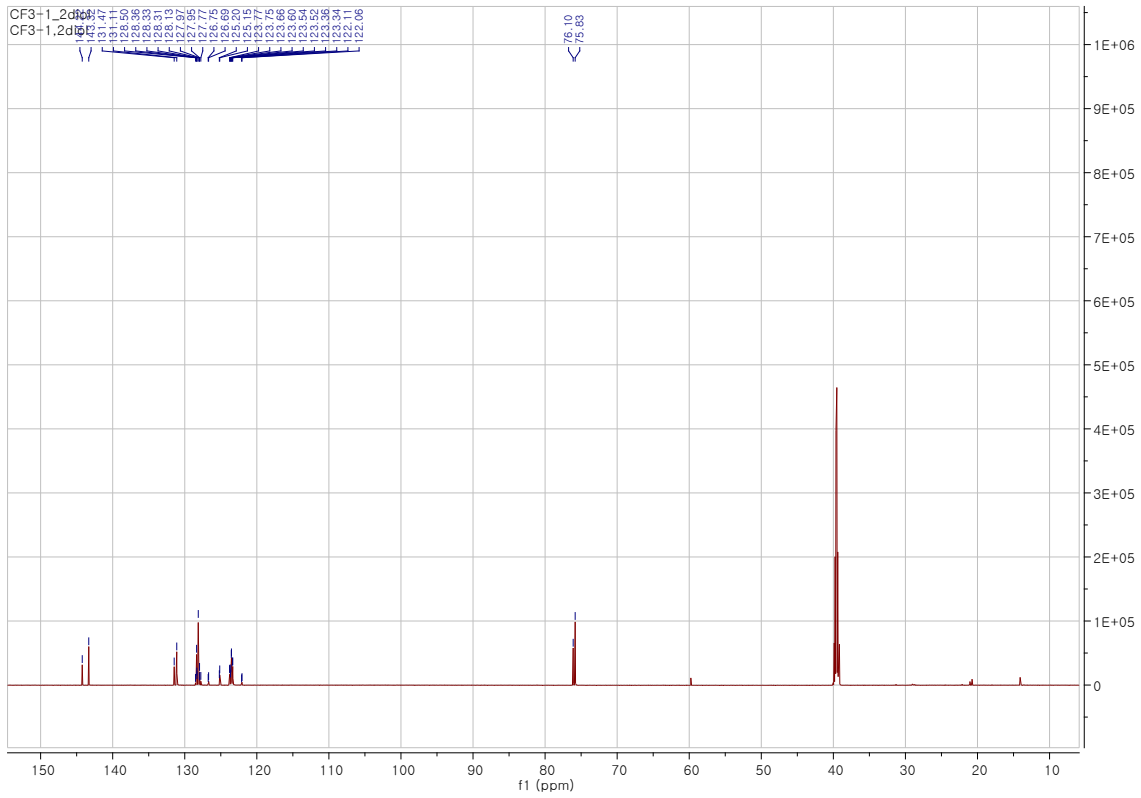


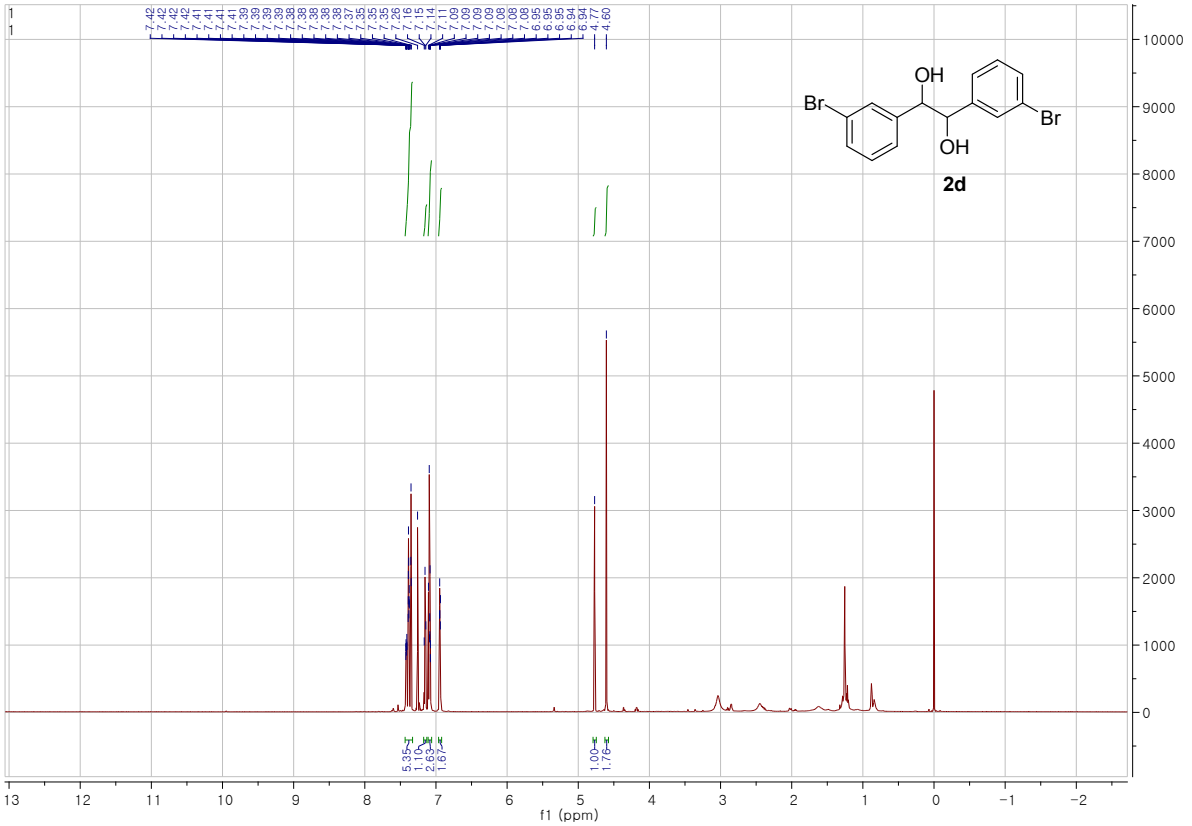


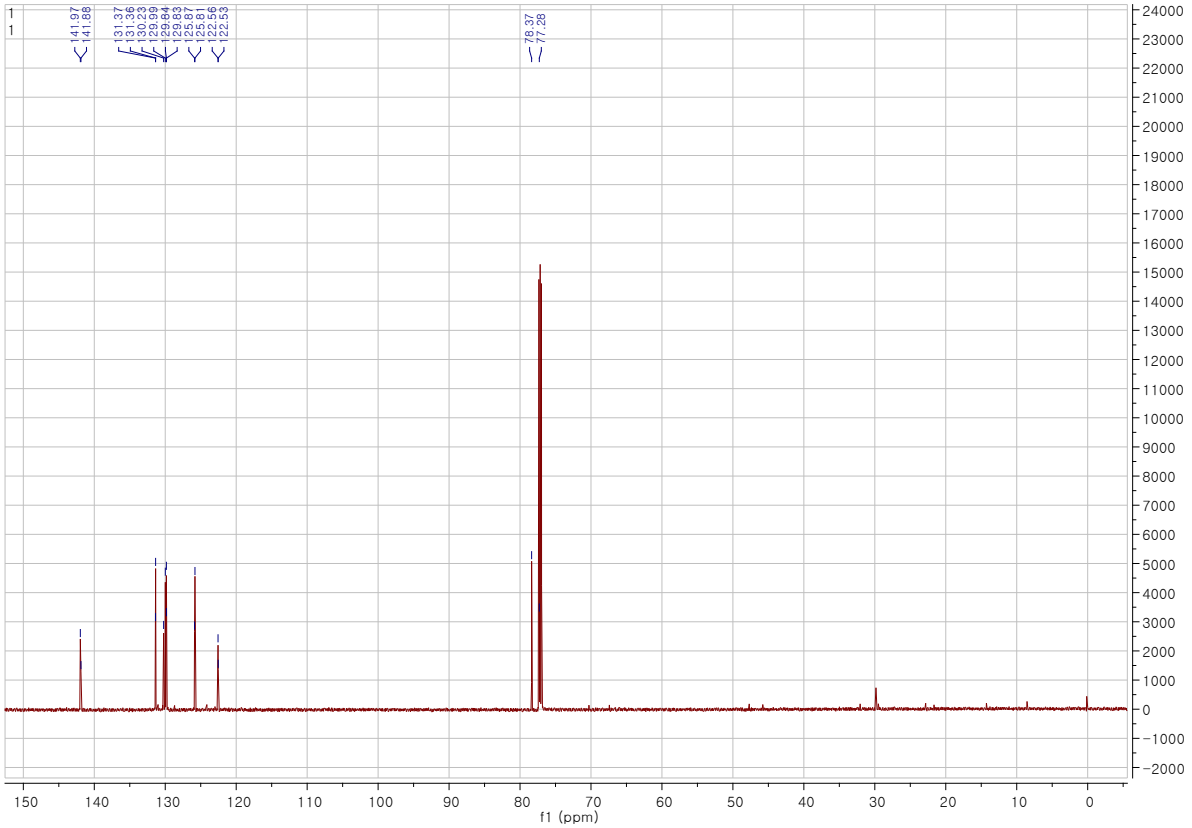
1,2-Bis(3-(trifluorometyl)phenyl)ethane-1,2-diol (Table 2, Entry 3)





1,2-Bis(3-bromophenyl)ethane-1,2diol (Table 2, Entry 4)





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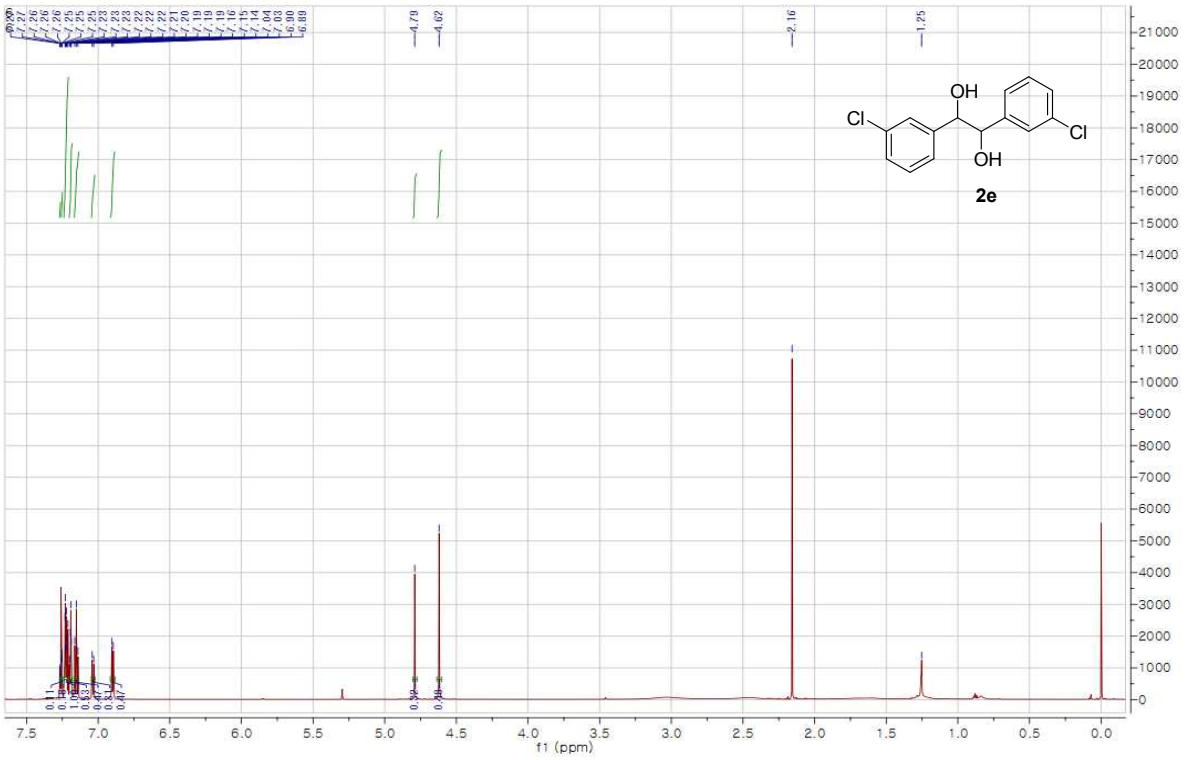

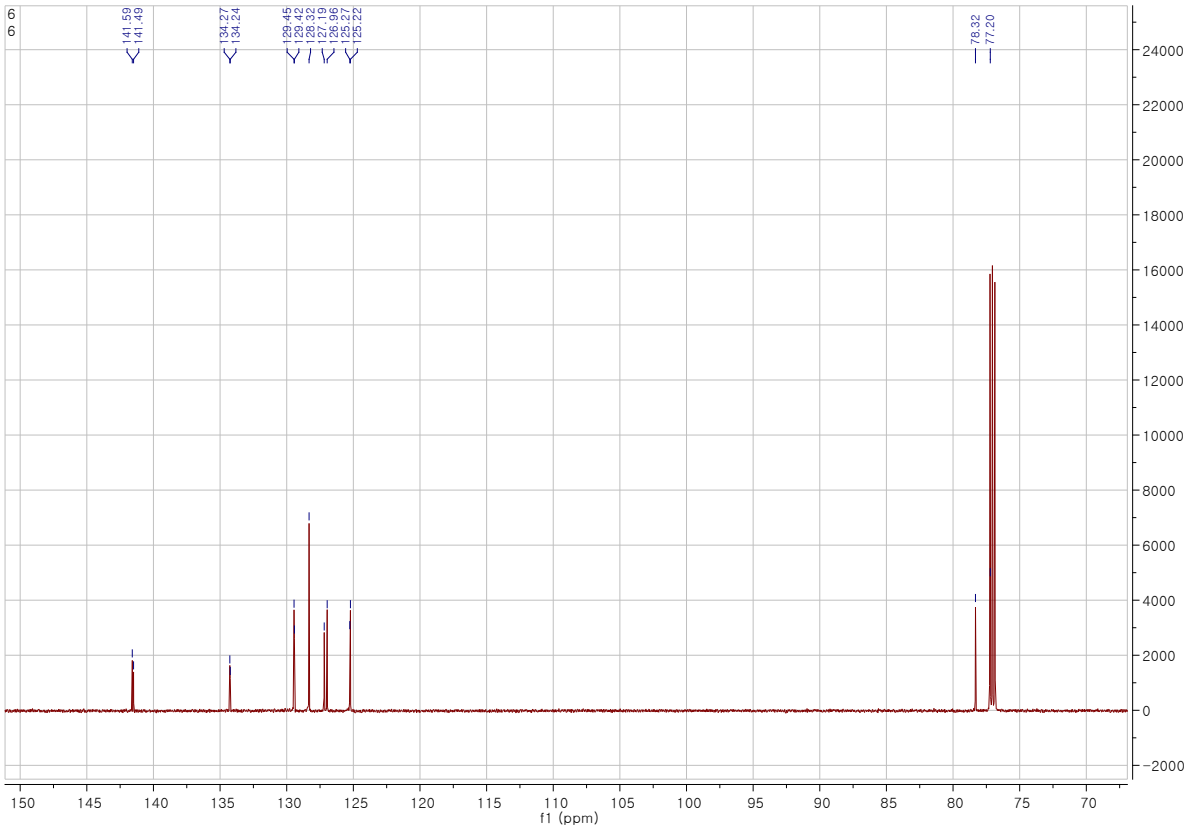

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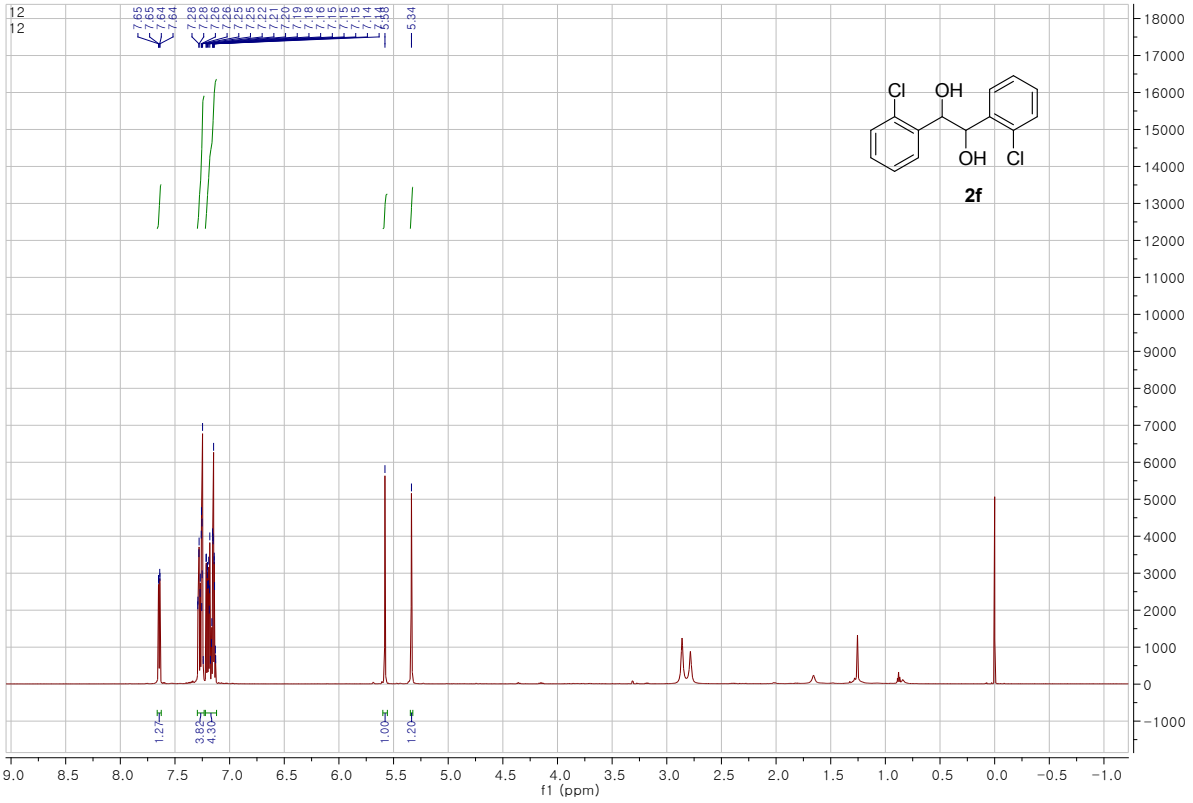
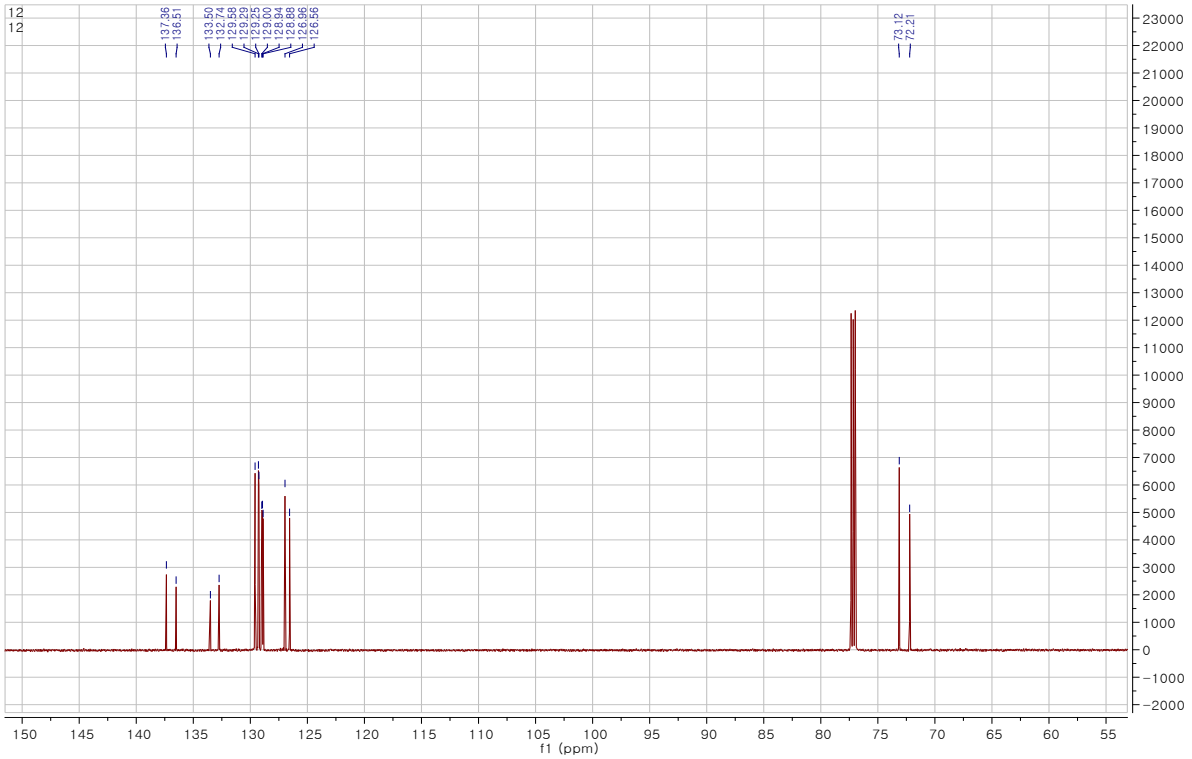
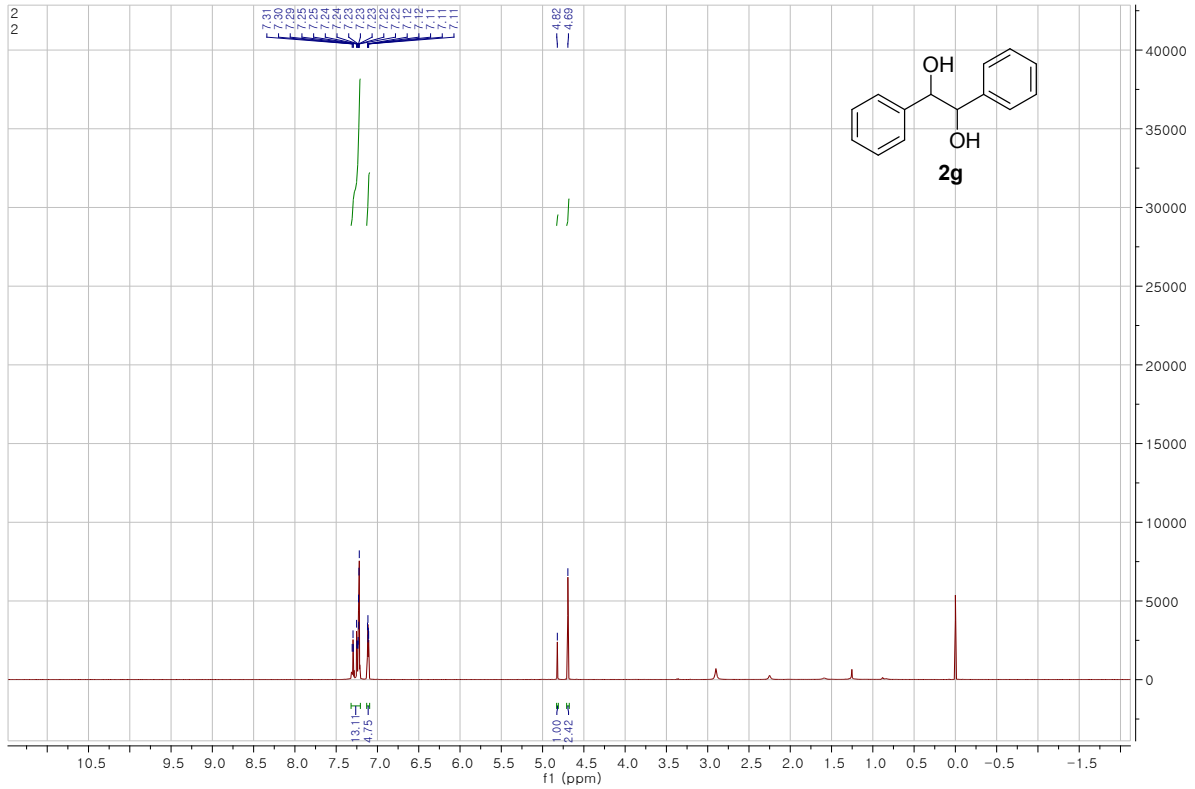
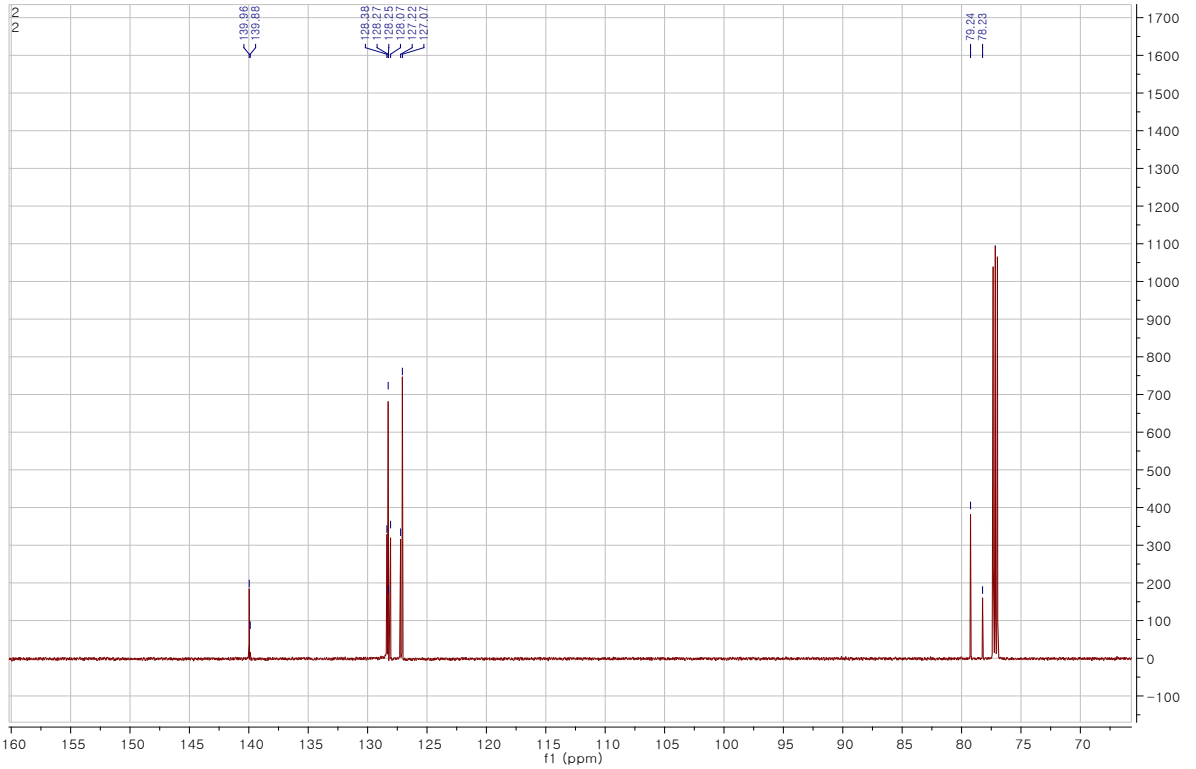


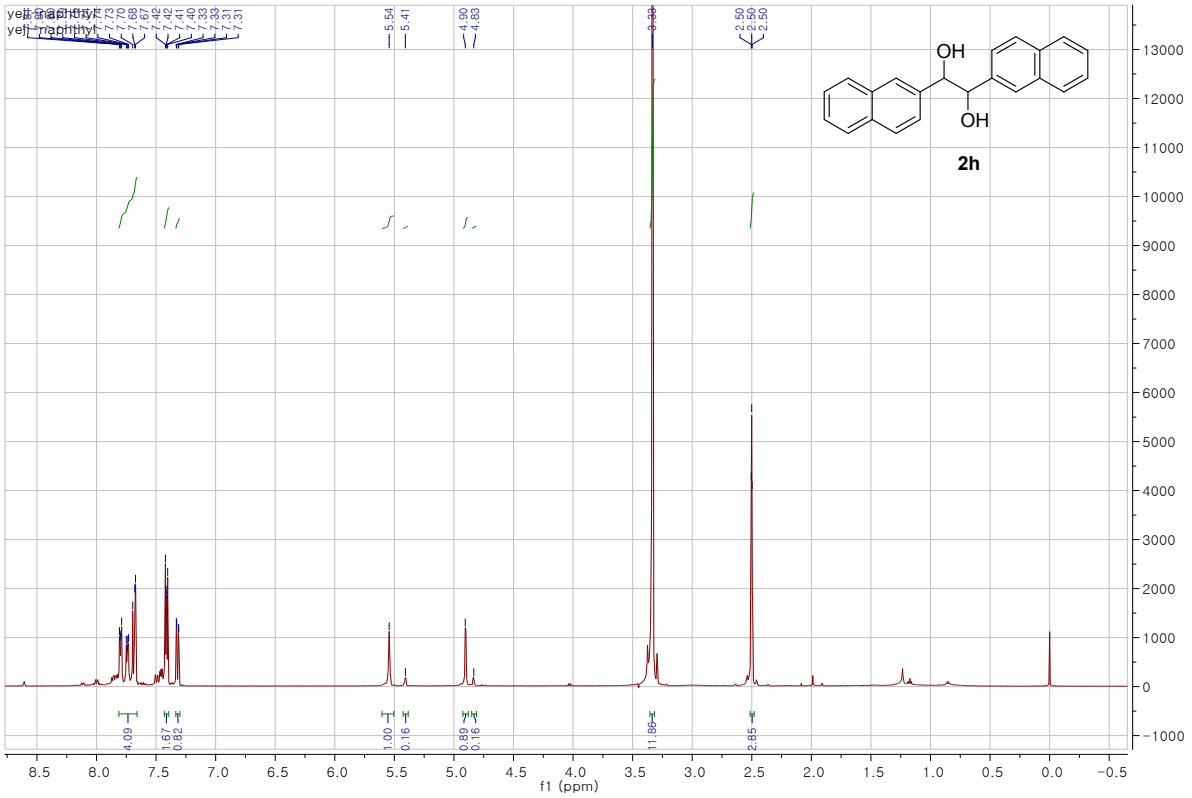


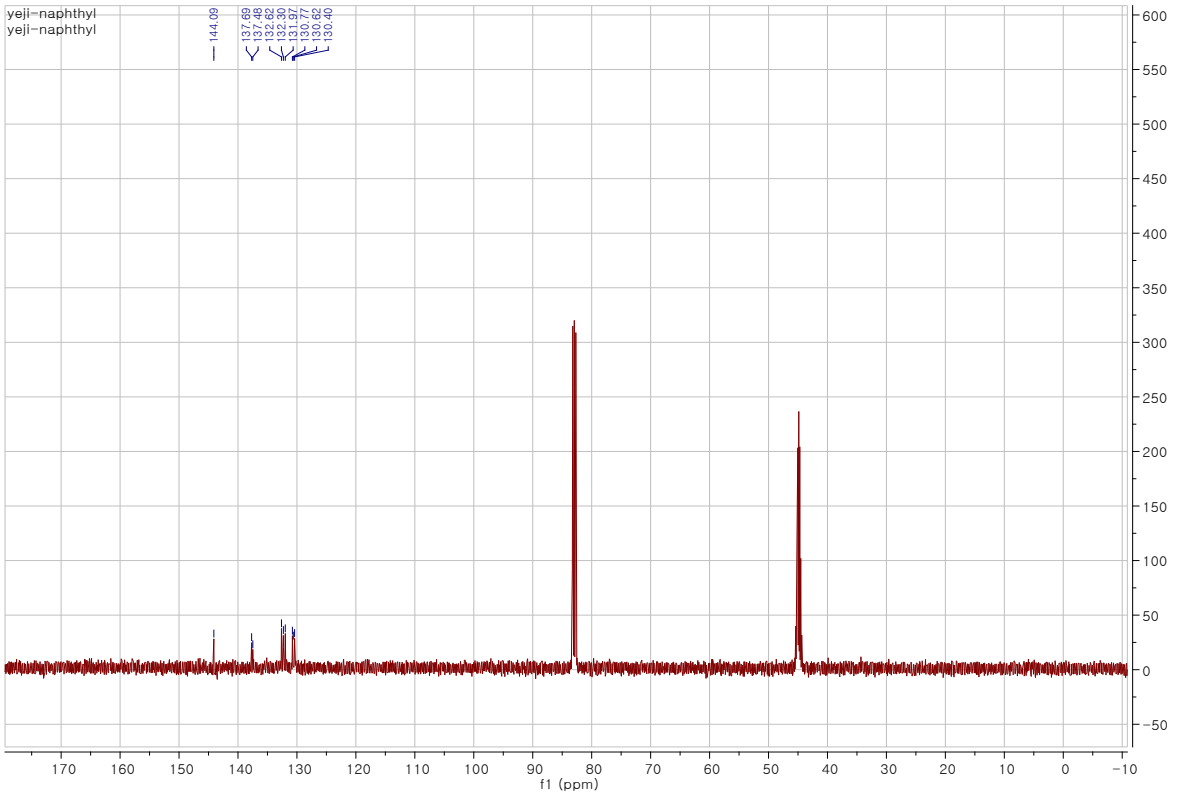
1,2-Diphenylethane-1,2diol (Table 2, Entry 7)



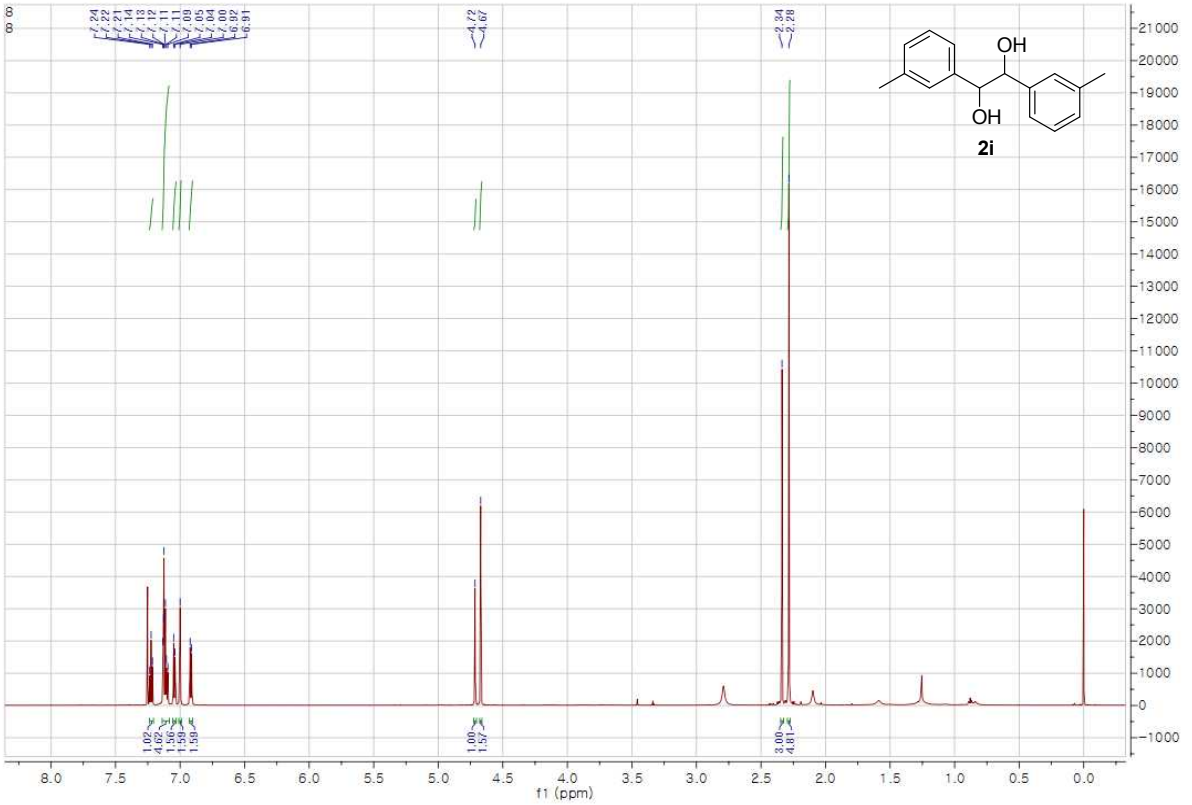


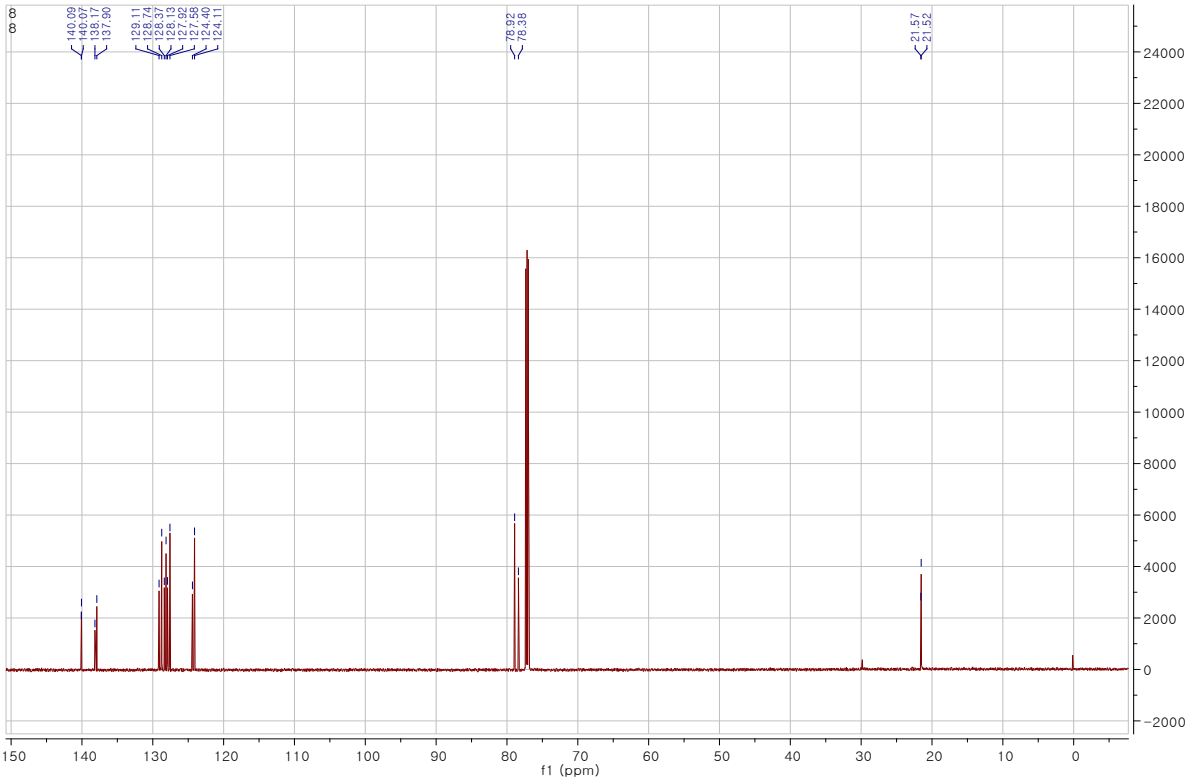
1,2-Di(naphthalene-2-yl)ethane-1,2-diol (Table 2, Entry 8)



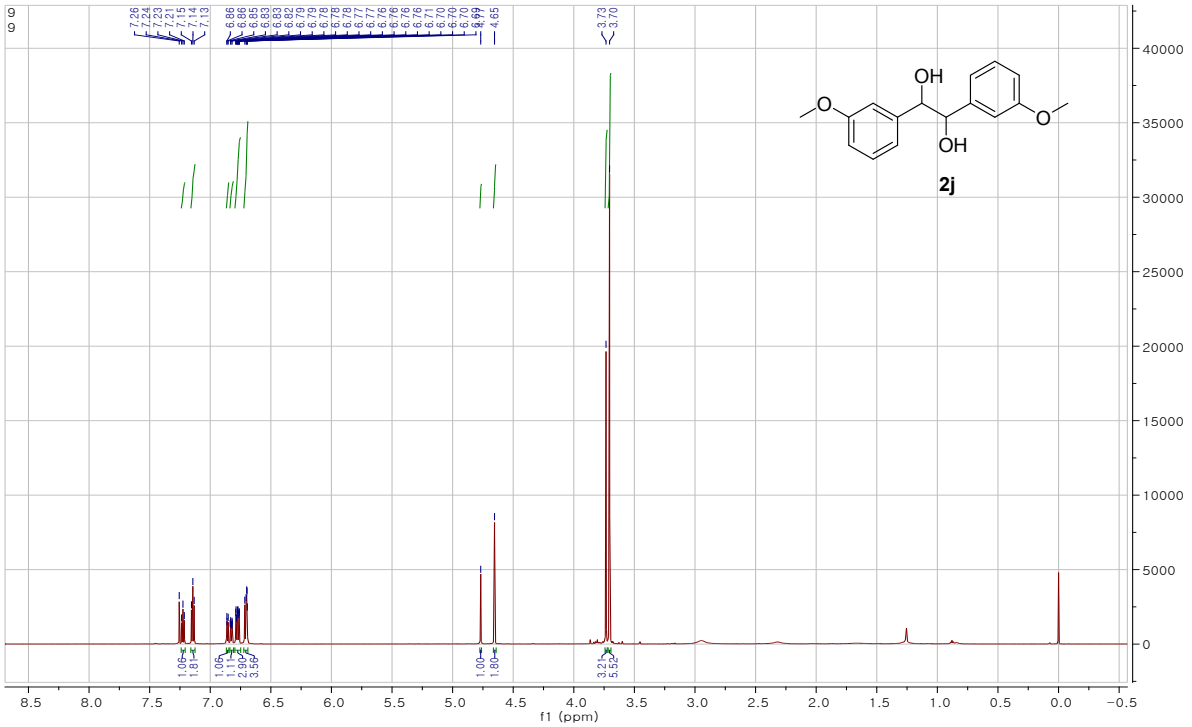


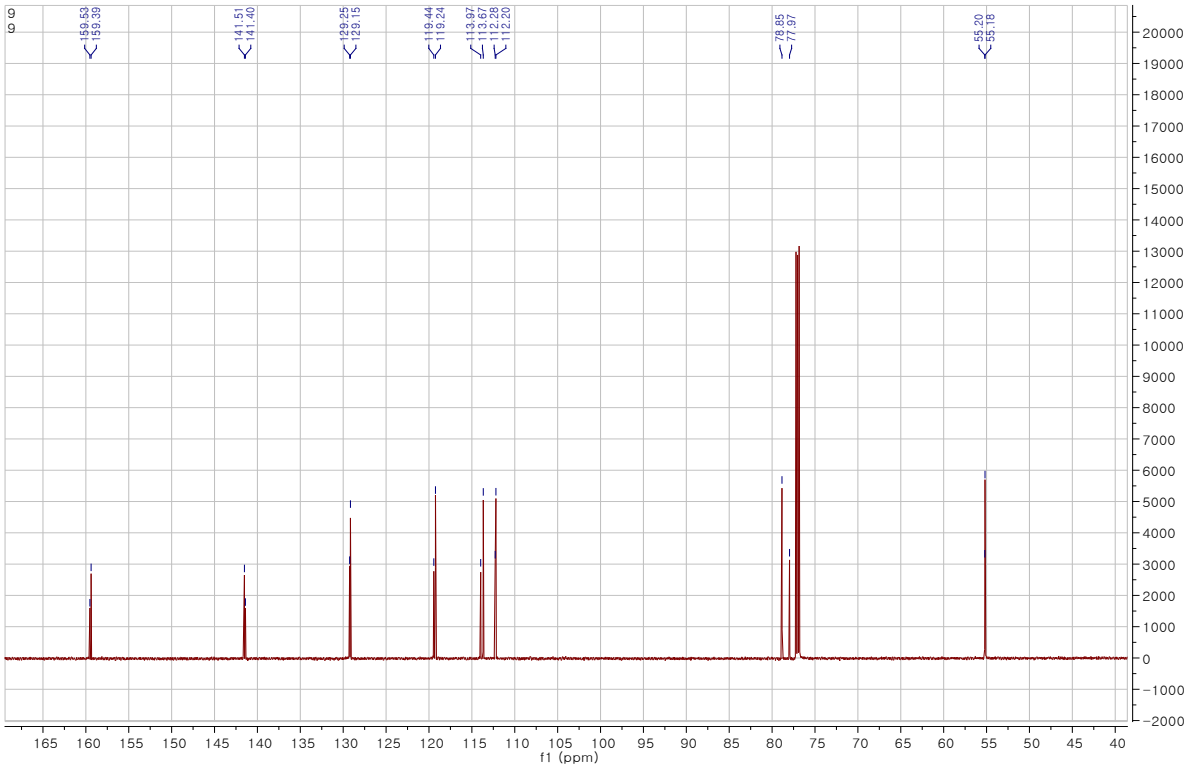
1,2-Di-*m*-tolyethane-1,2-diol (Table 2, Entry 9)



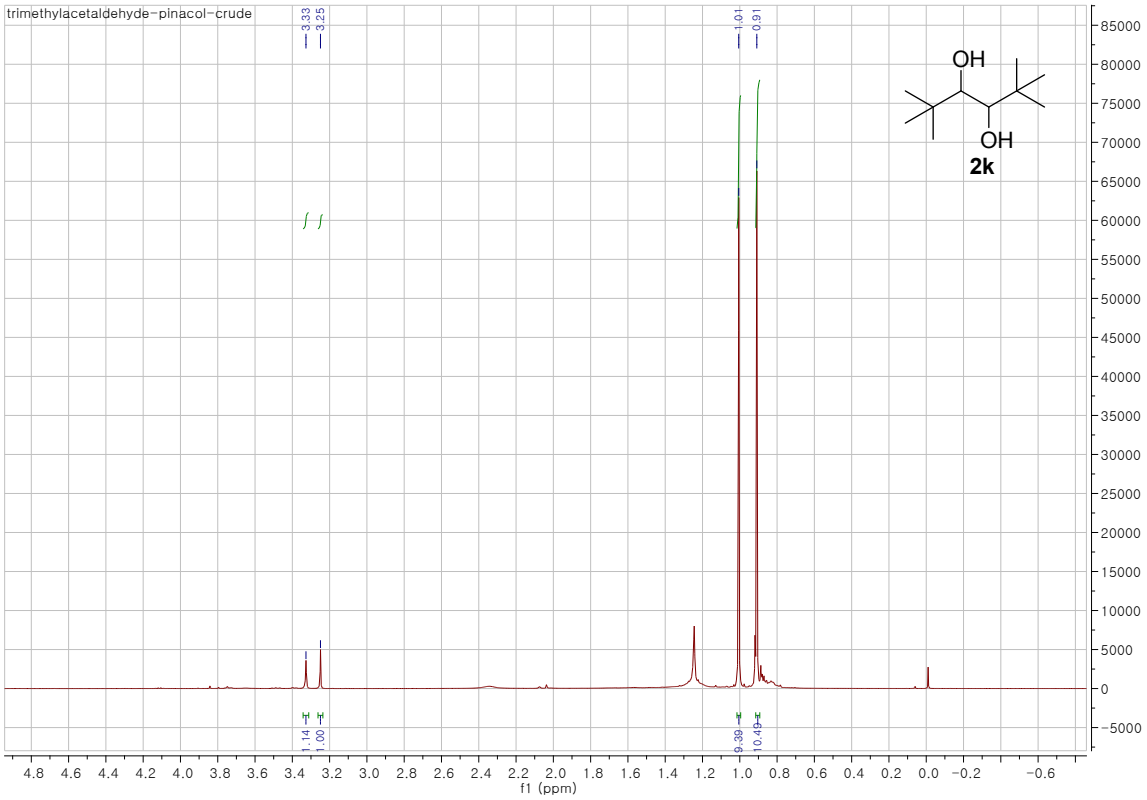


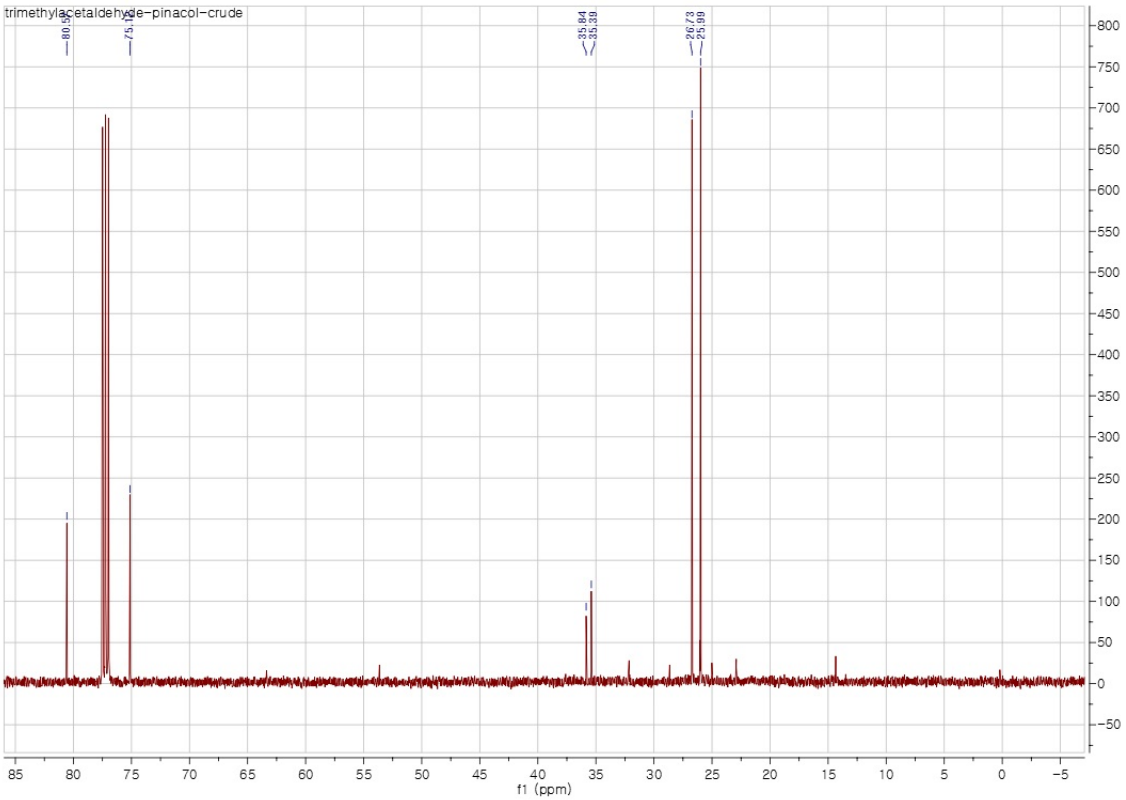
1,2-Bis(3-methoxyphenyl)ethane-1,2-diol (Table 2, Entry 10)



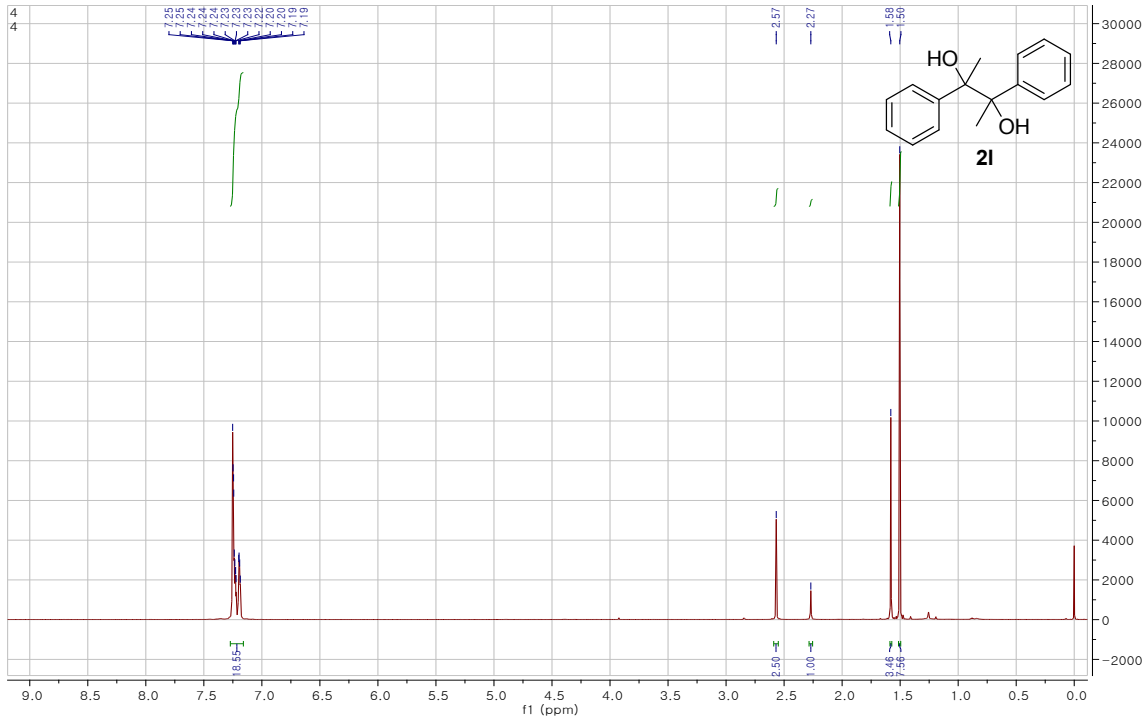


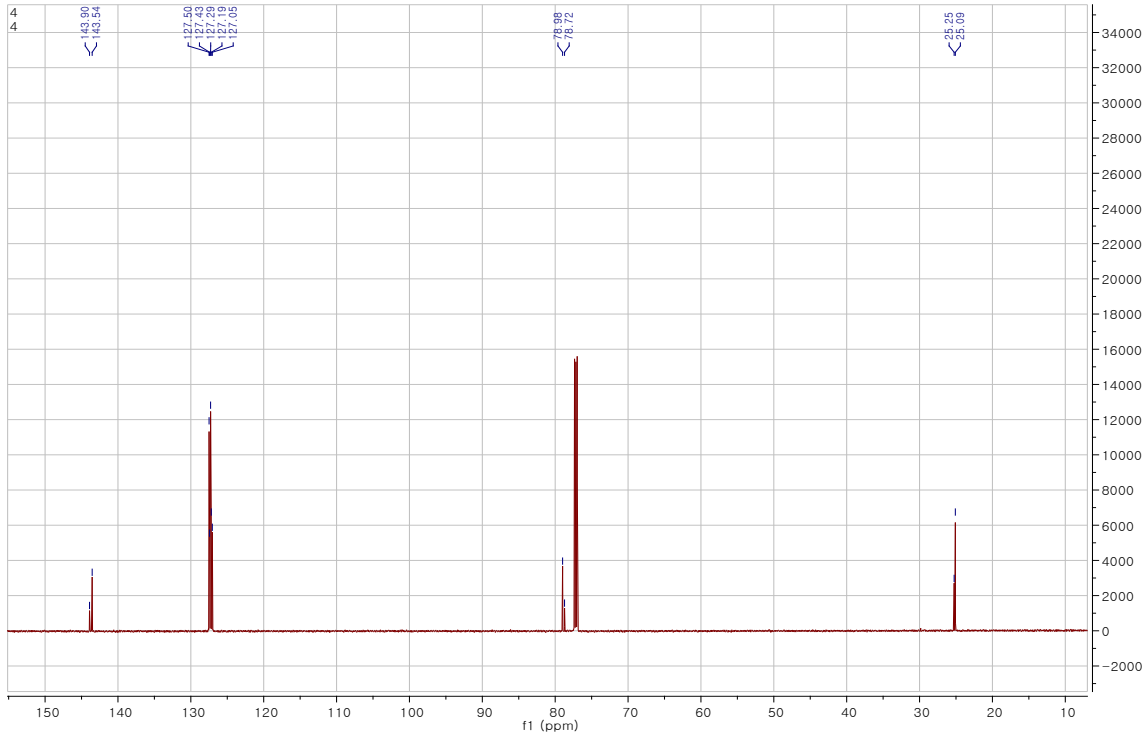
2,2,5,5-Tetrametylhexane-3,4-diol (Table 2, Entry 11)





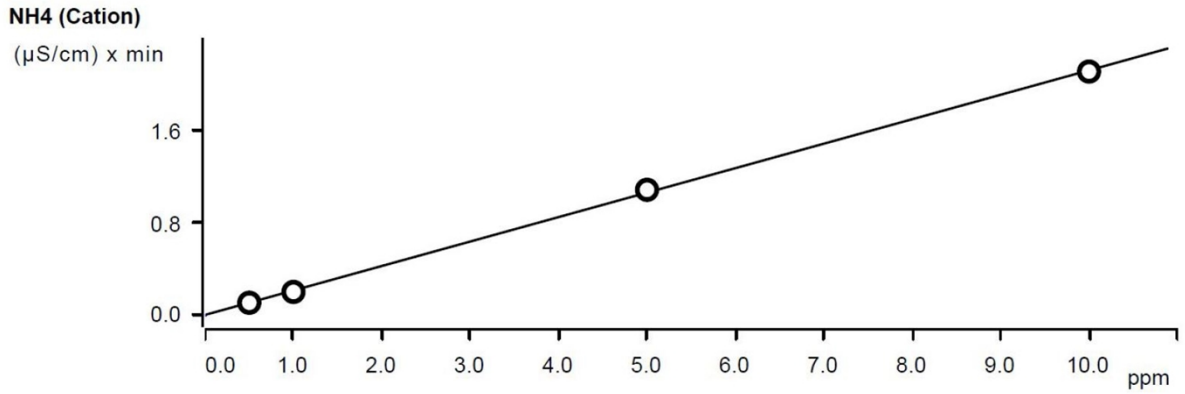
2,3-Diphenylbutane-2,3-diol (Table 2, Entry 12)





Calibrations and Results of Ion Chromatography

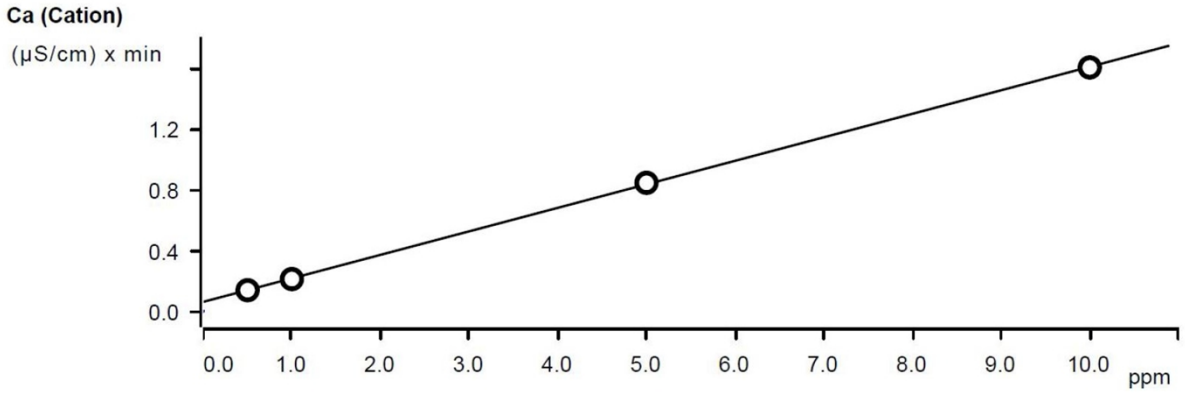
1) NH_4^+ cation calibration curve



Function: A = 4.15059E-3 + 0.0211598 × Q
Relative standard deviation: 2.732093%
Correlation coefficient: 0.999834

Sample	Conc.(mg/L)	Volume(µL)	Dilution	Area
Standard 1	0.500	10	1.0	0.109
Standard 2	1.000	10	1.0	0.203
Standard 3	5.000	10	1.0	1.086
Standard 4	10.000	10	1.0	2.109

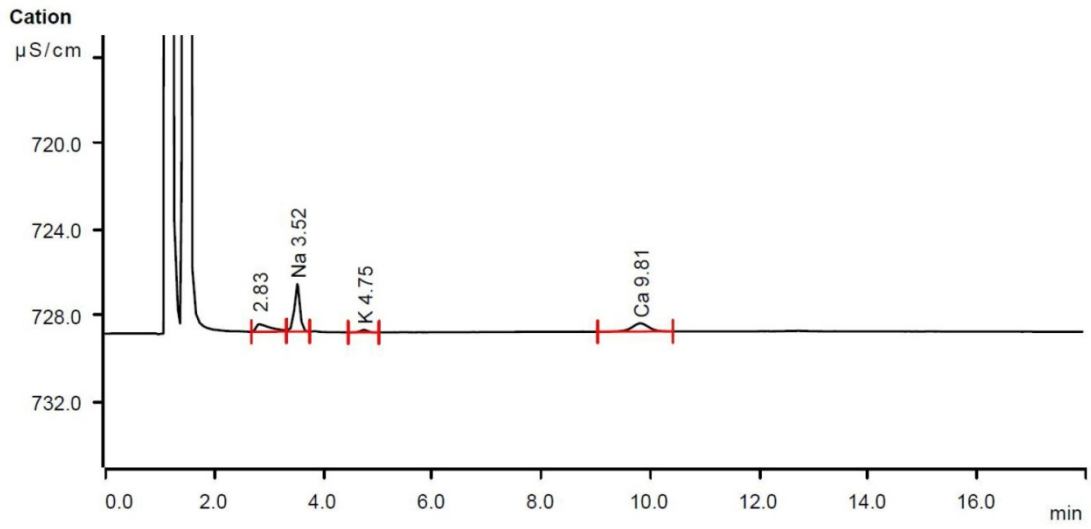
2) Ca^{2+} cation calibration curve



Function: A = 0.00617120 + 0.0154480 × Q
Relative standard deviation: 1.194612%
Correlation coefficient: 0.999950

Sample	Conc.(mg/L)	Volume(μL)	Dilution	Area
Standard 1	0.500	10	1.0	0.138
Standard 2	1.000	10	1.0	0.211
Standard 3	5.000	10	1.0	0.844
Standard 4	10.000	10	1.0	1.602

3) THF Sample Result

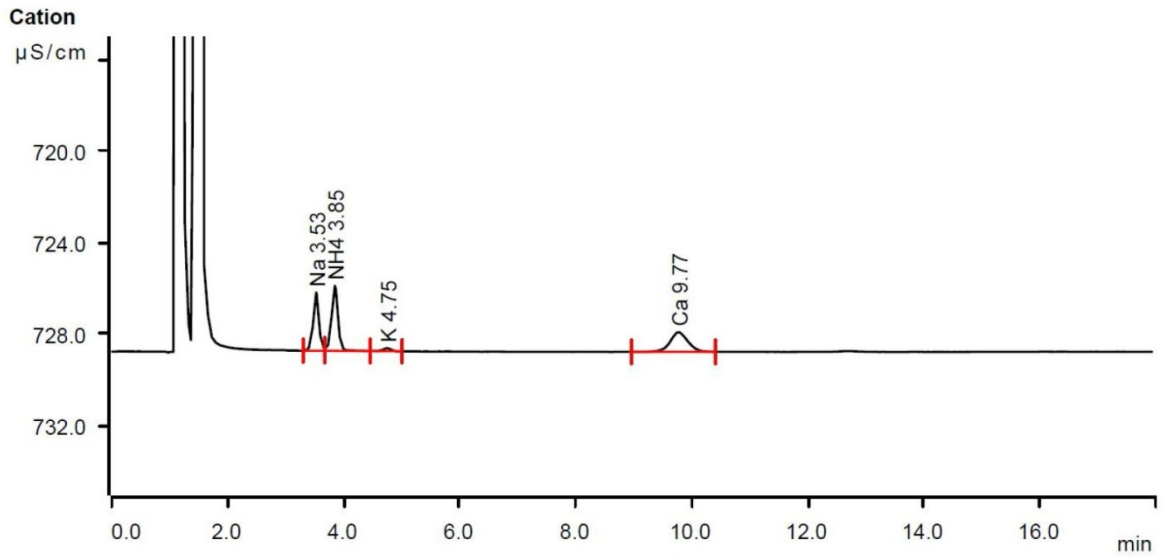


Sample	
Electride	$[Ca_2N]^{+}\cdot e^{-}$ (94 mg, 1 mmol)
Aldehyde	4-chlorobenzaldehyde (70.3 mg, 0.5 mmol)
Solvent	THF 4 mL
Washed Solvent	THF 8 mL
Dilution	200 times
Pressure / Flow	7.88 MPa / 0.700 mL/min

Result

Peak #	Retention Time (min)	Area (μS/cm)×min	Height (μS/cm)	Concentration (ppm)	Component name
1	2.827	0.1127	0.351	invalid	-
2	3.523	0.2556	2.205	0.025	Na
3	4.748	0.0181	0.117	0.096	K
4	9.813	0.1364	0.385	0.483	Ca

4) MeOH Sample Result

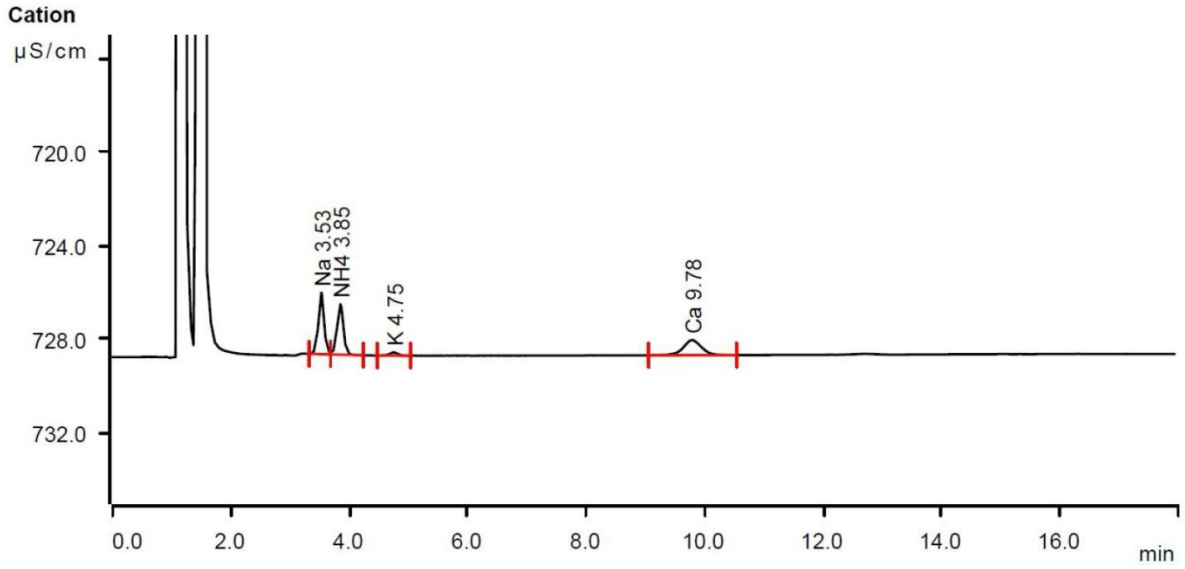


Sample	
Electride	$[Ca_2N]^{+}\cdot e^{-}$ (94 mg, 1 mmol)
Aldehyde	4-chlorobenzaldehyde (70.3 mg, 0.5 mmol)
Solvent	MeOH 4 mL
Washed Solvent	MeOH 4 mL
Dilution	200 times
Pressure / Flow	7.88 MPa / 0.700 mL/min

Result

Peak #	Retention Time (min)	Area (µS/cm)×min	Height (µS/cm)	Concentration (ppm)	Component name
1	3.530	0.2902	2.543	0.208	Na
2	3.852	0.3584	2.841	1.674	NH_4
3	4.752	0.0206	0.132	0.122	K
4	9.768	0.3036	0.858	1.566	Ca

5) MeOH/THF Sample Result



Sample	
Electride	$[Ca_2N]^{+}\cdot e^{-}$ (94 mg, 1 mmol)
Aldehyde	4-chlorobenzaldehyde (70.3 mg, 0.5 mmol)
Solvent	MeOH 2 mL / THF 2 mL
Washed Solvent	MeOH 8 mL
Dilution	200 times
Pressure / Flow	7.88 MPa / 0.700 mL/min

Result

Peak #	Retention Time (min)	Area (µS/cm)×min	Height (µS/cm)	Concentration (ppm)	Component name
1	3.530	0.2973	2.626	0.246	Na
2	3.582	0.2661	2.156	1.238	NH_4
3	4.753	0.0221	0.140	0.137	K
4	9.783	0.2306	0.648	1.093	Ca