Supporting Information

Enantioselective Conjugate Addition of Cyanide to Chalcones Catalyzed by Magnesium-Py-BINMOL Complex

Cheng Dong[a], Tao Song[a], Xing-Feng Bai[a,b], Yu-Ming Cui[a], Zheng Xu[a], and Li-Wen Xu*[a,b]

[a] *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, and College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310012, P. R. China. Fax: 86 2886 5135; Tel: 86 2886 5135; E-mail: liwenxu@hznu.edu.cn.*

[b] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, P. R. China. E-mail: licpxulw@yahoo.com*

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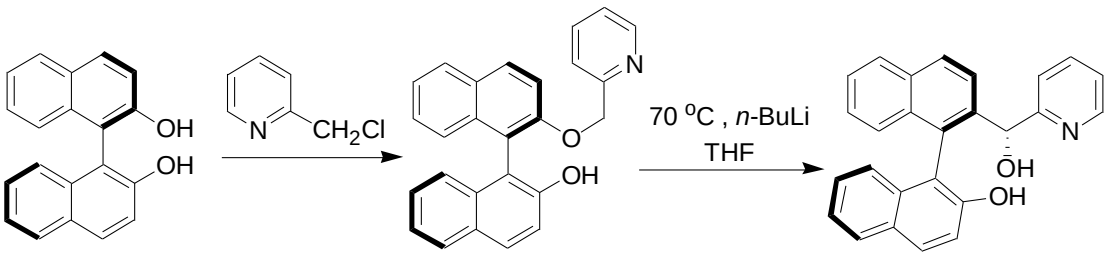
General Information

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All solvents were freshly distilled according to standard methods prior to use. Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin layer chromatography using silica gel. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of nitrogen. Air-and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula.

The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The ^{19}F NMR spectra was recorded at 470 MHz .The chemical shifts (δ) are referenced to residual signals of the solvents ($CHCl_3$: 7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). The ESI - MS analysis of the samples was operated on an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software.

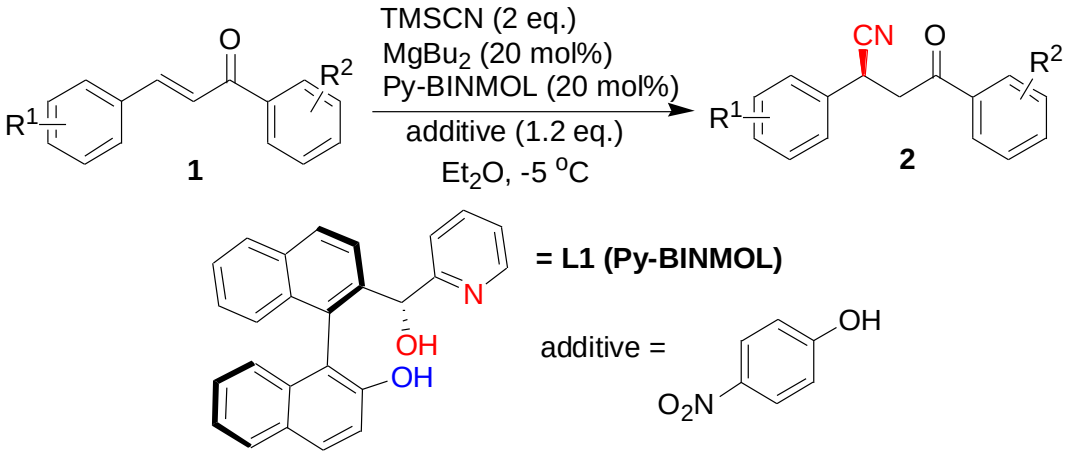
2. Synthesis of Py-BINMOL ligand[1,2]



(*R*)-BINOL (5.72 g, 20 mmol) was dissolved in 40 mL of acetone in a round bottom flask and a solution of K_2CO_3 (8.0 g, 57.89 mmol) in 12 mL of water was added. Next, the corresponding chloromethyl pyridine hydrochloride (3.28g, 20 mmol) was added and the mixture was heated at 65 ℃ during 12 h. The reaction crude was filtered under vacuum over celite, washing the cake with EtOAc (3 × 50 mL) and solvent was evaporated under vacuum. The benzyl oxide was purified by flash silica gel

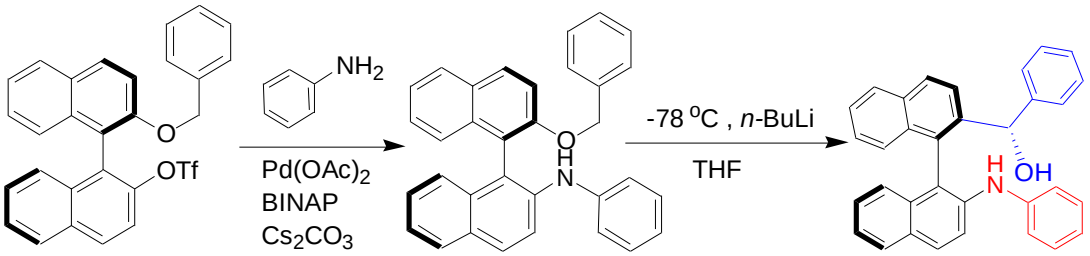
chromatography while the synthetic intermediate benzyl oxide was used in the next step without further purification. *n*-BuLi (8 mL, 20 mmol) was slowly added to a solution of the corresponding precursor benzyl oxide in dry THF (20 ml) at -78 ℃. The mixture was stirred for 12 h at 70 ℃ and then the reaction was quenched with water at 0 ℃. The resulting mixture was extracted with EtOAc and the combined organic layers were dried over magnesium sulfate and concentrated under vacuum. The crude product was purified by chromatography on flash silica gel (CH_2Cl_2/MeOH = 20/1) to give the desired products (3.4g, 90%) as pale yellow solid.

3. Typical procedure for the catalytic conjugate addition of TMSCN to chalcones



20 mol% Mg(*n*-Bu)$_2$ was added to a stirred solution of chiral ligand in Et_2O (4.0 mL), and then the reaction mixture was stirred and cooled to -5 ^oC for 15 min. Subsequently the enone (0.25 mmol) was added to the solution. After the addition of TMSCN (2 eq) and *para*-nitrophenol (1.2 eq), the resulting mixture was stirred for 12 hours at -5 ^oC until the reaction was accomplished (monitored by TLC analysis). The reaction mixture was quenched with saturated K_2CO_3 solution slowly and the resulting reaction mixture was extracted with EtOAc, and then the combined organic layers were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 10/1) to afford the desired product.

4. The synthesis of chiral amino alcohol ligand L7



7-a
ref. 1

7-b

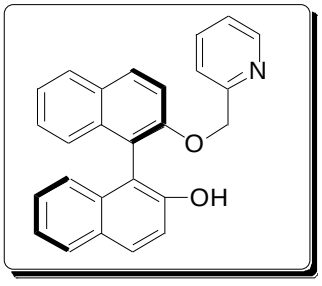
L7

To a solution of (*R*)-(+)-BINOL (5.72 g, 20.00 mmol) and dry K_2CO_3 (8.00 g, 57.89 mmol) in 50 mL dry acetone was added benzyl bromide (2.62 mL, 22.00 mmol) dropwise. The mixture was stirred vigorously and heated to reflux. After being refluxed for overnight, the reaction mixture was cooled to room temperature. After evaporation of solvents, the mixture was poured into water and extracted with EtOAc. The combined organic layers were washed with brine, dried by anhydrous Na_2SO_4 and concentrated in vacuum to give a pale yellow oil. The crude product was chromatographed on silica gel (hexane/EtOAc = 8/1) to give white solid (6.8 g, 90%). The crude product was dissolved in DCM (30 ml) and pyridine (21.6 mmol, 1.7 ml). To this was added Tf_2O (3.4 ml,21.6 mmol) at 0 °C, stirred for 6h at 0 °C, then the mixture was stirred at rt for 2h. The solution was extracted with CH_2Cl_2, washed with 10% HCl, saturated $NaHCO_3$, and saturated NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the intermediate (sulphonic acid ester) was chromatographed on silica gel (hexane/EtOAc = 10/1) to give pale yellow solid **7-a** (9.1 g, 99%).

To a mixture of palladium acetate (225 mg, 1 mmol), BINAP (1.245 g, 2 mmol) and cesium carbonate (6.52 g, 20 mmol) was added with a solution of sulphonic acid ester

(5.08g, 10 mmol) and aniline (2.7 mL, 30 mmol) in dioxane under N_2, and the reaction mixture was heated at 110 ℃ for overnight with stirring. After cooling to room temperature, removed of solvents, the mixture was extracted with EtOAc, washed with brine. The organic layer was dried over Na_2SO_4 and chromatographed on silica gel (hexane/EtOAc = 10/1) afforded the desired product **7-b** (4.3g, 95%) as yellow oil. The crude product was dissolved by THF (20 mL) under N_2 and cooled at -78 ℃ for 0.5 hour with stirring. Then the solution was added with *n*-BuLi (8 mL, 20 mmol) dropwise and with stirring for 1 hour at -70 ^{o}C. The reaction mixture was then allowed to warm up to room temperature slowly and stirred for further 6 hours at room temperature. After removal of the most of solvents in vacuo, the mixture was extracted with EtOAc, and washed with brine. The organic layer was dried over Na_2SO_4 and purification of the residual oil by column chromatography on silica gel (hexane/EtOAc = 5/1) afforded the desired product **L7** (95%) as pale yellow solid.

5. The characterization of data of product

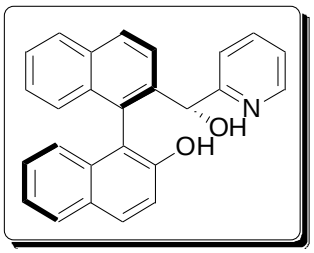


2'-(Pyridin-2-ylmethoxy)-[1,1']binaphthalenyl-2-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (d, J = 4.2 Hz, 1H), 7.85 (ddd, J = 21.4, 16.9, 10.4 Hz, 5H), 7.53 – 7.39 (m, 2H), 7.32 – 7.15 (m, 8H), 6.95 (d, J = 7.9 Hz, 1H), 5.32 (d, J = 14.7 Hz, 1H), 5.19 (d, J = 11.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=156.5,

153.9, 152.3, 148.13, 137.4, 134.1, 130.4, 129.6, 129.2, 128.1, 127.1, 126.3, 125.4, 125.1, 124.3, 123.1, 122.6, 121.3, 118.9, 115.8, 114.8ppm.

HRMS (ESI) calcd. for $C_{26}H_{19}NONa$ $[M+Na]^+$ 399.1704.Found 399.1700.

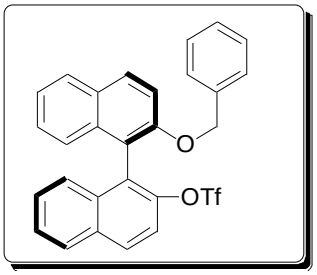


2'-(Hydroxy-pyridin-2-yl-methyl)-[1,1']binaphthalenyl-2-ol

^1H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, J = 4.9 Hz, 1H), 7.97 – 7.81 (m, 4H), 7.44 (dddd, J = 17.1, 7.7, 5.9, 1.5 Hz, 3H), 7.37 – 7.05 (m, 7H), 7.00 (d, J = 8.4 Hz, 1H), 6.67 (d, J = 7.9 Hz, 1H), 5.64 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.7, 152.1, 147.5, 140.9, 136.8, 134.3, 133.6, 133.0, 130.8, 130.2, 129.7, 129.1, 128.3, 128.1, 127.0, 126.5, 125.2, 124.9, 123.4, 122.5, 121.9, 118.8, 117.0 ppm.

HRMS (ESI) calcd. for $C_{26}H_{20}NO$ $[M+H]^+$ 378.1489, Found 378.1484.



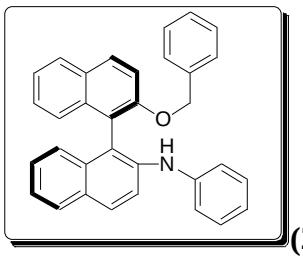
Trifluoro-methanesulfonic acid 2'-benzyloxy-[1,1']binaphthalenyl-2-yl ester

yellow soild; yield 95%; m.p. 88–89 ℃;

^1H NMR (400 MHz, $CDCl_3$) δ = 8.10–7.91 (m, 3H), 7.84 (d, J = 8.0 Hz, 1H),7.62–7.47(m,2H), 7.38(dt, J = 35.0,7.2 Hz,4H),7.27–7.00 (m, 7H), 5.12 (d, J = 3.0 Hz, 2H) ppm.

^{13}C NMR (100MHz, $CDCl_3$) δ = 154.4, 145.7, 137.2, 133.8, 133.7, 132.6, 130.9, 130.3, 129.1, 128.3, 128.2, 128.1, 127.5, 127.4, 127.1, 126.9, 126.8, 126.6, 125.1, 123.9, 119.6, 116.2, 114.7, 70.8ppm.

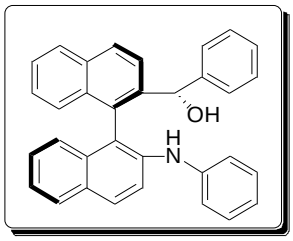
HRMS (ESI) calcd. for $C_{28}H_{19}F_3O_4SNa$ $[M+Na]^+$ 509.1029. Found509.1028.



(2'-Benzyloxy-[1,1']binaphthalenyl-2-yl)-phenyl-amine

yellow oil; yield 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.09–7.76 (m, 6H), 7.73–7.63 (m, 1H), 7.39–7.22 (m, 6H), 7.19–7.05 (m, 8H), 5.46 (s, 1H), 5.01 (d, J = 6.1 Hz, 2H) ppm.

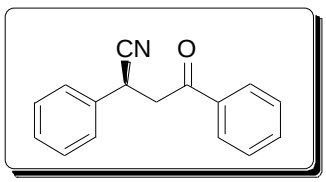
^{13}C NMR (100MHz, $CDCl_3$) δ = 146.9, 141.1, 140.7, 137.4, 133.7, 131.4, 131.1, 130.0, 129.3, 128.9, 128.3, 128.1, 127.9, 127.8, 127.4, 127.3, 126.9, 126.7, 125.4, 125.3, 125.1, 125.0, 123.7, 122.2, 121.9, 119.9, 100.0, 66.8, 31.4, 30.2, 29.7ppm. HRMS (ESI) calcd. for $C_{33}H_{26}NO$ $[M+H]^+$ 452.2009.Found452.1986.



Phenyl-(2'-phenylamino-[1,1']binaphthalenyl-2-yl)-methanol

yellow soild; yield 95%; m.p. 77–79 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (ddd, J = 23.5, 16.0, 8.4 Hz, 4H), 7.68 (d, J = 9.0 Hz, 1H), 7.58 (d, J = 8.7 Hz, 1H), 7.46 (ddd, J= 8.1, 5.1, 2.9 Hz, 1H), 7.36–7.08 (m, 12H), 6.99 (d, J = 7.8 Hz, 2H), 6.93 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 5.73 (s, 1H), 5.53 (s, 1H), 2.54 (s, 1H).

^{13}C NMR (100MHz, $CDCl_3$) δ = 129.5, 129.4, 129.3, 128.2, 128.07, 128.1, 128.0, 126.9, 126.8, 126.7, 126.4, 126.3, 126.1, 125.6, 125.2, 119.8, 73.1ppm. HRMS (ESI) calcd. for $C_{33}H_{26}NO$ $[M+H]^+$ 452.2009.Found452.2008.



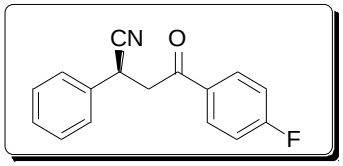
4-Oxo-2,4-diphenylbutanenitrile (2a): White solid; yield 89% (PE/EtOAc = 10:1, v/v), 92% *ee*, m.p. 123–124 ℃; HRMS (ESI) calcd. for $C_{16}H_{13}NONa$ $[M+Na]^+$ 258.0889, Found 258.0895.

IR (neat): ν = 1683, 2242 cm^{-1}. $[\alpha]^{20}_D$= -29.3 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.93 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 7.2 Hz, 1H), 7.49 – 7.32 (m, 7H), 4.64 – 4.52 (m, 1H), 3.73 (dd, J = 17.9, 8.0 Hz, 1H), 3.51 (dd, J = 17.9, 6.0 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.9, 44.6, 120.6, 127.5, 128.1, 128.4, 128.8, 129.3, 133.9, 135.3, 135.7, 194.6 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) = 8.9 min, t_R(minor) = 13.581 min.



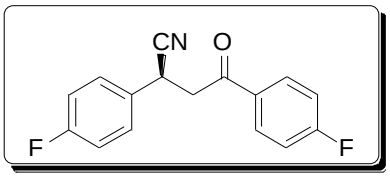
4-(4-Fluoro-phenyl)-4-oxo-2-phenyl-butyronitrile (2b): White solid; yield 71% (PE/EtOAc = 10:1, v/v), 45% *ee*, m.p. 100–103 ℃; HRMS (ESI) calcd. for $C_{16}H_{12}FNONa$ $[M+Na]^+$ 276.0795, Found 276.0799.

IR (neat): ν = 1677, 2242 cm^{-1}. $[\alpha]^{20}_D$ = -16.2 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, J = 8.9, 5.3 Hz, 2H), 7.40 (ddd, J = 22.0, 11.6, 7.1 Hz, 5H), 7.14 (t, J = 8.6 Hz, 2H), 4.55 (dd, J = 8.0, 5.9 Hz, 1H), 3.70 (dd, J = 17.9, 8.1 Hz, 1H), 3.47 (dd, J = 17.9, 5.9 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.9, 44.5, 115.9, 116.2, 120.5, 127.5, 128.5, 129.3, 130.8 (d, J = 9.5 Hz), 132.2 (d, J = 3.0 Hz,) , 135.2, 164.9, 167.5, 193.1 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = -103.42 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) = 10.457 min, t_R(minor) = 16.786 min.



2,4-Bis-(4-fluoro-phenyl)-4-oxo-butyronitrile (2c): White solid; yield 81% (PE/EtOAc = 10:1, v/v), 72% *ee*, m.p. 106–108 ℃; HRMS (ESI) calcd. for $C_{16}H_{11}F_2NONa$ $[M+Na]^+$ 294.0701, Found 294.0685.

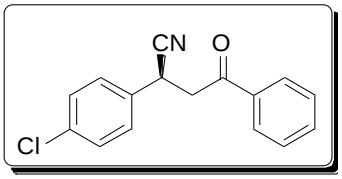
IR (neat): ν = 1680, 2241 cm^{-1}. $[\alpha]^{20}_D$=-21.2(c = 0.1, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, J = 8.9, 5.3 Hz, 2H), 7.48 – 7.38 (m, 2H), 7.11 (dt, J = 25.8, 8.6 Hz, 4H), 4.62 – 4.49 (t,J = 8.0, 1H), 3.69 (dd, J = 17.9, 7.5 Hz, 1H), 3.47 (dd, J = 17.9, 6.3 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.9, 42.0, 113.6, 113.8 (d, J = 1.7 Hz) , 114.1, 118.0, 126.9 (d, J = 8.3 Hz) , 128.5 (dd, J = 13.4, 6.4 Hz) , 129.7 (d, J = 3.0 Hz) , 158.9, 161.4, 162.6, 165.2, 190.5 ppm.

^{19}F NMR (470 MHz, $CDCl_3$): δ = -113.10, -103.21 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) = 11.15 min, t_R(minor) = 18.576 min.



2-(4-Chloro-phenyl)-4-oxo-4-phenyl-butyronitrile (2d): White solid; yield 70% (PE/EtOAc = 10:1, v/v), 64% *ee*, m.p. 115–117 ℃; HRMS (ESI) calcd. for $C_{16}H_{12}ClNONa$ $[M+Na]^+$ 292.0500, Found 292.0496.

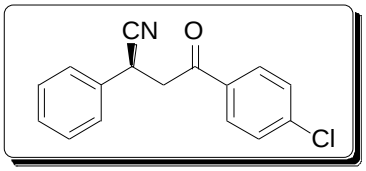
IR (neat): ν = 1680, 2242 cm^{-1}. $[\alpha]^{20}_D$ = -31.6 (c = 0.1, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$): δ =7.96 – 7.87 (m, 2H), 7.64 – 7.56 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.41 – 7.30 (m, 4H), 4.56 (t, J = 6.9 Hz, 1H), 3.71 (dd, J = 17.9, 7.4 Hz, 1H), 3.51 (dd, J = 18.0, 6.4 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ=194.33, 135.57, 134.45, 134.04, 133.79, 129.45,

128.94, 128.10, 120.26, 77.37, 77.05, 76.73, 44.28, 31.33 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) = 8.421 min, t_R(minor) = 10.826 min.



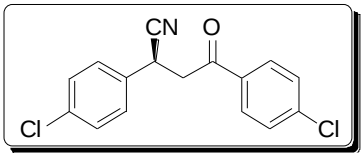
4-(4-Chloro-phenyl)-4-oxo-2-phenyl-butyronitrile (2e): White solid; yield 84% (PE/EtOAc = 10:1, v/v), 79% *ee*, m.p. 114–115 ℃; HRMS (ESI) calcd. for $C_{16}H_{12}ClNONa$ $[M+Na]^+$ 292.0500, Found 292.0499.

IR (neat): ν = 1677, 2242 cm^{-1}. $[\alpha]^{20}_D$=-29.7(c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 – 7.83 (m, 2H), 7.50 – 7.28 (m, 7H), 4.54 (dd, J = 8.0, 5.9 Hz, 1H), 3.69 (dd, J = 17.9, 8.1 Hz, 1H), 3.47 (dd, J = 17.9, 5.9 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.9, 44.5, 120.5, 127.5, 129.3, 140.5, 193.5ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) = 10.038 min, t_R(minor) = 14.699 min.



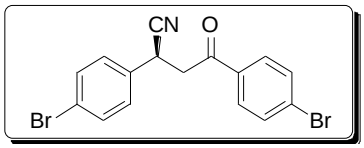
2,4-Bis-(4-chloro-phenyl)-4-oxo-butyronitrile (2f): White solid; yield 72% (PE/EtOAc = 10:1, v/v), 70% *ee*, m.p. 88–90 ℃; HRMS (ESI) calcd. for $C_{16}H_{11}Cl_2NONa$ $[M+Na]^+$ 326.0110, Found 292.0100.

IR (neat): ν = 1674,2241 cm^{-1}. $[\alpha]^{20}_D$ = -30.2 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, J = 7.5, 5.6 Hz, 2H), 7.42 (dd, J = 7.4, 5.3 Hz, 2H), 7.12 (dt, J = 26.0, 8.2 Hz, 4H), 4.56 (t, J = 6.9 Hz, 1H), 3.69 (dd, J = 17.8, 7.5 Hz, 1H), 3.47 (dd, J = 17.9, 6.3 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.0, 44.0, 119.8, 121.6, 128.6, 128.9, 129.2, 129.4, 132.9, 133.6, 136.1, 143.5, 188.6, 192.8 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) = 9.697 min, t_R(minor) = 13.329 min.



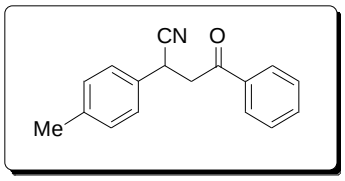
2,4-Bis-(4-bromo-phenyl)-4-oxo-butyronitrile (2g): White solid; yield 77% (PE/EtOAc = 10:1, v/v), 80% *ee*, m.p. 124–125 ℃; HRMS (ESI) calcd. for $C_{16}H_{11}Br_2NONa$ $[M+Na]^+$ 415.9076, Found 415.9075.

IR (neat): ν = 1674, 2242 cm^{-1}. $[\alpha]^{20}_D$ = -17.4 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 8.6 Hz, 2H), 7.68 – 7.61 (m, 3H), 7.31 (d, J = 8.5 Hz, 2H), 4.57 – 4.47 (t, J = 8.0 Hz,1H), 3.67 (dd, J = 18.0, 7.5 Hz, 1H), 3.45 (dd, J = 18.0, 6.4 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4, 44.2, 119.9, 122.6, 128.1, 129.4, 129.8, 132.0, 132.3, 134.2, 143.9, 189.1, 193.3 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) = 13.186 min, t_R(minor) = 17.556 min.



4-Oxo-4-phenyl-2-p-tolyl-butyronitrile (2h): White solid; yield 67% (PE/EtOAc = 10:1, v/v), 51% *ee*, m.p. 123–125 ℃; HRMS (ESI) calcd. for $C_{17}H_{15}NONa$ $[M+Na]^+$ 272.1046, Found 272.1054.

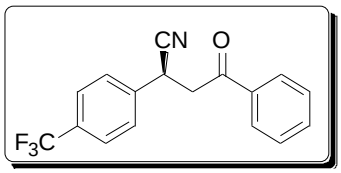
IR (neat): ν = 1675, 2239 cm^{-1}. $[\alpha]^{20}_D$ = -16.0 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.91 (dd, J = 5.2, 3.4 Hz, 2H), 7.64 – 7.55 (m, 1H),

7.46 (dd, J = 10.6, 4.8 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.53 (dd, J = 7.8, 6.1 Hz, 1H), 3.70 (dd, J = 17.9, 7.9 Hz, 1H), 3.49 (dd, J = 17.9, 6.1 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4, 120.0, 127.3, 137.2, 139.9, 143.8, 189.5 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) = 8.411 min, t_R(minor) = 9.894 min.



4-Oxo-4-phenyl-2-(4-trifluoromethyl-phenyl)-butyronitrile (2i): White solid; yield 90% (PE/EtOAc = 10:1, v/v), 79% *ee*, m.p. 96–98 ℃; HRMS (ESI) calcd. for $C_{17}H_{12}F_3NONa$ $[M+Na]^+$ 326.0763, Found 326.0765.

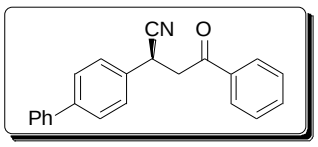
IR (neat): ν = 1679,2246 cm^{-1}. $[\alpha]^{20}_D$ = -37.4 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 – 7.80 (m, 2H), 7.64 – 7.51 (m, 4H), 7.39 (t, J = 7.7 Hz, 3H), 4.58 (t, J = 6.9 Hz, 1H), 3.68 (dd, J = 18.0, 7.3 Hz, 1H), 3.47 (dd, J = 18.0, 6.4 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ=31.7, 44.2, 119.9, 125.1, 126.2, 126.3, 128.1 (d, J = 1.6 Hz), 128.6, 134.1, 135.4, 139.3, 194.1 ppm.

^{19}F NMR (470 MHz, $CDCl_3$): δ = -62.77 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30,1.0 mL/min, 254 nm), t_S(major) =6.177 min, t_R(minor) = 7.02 min.



2-Biphenyl-4-yl-4-oxo-4-phenyl-butyronitrile (2j): White solid; yield 71% (PE/EtOAc = 10:1, v/v), 59% *ee*, m.p. 82–84 ℃; HRMS (ESI) calcd. for$C_{22}H_{17}NONa$

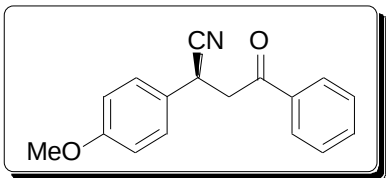
$[M+Na]^+$ 334.1201, Found 334.1200.

IR (neat): ν = 1685,2244 cm^{-1}. $[\alpha]^{20}_D$ = -20.6 (c = 0.1, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.90 (m, 2H), 7.63 – 7.55 (m, 5H), 7.53 – 7.42 (m, 6H), 7.39 – 7.35 (m, 1H), 4.61 (dd, J = 7.7, 6.2 Hz, 1H), 3.76 (dd, J = 18.0, 7.8 Hz, 1H), 3.55 (dd, J = 18.0, 6.1 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2, 44.1, 120.2, 126.7, 127.3, 127.5, 127.7, 128.4, 128.5, 133.5, 133.8, 139.7, 194.2 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) =10.221 min, t_R(minor) = 11.974 min.



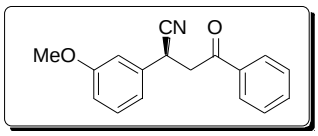
2-(4-Methoxy-phenyl)-4-oxo-4-phenyl-butyronitrile (2k): White solid; yield72% (PE/EtOAc = 10:1, v/v), 58% *ee*, m.p. 119–121 ℃; HRMS (ESI) calcd. for $C_{17}H_{15}NO_2Na$ $[M+H]^+$ 266.1176, Found 266.1172.

IR (neat): ν = 1689,2238 cm^{-1}. $[\alpha]^{20}_D$ = -19.7 (c = 0.1, $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (dd, J = 8.3, 1.1 Hz, 2H), 7.58 (d, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.37 – 7.32 (m, 2H), 6.92 – 6.89 (m, 2H), 4.52 (dd, J = 7.6, 6.3 Hz, 1H), 3.80 (s, 3H), 3.69 (dd, J = 17.9, 7.7 Hz, 1H), 3.49 (dd, J = 17.9, 6.3 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2, 44.6, 55.4, 114.6, 115.7, 120.9, 126.2, 127.2, 128.1, 128.7, 128.8, 159.6, 194.8 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak OD-H (*n*-hexane/2-propanol, 85:15, 1.0 mL/min, 254 nm), t_S(major) =17.03 min, t_R(minor) = 18.511 min.



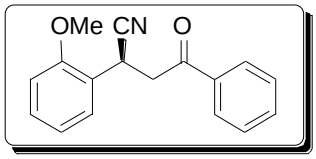
2-(3-Methoxy-phenyl)-4-oxo-4-phenyl-butyronitrile (2l): White solid; yield 85% (PE/EtOAc = 10:1, v/v), 82% *ee*, m.p. 105–107 ℃; HRMS (ESI) calcd. for $C_{17}H_{15}NO_2Na$ $[M+Na]^+$ 288.0995, Found 288.0998.

IR (neat): ν = 1682,2242 cm^{-1}. $[\alpha]^{20}_D$ = -22.5 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (dd, J = 8.1, 0.8 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.29 (dd, J = 16.3, 8.3 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.89 – 6.82 (m, 1H), 4.53 (dd, J = 7.9, 6.0 Hz, 1H), 3.81 (s, 3H), 3.72 (dd, J = 17.9, 8.1 Hz, 1H), 3.50 (dd, J = 18.0, 5.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.9, 44.5, 55.4, 113.3, 113.8, 119.6, 128.1, 128.8, 130.4, 133.9, 160.2, 194.6 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) =13.669min, t_R(minor) =26.122 min.



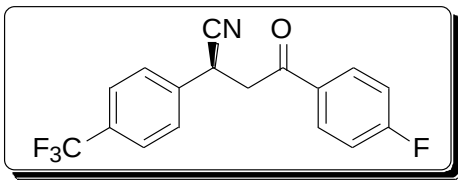
2-(2-Methoxy-phenyl)-4-oxo-4-phenyl-butyronitrile (2m): White solid; yield 76% (PE/EtOAc = 10:1, v/v), 56% *ee*, m.p. 85–87 ℃; HRMS (ESI) calcd. for $C_{17}H_{15}NO_2Na$ $[M+Na]^+$ 288.0995, Found 288.0996.

IR (neat): ν = 1656 cm^{-1}. $[\alpha]^{20}_D$ = -18.3 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.98 – 7.88 (m, 2H), 7.58 (d, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.04 – 6.93 (m, 2H), 6.87 (dd, J = 8.2, 2.1 Hz, 1H), 4.54 (dd, J = 8.1, 5.8 Hz, 1H), 3.82 (s, 3H), 3.75 – 3.66 (m, 1H), 3.50 (dd, J = 17.9, 5.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.5, 115.6, 115.9, 116.4, 121.1, 131.2, 144.9, 160.0, 164.4, 166.9, 188.8 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) =11.622min, t_R(minor) =23.853 min.



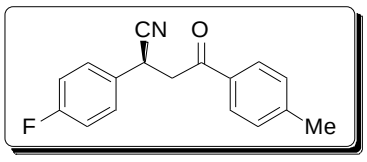
4-(4-Fluoro-phenyl)-4-oxo-2-(4-trifluoromethyl-phenyl)-butyronitrile (2n): White solid; yield 91% (PE/EtOAc = 10:1, v/v), 75% ee, m.p. 113–115 ℃; HRMS (ESI) calcd. for $C_{17}H_{11}F_4NONa$ $[M+Na]^+$ 344.0669, Found 344.0668.

IR (neat): ν = 1679, 2249 cm^{-1}. $[\alpha]^{20}_D$ = -38.6 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 – 7.92 (m, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.21 – 7.08 (m, 2H), 4.64 (t, J = 6.9 Hz, 1H), 3.73 (dd, J = 18.0, 7.4 Hz, 1H), 3.51 (dd, J = 18.0, 6.3 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.7, 44.1, 116.0, 116.2, 119.8, 122.4, 125.1, 126.3 (q, J=3.7) , 128.1,130.5, 131.3, 131.9 (d, J=3.0) , 139.1, 165.0, 167.6, 192.6ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = -102.98, -62.78 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) =7.65 min, t_R(minor) = 8.808 min.



2-(4-Fluoro-phenyl)-4-oxo-4-p-tolyl-butyronitrile (2o): White solid; yield 90% (PE/EtOAc = 10:1, v/v), 80% *ee*, m.p. 102–103 ℃; HRMS (ESI) calcd. for $C_{17}H_{14}FNONa$ $[M+Na]^+$ 290.0952, Found 290.0958.

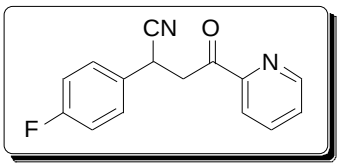
IR (neat): ν = 1678, 2247 cm^{-1}. $[\alpha]^{20}_D$ = -28.6 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.81 (d, J = 8.3 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.28 – 7.25 (m, 2H), 7.12 – 7.03 (m, 2H), 4.56 (t, J = 6.9 Hz, 1H), 3.68 (dd, J = 17.8, 7.4 Hz,

1H), 3.48 (dd, J = 17.8, 6.5 Hz, 1H), 2.41 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 31.2, 44.3, 116.1, 120.6, 128.2,129.2, 129.6, 131.2 (d, J = 3.4 Hz) , 133.2, 145.0, 161.3, 163.7, 194.0ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = -113.34 ppm.

The enantiomeric excess was determined by HPLC on Chiralpak AS-H (*n*-hexane/2-propanol, 70:30, 1.0 mL/min, 254 nm), t_S(major) =9.765 min, t_R(minor) = 15.222min.



2-(4-Fluoro-phenyl)-4-oxo-4-pyridin-2-yl-butyronitrile (2p)

White solid; yield 88% (PE/EtOAc = 10:1, v/v), 50% *ee*, m.p. 100–102 ℃; HRMS (ESI) calcd. for $C_{15}H_{11}N_2OFNa$ $[M+Na]^+$ 277.0748.Found 277.0747. $[\alpha]^{20}_D$ = -27.6 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.81 (d, J = 4.7 Hz, 1H), 10.22 (d, J = 7.8 Hz, 1H), 10.02 (td, J = 7.7, 1.5 Hz, 1H), 9.73 – 9.53 (m, 3H), 9.23 (t, J = 8.6 Hz, 2H), 6.75 – 6.58 (m, 1H), 6.13 (dd, J = 18.6, 8.0 Hz, 1H), 5.97 (dd, J = 18.6, 6.3 Hz, 1H)ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ=196.5, 163.7, 161.3, 152.2, 149.1, 137.1, 131.2, 131.2, 129.4, 129.3, 127.9, 122.1, 120.5, 116.2, 116.0, 43.7, 31.2, 29.7ppm.

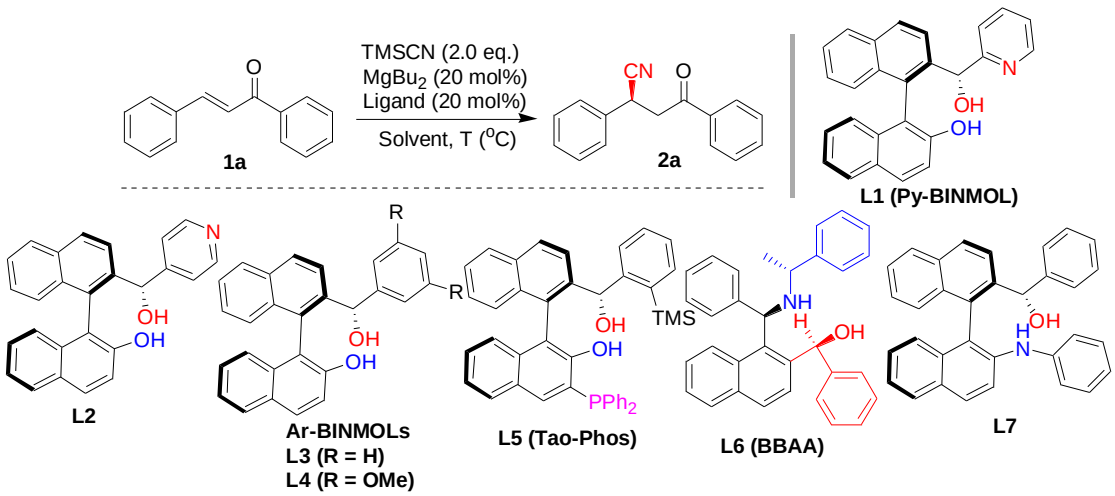
The enantiomeric excess was determined by HPLC on Chiralpak AS-H (n-hexane/2-propanol, 70:30,1.0 mL.min^{-1}, 254 nm), t_S(major) =11.717 min, t_R(minor) = 14.018 min.

References

[1] a) G. Gao, F. L. Gu, J. X. Jiang, K. Jiang, C. Q. Sheng, G. Q. Lai, L. W. Xu, *Chem. Eur. J.* 2011, **17**, 2698-2703; b) L. S. Zheng, K. Z. Jiang, Y. Deng, X. F. Bai, G. Gao, F. L. Gu, L. W. Xu, *Eur. J. Org. Chem.* 2013, 748-755.

[2] E. Fernández-Mateos, B. Maciá, M. Yus, *Adv. Synth. Catal.* 2013, **355**, 1249-1254.

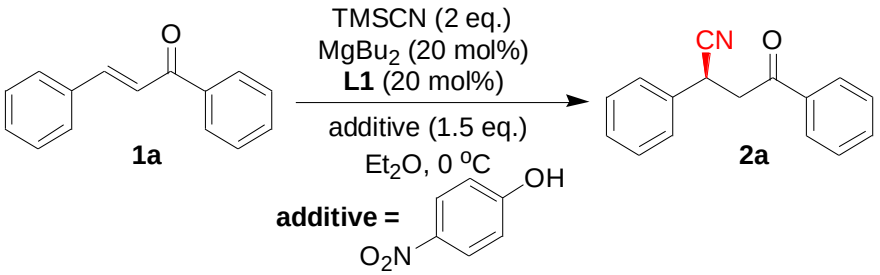
Table S1. Effect of chiral ligands and solvents on the catalytic asymmetric conjugate addition of cyanide to chalcone **1a**.

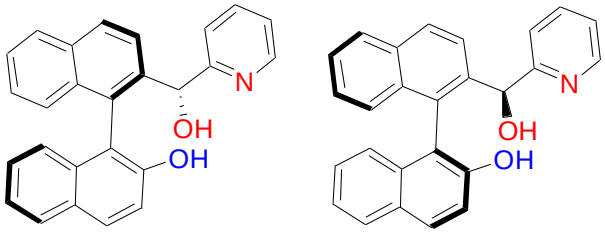


Entry[a]	Ligand	Solvent	T (°C)	Yield (%)[b]	Ee (%)[c]
1	**L1**	DCM	0	50	24
2	**L1**	THF	0	<5	-
3	**L1**	toluene	0	56	30
4	**L1**	1,4-dioxane	20	40	19
5	**L1**	CH_3CN	0	<5	-
6	**L1**	Et_2O	20	81	48
7	**L2**	Et_2O	20	68	38
8	**L3**	Et_2O	20	72	25
9	**L4**	Et_2O	20	91	0
10	**L5**	Et_2O	20	40	15
11	**L6**	Et_2O	20	71	0
12	**L7**	Et_2O	20	52	0
13	**No ligand**	Et_2O	20	86	-
14	**L1**[e]	Et_2O	20	NR[d]	-
15	**L1**[e,f]	Et_2O	20	NR[d]	-

Note: [a] Reaction conditions: 20 mol% of $MgBu_2$, 20 mol% of ligand (**L1-L7**), **1a** (0.25 mmol), and TMSCN (0.5 mmol). [b] Isolated yields. [c] The *ee* value or *e.r.* was determined by chiral HPLC. [d] No reaction. [e] It should be noted that both no Bu_2Mg and the use of Et_2Zn or Et_3Al as catalyst led to no reaction. [f] The addition of 1.2 eq. of *para*-nitrophenol.

Table S2. Effect of chiral ligand **L1** with varied optical purity on the catalytic asymmetric conjugate addition of cyanide to chalcone **1a**.





(*R*,*R*)-**L1** (*S*,*S*)-**L1**

(*R*,*R*)-**L1**/(*S*,*S*)-**L1**	de/%	yield/%	ee/%
50:50	0	47	0
55:45	10	51	8
60:40	20	71	15
65:35	30	68	18
70:30	40	77	32
75:25	50	81	40
80:20	60	75	50
85:15	70	90	54
90:10	80	86	60
95:5	90	85	72
100:0	100	89	92

Table S3. The effect of solvent amount on the catalytic asymmetric conjugate addition of cyanide to chalcone **1a**

Solvent/mL	yield/%	ee/%
1	88	84
2	80	83
4	89	92
6	94	78
8	76	77
10	76	70

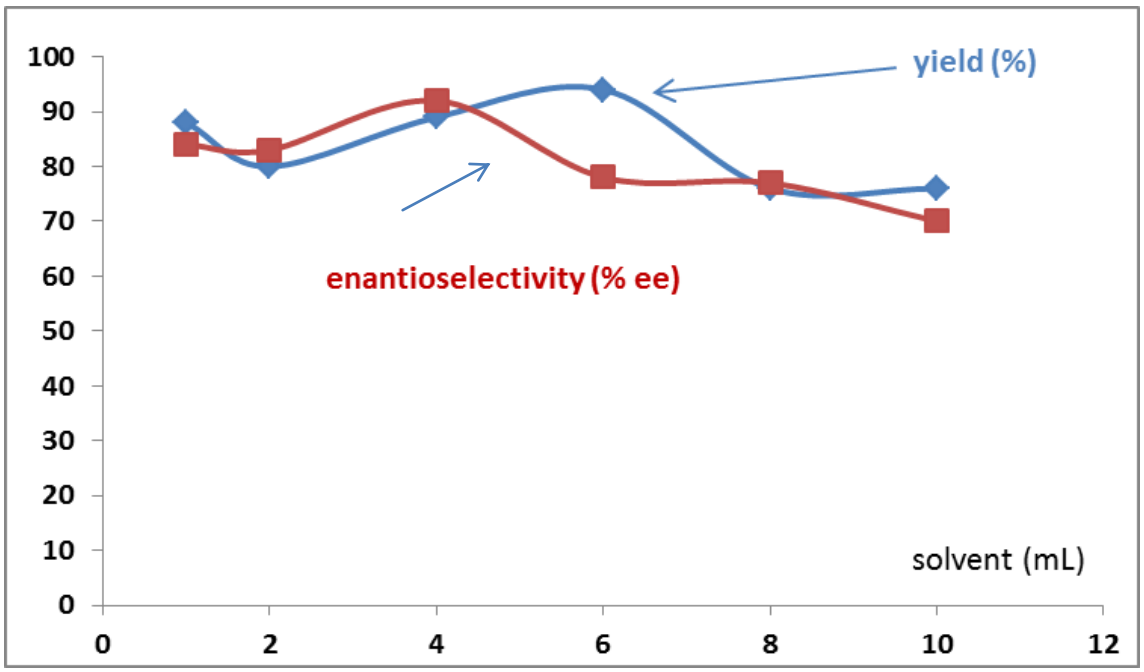


Table S4. Conversion/reaction time data for magnesium-catalyzed conjugate addition of cyanide to chalcone

Reaction time/hour	GC-MS yield/%	
	no ligand	With ligand **L1**
1	30	37
2	33	42
3	41	46
4	44	48
5	51	56
6	54	62
7	63	79

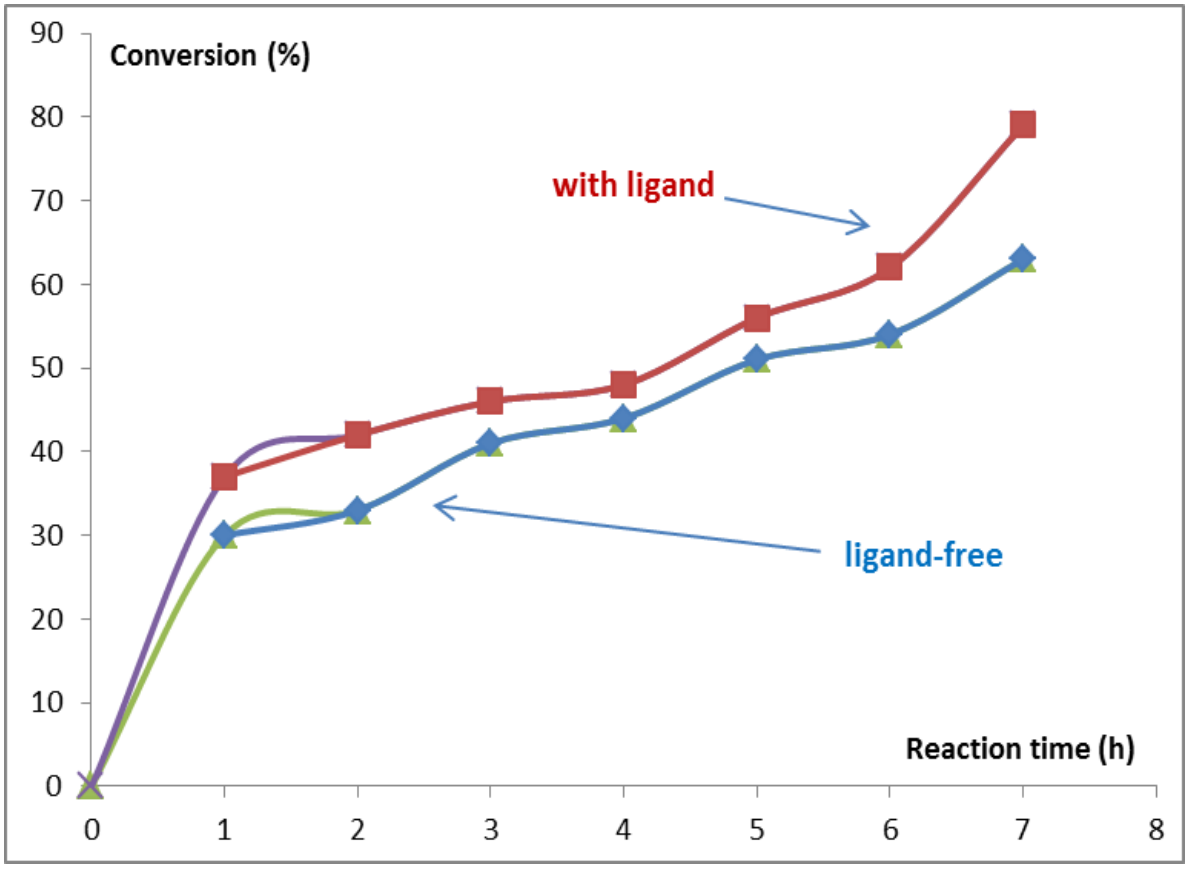


Figure S1-S6

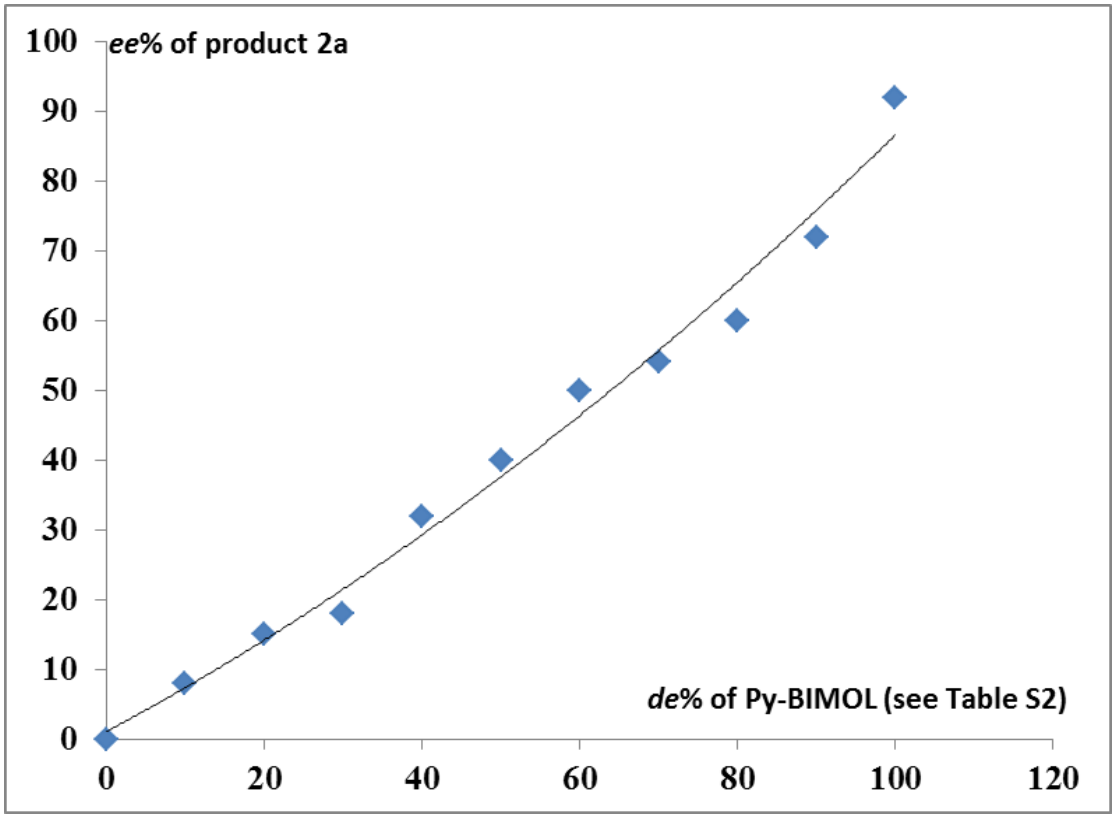


Figure S1. Correlation between the *de* of Py-BINMOL **L1** and the *ee* of product **2a** of benzaldehyde under optimal conditions.

6. ESI-MS analysis of catalyst systems

As showed in Figure S3 and S4, a major peak at *m/z* = 920.5 (Figure S1, *see* Supporting Information) was found, which could be identified as the silylated magnesium complex came from the cation $[2\text{Py-BINOL} + \text{Mg} + 2\text{TMS}]^+$ (*m/z* = 920.3).

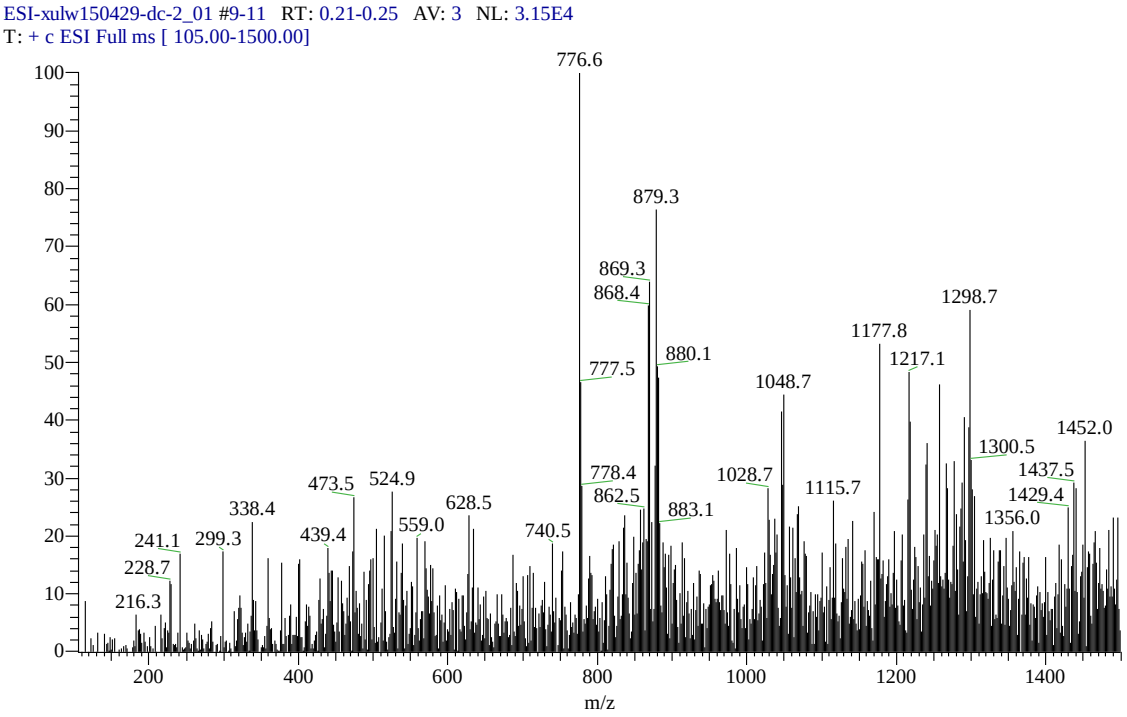
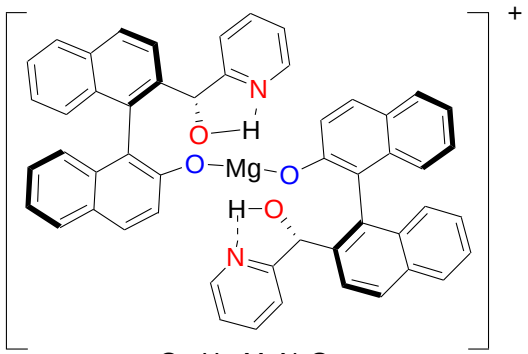


Figure S2. The ESI-MS spectra of the mixture of Py-BINMOL and Mg(*n*-Bu)$_2$



$C_{52}H_{36}MgN_2O_4$
Exact Mass: 776.3

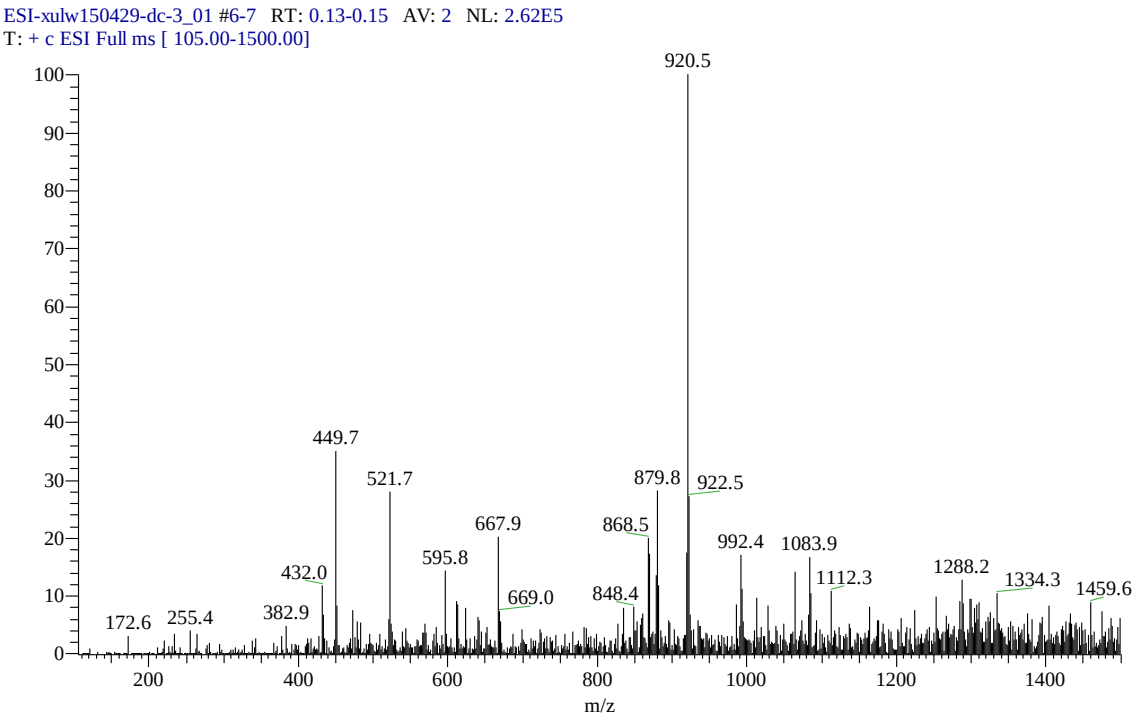
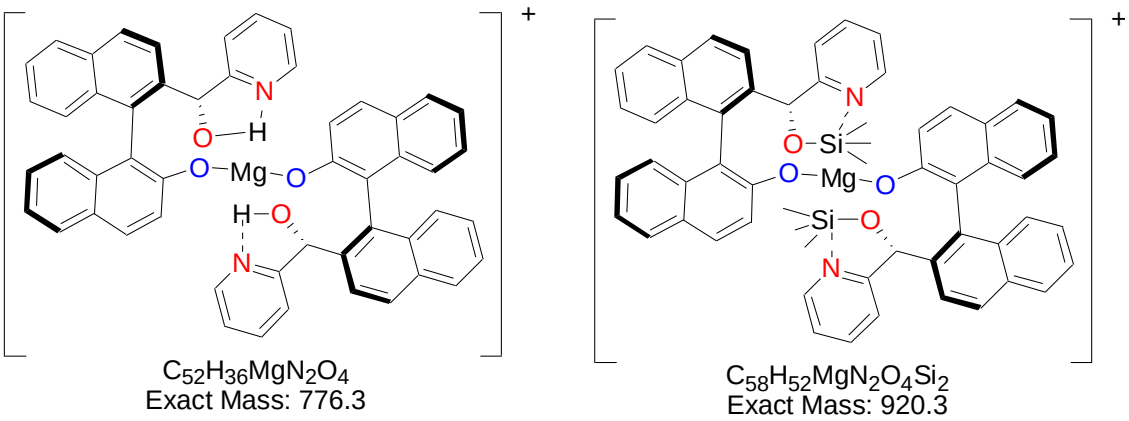


Figure S3. The ESI-MS spectra of the mixture of Py-BINMOL, TMSCN, and Mg(*n*-Bu)$_2$



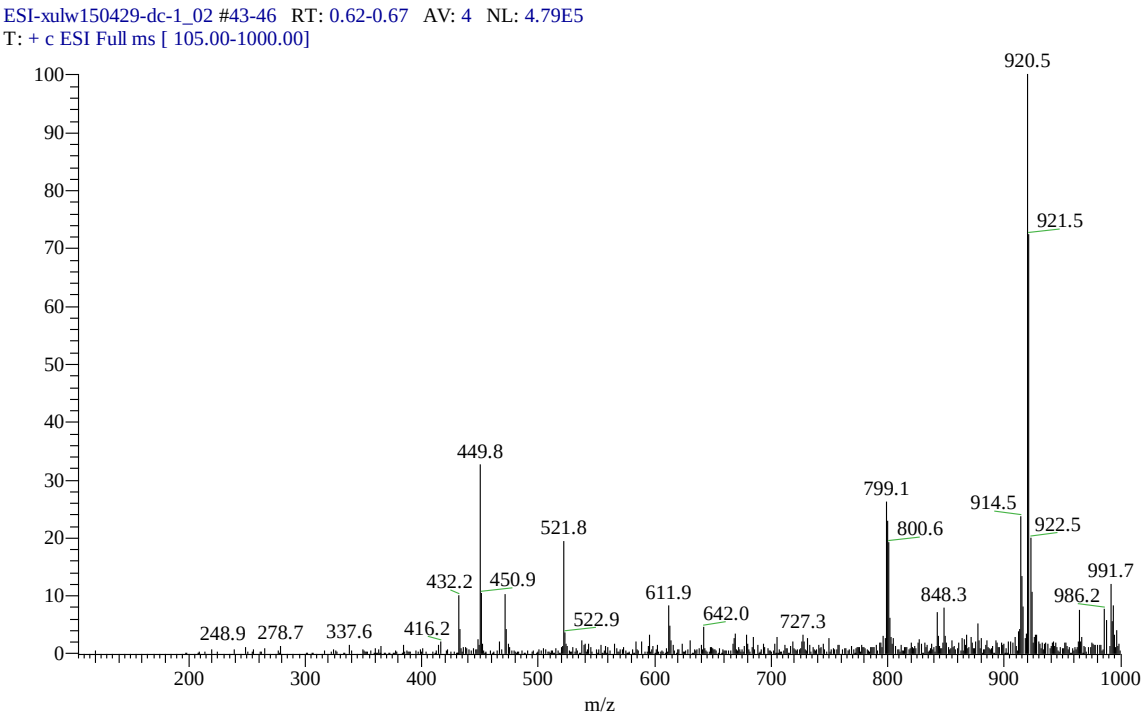
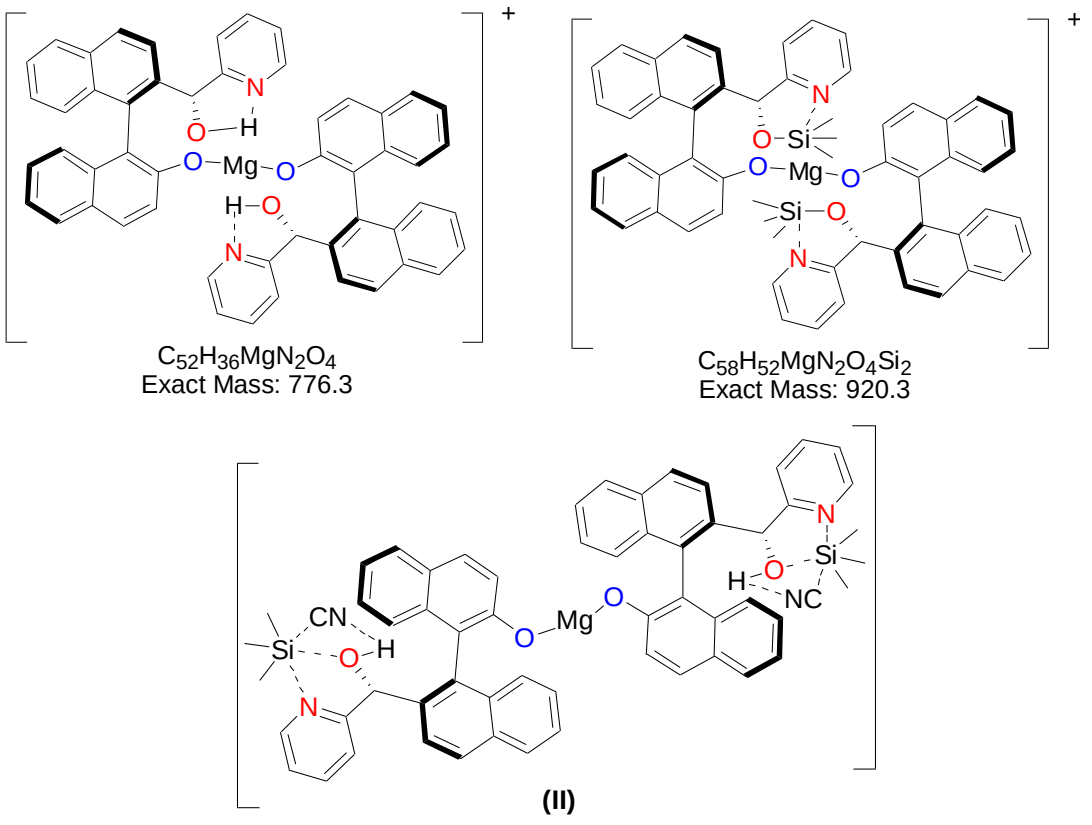
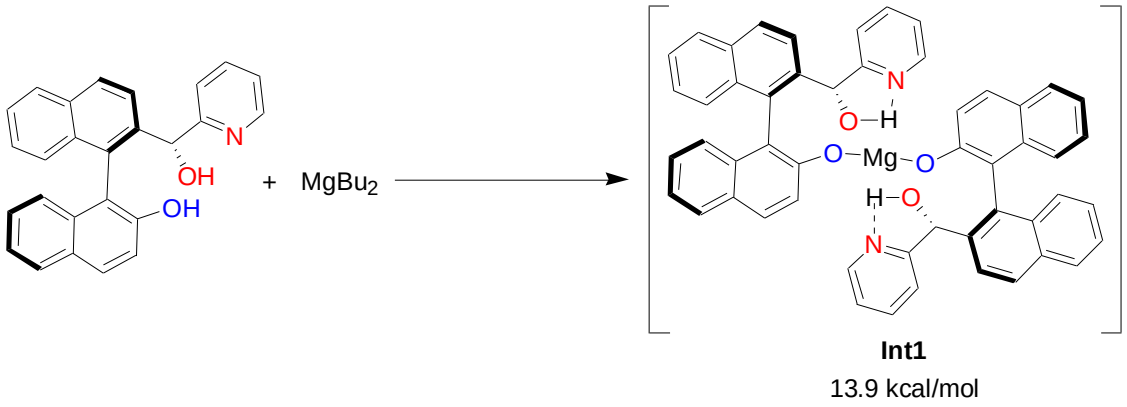


Figure S4. The ESI-MS spectra of the reaction mixture of Py-BINMOL, TMSCN, Mg(*n*-Bu)$_2$, *para*-nitrophenol, and chalcone **1a**





Int1

13.9 kcal/mol

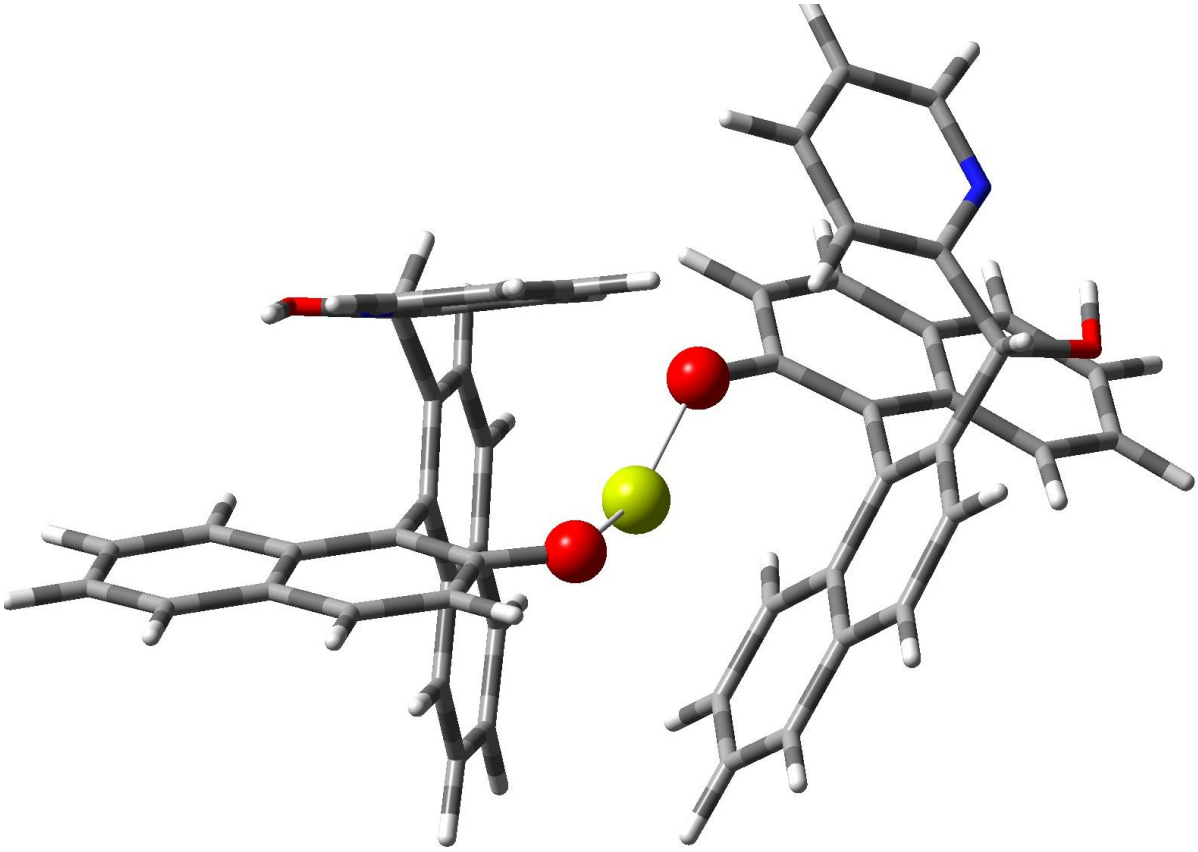
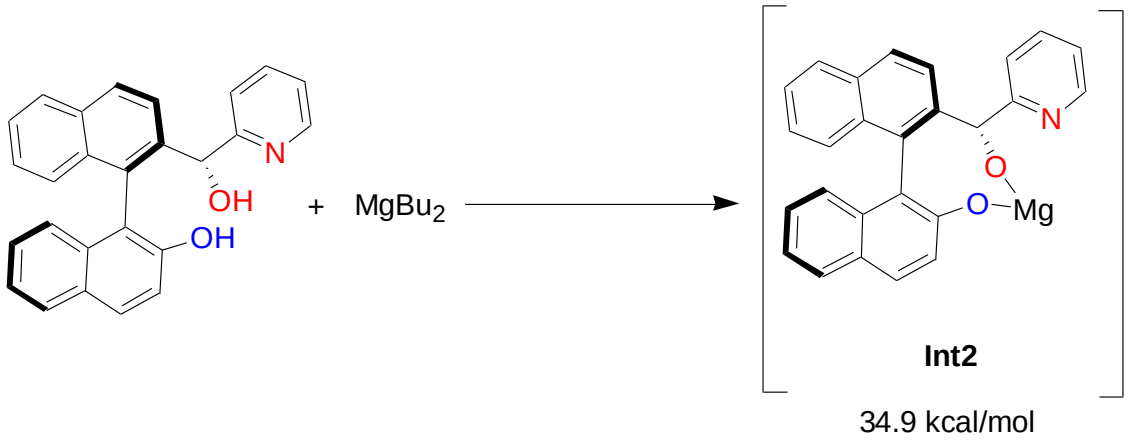


Figure S5. Frontier orbital energy calculated at B3LYP/6-31G(d,p) level of theory for possible Mg-complex with two molecules of Py-BINMOL (**Ia**: **13.9** kcal/mol).



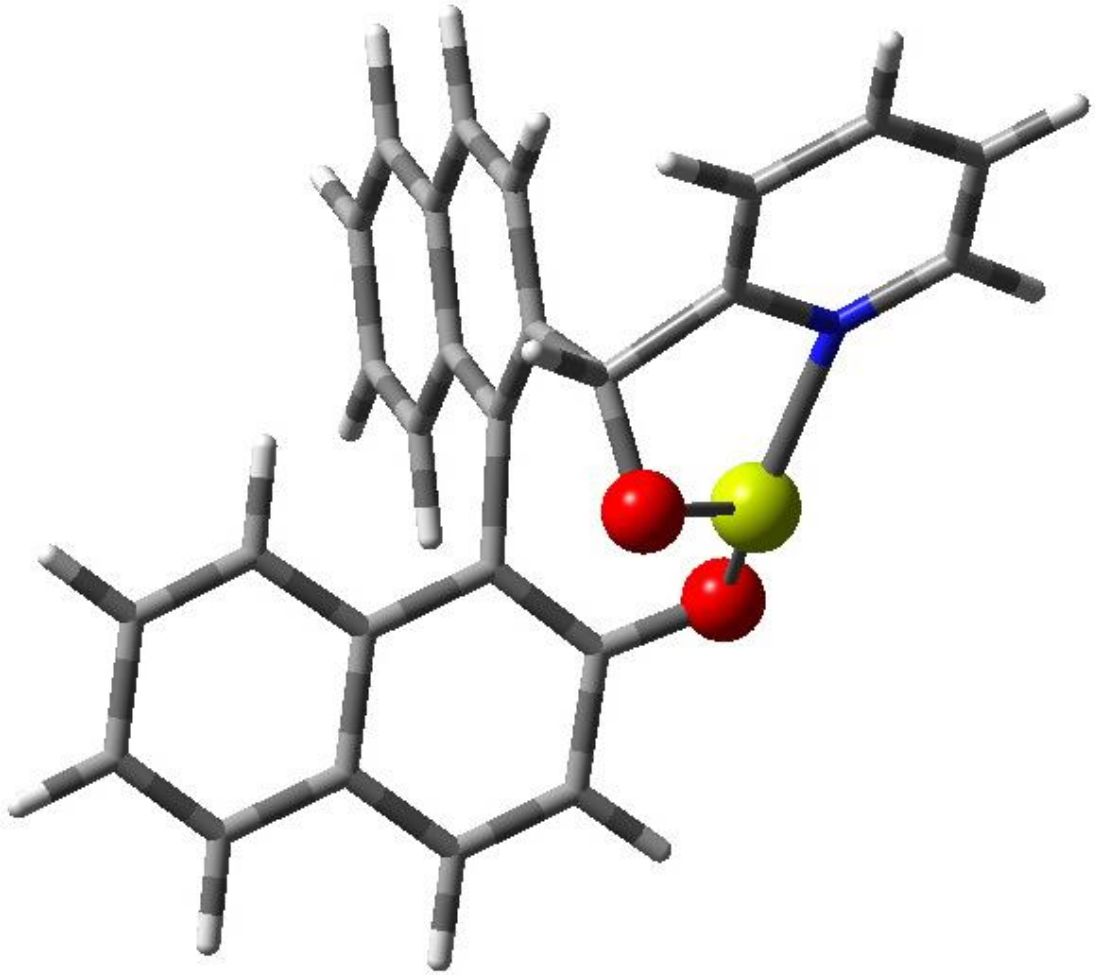
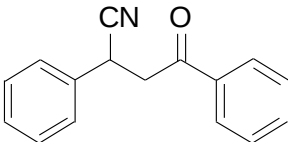
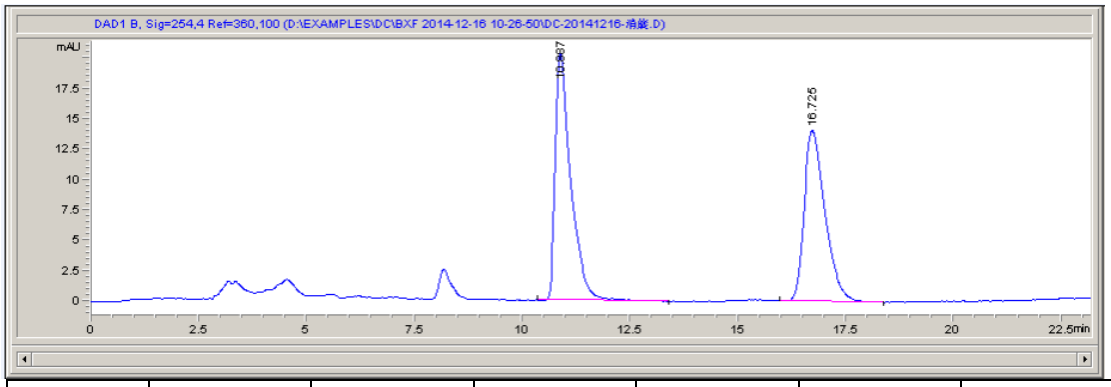


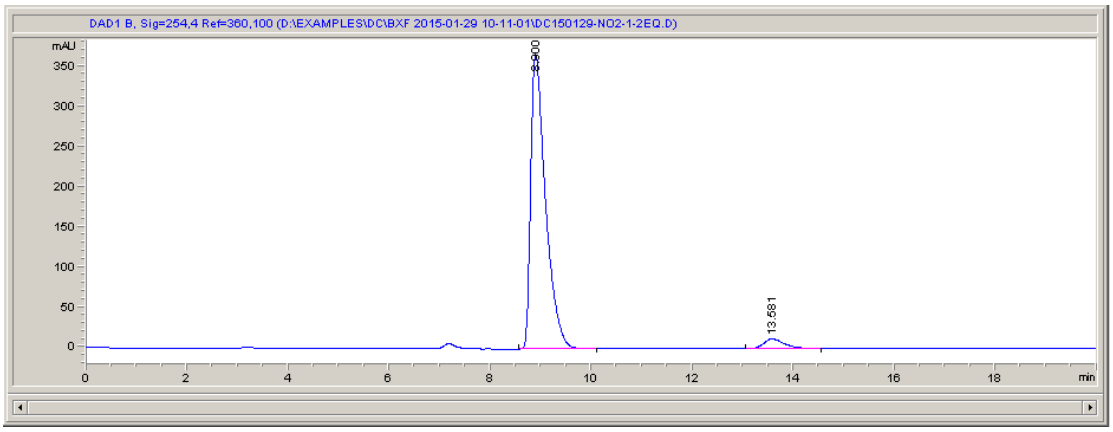
Figure S6. Frontier orbital energy calculated at B3LYP/6-31G(d,p) level of theory for possible Mg-complex with one molecule of Py-BINMOL (**Ib**: **34.9** kcal/mol).

7. HPLC analysis of chiral product 2

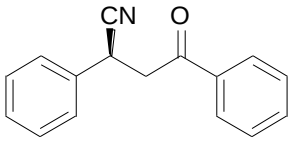


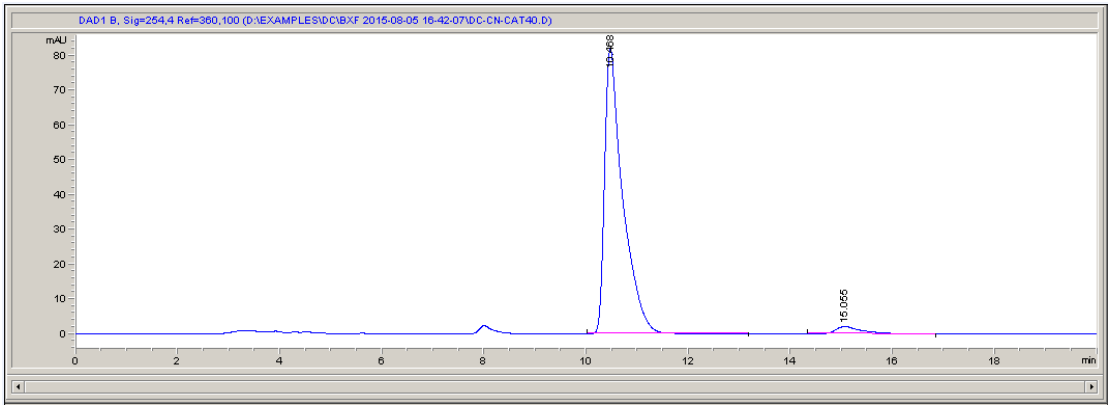


#	Time	Area	Height	Width	Symmetry	Area %
1	10.887	506.6	20.4	0.3584	0.468	51.592
2	16.725	475.4	14	0.5111	0.64	48.408

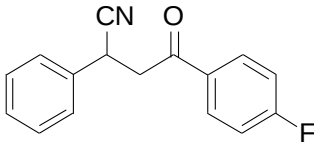


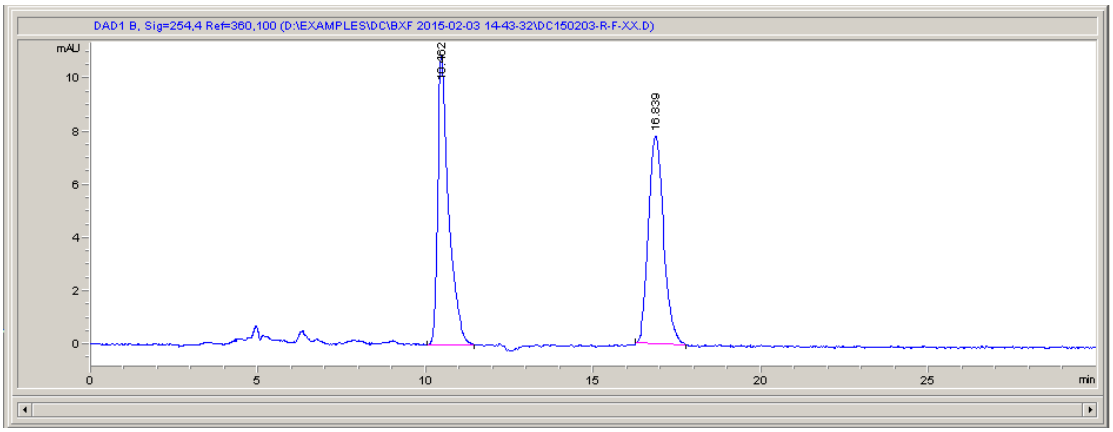
#	Time	Area	Height	Width	Symmetry	Area %
1	8.9	7451.8	366.4	0.3013	0.459	95.797
2	13.581	327	11.8	0.4187	0.654	4.203



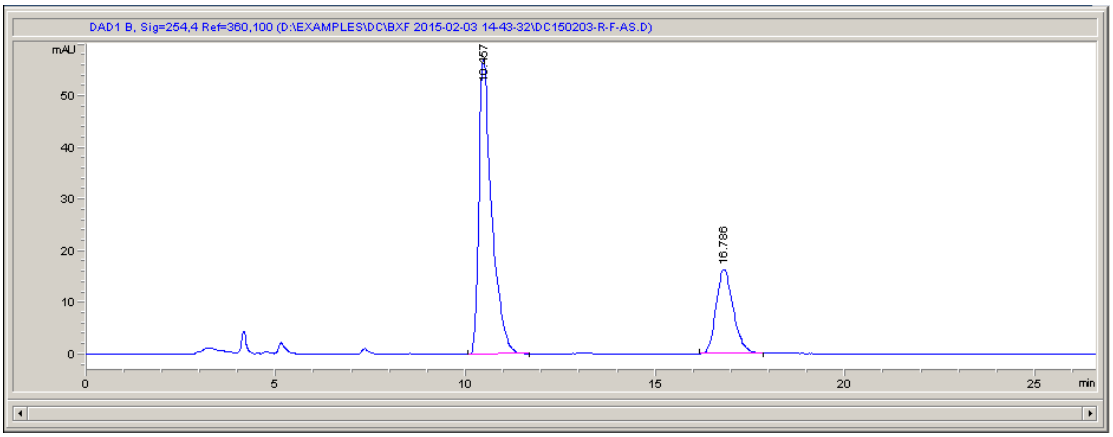


#	Time	Area	Height	Width	Symmetry	Area %
1	10.468	2039.9	81.7	0.3591	0.422	96.372
2	15.055	76.8	2.1	0.5195	0.467	3.628

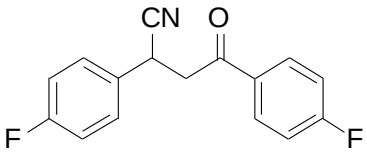


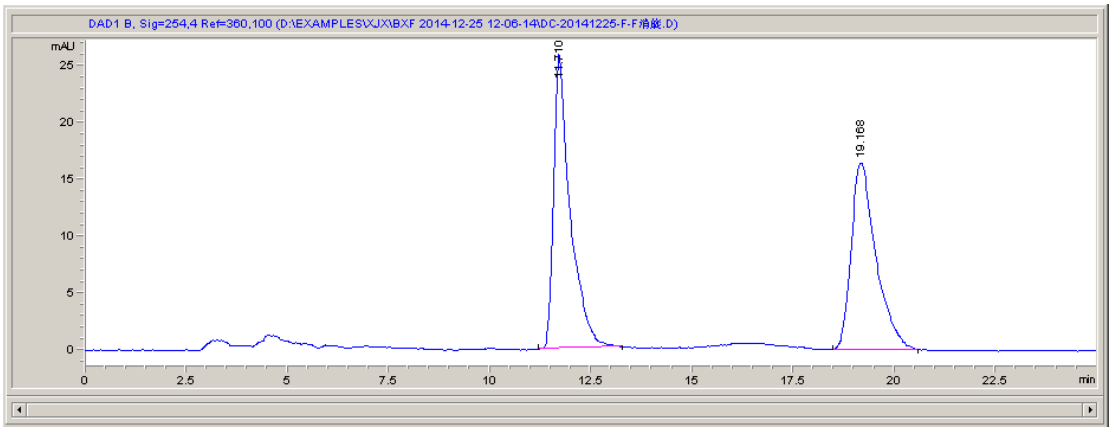


#	Time	Area	Height	Width	Symmetry	Area %
1	10.462	251.8	10.8	0.3349	0.526	50.599
2	16.839	245.9	7.8	0.4534	0.821	49.401

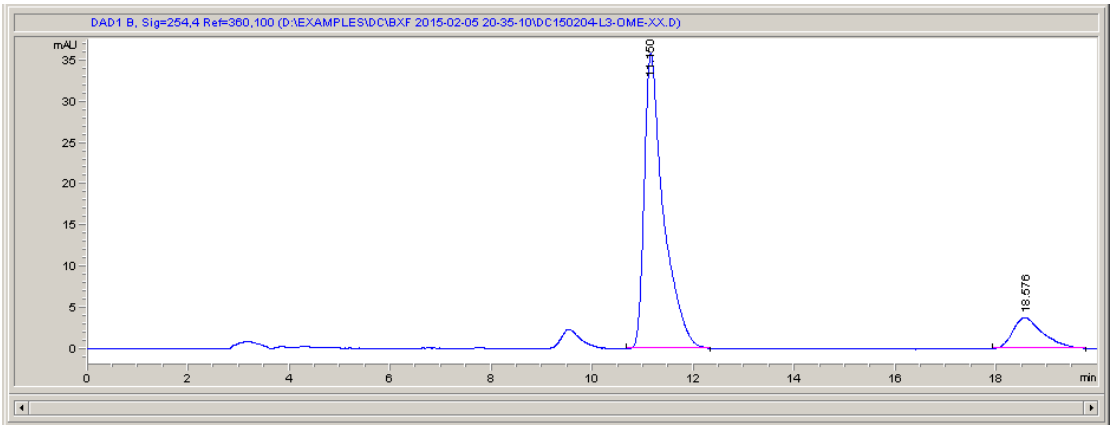


#	Time	Area	Height	Width	Symmetry	Area %
1	10.457	1348.1	57.4	0.3422	0.501	72.467
2	16.786	512.2	16.3	0.4786	0.783	27.533

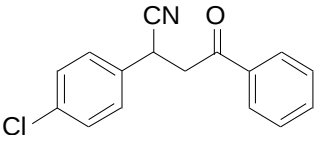


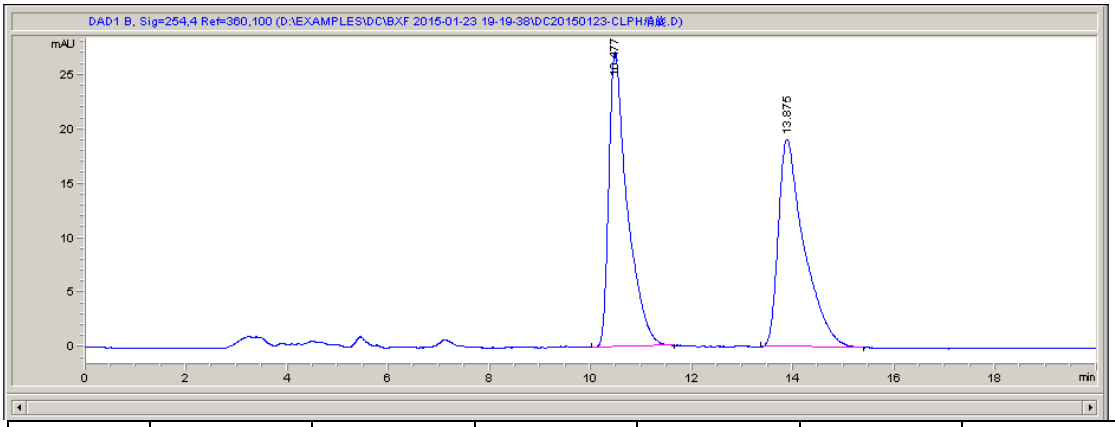


#	Time	Area	Height	Width	Symmetry	Area %
1	11.71	738.7	25.8	0.4096	0.459	51.349
2	19.168	699.9	16.4	0.5732	0.605	48.651

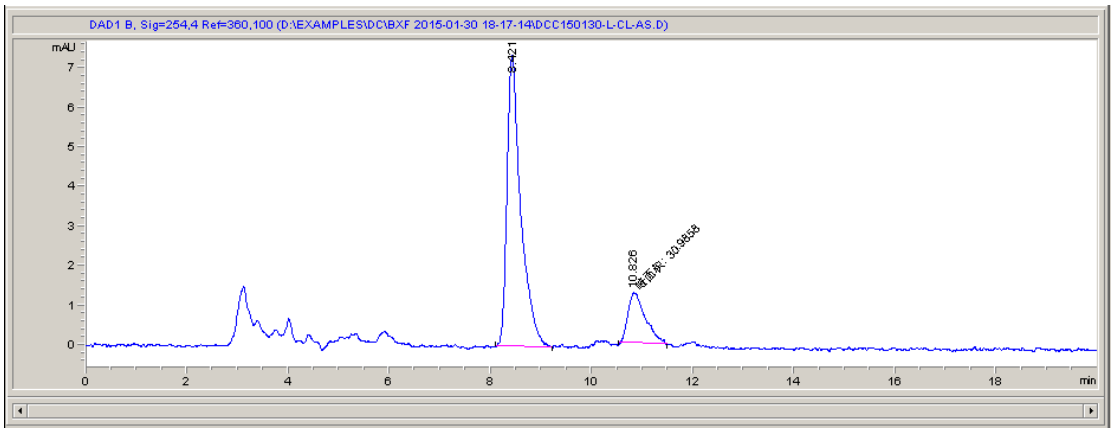


#	Time	Area	Height	Width	Symmetry	Area %
1	11.15	946.3	35.8	0.3782	0.437	85.915
2	18.576	155.1	3.8	0.5036	0.719	14.085

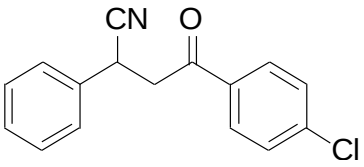


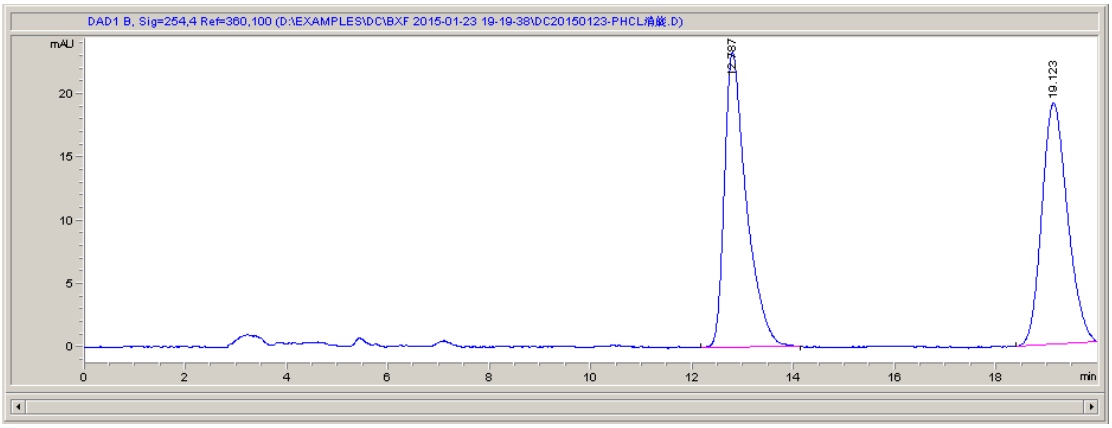


#	Time	Area	Height	Width	Symmetry	Area %
1	10.477	687.5	27	0.3646	0.462	50.286
2	13.875	679.7	19.1	0.5054	0.461	49.714



#	Time	Area	Height	Width	Symmetry	Area %
1	8.421	140.8	7.4	0.2753	0.529	81.964
2	10.826	31	1.3	0.4029	0.483	18.036





#	Time	Area	Height	Width	Symmetry	Area %
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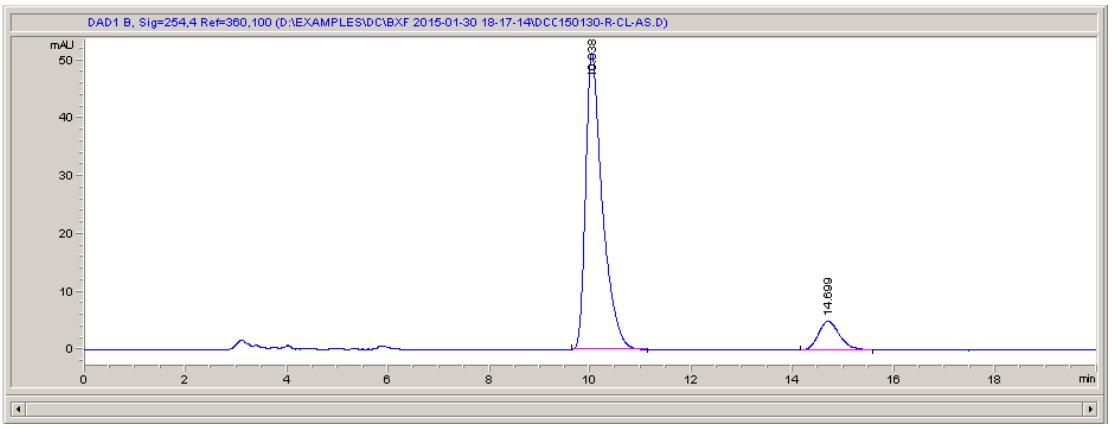
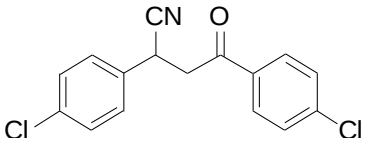
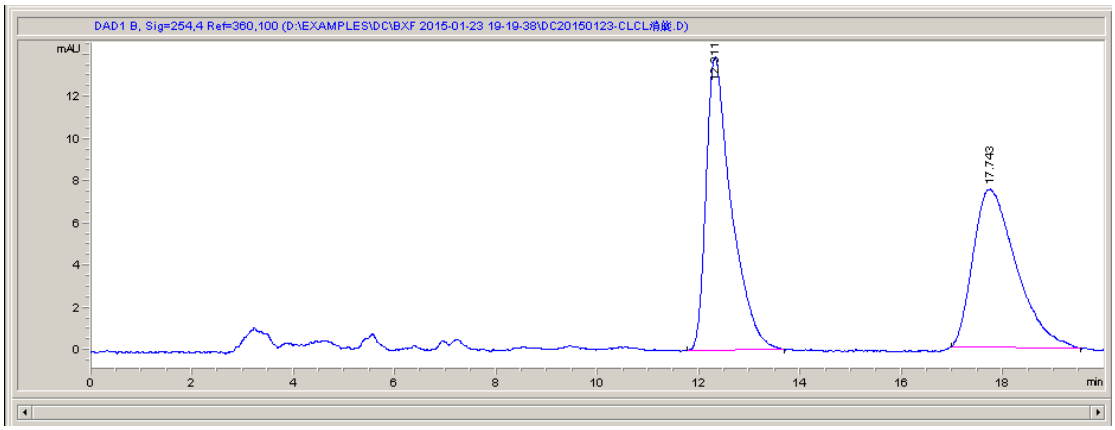
2	19.123	672.2	19	0.5179	0.802	48.773

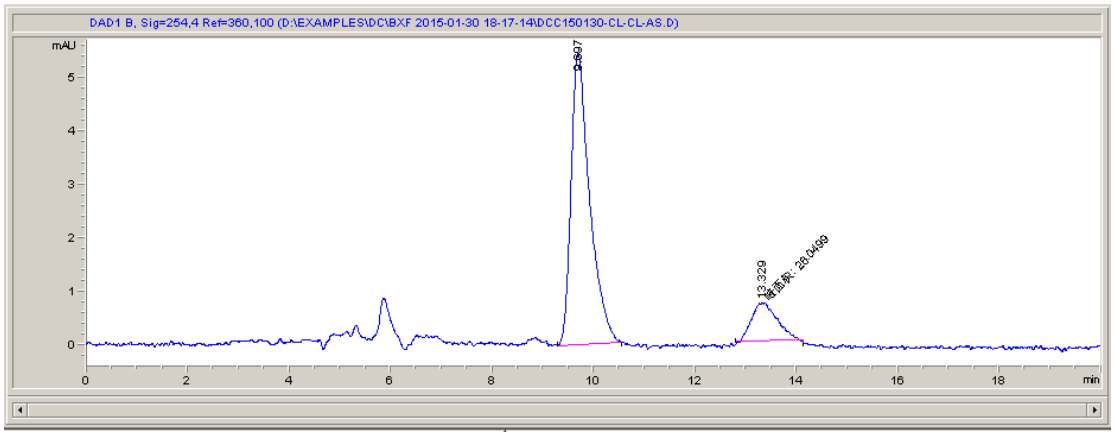


#	Time	Area	Height	Width	Symmetry	Area %
1	10.038	1188.4	51.2	0.3429	0.556	89.247
2	14.699	143.2	5	0.3832	0.799	10.753

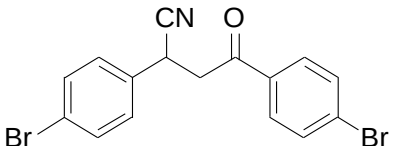


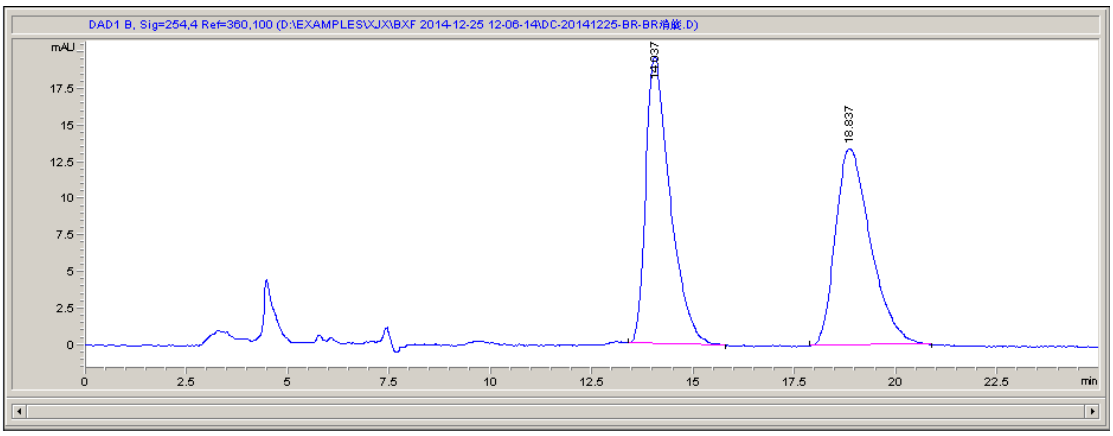


#	Time	Area	Height	Width	Symmetry	Area %
1	12.311	484	13.9	0.4843	0.502	52.146
2	17.743	445.9	7.5	0.7071	0.633	47.854



#	Time	Area	Height	Width	Symmetry	Area %
1	9.697	139.7	5.4	0.3613	0.581	84.280
2	13.329	26	0.72	0.6017	0.713	15.720





#	Time	Area	Height	Width	Symmetry	Area %
1	14.037	820.4	19.7	0.5826	0.535	50.184
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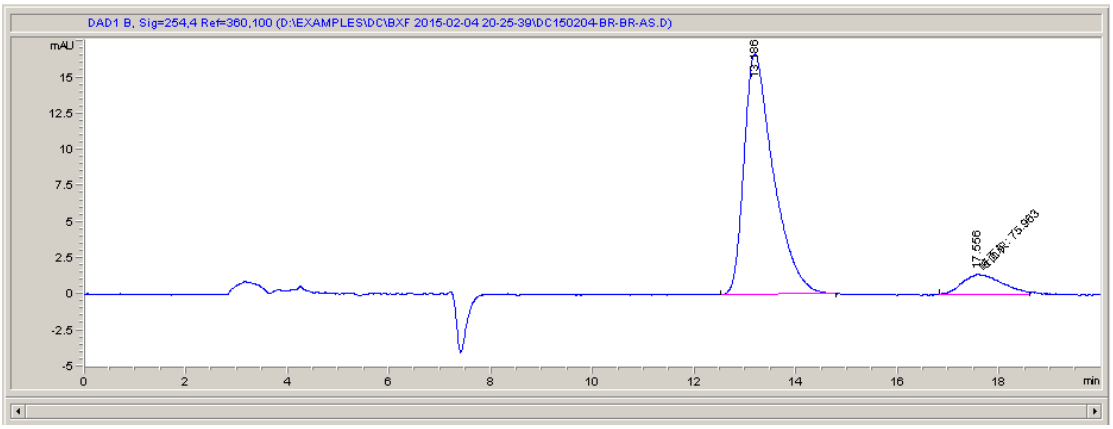

#	Time	Area	Height	Width	Symmetry	Area %
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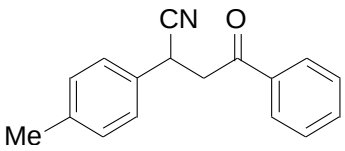
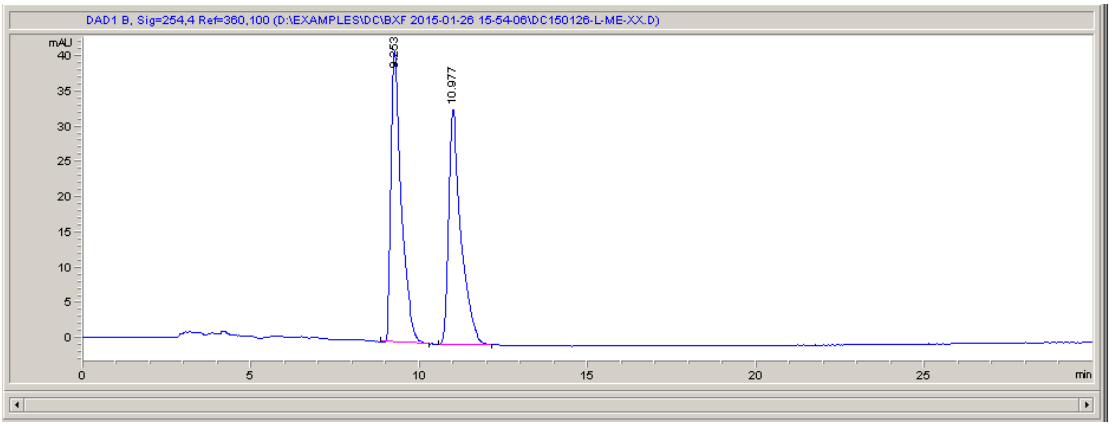
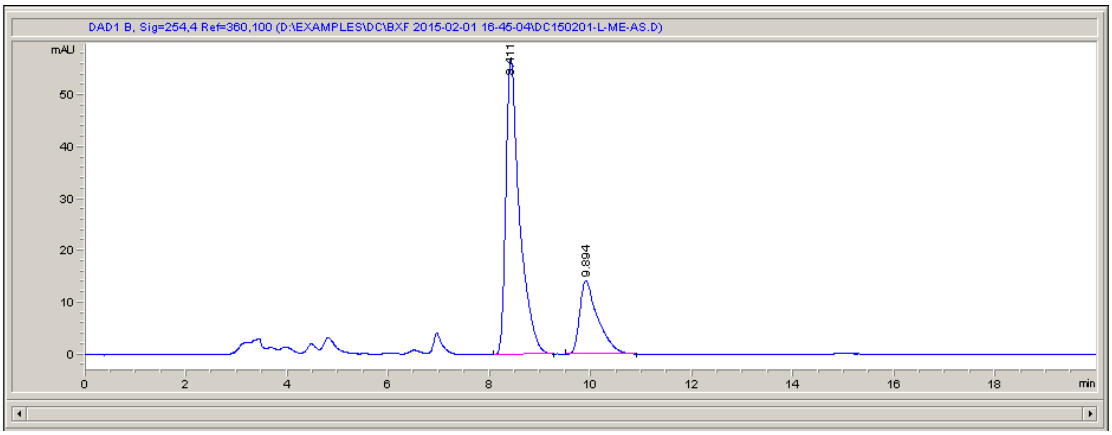
2	17.556	76	1.4	0.8963	0.58	10.165

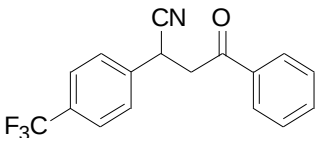


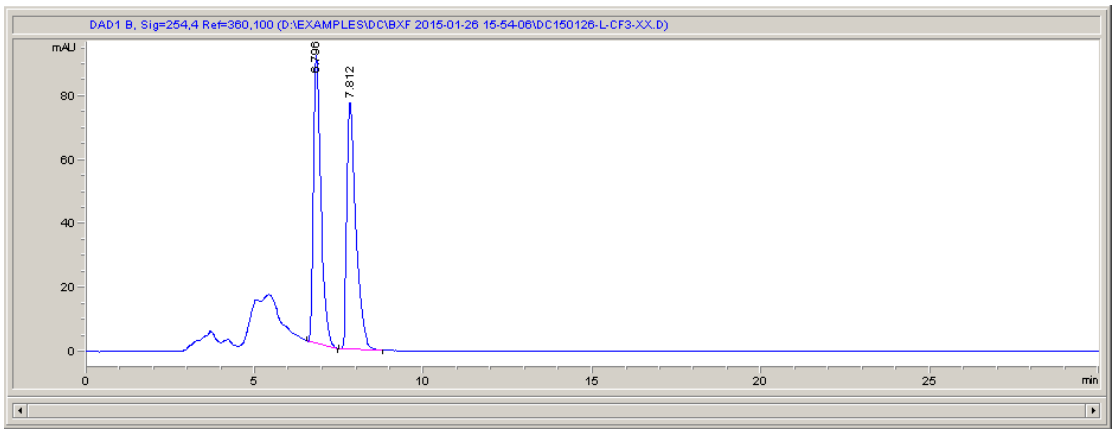


#	Time	Area	Height	Width	Symmetry	Area %
1	9.253	862	41.3	0.2996	0.492	49.981
2	10.977	862.7	33.3	0.3725	0.485	50.019

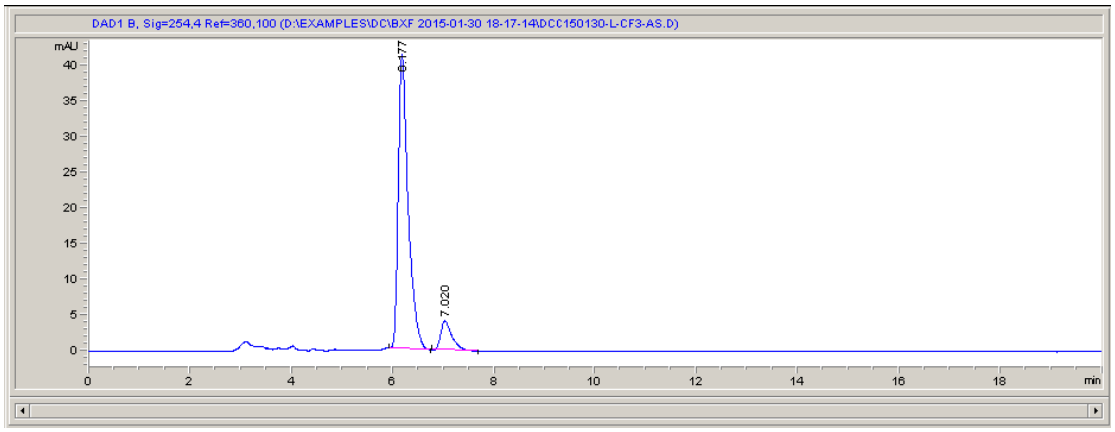


#	Time	Area	Height	Width	Symmetry	Area %
1	8.411	1084.9	57.1	0.2736	0.505	75.439
2	9.894	353.2	14.1	0.3561	0.465	24.561

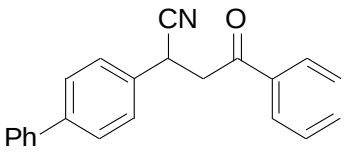


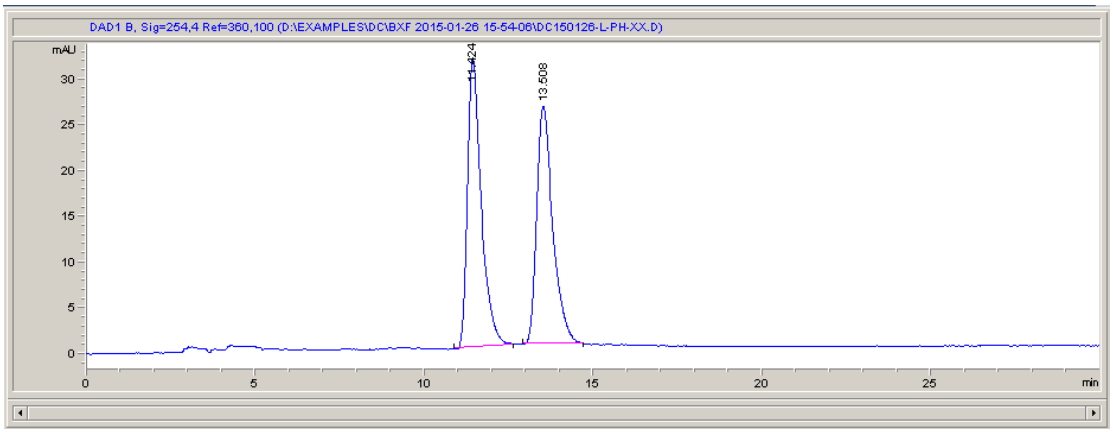


#	Time	Area	Height	Width	Symmetry	Area %
1	6.796	1388.2	90	0.2259	0.528	49.645
2	7.812	1408.1	77.3	0.2665	0.525	50.355



#	Time	Area	Height	Width	Symmetry	Area %
1	6.177	556.7	41.2	0.1996	0.557	89.633
2	7.020	64.4	4.1	0.2216	0.551	10.367





#	Time	Area	Height	Width	Symmetry	Area %
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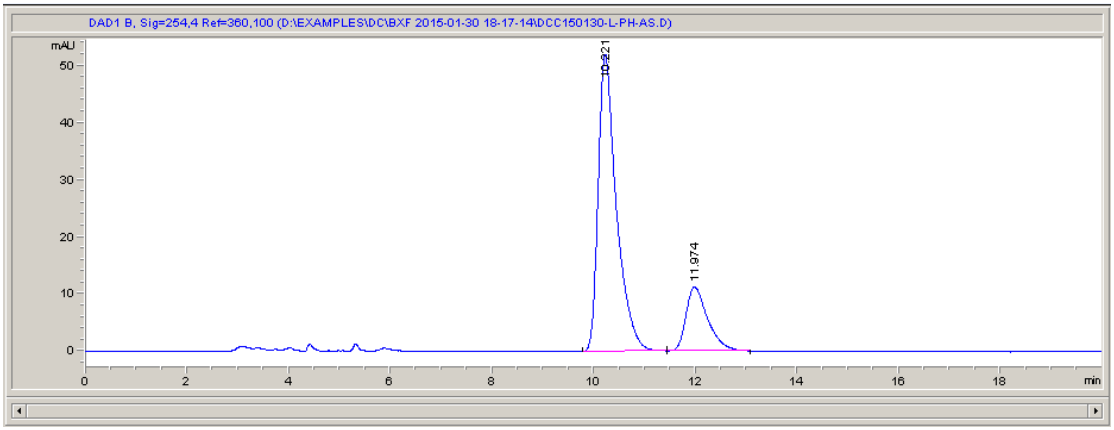
2	13.508	849.1	26	0.4796	0.605	49.177



#	Time	Area	Height	Width	Symmetry	Area %
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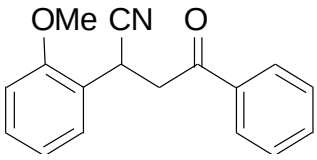
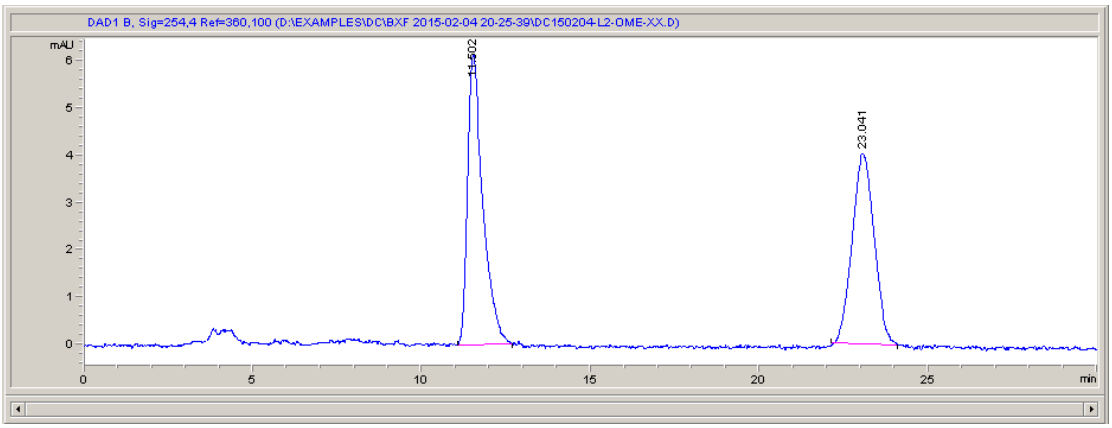
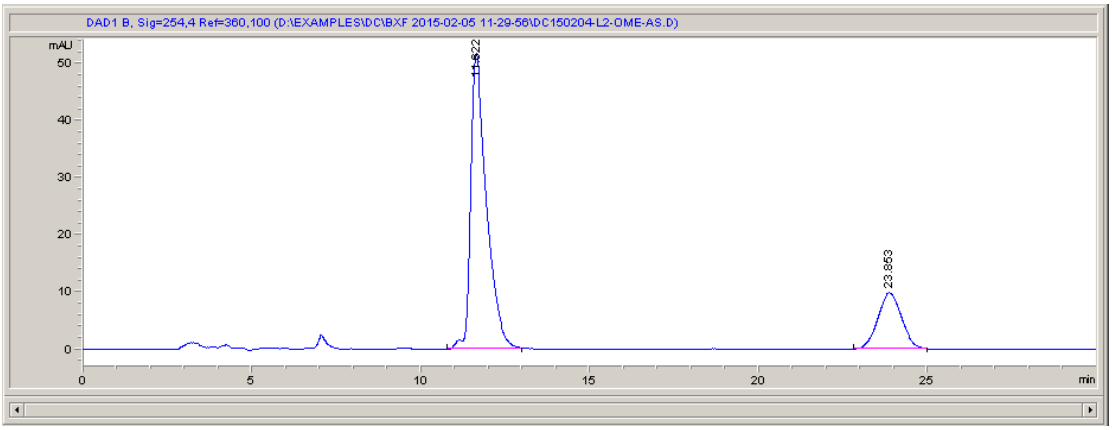
2	11.974	330.6	11.2	0.4182	0.591	20.400





#	Time	Area	Height	Width	Symmetry	Area %
1	11.502	193.6	6.1	0.4274	0.514	51.329
2	23.041	183.6	4	0.5571	0.901	48.671



#	Time	Area	Height	Width	Symmetry	Area %
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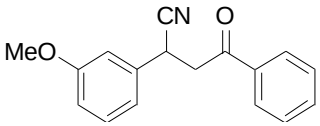
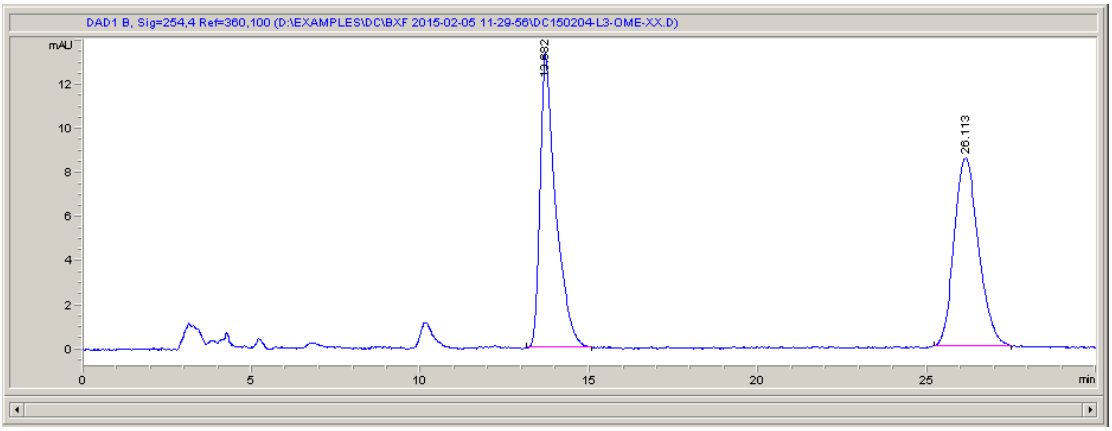
2	23.853	479.9	9.9	0.606	0.937	22.076





#	Time	Area	Height	Width	Symmetry	Area %
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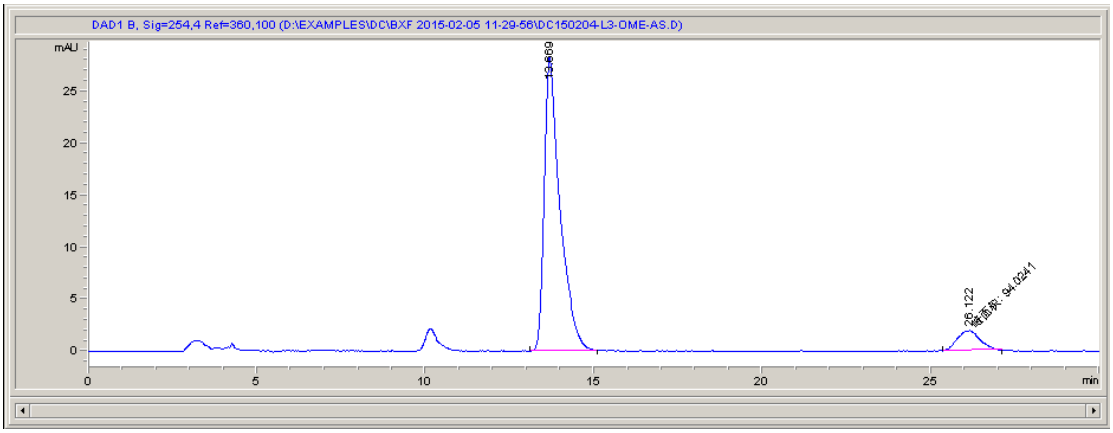
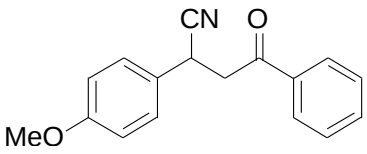
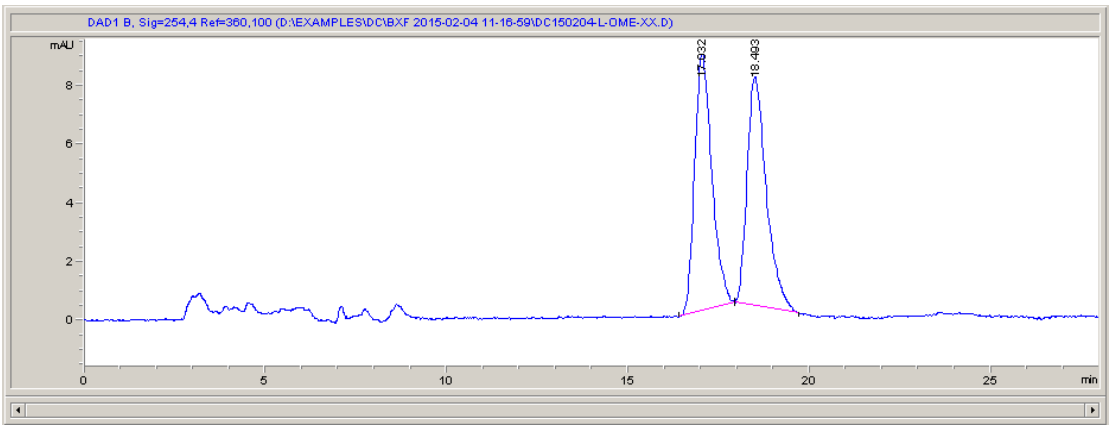
2	26.113	427.6	8.5	0.613	0.832	49.463

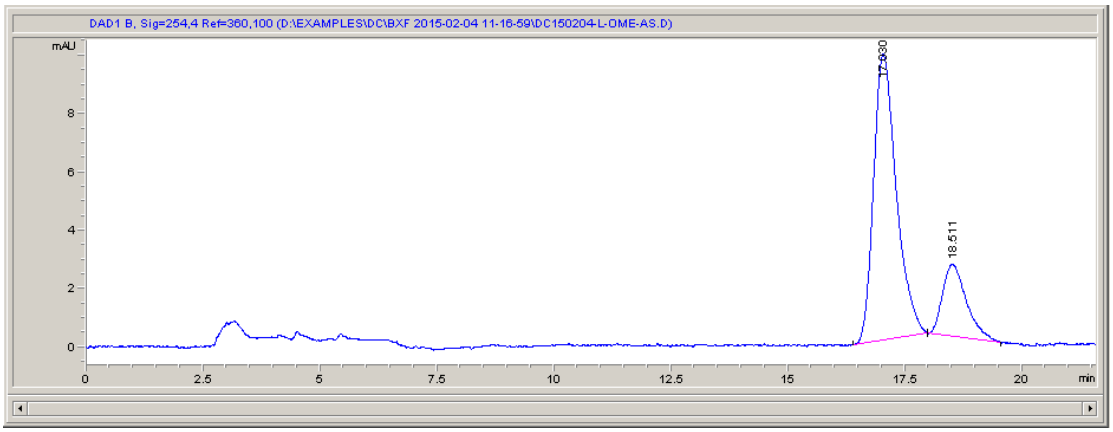


#	Time	Area	Height	Width	Symmetry	Area %
1	13.669	938.8	28.4	0.474	0.5	90.896
2	26.122	94	2	0.7982	1.092	9.104

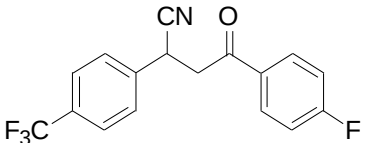


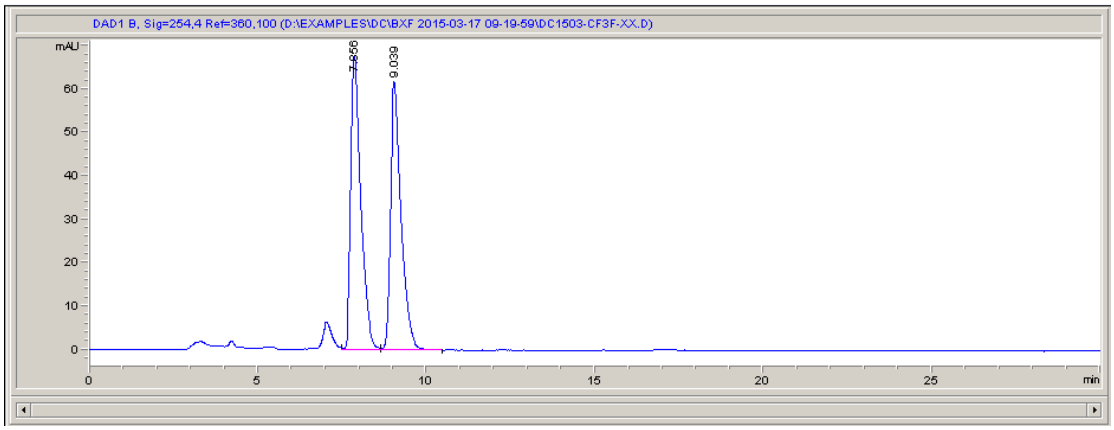


#	Time	Area	Height	Width	Symmetry	Area %
1	17.032	289.5	8.8	0.4877	0.726	50.046
2	18.493	289	7.8	0.4835	0.666	49.954

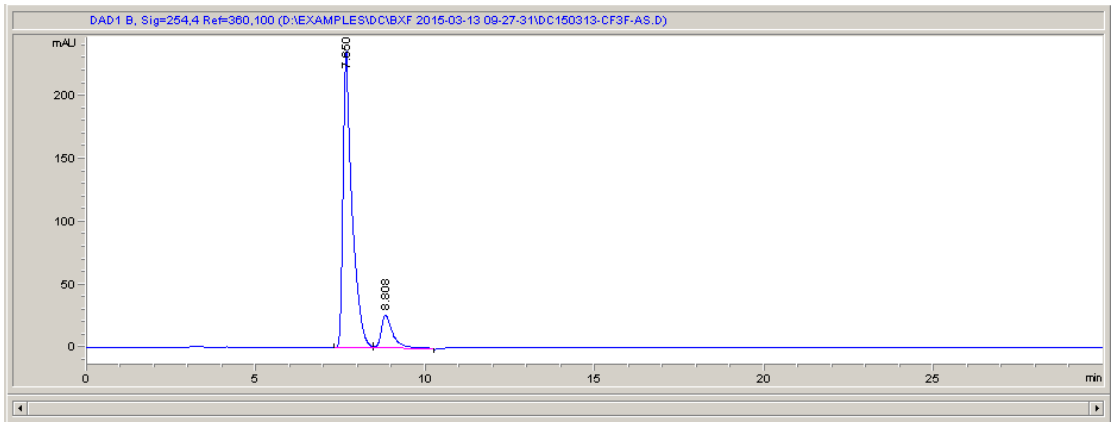


#	Time	Area	Height	Width	Symmetry	Area %
1	17.03	332.5	9.8	0.4619	0.681	78.707
2	18.511	90	2.5	0.4344	0.674	21.293

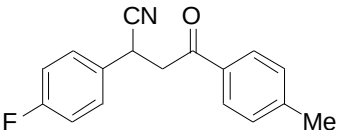


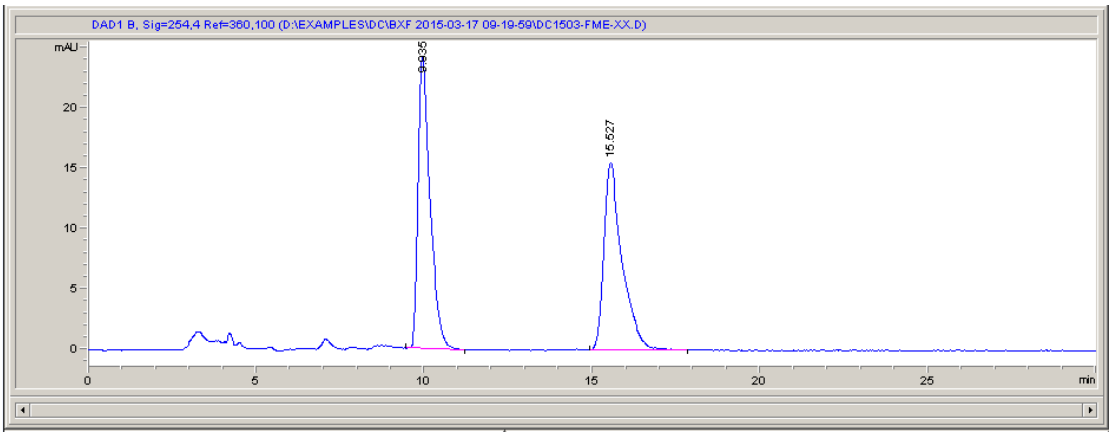


#	Time	Area	Height	Width	Symmetry	Area %
1	7.856	1371.7	67.8	0.2999	0.555	49.970
2	9.039	1373.3	61.8	0.3314	0.574	50.030

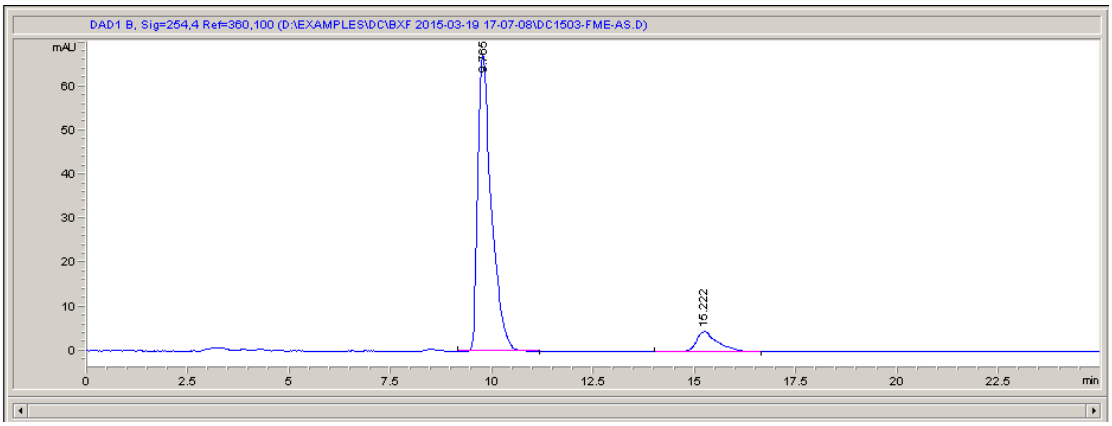


#	Time	Area	Height	Width	Symmetry	Area %
1	7.65	4613.7	235.9	0.2882	0.482	87.262
2	8.808	673.5	27	0.3514	0.455	12.738

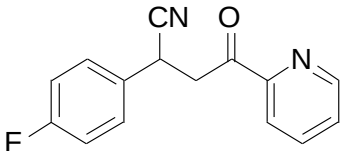


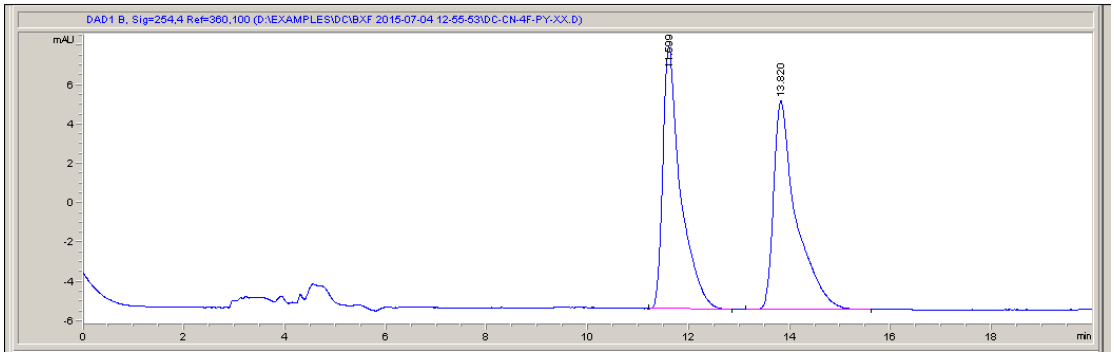


#	Time	Area	Height	Width	Symmetry	Area %
1	9.935	587.2	24.3	0.3504	0.524	50.060
2	15.527	585.8	15.5	0.5438	0.513	49.940

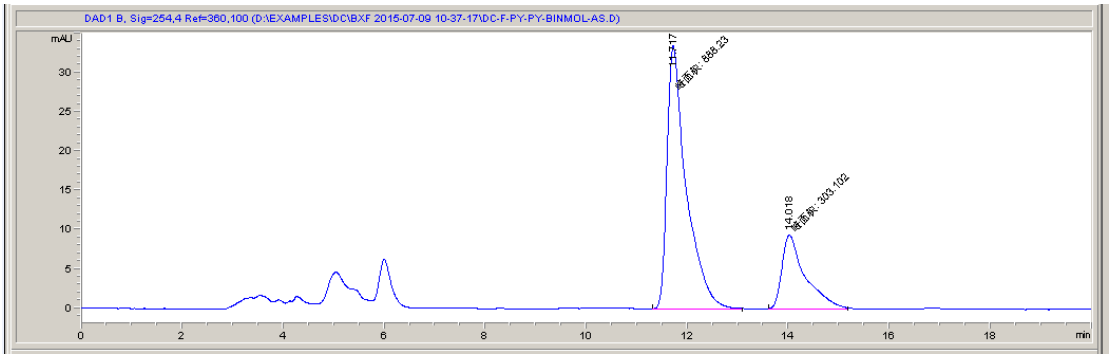


#	Time	Area	Height	Width	Symmetry	Area %
1	9.765	1556	67	0.3389	0.503	90.348
2	16.222	166.2	4.5	0.5272	0.54	9.652



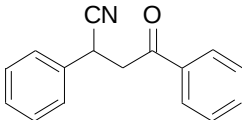


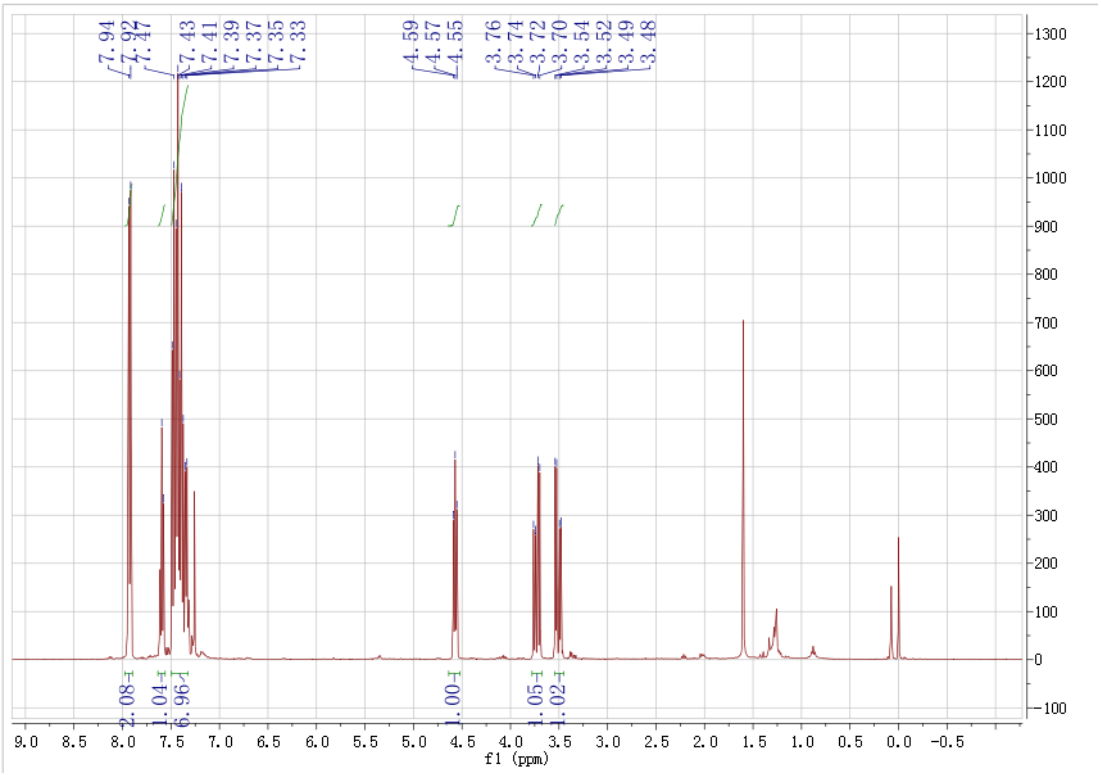
#	Time	Area	Height	Width	Symmetry	Area %
1	11.599	327.8	13.3	0.3556	0.467	49.719
2	13.82	330.6	10.6	0.4439	0.431	50.209

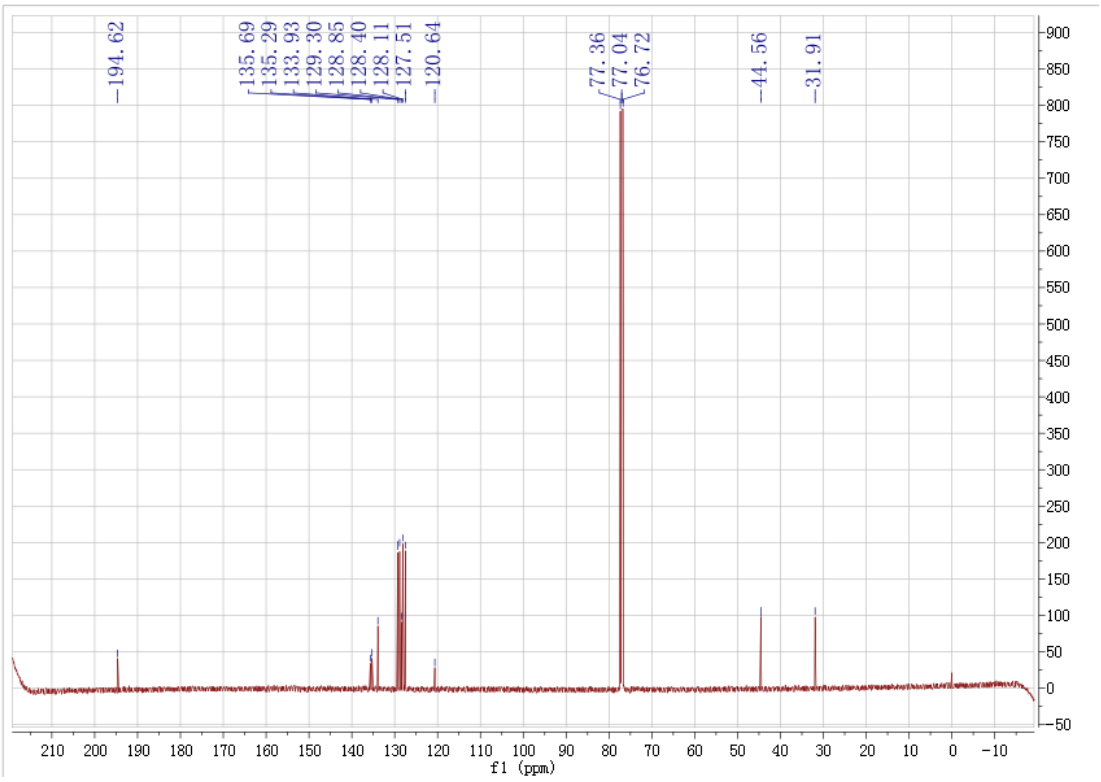


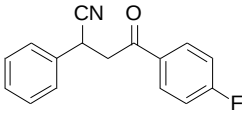
#	Time	Area	Height	Width	Symmetry	Area %
1	11.717	888.2	33.5	0.4423	0.468	74.858
2	14.018	303.1	9.4	0.5351	0.465	25.142

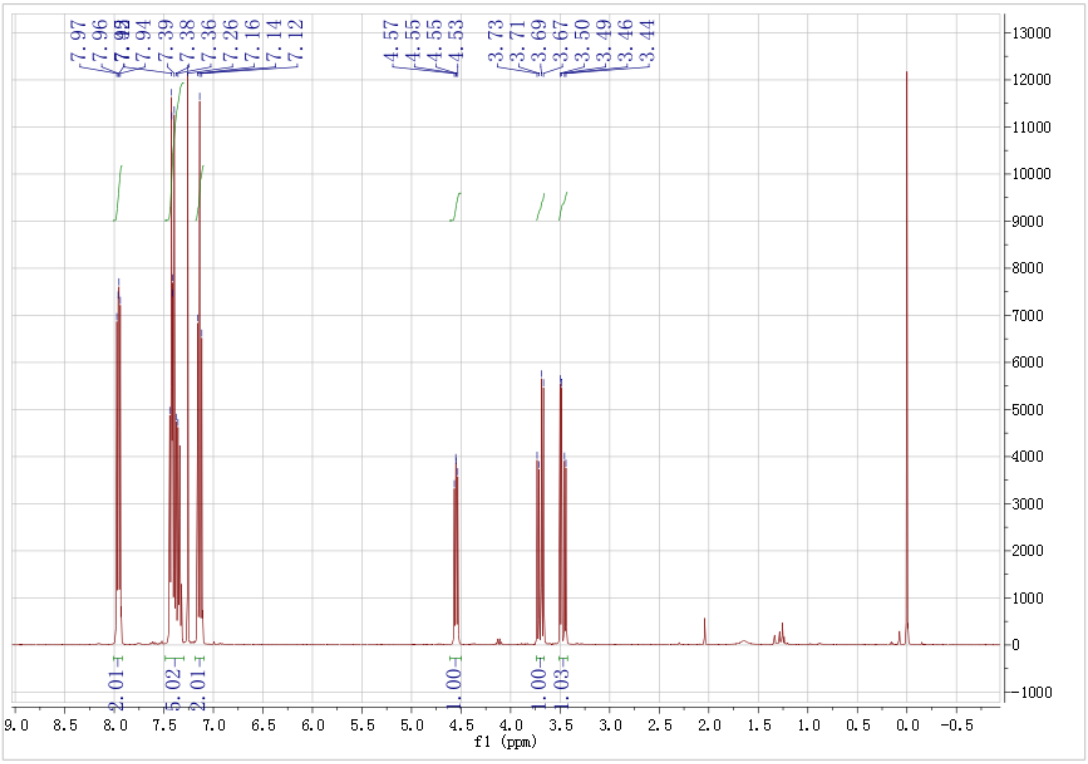
8. NMR Charts of products








CN
O
F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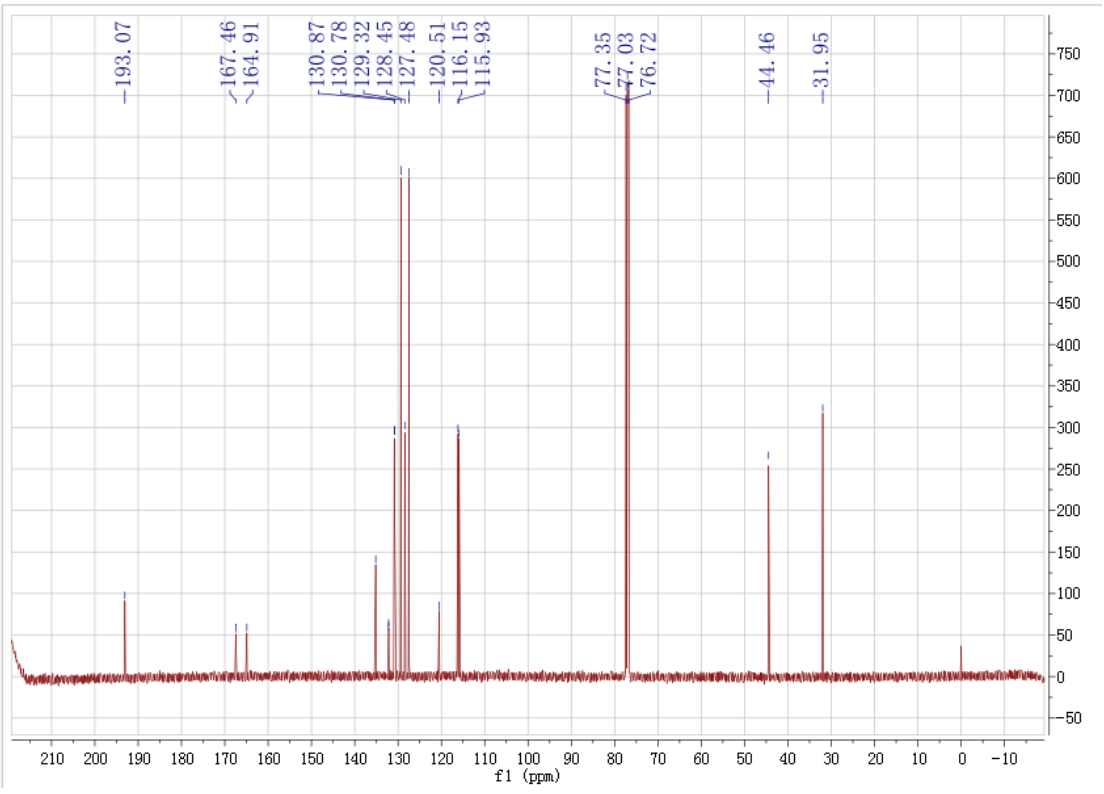
7.96
7.94
7.39
7.38
7.36
7.26
7.16
7.14
7.12
4.57
4.55
4.55
4.53
3.73
3.71
3.69
3.67
3.50
3.49
3.46
3.44
2.01
5.02
2.01
1.00
1.00
1.03
f1 (ppm)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128.45
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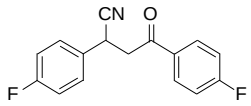
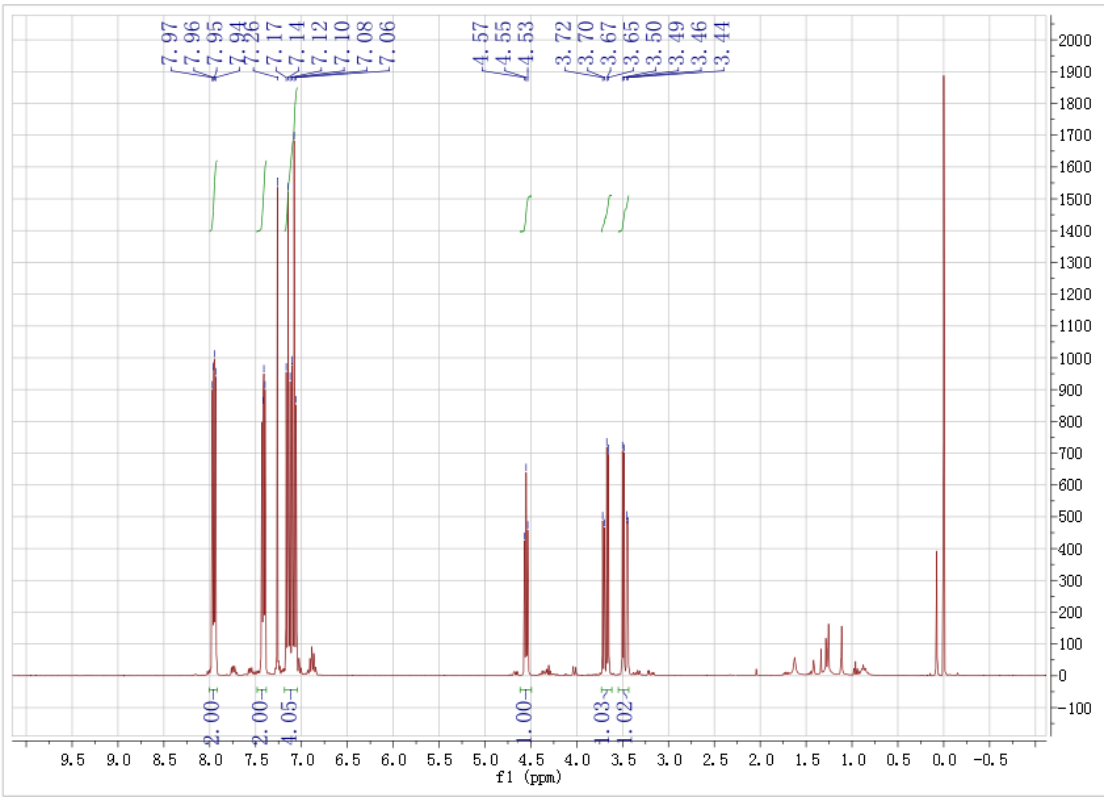
115.93
77.35
77.03
76.72
44.46
31.95
f1 (ppm)


CN
O
F
F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7.94
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7.17
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7.12
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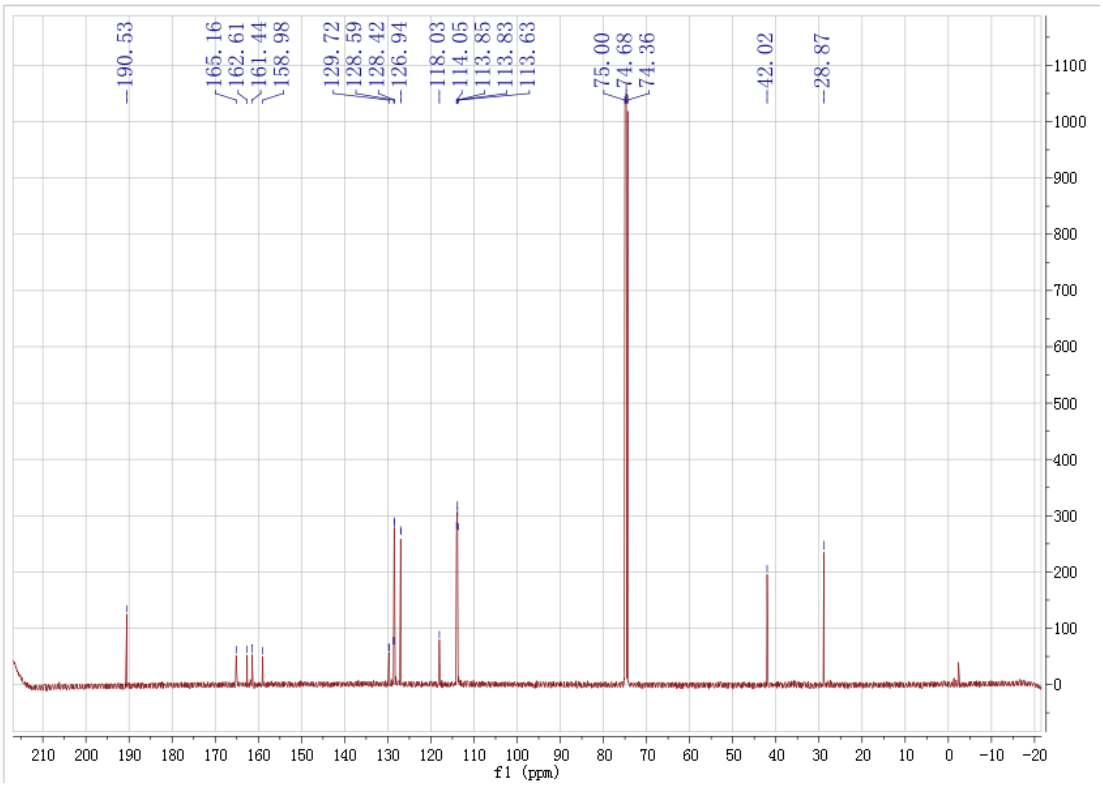
7.08
7.06
4.57
4.55
4.53
3.72
3.70
3.67
3.65
3.50
3.49
3.46
3.44
2.00
2.00
4.05
1.00
1.03
1.02
f1 (ppm)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165.16
162.61
161.44
158.98
129.72
128.59
128.42
126.94
118.03
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113.85
113.83
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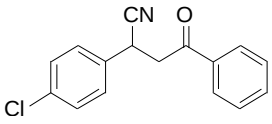
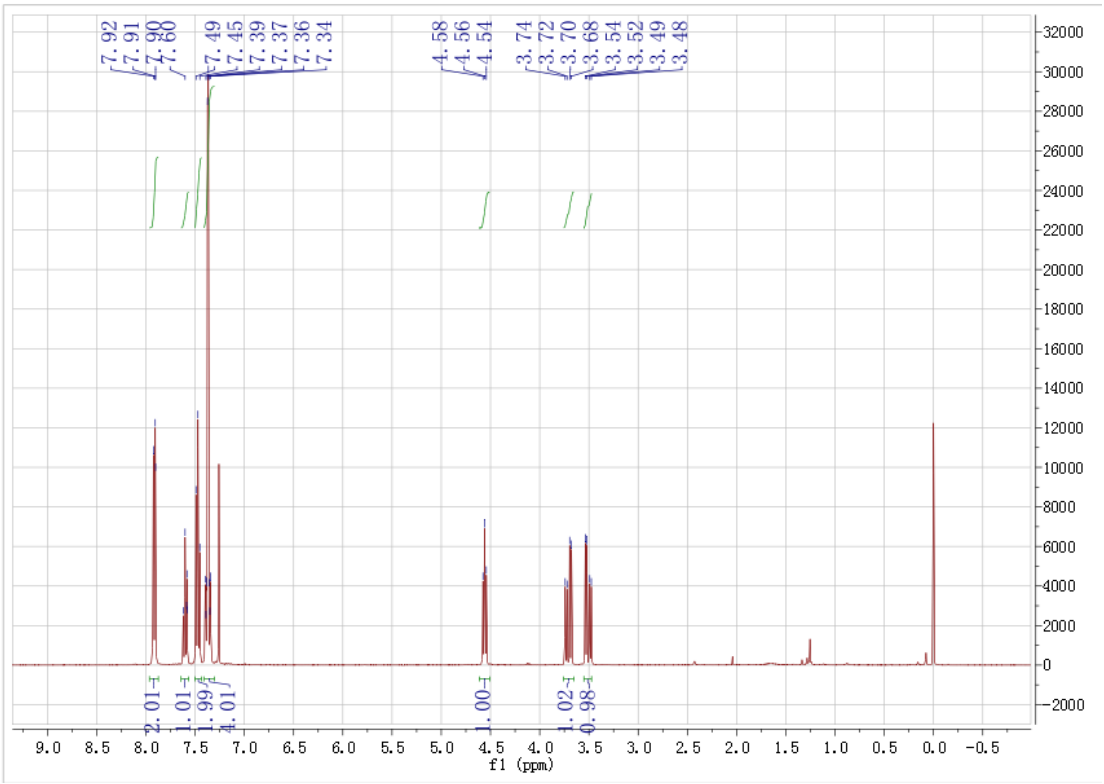
74.68
74.36
42.02
28.87
f1 (ppm)


CN
O
Cl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7.91
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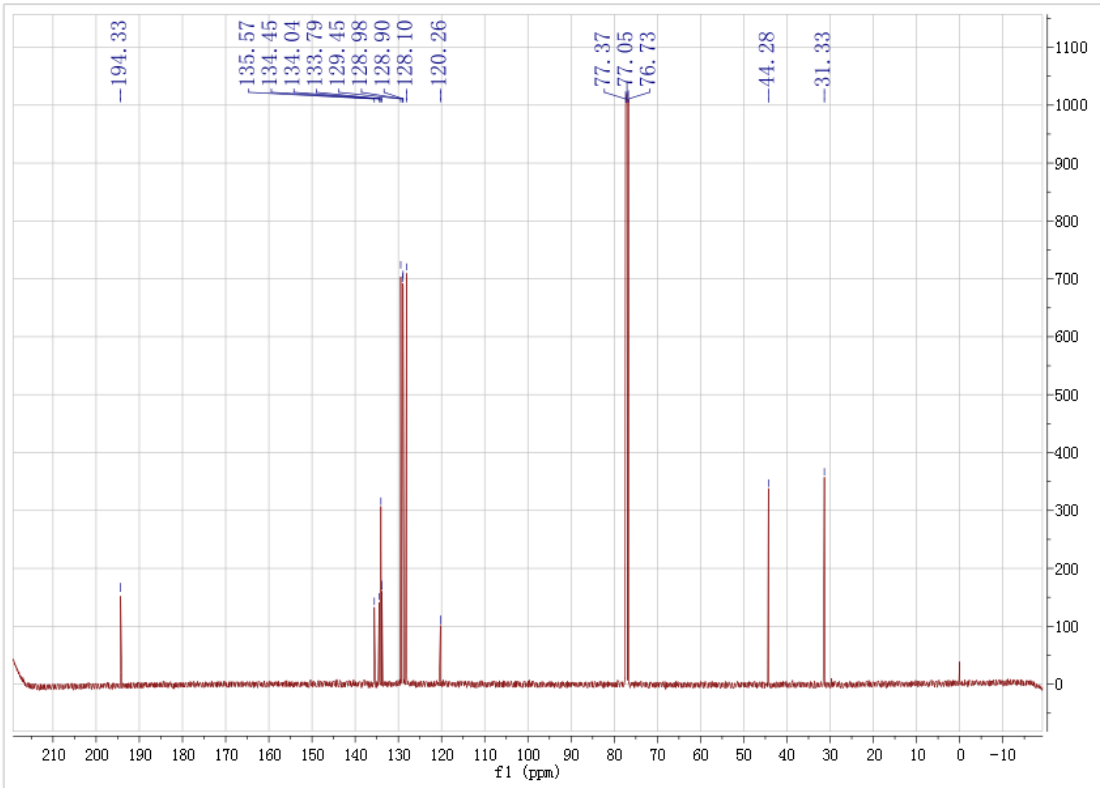
7.45
7.39
7.37
7.36
7.34
4.58
4.56
4.54
3.74
3.72
3.70
3.68
3.54
3.52
3.49
3.48
2.01
1.01
1.99
4.01
1.00
1.02
0.98
f1 (ppm)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135.57
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129.45
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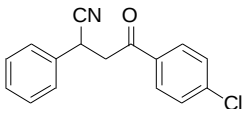
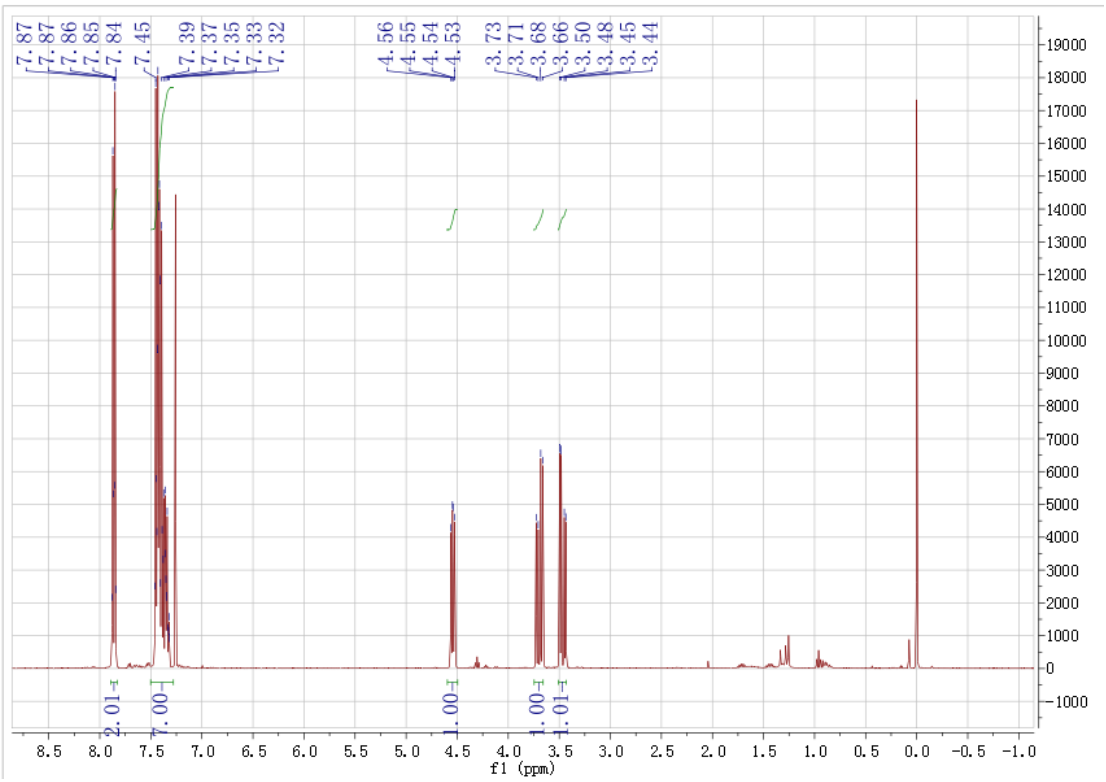
128.90
128.10
120.26
77.37
77.05
76.73
44.28
31.33
f1 (ppm)


CN
O
Cl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7.37
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7.33
7.32
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4.55
4.54
4.53
3.73
3.71
3.68
3.66
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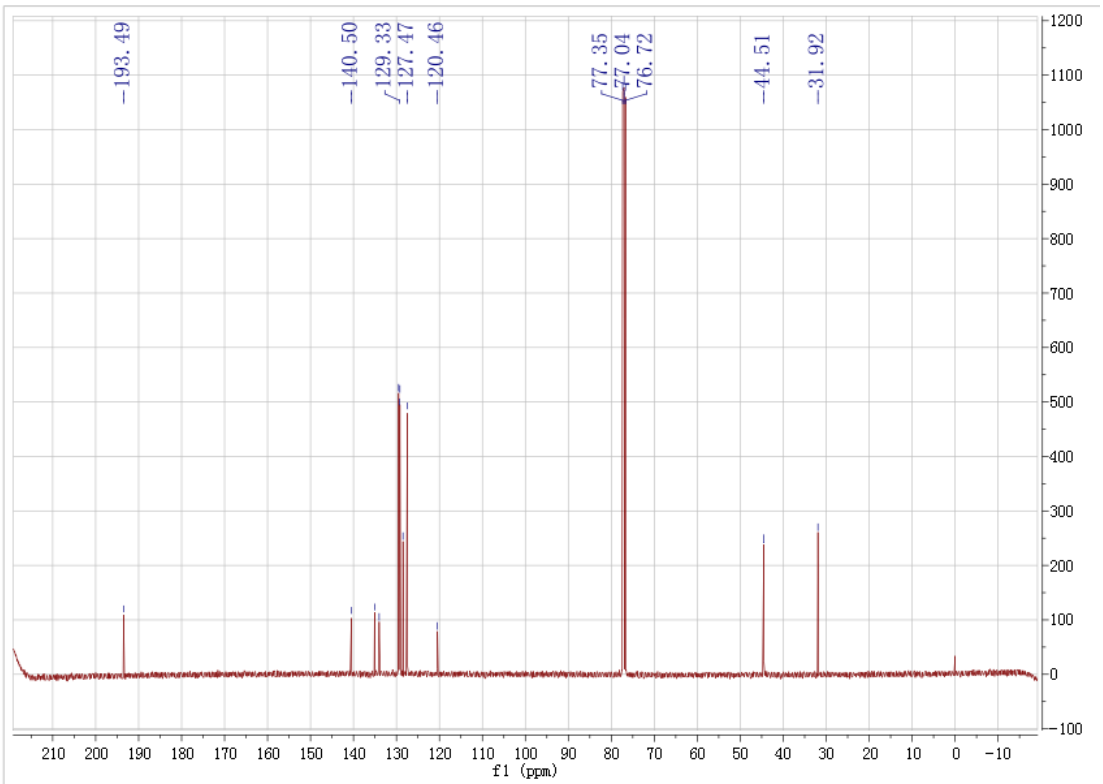
3.48
3.45
3.44
2.01
7.00
1.00
1.00
1.01
f1 (ppm)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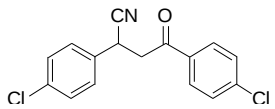
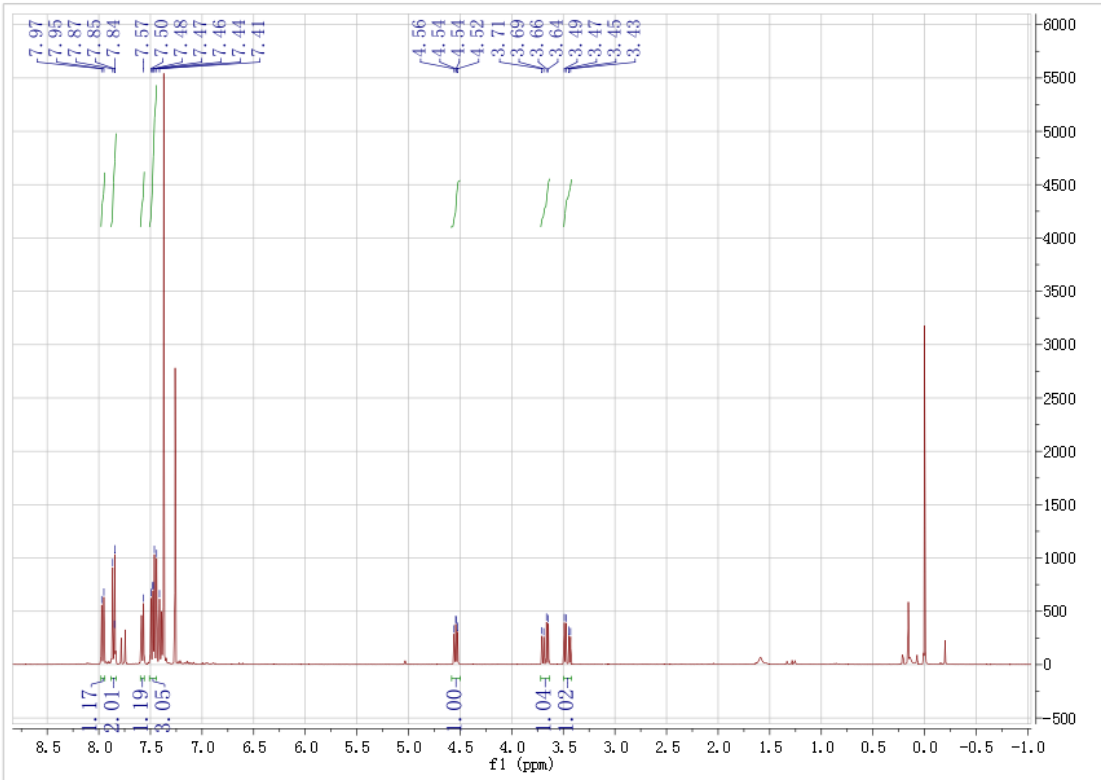
77.35
77.04
76.72
44.51
31.92
f1 (ppm)


CN
O
Cl
Cl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7.48
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7.46
7.44
7.41
4.56
4.54
4.54
4.52
3.71
3.69
3.66
3.64
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3.47
3.45
3.43
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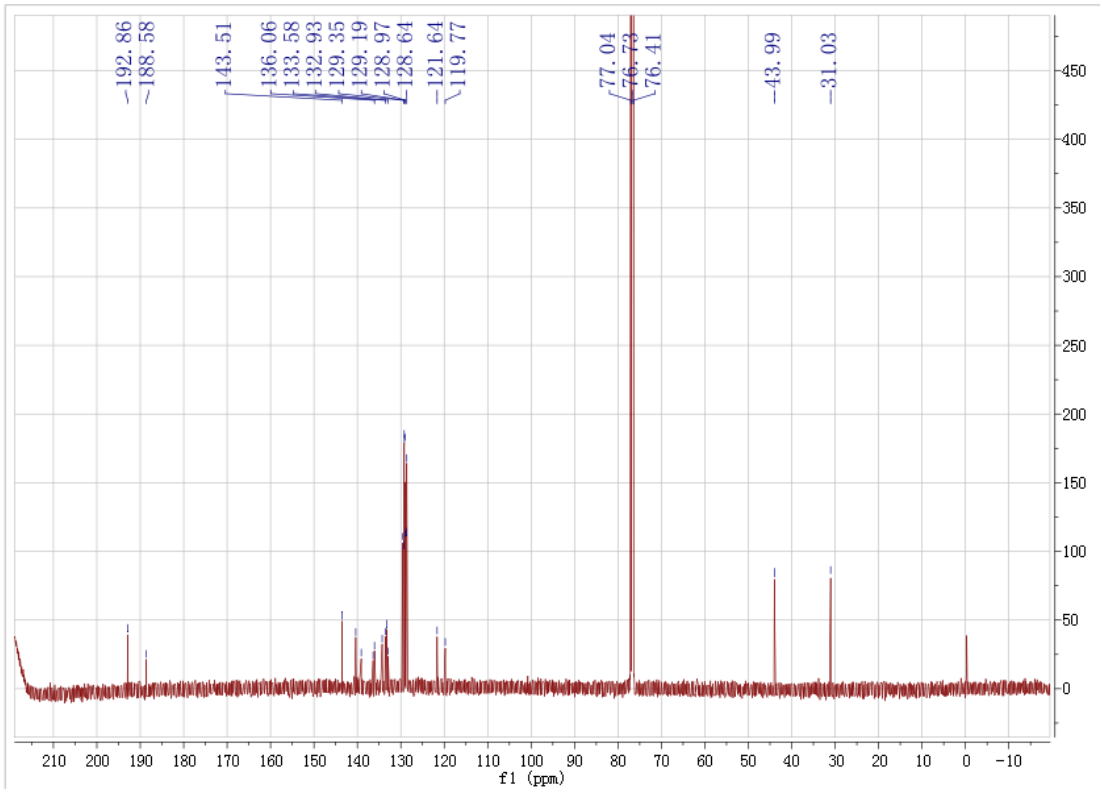
2.01
1.19
3.05
1.00
1.04
1.02
f1 (ppm)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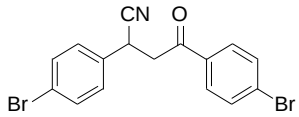
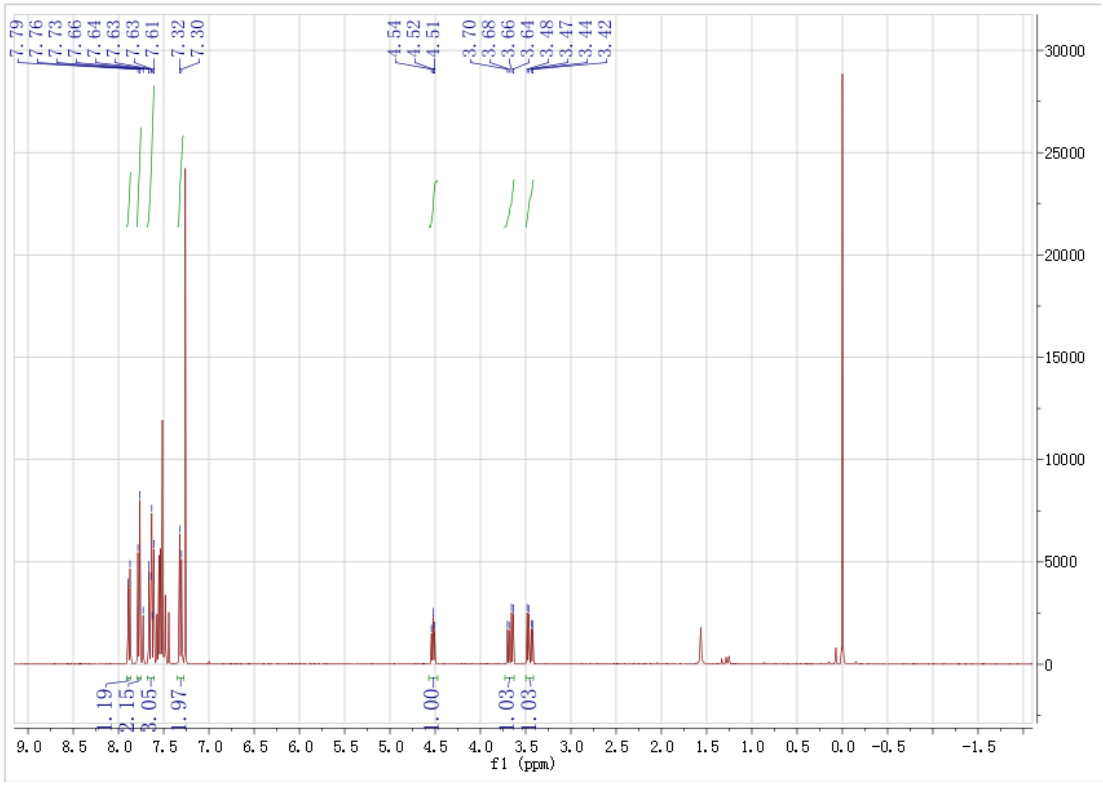
76.41
43.99
31.03
f1 (ppm)


CN
O
Br
Br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3.66
3.64
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3.05
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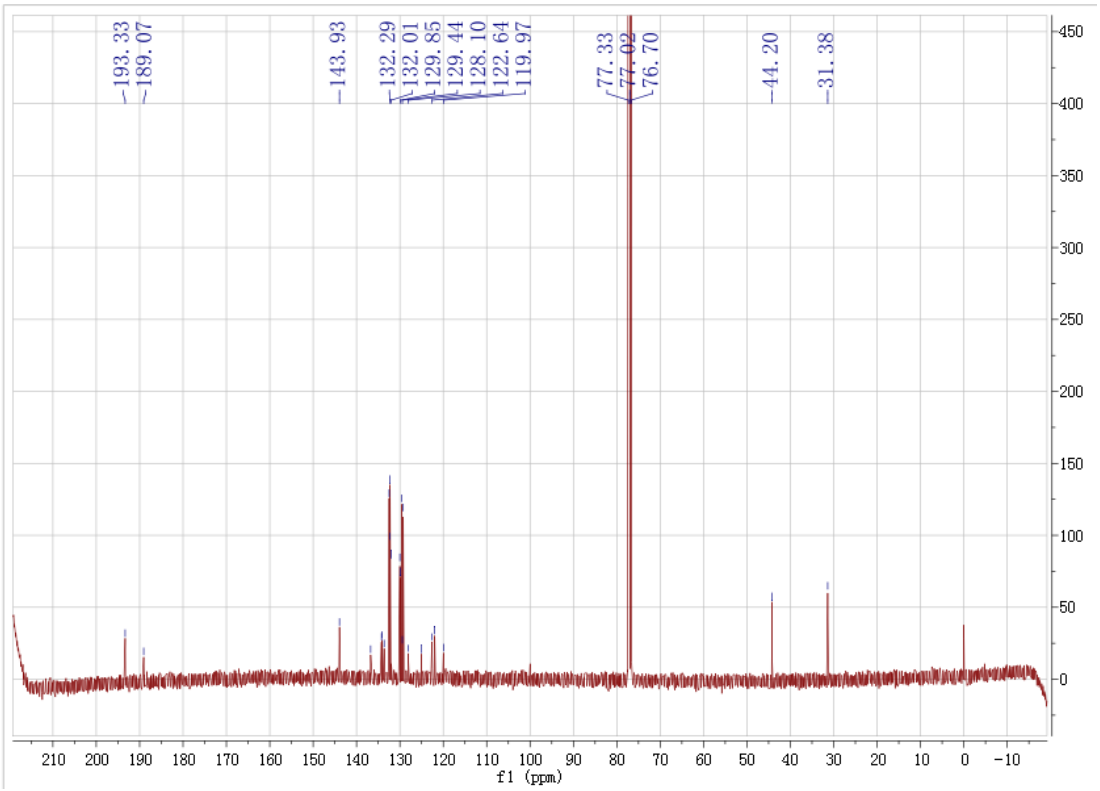
1.00
1.03
1.03
f1 (ppm)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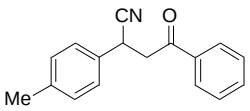
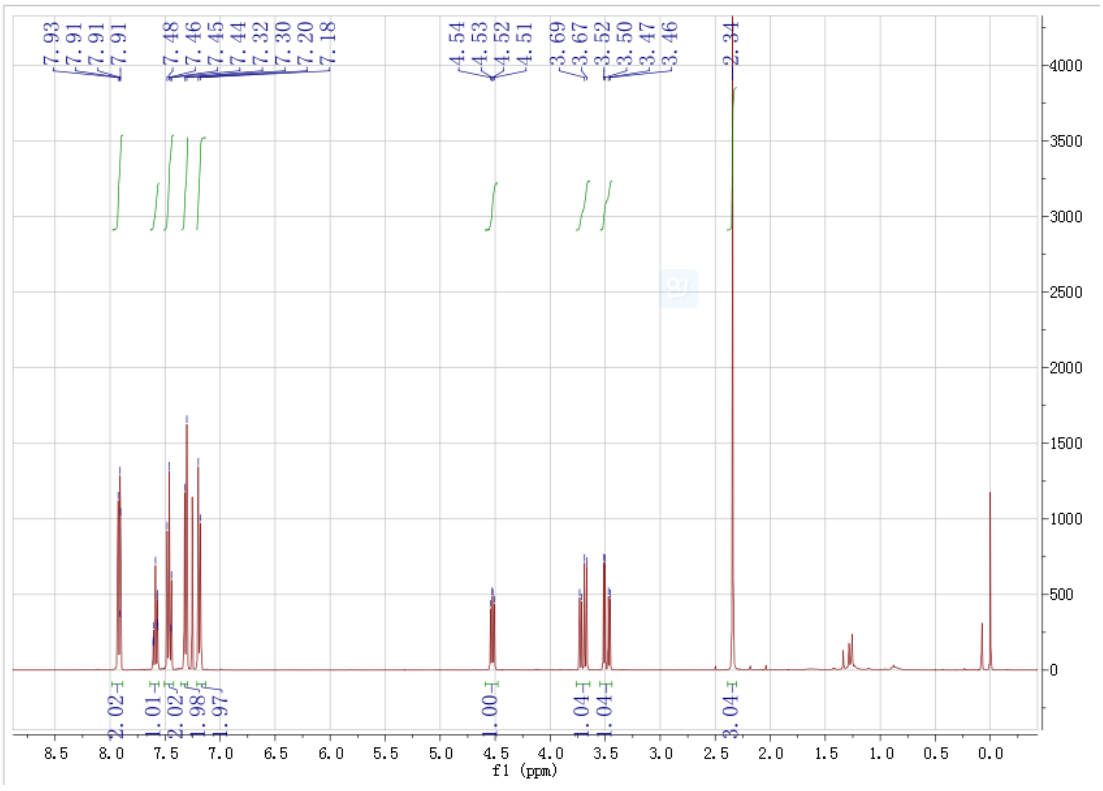
119.97
77.33
77.02
76.70
44.20
31.38
f1 (ppm)


CN
O
Me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4.52
4.51
3.69
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3.50
3.47
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1.97
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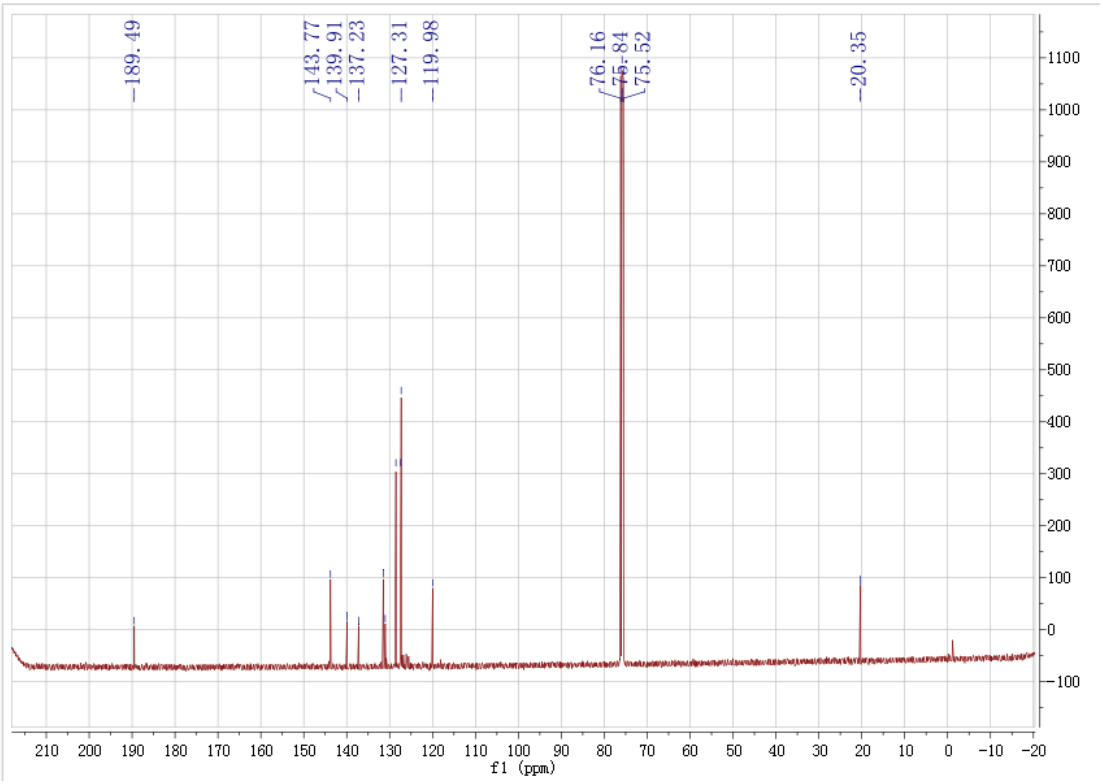
1.04
1.04
3.04
f1 (ppm)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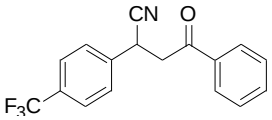
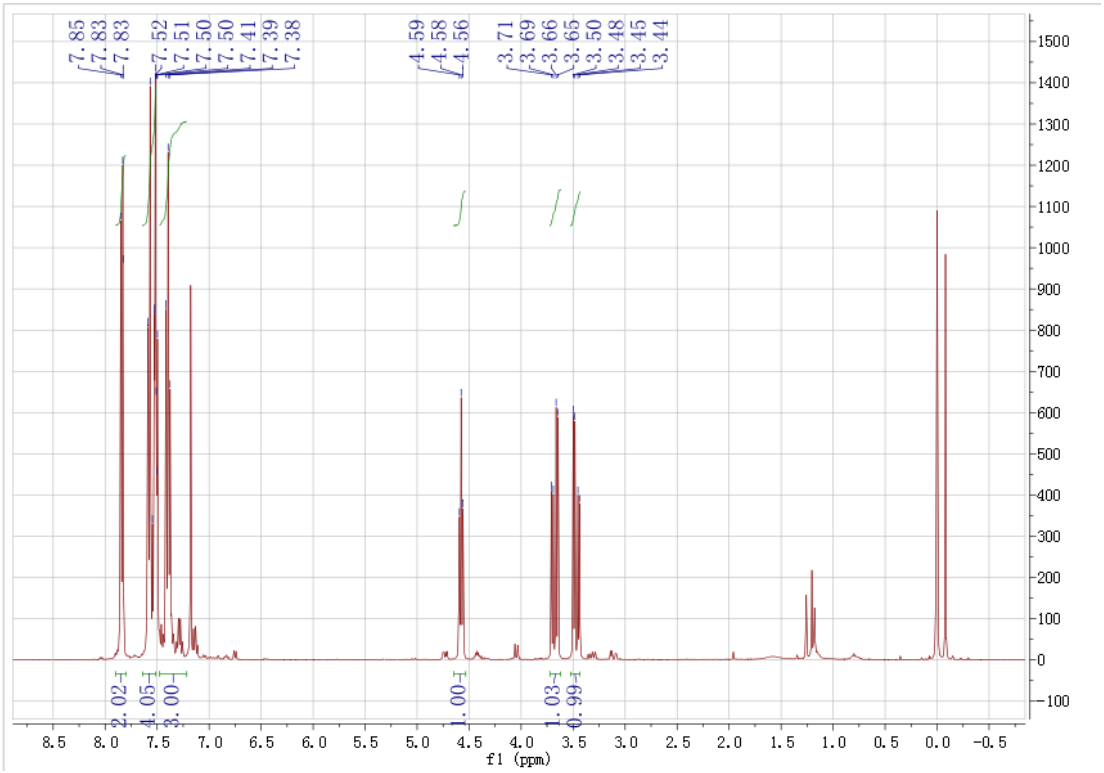
75.84
75.52
20.35
f1 (ppm)


CN
O
F3C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3.69
3.66
3.65
3.50
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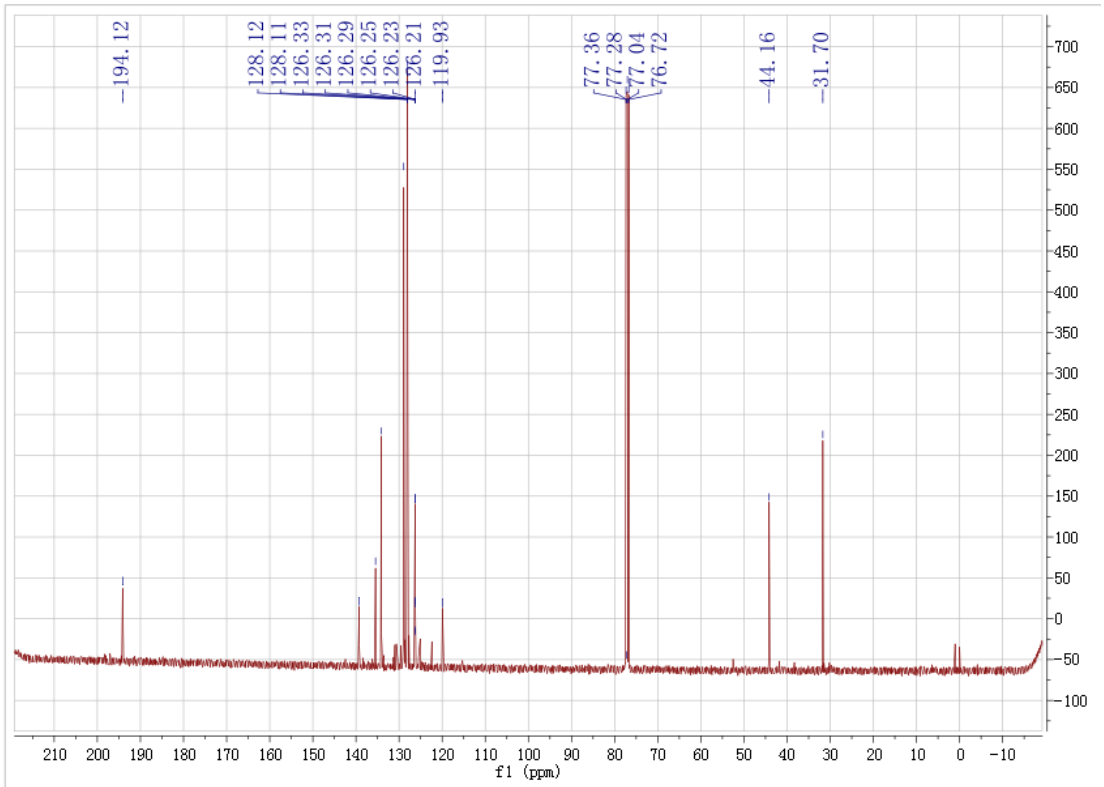
3.45
3.44
2.02
4.05
3.00
1.00
1.03
0.99
f1 (ppm)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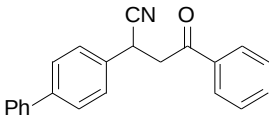
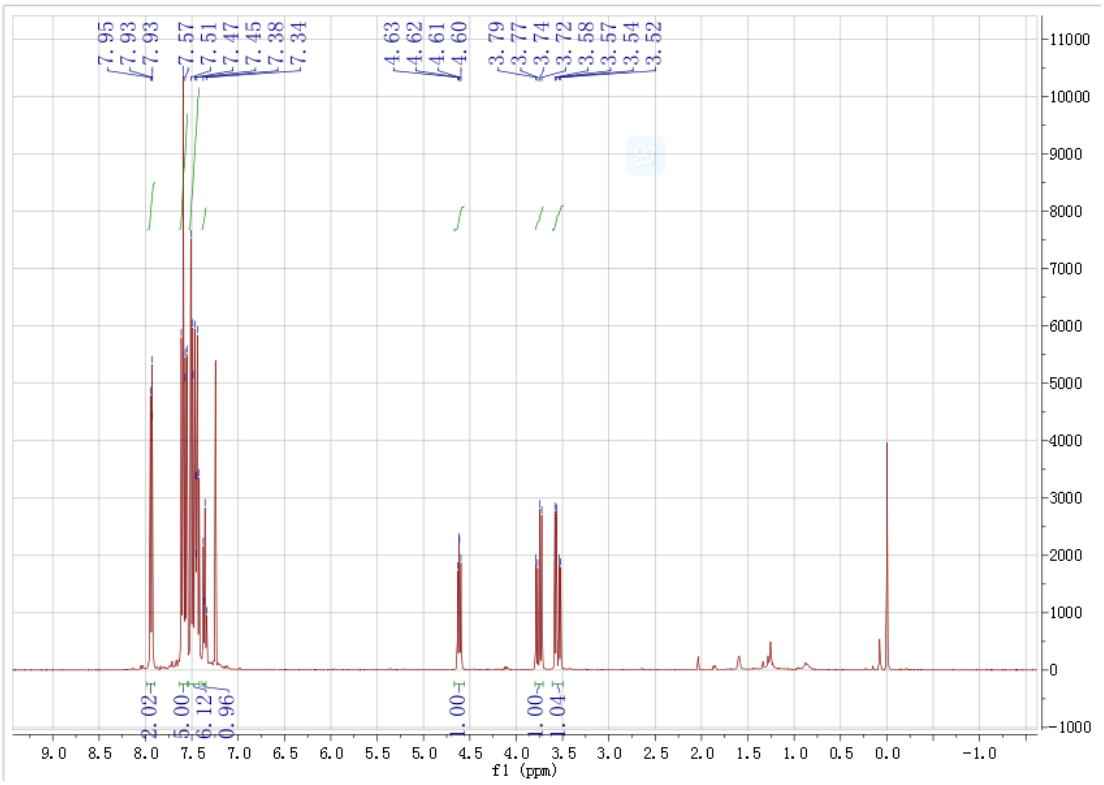
76.72
44.16
31.70
f1 (ppm)


CN
O
Ph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3.79
3.77
3.74
3.72
3.58
3.57
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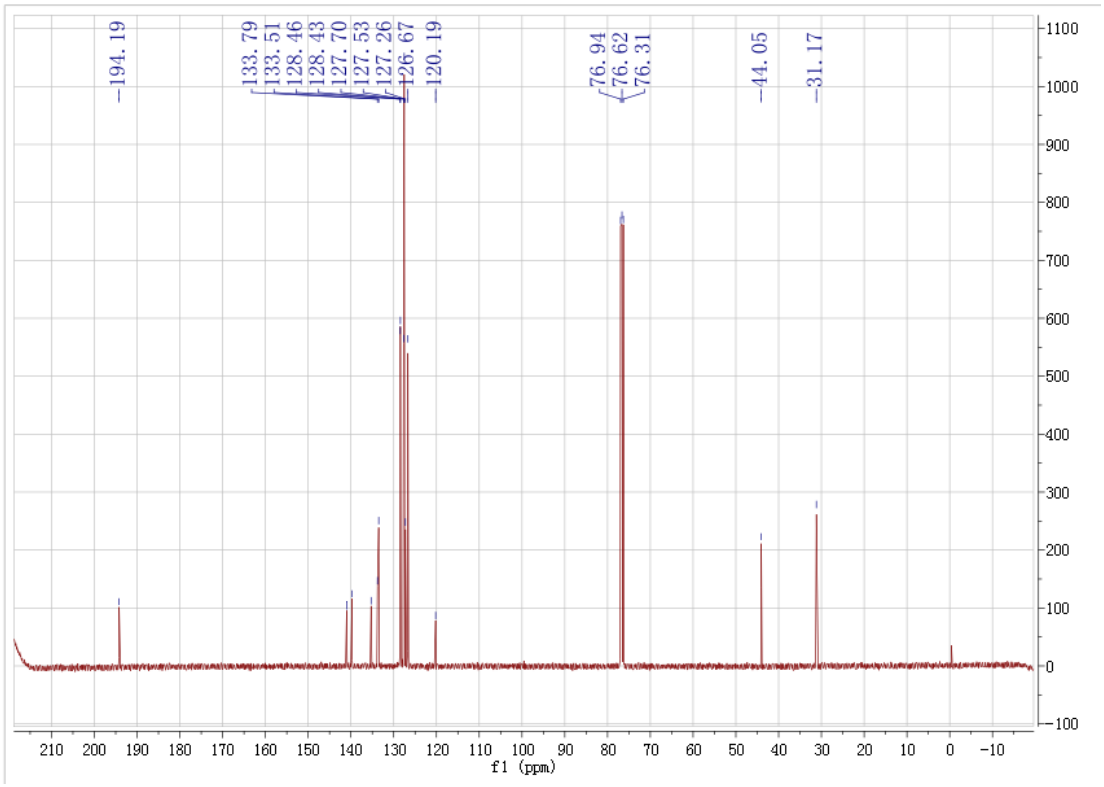
3.52
2.02
5.00
6.12
0.96
1.00
1.00
1.04
f1 (ppm)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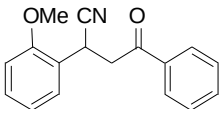
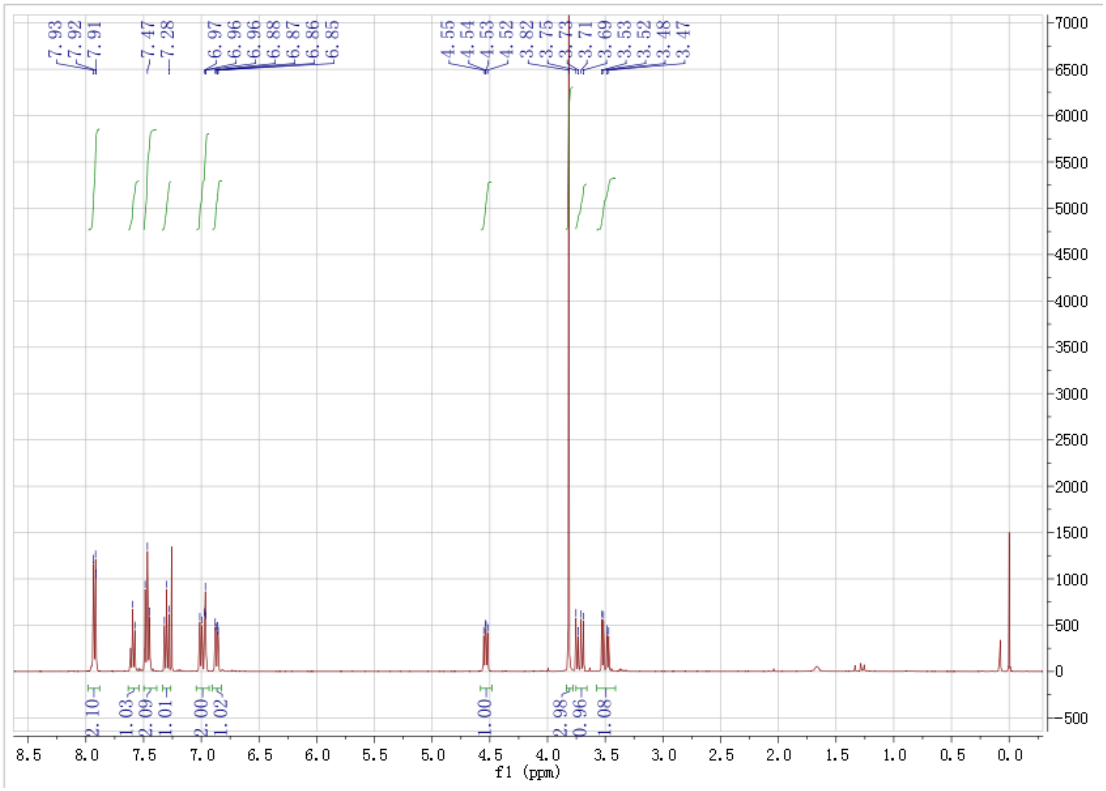
76.62
76.31
44.05
31.17
f1 (ppm)


OMe CN O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6.86
6.85
4.55
4.54
4.53
4.52
3.82
3.75
3.73
3.71
3.69
3.53
3.52
3.48
3.47
2.10
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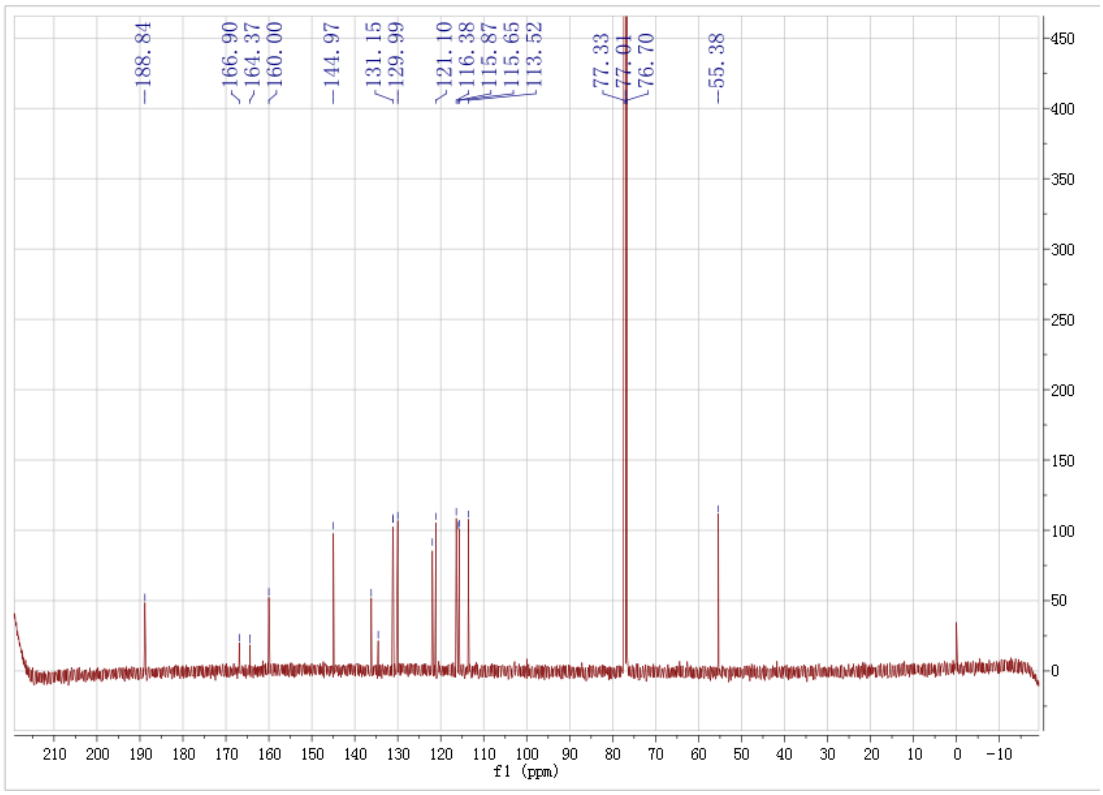
2.09
1.01
2.00
1.02
1.00
2.98
0.96
1.08
f1 (ppm)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121.10
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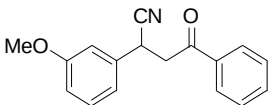
115.65
113.52
77.33
77.01
76.70
55.38
f1 (ppm)


CN
O
MeO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7.91
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6.96
6.88
6.87
6.86
6.85
4.55
4.53
4.51
3.81
3.75
3.71
3.69
3.53
3.51
3.48
3.47
2.03
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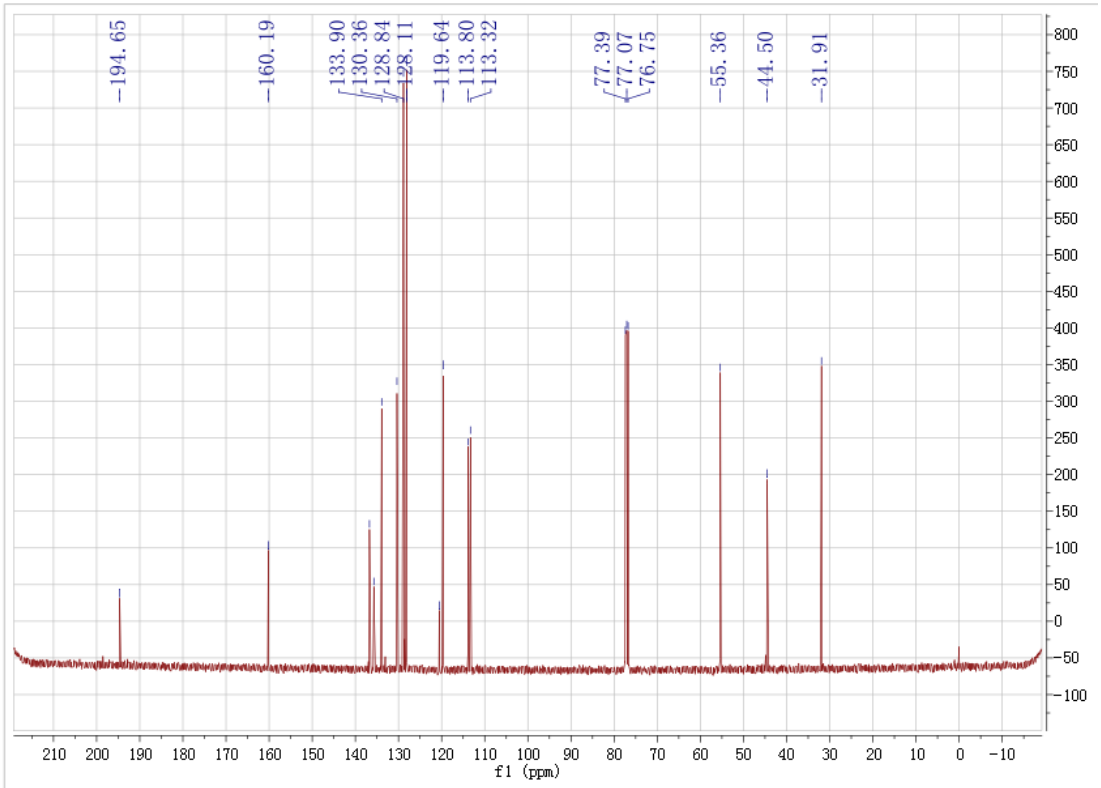
2.00
1.08
2.00
1.01
1.00
3.00
1.13
1.04
f1 (ppm)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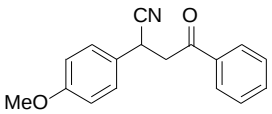
77.07
76.75
55.36
44.50
31.91
f1 (ppm)


CN
O
MeO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6.90
6.89
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4.52
4.52
4.50
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3.71
3.68
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3.52
3.51
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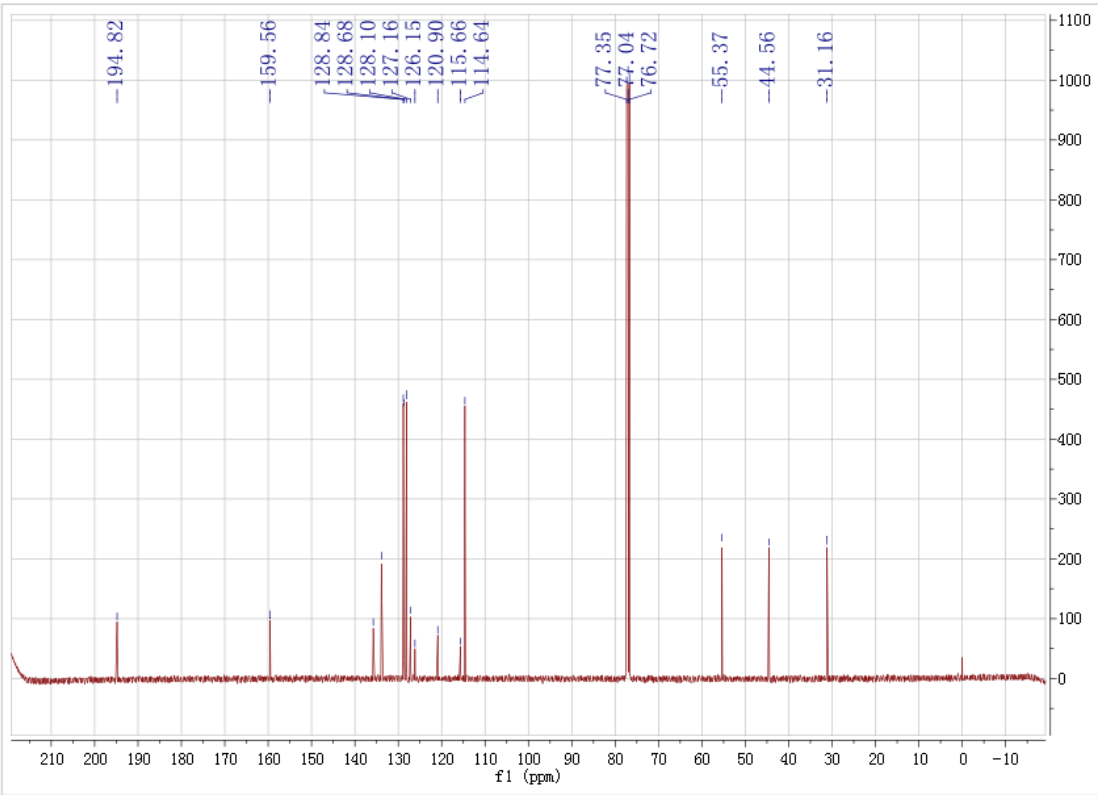
1.00
3.03
1.00
1.04
f1 (ppm)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77.04
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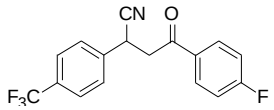
55.37
44.56
31.16
f1 (ppm)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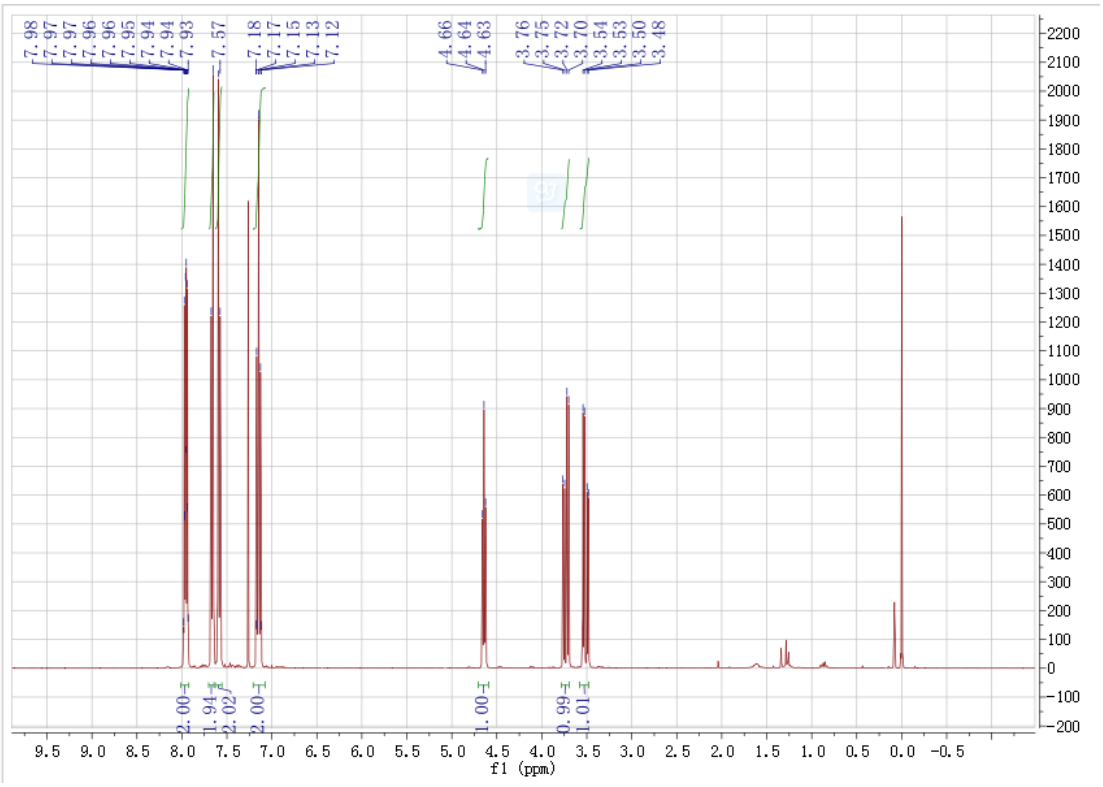
O
F3C
F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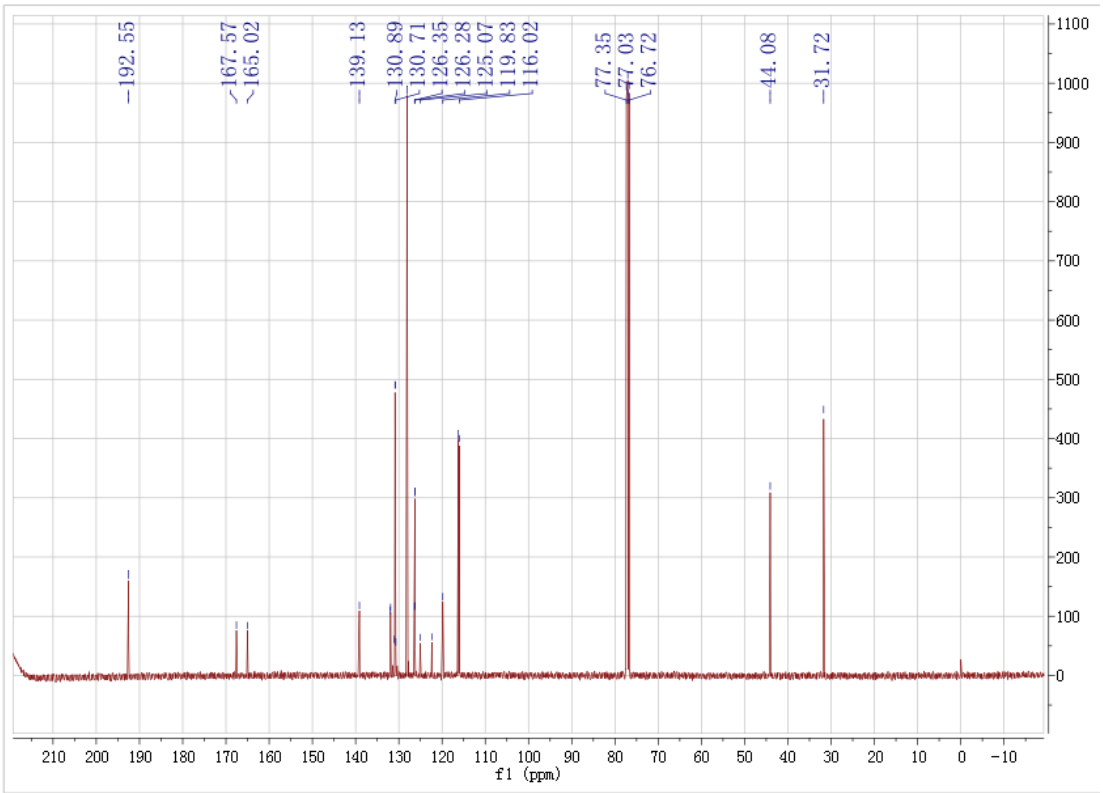
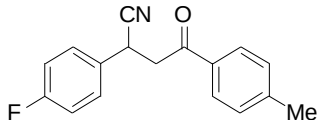
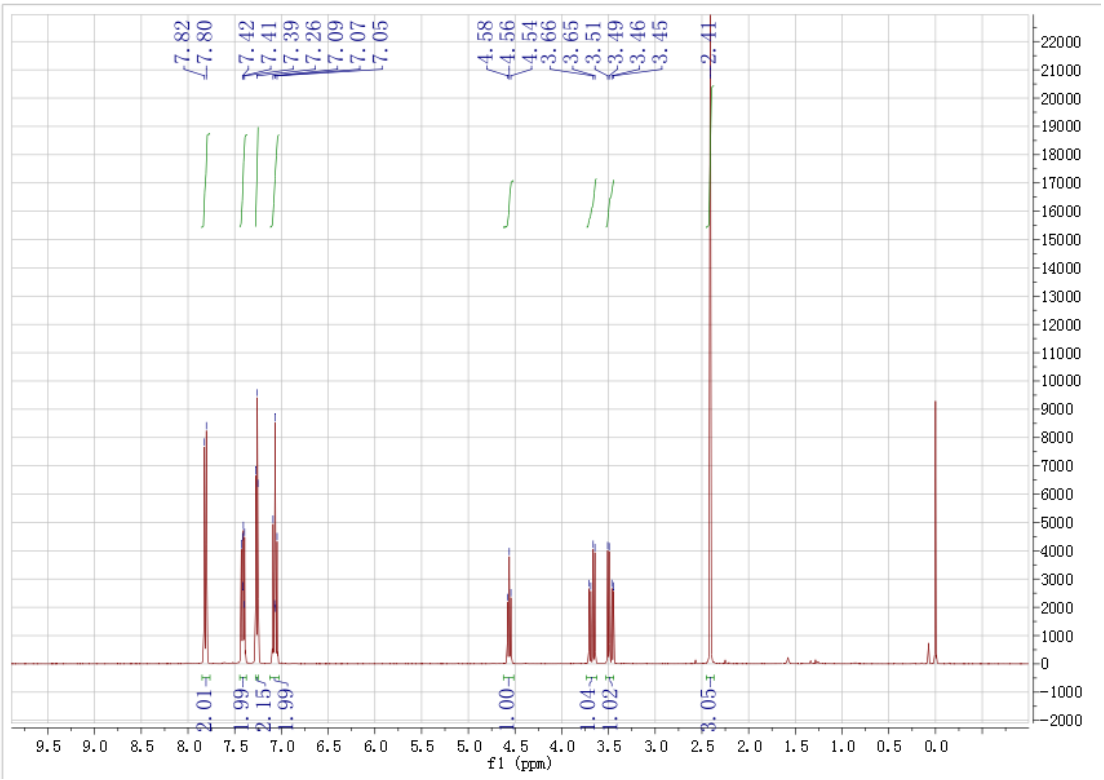
7.94
7.94
7.93
7.57
7.18
7.17
7.15
7.13
7.12
4.66
4.64
4.63
3.76
3.75
3.72
3.70
3.54
3.53
3.50
3.48
2.00
1.94
2.02
2.00
1.00
0.99
1.01
f1 (ppm)


192.55
167.57
165.02
139.13
130.89
130.71
126.35
126.28
125.07
119.83
116.02
77.35
77.03
76.72
44.08
31.72
f1 (ppm)


CN
O
F
Me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7.42
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7.26
7.09
7.07
7.05
4.58
4.56
4.54
3.66
3.65
3.51
3.49
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3.45
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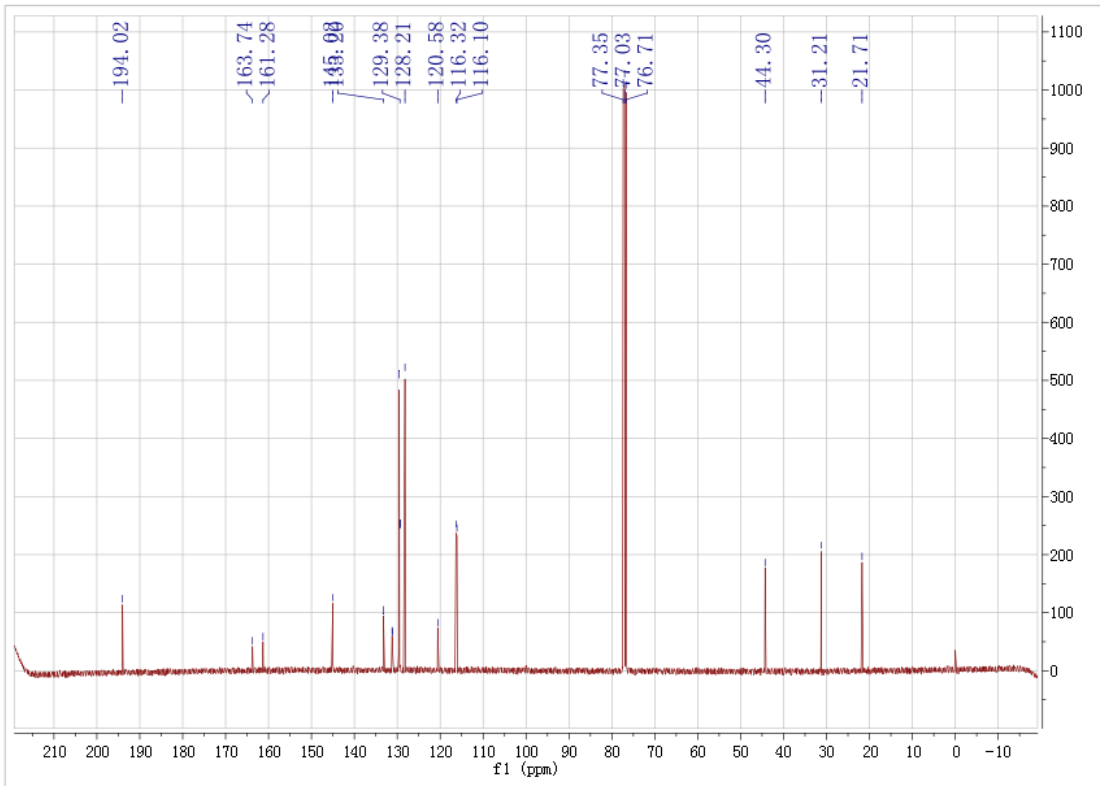
2.01
1.99
2.15
1.99
1.00
1.04
1.02
3.05
f1 (ppm)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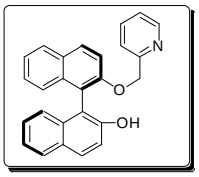
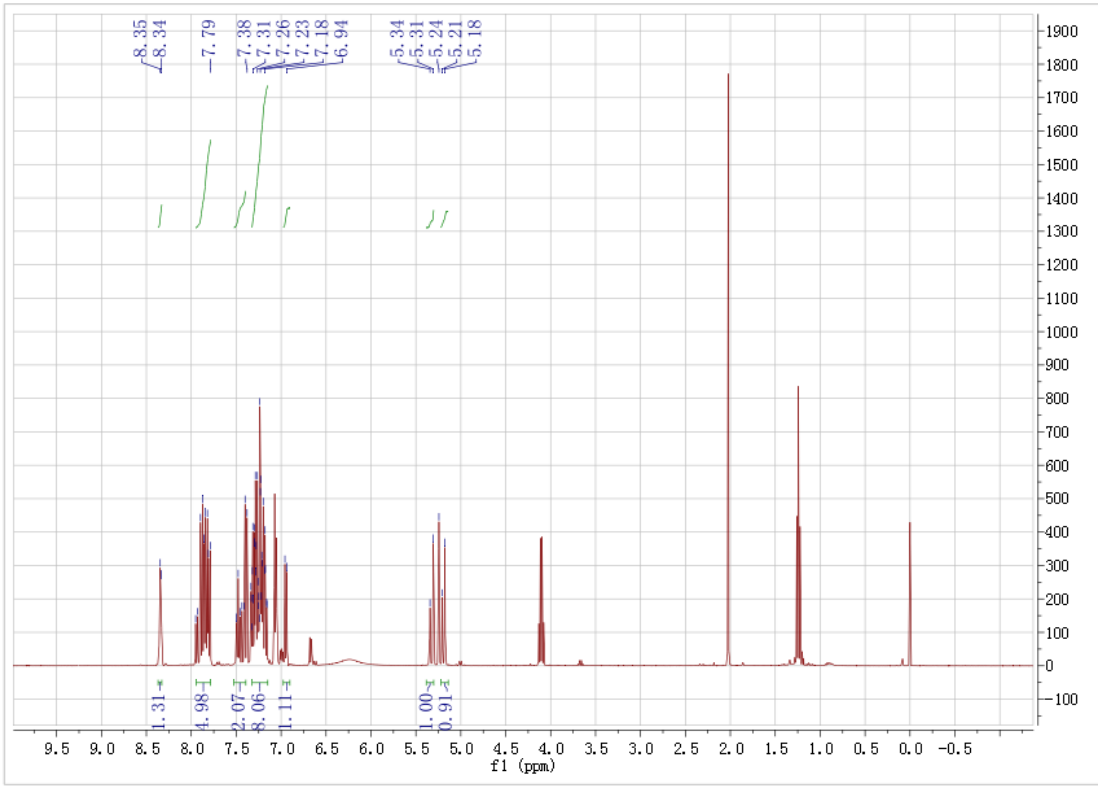
116.32
116.10
77.35
77.03
76.71
44.30
31.21
21.71
f1 (ppm)


N
O
OH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8.34
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7.38
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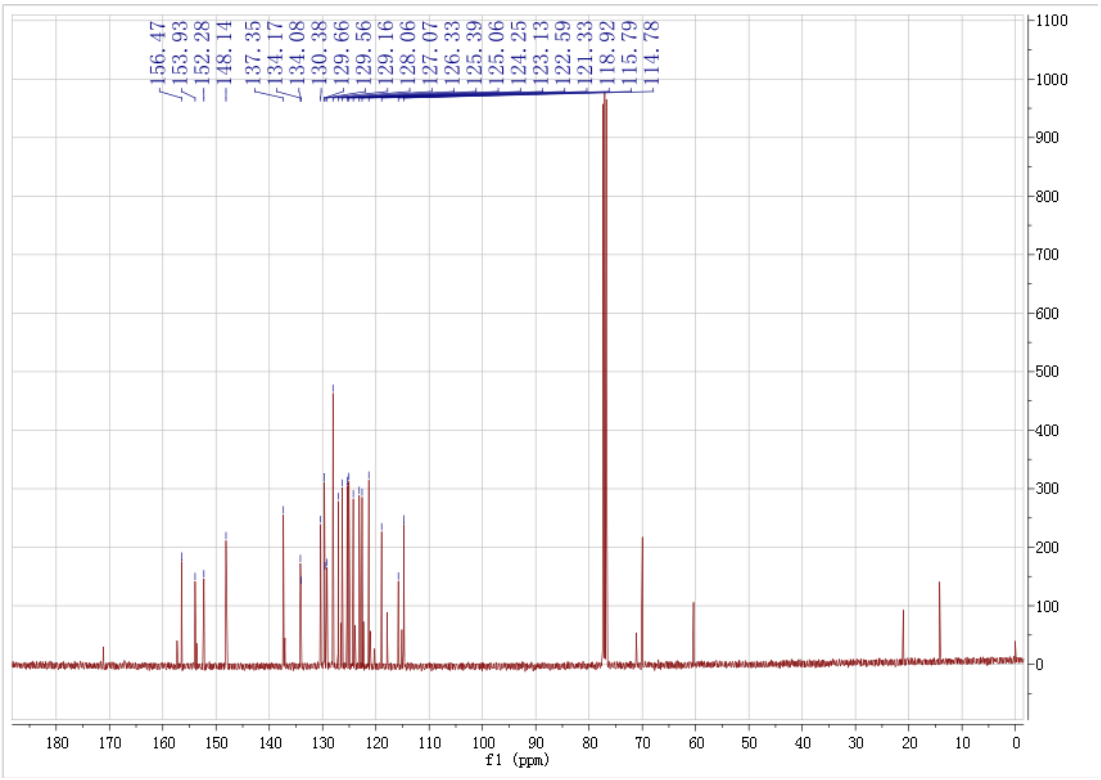
7.26
7.23
7.18
6.94
5.34
5.31
5.24
5.21
5.18
1.31
4.98
2.07
8.06
1.11
1.00
0.91
f1 (ppm)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130.38
129.66
129.56
129.16
128.06
127.07
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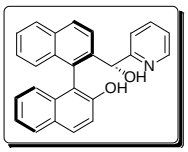
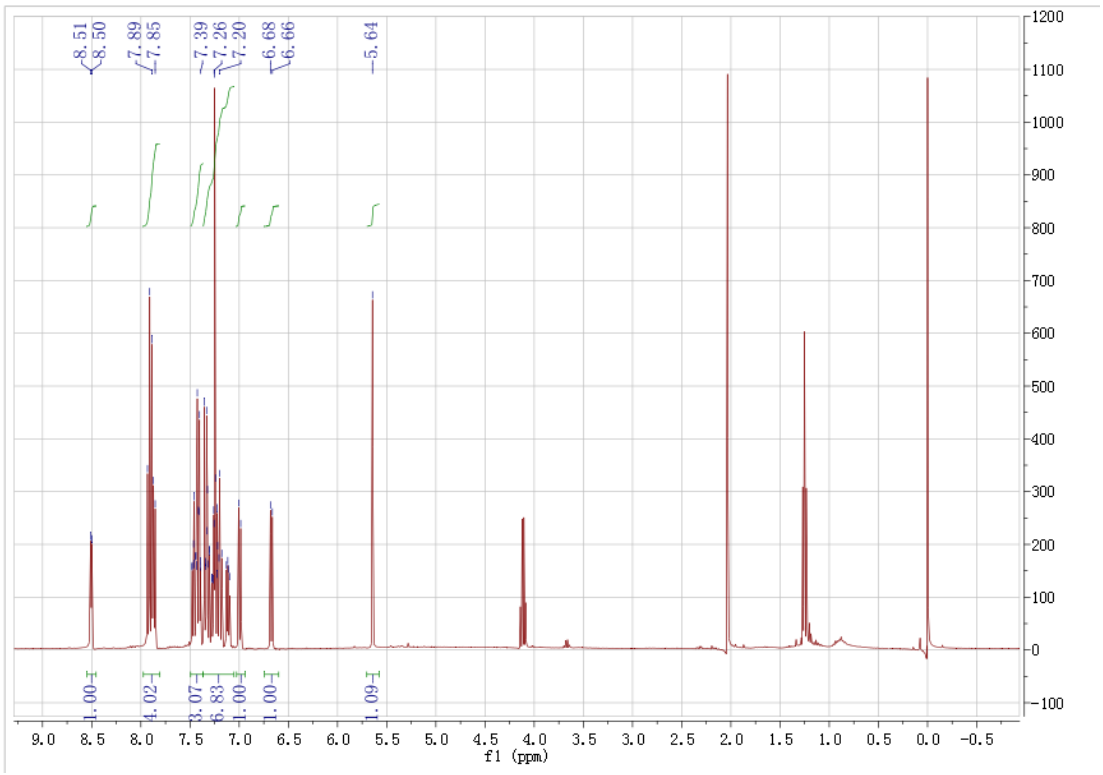
125.39
125.06
124.25
123.13
122.59
121.33
118.92
115.79
114.78
f1 (ppm)


OH
N
OH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7.26
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6.68
6.66
5.64
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4.02
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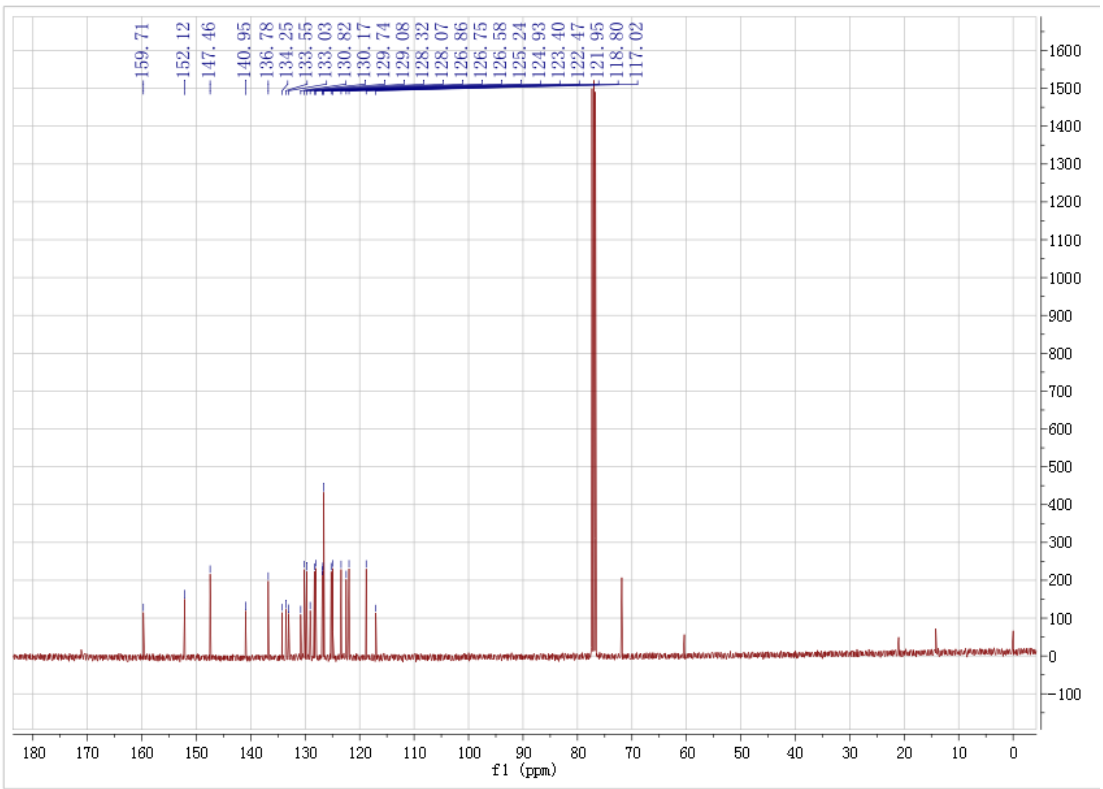
6.83
1.00
1.00
1.09
f1 (ppm)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133.03
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129.74
129.08
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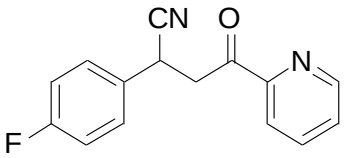
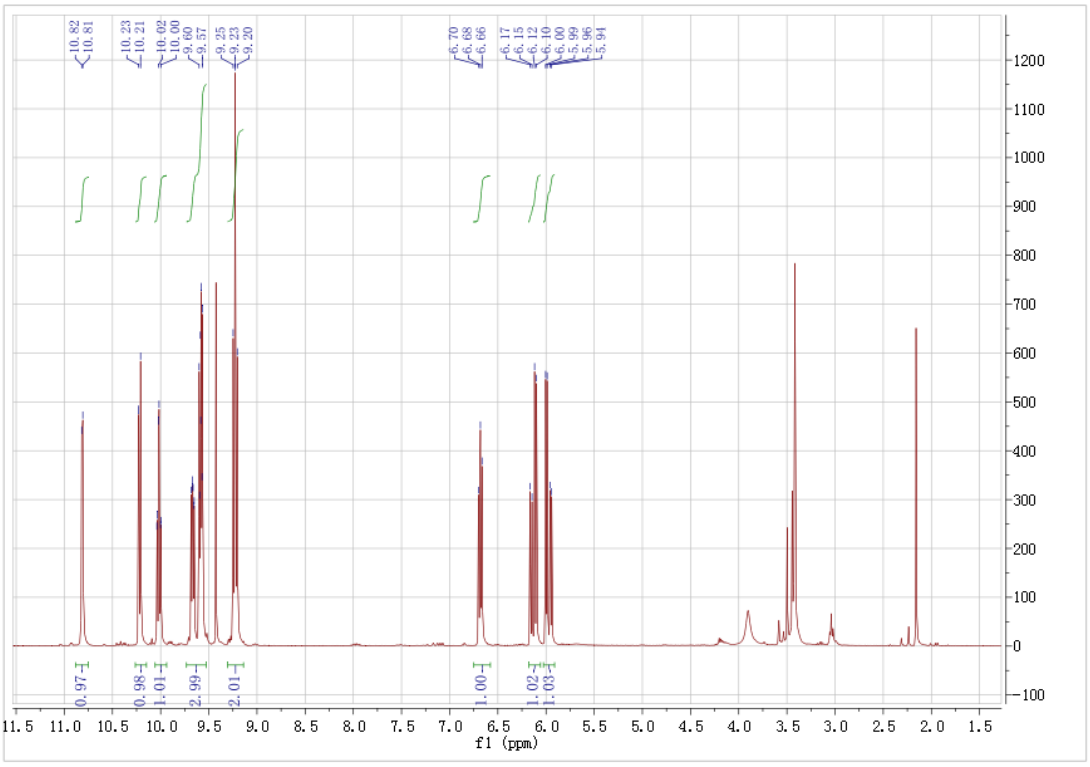
121.95
118.80
117.02
f1 (ppm)


CN
O
N
F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9.23
9.20
6.70
6.68
6.66
6.17
6.15
6.12
6.10
6.00
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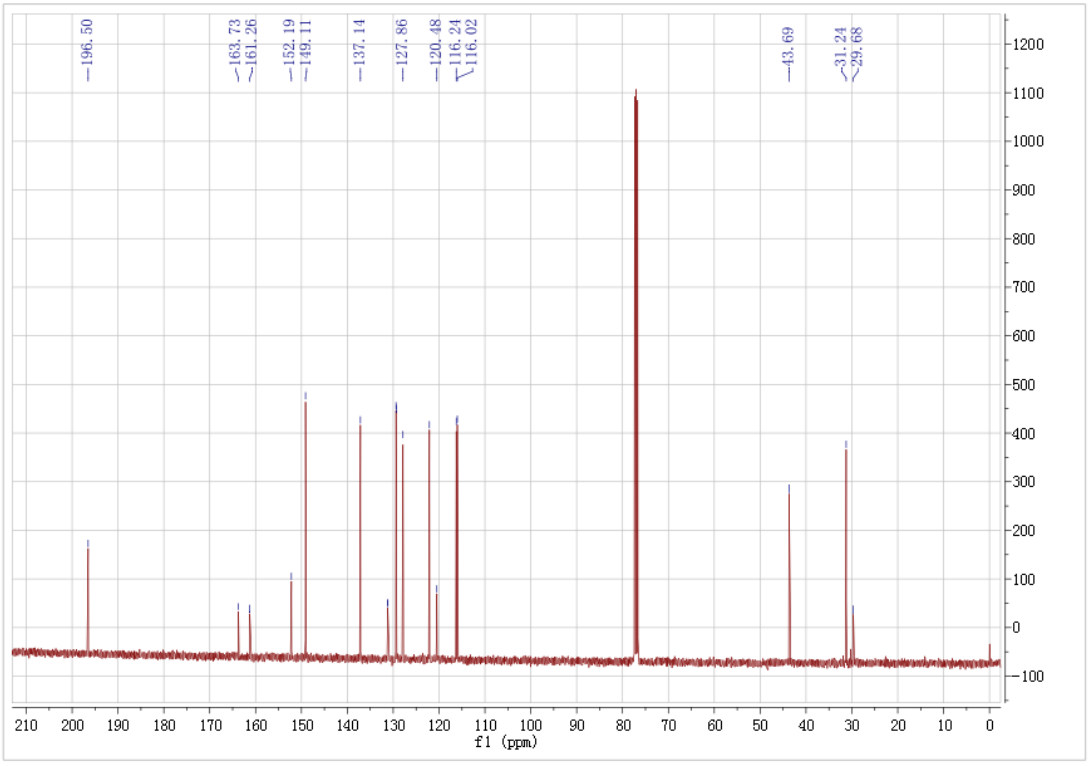
0.97
0.98
1.01
2.99
2.01
1.00
1.02
1.03
f1 (ppm)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43.69
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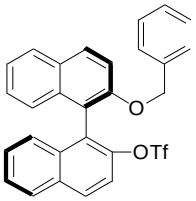
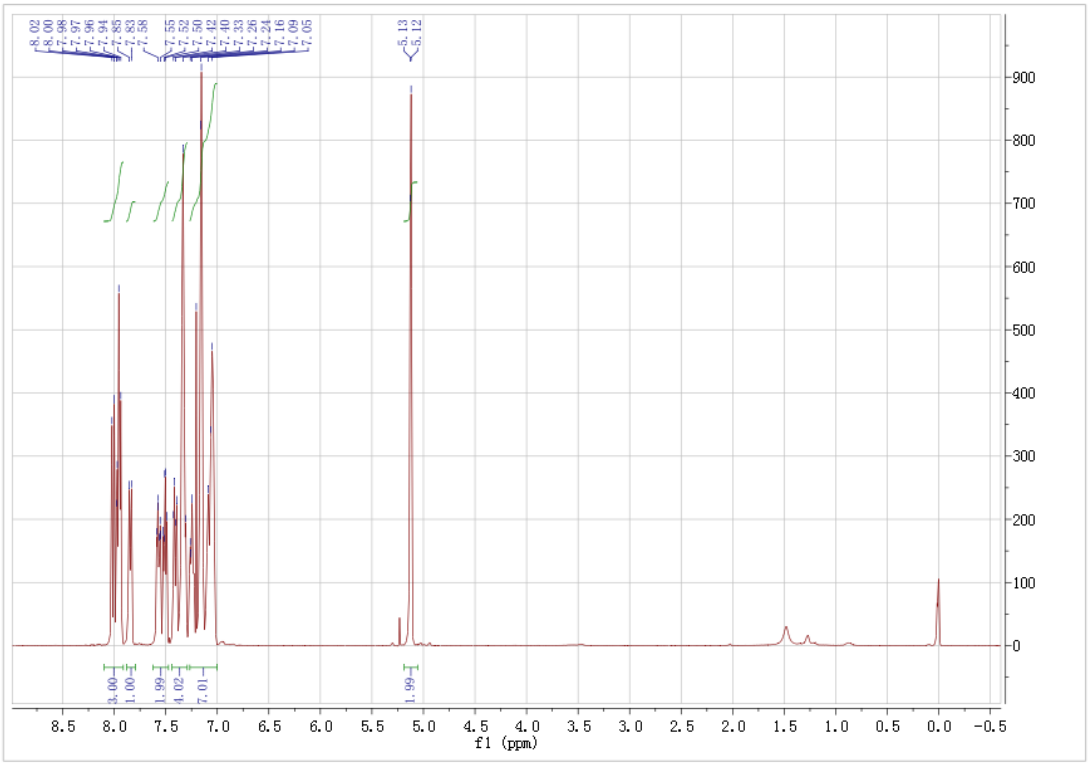
f1 (ppm)


O
OTf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7.83
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7.50
7.42
7.40
7.33
7.26
7.24
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7.09
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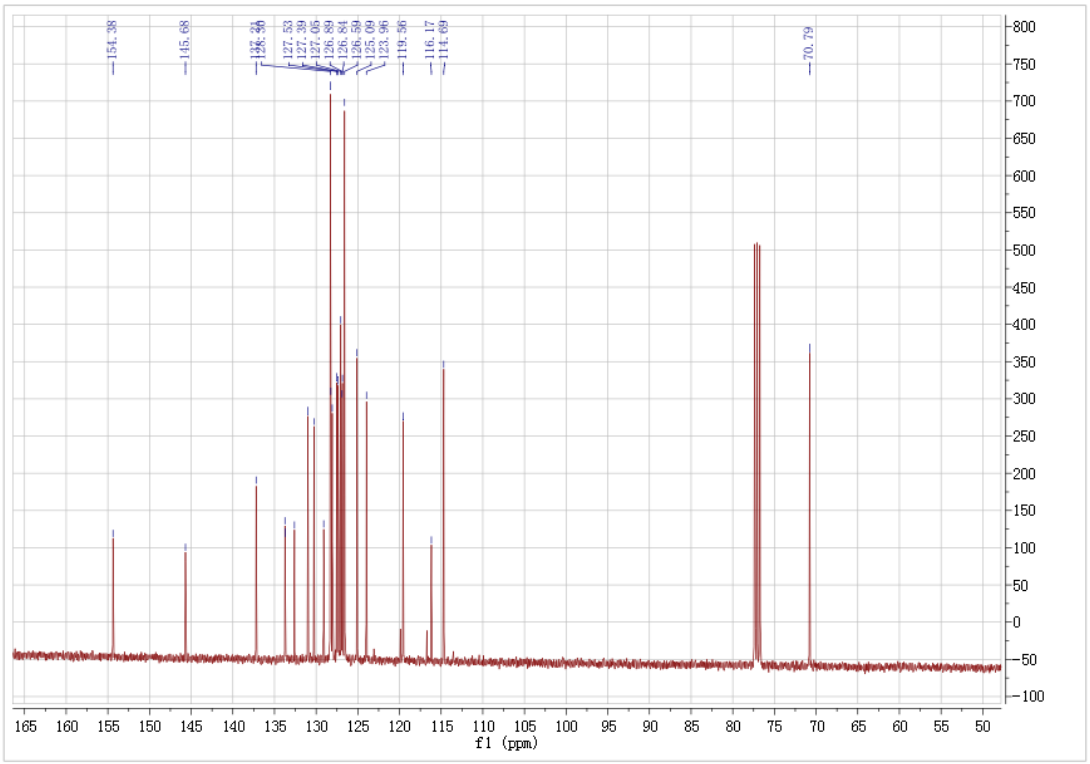
5.12
3.00
1.00
1.99
4.02
7.01
1.99
f1 (ppm)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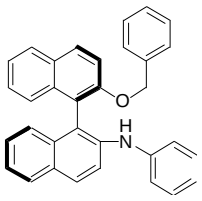
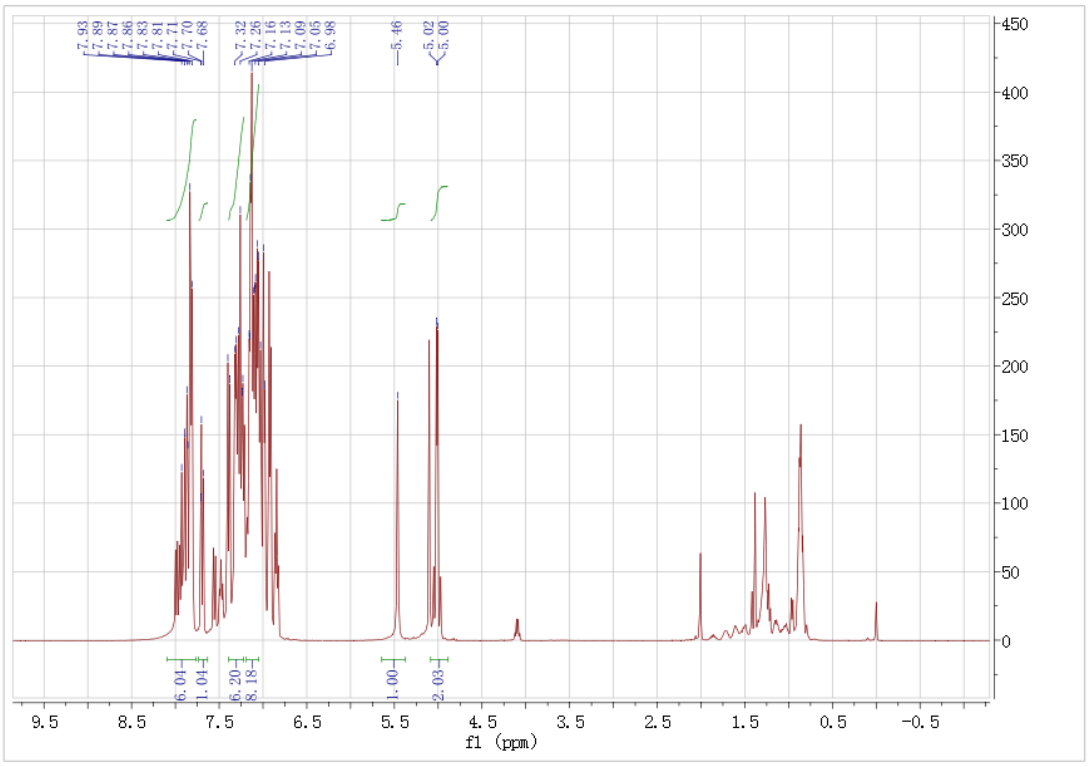
125.09
123.96
119.56
116.17
114.69
70.79
f1 (ppm)

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7.32
7.26
7.16
7.13
7.09
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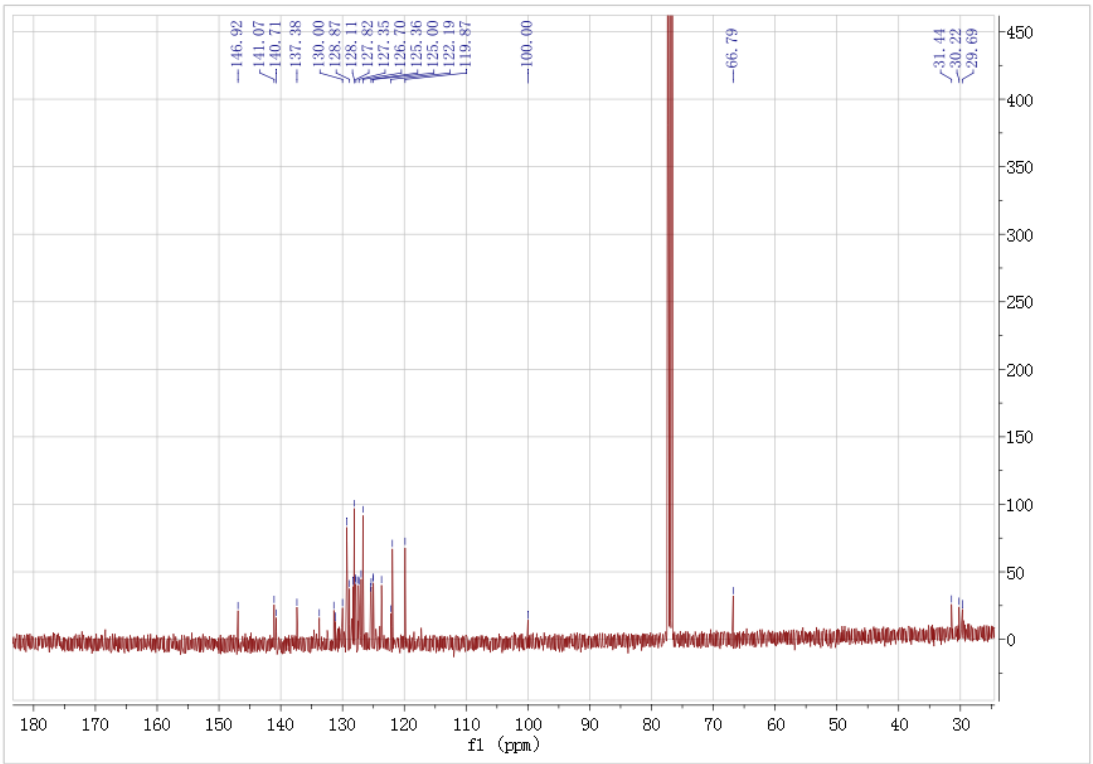
1.04
6.20
8.18
1.00
2.03
f1 (ppm)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128.11
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125.00
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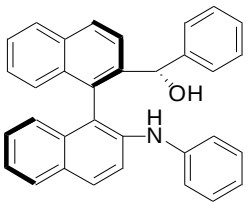
66.79
31.44
30.22
29.69
f1 (ppm)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H
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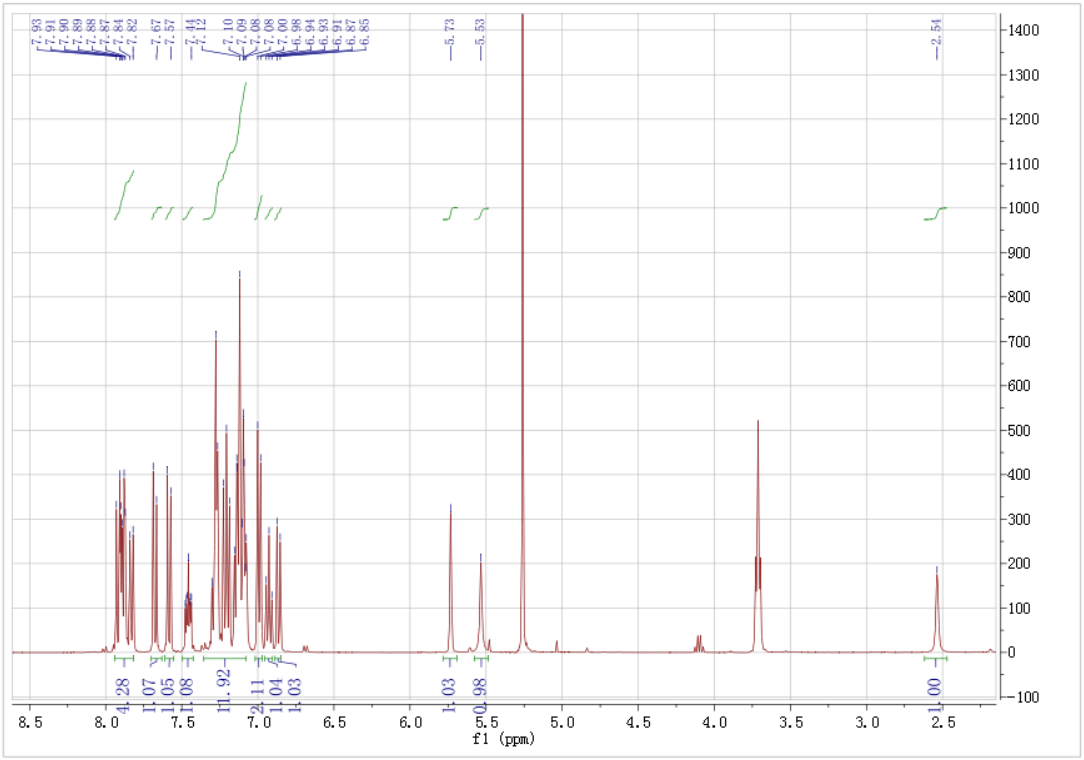
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7.09
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5.53
2.54
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1.08
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2.11
1.04
1.03
1.03
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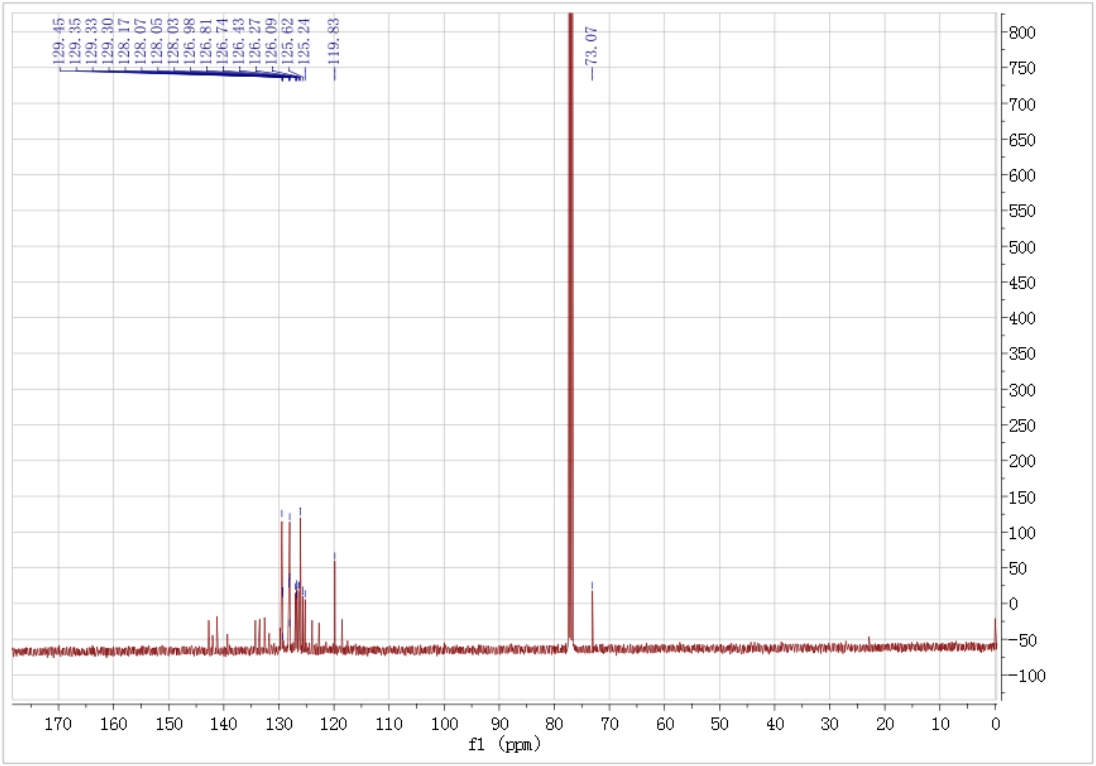
1.00
f1 (ppm)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126.74
126.43
126.27
126.09
125.62
125.24
119.83
73.07
f1 (ppm)