Pd-catalyzed Enantioselective C–H Iodination: Asymmetric Synthesis of Chiral Diarylmethylamines

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SUPPORTING INFORMATION

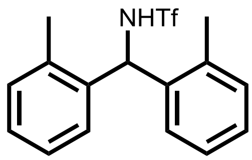
Table of Contents

General Information:

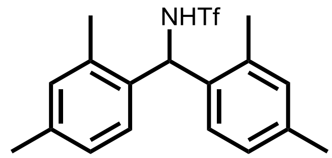
Unless otherwise noted all commercial materials were used without further purification. Solvents were obtained from Acros or Sigma-Aldrich and used directly without further purification. Nuclear magnetic resonance (NMR) spectra were recorded with Varian Inova-500, Bruker DRX-600. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CHCl_3$ = 7.26) unless otherwise noted. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. High resolution mass spectra for new compounds were recorded on an Agilent LC/MSD TOF mass spectrometer or an Agilent 6230 APCI-TOF mass spectrometer. Enantiomeric excesses (ee) were determined on a Hitachi LaChrow Elite HPLC system using commercially available chiral columns. X-ray crystallographic analysis of 2a was done at the X-ray crystallography facility, Department of Chemistry and Biochemistry, University of California, San Diego (UCSD).

All amino acids were purchased from Bachem or EMD or synthesized according to literature procedures as described in the following experimental section. All the substrates were synthesized according to the literature procedures.[1, 2]

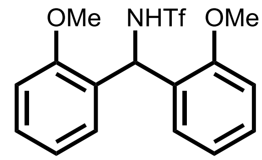
Substrates



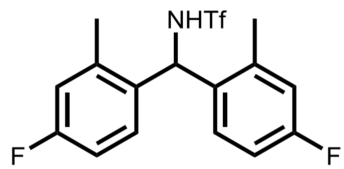
1a



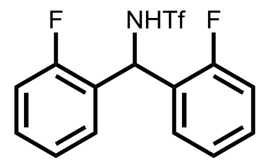
1b



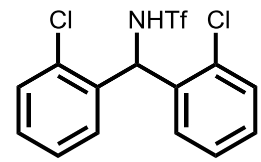
1c



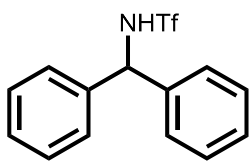
1d



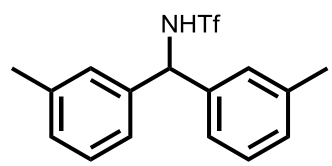
1e



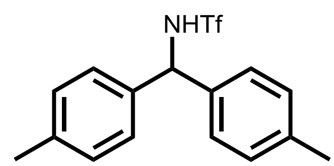
1f



1g



1h



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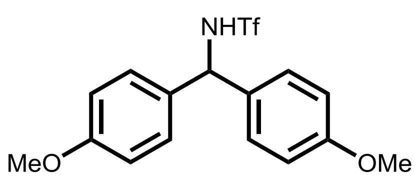

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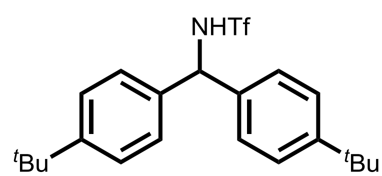
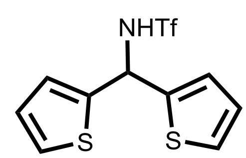


1k



1l

Experimental Procedures and Compound Characterizations:

Procedure for preparation of substrate 1g:

To a stirred solution of diphenylmethylamine (5 mmol, 1.0 equiv.) in dichloromethane (20 mL) was added triethylamine (5 mmol, 1.0 equiv.) at -78 °C under nitrogen. After stirring for 10 min at -78 °C, trifluoromethanesulfonic anhydride (5.3 mmol, 1.05 equiv.) was added dropwise and the mixture was stirred for 1 h at that temperature before being quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (10 mL × 2). The combined organic phase was washed with brine (20 mL), and then dried over $MgSO_4$. Evaporation and column chromatography on silica gel (ethyl acetate/hexane= 1:20 as eluant) afforded corresponding trifluoromethanesulfonamide **1g** (95% Yield).

General procedure for preparation of diarylmethylamines:[1]

To a flame-dried 500 mL three-necked round-bottomed flask filled with nitrogen and equipped with a refluxing condenser was added magnesium (22 mmol), THF (30 mL), the corresponding arylbromide (22 mmol) and a catalytic amount of iodine. The mixture was heated to reflux under a nitrogen atmosphere and kept at reflux for 3 h. The resulting solution was allowed to cool to room temperature and then the corresponding arylnitrile (20mmol) was added. The resulting mixture was heated to reflux for 24 h and then allowed to cool to room temperature, and then to 0 ºC. To this mixture was transferred a suspension of $LiAlH_4$ (20 mmol) in THF (20 mL) via cannula. The ice bath was then removed, and the reaction mixture was heated to reflux, which was maintained for 15 h. Upon completion, the mixture was cooled to room temperature, and carefully quenched by slow addition of water (0.8 mL), then 10% aq NaOH (1.6 mL), and finally H_2O (2.4 mL). The resulting slurry was filtered through a Celite pad and washed with DCM until no amine was left. The combined organic layer was washed with sat. aq. NaCl and concentrated under reduced pressure to give the crude amine, which could be used directly into the next step without purification. And the corresponding trifluoromethanesulfonamides **1a**, **1b**, **1d**, **1h**, **1i**, **1j** and **1k** could be synthesized using the same protocol shown above.

General procedure for preparation of substrate 1e, 1l:[1]

To a stirred solution of the corresponding arylbromide (1.0 equiv.) in THF was added n-BuLi (2.5 M in hexane, 1.0 equiv.) dropwise at -78 ^{o}C under nitrogen and the mixture was stirred for 1 h at -78 ^{o}C. The resulting solution was transferred via cannula to a 250 mL round bottle containing the corresponding arylaldehyde (1.0 equiv.) dissolved in THF at -78 ^{o}C under nitrogen. And the mixture was stirred for another 1 h at -78 ^{o}C and allowed to warm to room temperature while stirring. The resulting solution was quenched with 1 mL of MeOH, diluted with EtOAc and washed with water. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with brine, dried with $MgSO_4$. Evaporation of the solvent afforded the corresponding alcohol, which could be used directly into the next step without purification.

To a 250 mL round bottle was added the alcohol, PCC (5 equiv.) and DCM. The mixture was stirred vigorously at room temperature. Upon completion (Monitored by TLC), the dark slurry was filtered through a Celite pad. Evaporation and column chromatography on silica gel (ethyl acetate/hexane= 1:20 as eluant) afforded the corresponding ketone (81% yield for **1e** and 73% yield for **1l**, over 2 steps).

To a 100 mL pressure vessel was added the ketone, hydroxylamine hydrochloride (5 equiv.), pyridine and EtOH (1:5). The flask was sealed and the solution was heated to reflux for 10 hours. After completion, the solvent was removed under reduced pressure and the residue was partitioned between EtOAc and H_2O (1:1). The aqueous layer was extracted with EtOAc twice and the combined organic layer was washed with brine, dried over $MgSO_4$. Evaporation afforded the crude oxime, which could be used directly into the next step without purification.

To a stirred suspension of oxime in EtOH and concentrated ammonia solution (1:4) was added NH_4OAc (0.5 equiv.), followed by portion-wise addition of zinc powder (5 equiv.). The mixture was heated to 50 ºC and once the vigorous bubbling stopped, the solution was heated to reflux for 8 h. The mixture was then cooled to room temperature and diluted with 100 mL of EtOAc, stirred for 30 min and filtered. The filtrate was transferred to a separation funnel, the organic layer was collected and the aqueous layer was extracted with EtOAc (2 × 50 mL). The combined organic layer was dried over $MgSO_4$, concentrated under reduced pressure to give the crude amine. And the corresponding trifluoromethanesulfonamides **1e, 1l** could be synthesized using the same protocol shown above (52% yield for **1e** and 61% yield for **1l**, over 3 steps).

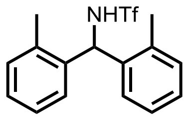
Procedure for preparation of substrate 1f:

To a stirred solution of Mg (1.1 equiv.), I_2 (cat.) in anhydrous THF was added 2-bromo-1-chlorobenzene (1.0 equiv.) dropwise. The resulting solution was stirred for another 1 h at room temperature. Then the solution was cooled to 0 ^{o}C and 2-chlorobenzaldehyde was added slowly. The resulting solution was warmed to room temperature and stirred for 1 h. Upon completion, the resulting solution was quenched with 1 mL of MeOH, diluted with EtOAc and washed with water. The aqueous layer was extracted with EtOAc and the combined organic layer was washed with brine, dried with $MgSO_4$. Evaporation of the solvent afforded the corresponding alcohol, which could be used directly into the next step without purification. And the correspongding trifluoromethanesulfonamides **1f** could be synthesized using the same protocol shown above.

Procedure for preparation of substrate 1c:[1, 2]

To a 100 mL pressure vessel was added benzophenone (10 mmol), $K_2S_2O_8$ (40 mmol), $Pd(OAc)_2$ (1 mmol) and TFA/DCE (25 mL/25 mL). The mixture was heated at 80 ^{o}C for 12 h. After completion, the mixture was filtered through a pad of Celite. Evaporation and column chromatography on silica gel (ethyl acetate/hexane= 1:10 as eluant) afforded 2,2’-dihydroxy-benzophenone (87% yield).

To a flame-dried 150 mL three-necked round-bottomed flask filled with nitrogen and equipped with a refluxing condenser was added 2,2’-dihydroxy-benzophenone (1.0 equiv.), methyl iodine (2 equiv.), K_2CO_3 (10 equiv.) and acetone. The mixture was heated to reflux for 12h. Upon completion, the resulting solution was filtered through a pad of Celite and evaporated to afford the crude 2,2’-dimethoxy-benzophenone, which could be used in the next step directly without purification. And the corresponding trifluoromethanesulfonamides **1c** could be synthesized using the same protocol shown above.

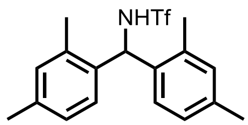


1a (2,2'-dimethyl)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.12 (m, 8H), 6.18 (d, *J* = 7.8 Hz, 1H), 5.29 (s, 1H), 2.30 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.01, 135.77, 131.09, 128.32, 126.76, 126.34, 119.18 (q, *J* = 321.1 Hz), 56.54, 19.00.

HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{15}F_3NO_2S^-$ $[M-H]^-$ 342.0781, found 342.0792.

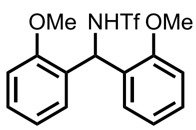


1b (2,2',4,4'-tetramethyl)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.7 Hz, 2H), 7.02 – 6.97 (m, 4H), 6.11 (d, *J* = 7.8 Hz, 1H), 5.14 (s, 1H), 2.31 (s, 6H), 2.27 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.97, 135.48, 134.35, 131.86, 126.93, 126.67, 119.22 (q, *J* = 321.1 Hz), 56.33, 20.94, 18.93.

HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{19}F_3NO_2S^-$ $[M-H]^-$ 370.1094, found 370.1093.

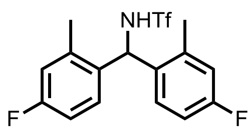


1c (2,2'-methoxyl)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.9 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.60 (d, *J* = 9.3 Hz, 1H), 6.17 (d, *J* = 9.2 Hz, 1H), 3.82 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.26, 129.15, 128.35, 127.40, 119.42 (q, *J* = 321.4 Hz), 120.49, 110.98, 55.87, 55.37.

HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{15}F_3NO_4S^-$ $[M-H]^-$ 374.0679, found 374.0677.

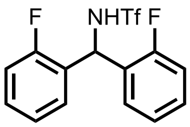


1d (2,2'-dimethyl-4,4'-difluoro)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.06 (m, 2H), 6.98 – 6.86 (m, 4H), 6.10 (d, *J* = 7.9 Hz, 1H), 5.16 (s, 1H), 2.30 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.36 (d, *J* = 247.9 Hz), 138.38 (d, *J* = 8.1 Hz), 132.71 (d, *J* = 3.1 Hz), 128.44 (d, *J* = 8.7 Hz), 119.13 (q, J = 320.9 Hz), 118.05 (d, *J* = 21.4 Hz), 113.17 (d, *J* = 21.3 Hz), 55.63, 19.09.

HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{13}F_5NO_2S^-$ $[M-H]^-$ 378.0593, found 378.0597.

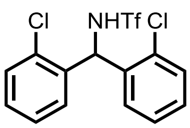


1e (2,2'-difluoro)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 9.5 Hz, 2H), 6.22 (d, *J* = 4.4 Hz, 1H), 5.85 (br, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.83 (d, *J* = 247.6 Hz), 130.49 (d, *J* = 8.9 Hz), 128.18 (d, *J* = 2.6 Hz), 128.17 (d, *J* = 2.7 Hz), 125.96 (d, *J* = 12.6 Hz), 124.66 (d, *J* = 3.6 Hz), 119.34 (d, *J* = 318.7 Hz), 116.16 (d, *J* = 21.0 Hz), 53.40.

HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_9F_5NO_2S^-$ $[M-H]^-$ 350.0280, found 350.0281.



1f (2,2'-dichloro)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.37 – 7.28 (m, 6H), 6.60 (s, 1H), 5.40 (br, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.78, 133.50, 130.46, 129.95, 128.71, 127.15, 119.18 (q, *J* =321.0 Hz), 57.17.

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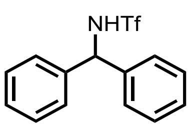

1g diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.30 (m, 7H), 7.29 – 7.20 (m, 3H), 5.87 (s, 1H), 5.52 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.53, 128.98, 128.36, 127.16, 119.41 (q, *J* = 321.1 Hz), 62.41.

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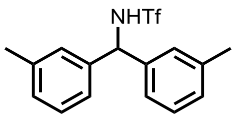
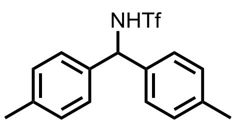


1h (3,3'-dimethyl)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.4 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 2H), 7.07 – 7.00 (m, 4H), 5.79 (d, *J* = 8.7 Hz, 1H), 5.48 (s, 1H), 2.34 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.63, 138.75, 129.03, 128.81, 127.74, 124.10, 119.43 (q, *J* = 321.2 Hz), 62.44, 21.43.

HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{15}F_3NO_2S^-$ [M-H]$^-$ 342.0781, found 342.0785.

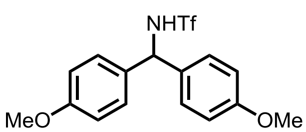


1i (4,4'-dimethyl)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.03 (m, 8H), 5.79 (d, *J* = 6.3 Hz, 1H), 5.58 (s, 1H), 2.33 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.04, 138.03, 136.89, 136.85, 129.56, 126.99, 119.45 (q, *J* = 321.1 Hz), 62.07, 21.04.

HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{15}F_3NO_2S^-$ [M-H]$^-$ 342.0781, found 342.0784.

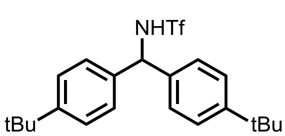


1j (4,4'-dimethoxyl)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.5 Hz, 4H), 6.89 (d, *J* = 7.3 Hz, 4H), 5.80 (d, *J* = 8.0 Hz, 1H), 5.36 (d, *J* = 6.3 Hz, 1H), 3.81 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.40, 131.92, 128.41, 119.45 (q, *J* = 321.45 Hz), 114.23, 61.56, 55.32.

HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{15}F_3NO_4S^-$ [M-H]$^-$ 374.0679, found 374.0679.

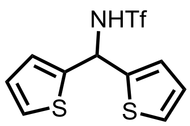


1k (4,4'-di-*tert*-butyl)diphenylmethyl-trifluoromethanesulfonamide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 4H), 7.17 (d, *J* = 8.1 Hz, 4H), 5.82 (d, *J* = 8.3 Hz, 1H), 5.35 (s, 1H), 1.31 (s, 18H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.26, 136.68, 126.85, 125.82, 119.47 (q, *J* = 321.3 Hz), 62.01, 34.57, 31.25.

HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{27}F_3NO_2S^-$ [M-H]$^-$ 426.1720, found 426.1726.



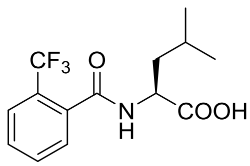
1l di(2-thiophene)methyl- trifluoromethanesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 5.1, 1.2 Hz, 2H), 7.08 – 7.02 (m, 2H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 2H), 6.30 (s, 1H), 5.75 (s, 1H).

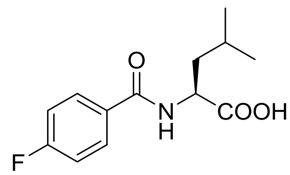
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.73, 127.11, 126.76, 126.54, 119.33 (q, *J* = 320.8 Hz), 54.57.

HRMS (ESI-TOF) *m/z* Calcd for $C_{10}H_7F_3NO_2S_3^-$ [M-H]$^-$ 325.9596, found 325.9597.

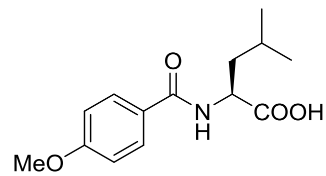
Ligands:



L1



L2



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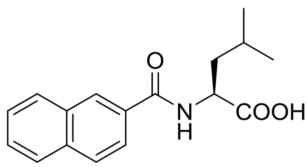
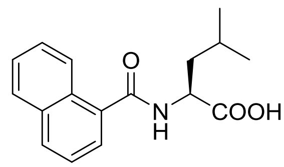
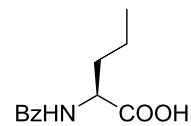


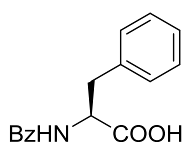
L4



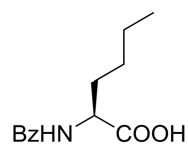
L5



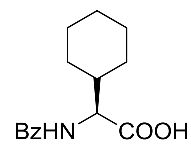
L6



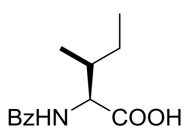
L7



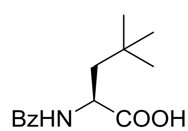
L8



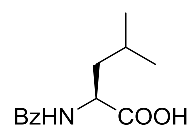
L9



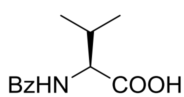
L10



L11



L12



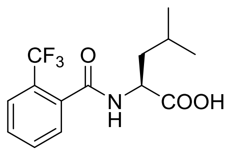
L13

L7, L8, L12 and L13 are commercially available. The rest of the ligands were synthesized according to the general procedure shown below.

General procedure for the preparation of *N*-protected amino acids L1-L11:

To a magnetically stirred solution at 0 °C of L-amino acid (5 mmol) and 1 N NaOH (20 mL) was added the corresponding aroyl chloride (7 mmol) in portions over 0.5 h. The reaction mixture was allowed to warm to r.t. and stirred overnight, and then was extracted with ether. The aqueous phase was then cooled to 0 °C, adjusted to pH 1 by the addition of HCl and then extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (methanol: dichloromethane = 1:50) to give the corresponding *N*-protected amino acid.

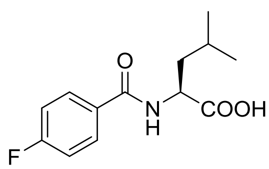
L1



^{1}H NMR (600 MHz, $CDCl_3$) δ 9.70 (br, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.62 – 7.50 (m, 3H), 6.31 (s, 1H), 4.82 (s, 1H), 1.90 – 1.73 (m, 2H), 1.73 – 1.57 (m, 1H), 1.06 – 0.92 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.17, 167.94, 134.90, 132.04, 130.13, 128.65, 127.32 (q, *J* = 32.2 Hz), 126.38 (q, *J* = 4.9 Hz), 123.43 (q, *J* = 273.5 Hz), 51.24, 41.02, 24.76, 22.79 21.61.

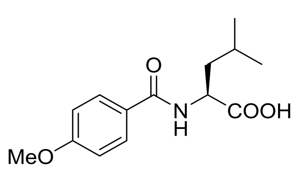
L2



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.17 – 7.02 (m, 2H), 6.62 (s, 1H), 4.80 (s, 1H), 1.89 – 1.64 (m, 3H), 1.04 – 0.92 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.96, 166.86, 164.99 (d, *J* = 252.8 Hz), 129.66 (d, *J* = 3.0 Hz), 129.55 (d, *J* = 9.0 Hz), 115.71 (d, *J* = 21.9 Hz), 51.39, 41.15, 25.00, 22.83, 21.87.

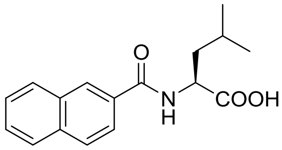
L3



^{1}H NMR (600 MHz, $CDCl_3$) δ 8.91 (br, 1H), 7.74 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.62 (s, 1H), 4.78 (s, 1H), 3.82 (s, 3H), 1.86 – 1.63 (m, 3H), 1.03 – 0.90 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.79, 167.56, 162.54, 129.06, 125.64, 113.79, 55.40, 51.45, 41.15, 24.97, 22.85, 21.92.

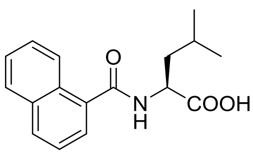
L4



^{1}H NMR (600 MHz, $CDCl_3$) δ 10.70 (br, 1H), 8.27 (s, 1H), 7.92 – 7.73 (m, 4H), 7.52 (t, J = 7.1 Hz, 1H), 7.47 (t, J = 7.0 Hz, 1H), 6.97 (s, 1H), 4.90 (s, 1H), 1.87 – 1.68 (m, 3H), 0.96 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.07, 168.14, 134.85, 132.45, 130.61, 128.95, 128.46, 127.89, 127.80, 127.67, 126.75, 123.47, 51.47, 41.21, 24.99, 22.82, 21.89.

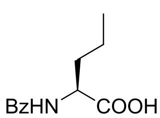
L5



^{1}H NMR (600 MHz, $CDCl_3$) δ 10.59 (br, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 6.6 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.34 (t, J = 7.3 Hz, 1H), 6.62 (s, 1H), 4.88 (s, 1H), 1.81 – 1.67 (m, 2H), 1.60 (t, J = 8.7 Hz, 1H), 1.00 (d, J = 4.9 Hz, 3H), 0.94 (d, J = 5.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.04, 170.05, 133.49, 133.25, 130.90, 129.97, 128.20, 127.19, 126.40, 125.28, 125.22, 124.55, 51.26, 40.96, 25.00, 22.85, 21.74.

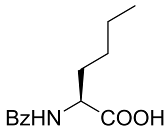
L6



^{1}H NMR (600 MHz, $CDCl_3$) δ 10.48 (br, 1H), 7.78 (s, 2H), 7.50 (s, 1H), 7.41 (s, 2H), 6.85 (s, 1H), 4.81 (s, 1H), 1.97 (s, 1H), 1.81 (s, 1H), 1.43 (s, 2H), 0.94 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.52, 167.89, 133.48, 131.98, 128.62, 127.14, 52.65, 34.21, 18.60, 13.67.

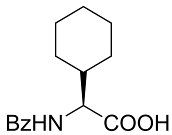
L8



^{1}H NMR (500 MHz, $CDCl_3$) δ 10.50 (br, 1H), 7.79 (s, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 6.9 Hz, 2H), 7.07 (s, 1H), 4.80 (s, 1H), 1.98 (s, 1H), 1.82 (s, 1H), 1.33 (s, 4H), 0.87 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.08, 168.03, 133.41, 131.92, 128.53, 127.16, 52.85, 31.80, 27.30, 22.25, 13.76.

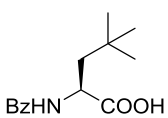
L9



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.56 – 7.36 (m, 3H), 6.82 (s, 1H), 4.76 (s, 1H), 2.00 – 1.52 (m, 6H), 1.32 – 1.00 (m, 5H).

^{13}C NMR (151 MHz, CDCl3) δ 176.60, 167.82, 133.70, 131.91, 128.60, 127.16, 57.58, 40.89, 29.57, 28.30, 25.93, 25.91.

L11

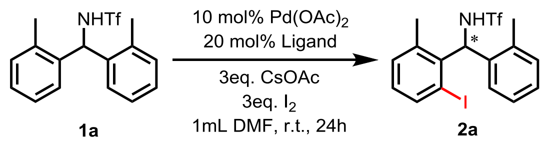


^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (br, 1H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.50 (s, 1H), 7.41 (s, 2H), 6.57 (s, 1H), 4.83 (s, 1H), 2.02 – 1.89 (m, 1H), 1.73 – 1.54 (m, 1H), 1.01 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.62, 167.79, 133.53, 131.96, 128.65, 127.11, 77.21, 77.00, 76.79, 50.64, 45.62, 30.85, 29.62.

Optimization of reaction conditions:

Table S1. Ligand Screening[a]



Entry	Ligand	Yield(%)[b]	ee(%)[c]	Entry	Ligand	Yield(%)	ee(%)
1	Boc-Leu-OH	25	25	11	Form-Leu-OH	10	30
2	Boc-Val-OH	20	33	12	Ac-Leu-OH	n.r.	n.r.
3	Boc-Ala-OH	11	23	13	TFA-Leu-OH	10	3
4	Boc-Ile-OH	30	26	14	TcBoc-Leu-OH	13	8
5	Boc-Phe-OH	26	25	15	Me-Leu-OH	n.r.	n.r.
6	Boc-D-Val-OH	18	-33	16	Bn-Leu-OH	n.r.	n.r.
7	Boc-Nle-OH	20	15	17	MeO_2C-Leu-OH	43	15
8	Boc-Try(tBu)-OH	20	35	18	Piv-Leu-OH	30	0
9	Boc-Asn-OH	n.r.	n.r.	19	Bz-Leu-OH	20	67
10	Boc-MeAla-OH	34	2	**20[d]**	**Bz-Leu-OH**	**18(47[e])**	**89(78[e])**

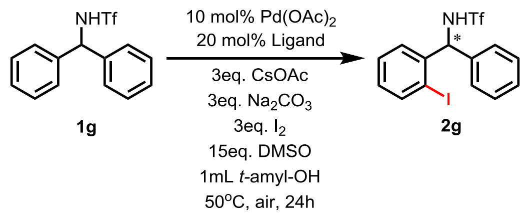
[a]Conducted on 0.1 mmol scale. [b]Determined by ^{1}H-NMR analysis using CH_2Br_2 as the internal standard. [c]Determined by chiral HPLC analysis. [d]*t*-Amyl-OH used as solvent with 15eq. DMF as an additive. [e]Conducted at 50 °C, 12 h.

Table S2. Base Screening[a]

Entry	Base	Yield(%)[b]	ee(%)[c]	Entry	Base	Yield(%)	ee(%)
1	None	n.r.	n.r.	10	K_2CO_3	38	99
2	CsOAc	47	78	11	Cs_2CO_3	40	98
3	LiOAc	n.r.	n.r.	12	Na_2HPO_4	n.r.	n.r.
4	NaOAc	12	53	13	K_2HPO_4	20	83
5	KOAc	40	60	14	K_3PO_4	33	97
6	$NaHCO_3$	n.r.	n.r.	15	LiH_2PO_4	58	75
7	$KHCO_3$	n.r.	n.r.	16	CsOAc+Na_2CO_3[d]	82	89
8	Li_2CO_3	n.r.	n.r.	**17[e]**	**CsOAc+Na_2CO_3[d]**	**81(80[f])**	**98(98[f])**
9	Na_2CO_3	6	77	18[e]	CsOAc	45	90

[a]Conducted on 0.1 mmol scale. [b]Determined by ^{1}H-NMR analysis using CH_2Br_2 as the internal standard. [c]By chiral HPLC analysis. [d]3eq. of CsOAc and 3eq. Na_2CO_3.
[e]15eq. DMSO as an additive instead of DMF. [f]Conducted on 30 °C, 48 h.

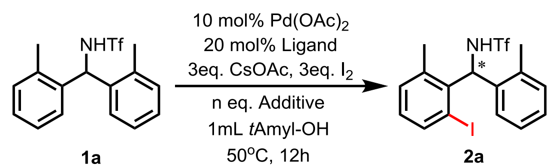
Table S3. Ligand Screening[a]



Entry	Ligand	Yield(%)[b]	ee(%)[c]
1	L1	60	75
2	L2	57	75
3	L3	53	75
4	L4	63	75
5	L5	55	75
6	L6	45	72
7	L7	49	50
8	L8	44	71
9	L9	66	63
10	L10	50	67
11	L11	46	55
12	L12	59	75
13	L13	46	73

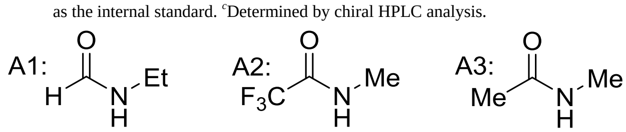
[a]Conducted on 0.1 mmol scale. [b]Determined by ^{1}H-NMR analysis using CH_2Br_2 as the internal standard. [b]Total yield of mono and di product [c]Determined by chiral HPLC analysis using AS-H chiral column.ee were of mono product

Table S4. Additive effect[a]



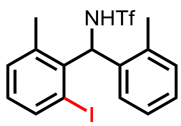
Entry	Additive(eq.)	Yield(%)[b]	ee(%)[c]
1	DMF(15)	47	78
2	NMF(15)	22	n.d.
3	DMA(15)	41	n.d.
4	DMSO(15)	47	91
5	NMP(15)	47	75
6	A1(15)	58	75
7	A2(15)	15	n.d.
8	A3(15)	40	n.d.

[a]Conducted on 0.1 mmol scale. [b]Determined by ^{1}H-NMR analysis using CH_2Br_2 as the internal standard. [c]Determined by chiral HPLC analysis.



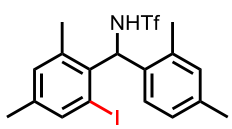
General procedure for the enantioselective C–H iodination reactions:

To a 15 mL sealed tube was added substrates **1** (1 equiv., 0.2 mmol), $Pd(OAc)_2$ (10 mol%, 0.02 mmol), Bz-Leu-OH (40 mol%, 0.08 mmol), CsOAc (3 equiv., 0.6 mmol), I_2 (3 equiv., 0.6 mmol), Na_2CO_3 (3 equiv., 0.6 mmol), DMSO (15 equiv.) and *t*-amyl-OH (2 mL). The mixture was stirred at 30 ^{o}C for 48 h under air. The resulting mixture was diluted by EtOAc, filtered through a pad of celite and washed with $Na_2S_2O_3$. The aqueous layer was extracted twice with EtOAc and the combined organic layer was dried over $MgSO_4$, evaporated and purified by prep-TLC (EtOAc: Hexanes= 1:5-1:15) to give the product and ee was determined on a Hitachi LaChrow HPLC system using commercially available chiral columns as described below.



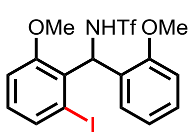
2a (2-iodo-6, 2'-dimethyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2a** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 80% yield (75 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.20 (m, 3H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.0 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.57 (s, 1H), 5.85 (br, 1H), 2.55 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.47, 138.73, 137.87, 137.77, 132.74, 132.03, 131.93, 129.71, 129.15, 128.99, 125.98, 119.01 (q, *J* = 321.6 Hz), 67.00, 21.73, 20.27. HPLC chiralcel AS-H column (5% isopropanol in hexanes, 0.3 mL/min) t_r= 27.320 min (major), 47.307 min (minor): 98% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{14}F_3INO_2S^-$ [M-H]$^-$ 467.9748, found 467.9753. $[\alpha]^{22}_D$= -84.6 (c= 1.00, $CHCl_3$). The absolute configuration is assigned to R according to the X-ray data.



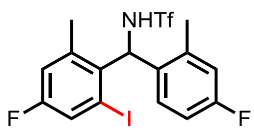
2b (2-iodo-4,6,2',4'-tetramethyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2b** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 85% yield (85 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.09 (s, 1H), 7.04 (s, 1H), 6.95 – 6.78 (m, 2H), 6.49 (s, 1H), 5.81 (br, 1H), 2.50 (s, 3H), 2.33 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.82, 139.59, 138.77, 138.10, 137.52, 135.00, 132.89, 132.69, 130.06, 129.19, 126.51, 119.03 (q, *J* = 321.5 Hz), 99.56, 60.41, 20.91, 20.25, 20.15. HPLC chiralcel AS-H column (2% isopropanol in hexanes, 0.2mL/min) t_r= 53.907 min (major), 67.027 min (minor): 98% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{18}F_3INO_2S^-$ [M-H]$^-$ 496.0061, found 496.0075. $[\alpha]^{23}_D$= -63.6 (c= 0.60, $CHCl_3$).



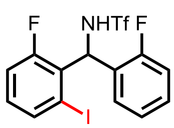
2c (2-iodo-6, 2'-dimethoxyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2c** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 75% yield (75 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.09 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.93 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.52 (s, 2H), 3.86 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.32, 157.06, 133.04, 130.40, 129.84, 129.40, 127.93, 125.74, 119.79, 119.32 (q, *J* = 321.4 Hz), 112.03, 110.87, 101.02, 62.00, 55.80, 55.17. HPLC chiralcel OD-H column (5% isopropanol in hexanes, 0.3mL/min) t_r= 26.693 min (major), 38.107 min (minor): 97% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{14}F_3INO_4S^-$ [M-H]$^-$ 499.9646, found 499.9653. $[\alpha]^{24}_D$= -29.1 (c= 0.92, $CHCl_3$).



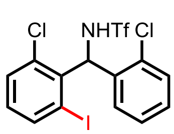
2d (2-iodo-6, 2'-dimethyl-4, 4'-difluoro)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2d** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 78% yield (79 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 5.5 Hz, 1H), 7.01 (td, *J* = 8.8, 2.4 Hz, 2H), 6.92 (m, 1H), 6.80 (td, *J* = 8.4, 2.6 Hz, 1H), 6.49 (s, 1H), 5.82 (br, 1H), 2.53 (s, 1H), 2.39 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.73 (d, *J* = 249.1 Hz), 161.01 (d, *J* = 253.4 Hz), 140.47 (d, *J* = 8.2 Hz), 133.91, 130.91, 128.40, 126.35, 119.05, 118.96 (q, *J* = 321.4 Hz), 118.80 (d, *J* = 21.4 Hz), 112.69 (d, *J* = 21.1 Hz), 97.98, 21.83, 20.34. HPLC chiralcel AS-H column (5% isopropanol in hexanes, 0.3 mL/min) t_r= 25.013 min (major), 48.240 min (minor): 99% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{12}F_5INO_2S^-$ [M-H]$^-$ 503.9559, found 503.9574. $[\alpha]^{23}_D$= -97.8 (c= 1.09, $CHCl_3$).



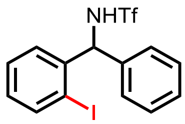
2e (2-iodo-6, 2'-difluoro)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2e** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 62% yield (59 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.31 (m, 1H), 7.26 – 7.22 (m, 1H), 7.19 – 7.05 (m, 4H), 6.56 (d, *J* = 9.9 Hz, 1H), 6.05 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.33 (d, *J* = 250.0 Hz), 160.17 (d, *J* = 250.6 Hz), 136.48 (d, *J* = 3.3 Hz), 131.61 (d, *J* = 9.7 Hz), 130.80 (d, *J* = 8.4 Hz), 129.05 (d, *J* = 12.6 Hz), 128.37 (d, *J* = 2.9 Hz), 128.35 (d, *J* = 2.9 Hz), 124.36 (d, *J* = 3.8 Hz), 123.99 (d, *J* = 12.8 Hz), 119.21 (q, *J* = 320.9 Hz), 116.83 (d, *J* = 23.1 Hz), 116.37 (d, *J* = 21.4 Hz), 98.90 (d, *J* = 3.2 Hz), 59.73. HPLC chiralcel AS-H column (5% isopropanol in hexanes, 0.3 mL/min) t_r= 52.280 min (major), 69.700 min (minor): 99% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_8F_5INO_2S^-$ [M-H]$^-$ 475.9246, found 475.9263. $[\alpha]^{23}_D$= -8.5 (c= 0.34, $CHCl_3$).



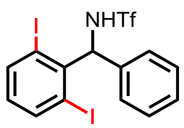
2f (2-iodo-6, 2'-dichloro)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2f** was prepared according to the general procedure and was purified by prep-TLC to give a colorless solid in 54% yield (55 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 – 7.28 (m, 1H), 7.28 – 7.16 (m, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 5.09 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.83, 136.83, 134.45, 133.89, 132.46, 131.66, 130.91, 130.31, 126.66, 119.09 (q, *J* = 321.4 Hz), 101.86, 64.83. HPLC chiralcel AS-H column (5% isopropanol in hexanes, 0.3 mL/min) t_r= 52.740 min (major), 57.033 min (minor): 99% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_8Cl_2F_3INO_2S^-$ [M-H]$^-$ 507.8655, found 507.8650.



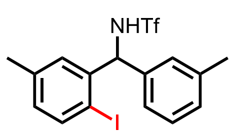
2g-mono 2-iododiphenylmethyl-trifluoromethanesulfonamide

The compound **2g-mono** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 20% yield (18 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.08 (td, *J* = 7.8, 1.6 Hz, 1H), 6.13 (d, *J* = 5.7 Hz, 1H), 5.65 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.37, 140.54, 137.99, 130.02, 129.09, 128.77, 128.59, 128.40, 127.73, 119.38 (q, *J* = 321.6 Hz), 98.18, 65.81. HPLC chiralcel AS-H column (5% isopropanol in hexanes, 0.3 mL/min) t_r= 51.513min (major), 67.300 min (minor): 87% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{10}F_3INO_2S^-$ [M-H]$^-$ 439.9435, found 439.9440.



2g-di (2, 6-diiodo)-diphenylmethyl-trifluoromethanesulfonamide

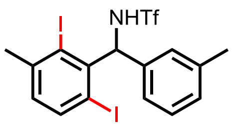
The compound **2g-di** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 46% yield (52 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.32 (m, 3H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.82 (d, *J* = 10.3 Hz, 1H), 6.76 – 6.70 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.50, 141.49, 140.60, 136.22, 131.47, 128.98, 128.08, 126.15, 119.25 (q, *J* = 321.1 Hz), 103.79, 95.01, 68.36. HPLC chiralcel AS-H column (5% isopropanol in hexanes, 0.2mL/min) t_r= 23.220 min (major), 26.680 min (minor): 99% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_9F_3I_2NO_2S^-$ [M-H]$^-$ 565.8410, found 565.8407.



2h-mono (2-iodo-5, 3'-dimethyl)-diphenylmethyl-trifluoromethanesulfonamide

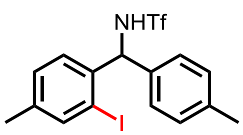
The compound **2h-mono** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 39% yield (37 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.20 (s, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.03 (s, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.88 (dd,

J = 8.0, 1.5 Hz, 1H), 6.05 (d, J = 8.3 Hz, 1H), 5.65 (d, J = 8.0 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.21, 140.15, 138.90, 138.87, 138.07, 130.99, 129.27, 129.22, 128.86, 128.22, 124.64, 119.38 (q, J = 321.3 Hz), 94.11, 65.62, 21.49, 21.15. HPLC chiralcel AS-H column (5% isopropanol in hexanes, 0.2mL/min) t_r= 56.300 min (major), 74.267 min (minor): 93% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{14}F_3INO_2S^-$ $[M-H]^-$ 467.9748, found 467.9761.



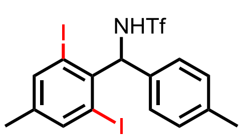
2h-di (2, 6-diiodo-3, 3'-dimethyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2h-di** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 22% yield (26 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 0.5H), 7.78 (d, J = 8.0 Hz, 0.5H), 7.23 (td, J = 7.7, 1.9 Hz, 1H), 7.14 (d, J = 7.3 Hz, 1H), 7.01 (s, 1H), 6.98 – 6.89 (m, 2.5H), 6.71 (s, 0.5H), 2.56 (s, 1.5H), 2.44 (s, 1.5H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.93, 143.89, 142.33, 142.18, 141.55, 140.17, 138.69, 138.67, 136.97, 136.80, 131.07, 130.91, 128.71, 128.70, 128.63, 128.53, 126.85, 126.55, 123.44, 123.15, 119.48 (q, J = 322.5 Hz), 119.43 (q, J = 322.5 Hz), 111.95, 103.16, 100.40, 91.33, 69.12, 69.08, 31.12, 29.95, 21.64, 21.63. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{13}F_3I_2NO_2S^-$ $[M-H]^-$ 593.8714, found 593.8724.



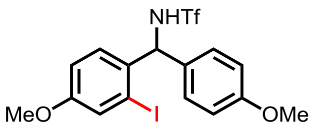
2i-mono (2-iodo-4, 4'-dimethyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2i-mono** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 24% yield (22 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 8.7 Hz, 1H), 7.15 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.05 (s, 1H), 2.33 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.85, 140.10, 138.61, 138.40, 135.31, 129.69, 129.54, 127.92, 127.57, 119.40 (J = 321.4 Hz), 98.05, 65.38, 21.10, 20.47. HPLC chiralcel AS-H column (5% isopropanol in hexanes, 0.2 mL/min) t_r= 61.980 min (major), 90.100 min (minor): 90% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{14}F_3INO_2S^-$ $[M-H]^-$ 467.9748, found 467.9757.



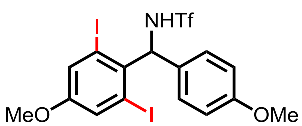
2i (2, 6-diiodo-4, 4'-dimethyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2i-di** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 47% yield (56 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.76 (s, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 6.75 (d, J = 9.5 Hz, 1H), 6.63 (d, J = 9.0 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.09, 141.91, 141.07, 138.45, 137.88, 133.41, 129.61, 126.12, 119. 26 (q, J = 321.2 Hz), 103.32, 94.56, 67.92, 21.08, 19.73. HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{13}F_3I_2NO_2S^-$ [M-H]$^-$ 593.8714, found 593.8727.



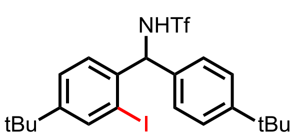
2j-mono (2-iodo-4, 4'-dimethoxyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2j-mono** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 22% yield (22 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 2.6 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 8.7 Hz, 2H), 6.99 (dd, J = 8.6, 2.6 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.02 (s, 1H), 5.55 (br, 1H), 3.81 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.54, 159.46, 133.69, 130.46, 128.95, 128.57, 125.45, 119.40 (q, J = 321.4 Hz), 114.62, 114.32, 98.19, 64.93, 55.56, 55.31. HPLC chiralcel AS-H column (10% isopropanol in hexanes, 0.3 mL/min) t_r= 80.367 min (major), 97.073 min (minor): 94% ee. HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{14}F_3INO_4S^-$ [M-H]$^-$ 499.9646, found 499.9649.



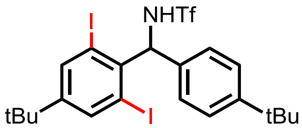
2j-di (2, 6-diiodo-4, 4'-dimethoxyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2j-di** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 32% yield (40 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.51 (s, 1H), 7.07 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 10.2 Hz, 1H), 6.58 (d, J = 10.2 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.30, 159.20, 133.42, 128.64, 128.53, 127.53, 125.62, 119.27 (q, J = 321. 1 Hz), 114.24, 102.94, 94.08, 67.49, 55.79, 55.29. HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{13}F_3I_2NO_4S^-$ [M-H]$^-$ 625.8612, found 625.8622.



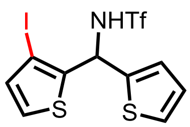
2k-mono (2-iodo-4, 4'-di-*tert*-butyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2k-mono** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 20% yield (22 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 6.8 Hz, 2H), 7.32 (dd, J = 8.2, 1.2 Hz, 1H), 7.13 (d, J = 7.2 Hz, 2H), 6.07 (d, J = 8.1 Hz, 1H), 5.60 (d, J = 8.0 Hz, 1H), 1.31 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.29, 151.54, 138.67, 137.44, 135.21, 127.76, 127.35, 125.94, 125.91, 119.42 (q, J = 321.3 Hz), 98.38, 65.41, 34.58, 34.52, 31.21, 31.11. HPLC chiralcel AS-H column (2% isopropanol in hexanes, 0.1 mL/min) t_r= 97.840 min (major), 137.033 min (minor): 77% ee. HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{26}F_3INO_2S^-$ [M-H]$^-$ 552.0687, found 552.0696.



2k-di (2, 6-diiodo-4, 4'-di-tert-butyl)-diphenylmethyl-trifluoromethanesulfonamide

The compound **2k-di** was prepared according to the general procedure and was purified by prep-TLC to give a colorless oil in 47% yield (61 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.88 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.76 (s, 1H), 6.65 (s, 1H), 1.31 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.96, 151.04, 139.92, 138.63, 137.83, 133.42, 125.88, 125.80, 119.32 (q, *J* = 321.3 Hz), 103.57, 94.87, 67.95, 34.54, 34.42, 31.25, 30.91. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{25}F_3I_2NO_2S^-$ [M-H]$^-$ 677.9653, found 677.9648.



2l (2-iodo-di-(2-thiophenyl))methyl-trifluoromethanesulfonamide

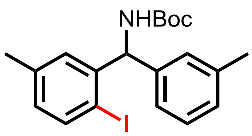
The compound **2l** was prepared according to the general procedure and was purified by prep-TLC to give a brown oil in 51% yield (46 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (s, 2H), 7.12 – 6.99 (m, 1H), 6.95 (s, 1H), 6.92 (s, 1H), 6.25 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.73, 142.28, 136.99, 135.49, 127.23, 127.03, 126.60, 119.58 (*J* = 321.8 Hz), 80.21, 56.51. HPLC chiralcel AS-H column (10% isopropanol in hexanes, 0.3mL/min) t_r= 37.773 min (major), 76.487 min (minor): 99% ee. HRMS (ESI-TOF) *m/z* Calcd for $C_{10}H_6F_3INO_2S_3^-$ [M-H]$^-$ 451.8563, found 451.8567. $[\alpha]^{23}_D$= -2.5 (c= 0.30, $CHCl_3$).

Procedure for the deprotection of trifluoromethanesulfonamides 2h:

To a 20 mL round bottle was added **2h** (1 equiv. 0.2 mmol), K_2CO_3 (2 equiv. 0.4 mmol), 4-nitrobenzylbromide (1.1 equiv. 0.22 mmol) and acetone (3 mL). The mixture was stirred at room temperature for 48 h under nitrogen. Upon completion (monitored by TLC), the resulting solution was diluted by EtOAc, filtered and evaporated to afford the alkylated trifluoromethanesulfonamide, which could be used directly into the next step without purification.

To a 20 mL round bottle was added the alkylated trifluoromethanesulfonamide, Cs_2CO_3 (3 equiv.) and anhydrous THF. The mixture was stirred at 30 ^{o}C overnight under nitrogen. Upon completion, the resulting solution was cooled to 0 ^{o}C, at which time aq. HCl (3 M) was added. The mixture was stirred for another 2 h at room temperature and all the solvent was evaporated. The resulting solid was dissolved in Et_2O and H_2O (1 : 1). The aqueous layer was washed twice with Et_2O. The combined organic solvent was washed with aq. HCl until no free amine was left. And the combined aqueous solution was evaporated to give a white solid.

To a 20 mL round bottle was added the white solid that was obtained in the previous step, catalytic amount of DMAP, Boc_2O (3 equiv.) and DCM. The mixture was cooled to 0 ^{o}C, and Et_3N (3 equiv.) was added while stirring. The resulting solution was allowed to warm to room temperature and stirred overnight under nitrogen. Upon completion (monitored by TLC), the resulting solution was washed with H_2O. The aqueous layer was extracted twice with DCM and the combined organic solution was evaporated and purified by flash chromatography (EtOAc: hexane = 1:10) to give the Boc-protected amide **3h** as a colorless oil in 67% yield. And the ee was measured by converting the Boc-protected amide back to the corresponding triflate amide (93% ee).



3h *tert*-butyl (2-iodo-5,3'-dimethyl-diphenyl)methyl carbamate

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.12 – 7.02 (m, 3H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.01 (s, 1H), 5.12 (s, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 1.45 (s, 9H).

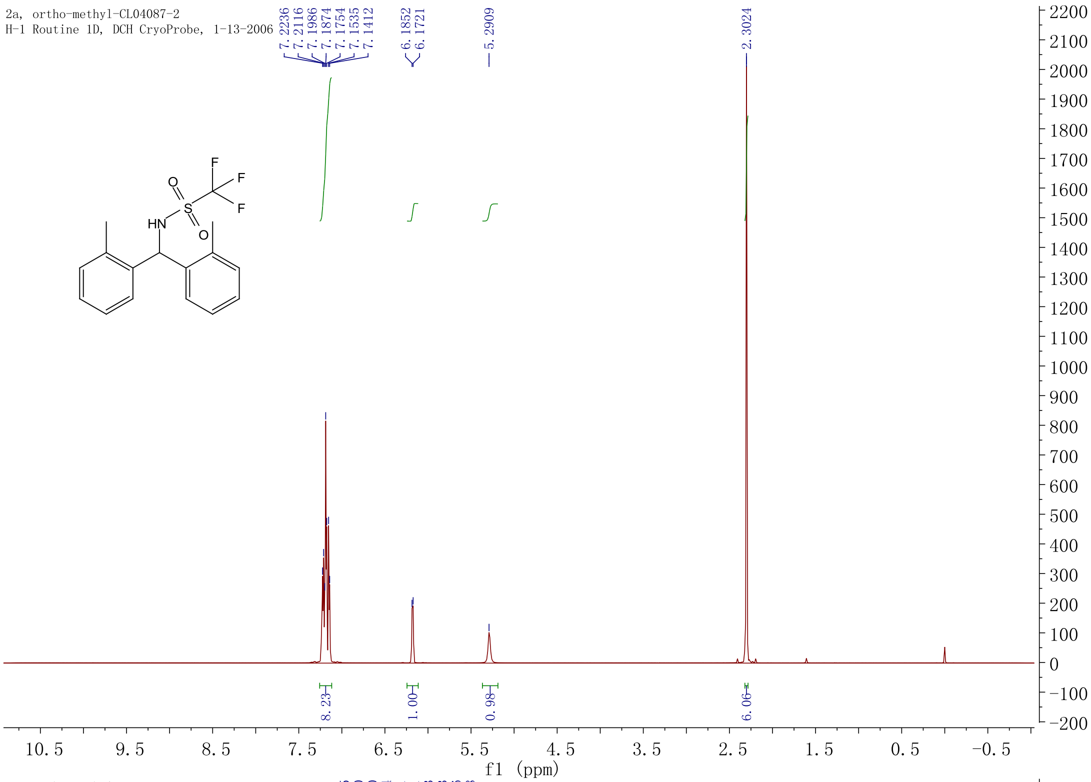
^{13}C NMR (151 MHz, $CDCl_3$) δ 154.69, 143.59, 140.44, 139.82, 138.34, 138.22, 130.09, 128.97, 128.48, 128.42, 128.26, 124.80, 95.60, 79.84, 62.04, 28.37, 21.49, 21.13.

HRMS (APCI-TOF) *m/z* Calcd for $C_{20}H_{24}INO_2Na^+$ $[M+Na]^+$ 460.0744, found 460.0746.

References:

(1) Zhang, Y.; Lu, Z.; Desai, A.; Wulff, W. D. *Org. Lett.* **2008**, 10, 5429.

(2) Mo, F.; Trzepkowski, L. J.; Dong, G. *Angew. Chem. Int. Ed.* **2012**, 51, 13075.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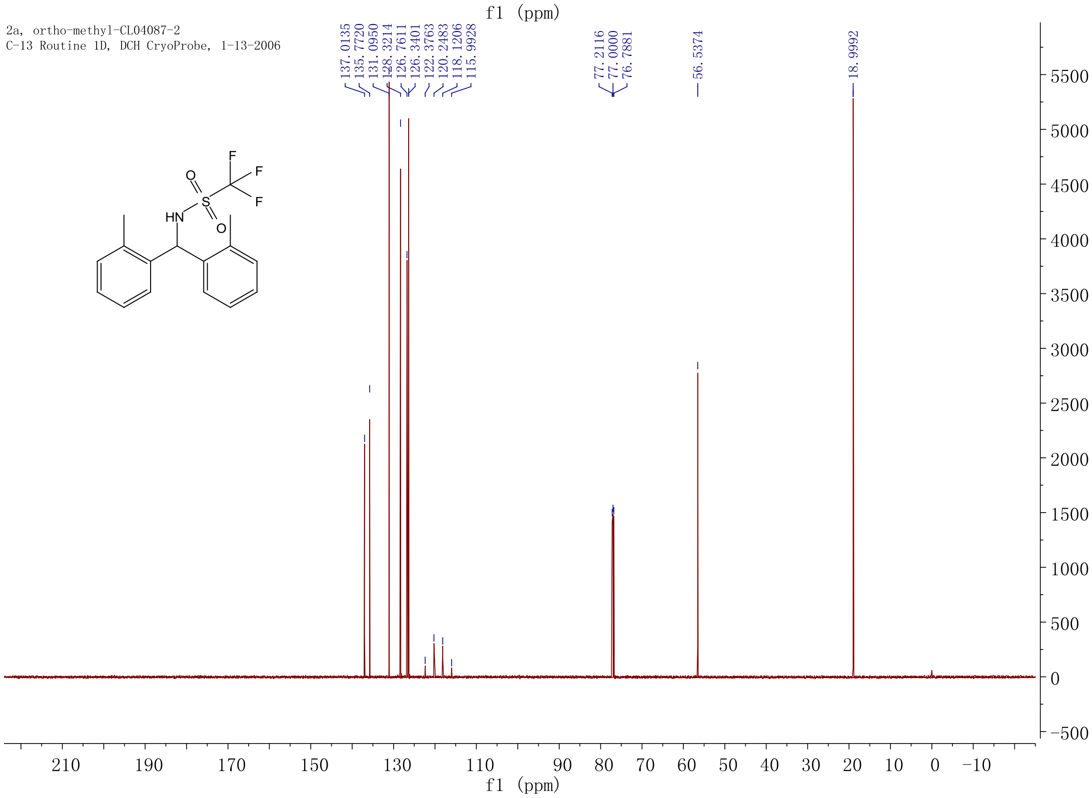
f1 (ppm)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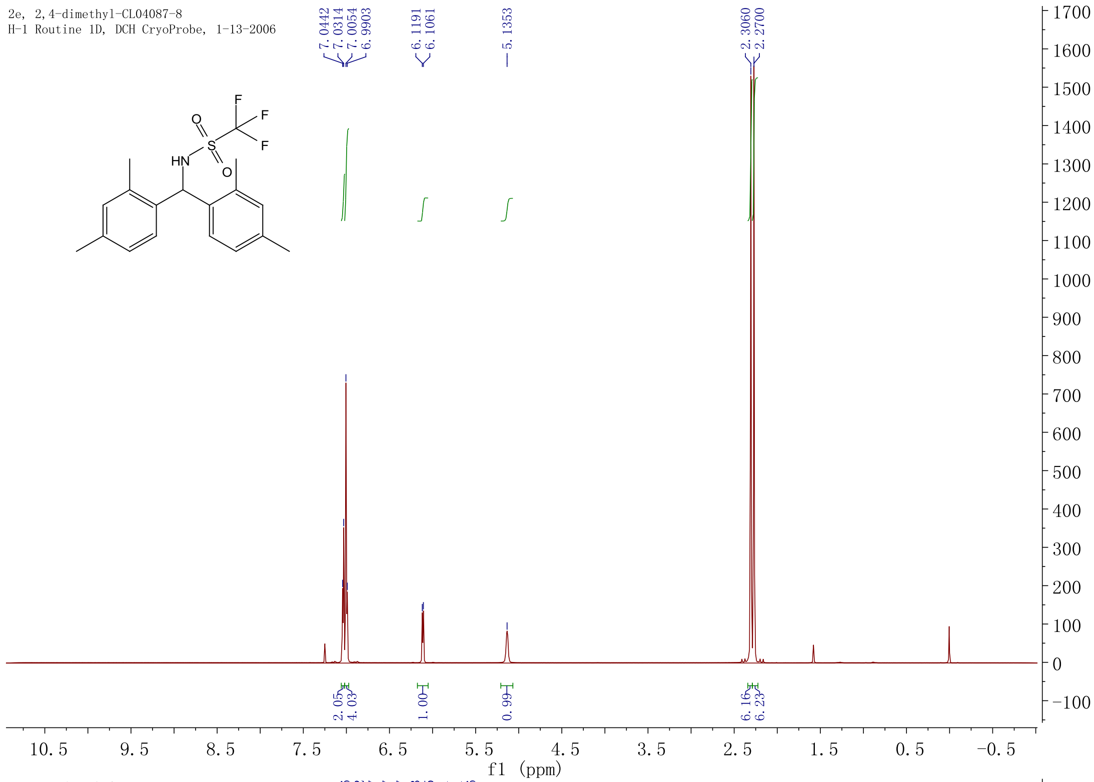
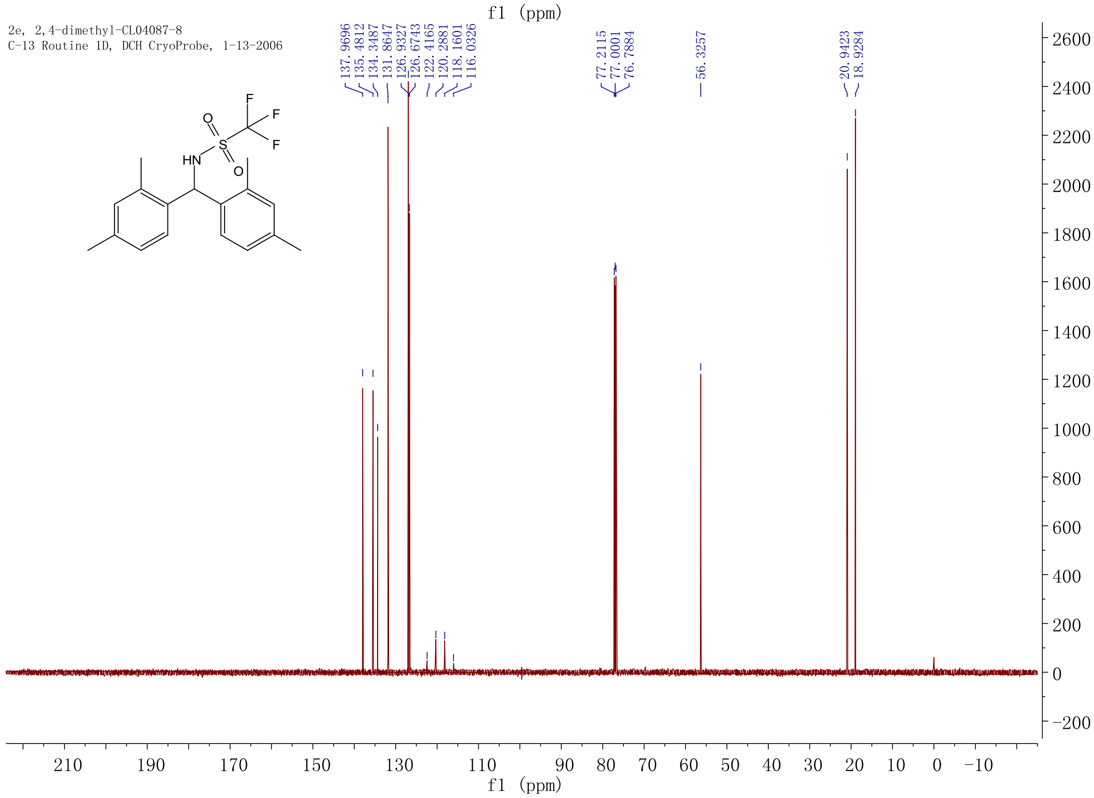
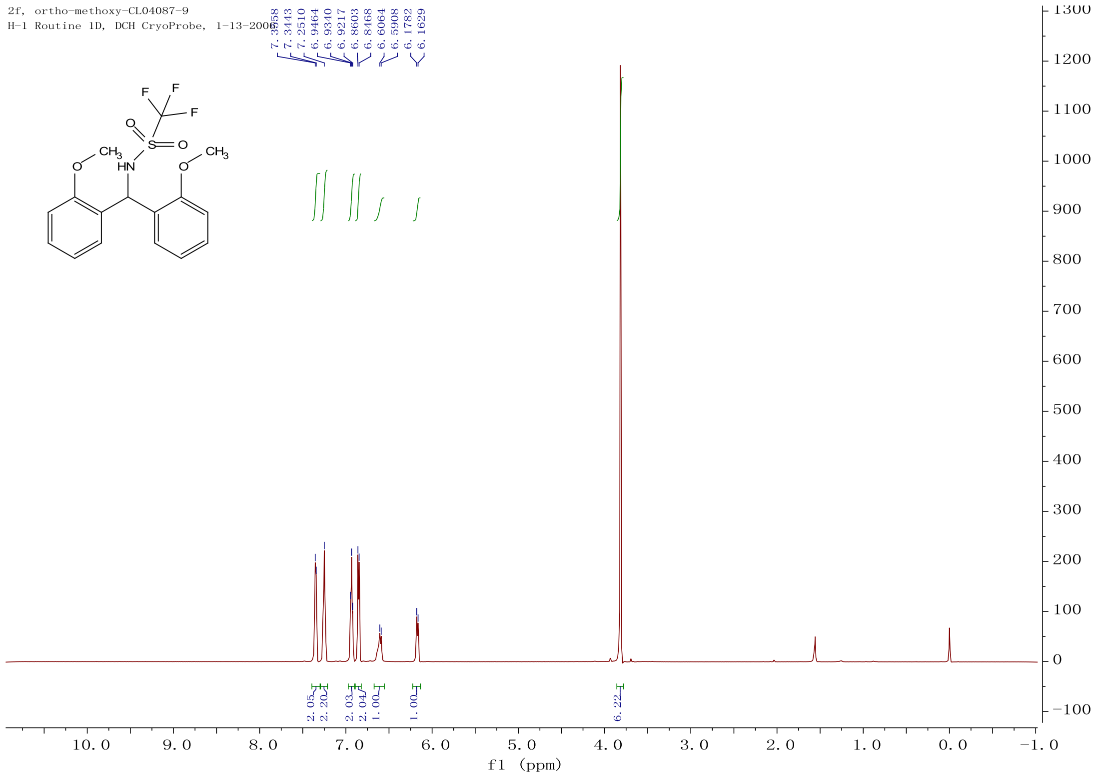
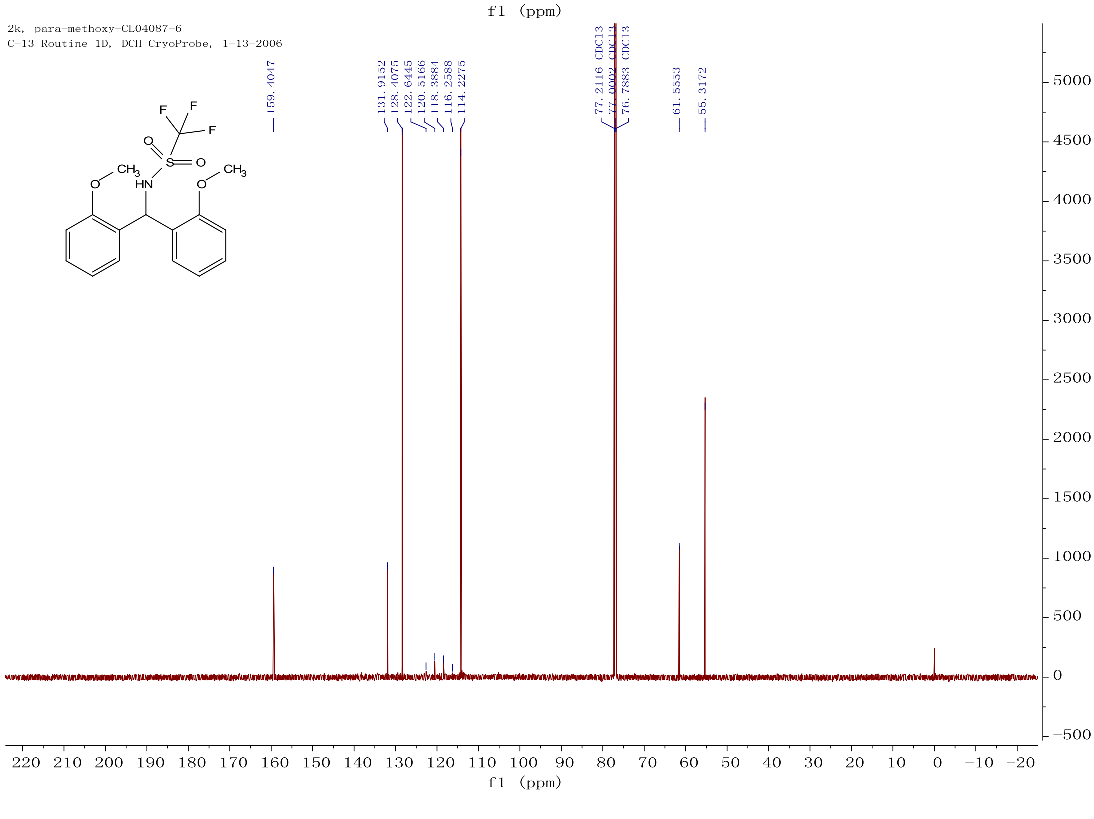
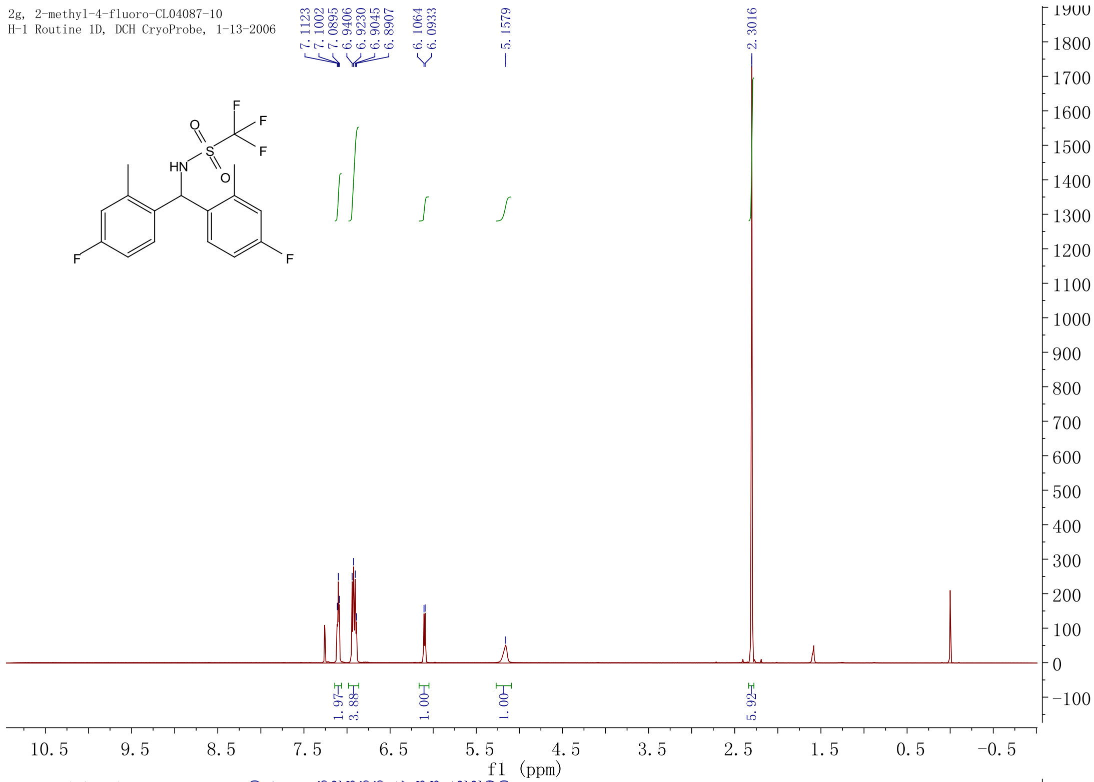
18.9992
f1 (ppm)

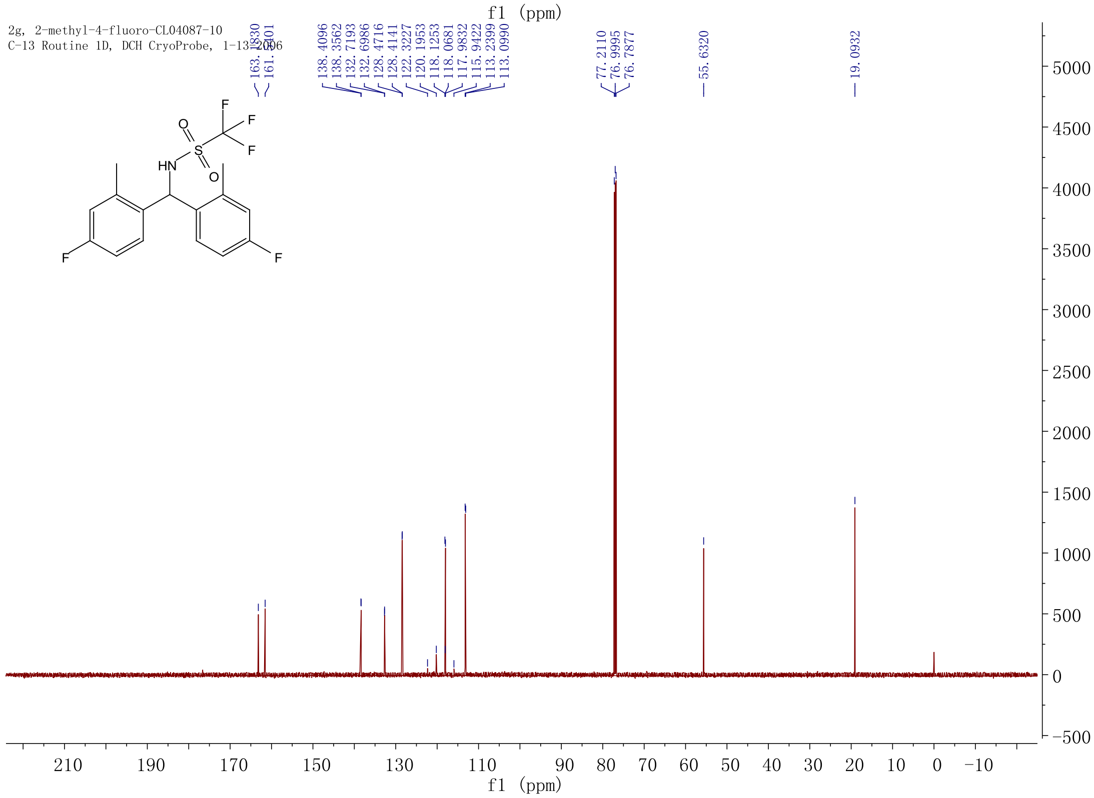

2e, 2,4-dimethyl-CL04087-8
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.0442
7.0314
7.0054
6.9903
6.1191
6.1061
5.1353
2.3060
2.2700
HN
S
O
O
F
F
F
2.05
4.03
1.00
0.99
6.16
6.23
f1 (ppm)

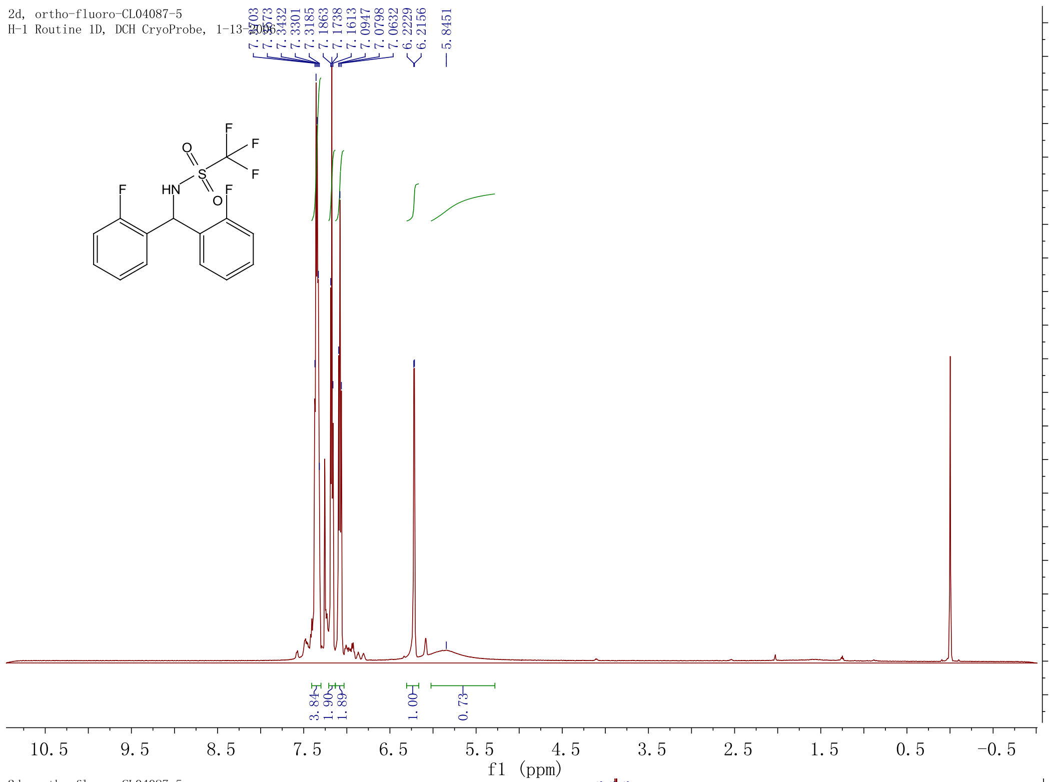

2e, 2,4-dimethyl-CL04087-8
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
137.9696
135.4812
134.3487
131.8647
126.9327
126.6743
122.4165
120.2881
118.1601
116.0326
77.2115
77.0001
76.7884
56.3257
20.9423
18.9284
HN
S
O
O
F
F
F
f1 (ppm)

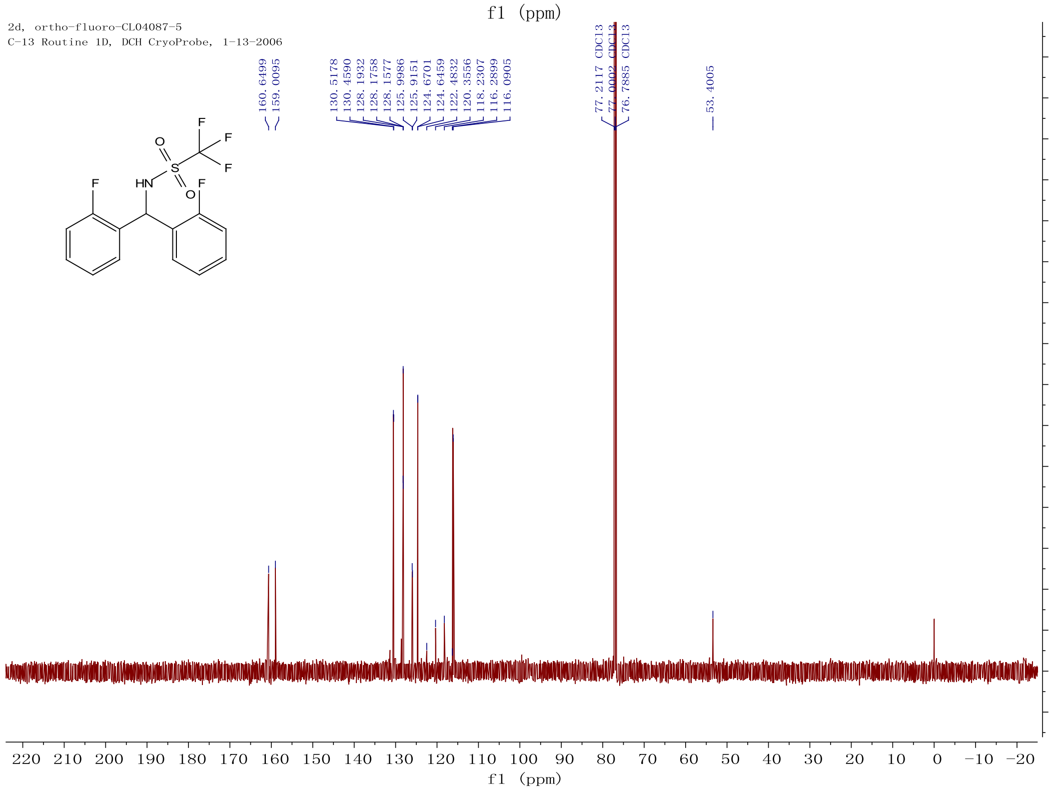

2f, ortho-methoxy-CL04087-9
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.3958
7.3443
7.2510
6.9464
6.9340
6.9217
6.8603
6.8468
6.6064
6.5908
6.1782
6.1629
2.05
2.20
2.03
2.04
1.00
1.00
6.22
f1 (ppm)

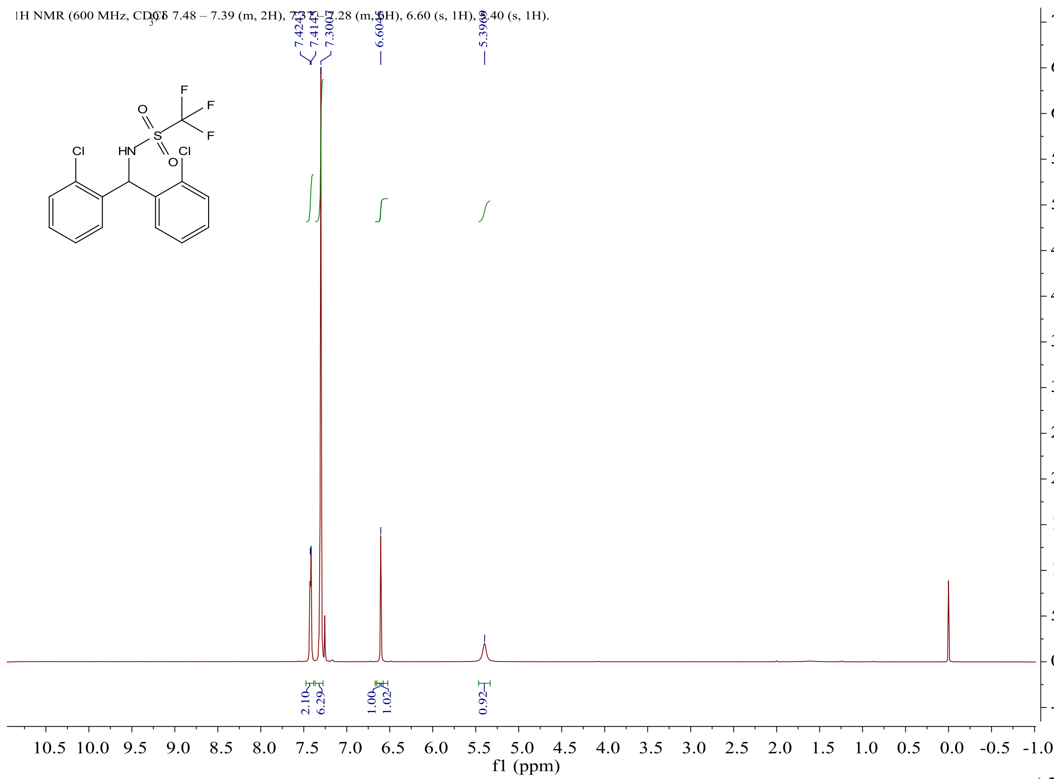

2k, para-methoxy-CL04087-6
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
159.4047
131.9152
128.4075
122.6445
120.5166
118.3884
116.2588
114.2275
77.2116 CDCl3
77.0002 CDCl3
76.7883 CDCl3
61.5553
55.3172
f1 (ppm)

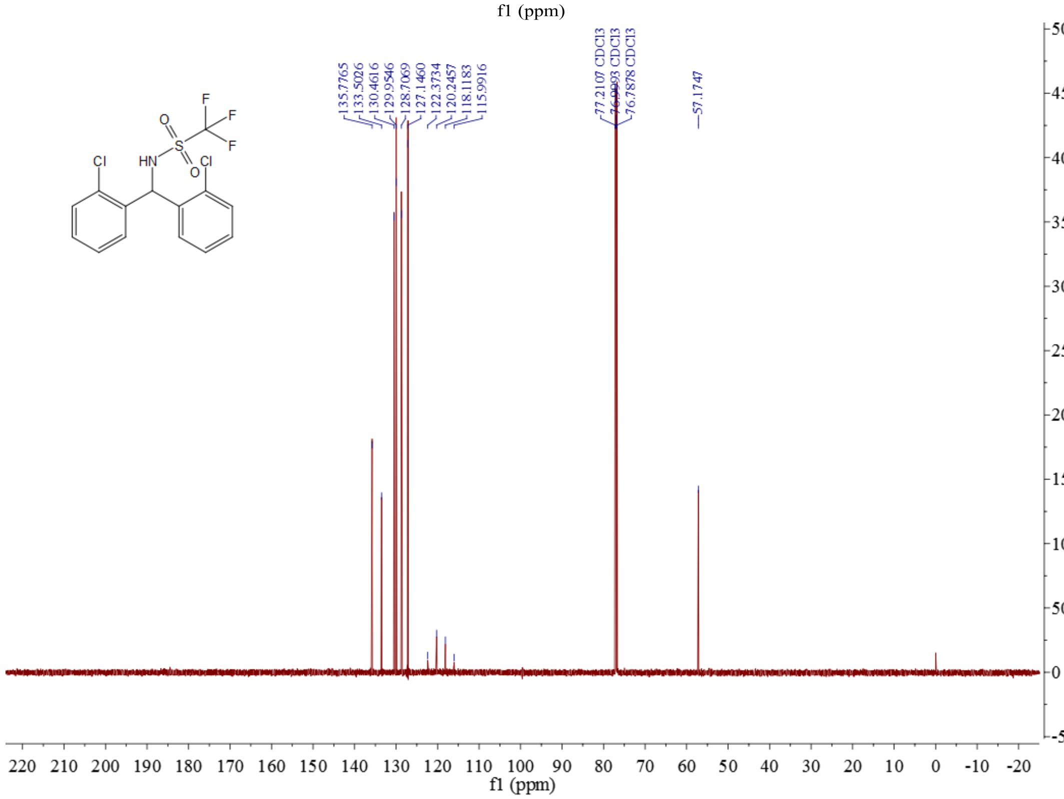

2g, 2-methyl-4-fluoro-CL04087-10
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.1123
7.1002
7.0895
6.9406
6.9230
6.9045
6.8907
6.1064
6.0933
5.1579
2.3016
1.97
3.88
1.00
1.00
5.92
f1 (ppm)

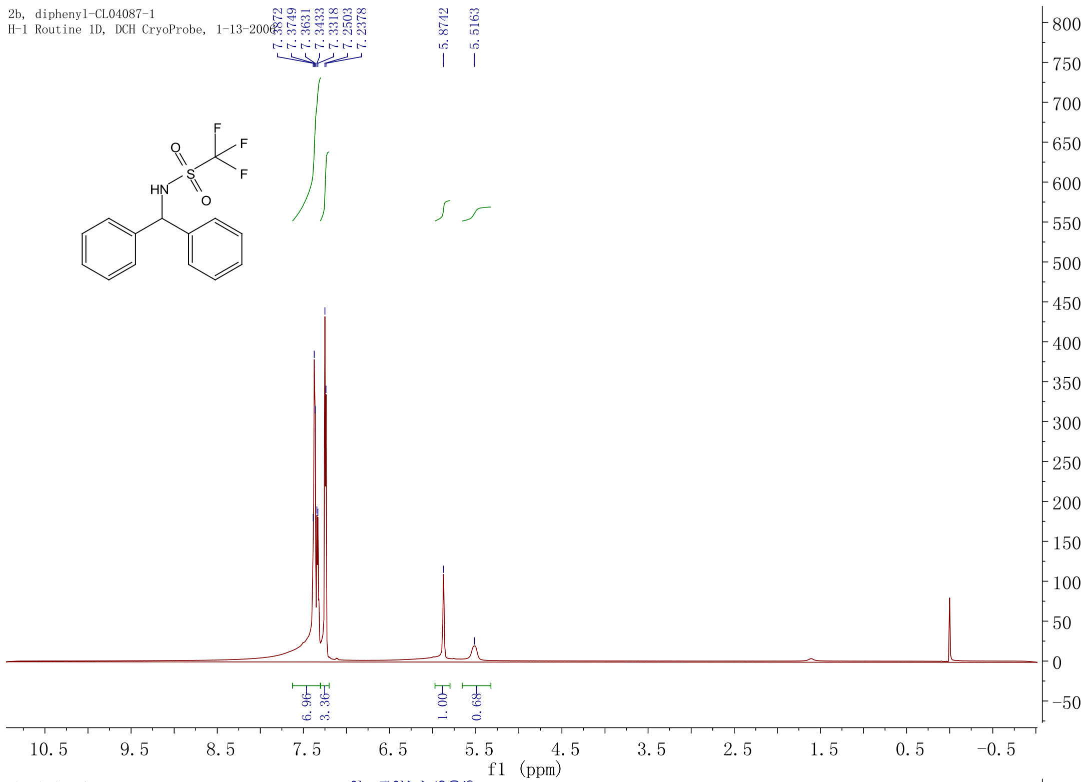

2g, 2-methyl-4-fluoro-CL04087-10
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
163.1830
161.2301
138.4096
138.3562
132.7193
132.6986
128.4716
128.4141
122.3227
120.1953
118.1253
118.0681
117.9832
115.9422
113.2399
113.0990
77.2110
76.9995
76.7877
55.6320
19.0932
f1 (ppm)

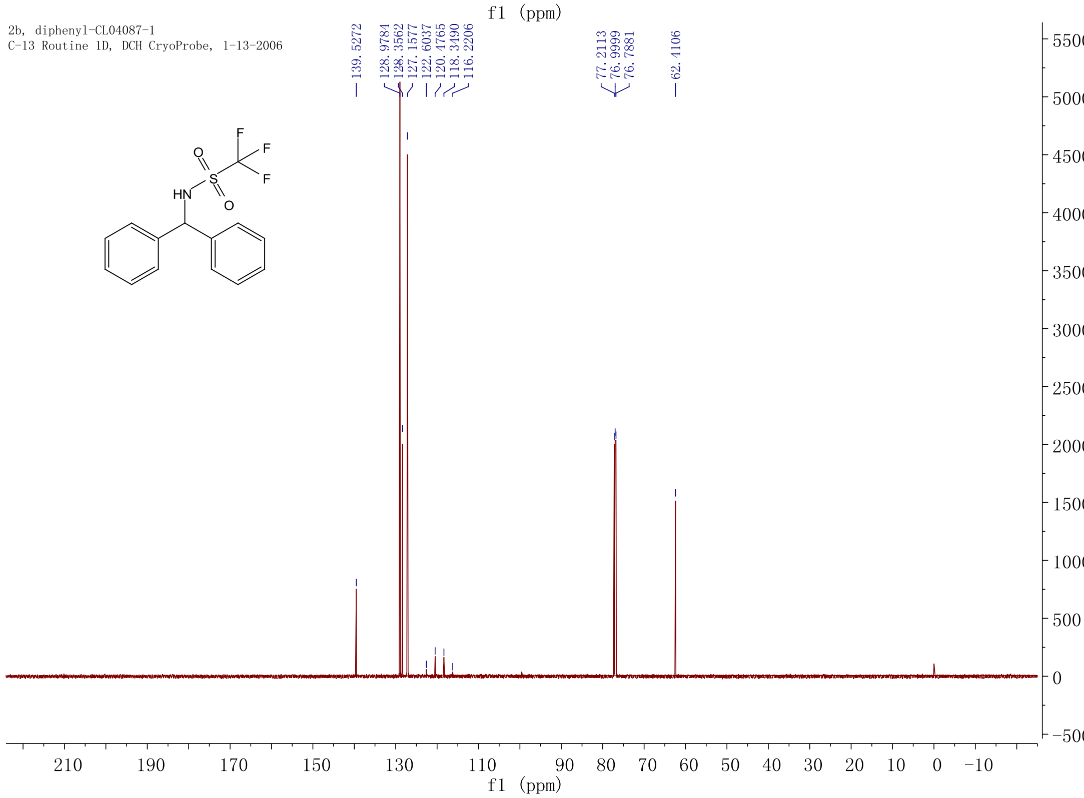

2d, ortho-fluoro-CL04087-5
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.3573
7.3432
7.3301
7.3185
7.1863
7.1738
7.1613
7.0947
7.0798
7.0632
6.2229
6.2156
5.8451
3.84
1.90
1.89
1.00
0.73
f1 (ppm)

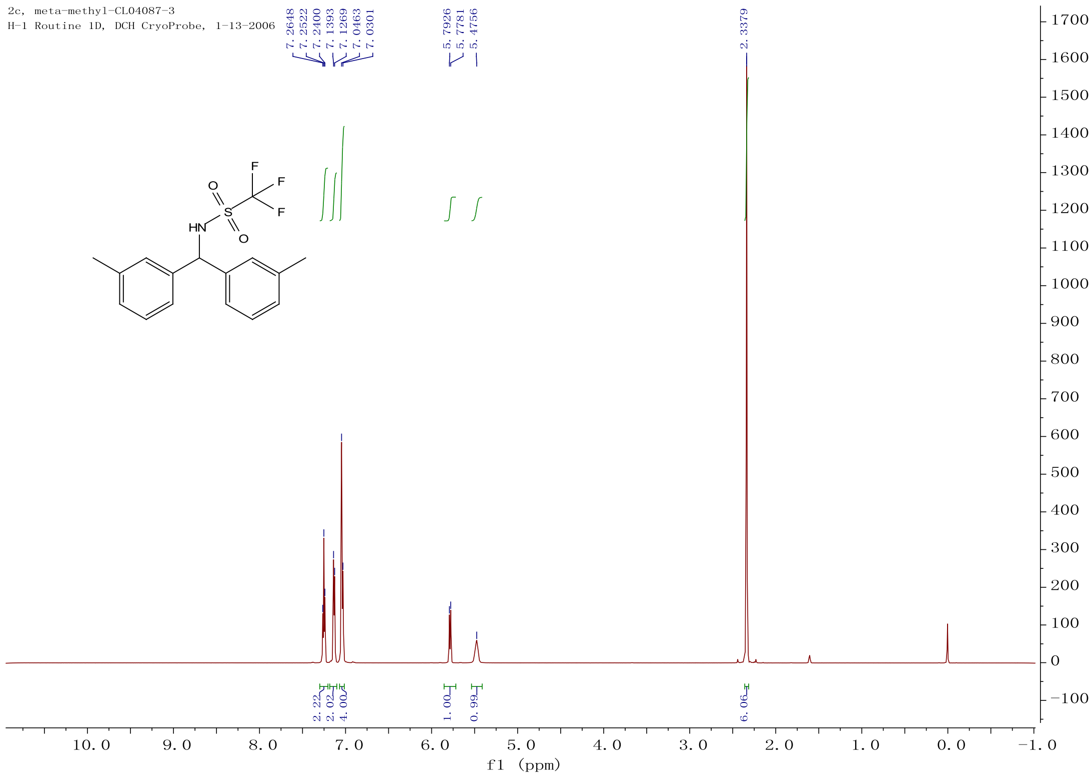

2d, ortho-fluoro-CL04087-5
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
160.6499
159.0095
130.5178
130.4590
128.1932
128.1758
128.1577
125.9986
125.9151
124.6701
124.6459
122.4832
120.3556
118.2307
116.2899
116.0905
77.2117 CDCl3
77.0002 CDCl3
76.7885 CDCl3
53.4005
f1 (ppm)

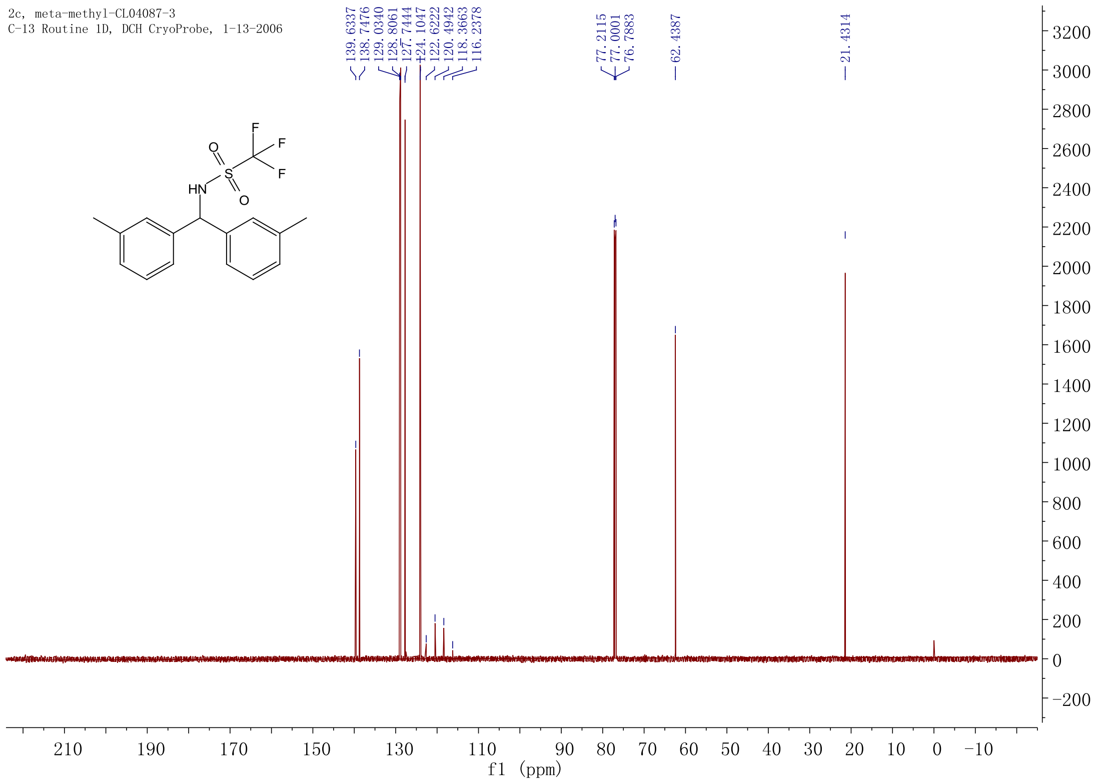

1H NMR (600 MHz, CDCl3) δ 7.48 – 7.39 (m, 2H), 7.37 – 7.28 (m, 6H), 6.60 (s, 1H), 5.40 (s, 1H).
7.4243
7.4143
7.3007
6.6045
5.3969
2.10
6.29
1.00
1.02
0.92
f1 (ppm)

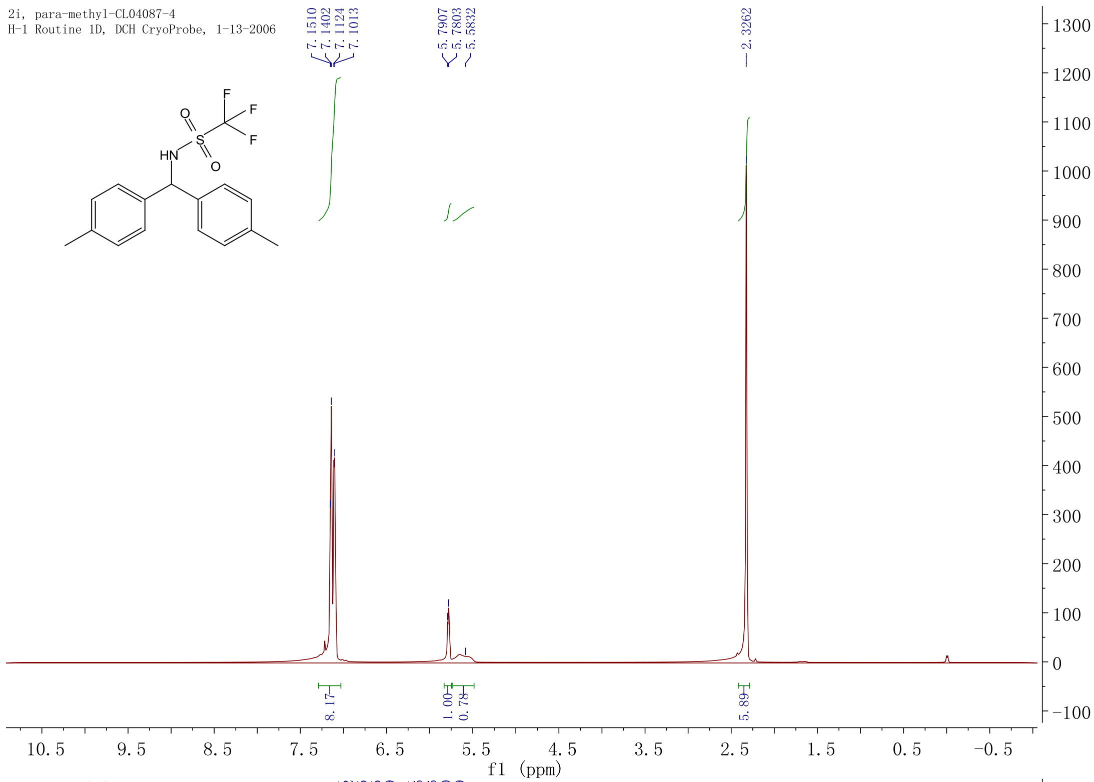

135.7765
133.5026
130.4616
129.9546
128.7069
127.1460
122.3734
120.2457
118.1183
115.9916
77.2107 CDCl3
76.9993 CDCl3
76.7878 CDCl3
57.1747
f1 (ppm)

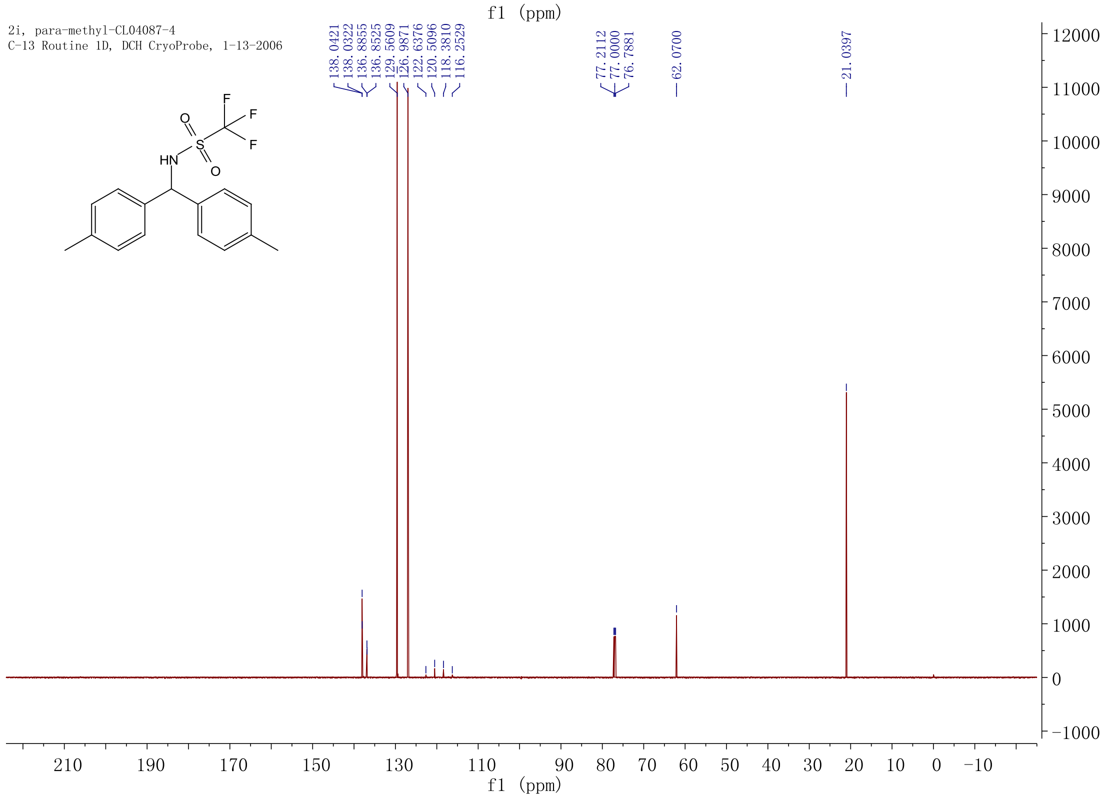

2b, diphenyl-CL04087-1
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.3872
7.3749
7.3631
7.3433
7.3318
7.2503
7.2378
5.8742
5.5163
6.96
3.36
1.00
0.68
f1 (ppm)

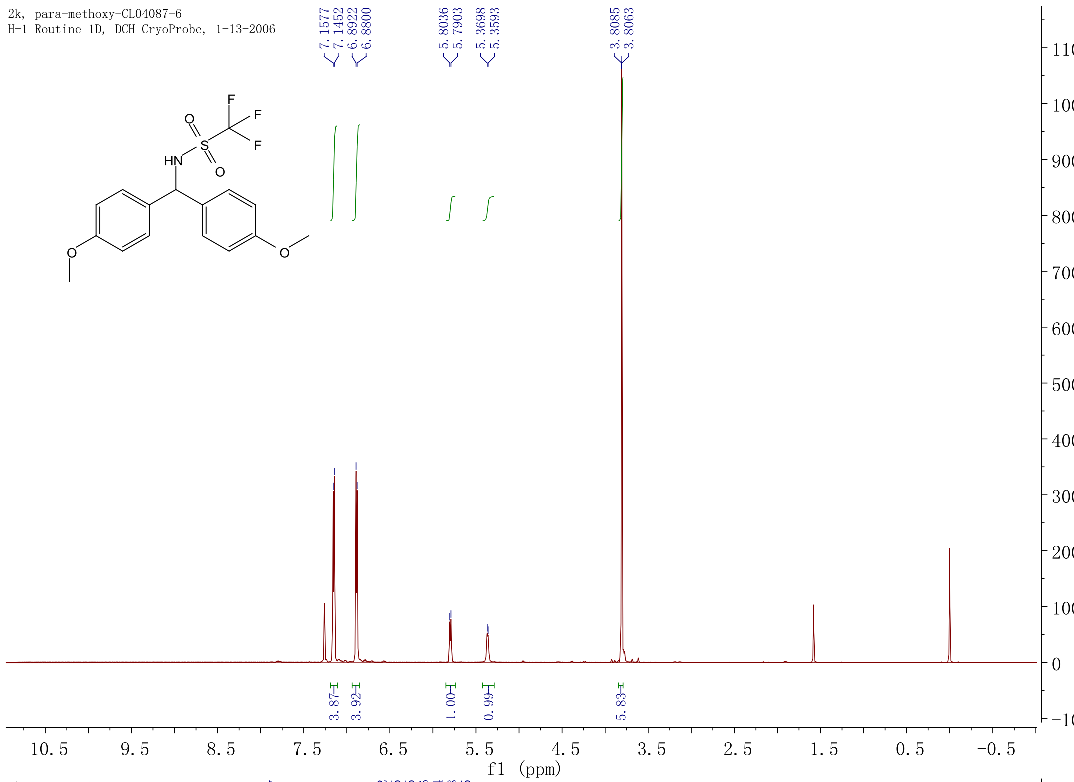

2b, diphenyl-CL04087-1
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
139.5272
128.9784
128.3562
127.1577
122.6037
120.4765
118.3490
116.2206
77.2113
76.9999
76.7881
62.4106
f1 (ppm)

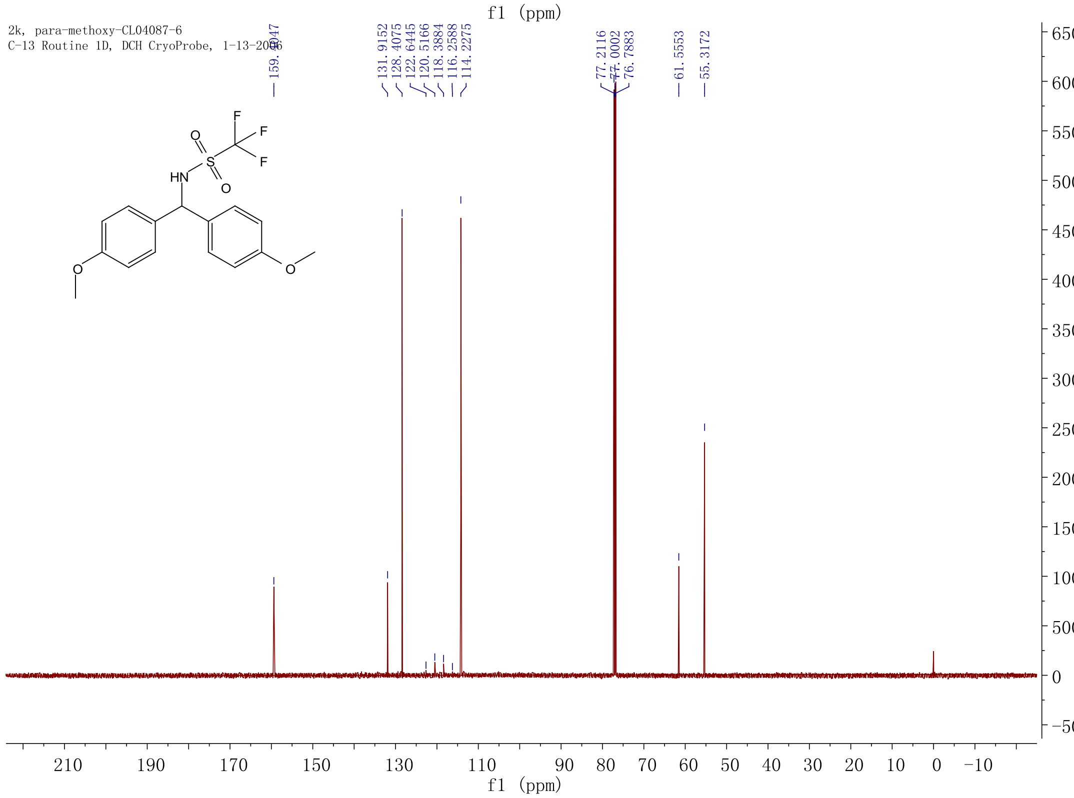

2c, meta-methyl-CL04087-3
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.2648
7.2522
7.2400
7.1393
7.1269
7.0463
7.0301
5.7926
5.7781
5.4756
2.3379
2.22
2.02
4.00
1.00
0.99
6.06
f1 (ppm)

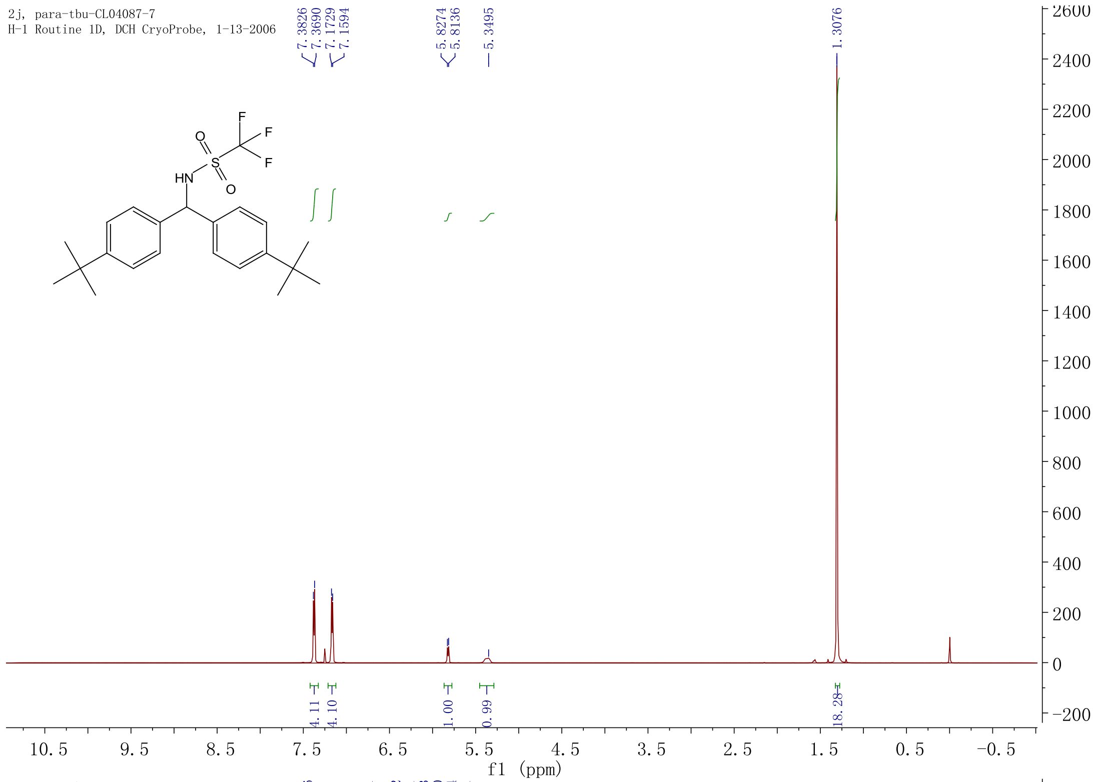

2c, meta-methyl-CL04087-3
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
139.6337
138.7476
129.0340
128.8061
127.7444
124.1047
122.6222
120.4942
118.3663
116.2378
77.2115
77.0001
76.7883
62.4387
21.4314
f1 (ppm)

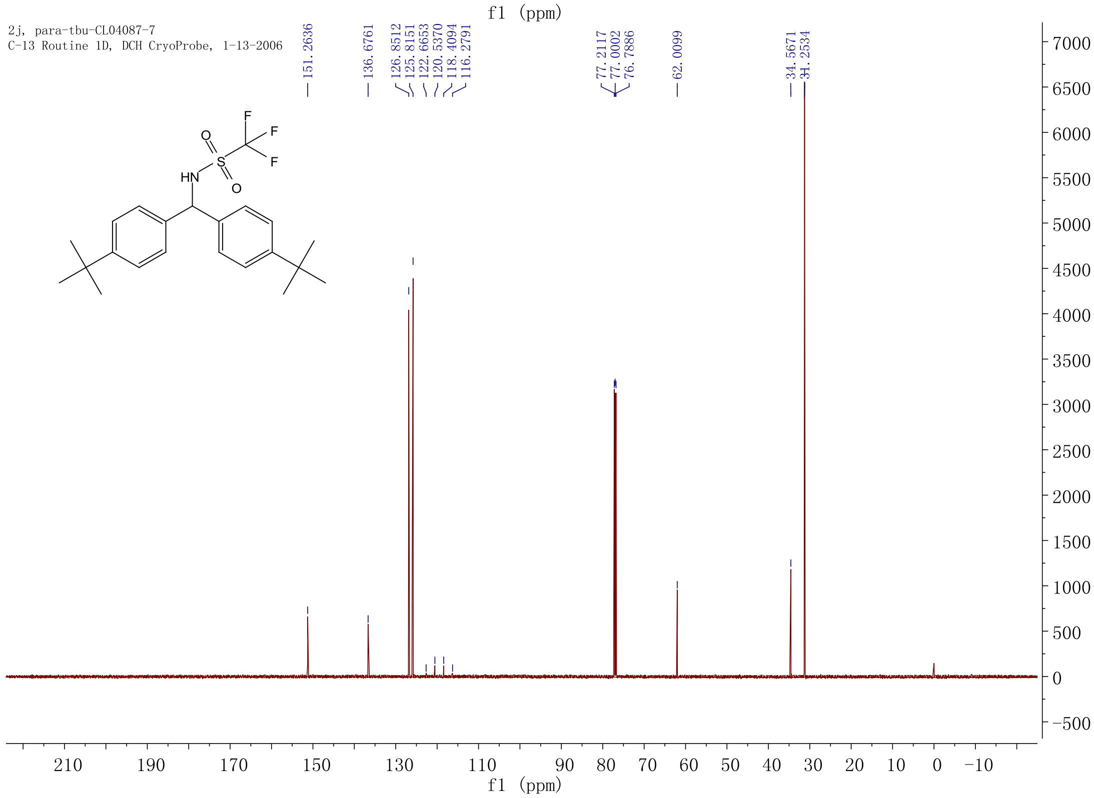

2i, para-methyl-CL04087-4
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.1510
7.1402
7.1124
7.1013
5.7907
5.7803
5.5832
2.3262
8.17
1.00
0.78
5.89
f1 (ppm)

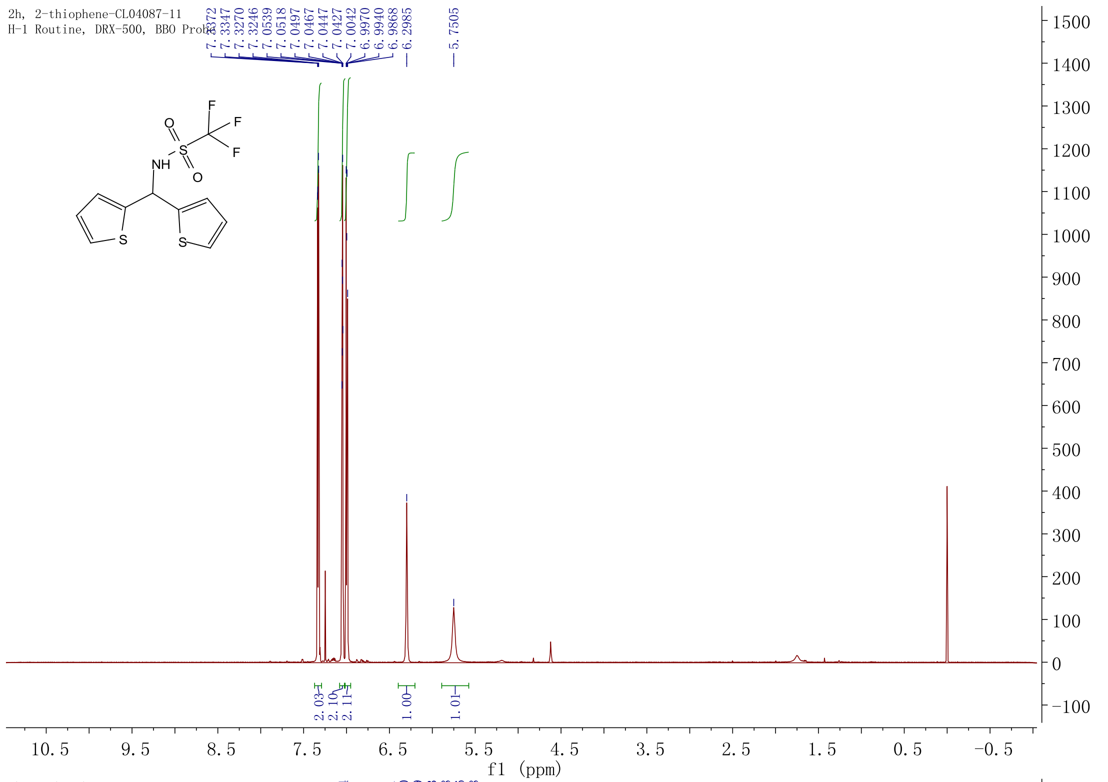

2i, para-methyl-CL04087-4
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
138.0421
138.0322
136.8855
136.8525
129.5609
126.9871
122.6376
120.5096
118.3810
116.2529
77.2112
77.0000
76.7881
62.0700
21.0397
f1 (ppm)

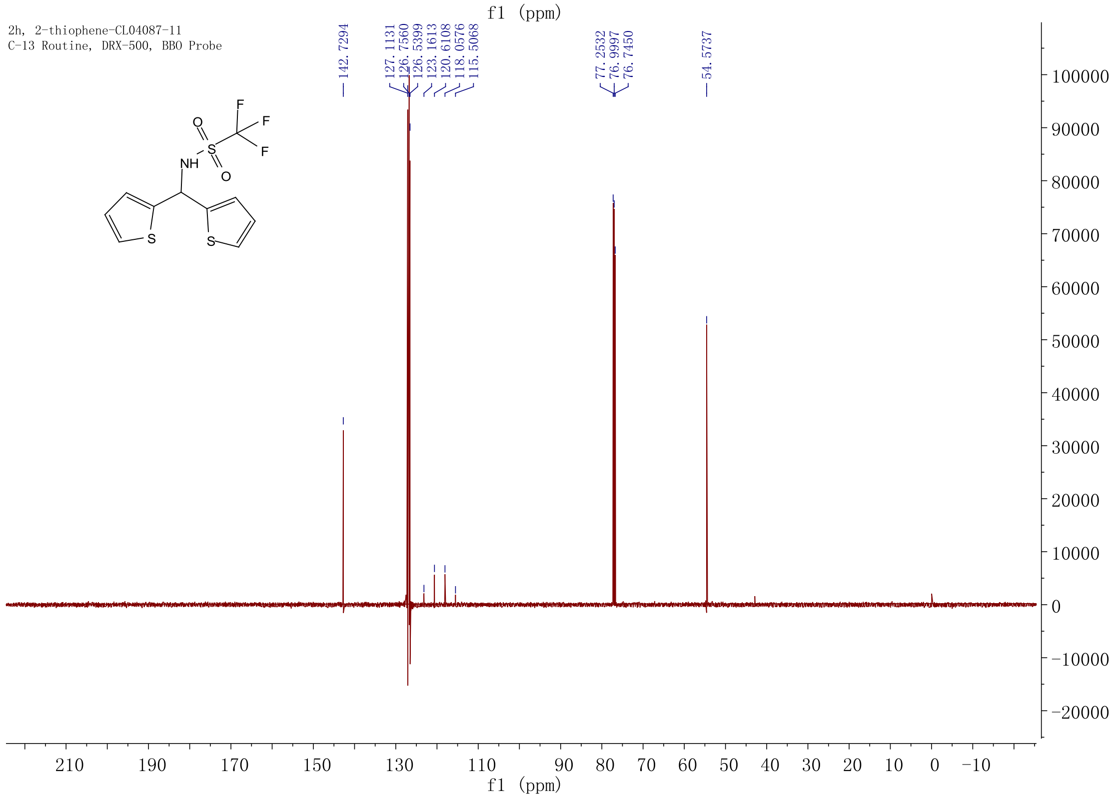

2k, para-methoxy-CL04087-6
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.1577
7.1452
6.8922
6.8800
5.8036
5.7903
5.3698
5.3593
3.8085
3.8063
3.87
3.92
1.00
0.99
5.83
f1 (ppm)

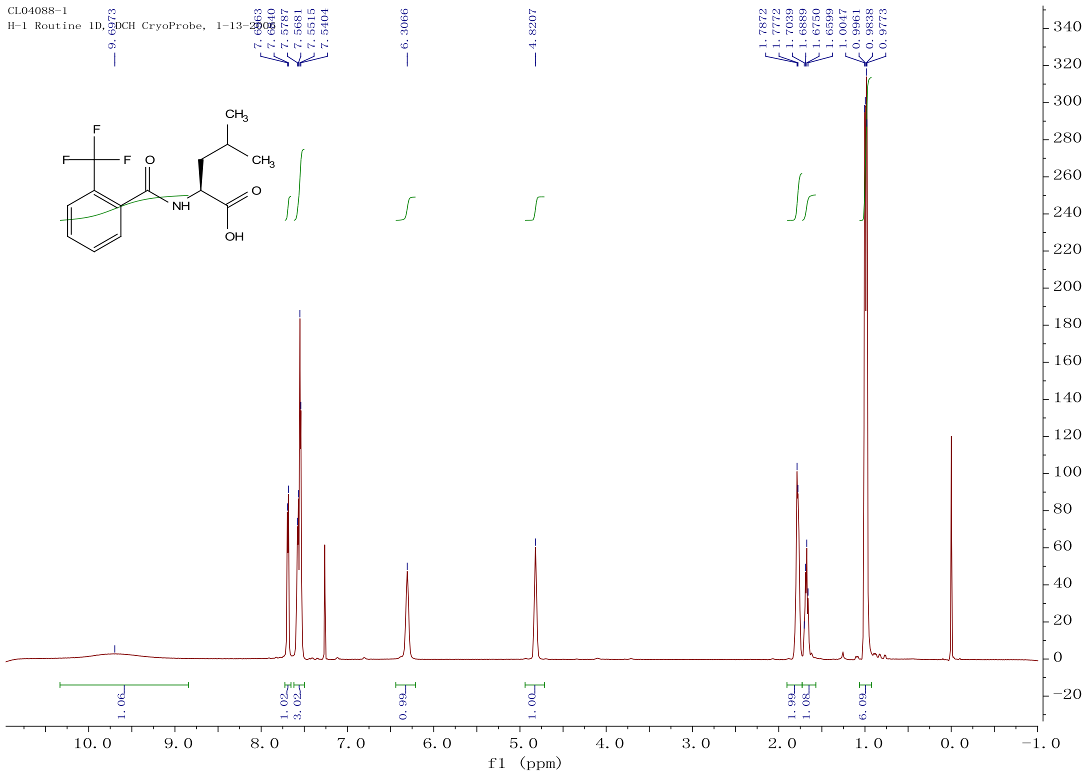

2k, para-methoxy-CL04087-6
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
159.0047
131.9152
128.4075
122.6445
120.5166
118.3884
116.2588
114.2275
77.2116
77.0002
76.7883
61.5553
55.3172
f1 (ppm)


2j, para-tbu-CL04087-7
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.3826
7.3690
7.1729
7.1594
5.8274
5.8136
5.3495
1.3076
4.11
4.10
1.00
0.99
18.28
HN
S
O
O
F
F
F
f1 (ppm)

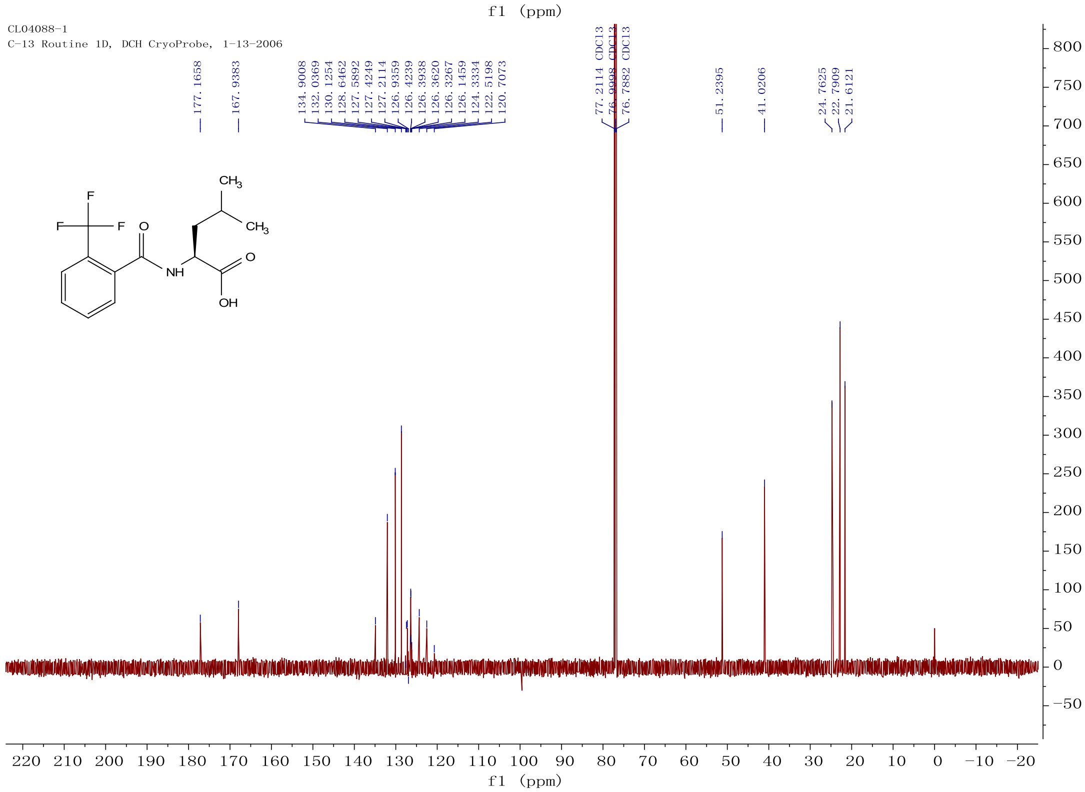

2j, para-tbu-CL04087-7
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
151.2636
136.6761
126.8512
125.8151
122.6653
120.5370
118.4094
116.2791
77.2117
77.0002
76.7886
62.0099
34.5671
31.2534
HN
S
O
O
F
F
F
f1 (ppm)


2h, 2-thiophene-CL04087-11
H-1 Routine, DRX-500, BBO Probe
7.3372
7.3347
7.3270
7.3246
7.0539
7.0518
7.0497
7.0467
7.0447
7.0427
7.0042
6.9970
6.9940
6.9868
6.2985
5.7505
2.03
2.10
2.11
1.00
1.01
f1 (ppm)

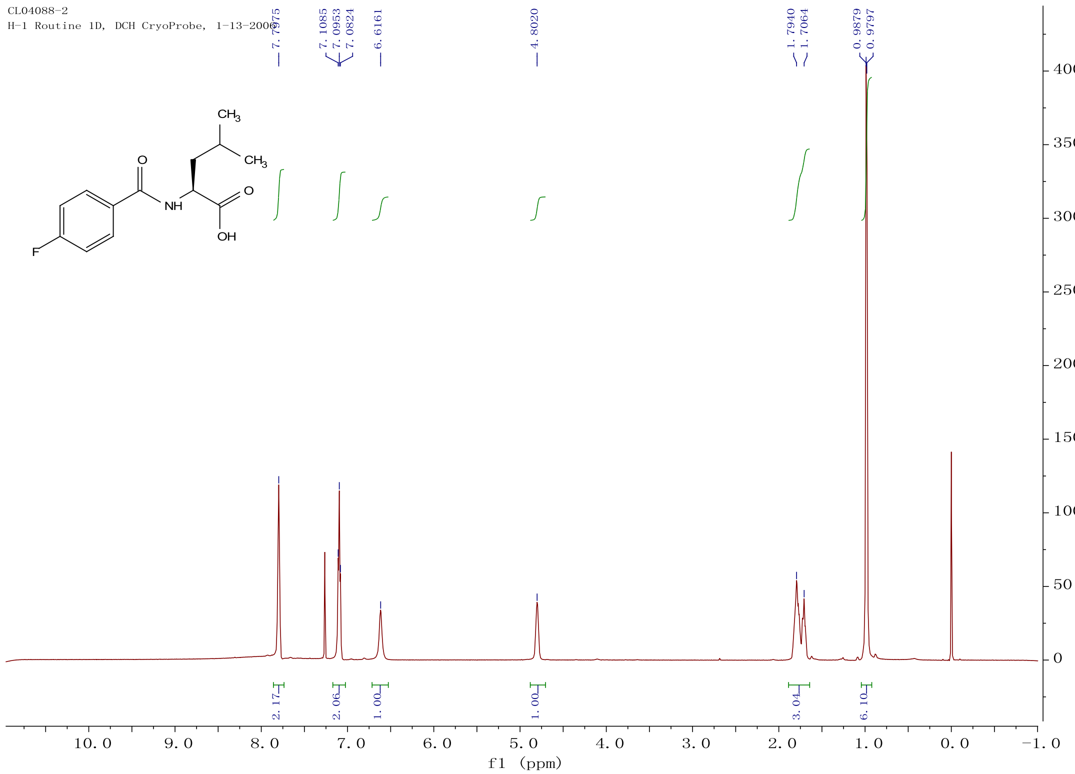

2h, 2-thiophene-CL04087-11
C-13 Routine, DRX-500, BBO Probe
142.7294
127.1131
126.7560
126.5399
123.1613
120.6108
118.0576
115.5068
77.2532
76.9997
76.7450
54.5737
f1 (ppm)

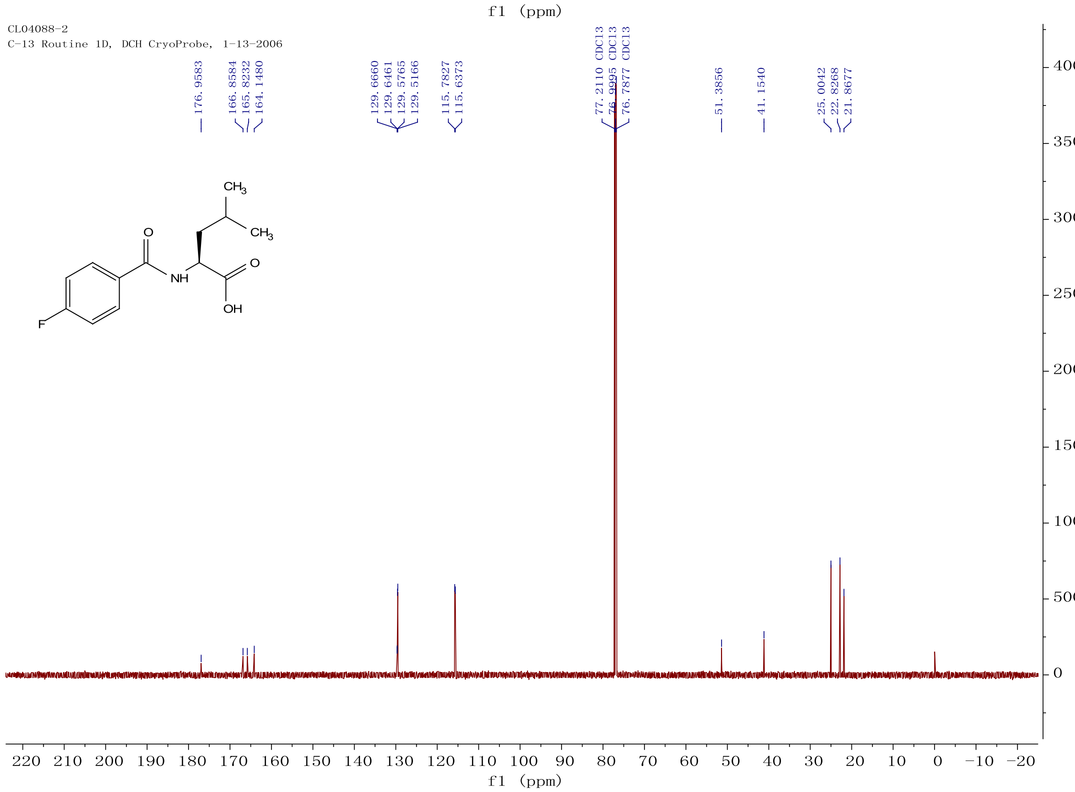


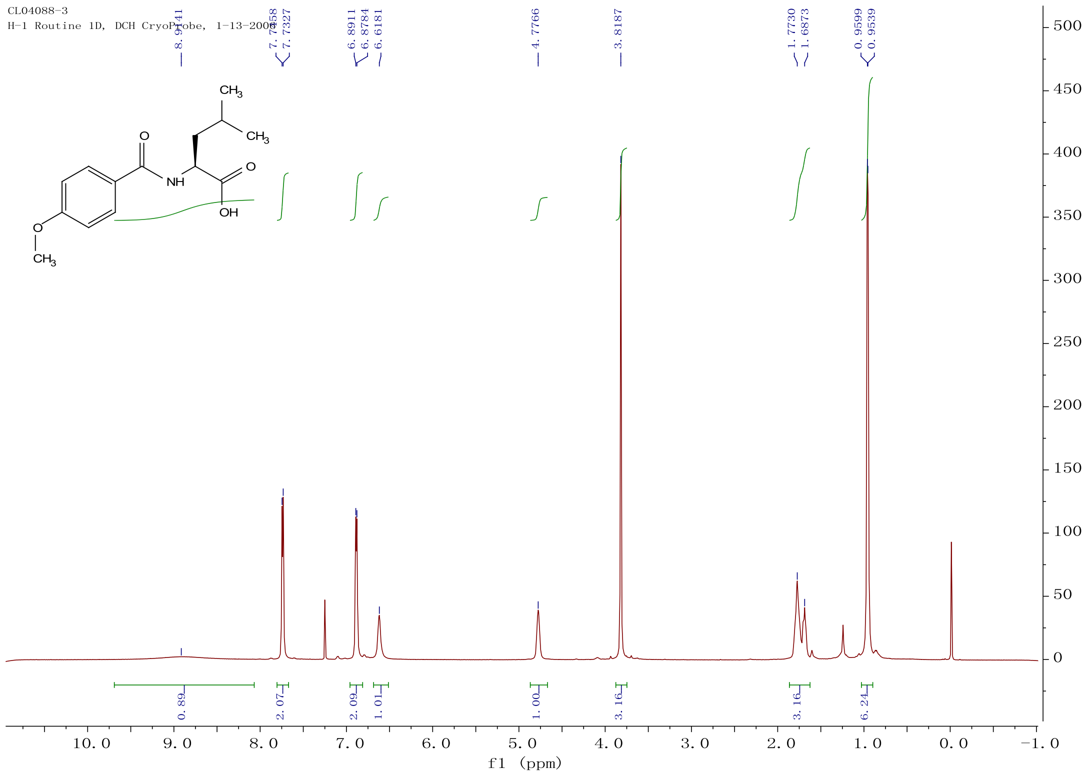
CL04088-1
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
9.6973
7.6963
7.6840
7.5787
7.5681
7.5515
7.5404
6.3066
4.8207
1.7872
1.7772
1.7039
1.6889
1.6750
1.6599
1.0047
0.9961
0.9838
0.9773
1.06
1.02
3.02
0.99
1.00
1.99
1.08
6.09
f1 (ppm)

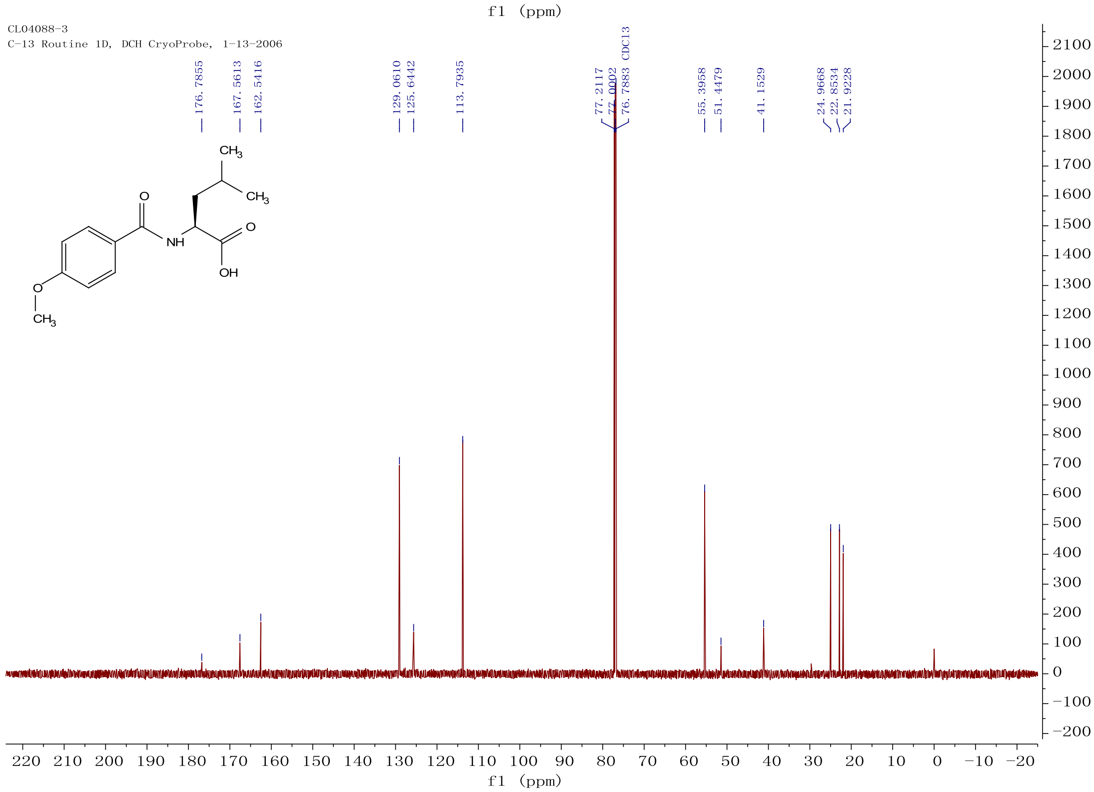


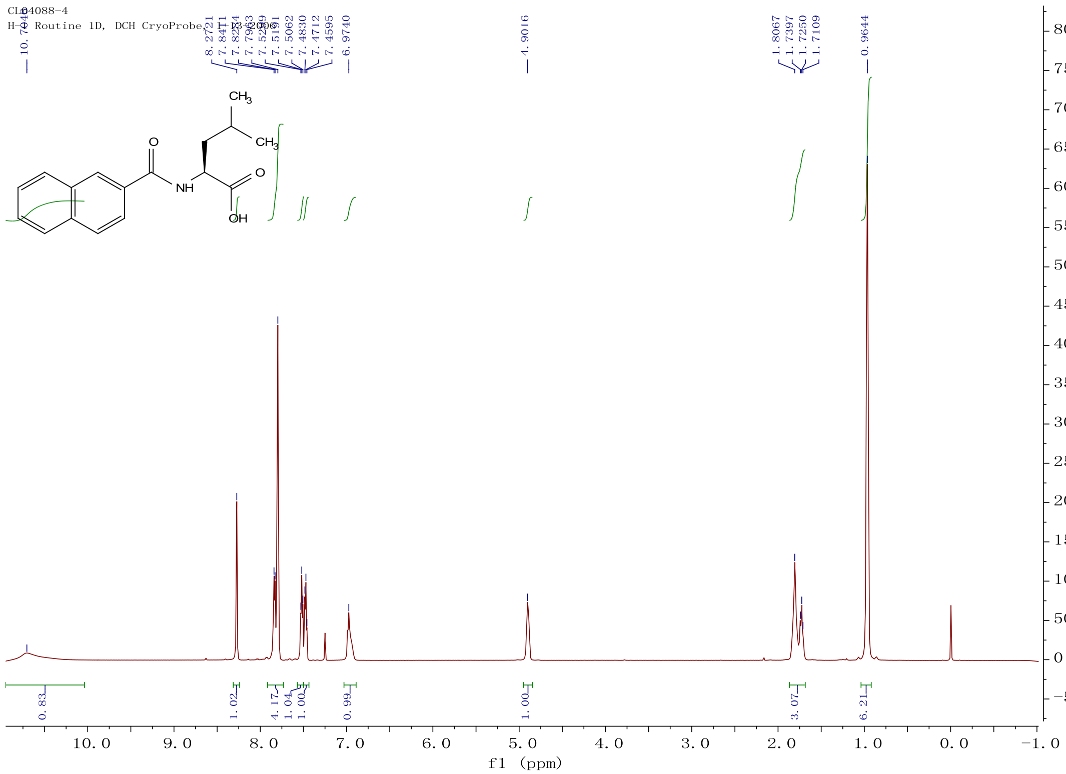
CL04088-1
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
177.1658
167.9383
134.9008
132.0369
130.1254
128.6462
127.5892
127.4219
127.2114
126.9359
126.4239
126.3938
126.3620
126.3267
126.1459
124.3334
122.5198
120.7073
77.2114 CDCl3
76.9998 CDCl3
76.7882 CDCl3
51.2395
41.0206
24.7625
22.7909
21.6121
f1 (ppm)

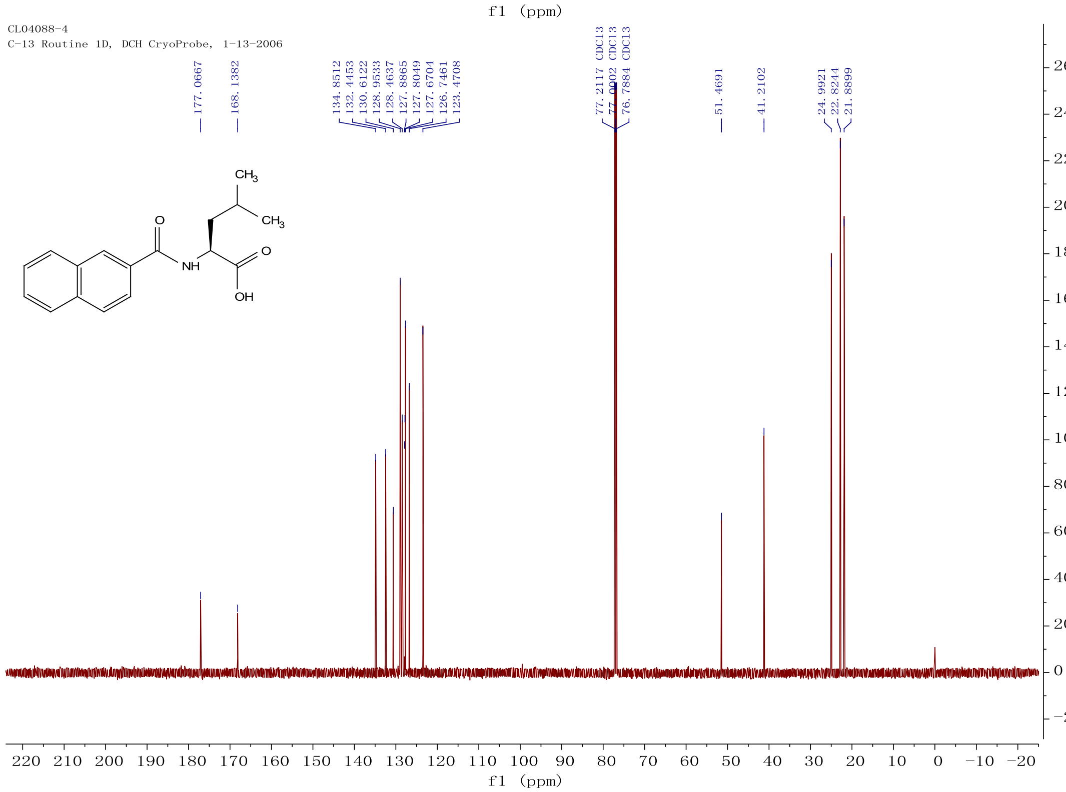

CL04088-2
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

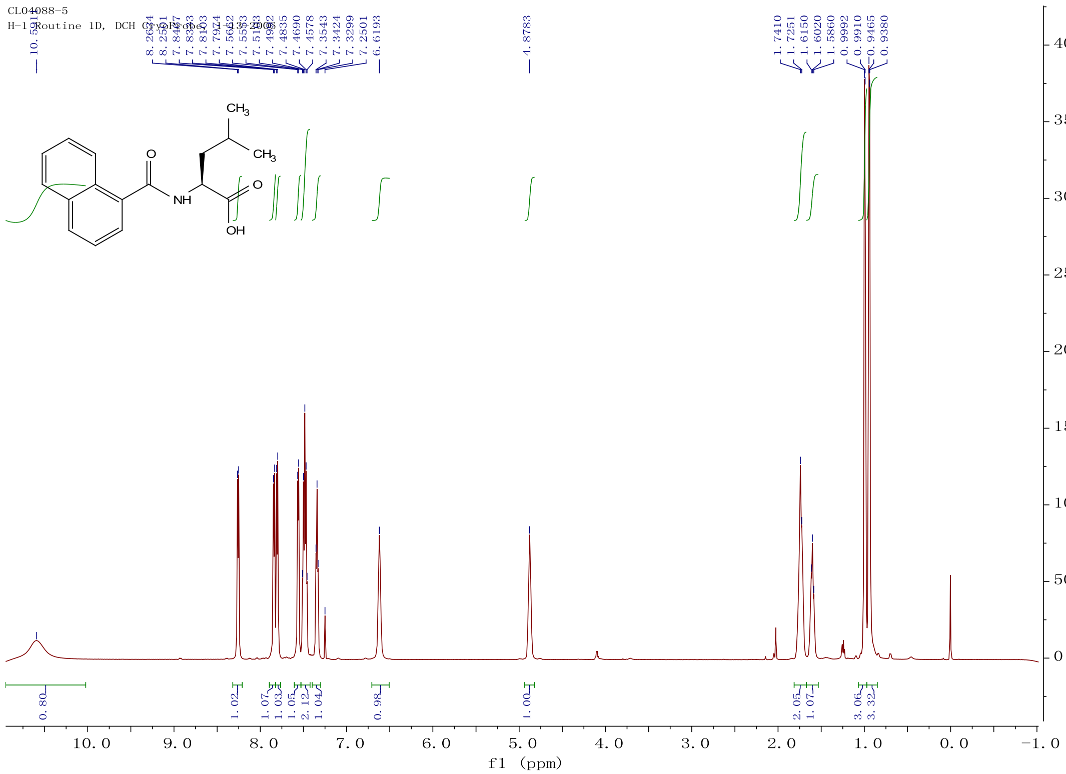

CL04088-2
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

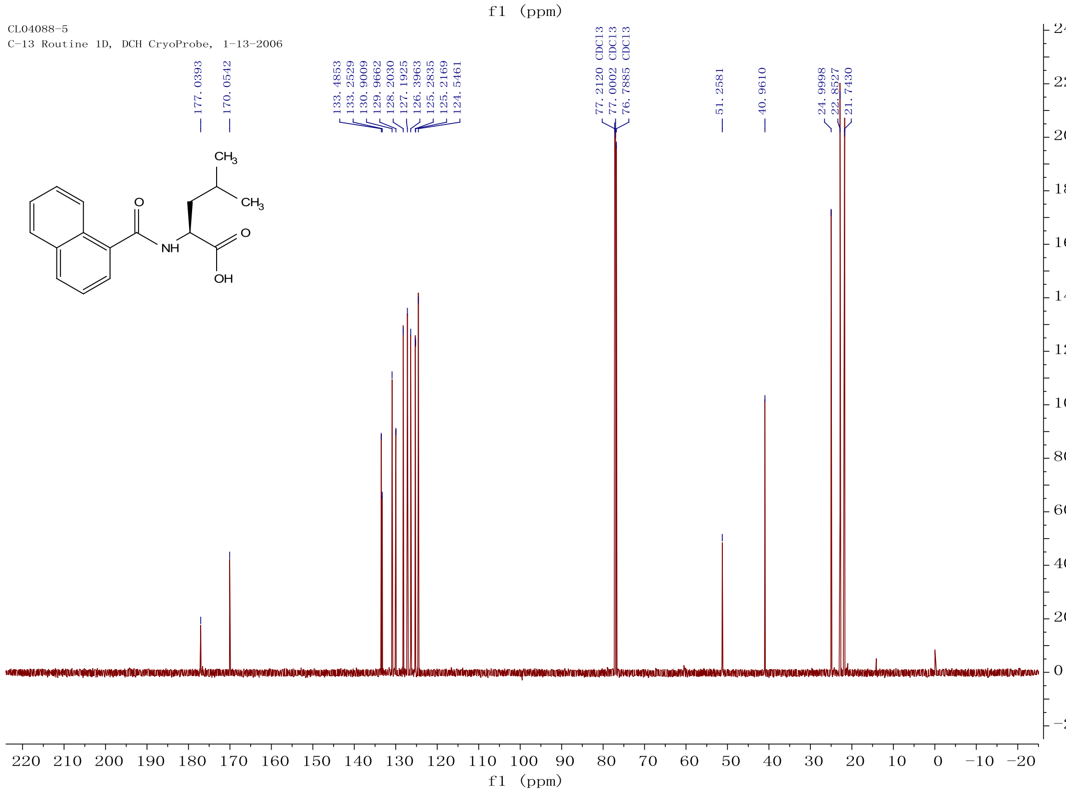

CL04088-3
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
8.9411
7.7458
7.7327
6.8911
6.8784
6.6181
4.7766
3.8187
1.7730
1.6873
0.9599
0.9539
0.89
2.07
2.09
1.01
1.00
3.16
3.16
6.24
CH3
CH3
O
NH
O
OH
O
CH3
f1 (ppm)

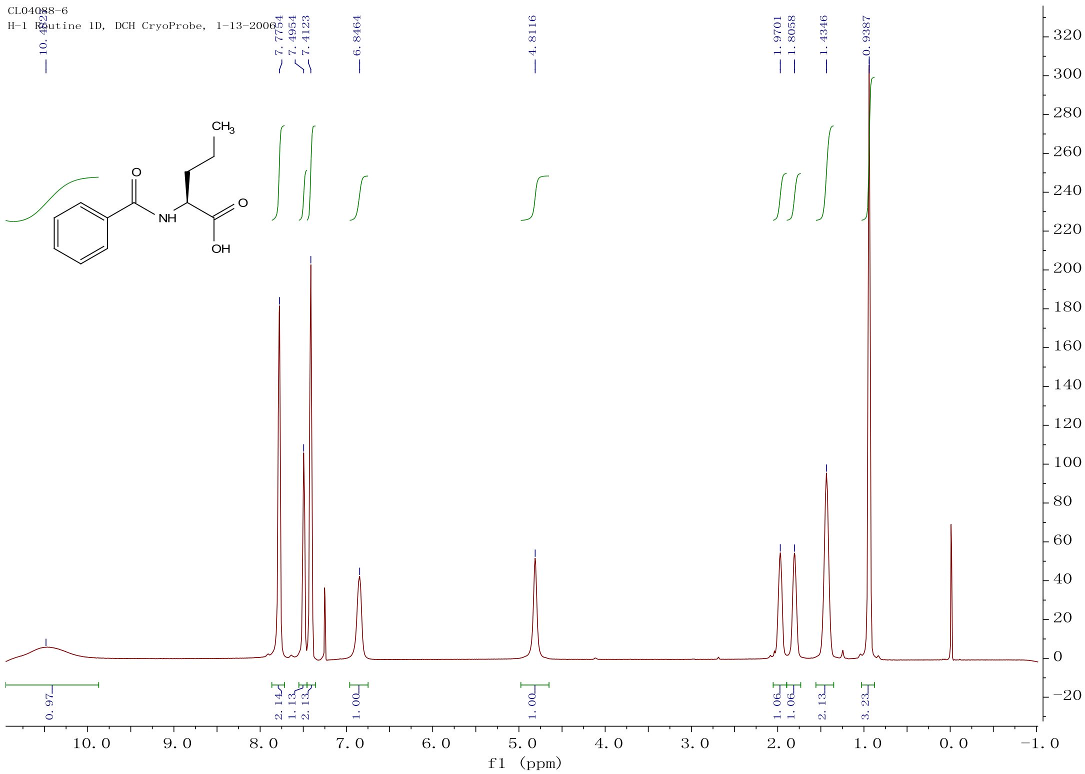

CL04088-3
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
176.7855
167.5613
162.5416
129.0610
125.6442
113.7935
77.2117
77.0002
76.7883
CDCl3
55.3958
51.4479
41.1529
24.9668
22.8534
21.9228
CH3
CH3
O
NH
O
OH
O
CH3
f1 (ppm)

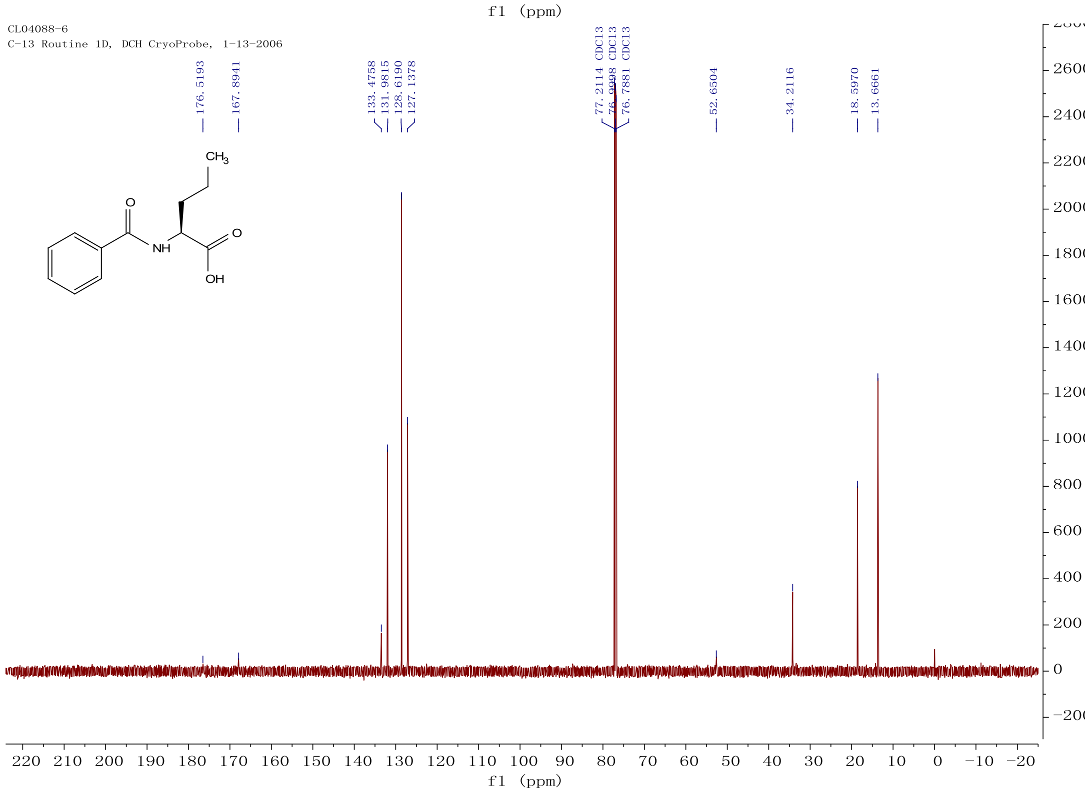

CL04088-4
H-1 Routine 1D, DCH CryoProbe
f1 (ppm)

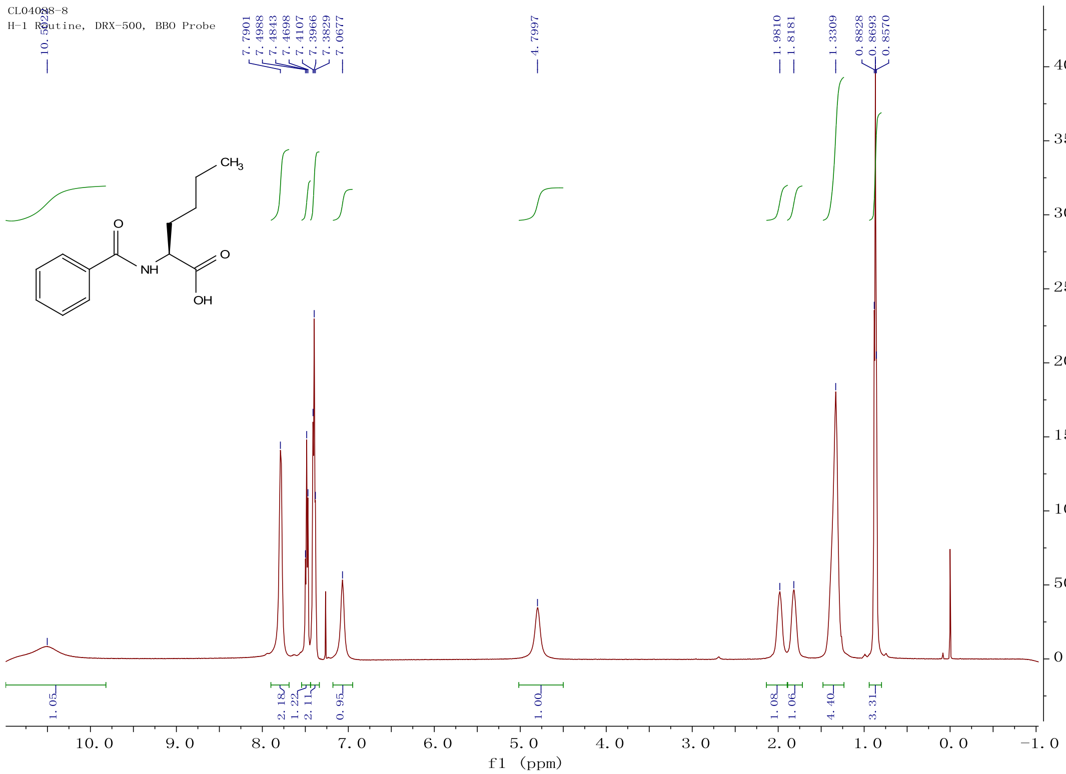

CL04088-4
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

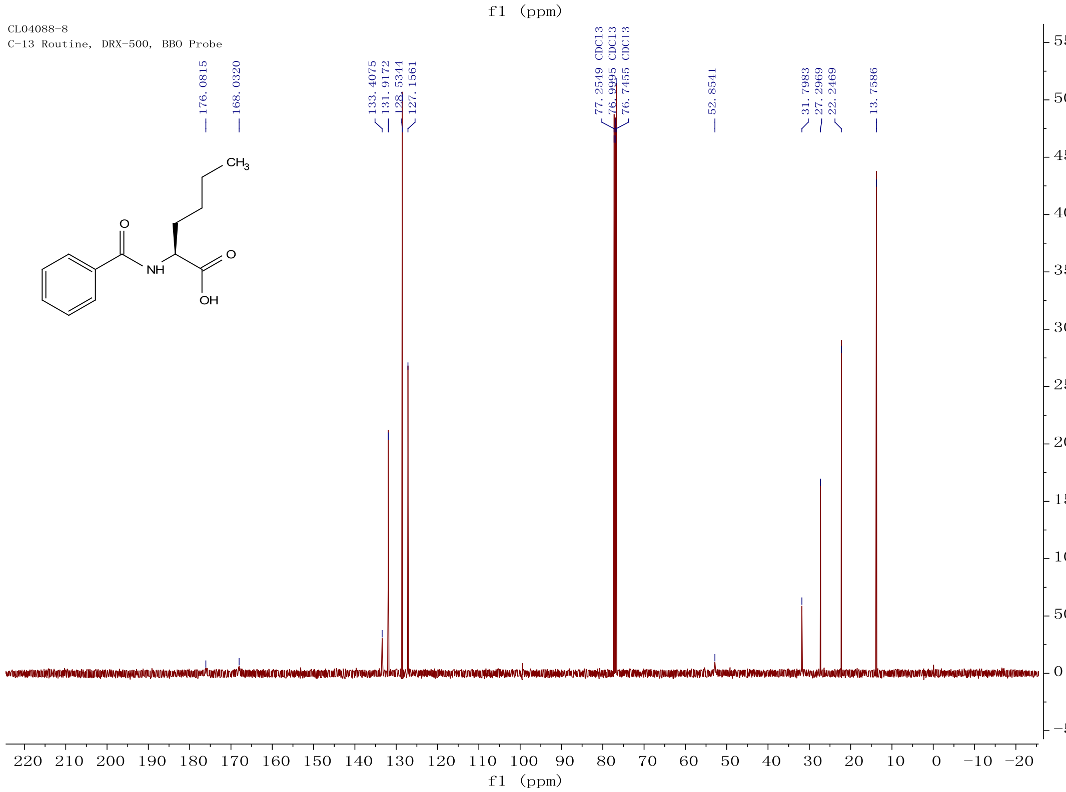

CL04088-5
H-1 Routine 1D, DCH CryoProbe
10.5910
8.2654
8.2501
7.8447
7.8363
7.8163
7.7924
7.5662
7.5533
7.5163
7.4992
7.4835
7.4690
7.4578
7.3543
7.3424
7.3299
7.2501
6.6193
4.8783
1.7410
1.7251
1.6150
1.6020
1.5860
0.9992
0.9910
0.9465
0.9380
CH3
CH3
O
NH
O
OH
0.80
1.02
1.07
1.03
1.05
2.12
1.04
0.98
1.00
2.05
1.07
3.06
3.32
f1 (ppm)

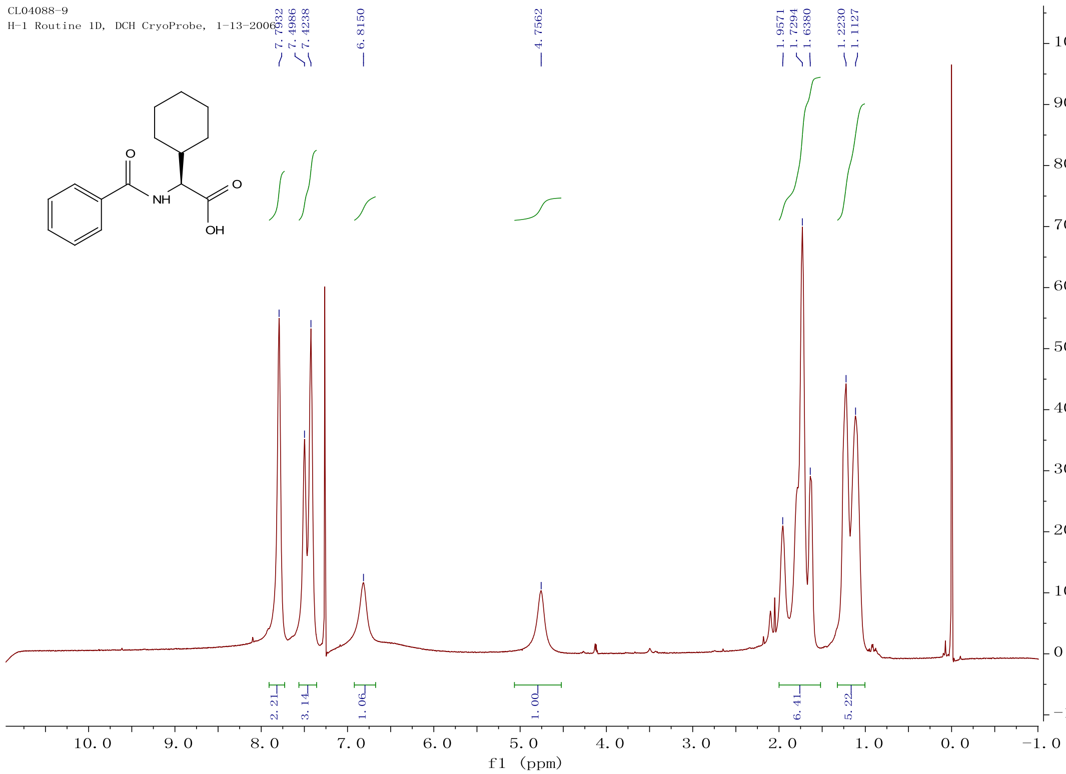

CL04088-5
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
177.0393
170.0542
133.4853
133.2529
130.9009
129.9662
128.2030
127.1925
126.3963
125.2835
125.2169
124.5461
77.2120 CDCl3
77.0002 CDCl3
76.7885 CDCl3
51.2581
40.9610
24.9998
22.8527
21.7430
CH3
CH3
O
NH
O
OH
f1 (ppm)

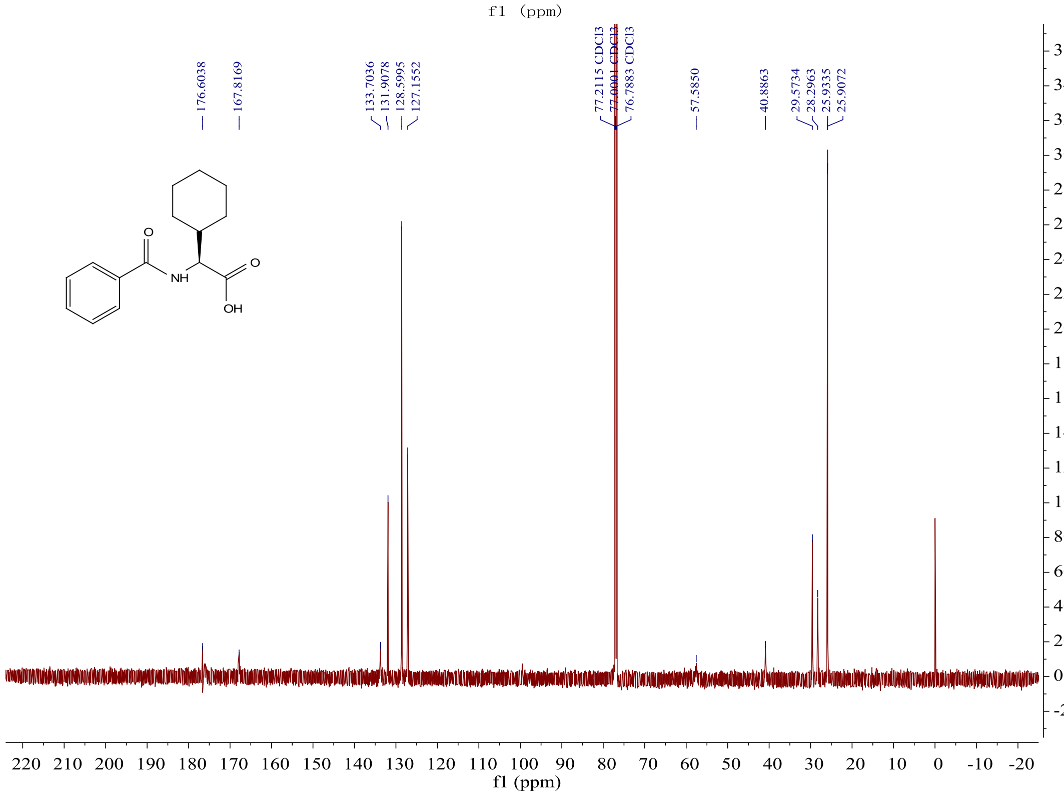

CL04088-6
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
CH3
O
NH
O
OH
f1 (ppm)

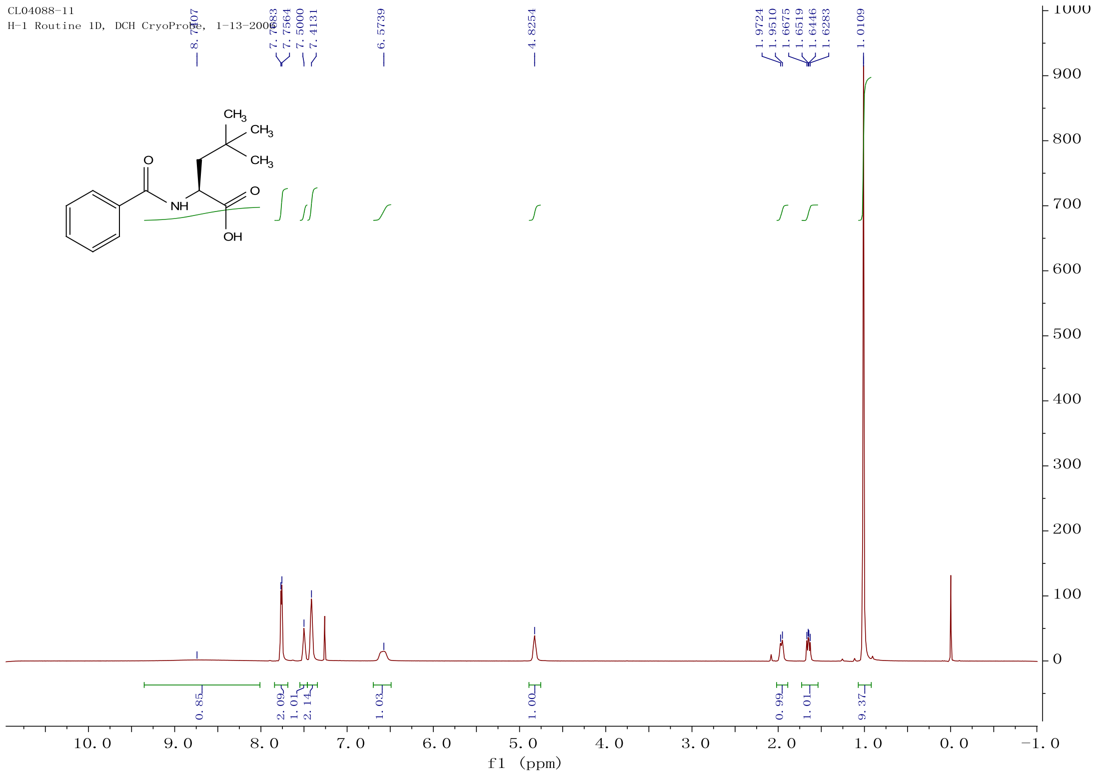

CL04088-6
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
176.5193
167.8941
133.4758
131.9815
128.6190
127.1378
77.2114 CDCl3
76.9998 CDCl3
76.7881 CDCl3
52.6504
34.2116
18.5970
13.6661
CH3
O
NH
O
OH
f1 (ppm)

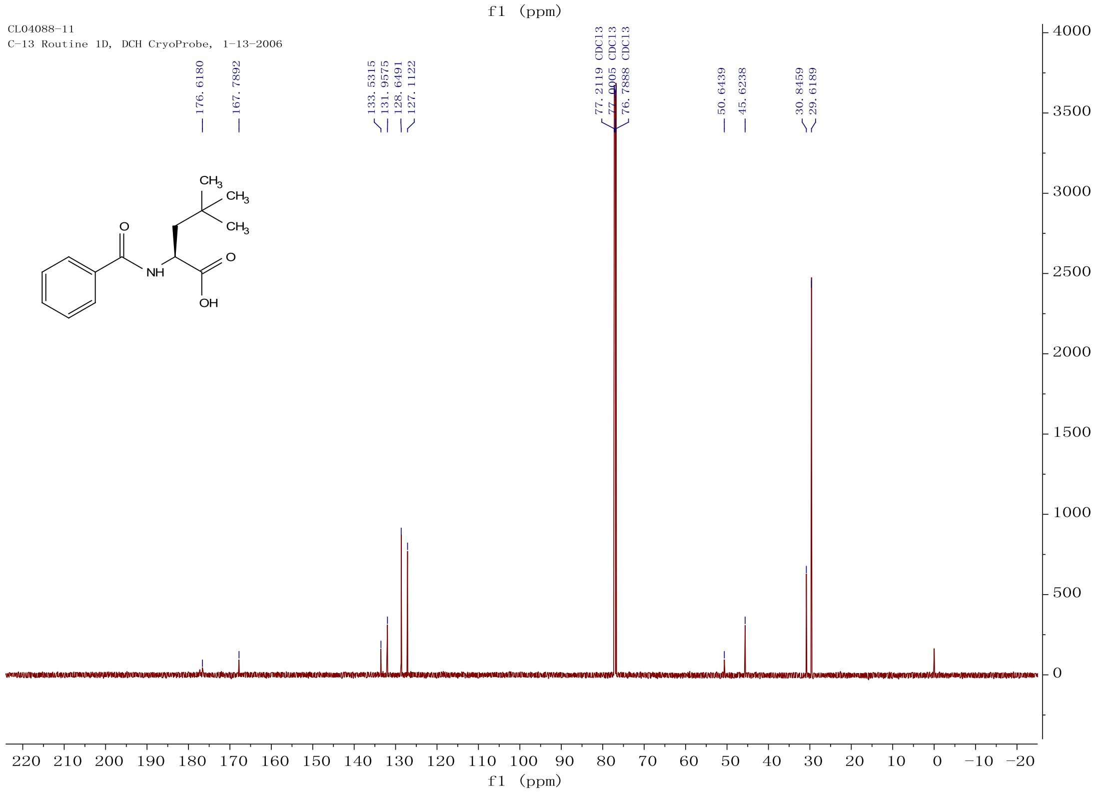

CL04088-8
H-1 Routine, DRX-500, BBO Probe
f1 (ppm)

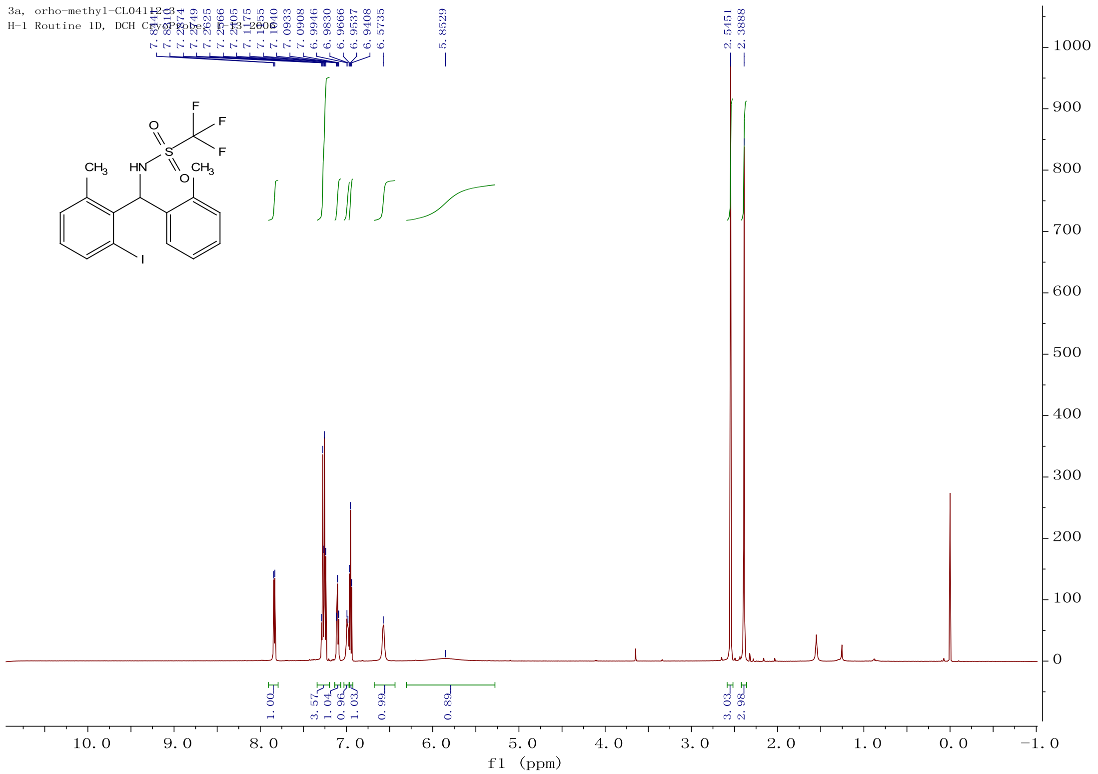

CL04088-8
C-13 Routine, DRX-500, BBO Probe
f1 (ppm)

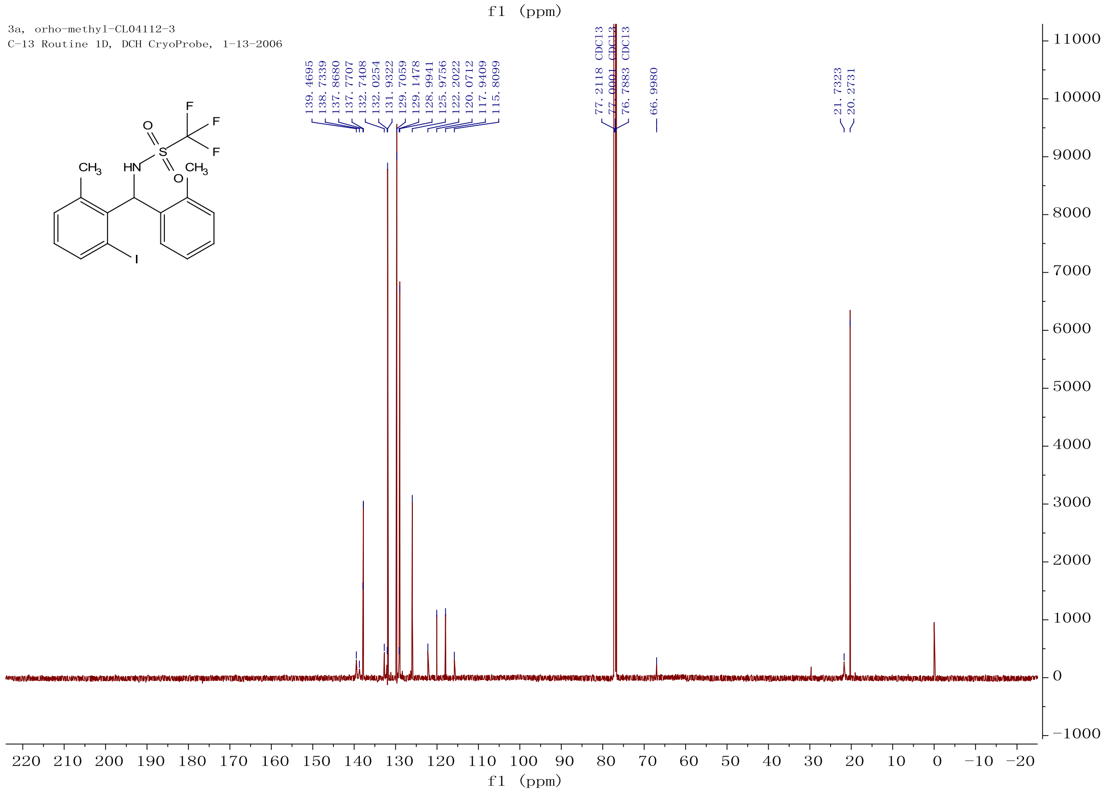

CL04088-9
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.7932
7.4986
7.4238
6.8150
4.7562
1.9571
1.7294
1.6380
1.2230
1.1127
NH
O
O
OH
2.21
3.14
1.06
1.00
6.41
5.22
f1 (ppm)

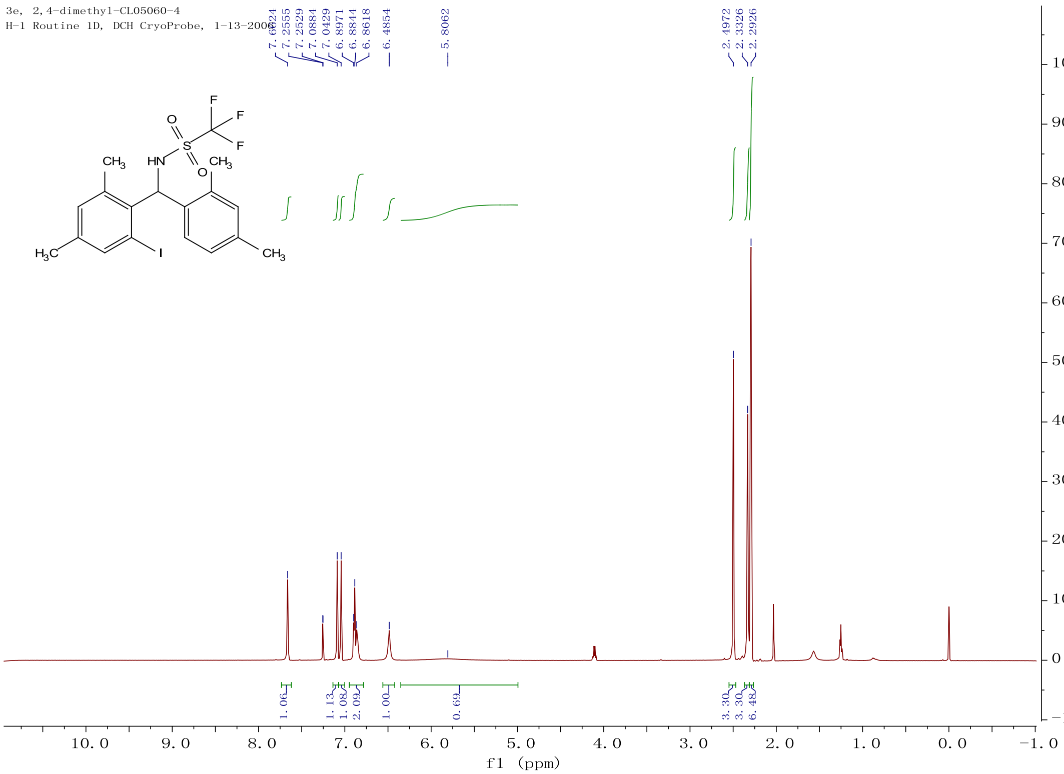

176.6038
167.8169
133.7036
131.9078
128.5995
127.1552
77.2115 CDCl3
77.0001 CDCl3
76.7883 CDCl3
57.5850
40.8863
29.5734
28.2963
25.9335
25.9072
NH
O
O
OH
f1 (ppm)

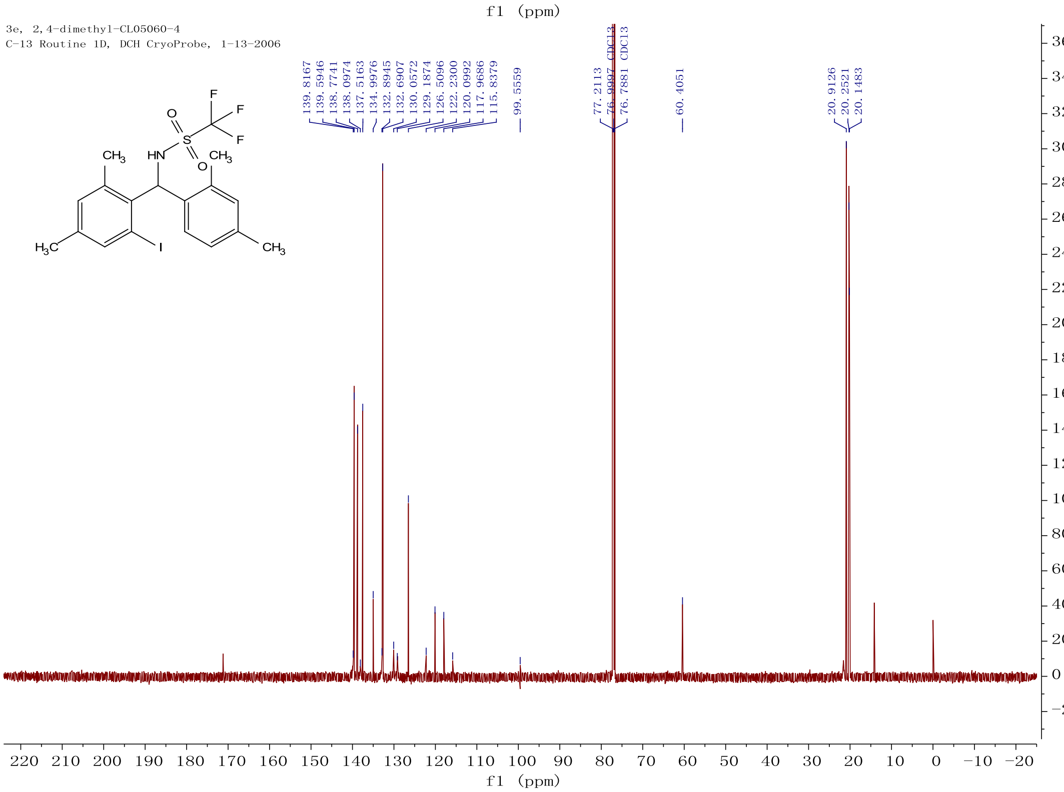

CL04088-11
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
8.7307
7.7683
7.7564
7.5000
7.4131
6.5739
4.8254
1.9724
1.9510
1.6675
1.6519
1.6446
1.6283
1.0109
0.85
2.09
1.01
2.14
1.03
1.00
0.99
1.01
9.37
f1 (ppm)

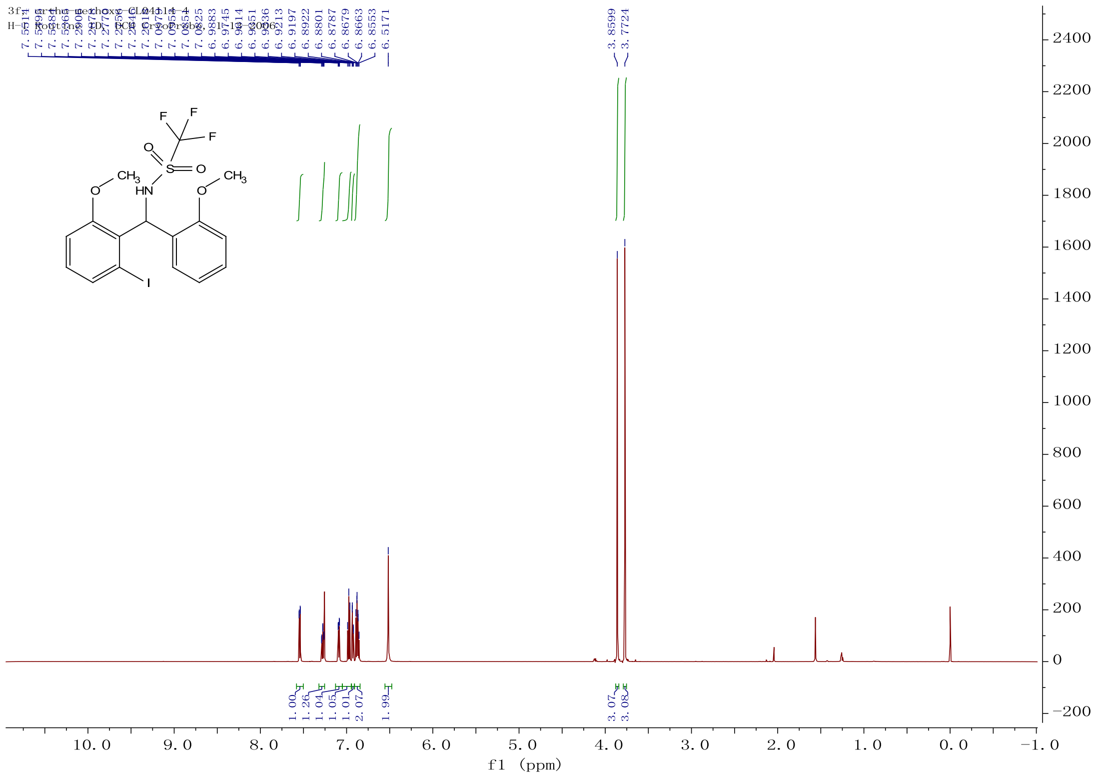

CL04088-11
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
176.6180
167.7892
133.5315
131.9575
128.6491
127.1122
77.2119 CDCl3
77.0005 CDCl3
76.7888 CDCl3
50.6439
45.6238
30.8459
29.6189
f1 (ppm)

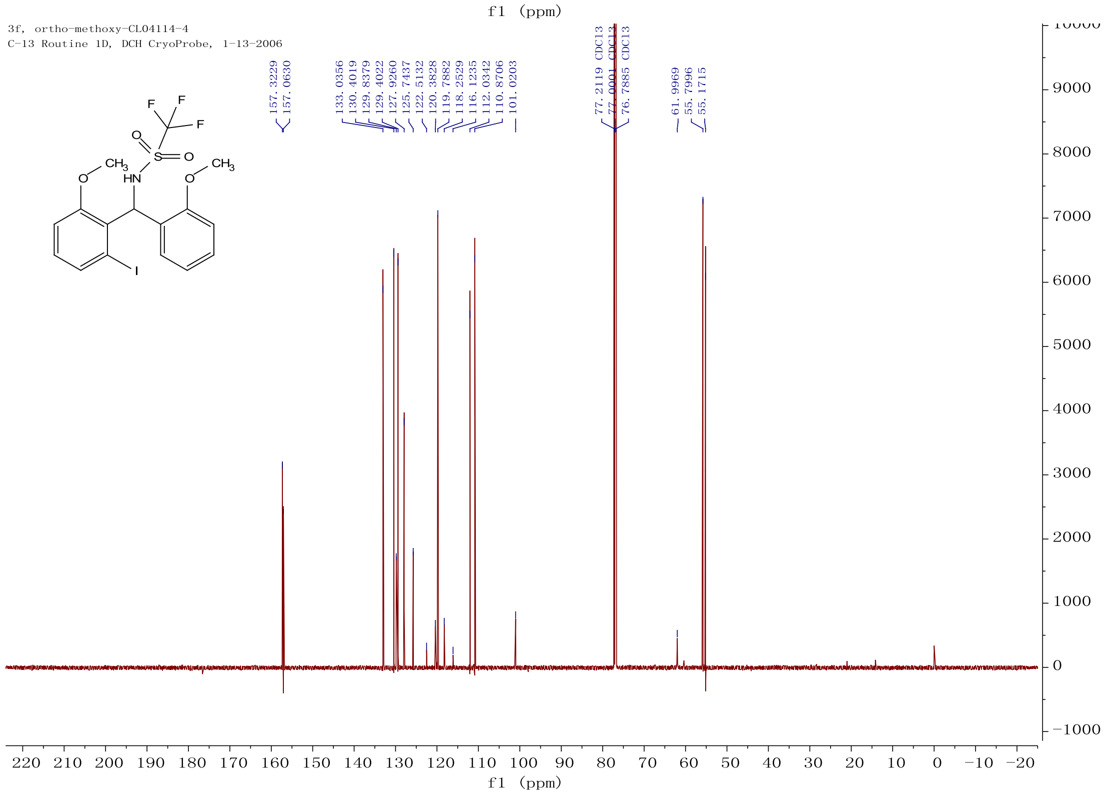

3a, orho-methyl-CL04112-3
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

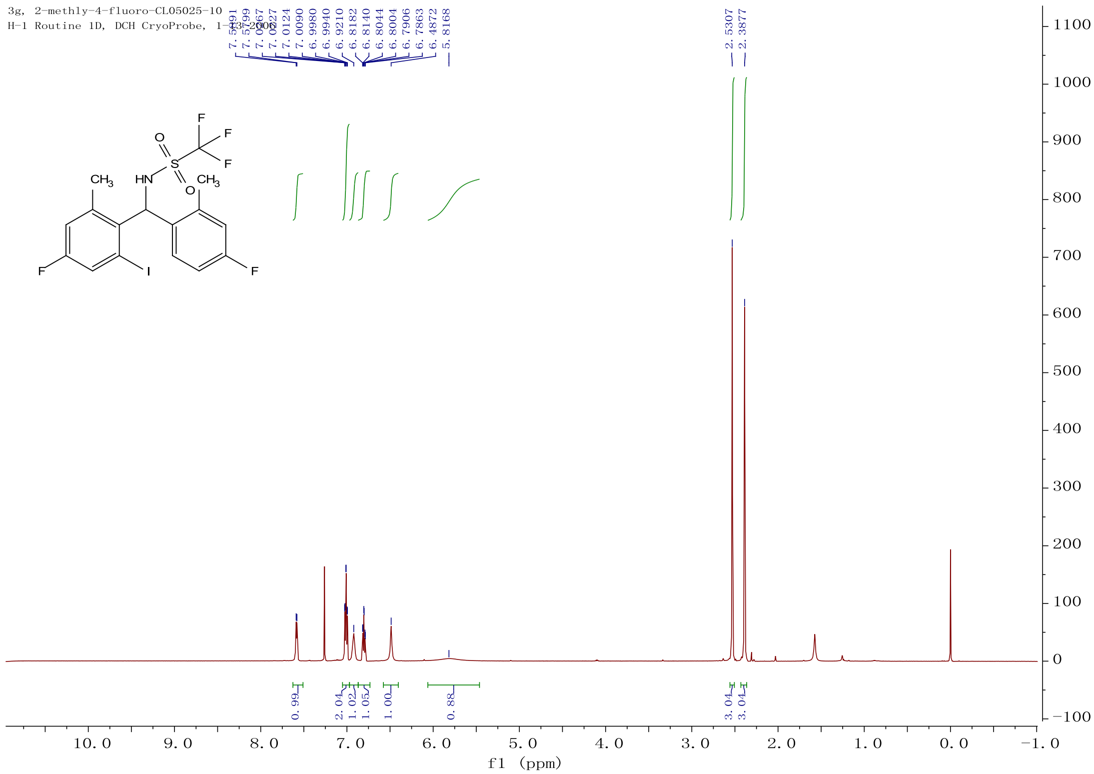

3a, orho-methyl-CL04112-3
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

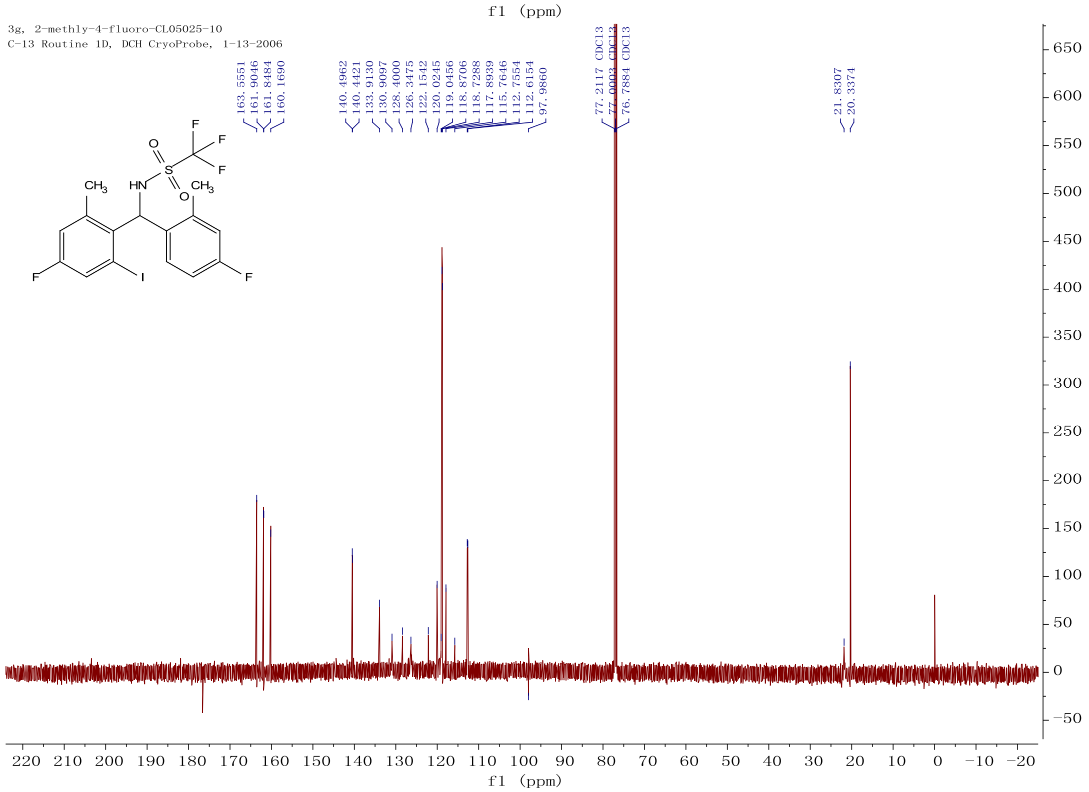

3e, 2,4-dimethyl-CL05060-4
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.6824
7.2555
7.2529
7.0884
7.0429
6.8971
6.8844
6.8618
6.4854
5.8062
2.4972
2.3326
2.2926
1.06
1.13
1.08
2.09
1.00
0.69
3.30
3.30
6.48
f1 (ppm)

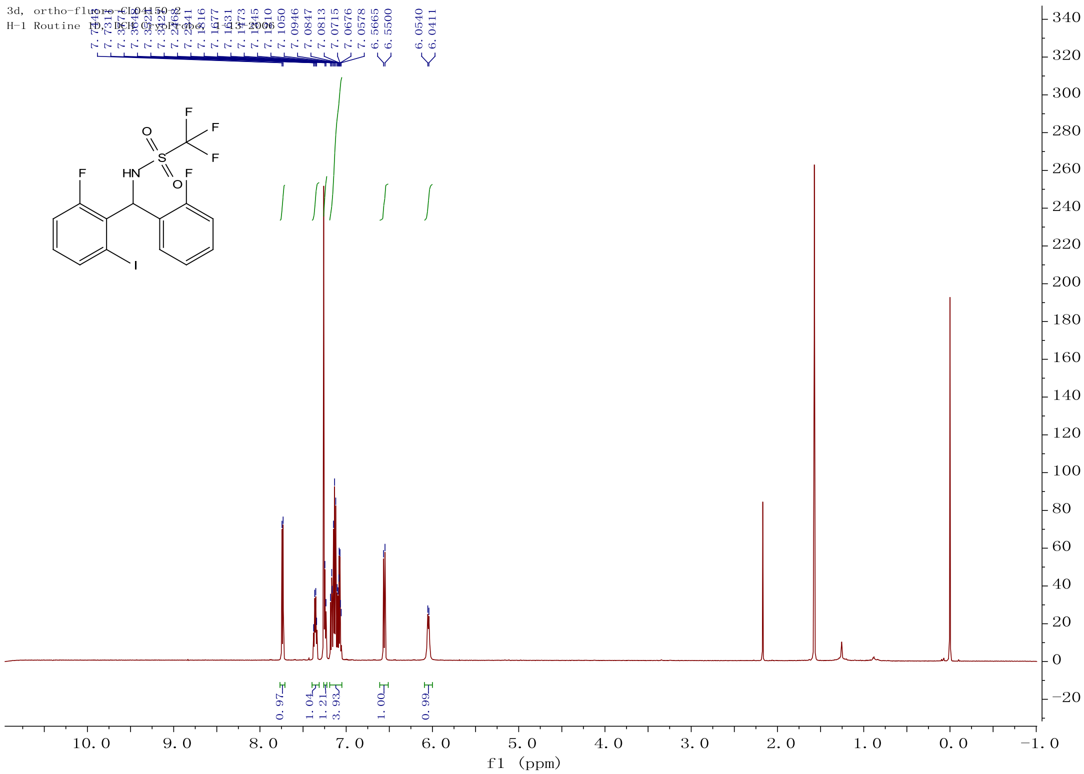

3e, 2,4-dimethyl-CL05060-4
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
139.8167
139.5946
138.7741
138.0974
137.5163
134.9976
132.8945
132.6907
130.0572
129.1874
126.5096
122.2300
120.0992
117.9686
115.8379
99.5559
77.2113
76.9997 CDCl3
76.7881 CDCl3
60.4051
20.9126
20.2521
20.1483
f1 (ppm)

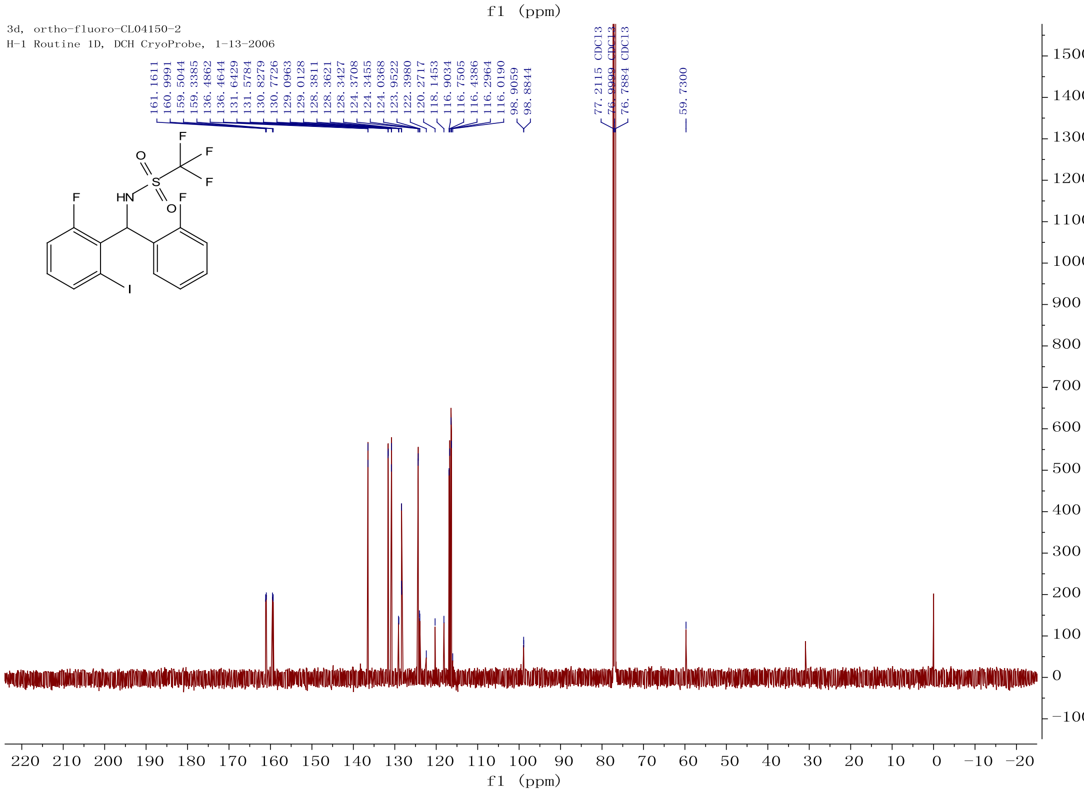

3f, ortho-methoxy-CL04114-4
f1 (ppm)

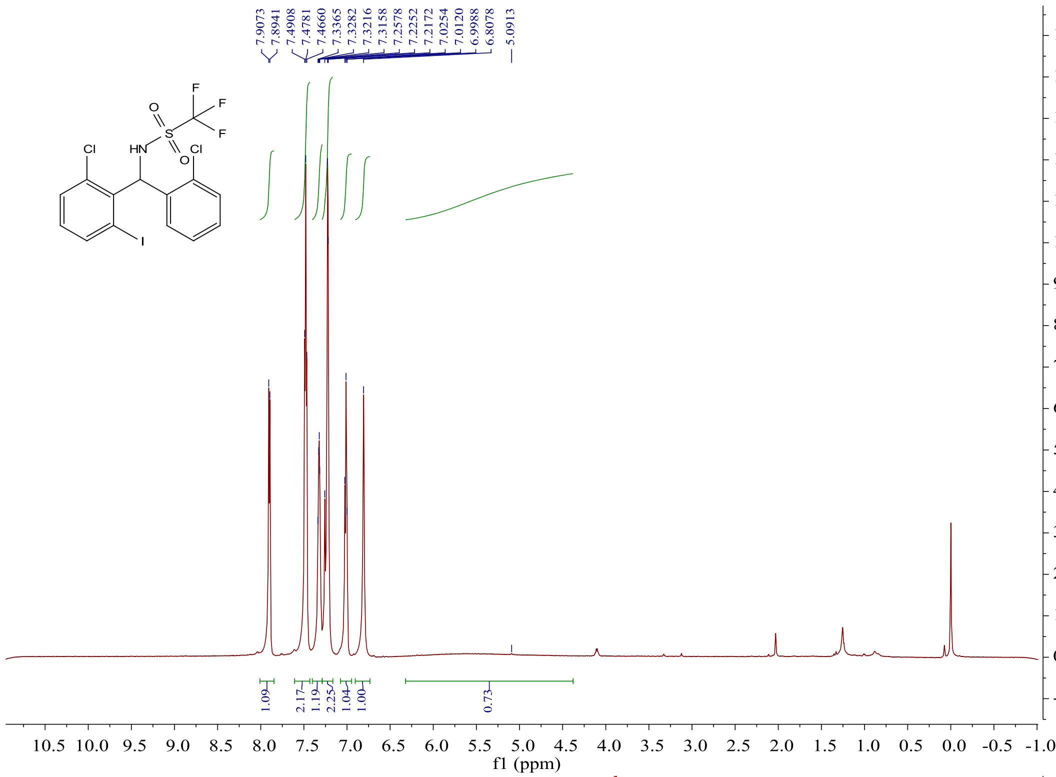

3f, ortho-methoxy-CL04114-4
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
157.3229
157.0630
133.0356
130.4019
129.8379
129.4022
127.9260
125.7437
122.5132
120.3828
119.7882
118.2529
116.1235
112.0342
110.8706
101.0203
77.2119 CDCl3
77.0001 CDCl3
76.7885 CDCl3
61.9969
55.7996
55.1715
f1 (ppm)

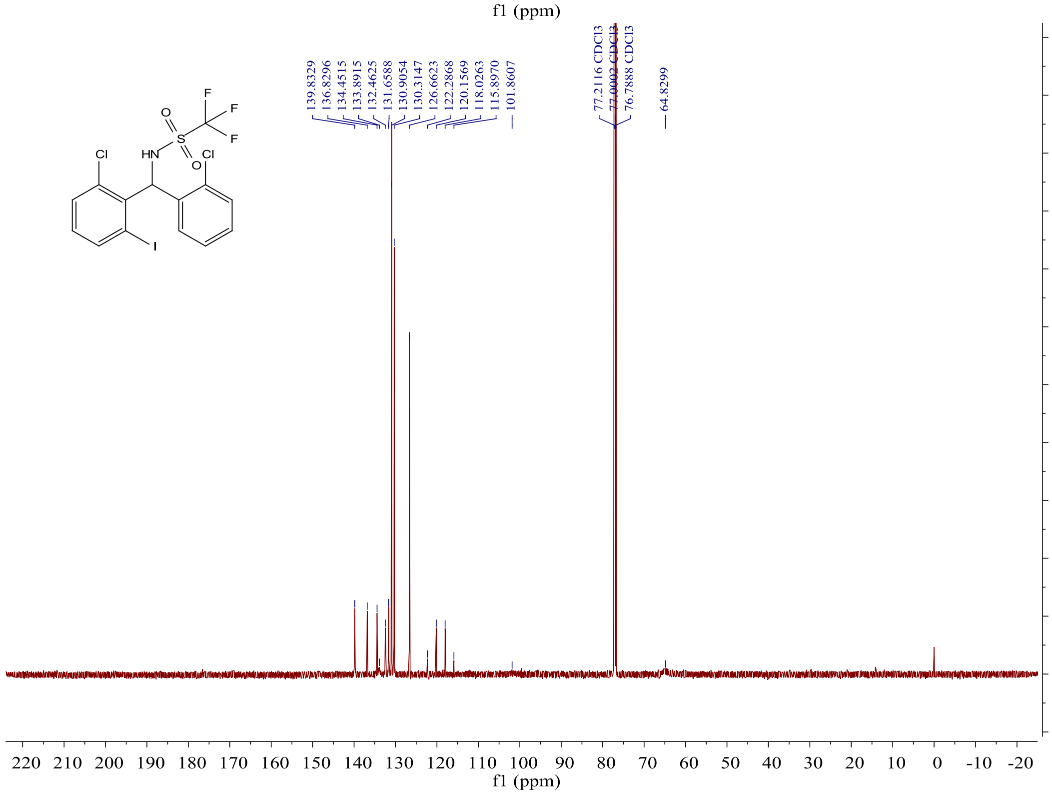

3g, 2-methly-4-fluoro-CL05025-10
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

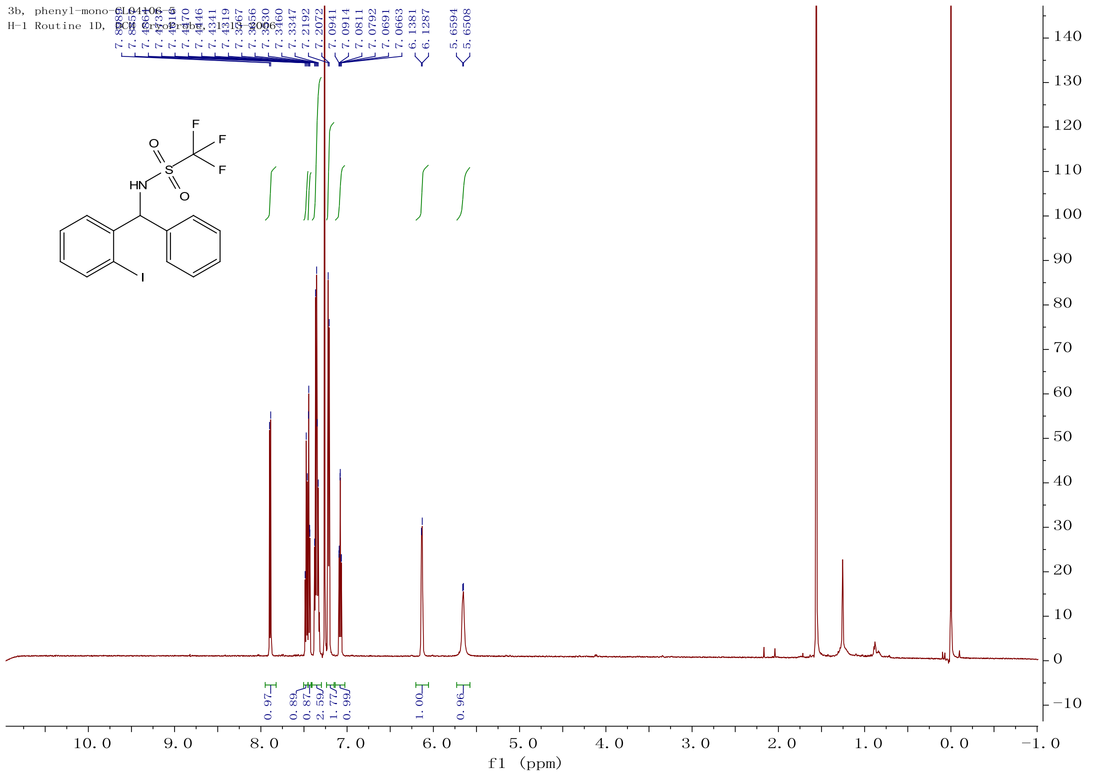

3g, 2-methly-4-fluoro-CL05025-10
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

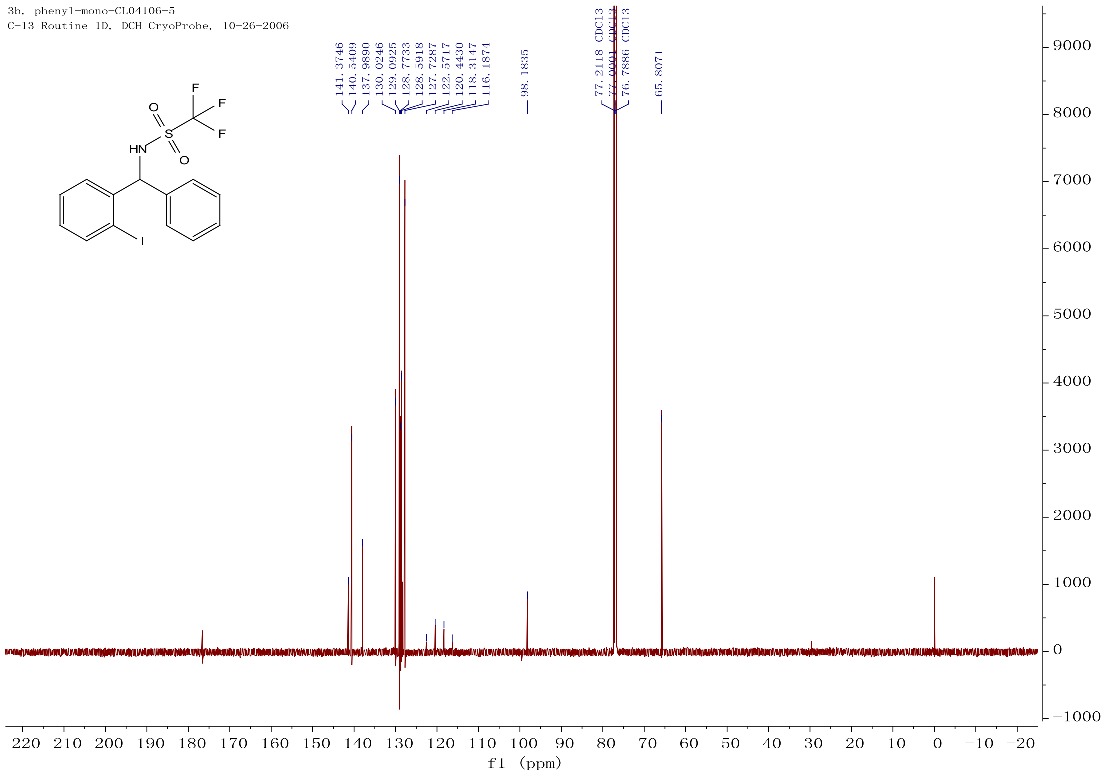


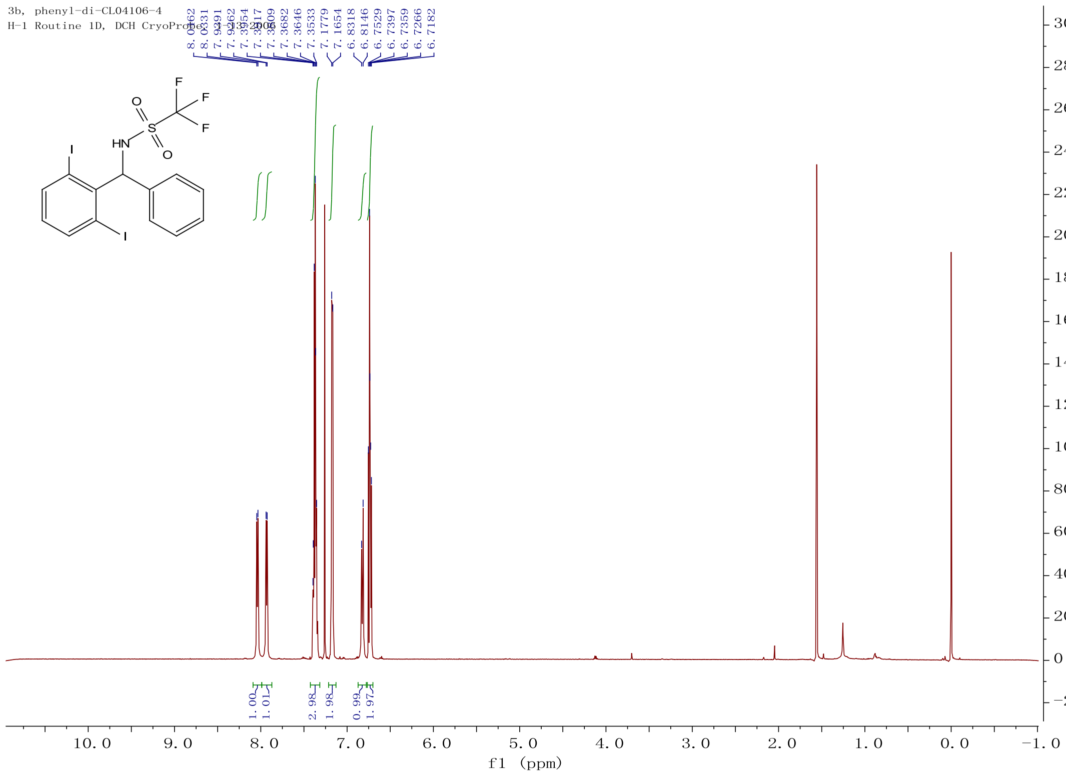


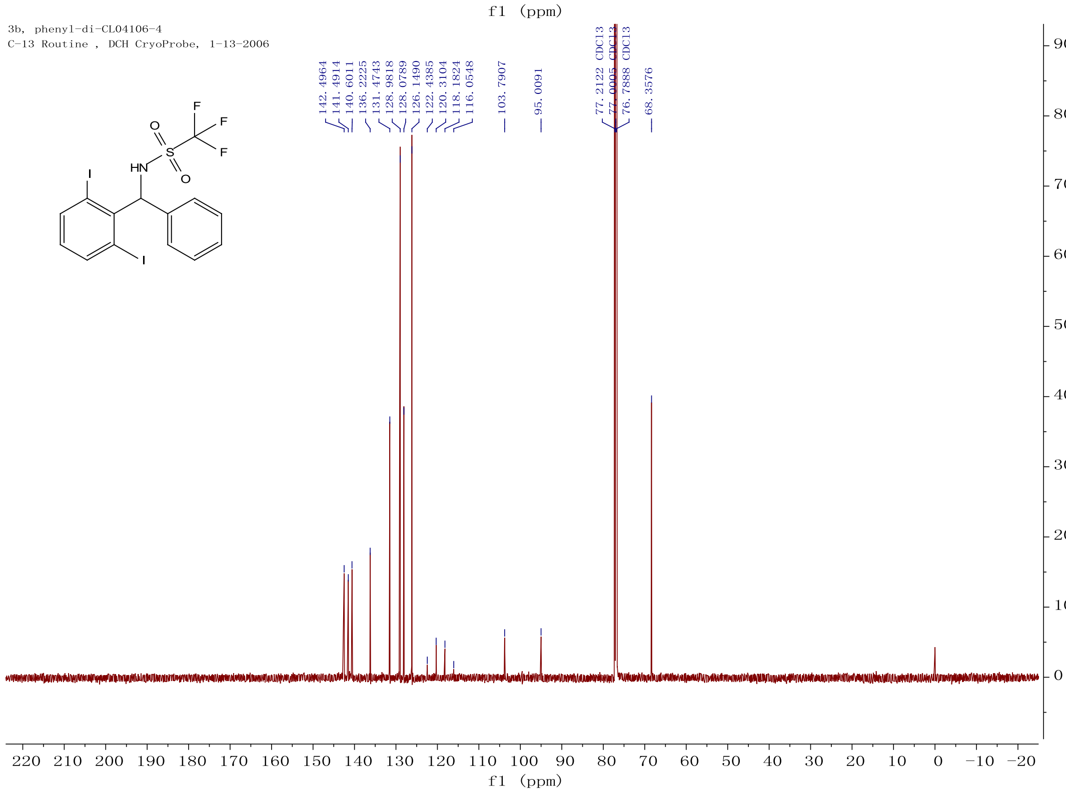

7.9073
7.8941
7.4908
7.4781
7.4660
7.3365
7.3282
7.3216
7.3158
7.2578
7.2252
7.2172
7.0254
7.0120
6.9988
6.8078
5.0913
1.09
2.17
1.19
2.25
1.04
1.00
0.73
f1 (ppm)

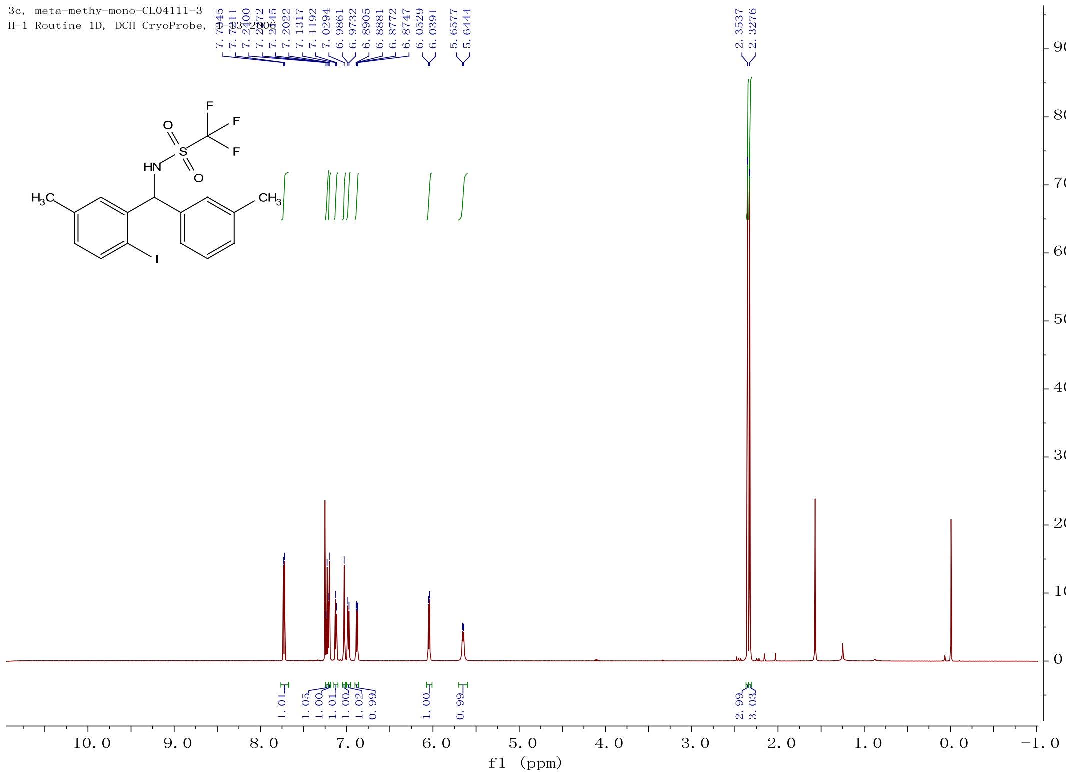

139.8329
136.8296
134.4515
133.8915
132.4625
131.6588
130.9054
130.3147
126.6623
122.2868
120.1569
118.0263
115.8970
101.8607
77.2116 CDCl3
77.0002 CDCl3
76.7888 CDCl3
64.8299
f1 (ppm)



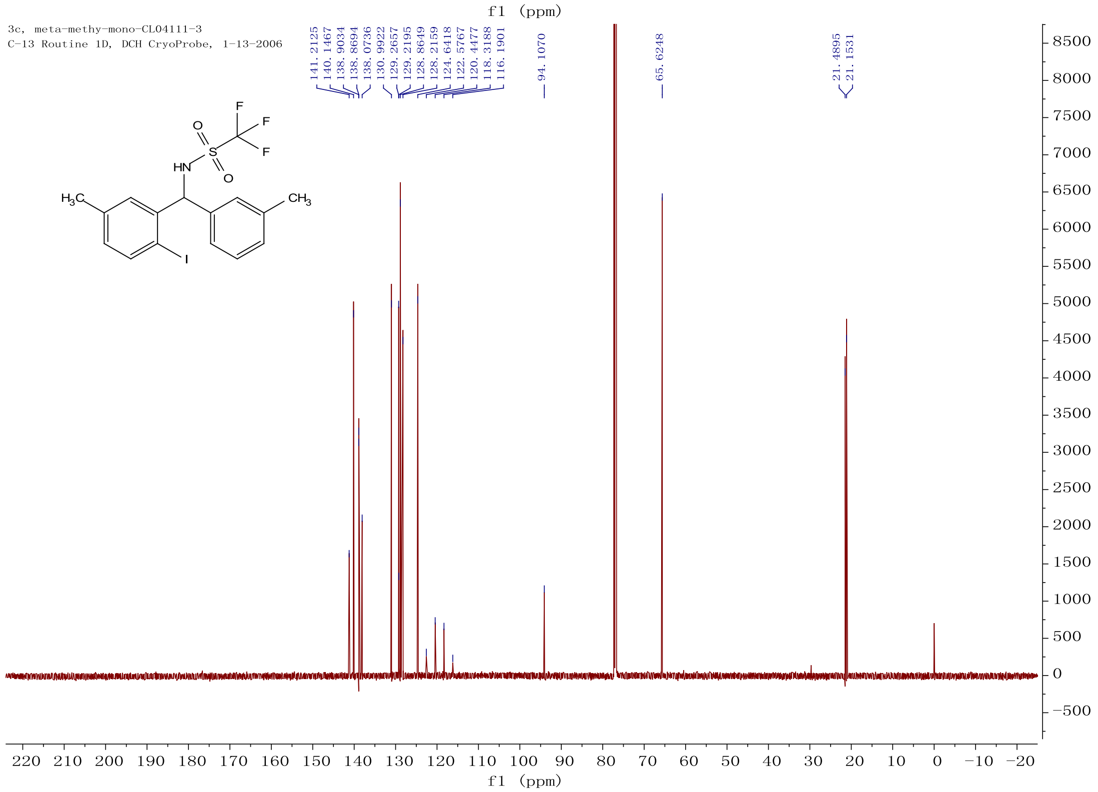



3b, phenyl-di-CL04106-4
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
8.0462
8.0331
7.9391
7.9262
7.3954
7.3817
7.3699
7.3682
7.3646
7.3533
7.1779
7.1654
6.8318
6.8146
6.7529
6.7397
6.7359
6.7266
6.7182
1.00
1.01
2.98
1.98
0.99
1.97
f1 (ppm)

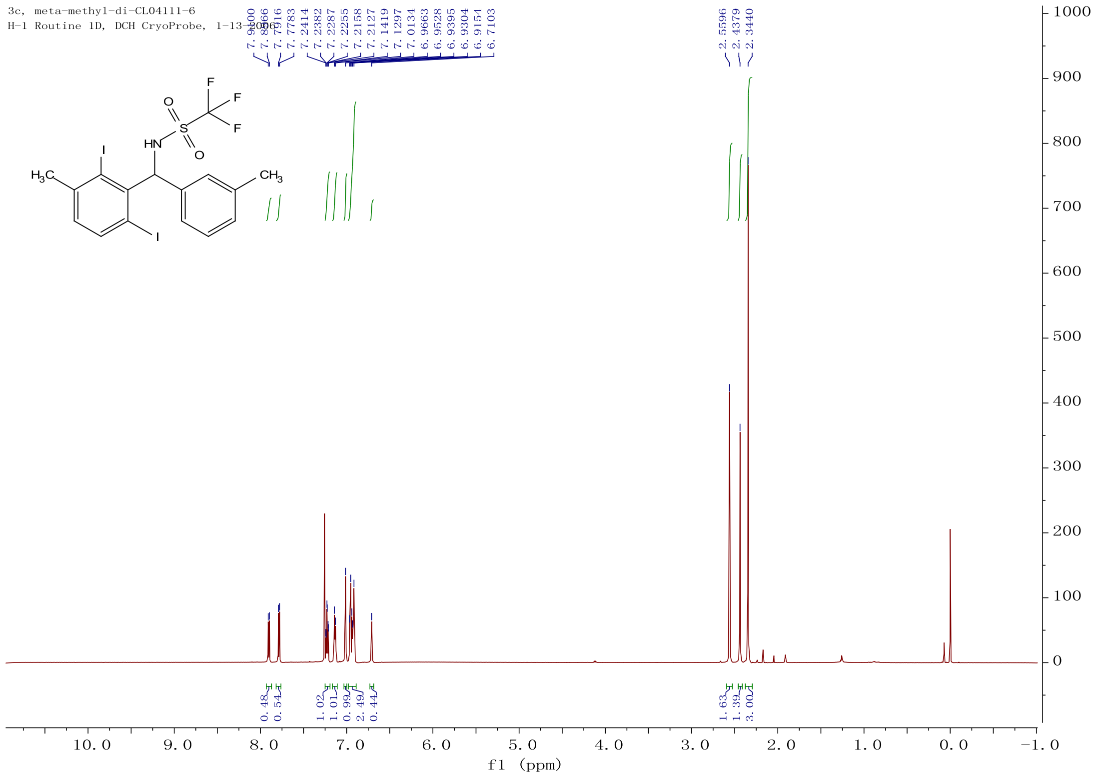

3b, phenyl-di-CL04106-4
C-13 Routine , DCH CryoProbe, 1-13-2006
142.4964
141.4914
140.6011
136.2225
131.4743
128.9818
128.0789
126.1490
122.4385
120.3104
118.1824
116.0548
103.7907
95.0091
77.2122 CDCl3
77.0005 CDCl3
76.7888 CDCl3
68.3576
f1 (ppm)

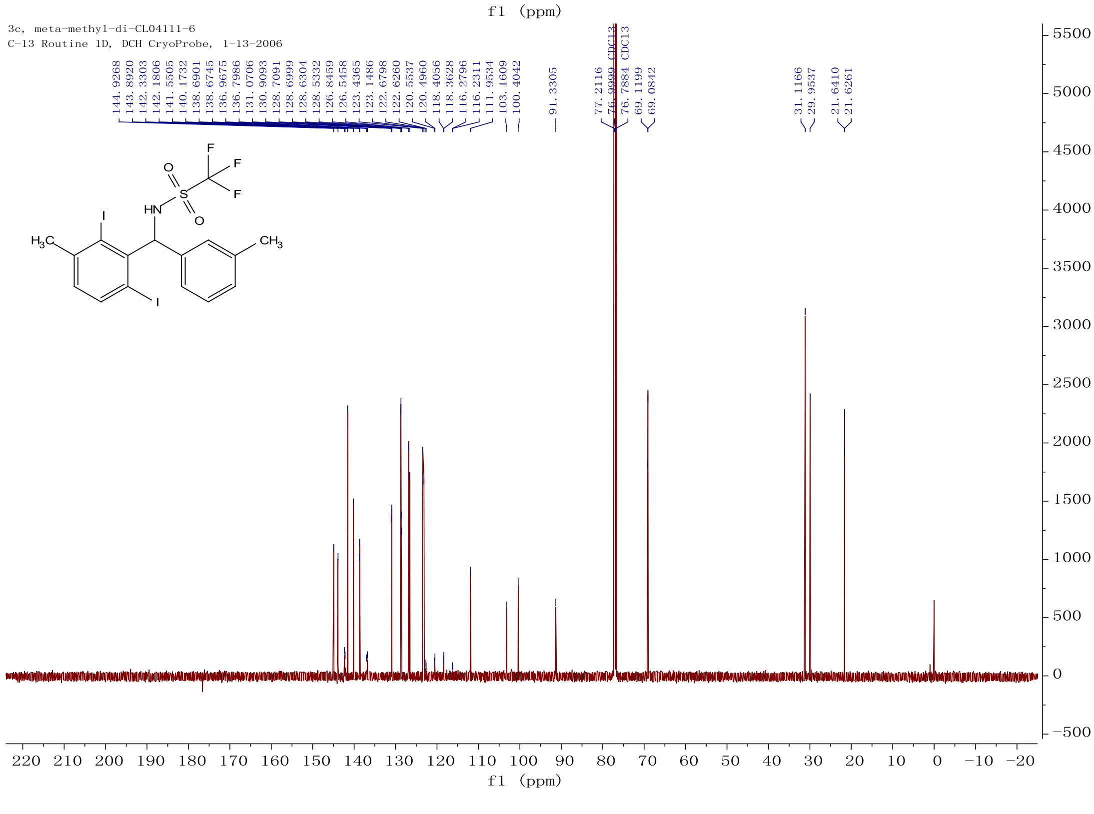


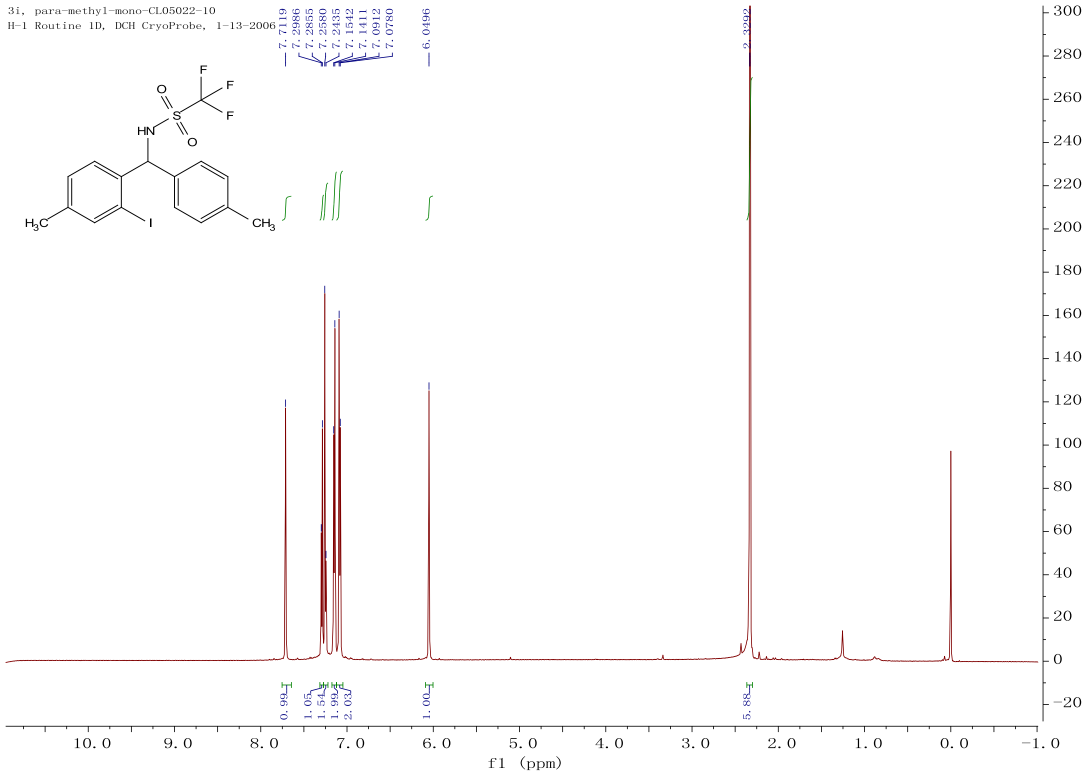
3c, meta-methy-mono-CL04111-3
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.7445
7.7311
7.2400
7.2272
7.2145
7.2022
7.1317
7.1192
7.0294
6.9861
6.9732
6.8905
6.8881
6.8772
6.8747
6.0529
6.0391
5.6577
5.6444
2.3537
2.3276
1.01
1.05
1.00
1.01
1.00
1.02
0.99
1.00
0.99
2.99
3.03
f1 (ppm)

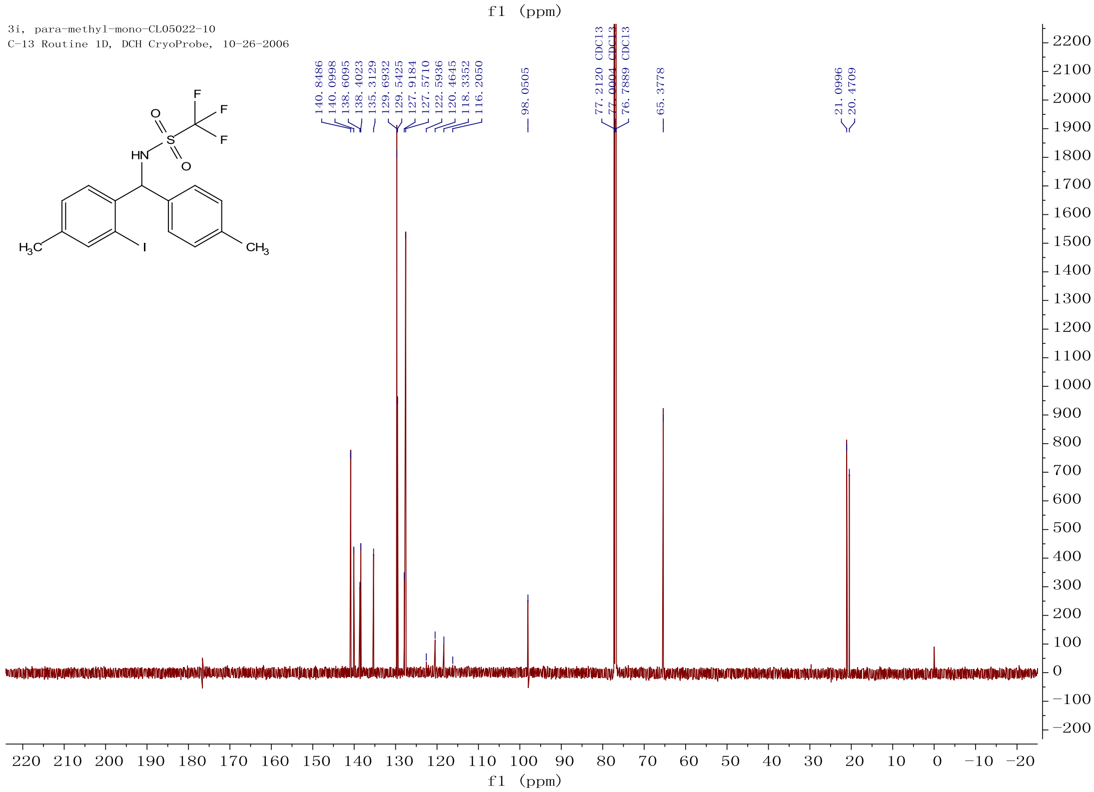


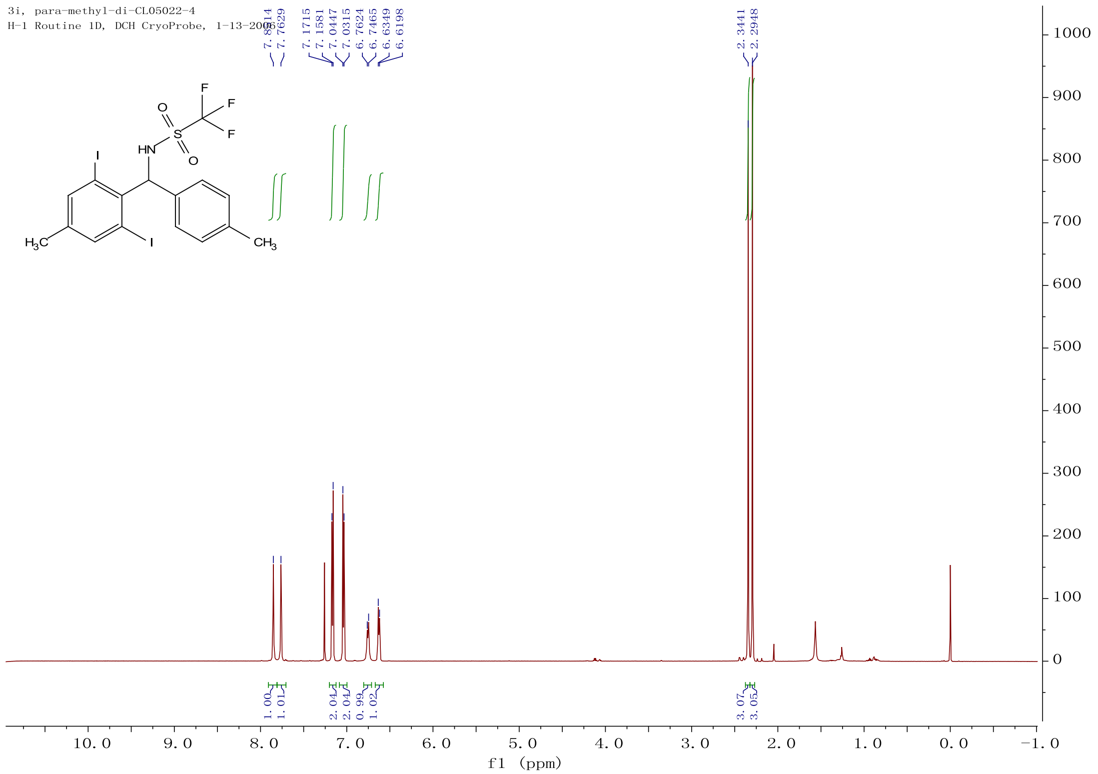
3c, meta-methy-mono-CL04111-3
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
141.2125
140.1467
138.9034
138.8694
138.0736
130.9922
129.2657
129.2195
128.8649
128.2159
124.6418
122.5767
120.4477
118.3188
116.1901
94.1070
65.6248
21.4895
21.1531
f1 (ppm)

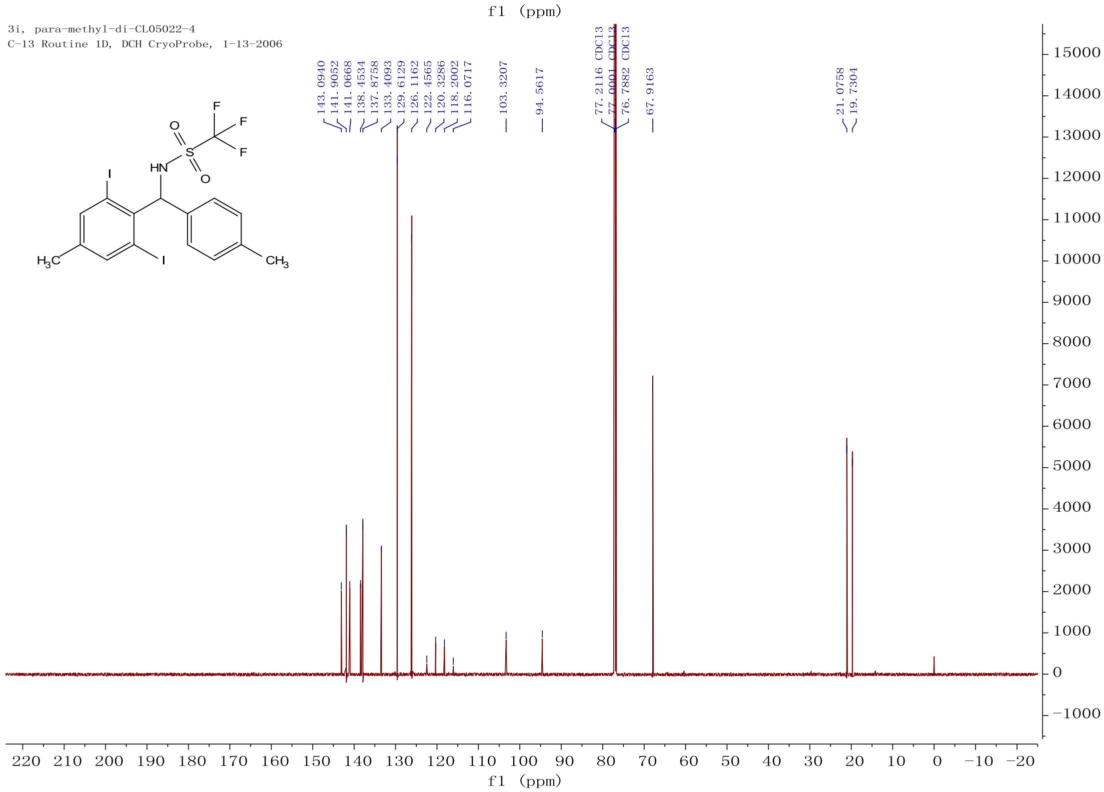

3c, meta-methyl-di-CL04111-6
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

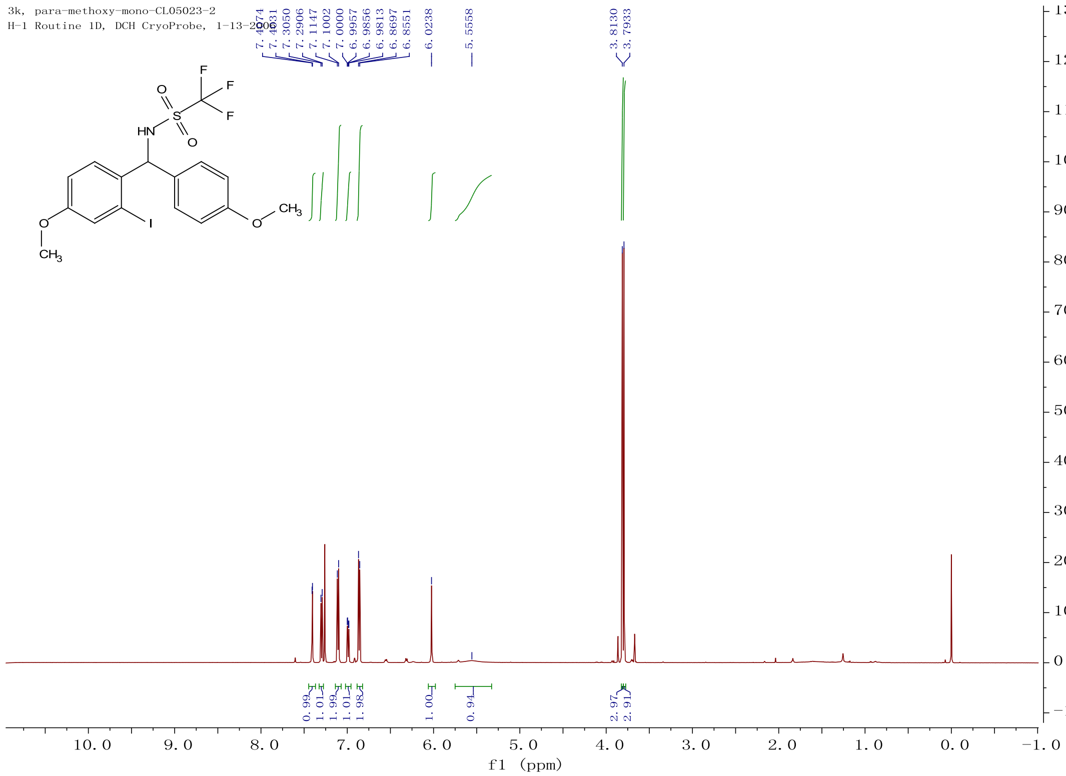

3c, meta-methyl-di-CL04111-6
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

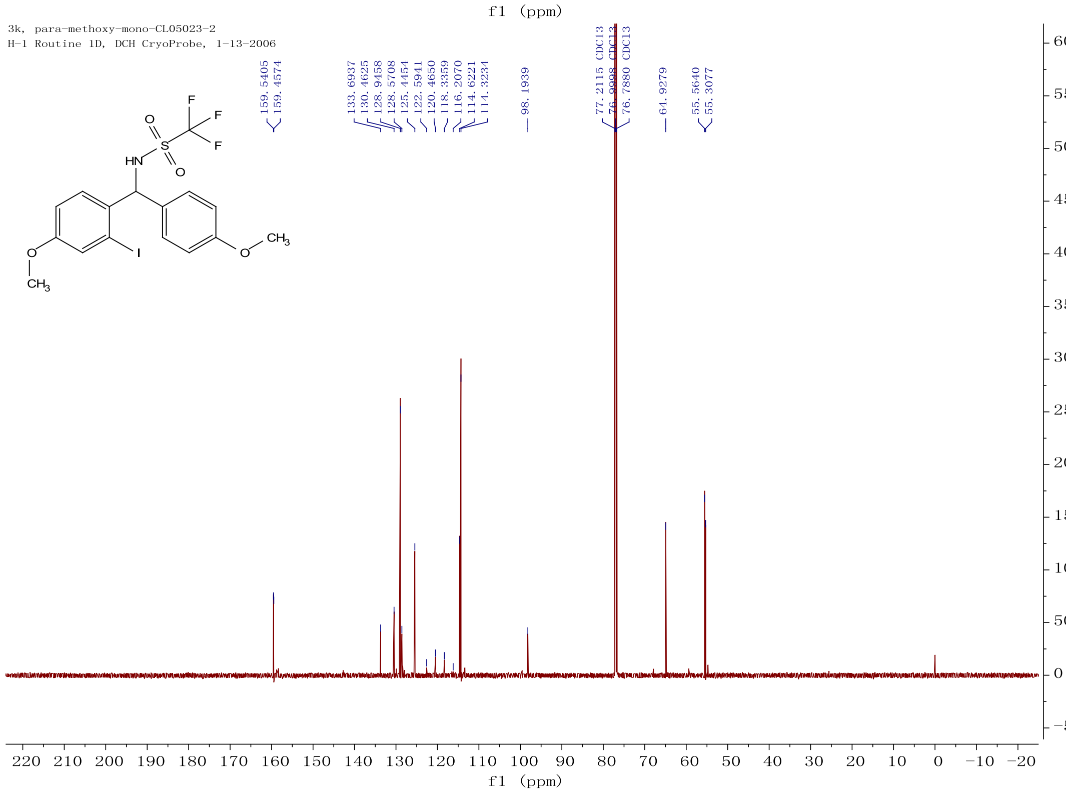

3i, para-methyl-mono-CL05022-10
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.7119
7.2986
7.2855
7.2580
7.2435
7.1542
7.1411
7.0912
7.0780
6.0496
2.3292
0.99
1.05
1.54
1.99
2.03
1.00
5.88
f1 (ppm)

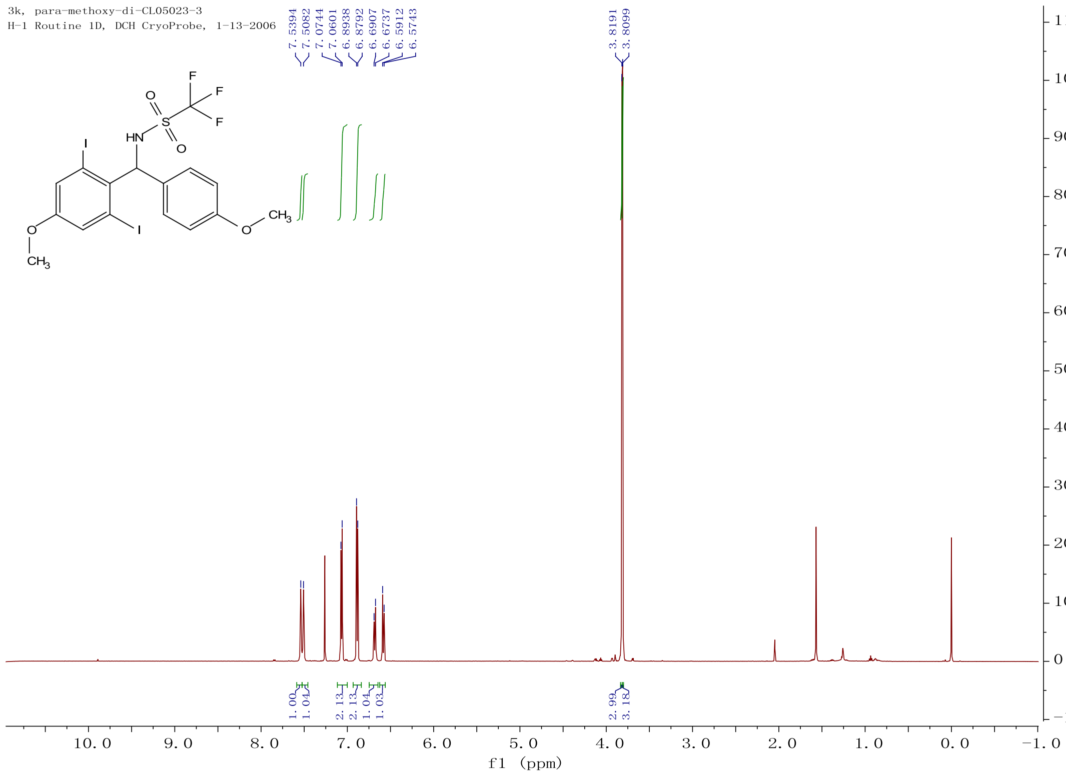

3i, para-methyl-mono-CL05022-10
C-13 Routine 1D, DCH CryoProbe, 10-26-2006
140.8486
140.0998
138.6095
138.4023
135.3129
129.6932
129.5425
127.9184
127.5710
122.5936
120.4645
118.3352
116.2050
98.0505
77.2120 CDCl3
77.0004 CDCl3
76.7889 CDCl3
65.3778
21.0996
20.4709
f1 (ppm)

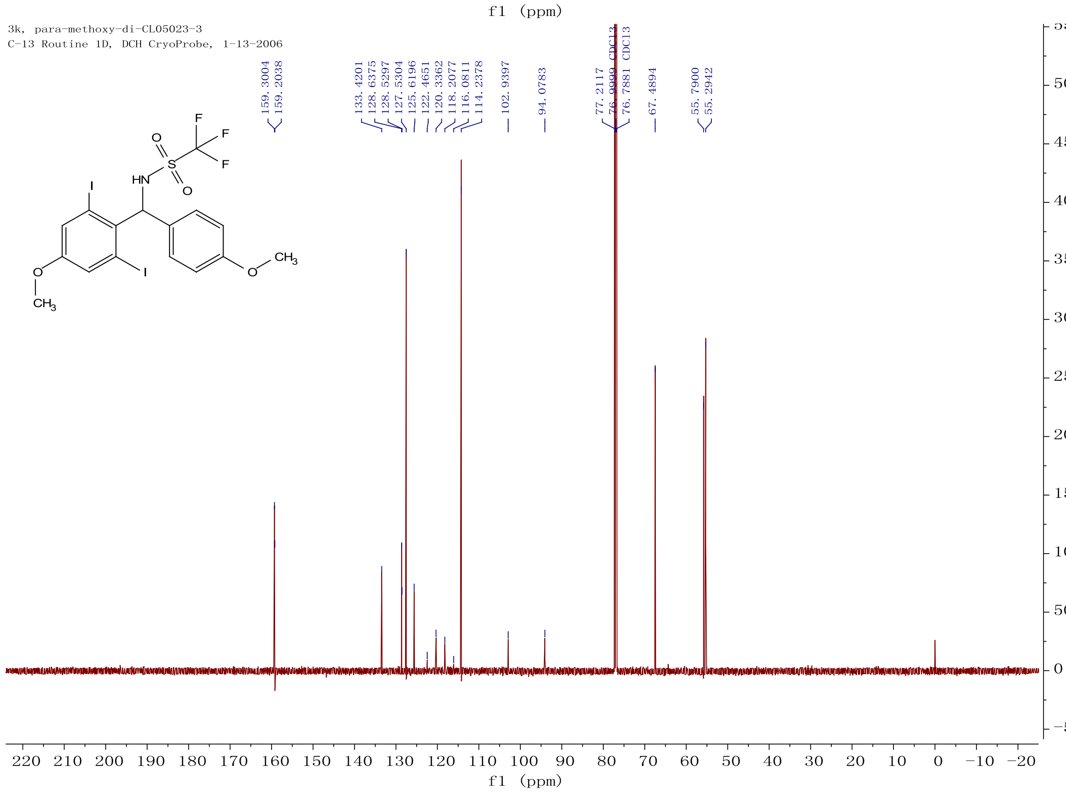

3i, para-methyl-di-CL05022-4
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.8014
7.7629
7.1715
7.1581
7.0447
7.0315
6.7624
6.7465
6.6349
6.6198
2.3441
2.2948
1.00
1.01
2.04
2.04
0.99
1.02
3.07
3.05
f1 (ppm)

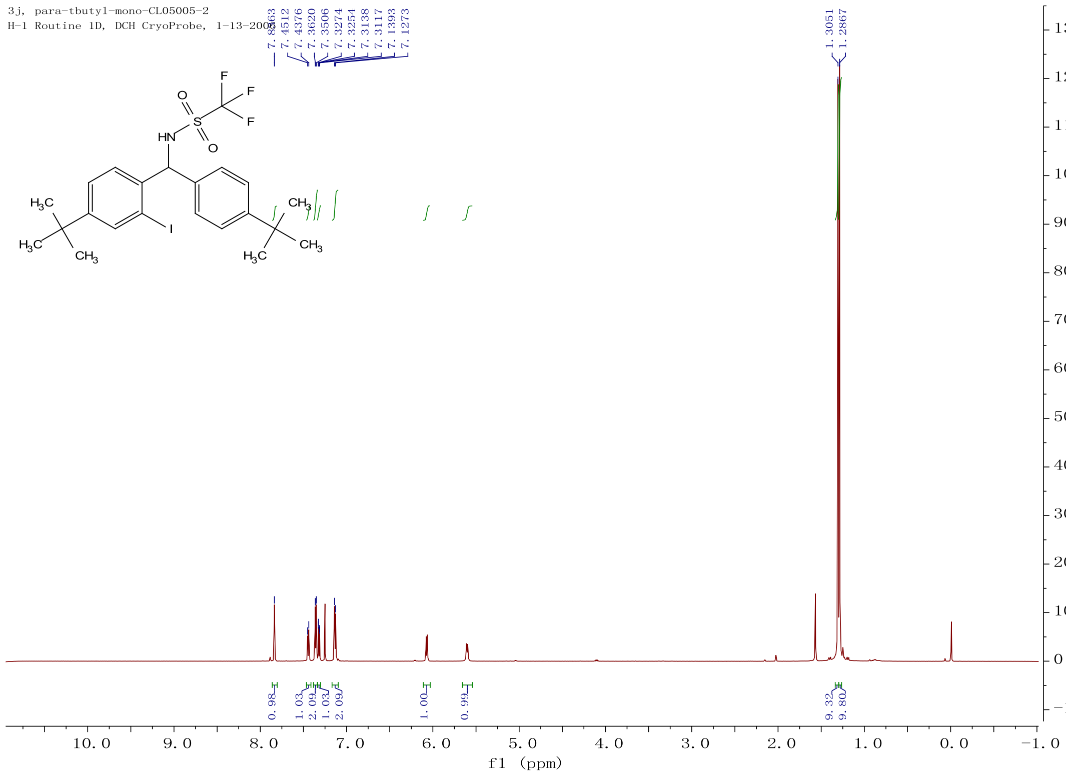

3i, para-methyl-di-CL05022-4
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
143.0940
141.9052
141.0668
138.4534
137.8758
133.4093
129.6129
126.1162
122.4565
120.3286
118.2002
116.0717
103.3207
94.5617
77.2116 CDCl3
77.0001 CDCl3
76.7882 CDCl3
67.9163
21.0758
19.7304
f1 (ppm)

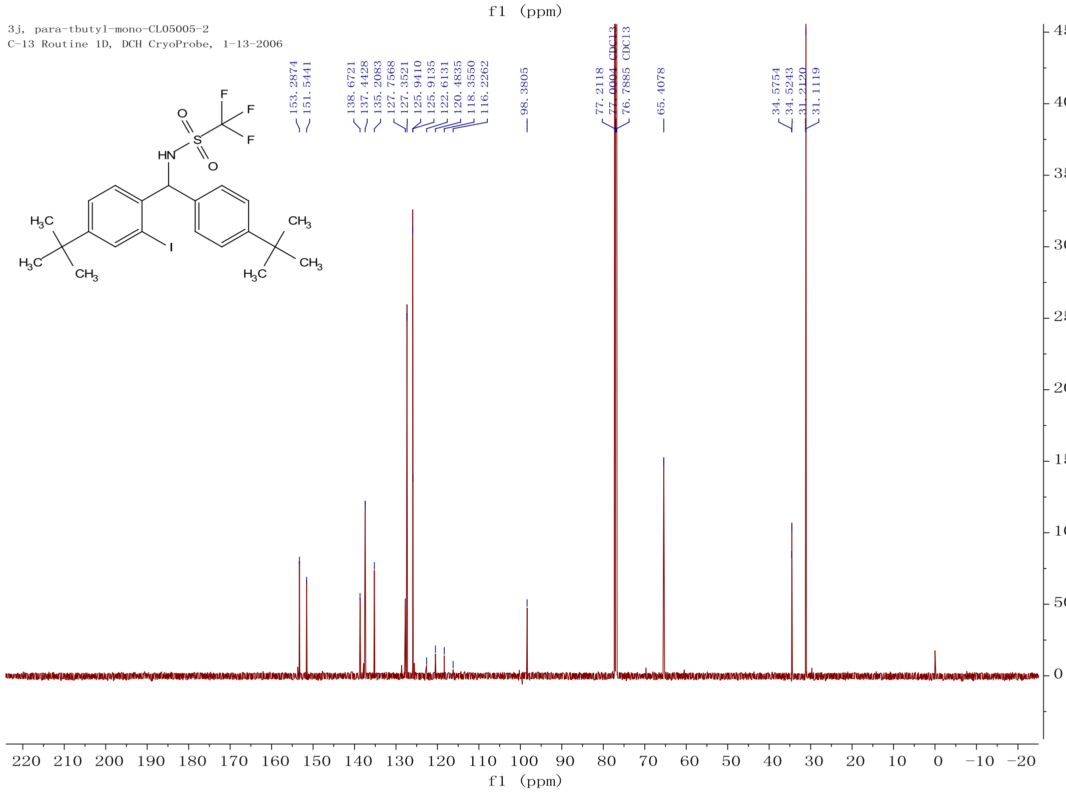

3k, para-methoxy-mono-CL05023-2
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

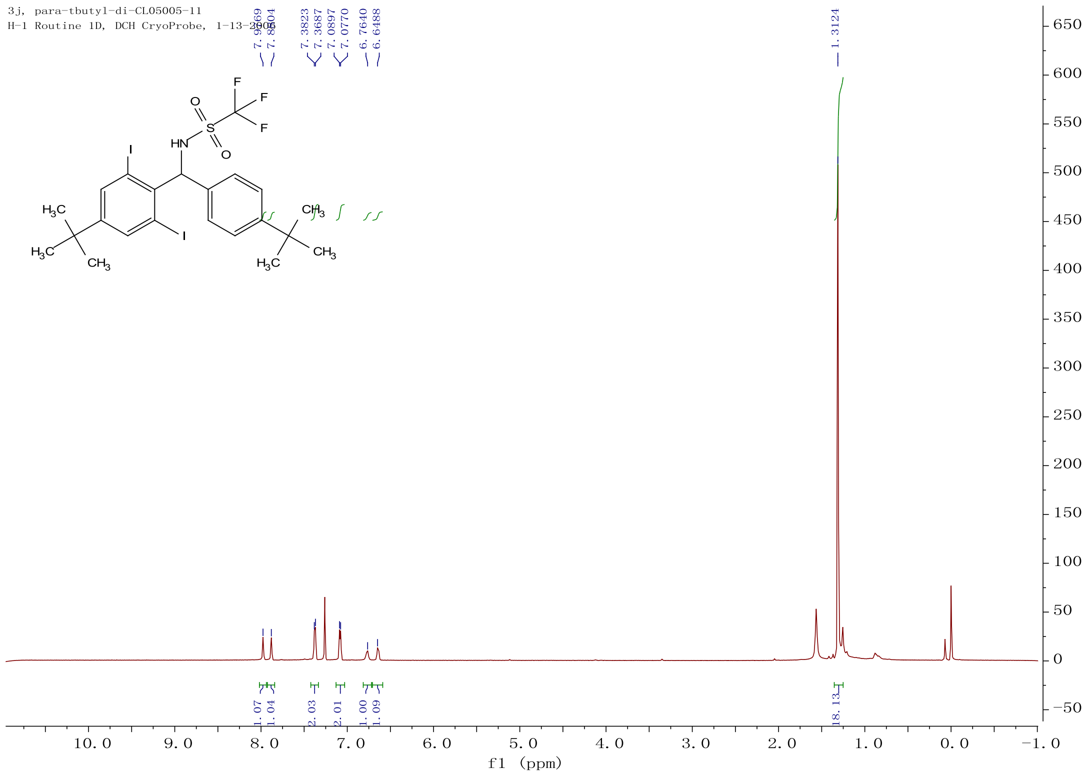

3k, para-methoxy-mono-CL05023-2
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)


3k, para-methoxy-di-CL05023-3
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.5394
7.5082
7.0744
7.0601
6.8938
6.8792
6.6907
6.6737
6.5912
6.5743
3.8191
3.8099
1.00
1.04
2.13
2.13
1.04
1.03
2.99
3.18
f1 (ppm)

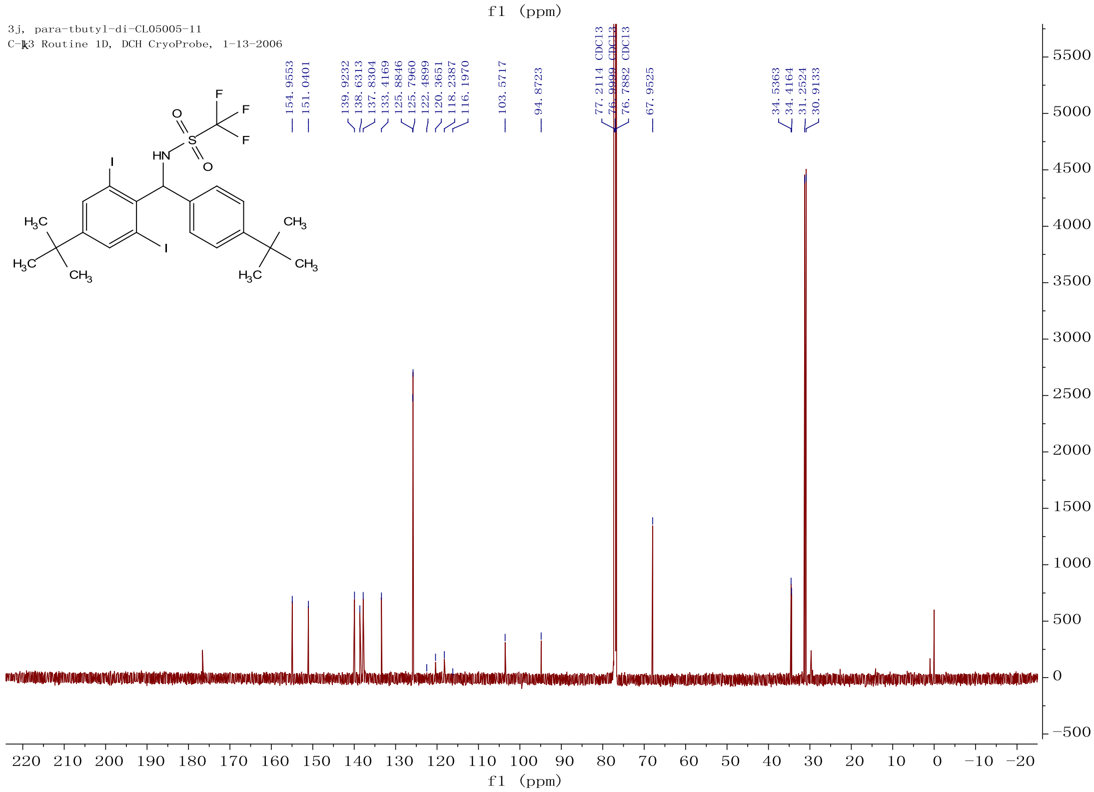

3k, para-methoxy-di-CL05023-3
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
159.3004
159.2038
133.4201
128.6375
128.5297
127.5304
125.6196
122.4651
120.3362
118.2077
116.0811
114.2378
102.9397
94.0783
77.2117
76.9999 CDCl3
76.7881 CDCl3
67.4894
55.7900
55.2942
f1 (ppm)


3j, para-tbutyl-mono-CL05005-2
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.8563
7.4512
7.4376
7.3620
7.3506
7.3274
7.3254
7.3138
7.3117
7.1393
7.1273
1.3051
1.2867
0.98
1.03
2.09
1.03
2.09
1.00
0.99
9.32
9.80
f1 (ppm)

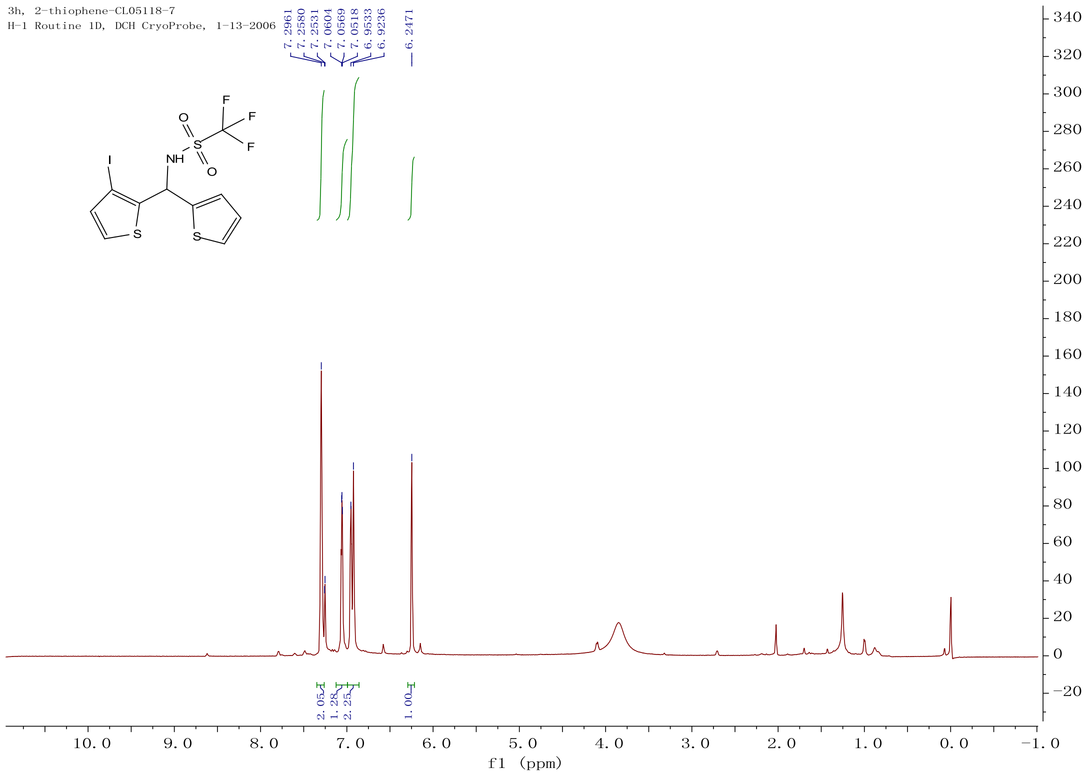

3j, para-tbutyl-mono-CL05005-2
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
153.2874
151.5441
138.6721
137.4428
135.2083
127.7568
127.3521
125.9410
125.9135
122.6131
120.4835
118.3550
116.2262
98.3805
77.2118
77.0004 CDCl3
76.7885 CDCl3
65.4078
34.5754
34.5243
31.2120
31.1119
f1 (ppm)

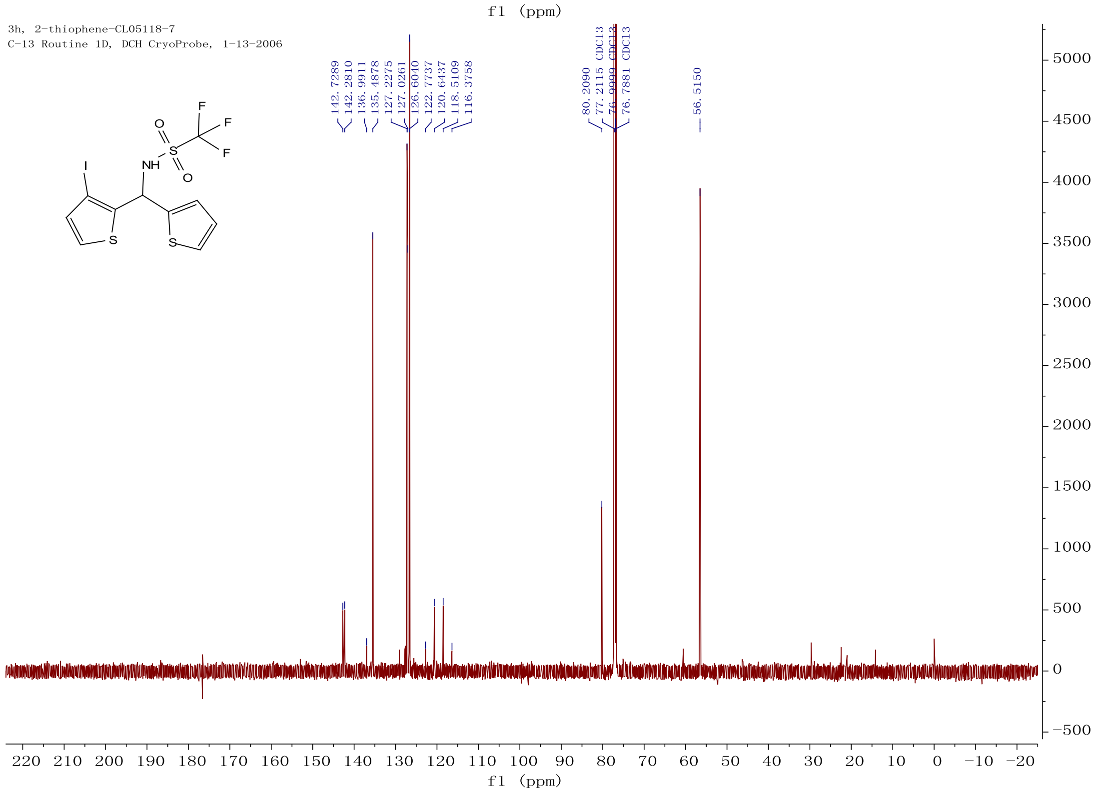


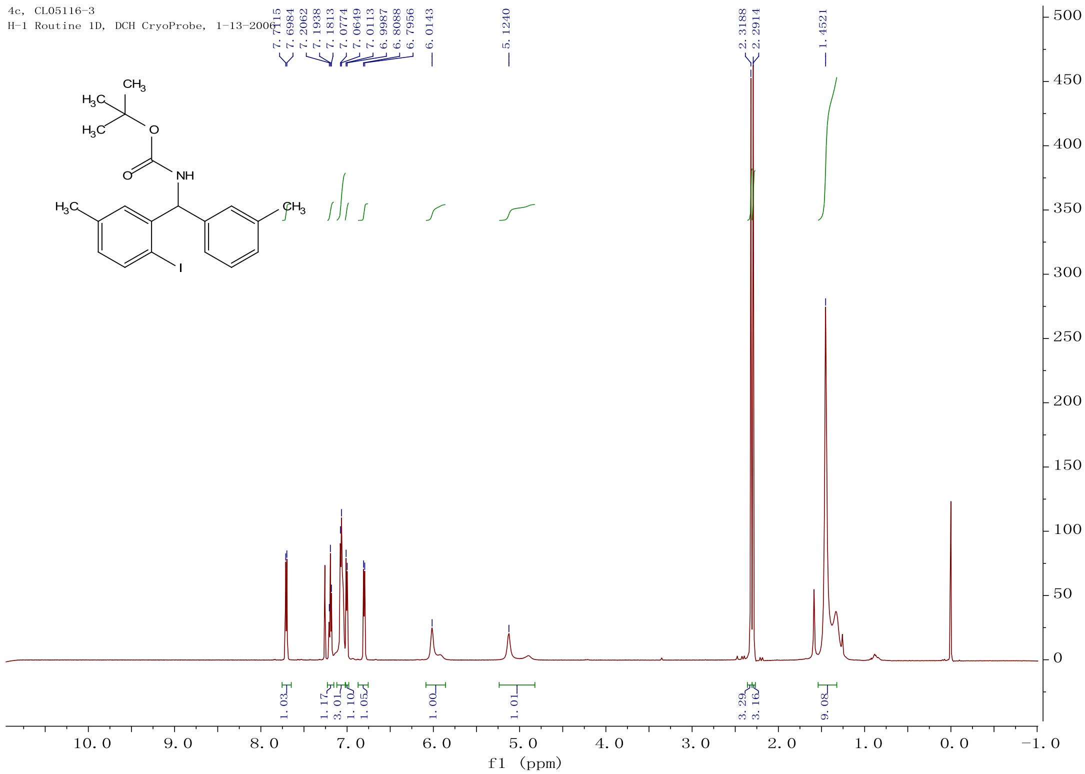
3j, para-tbutyl-di-CL05005-11
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.9569
7.8604
7.3823
7.3687
7.0897
7.0770
6.7640
6.6488
1.3124
1.07
1.04
2.03
2.01
1.00
1.09
18.13
f1 (ppm)

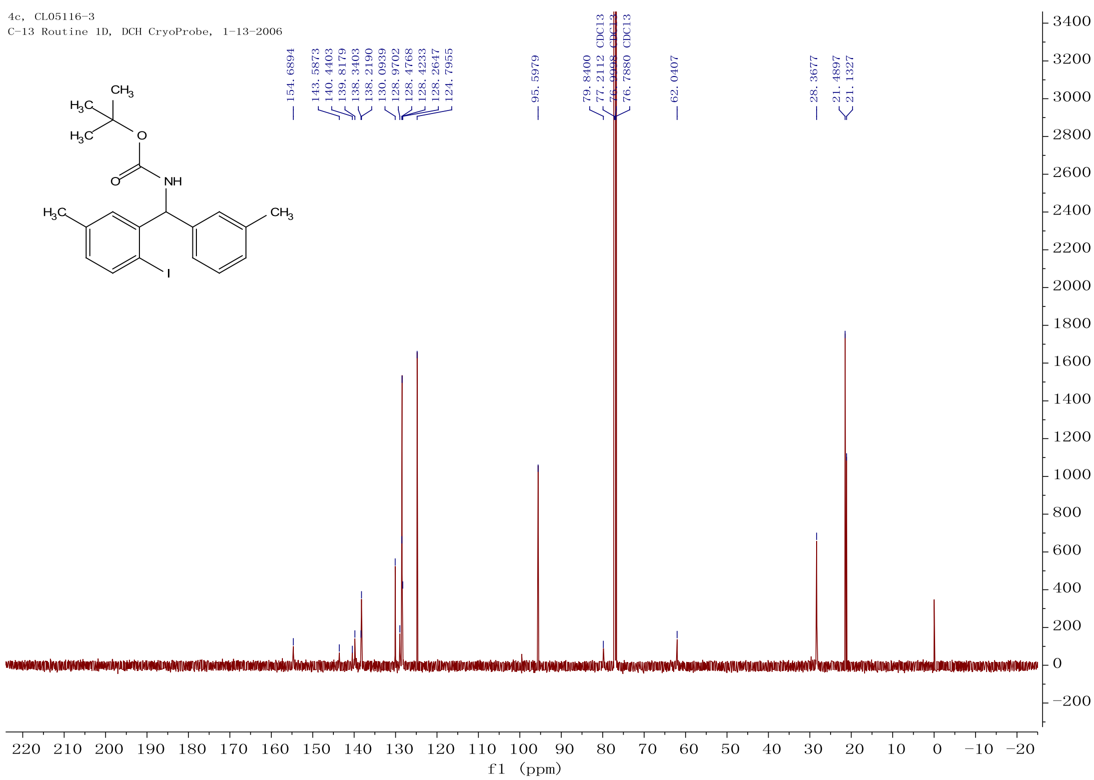


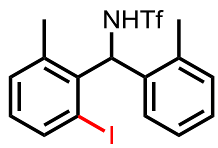
3j, para-tbutyl-di-CL05005-11
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
154.9553
151.0401
139.9232
138.6313
137.8304
133.4169
125.8846
125.7960
122.4899
120.3651
118.2387
116.1970
103.5717
94.8723
77.2114 CDCl3
76.9999 CDCl3
76.7882 CDCl3
67.9525
34.5363
34.4164
31.2524
30.9133
f1 (ppm)


3h, 2-thiophene-CL05118-7
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
7.2961
7.2580
7.2531
7.0604
7.0569
7.0518
6.9533
6.9236
6.2471
2.05
1.28
2.25
1.00
f1 (ppm)


3h, 2-thiophene-CL05118-7
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
142.7289
142.2810
136.9911
135.4878
127.2275
127.0261
126.6040
122.7737
120.6437
118.5109
116.3758
80.2090
77.2115 CDCl3
76.9999 CDCl3
76.7881 CDCl3
56.5150
f1 (ppm)


4c, CL05116-3
H-1 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)

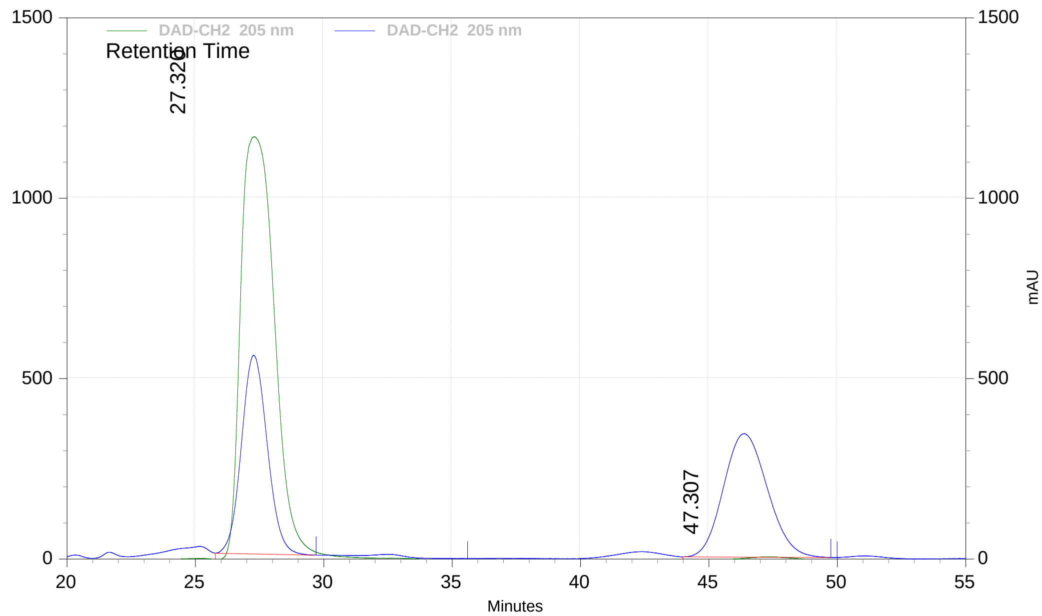

4c, CL05116-3
C-13 Routine 1D, DCH CryoProbe, 1-13-2006
f1 (ppm)



2a

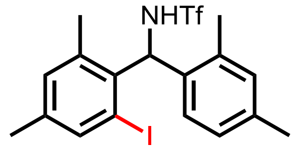
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL04132-1-ee-5%-0.3mL-90min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 2/17/2013 10:25:51 PM
Printed: 5/8/2013 5:09:10 PM



DAD-CH2 205 nm Results

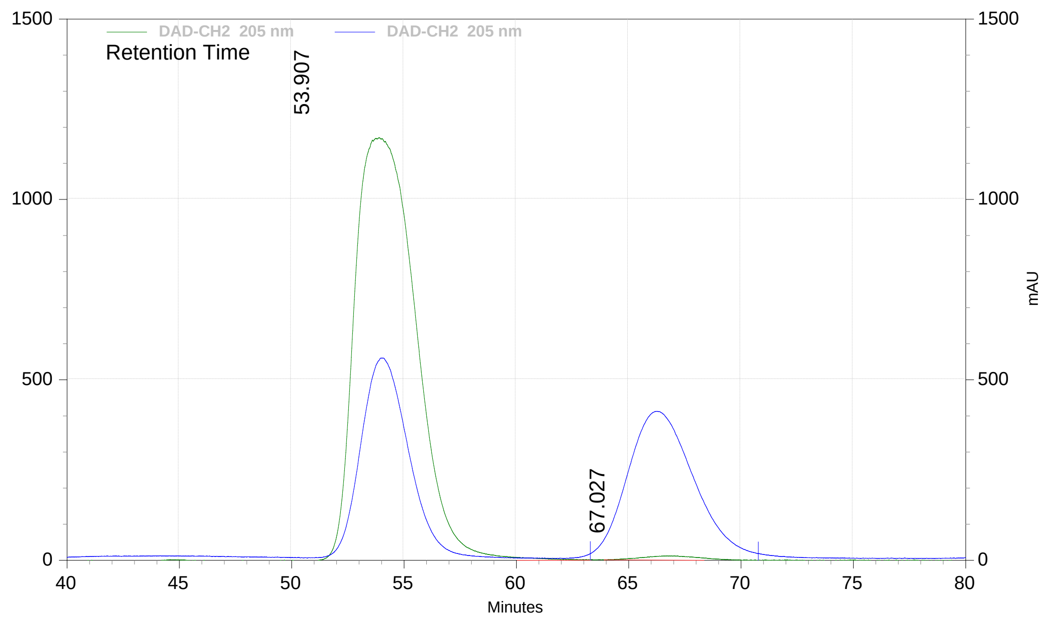
Retention Time	Area	Area %	Height	Height %
27.320	436407760	99.01	4688775	99.27
47.307	4350842	0.99	34605	0.73
Totals	440758602	100.00	4723380	100.00



2b

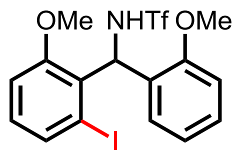
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL05060-1-ee-2%-0.2mL-120min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 4/3/2013 6:13:07 PM
Printed: 5/8/2013 5:22:29 PM



DAD-CH2 205 nm Results

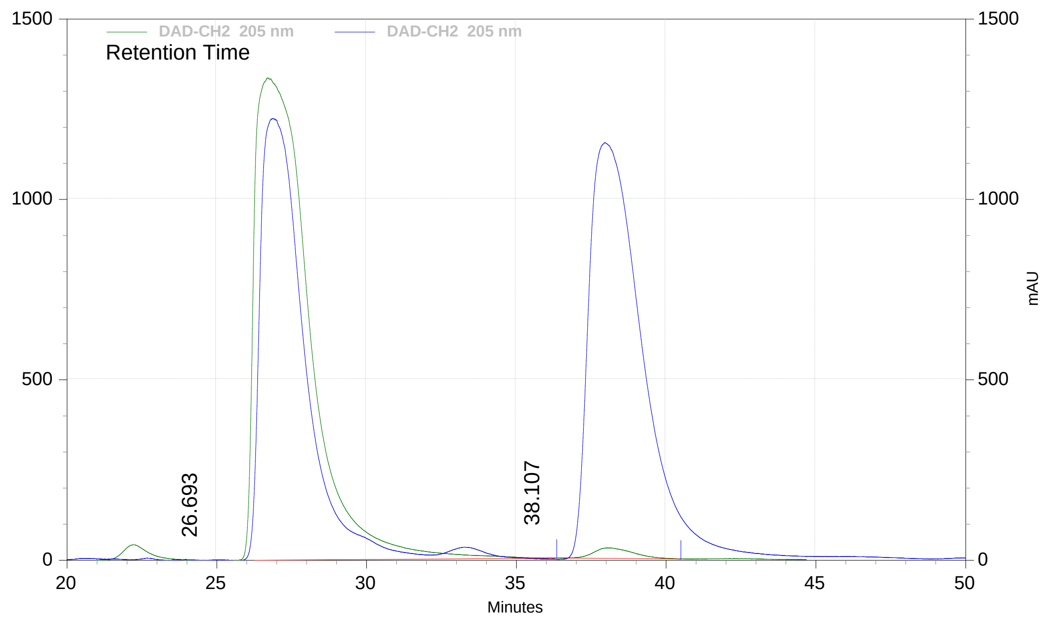
Retention Time	Area	Area %	Height	Height %
53.907	879891408	99.01	4688253	99.00
67.027	8785438	0.99	47558	1.00
Totals	888676846	100.00	4735811	100.00



2c

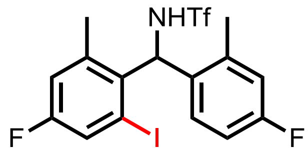
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL04142-3-ee-5%-0.3mL-60min-ODH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 2/22/2013 5:44:07 PM
Printed: 5/8/2013 5:25:09 PM



DAD-CH2 205 nm Results

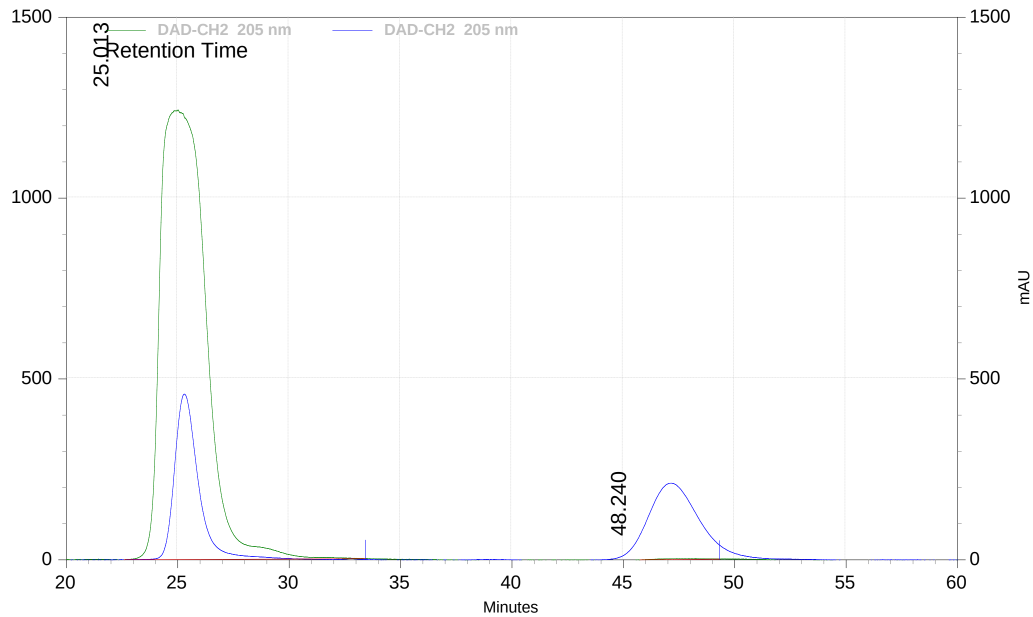
Retention Time	Area	Area %	Height	Height %
26.693	677980583	98.45	5346009	97.86
38.107	10695083	1.55	116885	2.14
Totals	688675666	100.00	5462894	100.00



2d

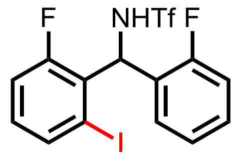
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL05025-1-ee-5%-0.3mL-75min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 3/17/2013 5:29:10 AM
Printed: 5/8/2013 5:26:31 PM



DAD-CH2 205 nm Results

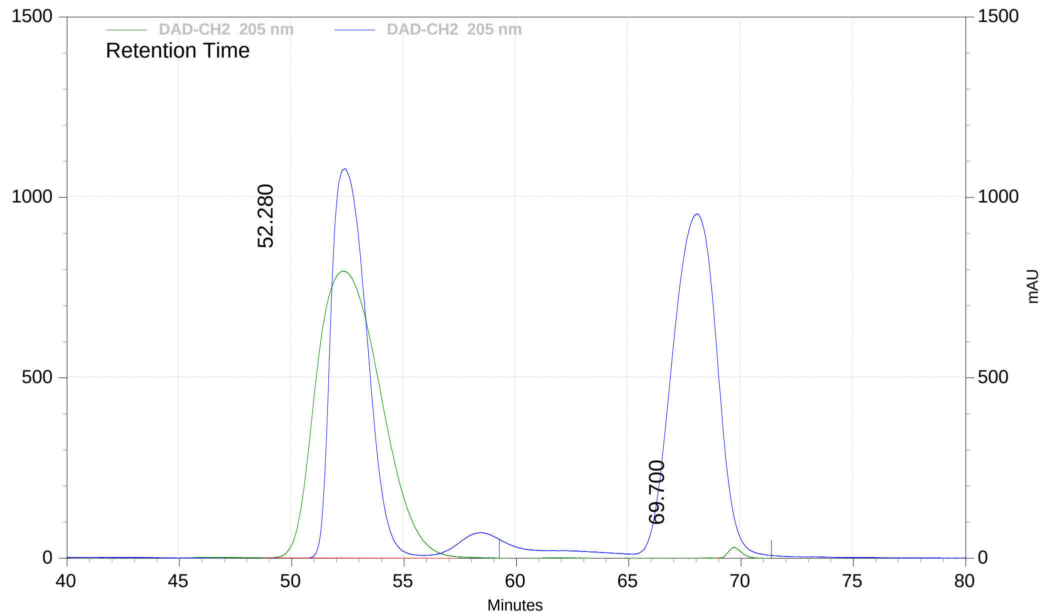
Retention Time	Area	Area %	Height	Height %
25.013	702486778	99.82	4972037	99.84
48.240	1249434	0.18	7924	0.16
Totals	703736212	100.00	4979961	100.00



2e

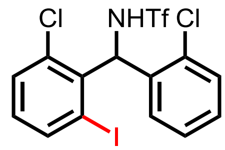
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL04150-1-ee-5%-0.3mL-90min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 3/8/2013 11:29:44 AM
Printed: 5/8/2013 4:59:02 PM



DAD-CH2 205 nm Results

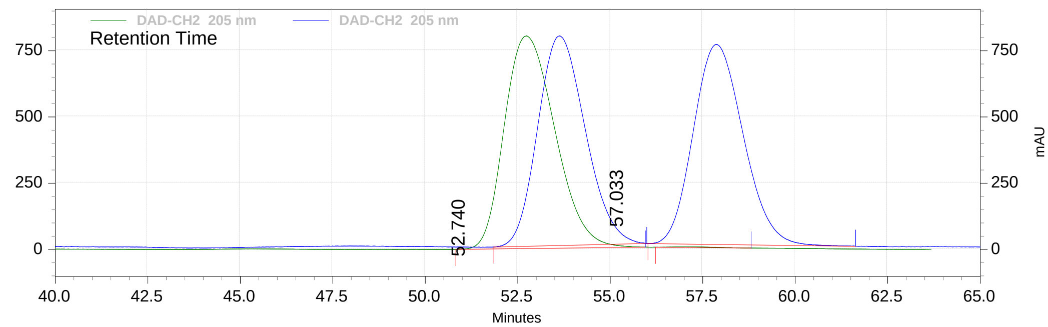
Retention Time	Area	Area %	Height	Height %
52.280	635341977	99.20	3180337	96.36
69.700	5152614	0.80	120226	3.64
Totals	640494591	100.00	3300563	100.00



2f

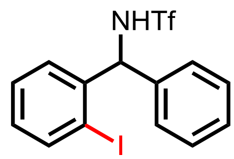
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\LingChu\CL06115-1-ee-5%-0.2mL-90min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\shutdown A.met
Acquired: 7/30/2013 4:10:43 PM
Printed: 8/20/2013 1:10:38 PM



DAD-CH2 205 nm Results

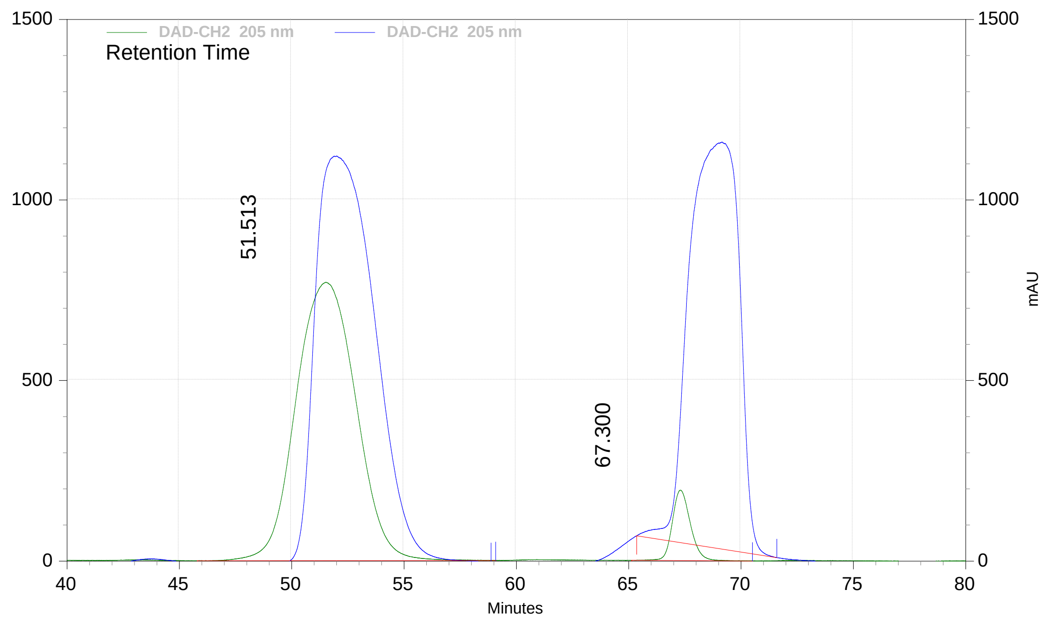
Retention Time	Area	Area %	Height	Height %
52.740	305631699	99.73	3212266	99.67
57.033	842743	0.27	10522	0.33
Totals	306474442	100.00	3222788	100.00



2g-mono

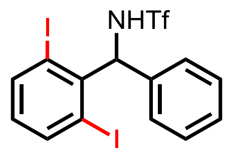
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL04131-1-ee-5%-0.3mL-90min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 2/18/2013 1:00:32 AM
Printed: 5/8/2013 5:10:48 PM



DAD-CH2 205 nm Results

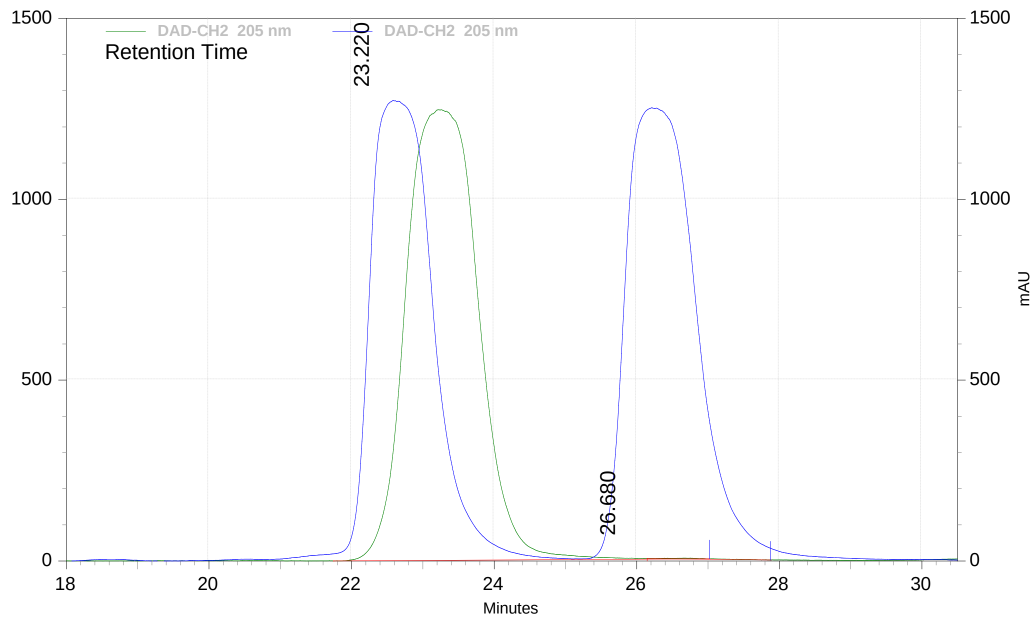
Retention Time	Area	Area %	Height	Height %
51.513	571009600	92.89	3084307	79.81
67.300	43704461	7.11	780281	20.19
Totals	614714061	100.00	3864588	100.00



2g-di

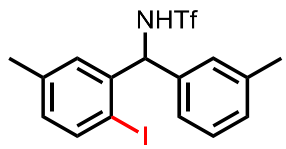
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL04131-2-ee-5%-0.3mL-60min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 3/8/2013 4:40:03 PM
Printed: 5/8/2013 5:02:27 PM



DAD-CH2 205 nm Results

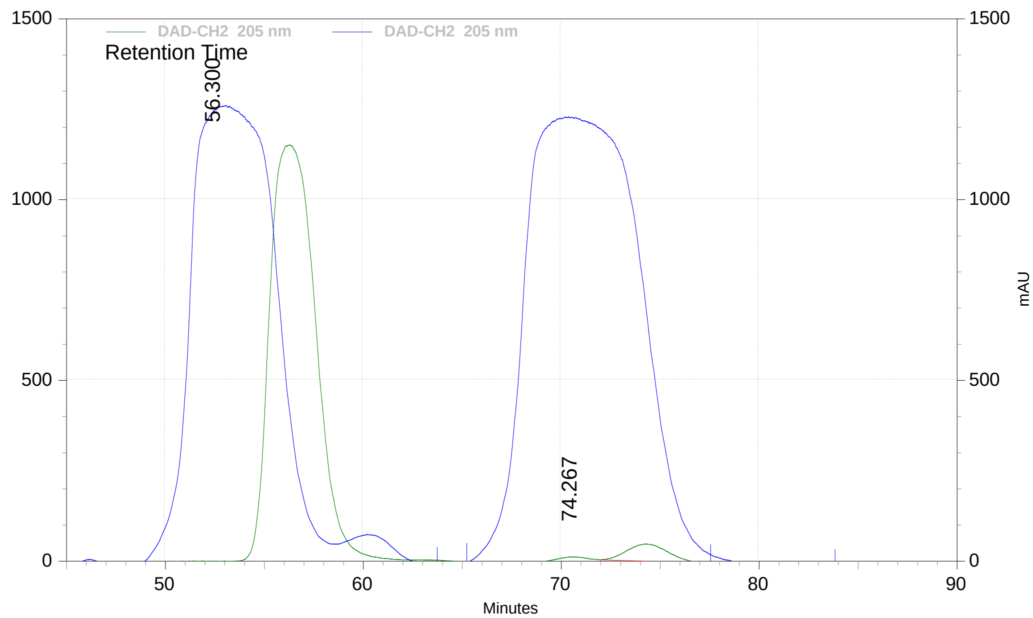
Retention Time	Area	Area %	Height	Height %
23.220	350283441	99.88	4983492	99.81
26.680	429389	0.12	9468	0.19
Totals	350714416	100.00	4992960	100.00



2h-mono

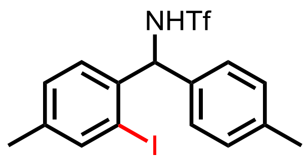
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL04130-1-ee-5%-0.2mL-90min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 2/18/2013 10:08:06 AM
Printed: 5/8/2013 4:54:01 PM



DAD-CH2 205 nm Results

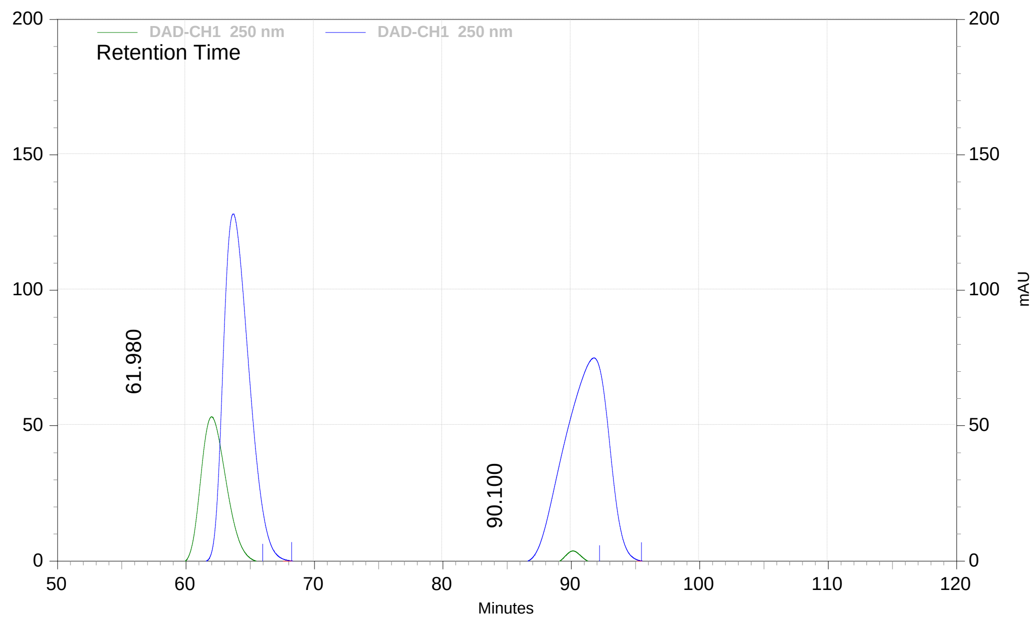
Retention Time	Area	Area %	Height	Height %
56.300	744451507	96.47	4608737	96.04
74.267	27259508	3.53	190269	3.96
Totals	771711015	100.00	4799006	100.00



2i-mono

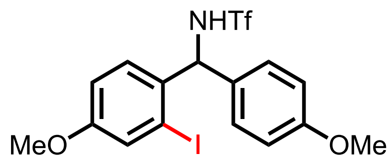
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL05022-3-ee-5%-0.2mL-120min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 4/1/2013 4:33:19 PM
Printed: 5/8/2013 5:36:35 PM



DAD-CH1 250 nm Results

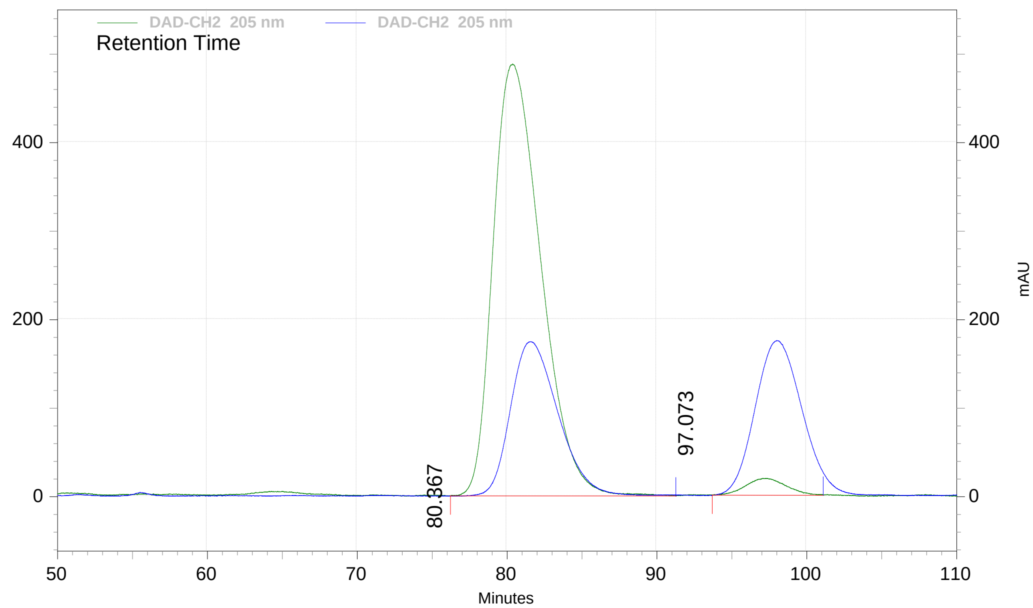
Retention Time	Area	Area %	Height	Height %
61.980	29851980	94.77	215138	92.10
90.100	1647949	5.23	18446	7.90
Totals	31499929	100.00	233584	100.00



2j-mono

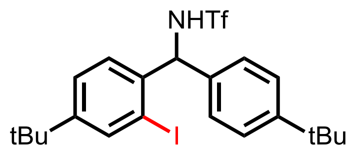
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL05023-1-ee-10%-0.3mL-120min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 3/18/2013 11:36:19 AM
Printed: 5/8/2013 5:45:35 PM



DAD-CH2 205 nm Results

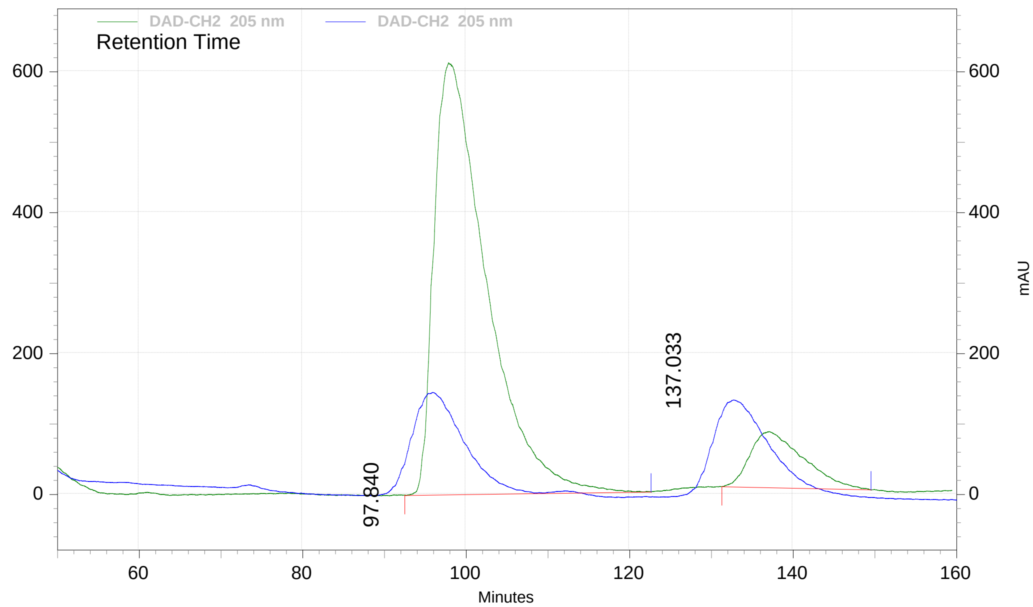
Retention Time	Area	Area %	Height	Height %
80.367	433033093	96.78	1951677	96.22
97.073	14386495	3.22	76675	3.78
Totals	447419588	100.00	2028352	100.00



2k-mono

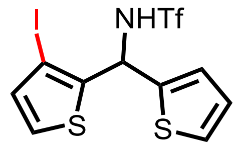
Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL05005-1-ee-2%-0.1mL-160min-ODH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 3/9/2013 1:35:31 PM
Printed: 5/8/2013 5:42:07 PM



DAD-CH2 205 nm Results

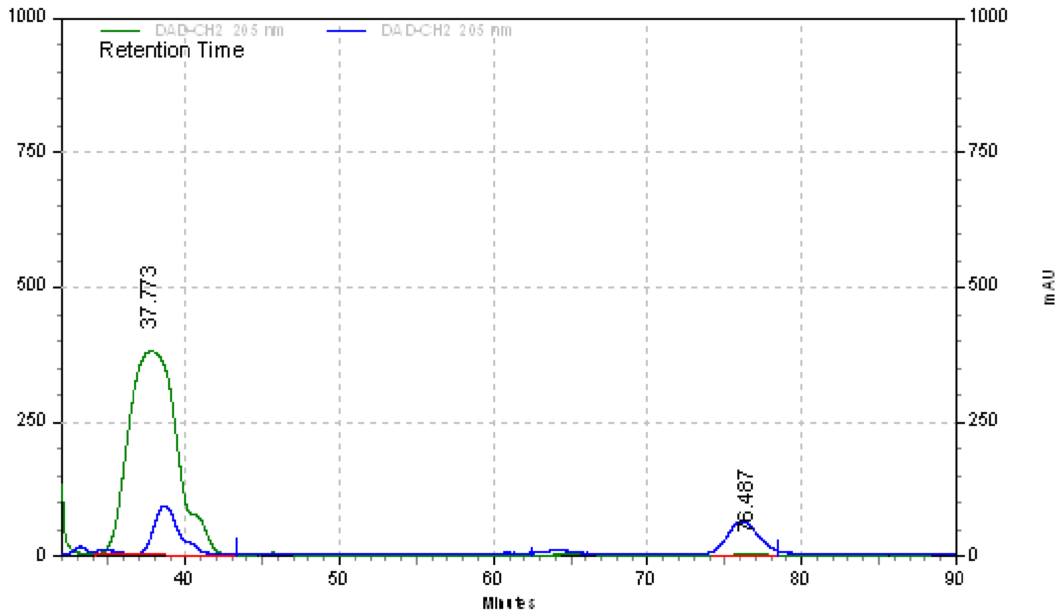
Retention Time	Area	Area %	Height	Height %
97.840	1090123095	88.25	2452601	88.49
137.033	145075078	11.75	319113	11.51
Totals	1235198173	100.00	2771714	100.00



2l

Area % Report

Data File: C:\Documents and Settings\Yu lab hplc\Desktop\LingChu-C–H iodination data\CL05118-1-ee-10%-0.3mL-120min-ASH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 4/25/2013 6:41:33 PM
Printed: 5/8/2013 5:33:51 PM



DAD-CH2 205 nm Results

Retention Time	Area	Area %	Height	Height %
37.773	331614321	99.31	1513931	98.81
76.487	2298226	0.69	16957	1.11
Totals	333913470	100.00	1532188	100.00

X-ray Crystallographic Data of 2a

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Mo K_α radiation (λ = 0.71073 Å). A 0.257 x 0.133 x 0.053 mm colorless block was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm and exposure time was 5 seconds per frame using a scan width of 0.6°. Data collection was 99.7% complete to 25.00° in θ. A total of 39833 reflections were collected covering the indices, -15<=h<=21, -17<=k<=14, -27<=l<=24. 18334 reflections were found to be symmetry independent, with a R_{int} of 0.0598. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2013. Crystallographic data are summarized in Table S5.

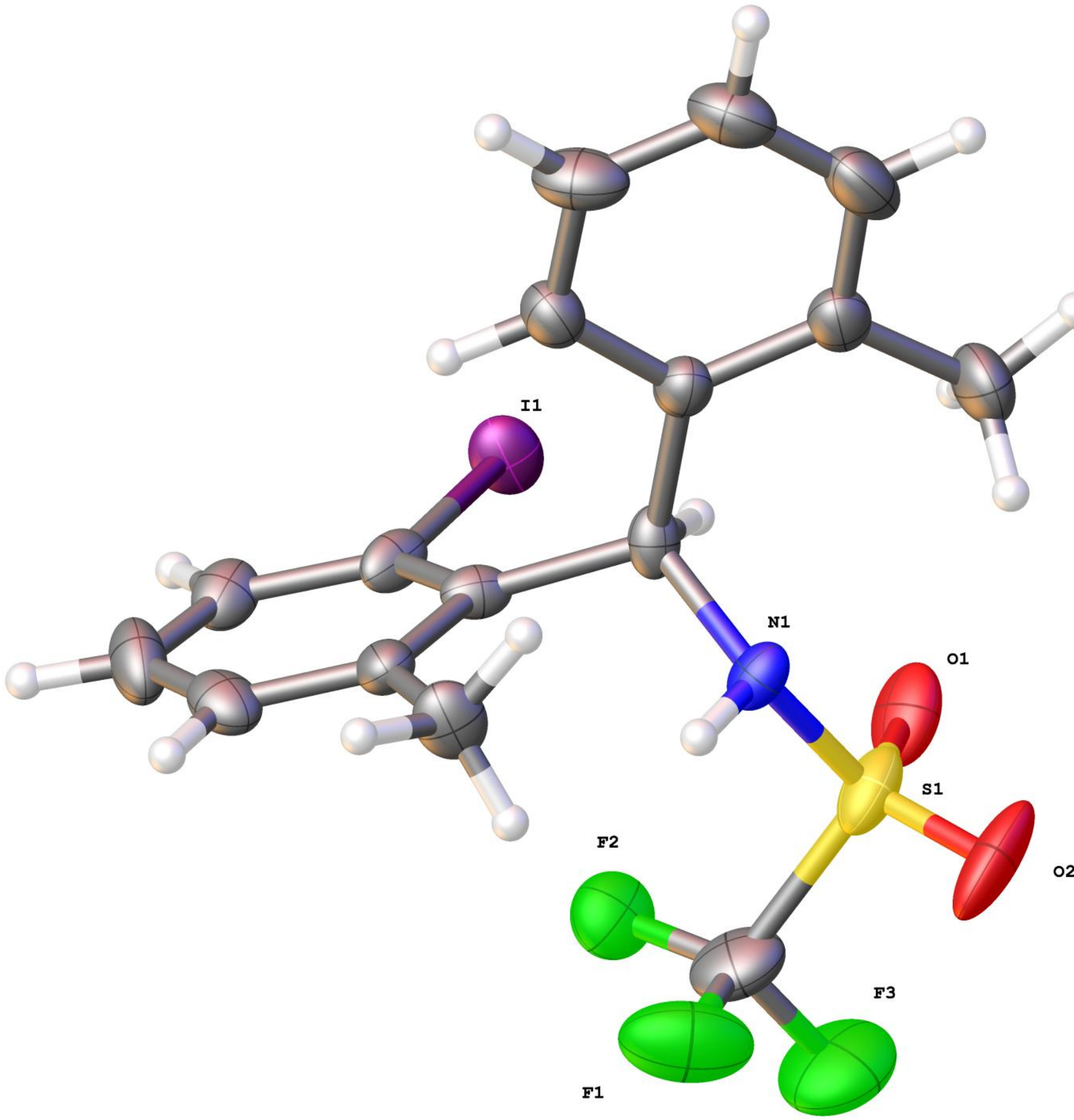

I1
N1
O1
S1
O2
F2
F3
F1

Table S5. Crystal data and structure refinement for Yu27.

Identification code	Yu27	
Empirical formula	C16 H15 F3 I N O2 S	
Molecular formula	C16 H15 F3 I N O2 S	
Formula weight	469.25	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 15.0973(9) Å	α= 90°.
	b = 12.2302(7) Å	β= 90.396(2)°.
	c = 18.9196(10) Å	γ = 90°.
Volume	3493.3(3) $Å^3$	
Z	8	
Density (calculated)	1.784 Mg/m^3	
Absorption coefficient	1.991 mm^{-1}	
F(000)	1840	
Crystal size	0.257 x 0.133 x 0.053 mm^3	
Crystal color, habit	Colorless Block	
Theta range for data collection	1.076 to 30.581°.	
Index ranges	-15<=h<=21, -17<=k<=14, -27<=l<=24	
Reflections collected	39833	
Independent reflections	18334 [R(int) = 0.0598]	
Completeness to theta = 25.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0474 and 0.0226	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18334 / 117 / 842	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0764, wR2 = 0.2088	
R indices (all data)	R1 = 0.1026, wR2 = 0.2247	
Absolute structure parameter	0.07(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.358 and -0.790 e.$Å^{-3}$	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Yu27. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	11438(1)	4771(1)	15269(1)	38(1)
S(1)	12333(2)	6412(3)	13060(2)	41(1)
F(1)	13188(6)	8144(9)	13484(6)	76(3)
F(2)	13149(5)	6875(7)	14254(4)	49(2)
F(3)	13997(6)	6706(11)	13308(6)	80(3)
O(1)	12426(6)	5291(9)	13258(5)	51(3)
O(2)	12452(7)	6781(12)	12348(5)	68(4)
N(1)	11428(5)	6907(7)	13340(5)	27(2)
C(1)	10919(7)	6450(9)	13941(5)	26(2)
C(2)	11094(6)	7048(9)	14631(6)	26(2)
C(3)	11295(6)	6472(10)	15245(5)	30(2)
C(4)	11404(7)	6981(11)	15909(6)	34(2)
C(5)	11319(8)	8075(12)	15968(7)	44(3)
C(6)	11153(7)	8695(11)	15325(7)	37(3)
C(7)	11039(7)	8192(9)	14693(5)	28(2)
C(8)	10885(11)	8963(11)	14108(8)	38(1)
C(9)	9936(7)	6354(9)	13720(6)	29(2)
C(10)	9285(8)	6920(10)	14097(6)	34(2)
C(11)	8401(8)	6882(12)	13875(8)	46(3)
C(12)	8172(8)	6272(11)	13311(8)	44(3)
C(13)	8808(9)	5677(12)	12945(7)	48(3)
C(14)	9698(7)	5707(10)	13144(6)	33(2)
C(15)	10343(9)	5034(12)	12738(8)	49(3)
C(16)	13218(8)	7091(14)	13581(9)	52(4)
I(1')	10869(9)	9204(9)	14028(7)	38(1)
I(1A)	13392(1)	9577(1)	15183(1)	39(1)
I(1AB)	13820(2)	13897(2)	14232(2)	49(1)
S(1A)	15030(2)	10973(2)	13205(2)	31(1)
F(1A)	15996(5)	12545(8)	13722(5)	61(2)
F(2A)	15678(5)	11280(8)	14475(4)	52(2)
F(3A)	16628(5)	10960(8)	13668(5)	60(2)

O(1A)	14919(5)	9857(7)	13380(4)	37(2)
O(2A)	15354(6)	11309(8)	12518(5)	45(2)
N(1A)	14154(5)	11634(8)	13374(5)	28(2)
C(1A)	13481(7)	11255(11)	13891(6)	37(2)
C(2A)	13741(13)	11891(14)	14599(6)	30(2)
C(3A)	13787(12)	11191(10)	15177(8)	38(2)
C(4A)	14063(11)	11586(12)	15832(7)	39(3)
C(5A)	14293(12)	12680(13)	15908(7)	47(4)
C(6A)	14247(11)	13380(11)	15330(9)	38(5)
C(7A)	13972(12)	12985(13)	14676(7)	44(2)
C(2AB)	13649(12)	11523(13)	14662(5)	30(2)
C(7AB)	13646(11)	10646(10)	15129(7)	38(2)
C(6AB)	13876(10)	10805(11)	15834(6)	39(3)
C(5AB)	14108(11)	11841(13)	16072(6)	38(2)
C(4AB)	14110(11)	12719(10)	15606(8)	47(4)
C(3AB)	13881(12)	12560(11)	14901(8)	44(2)
C(8A)	13630(40)	13820(40)	14170(30)	49(1)
C(8AB)	13390(20)	9310(30)	14945(19)	39(1)
C(9A)	12550(7)	11494(10)	13616(6)	32(2)
C(10A)	11963(8)	12092(12)	14012(6)	41(3)
C(11A)	11079(8)	12292(14)	13797(7)	46(3)
C(12A)	10822(8)	11814(11)	13161(7)	41(3)
C(13A)	11360(8)	11208(10)	12766(7)	40(3)
C(14A)	12251(8)	11050(10)	12981(6)	34(2)
C(15A)	12833(9)	10364(11)	12508(7)	44(3)
C(16A)	15895(8)	11463(13)	13824(8)	48(3)
I(1B)	11219(1)	10711(1)	9244(1)	52(1)
I(1BB)	11586(3)	15003(4)	10228(2)	42(1)
S(1B)	9929(2)	13637(2)	8256(2)	30(1)
F(1B)	8998(6)	12069(8)	8801(5)	65(3)
F(2B)	9353(5)	13342(9)	9536(4)	59(2)
F(3B)	8337(5)	13613(9)	8758(5)	64(3)
O(1B)	10029(5)	14761(8)	8427(4)	38(2)
O(2B)	9594(6)	13295(8)	7591(5)	45(2)
N(1B)	10823(6)	12995(7)	8420(5)	32(2)
C(1B)	11517(7)	13405(9)	8929(5)	28(2)

C(2B)	11351(7)	13129(8)	9690(4)	28(2)
C(7B)	11360(7)	13978(6)	10179(5)	38(2)
C(6B)	11168(7)	13769(8)	10883(4)	44(2)
C(5B)	10967(7)	12712(9)	11100(4)	44(2)
C(4B)	10959(7)	11864(7)	10611(5)	41(2)
C(3B)	11151(7)	12072(7)	9906(5)	41(2)
C(2BB)	11280(30)	12750(20)	9627(14)	28(2)
C(3BB)	11230(30)	13447(18)	10205(18)	38(2)
C(4BB)	10970(30)	13040(30)	10858(15)	44(2)
C(5BB)	10760(20)	11940(30)	10932(14)	44(2)
C(6BB)	10820(30)	11242(18)	10353(18)	41(2)
C(7BB)	11080(30)	11650(20)	9701(15)	41(2)
C(8B)	11641(18)	15164(13)	9994(13)	42(1)
C(8BB)	11030(60)	10820(30)	9090(20)	52(1)
C(9B)	12440(7)	13172(9)	8636(5)	29(2)
C(10B)	13054(7)	12600(12)	9028(7)	41(3)
C(11B)	13919(8)	12459(12)	8822(6)	40(3)
C(12B)	14171(7)	12839(13)	8166(7)	44(3)
C(13B)	13582(9)	13399(12)	7761(7)	49(3)
C(14B)	12696(8)	13576(9)	7966(6)	32(2)
C(15B)	12070(11)	14220(11)	7489(7)	51(4)
C(16B)	9088(8)	13108(12)	8883(7)	41(3)
I(1C)	16412(1)	14848(1)	9747(1)	45(1)
I(1CB)	15906(2)	10448(3)	10889(2)	53(1)
S(1C)	17393(2)	13098(3)	11933(2)	45(1)
F(1C)	18160(7)	11335(10)	11451(7)	87(4)
F(2C)	18144(5)	12674(8)	10726(5)	57(2)
F(3C)	19030(6)	12697(17)	11636(6)	114(6)
O(1C)	17509(7)	14180(10)	11756(5)	63(3)
O(2C)	17560(8)	12674(15)	12618(6)	92(5)
N(1C)	16461(6)	12680(9)	11646(5)	34(2)
C(1C)	15935(7)	13162(9)	11062(5)	32(2)
C(2C)	16104(8)	12529(7)	10351(4)	23(2)
C(7C)	16032(9)	11400(7)	10295(4)	28(2)
C(6C)	16138(8)	10894(6)	9644(5)	32(3)
C(5C)	16315(7)	11518(8)	9047(4)	35(3)

C(4C)	16387(7)	12648(8)	9102(4)	32(3)
C(3C)	16281(7)	13153(6)	9754(5)	28(2)
C(2CB)	16040(30)	12860(20)	10329(11)	23(2)
C(3CB)	16060(30)	11740(20)	10211(14)	28(2)
C(4CB)	16180(30)	11340(19)	9532(17)	32(3)
C(5CB)	16300(20)	12060(30)	8972(12)	35(3)
C(6CB)	16290(20)	13180(20)	9090(12)	32(3)
C(7CB)	16160(20)	13583(19)	9769(14)	28(2)
C(8C)	15906(2)	10448(3)	10889(2)	53(1)
C(8CB)	16412(1)	14848(1)	9747(1)	45(1)
C(9C)	14984(7)	13262(9)	11307(6)	30(2)
C(10C)	14313(7)	12702(10)	10961(6)	32(2)
C(11C)	13441(8)	12757(12)	11178(7)	43(3)
C(12C)	13234(9)	13405(12)	11744(7)	48(3)
C(13C)	13890(9)	13997(11)	12086(6)	43(3)
C(14C)	14761(8)	13929(10)	11869(6)	35(2)
C(15C)	15444(10)	14629(14)	12248(7)	57(4)
C(16C)	18235(9)	12427(16)	11410(9)	58(4)

Table S7. Bond lengths [Å] and angles [°] for Yu27.

I(1)-C(3)	2.092(13)	C(13)-H(13)	0.9500
S(1)-O(1)	1.427(11)	C(13)-C(14)	1.393(17)
S(1)-O(2)	1.432(10)	C(14)-C(15)	1.492(17)
S(1)-N(1)	1.589(8)	C(15)-H(15J)	0.9800
S(1)-C(16)	1.852(16)	C(15)-H(15K)	0.9800
F(1)-C(16)	1.302(18)	C(15)-H(15L)	0.9800
F(2)-C(16)	1.305(17)	I(1A)-C(3A)	2.063(13)
F(3)-C(16)	1.372(15)	I(1AB)-C(3AB)	2.069(11)
N(1)-H(1)	0.8603	S(1A)-O(1A)	1.415(9)
N(1)-C(1)	1.486(13)	S(1A)-O(2A)	1.450(9)
C(1)-H(1D)	1.0000	S(1A)-N(1A)	1.586(9)
C(1)-C(2)	1.519(15)	S(1A)-C(16A)	1.848(14)
C(1)-C(9)	1.543(15)	F(1A)-C(16A)	1.346(18)
C(2)-C(3)	1.389(14)	F(2A)-C(16A)	1.296(17)
C(2)-C(7)	1.407(15)	F(3A)-C(16A)	1.301(15)
C(3)-C(4)	1.411(16)	N(1A)-H(1A)	0.8599
C(4)-H(4)	0.9500	N(1A)-C(1A)	1.489(14)
C(4)-C(5)	1.348(19)	C(1A)-H(1AB)	1.0000
C(5)-H(5)	0.9500	C(1A)-H(1AA)	1.0000
C(5)-C(6)	1.45(2)	C(1A)-C(2A)	1.596(16)
C(6)-H(6)	0.9500	C(1A)-C(2AB)	1.514(16)
C(6)-C(7)	1.354(16)	C(1A)-C(9A)	1.524(16)
C(7)-C(8)	1.471(15)	C(2A)-C(3A)	1.3900
C(8)-H(8A)	0.9800	C(2A)-C(7A)	1.3900
C(8)-H(8B)	0.9800	C(3A)-C(4A)	1.3900
C(8)-H(8C)	0.9800	C(4A)-H(4A)	0.9500
C(9)-C(10)	1.401(15)	C(4A)-C(5A)	1.3900
C(9)-C(14)	1.392(16)	C(5A)-H(5A)	0.9500
C(10)-H(10)	0.9500	C(5A)-C(6A)	1.3900
C(10)-C(11)	1.397(17)	C(6A)-H(6A)	0.9500
C(11)-H(11)	0.9500	C(6A)-C(7A)	1.3900
C(11)-C(12)	1.35(2)	C(7A)-C(8A)	1.49(3)
C(12)-H(12)	0.9500	C(2AB)-C(7AB)	1.3900
C(12)-C(13)	1.39(2)	C(2AB)-C(3AB)	1.3900

C(7AB)-C(6AB)	1.3900	F(3B)-C(16B)	1.311(14)
C(7AB)-C(8AB)	1.71(4)	N(1B)-H(1B)	0.8599
C(6AB)-H(6AB)	0.9500	N(1B)-C(1B)	1.504(13)
C(6AB)-C(5AB)	1.3900	C(1B)-H(1BA)	1.0000
C(5AB)-H(5AB)	0.9500	C(1B)-H(1BB)	1.0000
C(5AB)-C(4AB)	1.3900	C(1B)-C(2B)	1.502(12)
C(4AB)-H(4AB)	0.9500	C(1B)-C(2BB)	1.59(3)
C(4AB)-C(3AB)	1.3900	C(1B)-C(9B)	1.530(14)
C(8A)-H(8AA)	0.9800	C(2B)-C(7B)	1.3900
C(8A)-H(8AB)	0.9800	C(2B)-C(3B)	1.3900
C(8A)-H(8AC)	0.9800	C(7B)-C(6B)	1.3900
C(8AB)-H(8AD)	0.9800	C(7B)-C(8B)	1.551(12)
C(8AB)-H(8AE)	0.9800	C(6B)-H(6B)	0.9500
C(8AB)-H(8AF)	0.9800	C(6B)-C(5B)	1.3900
C(9A)-C(10A)	1.376(16)	C(5B)-H(5B)	0.9500
C(9A)-C(14A)	1.391(16)	C(5B)-C(4B)	1.3900
C(10A)-H(10A)	0.9500	C(4B)-H(4B)	0.9500
C(10A)-C(11A)	1.414(17)	C(4B)-C(3B)	1.3900
C(11A)-H(11A)	0.9500	C(2BB)-C(3BB)	1.3900
C(11A)-C(12A)	1.391(18)	C(2BB)-C(7BB)	1.3900
C(12A)-H(12A)	0.9500	C(3BB)-C(4BB)	1.3900
C(12A)-C(13A)	1.332(19)	C(4BB)-H(4BB)	0.9500
C(13A)-H(13A)	0.9500	C(4BB)-C(5BB)	1.3900
C(13A)-C(14A)	1.416(17)	C(5BB)-H(5BB)	0.9500
C(14A)-C(15A)	1.513(17)	C(5BB)-C(6BB)	1.3900
C(15A)-H(15A)	0.9800	C(6BB)-H(6BB)	0.9500
C(15A)-H(15B)	0.9800	C(6BB)-C(7BB)	1.3900
C(15A)-H(15C)	0.9800	C(7BB)-C(8BB)	1.539(13)
I(1B)-C(3B)	2.086(7)	C(8B)-H(8BA)	0.9800
I(1BB)-C(3BB)	1.98(2)	C(8B)-H(8BB)	0.9800
S(1B)-O(1B)	1.421(10)	C(8B)-H(8BC)	0.9800
S(1B)-O(2B)	1.415(9)	C(8BB)-H(8BD)	0.9800
S(1B)-N(1B)	1.591(10)	C(8BB)-H(8BE)	0.9800
S(1B)-C(16B)	1.860(12)	C(8BB)-H(8BF)	0.9800
F(1B)-C(16B)	1.288(17)	C(9B)-C(10B)	1.374(16)
F(2B)-C(16B)	1.326(16)	C(9B)-C(14B)	1.417(14)

C(10B)-H(10B)	0.9500	C(4C)-C(3C)	1.3900
C(10B)-C(11B)	1.377(16)	C(2CB)-C(3CB)	1.3900
C(11B)-H(11B)	0.9500	C(2CB)-C(7CB)	1.3900
C(11B)-C(12B)	1.380(18)	C(3CB)-C(4CB)	1.3900
C(12B)-H(12B)	0.9500	C(4CB)-H(4CB)	0.9500
C(12B)-C(13B)	1.36(2)	C(4CB)-C(5CB)	1.3900
C(13B)-H(13B)	0.9500	C(5CB)-H(5CB)	0.9500
C(13B)-C(14B)	1.411(17)	C(5CB)-C(6CB)	1.3900
C(14B)-C(15B)	1.521(19)	C(6CB)-H(6CB)	0.9500
C(15B)-H(15D)	0.9800	C(6CB)-C(7CB)	1.3900
C(15B)-H(15E)	0.9800	C(9C)-C(10C)	1.384(16)
C(15B)-H(15F)	0.9800	C(9C)-C(14C)	1.382(16)
I(1C)-C(3C)	2.082(7)	C(10C)-H(10C)	0.9500
I(1CB)-C(3CB)	2.05(2)	C(10C)-C(11C)	1.383(16)
S(1C)-O(1C)	1.376(12)	C(11C)-H(11C)	0.9500
S(1C)-O(2C)	1.417(11)	C(11C)-C(12C)	1.370(19)
S(1C)-N(1C)	1.589(10)	C(12C)-H(12C)	0.9500
S(1C)-C(16C)	1.813(18)	C(12C)-C(13C)	1.38(2)
F(1C)-C(16C)	1.34(2)	C(13C)-H(13C)	0.9500
F(2C)-C(16C)	1.335(17)	C(13C)-C(14C)	1.382(17)
F(3C)-C(16C)	1.313(17)	C(14C)-C(15C)	1.52(2)
N(1C)-H(1C)	0.8598	C(15C)-H(15G)	0.9800
N(1C)-C(1C)	1.479(15)	C(15C)-H(15H)	0.9800
C(1C)-H(1CA)	1.0000	C(15C)-H(15I)	0.9800
C(1C)-H(1CB)	1.0000		
C(1C)-C(2C)	1.575(12)	O(1)-S(1)-O(2)	122.5(7)
C(1C)-C(2CB)	1.444(19)	O(1)-S(1)-N(1)	111.2(5)
C(1C)-C(9C)	1.517(16)	O(1)-S(1)-C(16)	102.8(7)
C(2C)-C(7C)	1.3900	O(2)-S(1)-N(1)	107.9(5)
C(2C)-C(3C)	1.3900	O(2)-S(1)-C(16)	105.3(8)
C(7C)-C(6C)	1.3900	N(1)-S(1)-C(16)	105.6(6)
C(6C)-H(6C)	0.9500	S(1)-N(1)-H(1)	108.3
C(6C)-C(5C)	1.3900	C(1)-N(1)-S(1)	124.3(7)
C(5C)-H(5C)	0.9500	C(1)-N(1)-H(1)	108.4
C(5C)-C(4C)	1.3900	N(1)-C(1)-H(1D)	106.3
C(4C)-H(4C)	0.9500	N(1)-C(1)-C(2)	112.9(9)

N(1)-C(1)-C(9)	108.9(8)	C(12)-C(11)-H(11)	120.1
C(2)-C(1)-H(1D)	106.3	C(11)-C(12)-H(12)	119.7
C(2)-C(1)-C(9)	115.5(8)	C(11)-C(12)-C(13)	120.5(12)
C(9)-C(1)-H(1D)	106.3	C(13)-C(12)-H(12)	119.7
C(3)-C(2)-C(1)	120.7(10)	C(12)-C(13)-H(13)	119.3
C(3)-C(2)-C(7)	116.6(10)	C(14)-C(13)-C(12)	121.3(12)
C(7)-C(2)-C(1)	122.7(9)	C(14)-C(13)-H(13)	119.3
C(2)-C(3)-I(1)	123.0(8)	C(9)-C(14)-C(13)	118.0(11)
C(2)-C(3)-C(4)	123.0(12)	C(9)-C(14)-C(15)	123.4(11)
C(4)-C(3)-I(1)	114.1(8)	C(13)-C(14)-C(15)	118.6(11)
C(3)-C(4)-H(4)	120.0	C(14)-C(15)-H(15J)	109.5
C(5)-C(4)-C(3)	120.1(12)	C(14)-C(15)-H(15K)	109.5
C(5)-C(4)-H(4)	120.0	C(14)-C(15)-H(15L)	109.5
C(4)-C(5)-H(5)	121.2	H(15J)-C(15)-H(15K)	109.5
C(4)-C(5)-C(6)	117.6(11)	H(15J)-C(15)-H(15L)	109.5
C(6)-C(5)-H(5)	121.2	H(15K)-C(15)-H(15L)	109.5
C(5)-C(6)-H(6)	119.3	F(1)-C(16)-S(1)	110.1(11)
C(7)-C(6)-C(5)	121.5(12)	F(1)-C(16)-F(2)	109.6(14)
C(7)-C(6)-H(6)	119.3	F(1)-C(16)-F(3)	108.4(13)
C(2)-C(7)-C(8)	125.8(11)	F(2)-C(16)-S(1)	111.6(10)
C(6)-C(7)-C(2)	121.2(11)	F(2)-C(16)-F(3)	111.9(12)
C(6)-C(7)-C(8)	113.0(11)	F(3)-C(16)-S(1)	105.2(11)
C(7)-C(8)-H(8A)	109.5	O(1A)-S(1A)-O(2A)	121.6(5)
C(7)-C(8)-H(8B)	109.5	O(1A)-S(1A)-N(1A)	110.1(5)
C(7)-C(8)-H(8C)	109.5	O(1A)-S(1A)-C(16A)	104.4(7)
H(8A)-C(8)-H(8B)	109.5	O(2A)-S(1A)-N(1A)	108.9(5)
H(8A)-C(8)-H(8C)	109.5	O(2A)-S(1A)-C(16A)	103.6(6)
H(8B)-C(8)-H(8C)	109.5	N(1A)-S(1A)-C(16A)	107.1(6)
C(10)-C(9)-C(1)	120.1(10)	S(1A)-N(1A)-H(1A)	109.7
C(14)-C(9)-C(1)	119.8(9)	C(1A)-N(1A)-S(1A)	123.2(8)
C(14)-C(9)-C(10)	120.1(10)	C(1A)-N(1A)-H(1A)	109.2
C(9)-C(10)-H(10)	119.9	N(1A)-C(1A)-H(1AB)	103.9
C(11)-C(10)-C(9)	120.1(12)	N(1A)-C(1A)-H(1AA)	109.4
C(11)-C(10)-H(10)	119.9	N(1A)-C(1A)-C(2A)	103.5(10)
C(10)-C(11)-H(11)	120.1	N(1A)-C(1A)-C(2AB)	117.0(11)
C(12)-C(11)-C(10)	119.8(13)	N(1A)-C(1A)-C(9A)	110.3(10)

C(2A)-C(1A)-H(1AA)	109.4	C(5AB)-C(4AB)-H(4AB)	120.0
C(2AB)-C(1A)-H(1AB)	103.9	C(5AB)-C(4AB)-C(3AB)	120.0
C(2AB)-C(1A)-C(9A)	115.8(11)	C(3AB)-C(4AB)-H(4AB)	120.0
C(9A)-C(1A)-H(1AB)	103.9	C(2AB)-C(3AB)-I(1AB)	120.8(9)
C(9A)-C(1A)-H(1AA)	109.4	C(4AB)-C(3AB)-I(1AB)	119.1(9)
C(9A)-C(1A)-C(2A)	114.5(11)	C(4AB)-C(3AB)-C(2AB)	120.0
C(3A)-C(2A)-C(1A)	111.8(11)	C(7A)-C(8A)-H(8AA)	109.5
C(3A)-C(2A)-C(7A)	120.0	C(7A)-C(8A)-H(8AB)	109.5
C(7A)-C(2A)-C(1A)	128.1(11)	C(7A)-C(8A)-H(8AC)	109.5
C(2A)-C(3A)-I(1A)	125.5(8)	H(8AA)-C(8A)-H(8AB)	109.5
C(2A)-C(3A)-C(4A)	120.0	H(8AA)-C(8A)-H(8AC)	109.5
C(4A)-C(3A)-I(1A)	114.3(8)	H(8AB)-C(8A)-H(8AC)	109.5
C(3A)-C(4A)-H(4A)	120.0	C(7AB)-C(8AB)-H(8AD)	109.5
C(5A)-C(4A)-C(3A)	120.0	C(7AB)-C(8AB)-H(8AE)	109.5
C(5A)-C(4A)-H(4A)	120.0	C(7AB)-C(8AB)-H(8AF)	109.5
C(4A)-C(5A)-H(5A)	120.0	H(8AD)-C(8AB)-H(8AE)	109.5
C(6A)-C(5A)-C(4A)	120.0	H(8AD)-C(8AB)-H(8AF)	109.5
C(6A)-C(5A)-H(5A)	120.0	H(8AE)-C(8AB)-H(8AF)	109.5
C(5A)-C(6A)-H(6A)	120.0	C(10A)-C(9A)-C(1A)	120.8(10)
C(5A)-C(6A)-C(7A)	120.0	C(10A)-C(9A)-C(14A)	118.1(11)
C(7A)-C(6A)-H(6A)	120.0	C(14A)-C(9A)-C(1A)	120.9(10)
C(2A)-C(7A)-C(8A)	120(3)	C(9A)-C(10A)-H(10A)	118.5
C(6A)-C(7A)-C(2A)	120.0	C(9A)-C(10A)-C(11A)	123.0(12)
C(6A)-C(7A)-C(8A)	116(3)	C(11A)-C(10A)-H(10A)	118.5
C(7AB)-C(2AB)-C(1A)	116.3(11)	C(10A)-C(11A)-H(11A)	122.1
C(7AB)-C(2AB)-C(3AB)	120.0	C(12A)-C(11A)-C(10A)	115.7(12)
C(3AB)-C(2AB)-C(1A)	123.4(11)	C(12A)-C(11A)-H(11A)	122.1
C(2AB)-C(7AB)-C(6AB)	120.0	C(11A)-C(12A)-H(12A)	118.3
C(2AB)-C(7AB)-C(8AB)	127.5(14)	C(13A)-C(12A)-C(11A)	123.4(12)
C(6AB)-C(7AB)-C(8AB)	112.5(14)	C(13A)-C(12A)-H(12A)	118.3
C(7AB)-C(6AB)-H(6AB)	120.0	C(12A)-C(13A)-H(13A)	120.1
C(7AB)-C(6AB)-C(5AB)	120.0	C(12A)-C(13A)-C(14A)	119.8(11)
C(5AB)-C(6AB)-H(6AB)	120.0	C(14A)-C(13A)-H(13A)	120.1
C(6AB)-C(5AB)-H(5AB)	120.0	C(9A)-C(14A)-C(13A)	119.8(11)
C(4AB)-C(5AB)-C(6AB)	120.0	C(9A)-C(14A)-C(15A)	122.7(11)
C(4AB)-C(5AB)-H(5AB)	120.0	C(13A)-C(14A)-C(15A)	117.5(11)

C(14A)-C(15A)-H(15A)	109.5	C(2B)-C(7B)-C(8B)	123.3(11)
C(14A)-C(15A)-H(15B)	109.5	C(6B)-C(7B)-C(8B)	116.5(11)
C(14A)-C(15A)-H(15C)	109.5	C(7B)-C(6B)-H(6B)	120.0
H(15A)-C(15A)-H(15B)	109.5	C(7B)-C(6B)-C(5B)	120.0
H(15A)-C(15A)-H(15C)	109.5	C(5B)-C(6B)-H(6B)	120.0
H(15B)-C(15A)-H(15C)	109.5	C(6B)-C(5B)-H(5B)	120.0
F(1A)-C(16A)-S(1A)	107.9(11)	C(4B)-C(5B)-C(6B)	120.0
F(2A)-C(16A)-S(1A)	111.3(9)	C(4B)-C(5B)-H(5B)	120.0
F(2A)-C(16A)-F(1A)	109.6(12)	C(5B)-C(4B)-H(4B)	120.0
F(2A)-C(16A)-F(3A)	110.9(13)	C(3B)-C(4B)-C(5B)	120.0
F(3A)-C(16A)-S(1A)	107.5(10)	C(3B)-C(4B)-H(4B)	120.0
F(3A)-C(16A)-F(1A)	109.6(11)	C(2B)-C(3B)-I(1B)	123.6(5)
O(1B)-S(1B)-N(1B)	110.1(5)	C(4B)-C(3B)-I(1B)	116.2(5)
O(1B)-S(1B)-C(16B)	105.3(6)	C(4B)-C(3B)-C(2B)	120.0
O(2B)-S(1B)-O(1B)	121.7(5)	C(3BB)-C(2BB)-C(1B)	111.2(19)
O(2B)-S(1B)-N(1B)	109.0(5)	C(3BB)-C(2BB)-C(7BB)	120.0
O(2B)-S(1B)-C(16B)	102.9(6)	C(7BB)-C(2BB)-C(1B)	128.6(19)
N(1B)-S(1B)-C(16B)	106.6(5)	C(2BB)-C(3BB)-I(1BB)	126.0(18)
S(1B)-N(1B)-H(1B)	109.5	C(2BB)-C(3BB)-C(4BB)	120.0
C(1B)-N(1B)-S(1B)	123.2(7)	C(4BB)-C(3BB)-I(1BB)	113.8(18)
C(1B)-N(1B)-H(1B)	109.4	C(3BB)-C(4BB)-H(4BB)	120.0
N(1B)-C(1B)-H(1BA)	104.3	C(5BB)-C(4BB)-C(3BB)	120.0
N(1B)-C(1B)-H(1BB)	110.1	C(5BB)-C(4BB)-H(4BB)	120.0
N(1B)-C(1B)-C(2BB)	101.9(16)	C(4BB)-C(5BB)-H(5BB)	120.0
N(1B)-C(1B)-C(9B)	109.8(8)	C(4BB)-C(5BB)-C(6BB)	120.0
C(2B)-C(1B)-N(1B)	114.8(9)	C(6BB)-C(5BB)-H(5BB)	120.0
C(2B)-C(1B)-H(1BA)	104.3	C(5BB)-C(6BB)-H(6BB)	120.0
C(2B)-C(1B)-C(9B)	117.7(9)	C(7BB)-C(6BB)-C(5BB)	120.0
C(2BB)-C(1B)-H(1BB)	110.1	C(7BB)-C(6BB)-H(6BB)	120.0
C(9B)-C(1B)-H(1BA)	104.3	C(2BB)-C(7BB)-C(8BB)	125.0(11)
C(9B)-C(1B)-H(1BB)	110.1	C(6BB)-C(7BB)-C(2BB)	120.0
C(9B)-C(1B)-C(2BB)	114.6(18)	C(6BB)-C(7BB)-C(8BB)	114.7(13)
C(7B)-C(2B)-C(1B)	118.0(7)	C(7B)-C(8B)-H(8BA)	109.5
C(7B)-C(2B)-C(3B)	120.0	C(7B)-C(8B)-H(8BB)	109.5
C(3B)-C(2B)-C(1B)	121.9(7)	C(7B)-C(8B)-H(8BC)	109.5
C(2B)-C(7B)-C(6B)	120.0	H(8BA)-C(8B)-H(8BB)	109.5

H(8BA)-C(8B)-H(8BC)	109.5	F(3B)-C(16B)-S(1B)	108.3(9)
H(8BB)-C(8B)-H(8BC)	109.5	F(3B)-C(16B)-F(2B)	108.8(12)
C(7BB)-C(8BB)-H(8BD)	109.5	O(1C)-S(1C)-O(2C)	123.5(9)
C(7BB)-C(8BB)-H(8BE)	109.5	O(1C)-S(1C)-N(1C)	109.9(7)
C(7BB)-C(8BB)-H(8BF)	109.5	O(1C)-S(1C)-C(16C)	102.2(8)
H(8BD)-C(8BB)-H(8BE)	109.5	O(2C)-S(1C)-N(1C)	110.2(6)
H(8BD)-C(8BB)-H(8BF)	109.5	O(2C)-S(1C)-C(16C)	102.3(9)
H(8BE)-C(8BB)-H(8BF)	109.5	N(1C)-S(1C)-C(16C)	106.9(6)
C(10B)-C(9B)-C(1B)	120.7(9)	S(1C)-N(1C)-H(1C)	108.3
C(10B)-C(9B)-C(14B)	118.3(10)	C(1C)-N(1C)-S(1C)	126.6(8)
C(14B)-C(9B)-C(1B)	120.9(10)	C(1C)-N(1C)-H(1C)	107.8
C(9B)-C(10B)-H(10B)	118.4	N(1C)-C(1C)-H(1CA)	106.7
C(9B)-C(10B)-C(11B)	123.2(12)	N(1C)-C(1C)-H(1CB)	102.2
C(11B)-C(10B)-H(10B)	118.4	N(1C)-C(1C)-C(2C)	110.7(9)
C(10B)-C(11B)-H(11B)	120.7	N(1C)-C(1C)-C(9C)	108.0(8)
C(10B)-C(11B)-C(12B)	118.7(12)	C(2C)-C(1C)-H(1CA)	106.7
C(12B)-C(11B)-H(11B)	120.7	C(2CB)-C(1C)-N(1C)	123.5(18)
C(11B)-C(12B)-H(12B)	120.2	C(2CB)-C(1C)-H(1CB)	102.2
C(13B)-C(12B)-C(11B)	119.7(11)	C(2CB)-C(1C)-C(9C)	115.3(19)
C(13B)-C(12B)-H(12B)	120.2	C(9C)-C(1C)-H(1CA)	106.7
C(12B)-C(13B)-H(13B)	118.6	C(9C)-C(1C)-H(1CB)	102.2
C(12B)-C(13B)-C(14B)	122.8(12)	C(9C)-C(1C)-C(2C)	117.4(9)
C(14B)-C(13B)-H(13B)	118.6	C(7C)-C(2C)-C(1C)	122.7(7)
C(9B)-C(14B)-C(15B)	122.6(10)	C(7C)-C(2C)-C(3C)	120.0
C(13B)-C(14B)-C(9B)	117.2(11)	C(3C)-C(2C)-C(1C)	117.2(7)
C(13B)-C(14B)-C(15B)	120.2(11)	C(2C)-C(7C)-C(6C)	120.0
C(14B)-C(15B)-H(15D)	109.5	C(7C)-C(6C)-H(6C)	120.0
C(14B)-C(15B)-H(15E)	109.5	C(5C)-C(6C)-C(7C)	120.0
C(14B)-C(15B)-H(15F)	109.5	C(5C)-C(6C)-H(6C)	120.0
H(15D)-C(15B)-H(15E)	109.5	C(6C)-C(5C)-H(5C)	120.0
H(15D)-C(15B)-H(15F)	109.5	C(6C)-C(5C)-C(4C)	120.0
H(15E)-C(15B)-H(15F)	109.5	C(4C)-C(5C)-H(5C)	120.0
F(1B)-C(16B)-S(1B)	109.7(10)	C(5C)-C(4C)-H(4C)	120.0
F(1B)-C(16B)-F(2B)	110.9(11)	C(3C)-C(4C)-C(5C)	120.0
F(1B)-C(16B)-F(3B)	110.7(11)	C(3C)-C(4C)-H(4C)	120.0
F(2B)-C(16B)-S(1B)	108.5(8)	C(2C)-C(3C)-I(1C)	124.8(5)

C(4C)-C(3C)-I(1C)	115.2(5)
C(4C)-C(3C)-C(2C)	120.0
C(3CB)-C(2CB)-C(1C)	114(2)
C(3CB)-C(2CB)-C(7CB)	120.0
C(7CB)-C(2CB)-C(1C)	126(2)
C(2CB)-C(3CB)-I(1CB)	131.2(17)
C(4CB)-C(3CB)-I(1CB)	108.8(17)
C(4CB)-C(3CB)-C(2CB)	120.0
C(3CB)-C(4CB)-H(4CB)	120.0
C(3CB)-C(4CB)-C(5CB)	120.0
C(5CB)-C(4CB)-H(4CB)	120.0
C(4CB)-C(5CB)-H(5CB)	120.0
C(4CB)-C(5CB)-C(6CB)	120.0
C(6CB)-C(5CB)-H(5CB)	120.0
C(5CB)-C(6CB)-H(6CB)	120.0
C(7CB)-C(6CB)-C(5CB)	120.0
C(7CB)-C(6CB)-H(6CB)	120.0
C(6CB)-C(7CB)-C(2CB)	120.0
C(10C)-C(9C)-C(1C)	120.5(10)
C(14C)-C(9C)-C(1C)	121.2(10)
C(14C)-C(9C)-C(10C)	118.3(11)
C(9C)-C(10C)-H(10C)	119.0
C(11C)-C(10C)-C(9C)	122.1(11)
C(11C)-C(10C)-H(10C)	119.0
C(10C)-C(11C)-H(11C)	120.6
C(12C)-C(11C)-C(10C)	118.8(13)
C(12C)-C(11C)-H(11C)	120.6
C(11C)-C(12C)-H(12C)	120.0
C(11C)-C(12C)-C(13C)	120.1(12)
C(13C)-C(12C)-H(12C)	120.0
C(12C)-C(13C)-H(13C)	119.7
C(14C)-C(13C)-C(12C)	120.6(11)
C(14C)-C(13C)-H(13C)	119.7
C(9C)-C(14C)-C(15C)	121.8(11)
C(13C)-C(14C)-C(9C)	120.1(12)
C(13C)-C(14C)-C(15C)	118.1(11)
C(14C)-C(15C)-H(15G)	109.5
C(14C)-C(15C)-H(15H)	109.5
C(14C)-C(15C)-H(15I)	109.5
H(15G)-C(15C)-H(15H)	109.5
H(15G)-C(15C)-H(15I)	109.5
H(15H)-C(15C)-H(15I)	109.5
F(1C)-C(16C)-S(1C)	111.0(10)
F(2C)-C(16C)-S(1C)	111.1(11)
F(2C)-C(16C)-F(1C)	105.8(15)
F(3C)-C(16C)-S(1C)	110.5(14)
F(3C)-C(16C)-F(1C)	108.0(16)
F(3C)-C(16C)-F(2C)	110.3(12)

Table S8. Anisotropic displacement parameters ($Å^2$x 10^3) for Yu27. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	52(1)	27(1)	34(1)	8(1)	-4(1)	-1(1)
S(1)	36(1)	60(2)	27(1)	1(1)	7(1)	19(1)
F(1)	58(5)	63(6)	105(8)	38(6)	-15(5)	-13(5)
F(2)	47(4)	57(5)	42(4)	6(4)	-9(3)	6(4)
F(3)	35(4)	111(9)	94(8)	6(7)	4(4)	15(5)
O(1)	49(5)	65(7)	41(5)	-7(5)	4(4)	30(5)
O(2)	62(6)	113(11)	28(5)	14(6)	22(4)	41(7)
N(1)	29(4)	26(4)	27(4)	4(4)	7(3)	9(3)
C(1)	38(5)	22(5)	19(5)	1(4)	-2(4)	7(4)
C(2)	19(4)	30(5)	29(5)	9(4)	-4(4)	0(4)
C(3)	21(4)	49(7)	19(5)	9(4)	-4(3)	3(4)
C(4)	23(5)	50(7)	28(6)	2(5)	-4(4)	8(5)
C(5)	37(6)	57(8)	39(7)	-23(6)	-5(5)	10(6)
C(6)	23(5)	40(7)	48(7)	-9(6)	-5(4)	1(4)
C(7)	24(4)	33(5)	28(5)	-4(4)	5(4)	-3(4)
C(8)	52(1)	27(1)	34(1)	8(1)	-4(1)	-1(1)
C(9)	31(5)	27(5)	29(5)	-2(4)	4(4)	-2(4)
C(10)	37(6)	32(6)	33(6)	-4(5)	-2(4)	-4(4)
C(11)	27(5)	43(7)	69(9)	6(7)	-3(6)	-3(5)
C(12)	36(6)	37(7)	60(8)	0(6)	-7(6)	-9(5)
C(13)	59(8)	44(7)	43(7)	-6(6)	-6(6)	-21(6)
C(14)	40(5)	30(5)	29(5)	0(5)	4(4)	-7(5)
C(15)	53(7)	45(8)	48(7)	-22(6)	2(6)	-7(6)
C(16)	28(6)	62(9)	66(10)	4(8)	11(6)	7(6)
I(1')	52(1)	27(1)	34(1)	8(1)	-4(1)	-1(1)
I(1A)	44(1)	30(1)	44(1)	14(1)	1(1)	-8(1)
I(1AB)	48(2)	29(1)	69(1)	-15(1)	6(1)	2(1)
S(1A)	32(1)	30(1)	31(1)	-2(1)	13(1)	-1(1)
F(1A)	46(4)	49(5)	88(7)	-23(5)	3(4)	-13(4)
F(2A)	31(4)	82(6)	43(4)	-13(4)	-1(3)	8(4)
F(3A)	26(3)	78(6)	76(6)	-18(5)	13(3)	13(4)
O(1A)	37(4)	33(4)	41(4)	-2(4)	11(3)	5(4)
O(2A)	46(5)	46(5)	42(5)	-1(4)	22(4)	-2(4)

N(1A)	23(4)	31(5)	31(5)	-4(4)	6(3)	0(3)
C(1A)	33(5)	45(7)	33(5)	-4(5)	4(4)	1(5)
C(2A)	17(6)	46(6)	27(5)	-5(5)	11(5)	-1(7)
C(3A)	29(4)	54(5)	31(3)	-8(4)	-4(3)	5(5)
C(4A)	32(7)	56(8)	28(6)	-19(7)	-3(6)	14(8)
C(5A)	32(10)	58(8)	50(10)	-19(7)	-14(9)	10(8)
C(6A)	44(13)	35(13)	36(13)	5(10)	-9(10)	-10(10)
C(7A)	31(4)	67(5)	33(4)	-4(3)	3(3)	13(4)
C(2AB)	17(6)	46(6)	27(5)	-5(5)	11(5)	-1(7)
C(7AB)	29(4)	54(5)	31(3)	-8(4)	-4(3)	5(5)
C(6AB)	32(7)	56(8)	28(6)	-19(7)	-3(6)	14(8)
C(5AB)	29(4)	54(5)	31(3)	-8(4)	-4(3)	5(5)
C(4AB)	32(10)	58(8)	50(10)	-19(7)	-14(9)	10(8)
C(3AB)	31(4)	67(5)	33(4)	-4(3)	3(3)	13(4)
C(8A)	48(2)	29(1)	69(1)	-15(1)	6(1)	2(1)
C(8AB)	44(1)	30(1)	44(1)	14(1)	1(1)	-8(1)
C(9A)	26(5)	44(6)	26(5)	-2(5)	5(4)	-6(4)
C(10A)	36(6)	54(8)	32(6)	-12(6)	-5(5)	8(5)
C(11A)	34(6)	69(9)	34(7)	-4(6)	-12(5)	0(6)
C(12A)	31(6)	49(7)	43(7)	7(6)	-10(5)	3(5)
C(13A)	46(6)	38(7)	34(6)	11(5)	-19(5)	-12(5)
C(14A)	47(6)	28(5)	28(6)	-1(4)	-9(5)	-5(4)
C(15A)	50(7)	31(6)	50(8)	-14(5)	-11(6)	0(5)
C(16A)	29(6)	58(9)	57(9)	-17(7)	6(5)	-8(5)
I(1B)	56(1)	26(1)	74(1)	11(1)	-10(1)	3(1)
I(1BB)	47(2)	36(2)	44(3)	-5(2)	5(2)	-11(2)
S(1B)	32(1)	30(1)	30(1)	2(1)	-9(1)	-2(1)
F(1B)	60(5)	52(5)	83(7)	24(5)	4(5)	-20(4)
F(2B)	40(4)	92(7)	45(5)	17(5)	3(3)	9(4)
F(3B)	29(4)	95(7)	69(6)	22(5)	-4(4)	6(4)
O(1B)	41(4)	33(4)	39(4)	-4(4)	-10(3)	8(4)
O(2B)	46(5)	39(5)	49(5)	0(4)	-19(4)	0(4)
N(1B)	39(5)	19(4)	37(5)	1(4)	-12(4)	-7(3)
C(1B)	27(5)	36(5)	21(4)	0(4)	-3(4)	4(4)
C(2B)	19(5)	38(6)	27(5)	1(4)	1(4)	4(6)
C(7B)	29(4)	54(5)	31(3)	-8(4)	-4(3)	5(5)
C(6B)	31(4)	67(5)	33(4)	-4(3)	3(3)	13(4)
C(5B)	31(4)	67(5)	33(4)	-4(3)	3(3)	13(4)

C(4B)	33(5)	52(5)	38(5)	14(4)	4(4)	7(5)
C(3B)	33(5)	52(5)	38(5)	14(4)	4(4)	7(5)
C(2BB)	19(5)	38(6)	27(5)	1(4)	1(4)	4(6)
C(3BB)	29(4)	54(5)	31(3)	-8(4)	-4(3)	5(5)
C(4BB)	31(4)	67(5)	33(4)	-4(3)	3(3)	13(4)
C(5BB)	31(4)	67(5)	33(4)	-4(3)	3(3)	13(4)
C(6BB)	33(5)	52(5)	38(5)	14(4)	4(4)	7(5)
C(7BB)	33(5)	52(5)	38(5)	14(4)	4(4)	7(5)
C(8B)	47(2)	36(2)	44(3)	-5(2)	5(2)	-11(2)
C(8BB)	56(1)	26(1)	74(1)	11(1)	-10(1)	3(1)
C(9B)	29(5)	34(5)	24(5)	-2(4)	1(4)	-2(4)
C(10B)	32(6)	52(8)	38(7)	12(6)	2(5)	5(5)
C(11B)	31(5)	58(8)	31(6)	-7(6)	2(4)	1(5)
C(12B)	25(5)	64(9)	44(7)	-15(6)	13(5)	-5(5)
C(13B)	58(8)	54(8)	35(7)	-7(6)	21(6)	-14(6)
C(14B)	46(6)	26(5)	24(5)	1(4)	8(4)	-7(4)
C(15B)	85(10)	35(7)	33(7)	13(5)	12(6)	1(6)
C(16B)	26(5)	51(8)	45(7)	14(6)	-4(5)	-2(5)
I(1C)	66(1)	32(1)	39(1)	7(1)	7(1)	1(1)
I(1CB)	49(2)	53(2)	58(2)	2(1)	-8(1)	-2(1)
S(1C)	34(1)	72(2)	30(2)	4(2)	-7(1)	-22(1)
F(1C)	68(6)	79(8)	116(9)	35(7)	12(6)	43(6)
F(2C)	45(4)	68(6)	58(5)	13(4)	11(4)	-12(4)
F(3C)	33(5)	233(19)	75(7)	12(9)	-7(4)	-15(7)
O(1C)	63(6)	73(8)	52(6)	-14(6)	-1(5)	-42(6)
O(2C)	71(7)	165(15)	40(6)	40(8)	-29(5)	-64(9)
N(1C)	35(5)	40(5)	28(5)	-6(4)	-3(4)	-7(4)
C(1C)	41(6)	26(5)	29(5)	2(4)	-2(4)	-9(4)
C(2C)	15(4)	32(6)	22(5)	-3(4)	0(4)	3(6)
C(7C)	20(5)	27(6)	37(6)	-9(5)	0(4)	10(6)
C(6C)	29(5)	19(6)	49(6)	-12(5)	-7(5)	-4(6)
C(5C)	39(7)	35(7)	33(6)	-18(6)	13(5)	1(7)
C(4C)	35(6)	35(6)	27(5)	2(5)	-1(5)	-3(7)
C(3C)	27(6)	26(5)	30(5)	-4(5)	4(5)	7(6)
C(2CB)	15(4)	32(6)	22(5)	-3(4)	0(4)	3(6)
C(3CB)	20(5)	27(6)	37(6)	-9(5)	0(4)	10(6)
C(4CB)	29(5)	19(6)	49(6)	-12(5)	-7(5)	-4(6)
C(5CB)	39(7)	35(7)	33(6)	-18(6)	13(5)	1(7)

C(6CB)	35(6)	35(6)	27(5)	2(5)	-1(5)	-3(7)
C(7CB)	27(6)	26(5)	30(5)	-4(5)	4(5)	7(6)
C(8C)	49(2)	53(2)	58(2)	2(1)	-8(1)	-2(1)
C(8CB)	66(1)	32(1)	39(1)	7(1)	7(1)	1(1)
C(9C)	41(6)	23(5)	27(5)	4(4)	-3(4)	3(4)
C(10C)	33(5)	36(6)	28(5)	1(5)	3(4)	3(4)
C(11C)	34(6)	50(8)	44(7)	-1(6)	-2(5)	10(5)
C(12C)	43(7)	62(9)	38(7)	5(6)	9(5)	28(6)
C(13C)	57(7)	48(7)	24(5)	0(5)	-3(5)	32(6)
C(14C)	50(6)	32(6)	22(5)	3(4)	-3(4)	10(5)
C(15C)	74(9)	59(10)	37(7)	-2(7)	-4(6)	30(8)
C(16C)	37(7)	79(12)	57(9)	17(8)	-6(6)	-17(7)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Yu27.

	x	y	z	U(eq)
H(1)	11503	7595	13412	33
H(1D)	11137	5686	14011	32
H(4)	11537	6553	16315	41
H(5)	11366	8428	16414	53
H(6)	11123	9470	15349	45
H(8A)	11436	9062	13844	56
H(8B)	10693	9669	14299	56
H(8C)	10425	8673	13793	56
H(10)	9445	7329	14505	41
H(11)	7963	7286	14121	55
H(12)	7570	6247	13160	53
H(13)	8632	5242	12553	58
H(15J)	10754	5517	12489	73
H(15K)	10022	4581	12394	73
H(15L)	10675	4563	13064	73
H(1A)	14283	12307	13460	34
H(1AB)	13526	10439	13872	45
H(1AA)	13549	10450	13968	45
H(4A)	14094	11108	16227	47
H(5A)	14482	12950	16355	56
H(6A)	14405	14128	15382	46
H(6AB)	13874	10205	16153	47
H(5AB)	14265	11950	16554	46
H(4AB)	14269	13428	15769	56
H(8AA)	13090	13542	13939	73
H(8AB)	14078	13970	13811	73
H(8AC)	13490	14495	14425	73
H(8AD)	12752	9194	15019	59
H(8AE)	13727	8828	15258	59
H(8AF)	13533	9150	14452	59
H(10A)	12160	12383	14451	49
H(11A)	10686	12725	14069	55

H(12A)	10231	11926	12999	49
H(13A)	11146	10882	12342	47
H(15A)	13228	10843	12239	65
H(15B)	12462	9942	12180	65
H(15C)	13188	9863	12798	65
H(1B)	10705	12323	8514	38
H(1BA)	11462	14219	8907	33
H(1BB)	11441	14208	9008	33
H(6B)	11174	14350	11217	52
H(5B)	10836	12570	11581	52
H(4B)	10822	11141	10759	49
H(4BB)	10928	13517	11253	52
H(5BB)	10587	11661	11378	52
H(6BB)	10682	10489	10404	49
H(8BA)	12284	15235	10046	63
H(8BB)	11347	15676	10314	63
H(8BC)	11468	15328	9505	63
H(8BD)	11562	10369	9087	78
H(8BE)	10974	11213	8640	78
H(8BF)	10505	10351	9152	78
H(10B)	12872	12287	9463	49
H(11B)	14334	12106	9125	48
H(12B)	14754	12709	8000	53
H(13B)	13773	13685	7321	59
H(15D)	11703	13711	7214	76
H(15E)	12415	14678	7167	76
H(15F)	11688	14684	7779	76
H(1C)	16498	11988	11573	41
H(1CA)	16160	13923	10993	38
H(1CB)	16138	13940	11066	38
H(6C)	16089	10121	9606	39
H(5C)	16388	11172	8601	43
H(4C)	16508	13074	8695	39
H(4CB)	16193	10573	9451	39
H(5CB)	16390	11785	8508	43
H(6CB)	16370	13673	8708	39
H(8CA)	16405	10467	11222	80
H(8CB)	15884	9732	10657	80

H(8CC)	15353	10572	11144	80
H(8CD)	16164	15216	10161	68
H(8CE)	16168	15178	9316	68
H(8CF)	17058	14928	9751	68
H(10C)	14456	12266	10562	39
H(11C)	12993	12352	10939	51
H(12C)	12639	13448	11902	57
H(13C)	13741	14454	12473	51
H(15G)	15695	14220	12647	85
H(15H)	15161	15297	12422	85
H(15I)	15918	14824	11919	85