Chiral Pentanidium and Pyridinyl-Sulphonamide Ion Pair as Enantioselective Organocatalyst for Steglich rearrangement

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1. General information

General

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker AVIII 400 (400 MHz) spectrometer, JEOL JNM-ECA 400 (400 MHz) spectrometer or JEOL JNM-ECZL 500 (500MHz) spectrometer. The residual solvent peak was used as an internal reference. 2D NOESY and 2D ROESY spectra were obtained on a Bruker AVIII 400 (400MHz) spectrometer. Chemical shifts are recorded as δ in units of parts per million (ppm). High resolution mass spectra (HRMS) were obtained on the Q-Tof Premier mass spectrometer (Waters Corporation) and reported in units of mass of charge ratio (m/z). Enantiomeric excess values were determined by HPLC analysis on Shimadzu LC-20AT and LC-2010CHT HPLC workstations. Optical rotations were measured in DCM using a 1 mL cell with a 1 dm path length on a Jasco P-1030 polarimeter with a sodium lamp of wavelength 589 nm and reported as follows: $[\alpha]^{T}_{D}$ (c = g/100 mL, solvent). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Flash column chromatography were performed on Merck 60 (0.040-0.063mm) mesh silica gel. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Visualization was performed using a UV lamp.

Materials

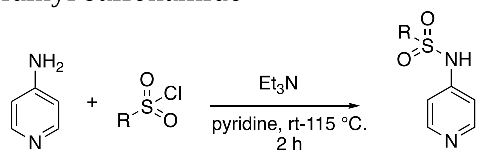
THF were distilled over sodium/benzophenone under N_2 atmosphere. Toluene, acetonitrile and dichloromethane were distilled over CaH_2 under N_2 atmosphere. Other reagents and solvents were commercial grade and were used as supplied without further purification, unless otherwise stated. Experiments involving moisture and/or air sensitive components were performed under a positive pressure of nitrogen in oven-dried glassware equipped with a rubber septum inlet. All compounds synthesized were stored in 4 °C fridge or –20 °C freezer.

2. Preparation of chiral guanidinium salt

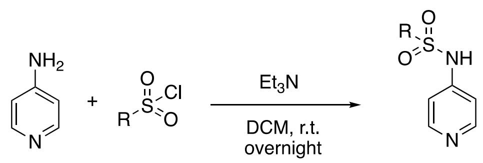
All pentanidium chloride (**1a-Cl - 1c-Cl**) were synthesized following reported procedures.[1] All synthesized chiral pentanidium chloride are used for ion-pair formation directly.

3. Preparation and characterization of neutral pyridinyl sulfonamide

a. Preparation of neutral pyridinyl sulfonamide

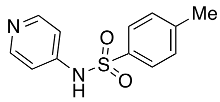


Method A: The synthesis of **H-2a** and **H-2e** were synthesized by this method.[2] Sulfonyl chloride (10 mmol, 1 equiv.) was added into the solution of 4-aminopyridine (10 mmol, 1 equiv.) in 10 mL pyridine. The mixture was stirred at room temperature for 10 min. Then Et_3N (30 mmol, 3 equiv.) was added and reflux for 2 h. The mixture was cooled down to evaporate solvent in vacuum. The solid residue was washed with boiling water and boiling acetone to afford neutral pyridinyl sulfonamide product.

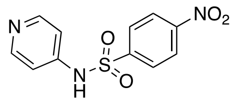


Method B: All neutral catalysts except **H-2a** and **H-2e** were synthesized by this method. 4-aminopyridine (10 mmol, 1 equiv.) and Et_3N (15 mmol, 1.5 equiv.) was dissolved in distilled DCM, then sulfonyl chloride (15 mmol, 1.5 equiv.) was added slowly under 0 °C and stirred at room temperature overnight. Solvent was evaporated after reaction finished. The solid was collected and dried after washing with cold water and cold acetone.

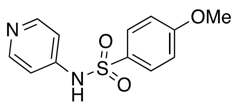
b. Characterization of neutral pyridinyl sulfonamide



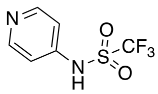
4-methyl-N-(pyridin-4-yl)benzenesulfonamide (H-2a): white solid; ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.01 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 7.9 Hz, 1H), 6.91 (d, J = 6.5 Hz, 1H), 2.33 (s, 2H); ^{13}C NMR (101 MHz, DMSO-*d6*): δ 129.3, 126.2, 114.0, 87.8, 74.5, 20.9; HRMS (ESI) calcd for $C_{12}H_{13}N_2O_2S$ *m/z* $[M+H]^+$: 249.0692; found: 249.069.



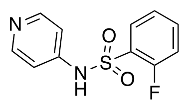
4-nitro-N-(pyridin-4-yl)benzenesulfonamide (H-2b): pale yellow solid; ^{1}H NMR (396 MHz, DMSO-*d6*): δ 8.32-8.25 (m, 2H), 8.05-7.93 (m, 4H), 6.88 (d, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*): δ 160.8, 150.6, 148.5, 141.9, 127.5, 124.0, 115.3; HRMS (ESI) calcd for $C_{11}H_{10}N_3O_4S$ *m/z* $[M+H]^+$: 280.0387; found: 280.0384.



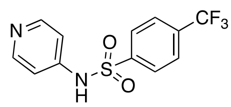
4-methoxy-N-(pyridin-4-yl)benzenesulfonamide (H-2c): white solid; ^{1}H NMR (400 MHz, DMSO-*d6*): δ 8.03 (s, 2H), 7.74 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 5.9 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, DMSO-*d6*): δ 128.3, 114.0, 55.5; HRMS (ESI) calcd for $C_{12}H_{11}N_2O_3S$ *m/z* $[M-H]^-$: 263.0496; found: 263.0489.



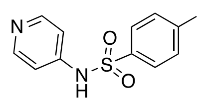
1,1,1-trifluoro-N-(pyridin-4-yl)methanesulfonamide (H-2d): white solid; ^{1}H NMR (400 MHz, DMSO-*d6*): δ 13.62 (s, 1H), 8.28 (d, J = 7.3 Hz, 2H), 7.28 (d, J = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-*d6*): δ 163.7, 140.1, 122.3, 119.1, 116.9; HRMS (ESI) calcd for $C_6H_6F_3N_2O_2S$ *m/z* $[M+H]^+$: 227.0097; found: 227.0101.



2-fluoro-N-(pyridin-4-yl)benzenesulfonamide (H-2e): white solid; ^{1}H NMR (396 MHz, DMSO-*d6*): δ 8.00 (d, J = 6.4 Hz, 2H), 7.86 (t, J = 7.2 Hz, 1H), 7.57 (q, J = 6.1 Hz, 1H), 7.29 (q, J = 8.5, 7.9 Hz, 2H), 6.94 (d, J = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*): δ 159.7, 157.2, 133.8, 129.2, 124.3, 117.1, 116.9; ^{19}F NMR (373 MHz, DMSO-*d6*): δ –109.5; HRMS (ESI) calcd for $C_{11}H_{10}FN_2O_2S$ *m/z* $[M+H]^+$: 253.0442; found: 253.0443.



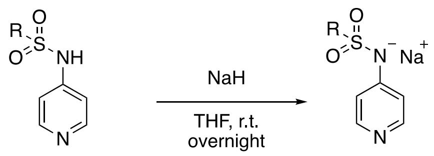
N-(pyridin-4-yl)-4-(trifluoromethyl)benzenesulfonamide (H-2f): white solid; ^{1}H NMR (396 MHz, DMSO-*d6*): δ 8.34-7.92 (m, 4H), 7.86 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*): δ 127.8, 126.9, 126.0, 125.9, 125.1, 122.3, 115.0; ^{19}F NMR (373 MHz, DMSO-*d6*): δ –61.3; HRMS (ESI) calcd for $C_{12}H_8F_3N_2O_2S$ *m/z* $[M-H]^-$: 301.0264; found: 301.0259.



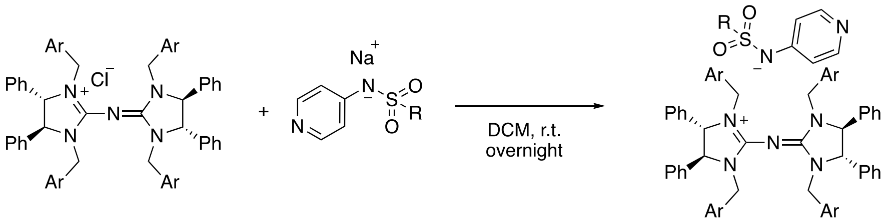
4-iodo-N-(pyridin-4-yl)benzenesulfonamide (H-2g): white solid; ^{1}H NMR (396 MHz, DMSO-*d6*): δ 7.99 (d, *J* = 7.0 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*): δ 137.6, 128.0, 114.7; HRMS (ESI) calcd for $C_{11}H_{10}IN_2O_2S$ *m/z* $[M+H]^+$: 360.9502; found: 360.9501.

4. Preparation and characterization of chiral pentanidium pyridinyl-sulfonamide ion pairs

a. Preparation of chiral pentanidium pyridinyl-sulfonamide ion pairs

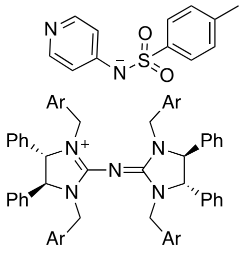


Step 1: The produced pyridine sulfonamide (1 equiv., 3mmol) was added in 10 mL distilled THF, and sodium hydride (1 equiv., 3mmol) was added slowly into the suspension. The whole mixture was stirred overnight at room temperature. The product was obtained by gravity filtration after reaction finished.

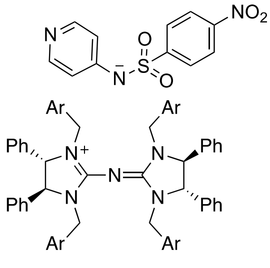


Step 2: The mixture of pentanidium chloride (0.01 mmol, 1 equiv.) and sodium salt of pyridinyl-sulfonamide (0.03 mmol, 3 equiv.) in 1 mL DCM was stirred overnight in a 4 mL vial at room temperature. The mixture was passed through a Kimwipe-plugged pipette and clear solution was obtained. The pentanidium pyridinyl-sulfonamide was obtained after solvent evaporation.

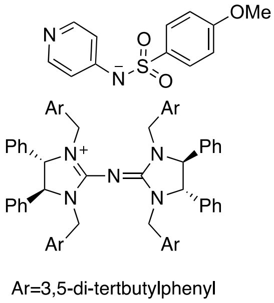
b. Characterization of chiral pentanidium pyridinyl-sulfonamide ion pairs



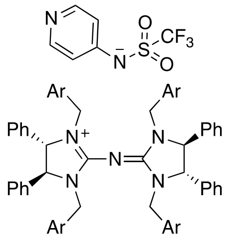
(4S,5S)-2-(((4S,5S)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenylimidazolidin-2-ylidene)amino)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium pyridin-4-yl(tosyl)amide (1a-2a): white solid; ^{1}H NMR (396 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 6.8 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 4H), 7.33 – 7.27 (m, 12H), 7.15 (d, J = 8.1 Hz, 2H), 7.01 (d, *J* = 6.6 Hz, 2H), 7.02 – 6.71 (m, 16H), 5.19 (d, *J* = 14.8 Hz, 4H), 4.40 (s, 4H), 4.10 (d, *J* = 14.8 Hz, 4H), 2.32 (s, 3H), 1.11 (s, 72H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.5, 152.2, 136.5, 131.7, 131.0, 129.9, 129.7, 129.1, 128.9, 127.3, 126.9, 123.4, 122.5, 115.5, 68.2, 49.3, 34.8, 31.3, 29.8; HRMS (+ESI) *m/z* $[C_{90}H_{116}N_5]^+$: 1266.9231; found: 1266.9231; HRMS (–ESI) *m/z* $[C_{12}H_{11}N_2O_2S]^-$: 247.0547; found: 247.0545; $[\alpha]^{23}_{D}$= –77.40 (*c* 1.0, CH_2Cl_2).



(4S,5S)-2-(((4S,5S)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenylimidazolidin-2-ylidene)amino)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium ((4-nitrophenyl)sulfonyl)(pyridin-4-yl)amide (1a-2b): yellow solid; ^{1}H NMR (396 MHz, Chloroform-*d*) δ 8.30 – 8.08 (m, 4H), 7.92 (d, *J* = 6.9 Hz, 2H), 7.61 (ddd, *J* = 70.1, 5.7, 3.3 Hz, 1H), 7.41 – 7.27 (m, 16H), 7.05 (d, *J* = 7.0 Hz, 2H), 7.03 – 6.65 (m, 16H), 5.20 (d, *J* = 14.8 Hz, 4H), 4.40 (s, 4H), 4.11 (d, *J* = 14.8 Hz, 4H), 1.11 (s, 72H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.5, 152.2, 136.5, 132.6, 131.7, 131.0, 129.9, 129.7, 128.9, 128.0, 127.3, 123.7, 123.4, 122.5, 116.1, 68.2, 49.3, 34.8, 31.3; HRMS (+ESI) *m/z* $[C_{90}H_{116}N_5]^+$: 1266.9231; found: 1266.9231; HRMS (–ESI) *m/z* $[C_{11}H_8N_3O_4S]^-$: 278.0241; found: 278.0243; $[\alpha]^{23}_{D}$= –81.94 (*c* 1.7, CH_2Cl_2).

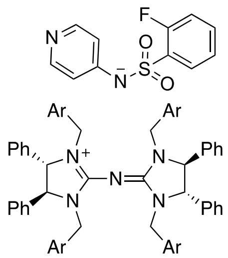


(4S,5S)-2-(((4S,5S)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenylimidazolidin-2-ylidene)amino)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium ((4-methoxyphenyl)sulfonyl)(pyridin-4-yl)amide (1a-2c): white solid; ^{1}H NMR (396 MHz, Chloroform-*d*) δ 7.91 – 7.81 (m, 4H), 7.40 – 7.27 (m, 16H), 7.00 (d, *J* = 7.2 Hz, 2H), 6.92 – 6.85 (m, 16H), 5.19 (d, *J* = 14.8 Hz, 4H), 4.40 (s, 4H), 4.11 (d, *J* = 14.8 Hz, 4H), 3.79 (s, 3H), 1.11 (s, 72H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.5, 152.2, 136.5, 131.7, 129.9, 129.7, 128.8, 127.3, 123.4, 122.5, 115.4, 113.7, 68.2, 55.5, 49.4, 34.8, 31.3; HRMS (+ESI) *m/z* $[C_{90}H_{116}N_5]^+$: 1266.9231; found: 1266.9231; HRMS (–ESI) *m/z* $[C_{12}H_{11}N_2O_5S]^-$: 263.0495; found: 263.0493; $[\alpha]^{23}_{D}$= –97.41 (*c* 1.7, CH_2Cl_2).



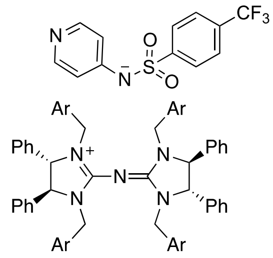
Ar=3,5-di-tertbutylphenyl

(4S,5S)-2-(((4S,5S)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenylimidazolidin-2-ylidene)amino)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium pyridin-4-yl((trifluoromethyl)sulfonyl)amide (1a-2d): white solid; ^{1}H NMR (396 MHz, Chloroform-*d*) δ 8.16 – 8.09 (m, 2H), 7.39 – 7.34 (m, 4H), 7.33 – 7.27 (m, 12H), 7.23 – 7.20 (m, 2H), 6.93 – 6.84 (m, 16H), 5.19 (d, *J* = 14.8 Hz, 4H), 4.40 (s, 4H), 4.11 (d, *J* = 14.8 Hz, 4H), 1.11 (s, 72H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.48, 152.21, 136.47, 131.70, 129.93, 129.67, 127.31, 123.39, 122.55, 118.03, 68.25, 49.36, 34.83, 31.31;^{19}F NMR (373 MHz, Chloroform-*d*) δ –76.95; HRMS (+ESI) *m/z* $[C_{90}H_{116}N_5]^+$: 1266.9231; found: 1266.9232; HRMS (–ESI) *m/z* $[C_6H_4F_3N_2O_2S]^-$: 224.9951; found: 224.9954; $[\alpha]^{23}_{D}$= –24.19 (*c* 1.6, CH_2Cl_2).



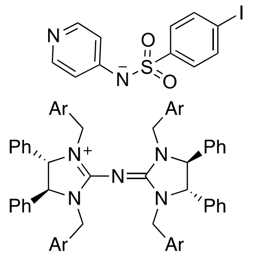
Ar=3,5-di-tertbutylphenyl

(4S,5S)-2-(((4S,5S)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenylimidazolidin-2-ylidene)amino)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium ((2-fluorophenyl)sulfonyl)(pyridin-4-yl)amide (1a-2e): white solid; ^{1}H NMR (396 MHz, Chloroform-*d*) δ 7.98 (t, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 6.7 Hz, 2H), 7.61 (ddd, *J* = 70.1, 5.6, 3.3 Hz, 1H), 7.40 – 7.28 (m, 16H), 7.12 – 7.00 (m, 4H), 6.93 – 6.84 (m, 16H), 5.20 (d, *J* = 14.8 Hz, 4H), 4.40 (s, 4H), 4.11 (d, *J* = 14.8 Hz, 4H), 1.11 (s, 72H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.5, 152.2, 136.5, 131.7, 130.2, 129.9, 129.7, 128.9, 127.3, 123.4, 122.5, 116.7, 115.9, 68.2, 49.4, 34.8, 31.3; ^{19}F NMR (373 MHz, Chloroform-d) δ –108.8; HRMS (+ESI) *m/z* $[C_{90}H_{116}N_5]^+$: 1266.9231; found: 1266.9231; HRMS (–ESI) *m/z* $[C_{11}H_8N_2O_2SF]^-$: 251.0296; found: 251.0300; $[\alpha]^{23}_{D}$= –62.53 (*c* 1.5, CH_2Cl_2).



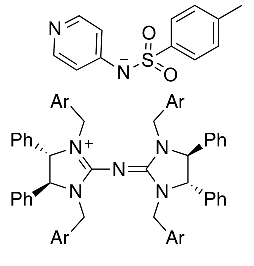
Ar=3,5-di-tertbutylphenyl

(4S,5S)-2-(((4S,5S)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenylimidazolidin-2-ylidene)amino)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium pyridin-4-yl((4-(trifluoromethyl)phenyl)sulfonyl)amide (1a-2f): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, J = 8.7 Hz, 2H), 7.95 (d, *J* = 6.8 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.39 – 7.33 (m, 4H), 7.32 – 7.25 (m, 12H), 6.97 (d, *J* = 6.8 Hz, 2H), 6.93 – 6.83 (m, 16H), 5.19 (d, *J* = 14.8 Hz, 4H), 4.40 (s, 4H), 4.11 (d, *J* = 14.8 Hz, 4H), 1.11 (s, 72H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.5, 152.2, 136.4, 131.7, 129.9, 129.7, 127.3, 127.3, 125.4, 125.3, 123.4, 122.5, 116.2, 68.2, 49.3, 34.8, 31.3; HRMS (+ESI) *m/z* $[C_{90}H_{116}N_5]^+$: 1266.9231; found: 1266.9231; HRMS (–ESI) *m/z* $[C_{12}H_8N_2O_2SF_3]^-$: 301.0259; found: 301.0264; $[\alpha]^{23}_{D}$= –106.41 (*c* 1.7, CH_2Cl_2).



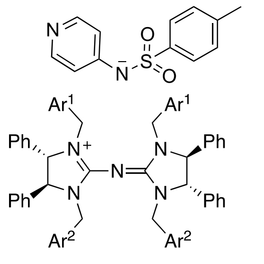
Ar=3,5-di-tertbutylphenyl

(4S,5S)-2-(((4S,5S)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenylimidazolidin-2-ylidene)amino)-1,3-bis(3,5-di-tert-butylbenzyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium ((4-iodophenyl)sulfonyl)(pyridin-4-yl)amide (1a-2g): white solid; ^{1}H NMR (396 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.1 Hz, 2H), 7.69 (s, 4H), 7.41 – 7.27 (m, 16H), 7.03 (d, *J* = 7.2 Hz, 2H), 6.92 – 6.83 (m, 16H), 5.19 (d, *J* = 14.8 Hz, 4H), 4.40 (s, 4H), 4.11 (d, *J* = 14.8 Hz, 4H), 1.11 (s, 72H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.5, 152.2, 139.3, 137.6, 136.5, 131.7, 129.9, 129.7, 128.6, 127.3, 123.4, 122.5, 115.8, 68.2, 49.4, 34.8, 31.3; HRMS (+ESI) *m/z* $[C_{90}H_{116}N_5]^+$: 1266.9231; found: 1266.9264; HRMS (–ESI) *m/z* $[C_{11}H_8N_2O_2SI]^-$: 358.9356; found: 358.9357; $[\alpha]^{23}_{D}$= –50.65 (*c* 1.7, CH_2Cl_2).



Ar=3,5-di-trifluoromethylphenyl

(4S,5S)-2-(((4S,5S)-1,3-bis(3,5-bis(trifluoromethyl)benzyl)-4,5-diphenylimidazolidin-2-ylidene)amino)-1,3-bis(3,5-bis(trifluoromethyl)benzyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium pyridin-4-yl(tosyl)amide (1b-2a): white solid; ^{1}H NMR (396 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 6.5 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.69 (s, 4H), 7.51 (s, 8H), 7.23 (d, *J* = 7.5 Hz, 4H), 7.16-7.10 (m, 10H), 6.99 (d, *J* = 7.5 Hz, 8H), 6.87 (d, *J* = 6.5 Hz, 2H), 5.09 (d, J = 16.2 Hz, 4H), 4.89 (s, 4H), 4.81 (d, J = 16.2 Hz, 4H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.8, 137.3, 134.2, 132.5, 132.2, 130.3, 129.6, 129.2, 128.1, 126.8, 124.3, 121.5, 115.5, 70.3, 49.2; ^{19}F NMR (373 MHz, Chloroform-*d*) δ –63.1; HRMS (+ESI) *m/z* $[C_{66}H_{44}F_{24}N_5]^+$: 1362.3213; found: 1362.3203; HRMS (–ESI) *m/z* $[C_{12}H_{11}N_2O_2S]^-$: 247.0547; found: 247.0546; $[\alpha]^{23}_{D}$= –6.80 (*c* 0.5, CH_2Cl_2).

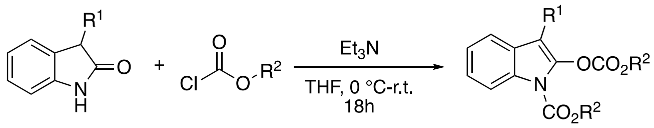


(4S,5S)-1-(3,5-bis(trifluoromethyl)benzyl)-2-(((4S,5S)-1-(3,5-bis(trifluoromethyl)benzyl)-3-(3,5-di-tert-butylbenzyl)-4,5-diphenylimidazolidin-2-ylidene)amino)-3-(3,5-di-tert-butylbenzyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium pyridin-4-yl(tosyl)amide (1c-2a): white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, J = 6.5 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 7.56 (s, 2H), 7.50 (s, 4H), 7.30 (d, J = 6.7 Hz, 4H), 7.16 (dt, J = 23.3, 7.6 Hz, 8H), 7.04 (q, J = 8.9, 7.7 Hz, 12H), 6.91 – 6.77 (m, 10H), 5.46 (d, J = 15.9 Hz, 2H), 5.22 (d, J = 14.8 Hz, 2H), 5.00 – 4.91 (m, 4H), 4.37 (d, J = 8.9 Hz, 2H), 3.90 (d, J = 14.8 Hz, 2H), 2.30 (s, 3H), 1.07 (s, 36H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.4, 152.2, 142.1, 138.5, 136.5, 135.2, 132.2, 131.4, 131.1, 129.7, 129.6, 129.4, 129.1, 128.3, 128.1, 126.8, 124.5, 123.1, 122.3, 115.8, 71.5, 68.1, 51.7, 49.1, 34.7, 31.2, 21.4; ^{19}F NMR (377 MHz, Chloroform-*d*) δ –62.7; HRMS (+ESI) *m/z* $[C_{78}H_{80}F_{12}N_5]^+$: 1314.6222; found: 1314.6224; HRMS (–ESI) *m/z* $[C_{12}H_{11}N_2O_2S]^-$: 247.0547; found: 247.0547; $[\alpha]^{23}_{D}$= –100.25 (*c* 0.4, CH_2Cl_2).

5. General procedure and characterisation of asymmetric Steglich rearrangement

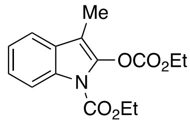
a. General synthetic procedure of Steglich rearrangement substrates

The substrates **3a-3m** were synthesized following reported procedure.[3–7] The compound **3c** is reported for the first time.



3-substituted oxindole derivative (3 mmol, 1 equiv.) was added in 10 mL distilled THF, then Et_3N (9 mmol, 3 equiv.) was added into the solution. The whole mixture was cooled down to 0 °C in ice bath and the chloroformate (9 mmol, 3 equiv.) was added slowly into the mixture. Then the mixture was warmed up to room temperature and stirred at this temperature overnight. The product was purified and isolated by flash column chromatography (n-hexane : ethyl acetate=10:1 – 4:1).

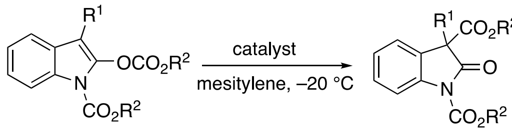
b. Characterisation of Steglich rearrangement substrates



ethyl 2-((ethoxycarbonyl)oxy)-3-methyl-1*H*-indole-1-carboxylate (3c): colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.21 (m, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.6, 150.4, 137.7, 132.2, 128.1, 124.7, 123.3, 118.9, 115.4, 105.2, 65.8, 63.3, 14.3, 14.3, 7.0; HRMS (ESI) calcd for $C_{15}H_{17}NO_5$ *m/z* $[M+H]^+$: 292.1180; found: 292.1180.

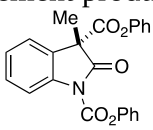
6. General procedure and characterisation of enantioselective Steglich rearrangement products

a. General procedure of enantioselective Steglich rearrangement

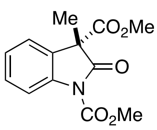


A solution of *O*-acylated oxindole (0.040 mmol, 1 equiv.) and catalyst (0.002 mmol, 5 mol%) in mesitylene (0.4 mL) was cooled to –20 °C and stirred at this temperature for 24 h. The reaction was monitored by TLC (n-hexane : ethyl acetate=4:1) and the mixture was purified by flash column chromatography (n-hexane : ethyl acetate=20:1) after reaction finished.

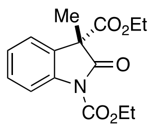
b. Characterisation of Steglich rearrangement products



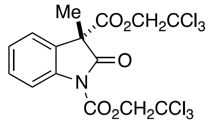
diphenyl 3-methyl-2-oxoindoline-1,3-dicarboxylate (4a): white solid; 99% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.39 – 7.27 (m, 6H), 7.26 – 7.17 (m, 1H), 7.01 – 6.91 (m, 2H), 1.90 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 167.7, 150.4, 150.2, 149.4, 139.2, 130.0, 129.8, 129.6, 128.8, 126.7, 126.6, 125.8, 123.1, 121.6, 121.3, 116.1, 56.1, 21.0; HRMS (ESI) calcd for $C_{23}H_{18}NO_5$ *m/z* $[M+H]^+$: 388.1180; found: 388.1180; $[\alpha]^{26}_D$= +63.75 (*c* 0.24, CH_2Cl_2); HPLC analysis: Chiralcel AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 22°C), 23.8 min, 37.5 min (major), 92% ee.



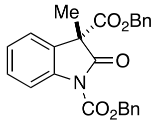
dimethyl 3-methyl-2-oxoindoline-1,3-dicarboxylate (4b): white solid; 82% yield; ^{1}H NMR (396 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.37 (td, *J* = 8.2, 1.5 Hz, 1H), 7.27 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 4.04 (s, 3H), 3.66 (s, 3H),1.73 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3, 169.6, 151.5, 139.3, 129.6, 129.0, 125.4, 123.1, 115.6, 55.7, 54.2, 53.4, 21.0; HRMS (ESI) calcd for $C_{13}H_{14}NO_5$ *m/z* $[M+H]^+$: 264.0867; found: 264.0868; $[\alpha]^{23}_D$= +26.13 (*c* 1.1, CH_2Cl_2); HPLC analysis: Chiralcel IG-3 (Hex/IPA = 95/5, 1.0 mL/min, 254 nm, 22°C), 15.9 min (major), 16.8 min, 99% ee.



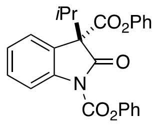
diethyl 3-methyl-2-oxoindoline-1,3-dicarboxylate (4c): white solid; 48% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.30 – 7.24 (m, 1H), 7.19 (td, *J* = 7.5, 1.0 Hz, 1H), 4.52 – 4.47 (m, 2H), 4.32 – 3.81 (m, 2H), 1.72 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3, 169.1, 151.0, 139.4, 129.4, 129.2, 125.2, 123.0, 115.6, 63.8, 62.4, 55.8, 21.0, 14.4, 14.0; HRMS (ESI) calcd for $C_{15}H_{17}NO_5$ *m/z* $[M+H]^+$: 292.1180; found: 292.1180; $[\alpha]^{23}_{D}$= +32.43 (*c* 1.4, CH_2Cl_2); HPLC analysis: Amylose-2 (Hex/IPA = 98/2, 1.0 mL/min, 210 nm, 22°C), 15.6 min, 17.5 min (major), 87% ee.



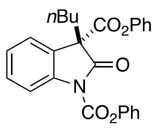
bis(2,2,2-trichloroethyl) 3-methyl-2-oxoindoline-1,3-dicarboxylate (4d): white solid; 85% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.38 (m, 1H), 7.34 (d, *J* = 6.7 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 5.06 (q, *J* = 11.8 Hz, 2H), 4.83 – 4.50 (m, 2H), 1.83 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.9, 167.2, 149.2, 138.9, 130.1, 128.1, 125.8, 123.6, 115.9, 94.2, 94.2, 75.9, 74.6, 55.7, 20.1; HRMS (ESI) calcd for C15H12Cl_6NO_5 *m/z* $[M+H]^+$: 494.8841; found: 494.8842; $[\alpha]^{23}_{D}$= +35.54 (*c* 2.1, CH_2Cl_2); HPLC analysis: Chiralcel OD-H (Hex/IPA = 90/10, 1.0 mL/min, 210 nm, 22°C), 5.5 min (major), 5.9 min, 73% ee.



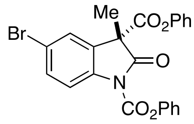
dibenzyl 3-methyl-2-oxoindoline-1,3-dicarboxylate (4e): white solid; 97% yield; ^{1}H NMR (396 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.48 – 7.28 (m, 4H), 7.27 – 7.21 (m, 3H), 7.21 – 7.12 (m, 2H), 7.09 (dd, *J* = 6.5, 3.0 Hz, 2H), 5.45 (s, 2H), 5.11 (s, 2H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.0, 168.8, 150.8, 139.3, 135.3, 135.0, 129.6, 128.8, 128.6, 128.6, 128.3, 128.2, 127.4, 125.2, 123.1, 115.7, 68.9, 67.6, 55.9, 20.7; HRMS (ESI) calcd for $C_{25}H_{22}NO_5$ *m/z* $[M+H]^+$: 416.1493; found: 416.1493; $[\alpha]^{23}_{D}$= +45.14 (*c* 1.5, CH_2Cl_2); HPLC analysis: Chiralcel AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 22°C), 25.0 min (major), 30.1 min, 88% ee.



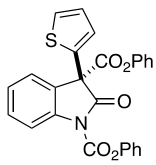
diphenyl 3-isopropyl-2-oxoindoline-1,3-dicarboxylate (4f): white solid; 86% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, J = 8.1 Hz, 1H), 7.83 – 7.57 (m, 1H), 7.50 – 7.18 (m, 17H), 7.15 – 7.04 (m, 2H), 3.27 (hept, *J* = 7.1 Hz, 1H), 1.46 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 167.2, 150.5, 150.3, 149.4, 139.8, 129.8, 129.7, 129.6, 126.7, 126.6, 126.5, 125.6, 124.0, 121.7, 121.4, 115.6, 63.9, 36.2, 17.5, 17.2; HRMS (ESI) calcd for $C_{25}H_{22}NO_5$ *m/z* $[M+H]^+$: 416.1493; found: 416.1493; $[\alpha]^{23}_{D}$= –3.05 (*c* 1.5, CH_2Cl_2); HPLC analysis: Chiralcel AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 22°C), 16.2 min (major), 23.9 min, 96% ee.



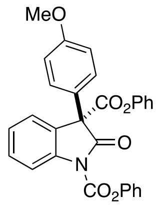
diphenyl 3-butyl-2-oxoindoline-1,3-dicarboxylate (4g): white solid; 94% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.41 (m, 6H), 7.37 – 7.29 (m, 6H), 7.25 – 7.19 (m, 1H), 7.01 – 6.95 (m, 2H), 2.56 – 2.45 (m, 1H), 2.42 – 2.33 (m, 1H), 1.42 – 1.25 (m, 3H), 1.15 – 1.01 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.9, 167.5, 150.4, 150.2, 149.4, 139.9, 129.9, 129.7, 129.6, 127.0, 126.7, 126.5, 125.8, 123.3, 121.6, 121.3, 115.9, 60.4, 34.8, 25.8, 22.8, 13.8; HRMS (ESI) calcd for $C_{26}H_{24}NO_5$ *m/z* $[M+H]^+$: 430.1649; found: 430.1648; $[\alpha]^{26}_{D}$= +50.29 (*c* 0.7, CH_2Cl_2); HPLC analysis: Chiralcel AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 210 nm, 22°C), 11.9 min, 13.9 min (major), 94% ee.



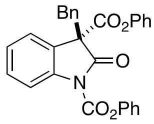
diphenyl 5-bromo-3-methyl-2-oxoindoline-1,3-dicarboxylate (2h): white solid; 70% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.6 Hz, 1H), 7.68 – 7.53 (m, 2H), 7.50 – 7.41 (m, 2H), 7.39 – 7.09 (m, 6H), 7.05 – 6.97 (m, 2H), 1.89 (s, 3H).; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.5, 167.0, 150.0, 138.1, 132.9, 130.5, 129.7, 129.6, 129.2, 126.7, 126.6, 126.2, 125.0, 121.8, 121.4, 121.1, 117.6, 55.8, 20.9; HRMS (ESI) calcd for $C_{23}H_{17}{}^{79}BrNO_5$ *m/z* $[M+H]^+$: 466.0285; found: 466.0284; HRMS (ESI) calcd for $C_{23}H_{17}{}^{81}BrNO_5$ *m/z* $[M+H]^+$: 468.0265; found: 468.0268; $[\alpha]^{23}_{D}$= +4.17 (*c* 0.4, CH_2Cl_2); HPLC analysis: Chiralcel AD-H (Hex/IPA = 90/10, 1.0 mL/min, 254 nm, 22°C), 10.4 min, 13.0 min (major), 92% ee.



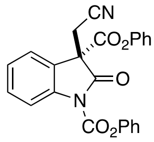
diphenyl 2-oxo-3-(thiophen-2-yl)indoline-1,3-dicarboxylate (4i): pale yellow solid; 86% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.71 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.55 (td, *J* = 7.9, 1.4 Hz, 1H), 7.48 – 7.27 (m, 9H), 7.25 – 7.18 (m, 2H), 7.13 – 6.98 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 166.3, 150.5, 150.2, 149.4, 139.8, 136.8, 130.9, 129.8, 129.7, 128.4, 127.4, 127.2, 126.8, 126.7, 125.9, 125.3, 121.6, 121.2, 116.3, 115.4, 61.5; HRMS (ESI) calcd for $C_{26}H_{18}NO_5S$ *m/z* $[M+H]^+$: 456.0900; found: 456.0902; $[\alpha]^{23}_{D}$= +47.06 (*c* 0.5, CH_2Cl_2); HPLC analysis: Chiralcel AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 215 nm, 22°C), 20.9 min, 27.0 min (major), 98% ee.



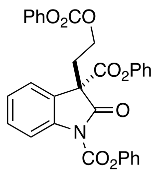
diphenyl 3-(4-methoxyphenyl)-2-oxoindoline-1,3-dicarboxylate (4j): white solid; 95% yield; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.14 (d, J = 8.3 Hz, 1H), 7.63 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.55 (td, *J* = 8.0, 1.4 Hz, 1H), 7.46 – 7.32 (m, 7H), 7.32 – 7.20 (m, 4H), 7.05 – 7.01 (m, 2H), 6.96 – 6.90 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 167.5, 160.2, 150.6, 150.2, 149.5, 140.2, 130.6, 129.7, 129.6, 127.0, 126.7, 126.6, 125.9, 125.8, 121.6, 121.2, 116.3, 114.4, 64.1, 55.5; HRMS (ESI) calcd for $C_{29}H_{22}NO_6$ *m/z* $[M+H]^+$: 480.1442; found: 480.1443; $[\alpha]^{26}_{D}$= +128.98 (*c* 1.9, CH_2Cl_2); HPLC analysis: Chiralcel IG-3 (Hex/IPA = 90/10, 1.0 mL/min, 254 nm, 22°C), 38.4 min, 40.9 min (major), 91% ee.



diphenyl 3-benzyl-2-oxoindoline-1,3-dicarboxylate (4k): white solid; 96% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.47 – 7.25 (m, 13H), 7.26 – 7.06 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 6.6 Hz, 1H), 3.85 – 3.64 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.3, 167.3, 150.4, 150.1, 148.9, 139.9, 133.5, 130.2, 130.0, 129.7, 129.6, 128.2, 127.5, 126.7, 126.6, 126.3, 125.5, 123.7, 121.6, 121.3, 115.8, 61.8, 41.1; HRMS (ESI) calcd for $C_{29}H_{22}NO_5$ *m/z* $[M+H]^+$: 464.1493; found: 464.1493; $[\alpha]^{26}_{D}$= +21.69 (*c* 1.5, CH_2Cl_2); HPLC analysis: Chiralcel IE (Hex/IPA = 90/10, 1.0 mL/min, 215 nm, 22°C), 12.8 min, 15.4 min (major), 96% ee.

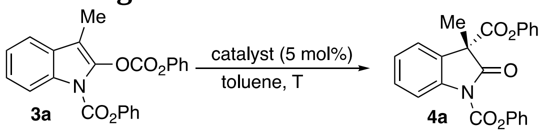


diphenyl 3-(cyanomethyl)-2-oxoindoline-1,3-dicarboxylate (4l): pale yellow solid; 90% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.52 (m, 2H), 7.50 – 7.19 (m, 9H), 7.05 – 6.94 (m, 2H), 3.59 – 3.23 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 165.3, 150.1, 148.9, 140.1, 131.5, 129.9, 129.8, 127.0, 127.0, 126.4, 124.1, 123.4, 121.5, 121.0, 116.7, 115.4, 114.9, 56.8, 23.4; HRMS (ESI) calcd for $C_{24}H_{17}N_2O_5$ *m/z* $[M+H]^+$: 413.1132; found: 413.1132; $[\alpha]^{26}_{D}$= +50.60 (*c* 0.7, CH_2Cl_2); HPLC analysis: Chiralcel IG-3 (Hex/IPA = 90/10, 1.0 mL/min, 210 nm, 22°C), 29.1 min, 33.1 min (major), 92% ee.



diphenyl 2-oxo-3-(2-((phenoxycarbonyl)oxy)ethyl)indoline-1,3-dicarboxylate (4m): white solid; 67% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.47 (m, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.38 – 7.17 (m, 12H), 7.09 (s, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 4.44 (dt, *J* = 9.1, 5.0 Hz, 1H), 4.01 (td, *J* = 10.9, 4.5 Hz, 1H), 3.14 (ddd, *J* = 15.8, 10.6, 5.6 Hz, 1H), 2.85 (dt, *J* = 14.9, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.7, 167.1, 153.2, 151.0, 150.4, 150.2, 146.5, 140.4, 130.6, 129.6, 129.6, 129.6, 126.7, 126.6, 126.3, 125.9, 125.2, 123.4, 121.6, 116.5, 64.1, 58.5, 33.0; HRMS (ESI) calcd for $C_{31}H_{24}NO_8$ *m/z* $[M+H]^+$: 538.1497; found: 538.1497; $[\alpha]^{26}_{D}$= +43.55 (*c* 2.0, CH_2Cl_2); HPLC analysis: Chiralcel AD-H (Hex/IPA = 90/10, 1.0 mL/min, 254 nm, 22°C), 38.4 min, 41.7 min (major), 97% ee.

7. Table S1. Proof of concept experiments to apply chiral ion pair catalyst in enantioselective Steglich rearrangement of oxindole derivatives[a]



entry	catalyst	T	yield[b]	ee[c]
1	**1a-Cl**	r.t.	-	-
2	**H-2a**	r.t.	-	-
3	**1a-Cl**, DMAP	r.t.	39%	0%
4	TBAB, **Na-2a**	r.t.	38%	-
5	**1a-Cl**, **Na-2a**	r.t.	8%	7%
6	**1a-2a**	r.t.	99%	0%
7	**1a-2a**	–20 °C	74%	87%

[a] Reaction condition: **3a** (0.04 mmol, 1.0 equiv.), catalyst (5 mol%), and solvent (0.4 mL) at room temperature for 24 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

8. 2D NOESY and 2D ROESY spectra for catalyst 1a-2f

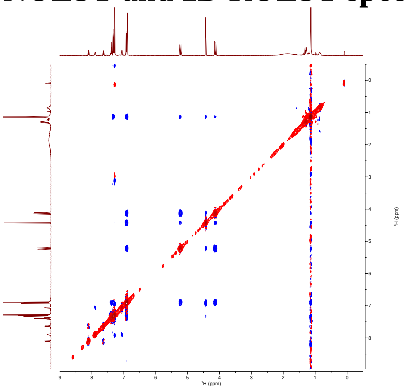


Figure S1. *2D ROESY spectrum of pentanidium ion pair* ***1a-2f***
(room temperature, chloroform-d, τ_m = 0.2 s)

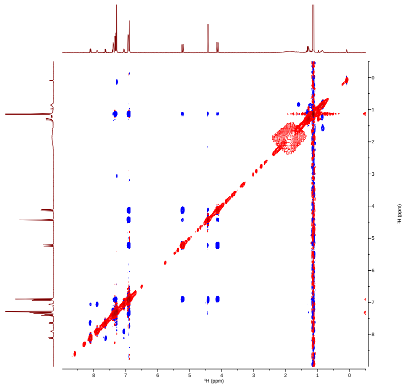


Figure S2. *2D NOESY spectrum of pentanidium ion pair* ***1a-2f***
(room temperature, chloroform-d, τ_m = 0.5 s)

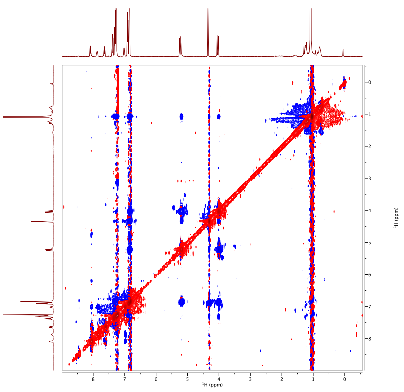


Figure S3. *2D ROESY spectrum of pentanidium ion pair* ***1a-2f***
(–20 °C, chloroform-d, τ_m = 0.2 s)

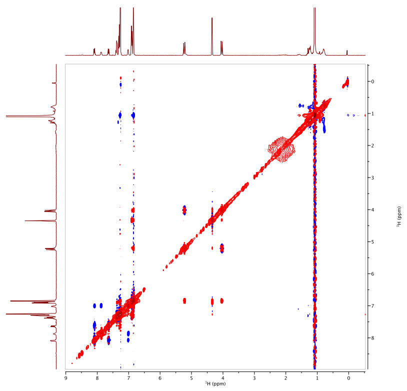


Figure S4. *2D NOESY spectrum of pentanidium ion pair* ***1a-2f***
(–20 °C chloroform-d, τ_m = 0.5 s)

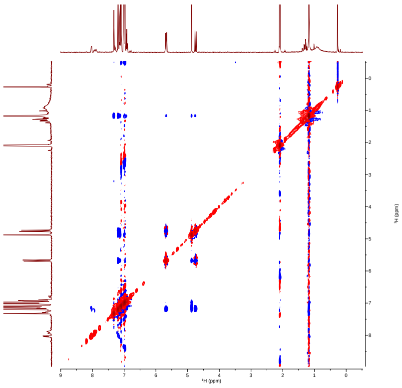


Figure S5. *2D ROESY spectrum of pentanidium ion pair* ***1a-2f***
(room temperature, toluene-d8, τm = 0.2 s)

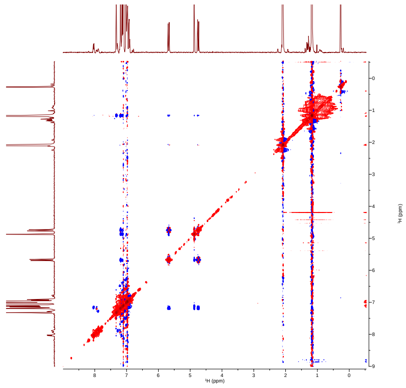


Figure S6. *2D NOESY spectrum of pentanidium ion pair* ***1a-2f***
(room temperature, toluene-d8, τm = 0.5 s)

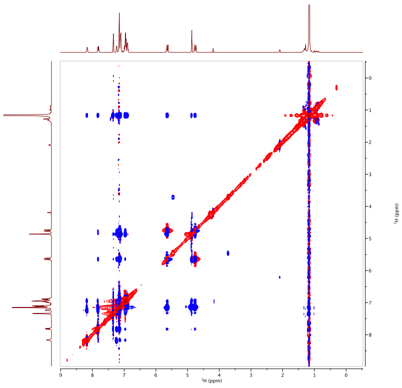


Figure S7. *2D ROESY spectrum of pentanidium ion pair* ***1a-2f***
(–20 °C, toluene-d8, τm = 0.2 s)

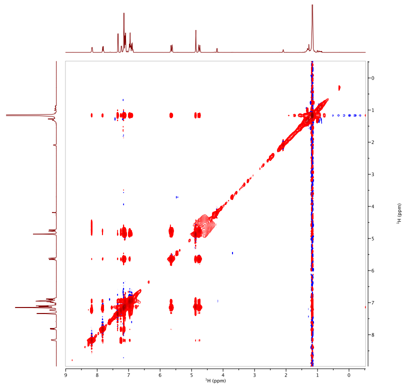


Figure S8. *2D NOESY spectrum of pentanidium ion pair* ***1a-2f***
(–20 °C, toluene-d8, τm = 0.5 s)

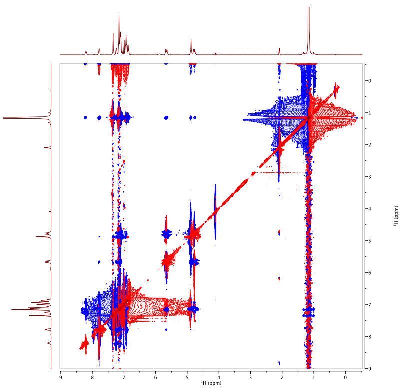


Figure S9. *2D ROESY spectrum of pentanidium ion pair* ***1a-2f***
(–40 °C, toluene-d8, τm = 0.2 s)

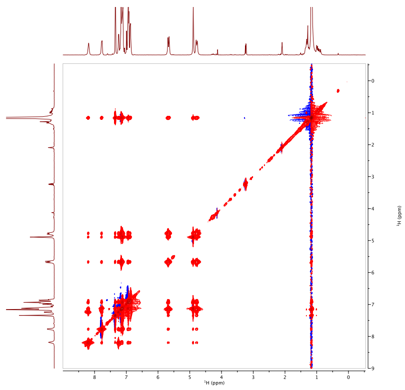


Figure S10. *2D NOESY spectrum of pentanidium ion pair* ***1a-2f***
(–40 °C, toluene-d8, τm = 0.5 s)

9. Computational details

All calculations are performed with ORCA 5.0[8] (5.0.4 for all calculations which involve the DFT-D4 corrections and 5.0.3 or 5.0.4 for all calculations which do not). Conformation sampling was performed with CREST[9] using GFN2-XTB[10] method to evaluate the required energies and forces. For all stationary points that are optimized at ALPB(toluene)/GFN2-XTB:r^{2}SCAN-3c[11], numerical frequencies were calculated to characterize the stationary points. Selected geometries are optimized at CPCM(toluene)/r^{2}SCAN-3c, for these stationary points. Intrinsic reaction coordinates were performed on key TS structures to confirm that the minimum energy path traversed by the TS correspond to the required elementary step.

IGMplot 3.0.3 was used to calculate the isosurfaces.[12] VMD[13] was used to produce the isosurface together with the corresponding 3D models of the complexes.

Examples of relevant ORCA 5 keywords in input file:

QM/QM2 geometry optimization

```
!QMMM
!QM/QM2 optTS verytightopt r2scan-3c verytightscf
%qmmm
	QMAtoms {211:284} end
	Charge_Total 0
	Mult_Total 1
	QM2CustomFile "/scratch/QM2method.txt"
end
```

```
!QMMM
!QM/QM2 opt verytightopt r2scan-3c verytightscf
%qmmm
	QMAtoms {211:284} end
	Charge_Total 0
	Mult_Total 1
	QM2CustomFile "/scratch/QM2method.txt"
end
```

QM2 Numerical Frequency

```
!QMMM
!QM/QM2 opt verytightopt r2scan-3c verytightscf
%qmmm
	QMAtoms {211:284} end
	Charge_Total 0
	Mult_Total 1
	QM2CustomFile "/scratch/QM2method.txt"
end
```

QM/QM2 Molecular Dynamics

```
!QM/QM2 r2scan-3c verytightscf
!MD
%qmmm
	QMAtoms {211:238} end
	Charge_Total 0
	Mult_Total 1
	QM2CustomFile "/scratch/QM2method.txt"
end
%md
	SCFlog last
	Timestep 0.5_fs
	Initvel 278_K No_overwrite
	Thermostat NHC 278_K Timecon 25.0_fs
```

```
        Dump Position Stride 4 Filename "/scratch/trajectory.xyz"
        Restart IfExists
        Run 1000 Centercom
end
```

QM2method.txt

```
!XTB ALPB(toluene)
%XTB
XTBINPUTSTRING "--acc 0.0001"
end
```

r^{2}SCAN-3c optimization

```
!opt verytightopt r2scan-3c verytightscf
```

r^{2}SCAN-3c numerical frequency

```
!NumFreq r2scan-3c verytightscf
%Freq
        Temp 253.15
end
```

CPCM/r^{2}SCAN-3c optimization

```
!optTS verytightopt verytightscf r2scan-3c CPCM(toluene) soscf notrah defgrid3
%geom
        UseGDIIS False
        MaxIter 300
        GDIISMaxEq 20
        InHess read
        InHessName "run.Hess.grid2.CPCM.r2scan-3c.hess"
        Trust 0.2
        TS_Active_Atoms {217 225}   end
          TS_Active_Atoms_Factor 1.5
        ENFORCESTRICTCONVERGENCE True
end
```

```
!opt verytightopt verytightscf r2scan-3c CPCM(toluene) soscf notrah defgrid3
%geom
        MaxIter 300
        Trust 0.3
end
```

CPCM/r^{2}SCAN-3c frequency

```
!AnFreq verytightscf r2scan-3c CPCM(toluene) soscf notrah defgrid3
%Freq
      Temp 253.15
end
```

Single point calculations

```
!M062X def2-tzvpp RIJCOSX VeryTightSCF autoaux defgrid3
```

```
!wB97M-V def2-tzvpp RIJCOSX VeryTightSCF autoaux
```

10. Supplementary computational results

Achiral nucleophilic catalysts calculations

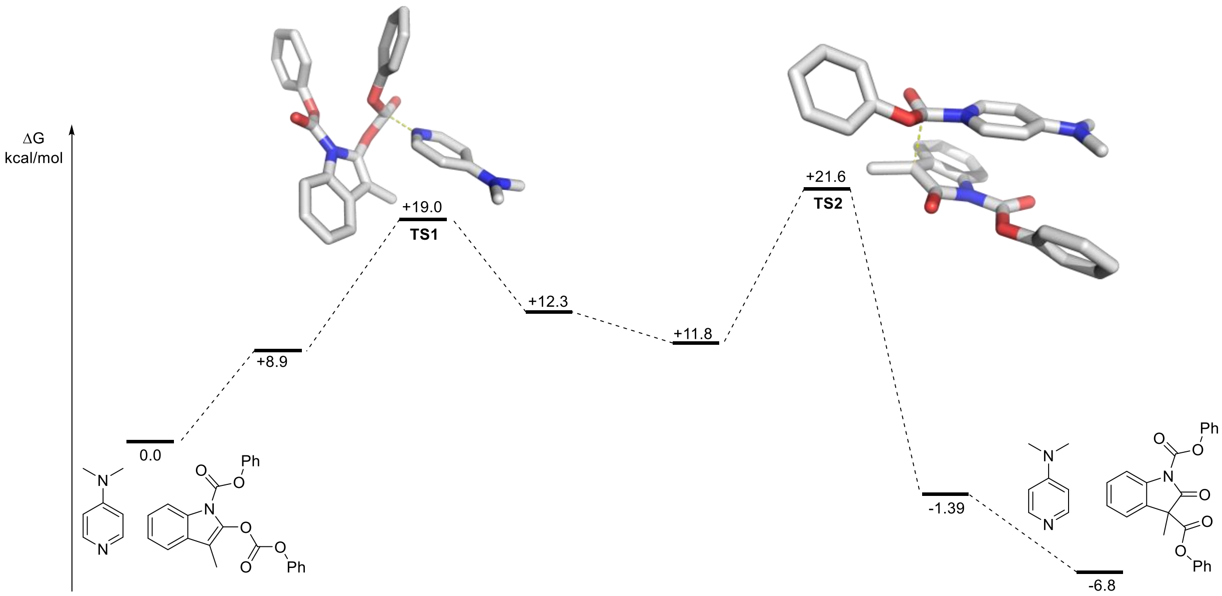


Figure S11. Free energy profile of DMAP catalyzed Steglich Rearrangement. Values are calculated at SMD(Toluene)/M06-2X/def2-TZVPP//CPCM(toluene)/r^{2}SCAN-3c. Thermochemical correction to the Gibbs free energy is calculated at 253.15K and 1 atm.

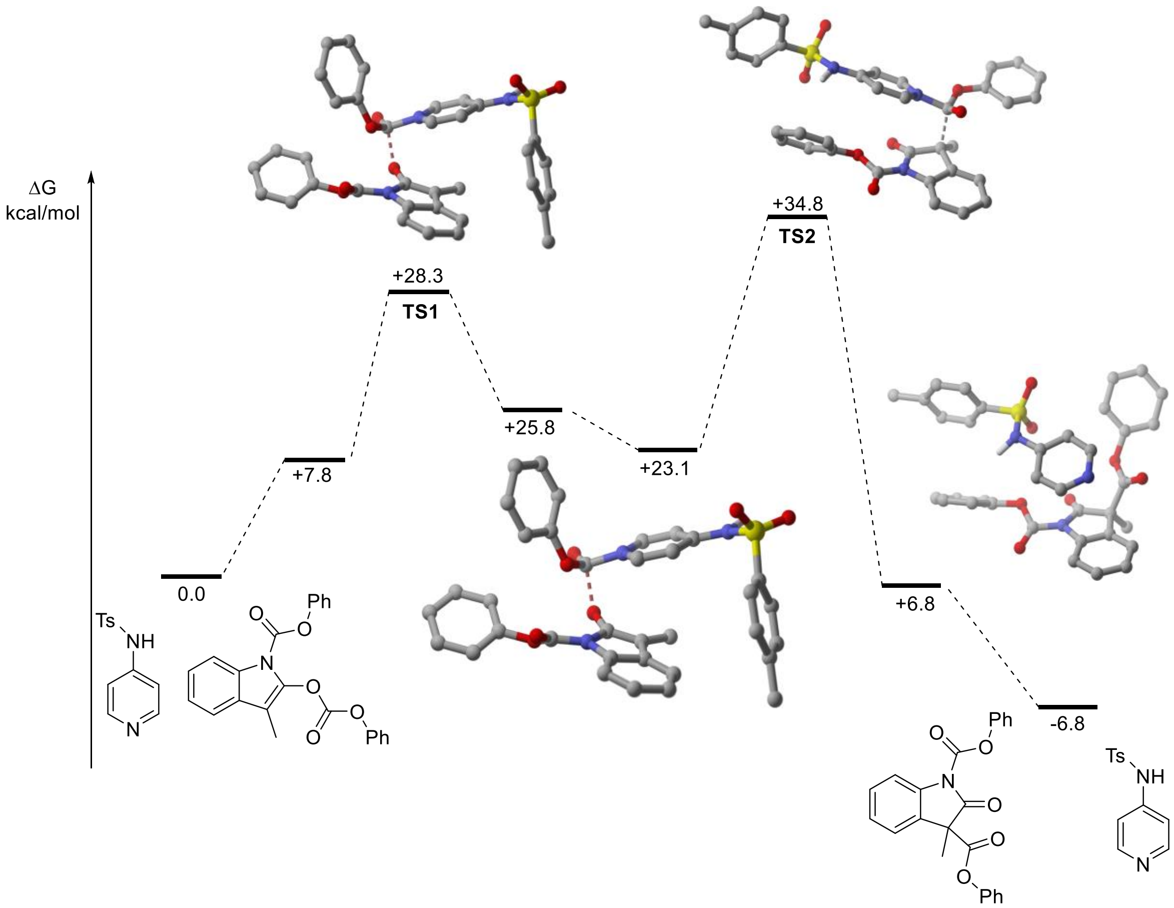


Figure S12. Free energy profile of **H-2a** catalyzed Steglich Rearrangement. Values are calculated at SMD(Toluene)/M06-2X/def2-TZVPP//CPCM(toluene)/r^{2}SCAN-3c. Thermochemical correction to the Gibbs free energy is calculated at 253.15K and 1 atm.

Table S2. Turnover Frequency from energy profiles shown above.

	$TOF_{298.15K}$ (h^{-1})
DMAP	2.75
H-2a	6.9×10^{-10}

TOF is calculated with AUTOTOF 0.9.1 excel.[14]

Post-processing of MD results.

Molecular dynamics simulations with ORCA were performed with the following workflow.

1. Equilibrate the optimized geometries at 253K for 1 ps (0.5fs/step)
2. Production for 20 ps (0.5fs/step) run to collect the data.

The details can be found in the ORCA input section above. The PYTHON script used to post-process the MD trajectories is attached as a jupyter notebook in the supplementary file.

Relevant MD trajectories are available from the authors as requested. They are not included due to their large size (2.19GB in total).

Entropy contribution to $\Delta\Delta G^‡$

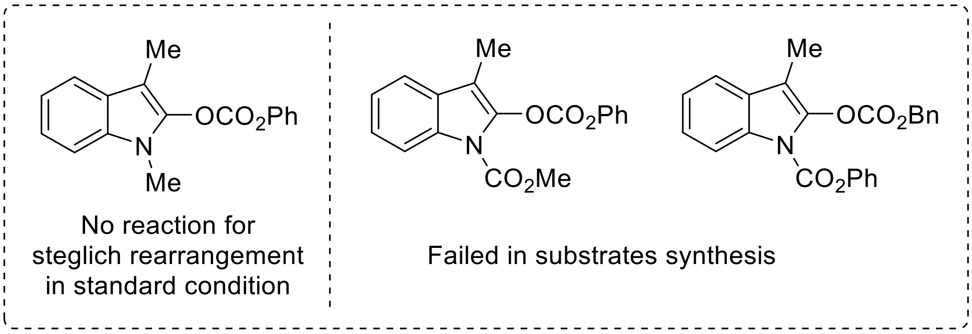
Table S3. Entropy contribution to $\Delta\Delta G^‡$

Transition state structures optimized at	$-T\Delta\Delta S^‡$ (kcal/mol)
ALPB(toluene)/GFN2-XTB:r^{2}SCAN-3c	+0.80
CPCM(toluene)/r^{2}SCAN-3c	+0.68

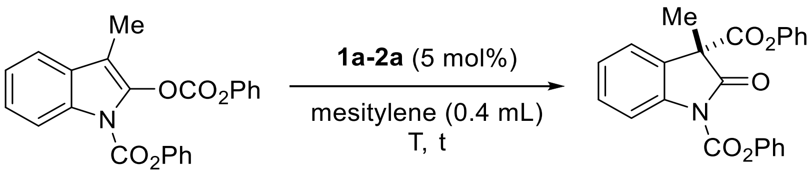
Please refer to spreadsheet “ee.xlsx” in SI_coordinates_and_data\CPCM_r2SCAn-3c\1a-2f for details.

11. The Optimization of Reaction Conditions

N-Protecting group:



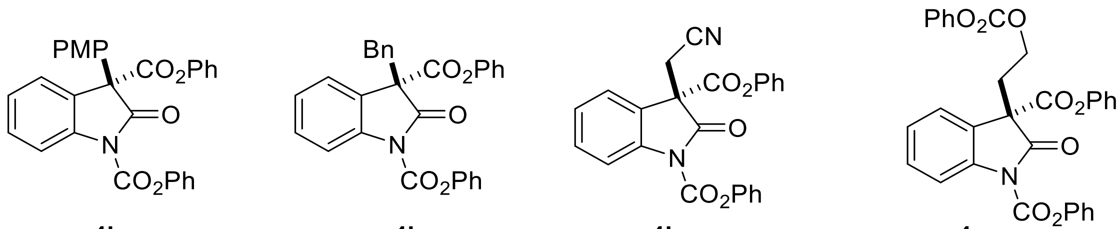
Optimization of temperature [a]



T (°C)	t (h)	yield (%) [b]	ee (%) [c]
0	24 h	81	86
-20	24 h	99	92
-40	24 h	N.R.	-
-40	48 h	N.R.	-

[a] Reaction condition: **3a** (0.04 mmol, 1.0 equiv.), catalyst (5 mol%), and solvent (0.4 mL) at T °C for t h. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Results for 4j, 4k, 4l, 4m using 1a-2a as catalyst (standard condition)



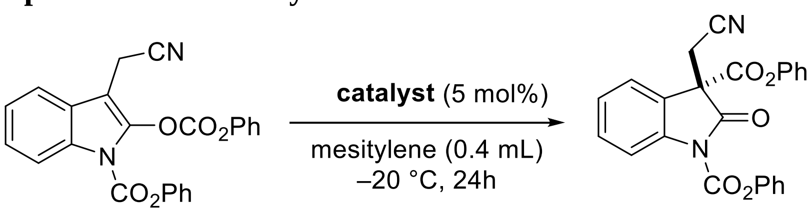
4j 78% yield, 84% ee

4k 53% yield, 90% ee

4l 53% yield, 66% ee

4m 30% yield, 70% ee (48 h)

Optimization of catalysts for 4l [a]



catalyst	yield (%) [b]	ee (%) [c]
1a-2a	53	66
1a-2c	20	50
1a-2e	24	67

1a-2f	90	92
1a-2g	12	40

[a] Reaction condition: **3l** (0.04 mmol, 1.0 equiv.), catalyst (5 mol%), and solvent (0.4 mL) at -20 °C for 24 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Reference

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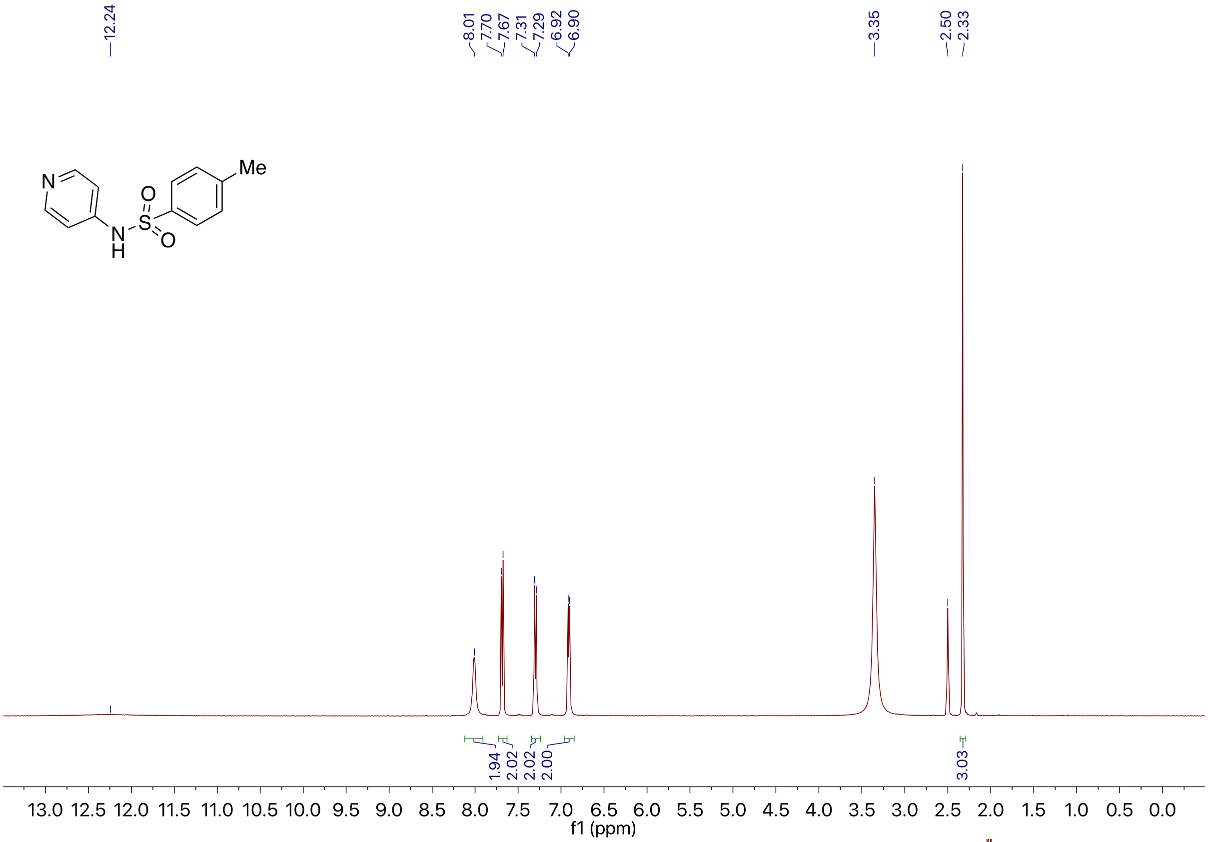
NMR spectra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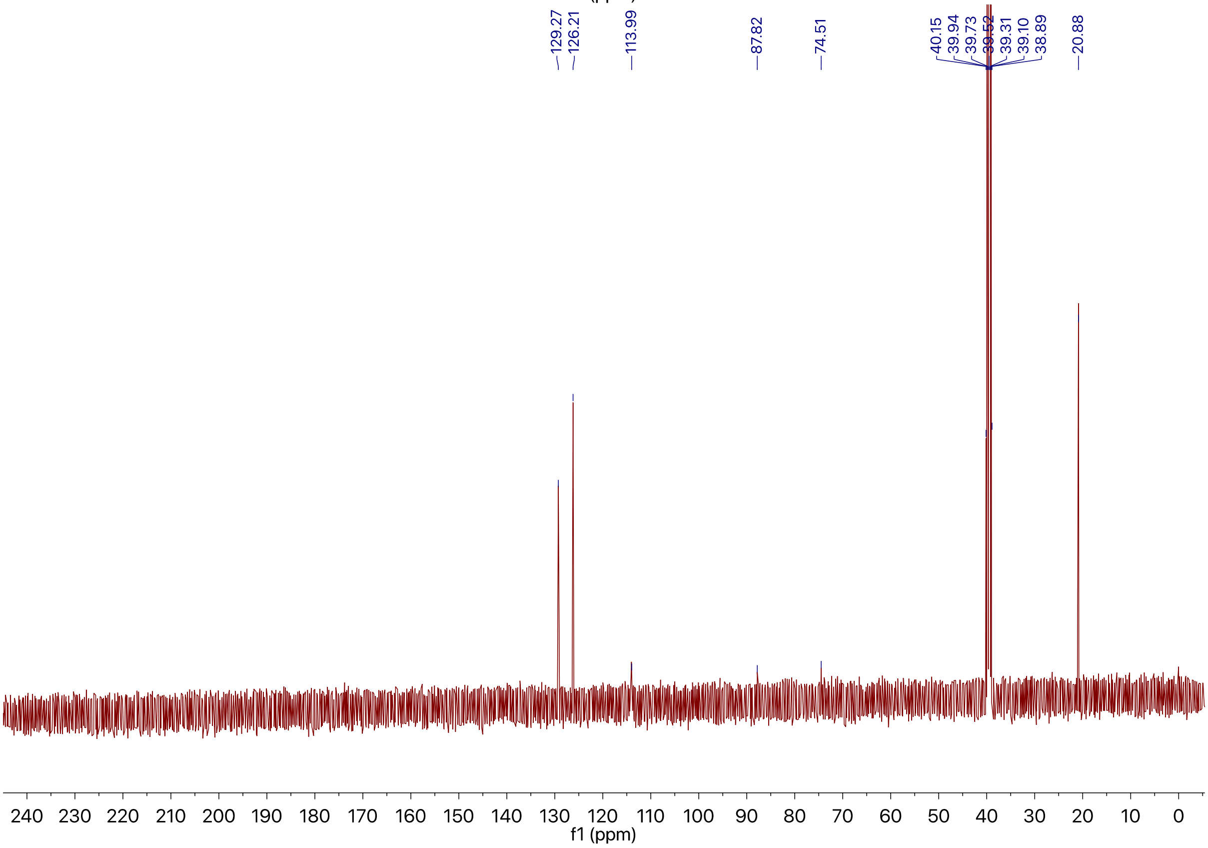
8.01
7.70
7.67
7.31
7.29
6.92
6.90
3.35
2.50
2.33
Me
N
O
S
O
N
H
1.94
2.02
2.02
2.00
3.03
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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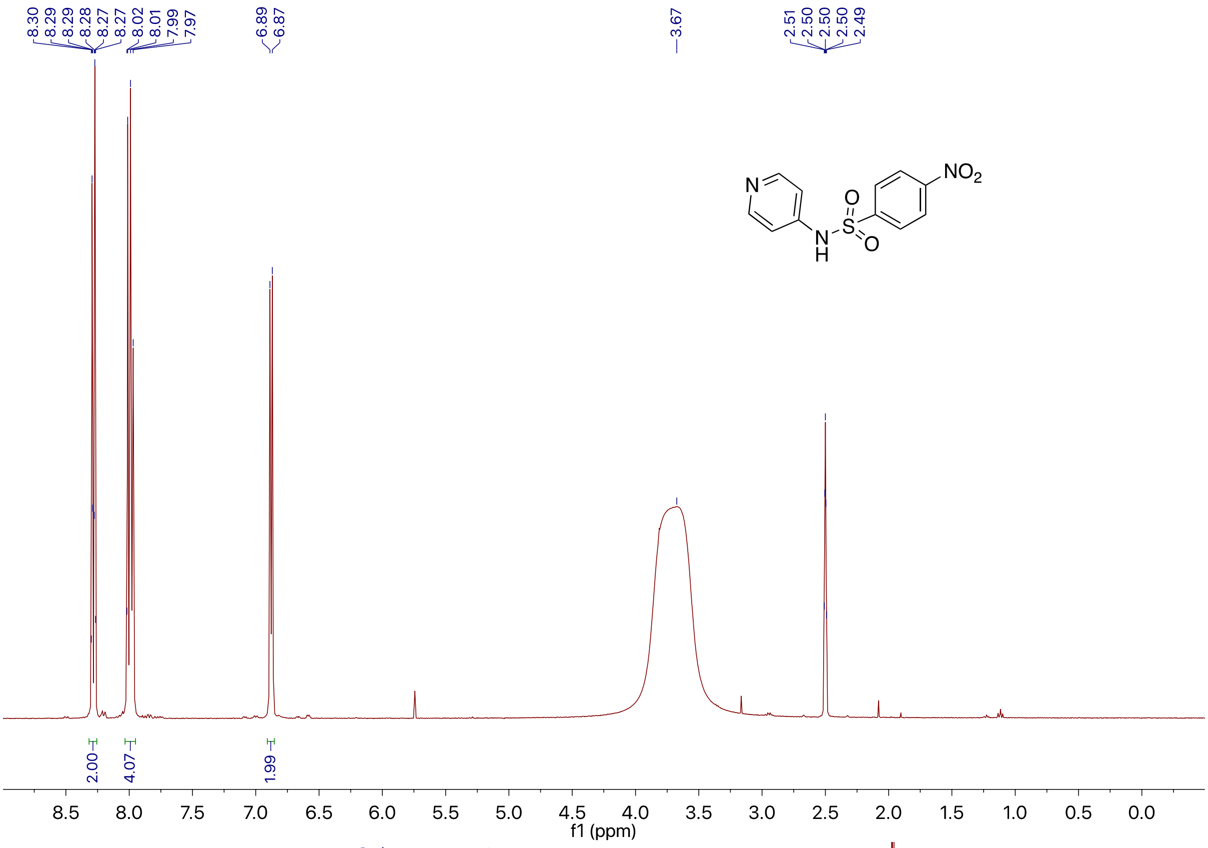
126.21
113.99
87.82
74.51
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.88
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.01
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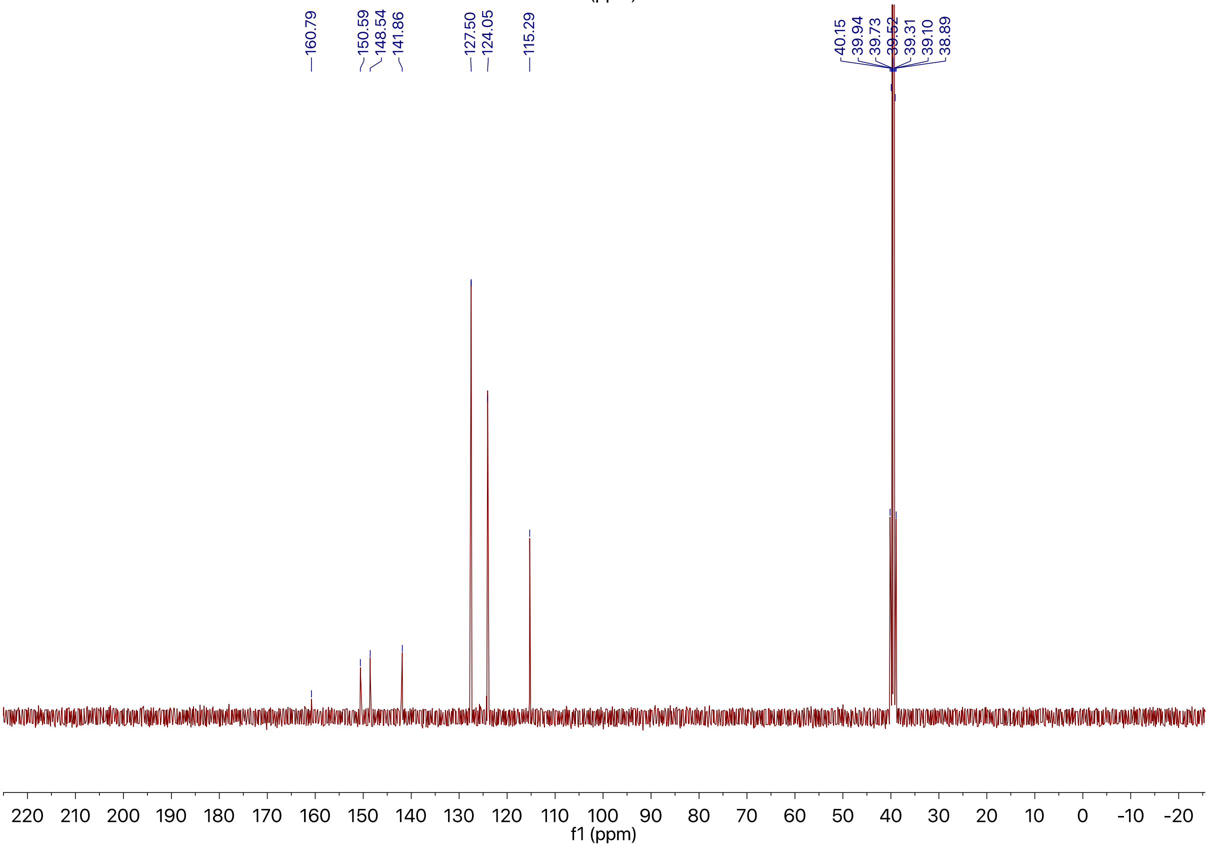
2.50
2.50
2.50
2.49
NO2
N
O
S
N
H
O
2.00
4.07
1.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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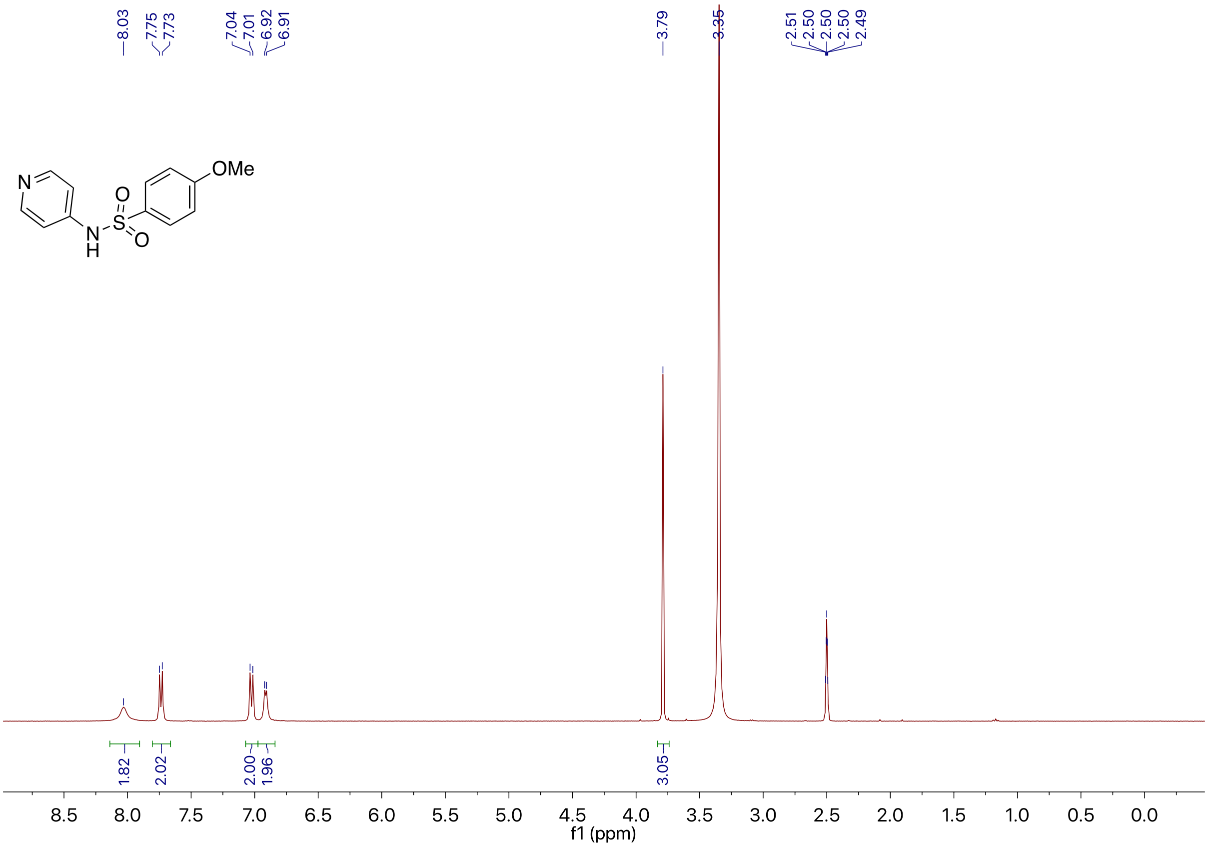
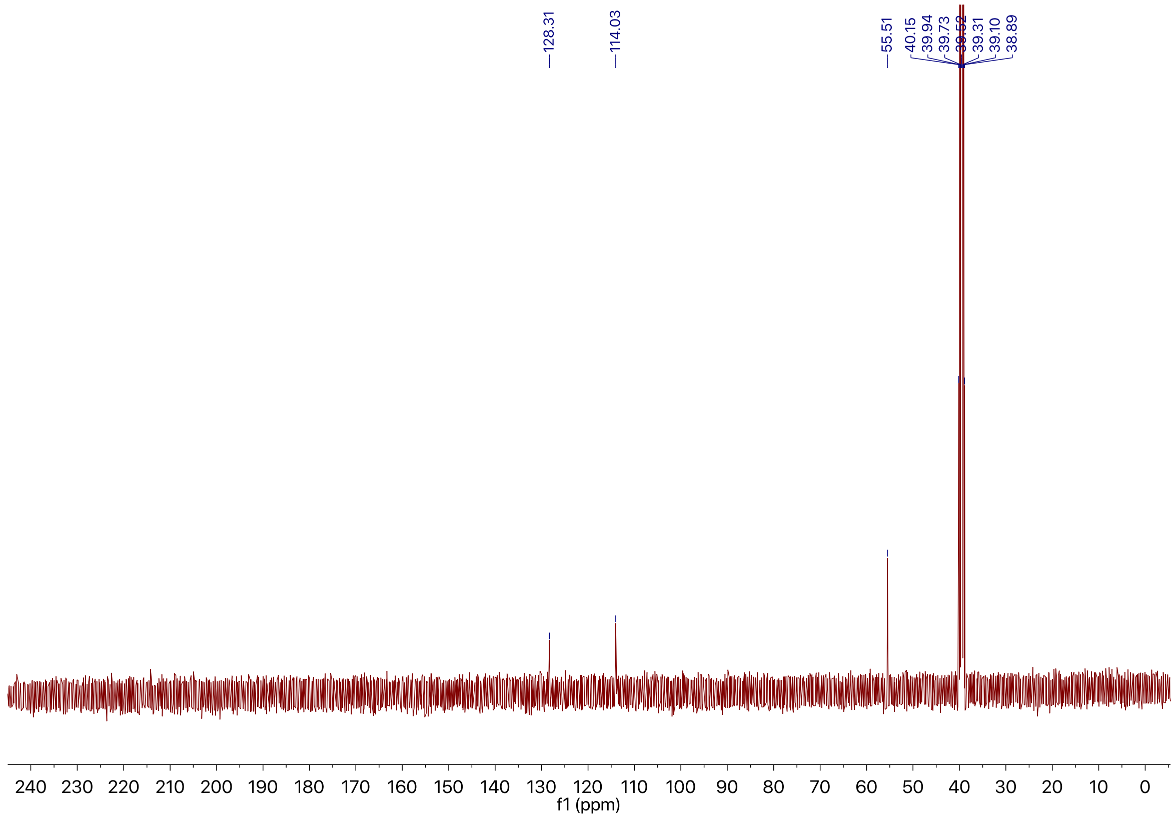
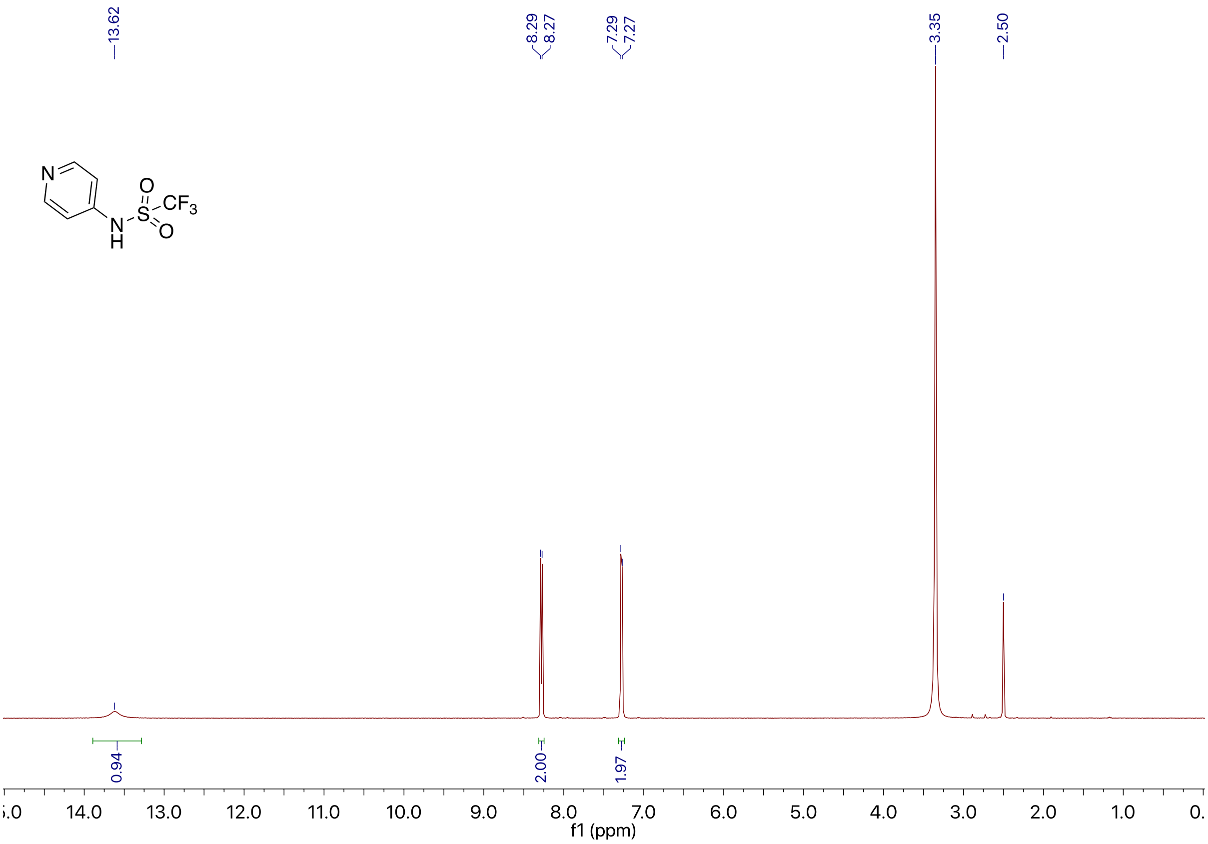
f1 (ppm)



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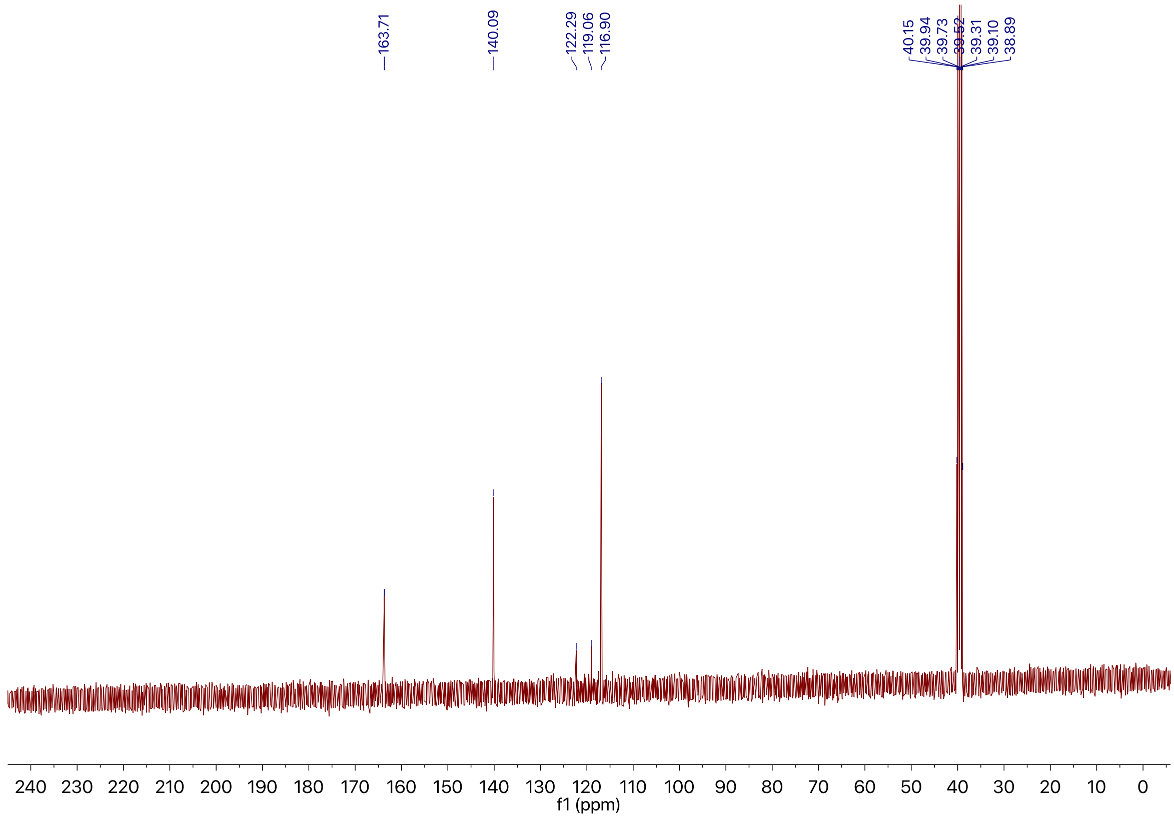
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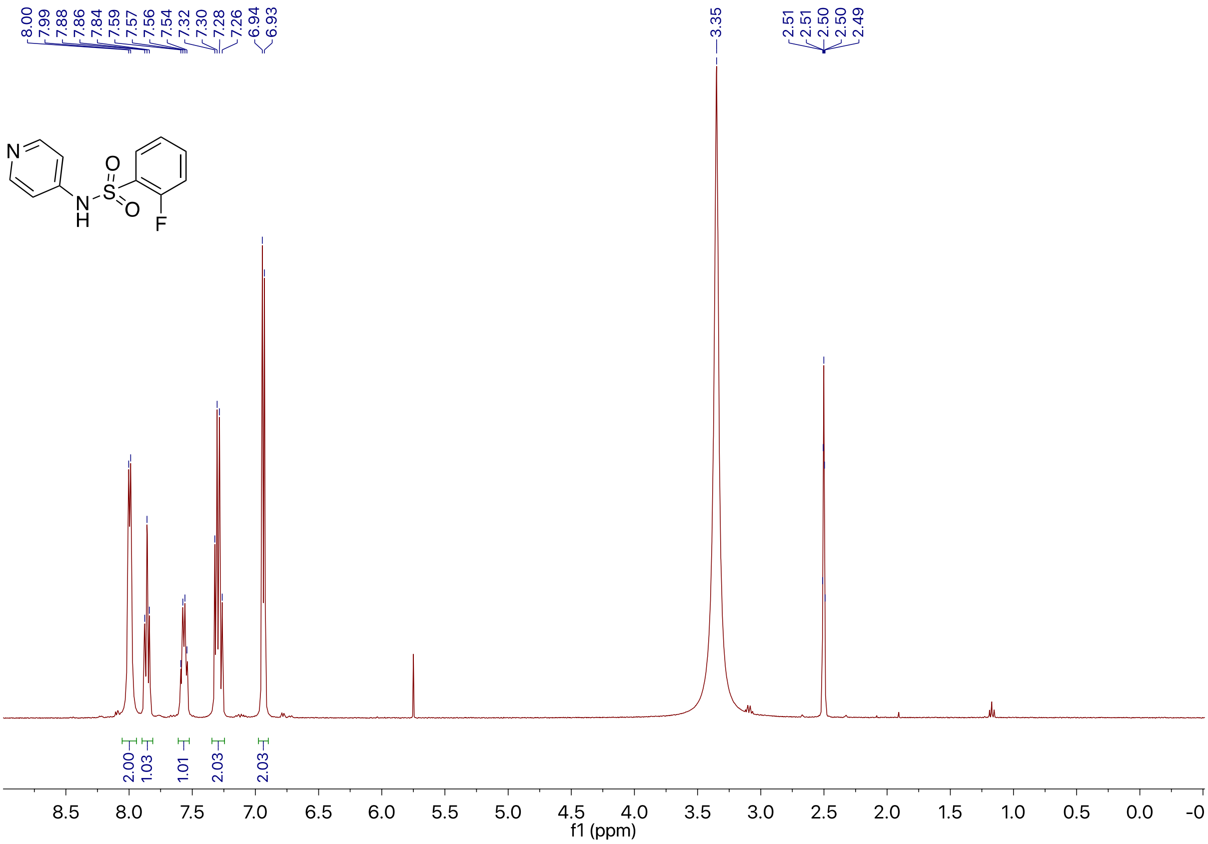
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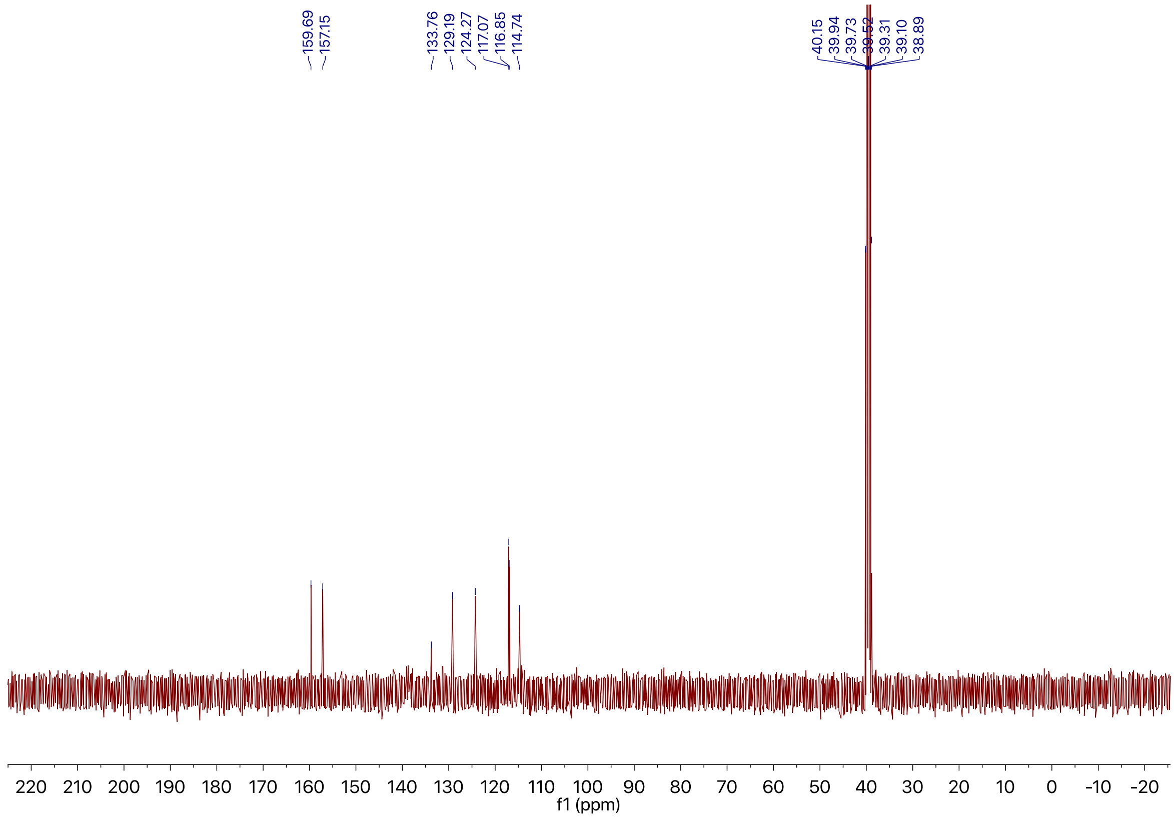
2.51
2.50
2.50
2.49
N
O
S
N
H
O
F
2.00
1.03
1.01
2.03
2.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

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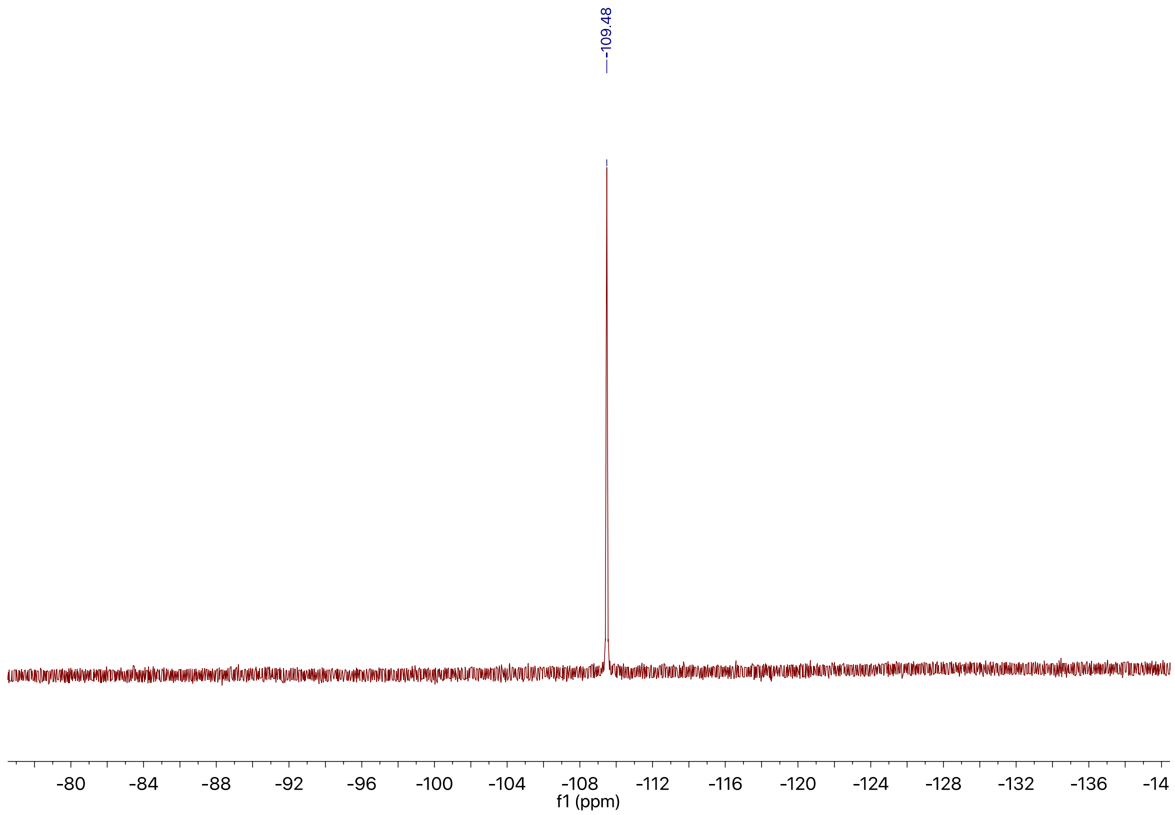
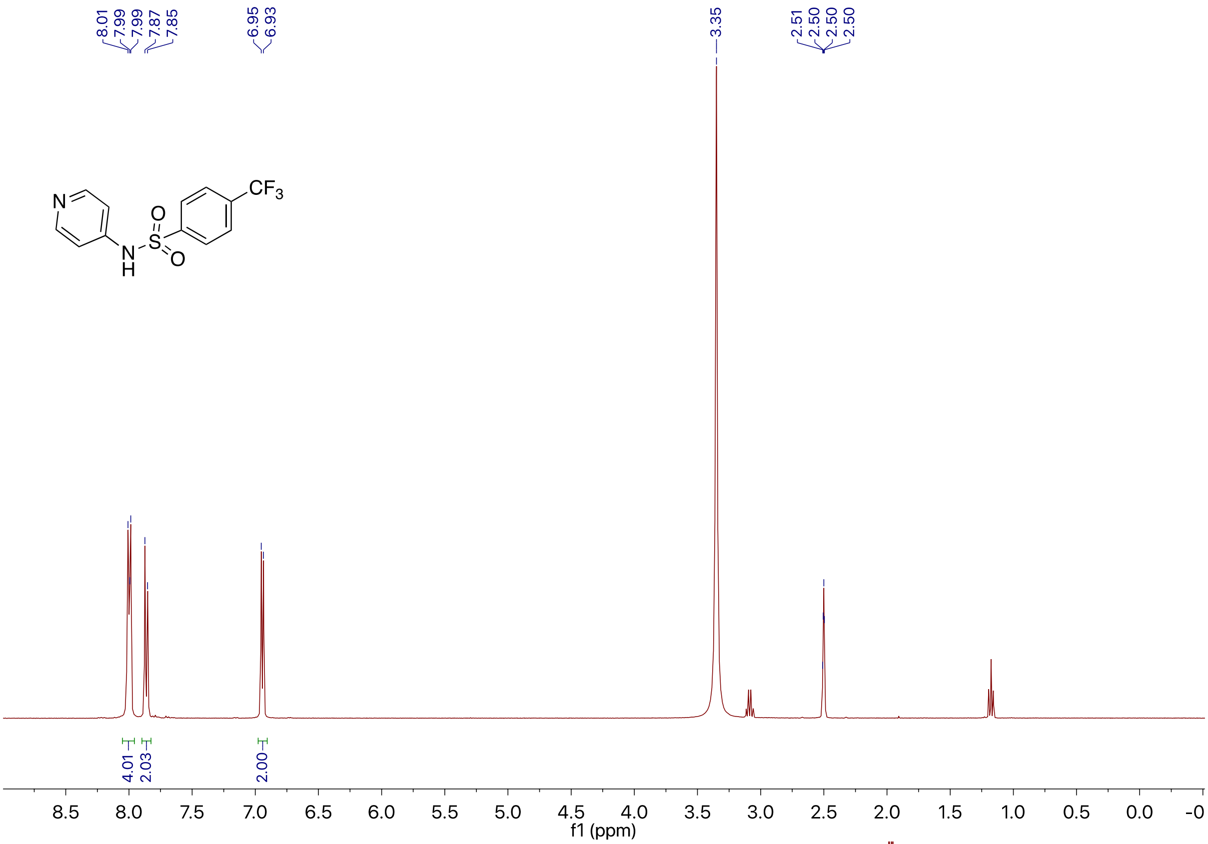
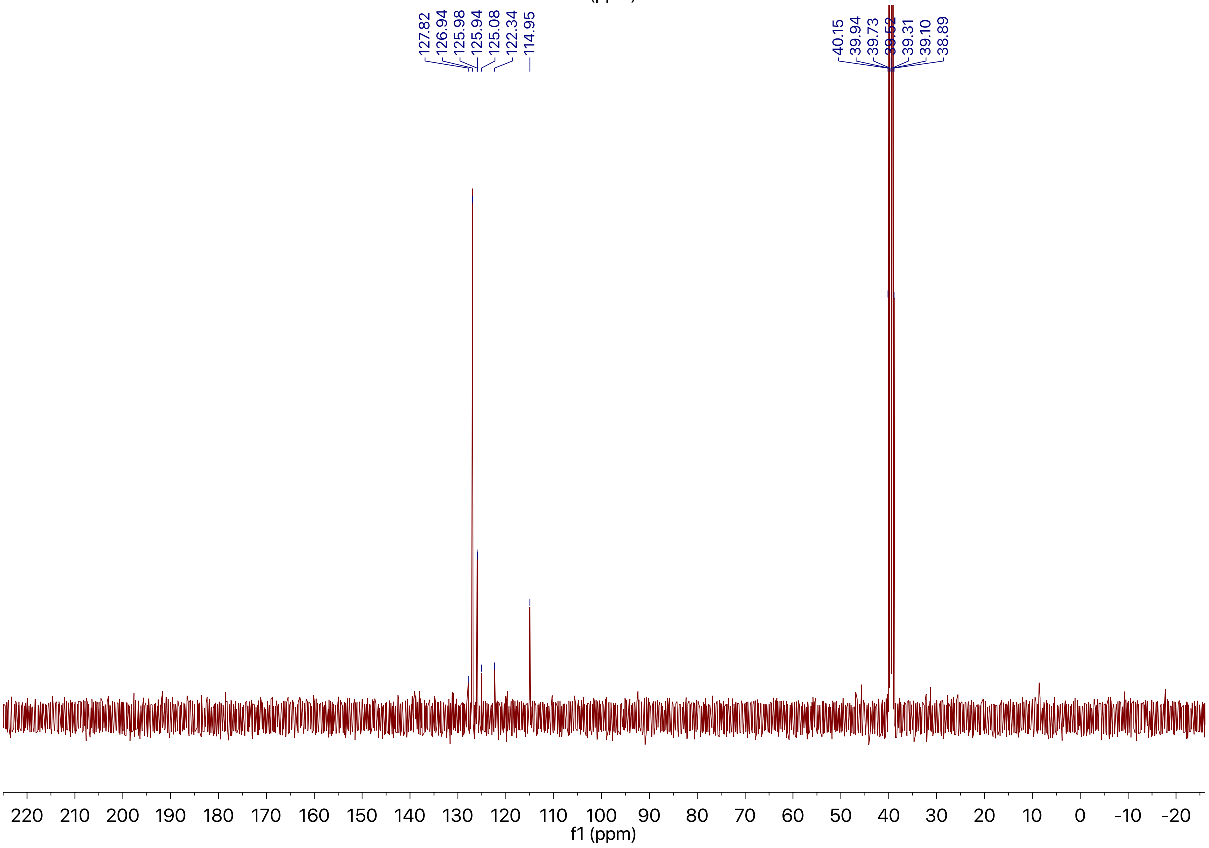
157.15
133.76
129.19
124.27
117.07
116.85
114.74
40.15
39.94
39.73
39.52
39.31
39.10
38.89
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

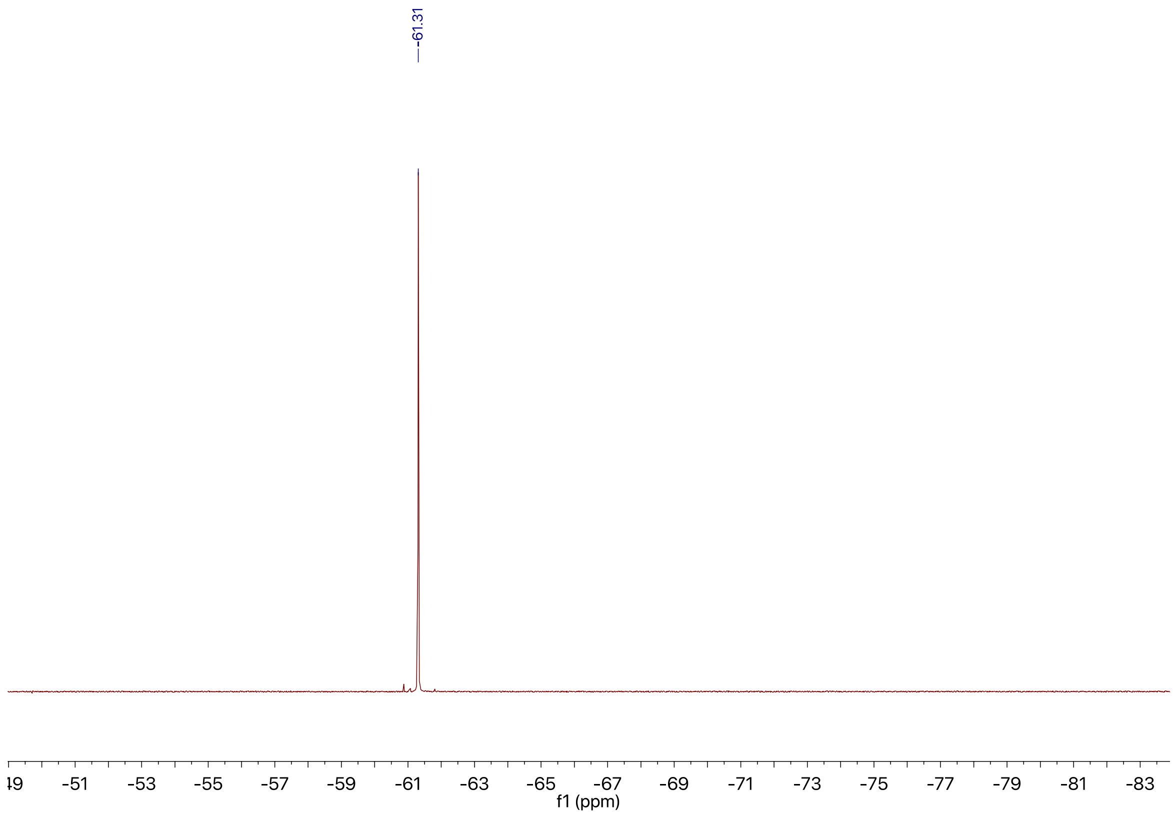

-109.48
-80
-84
-88
-92
-96
-100
-104
-108
-112
-116
-120
-124
-128
-132
-136
-14
f1 (ppm)



8.01
7.99
7.99
7.87
7.85
6.95
6.93
3.35
2.51
2.50
2.50
2.50
CF3
N
N
H
S
O
O
4.01
2.03
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)



127.82
126.94
125.98
125.94
125.08
122.34
114.95
40.15
39.94
39.73
39.52
39.31
39.10
38.89
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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-49
-51
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-55
-57
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-61
-63
-65
-67
-69
-71
-73
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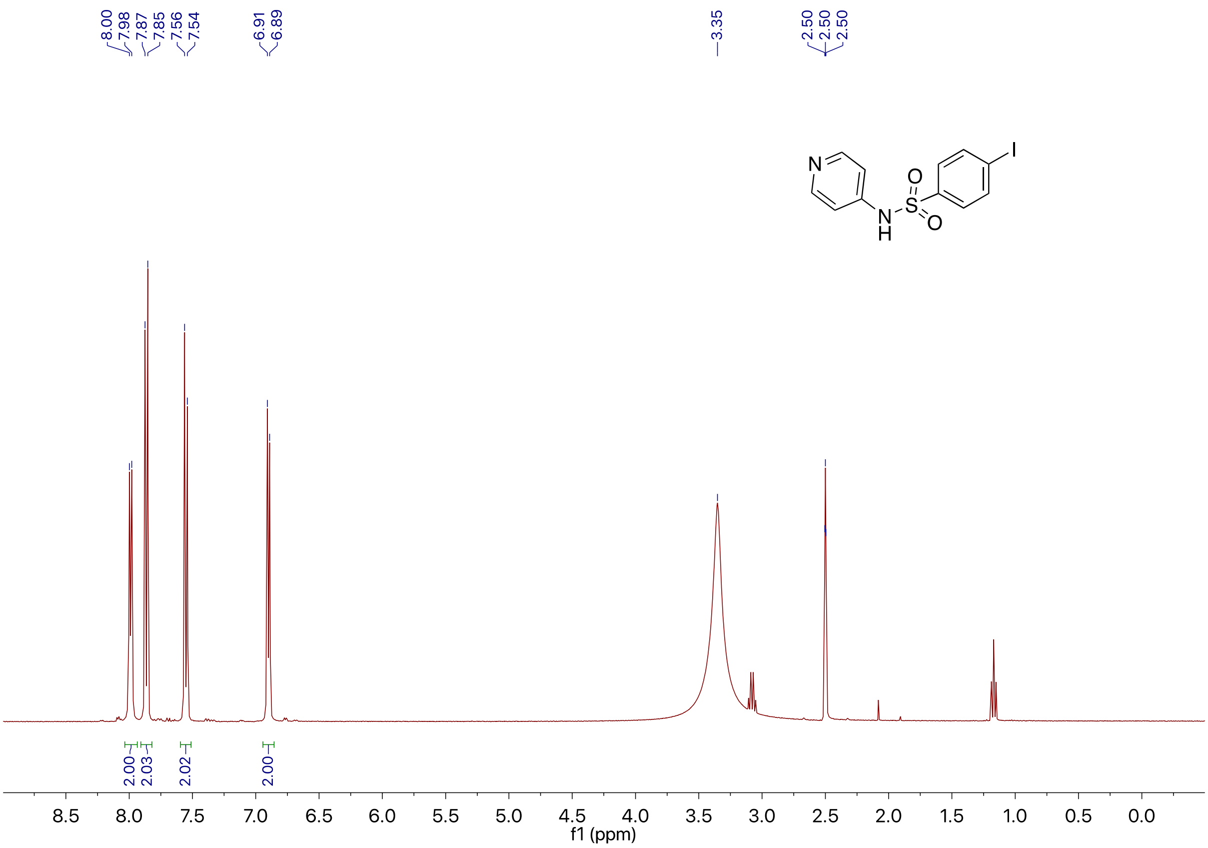
-81
-83
f1 (ppm)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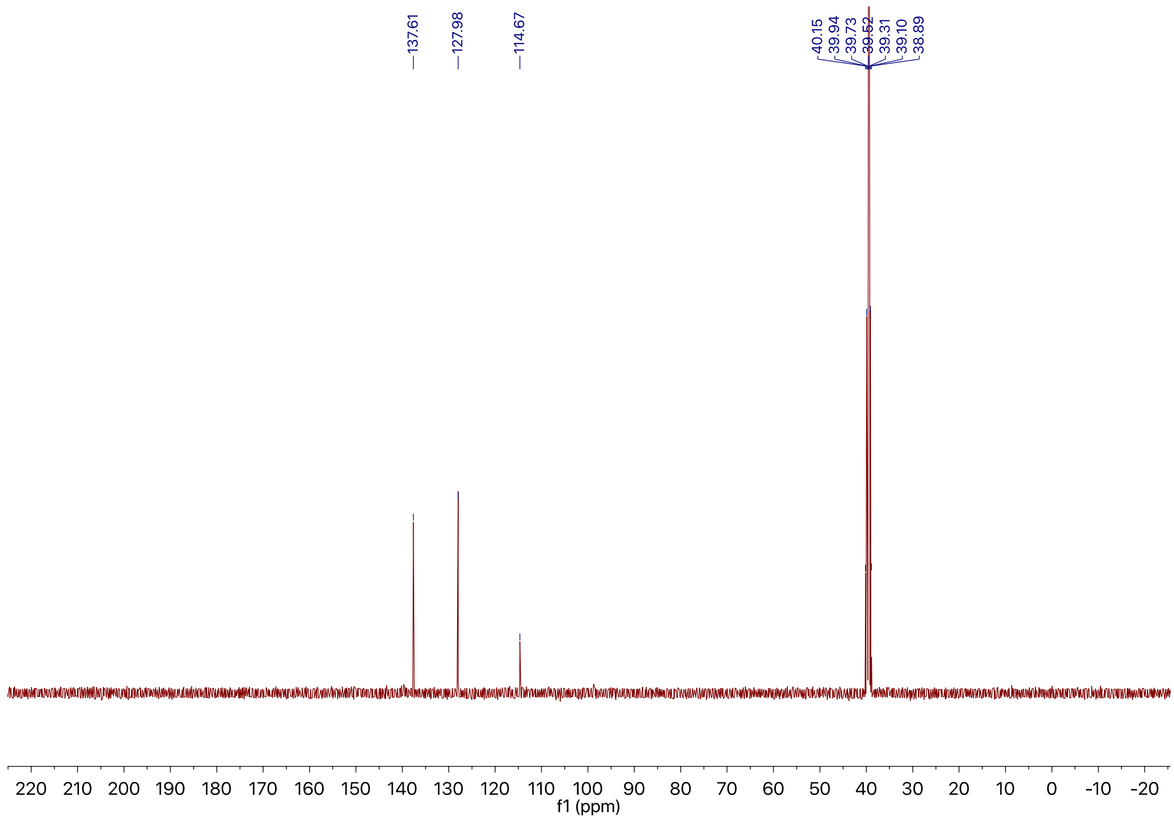
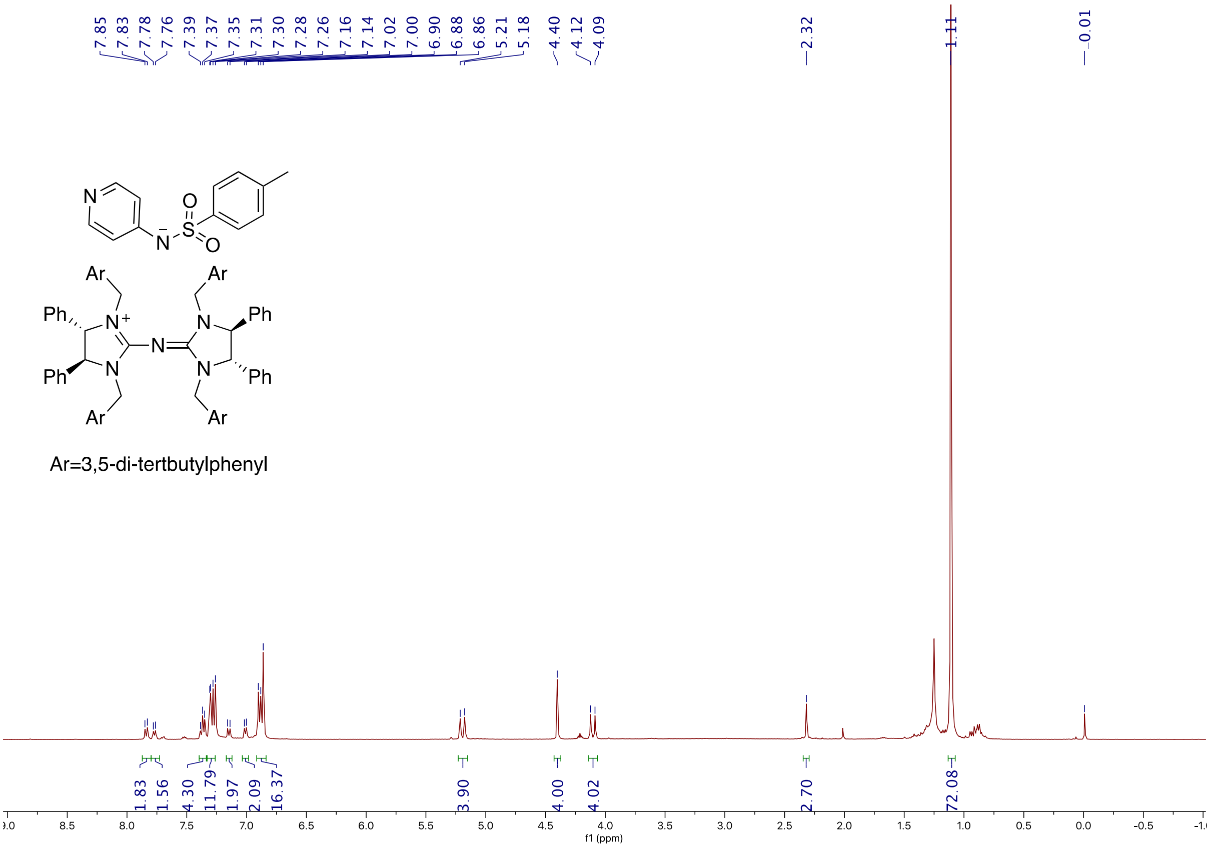
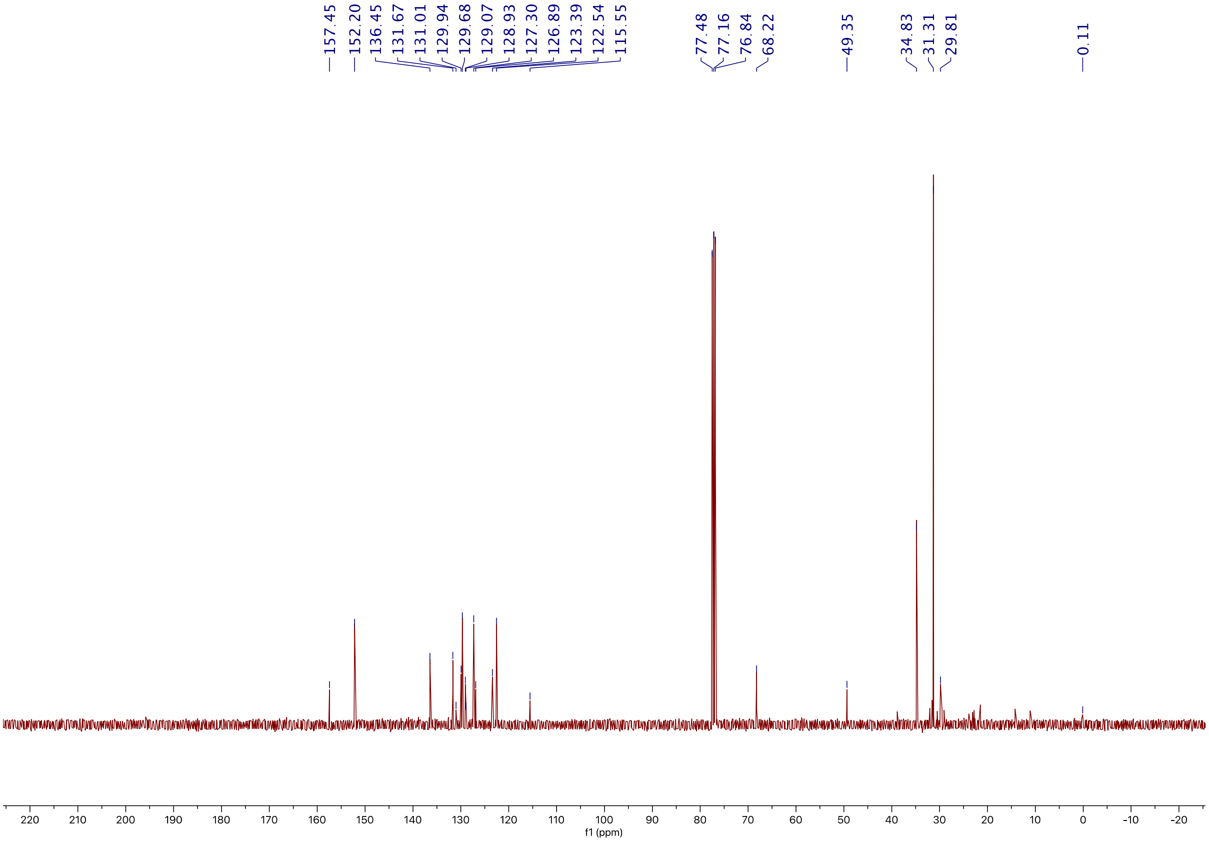
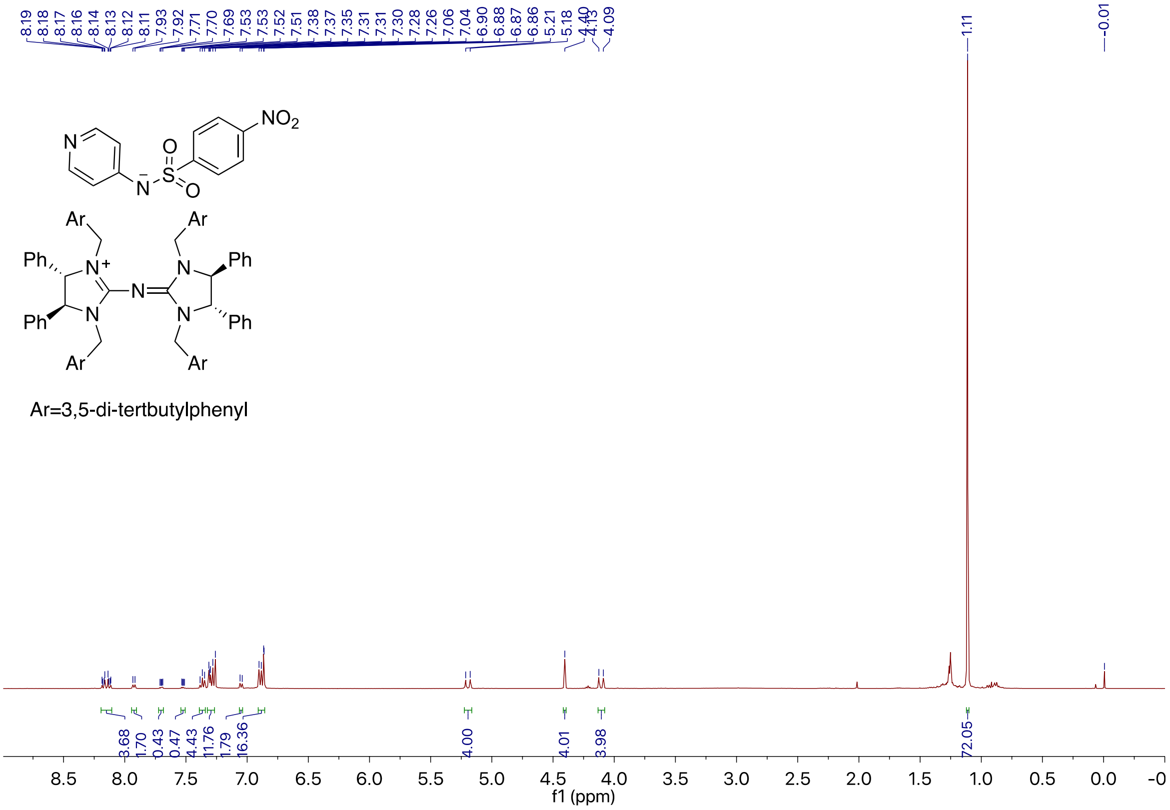
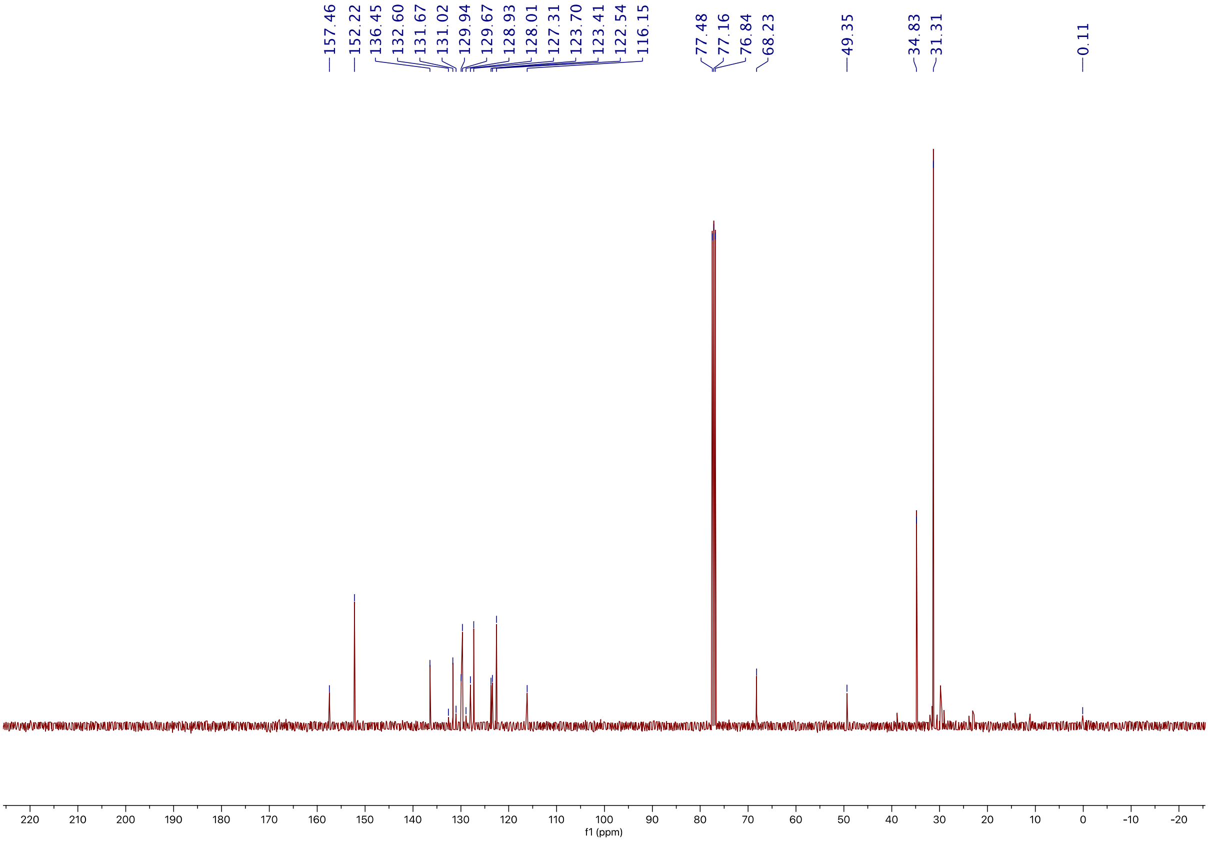
7.98
7.87
7.85
7.56
7.54
6.91
6.89
3.35
2.50
2.50
2.50
2.00
2.03
2.02
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

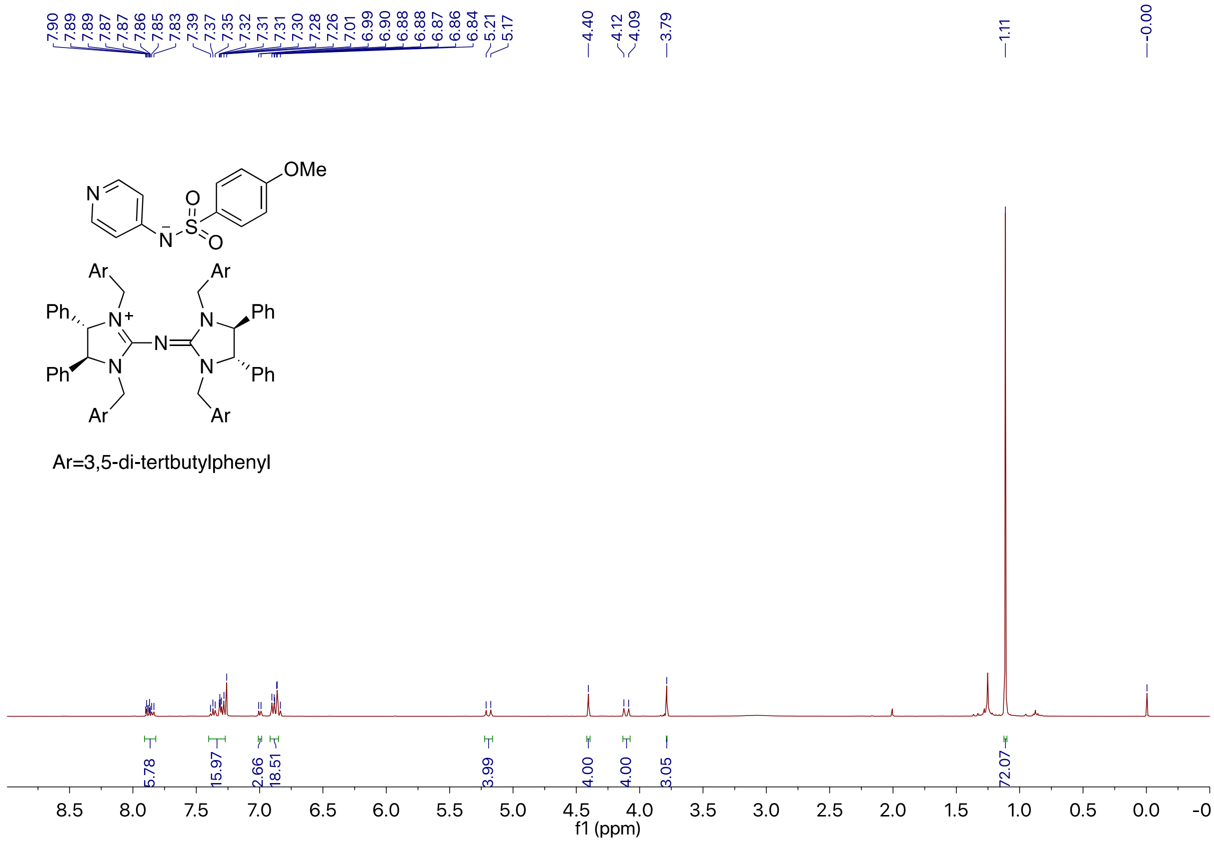

137.61
127.98
114.67
40.15
39.94
39.73
39.52
39.31
39.10
38.89
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

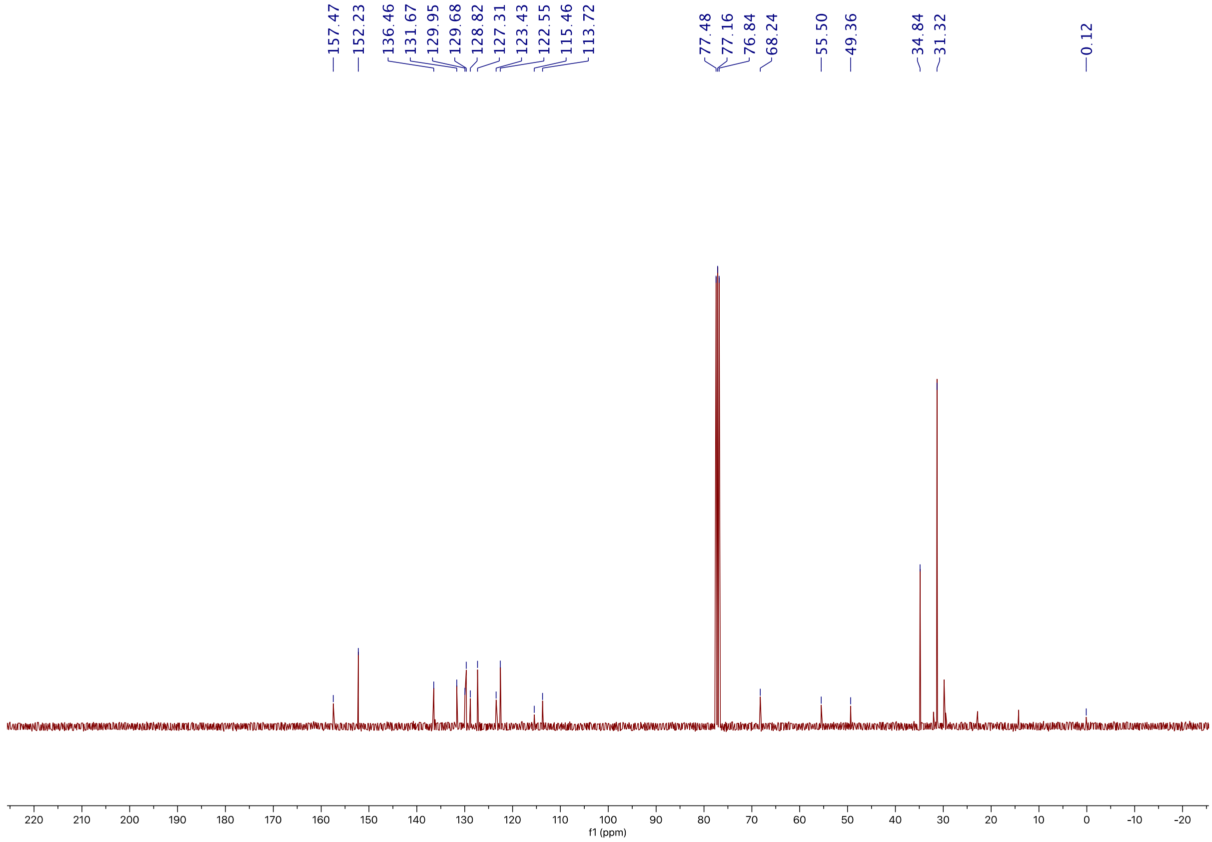

7.85 7.83 7.78 7.76 7.39 7.37 7.35 7.31 7.30 7.28 7.26 7.16 7.14 7.02 7.00 6.90 6.88 6.86 5.21 5.18 4.40 4.12 4.09
2.32
1.11
-0.01
Ar=3,5-di-tertbutylphenyl
1.83 1.56 4.30 11.79 1.97 2.09 16.37 3.90 4.00 4.02 2.70 72.08
f1 (ppm)

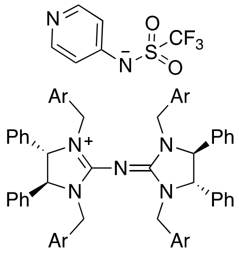

157.45 152.20 136.45 131.67 131.01 129.94 129.68 129.07 128.93 127.30 126.89 123.39 122.54 115.55
77.48 77.16 76.84 68.22
49.35
34.83 31.31 29.81
0.11
f1 (ppm)


8.19 8.18 8.17 8.16 8.14 8.13 8.12 8.11 7.93 7.92 7.71 7.70 7.69 7.53 7.53 7.52 7.51 7.38 7.37 7.35 7.31 7.31 7.30 7.28 7.26 7.06 7.04 6.90 6.88 6.87 6.86 5.21 5.18 4.40 4.13 4.09
1.11
-0.01
Ar=3,5-di-tertbutylphenyl
3.68 1.70 0.43 0.47 4.43 11.76 1.79 16.36
4.00
4.01
3.98
72.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

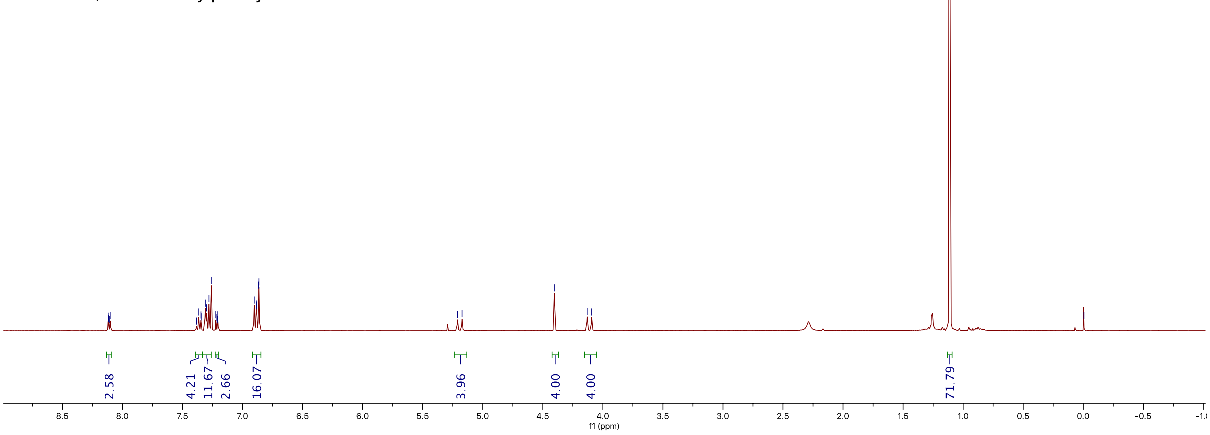

157.46 152.22 136.45 132.60 131.67 131.02 129.94 129.67 128.93 128.01 127.31 123.70 123.41 122.54 116.15
77.48 77.16 76.84 68.23
49.35
34.83 31.31
0.11
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

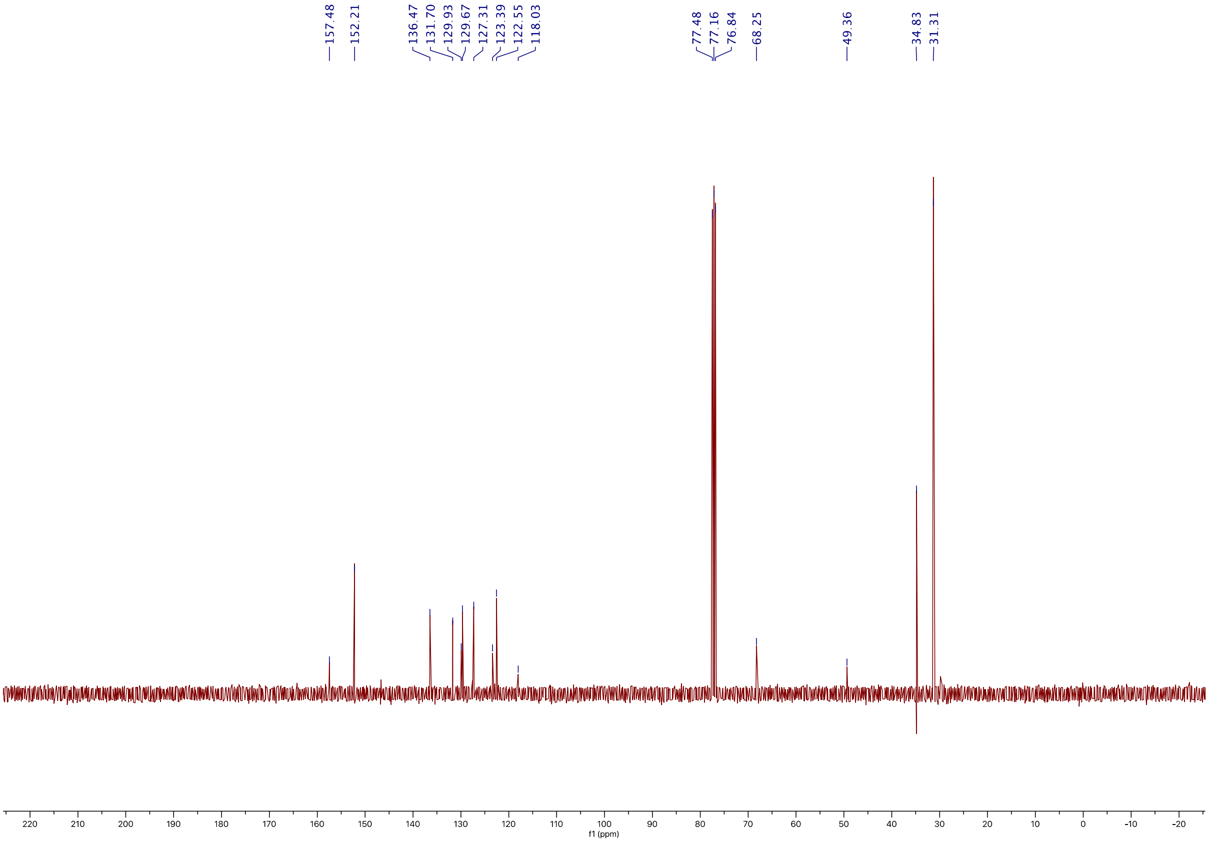

7.90
7.89
7.89
7.87
7.86
7.85
7.83
7.39
7.37
7.35
7.32
7.31
7.31
7.30
7.28
7.26
7.01
6.99
6.90
6.88
6.88
6.87
6.86
6.84
5.21
5.17
4.40
4.12
4.09
3.79
1.11
0.00
OMe
N
O
S
N
O
Ar
Ar
Ph
N+
N
Ph
N
N
Ph
N
Ph
Ar
Ar
Ar=3,5-di-tertbutylphenyl
5.78
15.97
2.66
18.51
3.99
4.00
4.00
3.05
72.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

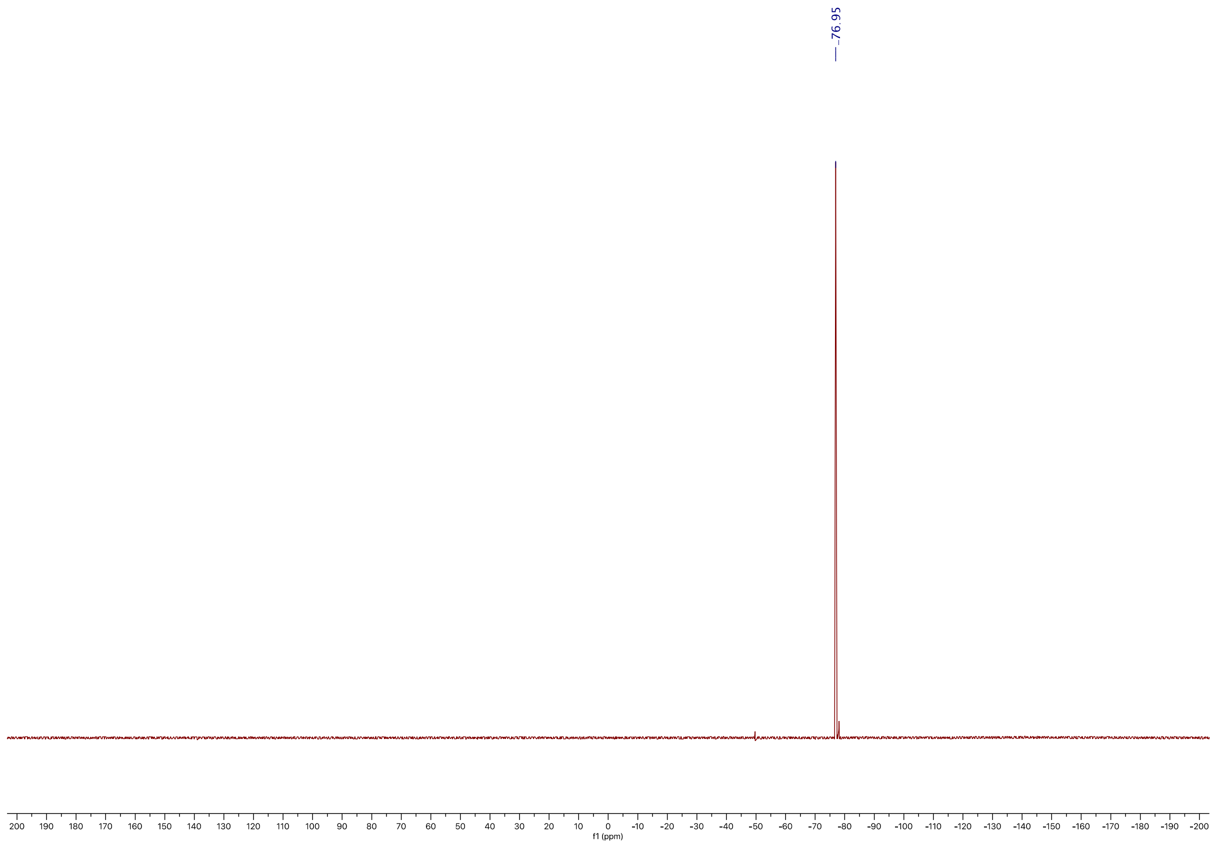

157.47
152.23
136.46
131.67
129.95
129.68
128.82
127.31
123.43
122.55
115.46
113.72
77.48
77.16
76.84
68.24
55.50
49.36
34.84
31.32
0.12
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

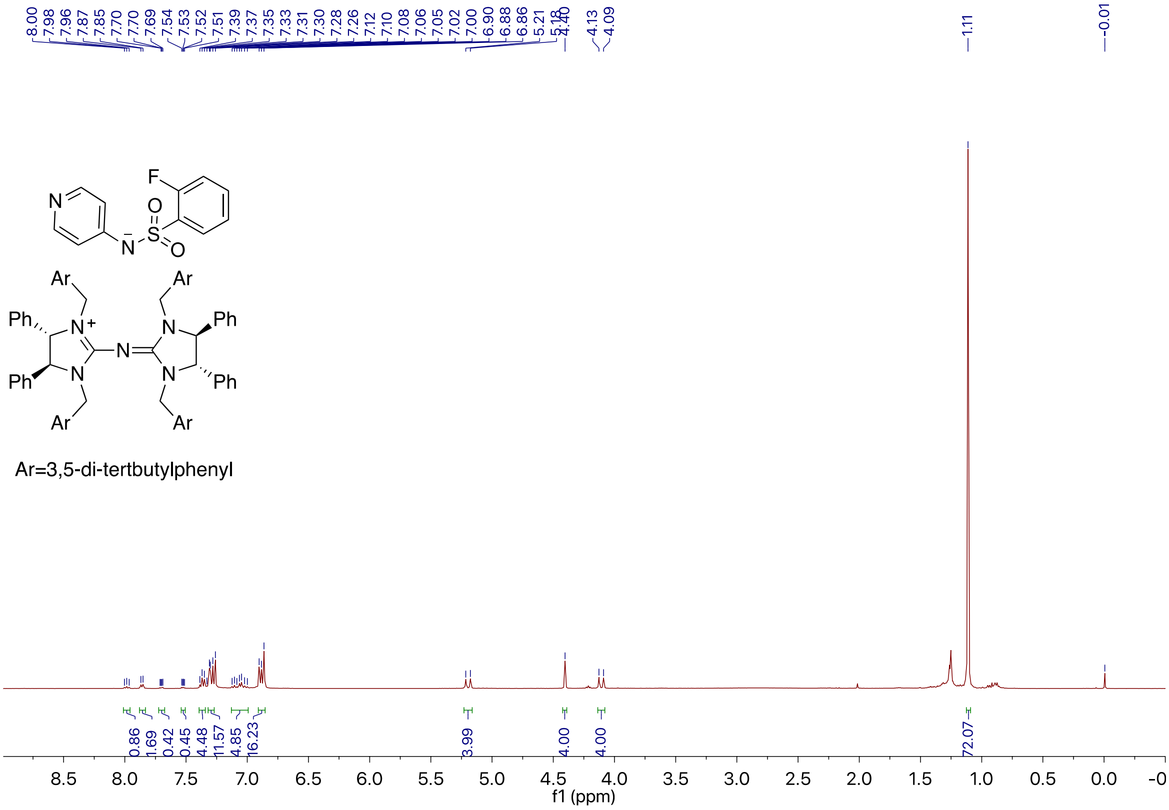


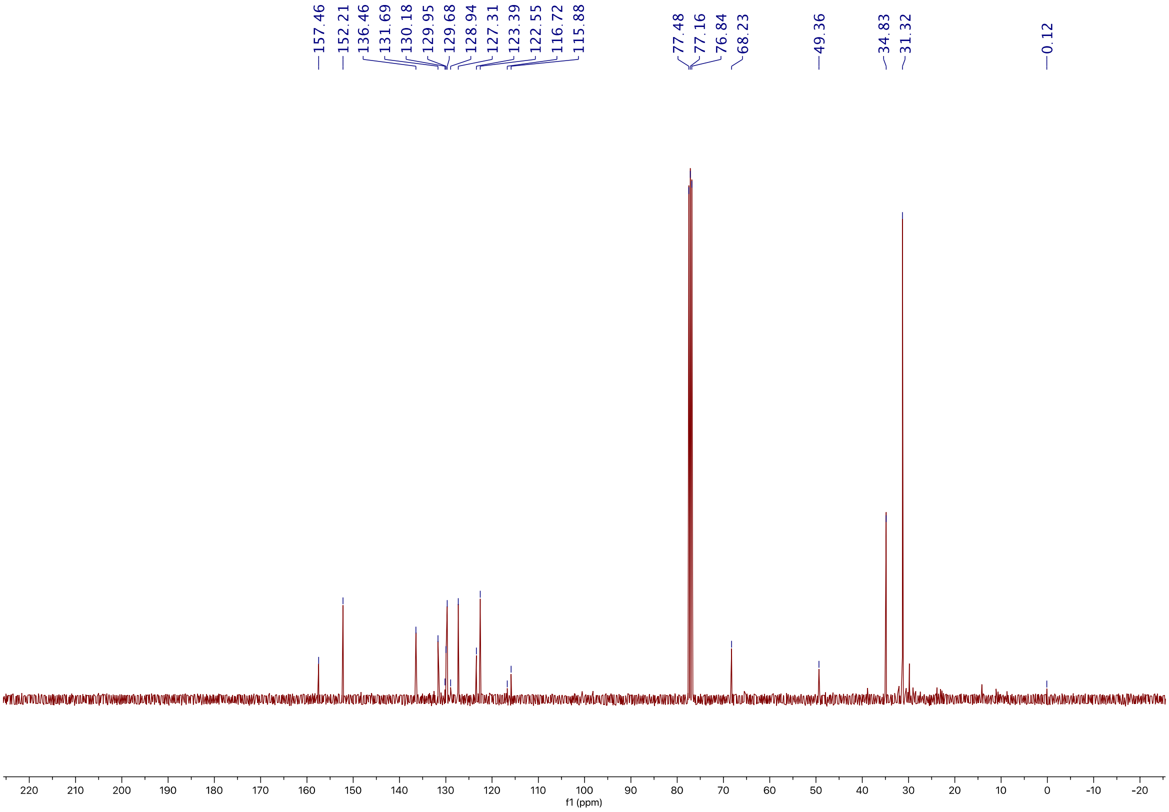
Ar=3,5-di-tertbutylphenyl

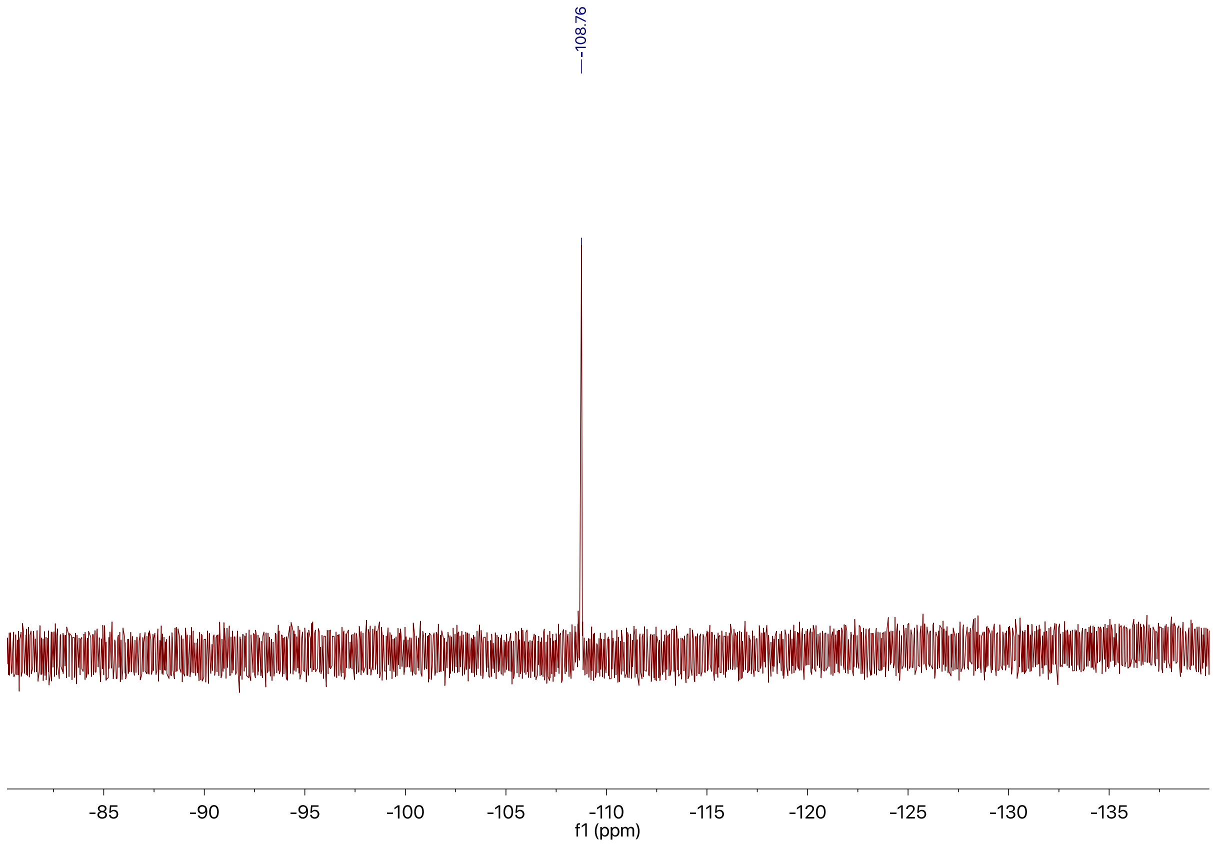


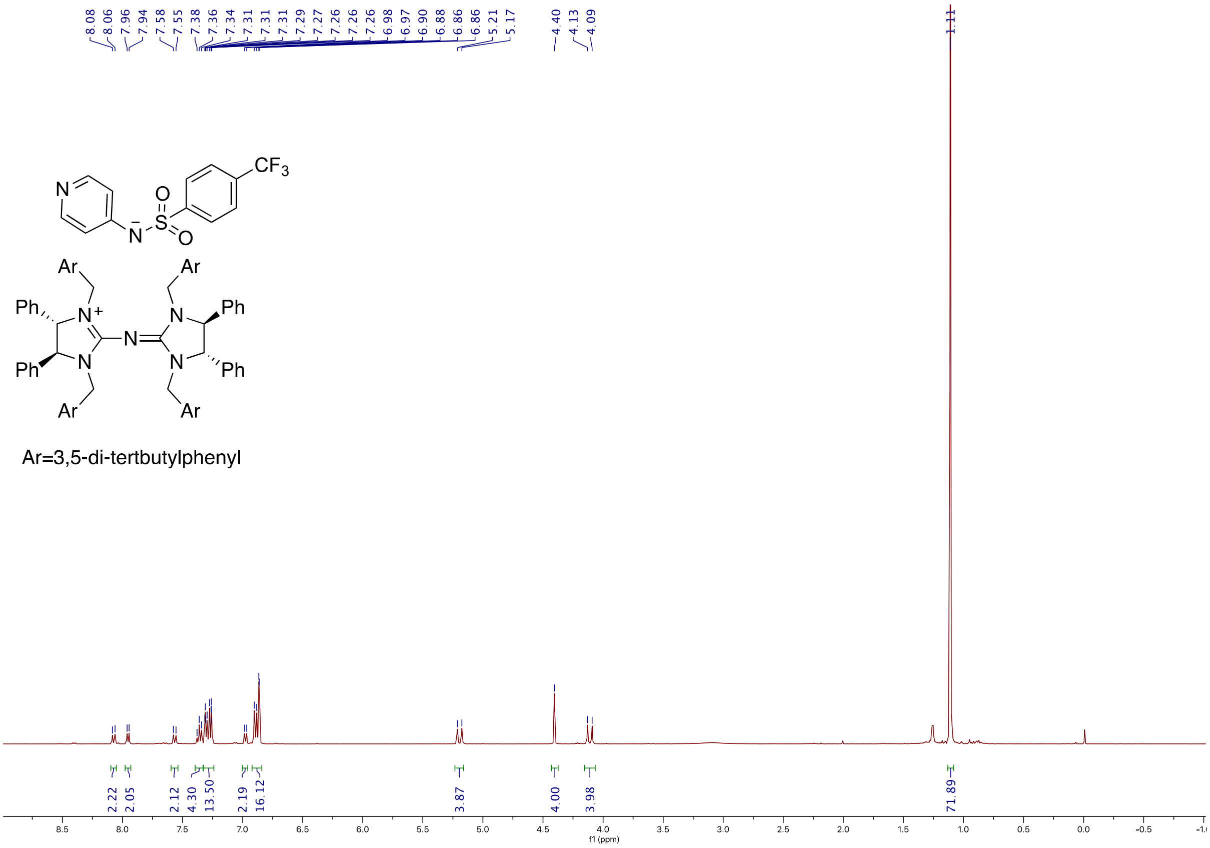



-76.95
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

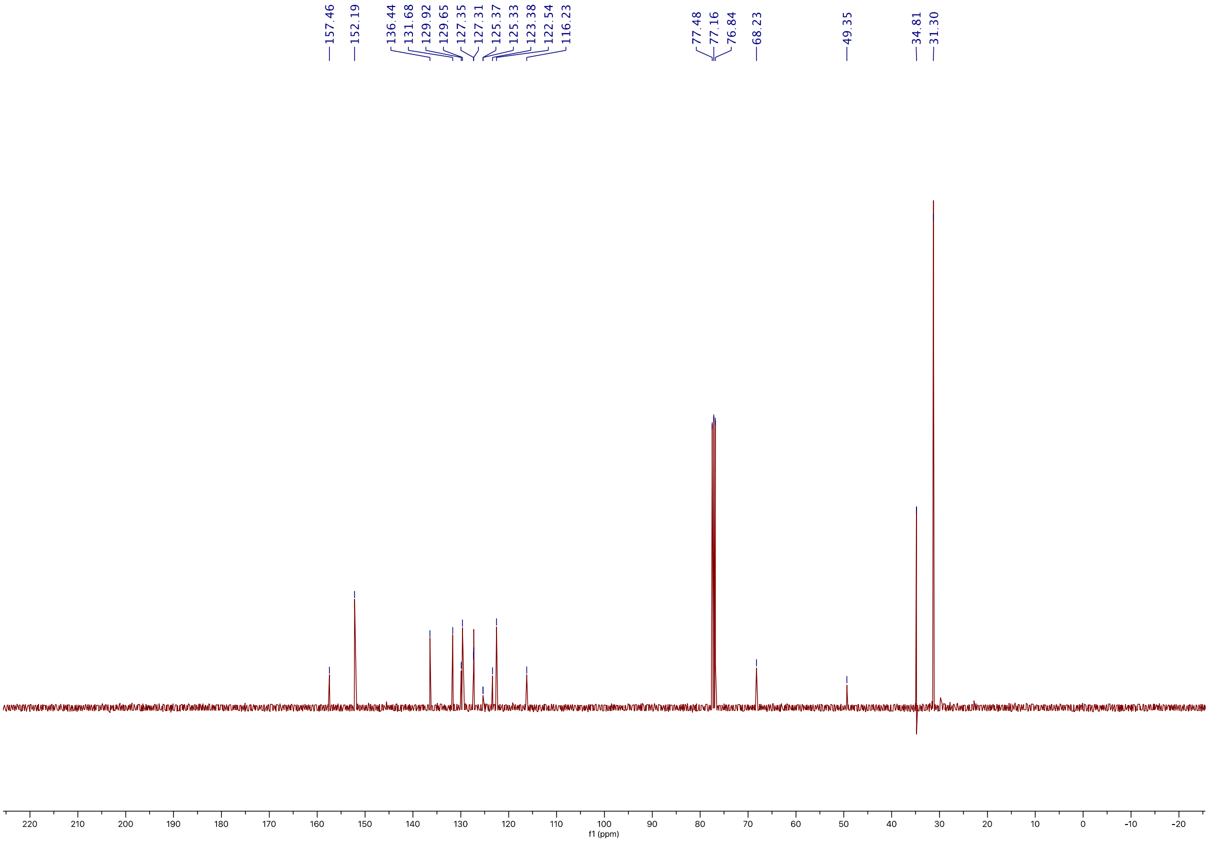

8.00
7.98
7.96
7.87
7.85
7.70
7.69
7.54
7.53
7.52
7.51
7.39
7.37
7.35
7.33
7.31
7.30
7.28
7.26
7.12
7.10
7.08
7.06
7.05
7.02
7.00
6.90
6.88
6.86
5.21
5.18
4.40
4.13
4.09
1.11
-0.01
F
N
O
S
N
O
Ar
Ar
Ph
N+
N
Ph
N
N
Ph
N
Ph
Ar
Ar
Ar=3,5-di-tertbutylphenyl
0.86
1.69
0.42
0.45
4.48
11.57
4.85
16.23
3.99
4.00
4.00
72.07
f1 (ppm)

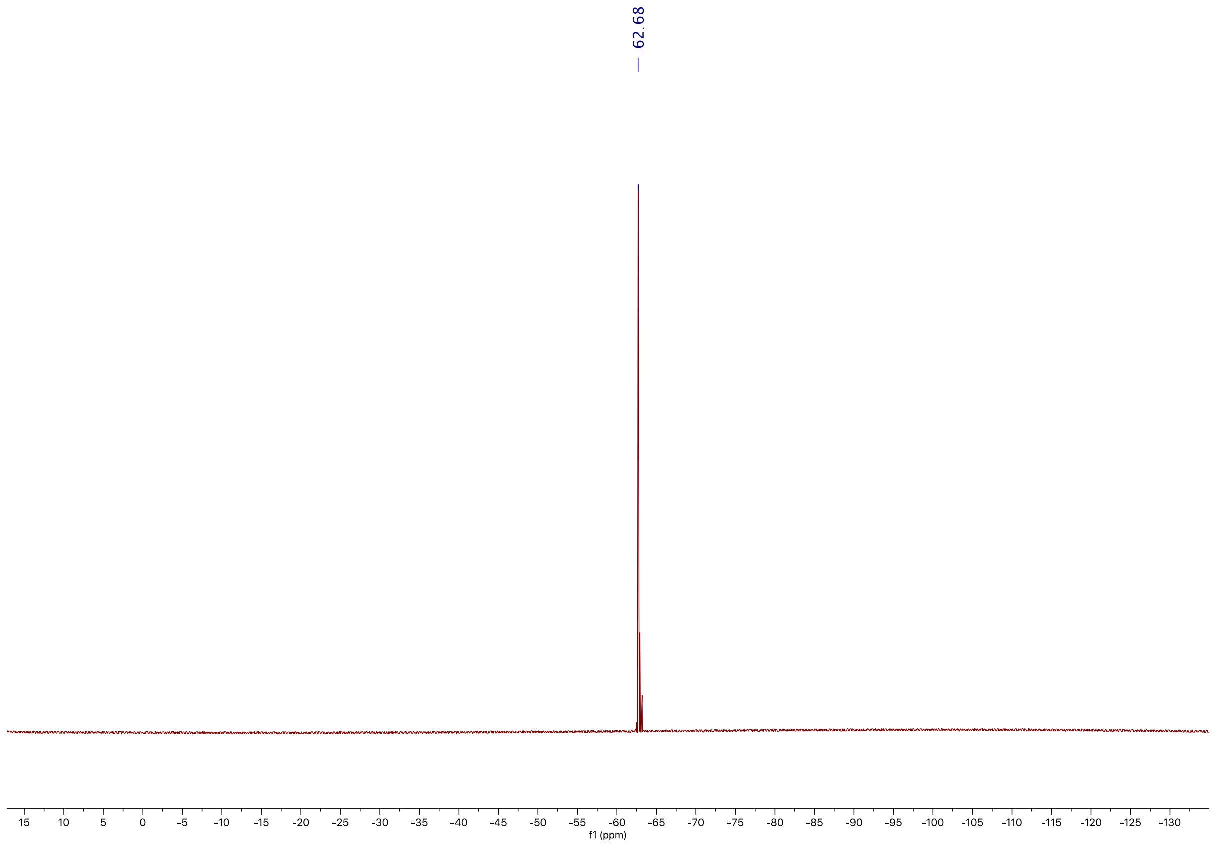

157.46
152.21
136.46
131.69
130.18
129.95
129.68
128.94
127.31
123.39
122.55
116.72
115.88
77.48
77.16
76.84
68.23
49.36
34.83
31.32
0.12
f1 (ppm)


-108.76
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
f1 (ppm)

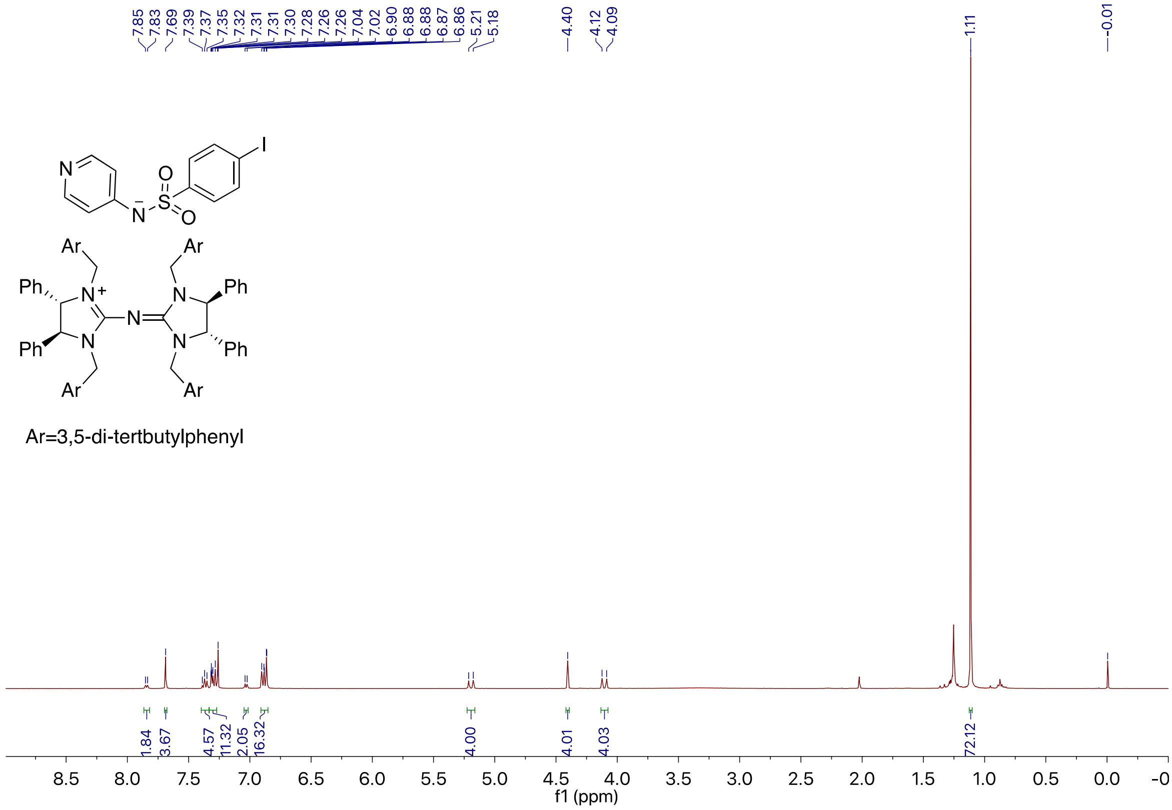


Ar=3,5-di-tertbutylphenyl

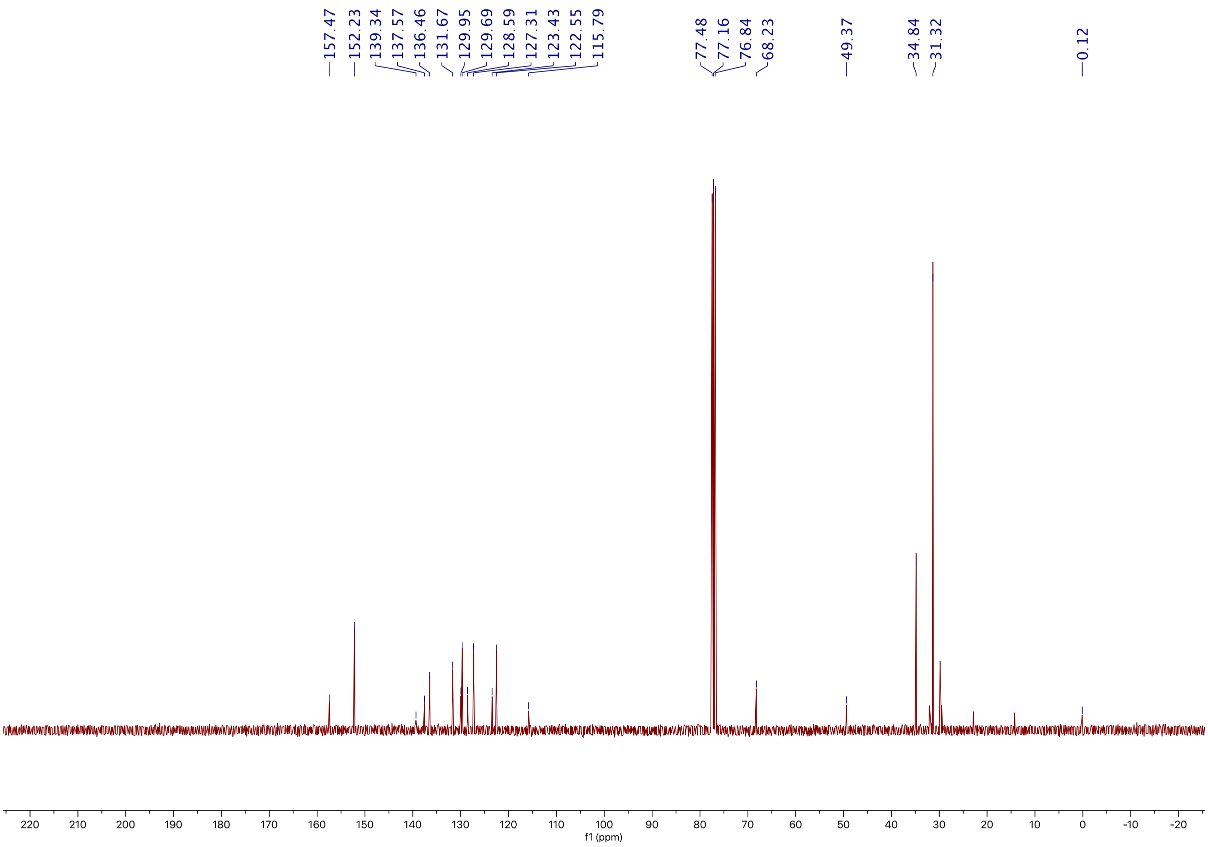


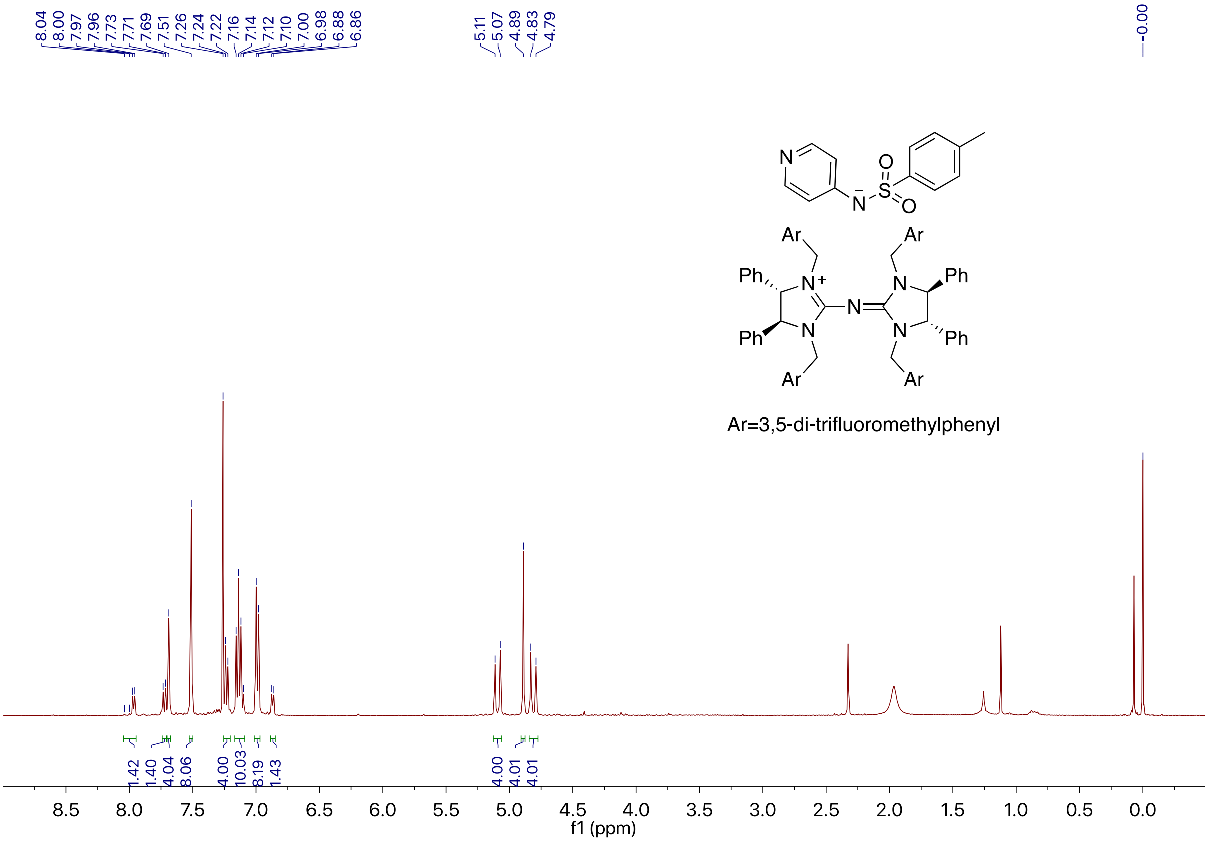


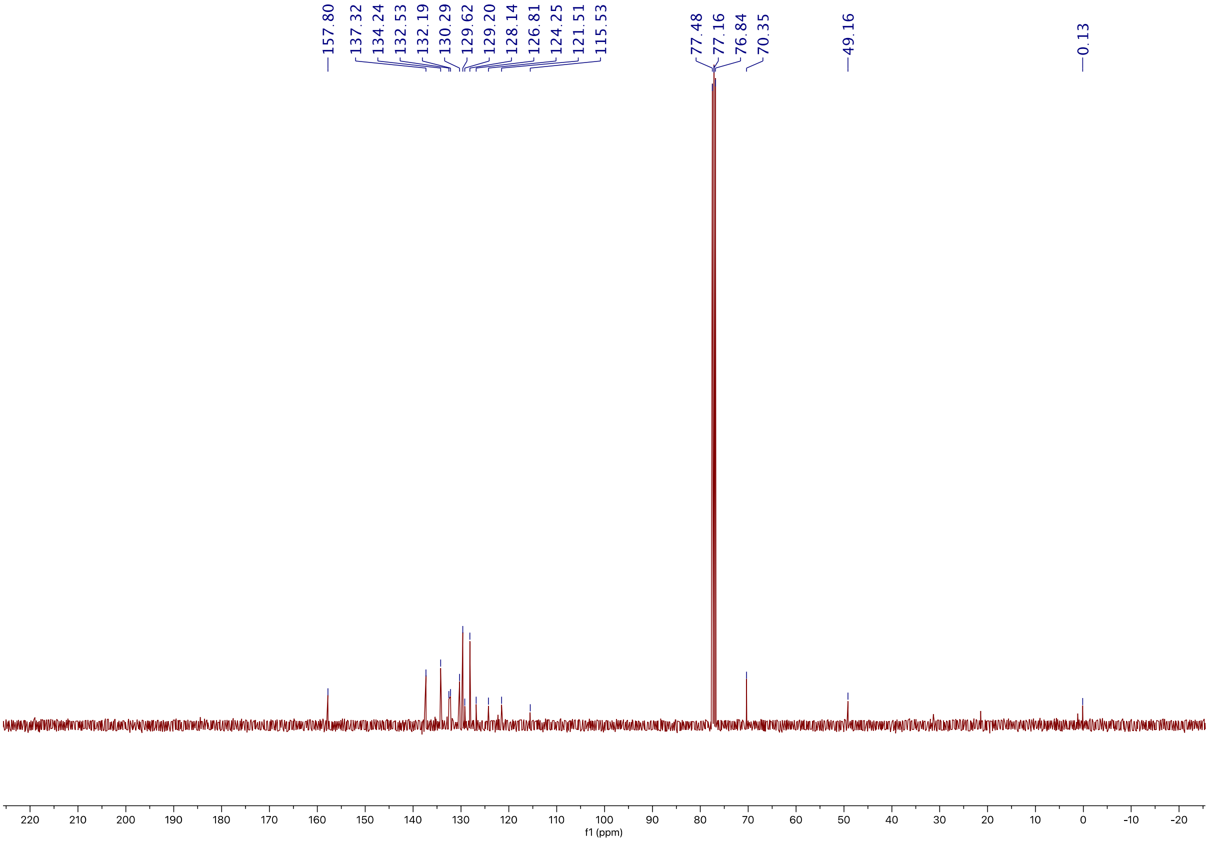
—-62.68
15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

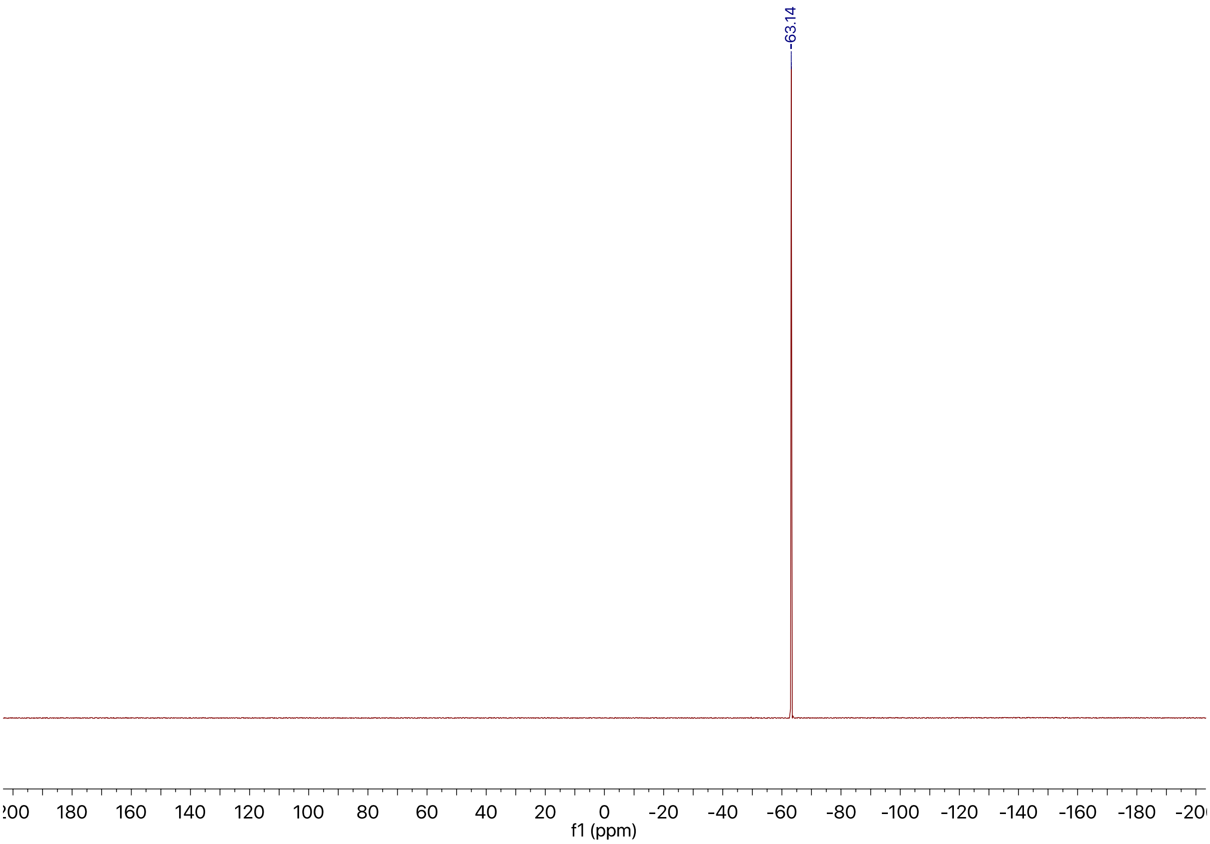


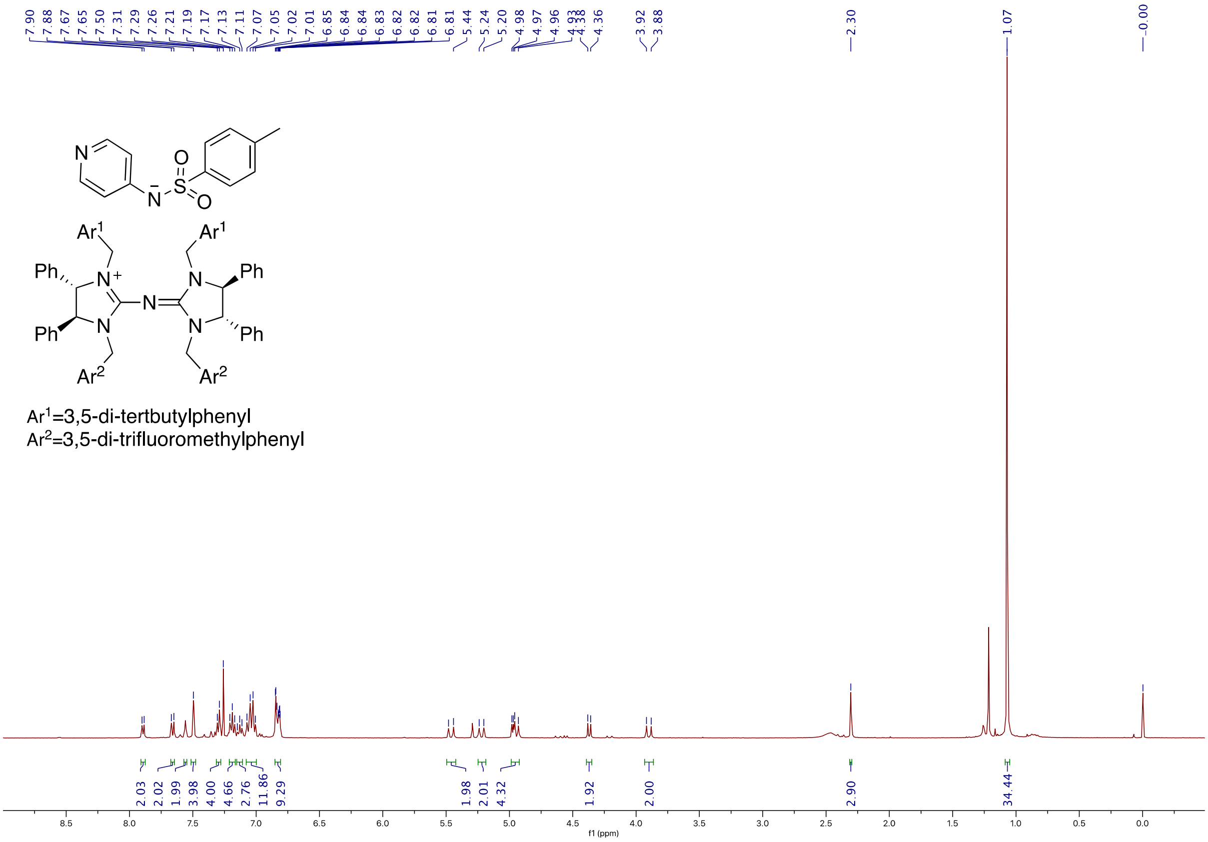
Ar=3,5-di-tertbutylphenyl



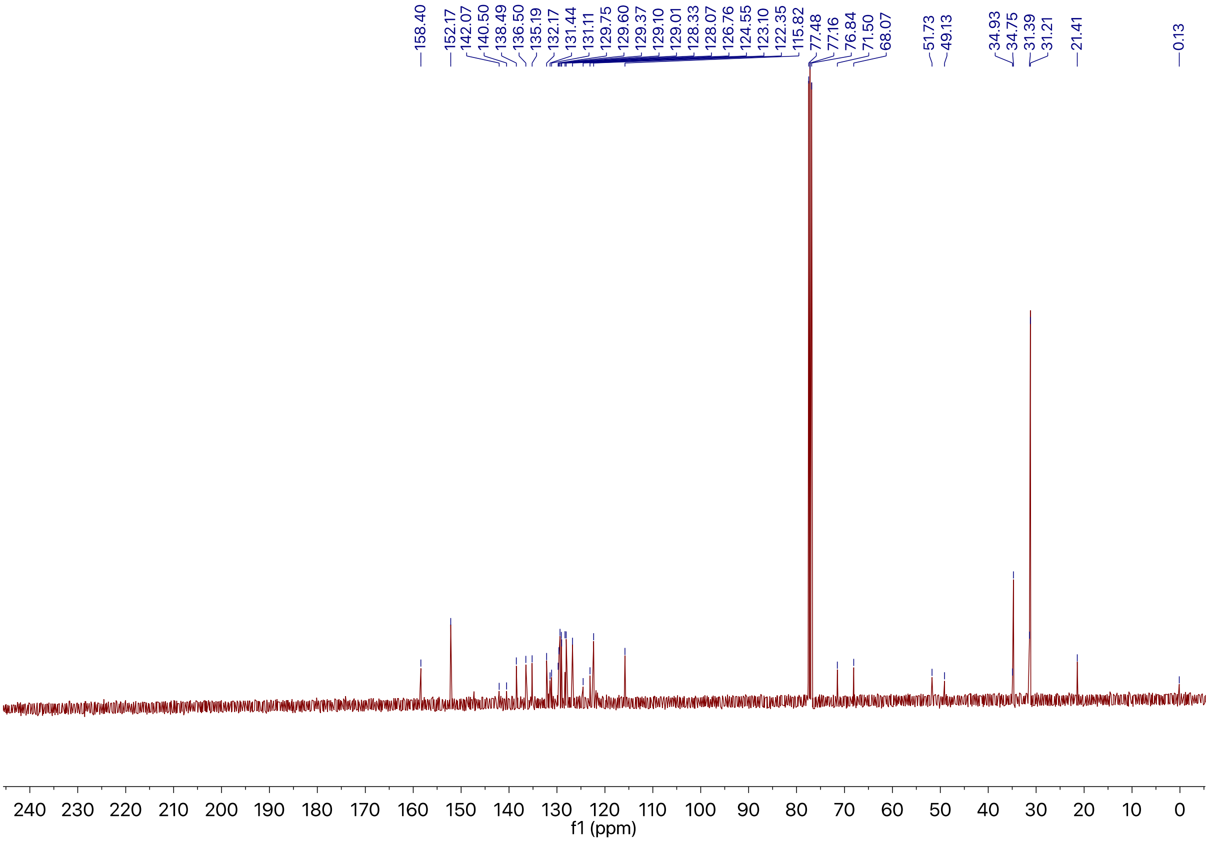

8.04
8.00
7.97
7.96
7.73
7.71
7.69
7.51
7.26
7.24
7.22
7.16
7.14
7.12
7.10
7.00
6.98
6.88
6.86
5.11
5.07
4.89
4.83
4.79
0.00
Ar=3,5-di-trifluoromethylphenyl
1.42
1.40
4.04
8.06
4.00
10.03
8.19
1.43
4.00
4.01
4.01
f1 (ppm)

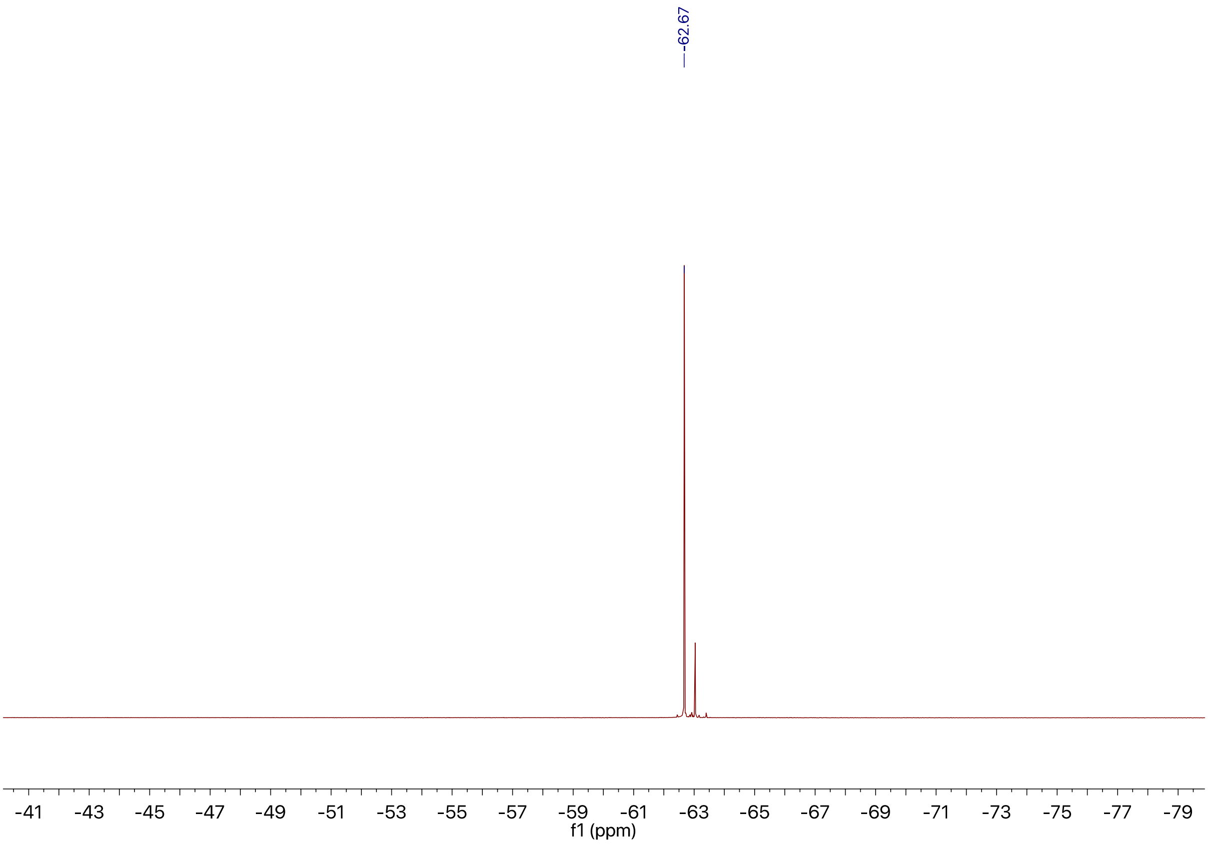

157.80
137.32
134.24
132.53
132.19
130.29
129.62
129.20
128.14
126.81
124.25
121.51
115.53
77.48
77.16
76.84
70.35
49.16
0.13
f1 (ppm)


-63.14
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

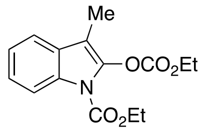


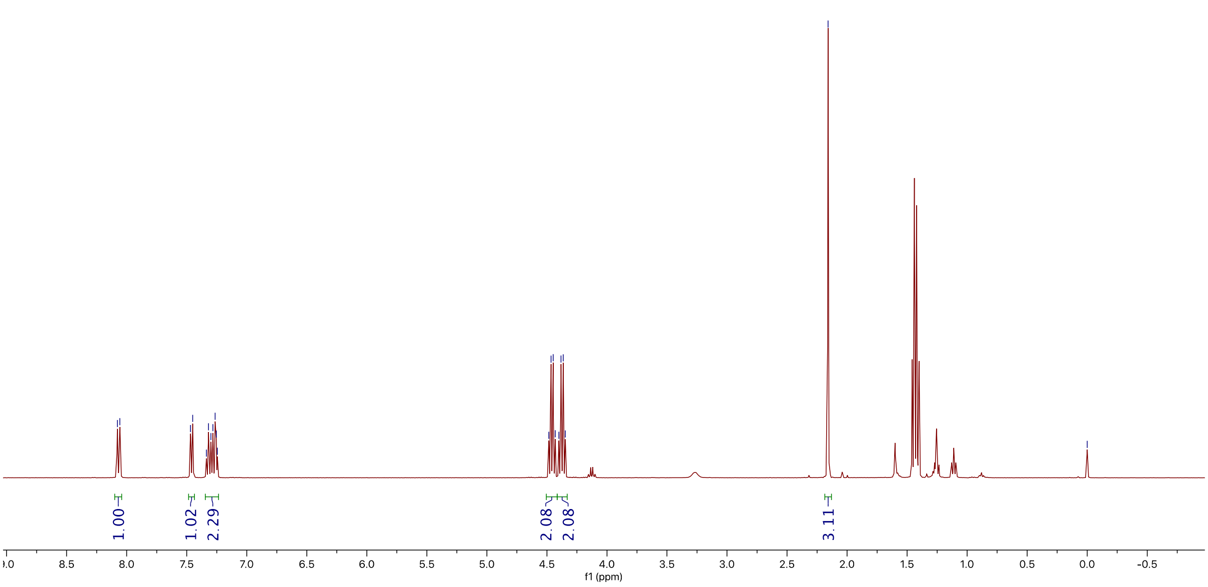
Ar[1]=3,5-di-tertbutylphenyl
Ar[2]=3,5-di-trifluoromethylphenyl

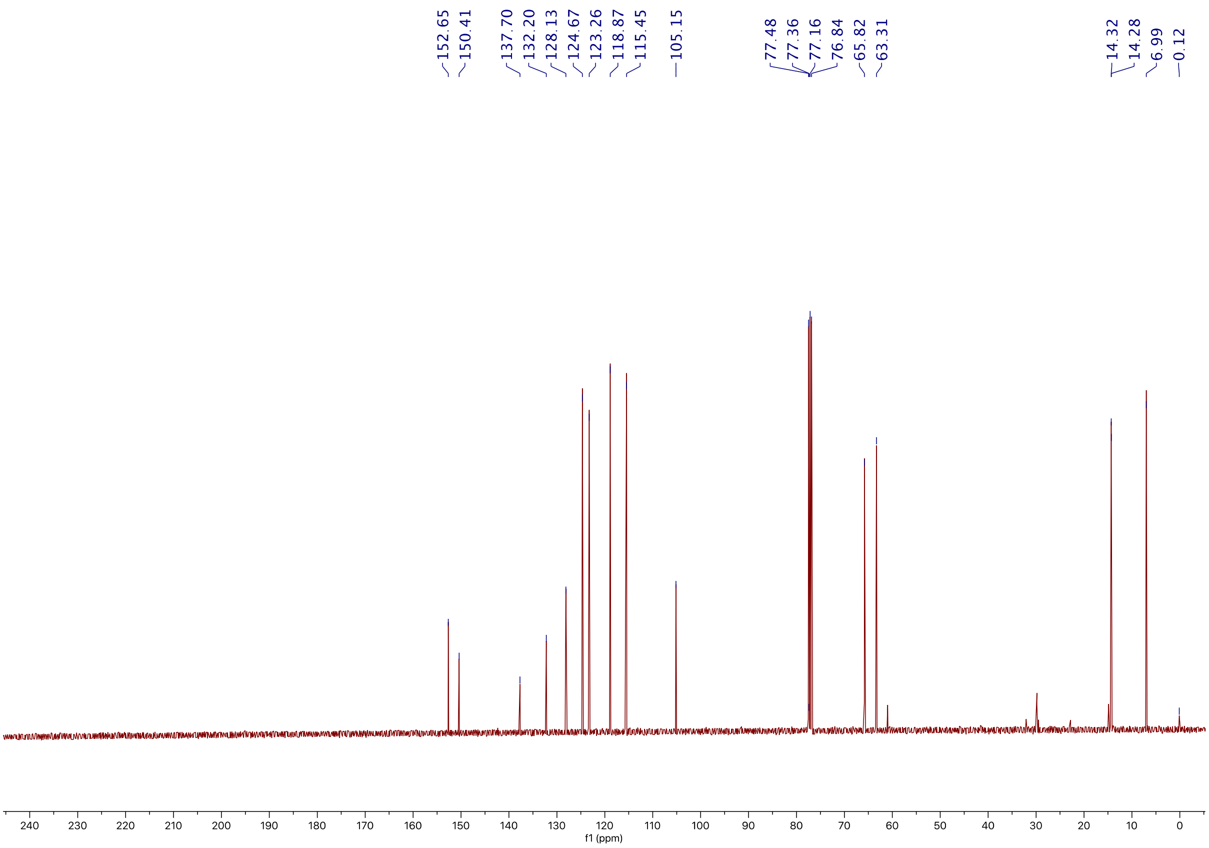


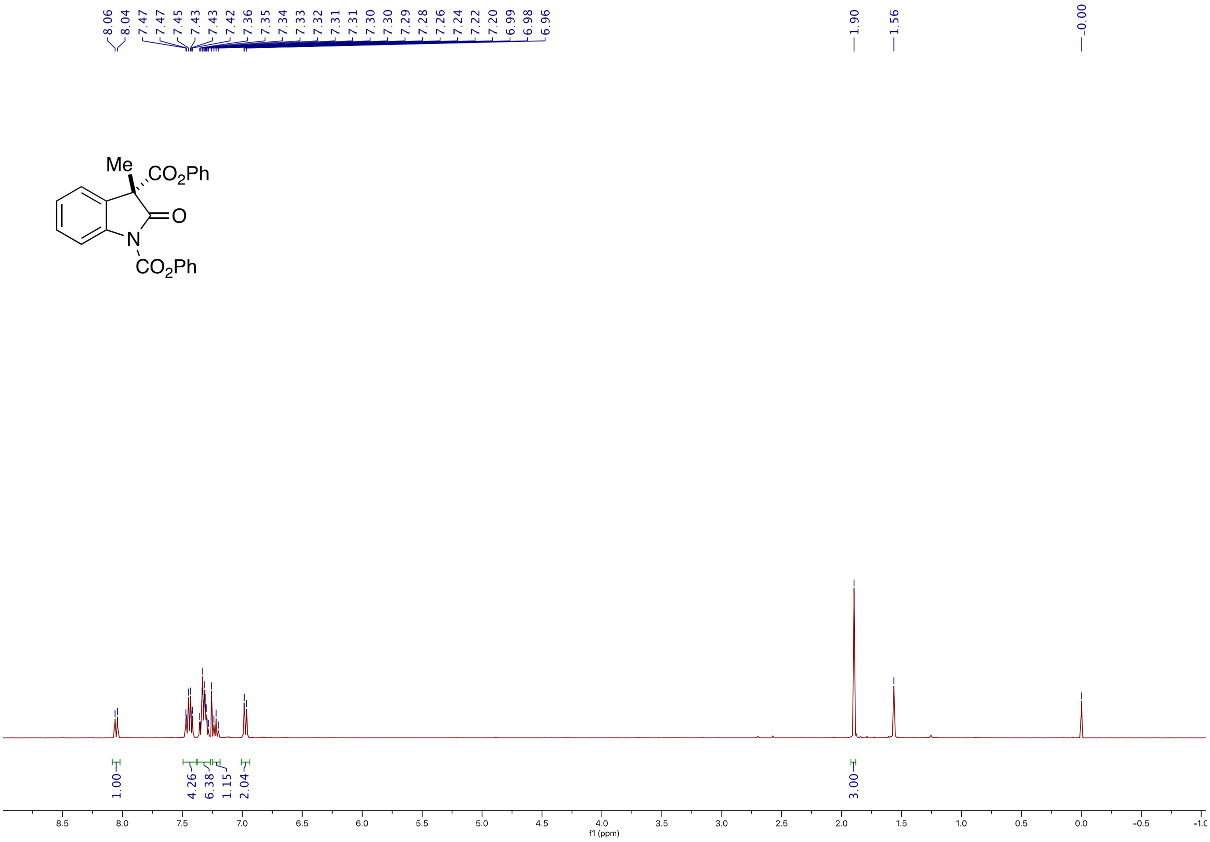


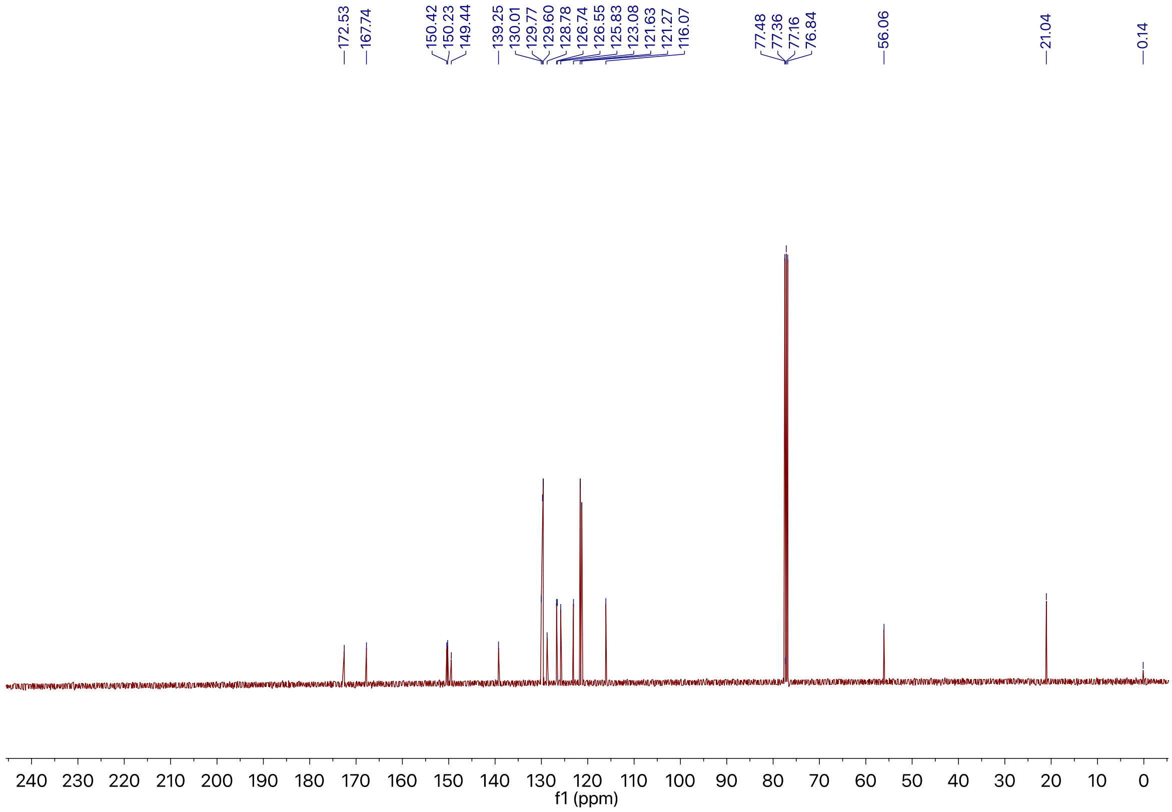
-62.67
-41
-43
-45
-47
-49
-51
-53
-55
-57
-59
-61
-63
-65
-67
-69
-71
-73
-75
-77
-79
f1 (ppm)


Me
OCO2Et
N
CO2Et


8.08
8.06
7.47
7.45
7.34
7.32
7.30
7.28
7.26
7.25
7.24
4.48
4.47
4.45
4.43
4.40
4.38
4.36
4.35
2.16
0.00
1.00
1.02
2.29
2.08
2.08
3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


152.65
150.41
137.70
132.20
128.13
124.67
123.26
118.87
115.45
105.15
77.48
77.36
77.16
76.84
65.82
63.31
14.32
14.28
6.99
0.12
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.06
8.04
7.47
7.47
7.45
7.43
7.43
7.43
7.42
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.26
7.24
7.22
7.20
6.99
6.98
6.96
1.90
1.56
0.00
Me
CO_2Ph
O
N
CO_2Ph
1.00
4.26
6.38
1.15
2.04
3.00
f1 (ppm)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167.74
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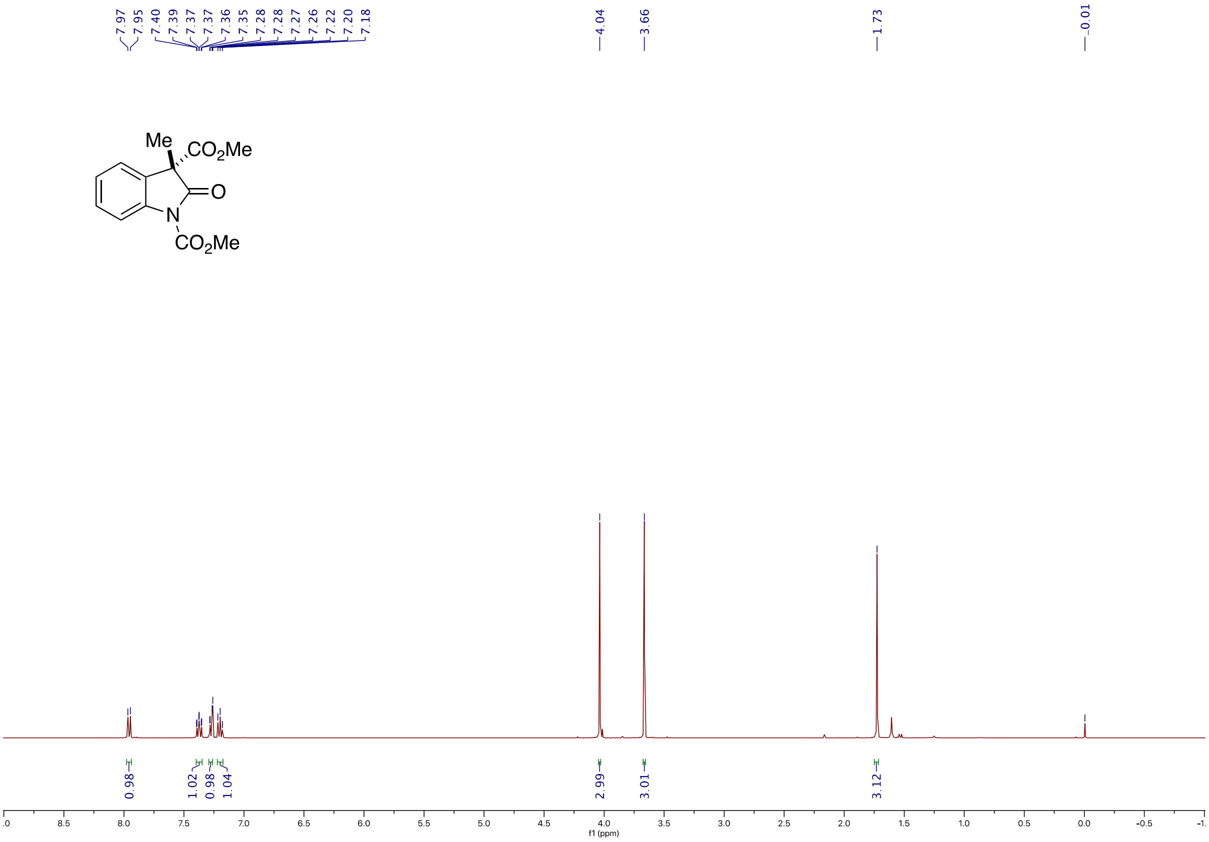
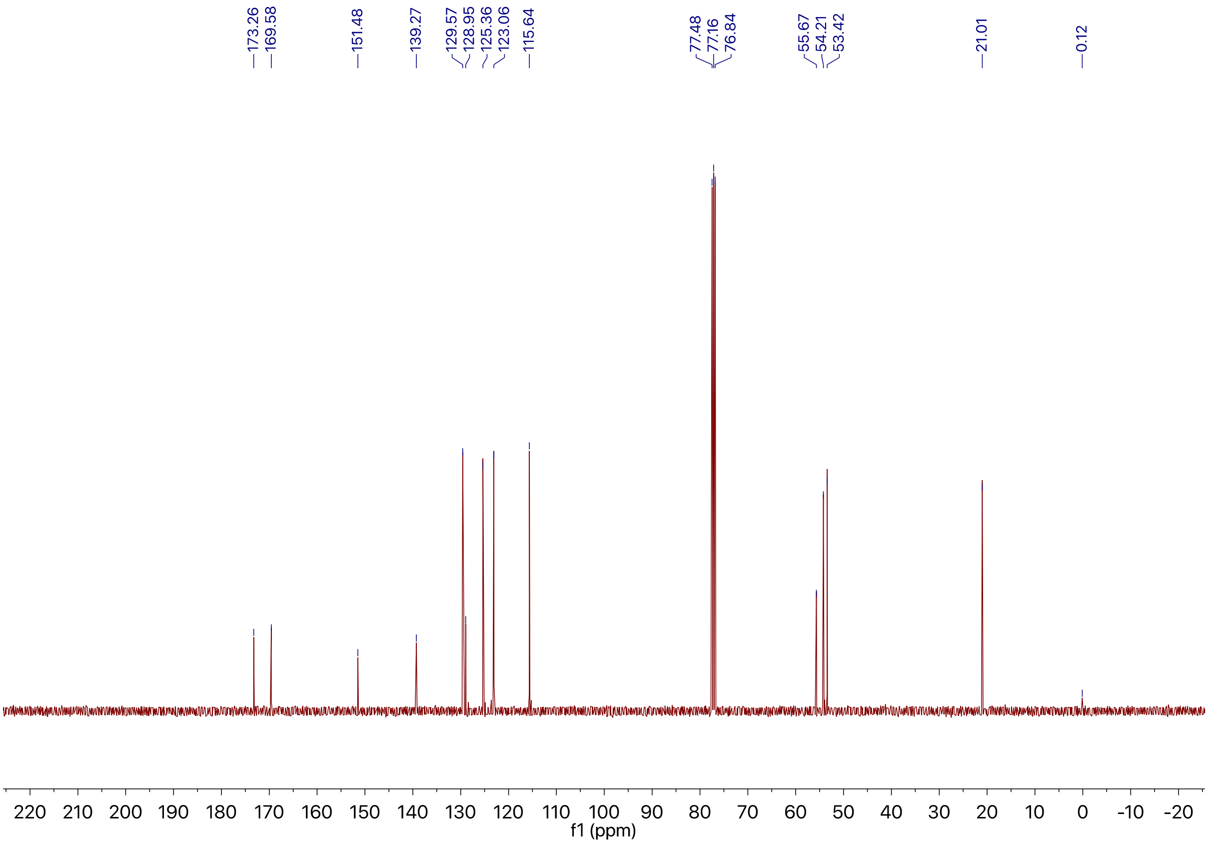
149.44
139.25
130.01
129.77
129.60
128.78
126.74
126.55
125.83
123.08
121.63
121.27
116.07
77.48
77.36
77.16
76.84
56.06
21.04
0.14
f1 (ppm)


7.97
7.95
7.40
7.39
7.37
7.37
7.36
7.35
7.28
7.28
7.27
7.26
7.22
7.20
7.18
4.04
3.66
1.73
0.01
Me
CO_2Me
O
N
CO_2Me
0.98
1.02
0.98
1.04
2.99
3.01
3.12
f1 (ppm)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169.58
151.48
139.27
129.57
128.95
125.36
123.06
115.64
77.48
77.16
76.84
55.67
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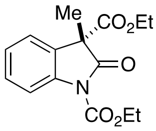
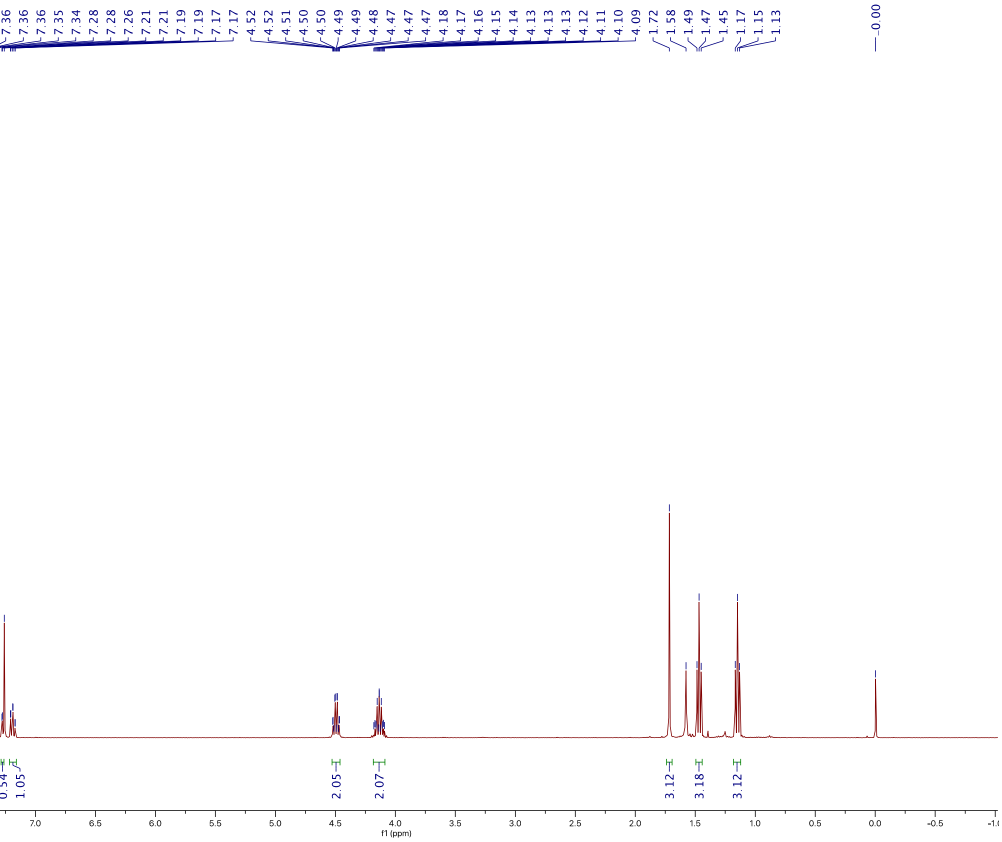
53.42
21.01
0.12
f1 (ppm)





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1.45
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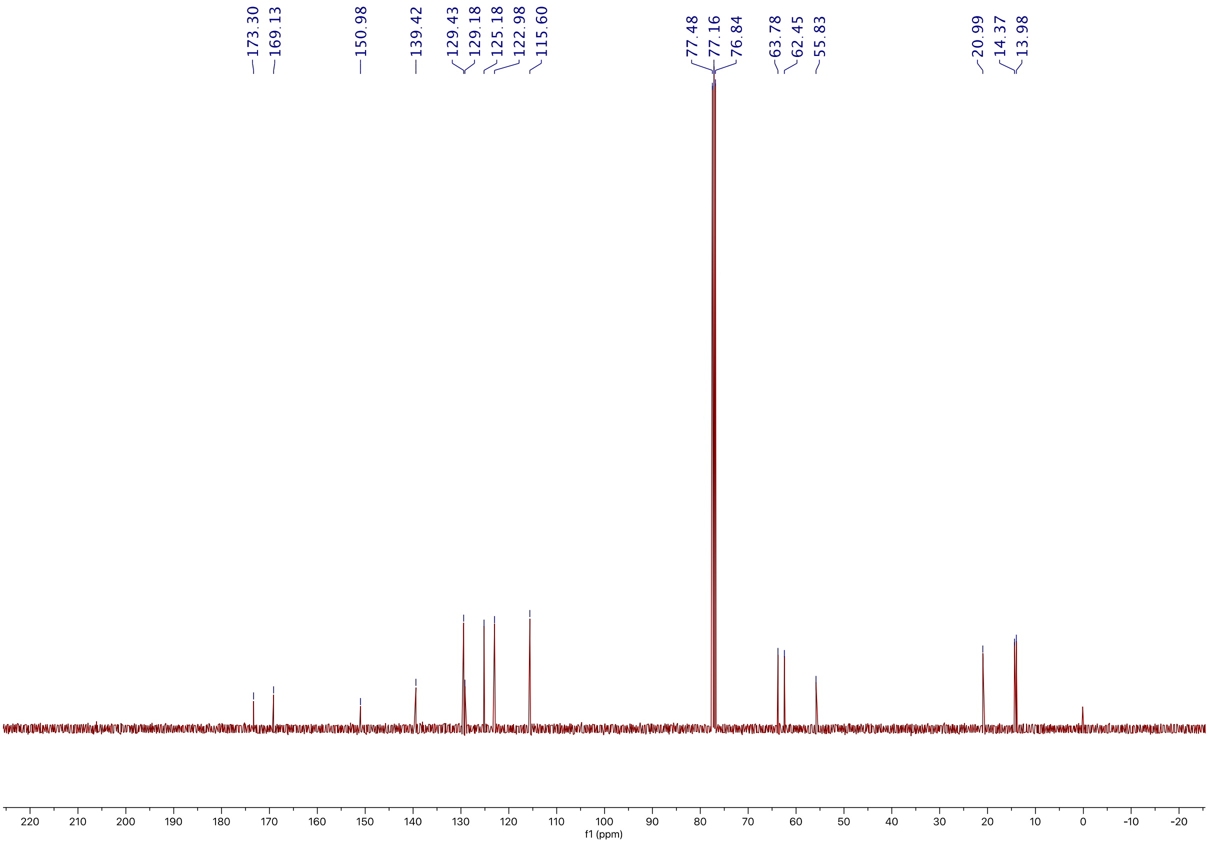

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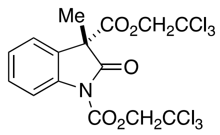
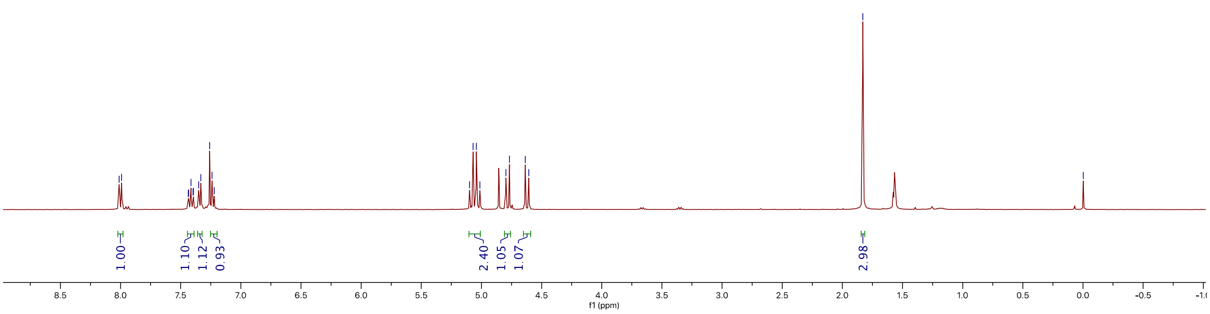
f1 (ppm)

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5.07
5.04
5.01
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4.77
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1.10
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1.05
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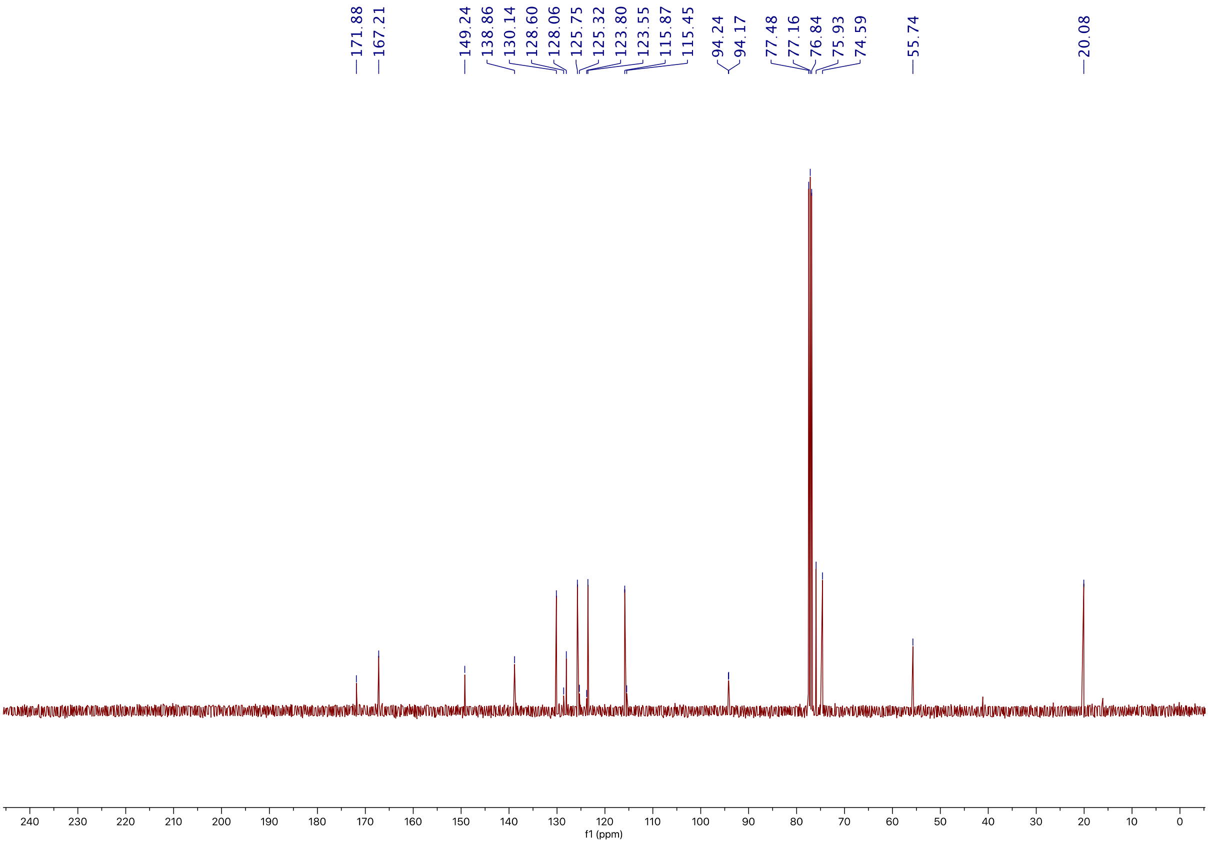
2.98
f1 (ppm)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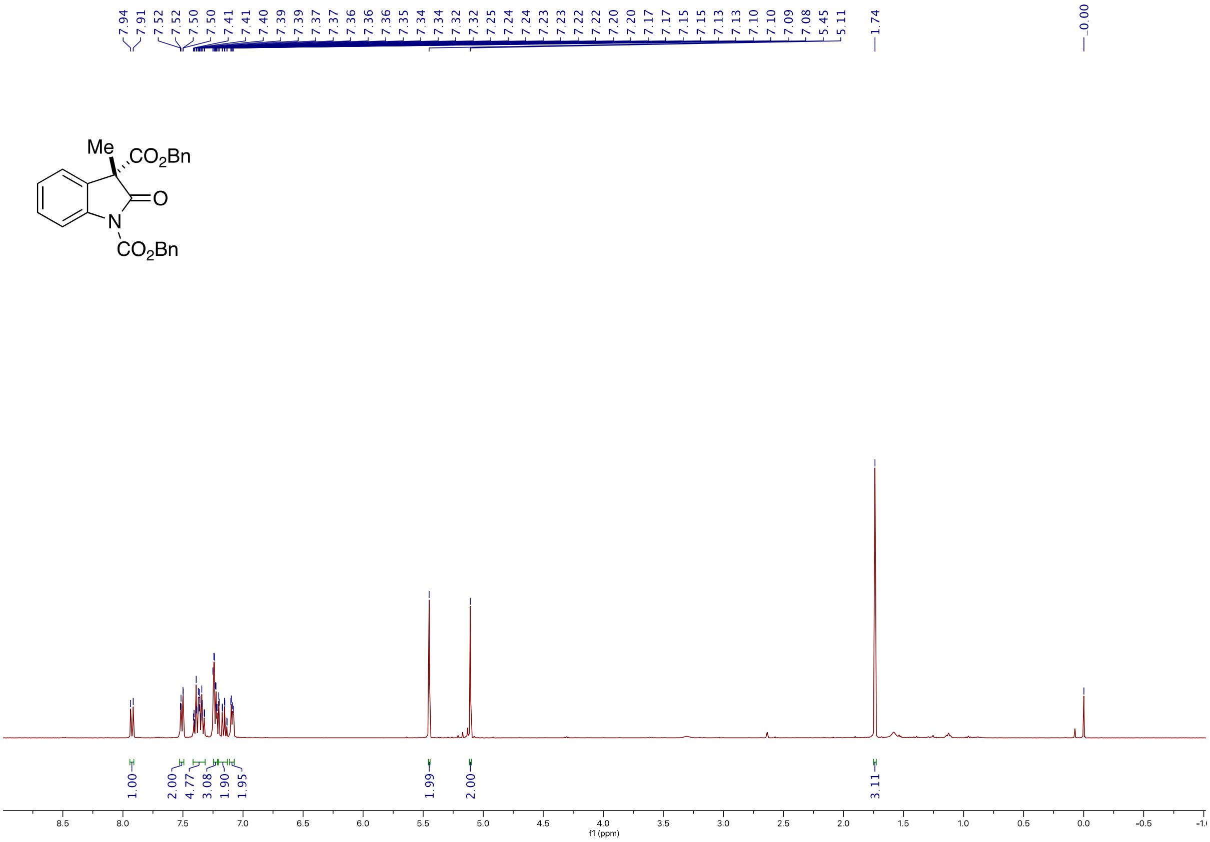
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7.13
7.13
7.10
7.10
7.09
7.08
5.45
5.11
1.74
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Me
CO2Bn
O
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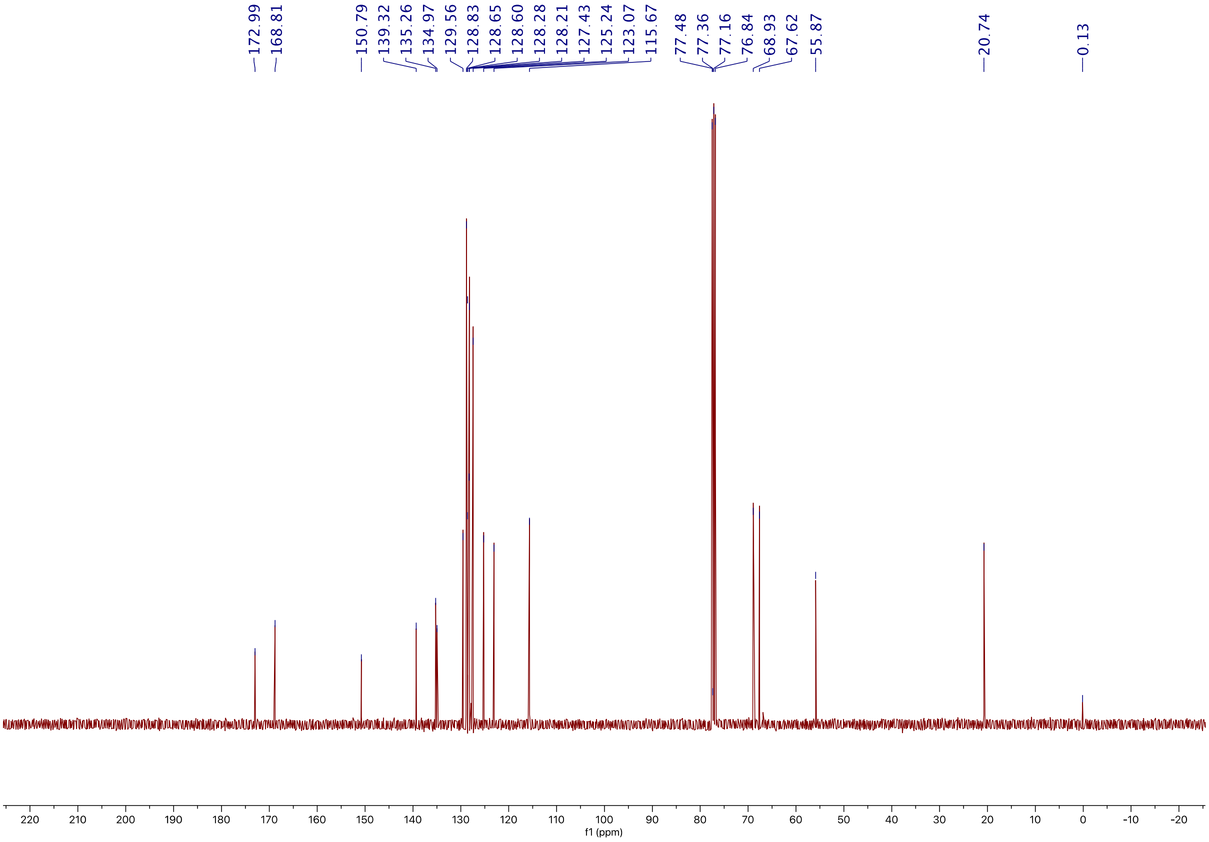
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125.24
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55.87
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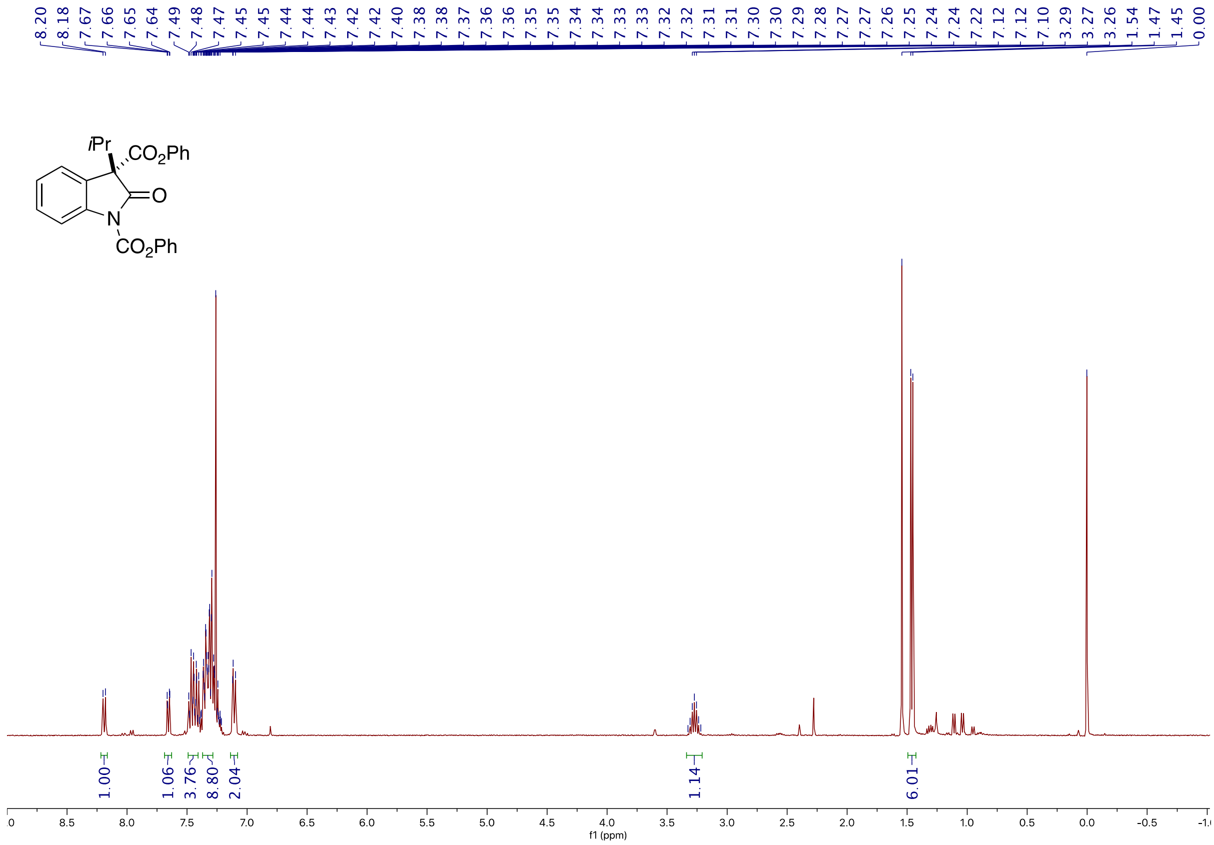
0.13
f1 (ppm)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O
N
CO2Ph
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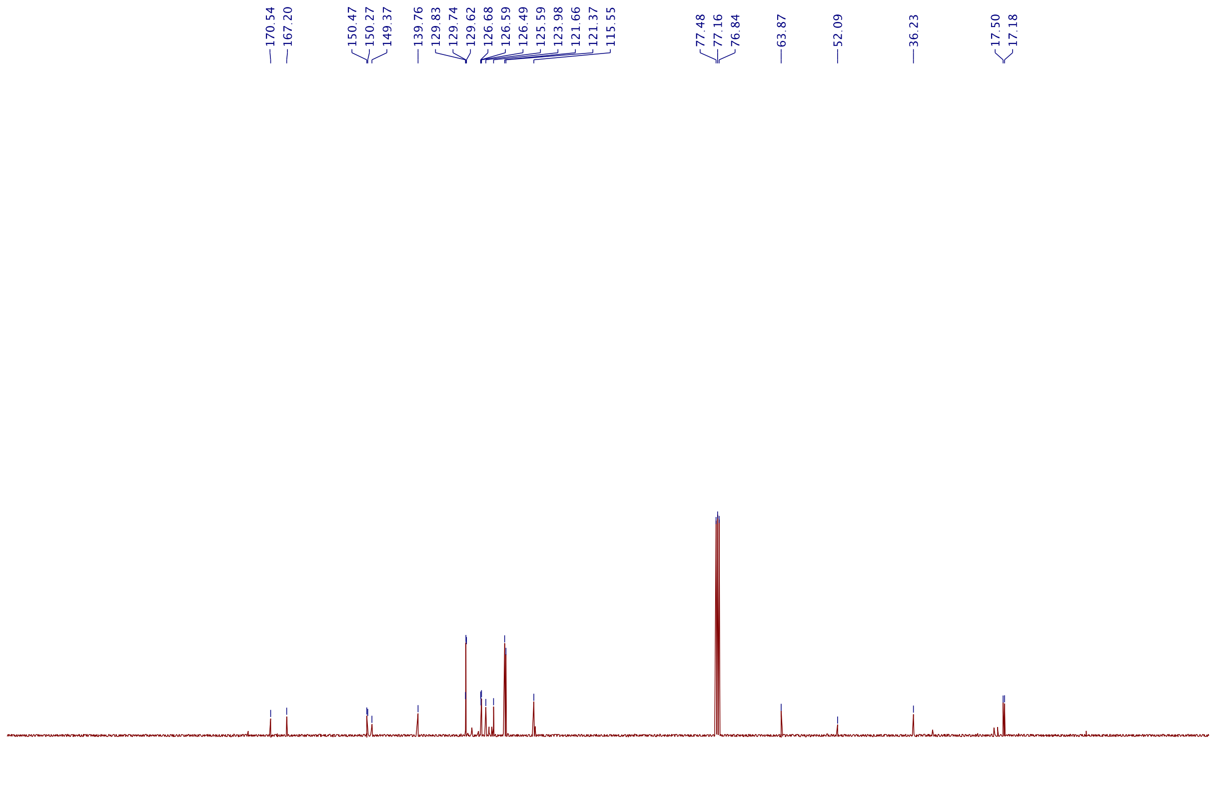
f1 (ppm)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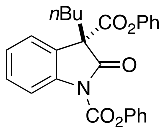
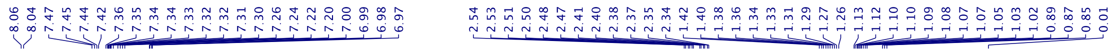
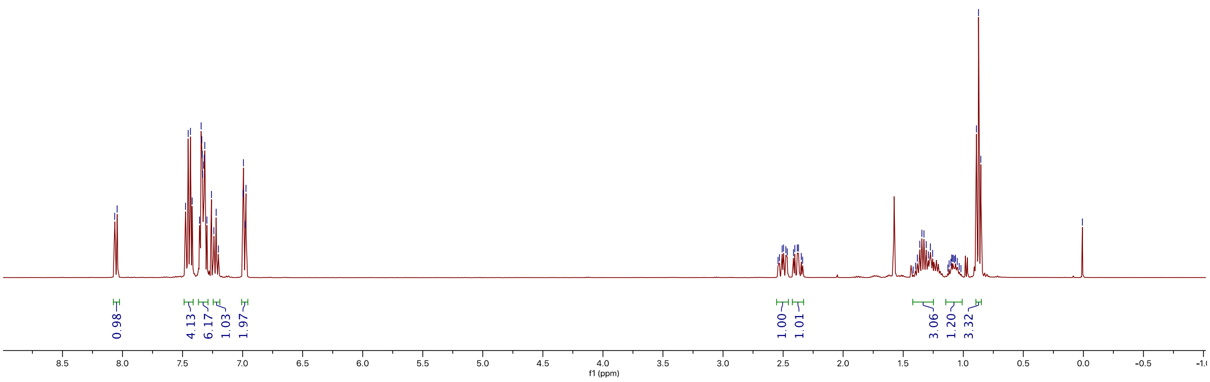
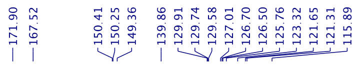
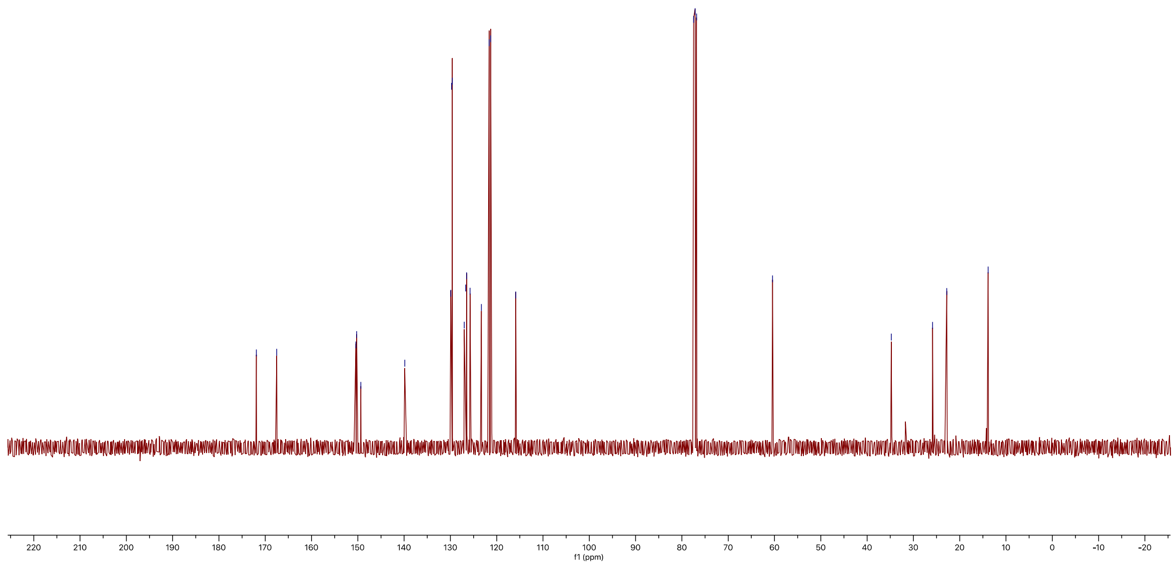
f1 (ppm)

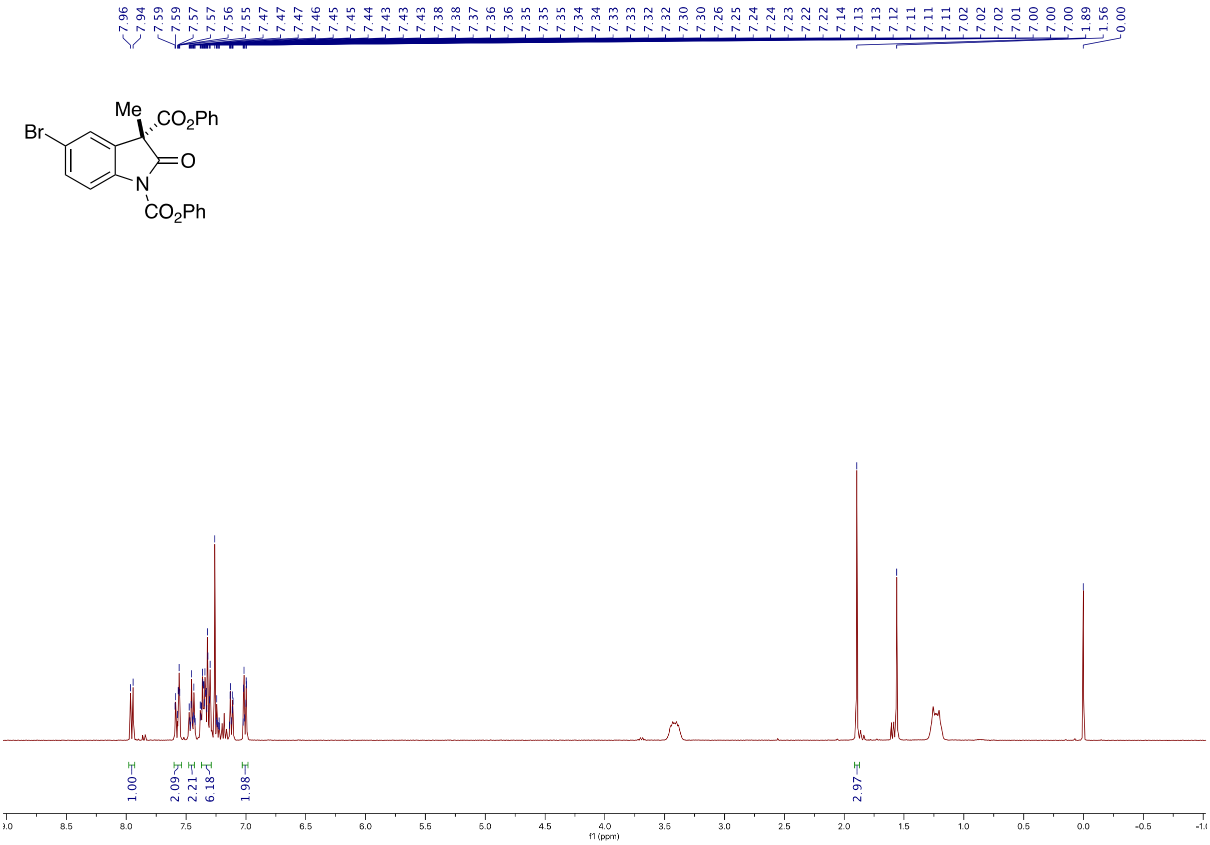


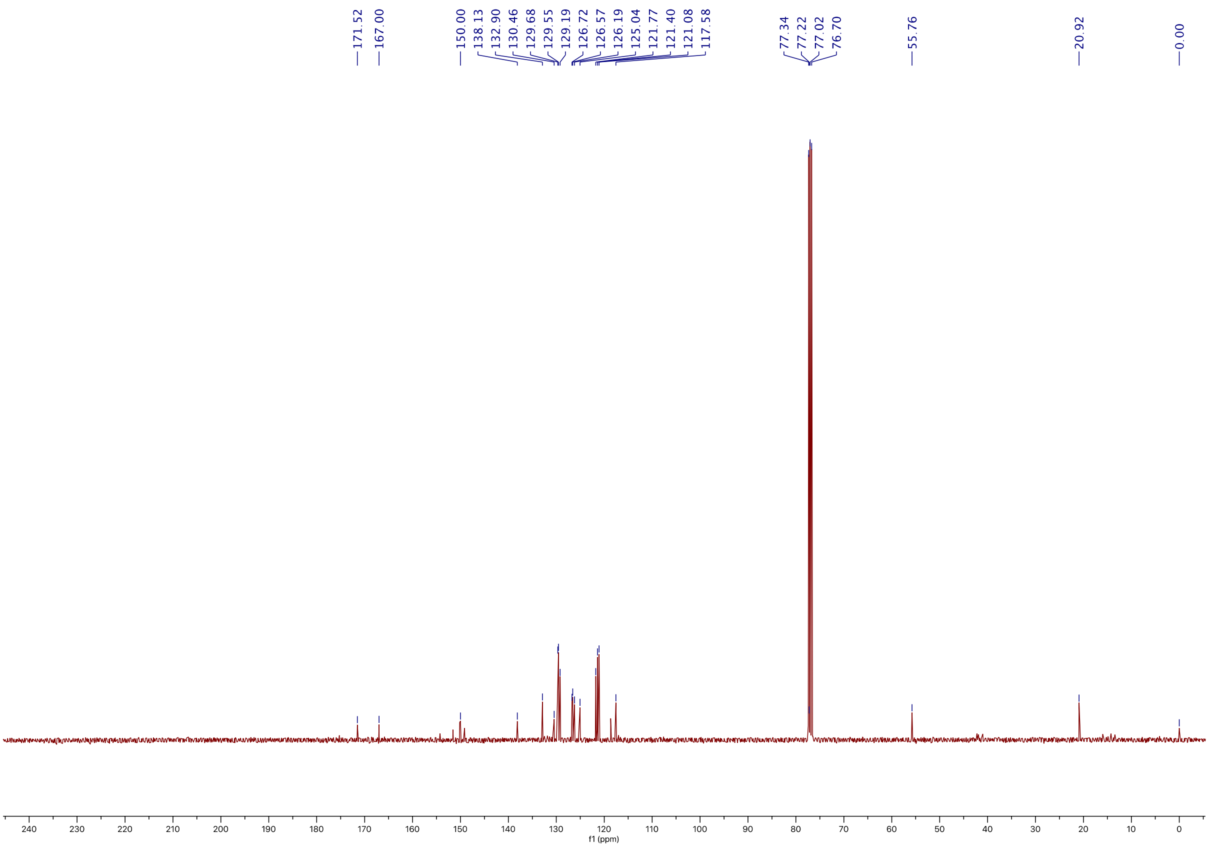


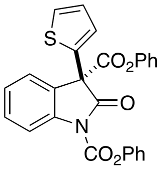








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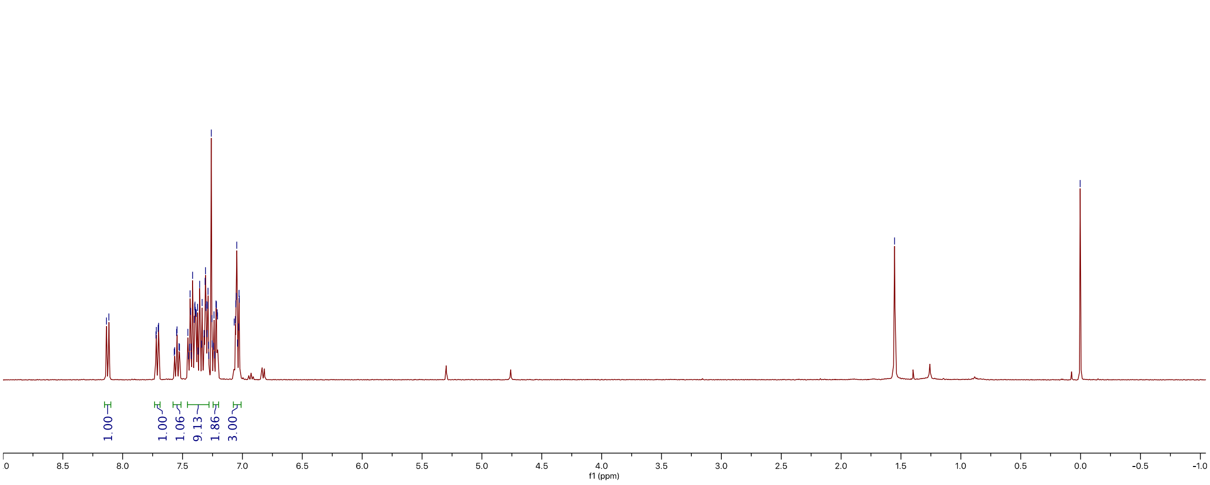
O
N
CO2Ph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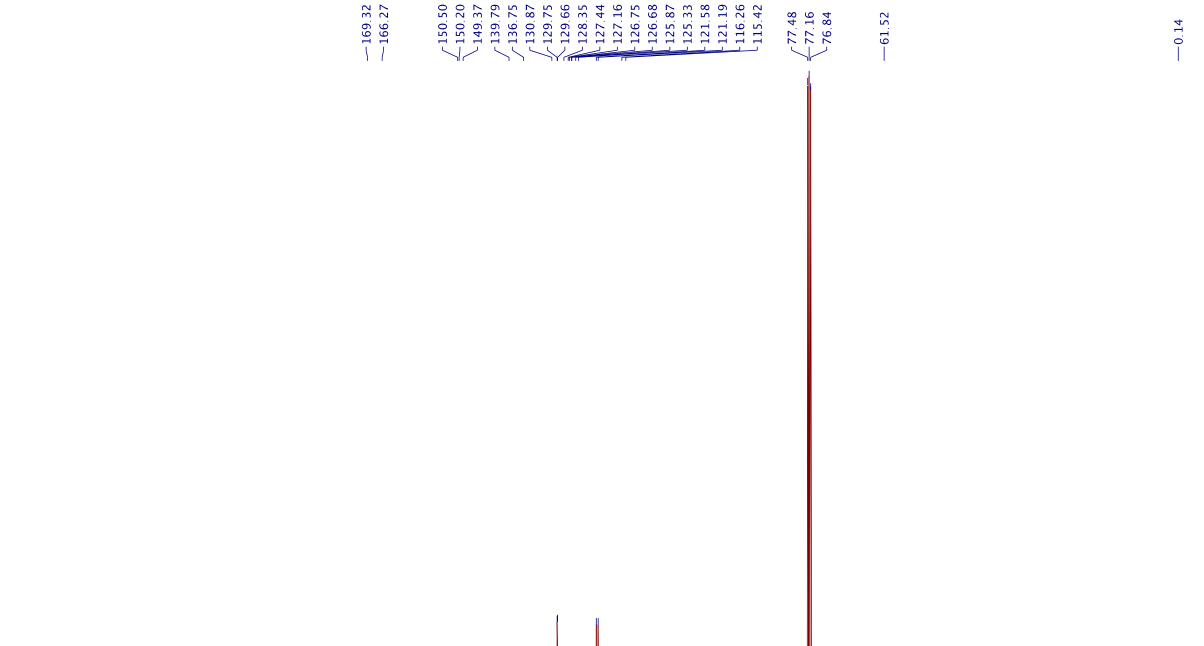
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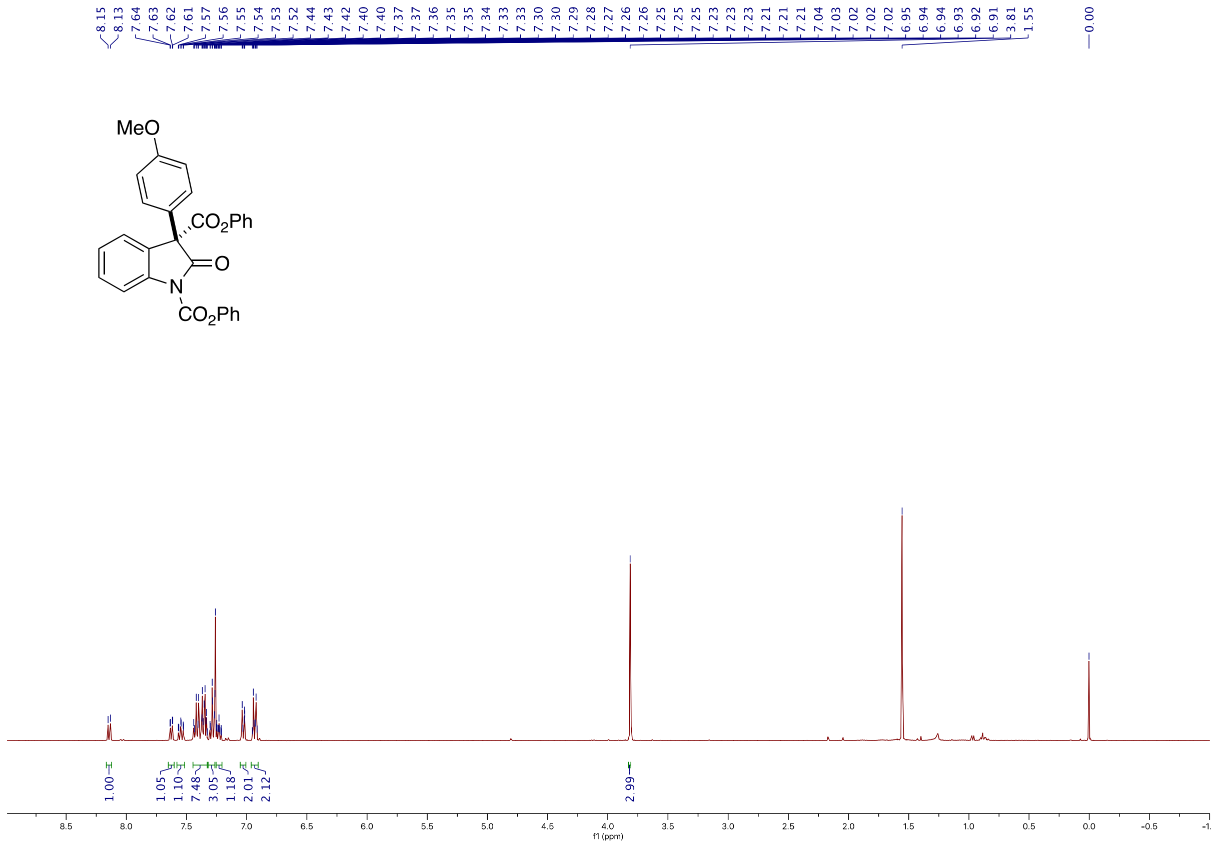
77.16
76.84
61.52
0.14
f1 (ppm)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7.03
7.02
7.02
7.02
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6.92
6.91
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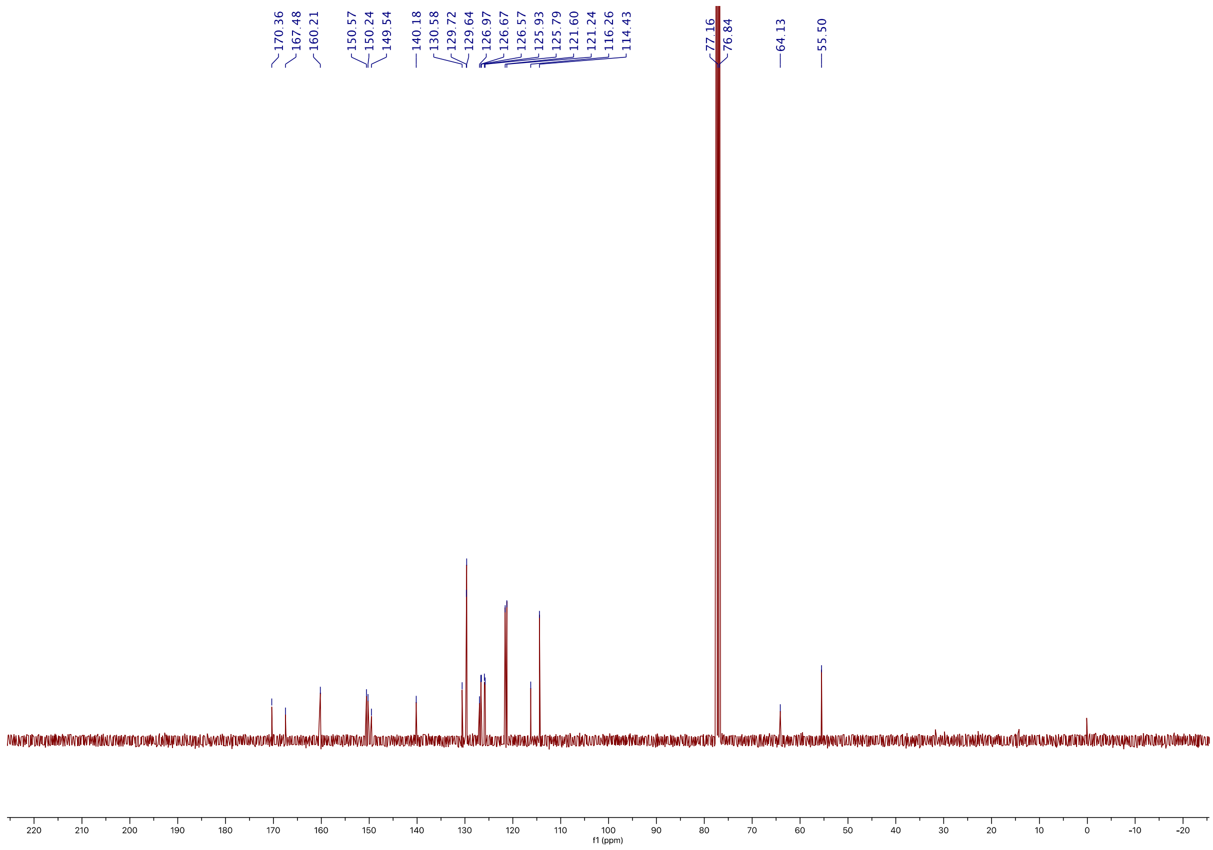
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116.26
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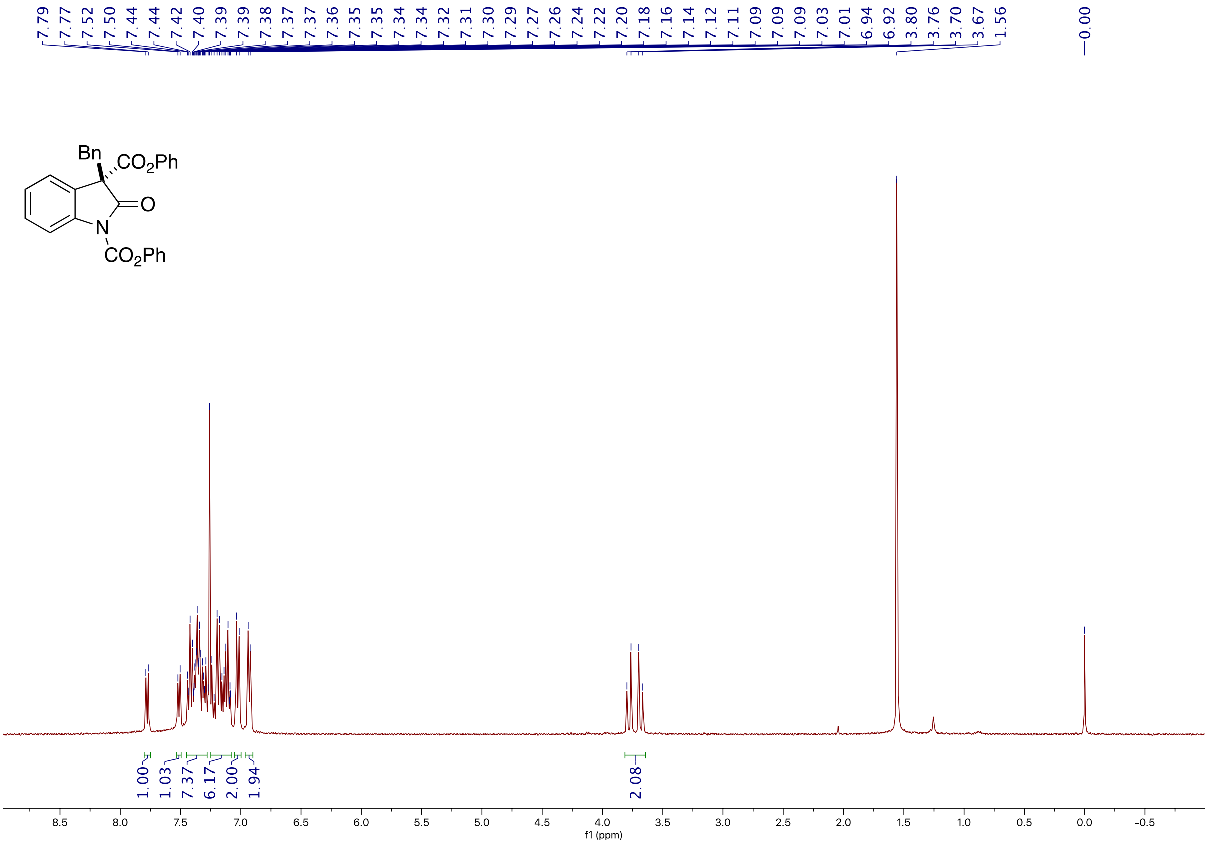
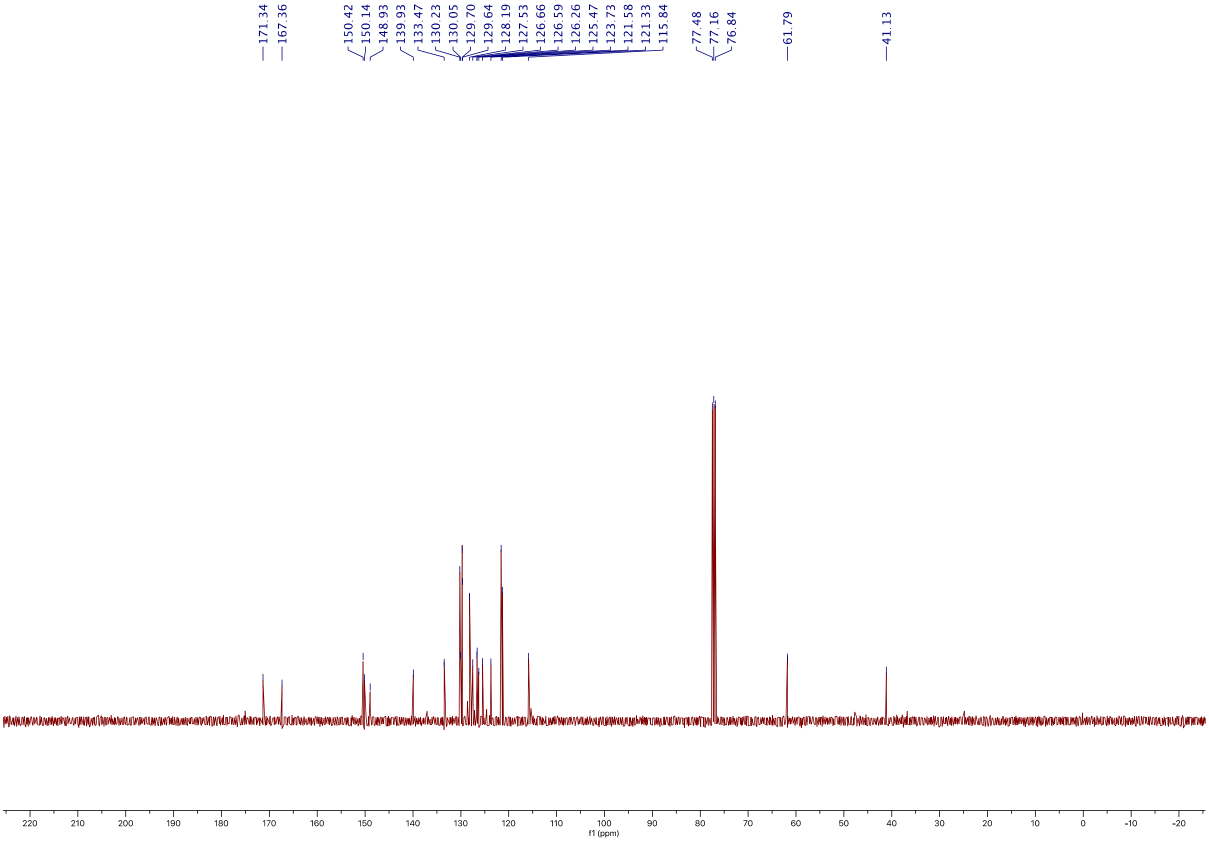
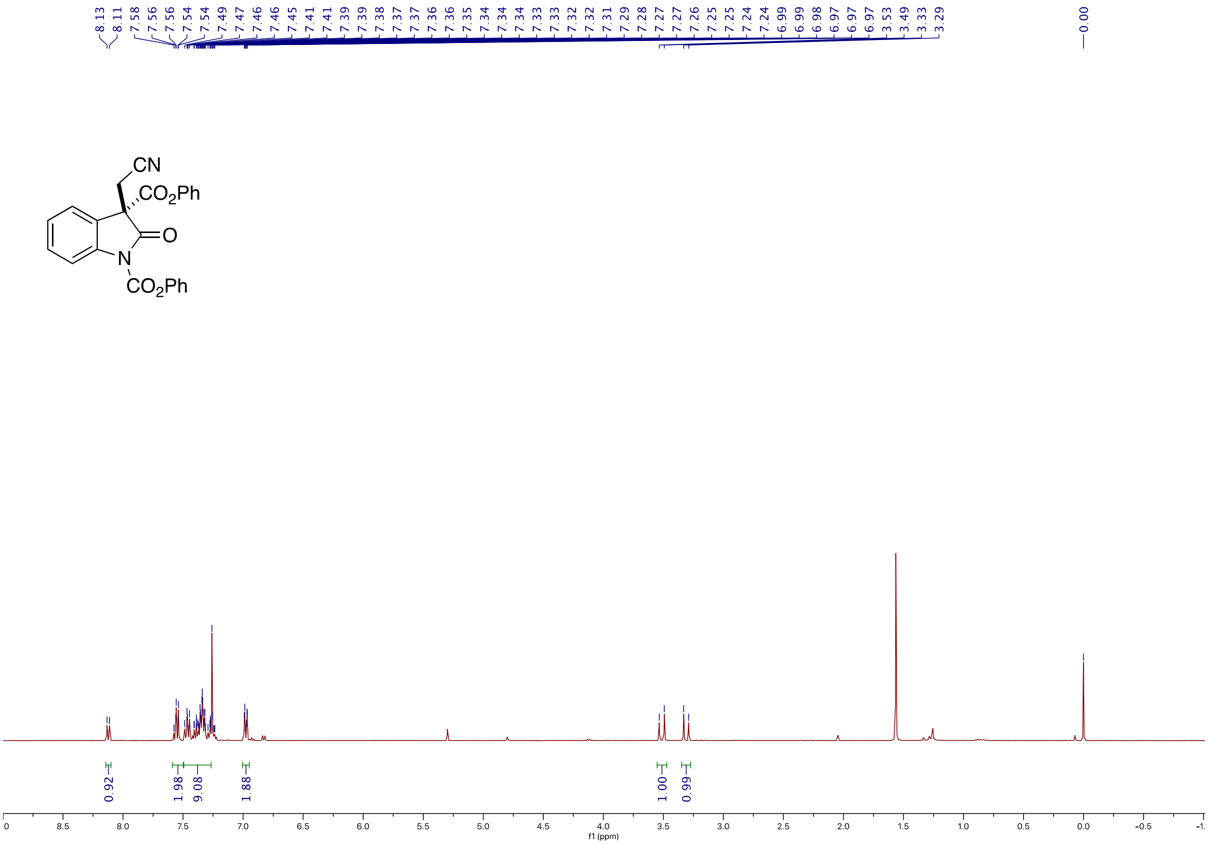
64.13
55.50
f1 (ppm)



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O
N
CO2Ph
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6.97
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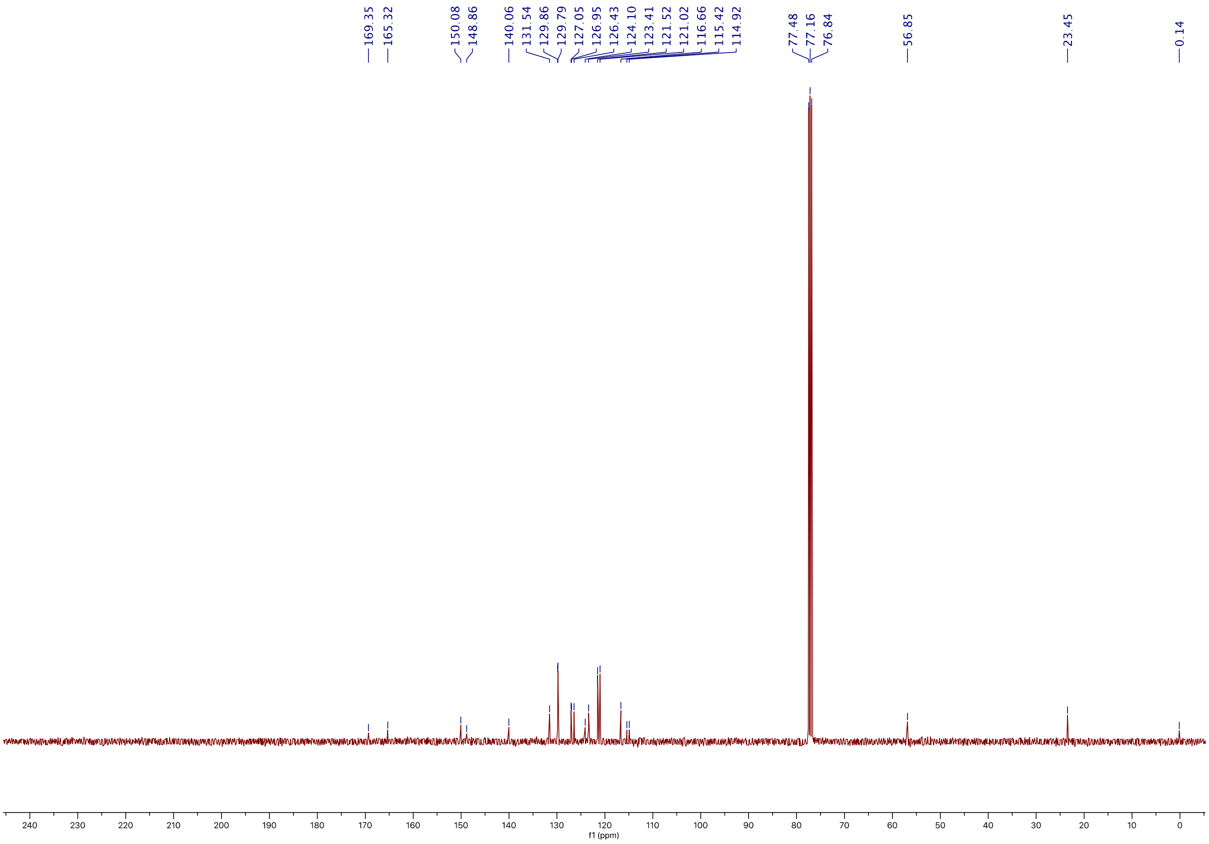
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56.85
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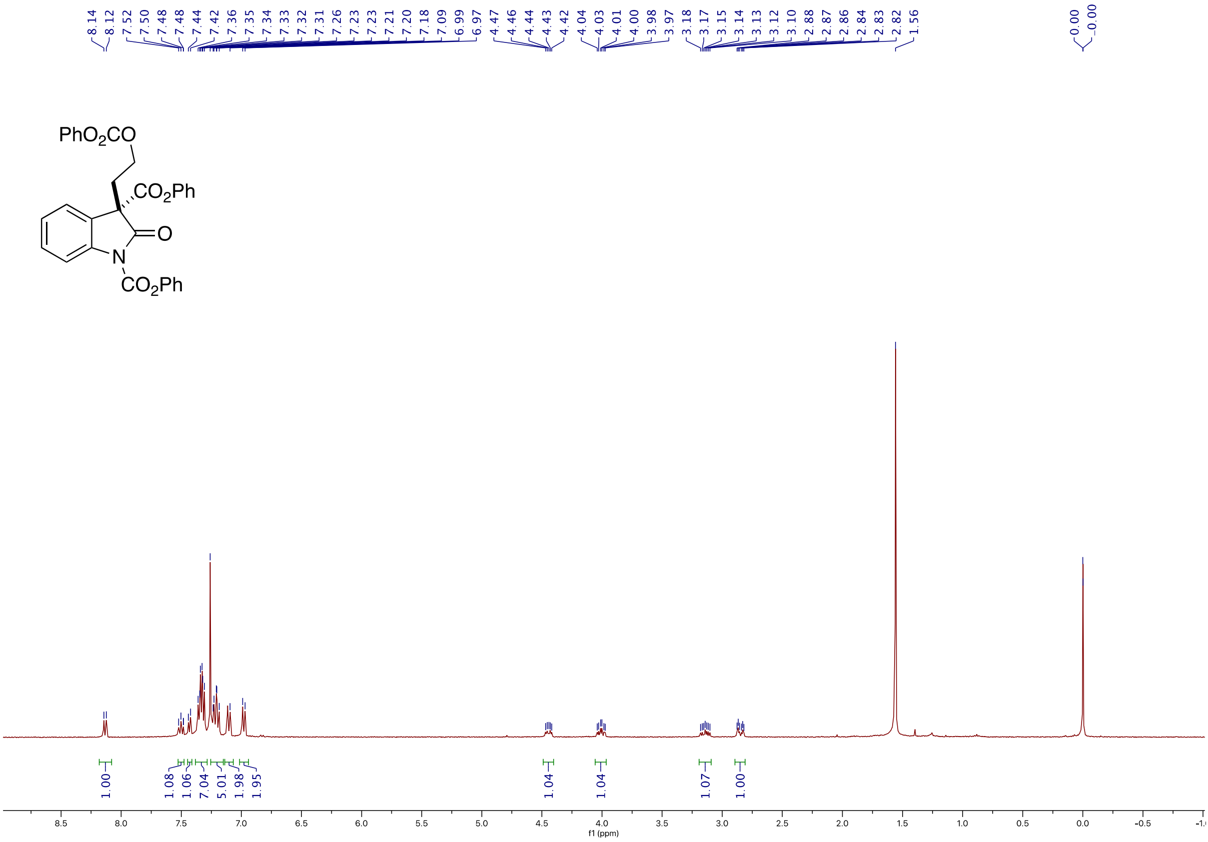
f1 (ppm)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O
N
CO2Ph
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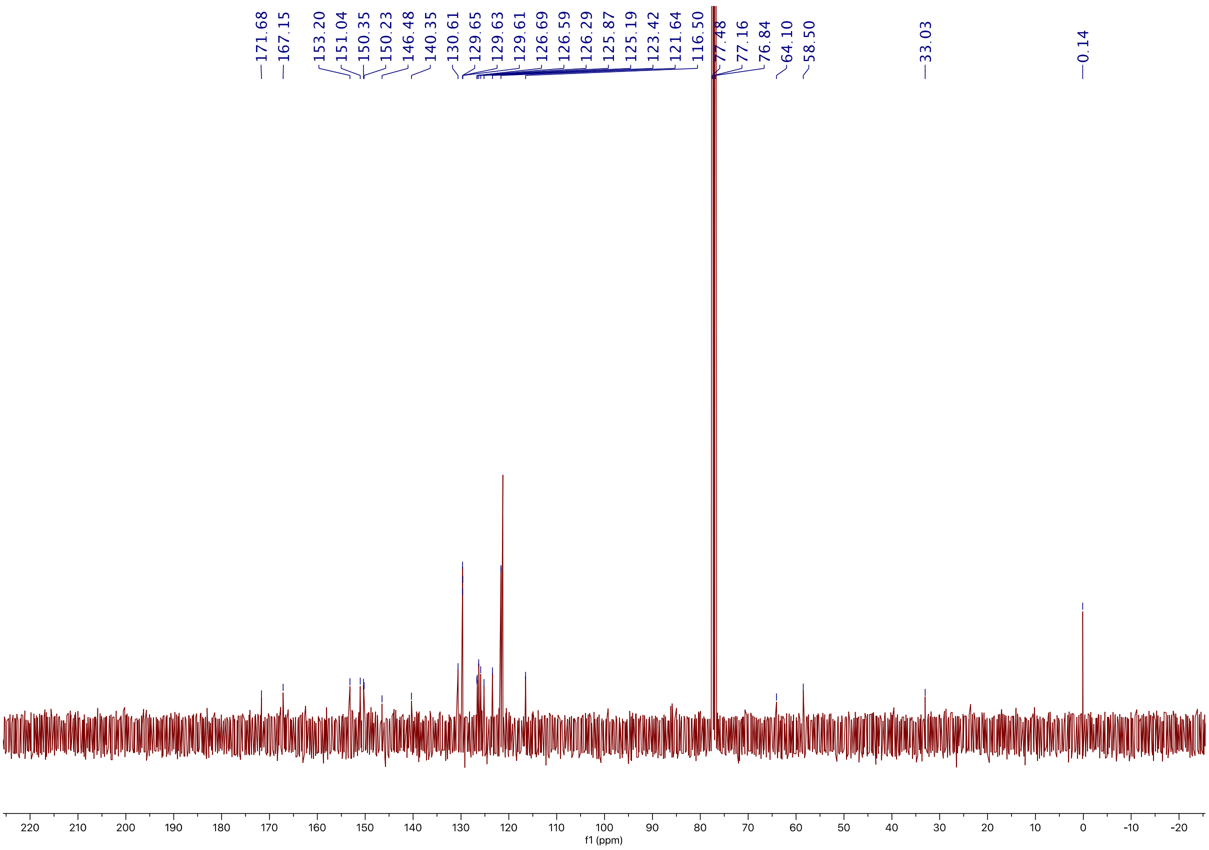
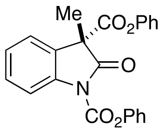
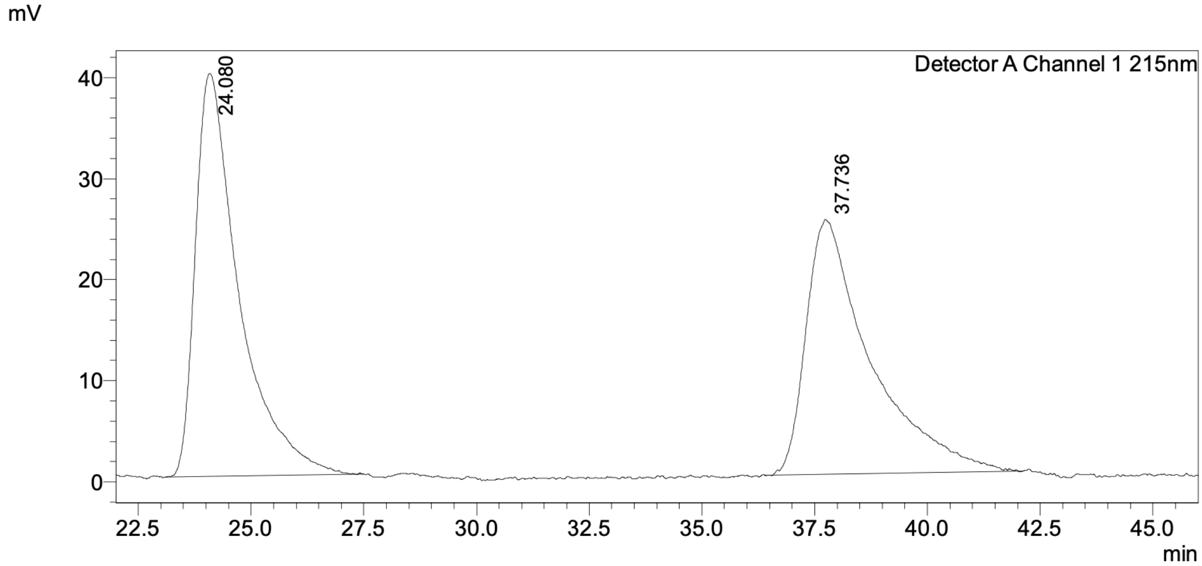
0.00 0.00
1.00 1.08 1.06 7.04 5.01 1.98 1.95 1.04 1.04 1.07 1.00
f1 (ppm)

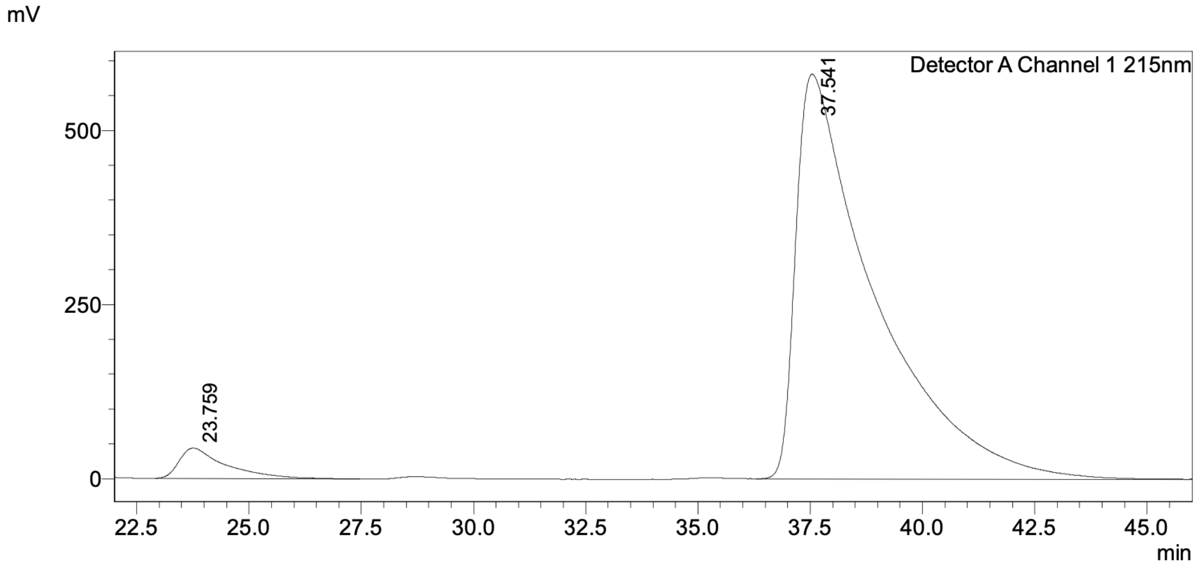

171.68 167.15 153.20 151.04 150.35 150.23 146.48 140.35 130.61 129.65 129.63 129.61 126.69 126.59 126.29 125.87 125.19 123.42 121.64 116.50 77.48 77.16 76.84 64.10 58.50 33.03 0.14
f1 (ppm)





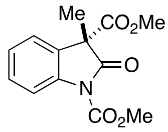
Detector A Channel 1 215nm

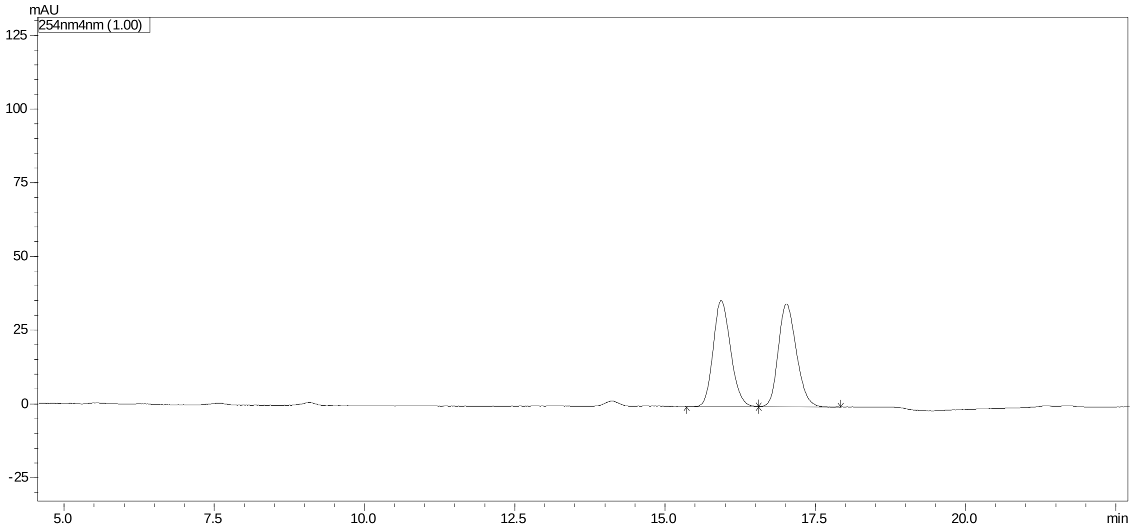
Peak#	Ret. Time	Area	Area%
1	24.080	2669698	51.697
2	37.736	2494450	48.303
Total		5164148	100.000



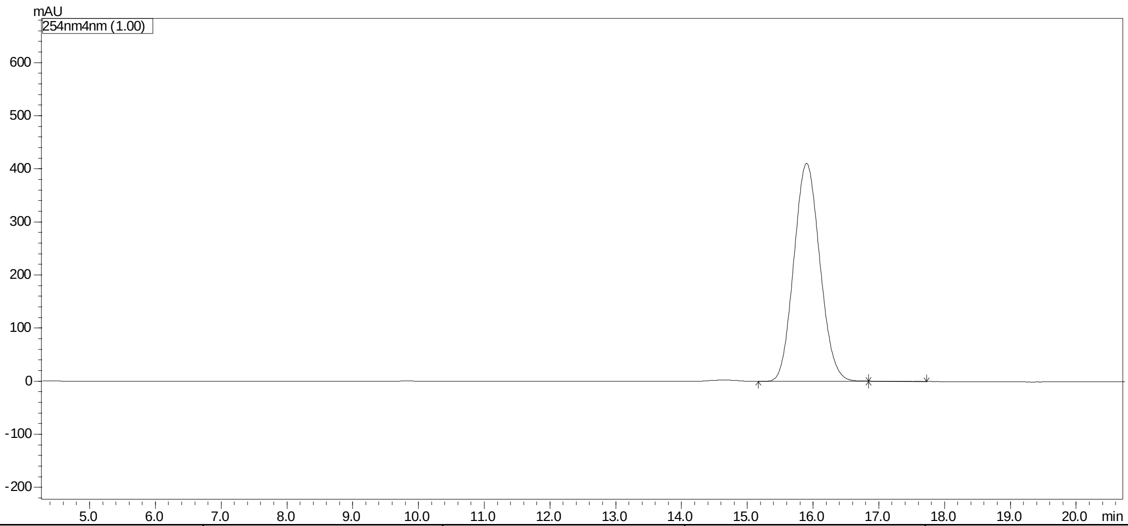
Detector A Channel 1 215nm

Peak#	Ret. Time	Area	Area%
1	23.759	3167251	4.275
2	37.541	70920263	95.725
Total		74087514	100.000





Peak	Ret. Time	Area	Height	Area%
1	15.933	728079	35958	49.814
2	17.021	733509	34941	50.186
Total		1461588	70900	100.000



Peak#	Ret. Time	Area	Height	Area%
1	15.902	11319088	411153	99.912
2	16.859	9971	841	0.088
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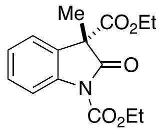

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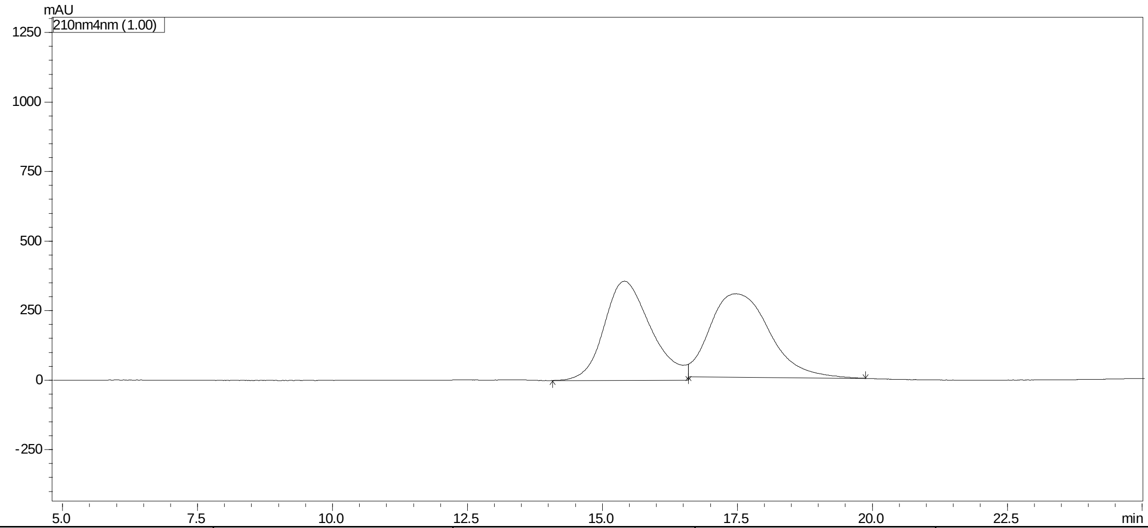
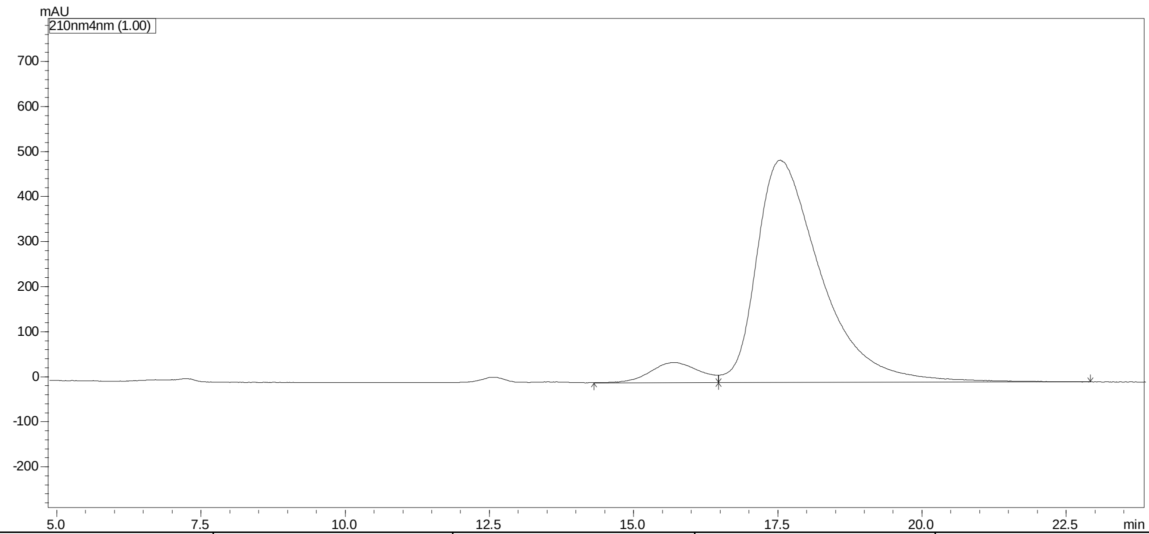
Sample Name:yzq-R-COOEt-Amy-2-98-1.0
Sample ID:1

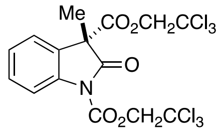


Peak#	Ret. Time	Area	Height	Area%
1	15.406	21734049	357149	48.423
2	17.440	23150074	300064	51.577
Total		44884123	657213	100.000

Datafile Name:yzq-C-COOEt-Amy-2-98-1.0.lcd
Sample Name:yzq-C-COOEt-Amy-2-98-1.0
Sample ID:1



Peak#	Ret. Time	Area	Height	Area%
1	15.684	2648357	44807	6.462
2	17.547	38333899	494271	93.538
Total		40982256	539078	100.000



Datafile Name:yzq-R-CCl3-90-1.0.lcd
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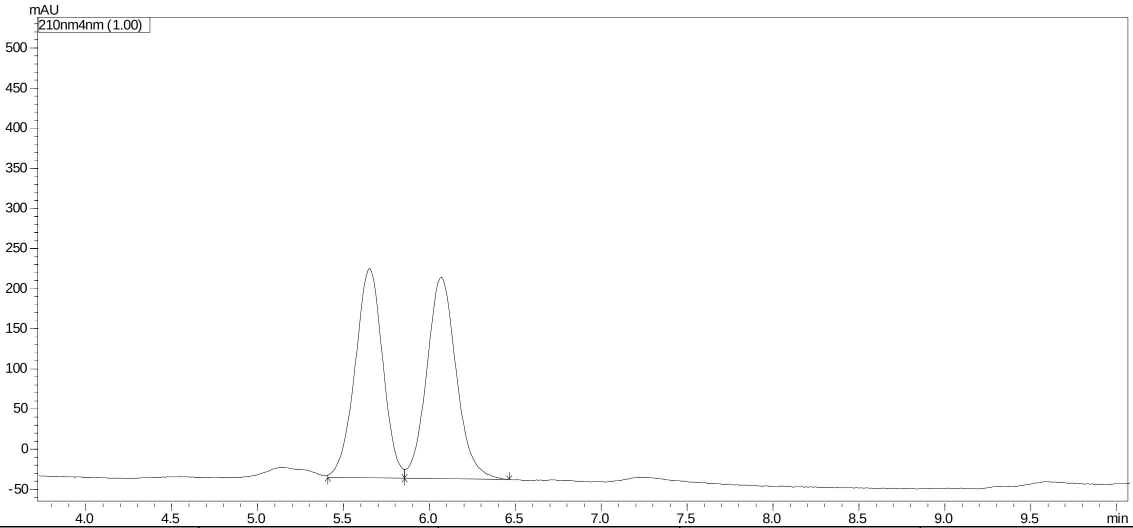
Sample ID:1



Peak#	Ret. Time	Area	Height	Area%
1	5.651	2912816	260678	49.367
2	6.068	2987467	250846	50.633
Total		5900283	511523	100.000

Datafile Name:yzq-C-CCl3-ODH-90-1.0-3.lcd
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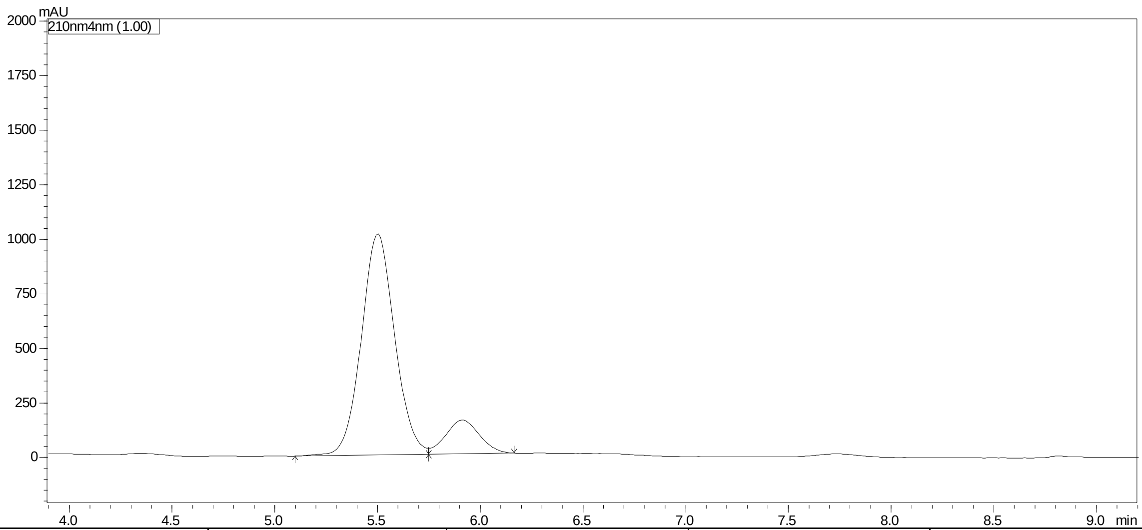
Sample ID:1



Peak#	Ret. Time	Area	Height	Area%
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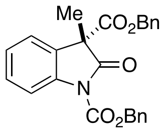
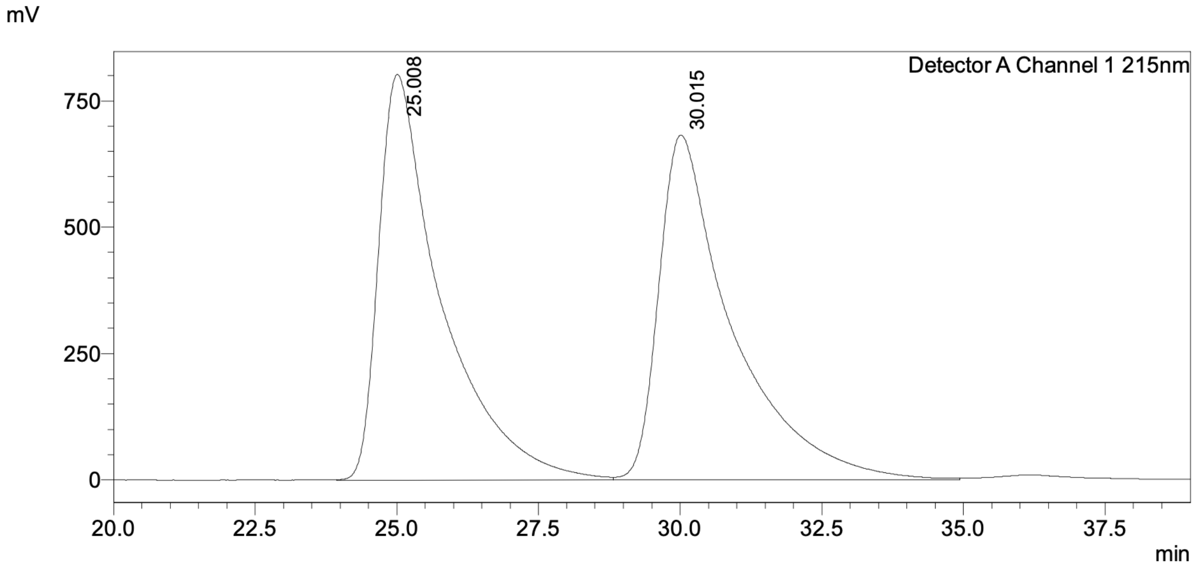
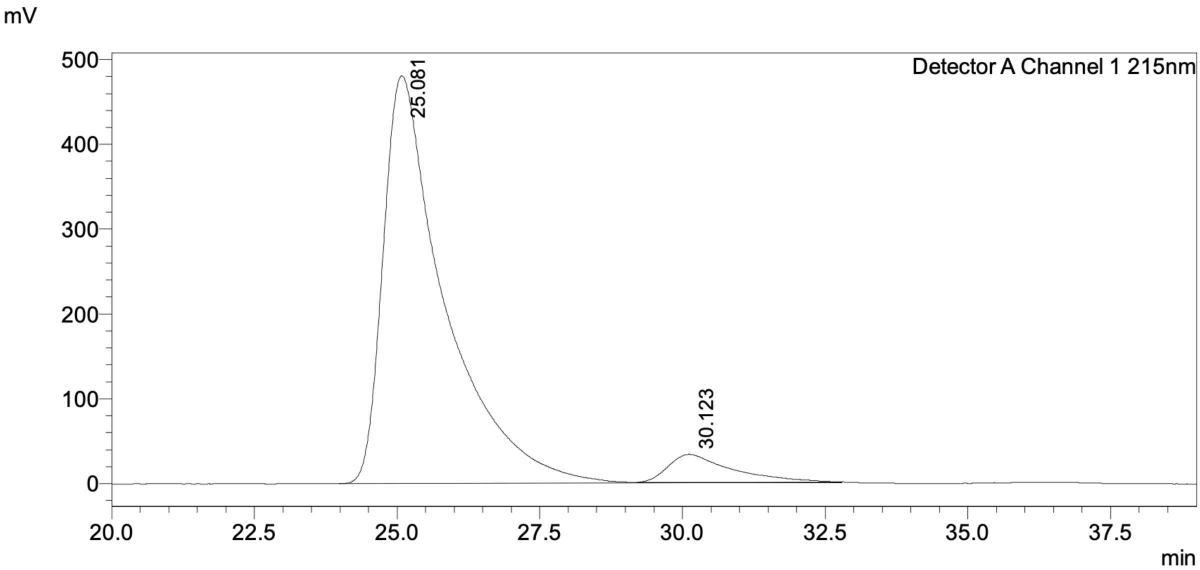
Total		13273340	1169832	100.000





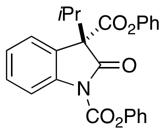
Detector A Channel 1 215nm

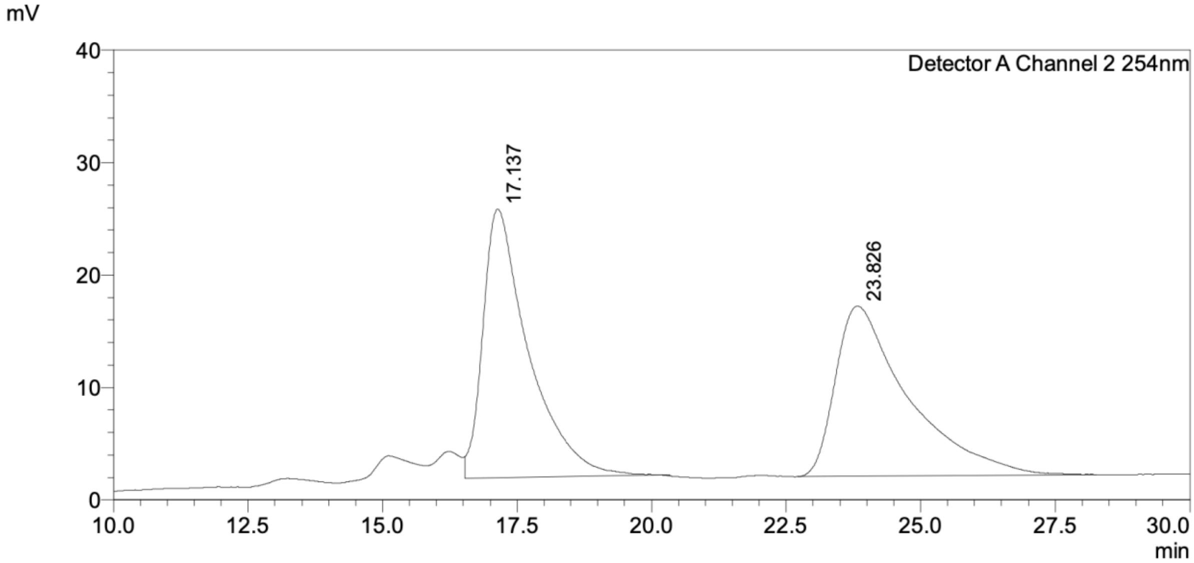
Peak#	Ret. Time	Area	Area%
1	25.008	61536117	50.039
2	30.015	61439966	49.961
Total		122976083	100.000



Detector A Channel 2 254nm

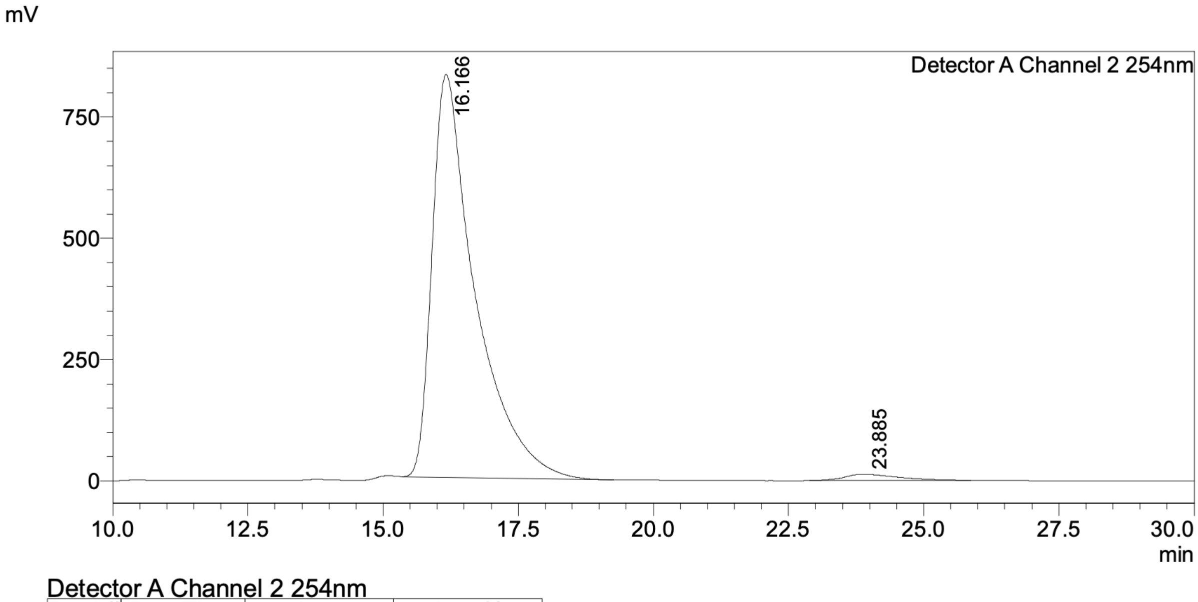
Peak#	Ret. Time	Area	Area%
1	25.082	2460999	93.856
2	30.100	161106	6.144
Total		2622105	100.000





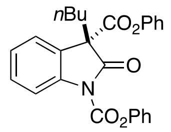
Detector A Channel 2 254nm

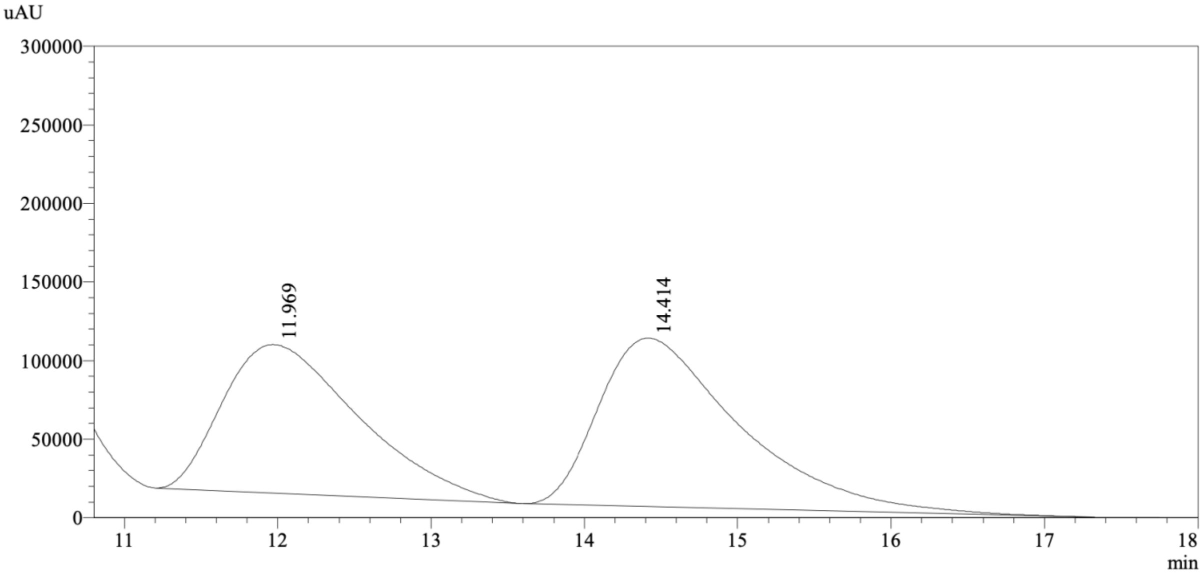
Peak#	Ret. Time	Area	Area%
1	17.137	1408131	49.741
2	23.826	1422795	50.259
Total		2830925	100.000



Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	16.166	46003423	98.070
2	23.885	905213	1.930
Total		46908636	100.000

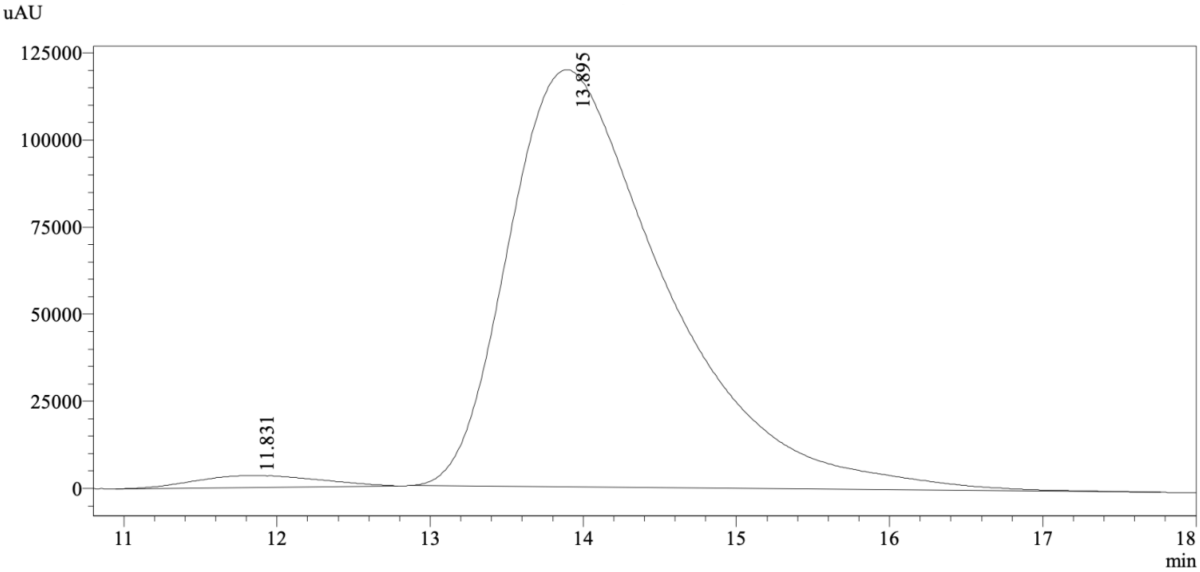




Peak Table

PDA Ch1 210nm

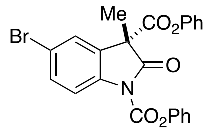
Peak#	Ret. Time	Height	Area	Area%
1	11.973	167926	10516360	46.668
2	14.416	184677	12018254	53.332
Total		352603	22534614	100.000



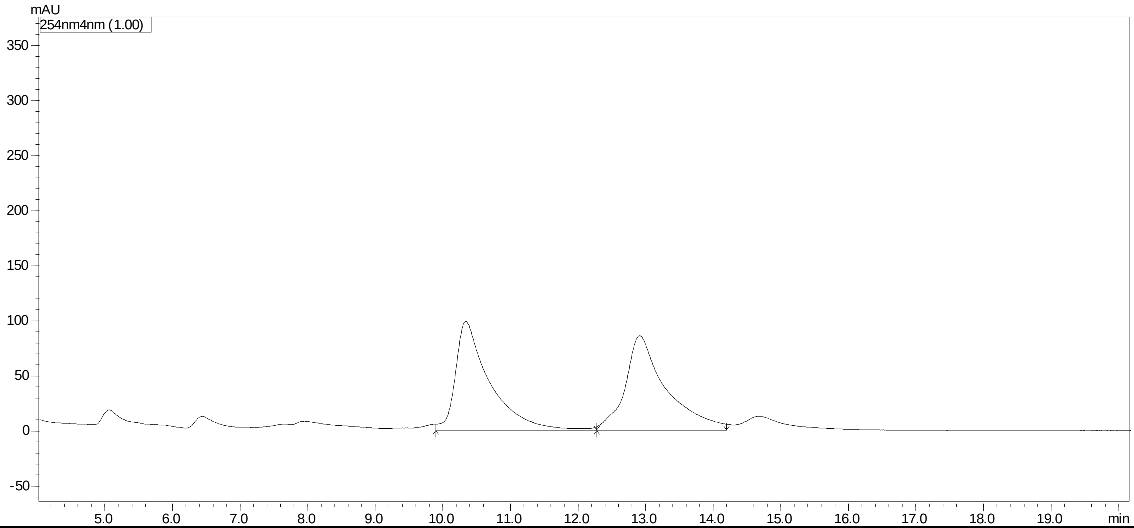
Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Height	Area	Area%
1	11.871	7230	478160	3.073
2	13.880	207600	15083779	96.927
Total		214829	15561939	100.000

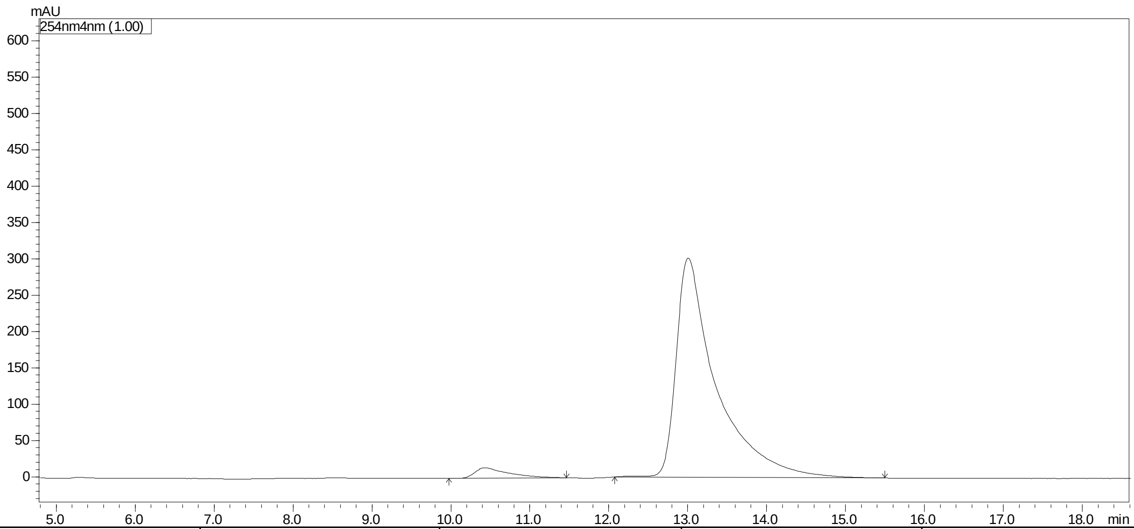


Datafile Name:yzq-R-Br-ADH-90-1.0-3.lcd
Sample Name:yzq-R-Br-ADH-90-1.0-3
Sample ID:1

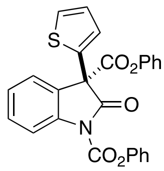


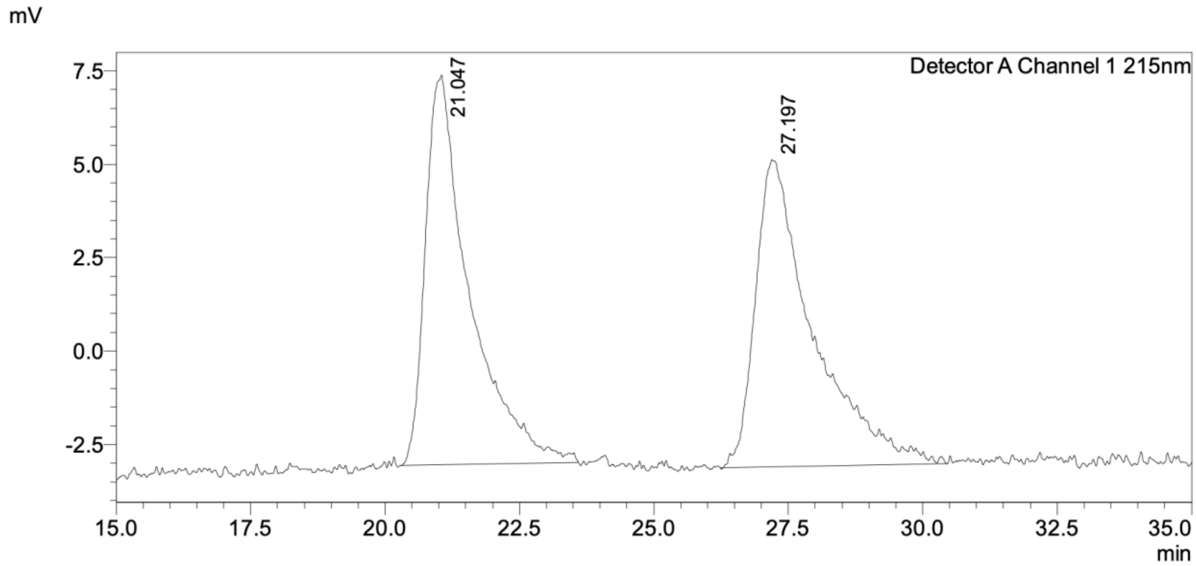
Peak#	Ret. Time	Area	Height	Area%
1	10.340	3474912	98893	49.055
2	12.913	3608816	85957	50.94
Total		7083728	184850	100.000

Datafile Name:yzq-C-Br-ADH-90-1.0.lcd
Sample Name:yzq-C-Br-ADH-90-1.0
Sample ID:1



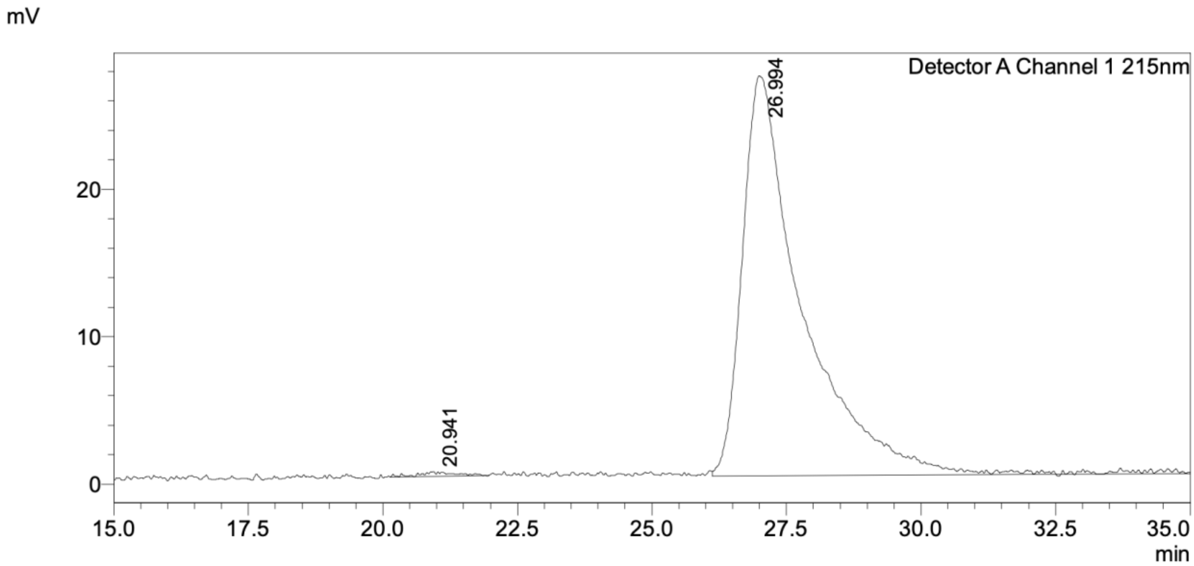
Peak#	Ret. Time	Area	Height	Area%
1	10.430	425742	14513	3.852
2	13.006	10628081	301389	96.148
Total		11053823	315902	100.000





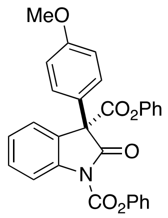
Detector A Channel 1 215nm

Peak#	Ret. Time	Area	Area%
1	21.047	593290	49.308
2	27.197	609940	50.692
Total		1203229	100.000

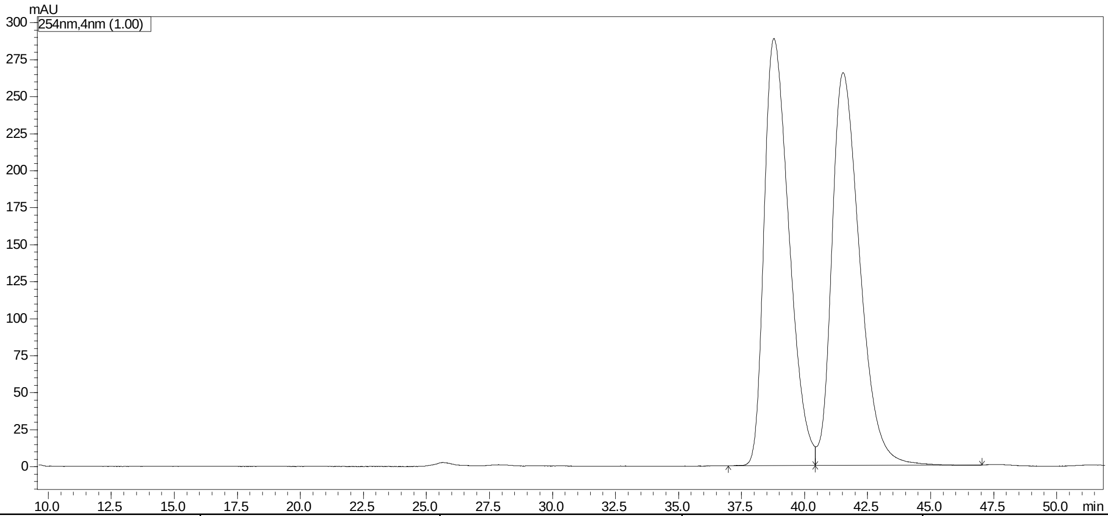


Detector A Channel 1 215nm

Peak#	Ret. Time	Area	Area%
1	20.941	13553	0.708
2	26.994	1899805	99.292
Total		1913358	100.000

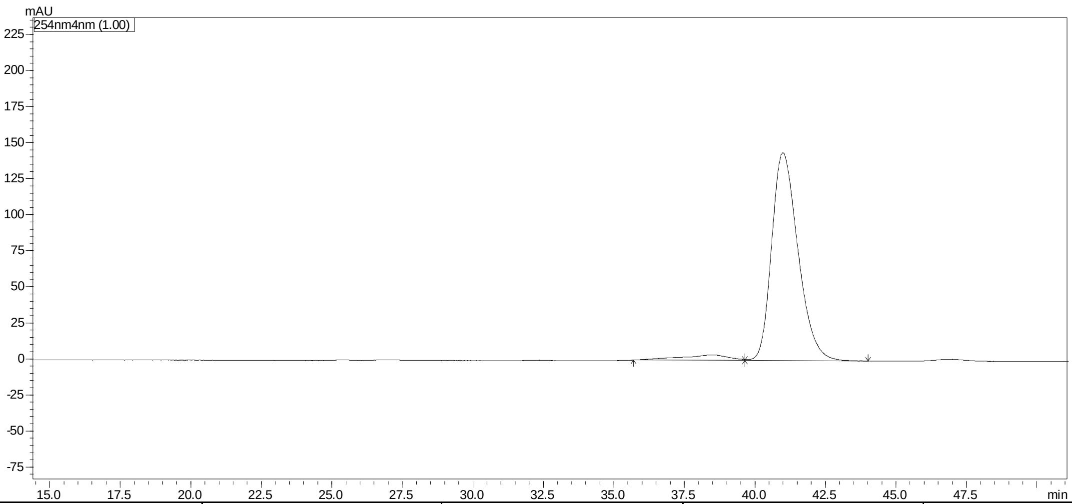


Datafile Name:yzq-R-OMe-IG3-90-1.0.lcd
Sample Name:yzq-R-OMe-IG3-90-1.0
Sample ID:1

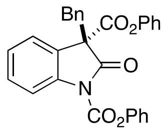


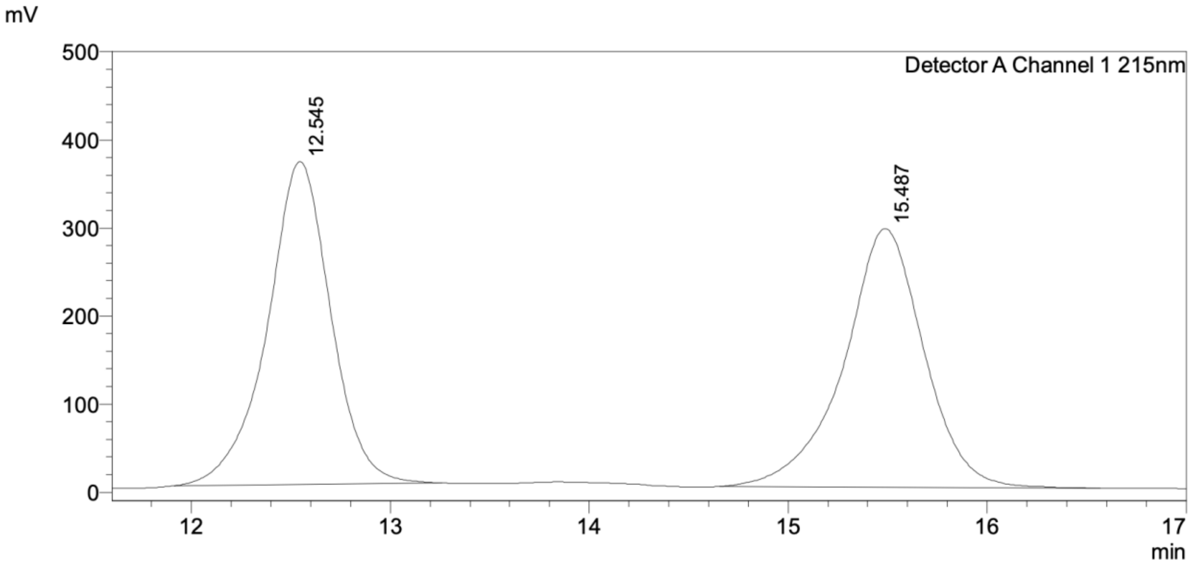
Peak#	Ret. Time	Area	Height	Area%
1	38.785	19858619	288712	49.270
2	41.524	20446899	265380	50.730
Total		40305518	554092	100.000

Datafile Name:yzq-C-OMe-IG3-90-1.0-2.lcd
Sample Name:yzq-C-OMe-IG3-90-1.0-2
Sample ID:1



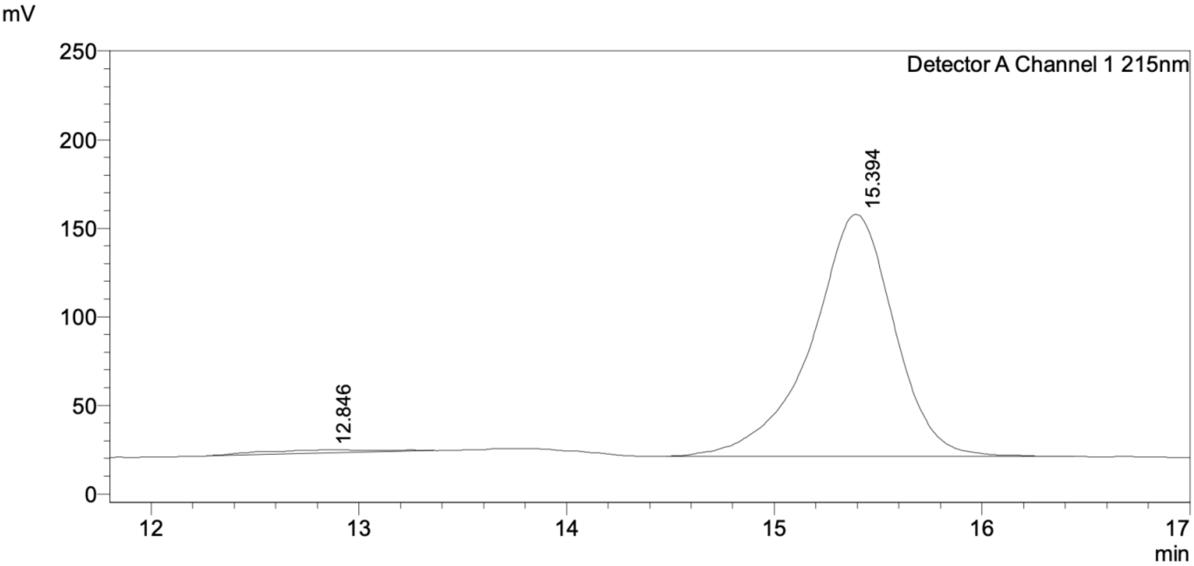
Peak#	Ret. Time	Area	Height	Area%
1	38.473	448611	3856	4.562
2	40.991	9384610	144253	95.438
Total		9833221	148110	100.000





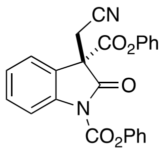
Detector A Channel 1 215nm

Peak#	Ret. Time	Area	Area%
1	12.545	8124336	49.718
2	15.487	8216564	50.282
Total		16340900	100.000

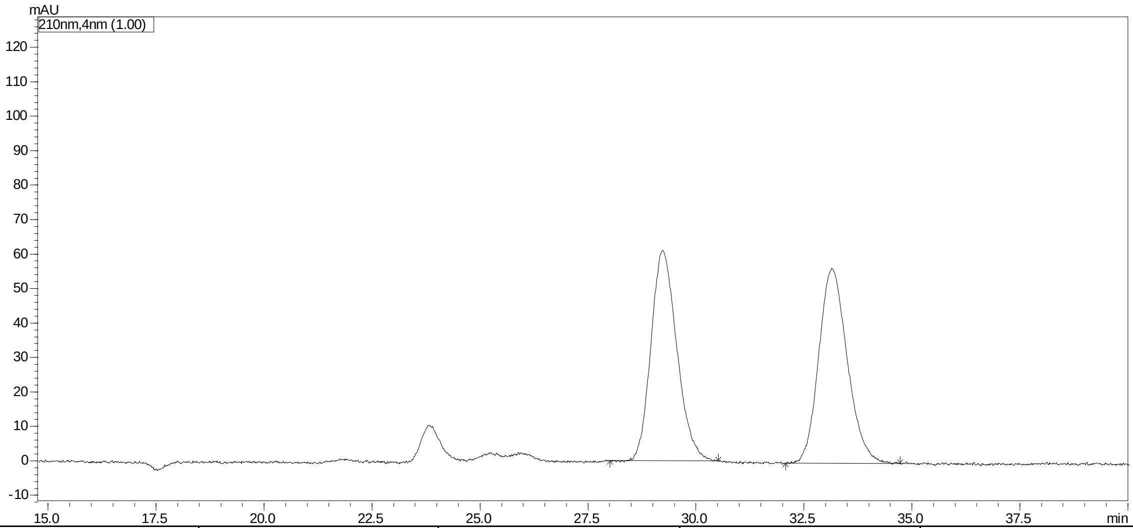


Detector A Channel 1 215nm

Peak#	Ret. Time	Area	Area%
1	12.846	78494	2.027
2	15.394	3793927	97.973
Total		3872421	100.000

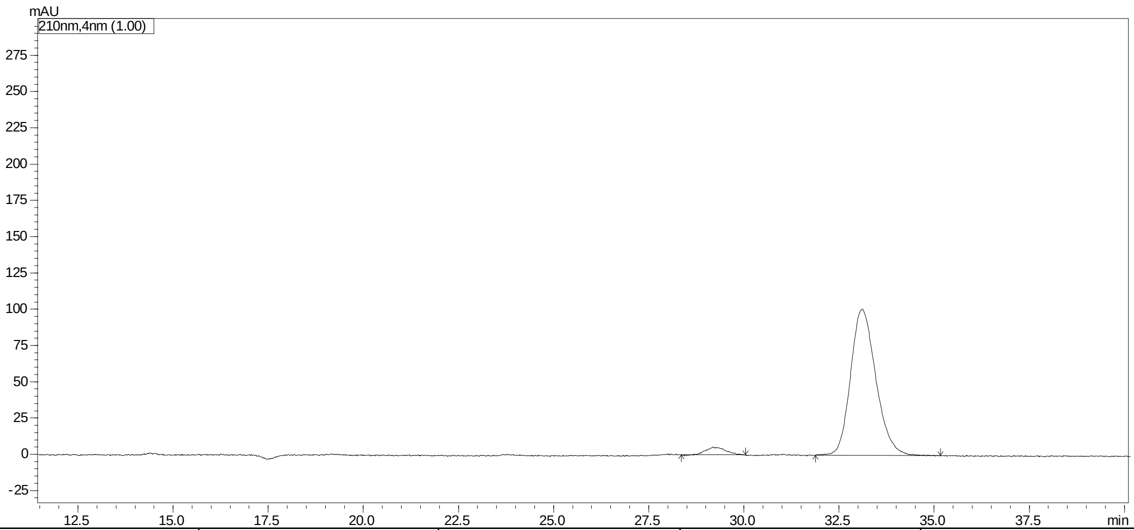


Datafile Name:yzq-R-CN-IG3-90-1.0-2.lcd
Sample Name:yzq-R-CN-IG3-90-1.0-2
Sample ID:1

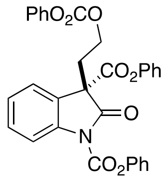


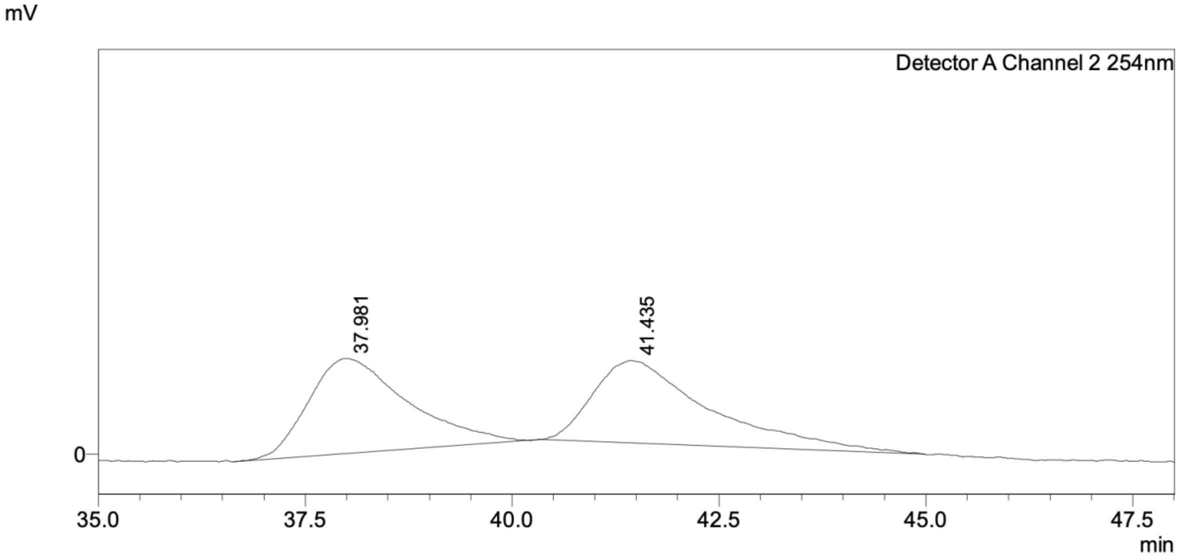
Peak#	Ret. Time	Area	Height	Area%
1	29.235	2536195	60969	49.347
2	33.144	2603317	56586	50.653
Total		5139512	117555	100.000

Datafile Name:yzq-C-CN-IG3-90-1.0.lcd
Sample Name:yzq-C-CN-IG3-90-1.0
Sample ID:1



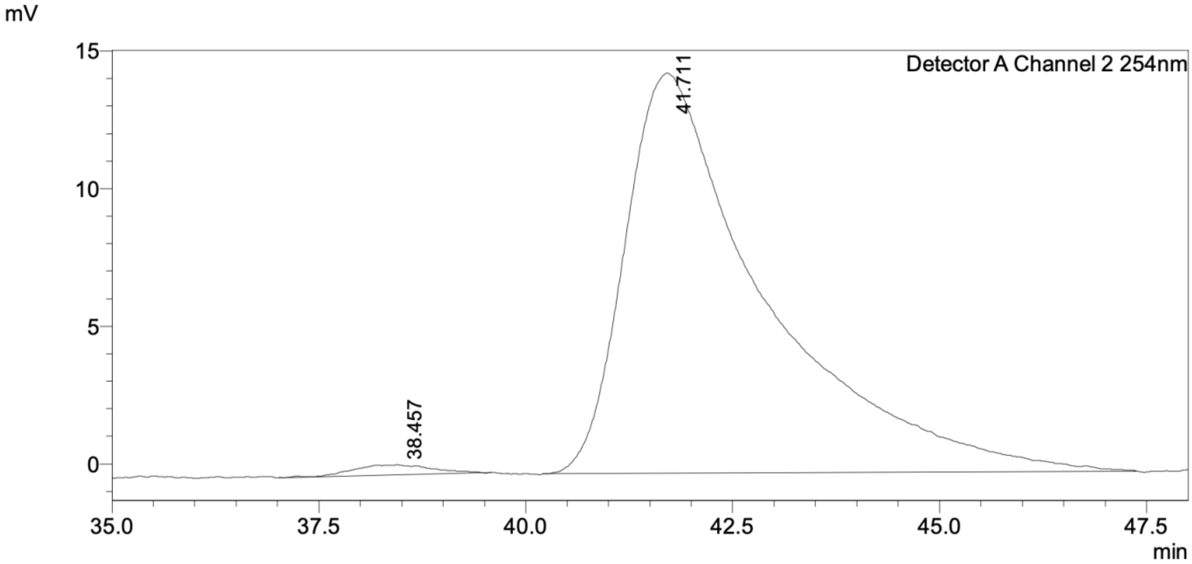
Peak#	Ret. Time	Area	Height	Area%
1	29.198	190478	5588	3.924
2	33.111	4664018	100886	96.076
Total		4854496	106474	100.000





Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	37.981	389766	49.550
2	41.435	396845	50.450
Total		786612	100.000



Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Area%
1	38.457	23563	1.352
2	41.711	1719001	98.648
Total		1742564	100.000