Supporting Information

Asymmetric Synthesis of Trifluoromethylated amines *via* Catalytic Enantioselective Isomerization of imines

Yongwei Wu, Li Deng*

Department of Chemistry
Brandeis University
Waltham, Massachusetts 02454-9110

Table of contents:

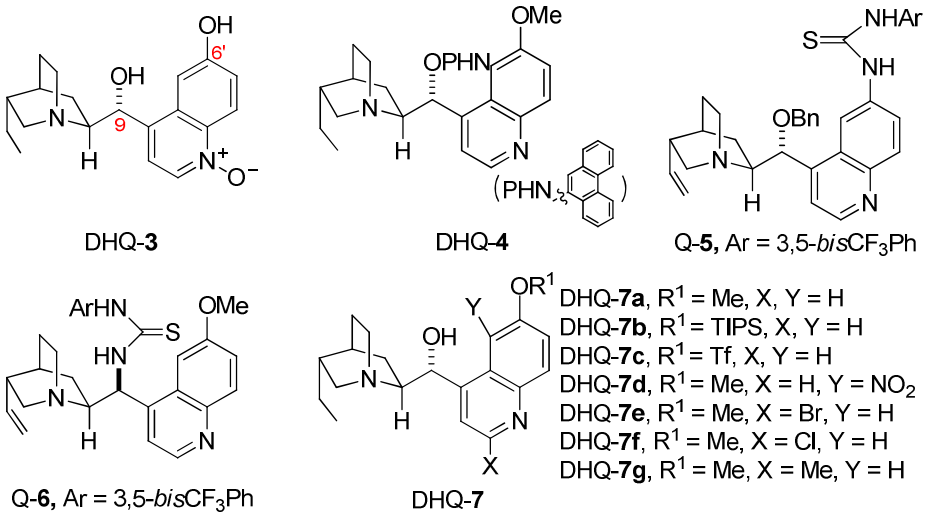
1. General Information.

^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration, coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrometer and are reported in frequency of absorption. Low resolution and high resolution mass spectra were recorded on either a Micromass 70-VSE-B instrument (EI, CI) or a Micromass Q-TOF instrument (ESI). Specific rotations were measured on a Jasco Digital Polarimeter.

High performance liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1100 Series instrument equipped with a quaternary pump, using Daicel Chiralpak AD, Daicel Chiralcel OJ-H or AS-H Columns (250 x 4.6 mm). UV absorption was monitored at 254 nm.

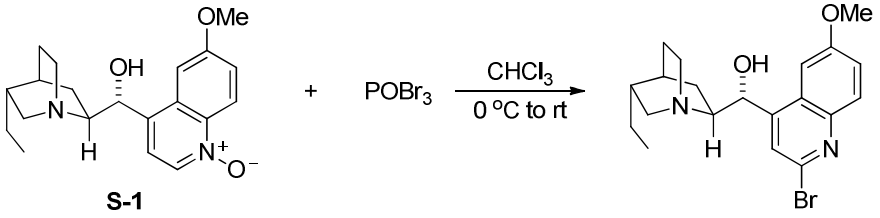
2. Materials:

A. Catalysts (S-Figure 1): Catalysts triethylamine (TEA), DHQ-**4** and DHQ-**7a** were purchased from Sigma-Aldrich Inc. and used as received. DHQ-**3**[1], Q-**6**[2] and DHQ-**7b**[3] were synthesized according to our previous reports. Q-**5**[4], DHQ-**7c**[5] and DHQ-**7d**[6] were prepared from known procedures.



S-Figure 1. Structures of cinchona alkaloids catalysts

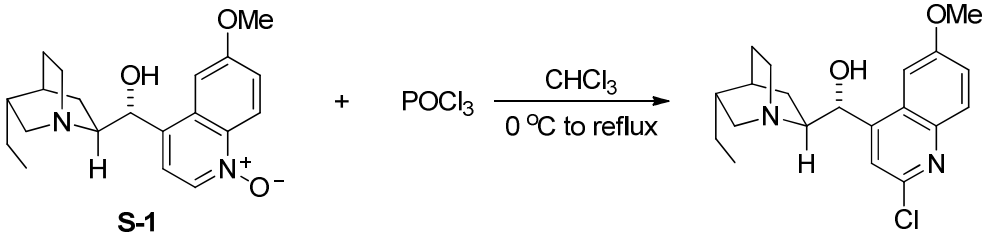
Preparation of catalyst DHQ-7e



S-1 DHQ-**7e**

At 0 °C, to the solution of **S-1**[1] (342 mg, 1.0 mmol) in $CHCl_3$ (3.0 mL) was added dropwise the solution of $POBr_3$ (4.0 mmol, 1.15 g) in $CHCl_3$ (1.0 mL) under N_2. The orange solution was allowed to warm up to room temperature and stirred overnight. $CHCl_3$ (10 mL) was added and the mixture was poured into ice-water (12.0 mL). Then it was adjusted to pH=10 with NH_4OH (sat.). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL×3). The organic layers were combined, dried over Na_2SO_4 and concentrated. The yellow residue was applied to silica (CH_2Cl_2/MeOH/Et_3N = 50/1/1 to 10/1/0.2) to afford DHQ-**7e** as a white solid (210 mg, 52% yield). The catalyst was dried in a vacuum drier at 90 °C for 6h prior to use. m. p. 187-189 °C; $[\alpha]_D^{23}$ = -51.0 (c = 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.2 Hz, 1H), 7.66 (s, 1H), 7.33 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.17 (s, 1H), 5.50 (s, 1H), 3.89 (s, 3H), 3.51 – 3.28 (m, 1H), 3.14 – 2.86 (m, 2H), 2.66 (t, *J* = 10.0 Hz, 1H), 2.39 (d, *J* = 13.4 Hz, 1H), 1.95 – 1.60 (m, 4H), 1.56 – 1.35 (m, 3H), 1.35 – 1.14 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 150.9, 144.7, 139.5, 130.9, 125.7, 123.2, 122.3, 102.0, 71.9, 59.9, 58.8, 56.0, 43.6, 37.6, 28.3, 27.9, 25.5, 21.3, 12.3; IR ($CHCl_3$) ν 2929, 2866, 1620, 1578, 1556, 1504, 1454, 1288, 1233, 1093, 897, 748 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{20}H_{26}BrN_2O_2$ requires m/z 405.1178, found m/z 405.1172.

Preparation of catalyst DHQ-7f

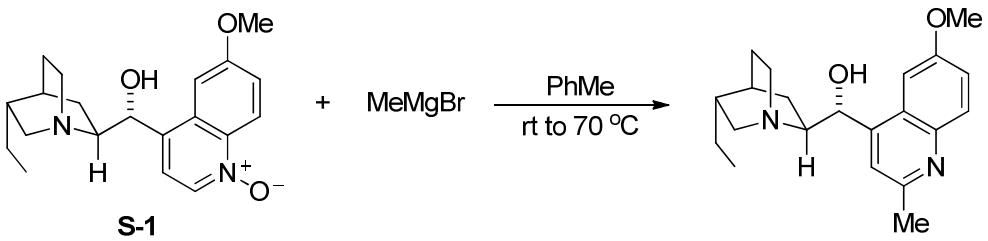


S-1 DHQ-**7f**

At 0 °C, to the solution of **S-1**[1] (1.37 g, 4.0 mmol) in $CHCl_3$ (18.0 mL) was added dropwise the solution of $POCl_3$ (16.0 mmol, 1.5 mL) under N_2. The orange solution was stirred at 0 °C for 30 min before it was moved to a 70 °C oil bath. After being refluxed for 2h, the reaction mixture was poured into ice-water (30 mL). Then it was adjusted to pH=10 with NH_4OH (sat.). The mixture was extracted with CH_2Cl_2 (50 mL×4). The organic layers were combined, washed with brine (40 mL), dried over Na_2SO_4 and concentrated. The yellow residue was applied to silica (CH_2Cl_2/MeOH = 20/1 + 1% NH_4OH) to afford DHQ-**7f** as a white solid (1.27 g, 88% yield). The catalyst was dried in a vacuum drier at 90 °C for 6 h prior to use. m. p. 196-198 °C; $[\alpha]_D^{23}$ = -78.6 (c = 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.89 (d, *J* = 9.2 Hz, 1H), 7.54 (s, 1H), 7.33 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 5.55 (s, 1H), 3.88 (s, 3H), 3.46 (bs, 1H), 3.08 (dd, *J* = 13.3, 9.8 Hz, 2H), 2.67 (t, *J* = 9.9 Hz, 1H), 2.39 (d, *J* = 13.5 Hz, 1H), 2.00 (bs, 1H), 1.84 – 1.62

(m, 3H), 1.59 – 1.32 (m, 3H), 1.32 – 1.09 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 151.8, 148.4, 143.8, 130.5, 125.4, 122.0, 119.7, 102.0, 71.8, 59.8, 58.7, 55.8, 43.4, 37.5, 28.2, 27.8, 25.4, 21.2, 12.2; IR ($CHCl_3$) ν 2930, 2888, 1620, 1590, 1503, 1296, 1235, 1099, 1031, 911, 831, 753 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{20}H_{26}N_2O_2Cl$ requires m/z 361.1683, found m/z 361.1685.

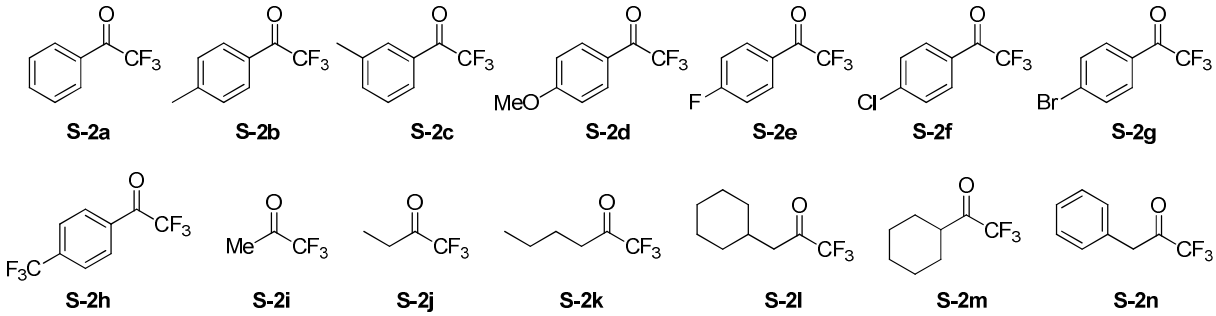
Preparation of catalyst DHQ-7g



A modified procedure from a reported 2'-Methylquinidine synthesis[7] was used here. At ambient temperature, to a dry 25 mL flask charged with MeMgBr (3.12 M in ether, 4.0 mL) was added dropwise the solution of **S-1** (342 mg, 1.0 mmol) in PhMe (7.0 mL) over 15 min. The resulting dark red solution was moved to a 70 °C oil bath. After 2.5 h, the reaction was quenched by the addition of ice-water (10.0 mL). HCl (conc., 12.1 M) was added to make the solution acidic as indicated by pH paper. The aqueous layer was washed with Et_2O (10 mL×2), basified with NaOH (sat.), and extracted with $CHCl_3$ (20 mL×4). The organic extracts were combined, washed with brine, dried over Na_2SO_4 and concentrated. The residue was applied to silica gel column (CH_2Cl_2/MeOH =20/1 + 1% NH_4OH) to afford DHQ-**7g** as a light yellow solid (182 mg, 54% yield). The catalyst was vacuumed for 6h prior to use. m. p. 113-115 °C; $[\alpha]_D^{23}$ = -77.0 (c = 0.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 9.2 Hz, 1H), 7.39 (s, 1H), 7.29 (dd, J = 9.2, 2.8 Hz, 1H), 7.15 (d, J = 2.6 Hz, 1H), 5.51 (d, J = 3.8 Hz, 1H), 3.88 (s, 3H), 3.46 (bs, 1H), 3.15 – 3.00 (m, 2H), 2.72 – 2.59 (m, 4H), 2.44 – 2.33 (m, 1H), 1.83 – 1.64 (m, 3H), 1.54 – 1.35 (m, 3H), 1.31 – 1.15 (m, 3H), 0.81 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 156.1, 147.8, 144.0, 130.8, 124.8, 121.3, 119.4, 101.4, 72.0, 59.9, 58.7, 55.8, 43.5, 37.6, 28.3, 27.8, 25.6, 25.2, 21.5, 12.2; IR ($CHCl_3$) ν 2930, 2867, 1621, 1602, 1505, 1455, 1379, 1343, 1232, 1121, 1034, 831, 752 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{21}H_{29}N_2O_2$ requires m/z 341.2229, found m/z 341.2236.

B. Trifluoromethyl ketones (S-Figure 2)

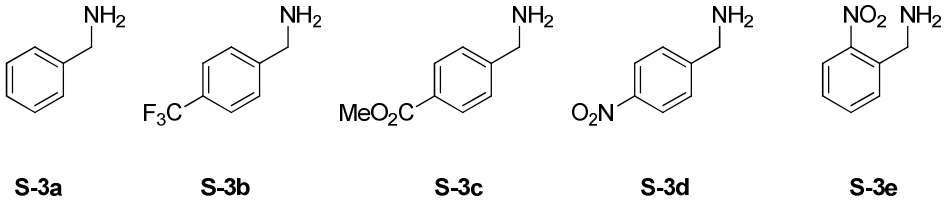
Trifluoromethyl ketones **S-2a** to **S-2k** and **S-2n** were purchased from VWR international Inc. and used directly. **S-2l** and **S-2m** were synthesized via a literature reported procedure[8].



S-Figure 2. Structures of trifluoromethyl ketones

C. Benzylamines (S-Figure 3)

Benzylamines **S-3a**, **S-3b** and hydrochloride salts of benzylamines **S-3c** to **S-3e** were purchased from VWR International Inc., benzylamines **S-3c** to **S-3e** were obtained *via* neutralization of the corresponding benzylamine hydrochloride salts with NH_4OH (sat.) followed by extraction with CH_2Cl_2.

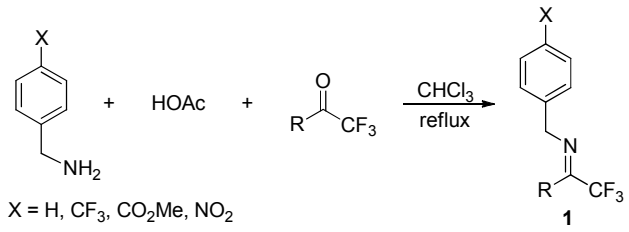


S-Figure 3. Structures of benzylamines

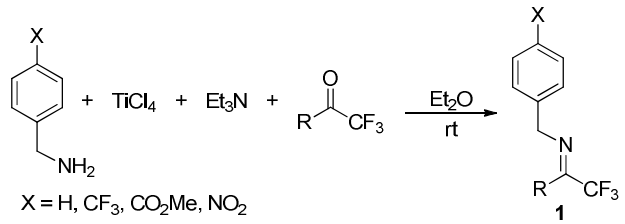
D. *N*-benzyl trifluoromethyl imines

General procedure for the preparation of *N*-benzyl imines **1**

Method A



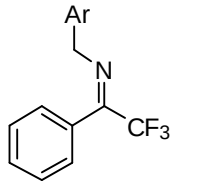
Method B



Method A: To the mixture of benzyl amine (1.0 eq.) and acetic acid (1.0 eq.) in $CHCl_3$ (1.0 mL/mmol) was added the solution of trifluoromethyl ketone (1.0 eq.) in $CHCl_3$ (0.2 mL/mmol) in one portion. The resulting mixture was refluxed until all the ketone was consumed (indicated by TLC or by the disappearance of the insoluble solid). After cooling down to room temperature, CH_2Cl_2 (4.0 mL/mmol) was added and the mixture was washed with $NaHCO_3$ (sat., 2.0 mL/mmol). The aqueous layer was extracted with CH_2Cl_2 (4.0 mL/mmol×2). The organic phase was combined, washed with brine, dried over Na_2SO_4 and concentrated. The yellow residue was applied to silica gel columatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) to afford the benzyl imine.

Method B: At -40 ^oC to the solution of trifluoroketone (1.0 eq.) in ethyl ether (0.6 mL/mmol) was added the solution of 4-NO_2 benzylamine (1.0 eq.) and triethylamine (2.0 eq.) in ethyl ether (0.4 mL/mmol). After 5 mins, the reaction mixture was raised to 0 ^oC and $TiCl_4$ (0.5 eq.) in hexanes (4.0 mL/mmol $TiCl_4$) was added dropwise. After the addition, the orange suspension was allowed to warm up to room temperature. The reaction was monitored by ^1H NMR. After the consumption of benzyl amine, ethyl ether (2.0 mL/mmol ketone) was then added. The solid was filtered and washed with ether (2.0 mL/mmol ketone). The filtrate was combined and concentrated to afford a yellow liquid which was applied to silica (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) to afford the desired benzyl imine.

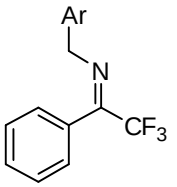
Benzylamines **1Aa** and **1Ba** were synthesized according to a literature procedure[9].



Ar = 4-CO_2MePh

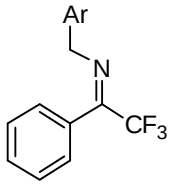
1Ca

4-Carboxylate benzyl imine 1Ca. This compound was synthesized *via* method A and was isolated by flash chromatography (Hexanes/EA = 50/1 to Hexanes/EA = 5/1) as a yellow liquid in 73% yield. The compound could be stored for months under -50 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.01 (d, J = 8.2 Hz, 2H), 7.54 – 7.45 (m, 3H), 7.34 (d, J = 8.1 Hz, 2H), 7.31 – 7.26 (m, 2H), 4.64 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.9, 159.6 (q, $J_{C\text{-}F}$ = 33.9 Hz), 143.3, 130.4, 130.0, 129.9, 129.1, 129.0, 127.5, 127.4, 119.7 (q, $J_{C\text{-}F}$ = 278.8 Hz), 56.4, 52.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -71.3; IR($CHCl_3$) ν 2953, 1719, 1669, 1613, 1577, 1436, 1332, 1277, 1190, 1128, 1019, 963, 838, 754 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{17}H_{15}NO_2F_3$ m/z 322.1055, found m/z 322.1061.



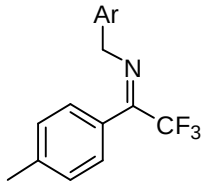
Ar = 4-NO_2Ph
1Da

4-NO_2 benzyl imine 1Da. This compound was synthesized *via* method A as a white solid in 41% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 8.5 Hz, 2H), 7.59 – 7.49 (m, 3H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.27 (m, 2H), 4.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4 (d, J_{C-F} = 34.2 Hz), 147.3, 145.6, 130.8, 129.9, 129.3, 128.3, 127.5, 123.9, 119.7 (d, J_{C-F} = 278.7 Hz), 56.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -71.4; IR($CHCl_3$) ν 1670, 1604, 1518, 1340, 1190, 1126, 1017, 943, 841, 701 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{15}H_{12}N_2O_2F_3$ m/z 309.0851, found m/z 309.0847.



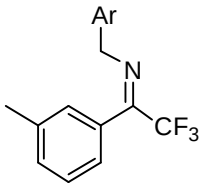
Ar = 2-NO_2Ph
1Ea

2-NO_2 benzyl imine 1Ea. This compound was synthesized *via* method A as a yellow solid in 40% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.61 (m, 2H), 7.54 – 7.41 (m, 4H), 7.38 – 7.28 (m, 2H), 4.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4 (q, J_{C-F} = 34.2 Hz), 148.1, 134.21, 134.0, 130.8, 130.3, 130.1, 129.3, 128.4, 127.6, 125.2, 119.8 (q, J_{C-F} = 278.8 Hz), 54.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -71.2; IR($CHCl_3$) ν 1670, 1613, 1526, 1445, 1340, 1196, 1131, 1014, 961, 858, 731 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{15}H_{12}N_2O_2F_3$ m/z 309.0851, found m/z 309.0842.



Ar = 4-NO_2Ph
1Db

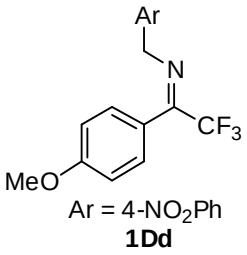
4-NO_2 benzyl imine 1Db. This compound was synthesized *via* method A as a white solid in 35% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.71 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5 (q, J_{C-F} = 34.0 Hz), 147.2, 145.8, 141.1, 129.9, 129.6, 128.3, 127.5, 126.9, 124.0, 123.9, 119.7 (q, J_{C-F} = 278.8 Hz), 56.0, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -71.3. IR($CHCl_3$) ν 1667, 1605, 1520, 1341, 1193, 1130, 1036, 843, 736 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{16}H_{14}N_2O_2F_3$ m/z 323.1007, found m/z 323.0999.



Ar = 4-NO_2Ph
1Dc

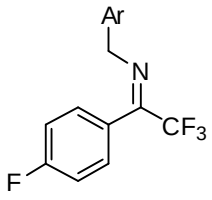
4-NO_2 benzyl imine 1Dc. This compound was synthesized *via* method A as a white solid in 50% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.06 (m, 2H), 4.68 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.6 (q, J_{C-F} = 34.1 Hz), 147.2, 145.8, 139.2, 131.5, 129.9, 129.1, 128.3, 127.9, 124.6, 123.9, 119.7 (d, J_{C-F} = 278.7 Hz), 56.0, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -71.4. IR($CHCl_3$) ν 1670, 1604, 1520, 1342, 1242, 1194, 1131, 1039, 968, 854, 718cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for

$C_{16}H_{14}N_2O_2F_3$ m/z 323.1007, found m/z 323.1008.



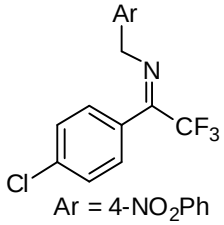
Ar = 4-NO_2Ph
1Dd

4-NO_2 benzyl imine 1Dd. This compound was synthesized *via* method A as a white solid in 49% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 4.73 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.4, 160.2 (q, $J_{C\text{-}F}$ = 33.9 Hz), 147.3, 146.1, 129.4, 128.4, 124.0, 121.8, 119.9 (q, $J_{C\text{-}F}$ = 278.7 Hz), 114.7, 56.0, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -71.2. IR($CHCl_3$) ν 1664, 1604, 1558, 1463, 1340, 1294, 1255, 1176, 1126, 1024, 935, 835, 737cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{16}H_{14}N_2O_3F_3$ m/z 339.0957, found m/z 339.0950.



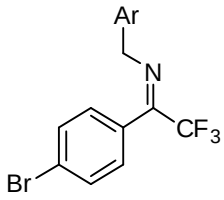
Ar = 4-NO_2Ph
1De

4-NO_2 benzyl imine 1De. This compound was synthesized *via* method A as a white solid in 28% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 2/1). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 2H), 4.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.0 (d, $J_{C\text{-}F}$ = 252.2 Hz), 159.4 (q, $J_{C\text{-}F}$ = 34.3 Hz), 147.4, 145.5, 130.0 (d, $J_{C\text{-}F}$ = 8.5 Hz), 128.3, 125.9, 125.9, 124.0, 119.6 (q, $J_{C\text{-}F}$ = 278.5 Hz), 116.7 (d, $J_{C\text{-}F}$ = 22.0 Hz), 56.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -71.4, -108.8; IR($CHCl_3$) ν 3081, 1660, 1601, 1517, 1343, 1226, 1195, 1132, 1007, 838, 771 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{15}H_{11}N_2O_2F_4$ m/z 327.0757, found m/z 327.0751.



Ar = 4-NO_2Ph
1Df

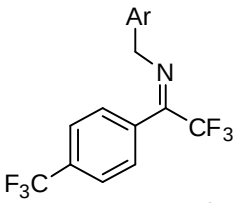
4-NO_2 benzyl imine 1Df. This compound was synthesized *via* method A as a white solid after in 62% yield (based on recovered ketone) after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.1 (q, $J_{C\text{-}F}$ = 34.5 Hz), 147.2, 145.3, 137.1, 129.6, 129.0, 128.2, 128.1, 123.9, 119.5 (d, *J* = 278.8 Hz), 56.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -71.3. IR($CHCl_3$) ν 1918, 1671, 1603, 1519, 1491, 1341, 1192, 1130, 1092, 1014, 937, 830, 767, 737 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{15}H_{11}N_2O_2F_3Cl$ m/z 343.0461, found m/z 343.0464.



Ar = 4-NO_2Ph
1Dg

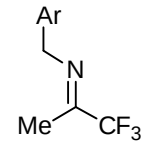
4-NO_2 benzyl imine 1Dg. This compound was synthesized *via* method A as a white solid in 37% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/2). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 4.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.4 (q, $J_{C\text{-}F}$ = 34.8 Hz), 147.4, 145.3, 132.7, 129.3, 128.7, 128.3, 125.6, 124.1, 119.5 (d, $J_{C\text{-}F}$ = 278.6 Hz), 56.2; ^{19}F

NMR (376 MHz, $CDCl_3$) δ = -71.4. IR($CHCl_3$) ν 1671, 1603, 1518, 1487, 1341, 1191, 1130, 1072, 1011, 937, 825, 736 cm^{-1}; HRMS (EI/$[M]^+$) Calcd. for $C_{15}H_{10}BrF_3N_2O_2$ m/z 385.9878, found m/z 385.9808.



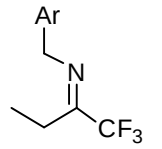
Ar = 4-NO_2Ph
1Dh

4-NO_2 benzyl imine 1Dh. This compound was synthesized *via* method A as a white solid after in 63% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 4.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.0 (q, J_{C-F} = 34.8 Hz), 147.4, 145.2, 133.6, 132.9 (q, J_{C-F} = 33.0 Hz), 128.4, 128.3, 126.5 (q, J_{C-F} = 3.7 Hz), 125.0 (q, J_{C-F} = 266.7 Hz), 124.0, 119.5 (q, J_{C-F} = 278.6 Hz), 56.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.6, -71.4. IR($CHCl_3$) ν 1672, 1605, 1520, 1323, 1195, 1124, 1066, 1016, 942, 842, 736, 695 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{16}H_{11}N_2O_2F_6$ m/z 377.0725, found m/z 377.0726.



Ar = 4-NO_2Ph
1Di

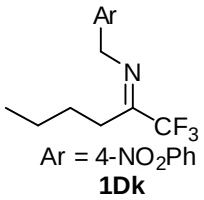
4-NO_2 benzyl imine 1Di. This compound was synthesized *via* method B as a yellow liquid which was solidified as a yellow solid at -50 °C in 33% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 4.72 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.3 (q, J_{C-F} = 33.7 Hz), 147.2, 145.8, 128.3, 123.9, 119.7 (q, J_{C-F} = 278.1 Hz), 54.3, 13.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -75.1; IR($CHCl_3$) ν 1688, 1606, 1518, 1339, 1195, 1118, 1050, 842, 736 cm^{-1}; HRMS (EI/$[M]^+$) Calcd. for $C_{10}H_9O_2N_2F_3$ m/z 246.0616, found m/z 246.0613.



Ar = 4-NO_2Ph
1Dj

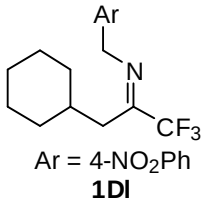
4-NO_2 benzyl imine 1Dj. This compound was synthesized *via* a modified procedure from method A. To the mixture of 4-NO_2 benzyl amine (5.0 mmol) and acetic acid (5.0 mmol) in benzene (5.0 mL) was added the solution of trifluoromethyl ketone (5.0 mmol) in benzene (1.0 mL) in one portion. Then 500 mg 4 Å MS was added. The mixture was refluxed for 24h. After cooling down to rt, CH_2Cl_2 (20.0 mL) was added and the mixture was washed with $NaHCO_3$ (sat., 10.0 mL). The aqueous layer was extracted with CH_2Cl_2 (20 mL×2). The organic solvents were combined, washed with brine, dried over Na_2SO_4 and concentrated. The yellow residue was applied to silica gel columatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) to afford **4-NO_2 benzyl imine 1Dj** as a yellow liquid which was solidified as a yellow solid at -50 °C in 23% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 4.80 (s, 2H), 2.57 (q, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8 (q, J_{C-F} = 32.2 Hz), 147.2, 145.9, 128.2, 123.8, 120.0 (q, J_{C-F} = 279.3 Hz), 53.5, 21.0, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -73.4;

IR($CHCl_3$) ν 2967, 2847, 1707, 1604, 1521, 1344, 1197, 1126, 1052, 936, 850, 816 cm^{-1}; HRMS (EI/$[M]^+$) Calcd. for $C_{11}H_{11}O_2N_2F_3$ m/z 260.0773, found m/z 260.0769.



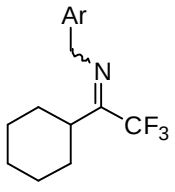
1Dk

4-NO_2 benzyl imine 1Dk. This compound was synthesized *via* method B as a yellow liquid in 41% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 4.79 (s, 2H), 2.60 – 2.44 (m, 2H), 1.68 – 1.50 (m, 2H), 1.50 – 1.32 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.0 (q, $J_{C\text{-}F}$ = 32.3 Hz), 147.1, 146.0, 128.2, 123.7, 119.9 (q, $J_{C\text{-}F}$ = 279.5 Hz), 53.6, 28.0, 27.6, 23.0, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -73.2; IR($CHCl_3$) ν 2964, 2875, 1683, 1605, 1520, 1342, 1188, 1127, 1076, 980, 841, 737 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{13}H_{16}N_2O_2F_3$ m/z 289.1164, found m/z 289.1155.



1Dl

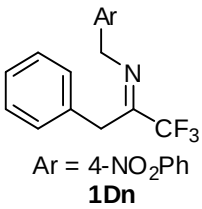
4-NO_2 benzyl imine 1Dl. This compound was synthesized *via* method B as a yellow solid in 18% yield after flash chromatography (Hexanes/CH_2Cl_2 = 5/1 to Hexanes/CH_2Cl_2 = 1/1). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 4.79 (s, 2H), 2.44 (d, *J* = 7.3 Hz, 2H), 1.84 – 1.61 (m, 5H), 1.35 – 0.73 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.5 (q, $J_{C\text{-}F}$ = 32.1 Hz), 147.2, 146.3, 128.3, 123.8, 119.9 (d, $J_{C\text{-}F}$ = 279.9 Hz), 54.4, 36.2, 35.6, 33.6, 26.3, 26.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -72.0; IR($CHCl_3$) ν 2926, 2853, 1682, 1604, 1520, 1450, 1340, 1186, 1130, 1090, 839, 737 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{16}H_{20}N_2O_2F_3$ m/z 329.1477, found m/z 329.1487.



1Dm

4-NO_2 benzyl imine 1Dm. This compound was synthesized *via* a modified procedure from method A. To the mixture of 4-NO_2 benzyl amine (3.0 mmol) and acetic acid (3.0 mmol) in benzene (3.0 mL) was added the solution of trifluoromethyl ketone (3.0 mmol) in benzene (1.0 mL) in one portion. The mixture was refluxed with Dean-Stark apparatus for 24h. After cooling down to rt, CH_2Cl_2 (20.0 mL) was added and the mixture was washed with $NaHCO_3$ (sat., 10.0 mL). The aqueous layer was extracted with CH_2Cl_2 (20 mL×2). The organic solvents were combined, washed with brine, dried over Na_2SO_4 and concentrated. The yellow residue was applied to silica gel columatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) to afford **4-NO_2 benzyl imine 1Dm** as a mixture of E/Z imine stereoisomers (2/1 ratio) in 32% yield as a yellow solid after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) (About 6% enamine was also present, but it won't affect the isomerization.). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = Major isomer: 8.22 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 4.83 (s, 2H), 2.81 (t, *J* = 12.1 Hz, 1H), 2.00 – 1.58 (m, 6H), 1.45 – 1.08 (m, 4H); Minor isomer: 4.90 (s, 2H), 2.60 (t, *J* = 9.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = Major isomer: 164.2 (q, *J*

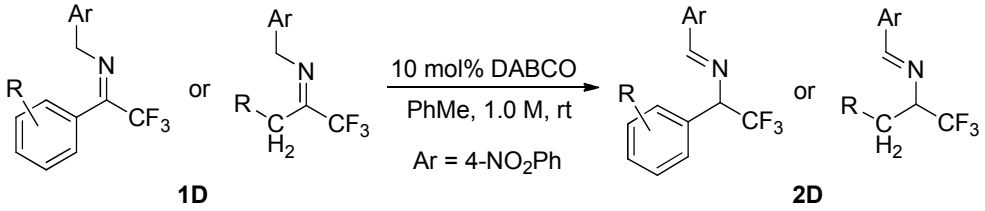
$J_{C\text{-}F}$ = 30.4 Hz), 147.3, 146.4, 128.3, 123. 9, 120.3 (q, J = 280.9 Hz), 53.3, 40.2, 30.6, 28.5, 26.3, 25.7. Minor isomer: 162.4 (q, $J_{C\text{-}F}$ = 25.7 Hz), 128.2, 123.8, 54.6, 54.5, 43.2, 30.1, 26.2, 26.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = Minor: -65.6, Major: -69.2; IR($CHCl_3$) ν 2937, 2860, 1675, 1520, 1468, 1342, 1192, 1120, 1017, 843, 738 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{15}H_{18}N_2O_2F_3$ m/z 315.1320, found m/z 315.1318.



4-NO_2 benzyl imine 1Dn. This compound was synthesized *via* method B as a yellow solid in 39% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 3/2). The compound could be stored for months under -50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.17 (d, J = 7.3 Hz, 2H), 4.73 (s, 2H), 3.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.2 (q, $J_{C\text{-}F}$ = 32.9 Hz), 147.0, 145.5, 133.2, 129.2, 128.2, 127.3, 123.6, 119.7 (d, $J_{C\text{-}F}$ = 279.1 Hz), 54.4, 33.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -73.2; IR($CHCl_3$) ν 3032, 2936, 1683, 1603, 1518, 1455, 1341, 1193, 1126, 1088, 997, 840, 735 cm^{-1}; HRMS (EI/[M]$^+$) Calcd. for $C_{16}H_{13}O_2N_2F_3$ m/z 322.0929, found m/z 322.0923.

3. Isomerization of trifluoromethyl imines

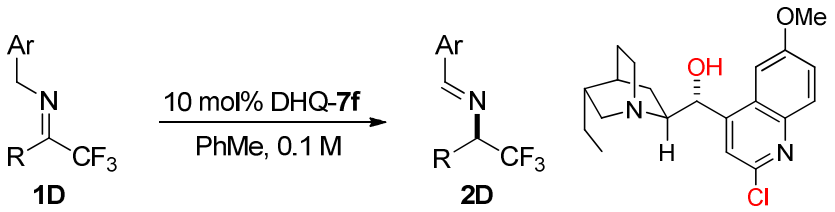
Synthesis of racemic trifluoromethylated amines:



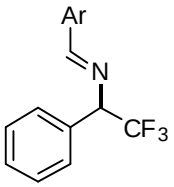
1D **2D**

To the solution of trifluoromethyl imine **1D** (0.05 mmol) in PhMe (0.05 mL) was added DABCO (0.005 mmol), the mixture was stirred at room temperature for 2h (for aryl trifluoromethyl imines) or 12h (for alkyl trifluoromethyl imines) until all the imine was isomerized. The reaction was stopped by passing the reaction mixture through a plug of silica gel to remove DABCO. The silica gel plug was then washed with diethyl ether (1.0-2.0 mL). The solvent was evaporated *in vacuo* to afford the pure racemic trifluoromethylated amine **2D** in over 90% yield.

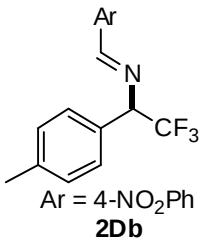
General procedure for the asymmetric isomerization of trifluomethyl imines:



To the solution of trifluoromethyl imine **1D** (0.20 mmol) in toluene (2.0 mL) was added 4 Å MS (20 mg). The suspension was stirred at room temperature for 10 min before being moved into the specified temperature in the Table. After the mixture was fully chilled, the solution of DHQ-**7f** (0.02 mmol) in CH_2Cl_2 (0.02 mL) was added in one portion. Then the mixture was allowed to stir for the designated time in Table 3 & 4. The reaction was stopped by passing the reaction mixture through a plug of silica gel to remove the catalyst. The silica gel plug was then washed with diethyl ether (2.0-4.0 mL). The filtrate was concentrated *in vacuo* to give a residue, which is purified by column chromatography on MeOH/Et_3N deactivated silica (eluent: Hexanes/ CH_2Cl_2 = 20/1 to 1/1) to yield the corresponding trifluoromethylated amines **2D**.

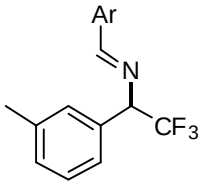


Trifluoromethylated amine 2Da. The product was obtained as a white solid in 75% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) and 90% ee[10] as determined by HPLC analysis [Daicel Chiralpak AD, Hexanes/IPA=80/20, 1.0 ml/min, λ 254 nm, t(major) = 8.66 min, t(minor) = 12.39 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at -30°C for 48h. $[\alpha]_D^{23}$ = +205.3 (c = 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 4.6 Hz, 2H), 7.46 – 7.29 (m, 3H), 4.84 (q, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.9, 149.8, 140.8, 134.5, 129.7, 129.5, 129.0, 124.7 (q, $J_{C\text{-}F}$ = 280.9 Hz), 124.1, 75.3 (q, $J_{C\text{-}F}$ = 28.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -74.1 (d, *J* = 7.1 Hz); IR($CHCl_3$) ν 2879, 1650, 1603, 1523, 1455, 1386, 1345, 1258, 1167, 1124, 1051, 871, 708 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{15}H_{12}N_2O_2F_3$ m/z 309.0851, found m/z 309.0860.



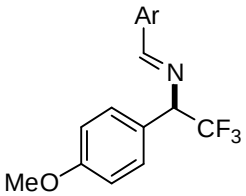
Trifluoromethylated amine 2Db. The product was obtained as a light yellow liquid in 76% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) and 90% ee as determined by HPLC analysis [Daicel Chiralcel OJ-H, Hexanes/IPA=70/30, 1.0 ml/min, λ 254 nm, t(major) = 21.64 min, t(minor) = 17.55 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at -30°C for 72h. $[\alpha]_D^{23}$ = +143.2 (c = 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.84 (q, *J* = 7.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.5, 149.7, 140.7, 139.4, 131.4, 129.6, 128.7, 124.6 (q, $J_{C\text{-}F}$ = 280.6 Hz), 124.0, 74.9 (q, $J_{C\text{-}F}$ = 28.8 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -74.3 (d, *J* = 7.1 Hz); IR($CHCl_3$) ν 1649, 1602, 1523, 1345, 1257, 1164, 1125, 1058, 857, 806 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd.

for $C_{16}H_{14}N_2O_2F_3$ m/z 323.1007, found m/z 323.0999.



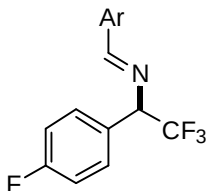
2Dc

Trifluoromethylated amine 2Dc. This product was obtained as a light yellow liquid in 70% yield after flash chromatography (from Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) and 90% ee as determined by HPLC analysis [Daicel Chiralpak OJ-H, Hexanes/IPA=80/20, 1.0 ml/min, λ 254nm, t(major) = 28.39 min, t(minor) = 18.96 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at -30°C for 72h. $[\alpha]_D^{23}$ = +160.3 (c = 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.24 – 7.17 (m, 1H), 4.83 (q, *J* = 7.4 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ = 163.6, 149.6, 140.6, 138.7, 134.2, 130.1, 129.6, 129.4, 128.7, 125.9, 124.5 (q, $J_{C\text{-}F}$ = 280.8 Hz), 124.0, 75.2 (q, $J_{C\text{-}F}$ = 28.8 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -74.1 (d, *J* = 6.9 Hz); IR ($CHCl_3$) ν 2872, 2360, 1649, 1603, 1524, 1346, 1260, 1168, 1125, 1057, 857, 713 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{16}H_{14}F_3N_2O_2$ requires m/z 323.1007, found m/z 323.1001.



2Dd

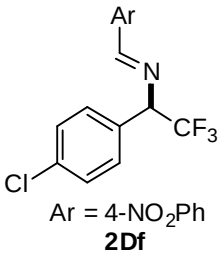
Trifluoromethylated amine 2Dd. The product was obtained as a light yellow liquid in 71% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) and 90% ee as determined by HPLC analysis [Daicel Chiralpak AD, Hexanes/IPA=80/20, 1.0 ml/min, λ 254 nm, t(major) = 12.43 min, t(minor) = 14.53 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at -10°C for 24h. $[\alpha]_D^{23}$ = +173.1 (c = 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 8.27 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.80 (q, *J* = 7.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.5, 160.4, 149.8, 140.8, 130.1, 129.7, 126.4, 124.7 (q, $J_{C\text{-}F}$ = 280.7 Hz), 124.1, 114.4, 74.7 (q, $J_{C\text{-}F}$ = 29.0 Hz), 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -74.5 (d, *J* = 6.9 Hz); IR($CHCl_3$) ν 2843, 1650, 1603, 1515, 1346, 1250, 1165, 1125, 1058, 1032, 813, 749 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{16}H_{14}F_3N_2O_3$ m/z 339.0957, found m/z 339.0957.



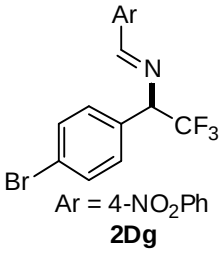
2De

Trifluoromethylated amine 2De. The product was obtained as a white solid in 79% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) and 91% ee as determined by HPLC analysis [Daicel Chiralcel OJ-H, Hexanes/IPA=70/30, 1.0 ml/min, λ 254 nm, t(major) = 20.97 min, t(minor) = 13.18 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at -30°C for 48h. $[\alpha]_D^{23}$ = +188.6 (c = 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.48 (s, 1H), 8.31 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.54 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.11 (t, *J* = 8.7 Hz, 2H), 4.85 (q, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.0, 163.4 (d, $J_{C\text{-}F}$ = 248.4 Hz), 149.9, 140.6, 130.7 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.2, 129.8, 124.2, 124.4 (q, $J_{C\text{-}F}$ = 280.9 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.7 Hz), 74.6 (q, $J_{C\text{-}F}$ = 29.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -74.52 (d, *J* = 7.0 Hz), -112.5; IR($CHCl_3$) 1650, 1604, 1525, 1511, 1346, 1258, 1168, 1126, 1058, 876, 856, 749 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for

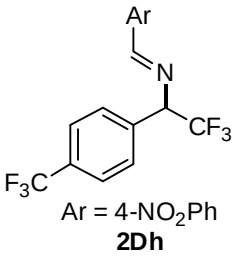
$C_{15}H_{11}N_2O_2F_4$ m/z 327.0757, found m/z 327.0752.



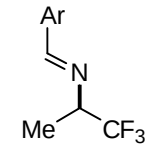
Trifluoromethylated amine 2Df. This product was obtained as a white solid in 69% yield after flash chromatography (from Hexanes/ CH_2Cl_2/diethyl ether = 20/1/0.01 to Hexanes/CH_2Cl_2/diethyl ether = 1/1/0.01) and 88% ee as determined by HPLC analysis [Daicel chiralcel OJ-H, Hexanes/IPA=80/20, 1.0 ml/min, λ 254nm, t(major) = 18.22 min, t(minor) = 14.92 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at -50°C for 72h. $[\alpha]_D^{23}$ = +199.4 (c = 0.46, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.31 (d, *J* = 8.8 Hz, 2H), 8.06 – 7.95 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.84 (q, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 164.2, 149.9, 140.5, 135.5, 132.8, 130.3, 129.8, 129.2, 124.3 (q, J_{C-F} = 281.0 Hz), 124.2, 74.6 (q, J_{C-F} = 29.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.4 (d, *J* = 6.8 Hz); IR ($CHCl_3$) ν 2876, 1650, 1602, 1523, 1492, 1345, 1257, 1167, 1126, 1091, 1016, 873, 808 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{15}H_{11}N_2O_2F_3Cl$ requires m/z 343.0461, found m/z 343.0456.



Trifluoromethylated amine 2Dg. The product was obtained as a white solid in 79% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) and 86% ee as determined by HPLC analysis [Daicel Chiralcel OJ-H, Hexanes/IPA=80/20, 1.0 ml/min, λ 254 nm, t(major) = 17.10 min, t(minor) = 15.12 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at -30°C for 48h. $[\alpha]_D^{23}$ = +163.5 (c = 0.46, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.06 – 7.92 (m, 2H), 7.60 – 7.49 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 4.80 (q, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 149.8, 140.4, 133.2, 132.1, 130.4, 129.7, 124.1 (q, J_{C-F} = 281.2 Hz), 124.0, 123.6, 74.6 (q, J_{C-F} = 29.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -74.4 (d, *J* = 7.4 Hz); IR($CHCl_3$) ν 2878, 1650, 1603, 1522, 1344, 1256, 1167, 1126, 1057, 1012, 873, 806, 749cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{15}H_{11}N_2O_2F_3Br$ m/z 386.9956, found m/z 386.9956.

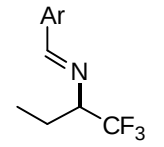


Trifluoromethylated amine 2Dh. The product was obtained as a white solid in 81% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 1/1) and 80% ee as determined by HPLC analysis [Daicel Chiralpak AD, Hexanes/IPA = 90/10, 1.0 ml/min, λ 254 nm, t(major) = 11.44 min, t(minor) = 12.97 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at -50°C for 72h. $[\alpha]_D^{23}$ = +150.1 (c = 0.46, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.48 (s, 1H), 8.29 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.76 – 7.58 (m, 4H), 4.90 (q, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.5, 149.9, 140.3, 138.1, 131.6 (q, J_{C-F} = 32.8 Hz), 129.8, 129.3, 125.8 (dd, J_{C-F} = 7.4, 3.7 Hz), 124.1, 123.9 (q, J_{C-F} = 268.1 Hz), 74.8 (q, J_{C-F} = 29.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.3, -74.1 (d, *J* = 6.9 Hz); IR($CHCl_3$) ν 2875, 1651, 1604, 1525, 1347, 1325, 1257, 1167, 1126, 1069, 1020, 857, 814 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{16}H_{11}N_2O_2F_6$ m/z 377.0725, found m/z 377.0729.



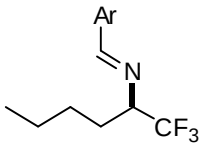
Ar = 4-NO_2Ph
2Di

Trifluoromethylated amine 2Di. The product was obtained as a yellow solid in 61% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 2/1) and 90% ee as determined by HPLC analysis [Daicel Chiralcel OJ-H, Hexanes/IPA=97/3, 1.0 ml/min, λ 254 nm, t(major) = 15.82 min, t(minor) = 15.00 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at 10 °C for 48h. $[\alpha]_D^{23}$ = +73.7 (c = 0.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 (s, 1H), 8.30 – 8.23 (m, 2H), 7.97 – 7.87 (m, 2H), 3.89 (dq, *J* = 13.7, 6.8 Hz, 1H), 1.45 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.3, 149.6, 140.7, 129.5, 125.4 (d, $J_{C\text{-}F}$ = 281.4 Hz), 124.3, 66.7 (q, $J_{C\text{-}F}$ = 28.9 Hz), 15.8 (d, $J_{C\text{-}F}$ = 2.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ = -76.7 (d, *J* = 7.6 Hz); IR($CHCl_3$) ν 2886, 1651, 1603, 1524, 1453, 1346, 1270, 1172, 1146, 1124, 1084, 1020, 855, 750 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{10}H_{10}N_2O_2F_3$ m/z 247.0694, found m/z 247.0691.



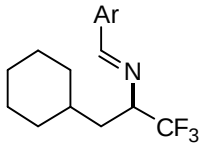
Ar = 4-NO_2Ph
2Dj

Trifluoromethylated amine 2Dj. The product was obtained as a yellow liquid in 66% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 3/2) and 93% ee as determined by HPLC analysis [Daicel Chiralcel AS-H, Hexanes/IPA=90/10, 1.0 ml/min, λ 254 nm, t(major) = 8.16 min, t(minor) = 17.00 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at 10 °C for 48h. $[\alpha]_D^{23}$ = +131.2 (c = 0.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 8.30 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H), 3.67 – 3.49 (m, 1H), 2.10 – 1.79 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 149.7, 140.6, 129.6, 125.4 (q, $J_{C\text{-}F}$ = 280.2 Hz), 124.1, 73.6 (q, $J_{C\text{-}F}$ = 27.6 Hz), 22.3, 10.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -75.0 (d, *J* = 7.8 Hz); IR($CHCl_3$) ν 2978, 2880, 1651, 1603, 1526, 1348, 1273, 1174, 1124, 1046, 856, 823 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{11}H_{12}N_2O_2F_3$ m/z 261.0851, found m/z 261.0856.



Ar = 4-NO_2Ph
2Dk

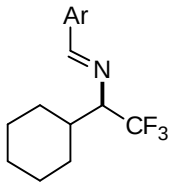
Trifluoromethylated amine 2Dk. The product was obtained as a yellow solid in 69% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 2/1) and 92% ee as determined by HPLC analysis [Daicel Chiralcel OJ-H, Hexanes/IPA=95/5, 1.0 ml/min, λ 254 nm, t(major) = 7.24 min, t(minor) = 6.82 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at 10 °C for 48h. $[\alpha]_D^{23}$ = +155.8 (c = 0.31, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (s, 1H), 8.31 – 8.22 (m, 2H), 8.01 – 7.87 (m, 2H), 3.69 – 3.56 (m, 1H), 1.99 – 1.75 (m, 2H), 1.41 – 1.06 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9, 149.6, 140.6, 129.6, 125.3 (d, $J_{C\text{-}F}$ = 280.3 Hz), 124.0, 72.2 (q, $J_{C\text{-}F}$ = 27.5 Hz), 28.5, 27.7, 22.3, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -75.1 (d, *J* = 6.8 Hz); IR($CHCl_3$) ν 2935, 2871, 1651, 1603, 1524 1346, 1268, 1167, 1129, 1105, 855, 749 cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{13}H_{16}N_2O_2F_3$ m/z 289.1164, found m/z 289.1167.



Ar = 4-NO_2Ph
2Dl

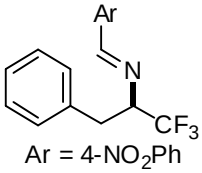
Trifluoromethylated amine 2Dl. The product was obtained as a yellow liquid in 60% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to

Hexanes/CH_2Cl_2 = 2/1) and 94% ee as determined by HPLC analysis [Daicel Chiralcel OJ-H, Hexanes/IPA=90/10, 1.0 ml/min, λ 254 nm, t(major) = 5.37 min, t(minor) = 15.52 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at 10 °C for 48h. $[\alpha]_D^{23}$ = +156.9 (c = 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 8.31 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 3.90 – 3.74 (m, 1H), 1.87 (ddd, *J* = 14.2, 10.3, 4.0 Hz, 1H), 1.79 – 1.60 (m, 6H), 1.26 – 1.09 (m, 4H), 1.09 – 0.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 149.7, 140.7, 129.6, 125.5 (q, $J_{C\text{-}F}$ = 286.1 Hz), 124.1, 69.4 (q, $J_{C\text{-}F}$ = 27.4 Hz), 36.2, 34.2, 33.1, 31.9, 26.5, 26.2, 26.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -75.1 (d, *J* = 7.7 Hz); IR($CHCl_3$) ν 2926, 2852, 1650, 1603, 1525, 1450, 1346, 1268, 1164, 1129, 1069, 855, 750 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{16}H_{20}N_2O_2F_3$ m/z 329.1477, found m/z 329.1475.



Ar = 4-NO_2Ph
2Dm

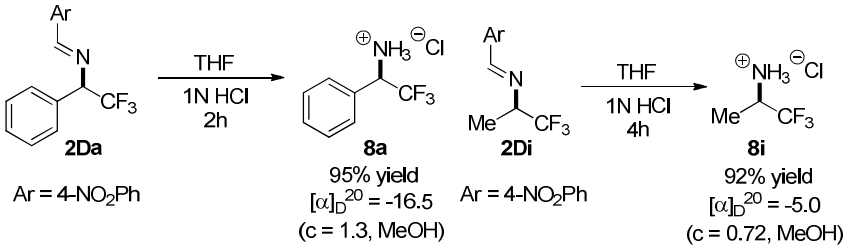
Trifluoromethylated amine 2Dm. The product was obtained as a yellow solid in 58% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 3/2) and 91% ee as determined by HPLC analysis [Daicel Chiralcel AS-H, Hexanes/IPA=90/10, 1.0 ml/min, λ 254 nm, t(major) = 5.79 min, t(minor) = 25.58 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at 10 °C for 48h. $[\alpha]_D^{23}$ = +147.5 (c = 0.26, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 – 8.27 (m, 3H), 8.01 – 7.94 (m, 2H), 3.53 – 3.38 (m, 1H), 2.10 – 1.94 (m, 1H), 1.89 – 1.58 (m, 5H), 1.40 – 1.17 (m, 2H), 1.17 – 1.00 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8, 149.6, 140.6, 129.6, 125.4 (q, $J_{C\text{-}F}$ = 281.7 Hz), 124.0, 77.0 (q, $J_{C\text{-}F}$ = 26.1 Hz), 38.3, 30.3, 28.5, 26.2, 26.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -70.6 (d, *J* = 8.1 Hz); IR($CHCl_3$) ν 2933, 2858, 1651, 1603, 1526, 1347, 1269, 1162, 1122, 851, 773 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{15}H_{18}N_2O_2F_3$ m/z 315.1320, found m/z 315.1311.



Ar = 4-NO_2Ph
2Dn

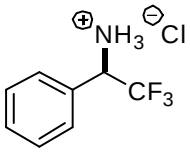
Trifluoromethylated amine 2Dn. The product was obtained as a yellow liquid in 65% yield after flash chromatography (Hexanes/CH_2Cl_2 = 20/1 to Hexanes/CH_2Cl_2 = 2/1) and 87% ee as determined by HPLC analysis [Daicel Chiralcel OJ-H, Hexanes/IPA=90/10, 1.0 ml/min, λ 254 nm, t(major) = 11.56 min, t(minor) = 10.80 min] from a reaction catalyzed by DHQ-**7f** (10 mol%) at 5 °C for 48h. $[\alpha]_D^{23}$ = +286.7 (c = 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.66 (s, 1H), 7.25 – 7.17 (m, 3H), 7.07 (d, *J* = 7.5 Hz, 2H), 3.91 – 3.77 (m, 1H), 3.31 (dd, *J* = 13.5, 2.3 Hz, 1H), 3.05 (dd, *J* = 13.5, 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.2, 149.6, 140.4, 135.8, 130.0, 129.3, 128.7, 127.2, 125.1 (q, $J_{C\text{-}F}$ = 280.4 Hz), 124.0, 73.4 (q, $J_{C\text{-}F}$ = 27.7 Hz), 35.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -75.7 (d, *J* = 7.0 Hz); IR($CHCl_3$) ν 2887, 1650, 1603, 1524, 1347, 1270, 1166, 1129, 1082, 854, 828, 749 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{16}H_{14}N_2O_2F_3$ m/z 323.1007, found m/z 323.1007.

4. Hydrolysis of chiral amines 2D



A modified procedure from a literature report[11] was used here:

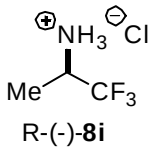
At 0 °C, to the solution of amine **2D** (0.14 mmol) in THF (0.7 mL) was added HCl (1N, 0.7 mL). The mixture was stirred at room temperature until all the *N*-benzyl trifluoromethylated amine was consumed (indicated by TLC analysis). The THF was evaporated under vacuum. Another 0.7 mL HCl (1N) was added. The aqueous layer was then washed with Et_2O (2.0 mL×3) and concentrated under vacuum to afford the trifluoromethyl amine hydrochloride salt **8** as indicated by ^{1}H NMR.



R-(-)-**8a**

The product was obtained as a white solid in 95% yield. $[\alpha]_D^{23}$ = -16.5 (c = 1.3, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.56 (s, 5H), 5.35 (q, *J* = 7.2 Hz, 1H). ^{19}F NMR (376 MHz, CD_3OD) δ = -75.5. The spectral data was consistent with that reported in the literature[12]. The ee value was determined to be 90% by HPLC analysis of the corresponding *N*-benzoyl derivative (the NMR and HPLC spectrums were attached).

The absolute configuration of (-)-8a was determined to be R by comparing the specific optical rotation with a literature value. $[\alpha]_D^{23}$ =-16.5 (*c* = 1.3, MeOH) for 90% ee [lit.[12] $[\alpha]_D^{25}$ = +28.6 (c = 0.65, MeOH) for 94% ee].



R-(-)-**8i**

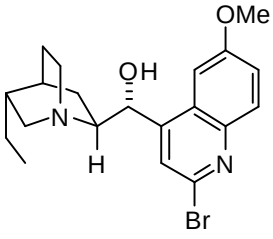
The product was obtained as a white solid in 92% yield. $[\alpha]_D^{23}$ = -5.0 (c = 0.72, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 4.27 – 4.15 (m, 1H), 1.49 (d, *J* = 6.9 Hz, 3H). ^{19}F NMR (376 MHz, CD_3OD) δ -78.5 (d, *J* = 6.5 Hz). The spectral data was consistent with that reported in the literature[11]. The ee value was determined to be 90% by HPLC analysis of the corresponding *N*-benzoyl derivative (the NMR and HPLC spectrums were attached).

The absolute configuration of (-)-8i was determined to be R by comparing the specific optical rotation with a literature value. $[\alpha]_D^{23}$ =-5.0 (*c* = 0.72, MeOH) for 90% ee [lit.[11] $[\alpha]_D^{25}$ = -2.94 (c = 1.0, MeOH) for 98% ee].

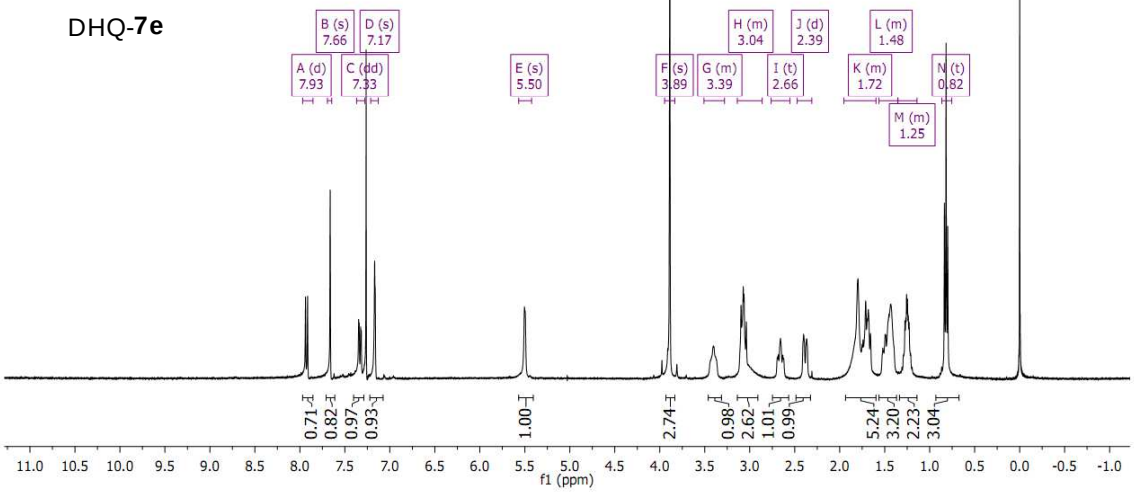
5. Reference

(1) Wu, Y.; Singh, R. P.; Deng, L. *J. Am. Chem. Soc.* **2011**, *133*, 12458.
(2) Song, J.; Shih, H.-W.; Deng, L. *Org. Lett.* **2007**, *9*, 603.
(3) Wu, F.; Hong, R.; Khan, J.; Liu, X.; Deng, L. *Angew. Chem.* **2006**, *45*, 4301.
(4) Marcelli, T.; van der Haas, R. N. S.; van Maarseveen, J. H.; Hiemstra, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 929.
(5) Corey, E. J.; Zhang, J. *Org. Lett.* **2001**, *3*, 3211.
(6) Palacio, C.; Connon, S. J. *Org. Lett.* **2011**, *13*, 1298.
(7) Yardley, J. P.; Bright, R. E.; Rane, L.; Rees, R. W.; Russell, P. B.; Smith, H. *J. Med. Chem.* **1971**, *14*, 62.
(8) Creary, X. *J. Org. Chem.* **1987**, *52*, 5026.
(9) Berbasov, D. O.; Ojemaye, I. D.; Soloshonok, V. A. *J. Fluorine Chem.* **2004**, *125*, 603.
(10) Previously, Self-dispropotionation of trifluoromethylated amines on silica column was reported, see: Soloshonok, V. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 766. The ee value of product in this manuscript stayed the same after the separation.
(11) Soloshonok, V. A.; Ono, T. *J. Org. Chem.* **1997**, *62*, 3030.
(12) Prakash, G. K. S.; Mandal, M.; Olah, G. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 589.

wuyw-IV-4
wuyw-IV-4 ^{1}H and ^{13}C NMR spectra for the cinchona alkaloids

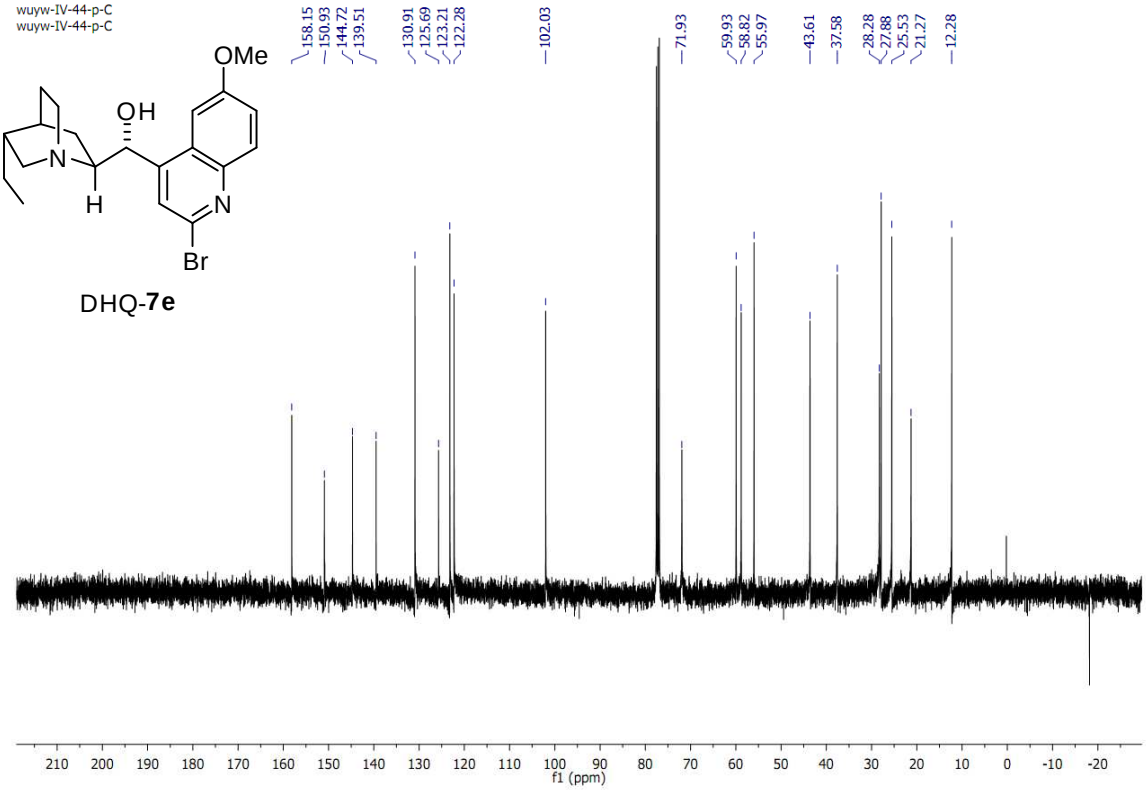


DHQ-**7e**

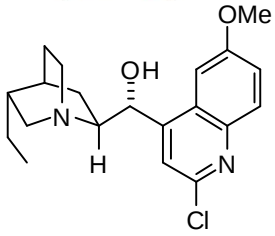


wuyw-IV-44-p-C
wuyw-IV-44-p-C

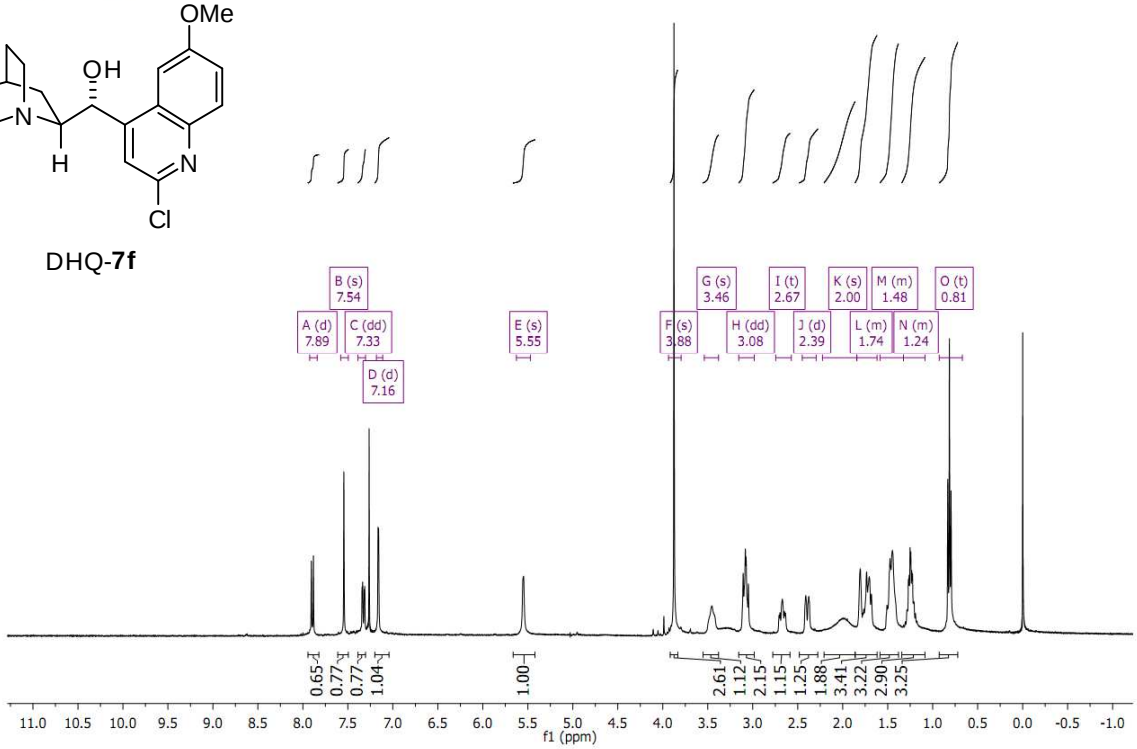
DHQ-**7e**



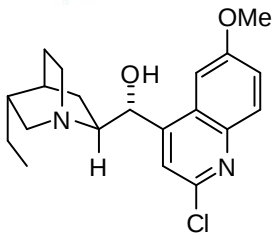
wuyw-IV-46-2-ClDHQ
wuyw-IV-46-2-ClDHQ



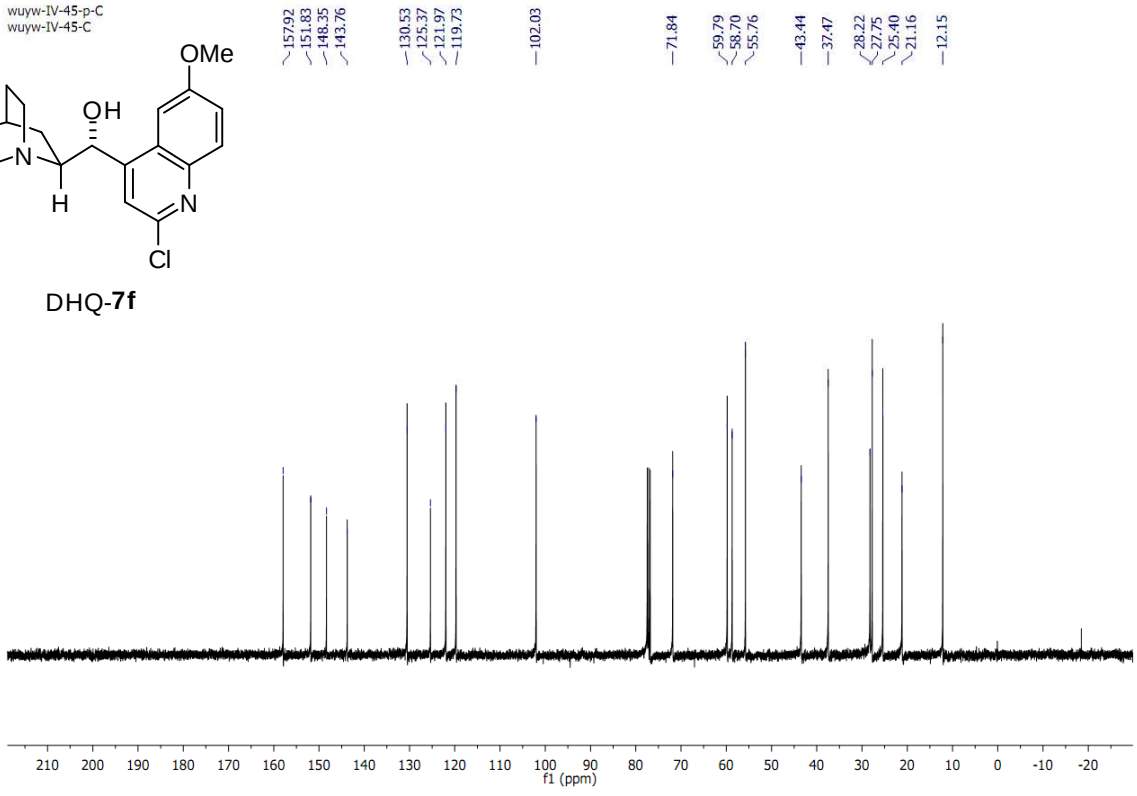
DHQ-**7f**



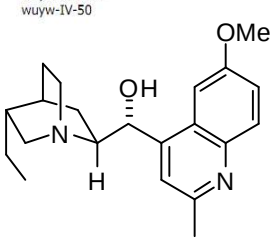
wuyw-IV-45-p-C
wuyw-IV-45-C



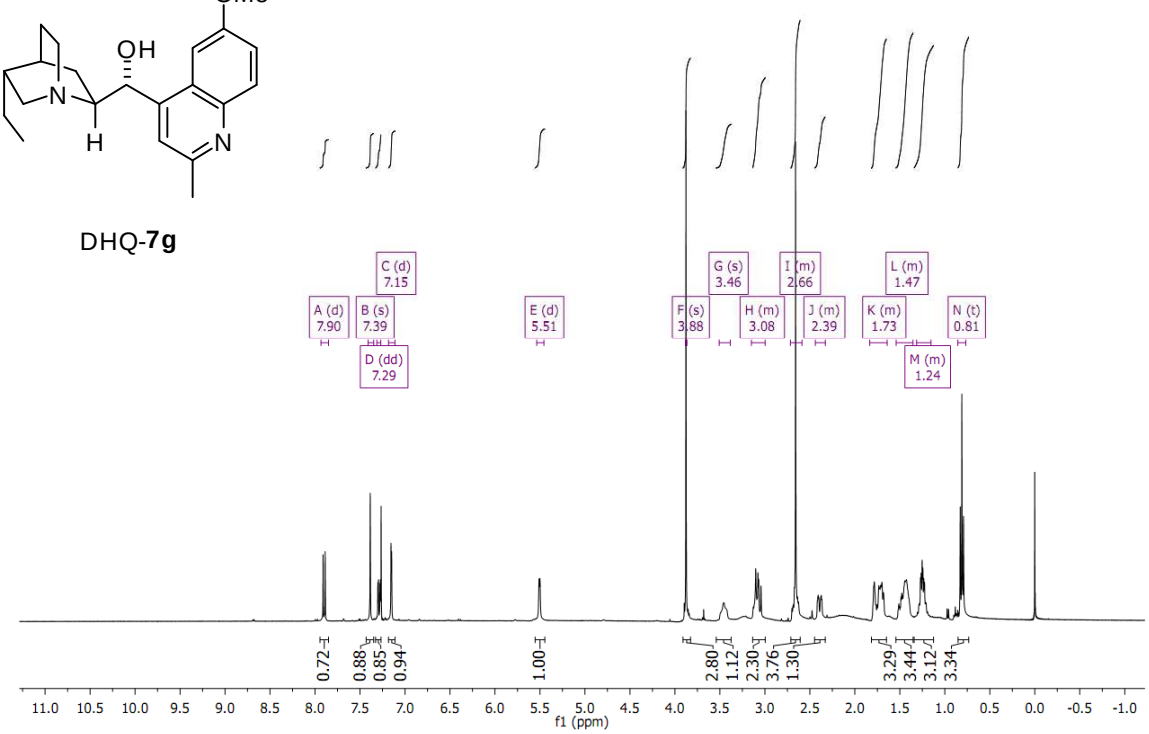
DHQ-**7f**



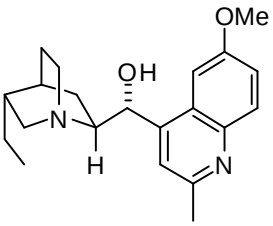
wuyw-IV-50-1
wuyw-IV-50



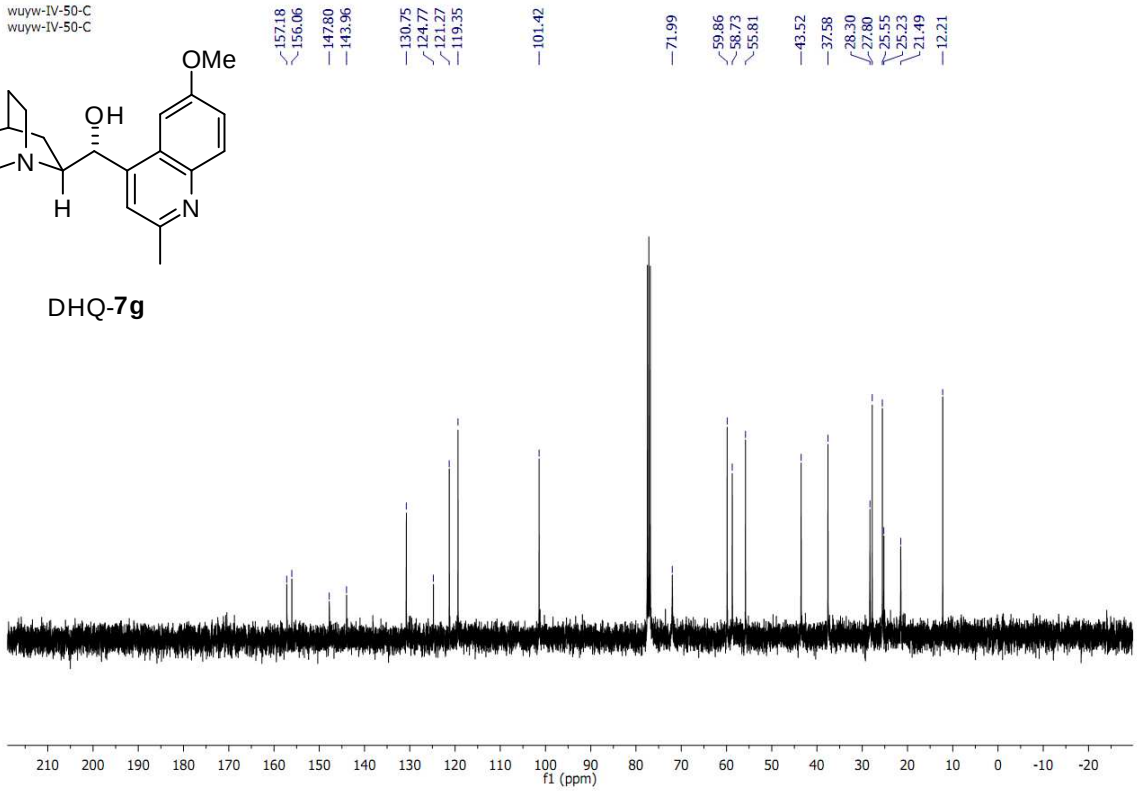
DHQ-**7g**



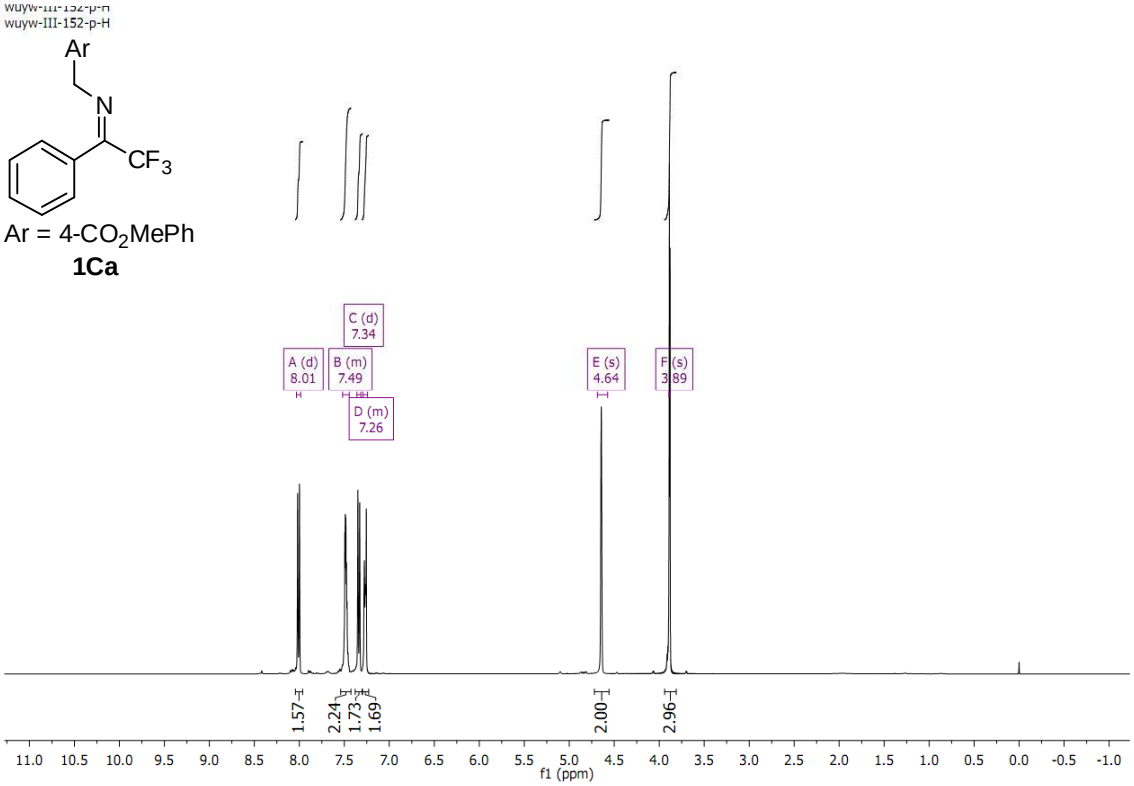
wuyw-IV-50-C
wuyw-IV-50-C

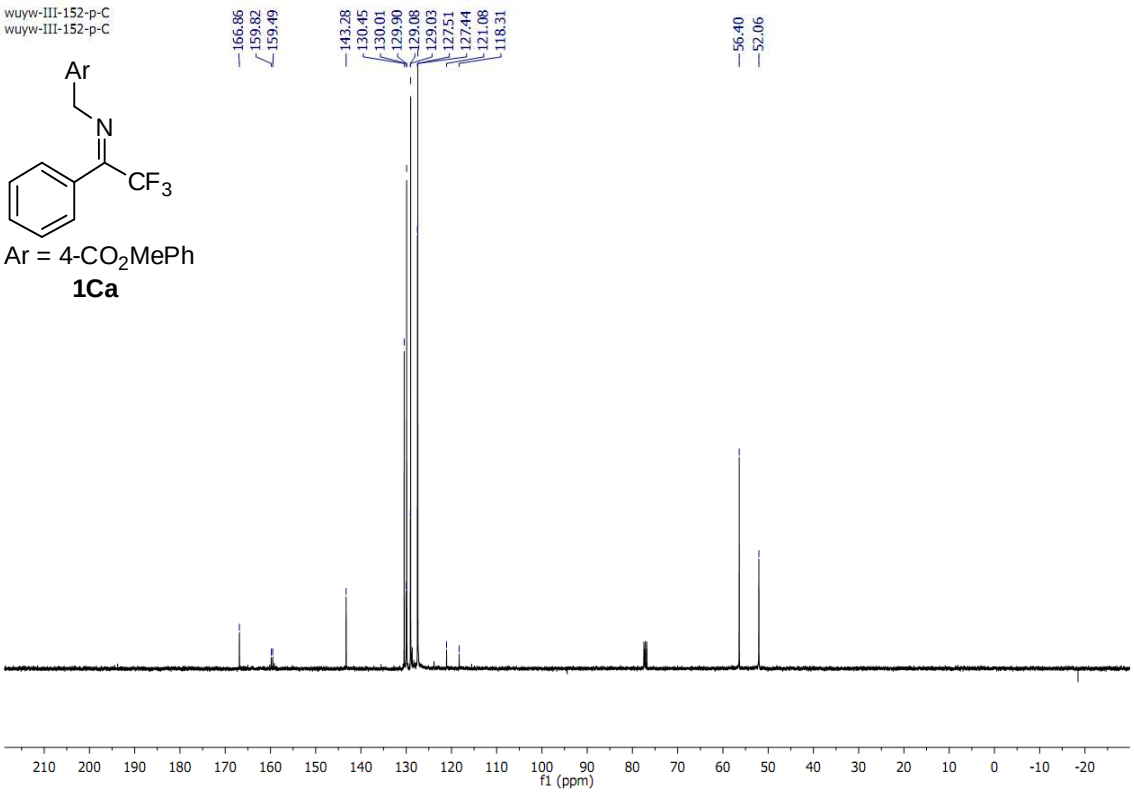


DHQ-**7g**



^{1}H, ^{13}C and ^{19}F NMR spectra for imine **1**

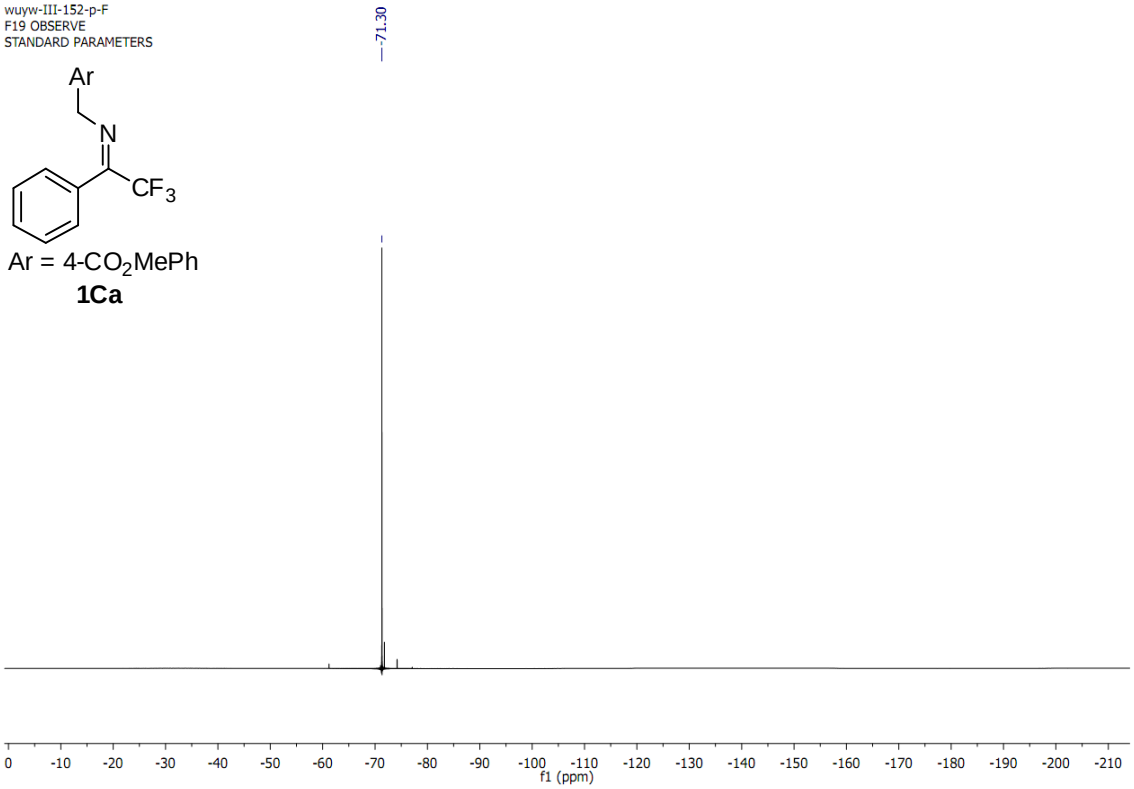




wuyw-III-152-p-F
F19 OBSERVE
STANDARD PARAMETERS

Ar = 4-CO_2MePh

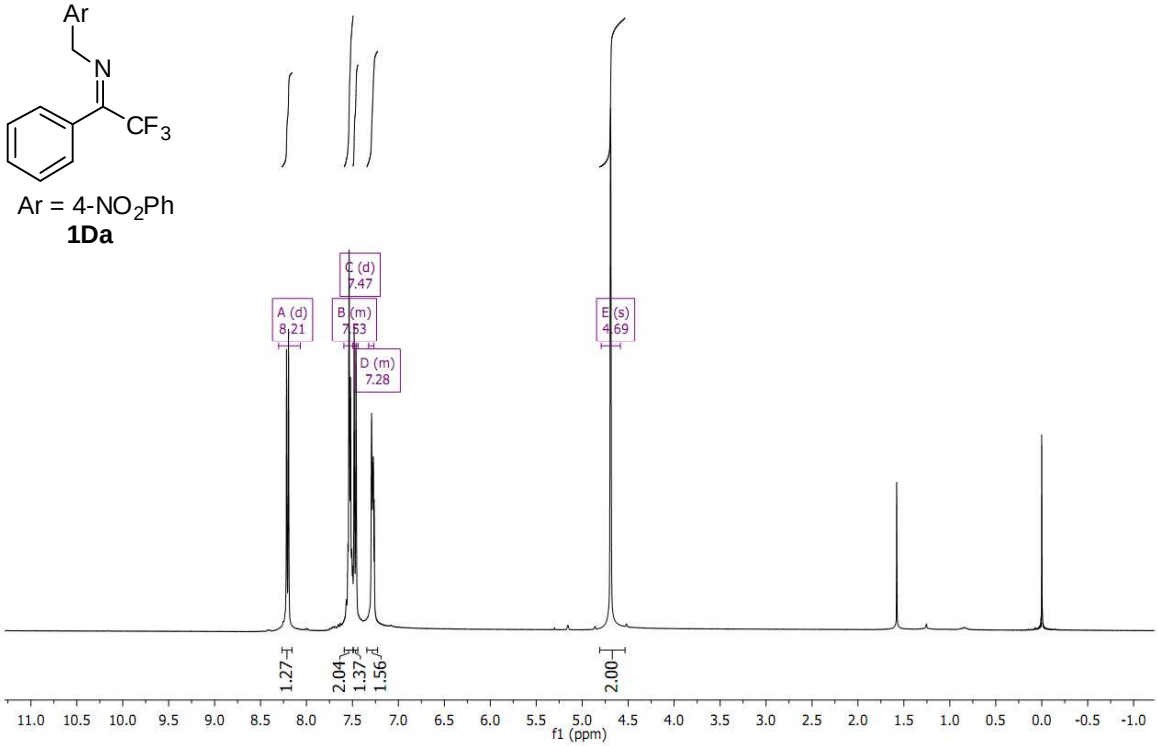
1Ca

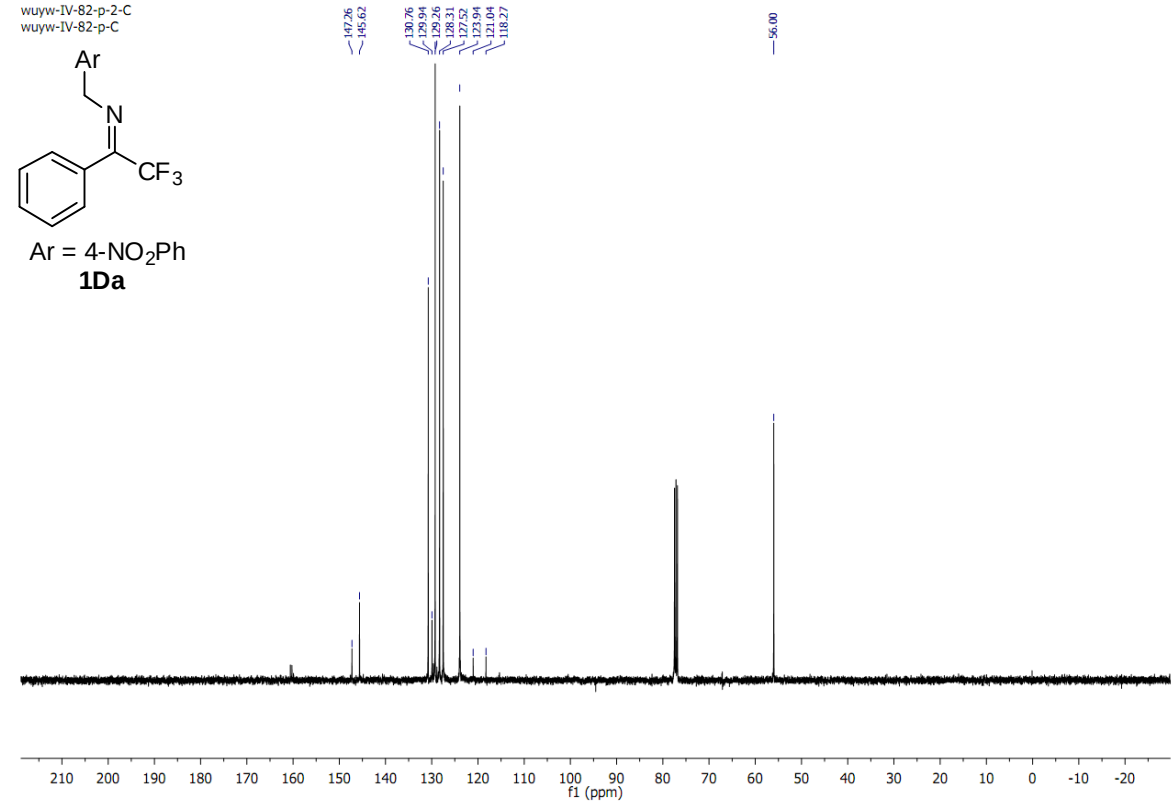


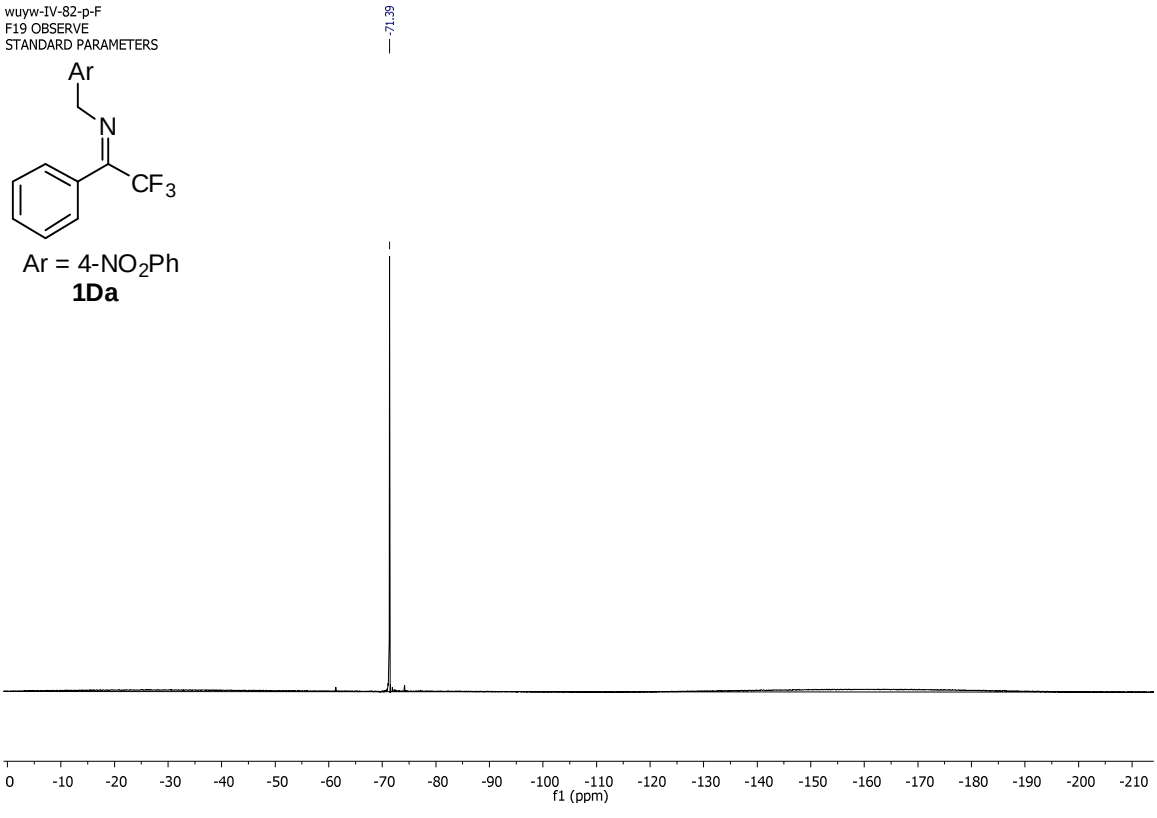
wuyw-IV-82-p-H
wuyw-IV-82-p-H

Ar = 4-NO_2Ph

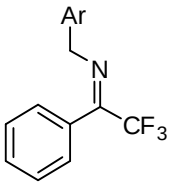
1Da




wuyw-IV-82-p-2-C
wuyw-IV-82-p-C
147.26
145.62
130.76
129.94
129.26
128.31
127.52
123.94
121.04
118.27
56.00
Ar
N
CF3
Ar = 4-NO2Ph
1Da
f1 (ppm)

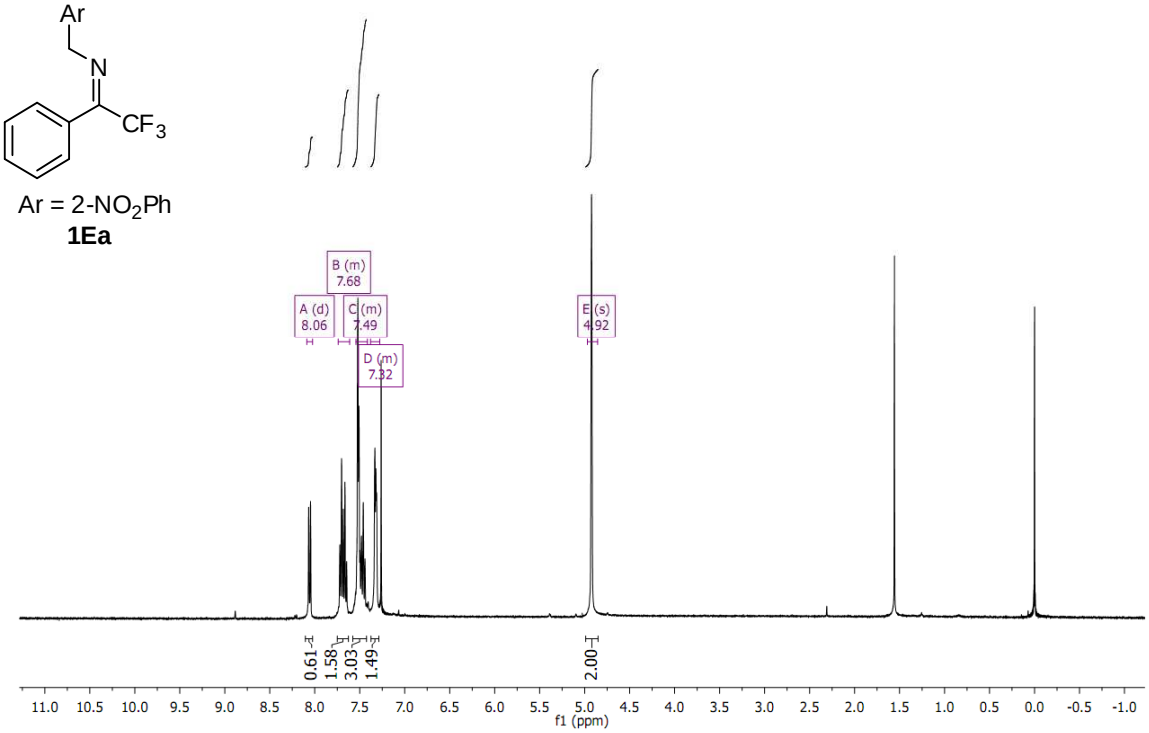

wuyw-IV-82-p-F
F19 OBSERVE
STANDARD PARAMETERS
71.39
Ar
N
CF3
Ar = 4-NO2Ph
1Da
f1 (ppm)

wuyw-IV-55-p
wuyw-IV-55



Ar = 2-NO_2Ph

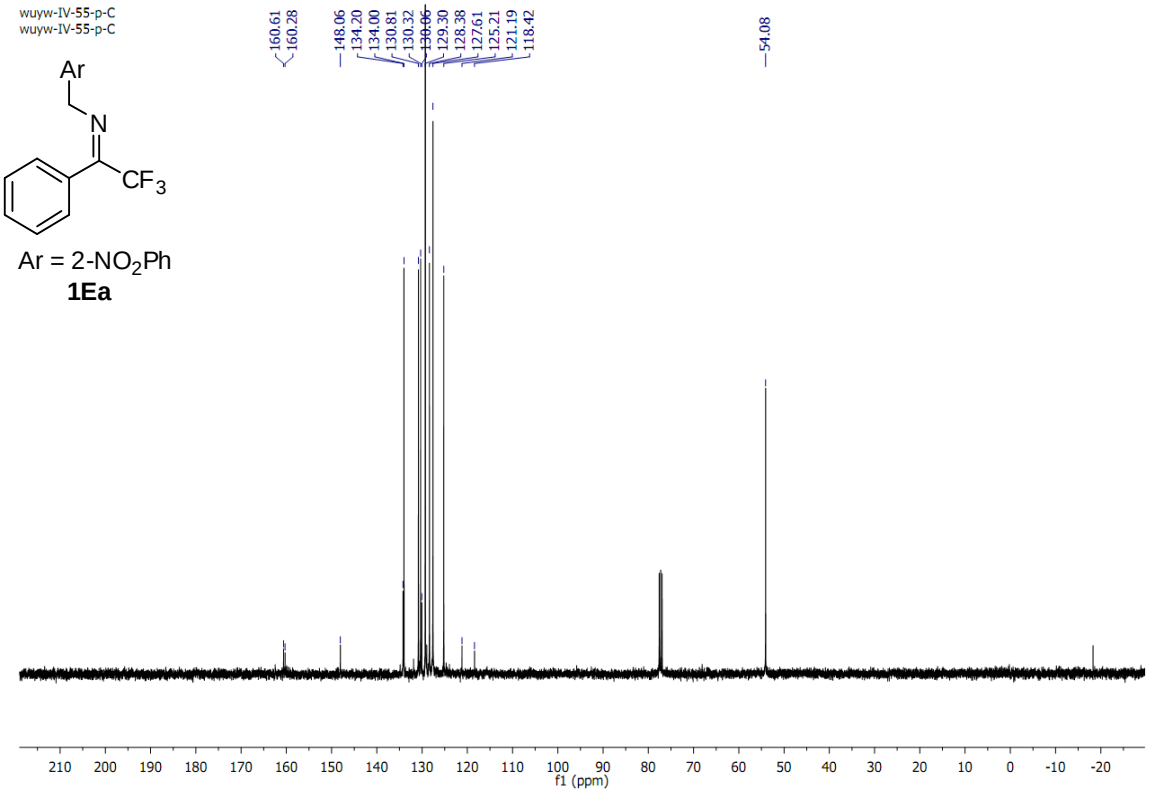
1Ea



wuyw-IV-55-p-C
wuyw-IV-55-p-C

Ar = 2-NO_2Ph

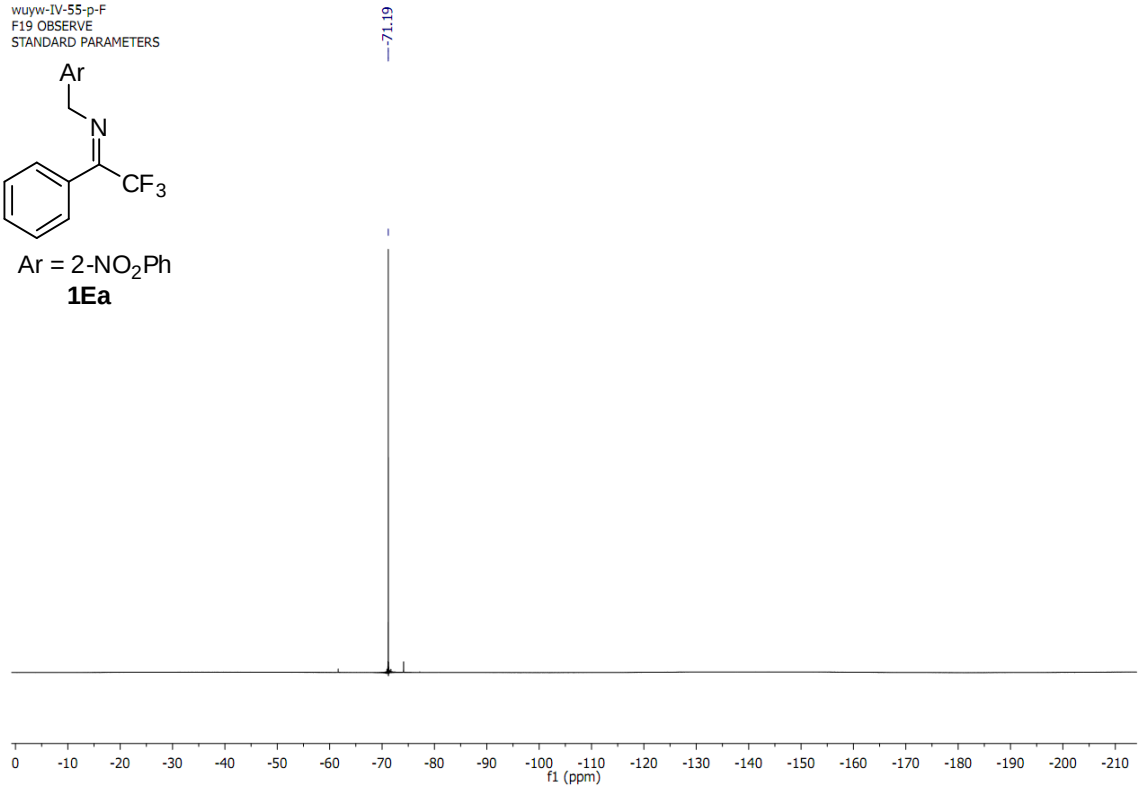
1Ea



wuyw-IV-55-p-F
F19 OBSERVE
STANDARD PARAMETERS

Ar = 2-NO_2Ph

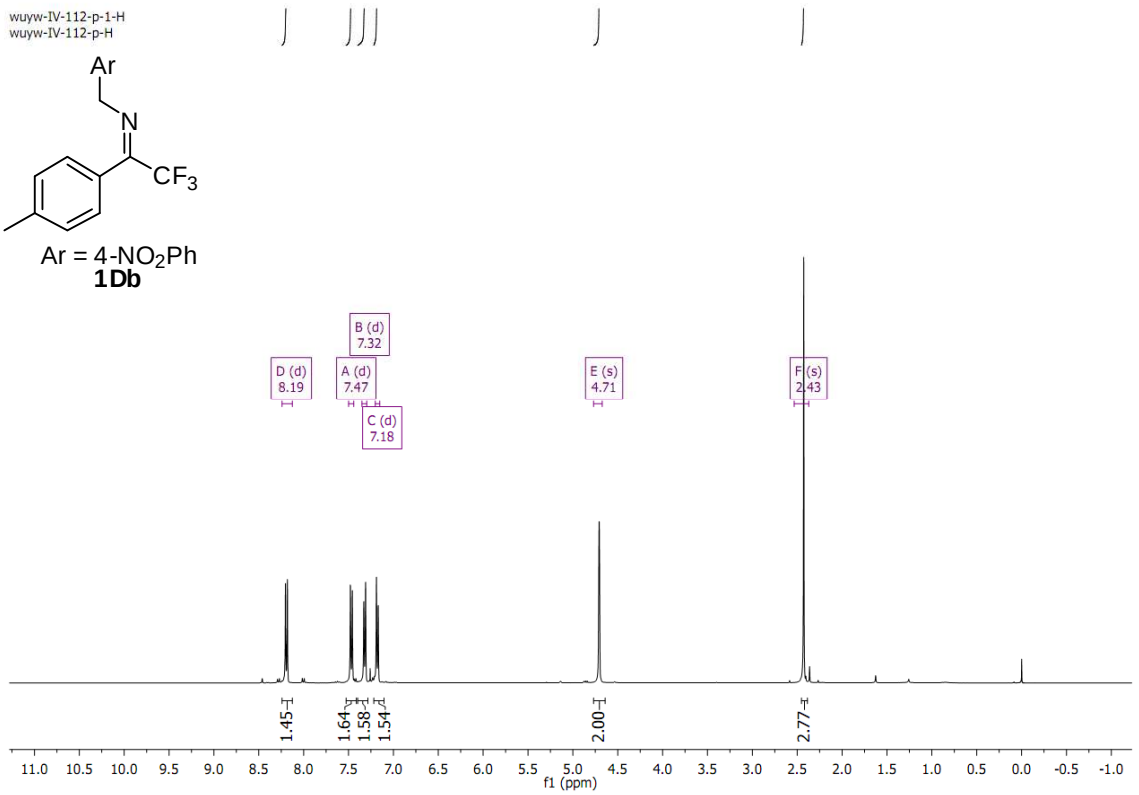
1Ea

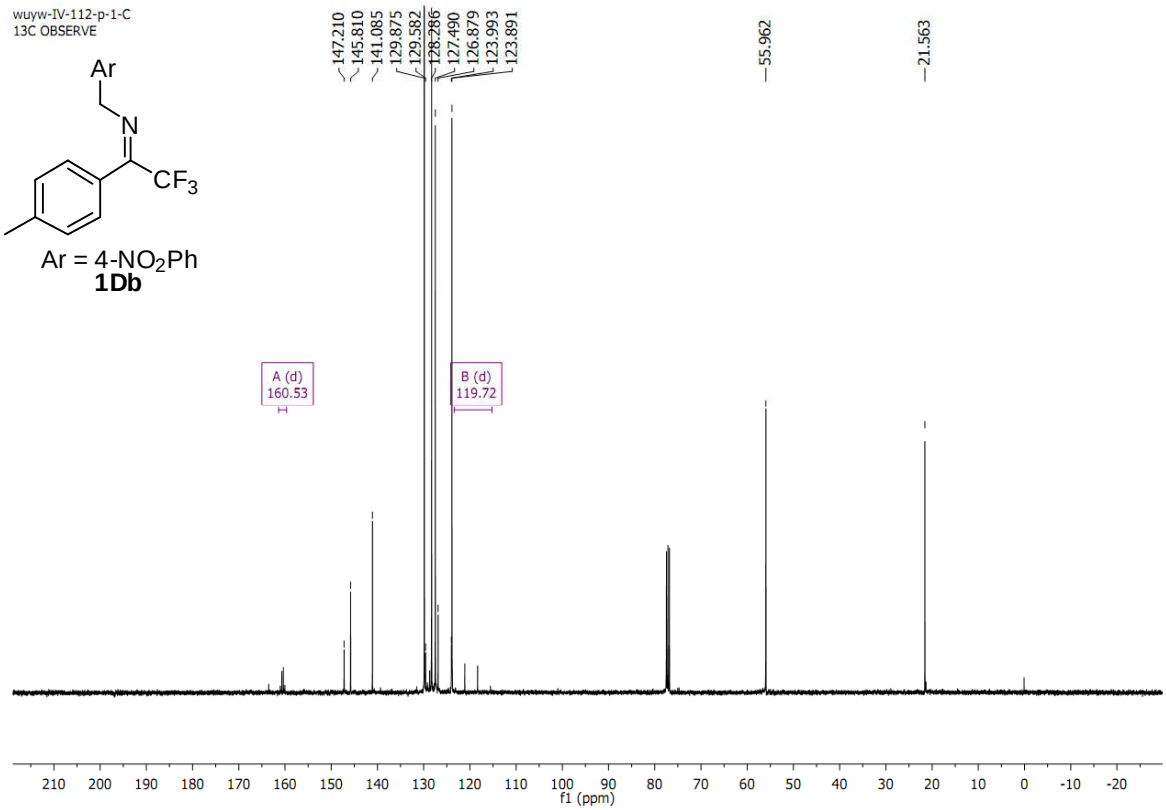


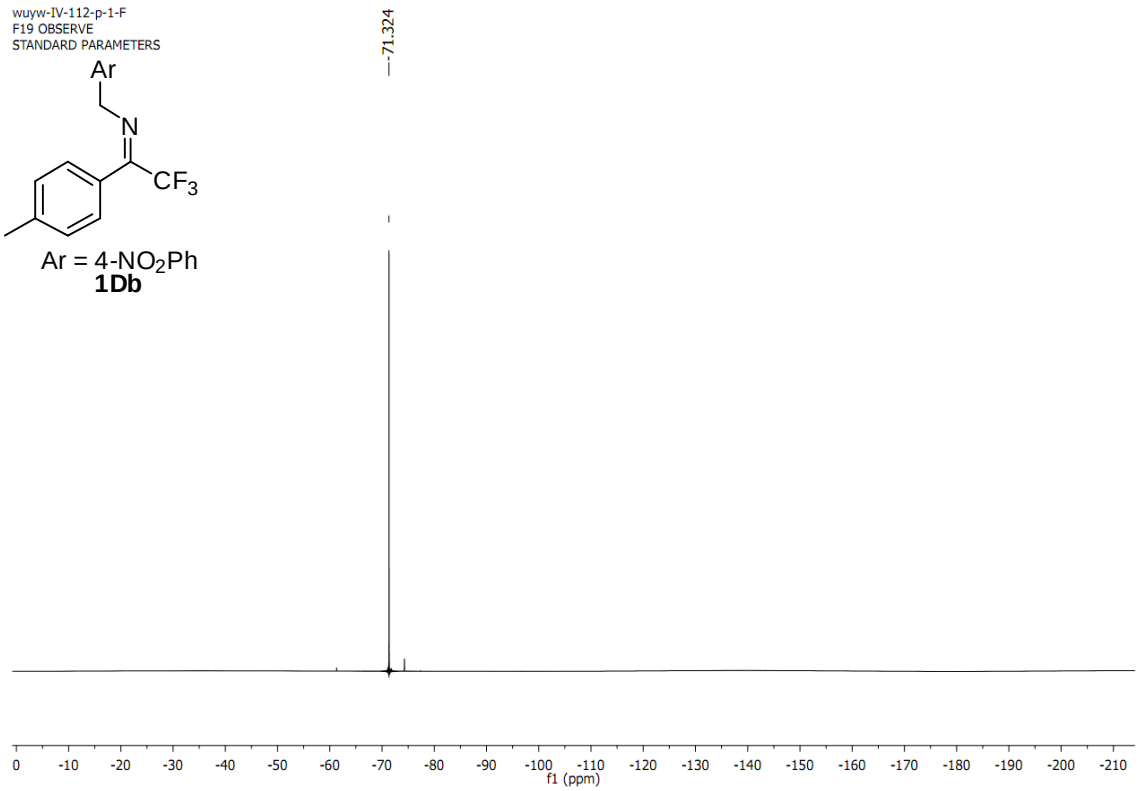
wuyw-IV-112-p-1-H
wuyw-IV-112-p-H

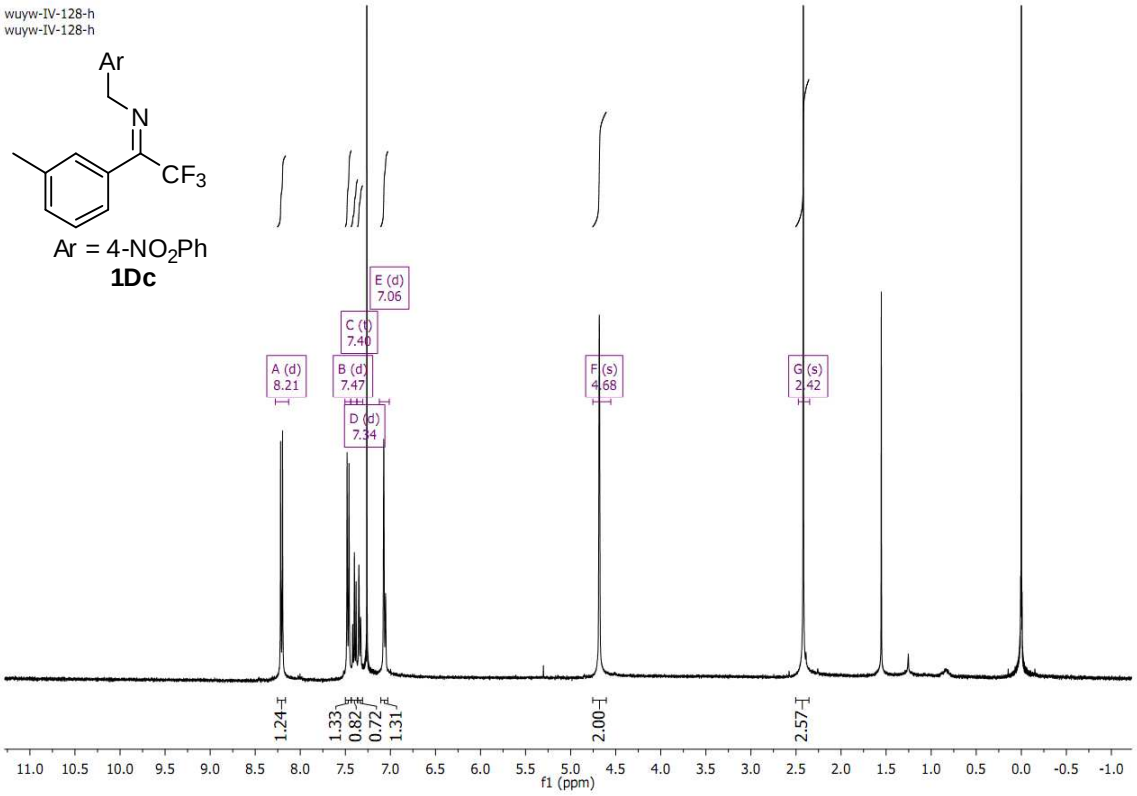
Ar = 4-NO_2Ph

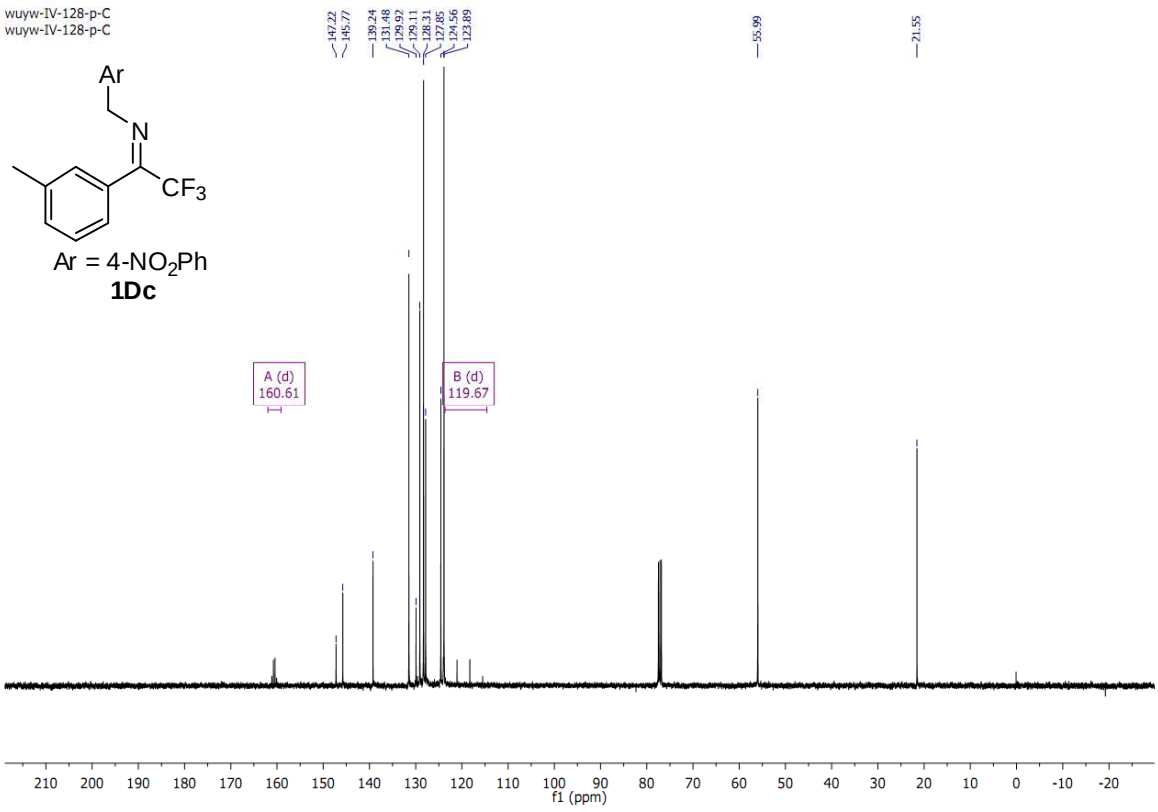
1Db




wuyw-IV-112-p-1-C
13C OBSERVE
Ar
N
CF3
Ar = 4-NO2Ph
1Db
147.210
145.810
141.085
129.875
129.582
128.286
127.490
126.879
123.993
123.891
55.962
21.563
A (d)
160.53
B (d)
119.72
f1 (ppm)


wuyw-IV-112-p-1-F
F19 OBSERVE
STANDARD PARAMETERS
Ar
N
CF3
Ar = 4-NO2Ph
1Db
-71.324
f1 (ppm)

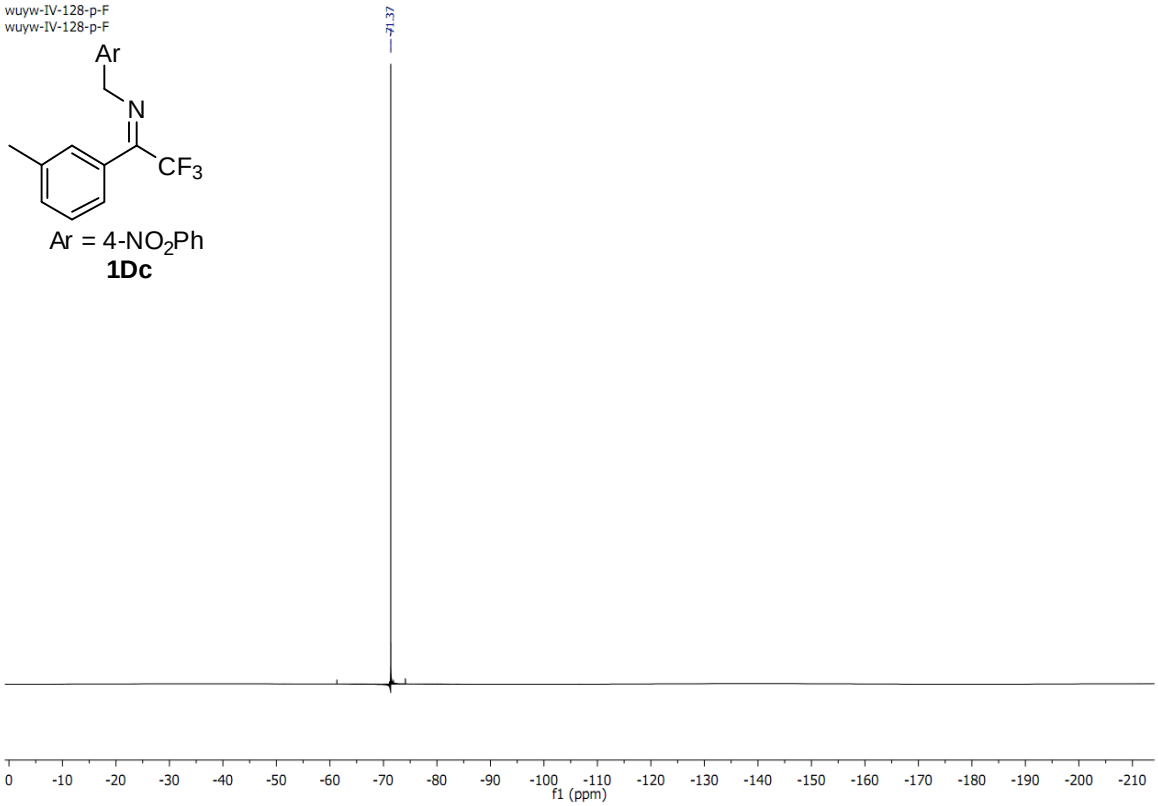

wuyw-IV-128-h
wuyw-IV-128-h
Ar
N
CF3
Ar = 4-NO2Ph
1Dc
E (d) 7.06
C (t) 7.40
A (d) 8.21
B (d) 7.47
D (d) 7.34
F (s) 4.68
G (s) 2.42
1.24
1.33
0.82
0.72
1.31
2.00
2.57
f1 (ppm)


wuyw-IV-128-p-C
wuyw-IV-128-p-C
147.22
145.77
129.24
131.48
129.92
129.11
128.31
127.85
124.56
123.89
55.99
21.55
Ar
N
CF3
Ar = 4-NO2Ph
1Dc
A (d) 160.61
B (d) 119.67
f1 (ppm)

wuyw-IV-128-p-F
wuyw-IV-128-p-F

Ar = 4-NO_2Ph

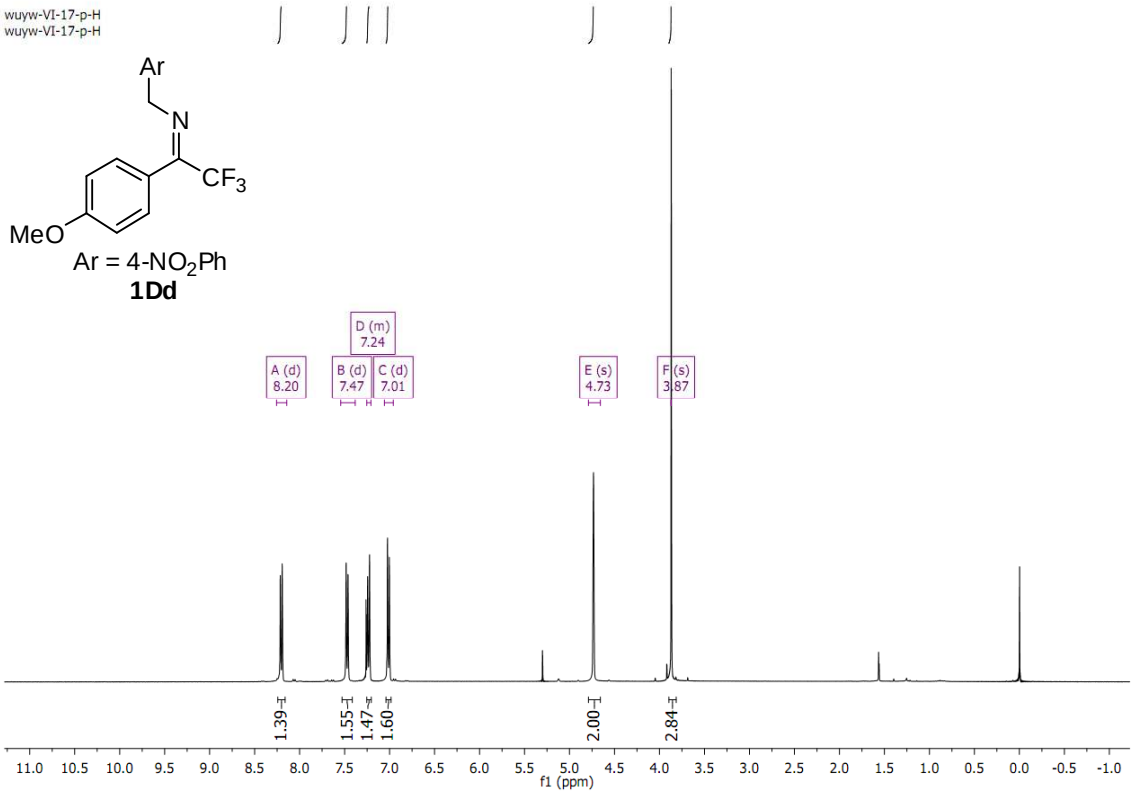
1Dc

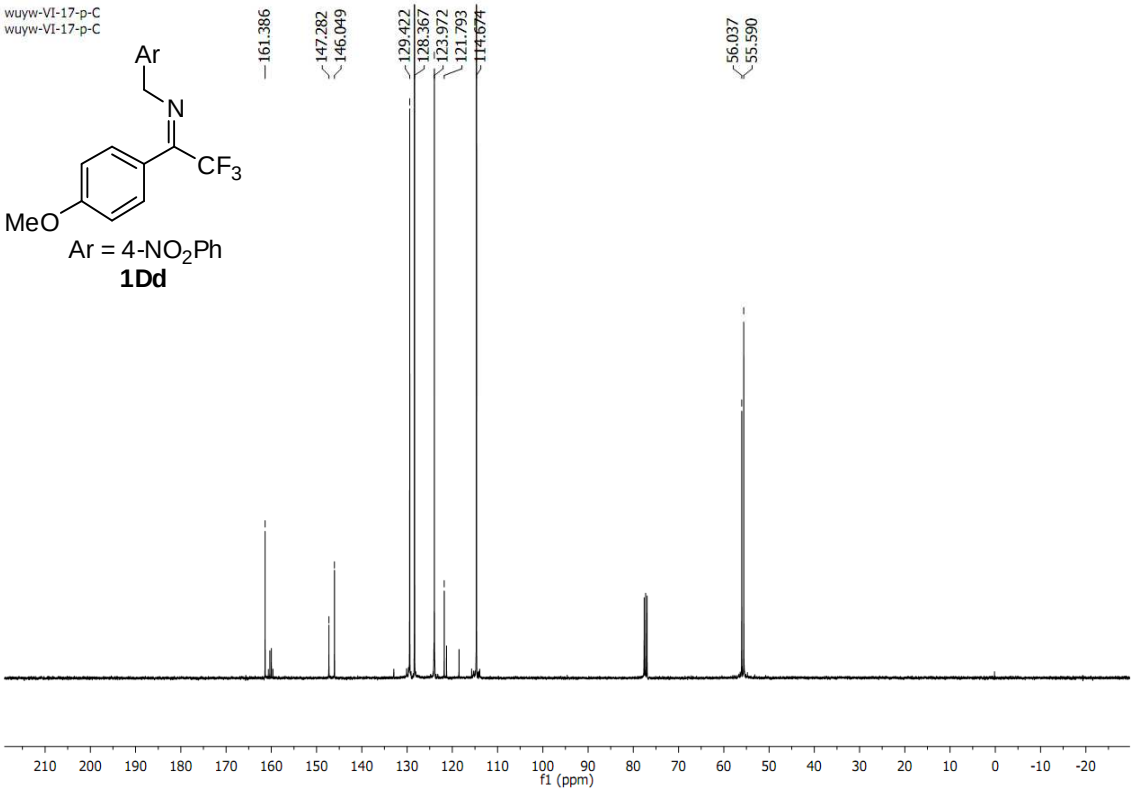


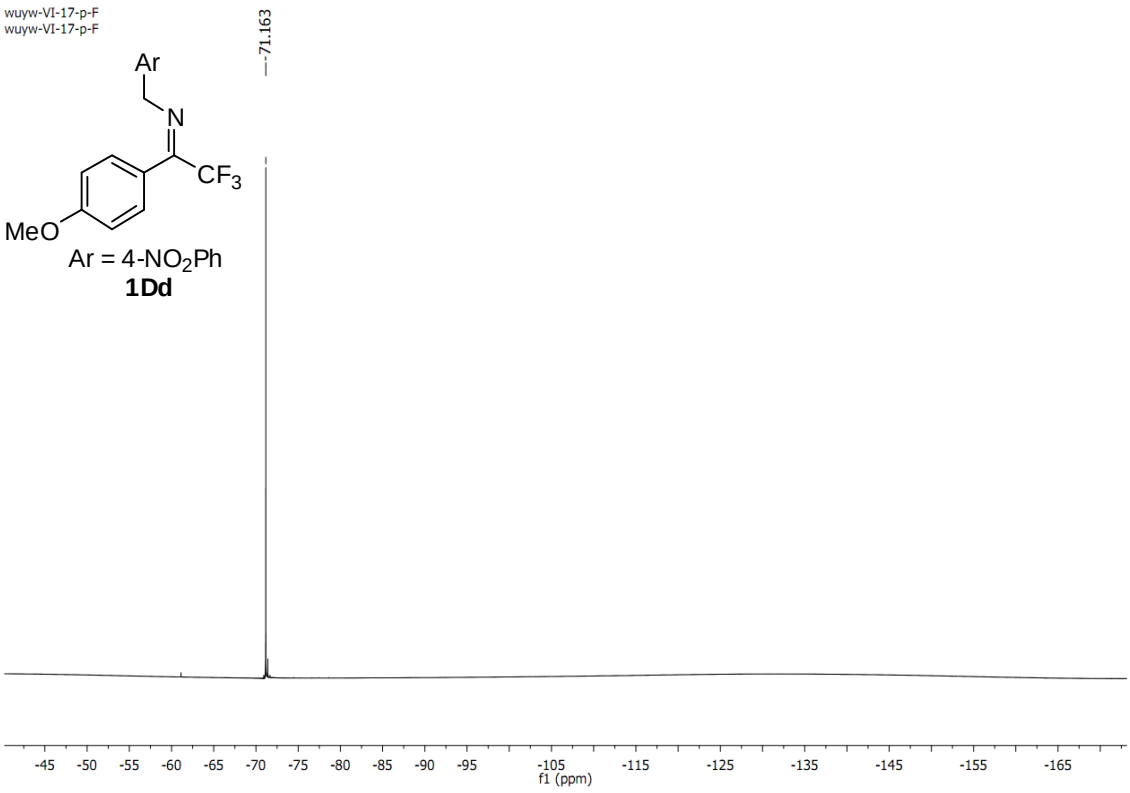
wuyw-VI-17-p-H
wuyw-VI-17-p-H

Ar = 4-NO_2Ph

1Dd



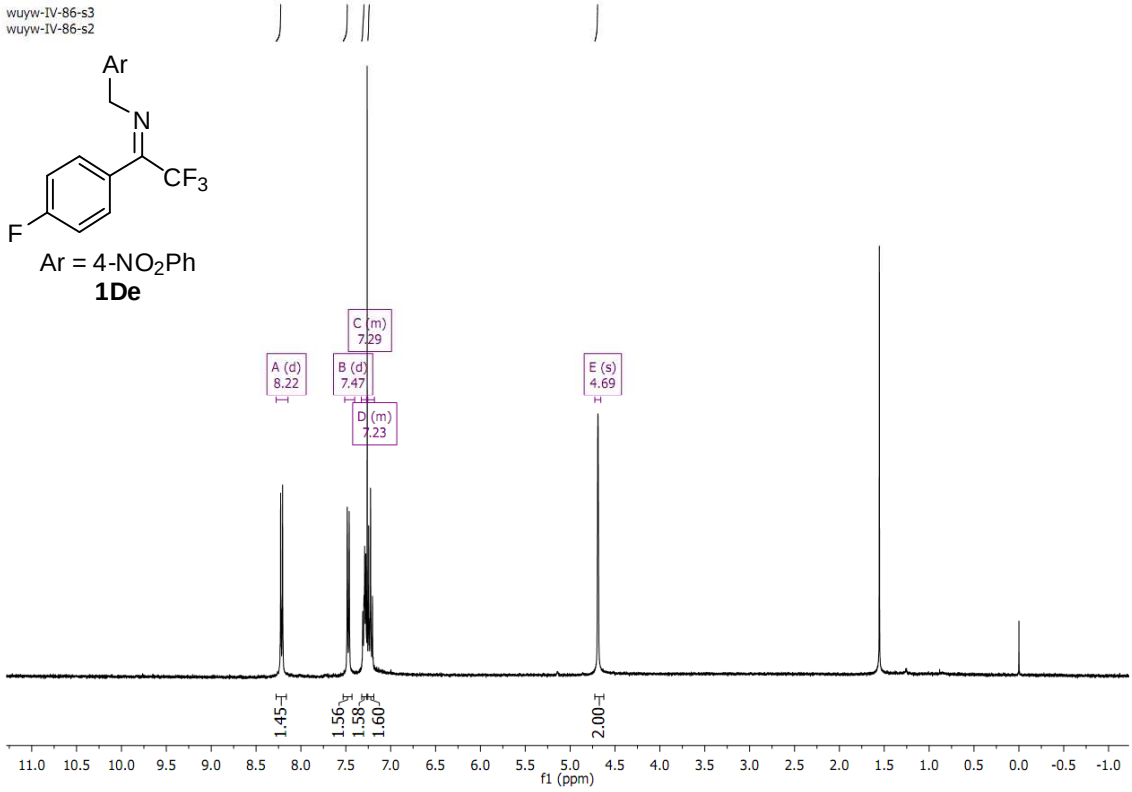

wuyw-VI-17-p-C
wuyw-VI-17-p-C
161.386
147.282
146.049
129.422
128.367
123.972
121.793
114.674
56.037
55.590
Ar
N
CF3
MeO
Ar = 4-NO2Ph
1Dd
f1 (ppm)


wuyw-VI-17-p-F
wuyw-VI-17-p-F
-71.163
Ar
N
CF3
MeO
Ar = 4-NO2Ph
1Dd
f1 (ppm)

wuyw-IV-86-s3
wuyw-IV-86-s2

Ar = 4-NO_2Ph

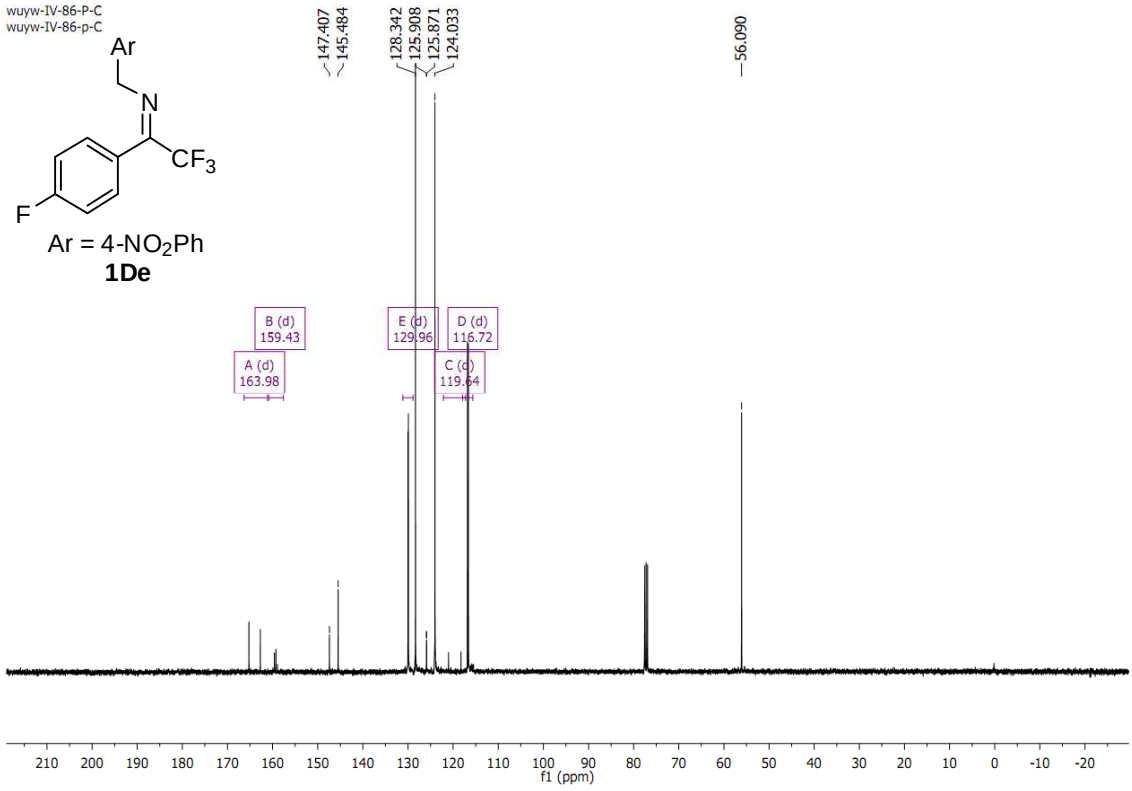
1De



wuyw-IV-86-P-C
wuyw-IV-86-p-C

Ar = 4-NO_2Ph

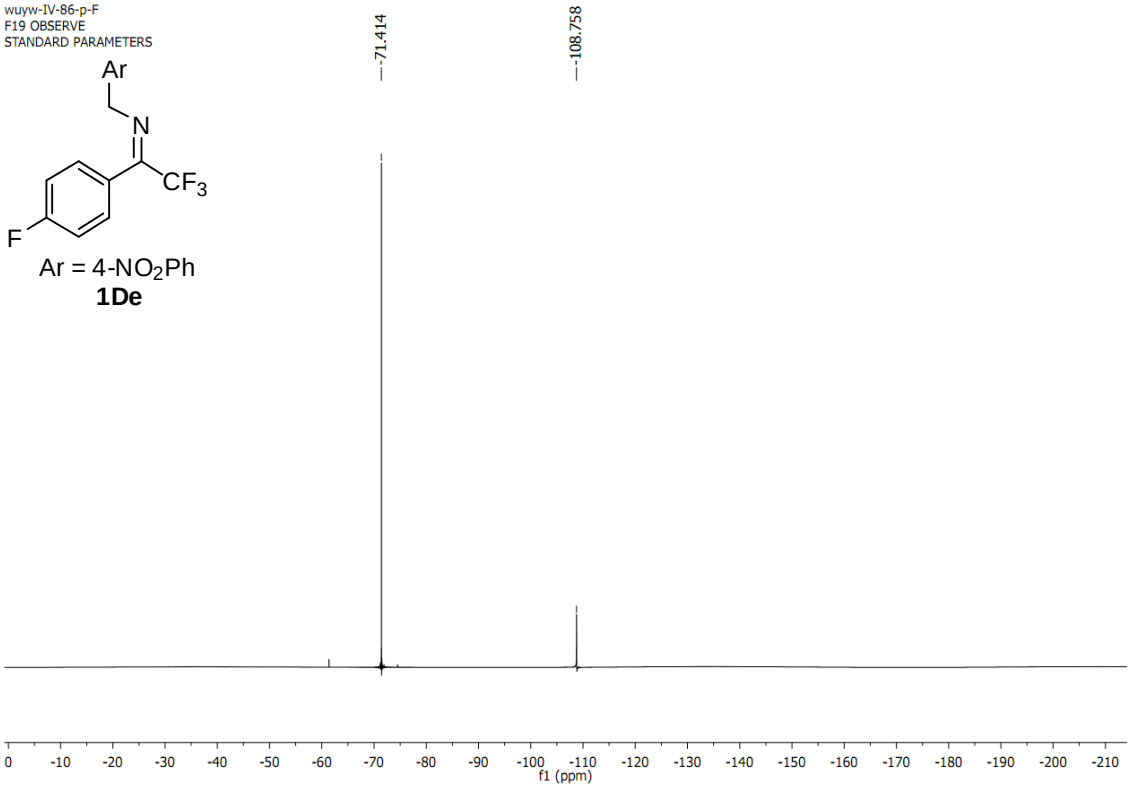
1De



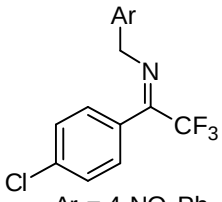
wuyw-IV-86-p-F
F19 OBSERVE
STANDARD PARAMETERS

Ar = 4-NO_2Ph

1De

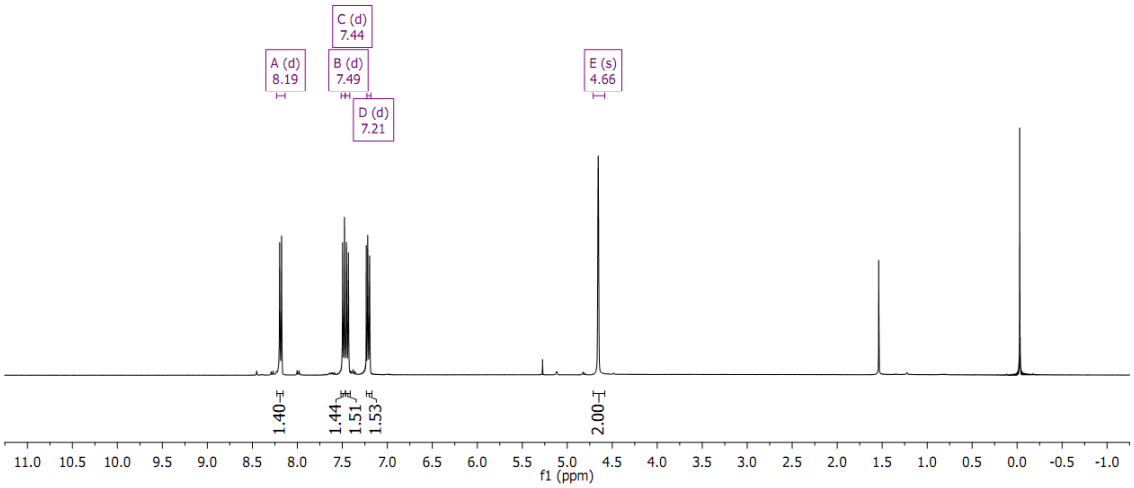


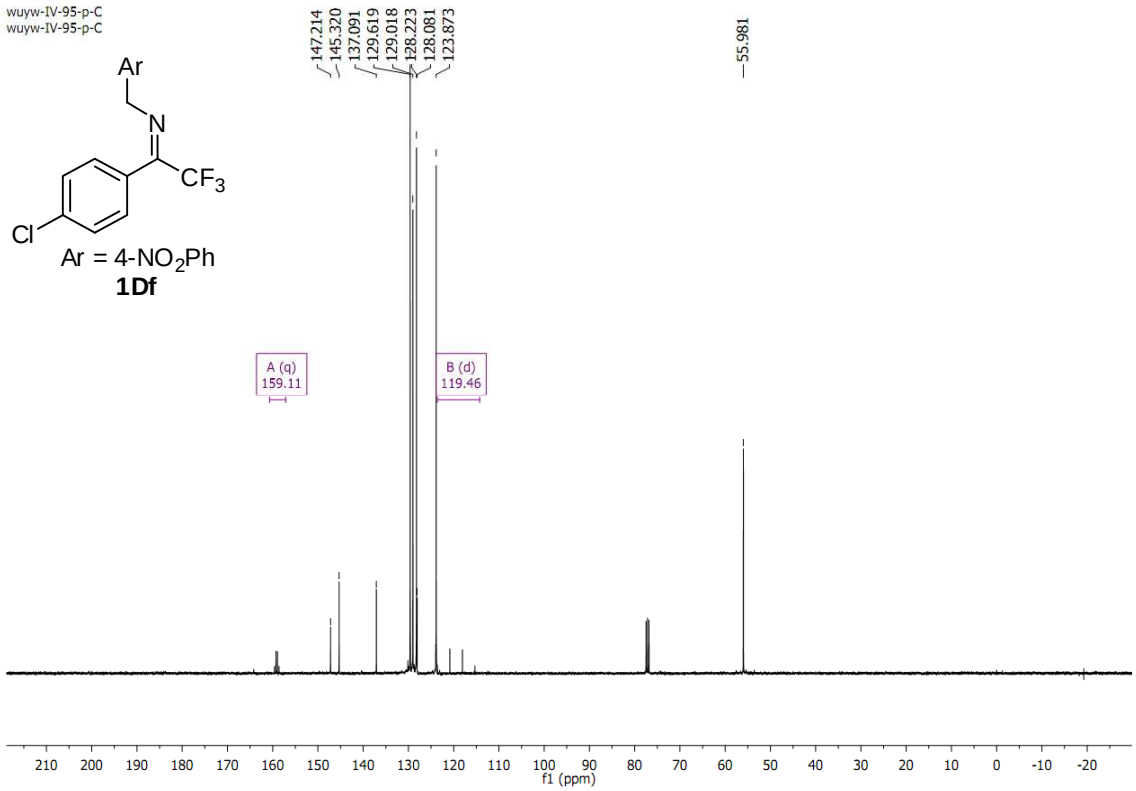
wuyw-IV-95-p-H
STANDARD 1H OBSERVE

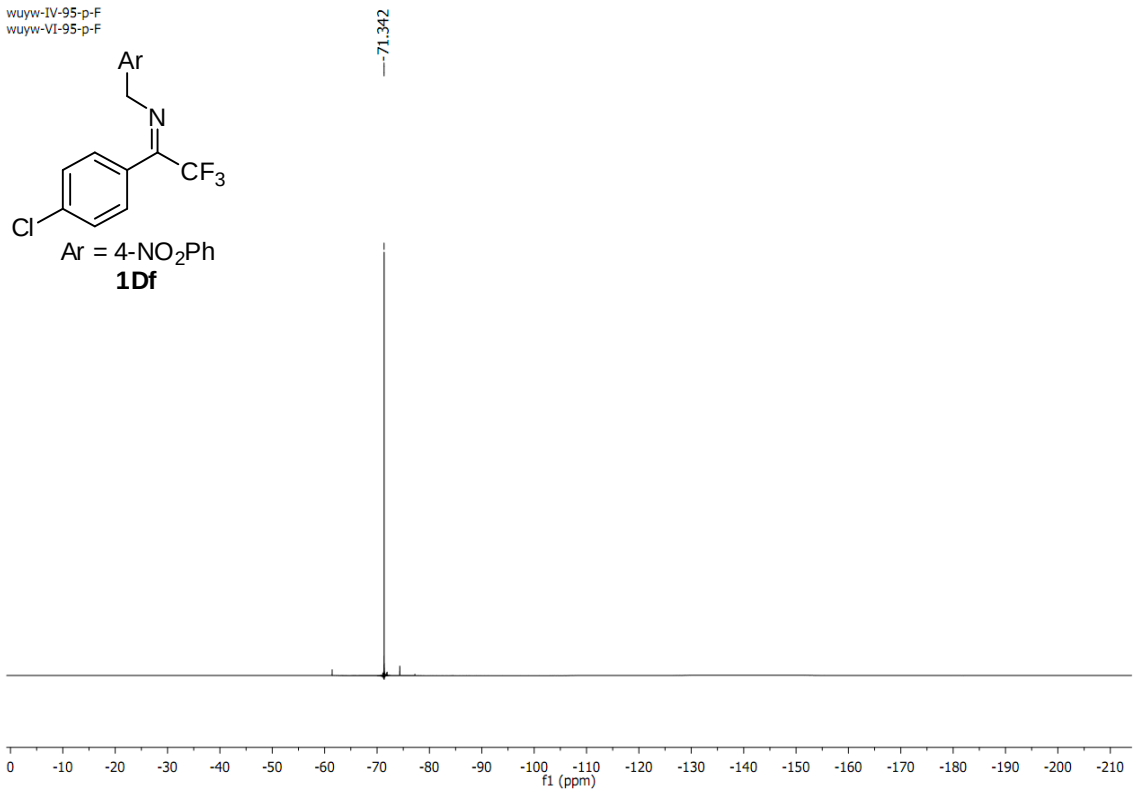


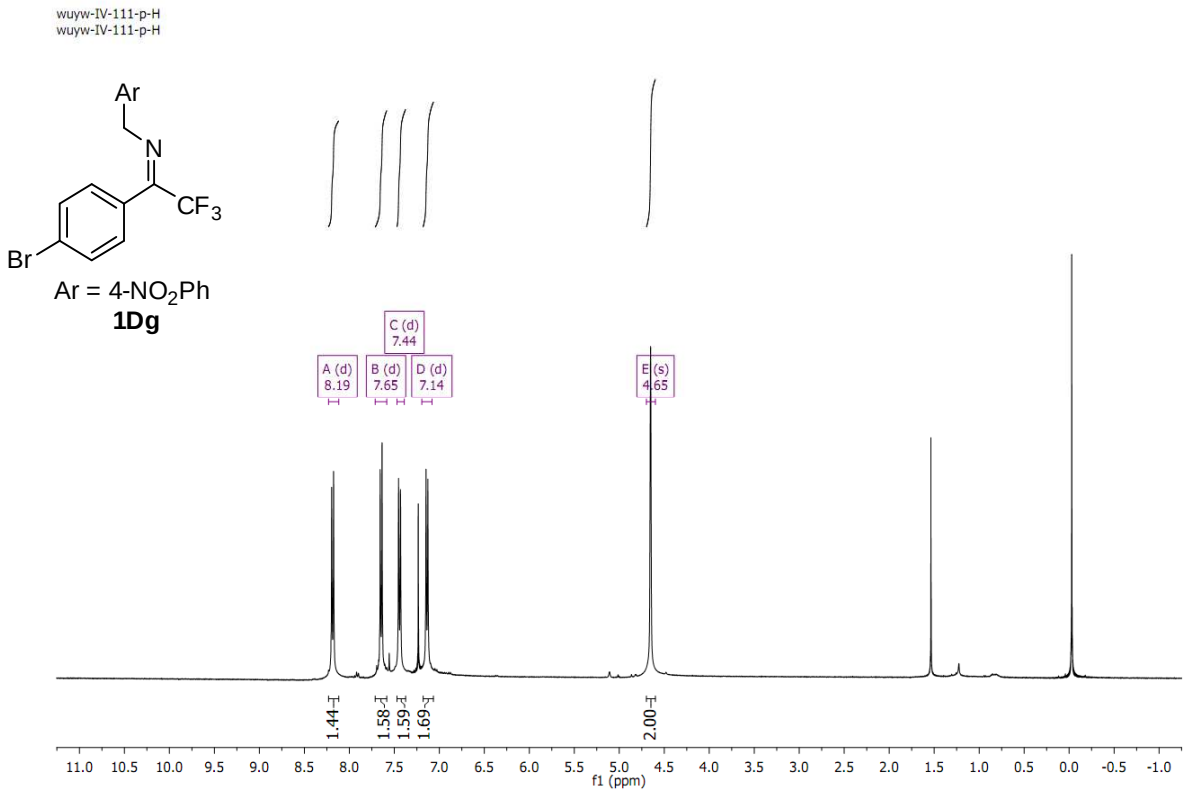
Ar = 4-NO_2Ph

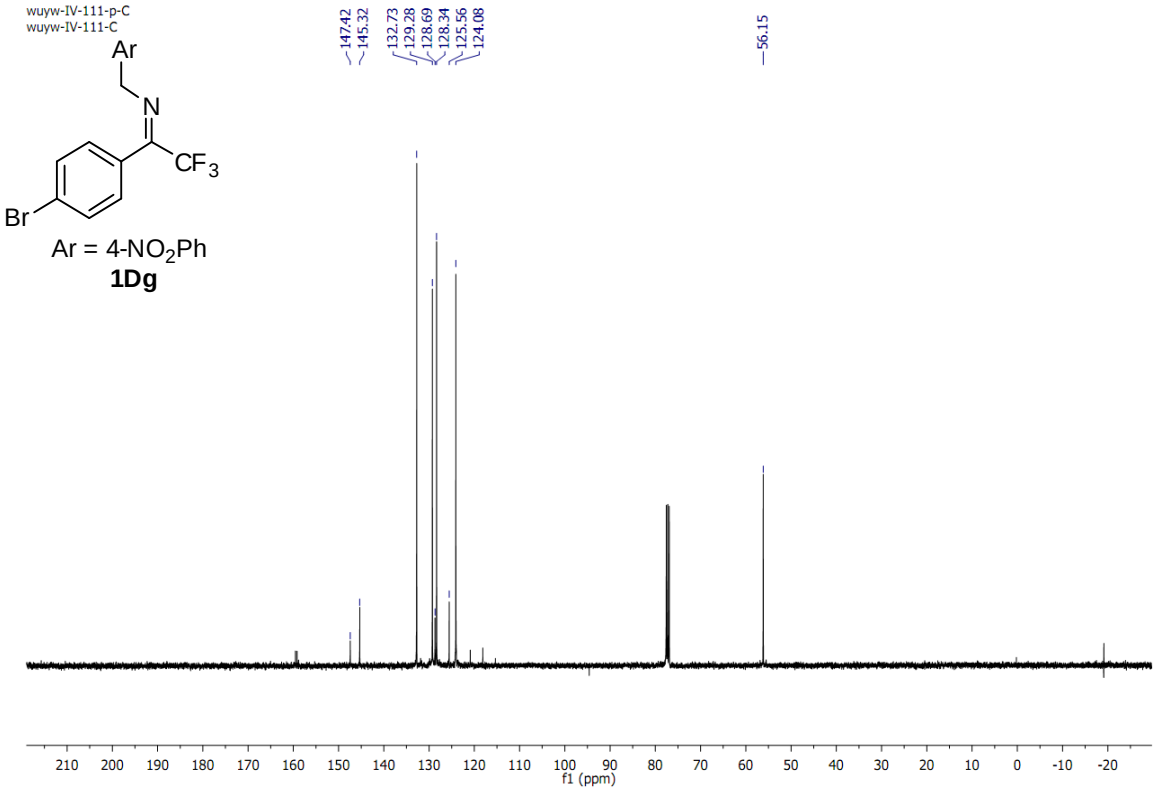
1Df

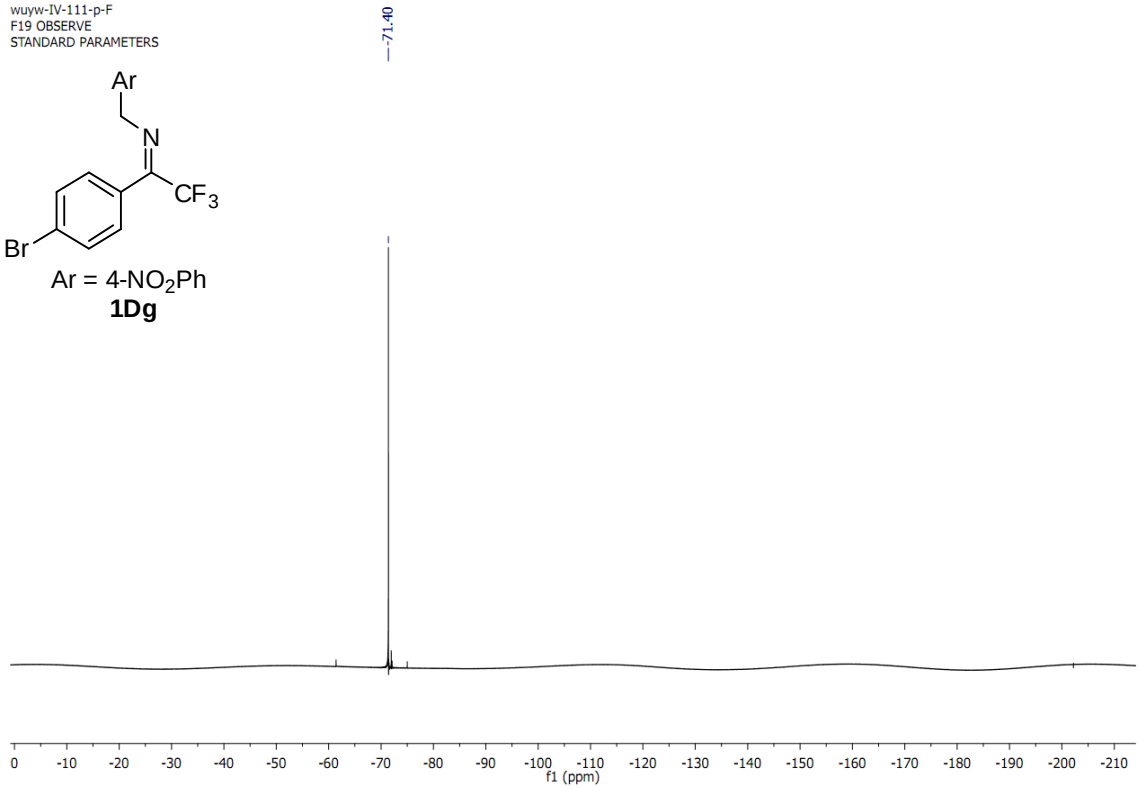


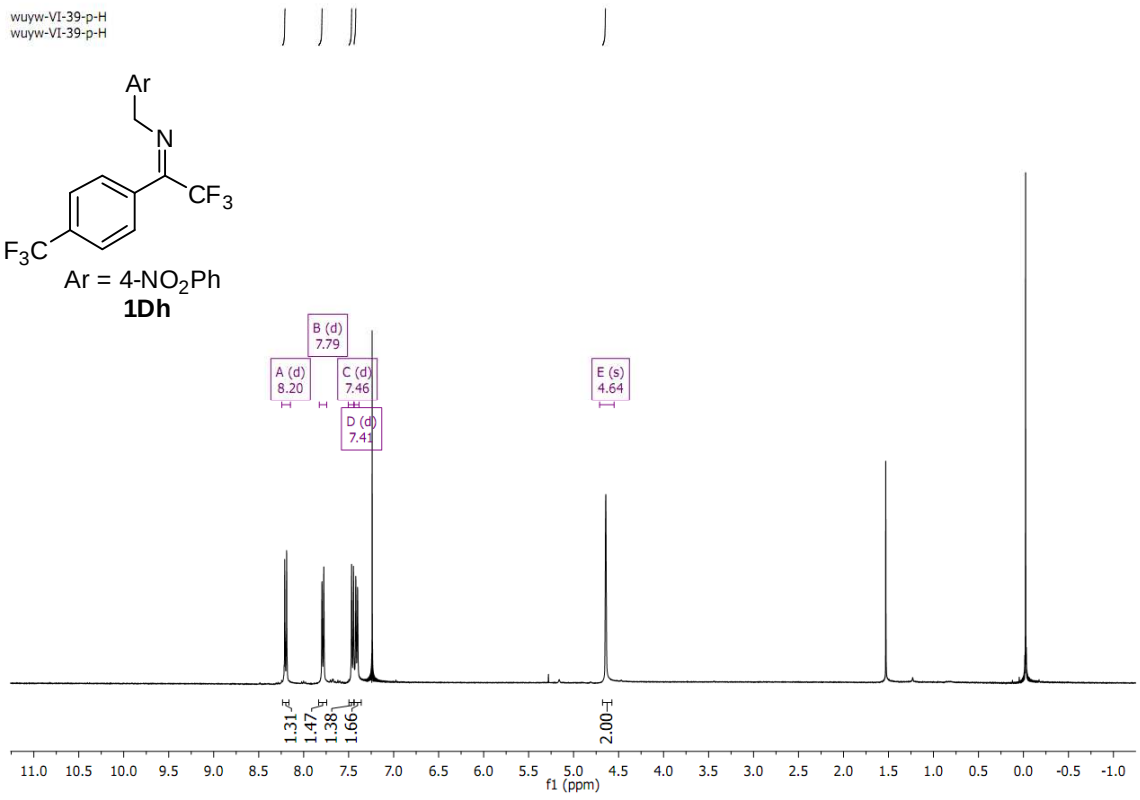

wuyw-IV-95-p-C
wuyw-IV-95-p-C
147.214
145.320
137.091
129.619
129.018
128.223
128.081
123.873
55.981
Ar
N
CF3
Cl
Ar = 4-NO2Ph
1Df
A (q)
159.11
B (d)
119.46
f1 (ppm)

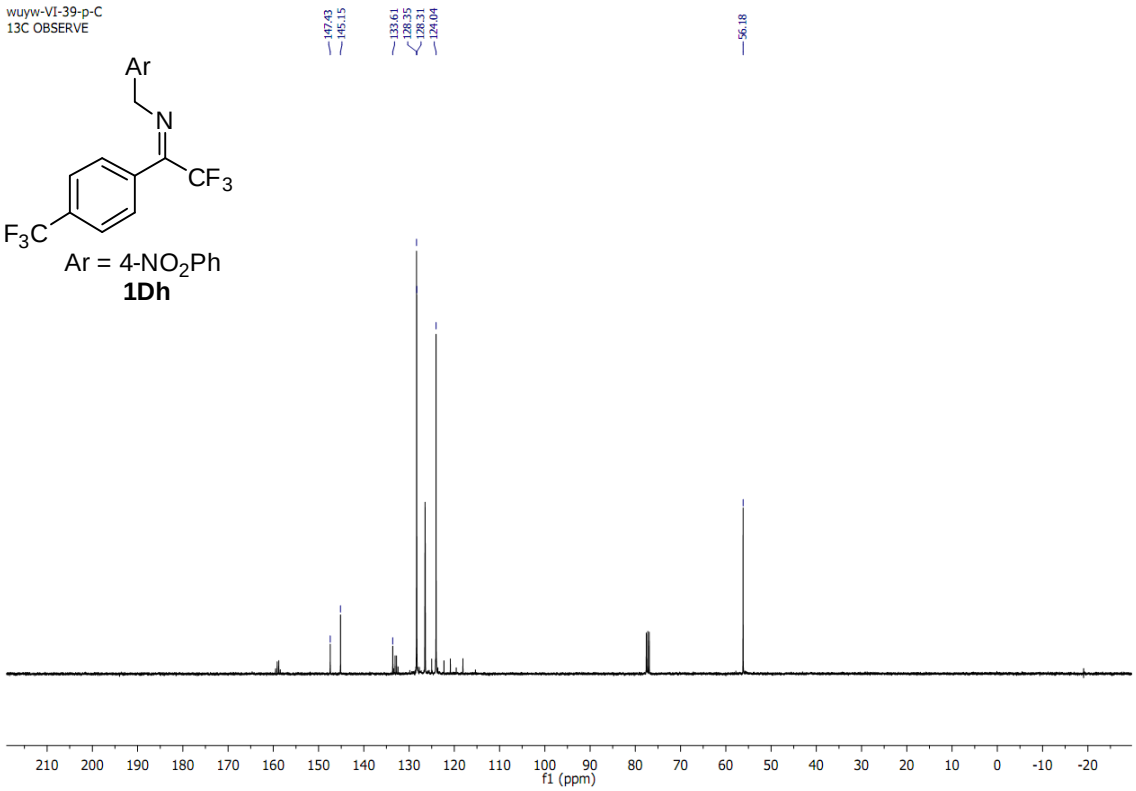

wuyw-IV-95-p-F
wuyw-VI-95-p-F
-71.342
Ar
N
CF3
Cl
Ar = 4-NO2Ph
1Df
f1 (ppm)

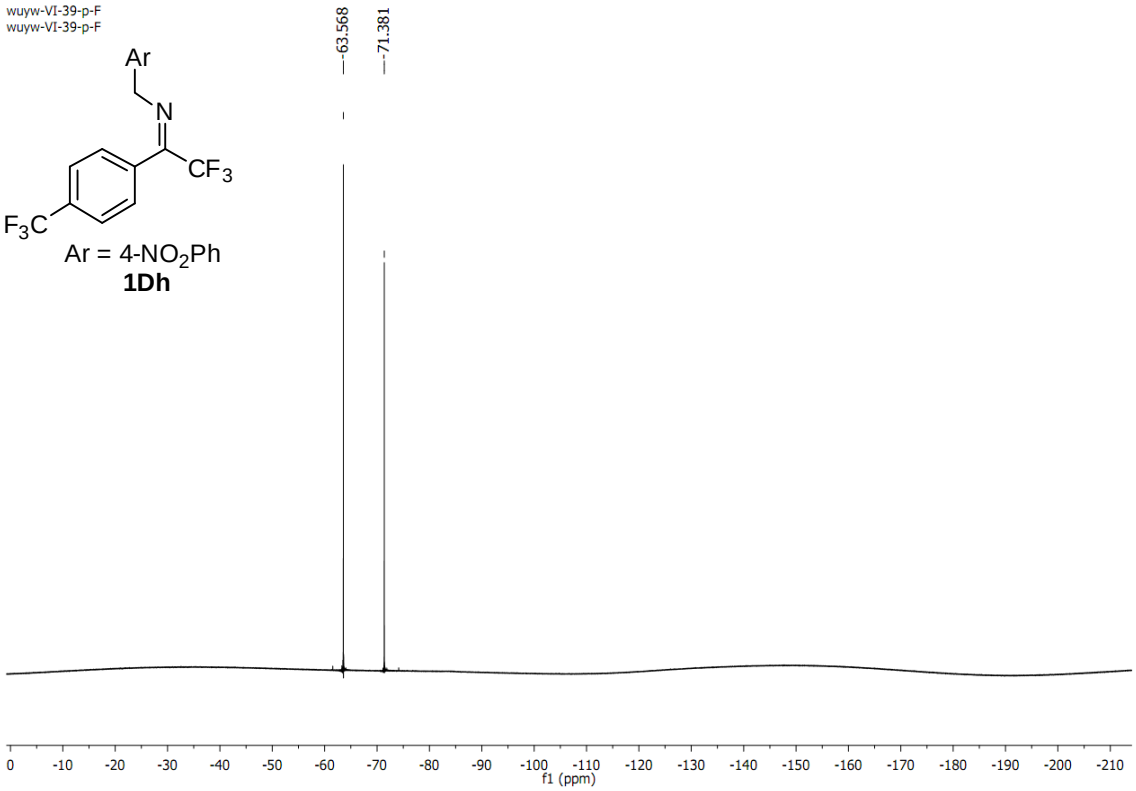

wuyw-IV-111-p-H
wuyw-IV-111-p-H
Ar
N
CF3
Br
Ar = 4-NO2Ph
1Dg
C (d) 7.44
A (d) 8.19
B (d) 7.65
D (d) 7.14
E (s) 4.65
1.44
1.58
1.59
1.69
2.00
f1 (ppm)


wuyw-IV-111-p-C
wuyw-IV-111-C
Ar
N
CF3
Br
Ar = 4-NO2Ph
1Dg
147.42
145.32
132.73
129.28
128.69
128.34
125.56
124.08
56.15
f1 (ppm)

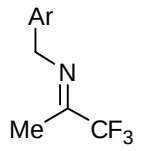

wuyw-IV-111-p-F
F19 OBSERVE
STANDARD PARAMETERS
-71.40
Ar
N
CF3
Br
Ar = 4-NO2Ph
1Dg
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


wuyw-VI-39-p-H
wuyw-VI-39-p-H
Ar
N
CF3
F3C
Ar = 4-NO2Ph
1Dh
B (d) 7.79
A (d) 8.20
C (d) 7.46
D (d) 7.41
E (s) 4.64
1.31
1.47
1.38
1.66
2.00
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 -0.5 -1.0
f1 (ppm)


wuyw-VI-39-p-C
13C OBSERVE
147.43
145.15
133.61
128.35
128.31
124.04
56.18
Ar
N
CF3
F3C
Ar = 4-NO2Ph
1Dh
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)

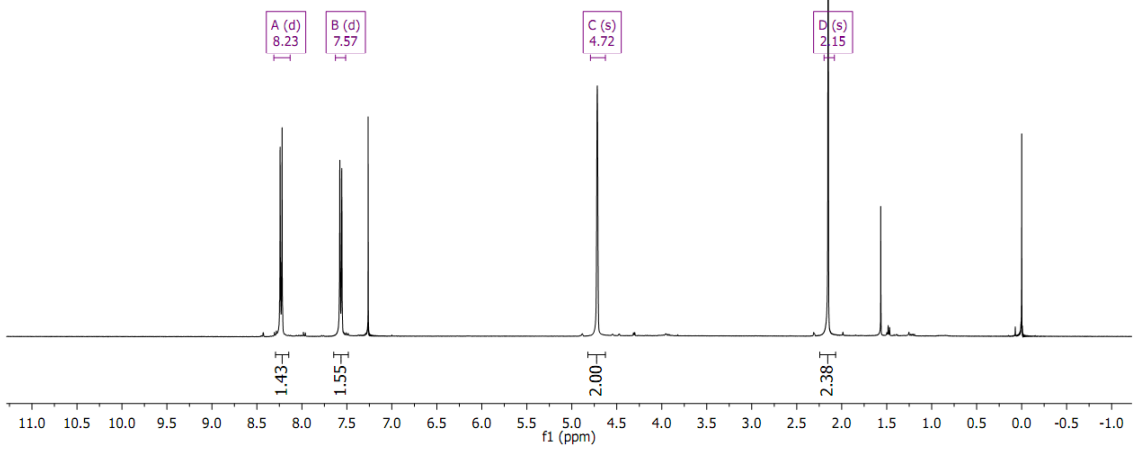

wuyw-VI-39-p-F
wuyw-VI-39-p-F
-63.568
-71.381
Ar
N
CF3
F3C
Ar = 4-NO2Ph
1Dh
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

wuyw-VI-32-C1-32
wuyw-VI-32-C1-32



Ar = 4-NO_2Ph

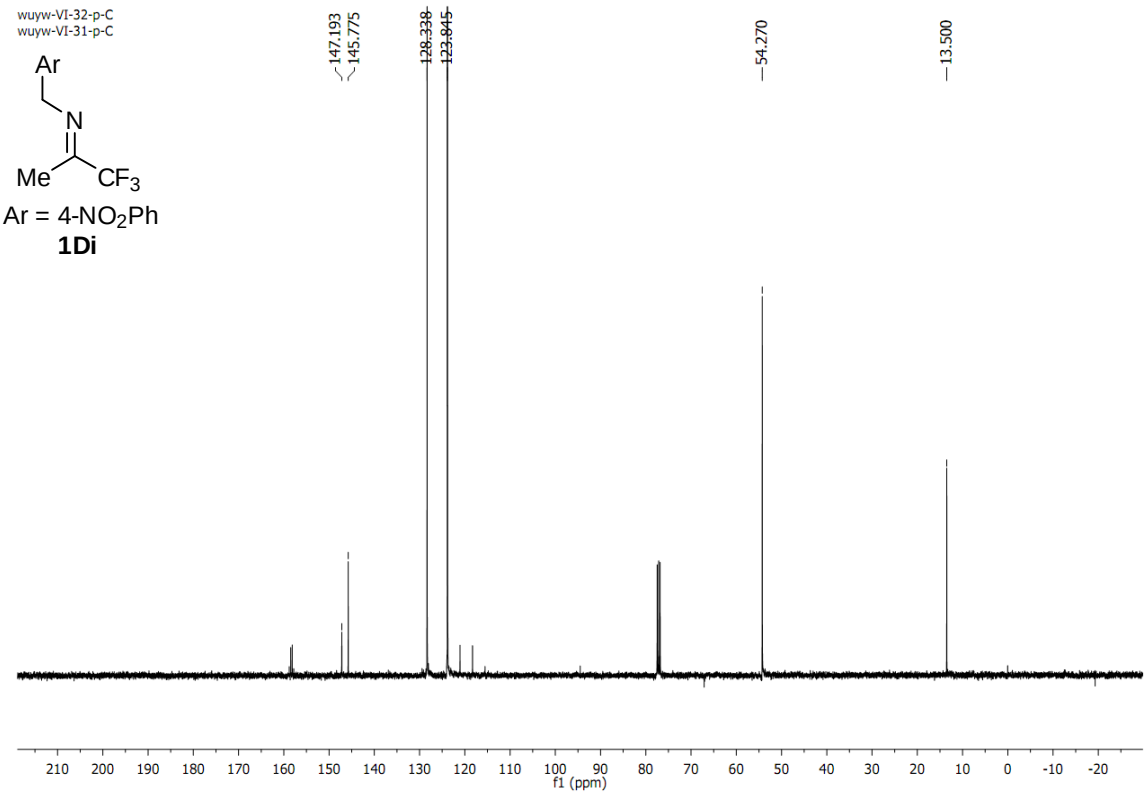
1Di



wuyw-VI-32-p-C
wuyw-VI-31-p-C

Ar = 4-NO_2Ph

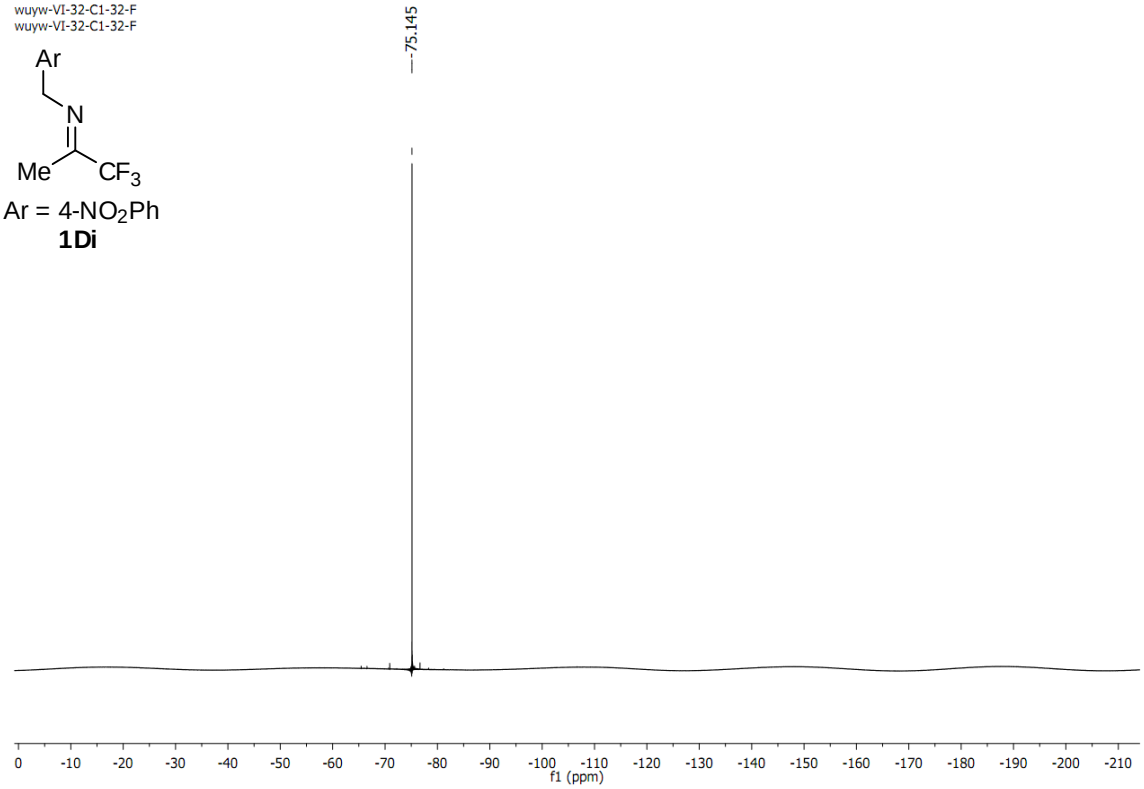
1Di



wuyw-VI-32-C1-32-F
wuyw-VI-32-C1-32-F

Ar = 4-NO_2Ph

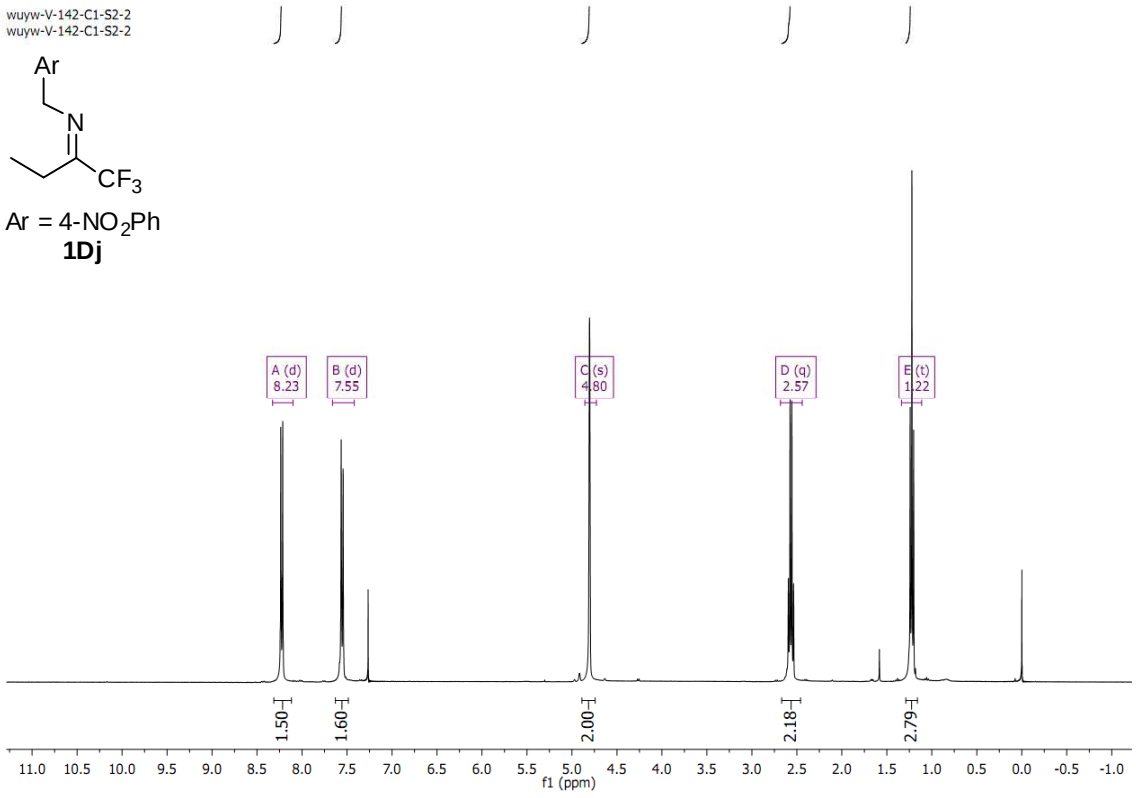
1Di



wuyw-V-142-C1-S2-2
wuyw-V-142-C1-S2-2

Ar = 4-NO_2Ph

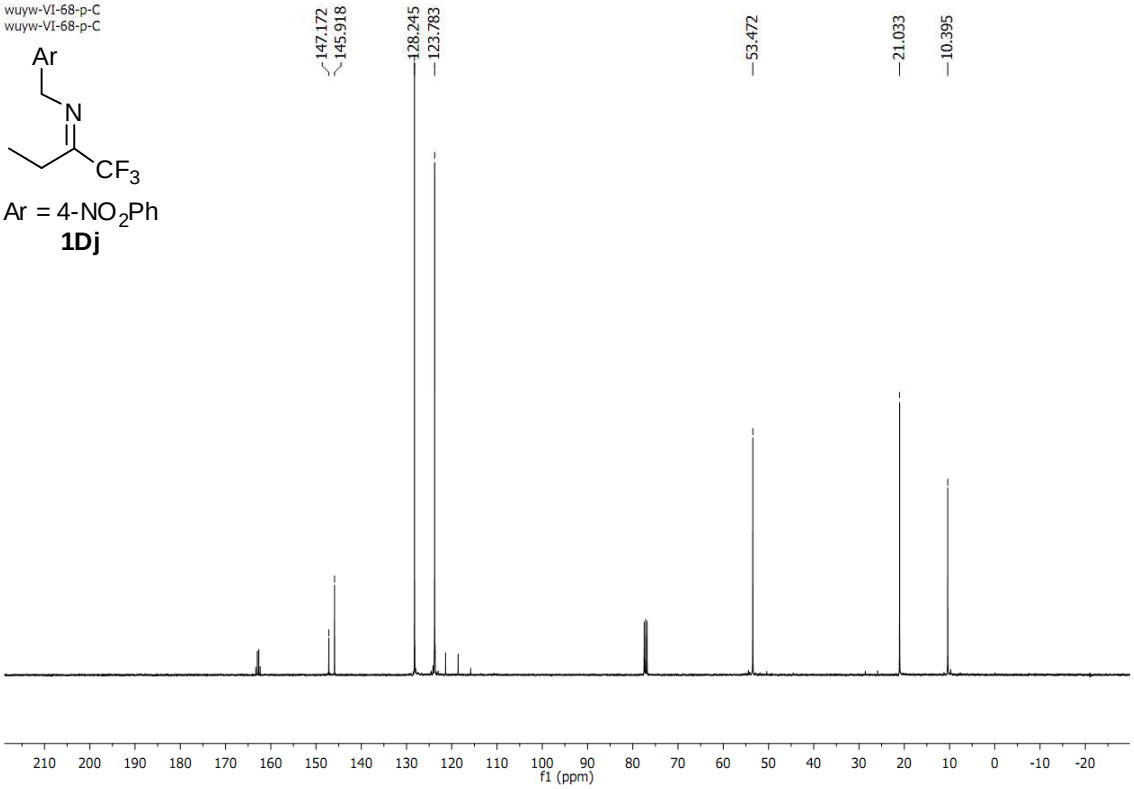
1Dj



wuyw-VI-68-p-C
wuyw-VI-68-p-C

Ar = 4-NO_2Ph

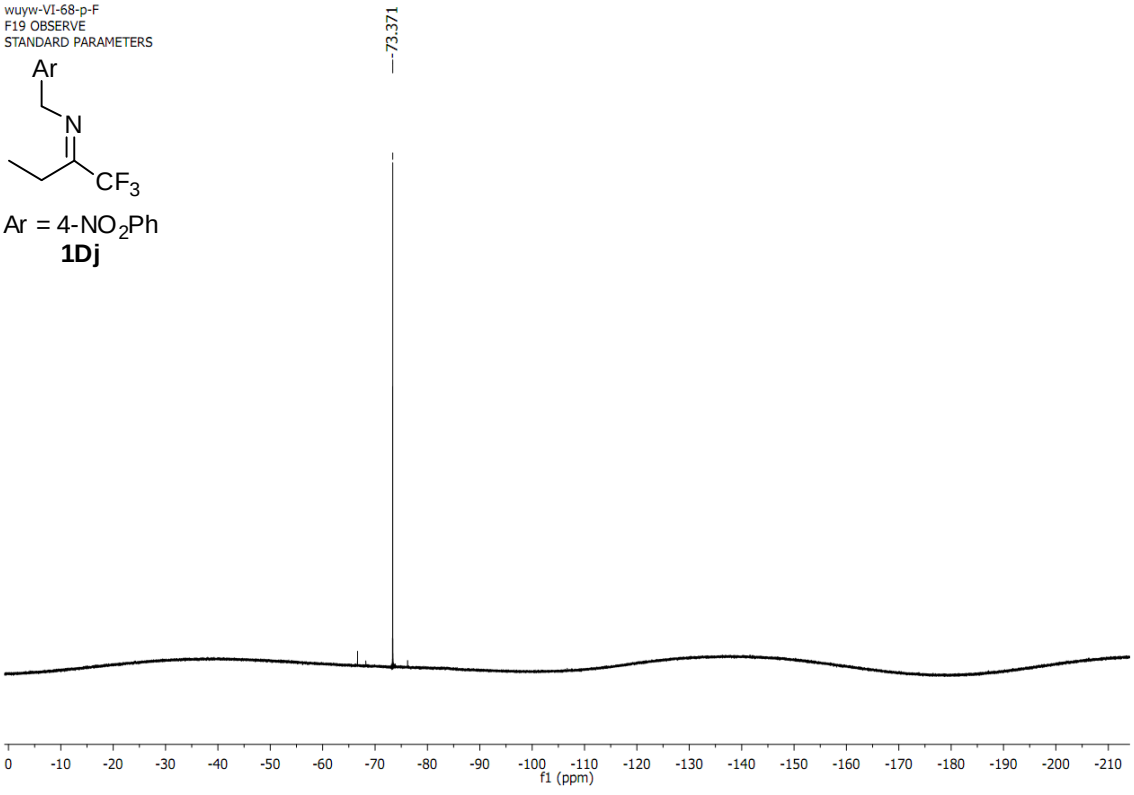
1Dj

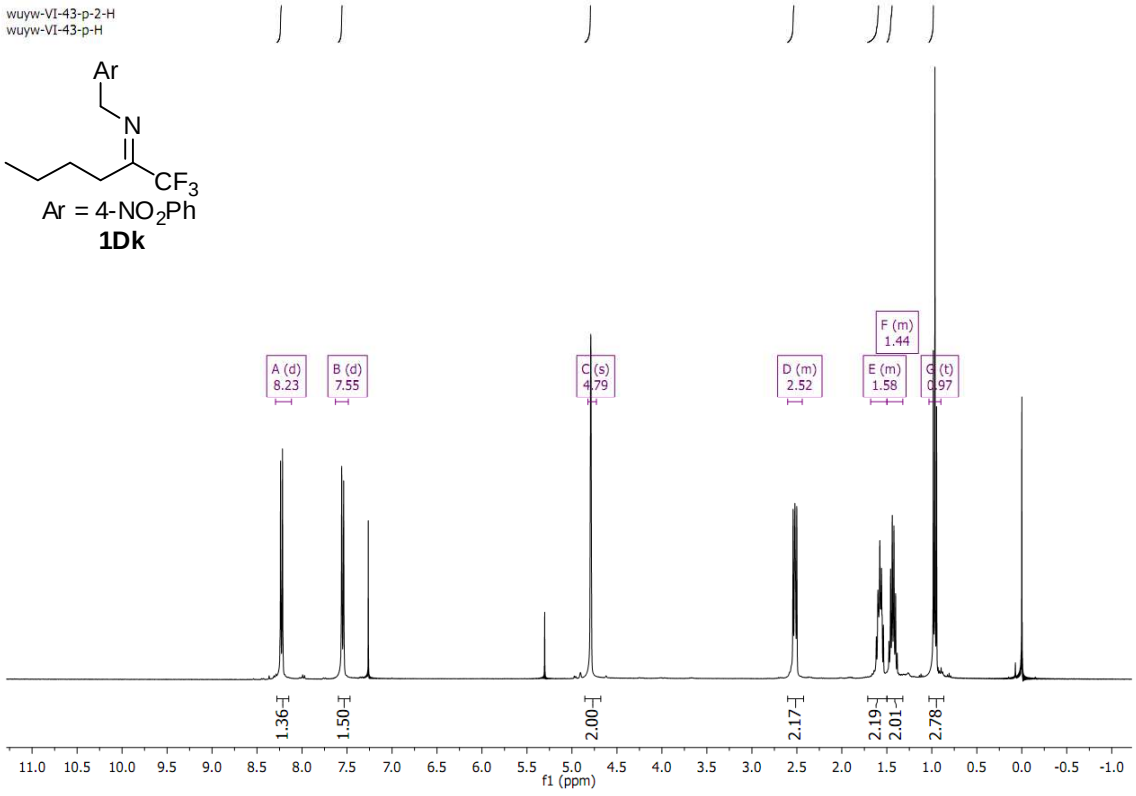


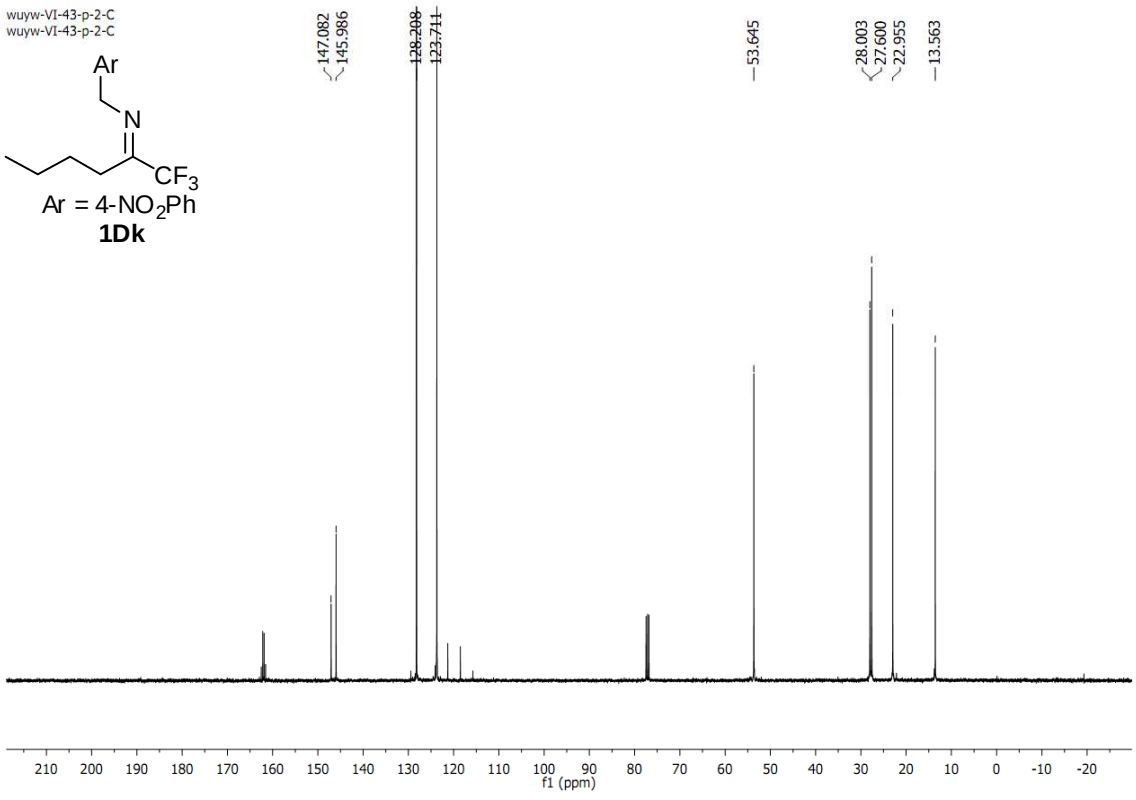
wuyw-VI-68-p-F
F19 OBSERVE
STANDARD PARAMETERS

Ar = 4-NO_2Ph

1Dj



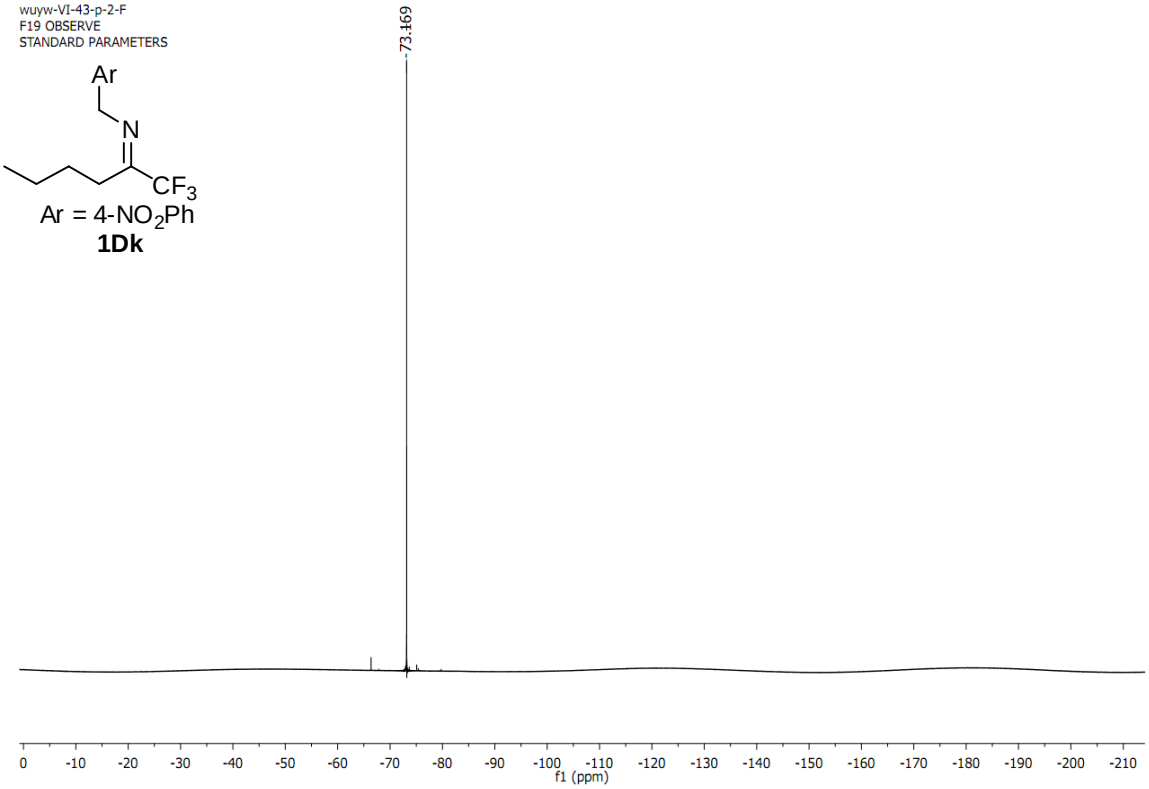

wuyw-VI-43-p-2-H
wuyw-VI-43-p-H
Ar
N
CF3
Ar = 4-NO2Ph
1Dk
A (d) 8.23
B (d) 7.55
C (s) 4.79
D (m) 2.52
E (m) 1.58
F (m) 1.44
G (t) 0.97
1.36
1.50
2.00
2.17
2.19
2.01
2.78
f1 (ppm)


wuyw-VI-43-p-2-C
wuyw-VI-43-p-2-C
Ar
N
CF3
Ar = 4-NO2Ph
1Dk
147.082
145.986
128.208
123.711
53.645
28.003
27.600
22.955
13.563
f1 (ppm)

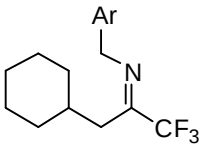
wuyw-VI-43-p-2-F
F19 OBSERVE
STANDARD PARAMETERS

Ar = 4-NO_2Ph

1Dk

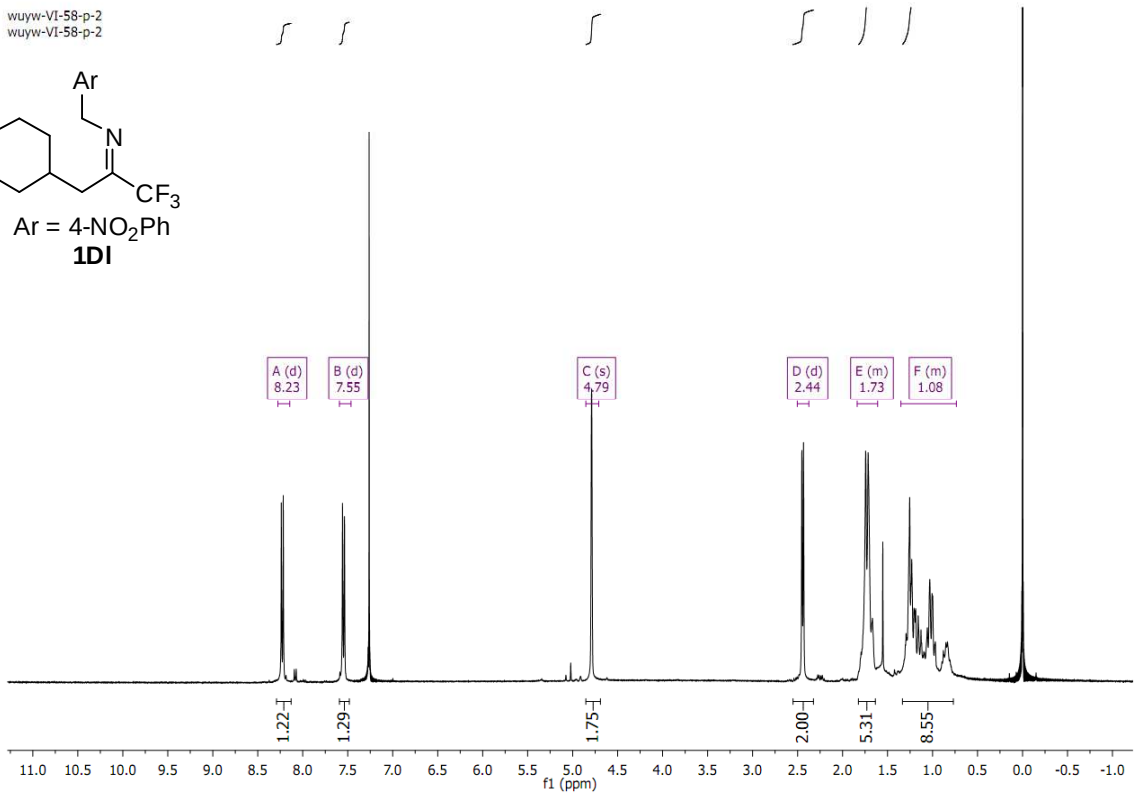


wuyw-VI-58-p-2
wuyw-VI-58-p-2

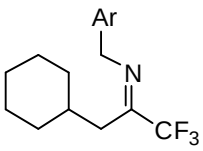


Ar = 4-NO_2Ph

1Dl



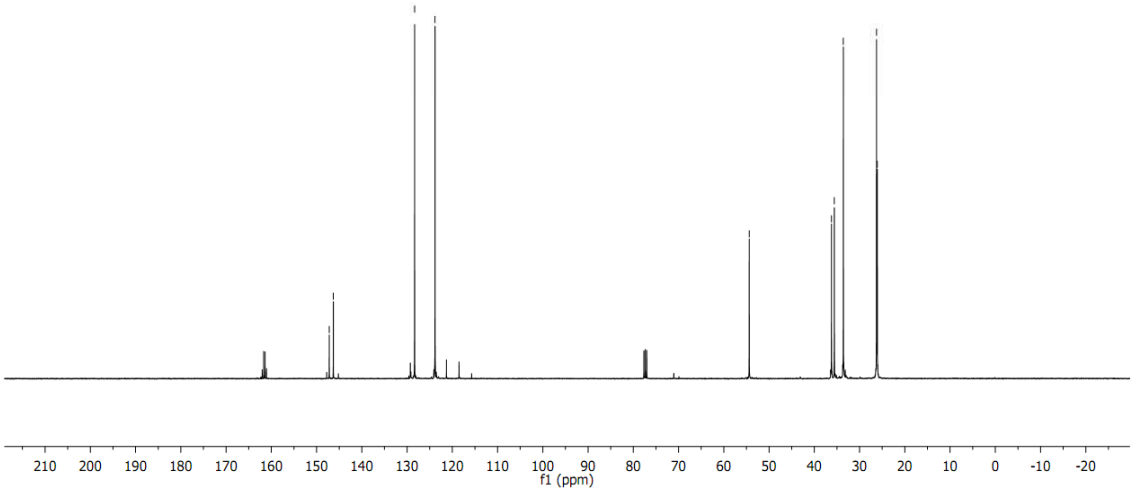
wuyw-VI-58-p-2-C
wuyw-VI-58-p-2-C



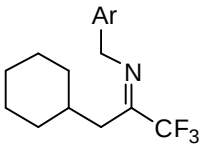
Ar = 4-NO_2Ph

1DI

147.203
146.300
128.338
123.833
54.392
36.213
35.574
33.588
26.257
26.082



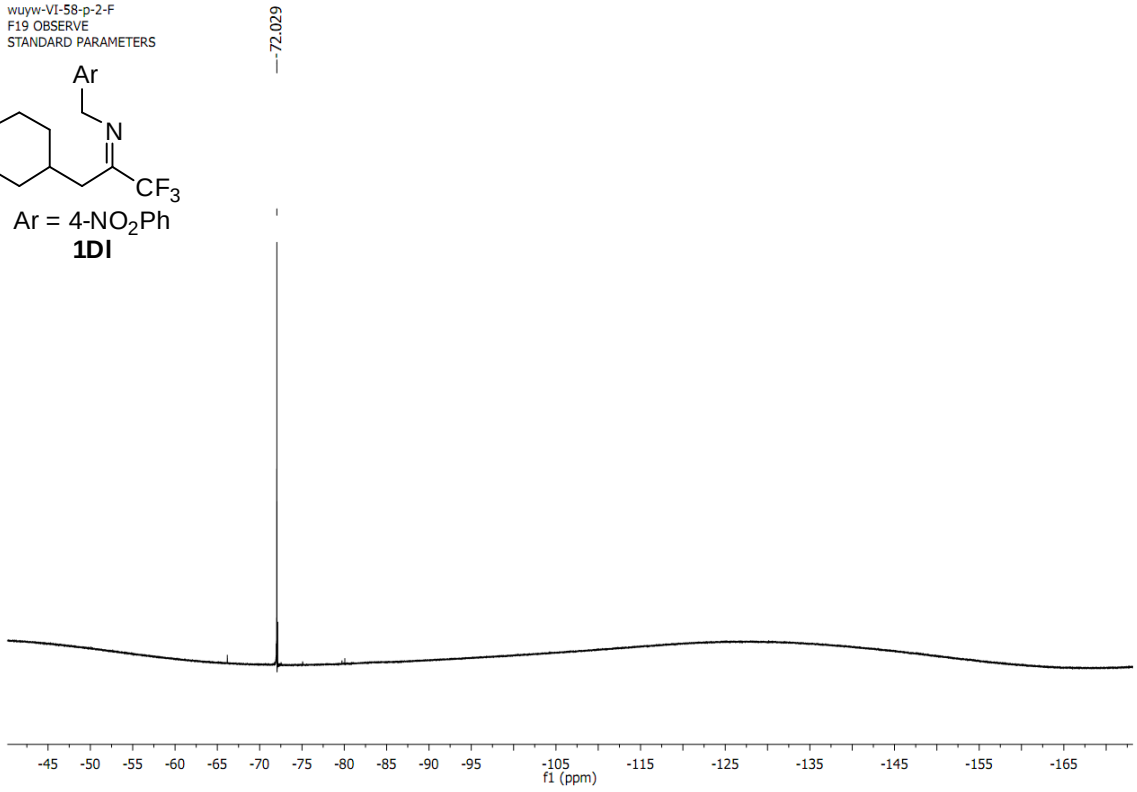
wuyw-VI-58-p-2-F
F19 OBSERVE
STANDARD PARAMETERS

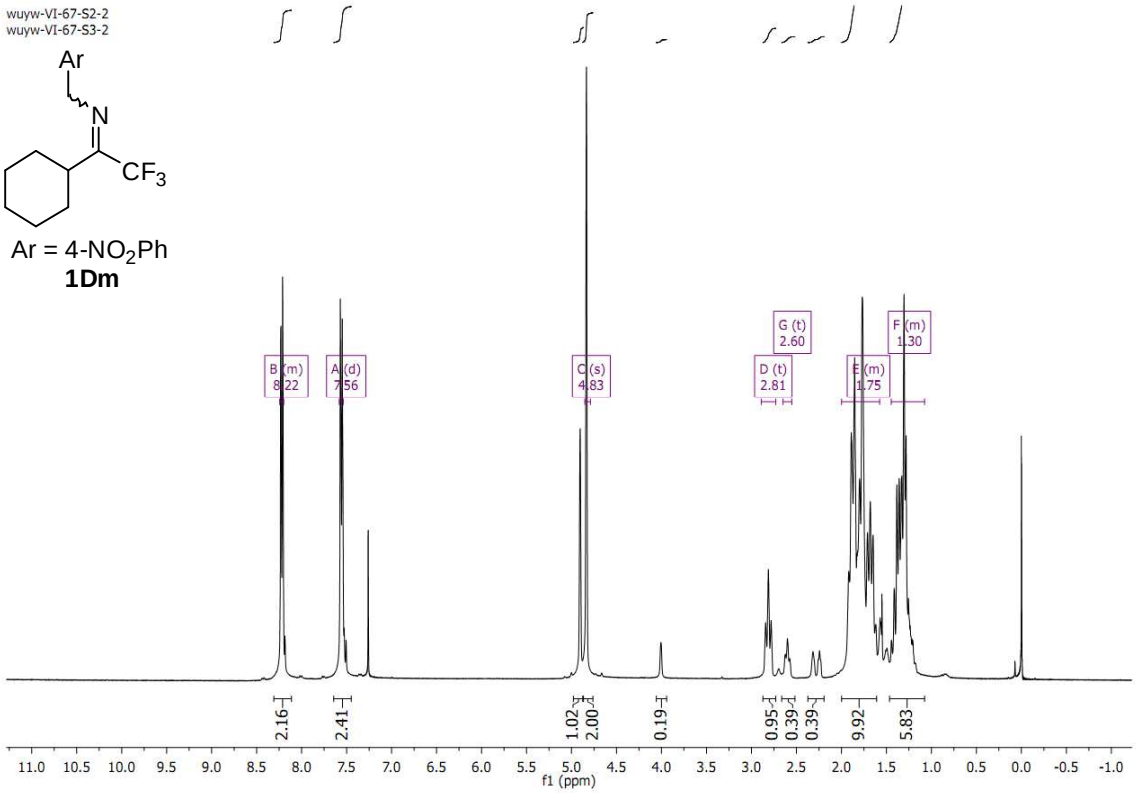


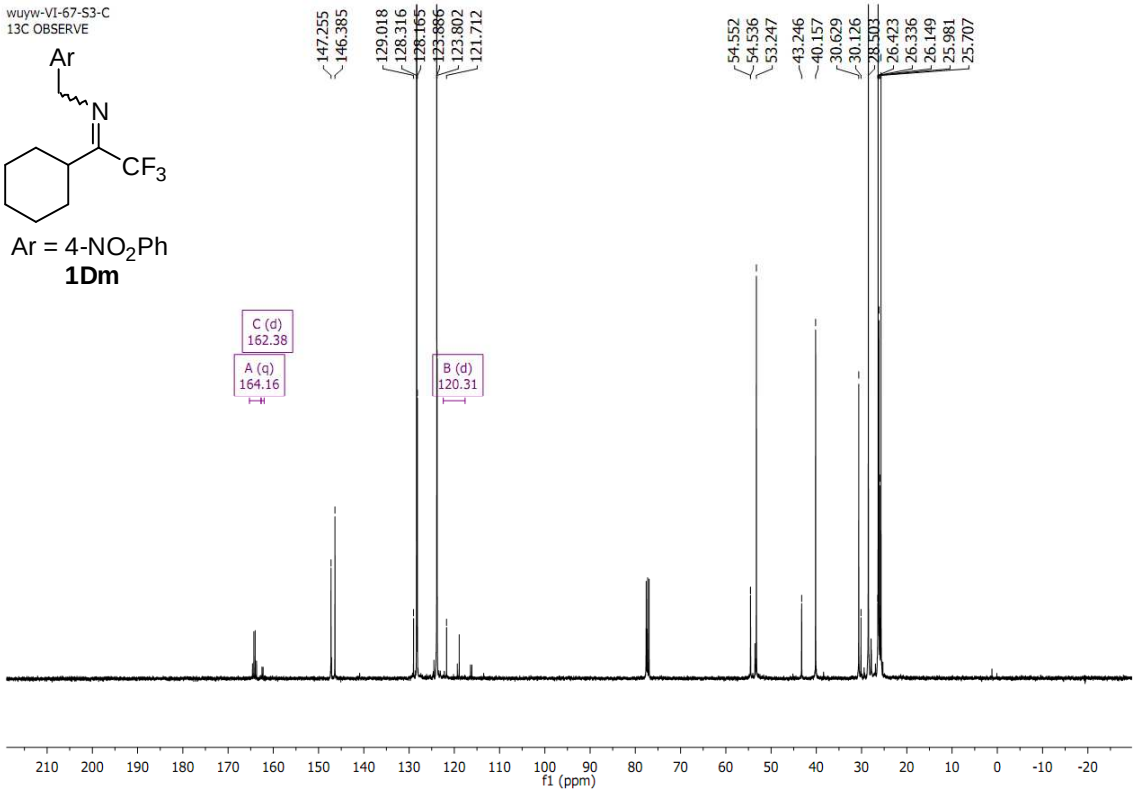
Ar = 4-NO_2Ph

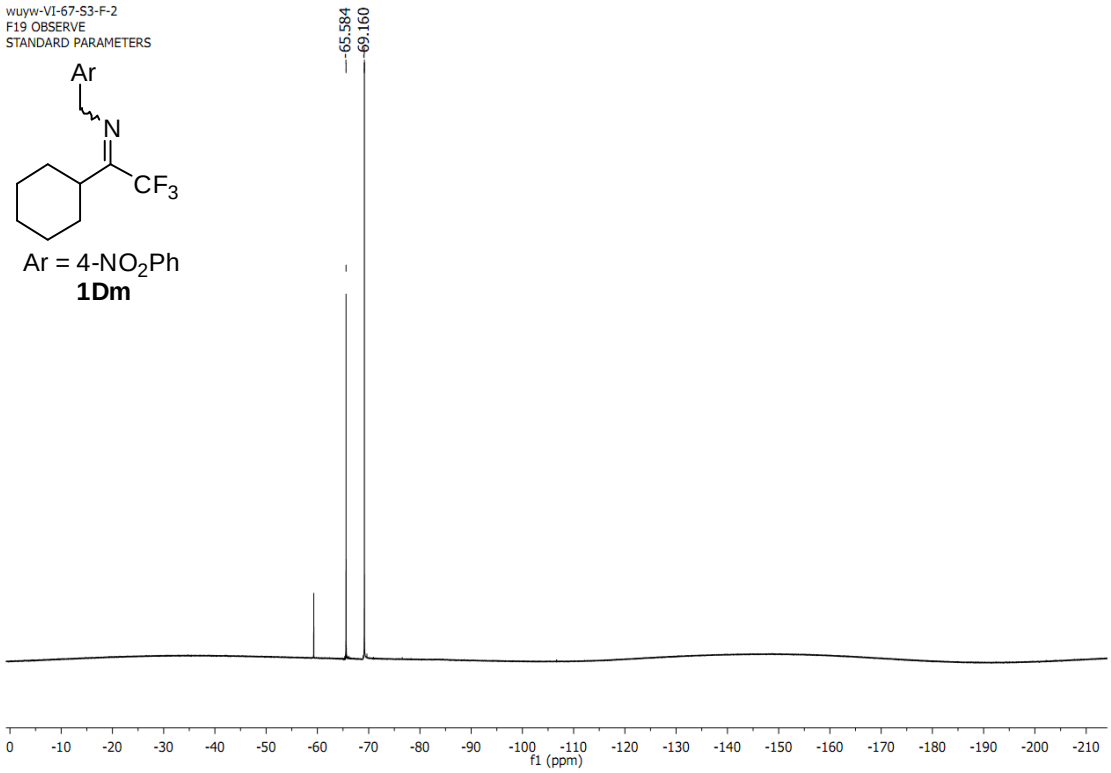
1DI

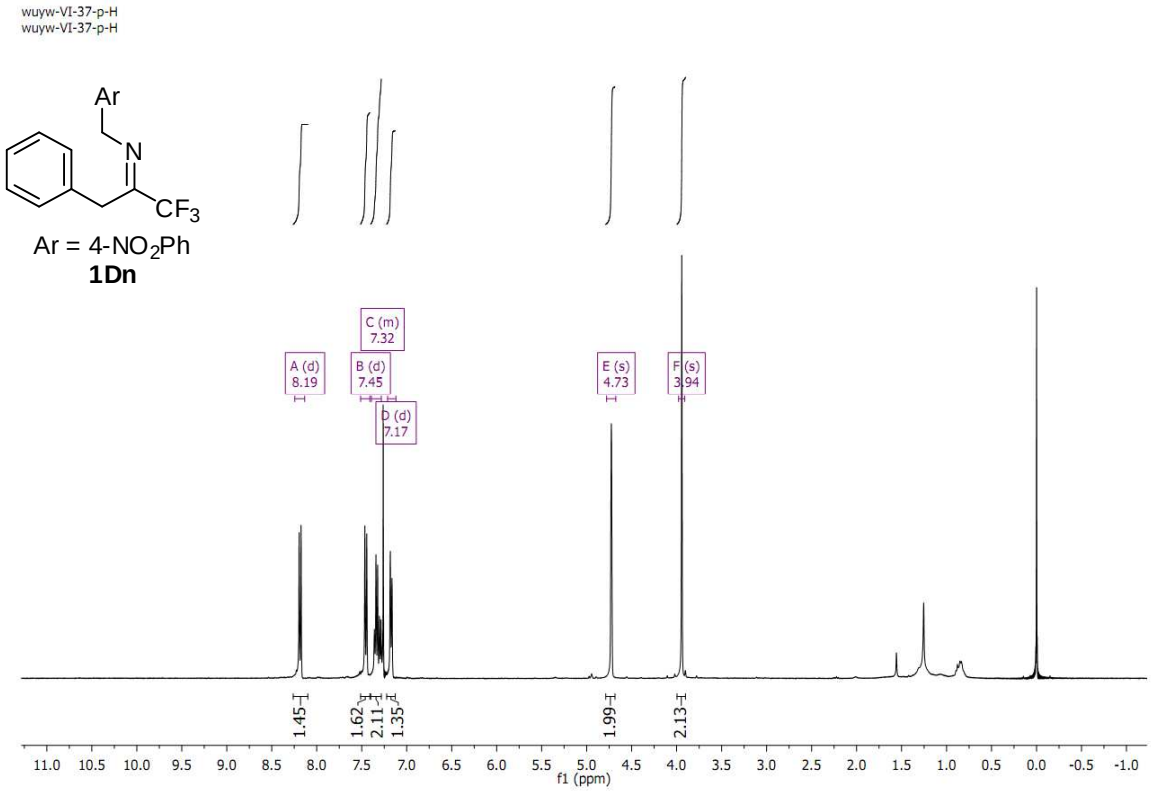
-72.029

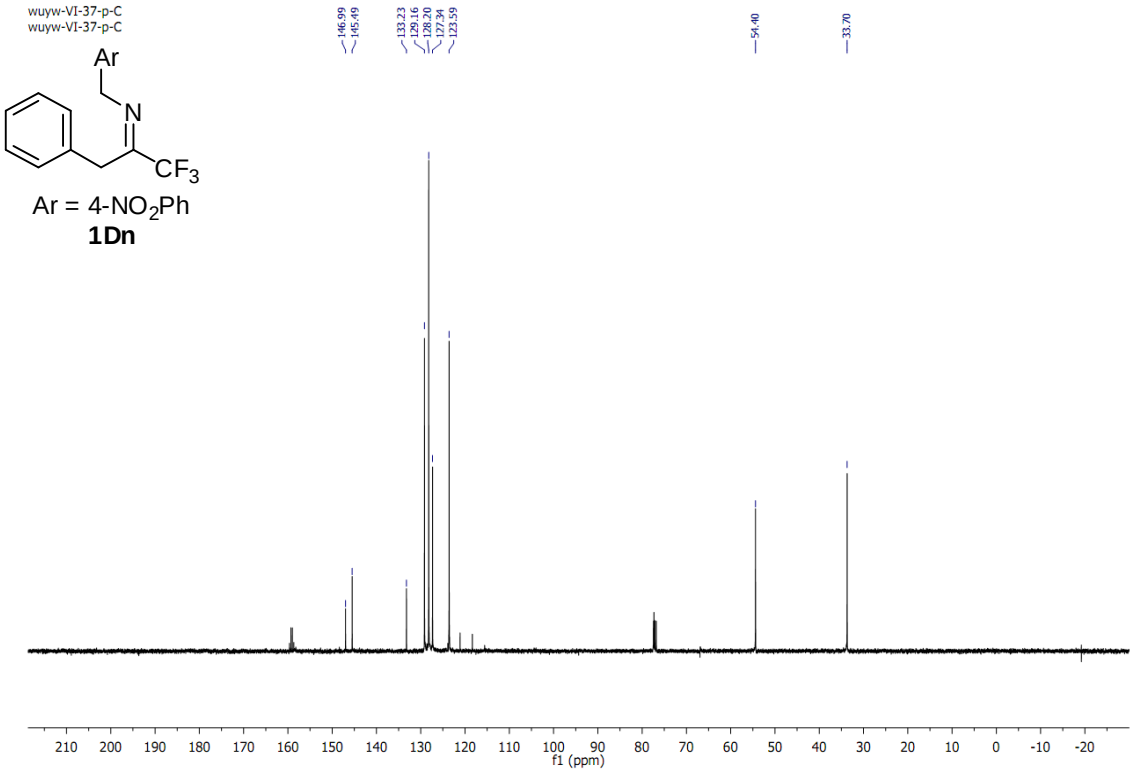


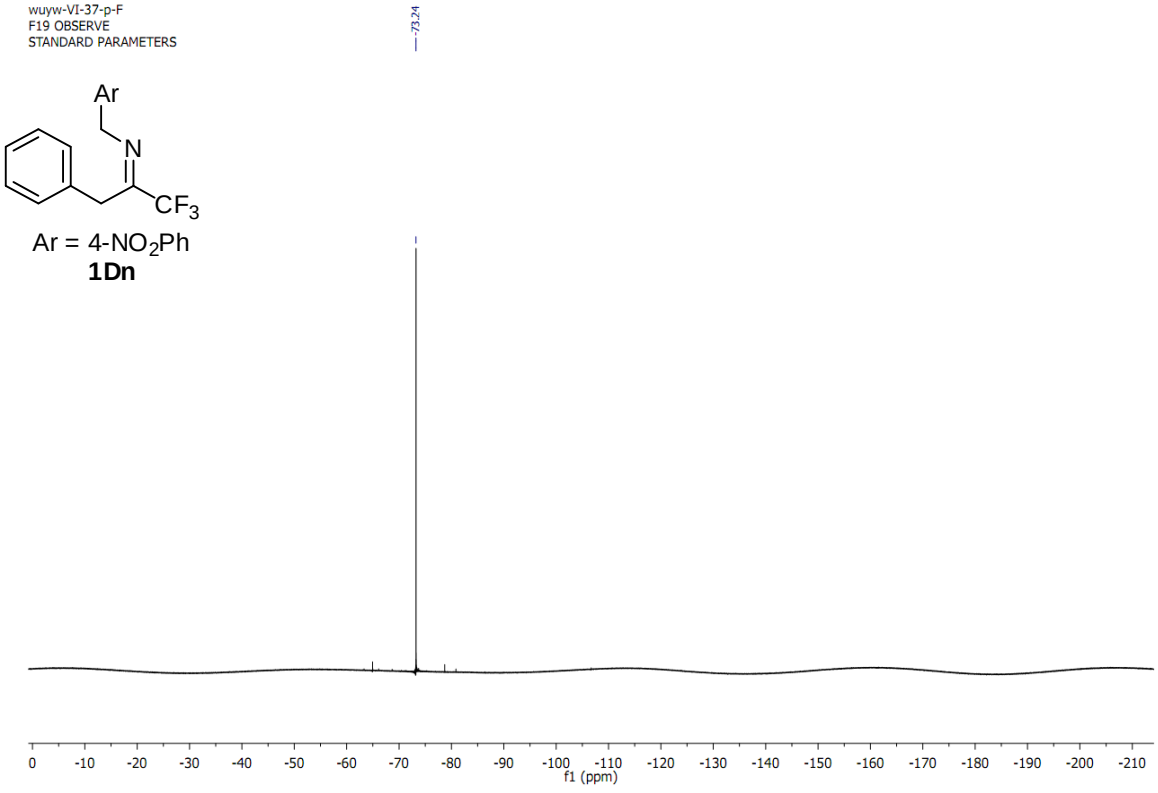

wuyw-VI-67-S2-2
wuyw-VI-67-S3-2
Ar
N
CF3
Ar = 4-NO2Ph
1Dm
B (m) 8.22
A (d) 7.56
C (s) 4.83
D (t) 2.81
G (t) 2.60
E (m) 1.75
F (m) 1.30
2.16
2.41
1.02
2.00
0.19
0.95
0.39
0.39
9.92
5.83
f1 (ppm)


wuyw-VI-67-S3-C
13C OBSERVE
Ar
N
CF3
Ar = 4-NO2Ph
1Dm
147.255
146.385
129.018
128.316
128.165
123.886
123.802
121.712
54.552
54.536
53.247
43.246
40.157
30.629
30.126
28.503
26.423
26.336
26.149
25.981
25.707
C (d) 162.38
A (q) 164.16
B (d) 120.31
f1 (ppm)

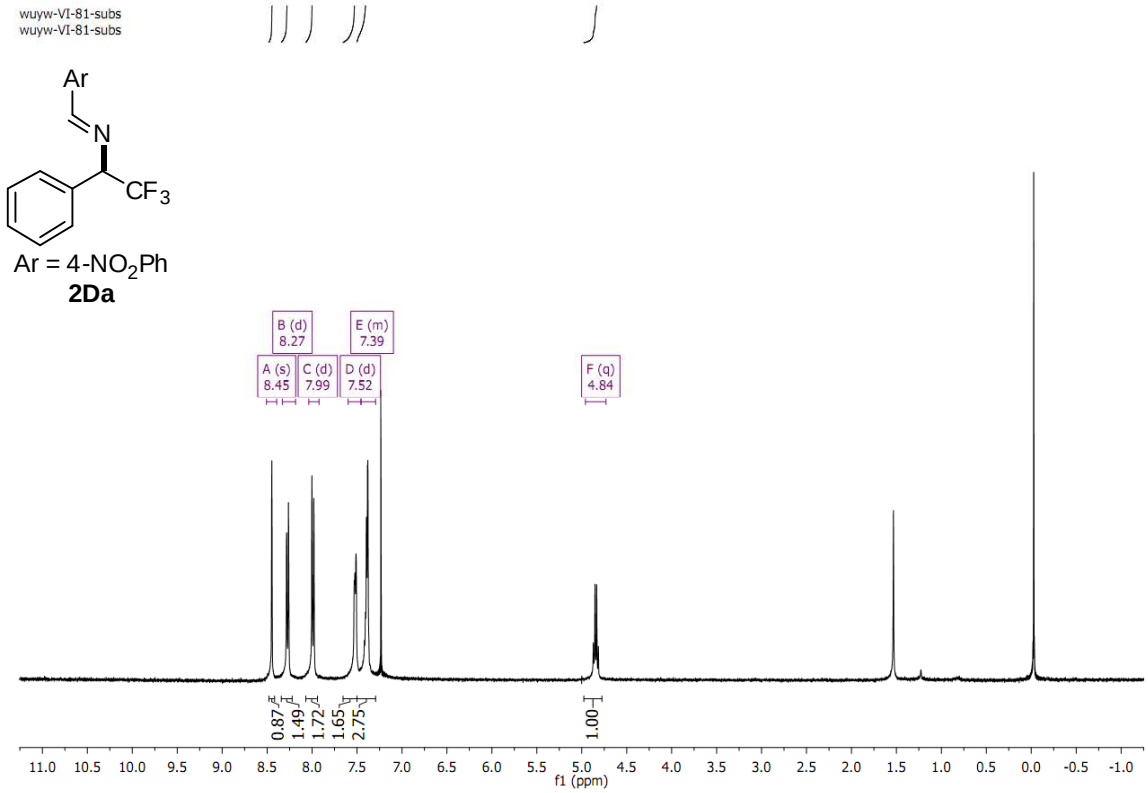

wuyw-VI-67-S3-F-2
F19 OBSERVE
STANDARD PARAMETERS
Ar
N
CF3
Ar = 4-NO2Ph
1Dm
-65.584
-69.160
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

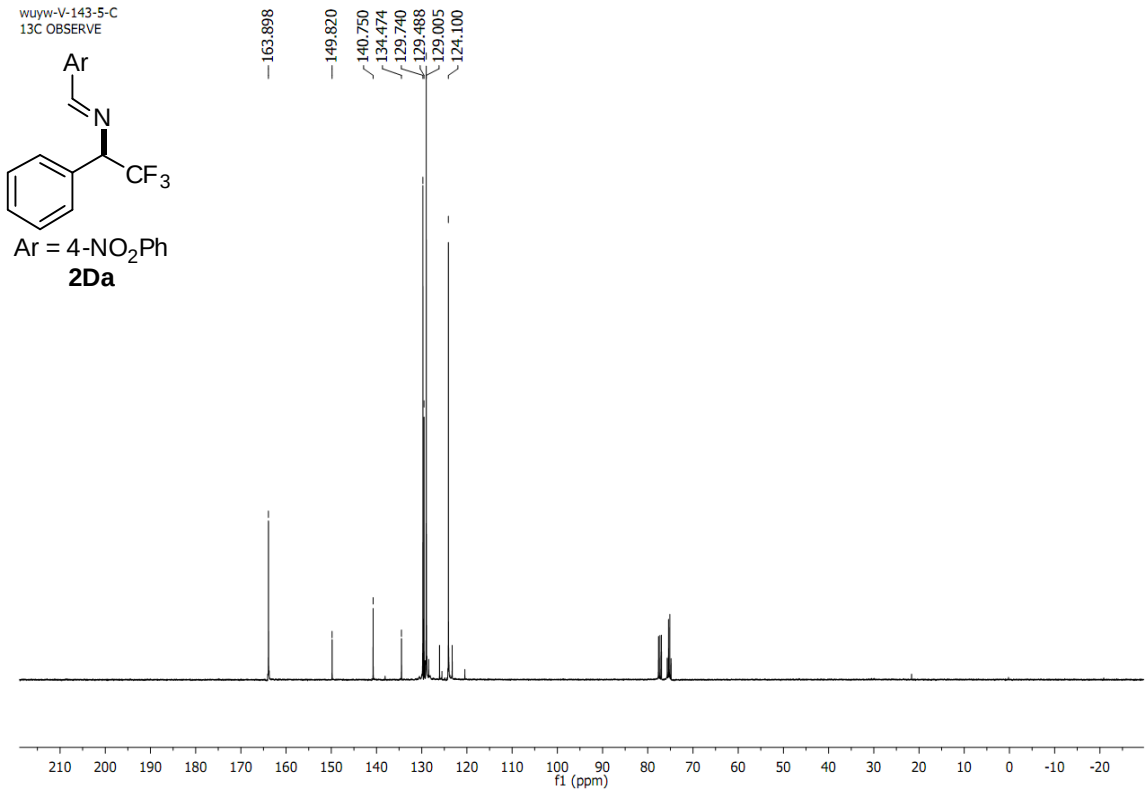

wuyw-VI-37-p-H
wuyw-VI-37-p-H
Ar
N
CF3
Ar = 4-NO2Ph
1Dn
A (d) 8.19
B (d) 7.45
C (m) 7.32
D (d) 7.17
E (s) 4.73
F (s) 3.94
1.45
1.62
2.11
1.35
1.99
2.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wuyw-VI-37-p-C
wuyw-VI-37-p-C
146.99
145.49
133.23
129.16
128.20
127.34
123.59
54.40
33.70
Ar
N
CF3
Ar = 4-NO2Ph
1Dn
f1 (ppm)

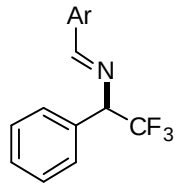

wuyw-VI-37-p-F
F19 OBSERVE
STANDARD PARAMETERS
-73.24
Ar
N
CF3
Ar = 4-NO2Ph
1Dn
f1 (ppm)

^{1}H and ^{13}C NMR spectra and HPLC spectra for **Amine 2**





wuyw-V-143-5-F
F19 OBSERVE
STANDARD PARAMETERS

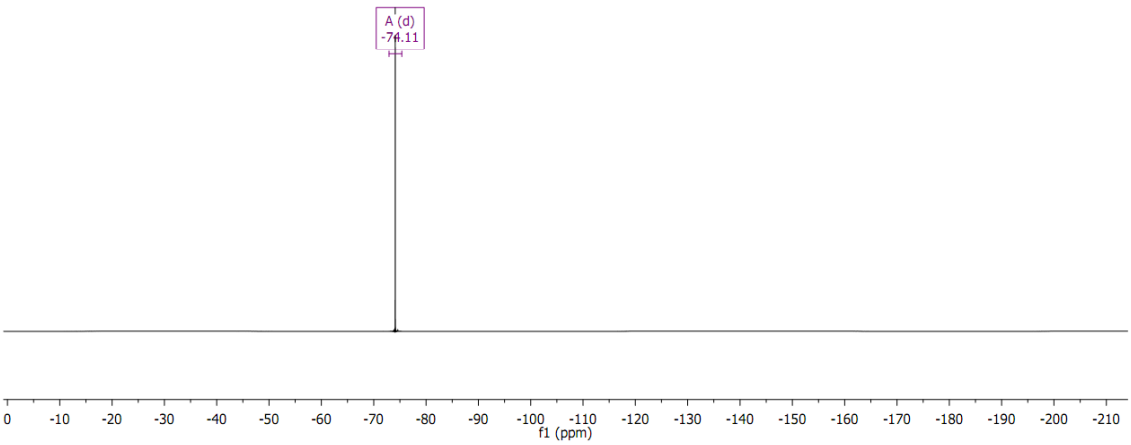


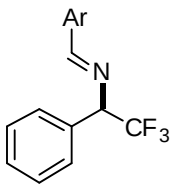
Ar = 4-NO_2Ph

2Da

-74.100
-74.119

A (d)
-74.11

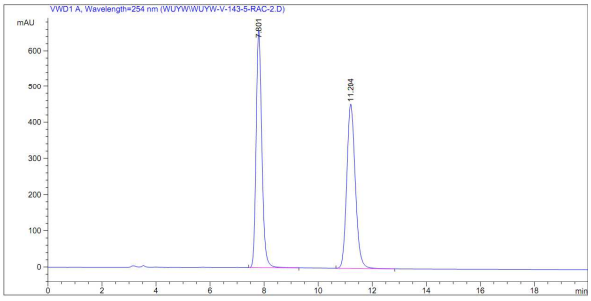




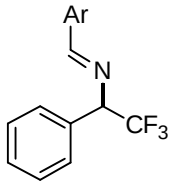
Ar = 4-NO_2Ph

Racemic 2Da

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-V-143-5-RAC-2.D
 Sample Name: wuyw-V-143-5-rac

================================================================================
Acq. Operator   : wuyw
Acq. Instrument : Instrument 1                    Location : Vial 21
Injection Date  : 4/30/2012 12:20:32 PM
                                                  Inj Volume : 8 µl
Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 4/30/2012 12:16:52 PM by wuyw
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 4/24/2012 11:01:01 AM by DAVID
                  (modified after loading)
Sample Info     : AD, Hex/IPA=80/20, 1.0 mL/min, 254nm, left, 25C, 28bar
```



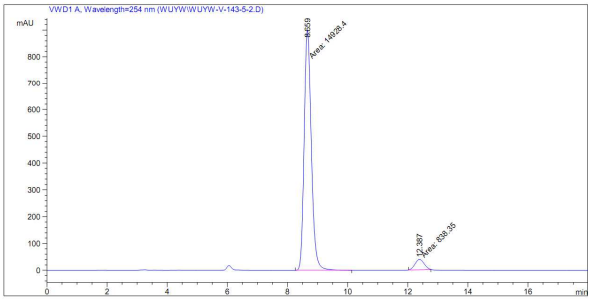

```
================================================================================
                          Area Percent Report
--------------------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      5.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1   7.801 BB    0.2247 9660.23145  659.85828  49.2992
   2  11.204 BB    0.3383 9934.87402  453.98557  50.7008

Totals :                 1.95951e4  1113.84384

--------------------------------------------------------------------------------
                          *** End of Report ***

Instrument 1 5/1/2012 10:34:51 AM DAVID                    Page   1 of 1
```



Ar = 4-NO_2Ph

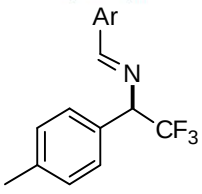
(R)-2Da, 90%ee from 10 mol% DHQ-7f catalyzed reaction.

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-V-143-5-2.D
 Sample Name: wuyw-V-143-5

================================================================================
Acq. Operator   : wuyw                          Seq. Line :   3
Acq. Instrument : Instrument 1                   Location : Vial 21
Injection Date  : 11/22/2011 10:58:16 PM            Inj :   1
                                                 Inj Volume : 6 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 8 µl
Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 11/22/2011 10:55:51 PM by wuyw
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 11/23/2011 5:51:02 PM by wuyw
Sample Info     : AD, Hex/IPA=80/20, 1.0 mL/min, 254nm, 25C, 28bar, left
```



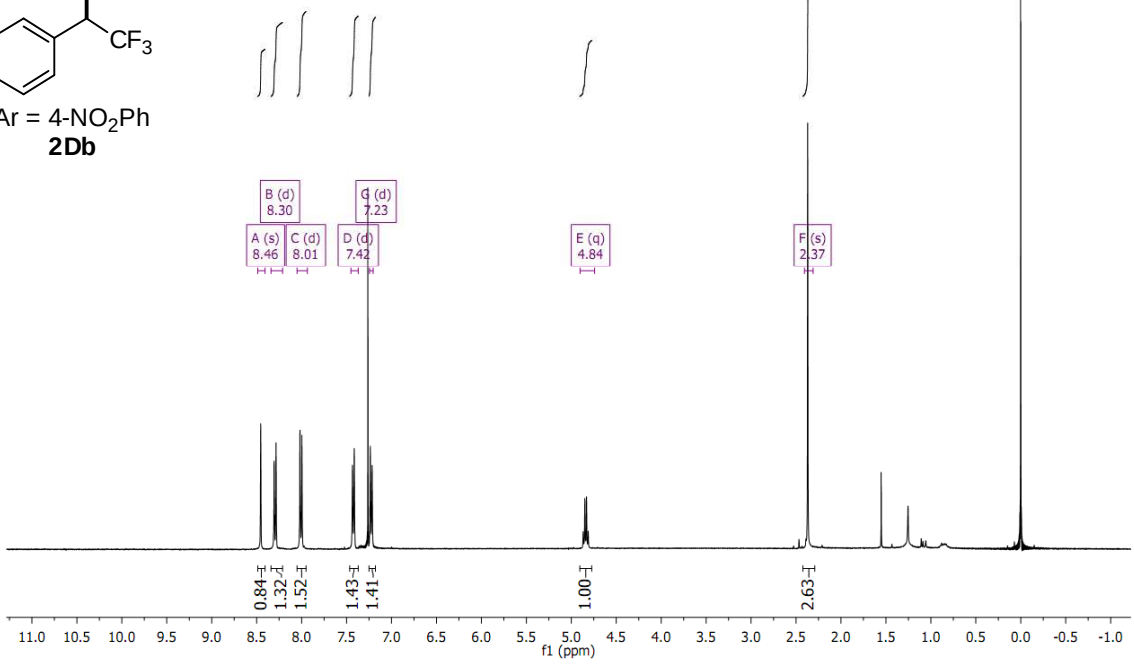

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|------|----------|----------|--------|
   1   8.659 MM    0.2767 1.49284e4   899.14563  94.6828
   2  12.387 MM    0.3569  838.34991   39.14538   5.3172

Totals :                  1.57668e4   938.29101

================================================================================
                          *** End of Report ***
```

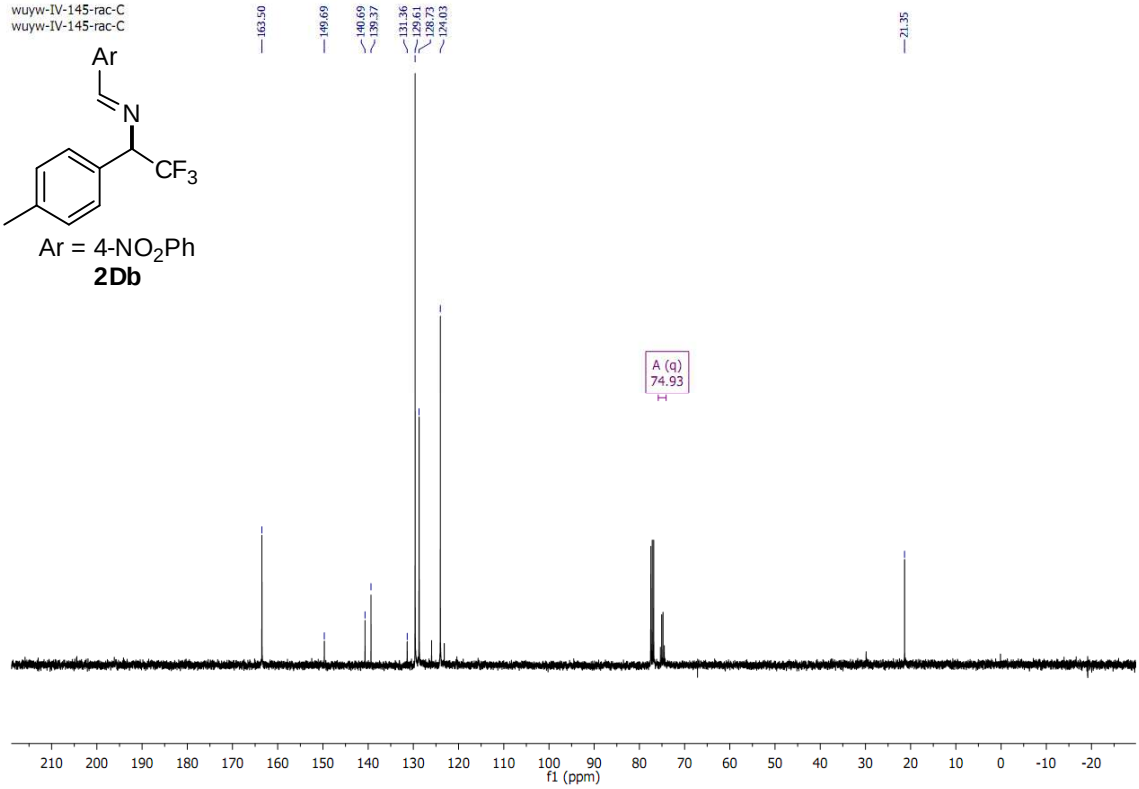

wuyw-IV-145-rac-H
wuyw-VI-19-p-H

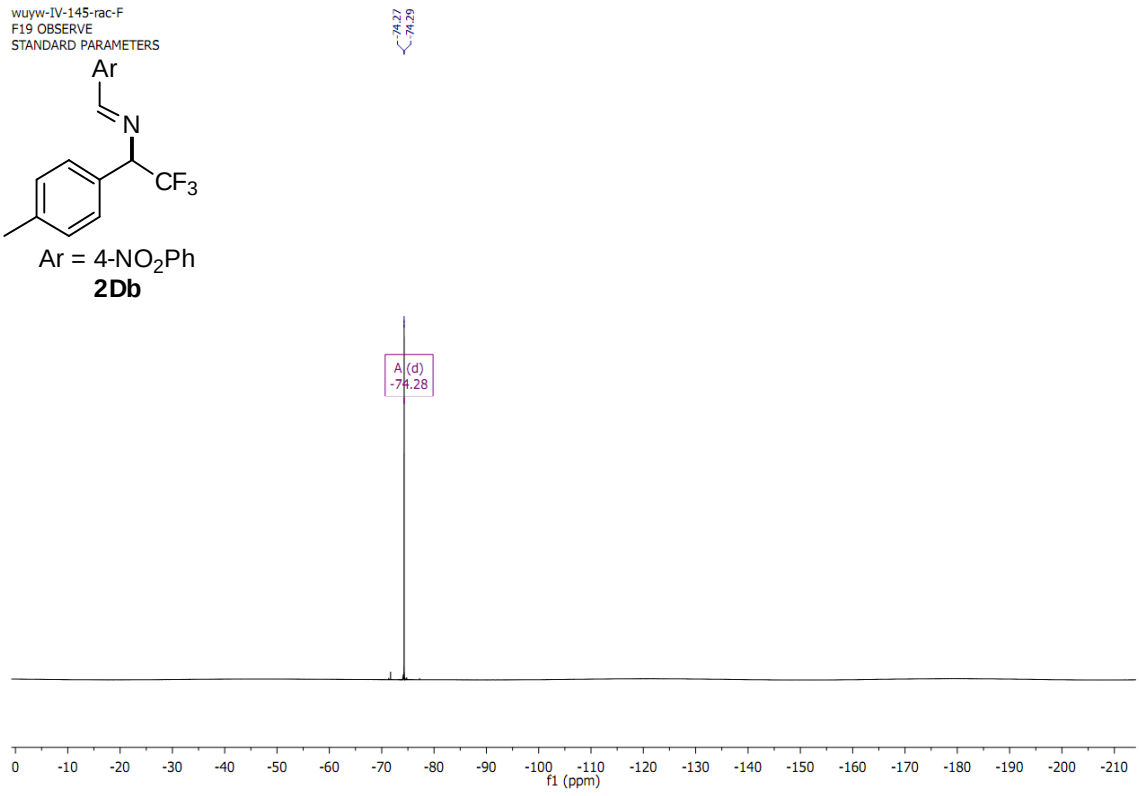


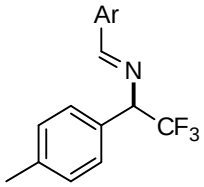
Ar = 4-NO_2Ph

2Db




wuyw-IV-145-rac-C
wuyw-IV-145-rac-C
163.50
149.69
140.69
139.37
131.36
129.61
128.73
124.03
21.35
Ar
N
CF3
Ar = 4-NO2Ph
2Db
A (q)
74.93
f1 (ppm)

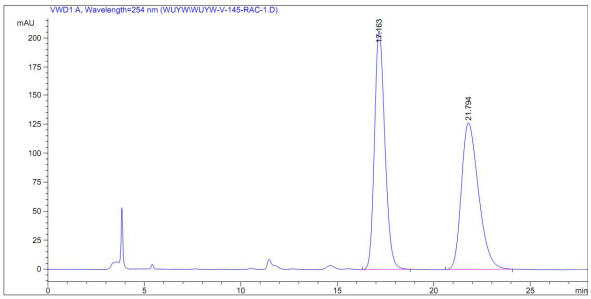

wuyw-IV-145-rac-F
F19 OBSERVE
STANDARD PARAMETERS
74.27
74.29
Ar
N
CF3
Ar = 4-NO2Ph
2Db
A (d)
-74.28
f1 (ppm)



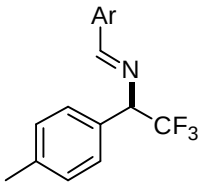
Ar = 4-NO_2Ph

Racemic 2Db

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-V-145-RAC-1.D
 Sample Name: wuyw-V-145-rac

    ========================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                  Location : Vial 21
    Injection Date  : 4/30/2012 1:39:21 PM
                                                    Inj Volume : 8 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 4/30/2012 1:37:14 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 4/24/2012 11:01:01 AM by DAVID
                      (modified after loading)
    Sample Info     : OJ-H, Hex/IPA=70/30, 1.0 mL/min, 254nm, left, 25C, 66ba
                      r
```



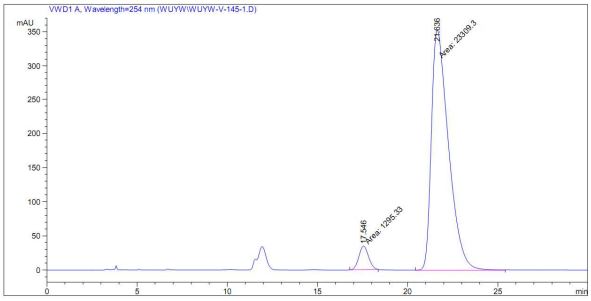

```
    ========================================================================
                                Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      5.00000  [ng/ul]   (not used in calc.)
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]      [min]  mAU   *s    [mAU   ]      %
    ----|-------|----|-------|---------|---------|--------|
       1  17.163 BB    0.5760 7724.16553  206.56525  49.7810
       2  21.794 BB    0.9480 7792.11914  126.35801  50.2190

    Totals :                 1.55163e4   332.92326

    ========================================================================
                              *** End of Report ***

Instrument 1 5/1/2012 10:36:44 AM DAVID                          Page  1 of 1
```



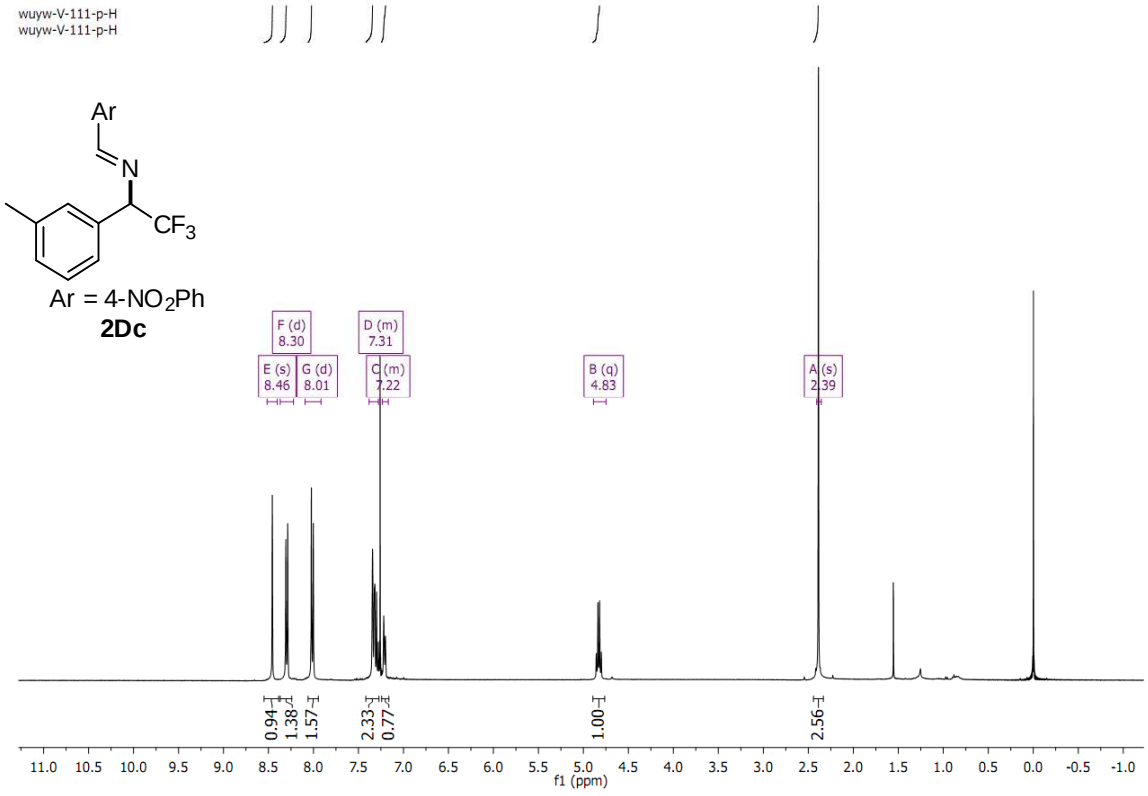
Ar = 4-NO_2Ph

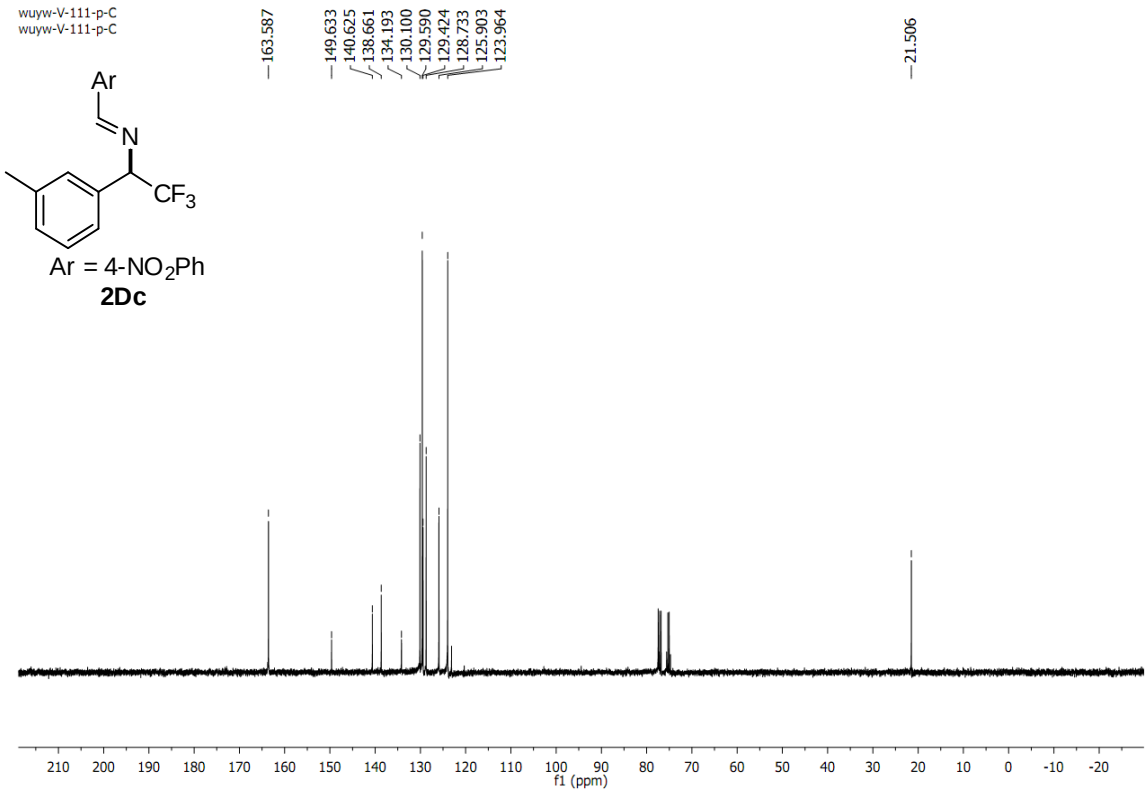
(R)-2Db, 90%ee from 10 mol% DHQ-7f catalyzed reaction.

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-V-145-1.D
 Sample Name: wuyw-V-145

    ========================================================================
    Acq. Operator   : wuyw                          Seq. Line :  2
    Acq. Instrument : Instrument 1                  Location : Vial 22
    Injection Date  : 11/23/2011 10:57:23 PM            Inj :  1
                                                    Inj Volume : 8 µl
    Different Inj Volume from Sequence !     Actual Inj Volume : 6 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 11/23/2011 10:42:34 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 11/23/2011 5:51:02 PM by wuyw
    Sample Info     : OJ-H, Hex/IPA = 70/30, 1.0ml/min, 254nm, 25C, left, 65b
                      ar
```




```
    ========================================================================
                                Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]      [min]  mAU   *s    [mAU   ]      %
    ----|-------|----|-------|---------|---------|--------|
       1  17.546 MM    0.6223 1295.32739   34.69467   5.2646
       2  21.636 MM    1.1007 2.33093e4   352.94885  94.7354

    Totals :                 2.46047e4   387.64352

    ========================================================================
                              *** End of Report ***

Ins Created with novaPDF Printer (www.novaPDF.com). Please register to remove this message.  Page  1 of 1
```

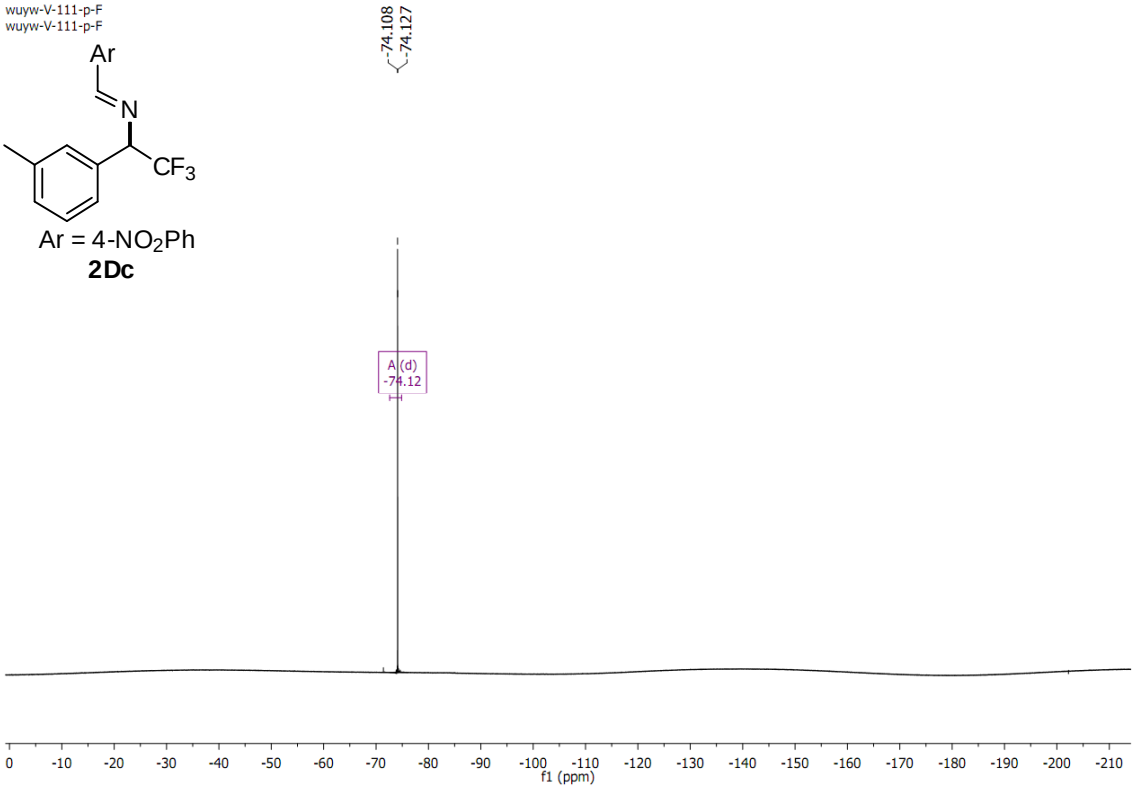

wuyw-V-111-p-H
wuyw-V-111-p-H
Ar
N
CF3
Ar = 4-NO2Ph
2Dc
F (d) 8.30
D (m) 7.31
E (s) 8.46
G (d) 8.01
C (m) 7.22
B (q) 4.83
A (s) 2.39
0.94
1.38
1.57
2.33
0.77
1.00
2.56
f1 (ppm)

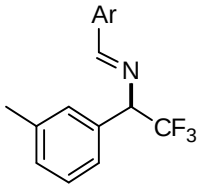

wuyw-V-111-p-C
wuyw-V-111-p-C
Ar
N
CF3
Ar = 4-NO2Ph
2Dc
163.587
149.633
140.625
138.661
134.193
130.100
129.590
129.424
128.733
125.903
123.964
21.506
f1 (ppm)

wuyw-V-111-p-F
wuyw-V-111-p-F

Ar = 4-NO_2Ph

2Dc





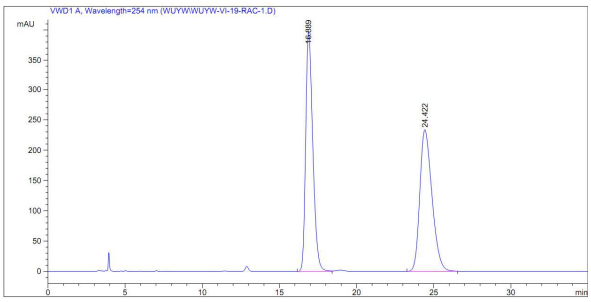
Ar = 4-NO_2Ph

Racemic 2Dc

Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-19-RAC-1.D
Sample Name: WUYW-VI-19-RAC

Acq. Operator : wuyw
Acq. Instrument : Instrument 1 Location : Vial 21
Injection Date : 5/1/2012 11:11:52 AM Inj Volume : 8 µl

Acq. Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed : 5/1/2012 10:46:45 AM by wuyw
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed : 5/1/2012 6:00:30 PM by wuyw
(modified after loading)
Sample Info : OJ-H, Hex/IPA=80/20, 1.0 mL/min, 254nm, left, 25C, 55bar



Area Percent Report

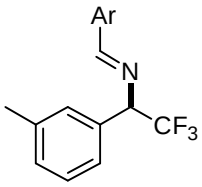
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 5.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.889	BB	0.4888	1.26769e4	397.21793	49.8582
2	24.422	BB	0.8424	1.27490e4	233.46429	50.1418
Totals :				2.54258e4	630.68222	

*** End of Report ***

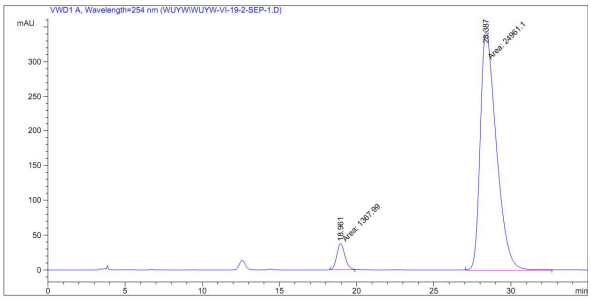
Instrument 1 5/1/2012 10:14:59 PM wuyw Page 1 of 1



Ar = 4-NO_2Ph

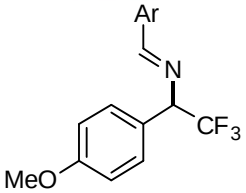
(R)-2Dc, 90%ee from 10 mol% DHQ-7f catalyzed reaction.

```
Data File C:\Chem32\1\DATA\WUYW\WUYW-VI-19-2-SEP-1.D
 Sample Name: wuyw-VI-19-2-sep

 ================================================================================
 Acq. Operator   : wuyw                          Seq. Line :   1
 Acq. Instrument : Instrument 1                   Location : Vial 21
 Injection Date  : 2/23/2012 10:26:49 PM             Inj :   1
                                                 Inj Volume : 8 µl

 Sequence File   : C:\CHEM32\1\SEQUENCE\DEF LC.S
 Method          : C:\CHEM32\1\METHODS\METHOD1.M
 Last changed    : 2/23/2012 10:24:18 PM by wuyw
 Sample Info     : OJ-H, Hex/IPA=80:20, 1.0ml/min, 254nm, 54bar, left
```



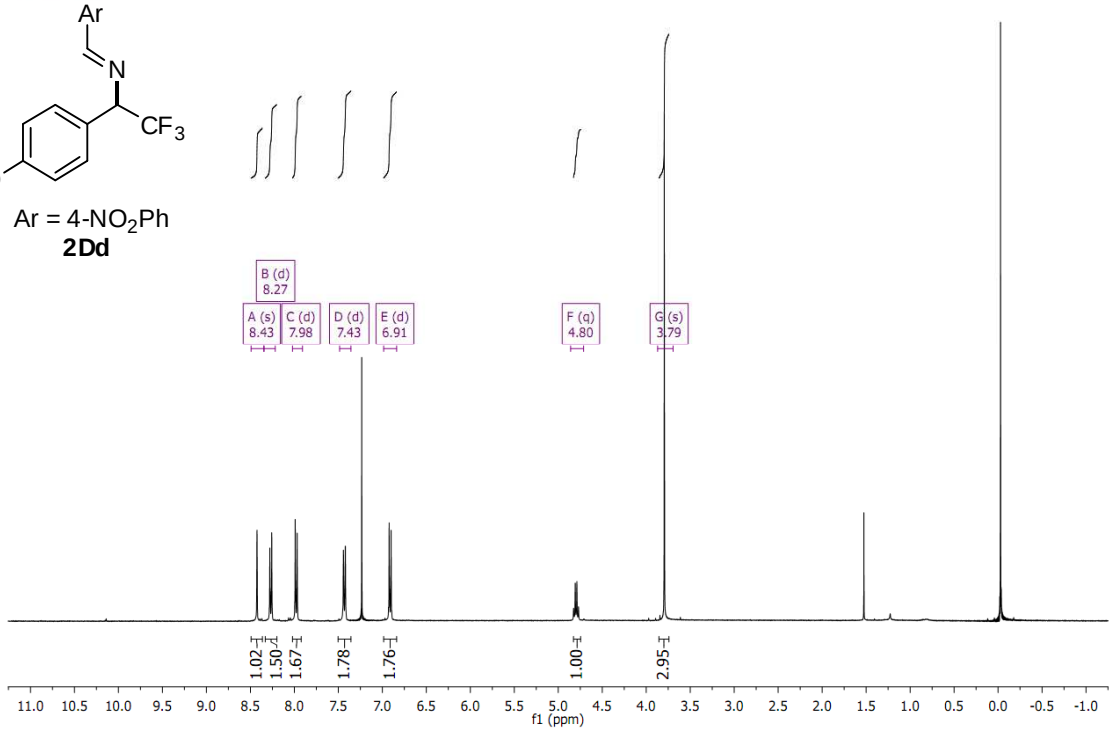

```
 ================================================================================
                                Area Percent Report
 ================================================================================

 Sorted By             :      Signal
 Multiplier            :      1.0000
 Dilution              :      1.0000
 Use Multiplier & Dilution Factor with ISTDs


 Signal 1: VWD1 A, Wavelength=254 nm

 Peak RetTime Type  Width     Area      Height     Area
    #  [min]      [min]  mAU   *s      [mAU   ]     %
 ----|-------|----|-------|---------|----------|--------|
    1  18.961 MM    0.6045 1367.99487   37.71764   5.1957
    2  28.387 MM    1.2070 2.49611e4   344.67096  94.8043

 Totals :                  2.63291e4   382.38860

 ================================================================================
                              *** End of Report ***

Instrument 1 2/24/2012 9:40:33 AM wuyw                          Page   1 of 1
```

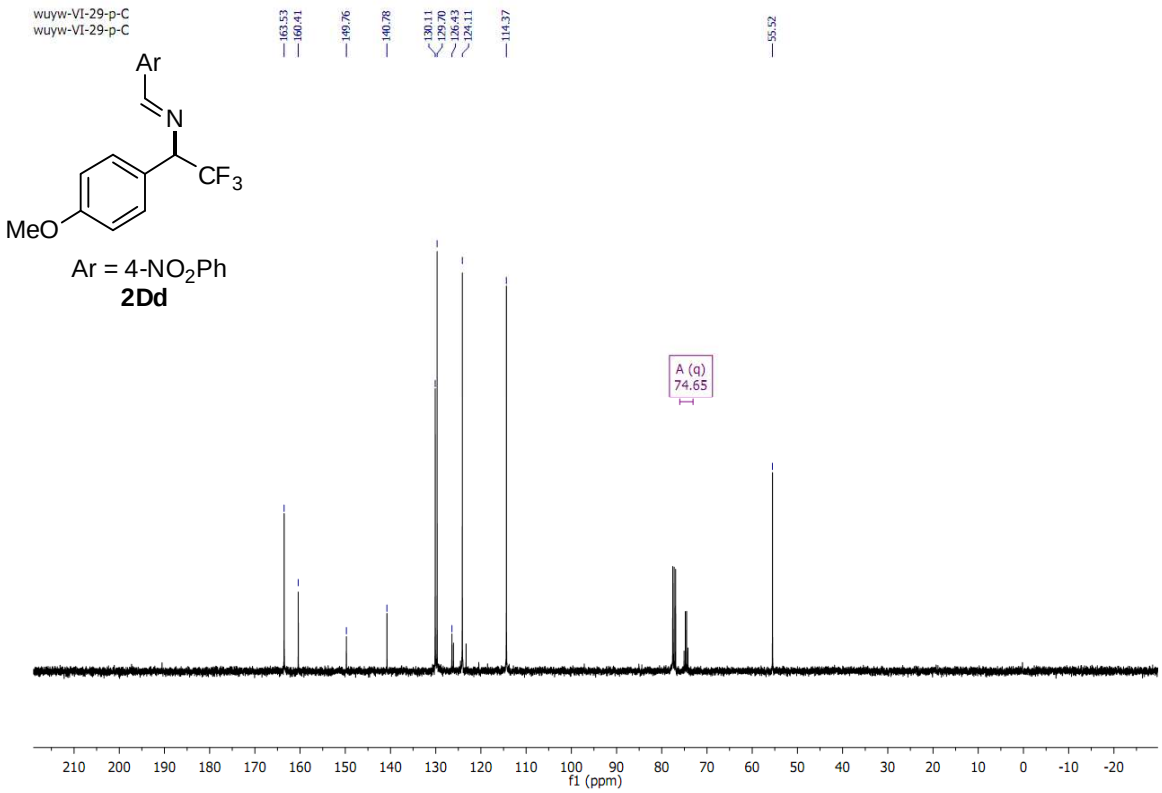
wuyw-VI-29-p-H
wuyw-VI-29-p-H

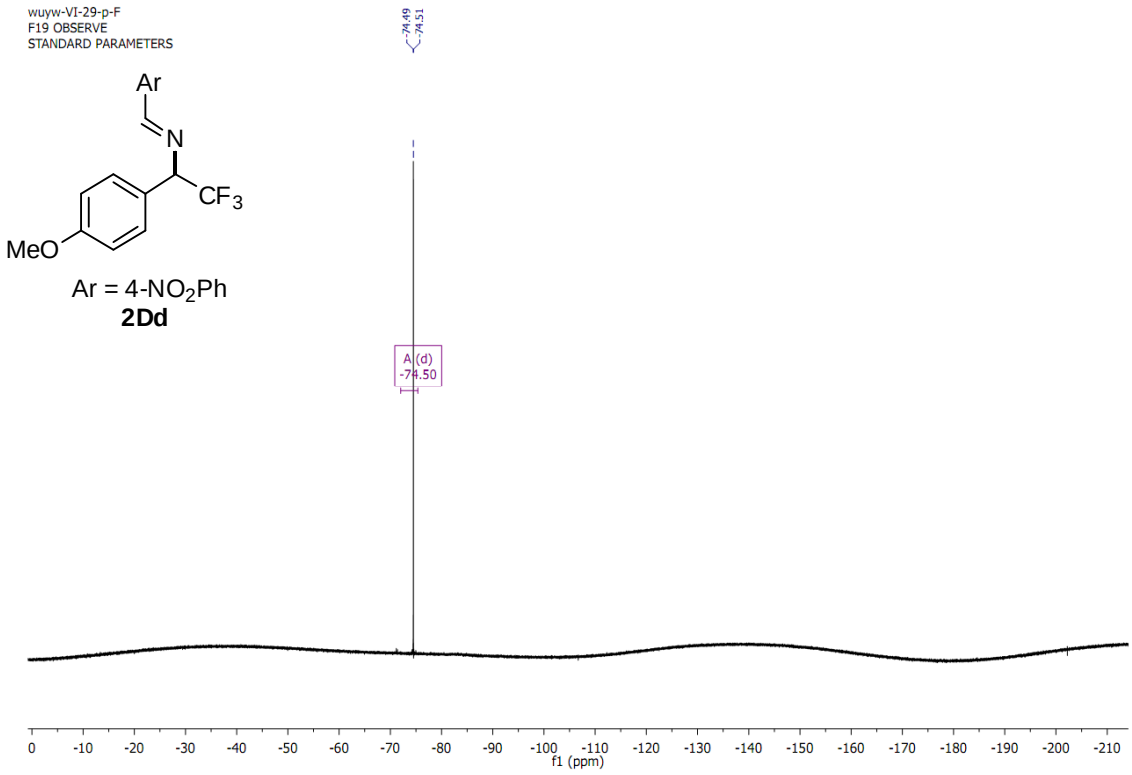


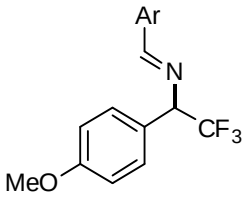
Ar = 4-NO_2Ph

2Dd




wuyw-VI-29-p-C
wuyw-VI-29-p-C
163.53
160.41
149.76
140.78
130.11
129.70
126.43
124.11
114.37
55.52
Ar
N
CF3
MeO
Ar = 4-NO2Ph
2Dd
A (q)
74.65
f1 (ppm)

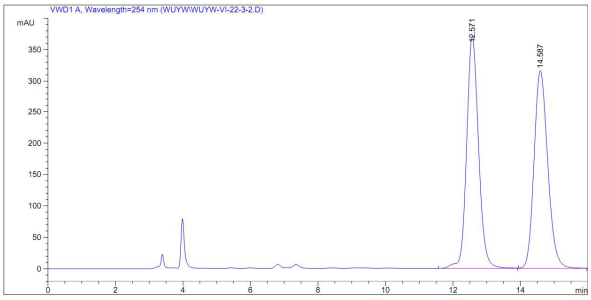

wuyw-VI-29-p-F
F19 OBSERVE
STANDARD PARAMETERS
-74.49
-74.51
Ar
N
CF3
MeO
Ar = 4-NO2Ph
2Dd
A (d)
-74.50
f1 (ppm)



Ar = 4-NO_2Ph

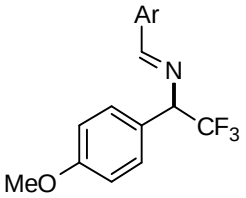
Racemic 2Dd

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-22-3-2.D
 Sample Name: wuyw-VI-22-3

    ========================================================================
    Acq. Operator   : wuyw                          Seq. Line :   1
    Acq. Instrument : Instrument 1                   Location : Vial 21
    Injection Date  : 1/9/2012 5:58:10 PM                Inj :   1
                                                   Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 1/9/2012 5:55:50 PM by wuyw
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/1/2012 1:49:44 PM by DAVID
                      (modified after loading)
    Sample Info     : AD, Hex/IPA=80/20, 1.0 mL/min, 254nm, 25C, left, 28bar
```




```
    ========================================================================
                           Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #  [min]       [min]  mAU   *s    [mAU   ]     %
    ----|-------|----|-------|----------|----------|-------|
       1  12.571 BB    0.3779 9106.03809  371.25906  50.5790
       2  14.587 BB    0.4342 8897.56543  316.54193  49.4210

    Totals :                  1.80036e4   687.80099

    ========================================================================
                           *** End of Report ***
```

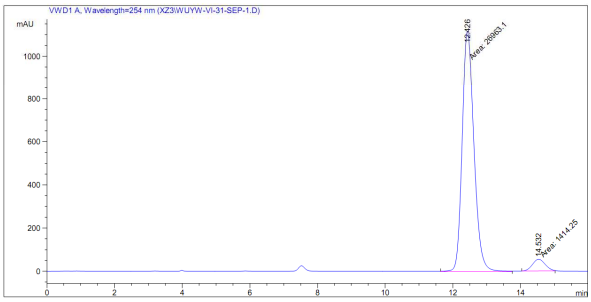
```
Instrument 1 5/1/2012 1:50:07 PM DAVID                          Page   1 of 1
```



Ar = 4-NO_2Ph

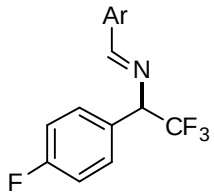
(R)-2Dd, 90%ee from 10 mol% DHQ-7f catalyzed reaction.

```
Data File C:\Chem32\1\DATA\XZ3\WUYW-VI-31-SEP-1.D
 Sample Name: wuyw-VI-31-sep

    ========================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                   Location : Vial 21
    Injection Date  : 1/19/2012 7:34:00 PM
                                                   Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 1/19/2012 7:28:18 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 1/19/2012 7:52:54 PM by wuyw
                      (modified after loading)
    Sample Info     : AD, Hex/IPA = 80/20, 1.0 mL/min, 254 nm, 28 bar,  Left
```



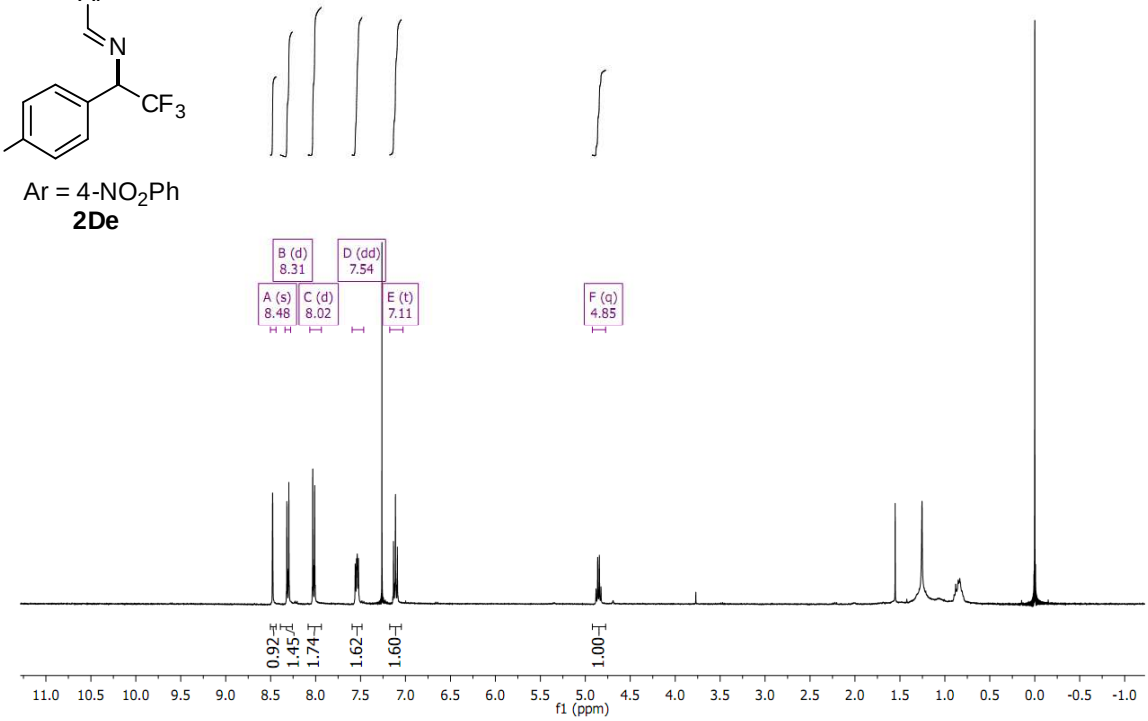

```
    ========================================================================
                           Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #  [min]       [min]  mAU   *s    [mAU   ]     %
    ----|-------|----|-------|----------|----------|-------|
       1  12.426 MM    0.4023 2.69631e4  1117.13525  95.0163
       2  14.532 MM    0.4352 1414.24915   54.16494   4.9837

    Totals :                  2.83773e4  1171.30020

    ========================================================================
                           *** End of Report ***
```

wuyw-V-144-H
wuyw-V-144-H

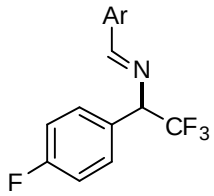


Ar = 4-NO_2Ph

2De

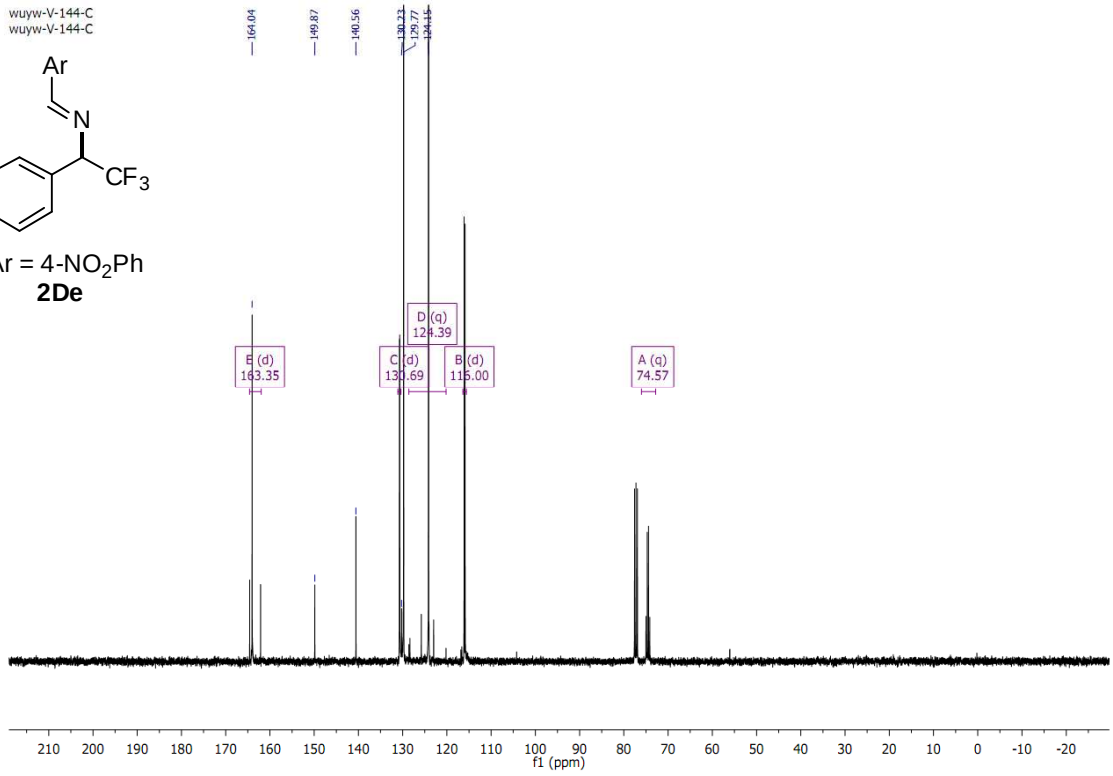


wuyw-V-144-C
wuyw-V-144-C



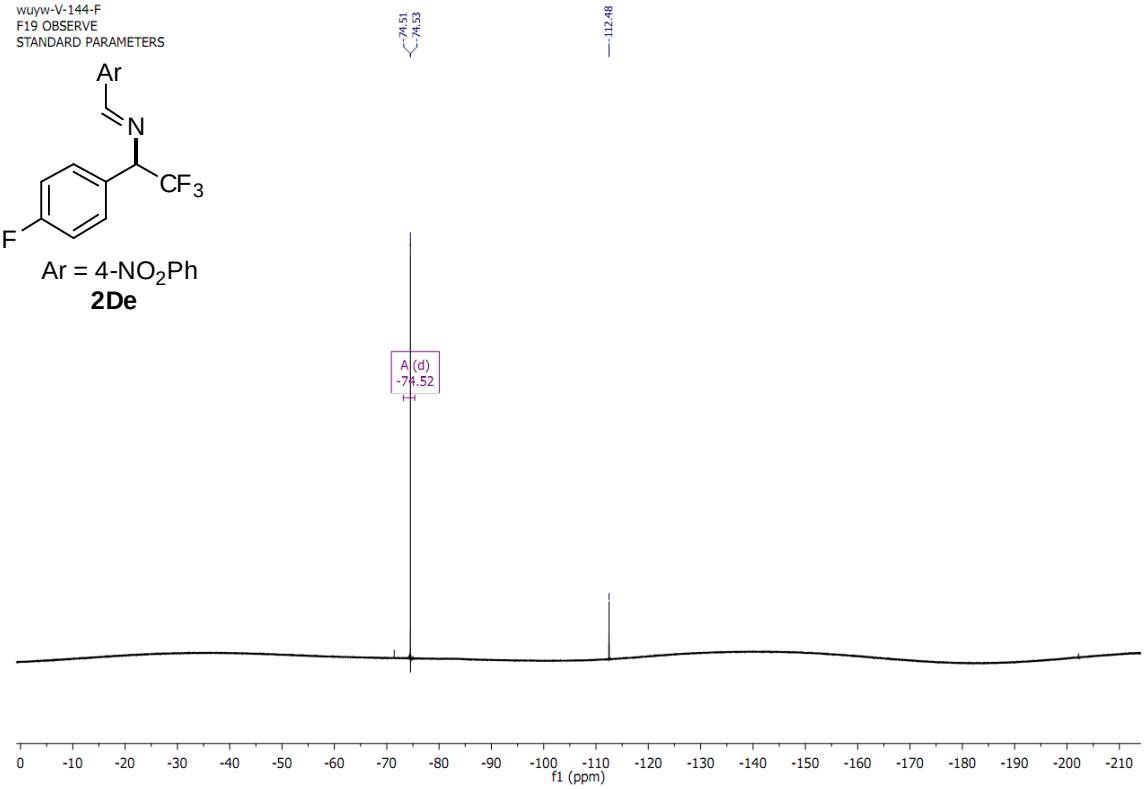
Ar = 4-NO_2Ph

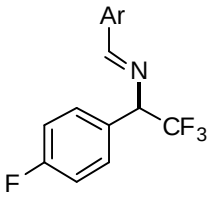
2De



wuyw-V-144-F
F19 OBSERVE
STANDARD PARAMETERS

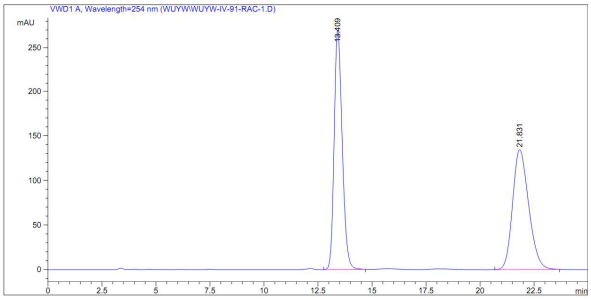
Ar = 4-NO_2Ph
2De



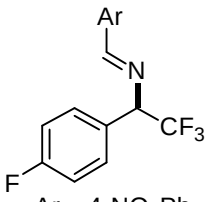


Ar = 4-NO_2Ph
Racemic 2De

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-IV-91-RAC-1.D
 Sample Name: wuyw-IV-91-rac

  ============================================================================
  Acq. Operator   : wuyw                          Seq. Line :   1
  Acq. Instrument : Instrument 1                   Location : Vial 21
  Injection Date  : 12/22/2010 10:54:12 PM            Inj :   1
                                                  Inj Volume : 10 µl
  Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
  Last changed    : 12/22/2010 10:56:26 PM by wuyw
                    (modified after loading)
  Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
  Last changed    : 5/1/2012 1:53:25 PM by DAVID
                    (modified after loading)
  Sample Info     : OJ-H, Hex:IPA = 70:30, 254nm, 1.0 mL/min, 67 bar, Left
```



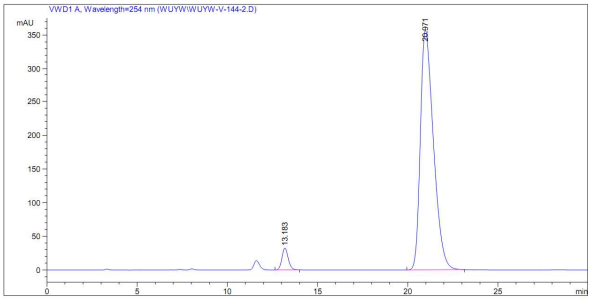

```
  ============================================================================
                              Area Percent Report
  ----------------------------------------------------------------------------

  Sorted By             :      Signal
  Multiplier            :      1.0000
  Dilution              :      1.0000
  Use Multiplier & Dilution Factor with ISTDs


  Signal 1: VWD1 A, Wavelength=254 nm

  Peak RetTime Type  Width     Area      Height     Area
     #   [min]       [min]  mAU   *s   [mAU   ]     %
  -----|-------|-----|-------|---------|---------|-------|
     1  13.409 BB    0.3959 6973.11279  270.04990  50.0055
     2  21.831 BB    0.7993 6971.58789  134.60960  49.9945

  Totals :                  1.39447e4   404.65950

  ============================================================================
                              *** End of Report ***

Instrument 1 5/1/2012 1:56:38 PM DAVID                    Page   1 of 1
```



Ar = 4-NO_2Ph

(R)-2De, 91%ee from 10 mol% DHQ-7f catalyzed reaction.

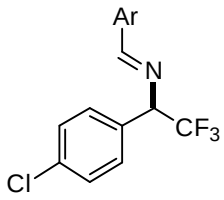
```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-V-144-2.D
 Sample Name: wuyw-V-144

================================================================================
Acq. Operator   : wuyw                          Seq. Line :   1
Acq. Instrument : Instrument 1                   Location : Vial 21
Injection Date  : 11/23/2011 10:24:54 PM            Inj :   1
                                                 Inj Volume : 8 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 6 µl
Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 11/23/2011 10:42:34 PM by wuyw
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 11/23/2011 5:51:02 PM by wuyw
Sample Info     : OJ-H, Hex/IPA = 70/30, 1.0ml/min, 254nm, 25C, left, 65b
                  ar
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.183 BB    0.3752  793.89240   32.50787  4.2260
   2  20.971 BB    0.7707 1.79920e4   357.45752 95.7740

Totals :                 1.87859e4   389.96539

================================================================================
                          *** End of Report ***
```

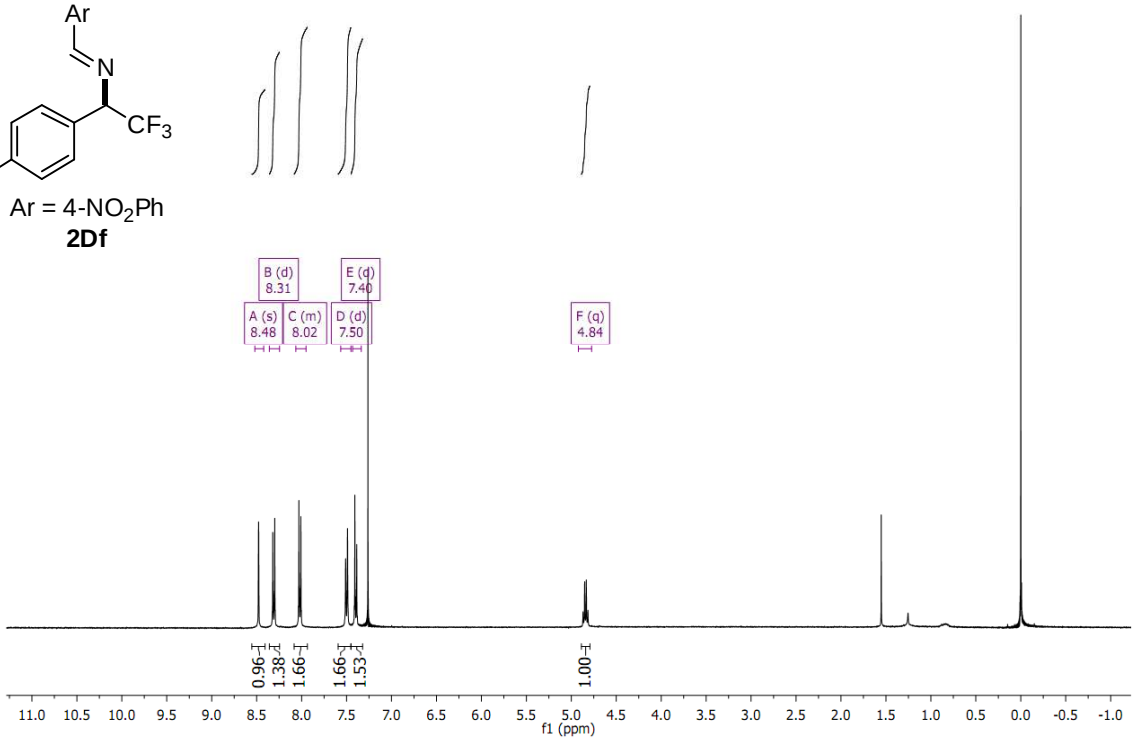

wuyw-VI-31-p-H

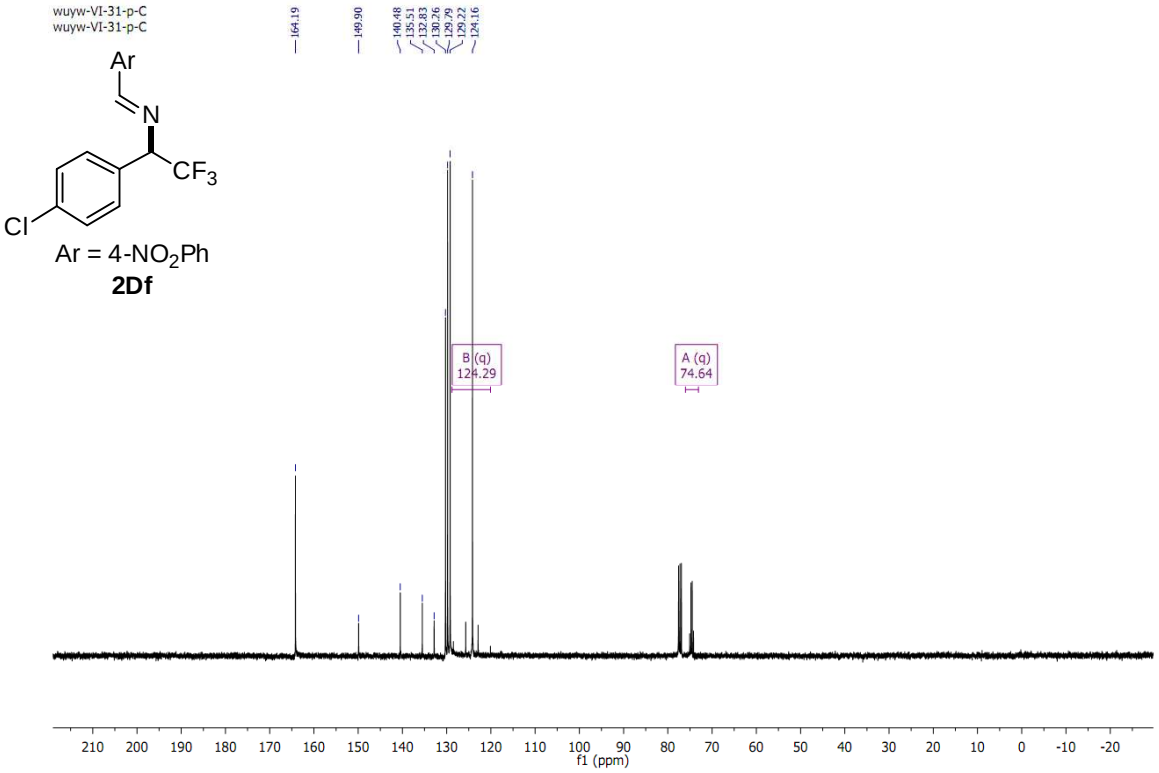
wuyw-VI-31-p-H

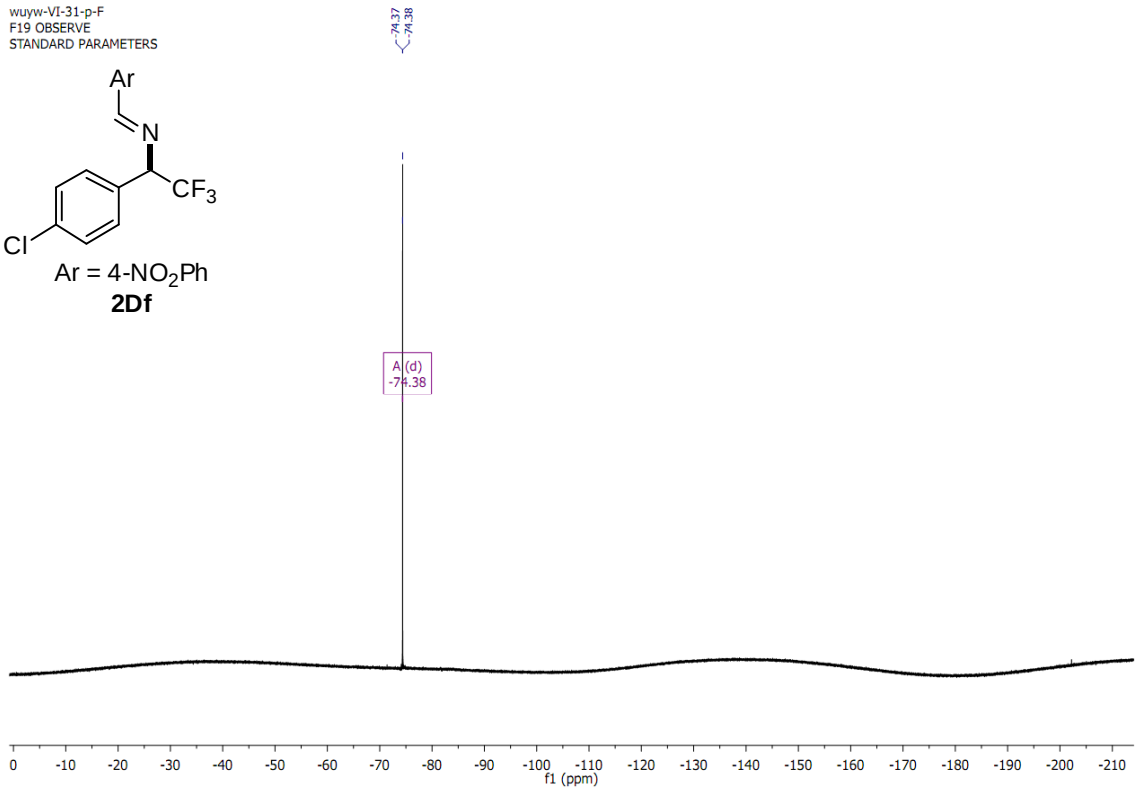


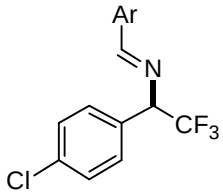
Ar = 4-NO_2Ph

2Df




wuyw-VI-31-p-C
wuyw-VI-31-p-C
164.19
149.90
140.48
135.51
132.83
130.26
129.79
129.22
124.16
Ar
N
CF3
Cl
Ar = 4-NO2Ph
2Df
B (q)
124.29
A (q)
74.64
f1 (ppm)

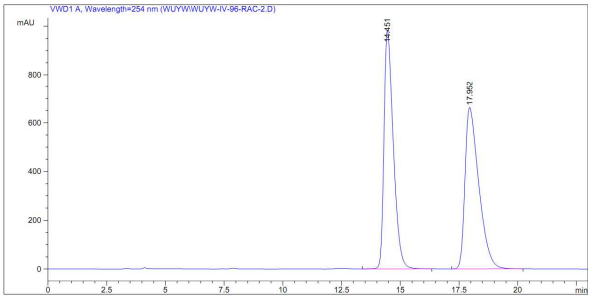

wuyw-VI-31-p-F
F19 OBSERVE
STANDARD PARAMETERS
74.37
74.38
Ar
N
CF3
Cl
Ar = 4-NO2Ph
2Df
A (d)
-74.38
f1 (ppm)



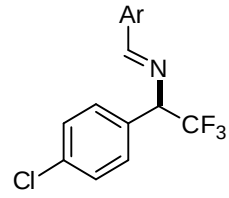
Ar = 4-NO_2Ph

Racemic 2Df

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-IV-96-RAC-2.D
 Sample Name: wuyw-IV-96-rac

    ==========================================================================
    Acq. Operator   : wuyw                          Seq. Line :   2
    Acq. Instrument : Instrument 1                   Location : Vial 22
    Injection Date  : 1/8/2011 2:44:07 PM              Inj :   1
                                                    Inj Volume : 10 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 1/8/2011 2:34:17 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/1/2012 1:59:48 PM by DAVID
                      (modified after loading)
    Sample Info     : OJ-H, Hex:IPA = 80:20, 254nm, 1.0 mL/min, 56 bar, Left
```



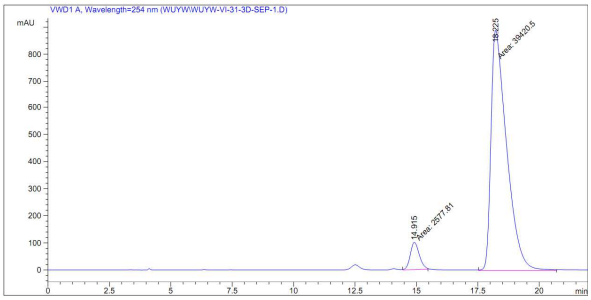

```
    ==========================================================================
                                Area Percent Report
    ==========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s    [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  14.451 BB    0.4154 2.70673e4   984.37512  49.9789
       2  17.952 BB    0.6152 2.70901e4   662.74390  50.0211

    Totals :                  5.41574e4  1647.11902

    ==========================================================================
                                *** End of Report ***

Instrument 1 5/1/2012 2:04:43 PM DAVID                              Page   1 of 1
```



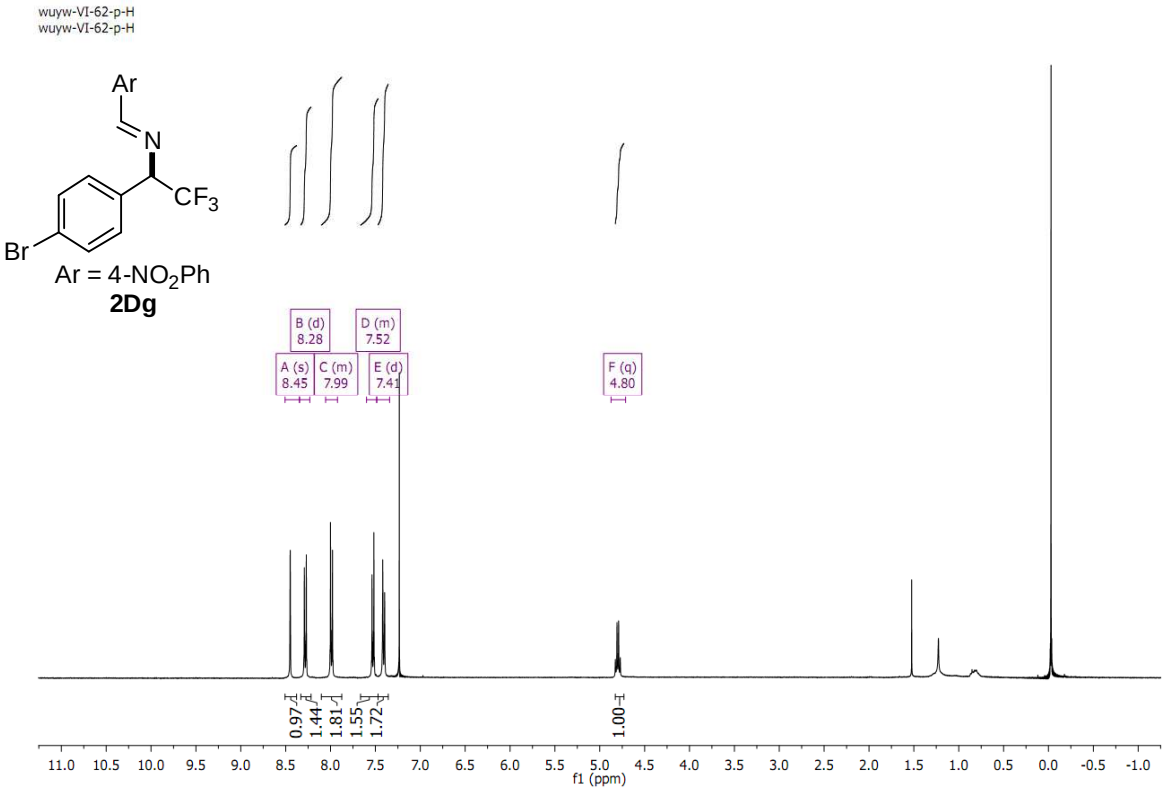
Ar = 4-NO_2Ph

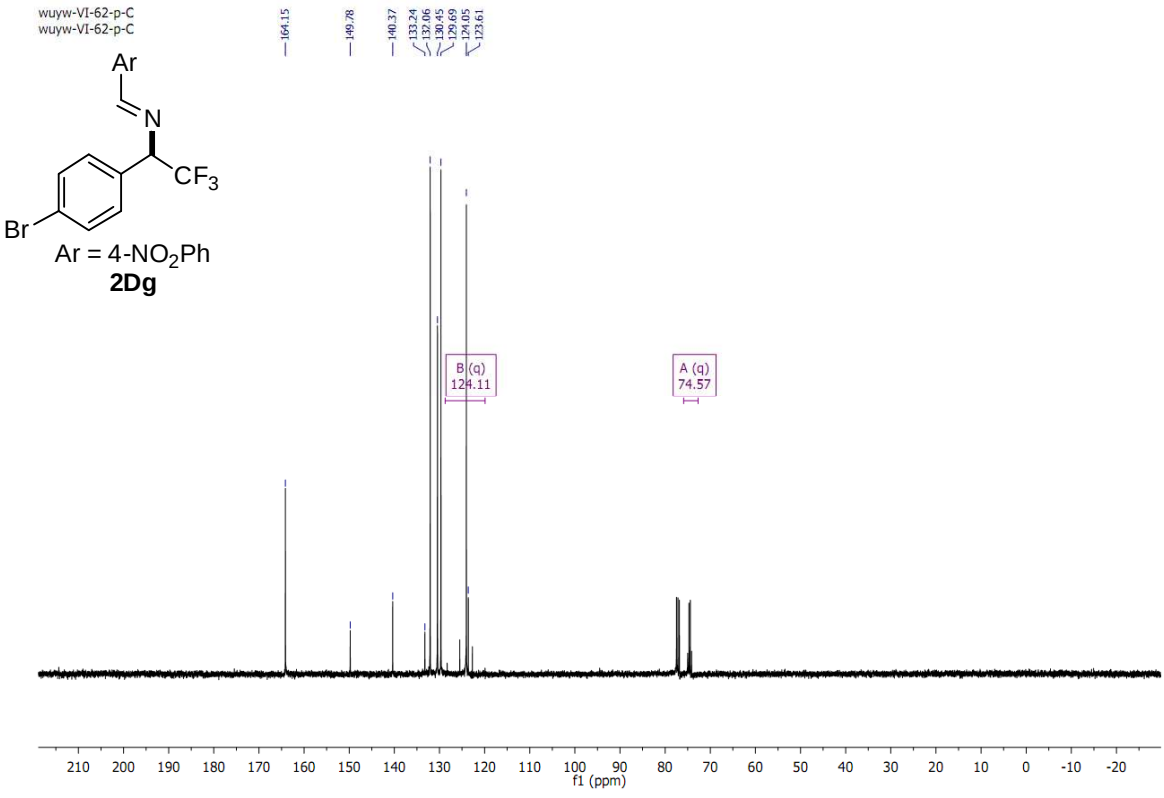
(R)-2Df, 88%ee from 10 mol% DHQ-7f catalyzed reaction.

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-31-3D-SEP-1.D
 Sample Name: wuyw-VI-31-3D-SEP

    ==========================================================================
    Acq. Operator   : wuyw                          Seq. Line :   1
    Acq. Instrument : Instrument 1                   Location : Vial 21
    Injection Date  : 1/23/2012 10:50:48 AM            Inj :   1
                                                    Inj Volume : 3 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 1/21/2012 5:28:07 PM by wuyw
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/1/2012 1:59:48 PM by DAVID
                      (modified after loading)
    Sample Info     : OJ-H, Hex/IPA=80/20, 1.0mL/min, 254nm, left, 25C, 54bar
```

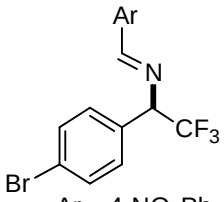



```
    ==========================================================================
                                Area Percent Report
    ==========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s    [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  14.915 MM    0.4262 2577.81006  100.79835   6.1379
       2  18.225 MM    0.7379 3.94205e4   890.39227  93.8621

    Totals :                  4.19983e4   991.19062

    ==========================================================================
                                *** End of Report ***

Instrument 1 5/1/2012 2:01:59 PM DAVID                              Page   1 of 1
```


wuyw-VI-62-p-H
wuyw-VI-62-p-H
Ar
N
CF3
Br
Ar = 4-NO2Ph
2Dg
B (d) 8.28
D (m) 7.52
A (s) 8.45
C (m) 7.99
E (d) 7.41
F (q) 4.80
0.97
1.44
1.81
1.55
1.72
1.00
f1 (ppm)

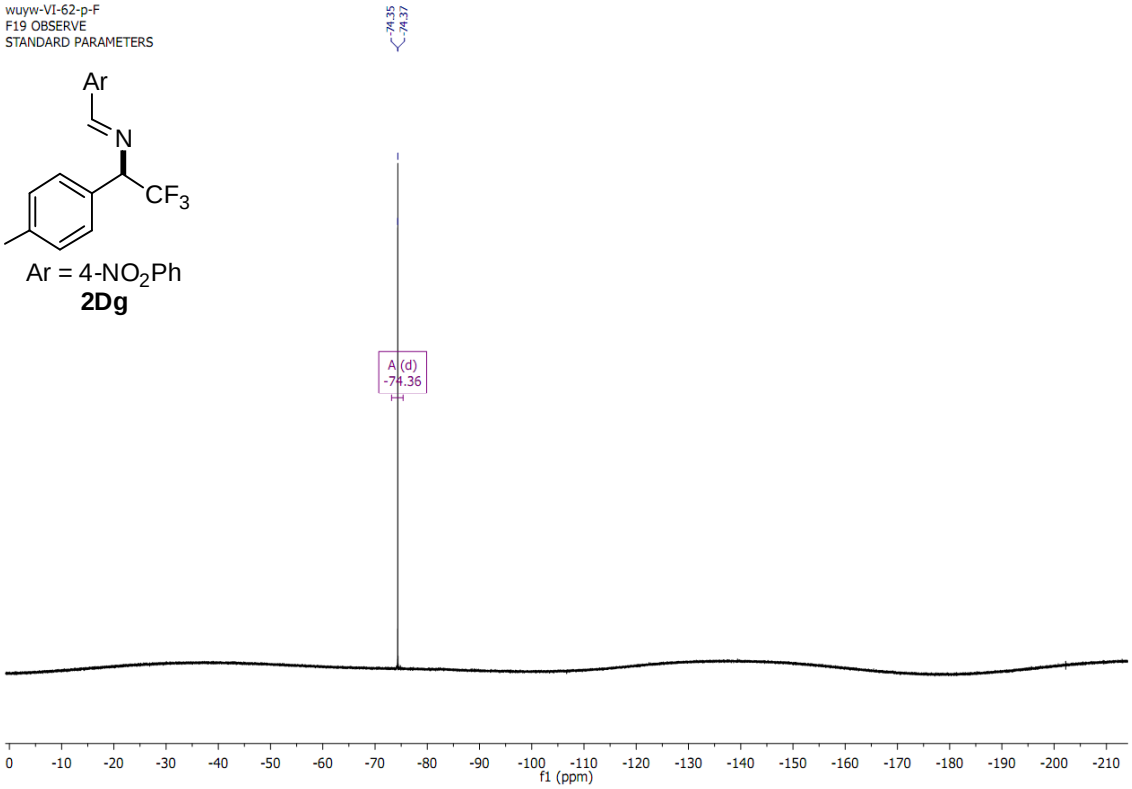

wuyw-VI-62-p-C
wuyw-VI-62-p-C
164.15
149.78
140.37
133.24
132.06
130.45
129.69
124.05
123.61
Ar
N
CF3
Br
Ar = 4-NO2Ph
2Dg
B (q) 124.11
A (q) 74.57
f1 (ppm)

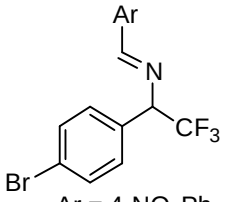
wuyw-VI-62-p-F
F19 OBSERVE
STANDARD PARAMETERS



Ar = 4-NO_2Ph

2Dg

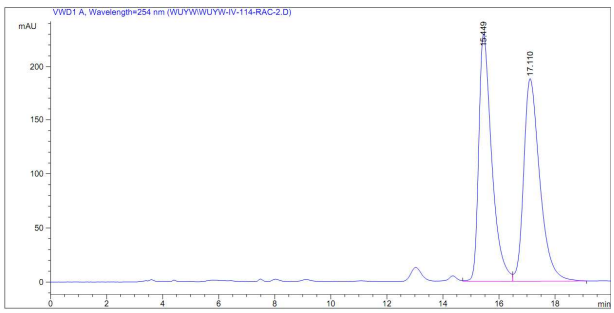




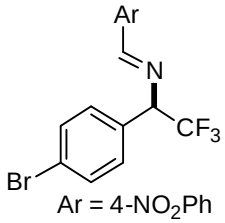
Ar = 4-NO_2Ph

Racemic 2Dg

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-IV-114-RAC-2.D
 Sample Name: wuyw-IV-114-rac

   ================================================================
   Acq. Operator   : wuyw
   Acq. Instrument : Instrument 1                    Location : Vial 21
   Injection Date  : 2/8/2011 12:01:08 PM
                                                     Inj Volume : 5 µl
   Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
   Last changed    : 2/8/2011 11:59:19 AM by wuyw
                     (modified after loading)
   Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
   Last changed    : 5/1/2012 1:59:48 PM by DAVID
                     (modified after loading)
   Sample Info     : OJ-H, Hex:IPA=80:20, 1.0 mL/min, 254 nm, Left, 56 bar
```



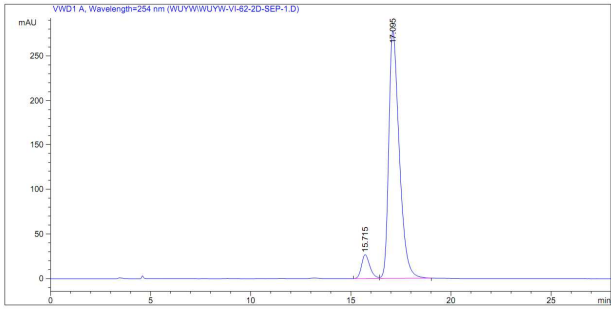

```
   ================================================================
                          Area Percent Report
   ================================================================

   Sorted By             :      Signal
   Multiplier            :      1.0000
   Dilution              :      1.0000
   Use Multiplier & Dilution Factor with ISTDs


   Signal 1: VWD1 A, Wavelength=254 nm

   Peak RetTime Type  Width     Area      Height     Area
     #   [min]       [min]  mAU   *s   [mAU   ]      %
   ----|-------|----|-------|----------|----------|--------|
      1  15.449 VV    0.4784 7352.54102  229.63155  49.5728
      2  17.110 VB    0.6007 7479.27197  188.11191  50.4272

   Totals :                  1.48318e4   417.74345

   ================================================================
                          *** End of Report ***

Instrument 1 5/1/2012 2:10:00 PM DAVID                    Page   1 of 1
```



Ar = 4-NO_2Ph

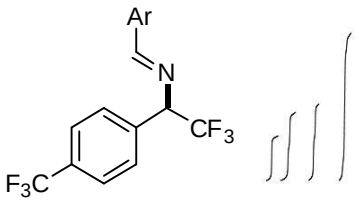
(R)-2Dg, 86% ee from 10 mol% DHQ-7f catalyzed reaction.

```
Data File C:\Chem32\1\DATA\WUYW\WUYW-VI-62-2D-SEP-1.D
 Sample Name: wuyw-VI-62-2d-sep

   ========================================================================
   Acq. Operator   : wuyw                          Seq. Line :   1
   Acq. Instrument : Instrument 1                   Location : Vial 21
   Injection Date  : 3/18/2012 7:23:01 PM             Inj :   1
                                                  Inj Volume : 5 µl

   Sequence File   : C:\CHEM32\1\SEQUENCE\DEF LC.S
   Method          : C:\CHEM32\1\METHODS\METHOD1.M
   Last changed    : 3/18/2012 7:20:23 PM by wuyw
   Sample Info     : OJ-H, Hex/IPA=80/20, 1.0ml/min, 1eft, 52bar, 254nm, 25C
```



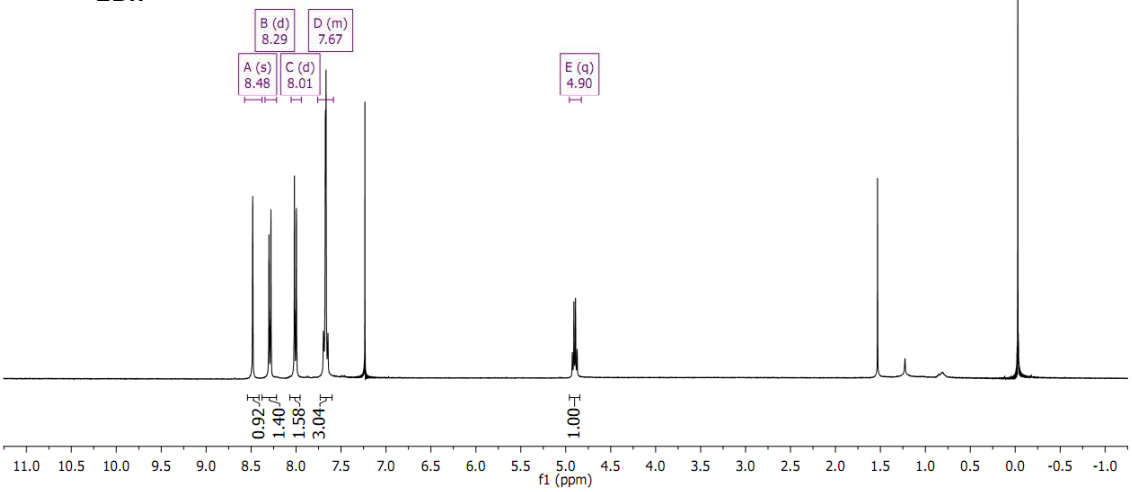

```
   ========================================================================
                              Area Percent Report
   ========================================================================

   Sorted By             :      Signal
   Multiplier            :      1.0000
   Dilution              :      1.0000
   Use Multiplier & Dilution Factor with ISTDs


   Signal 1: VWD1 A, Wavelength=254 nm

   Peak RetTime Type  Width     Area      Height     Area
     #   [min]      [min]  mAU   *s   [mAU   ]      %
   ----|-------|----|-------|----------|----------|--------|
      1  15.715 BV    0.4427  774.32281   26.73443   7.1422
      2  17.095 VB    0.5463 1.00671e4   277.99075  92.8578

   Totals :                  1.08415e4   304.72518

   ========================================================================
                              *** End of Report ***

Instrument 1 3/19/2012 9:44:26 AM wuyw                          Page   1 of 1
```

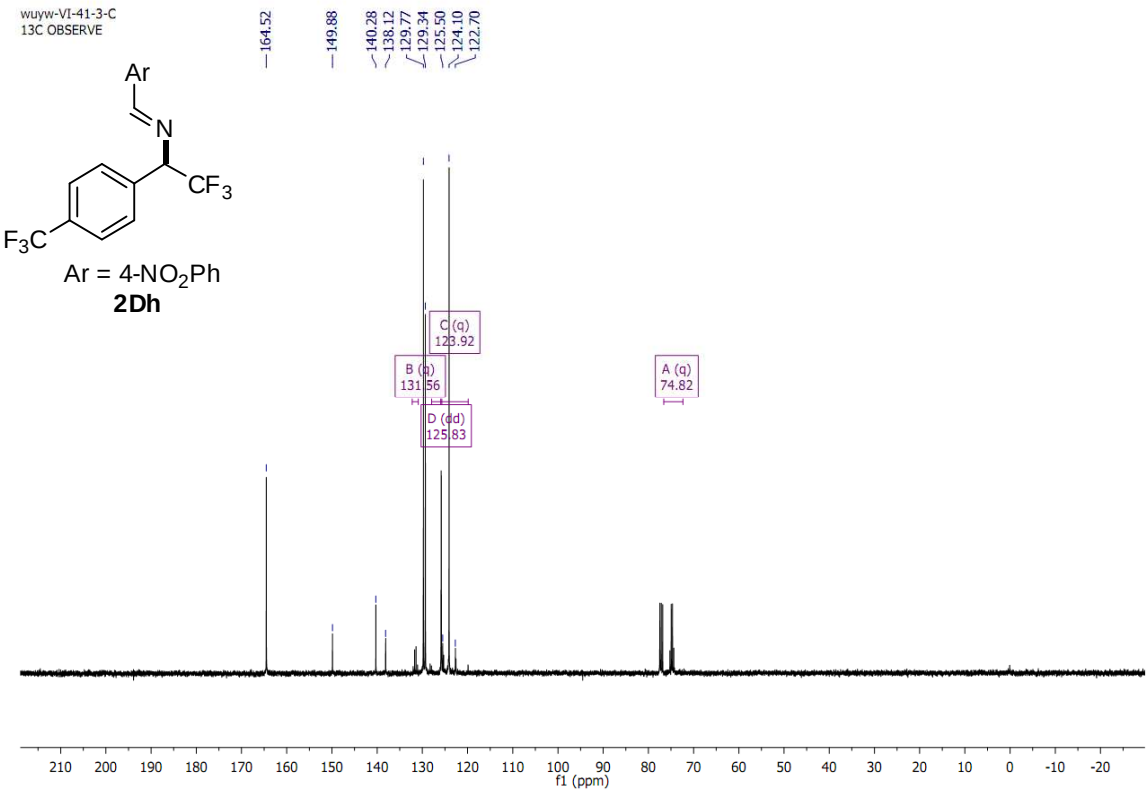
wuyw-VI-41-3-H
wuyw-VI-41-3-H

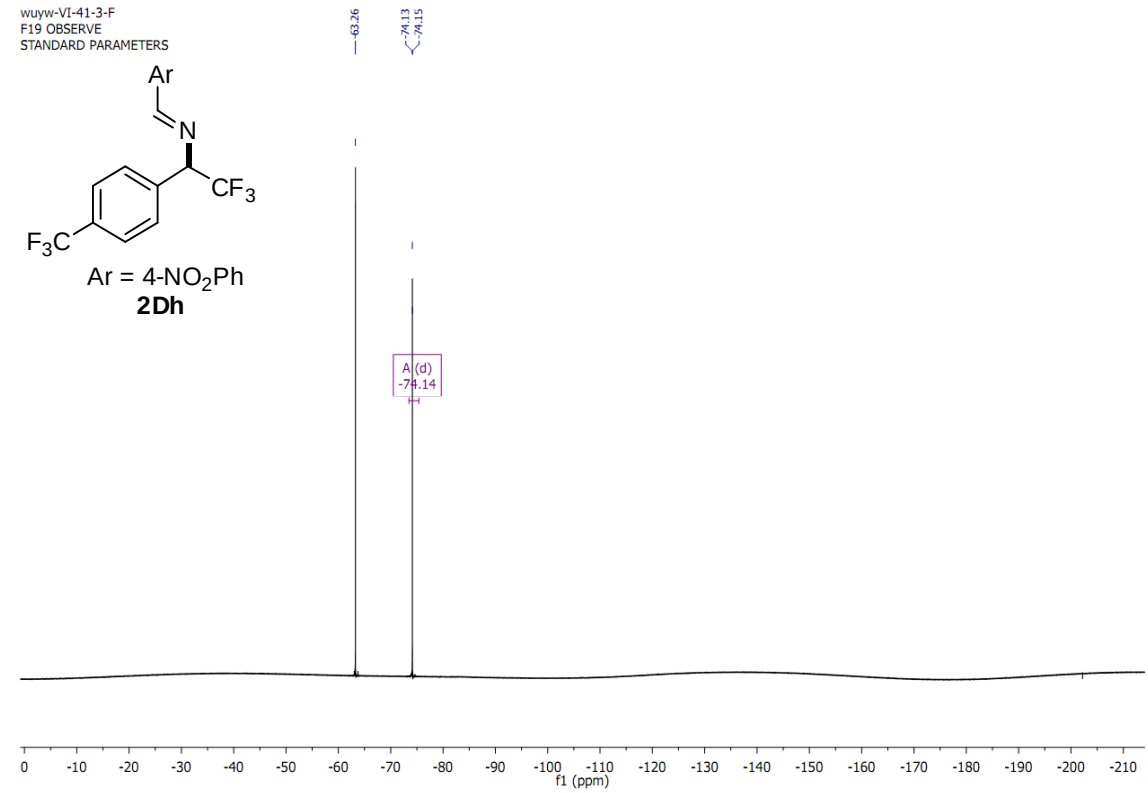


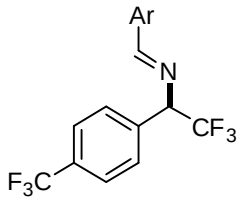
Ar = 4-NO_2Ph

2Dh




wuyw-VI-41-3-C
13C OBSERVE
164.52
149.88
140.28
138.12
129.77
129.34
125.50
124.10
122.70
Ar
N
CF3
F3C
Ar = 4-NO2Ph
2Dh
C (q)
123.92
B (q)
131.56
D (dd)
125.83
A (q)
74.82
f1 (ppm)

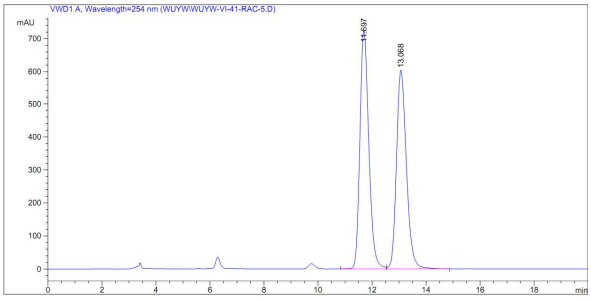

wuyw-VI-41-3-F
F19 OBSERVE
STANDARD PARAMETERS
-63.26
-74.13
-74.15
Ar
N
CF3
F3C
Ar = 4-NO2Ph
2Dh
A (d)
-74.14
f1 (ppm)



Ar = 4-NO_2Ph

Racemic 2Dh

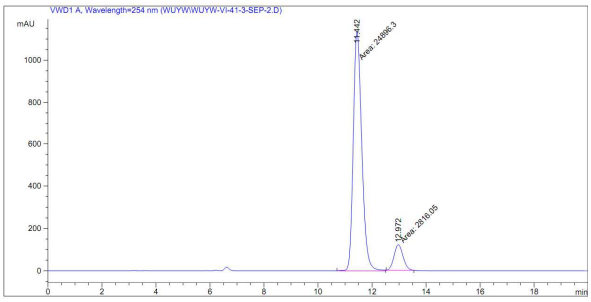
```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-41-RAC-5.D
 Sample Name: wuyw-VI-41-rac

    ================================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                    Location : Vial 21
    Injection Date  : 2/3/2012 1:16:09 PM
                                                      Inj Volume : 8 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 2/3/2012 1:13:51 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/1/2012 1:59:48 PM by DAVID
                      (modified after loading)
    Sample Info     : AD, Hex/IPA = 90:10, 1.0 mL/min, 254 nm, 27bar,  Left
```



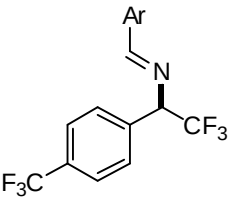

```
    ================================================================================
                                Area Percent Report
    ================================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]  mAU   *s     [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  11.697 BV    0.3502 1.65392e4   726.20599  51.8110
       2  13.068 VB    0.3913 1.53830e4   604.86804  48.1890

    Totals :                  3.19221e4  1331.07404

    ================================================================================
                                *** End of Report ***
```



```
Data File C:\Chem32\1\DATA\WUYW\WUYW-VI-41-3-SEP-2.D
 Sample Name: WUYW-VI-41-3-sep

    ================================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                    Location : Vial 21
    Injection Date  : 2/9/2012 10:15:27 AM
                                                      Inj Volume : 5 µl
    Method          : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 2/8/2012 10:52:03 PM by wuyw
    Sample Info     : AD, Hex/IPA-90/10, 1.0mL/min, 254nm, left, 25C, 25bar
```




```
    ================================================================================
                                Area Percent Report
    ================================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      5.00000  [ng/ul]   (not used in calc.)
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]  mAU   *s     [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  11.442 MM    0.3646 2.48963e4  1137.95068  89.8383
       2  12.972 MM    0.3883 2816.05420  120.85689  10.1617

    Totals :                  2.77124e4  1258.80757

    ================================================================================
                                *** End of Report ***
```



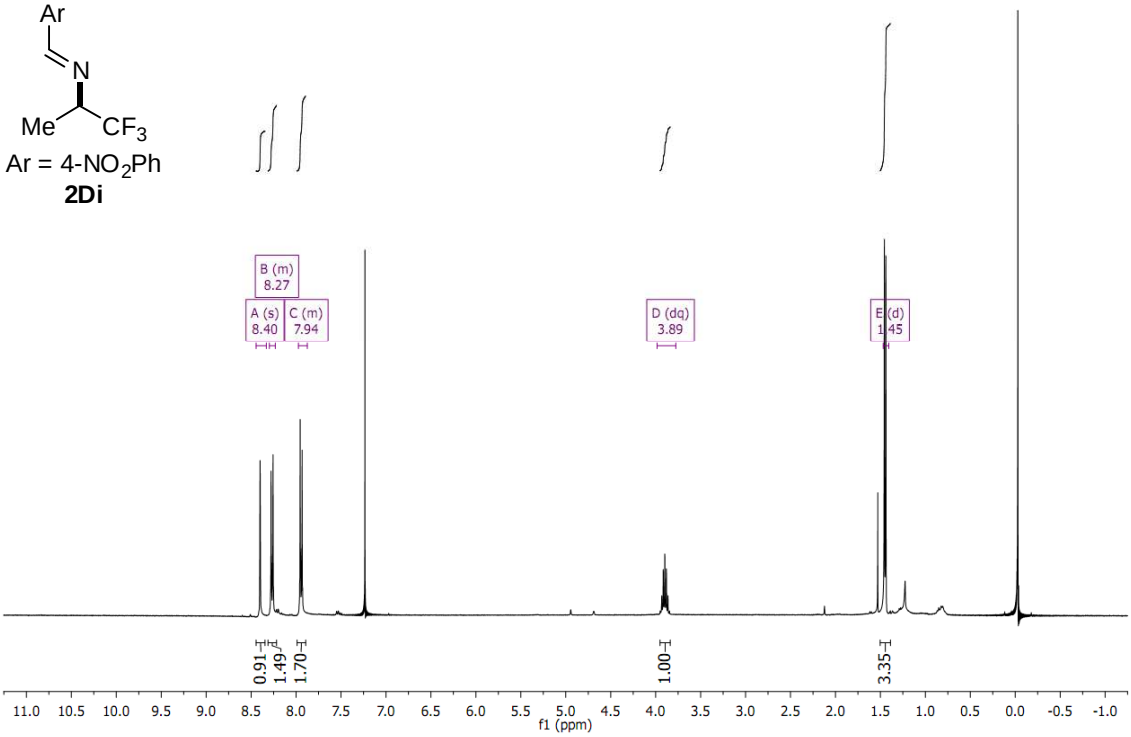
Ar = 4-NO_2Ph

(R)-2Dh, 80% ee from 10 mol% DHQ-7f catalyzed reaction.

wuyw-VI-38-4-H
wuyw-VI-38-4-H

Ar = 4-NO_2Ph

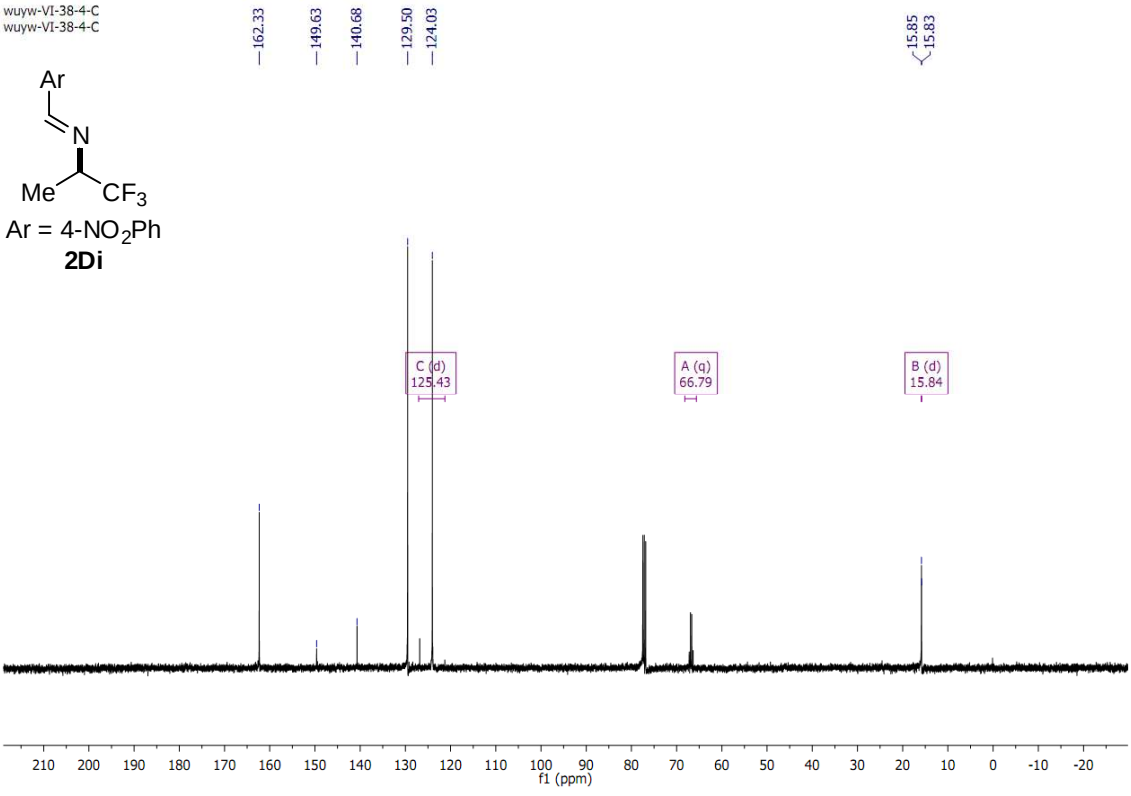
2Di



wuyw-VI-38-4-C
wuyw-VI-38-4-C

Ar = 4-NO_2Ph

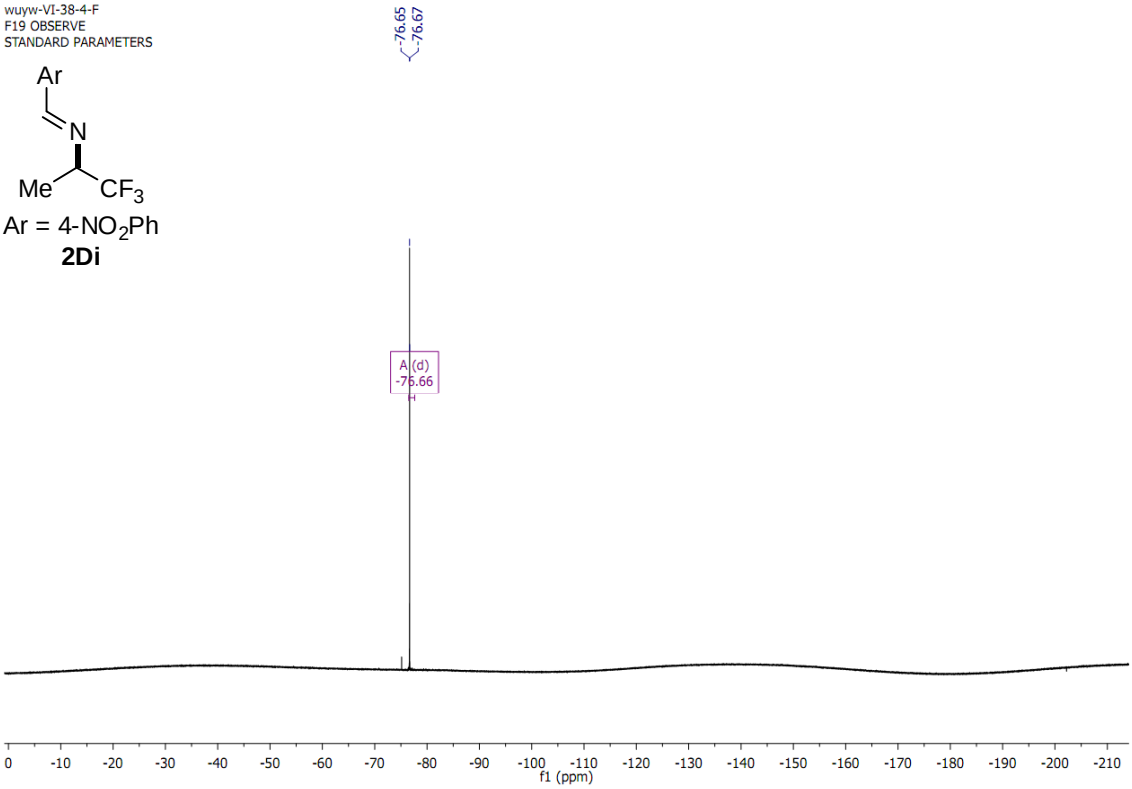
2Di

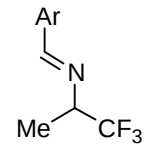


wuyw-VI-38-4-F
F19 OBSERVE
STANDARD PARAMETERS

Ar = 4-NO_2Ph

2Di

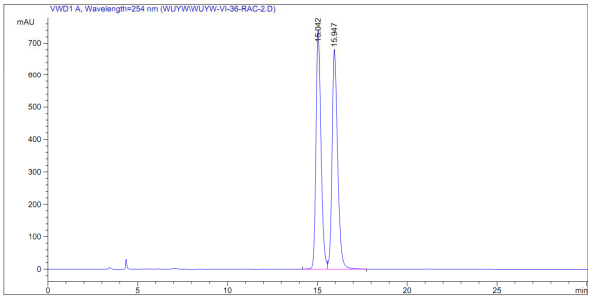




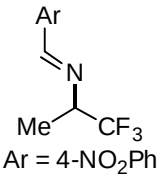
Ar = 4-NO_2Ph

Racemic 2Di

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-36-RAC-2.D
 Sample Name: WUYW-VI-36-rac

================================================================================
Acq. Operator   : wuyw
Acq. Instrument : Instrument 1                    Location : Vial 41
Injection Date  : 1/28/2012 2:33:16 PM
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 1/28/2012 2:31:02 PM by wuyw
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 5/1/2012 1:59:48 PM by DAVID
                  (modified after loading)
Sample Info     : OJ-H, Hex/IPA = 97/3, 1.0 mL/min, 254 nm, 25C, 45 bar,
                  Left
```



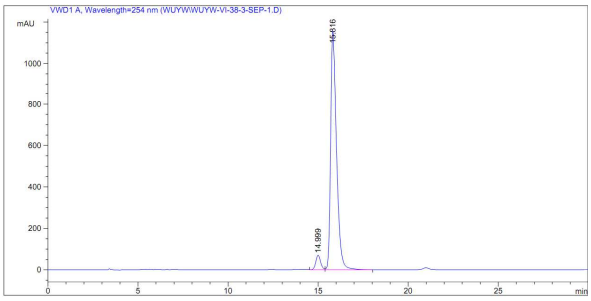

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.042 BV    0.2917 1.42907e4   741.89807  49.4448
   2  15.947 VB    0.3231 1.46116e4   681.05408  50.5552

Totals :                 2.89023e4  1422.95215

================================================================================
                          *** End of Report ***

Instrument 1 5/1/2012 2:23:15 PM DAVID                    Page   1 of 1
```



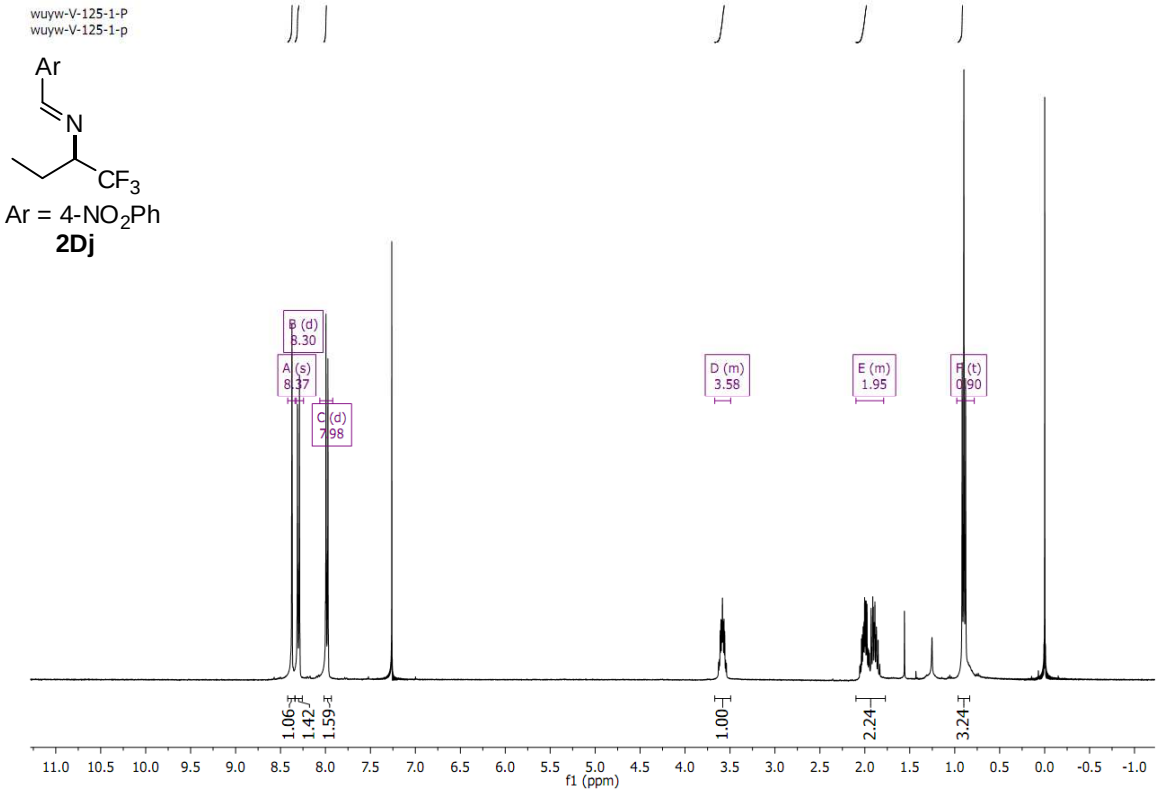
Ar = 4-NO_2Ph

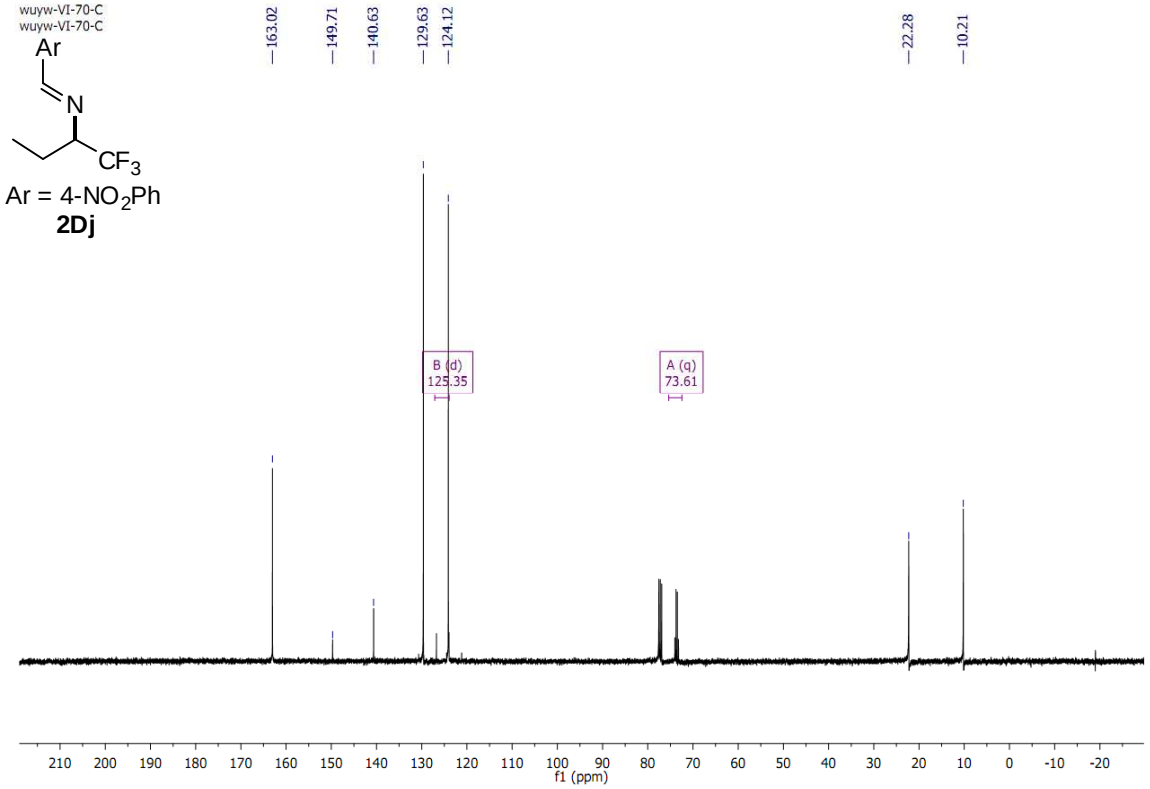
(R)-2Di, 90% ee from 10 mol% DHQ-7f catalyzed reaction.

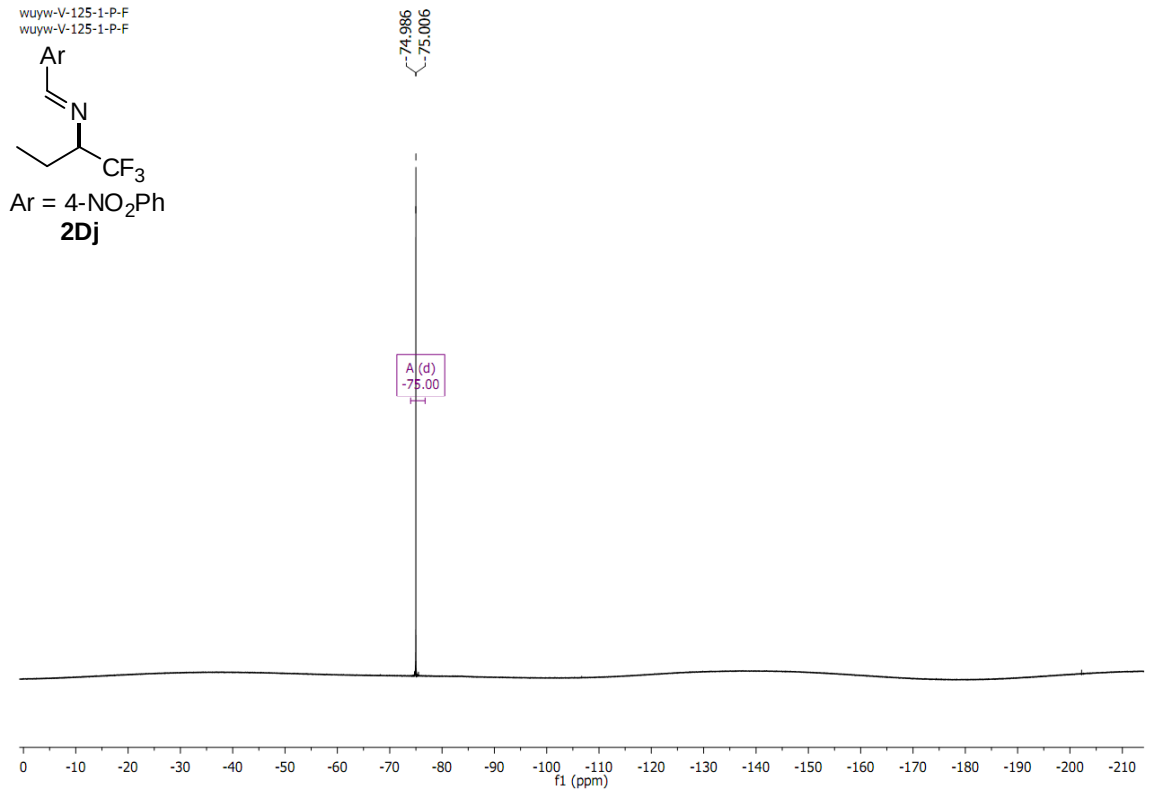
```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-38-3-SEP-1.D
 Sample Name: WUYW-VI-38-3-sep

    ------------------------------------------------------------------------
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                  Location : Vial 21
    Injection Date  : 2/8/2012 3:24:03 PM
                                                    Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 2/8/2012 2:20:11 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/1/2012 1:59:48 PM by DAVID
                      (modified after loading)
    Sample Info     : OJ-H, Hex/IPA=97/3, 1.0mL/min, 254nm, left, 25C, 44bar
```

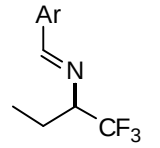



```
    ------------------------------------------------------------------------
                              Area Percent Report
    ------------------------------------------------------------------------

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      5.00000  [ng/ul]   (not used in calc.)
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #  [min]       [min]  mAU   *s     [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  14.999 BV    0.2854 1326.43323   70.83799   4.8434
       2  15.816 VB    0.3357 2.60602e4  1156.42700  95.1566

    Totals :                  2.73867e4  1227.26499

    ------------------------------------------------------------------------
                              *** End of Report ***

Instrument 1 5/1/2012 2:20:32 PM DAVID                        Page   1 of 1
```




wuyw-VI-70-C
wuyw-VI-70-C
Ar
N
CF3
Ar = 4-NO2Ph
2Dj
163.02
149.71
140.63
129.63
124.12
22.28
10.21
B (d)
125.35
A (q)
73.61
f1 (ppm)

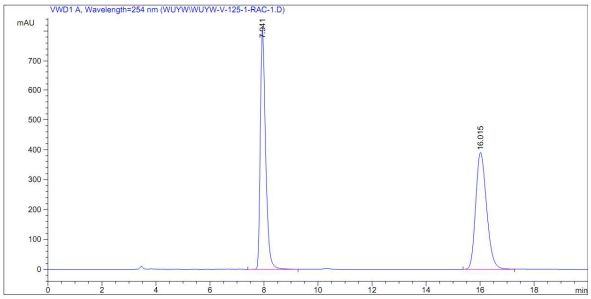

wuyw-V-125-1-P-F
wuyw-V-125-1-P-F
Ar
N
CF3
Ar = 4-NO2Ph
2Dj
-74.986
-75.006
A (d)
-75.00
f1 (ppm)



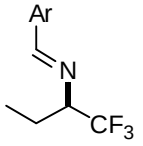
Ar = 4-NO_2Ph

Racemic 2Dj

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-V-125-1-RAC-1.D
 Sample Name: WUYW-V-125-1-rac

    ========================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                  Location : Vial 21
    Injection Date  : 11/1/2011 11:09:12 AM
                                                    Inj Volume : 3 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 11/1/2011 10:26:40 AM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/1/2012 1:59:48 PM by DAVID
                      (modified after loading)
    Sample Info     : AS-H, Hex:IPA = 90:10, 1.0 mL/min, 254 nm, 50 bar, 30C,
                      Left
```



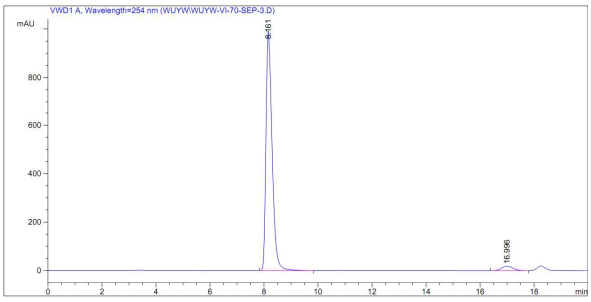

```
    ========================================================================
                               Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]  mAU   *s    [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1   7.941 VB    0.2054 1.09212e4   802.28192  49.8892
       2  16.015 BB    0.4369 1.09697e4   390.53619  50.1108

    Totals :                  2.18909e4  1192.81812

    ========================================================================
```

Ar = 4-NO_2Ph

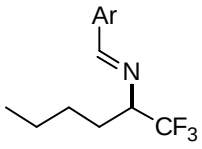
(R)-2Dj, 93% ee from 10 mol% DHQ-7f catalyzed reaction.

```
Data File C:\Chem32\1\DATA\WUYW\WUYW-VI-70-SEP-3.D
 Sample Name: WUYW-VI-70-sep

    ========================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                  Location : Vial 21
    Injection Date  : 5/1/2012 6:34:39 PM
                                                    Inj Volume : 8 µl
    Method          : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/1/2012 6:00:30 PM by wuyw
                      (modified after loading)
    Sample Info     : AS-H, Hex/IPA=90/10, 1.0 mL/min, 254nm, left, 30C, 50ba
                      r
```



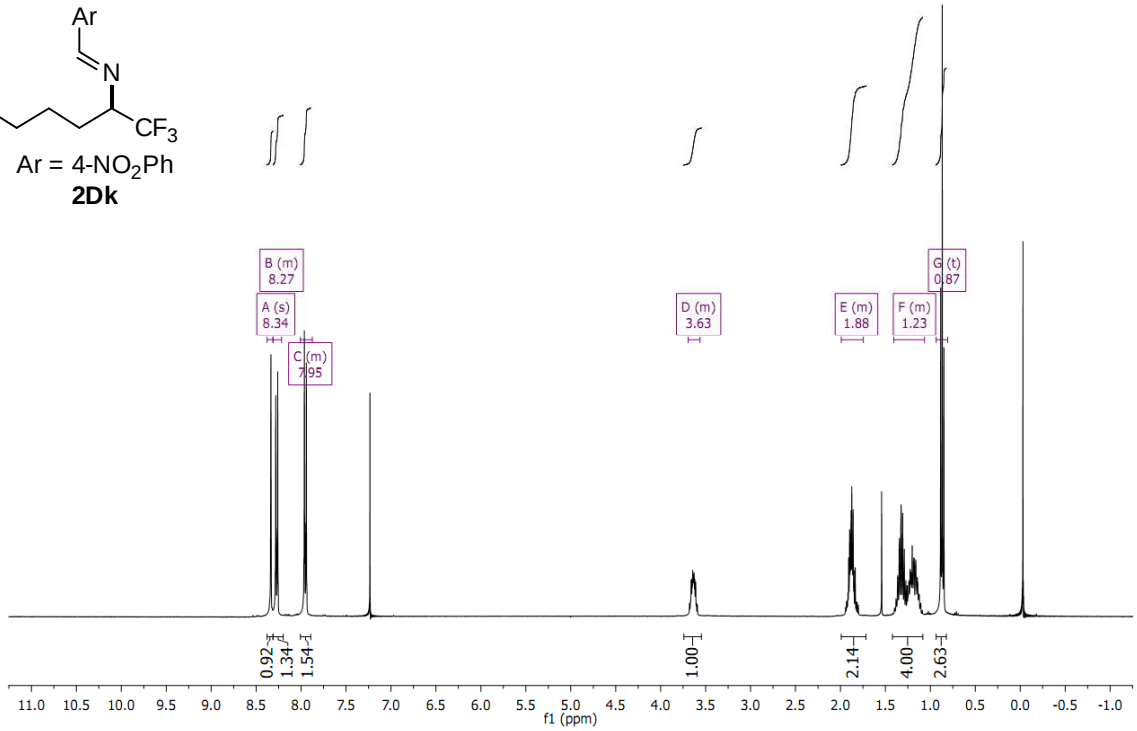

```
    ========================================================================
                               Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      5.00000  [ng/ul]   (not used in calc.)
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]  mAU   *s    [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1   8.161 BB    0.2390 1.55981e4   990.53473  96.5770
       2  16.996 BB    0.4610  552.84106   18.48866   3.4230

    Totals :                  1.61509e4  1009.02339

    ========================================================================
                               *** End of Report ***
```

wuyw-VI-44-2-H
wuyw-VI-44-2-H



Ar = 4-NO_2Ph

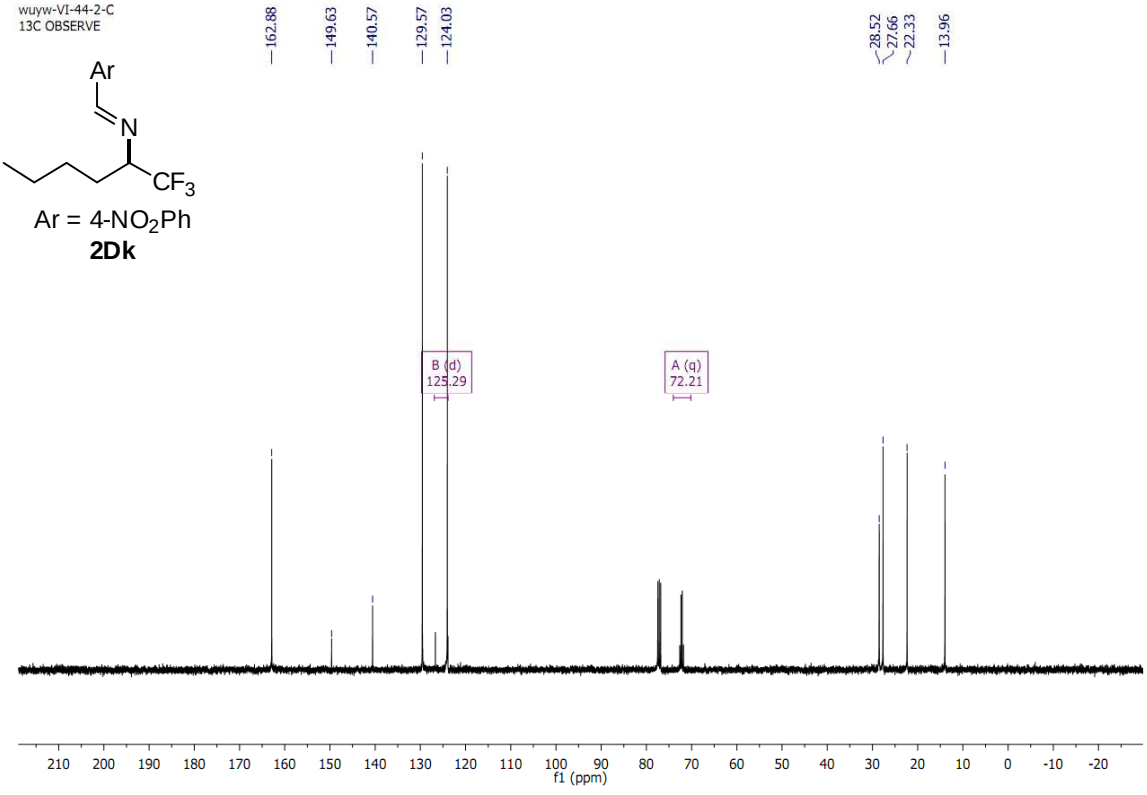
2Dk



wuyw-VI-44-2-C
13C OBSERVE

Ar = 4-NO_2Ph

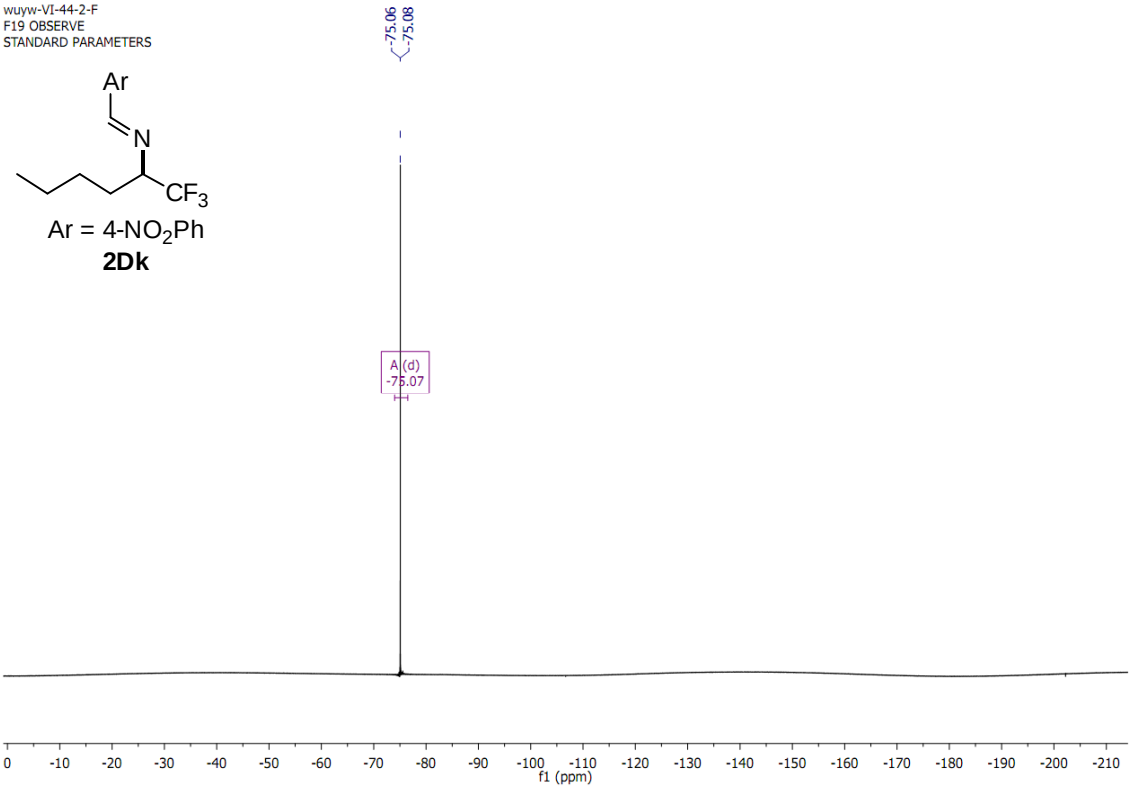
2Dk

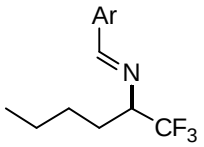


wuyw-VI-44-2-F
F19 OBSERVE
STANDARD PARAMETERS

Ar = 4-NO_2Ph

2Dk

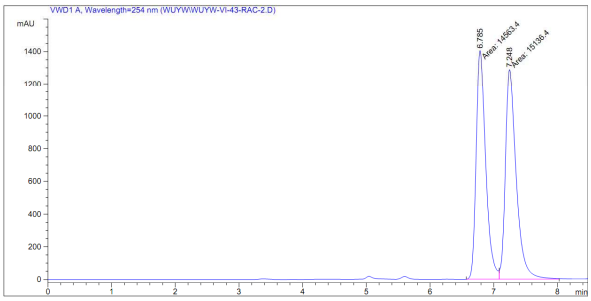




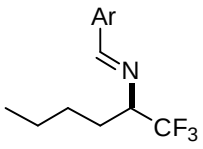
Ar = 4-NO_2Ph

Racemic 2Dk

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-43-RAC-2.D
 Sample Name: WUYW-VI-43-rac

 ========================================================================
 Acq. Operator   : wuyw
 Acq. Instrument : Instrument 1                    Location : Vial 21
 Injection Date  : 2/8/2012 5:24:43 PM
                                                   Inj Volume : 5 µl
 Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
 Last changed    : 2/8/2012 5:02:37 PM by wuyw
                   (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
 Last changed    : 5/1/2012 2:53:10 PM by DAVID
                   (modified after loading)
 Sample Info     : OJ-H, Hex/IPA=95/5, 1.0mL/min, 254nm, left, 25C, 45bar
```



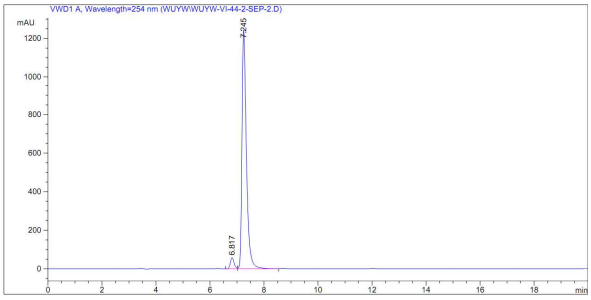

```
 ========================================================================
                          Area Percent Report
 ------------------------------------------------------------------------

 Sorted By             :      Signal
 Multiplier            :      1.0000
 Dilution              :      1.0000
 Sample Amount         :      5.00000  [ng/ul]   (not used in calc.)
 Use Multiplier & Dilution Factor with ISTDs


 Signal 1: VWD1 A, Wavelength=254 nm

 Peak RetTime Type  Width     Area      Height     Area
   #   [min]       [min]  mAU   *s    [mAU   ]     %
 ----|-------|----|-------|----------|----------|--------|
    1   6.785 MF    0.1728 1.45634e4  1404.46753  49.0354
    2   7.248 FM    0.1959 1.51364e4  1287.48560  50.9646

 Totals :                  2.96999e4  2691.95313

 ------------------------------------------------------------------------
                          *** End of Report ***

 Instrument 1 5/1/2012 2:54:00 PM DAVID                    Page   1 of 1
```



Ar = 4-NO_2Ph

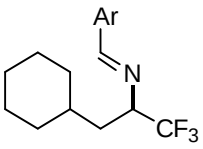
(R)-2Dk, 92% ee from 10 mol% DHQ-7f catalyzed reaction.

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-44-2-SEP-2.D
 Sample Name: wuyw-VI-44-2-sep

 ================================================================================
 Acq. Operator   : wuyw                          Seq. Line :   2
 Acq. Instrument : Instrument 1                   Location : Vial 21
 Injection Date  : 2/11/2012 7:10:49 PM              Inj :   1
                                                 Inj Volume : 3 µl
 Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
 Last changed    : 2/11/2012 6:57:01 PM by wuyw
                   (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
 Last changed    : 2/13/2012 10:02:42 AM by wuyw
                   (modified after loading)
 Sample Info     : OJ-H, Hex/IPA=95/5, 1.0mL/min, 254nm, left, 25C, 45bar
```



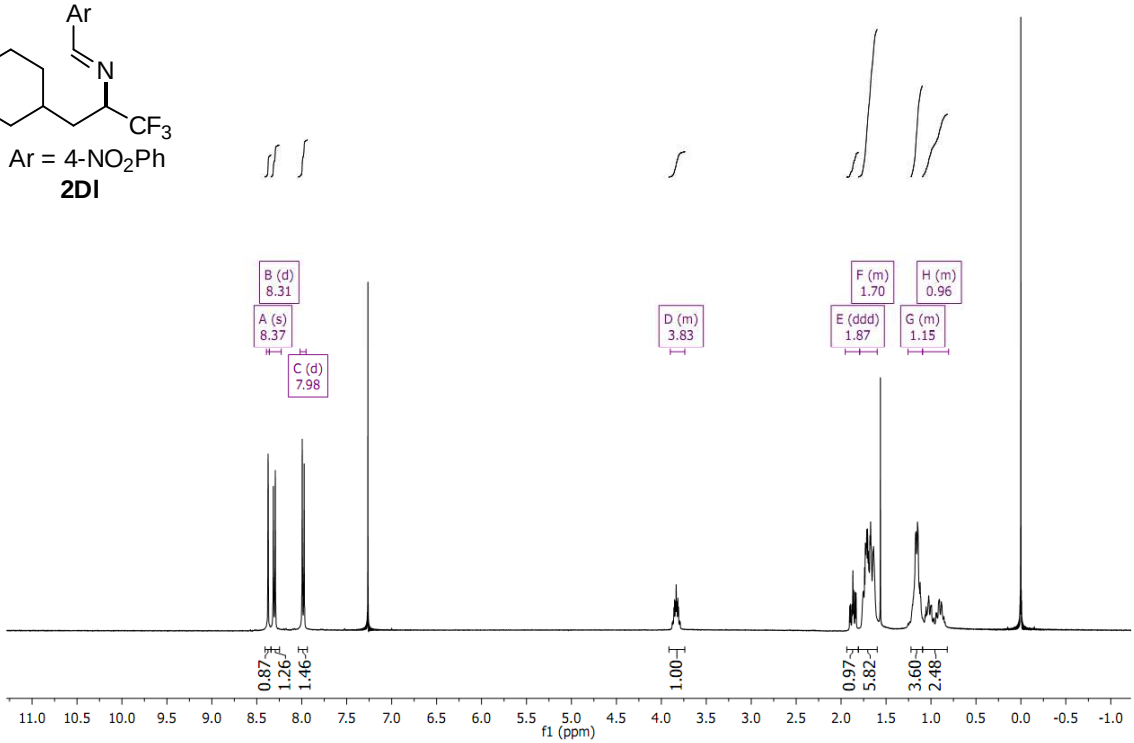

```
 ================================================================================
                            Area Percent Report
 ================================================================================

 Sorted By             :      Signal
 Multiplier            :      1.0000
 Dilution              :      1.0000
 Use Multiplier & Dilution Factor with ISTDs


 Signal 1: VWD1 A, Wavelength=254 nm

 Peak RetTime Type  Width     Area      Height     Area
    #   [min]        [min]  mAU   *s   [mAU   ]     %
 ----|-------|-----|-------|----------|----------|---------|
    1   6.817 BV    0.1481  564.92944   58.26552  3.8330
    2   7.245 VB    0.1708 1.41737e4  1243.48376 96.1670

 Totals :                   1.47386e4  1301.74929

 ================================================================================
                            *** End of Report ***
```

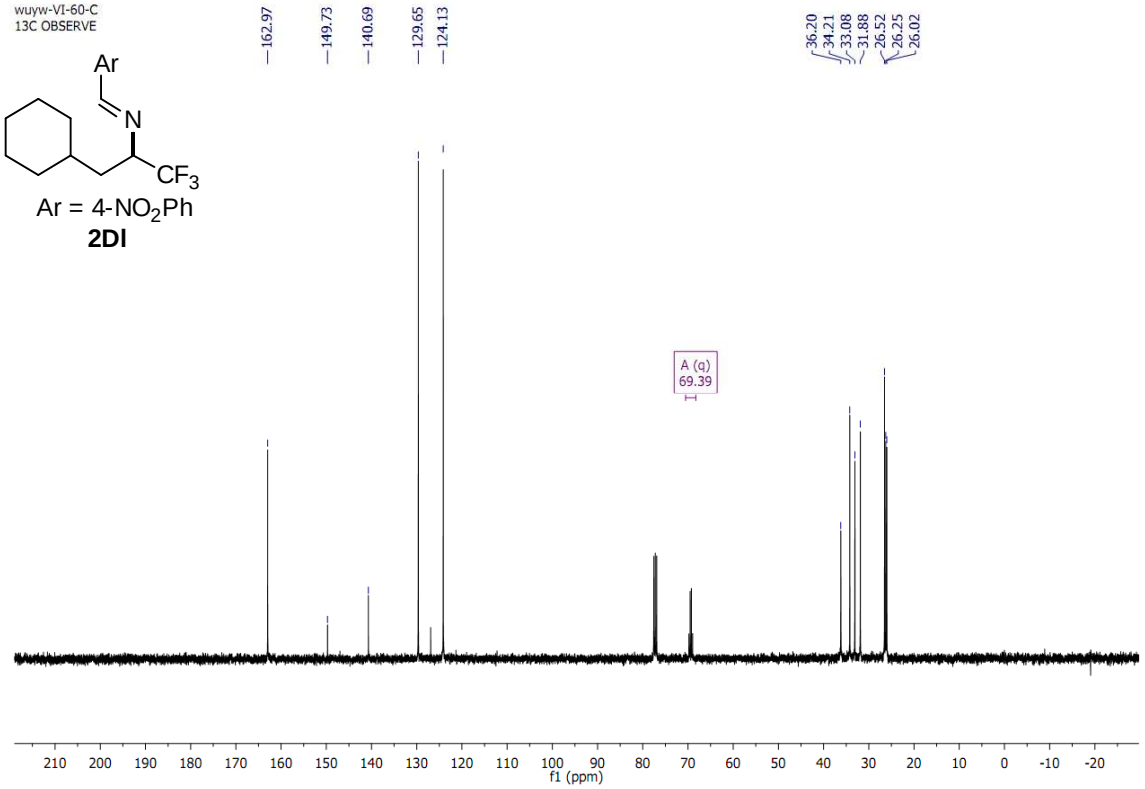

wuyw-VI-60-H
wuyw-VI-60-H

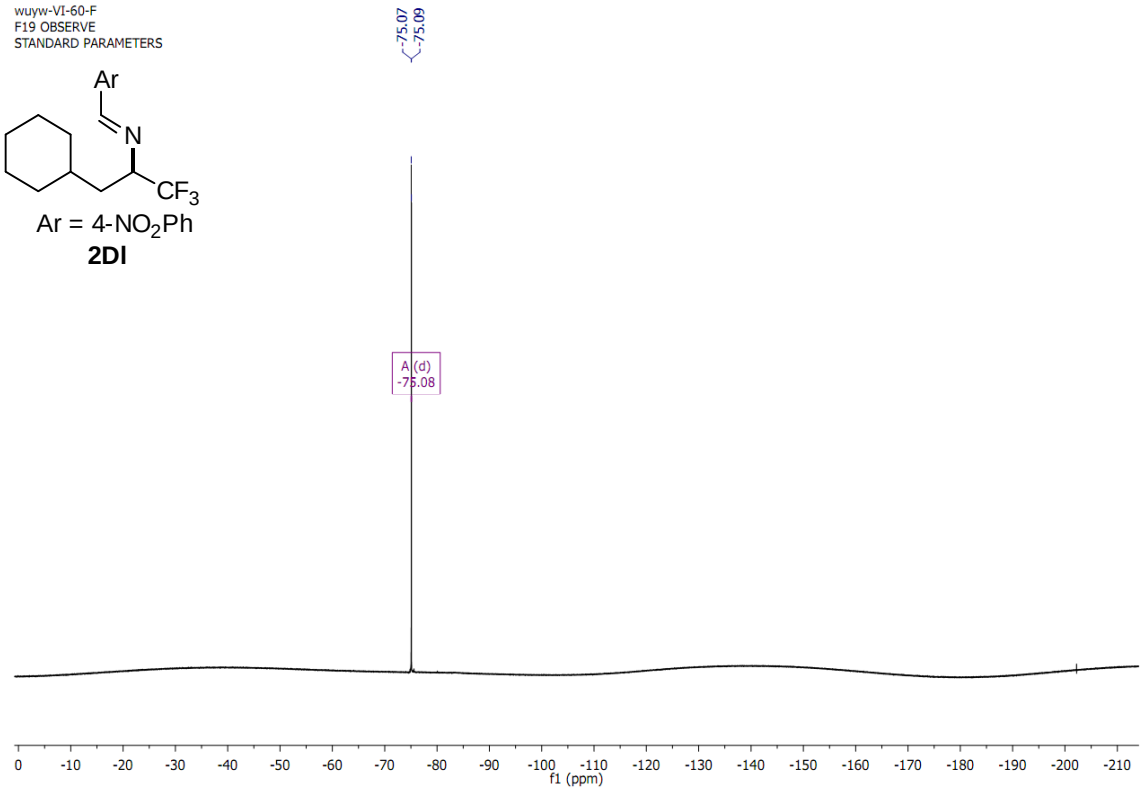


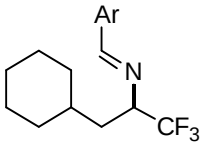
Ar = 4-NO_2Ph

2DI




wuyw-VI-60-C
13C OBSERVE
Ar
N
CF3
Ar = 4-NO2Ph
2DI
162.97
149.73
140.69
129.65
124.13
36.20
34.21
33.08
31.88
26.52
26.25
26.02
A (q)
69.39
f1 (ppm)

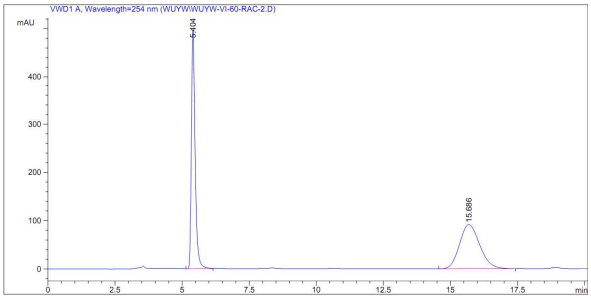

wuyw-VI-60-F
F19 OBSERVE
STANDARD PARAMETERS
Ar
N
CF3
Ar = 4-NO2Ph
2DI
-75.07
-75.09
A (d)
-75.08
f1 (ppm)



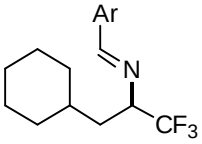
Ar = 4-NO_2Ph

Racemic 2DI

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-60-RAC-2.D
 Sample Name: wuyw-VI-60-rac

    ========================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                  Location : Vial 21
    Injection Date  : 3/14/2012 1:34:49 PM
                                                    Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 3/14/2012 1:13:20 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 3/13/2012 9:51:41 PM by xiao
    Sample Info     : AS-H, Hep/IPA-90/10, 1.0 mL/min, 254 nm, left, 25C, 51b
                      ar
```



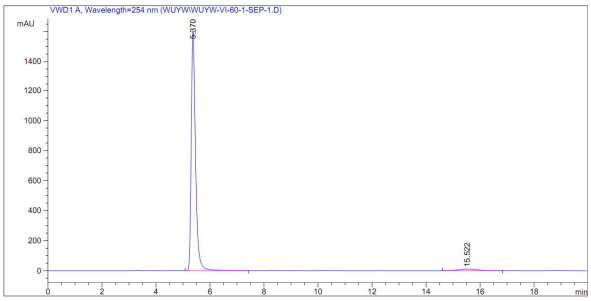

```
    ========================================================================
                                Area Percent Report
    ------------------------------------------------------------------------

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s    [mAU   ]     %
    ----|-------|-----|-------|---------|----------|--------|
       1   5.404 VB    0.1455 4773.54492  497.40454  49.8012
       2  15.686 BB    0.8152 4811.64893   91.81660  50.1988

    Totals :                  9585.19385  589.22115

    ========================================================================
                                *** End of Report ***

Instrument 1 3/20/2012 9:26:29 AM jpchen                        Page   1 of 1
```



Ar = 4-NO_2Ph

(R)-2DI, 94% ee from 10 mol% DHQ-7f catalyzed reaction

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-60-1-SEP-1.D
 Sample Name: WUYW-VI-60-1-sep

    ========================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                  Location : Vial 21
    Injection Date  : 3/19/2012 9:42:27 PM
                                                    Inj Volume : 10 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 3/19/2012 9:39:49 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 3/13/2012 9:51:41 PM by xiao
    Sample Info     : OJ-H, Hep/IPA-90/10, 1.0 mL/min, 254nm, left, 25C, 51ba
                      r
```

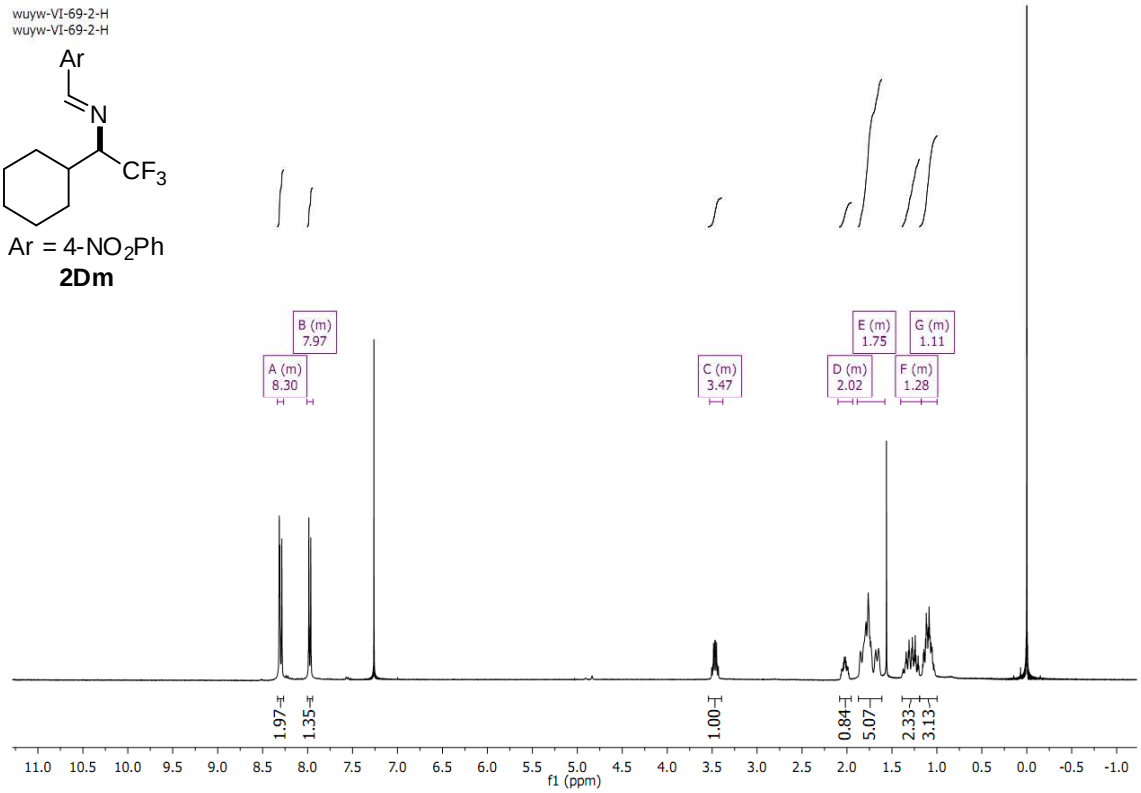



```
    ========================================================================
                                Area Percent Report
    ------------------------------------------------------------------------

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s    [mAU   ]     %
    ----|-------|-----|-------|---------|----------|--------|
       1   5.370 VB    0.1662 1.76488e4 1604.89795  97.0981
       2  15.522 BB    0.7618  527.44861   10.58724   2.9019

    Totals :                  1.81760e4  1615.48519

    ========================================================================
                                *** End of Report ***

Instrument 1 3/20/2012 9:27:45 AM jpchen                        Page   1 of 1
```

wuyw-VI-69-2-H
wuyw-VI-69-2-H

Ar = 4-NO_2Ph

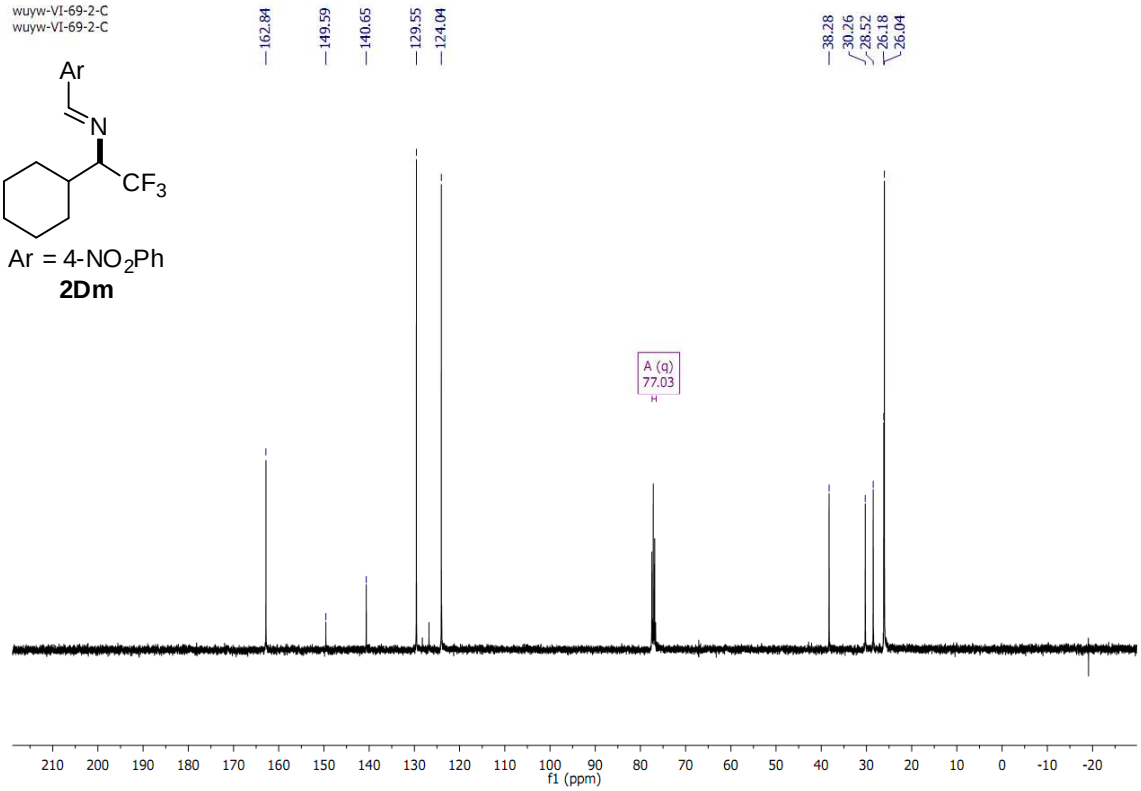
2Dm



wuyw-VI-69-2-C
wuyw-VI-69-2-C

Ar = 4-NO_2Ph

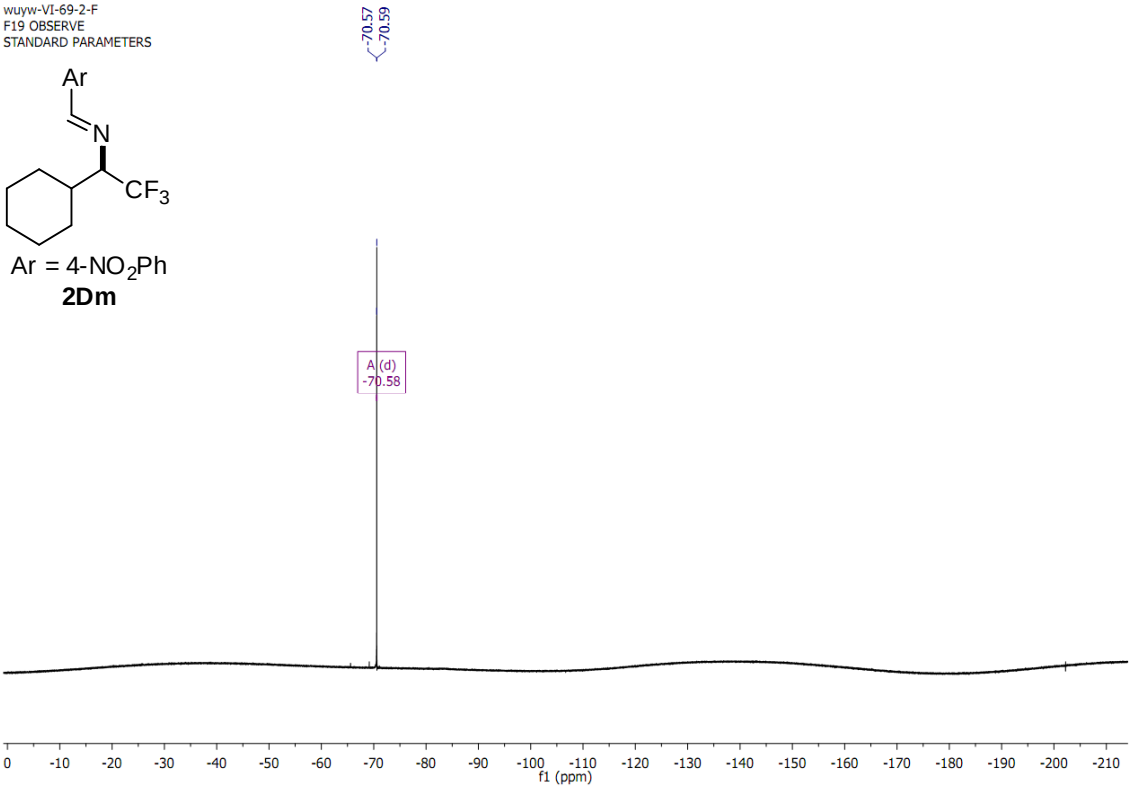
2Dm

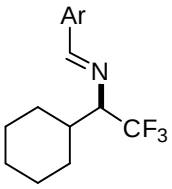


wuyw-VI-69-2-F
F19 OBSERVE
STANDARD PARAMETERS

Ar = 4-NO_2Ph

2Dm



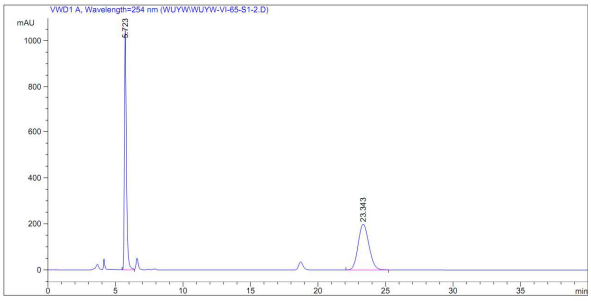


Ar = 4-NO_2Ph

Racemic 2Dm

Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-65-S1-2.D
Sample Name: wuyw-VI-65-S1

Acq. Operator	: wuyw	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 21
Injection Date	: 3/24/2012 6:50:48 PM	Inj	: 1
		Inj Volume	: 6 µl
Acq. Method	: C:\CHEM32\1\METHODS\METHOD1.M		
Last changed	: 3/24/2012 6:40:19 PM by wuyw		
Analysis Method	: C:\CHEM32\1\METHODS\METHOD1.M		
Last changed	: 5/2/2012 10:52:57 AM by DAVID (modified after loading)		
Sample Info	: AS-H, Hex/IPA=90/10, 1.0ml/min, left, 51bar, 254nm, 25C		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

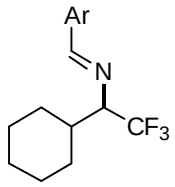
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.723	BV	0.1533	1.07373e4	1045.21301	49.3427
2	23.343	BB	0.8639	1.10234e4	198.79279	50.6573
Totals :				2.17607e4	1244.00580	

*** End of Report ***

Instrument 1 5/2/2012 11:05:52 AM DAVID

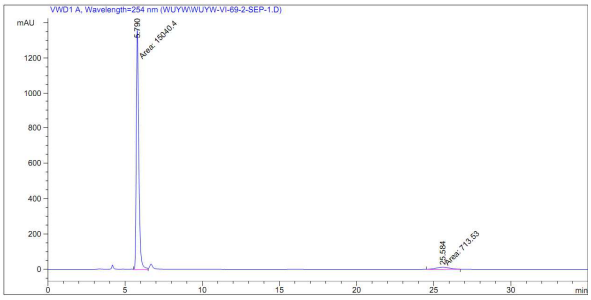
Page 1 of 1



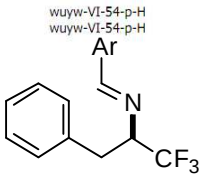
Ar = 4-NO_2Ph

(R)-2Dm, 91% ee from 10 mol% DHQ-7f catalyzed reaction.

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-69-2-SEP-1.D
 Sample Name: wuyw-VI-69-2-sep

 ================================================================================
 Acq. Operator   : wuyw                          Seq. Line :   1
 Acq. Instrument : Instrument 1                   Location : Vial 21
 Injection Date  : 3/30/2012 6:05:31 PM              Inj :   1
                                                 Inj Volume : 10 µl
 Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
 Last changed    : 3/30/2012 6:02:57 PM by wuyw
 Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
 Last changed    : 5/2/2012 10:52:57 AM by DAVID
                   (modified after loading)
 Sample Info     : AS-H, Hex/IPA-90/10, 1.0ml/min, left, 51bar, 254nm, 25C
```

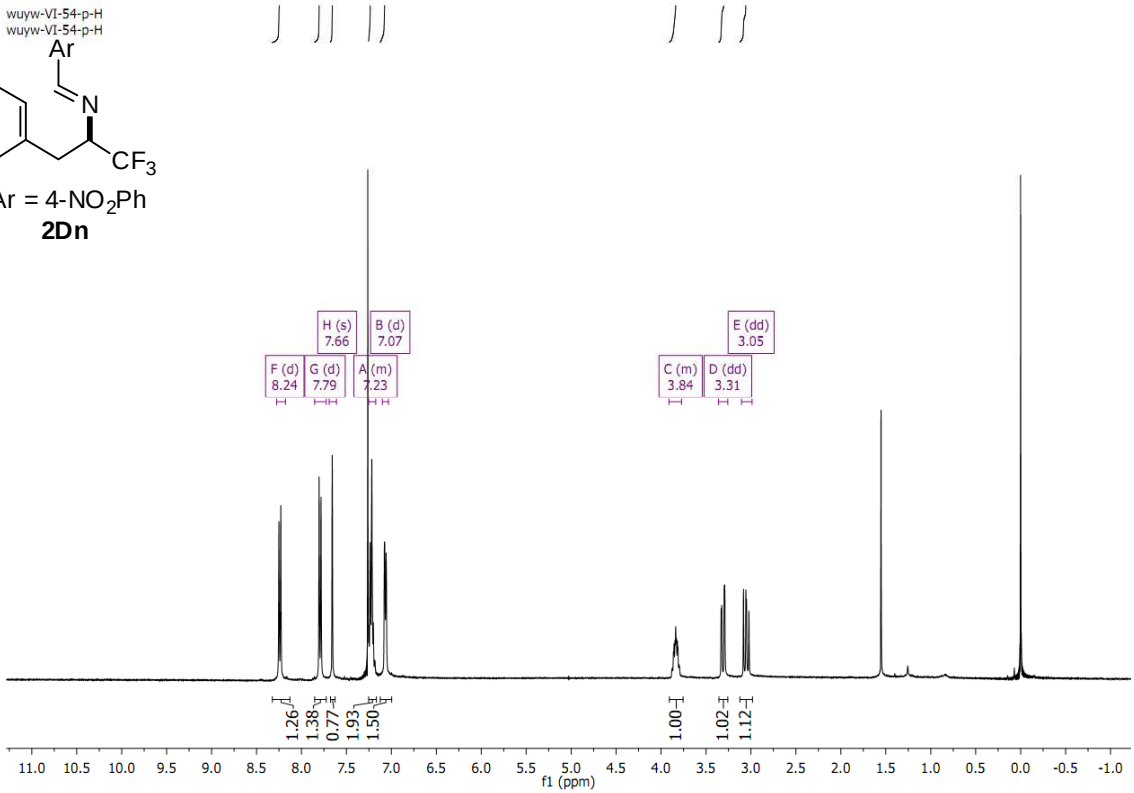


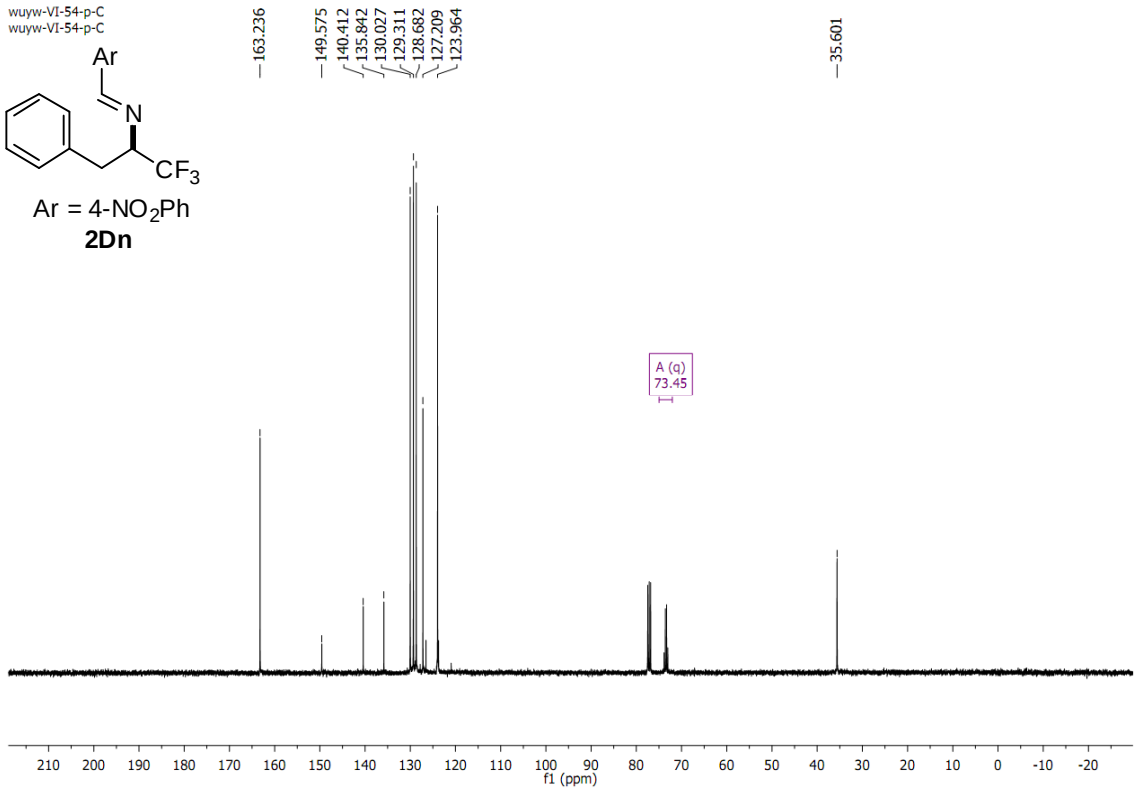

```
 ================================================================================
                              Area Percent Report
 ================================================================================

 Sorted By             :      Signal
 Multiplier            :      1.0000
 Dilution              :      1.0000
 Use Multiplier & Dilution Factor with ISTDs


 Signal 1: VWD1 A, Wavelength=254 nm

 Peak RetTime Type  Width     Area      Height      Area
   #   [min]       [min]  mAU   *s    [mAU   ]      %
 ----|-------|----|-------|----------|----------|--------|
    1   5.790 MM    0.1847 1.50404e4  1357.48755  95.4708
    2  25.584 MM    1.0283  713.52979   11.56446   4.5292

 Totals :                  1.57539e4  1369.05201

 ================================================================================
                              *** End of Report ***

 Instrument 1 5/2/2012 10:59:24 AM DAVID                        Page   1 of 1
```

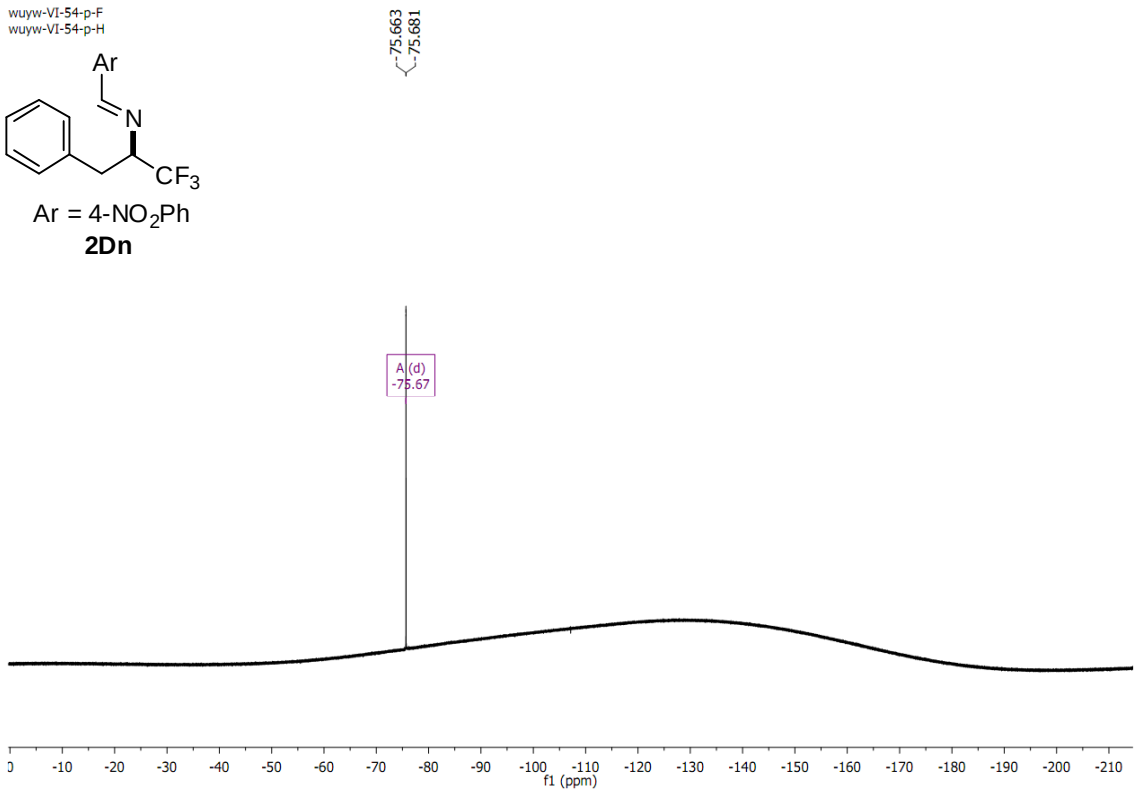


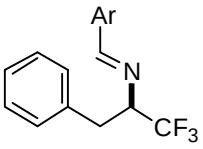
Ar = 4-NO_2Ph

2Dn




wuyw-VI-54-p-C
wuyw-VI-54-p-C
Ar
N
CF3
Ar = 4-NO2Ph
2Dn
163.236
149.575
140.412
135.842
130.027
129.311
128.682
127.209
123.964
35.601
A (q)
73.45
f1 (ppm)

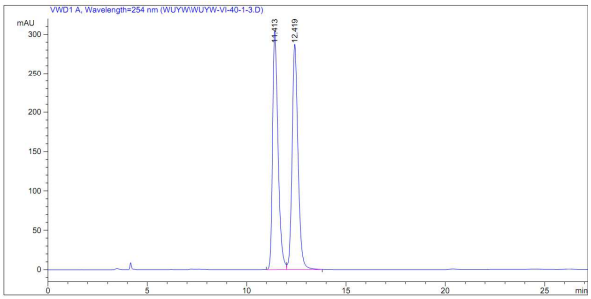

wuyw-VI-54-p-F
wuyw-VI-54-p-H
Ar
N
CF3
Ar = 4-NO2Ph
2Dn
-75.663
-75.681
A (d)
-75.67
f1 (ppm)



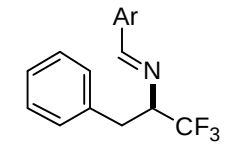
Ar = 4-NO_2Ph

Racemic 2Dn

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-40-1-3.D
 Sample Name: wuyw-VI-40-1

    ================================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                    Location : Vial 21
    Injection Date  : 3/29/2012 10:40:24 AM
                                                      Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 3/29/2012 10:37:46 AM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/2/2012 10:52:57 AM by DAVID
                      (modified after loading)
    Sample Info     : OJ-H, Hep/IPA=90/10, 1.0 mL/min, 254nm, left, 25C, 47ba
                      r
```



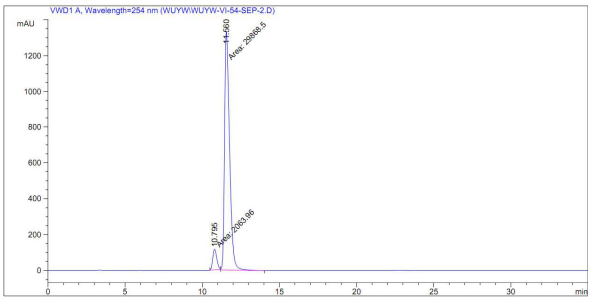

```
    ================================================================================
                                Area Percent Report
    ================================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #  [min]       [min]  mAU   *s      [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  11.413 BV    0.2877 5798.15088  304.49158  49.4558
       2  12.419 VB    0.3134 5925.74316  287.33719  50.5442

    Totals :                  1.17239e4   591.82877

    ================================================================================
                                *** End of Report ***

Instrument 1 5/2/2012 11:12:32 AM DAVID                                Page   1 of 1
```



Ar = 4-NO_2Ph

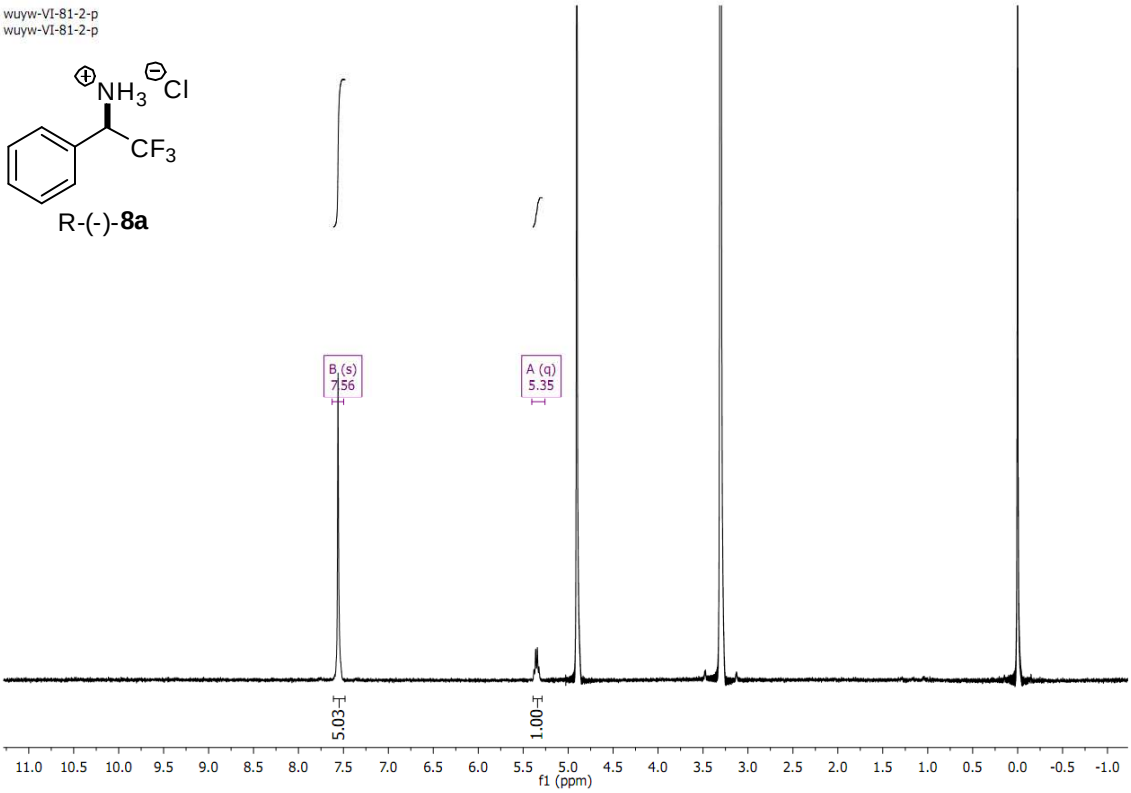
(R)-2Dn, 87% ee from 10 mol% DHQ-7f catalyzed reaction.

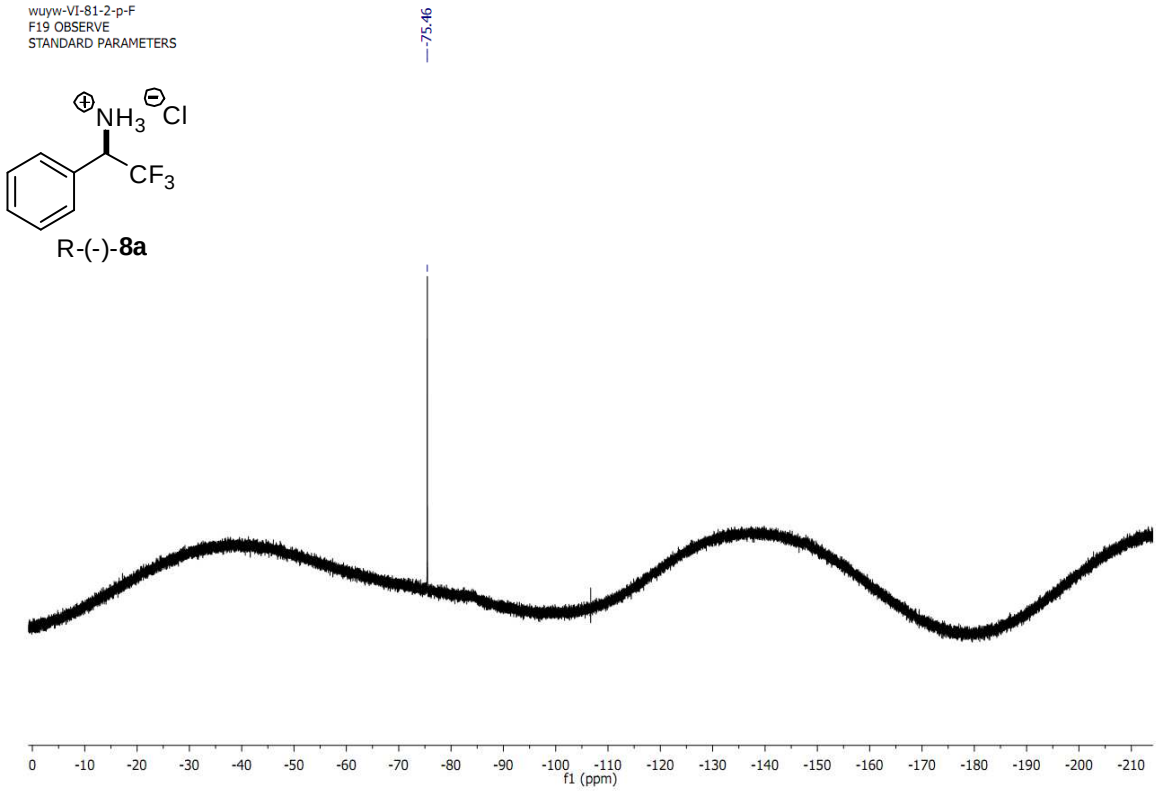
```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-54-SEP-2.D
 Sample Name: wuyw-VI-54-sep

    ================================================================================
    Acq. Operator   : wuyw                            Seq. Line :  1
    Acq. Instrument : Instrument 1                    Location : Vial 21
    Injection Date  : 3/6/2012 12:14:42 PM              Inj :  1
                                                      Inj Volume : 15 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 3/6/2012 12:12:15 PM by wuyw
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/26/2012 4:20:13 PM by wuyw
    Sample Info     : OJ-H, Hex/IPA=90/10, 1.0mL/min, 254nm, 25C, left, 47bar
```




```
    ================================================================================
                                Area Percent Report
    ================================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #  [min]       [min]  mAU   *s      [mAU   ]     %
    ----|-------|----|-------|----------|----------|--------|
       1  10.795 MM    0.3003 2063.96069  114.55701   6.4635
       2  11.560 MM    0.3739 2.98685e4  1331.34167  93.5365

    Totals :                  3.19325e4  1445.89868

    ================================================================================
                                *** End of Report ***

Instrument 1 6/8/2012 2:38:26 PM xiao                                  Page   1 of 1
```

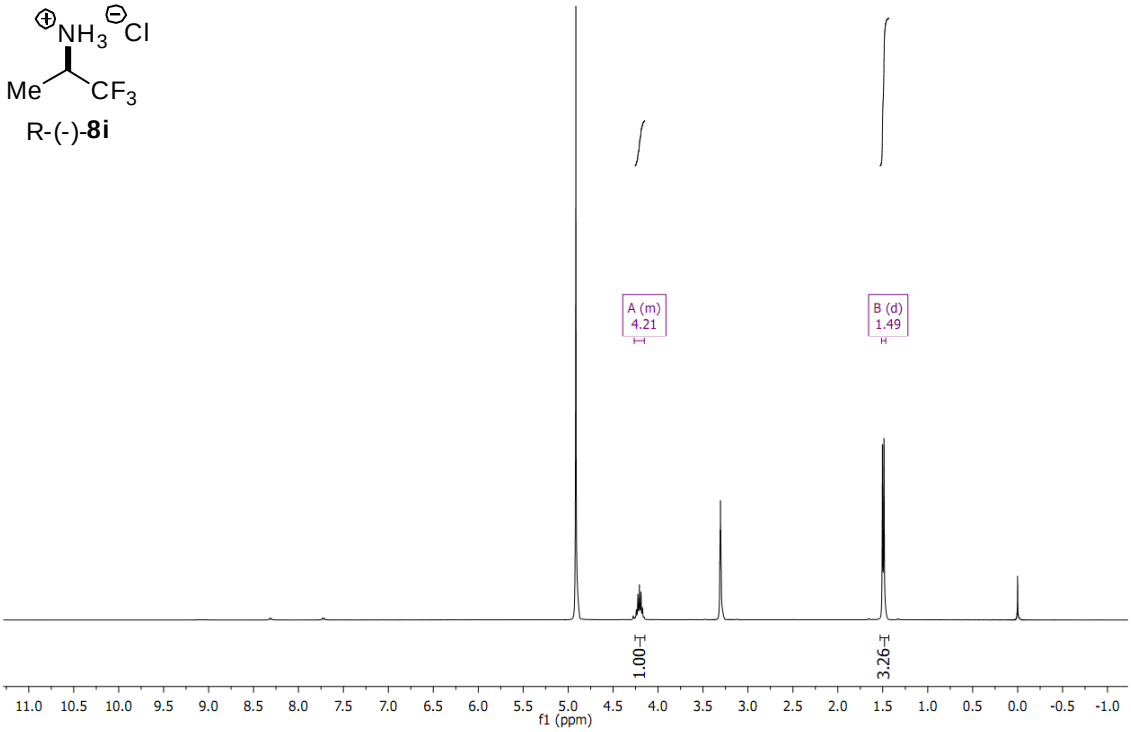
^{1}H and ^{13}C NMR spectra and HPLC spectra for **Amine salts 8**





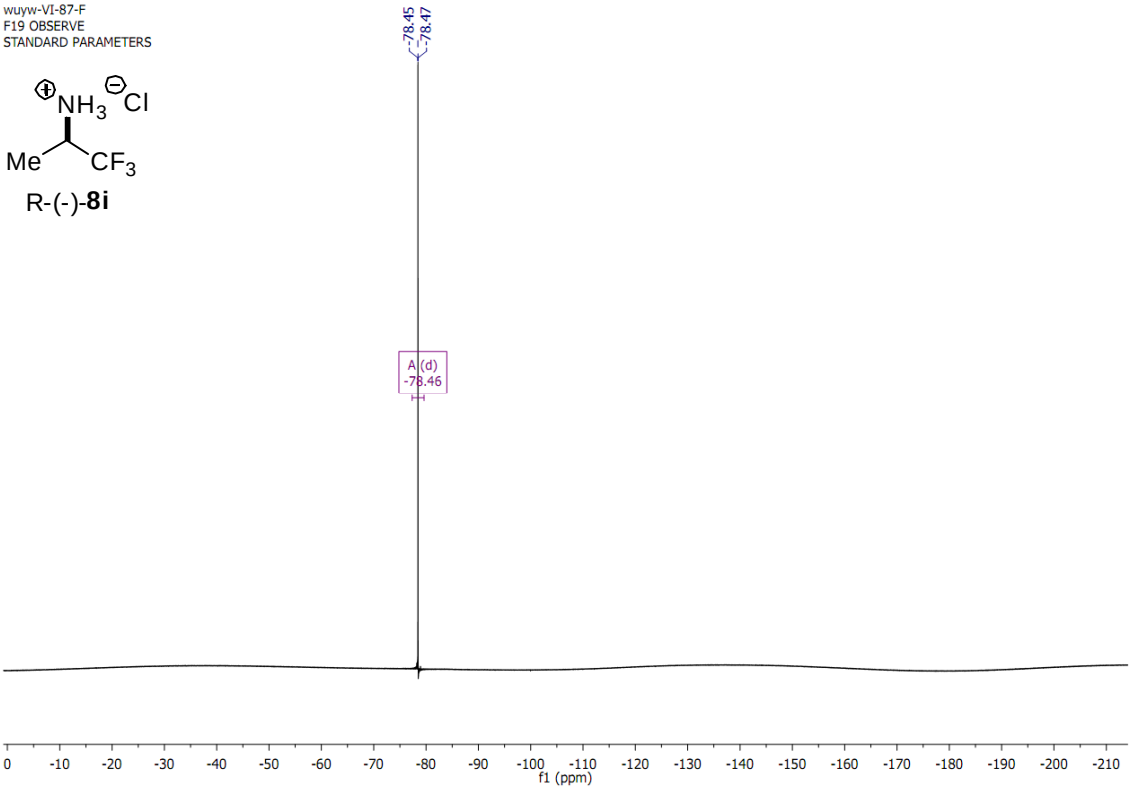
wuyw-VI-87-H
wuyw-VI-87-H

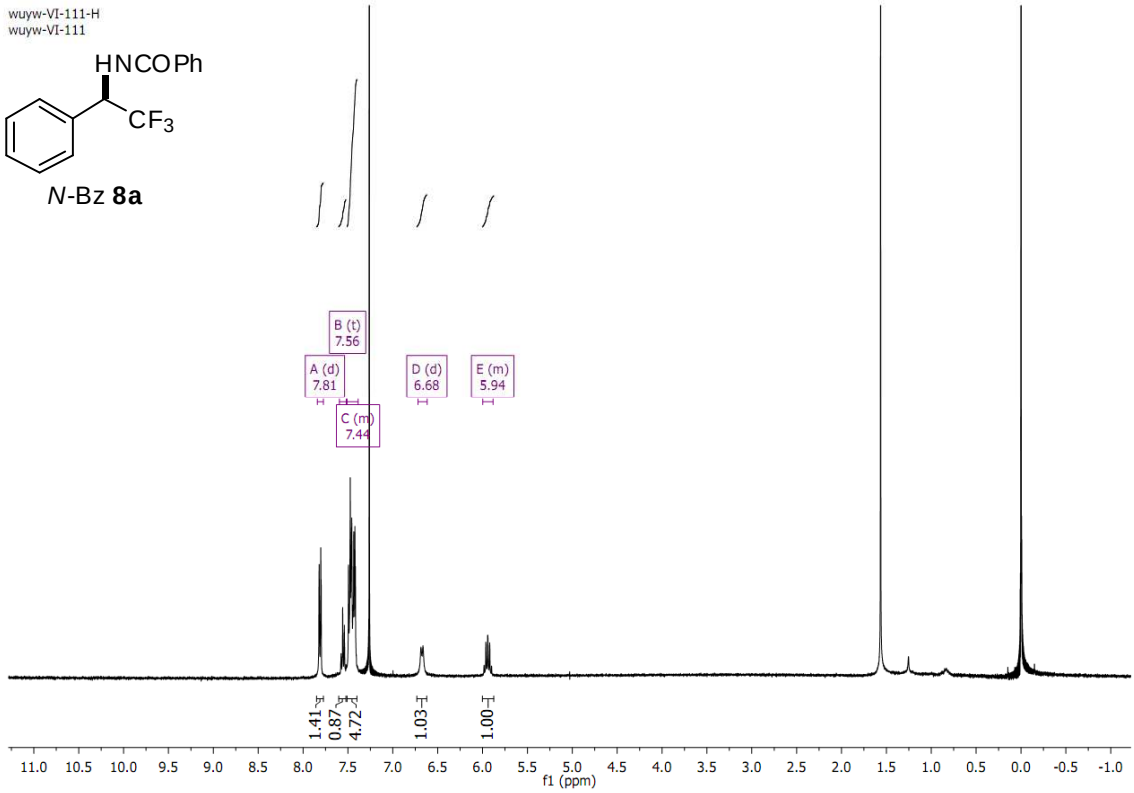
R-(-)-**8i**

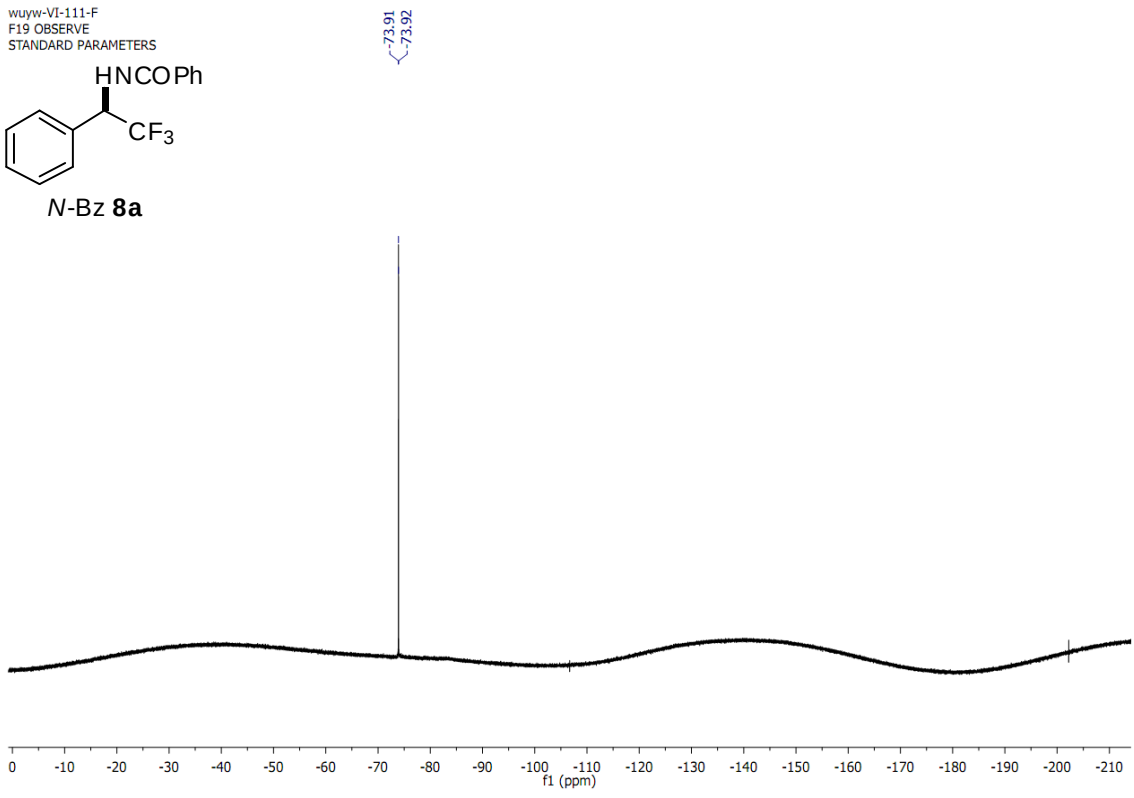


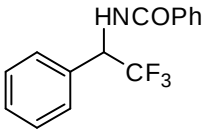
wuyw-VI-87-F
F19 OBSERVE
STANDARD PARAMETERS

R-(-)-**8i**



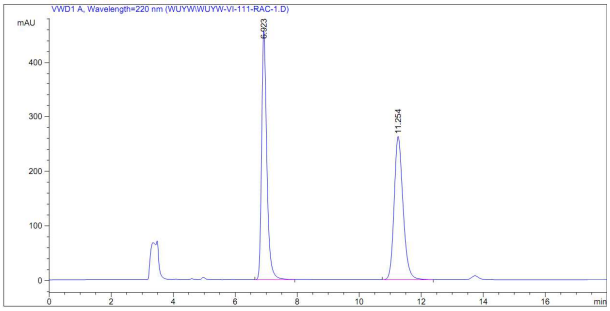

wuyw-VI-111-H
wuyw-VI-111
HNCOPh
CF3
N-Bz 8a
B (t)
7.56
A (d)
7.81
D (d)
6.68
E (m)
5.94
C (m)
7.44
1.41
0.87
4.72
1.03
1.00
f1 (ppm)


wuyw-VI-111-F
F19 OBSERVE
STANDARD PARAMETERS
-73.91
-73.92
HNCOPh
CF3
N-Bz 8a
f1 (ppm)

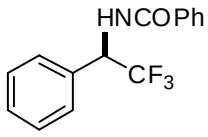


Racemic *N*-Bz **8a**

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-111-RAC-1.D
 Sample Name: wuyw-VI-111-rac-1

    ======================================================================
    Acq. Operator   : wuyw                          Seq. Line :   1
    Acq. Instrument : Instrument 1                   Location : Vial 21
    Injection Date  : 6/20/2012 2:57:38 PM             Inj :   1
                                                   Inj Volume : 10 µl
    Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 6/20/2012 3:13:59 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 6/18/2012 3:42:28 PM by wuyw
                      (modified after loading)
    Sample Info     : OJ-H, Hex/IPA=80/20, 1.0 mL/min, 220nm, 54bar, left
```

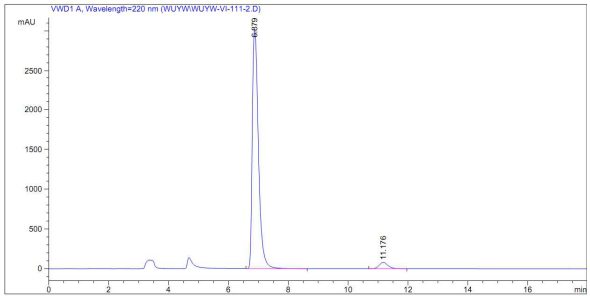



```
    ======================================================================
                                Area Percent Report
    ----------------------------------------------------------------------

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
       #   [min]      [min]   mAU   *s    [mAU   ]     %
    ----|-------|----|--------|---------|----------|--------|
       1   6.923 BB    0.1739 5267.27197  456.59460  50.2084
       2  11.254 BB    0.3057 5223.55566  261.63541  49.7916

    Totals :                  1.04908e4   718.23001

    ======================================================================
                                *** End of Report ***

Instrument 1 6/21/2012 11:36:57 AM wuyw                          Page   1 of 1
```

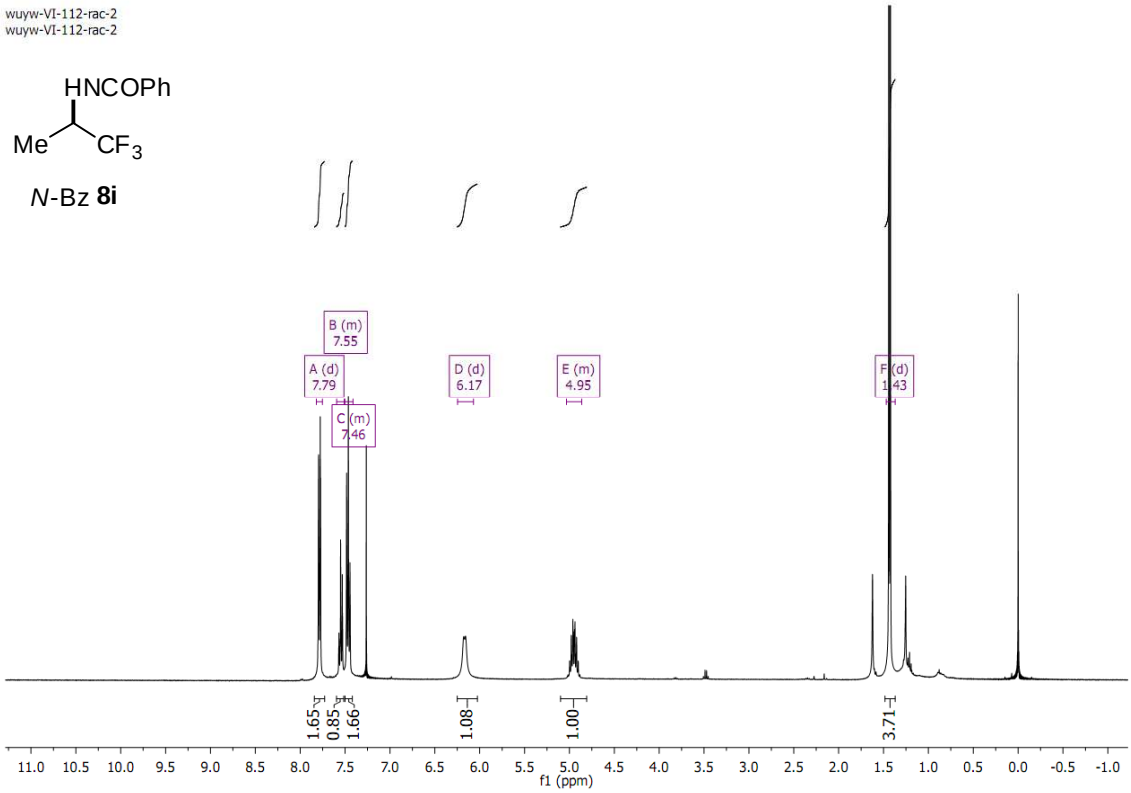


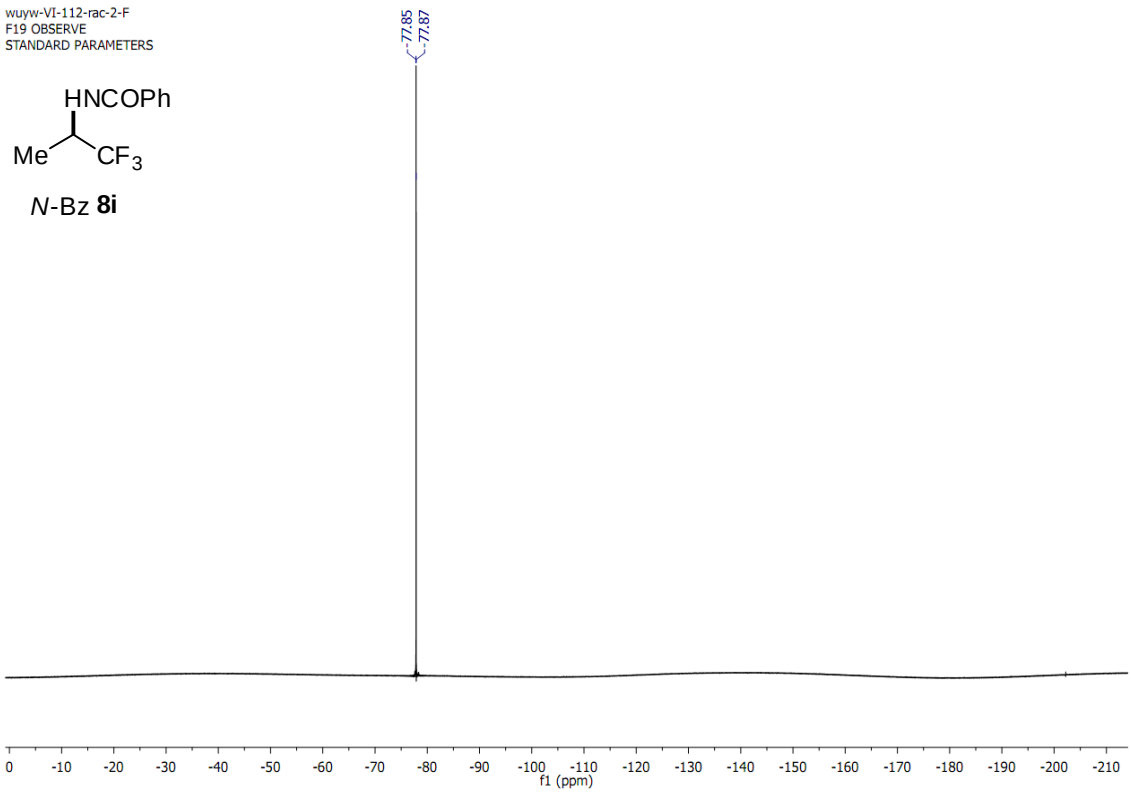
N-Bz **8a**, 90% ee

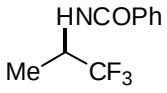
```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-111-2.D
 Sample Name: wuyw-VI-111

    ======================================================================
    Acq. Operator   : wuyw                          Seq. Line :   2
    Acq. Instrument : Instrument 1                   Location : Vial 22
    Injection Date  : 6/20/2012 3:18:12 PM             Inj :   1
                                                   Inj Volume : 10 µl
    Different Inj Volume from Sequence !     Actual Inj Volume : 8 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 6/20/2012 3:13:59 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 6/18/2012 3:42:28 PM by wuyw
                      (modified after loading)
    Sample Info     : OJ-H, Hex/IPA=80/20, 1.0 mL/min, 220nm, 54bar, left
```




```
    ======================================================================
                                Area Percent Report
    ----------------------------------------------------------------------

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
       #   [min]      [min]   mAU   *s    [mAU   ]     %
    ----|-------|----|--------|---------|----------|--------|
       1   6.879 BB    0.2192 4.27329e4  3014.76904  96.3566
       2  11.176 BB    0.3093 1615.81470   80.20595   3.6434

    Totals :                  4.43487e4  3094.97499

    ======================================================================
                                *** End of Report ***

Instrument 1 6/21/2012 1:11:53 PM wuyw                           Page   1 of 1
```

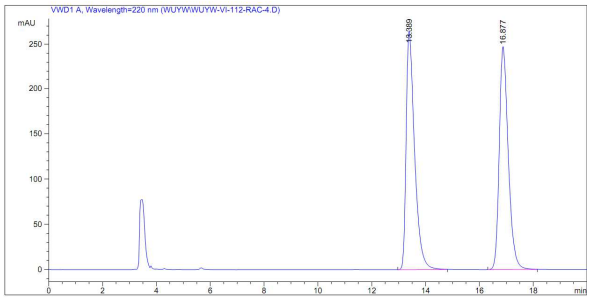

wuyw-VI-112-rac-2
wuyw-VI-112-rac-2
HNCOPh
Me
CF3
N-Bz 8i
B (m) 7.55
A (d) 7.79
C (m) 7.46
D (d) 6.17
E (m) 4.95
F (d) 1.43
1.65
0.85
1.66
1.08
1.00
3.71
f1 (ppm)


wuyw-VI-112-rac-2-F
F19 OBSERVE
STANDARD PARAMETERS
HNCOPh
Me
CF3
N-Bz 8i
-77.85
-77.87
f1 (ppm)

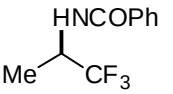


Racemic *N*-Bz **8i**

```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-VI-112-RAC-4.D
 Sample Name: WUYW-VI-112-rac

    ==========================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                  Location : Vial 21
    Injection Date  : 6/20/2012 10:22:20 AM
                                                   Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 6/20/2012 10:20:08 AM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 6/20/2012 11:48:54 AM by wuyw
                      (modified after loading)
    Sample Info     : OJ-H, Hex/IPA=95/5, 1.0 mL/min, 220nm, left, 47 bar, 25
                      C
```

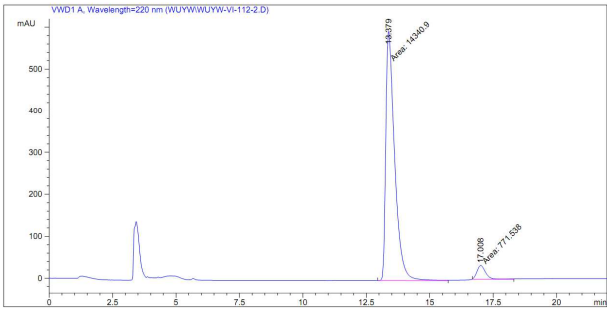



```
    ==========================================================================
                              Area Percent Report
    ==========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1  13.389 BB    0.3238 5733.17334  264.94153  50.0171
       2  16.877 BB    0.3519 5729.24414  247.25912  49.9829

    Totals :                 1.14624e4   512.20065

    ==========================================================================
                              *** End of Report ***

    Instrument 1 6/20/2012 2:21:43 PM wuyw                          Page   1 of 1
```



N-Bz **8i**, 90% ee

```
Data File C:\Chem32\1\DATA\WUYW\WUYW-VI-112-2.D
 Sample Name: WUYW-VI-112

    ==========================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                  Location : Vial 21
    Injection Date  : 6/20/2012 11:52:00 AM
                                                   Inj Volume : 10 µl
    Method          : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 6/20/2012 11:48:54 AM by wuyw
                      (modified after loading)
    Sample Info     : OJ-H, Hex/IPA=95/5, 1.0 mL/min, 220nm, left, 47 bar, 25
                      C
```




```
    ==========================================================================
                              Area Percent Report
    ==========================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1  13.379 MM    0.4016 1.43409e4  595.17163  94.8947
       2  17.008 MM    0.3939  771.53839   32.64733   5.1053

    Totals :                 1.51124e4   627.81896

    ==========================================================================
                              *** End of Report ***

    Instrument 1 6/20/2012 2:21:05 PM wuyw                          Page   1 of 1
```