Electronic Supplementary Material (ESI) for Chemical Communications.

Asymmetric Michael Addition of α-Fluoro-α-nitroalkanes to Nitroolefins: Facile Preparation of Fluorinated Amines and Tetrahydropyrimidines

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Supporting Information

A. General Information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. Solvent purification system was used to dry and purify toluene and diethyl ether while THF was dried and distilled from sodium benzophenone ketyl prior to use. $CHCl_3$ was distilled from CaH_2 prior to use. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker ACF300, AMX 400 or AMX500 (^{1}H and ^{13}C only) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0), fluorine $CFCl_3$ (AMX400) or TFA (ACF300). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL- T mass spectrometer in FAB mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with $KMnO_4$ aqueous solution or ninhydrine solution in ethanol, followed by heating with a heat gun. Flash chromatographic separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. The enantiomeric excesses of products were determined by chiral-phase HPLC analysis. Optical rotations were recorded on Jasco DIP-1000 Digital Polarimeter with 10 mm cell and 589 nm sodium lamp.

B. Preparation of Substrates and analytical data of new α-fluoro-α-nitroalkanes

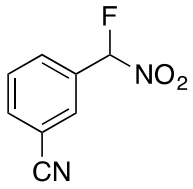
Nitroalkenes were prepared from respective aldehydes and nitromethane according to reported procedures.[1]

The α-fluoro-α-nitroalkanes were prepared form respective benzyl bromides by reacting with sodium nitrite and urea in DMF at -20 ^{o}C, according to previously reported procedure.[2] The fluorination was performed using selectfluor in acetonitrile/water (1/1) at room temperature over 12 h and KOH as base according to the reported procedure.[3] Yields of fluorination are high (>80%) however isolation is slightly more difficult for the 1-fluoro-1-aryl-nitromethanes having lower molecular weight due to their low boiling point. In such

[1] a) G. Kumaran, G. H. Kulkarni, *Tetrahedron Lett.*, 1994, **35**, 9099; b) J. Bourguignon, G. Le Nard, G. Queguiner, *Canadian Journal of Chemistry*, 1985, **63**, 2354.
[2] N. Kornblum , W. M. Weaver , *J. Am. Chem. Soc.,* 1958 , **80** , 4333.
[3] W. Peng, J. M. Shreeve, *Tetrahedron Letters*, 2005, **46**, 4905.

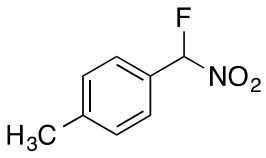
cases, pentane and diethyl ether were used instead of hexane and ethyl acetate for chromatographic purification and water pump instead of high vacuum pump to remove traces of solvents.

3-(Fluoro(nitro)methyl)benzonitrile (**1b**)



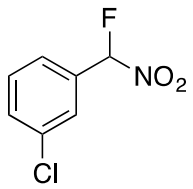
Yellow oil, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 4.8 Hz, 1H), 7.71 – 7.68 (m, 2H), 6.95 (d, J = 47.6 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 133.62, 133.52, 132.68, 132.41, 132.40, 126.72,115.49, 112.69, 106.65 (d, J = 241.3 Hz); ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -140.26 (d, J = 47.4 Hz); HRMS (ESI) m/z calcd for $C_8H_5FN_2O_2$ $[M]^-$=179.0257, found = 179.0251.

1-(Fluoro(nitro)methyl)-4-methylbenzene (**1c**)



Yellow oil, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.59 (d, J = 48.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 142.47, 129.75, 127.54, 127.33, 126.51, 126.45, 111.38, 109.00, 21.41; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -138.93 (d, J = 48.5 Hz); HRMS (ESI) m/z calcd for $C_8H_8FNO_2$ $[M]^+$= 168.0461, found = 168.0458.

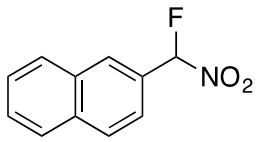
1-Chloro-3-(fluoro(nitro)methyl)benzene (**1d**)



Yellow oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.52 (d, J = 9.6 Hz, 2H), 7.43 (m, 1H), 6.58 (d, J = 48.4 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 135.31, 132.19, 130.48,

126.72, 126.65, 124.69, 124.63; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ −141.29 (d, J = 48.1 Hz); HRMS (ESI) m/z calcd for $C_{13}H_{14}FN_3O_4$ $[M]^-$=187.9915, found = 187.9899.

2-(Fluoro(nitro)methyl)naphthalene (**1e**)



Pale yellow solid, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.96 – 7.88 (m, 3H), 7.65 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.62 – 7.58 (m, 2H), 6.77 (d, J = 48.8 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 135.43, 134.38, 131.82, 129.41, 128.00, 127.92, 127.77, 127.54, 126.83; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -139.08 (d, J = 48.6 Hz); HRMS (ESI) m/z calcd for $C_{11}H_8FNO_2$ $[M]^-$ = 204.0461, found = 204.0532.

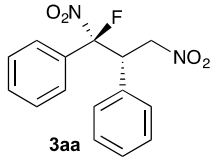
C. Representative procedure: Michael addition of ethyl fluoronitroacetate to nitroalkenes

To a sample vial containing 1-fluoro-1-aryl-nitromethane (0.1 mmol, **1a**-**f**) in toluene (1 mL), **9c** (0.01 mmol, 10 mg) was added. The vial was then capped and the reaction mixture was stirred at 0 ^{o}C for 5 minutes. Subsequently nitroalkene (0.11 mmol) was added in one portion under nitrogen protection, the vial was sealed and the reaction mixture was stirred at 0 ^{o}C for the time indicated. Upon completion of the reaction, the mixture was passed through a short silica gel column, and then concentrated and analyzed by ^{1}H NMR. The crude product was then subjected to column chromatographic separation eluting with hexane/ethyl acetate (20:1 – 10:1) to afford the diastereomerically pure Michael products (**3aa**–**bk**).

D. Analytical Data and HPLC Chromatograms of the Michael Reaction Products

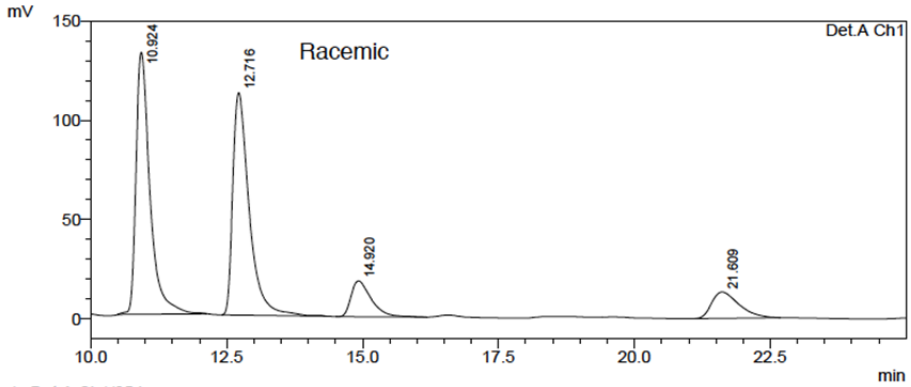
All products could be obtained in diastereoselectively pure form upon simple flush chromatography on a silica gel column with exception of **3ag** and **3bk** where only partial separation of diastereomers was achieved (trace amount of the minor diastereomer can also be detected in case of **3ei** and **3ac**).

((1S,2S)-1-Fluoro-1,3-dinitropropane-1,2-diyl)dibenzene (**3aa**)



3aa

White solid. $[\alpha]^{270}_{D}$ = +51.6 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.87 (m, 2H), 7.58 – 7.54 (m, 3H), 7.44 – 7.42 (m, 2H), 7.39 – 7.37 (m, 3H), 5.10 (ddd, J = 38.4 Hz, 10.8 Hz, 4.0 Hz, 1H), 4.77 (dd, J = 13.6 Hz, 10.8 Hz, 1H), 4.49 (dd, J = 13.2 Hz, 3.6 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 131.91, 131.01, 130.78, 130.71, 129.62, 129.61, 129.59, 129.53, 129.51, 129.19, 125.41, 125.31, 118.90 (d, J = 244.1 Hz), 75.33 (d, J = 2.1 Hz), 50.14 (d, J = 18.3 Hz); ^{19}F NMR (376.46 Hz, $CDCl_3$) δ −136.63 (d, J = 31.6 Hz); HRMS (ESI) m/z calcd for $C_{15}H_{12}FN_2O_4$ $[M-H]^-$ = 303.8787, found = 303.8789; the ee value was 90%, t_R (major) = 12.1 min, t_R (minor) = 10.6 min (Chiralcel IB, λ = 254 nm, 10% *i*PrOH/hexanes, flow rate = 1 mL/min).

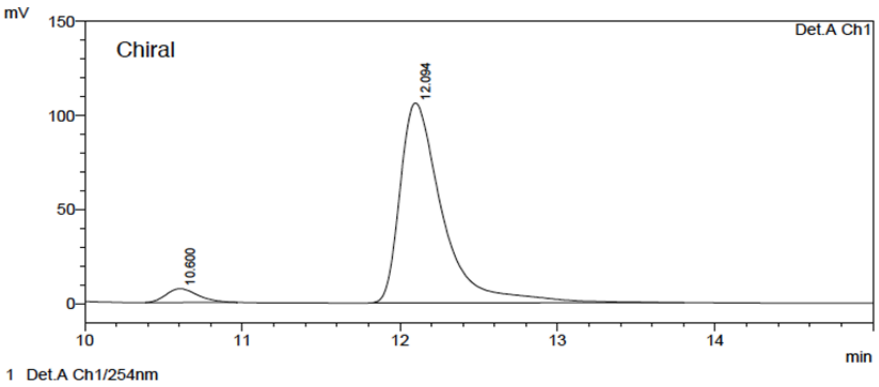


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.924	2355184	131979	41.750	47.952
2	12.716	2355064	112014	41.748	40.698
3	14.920	466296	18015	8.266	6.545
4	21.609	464593	13224	8.236	4.805
Total		5641137	275232	100.000	100.000

Racemic **3aa**



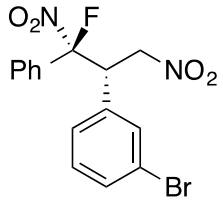
PeakTable

Detector A Ch1 254nm

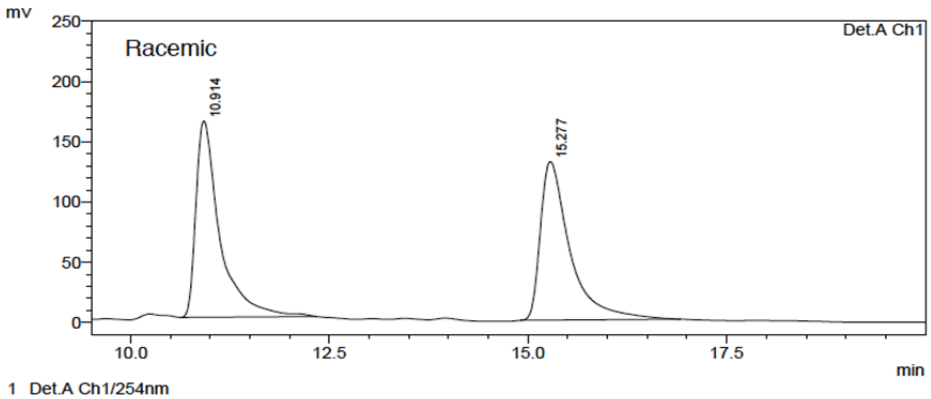
Peak#	Ret. Time	Area %
1	10.600	4.878
2	12.094	95.122
Total		100.000

Enantiomerically enriched **3aa**

1-Bromo-3-((1*S*,2*S*)-1-fluoro-1,3-dinitro-1-phenylpropan-2-yl)benzene (**3ae**)



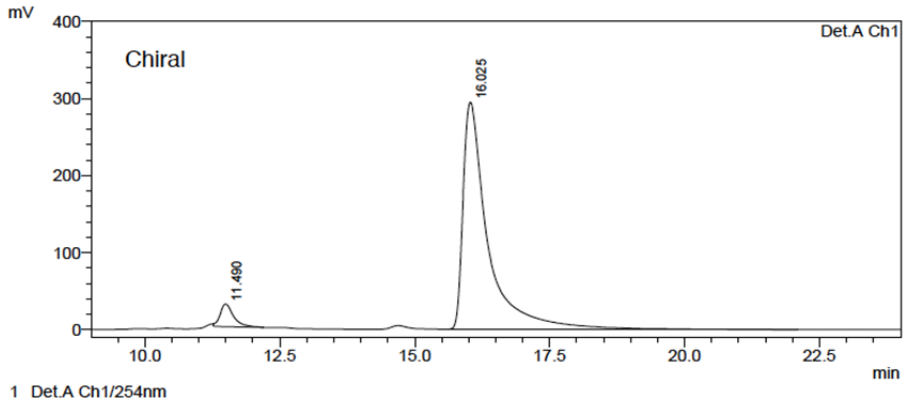
Pale yellow oil. $[\alpha]^{270}_{D}$ = +53.1 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 7.61 – 7.53 (m, 5H), 7.39 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 5.08 (ddd, J = 30.8 Hz, 10.8 Hz, 3.6 Hz, 1H), 4.74 (dd, J = 13.6 Hz, 10.8 Hz, 1H); 4.49 (dd, J = 14.0 Hz, 4.0 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 132.92, 132.51, 132.08, 130.68, 130.41, 128.27, 128.25, 125.30, 125.20, 123.17, 118.64 (d, J = 244.3 Hz), 75.09, 49.65 (d, J = 18.4 Hz); ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -136.55 (d, J = 30.8 Hz); HRMS (ESI) m/z calcd for $C_{15}H_{11}BrFN_2O_4$ $[M\text{-}H]^-$ = 380.0892, found = 380.9873; the ee value was 90%, t_R (major) = 16.0 min, t_R (minor) = 11.5 min (Chiralcel IB, λ = 254 nm, 10% *i*PrOH/hexanes, flow rate = 1 mL/min).



PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	10.914	50.028
2	15.277	49.972
Total		100.000

Racemic **3ae**



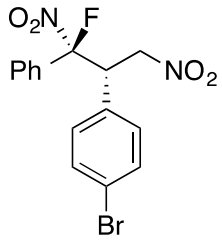
PeakTable

Detector A Ch1 254nm

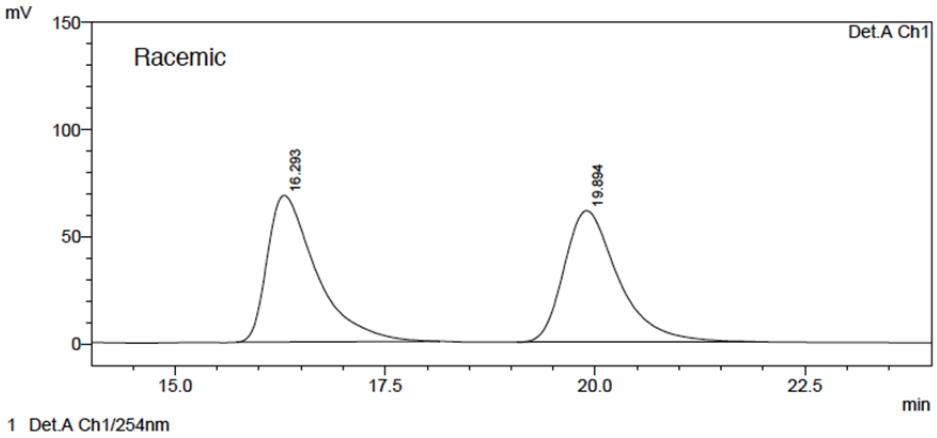
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.490	506512	29286	5.078	9.041
2	16.025	9467853	294642	94.922	90.959
Total				100.000	

Enantiomerically enriched **3ae**

1-Bromo-4-((1*S*,2*S*)-1-fluoro-1,3-dinitro-1-phenylpropan-2-yl)benzene (**3ab**)



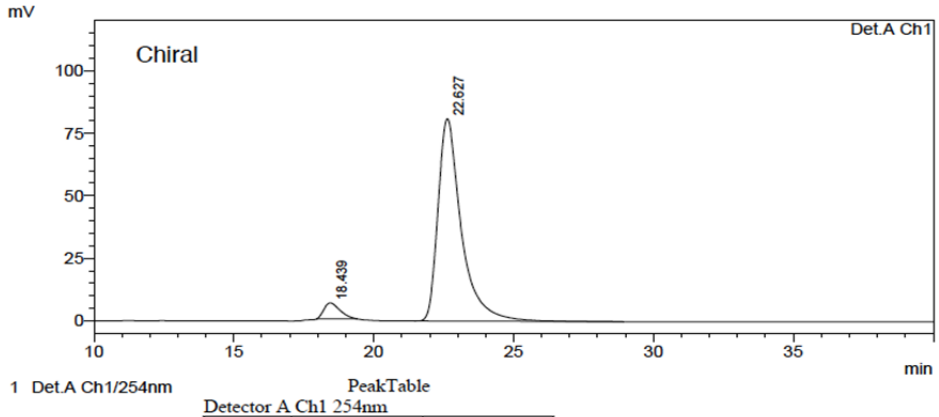
White solid. $[\alpha]^{270}_{D}$ = +22.2 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.6 Hz, 1.2 Hz, 2H), 7.58 – 7.51 (m, 5H), 7.31 (dd, J = 8.4 Hz, 1.6 Hz, 2H), 5.07 (ddd, J = 30.8 Hz, 10.8 Hz, 3.6 Hz, 1H), 4.72 (dd, J = 13.2 Hz, 10.8 Hz, 1H); 4.47 (dd, J = 13.6 Hz, 3.6 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 132.48, 132.07, 131.14, 131.1, 130.07, 130.42, 129.70, 129.68, 125.31, 125.21, 124.16, 118.64 (d, J = 244.2 Hz), 75.08, 49.65 (d, J = 18.5 Hz); ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -136.77 (d, J = 30.9 Hz); HRMS (ESI) m/z calcd for $C_{15}H_{11}BrFN_2O_4$ $[M\text{-}H]^-$ = 380.9892, found = 380.9880; the ee value was 90%, t_R (major) = 22.6 min, t_R (minor) = 18.4 min (Chiralcel AD-H, λ = 254 nm, 2% *i*PrOH/hexanes, flow rate = 1 mL/min).



PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	16.293	50.203
2	19.894	49.797
Total		100.000

Racemic **3ab**

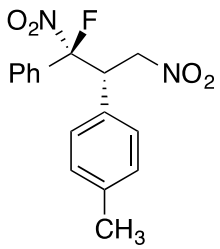


PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	18.439	5.124
2	22.627	94.876
Total		100.000

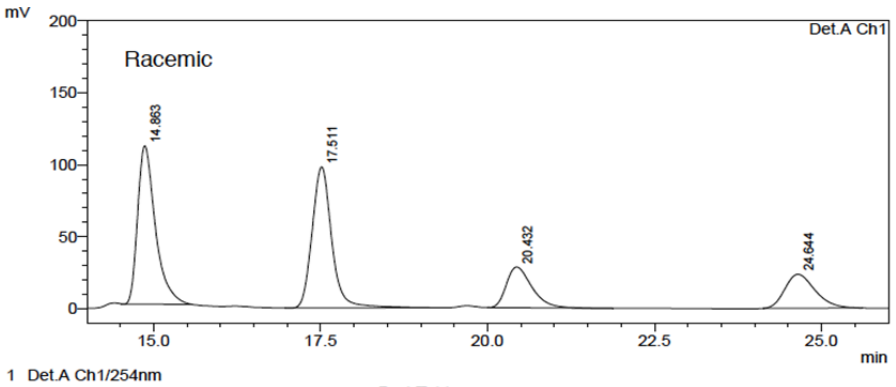
Enantiomerically enriched **3ab**

1-((1S,2S)-1-Fluoro-1,3-dinitro-1-phenylpropan-2-yl)-4-methylbenzene (**3ac**)



Pale yellow oil. $[\alpha]^{270}_{D}$ = +65.4 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, J = 8.4 Hz, 1.6 Hz, 2H), 7.55 (m, 3H), 7.30 (dd, J = 8.4 Hz, 1.6 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.06 (ddd, J = 31.6 Hz, 10.8 Hz, 4.0 Hz, 1H), 4.75 (dd, J = 11.2 Hz, 10.8 Hz, 1H); 4.47 (dd, J = 13.2 Hz, 3.6 Hz,

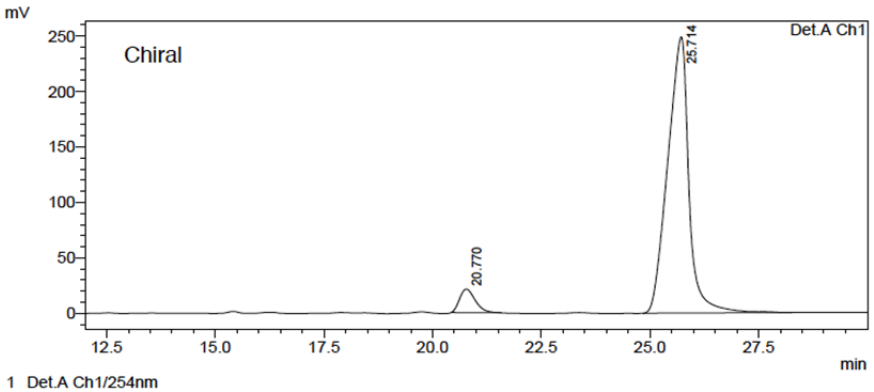
1H), 2.33 (s, 3H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 131.85, 131.09, 130.86, 129.89, 129.57, 129.55, 129.35, 128.71, 127.55, 125.42, 118.98 (d, J = 244.2 Hz), 75.40, 49.85 (d, J = 18.5 Hz), 21.13 ; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -136.70 (d, J = 31.5 Hz); HRMS (ESI) m/z calcd for $C_{16}H_{15}FN_2O_4$ $[M-H]^-$ = 317.0943, found = 317.0949; the ee value was 88%, t_R (major) = 25.7 min, t_R (minor) = 20.8 min (Chiralcel IA, λ = 254 nm, 10% *i*PrOH/hexanes, flow rate = 1 mL/min).



PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.863	36.660
2	17.511	36.276
3	20.432	13.617
4	24.644	13.447
Total		100.000

Racemic **3ac**

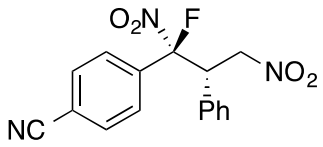


PeakTable
Detector A Ch1 254nm

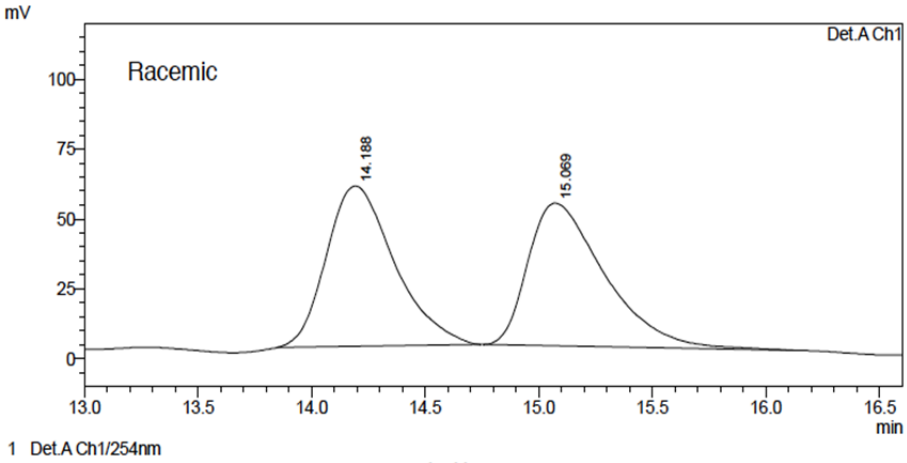
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.770	532247	21239	5.929	7.856
2	25.714	8444573	249130	94.071	92.144
Total		8976820	270369	100.000	100.000

Enantiomerically enriched **3ac**

4-((1S,2S)-1-Fluoro-1,3-dinitro-2-phenylpropyl)benzonitrile (**3ba**)



Pale yellow oil. $[\alpha]^{270}_{D}$ = +68.2 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.40 (s, 5H), 5.05 (ddd, J = 31.6 Hz, 10.4 Hz, 4.4 Hz, 1H), 4.75 (dd, J = 13.6 Hz, 10.0 Hz, 1H); 4.44 (dd, J = 13.6 Hz, 4.4 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 135.19, 134.95, 133.21, 133.19, 130.07, 129.95, 129.37, 129.34, 126.55, 126.44 117.94 (d, J = 245.9 Hz), 117.09, 116.22, 74.89, 50.14 (d, J = 18.4 Hz) ; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -136.70 (d, J = 31.2 Hz); HRMS (ESI) m/z calcd for $C_{32}H_{22}F_2NaN_6O_8$ $[2M-2H+Na]^-$ = 679.1370, found = 679.1342; the ee value was 88%, t_R (major) = 17.3 min, t_R (minor) = 16.4 min (Chiralcel IB+ID, λ = 254 nm, 10% *i*PrOH/hexanes, flow rate = 1 mL/min).

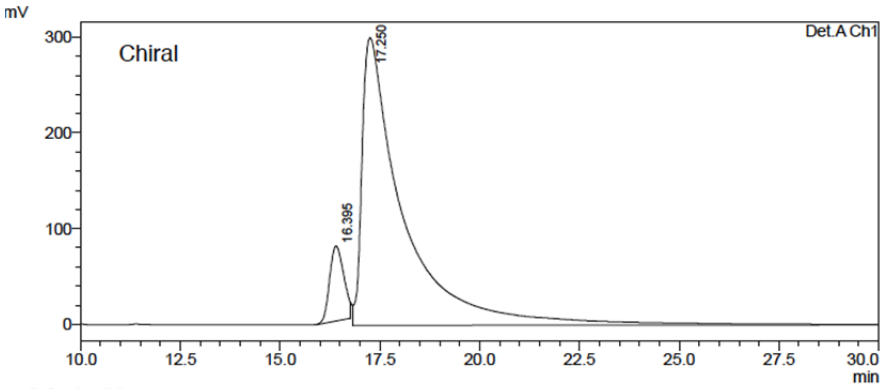


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.188	49.885
2	15.069	50.115
Total		100.000

Racemic **3ba**



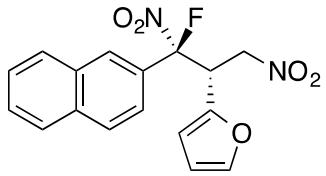
PeakTable

Detector A Ch1 254nm

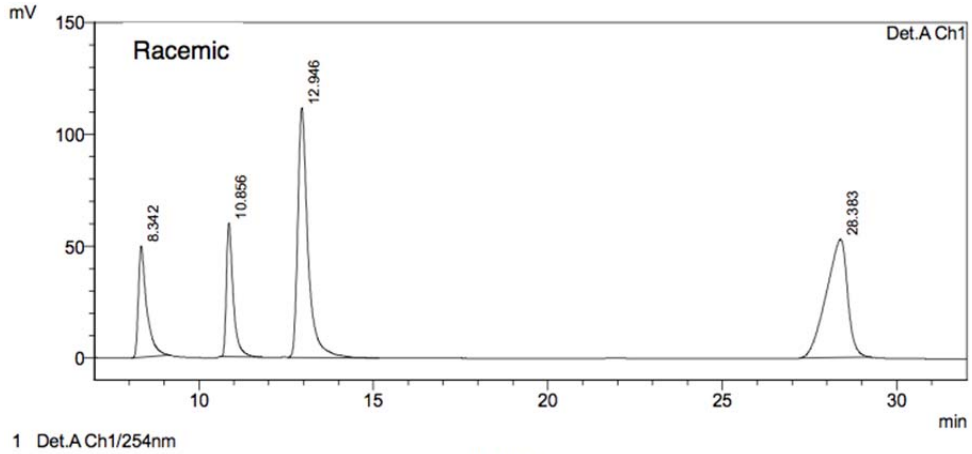
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.395	1919795	77956	8.025	20.623
2	17.250	22003265	300055	91.975	79.377
Total		23923060	378010	100.000	100.000

Enantiomerically enriched **3ba**

2-((1*S*,2*R*)-1-Fluoro-1-(naphthalen-2-yl)-1,3-dinitropropan-2-yl)furan (**3ei**)



Pale yellow solid. $[\alpha]^{270}_{D}$ = +40.1 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 1.6 Hz, 1H), 8.08 – 7.92 (m, 3H), 7.67 – 7.61 (m, 3H), 7.48 (dd, J = 6.8 Hz, 1.6 Hz, 1H), 7.36 – 7.32 (m, 2H), 6.12 – 6.01 (m, 1H), 4.83 – 4.71 (m, 1H), 4.59 (dd, J = 13.2 Hz, 4.0 Hz, 1H); ^{13}C NMR (100.62 Hz,$CDCl_3$)δ 134.43, 132.42, 130.71, 130.41, 129.93, 128.94, 128.77, 128.58, 127.83, 127.72, 127.62, 126.31, 121.32, 118.67 (d, J = 245.6 Hz), 75.50, 45.16 (d, J = 18.0 Hz) ; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -134.92 (d, J = 30.8 Hz); HRMS (ESI) m/z calcd for $C_{17}H_{12}FN_2O_5$ $[M-H]^-$ = 343.0736, found = 343.0738; the ee value was 88%, t_R (major) = 15.4 min, t_R (minor) = 34.5 min (Chiralcel IB, λ = 254 nm, 10% *i*PrOH/hexanes, flow rate = 1 mL/min).

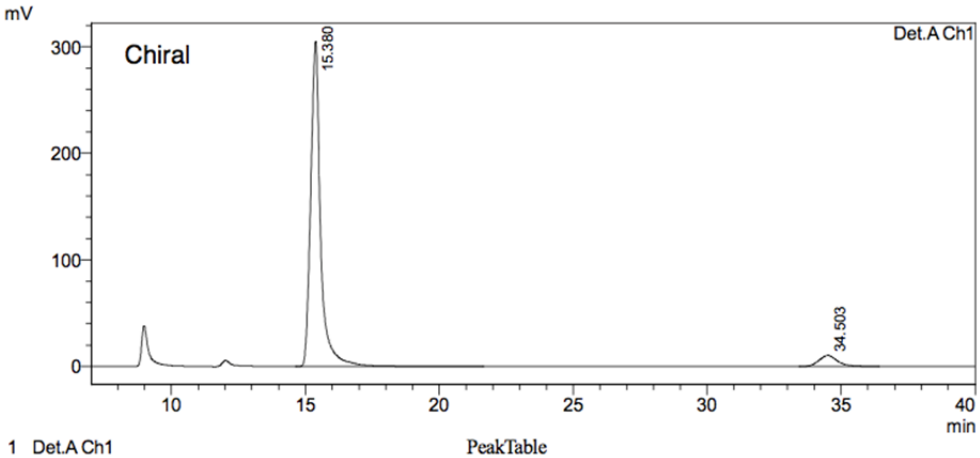


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.342	832316	50013	13.477	18.190
2	10.856	817791	59929	13.242	21.796
3	12.946	2273086	111974	36.807	40.725
4	28.383	2252468	53038	36.473	19.290
Total		6175661	274953	100.000	100.000

Racemic **3ei**



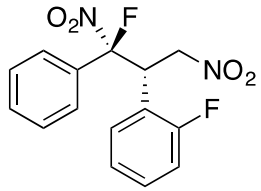
PeakTable

Detector A Ch1 254nm

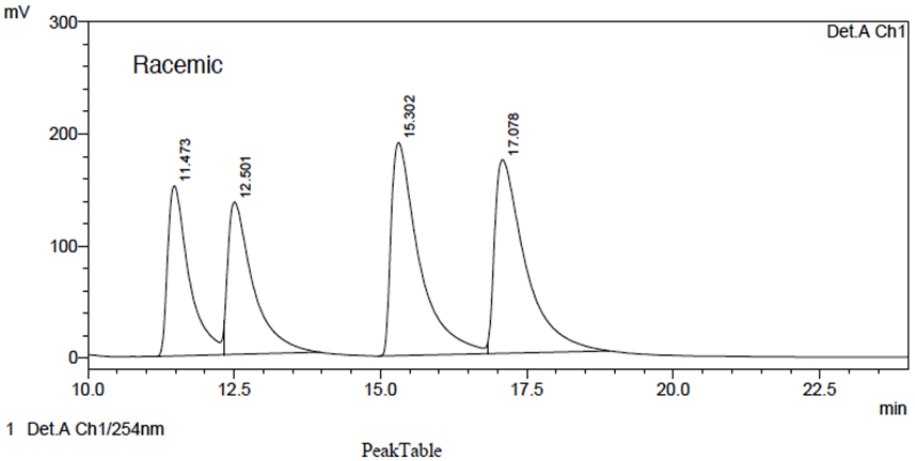
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.380	7856621	305096	94.008	96.723
2	34.503	500814	10335	5.992	3.277
Total		8357435	315431	100.000	100.000

Enantiomerically enriched **3ei**

1-Fluoro-2-((1*S*,2*S*)-1-fluoro-1,3-dinitro-1-phenylpropan-2-yl)benzene (**3ag**)



Pale yellow oil. $[\alpha]^{270}_{D}$ = +45.0 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.48 – 7.40 (m, 1H), 7.39 – 7.34 (m, 1H), 7.21 – 7.10 (m, 2H), 5.53 (ddd, J = 30.0 Hz, 10.0 Hz, 3.6 Hz, 1H), 4.80 (dd, J = 13.6 Hz, 10.4 Hz, 1H); 4.52 (dd, J = 14.0 Hz, 4.0 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 162.39, 132.02, 131.60, 131.51, 129.84, 129.59, 128.04, 125.44, 125.34, 124.93, 118.75 (d, J = 245.7 Hz), 116.67, 116.44, 74.52 (d, 2.0 Hz), 43.43 (d, J = 18.8 Hz); ^{19}F NMR (376.46 Hz, $CDCl_3$) δ −114.29, -135.93 (dd, J = 31.2 Hz, 14.7 Hz); HRMS (ESI) m/z calcd for $C_{15}H_{11}F_2N_2O_4$ $[M\text{-}H]^-$ = 321.0692, found = 321.0687; the ee value was 85%, t_R (major) = 18.8 min, t_R (minor) = 17.7 min (Chiralcel IB, λ = 254 nm, 2% *i*PrOH/hexanes, flow rate = 1 mL/min).

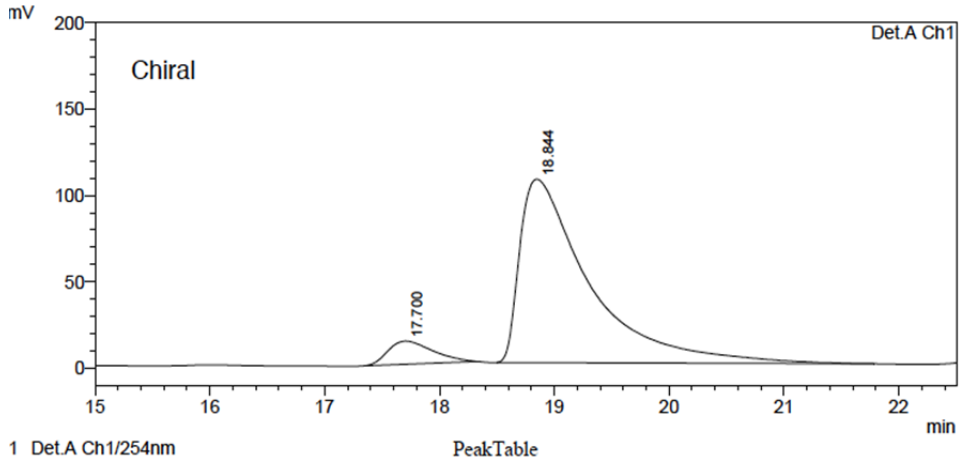


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	11.473	19.026
2	12.501	19.593
3	15.302	30.787
4	17.078	30.594
Total		100.000

Racemic **3ag**



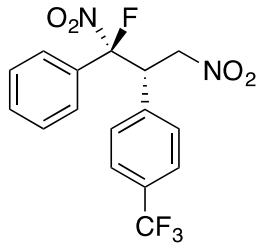
PeakTable

Detector A Ch1 254nm

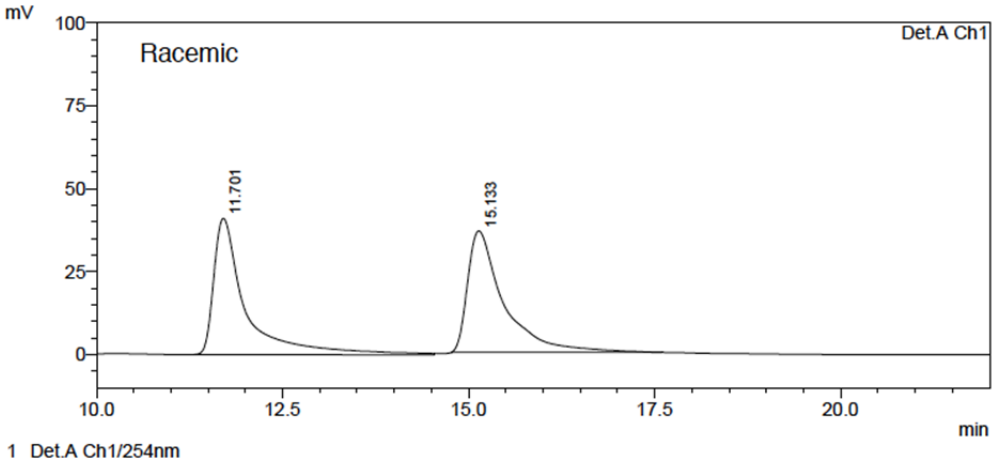
Peak#	Ret. Time	Area %
1	17.700	7.468
2	18.844	92.532
Total		100.000

Enantiomerically enriched **3ag**

1-((1S,2S)-1-Fluoro-1,3-dinitro-1-phenylpropan-2-yl)-4-(trifluoromethyl)benzene (**3ad**)



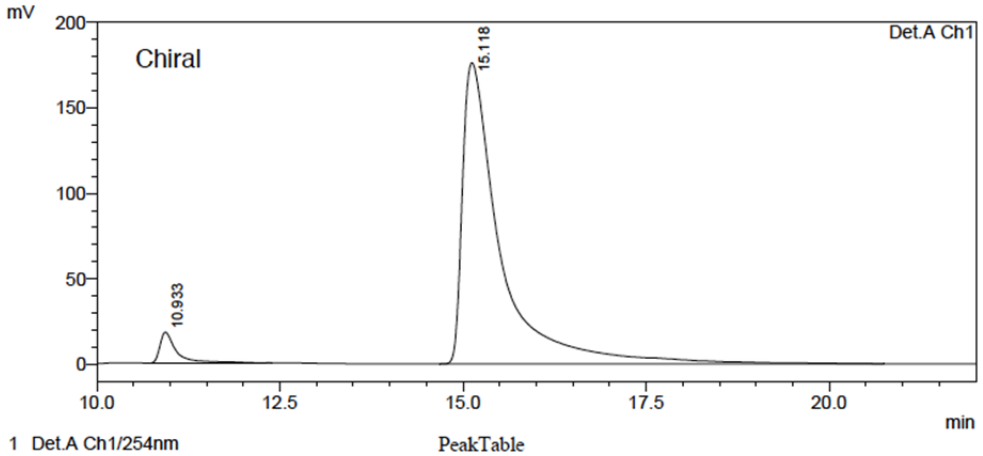
Pale yellow oil. $[\alpha]^{270}_{D}$ = +61.9 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.59 (m, 5H), 5.19 (ddd, J = 31.2 Hz, 11.2 Hz, 3.6 Hz, 1H), 4.77 (dd, J = 13.6 Hz, 10.8 Hz, 1H); 4.51 (dd, J = 13.6 Hz, 3.8 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 134.83, 132.18, 131.73, 130.51, 130.28, 130.07, 129.77, 126.21, 126.17, 125.29, 125.19, 124.93, new 118.62 (d, J = 244.7 Hz), 75.00, 49.85 (d, J = 18.6 Hz) ; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ −63.02, -136.54 (d, J = 30.8 Hz); HRMS (ESI) m/z calcd for $C_{16}H_{13}F_4N_2O_5$ $[M\text{-}H]^-$ = 371.0660, found = 371.0650; the ee value was 91%, t_R (major) = 15.1 min, t_R (minor) = 10.9 min (Chiralcel IB, λ = 254 nm, 10% *i*PrOH/hexanes, flow rate = 1 mL/min).



PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	11.701	49.979
2	15.133	50.021
Total		100.000

Enantiomerically enriched **3ad**

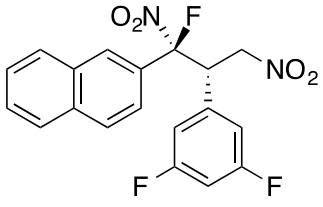


PeakTable
Detector A Ch1 254nm

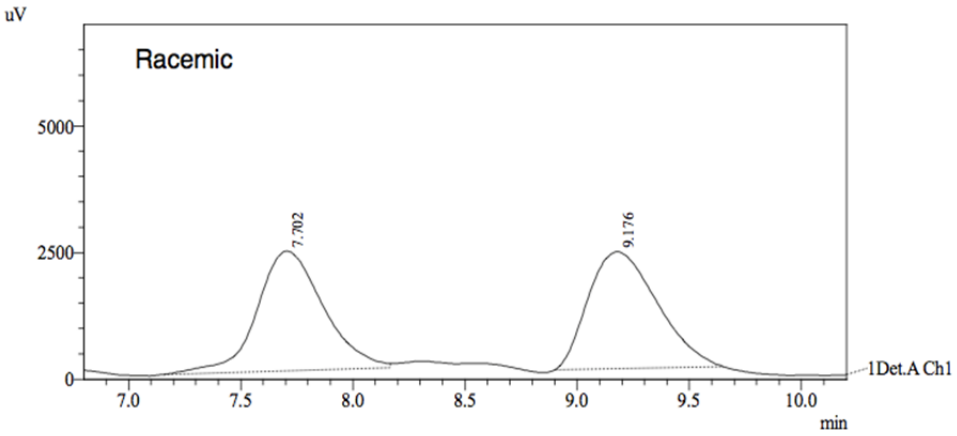
Peak#	Ret. Time	Area %
1	10.933	4.442
2	15.118	95.558
Total		100.000

Enantiomerically enriched **3ad**

2-((1*S*,2*S*)-2-(3,5-Difluorophenyl)-1-fluoro-1,3-dinitropropyl)naphthalene (**3eh**)



Pale yellow solid. $[\alpha]^{270}_{D}$ = +58.1 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 2.0 Hz, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.95 (dd, J = 6.8 Hz, 3.6 Hz, 2H), 7.88 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.65 (m, 2H), 7.04 (dd, J = 5.6 Hz, 1.2 Hz, 2H), 6.90 – 6.84 (m, 1H), 5.23 (ddd, J = 30.0 Hz, 10.8 Hz, 3.6 Hz, 1H), 4.73 (dd, J = 14.0 Hz, 11.2 Hz, 1H); 4.50 (dd, J = 13.6 Hz, 3.6 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 164.35 (d, J = 12.6 Hz), 161.85 (d, J = 12.5 Hz), 134.48, 134.33, 132.51, 130.22, 128.92, 128.76, 127.87, 127.38, 127.15, 126.17, 126.06, 118.67 (d, J = 244.9 Hz), 113.14, 112.85, 105.56, 75.00, 49.65 (d, J = 18.5 Hz); ^{19}F NMR (376.46 Hz, $CDCl_3$) δ −107.20, -135.87 (d, J = 30.1 Hz); HRMS (ESI) m/z calcd for $C_{19}H_{12}F_3N_2O_4$ $[M\text{-}H]^-$ = 389.0755, found = 389.0757; the ee value was 96%, t_R (major) = 7.7 min, t_R (minor) = 9.1 min (Chiralcel AD-H, λ = 254 nm, 5% *i*PrOH/hexanes, flow rate = 1 mL/min).

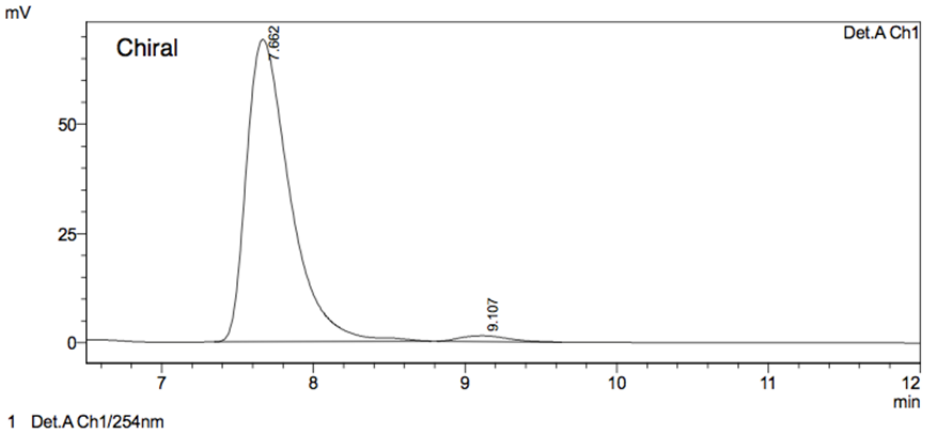


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.702	49019	2364	49.818	50.604
2	9.176	49377	2307	50.182	49.396
Total		98396	4671	100.000	100.000

Enantiomerically enriched **3eh**



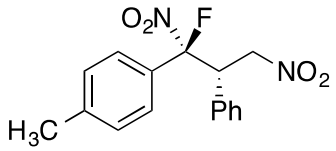
PeakTable

Detector A Ch1 254nm

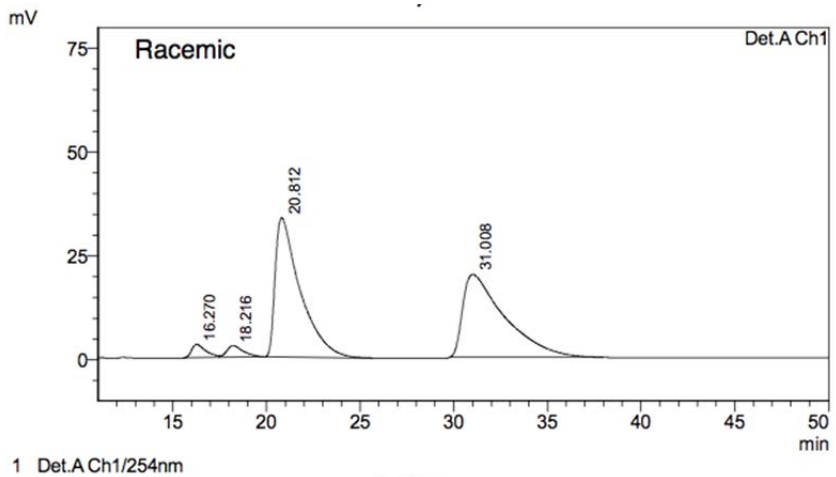
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.662	1373964	69172	97.968	98.138
2	9.107	28494	1313	2.032	1.862
Total		1402458	70485	100.000	100.000

Enantiomerically enriched **3eh**

1-((1*S*,2*S*)-1-Fluoro-1,3-dinitro-2-phenylpropyl)-4-methylbenzene (**3ca**)



Pale yellow oil. $[\alpha]^{270}_{D}$ = +95.1 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 8.4 Hz, 1.6 Hz, 2H), 7.42 (m, 2H), 7.38 – 7.34 (m, 5H), 5.08 (ddd, J = 31.2 Hz, 10.8 Hz, 3.6 Hz, 1H), 4.75 (dd, J = 13.6 Hz, 10.8 Hz, 1H); 4.50 (dd, J = 13.2 Hz, 3.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 142.45, 130.84, 130.23, 130.22, 129.55, 129.53, 129.50, 129.15, 128.14, 127.91, 125.33, 125.23, 119.11 (d, J = 243.7 Hz), 75.44, 50.10 (d, J = 18.3 Hz), 21.29; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -136.54 (d, J = 31.2 Hz); HRMS (ESI) m/z calcd for $C_{32}H_{28}F_2NaN_4O_8$ $[2M-2H+Na]^-$ = 657.1778, found = 657.1794; the ee value was 90%, t_R (major) = 30.6 min, t_R (minor) = 20.6 min (Chiralcel IB, λ = 254 nm, 2% *i*PrOH/hexanes, flow rate = 1 mL/min).



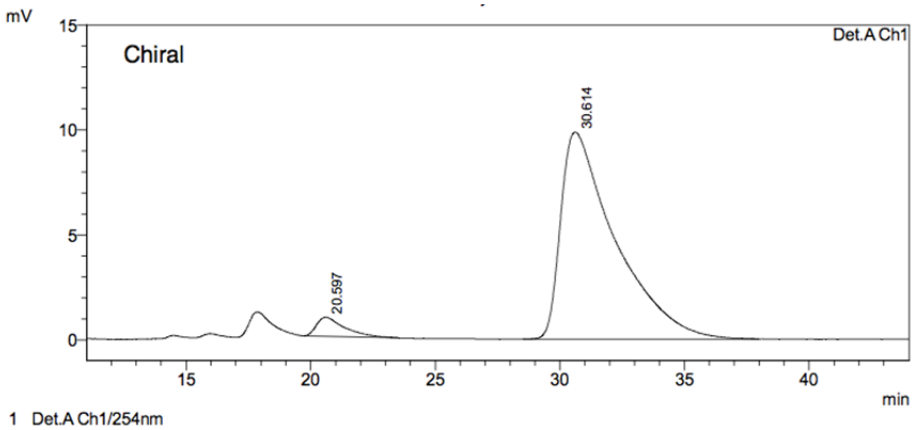
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.270	173056	3244	2.629	5.436
2	18.216	171878	2813	2.611	4.713
3	20.812	3115365	33599	47.332	56.298
4	31.008	3121694	20026	47.428	33.554
Total		6581993	59681	100.000	100.000

Racemic **3ca**



1 Det.A Ch1/254nm

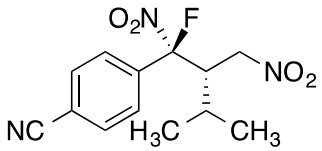
PeakTable

Detector A Ch1 254nm

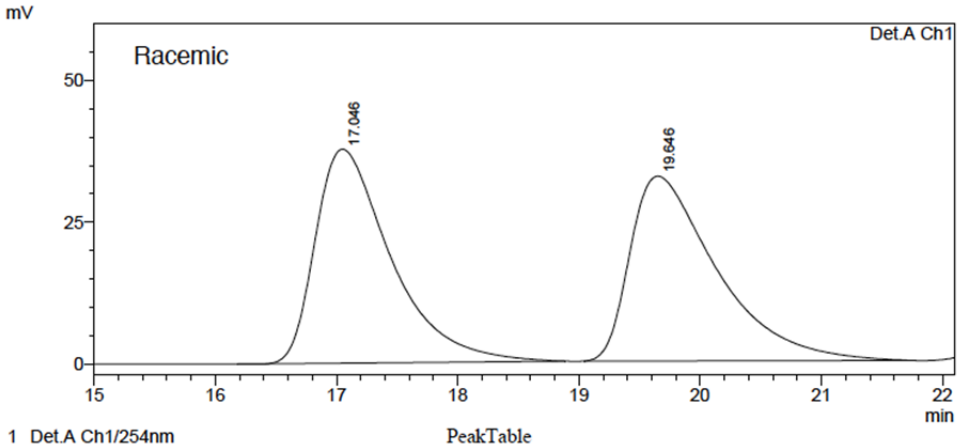
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.597	71233	907	4.533	8.420
2	30.614	1500079	9865	95.467	91.580
Total		1571312	10772	100.000	100.000

Enantiomerically enriched **3ca**

4-((1*S*,2*S*)-1-Fluoro-3-methyl-1-nitro-2-(nitromethyl)butyl)benzonitrile (**3bk**)



Pale yellow oil. $[\alpha]^{270}_{D}$ = +45.5 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 7.8 Hz, 2H), 7.77 (t, J = 7.6 Hz, 2H), 4.43 (dd, J = 14.4 Hz, 4.8 Hz, 1H), 4.16 (dd, J = 14.4 Hz, 5.6 Hz, 1H), 3.99 (dtd, J = 34.0 Hz, 5.2 Hz, 2.4 Hz, 1H), 2.06 (m, 1H), 1.10 (d, J = 6.8 Hz, 3H), 1.05 (dd, J = 6.8 Hz, 2.0 Hz, 3H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 135.42, 132.83, 127.21, 126.60, 126.49, 120.29 (d, J = 247.98 Hz), 117.20, 115.96, 70.76, 48.20 (d, J = 19.1 Hz), 27.86, 21.88, 17.56; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ −137.87 (d, J = 33.8 Hz); HRMS (ESI) m/z calcd for $C_{13}H_{13}FN_3O_4$ $[M\text{-}H]^-$ = 294.0896, found = 294.0893; the ee value was 82%, t_R (major) = 17.1 min, t_R (minor) = 19.8 min (Chiralcel AD-H, λ = 254 nm, 5% *i*PrOH/hexanes, flow rate = 1 mL/min).

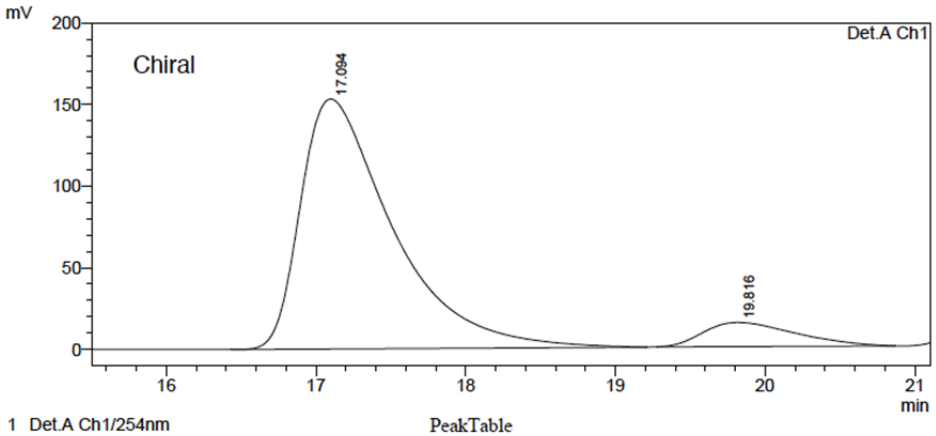


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	17.046	50.235
2	19.646	49.765
Total		100.000

Racemic **3bk**



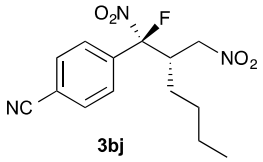
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	17.094	91.190
2	19.816	8.810
Total		100.000

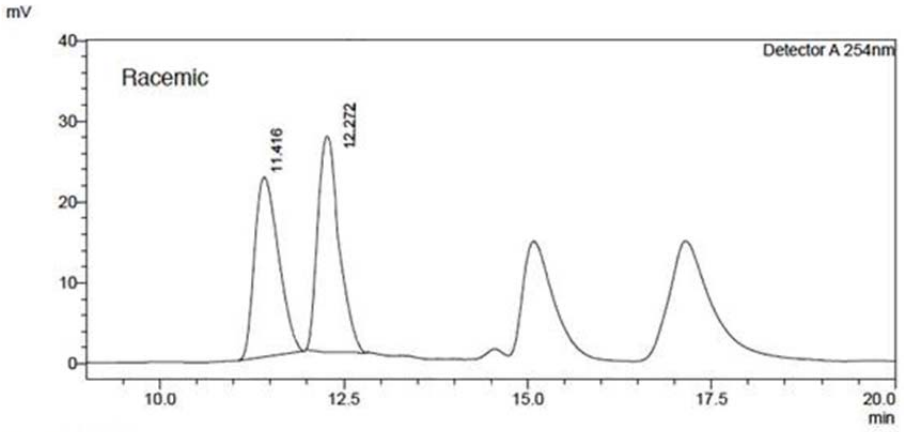
Enantiomerically enriched **3bk**

4-((1S,2S)-1-Fluoro-1-nitro-2-(nitromethyl)hexyl)benzonitrile (**3bj**)



3bj

Pale yellow oil. $[\alpha]^{270}_{D}$ = +72.0 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.70 (m, 4H), 4.33 – 4.20 (m, 2H), 3.94 (dd, J = 30.4 Hz, 5.2 Hz, 1H), 1.62 – 1.34 (m, 7H), 0.91 (m, 2H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 135.22, 132.95, 126.50, 119.36 (d, J = 244.5 Hz), 117.17, 115.99, 74.03 (d, J = 4.2 Hz), 43.90 (d, J = 20.6 Hz), 28.32, 26.99, 22.32, 13.60; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ −139.01 (d, J = 31.6 Hz); HRMS (ESI) m/z calcd for $C_{14}H_{15}FN_3O_4$ $[M\text{-}H]^-$ = 308.1052, found = 308.1053; the ee value was 82%, t_R (major) = 12.5 min, t_R (minor) = 11.4 min (Chiralcel ID, λ = 254 nm, 5% *i*PrOH/hexanes, flow rate = 1 mL/min).

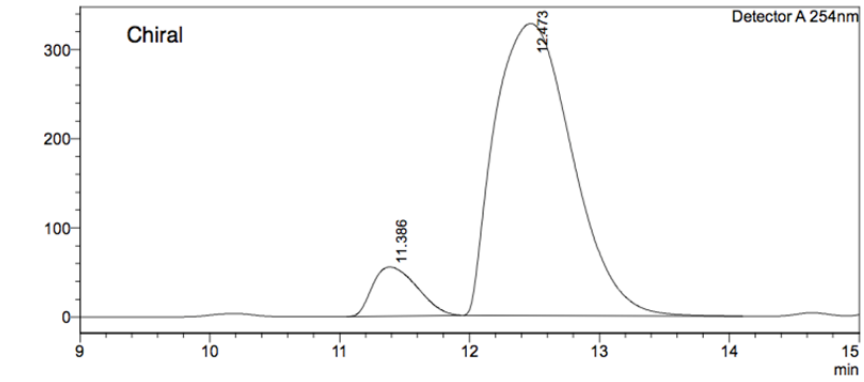


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area%
1	11.416	45.787
2	12.272	54.213
Total		100.000

Racemic **3bj**



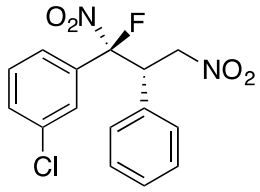
<Peak Table>

Detector A 254nm

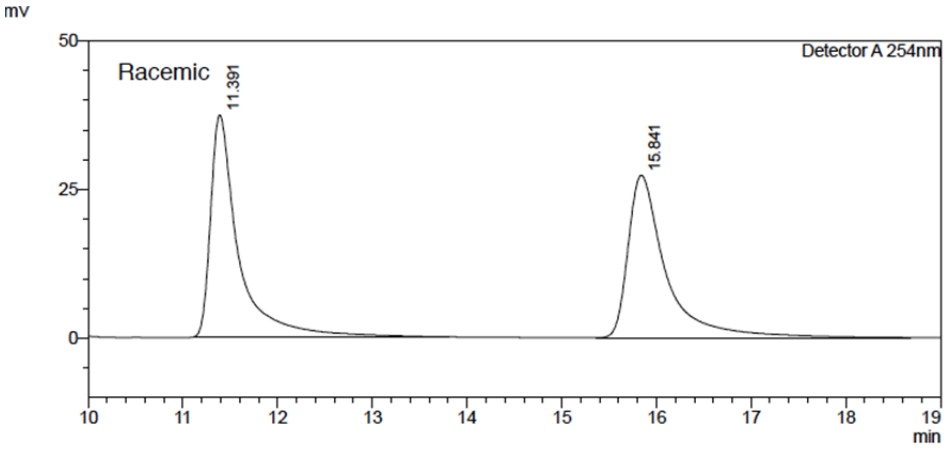
Peak#	Ret. Time	Area%
1	11.386	8.818
2	12.473	91.182
Total		100.000

Enantiomerically enriched **3bj**

1-Chloro-3-((1*S*,2*S*)-1-fluoro-1,3-dinitro-2-phenylpropyl)benzene (**3da**)



Pale yellow oil. $[\alpha]^{270}_{D}$ = +81.3 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (m, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 2Hz, 1H), 7.40 – 7.26 (m, 5H), 5.03 (ddd, J = 31.2 Hz, 10.8 Hz, 4.0 Hz, 1H), 4.78 (dd, J = 13.6 Hz, 10.8 Hz, 1H), 4.48 (dd, J = 13.6 Hz, 4.0 Hz, 1H); ^{13}C NMR (100.62 Hz, $CDCl_3$) δ 135.95, 132.76, 132.53, 132.22, 130.94, 130.93, 130.35, 129.78, 129.46, 129.44, 129.27, 125.80, 123.70, 118.07 (d, J = 245.36 Hz), 75.10, 50.19 (d, J = 18.40 Hz); ^{19}F NMR (376.46 Hz, $CDCl_3$) δ −136.29 (d, J = 31.2 Hz); HRMS (ESI) m/z calcd for $C_{15}H_{11}ClFN_2O_4$ $[M-H]^-$ = 337.0397, found = 337.0392; the ee value was 87%, t_R (major) = 15.8 min, t_R (minor) = 11.4 min (Chiralcel IB, λ = 254 nm, 10% *i*PrOH/hexanes, flow rate = 1 mL/min).

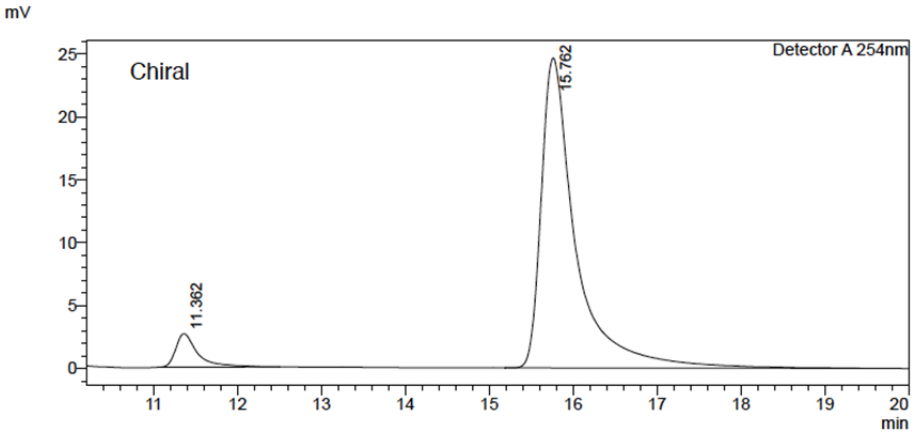


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area%
1	11.391	50.082
2	15.841	49.918
Total		100.000

Racemic **3da**



<Peak Table>

Detector A 254nm

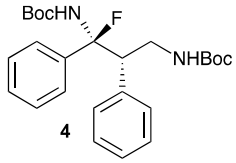
Peak#	Ret. Time	Area%
1	11.362	6.407
2	15.762	93.593
Total		100.000

Enantiomerically enriched **3da**

E. Catalytic hydrogenation and analytical data of fluoroamine **4**

Experimental procedure:

Michael adduct (**3aa**, 0.2 mmol, 61 mg) was dissolved in MeOH (2 ml). Boc anhydride was then added (2.5 equiv. 109 mg), followed by 2-3 drops of glacial acetic acid, $Pd/BaSO_4$ (5 mol% Pd, 0.01 mmol, 21.3 mg of 5 wt% $Pd/BaSO_4$) and freshly activated 4 Å molecular sieves (~20 mg). The reaction mixture was placed in autoclave and stirred for 48 h at 15 atm H_2 with stirring at room temperature. After that time, the reaction mixture was filtered through celite and concentrated *in vacuo*, below 20 °C.[4] The crude reaction mixture was purified on silica gel column eluting with hexane/chloroform (10/1). The pure product was obtained as a pale yellow oil (55 mg, 62%).



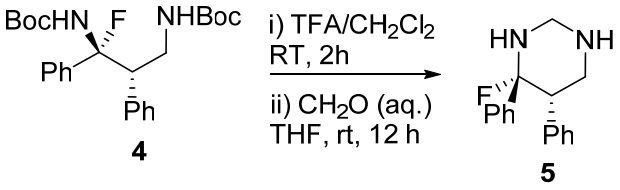
4

Yellow oil. $[\alpha]^{270}_D$ = -52.0 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (m, 2H), 7.49 (m, 3H), 7.42 (m, 2H), 7.36 - 7.30 (m, 3H), 4.59 (ddd, J = 32.8 Hz, 10.4 Hz, 3.6 Hz, 1H), 4.13 (m, 1H), 3.73 (m, 1H), 1.44 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (125 Hz, $CDCl_3$) δ 151.72, 151.70, 133.27,

[4] Heating should be avoided and it is recommended to remove acetic acid together with solvent to avoid defluorination - thus the use of vaccum; other work-up procedures resulted in lower isolated yield of product.

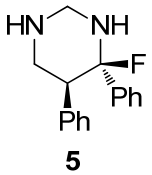
132.30, 132.11, 131.12, 129.98, 120.06, 128.60, 128.55, 125.59, 125.51, 120.24 (d, J = 246.2 Hz), 85.17, 82.62, 50.52, 49.76 (d J = 18.1 Hz), 27.83, 27.54; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -137.84 (d, J = 32.7 Hz); HRMS (ESI) m/z calcd for $C_{25}H_{34}FN_2O_4$ $[M+H]^+$ = 445.2503, found = 445.2504.

F. Preparation of tetrahydropyrimidine (**5**) and analytical data



Experimental procedure:

Diamine **4** (0.1 mmol, 44 mg) was dissolved in CH_2Cl_2 (2 mL) and 0.2 mL of TFA was added dropwise while stirring at room temperature. The reaction was stirred for an additional 2 h. The reaction was quenched by addition of water (2 mL), diluted with CH_2Cl_2 and brought to pH 10 by slow addition of saturated aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (3x 10 ml) and the organic phase was dried over sodium sulfate and concentrated. The crude product was dissolved in THF (1 ml) and 37 wt% aqueous formaldehyde was added dropwise at room temperature (1 equiv., 8 mg). The mixtue was then stirred at room temperature for 12 h.[5] The reaction mixture was diluted with CH_2Cl_2 (2 mL), dried over sodium sulfate and concentrated. The pure product was obtained after column chromatography on silica gel eluting with toluene/chloroform (10/1 - 5/1) as a pale yellow oil (23.5 mg, 92%).



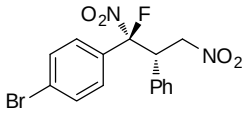
5

Pale yellow oil. $[\alpha]^{270}_D$ = +65.6 (c 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (m, 2H), 7.53 (dd, J = 5.5 Hz, 2.0 Hz, 3H), 7.48 – 7.45 (m, 2H), 7.38 – 7.34 (m, 3H), 6.10 (d, J = 7.2 Hz, 1H), 5.82 (d, J = 7.2 Hz, 1H), 5.22 (ddd, J = 33.5 Hz, 10.5 Hz, 3.7 Hz, 1H), 4.08 (dd, J = 11.8 Hz, 10.7

[5] The change of ninhydrine stain color on TLC suggested that the reaction proceeded fast - within 0.5 h; however it is difficult to distinguish product and starting material spot on TLC and therefore the reaction was stirred for additional time.

Hz, 1H), 3.97 (dd, J = 12.0 Hz, 3.7 Hz, 1H), ; ^{13}C NMR (125 Hz, $CDCl_3$) δ 132.22, 131.52, 131.39, 129.53, 129.51, 129.32, 129.08, 129.03, 128.20, 125.72, 125.64, 124.94, 119.98 (d, J = 243.6 Hz), 65.75, 49.06, 48.92; ^{19}F NMR (376.46 Hz, $CDCl_3$) δ -59.15 (d, J = 44.7 Hz); HRMS (ESI) m/z calcd for $C_{16}H_{16}FN_2$ $[M-H]^-$ = 255.2330, found = 255.2336.

G. X-Ray Crystallographic Analysis and Determination of Configurations of Products



3ab

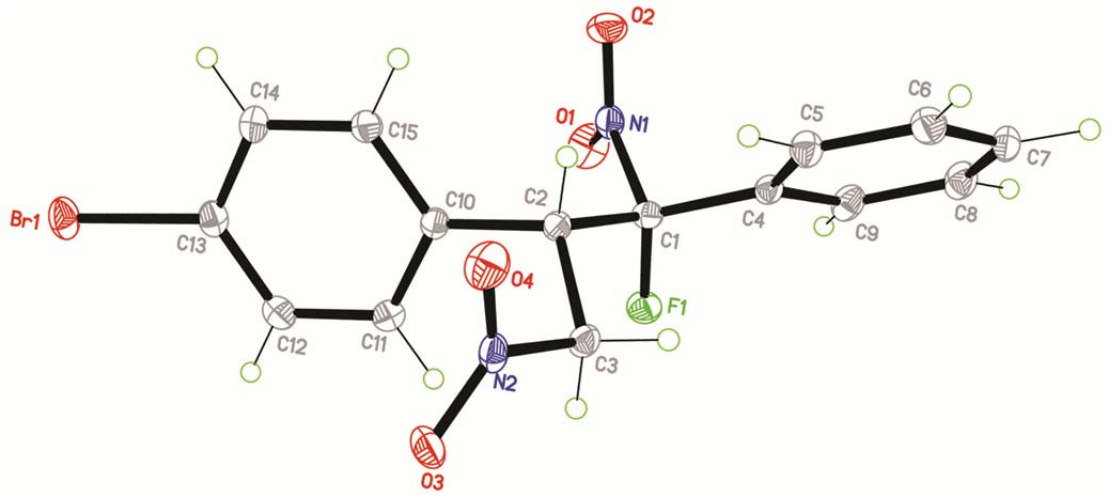


Table 1. Crystal data and structure refinement for D345.

Identification code	d345	
Empirical formula	C15 H12 Br F N2 O4	
Formula weight	383.18	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 5.6907(11) Å	α= 108.137(3)°.
	b = 7.4227(14) Å	β= 100.781(3)°.
	c = 9.3653(18) Å	γ = 90.415(3)°.
Volume	368.39(12) Å^3	
Z	1	
Density (calculated)	1.727 Mg/m^3	
Absorption coefficient	2.823 mm^{-1}	

F(000)	192
Crystal size	0.52 x 0.50 x 0.20 mm^3
Theta range for data collection	2.34 to 27.50°.
Index ranges	-7<=h<=7, -9<=k<=9, -12<=l<=12
Reflections collected	4816
Independent reflections	3338 [R(int) = 0.0145]
Completeness to theta = 27.50°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8372 and 0.5831
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3338 / 3 / 208
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0946
R indices (all data)	R1 = 0.0379, wR2 = 0.0947
Absolute structure parameter	0.000(6)
Largest diff. peak and hole	0.455 and -0.338 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for D345. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	11585	8390	12936	21(1)
F(1)	4095(3)	3923(3)	5634(2)	18(1)
O(1)	5131(5)	7334(4)	6030(3)	26(1)
O(2)	8353(5)	6780(4)	5075(3)	24(1)
O(3)	9475(5)	212(4)	7936(3)	23(1)
O(4)	11720(4)	898(4)	6516(3)	23(1)
N(1)	6571(5)	6292(4)	5454(4)	16(1)
N(2)	9795(5)	796(4)	6892(3)	15(1)
C(1)	6169(5)	4129(4)	5135(4)	13(1)
C(2)	8276(5)	3518(4)	6129(4)	13(1)
C(3)	7668(5)	1448(4)	6018(4)	15(1)
C(4)	5776(5)	3205(4)	3424(4)	13(1)
C(5)	7490(6)	2157(5)	2701(4)	16(1)
C(6)	7034(6)	1314(5)	1115(4)	19(1)
C(7)	4857(6)	1537(5)	238(4)	18(1)
C(8)	3170(6)	2630(5)	954(4)	20(1)
C(9)	3599(6)	3448(5)	2527(4)	17(1)
C(10)	8918(5)	4816(4)	7783(4)	13(1)
C(11)	7527(5)	4802(5)	8869(4)	16(1)
C(12)	8284(6)	5894(5)	10401(4)	17(1)
C(13)	10443(6)	6999(4)	10833(4)	16(1)
C(14)	11817(6)	7066(5)	9777(4)	18(1)
C(15)	11034(6)	5972(5)	8254(4)	16(1)

Table 3. Bond lengths [Å] and angles [°] for D345.

Br(1)-C(13)	1.901(3)
F(1)-C(1)	1.372(3)
O(1)-N(1)	1.214(4)
O(2)-N(1)	1.223(4)
O(3)-N(2)	1.228(4)
O(4)-N(2)	1.221(4)
N(1)-C(1)	1.546(4)
N(2)-C(3)	1.501(4)
C(1)-C(4)	1.506(4)
C(1)-C(2)	1.537(4)
C(2)-C(10)	1.522(4)
C(2)-C(3)	1.540(4)
C(2)-H(2A)	1.0000
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.395(4)
C(4)-C(9)	1.407(4)
C(5)-C(6)	1.392(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.395(5)
C(6)-H(6)	0.9500
C(7)-C(8)	1.394(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.380(5)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-C(15)	1.390(4)
C(10)-C(11)	1.403(4)
C(11)-C(12)	1.393(5)
C(11)-H(11)	0.9500
C(12)-C(13)	1.393(4)
C(12)-H(12)	0.9500
C(13)-C(14)	1.382(4)
C(14)-C(15)	1.389(5)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500

O(1)-N(1)-O(2)	126.2(3)
O(1)-N(1)-C(1)	118.8(3)
O(2)-N(1)-C(1)	114.9(3)
O(4)-N(2)-O(3)	124.9(3)
O(4)-N(2)-C(3)	117.4(3)
O(3)-N(2)-C(3)	117.7(3)
F(1)-C(1)-C(4)	109.7(2)
F(1)-C(1)-C(2)	109.4(2)
C(4)-C(1)-C(2)	117.6(3)
F(1)-C(1)-N(1)	104.6(2)
C(4)-C(1)-N(1)	107.0(2)
C(2)-C(1)-N(1)	107.6(2)
C(10)-C(2)-C(1)	114.4(2)
C(10)-C(2)-C(3)	112.1(2)
C(1)-C(2)-C(3)	107.5(2)
C(10)-C(2)-H(2A)	107.5
C(1)-C(2)-H(2A)	107.5
C(3)-C(2)-H(2A)	107.5
N(2)-C(3)-C(2)	107.8(2)
N(2)-C(3)-H(3A)	110.2
C(2)-C(3)-H(3A)	110.2
N(2)-C(3)-H(3B)	110.2
C(2)-C(3)-H(3B)	110.2
H(3A)-C(3)-H(3B)	108.5
C(5)-C(4)-C(9)	119.2(3)
C(5)-C(4)-C(1)	122.7(3)
C(9)-C(4)-C(1)	118.1(3)
C(6)-C(5)-C(4)	120.6(3)
C(6)-C(5)-H(5)	119.7
C(4)-C(5)-H(5)	119.7
C(5)-C(6)-C(7)	119.8(3)
C(5)-C(6)-H(6)	120.1
C(7)-C(6)-H(6)	120.1
C(8)-C(7)-C(6)	119.6(3)
C(8)-C(7)-H(7)	120.2
C(6)-C(7)-H(7)	120.2
C(9)-C(8)-C(7)	120.8(3)

C(9)-C(8)-H(8)	119.6
C(7)-C(8)-H(8)	119.6
C(8)-C(9)-C(4)	120.0(3)
C(8)-C(9)-H(9)	120.0
C(4)-C(9)-H(9)	120.0
C(15)-C(10)-C(11)	118.9(3)
C(15)-C(10)-C(2)	118.6(3)
C(11)-C(10)-C(2)	122.3(3)
C(12)-C(11)-C(10)	120.5(3)
C(12)-C(11)-H(11)	119.7
C(10)-C(11)-H(11)	119.7
C(13)-C(12)-C(11)	118.8(3)
C(13)-C(12)-H(12)	120.6
C(11)-C(12)-H(12)	120.6
C(14)-C(13)-C(12)	121.7(3)
C(14)-C(13)-Br(1)	119.0(2)
C(12)-C(13)-Br(1)	119.3(2)
C(13)-C(14)-C(15)	118.8(3)
C(13)-C(14)-H(14)	120.6
C(15)-C(14)-H(14)	120.6
C(14)-C(15)-C(10)	121.2(3)
C(14)-C(15)-H(15)	119.4
C(10)-C(15)-H(15)	119.4

Symmetry transformations used to generate equivalent atoms:

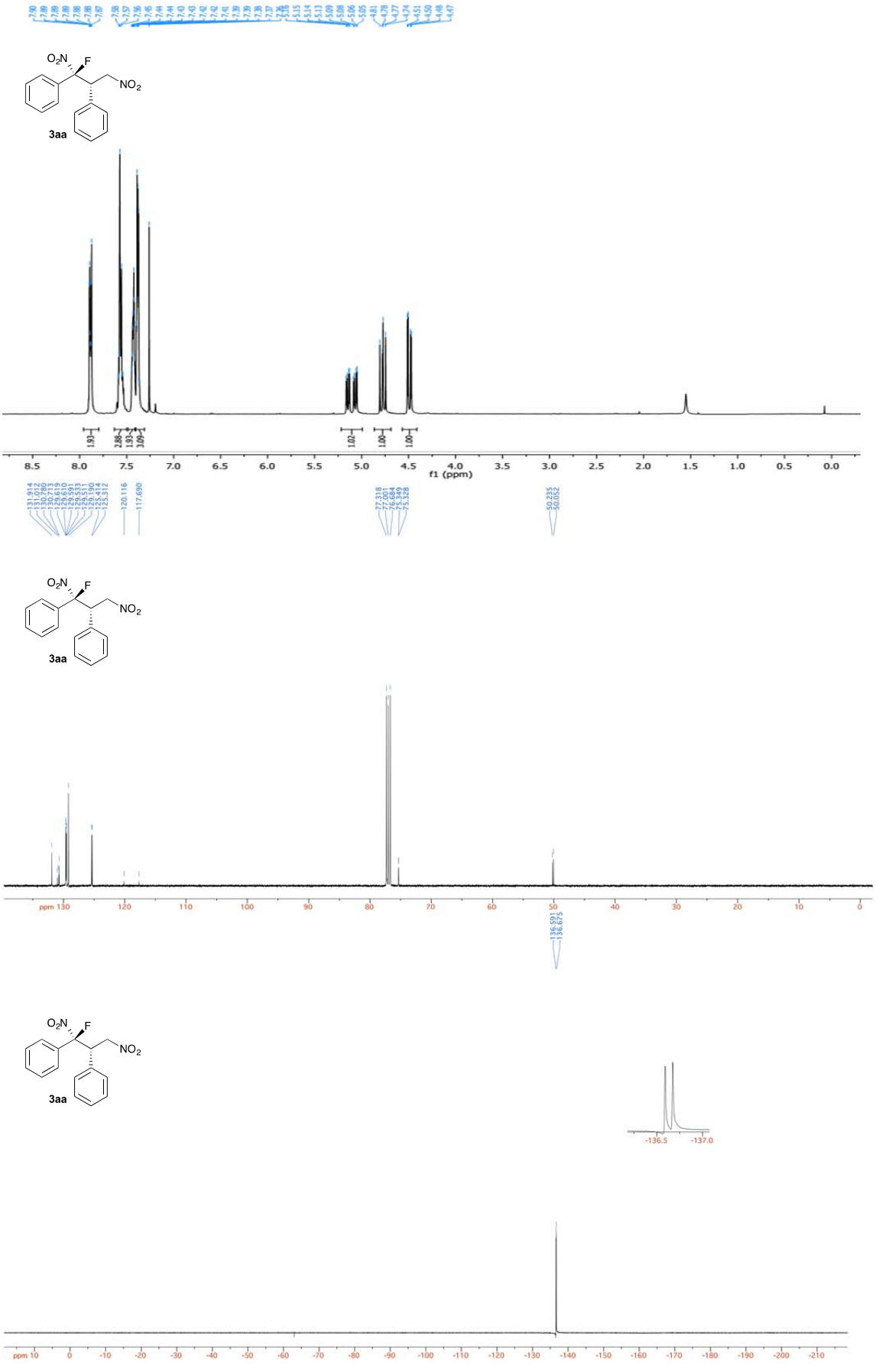
Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for D345. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

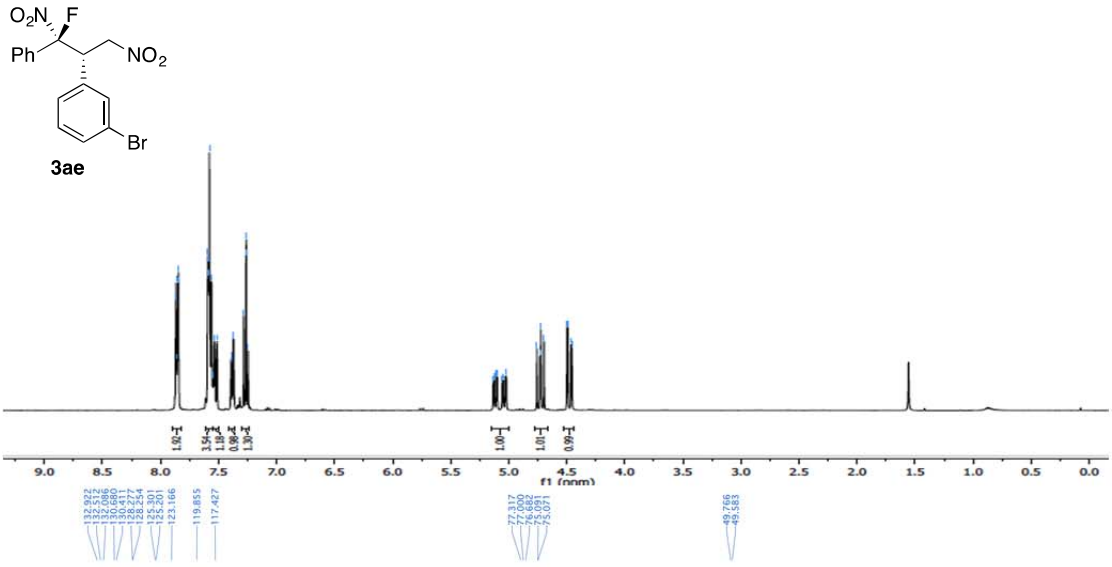
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	30(1)	18(1)	13(1)	1(1)	1(1)	2(1)
F(1)	14(1)	22(1)	19(1)	7(1)	5(1)	1(1)
O(1)	27(1)	19(1)	31(1)	4(1)	5(1)	8(1)
O(2)	31(1)	17(1)	23(1)	5(1)	8(1)	-7(1)
O(3)	33(1)	22(1)	14(1)	9(1)	-1(1)	-1(1)
O(4)	17(1)	25(1)	25(1)	6(1)	3(1)	3(1)
N(1)	21(1)	12(1)	13(1)	4(1)	0(1)	1(1)
N(2)	20(1)	11(1)	12(1)	2(1)	-2(1)	1(1)
C(1)	13(1)	13(1)	14(1)	5(1)	3(1)	0(1)
C(2)	13(1)	12(1)	13(1)	5(1)	1(1)	0(1)
C(3)	16(1)	12(1)	15(1)	5(1)	-1(1)	-1(1)
C(4)	13(1)	12(1)	14(1)	5(1)	0(1)	-1(1)
C(5)	14(1)	17(1)	15(2)	4(1)	2(1)	1(1)
C(6)	21(2)	17(2)	17(2)	5(1)	5(1)	1(1)
C(7)	25(2)	16(1)	12(1)	3(1)	-1(1)	-5(1)
C(8)	19(1)	20(2)	19(2)	8(1)	-4(1)	-1(1)
C(9)	15(1)	15(1)	20(2)	5(1)	-2(1)	1(1)
C(10)	15(1)	10(1)	13(1)	4(1)	0(1)	1(1)
C(11)	15(1)	17(1)	17(2)	6(1)	3(1)	-1(1)
C(12)	19(1)	20(2)	16(2)	7(1)	5(1)	2(1)
C(13)	22(2)	10(1)	13(2)	2(1)	1(1)	2(1)
C(14)	18(1)	18(2)	13(2)	3(1)	0(1)	-1(1)
C(15)	18(1)	15(1)	13(2)	3(1)	4(1)	-1(1)

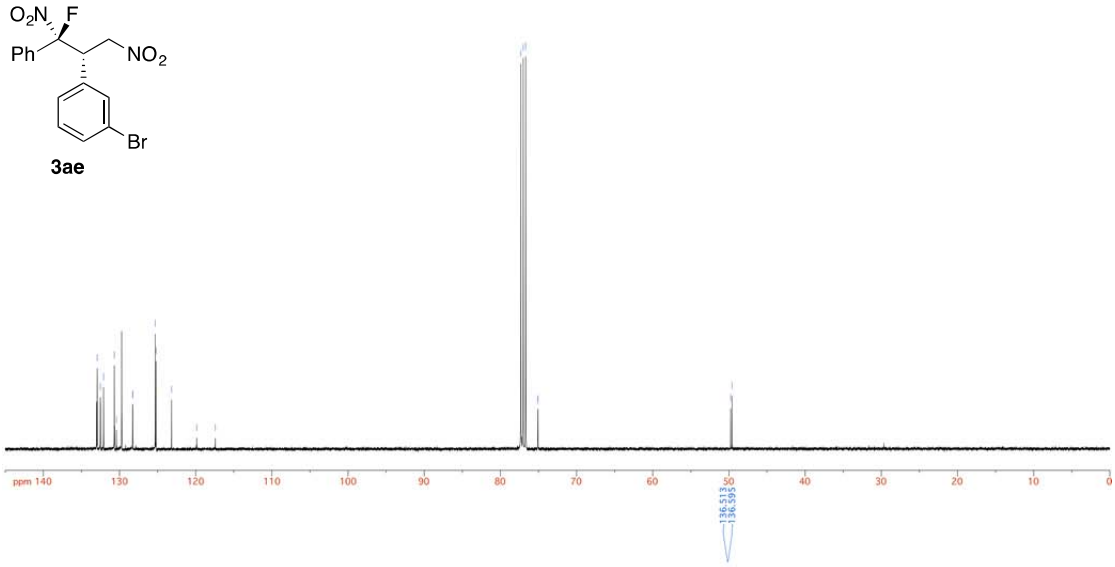
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for D345.

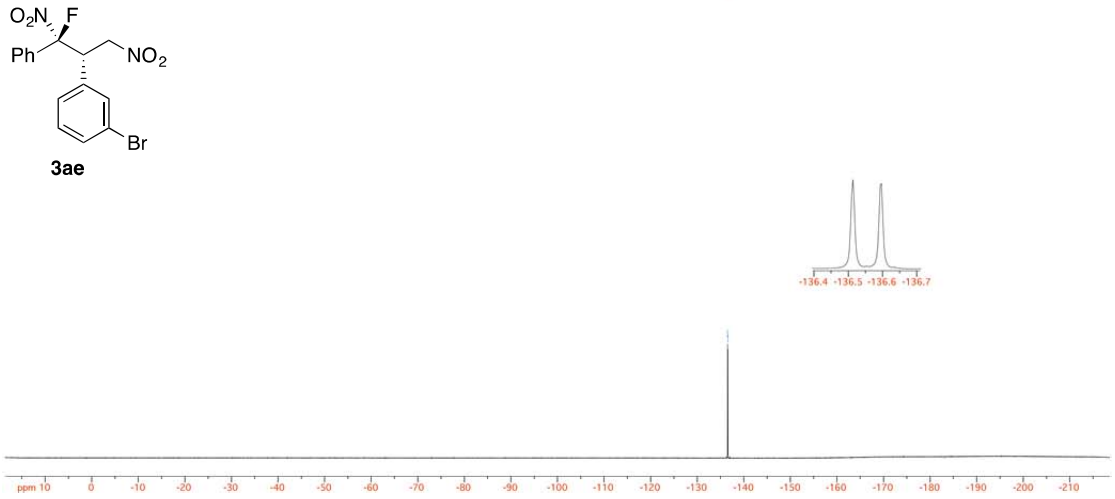
	x	y	z	U(eq)
H(2A)	9714	3530	5660	15
H(3A)	6237	1371	6462	18
H(3B)	7321	632	4932	18
H(5)	8982	2017	3296	19
H(6)	8203	589	633	22
H(7)	4525	947	-843	22
H(8)	1708	2814	353	24
H(9)	2427	4175	3003	21
H(11)	6057	4042	8557	19
H(12)	7345	5884	11138	21
H(14)	13271	7846	10088	21
H(15)	11962	6015	7519	19

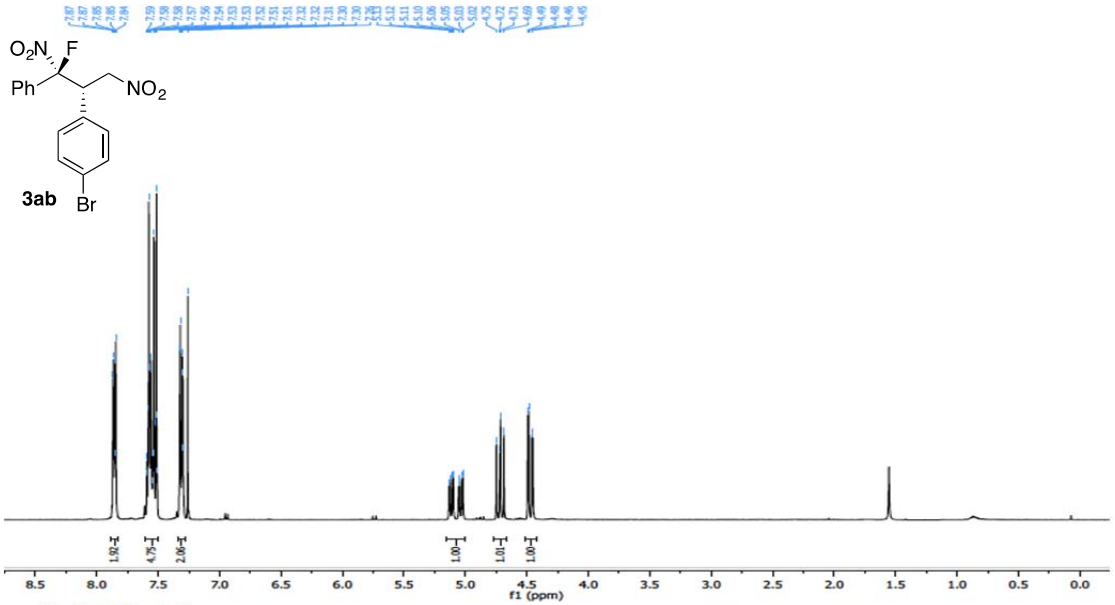
H. NMR Spectra of the Michael Products

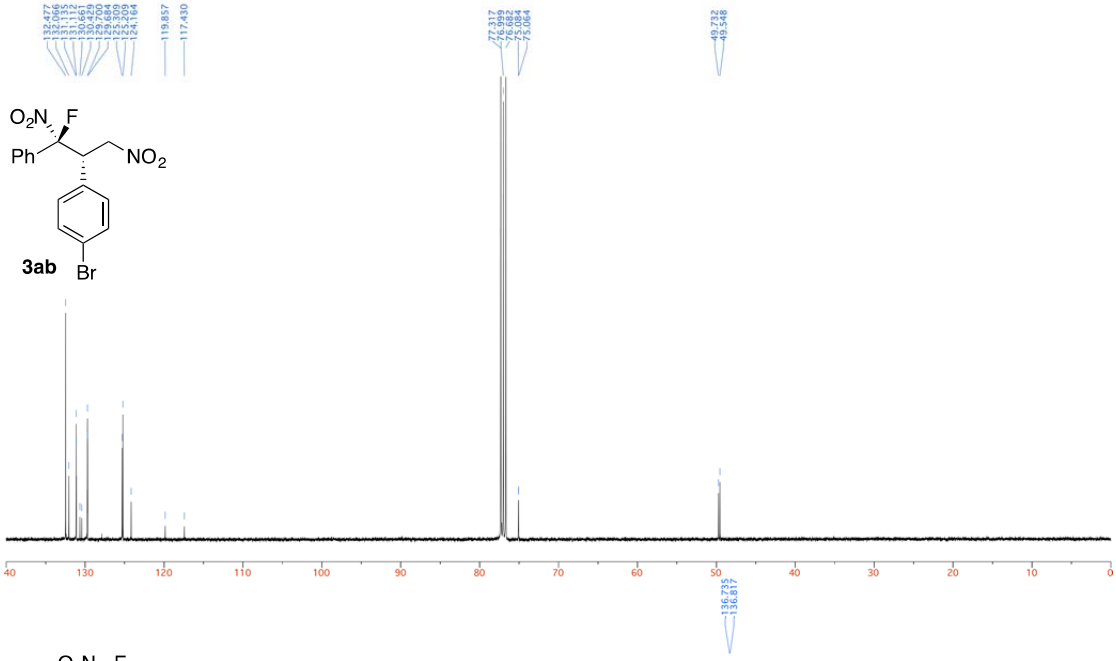


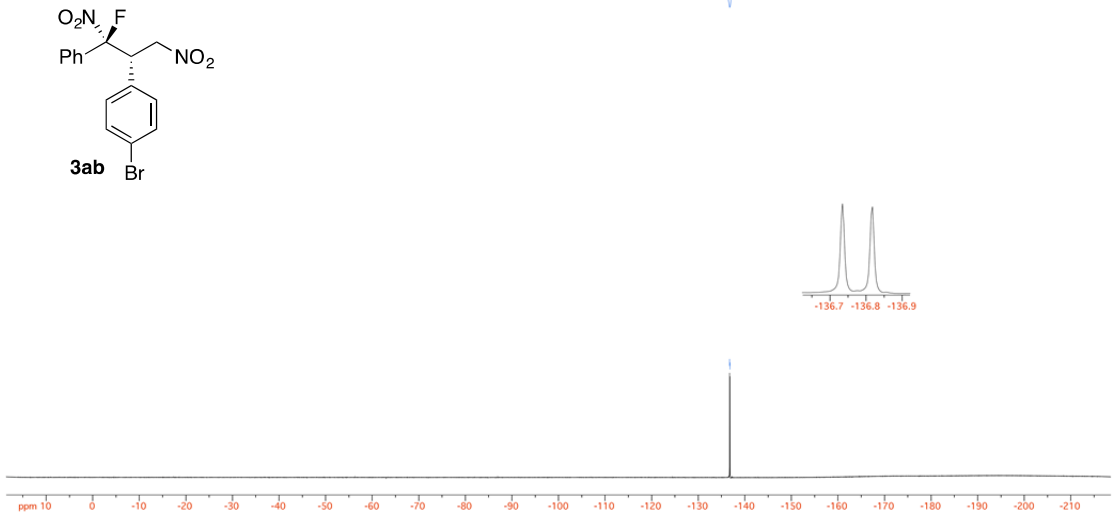

O2N
F
Ph
NO2
Br
3ae
f1 (ppm)


O2N
F
Ph
NO2
Br
3ae
ppm


O2N
F
Ph
NO2
Br
3ae
ppm


O2N
F
Ph
NO2
3ab
Br
f1 (ppm)


O2N
F
Ph
NO2
3ab
Br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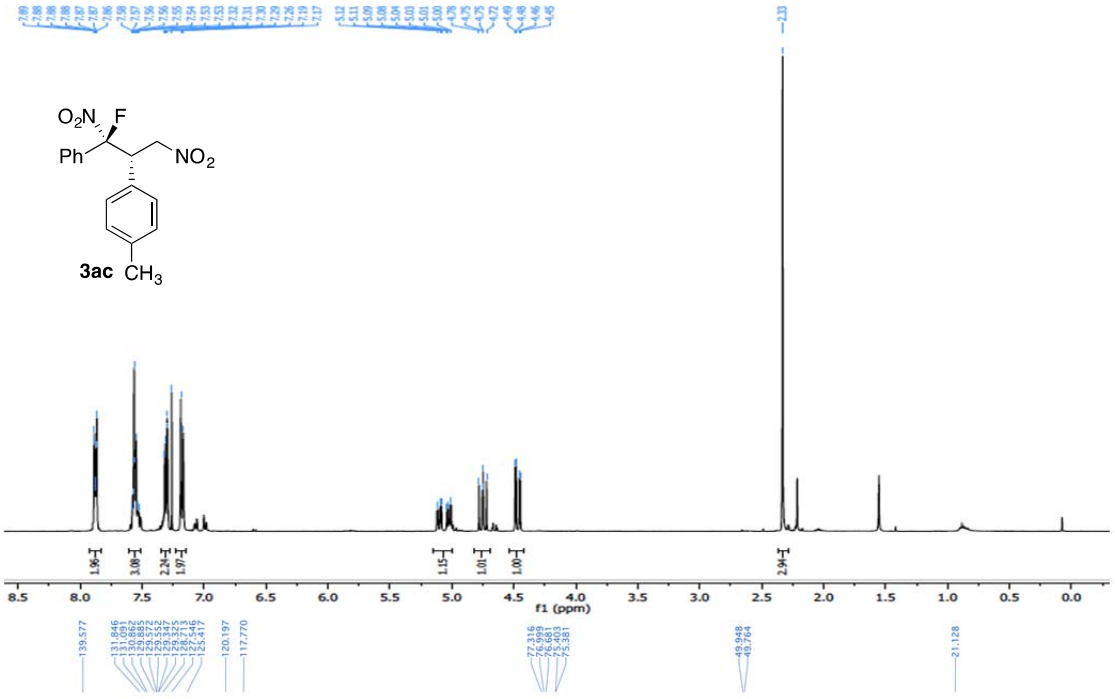
F
Ph
NO2
3ab
Br
-136.7
-136.8
-136.9
ppm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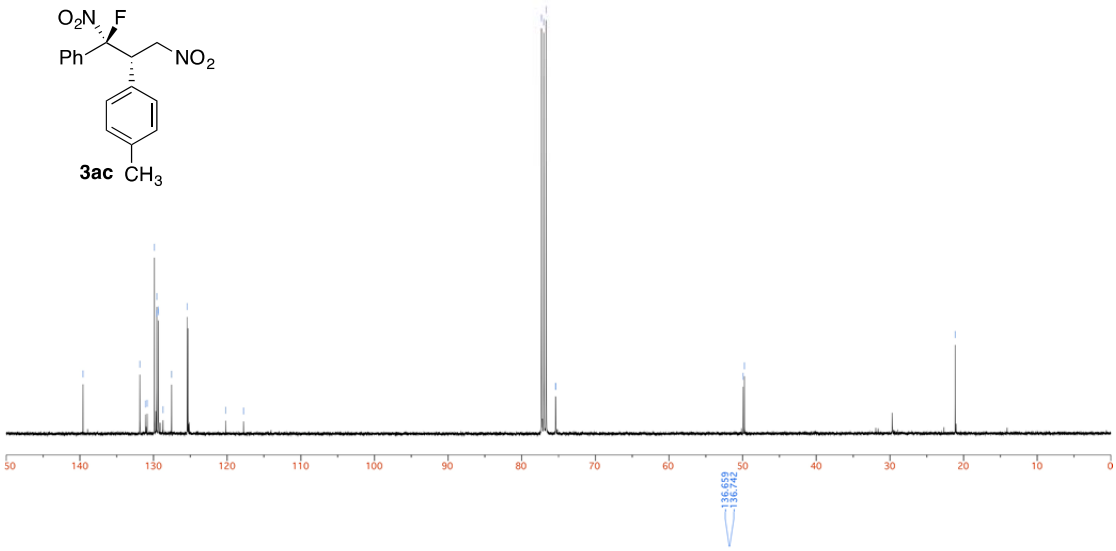
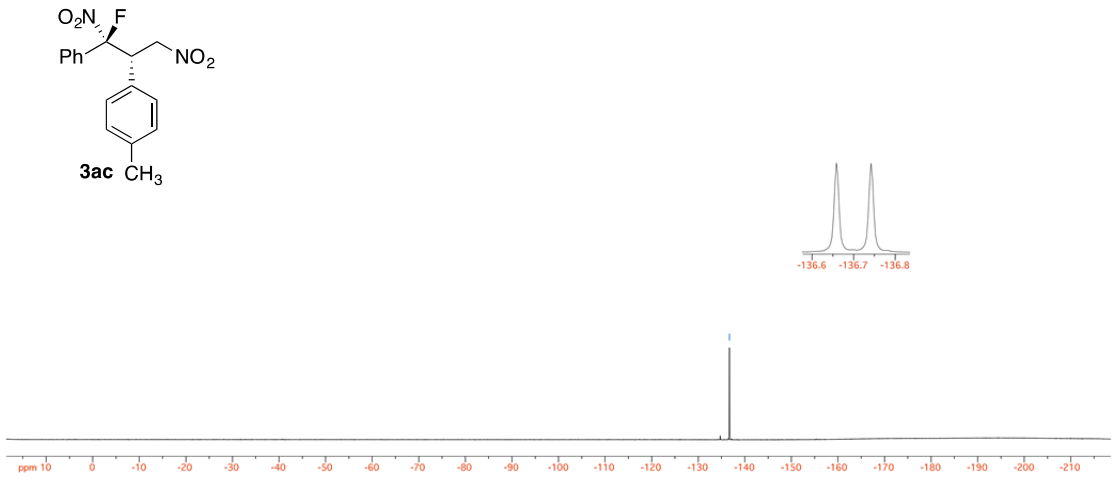
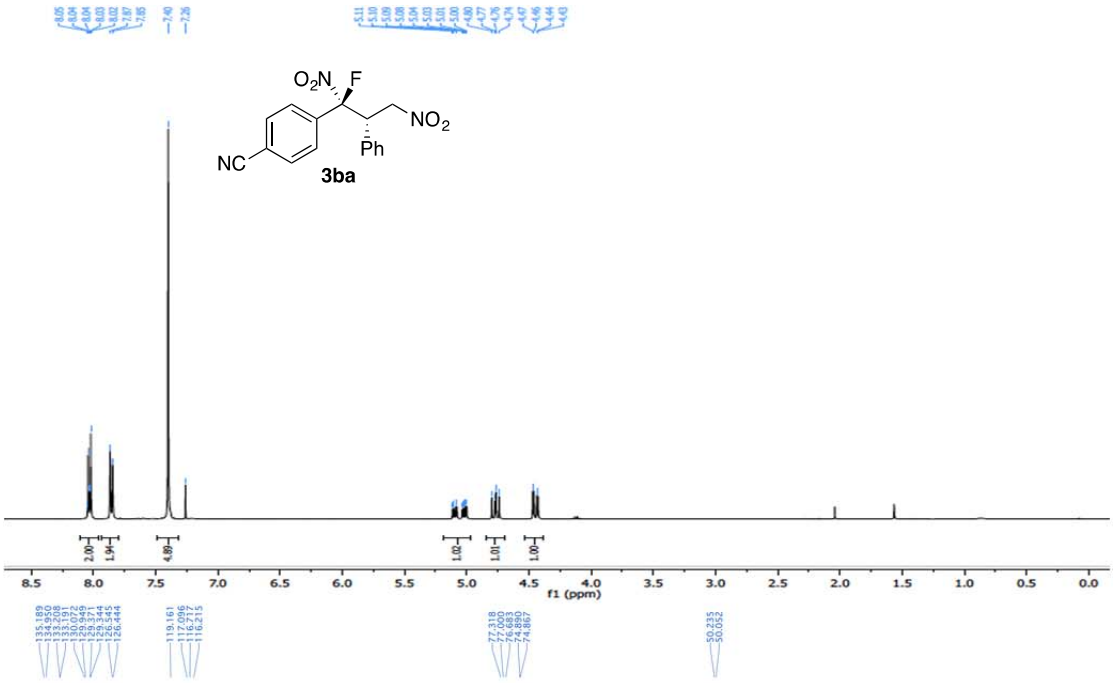
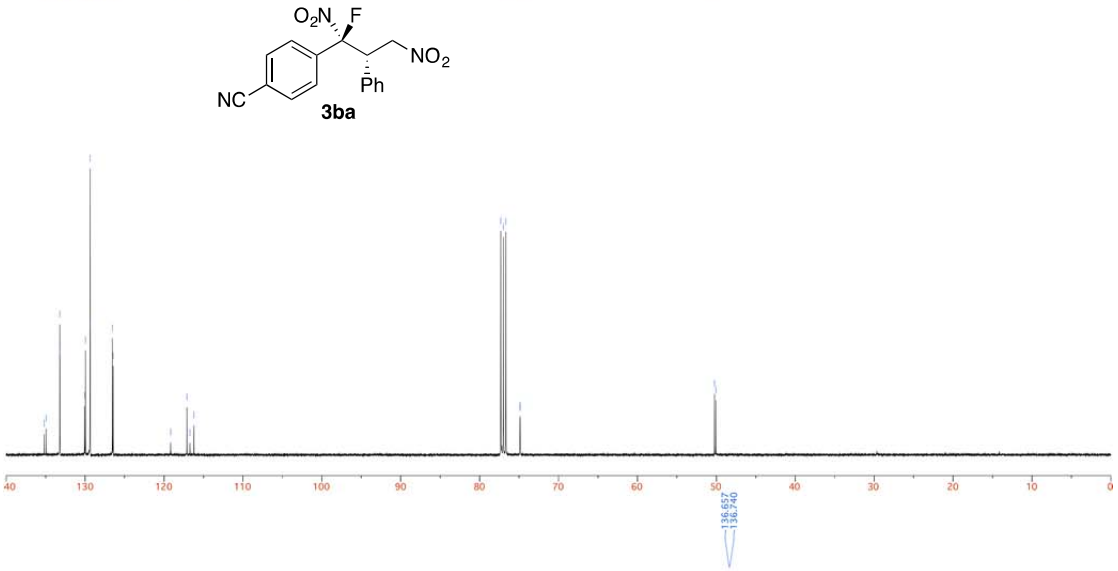
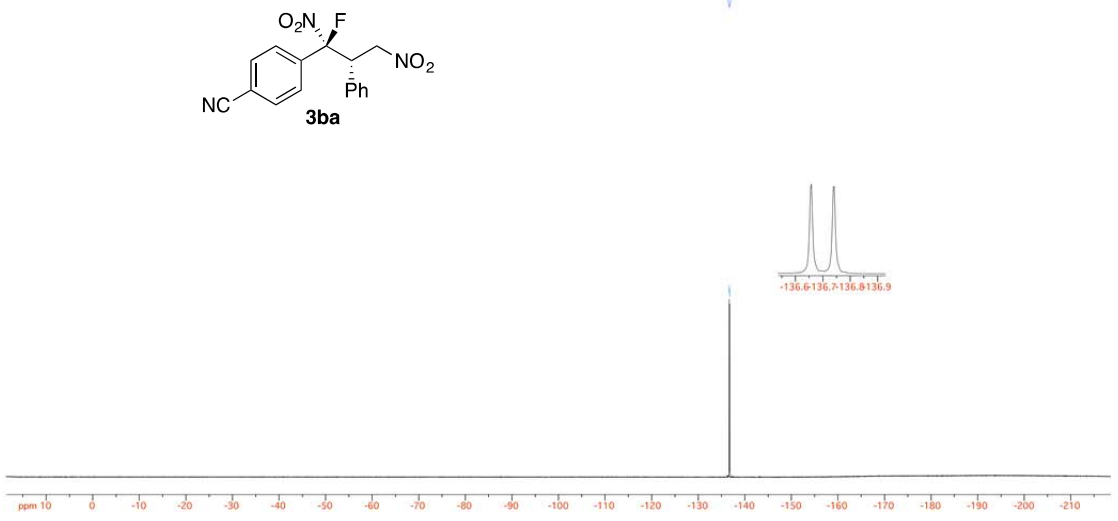
F
Ph
NO2
3ac
CH3
f1 (ppm)

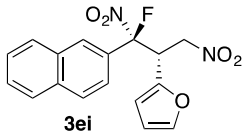

O2N
F
Ph
NO2
3ac
CH3


O2N
F
Ph
NO2
3ac
CH3

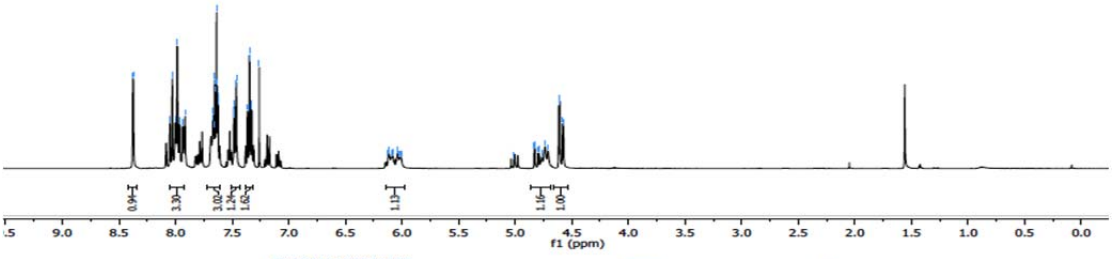

O2N
F
NO2
NC
Ph
3ba
f1 (ppm)

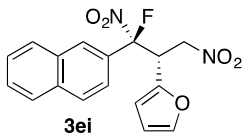

O2N
F
NO2
NC
Ph
3ba


O2N
F
NO2
NC
Ph
3ba

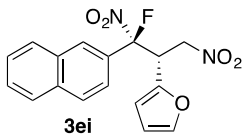


3ei





3ei



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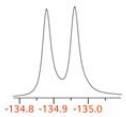
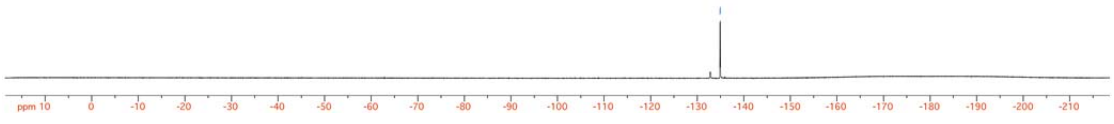
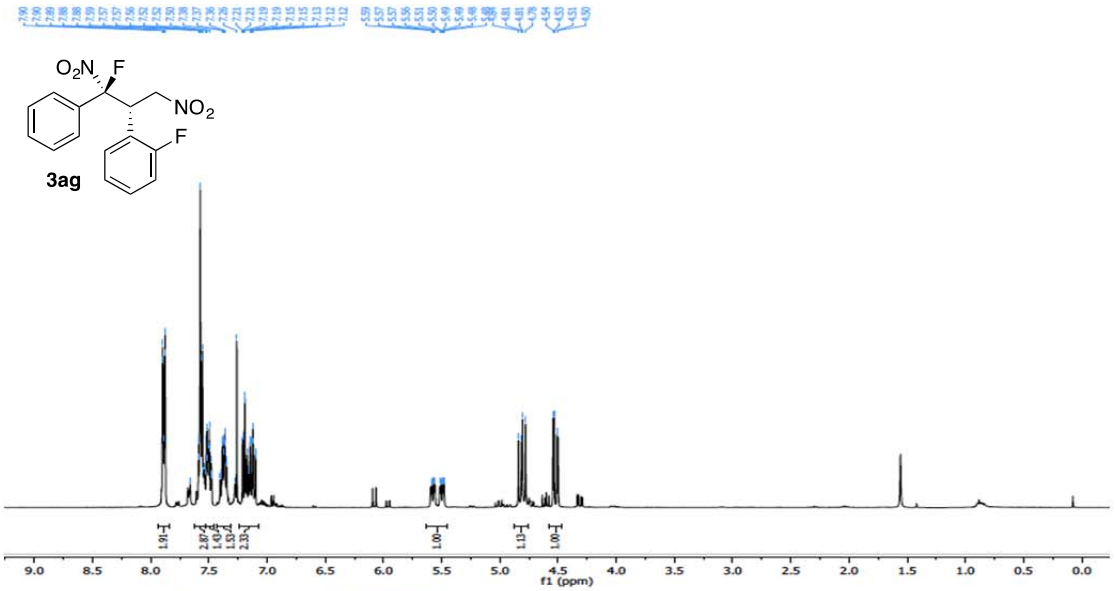
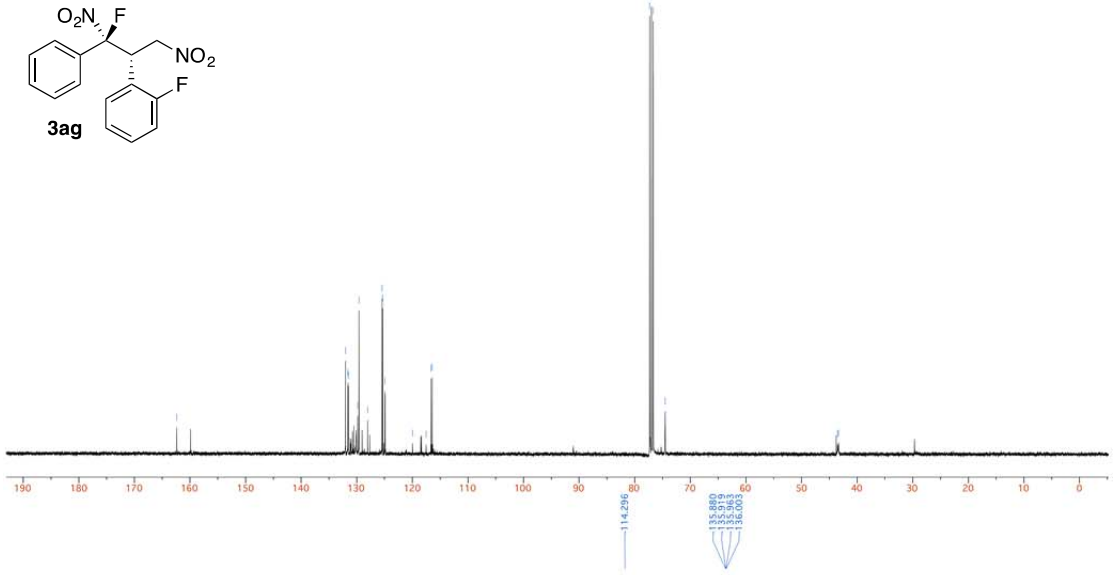





3ag
f1 (ppm)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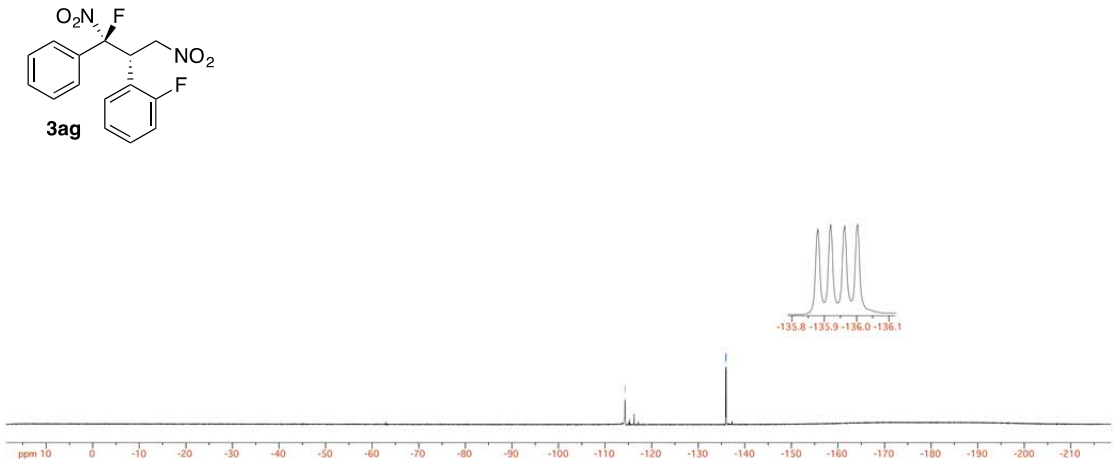
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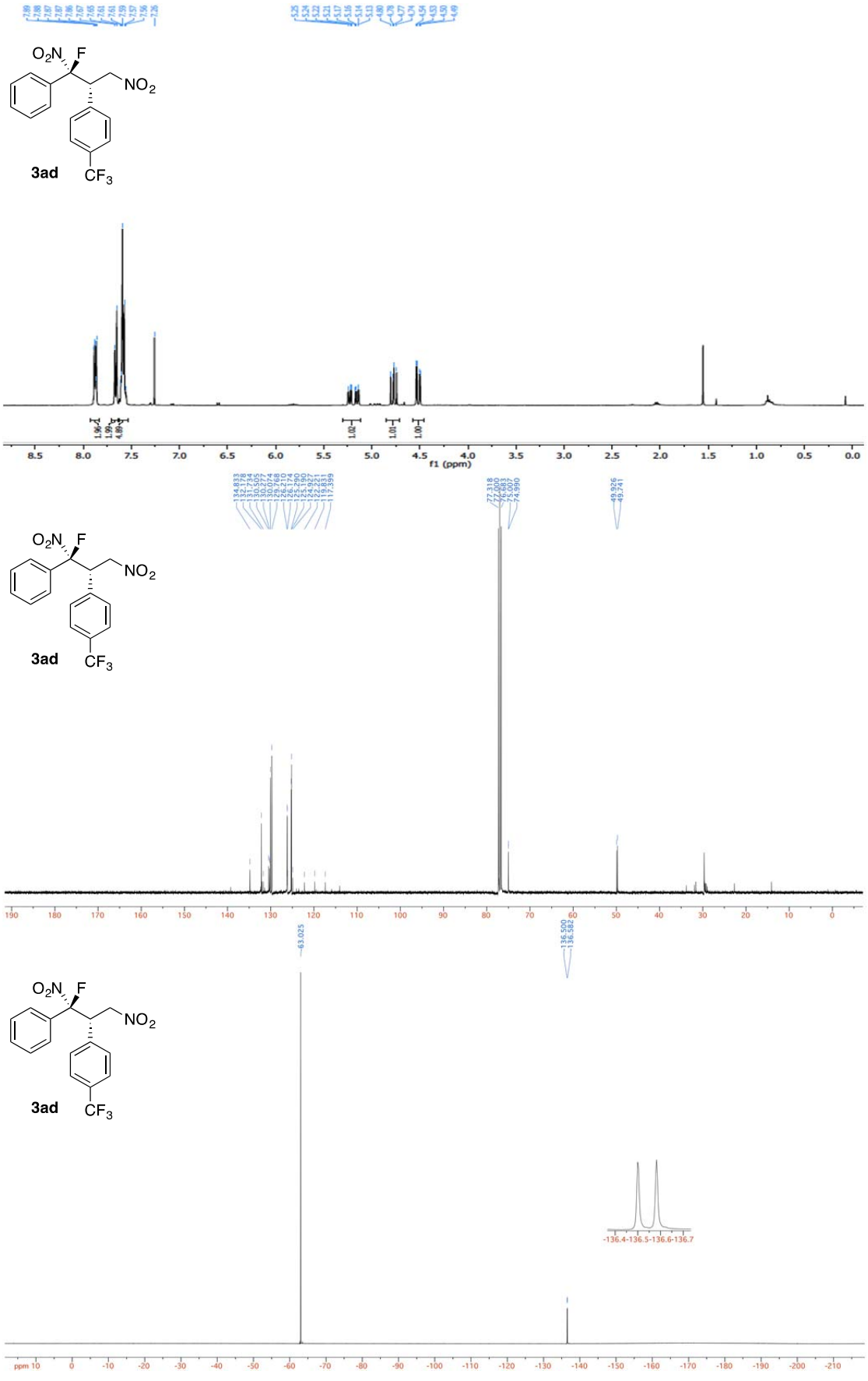
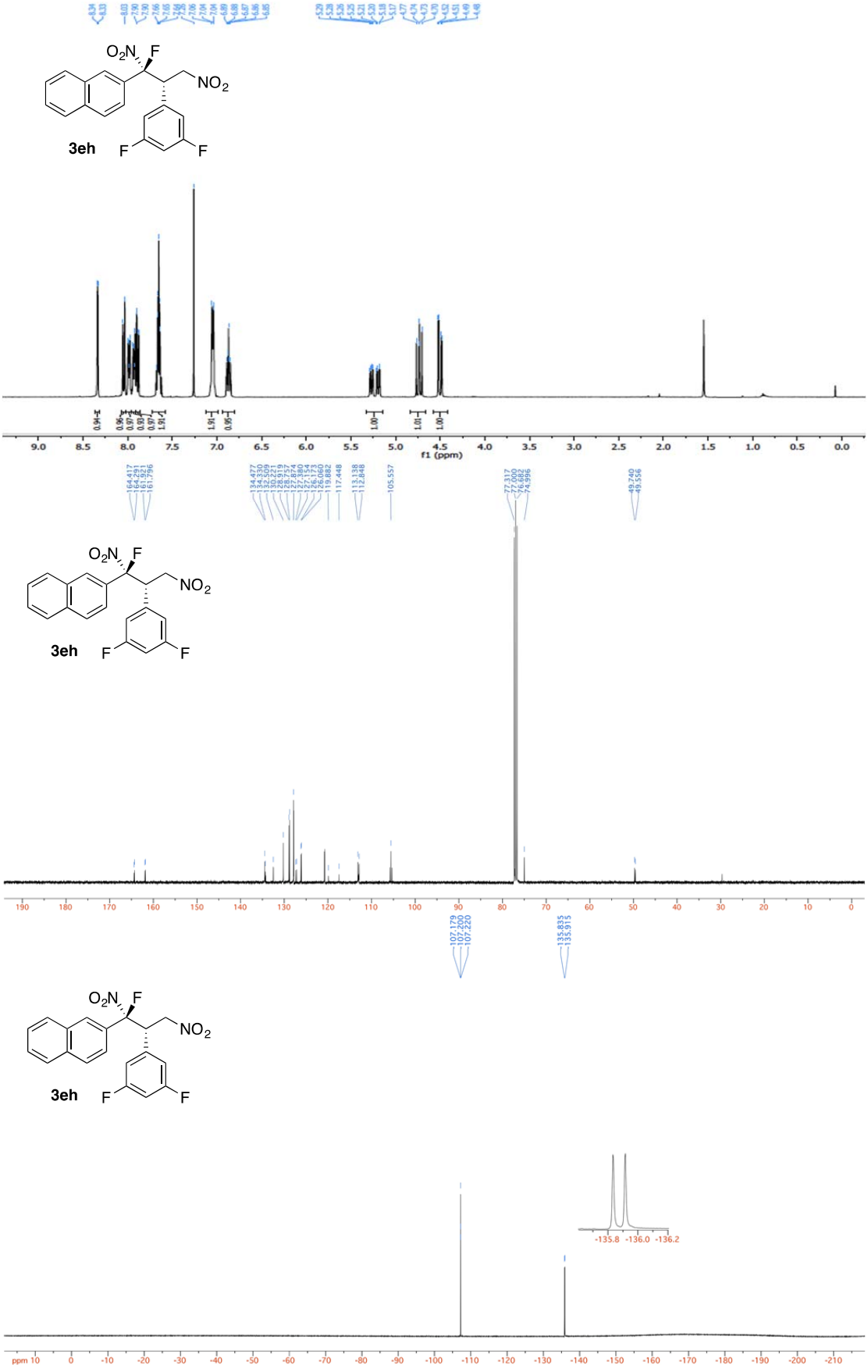
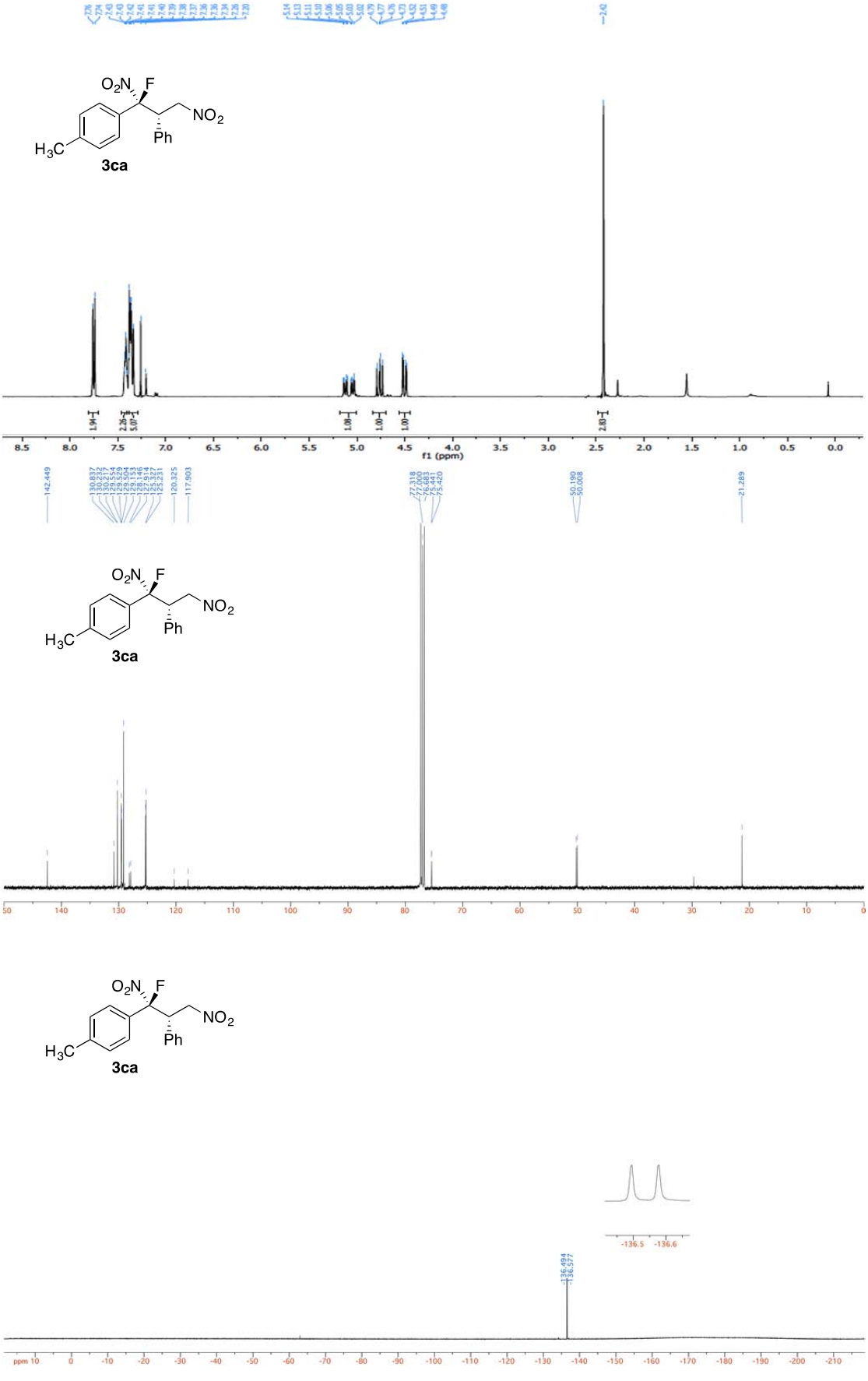
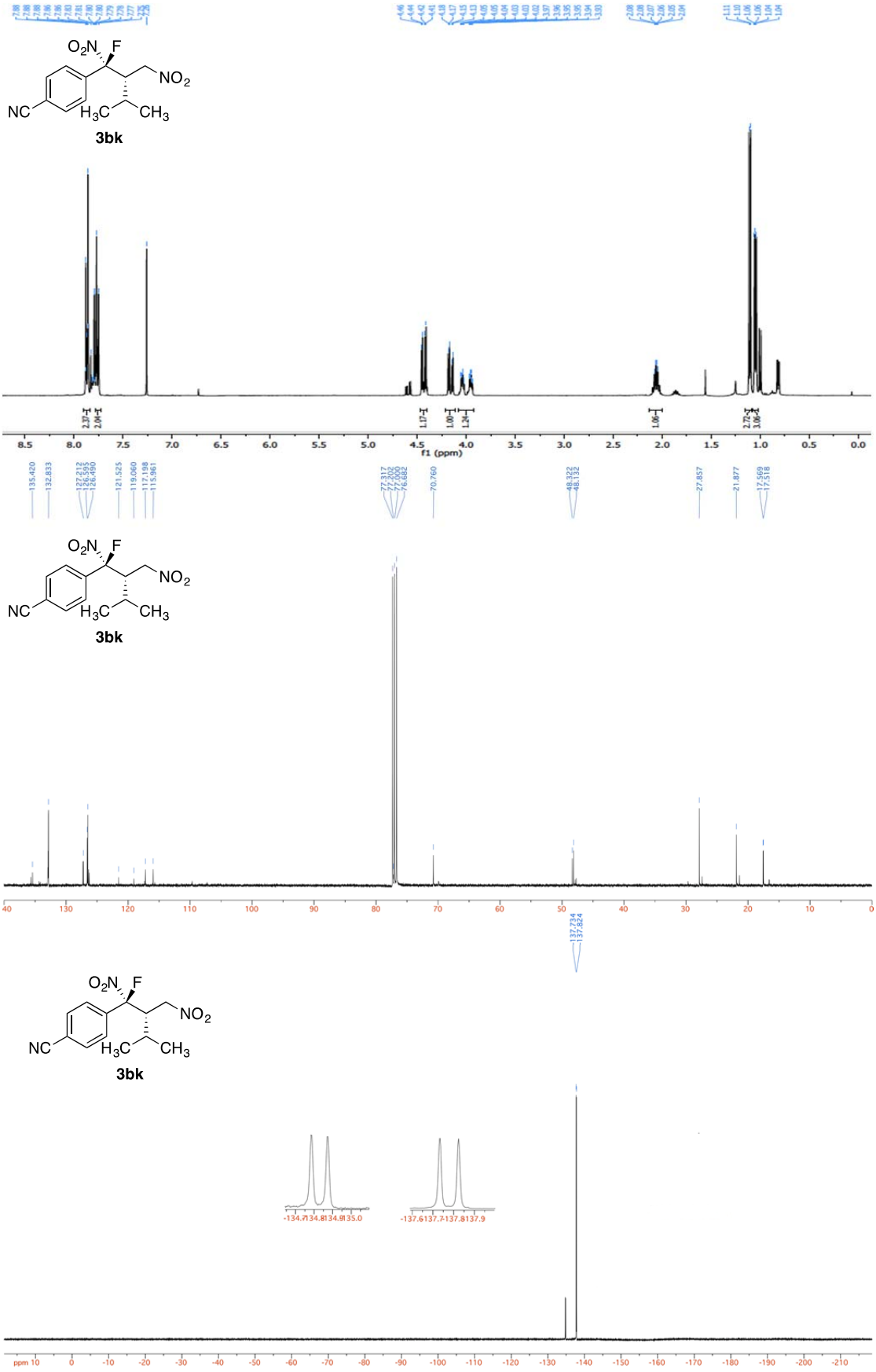
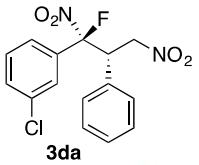

O2N
F
NO2
3ad
CF3
f1 (ppm)
-136.4-136.5-136.6-136.7

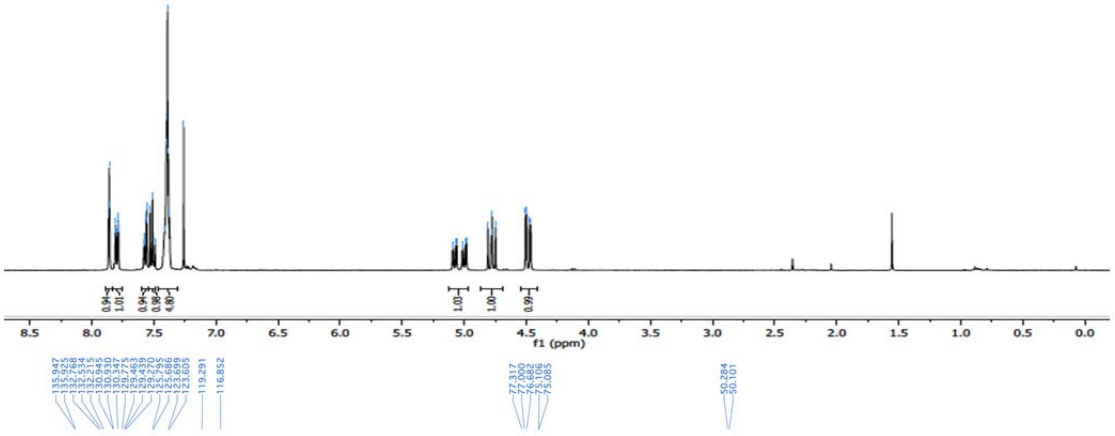

O2N
F
NO2
3eh
F
F
f1 (ppm)

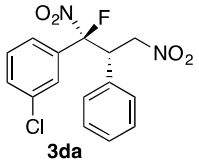

O2N
F
NO2
Ph
H3C
3ca
f1 (ppm)


O2N
F
NO2
NC
H3C
CH3
3bk
f1 (ppm)


O_2N
F
NO_2
Cl

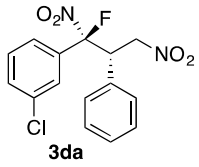
3da


0.94
1.01
0.94
0.98
4.00
1.03
1.00
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

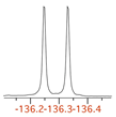

O_2N
F
NO_2
Cl

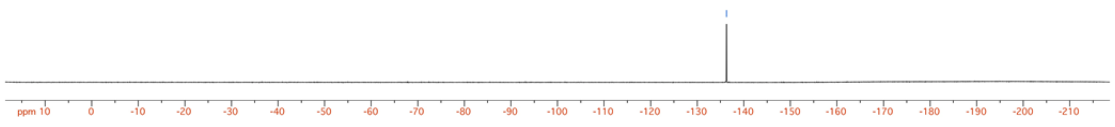
3da

ppm 140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O_2N
F
NO_2
Cl

3da


-136.2
-136.3
-136.4


ppm 10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
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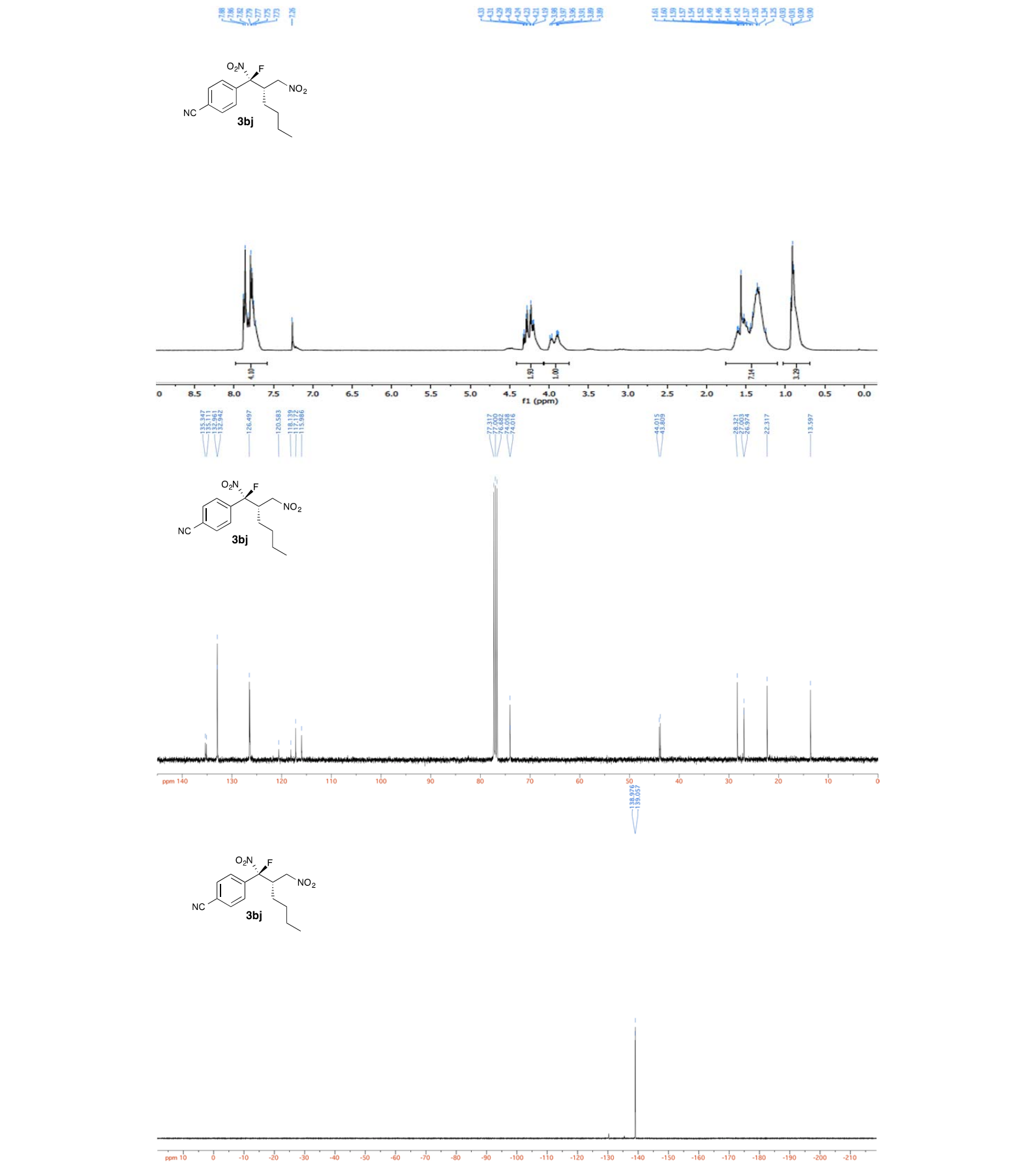
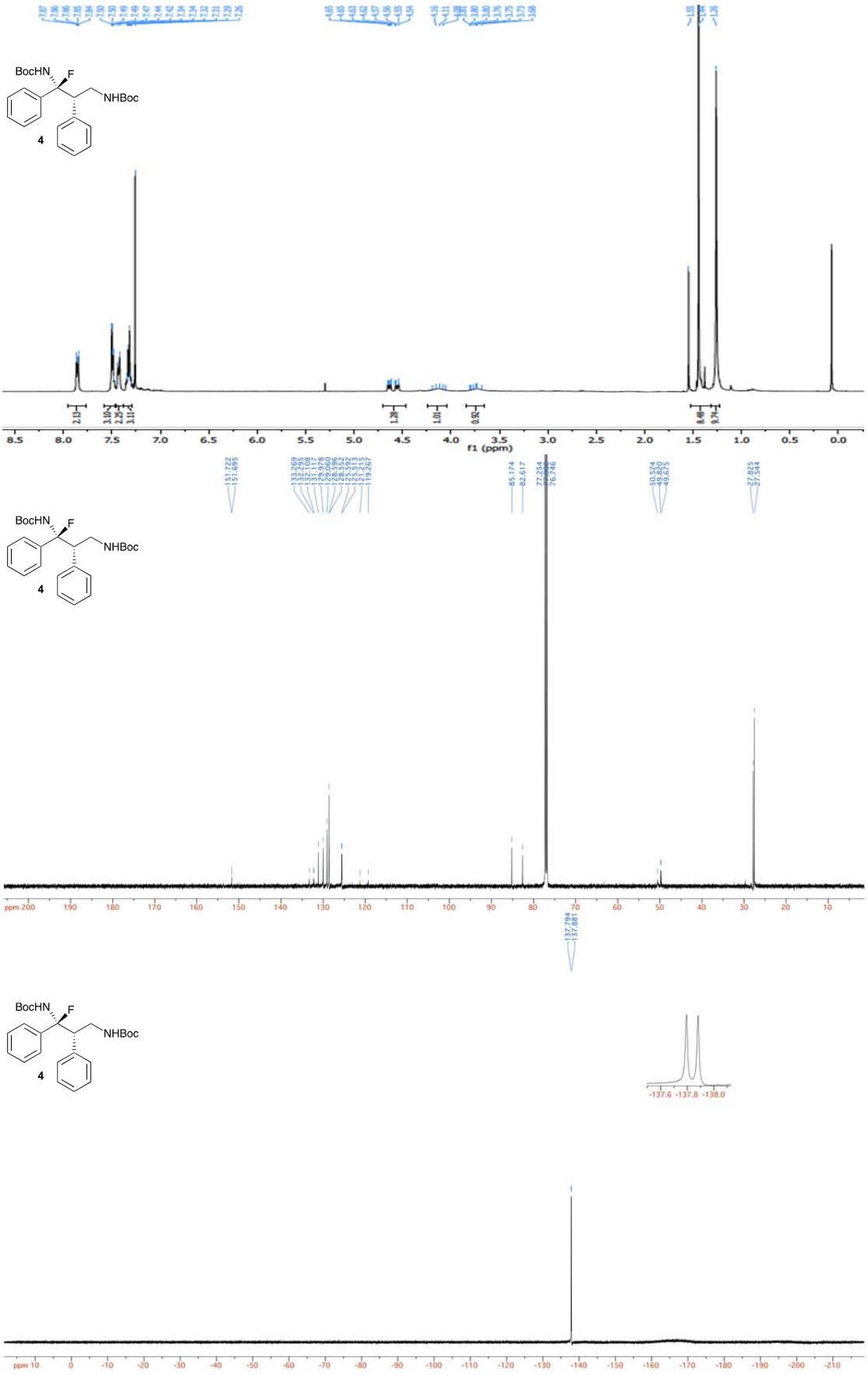
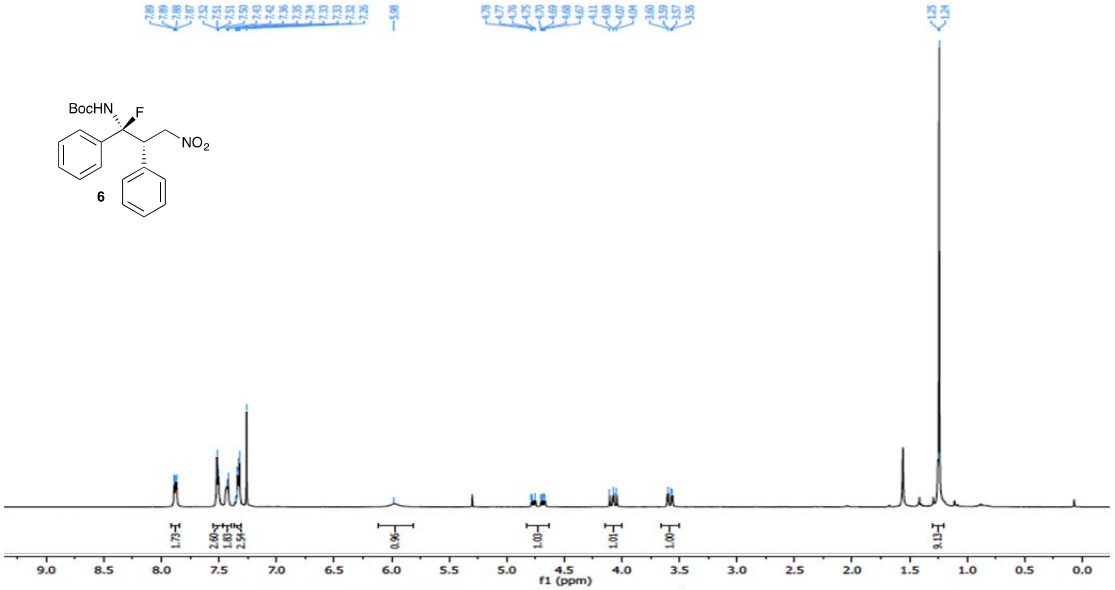
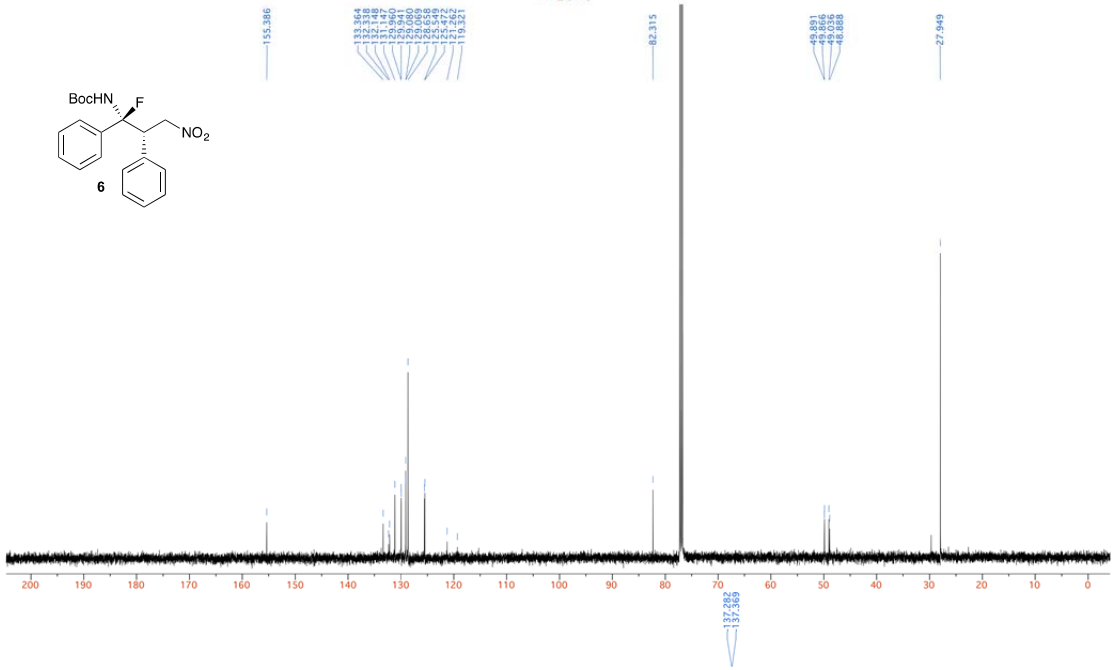
-150
-160
-170
-180
-190
-200
-210

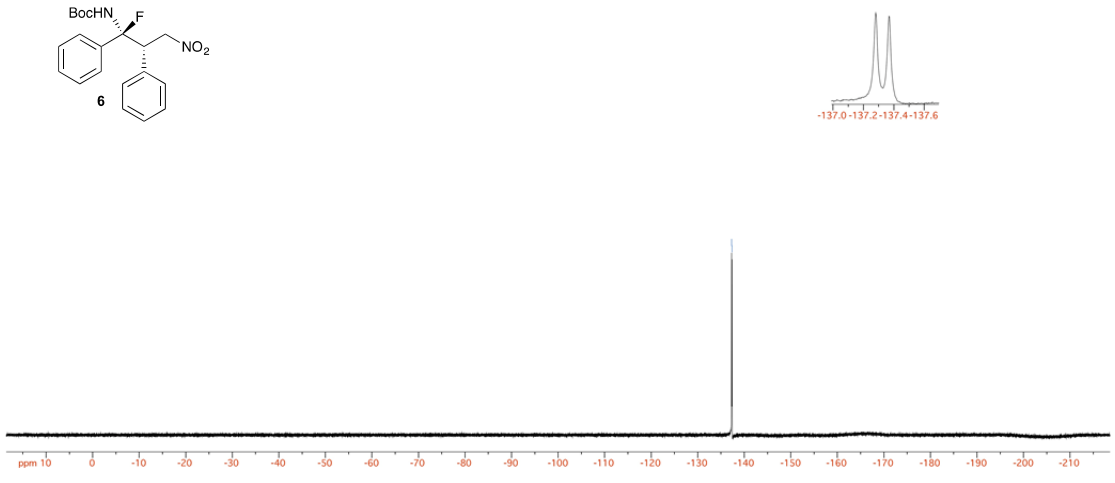

O2N
F
NO2
NC
3bj
f1 (ppm)
ppm 140
ppm 10

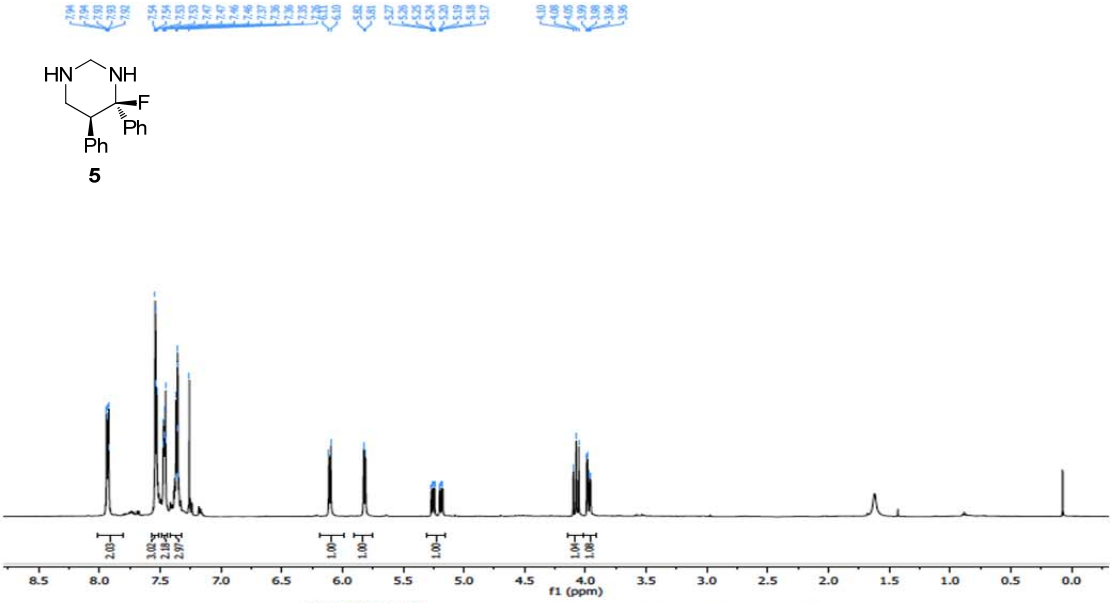
I. NMR Spectra of the Derivatives

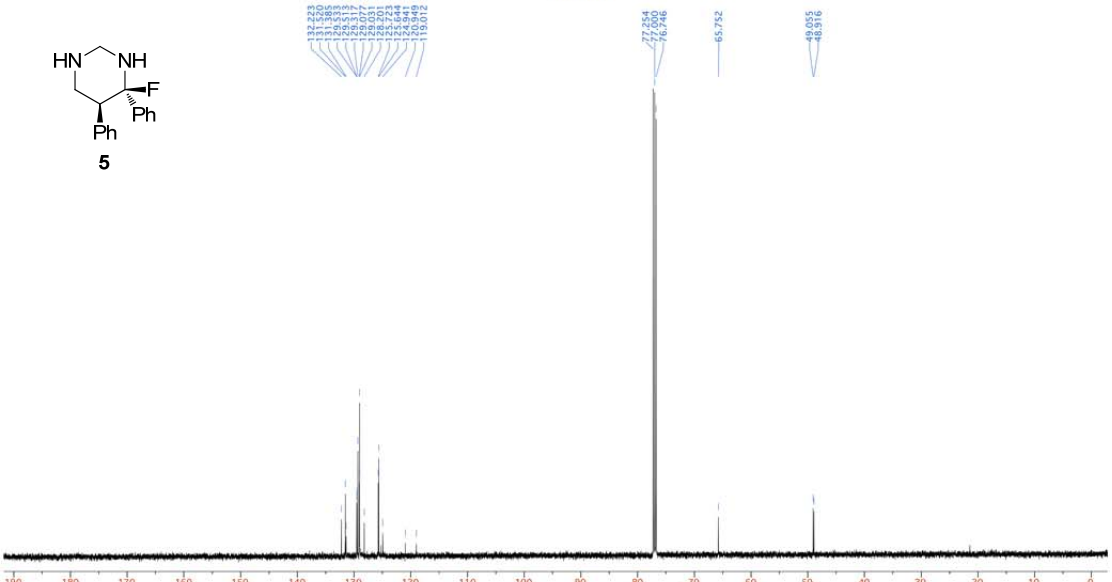


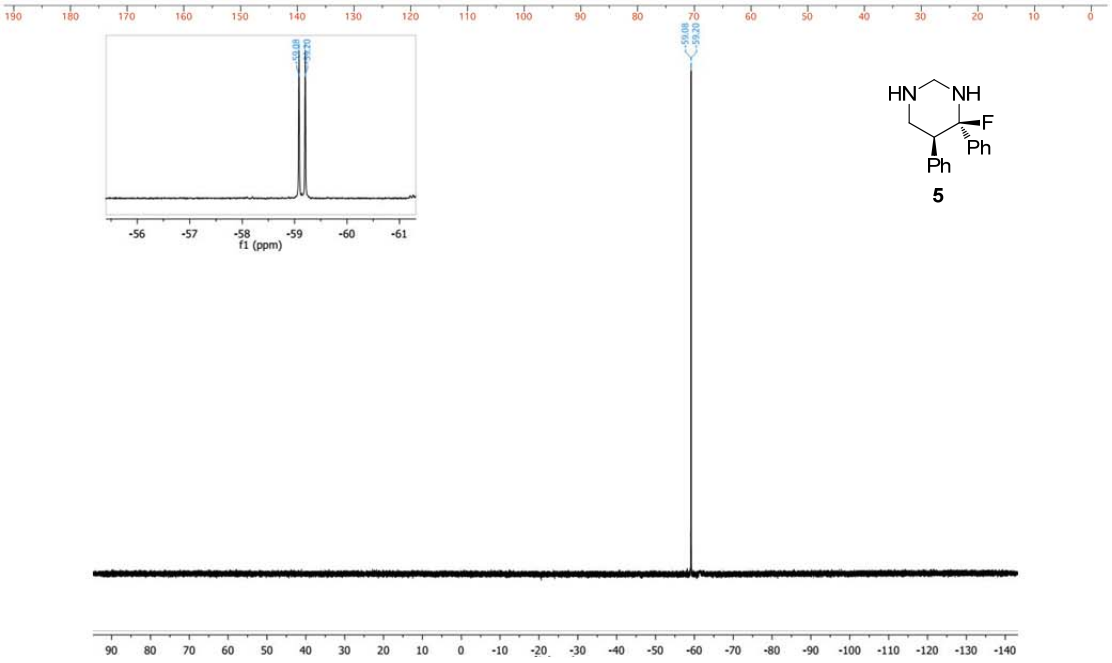

BocHN
F
NO2
6
f1 (ppm)


BocHN
F
NO2
6


BocHN
F
NO2
6


HN
NH
F
Ph
Ph
5
f1 (ppm)


HN
NH
F
Ph
Ph
5
f1 (ppm)


HN
NH
F
Ph
Ph
5
f1 (ppm)