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Enantioselective organocatalytic oxa-Michael addition of oximes to β-CF_3-β-disubstituted nitroalkenes: efficient synthesis of β-amino-α-trifluoromethyl alcohol

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Supporting Information

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1. General Information

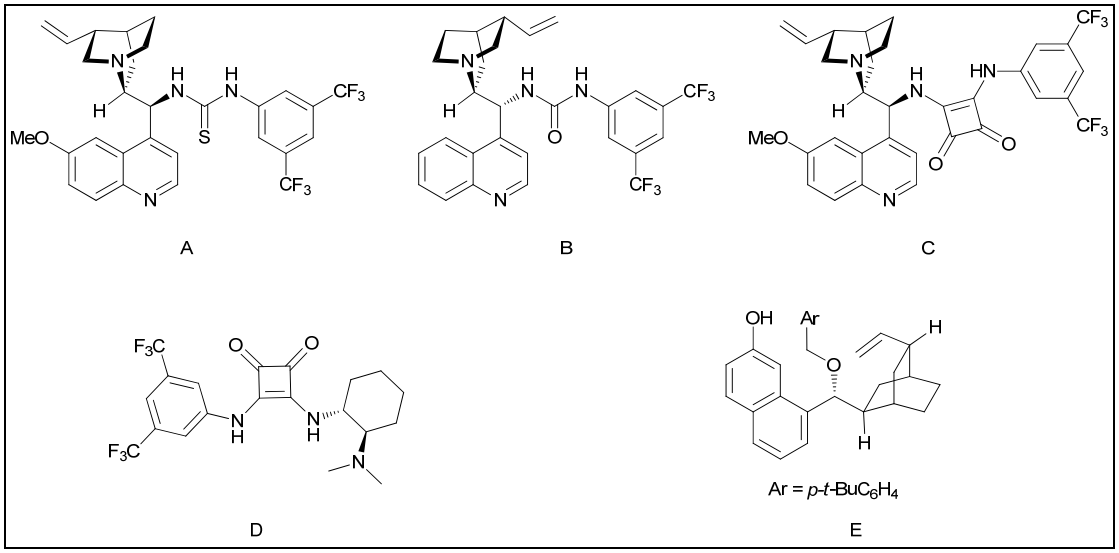
^{1}H NMR spectra were recorded on Varian-Mercury 400 MHz or 600 MHz spectrophotometers. Solvent for NMR is $CDCl_3$, unless otherwise noted. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on recorded on Varian Mercury 400/600 (100/150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm relative to the central line of the heptalet at 77.0 ppm for $CDCl_3$. Mass spectra were measured on a Bruker micrOTOF Q II. Enantiomeric ratios were determined by chiral HPLC on Agilent 1100 series with chiral columns (chiralpak IC column, chiralpak AD-H column) with hexane and *i*-PrOH as solvents. Optical rotations were measured with JASCO P-1020 polarimeter.

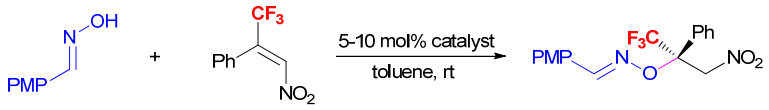
2. Materials

Unless otherwise noted, all trifluoromethylated nitroalkenes were prepared according to the known literature;[1] difluoromethylated nitroalkene **4** was prepared according to the known literature.[1, 2] Bifuntional organocatalysts **A**[3a], **B**[3b], **C**[3c], **D**[3d], **E**[3e] were prepared according to literature procedures. Dichloromethane was freshly distilled from calcium hydride. Ethyl ether, tetrahydrofuran (THF) and toluene were distilled from sodium / benzophenone. Other solvents were also purified before using. Reactions were monitored by thin layer chromatography (TLC), and column chromatography purifications were performed using 200-300 mesh silica gel.

3. Reaction Optimization

Table S1 Catalyst Screen for Conjugate Addition of 4-Methoxybenzaldehyde Oxime **1a** to (*E*)-(3,3,3-trifluoro-1-nitroprop-1-en-2-yl)benzene **2a**[a]



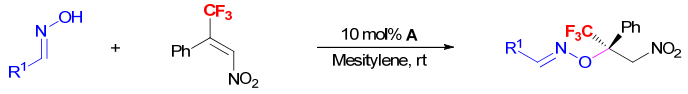


1a **2a** **3a**

Entry	Catslyst	*t*	Yield (%)[b]	e.r.[c]
1	**B**	6 d	31	42:58
2	**C**	7 d	47	84:16
3	**D**	6 d	trace	n.d.[e]
4	**E**	6 d	46	40:60
5	**B**	96 h	71	30:70[d]
6	**C**	105 h	54	84:16[d]
7	**A**	**72 h**	**75**	**88:12**[d]

[a] The reactions were carried out with 0.40 mmol (2.0 equiv) of **1a**, 0.20 mmol (1.0 equiv) of **2a** and 5 mol% **B-E** in toluene (1.0 mL) at rt. [b] Isolated yield. [c] Determined by chiral HPLC. [d] 10 mol% catalyst was uesd. [e] Not determined.

Table S2 Conjugated Addition of 4-Methoxybenzaldehyde Oximes **1a-h** to (*E*)-(3,3,3-trifluoro-1-nitroprop-1-en-2-yl)benzene **2a**[a]

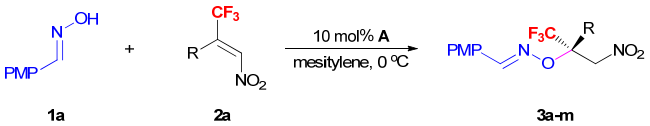


1a-h **2a** **3a, 3b'-h'**

Entry	R^1	Product	*t* (h)	Yield (%)[b]	e.r.[c]
1	**4-MeOPh (1a)**	**3a**	**50**	**91**	**92:8**
2	2-MeOPh (**1b**)	**3b′**	48	74	74:26
3	3-MeOPh (**1c**)	**3c′**	48	95	86:15
4	2,4-MeOPh (**1d**)	**3d′**	48	89	78:22
5	4-MePh (**1e**)	**3e′**	48	90	88:12
6	4-^{t}BuPh (**1f**)	**3f′**	48	87	87:13
7	2-naphthyl (**1g**)	**3g′**	48	95	60:40
8	3-PhO (**1h**)	**3h′**	48	85	89:11

[a] The reactions were carried out with 0.40 mmol (2.0 equiv) of **1**, 0.20 mmol (1.0 equiv) of **2a** and 10 mol% **A** in mesitylene (1.0 mL) at rt. [b] Isolated yield. [c] Determined by chiral HPLC.

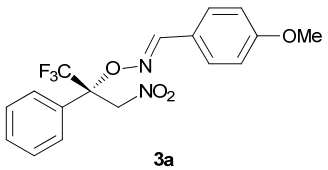
4. Experimental Procedure and Characterizations.



1a 2a 3a-m

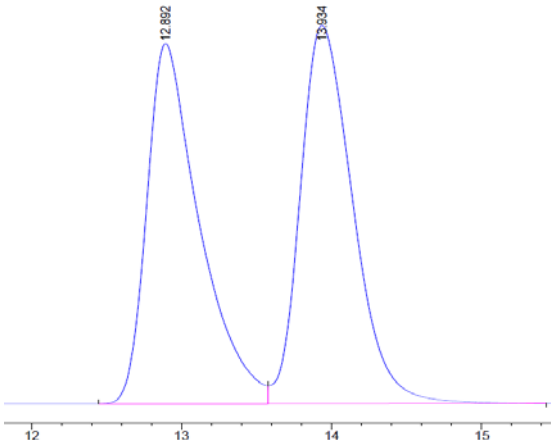
Oxime **1a** (0.40 mmol) was added to a solution of trifluoromethylated alkenes **2** (0.20 mmol) and organocatalyst **A** (0.02 mmol) in 1.0 mL of mesitylene at 0 °C. After completion (monitored by TLC analysis), the desired products **3** were purified by flash column chromatography.

(*S, E*)-4-methoxybenzaldehyde O-(1,1,1-trifluoro-3-nitro-2-phenylpropan-2-yl) oxime (**3a**)

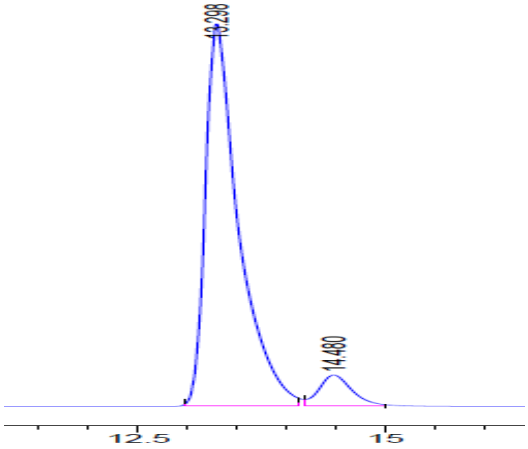


3a

Prepared according to the general procedure from **1a** (0.40 mmol), **2a** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a white solid (75% yield, 93:7 e.r.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 1H), 7.61 (s, 1H), 7.60 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 7.44 (d, *J* = 3.7 Hz, 3H), 6.93 (s, 1H), 6.90 (s, 1H), 5.74 (d, *J* = 13.5 Hz, 1H), 5.27 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 151.5, 131.8, 129.5, 129.2, 128.4, 126.7, 123.4(q, *J* = 287.6 Hz), 123.3, 114.2, 83.2 (q, *J* = 27.3 Hz), 73.6, 55.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.6 (s, 3F). HRMS m/z (ESI): calcd for $[C_{17}H_{15}F_3N_2O_4 + H]^+$: 369.1057, found 369.1062. M.P. = 79.7-81.7 °C; $[\alpha]_D^{25}$ = - 67.2 (C = 1.00, $CHCl_3$); HPLC (Chiralpak IC-H column, hexane/2-propanol = 98:2, 0.7 mL/min; 254 nm, 25 °C, t_1 = 13.30 min, t_2 = 14.48 min).

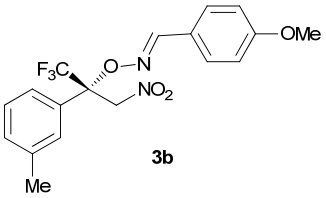


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.892	BV	0.3536	1.49966e4	613.57440	48.8342
2	13.934	VB	0.3865	1.57126e4	644.24139	51.1658



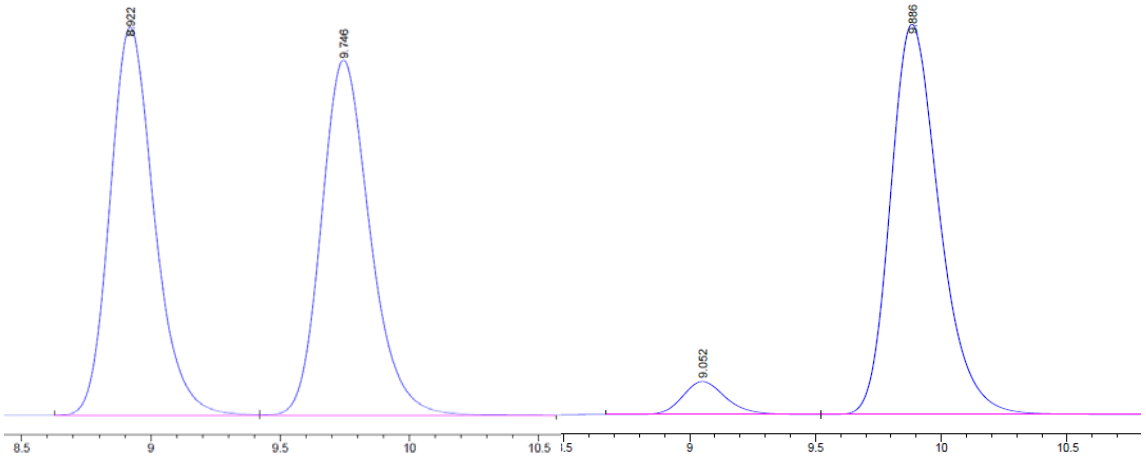
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.298	BB	0.3381	2.55856e4	1089.40027	92.5382
2	14.480	BB	0.3485	2063.10425	89.17475	7.4618

(*S,E*)-4-methoxybenzaldehyde O-(1,1,1-trifluoro-3-nitro-2-(m-tolyl)propan-2-yl) oxime (**3b**)



3b

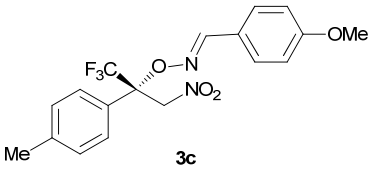
Prepared according to the general procedure from **1a** (0.40 mmol), **2b** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a white solid (74% yield, 93:7 e.r.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 7.41 (s, 1H), 7.38 (s, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 6.90 (s, 1H), 5.74 (d, *J* = 13.5 Hz, 1H), 5.26 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 151.5, 138.3, 131.8, 130.4, 129. 3, 128.4, 127.2, 123.8, 123.5, 123.4 (q, *J* = 287.6 Hz), 121.9, 114.3, 83.2 (q, *J* = 27.7 Hz), 73.6, 55.3, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.7 (s, 3F). HRMS m/z (ESI): calcd for $[C_{18}H_{17}F_3N_2O_4+H]^+$: 383.1213, found 383.1219. M.P. = 83.6-85.2 °C; $[\alpha]_D^{27}$ = -71.7 (C = 1.00, $CHCl_3$); HPLC (Chiralpak AD-H column, hexane/2-propanol = 95:5, 1.0 mL/min; 254 nm, 25 °C, t_1 = 9.05 min, t_2 = 9.89 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.922	BV	0.1918	7223.97021	604.56085	49.8982
2	9.746	VB	0.2058	7253.45654	551.57782	50.1018

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.052	BV	0.1869	1170.97705	97.36171	6.9569
2	9.886	VB	0.2110	1.56608e4	1151.77673	93.0431

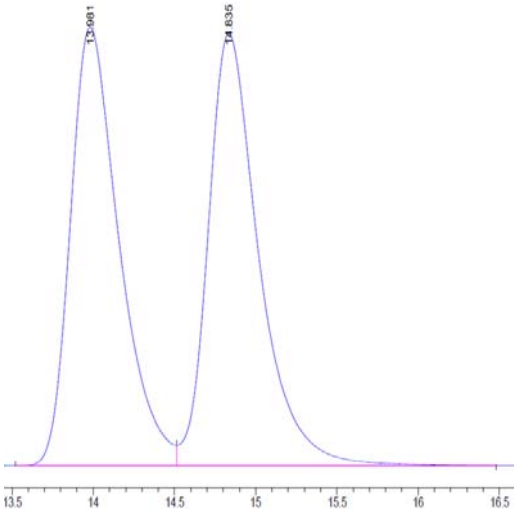
(*S,E*)-4-methoxybenzaldehyde O-(1,1,1-trifluoro-3-nitro-2-(p-tolyl)propan-2-yl) oxime (**3c**)



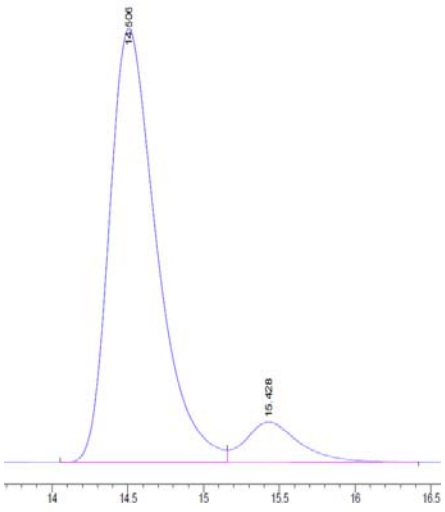
3c

Prepared according to the general procedure from **1a** (0.40 mmol), **2c** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a white solid (70% yield, 90.5:9.5 e.r.). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 8.36 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 7.49 (s, 1H), 7.47 (s, 1H), 7.25 (s, 1H), 7.24 (s, 1H), 6.92 (s, 1H), 6.91 (s, 1H), 5.72 (d, *J* = 13.5 Hz, 1H), 5.25 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 151.5, 139.6, 129.2, 128.8, 126.6, 123.5, 123.4 (q, *J* = 287.4 Hz),114.2, 83.2 (q, *J* = 27.8 Hz), 73.7, 55.2, 21.0; ^{19}F NMR (376

MHz, $CDCl_3$): δ = -74.8 (s, 3F). HRMS m/z (ESI): calcd for $[C_{18}H_{17}F_3N_2O_4 + H]^+$: 383.1213, found 383.1214. M.P. = 103.7-105.1 °C; $[\alpha]_D^{28}$ = -59.9 (C = 1.00, $CHCl_3$); HPLC (Chiralpak IC-H column, hexane/2-propanol = 95:5, 0.5 mL/min; 254 nm, 25 °C, t_1 = 14.51 min, t_2 = 15.43 min).

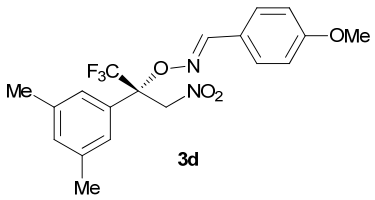


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.981	VV	0.3141	1.34727e4	647.36072	49.3377
2	14.835	VB	0.3226	1.38344e4	638.56219	50.6623



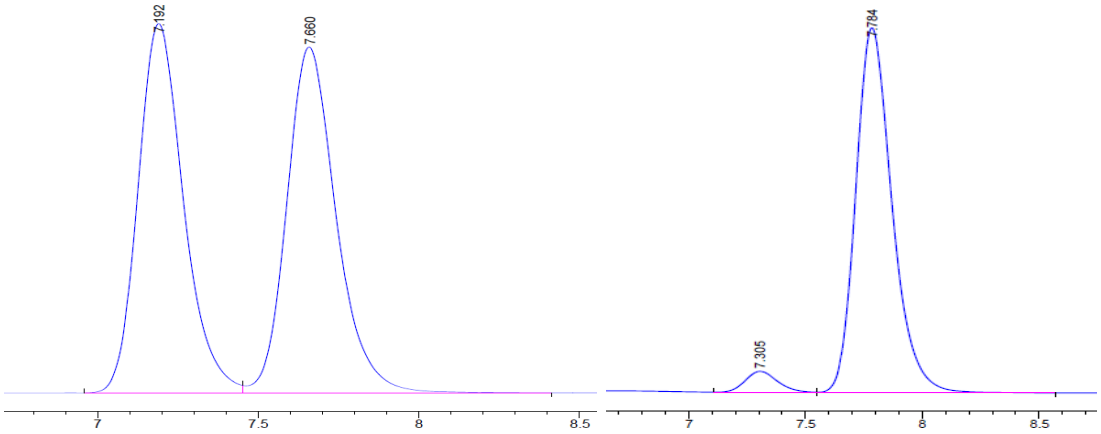
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.506	BV	0.3254	8684.59375	401.14392	90.3882
2	15.428	VB	0.3665	923.51331	37.23448	9.6118

(*S,E*)-4-methoxybenzaldehyde O-(2-(3,5-dimethylphenyl)-1,1,1-trifluoro-3-nitropropan-2-yl) oxime (**3d**)



3d

Prepared according to the general procedure from **1a** (0.40 mmol), **2d** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a white solid (77% yield, 95:5 e.r.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 7.19 (s, 2H), 7.05 (s, 1H), 6.93 (s, 1H), 6.90 (s, 1H), 5.74 (d, *J* = 13.5 Hz, 1H), 5.24 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 151.4, 138.1, 131.7, 131.3, 129.2, 124.3, 123.5, 123.4 (q, *J* = 287.4 Hz), 114.2, 83.2 (q, *J* = 27.4 Hz), 73.5, 55.2, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.7 (s, 3F). HRMS m/z (ESI): calcd for $[C_{19}H_{19}F_3N_2O_4 + H]^+$: 397.1370, found 397.1374. M.P. = 115.0-116.8 °C; $[\alpha]_D^{28}$ = -54.5 (C = 0.2, $CHCl_3$); HPLC (Chiralpak AD-H column, hexane/2-propanol = 95:5, 1.0 mL/min; 254 nm, 25 °C, t_1 = 7.30 min, t_2 = 7.78 min).



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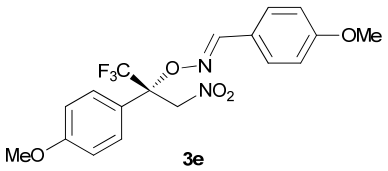
1	7.192	BV	0.1561	6867.12988	694.69318	49.5322
2	7.660	VB	0.1661	6996.84375	651.45093	50.4678

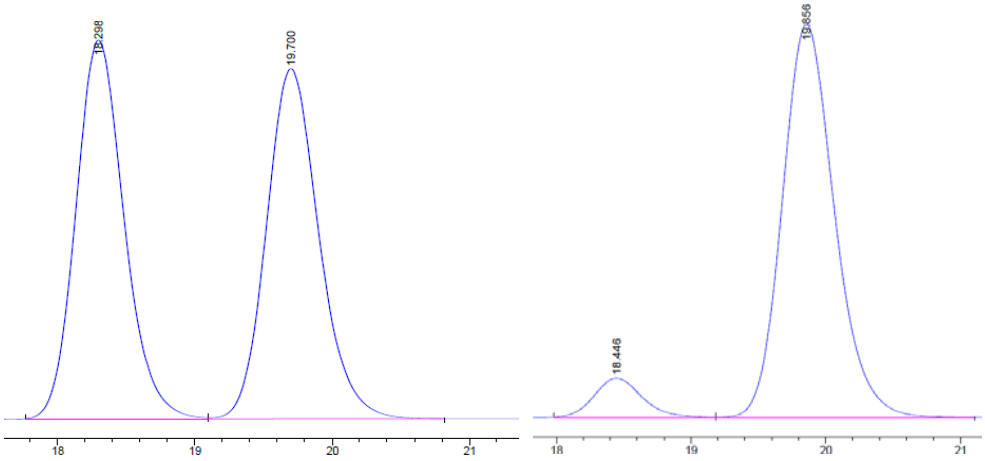
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.305	VV	0.1539	507.76868	50.43239	5.2217
2	7.784	VB	0.1657	9216.40430	850.83020	94.7783

(*S*,*E*)-4-methoxybenzaldehyde O-(1,1,1-trifluoro-2-(4-methoxyphenyl)-3-nitropropan-2-yl) oxime (**3e**)



3e

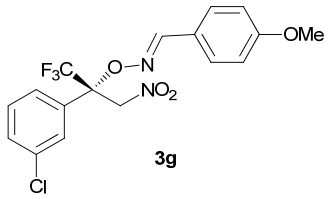
Prepared according to the general procedure from **1a** (0.40 mmol), **2e** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 4 d to provide the title compound as a white solid (71% yield, 92:8 e.r.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 7.53 (s, 1H), 7.51 (s, 1H), 6.96 (s, 1H), 6.94 (s, 1H), 6.92 (s, 1H), 6.90 (s, 1H), 5.71 (d, *J* = 13.5 Hz, 1H), 5.23 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 160.4, 151.5, 129.3, 128.2, 123.50, 123.4 (q, *J* = 287.3 Hz), 114.3, 113.9, 83.2 (q, *J* = 27.7 Hz), 73.7, 55.3, 55.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -75.0 (s, 3F). HRMS m/z (ESI): calcd for $[C_{18}H_{17}F_3N_2O_5 + H]^+$: 399.1162, found 399.1169. M.P. = 115.6-117.4 °C; $[\alpha]_D^{25}$ = -77.7 (C = 1.00, $CHCl_3$); HPLC (Chiralpak AD-H column, hexane/2-propanol = 95:5, 1.0 mL/min; 254 nm, 25 °C, t_1 = 18.45 min, t_2 = 19.86 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.298	BV	0.3790	4459.86963	182.04749	49.9022
2	19.700	VB	0.4153	4477.34570	168.26591	50.0978

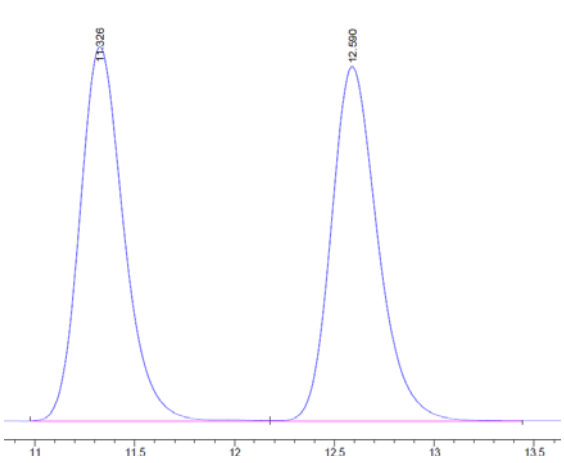
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.446	BV	0.3800	1018.35699	41.41745	8.2899
2	19.856	VB	0.4191	1.12659e4	418.25153	91.7101

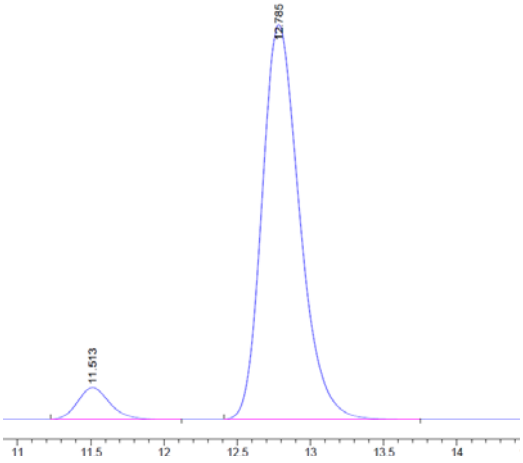
(*S,E*)-4-methoxybenzaldehyde O-(2-(3-chlorophenyl)-1,1,1-trifluoro-3-nitropropan-2-yl) oxime (**3g**)



3g

Prepared according to the general procedure from **1a** (0.40 mmol), **2g** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a colourless oil (87% yield, 93.5:6.5 e.r.). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 7.64 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 6.93 (s, 1H), 6.92 (s, 1H), 5.74 (d, *J* = 13.5 Hz, 1H), 5.22 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.9, 151.9, 134.7, 133.9, 129.9, 129.7, 129.4, 127.2, 124.9, 123.1 (q, *J* = 287.7 Hz), 114.3, 82.8 (q, *J* = 28.0 Hz), 73.5, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.8 (s, 3F). HRMS m/z (ESI): calcd for $[C_{17}H_{14}ClF_3N_2O_4 + H]^+$: 403.0667, found 403.0669. $[\alpha]_D^{25}$ = -79.2 (C = 1.00, $CHCl_3$); HPLC (Chiralpak AD-H column, hexane/2-propanol = 95:5, 1.0 mL/min; 254 nm, 25 °C, t_1 = 11.51 min, t_2 = 12.78 min).

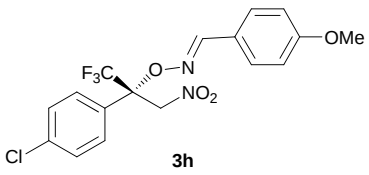




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.326	BV	0.2427	5265.84766	343.98962	49.9235
2	12.590	VB	0.2530	5281.99414	326.12439	50.0765

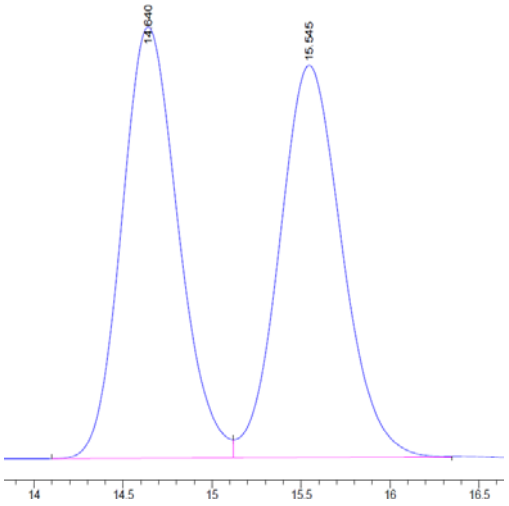
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.513	BB	0.2369	607.28027	39.65477	6.4389
2	12.785	BB	0.2777	8824.19824	495.49100	93.5611

(*S,E*)-4-methoxybenzaldehyde O-(2-(4-chlorophenyl)-1,1,1-trifluoro-3-nitropropan-2-yl) oxime (**3h**)

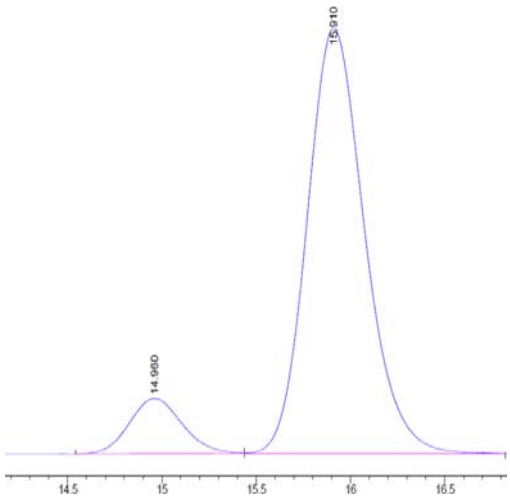


3h

Prepared according to the general procedure from **1a** (0.40 mmol), **2h** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a white solid (67% yield, 89:11 e.r.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.55 (s, 2H), 7.54 (s, 2H), 7.44 (s, 1H), 7.42 (s, 1H), 6.93 (s, 1H), 6.91 (s, 1H), 5.73 (d, *J* = 13.5 Hz, 1H), 5.22 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 151.8, 135.9, 130.4, 129.3, 128.8, 128.2, 123.2, 123.1 (q, *J* = 287.5 Hz) 114.3, 83.0 (q, *J* = 27.9 Hz), 73.6, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.9 (s, 3F). HRMS m/z (ESI): calcd for $[C_{17}H_{14}ClF_3N_2O_4+H]^+$: 403.0667, found 403.0674. M.P. = 105.2-107.3 °C; $[\alpha]_D^{27}$ = -51.6 (C = 1.00, $CHCl_3$); HPLC (Chiralpak AD-H column, hexane/2-propanol = 95:5, 1.0 mL/min; 254 nm, 25 °C, t_1 = 14.96 min, t_2 = 15.91 min).

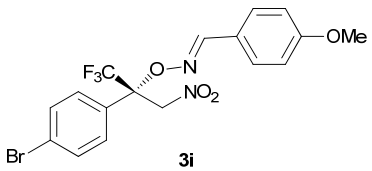


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.640	PV	0.3414	6308.65430	286.39630	49.7976
2	15.545	VB	0.3765	6359.94092	260.57272	50.2024



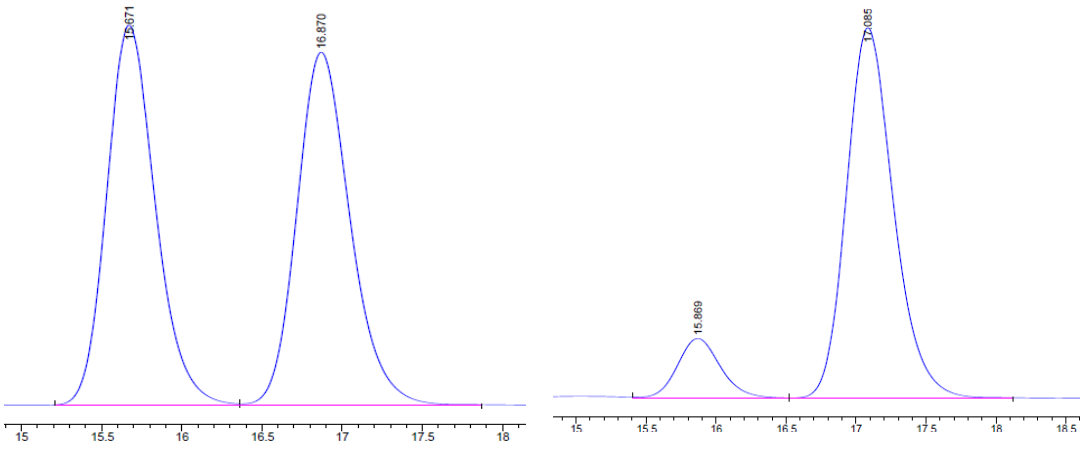
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.960	BV	0.3030	391.02756	19.94643	10.7915
2	15.910	VB	0.3275	3232.45752	152.40593	89.2085

(*S,E*)-4-methoxybenzaldehyde O-(2-(4-bromophenyl)-1,1,1-trifluoro-3-nitropropan-2-yl) oxime (**3i**)



3i

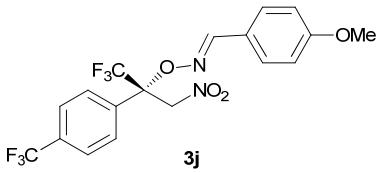
Prepared according to the general procedure from **1a** (0.40 mmol), **2i** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a white solid (86% yield, 87:13 e.r.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.59 (s, 1H), 7.58 (s, 1H), 7.55 (s, 1H), 7.53 (s, 1H), 7.49 (s, 1H), 7.47 (s, 1H), 6.92 (s, 1H), 6.91 (s, 1H), 5.71 (d, *J* = 13.5 Hz, 1H), 5.21 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.8, 151.9, 131.7, 130.9, 129.3, 128.5, 124.2, 123.2, 123.0 (q, *J* = 287.8 Hz), 114.3, 83.0 (q, *J* = 27.8 Hz), 73.5, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.9 (s, 3F). HRMS m/z (ESI): calcd for $[C_{17}H_{14}BrF_3N_2O_4+H]^+$: 447.0162, found 447.0168. M.P. = 111.1-113.2 °C; $[\alpha]_D^{28}$ = -40.4 (C = 1.00, $CHCl_3$); HPLC (Chiralpak AD-H column, hexane/2-propanol = 95:5, 1.0 mL/min; 254 nm, 25 °C, t_1 = 15.87 min, t_2 =17.08 min)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.671	BV	0.3289	6064.44775	286.07990	49.6195
2	16.870	VB	0.3578	6157.45361	265.65051	50.3805

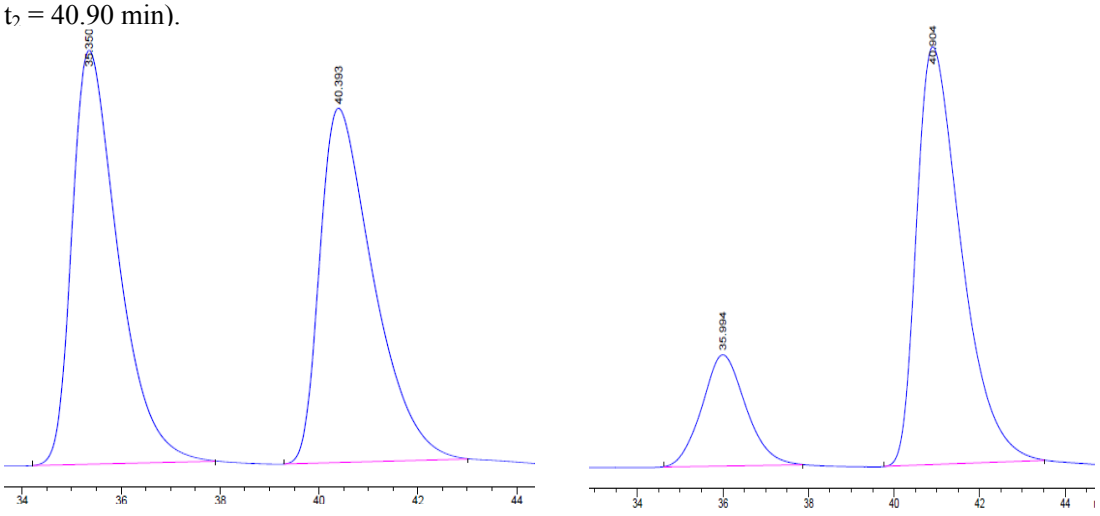
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.869	VV	0.3380	943.92639	43.93519	12.8673
2	17.085	VB	0.3671	6391.92871	272.25156	87.1327

(*S,E*)-4-methoxybenzaldehyde O-(1,1,1-trifluoro-3-nitro-2-(4-(trifluoromethyl)phenyl)propan-2-yl) oxime (**3j**)



3j

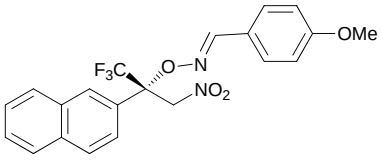
Prepared according to the general procedure from **1** (0.40 mmol), **2j** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a colourless oil (80% yield, 79:21 e.r.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.37 (s, 1H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.55 (s, 1H), 7.54 (s, 1H), 6.93 (s, 1H), 6.92 (s, 1H), 5.77 (d, *J* = 13.5 Hz, 1H), 5.27 (d, *J* = 13.5 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 152.1, 135.8, 131.7 (q, *J* = 32.7 Hz), 129.4, 127.4, 125.5, 123.6 (q, *J* = 270.3 Hz), 123.1, 121.6 (q, *J* = 287.5 Hz), 114.3, 83.0 (q, *J* = 27.7 Hz), 73.5, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -63.4 (s, 3F), -74.7 (s, 3F). HRMS m/z (ESI): calcd for $[C_{18}H_{14}F_6N_2O_4 + Na]^+$: 459.0755, found 459.0751. $[\alpha]_D^{26}$ = -44.4 (C = 1.00, $CHCl_3$); HPLC (Chiralpak OD-H column, hexane/2-propanol = 99:1, 0.7 mL/min; 254 nm, 25 °C, t_1 = 35.99 min, t_2 = 40.90 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.350	BB	0.9783	1.00667e4	155.13893	50.1322
2	40.393	BB	1.1083	1.00136e4	132.79504	49.8678

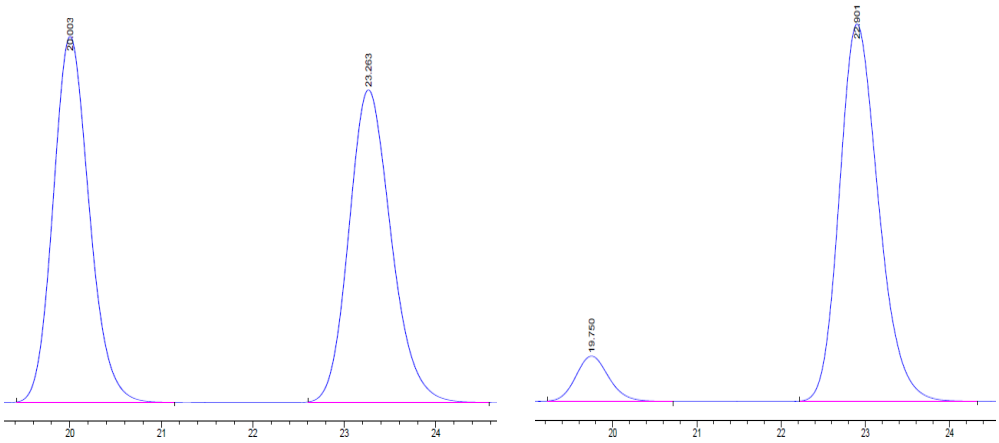
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.994	BB	1.0486	2275.68311	31.81261	20.7450
2	40.904	BB	1.0927	8694.08496	119.39623	79.2550

(*S,E*)-4-methoxybenzaldehyde O-(1,1,1-trifluoro-2-(naphthalen-2-yl)-3-nitropropan-2-yl) oxime (**3k**)



3k

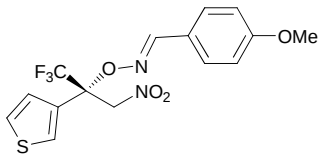
Prepared according to the general procedure from **1a** (0.40 mmol), **2k** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a white solid (83% yield, 91:9 er). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1H), 8.11 (s, 1H), 7.94 – 7.85 (m, 3H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.57 (s, 1H), 7.55 (d, *J* = 2.7 Hz, 2H), 7.54 (s, 1H), 6.93 (s, 1H), 6.91 (s, 1H), 5.83 (d, *J* = 13.5 Hz, 1H), 5.39 (d, *J* = 13.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 151.7, 133.4, 132.7, 129.3, 128.6, 128.3, 127.5, 127.2, 127.0, 126.6, 123.5, 123.4, 123.4 (q, *J* = 287.3 Hz), 114.3, 83.5 (q, *J* = 27.7 Hz), 73.8, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.5 (s, 3F). HRMS m/z (MALDI): calcd for $[C_{21}H_{17}F_3N_2O_4+H]^+$: 419.1219, found 419.1213. M.P. = 128.5-130.0 °C; $[\alpha]_D^{26}$ = -47.3 (C = 1.00, $CHCl_3$); HPLC (Chiralpak AD-H column, hexane/2-propanol = 95:5, 1.0 mL/min; 254 nm, 25 °C, t_1 = 19.75 min, t_2 = 22.90 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.003	BB	0.4257	4680.77539	170.21399	49.9820
2	23.263	BB	0.4982	4684.14014	145.37614	50.0180

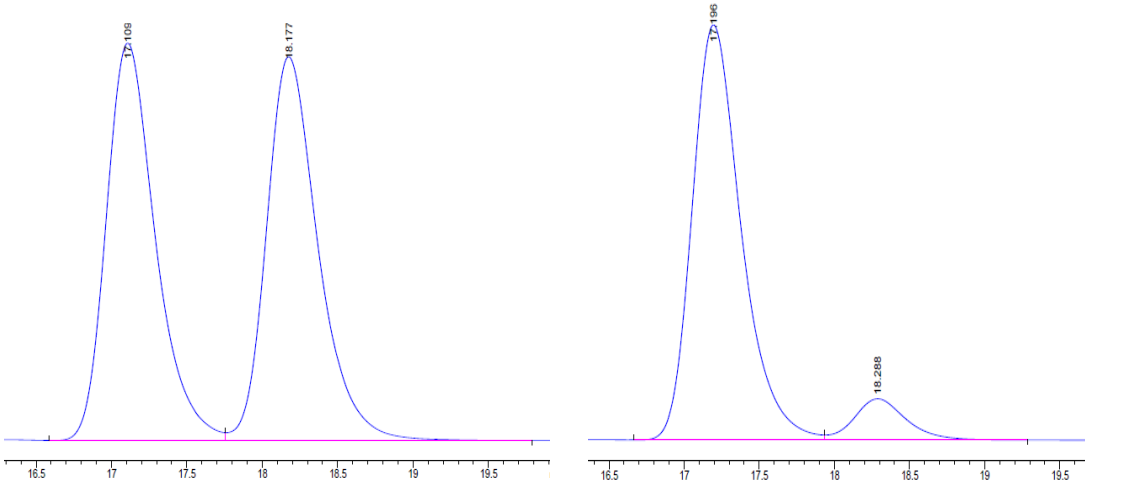
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.750	BB	0.4253	940.95007	34.26040	9.2772
2	22.901	BB	0.4994	9201.62891	284.67352	90.7228

(*S,E*)-4-methoxybenzaldehyde O-(1,1,1-trifluoro-3-nitro-2-(thiophen-3-yl)propan-2-yl) oxime (**3l**)



3l

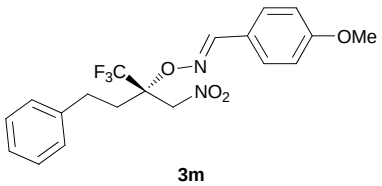
Prepared according to the general procedure from **1a** (0.40 mmol), **2l** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a yellow solid (69% yield, 90.5:9.5 e.r.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.57 (s, 2H), 7.55 (s, 1H), 7.39 (s, 1H), 7.23 (s, 1H), 6.93 (s, 1H), 6.92 (s, 1H), 5.65 (d, *J* = 13.5 Hz, 1H), 5.16 (d, *J* = 13.5 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 151.5, 132.2, 129.2, 126.2, 125.9, 125.4, 123.3, 123.1 (*J* = 287.1 Hz), 114.3, 82.4 (q, *J* = 28.6 Hz), 74.4, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -75.1 (s, 3F). HRMS m/z (ESI): calcd for $[C_{15}H_{13}F_3N_2O_4S+H]^+$: 375.0621, found 375.0623. M.P. = 84.0-85.7 °C; $[\alpha]_D^{21}$ = -57.6 (C = 1.00, $CHCl_3$); HPLC (Chiralpak IC-H column, hexane/2-propanol = 95:5, 0.5 mL/min; 254 nm, 25 °C, t_1 = 17.20 min, t_2 = 18.29 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	17.109	VV	0.3461	1.53999e4	679.12683	49.5979
2	18.177	VB	0.3657	1.56496e4	655.96265	50.4021

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	17.196	VV	0.3469	1.35138e4	594.20599	90.4254
2	18.288	VB	0.3641	1430.90613	59.08576	9.5746

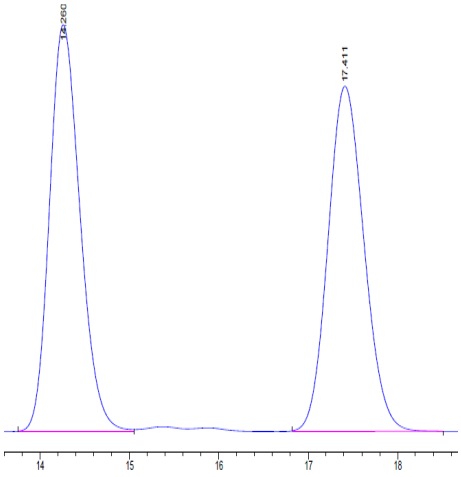
(*S,E*)-4-methoxybenzaldehyde O-(1,1,1-trifluoro-2-(nitromethyl)-4-phenylbutan-2-yl) oxime (**3m**)



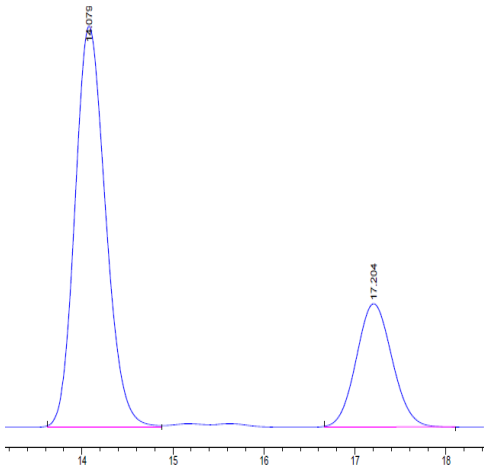
3m

Prepared according to the general procedure from **1a** (0.40 mmol), **2m** (0.20 mmol), mesitylene (1.0 mL) at 0 °C for 3 d to provide the title compound as a colourless oil (71% yield, 73:27 e.r.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 7.31 (s, 2H), 7.24 (s, 1H), 7.23 (s, 2H), 6.93 (s, 1H), 6.92 (s, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 4.96 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 3H), 2.89 (s, 2H), 2.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.7, 151.6, 140.5, 129.1, 128.6, 128.3, 126.3, 124.1 (q, *J* = 287.5 Hz), 123.3, 114.3, 81.8 (q, *J* = 27.4 Hz), 75.0, 55.2, 33.0, 28.9; ^{19}F

NMR (376 MHz, $CDCl_3$): δ = -74.1 (s, 3F). HRMS m/z (ESI): calcd for $[C_{19}H_{19}F_3N_2O_4 + H]^+$: 397.1370, found 397.1370. $[\alpha]_D^{26}$ = -26.3 (C = 1.00, $CHCl_3$); HPLC (Chiralpak OD-H column, hexane/2-propanol = 95:5, 1.0 mL/min; 254 nm, 25 °C, t_1 = 14.08 min, t_2 = 17.20 min).

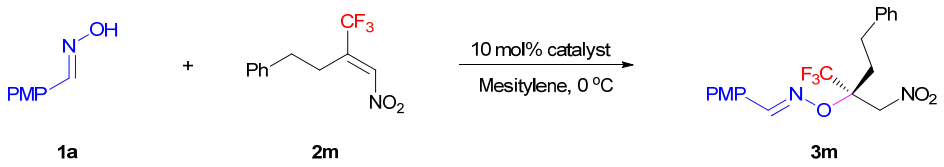


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.260	BV	0.3705	5656.17285	237.95988	49.9844
2	17.411	BB	0.4377	5659.69678	201.89621	50.0156

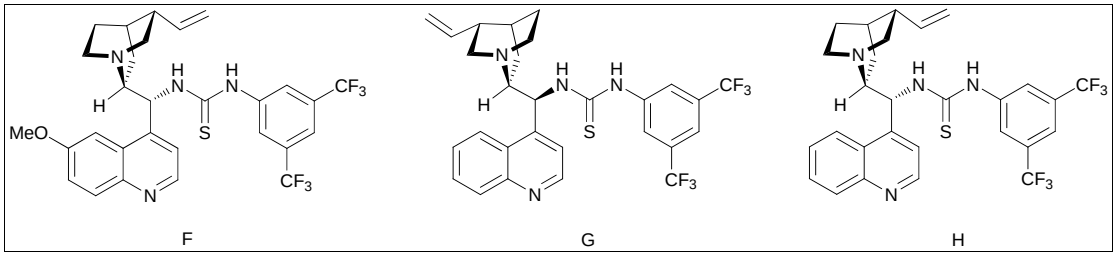


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.079	BV	0.3603	2881.07373	123.16792	73.4421
2	17.204	BB	0.4312	1041.84277	37.91815	26.5579

Table S3 Catalyst screen for the reaction with substrate **2m**[a]



1a **2m** **3m**



F G H

Entry	Catslyst	*t*	Yield (%)[b]	e.r.[c]
1	**F**	3 d	48	39:61
2	**G**	**3d**	**52**	**85:15**
3	**H**	3d	32	31.5:68.5

[a] The reactions were carried out with 0.40 mmol (2.0 equiv) of **1a**, 0.20 mmol (1.0 equiv) of **2m** and 10 mol% catalyst in mesitylene (1.0 mL) at 0 °C. [b] Isolated yield. [c] Determined by chiral HPLC.

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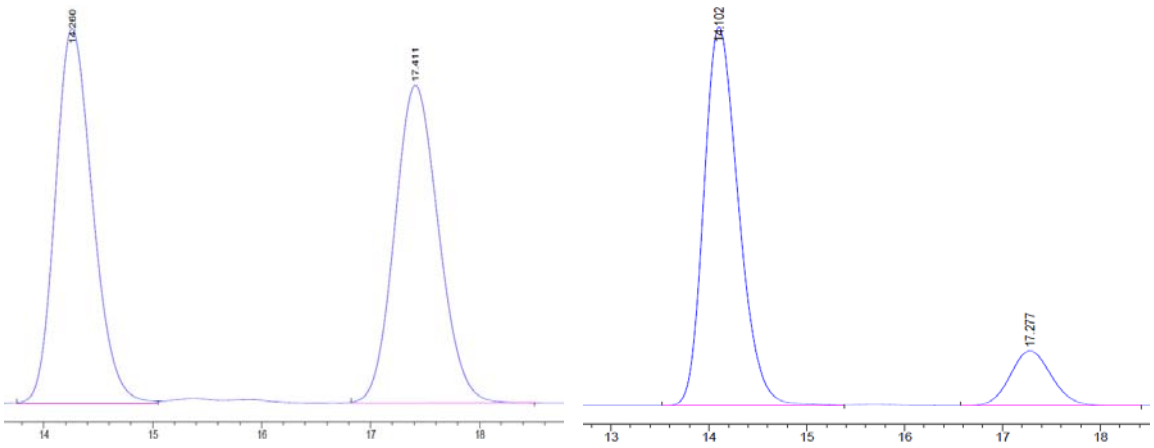
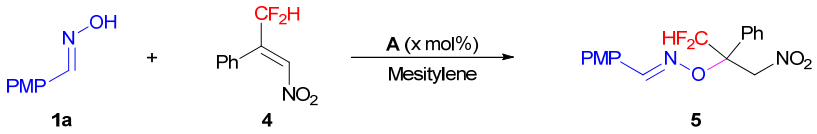


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.260	BV	0.3705	5656.17285	237.95988	49.9844
2	17.411	BB	0.4377	5659.69678	201.89621	50.0156

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.102	BV	0.3825	9993.60547	407.03305	85.4438
2	17.277	BB	0.4520	1702.50757	58.68724	14.5562

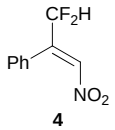
Table S4 Oxa-Michael addition of oxime to *β*-CF_2H-*β*-disubstituted nitroalkene **5**[a]



Entry	x	*t* (h)	Yield (%)[e]	e.r.[f]
1	10	24	91	83:17[b]
2	10	42	88	84:16
3	**10**	**42**	**80**	**85:15**[c]
4	20	42	90	84:16[d]

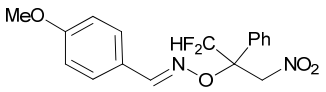
[a] The reactions were carried out with 0.40 mmol (2.0 equiv) of **1a**, 0.20 mmol (1.0 equiv) of **4** and 10 mol% catalyst in mesitylene (1.0 mL) at 0 °C. [b] Conducted at room temperature. [c] Conducted at -10 °C. [d] Conducted at -10 °C, x = 20. [e] Isolated yield. [f] Determined by chiral HPLC.

(*E*)-(3,3-difluoro-1-nitroprop-1-en-2-yl)benzene (**4**)



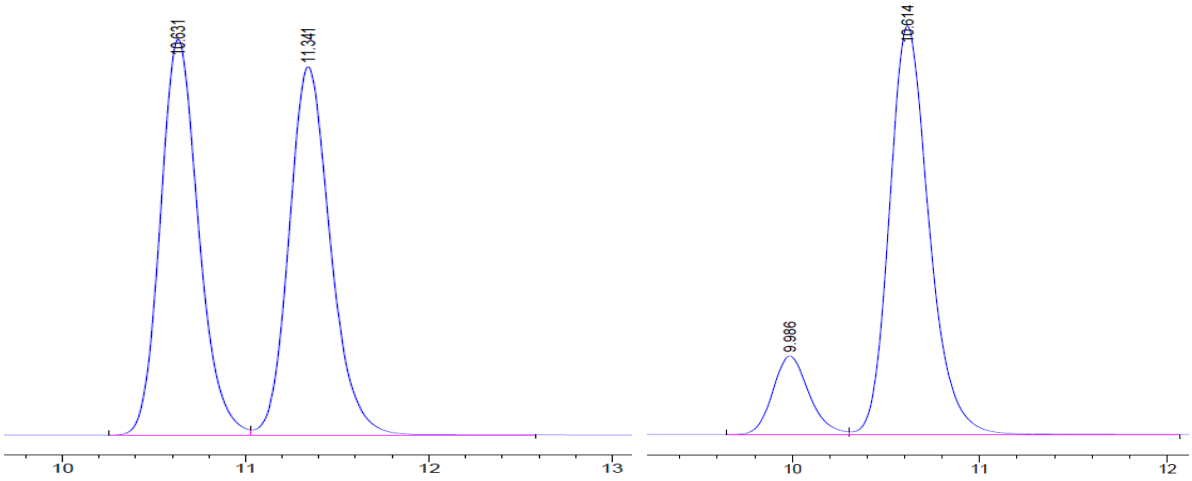
Prepared according to the known literature (yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, 3H), 7.35 (s, 1H), 7.28 (s, 2H), 6.34 (t, *J* = 54.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8 (t, *J* = 20.0 Hz), 138.5 (t, *J* = 12.5 Hz), 130.0, 128.8, 128.6, 127.7, 112.5(t, *J* = 243.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -119.0 (s, 2F). HRMS m/z (ESI): calcd for $[C_9H_7F_2NO_2+Na]^+$: 222.0337, found 222.0335.

(*E*)-4-methoxybenzaldehyde O-(1,1-difluoro-3-nitro-2-phenylpropan-2-yl) oxime (**5**)



5

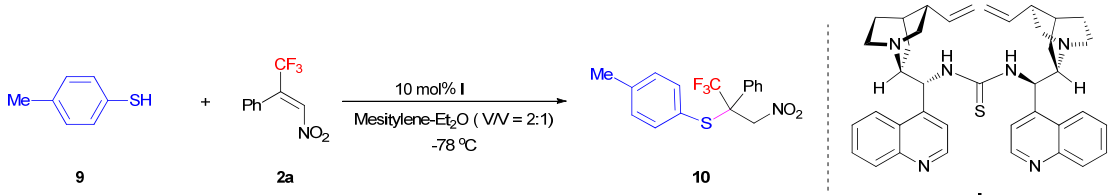
Prepared according to the general procedure from **1a** (0.40 mmol), **4** (0.20 mmol), mesitylene (1.0 mL) at -10 °C for 42 h to provide the title compound as a colourless oil (80% yield, 85:15 e.r.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 4H), 7.42 (d, *J* = 7.4 Hz, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.52 (t, *J* = 54.0 Hz, 1H), 5.37 (d, *J* = 13.0 Hz, 1H), 5.21 (d, *J* = 13.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 151.6, 132.7, 129.2, 129.1, 128.4, 126.8, 123.4, 114.2, 113.3 (t, *J* = 247.5 Hz), 82.8 (t, *J* = 23.0 Hz), 76.5, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -128.5 – -131.92 (m, 2F). HRMS m/z (ESI): calcd for $[C_{17}H_{16}F_2N_2O_4+H]^+$: 351.1151, found 351.1154. $[\alpha]_D^{19}$ = 17.3 (C = 1.00, $CHCl_3$); HPLC (Chiralpak AD-H column, hexane/2-propanol = 85:15, 1.0 mL/min; 254 nm, 25 °C, t_1 = 9.99 min, t_2 = 10.61 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.631	BV	0.2246	5285.97705	364.40561	49.7861
2	11.341	VB	0.2446	5331.39502	339.14377	50.2139

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.986	BV	0.2095	1629.51013	121.02731	14.9200
2	10.614	VB	0.2274	9292.15039	630.16931	85.0800

Michael addition of thiol **8** to *β*-CF_3-*β*-disubstituted nitroalkene **2a**



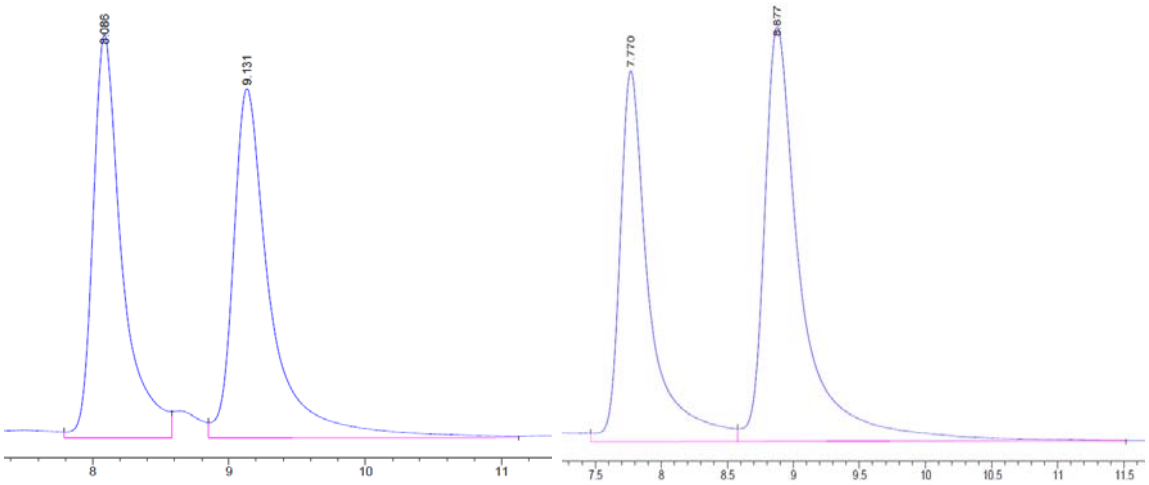
9 **2a** **10** **I**

70% yield
58:42 er

Thiol **9** (0.22 mmol) was added to a solution of trifluoromethylated alkene **2a** (0.20 mmol) and organocatalyst **I** (0.02 mmol) in 1.5 mL of mesitylene-Et_2O (V/V = 2:1) at -78 °C. After

completion (monitored by TLC analysis), the desired products **10** were purified by flash column chromatography.

Prepared according to the general procedure from **9** (0.22 mmol), **2a** (0.20 mmol), mesitylene-Et_2O (1.5 mL, V/V = 2:1) at -78 °C for 30 min to provide the title compound as a colourless oil (70% yield, 58:42 e.r.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.0 Hz, 2H), 7.41 – 7.39 (m, 5H), 7.13 (d, *J* = 7.7 Hz, 2H), 5.11 – 5.03 (m, 2H), 2.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.4, 137.9, 131.51, 130.0, 129.1, 128.5, 127.7, 125.3 (q, *J* = 283.0 Hz), 124.0, 75.5, 60.3 (q, *J* = 26.7 Hz), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -66.1 (s, 3F). HRMS m/z (ESI): calcd for $[C_{16}H_{14}F_3NO_2S + Na]^+$: 364.0595, found 364.0607. HPLC (Chiralpak OD-H column, hexane/2-propanol = 95:5, 1.0 mL/min; 254 nm, 25 °C, t_1 = 7.77 min, t_2 = 8.88 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.086	VV	0.2203	1751.56042	117.65757	47.4200
2	9.131	VV	0.2774	1942.15247	102.02345	52.5800

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.770	VV	0.2260	1480.59912	94.71944	41.8567
2	8.877	VB	0.2821	2056.70239	105.81108	58.1433

5. References

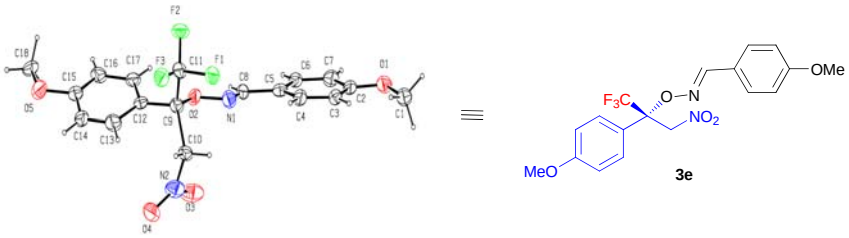
(1) J.-R. Gao, H. Wu, B. Xiang, W.-B. Yu, L. Han and Y.-X. Jia, *J. Am. Chem. Soc.*, 2013, **135**, 2983.

(2) T. Kitazume, M. Asai, T. Tsukamoto and T. Yamazaki, *J. Fluorine Chem.*, 1992, **56**, 271.

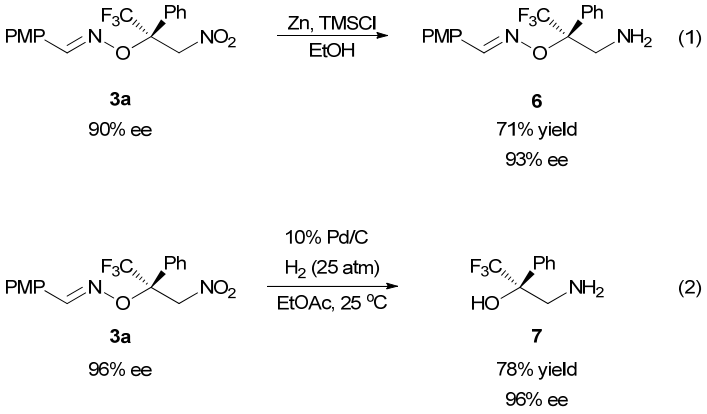
(3) (a) B. Vakulya, S. Varga, A. Csampai and T. Soos, *Org. Lett.*, 2005, **7**, 1967; (b) M. Amere, M. C. Lasne and J. Rouden, *Org. Lett.*, 2007, **9**, 2621; (c) W. Yang and D.-M. Du, *Org. Lett.*, 2010, **12**, 5450; (d) J. P. Malerich, K. Hagihara and V. H. Rawal, *J. Am. Chem. Soc.*, 2008, **130**, 14416; (e) F.-G. Zhang, Q.-Q. Yang, J. Xuan, H.-H. Lu, S.-W. Duan, J.-R. Chen and W.-J. Xiao, *Org. Lett.*, 2010, **12**, 5636.

(4) J. Weng, Y.-B. Li, R.-B. Wang, F.-Q. Li, C. Liu, A.-S. Chan and G. Lu, *J. Org. Chem.*, 2010, **75**, 3125.

6. X-Ray Single Crystal Structure of Product 3e



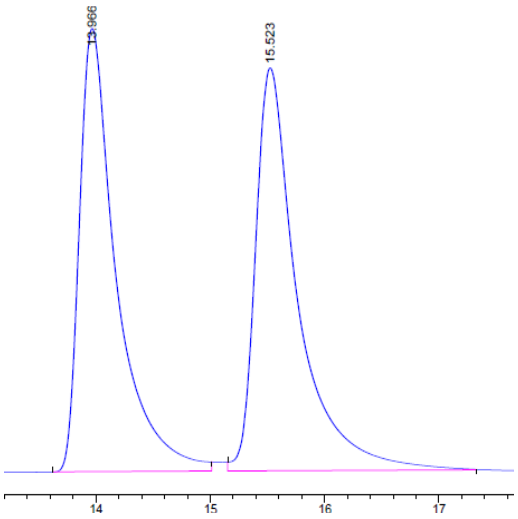
7. Application of the Michael Reaction Product 3a



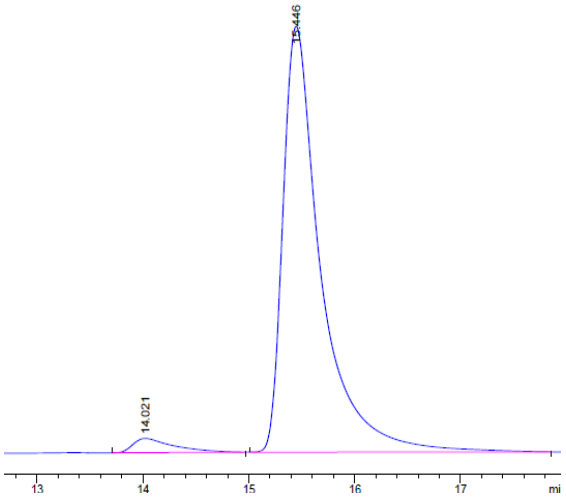
(*S*,*E*)-4-methoxybenzaldehyde O-(3-amino-1,1,1-trifluoro-2-phenylpropan-2-yl) oxime 6[4]

Activated Zn powder (975 mg, 15 mmol) was added carefully to a solution of **3a** (110.5 mg, 0.30 mmol) and trimethylsilyl chloride (1.14 mL, 37.2 mmol) in EtOH (5.0 mL) at room temperature. The mixture was stirred at 70 °C for 2 h, cooled to rt and adjusted to weakly basic (pH = 8) with 28% NH_4OH in H_2O. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with saturated brine, dried over $MgSO_4$ and then removed under reduced pressure. Finally, purification by flash chromatography gave **6** as a white solid (72 mg, 71% yield, 93% ee).

^{1}H NMR (600 MHz, $CDCl_3$): 8.36 (s, 1H), 7.55 (s, 2H), 7.54 (d, J = 2.4 Hz , 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.39 (d, J = 6.6 Hz, 1H), 6.91 (s, 1H), 6.89 (s, 1H), 3.88 (d, J = 14.7 Hz, 1H), 3.83 (s, 3H), 3.47 (d, J = 14.7 Hz, 1H).1.67 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 151.0, 134.6, 129.0, 128.7, 128.4, 127.2, 125.1 (q, J = 274.4 Hz), 123.9, 114.2, 85.4 (q, J = 21.8 Hz), 55.3, 44.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -74.6 (s, 3F). HRMS m/z (MALDI): calcd for $[C_{17}H_{17}F_3N_2O_2+H]^+$: 339.1415, found 339.1419. M.P. = 63.2-65.7 °C; $[\alpha]_D^{25}$ = -18.7 (C = 1.00, $CHCl_3$); HPLC (Chiralpak AD-H column, hexane/2-propanol = 90:10, 0.7 mL/min; 254 nm, 25 °C, t_1 = 14.02 min, t_2 = 15.45 min).



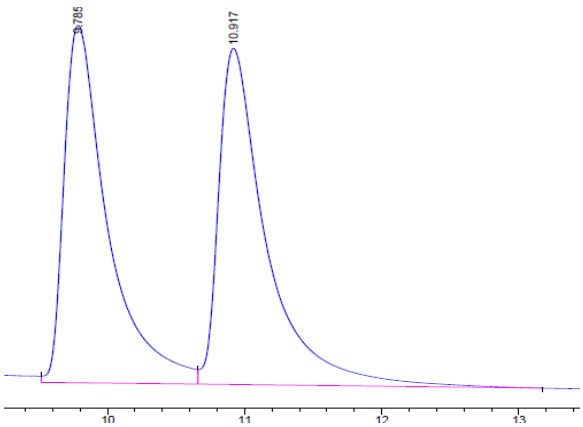
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.966	BB	0.3271	3914.14917	174.55135	48.9378
2	15.523	BB	0.3732	4084.06055	158.63531	51.0622



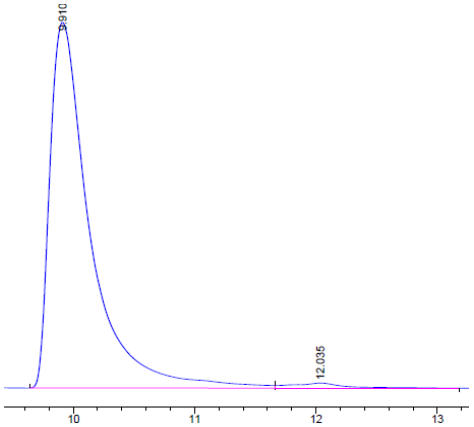
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.021	PB	0.3926	462.47064	16.79652	3.5821
2	15.446	BB	0.3660	1.24481e4	497.86438	96.4179

(*S*)-3-amino-1,1,1-trifluoro-2-phenylpropan-2-ol 7[3e]

A suspension solution of **3a** (147.3 mg, 0.40 mmol) and 10% Pd/C (221 mg) in EtOAc (6 mL) was stirred under 25 atm of hydrogen for 24 h. After the reaction mixture was filtered from Celite, the solvent was removed under reduced pressure and the residue was purified by flash chromatography to give **7** as a white solid (64.4 mg, 78% yield, 96% ee). ^{1}H NMR (600 MHz, $CDCl_3$):δ = 7.58 (s, 1H), 7.57 (s, 1H), 7.41 – 7.34 (m, 3H), 3.56 (d, J = 13.2 Hz, 1H), 3.03 (d, J = 13.3 Hz, 1H), 1.44 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.3, 128.5, 128.3, 126.2, 125.7 (q, J = 285.3 Hz), 74.0 (q, J = 27.0 Hz), 45.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -79.0 (s, 3F). HRMS m/z (MALDI): calcd for $[C_9H_{10}F_3NO+H]^+$: 206.0787, found 206.0780. M.P. = 89.1-90.8 °C; $[\alpha]_D^{26}$ = +36.75 (C = 1.00, $CHCl_3$); HPLC (Chiralpak IC-H column, hexane/2-propanol = 90:10, 0.7 mL/min; 215 nm, 25 °C, t_1 = 9.91 min, t_2 = 12.04 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.785	BV	0.3172	5761.80664	261.02951	49.2172
2	10.917	VB	0.3522	5945.07959	245.66129	50.7828



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.910	PB	0.3403	1.05305e4	456.81915	98.1140
2	12.035	BB	0.4143	202.42809	6.42273	1.8860

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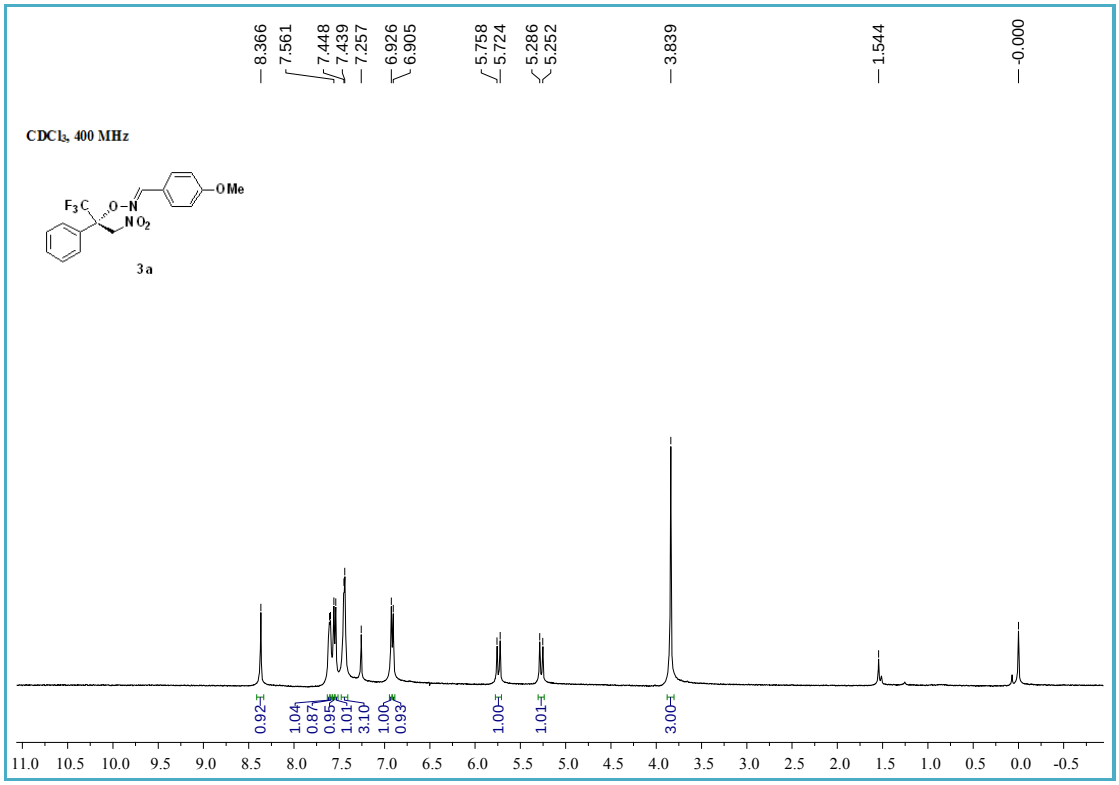
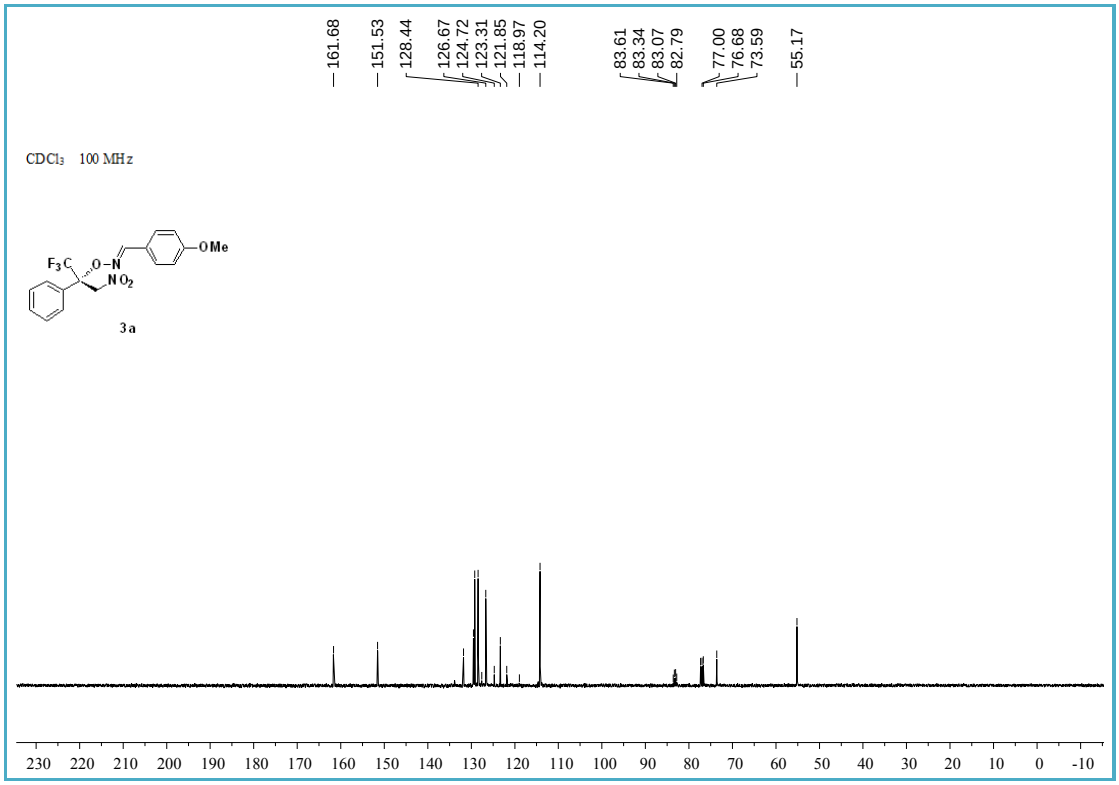
8. Copies of ^{1}H NMR ^{13}C NMR and ^{19}F NMR Spectra

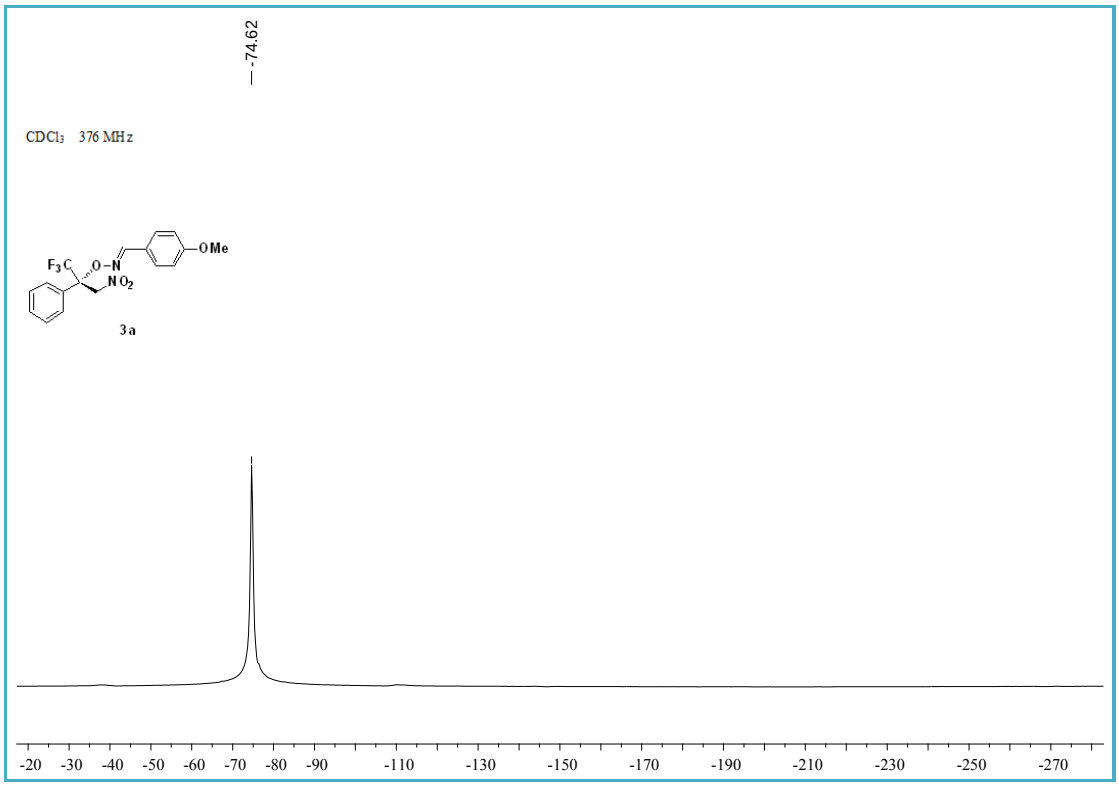
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3a



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3a



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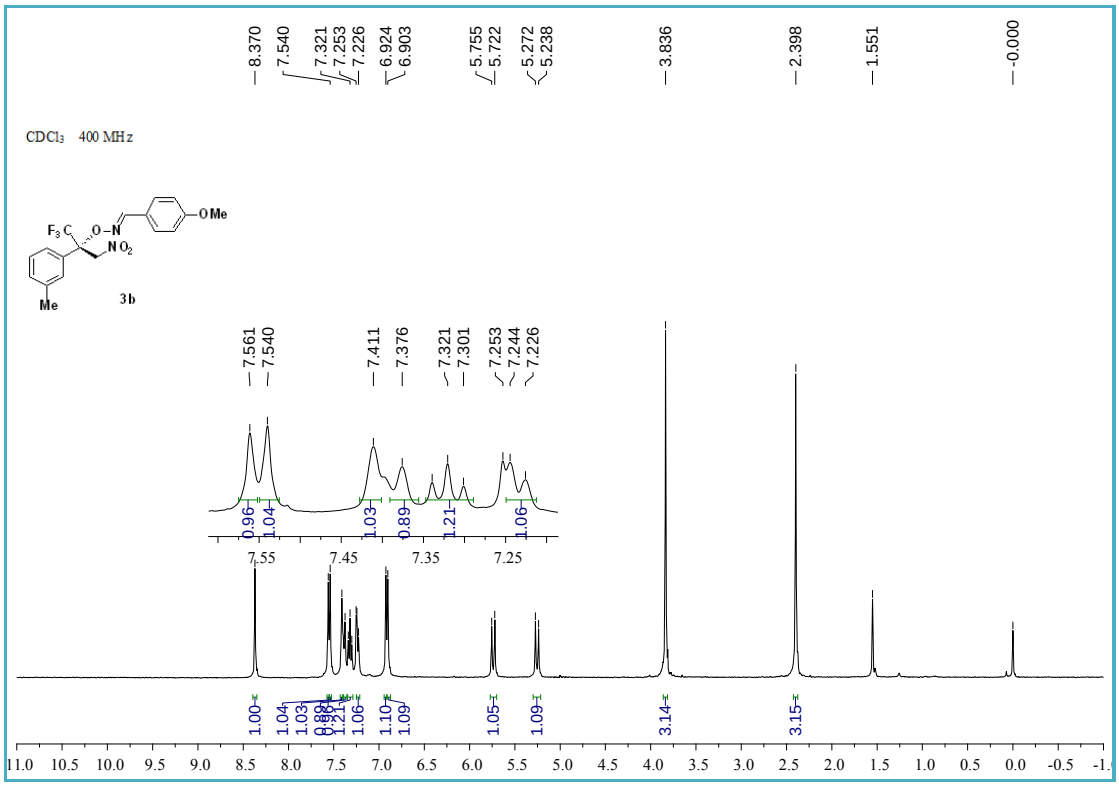
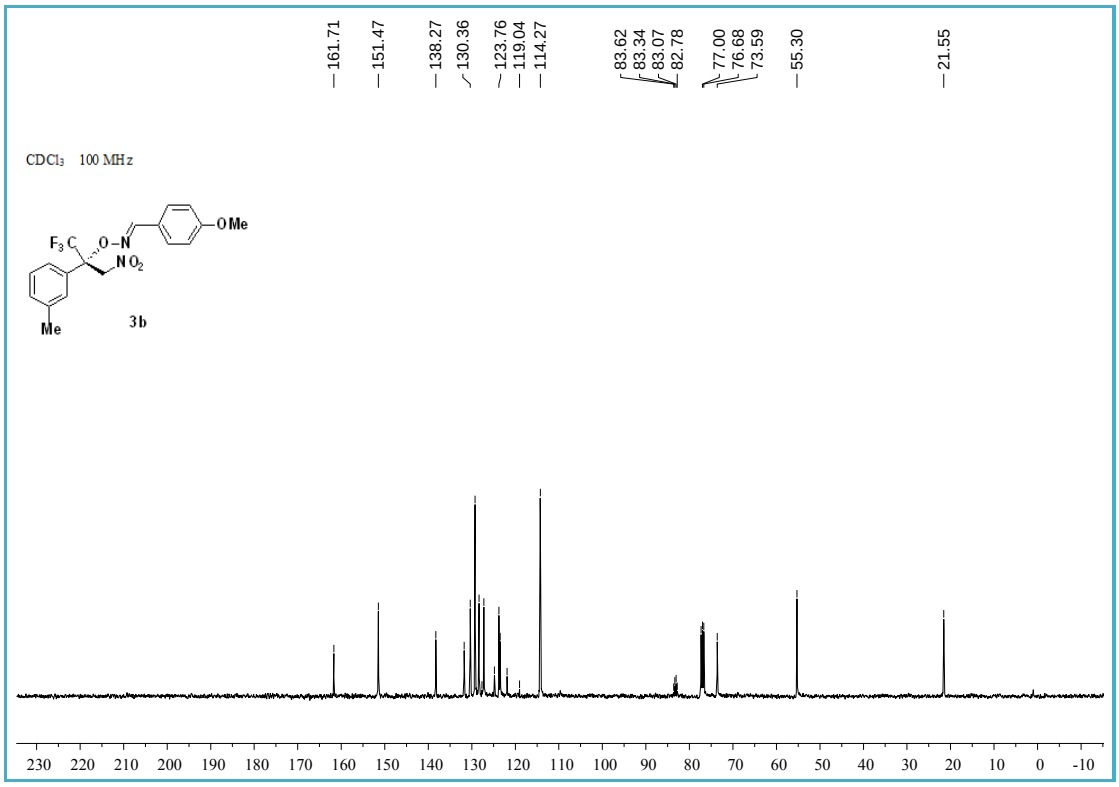
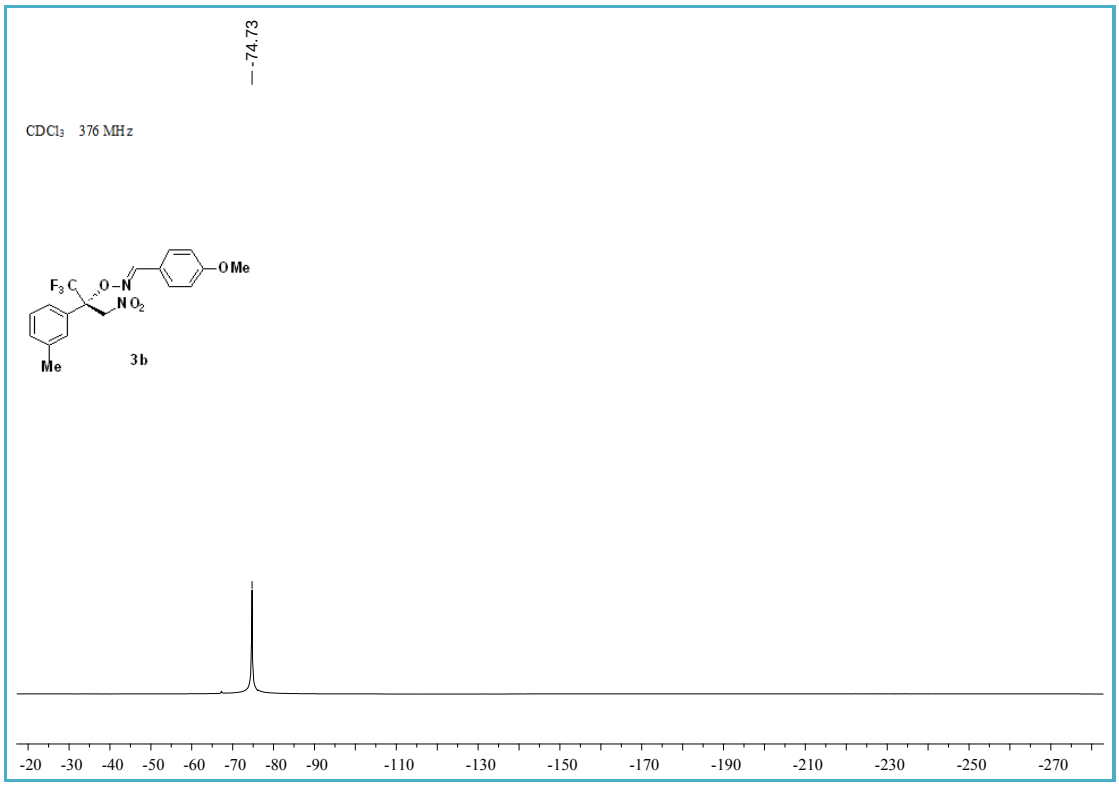
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3b



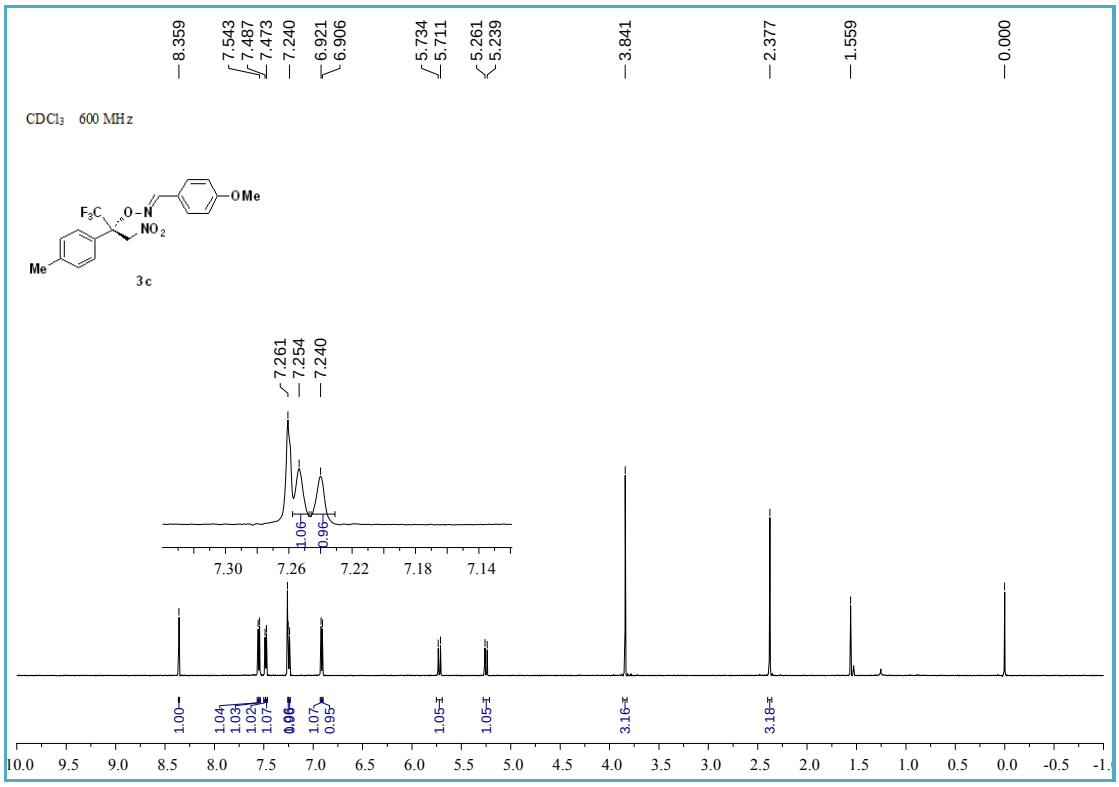
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3b



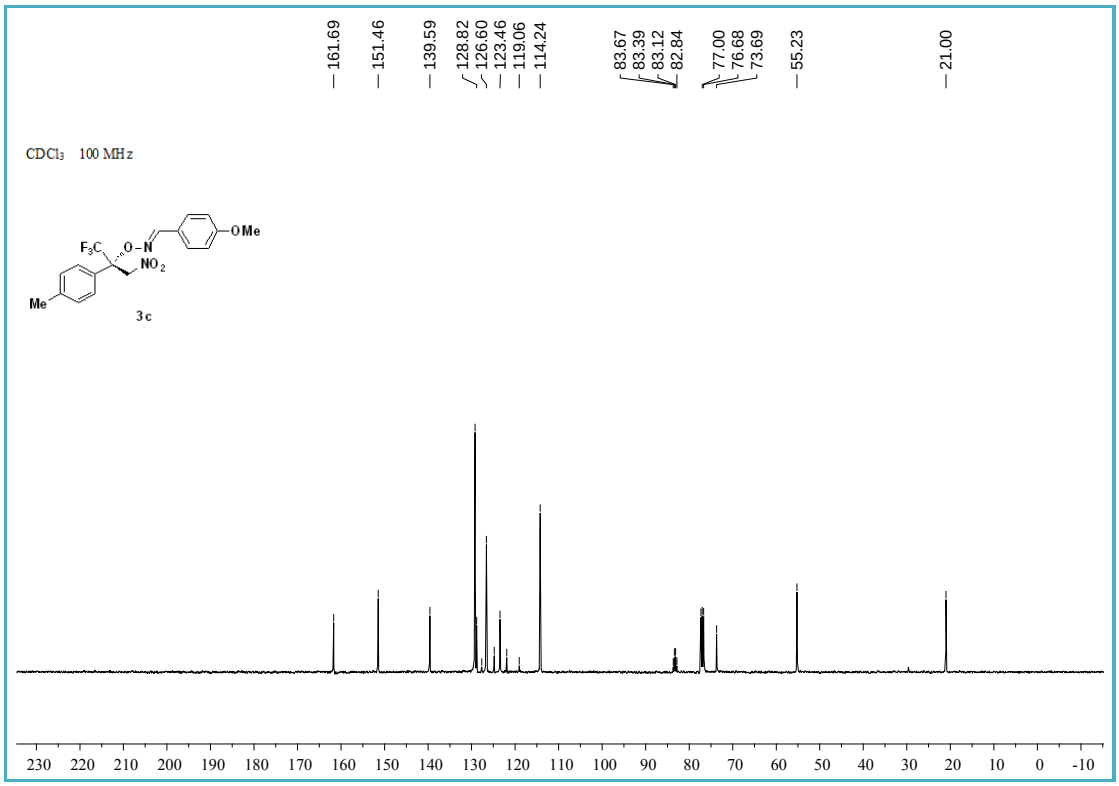
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3b



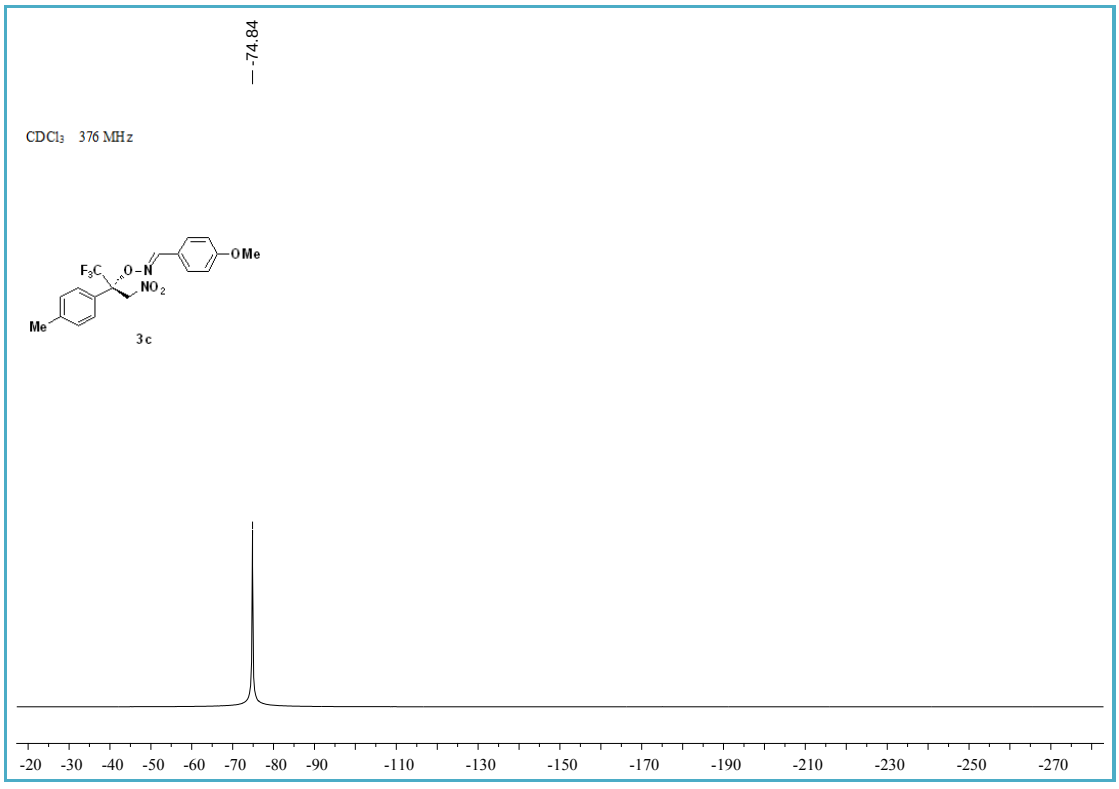
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3c



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3c



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3c



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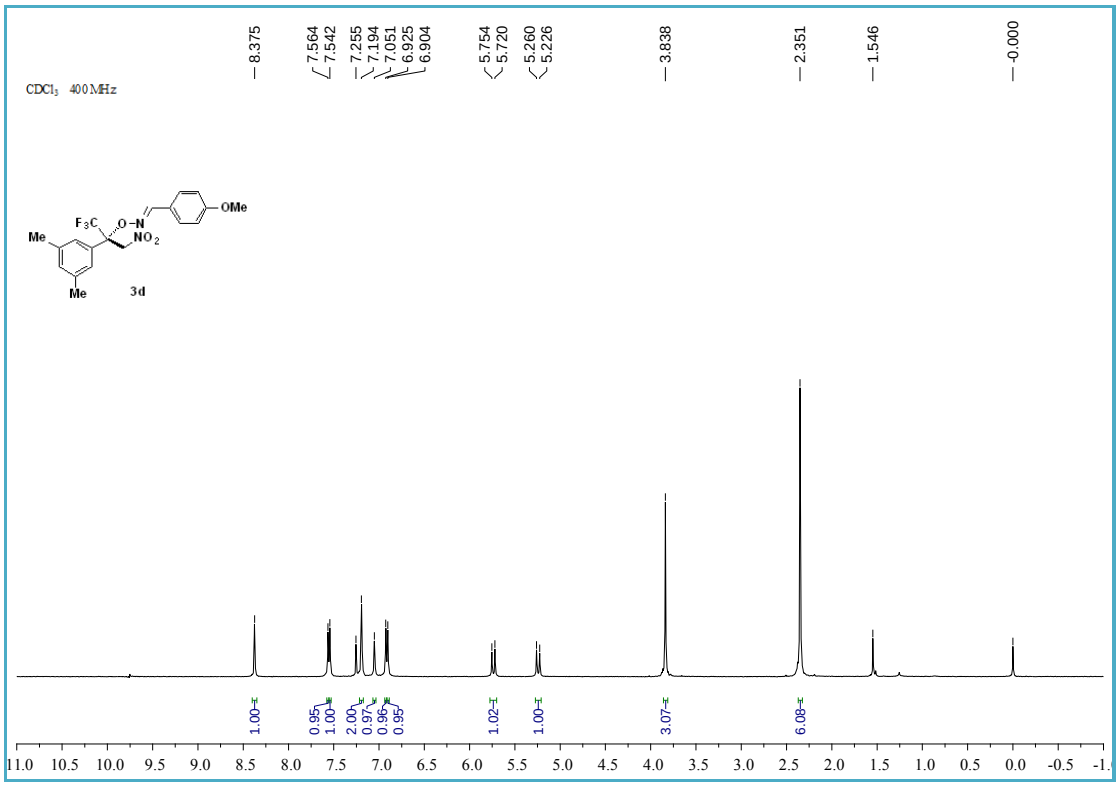
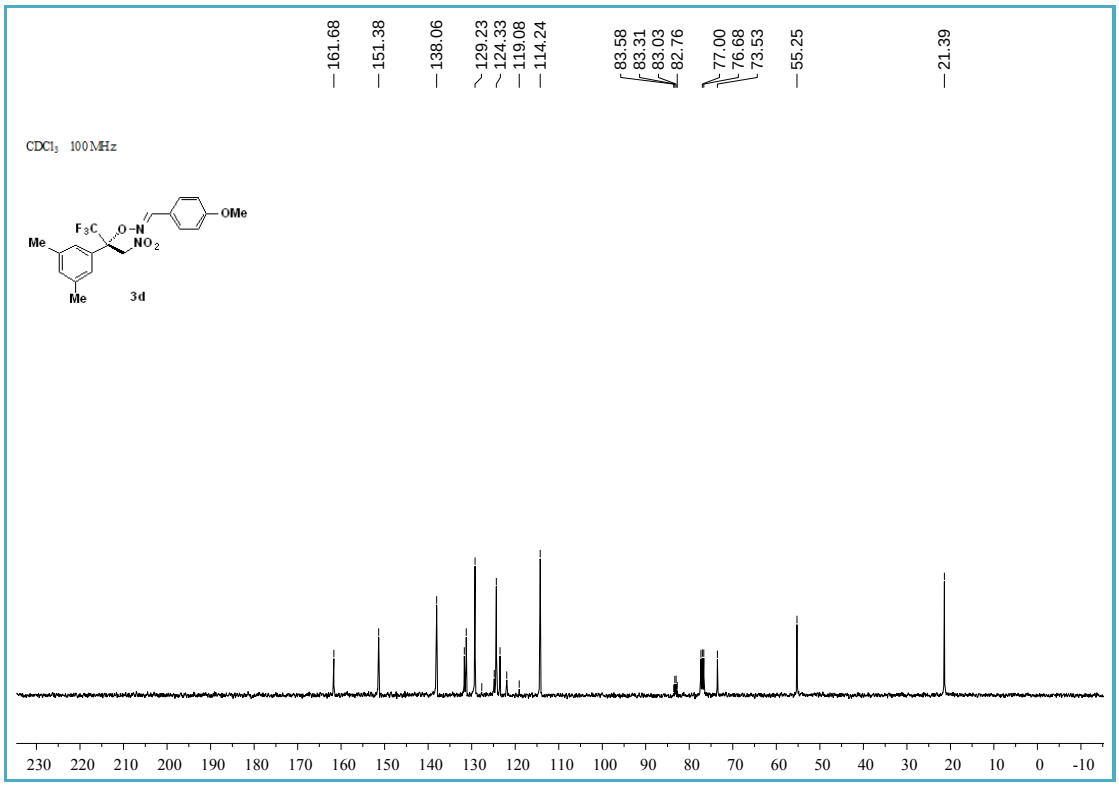
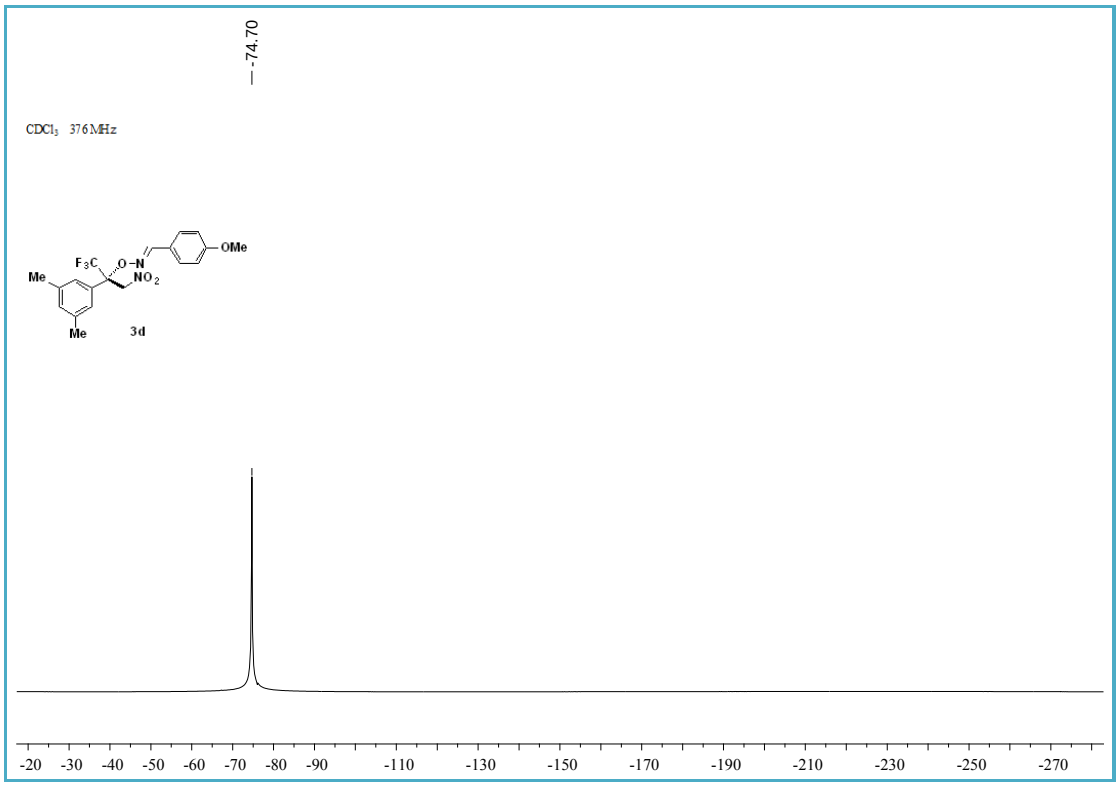
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3d



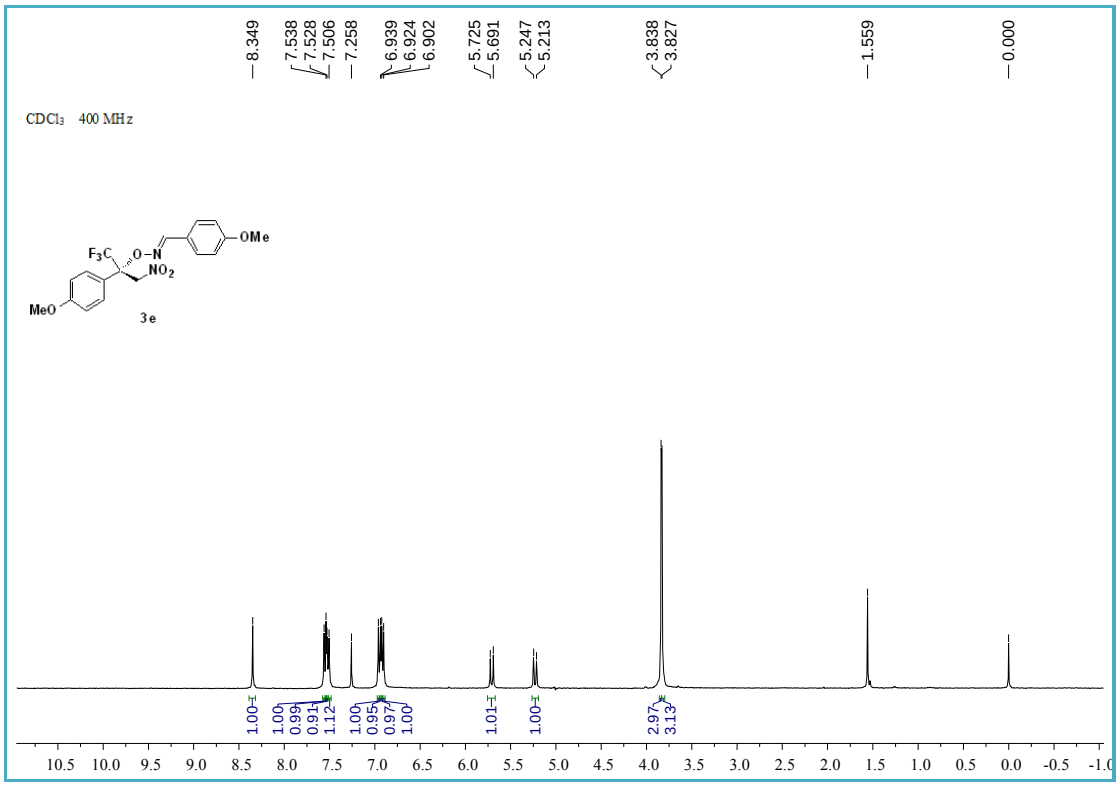
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3d



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3d



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3e



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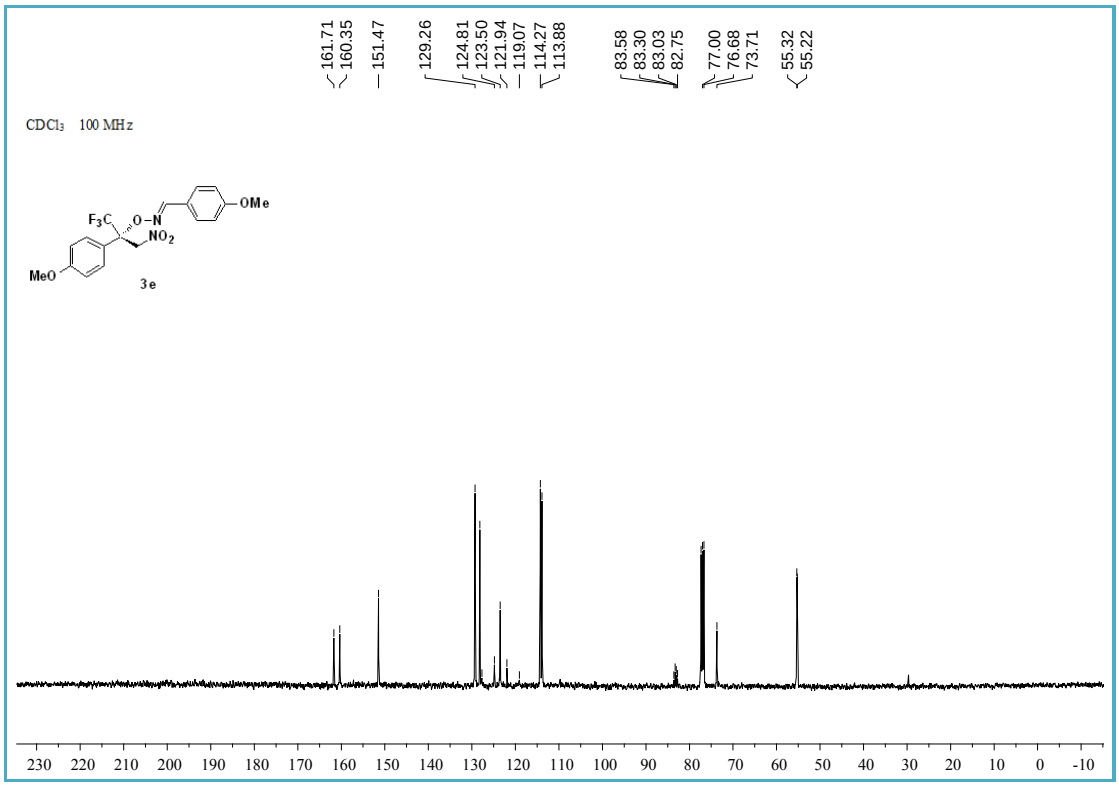
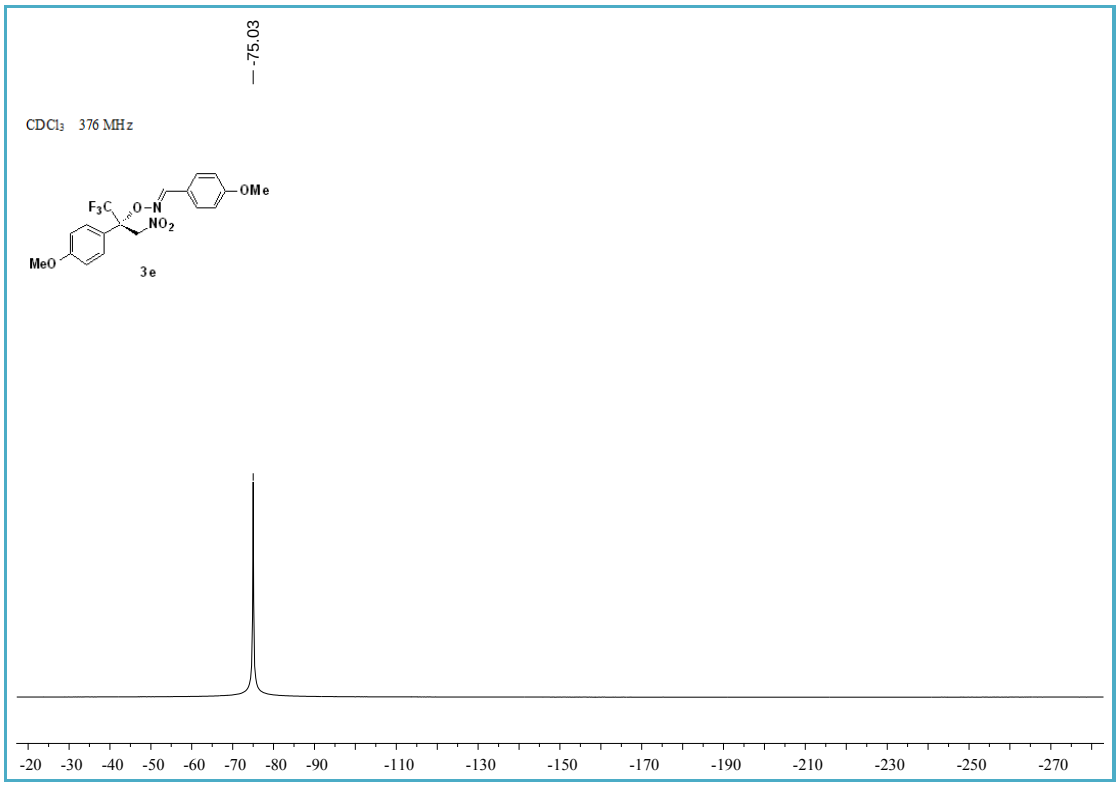
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3e



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3e



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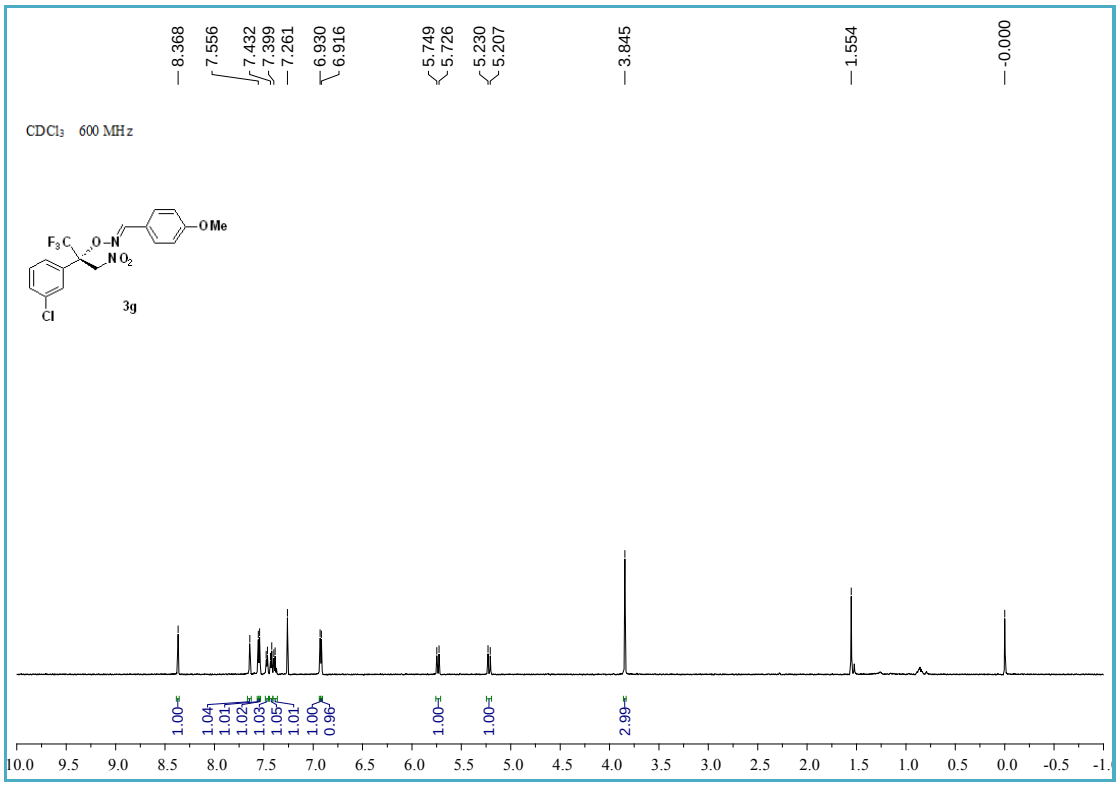
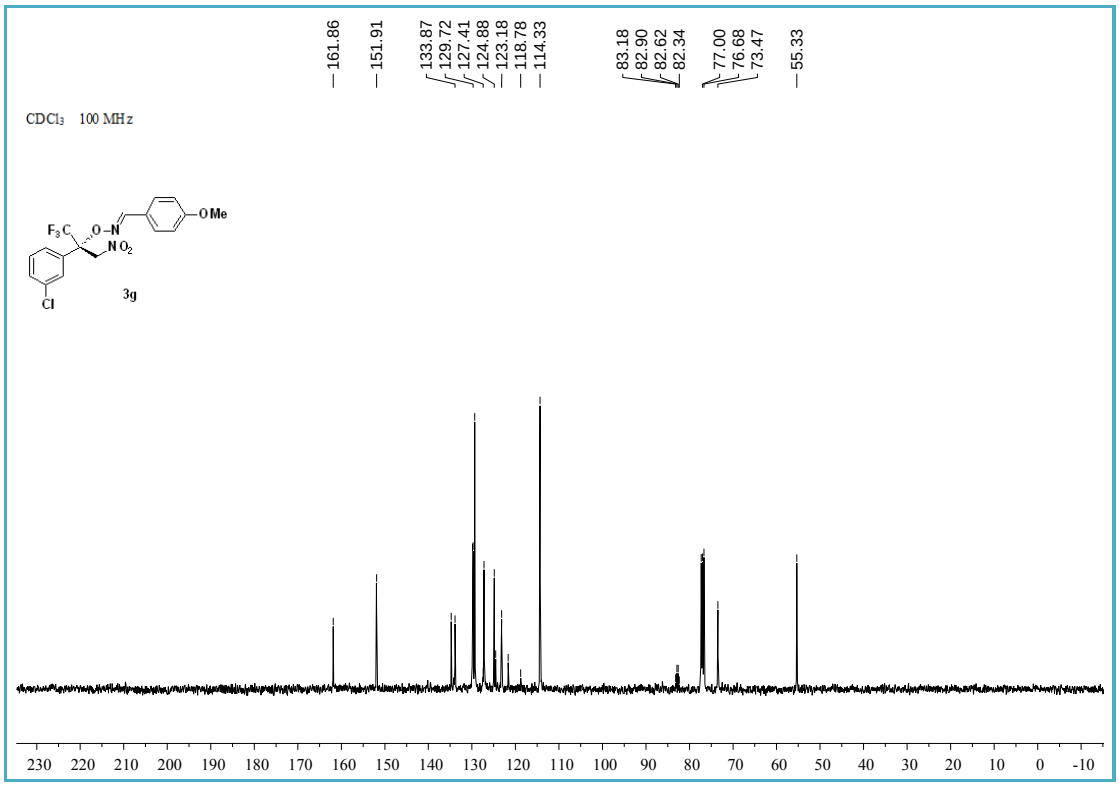
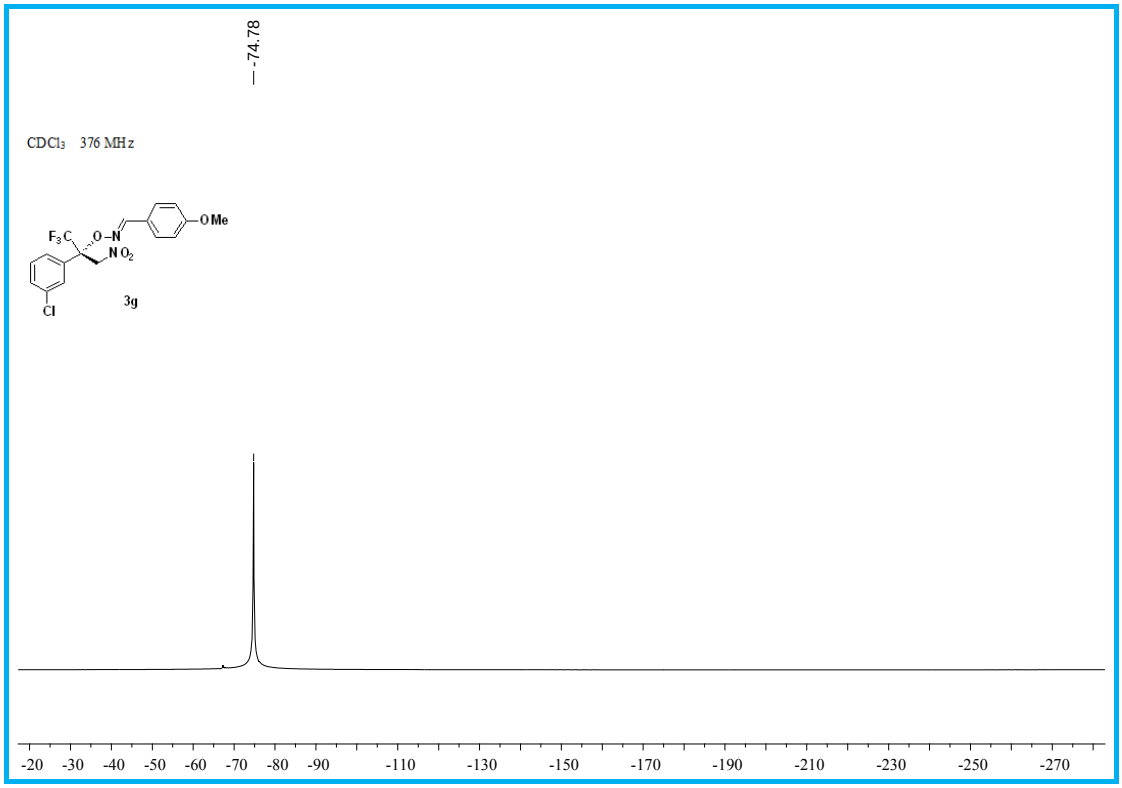
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3g



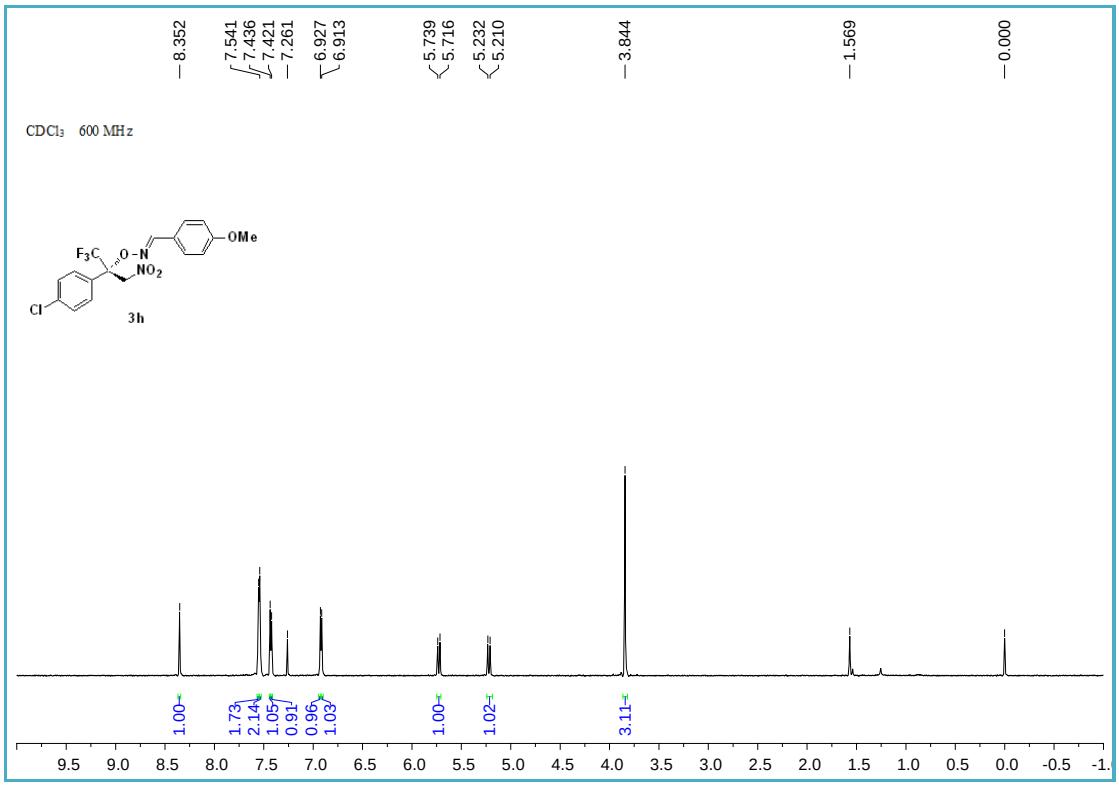
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3g



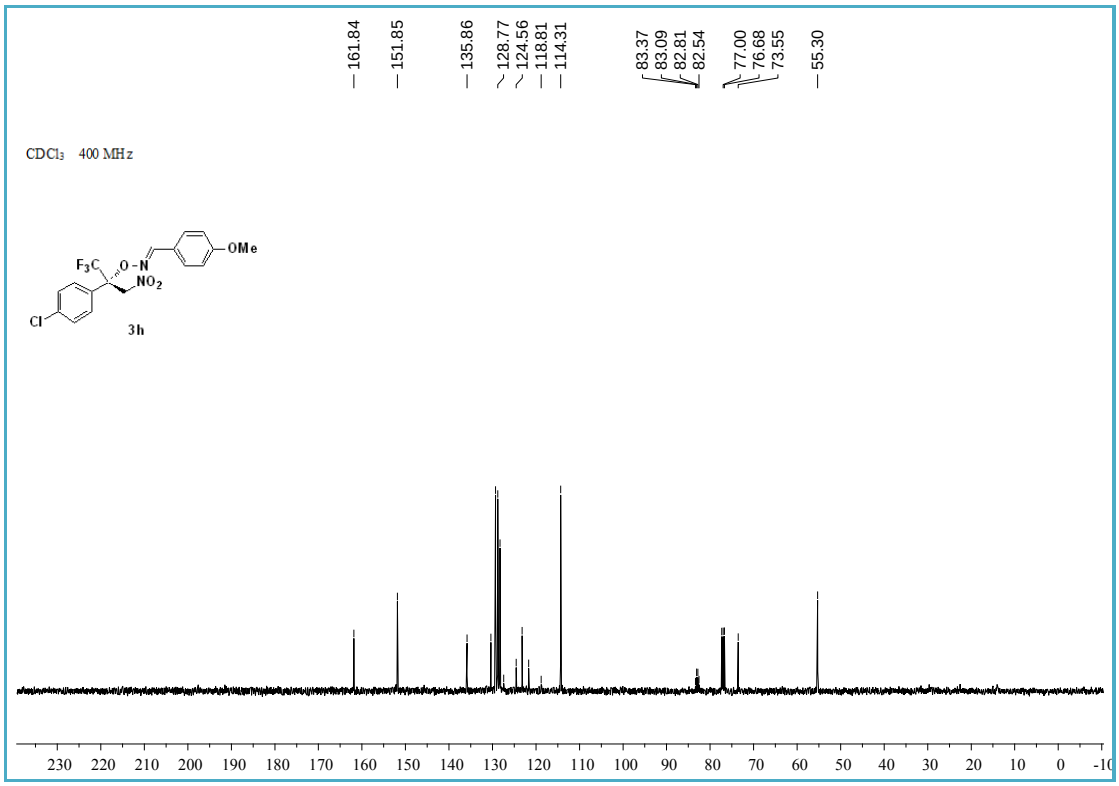
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3g



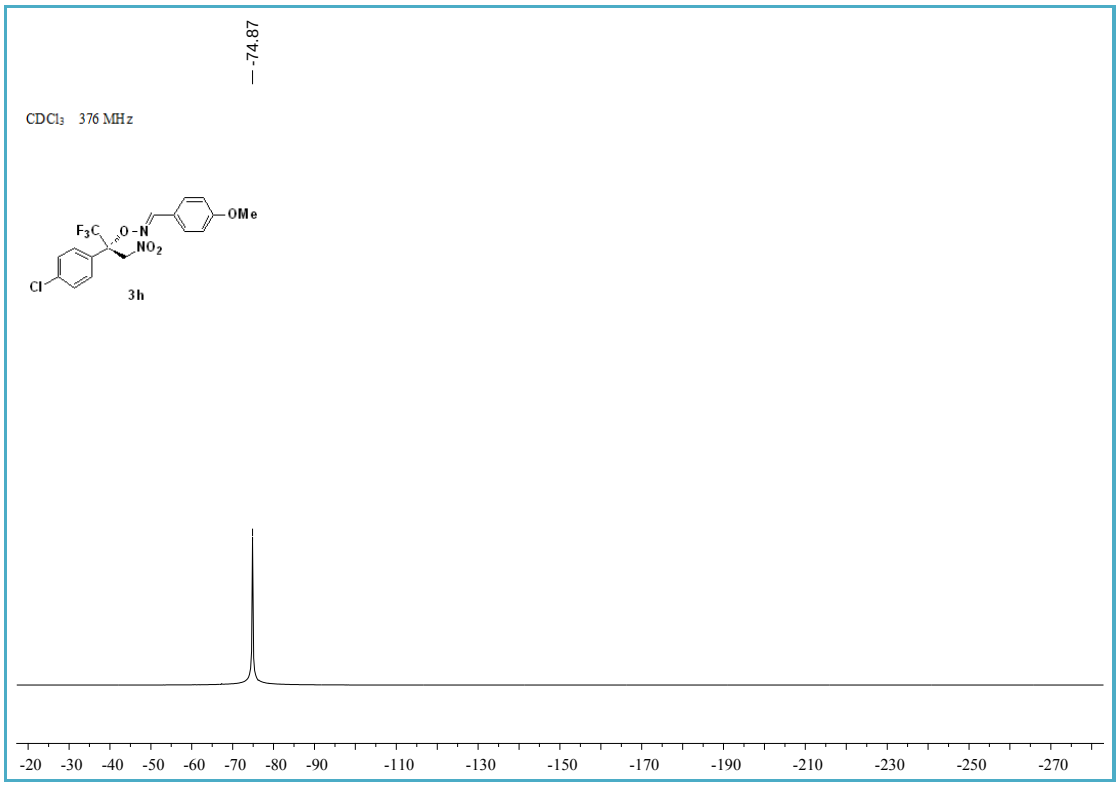
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3h



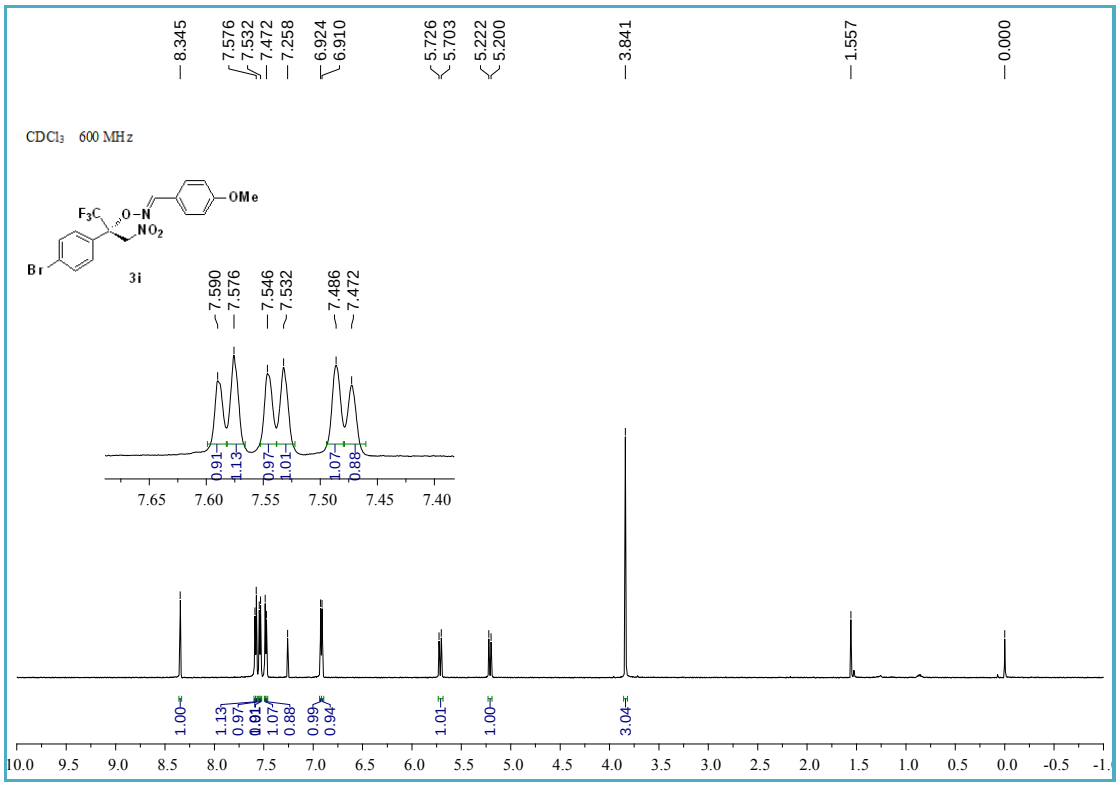
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3h



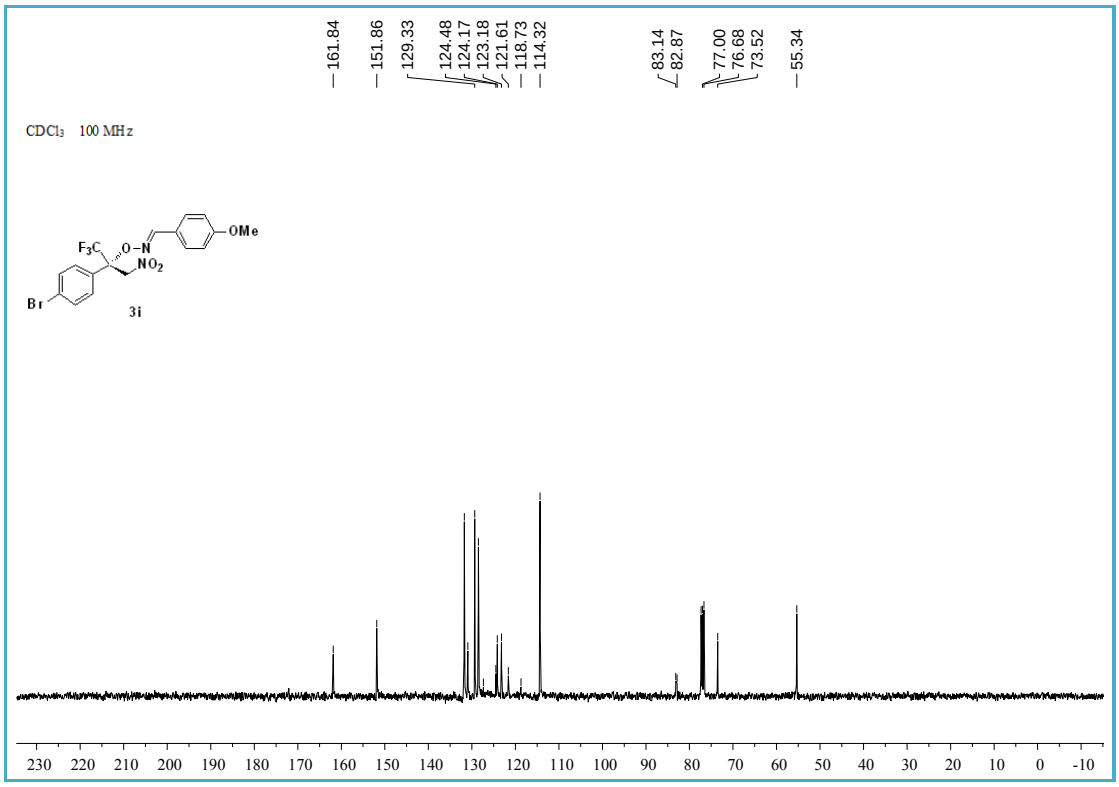
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3h



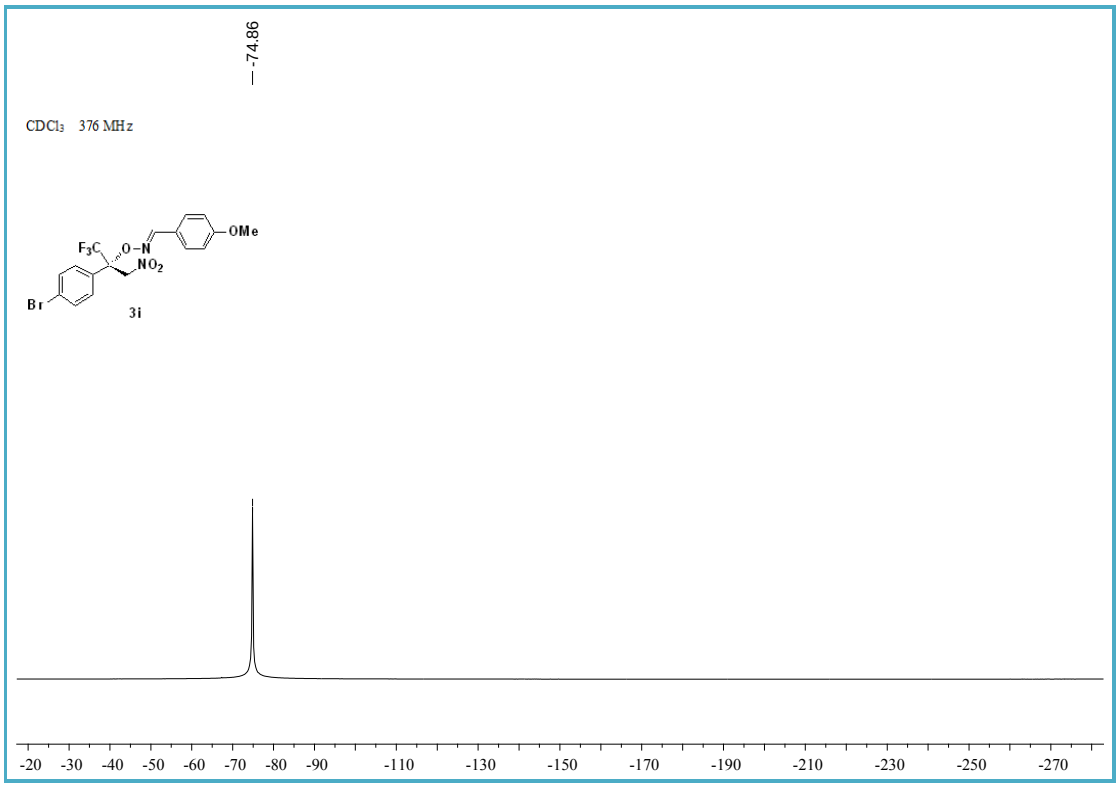
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3i



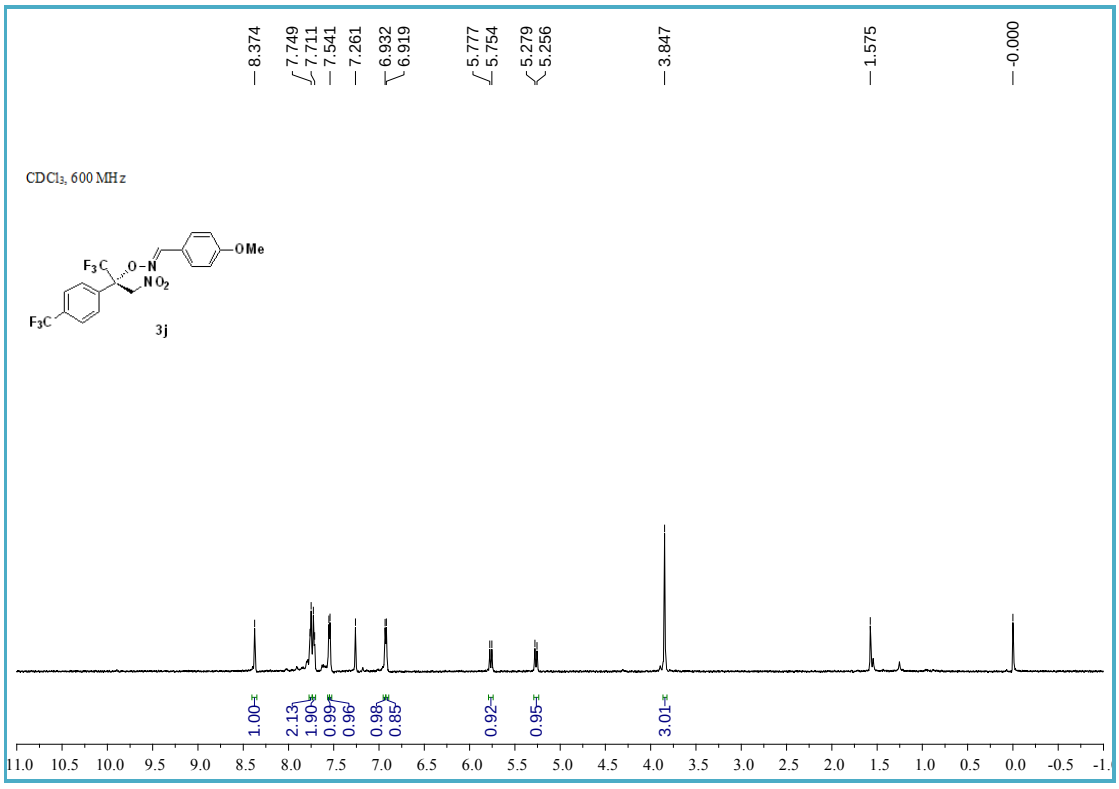
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3i



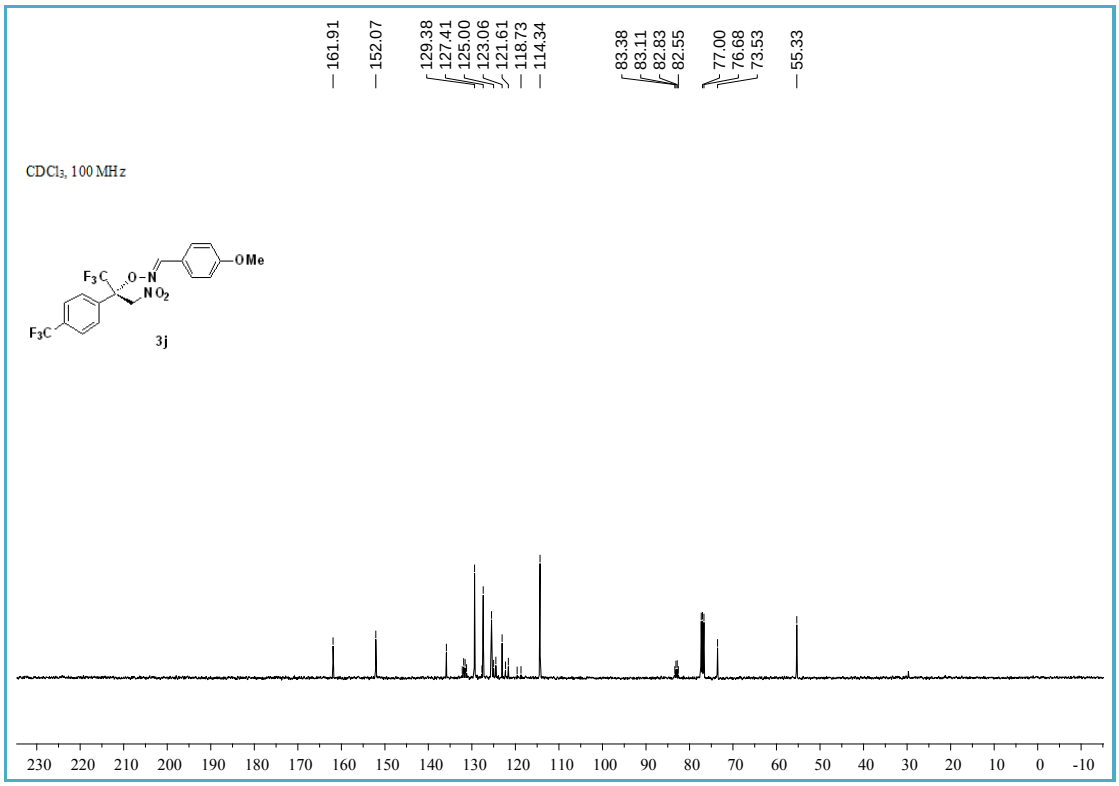
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3i



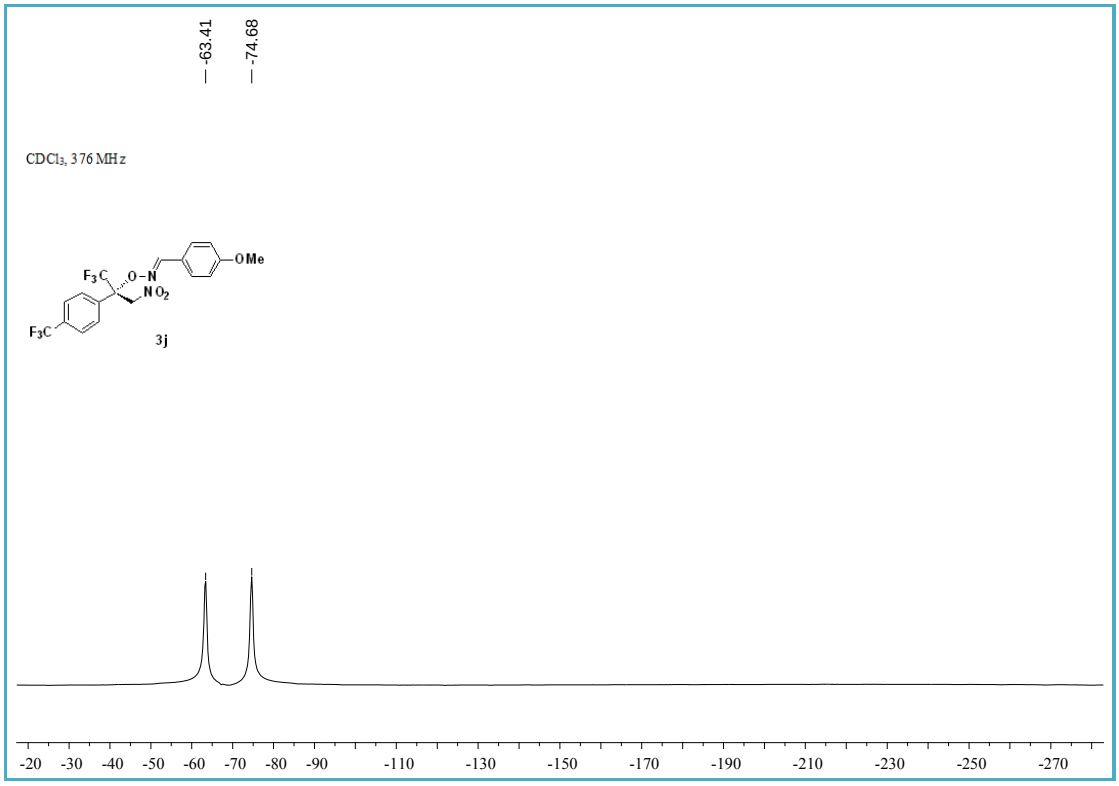
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3j



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3j



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3j



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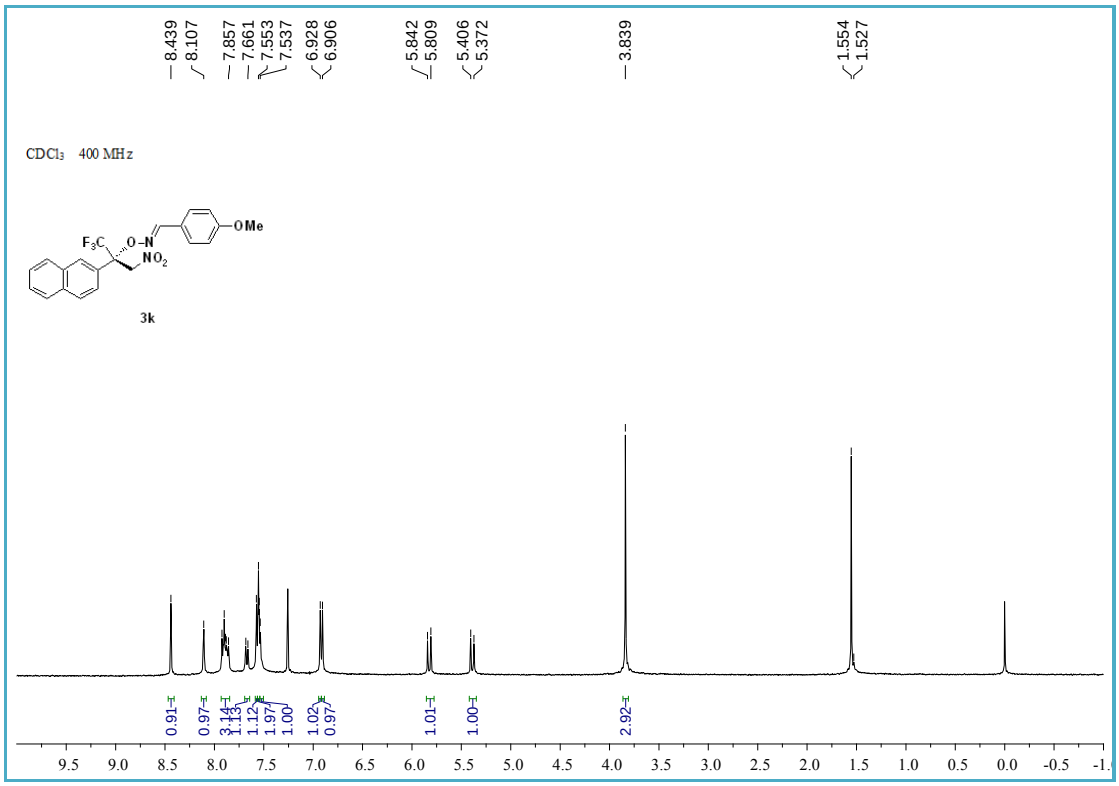
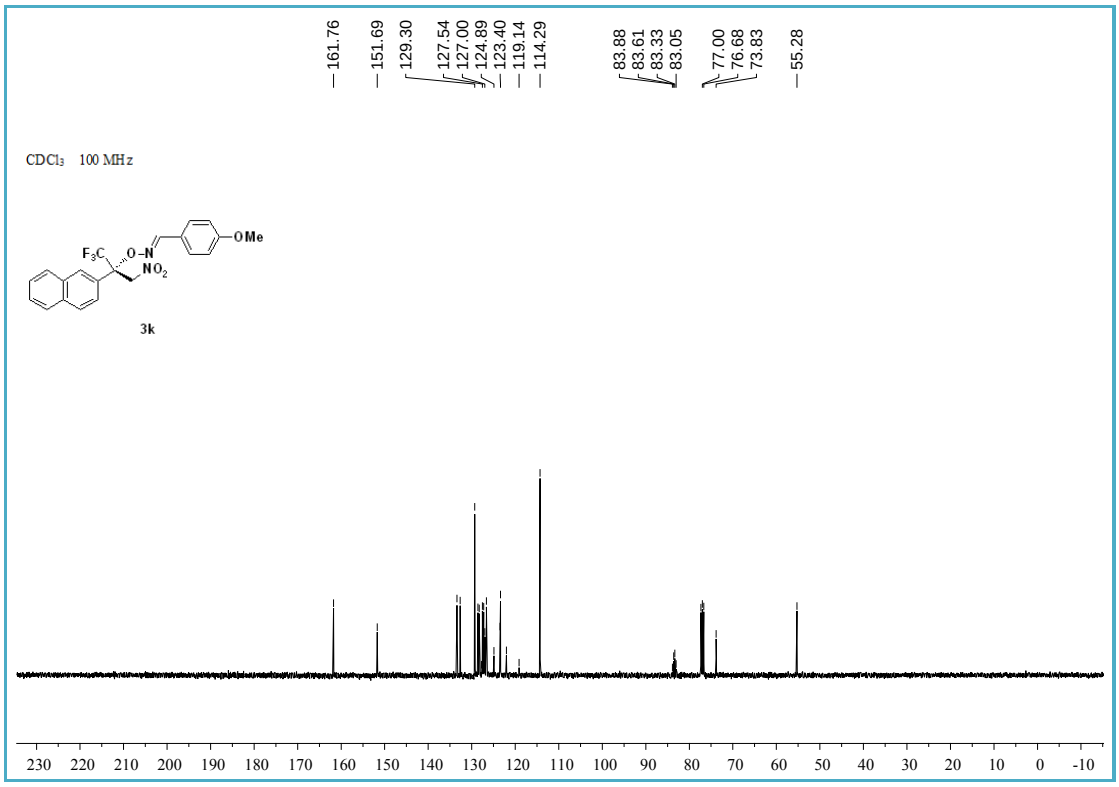
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3k



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3k



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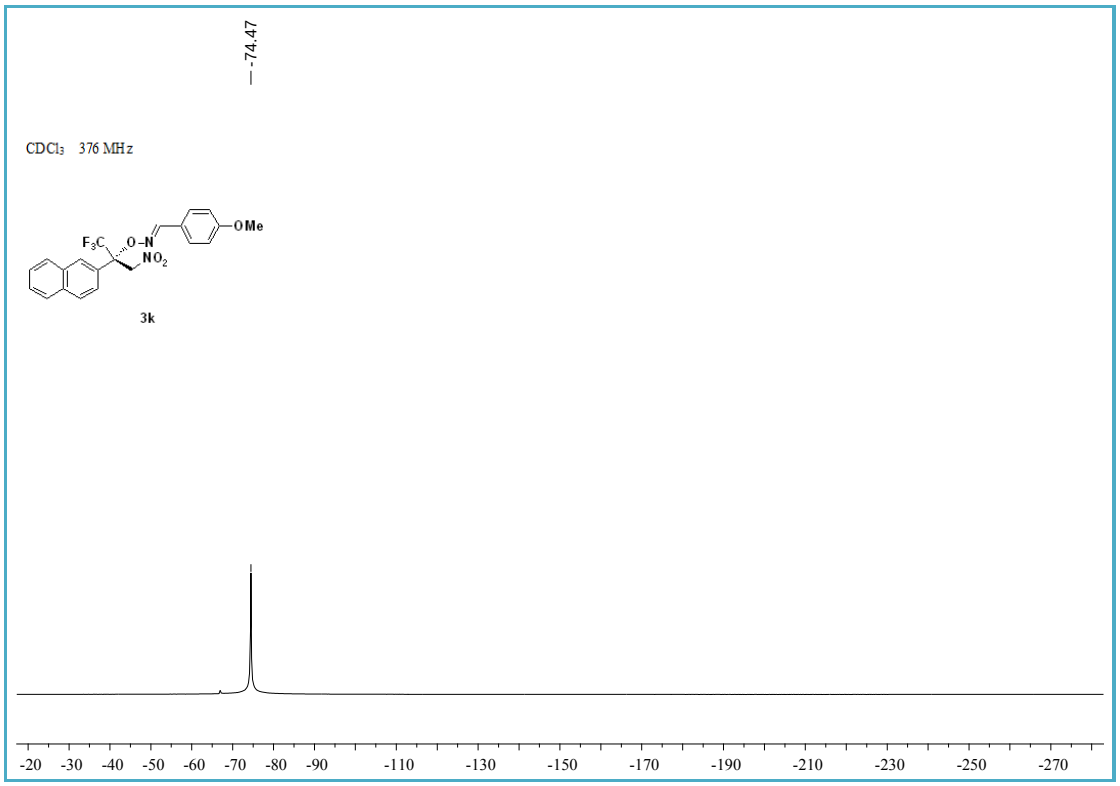
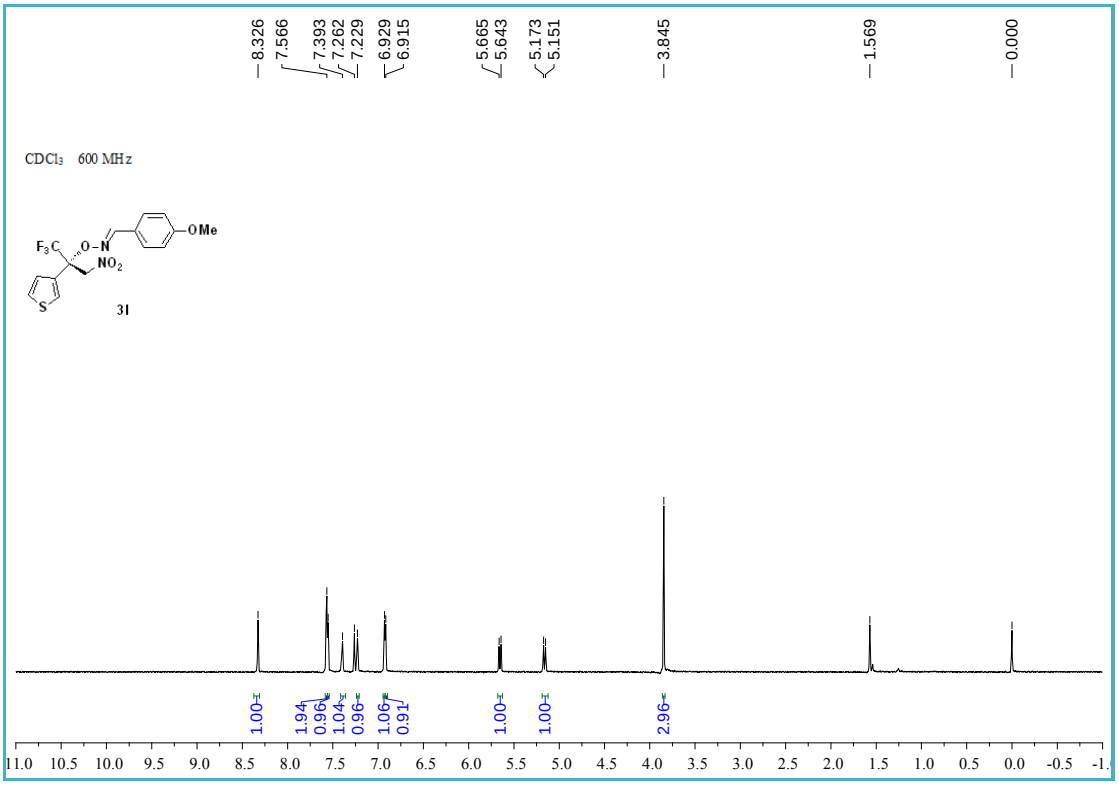
^{19}F NMR (100 MHz, $CDCl_3$) spectrum of 3k



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3l



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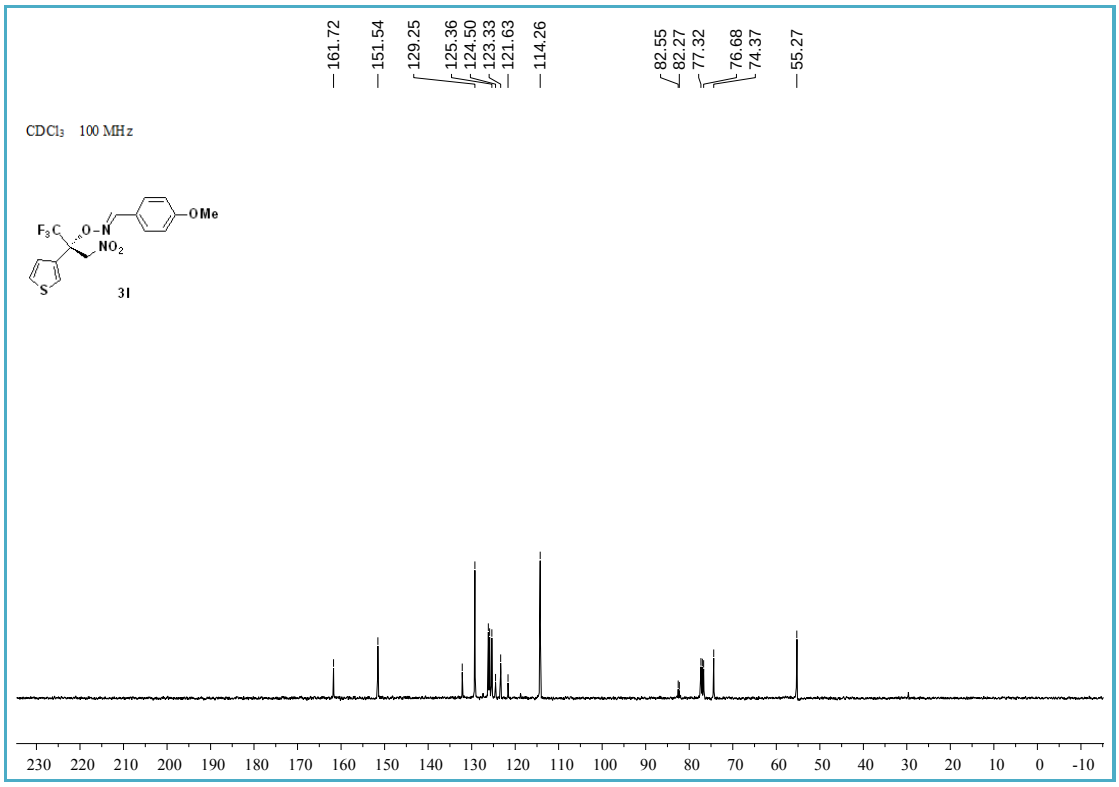
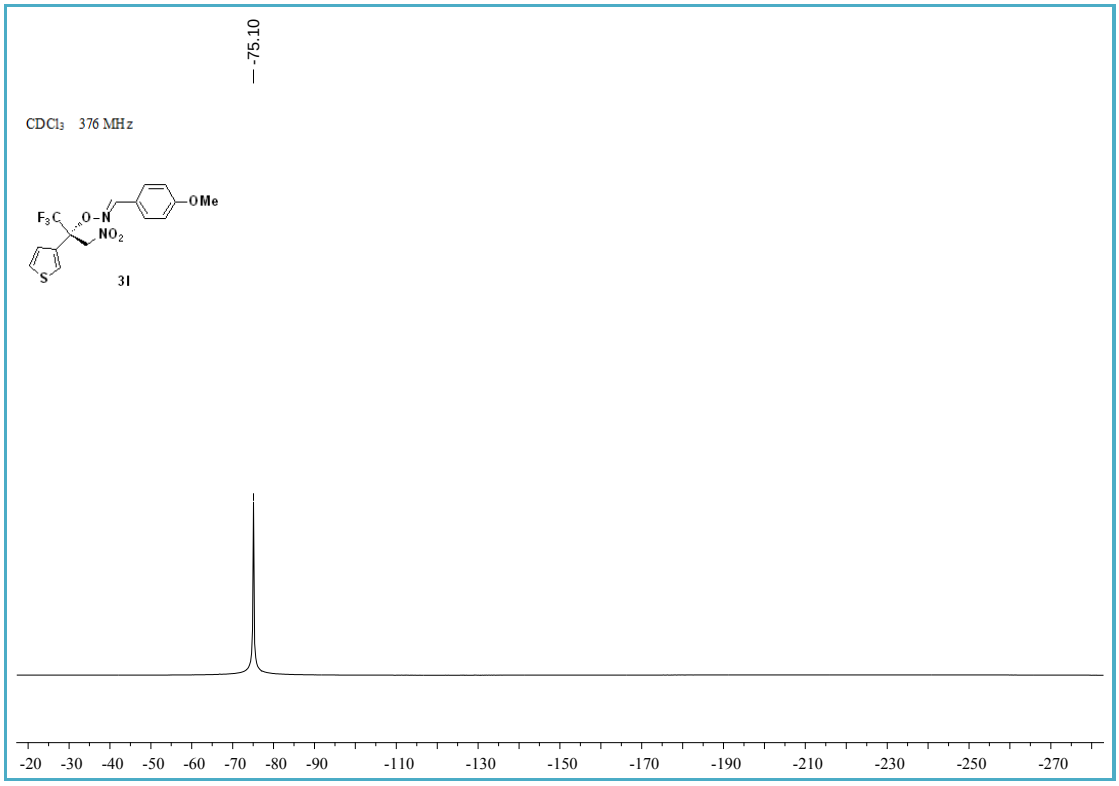
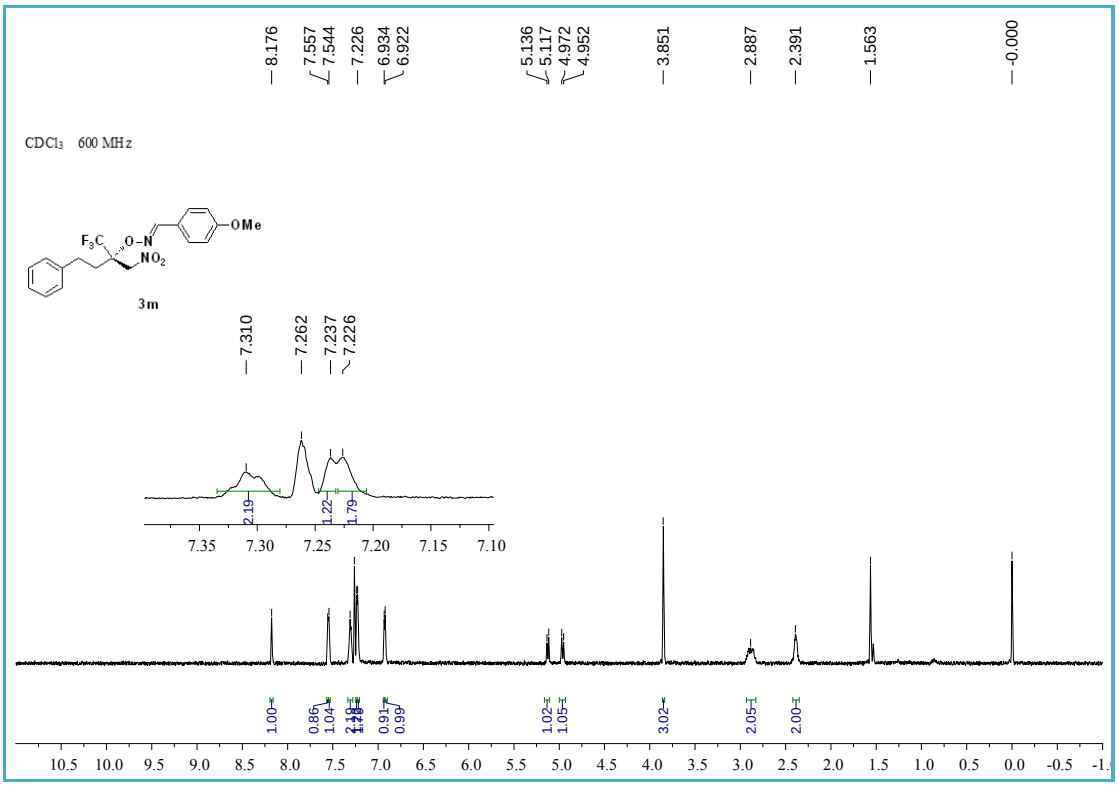
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3l



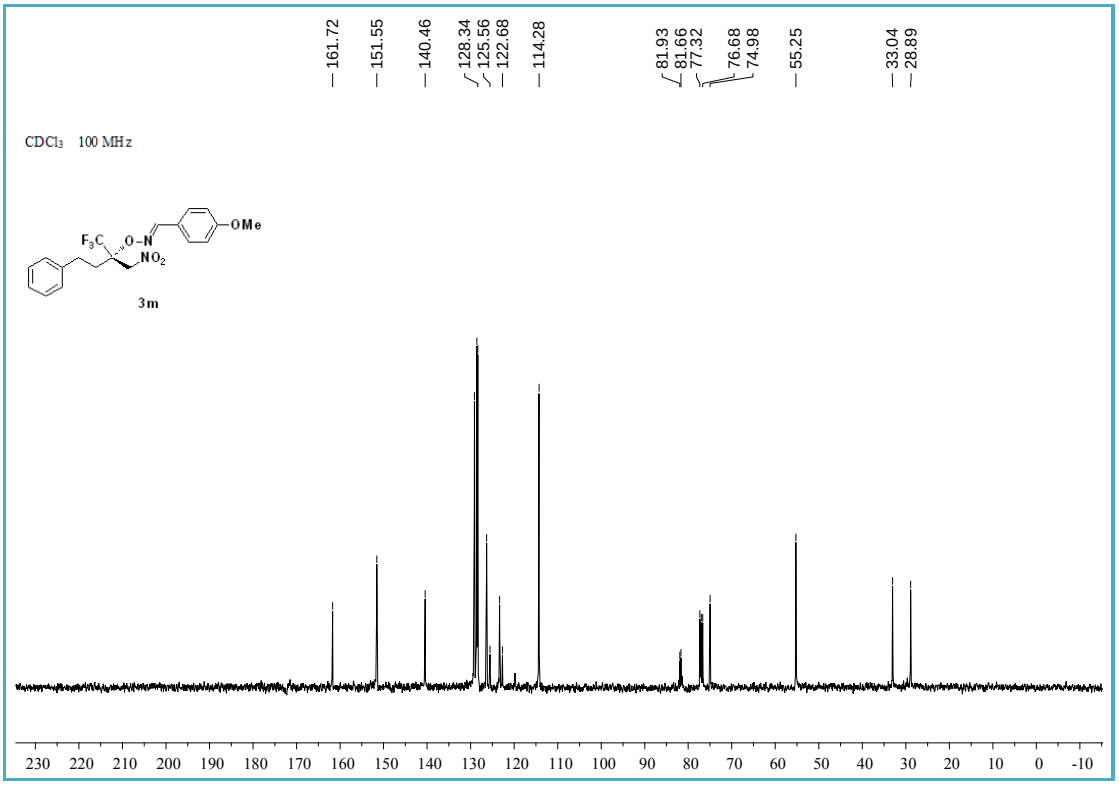
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3l



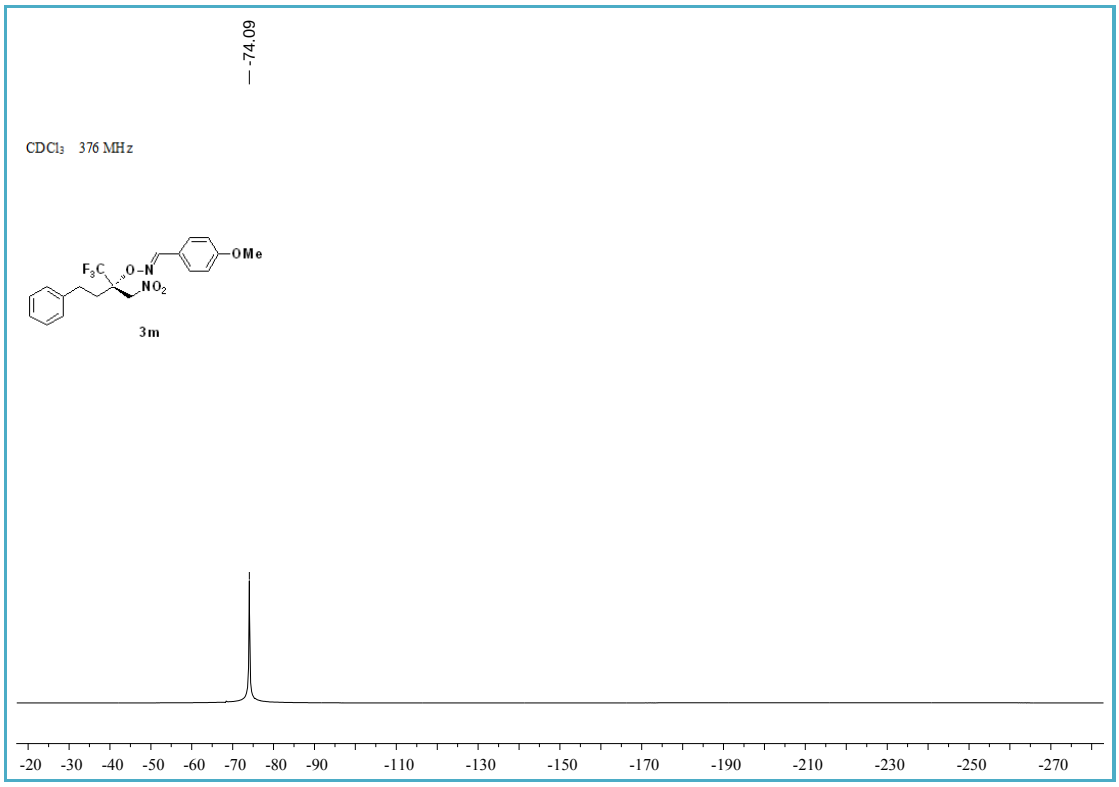
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3m



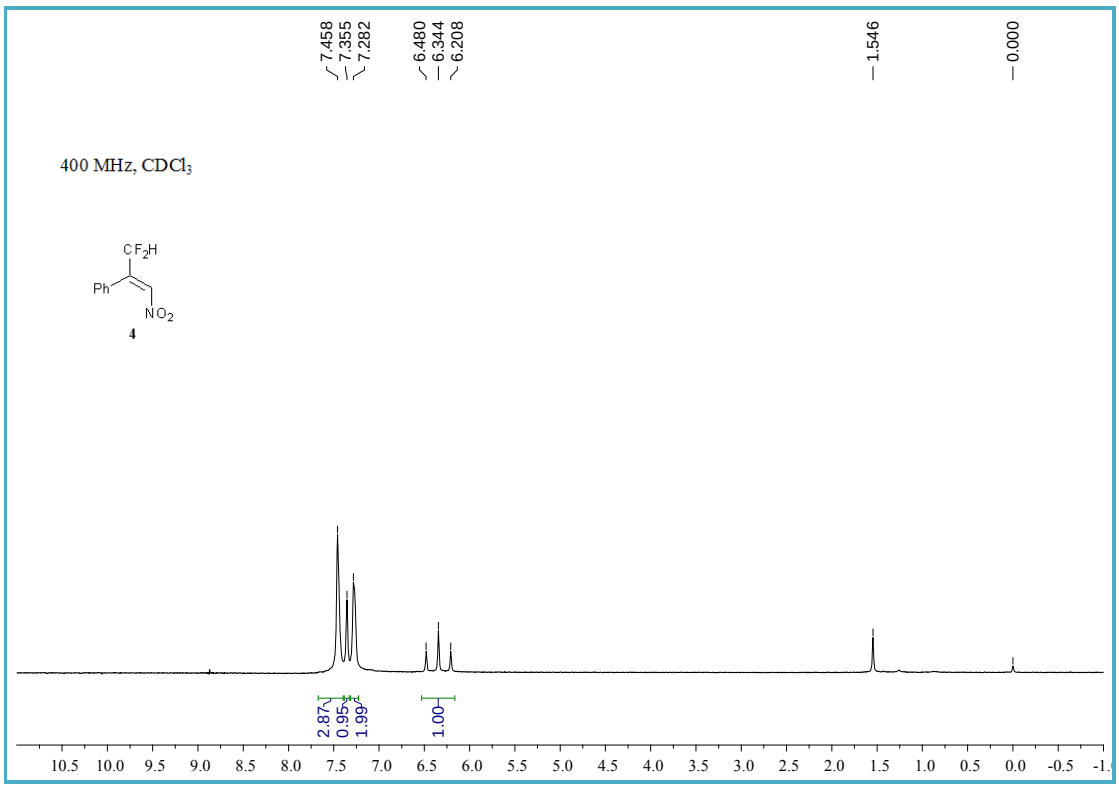
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3m



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 3m



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4



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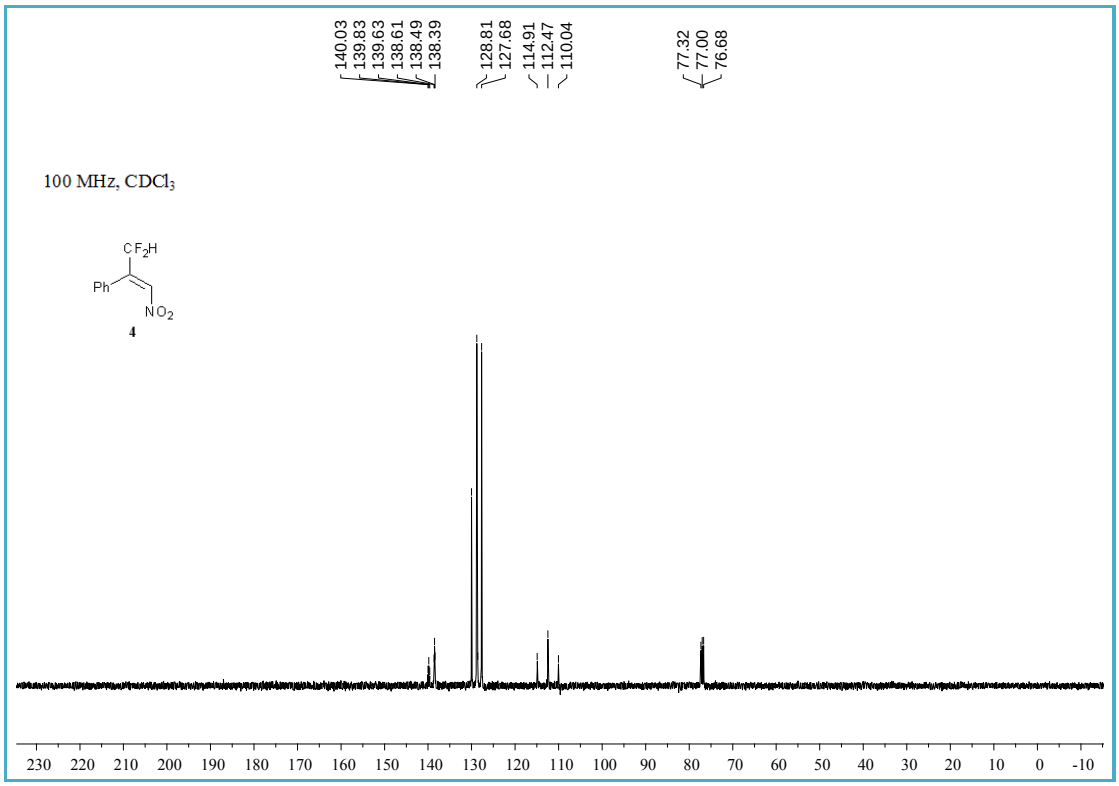
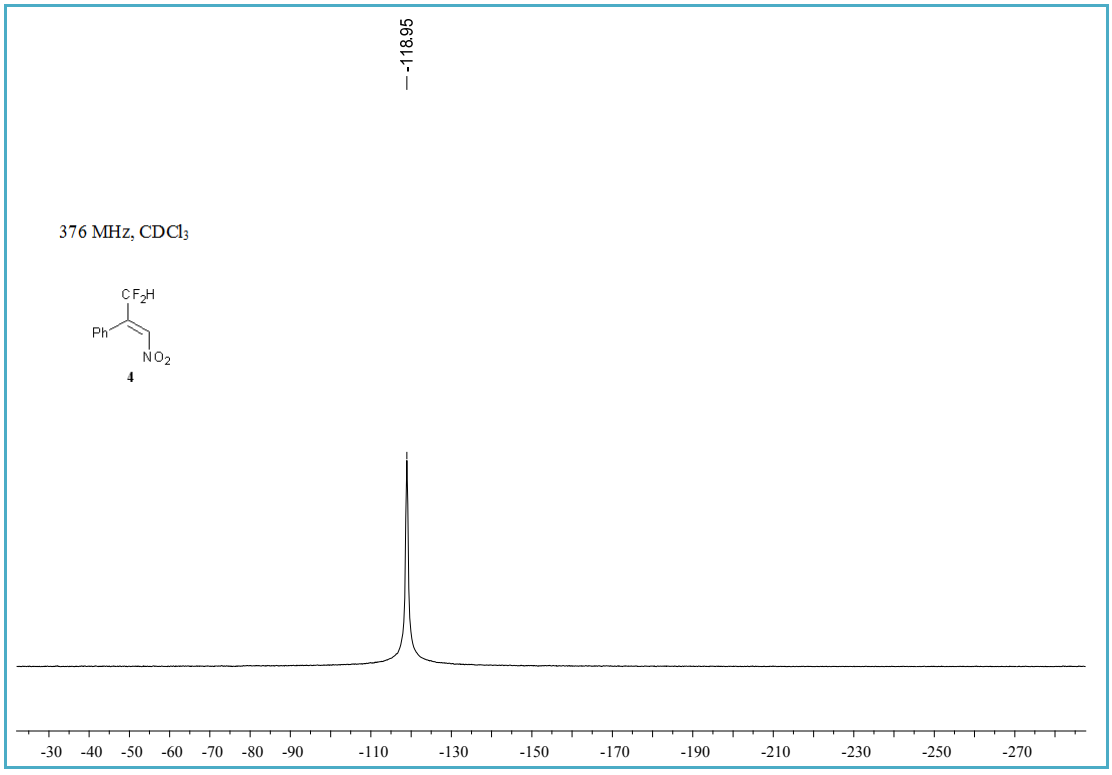
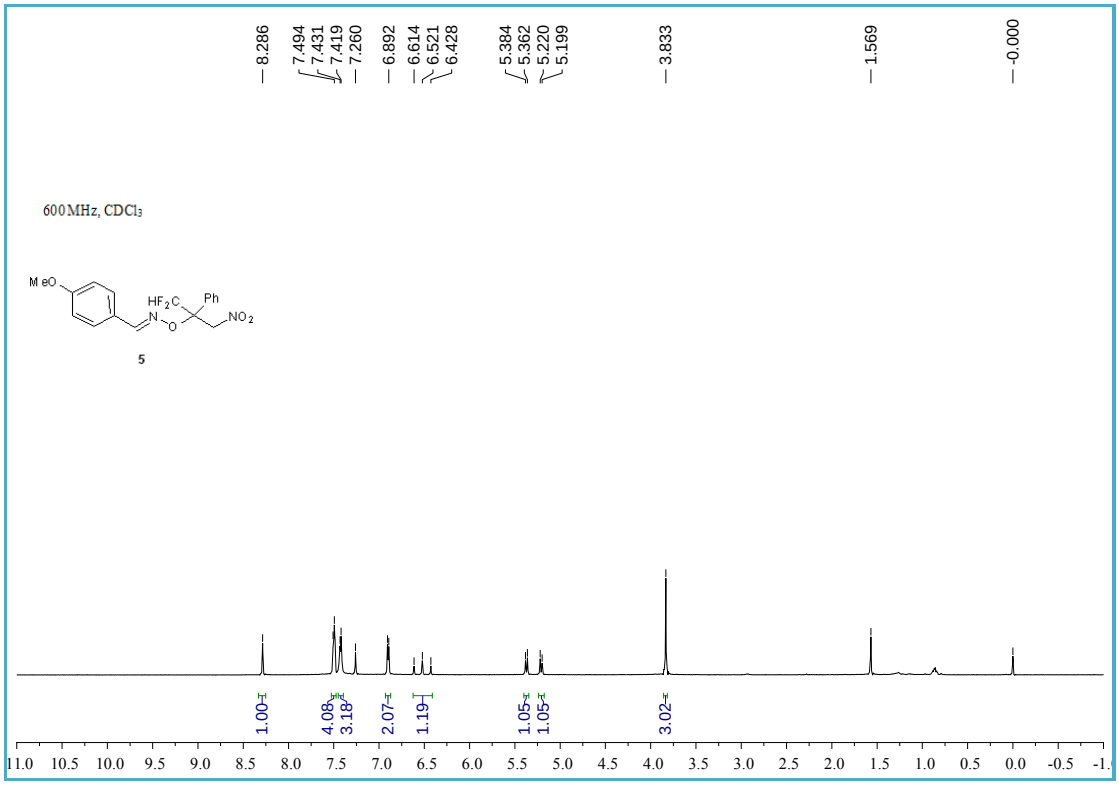
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4



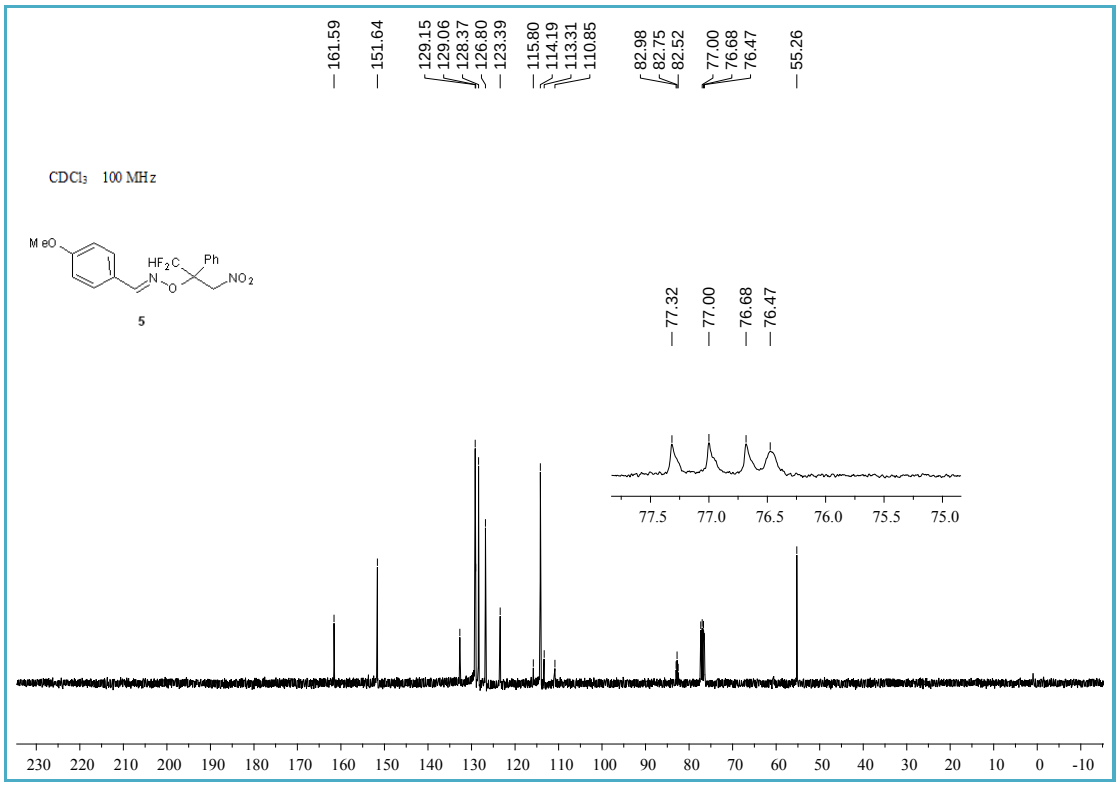
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4



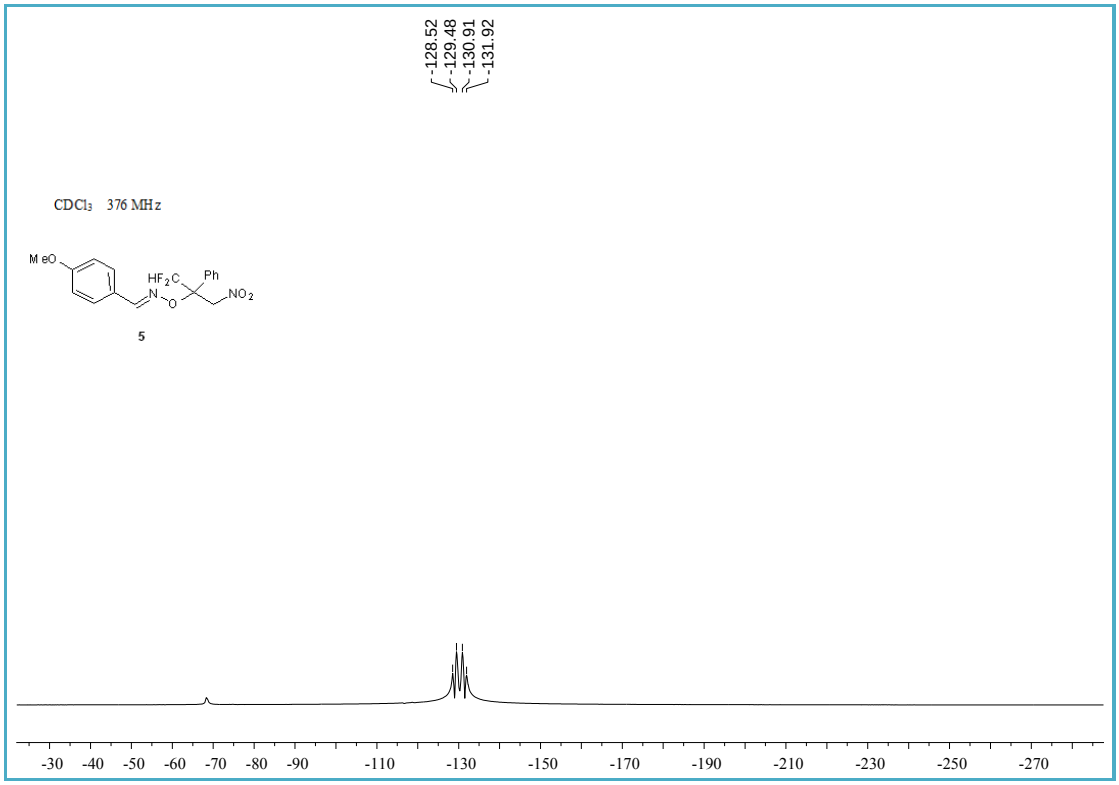
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5



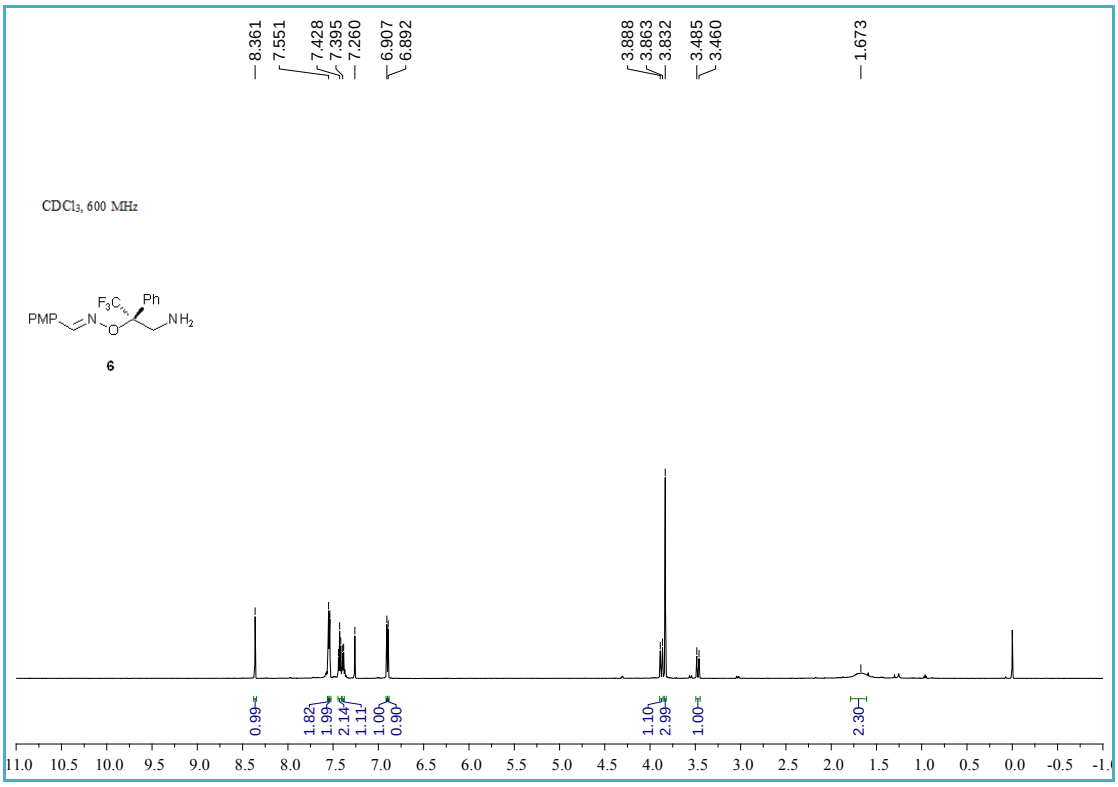
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 5



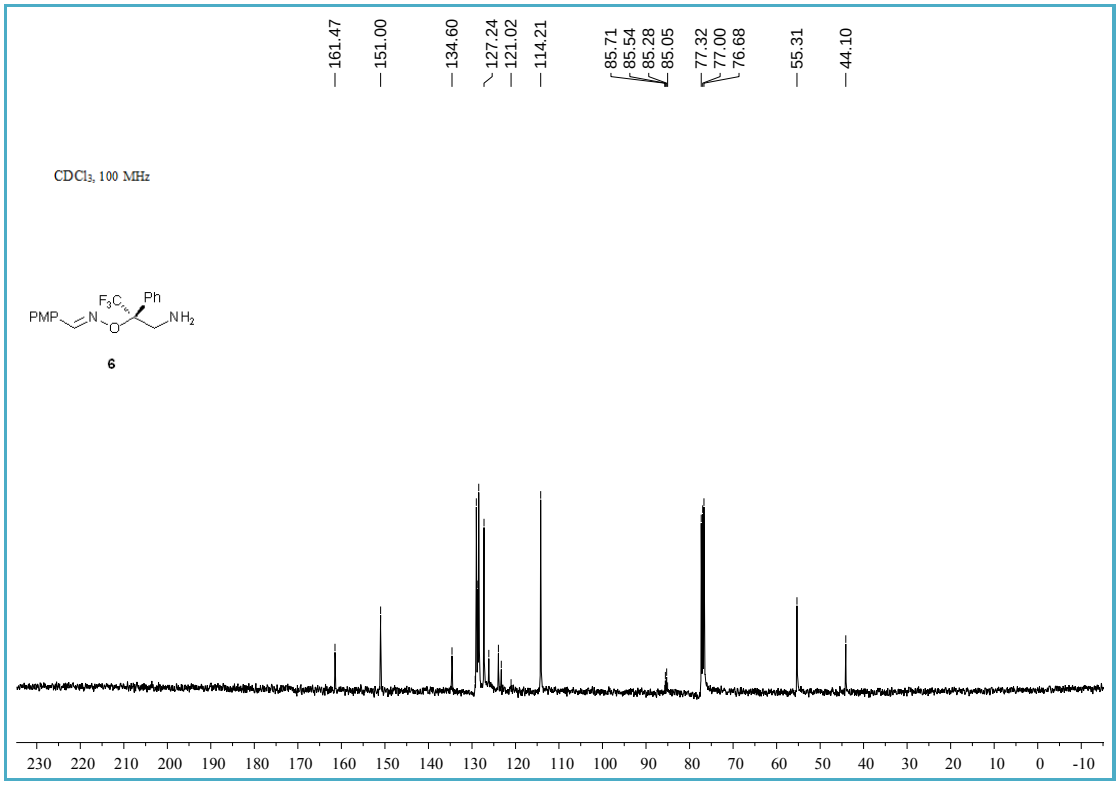
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5



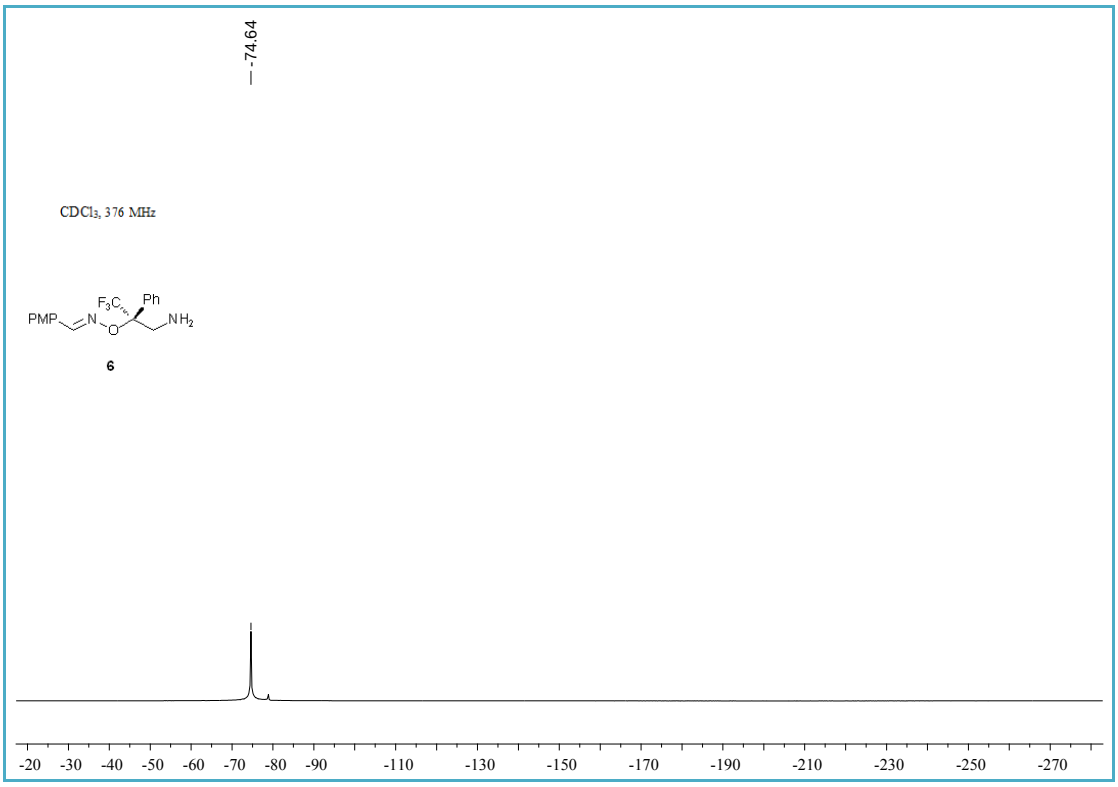
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 6



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of product 7

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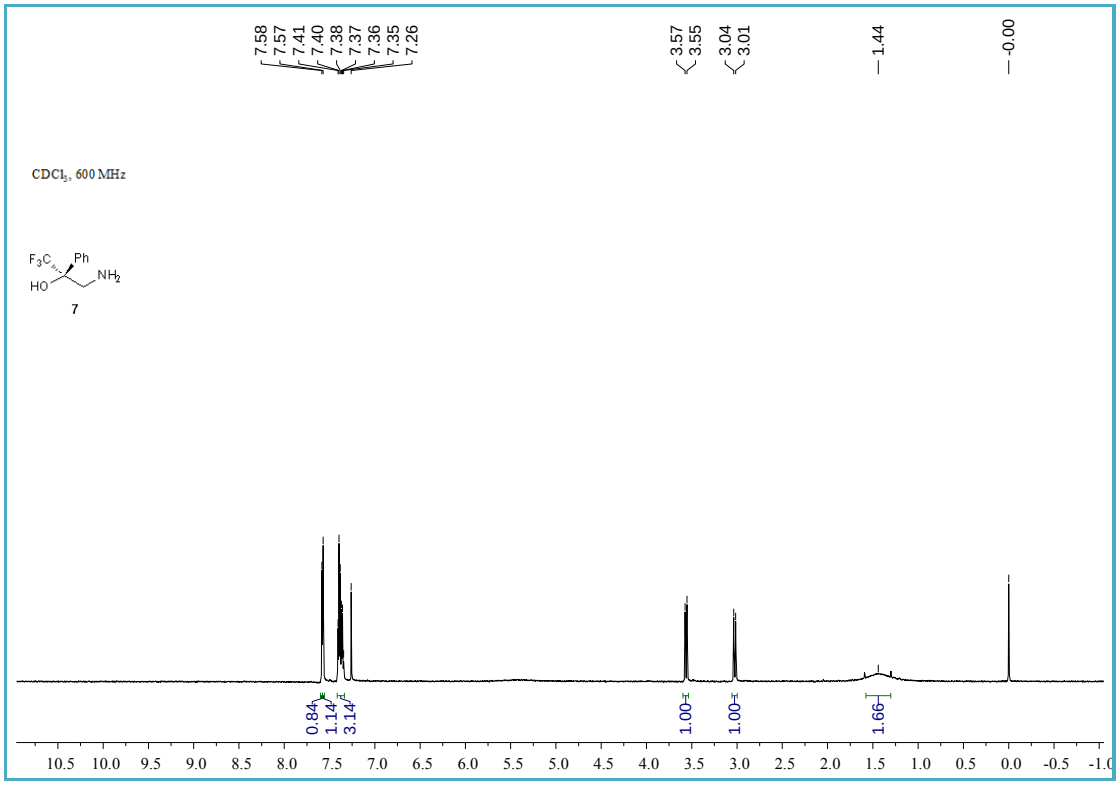
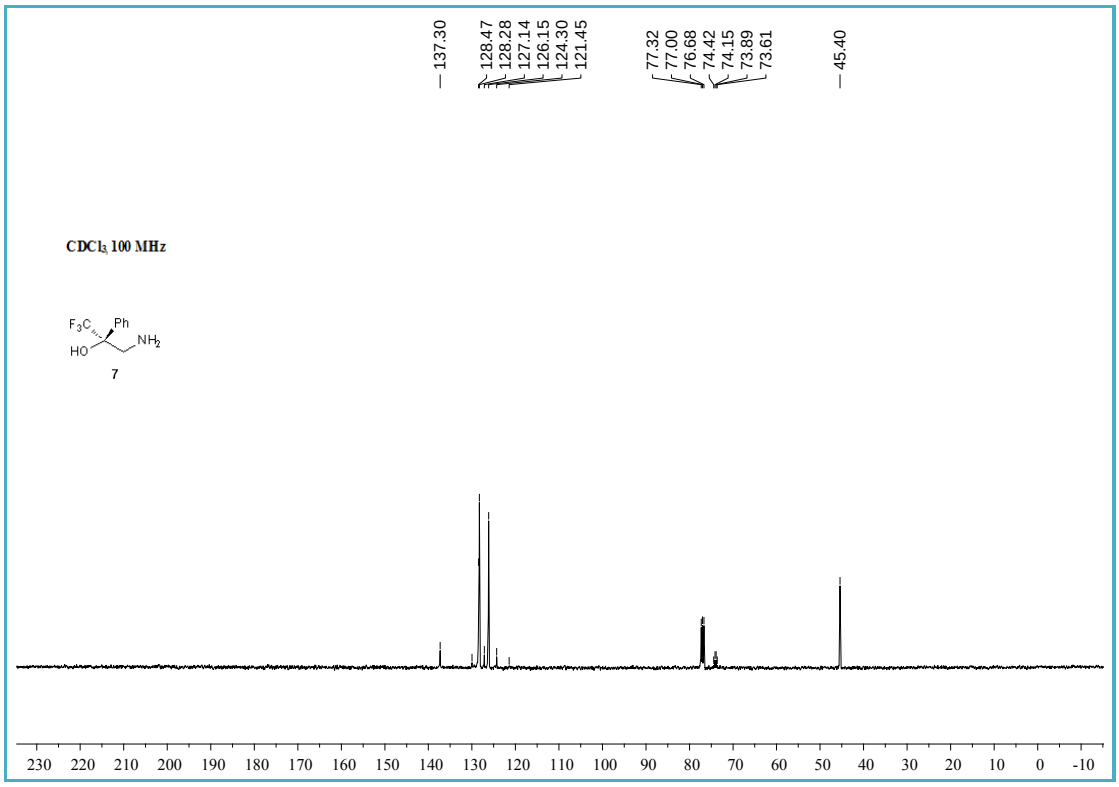


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 7

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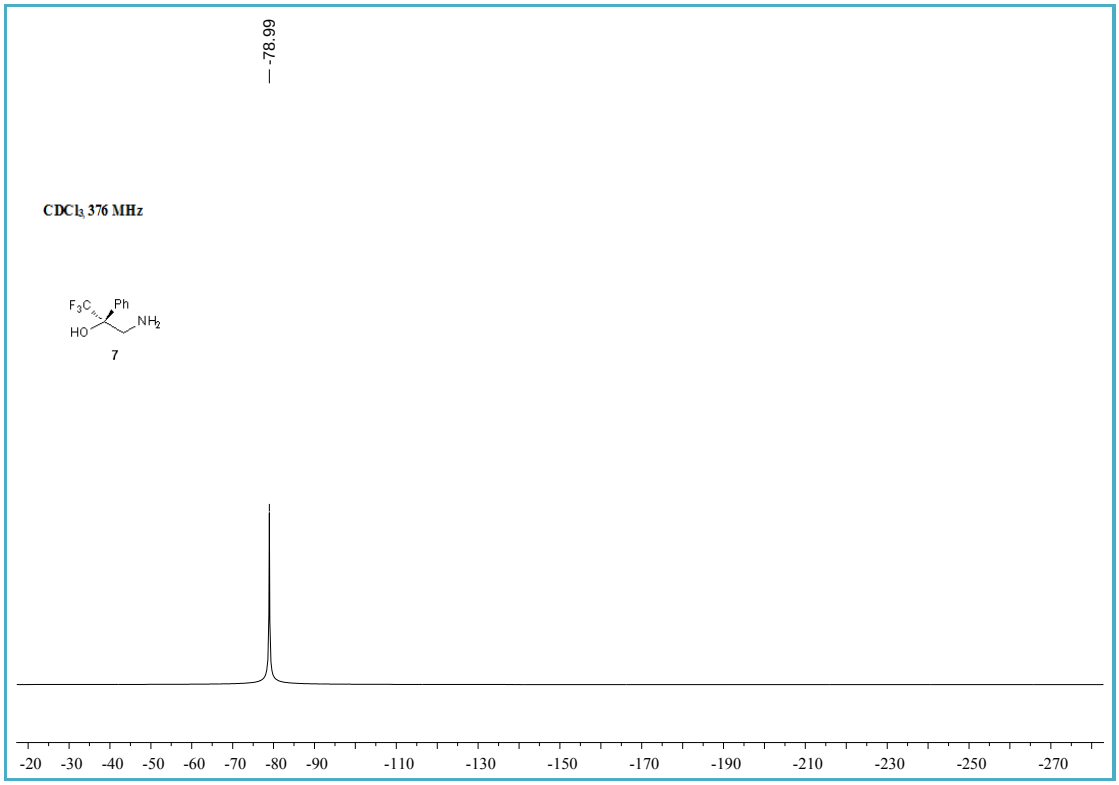
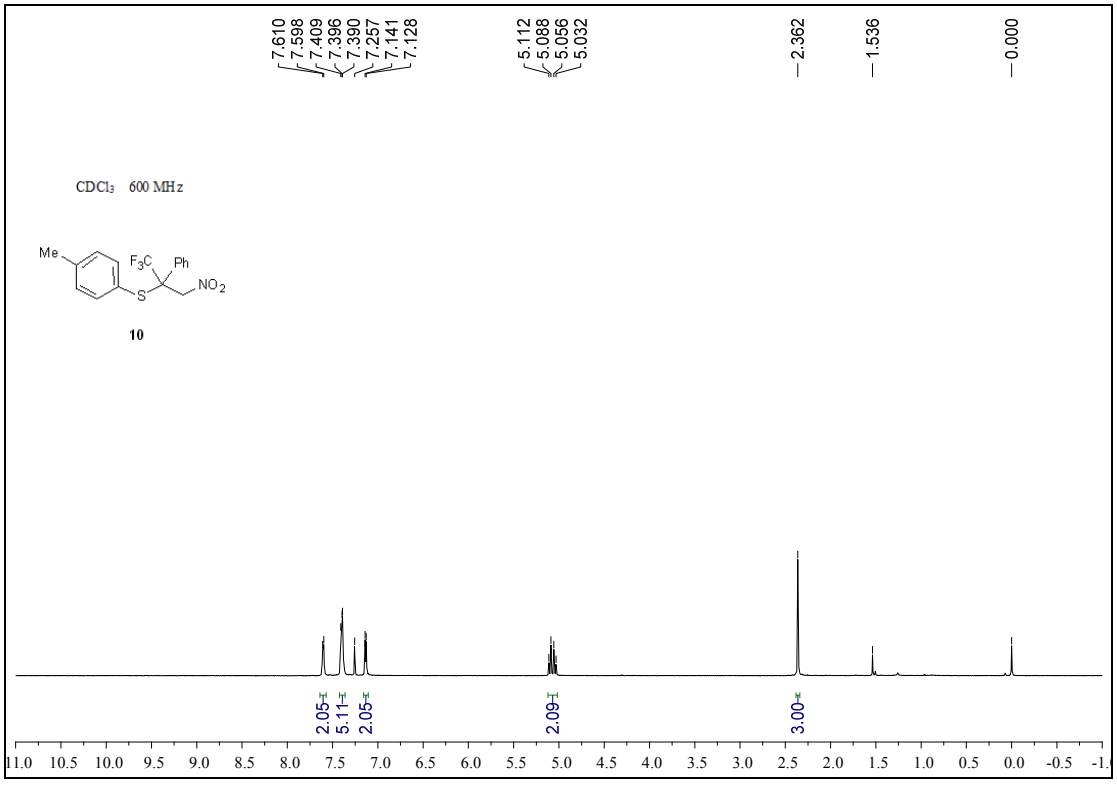
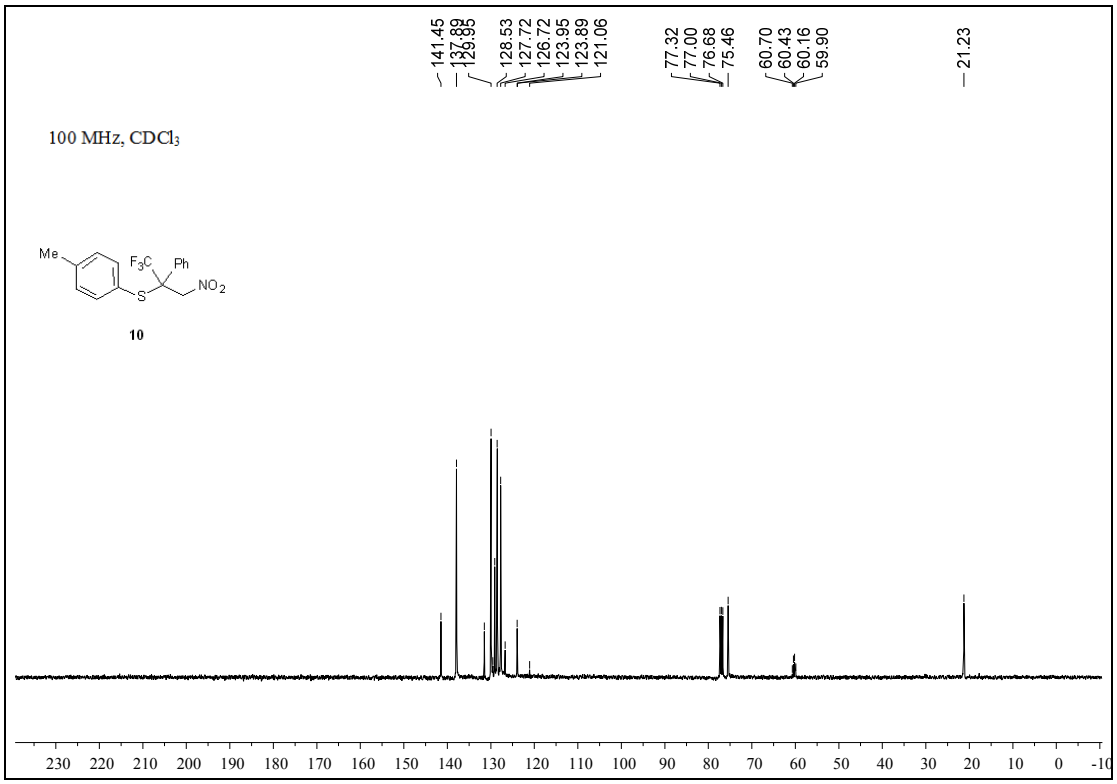


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of product 10



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 10



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 10