Supplementary Information

Synthesis of *N*-triflyl aldimines catalyzed by imino-λ^3-iodane

Shun Sunagawa,[a] Yoko Tezuka,[a] Akira Tsubouchi,[a] Akira Yoshimura[b] and Akio Saito*[,a]

[a] Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan.

[b] Faculty of Pharmaceutical Sciences, Aomori University, 2-3-1 Kobata, Aomori 030-0943, Japan.

* Correspondence: akio-sai@cc.tuat.ac.jp; Tel.: +81-42-388-7667

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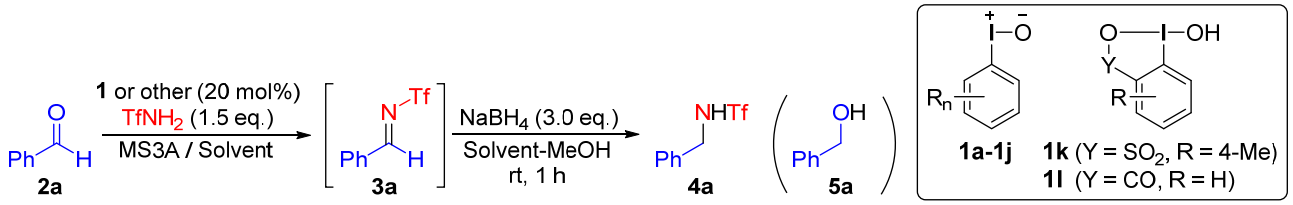
1. Optimization of Reaction Conditions

Table S1. Evaluation of iodine reagents, additives and solvents.



entry	Catalyst	R_n (**1a-1j**)	MS3A (mg)	Solvent	Temp. (ºC)	Time (h)	**4a**[a] (%)	**5a**[a] (%)
1	**1a**	H	120	$CHCl_3$	50	24	19	65
2	**1b**	4-Me	120	$CHCl_3$	50	24	39	45
3	**1c**	2-Me	120	$CHCl_3$	50	24	22	67
4	**1d**	4-OMe	120	$CHCl_3$	50	24	30	58
5	**1e**	2-OMe	120	$CHCl_3$	50	24	65	35
6	**1f**	4-Cl	120	$CHCl_3$	50	24	24	46
7	**1g**	4-CF_3	120	$CHCl_3$	50	24	20	56
8	**1h**	2-NO_2	120	$CHCl_3$	50	24	18	61
9	**1i**	F_5	120	$CHCl_3$	50	24	18	61
10	**1j**	2-CO_2NMe_2	120	$CHCl_3$	50	24	2	87
11	**1k**	-	120	$CHCl_3$	50	24	trace	84
12	**1l**	-	120	$CHCl_3$	50	24	trace	85
13	$BF_3{\cdot}Et_2O$	-	120	$CHCl_3$	50	24	0	90
14	-	-	120	$CHCl_3$	50	24	0	93
15	**1e**	2-OMe	120	MeCN	50	24	3	96
16	**1e**	2-OMe	120	$CHCl_3$	rt	4	50	31
17	**1e**	2-OMe	120	CH_2Cl_2	rt	2	66	29
18	**1e**	2-OMe	120	Hexane	rt	2	60	37
19	**1e**	2-OMe	120	Toluene	rt	2	62	27
20	**1e**	2-OMe	120	HFIP[b]	rt	2	0	97
21	**1e**	2-OMe	360	CH_2Cl_2	rt	4	94	6
22[c]	**1e**	2-OMe	360	CH_2Cl_2	rt	4	94 (86)[d]	6
23	-	-	360	CH_2Cl_2	rt	4	0	98
24	TiO_2	-	-	CH_2Cl_2	rt	3	0	99

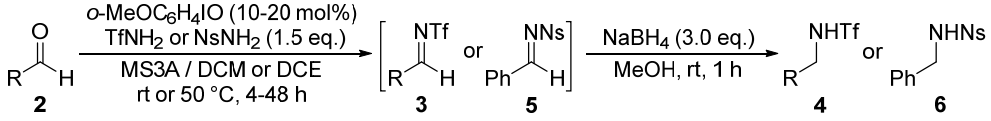
[a] Determined by ^{1}H NMR analysis using an internal standard. **2a**: 0.4 mmol. [b] HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol. [c] **1g**: 10 mol%. [d] Isolated yield.

2. General Information

All reactions were carried out under an argon atmosphere. According to procedures reported in the literatures, iodosylarenes **1a**-**1j**[1a] or **1k**[1b] and **1l**[1c] were prepared from the corresponding (diacetoxyiodo)arenes[1d] or iodoarenes. Triflylamide ($TfNH_2$), *p*-nosylamide (*p*-$NsNH_2$) and carbonyls **2a**-**2o** are commercially available. All solvents were purchased as the "anhydrous" and used without further purification. For the thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Column chromatography was performed on silica gel 60N (63-200 μm, neutral, Kanto Kagaku Co., Ltd.). Preparative thin layer chromatography (PTLC) was performed on Wakogel® B-5F (FUJIFILM Wako Pure Chemical Corp.). Medium pressure liquid chromatography (MPLC) was carried out with YAMAZEN EPCLC-Wprep 2XY.

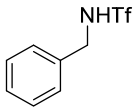
^1H, ^{19}F and ^{13}C NMR spectra were measured at 500, 470 and 125 MHz in $CDCl_3$ and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^1H NMR, using C_6F_6 (-162.9) for ^{19}F NMR and using $CDCl_3$ (77.0 ppm) for ^{13}C NMR as an internal standard, respectively. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). Mass spectra and HRMS were recorded on double-focusing magnetic sector by FAB or ESI methods.

3. Preparation and Characterization of N-Tryflylamine 4a-4l and N-p-Nosylamine 6

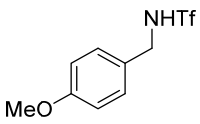


To a suspension of 1-iodosyl-2-methoxybenzene (10.0 mg, 0.04 mmol for **4a**, **4d** and **4f**-**4l**; 20.0 mg, 0.08 mmol for **4b**, **4c** and **4e**) and MS3A (360 mg) in dichloromethane (DCM, 1.0 mL for **4a** and **4c**-**4l**) or 1,2-dichloroethane (DCE, 1.0 mL for **4b**) was added $TfNH_2$ (89.5 mg, 0.6 mmol) or *p*-$NsNH_2$ (121.4 mg, 0.6 mmol) and aldehyde **2** (0.4 mmol) at room temperature. After the reaction mixture was stirred at same temperature (for **4a** and **4c**-**4l**) or 50 ºC (for **4b** and **6**) for 4-48 h, $NaBH_4$ (45.4 mg, 1.2 mmol) and methanol (1.0 mL) were added at 0 ºC. The reaction mixture was stirred at room temperature for 1 h and then was filtered through celite pad. The filtrate was quenched with H_2O and extracted with DCM. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by PTLC to give **4a**-**4l** and **6**.

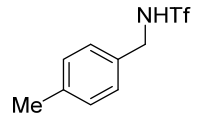
Scale-up experiment: To a suspension of 1-iodosyl-2-methoxybenzene (50.0 mg, 0.2 mmol) stirred for 15 minutes in the presence of MS3A (1.8 g) in dichloromethane (DCM, 5.0 mL) was added $TfNH_2$ (447.3 mg, 3.0 mmol) and aldehyde **2a** (202 μL, 2.0 mmol) at room temperature. After the reaction mixture was stirred at same temperature for 4 h, $NaBH_4$ (227 mg, 6.0 mmol) and methanol (5.0 mL) were added at 0 ºC. The reaction mixture was stirred at room temperature for 1 h and then was filtered through celite pad. The filtrate was quenched with H_2O and extracted with DCM. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by silica gel chromatography (hexane:AcOEt = 9:1) to give **4a** (409.3 mg, 86%) as a white solid.



***N*-Benzyl-1,1,1-trifluoromethanesulfonamide** (**4a**): 86% (82.1 mg). R_f = 0.61 (hexane:AcOEt = 3:1). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.57-7.29 (m, 5H), 5.03 (brs, 1H), 4.45 (d, J = 5.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 135.1, 129.1, 128.6, 127.8, 119.6 (q, J_{CF} = 321.1 Hz), 48.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.3 (s, 3F). The ^1H, ^{19}F and ^{13}C NMR spectra of the product were identical to those reported in the literature.[2a]



1,1,1-Trifluoro-*N*-(4-methoxybenzyl)methanesulfonamide (**4b**): 76% (81.9 mg). R_f = 0.53 (hexane:AcOEt = 3:1). White solid. Mp 66-68 ºC. IR (KBr) ν cm^{-1}; 3187, 1612, 1515, 1444, 1373, 1232, 1181, 1147, 1047, 817, 616. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.25 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 4.99 (brs, 1H), 4.38 (d, J = 5.7 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 159.7, 129.4, 127.2, 119.7 (q, J_{CF} = 321.1 Hz), 114.4, 55.3, 47.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.3 (s, 3F). HRMS (FAB, m/z): calcd. for $C_9H_{10}F_3NO_3S$ [M] 269.0333; found, 269.0337.

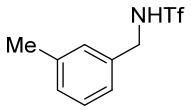


1,1,1-Trifluoro-*N*-(4-methylbenzyl)methanesulfonamide (**4c**): 92% (93.2 mg). R_f = 0.61 (hexane:AcOEt = 3:1). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.21 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 4.99 (brs, 1H), 4.40 (d, J = 5.7 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 138.6, 132.1, 129.7, 127.8, 119.7 (q, J_{CF} = 321.1 Hz), 48.0, 21.1. ^{19}F NMR

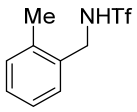
[1] (*a*) A. Maity, S.-M. Hyun and D. C. Powers, *Nat. Chem.*, 2018, **10**, 200; (*b*) S. Sunagawa, F. Morisaki, T. Baba, A. Tsubouchi, A. Yoshimura, K. Miyamoto, M. Uchiyama and A. Saito, *Org. Lett.*, 2022, **24**, 5230; (*c*) L. Kraszkiewicz and L. Skulski, *ARKIVOC*, 2003, 120; (*d*) A. Watanabe, K. Miyamoto, T. Okada, T. Asawa and M. Uchiyama, *J. Org. Chem.*, 2018, **83**, 14262.

[2] (*a*) A. U. Meyer, A. L. Berger and B. König, *Chem. Commun.*, 2016, **52**, 10918; (*b*) X. Wang, T.-S. Mei and J.-Q. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7520; (*c*) R. Pirwerdjan, P. Becker and C. Bolm, *Org. Lett.*, 2015, **17**, 5008.

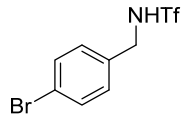
(470 MHz, $CDCl_3$) δ ppm; -78.3 (s, 3F). The ^1H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[2b]



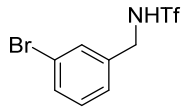
1,1,1-Trifluoro-*N*-(3-methylbenzyl)methanesulfonamide (**4d**): 84% (85.0 mg). R_f = 0.70 (hexane:AcOEt = 3:1). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.28 (dd, J = 7.5, 7.5 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.14 (s, 1H), 7.12 (d, J = 7.5 Hz, 1H), 4.95 (brs, 1H), 4.41 (d, J = 5.7 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 138.9, 135.0, 129.3, 128.9, 128.5, 124.8, 119.7 (q, J_{CF} = 320.7 Hz), 48.1, 21.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.3 (s, 3F). The ^1H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[2b]



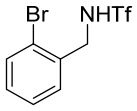
1,1,1-Trifluoro-*N*-(2-methylbenzyl)methanesulfonamide (**4e**): 76% (76.7 mg). R_f = 0.63 (hexane:AcOEt = 3:1). Yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.31-7.27 (m, 2H), 7.25-7.20 (m, 2H), 4.90 (brs, 1H), 4.45 (d, J = 4.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 136.5, 132.8, 130.9, 128.9, 128.8, 126.6, 119.7 (q, J_{CF} = 321.1 Hz), 46.2, 18.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.2 (s, 3F). The ^1H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[2b]



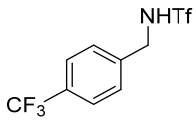
***N*-(4-Bromobenzyl)-1,1,1-trifluoromethanesulfonamide** (**4f**): 85% (108.0 mg). R_f = 0.56 (hexane:AcOEt = 3:1). White solid. Mp 61-63 ºC. IR (KBr) ν cm^{-1}; 3301, 1451, 1365, 1230, 1197, 1143, 1057, 865, 795, 610. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.53 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 4.99 (brs, 1H), 4.42 (d, J = 5.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 134.2, 132.2, 129.5, 122.7, 119.6 (q, J_{CF} = 320.7 Hz), 47.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.3 (s, 3F). HRMS (FAB, m/z): calcd. for $C_8H_8BrF_3NO_2S$, [M+H] 317.9411; found, 317.9407.



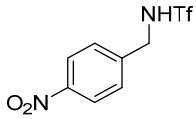
***N*-(3-Bromobenzyl)-1,1,1-trifluoromethanesulfonamide** (**4g**): 70% (89.5 mg). R_f = 0.56 (hexane:AcOEt = 3:1). Yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.52-7.47 (m, 2H), 7.29-7.26 (m, 2H), 5.09 (brs, 1H), 4.43 (d, J = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 137.4, 131.7, 130.8, 130.6, 126.3, 122.9, 119.6 (q, J_{CF} = 321.1 Hz), 47.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.3 (s, 3F). The ^1H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[2b]



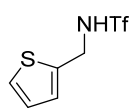
***N*-(2-Bromobenzyl)-1,1,1-trifluoromethanesulfonamide** (**4h**): 75% (95.5 mg). R_f = 0.70 (hexane:AcOEt = 3:1). Yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.60 (d, J = 7.5 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.36 (dd, J = 7.5, 7.5 Hz, 1H), 7.25 (dd, J = 7.5, 7.5 Hz, 1H), 5.36 (brs, 1H), 4.54 (d, J = 6.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 134.7, 133.1, 130.5, 130.4, 128.1, 123.6, 119.5 (q, J_{CF} = 320.7 Hz), 48.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.5 (s, 3F). The ^1H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[2b]



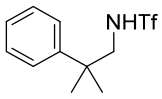
1,1,1-Trifluoro-*N*-[4-(trifluoromethyl)benzyl]methanesulfonamide (**4i**): 67% (82.8 mg). R_f = 0.58 (hexane:AcOEt = 3:1). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.67 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 5.25 (brs, 1H), 4.53 (d, J = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 139.2, 130.9 (q, J_{CF} = 32.8 Hz), 128.0, 126.0 (q, J_{CF} = 3.6 Hz), 123.8 (q, J_{CF} = 272.3 Hz), 119.6 (q, J_{CF} = 321.1 Hz), 47.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -63.9 (s, 3F), -78.3 (s, 3F). The ^1H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[2b]



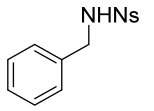
1,1,1-Trifluoro-*N*-(4-nitrobenzyl)methanesulfonamide (**4j**): 39% (44.1 mg). R_f = 0.33 (hexane:AcOEt = 3:1). Brown solid. Mp 39-41 ºC. IR (KBr) ν cm^{-1}; 3297, 1608, 1528,1441, 1372, 1354, 1231, 1194, 1149, 1065, 863, 744, 608. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 8.26 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 5.44 (brs, 1H), 4.58 (d, J = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 147.7, 142.8, 128.4, 124.1, 119.5 (q, J_{CF} = 320.7 Hz), 47.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.2 (s, 3F). HRMS (FAB, m/z): calcd. for $C_8H_8F_3N_2O_4S$ [M+H] 285.0157; found, 285.0150.



1,1,1-Trifluoro-*N*-(thiophen-2-ylmethyl)methanesulfonamide (**4k**): 56% (55.3 mg). R_f = 0.58 (hexane:AcOEt = 3:1). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.33 (dd, J = 5.2, 1.2 Hz, 1H), 7.06 (dd, J = 3.4, 1.2 Hz, 1H), 7.00 (dd, J = 5.2, 3.4 Hz, 1H), 5.04 (brs, 1H), 4.65 (d, J = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 137.4, 127.5, 127.3, 126.8, 119.5 (q, J_{CF} = 320.7 Hz), 42.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.5 (s, 3F). The ^1H, ^{19}F and ^{13}C NMR spectra of the product were identical to those reported in the literature.[2c]



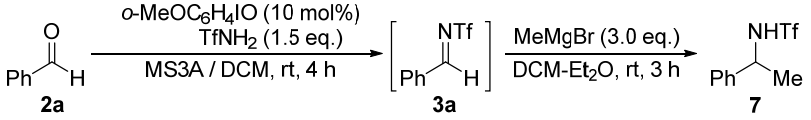
1,1,1-Trifluoro-*N*-(2-methyl-2-phenylpropyl)methanesulfonamide (**4l**): 57% (64.1 mg). R_f = 0.66 (hexane:AcOEt = 3:1). White solid. Mp 64-66 ºC. IR (KBr) ν cm^{-1}; 3280, 2978, 1434, 1377, 1232, 1178, 1154, 1071, 875, 765, 607. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.41-7.26 (m, 5H), 4.34 (brs, 1H), 3.41 (d, J = 5.7 Hz, 2H), 1.41 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 144.3, 129.0, 127.1, 125.8, 119.6 (q, J_{CF} = 321.5 Hz), 55.7, 38.4, 26.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.2 (s, 3F). HRMS (FAB, m/z): calcd. for $C_{11}H_{15}F_3NO_2S$ [M+H] 282.0776; found, 282.0765.



***N*-Benzyl-4-nitrobenzenesulfonamide** (**6**): 71% (83.2 mg). R_f = 0.32 (hexane:AcOEt = 3:1). Pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 8.31 (d, J = 8.6 Hz, 2H), 7.99 (d, J = 8.6 Hz, 2H), 7.30-7.25 (m, 3H), 7.20-7.14 (m, 2H), 4.89 (brs, 1H), 4.24 (d, J = 6.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 150.0, 146.0, 135.4, 128.8, 128.3, 127.9, 124.3, 48.4 (Note that the two carbon peaks overlap each other). The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[3]

4. Other Conversion Reactions of N-Tryflylimine 3a

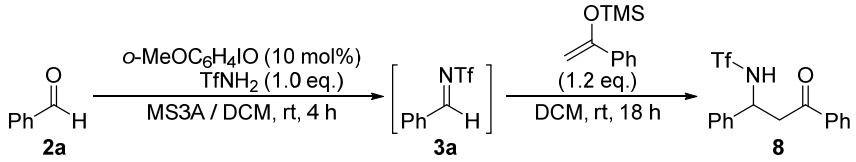
a) Preparation of **1,1,1-trifluoro-*N*-(1-phenylethyl)methanesulfonamide** (**7**)



To a suspension of 1-iodosyl-2-methoxybenzene (10.0 mg 0.04 mmol) and MS3A (360 mg) in dichloromethane (DCM, 1.0 mL) was added $TfNH_2$ (89.5 mg, 0.6 mmol) and benzaldehyde (**2a**, 40.8 μL, 0.4 mmol) at room temperature. After the reaction mixture was stirred at same temperature for 4 h, Et_2O (3.0 mL) and MeMgBr (3.0 M in Et_2O solution, 0.4 mL, 1.2 mmol) were added at 0 ºC. The reaction mixture was stirred at room temperature for 3 h and then was filtered through celite pad. The filtrate was quenched with sat. NH_4Cl and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC (hexane:AcOEt = 9:1) to give **7** (86.1 mg, 85%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.43-7.36 (m, 2H), 7.36-7.30 (m, 3H), 5.17 (brs, 1H), 4.80 (dq, J = 6.8, 6.8 Hz, 1H), 1.65 (d, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 140.9, 129.0, 128.3, 125.9, 119.5 (q, J_{CF} = 320.9 Hz), 55.3, 23.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.8 (s, 3F). The ^{1}H and ^{13}C NMR spectra of the product were identical to those reported in the literature.[4]

b) Preparation of **1,1,1-trifluoro-*N*-(3-oxo-1,3-diphenylpropyl)methanesulfonamide** (**8**)

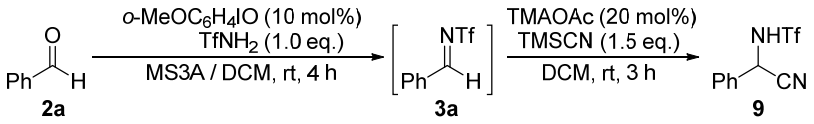


To a suspension of 1-iodosyl-2-methoxybenzene (10.0 mg 0.04 mmol) and MS3A (360 mg) in dichloromethane (DCM, 1.0 mL) was added $TfNH_2$ (59.6 mg, 0.4 mmol) and benzaldehyde (**2a**, 40.8 μL, 0.4 mmol) at room temperature. After the reaction mixture was stirred at same temperature for 4 h, 1-phenyl-1-trimethylsiloxyethylene (98.4 μL, 0.48 mmol) were added at room temperature. The reaction mixture was stirred at room temperature for 18 h and then was filtered through celite pad. The filtrate was concentrated in vacuo to dryness. The residue was purified by PTLC (R_f = 0.44, hexane:AcOEt = 3:1) to give **8** (86.1 mg, 85%) as a white solid.

Mp 111-113 ºC. IR (KBr) ν cm^{-1}; 3247, 1675, 1377, 1234, 1189, 1150, 1053, 597. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.91-7.83 (m, 2H), 7.60 (t, J = 7.7 Hz, 1H), 7.46 (dd, J = 7.7 Hz, 2H), 7.39-7.32 (m, 4H), 7.30-7.26 (m, 1H), 6.84 (d, J = 9.2 Hz, 1H), 5.18 (ddd, J = 9.2, 5.7, 4.0 Hz, 1H), 3.84 (dd, J = 17.8, 4.0 Hz, 1H), 3.58 (dd, J = 17.8, 5.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 198.1, 139.1, 136.0, 134.1, 128.84, 128.80, 128.11, 128.08, 126.1, 119.4 (q, J_{CF} = 321.1 Hz), 55.6, 43.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.8 (s, 3F). HRMS (ESI, m/z): calcd. for $C_{16}H_{14}F_3NKO_3S^+$ $[M+K]^+$ 396.0278; found, 396.0289.

[3] I. Nageli, C. Baud, G. Bernardinelli, Y. Jacqnier, M. Moran and P. Müller, *Helv. Chim. Acta*, 1997, **80**, 1087.
[4] K. W. Fiori and J. Du Bois, *J. Am. Chem. Soc.*, 2007, **129**, 562.

c) Preparation of ***N*-[cyano(phenyl)methyl]-1,1,1-trifluoromethanesulfonamide (9)**

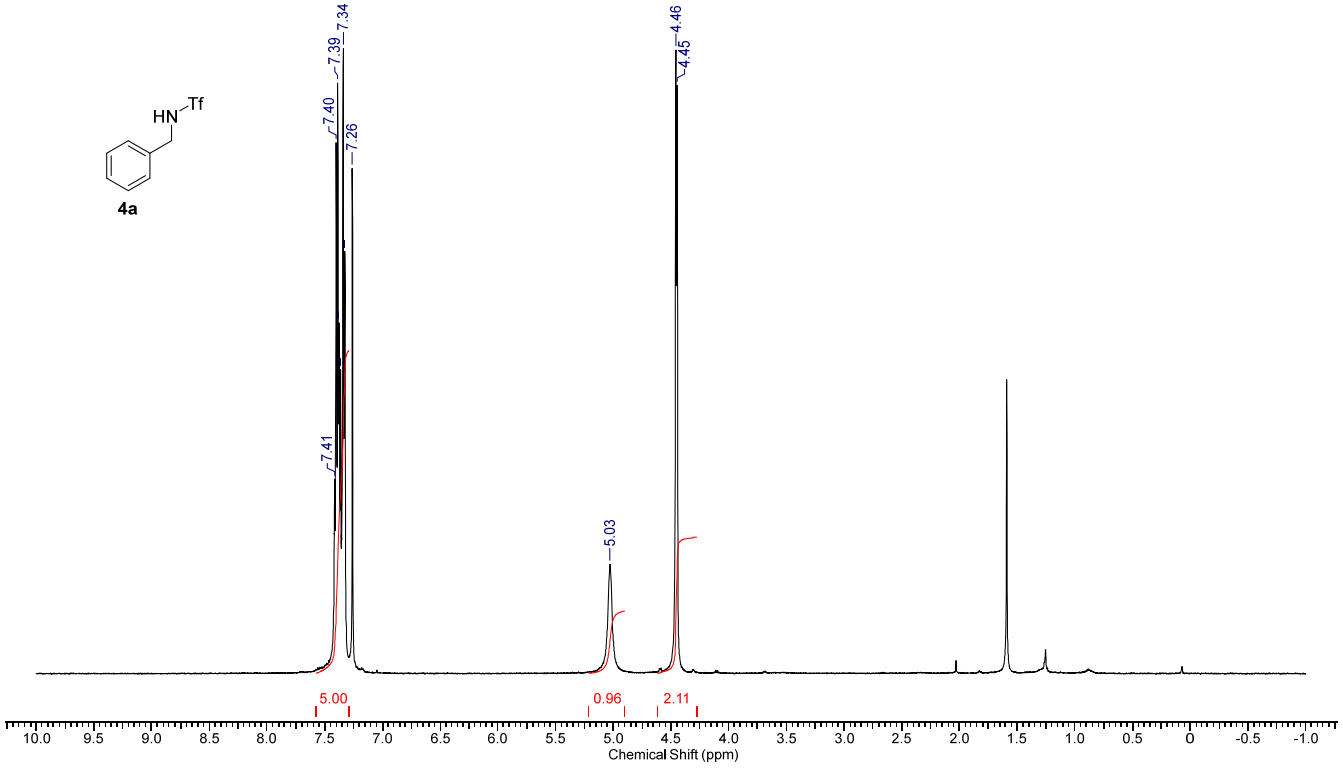


To a suspension of 1-iodosyl-2-methoxybenzene (10.0 mg 0.04 mmol) and MS3A (360 mg) in dichloromethane (DCM, 1.0 mL) was added $TfNH_2$ (59.6 mg, 0.4 mmol) and benzaldehyde (**2a**, 40.8 μL, 0.4 mmol) at room temperature. After the reaction mixture was stirred at same temperature for 4 h, trimethylsilyl cyanide (TMSCN, 74.8 μL, 0.6 mmol) and tetramethylammonium acetate (10.7 mg, 0.08 mmol) were added at room temperature. The reaction mixture was stirred at room temperature for 3 h and then was filtered through celite pad. The filtrate was concentrated in vacuo to dryness. The residue was purified by MPLC (hexane:AcOEt = 3:1) to give **9** (81.4 mg, 77%) as a white solid.

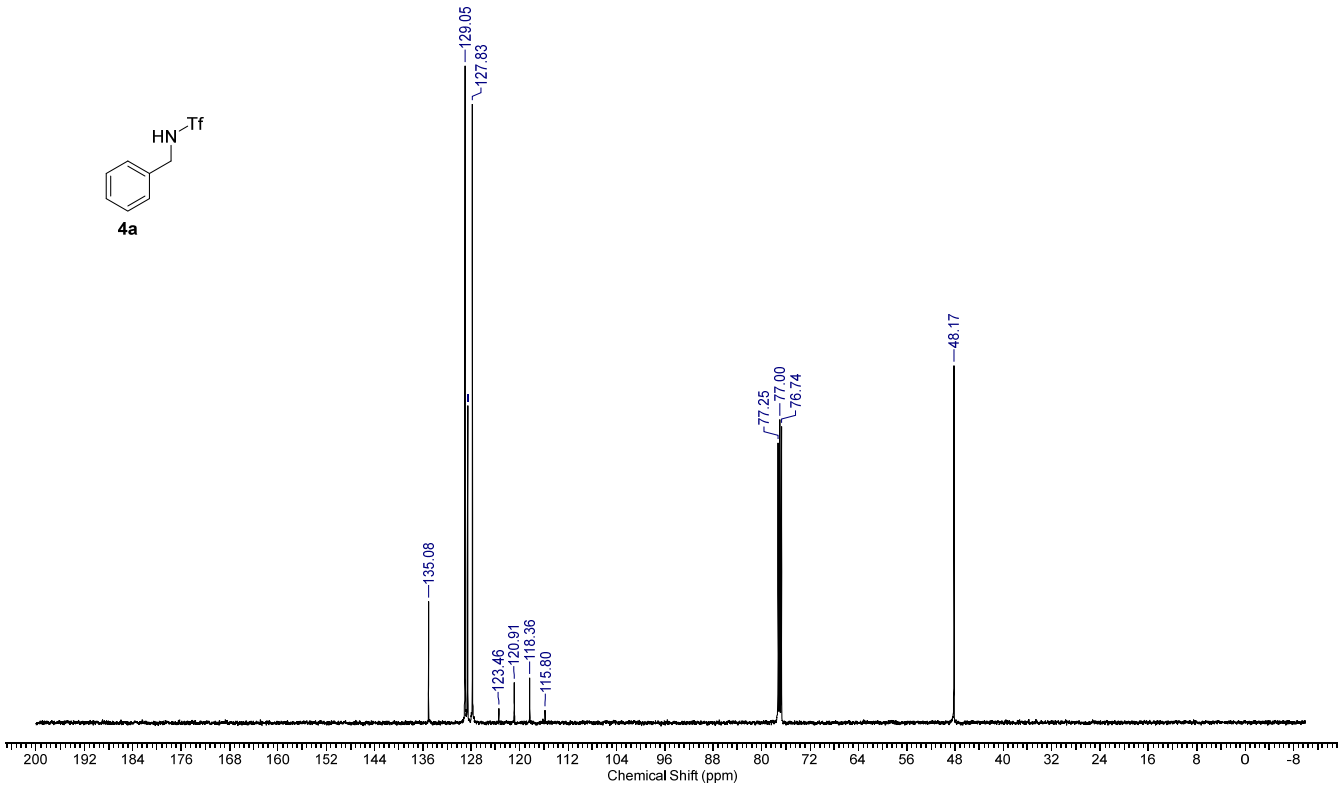
Mp 105-106 ºC. IR (KBr) ν cm^{-1}; 3119, 2269, 1462, 1378, 1232, 1194, 1145, 1065, 613. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.69-7.46 (m, 5H), 5.62 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm; 131.1, 130.6, 129.8, 127.0, 119.2 (q, J_{CF} = 320.3 Hz), 115.7, 49.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm; -78.4 (s, 3F). HRMS (ESI, m/z): calcd. for $C_8H_7F_3NO_2S^+$ $[M\text{-}CN]^+$ 238.0144; found, 238.0148.

5. ^{1}H and ^{13}C NMR Spectra of 4a-4h and 6-9

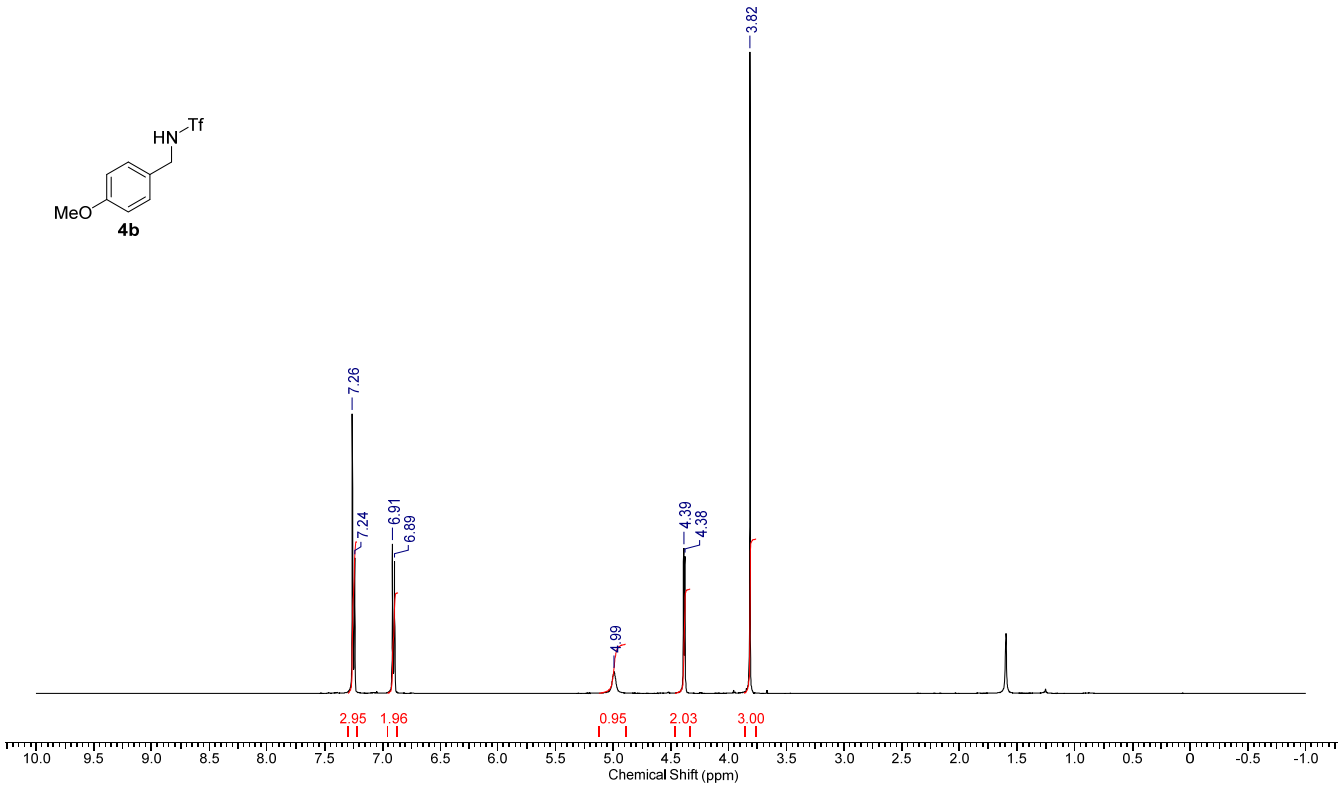
^{1}H NMR (500 MHz, $CDCl_3$) of **4a**



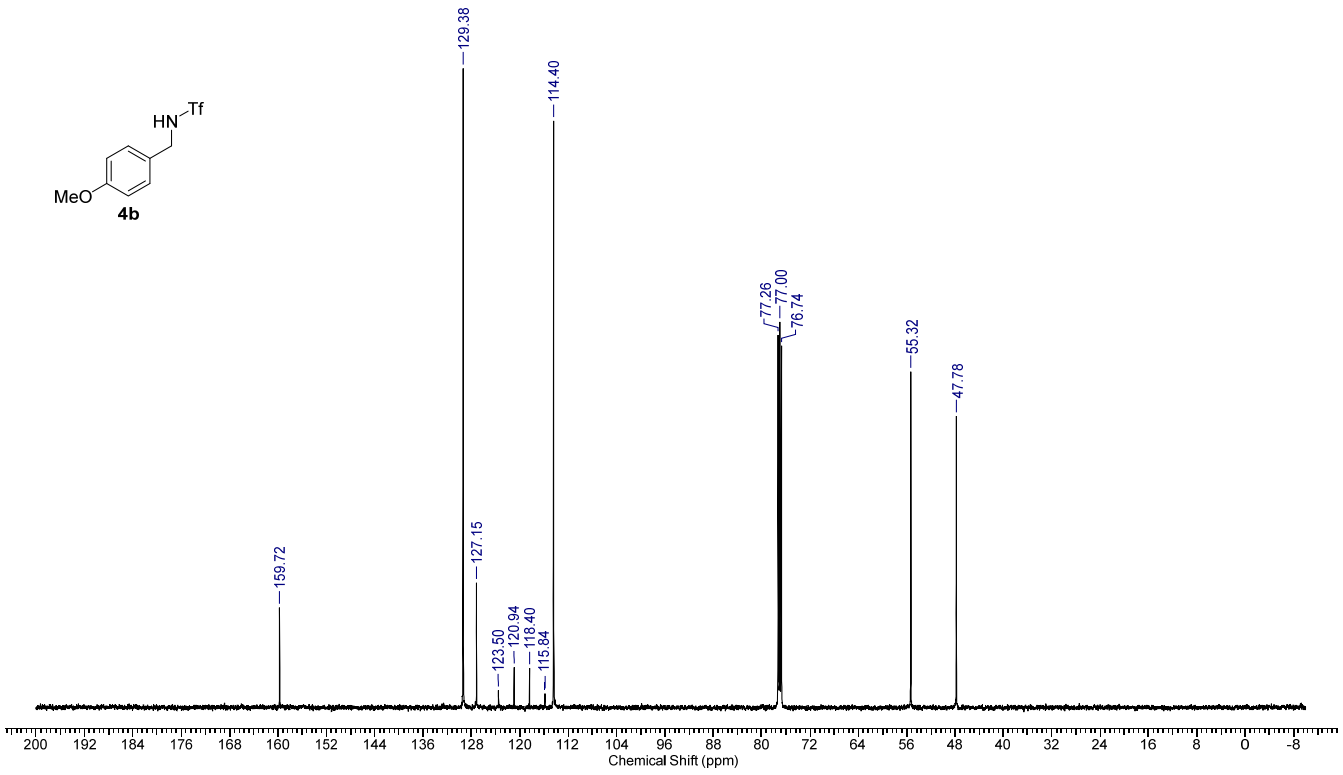
^{13}C NMR (125 MHz, $CDCl_3$) of **4a**



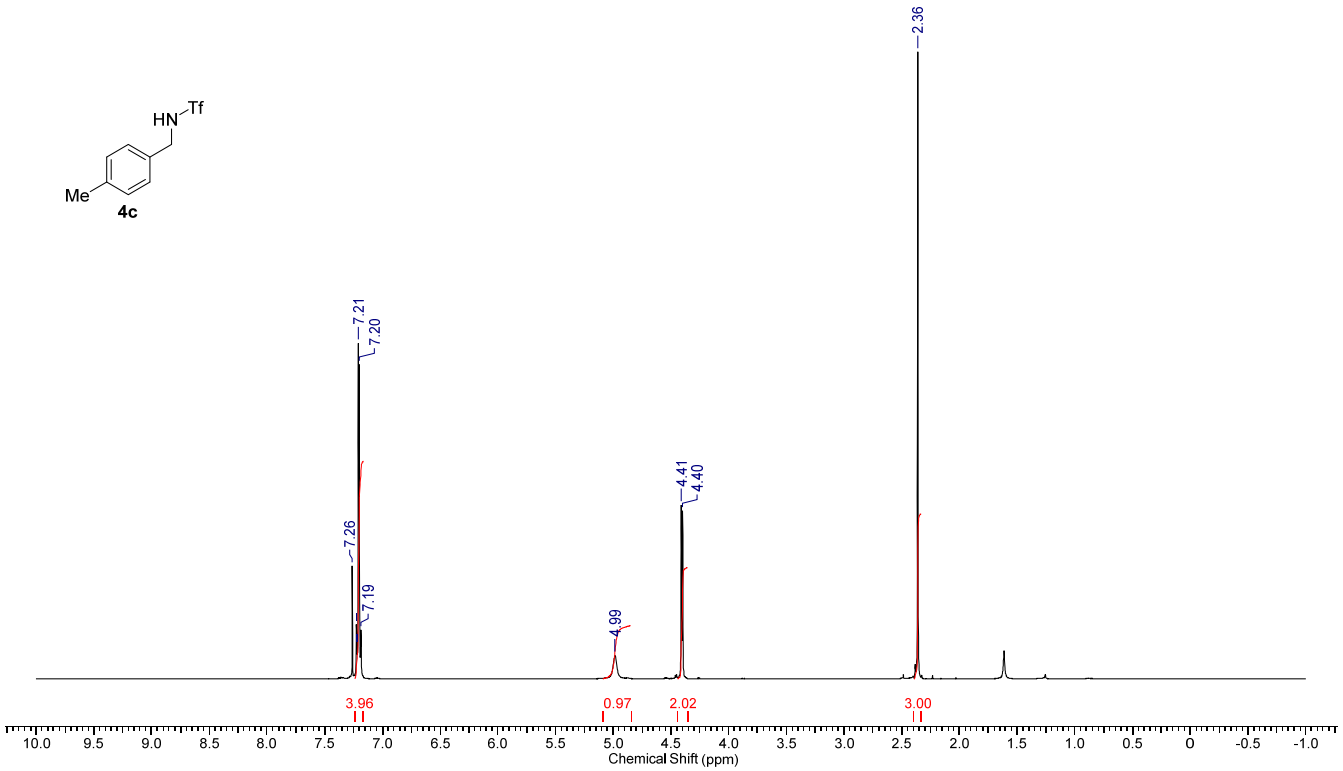
^{1}H NMR (500 MHz, $CDCl_3$) of **4b**



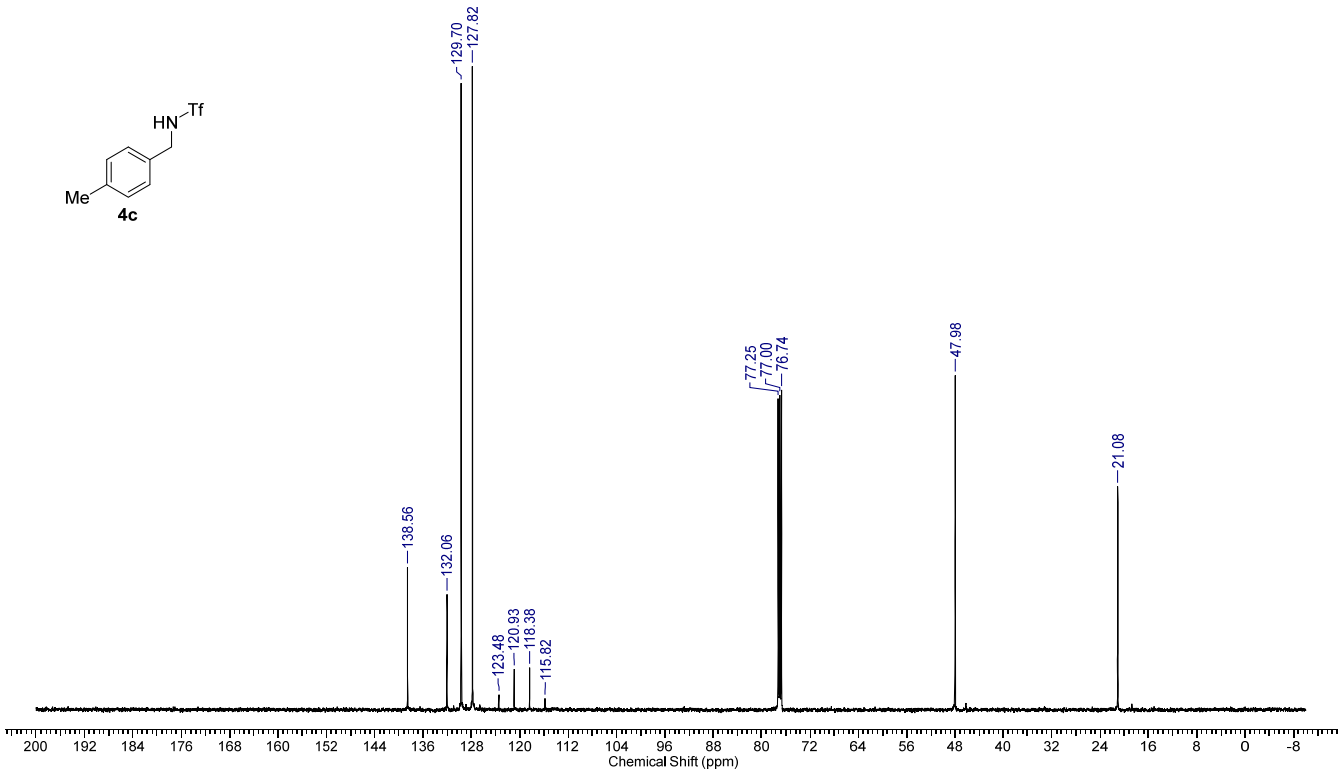
^{13}C NMR (125 MHz, $CDCl_3$) of **4b**



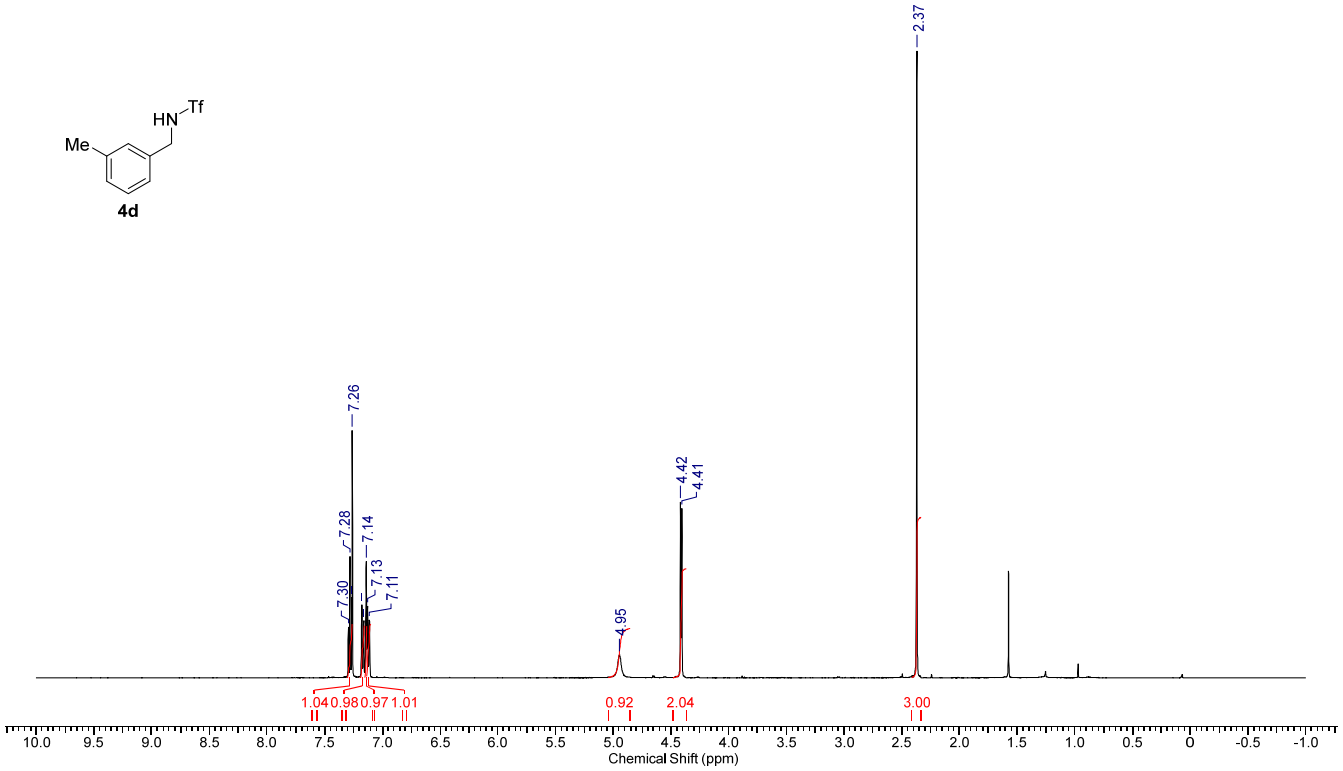
^{1}H NMR (500 MHz, $CDCl_3$) of **4c**



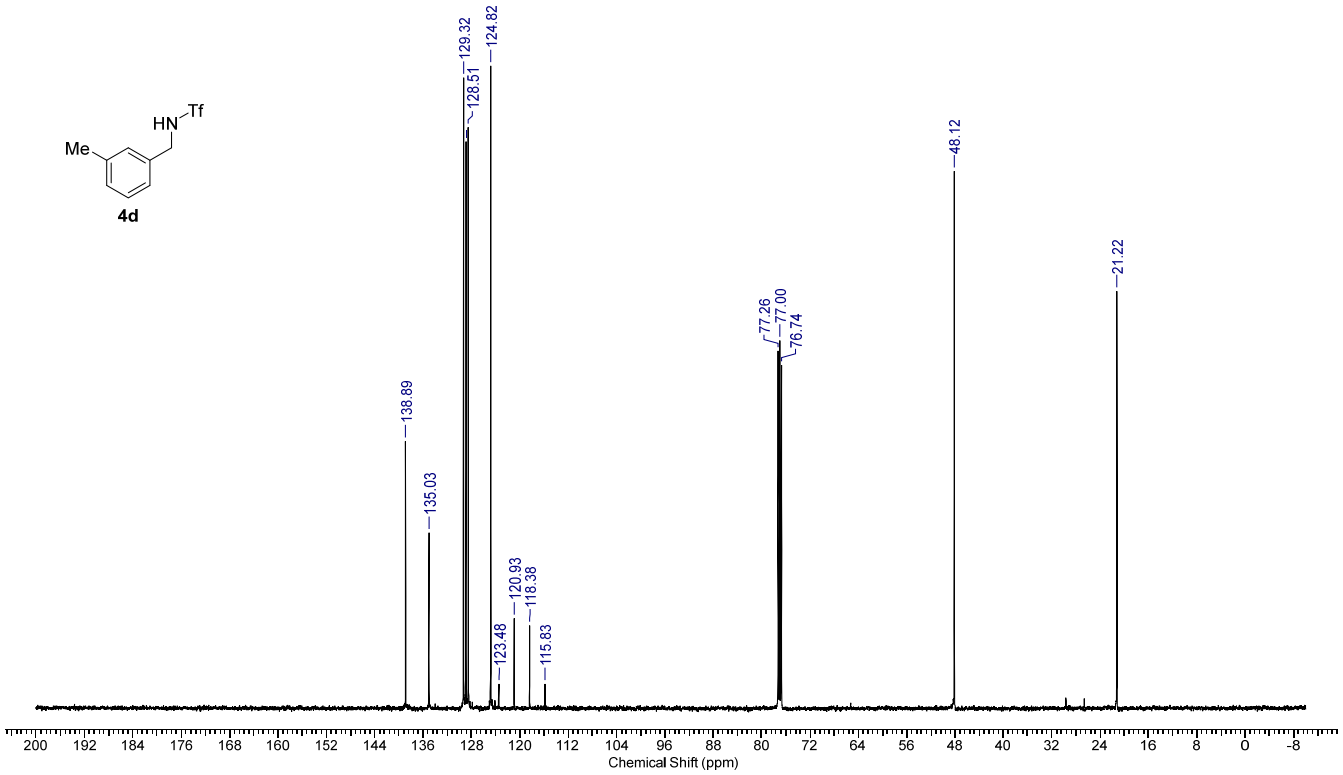
^{13}C NMR (125 MHz, $CDCl_3$) of **4c**



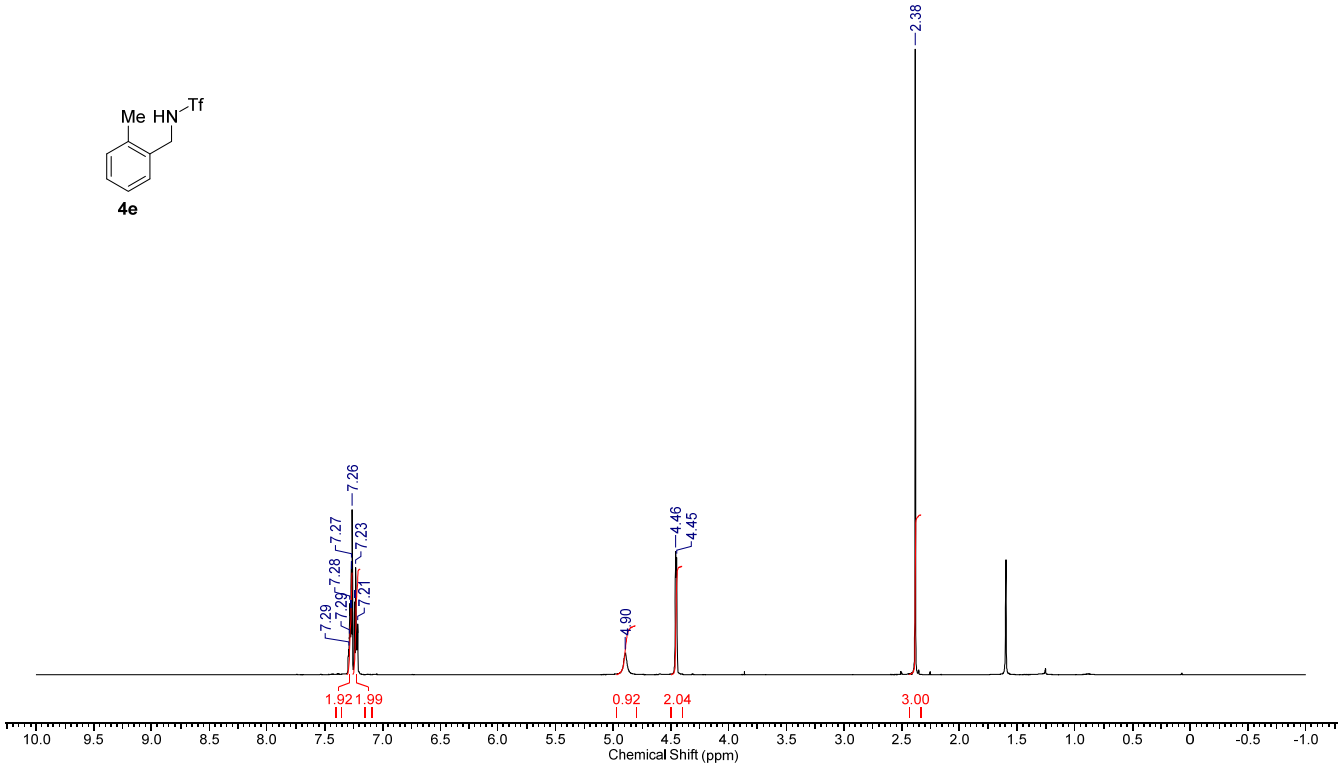
^{1}H NMR (500 MHz, $CDCl_3$) of **4d**



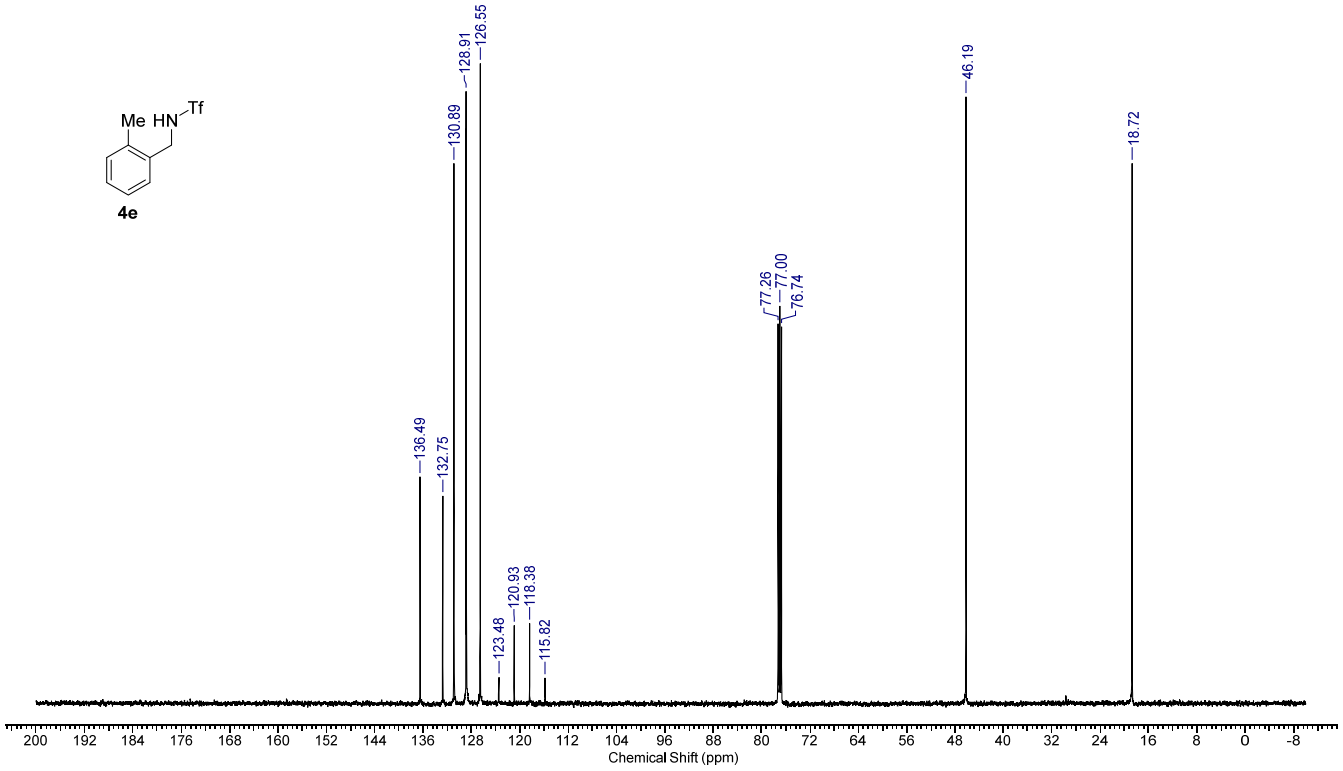
^{13}C NMR (125 MHz, $CDCl_3$) of **4d**



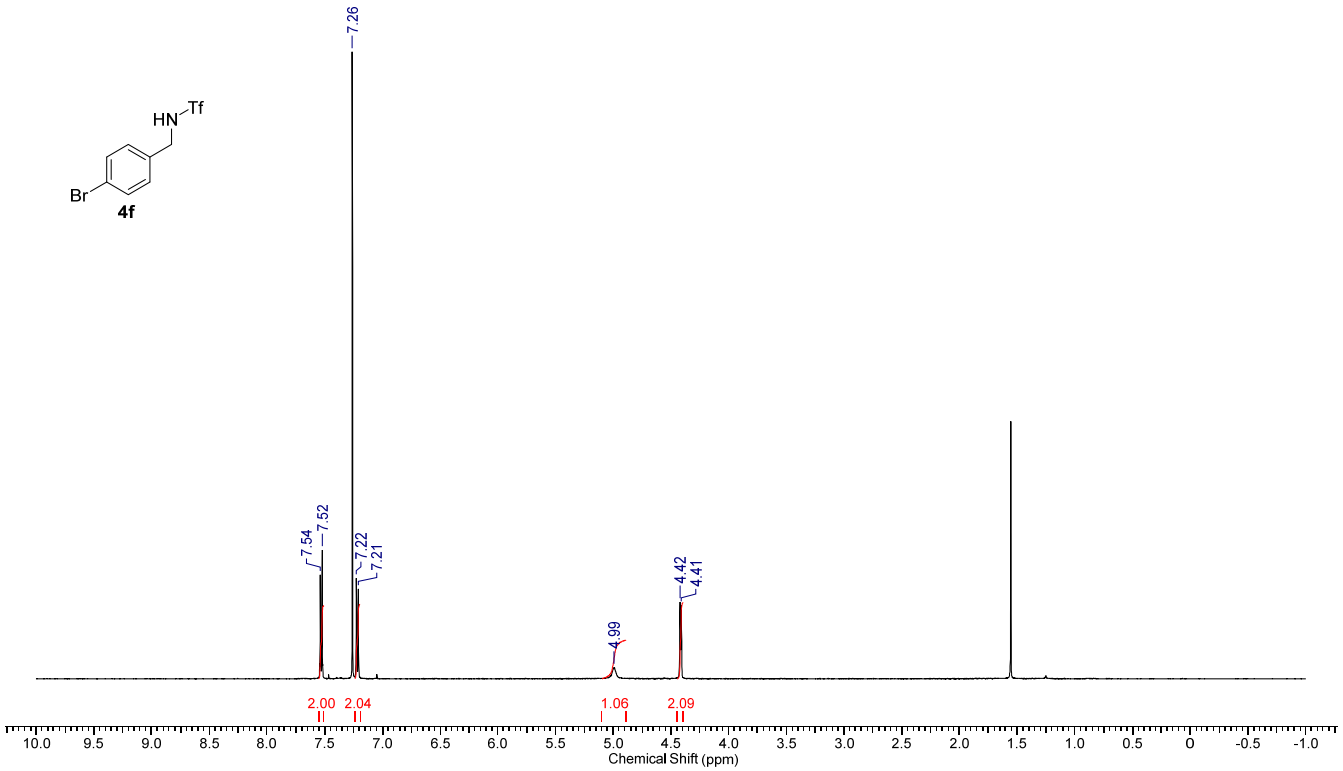
^{1}H NMR (500 MHz, $CDCl_3$) of **4e**



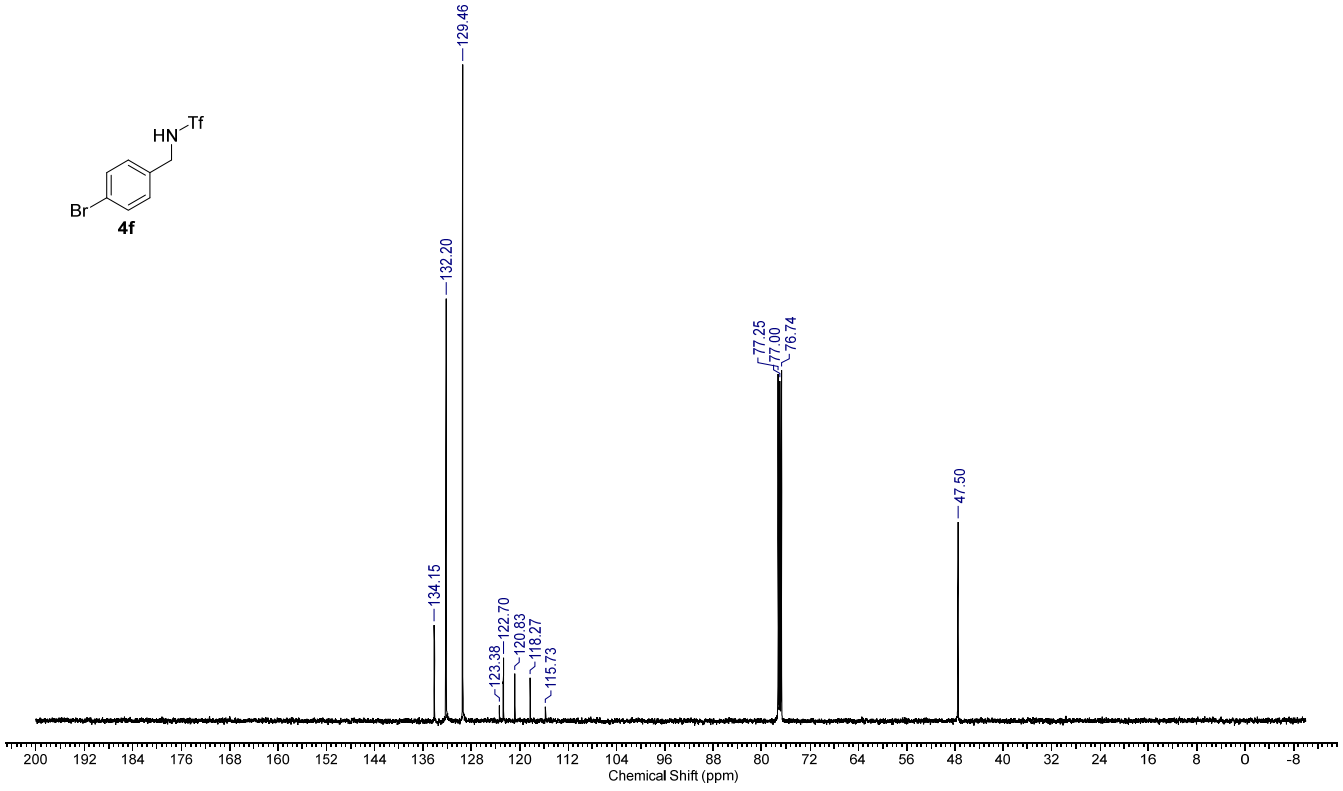
^{13}C NMR (125 MHz, $CDCl_3$) of **4e**



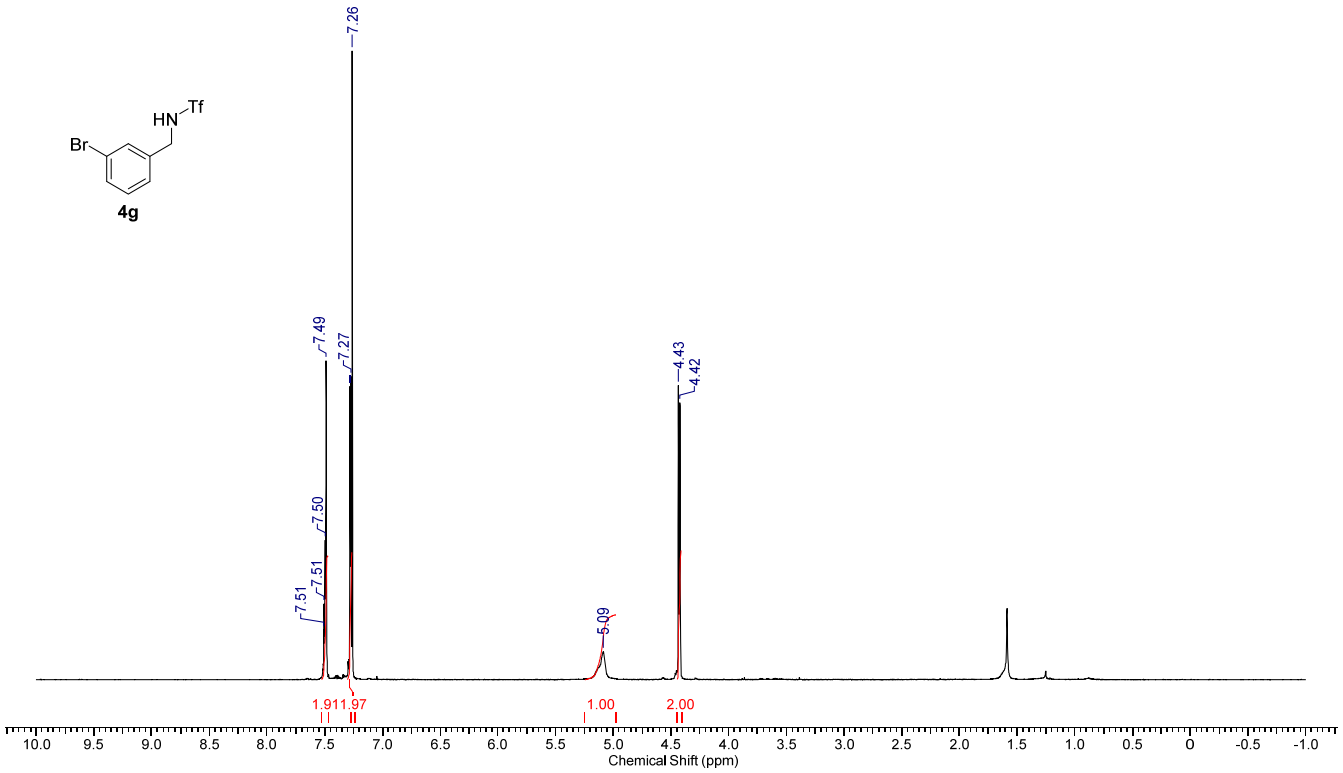
^{1}H NMR (500 MHz, $CDCl_3$) of **4f**



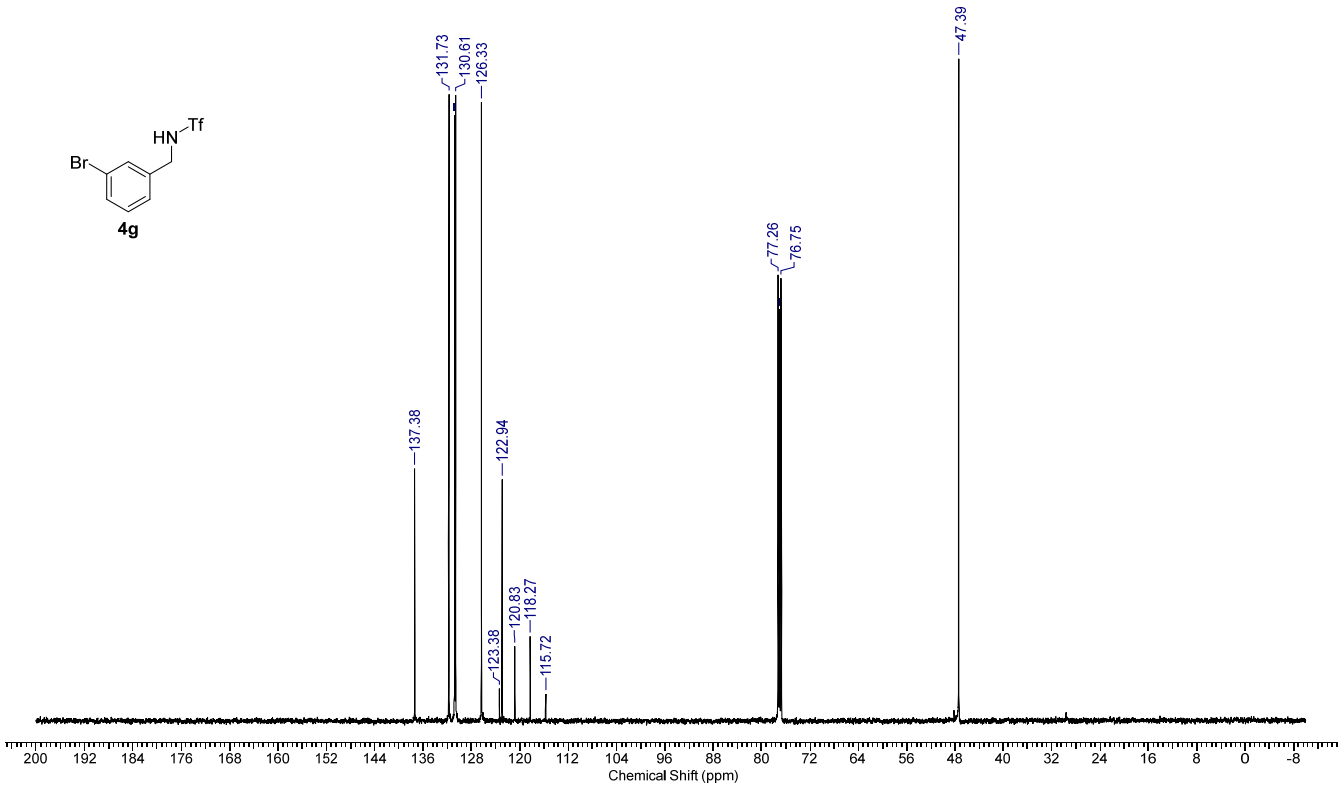
^{13}C NMR (125 MHz, $CDCl_3$) of **4f**



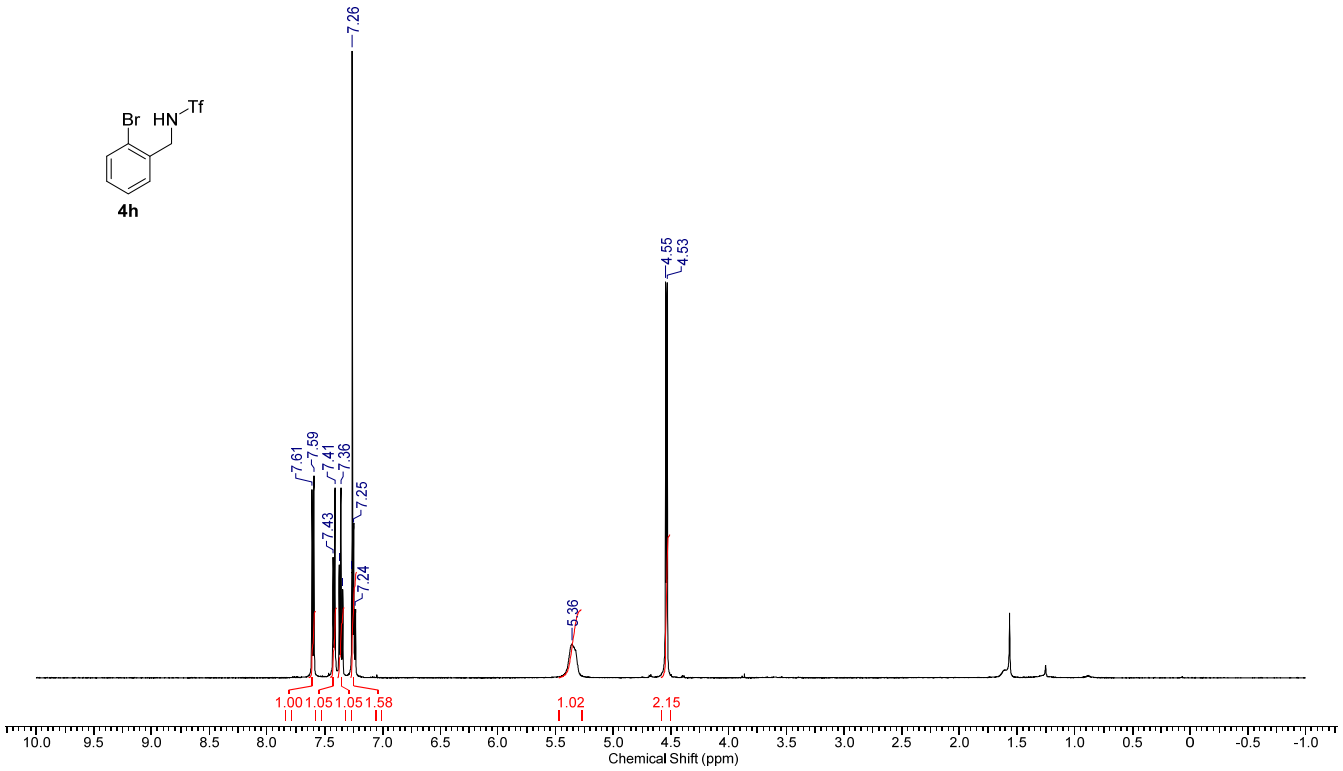
^{1}H NMR (500 MHz, $CDCl_3$) of **4g**



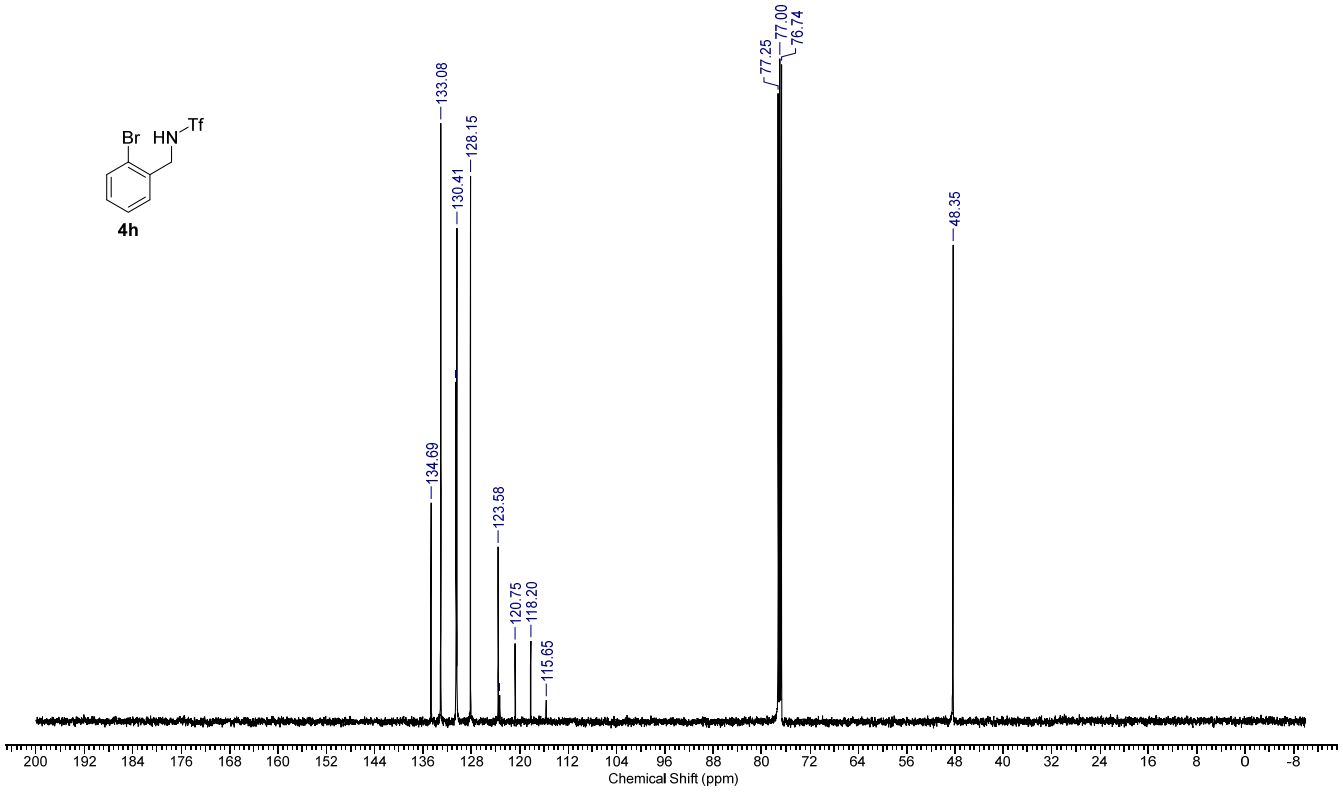
^{13}C NMR (125 MHz, $CDCl_3$) of **4g**



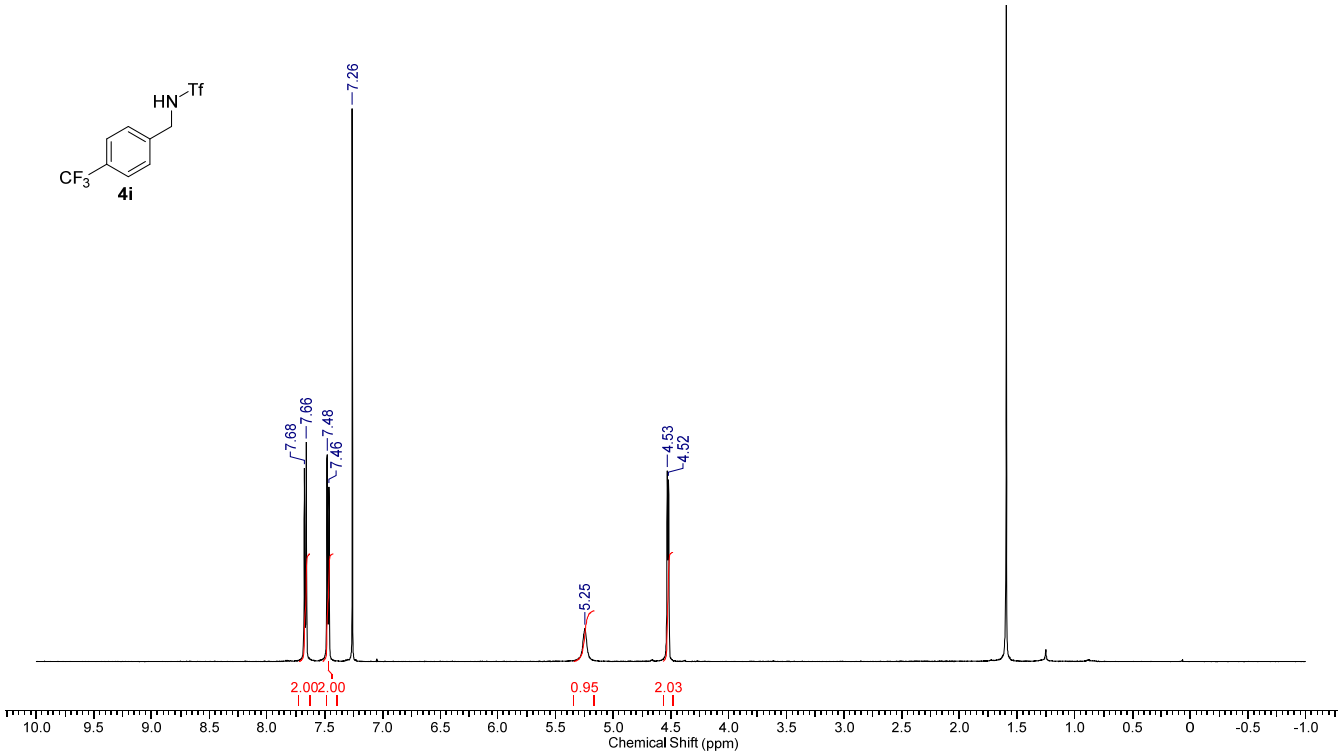
^{1}H NMR (500 MHz, $CDCl_3$) of **4h**



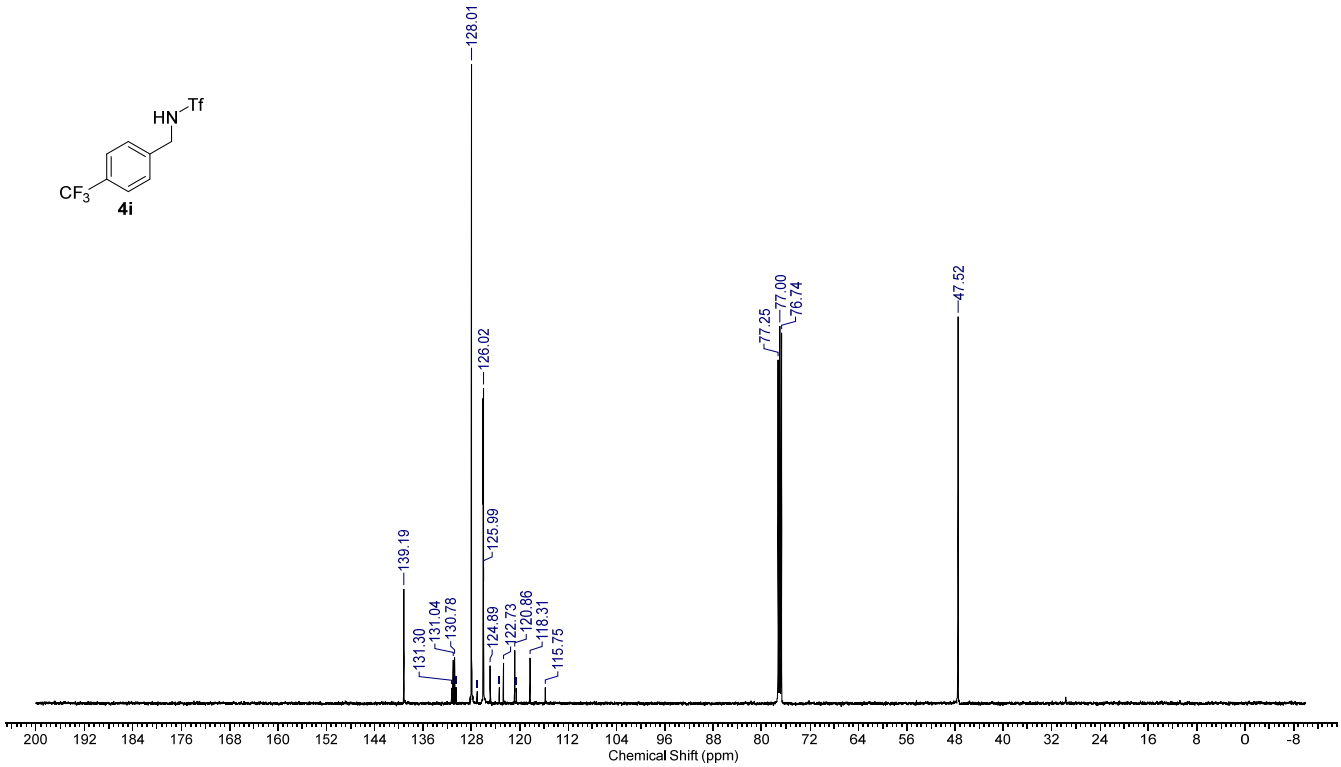
^{13}C NMR (125 MHz, $CDCl_3$) of **4h**



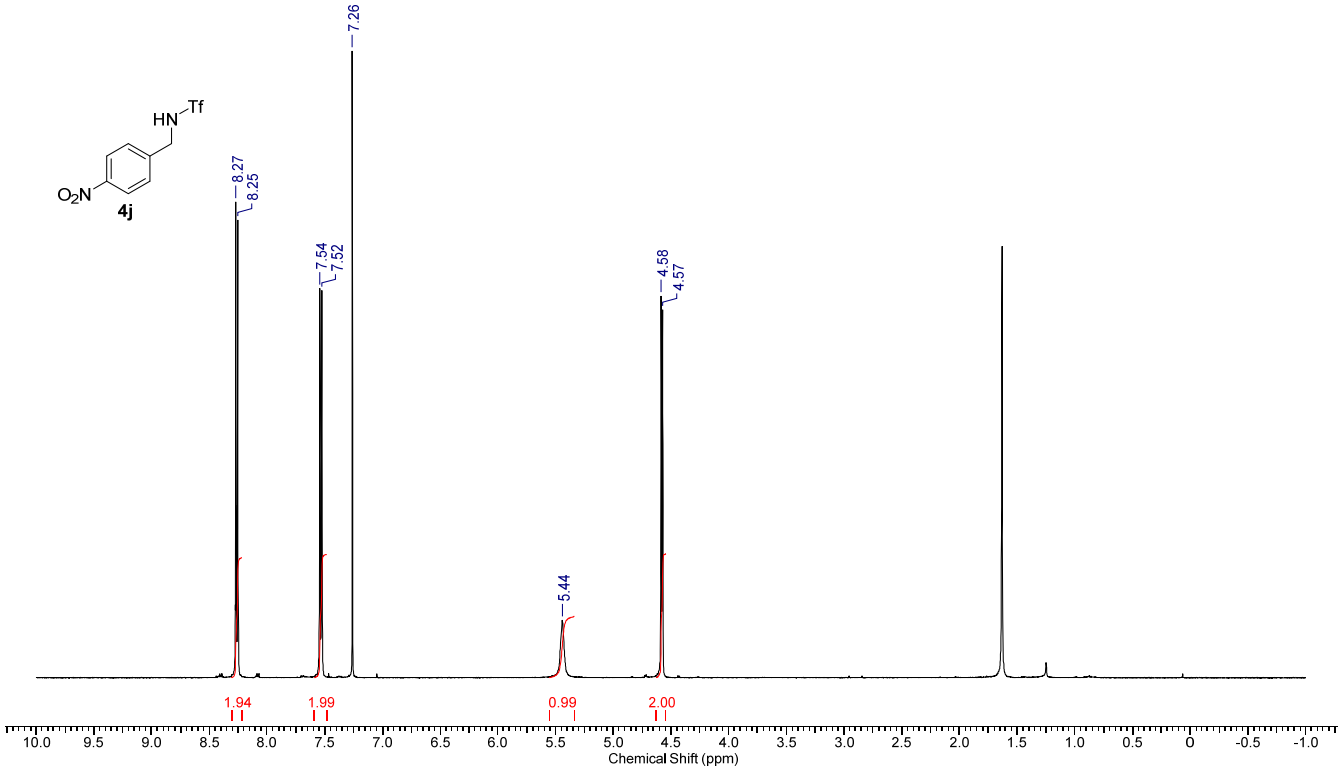
^{1}H NMR (500 MHz, $CDCl_3$) of **4i**



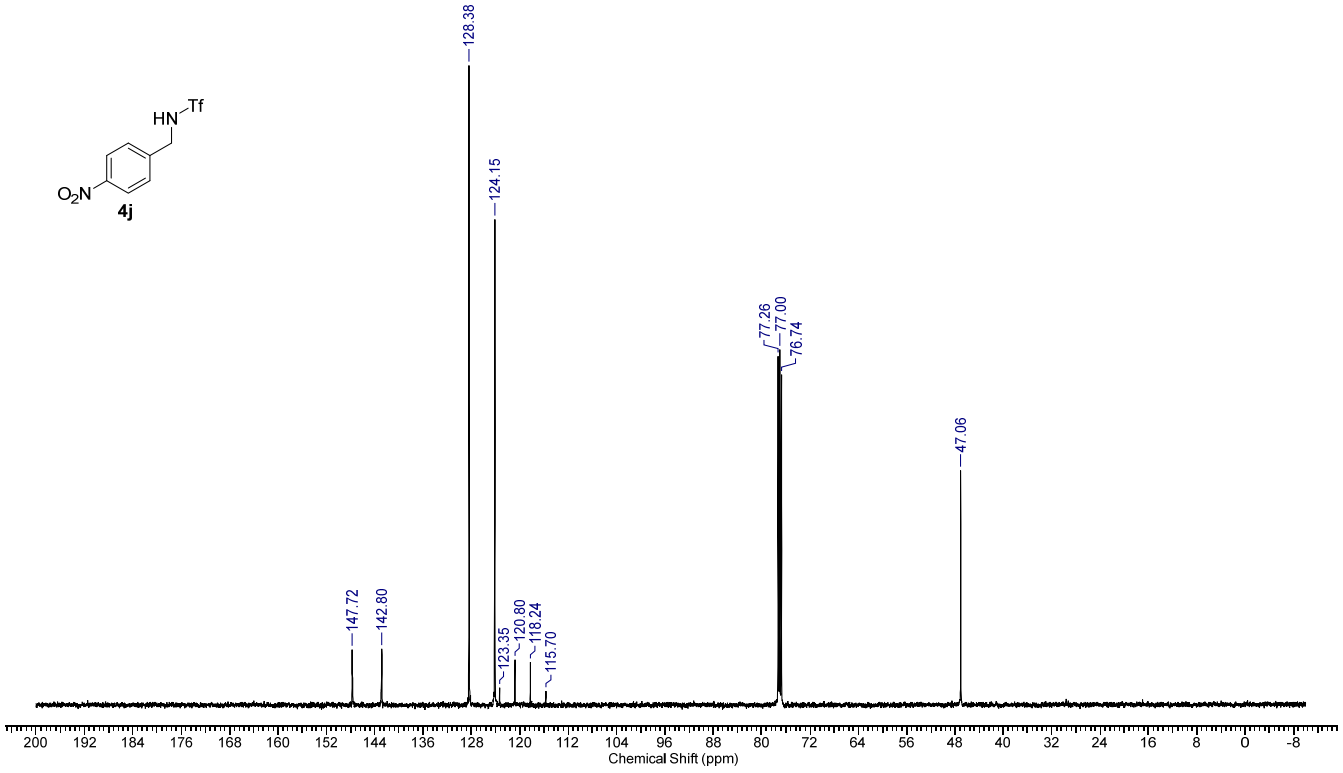
^{13}C NMR (125 MHz, $CDCl_3$) of **4i**



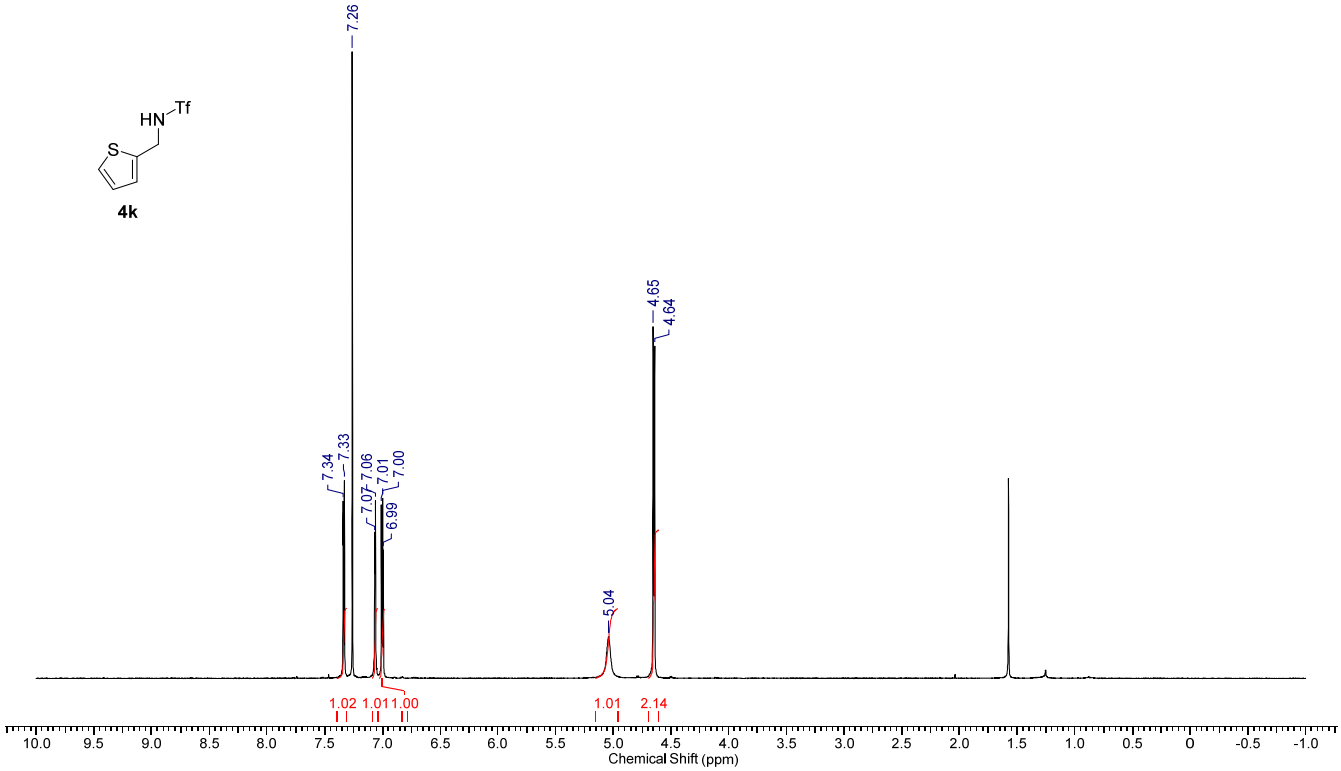
^{1}H NMR (500 MHz, $CDCl_3$) of **4j**



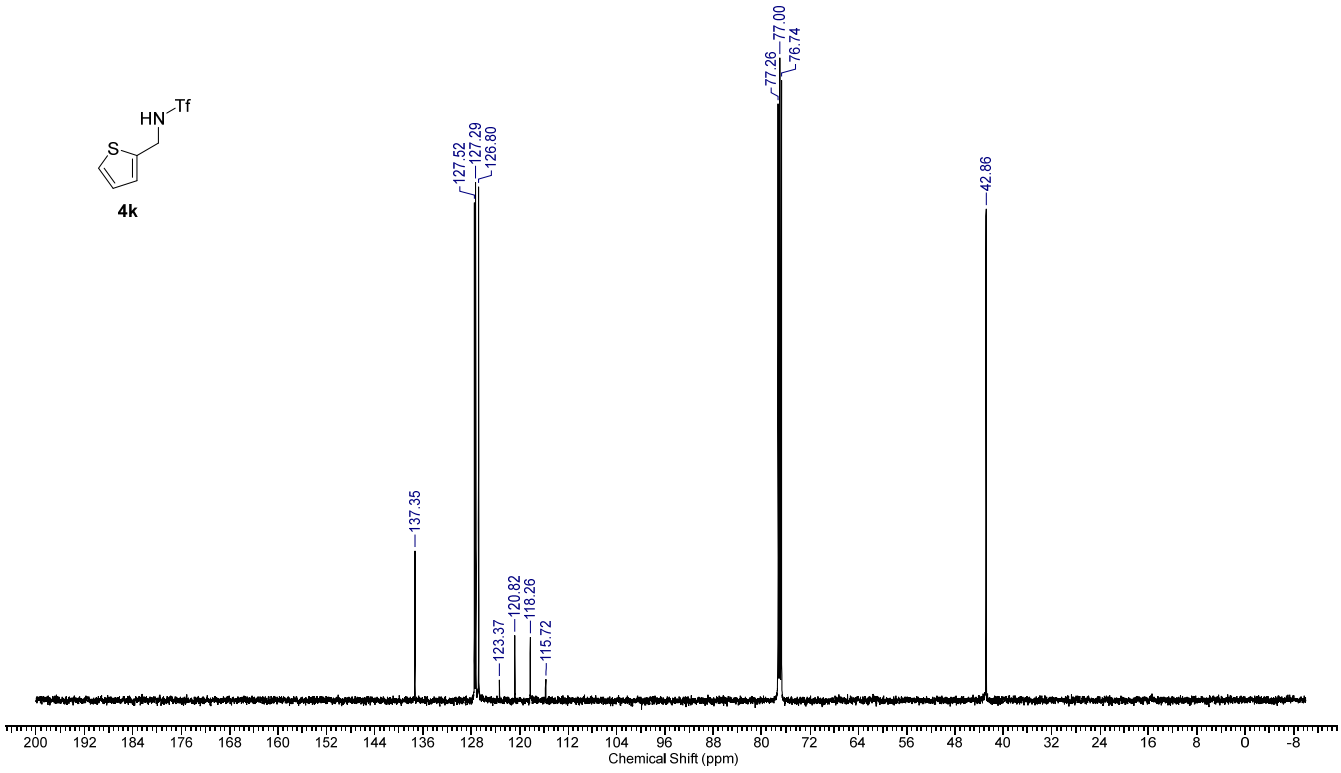
^{13}C NMR (125 MHz, $CDCl_3$) of **4j**



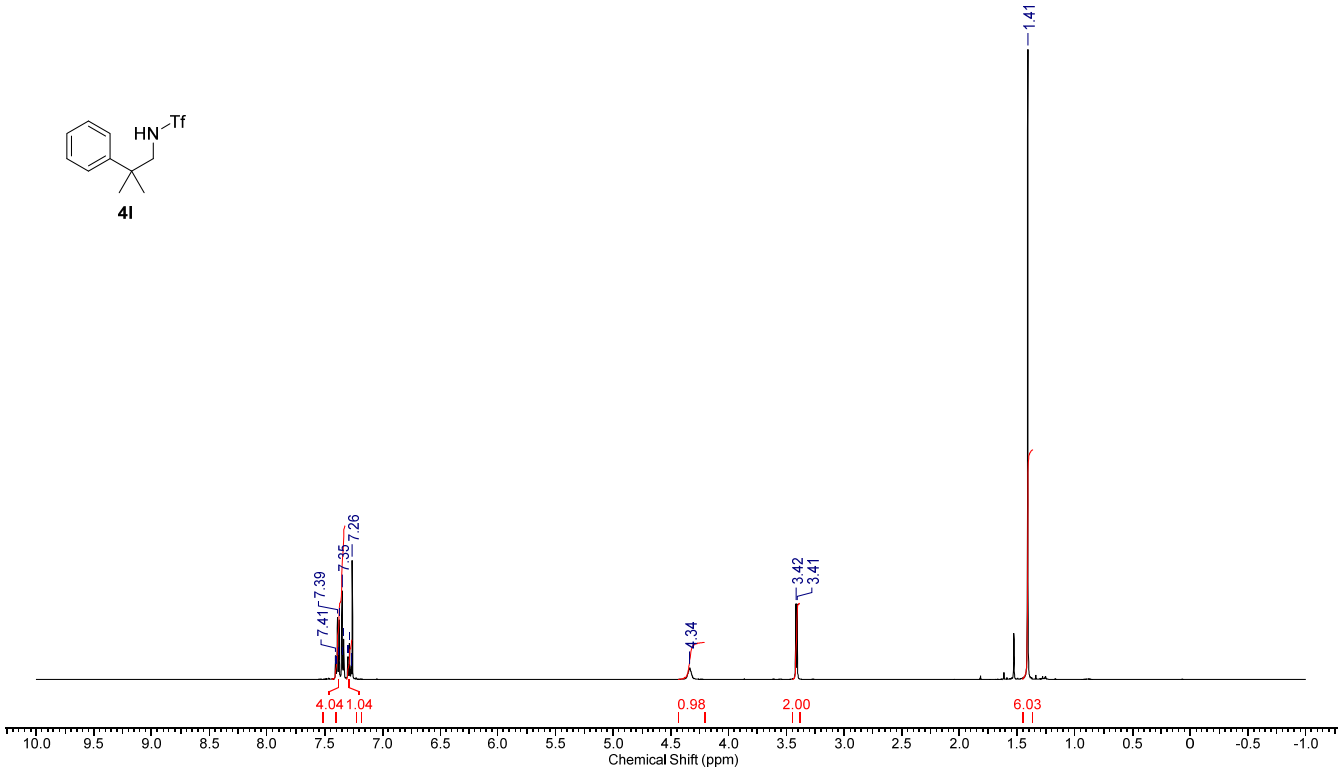
^{1}H NMR (500 MHz, $CDCl_3$) of **4k**



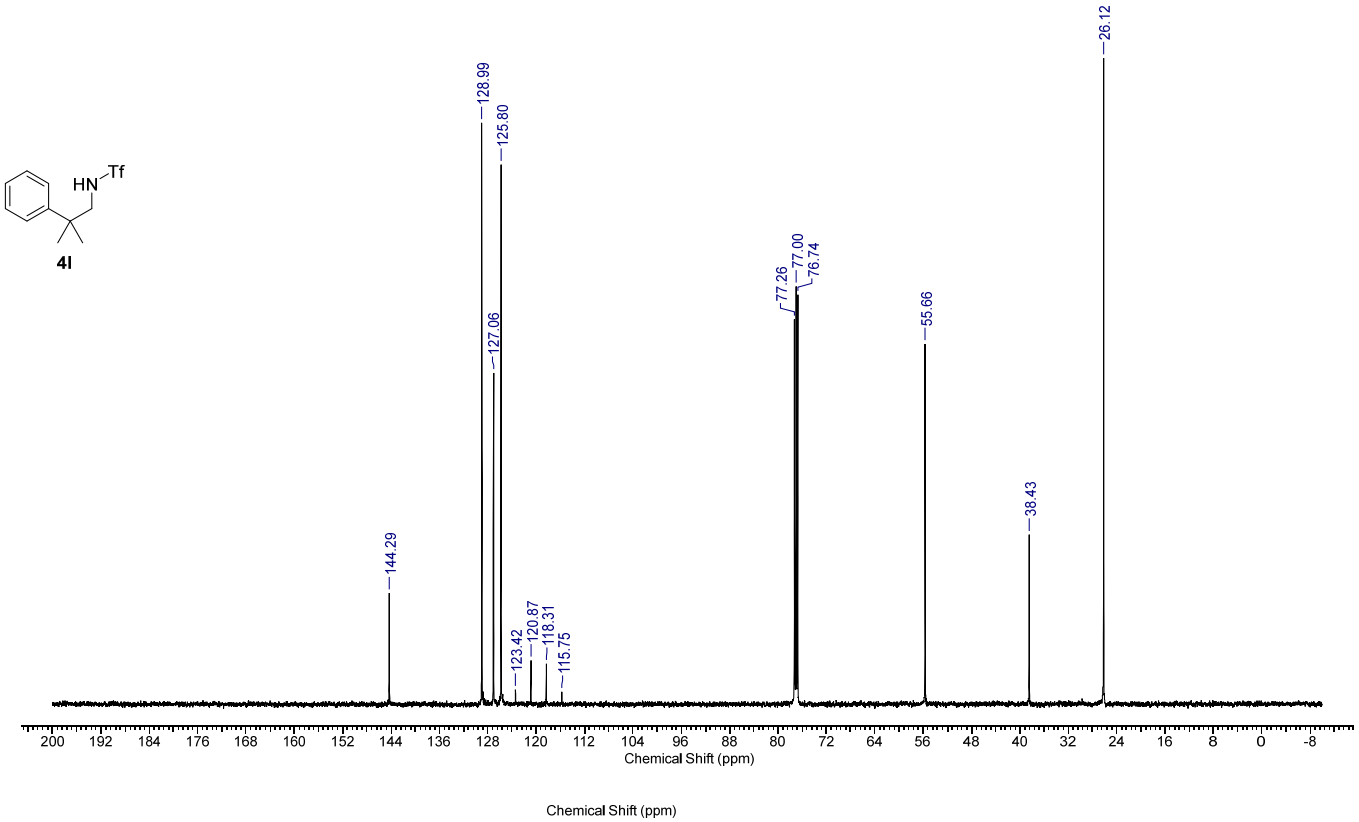
^{13}C NMR (125 MHz, $CDCl_3$) of **4k**



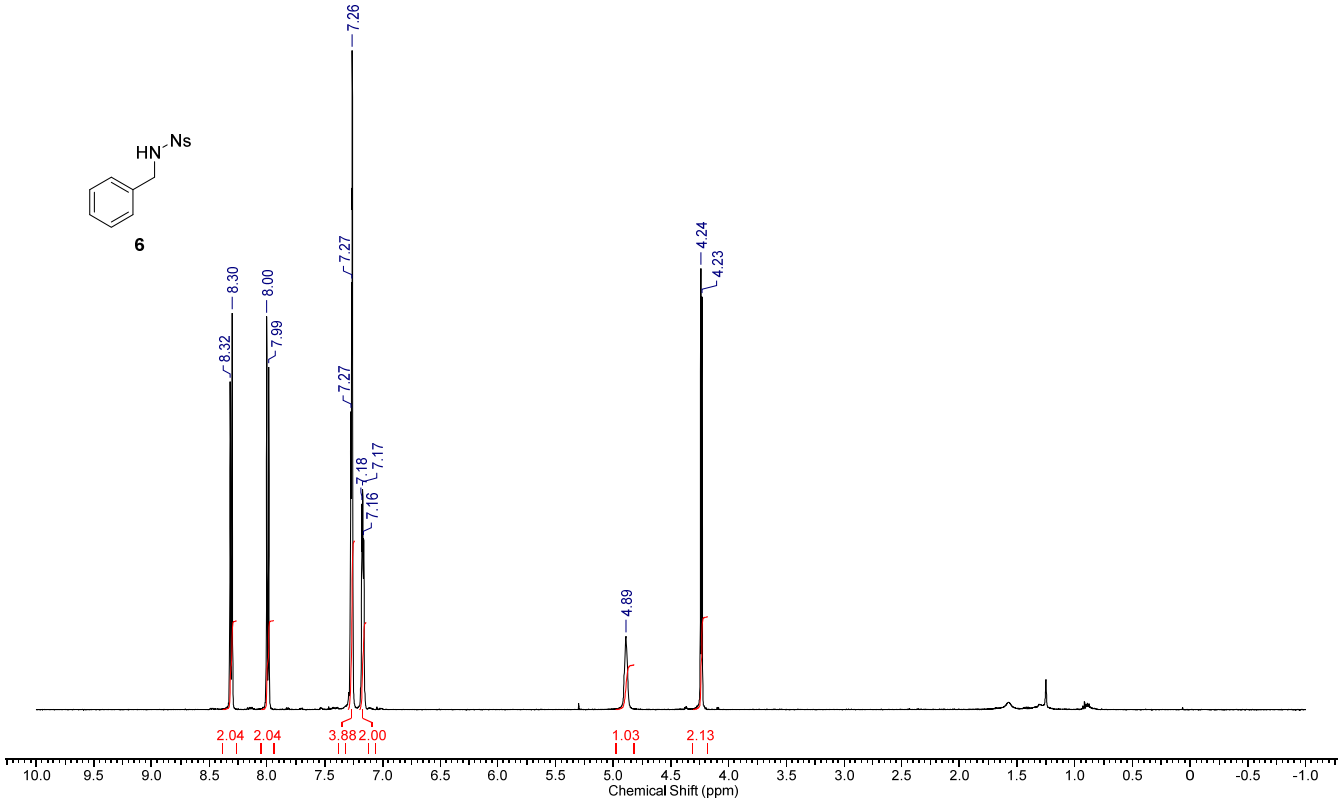
^{1}H NMR (500 MHz, $CDCl_3$) of **4l**



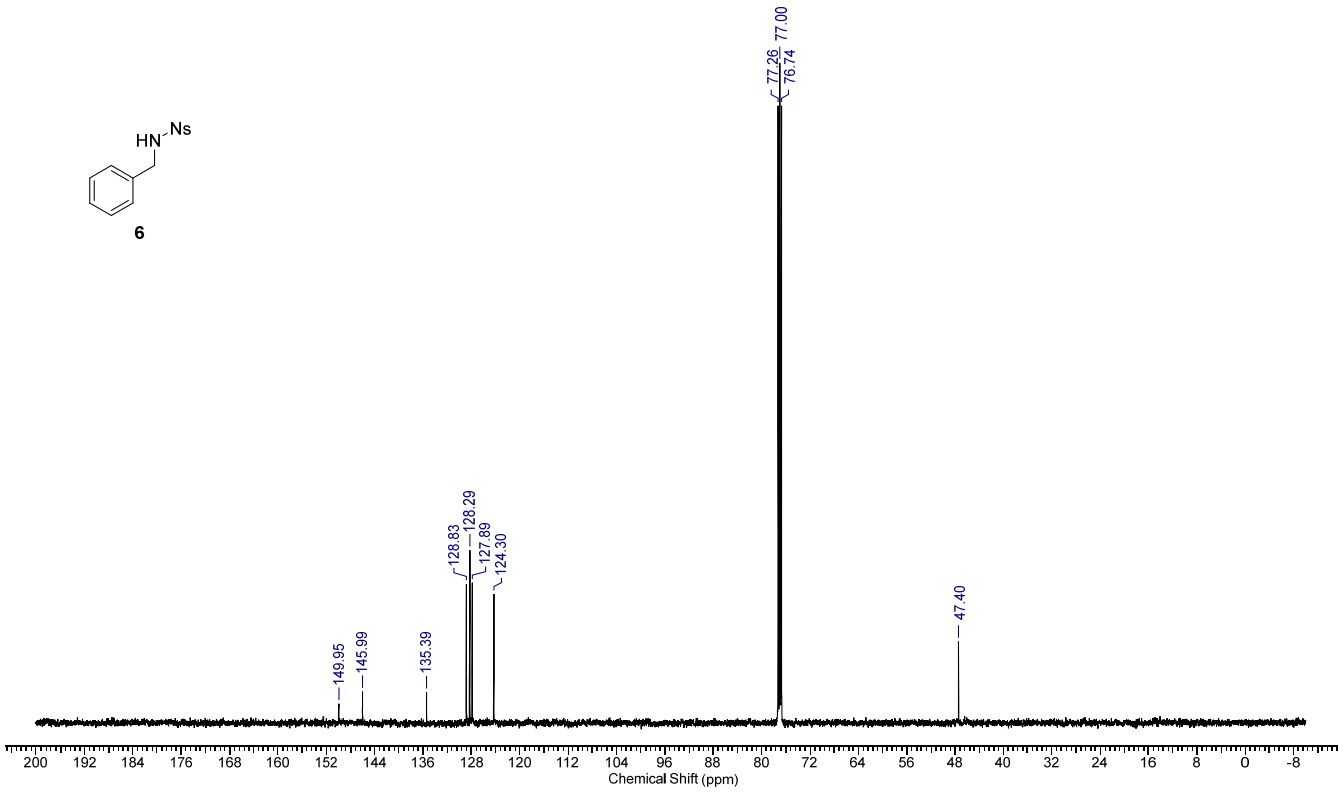
^{13}C NMR (125 MHz, $CDCl_3$) of **4l**



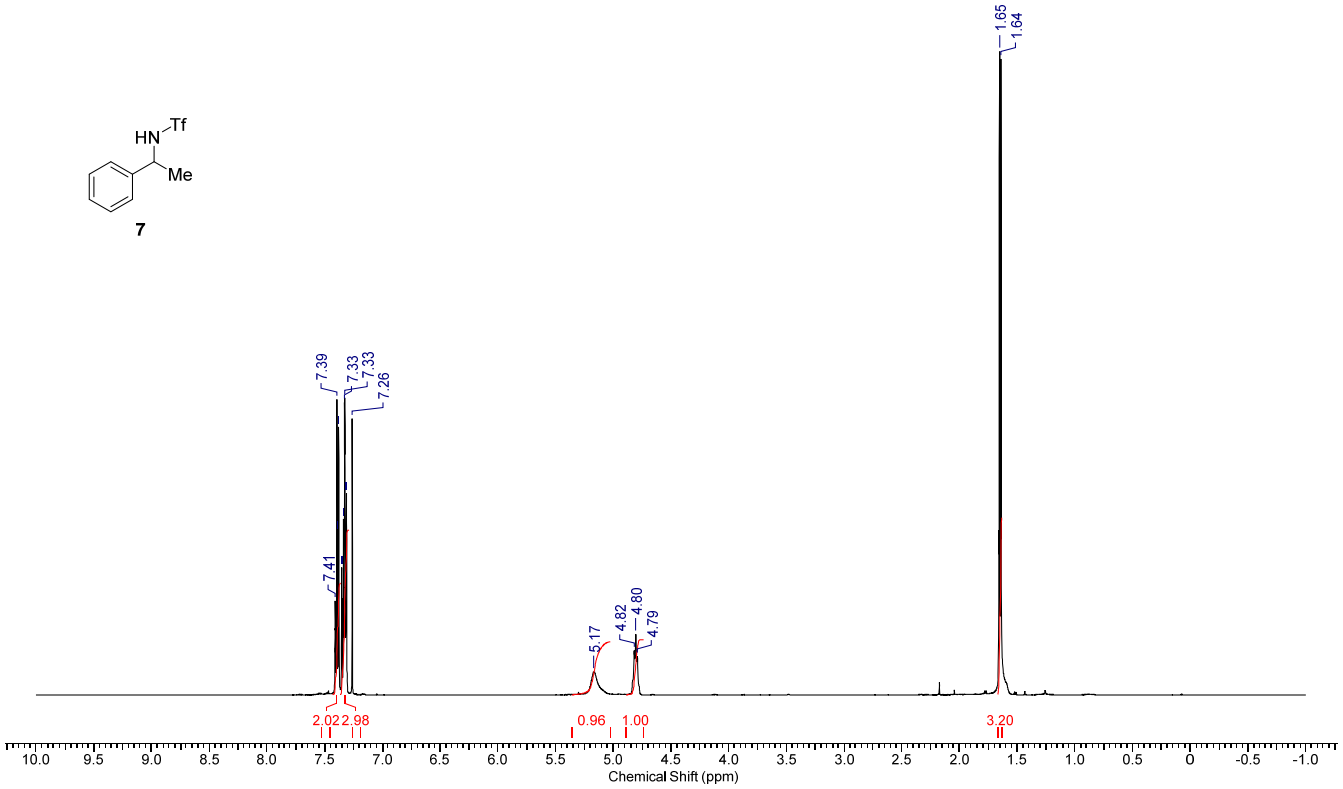
^{1}H NMR (500 MHz, $CDCl_3$) of **6**



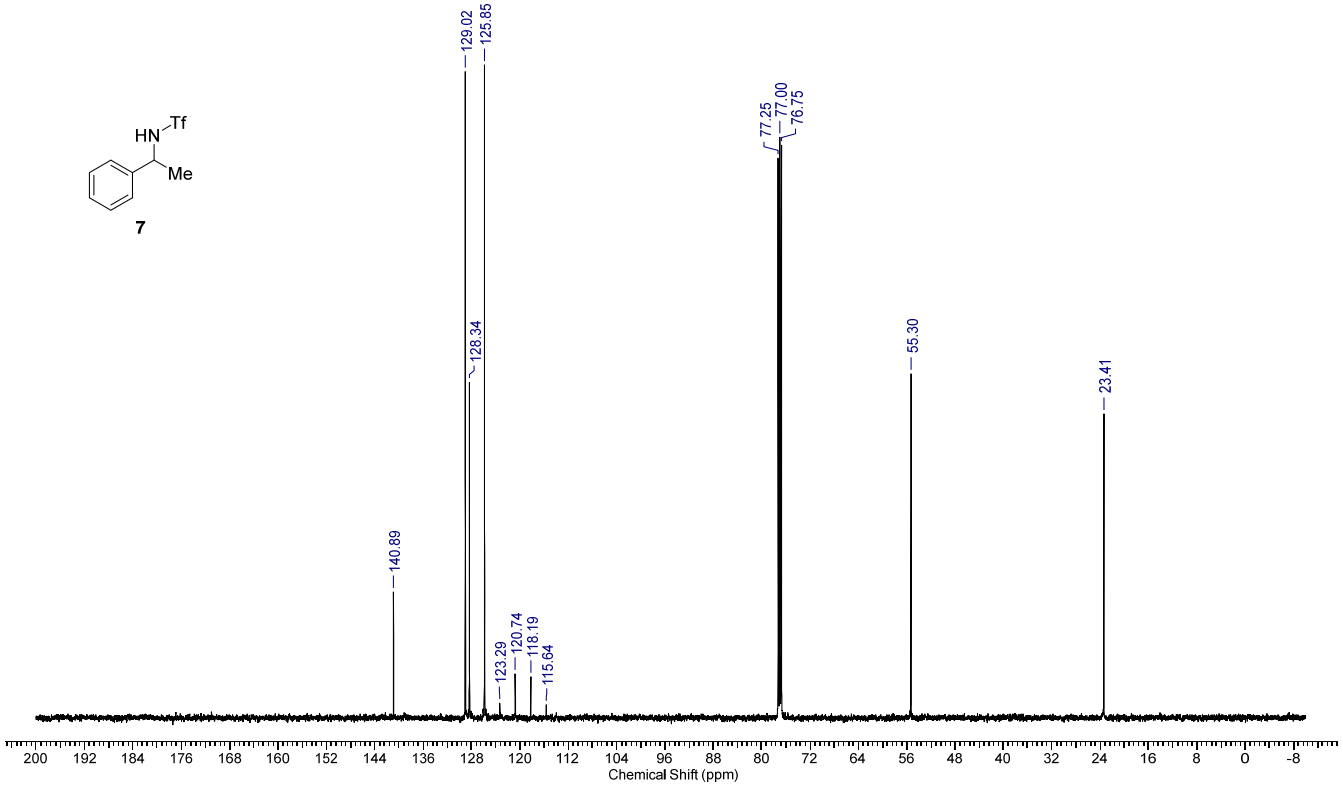
^{13}C NMR (125 MHz, $CDCl_3$) of **6**



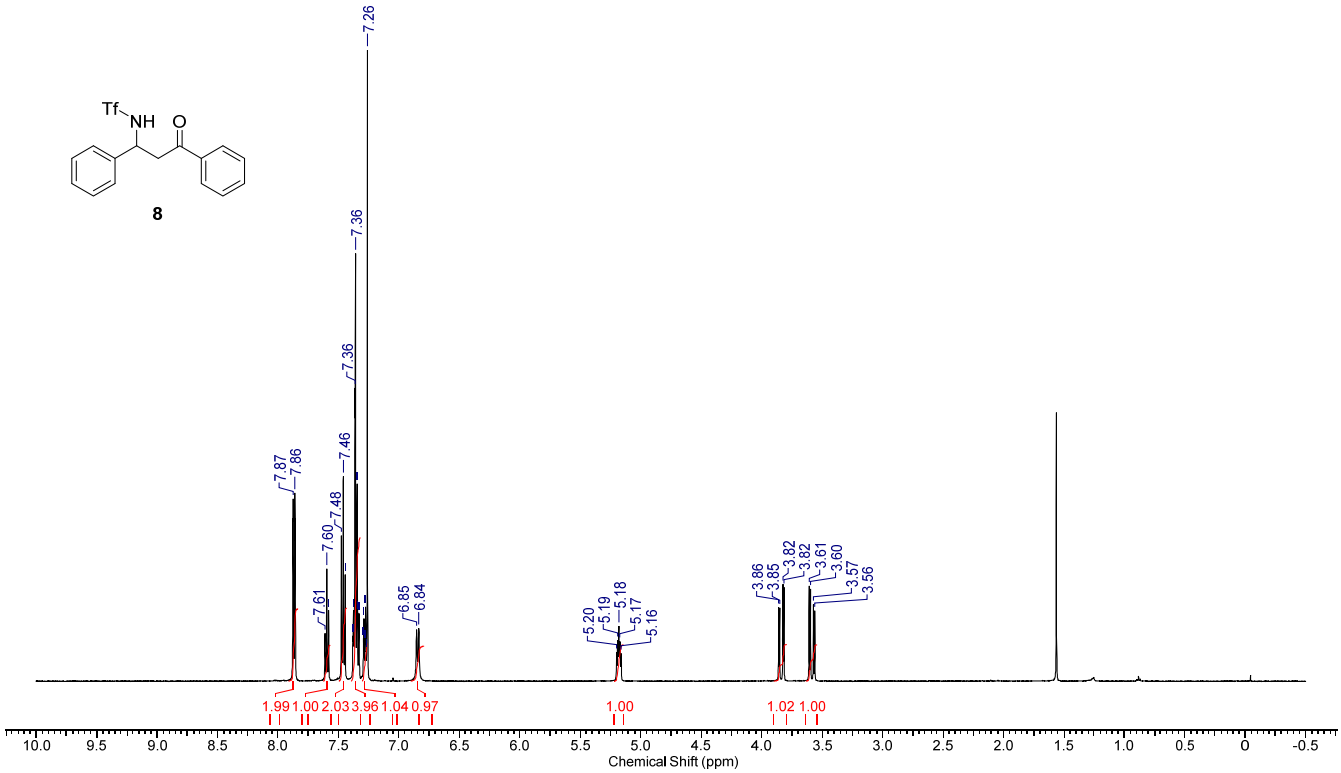
^{1}H NMR (500 MHz, $CDCl_3$) of **7**



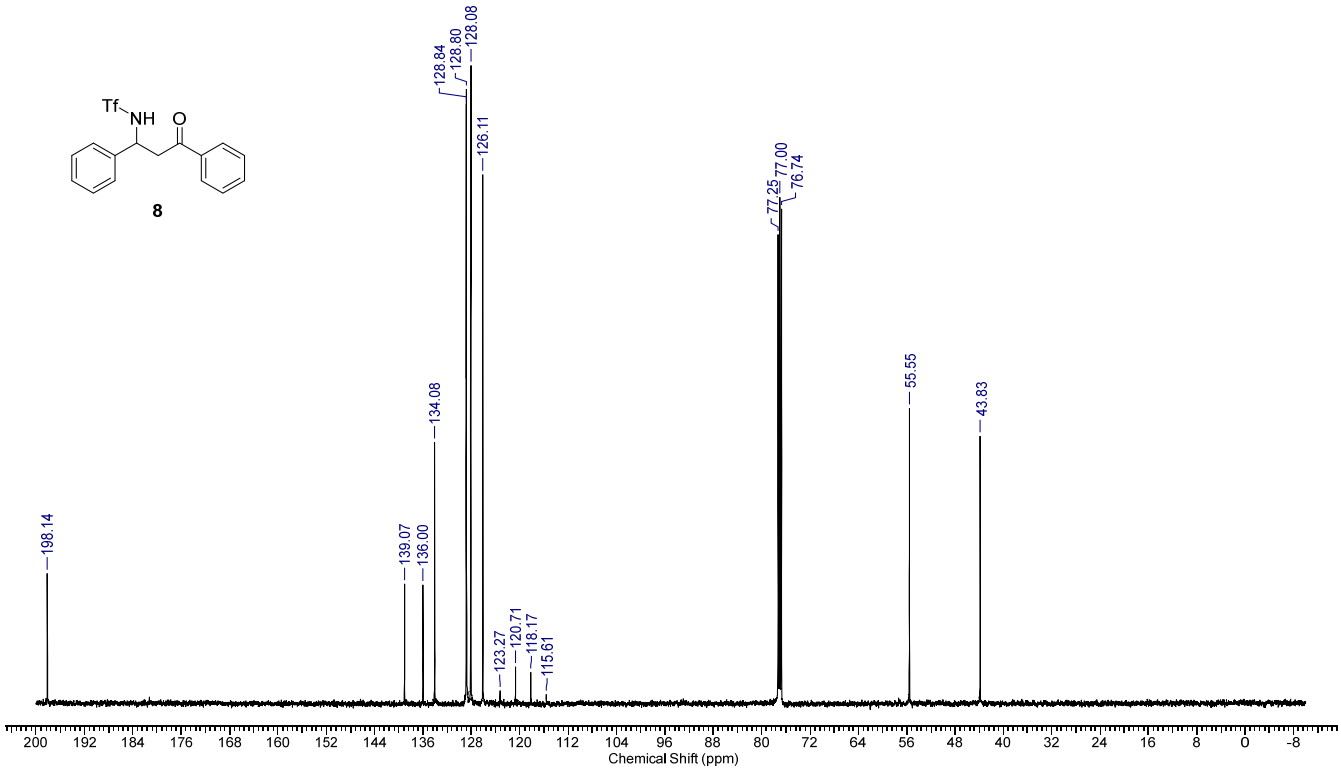
^{13}C NMR (125 MHz, $CDCl_3$) of **7**



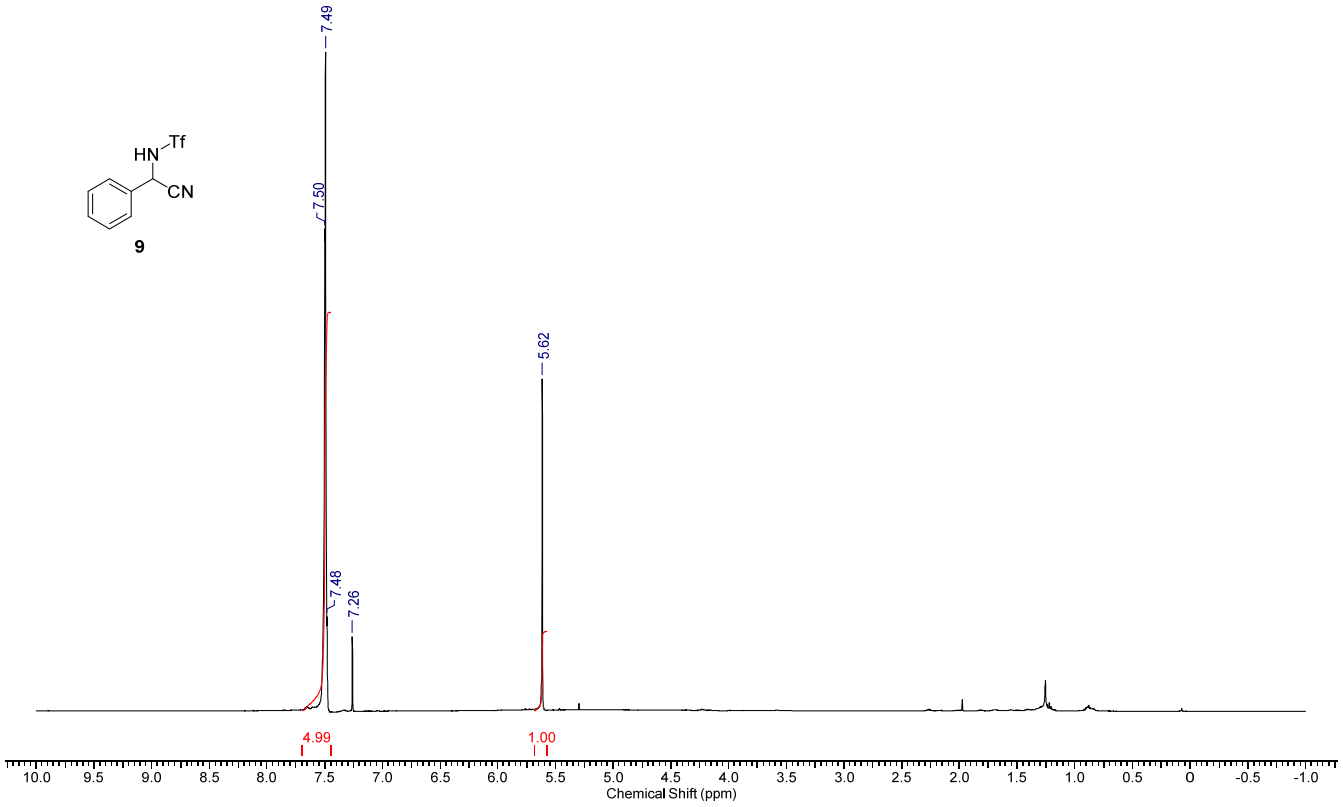
^{1}H NMR (500 MHz, $CDCl_3$) of **8**



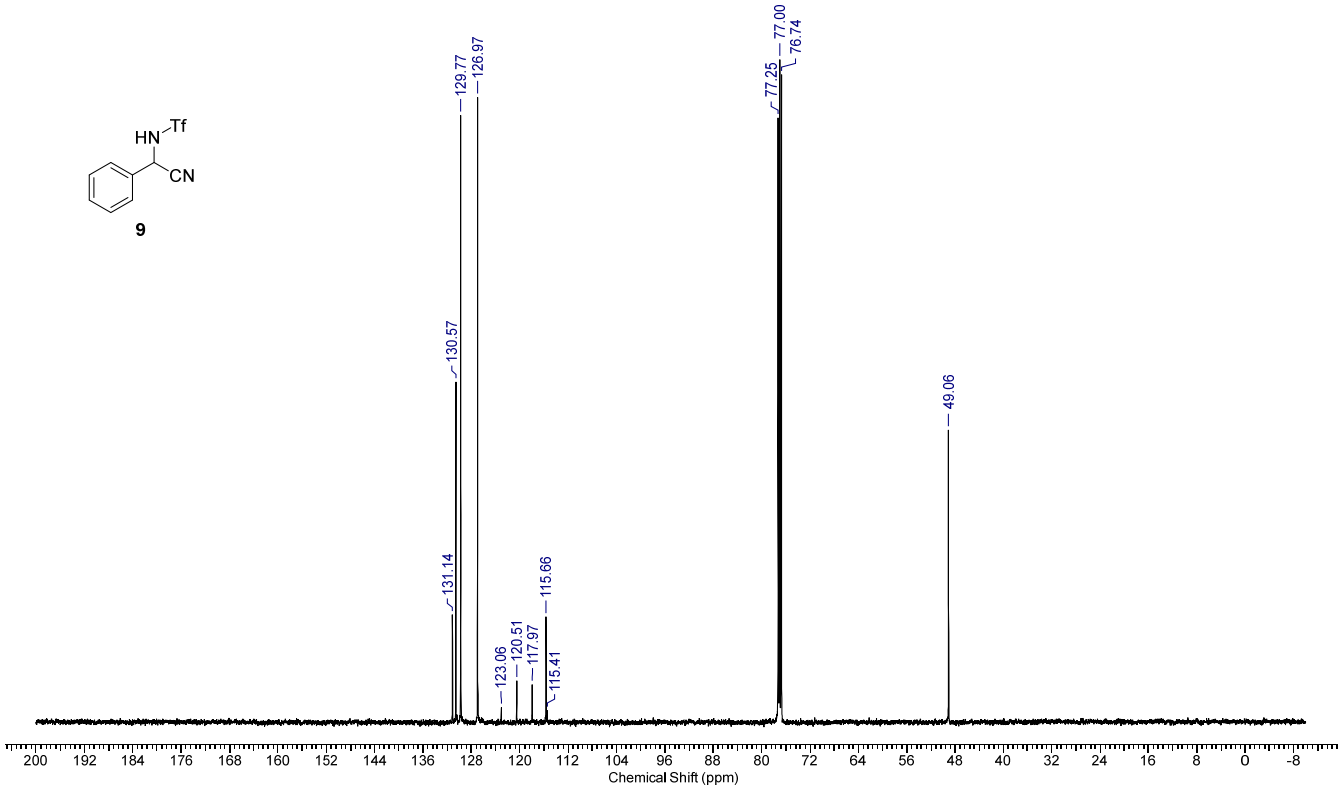
^{13}C NMR (125 MHz, $CDCl_3$) of **8**



^{1}H NMR (500 MHz, $CDCl_3$) of **9**

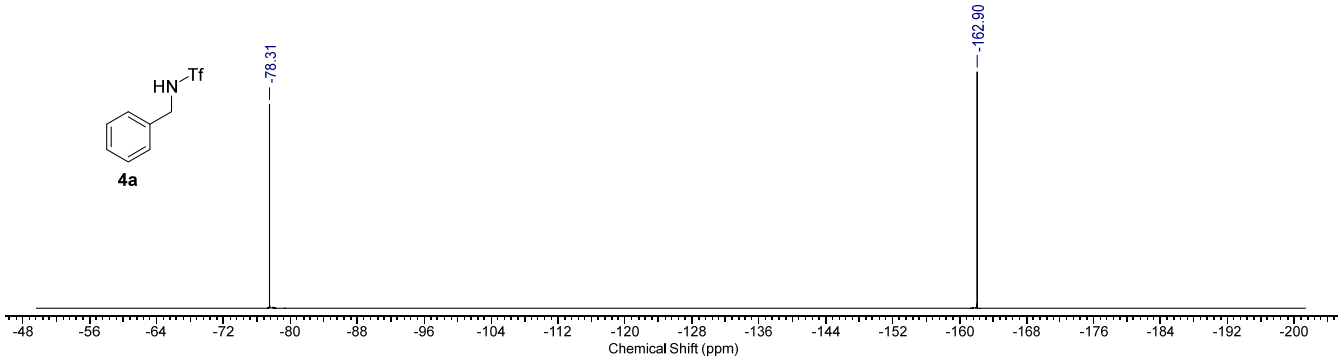


^{13}C NMR (125 MHz, $CDCl_3$) of **9**

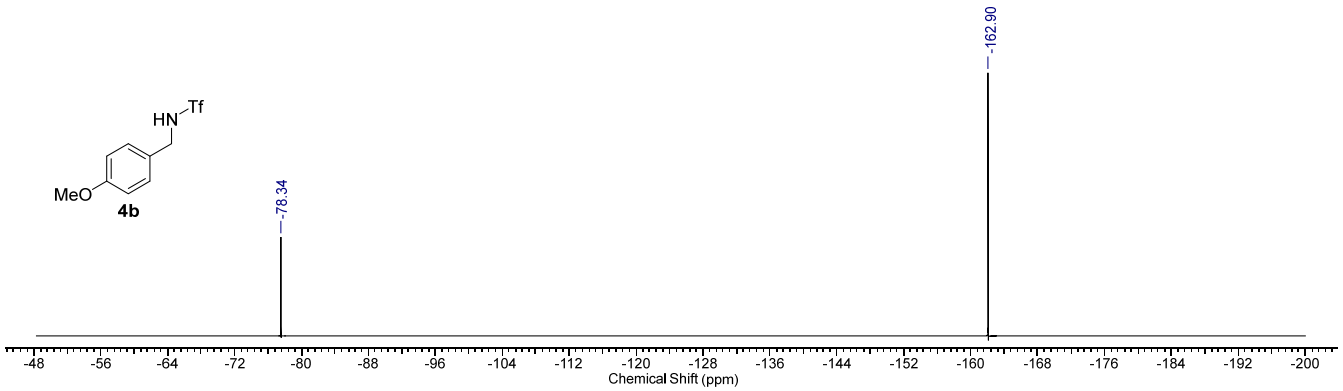


6. ^{19}F NMR Spectra of 4a-4h and 6-9

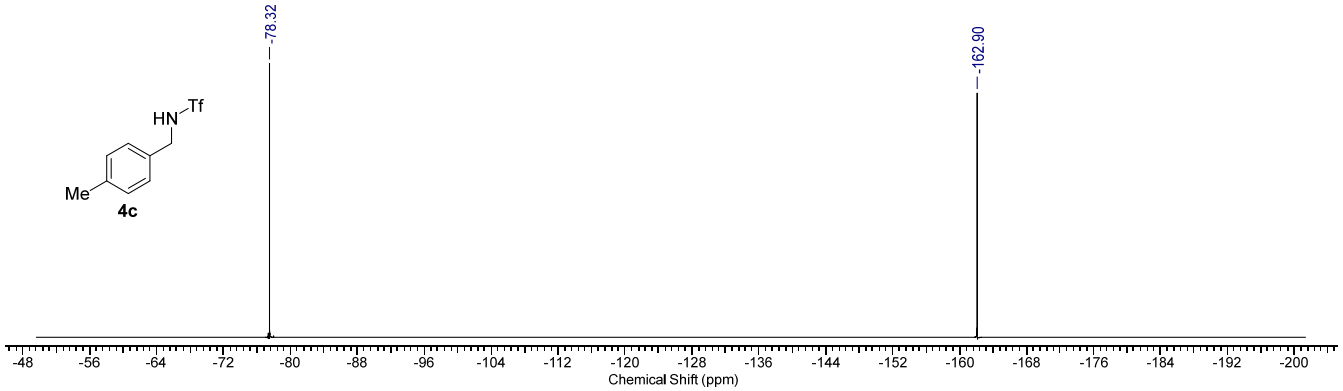
^{19}F NMR (470 MHz, $CDCl_3$) of **4a**



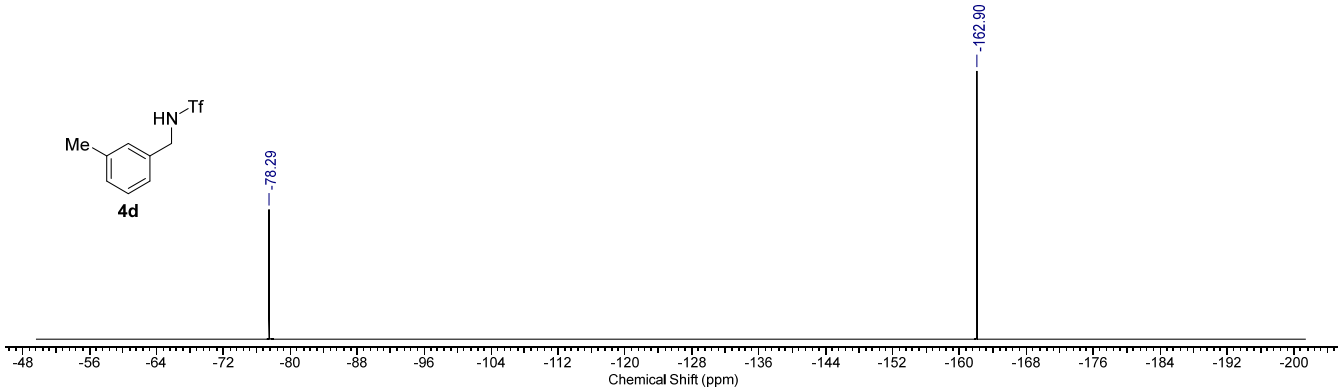
^{19}F NMR (470 MHz, $CDCl_3$) of **4b**



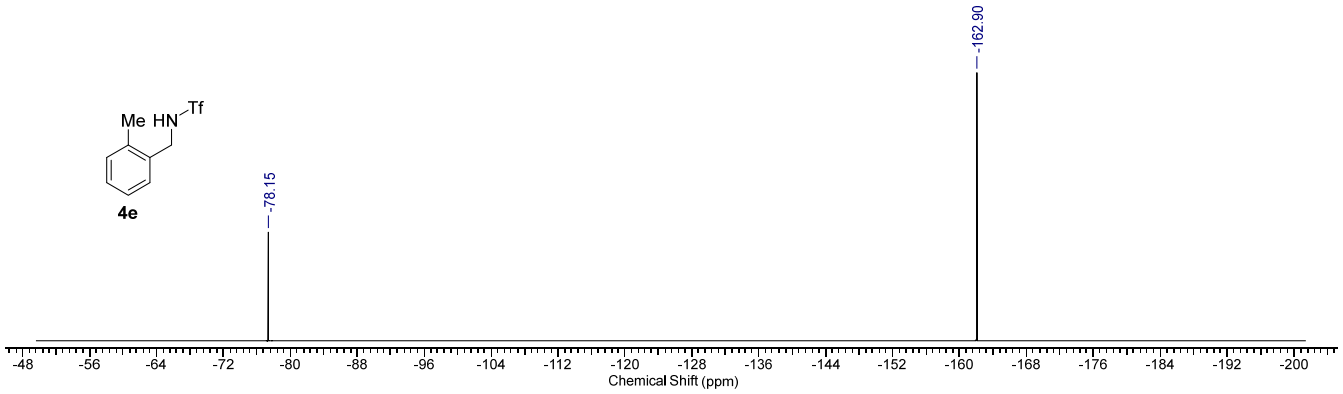
^{19}F NMR (470 MHz, $CDCl_3$) of **4c**



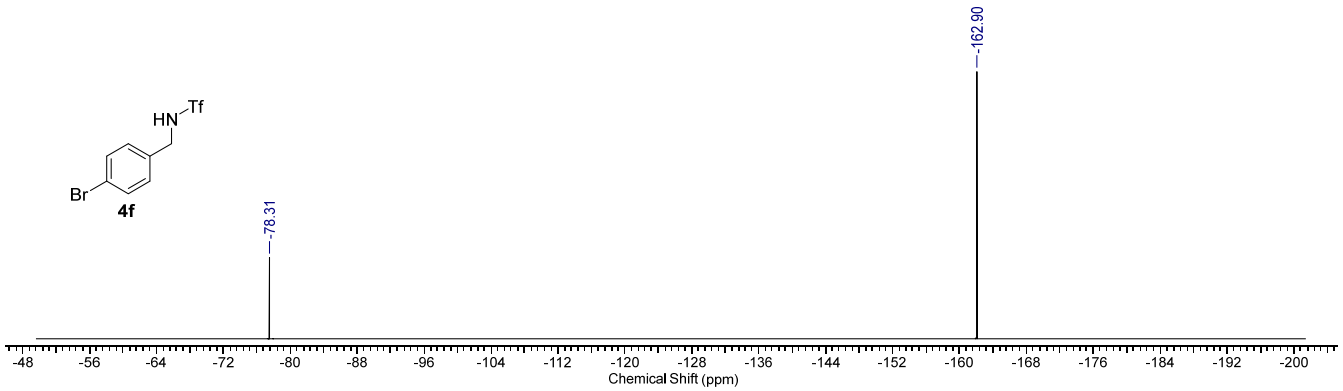
^{19}F NMR (470 MHz, $CDCl_3$) of **4d**



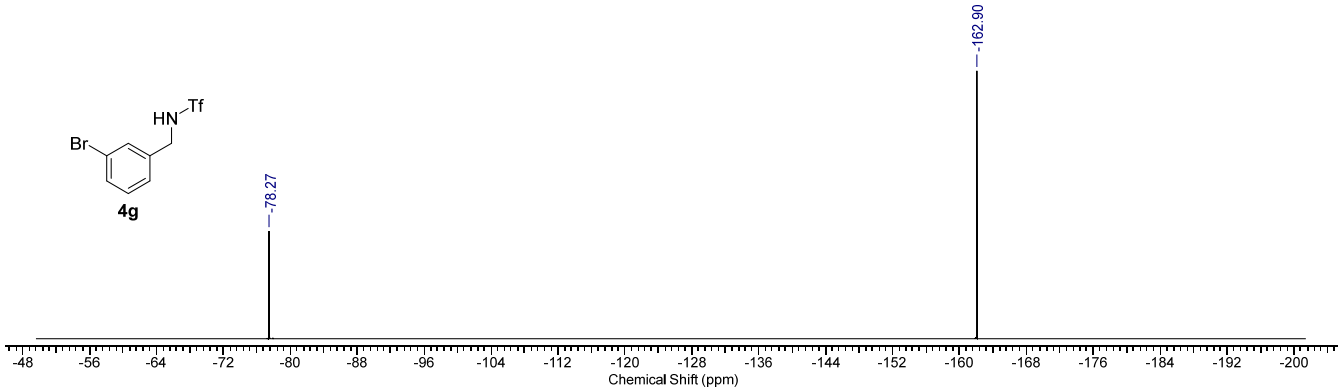
^{19}F NMR (470 MHz, $CDCl_3$) of **4e**



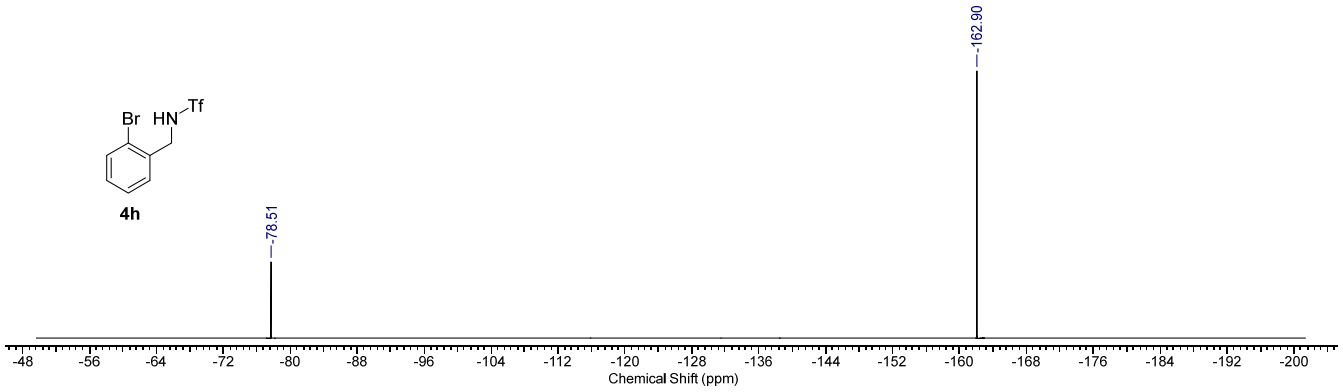
^{19}F NMR (470 MHz, $CDCl_3$) of **4f**



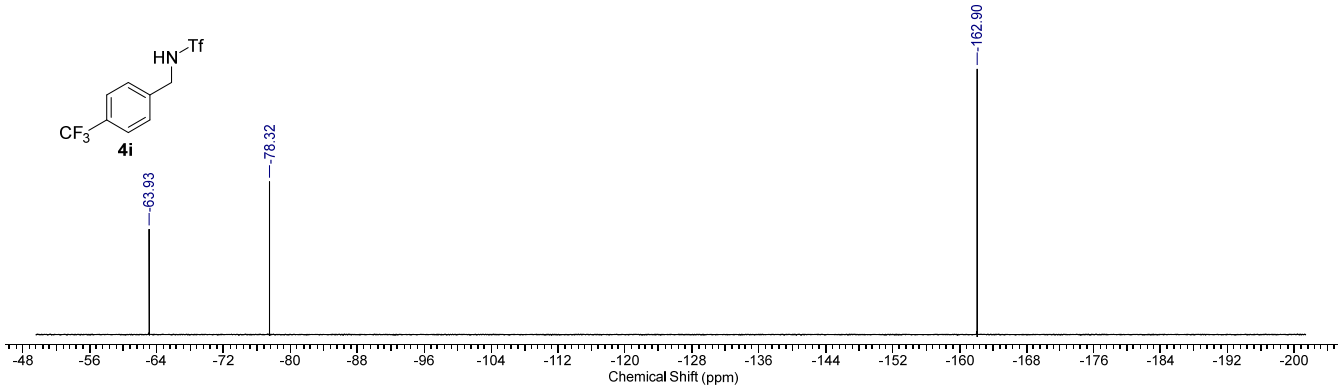
^{19}F NMR (470 MHz, $CDCl_3$) of **4g**



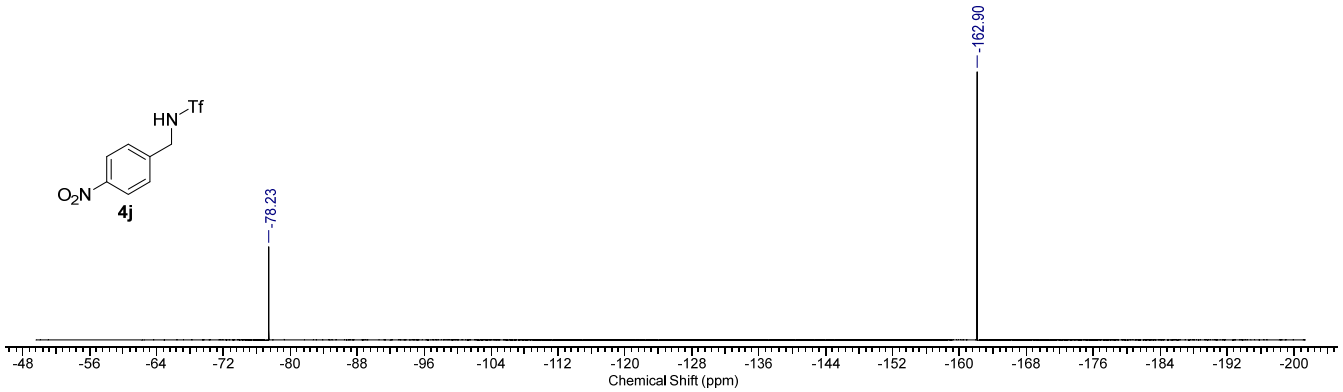
^{19}F NMR (470 MHz, $CDCl_3$) of **4h**



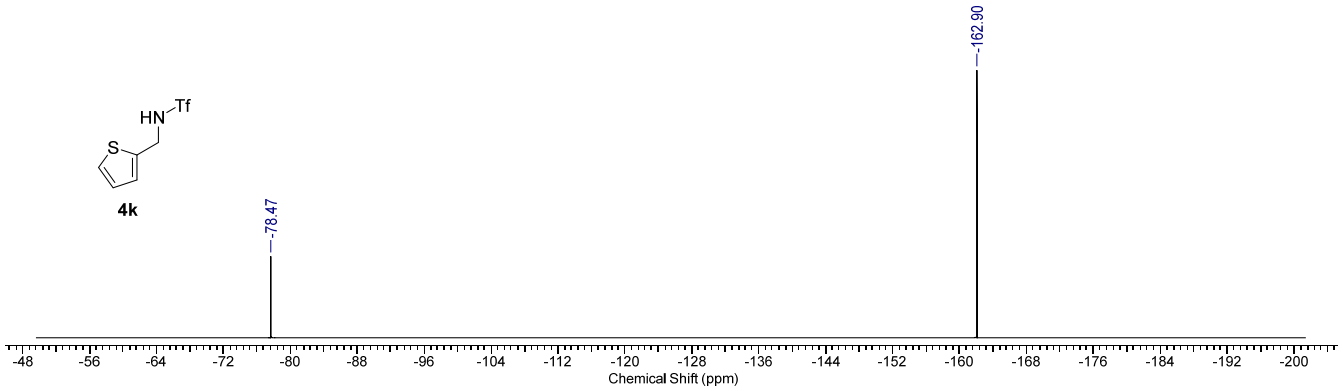
^{19}F NMR (470 MHz, $CDCl_3$) of **4i**



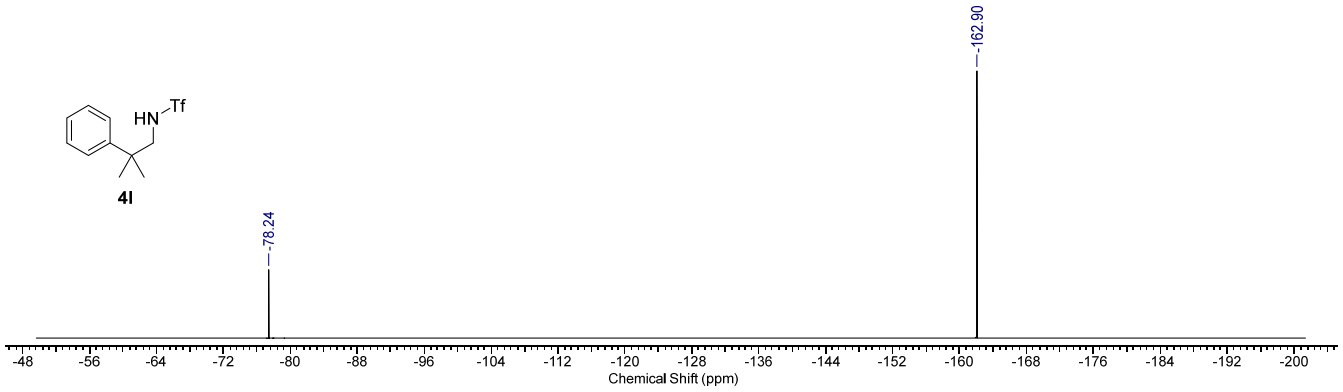
^{19}F NMR (470 MHz, $CDCl_3$) of **4j**



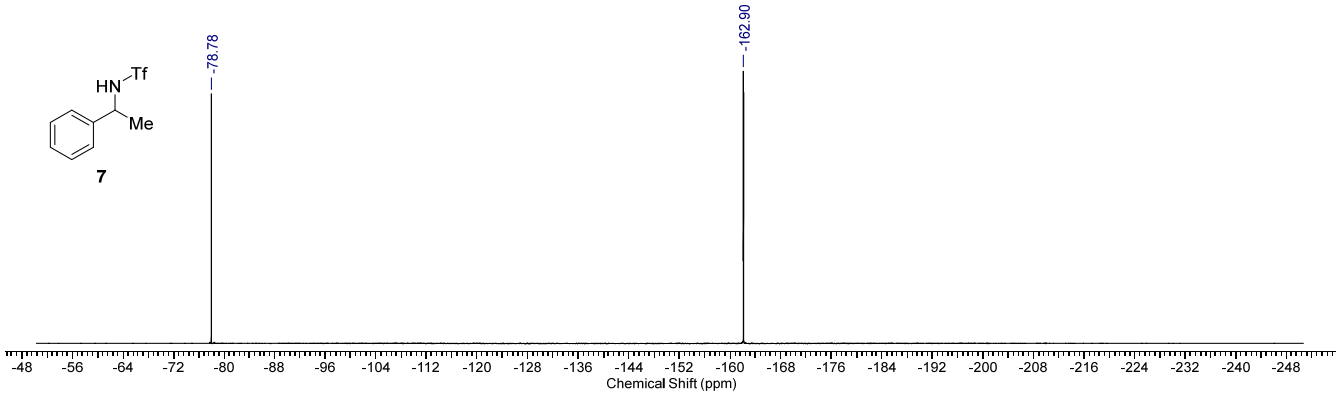
^{19}F NMR (470 MHz, $CDCl_3$) of **4k**



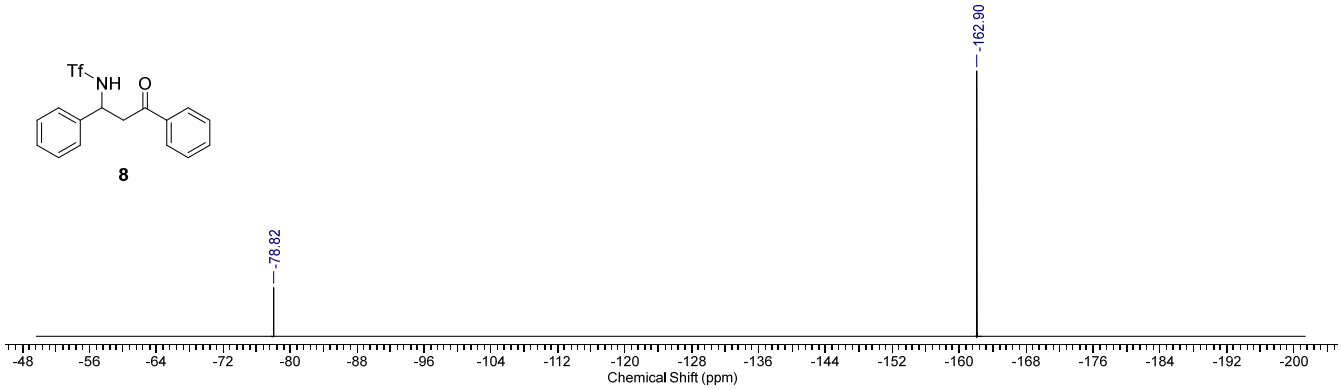
^{19}F NMR (470 MHz, $CDCl_3$) of **4l**



^{19}F NMR (470 MHz, $CDCl_3$) of **7**



^{19}F NMR (470 MHz, $CDCl_3$) of **8**



^{19}F NMR (470 MHz, $CDCl_3$) of **9**