N-Acyl-1,2,3-triazoles – key intermediates in denitrogenative transformations

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General

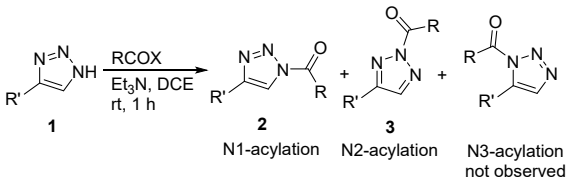
All solvents were dried by activated molecular sieves (3 and 4 Å) and stored under nitrogen. All commercially available chemicals were used as received, unless stated otherwise. Triethylamine was dried with activated 3 Å molecular sieves before use. Starting NH-1,2,3-triazoles were prepared according to procedures published in literature.[1-2] Flash column chromatography was performed using silica gel 60 (0.040–0.063 mm). ^{1}H, ^{13}C and ^{19}F NMR spectra were measured at ambient temperature using 5 mm diameter NMR tubes. ^{13}C NMR spectra were proton decoupled. The chemical shift values (δ) are reported in ppm relative to internal Me_4Si (0 ppm for ^{1}H, ^{13}C NMR) or residual solvents ($CDCl_3$, 7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C NMR) and internal $CFCl_3$ (0 ppm for ^{19}F NMR). Coupling constants (J) are reported in Hertz. For ^{19}F NMR yields, $PhCF_3$ was used as an internal standard which was added directly into the crude reaction mixture. High resolution MS spectra (HRMS) were recorded on a Waters Micromass AutoSpec Ultima or Agilent 7890A GC coupled with Waters GCT Premier orthogonal acceleration time-of-flight (TOF) detector using electron impact (EI) ionization or on an LTQ Orbitrap XL using electrospray ionization (ESI).

Acylation of NH-1,2,3-triazoles

General procedure 1. To a suspension of NH-1,2,3-triazole **1** (0.1 mmol) in dry DCE (0.5 ml) in a 10 ml vial Et_3N (1.1 equiv., 0.11 mmol, 15.6 µl) was added, followed by the addition of acylating agent (1.03-1.10 equiv.). The mixture was stirred at rt for 1 h, then extracted with DCM/H_2O. The aqueous layer was washed with DCM, the combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to give pure acylation product **3**.

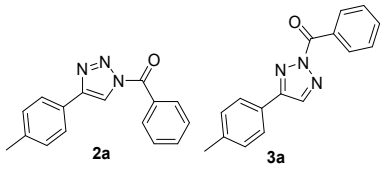
Note: Acylation studies were performed with model triazole 4-(*p*-tolyl)-1,2,3-NH-triazole (**1a**) in DCE. The results of all test experiments for several other substituted triazoles and other applicable solvents are shown in Table S1. Solvent and substituent effects affect the regioselectivity of acylation only slightly (see entries 10-17) compared to the remarkable effects of the nature of the acylating agent.

Table S1.



Entry	R'	RCOX	Solvent	Acylation ratio (NMR), **2**/**3**
1	*p*-Tol	PhCOCl	DCE	14:86
2	*p*-Tol	$(PhCO)_2O$	DCE	8:92
3	*p*-Tol	4-O_2N-C_6H_4COCl	DCE	<1:99
4	*p*-Tol	4-MeO-C_6H_4COCl	DCE	75:25
5	*p*-Tol	2-Cl-C_6H_4COCl	DCE	80:20
6	*p*-Tol	2-Br-C_6H_4COCl	DCE	80:20
7	*p*-Tol	Ac_2O	DCE	5:95
8	*p*-Tol	$(HCF_2CO)_2O$	DCE	<1:99
9	*p*-Tol	$(CF_3CO)_2O$	DCE	<1:99
10	*p*-Tol	$ClCO_2Et$	DCE	45:55
11	*p*-Tol	$ClCO_2Et$	PhMe	47:53
12	*p*-Tol	$ClCO_2Et$	MeCN	40:60
13	*p*-Tol	$ClCO_2Et$	DMF	43:57
14	*p*-Tol	$ClCO_2Et$	*c*-C_6H_{12}	33:67
15	4-MeO-C_6H_4	$ClCO_2Et$	DCE	48:52
16	4-O_2N-C_6H_4	$ClCO_2Et$	DCE	47:53
17	H	$ClCO_2Et$	DCE	61:39

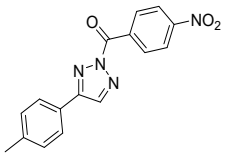
*Phenyl(4-(p-tolyl)-2H-1,2,3-triazol-2-yl)methanone **2a** and phenyl(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)methanone **3a***



N-acyltriazoles **2a**/**3a** were obtained from NH-triazole **1a** (15.9 mg, 0.1 mmol) and benzoyl chloride according to general procedure 1. **2a**/**3a** = 1:6, yield 26 mg (quant.), colorless oil, which solidified upon storage.

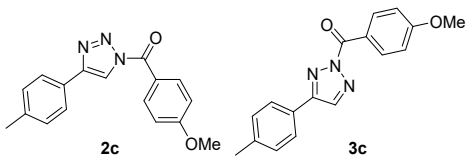
N-acyltriazoles **2a**/**3a** were obtained from NH-triazole **1a** (15.9 mg, 0.1 mmol) and benzoic anhydride according to general procedure 1. N2/N1 = 11:1, yield 26 mg (quant.), colorless oil, which solidified upon storage. Major isomer **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H, H5), 8.20-8.17 (m, 2H), 7.84-7.81 (m, 2H), 7.69-7.65 (m, 1H), 7.58-7.50 (m, 2H), 7.30-7.28 (m, 2H), 2.41 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (C=O), 140.3 (C4), 135.8 (C5-H), 134.3, 133.5 (CH), 131.8 (CH), 129.7 (CH), 128.8, 128.2 (CH), 126.7 (CH), 125.5, 21.4 (Me). Minor isomer **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H, H5), 8.30-8.27 (m, 2H), 7.85-7.83 (m, 2H), 7.73-7.69 (m, 1H), 7.59-7.55 (m, 2H), 7.31-7.29 (m, 2H), 2.42 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8 (C=O), 147.5 (C4), 139.1, 134.4 (CH), 132.2 (CH), 130.0, 129.8 (CH), 128.6 (CH), 126.2, 126.1 (CH), 118.4 (C5-H), 21.4 (Me); HRMS (EI$^+$) *m/z* calcd for $C_{16}H_{13}N_3O$ $[M]^+$: 263.1053, found 263.1044.

*(4-Nitrophenyl)(4-(p-tolyl)-2H-1,2,3-triazol-2-yl)methanone **3b***



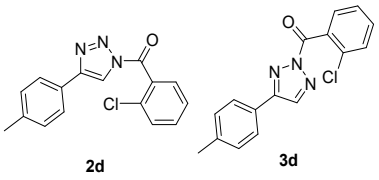
N-acyltriazole **3b** was obtained from NH-triazole **1a** (15.9 mg, 0.1 mmol) and 4-nitrobenzoyl chloride as a single isomer according to general procedure 1. The product was characterized without work-up due to hydrolytic instability; quantitative yield by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.19 (m, 4H), 7.89 (s, 1H, H5), 7.68-7.66 (m, 2H), 7.21-7.19 (m, 2H), 2.35 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4 (C=O), 149.2 (C4), 145.8, 141.8, 138.2, 130.4 (CH), 129.5 (CH), 128.0 (C5-H), 127.1, 125.8 (CH), 123.0 (CH), 21.2 (Me).

*(4-Methoxyphenyl)(4-(p-tolyl)-2H-1,2,3-triazol-2-yl)methanone **2c** and (4-methoxyphenyl)(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)methanone **3c***



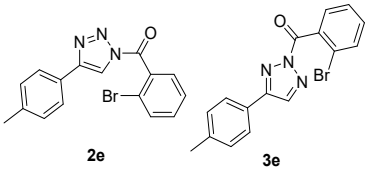
N-acyltriazoles **2c**/**3c** were obtained from NH-triazole **1a** (15.9 mg, 0.1 mmol) and 4-methoxybenzoyl chloride according to general procedure 1. **2c**/**3c** = 3:1, yield 29.5 mg (quant.), colorless oil, which solidified upon storage. Pure sample of N1-isomer **2c** was obtained in 48% yield by recrystallization of the mixture **2c**/**3c** (0.2 mmol) from hexane/EtOAc. Major isomer **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H, H5), 8.39-8.35 (m, 2H), 7.84-7.82 (m, 2H), 7.30-7.28 (m, 2H), 7.06-7.02 (m, 2H), 3.93 (s, 3H, OMe), 2.41 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8 (C-OMe), 163.6 (C=O), 147.2 (C4), 138.9, 134.9 (CH), 129.7 (CH), 126.5, 126.0 (CH), 122.0, 118.7 (C5-H), 114.0 (CH), 55.6 (OMe), 21.3 (Me). Minor isomer **3c** (characteristic signals): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H, H5), 8.09-8.05 (m, 2H), 6.97-6.93 (m, 2H). HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{16}N_3O_2$ $[M+H]^+$: 294.1237, found 294.1237.

*(2-Chlorophenyl)(4-(p-tolyl)-2H-1,2,3-triazol-2-yl)methanone **3d** and (2-chlorophenyl)(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)methanone **2d***



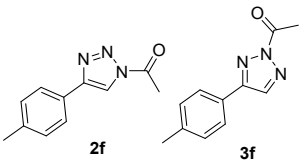
N-acyltriazoles **2d**/**3d** were obtained from NH-triazole **1a** (15.9 mg, 0.1 mmol) and 2-chlorobenzoyl chloride according to general procedure 1. **2d**/**3d** = 4:1, yield 28 mg (94%), colorless oil, which solidified upon storage. Major isomer **2d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H, H5), 7.83-7.81 (m, 2H), 7.65 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.58-7.54 (m, 2H), 7.44 (ddd, *J* = 7.5, 6.0, 2.6 Hz, 1H), 7.30-7.28 (m, 2H), 2.41 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (C=O), 148.3 (C4), 139.3, 133.1 (CH), 132.9, 131.5, 130.7 (CH), 130.4 (CH), 129.6 (CH), 126.6 (CH), 126.2 (CH), 126.1, 116.8 (C5-H), 21.4 (Me). Minor isomer **3d** (characteristic signal): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H, H5); HRMS (EI$^+$) *m/z* calcd for $C_{16}H_{12}ClN_3O$ [M]$^+$: 297.0664, found 297.0663.

*(2-Bromophenyl)(4-(p-tolyl)-2H-1,2,3-triazol-2-yl)methanone **3e** and (2-bromophenyl)(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)methanone **2e***



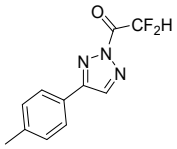
N-acyltriazoles **2e**/**3e** were obtained from NH-triazole **1a** (15.9 mg, 0.1 mmol) and 2-bromobenzoyl chloride according to general procedure 1. **2e**/**3e** = 4:1, yield 33 mg (96%), colorless oil, which solidified upon storage. **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H, H5), 7.82-7.80 (m, 2H), 7.70 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.59-7.57 (m, 1H), 7.50-7.42 (m, 2H), 7.29-7.27 (m, 2H), 2.41 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (C=O), 152.3 (C4), 140.6, 136.8 (C5-H), 134.7, 133.0 (CH), 132.4 (CH), 130.0 (CH), 129.8 (CH), 126.6 (CH), 126.9 (CH), 125.3, 120.6, 21.4 (Me); HRMS (EI$^+$) *m/z* calcd for $C_{16}H_{12}BrN_3O$ [M]$^+$: 341.0158, found 341.0154. **2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H, H5), 7.84-7.82 (m, 2H), 7.73-7.71 (m, 1H), 7.63-7.61 (m, 1H), 7.49-7.46 (m, 2H), 7.30-7.28 (m, 2H), 2.41 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8 (C=O), 148.3 (C4), 139.3, 133.6, 133.4 (CH), 133.1 (CH), 130.6 (CH), 129.7 (CH), 127.1 (CH), 126.2 (CH), 126.0, 120.9, 116.8 (C5-H), 21.4 (Me); HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{12}BrN_3ONa$ [M+Na]$^+$: 364.0056, found 364.0055.

*1-(4-(p-tolyl)-2H-1,2,3-triazol-2-yl)ethan-1-one **3f** and 1-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)ethan-1-one **2f***



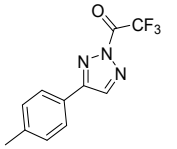
N-acyltriazoles **2f**/**3f** were obtained from NH-triazole **1a** (32.8 mg, 0.2 mmol) and acetic anhydride according to general procedure 1. **3f**/**2f** = 19:1, yield 39.5 mg (98%), colorless oil, which solidified upon storage. Single crystal of **3f** was obtained after recrystallization from $CHCl_3$. Major isomer **3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H, H5), 7.82-7.79 (m, 2H), 7.30-7.28 (m, 2H), 2.86 (s, 3H, COMe), 2.41 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C=O), 151.4 (C4), 140.3, 135.9 (C5-H), 129.8 (CH), 126.7 (CH), 125.6, 22.2 (CO*Me*), 21.4 (Me); Minor isomer **2f** (characteristic signal): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H, H5); HRMS (EI$^+$) *m/z* calcd for $C_{11}H_{11}N_3O$ [M]$^+$: 201.0897, found 201.0890.

2,2-difluoro-1-(4-(p-tolyl)-2H-1,2,3-triazol-2-yl)ethan-1-one ***3g***



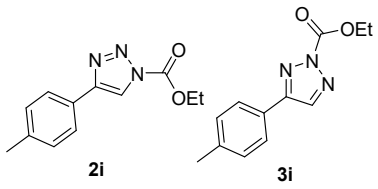
N-acyltriazole **3g** was obtained from NH-triazole **1a** (15.9 mg, 0.1 mmol) and difluoroacetic anhydride as a single isomer according to general procedure 1. Compound was characterized without work-up due to hydrolytic instability; quantitative yield by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H, H5), 7.83-7.81 (m, 2H), 7.33-7.30 (m, 2H), 7.07 (t, *J* = 52.8 Hz, 1H, CF_2H), 2.42 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (t, *J* = 29.6 Hz, C=O), 153.3 (C4), 141.4, 138.1 (C5-H), 129.9 (CH), 127.0 (CH), 124.3, 105.8 (t, *J* = 247.6 Hz), 21.4 (Me); ^{19}F NMR (282 MHz, $CDCl_3$) δ -126.7 (d, *J* = 52.8 Hz); HRMS (APCI$^+$) *m/z* calcd for $C_{11}H_{10}N_3F_2O$ $[M]^+$: 237.0708, found 237.0711.

2,2,2-trifluoro-1-(4-(p-tolyl)-2H-1,2,3-triazol-2-yl)ethan-1-one ***3h***



N-acyltriazole **3h** was obtained from NH-triazole **1a** (15.9 mg, 0.1 mmol) and trifluoroacetic anhydride as a single isomer according to general procedure 1. Compound was characterized without work-up due to hydrolytic instability; quantitative yield by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H, H5), 7.82-7.80 (m, 2H), 7.31-7.28 (m, 2H), 2.40 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (q, *J* = 35.3 Hz, C=O), 153.8, 141.7, 138.9 (C5-H), 130.0 (CH), 127.1 (CH), 124.1, 115.2 (q, *J* = 287.0 Hz, CF_3), 21.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -70.2 ppm; HRMS (APCI$^+$) *m/z* calcd for $C_{11}H_9N_3F_3O$ $[M+H]^+$: 256.0692, found 256.0687.

Ethyl 4-(p-tolyl)-2H-1,2,3-triazole-2-carboxylate ***3i*** *and ethyl 4-(p-tolyl)-1H-1,2,3-triazole-1-carboxylate* ***2i***



2i **3i**

N-acyltriazoles **3i**/**2i** were obtained from NH-triazole **1a** (15.9 mg, 0.1 mmol) and ethyl chloroformate according to general procedure 1. **3i**/**2i** = 1.1:1, yield 22.5 mg (97%), colorless oil, which solidified upon storage. Major isomer **3i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H, H5), 7.79-7.78 (m, 2H), 7.27-7.25 (m, 2H), 4.63 (q, *J* = 7.1 Hz, 2H, CH_2), 2.39 (s, 3H, Me), 1.52 (t, *J* = 7.1 Hz, 3H, CH_2CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 147.5, 140.2, 135.7 (C5-H), 129.7 (CH), 126.7 (CH), 125.5, 65.7 (CH_2), 21.3 (Me), 14.2 (CH_2CH_3); Minor isomer **2i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H, H5), 7.77-7.75 (m, 2H), 7.27-7.25 (m, 2H), 4.62 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H, Me), 1.52 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.6, 139.0, 129.6 (CH), 126.2, 126.0 (CH), 118.6 (C5-H), 65.8 (CH_2), 21.3 (Me), 14.1 (CH_2CH_3); HRMS (EI$^+$) *m/z* calcd for $C_{12}H_{13}N_3O_2$ $[M]^+$: 231.1002, found 231.0998.

Synthesis of pure N2-acyltriazole 3e from NH-triazole

Preparation of (2-bromophenyl)(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)methanone ***3e***

To a suspension of 4-(*p*-tolyl)-NH-1,2,3-triazole **1a** (159 mg, 1 mmol) in dry DCE (5 ml) in a 10 ml vial Et_3N (1.03 equiv., 1.03 mmol, 143 µl) was added, followed by the addition of 2-bromobenzoyl chloride (1.03 equiv., 1.03 mmol, 131 µl). The resulting mixture was stirred at rt for 1 h, then poured into DCM/H_2O (50 + 50 ml). The aqueous layer was extracted with DCM (50 ml), the combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was redissolved in cyclohexane/EtOAc mixture (5:1) and cyclohexane was carefully added to the top. After standing at rt for 3 days colorless crystals of pure **3e** (265 mg, 77%) precipitated, which were collected by filtration and dried.

Confirmation of N-acyltriazole structures

Structures of the obtained N1- and N2-acyltriazoles were determined by analysis of H,N-HMBC spectra and by comparison of DFT calculated ^{15}N chemical shifts and $J_{H,N}$ couplings. Model compound depicted in Figure S1 was used for calculation. Geometry optimization was performed for two orientations of fluoroacyl (difluoromethylcarbonyl or trifluoromethylcarbonyl) group at B3LYP/6-31G* level of theory and NMR parameters (chemical shifts and *J*-couplings) were calculated at B3LYP/6-311++G** level of theory. Results of DFT calculations are shown in Figure S1.

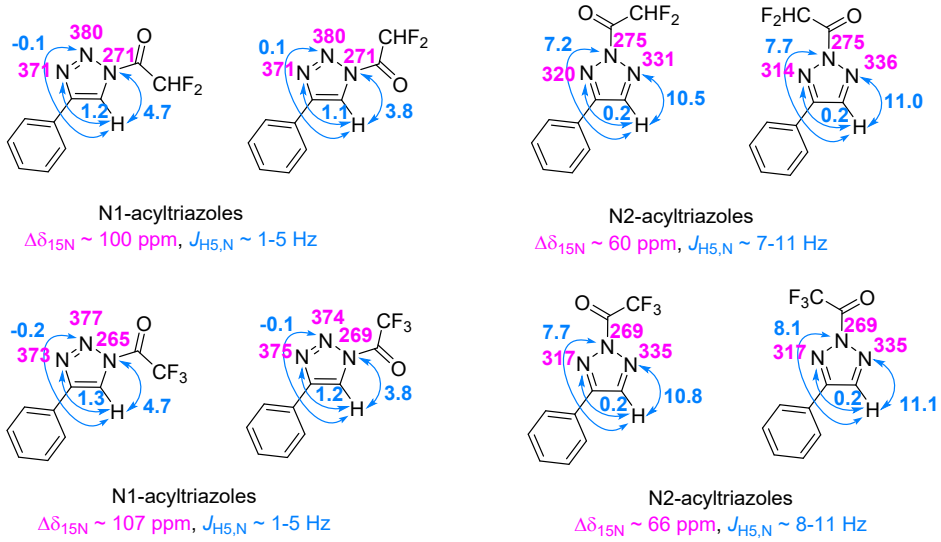


Figure S1. DFT calculated values of δ_{15N} and $J_{H5,N}$ for model compounds.

We observed good correlation of predicted and experimental NMR parameters, which is illustrated by experimental H,N-HMBC spectrum of a mixture of **3e** and **2e** (Figure S2). The same trend also fits for other compounds.

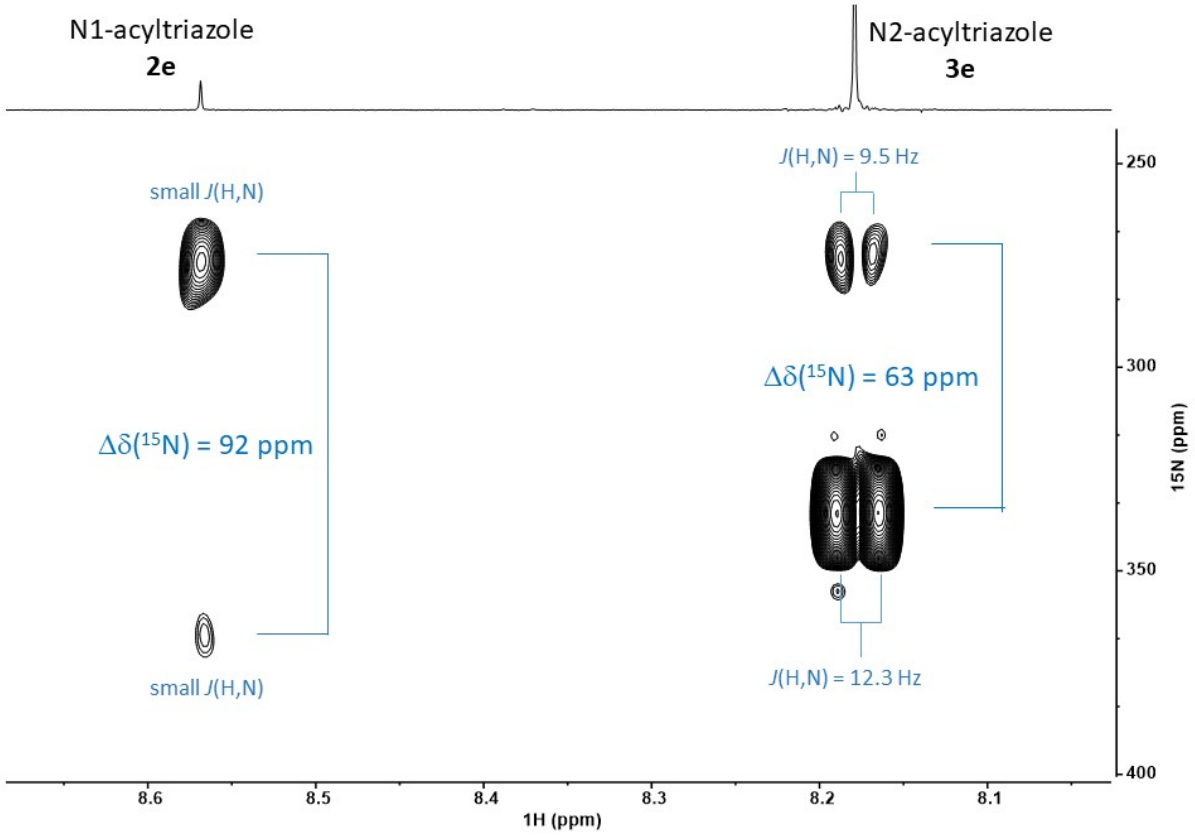
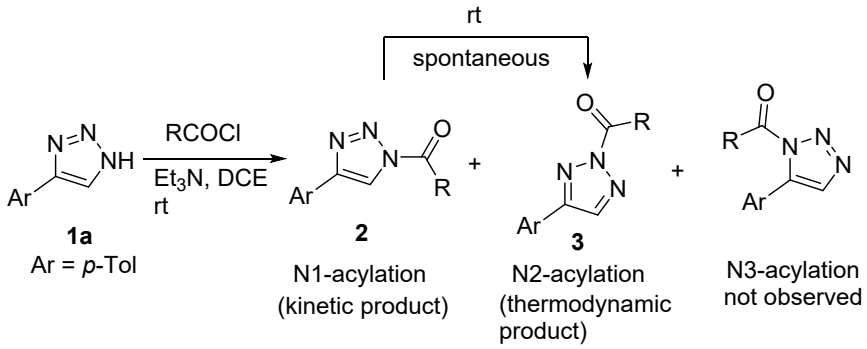


Figure S2. H,N-HMBC spectrum of **3e** contaminated with **2e** (H5-region shown only).

Study of N1 to N2 interconversion of N-acyltriazole isomers

For the N1/N2 acyltriazoles **2c**/**3c** and **2e**/**3e**, where N1-isomer was found to be major under standard conditions (general procedure 1), it was possible to monitor the process of N1 to N2-acyltriazole by ^{1}H NMR of reaction mixtures in time (Table S2).

Table S2.



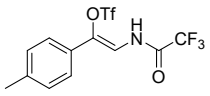
2, **3**	R	Time	**2**/**3** ratio
2c, **3c**	4-MeO-C_6H_4	2 min	76:24
2c, **3c**	4-MeO-C_6H_4	18 h	68:32
2c, **3c**	4-MeO-C_6H_4	40 h	50:50
2c, **3c**	4-MeO-C_6H_4	68 h	50:50
2e, **3e**	2-Br-C_6H_4	2 min	82:18
2e, **3e**	2-Br-C_6H_4	1 h	81:19
2e, **3e**	2-Br-C_6H_4	3 h	81:19
2e, **3e**	2-Br-C_6H_4	6 h	81:19
2e, **3e**	2-Br-C_6H_4	21 h	80:20

Reaction conditions: **1a** (0.1 mmol), acyl chloride (0.103 mmol), Et_3N (0.103 mmol), DCE (1 ml), rt.

General procedure 2 for the synthesis of β-trifluoroacetamido triflates 4 from NH-1,2,3-triazoles

To a suspension of NH-1,2,3-triazole **1** (0.3 mmol) in DCE (1 ml) in a 10 ml vial, Et_3N (0.33 mmol, 1.1.equiv., 46 µl) was added, followed by acid anhydride (0.33 mmol, 1.1 equiv.). The mixture was stirred at room temperature for 1 h, then TfOH (1.5-1.8 equiv.) was added and the mixture was heated at 50-80 °C until complete consumption of N-acyltriazole by NMR (3-20 h). The mixture was subjected to column chromatography (silica gel, EtOAc/cyclohexane, 2:98 to 20:80) to give the target β-(trifluoroacetamido)-triflates **4**.

*(Z)-1-(p-tolyl)-2-(2,2,2-trifluoroacetamido)vinyl trifluoromethanesulfonate **4a***

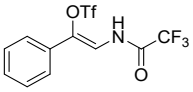


4a was prepared from NH-triazole (48 mg, 0.3 mmol), trifluoroacetic anhydride and TfOH (1.5 equiv.) according to General procedure 2 (60°C, 4 h for the second step). Yield 70 mg (62%), white solid.

For the 1 mmol scale synthesis, **4a** was prepared from NH-triazole (159 mg, 1 mmol) trifluoroacetic anhydride and TfOH (1.5 equiv.) according to General procedure 2 (50°C, 14 h for the second step). Yield 244 mg (65%), white solid.

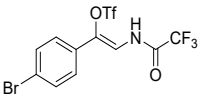
NMR matched previously reported data.[3]

(Z)-1-phenyl-2-(2,2,2-trifluoroacetamido)vinyl trifluoromethanesulfonate ***4b***



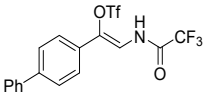
4b was prepared from NH-triazole (45 mg, 0.3 mmol), trifluoroacetic anhydride and TfOH (1.5 equiv.) according to General procedure 2 (70°C, 7 h for the second step). Yield 67 mg (61%), white solid. NMR matched previously reported data.[3]

(Z)-1-(4-bromophenyl)-2-(2,2,2-trifluoroacetamido)vinyl trifluoromethanesulfonate ***4c***



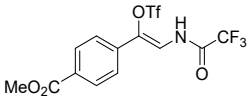
4c was prepared from NH-triazole (67 mg, 0.3 mmol), trifluoroacetic anhydride and TfOH (1.8 equiv.) according to General procedure 2. Yield 81 mg (61%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 10.8 Hz, 1H, NH), 7.60-7.57 (m, 2H), 7.36-7.33 (m, 2H), 7.32 (d, *J* = 10.7 Hz, 1H, =CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3 (q, *J* = 39.6 Hz), 135.4, 132.5, 129.3, 126.5, 124.7, 118.3 (q, *J* = 320.2 Hz), 115.1 (q, *J* = 287.2 Hz), 113.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.8 (s, 3F, OTf), -76.3 (s, 3F, $COCF_3$); HRMS (ESI^-) *m/z* calcd for $C_{11}H_5F_6BrNO_3S$ $[M-H]^-$: 439.9032, found 439.9027.

(Z)-1-([1,1'-biphenyl]-4-yl)-2-(2,2,2-trifluoroacetamido)vinyl trifluoromethanesulfonate ***4d***



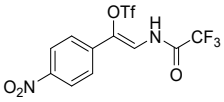
4d was prepared from NH-triazole (22.1 mg, 0.1 mmol), trifluoroacetic anhydride and TfOH (1.5 equiv.) according to General procedure 2. Yield 23 mg (52%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 10.7 Hz, 1H, NH), 7.68-7.66 (m, 2H), 7.62-7.60 (m, 2H), 7.56-7.53 (m, 2H), 7.49-7.44 (m, 2H), 7.42-7.37 (m, 1H), 7.38 (d, *J* = 10.7 Hz, 1H, =CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3 (q, *J* = 39.6 Hz), 143.2, 139.6, 136.3, 129.1, 129.0, 128.1, 127.8, 127.1, 125.5, 118.4 (q, *J* = 320.2 Hz), 115.3 (q, *J* = 287.2 Hz), 112.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.8 (s, 3F, OTf), -76.2 (s, 3F, $COCF_3$) ppm; HRMS (ESI^-) *m/z* calcd for $C_{17}H_{10}F_6NO_4S$ $[M-H]^-$: 438.0240, found 438.0236.

Methyl (Z)-4-(2-(2,2,2-trifluoroacetamido)-1-(((trifluoromethyl)sulfonyl)oxy)vinyl)benzoate ***4e***



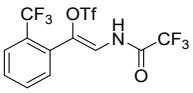
4e was prepared from NH-triazole (60.9 mg, 0.3 mmol), trifluoroacetic anhydride and TfOH (1.8 equiv.) according to General procedure 2 (70°C, 20 h for the second step). Yield 75.5 mg (60%), pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 10.7 Hz, 1H, NH), 8.11-8.08 (m, 2H), 7.56-7.53 (m, 2H), 7.44 (d, *J* = 10.7 Hz, 1H, =CH), 3.92 (s, 3H, CO_2Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 154.4 (q, *J* = 39.8 Hz), 135.2, 134.5, 131.6, 130.4, 124.8, 118.2 (q, *J* = 320.6 Hz), 115.2 (q, *J* = 287.2 Hz), 114.0, 52.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.7 (s, 3F, OTf), -76.2 (s, 3F, $COCF_3$) ppm; HRMS (ESI^-) *m/z* calcd for $C_{13}H_8F_6NO_6S$ $[M-H]^-$: 419.9982, found 419.9978.

(Z)-1-(4-nitrophenyl)-2-(2,2,2-trifluoroacetamido)vinyl trifluoromethanesulfonate ***4f***



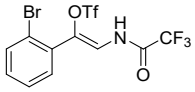
4f was prepared from NH-triazole (57 mg, 0.3 mmol), trifluoroacetic anhydride and TfOH (1.8 equiv.) according to General procedure 2 (80°C, 3 h for the second step). Yield 65 mg (53%), pale yellow solid. NMR matched previously reported data.[3]

(Z)-2-(2,2,2-trifluoroacetamido)-1-(2-(trifluoromethyl)phenyl)vinyl trifluoromethanesulfonate ***4g***



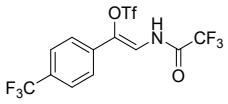
4g was prepared from NH-triazole (67 mg, 0.3 mmol), trifluoroacetic anhydride and TfOH (1.5 equiv.) according to General procedure 2 (70°C, 4 h for the second step). Yield 59.5 mg (46%), white solid. NMR matched previously reported data.[4]

(Z)-1-(2-bromophenyl)-2-(2,2,2-trifluoroacetamido)vinyl trifluoromethanesulfonate ***4h***



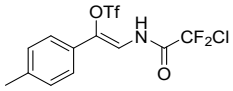
4h was prepared from NH-triazole (67 mg, 0.3 mmol), trifluoroacetic anhydride and TfOH (1.5 equiv.) according to General procedure 2 (70°C, 4 h for the second step). Yield 75 mg (57%), white solid. NMR matched previously reported data.[3]

*(Z)-2-(2,2,2-trifluoroacetamido)-1-(4-(trifluoromethyl)phenyl)vinyl trifluoromethanesulfonate **4i***



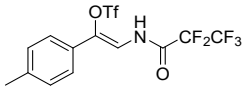
β-Enamido triflate **4i** was prepared from NH-triazole (64 mg, 0.3 mmol), trifluoroacetic anhydride and TfOH (1.8 equiv.) according to General procedure 2 (70°C, 5 h for the second step). Yield 62 mg (48%), white solid. NMR matched previously reported data.[3]

*(Z)-2-(2-chloro-2,2-difluoroacetamido)-1-(p-tolyl)vinyl trifluoromethanesulfonate **4j***



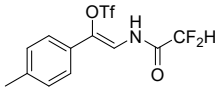
4j was prepared from NH-triazole (48 mg, 0.3 mmol), chlorodifluoroacetic anhydride and TfOH (1.5 equiv.) according to General procedure 2 (60°C, 5 h for the second step). Yield 73 mg (62%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 10.8 Hz, 1H, NH), 7.38-7.36 (m, 2H), 7.25-7.23 (m, 3H), 2.39 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (t, *J* = 32.3 Hz, C=O), 140.7, 136.8, 129.8, 127.6, 125.1, 118.3 (t, *J* = 301.5 Hz), 118.3 (q, *J* = 320.2 Hz), 112.1, 21.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.1 (s, 2F, CF_2Cl), -73.9 (s, 3F, OTf) ppm; HRMS (ESI^-) *m/z* calcd for $C_{12}H_8ClF_5NO_4S$ $[M-H]^-$: 391.9788, found 391.9784.

*(Z)-2-(2,2,3,3,3-pentafluoropropanamido)-1-(p-tolyl)vinyl trifluoromethanesulfonate **4k***



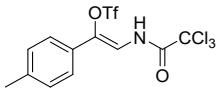
4k was prepared from NH-triazole (48 mg, 0.3 mmol) perfluoropropionic anhydride and TfOH (1.5 equiv.) according to General procedure 2 (60°C, 4 h for the second step). Yield 89 mg (70%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 10.7 Hz, 1H, NH), 7.39-7.36 (m, 2H), 7.28 (dt, *J* = 10.7, 0.9 Hz, 1H), 7.27-7.23 (m, 2H), 2.39 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (t, *J* = 27.1 Hz), 140.8, 136.9, 129.9, 127.5, 125.1, 118.4 (q, *J* = 320.2 Hz), 117.5 (qt, *J* = 286.7, 34.5 Hz), 106.6 (tq, *J* = 266.7, 39.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.0 (s, 3F, OTf), -83.2 (s, 3F, $CF_2\underline{CF_3}$), -123.8 (s, 2F, CF_2) ppm; HRMS (ESI^-) *m/z* calcd for $C_{13}H_8F_8NO_4S$ $[M-H]^-$: 426.0052, found 426.0047.

*(Z)-2-(2,2-difluoroacetamido)-1-(p-tolyl)vinyl trifluoromethanesulfonate **4l***



4l was prepared from NH-triazole (48 mg, 0.3 mmol), difluoroacetic anhydride and TfOH (1.5 equiv.) according to General procedure 2 (70°C, 6 h for the second step). Yield 33 mg (33%), white solid. NMR matches previously reported data.[5]

*(Z)-1-(p-tolyl)-2-(2,2,2-trichloroacetamido)vinyl trifluoromethanesulfonate **4m***

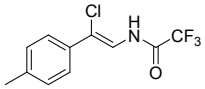


4m was prepared from NH-triazole (48 mg, 0.3 mmol), trichloroacetic anhydride and TfOH (1.5 equiv.) according to General procedure 2 (70°C, 3 h for the second step). Yield 64.5 mg (50%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 10.6 Hz, 1H, NH), 7.39-7.36 (m, 2H), 7.25-7.22 (m, 3H), 2.39 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1 (C=O), 140.5, 136.3, 129.8, 127.8, 125.0, 118.3 (q, *J* = 320.2 Hz), 113.6, 91.2 (CCl_3), 21.3 (Me); ^{19}F NMR (282 MHz, $CDCl_3$) δ -73.9 (s, 3F, OTf) ppm; HRMS (ESI^-) *m/z* calcd for $C_{12}H_8Cl_3F_3NO_4S$ $[M-H]^-$: 423.9197, found 423.9194.

Reaction of N-acyltriazoles with aluminum halides

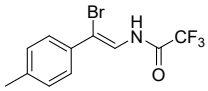
Synthesis of β-haloenamides 5

*(Z)-N-(2-chloro-2-(p-tolyl)vinyl)-2,2,2-trifluoroacetamide **5a***



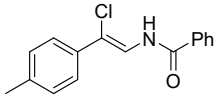
To a suspension of NH-triazole **1a** (0.3 mmol, 47.7 mg) in DCE (1 ml) in a 10 ml vial, Et_3N (0.33 mmol, 1.1.equiv., 46 µl) was added, followed by trifluoroacetic anhydride (0.33 mmol, 1.1 equiv.). The mixture was stirred at room temperature for 1 h, then $AlCl_3$ (0.36 mmol, 1.2 equiv., 48 mg) was added and the resulting mixture was stirred at 50 °C for 4 h. After the reaction was complete (NMR monitoring) it was subjected to column chromatography (silica gel, EtOAc/cyclohexane, 3:97) to give product **5a** (43.5 mg, 55%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (br d, *J* = 10.8 Hz, 1H, NH), 7.47 (d, *J* = 10.8 Hz, 1H, =CH), 7.47-7.43 (m, 2H), 7.22-7.18 (m, 2H), 2.38 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 (q, *J* = 39.2 Hz, **C**OCF_3), 139.5, 131.5, 129.5, 125.9, 121.8, 115.6, 115.5 (q, *J* = 287.2 Hz, CF_3), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.0 (s, 3F); HRMS (EI^+) *m/z* calcd for $C_{11}H_9ClF_3NO$ $[M]^+$: 263.0320, found 263.0323.

*(Z)-N-(2-bromo-2-(p-tolyl)vinyl)-2,2,2-trifluoroacetamide **5b***



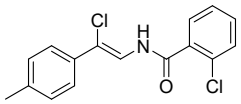
To a suspension of NH-triazole **1a** (0.3 mmol, 47.7 mg) in DCE (1 ml) in a 10 ml vial, Et_3N (0.33 mmol, 1.1.equiv., 46 µl) was added, followed by trifluoroacetic anhydride (0.33 mmol, 1.1 equiv.). The mixture was stirred at room temperature for 1 h. Then $AlBr_3$ (0.3 mmol, 1 equiv., 80 mg) was added and the resulting mixture was stirred at 50 °C for 4 h. After the reaction was complete (NMR monitoring) it was subjected to column chromatography (silica gel, EtOAc/cyclohexane, 3:97) to give product **5b** (32.5 mg, 35%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (br d, *J* = 10.8 Hz, 1H, NH), 7.48 (d, *J* = 10.8 Hz, 1H, =CH), 7.44-7.41 (m, 2H), 7.20-7.17 (m, 2H), 2.38 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2 (q, *J* = 38.9 Hz, **C**OCF_3), 139.5, 133.0, 129.4, 127.1, 121.8, 115.5 (q, *J* = 287.2 Hz, CF_3), 113.7, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.1 (s, 3F); HRMS (EI^+) *m/z* calcd for $C_{11}H_9BrF_3NO$ $[M]^+$: 306.9815, found 306.9817.

*(Z)-N-(2-chloro-2-(p-tolyl)vinyl)benzamide **5c***



To a suspension of NH-triazole **1a** (0.2 mmol, 31.8 mg) in DCE (0.7 ml) in a 10 ml vial, Et_3N (0.22 mmol, 1.1.equiv., 31 µl) was added, followed by benzoyl chloride (0.21 mmol, 1.05 equiv.). The mixture was stirred at room temperature for 1 h. Then $AlCl_3$ (0.2 mmol, 1 equiv., 27 mg) was added and the resulting mixture was stirred at 50 °C for 4 h. After the reaction was complete (NMR monitoring) it was subjected to column chromatography (silica gel, EtOAc/cyclohexane, 5:95) to give product **5c** (30 mg, 55%) as a colorless oil, which solidifies upon storage. NMR matches previously reported data.[6]

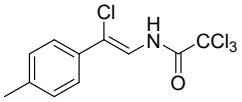
*(Z)-2-chloro-N-(2-chloro-2-(p-tolyl)vinyl)benzamide **5d***



To a suspension of NH-triazole **1a** (0.2 mmol, 31.8 mg) in DCE (0.7 ml) in a 10 ml vial, Et_3N (0.22 mmol, 1.1.equiv., 31 µl) was added, followed by 2-chlorobenzoyl chloride (0.21 mmol, 1.05 equiv.). The mixture was stirred at room temperature for 1 h. Then $AlCl_3$ (0.2 mmol, 1 equiv., 27 mg) was added and the resulting mixture was stirred at 50 °C for 4 h. After the reaction was complete (NMR monitoring) it was subjected to column chromatography (silica gel, EtOAc/cyclohexane, 5:95) to give product **5c** (28.5 mg, 47%) as a colorless oil, which solidifies upon

storage. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 10.7 Hz, 1H, NH), 7.91-7.88 (m, 1H), 7.80 (d, *J* = 10.7 Hz, 1H, =CH), 7.51-7.37 (m, 5H), 7.20-7.18 (m, 2H), 2.37 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 138.4, 132.8, 132.5, 132.4, 131.4, 131.0, 130.7, 129.3, 127.4, 125.6, 118.2, 117.8, 21.1; HRMS (EI$^+$) *m/z* calcd for $C_{16}H_{13}Cl_2NO$ [M]$^+$: 305.0368, found 305.0369.

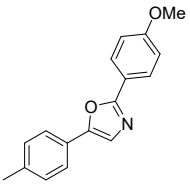
*(Z)-2,2,2-trichloro-N-(2-chloro-2-(p-tolyl)vinyl)acetamide **5e***



To a suspension of NH-triazole **1a** (0.2 mmol, 31.8 mg) in DCE (0.7 ml) in a 10 ml vial, Et_3N (0.22 mmol, 1.1.equiv., 31 µl) was added, followed by trichloroacetyl anhydride (0.21 mmol, 1.05 equiv.). The mixture was stirred at room temperature for 1 h. Then $AlCl_3$ (0.2 mmol, 1 equiv., 27 mg) was added and the resulting mixture was stirred at 50 °C for 4 h. After the reaction was complete (NMR monitoring) it was subjected to column chromatography (silica gel, EtOAc/cyclohexane, 5:95) to give product **5e** (21 mg, 34%) as a colorless oil, which solidifies upon storage. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 10.2 Hz, 1H, NH), 7.50-7.48 (m, 2H), 7.45 (d, *J* = 10.2 Hz, 1H, =CH), 7.24-7.21 (m, 2H), 2.40 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 139.3, 131.8, 129.4, 125.8, 121.2, 117.3, 91.7 (CCl_3), 21.2; HRMS (EI$^+$) *m/z* calcd for $C_{11}H_9Cl_4NO$ [M]$^+$: 310.9433, found 310.9437.

Synthesis of oxazoles 6

Reaction of N1/N2 acyltriazole mixture with $AlCl_3$

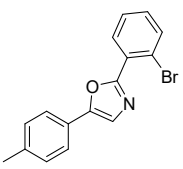


To the suspension of NH-1,2,3-triazole **1a** (0.3 mmol, 47.7 mg) in DCE (4 ml) in a 10 ml vial, Et_3N (0.315 mmol, 1.05 equiv., 44 µl) was added, followed by 4-methoxybenzoyl chloride (0.315 mmol, 1.05 equiv.). The mixture was stirred at room temperature for 1 h giving 71:29 mixture of **2c**/**3c** according to ^{1}H NMR. Then $AlCl_3$ (0.3 mmol, 1 equiv., 40 mg) was added and the resulting mixture was heated under nitrogen atmosphere at 80 °C for 18 h. After the reaction was complete (NMR monitoring) it was evaporated under reduced pressure after addition of silica gel. The crude product was purified by column chromatography (silica gel, EtOAc/cyclohexane, 10:90) to give 2-(4-methoxyphenyl)-5-(*p*-tolyl)oxazole (**6a**) (48 mg, 61%) as a yellow solid. NMR matches previously reported data.[7]

Reaction of N1-acyltriazole with $AlCl_3$

To a solution of pure N1-acyltriazole **2c** (0.1 mmol, 29.3 mg) in DCE (1 ml) $AlCl_3$ (0.1 mmol, 1 equiv., 13.4 mg) was added and the mixture was heated under nitrogen atmosphere at 80 °C for 18 h. After the reaction was complete (NMR monitoring) it was evaporated under reduced pressure after addition of silica gel. The crude product was purified by column chromatography (silica gel, EtOAc/cyclohexane, 10:90) to give oxazole **6a** (15 mg, 57%) as a yellow solid. NMR matches previously reported data.[7]

Reaction of N2-acyltriazole with $AlCl_3$



To a solution of N2-acyltriazole **3e** (24.2 mg, 0.07 mmol) in DCE (0.7 ml) $AlCl_3$ (9.5 mg, 0.07 mmol, 1 equiv.) was added, and the resulting mixture was heated under nitrogen atmosphere at 80 °C for 24 h. Then it was evaporated under reduced pressure after addition of silica gel and the crude product was purified by column chromatography (silica gel, EtOAc/cyclohexane, 3:97 to 10:90) to afford 2-(2-bromophenyl)-5-(*p*-tolyl)oxazole (**6b**) (16 mg, 71%) as a colorless oil, which solidified upon storage. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.74 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65-7.63 (m, 2H), 7.46 (s, 1H, H4), 7.43 (td, *J*

= 7.5, 1.2 Hz, 1H), 7.30 (ddd, *J* = 8.0, 7.5, 1.7 Hz, 1H), 7.29-7.25 (m, 2H, signal overlapped with solvent), 2.40 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 152.0, 138.8, 134.7, 131.1, 131.0, 129.7, 128.2, 127.4, 125.1, 124.4, 122.5, 120.7, 21.4; HRMS (EI$^+$) *m/z* calcd for $C_{16}H_{12}BrNO$ [M]$^+$: 313.0096, found 313.0097.

X-ray crystallography

Single-crystal diffraction data of **3f** and **2c** were collected using Bruker D8 VENTURE system equipped with a Photon 100 CMOS detector, a multilayer monochromator, and a CuKα Incoatec microfocus sealed tube (λ = 1.54178 Å) at 180 K. The frames were integrated with the with Bruker SAINT[8] software package. The structure was solved by direct methods with SIR92[9] and were refined by full-matrix least-squares on F with CRYSTALS.[10] The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. All hydrogen atoms were located in a difference Fourier map and then they were repositioned geometrically. They were initially refined with soft restraints on the bond lengths and angles to regularise their geometry, then their positions were refined with riding constraints

Crystal data for 2c (colourless, 0.156 x 0.184 x 0.323 mm):

$C_{17}H_{15}N_3O_2$, triclinic, space group *P*-1, *a* = 8.1806(6) Å, *b* = 9.0341(6) Å, *c* = 11.2117(8) Å, α = 93.215(2)°, *β* = 106.075(2)°, γ = 113.5933(19)°, *V* = 716.42(9) Å^3, *Z* = 2, *M* = 293.33, 20666 reflections measured, 2602 independent reflections. Final *R* = 0.044, *wR* = 0.047, *GoF* = 1.013 for 2489 reflections with $I > 2\sigma(I)$ and 244 parameters. CCDC 2244997.

Crystal data for 3f (colourless, 0.088 x 0.138 x 0.333 mm):

$C_{11}H_{11}N_3O_1$, monoclinic, space group $P2_1/n$, *a* = 7.7087(2) Å, *b* = 11.2855(2) Å, *c* = 12.0893(2) Å, *β* = 102.9689(6)°, *V* = 1024.90(4) Å^3, *Z* = 4, *M* = 201.23, 19496 reflections measured, 1876 independent reflections. Final *R* = 0.038, *wR* = 0.040, *GoF* = 1.070 for 1807 reflections with $I > 2\sigma(I)$ and 137 parameters. CCDC 2244996.

References

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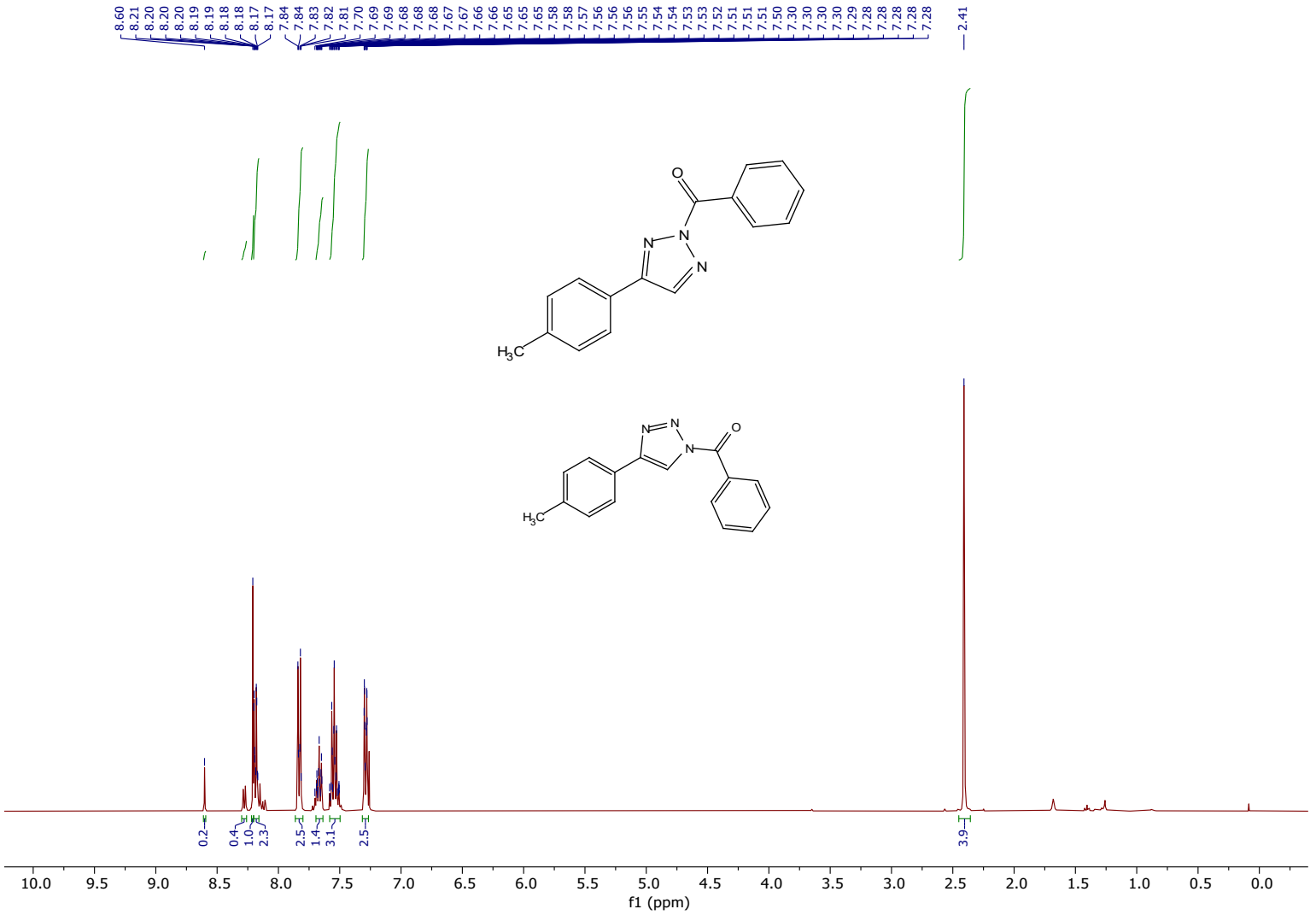
10. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K., Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487.

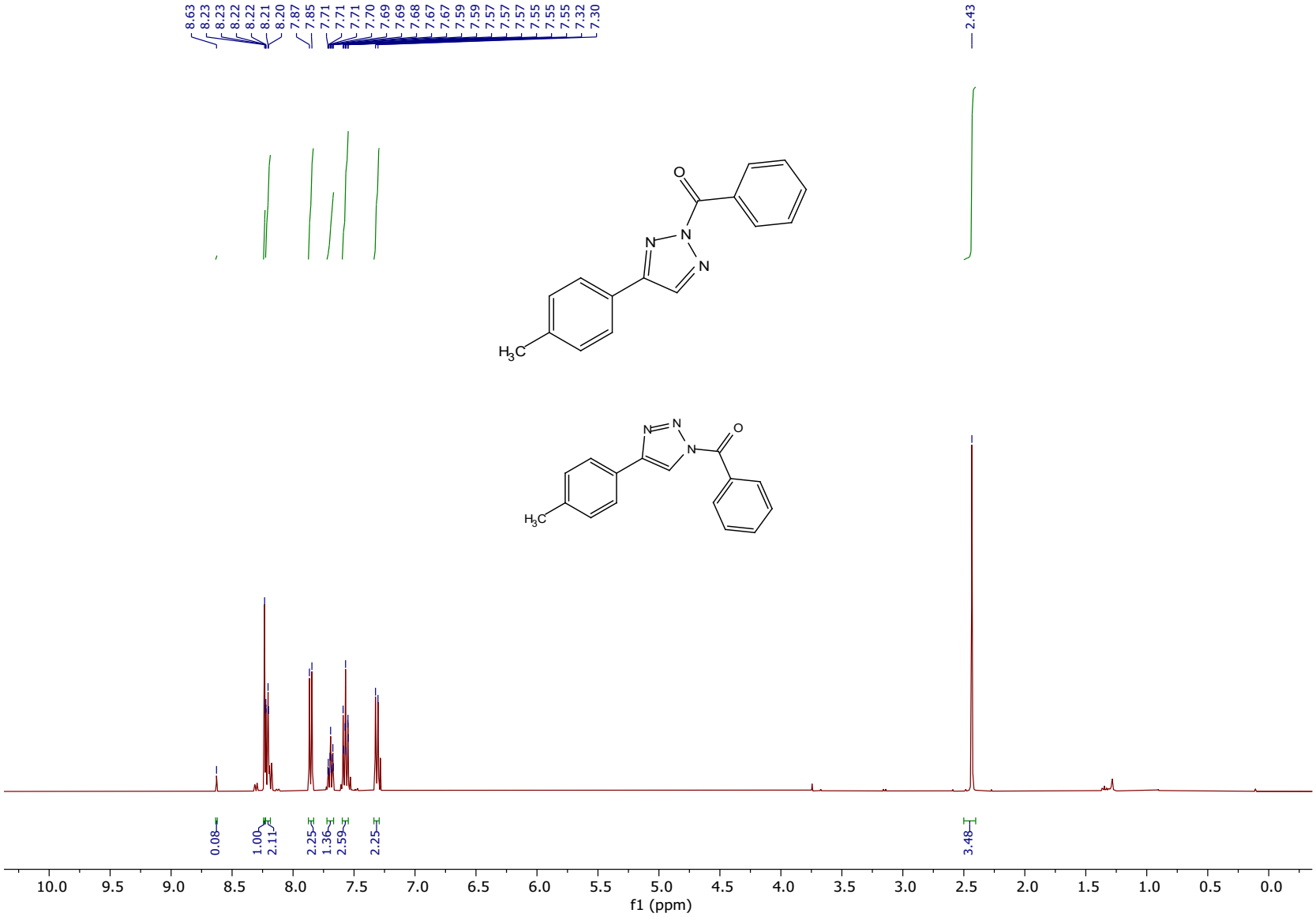
Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

Phenyl(4-(*p*-tolyl)-2H-1,2,3-triazol-2-yl)methanone **3a** and phenyl(4-(*p*-tolyl)-1H-1,2,3-triazol-1-yl)methanone **2a**

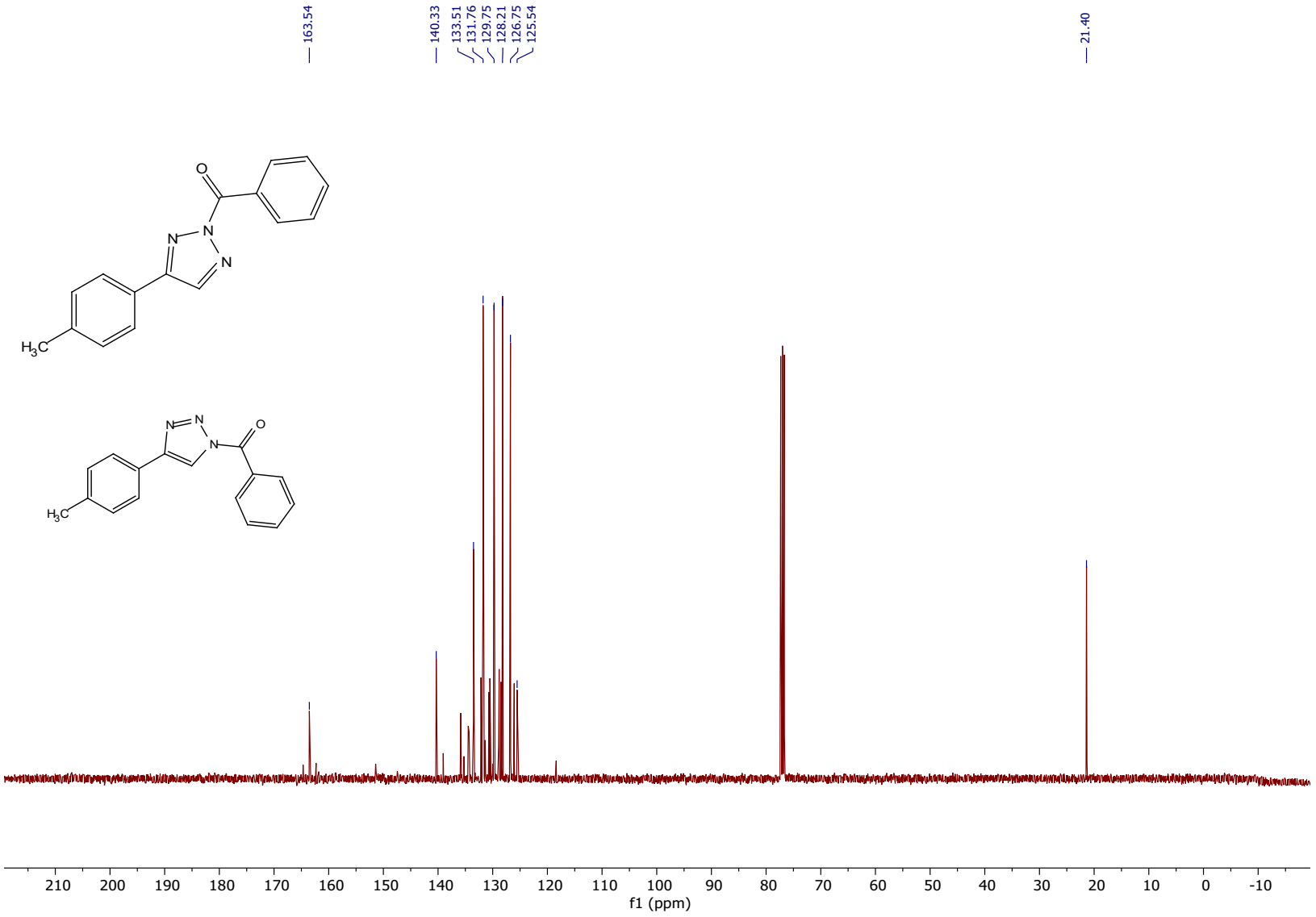
^{1}H NMR (reaction with benzoyl chloride)



^{1}H NMR (reaction with benzoic anhydride)

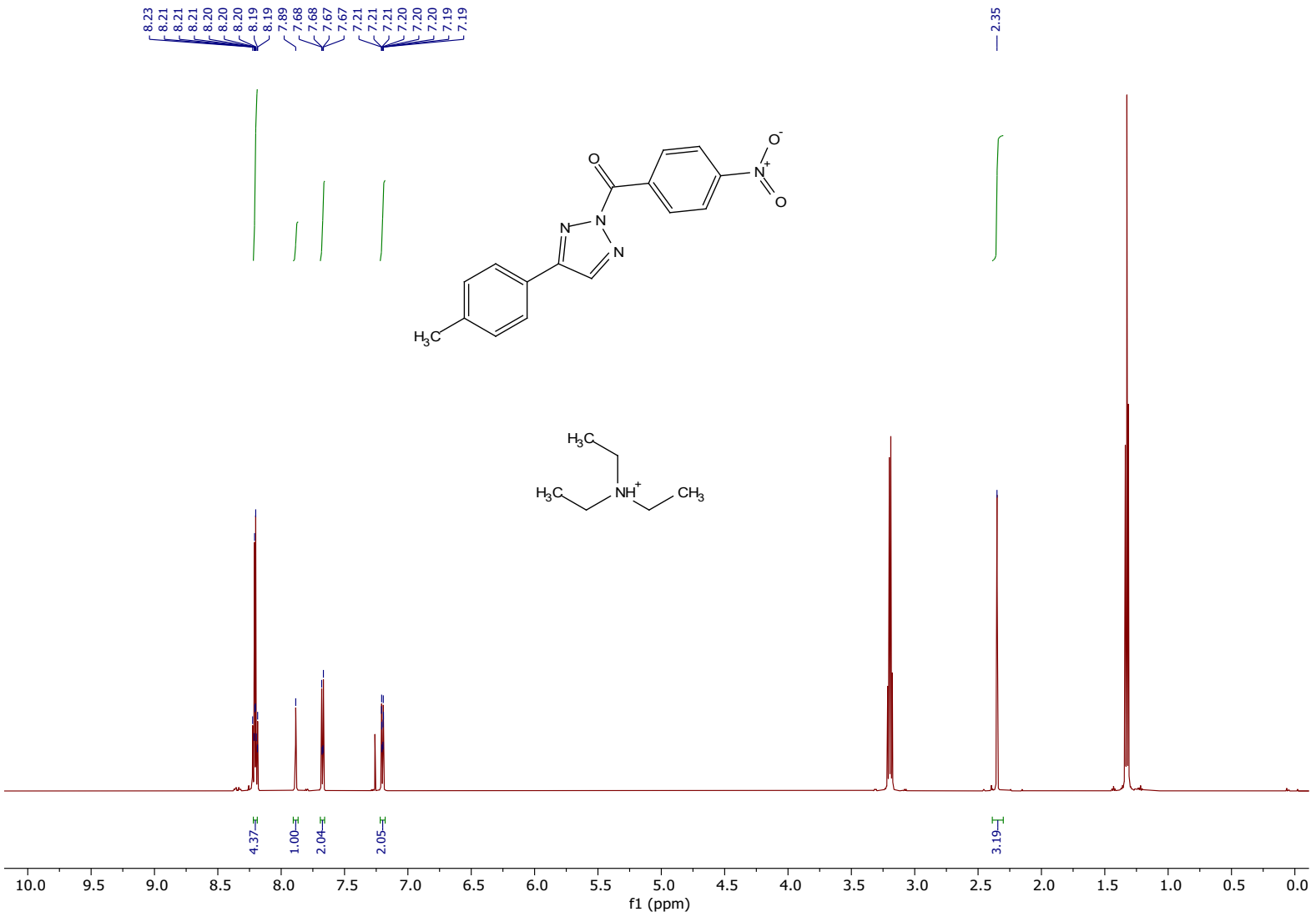


^{13}C NMR (reaction with benzoyl chloride)

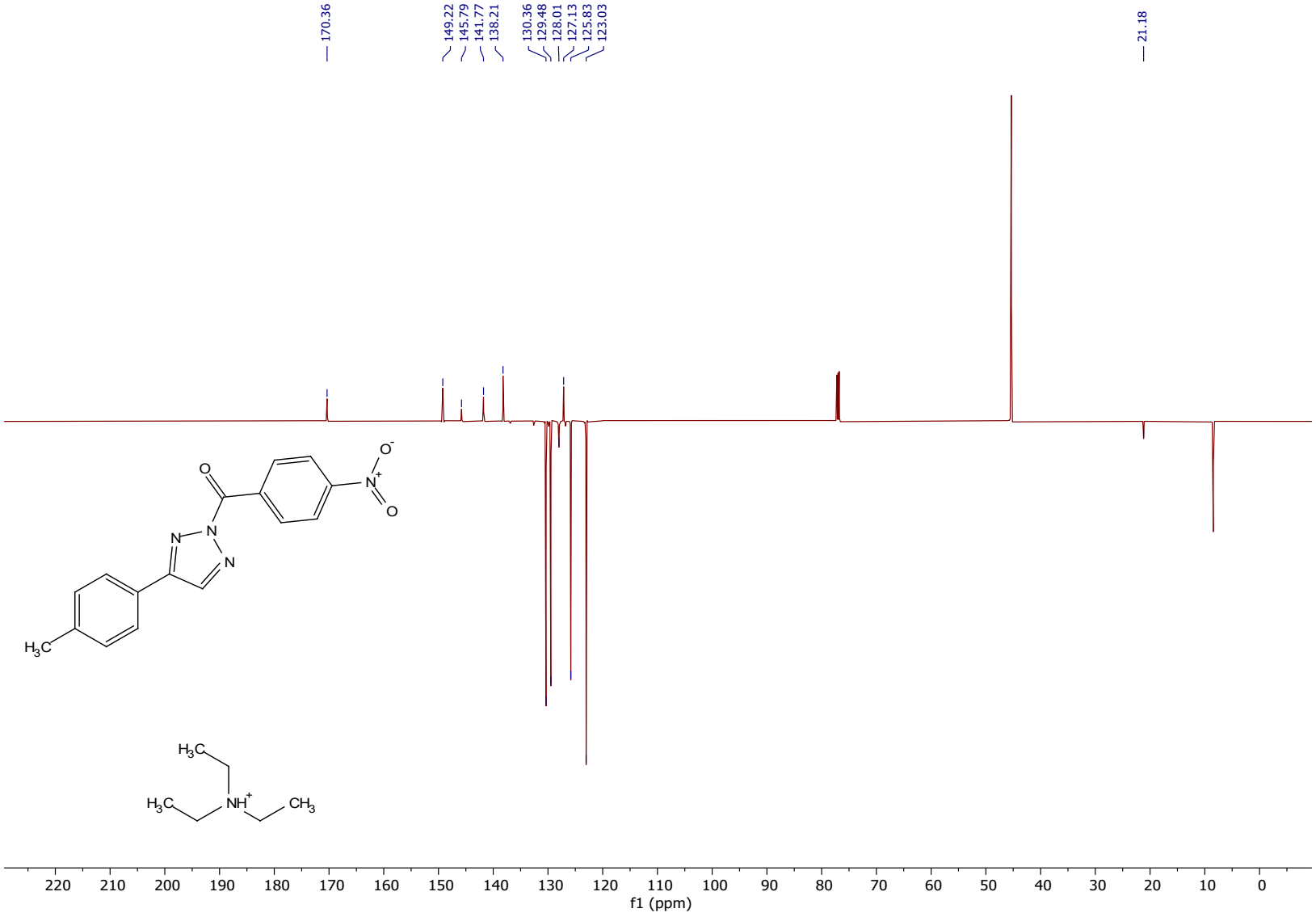


(4-Nitrophenyl)(4-(*p*-tolyl)-2H-1,2,3-triazol-2-yl)methanone **3b**

^{1}H NMR

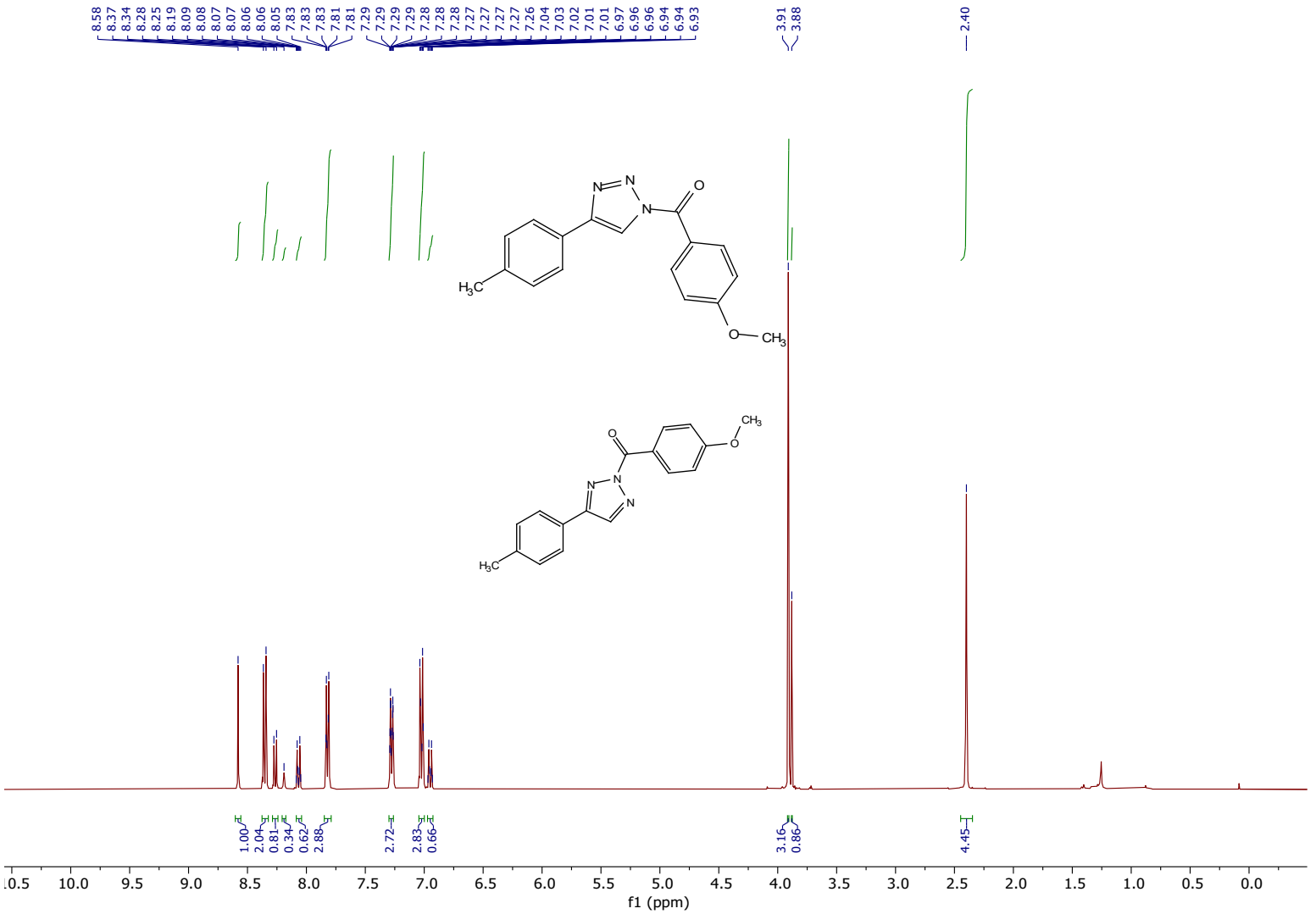


^{13}C NMR (APT)


170.36
149.22
145.79
141.77
138.21
130.36
129.48
128.01
127.13
125.83
123.03
21.18
f1 (ppm)

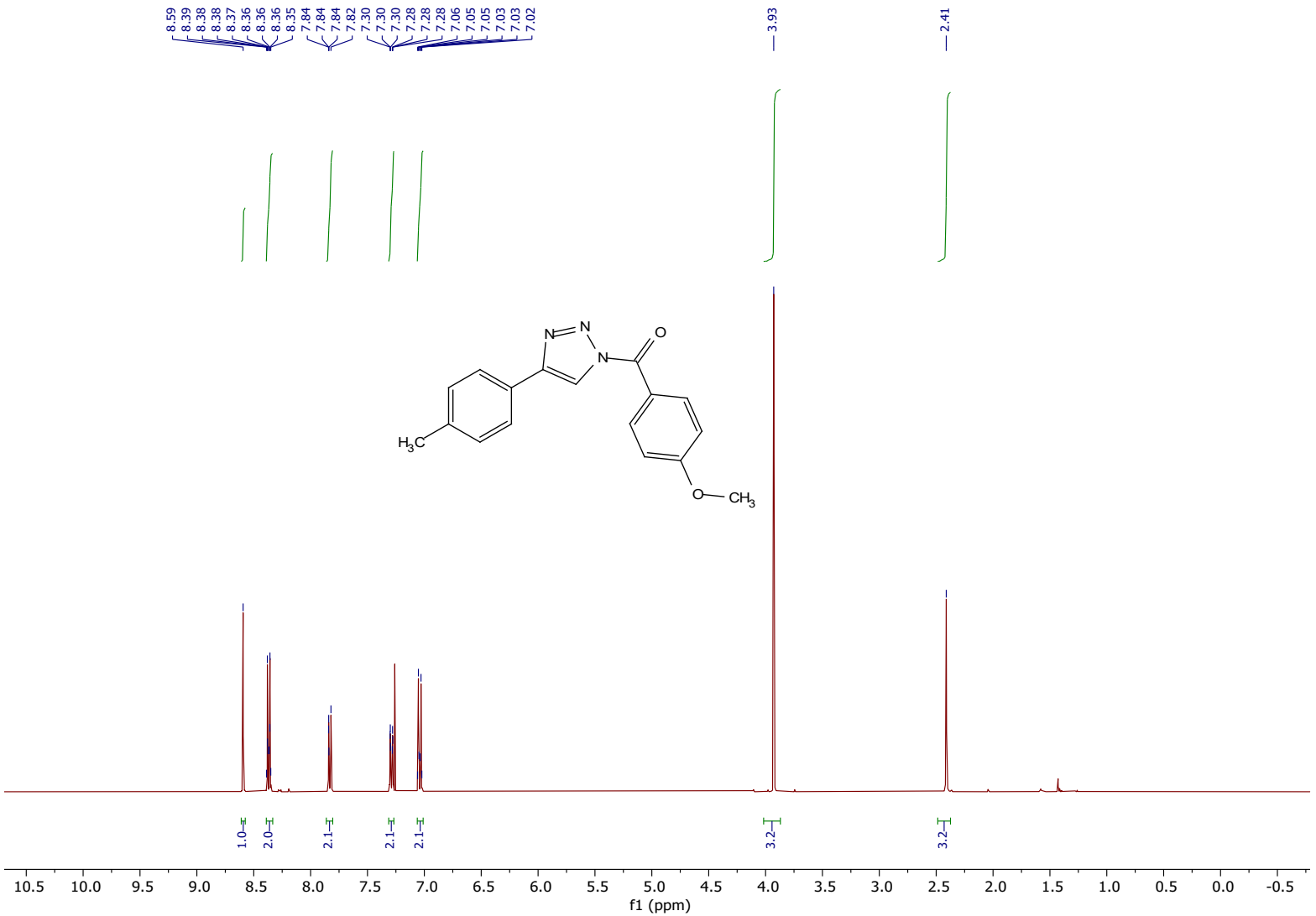
(4-Methoxyphenyl)(4-(*p*-tolyl)-2H-1,2,3-triazol-2-yl)methanone **3c** and (4-methoxyphenyl)(4-(*p*-tolyl)-1H-1,2,3-triazol-1-yl)methanone **2c**

^{1}H NMR

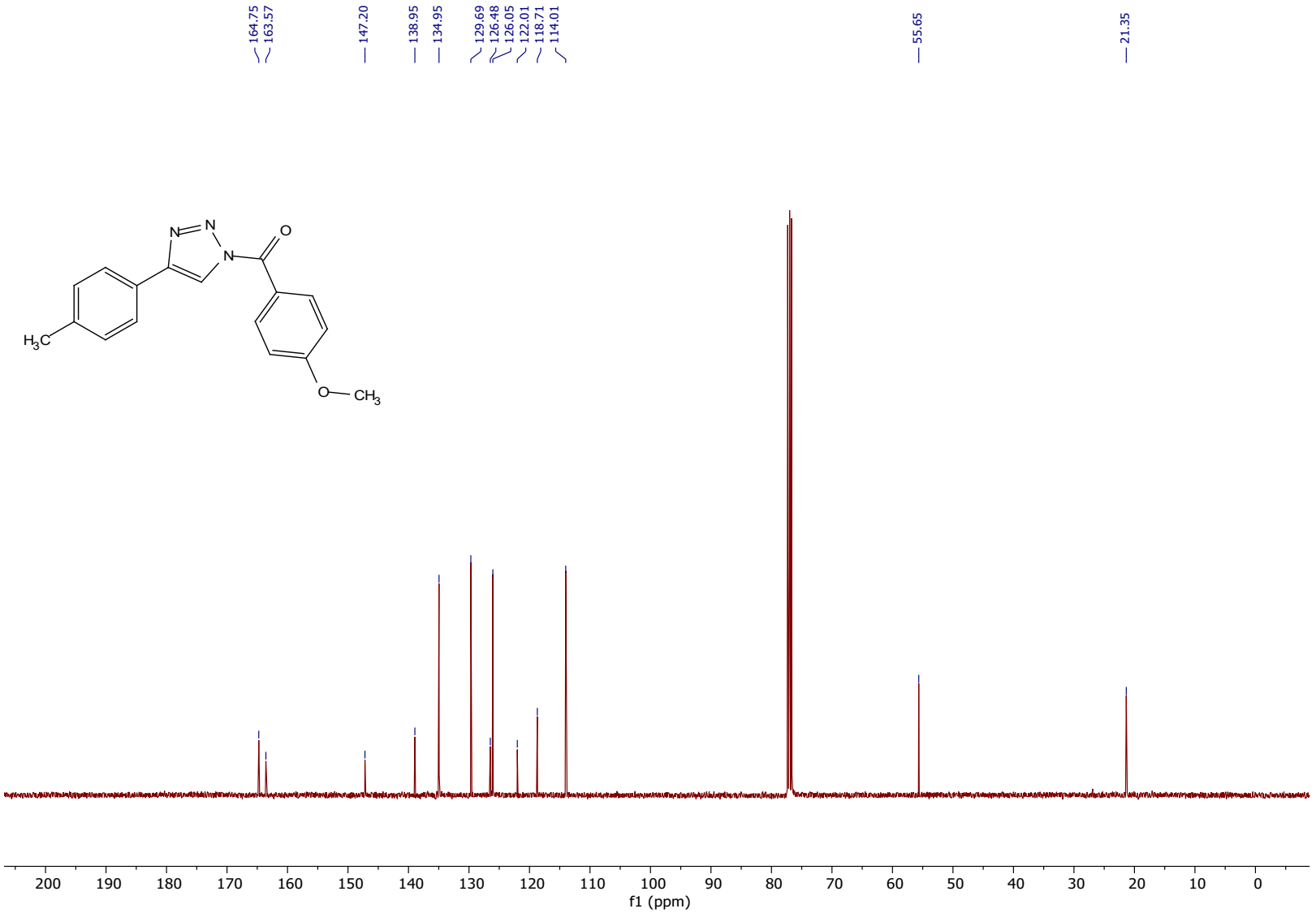


(4-methoxyphenyl)(4-(*p*-tolyl)-1H-1,2,3-triazol-1-yl)methanone **2c**

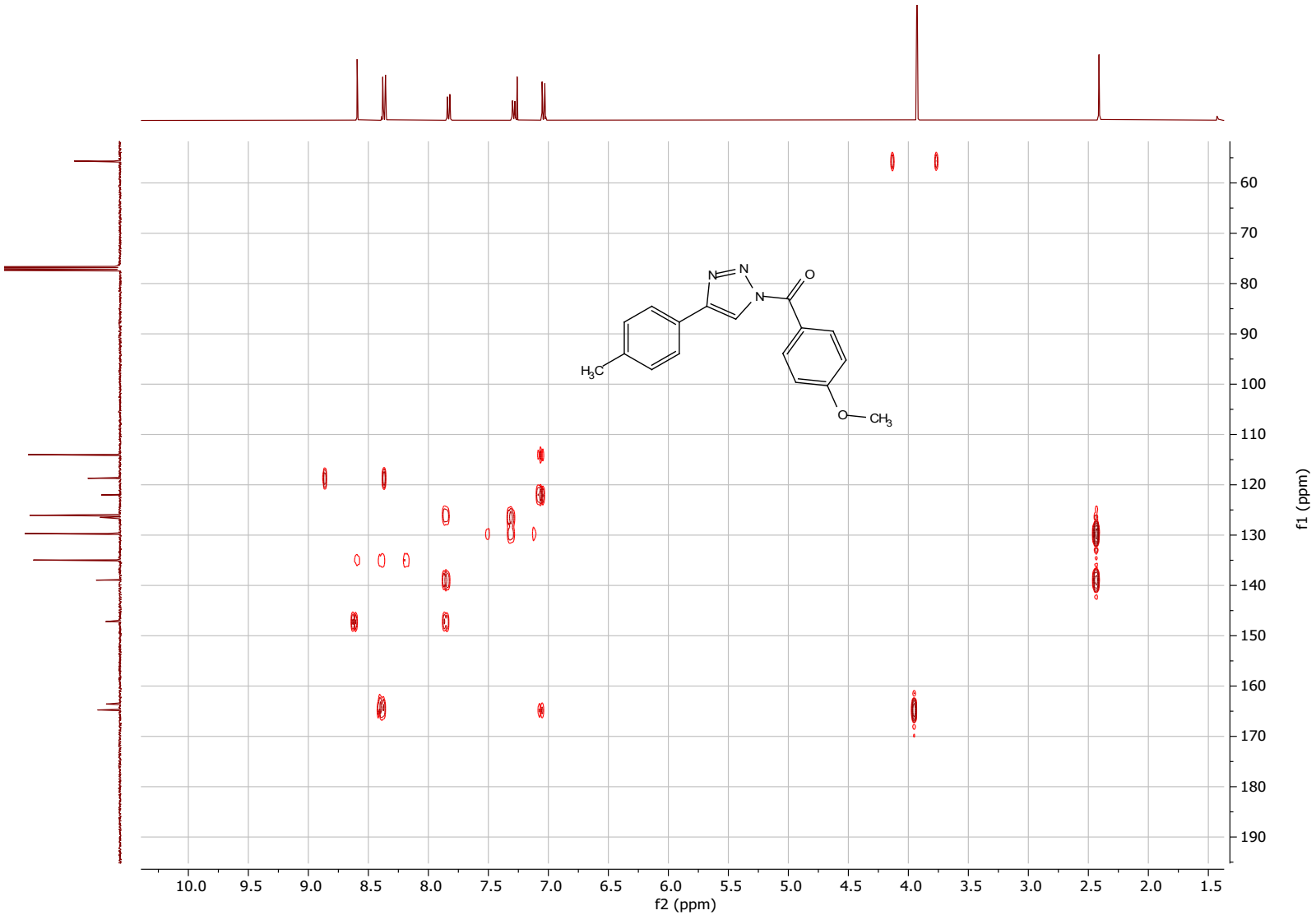
^{1}H NMR



^{13}C NMR

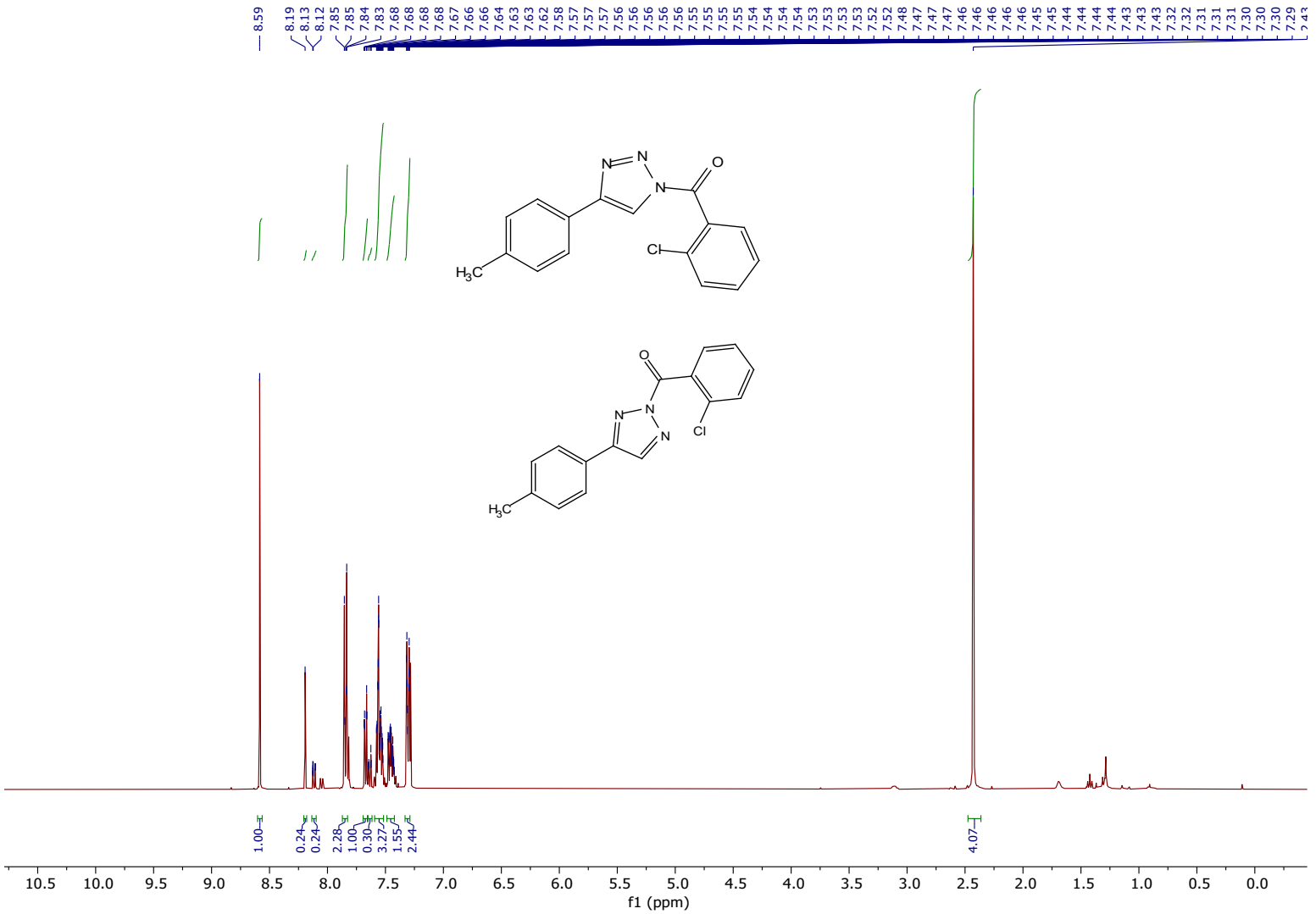

164.75
163.57
147.20
138.95
134.95
129.69
126.48
126.05
122.01
118.71
114.01
55.65
21.35
N
N
N
O
H3C
O
CH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H-^{13}C HMBC NMR

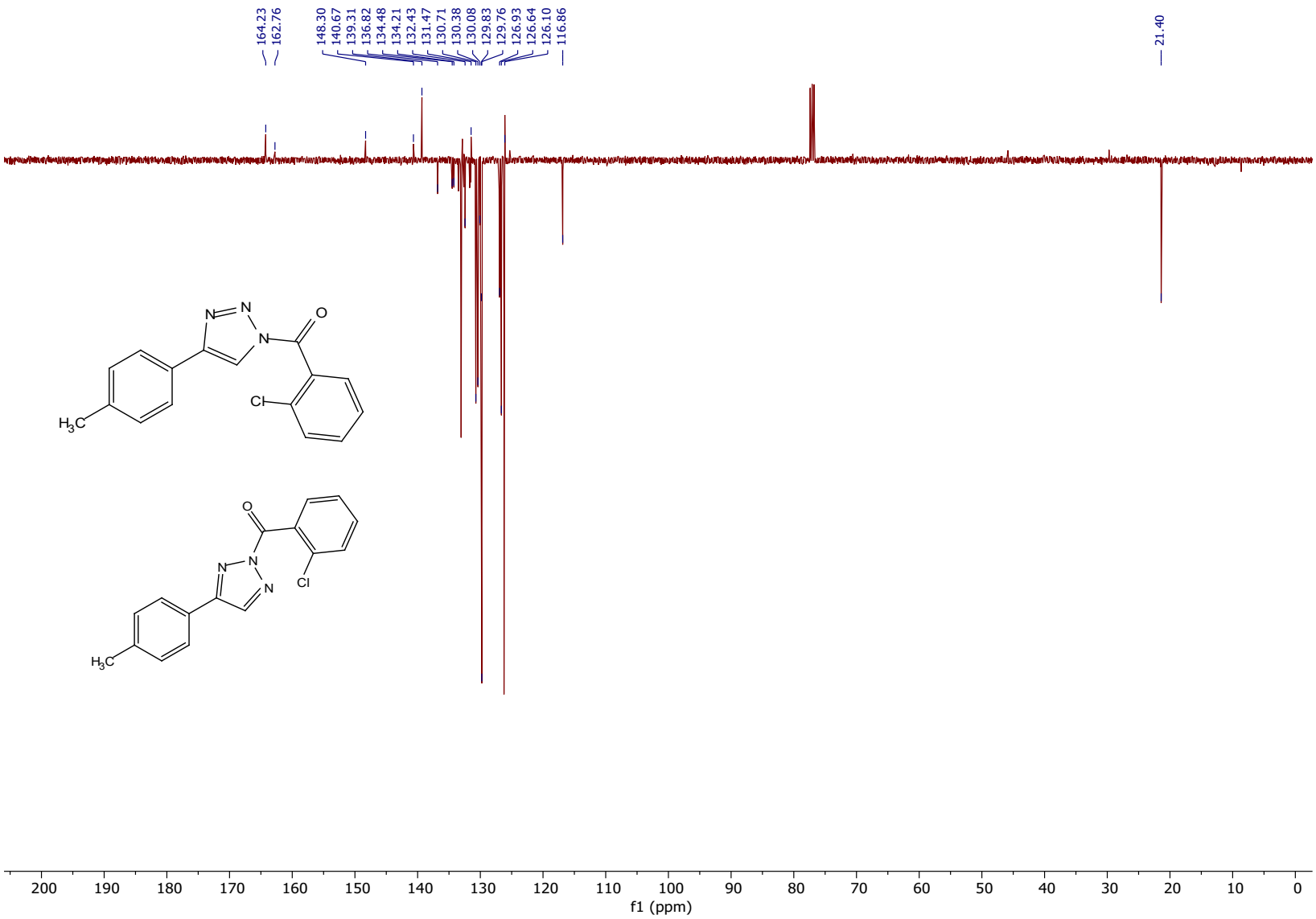


(2-Chlorophenyl)(4-(*p*-tolyl)-2H-1,2,3-triazol-2-yl)methanone **3d** and (2-chlorophenyl)(4-(*p*-tolyl)-1H-1,2,3-triazol-1-yl)methanone **2d**

^{1}H NMR

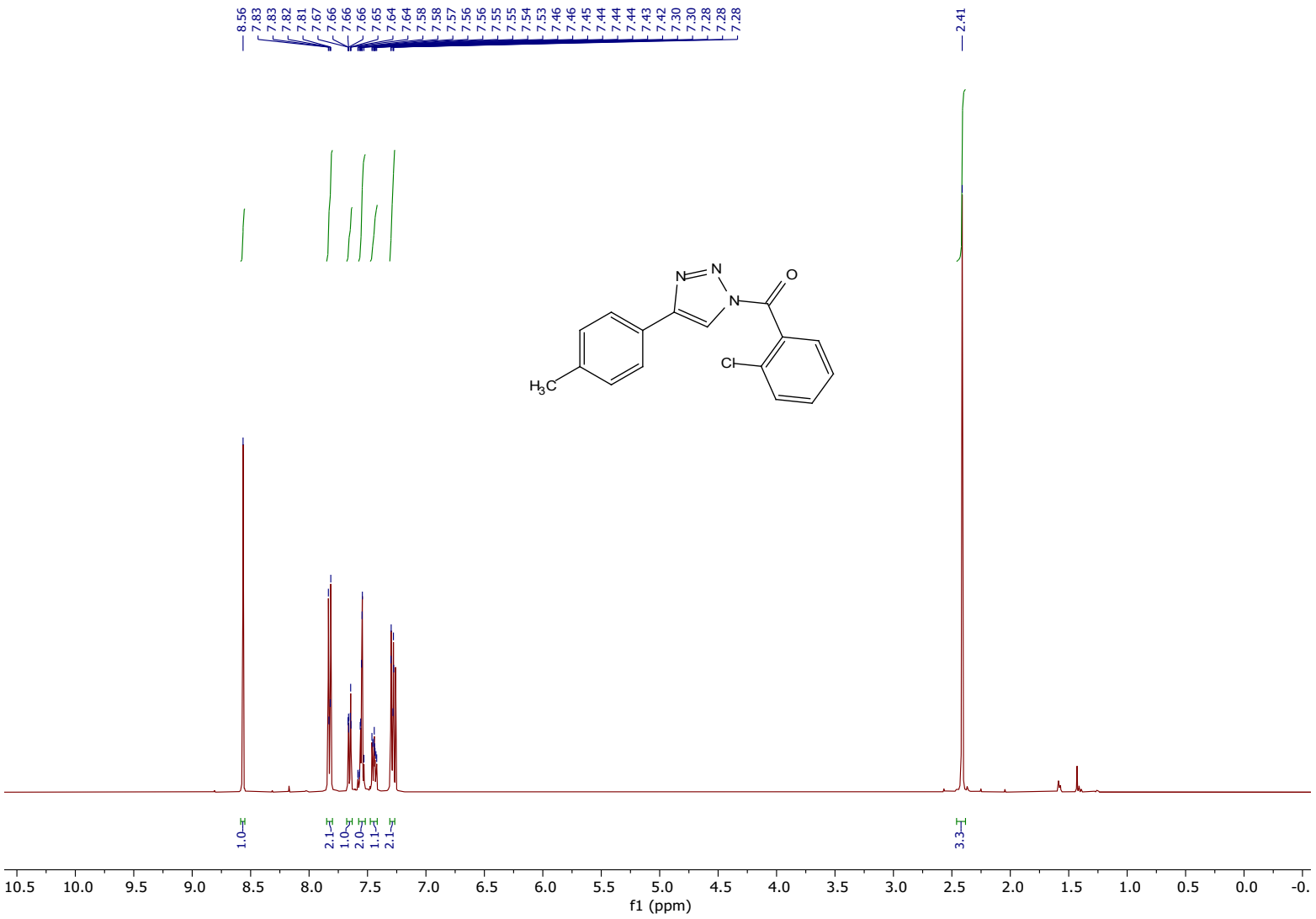


^{13}C NMR (APT)

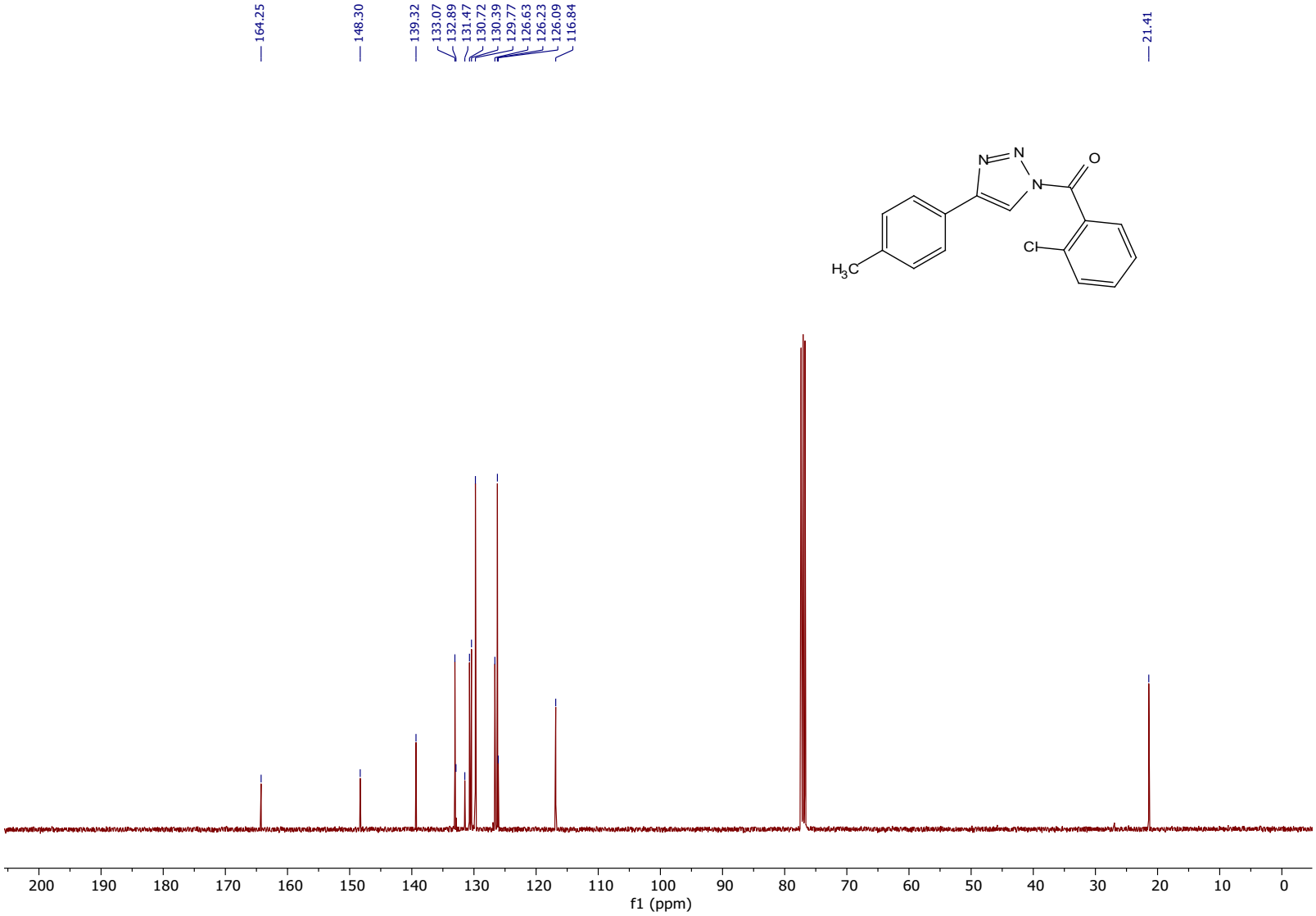

164.23
162.76
148.30
140.67
139.31
136.82
134.48
134.21
132.43
131.47
130.71
130.38
130.08
129.83
129.76
126.93
126.64
126.10
116.86
21.40
N
N
N
O
Cl
H3C
O
N
N
N
Cl
H3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(2-chlorophenyl)(4-(*p*-tolyl)-1H-1,2,3-triazol-1-yl)methanone **2d**

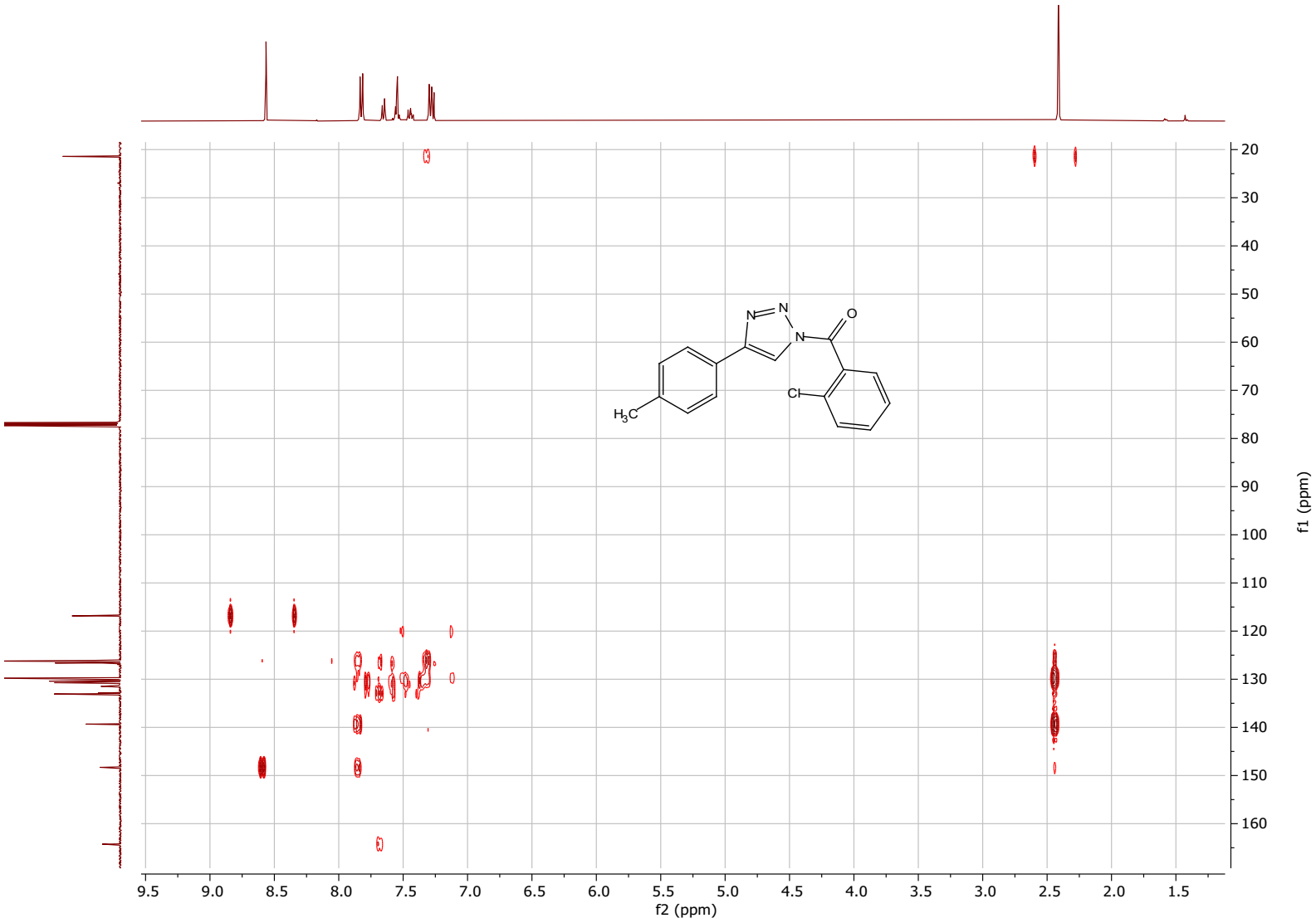
^{1}H NMR



^{13}C NMR

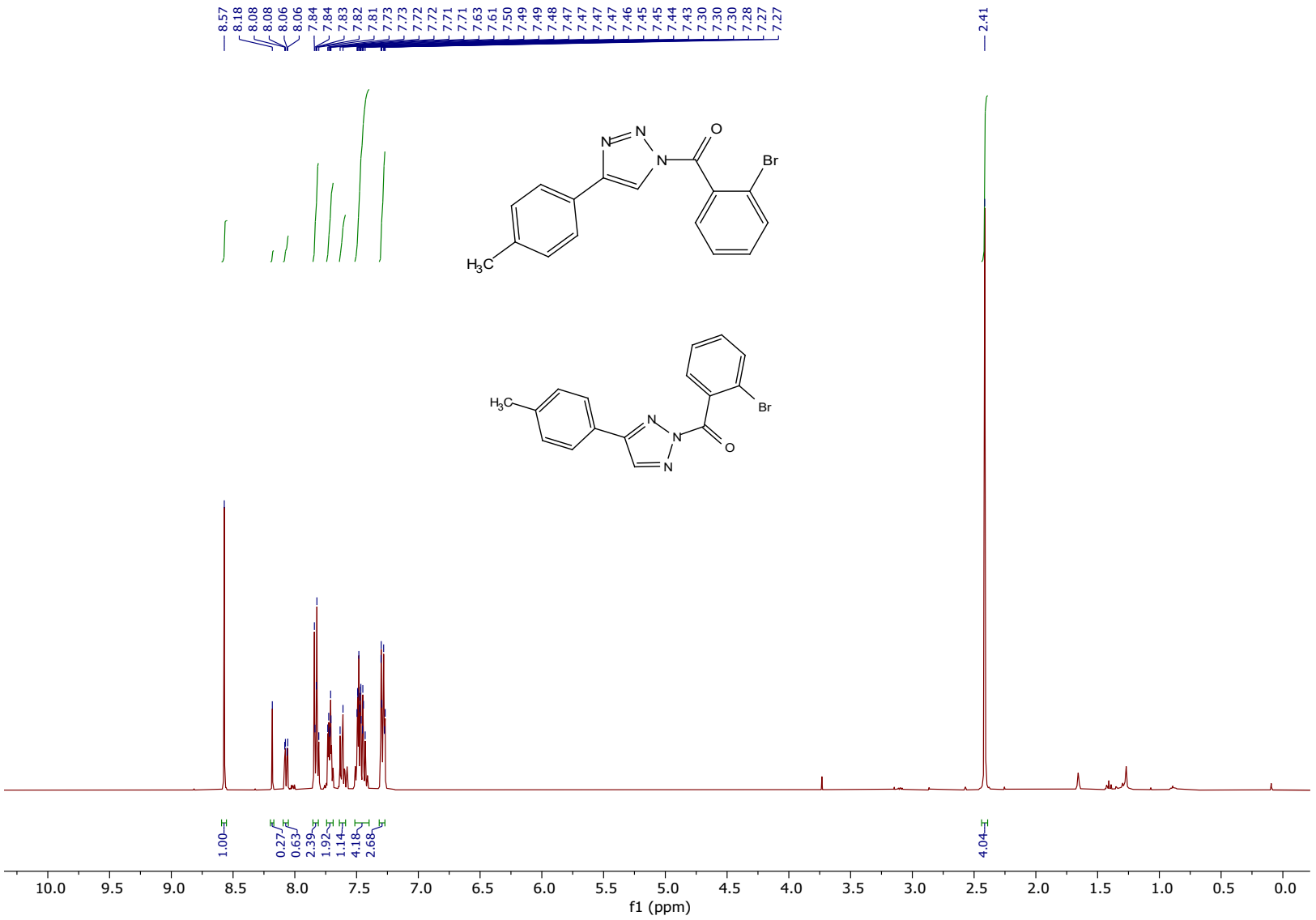

164.25
148.30
139.32
133.07
132.89
131.47
130.72
130.39
129.77
126.63
126.23
126.09
116.84
21.41
N
N
N
O
Cl
H3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H-^{13}C HMBC NMR



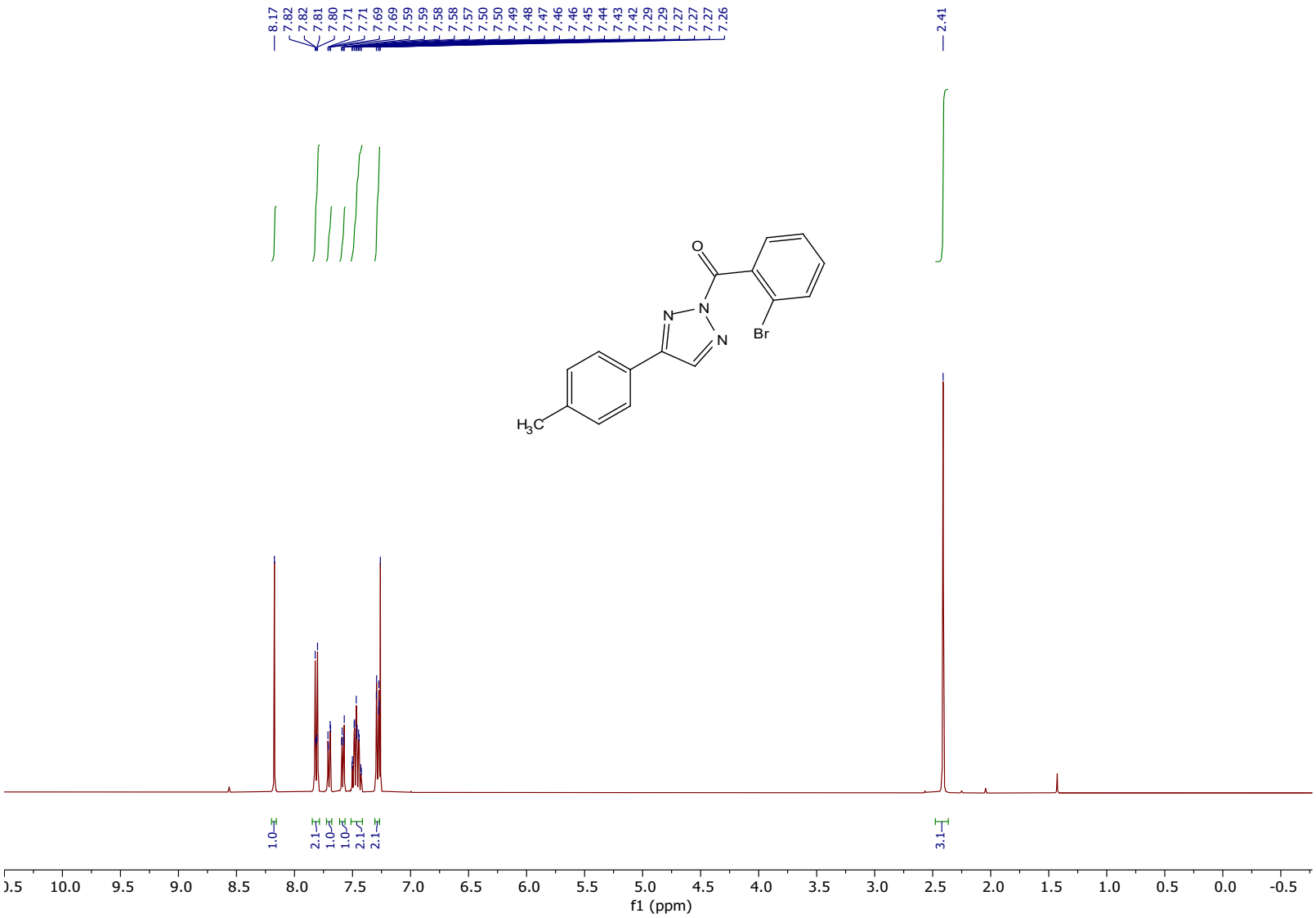
(2-Bromophenyl)(4-(*p*-tolyl)-2H-1,2,3-triazol-2-yl)methanone **3e** and (2-bromophenyl)(4-(*p*-tolyl)-1H-1,2,3-triazol-1-yl)methanone **2e**

^{1}H NMR

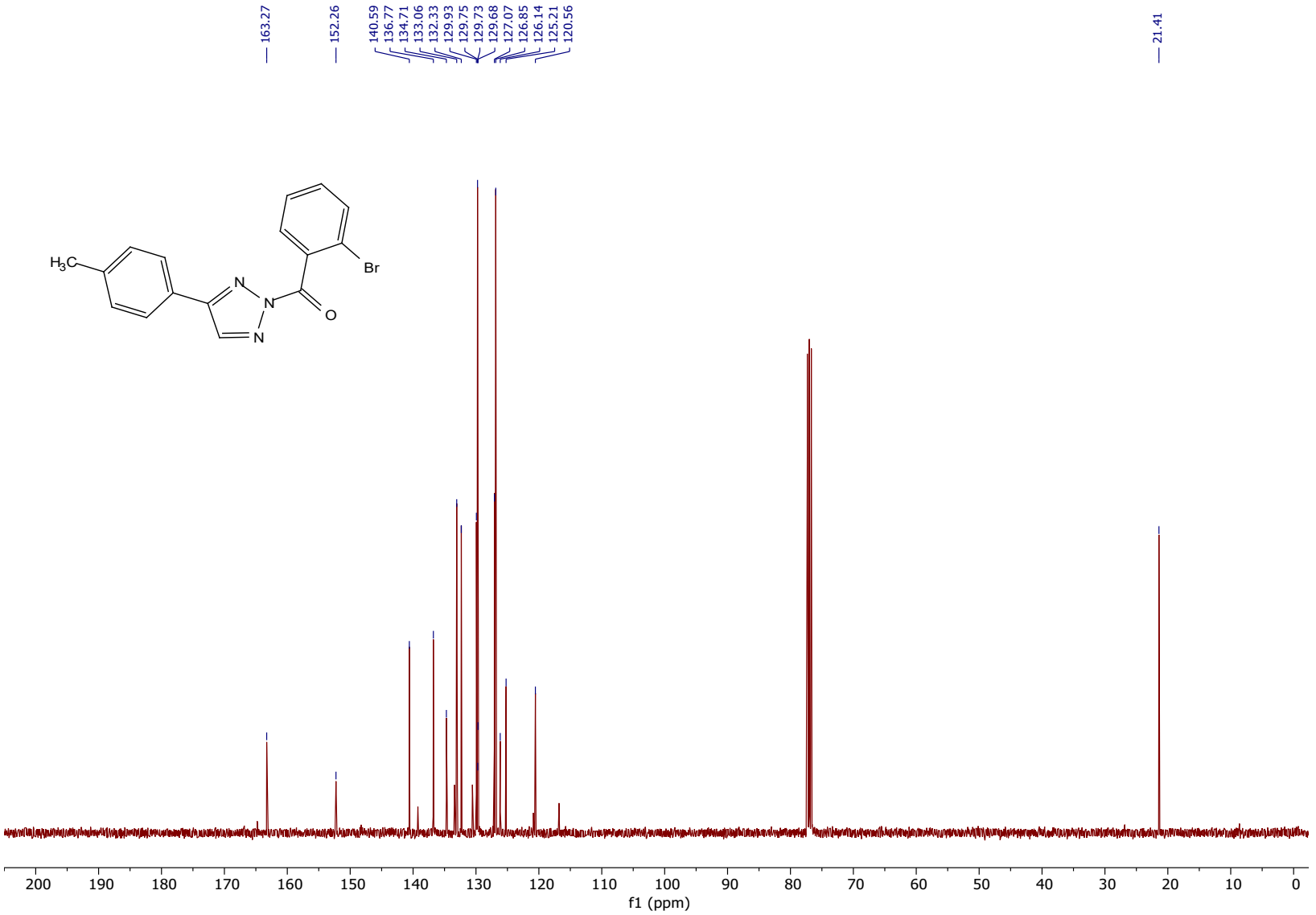


(2-Bromophenyl)(4-(*p*-tolyl)-2H-1,2,3-triazol-2-yl)methanone **3e** (crystallized, >20:1 N2/N1)

^{1}H NMR

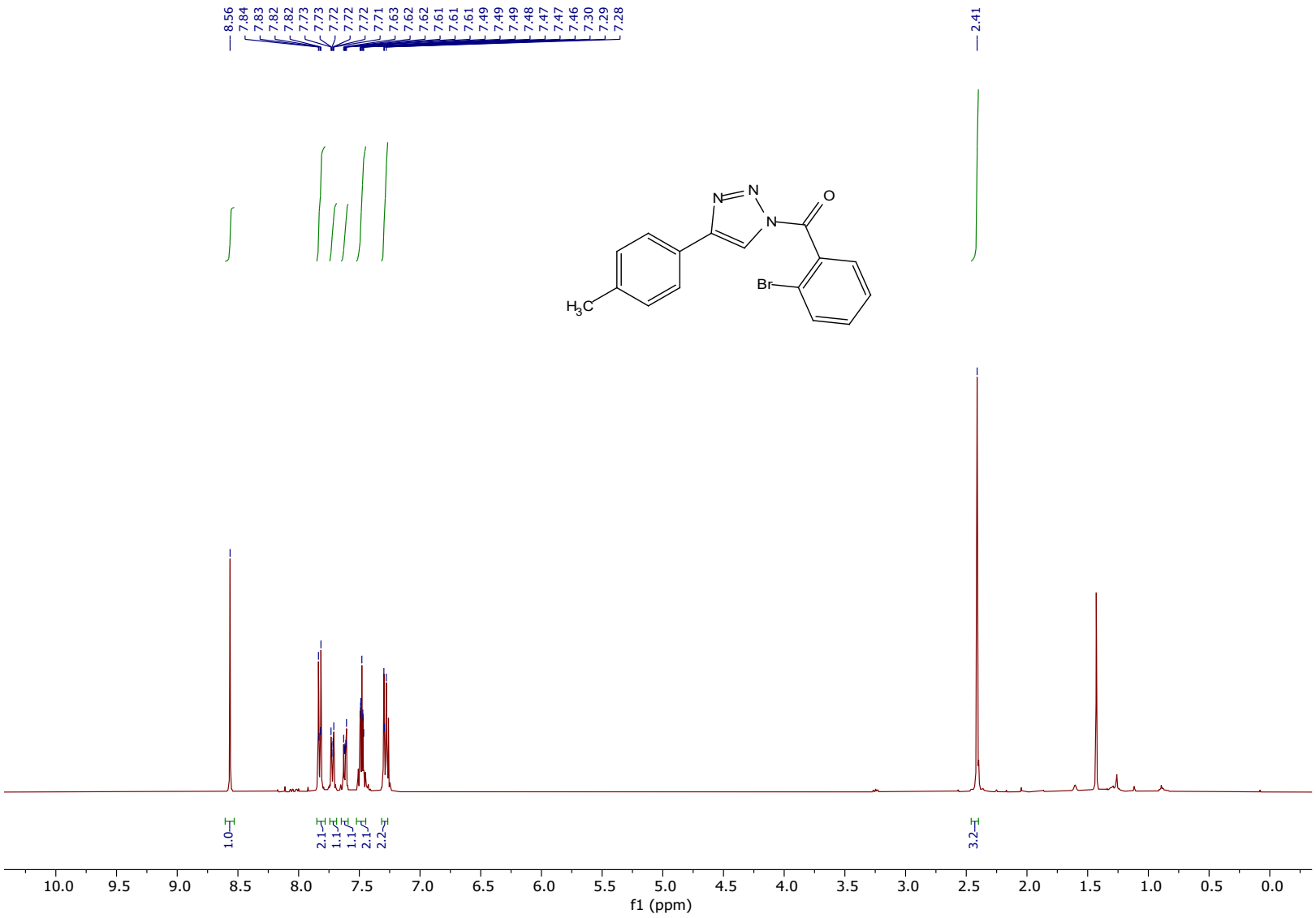


^{13}C NMR

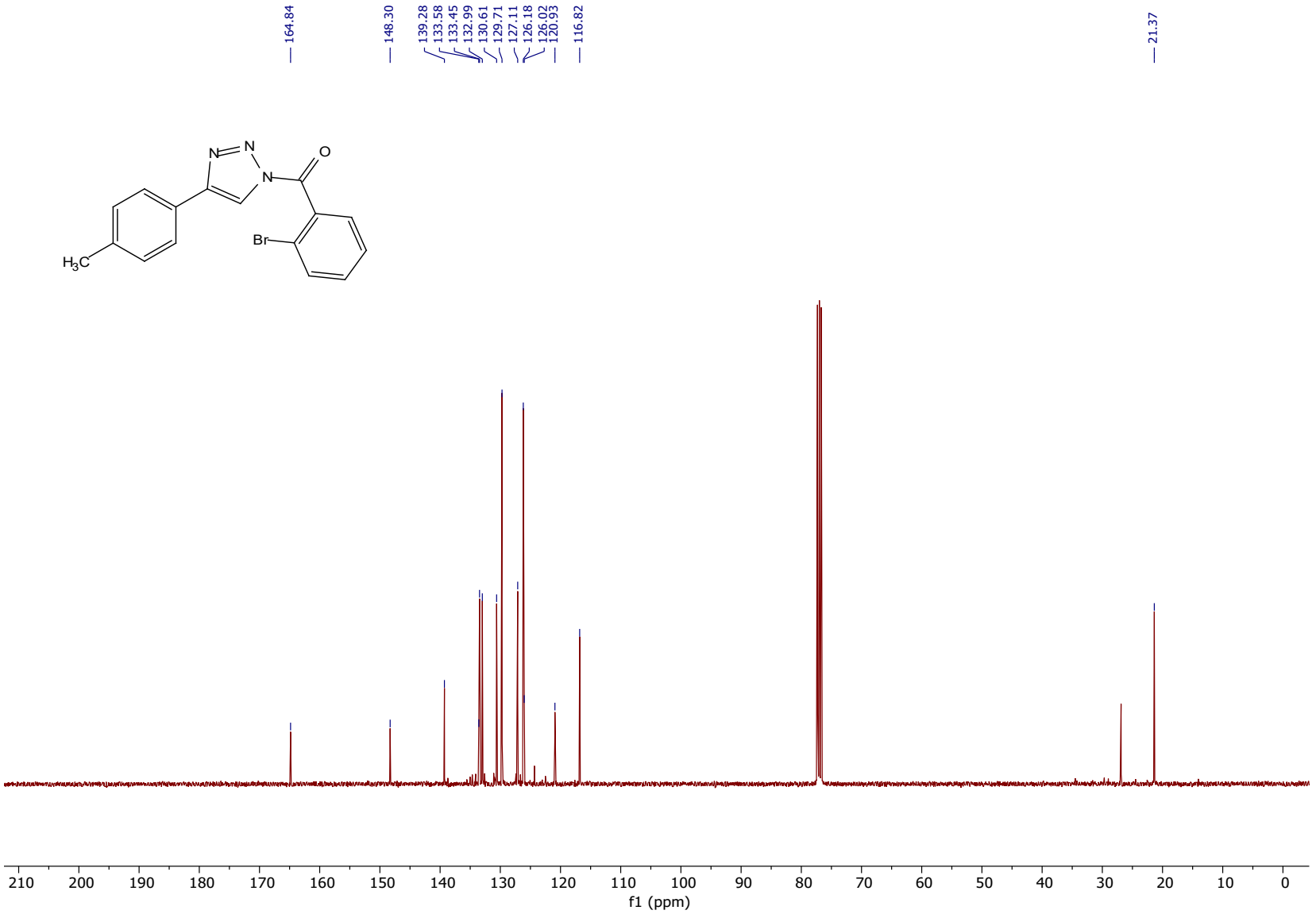

163.27
152.26
140.59
136.77
134.71
133.06
132.33
129.93
129.75
129.73
129.68
127.07
126.85
126.14
125.21
120.56
21.41
H3C
N
N
N
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(2-bromophenyl)(4-(*p*-tolyl)-1H-1,2,3-triazol-1-yl)methanone **2e**

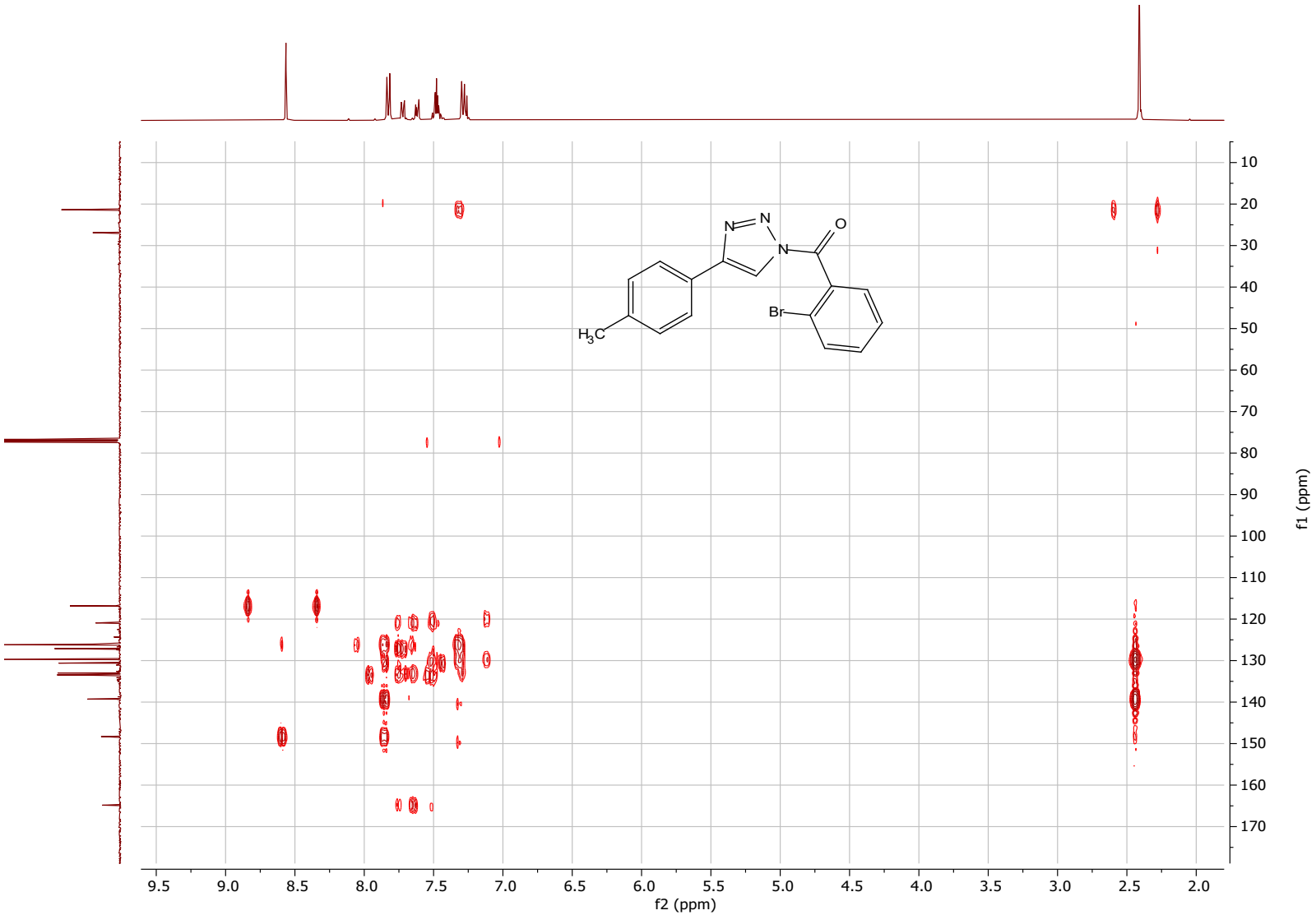
^{1}H NMR



^{13}C NMR

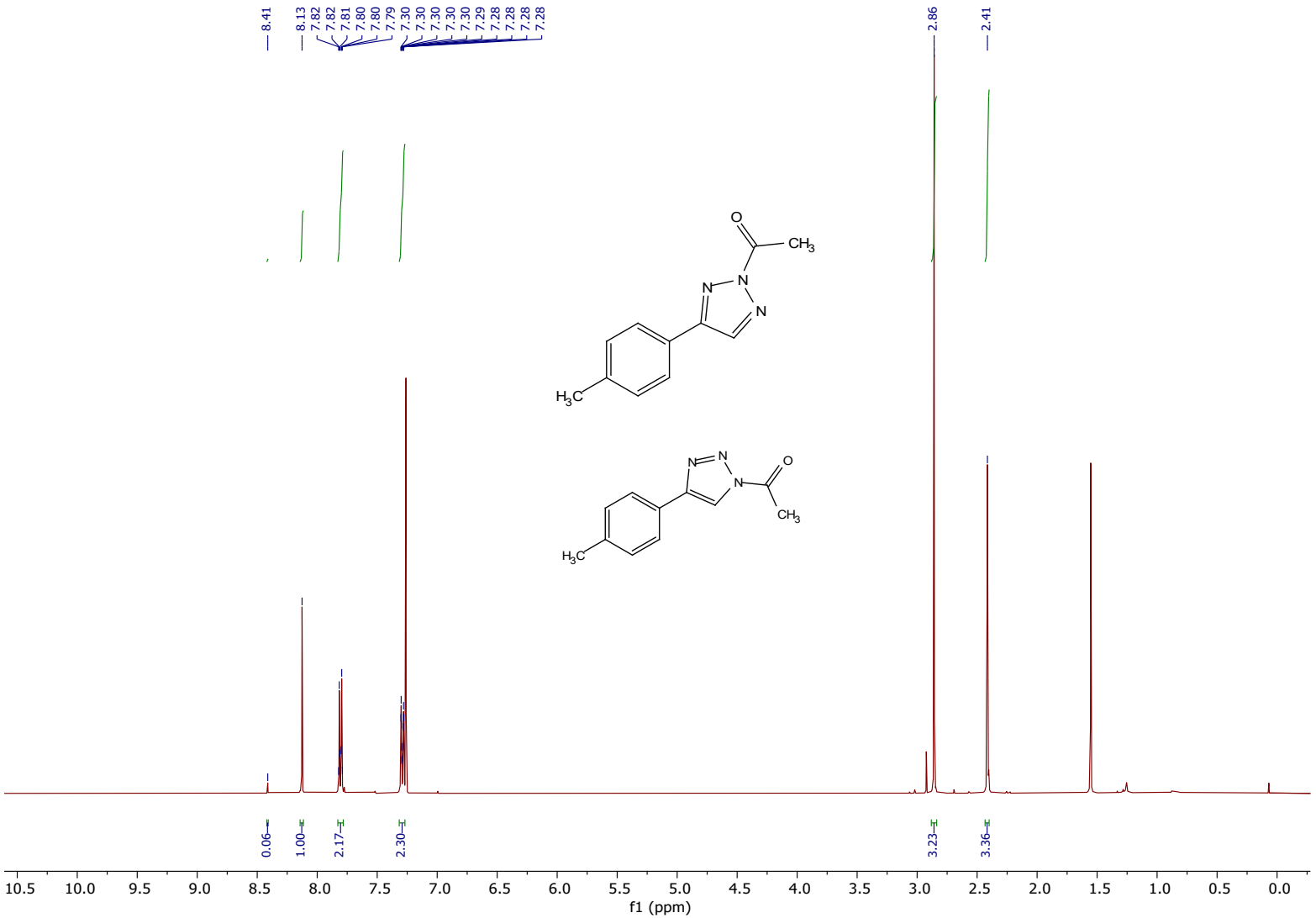

164.84
148.30
139.28
133.58
133.45
132.99
130.61
129.71
127.11
126.18
126.02
120.93
116.82
21.37
N
N
N
O
Br
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H-^{13}C HMBC NMR

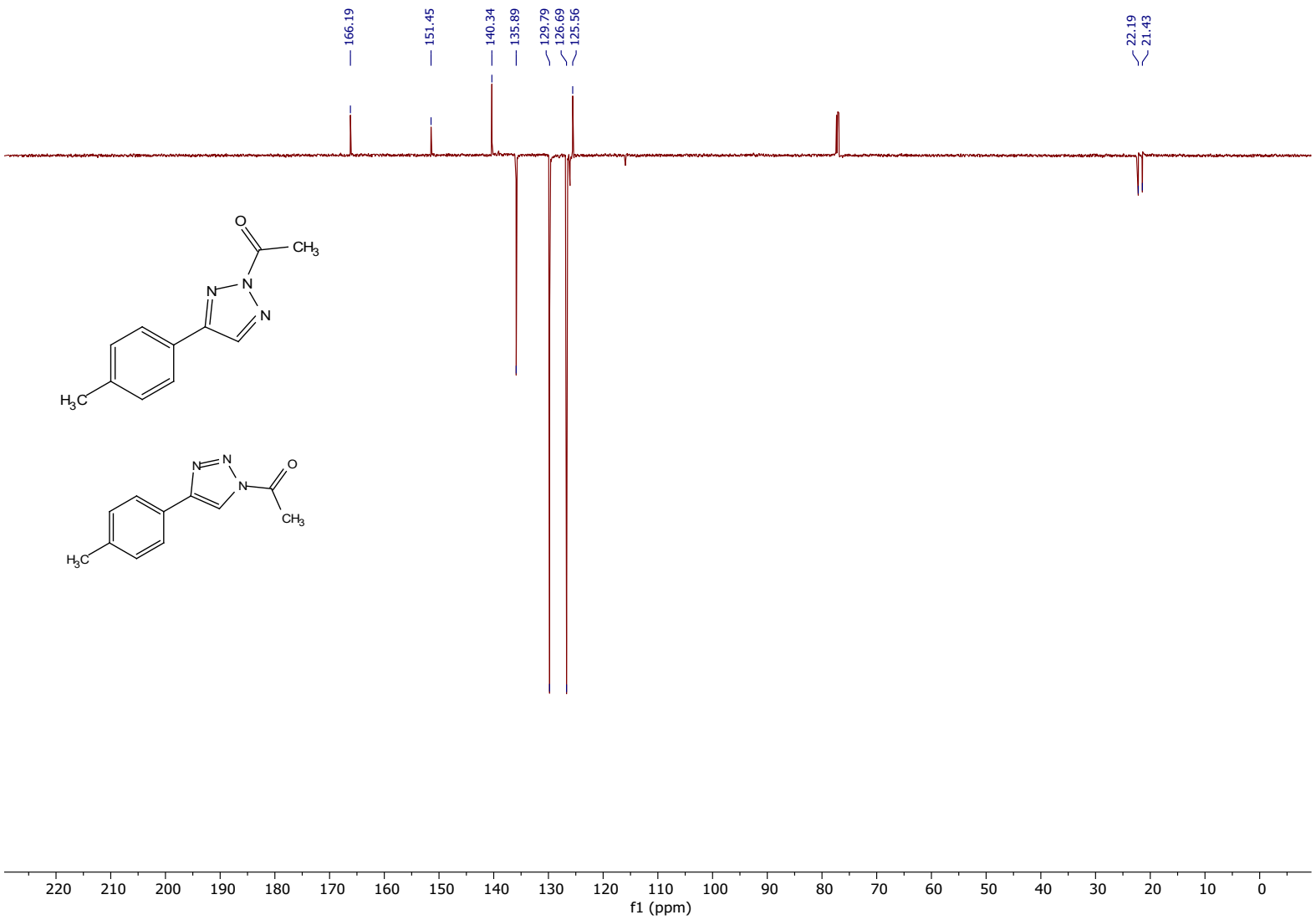


1-(4-(*p*-tolyl)-2H-1,2,3-triazol-2-yl)ethan-1-one **3f** and 1-(4-(*p*-tolyl)-1H-1,2,3-triazol-1-yl)ethan-1-one **2f**

^{1}H NMR

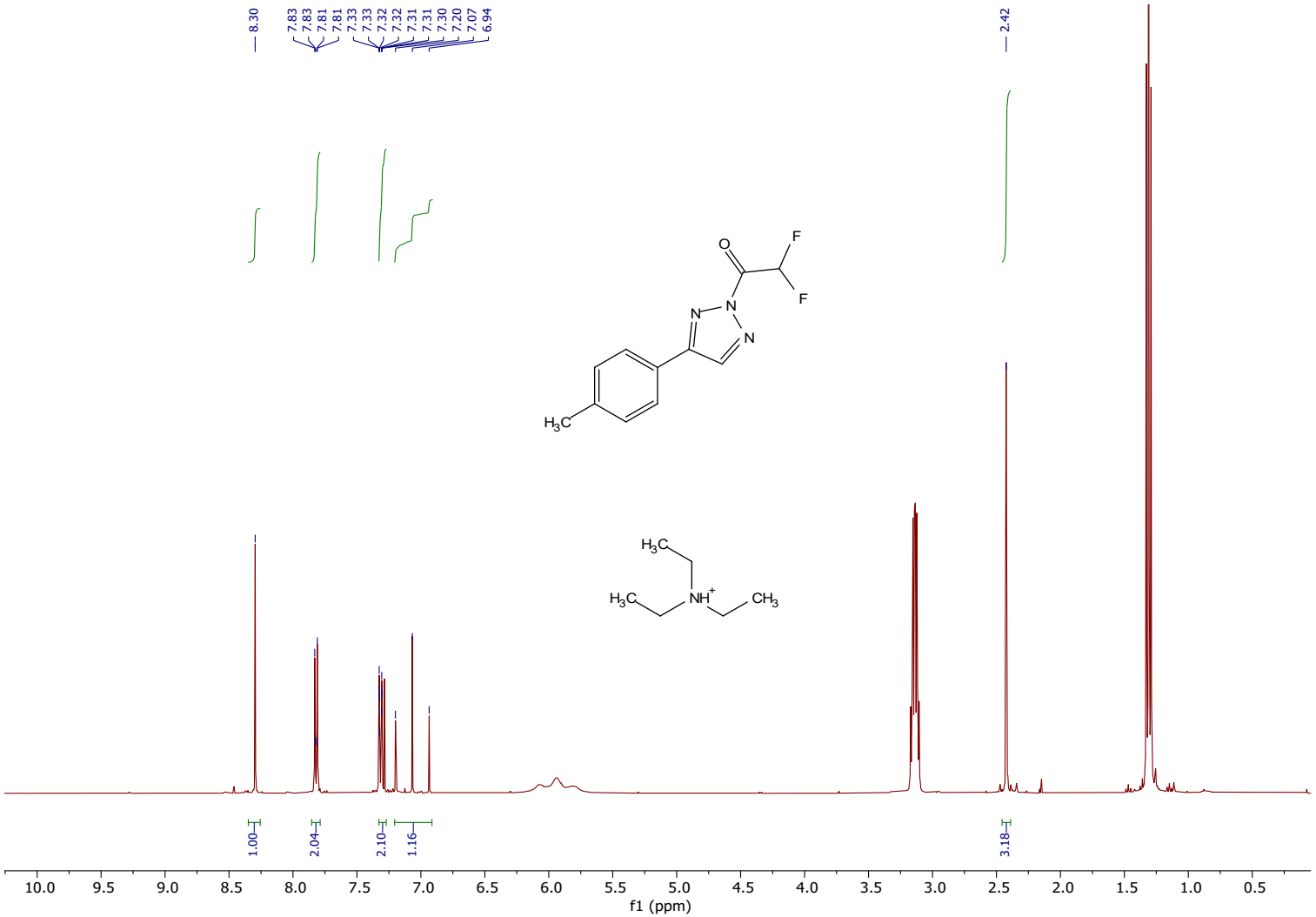


^{13}C NMR (APT)

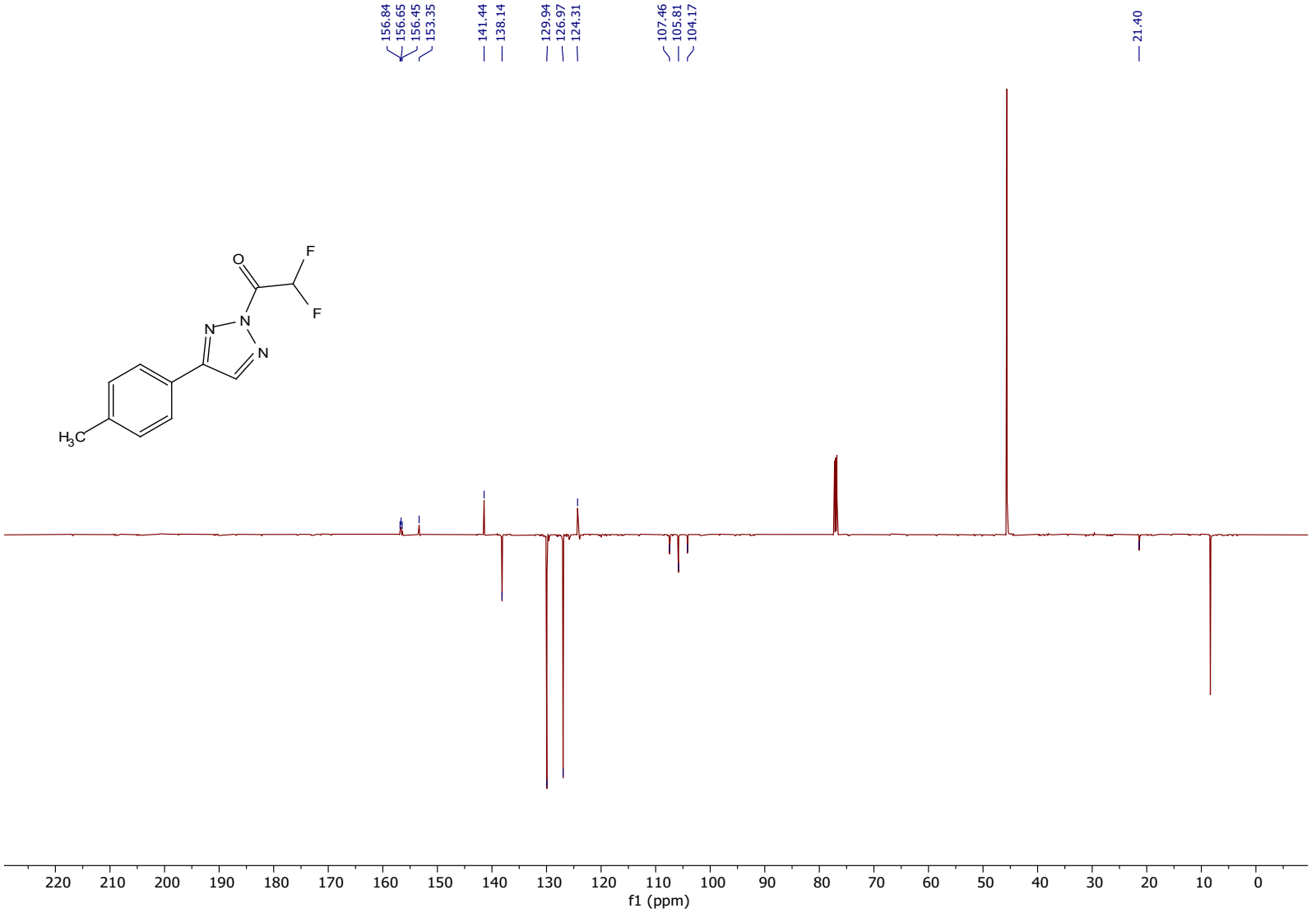

166.19
151.45
140.34
135.89
129.79
126.69
125.56
22.19
21.43
O
CH3
N
N
N
H3C
N
N
O
CH3
H3C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2,2-difluoro-1-(4-(*p*-tolyl)-2H-1,2,3-triazol-2-yl)ethan-1-one **3g**

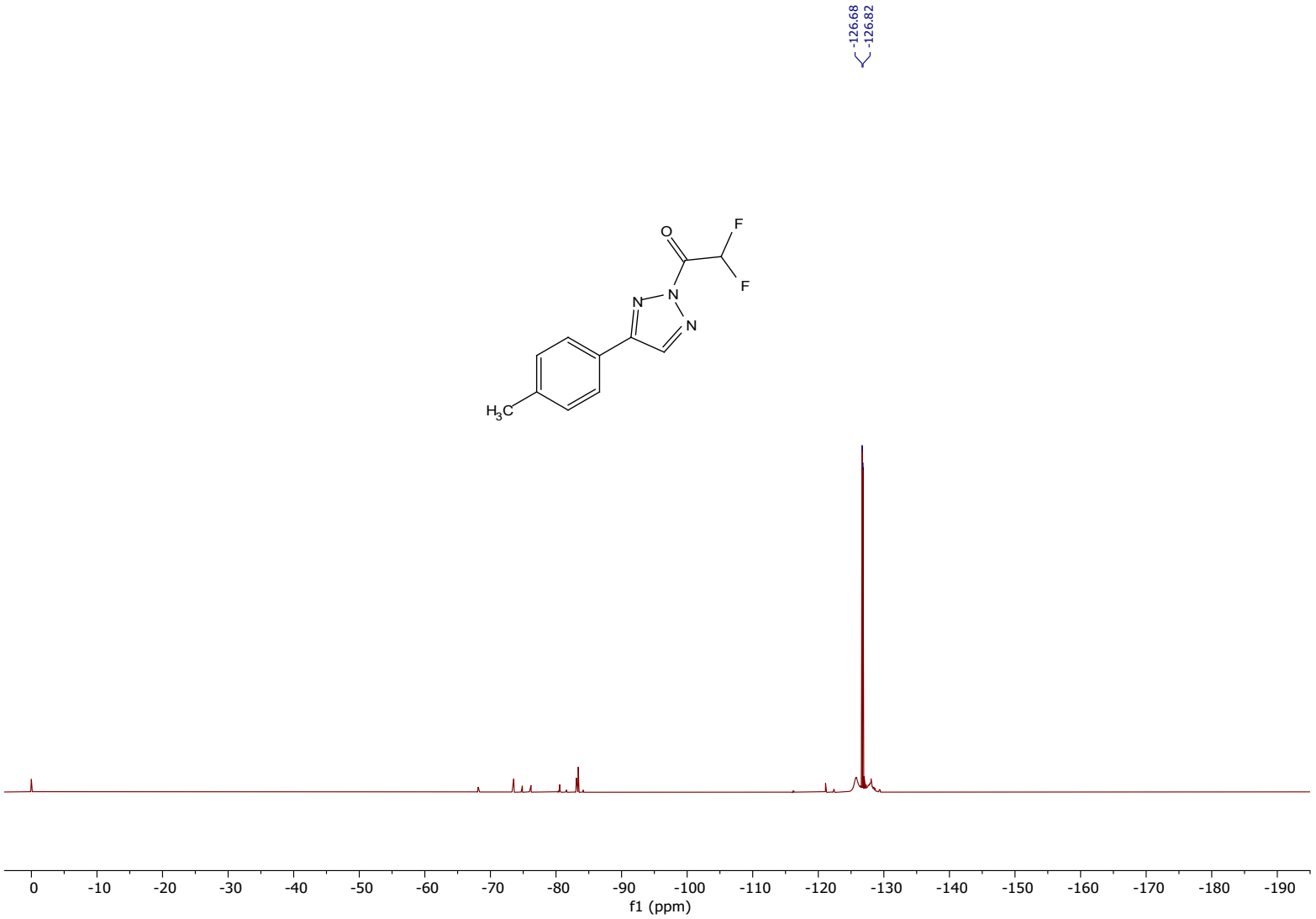
^{1}H NMR



^{13}C NMR (APT)

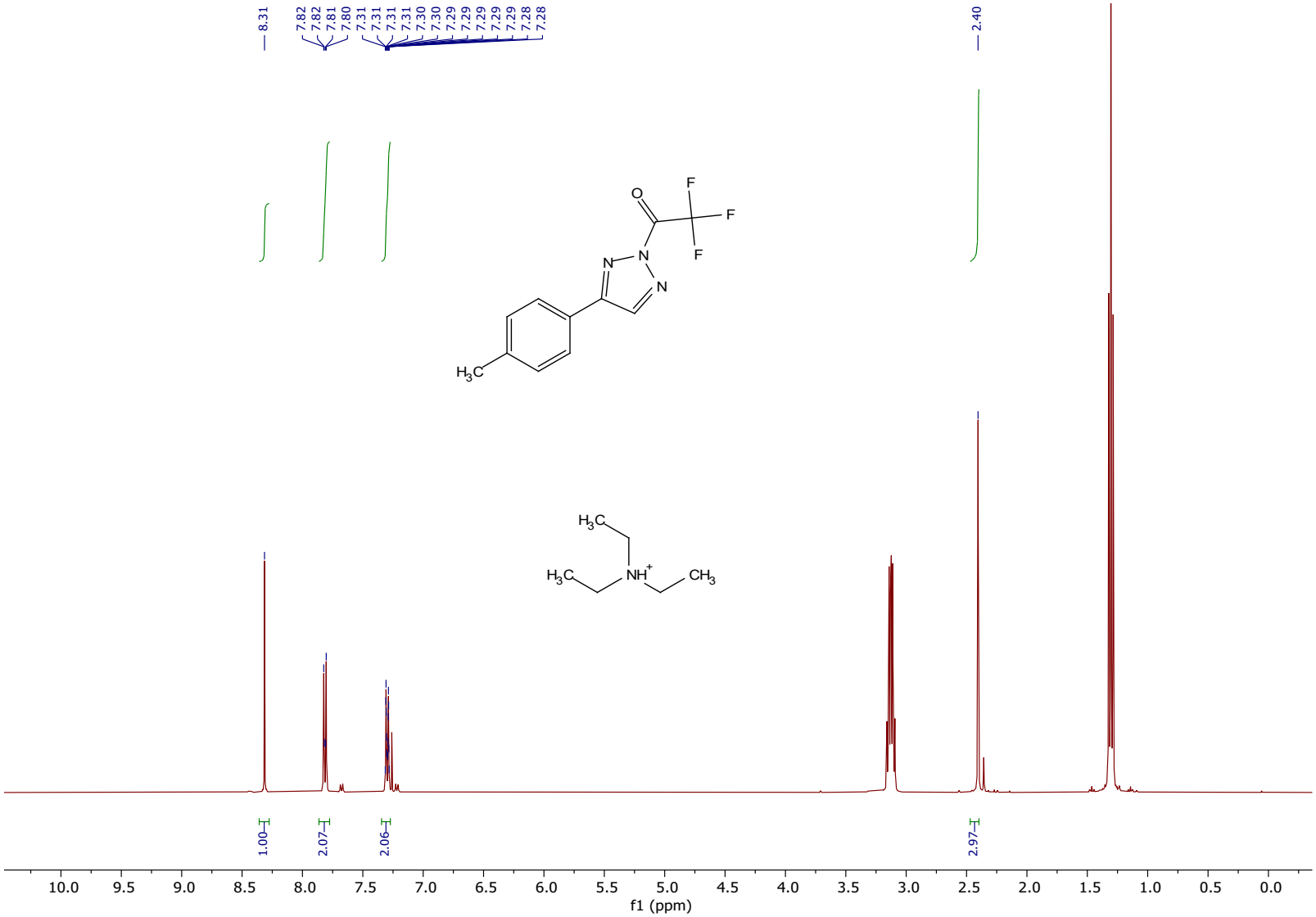

156.84
156.65
156.45
153.35
141.44
138.14
129.94
126.97
124.31
107.46
105.81
104.17
21.40
O
F
F
N
N
N
H3C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR

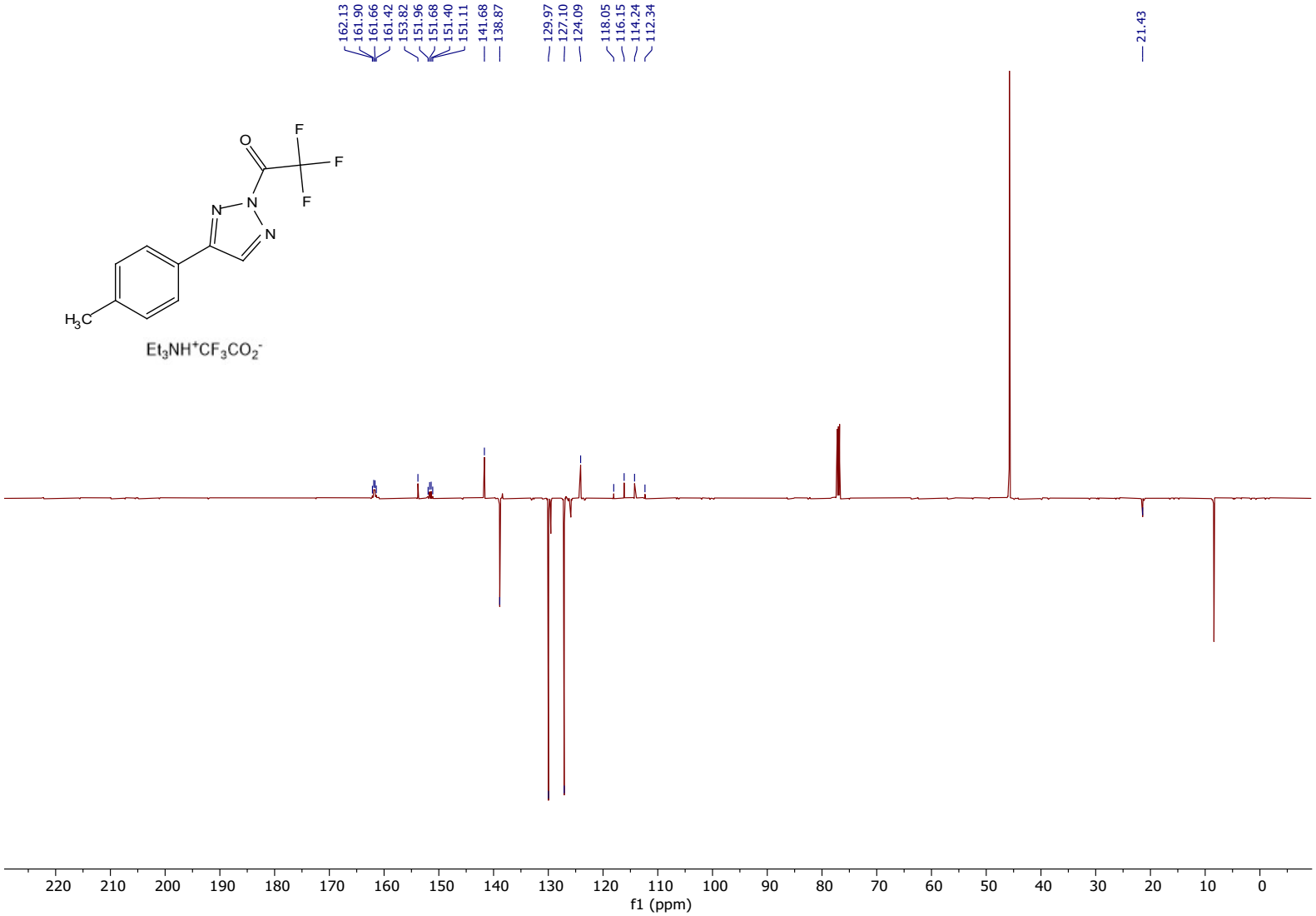

-126.68
-126.82
O
F
F
N
N
N
H3C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

2,2,2-trifluoro-1-(4-(*p*-tolyl)-2H-1,2,3-triazol-2-yl)ethan-1-one **3h**

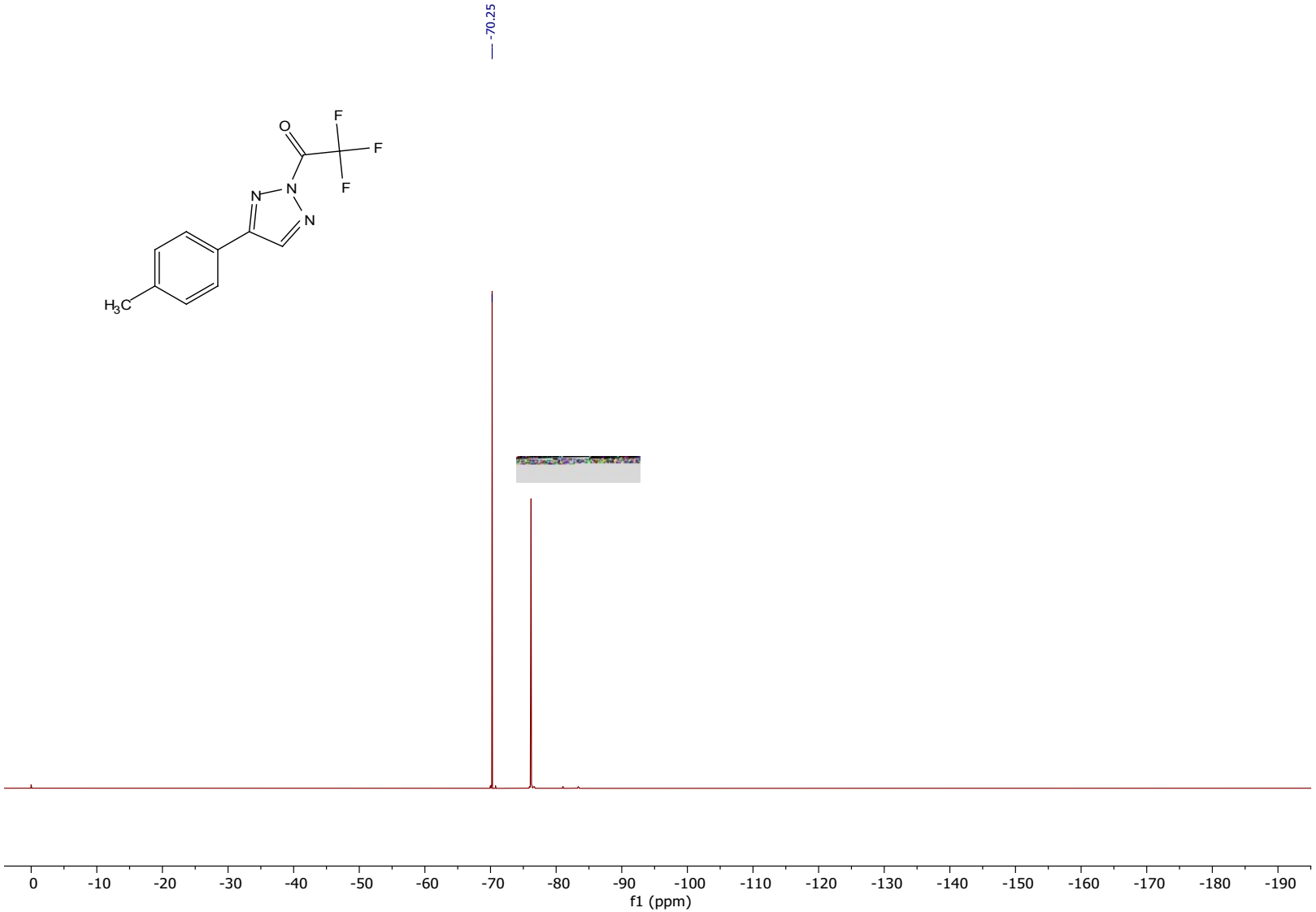
^{1}H NMR



^{13}C NMR

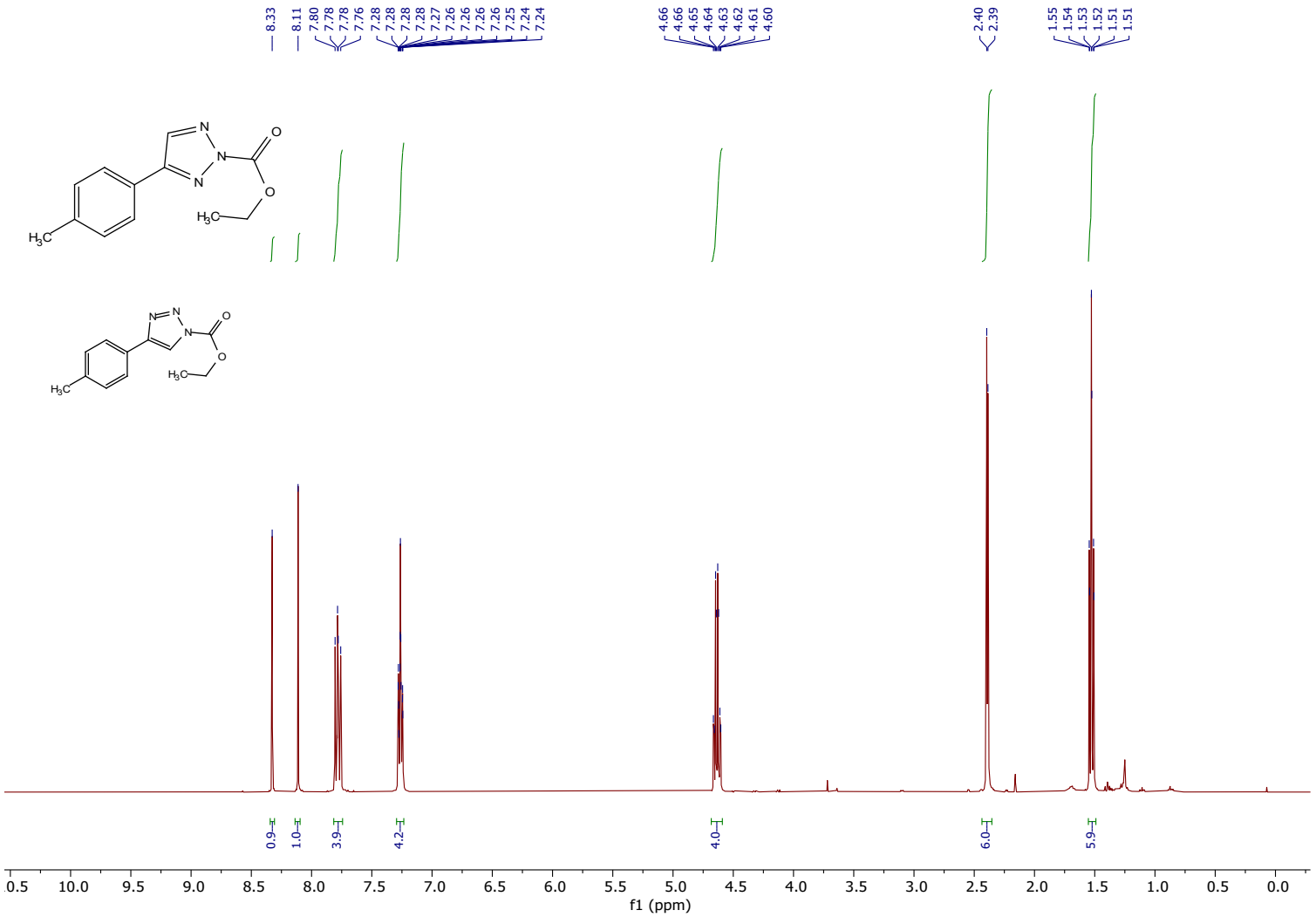

162.13
161.90
161.66
161.42
153.82
151.96
151.68
151.40
151.11
141.68
138.87
129.97
127.10
124.09
118.05
116.15
114.24
112.34
21.43
O
F
F
F
N
N
N
H3C
Et3NH+CF3CO2-
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{19}F NMR

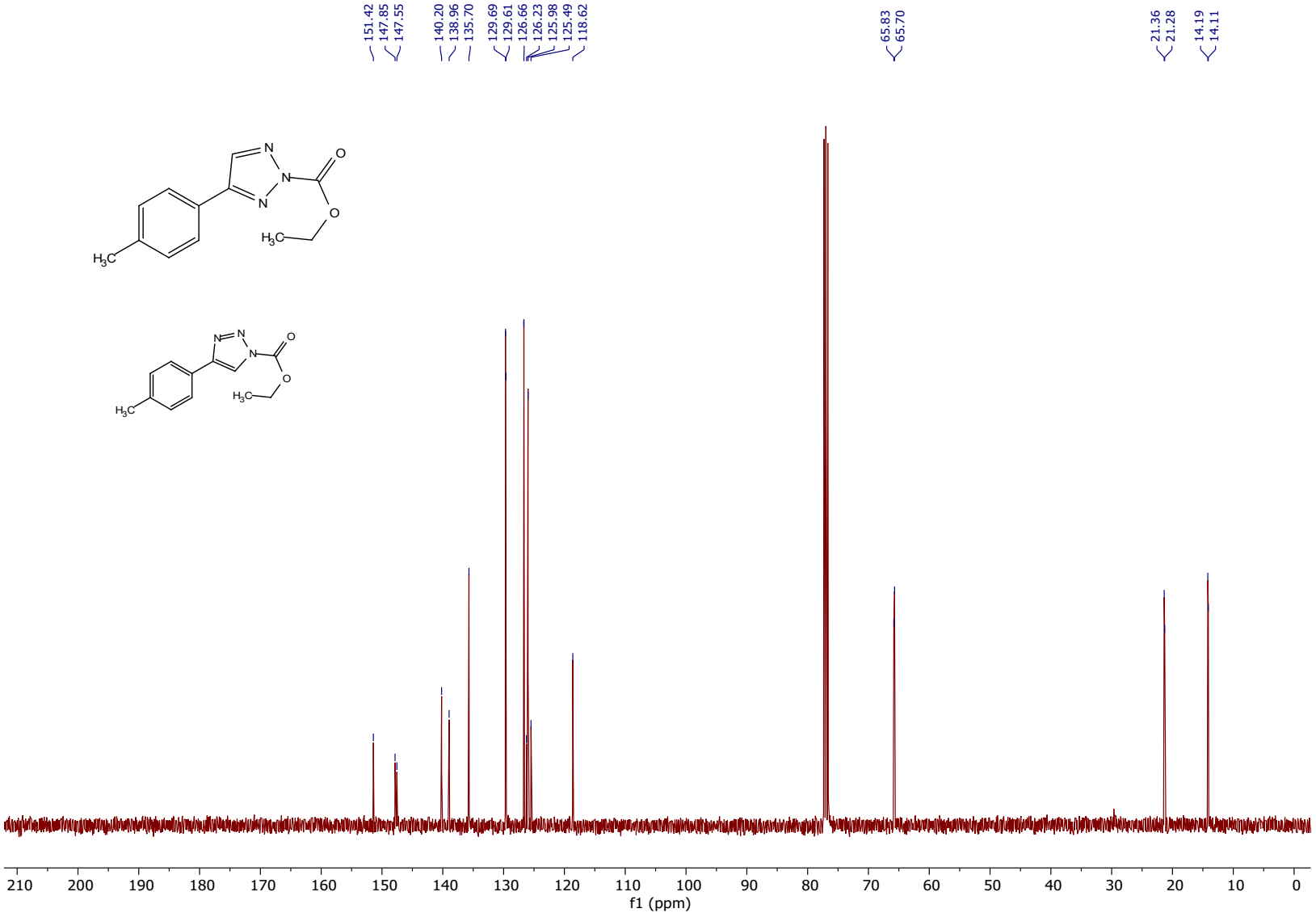

-70.25
O
F
F
F
N
N
N
H3C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Ethyl 4-(p-tolyl)-2H-1,2,3-triazole-2-carboxylate ***3i*** *and ethyl 4-(p-tolyl)-1H-1,2,3-triazole-1-carboxylate* ***2i***

^{1}H NMR

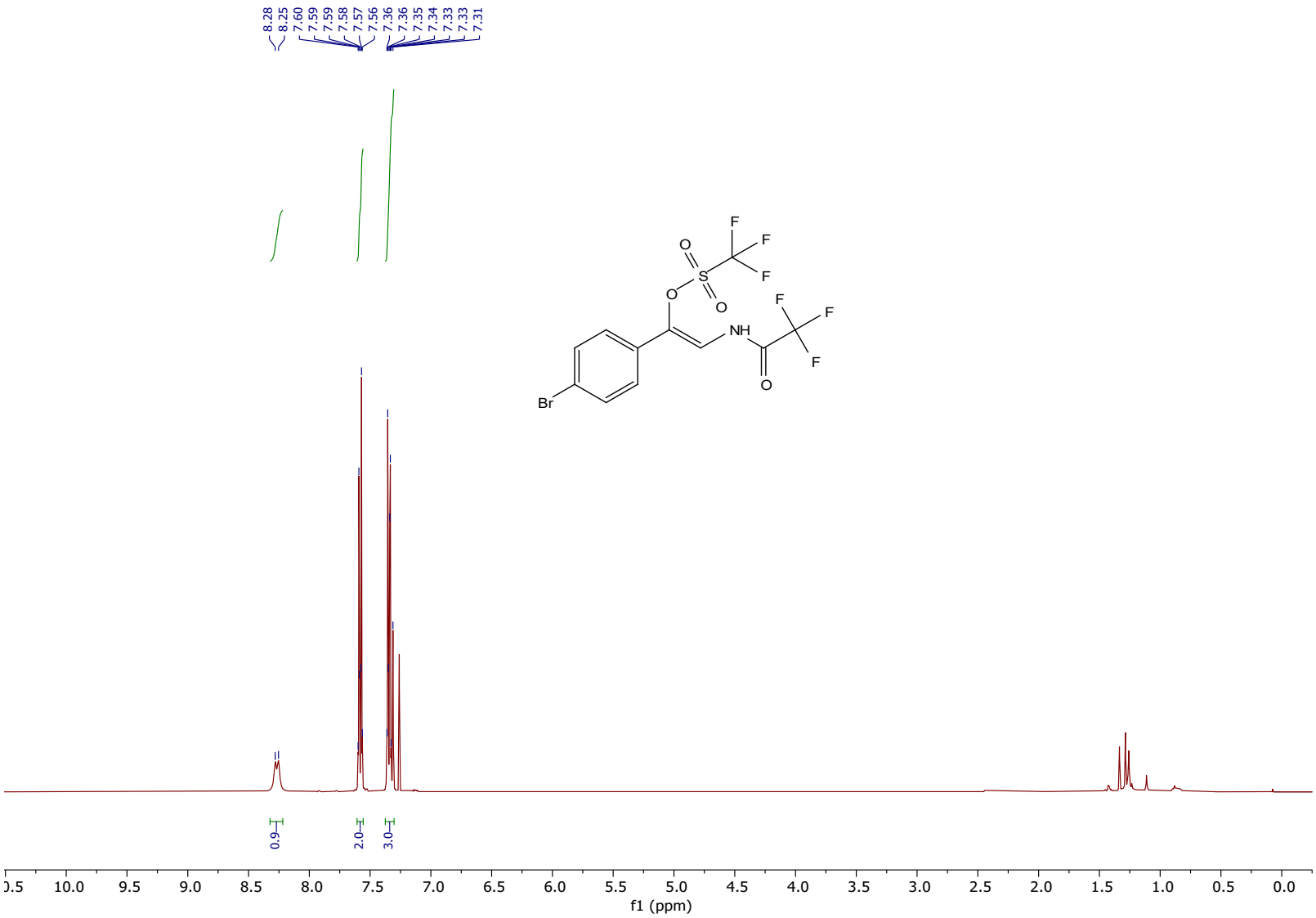


^{13}C NMR

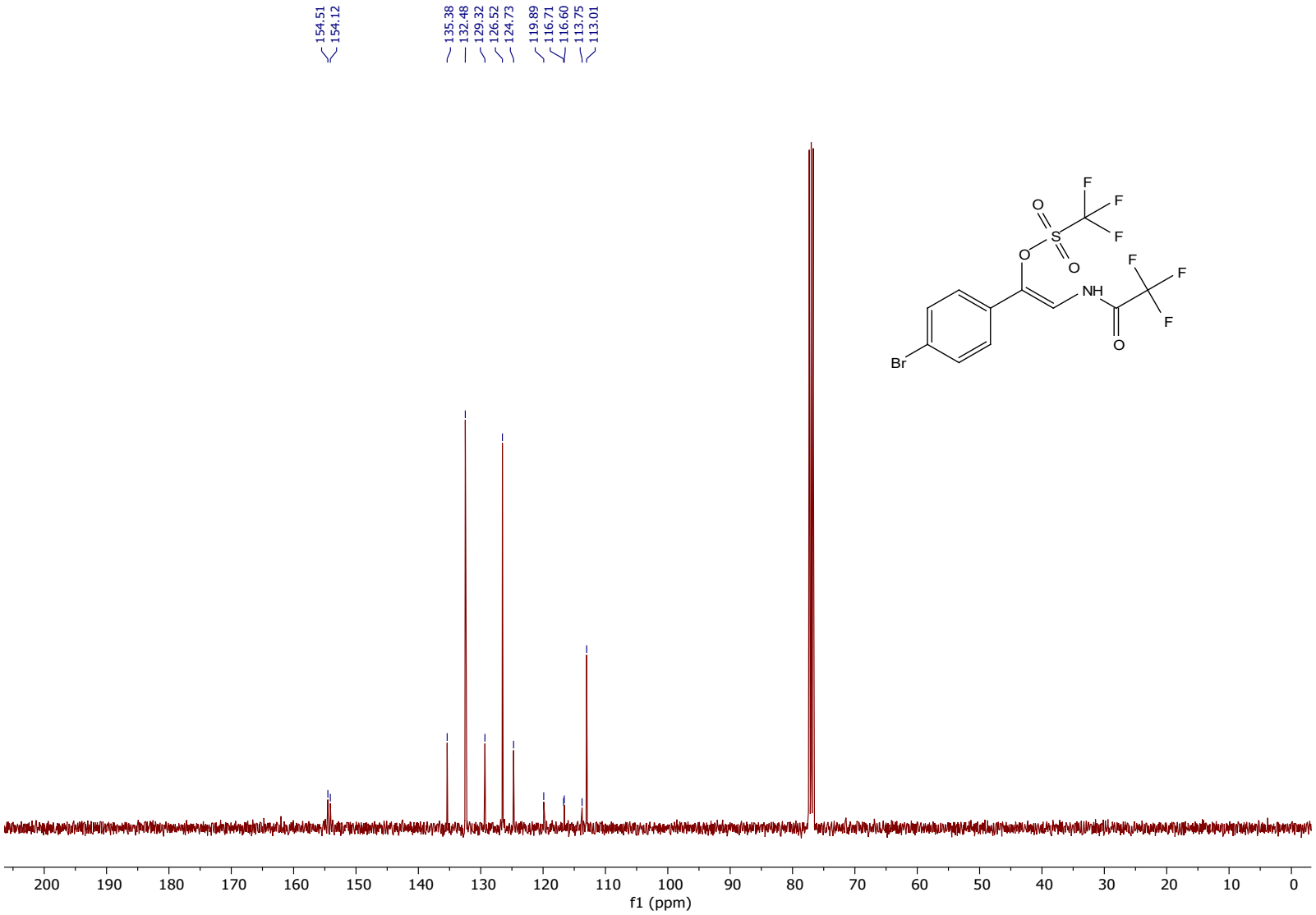

151.42
147.85
147.55
140.20
138.96
135.70
129.69
129.61
126.66
126.23
125.98
125.49
118.62
65.83
65.70
21.36
21.28
14.19
14.11
f1 (ppm)

(Z)-1-(4-bromophenyl)-2-(2,2,2-trifluoroacetamido)vinyl trifluoromethanesulfonate **4c**

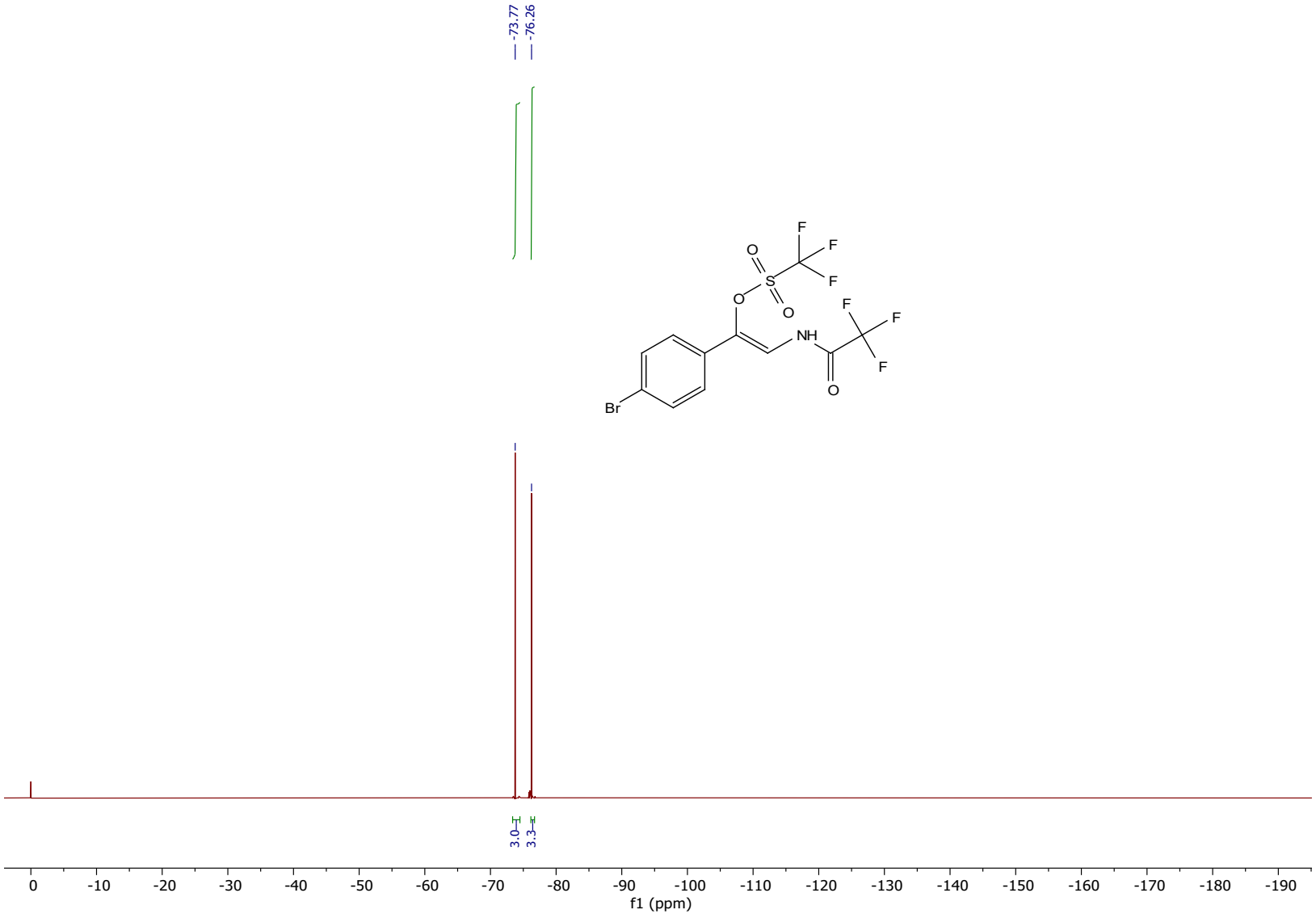
^{1}H NMR



^{13}C NMR

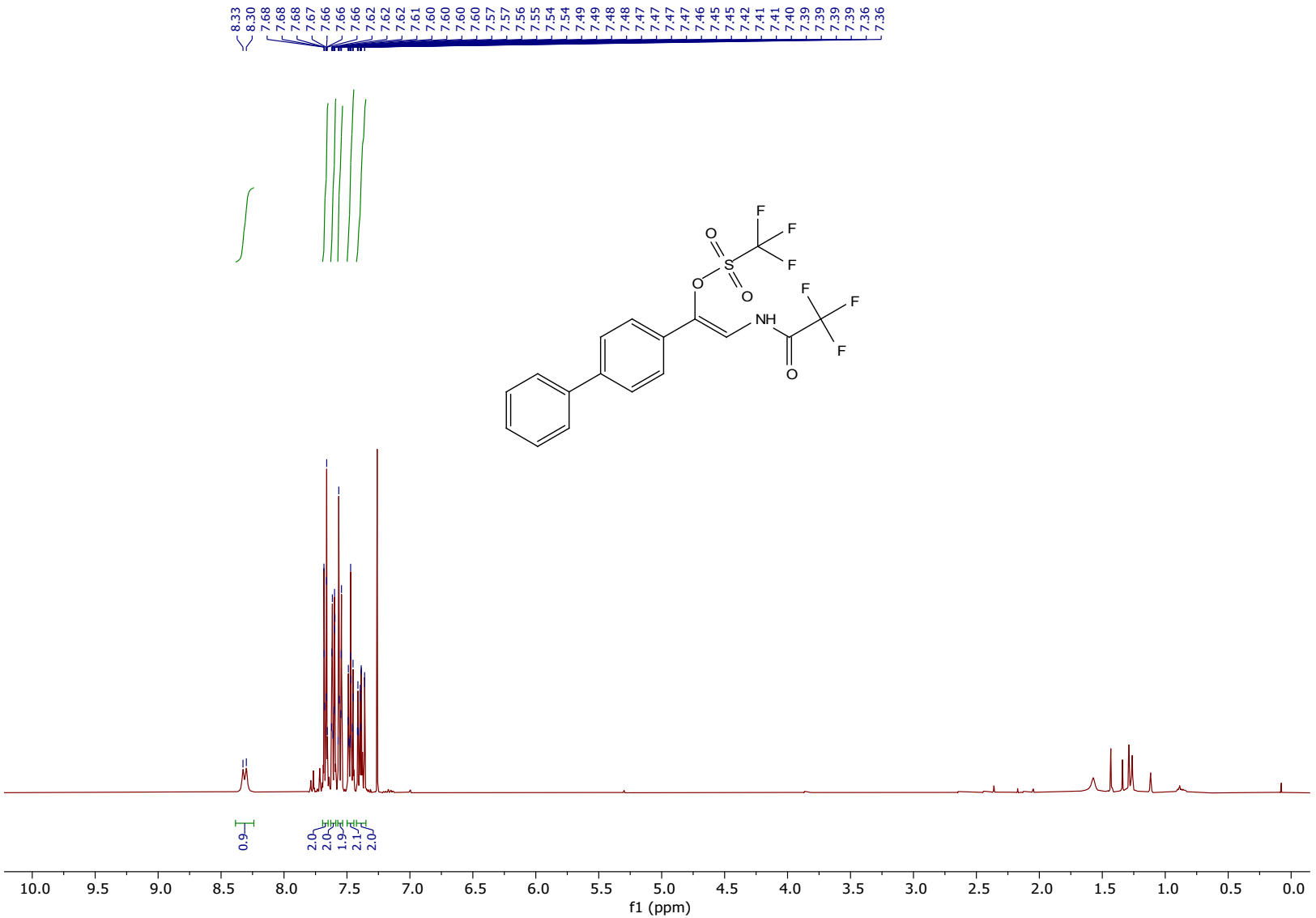

154.51
154.12
135.38
132.48
129.32
126.52
124.73
119.89
116.71
116.60
113.75
113.01
F
F
F
O
S
O
O
F
F
F
NH
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR

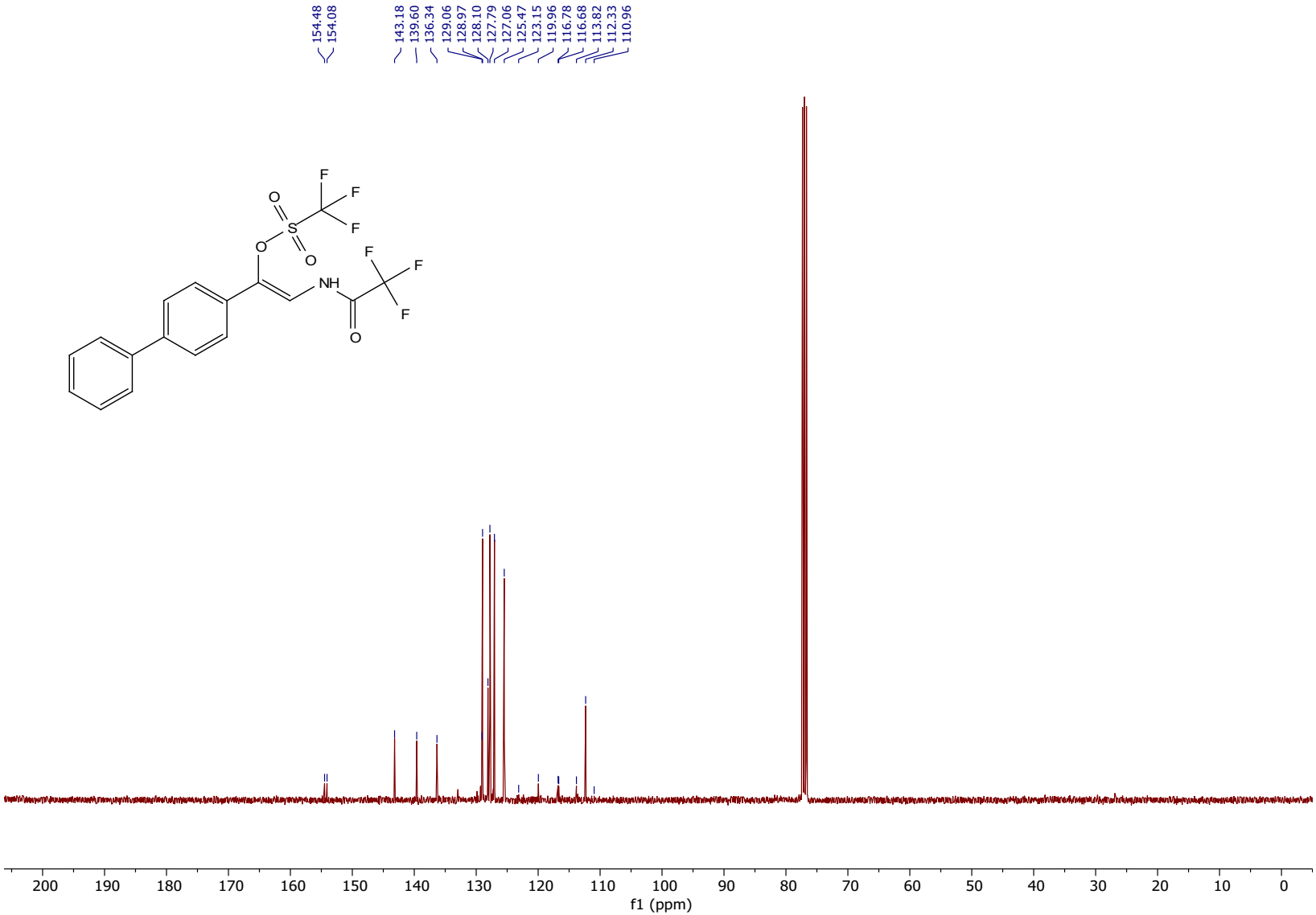

-73.77
-76.26
F
F
F
O
S
O
O
F
F
F
NH
O
Br
3.0
3.3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

(*Z*)-1-([1,1'-biphenyl]-4-yl)-2-(2,2,2-trifluoroacetamido)vinyl trifluoromethanesulfonate **4d**

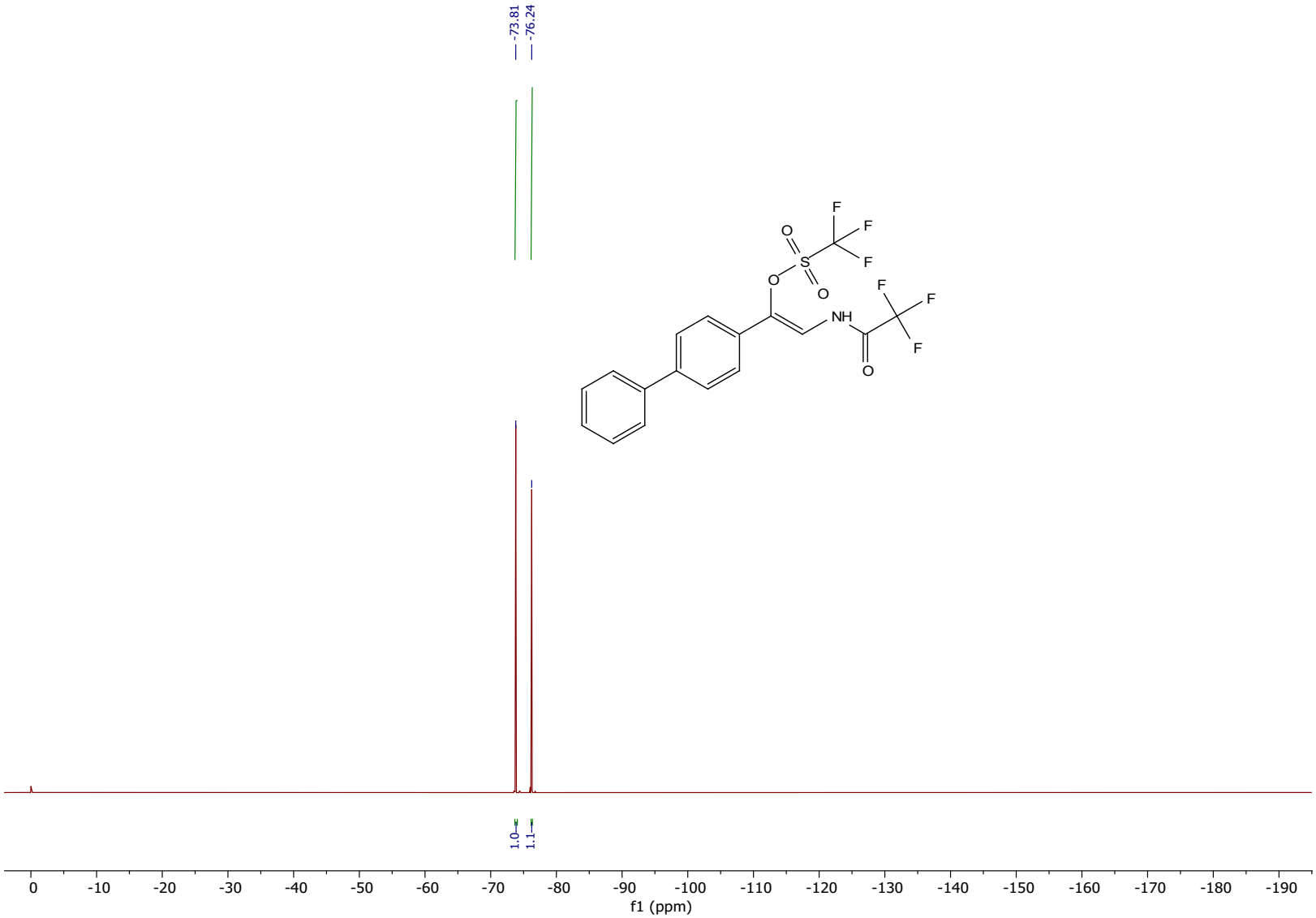
^{1}H NMR



^{13}C NMR

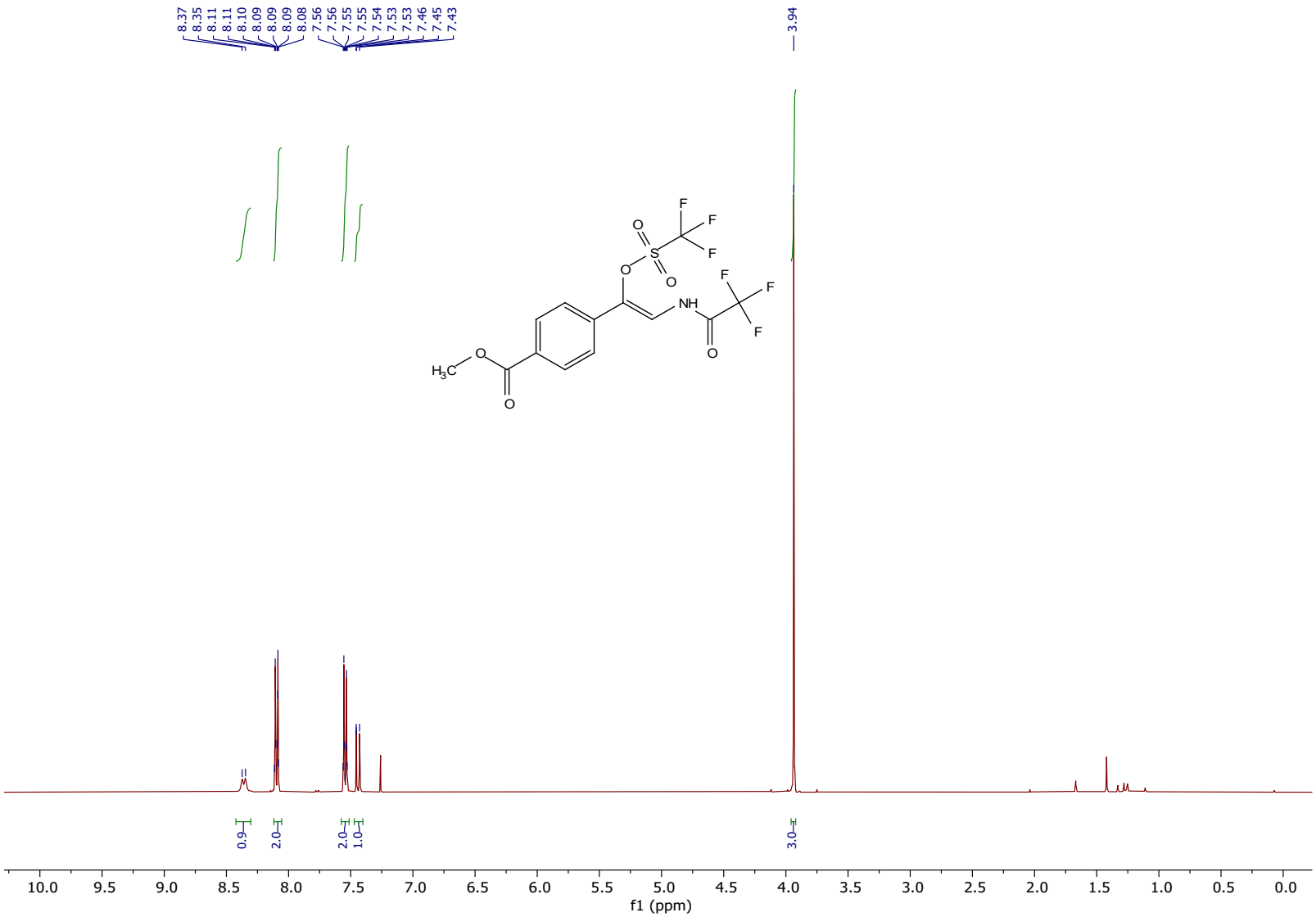

154.48
154.08
143.18
139.60
136.34
129.06
128.97
128.10
127.79
127.06
125.47
123.15
119.96
116.78
116.68
113.82
112.33
110.96
F
F
F
O
S
O
O
F
F
F
NH
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR

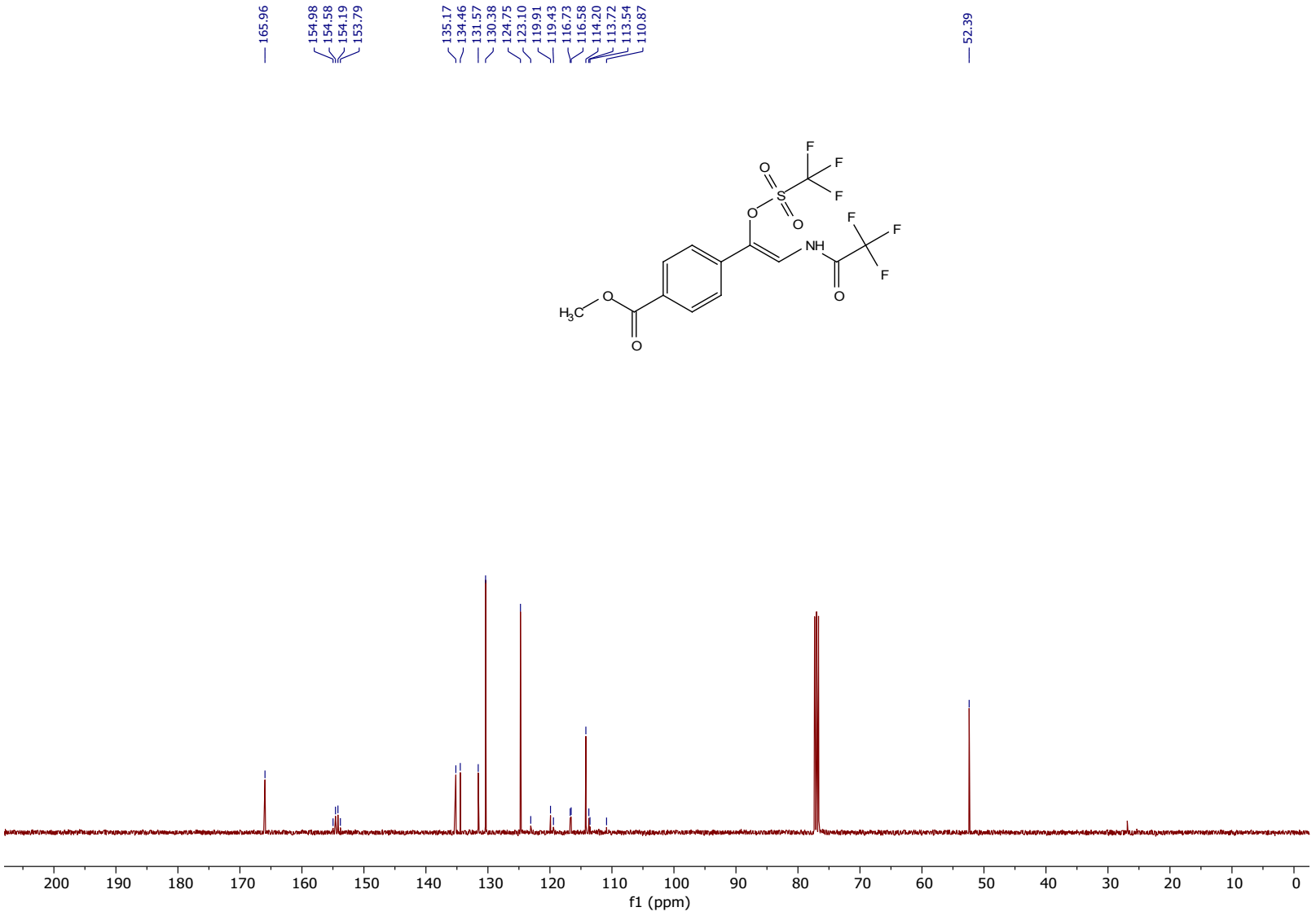

-73.81
-76.24
F
F
F
O
S
O
O
F
F
F
NH
O
1.0
1.1
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Methyl (*Z*)-4-(2-(2,2,2-trifluoroacetamido)-1-(((trifluoromethyl)sulfonyl)oxy)vinyl)benzoate **4e**

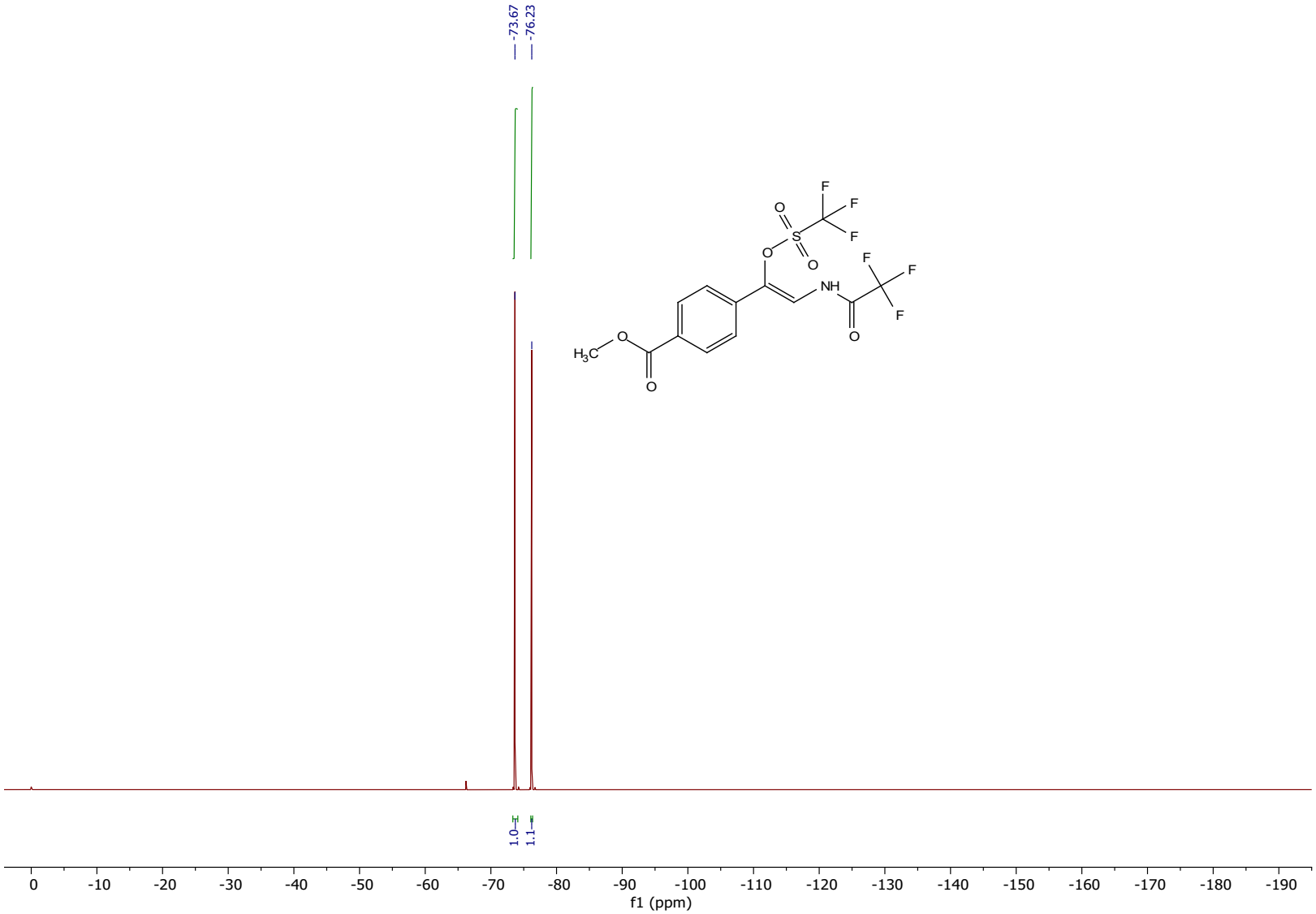
^{1}H NMR



^{13}C NMR

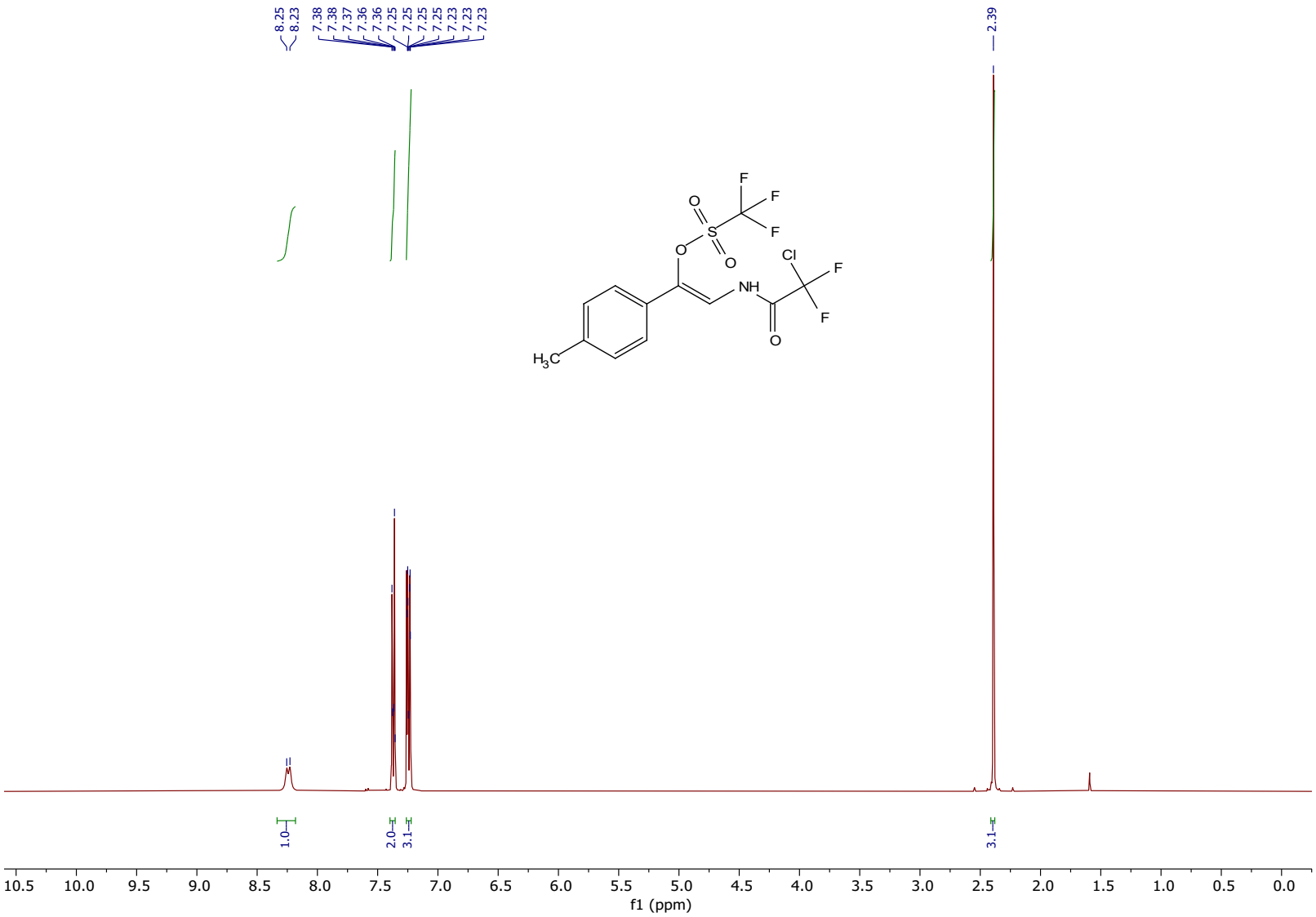

165.96
154.98
154.58
154.19
153.79
135.17
134.46
131.57
130.38
124.75
123.10
119.91
119.43
116.73
116.58
114.20
113.72
113.54
110.87
52.39
F
F
F
O
S
O
O
F
F
F
NH
O
O
H3C
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR

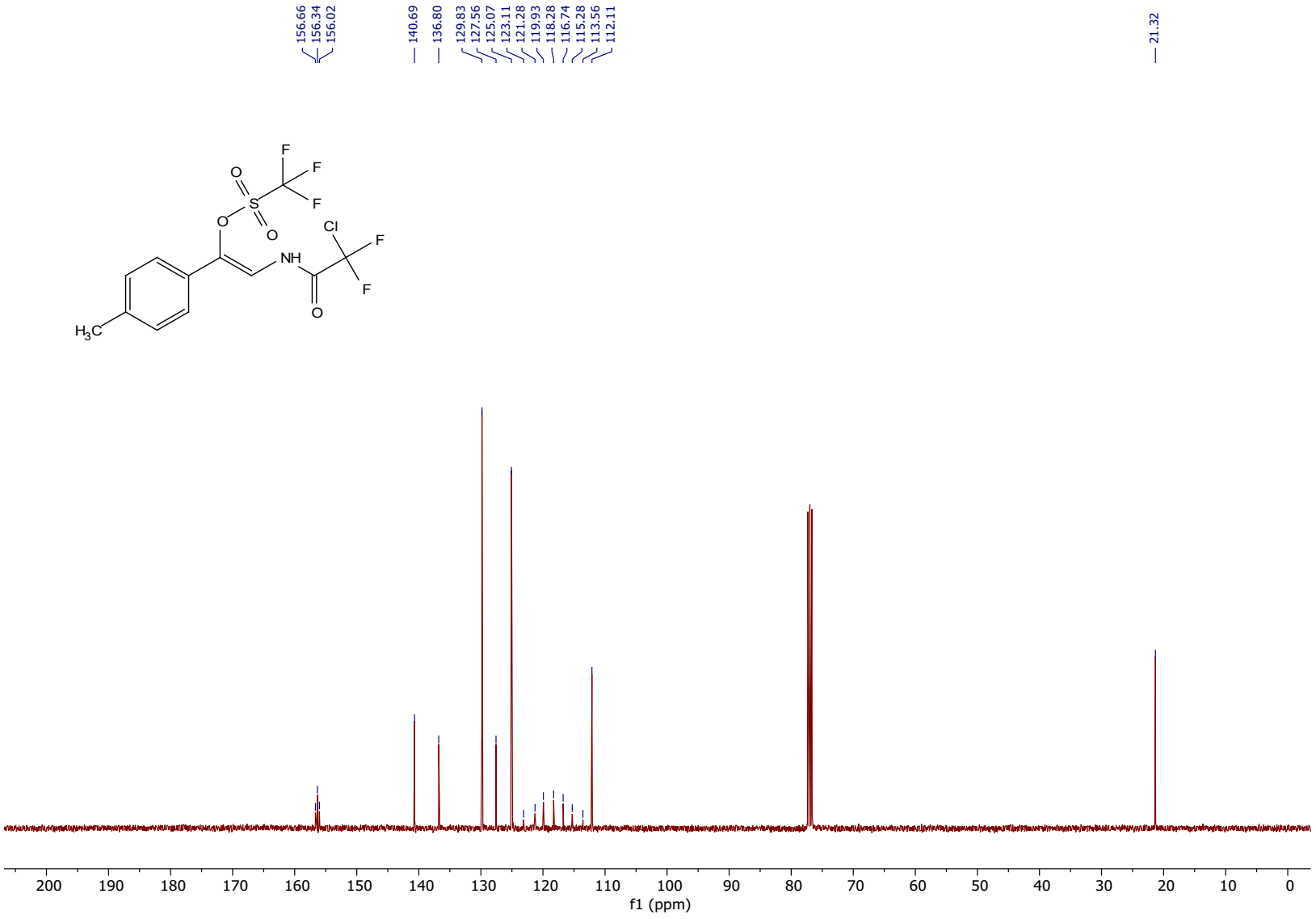

-73.67
-76.23
1.0
1.1
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

(*Z*)-2-(2-chloro-2,2-difluoroacetamido)-1-(*p*-tolyl)vinyl trifluoromethanesulfonate **4j**

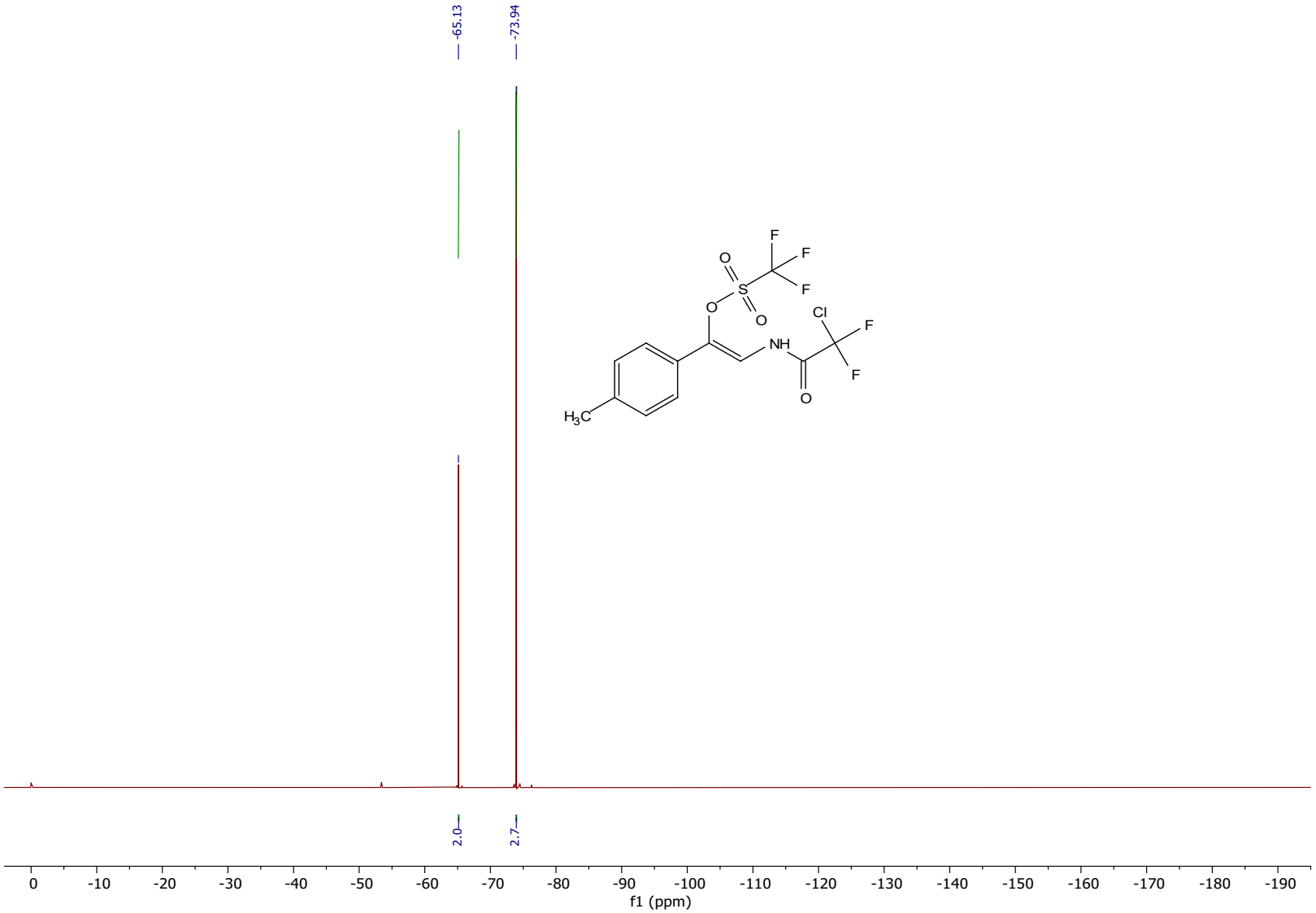
^{1}H NMR



^{13}C NMR

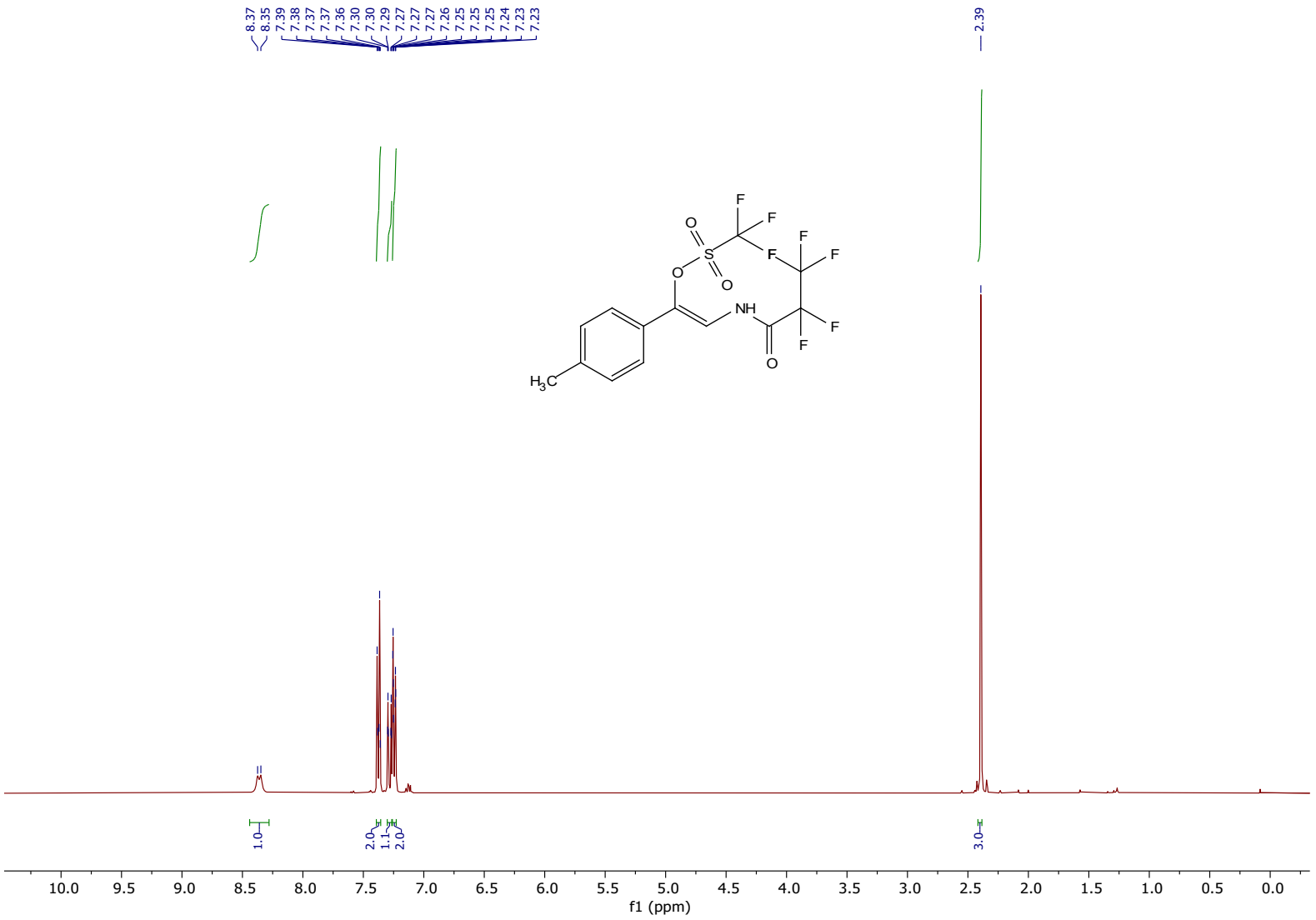

156.66
156.34
156.02
140.69
136.80
129.83
127.56
125.07
123.11
121.28
119.93
118.28
116.74
115.28
113.56
112.11
21.32
F
F
F
O
S
O
O
Cl
F
NH
F
O
H3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR

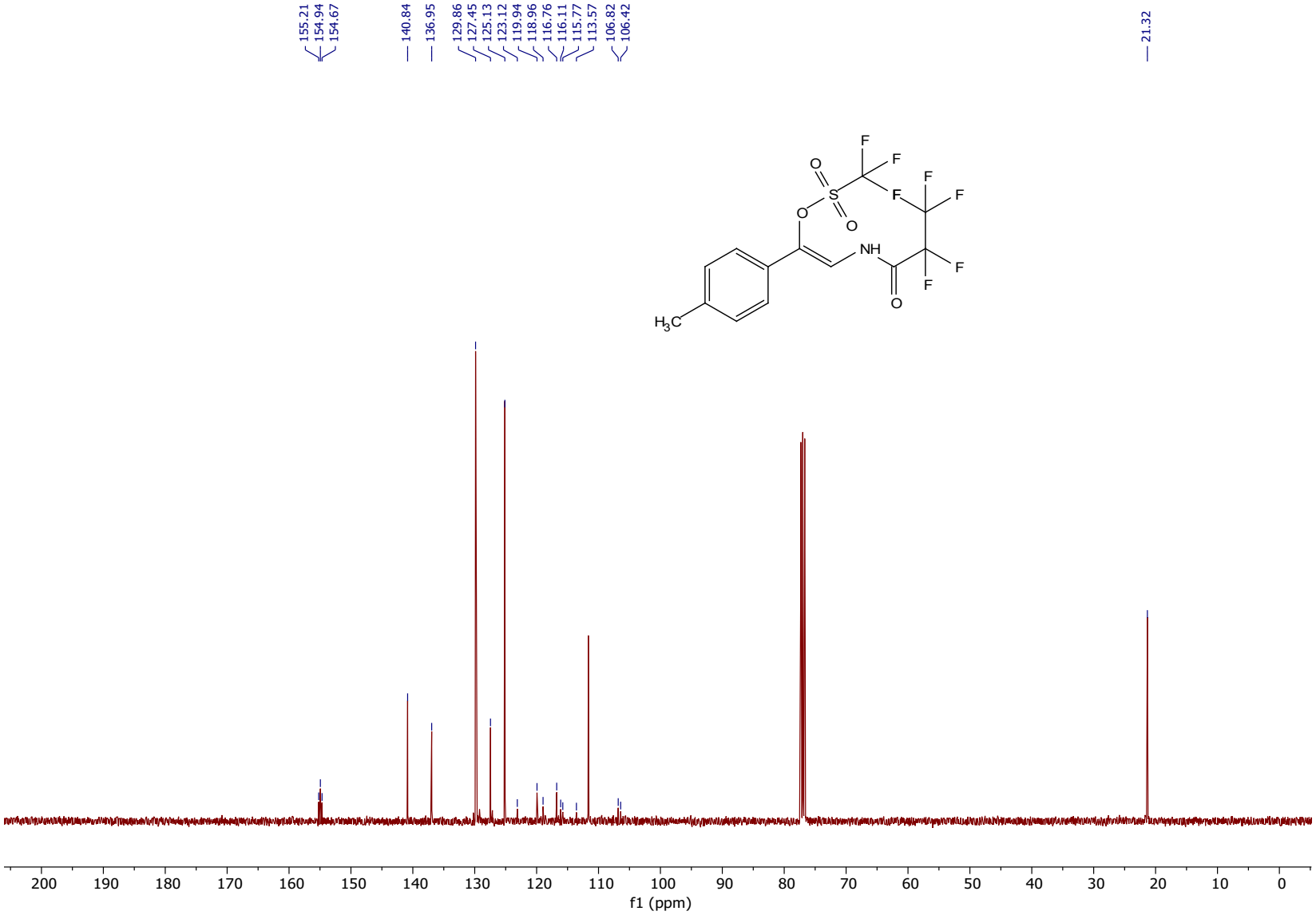

-65.13
-73.94
F
F
F
O
S
O
O
Cl
F
NH
F
O
H3C
2.0
2.7
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

(*Z*)-2-(2,2,3,3,3-pentafluoropropanamido)-1-(*p*-tolyl)vinyl trifluoromethanesulfonate **4k**

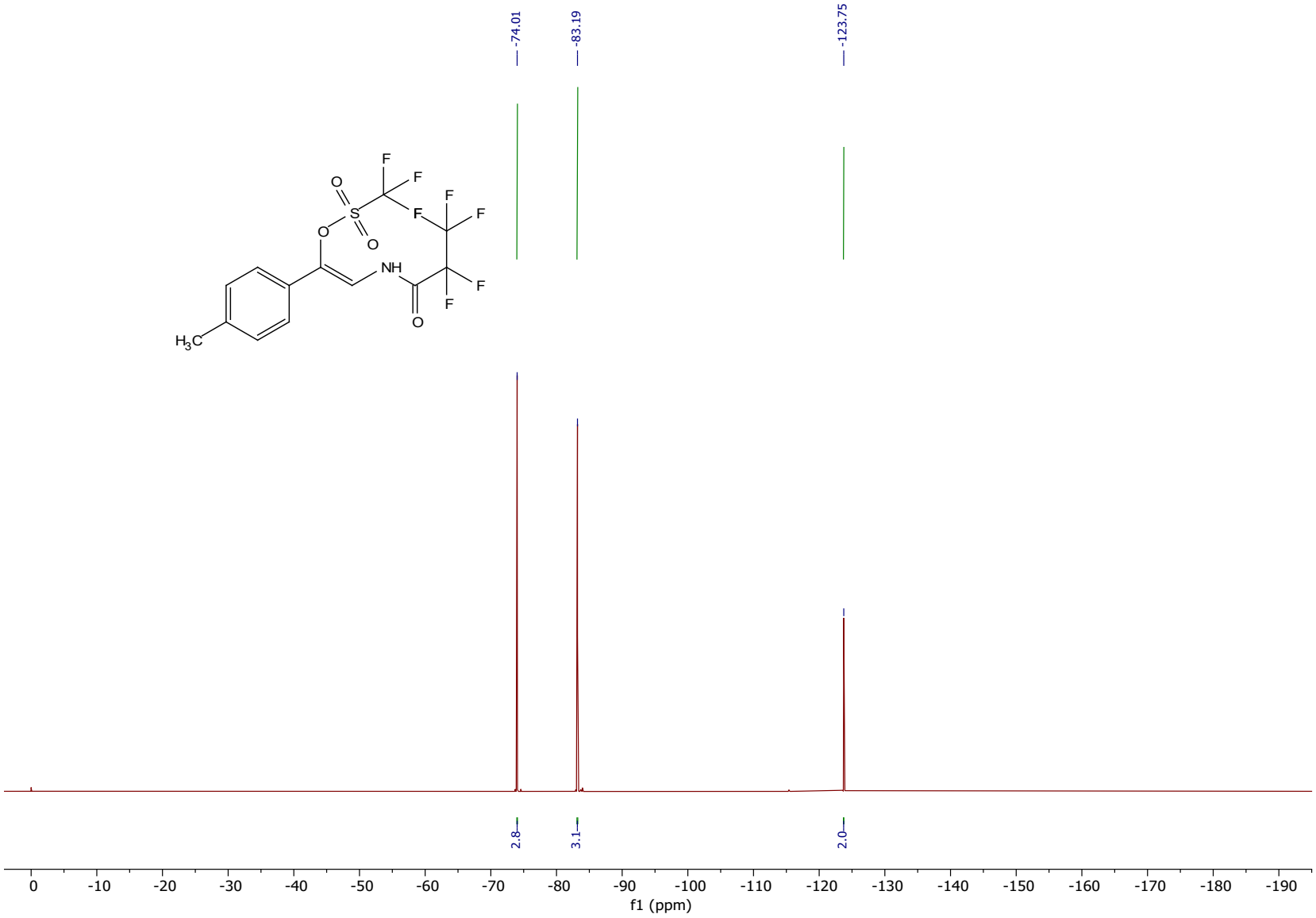
^{1}H NMR



^{13}C NMR

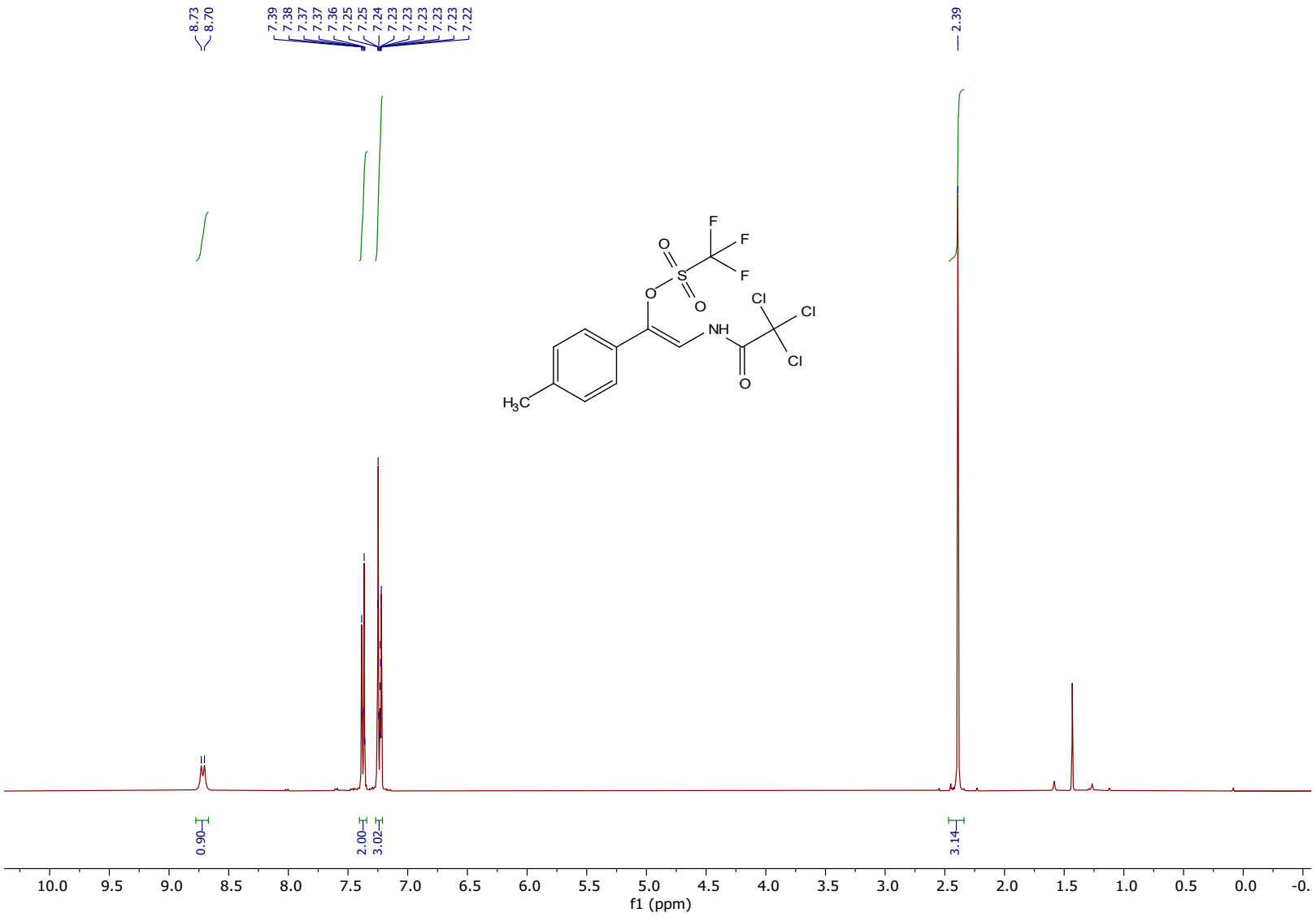

155.21
154.94
154.67
140.84
136.95
129.86
127.45
125.13
123.12
119.94
118.96
116.76
116.11
115.77
113.57
106.82
106.42
21.32
F
F
F
F
F
F
F
F
O
S
O
O
NH
O
H3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR

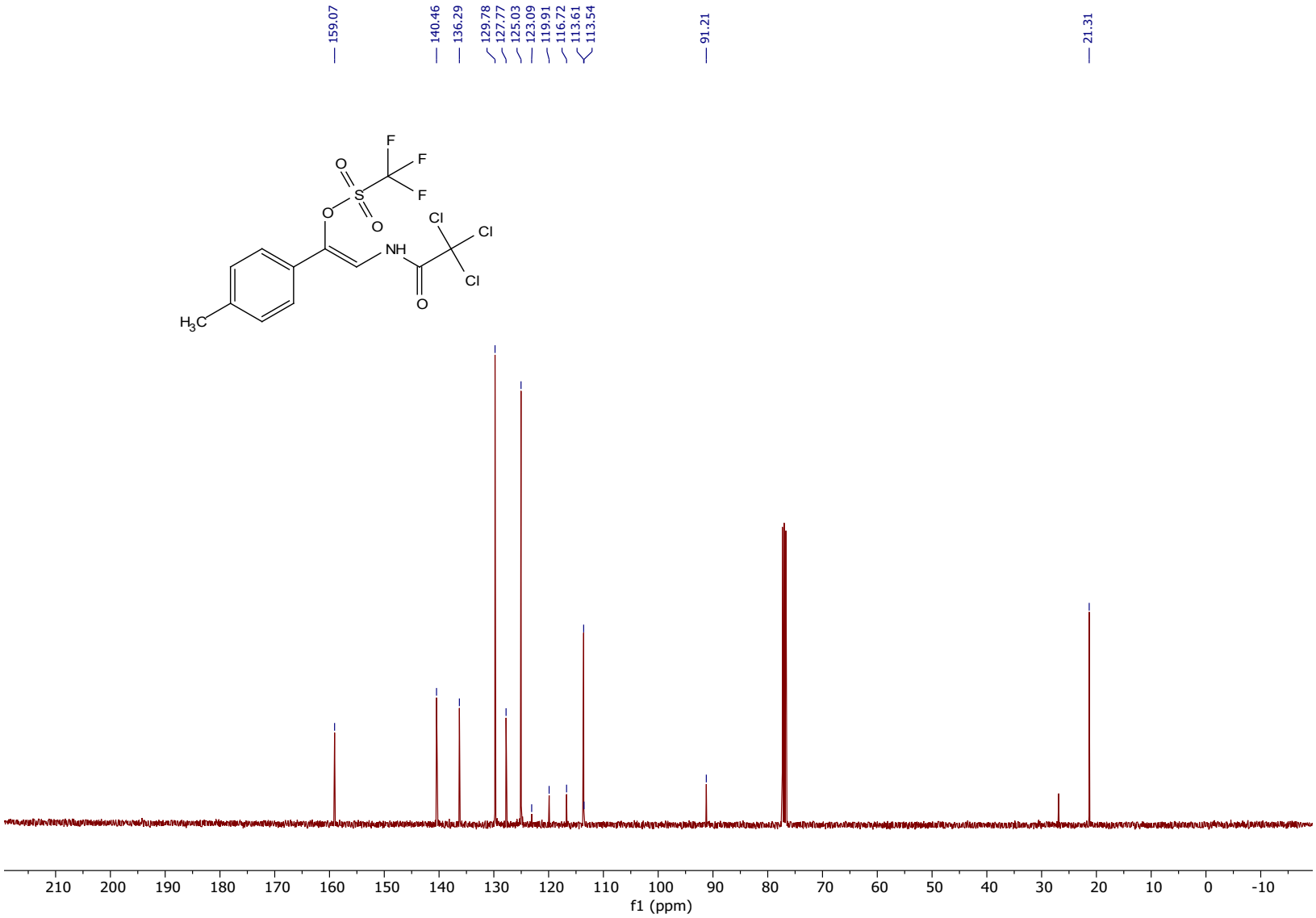

-74.01
-83.19
-123.75
F
F
F
F
F
F
F
O
S
O
O
NH
O
H3C
2.8
3.1
2.0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

(*Z*)-1-(*p*-tolyl)-2-(2,2,2-trichloroacetamido)vinyl trifluoromethanesulfonate **4m**

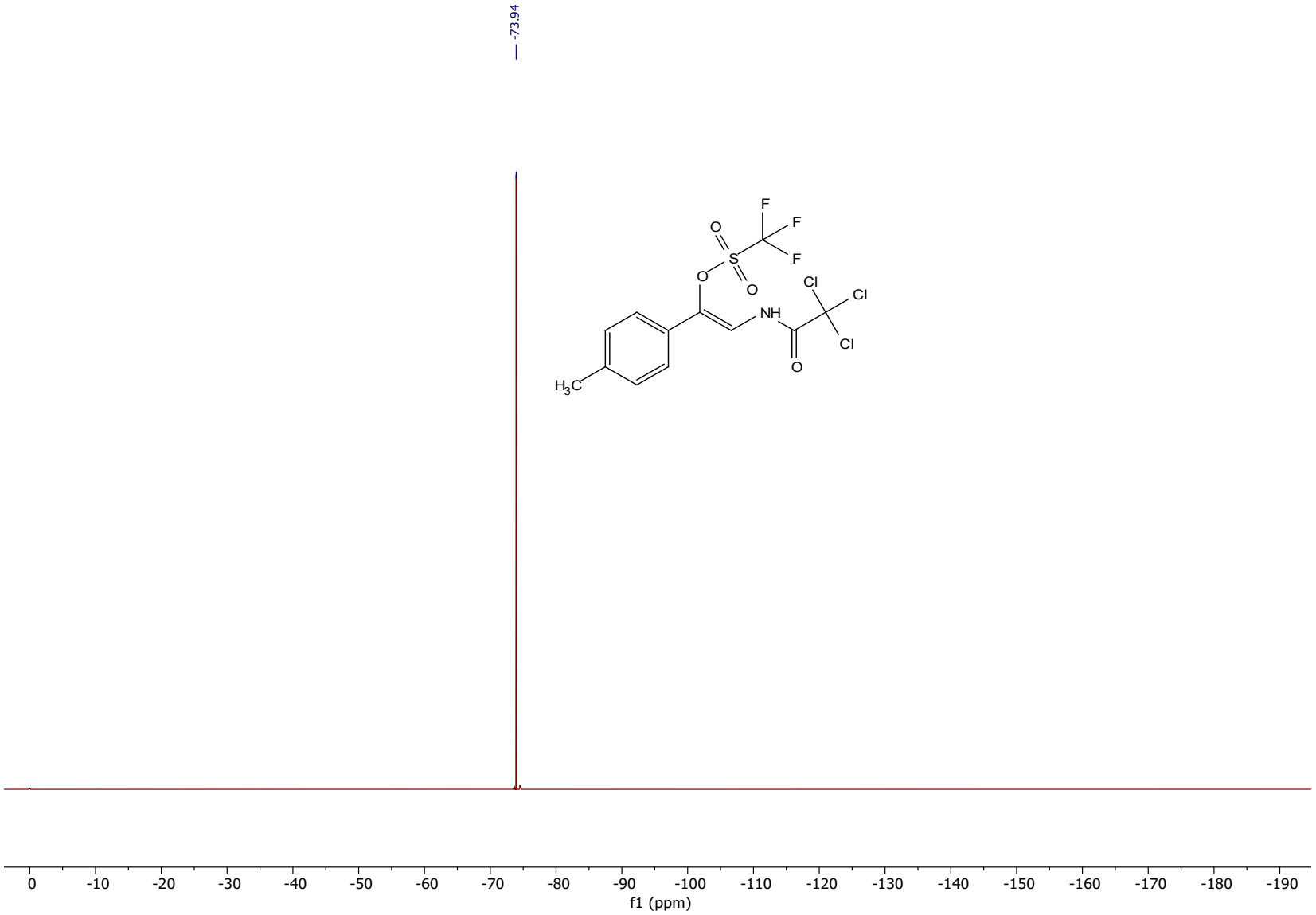
^{1}H NMR



^{13}C NMR

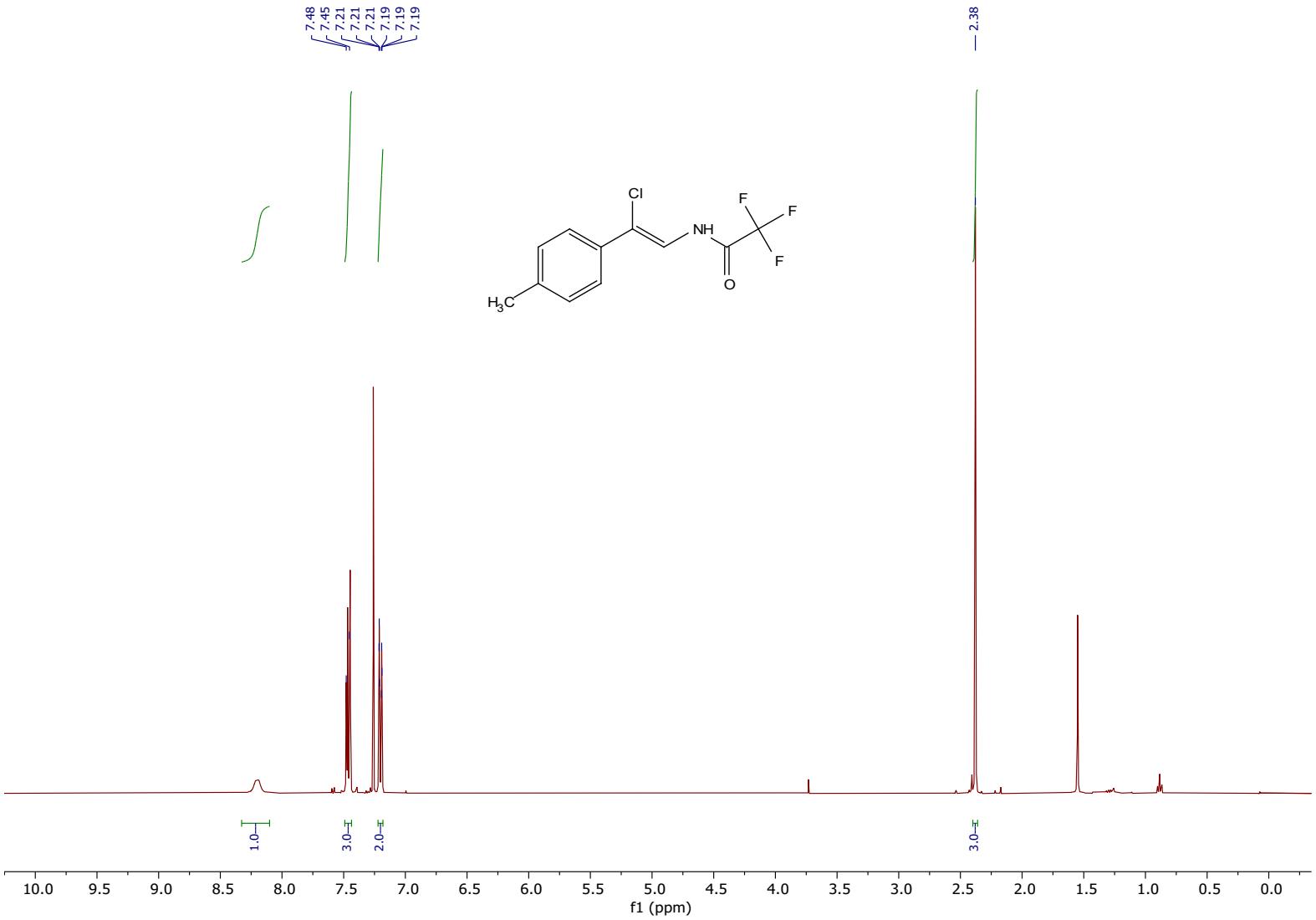

159.07
140.46
136.29
129.78
127.77
125.03
123.09
119.91
116.72
113.61
113.54
91.21
21.31
F
F
F
O
S
O
O
Cl
Cl
Cl
NH
O
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR

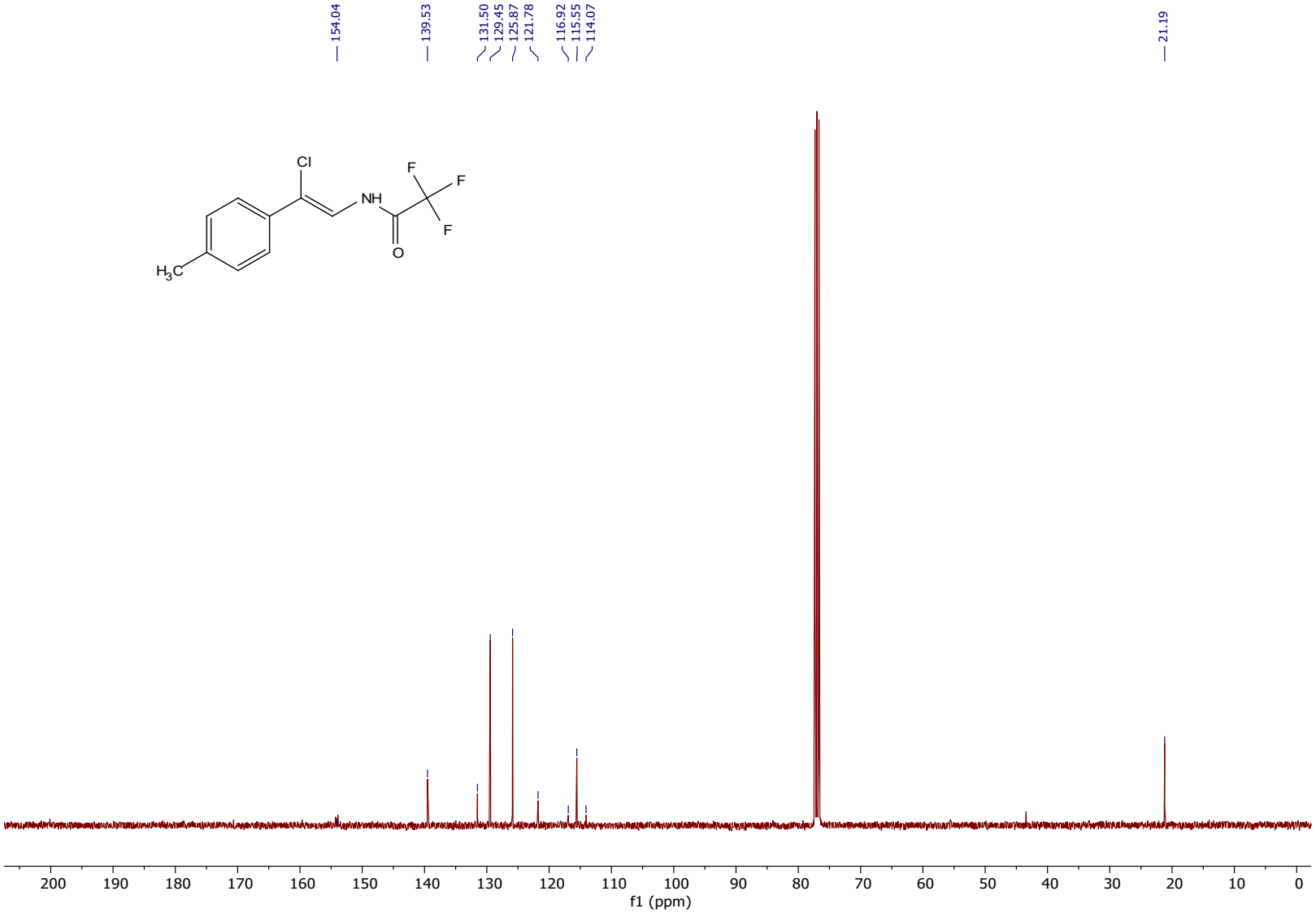

-73.94
F
F
F
O
S
O
O
Cl
Cl
Cl
NH
O
H3C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

(*Z*)-N-(2-chloro-2-(*p*-tolyl)vinyl)-2,2,2-trifluoroacetamide **5a**

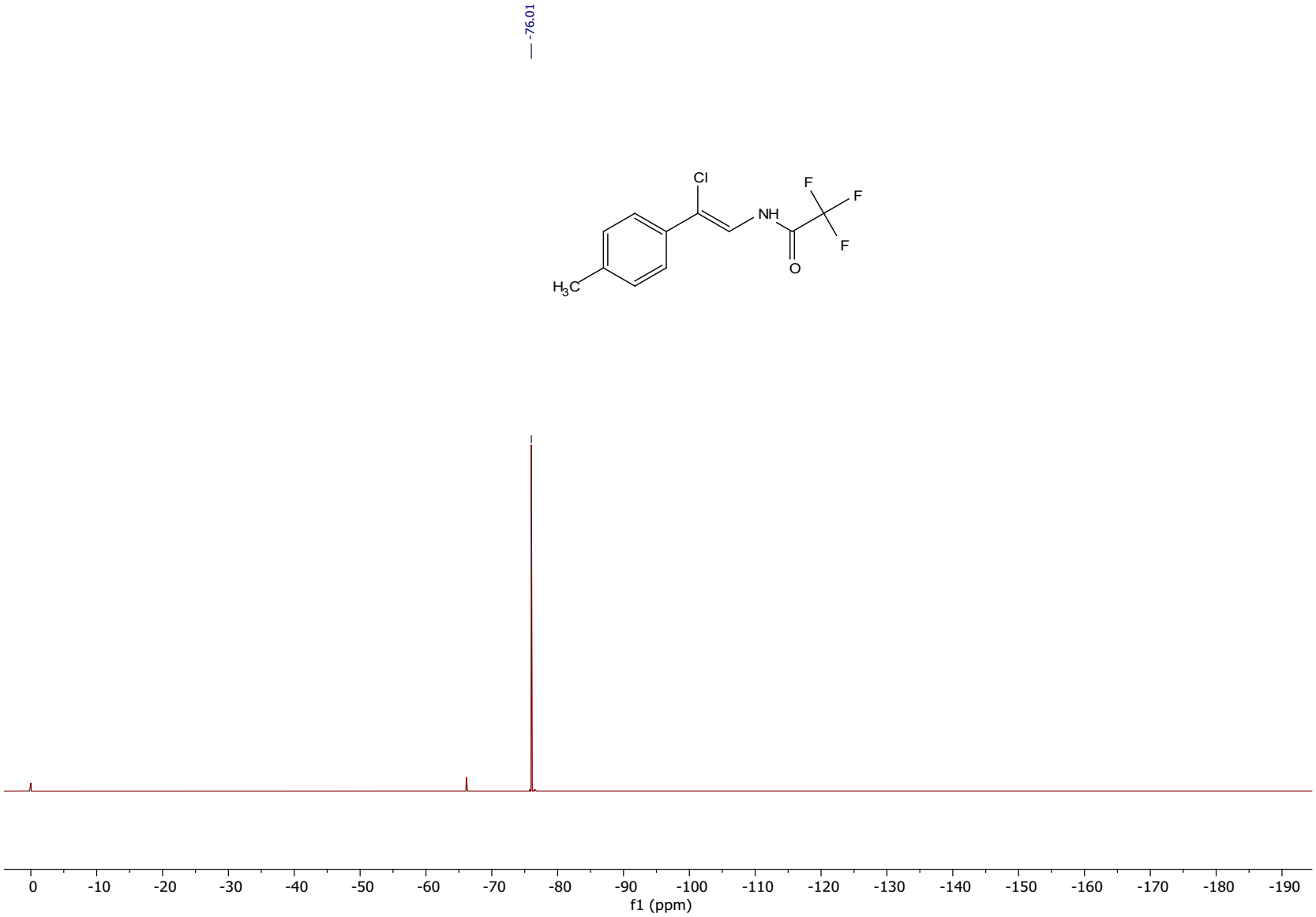
^{1}H NMR



^{13}C NMR

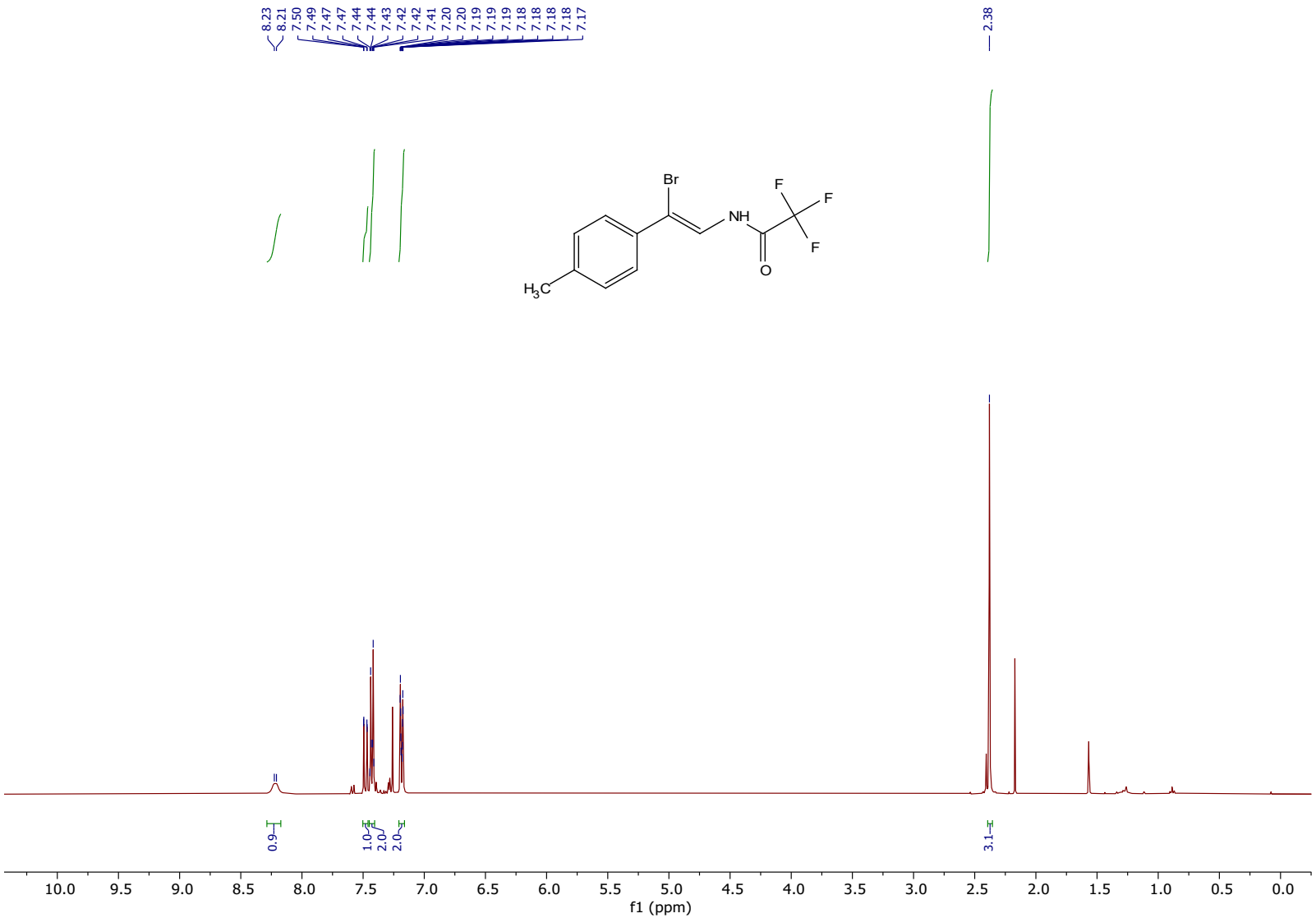

154.04
139.53
131.50
129.45
125.87
121.78
116.92
115.55
114.07
21.19
Cl
NH
F
F
F
O
H3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR

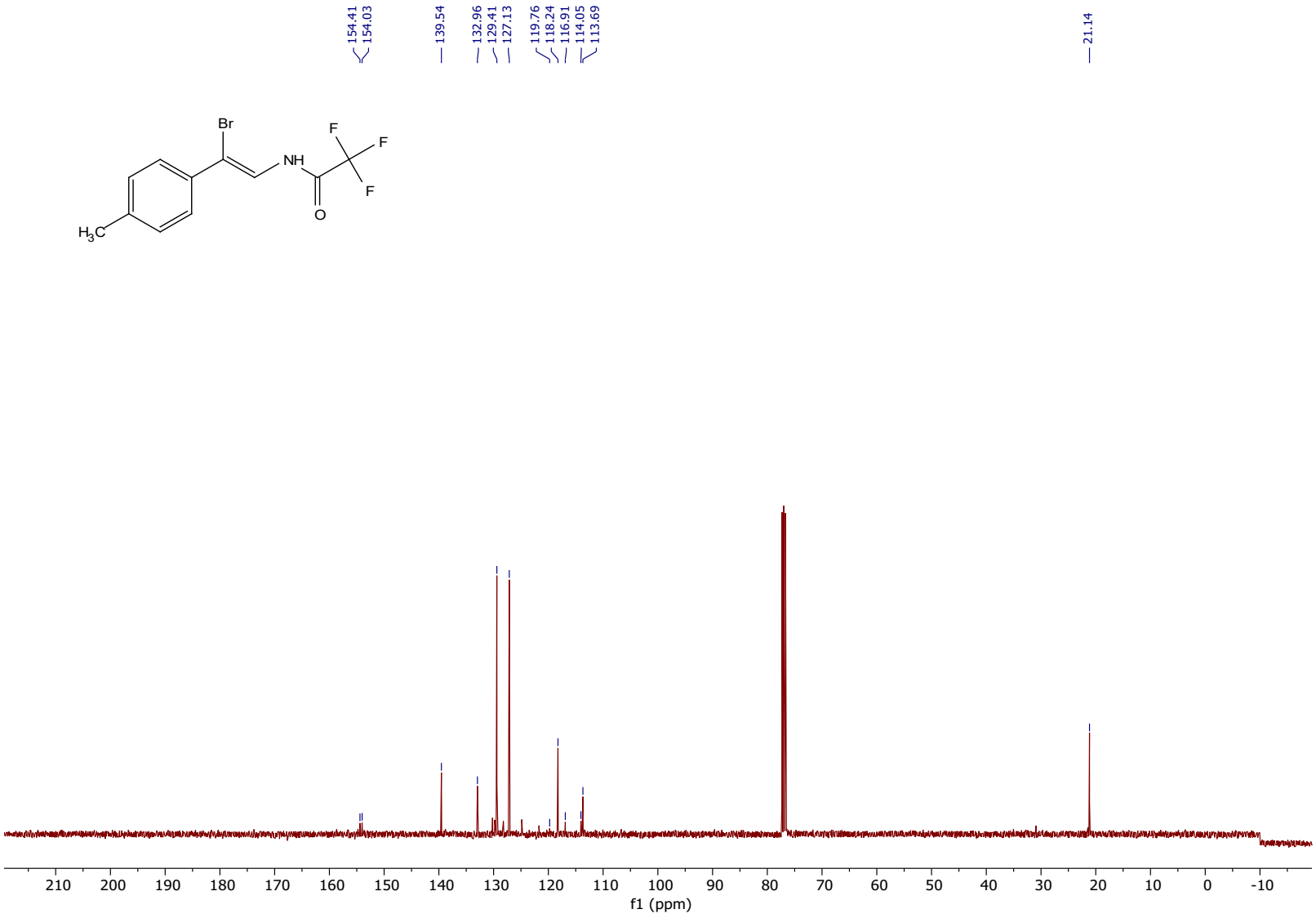

-76.01
Cl
NH
F
F
F
O
H3C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

(*Z*)-N-(2-bromo-2-(*p*-tolyl)vinyl)-2,2,2-trifluoroacetamide **5b**

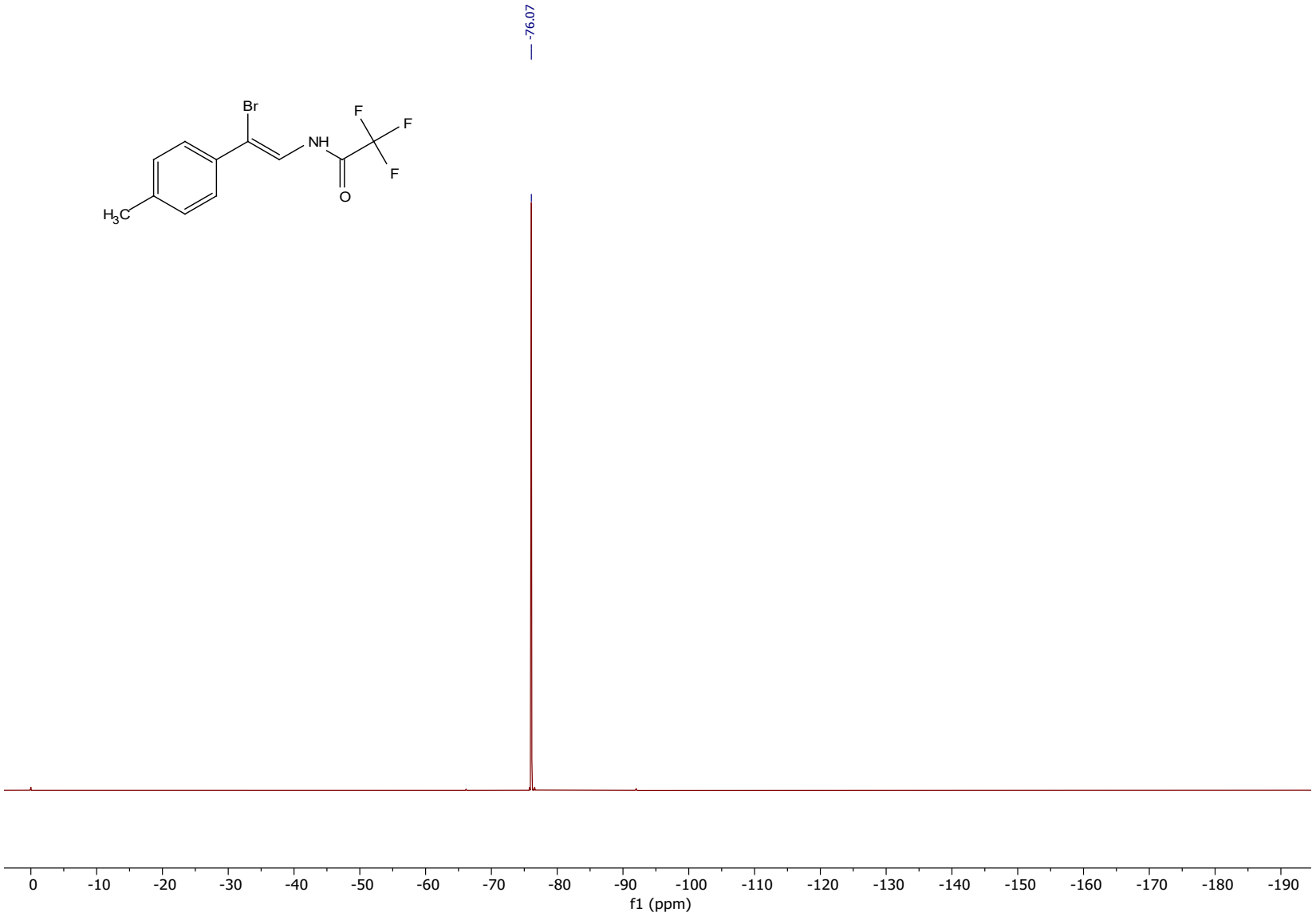
^{1}H NMR



^{13}C NMR

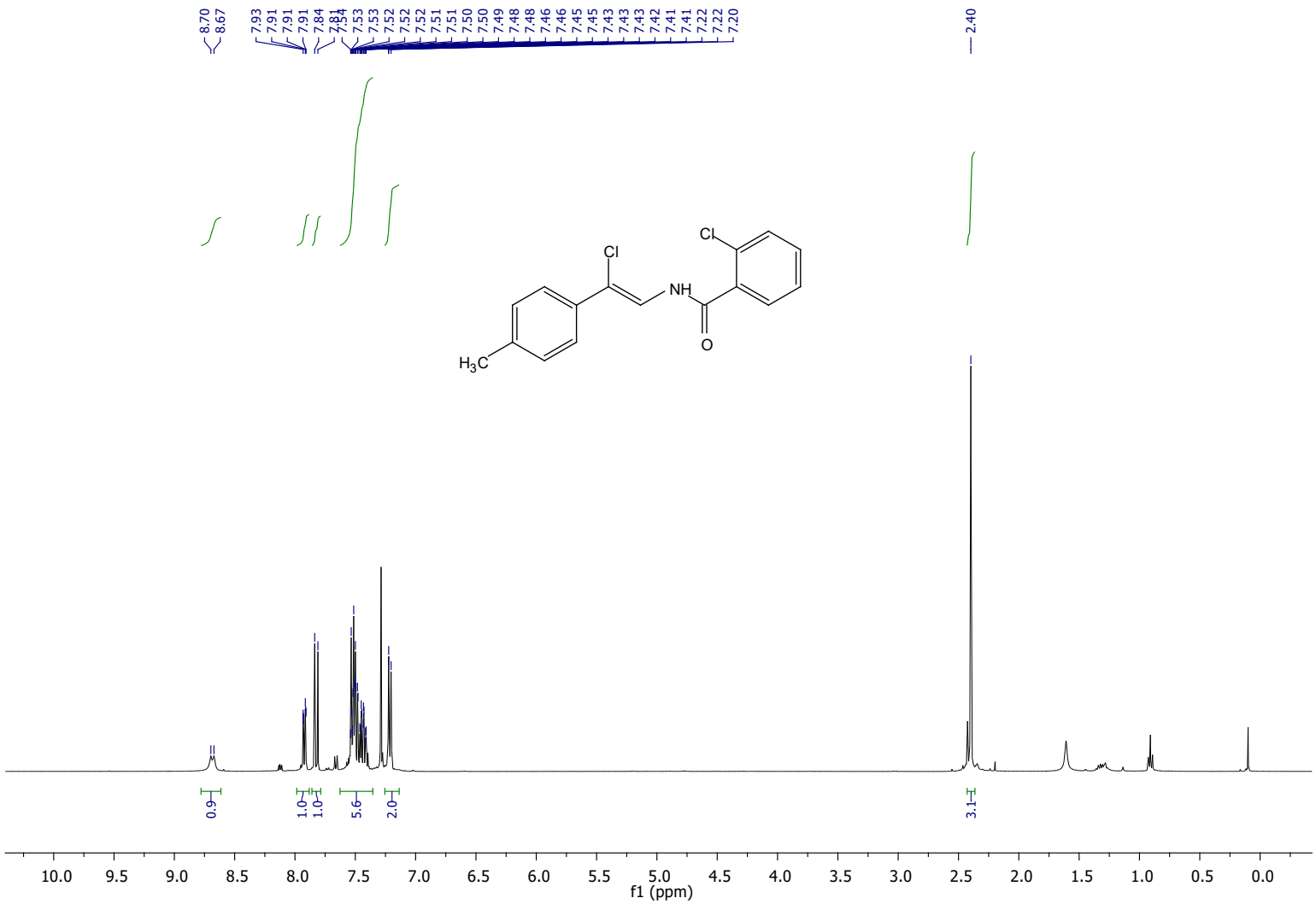

154.41
154.03
139.54
132.96
129.41
127.13
119.76
118.24
116.91
114.05
113.69
21.14
Br
NH
F
F
F
O
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR

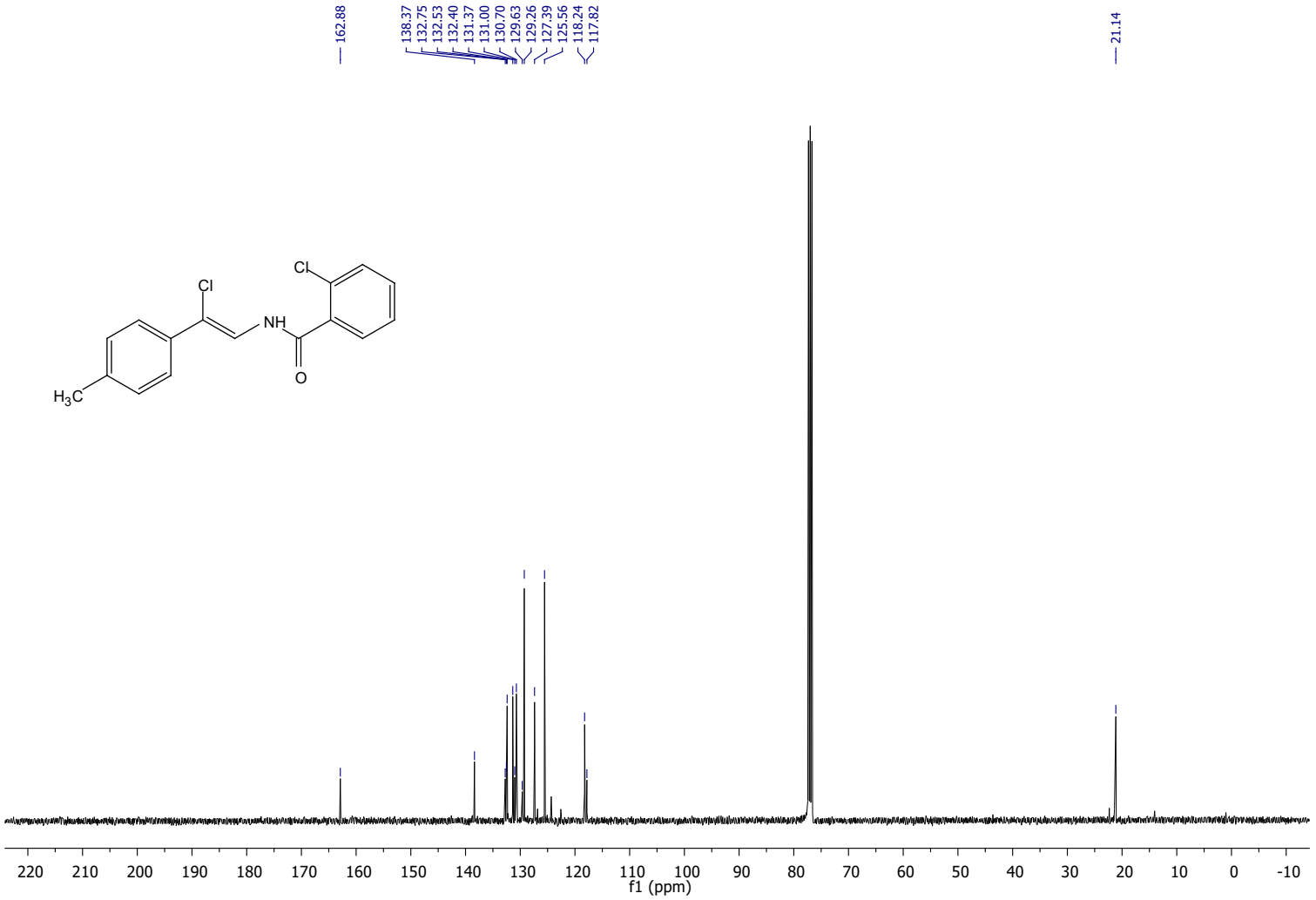

-76.07
Br
F
F
F
NH
O
H3C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

(Z)-2-chloro-N-(2-chloro-2-(p-tolyl)vinyl)benzamide **5d**

^{1}H NMR

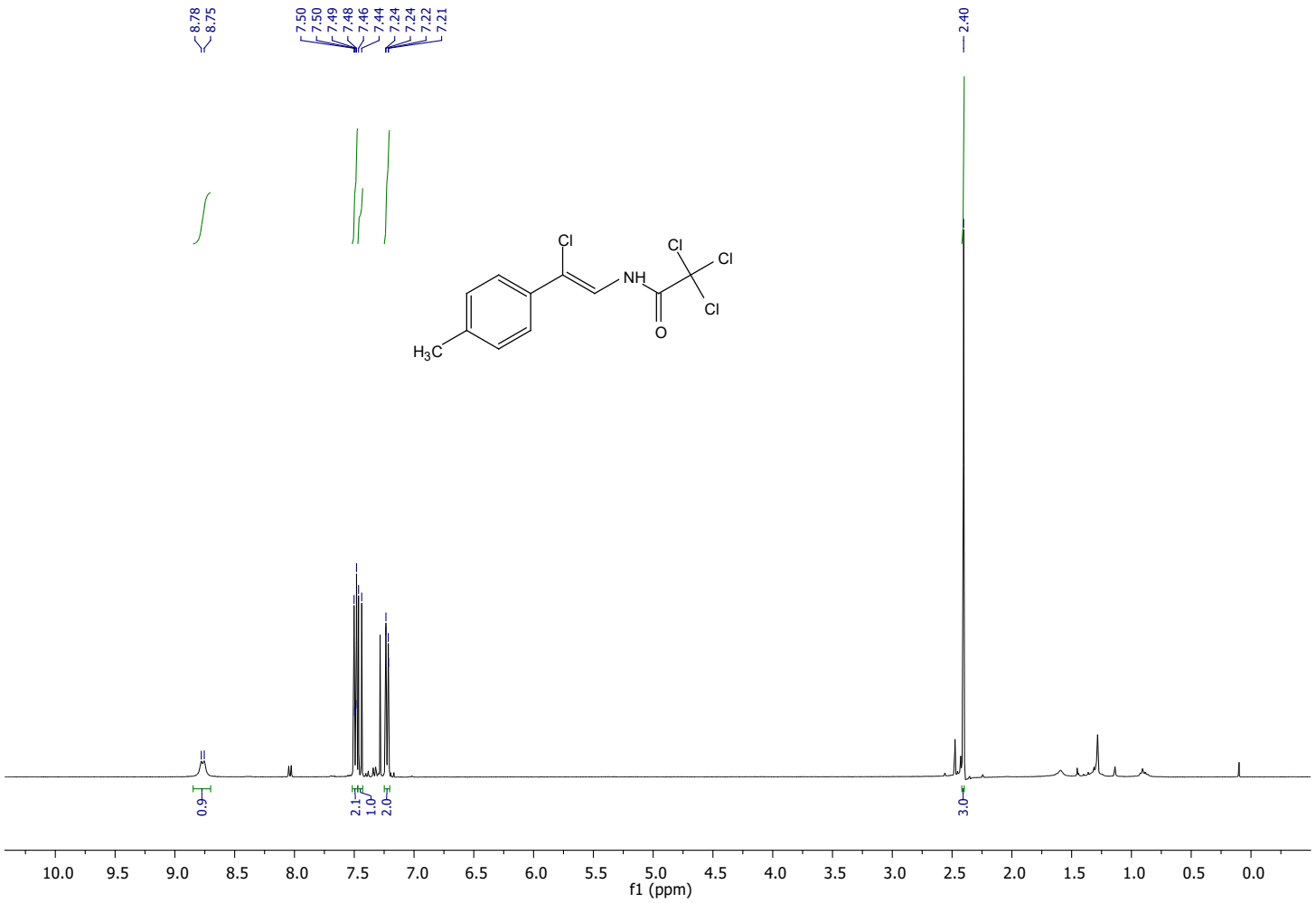


^{13}C NMR

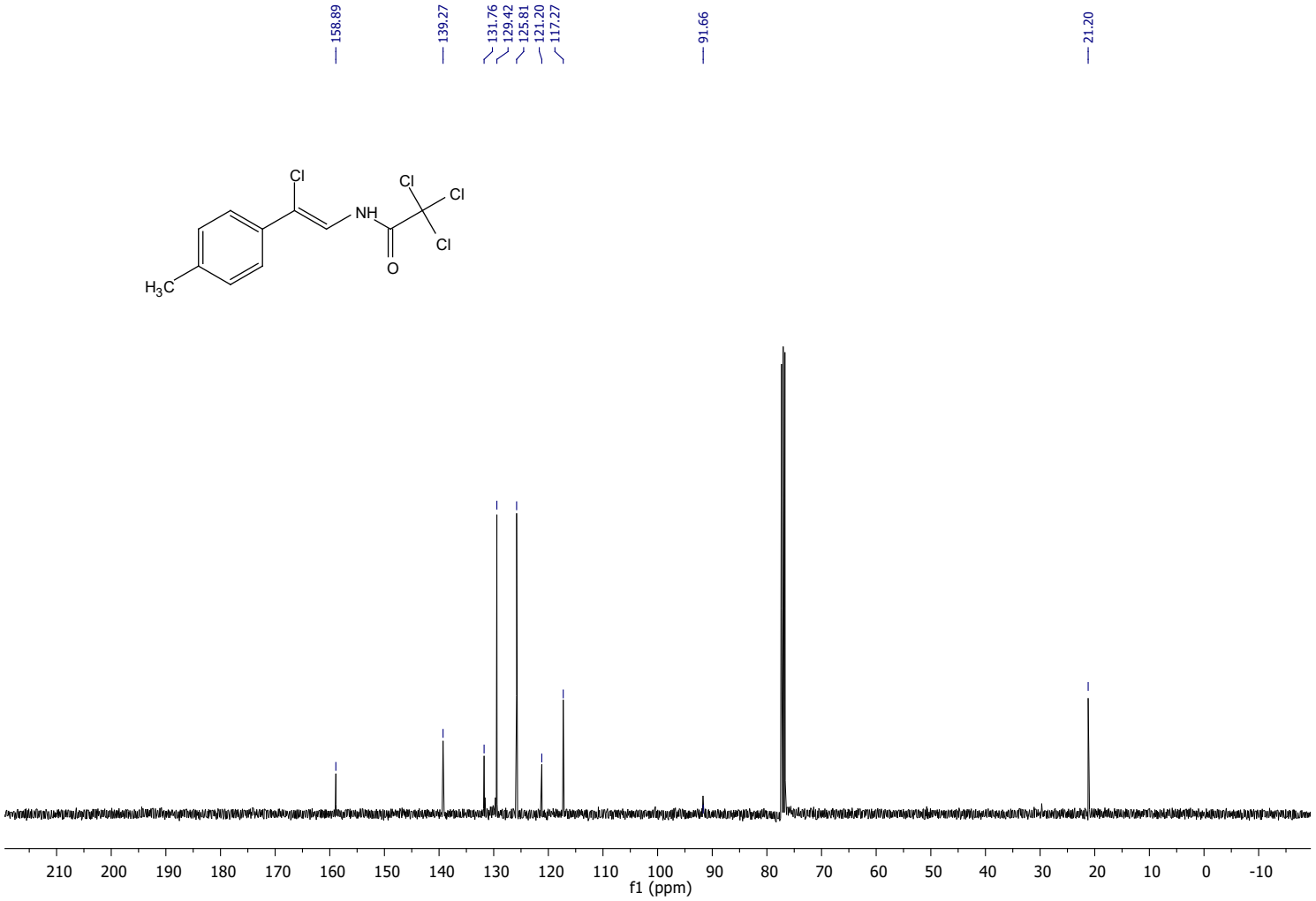

162.88
138.37
132.75
132.53
132.40
131.37
131.00
130.70
129.63
129.26
127.39
125.56
118.24
117.82
21.14
Cl
Cl
NH
O
H3C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(Z)-2,2,2-trichloro-N-(2-chloro-2-(p-tolyl)vinyl)acetamide **5e**

^{1}H NMR

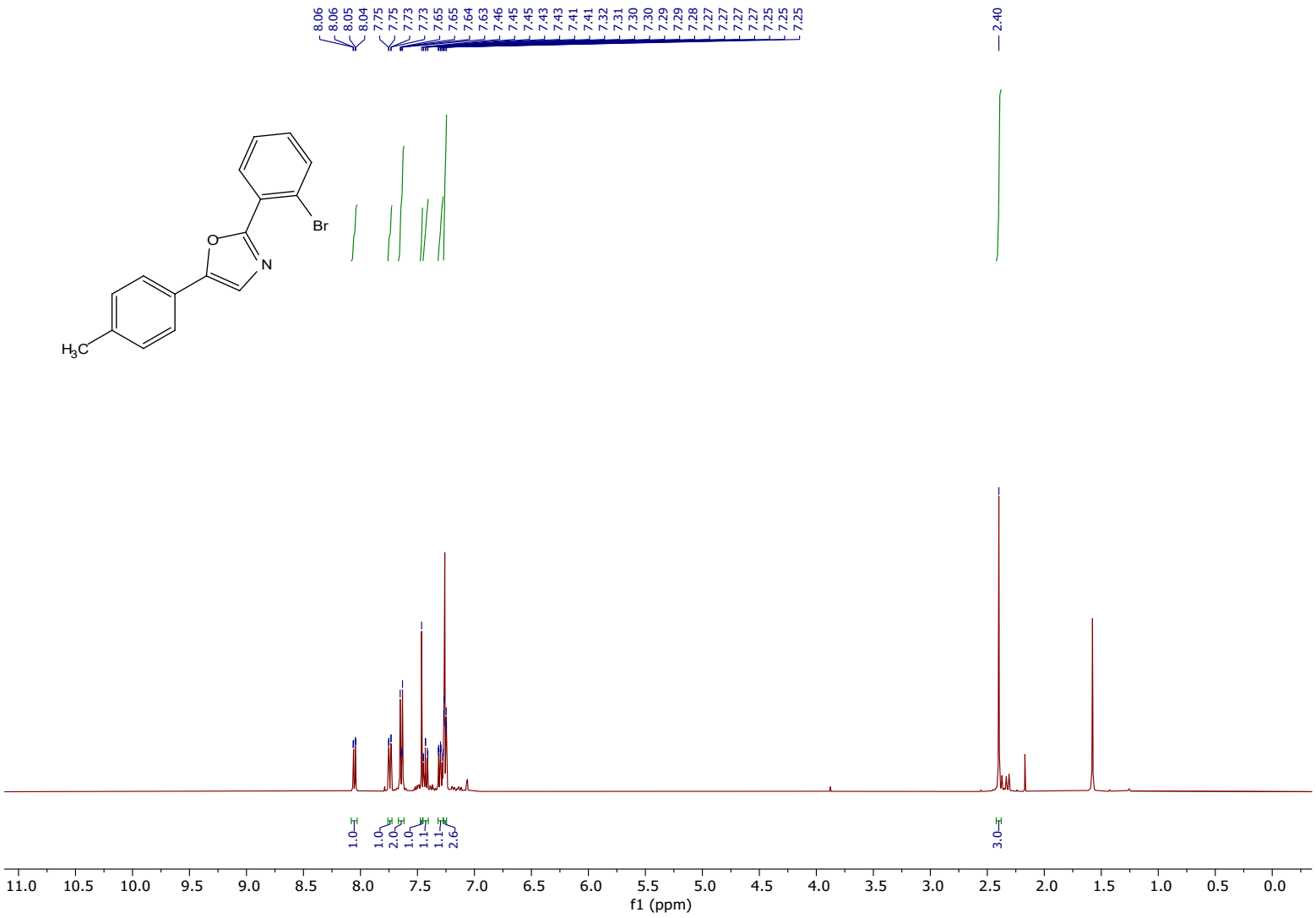


^{13}C NMR

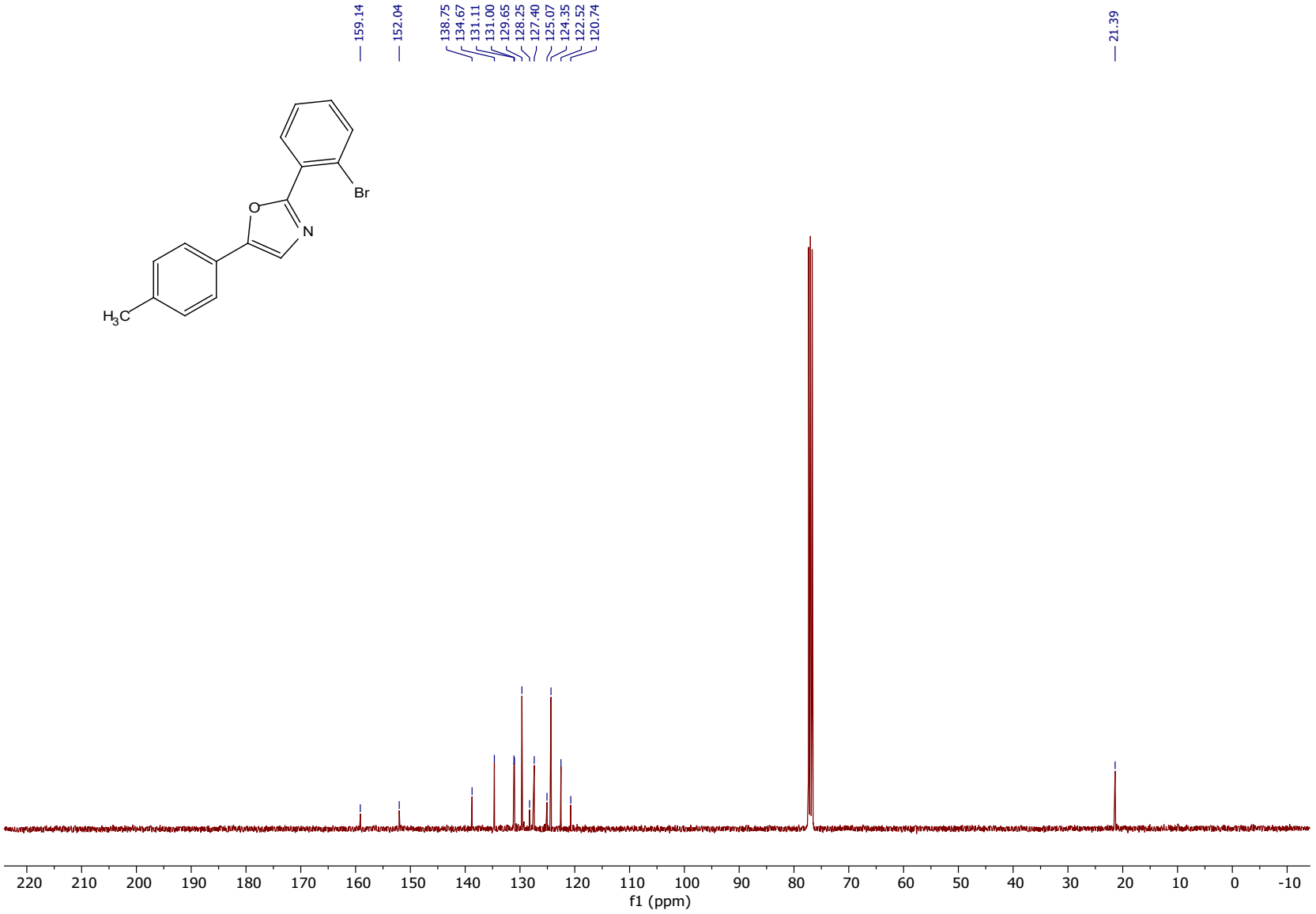

158.89
139.27
131.76
129.42
125.81
121.20
117.27
91.66
21.20
Cl
NH
Cl
Cl
Cl
O
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2-(2-bromophenyl)-5-(*p*-tolyl)oxazole **6b**

^{1}H NMR



^{13}C NMR


159.14
152.04
138.75
134.67
131.11
131.00
129.65
128.25
127.40
125.07
124.35
122.52
120.74
21.39
Br
O
N
H3C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)