Electronic supplementary materials *Mendeleev Commun.*, 2017, **27**, 293–295

Stereochemistry and mechanism of oxidative 1,4-addition of trifluoroacetamide to 2,3-dimethylbuta-1,3-diene

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Contents

Single crystal X-ray structure determinations:

Crystal data were collected on a Bruker D8 Venture diffractometer with MoKa radiation (λ = 0.71073) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set [1]. Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX programs set [1]. **CCDC 1483559 (3)** and **CCDC 1483560 (4)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

References:

[1] G.M. Sheldrick, *Acta Crystallogr*., 2008, **A64**,112.

Figure S1 Molecular structure (ORTEP diagram) of compound 3.

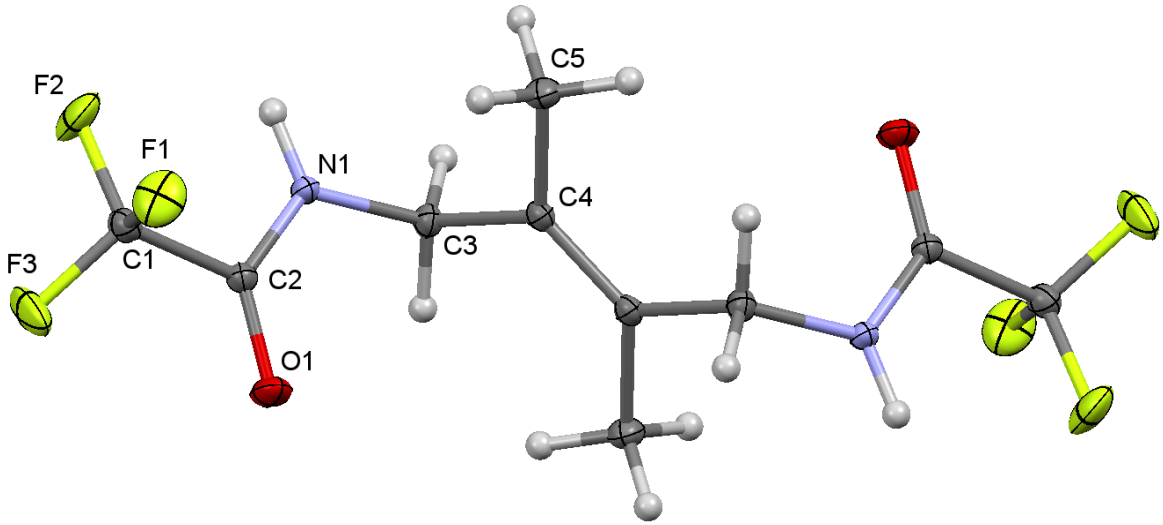

Table S1 Crystal Data, Details of Intensity Measurements, and Structure Refinement for compound **3.**

Empirical formula	$C_5H_6F_3NO$
Formula weight / g·mol^{-1}	153.11
Crystal system	triclinic
Space group	P-1
a / Å	5.0888(4)
b / Å	7.6270(6)
c / Å	9.1110(7)
α / °	112.328(3)
β / °	95.026(3)
γ / °	103.060(3)
Volume / Å^3	312.69(4)
Z	2
Density (calculated) / g·cm^{-3}	1.626
Absorptions coefficient / mm^{-1}	0.171
Radiation (λ / Å)	$Mo_{K\alpha}$ (0.71073)
Temperature / K	100(2)
2Θ range / °	4.92 – 60.24
Crystal size / mm	0.060 × 0.100 × 0.500
Crystal habit	colorless needle
F(000)	156
Index ranges	$-7 \leq h \leq 7$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$
Reflections collected	14733
Independent reflections	1835
Max. and min. transmission	0.919 / 0.990
Number of ref. parameters	92
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0367 / 0.0906
R_1 / wR_2 (all data)	0.0431 / 0.0947
Goodness-of-fit on F^2	1.070
Largest diff. peak and hole / e·Å^{-3}	0.486 / -0.373

$w=1/[\sigma^2(F_o^2)+(0.0421P)^2+ 0.1638P]$

Table S2 Selected bond lengths, bond and torsion angles in compound **3.**

Bond	*l*, Å	Angle	φ, ˚	Torsion angle	θ, ˚
F1-C1	1.336(1)	C2-N1-C3	121.5(1)	C3-N1-C2-O1	4.5(2)
F3-C1	1.322(1)	F3-C1-F1	107.2(1)	F3-C1-C2-O1	37.4(1)
N1-C2	1.324(1)	F3-C1-C2	111.7(1)	F1-C1-C2-O1	-80.9(1)
F2-C1	1.331(1)	F1-C1-C2	109.3(1)	F2-C1-C2-N1	-22.8(1)
O1-C2	1.227(1)	O1-C2-C1	118.6(1)	C2-N1-C3-C4	80.3 (1)
N1-C3	1.468(1)	N1-C3-C4	112.2(1)	N1-C3-C4-C5	49.5(1)
C3-C4	1.516(1)	C4-C4-C5	125.0(1)	C3-N1-C2-C1	-172.3(1)
C1-C2	1.538(2)	C5-C4-C3	112.8(1)	F2-C1-C2-O1	160.1(1)
C4-C5	1.511(1)	C4-C4-C3	122.2(1)	F3-C1-C2-N1	-145.5(1)
C4-C4	1.343(2)	O1-C2-N1	126.6(1)	F1-C1-C2-N1	96.1(1)

Figure S2 Molecular structure (ORTEP diagram) of compound 4.

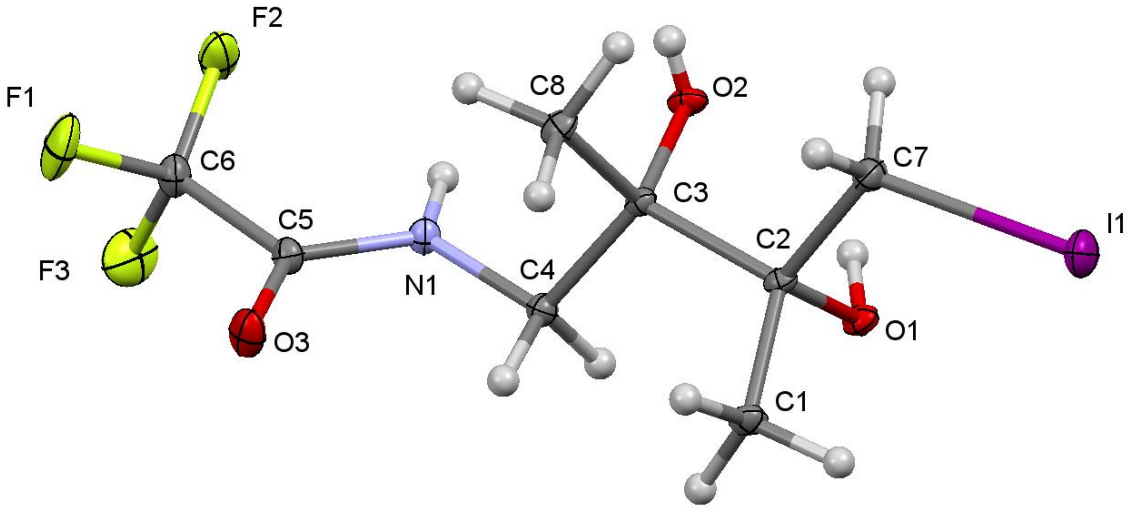

Table S3 Crystal Data, Details of Intensity Measurements, and Structure Refinement for compound **4.**

Empirical formula	$C_8H_{13}F_3INO_3$
Formula weight / g·mol^{-1}	355.09
Crystal system	monoclinic
Space group	P 21/c
a / Å	13.4477(5)
b / Å	9.5469(4)
c / Å	10.2342(4)
α / °	90
β / °	108.6020(10)
γ / °	90
Volume / Å^3	1245.26(9)
Z	4
Density (calculated) / g·cm^{-3}	1.894
Absorptions coefficient / mm^{-1}	2.602
Radiation (*λ* / Å)	MoKα (0.71073)
Temperature / K	100(2)
2*Θ* range / °	5.22 – 60.32
Crystal size / mm	0.310 × 0.410 × 0.500
Crystal habit	colorless prizm
F(000)	688
Index ranges	-18 ≤ h ≤ 16, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	28448
Independent reflections	3668
Max. and min. transmission	0.4223 / 0.7460
Number of ref. parameters	151
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0569 / 0.1344
R_1 / wR_2 (all data)	0.0883 / 0.1521
Goodness-of-fit on F^2	1.026
Largest diff. peak and hole / e·Å^{-3}	1.703 / -1.882

$w=1/[\sigma^2(F_o^2)+(0.0552P)^2+ 4.3976P]$ where $P=(F_o^2+2F_c^2)/3$

Table S4 Selected bond lengths, bond and torsion angles in compound **4.**

Bond	*l*, Å	Angle	φ, ˚	Torsion angle	θ, ˚
I1-C7	2.152(5)	O1-C2-C1	107.2(3)	O1-C2-C3-O2	-45.8(4)
F2-C6	1.299(7)	C1-C2-C7	112.2(4)	C7-C2-C3-O2	71.6(4)
O1-C2	1.432(5)	C1-C2-C3	112.9(4)	C1-C2-C3-C8	74.4(5)
N1-C5	1.332(6)	O2-C3-C8	111.4(3)	O1-C2-C3-C4	67.3(4)
C1-C2	1.525(6)	C8-C3-C4	111.2(4)	C7-C2-C3-C4	-175.3(4)
C2-C7	1.534(6)	C8-C3-C2	113.3(4)	O2-C3-C4-N1	-56.8(4)
C3-C8	1.521(6)	N1-C4-C3	110.9(4)	C2-C3-C4-N1	-169.9(3)
F1-C6	1.307(6)	O1-C2-C7	109.1(4)	C4-N1-C5-C6	-177.8(4)
F3-C6	1.316(7)	O1-C2-C3	107.0(3)	N1-C5-C6-F2	-29.3(7)
O2-C3	1.428(5)	C7-C2-C3	108.3(3)	N1-C5-C6-F1	-152.0(5)
O3-C5	1.216(6)	O2-C3-C4	105.6(3)	N1-C5-C6-F3	90.5(6)
N1-C4	1.455(6)	O2-C3-C2	105.5(3)	C1-C2-C7-I1	63.9(5)
C2-C3	1.566(6)	F1-C6-C5	111.5(4)	C1-C2-C3-O2	-163.5(3)
C3-C4	1.544(6)	F2-C6-C5	114.5(4)	O1-C2-C3-C8	-168.0(4)
C5-C6	1.529(7)	F3-C6-C5	109.7(5)	C7-C2-C3-C8	-50.5(5)

Figure S3 ^{1}H NMR spectrum of compound 3 (400 MHz, CD_3CN).

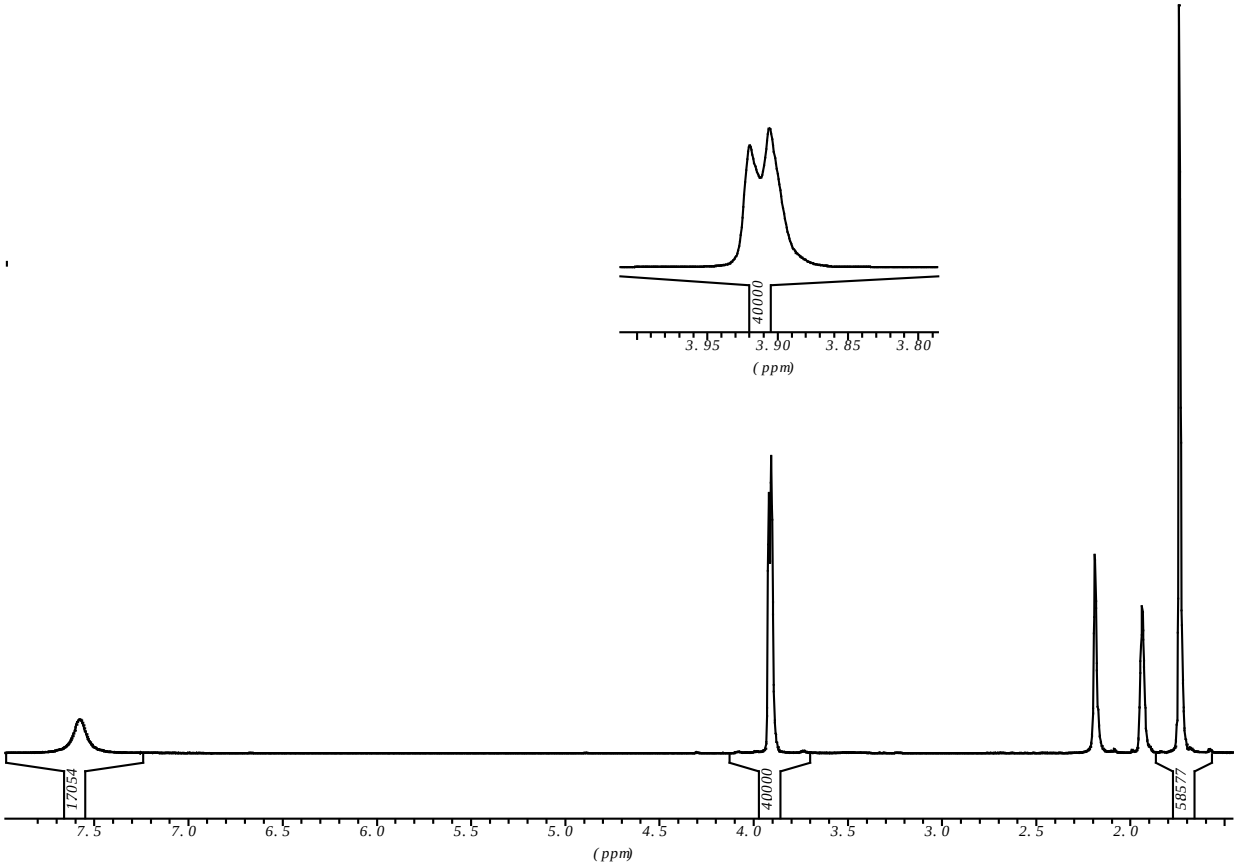

Figure S4 ^{13}C NMR spectrum of compound 3 (400 MHz, CD_3CN).

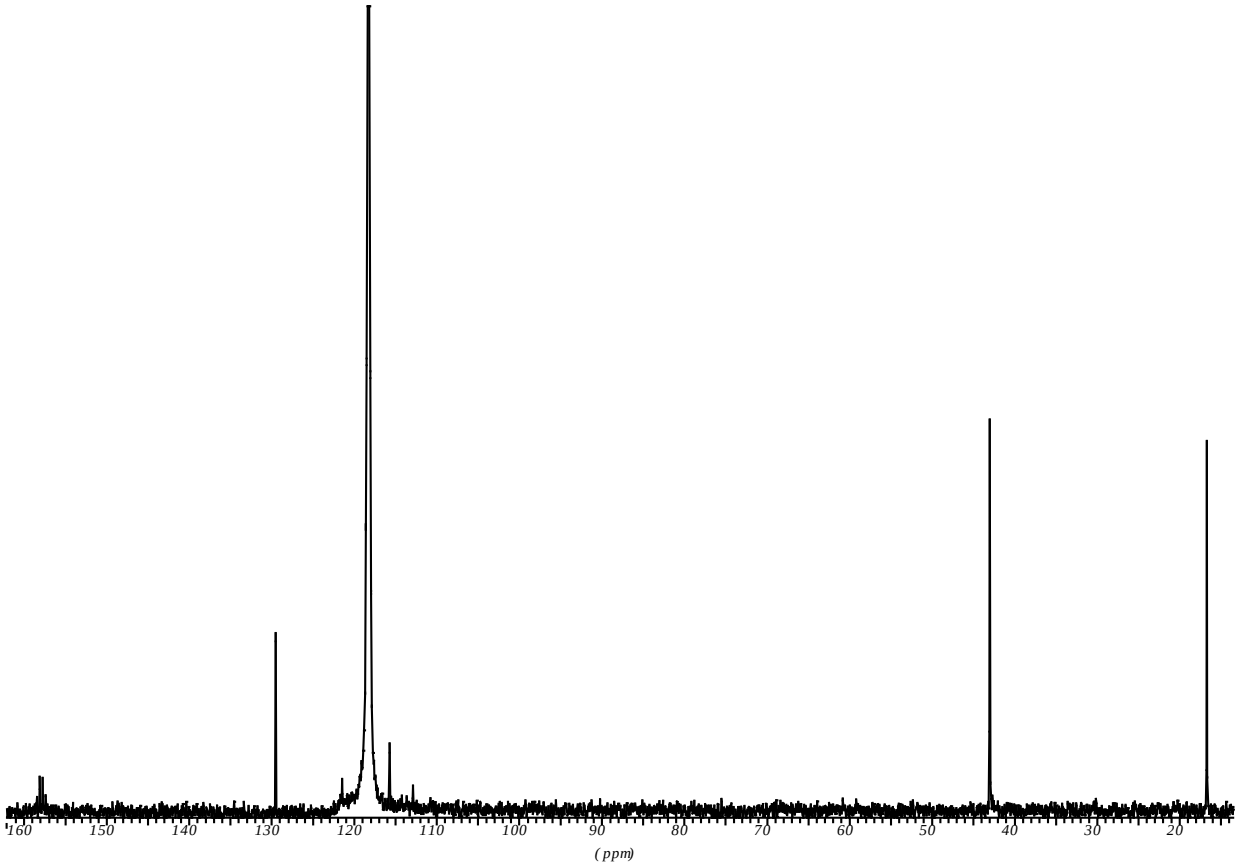

Figure S5 ^{19}F NMR spectrum of compound 3 (400 MHz, CD_3CN).

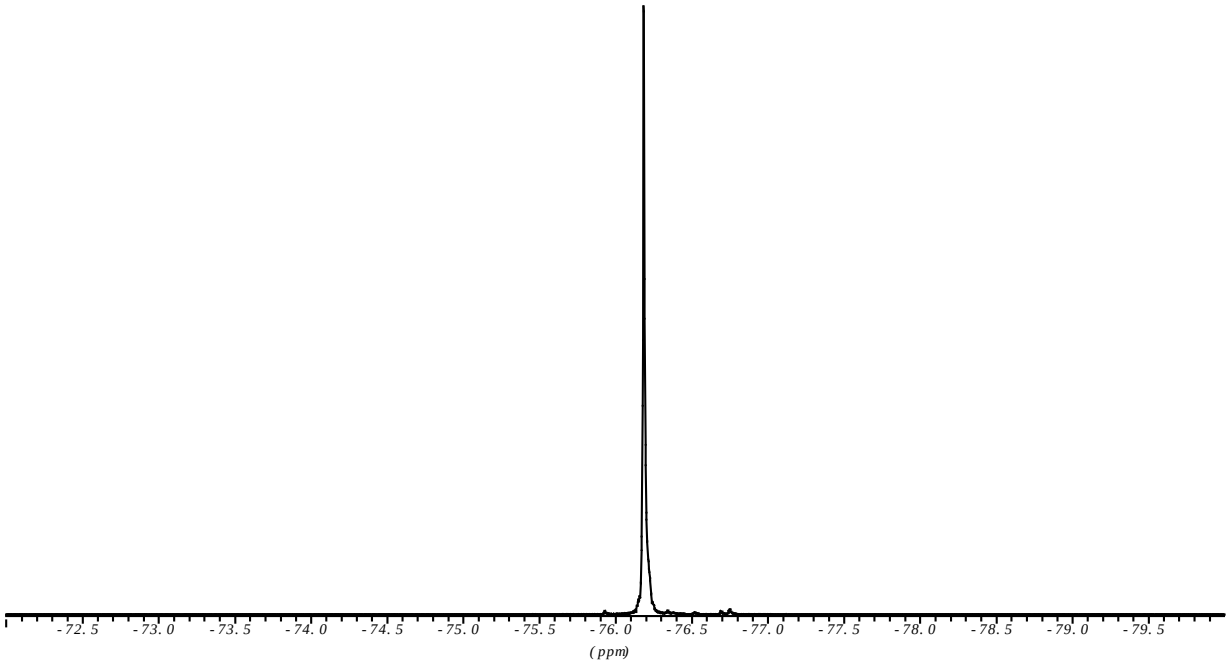

Figure S6 FT-IR spectrum of compound 3 (KBr).

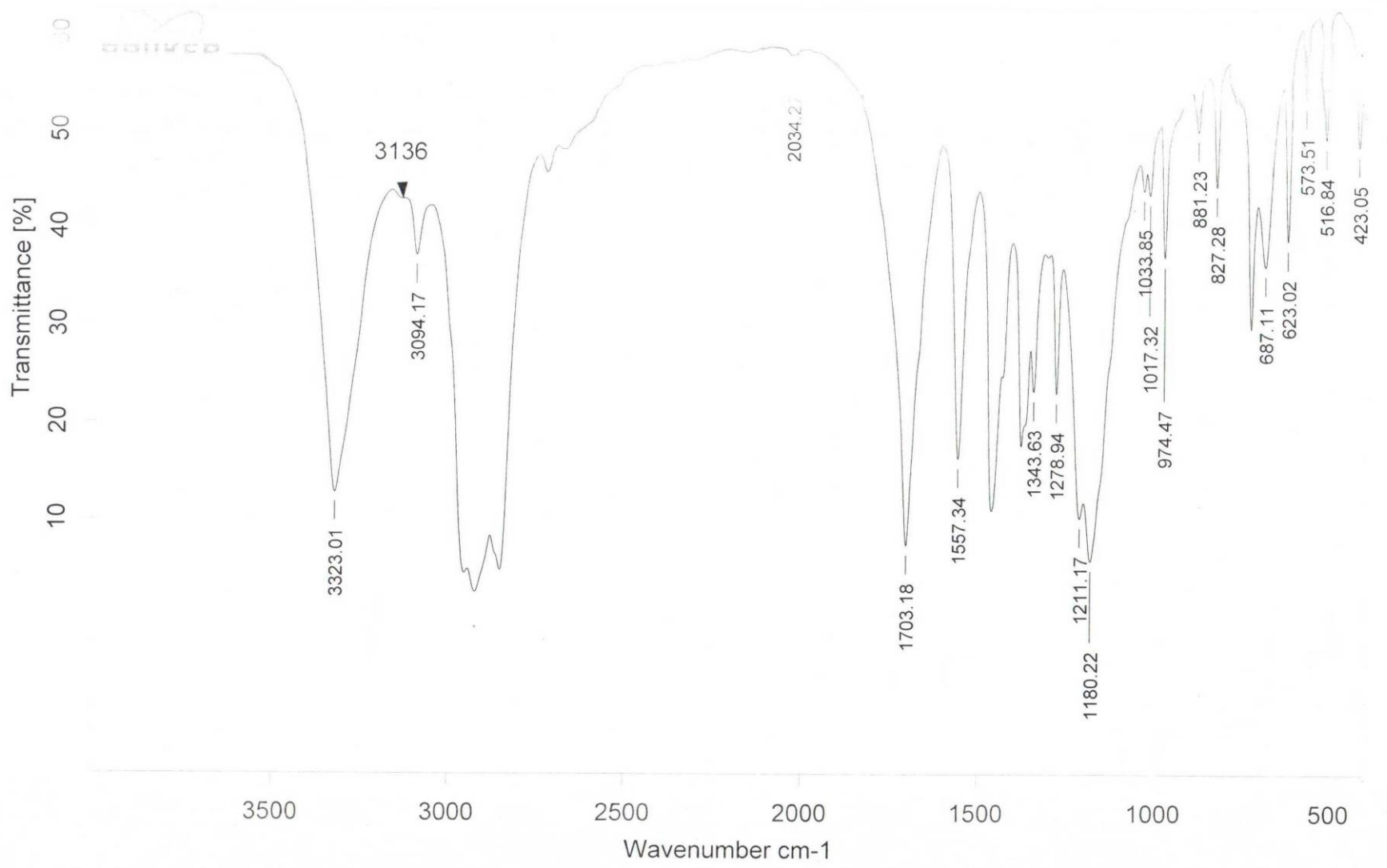

Figure S7 ^{1}H NMR spectrum of compound 4 (400 MHz, CD_3CN).

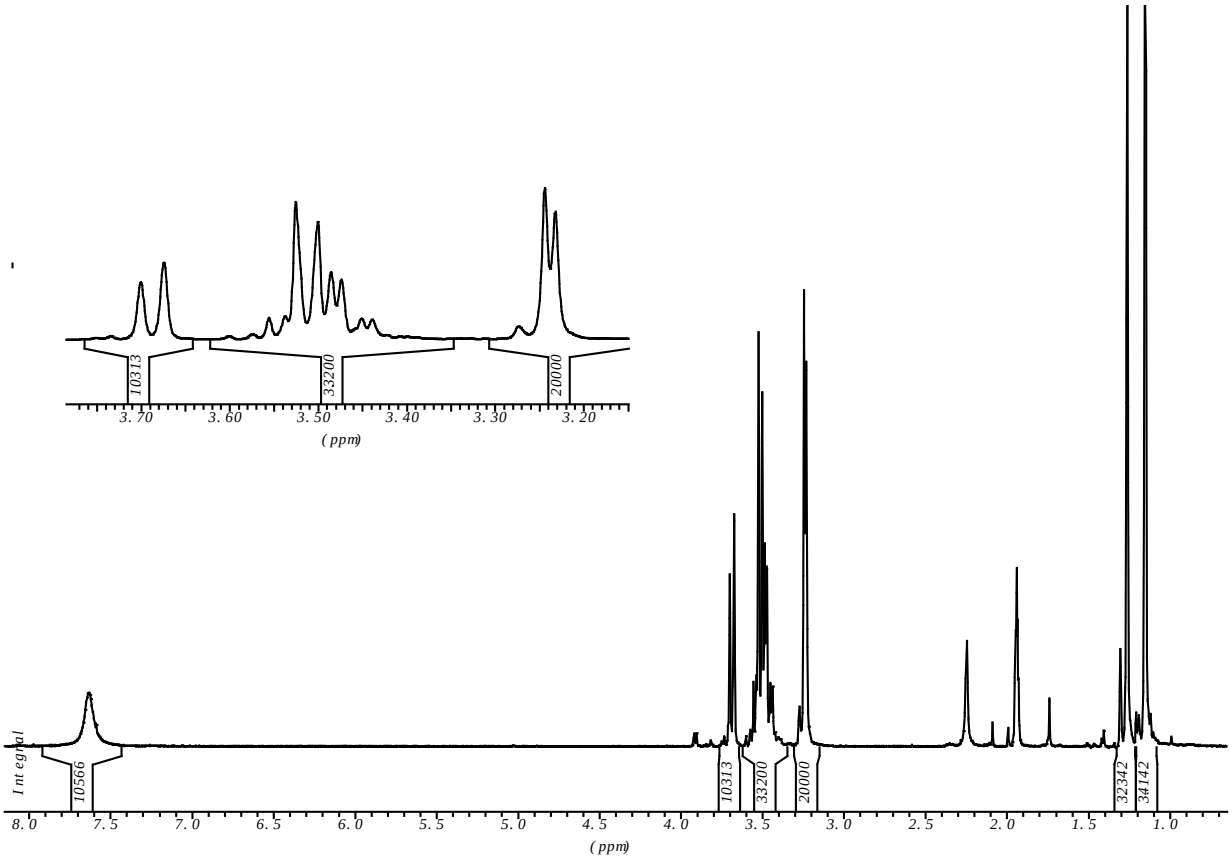

Figure S8 ^{13}C NMR spectrum of compound 4 (400 MHz, CD_3CN).

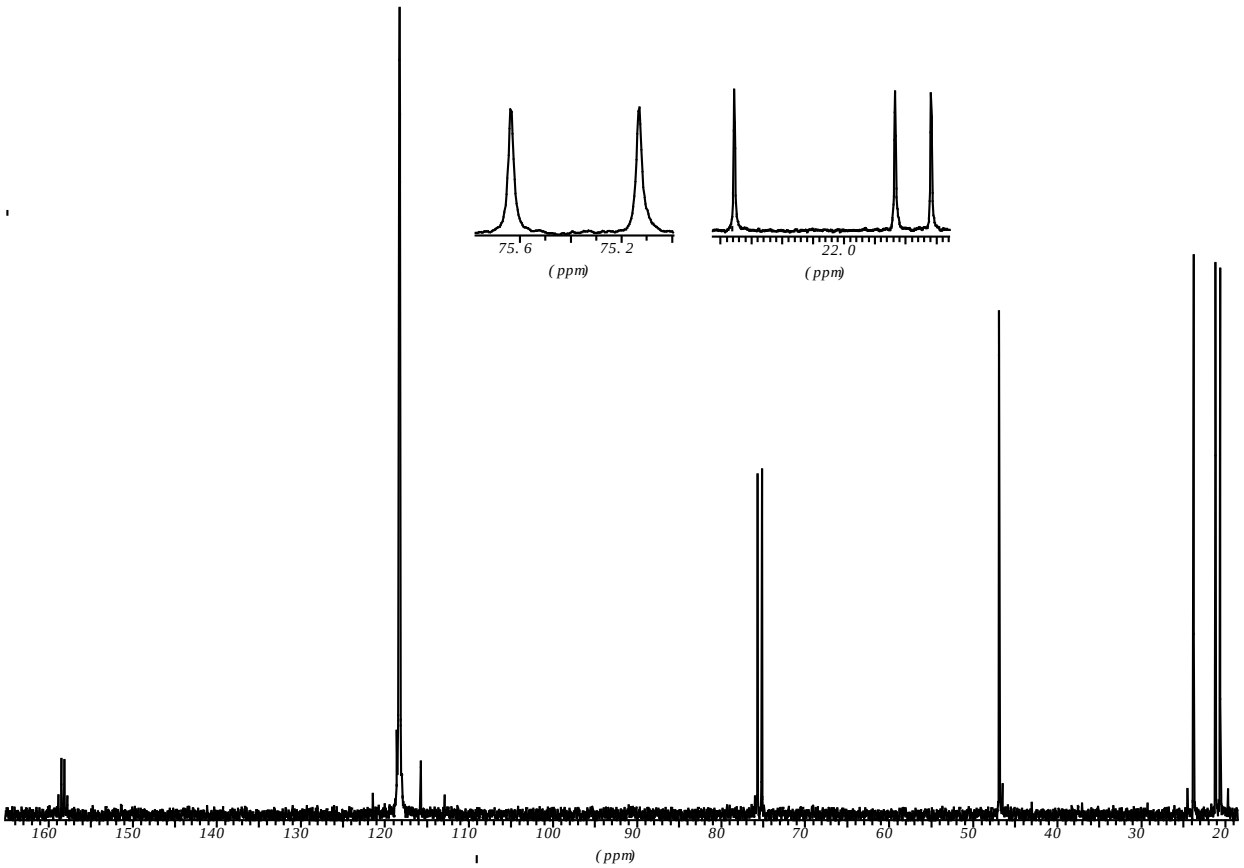

Figure S9 ^{13}C NMR (*J-modulation*) spectrum of compound 4 (400 MHz, CD_3CN).

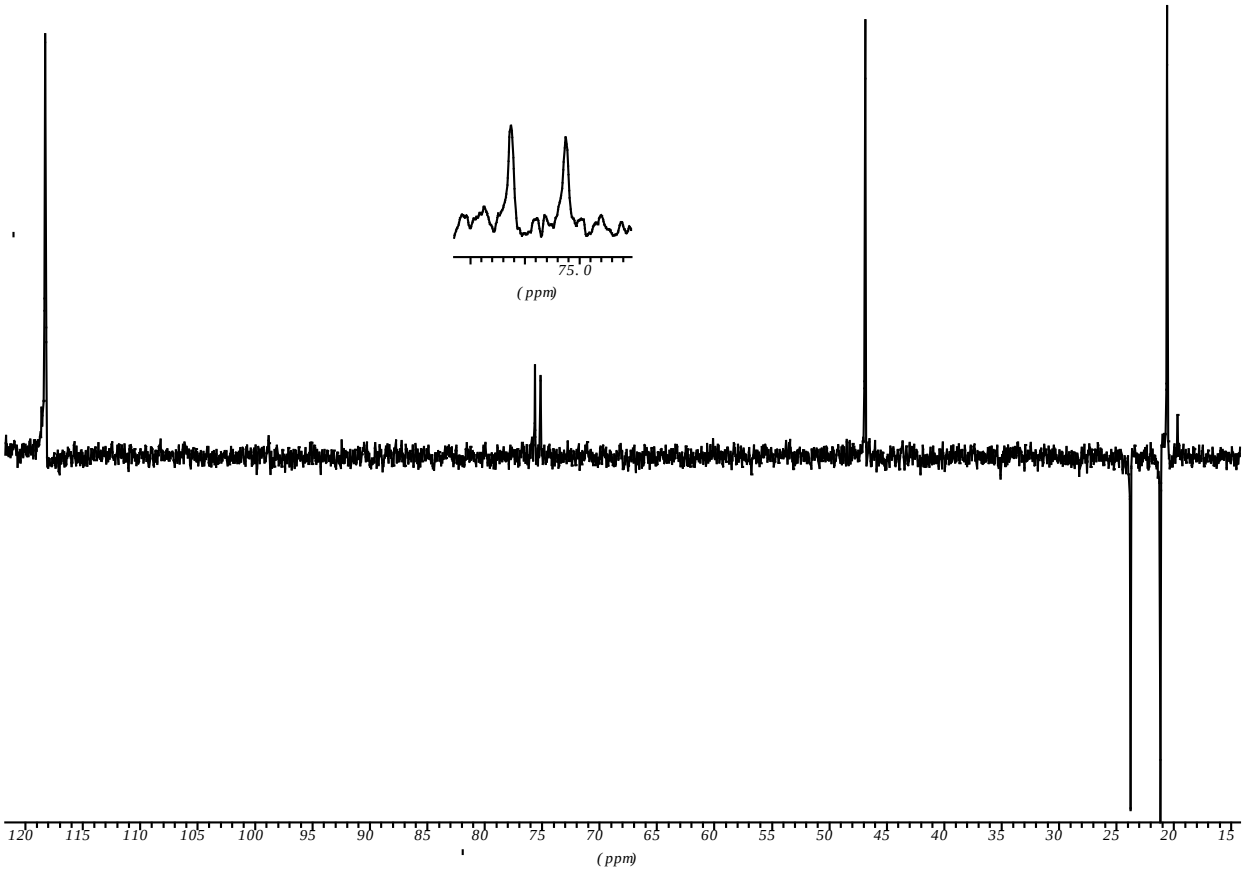

Figure S10 {^{1}H–^{13}C} NMR spectrum of compound 4 (400 MHz, CD_3CN).

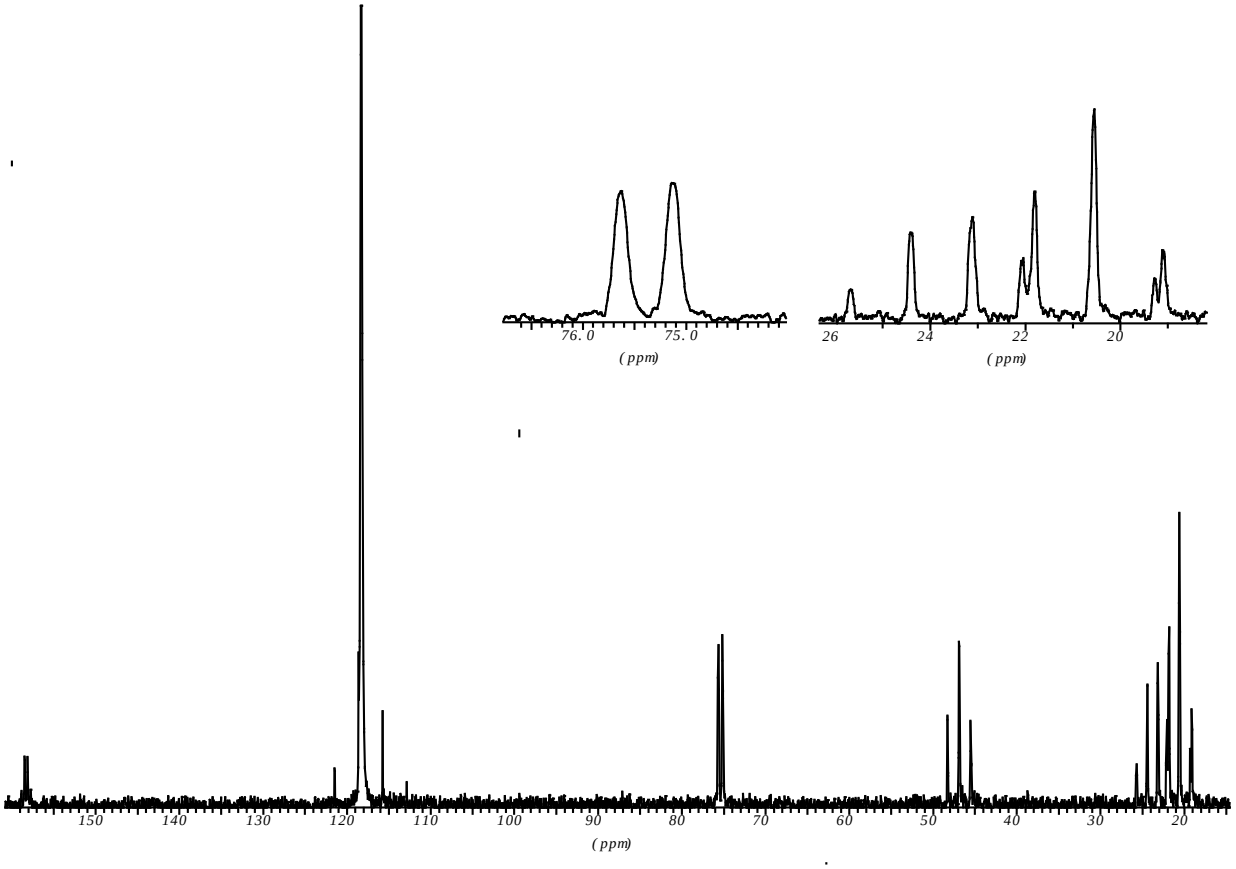

Figure S11 ^{19}F NMR spectrum of compound 4 (400 MHz, CD_3CN).

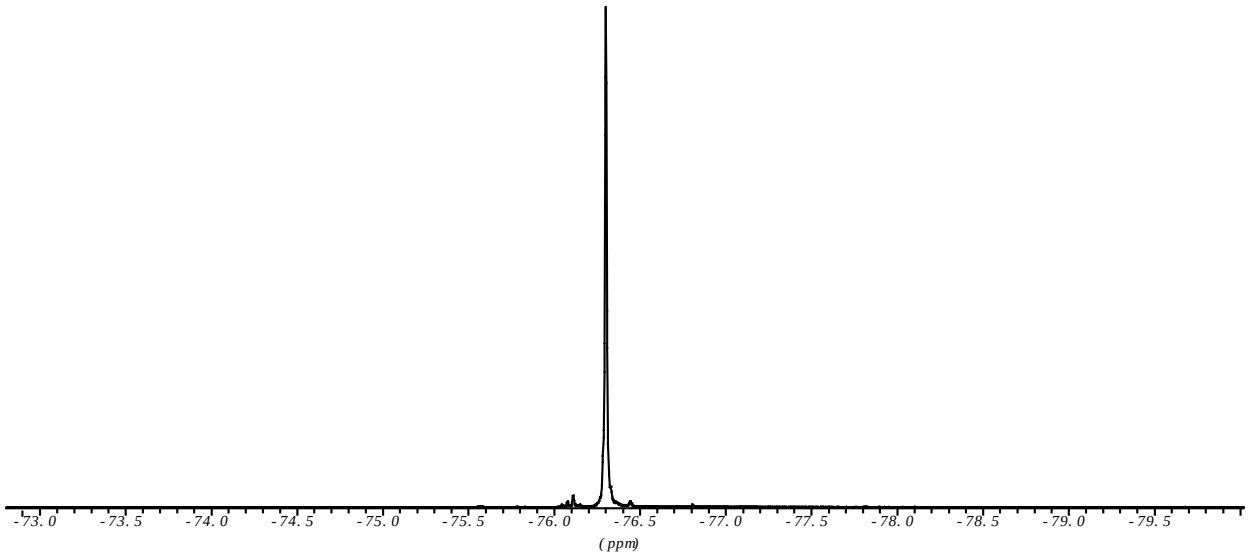

Figure S12 FT-IR spectrum of compound 4 (KBr).