Supporting Information

$n_N \rightarrow \pi^*_{Ar}$ interactions stabilize the E-ac isomers of arylhydrazides and facilitate their S_NAr autocyclizations

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A. General Experimental Information.

All reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Spectrochem, CDH, BLD pharm and TCI) and were used without further purification. Anhydrous solvents for reaction purposes were purchased from commercial sources (Chemlabs, Finar and Rankem) and were used without further purification. Column chromatography was performed on silica gel (100-200 mesh particle size) as a stationary phase using commercial solvents as mobile phase (hexane and ethylacetate). The reactions were monitored by thin layer chromatography (TLC) on silica gel 60 F_{254} (Merck). The NMR spectra were recorded in $CDCl_3$, $[CD_3]_2SO$, CD_3OD, CD_3CN and D_2O or as stated deuterated solvents. ^1H (400 MHz), ^{13}C (100 MHz) and ^{19}F (376 MHz) NMR were obtained on Bruker 400 MHz NMR spectrometer using tetramethylsilane (TMS) as an internal standard. ^1H and ^{19}F NMR spectra were recorded at ambient temperature in five different deutrated solvents which are $CDCl_3$, $[CD_3]_2SO$, CD_3OD, CD_3CN and D_2O. ^{13}C NMR spectra were recorded only in $CDCl_3$ at ambient temperature. Chemical shifts (δ) are reported in part per million (ppm) relative to residual undeuterated solvent as an internal reference (^1H: δ 7.26 ppm for $CDCl_3$; ^{13}C: δ 77.16 ppm for $CDCl_3$, δ 2.50 ppm for $[CD_3]_2SO$, δ 3.31 ppm for CD_3OD, δ 1.94 ppm for CD_3CN, δ 4.79 ppm for D_2O). Chemical shifts for fluorine are reported in parts per million from $CFCl_3$, $[CF_3]_2SO$, CF_3OF, CF_3CN, F_2O (δ 0 ppm) as the external standard. Abbreviations of NMR peak multiplicities were explained as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs and brd = broad singlet and doublet signals. NMR data were processed by using MestReNova software. HRMS data were obtained using "6540 UHD Accurate-Mass Q-TOF LC/MS system (Agilent Technologies, Santa Clara, CA, USA) equipped with Agilent 1290 UPLC system". In case of isotopic pattern, we reported the highest intensity peak mass.

B. X-ray crystal structure determination method

Single crystal structures of the compounds were determined by measuring x-ray intensity data on a D8 venture *APEX* 3[1] X-ray diffractometer equipped with monochromatised micro-focus sources of Mo Kα radiation (λ= 0.71073 Å). Data collection were done in phi (ϕ) and omega (ω) scan strategy at room temperature (295-302K). Data was processed by SAINT[2] and absorption correction was done using SADABS[3] implemented in APEX 3. The structures were solved by using XSHELL program based on SHELX[4] program implemented in APEX 3 and Olex2 1.3 (Dolomanov et al., 2009) (compiled 2020.06.28 svn.raecde09e for Olexsys, GUI svn.r6132). The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms

were assigned in idealized locations. All the structures were deposited in the CCDC[5] (CCDC No: **2087868-2087870, 2088424, 2093749** and **2093793**) database.

C. 2D-NOESY studies

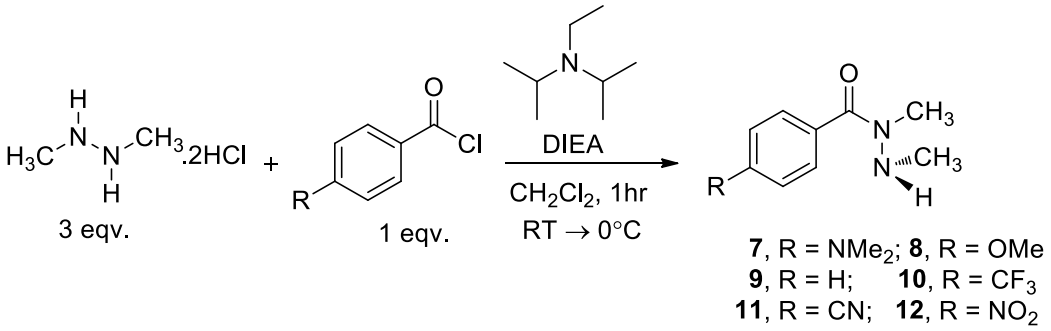
2D gradient Nuclear Overhauser Effect Spectroscopy (NOESY) ^{1}H-^{1}H Correlation (spin-lattice relaxation) NMR experiments were performed on a Bruker 400 MHz spectrometer using the following parameters – 5 mm PABBO BB/ probe, noesygpphpp pulse sequence, NS = 4 or 8 (number of scans, 8*n), DS = 32 (numbers of dummy scans were run prior to acquisition), D1= 1.98976004 sec (relaxation delay or mixing time between 1- 5 sec) and P1= 12.85 usec (^{1}H 90° pulse).

D. Computational Studies

All the calculations were performed by using Gaussian09 suite quantum chemistry program.[6] We optimized each conformer using the hybrid Minnesota functional (M06-2X)/6-311+G(2d,p) level of theory.[7] Frequency calculations were also done at the same level of theory. The stabilization energies due to the orbital interactions were evaluated using Natural Bond Orbital (NBO)[8] analyses. Noncovalent Interaction (NCI)[9] analyses were done with Multiwfn[10] software. For the NCI plots, we used VMD[11] graphical visualization software. To visualize the structures and determine the crystallographic parameters, Chemcraft[12] graphical visualization software was used. We observed that two π* (C=C) acceptor orbitals of the phenyl rings are involved in the $n_{N\beta} \rightarrow \pi^*_{Ar}$ interaction (Figure S3). There are four and eight isomers possible in symmetrical ($R_2 = R_3$) (Figure S1) and unsymmetrical ($R_2 \neq R_3$) (Figure S2) acylhydrazides, respectively, depending on whether the two substituents on the β-nitrogen atom R_2 and R_3 are same or different. In the unsymmetrical arylhydrazides (Figure S2), we used additional bH and fH designations for the isomers. For this purpose, the molecules were viewed by keeping the R-CO-N-N moiety in the plane of the screen by keeping R to the left and N-N to the right of the CO group and the viewer. In such a view, if the hydrogen on the β-nitrogen was pointed towards the viewer (frontside) fH designation was used and if the hydrogen on the β-nitrogen was pointed away from the viewer (backside) bH designation was used.

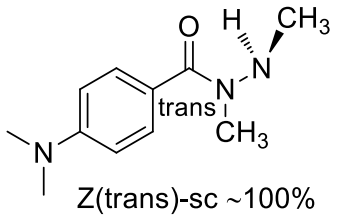
E. Synthetic protocols and characterizations

1. General Scheme for the synthesis of *N,N'*-dimethyl-monoacylhydrazines 7-12:



Procedure:

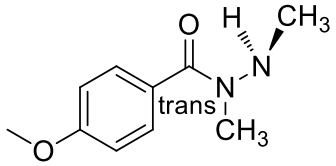
x mg of 1,2-Dimethylhydrazine-dihydrochloride [y mmol (3 eqv.)] were neutralized by using x' µL of N, N-diisopropylethylamine [DIEA-y' mmol (7 eqv.)] in CH_2Cl_2 (15 mL) at room temperature and stirred for 15 minutes. The reaction mixture was allowed to cool to 0° C and stirred for another 5 minutes. Then x" mg/ µL of Acyl chloride [y" mmol (1 eqv.)] in CH_2Cl_2 (2 mL) were added drop-wise manner to a reaction mixture over 10 minutes and stirred for another 30 minutes. The solvent was evaporated to dryness by using the rotary evaporator. Then the reaction mixture was dissolved in CH_2Cl_2 and washed twice with water, then a 10% citric acid solution followed by a saturated sodium bicarbonate ($NaHCO_3$) solution and finally with brine solution. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The final residue was then purified by the Column chromatography using Silica Gel (100-200 Mesh) and gradient of Hexane and ethyl acetate as an eluent.



Compound **7:** 4-(dimethylamino)-*N*, *N*'-dimethylbenzohydrazide.

x = 217 mg of 1,2-Dimethylhydrazine-dihydrochloride [y = 1.63 mmol (3 eqv.)], x' = 652 µL of N, N-diisopropylethylamine [DIEA (y') = 3.81 mmol (7 eqv.)] and x'' = 100 mg of 4-(dimethylamino)benzoyl chloride [y'' = 0.545 mmol (1 eqv.)]. Yield (%): 85 % as a semi-liquid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm Z(trans)-sc rotamer (~100 %): 7.46 [d, 2H, *J* = 8.0 Hz, Ph-N(CH_3)$_2$], 6.66 [d, 2H, *J* = 8.0 Hz, Ph-N(CH_3)$_2$], 5.46 [brs, 1H, NH-(CH_3)], 3.22 [s, 3H, C(O)NCH_3], 3.00 [s, 6H, N(CH_3)$_2$], 2.65 [s, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz [20mM, (CD_3)$_2$SO] δ ppm Z(trans)-sc rotamer (~100 %): 7.49 [d, 2H, *J* = 12.0 Hz, Ph-N(CH_3)$_2$], 6.65 [d, 2H, *J* = 8.0 Hz, Ph-N(CH_3)$_2$], 5.06 [brs, 1H, NH-(CH_3)], 3.07 [s, 3H, C(O)NCH_3], 2.94 [s, 6H, N(CH_3)$_2$], 2.45 [s, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz (20mM, CD_3OD) δ ppm Z(trans)-sc rotamer (~100 %): 7.48 [brd, 2H, *J* = 8.0 Hz, Ph-N(CH_3)$_2$], 6.73 [d, 2H, *J* = 8.0 Hz, Ph-N(CH_3)$_2$], 3.22 [s, 3H, C(O)NCH_3], 3.00 [s, 6H, N(CH_3)$_2$], 2.59 [s, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz (20mM, CD_3CN) δ ppm Z(trans)-sc rotamer (~100 %): 7.45 [brd, 2H, *J* = 8.0 Hz, Ph-N(CH_3)$_2$], 6.79 [d, 2H, *J* = 8.0 Hz, Ph-N(CH_3)$_2$], 3.12 [s, 3H, C(O)NCH_3], 2.96 [s, 6H, N(CH_3)$_2$], 2.53 [s, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz (20mM, D_2O) δ ppm Z(trans)-sc rotamer (~100 %): 7.48 [d, 2H, *J* = 12.0 Hz, Ph-N(CH_3)$_2$], 7.02 [d, 2H, *J* = 8.0 Hz, Ph-N(CH_3)$_2$], 3.23 [s, 3H, C(O)NCH_3], 2.99 [s, 6H, N(CH_3)$_2$], 2.62 [brs, 3H, H_3C-N(H)]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm Z(trans)-sc rotamer [~100 %]: 170.8, 151.7, 129.7, 121.8, 111.0, 40.3, 38.5, 36.3; HRMS $[M + H]^+$ calcd. for, $C_{11}H_{18}N_3O$, m/z: 208.1450; found m/z: 208.1445.

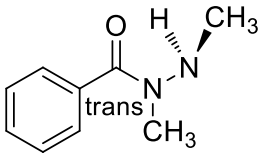


Z(trans)-sc ~100%

Compound **8:** 4-methoxy-*N*, *N*'-dimethylbenzohydrazide.

x = 234 mg of 1,2-Dimethylhydrazine-dihydrochloride [y = 1.76 mmol (3 eqv.)], x' = 702 µL of N, N-diisopropylethylamine [DIEA (y') = 4.10 mmol (7 eqv.)] and x'' = 79 µL of 4-methoxybenzoyl chloride [y'' = 0.586 mmol (1 eqv.)]. Yield (%): 82 % as a semi-liquid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm Z(trans)-sc rotamer (~100 %): 7.48 (brd, 2H, *J* = 8.0 Hz, Ph-OCH_3), 6.90 (d, 2H, *J* = 8.0 Hz, Ph-OCH_3), 5.76 [brs, 1H, NH-(CH_3)], 3.83 [s, 3H, O-CH_3], 3.19 [s, 3H, C(O)NCH_3], 2.65 [s, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm Z(trans)-sc rotamer (~100 %): 7.51 (brd, 2H, *J* = 8.0 Hz, Ph-OCH_3), 6.91 (brd, 2H, *J* = 8.0 Hz, Ph-OCH_3), 4.86 [brs, 1H, NH-(CH_3)], 3.78 [s, 3H, O-CH_3], 3.08 [s, 3H, C(O)NCH_3], 2.44 [brd, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz (20mM, CD_3OD) δ ppm Z(trans)-sc rotamer (~100 %): 7.52 (brs, 2H, Ph-OCH_3), 6.95 (brd, 2H, *J* = 8.0 Hz, Ph-OCH_3), 3.83 [s, 3H, O-CH_3], 3.20 [s, 3H, C(O)NCH_3], 2.58 [brs, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz (20mM, CD_3CN) δ ppm Z(trans)-sc rotamer (~100 %): 7.49 (brd, 2H, *J* = 8.0 Hz, Ph-OCH_3), 6.92 (d, 2H, *J* = 12.0 Hz, Ph-OCH_3), 3.81 [s, 3H, O-CH_3], 3.11 [s, 3H, C(O)NCH_3], 2.52 [s, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz (20mM, D_2O) δ ppm Z(trans)-sc rotamer (58 %): 7.48 (d, 2H, *J* = 8.0 Hz, Ph-OCH_3), 7.07 (brs, 2H, Ph-OCH_3), 3.89 [s, 3H, O-CH_3], 3.18 [s, 3H, C(O)NCH_3], 2.66 [s, 3H, H_3C-N(H)]; E(cis)-ac rotamer (42 %): 7.48 (d, 2H, *J* = 12.0 Hz, Ph-OCH_3), 7.07 (brs, 2H, Ph-OCH_3), 3.89 [s, 3H, O-CH_3], 3.25 [s, 3H, C(O)NCH_3], 2.54 [s, 3H, H_3C-N(H)]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm Z(trans)-sc rotamer [~100 %]: 170.0, 161.0, 129.6, 127.4, 113.5, 55.3, 38.0, 36.1; HRMS $[M + H]^+$ calcd. for, $C_{10}H_{15}N_2O_2$, m/z: 195.1134; found m/z: 195.1139.

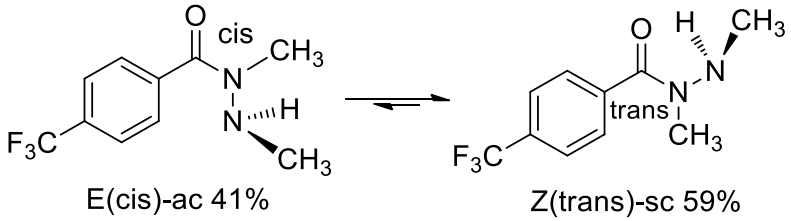


Z(trans)-sc ~100%

Compound **9:** *N*, *N*'-dimethylbenzohydrazide.

x = 284 mg of 1,2-Dimethylhydrazine-dihydrochloride [y = 2.13 mmol (3 eqv.)], x' = 851 µL of N, N-diisopropylethylamine [DIEA (y') = 4.98 mmol (7 eqv.)] and x'' = 83 µL of benzoyl chloride [y'' = 0.711 mmol (1 eqv.)]. Yield (%): 86 % as a semi-liquid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm Z(trans)-sc rotamer (~100 %): 7.46-7.42 (m, 5H, Ph), 5.78 [brs, 1H, NH-(CH_3)], 3.15 [brs, 3H, C(O)NCH_3], 2.67 [s, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm (~100 %): 7.45 (brd, 2H, *J* = 8.0 Hz, Ph), 7.36 (brs, 3H, Ph), 4.84 [brs, 1H, NH-(CH_3)], 3.10 [brs, 3H, C(O)NCH_3], 2.40 [brs, 3H, H_3C-N(H)]; ^{1}H NMR 400 MHz (20mM, CD_3OD) δ ppm E(cis)-ac rotamer (56 %): 7.48-7.39 (m, 5H, Ph), 3.24 [brs, 3H, C(O)NCH_3], 2.49 [brs, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (44 %): 7.48-7.39 (m, 5H, Ph), 3.13 [brs, 3H, C(O)NCH_3], 2.66 [brs, 3H, H_3C-(NH)]; ^{1}H NMR 400 MHz (20mM, CD_3CN) δ ppm E(cis)-ac rotamer (59 %): 7.44-7.39 (m, 5H, Ph), 3.90 [brs, 1H, H-N(CH_3)], 3.13 [brs, 3H, C(O)NCH_3], 2.49 [brs, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (41 %): 7.44-7.39 (m, 5H, Ph), 5.65 [brs, 1H, H-N(CH_3)], 3.13 [brs, 3H, C(O)NCH_3], 2.49 [brs, 3H, H_3C-(NH)]; ^{1}H NMR 400 MHz (20mM, D_2O) δ ppm E(cis)-ac rotamer (50 %): 7.56-7.43 (m, 5H, Ph), 3.27 [s, 3H, C(O)NCH_3], 2.51 [s, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (50 %): 7.56-7.43 (m, 5H, Ph), 3.13 [s, 3H, C(O)NCH_3], 2.67 [s, 3H, H_3C-(NH)]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [~100 %]: 169.6, 135.3, 130.1, 128.4, 127.4, 37.8, 36.1; HRMS $[M + H]^+$ calcd. for, $C_9H_{13}N_2O$, m/z: 165.1028; found m/z: 165.1031.

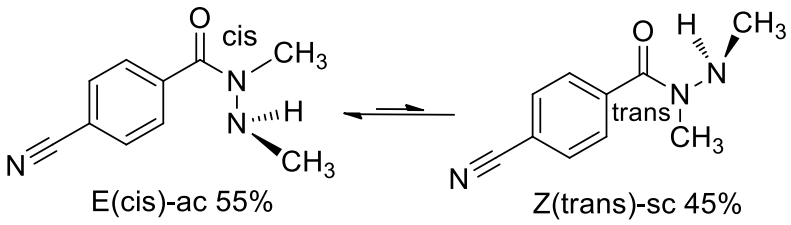


Compound **10:** *N*, *N*'-dimethyl-4-(trifluoromethyl)benzohydrazide.

x = 191 mg of 1,2-Dimethylhydrazine-dihydrochloride [y = 1.44 mmol (3 eqv.)], x' = 574 µL of N, N-diisopropylethylamine [DIEA (y') = 3.36 mmol (7 eqv.)] and x'' = 71 µL of 4-(trifluoromethyl)benzoyl chloride [y'' = 0.479 mmol (1 eqv.)]. Yield (%): 84 % as a solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm Z(trans)-sc rotamer (59 %): 7.66-7.59 (m, 4H, Ph-CF_3), 5.87 [brs, 1H, NH-(CH_3)], 3.11 [brs, 3H, C(O)NCH_3], 2.69 [brd, 3H, *J* = 4.0 Hz, H_3C-(NH)]; E(cis)-ac rotamer (41 %): 7.66-7.59 (m, 4H, Ph-CF_3), 3.37 [brs, 1H, NH-(CH_3)], 3.28 [brs, 3H, C(O)NCH_3], 2.59 [brs, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm Z(trans)-sc rotamer (59 %): -62.95 (s, 3F, Ph-CF_3); E(cis)-ac rotamer (41 %): -62.84 (s, 3F, Ph-CF_3); ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm E(cis)-ac rotamer (~100 %): 7.72 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 7.63 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 4.92 [q, 1H, *J* = 4.0 Hz, NH-(CH_3)], 3.13 [s, 3H, C(O)NCH_3], 2.39 [brd, 3H, *J* = 8.0 Hz, H_3C-N(H)]; ^{19}F NMR 376 MHz [20mM, $(CD_3)_2SO$] δ ppm E(cis)-ac rotamer (~100 %): -61.14 (s, 3F, Ph-CF_3); ^{1}H NMR 400 MHz (20mM, CD_3OD) δ ppm E(cis)-ac rotamer (74 %): 7.67 (brs, 4H, Ph-CF_3), 3.26 [s, 3H, C(O)NCH_3], 2.49 [s, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (26 %): 7.78 (brs, 2H, Ph-CF_3), 7.67 (brs, 2H, Ph-CF_3), 3.10 [s, 3H, C(O)NCH_3], 2.68 [s, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz (20mM, CD_3OD) δ ppm E(cis)-ac rotamer (74 %): -64.30 (s, 3F, Ph-CF_3); Z(trans)-sc rotamer (26 %): -64.47 (s, 3F, Ph-CF_3);^{1}H NMR 400 MHz (20mM, CD_3CN) δ ppm E(cis)-ac rotamer (76 %): 7.74-7.60 (m, 4H, Ph-CF_3), 3.93 [brs, 1H, H-N(CH_3)], 3.17 [s, 3H, C(O)NCH_3], 2.46 [brd, 3H, *J* = 4.0 Hz, H_3C-(NH)]; Z(trans)-sc rotamer (24 %): 7.74-7.60 (m, 4H, Ph-CF_3), 5.75 [brs, 1H, H-N(CH_3)], 3.01 [s, 3H, C(O)NCH_3], 2.61 [s, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz (20mM, CD_3CN) δ ppm E(cis)-ac rotamer (76 %): -63.20 (s, 3F, Ph-CF_3); Z(trans)-sc rotamer (24 %): -63.36 (s, 3F, Ph-CF_3); ^{1}H NMR 400 MHz (20mM, D_2O) δ ppm E(cis)-ac rotamer (57 %): 7.80 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 7.60 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 3.28 [s, 3H, C(O)NCH_3], 2.51 [s, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (43 %): 7.84 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 7.64 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 3.11 [s, 3H, C(O)NCH_3], 2.68 [s, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz

(20mM, D_2O) δ ppm E(cis)-ac rotamer (57 %): -62.69 (s, 3F, Ph-CF_3); Z(trans)-sc rotamer (43 %): -62.85 (s, 3F, Ph-CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [Z(trans)-sc (59 %)]: 168.2, 138.9, 132.1 (q, $^2J_{CF}$ = 30.0 Hz), 128.0-127.8 (m), 125.7 (brq,$^3J_{CF}$ = 4.0 Hz), 121.1 (q, $^1J_{CF}$ = 267.0 Hz), 37.8, 36.1; [E(cis)-ac (41 %)]: 171.2, 140.0, 132.1 (q, $^2J_{CF}$ = 30.0 Hz), 128.0-127.8 (m), 124.8 (brq,$^3J_{CF}$ = 4.0 Hz), 121.1 (q, $^1J_{CF}$ = 267.0 Hz), 36.1, 32.9; HRMS $[M + H]^+$ calcd. for, $C_{10}H_{12}F_3N_2O$, m/z: 233.0902; found m/z: 233.0905.

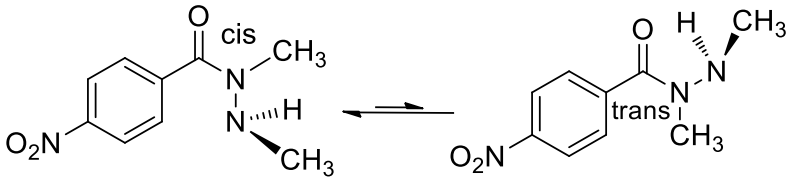


Compound **11:** 4-cyano-*N*, *N*'-dimethylbenzohydrazide.

x = 241 mg of 1,2-Dimethylhydrazine-dihydrochloride [y = 1.81 mmol (3 eqv.)], x' = 723 µL of N, N-diisopropylethylamine [DIEA (y') = 4.23 mmol (7 eqv.)] and x'' = 100 mg of 4-cyanobenzoyl chloride [y'' = 0.604 mmol (1 eqv.)]. Yield (%): 80 % as a light yellow solid.

^1H NMR 400 MHz (20mM, $CDCl_3$) δ ppm E(cis)-ac rotamer (55 %): 7.71-7.58 (m, 4H, Ph-CN), 3.41 [s, 1H, NH-(CH_3)], 3.28 [s, 3H, C(O)NCH_3], 2.58 [s, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (45 %): 7.71-7.58 (m, 4H, Ph-CN), 5.71 [s, 1H, NH-(CH_3)], 3.10 [s, 3H, C(O)NCH_3], 2.69 [s, 3H, H_3C-(NH)]; ^1H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm E(cis)-ac rotamer (~100 %): 7.83 (d, 2H, *J* = 8.0 Hz, Ph-CN), 7.58 (d, 2H, *J* = 8.0 Hz, Ph-CN), 4.94 [q, 1H, *J* = 4.0 Hz, NH-(CH_3)], 3.11 [s, 3H, C(O)NCH_3], 2.38 [brd, 3H, *J* = 4.0 Hz, H_3C-N(H)]; ^1H NMR 400 MHz (20mM, CD_3OD) δ ppm E(cis)-ac rotamer (78 %): 7.74 (d, 2H, *J* = 8.0 Hz, Ph-CN), 7.64 (d, 2H, *J* = 8.0 Hz, Ph-CN), 3.25 [s, 3H, C(O)NCH_3], 2.48 [s, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (22 %): 7.84 (brs, 2H, Ph-CN), 7.64 (d, 2H, *J* = 8.0 Hz, Ph-CN), 3.09 [s, 3H, C(O)NCH_3], 2.67 [s, 3H, H_3C-(NH)]; ^1H NMR 400 MHz (20mM, CD_3CN) δ ppm E(cis)-ac rotamer (80 %): 7.71 (d, 2H, *J* = 8.0 Hz, Ph-CN), 7.57 (d, 2H, *J* = 8.0 Hz, Ph-CN), 3.94 [brq,

1H, *J* = 4.0 Hz, NH-(CH_3)], 3.16 [s, 3H, C(O)NCH_3], 2.45 [brd, 3H, *J* = 4.0 Hz, H_3C-(NH)]; Z(trans)-sc rotamer (20 %): 7.78 (brs, 2H, Ph-CN), 7.57 (d, 2H, *J* = 8.0 Hz, Ph-CN), 5.61 [brs, 1H, NH-(CH_3)], 2.99 [s, 3H, C(O)NCH_3], 2.60 [s, 3H, H_3C-(NH)]; ^{1}H NMR 400 MHz (20mM, D_2O) δ ppm E(cis)-ac rotamer (62 %): 7.84 (d, 2H, *J* = 8.0 Hz, Ph-CN), 7.58 (d, 2H, *J* = 8.0 Hz, Ph-CN), 3.26 [s, 3H, C(O)NCH_3], 2.50 [s, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (38 %): 7.89 (d, 2H, *J* = 8.0 Hz, Ph-CN), 7.63 (d, 2H, *J* = 8.0 Hz, Ph-CN), 3.10 [s, 3H, C(O)NCH_3], 2.67 [s, 3H, H_3C-(NH)]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm E(cis)-ac rotamer (55 %): 170.7, 140.9, 131.5, 128.4, 118.6, 112.8, 35.8, 32.6; Z(trans)-sc rotamer (45 %): 167.5, 139.6, 132.4, 128.0, 118.1, 113.8, 37.6, 36.0; HRMS $[M + H]^+$ calcd. for, $C_{10}H_{12}N_3O$, m/z: 190.0980; found m/z: 190.0982.



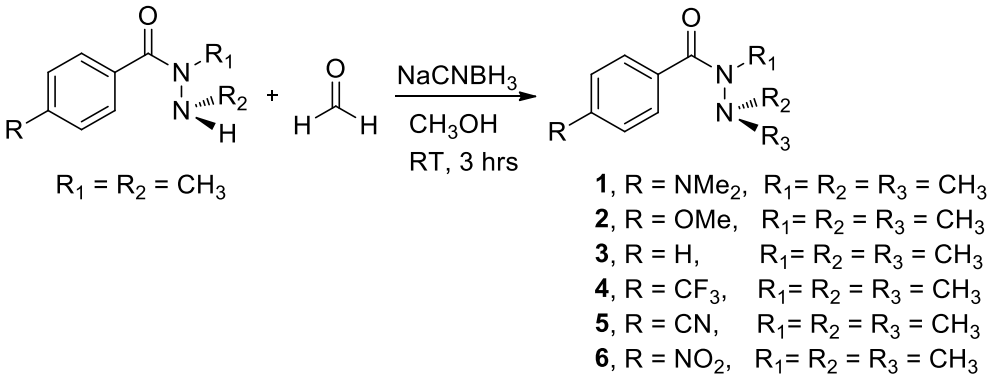
Compound **12:** *N*, *N*'-dimethyl-4-nitrobenzohydrazide.

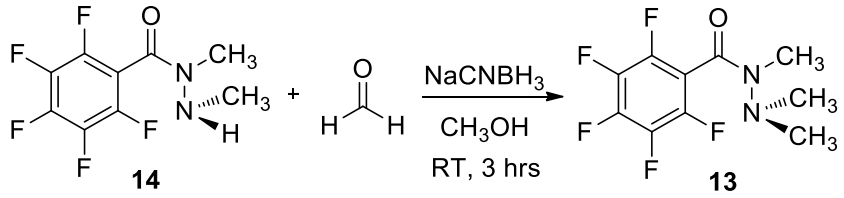
x = 215 mg of 1,2-Dimethylhydrazine-dihydrochloride [y = 1.62 mmol (3 eqv.)], x' = 645 µL of N, N-diisopropylethylamine [DIEA (y') = 3.77 mmol (7 eqv.)] and x'' = 100 mg of 4-nitrobenzoyl chloride [y'' = 0.539 mmol (1 eqv.)]. Yield (%): 82 % as a light yellow solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm E(cis)-ac rotamer (57 %): 8.23 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.67 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 3.42 [brs, 1H, NH-(CH_3)], 3.30 [s, 3H, C(O)NCH_3], 2.59 [s, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (43 %): 8.28 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.67 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 5.73 [brs, 1H, NH-(CH_3)], 3.11 [s, 3H, C(O)NCH_3], 2.71 [s, 3H, H_3C-(NH)]; ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm E(cis)-ac rotamer (~100 %): 8.21 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.67 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 4.97 [q, 1H, *J* = 8.0 Hz, NH-(CH_3)], 3.13 [s, 3H, C(O)NCH_3], 2.39 [brd, 3H, *J* = 4.0 Hz, H_3C-N(H)];

^{1}H NMR 400 MHz (20mM, CD_3OD) δ ppm E(cis)-ac rotamer (81 %): 8.24 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.70 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 3.26 [s, 3H, C(O)NCH_3], 2.49 [s, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (19 %): 8.33 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.70 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 4.57 [brs, 1H, NH-(CH_3)], 3.10 [s, 3H, C(O)NCH_3], 2.69 [s, 3H, H_3C-(NH)]; ^{1}H NMR 400 MHz (20mM, CD_3CN) δ ppm E(cis)-ac rotamer (83 %): 8.19 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.64 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 3.96 [brq, 1H, *J* = 8.0 Hz, NH-(CH_3)], 3.18 [s, 3H, C(O)NCH_3], 2.46 [brd, 3H, *J* = 4.0 Hz, H_3C-(NH)]; Z(trans)-sc rotamer (17 %): 8.25 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.64 (brd, 2H, *J* = 8.0 Hz, Ph-NO_2), 5.62 [brs, 1H, NH-(CH_3)], 3.01 [s, 3H, C(O)NCH_3], 2.62 [s, 3H, H_3C-(NH)]; ^{1}H NMR 400 MHz (20mM, D_2O) δ ppm E(cis)-ac rotamer (63 %): 8.31 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.65 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 3.27 [s, 3H, C(O)NCH_3], 2.50 [brd, 3H, *J* = 4.0 Hz, H_3C-(NH)]; Z(trans)-sc rotamer (37 %): 8.35 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.70 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 3.10 [s, 3H, C(O)NCH_3], 2.67 [s, 3H, H_3C-(NH)]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm E(cis)-ac rotamer (57 %): 170.6, 148.2, 142.9, 128.7, 123.0, 35.9, 32.7; Minor rotamer (45 %): 167.4, 148.7, 141.6, 128.5, 123.94, 37.7, 36.2; HRMS $[M + H]^+$ calcd. for, $C_9H_{12}N_3O_3$, m/z: 210.0879; found m/z: 210.0883.

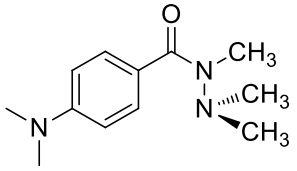
2. General Scheme for the synthesis of *N, N', N'*-trimethyl-monoacylhydrazines 1-6:





Procedure: (Reductive Amination)

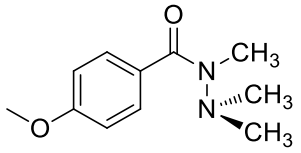
x mg/ µL of *N, N'*-dimethylbenzohydrazide derivatives (**7-12**) [y mmol (1 eqv.)] and x' µL of 37% formaldehyde solution [y' mmol (3 eqv.)] were dissolved in CH_3OH (5-10 mL) at room temperature and stirred for 1 hr. Then x" mg of sodiumcyanoborohydride [y" mmol (3 eqv.)] were added slowly to the above reaction mixture and stirred for another 2 hr. The solvent was evaporated to dryness by using the rotary evaporator. Then the reaction mixture was dissolved in CH_2Cl_2 and washed twice with water, then a 10% citric acid solution followed by a saturated sodium bicarbonate ($NaHCO_3$) solution and finally with brine solution. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The final residue was then purified by the Column chromatography using Silica Gel (100-200 Mesh) and gradient of Hexane and ethyl acetate as an eluent.



Compound **1**: 4-(dimethylamino)-*N, N', N'*-trimethylbenzohydrazide.

100 µL of 4-(dimethylamino)-*N*, *N*'-dimethylbenzohydrazide (**7**) [0.482 mmol (1 eqv.)], 109 µL of 37% formaldehyde solution [1.45 mmol (3 eqv.)] and 91 mg of sodiumcyanoborohydride [1.45 mmol (3 eqv.)]. Yield (%): 69 % as a solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 7.66 [d, 2H, *J* = 8.0 Hz, Ph-$N(CH_3)_2$], 6.64 [d, 2H, *J* = 12.0 Hz, Ph-$N(CH_3)_2$], 3.00 [s, 3H, C(O)N-CH_3], 2.99 [s, 6H, Ph-$N(CH_3)_2$], 2.52 [s, 6H, $N(CH_3)_2$]; ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm [E(cis)-ac: ~100 %]: 7.48 [d, 2H, *J* = 8.0 Hz, Ph-$N(CH_3)_2$], 6.64 [d, 2H, *J* = 12.0 Hz, Ph-$N(CH_3)_2$], 2.94 [s, 6H, Ph-$N(CH_3)_2$], 2.87 [s, 3H, C(O)N-CH_3], 2.43 [s, 6H, $N(CH_3)_2$]; ^{1}H NMR 400 MHz (20 mM, CD_3OD) δ ppm [E(cis)-ac: ~100 %]: 7.55 [d, 2H, *J* = 8.0 Hz, Ph-$N(CH_3)_2$], 6.69 [d, 2H, *J* = 8.0 Hz, Ph-$N(CH_3)_2$], 3.01 [s, 3H, C(O)N-CH_3], 2.99 [s, 6H, Ph-$N(CH_3)_2$], 2.53 [s, 6H, $N(CH_3)_2$]; ^{1}H NMR 400 MHz (20 mM, CD_3CN) δ ppm [E(cis)-ac: ~100 %]: 7.51 [d, 2H, *J* = 8.0 Hz, Ph-$N(CH_3)_2$], 6.67 [d, 2H, *J* = 12.0 Hz, Ph-$N(CH_3)_2$], 2.96 [s, 6H, Ph-$N(CH_3)_2$], 2.92 [s, 3H, C(O)N-CH_3], 2.46 [s, 6H, $N(CH_3)_2$]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 171.8, 151.6, 130.6, 122.8, 110.4, 43.3, 40.3, 23.5; HRMS $[M + H]^+$ calcd. for, $C_{12}H_{20}N_3O$, m/z: 222.1606; found m/z: 222.1607.



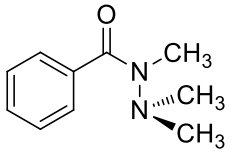
E(cis)-ac: ~100 %

Compound **2**: 4-methoxy-*N*, *N'*, *N'*-trimethylbenzohydrazide.

100 µL of 4-methoxy-*N*, *N*'-dimethylbenzohydrazide (**8**) [0.515 mmol (1 eqv.)], 117 µL of 37% formaldehyde solution [1.54 mmol (3 eqv.)] and 97 mg of sodiumcyanoborohydride [1.54 mmol (3 eqv.)]. Yield (%): 67 % as a solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 7.60 (d, 2H, *J* = 8.0 Hz, Ph-OCH_3), 6.86 (d, 2H, *J* = 8.0 Hz, Ph-OCH_3), 3.83 (s, 3H, OCH_3), 3.02 [s, 3H, C(O)N-CH_3], 2.50

[s, 6H, $N(CH_3)_2$]; ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm [E(cis)-ac: ~100 %]: 7.48 (d, 2H, *J* = 8.0 Hz, Ph-OCH_3), 6.90 (d, 2H, *J* = 8.0 Hz, Ph-OCH_3), 3.78 (s, 3H, OCH_3), 2.90 [s, 3H, C(O)N-CH_3], 2.42 [s, 6H, $N(CH_3)_2$]; ^{1}H NMR 400 MHz (20 mM, CD_3OD) δ ppm [E(cis)-ac: ~100 %]: 7.54 [d, 2H, *J* = 8.0 Hz, Ph-OCH_3], 6.91 [d, 2H, *J* = 8.0 Hz, Ph-OCH_3], 3.83 [s, 3H, OCH_3], 3.02 [s, 3H, C(O)N-CH_3], 2.51 [s, 6H, $N(CH_3)_2$]; ^{1}H NMR 400 MHz (20 mM, CD_3CN) δ ppm [E(cis)-ac: ~100 %]: 7.51 [d, 2H, *J* = 12.0 Hz, Ph- OCH_3], 6.89 [d, 2H, *J* = 8.0 Hz, Ph-OCH_3], 3.81 [s, 3H, OCH_3], 2.94 [s, 3H, C(O)N-CH_3], 2.45 [s, 6H, $N(CH_3)_2$]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 171.7, 160.8, 130.2, 128.4, 112.8, 55.4, 43.2, 23.2; HRMS $[M + H]^+$ calcd. for, $C_{11}H_{17}N_2O_2$, m/z: 209.1290; found m/z: 209.1292.

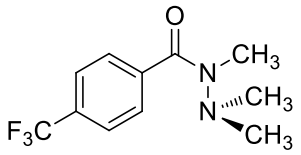


E(cis)-ac: ~100 %

Compound **3**: *N*, *N'*, *N'*-trimethylbenzohydrazide.

100 µL of *N*, *N*′-dimethylbenzohydrazide (**9**) [0.609 mmol (1 eqv.)], 138 µL of 37% formaldehyde solution [1.83 mmol (3 eqv.)] and 115 mg of sodiumcyanoborohydride [1.83 mmol (3 eqv.)]. Yield (%): 66 % as a solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 7.52-7.50 (m, 2H, Ph), 7.39-7.33 (m, 3H, Ph), 3.04 [s, 3H, C(O)N-CH_3], 2.48 [s, 6H, $N(CH_3)_2$]; ^{1}H NMR 400 MHz (20mM, $[CD_3]_2SO$) δ ppm [E(cis)-ac: ~100 %]: 7.43-7.34 (m, 5H, Ph), 2.92 [s, 3H, C(O)N-CH_3], 2.40 [s, 6H, $N(CH_3)_2$]; ^{1}H NMR 400 MHz (20 mM, CD_3OD) δ ppm [E(cis)-ac: ~100 %]: 7.48-7.45 (m, 2H, Ph), 7.40-7.35 (m, 3H, Ph), 3.04 [s, 3H, C(O)N-CH_3], 2.48 [s, 6H, $N(CH_3)_2$]; ^{1}H NMR 400 MHz (20 mM, CD_3CN) δ ppm [E(cis)-ac: ~100 %]: 7.45-7.34 (m, 5H, Ph), 2.96 [s, 3H, C(O)N-CH_3], 2.43 [s, 6H, $N(CH_3)_2$]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 171.6, 136.9, 129.4, 127.6, 127.5, 43.2, 22.9; HRMS $[M + H]^+$ calcd. for, $C_{10}H_{15}N_2O$, m/z: 179.1184; found m/z: 179.1184.

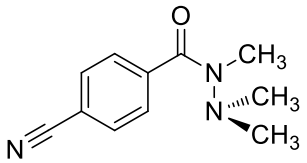


E(cis)-ac: ~100 %

Compound **4**: *N*, *N'*, *N'*-trimethyl-4-(trifluoromethyl)benzohydrazide.

100 µL of *N*, *N*'-dimethyl-4-(trifluoromethyl)benzohydrazide (**10**) [0.431 mmol (1 eqv.)], 98 µL of 37% formaldehyde solution [1.29 mmol (3 eqv.)] and 81 mg of sodiumcyanoborohydride [1.29 mmol (3 eqv.)]. Yield (%): 65 % as a solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 7.63-7.57 (m, 4H, Ph-CF_3), 3.05 [s, 3H, C(O)N-CH_3], 2.47 [s, 6H, N(CH_3)$_2$]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: -62.76 (s, 3F, Ph-CF_3); ^{1}H NMR 400 MHz (20mM, [CD_3]$_2$SO) δ ppm [E(cis)-ac: ~100 %]: 7.73 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 7.61 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 2.95 [s, 3H, C(O)N-CH_3], 2.40 [s, 6H, N(CH_3)$_2$]; ^{19}F NMR 376 MHz (20mM, [CD_3]$_2$SO) δ ppm [E(cis)-ac: ~100 %]: -61.11 (s, 3F, Ph-CF_3); ^{1}H NMR 400 MHz (20mM, CD_3OD) δ ppm [E(cis)-ac: ~100 %]: 7.69 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 7.62 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 3.07 [s, 3H, C(O)N-CH_3], 2.49 [s, 6H, N(CH_3)$_2$]; ^{19}F NMR 376 MHz (20mM, CD_3OD) δ ppm [E(cis)-ac: ~100 %]: -64.28 (s, 3F, Ph-CF_3); ^{1}H NMR 400 MHz (20mM, CD_3CN) δ ppm [E(cis)-ac: ~100 %]: 7.68 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 7.59 (d, 2H, *J* = 8.0 Hz, Ph-CF_3), 2.98 [s, 3H, C(O)N-CH_3], 2.42 [s, 6H, N(CH_3)$_2$]; ^{19}F NMR 376 MHz (20mM, CD_3CN) δ ppm [E(cis)-ac: ~100 %]: -64.28 (s, 3F, Ph-CF_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 171.2, 140.5, 131.1 (q, $^{2}J_{CF}$ = 32.0 Hz), 127.6, 124.7 (q,$^{3}J_{CF}$ = 3.0 Hz), 124.11 (q, $^{1}J_{CF}$ = 270.0 Hz), 43.2, 22.9; HRMS $[M + H]^+$ calcd. for, $C_{11}H_{14}F_3N_2O$, m/z: 247.1058; found m/z: 247.1064.

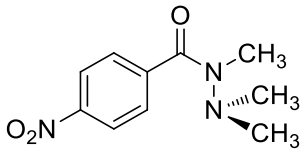


E(cis)-ac: ~100 %

Compound **5**: 4-cyano-*N*, *N'*, *N'*-trimethylbenzohydrazide.

100 mg of 4-cyano-*N*, *N*'-dimethylbenzohydrazide (**11**) [0.529 mmol (1 eqv.)], 120 µL of 37% formaldehyde solution [1.59 mmol (3 eqv.)] and 100 mg of sodiumcyanoborohydride [1.59 mmol (3 eqv.)]. Yield (%): 65 % as a solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 7.65 (d, 2H, *J* = 8.0 Hz, Ph-CN), 7.56 (d, 2H, *J* = 8.0 Hz, Ph-CN), 3.05 [s, 3H, C(O)N-CH_3], 2.46 [s, 6H, N(CH_3)$_2$]; ^{1}H NMR 400 MHz [20mM, (CD_3)$_2$SO] δ ppm [E(cis)-ac: ~100 %]: 7.84 (d, 2H, *J* = 8.0 Hz, Ph-CN), 7.57 (d, 2H, *J* = 8.0 Hz, Ph-CN), 2.94 [s, 3H, C(O)N-CH_3], 2.39 [s, 6H, N(CH_3)$_2$]; ^{1}H NMR 400 MHz (20 mM, CD_3OD) δ ppm [E(cis)-ac: ~100 %]: 7.75 (d, 2H, *J* = 8.0 Hz, Ph-CN), 7.60 (d, 2H, *J* = 8.0 Hz, Ph-CN), 3.06 [s, 3H, C(O)N-CH_3], 2.47 [s, 6H, N(CH_3)$_2$]; ^{1}H NMR 400 MHz (20 mM, CD_3CN) δ ppm [E(cis)-ac: ~100 %]: 7.72 (d, 2H, *J* = 8.0 Hz, Ph-CN), 7.56 (d, 2H, *J* = 12.0 Hz, Ph-CN), 2.97 [s, 3H, C(O)-NCH_3], 2.41 [s, 6H, N(CH_3)$_2$]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 170.7, 141.4, 131.6, 127.8, 118.7, 112.9, 43.2, 23.0; HRMS $[M + H]^+$ calcd. for, $C_{11}H_{14}N_3O$, m/z: 204.1137; found m/z: 204.1139.

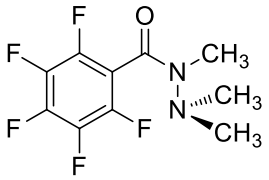


E(cis)-ac: ~100 %

Compound **6**: *N*, *N'*, *N'*-trimethyl-4-nitrobenzohydrazide.

100 mg of *N*, *N*'-dimethyl-4-nitrobenzohydrazide (**12**) [0.478 mmol (1 eqv.)], 108 µL of 37% formaldehyde solution [1.43 mmol (3 eqv.)] and 90 mg of sodiumcyanoborohydride [1.43 mmol (3 eqv.)]. Yield (%): 62 % as a solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 8.22 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.62 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 3.06 [s, 3H, C(O)N-CH_3], 2.47 [s, 6H, N(CH_3)$_2$]; ^{1}H NMR 400 MHz [20mM, (CD_3)$_2$SO] δ ppm [E(cis)-ac: ~100 %]: 8.21 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.66 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 2.96 [s, 3H, C(O)N-CH_3], 2.39 [s, 6H, N(CH_3)$_2$]; ^{1}H NMR 400 MHz (20mM, CD_3OD) δ ppm [E(cis)-ac: ~100 %]: 8.25 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.67 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 3.07 [s, 3H, C(O)N-CH_3], 2.48 [s, 6H, N(CH_3)$_2$]; ^{1}H NMR 400 MHz (20mM, CD_3CN) δ ppm [E(cis)-ac: ~100 %]: 8.20 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 7.62 (d, 2H, *J* = 8.0 Hz, Ph-NO_2), 2.99 [s, 3H, C(O)N-CH_3], 2.42 [s, 6H, N(CH_3)$_2$]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 170.5, 148.1, 143.4, 128.0, 123.1, 43.2, 23.0; HRMS $[M + H]^+$ calcd. for, $C_{10}H_{14}N_3O_3$, m/z: 224.1035; found m/z: 224.1034.



E(cis)-ac: ~100 %

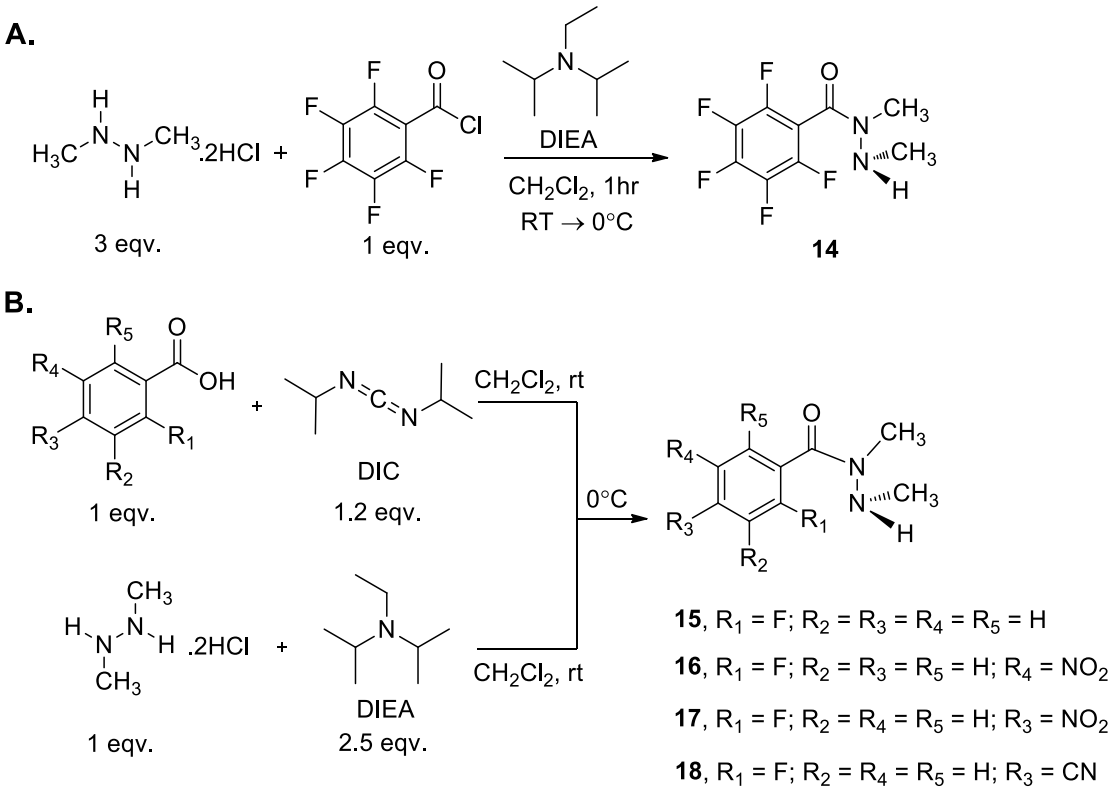
Compound **13**: 2,3,4,5,6-pentafluoro-*N*, *N'*, *N'*-trimethylbenzohydrazide.

100 mg of 2,3,4,5,6-pentafluoro-*N*, *N'*-dimethylbenzohydrazide (**14**) [0.393 mmol (1 eqv.)], 89 µL of 37% formaldehyde solution [1.18 mmol (3 eqv.)] and 74 mg of sodiumcyanoboro-hydride [1.18 mmol (3 eqv.)]. Yield (%): 50 % as a white solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 3.08 [s, 3H, C(O)N-CH_3], 2.47 [s, 6H, N(CH_3)$_2$]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: -142.44 to -142.54 (m, 2F, Ph-F5), -154.77 (t, 1F, *J* = 19 Hz, Ph-F5), -161.66 to -161.81 (m, 2F, Ph-F5); ^{1}H NMR 400 MHz [20mM, (CD_3)$_2$SO] δ ppm [E(cis)-ac: ~100 %]: 3.02 [s, 3H, C(O)N-CH_3], 2.42 [s, 6H, N(CH_3)$_2$]; ^{19}F NMR 376 MHz [20mM, (CD_3)$_2$SO] δ ppm [E(cis)-ac: ~100 %]: -143.65 to -143.74 (m, 2F, Ph-F5), -154.58 (t, 1F, *J* = 23 Hz, Ph-F5), -161.59 to -161.75 (m, 2F, Ph-F5); ^{1}H NMR 400 MHz (20mM, CD_3OD) δ ppm [E(cis)-ac: ~100 %]: 3.10 [s, 3H, C(O)N-

CH_3], 2.50 [s, 6H, $N(CH_3)_2$]; ^{19}F NMR 376 MHz [20mM, $(CD_3)_2SO$] δ ppm [E(cis)-ac: ~100 %]: -145.13 to -145.22 (m, 2F, Ph-F5), -157.61 (t, 1F, *J* = 19 Hz, Ph-F5), -164.57 to -164.69 (m, 2F, Ph-F5); ^1H NMR 400 MHz (20mM, CD_3CN) δ ppm [E(cis)-ac: ~100 %]: 3.03 [s, 3H, $C(O)N-CH_3$], 2.44 [s, 6H, $N(CH_3)_2$]; ^{19}F NMR 376 MHz [20mM, $(CD_3)_2SO$] δ ppm [E(cis)-ac: ~100 %]: -144.81 to -144.90 (m, 2F, Ph-F5), -157.60 (t, 1F, *J* = 19 Hz, Ph-F5), -163.83 to -163.97 (m, 2F, Ph-F5); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: ~100 %]: 160.5, 144.3-144.0 (m, Ph-F5), 142.5-142.3 (m, Ph-F5), 141.8-141.5 (m, Ph-F5), 140.0-139.7 (m, Ph-F5), 138.9-138.6 (m, Ph-F5), 136.6-136.1 (m, Ph-F5), 141.2-113.5 (m, Ph-F5), 43.6, 22.9; HRMS $[M + H]^+$ calcd. for, $C_{10}H_{10}F_5N_2O$, m/z: 269.0713; found m/z: 269.0702.

3. General Scheme for the synthesis of *N,N'*-dimethyl-monoacylhydrazines 14-18:



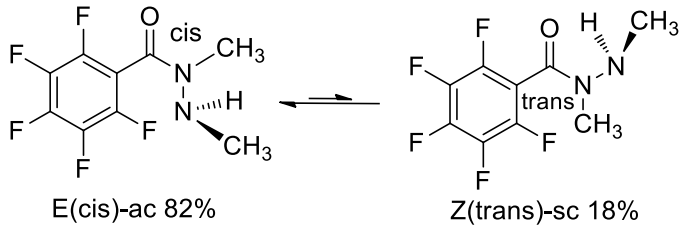
Procedure:

A. x mg of 1,2-Dimethylhydrazine-dihydrochloride [y mmol (3 eqv.)] were neutralized by using x' µL of N, N-diisopropylethylamine [DIEA-y' mmol (7 eqv.)] in CH_2Cl_2 (15 mL) at room temperature and stirred for 15 minutes. The reaction mixture was allowed to cool to

0° C and stirred for another 5 minutes. Then x" mg/ µL of Acyl chloride [y" mmol (1 eqv.)] in CH_2Cl_2 (2 mL) were added drop-wise manner to a reaction mixture over 10 minutes and stirred for another 30 minutes. The solvent was evaporated to dryness by using the rotary evaporator. Then the reaction mixture was dissolved in CH_2Cl_2 and washed twice with water, then a 10% citric acid solution followed by a saturated sodium bicarbonate ($NaHCO_3$) solution and finally with brine solution. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure and the temperature of the rota-vapor need to be maintained less than 40℃. The final residue was then purified by the Column chromatography using Silica Gel (100-200 Mesh) and gradient of Hexane and ethyl acetate as an eluent.

B. In two-neck Rb flask, x mg of substituted benzoic acid [y mmol (1.2 eqv.)] were activated by using x' µL of *N,N'*-diisopropylcarbodiimide (DIC) coupling reagent [y' mmol (1.2 eqv.)] in CH_2Cl_2 (10 mL) at room temperature and stirred for 1 hr (reaction mixture 1). In another two-neck Rb flask, x" mg of 1,2-Dimethylhydrazine-dihydrochloride [y" mmol (1 eqv.)] were neutralized by using x'" µL of N, N-diisopropylethylamine [DIEA-y'" mmol (2.5 eqv.)] in CH_2Cl_2 (10 mL) at room temperature and stirred for 1 hr (reaction mixture 2). Then both the reaction mixture was allowed to cool to 0° C and stirred for another 5 minutes. Then the reaction mixture 1 was slowly added into the rb flask of the reaction mixture 2 and stirred for another 1hr at 0° C. DIC-Urea were filtered off from the final reaction mixture. Then the solvent was evaporated to dryness by using the rotary evaporator. Then the reaction mixture was dissolved in CH_2Cl_2 and washed twice with water, then a 10% citric acid solution followed by a saturated sodium bicarbonate ($NaHCO_3$) solution and finally with brine solution. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure and the temperature of the rota-vapour need to be maintained less than 40℃. The final

residue was then purified by the Column chromatography using Silica Gel (100-200 Mesh) and gradient of Hexane and ethyl acetate as an eluent.

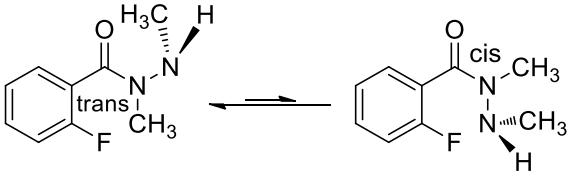


Compound **14**: 2,3,4,5,6-pentafluoro-*N*, *N'*-dimethylbenzohydrazide.

A. x = 173 mg of 1,2-Dimethylhydrazine-dihydrochloride [y = 1.30 mmol (3 eqv.)], x' = 519 µL of N, N-diisopropylethylamine [DIEA (y') = 3.05 mmol (7 eqv.)] and x'' = 63 µL of 2,3,4,5,6-pentafluorobenzoyl chloride [y'' = 0.434 mmol (1 eqv.)]. Yield (%): 85 % as a white solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm E(cis)-ac rotamer (82 %): 3.54 [brs, 1H, HN-(CH_3)], 3.30 [s, 3H, C(O)NCH_3], 2.58 [brs, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (18 %): 3.08 [s, 3H, C(O)NCH_3], 2.70 [s, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: 82 %]: -141.72 [brdd, 2F, *J* = 11.0 Hz, ortho-F (F5-Ph)], -154.34 [t, 1F, *J* = 23.0 Hz, para-F (F5-Ph)], -161.74 to -161.88 [m, 2F, meta-F (F5-Ph)]; Z(trans)-sc rotamer (18 %): -140.65 [brdd, 2F, *J* = 11.0 Hz, ortho-F (F5-Ph)], -150.97 [t, 1F, *J* = 23.0 Hz, para-F (F5-Ph)], -159.48 to -159.63 [m, 2F, meta-F (F5-Ph)]; ^{1}H NMR 400 MHz (20mM, $[CD_3]_2SO$) δ ppm E(cis)-ac rotamer (~100%): 5.32 [q, 1H, *J* = 8.0 Hz, HN-(CH_3)], 3.16 [s, 3H, C(O)NCH_3], 2.38 [d, 3H, *J* = 4.0 Hz, H_3C-(NH)]; ^{19}F NMR 376 MHz (20mM, $[CD_3]_2SO$) δ ppm [E(cis)-ac: ~100 %]: -143.03 [brdd, 2F, *J* = 15.0 Hz, ortho-F (F5-Ph)], -154.77 [t, 1F, *J* = 23.0 Hz, para-F (F5-Ph)], -161.98 to -162.13 [m, 2F, meta-F (F5-Ph)]; ^{1}H NMR 400 MHz (20mM, CD_3OD) δ ppm E(cis)-ac rotamer (94 %): 3.26 [s, 3H, C(O)NCH_3], 2.49 [d, 3H, *J* = 4.0 Hz, H_3C-(NH)]; Z(trans)-sc rotamer (6 %): 3.10 [s, 3H, C(O)NCH_3], 2.67 [s, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: 94 %]: -144.52 to -144.60 [m, 2F, ortho-F (F5-Ph)], -157.65 [t, 1F,

J = 19.0 Hz, para-F (F5-Ph)], -164.91 to -165.04 [m, 2F, meta-F (F5-Ph)]; Z(trans)-sc rotamer (6 %): -144.22 to -144.25 [m, 2F, ortho-F (F5-Ph)], -154.68 [t, 1F, *J* = 19.0 Hz, para-F (F5-Ph)], -162.93 to -163.05 [m, 2F, meta-F (F5-Ph)]; ^{1}H NMR 400 MHz (20mM, CD_3CN) δ ppm E(cis)-ac rotamer (92 %): 4.21 [brq, 1H, *J* = 4.0 Hz, HN-(CH_3)], 3.20 [s, 3H, C(O)NCH_3], 2.46 [d, 3H, *J* = 4.0 Hz, H_3C-(NH)]; Z(trans)-sc rotamer (8 %): 3.02 [s, 3H, C(O)NCH_3], 2.61 [s, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: 92 %]: -144.20 to -144.28 [m, 2F, ortho-F (F5-Ph)], -157.27 [t, 1F, *J* = 19.0 Hz, para-F (F5-Ph)], -164.03 to -164.16 [m, 2F, meta-F (F5-Ph)]; Z(trans)-sc rotamer (8 %): -143.83 to -143.91 [m, 2F, ortho-F (F5-Ph)], -154.96 [t, 1F, *J* = 19.0 Hz, para-F (F5-Ph)], -162.30 to -162.44 [m, 2F, meta-F (F5-Ph)]; ^{1}H NMR 400 MHz (20mM, D_2O) δ ppm E(cis)-ac rotamer (76 %): 3.29 [s, 3H, C(O)NCH_3], 2.51 [s, 3H, H_3C-(NH)]; Z(trans)-sc rotamer (24 %): 3.14 [s, 3H, C(O)NCH_3], 2.66 [s, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz (20mM, D_2O) δ ppm [E(cis)-ac: 76 %]: -142.67 to -142.78 [m, 2F, ortho-F (F5-Ph)], -153.23 [t, 1F, *J* = 23.0 Hz, para-F (F5-Ph)], -161.31 to -161.46 [m, 2F, meta-F (F5-Ph)]; Z(trans)-sc rotamer (24 %): -142.04 [m, 2F, ortho-F (F5-Ph)], -150.98 [t, 1F, *J* = 23.0 Hz, para-F (F5-Ph)], -160.25 to -160.39 [m, 2F, meta-F (F5-Ph)]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: 82 %]: 161.0, 144.3-144.1 (m, Ph-F5), 142.8-142.4 (m, Ph-F5), 141.9-141.6 (m, Ph-F5), 140.3-139.9 (m, Ph-F5), 138.9-138.5 (m, Ph-F5), 136.4-136.0 (m, Ph-F5), 113.3-112.8 (m, Ph-F5), 35.89, 31.97; [Z(trans)-sc: 18 %]: 156.9, 144.3-144.1 (m, Ph-F5), 142.8-142.4 (m, Ph-F5), 141.9-141.6 (m, Ph-F5), 140.3-139.9 (m, Ph-F5), 138.9-138.5 (m, Ph-F5), 136.4-136.0 (m, Ph-F5), 113.3-112.8 (m, Ph-F5), 36.3, 36.1; HRMS $[M + H]^+$ calcd. for, $C_9H_8F_5N_2O$, m/z: 255.0557; found m/z: 255.0565.

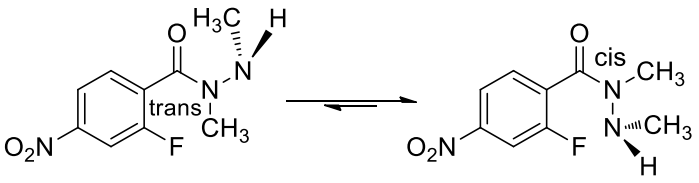


Z(trans)-sc: 63% E(cis)-ac: 37%

Compound **15**: 2-fluoro-*N*,*N'*-dimethylbenzohydrazide.

B. x = 158 mg of 2-fluorobenzoic acid [y = 1.13 mmol (1.2 eqv.)], x' = 210 µL of *N,N'*-diisopropylcarbodiimide (DIC) coupling reagent [y' = 1.35 mmol (1.2 eqv.)], x" = 150 mg of 1,2-Dimethylhydrazine-dihydrochloride [y" = 1.13 mmol (1 eqv.)] and x"' = 482 µL of N, N-diisopropylethylamine [DIEA-y"' = 2.82 mmol (2.5 eqv.)]. Yield (%): 89 % as a white semisolid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm Z(trans)-sc rotamer (63 %): 7.45-7.32 [m, 2H, Ph(ortho-F)], 7.24-7.02 [m, 2H, Ph(ortho-F)], 3.07 [brd, *J* = 4.0 Hz, 3H, C(O)N-CH_3], 2.70 [s, 3H, H_3C-(NH)]; E(cis)-ac rotamer (37 %): 7.45-7.32 [m, 2H, Ph(ortho-F)], 7.24-7.02 [m, 2H, Ph(ortho-F)], 3.28 [s, 3H, C(O)N-CH_3], 2.54 [s, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm Z(trans)-sc rotamer (63 %): -114.91 to -114.97 (m, 1F, J_{FC}, meta-NO_2-Ph-F); [E(cis)-ac: 37 %]: -113.74 to -113.79 (m, 1F, J_{FC}, meta-NO_2-Ph-F); ^{1}H NMR 400 MHz (20mM, $[CD_3]_2SO$) δ ppm E(cis)-ac rotamer (86 %): 7.40-7.35 [m, 1H, Ph(ortho-F)], 7.31-7.27 [m, 1H, Ph(ortho-F)], 7.20-7.14 [m, 2H, Ph(ortho-F)], 4.93 [q, 1H, *J* = 4.0 Hz, (CH_3)N-H] 3.11 [s, 3H, C(O)N-CH_3], 2.33 [d, 3H, *J* = 8.0 Hz, H_3C-(NH)]; Z(trans)-sc rotamer (14 %): 7.89-7.84 [m, 1H, Ph(ortho-F)], 7.67-7.61 [m, 1H, Ph(ortho-F)], 7.54-7.49 [m, 1H, Ph(ortho-F)], 7.31-7.27 [m, 1H, Ph(ortho-F)], 5.87 [brs, 1H, (CH_3)N-H] 2.92 [s, 3H, C(O)N-CH_3], 2.54 [s, 3H, H_3C-(NH)]; ^{19}F NMR 376 MHz [20mM, $(CD_3)_2SO$] δ ppm [E(cis)-ac: 86 %]: -115.28 to -115.34 (m, 1F, J_{FC}, meta-NO_2-Ph-F); [Z(trans)-sc: 14 %]: -116.60 to -116.66 (m, 1F, J_{FC}, meta-NO_2-Ph-F); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [Z(trans)-sc: 63 %]: 164.7, 158.4 (d, $^{1}J_{FC,}$ *J* = 247 Hz), 134.6 (d, $^{3}J_{FC,}$ *J* = 8.0 Hz), 131.8 (d, $^{2}J_{FC,}$ *J* = 8.0 Hz), 129.2 (d, $^{4}J_{FC,}$ *J* = 3.0 Hz), 124.7 (d, $^{3}J_{FC,}$ *J* = 3.0 Hz), 116.0 (d, $^{2}J_{FC,}$ *J* = 21.0 Hz), 36.5 [d, *J* = 3.0 Hz, C(O)N-CH_3···F-Ph] 36.1; [E(cis)-ac: 37 %]: 168.8, 158.5 (d, $^{1}J_{FC,}$ *J* = 246 Hz), 132.6 (brd, $^{3}J_{FC}$), 130.6 (d, $^{2}J_{FC,}$ *J* = 8.0 Hz), 128.6 (d, $^{3}J_{FC,}$ *J* = 4.0 Hz), 124.0 (d, $^{4}J_{FC,}$ *J* = 3.0 Hz), 115.2 (d, $^{2}J_{FC,}$ *J* = 22.0 Hz), 35.7 [brd, *J* = 4.0 Hz, (H)N-CH_3···F-Ph], 32.3; HRMS $[M + H]^+$ calcd. for, $C_9H_{12}FN_2O$, m/z: 183.0934; found m/z: 183.0929.

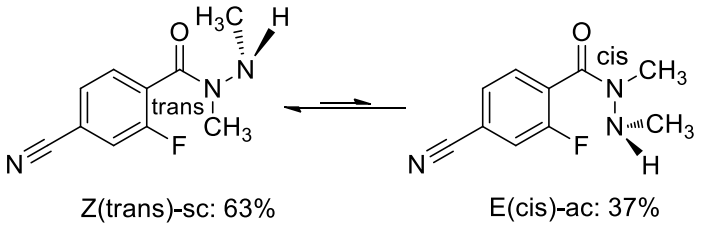


Compound **17**: 2-fluoro-*N*,*N'*-dimethyl-4-nitrobenzohydrazide.

B. x = 250 mg of 2-fluoro-4-nitrobenzoic acid [y = 1.35 mmol (1.2 eqv.)], x' = 210 µL of *N*,*N'*-diisopropylcarbodiimide (DIC) coupling reagent [y' = 1.35 mmol (1.2 eqv.)], x" = 150 mg of 1,2-Dimethylhydrazine-dihydrochloride [y" = 1.13 mmol (1 eqv.)] and x"' = 482 µL of N, N-diisopropylethylamine [DIEA-y"' = 2.82 mmol (2.5 eqv.)]. Yield (%): 82 % as an off-white semisolid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm E(cis)-ac rotamer (75 %): 8.06 (dd, 1H, *J* = 8.0 Hz, meta-NO_2-Ph-F), 7.92 (dd, 1H, *J* = 8.0 Hz, meta-NO_2-Ph-F), 7.53 (dd, 1H, *J* = 8.0 Hz, meta-NO_2-Ph-F), 3.52 [brq, *J* = 8.0 Hz, 1H, (CH_3)N-H] 3.29 [s, 3H, C(O)N-CH_3], 2.55 [d, 3H, *J* = 4.0 Hz, Ph-F···H_3C-(NH)]; Z(trans)-sc rotamer (25 %): 8.12 (dd, 1H, *J* = 8.0 Hz, meta-NO_2-Ph-F), 8.02 (dd, 1H, *J* = 8.0 Hz, meta-NO_2-Ph-F), 7.63 (dd, 1H, *J* = 8.0 Hz, meta-NO_2-Ph-F), 3.06 [d, 3H, C(O)N-CH_3···F-Ph], 2.71 [s, 3H, (H_3C)N-H]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: 75 %]: -109.48 (dd, 1F, *J* = 8.0 Hz, meta-NO_2-Ph-F); Z(trans)-sc rotamer (25 %): -110.48 (t, 1F, *J* = 8.0 Hz, meta-NO_2-Ph-F); ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm E(cis)-ac rotamer (~100 %): 8.13-8.07 (m, 2H, meta-NO_2-Ph-F), 7.64-7.61 (m, 1H, meta-NO_2-Ph-F), 5.11 [q, 1H, *J* = 4.0 Hz, (CH_3)N-H], 3.14 [s, 3H, C(O)-NCH_3], 2.34 [d, *J* = 8.0 Hz, 3H, (H)N-CH_3]; ^{19}F NMR 376 MHz (20mM, $[CD_3]_2SO$) δ ppm [E(cis)-ac: ~100 %]: - 111.46 (dd, *J* = 8.0 Hz, 1F, meta-NO_2-Ph-F); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: 75 %]: 166.7, 158.2 (d, $^{1}J_{FC,}$ *J* = 250 Hz), 132.8 (d, $^{2}J_{FC,}$ *J* = 18.0 Hz), 129.2 (d, $^{3}J_{FC,}$ *J* = 4.0 Hz), 119.4 (d, $^{4}J_{FC,}$ *J* = 4.0 Hz), 111.2 (d, $^{2}J_{FC,}$ *J* = 28.0 Hz), 35.6 [d, *J* = 1.0 Hz, (H)N-CH_3···F-Ph], 32.0; [Z(trans)-sc: 25 %]: 162.6, 158.1 (d, $^{1}J_{FC,}$ *J* = 250 Hz), 148.8 (d, $^{2}J_{FC,}$ *J* = 8.0 Hz), 130.3 (d,

$^{3}J_{FC,}$ J = 4.0 Hz), 120.0 (d, $^{4}J_{FC,}$ J = 3.0 Hz), 112.2 (d, $^{2}J_{FC,}$ J = 27.0 Hz), 36.6 [d, J = 3.0 Hz, C(O)N-CH_3···F-Ph] 36.1; HRMS $[M + H]^+$ calcd. for, $C_9H_{10}FN_3O_3$, m/z: 228.0784; found m/z: 228.0795.



Z(trans)-sc: 63% E(cis)-ac: 37%

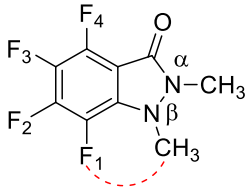
Compound **18**: 2-fluoro-*N*,*N'*-dimethyl-4-nitrobenzohydrazide.

B. x = 223 mg of 4-cyano-2-fluorobenzoic acid [y = 1.35 mmol (1.2 eqv.)], x' = 210 µL of *N*,*N'*-diisopropylcarbodiimide (DIC) coupling reagent [y' = 1.35 mmol (1.2 eqv.)], x'' = 150 mg of 1,2-Dimethylhydrazine-dihydrochloride [y'' = 1.13 mmol (1 eqv.)] and x''' = 482 µL of N, N-diisopropylethylamine [DIEA-y''' = 2.82 mmol (2.5 eqv.)]. Yield (%): 83 % as an off-white semisolid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm E(cis)-ac rotamer (71 %): 7.55-7.54 (m, 1H, meta-CN-Ph-F), 7.47-7.43 (m, 1H, meta-CN-Ph-F), 7.35-7.33 (d, 1H, J = 8.0 Hz, meta-CN-Ph-F), 3.51 [brq, J = 4.0 Hz, 1H, (CH_3)N-H] 3.28 [s, 3H, C(O)N-CH_3], 2.55 [d, 3H, J = 4.0 Hz, Ph-F···H_3C-(NH)]; Z(trans)-sc rotamer (29 %): 7.47-7.43 (m, 3H, meta-CN-Ph-F), 3.05 [bd, 3H, C(O)N-CH_3···F-Ph], 2.70 [s, 3H, (H_3C)N-H]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm [E(cis)-ac: 71 %]: -110.51 to -110.54 (m, 1F, meta-NO_2-Ph-F); Z(trans)-sc rotamer (29 %): -111.63 to -111.65 (m, 1F, meta-NO_2-Ph-F); ^{1}H NMR 400 MHz [20mM, (CD_3)$_2$SO] δ ppm E(cis)-ac rotamer (~100 %): 7.85 (dd, 1H, J = 8.0 Hz, meta-CN-Ph-F), 7.70 (dd, 1H, J = 8.0 Hz, meta-CN-Ph-F), 7.53 (t, 1H, J = 8.0 Hz, meta-CN-Ph-F), 5.06 [q, 1H, J = 4.0 Hz, (CH_3)N-H], 3.12 [s, 3H, C(O)-NCH_3], 2.33 [d, J = 4.0 Hz, 3H, (H)N-CH_3]; ^{19}F NMR 376 MHz (20mM, [CD_3]$_2$SO) δ ppm [E(cis)-ac: ~100 %]: -113.26 (dd, J = 8.0 Hz, 1F, meta-CN-Ph-F); ^{13}C NMR

(100 MHz, $CDCl_3$) δ ppm [E(cis)-ac: 71 %]: 166.9, 158.0 (d, $^1J_{FC,}$ J = 249.0 Hz), 131.3 (d, $^2J_{FC,}$ J = 18.0 Hz), 129.6 (d, $^3J_{FC,}$ J = 4.0 Hz), 128.2 (d, $^4J_{FC,}$ J = 4.0 Hz), 119.0 (d, $^2J_{FC,}$ J = 25.0 Hz), 117.5 (d, $^4J_{FC,}$ J = 3.0 Hz), 113.9 (d, $^3J_{FC,}$ J = 9.0 Hz), 35.6 [d, J = 1.0 Hz, (H)N-CH_3···F-Ph], 32.0; [Z(trans)-sc: 29 %]: 162.7, 158.2 (d, $^1J_{FC,}$ J = 197.0 Hz), 128.8 (d, $^2J_{FC,}$ J = 18.0 Hz), 130.5 (d, $^3J_{FC,}$ J = 5.0 Hz), 128.8 (d, $^4J_{FC,}$ J = 4.0 Hz), 120.0 (d, $^2J_{FC,}$ J = 25.0 Hz), 116.9 (d, $^4J_{FC,}$ J = 3.0 Hz), 115.4 (d, $^3J_{FC,}$ J = 9.0 Hz), 36.5[d, J = 3.0 Hz, C(O)N-CH_3···F-Ph], 36.8; HRMS $[M + H]^+$ calcd. for, $C_{10}H_{11}FN_3O$, m/z: 208.0886; found m/z: 208.0897.

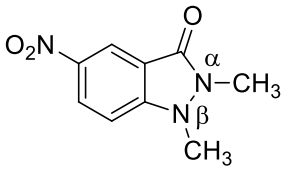
Cyclic compounds:



Compound **14C**: 4, 5, 6, 7-tetrafluoro-1, 2-dimethyl-*1H*-indazol-3(*2H*)-one.

Yield (%): 95 % as a white solid.

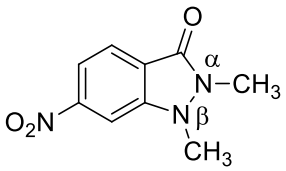
^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm (~100 %): 3.40 [s, 3H, C(O)-$N_α$-CH_3], 3.34 [s, 3H, $N_β$-CH_3]; ^{19}F NMR 376 MHz (20mM, $CDCl_3$) δ ppm (~100 %): -143.27 to -143.39 (m, 1F, PhF_4), -149.04 (td, 1F, J = 19.0 Hz), -156.16 (t, 1F, J = 19.0 Hz), -163.04 (td, 1F, J = 19.0 Hz); ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm (~100 %): 3.36 [s, 3H, C(O)-$N_α$-CH_3], 3.33 [s, 3H, $N_β$-CH_3]; ^{19}F NMR 376 MHz [20mM, $(CD_3)_2SO$] δ ppm (~100 %): -146.55 to -146.67 (m, 1F), -151.38 (td, 1F, J = 19.0 Hz), -156.47 (t, 1F, J = 19.0 Hz), -165.71 (td, 1F, J = 19.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm (~100 %): 159.0 (d, $^3J_{C-F4}$ = 3.0 Hz), 143.9 (dtd, $^1J_{CF}$ = 254 Hz, $^2J_{CF}$ = 15.0 Hz, $^3J_{CF}$ = 3.0 Hz), 142.7 (ddt, $^1J_{CF}$ = 260 Hz, $^2J_{CF}$ = 12.0 Hz, $^3J_{CF}$ = 3.0 Hz), 136.5 (dt, $^1J_{CF}$ = 248 Hz, $^2J_{CF}$ = 15.0 Hz), 134.9 (ddd, $^1J_{CF}$ = 250 Hz, $^2J_{CF}$ = 15.0 Hz, $^2J_{CF}$ = 15.0 Hz), 134.3-134.1 (m), 105.0 (d, $^2J_{C-F4}$ = 15.0 Hz), 38.2 (d, J = 5.0 Hz, F1···H_3C-Nβ), 29.1; HRMS $[M + H]^+$ calcd. for, $C_9H_7F_4N_2O$, m/z: 235.0495; found m/z: 235.0493.



Compound **16C**: 1, 2-dimethyl-5-nitro-*1H*-indazol-3(*2H*)-one.

Yield (%): 96 % as a yellow solid.

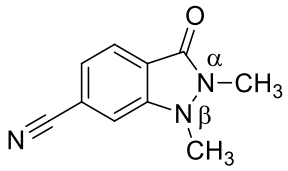
^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm (~100 %): 8.78 (d, 1H, *J* = 4.0 Hz, para-NO_2-Ph), 8.40 (dd, 1H, *J* = 8.0 Hz, para-NO_2-Ph), 7.22 (d, 1H, *J* = 12.0 Hz, para-NO_2-Ph), 3.52 [s, 3H, C(O)-N_α-CH_3], 3.47 [s, 3H, N_β-CH_3]; ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm (~100 %): 8.46 (d, 1H, *J* = 4.0 Hz, para-NO_2-Ph), 8.37 (dd, 1H, *J* = 8.0 Hz, para-NO_2-Ph), 7.68 (d, 1H, *J* = 12.0 Hz, para-NO_2-Ph), 3.60 [s, 3H, C(O)-N_α-CH_3], 3.45 [s, 3H, N_β-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm (~100 %): 161.4, 150.4, 142.7, 127.4, 121.6, 117.5, 110.7, 35.9, 29.3; HRMS $[M + H]^+$ calcd. for, $C_9H_{10}N_3O_3$, m/z: 208.0722; found m/z: 208.0721.



Compound **17C**: 1, 2-dimethyl-6-nitro-*1H*-indazol-3(*2H*)-one.

Yield (%): 93 % as an orange solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm (~100 %): 8.09 (brs, 1H, meta-NO_2-Ph), 8.01-8.00 (m, 1H, meta-NO_2-Ph), 3.51 [s, 3H, C(O)-N_α-CH_3], 3.40 [s, 3H, N_β-CH_3]; ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm (~100 %): 8.53 (brs, 1H, meta-NO_2-Ph), 7.91 (m, 2H, meta-NO_2-Ph-F), 3.49 [s, 3H, C(O)-N_α-CH_3], 3.43 [s, 3H, N_β-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm (~100 %): 161.1, 150.8, 148.8, 125.5, 123.0, 117.0, 107.4, 37.2, 29.4; HRMS $[M + H]^+$ calcd. for, $C_9H_{10}N_3O_3$, m/z: 208.0722; found m/z: 208.0732.



Compound **18C**: 1, 2-dimethyl-3-oxo-2, 3-dihydro-*1H*-indazole-6-carbonitrile.

Yield (%): 90 % as an off-white solid.

^{1}H NMR 400 MHz (20mM, $CDCl_3$) δ ppm (~100 %): 7.95 (d, 1H, *J* = 8.0 Hz, meta-CN-Ph), 7.50 (s, 1H, meta-CN-Ph), 7.41 (d, 1H, *J* = 8.0 Hz, meta-CN-Ph), 3.49 [s, 3H, C(O)-N_α-CH_3], 3.33 [s, 3H, N_β-CH_3]; ^{1}H NMR 400 MHz [20mM, $(CD_3)_2SO$] δ ppm (~100 %): 8.21 (s, 1H, meta-CN-Ph), 7.85 (d, 1H, *J* = 8.0 Hz, meta-CN-Ph), 7.51 (d, 1H, *J* = 8.0 Hz, meta-CN-Ph), 3.41 [s, 3H, C(O)-N_α-CH_3], 3.40 [s, 3H, N_β-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm (~100 %): 161.4, 148.7, 125.4, 125.1, 121.8, 118.4, 115.8, 115.4, 37.3, 29.3; HRMS $[M + H]^+$ calcd. for, $C_{10}H_{10}N_3O$, m/z: 188.0824; found m/z: 188.0835.

F. Supplementary figures and tables.

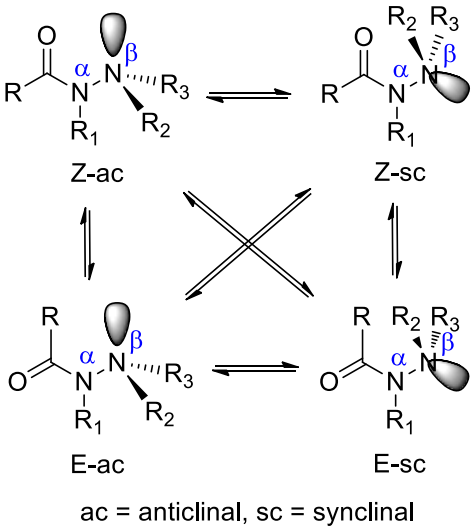


Figure S1. Four different rotamers were possible based on E/Z isomerisation of the amide bond, the lone pair of β-nitrogen and when the both substituent at β-nitrogen are same (R_2 = R_3).

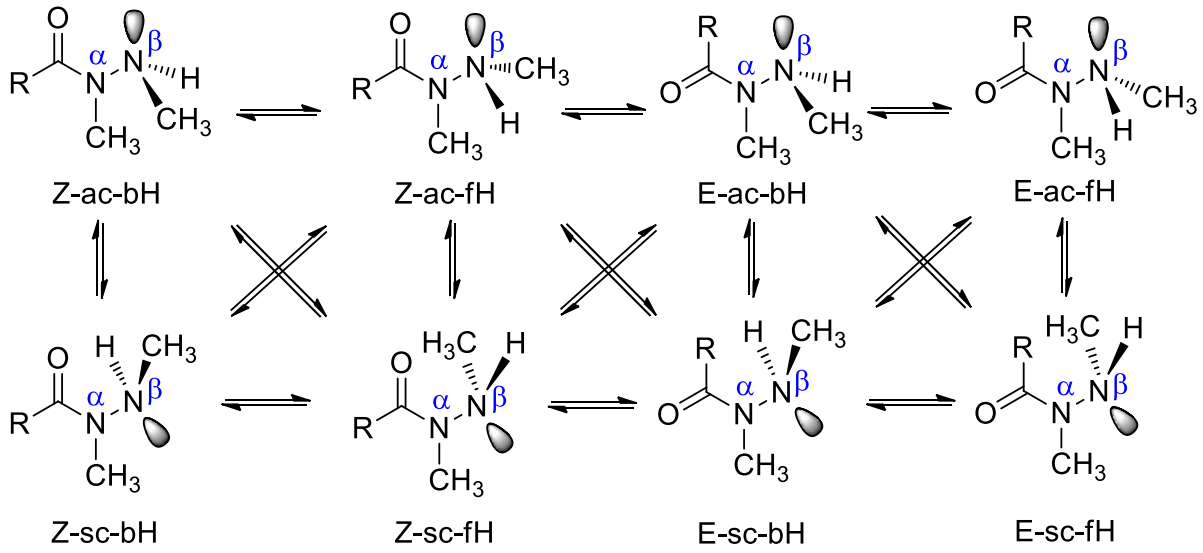
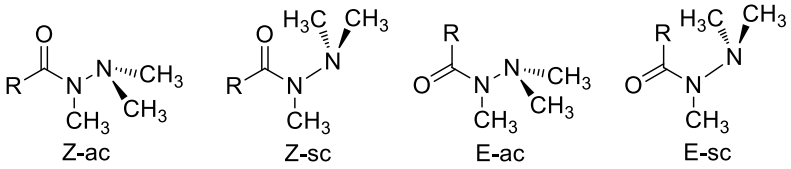


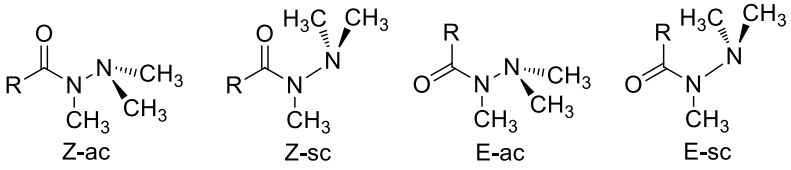
Figure S2. Eight different rotamers were possible based on E/Z isomerisation of the amide bond, the lone pair of β-nitrogen and when the both substituent at β-nitrogen are different ($R_2 \neq R_3$).

Table S1. Zero-point corrected relative electronic energies Δ(E+ZPE) of **1-6** in kcal·mol^{-1}.



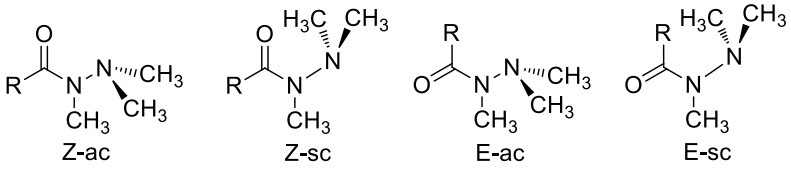
Comp	Conformation				
	R	Z-ac	Z-sc	E-ac	E-sc
1	NMe_2Ph	4.02	1.34	0.00	4.12
2	OMePh	4.56	1.84	0.00	4.49
3	Ph	4.16	1.36	0.00	4.23
4	CF_3Ph	4.96	1.99	0.00	4.88
5	CNPh	4.99	2.10	0.00	4.90
6	NO_2Ph	5.05	2.25	0.00	4.77

Table S2. Relative electronic energies ΔE of **1-6** in kcal·mol^{-1}.



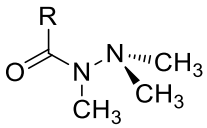
Comp	Conformation				
	R	Z-ac	Z-sc	E-ac	E-sc
1	NMe_2Ph	4.27	1.28	0.00	4.29
2	OMePh	4.42	1.50	0.00	4.66
3	Ph	4.37	1.39	0.00	4.35
4	CF_3Ph	4.88	1.93	0.00	4.93
5	CNPh	5.03	2.10	0.00	5.14
6	NO_2Ph	5.10	2.20	0.00	5.19

Table S3. Relative Gibbs free energies ΔG of **1-6** in kcal·mol^{-1}.



Comp	Conformation				
	R	Z-ac	Z-sc	E-ac	E-sc
1	NMe_2Ph	3.89	1.20	0.00	4.04
2	OMePh	4.71	1.99	0.00	4.13
3	Ph	4.11	1.20	0.00	3.95
4	CF_3Ph	5.21	1.82	0.00	4.79
5	CNPh	5.02	1.96	0.00	4.49
6	NO_2Ph	5.22	2.29	0.00	4.24

Table S4. Optimized structural parameters and NBO stabilization energies of the E-ac conformers of **1-6** computed at M06-2X/6-311+G(2d,p) level of theory.



E-ac

Comp	R	E^2 $n_{N\beta}\rightarrow\pi^*_{Ar}$ kcal.mol^{-1}	σ_P	ΔN_β Å	ΔC_{Ph} Å	$d_{N\cdots C}$ Å	E^2 $n_O\rightarrow\sigma^*_{C\text{-}H}$ kcal.mol^{-1}	$d_{O\cdots C}$ Å
1	NMe_2-Ph	1.27	-0.83	0.406	0.033	2.845	1.23	2.635
2	OMe-Ph	1.44	-0.27	0.407	0.034	2.833	1.17	2.644
3	Ph	1.47	0.00	0.407	0.035	2.826	1.11	2.653
4	CF_3-Ph	1.60	0.54	0.409	0.035	2.816	1.06	2.659
5	CN-Ph	1.62	0.66	0.410	0.036	2.815	1.06	2.661
6	NO_2-Ph	1.66	0.78	0.411	0.035	2.812	1.03	2.665

E^2 = Second order perturbation energies calculated as kcal.mol^{-1}, $n_{N\beta}\rightarrow\pi^*_{Ar}$ = lone pair of β-nitrogen delocalized into the antibonding π orbital of the Ph ring, σ_P = Hammett constant, ΔN_β = Pyramidiality at β-nitrogen, ΔC_{Ph} = Pyramidiality at Cipso in aromatic Ph ring, $d_{N\cdots C}$ = distances between β-nitrogen and Cipso of the Ph ring in Angstrom (Å), NBO values were observed at above 0.05 kcal.mol^{-1} threshold.

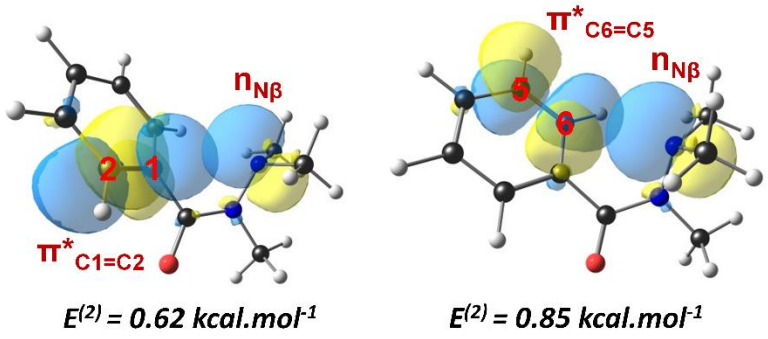
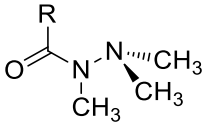


Figure S3. $n_{N\beta} \rightarrow \pi^*_{Ar}$ interaction NBO orbital overlaps involving the β-nitrogen lone pair ($n_{N\beta}$) and two different antibonding $\pi^*_{C=C}$ orbitals of the phenyl ring in **3**.

Table S5. X-ray crystallographic structural parameters and NBO stabilization energies of the E-ac conformers of **2-3** and **5-6** computed using crystallographic atomic coordinates.



E-ac

Comp	R	E^2 $n_N\rightarrow\pi^*_{Ar}$ kcal.mol^{-1}	σ_P	ΔN_β Å	ΔC_{Ph} Å	$d_{N\cdots C}$ Å
2	OMe-Ph	1.67	-0.27	0.421	0.041	2.785
3	Ph	2.09	0.00	0.426	0.032	2.712
5	CN-Ph	2.48	0.66	0.416	0.035	2.694
6	NO_2-Ph	2.53	0.78	0.425	0.037	2.691

NBO values were observed at above 0.05 kcal.mol^{-1} threshold.

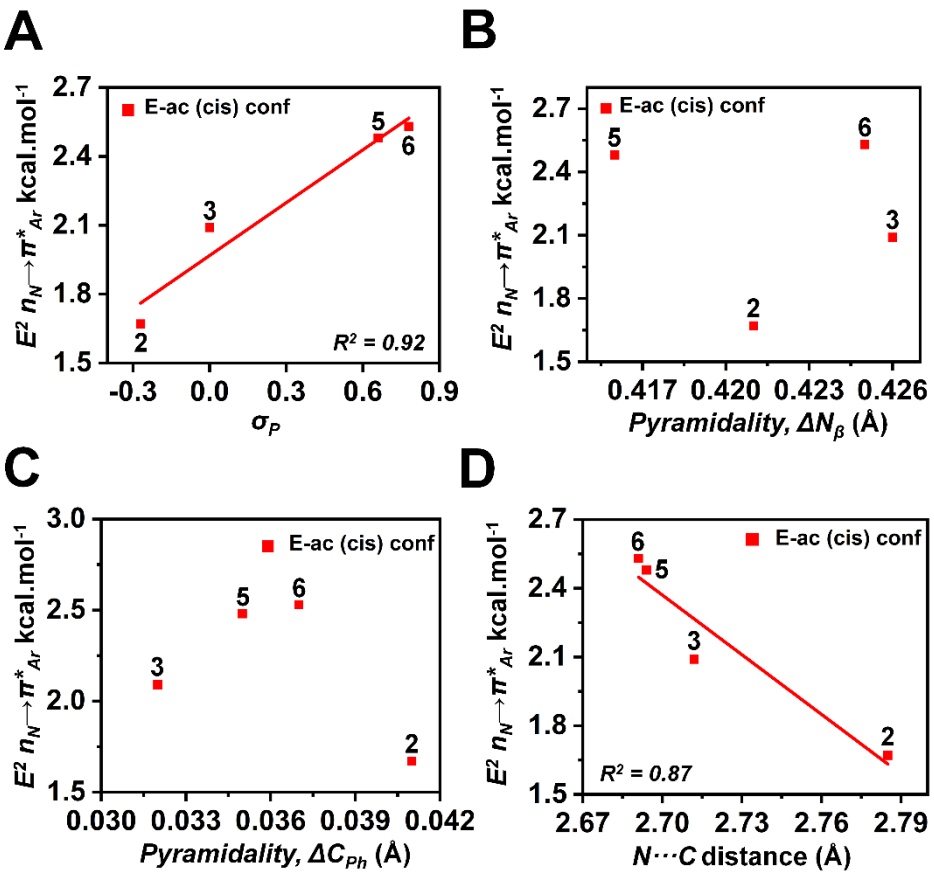


Figure S4. (A) Increase in the $n_N \rightarrow \pi^*_{Ar}$ interactions from **2, 3** to **5, 6** with increase in electron withdrawing ability of the p-substituent in the phenyl ring. (B) Positive pyramidality of the donor nitrogen vs $n_N \rightarrow \pi^*_{Ar}$ interactions of **2, 3** to **5, 6**. (C) Positive pyramidality of the phenyl carbon vs $n_N \rightarrow \pi^*_{Ar}$ interactions of **2, 3** to **5, 6** and (D) Increase in the $n_N \rightarrow \pi^*_{Ar}$ interactions from **2, 3** to **5, 6** with decrease in donor-acceptor distance (N···C).

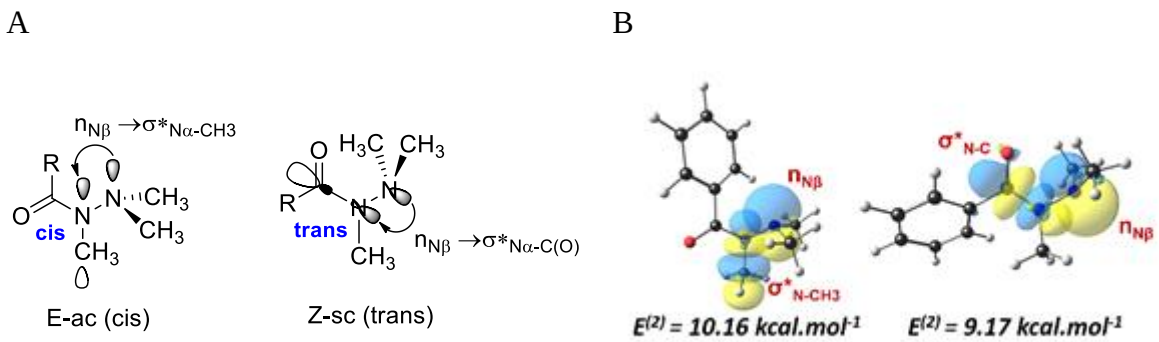


Figure S5. (A) Pictorial representations of $n_{N\beta} \rightarrow \sigma^*_{N\text{-}CH3}$ and $n_{N\beta} \rightarrow \sigma^*_{N\text{-}C(O)}$ interactions in the E-ac and Z-sc isomers, respectively. (B) NBO $n_{N\beta} \rightarrow \sigma^*_{N\text{-}CH3}$ orbital interaction in the E-ac isomer of **3** and (B) $n_{N\beta} \rightarrow \sigma^*_{N\text{-}C(O)}$ orbital interaction in the Z-sc isomer of **3**.

Table S6. NBO stabilization energies due to anomeric interactions in the E-ac, Z-sc, Z-ac and E-sc isomers of **1-6**. [cis and trans denotes for the amide bond O=C-Nα-CH_3]

Comp	E-ac (cis)		Z-sc (trans)		Z-ac (trans)		E-sc (cis)	
	E^2 $n_{N\beta} \rightarrow \sigma^*_{N\alpha\text{-}CH3}$	E^2 $n_{N\beta} \rightarrow \sigma^*_{N\alpha\text{-}C(O)}$	E^2 $n_{N\beta} \rightarrow \sigma^*_{N\alpha\text{-}CH3}$	E^2 $n_{N\beta} \rightarrow \sigma^*_{N\alpha\text{-}C(O)}$	E^2 $n_{N\beta} \rightarrow \sigma^*_{N\alpha\text{-}CH3}$	E^2 $n_{N\beta} \rightarrow \sigma^*_{N\alpha\text{-}C(O)}$	E^2 $n_{N\beta} \rightarrow \sigma^*_{N\alpha\text{-}CH3}$	E^2 $n_{N\beta} \rightarrow \sigma^*_{N\alpha\text{-}C(O)}$
	kcal.mol^{-1}							
1	10.12	2.16	1.59	9.15	9.74	1.47	2.90	7.78
2	10.13	2.16	1.63	9.18	9.77	1.50	2.92	7.93
3	10.16	2.18	1.66	9.17	9.76	1.51	3.04	8.11
4	10.23	2.19	1.66	9.20	9.79	1.49	3.15	8.33
5	10.27	2.20	1.67	9.21	9.80	1.50	3.14	8.36
6	10.32	2.23	1.67	9.22	9.82	1.51	3.25	8.45

Table S7. Sum of NBO stabilization energies listed in Table S6.

Comp	R	E-ac (cis)	Z-sc (trans)	Z-ac (trans)	E-sc (cis)
		Overall E^2 (kcal.mol^{-1})			
1	NMe_2-Ph	12.28	10.74	11.21	10.68
2	OMe-Ph	12.29	10.81	11.27	10.85
3	Ph	12.34	10.83	11.27	11.15
4	CF_3-Ph	12.42	10.86	11.28	11.48
5	CN-Ph	12.47	10.88	11.30	11.50
6	NO_2-Ph	12.55	10.89	11.33	11.70

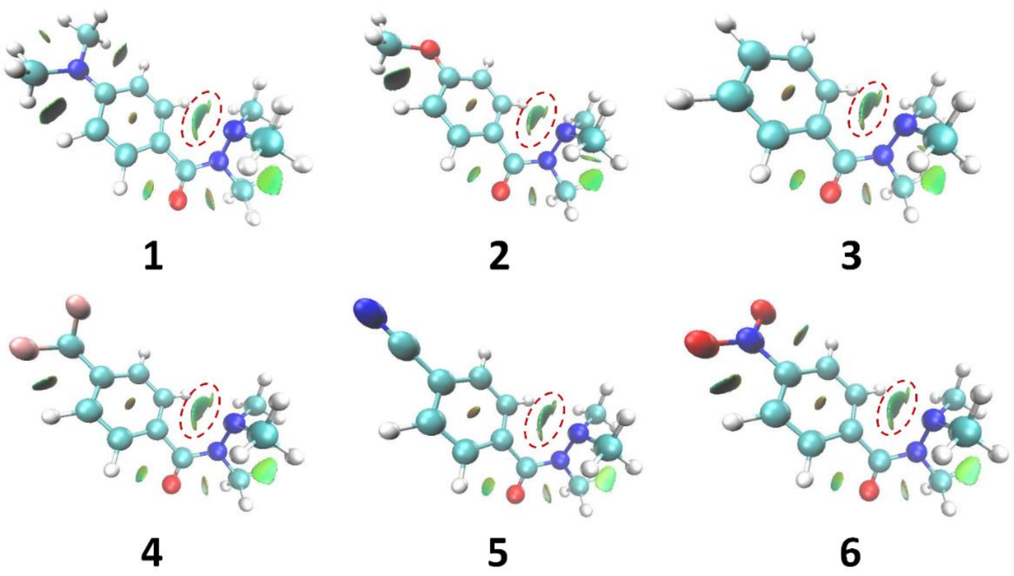


Figure S6. Noncovalent Interaction (NCI) plot showing the $n_N \rightarrow \pi^*_{Ar}$ interaction (red circle marked region) for the optimized geometries of arylhydrazides **1-6**. The reduced density gradient (RDG) isosurface is 0.5 a.u. and colour scale is -0.04 < sin(λ_2)ρ < 0.04 a.u.

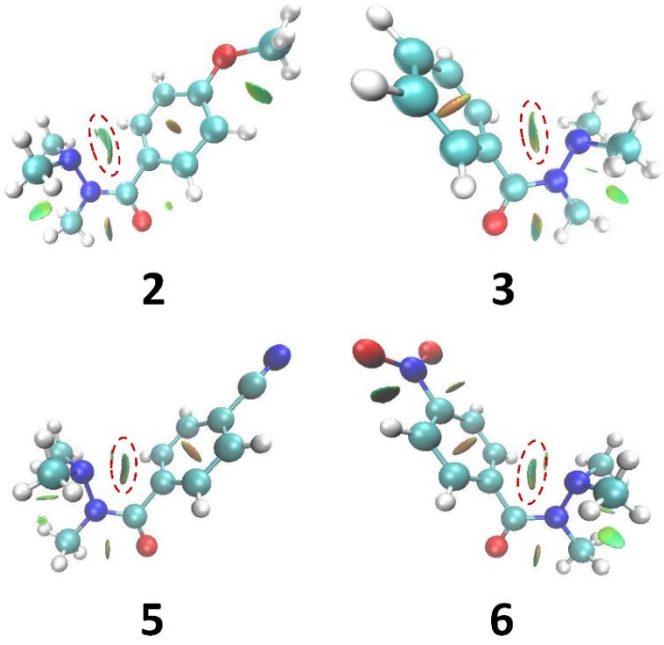


Figure S7. Noncovalent Interaction (NCI) plot showing the $n_N \rightarrow \pi^*_{Ar}$ interaction (red circle marked region) for the crystal geometries of arylhydrazides **2-3** and **5-6**. The reduced density gradient (RDG) isosurface is 0.5 a.u. and colour scale is $-0.04 < \sin(\lambda_2)\rho < 0.04$ a.u.

Table S8. Zero-point corrected relative electronic energies Δ(E+ZPE) of **7**, **9** and **12** in kcal.mol^{-1}.

Comp	Conformation								
	R	Z-sc-fH	E-ac-fH	E-sc-fH	Z-ac-fH	Z-sc-bH	E-ac-bH	E-sc-bH	Z-ac-bH
7	NMe_2Ph	0.00	1.66	3.28	6.00	1.00	1.84	2.11	5.81
9	Ph	0.00	1.37	3.18	6.05	0.53	1.12	1.83	5.41
12	NO_2Ph	0.00	0.81	NP	5.74	0.53	0.54	1.88	5.51

Table S9. Average zero-point corrected relative electronic energies Δ(E+ZPE) of **7**, **9** and **12** in kcal.mol^{-1}.

Comp	Conformation				
	R	Z-sc	E-ac	E-sc	Z-ac
		Average			
7	NMe_2Ph	0.50	1.75	2.70	5.91
9	Ph	0.27	1.25	2.51	5.73
12	NO_2Ph	0.27	0.68	1.88	5.63

Table S10. Relative electronic energies ΔE of **7**, **9** and **12** in kcal·mol^{-1}.

Comp	Conformation								
	R	Z-sc-fH	E-ac-fH	E-sc-fH	Z-ac-fH	Z-sc-bH	E-ac-bH	E-sc-bH	Z-ac-bH
7	NMe_2Ph	0.00	1.98	3.51	6.40	0.64	1.81	2.19	5.87
9	Ph	0.00	1.78	3.52	6.40	0.49	1.53	1.98	5.76
12	NO_2Ph	0.00	0.76	NP	6.22	0.36	0.45	2.13	5.50

Table S11. Average Relative electronic energies ΔE of **7**, **9** and **12** in kcal·mol^{-1}.

Comp	Conformation				
	R	Z-sc	E-ac	E-sc	Z-ac
			Average		
7	NMe_2Ph	0.32	1.90	2.85	6.14
9	Ph	0.25	1.66	2.75	6.08
12	NO_2Ph	0.18	0.61	2.13	5.86

Table S12. Relative Gibbs free energy ΔG of **7**, **9** and **12** in kcal·mol^{-1}.

Comp	Conformation								
	R	Z-sc-fH	E-ac-fH	E-sc-fH	Z-ac-fH	Z-sc-bH	E-ac-bH	E-sc-bH	Z-ac-bH
7	NMe_2Ph	0.00	1.91	3.43	6.06	1.48	2.20	2.33	6.17
9	Ph	0.00	1.72	3.14	6.27	1.05	1.37	2.27	5.87
12	NO_2Ph	0.00	1.00	NP	5.46	0.78	0.52	1.75	5.91

Table S13. Average relative Gibbs free energy ΔG of **7**, **9** and **12** in kcal·mol^{-1}.

Comp	Conformation				
	R	Z-sc	E-ac	E-sc	Z-ac
			Average		
7	NMe_2Ph	0.74	2.06	2.88	6.12
9	Ph	0.53	1.55	2.71	6.07
12	NO_2Ph	0.39	0.76	1.75	5.69

Table S14. Details of Crystallization conditions and their CCDC number. All compounds were crystallized at room temperature except compound **17C**.

Comp	Crystallization Solvents	CCDC	Resolution (Å)
2	Ethyl acetate (rt)	2087868	0.81
5	Dichloromethane (rt)	2093749	0.81
6	Ethyl acetate (rt)	2087869	0.80
11	Methanol (rt)	2093793	0.81
12	Acetonitrile (rt)	2087870	0.80
17C	DMSO-d_6 (50℃)	2088424	0.81

Table S15. Details of Crystal Structures for **2, 5-6, 11-12 and 17C**.

	2	**5**	**6**
Empirical formula	C11 H16 N2 O2	C11 H13 N3 O	C10 H13 N3 O3
Formula weight	208.26	203.24	223.23
Temperature	299 K	299 K	298 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P 21/n	P 21/n	P b c a
Unit cell dimensions	a = 9.779 (3), α = 90.00° b = 12.795 (4), β = 116.78° (10) c = 10.020 (3), γ = 90.00°	a = 6.6018 (4), α = 90.00° b = 13.8377 (10), β = 90.58° (2) c = 12.6315 (8), γ = 90.00°	a = 6.0949 (2) α = 90° b = 9.8024 (3) β = 90° c = 18.4664 (5) γ = 90°
Volume	1119.2 (6) $Å^3$	1153.9 (13) $Å^3$	1103.27 (6) $Å^3$
Z	4	4	4
Density	1.236 g/cm^3	1.170 g/cm^3	1.344 g/cm^3
Absorption coefficient	0.086	0.078	0.101
F (000)	448.0	432.0	472.0

Crystal size	0.065 X 0.120 X 0.170	0.066 X 0.099 X 0.236	0.115 X 0.172 X 0.278
Theta max.	26.13	25.91	26.15
Theta min.	2.78	3.23	2.35
Reflections collected	17371	10384	9571
Independent reflections	2186	2272	2246
Absorption correction	Multi-scan with SADABS	Multi-scan with SADABS	Multi-scan with SADABS
Max. and min. Transmission	0.971 and 0.907	0.971 and 0.854	0.971 and 0.877
Goodness-of-fit on F^2	1.071	1.090	1.079
R1 (I> 2σ (I))	0.0429	0.0456	0.0365
wR2 (I > 2σ (I))	0.1127	0.1245	0.0833
R1 (all data)	0.0560	0.0655	0.0473
wR2 (all data)	0.1238	0.1410	0.0914
R_{int} (all data)	0.0377	0.0310	0.0331

	11	**12**	**17C**
Empirical formula	C10 H11 N3 O	C9 H11 N3 O3	C9 H9 N3 O3
Formula weight	189.21	209.21	207.19
Temperature	297 K	295 K	302 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P 21/c	P 21/c	P n a 21
Unit cell dimensions	a = 7.4997 (6), α = 90.00° b = 18.7572 (15), β = 100.33 (3)° c = 7.4345 (7), γ = 90.00°	a = 6.8686 (9), α = 90.00° b = 21.053 (3), β = 95.02 (4)° c = 7.1521 (9), γ = 90.00°	a = 12.3475 (8), α = 90.00° b = 18.8728 (11), β = 90.00° c = 3.9943 (2), γ = 90.00°
Volume	1028.9 (15) $Å^3$	1030.2 (2) $Å^3$	930.80 (9) $Å^3$

Z	4	4	4
Density	1.222 g/cm^3	1.349 g/cm^3	1.479 g/cm^3
Absorption coefficient	0.083	0.104	0.114
F (000)	400.0	440.0	432.0
Crystal size	0.085 X 0.205 X 0.270	0.038 X 0.154 X 0.222	0.078 X 0.117 X 0.320
Theta max.	22.98	26.37	25.62
Theta min.	2.76	1.96	2.72
Reflections collected	26107	13985	9432
Independent reflections	2016	1079	1811
Absorption correction	Multi-scan with SADABS	Multi-scan with SADABS	Multi-scan with SADABS
Max. and min. Transmission	0.971 and 0.900	0.970 and 0.881	0.971 and 0.862
Goodness-of-fit on F^2	1.128	1.050	1.113
R1 (I> 2σ (I))	0.0586	0.0503	0.0348
wR2 (I > 2σ (I))	0.1639	0.1092	0.0860
R1 (all data)	0.1110	0.1246	0.0440
wR2 (all data)	0.2200	0.1519	0.0937
R_{int} (all data)	0.0682	0.0851	0.0325

G. Kinetics Studies for arylhydrazides 14-18.

The cyclization reactions of *N,N'*-dimethylarylhydrazides **14-18** were carried out in a sealed NMR tubes by ^{1}H NMR spectroscopy at ambient temperatures (between 22-25℃). These reactions were performed in $[CD_3]_2SO$ and $CDCl_3$. Compound **15** was performed with base t-BuOK (3 eqv.) in $[CD_3]_2SO$. Solvent-dependent reactions studies were also performed for compound **14** in D_2O and $[CD_3]_2CO$. ^{1}H NMR Spectra were recorded at various time intervals and the formation of the products for cyclization reaction and the half-life ($t_{1/2}$) values of arylhydrazides were calculated from the relative integration of the peak in arylhydrazide and the corresponding cyclic indazolone.

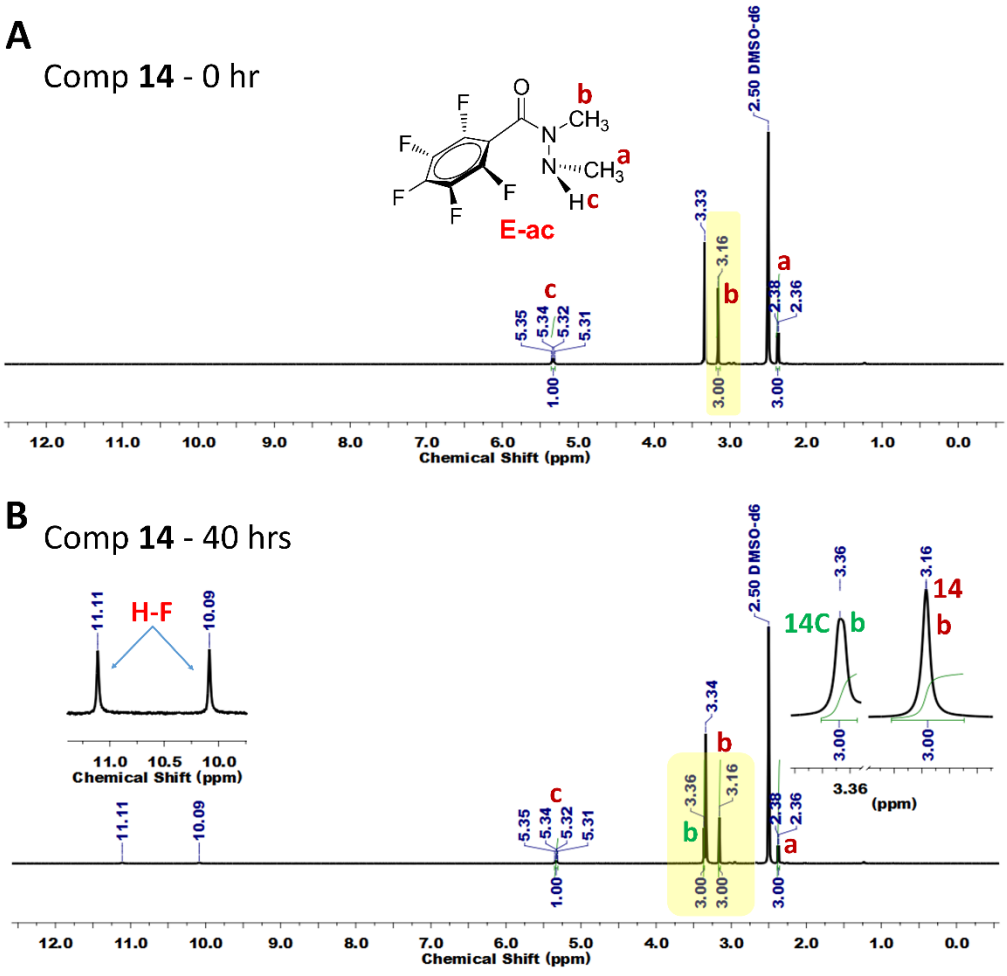


Figure S8: ^{1}H NMR spectra of **14** and **14C** were recorded in DMSO-d^6 at (A) 0 hr and (B) 40 hrs.

Similarly, ^{1}H NMR of the compounds **15-18** were integrated to find out the percentage of product formation and their $t_{1/2}$ values.

Table S16. ^{1}H nmr integration values of arylhydrazide **14-15** & **17-18** and cyclic indazolone **14C-15C** & **17C-18C** were recorded at different intervals of time.

SL. No	Comp **14C** [$(CD_3)_2SO$]					Comp **15C** [$(CD_3)_2SO$ + t-BuOK]				
	^{1}H-intergating peak				**14C**	^{1}H-intergating peak				**15C**
	Time	Nα-CH_3 **14**	Nα-CH_3 **14C**	Sum **(14 + 14C)**	Product formed	Time	Nα-CH_3 **15**	Nα-CH_3 **15C**	Sum **(15 + 15C)**	Product formed
	hrs			hrs	%	hrs			hrs	%
1	0	3.00	0.00	3.00	0	0	3.00	0.00	3.00	0
2	24	3.00	1.80	4.80	38	2	3.00	0.45	3.45	13
3	33	3.00	2.30	5.30	43	4	3.00	0.48	3.48	14
4	40	3.00	3.00	6.00	50	23	3.00	1.05	4.05	26
5	46	3.00	3.86	6.86	56	33	3.00	1.23	4.23	29
6	70	3.00	7.21	10.21	71	48	3.00	1.67	4.67	36
7	118	3.00	18.40	21.40	86	122	3.00	3.00	6.00	50
8	142	3.00	29.24	32.24	91	144	3.00	3.43	6.43	53
9	166	3.00	41.66	44.66	93	172	3.00	3.82	6.82	56
10	190	3.00	58.40	61.40	95	194	3.00	4.28	7.28	59
11	214	3.00	79.12	82.12	96	218	3.00	4.54	7.54	60
12	246	3.00	154.15	157.15	98	288	3.00	5.80	8.80	66
13	299	3.00	205.36	208.36	99	315	3.00	6.20	9.20	67
14	321	3.00	294.25	297.25	99	338	3.00	6.50	9.50	68
15	-	-	-	-	-	363	3.00	6.77	9.77	69
16	-	-	-	-	-	387	3.00	7.44	10.44	71

SL. No	Comp **17C** [$(CD_3)_2SO$]					Comp **18C** [$(CD_3)_2SO$]				
	^{1}H-intergating peak				**17C**	^{1}H-intergating peak				**18C**
	Time	Nα-CH_3 **17**	Nα-CH_3 **17C**	Sum **(17 + 17C)**	Product formed	Time	Nα-CH_3 **18**	Nα-CH_3 **18C**	Sum **(18 + 18C)**	Product formed
	hrs			hrs	%	hrs			hrs	%
1	0	3.00	0.00	3.00	0	0	3.00	0.00	3.00	0
2	18	3.00	0.14	3.14	5	23	3.00	0.16	3.16	5
3	71	3.00	0.44	3.44	13	47	3.00	0.23	3.23	7
4	138	3.00	0.86	3.86	22	118	3.00	0.52	3.52	15
5	184	3.00	1.28	4.28	30	166	3.00	0.80	3.80	21
6	233	3.00	1.77	4.77	37	191	3.00	1.00	4.00	25
7	282	3.00	2.40	5.40	44	286	3.00	1.62	4.62	35
8	328	3.00	3.00	6.00	50	334	3.00	1.86	4.86	38
9	377	3.00	3.80	6.80	56	382	3.00	1.96	4.96	40
10	400	3.00	4.19	7.19	58	405	3.00	2.10	5.10	41
11	448	3.00	5.35	8.35	64	453	3.00	2.40	5.40	44
12	496	3.00	6.60	9.60	69	502	3.00	2.71	5.71	47
13	546	3.00	7.75	10.75	72	550	3.00	2.90	5.90	49
14	616	3.00	10.05	13.05	77	580	3.00	3.00	6.00	50
15	664	3.00	11.50	14.50	79	622	3.00	3.40	6.40	53
16	689	3.00	12.75	15.75	81	670	3.00	3.60	6.60	55
17	784	3.00	19.00	22.00	86	863	3.00	4.85	7.85	62
18	880	3.00	23.05	26.05	88	1056	3.00	7.15	10.15	70
19	952	3.00	24.50	27.50	89	1127	3.00	8.06	11.06	73
20	1000	3.00	28.38	31.38	90	1319	3.00	11.60	14.60	79
21	1048	3.00	30.00	33.00	91	1470	3.00	14.73	17.73	83

22	1120	3.00	32.15	35.15	92	1654	3.00	21.00	24.00	88
23	1168	3.00	39.10	42.10	93	1729	3.00	23.85	26.85	89
24	1360	3.00	54.08	57.08	95	-	-	-	-	-
25	1624	3.00	80.04	83.04	96	-	-	-	-	-

SL. No	Comp **14C** [$(CD_3)_2CO$]					Comp **14C** [D_2O]				
	^{1}H-intergating peak				**14C**	^{1}H-intergating peak				**14C**
	Time	Nα-CH_3 **14**	Nα-CH_3 **14C**	Sum **(14 + 14C)**	Product formed	Time	Nα-CH_3 **14**	Nα-CH_3 **14C**	Sum **(14 + 14C)**	Product formed
	hrs			hrs	%	hrs			hrs	%
1	0	3.00	0.00	3.00	0	0	3.00	0.00	3.00	0
2	23	3.00	0.08	3.08	3	23	3.00	0.09	3.09	3
3	47	3.00	0.12	3.12	4	47	3.00	0.15	3.15	5
4	95	3.00	0.19	3.19	6	95	3.00	0.22	3.22	7
5	161	3.00	0.33	3.33	10	161	3.00	0.29	3.29	9
6	203	3.00	0.39	3.39	12	203	3.00	0.38	3.38	11
7	252	3.00	0.48	3.48	14	252	3.00	0.45	3.45	13
8	348	3.00	0.68	3.68	18	349	3.00	0.61	3.61	17
9	395	3.00	0.81	3.81	21	395	3.00	0.66	3.66	18
10	444	3.00	0.95	3.95	24	444	3.00	0.75	3.75	20
11	492	3.00	1.08	4.08	26	492	3.00	0.88	3.88	23
12	538	3.00	1.25	4.25	29	538	3.00	0.96	3.96	24
13	612	3.00	1.48	4.48	33	588	3.00	1.09	4.09	27
14	659	3.00	1.66	4.66	36	659	3.00	1.29	4.29	30
15	706	3.00	1.98	4.98	40	705	3.00	1.45	4.45	33
16	755	3.00	2.15	5.15	42	755	3.00	1.54	4.54	34
17	826	3.00	2.37	5.37	44	863	3.00	1.91	4.91	39
18	863	3.00	2.56	5.56	46	910	3.00	2.09	5.09	41
19	910	3.00	2.68	5.68	47	1006	3.00	2.40	5.40	44
20	1006	3.00	3.10	6.10	51	1054	3.00	2.56	5.56	46
21	1030	3.00	3.35	6.35	53	1103	3.00	2.70	5.70	47
22	1078	3.00	3.65	6.65	55	1174	3.00	2.88	5.88	49
23	1126	3.00	3.80	6.80	56	1222	3.00	3.00	6.00	50
24	1173	3.00	4.06	7.06	58	1270	3.00	3.07	6.07	51
25	1221	3.00	4.26	7.26	59	1342	3.00	3.25	6.25	52
26	1270	3.00	4.52	7.52	60	1390	3.00	3.51	6.51	54
27	1341	3.00	4.90	7.90	62	1582	3.00	3.88	6.88	56
28	1389	3.00	5.04	8.04	63	1773	3.00	4.50	7.50	60
29	1582	3.00	6.39	9.39	68	1844	3.00	4.81	7.81	62
30	1774	3.00	7.56	10.56	72	2036	3.00	5.88	8.88	66
31	1845	3.00	8.16	11.16	73	2189	3.00	7.10	10.10	70
32	2037	3.00	10.59	13.59	78	2372	3.00	8.29	11.29	73
33	2189	3.00	12.39	15.39	81	2447	3.00	9.09	12.09	75
34	2371	3.00	15.84	15.84	84	-	-	-	-	-
35	2446	3.00	21.18	18.18	86	-	-	-	-	-

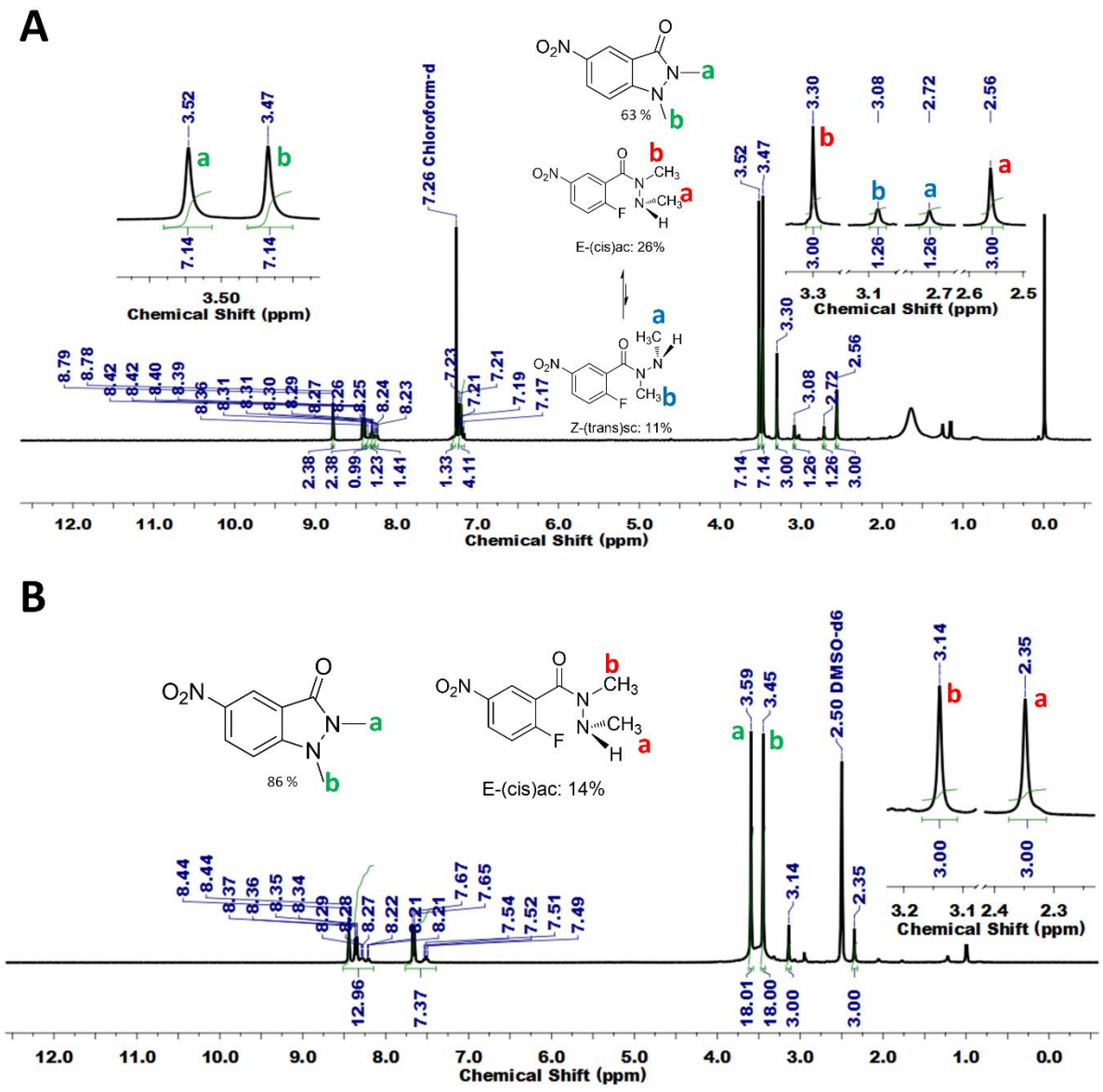
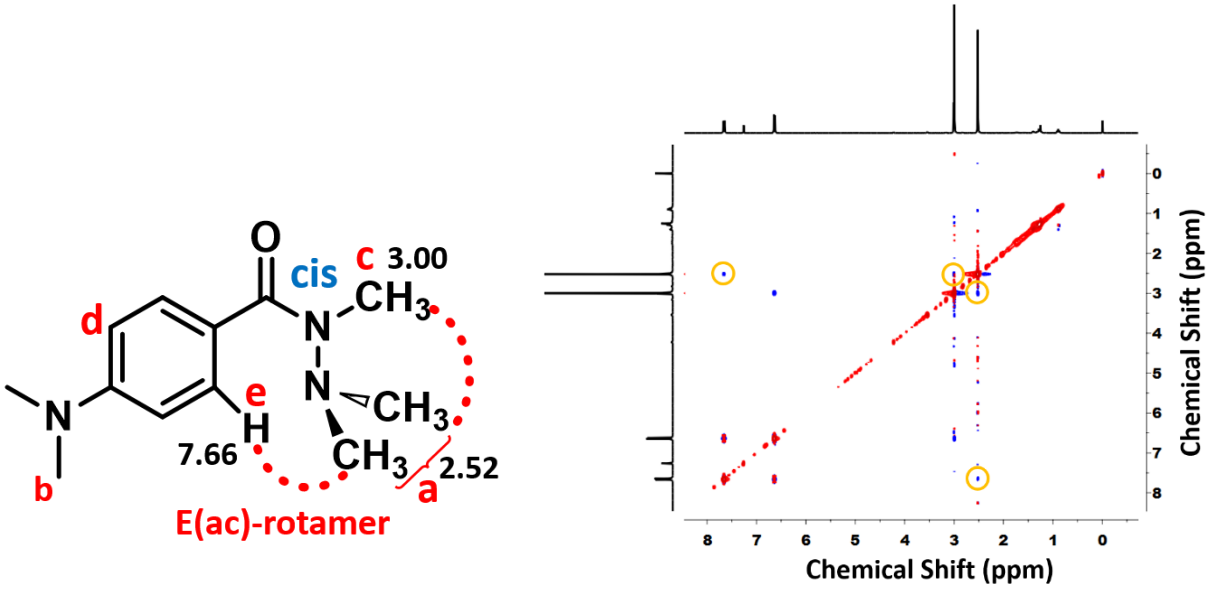


Figure S9. A) ^{1}H NMR spectra of **16** was recorded at 0 min. in $CDCl_3$ and showing their populations in %. B) ^{1}H NMR spectra of **16** recorded at 0 min. in $(CD_3)_2SO$ and showing their population in %.

H. 2D-NOESY spectra of the newly synthesized compounds.



Compound **1**

Figure S10 (A). 2D NOESY full spectra for **1** 4-(dimethylamino)-*N*, *N'*, *N'*-trimethylbenzohydrazide in $CDCl_3$.

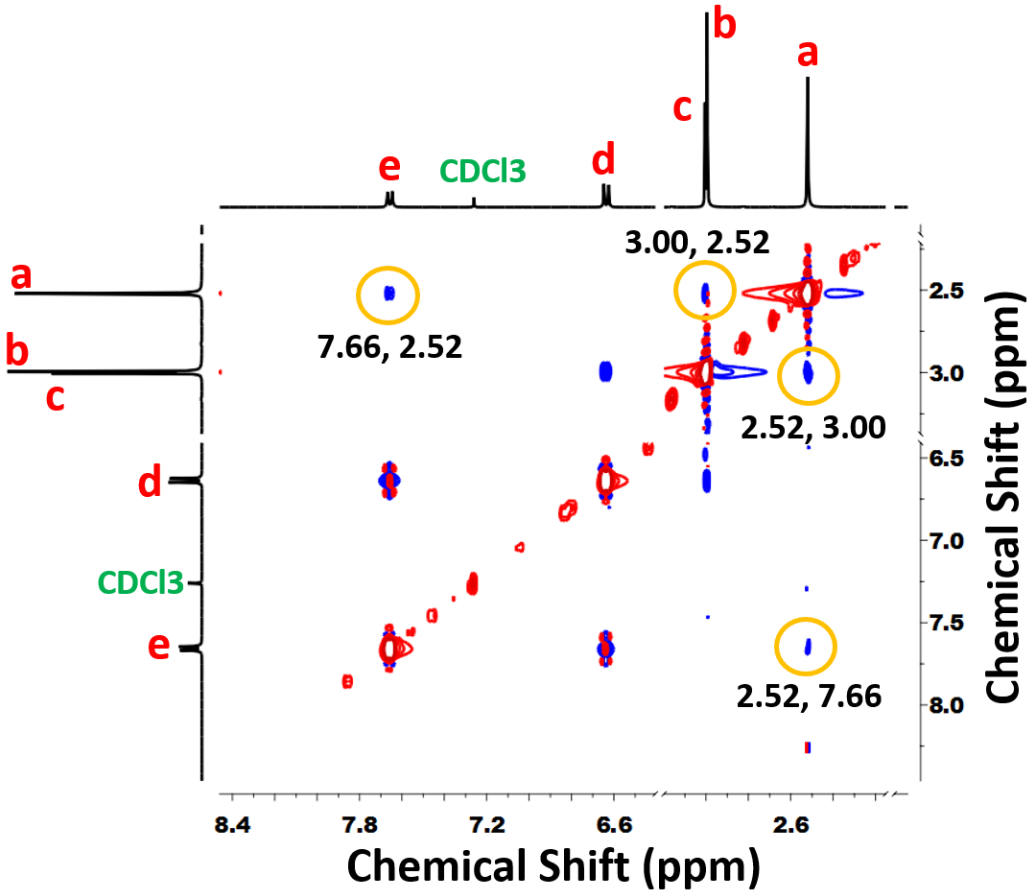
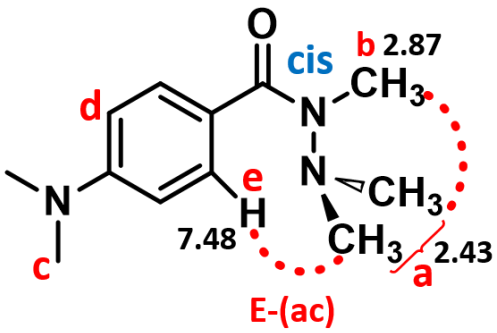


Figure S10 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **1** 4-(dimethylamino)-*N*, *N'*, *N'*-trimethylbenzohydrazide in $CDCl_3$.



Compound **1**

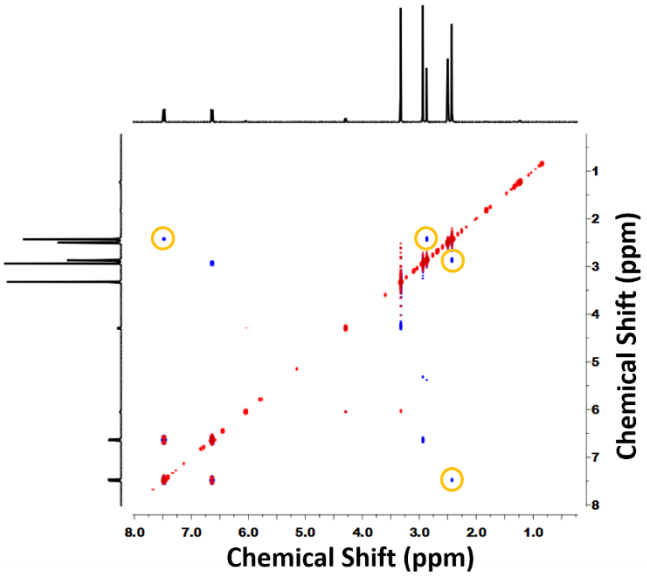


Figure S11 (A). 2D NOESY full spectra for **1** 4-(dimethylamino)-*N*, *N'*, *N'*-trimethylbenzohydrazide in $[CD_3]_2SO$.

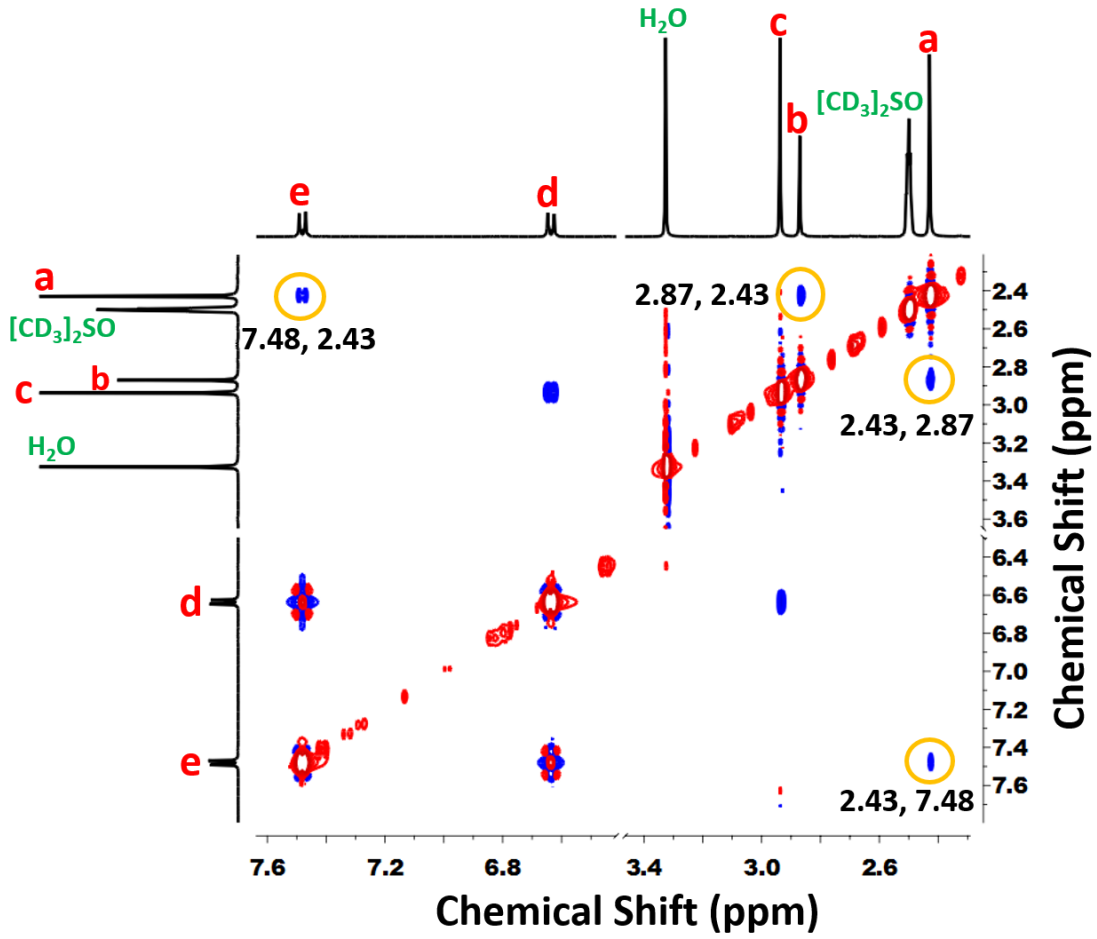
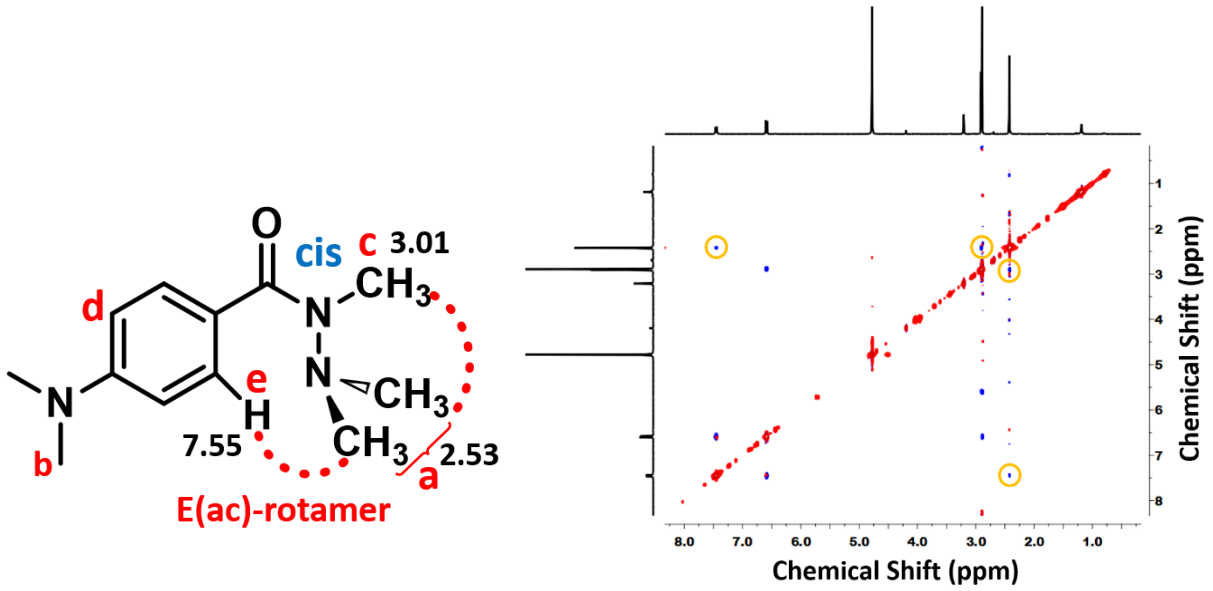


Figure S11 (B). 2D ^1H-^1H NOESY Correlation enlarged spectra for **1** 4-(dimethylamino)-*N*, *N'*, *N'*-trimethylbenzohydrazide in $[CD_3]_2SO$.



Compound **1**

Figure S12 (A). 2D NOESY full spectra for **1** 4-(dimethylamino)-*N*, *N*′, *N*′-trimethylbenzohydrazide in CD_3OD.

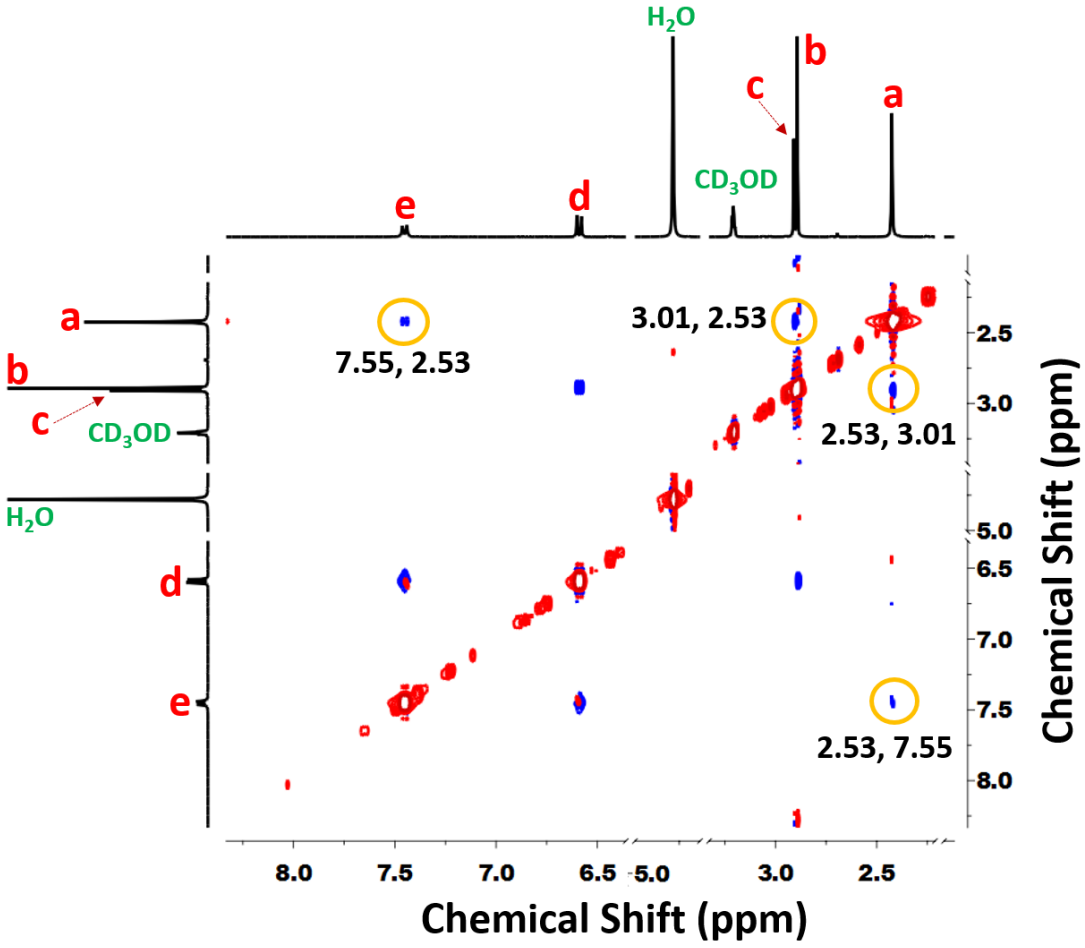
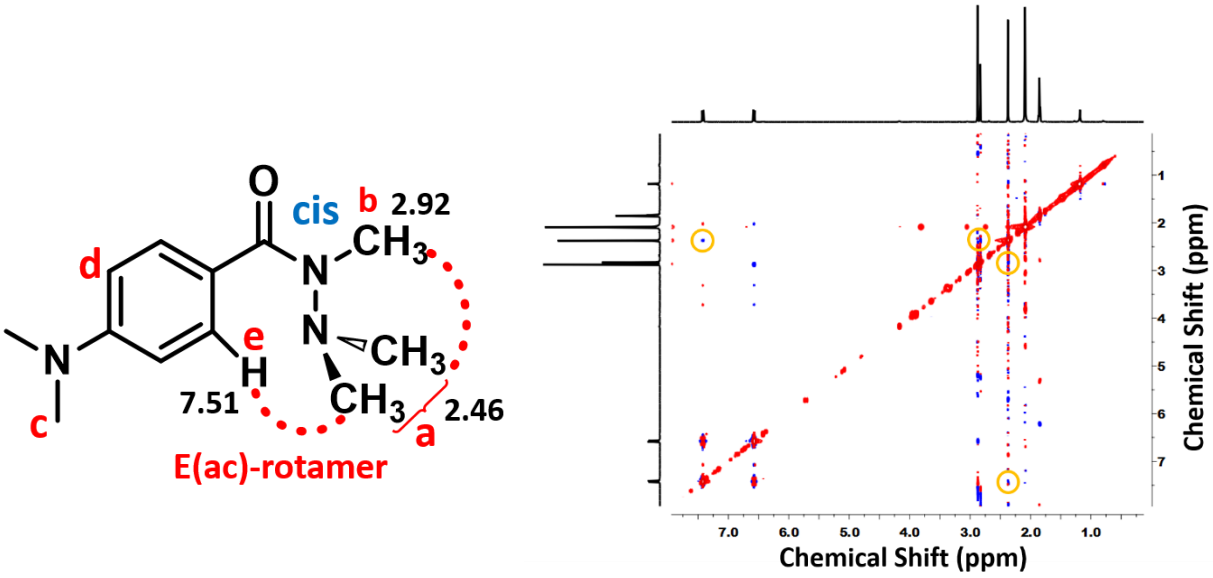


Figure S12 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **1** 4-(dimethylamino)-*N*, *N*′, *N*′-trimethylbenzohydrazide in CD_3OD.



Compound **1**

Figure S13 (A). 2D NOESY full spectra for **1** 4-(dimethylamino)-*N*, *N*′, *N*′-trimethylbenzohydrazide in CD_3CN.

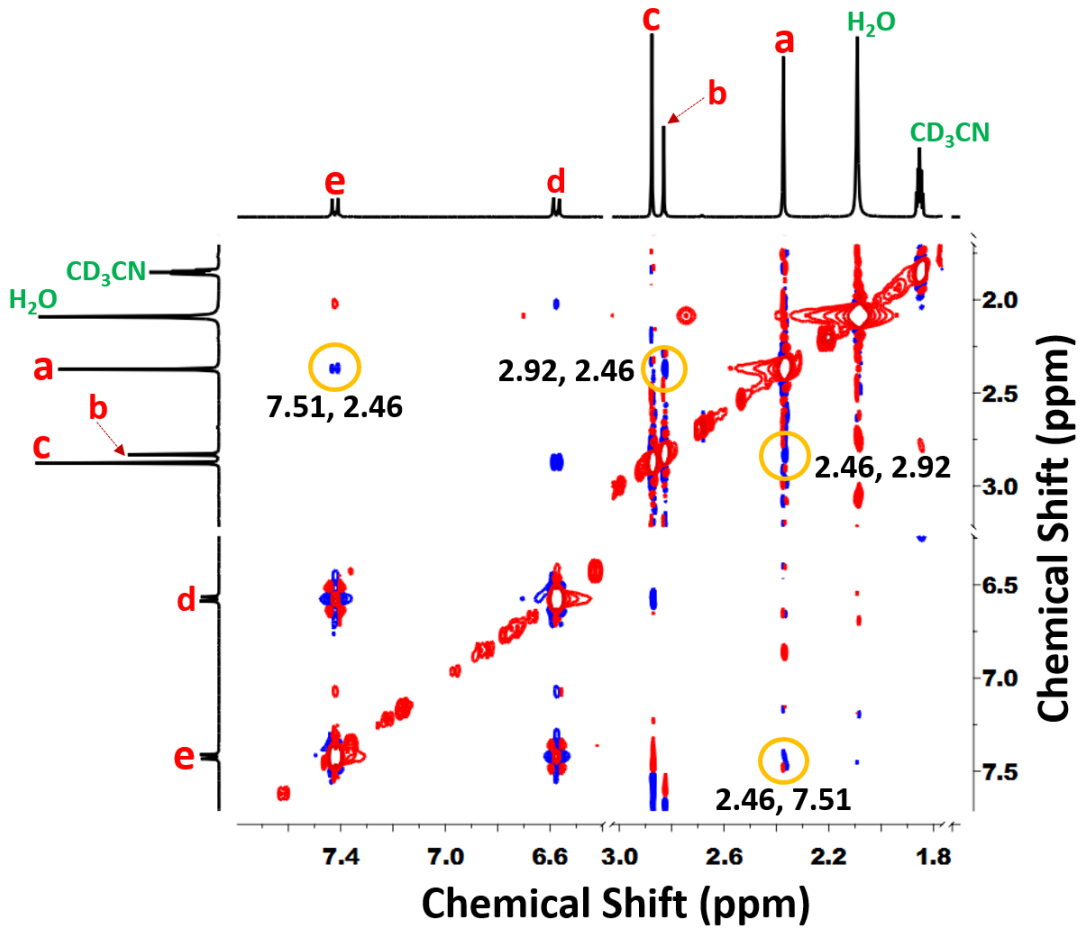
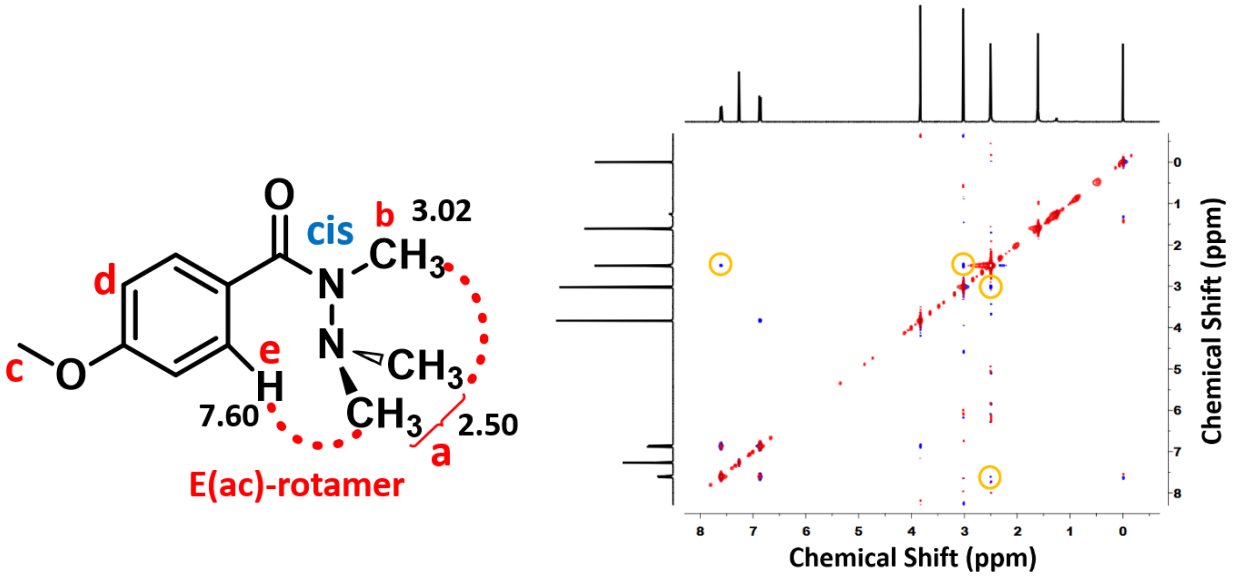


Figure S13 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **1** 4-(dimethylamino)-*N*, *N*′, *N*′-trimethylbenzohydrazide in CD_3CN.



Compound **2**

Figure S14 (A). 2D NOESY full spectra for **2** 4-methoxy-*N*, *N'*, *N'*-trimethylbenzohydrazide in $CDCl_3$.

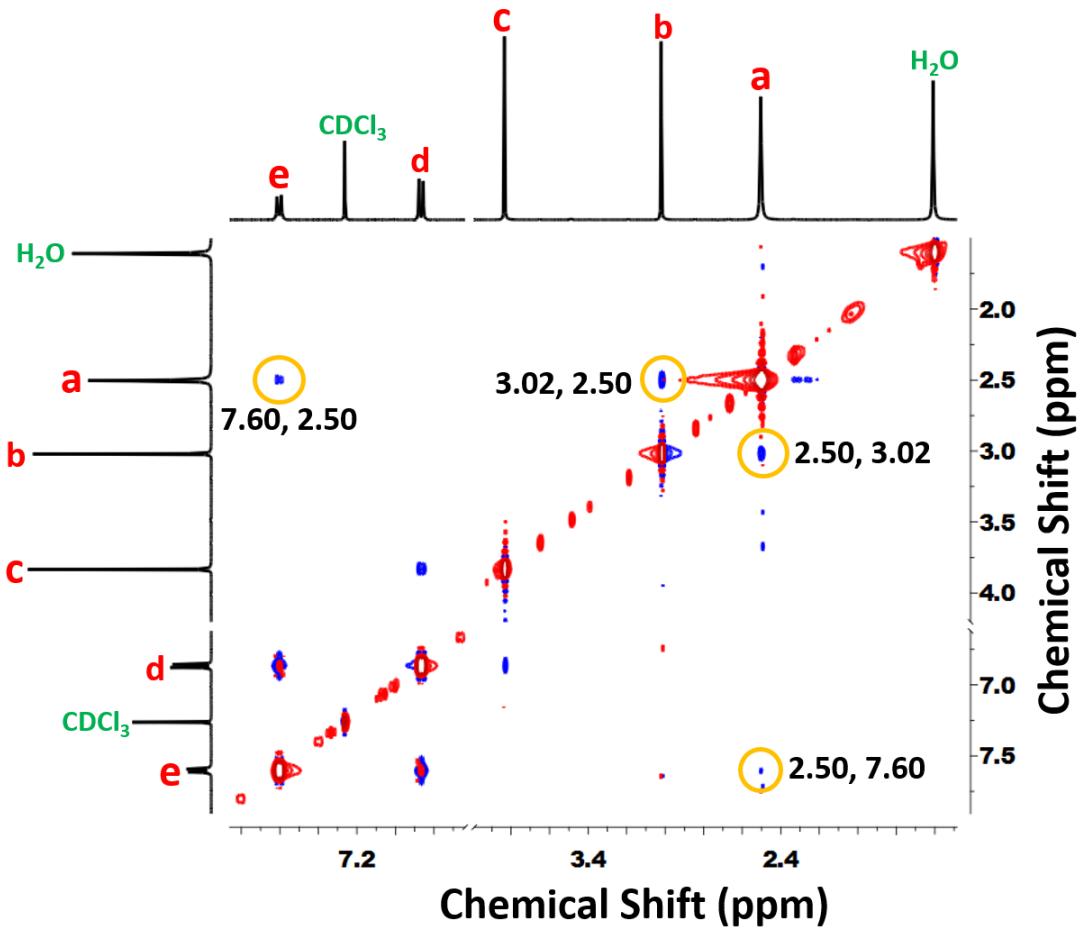
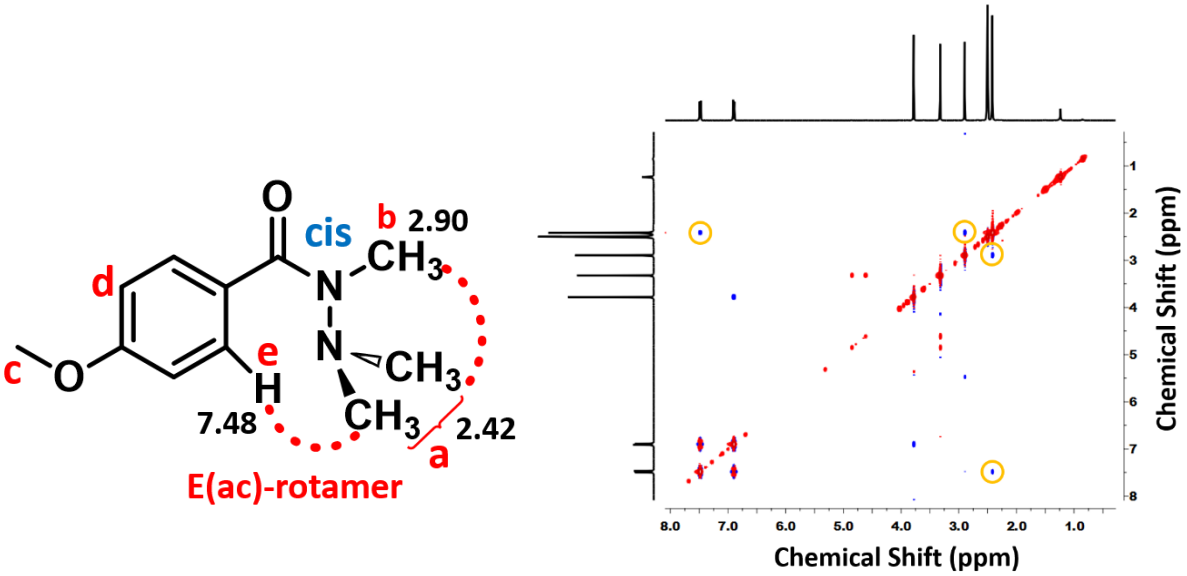


Figure S14 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **2** 4-methoxy-*N*, *N'*, *N'*-trimethylbenzohydrazide in $CDCl_3$.



Compound **2**

Figure S15 (A). 2D NOESY full spectra for **2** 4-methoxy-*N*, *N*′, *N*′-trimethylbenzohydrazide in $[CD_3]_2SO$.

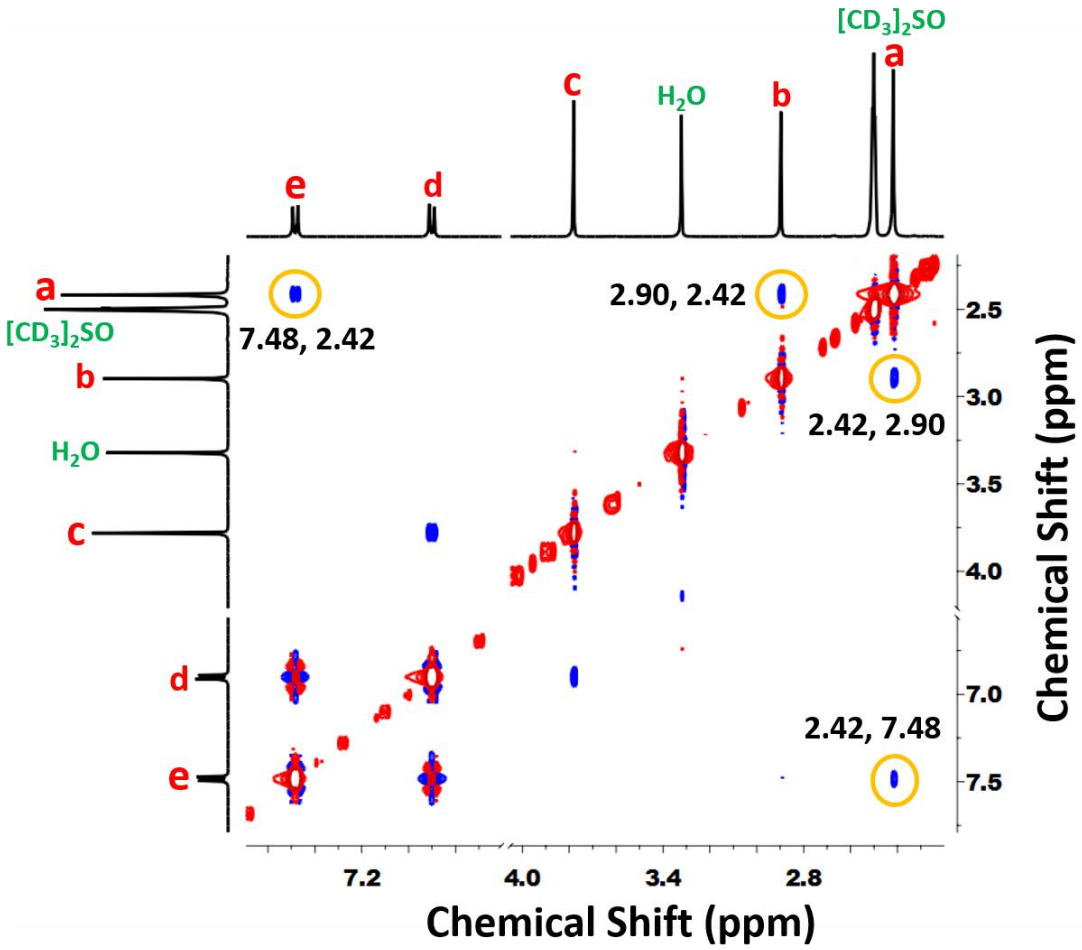
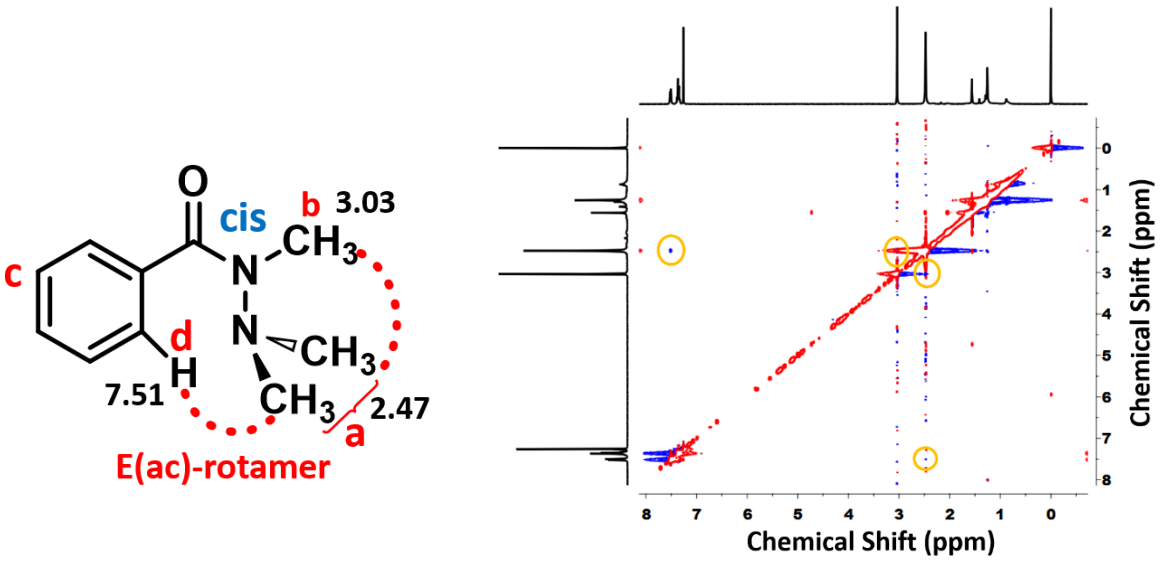


Figure S15 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **2** 4-methoxy-*N*, *N*′, *N*′-trimethylbenzohydrazide in $[CD_3]_2SO$.



Compound **3**

Figure S16 (A). 2D NOESY full spectra for **3** *N*, *N'*, *N'*-trimethylbenzohydrazide in $CDCl_3$.

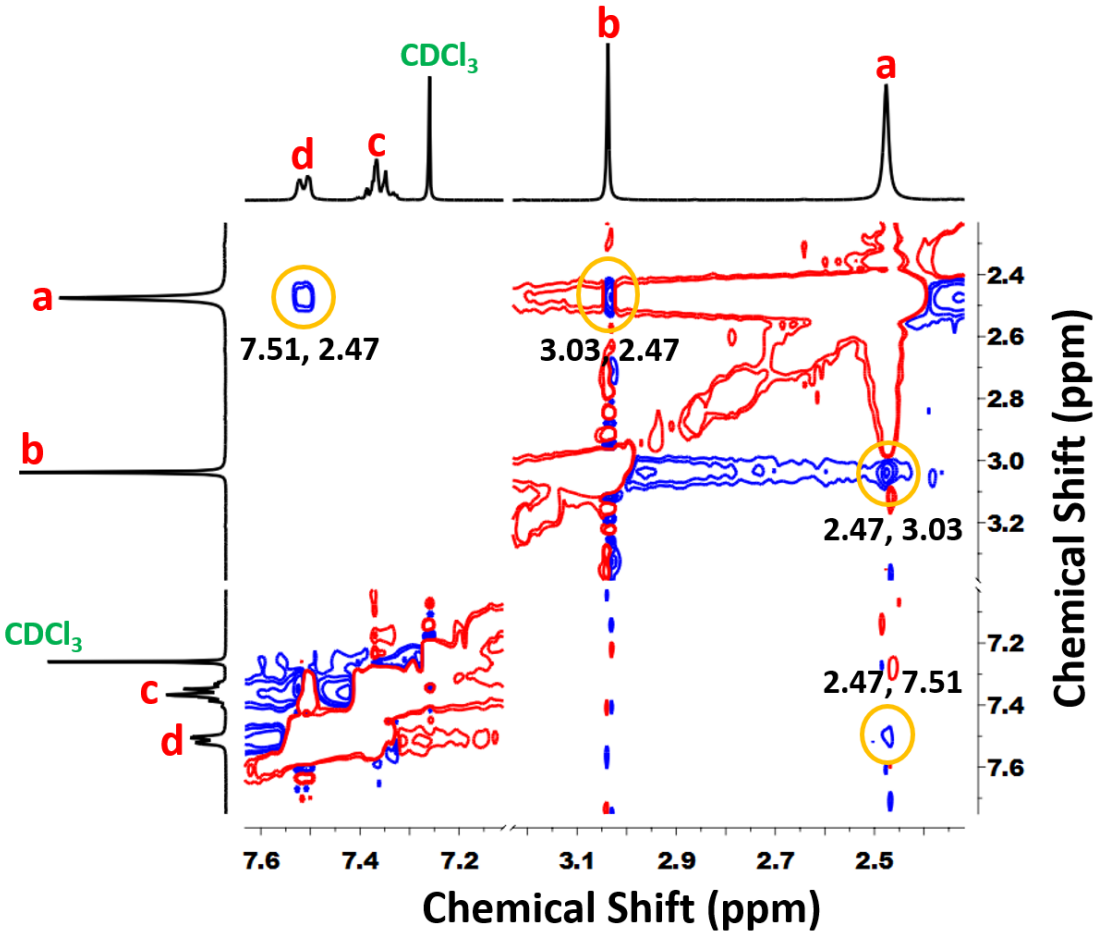
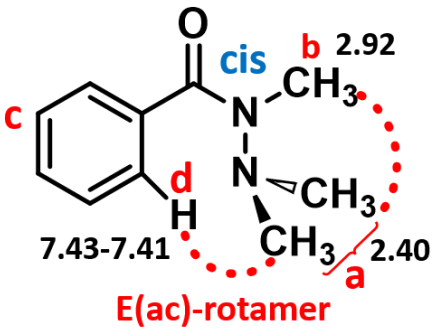


Figure S16 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **3** *N*, *N'*, *N'*-trimethyl-benzohydrazide in $CDCl_3$.



Compound **3**

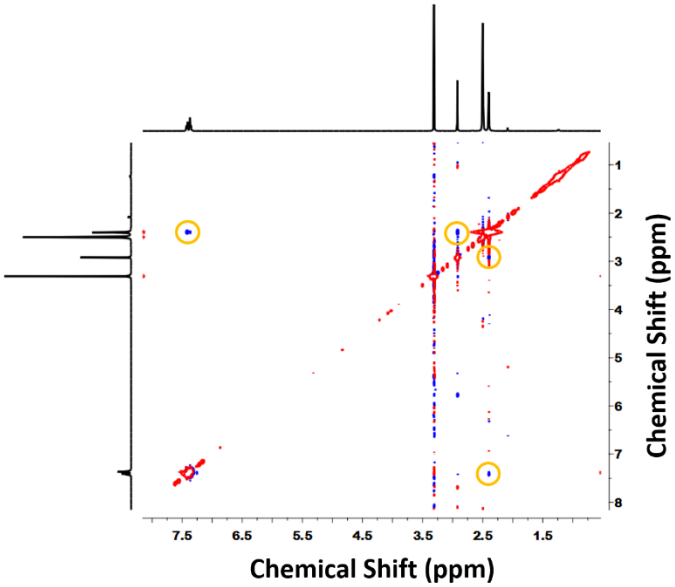


Figure S17 (A). 2D NOESY full spectra for **3** *N*, *N*′, *N*′-trimethylbenzohydrazide in $[CD_3]_2SO$.

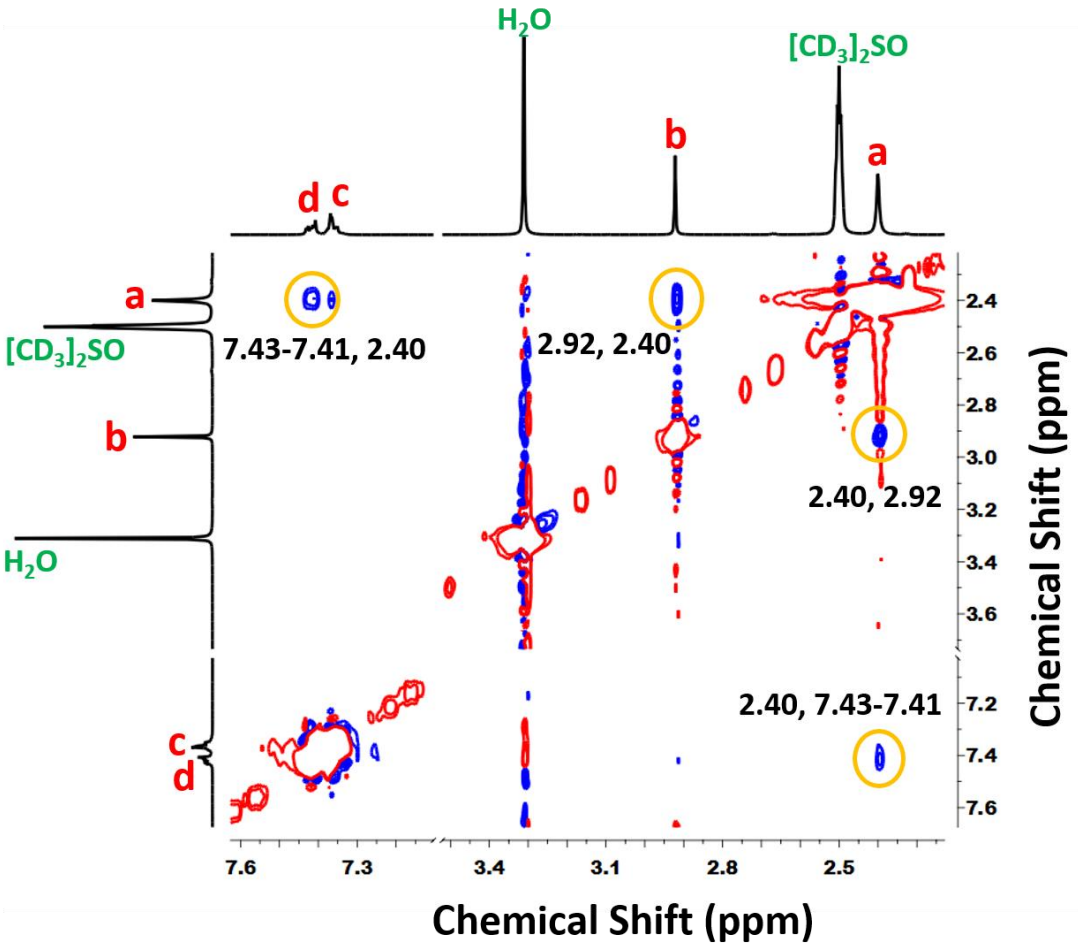
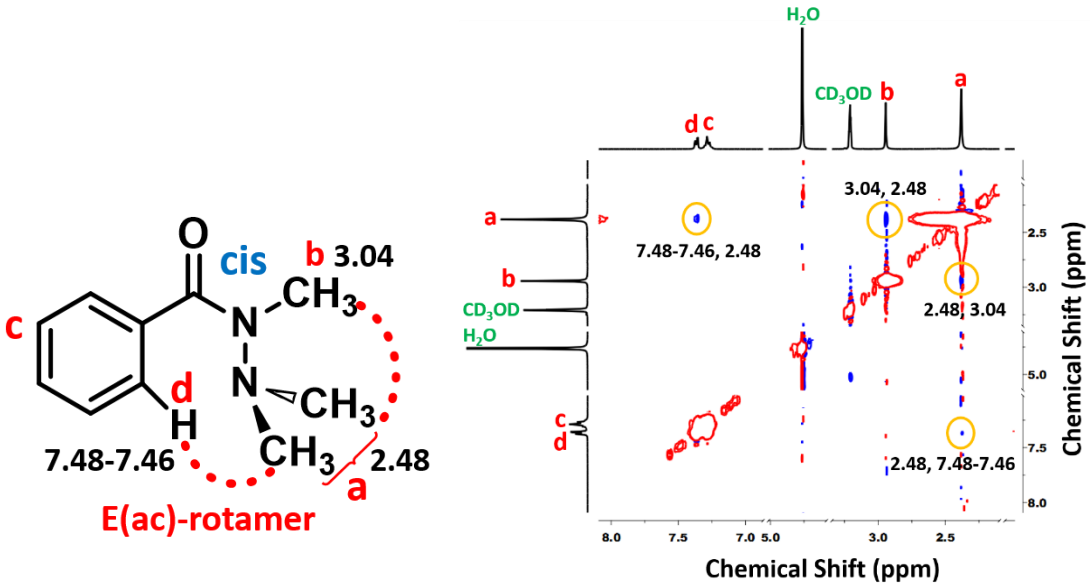


Figure S17 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **3** *N*, *N*′, *N*′-trimethyl-benzohydrazide in $[CD_3]_2SO$.



Compound **3**

Figure S18 (A). 2D NOESY full spectra for **3** *N*, *N'*, *N'*-trimethylbenzohydrazide in CD_3OD.

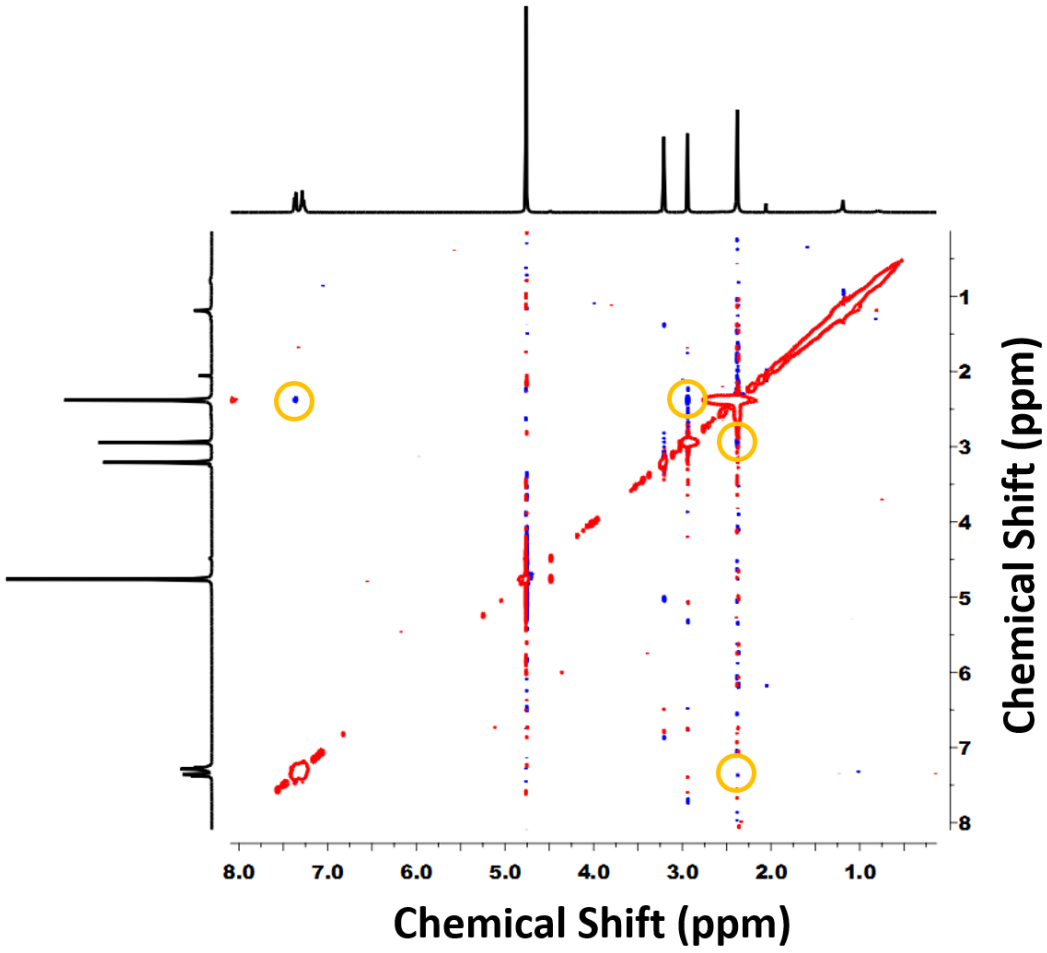
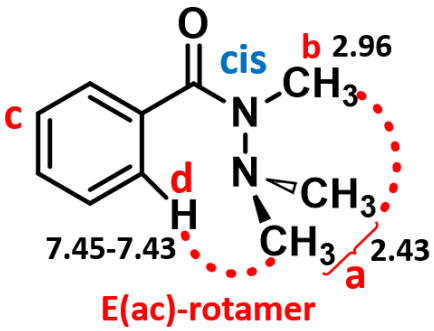


Figure S18 (B). 2D ^1H-^1H NOESY Correlation enlarged spectra for **3** *N*, *N'*, *N'*-trimethyl-benzohydrazide in CD_3OD.



Compound **3**

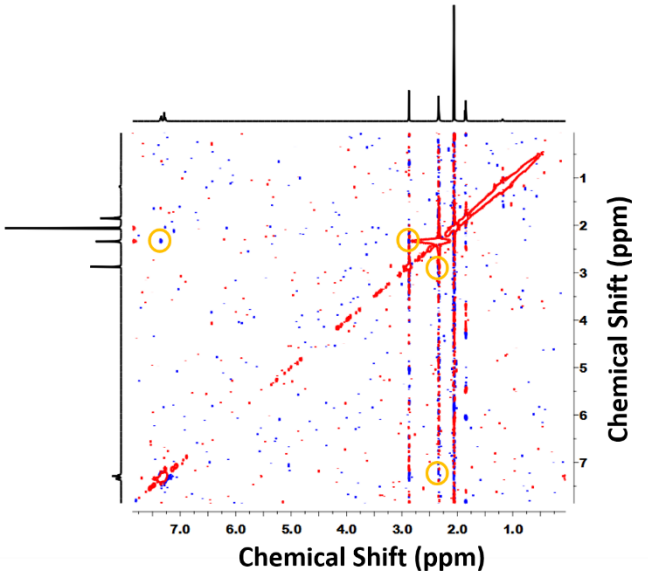


Figure S19 (A). 2D NOESY full spectra for **3** *N*, *N'*, *N'*-trimethylbenzohydrazide in CD_3CN.

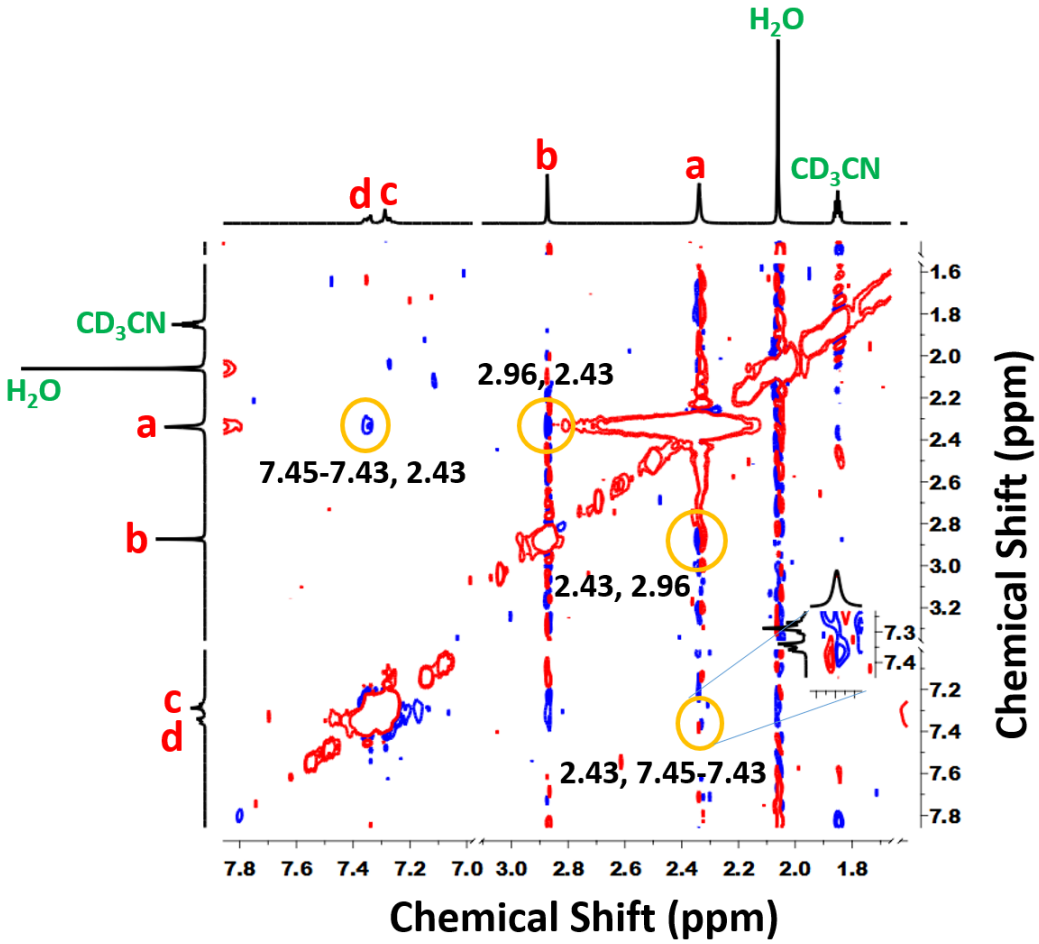
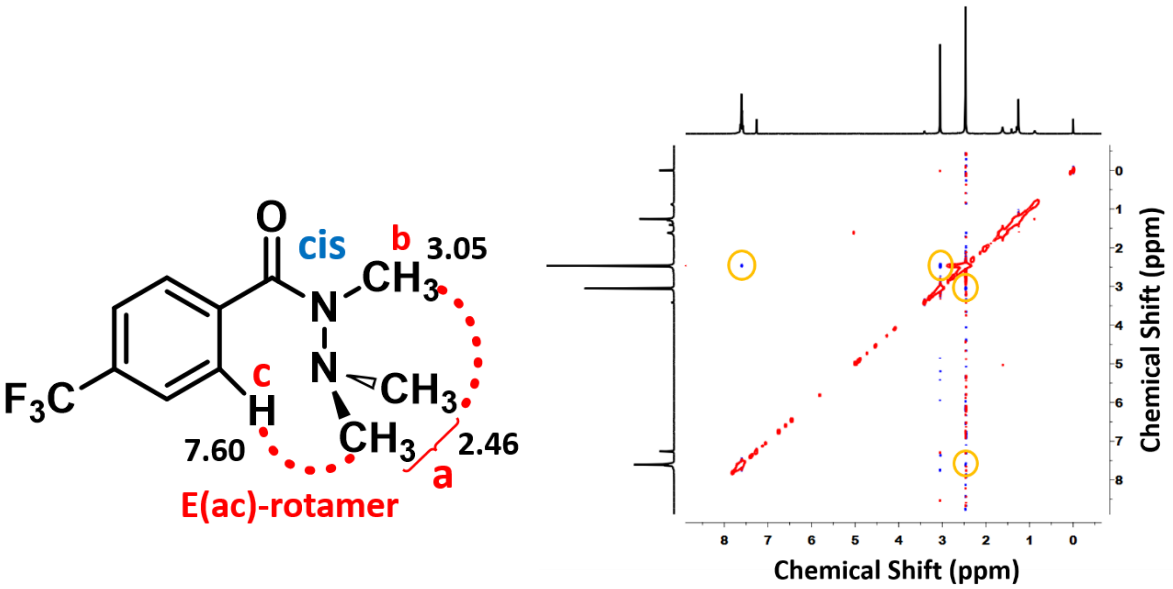


Figure S19 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **3** *N*, *N'*, *N'*-trimethyl-benzohydrazide in CD_3CN.



Compound **4**

Figure S20 (A). 2D NOESY full spectra for **4** *N*, *N'*, *N'*-trimethyl-4-(trifluoromethyl)benzohydrazide in $CDCl_3$.

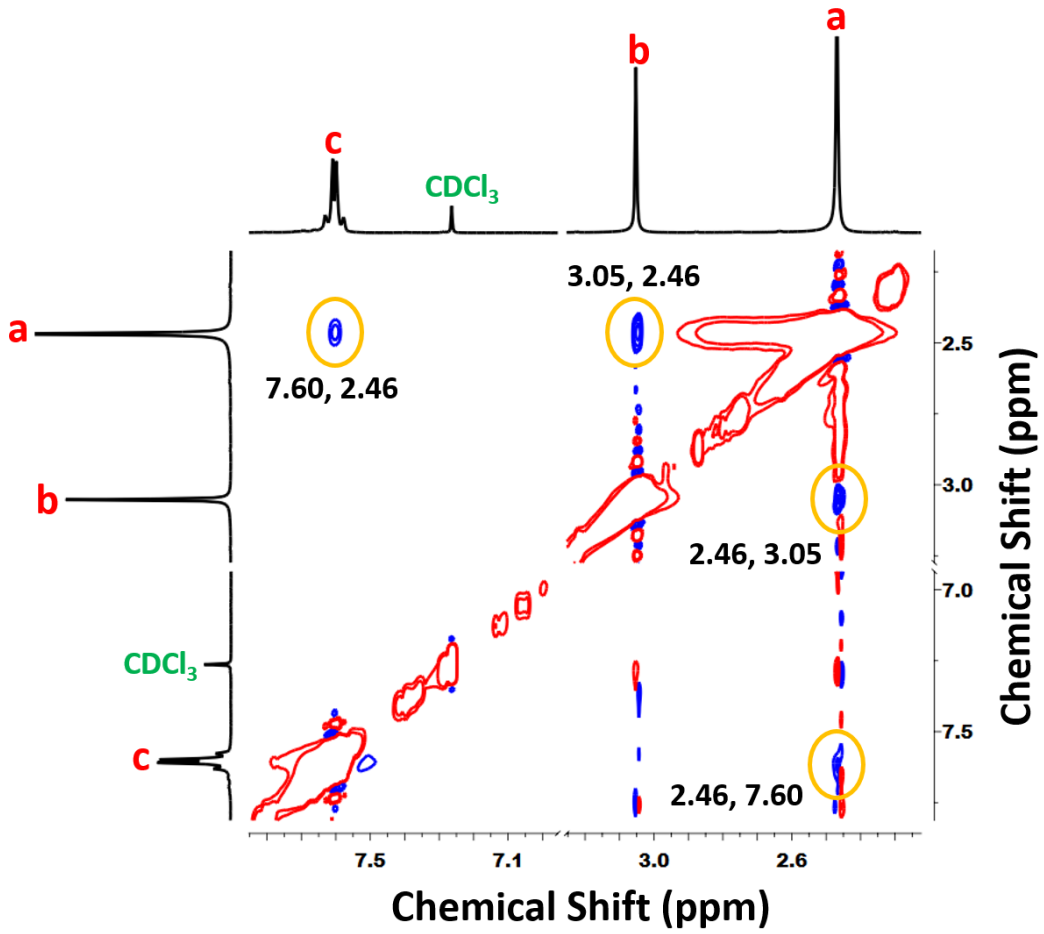
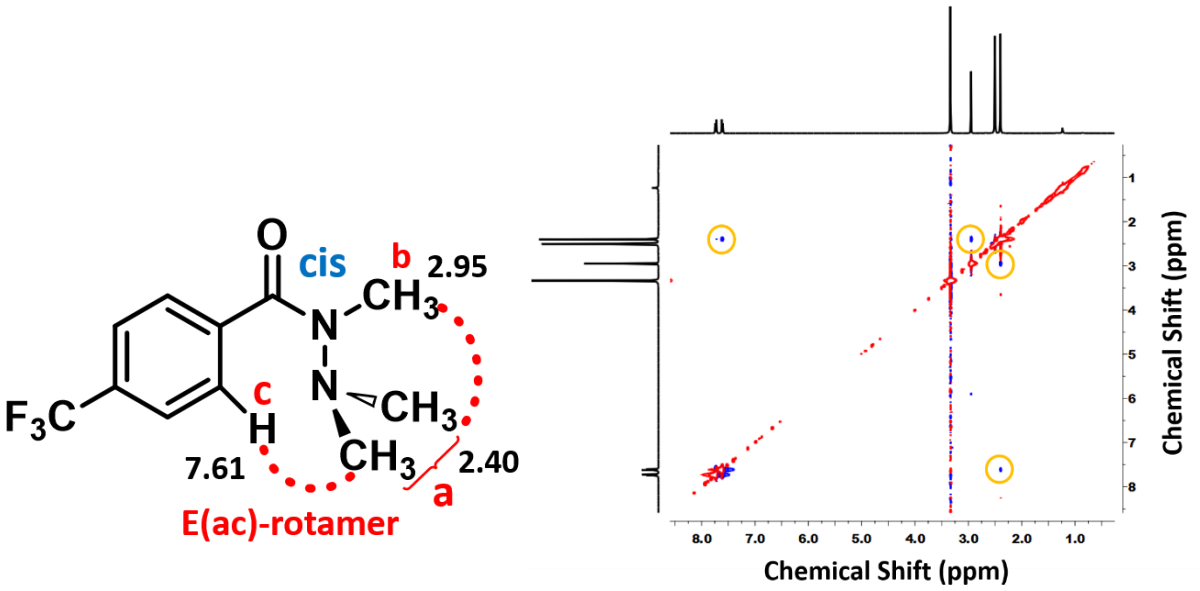


Figure S20 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **4** *N*, *N'*, *N'*-trimethyl-4-(trifluoromethyl)benzohydrazide in $CDCl_3$.



Compound **4**

Figure S21 (A). 2D NOESY full spectra for **4** *N*, *N'*, *N'*-trimethyl-4-(trifluoromethyl)benzohydrazide in $[CD_3]_2SO$.

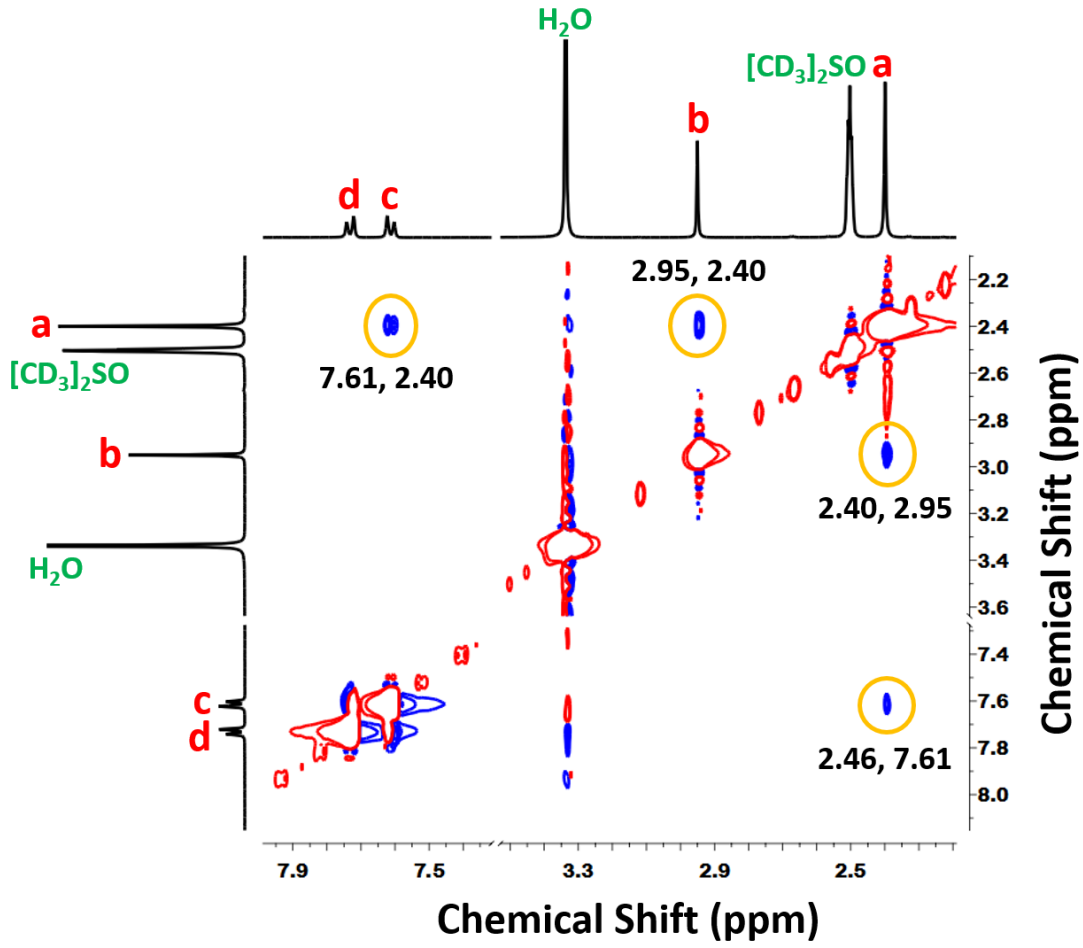
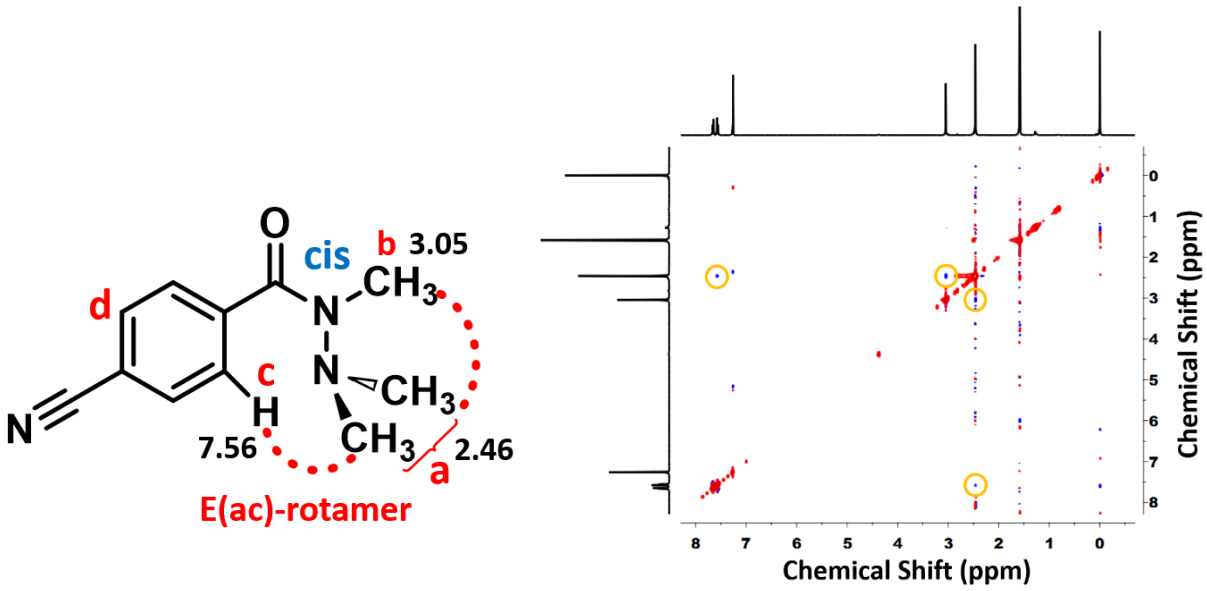


Figure S21 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **4** *N*, *N'*, *N'*-trimethyl-4-(trifluoromethyl)benzohydrazide in $[CD_3]_2SO$.



Compound **5**

Figure S22 (A). 2D NOESY full spectra for **5** 4-cyano-*N*, *N*′, *N*′-trimethylbenzohydrazide in $CDCl_3$.

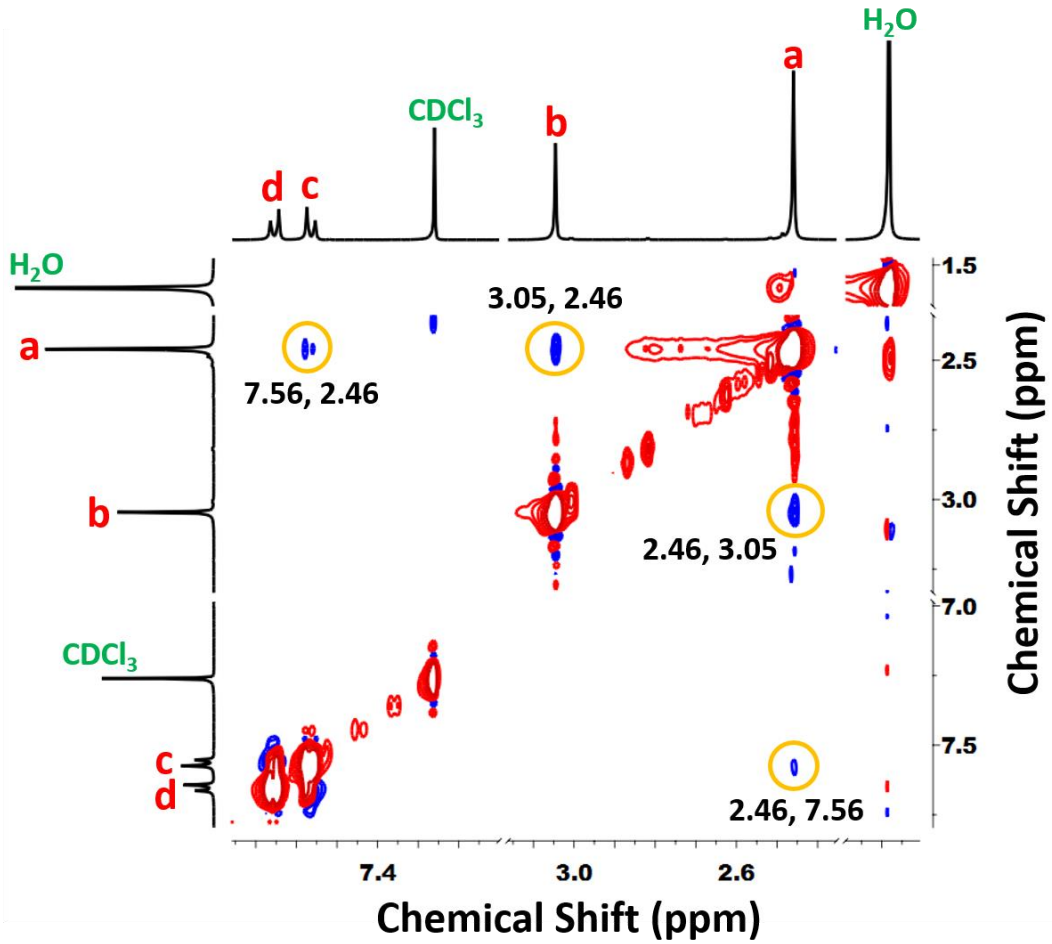
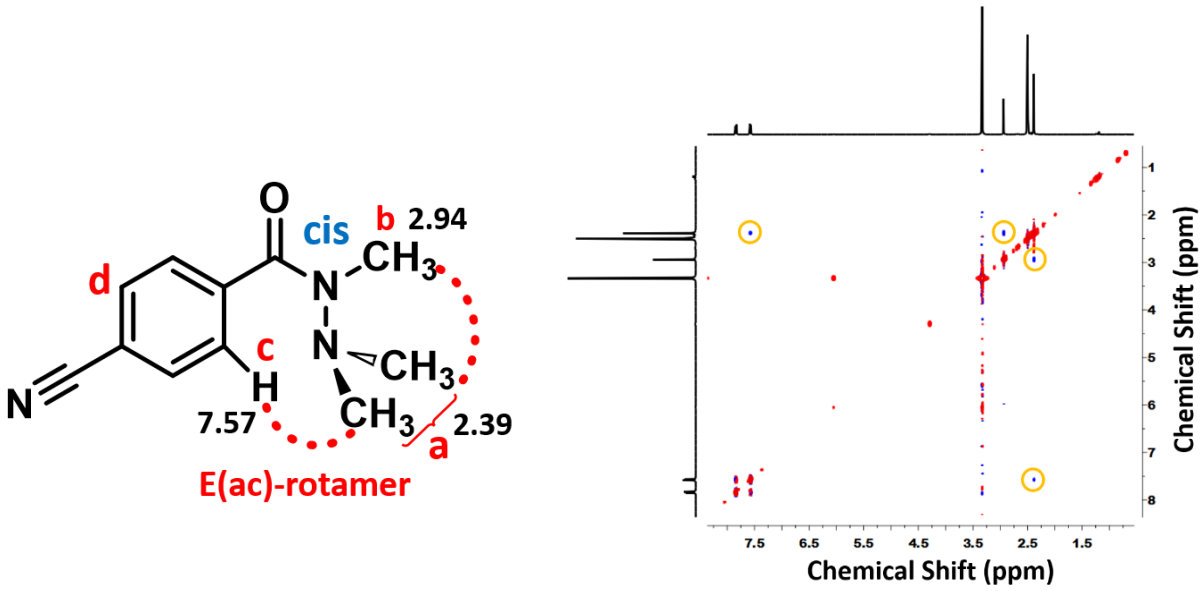


Figure S22 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **5** 4-cyano-*N*, *N*′, *N*′-trimethylbenzohydrazide in $CDCl_3$.



Compound **5**

Figure S23 (A). 2D NOESY full spectra for **5** 4-cyano-*N*, *N*′, *N*′-trimethylbenzohydrazide in $[CD_3]_2SO$.

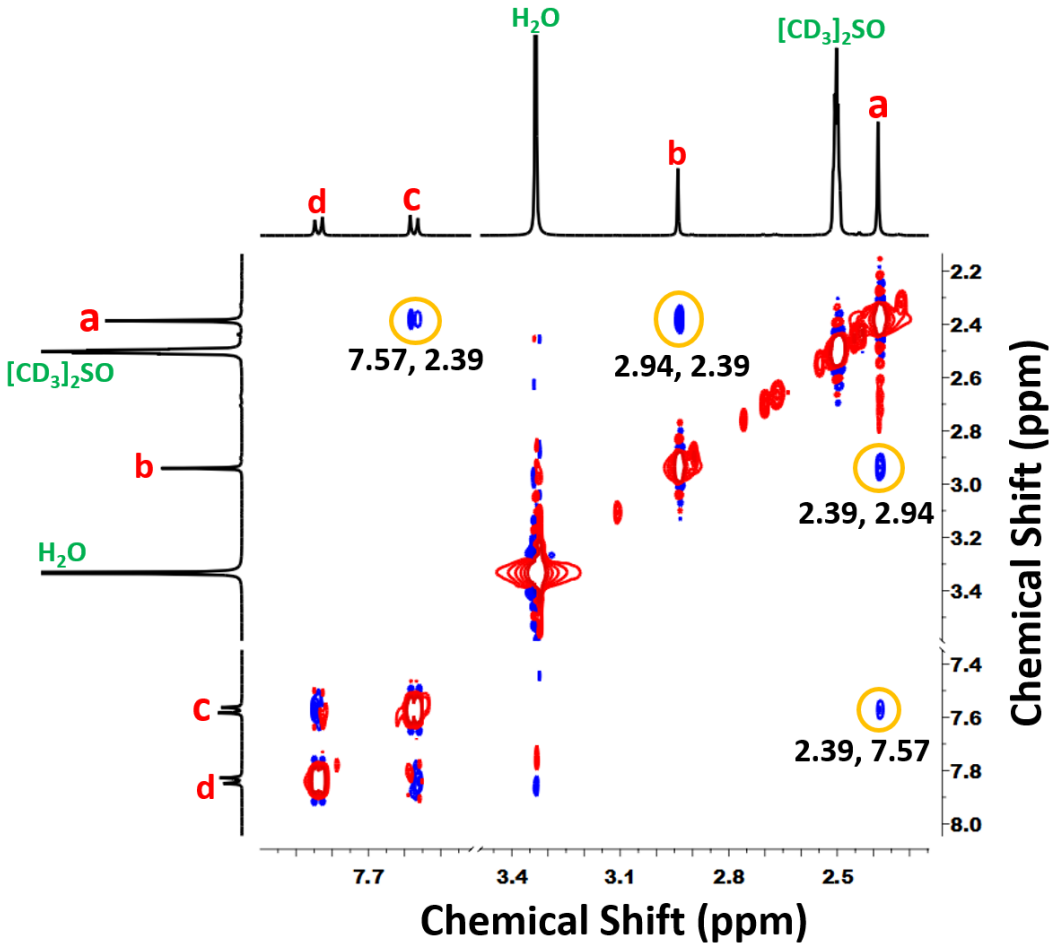
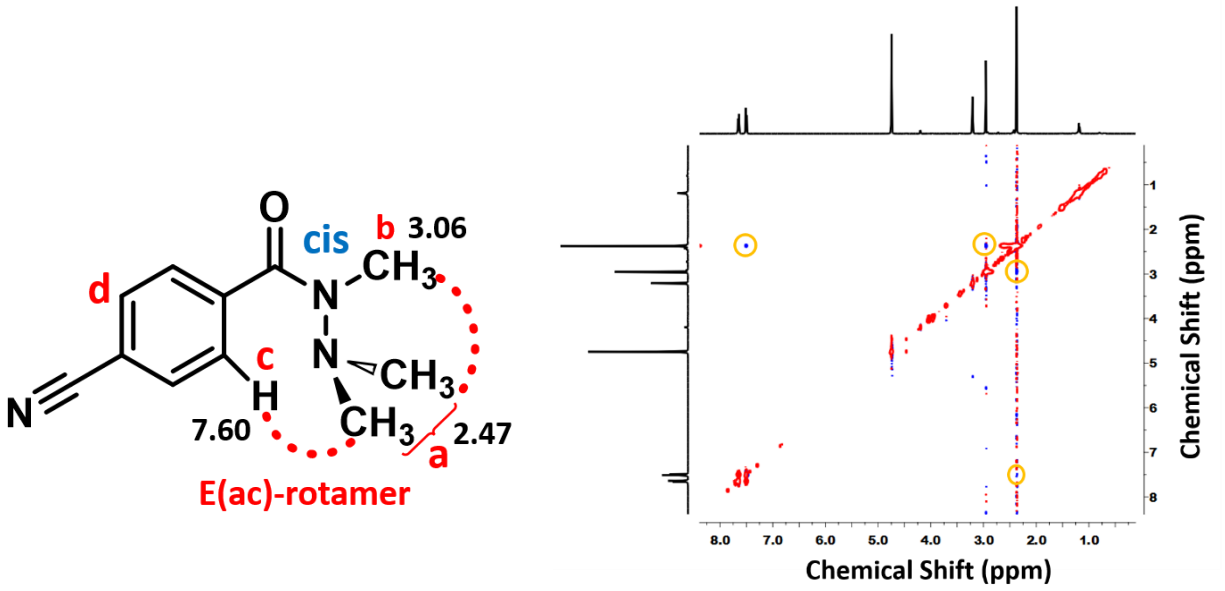


Figure S23 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **5** 4-cyano-*N*, *N*′, *N*′-trimethylbenzohydrazide in $[CD_3]_2SO$.



Compound **5**

Figure S24 (A). 2D NOESY full spectra for **5** 4-cyano-*N*, *N*′, *N*′-trimethylbenzohydrazide in CD_3OD.

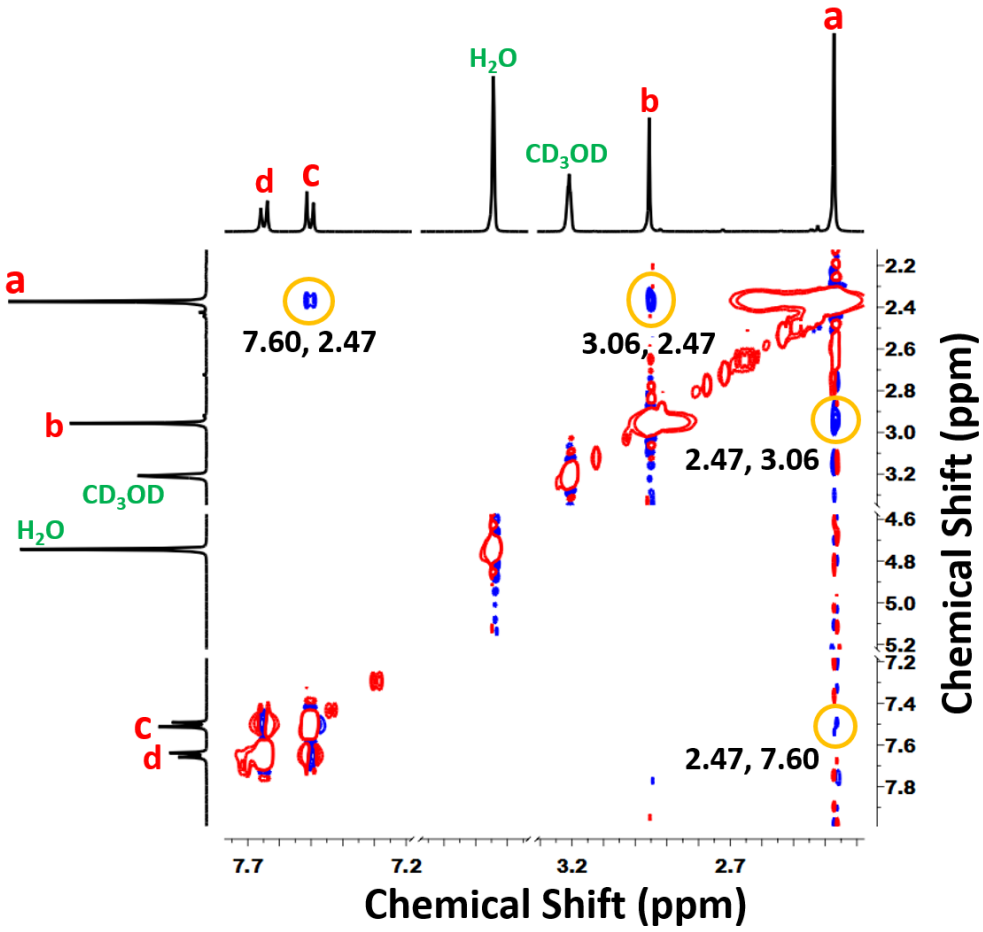
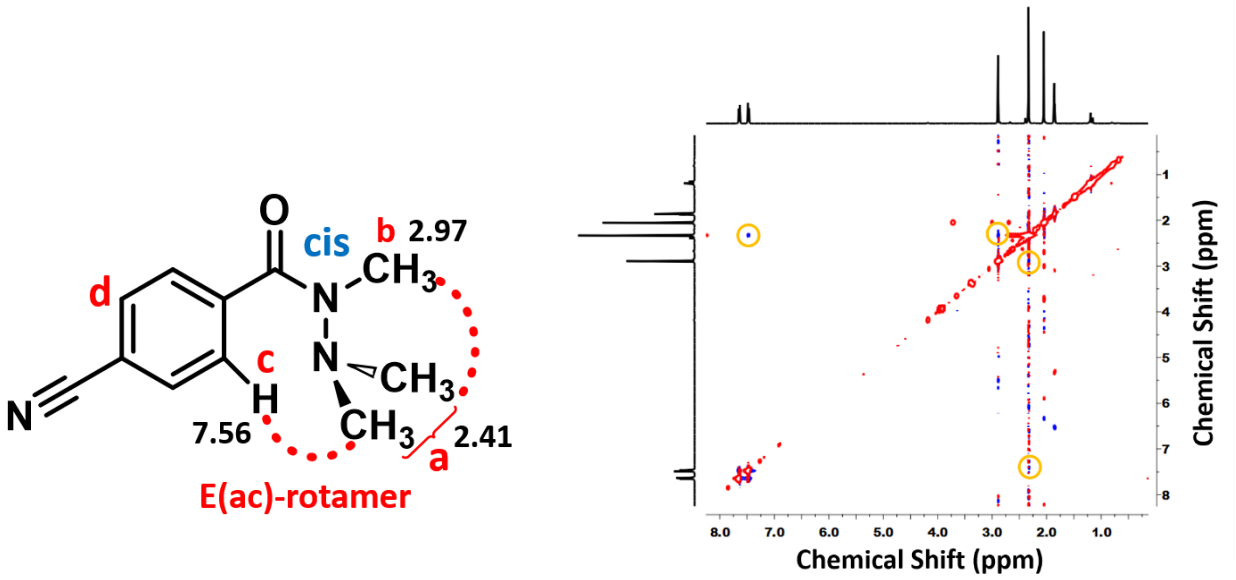


Figure S24 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **5** 4-cyano-*N*, *N*′, *N*′-trimethylbenzohydrazide in CD_3OD.



Compound **5**

Figure S25 (A). 2D NOESY full spectra for **5** 4-cyano-*N*, *N*′, *N*′-trimethylbenzohydrazide in CD_3CN.

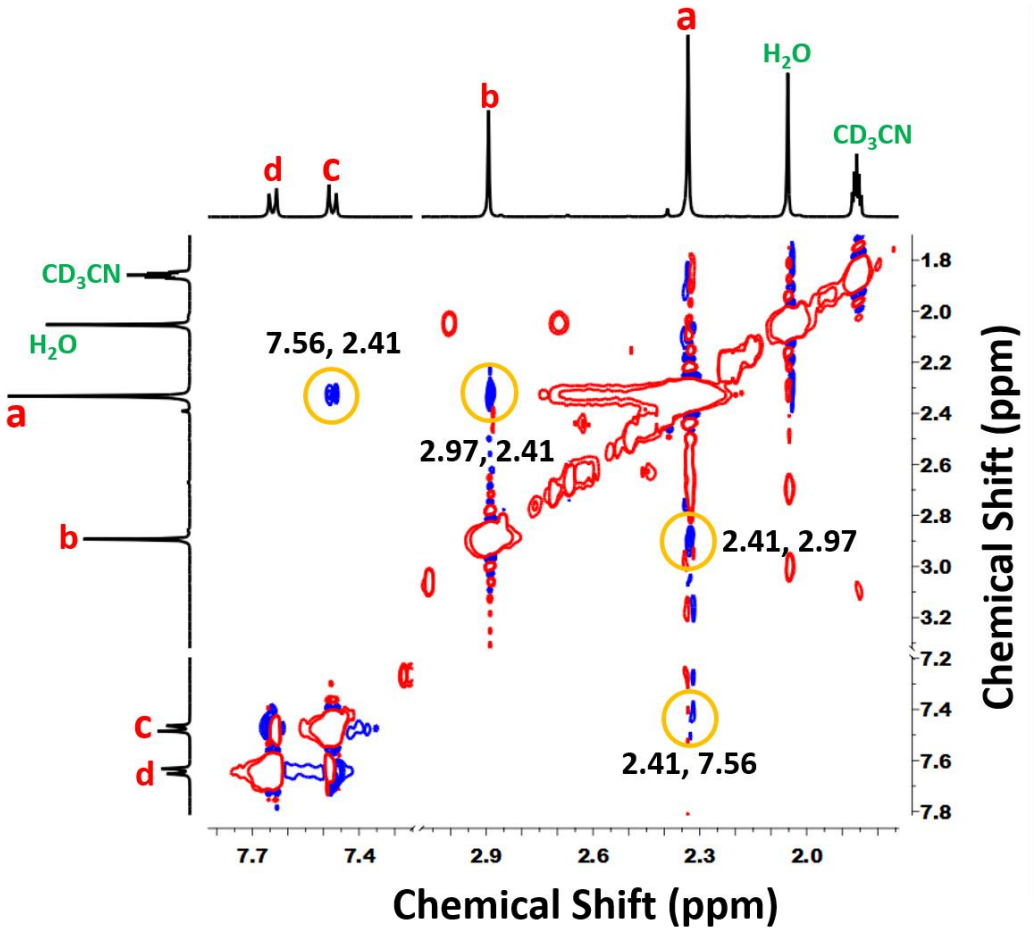
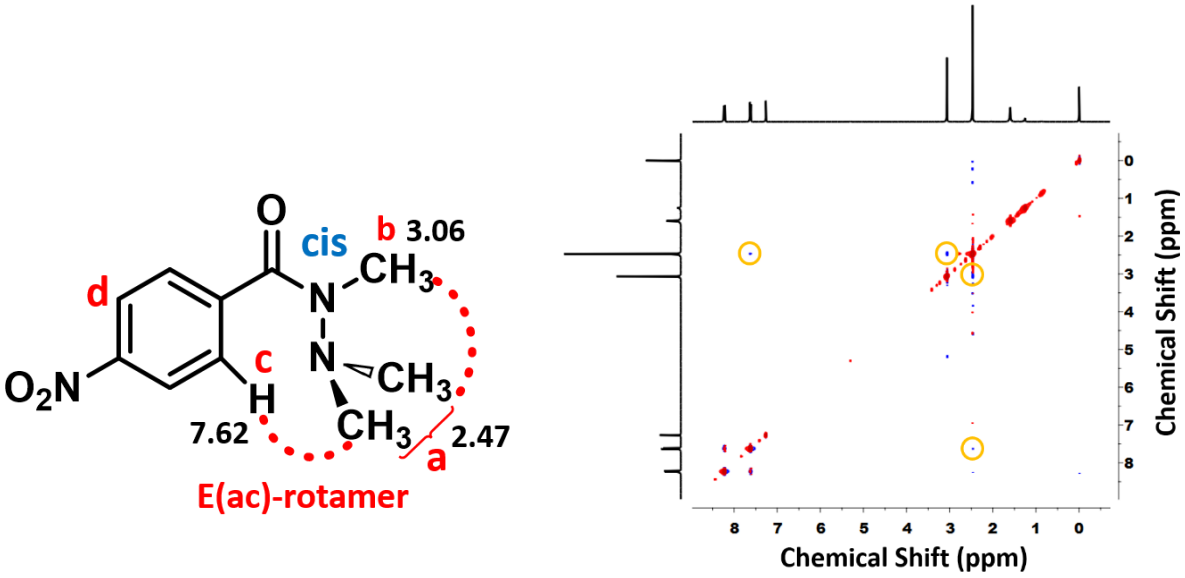


Figure S25 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **5** 4-cyano-*N*, *N*′, *N*′-trimethylbenzohydrazide in CD_3CN.



Compound **6**

Figure S26 (A). 2D NOESY full spectra for **6** *N*, *N*′, *N*′-trimethyl-4-nitrobenzohydrazide in $CDCl_3$.

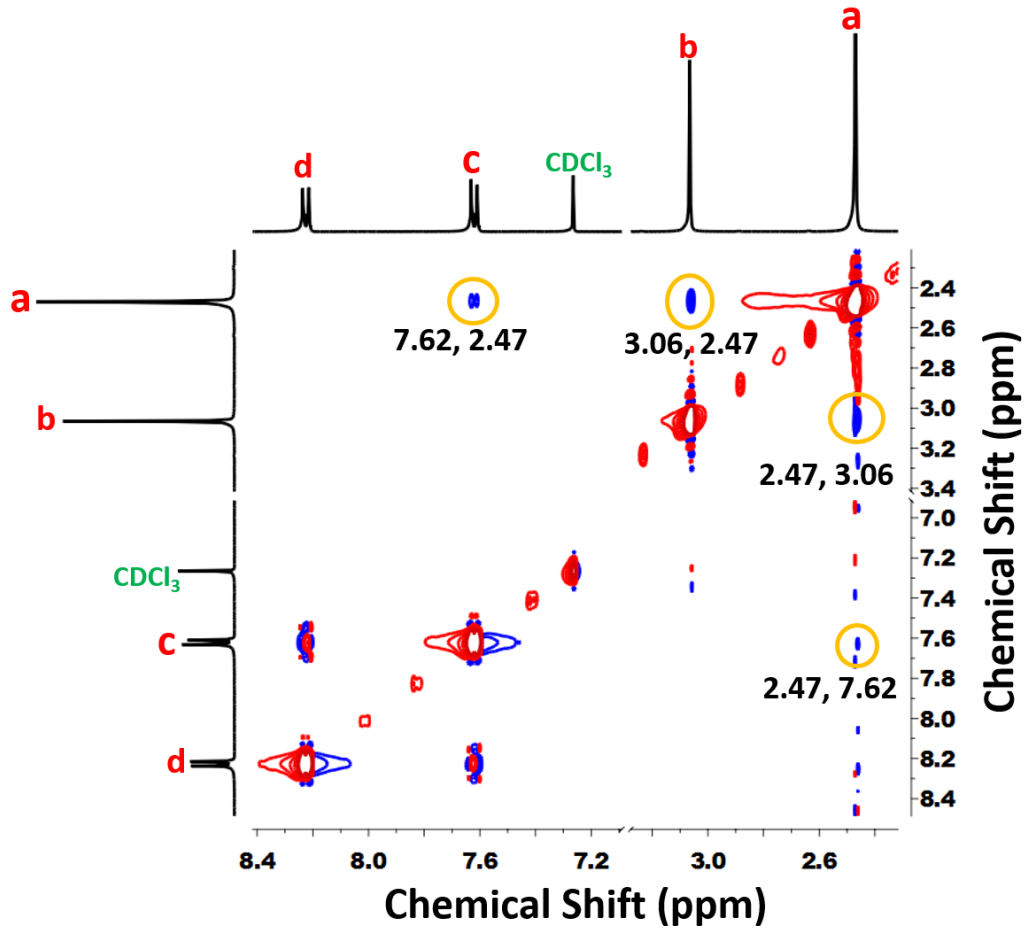
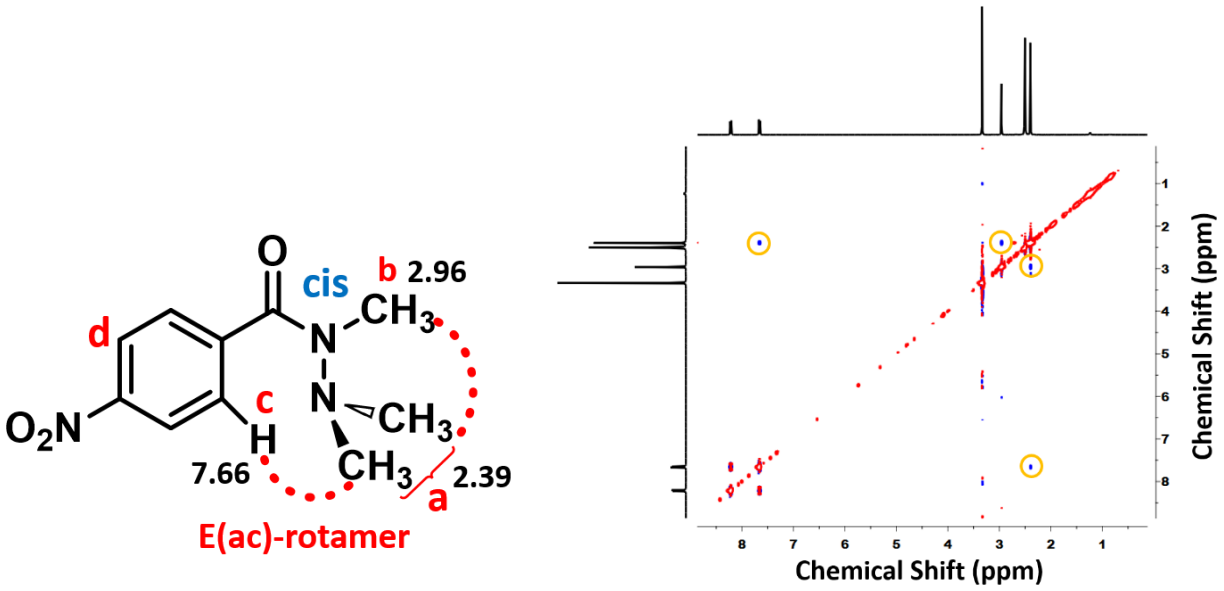


Figure S26 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **6** *N*, *N*′, *N*′-trimethyl-4-nitrobenzohydrazide in $CDCl_3$.



Compound **6**

Figure S27 (A). 2D NOESY full spectra for **6** *N*, *N'*, *N'*-trimethyl-4-nitrobenzohydrazide in $[CD_3]_2SO$.

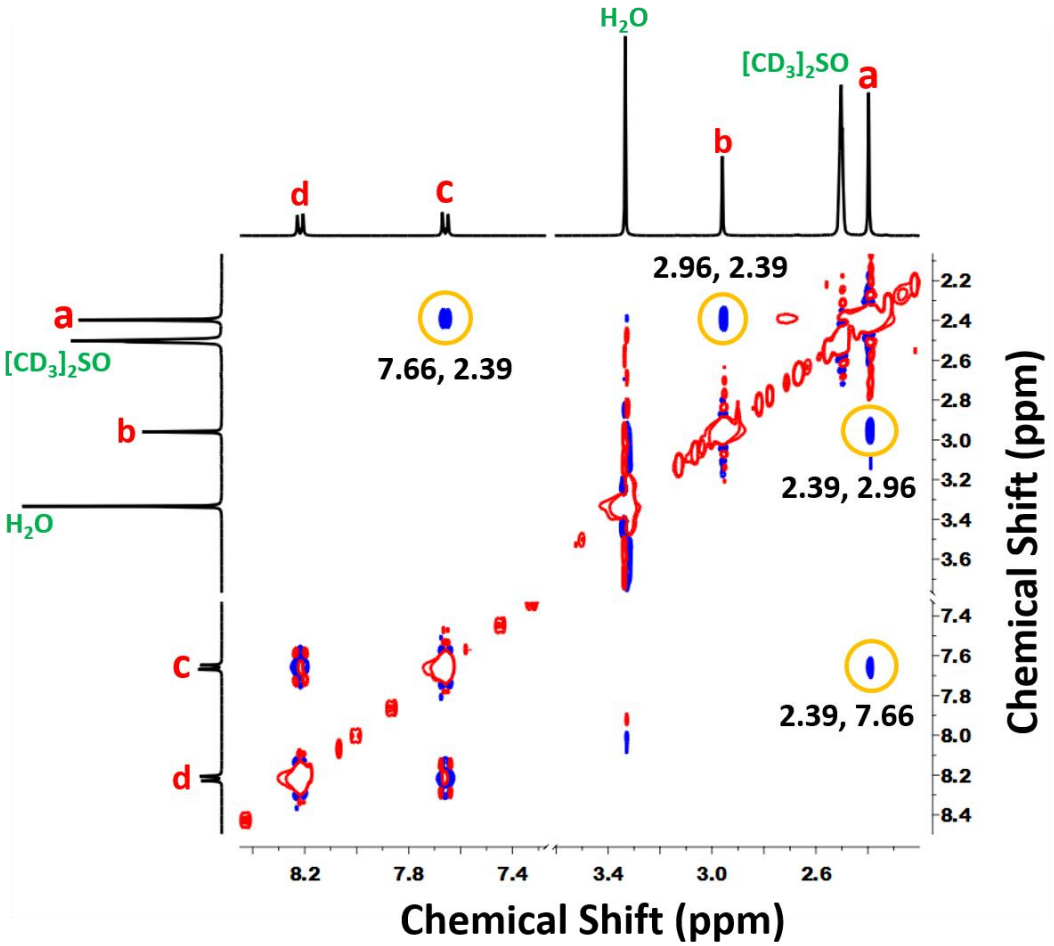
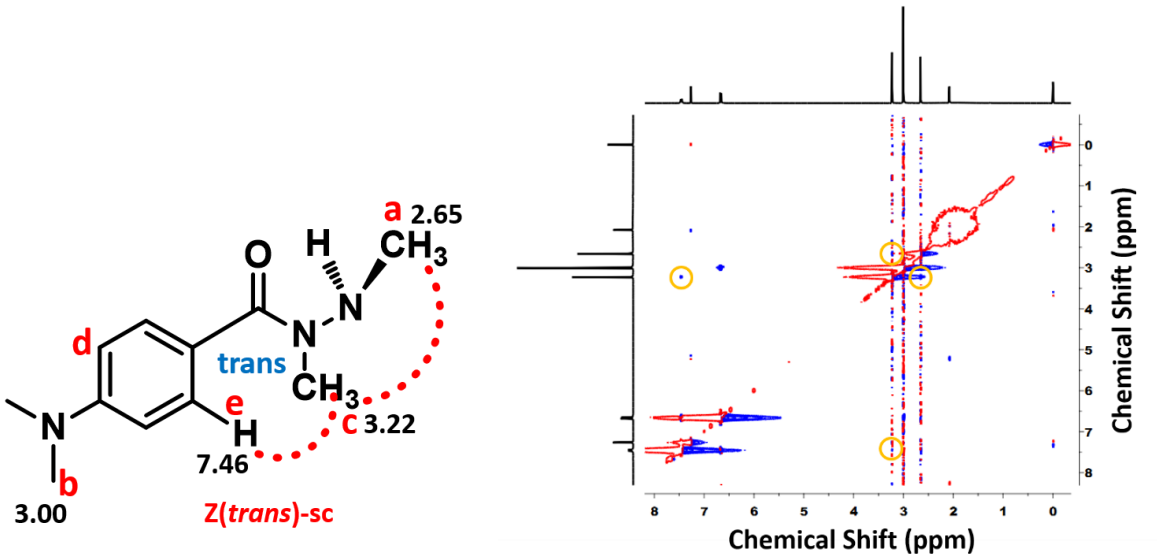


Figure S27 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **6** *N*, *N'*, *N'*-trimethyl-4-nitrobenzohydrazide in $[CD_3]_2SO$.



Compound **7**

Figure S28 (A). 2D NOESY full spectra for **7** 4-(dimethylamino)-*N*, *N*′-dimethylbenzohydrazide in $CDCl_3$.

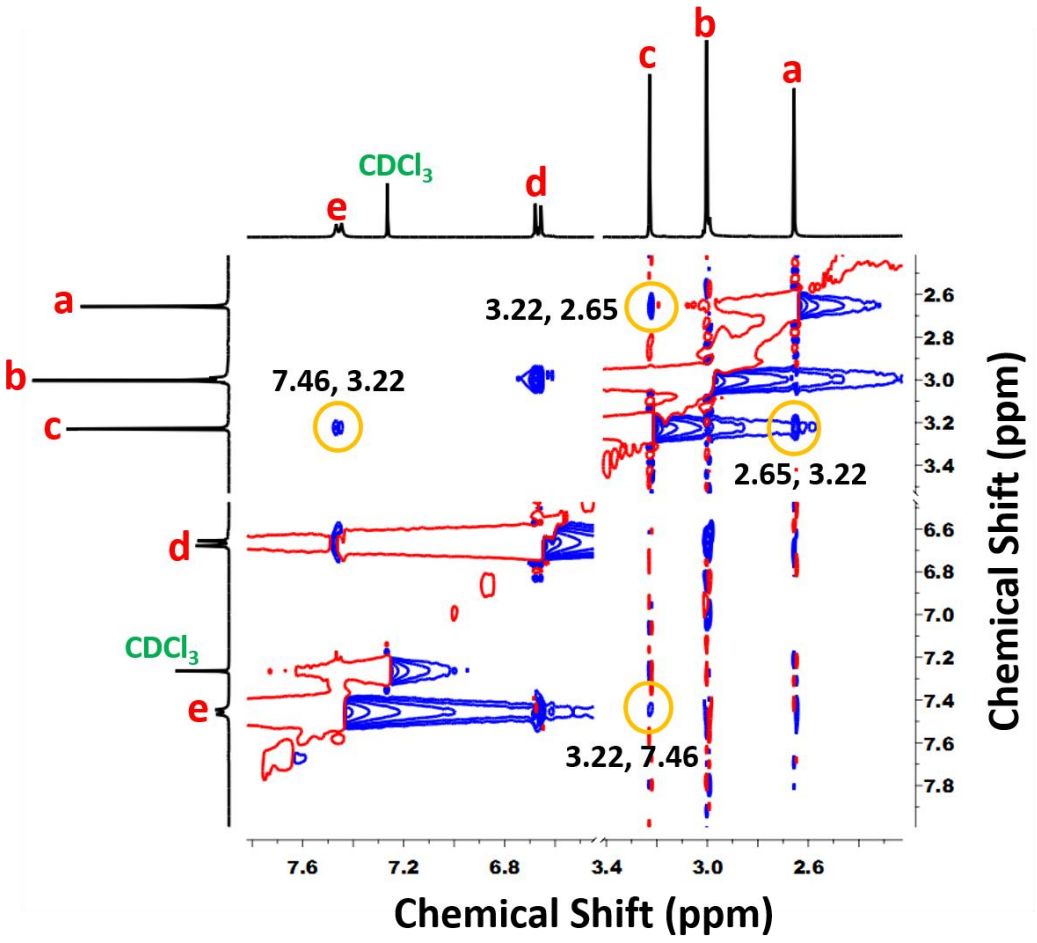
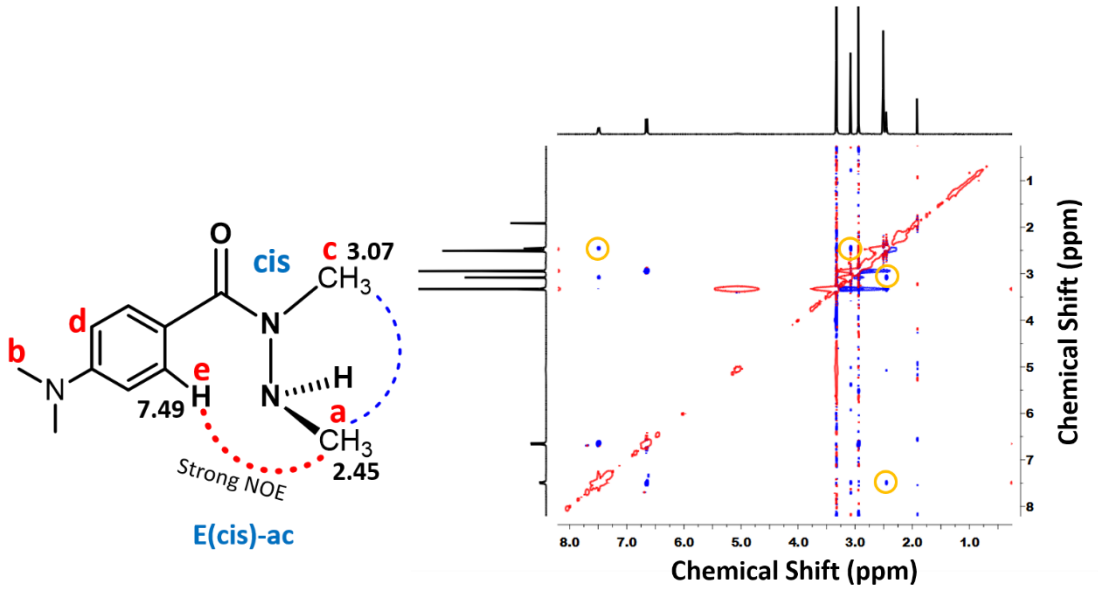


Figure S28 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **7** 4-(dimethylamino)-*N*, *N*′-dimethylbenzohydrazide in $CDCl_3$.



Compound **7**

Figure S29 (A). 2D NOESY full spectra for **7** 4-(dimethyl-amino)-*N*, *N*′-dimethylbenzohydrazide in $[CD_3]_2SO$.

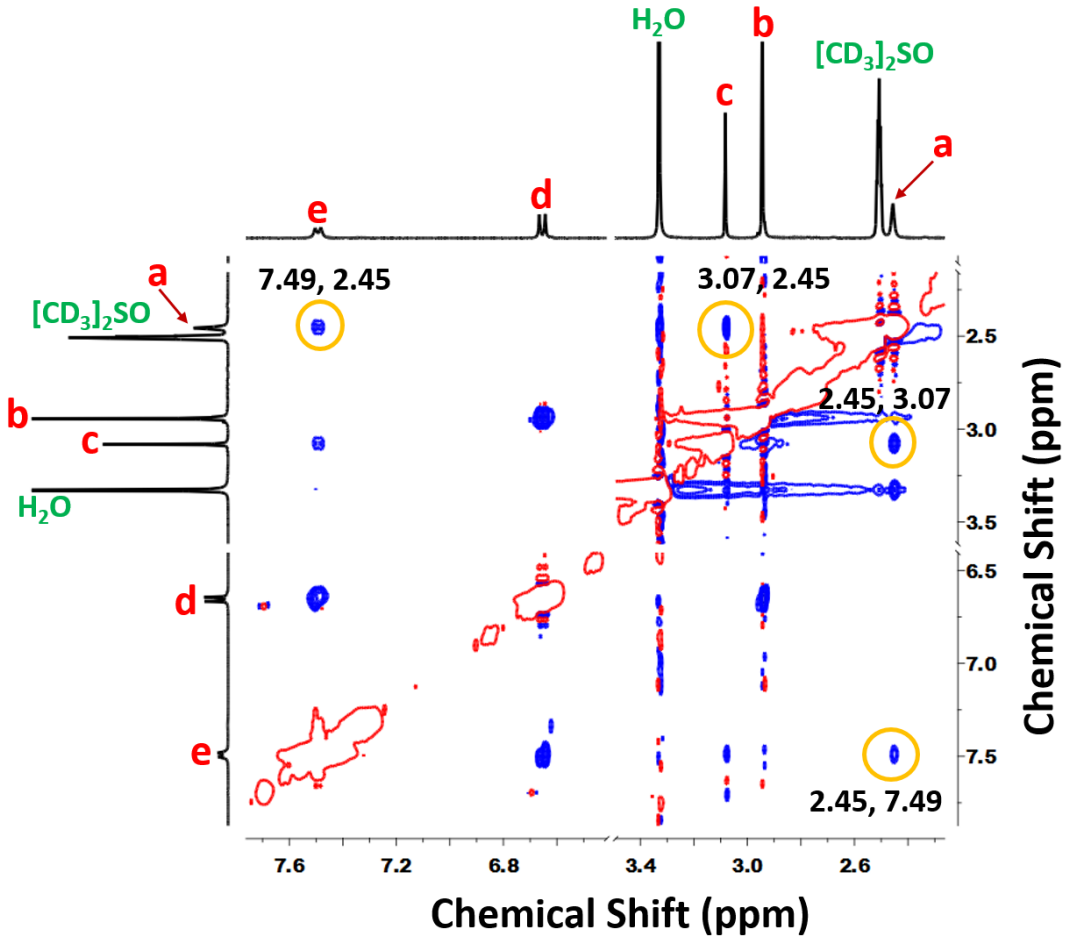
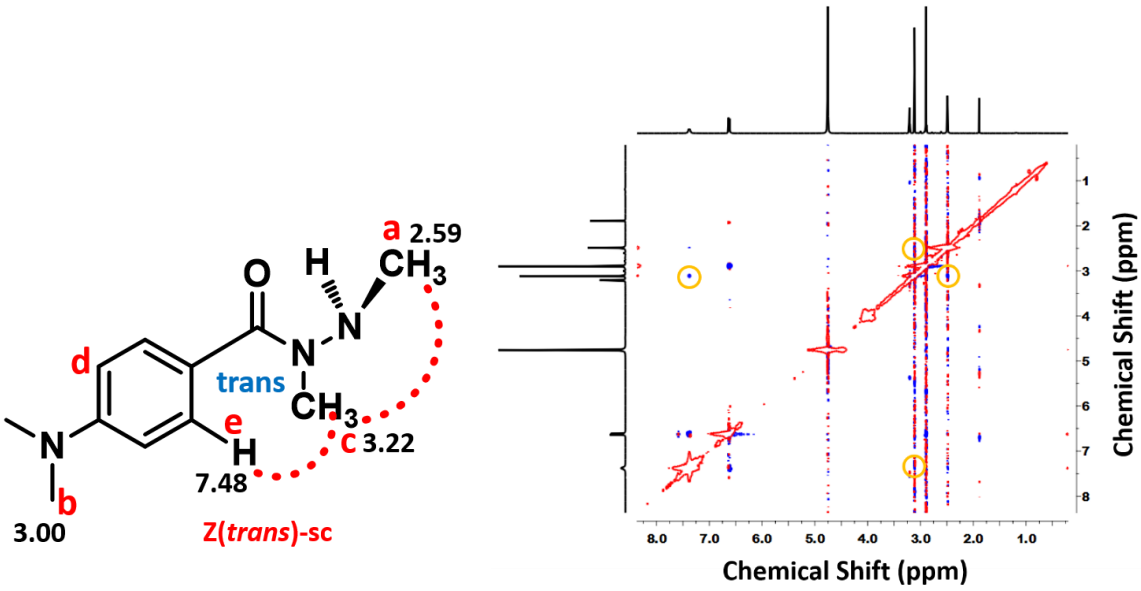


Figure S29 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **7** 4-(dimethylamino)-*N*, *N*′-dimethylbenzohydrazide in $[CD_3]_2SO$.



Compound **7**

Figure S30 (A). 2D NOESY full spectra for **7** 4-(dimethylamino)-*N*, *N*'-dimethylbenzohydrazide in CD_3OD.

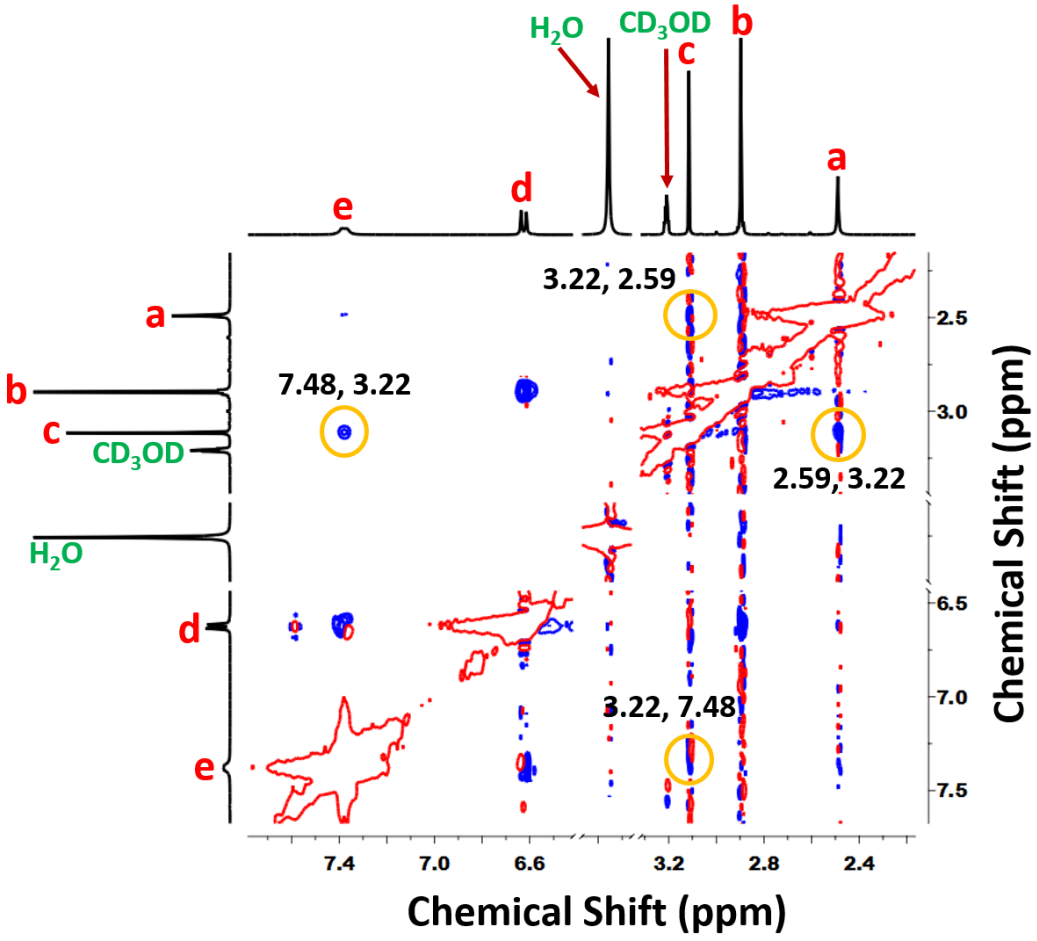
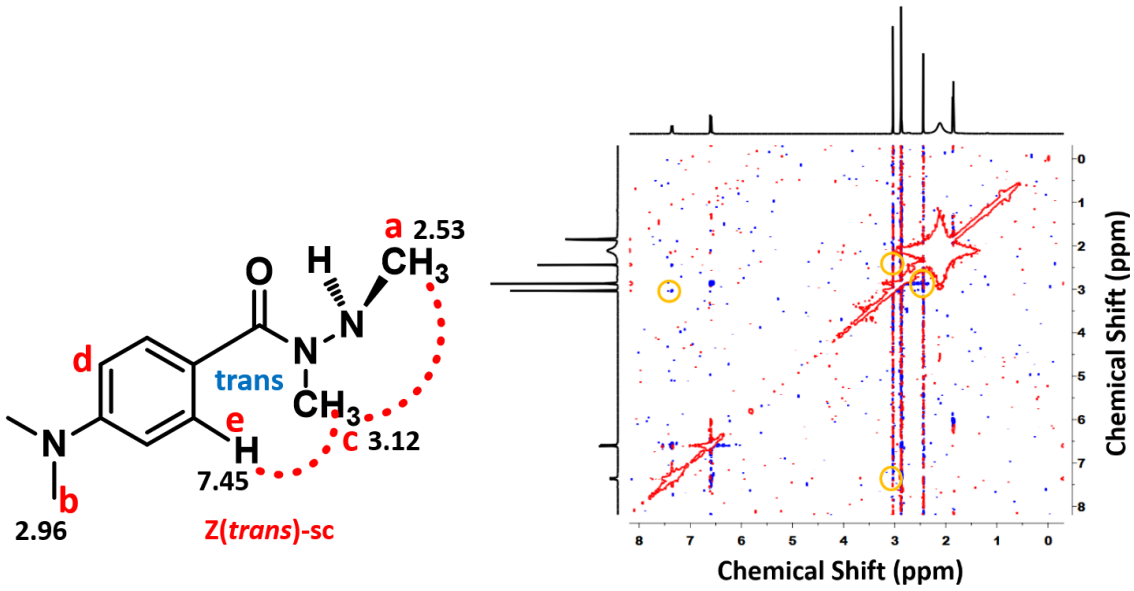


Figure S30 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **7** 4-(dimethylamino)-*N*, *N*'-dimethylbenzohydrazide in CD_3OD.



Compound **7**

Figure S31 (A). 2D NOESY full spectra for **7** 4-(dimethylamino)-*N*, *N*′-dimethylbenzohydrazide in CD_3CN.

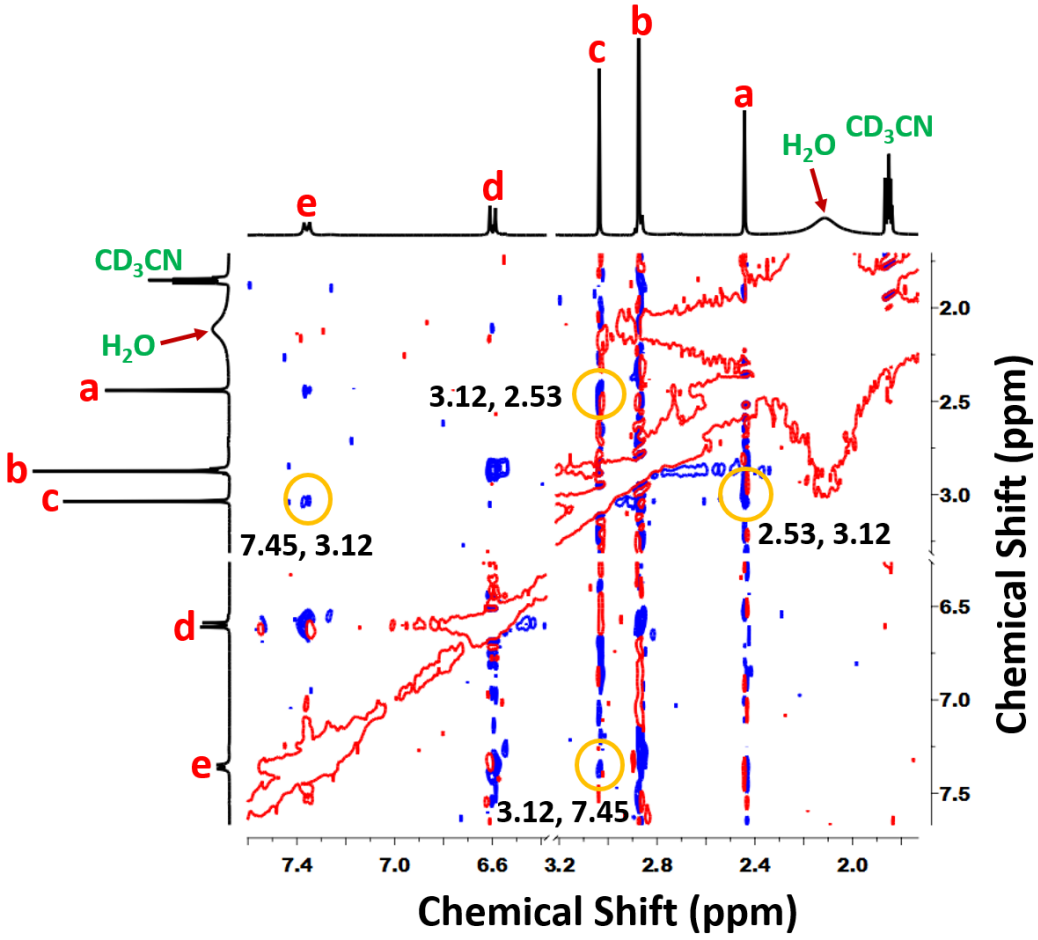
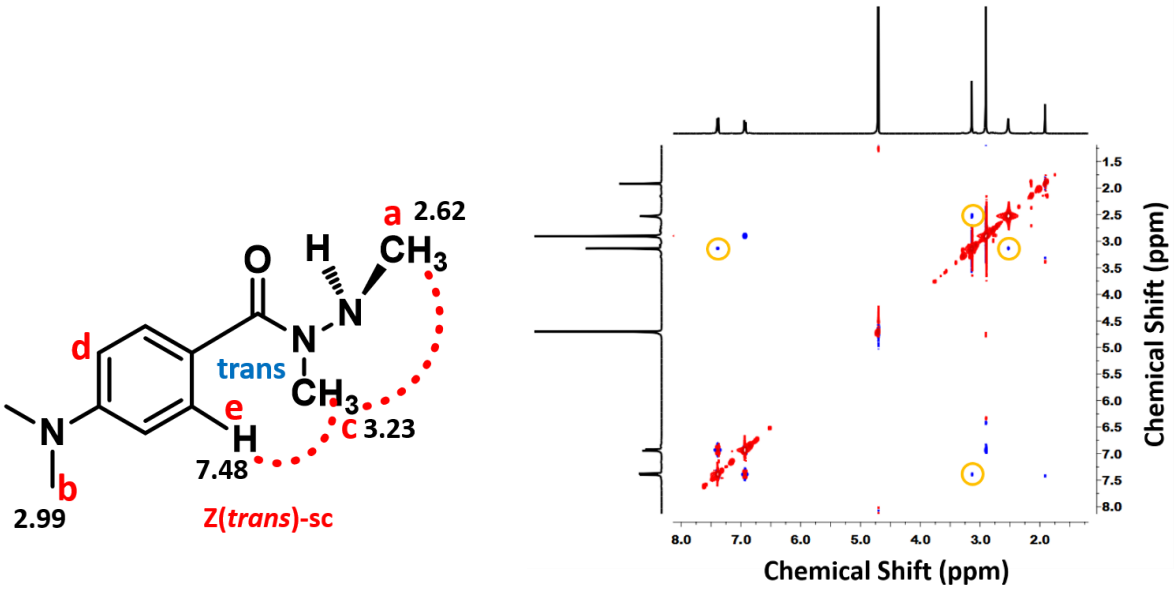


Figure S31 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **7** 4-(dimethylamino)-*N*, *N*′-dimethylbenzohydrazide in CD_3CN.



Compound **7**

Figure S32 (A). 2D NOESY full spectra for **7** 4-(dimethylamino)-*N*, *N*'-dimethylbenzohydrazide in D_2O.

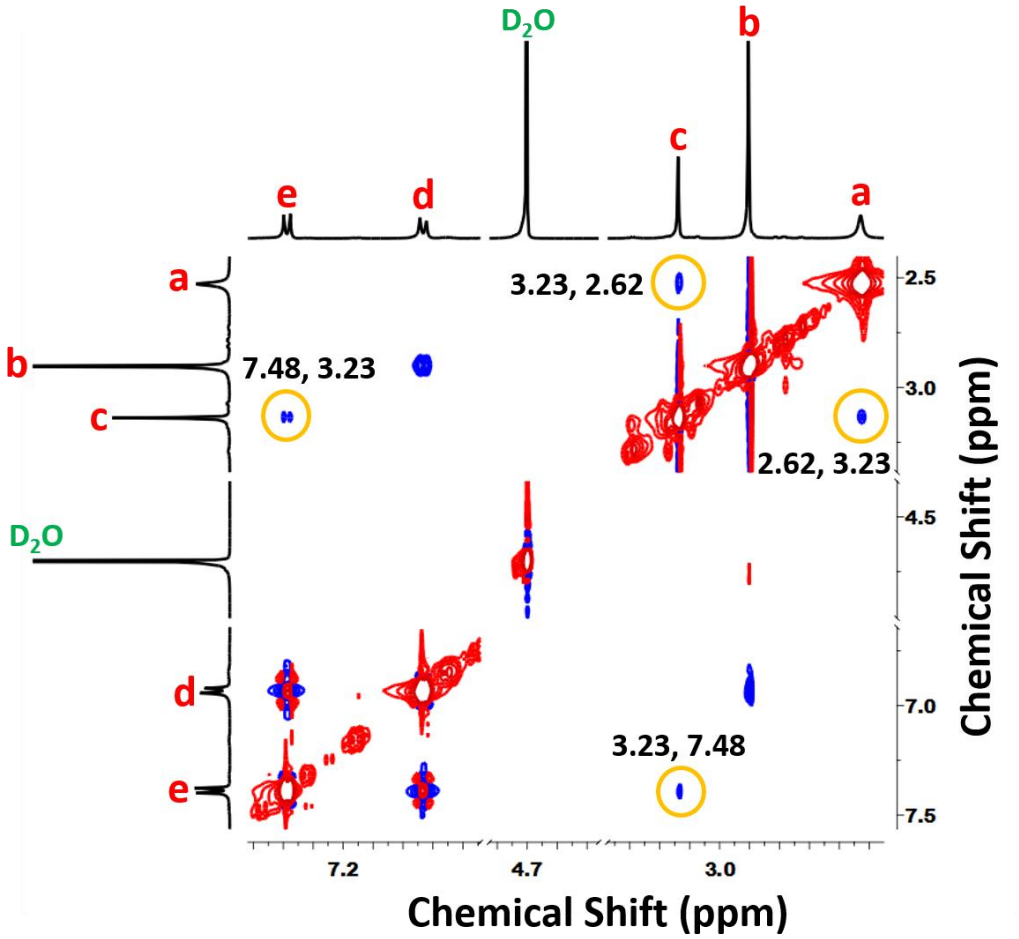
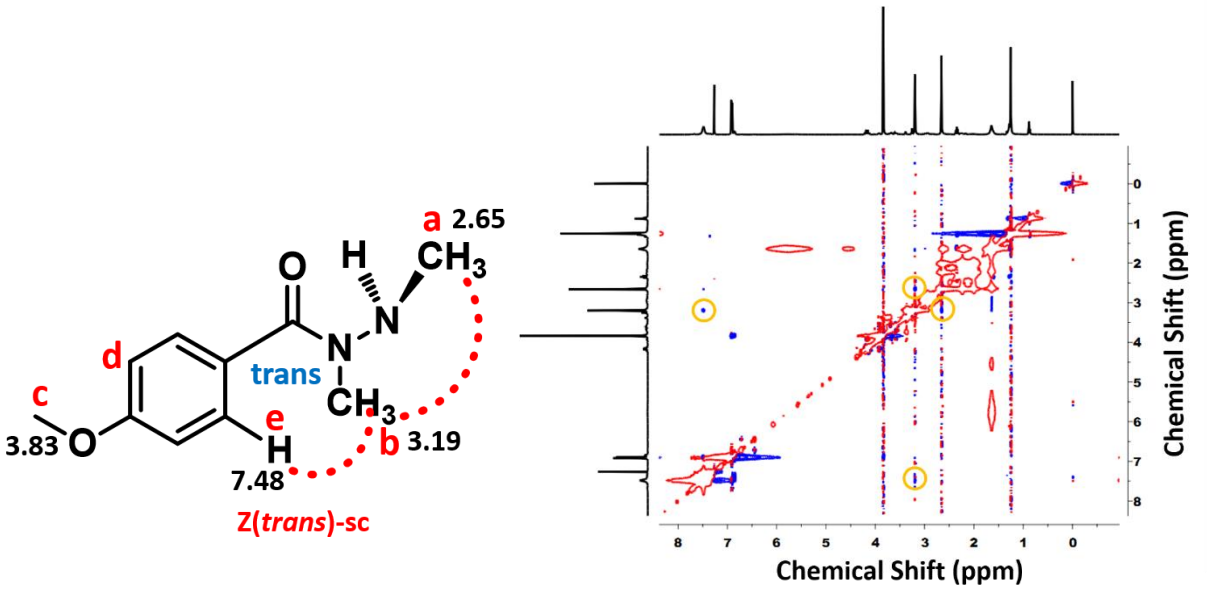


Figure S32 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **7** 4-(dimethylamino)-*N*, *N*'-dimethylbenzohydrazide in D_2O.



Compound **8**

Figure S33 (A). 2D NOESY full spectra for **8** 4-methoxy-*N*, *N*′-dimethylbenzohydrazide in $CDCl_3$.

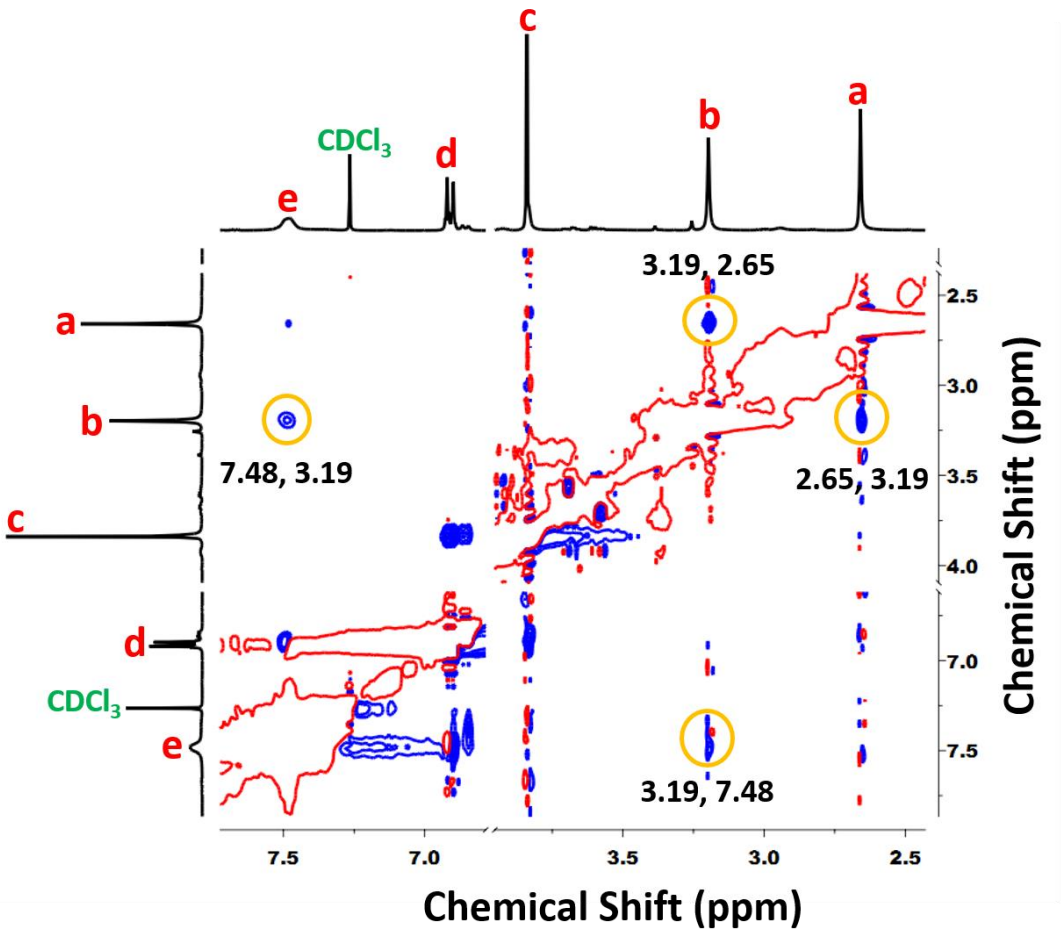
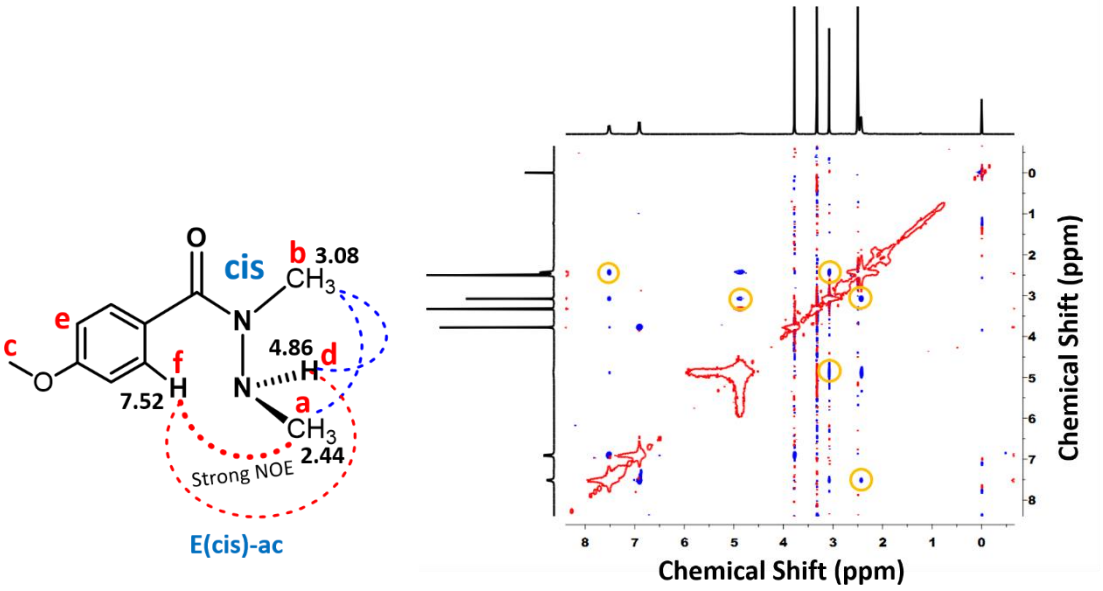


Figure S33 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **8** 4-methoxy-*N*, *N*′-dimethylbenzohydrazide in $CDCl_3$.



Compound **8**

Figure S34 (A). 2D NOESY full spectra for **8** 4-methoxy-*N*, *N*′-dimethylbenzohydrazide in $[CD_3]_2SO$.

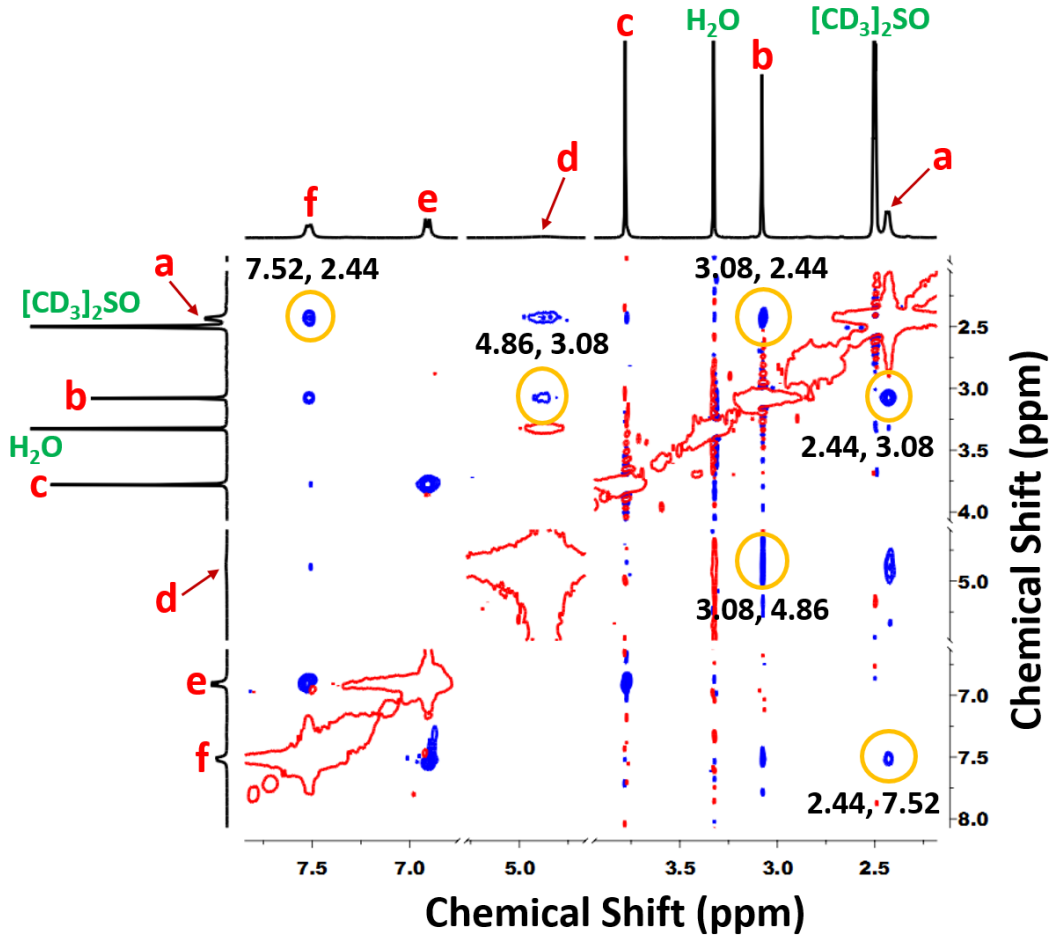
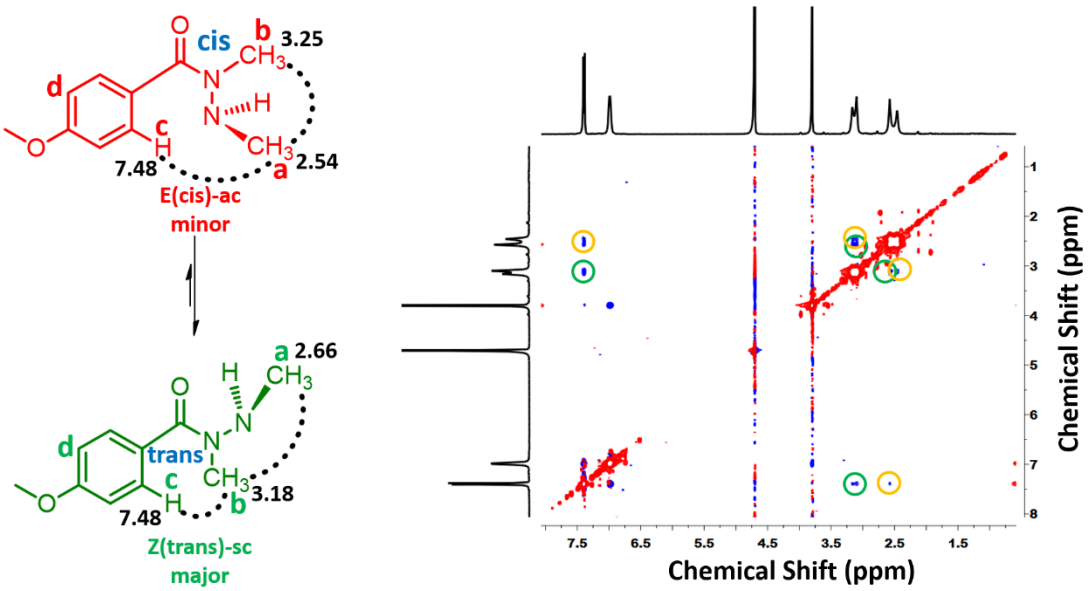


Figure S34 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **8** 4-methoxy-*N*, *N*′-dimethylbenzohydrazide in $[CD_3]_2SO$.



Compound **8**

Figure S35 (A). 2D NOESY full spectra for **8** 4-methoxy-*N*, *N*′-dimethylbenzohydrazide in D_2O.

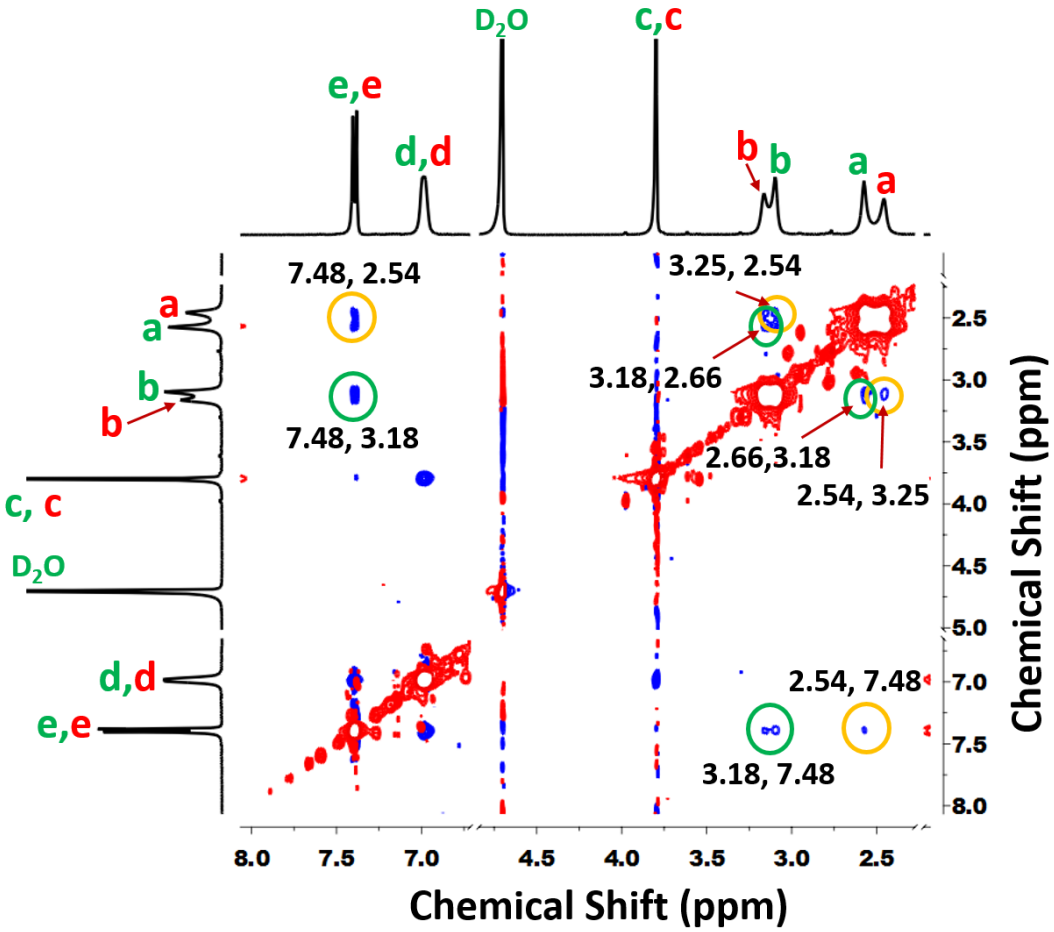
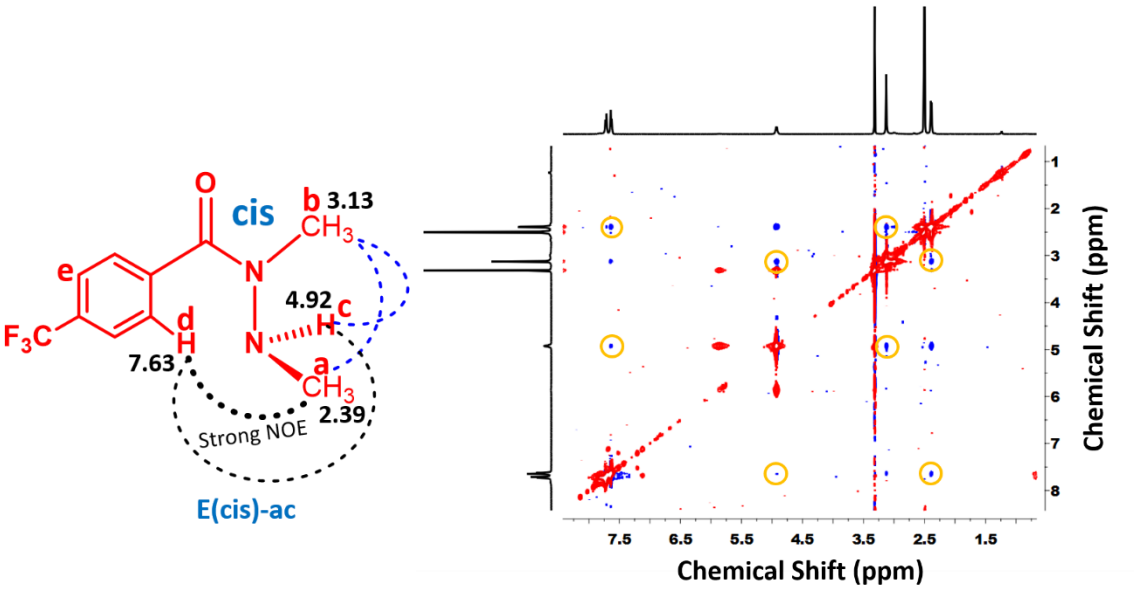


Figure S35 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **8** 4-methoxy-*N*, *N*′-dimethylbenzohydrazide in D_2O.



Compound **10**

Figure S36 (A). 2D NOESY full spectra for **10** *N*, *N*′-dimethyl-4-(trifluoromethyl)benzohydrazide in $[CD_3]_2SO$.

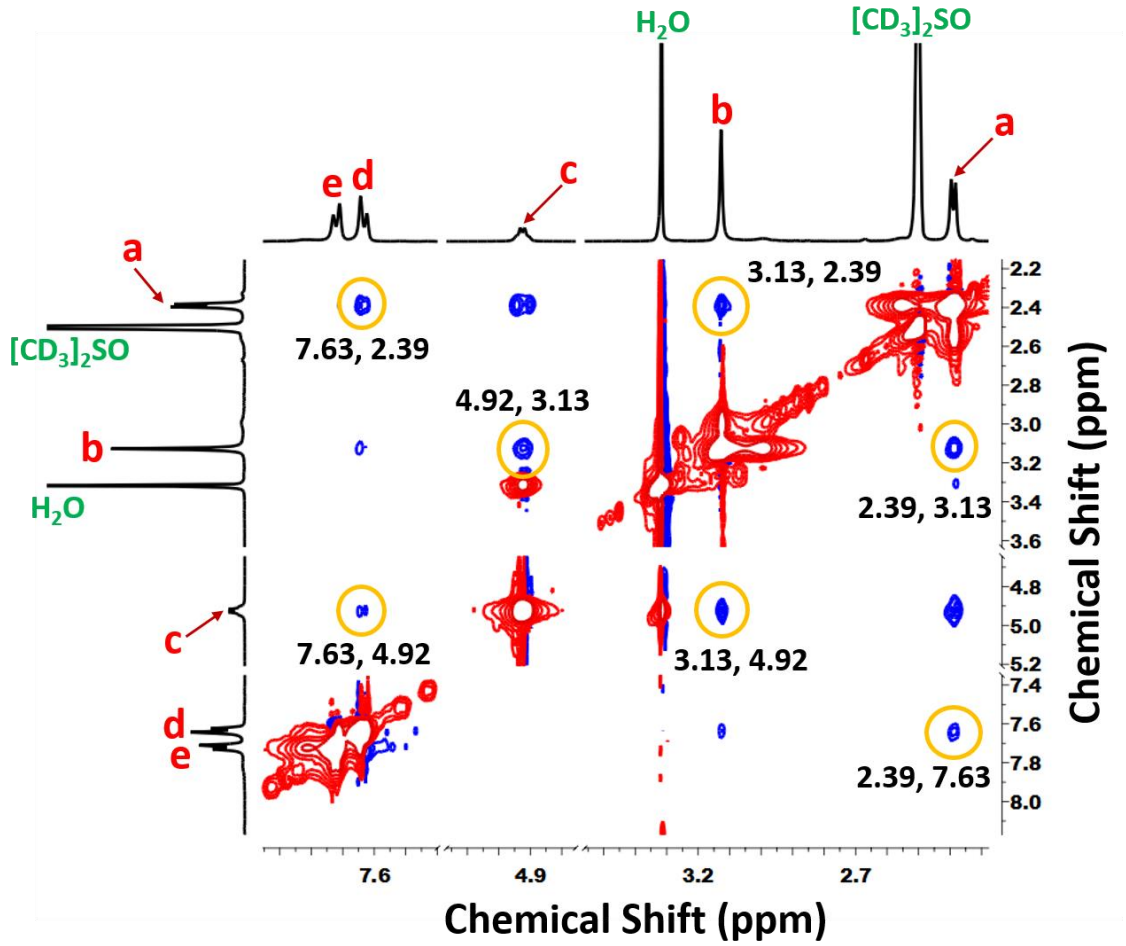
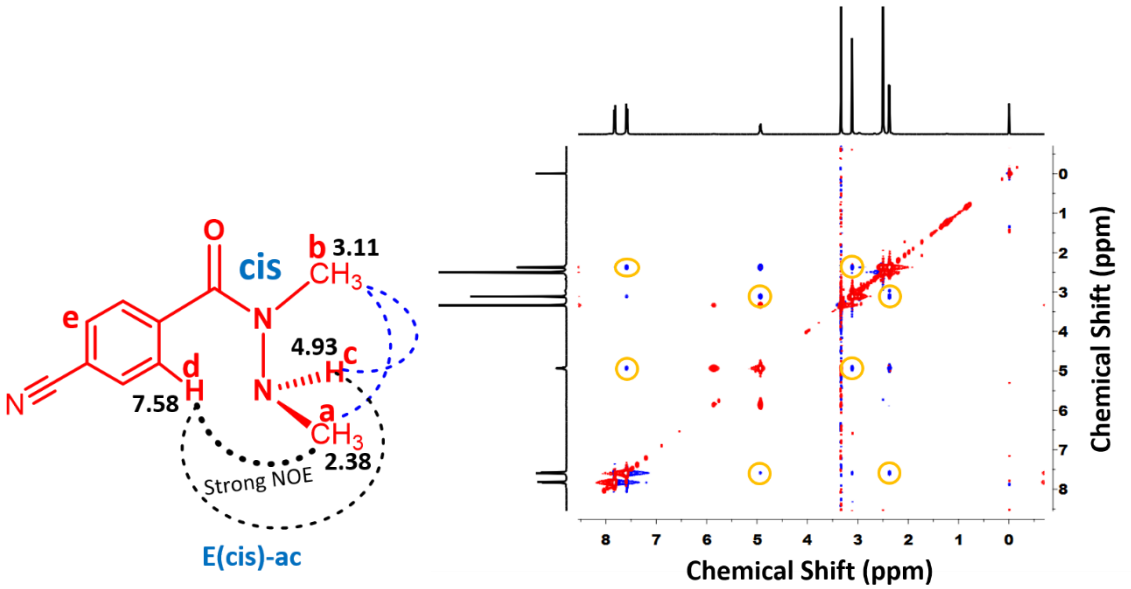


Figure S36 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **10** *N*, *N*′-dimethyl-4-(trifluoromethyl)benzohydrazide in $[CD_3]_2SO$.



Compound **11**

Figure S37 (A). 2D NOESY full spectra for **11** 4-cyano-*N*, *N*'-dimethylbenzohydrazide in $[CD_3]_2SO$.

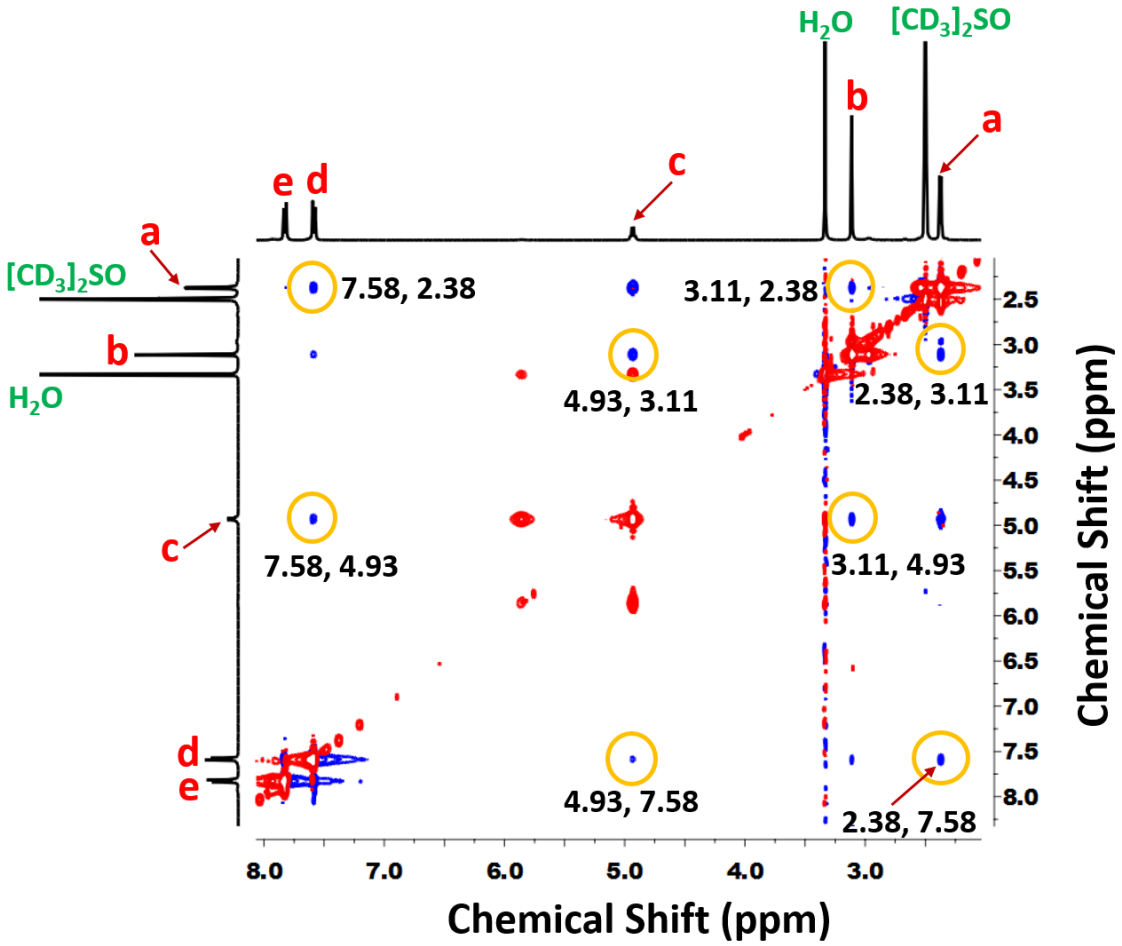
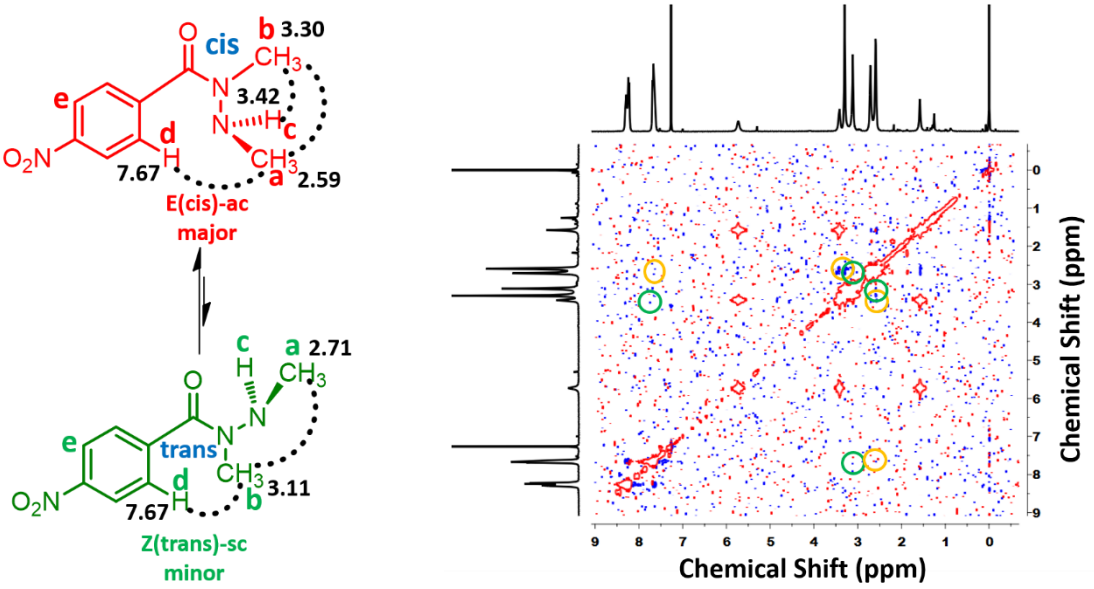


Figure S37 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **11** 4-cyano-*N*, *N*'-dimethylbenzohydrazide in $[CD_3]_2SO$.



Compound **12**

Figure S38 (A). 2D NOESY full spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in $CDCl_3$.

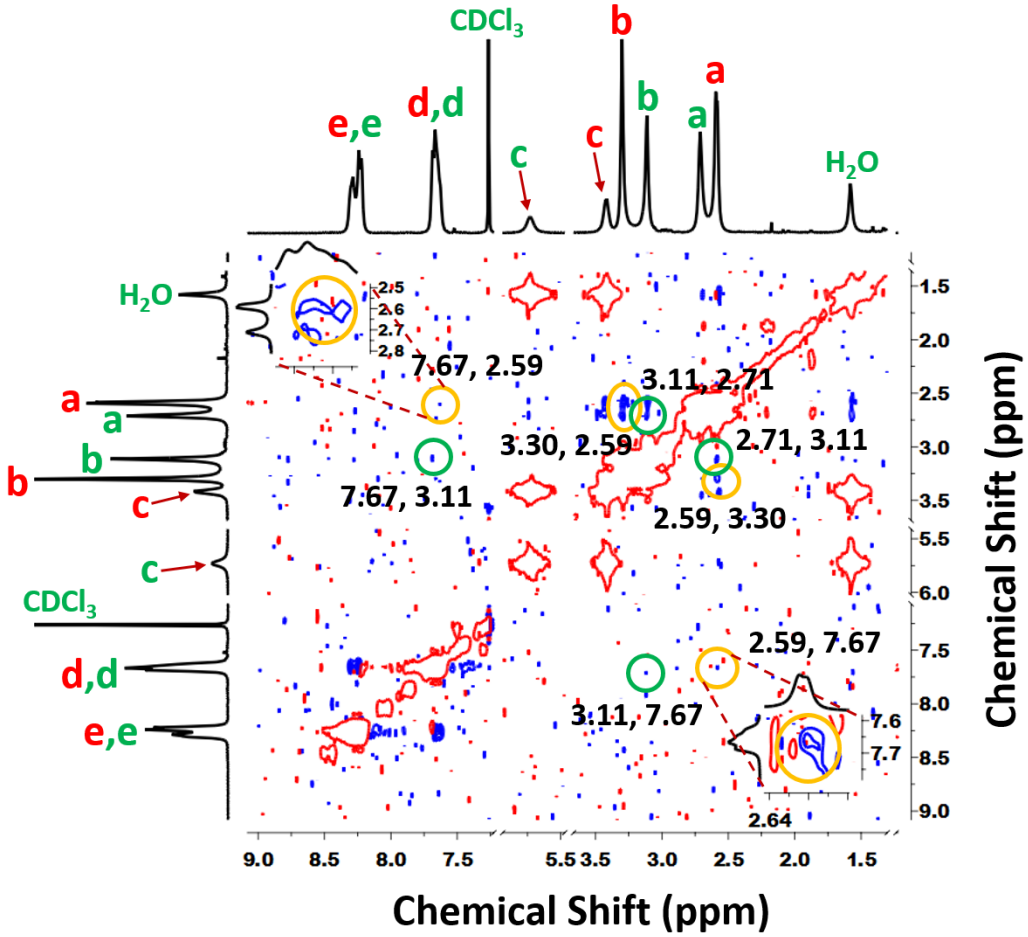
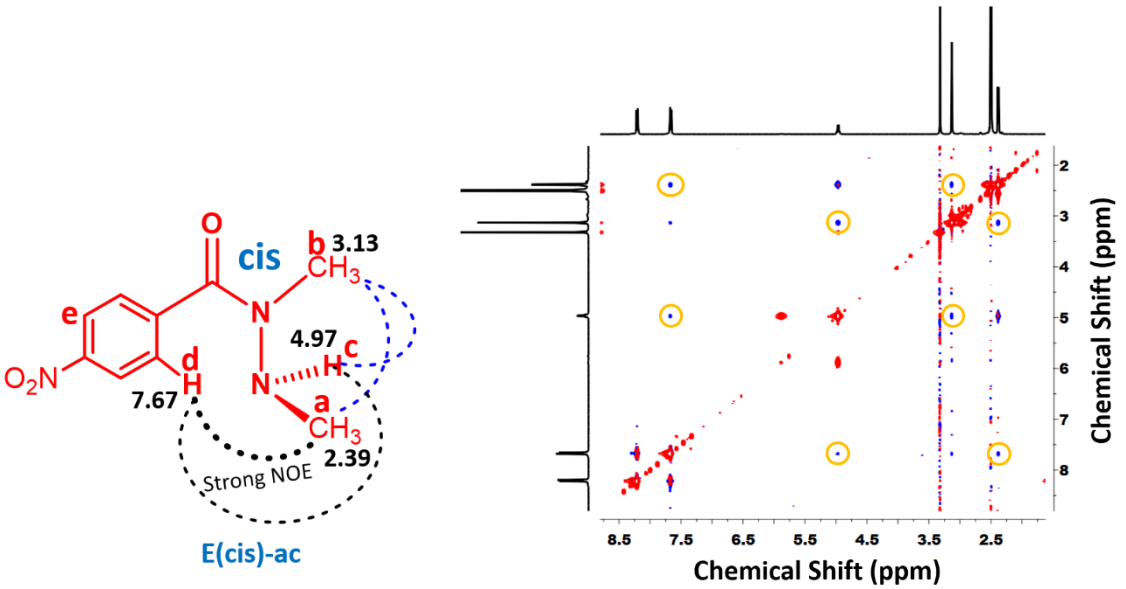


Figure S38 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in $CDCl_3$.



Compound **12**

Figure S39 (A). 2D NOESY full spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in $[CD_3]_2SO$.

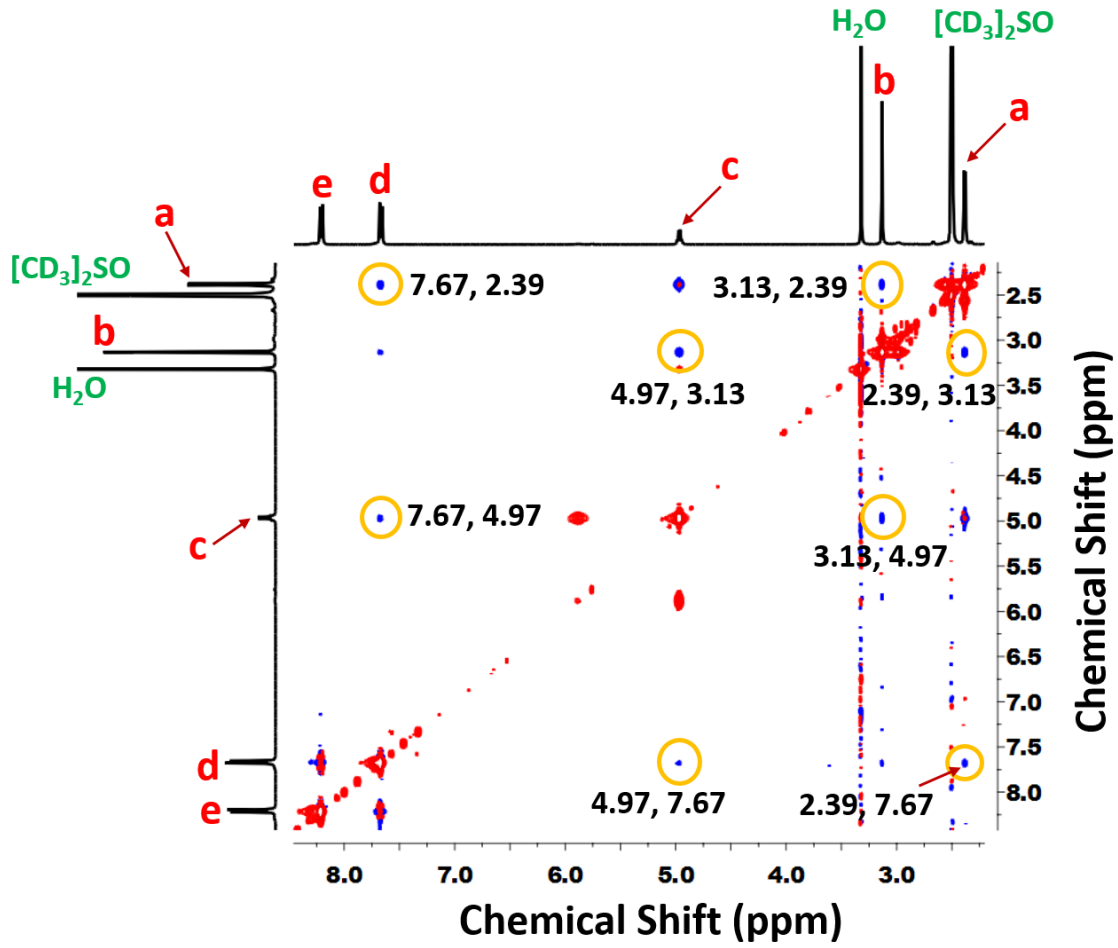
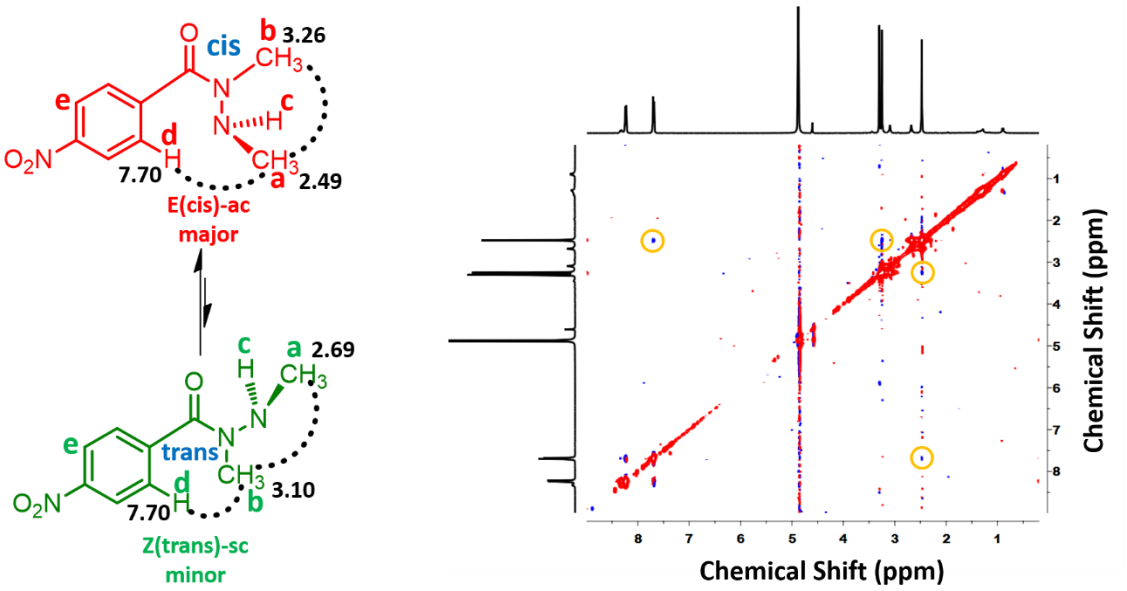


Figure S39 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in $[CD_3]_2SO$.



Compound **12**

Figure S40 (A). 2D NOESY full spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in CD_3OD.

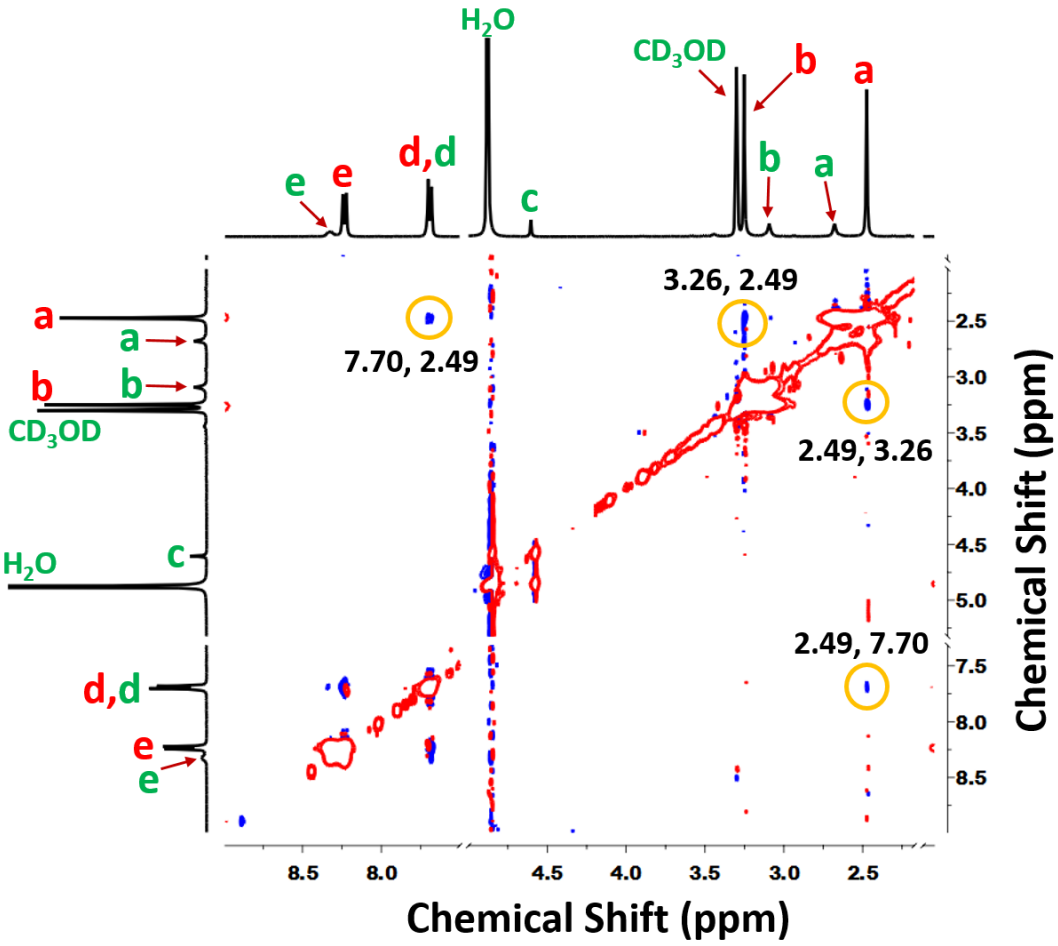
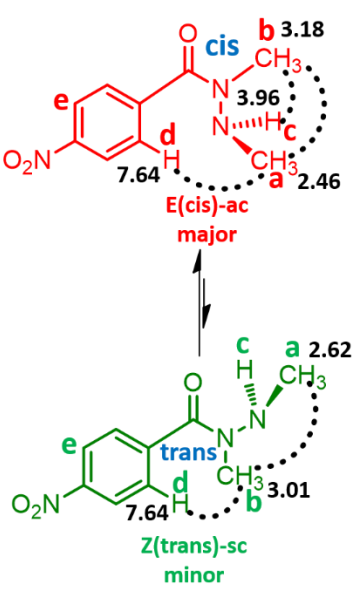


Figure S40 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in CD_3OD.



Compound **12**

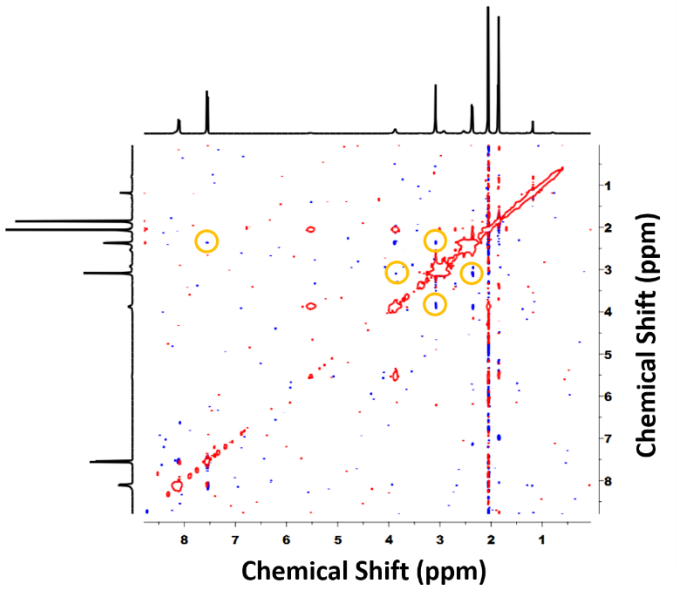


Figure S41 (A). 2D NOESY full spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in CD_3CN.

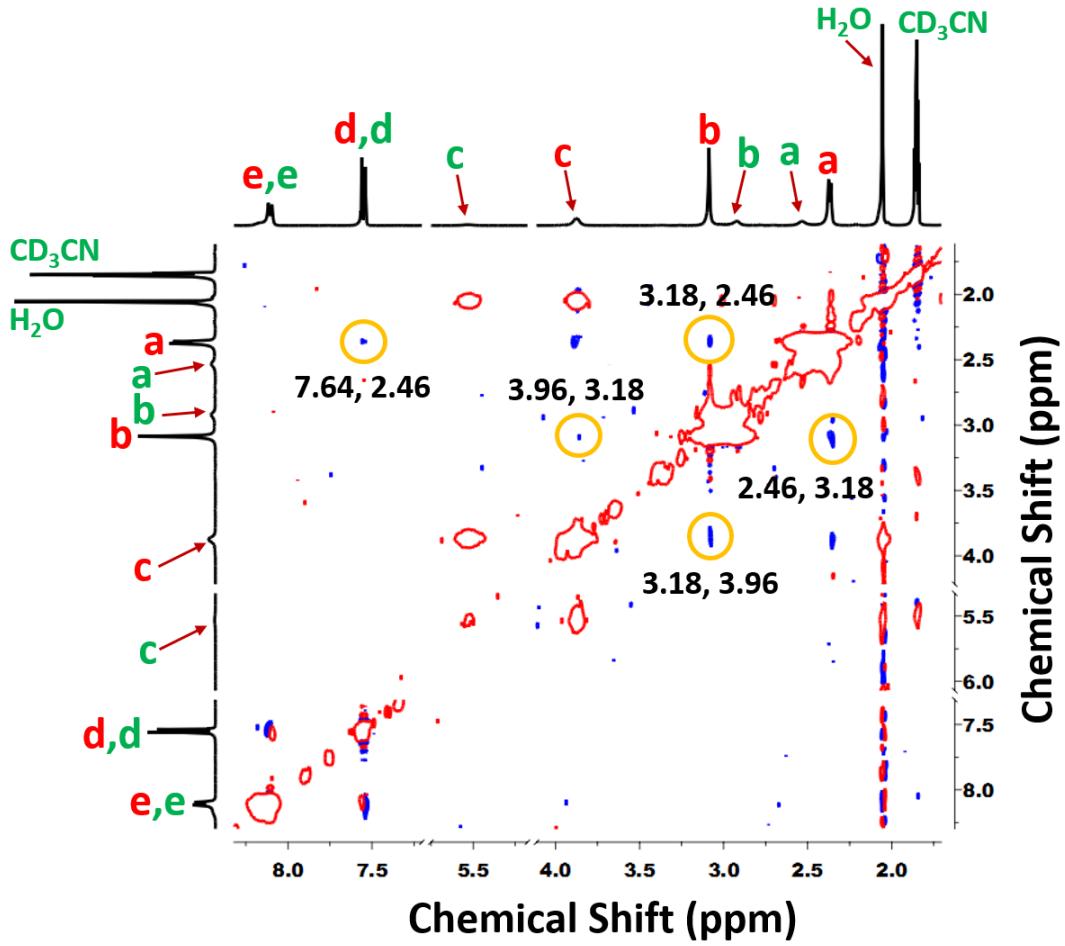
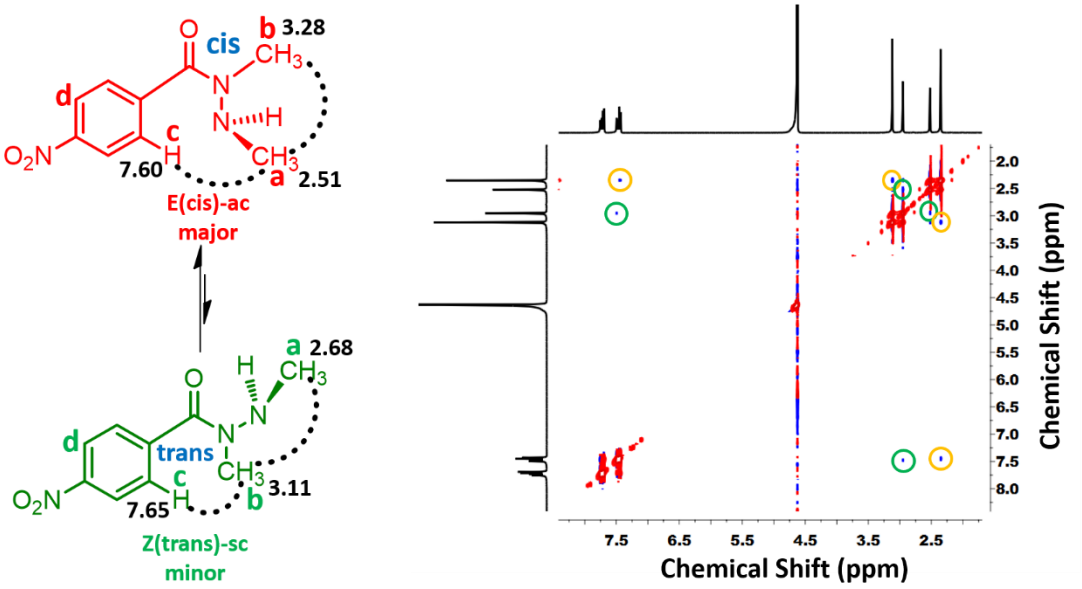


Figure S41 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in CD_3CN.



Compound **12**

Figure S42 (A). 2D NOESY full spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in D_2O.

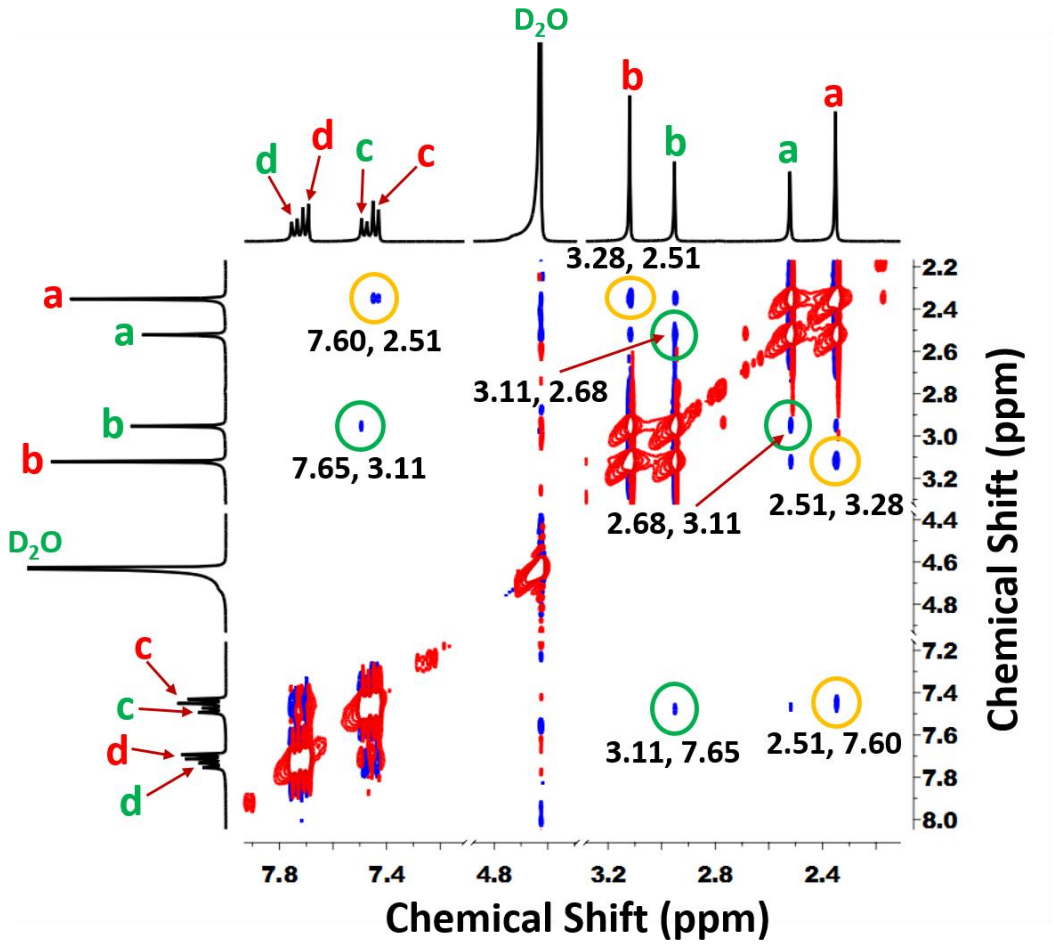
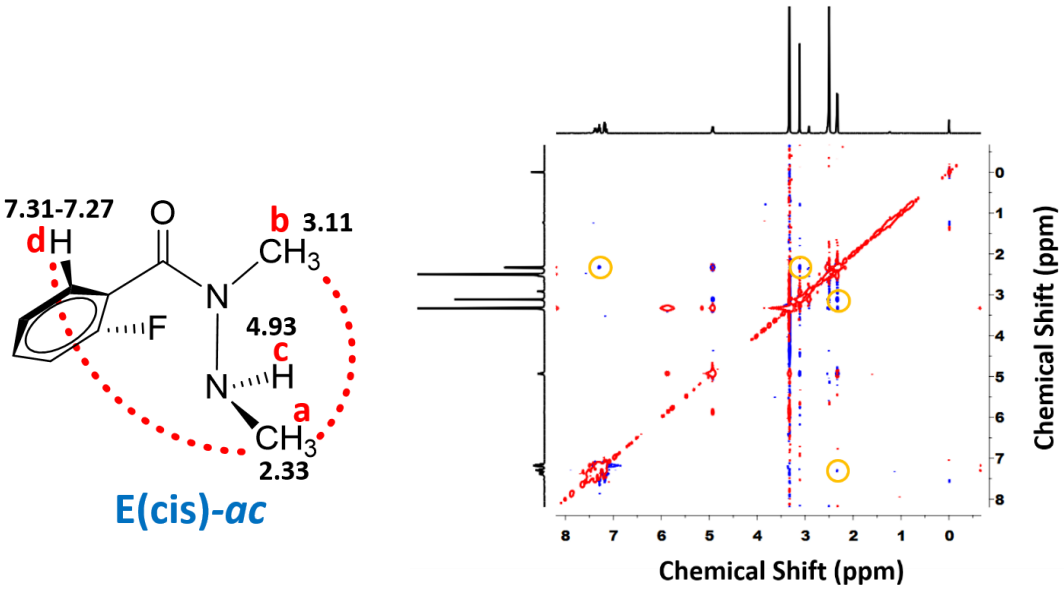


Figure S42 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **12** *N*, *N*′-dimethyl-4-nitrobenzohydrazide in D_2O.



Compound **15**

Figure S43 (A). 2D NOESY full spectra for **15** 2-fluoro-*N*, *N*'-dimethylbenzohydrazide in $[CD_3]_2SO$.

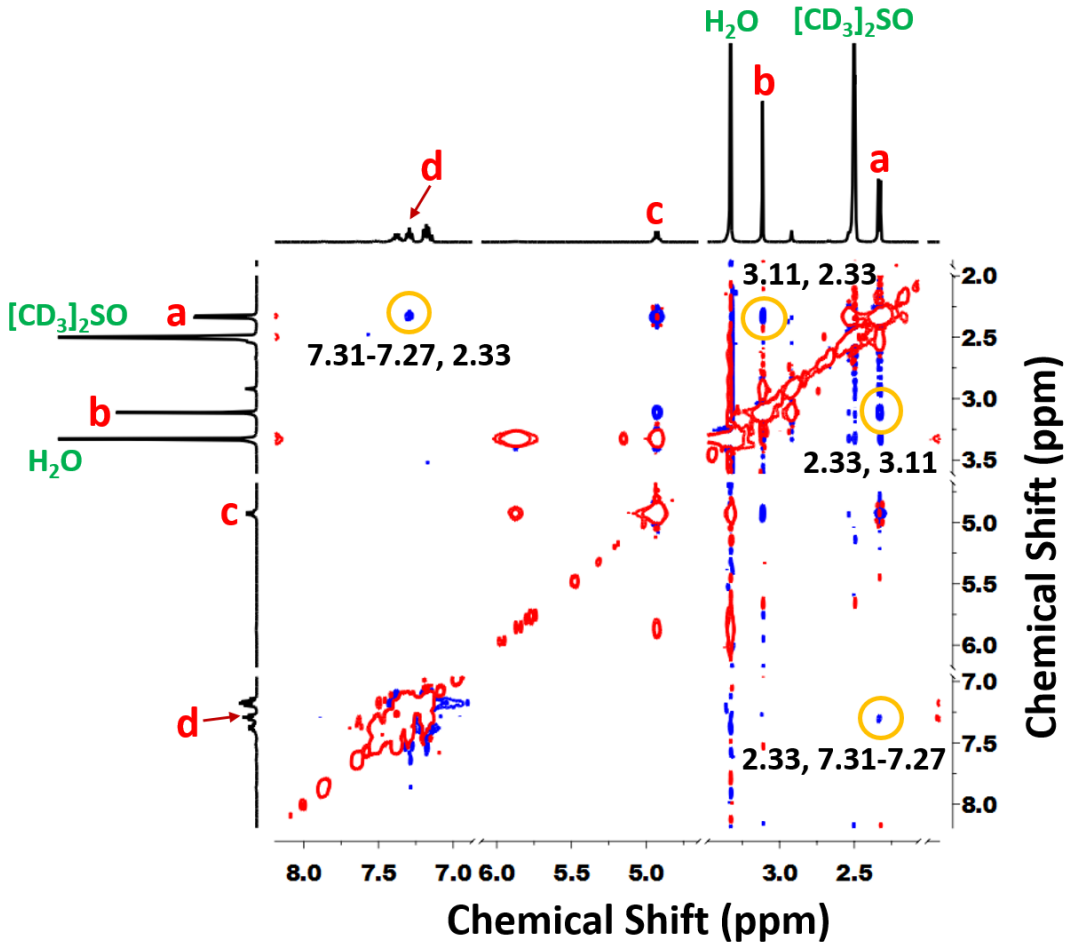
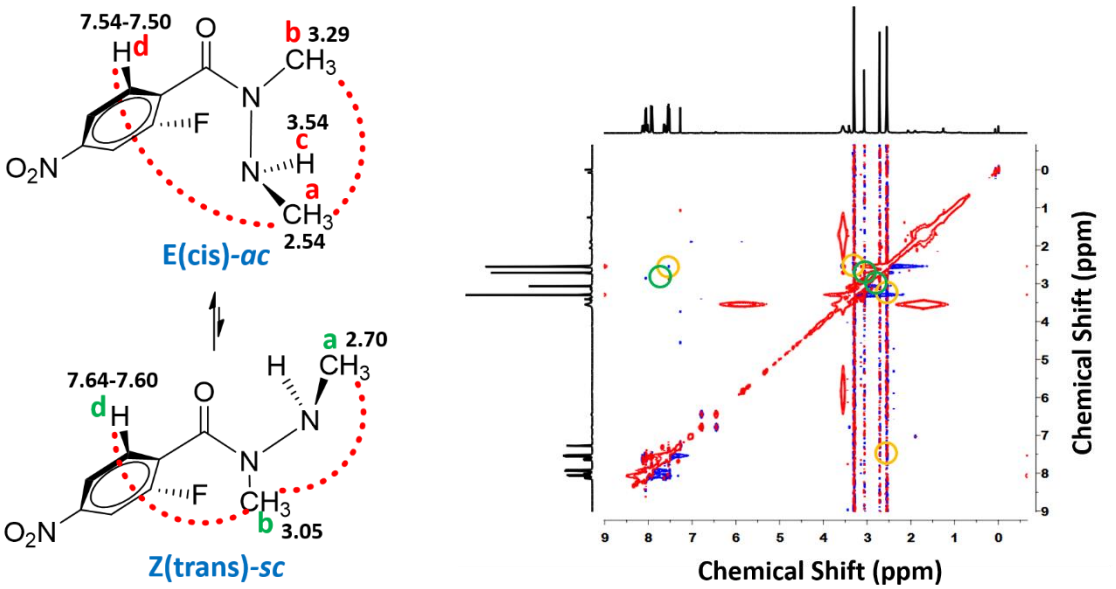


Figure S43 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **15** 2-fluoro-*N*, *N*'-dimethylbenzohydrazide in $[CD_3]_2SO$.



Compound **17**

Figure S44 (A). 2D NOESY full spectra for **17** 2-fluoro-*N*, *N*'-dimethyl-4-nitrobenzohydrazide in $CDCl_3$.

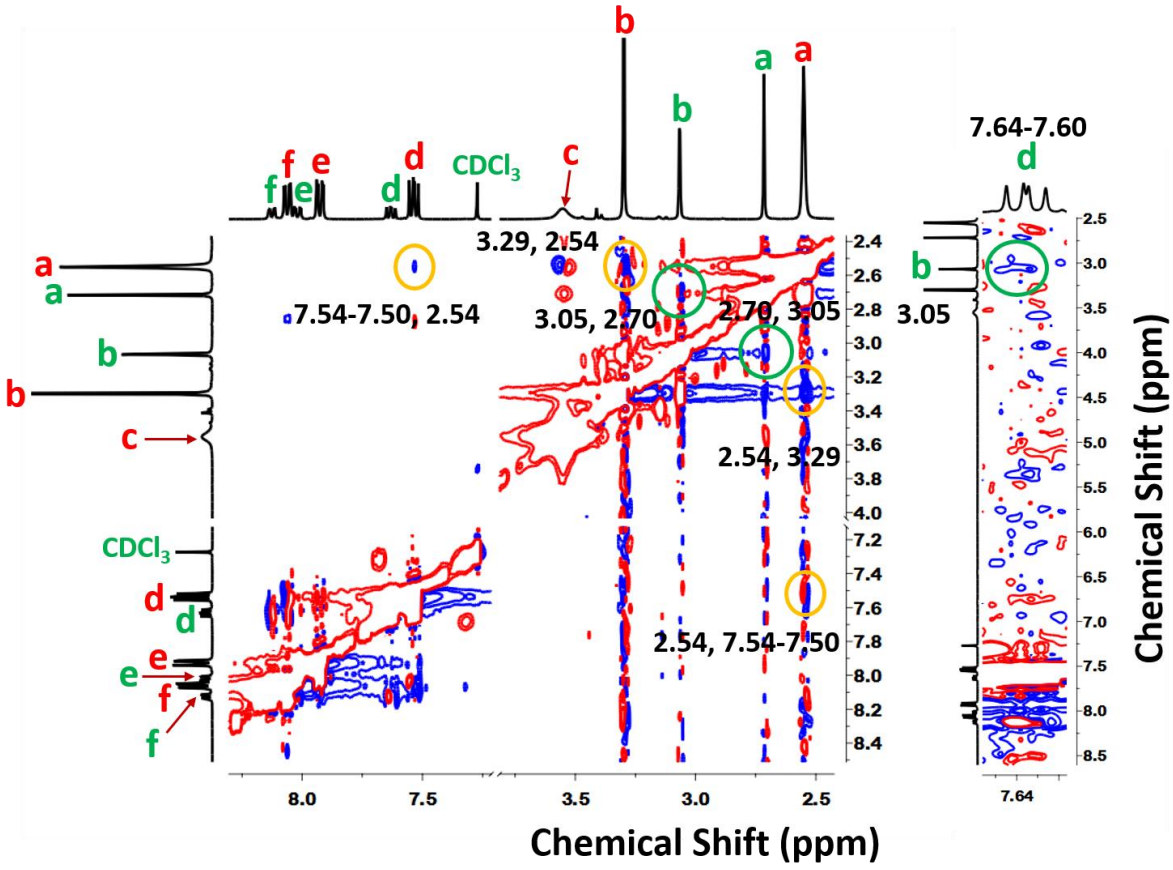
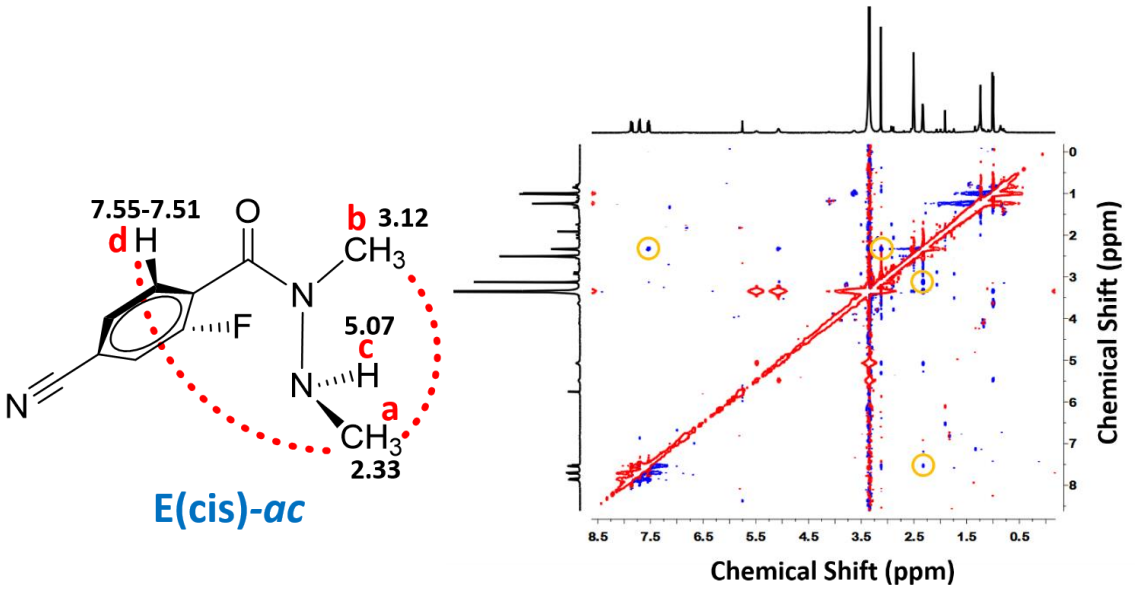


Figure S44 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **17** 2-fluoro-*N*, *N*'-dimethyl-4-nitrobenzohydrazide in $CDCl_3$.



Compound **18**

Figure S45 (A). 2D NOESY full spectra for **18** 4-cyano-2-fluoro-*N*, *N*′-dimethylbenzohydrazide in $[CD_3]_2SO$.

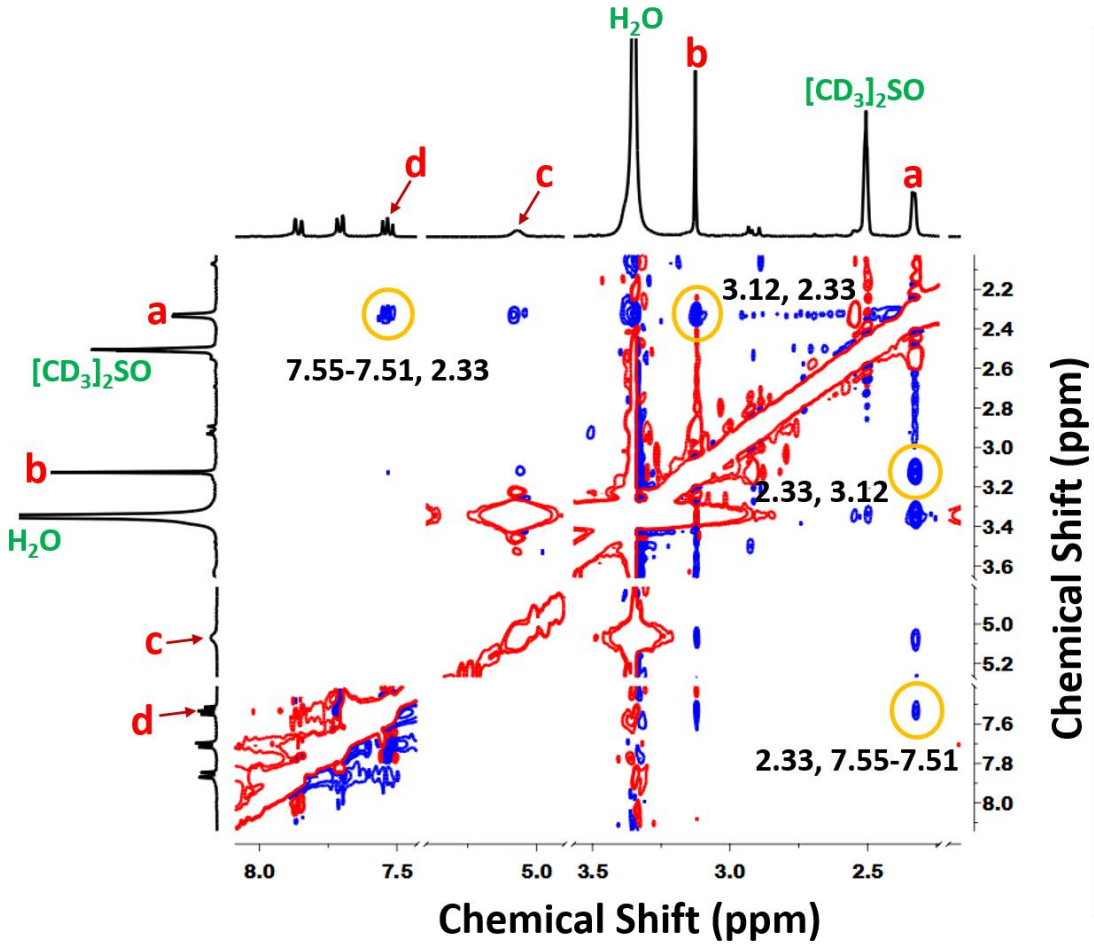
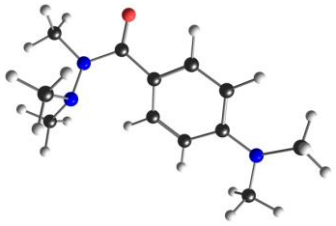


Figure S45 (B). 2D ^{1}H-^{1}H NOESY Correlation enlarged spectra for **18** 4-cyano-2-fluoro-*N*, *N*′-dimethylbenzohydrazide in $[CD_3]_2SO$.

I. Cartesian Coordinates



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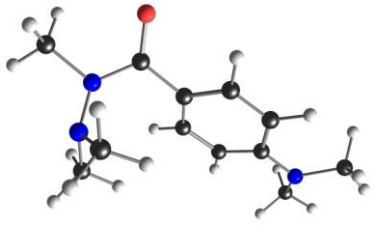

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6	2.339325000	-0.044272000	0.027193000
6	1.765855000	-1.179108000	-0.579442000
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6	-2.215374000	2.314240000	-0.165591000
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1	-4.764061000	0.501649000	0.783541000
1	-2.635740000	-0.373746000	-2.143622000
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1	-1.127230000	0.560062000	-1.967710000
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7	3.676937000	0.256810000	-0.140275000
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1	4.556699000	-1.677976000	-0.096710000
6	4.272415000	1.261778000	0.716890000
1	5.324041000	1.367260000	0.461167000
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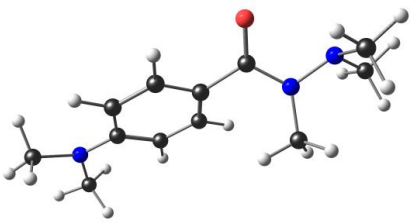
1	4.194710000	1.004856000	1.781193000



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Z-ac

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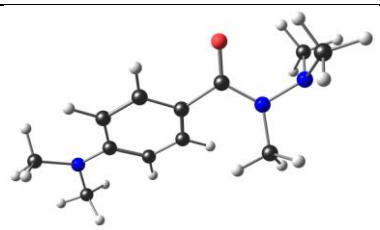

1
Z-sc

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6	2.158904000	1.277108000	-0.109130000	6	2.067499000	-1.276062000	0.176231000
6	2.720481000	0.005651000	0.116571000	6	2.691041000	-0.048277000	-0.116625000
6	1.838301000	-1.056892000	0.388345000	6	1.860180000	1.055234000	-0.386390000
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6	-1.534890000	0.707559000	0.329297000	6	-1.602182000	-0.512369000	-0.138733000
6	-2.143424000	-1.208164000	-1.158295000	6	-2.075145000	1.537831000	1.237795000
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1	-0.179272000	-1.685451000	0.659031000	1	-0.125385000	1.794105000	-0.595591000
1	-2.875313000	-1.049869000	-1.953655000	1	-2.771791000	1.479231000	2.076650000
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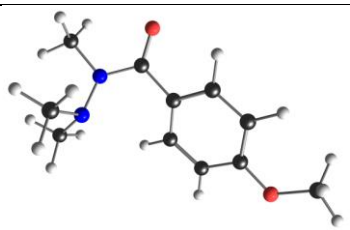
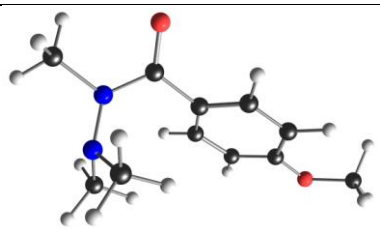


2
E-ac



2
E-sc

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7	-2.223324000	-0.972591000	0.314523000	7	2.418317000	1.039342000	0.483861000
6	0.463937000	-0.677231000	-0.781214000	6	-0.387811000	0.418277000	-1.113932000
6	1.774789000	-1.102561000	-0.752941000	6	-1.718687000	0.787194000	-1.119197000
6	2.756238000	-0.314417000	-0.147391000	6	-2.620153000	0.159251000	-0.259457000
6	2.413353000	0.915065000	0.405625000	6	-2.181042000	-0.859792000	0.583890000
6	1.091593000	1.340423000	0.346949000	6	-0.844478000	-1.234414000	0.560414000
6	0.103344000	0.551760000	-0.223408000	6	0.066248000	-0.587220000	-0.262040000
6	-1.271299000	1.134534000	-0.289391000	6	1.477705000	-1.072440000	-0.290069000
6	-3.671496000	0.924832000	-0.295751000	6	3.844742000	-0.641969000	-0.410238000
6	-2.644443000	-0.959572000	1.708303000	6	1.858855000	0.874883000	1.813240000
6	-2.867596000	-2.023852000	-0.452537000	6	2.021498000	2.263299000	-0.184068000
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1	2.072318000	-2.045494000	-1.193103000	1	-2.091245000	1.552242000	-1.788024000
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1	0.814537000	2.309122000	0.743751000	1	-0.497686000	-2.045274000	1.189662000
1	-3.866937000	1.455321000	0.640411000	1	4.180584000	-1.064535000	0.541696000
1	-3.710640000	1.646692000	-1.107095000	1	3.877172000	-1.421373000	-1.167095000

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1	-3.727257000	-0.811648000	1.828292000	1	2.220621000	1.691864000	2.440937000
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1	-2.114130000	-0.164523000	2.233277000	1	2.213867000	-0.065421000	2.237343000
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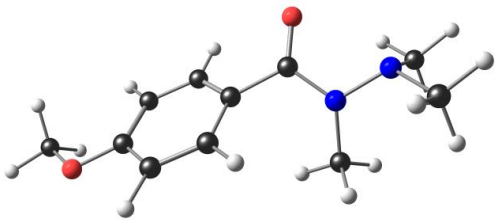

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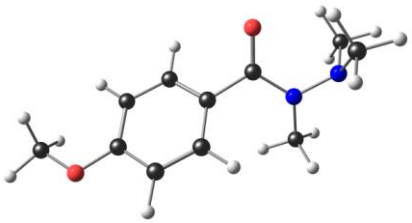

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7	3.417980000	-0.076000000	-0.277663000	7	-3.485815000	0.318578000	-0.040218000
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6	-2.091541000	1.313777000	-0.395852000	6	2.123676000	1.262688000	0.496839000
6	-3.014856000	0.319255000	-0.067263000	6	2.996027000	0.241699000	0.114614000
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6	-1.220176000	-1.265731000	0.108553000	6	1.113970000	-1.198644000	-0.270354000
6	-0.291978000	-0.279006000	-0.188574000	6	0.238141000	-0.181114000	0.076559000
6	1.144821000	-0.681250000	-0.320187000	6	-1.225134000	-0.499685000	0.123903000
6	1.885109000	1.224274000	1.120943000	6	-1.806191000	1.592451000	-1.141634000
6	4.195702000	1.103041000	-0.601684000	6	-3.827114000	0.159349000	1.367235000
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1	-0.866206000	-2.276387000	0.270336000	1	0.706666000	-2.166755000	-0.534595000
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1	0.893851000	1.108028000	1.548383000	1	-0.786138000	1.525399000	-1.508086000
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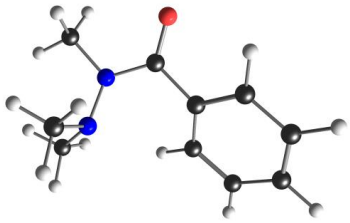

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6	1.205189000	-0.831139000	-0.732562000
6	2.474084000	-1.380240000	-0.629314000
6	3.470023000	-0.709251000	0.070888000
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6	0.930541000	0.404398000	-0.153114000
6	-0.382361000	1.111958000	-0.304964000
6	-2.788645000	1.113276000	-0.429320000
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6	-2.240330000	-1.895843000	-0.475240000
1	0.430532000	-1.355371000	-1.275326000
1	2.686682000	-2.334745000	-1.094289000
1	4.457295000	-1.145631000	0.160277000
1	3.976698000	1.054416000	1.184718000
1	1.717780000	2.063585000	0.933679000
1	-2.996161000	1.666676000	0.490761000
1	-2.712418000	1.828235000	-1.244026000
1	-3.602831000	0.419609000	-0.631854000
1	-3.096015000	-0.553296000	1.733990000
1	-1.864379000	-1.762896000	2.153455000
1	-1.452221000	-0.041602000	2.204585000
1	-1.853316000	-1.898946000	-1.493668000
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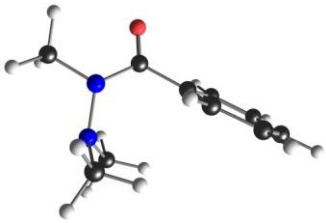

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6	2.912202000	-0.594135000	0.813257000
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6	2.474475000	0.931986000	-0.995415000
6	1.164077000	0.475353000	-1.062735000
6	0.726621000	-0.513464000	-0.190010000
6	-0.651984000	-1.089353000	-0.290853000
6	-3.037508000	-0.805328000	-0.486789000
6	-1.413314000	2.201400000	-0.292204000
6	-1.203564000	0.901921000	1.761826000
1	1.267715000	-1.866439000	1.375443000
1	3.595054000	-1.013650000	1.541393000
1	4.362692000	0.770536000	0.009430000
1	2.817717000	1.692199000	-1.685985000
1	0.484387000	0.867220000	-1.808924000
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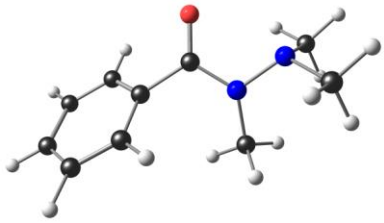

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6	-1.562480000	1.049390000	-0.425499000
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6	-3.385741000	-0.892765000	0.359448000
6	-2.042560000	-1.214647000	0.232863000
6	-1.123291000	-0.240522000	-0.141781000
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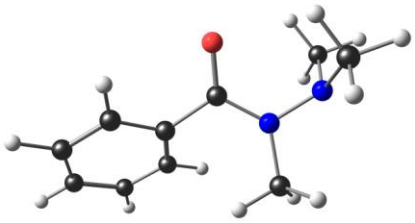

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6	-3.810837000	-0.156655000	-0.048867000
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6	0.963411000	-1.603242000	1.135458000
6	3.265114000	0.676310000	0.865872000
6	2.999264000	-0.221770000	-1.382557000

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1	-4.096194000	-1.651063000	0.663785000	1	-3.396959000	-2.107983000	-0.845060000
1	-1.687747000	-2.222250000	0.410299000	1	-0.948152000	-1.785210000	-0.842476000
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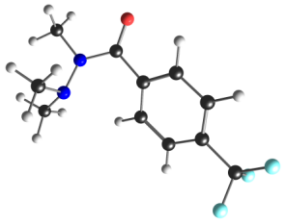

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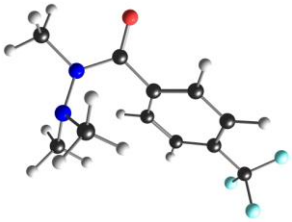

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6	-1.691140000	-1.248764000	0.590007000	6	-1.482873000	-1.069766000	0.787124000
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6	0.523880000	-0.696948000	-0.182811000	6	0.672972000	-0.696447000	-0.210244000
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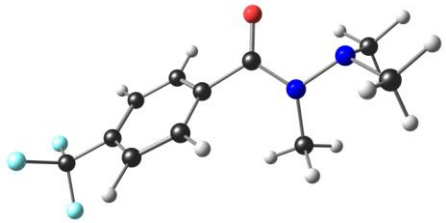

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Z-ac

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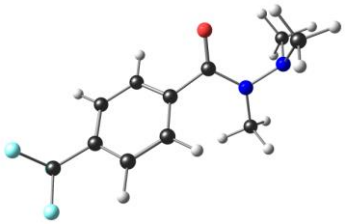
7	-2.676307000	-0.293616000	0.036443000
7	-4.026950000	-0.060009000	-0.286463000
6	0.214555000	-0.807180000	-0.500517000
6	1.584208000	-0.992290000	-0.433219000
6	2.399029000	0.058455000	-0.027701000
6	1.857867000	1.294729000	0.287894000
6	0.485703000	1.480640000	0.197799000
6	-0.340289000	0.429213000	-0.177007000
6	-1.810930000	0.713017000	-0.326639000
6	-2.395843000	-1.251725000	1.103026000
6	-4.714123000	-1.295687000	-0.606660000
6	-4.711560000	0.737091000	0.719743000
1	-0.427807000	-1.619028000	-0.819828000
1	2.024370000	-1.946822000	-0.694904000
1	2.504343000	2.106276000	0.593386000
1	0.040259000	2.445418000	0.404439000
1	-2.453995000	-2.278735000	0.736601000
1	-1.406365000	-1.081886000	1.516139000
1	-3.123043000	-1.127551000	1.908061000
1	-4.870430000	-1.951154000	0.263609000
1	-5.690530000	-1.041536000	-1.018866000
1	-4.147817000	-1.835932000	-1.365137000
1	-4.165539000	1.668742000	0.857879000
1	-5.706664000	0.973864000	0.343152000
1	-4.824511000	0.221101000	1.684604000
6	3.878209000	-0.181401000	0.047642000
9	4.389346000	-0.496825000	-1.150820000
9	4.545649000	0.885212000	0.495706000
9	4.168315000	-1.204349000	0.865710000



4
Z-sc

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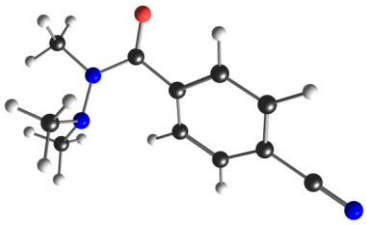
6	-0.207126000	0.900587000	-0.479540000
6	-1.589297000	1.030338000	-0.477095000
6	-2.370331000	-0.023237000	-0.030435000
6	-1.786680000	-1.212925000	0.390583000
6	-0.409922000	-1.344569000	0.365764000
6	0.385819000	-0.280581000	-0.050539000
6	1.871075000	-0.510802000	-0.129770000
6	2.341889000	1.606349000	1.136830000
6	4.415468000	0.299247000	-1.391134000
6	4.723037000	-0.589373000	0.857126000
1	0.409583000	1.719368000	-0.830360000
1	-2.055637000	1.944118000	-0.819933000
1	-2.412006000	-2.030470000	0.727936000
1	0.066894000	-2.272127000	0.655758000
1	2.446025000	2.566200000	0.627401000
1	1.325995000	1.492933000	1.503547000
1	3.024329000	1.594844000	1.988347000
1	3.905610000	1.088733000	-1.943030000
1	5.491027000	0.450025000	-1.490354000
1	4.145137000	-0.674250000	-1.810503000
1	4.457480000	-1.608386000	0.563401000
1	5.802195000	-0.454404000	0.776200000
1	4.438480000	-0.424558000	1.897324000
6	-3.867048000	0.080001000	-0.015003000
9	-4.428787000	-0.751052000	-0.904257000
9	-4.370638000	-0.246859000	1.183434000
9	-4.295180000	1.313290000	-0.302618000



5
E-ac

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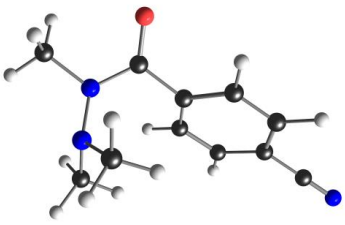
7	1.996592000	1.034664000	0.291037000
6	-0.680004000	0.544968000	-0.792128000
6	-2.015832000	0.896951000	-0.723595000
6	-2.907897000	0.088941000	-0.017841000
6	-2.466248000	-1.080884000	0.596006000
6	-1.131951000	-1.437440000	0.498512000
6	-0.231459000	-0.621076000	-0.177681000
6	1.178767000	-1.127648000	-0.291157000



5
E-sc

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7	2.207854000	1.129083000	0.406251000
6	-0.606964000	0.248384000	-1.096314000
6	-1.959830000	0.545777000	-1.046573000
6	-2.757709000	-0.049190000	-0.072308000
6	-2.210347000	-0.961637000	0.831654000
6	-0.863929000	-1.267920000	0.759078000
6	-0.053840000	-0.644989000	-0.186351000
6	1.385631000	-1.058385000	-0.281077000

6	3.558908000	-0.771794000	-0.347198000	6	3.721620000	-0.498989000	-0.466395000
6	2.447722000	1.066382000	1.676275000	6	1.702439000	1.008149000	1.761659000
6	2.556342000	2.116822000	-0.501499000	6	1.727095000	2.288385000	-0.319203000
1	0.013727000	1.172594000	-1.333622000	1	0.018731000	0.693991000	-1.858802000
1	-2.376836000	1.794363000	-1.208405000	1	-2.402120000	1.231757000	-1.757139000
1	-3.169114000	-1.704515000	1.132293000	1	-2.846341000	-1.427292000	1.572877000
1	-0.771773000	-2.360162000	0.934974000	1	-0.427201000	-1.995212000	1.432197000
1	3.810882000	-1.294549000	0.579249000	1	4.117101000	-0.875081000	0.481522000
1	3.621618000	-1.483869000	-1.165755000	1	3.774976000	-1.292582000	-1.206921000
1	4.266735000	0.037273000	-0.516685000	1	4.306571000	0.360179000	-0.786590000
1	3.538799000	0.978533000	1.773022000	1	2.120192000	0.111573000	2.221343000
1	2.135922000	2.013036000	2.117374000	1	2.041092000	1.874617000	2.332928000
1	1.971991000	0.253441000	2.225517000	1	0.606778000	0.966119000	1.818868000
1	2.215904000	2.021727000	-1.532080000	1	0.632587000	2.366683000	-0.341084000
1	2.194470000	3.061794000	-0.095021000	1	2.120961000	3.184073000	0.165537000
1	3.654885000	2.140883000	-0.492618000	1	2.107015000	2.253003000	-1.339534000
6	-4.293468000	0.464702000	0.067278000	6	-4.158464000	0.269978000	-0.005663000
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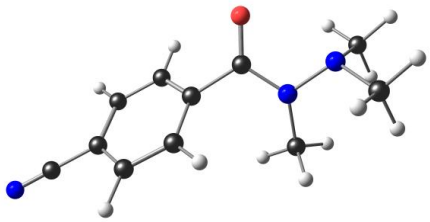
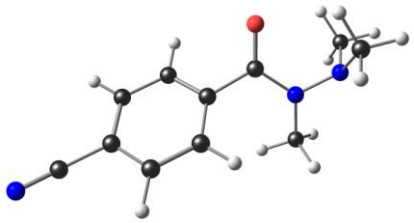


5
Z-ac



5
Z-sc

8	-1.350057000	1.757697000	-0.780704000	8	-1.509104000	1.561035000	-0.570360000
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7	-3.255160000	-0.018191000	-0.290465000	7	-3.310137000	-0.419146000	0.024425000
6	0.965142000	-0.887808000	-0.479579000	6	0.976364000	-0.917284000	-0.482409000
6	2.329310000	-1.113826000	-0.410432000	6	2.354218000	-1.053187000	-0.484714000
6	3.176530000	-0.082096000	-0.008665000	6	3.148844000	0.001498000	-0.038247000
6	2.661468000	1.176360000	0.301170000	6	2.566323000	1.195334000	0.386682000
6	1.298574000	1.396462000	0.208456000	6	1.189115000	1.327861000	0.364615000
6	0.444201000	0.363353000	-0.162838000	6	0.388998000	0.268030000	-0.049752000
6	-1.017601000	0.688808000	-0.319803000	6	-1.095837000	0.505280000	-0.127749000
6	-1.665704000	-1.259613000	1.105188000	6	-1.574434000	-1.610868000	1.136341000
6	-3.975004000	-1.234020000	-0.615459000	6	-3.643223000	-0.292649000	-1.389356000
6	-3.922137000	0.797387000	0.713022000	6	-3.947036000	0.596463000	0.859563000
1	0.301748000	-1.683208000	-0.797100000	1	0.354956000	-1.732381000	-0.833331000
1	2.745020000	-2.079354000	-0.666818000	1	2.819813000	-1.966255000	-0.831573000
1	3.332148000	1.970331000	0.601960000	1	3.196325000	2.009711000	0.719248000
1	0.877929000	2.373621000	0.408789000	1	0.716519000	2.257430000	0.655144000
1	-1.742747000	-2.283407000	0.733315000	1	-1.682790000	-2.569294000	0.625203000
1	-0.677573000	-1.113173000	1.530502000	1	-0.558039000	-1.502143000	1.503401000
1	-2.398913000	-1.123009000	1.902499000	1	-2.256330000	-1.597990000	1.988145000
1	-4.152910000	-1.886228000	0.253047000	1	-3.137690000	-1.084748000	-1.941479000
1	-4.942166000	-0.951669000	-1.030957000	1	-4.719511000	-0.437849000	-1.488308000
1	-3.421108000	-1.788372000	-1.372941000	1	-3.368140000	0.679562000	-1.808594000
1	-3.350722000	1.713171000	0.854842000	1	-3.678341000	1.614547000	0.565485000
1	-4.908105000	1.062714000	0.331660000	1	-5.026638000	0.465174000	0.779421000
1	-4.054527000	0.284210000	1.676829000	1	-3.662294000	0.430709000	1.899534000
6	4.592439000	-0.317856000	0.081113000	6	4.579775000	-0.141233000	-0.024712000
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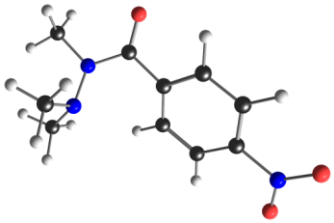

6
E-ac

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7	2.338742000	1.021710000	0.363378000
6	-0.313312000	0.541739000	-0.781433000
6	-1.656578000	0.864739000	-0.698221000
6	-2.506221000	-0.010530000	-0.042635000
6	-2.070204000	-1.201611000	0.507595000
6	-0.726974000	-1.522504000	0.393676000
6	0.156508000	-0.648538000	-0.231539000
6	1.578905000	-1.117258000	-0.365897000
6	3.951495000	-0.707448000	-0.363295000
6	2.775110000	0.984926000	1.753377000
6	2.881561000	2.160332000	-0.359470000
1	0.369640000	1.212761000	-1.282730000
1	-2.052030000	1.775911000	-1.123457000
1	-2.774982000	-1.856146000	0.999767000
1	-0.348775000	-2.460518000	0.778819000
1	4.208805000	-1.278735000	0.532489000
1	4.036429000	-1.367340000	-1.222555000
1	4.641107000	0.126665000	-0.477417000
1	3.866585000	0.910913000	1.856529000
1	2.442556000	1.900556000	2.242108000
1	2.308913000	0.134961000	2.252375000
1	2.560174000	2.113256000	-1.399453000
1	2.488351000	3.071832000	0.091583000
1	3.978758000	2.211858000	-0.330344000
7	-3.934845000	0.340216000	0.066666000
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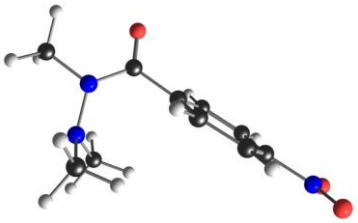

6
E-sc

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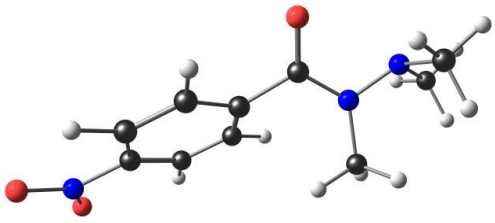
6	-0.483686000	1.394751000	0.583141000
6	-1.834507000	1.115819000	0.692941000
6	-2.361486000	0.104289000	-0.093326000
6	-1.596639000	-0.623775000	-0.985805000
6	-0.240072000	-0.346232000	-1.069074000
6	0.319454000	0.648029000	-0.275359000
6	1.766040000	1.029439000	-0.401845000
6	4.101812000	0.424612000	-0.433390000
6	2.104931000	-2.311358000	-0.097396000
6	1.949095000	-0.849574000	1.855272000
1	-0.037851000	2.195334000	1.159832000
1	-2.480299000	1.666680000	1.361648000
1	-2.063230000	-1.383579000	-1.596404000
1	0.381885000	-0.889297000	-1.768367000
1	4.671897000	-0.466634000	-0.686771000
1	4.184521000	1.165327000	-1.223820000
1	4.491615000	0.850864000	0.495187000
1	2.543131000	-2.363707000	-1.093495000
1	2.476978000	-3.154622000	0.488229000
1	1.014251000	-2.407211000	-0.174776000
1	0.851289000	-0.829527000	1.850983000
1	2.273241000	-1.651259000	2.521769000
1	2.323147000	0.095499000	2.250635000
7	-3.801291000	-0.199824000	0.015404000
8	-4.243462000	-1.076963000	-0.695586000
8	-4.450550000	0.445128000	0.810460000



6
Z-ac

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7	3.653432000	-0.045690000	-0.280802000
6	-0.883629000	1.442280000	0.130637000
6	-2.250824000	1.244933000	0.229340000
6	-2.751107000	-0.020019000	-0.026301000
6	-1.942436000	-1.087245000	-0.375530000
6	-0.574983000	-0.878010000	-0.449842000
6	-0.041968000	0.381768000	-0.189884000
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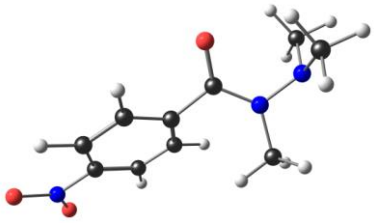

6
Z-sc

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6	2.164350000	-1.251931000	0.275893000
6	2.724247000	-0.025358000	-0.036308000
6	1.963018000	1.077901000	-0.379881000
6	0.583743000	0.947031000	-0.389020000
6	-0.007934000	-0.272147000	-0.070494000
6	-1.494344000	-0.494771000	-0.172957000
6	-1.968385000	1.493645000	1.285642000

6	4.328343000	0.817596000	0.676331000	6	-4.346330000	-0.675988000	0.793816000
6	4.359109000	-1.286712000	-0.535081000	6	-4.036456000	0.429169000	-1.355439000
1	-0.452078000	2.422573000	0.286534000	1	0.307156000	-2.322128000	0.442246000
1	-2.927250000	2.046709000	0.488369000	1	2.804630000	-2.085268000	0.527258000
1	-2.386765000	-2.050329000	-0.582157000	1	2.451489000	2.007730000	-0.633509000
1	0.080604000	-1.694437000	-0.726949000	1	-0.034098000	1.794443000	-0.660096000
1	2.775759000	-1.019393000	1.967185000	1	-2.653140000	1.403060000	2.130339000
1	1.056182000	-1.009295000	1.587932000	1	-0.953101000	1.348947000	1.643505000
1	2.110025000	-2.232760000	0.858799000	1	-2.073423000	2.495393000	0.865015000
1	4.448651000	0.359666000	1.669086000	1	-4.045477000	-0.627876000	1.841234000
1	5.319887000	1.044525000	0.284764000	1	-5.424962000	-0.523981000	0.743430000
1	3.770373000	1.748670000	0.760717000	1	-4.094972000	-1.659435000	0.387300000
1	3.794660000	-1.880090000	-1.254214000	1	-3.757652000	-0.496769000	-1.867058000
1	5.326739000	-1.040862000	-0.972071000	1	-5.113051000	0.580092000	-1.441236000
1	4.535136000	-1.886868000	0.370494000	1	-3.533097000	1.272851000	-1.827274000
7	-4.206959000	-0.240776000	0.071586000	7	4.193353000	0.110757000	-0.011713000
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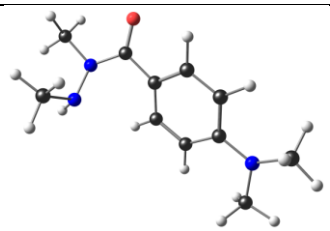

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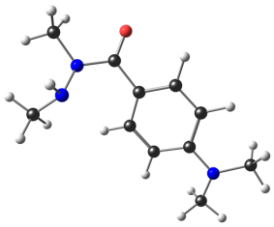

7
E-ac-fH

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7	-2.601570000	-1.416599000	0.181430000	7	2.673152000	1.071550000	0.756897000
6	0.061237000	-0.653555000	-0.792148000	6	0.006640000	0.704805000	-0.405348000
6	1.427001000	-0.859126000	-0.746944000	6	-1.344519000	0.988290000	-0.346496000
6	2.280141000	0.070670000	-0.122904000	6	-2.272394000	0.010516000	0.058898000
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6	0.325751000	1.415040000	0.369721000	6	-0.425592000	-1.544969000	0.259941000
6	-0.515527000	0.483920000	-0.232915000	6	0.493135000	-0.561742000	-0.095459000
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1	3.761134000	-2.229035000	0.184963000	1	-3.652047000	2.400116000	0.083946000
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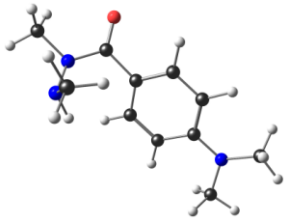

7
E-sc-bH

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6	-0.591611000	0.473886000	-0.308572000
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1	2.167693000	1.924910000	1.004383000
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1	-4.814333000	-1.023387000	-0.734034000
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1	-2.231346000	-2.026814000	2.426730000
1	-1.615617000	-0.400215000	2.042674000
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6	4.133126000	-1.342268000	-0.523958000
1	3.955421000	-1.504985000	-1.588928000
1	5.209034000	-1.323310000	-0.369368000
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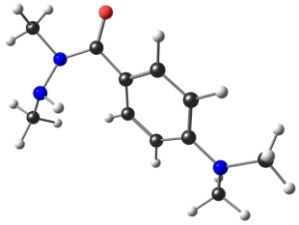

7
E-sc-fH

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6	-2.236824000	-0.004427000	0.048579000
6	-1.708783000	-1.252465000	0.430494000
6	-0.357706000	-1.514355000	0.318410000
6	0.531019000	-0.552495000	-0.155487000
6	1.965102000	-0.943412000	-0.302211000
6	4.310649000	-0.468782000	-0.076767000
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1	4.972579000	0.395114000	-0.071367000
1	2.321585000	2.559175000	-0.569548000
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1	3.972335000	2.491779000	0.064815000
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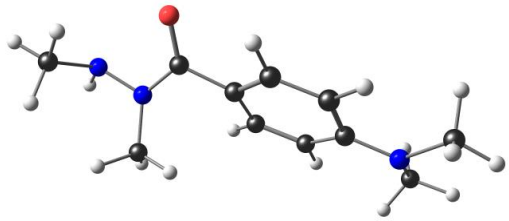

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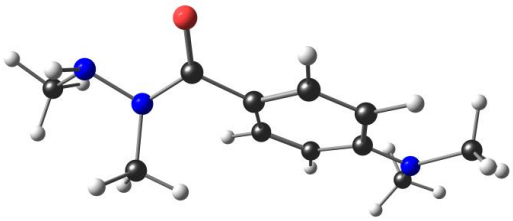

7
Z-ac-fH

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6	1.462400000	-1.071037000	-0.269277000
6	2.393704000	-0.058361000	0.029829000

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6	-0.409985000	0.277235000	-0.179831000	6	-0.377714000	0.485366000	-0.069685000
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6	-4.839260000	0.402337000	0.490815000	6	-4.858298000	-1.049942000	-0.470983000
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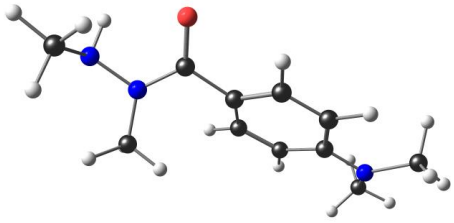

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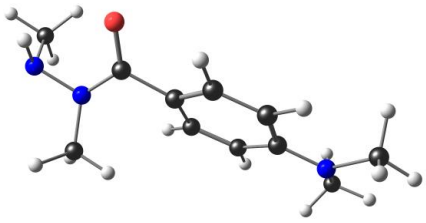
Z-sc-bH



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Z-sc-fH

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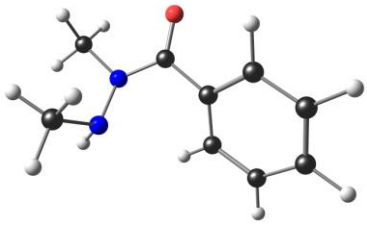

9
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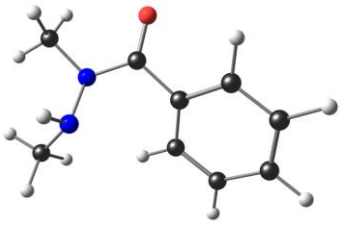

9
E-ac-fH

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6	-3.085821000	-0.606816000	0.469218000	6	3.034625000	-0.892003000	-0.120514000
6	-2.123447000	1.569126000	-1.307012000	6	2.347099000	2.095204000	0.121453000
1	0.462556000	1.239791000	1.556879000	1	-0.207989000	1.544865000	-0.920684000
1	2.826145000	1.935121000	1.433478000	1	-2.512416000	2.414594000	-0.839568000
1	4.383485000	0.768936000	-0.093706000	1	-4.335257000	1.014049000	0.073445000
1	3.580217000	-1.136405000	-1.454751000	1	-3.849454000	-1.281281000	0.861993000
1	1.214466000	-1.874224000	-1.264403000	1	-1.532468000	-2.169365000	0.714481000
1	-3.418281000	-0.944371000	-0.516214000	1	3.235062000	-1.424088000	0.815718000
1	-3.078319000	-1.466073000	1.134582000	1	3.023441000	-1.616335000	-0.929955000
1	-3.775112000	0.147225000	0.850061000	1	3.819764000	-0.160011000	-0.299315000
1	-3.184585000	1.326799000	-1.432116000	1	1.865424000	2.344145000	-0.824350000
1	-1.974014000	2.625746000	-1.527538000	1	2.235143000	2.940948000	0.799802000
1	-1.539814000	0.984629000	-2.019564000	1	3.414963000	1.938906000	-0.066739000
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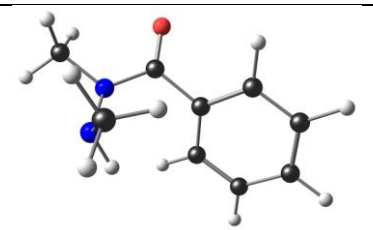

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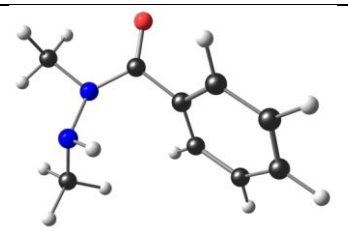
E-sc-bH



9
E-sc-fH

8	-1.096831000	-2.055354000	0.042779000	8	0.940299000	-2.126171000	-0.617909000
7	-1.799471000	0.067716000	0.417506000	7	1.793174000	-0.114180000	-0.032346000
7	-1.656591000	1.415695000	0.027330000	7	1.648563000	0.964459000	0.875371000
6	1.106817000	0.451991000	1.102666000	6	-1.062866000	0.695362000	-0.858549000
6	2.446789000	0.813487000	1.073399000	6	-2.377562000	1.128157000	-0.752860000
6	3.273808000	0.330210000	0.067737000	6	-3.268844000	0.450431000	0.068763000
6	2.765692000	-0.533797000	-0.894780000	6	-2.849950000	-0.675040000	0.767412000

6	1.431221000	-0.909963000	-0.855292000	6	-1.541312000	-1.120294000	0.648125000
6	0.592696000	-0.401921000	0.131108000	6	-0.638487000	-0.425014000	-0.150555000
6	-0.830910000	-0.876895000	0.167415000	6	0.753783000	-0.970687000	-0.289569000
6	-3.180125000	-0.378894000	0.498843000	6	3.134673000	-0.675806000	-0.041804000
6	-1.483978000	1.578632000	-1.413823000	6	1.809262000	2.263102000	0.232212000
1	0.465110000	0.804141000	1.903426000	1	-0.371812000	1.205014000	-1.518102000
1	2.846556000	1.466680000	1.838743000	1	-2.707510000	1.990434000	-1.318725000
1	4.317521000	0.617675000	0.041162000	1	-3.546567000	-1.212839000	1.398033000
1	3.413703000	-0.921981000	-1.670351000	1	-1.209344000	-2.013489000	1.163221000
1	1.025331000	-1.606275000	-1.579119000	1	3.321931000	-1.254223000	0.866232000
1	-3.619068000	-0.522083000	-0.493360000	1	3.239043000	-1.323219000	-0.907695000
1	-3.212669000	-1.328926000	1.025478000	1	3.850095000	0.142434000	-0.100868000
1	-3.742896000	0.378456000	1.039016000	1	1.082297000	2.458166000	-0.561127000
1	-2.368548000	1.190659000	-1.919628000	1	1.716756000	3.030804000	1.000407000
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1	-0.596062000	1.071924000	-1.808545000	1	0.738510000	0.893479000	1.316553000
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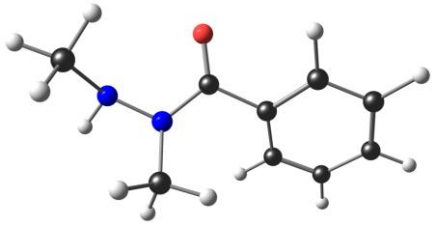

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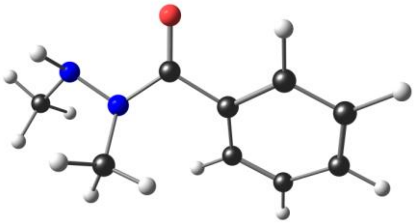
Z-ac-bH



9
Z-ac-fH

8	1.003514000	-1.619191000	-0.729096000	8	-0.757649000	1.972411000	-0.425460000
7	1.544738000	0.507136000	-0.146348000	7	-1.571371000	-0.082166000	0.149426000
7	2.871948000	0.238150000	-0.525487000	7	-2.863020000	0.403468000	-0.104358000
6	-1.382474000	0.976789000	-0.556732000	6	1.159822000	-1.013264000	-0.487990000
6	-2.749102000	1.172773000	-0.416007000	6	2.480346000	-1.439619000	-0.501388000
6	-3.537473000	0.181700000	0.154578000	6	3.491728000	-0.580015000	-0.091276000
6	-2.960751000	-1.013972000	0.565265000	6	3.183061000	0.712095000	0.315743000
6	-1.598280000	-1.217944000	0.406059000	6	1.865271000	1.144279000	0.312447000
6	-0.800942000	-0.216449000	-0.138054000	6	0.847282000	0.278407000	-0.073427000
6	0.654091000	-0.520509000	-0.355125000	6	-0.552711000	0.821772000	-0.120260000
6	1.348981000	1.591809000	0.804862000	6	-1.452866000	-1.068179000	1.220030000
6	3.629686000	-0.484349000	0.491434000	6	-3.776722000	-0.647615000	-0.517896000
1	-0.766562000	1.744473000	-1.010965000	1	0.368388000	-1.677153000	-0.815947000
1	-3.199481000	2.096395000	-0.757352000	1	2.721245000	-2.440731000	-0.836057000
1	-4.602885000	0.337714000	0.270031000	1	4.521451000	-0.915413000	-0.096341000
1	-3.576226000	-1.791463000	0.999938000	1	3.971767000	1.385465000	0.626756000
1	-1.134919000	-2.155449000	0.687334000	1	1.605360000	2.156682000	0.595392000
1	1.478007000	2.559633000	0.312472000	1	-1.802413000	-2.047873000	0.890611000
1	0.354630000	1.550540000	1.239265000	1	-0.419967000	-1.159061000	1.542081000
1	2.079096000	1.510475000	1.613659000	1	-2.056834000	-0.750788000	2.077194000
1	3.196289000	-1.478328000	0.589930000	1	-3.945934000	-1.431903000	0.230738000
1	4.654380000	-0.587511000	0.135505000	1	-4.734341000	-0.183126000	-0.751423000
1	3.646924000	0.005107000	1.472908000	1	-3.387754000	-1.107210000	-1.426786000
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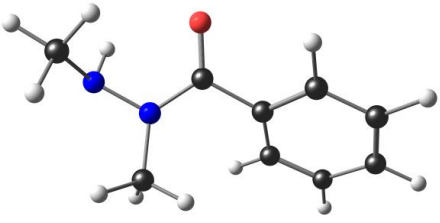

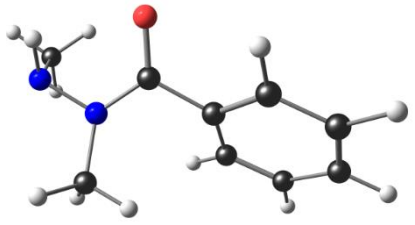

9 Z-sc-bH				9 Z-sc-fH			
8	1.034896000	-1.534372000	-0.851338000	8	-1.010092000	-1.767513000	0.239040000
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7	2.911461000	0.303774000	-0.414156000	7	-2.942147000	-0.052003000	-0.331068000
6	-1.407638000	0.967402000	-0.559905000	6	1.202725000	0.961417000	0.565937000
6	-2.776714000	1.129558000	-0.399850000	6	2.557515000	1.241662000	0.673037000
6	-3.531268000	0.124208000	0.190311000	6	3.494487000	0.325466000	0.212426000
6	-2.918622000	-1.053892000	0.599604000	6	3.076215000	-0.880464000	-0.336775000
6	-1.554205000	-1.225465000	0.420703000	6	1.723033000	-1.170086000	-0.425606000
6	-0.790327000	-0.207057000	-0.140292000	6	0.781752000	-0.242052000	0.007644000
6	0.667833000	-0.474219000	-0.368929000	6	-0.664039000	-0.633364000	-0.045354000
6	1.325783000	1.731243000	0.674397000	6	-1.337220000	1.497284000	-1.200984000
6	3.586964000	-0.527735000	0.588401000	6	-3.452834000	0.054945000	1.037447000
1	-0.821652000	1.748986000	-1.029295000	1	0.469242000	1.670110000	0.933210000
1	-3.254716000	2.039548000	-0.740019000	1	2.882741000	2.172874000	1.119527000
1	-4.598124000	0.255128000	0.322110000	1	4.551492000	0.547539000	0.290014000
1	-3.507102000	-1.843721000	1.049168000	1	3.806068000	-1.599136000	-0.687726000
1	-1.066088000	-2.150592000	0.700951000	1	1.376850000	-2.118031000	-0.818296000
1	1.369294000	2.603256000	0.018237000	1	-1.712326000	2.394522000	-0.704648000
1	0.361269000	1.690082000	1.171743000	1	-0.274422000	1.611647000	-1.392023000
1	2.103327000	1.834335000	1.432697000	1	-1.863996000	1.379320000	-2.148705000
1	3.084009000	-1.485016000	0.745635000	1	-3.446396000	1.103523000	1.335811000
1	4.606977000	-0.702130000	0.246699000	1	-4.484637000	-0.296345000	1.041171000
1	3.637221000	0.019698000	1.530438000	1	-2.867733000	-0.532422000	1.751223000
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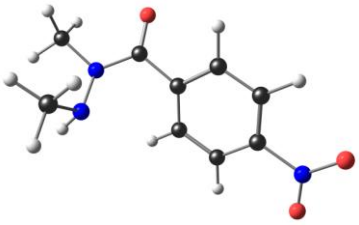

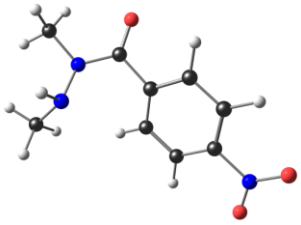

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7	2.790281000	0.141015000	-0.387145000	7	2.800332000	-0.030593000	-0.030783000
7	2.468820000	1.405954000	0.127123000	7	2.488591000	1.079742000	0.768390000
6	-0.163988000	0.590244000	-0.893254000	6	-0.089465000	0.673298000	-0.567212000
6	-1.527153000	0.820186000	-0.822666000	6	-1.443801000	0.955425000	-0.524878000
6	-2.299465000	-0.024787000	-0.043572000	6	-2.302736000	-0.009289000	-0.026158000
6	-1.767501000	-1.101022000	0.642564000	6	-1.863329000	-1.247790000	0.404605000
6	-0.405359000	-1.333234000	0.541188000	6	-0.507481000	-1.523327000	0.332722000
6	0.401399000	-0.481815000	-0.207503000	6	0.383747000	-0.561917000	-0.133278000
6	1.853127000	-0.857406000	-0.315216000	6	1.824449000	-0.977784000	-0.239853000
6	4.189186000	-0.265830000	-0.437945000	6	4.184886000	-0.478167000	-0.069402000
6	2.915686000	1.594860000	1.505186000	6	3.006724000	2.333567000	0.236997000
1	0.460893000	1.239914000	-1.488744000	1	0.598695000	1.412109000	-0.951946000
1	-1.996353000	1.636887000	-1.352012000	1	-1.840043000	1.900930000	-0.865993000
1	-2.414153000	-1.737377000	1.229408000	1	-2.574697000	-1.971131000	0.776386000
1	0.048252000	-2.184348000	1.032113000	1	-0.124481000	-2.490646000	0.630119000
1	4.537246000	-0.663336000	0.519048000	1	4.476937000	-0.932123000	0.883486000
1	4.302797000	-1.042331000	-1.189749000	1	4.296309000	-1.220209000	-0.854310000
1	4.786996000	0.603094000	-0.713129000	1	4.830026000	0.372388000	-0.280031000
1	3.994473000	1.466555000	1.643807000	1	4.096656000	2.367818000	0.137555000
1	2.636781000	2.601481000	1.814774000	1	2.566136000	2.510943000	-0.744362000
1	2.388798000	0.882116000	2.140969000	1	2.694189000	3.134617000	0.906376000
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8	-4.195106000	1.173444000	-0.566474000	8	-4.105732000	1.387459000	-0.342442000
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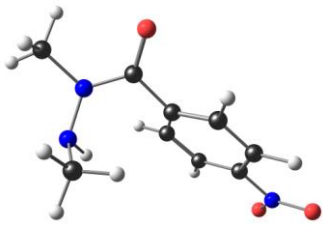

12
E-sc-bH

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6	1.490217000	0.692241000	0.974685000
6	2.228326000	-0.058842000	0.077434000
6	1.661653000	-1.030983000	-0.728560000
6	0.297134000	-1.248383000	-0.635019000
6	-0.476919000	-0.483636000	0.232339000
6	-1.944365000	-0.800422000	0.335462000
6	-4.233146000	-0.023491000	0.490214000
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1	1.986016000	1.420796000	1.600025000
1	2.287251000	-1.600991000	-1.400488000
1	-0.181153000	-2.019013000	-1.226225000
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1	-4.363605000	-0.835639000	1.200388000
1	-4.718461000	0.880740000	0.848407000
1	-3.206714000	0.957654000	-2.175630000
1	-2.132437000	2.356631000	-2.121161000
1	-1.455047000	0.717173000	-1.976004000
7	3.682033000	0.179188000	-0.013842000
8	4.307828000	-0.484011000	-0.812295000
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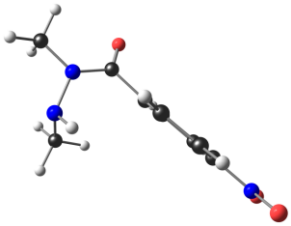

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E-sc-fH

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6	-0.297182000	-1.248574000	-0.634869000
6	-1.661694000	-1.031174000	-0.728376000
6	-2.228298000	-0.058873000	0.077474000
6	-1.490168000	0.692277000	0.974637000
6	-0.123017000	0.475015000	1.043754000
6	0.476918000	-0.483742000	0.232403000
6	1.944355000	-0.800495000	0.335410000
6	4.233119000	-0.023462000	0.490195000
6	2.303813000	1.359937000	-1.715525000
1	0.181112000	-2.019272000	-1.225972000
1	-2.287323000	-1.601290000	-1.400181000
1	-1.985930000	1.420932000	1.599880000
1	0.475256000	1.031146000	1.756406000
1	4.718369000	0.880862000	0.848298000
1	4.363590000	-0.835417000	1.200517000
1	4.676828000	-0.324868000	-0.463259000
1	1.455193000	0.717131000	-1.976064000
1	2.132114000	2.356824000	-2.120974000
1	3.206778000	0.958158000	-2.175652000
1	1.740145000	1.927655000	0.179998000
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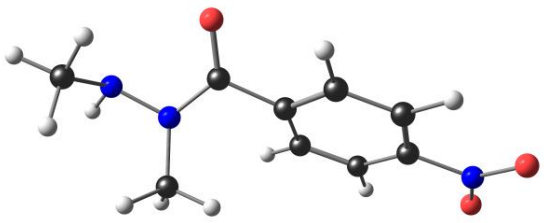

12
Z-ac-bH

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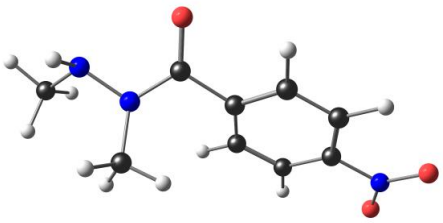
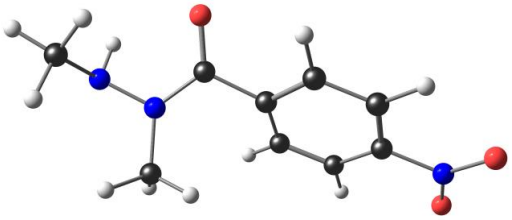
6	-0.328855000	-0.916296000	0.587032000
6	-1.704791000	-1.046241000	0.489484000
6	-2.432161000	0.028685000	0.010494000
6	-1.843920000	1.228539000	-0.350210000
6	-0.469675000	1.348628000	-0.228869000
6	0.292433000	0.274302000	0.219383000
6	1.770679000	0.497356000	0.402034000



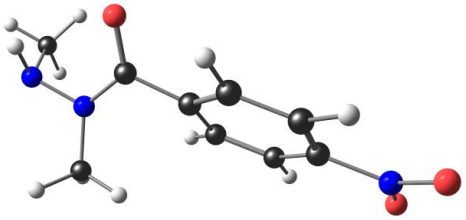
12
Z-ac-fH

8	-2.042096000	1.924396000	-0.608677000
7	-2.626849000	-0.136356000	0.185939000
7	-3.966402000	0.160659000	-0.104195000
6	0.202100000	-0.793776000	-0.427245000
6	1.560814000	-1.064553000	-0.416360000
6	2.428475000	-0.051321000	-0.048766000
6	1.994729000	1.220032000	0.285415000
6	0.634954000	1.480210000	0.249839000
6	-0.264097000	0.473531000	-0.087635000
6	-1.722158000	0.841988000	-0.181023000

6	2.317699000	-1.564646000	-0.917343000	6	-2.386214000	-1.046324000	1.302138000
6	4.700158000	0.406031000	-0.571116000	6	-4.728342000	-1.022098000	-0.470880000
1	0.263620000	-1.739631000	0.967024000	1	-0.500053000	-1.566222000	-0.716369000
1	-2.216289000	-1.953530000	0.777107000	1	1.952832000	-2.034105000	-0.687799000
1	-2.460389000	2.041445000	-0.706178000	1	2.715252000	1.978812000	0.555270000
1	0.028812000	2.279365000	-0.466518000	1	0.253097000	2.468531000	0.470856000
1	2.411489000	-2.562211000	-0.480047000	1	-2.602811000	-2.078292000	1.021623000
1	1.314930000	-1.449814000	-1.318067000	1	-1.353270000	-0.985128000	1.631304000
1	3.026357000	-1.475987000	-1.743626000	1	-3.031950000	-0.768728000	2.141506000
1	4.629774000	0.004300000	-1.589061000	1	-4.266578000	-1.474425000	-1.348669000
1	4.327924000	1.429071000	-0.558454000	1	-4.807681000	-1.779216000	0.318842000
1	5.747353000	0.415082000	-0.270682000	1	-5.733014000	-0.699236000	-0.741287000
7	-3.896483000	-0.108219000	-0.112419000	7	3.876129000	-0.337147000	-0.019820000
8	-4.513828000	0.845047000	-0.536046000	8	4.617020000	0.561895000	0.314811000
8	-4.388936000	-1.166590000	0.216117000	8	4.232497000	-1.453754000	-0.331055000
1	4.354316000	-1.279082000	0.567926000	1	-4.386902000	0.641490000	0.687722000



12
Z-sc-bH

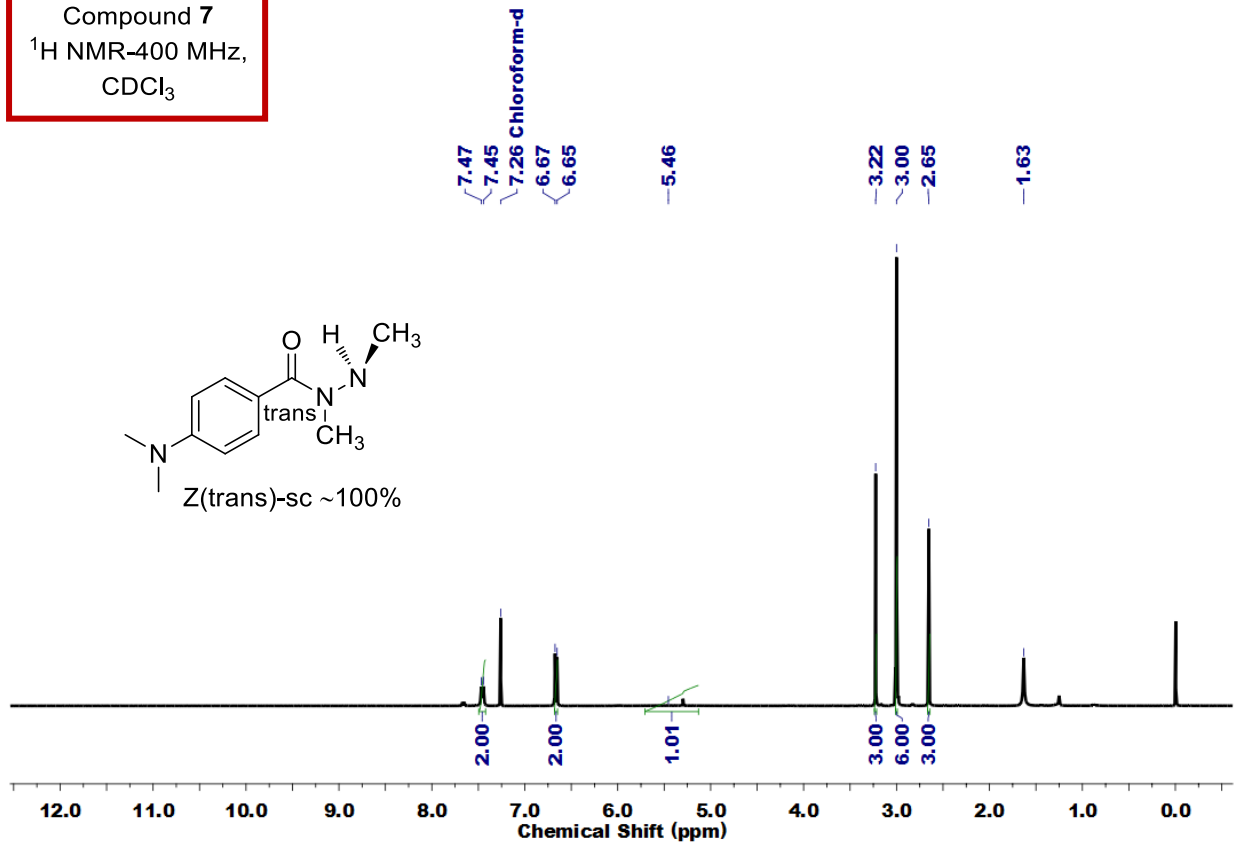


12
Z-sc-fH

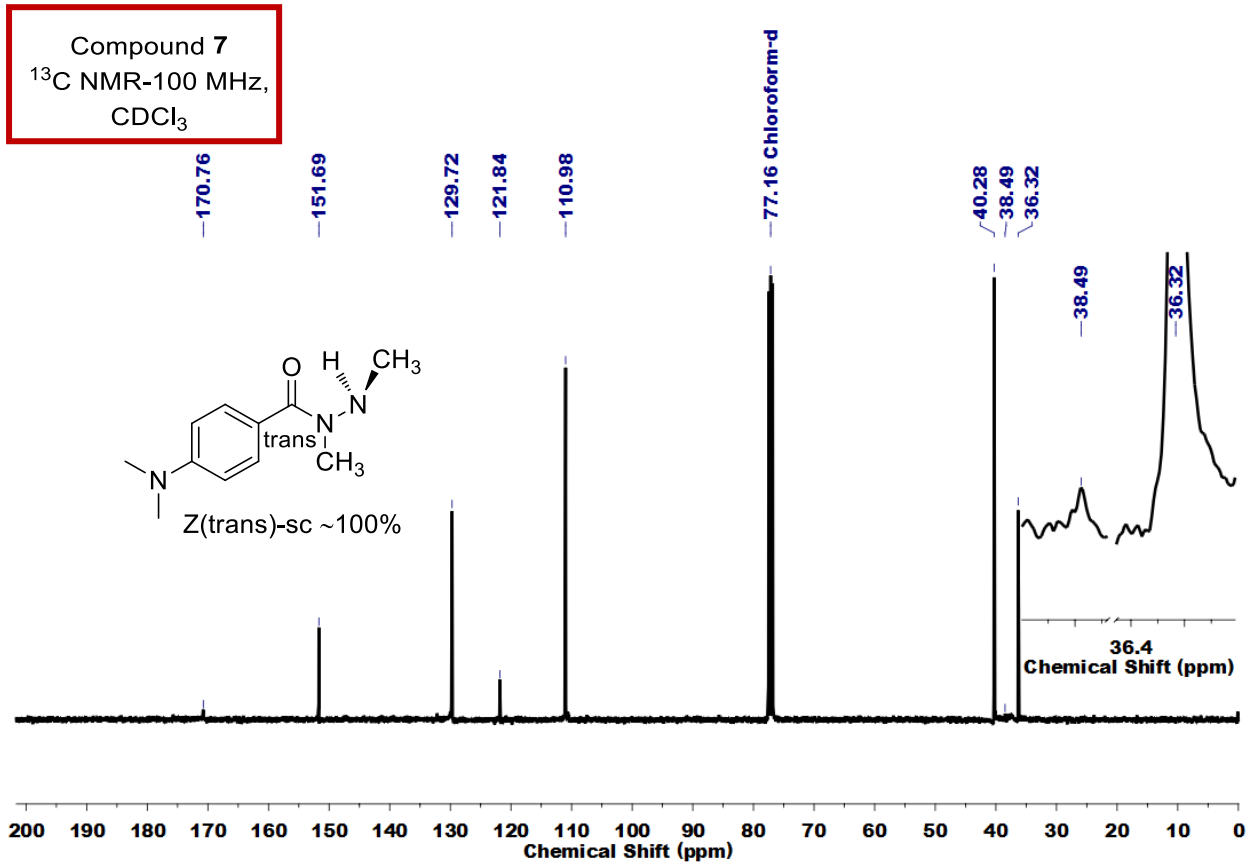
8	2.184092000	-1.458494000	-0.961283000	8	-2.184980000	1.697395000	-0.498115000
7	2.620845000	0.531522000	0.001661000	7	-2.639039000	-0.315688000	0.414291000
7	3.989232000	0.394029000	-0.306087000	7	-4.019012000	-0.053135000	0.286010000
6	-0.341510000	0.933854000	-0.594620000	6	0.219606000	-0.864436000	-0.399106000
6	-1.718837000	1.044089000	-0.489861000	6	1.591365000	-1.055118000	-0.438354000
6	-2.428172000	-0.038661000	-0.002648000	6	2.410468000	-0.006454000	-0.059378000
6	-1.820738000	-1.228613000	0.359189000	6	1.915414000	1.224811000	0.333942000
6	-0.445892000	-1.330211000	0.230587000	6	0.542567000	1.406316000	0.348799000
6	0.298364000	-0.245975000	-0.225010000	6	-0.306909000	0.360207000	0.002216000
6	1.776101000	-0.448968000	-0.410834000	6	-1.781914000	0.643980000	-0.036901000
6	2.314147000	1.695450000	0.809614000	6	-2.335261000	-1.366147000	1.372688000
6	4.659352000	-0.476132000	0.667114000	6	-4.481238000	-0.393272000	-1.062033000
1	0.233701000	1.765829000	-0.981676000	1	-0.444311000	-1.666583000	-0.697594000
1	-2.244283000	1.943231000	-0.777930000	1	2.029491000	-1.989916000	-0.757433000
1	-2.423655000	-2.049207000	0.720760000	1	2.599245000	2.014622000	0.609830000
1	0.064306000	-2.254441000	0.468709000	1	0.113645000	2.363138000	0.616872000
1	2.349475000	2.607733000	0.210544000	1	-2.633243000	-2.338095000	0.974931000
1	1.335807000	1.590389000	1.269536000	1	-1.273673000	-1.381114000	1.600758000
1	3.060573000	1.775739000	1.600583000	1	-2.897075000	-1.178158000	2.287916000
1	4.666981000	0.015655000	1.640517000	1	-3.922374000	0.129606000	-1.843482000
1	4.180910000	-1.454876000	0.752862000	1	-4.390724000	-1.470134000	-1.205505000
1	5.692946000	-0.601575000	0.346383000	1	-5.535468000	-0.126329000	-1.132515000
7	-3.893662000	0.077123000	0.127025000	7	3.872387000	-0.207630000	-0.086848000
8	-4.494448000	-0.884159000	0.556312000	8	4.571409000	0.722741000	0.251747000
8	-4.403198000	1.127112000	-0.201979000	8	4.280575000	-1.291661000	-0.445355000
1	4.019869000	-0.061865000	-1.214065000	1	-4.126483000	0.951008000	0.414591000

J. NMR Spectra of new synthesized compounds.

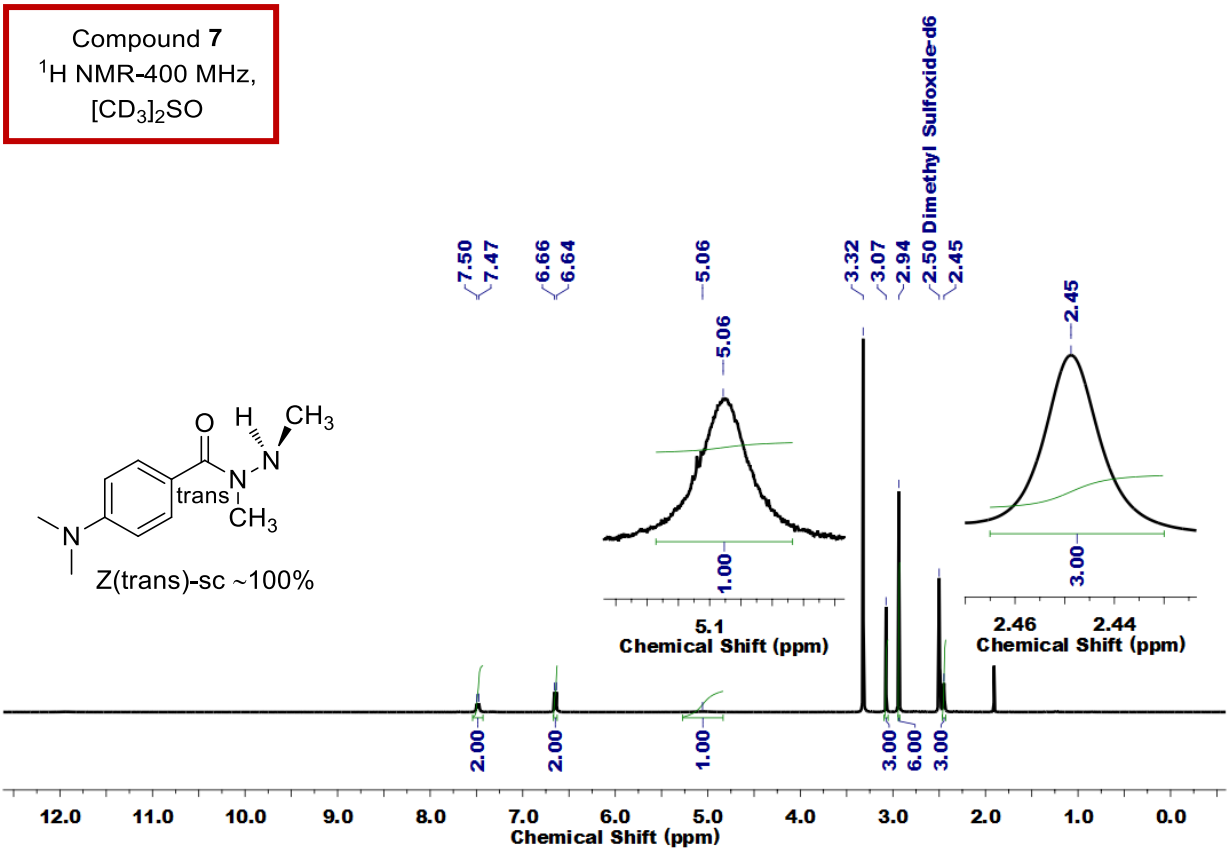
Compound **7**
^{1}H NMR-400 MHz,
$CDCl_3$



Compound **7**
^{13}C NMR-100 MHz,
$CDCl_3$

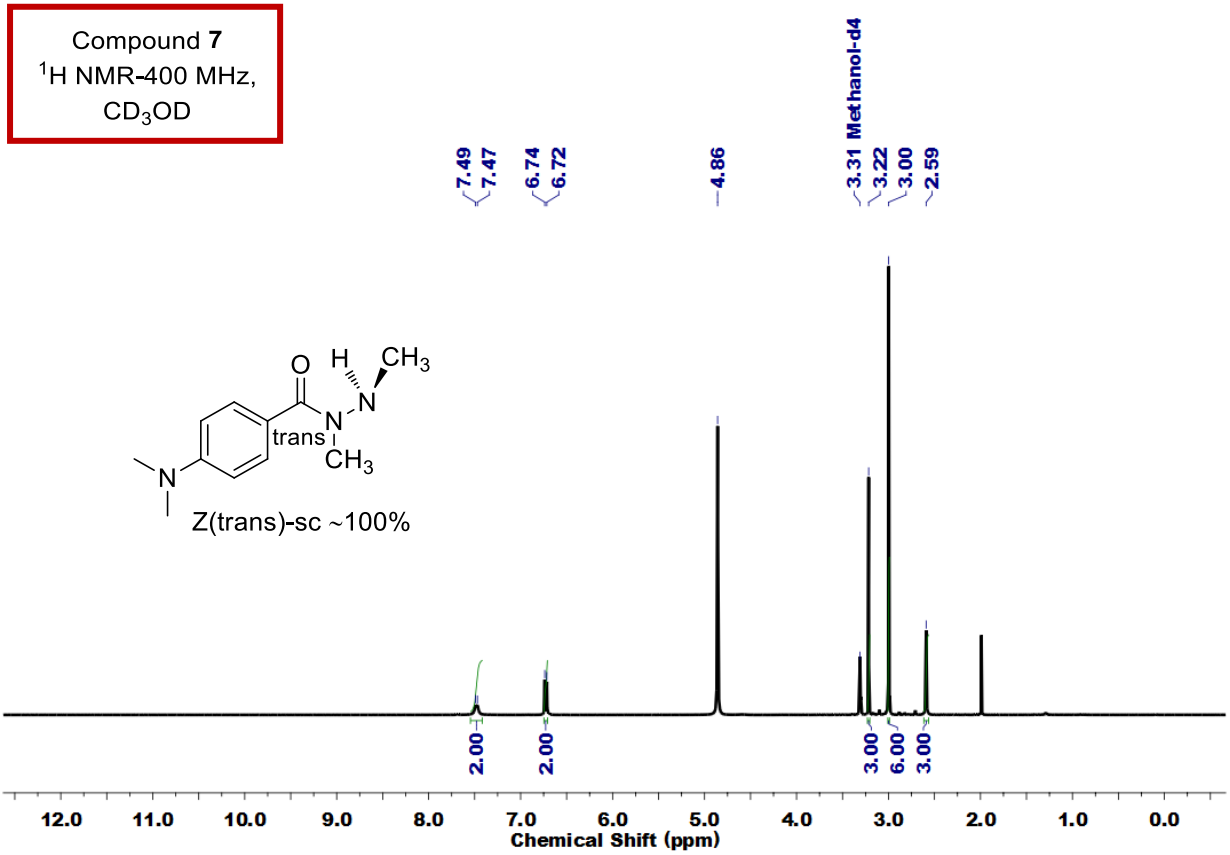


Compound **7**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



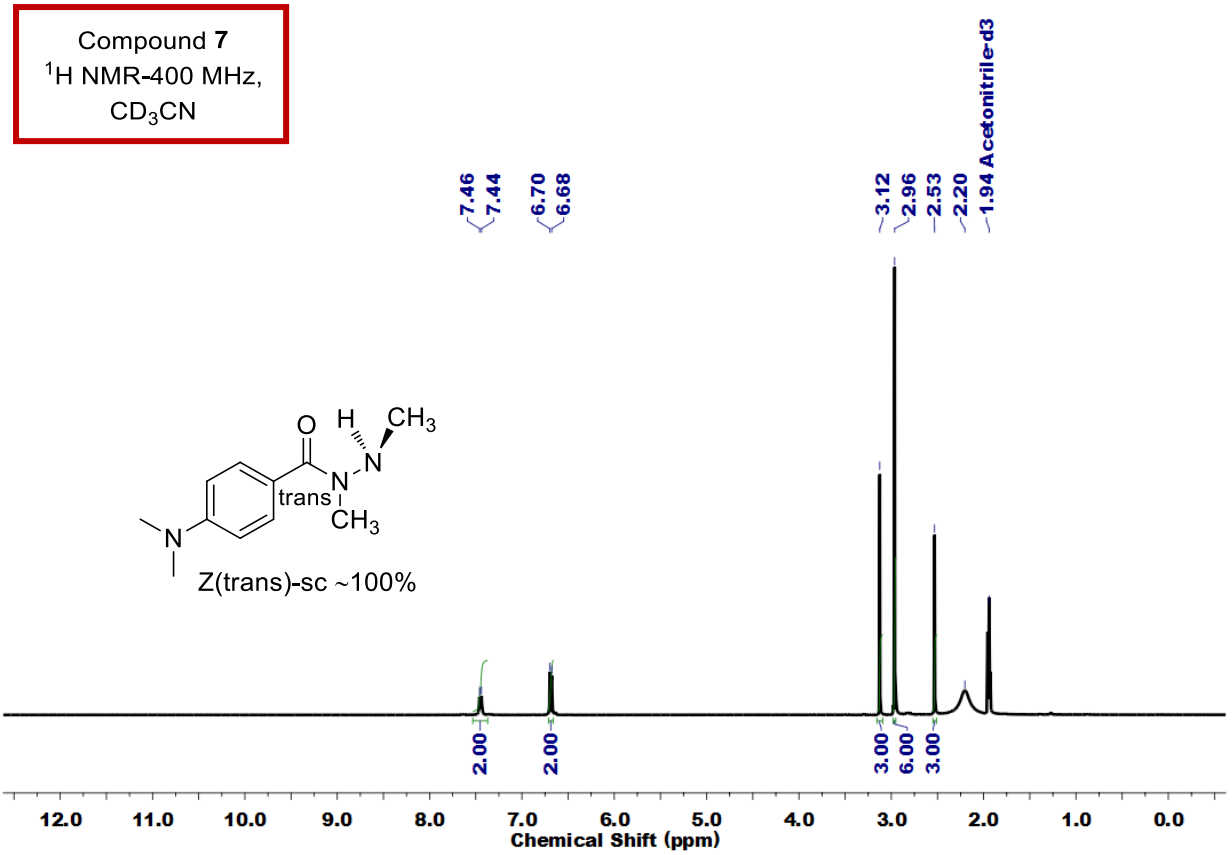
Z(trans)-sc ~100%

Compound **7**
^{1}H NMR-400 MHz,
CD_3OD

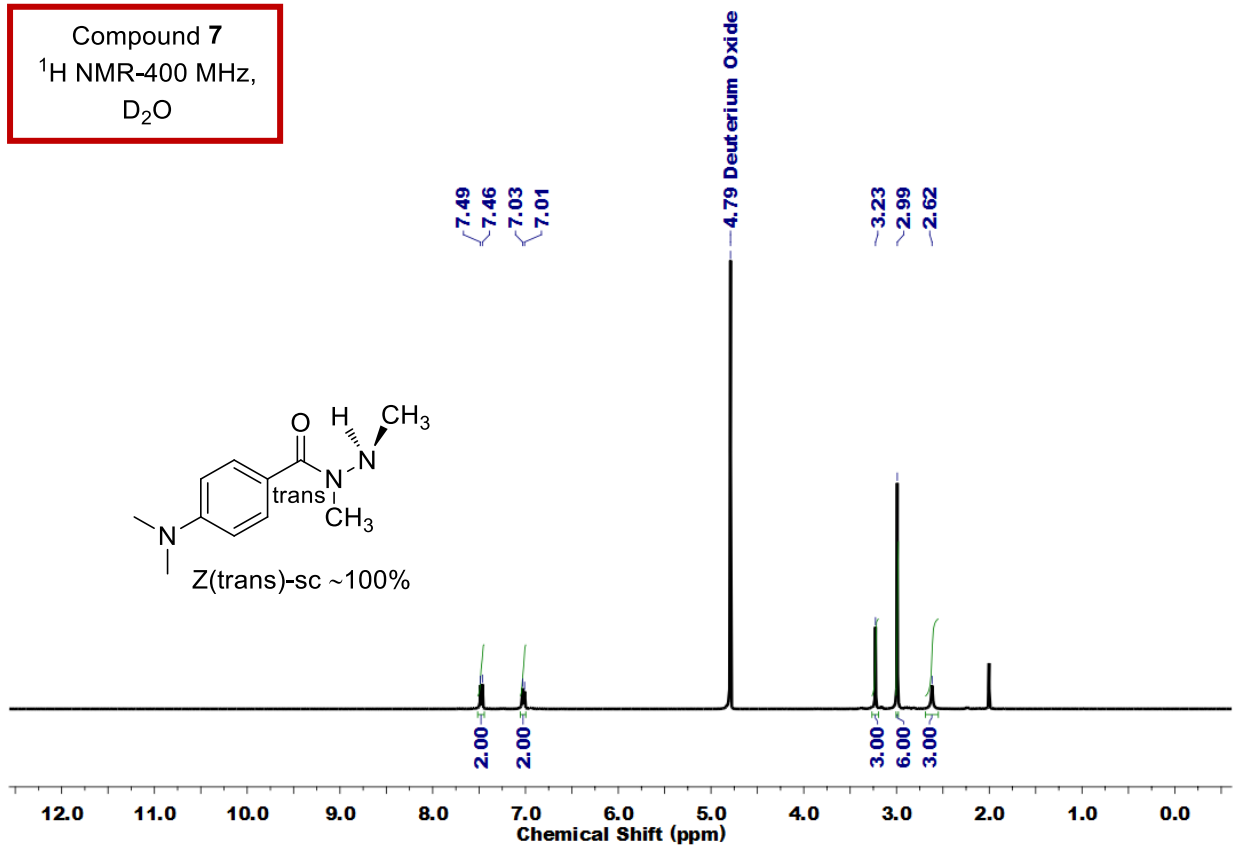


Z(trans)-sc ~100%

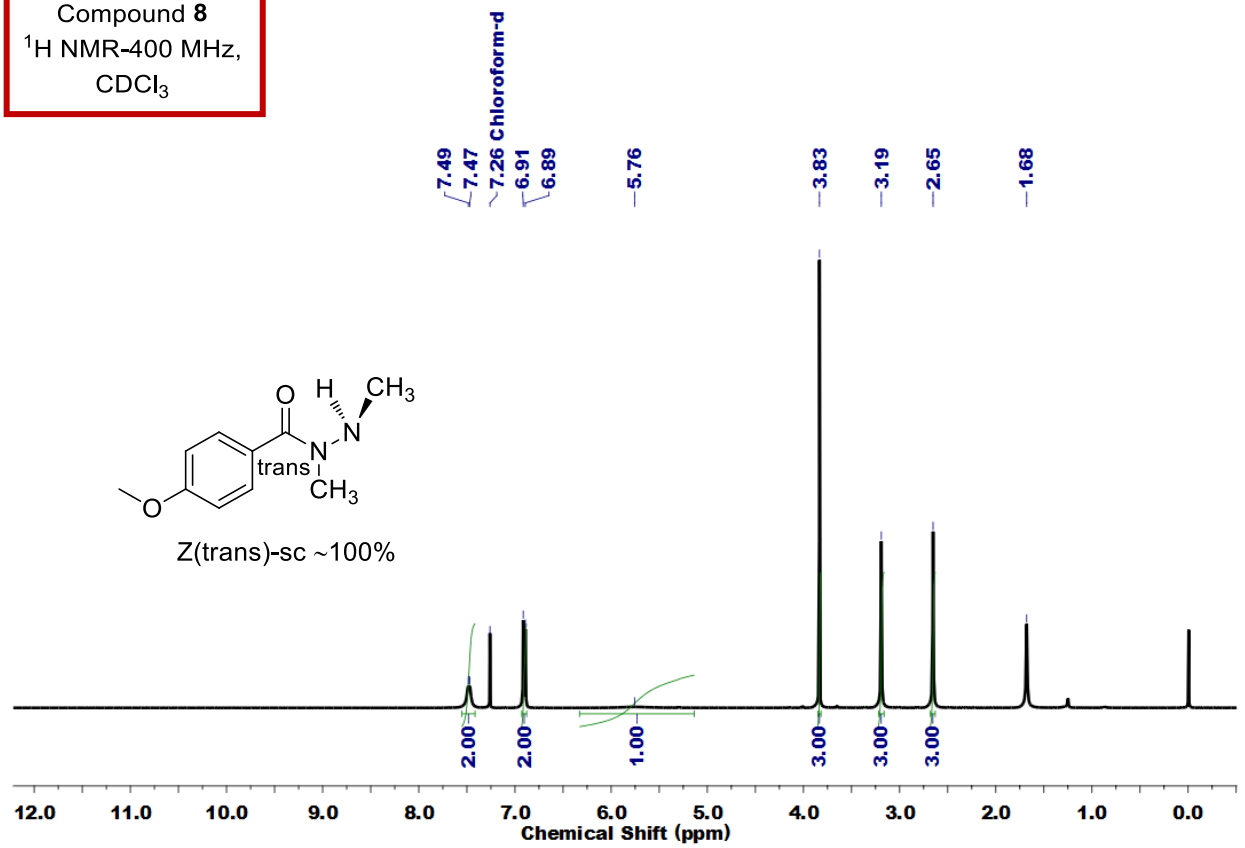
Compound **7**
^{1}H NMR-400 MHz,
CD_3CN



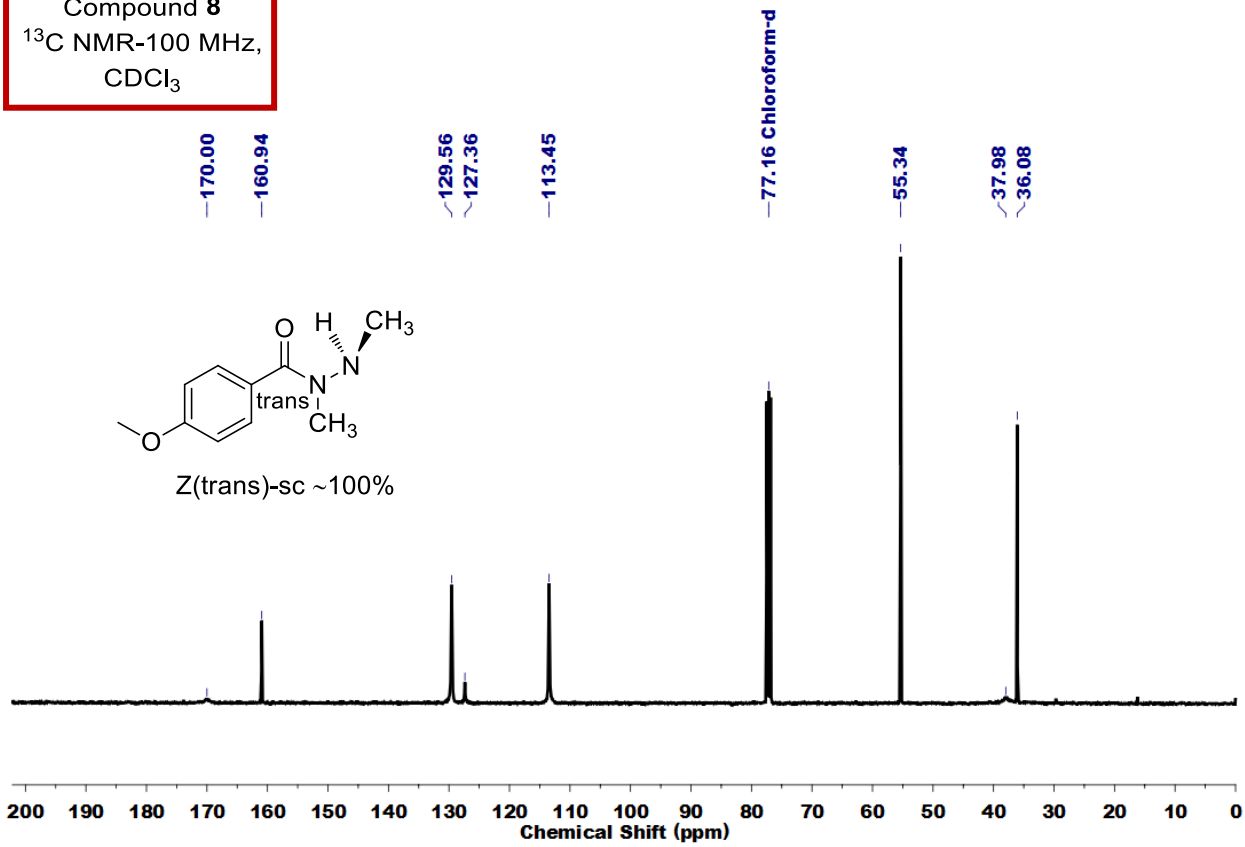
Compound **7**
^{1}H NMR-400 MHz,
D_2O



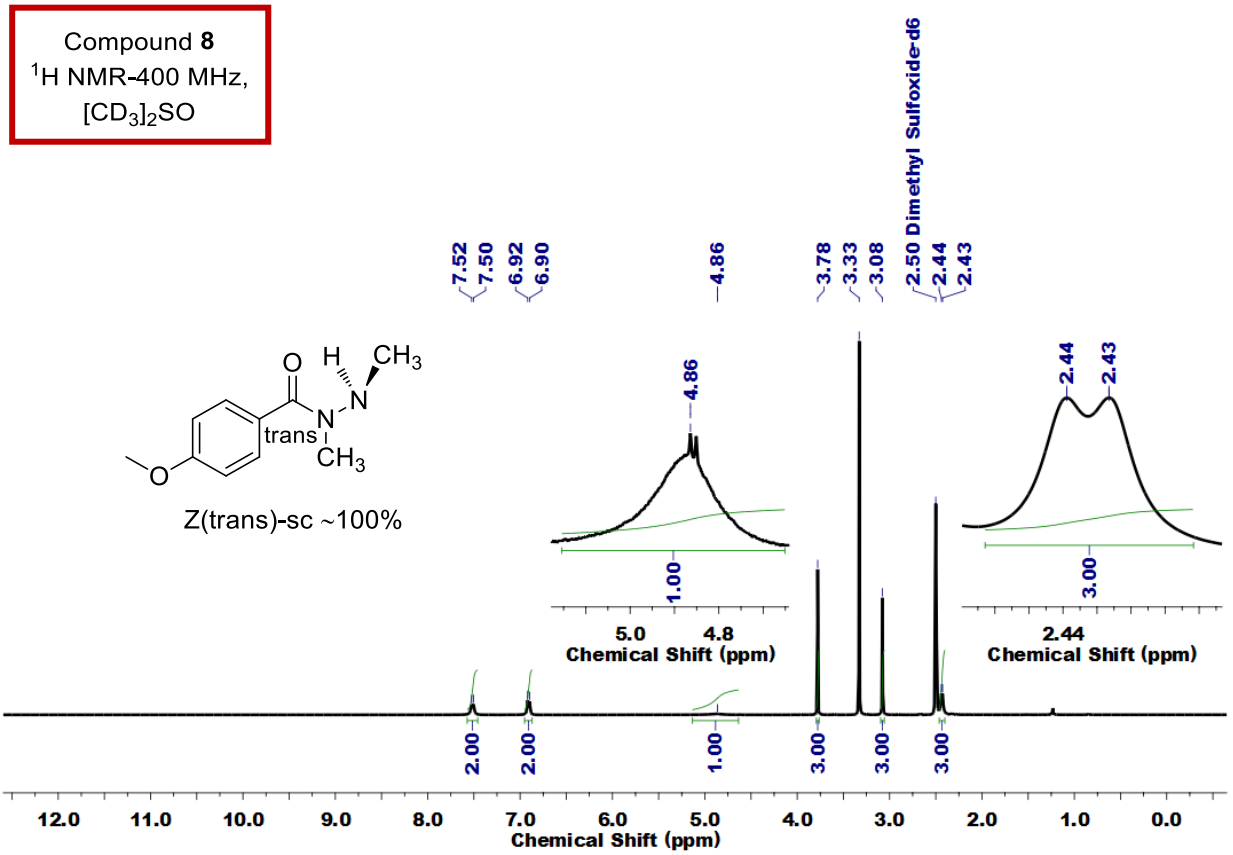
Compound **8**
^{1}H NMR-400 MHz,
$CDCl_3$



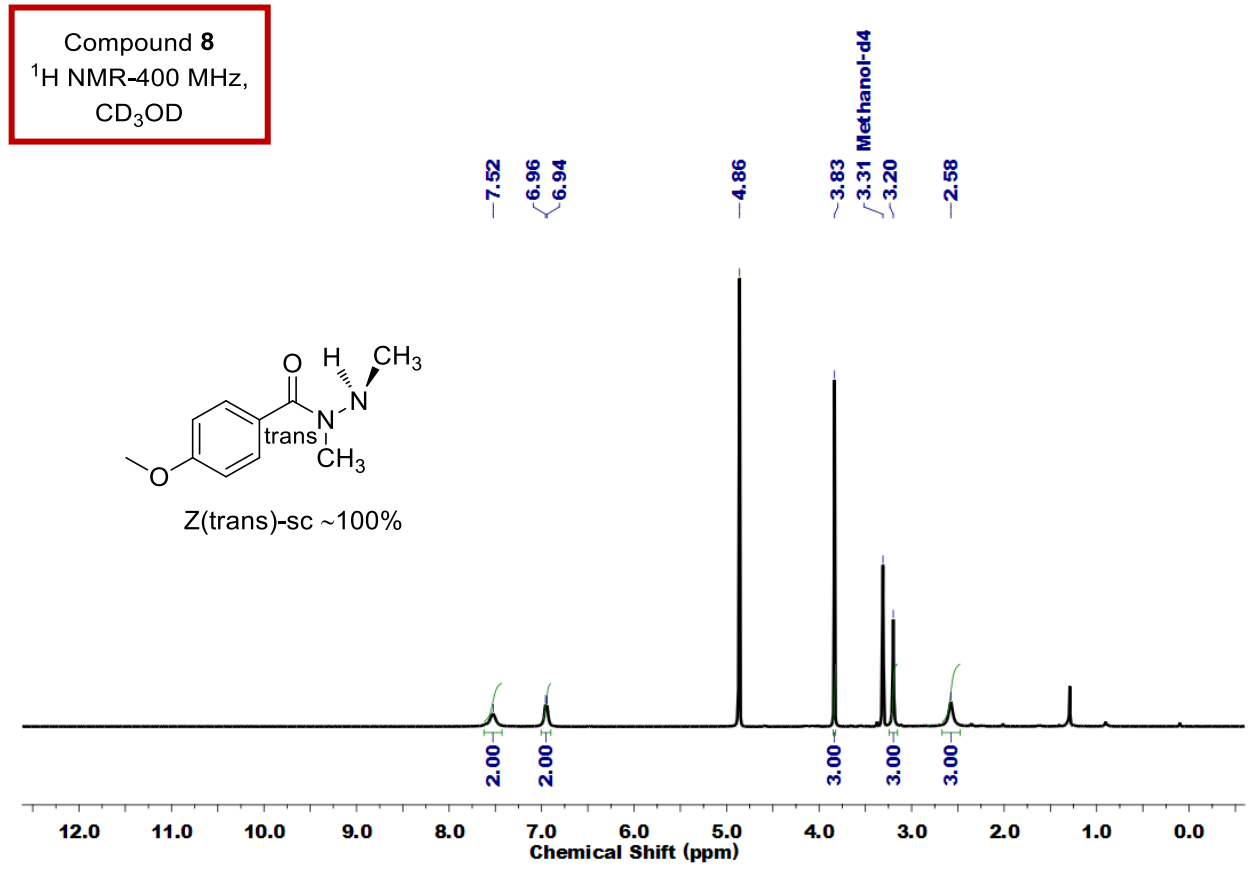
Compound **8**
^{13}C NMR-100 MHz,
$CDCl_3$



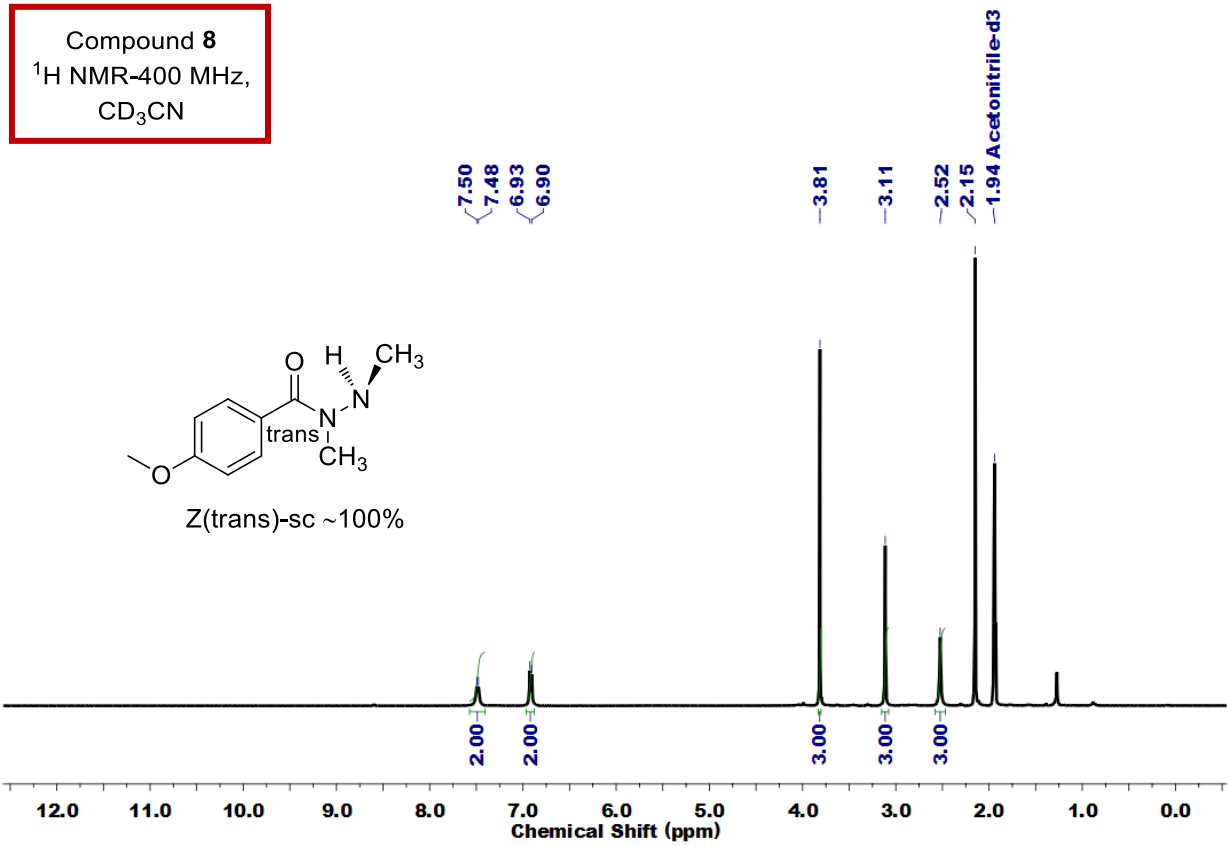
Compound **8**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



Compound **8**
^{1}H NMR-400 MHz,
CD_3OD

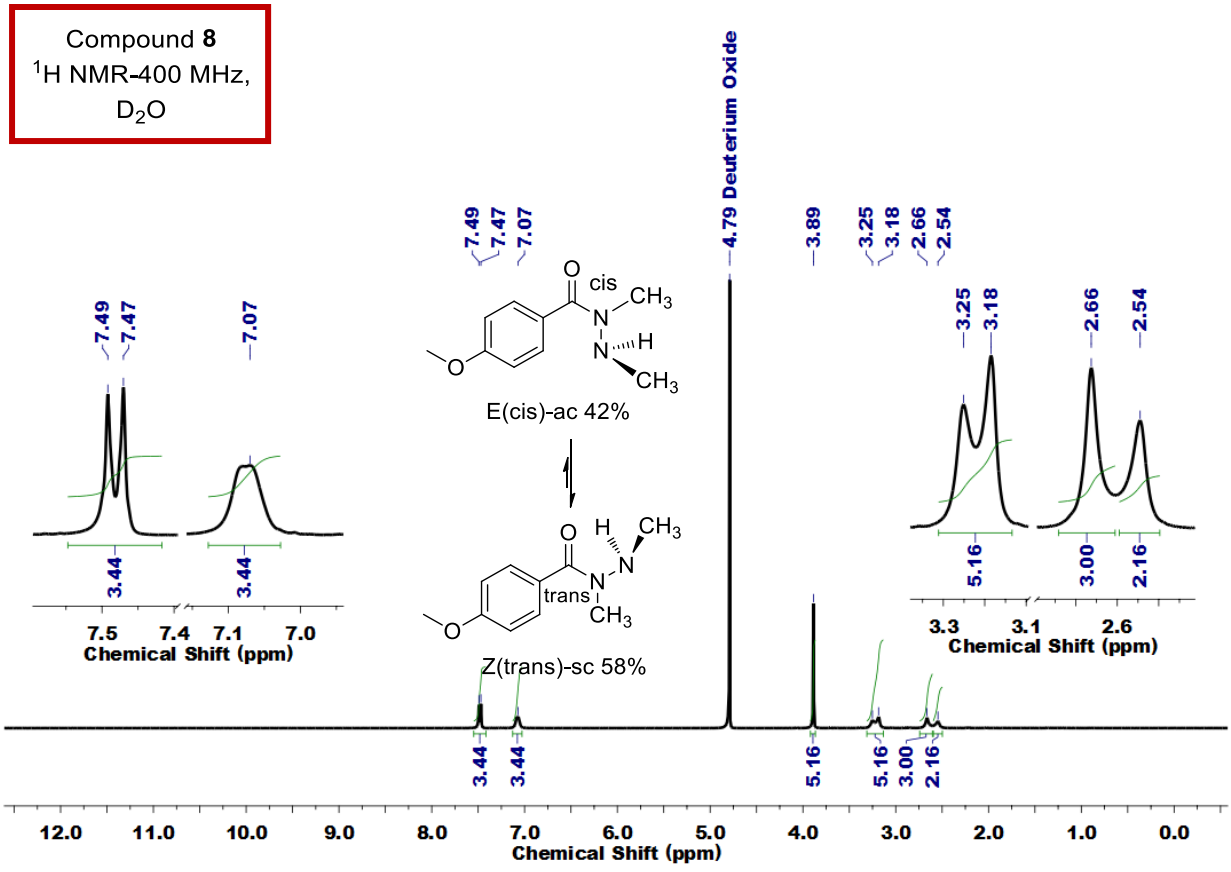


Compound **8**
^{1}H NMR-400 MHz,
CD_3CN

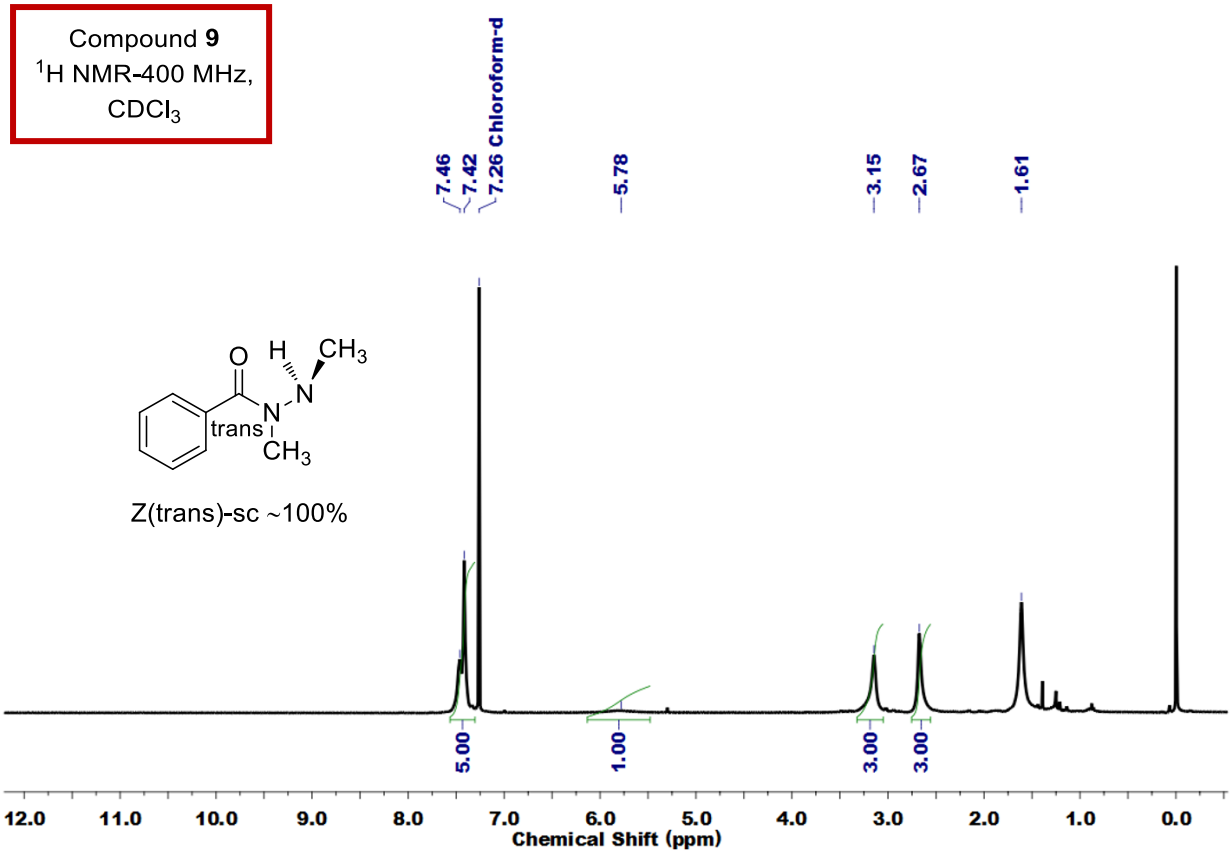


Z(trans)-sc ~100%

Compound **8**
^{1}H NMR-400 MHz,
D_2O

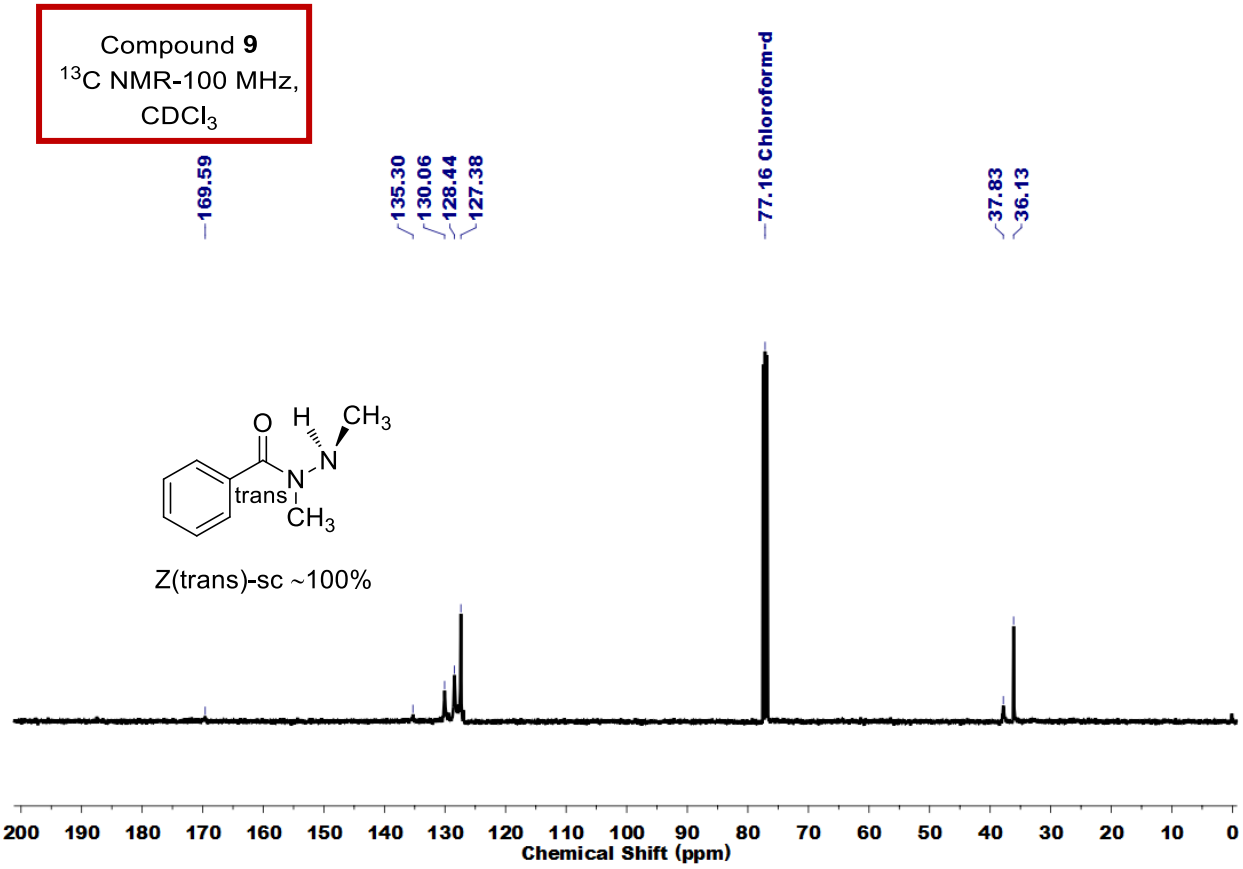


Compound **9**
^{1}H NMR-400 MHz,
$CDCl_3$



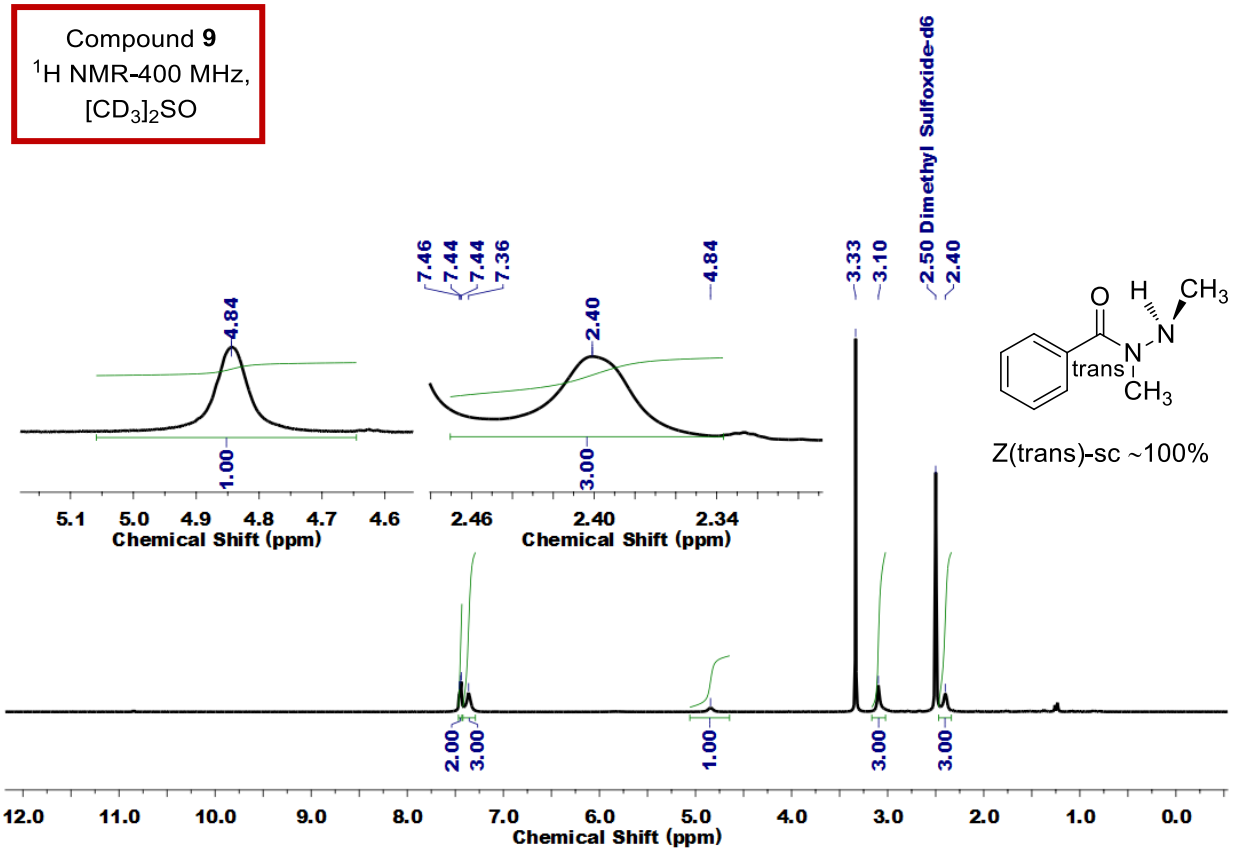
Z(trans)-sc ~100%

Compound **9**
^{13}C NMR-100 MHz,
$CDCl_3$

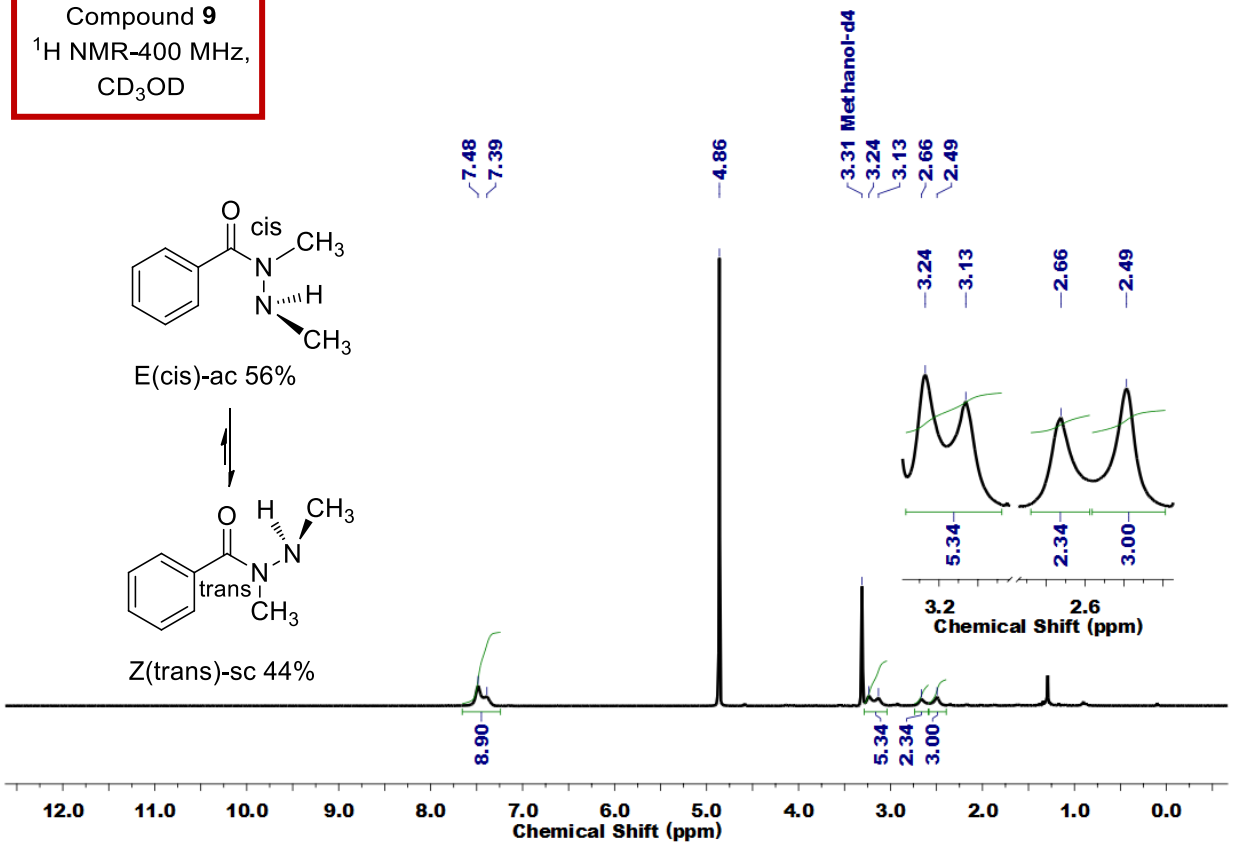


Z(trans)-sc ~100%

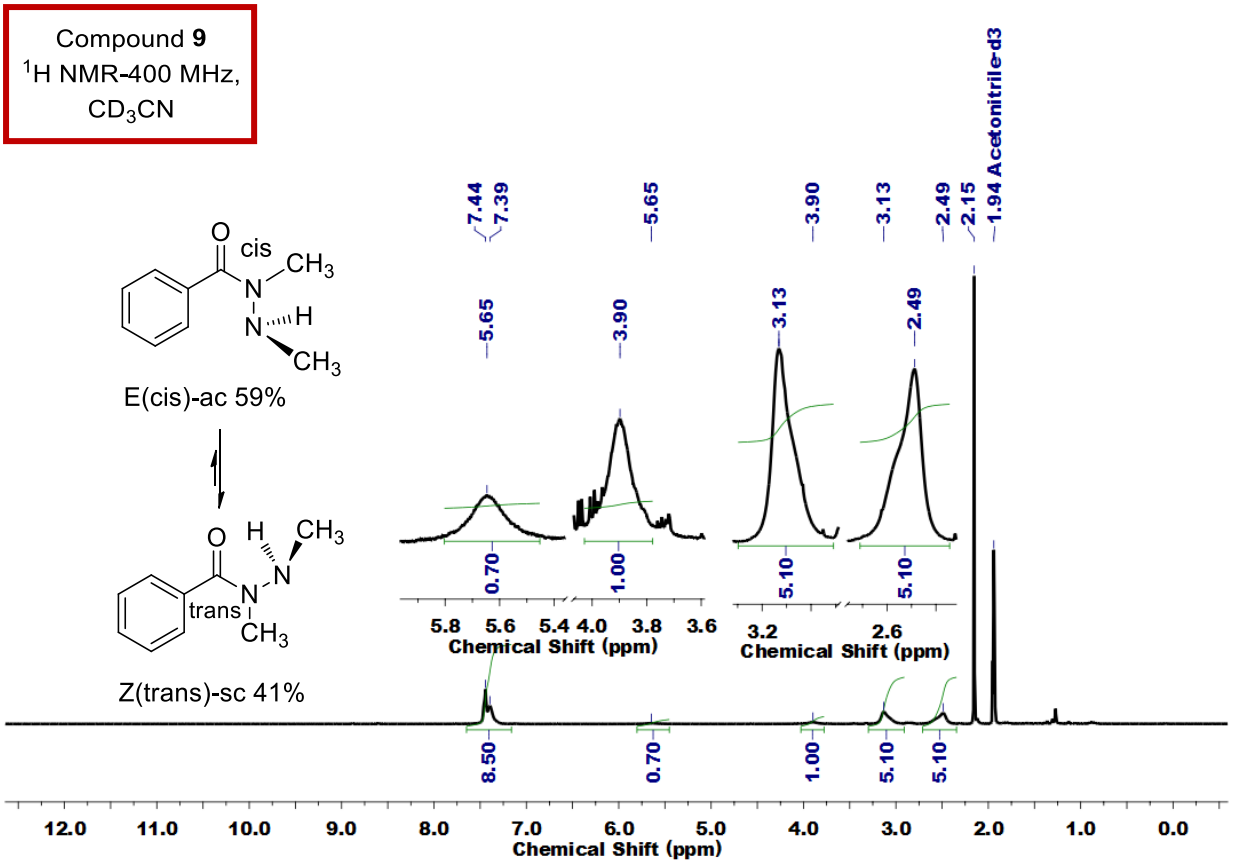
Compound **9**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



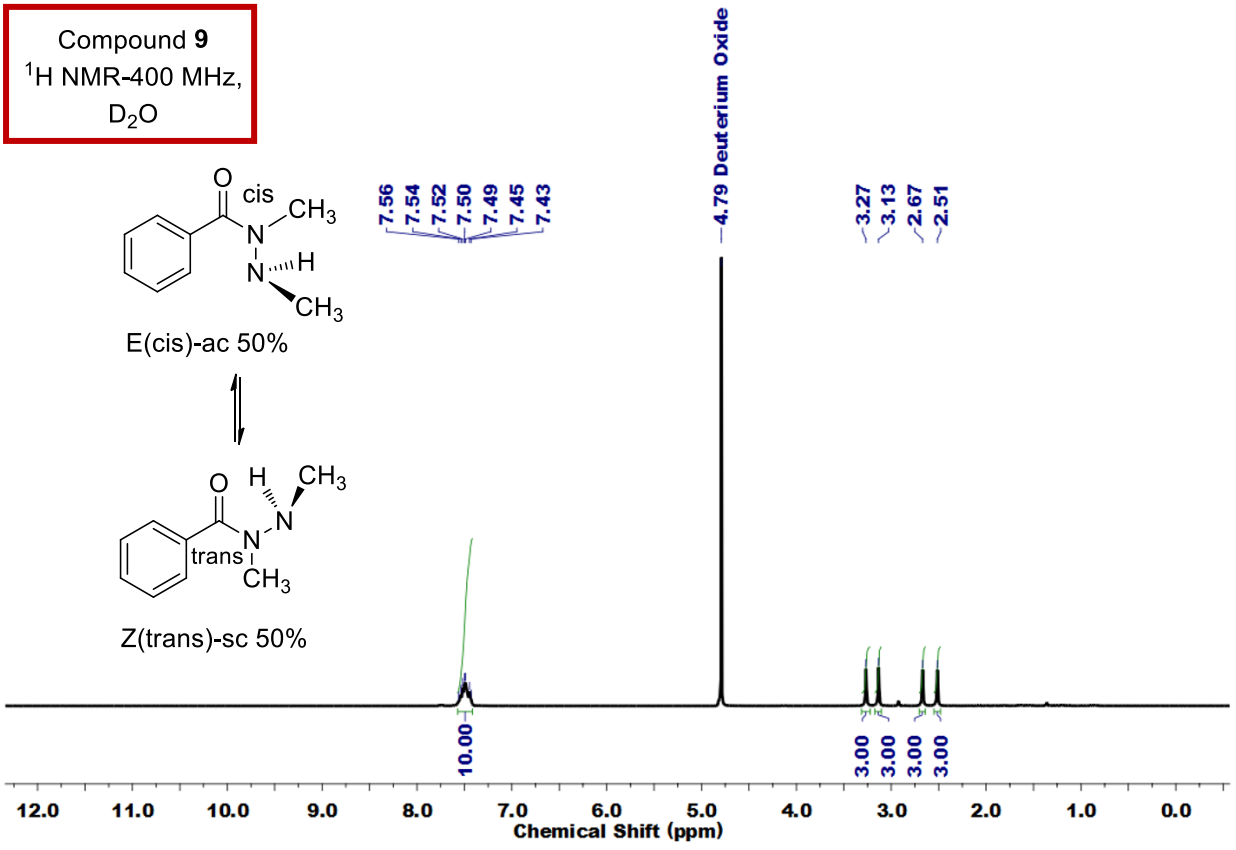
Compound **9**
^{1}H NMR-400 MHz,
CD_3OD



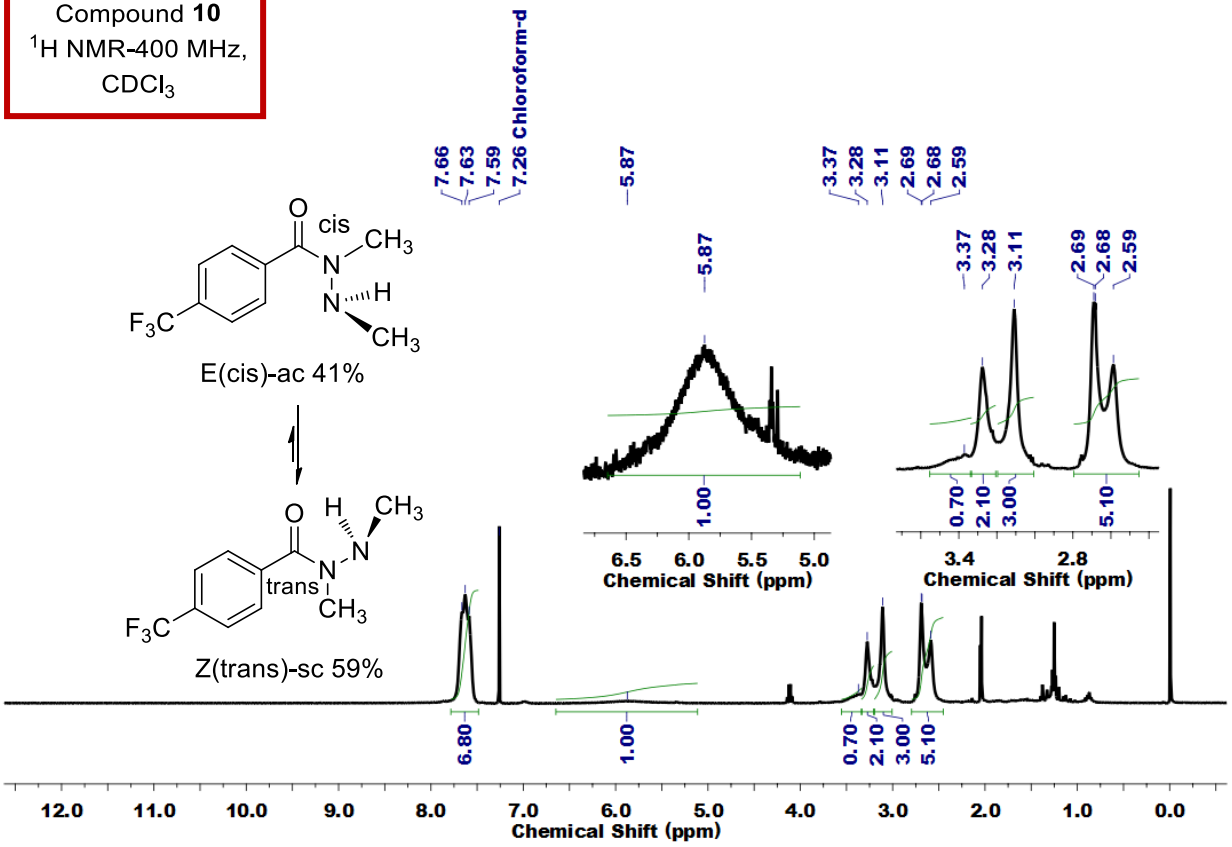
Compound **9**
^{1}H NMR-400 MHz,
CD_3CN



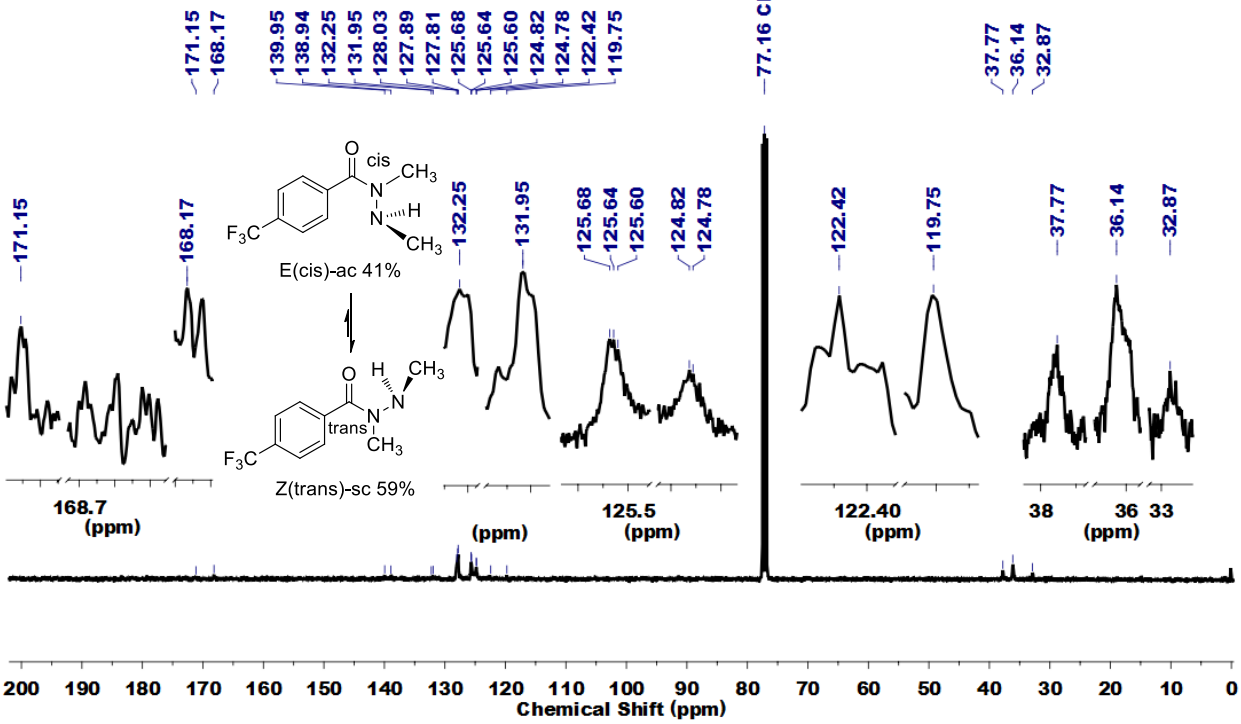
Compound **9**
^{1}H NMR-400 MHz,
D_2O



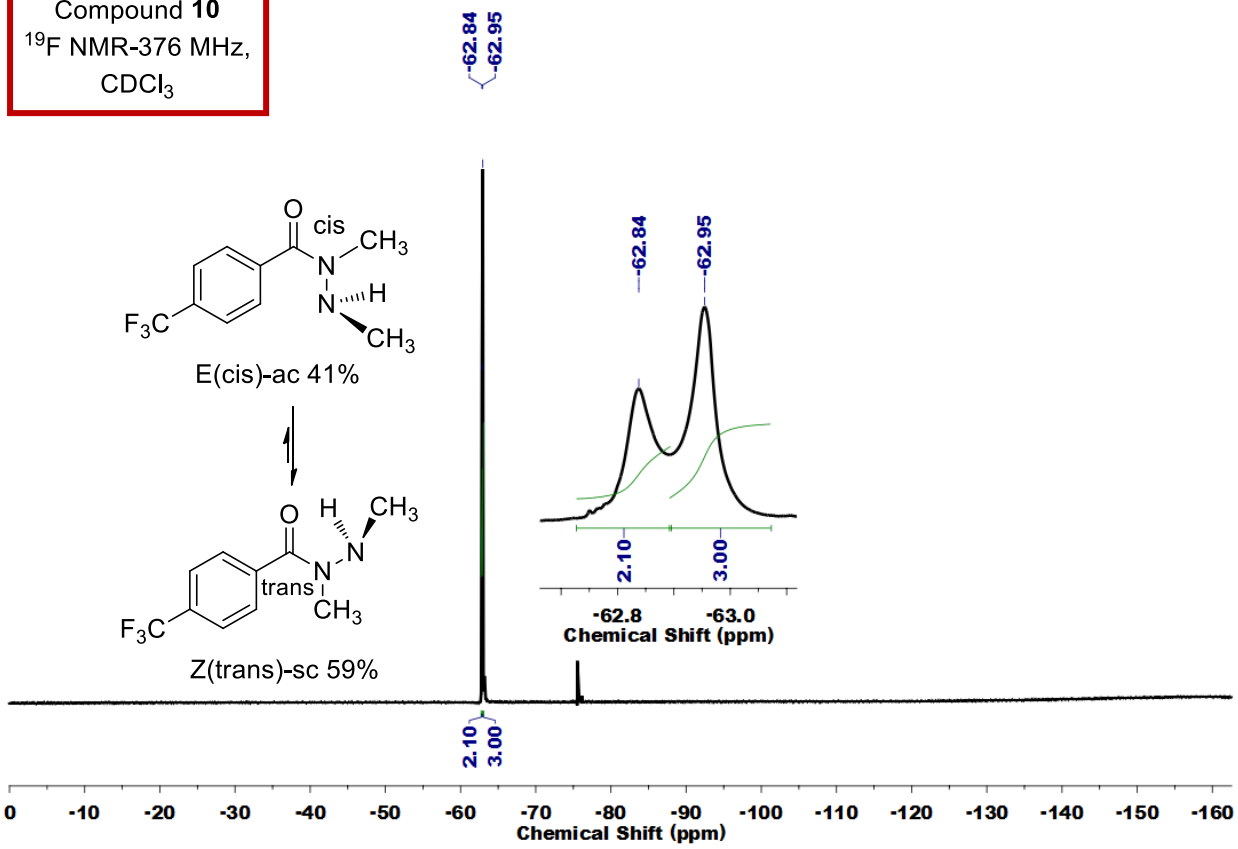
Compound **10**
^{1}H NMR-400 MHz,
$CDCl_3$



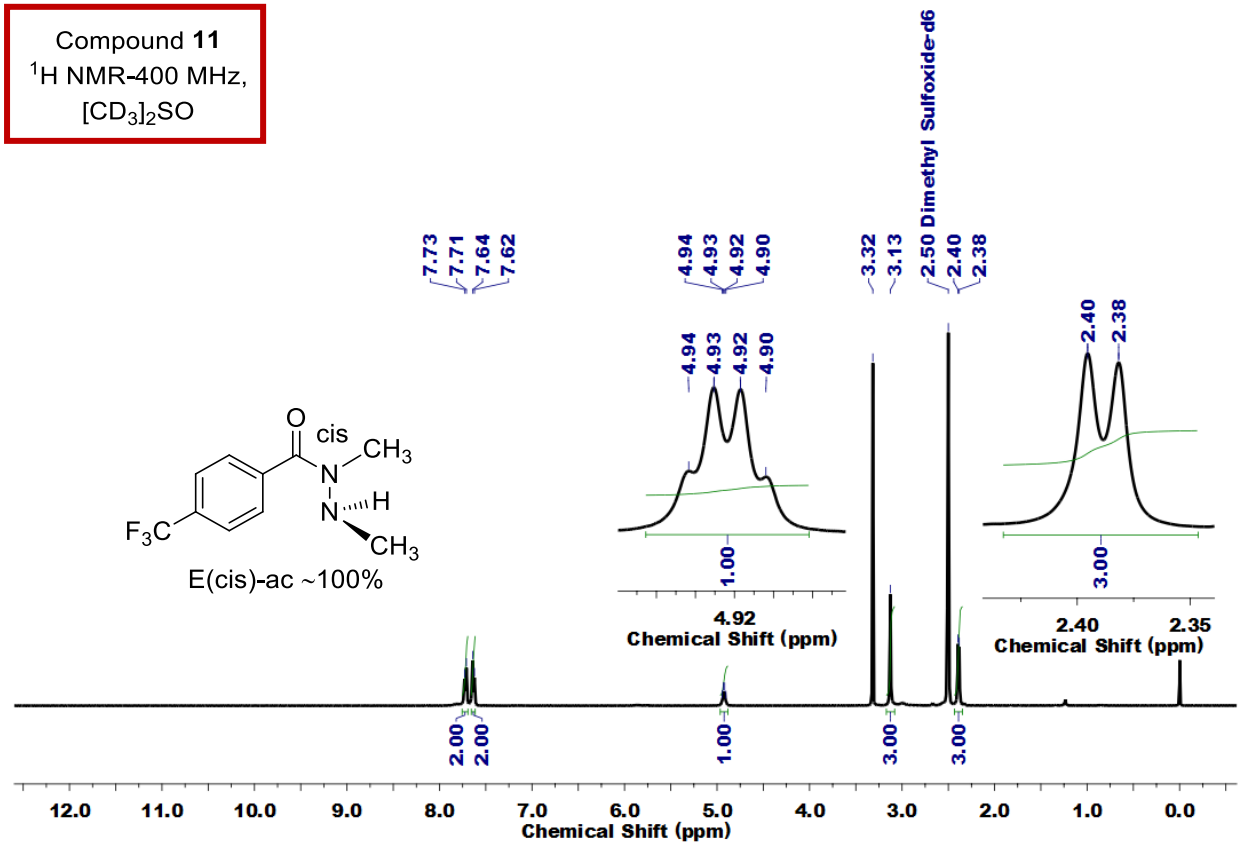
Compound **10**
^{13}C NMR-100 MHz,
$CDCl_3$



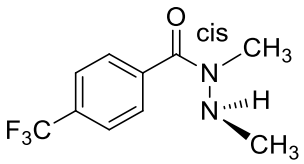
Compound **10**
^{19}F NMR-376 MHz,
$CDCl_3$



Compound **11**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$

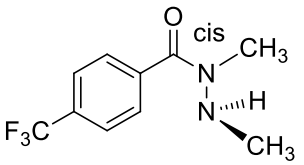


Compound **10**
^{19}F NMR-376 MHz,
$[CD_3]_2SO$

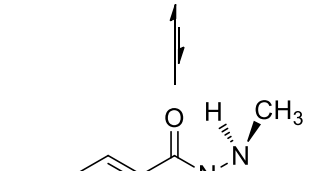


E(cis)-ac ~100%

Compound **10**
^{1}H NMR-400 MHz,
CD_3OD

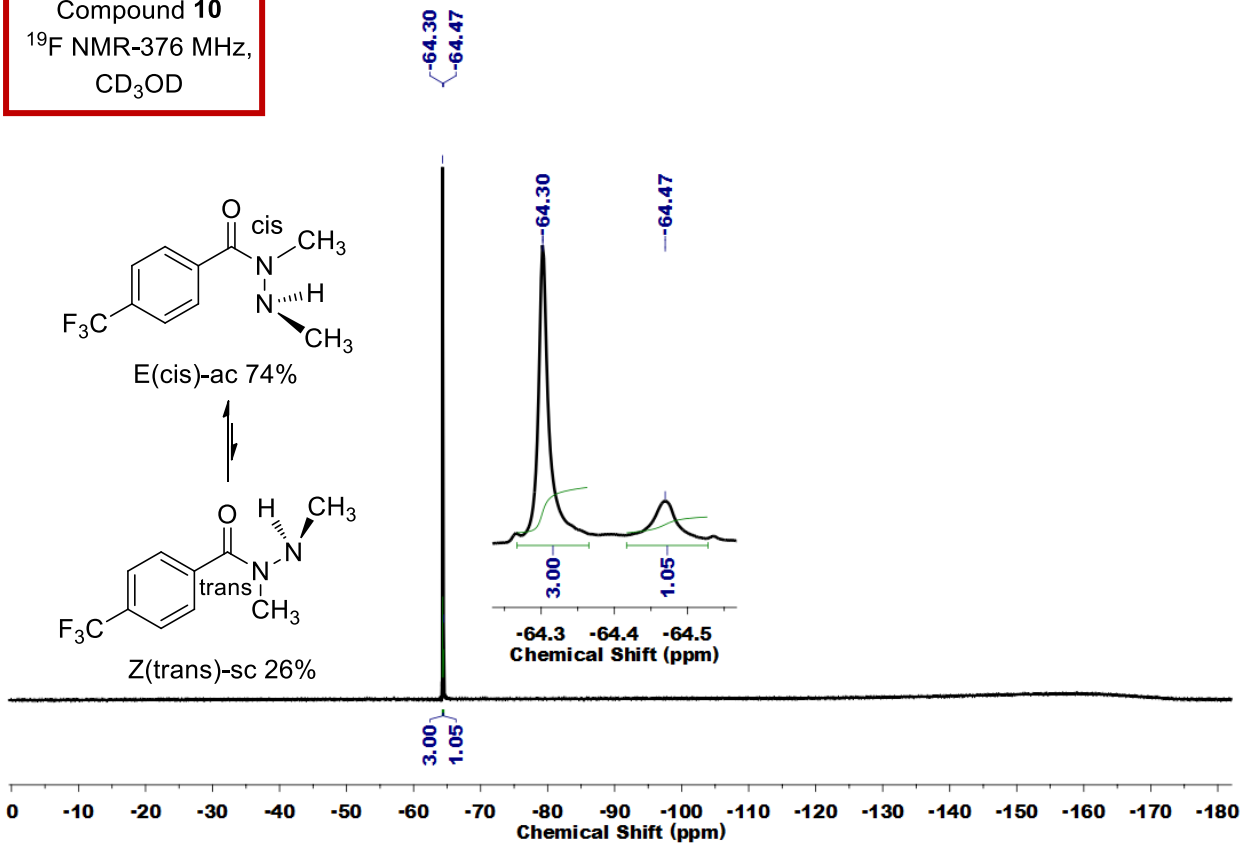


E(cis)-ac 74%

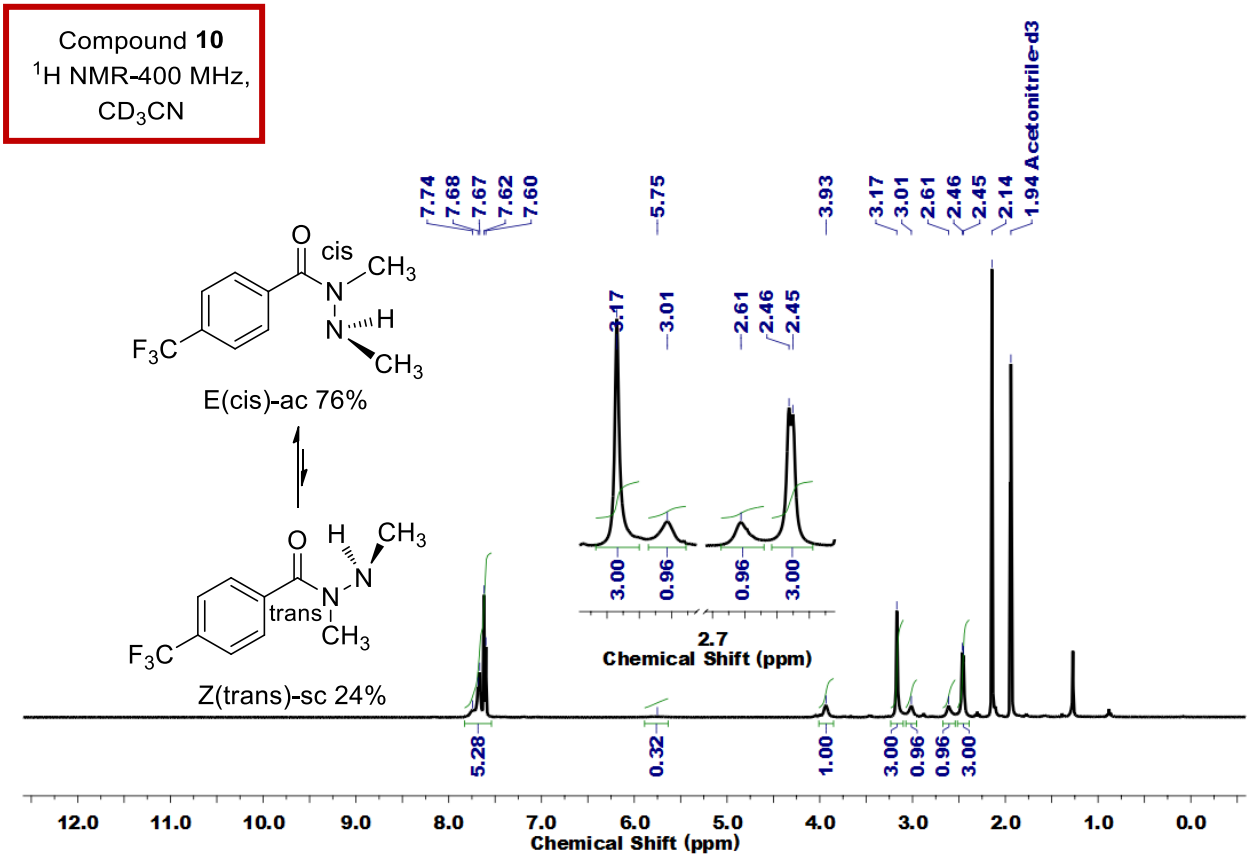


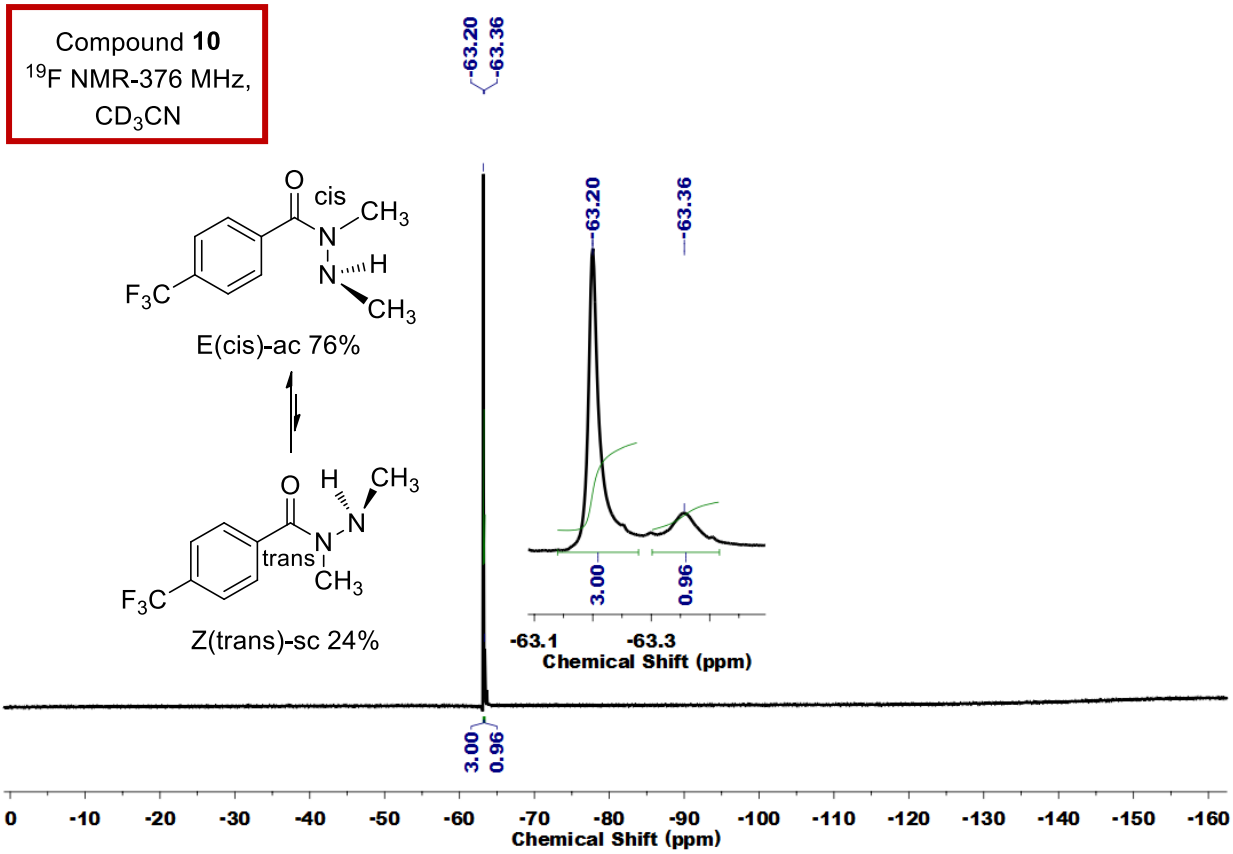
Z(trans)-sc 26%

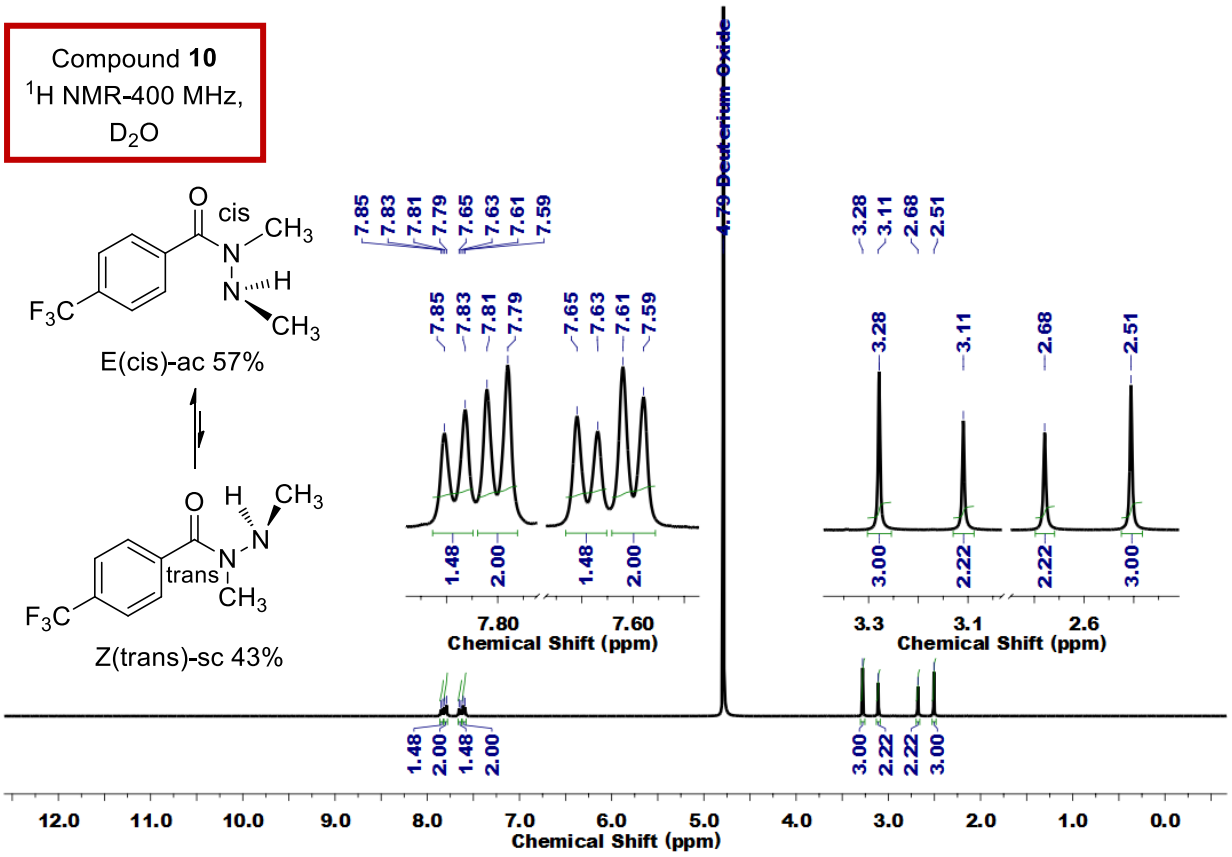
Compound **10**
^{19}F NMR-376 MHz,
CD_3OD



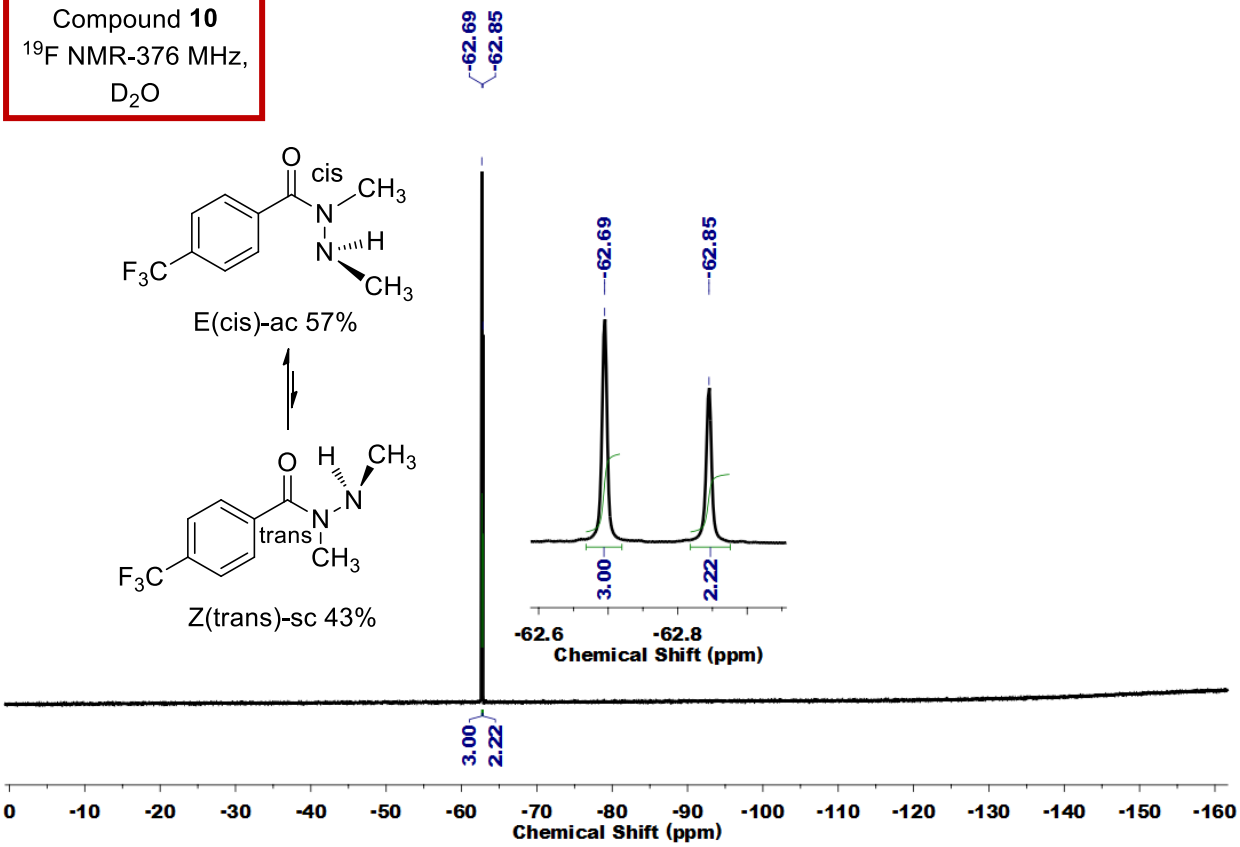
Compound **10**
^{1}H NMR-400 MHz,
CD_3CN



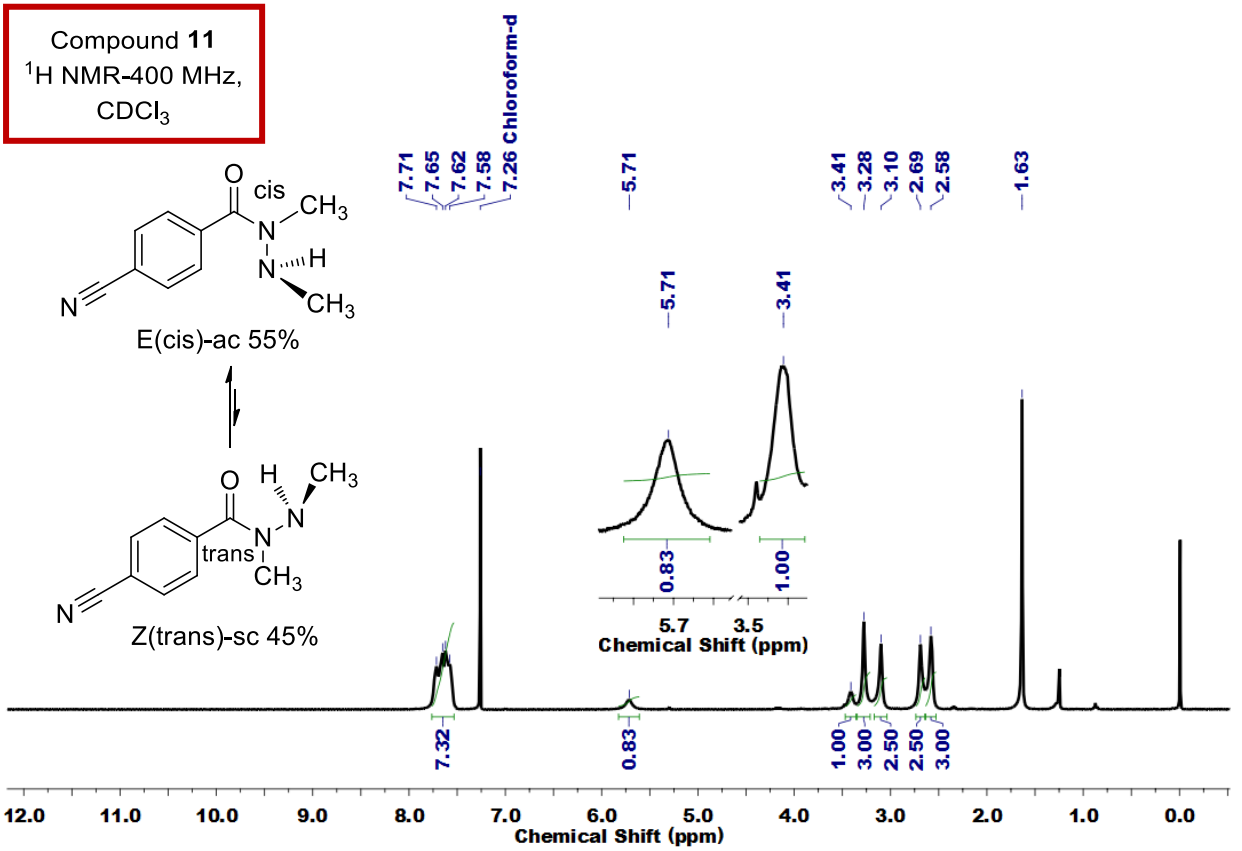

Compound 10
19F NMR-376 MHz,
CD3CN
-63.20
-63.36
cis
trans
E(cis)-ac 76%
Z(trans)-sc 24%
3.00
0.96
-63.1
-63.3
Chemical Shift (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
Chemical Shift (ppm)


Compound 10
1H NMR-400 MHz,
D2O
cis
trans
E(cis)-ac 57%
Z(trans)-sc 43%
7.85
7.83
7.81
7.79
7.65
7.63
7.61
7.59
4.79 Deuterium Oxide
3.28
3.11
2.68
2.51
1.48
2.00
3.00
2.22
7.80
7.60
3.3
3.1
2.6
Chemical Shift (ppm)
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical Shift (ppm)

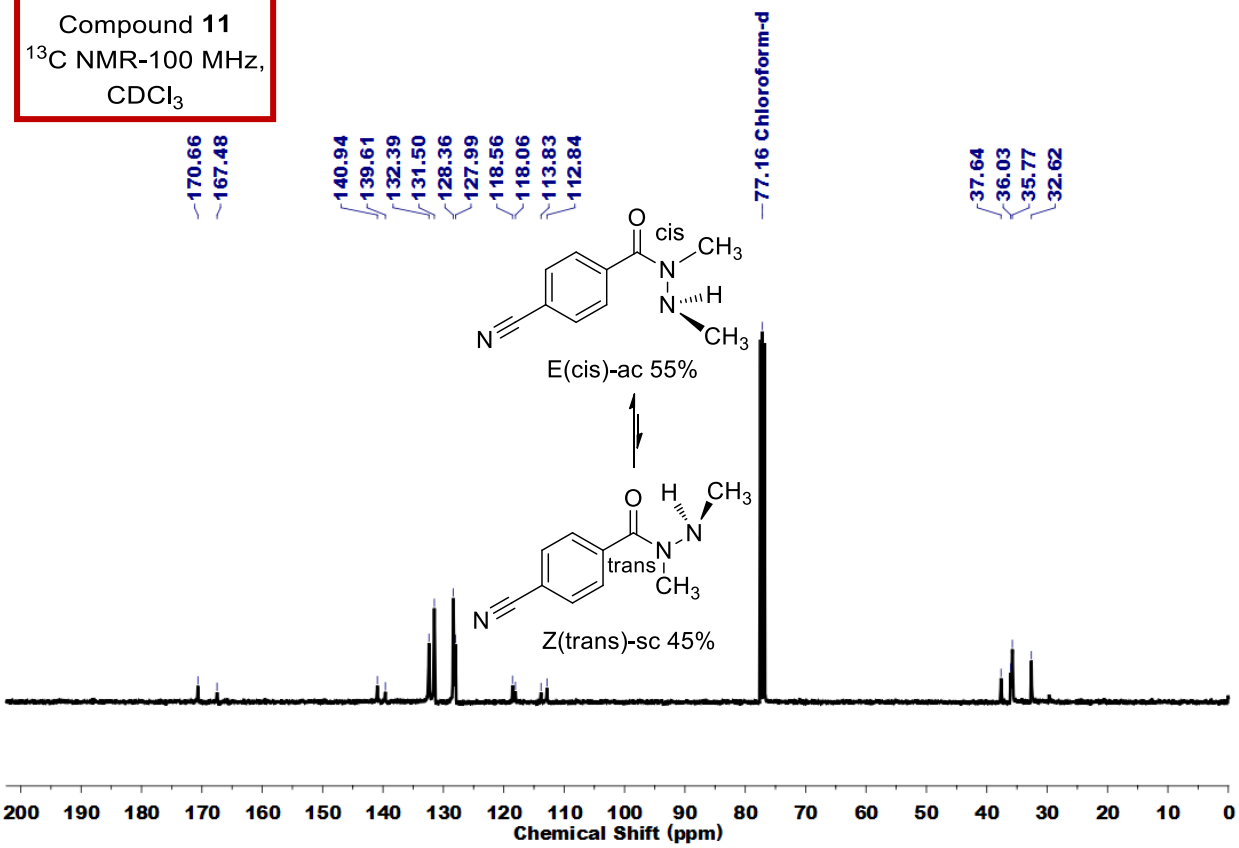
Compound **10**
^{19}F NMR-376 MHz,
D_2O



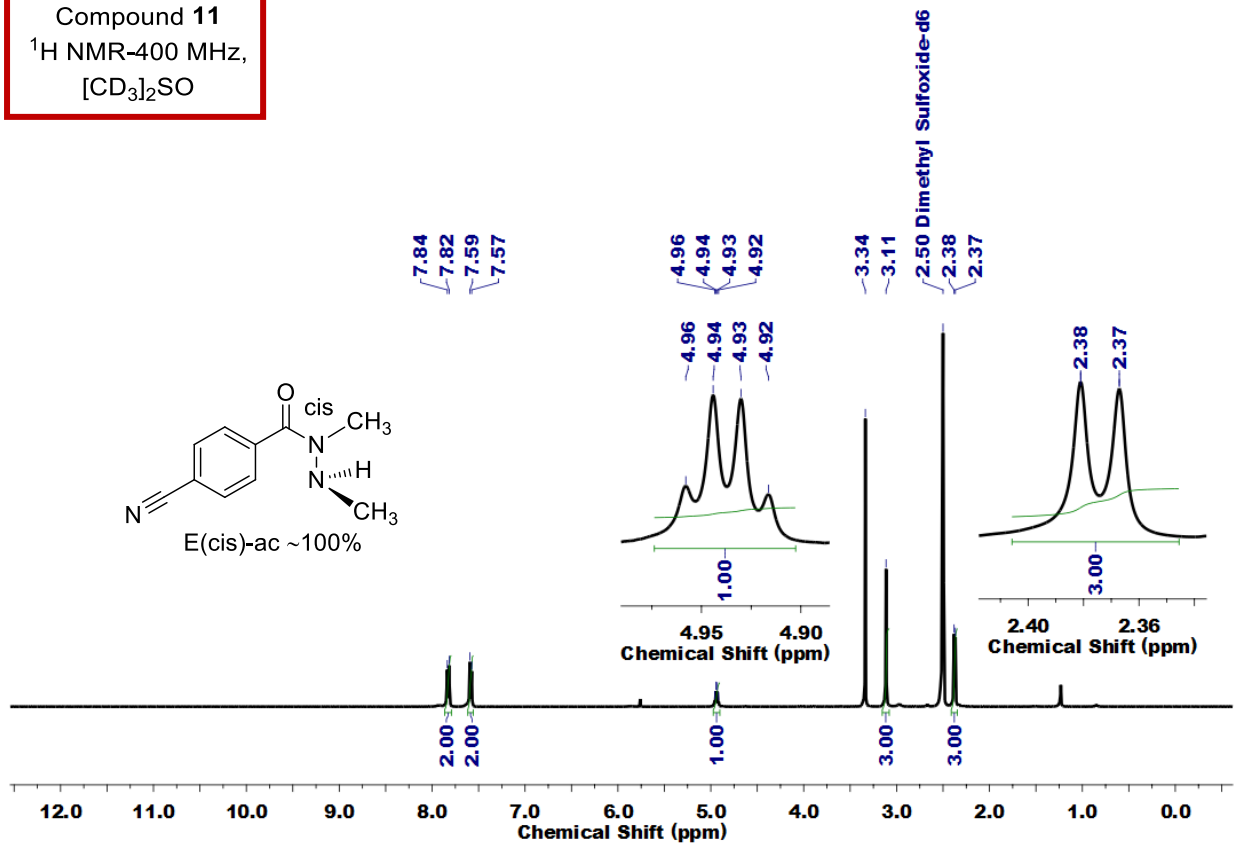
Compound **11**
^{1}H NMR-400 MHz,
$CDCl_3$



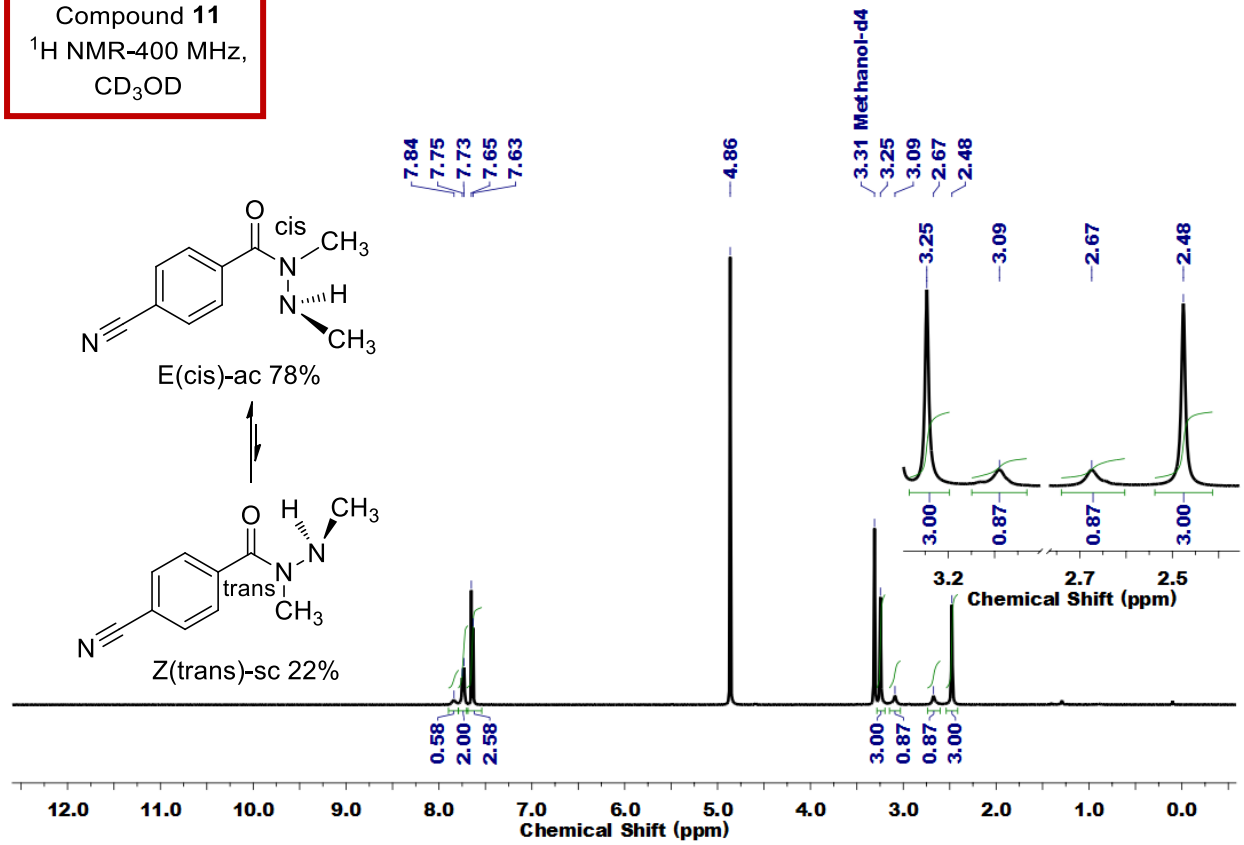
Compound **11**
^{13}C NMR-100 MHz,
$CDCl_3$



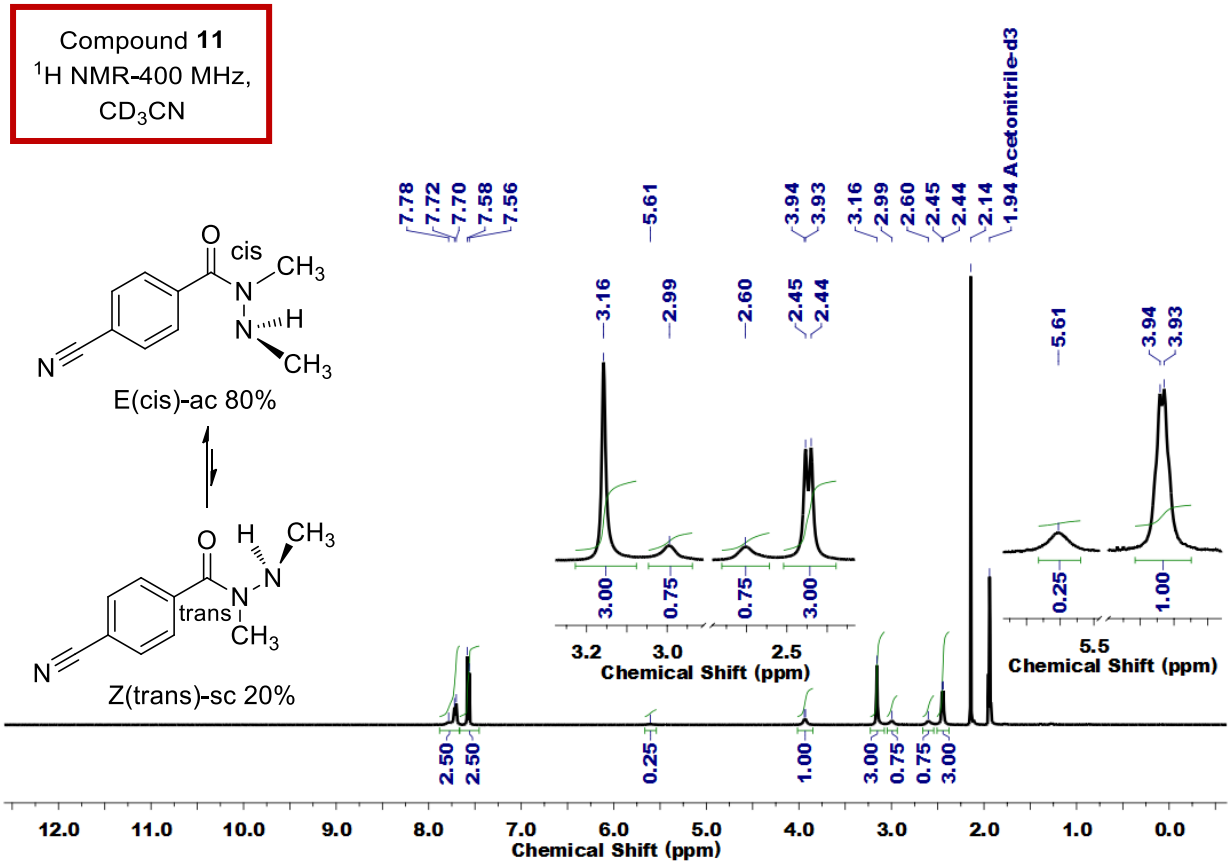
Compound **11**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



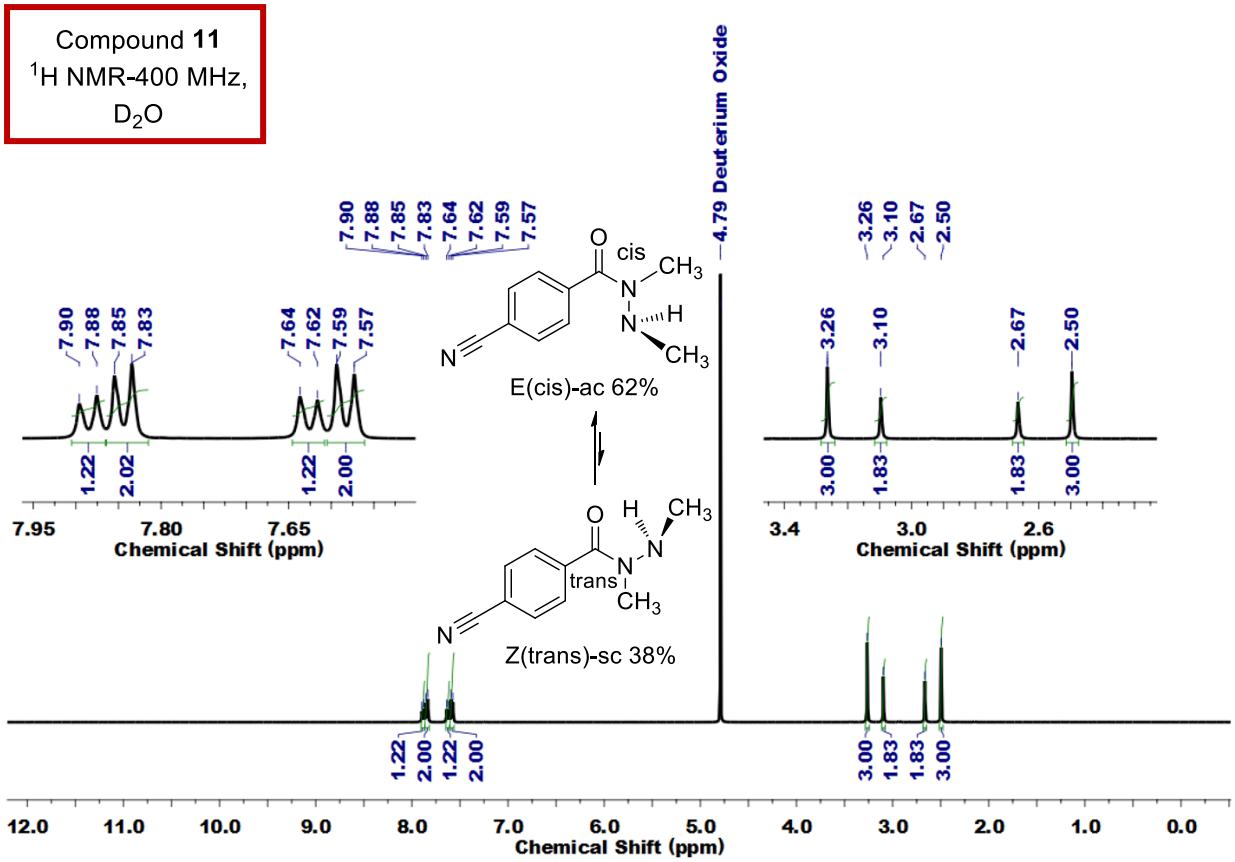
Compound **11**
^{1}H NMR-400 MHz,
CD_3OD



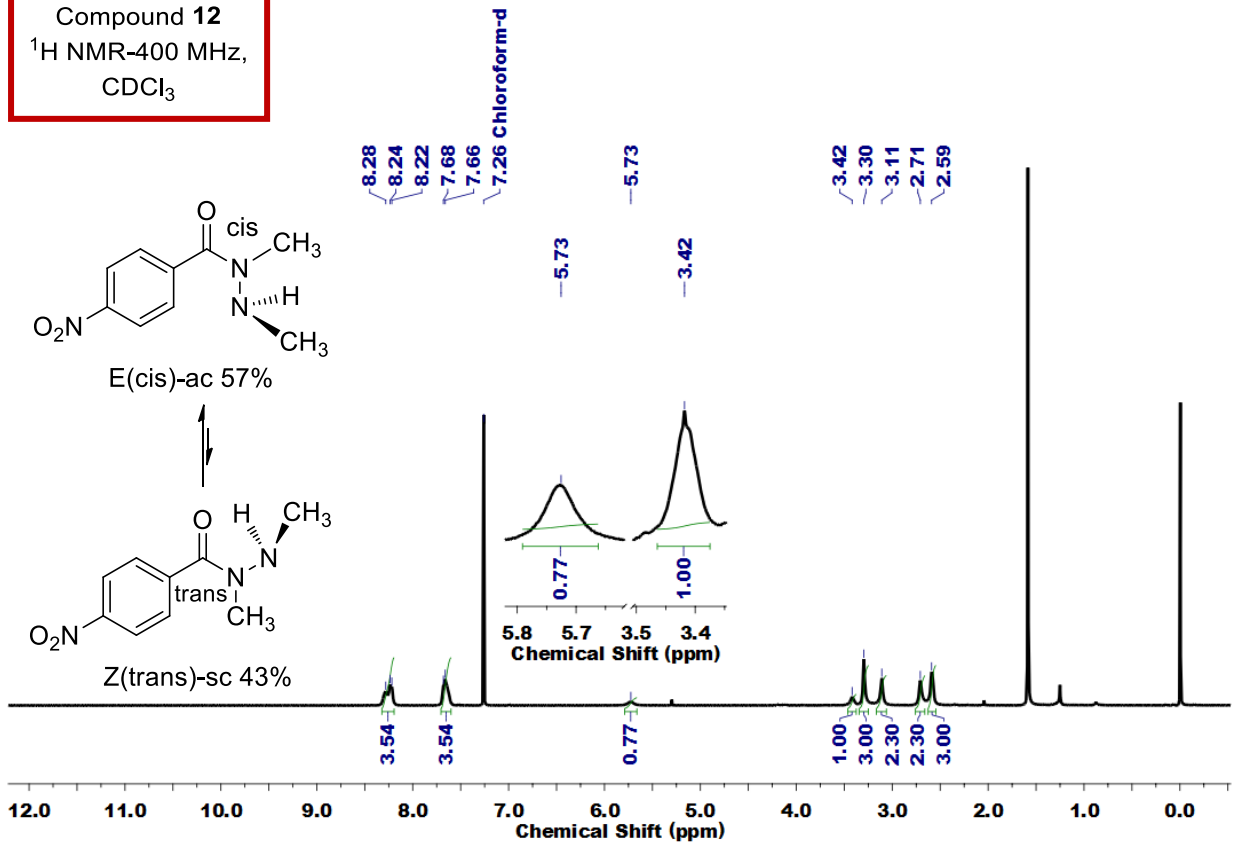
Compound **11**
^{1}H NMR-400 MHz,
CD_3CN

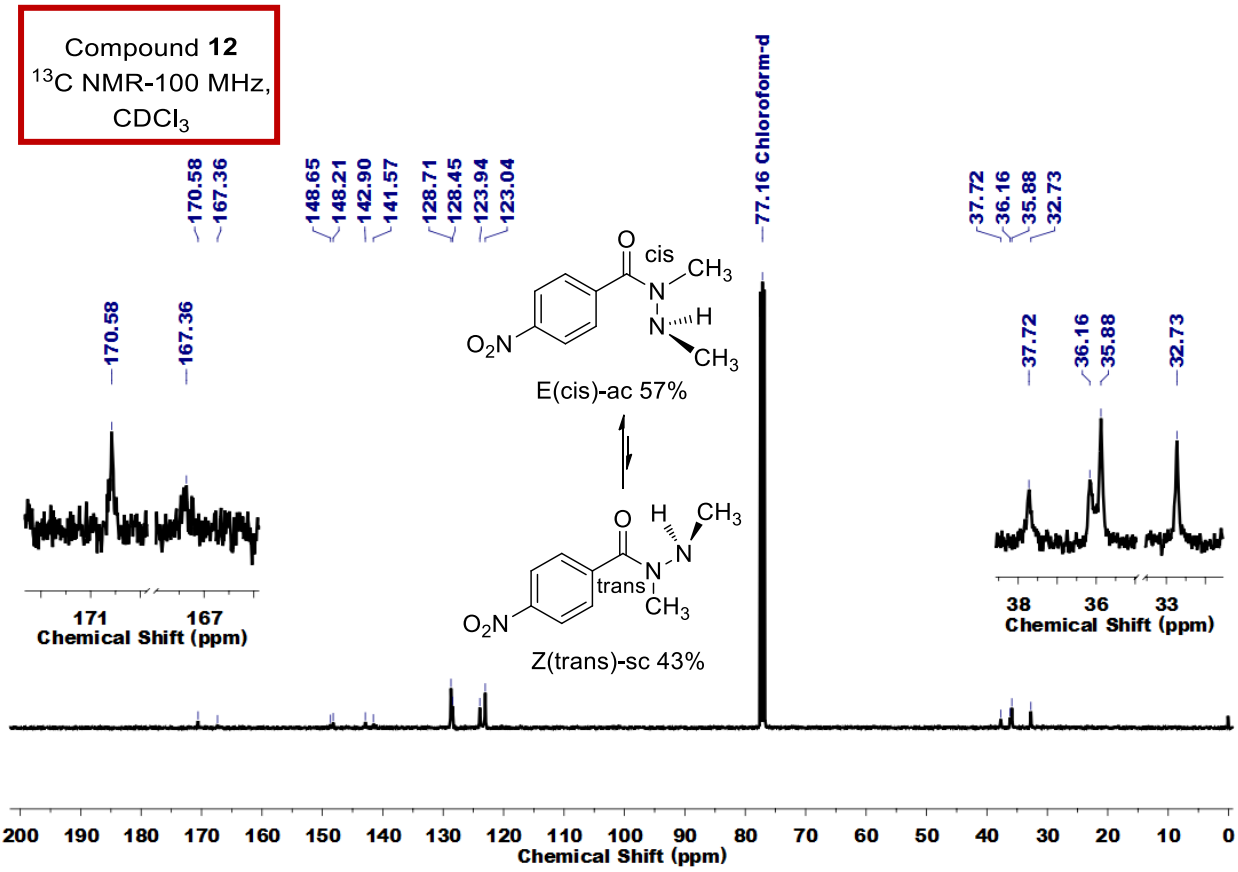


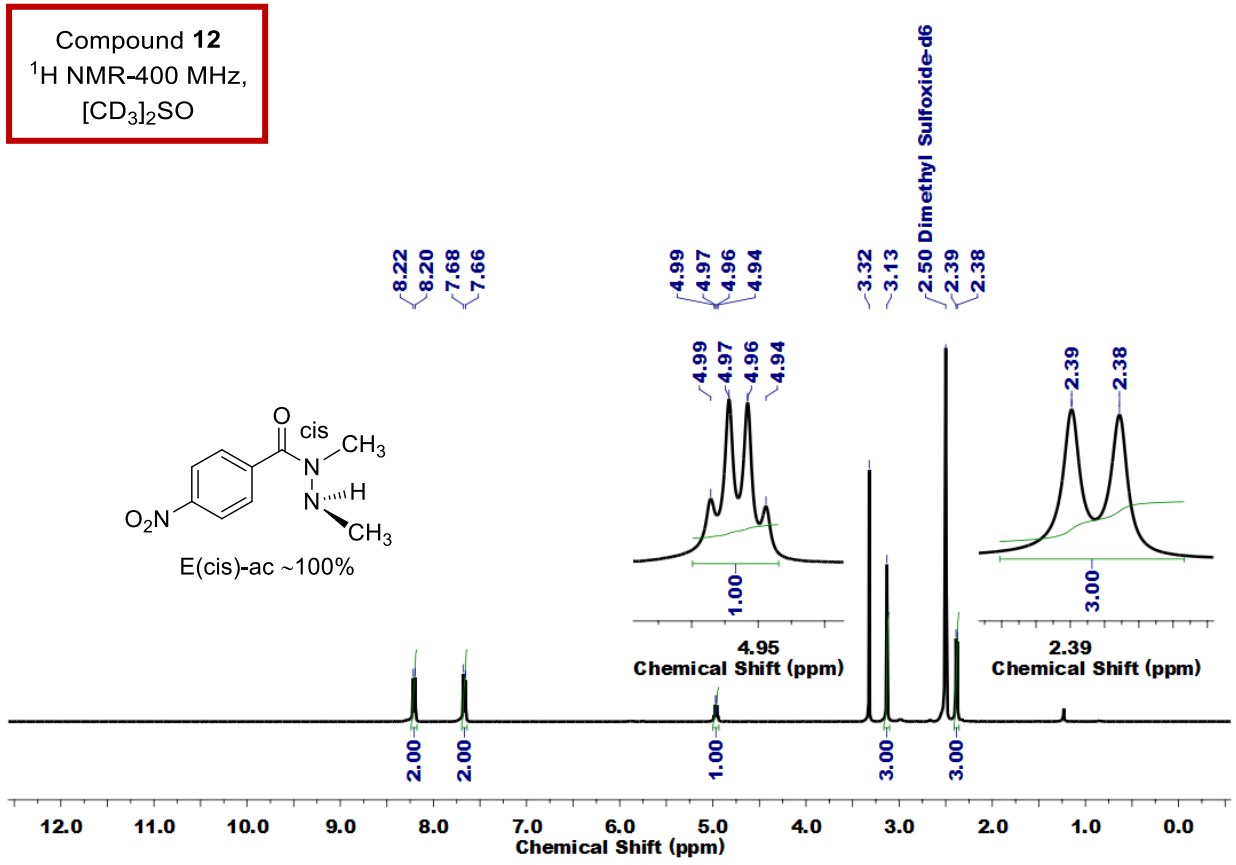
Compound **11**
^{1}H NMR-400 MHz,
D_2O



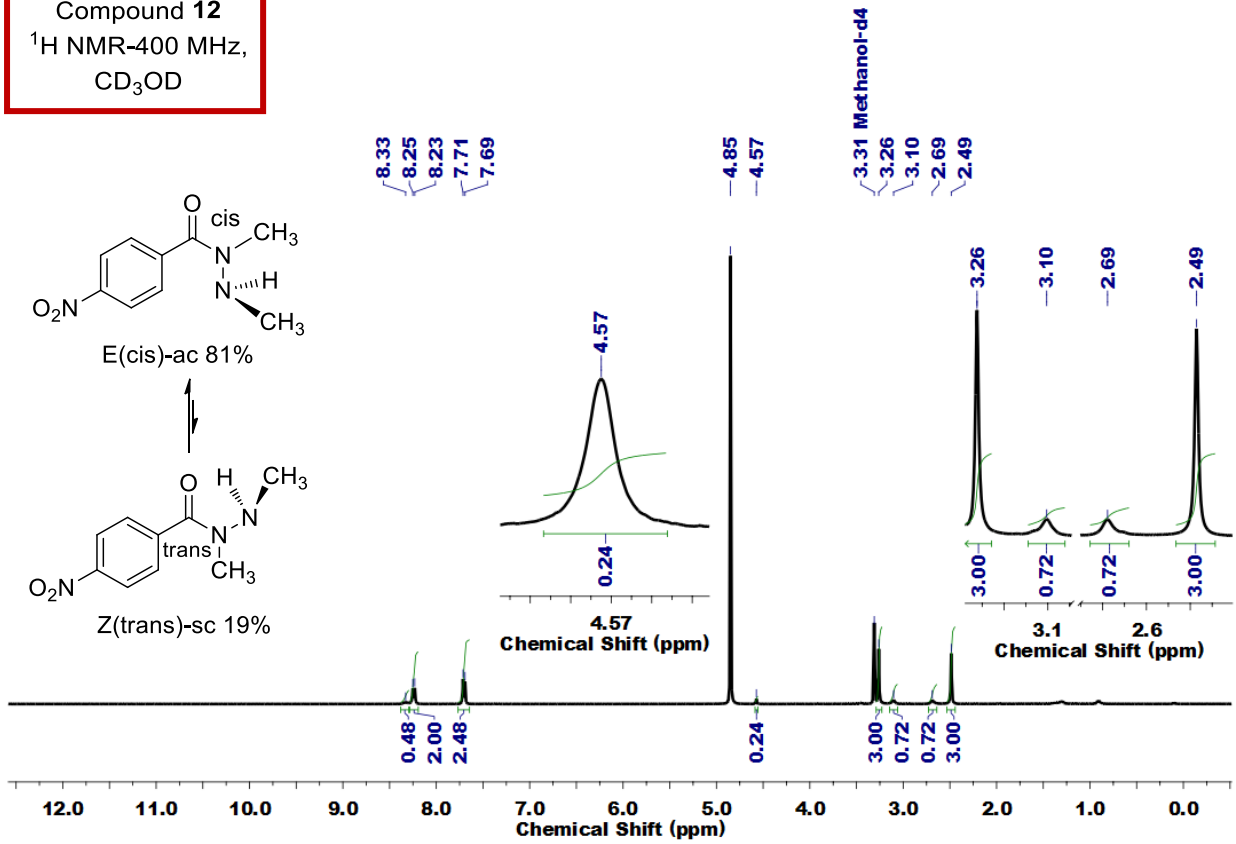
Compound **12**
^{1}H NMR-400 MHz,
$CDCl_3$



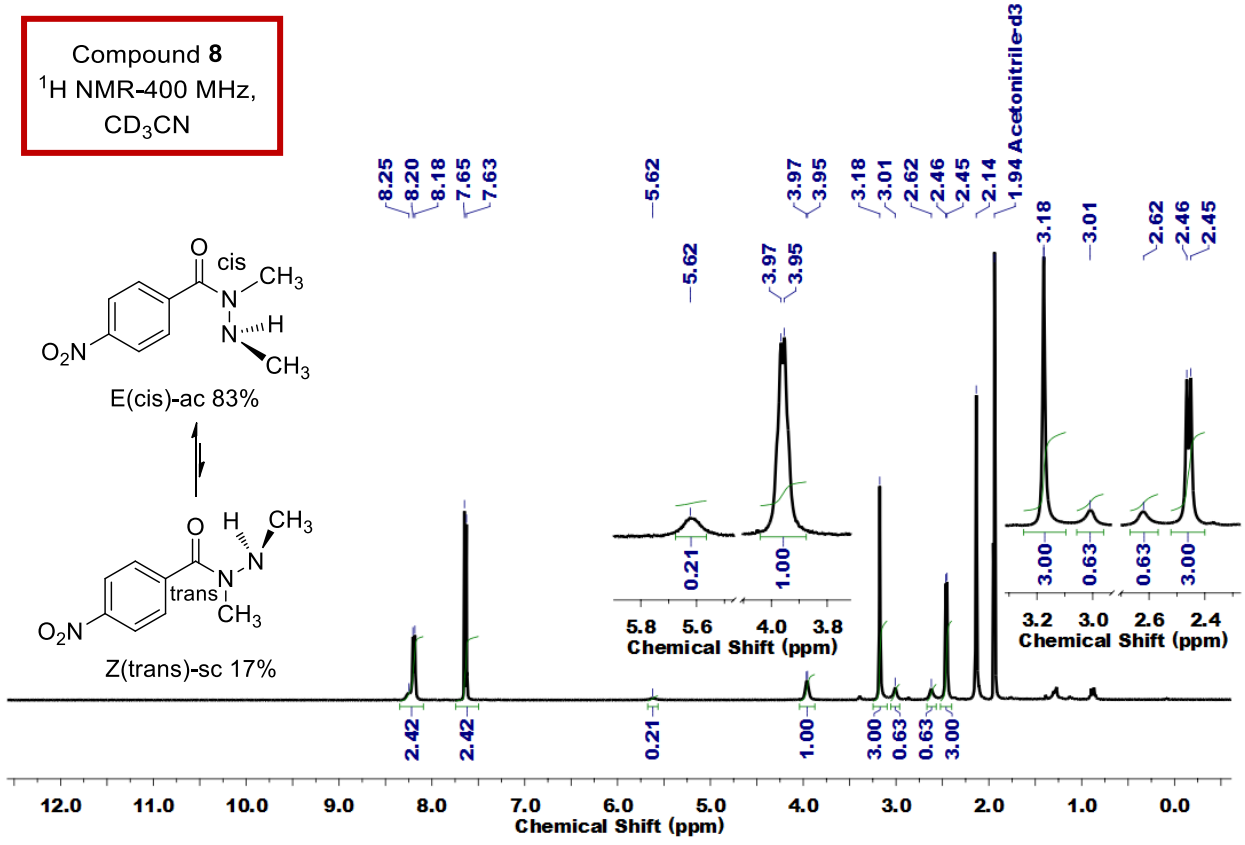

Compound 12
13C NMR-100 MHz,
CDCl3
170.58
167.36
148.65
148.21
142.90
141.57
128.71
128.45
123.94
123.04
77.16 Chloroform-d
37.72
36.16
35.88
32.73
cis
trans
E(cis)-ac 57%
Z(trans)-sc 43%
171
167
Chemical Shift (ppm)
38
36
33
Chemical Shift (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)


Compound 12
1H NMR-400 MHz,
[CD3]2SO
8.22
8.20
7.68
7.66
4.99
4.97
4.96
4.94
3.32
3.13
2.50 Dimethyl Sulfoxide-d6
2.39
2.38
cis
E(cis)-ac ~100%
1.00
4.95
Chemical Shift (ppm)
3.00
2.39
Chemical Shift (ppm)
2.00
2.00
1.00
3.00
3.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
Chemical Shift (ppm)

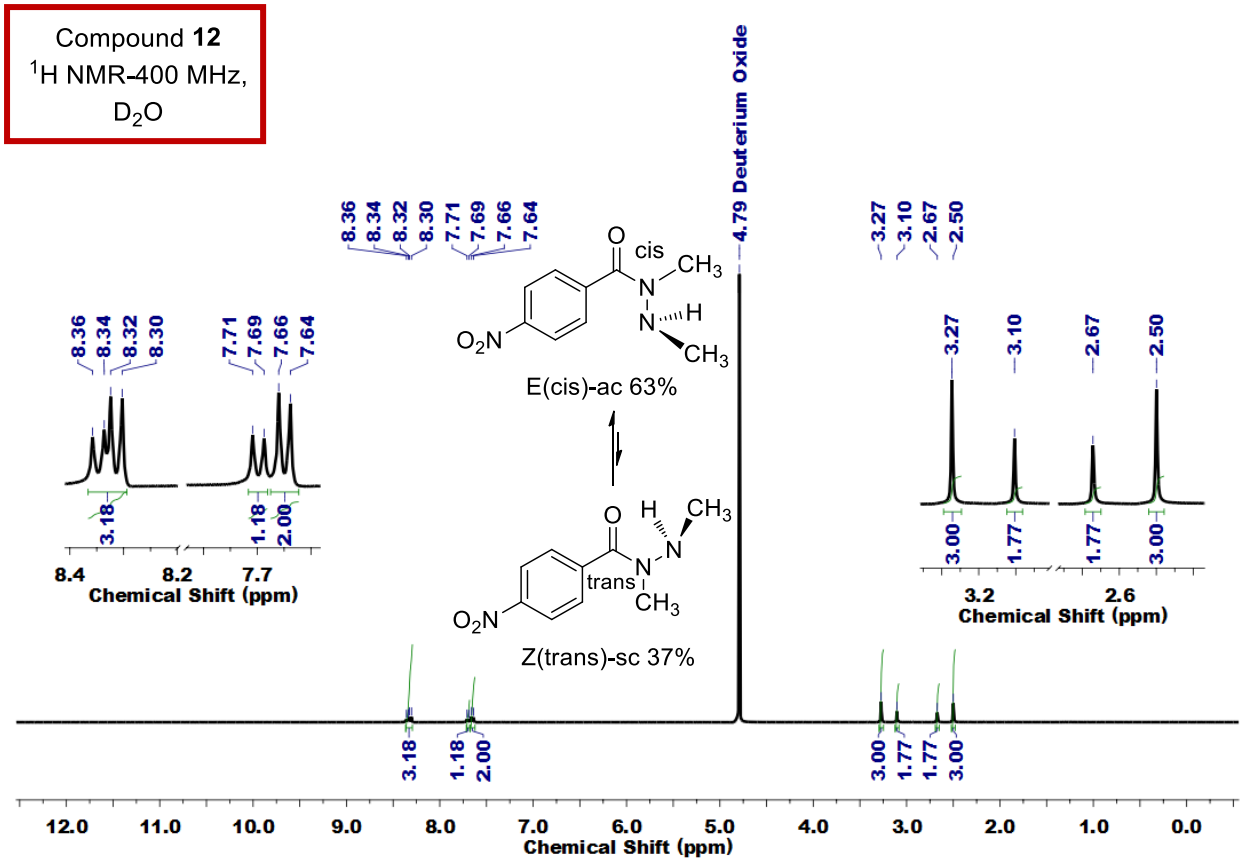
Compound **12**
^{1}H NMR-400 MHz,
CD_3OD



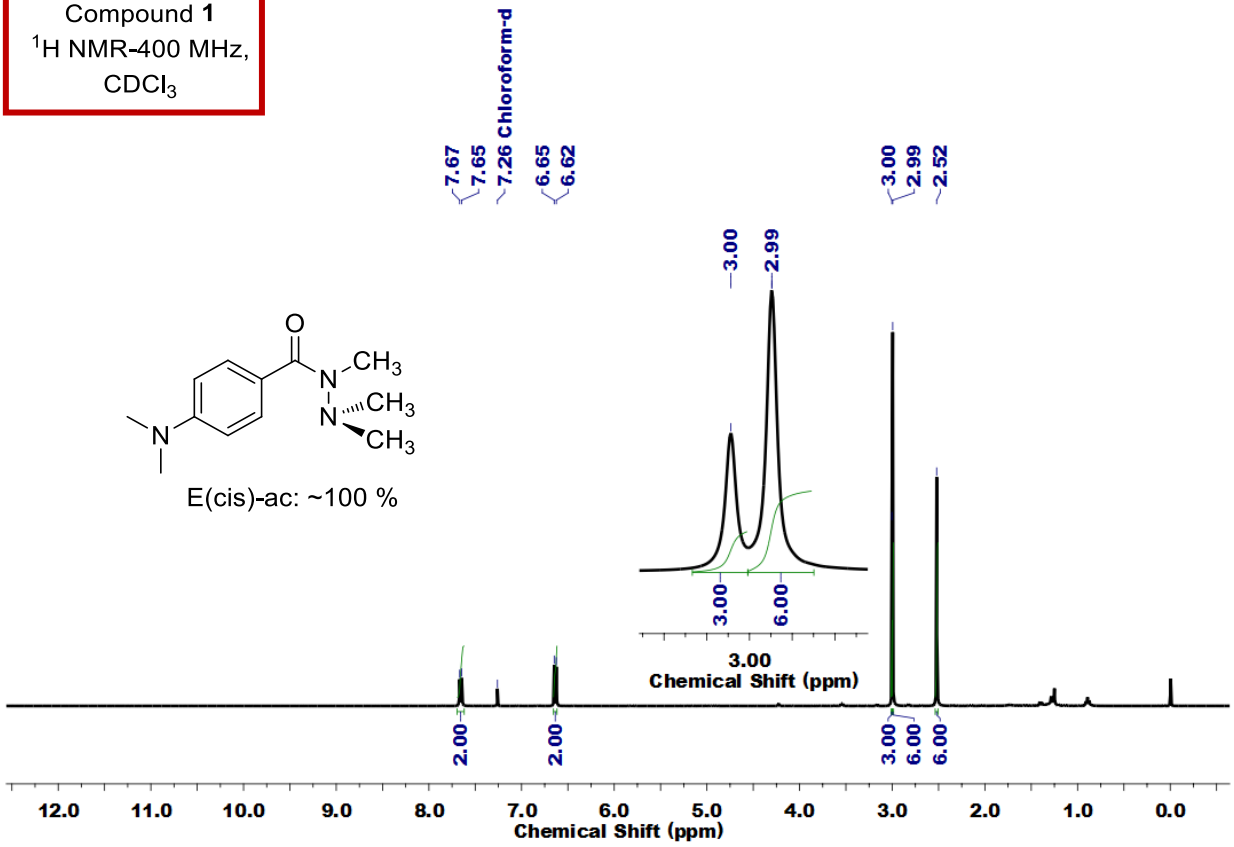
Compound **8**
^{1}H NMR-400 MHz,
CD_3CN



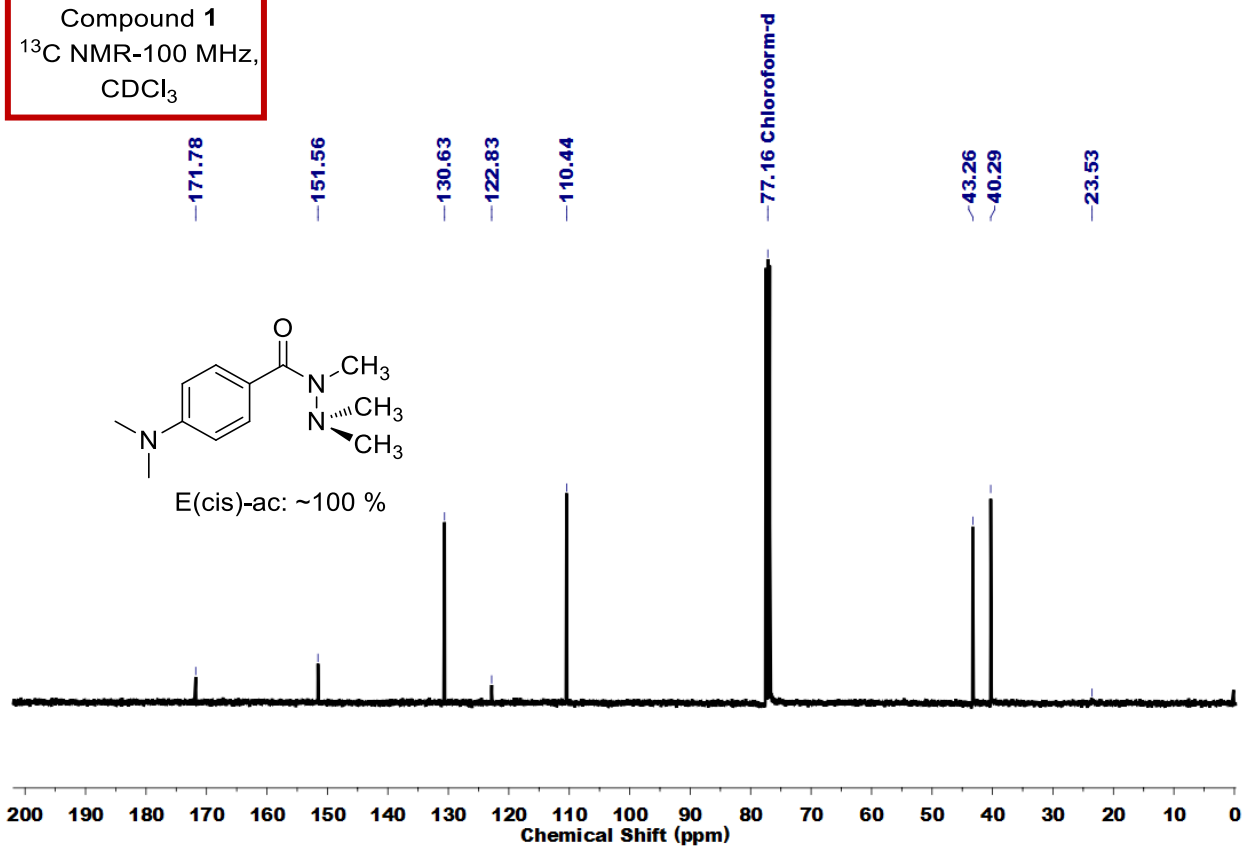
Compound **12**
^{1}H NMR-400 MHz,
D_2O



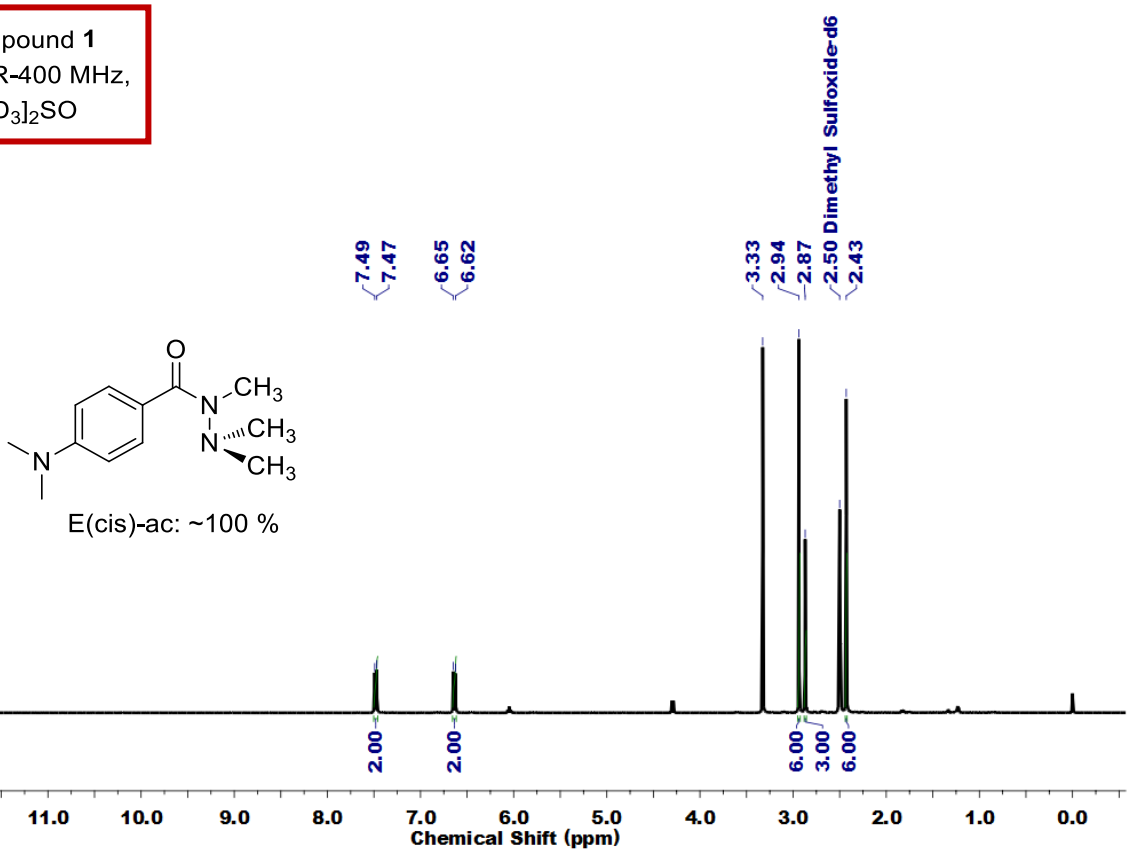
Compound **1**
^{1}H NMR-400 MHz,
$CDCl_3$



Compound **1**
^{13}C NMR-100 MHz,
$CDCl_3$

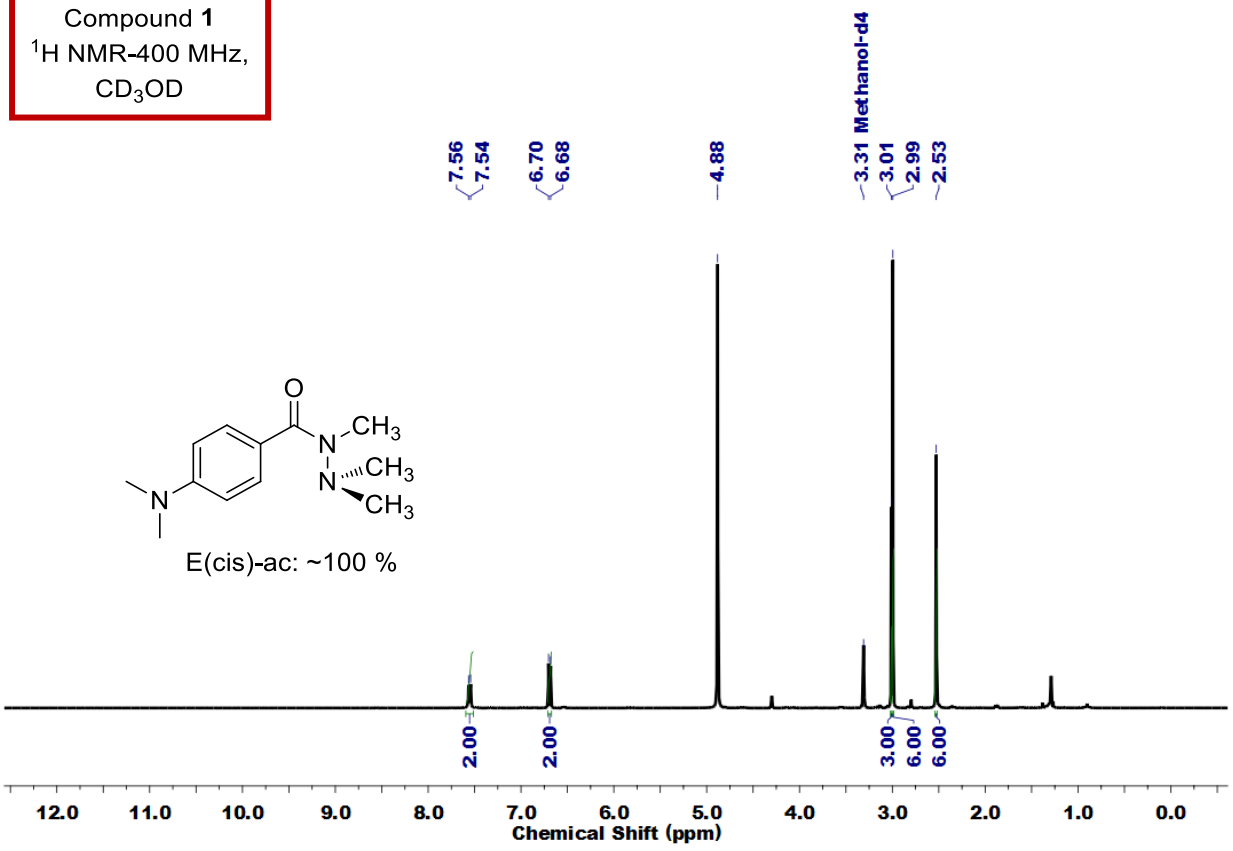


Compound **1**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



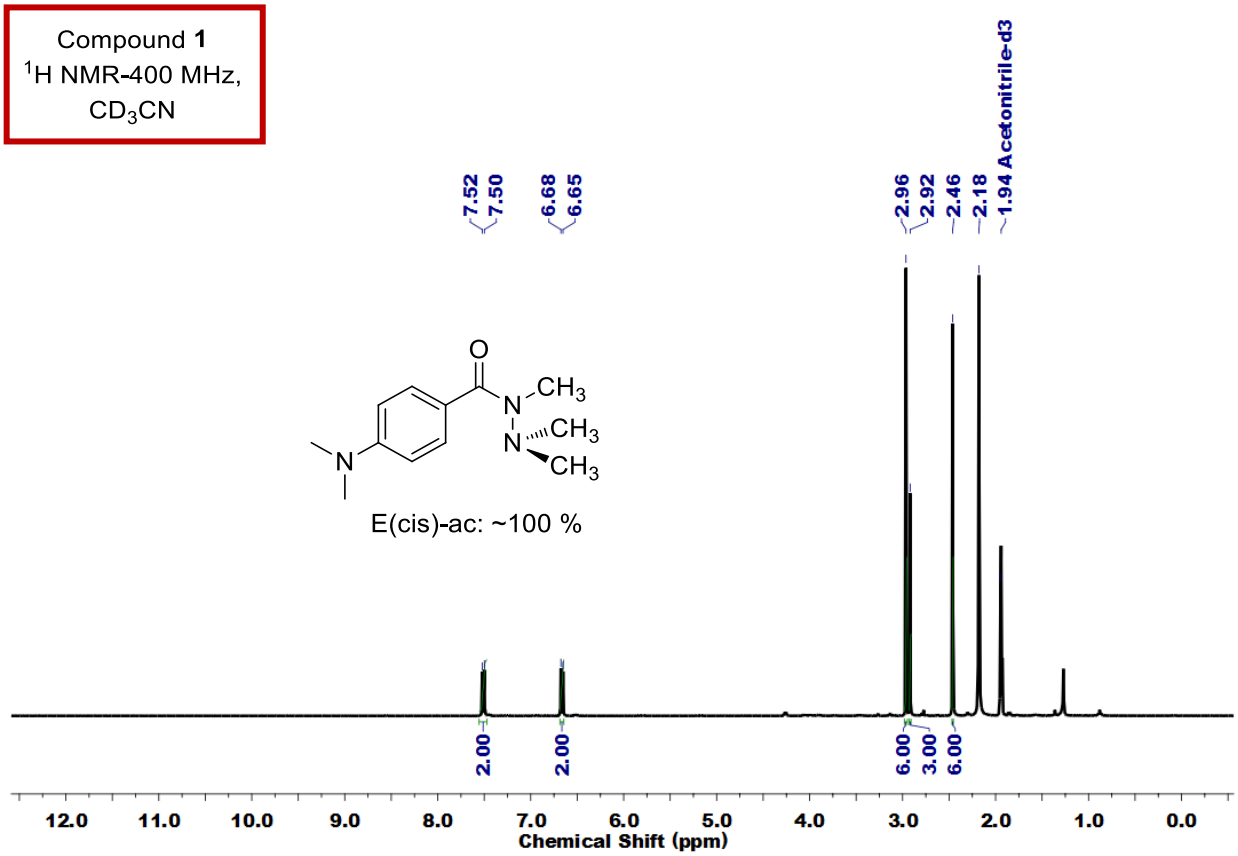
E(cis)-ac: ~100 %

Compound **1**
^{1}H NMR-400 MHz,
CD_3OD



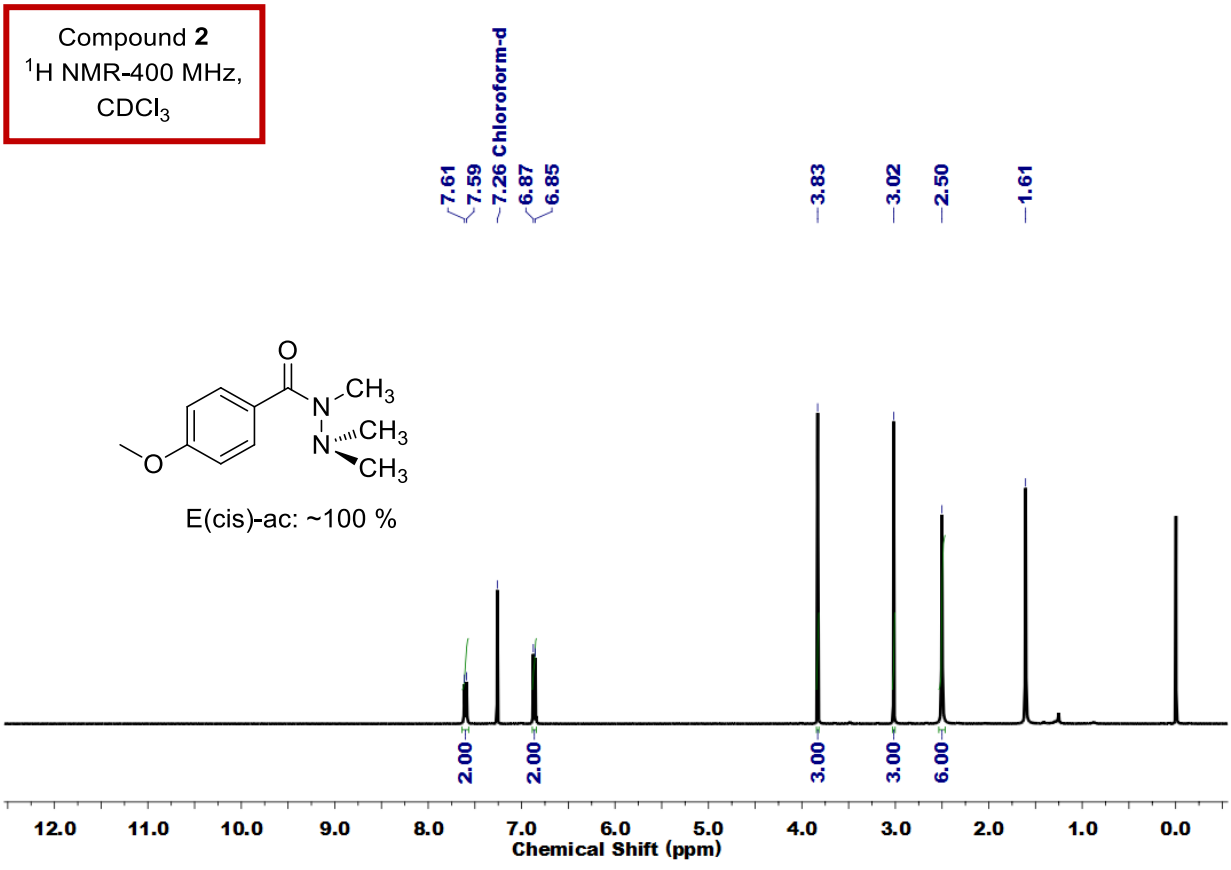
E(cis)-ac: ~100 %

Compound **1**
^{1}H NMR-400 MHz,
CD_3CN

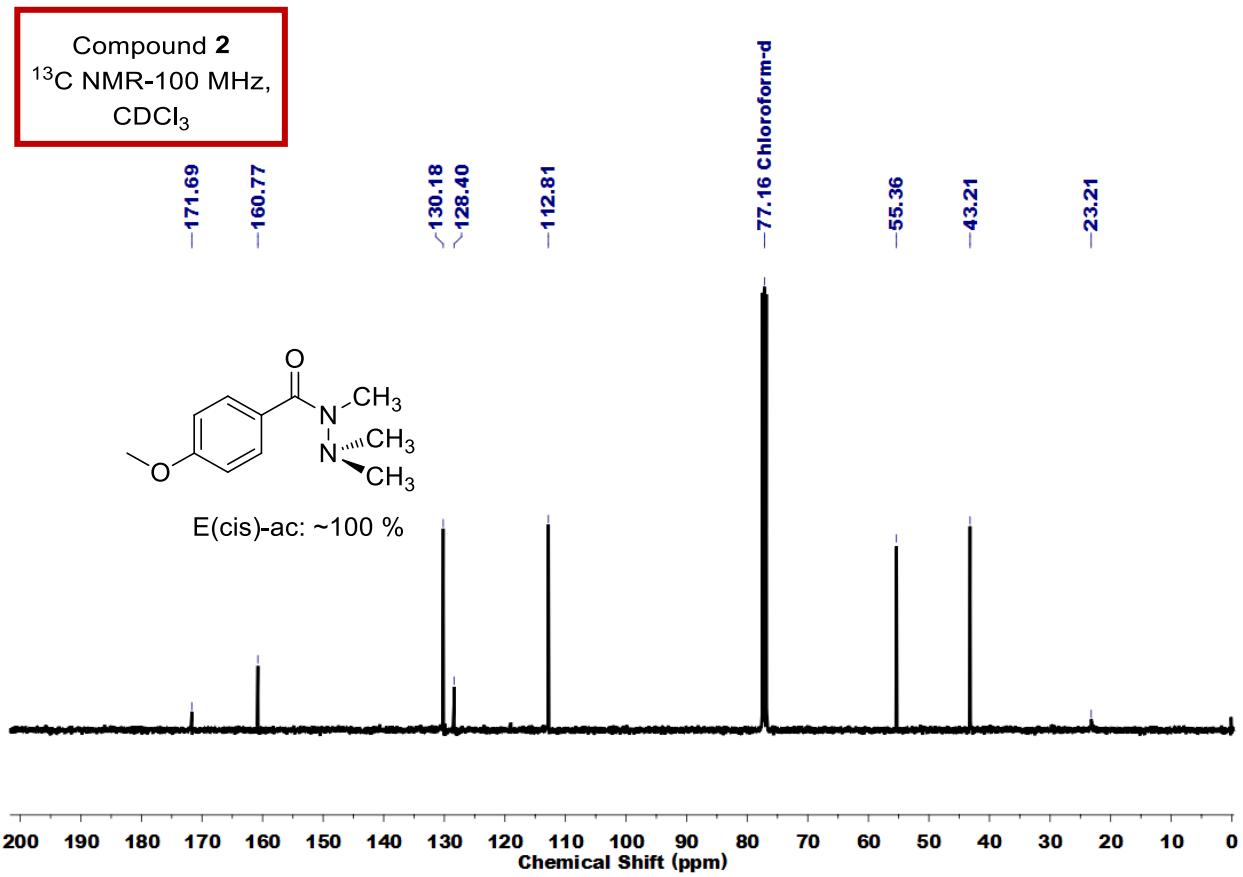


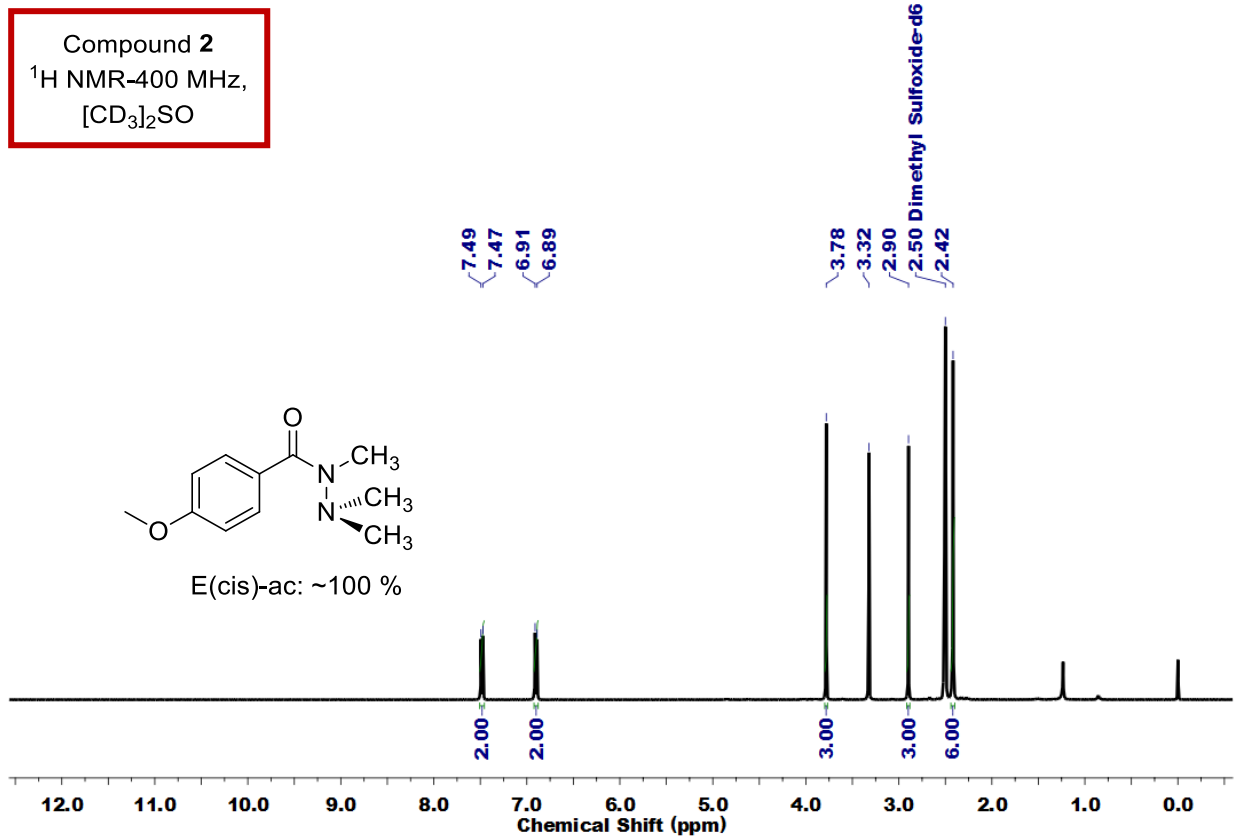
E(cis)-ac: ~100 %

Compound **2**
^{1}H NMR-400 MHz,
$CDCl_3$

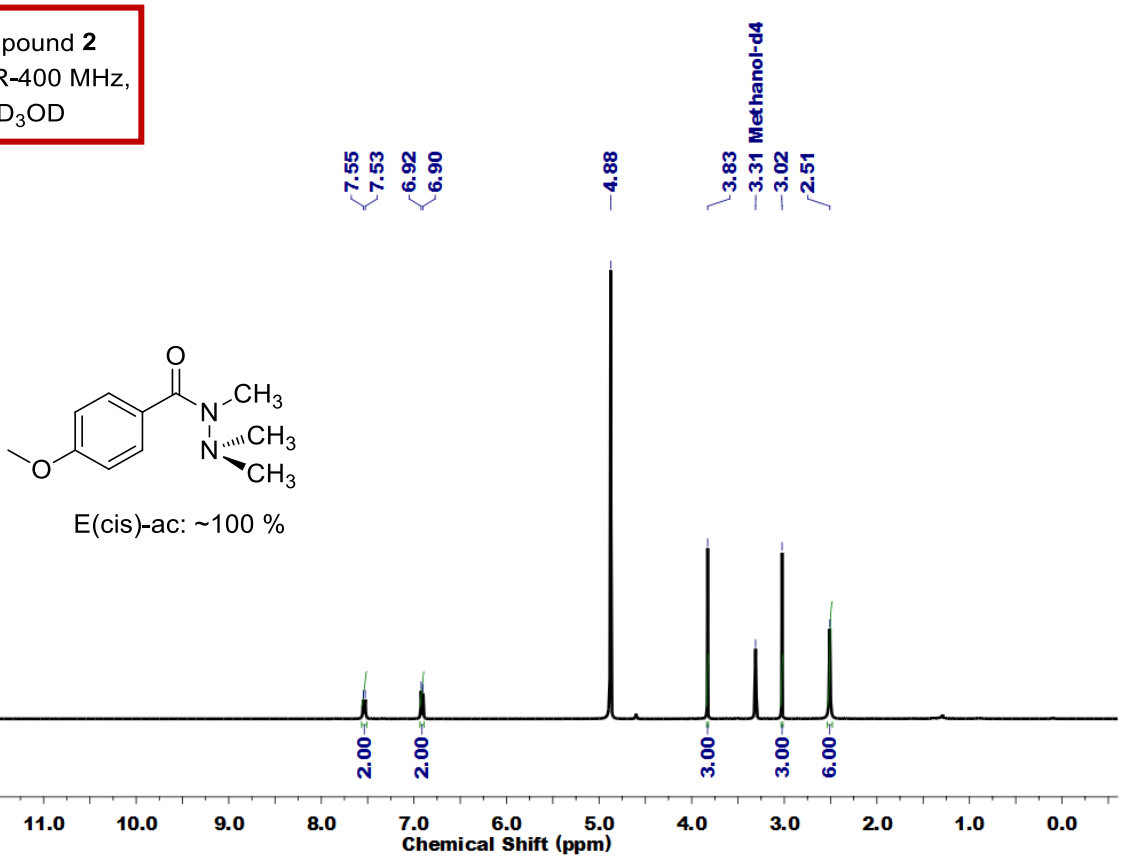


E(cis)-ac: ~100 %


Compound 2
13C NMR-100 MHz,
CDCl3
171.69
160.77
130.18
128.40
112.81
77.16 Chloroform-d
55.36
43.21
23.21
O
N
CH3
N
CH3
CH3
O
E(cis)-ac: ~100 %
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

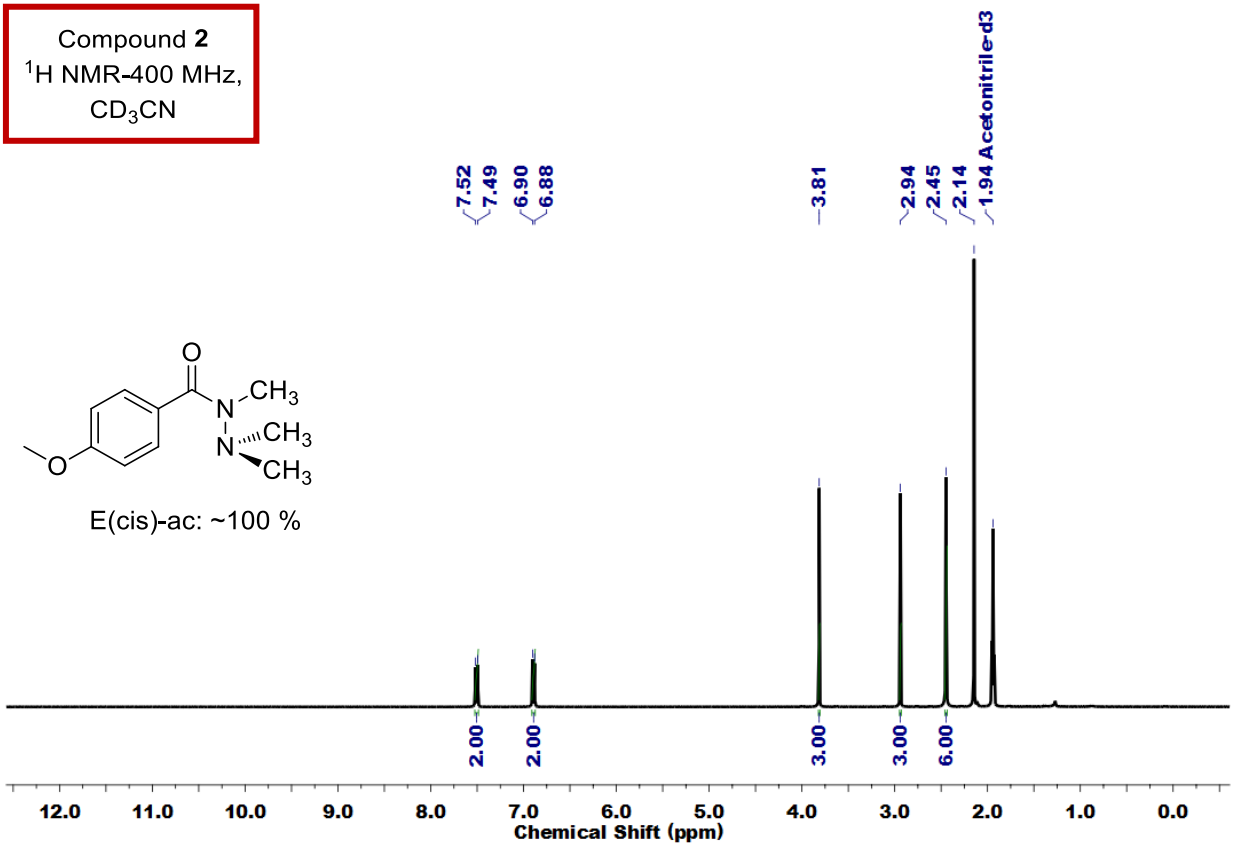

Compound 2
1H NMR-400 MHz,
[CD3]2SO
7.49
7.47
6.91
6.89
3.78
3.32
2.90
2.50 Dimethyl Sulfoxide-d6
2.42
O
N
CH3
N
CH3
CH3
O
E(cis)-ac: ~100 %
2.00
2.00
3.00
3.00
6.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
Chemical Shift (ppm)

Compound **2**
^{1}H NMR-400 MHz,
CD_3OD



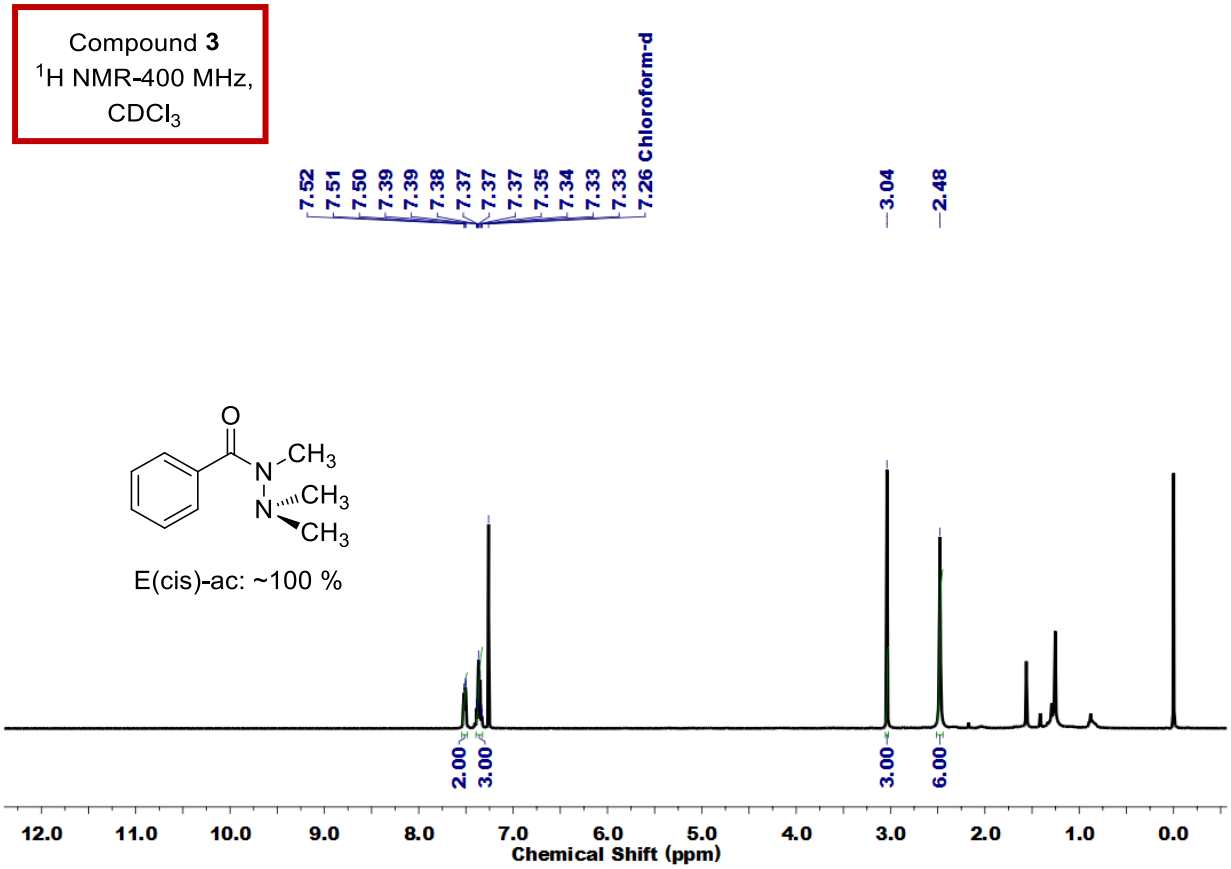
E(cis)-ac: ~100 %

Compound **2**
^{1}H NMR-400 MHz,
CD_3CN

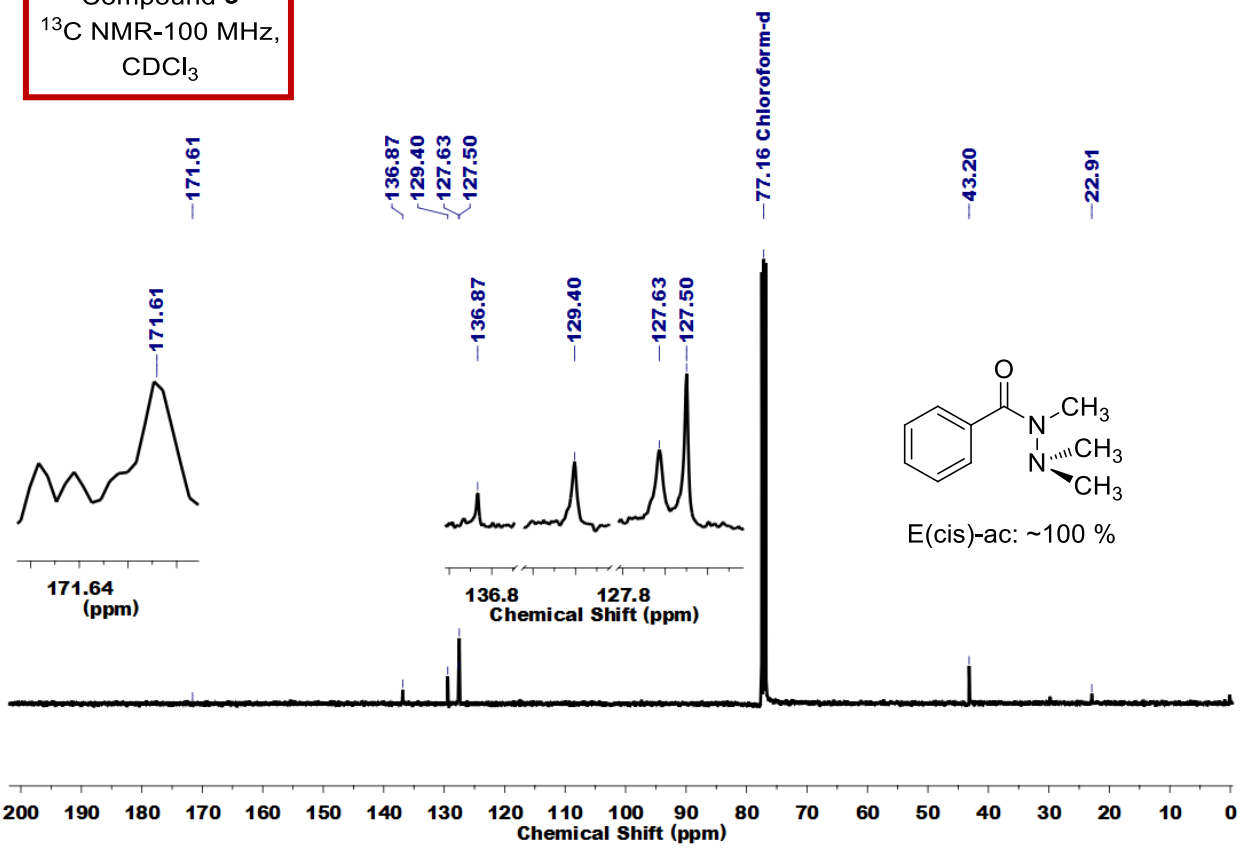


E(cis)-ac: ~100 %

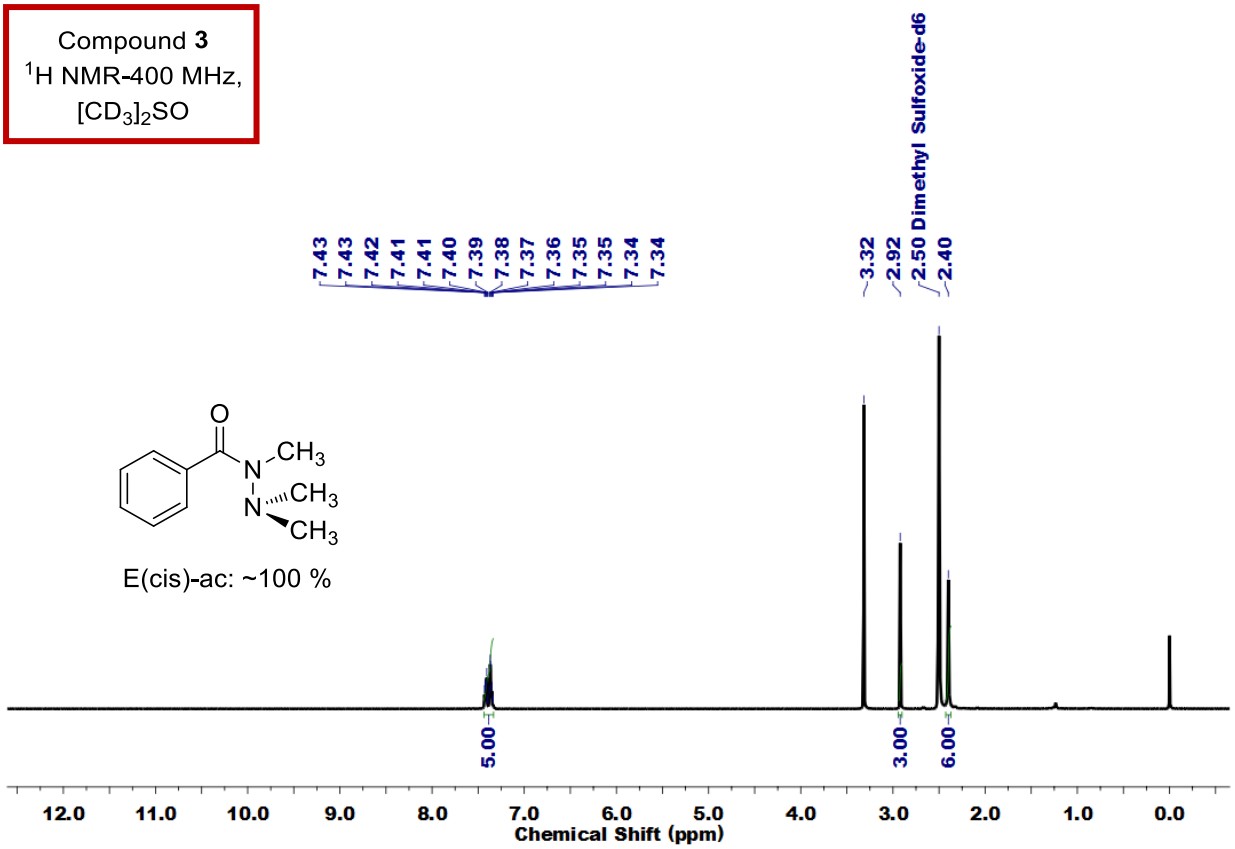
Compound **3**
^{1}H NMR-400 MHz,
$CDCl_3$



Compound **3**
^{13}C NMR-100 MHz,
$CDCl_3$

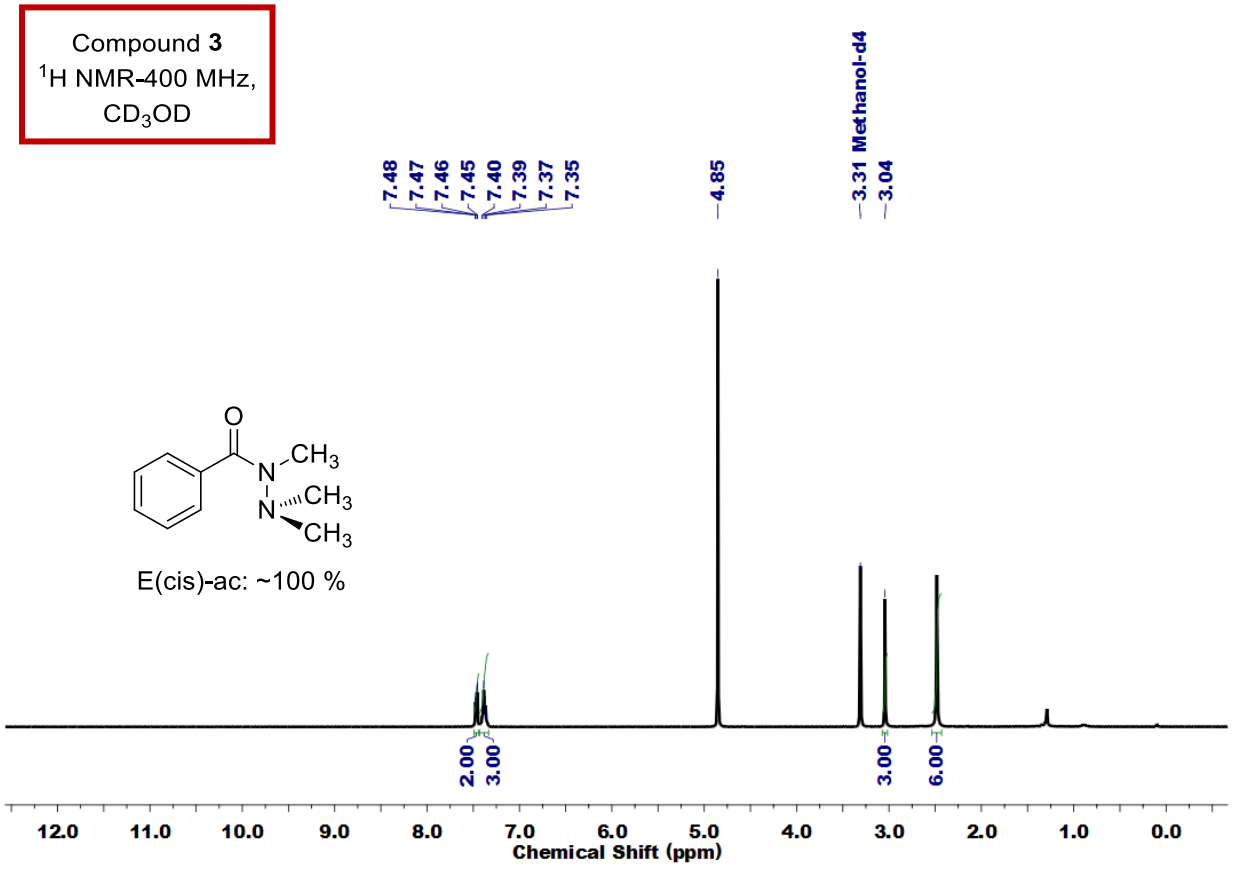


Compound **3**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



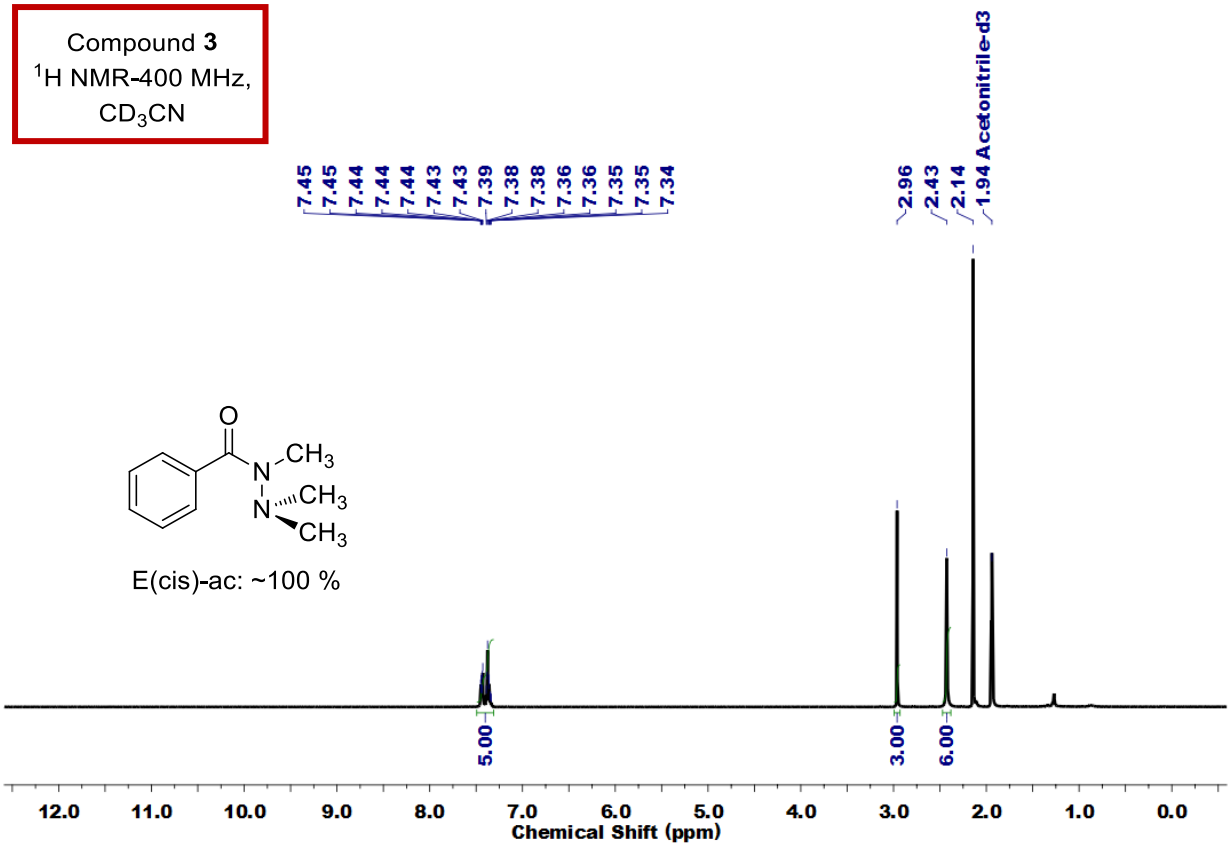
E(cis)-ac: ~100 %

Compound **3**
^{1}H NMR-400 MHz,
CD_3OD



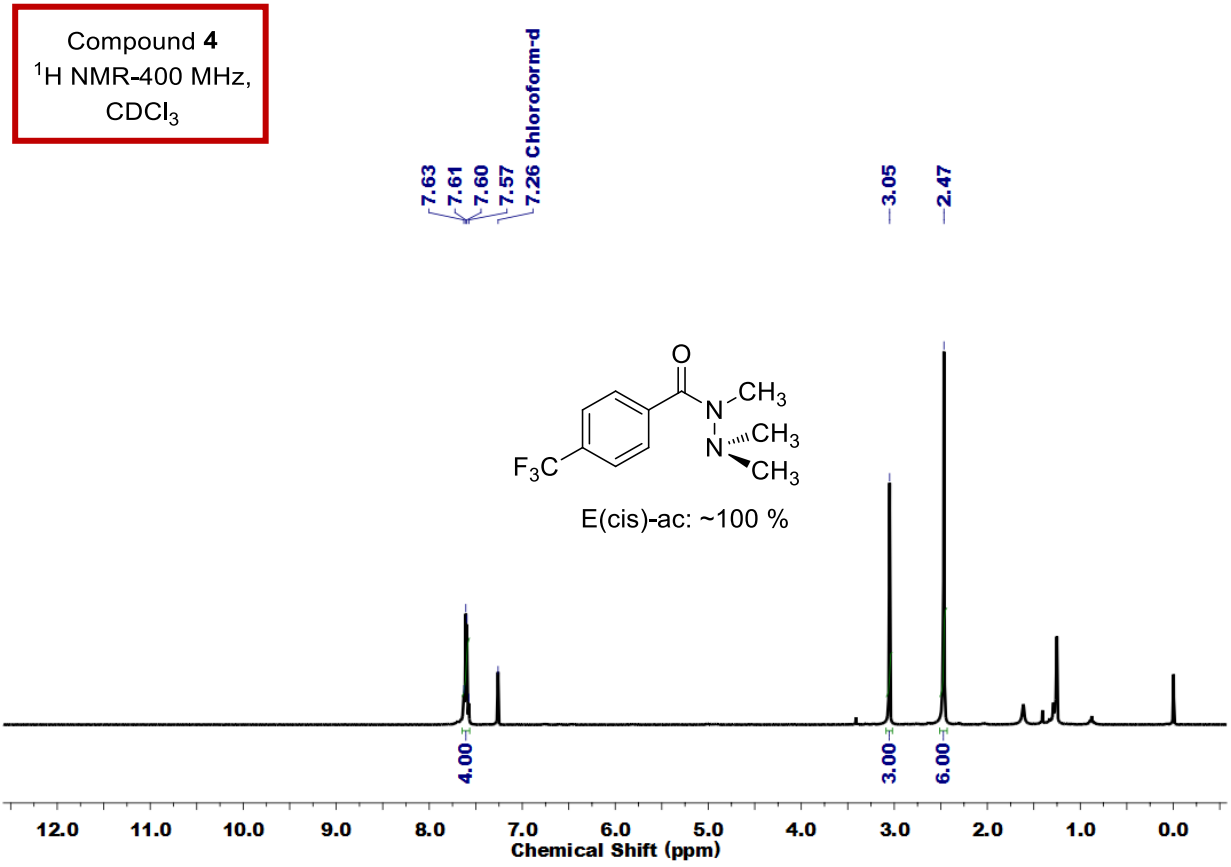
E(cis)-ac: ~100 %

Compound **3**
^{1}H NMR-400 MHz,
CD_3CN



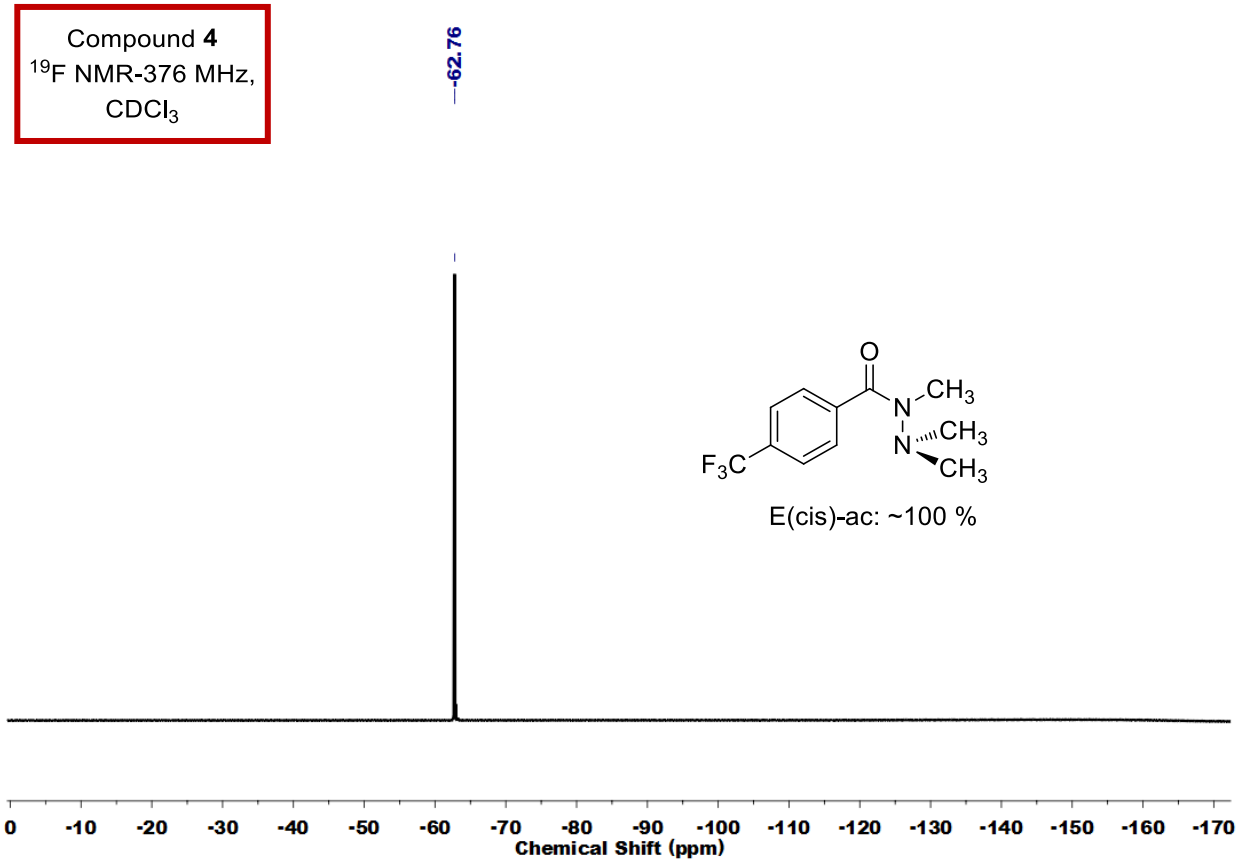
E(cis)-ac: ~100 %

Compound **4**
^{1}H NMR-400 MHz,
$CDCl_3$

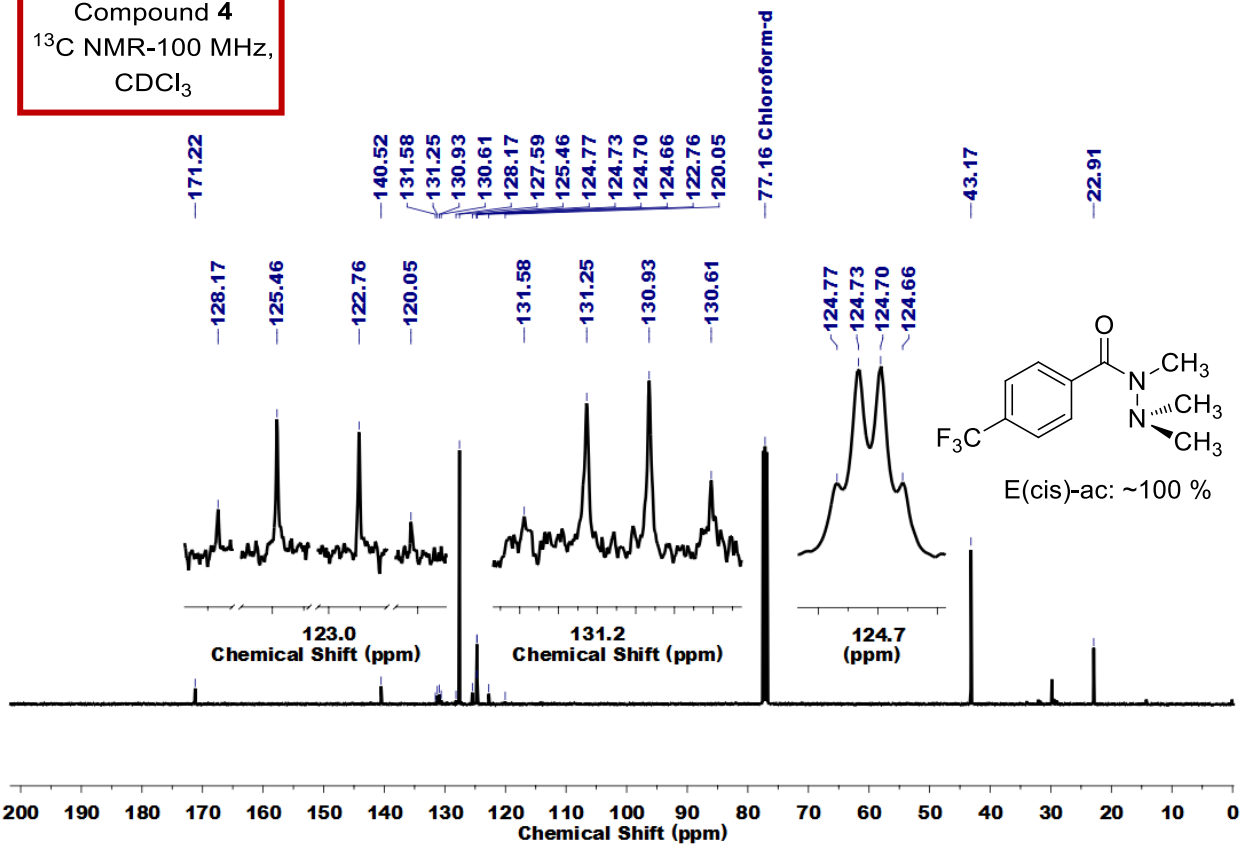


E(cis)-ac: ~100 %

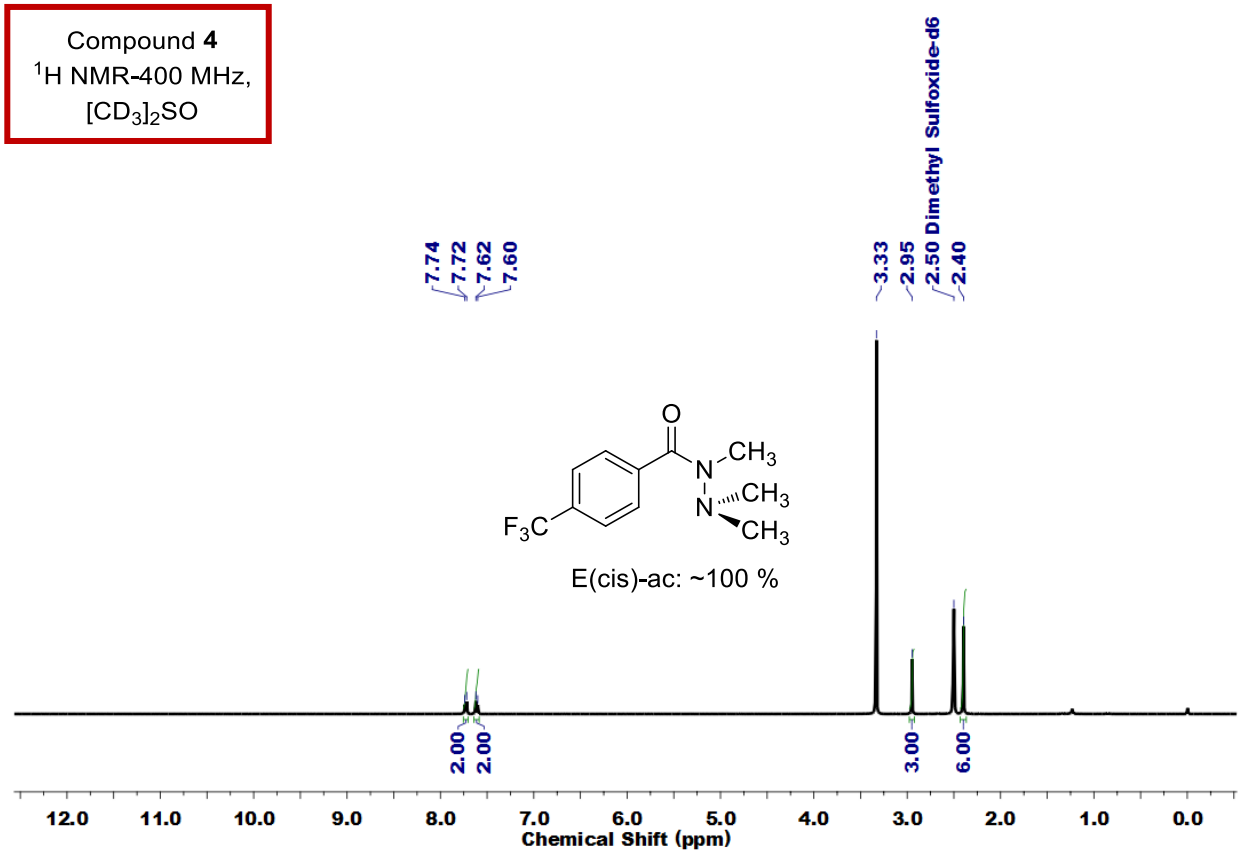
Compound **4**
^{19}F NMR-376 MHz,
$CDCl_3$



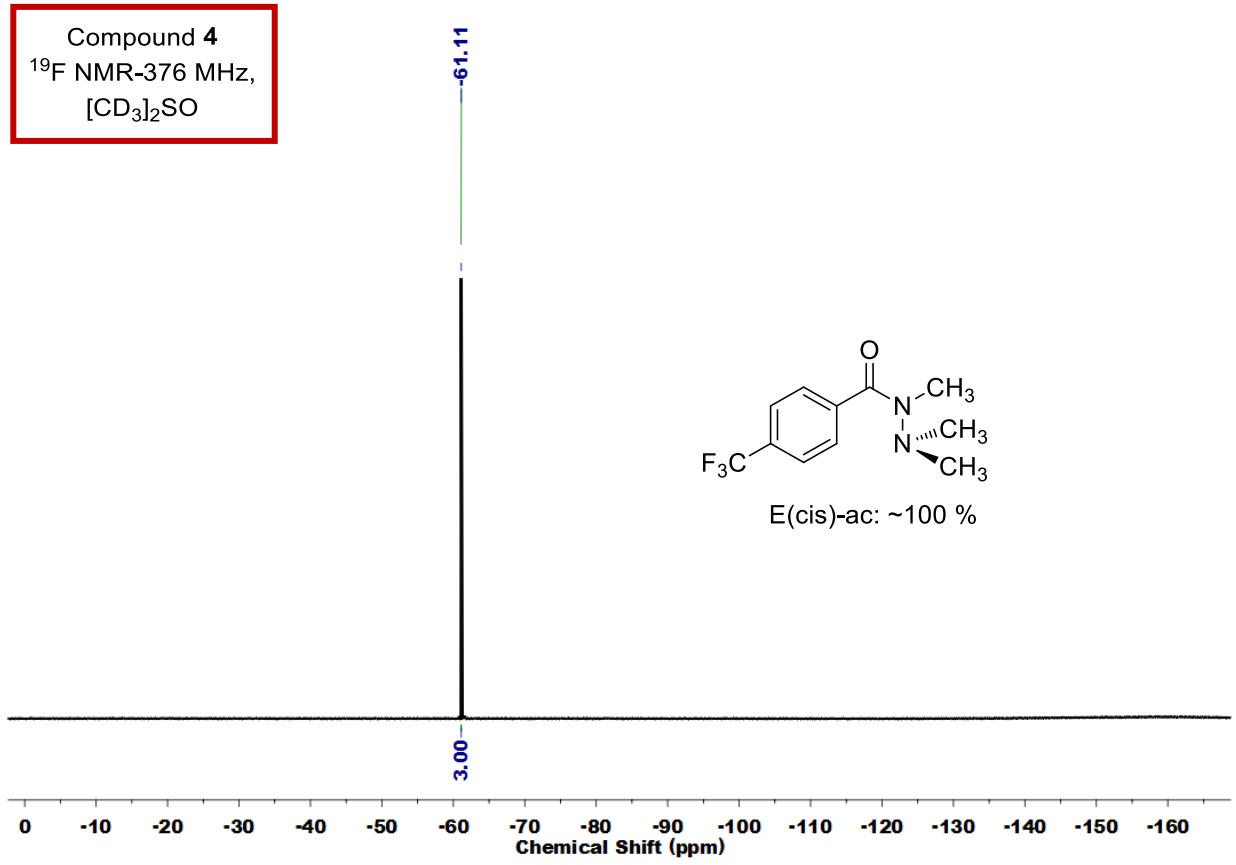
Compound **4**
^{13}C NMR-100 MHz,
$CDCl_3$



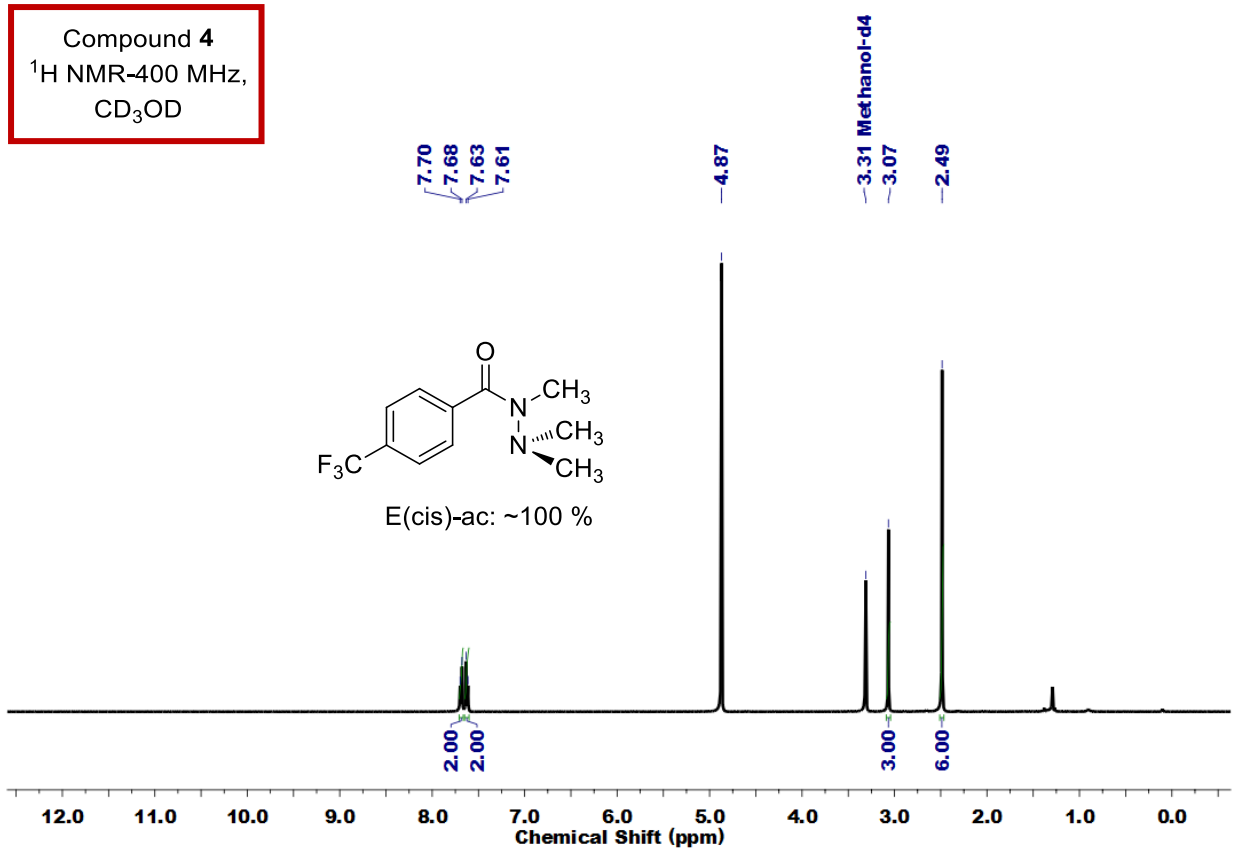
Compound **4**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



Compound **4**
^{19}F NMR-376 MHz,
$[CD_3]_2SO$

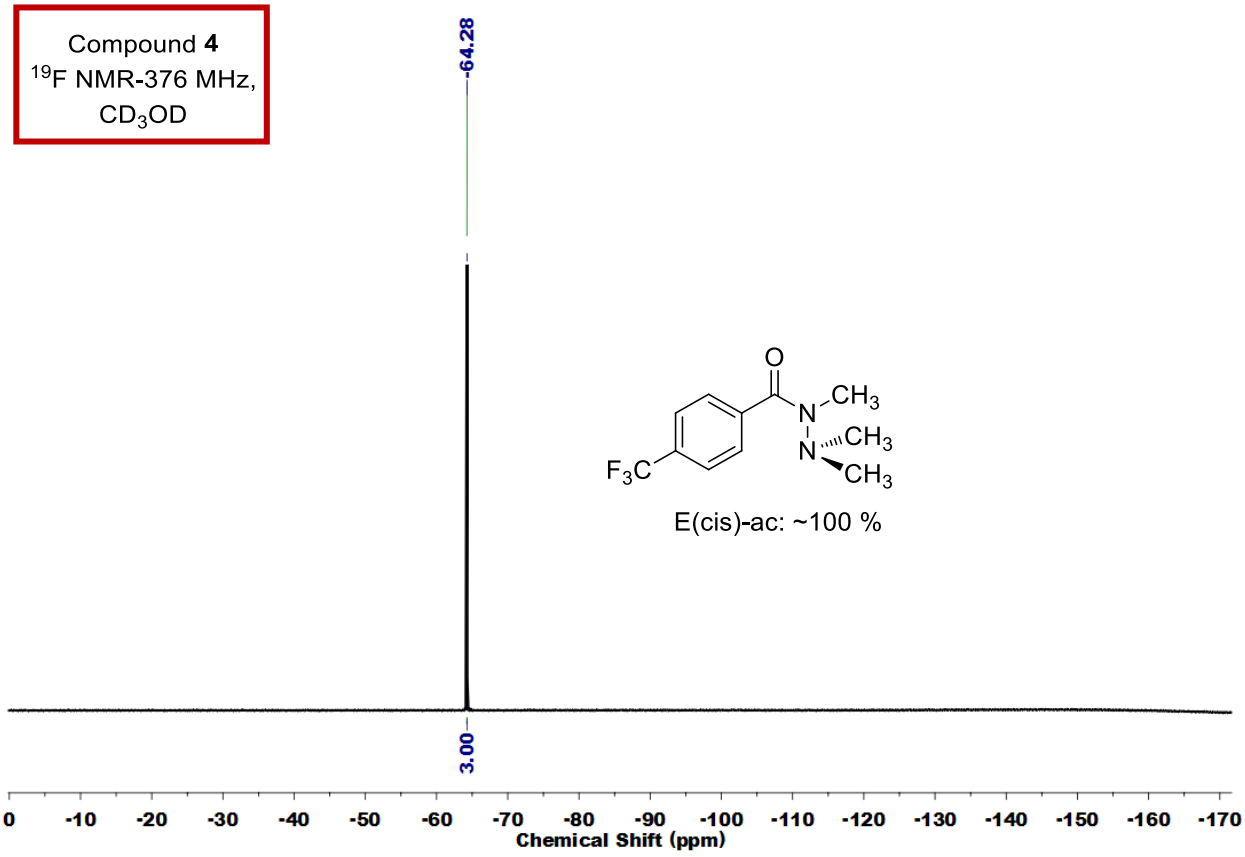


Compound **4**
^{1}H NMR-400 MHz,
CD_3OD



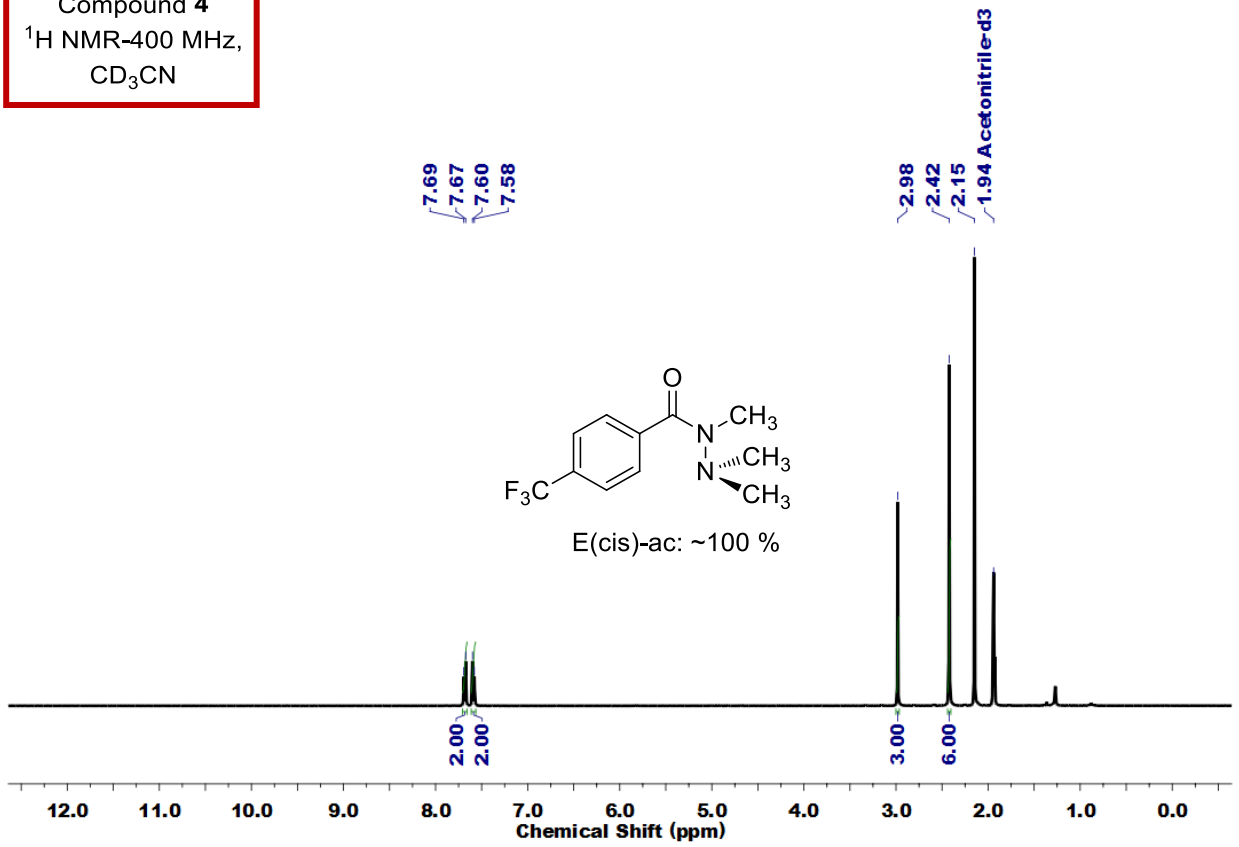
E(cis)-ac: ~100 %

Compound **4**
^{19}F NMR-376 MHz,
CD_3OD

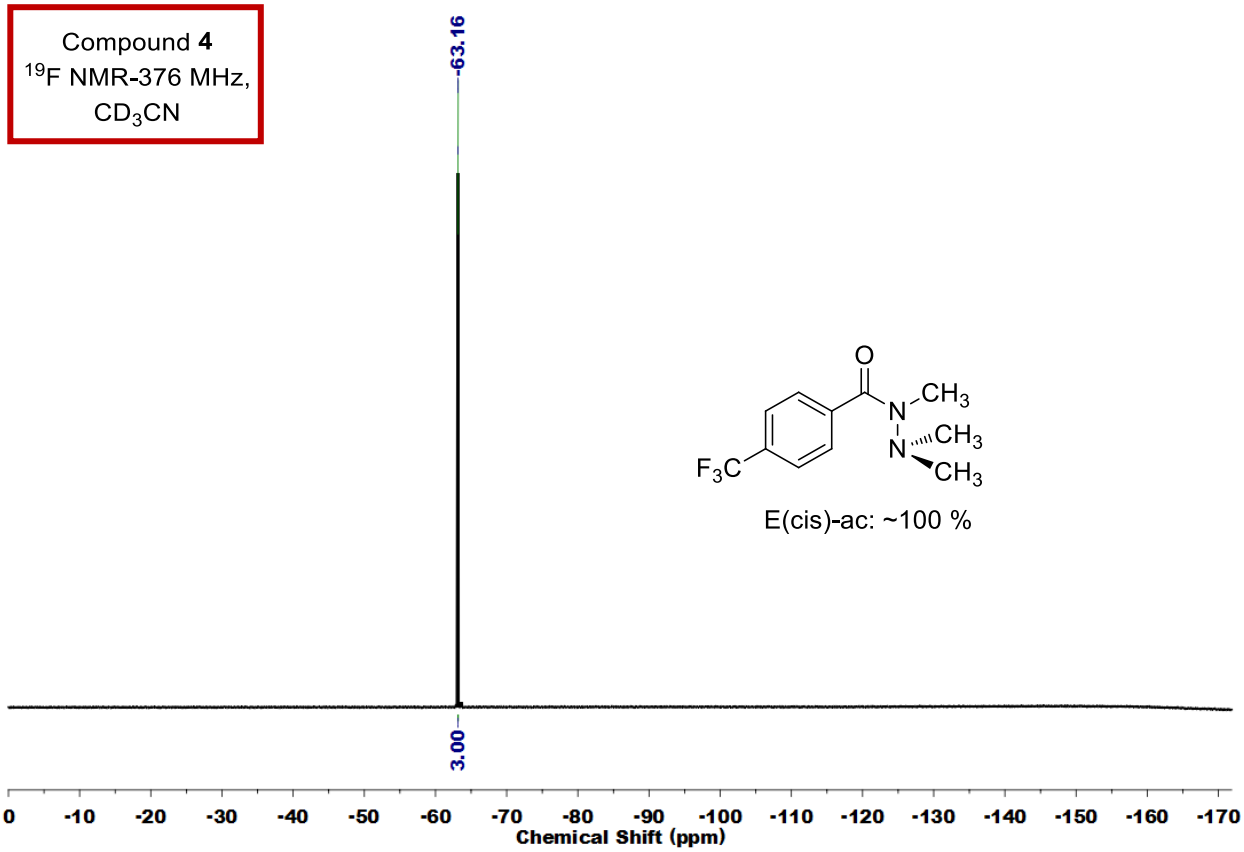


E(cis)-ac: ~100 %

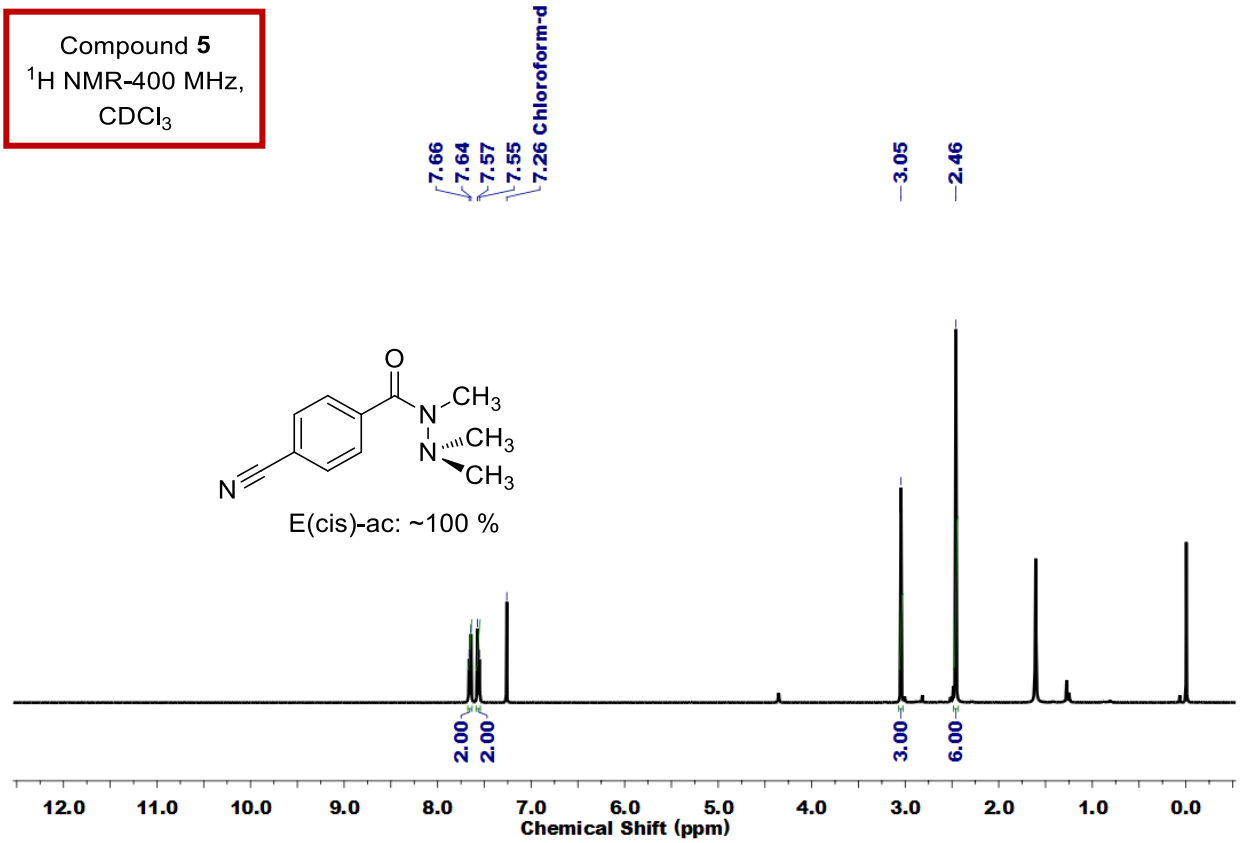
Compound **4**
^{1}H NMR-400 MHz,
CD_3CN



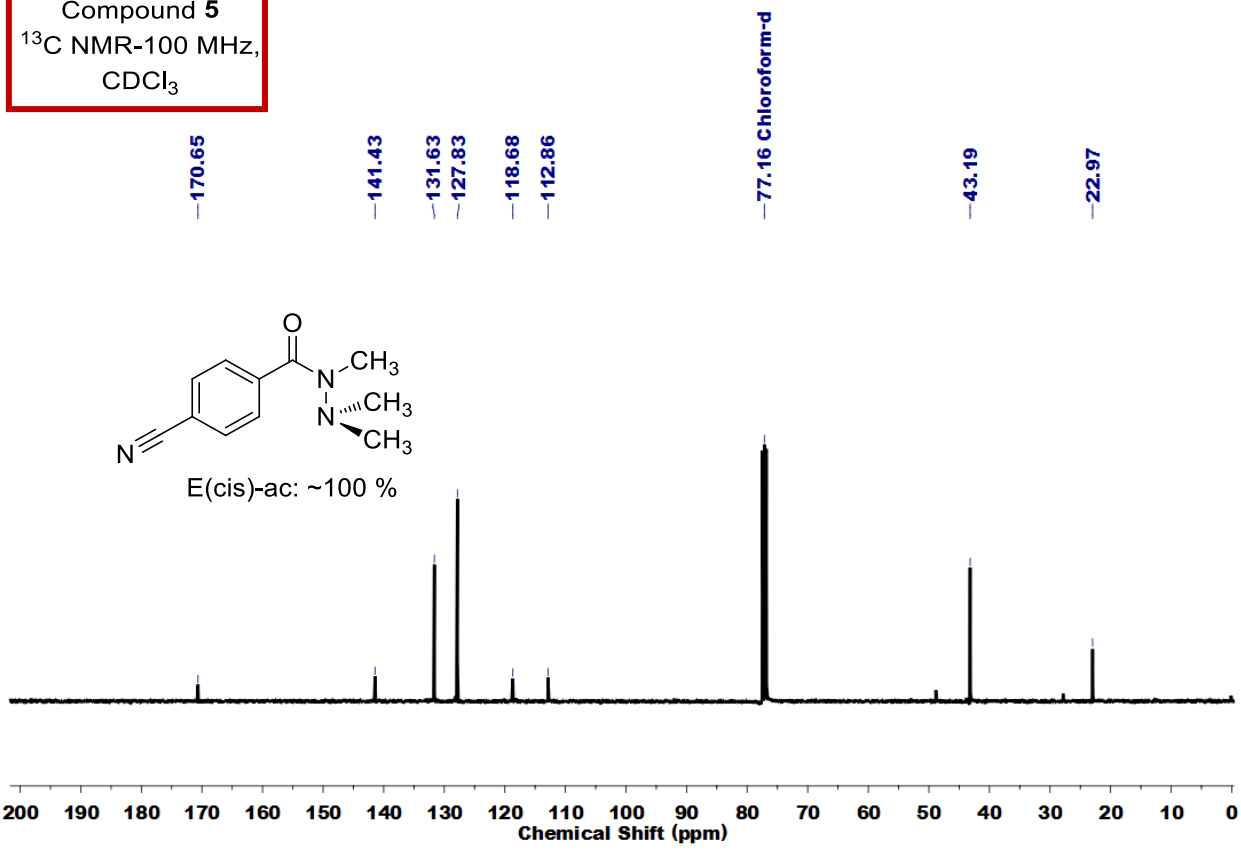
Compound **4**
^{19}F NMR-376 MHz,
CD_3CN



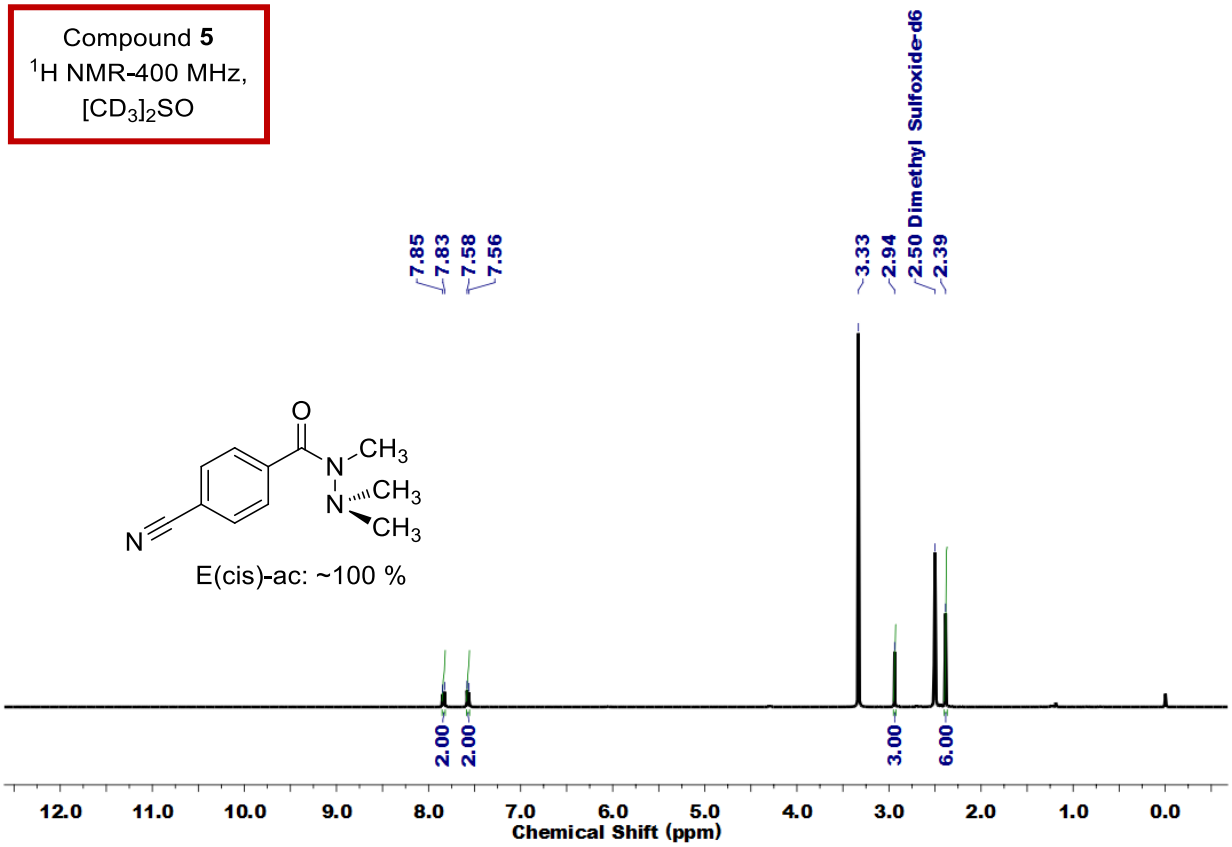
Compound **5**
^{1}H NMR-400 MHz,
$CDCl_3$



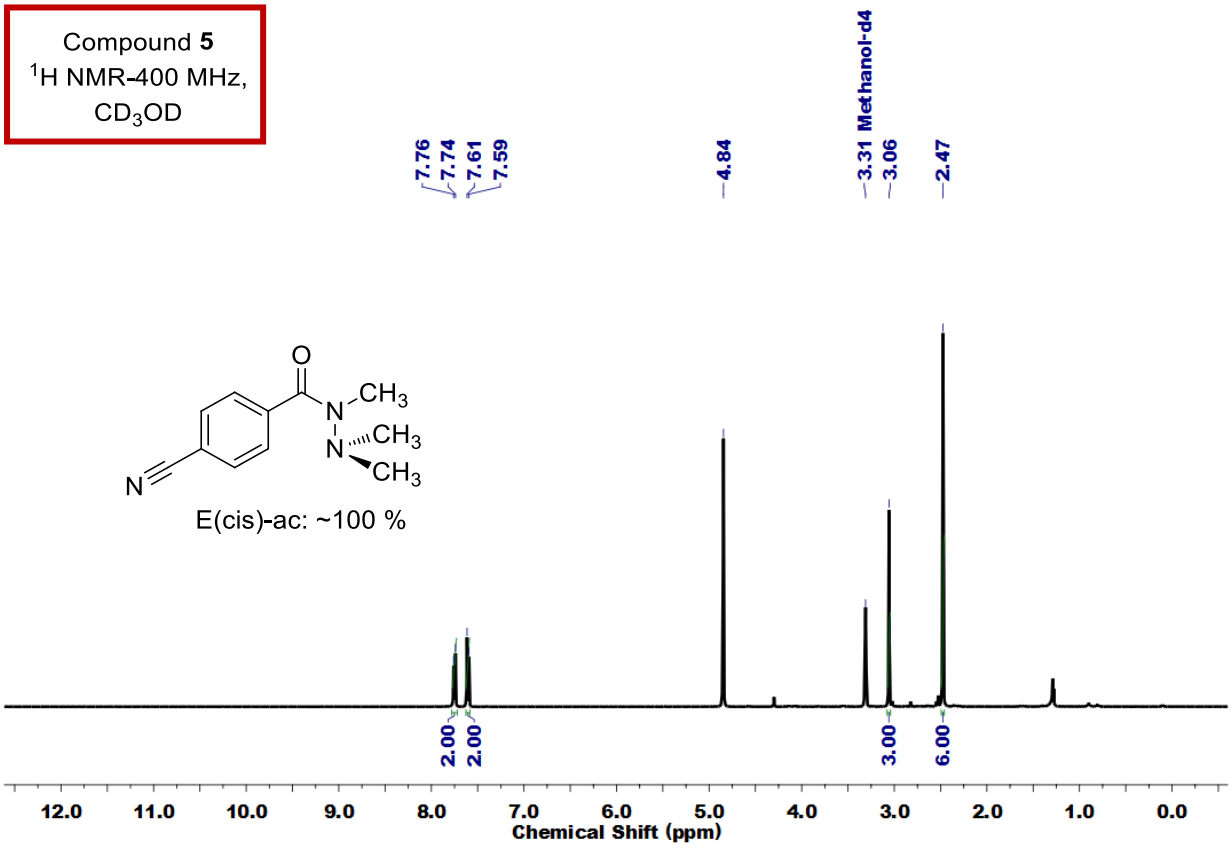
Compound **5**
^{13}C NMR-100 MHz,
$CDCl_3$



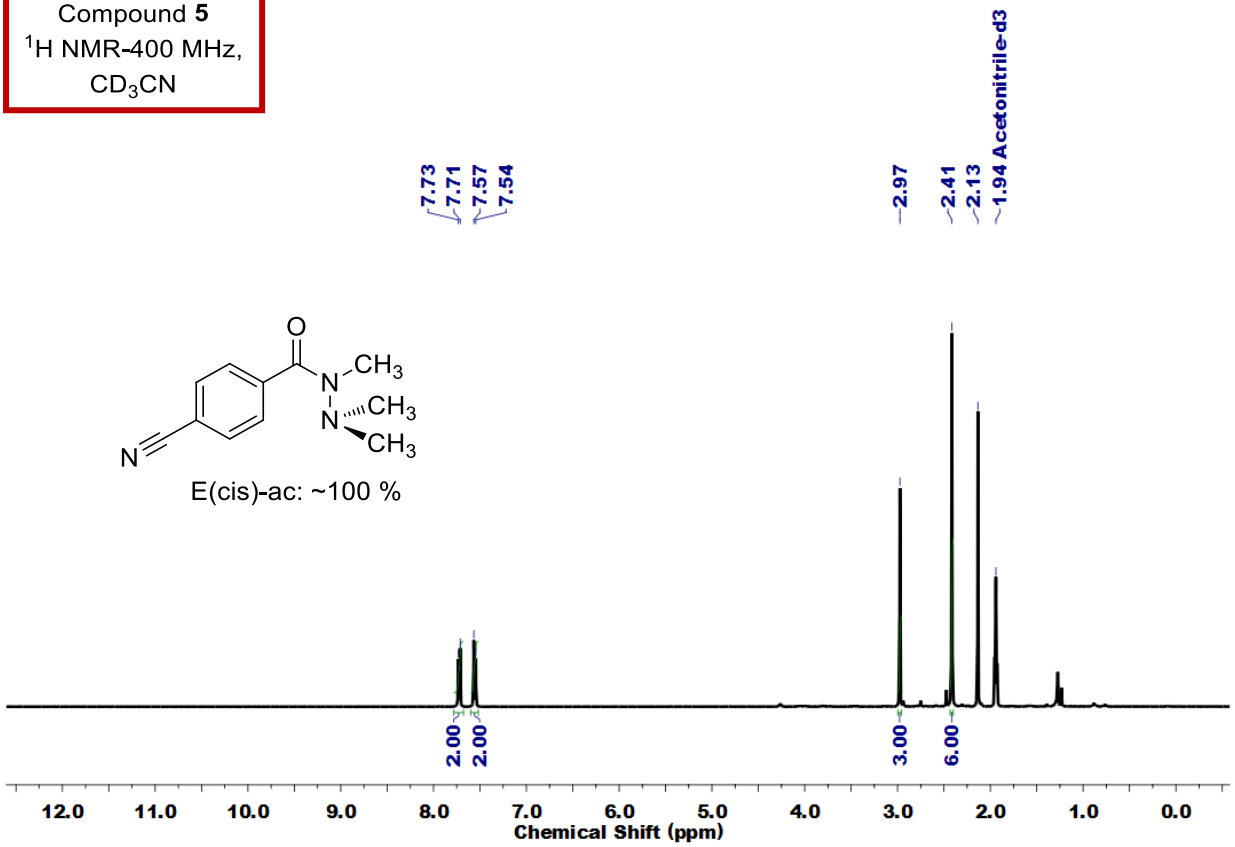
Compound **5**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



Compound **5**
^{1}H NMR-400 MHz,
CD_3OD

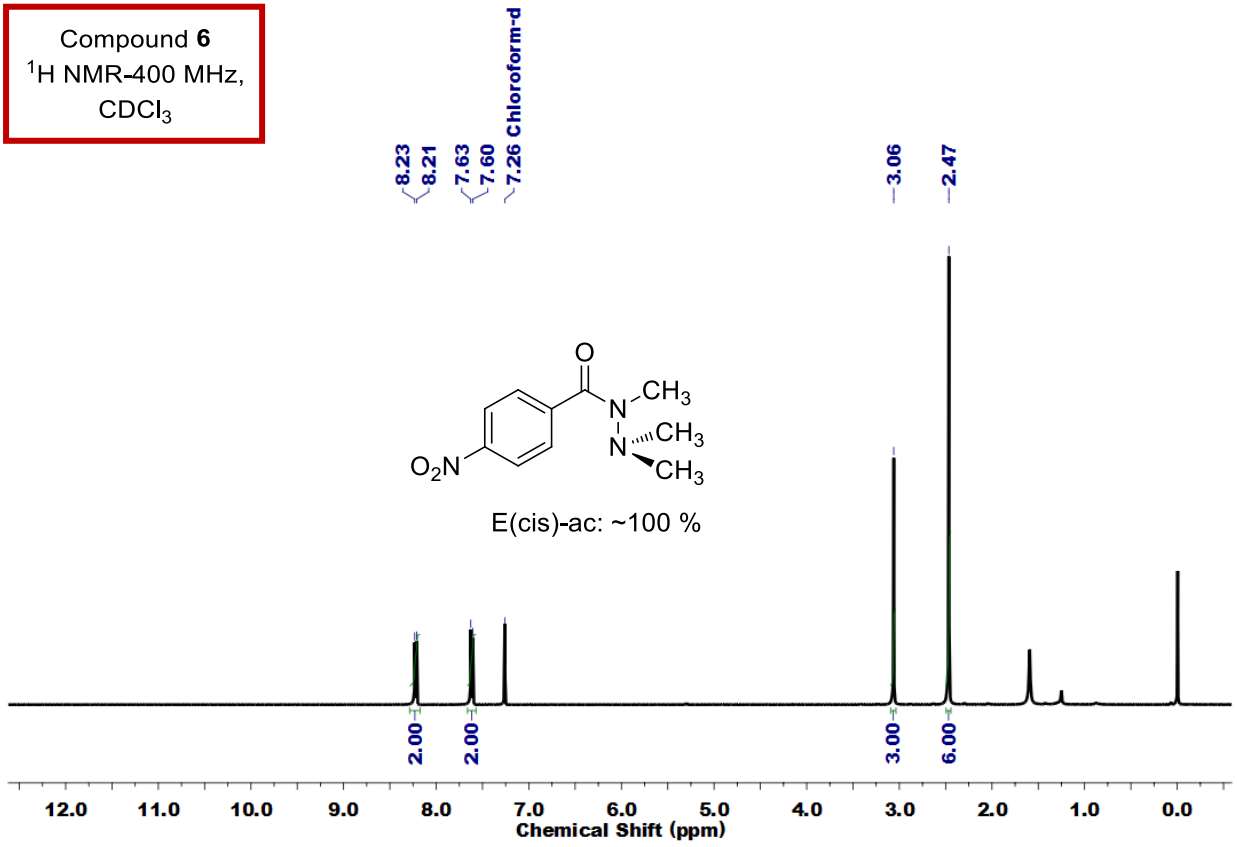


Compound **5**
^{1}H NMR-400 MHz,
CD_3CN



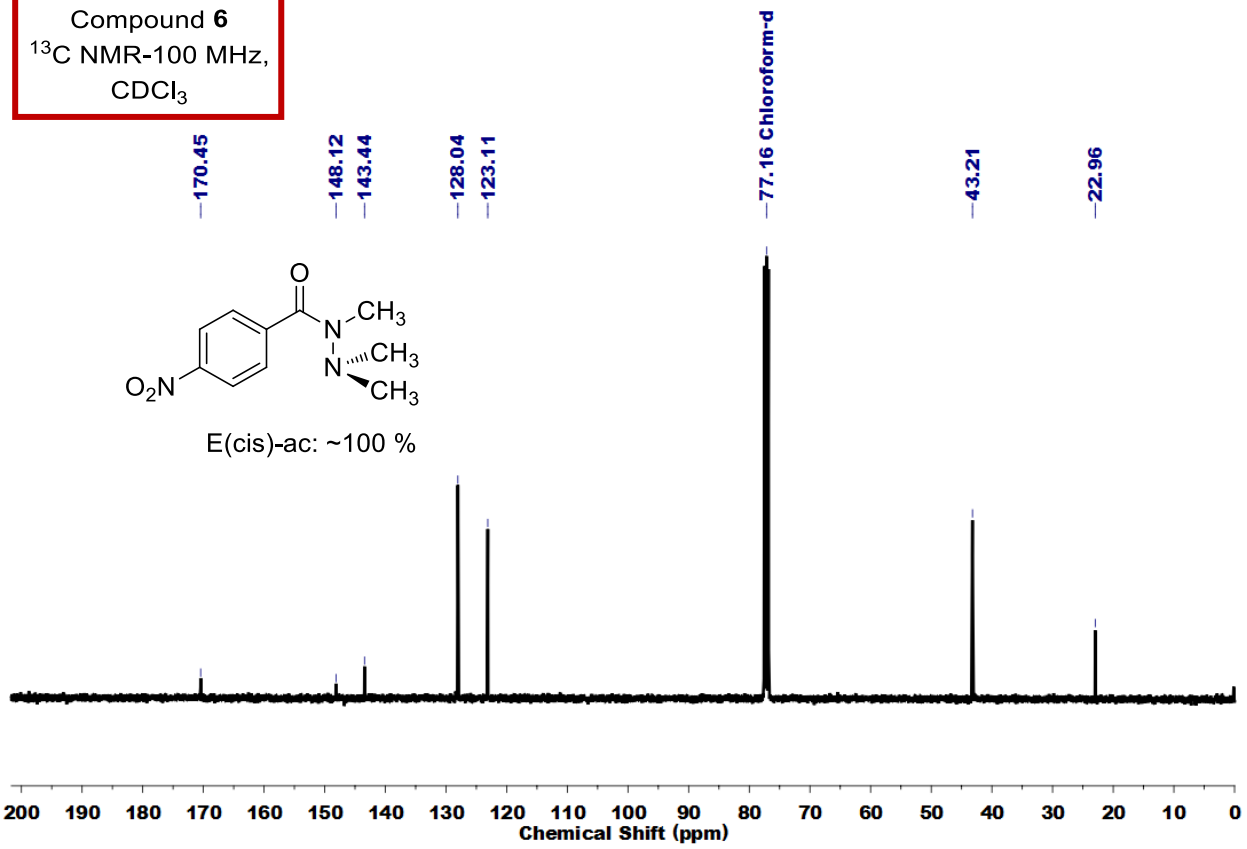
E(cis)-ac: ~100 %

Compound **6**
^{1}H NMR-400 MHz,
$CDCl_3$

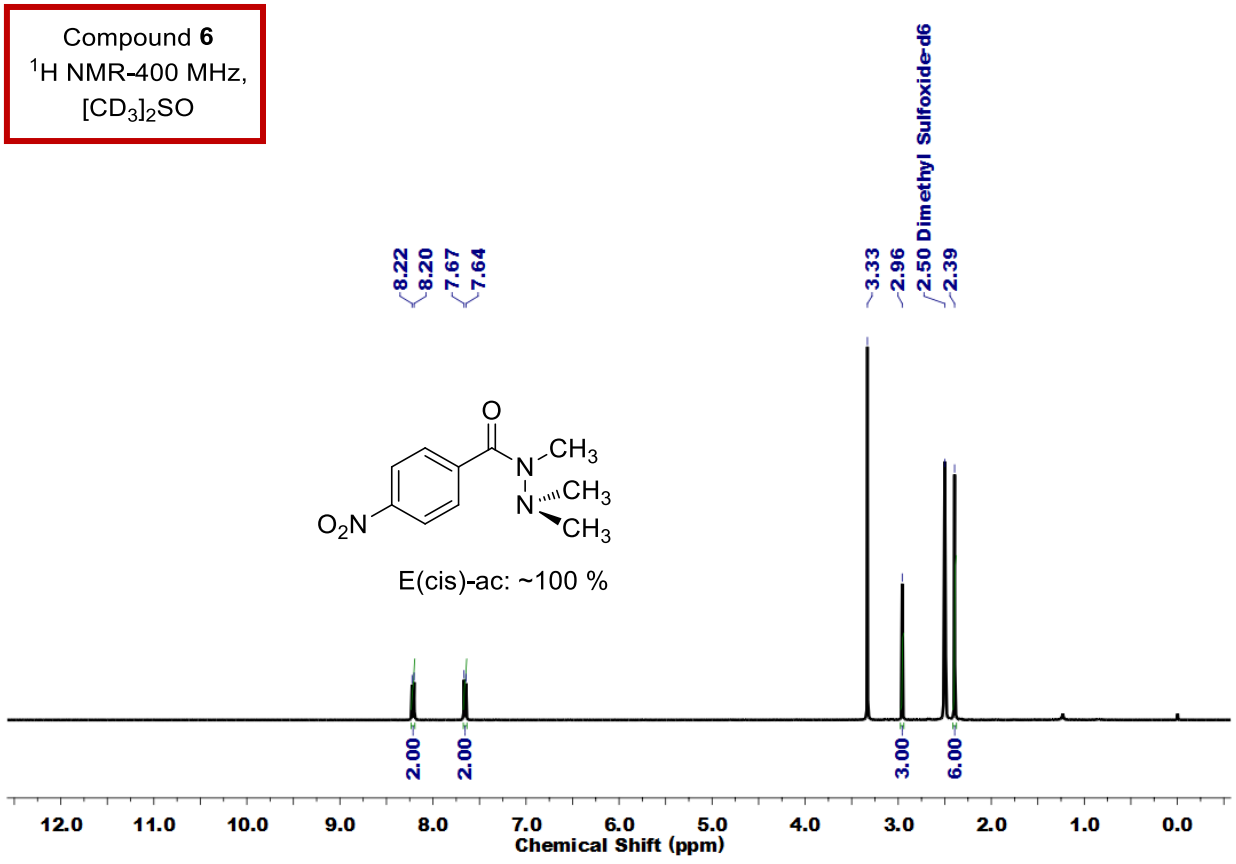


E(cis)-ac: ~100 %

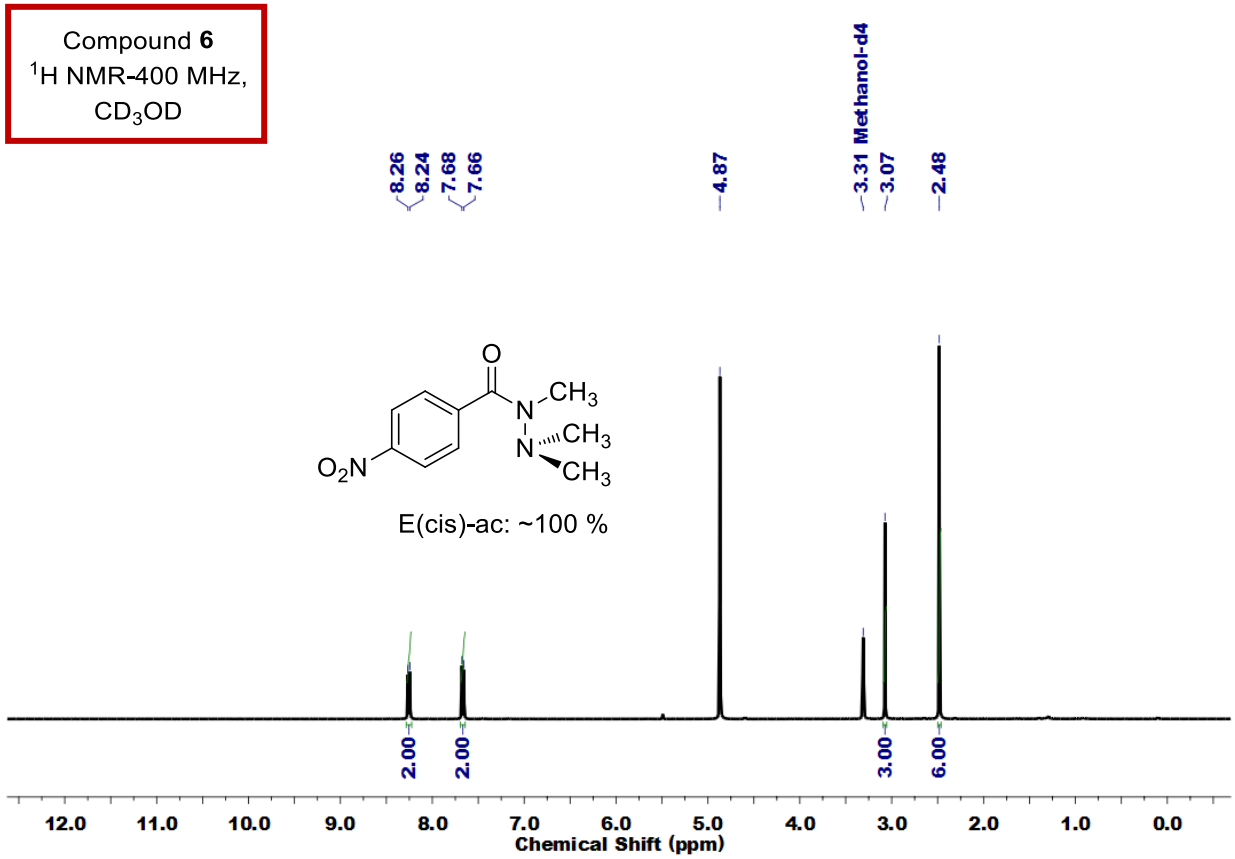
Compound **6**
^{13}C NMR-100 MHz,
$CDCl_3$



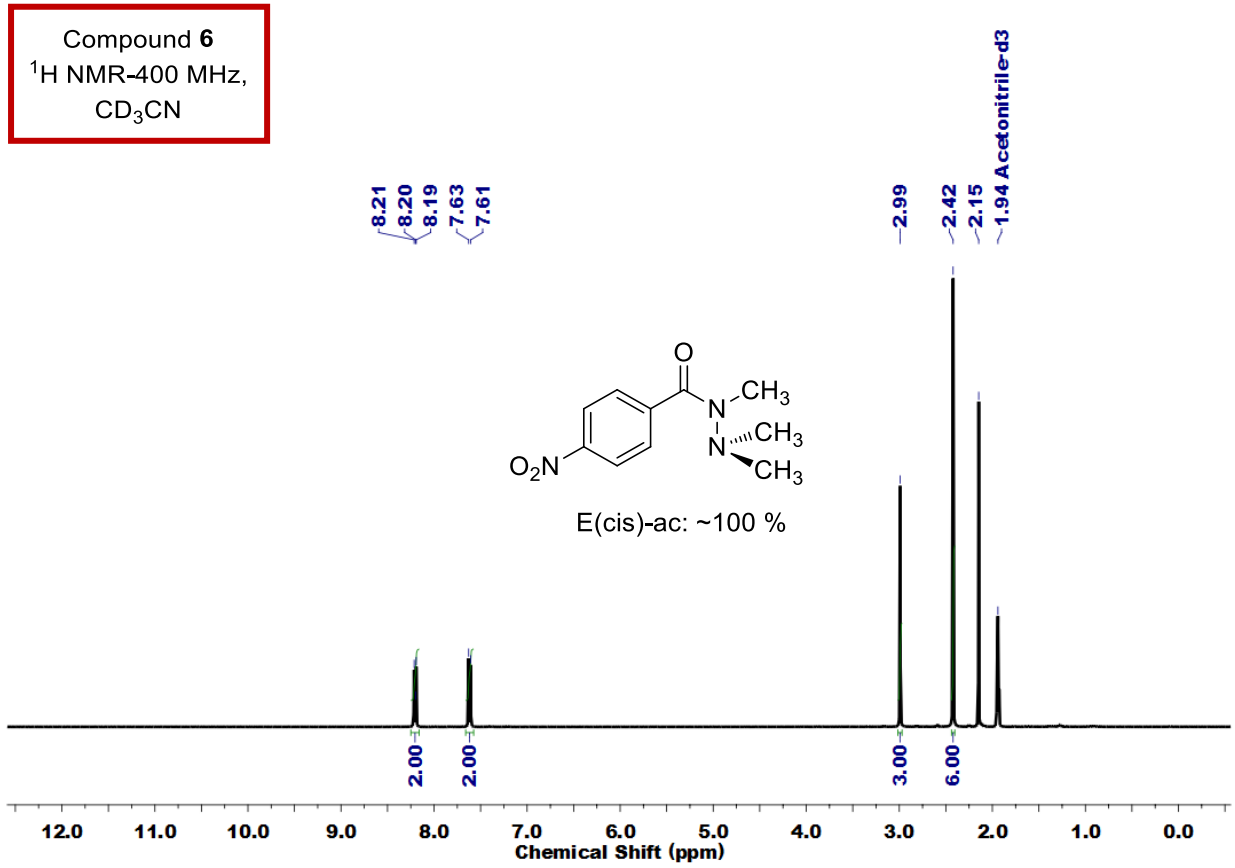
Compound **6**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



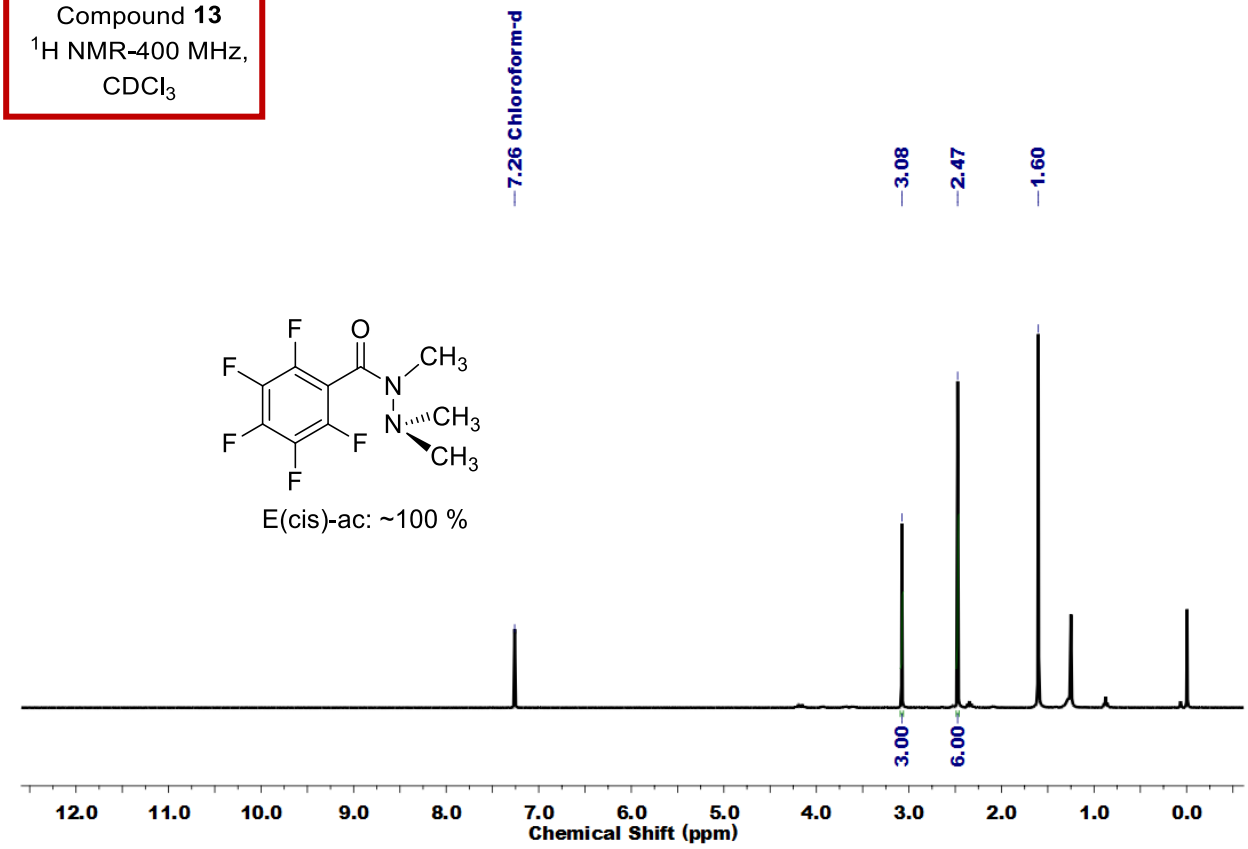
Compound **6**
^{1}H NMR-400 MHz,
CD_3OD



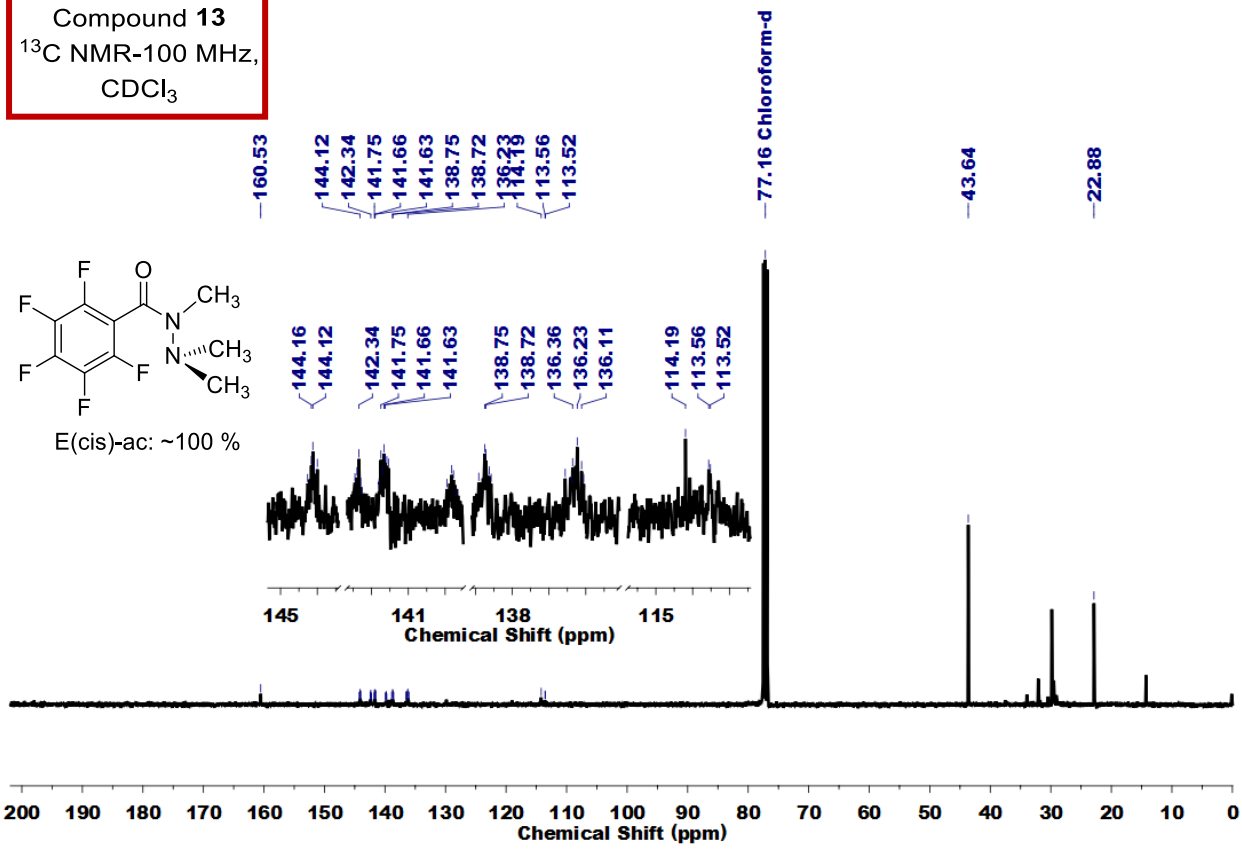
Compound **6**
^{1}H NMR-400 MHz,
CD_3CN



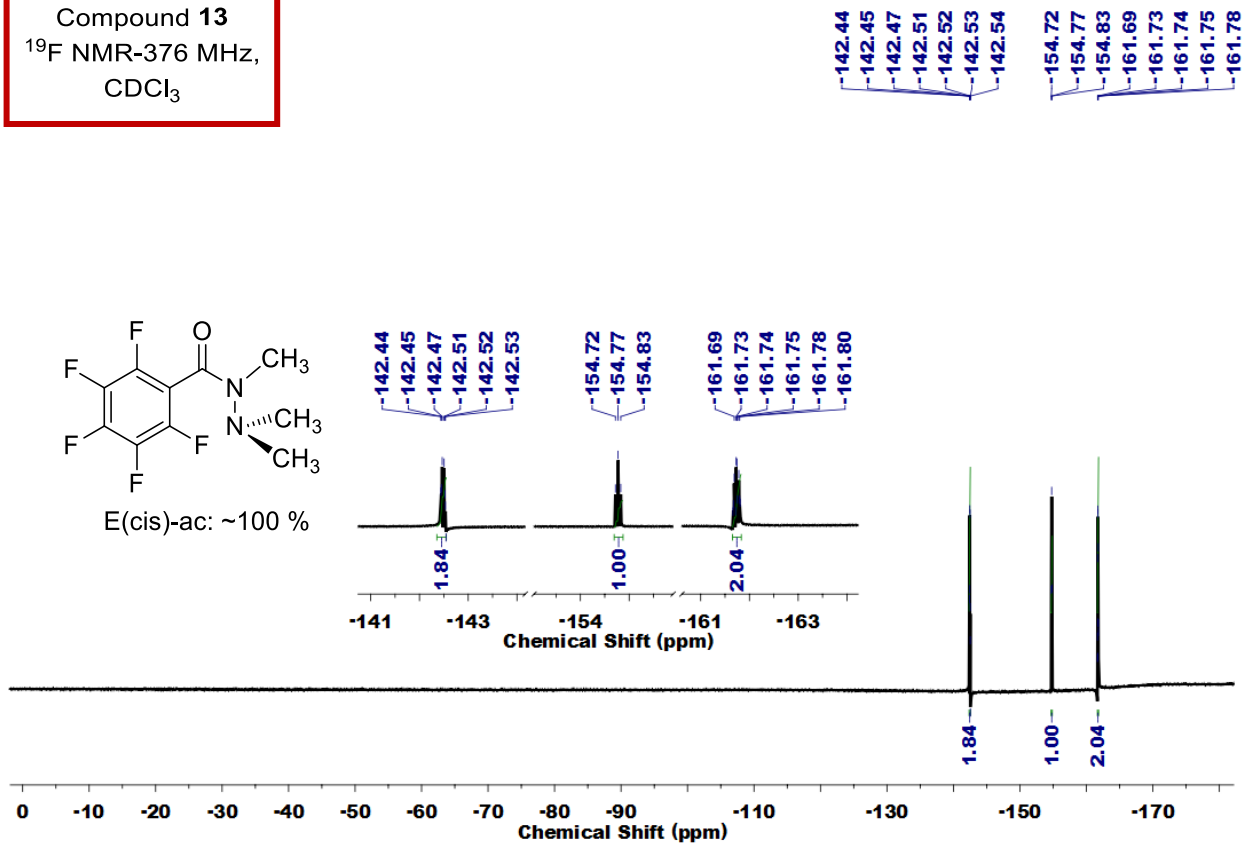
Compound **13**
^{1}H NMR-400 MHz,
$CDCl_3$



Compound **13**
^{13}C NMR-100 MHz,
$CDCl_3$

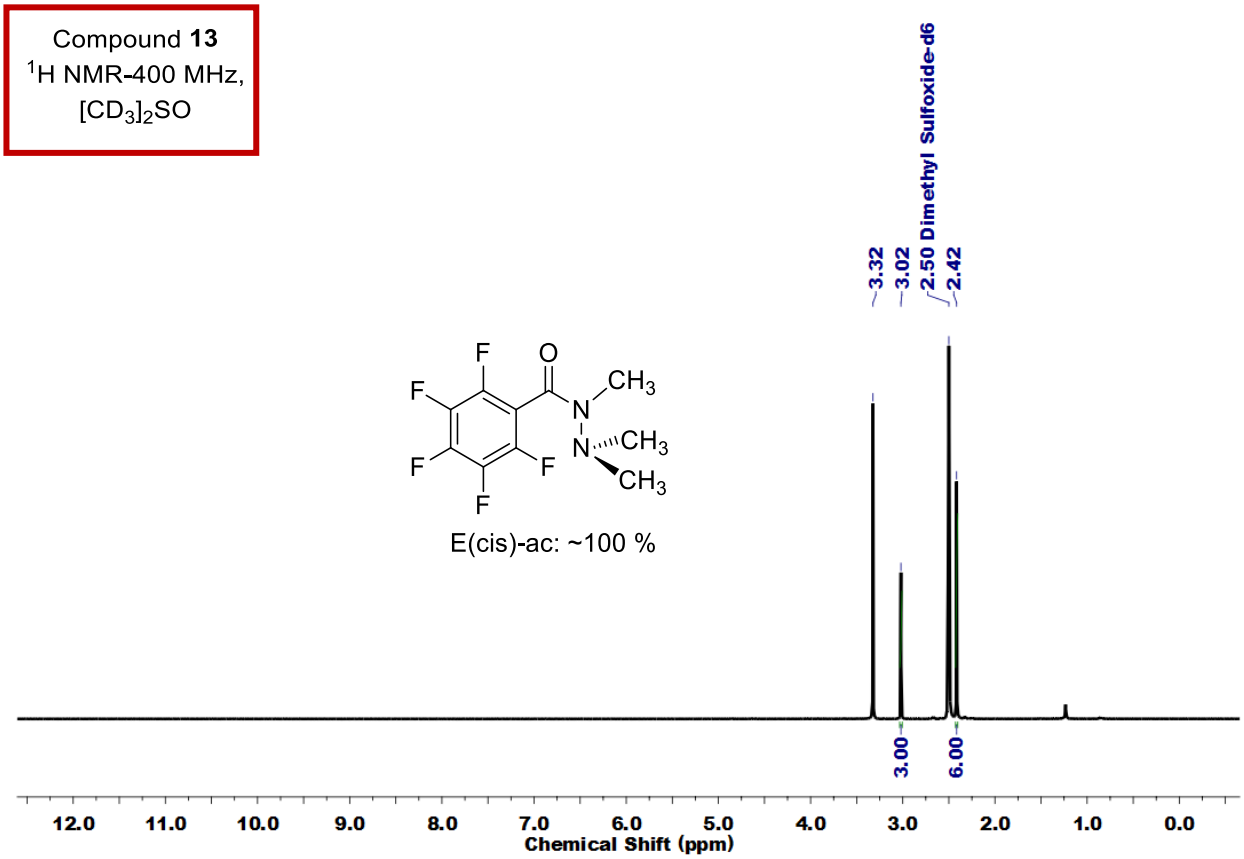


Compound **13**
^{19}F NMR-376 MHz,
$CDCl_3$



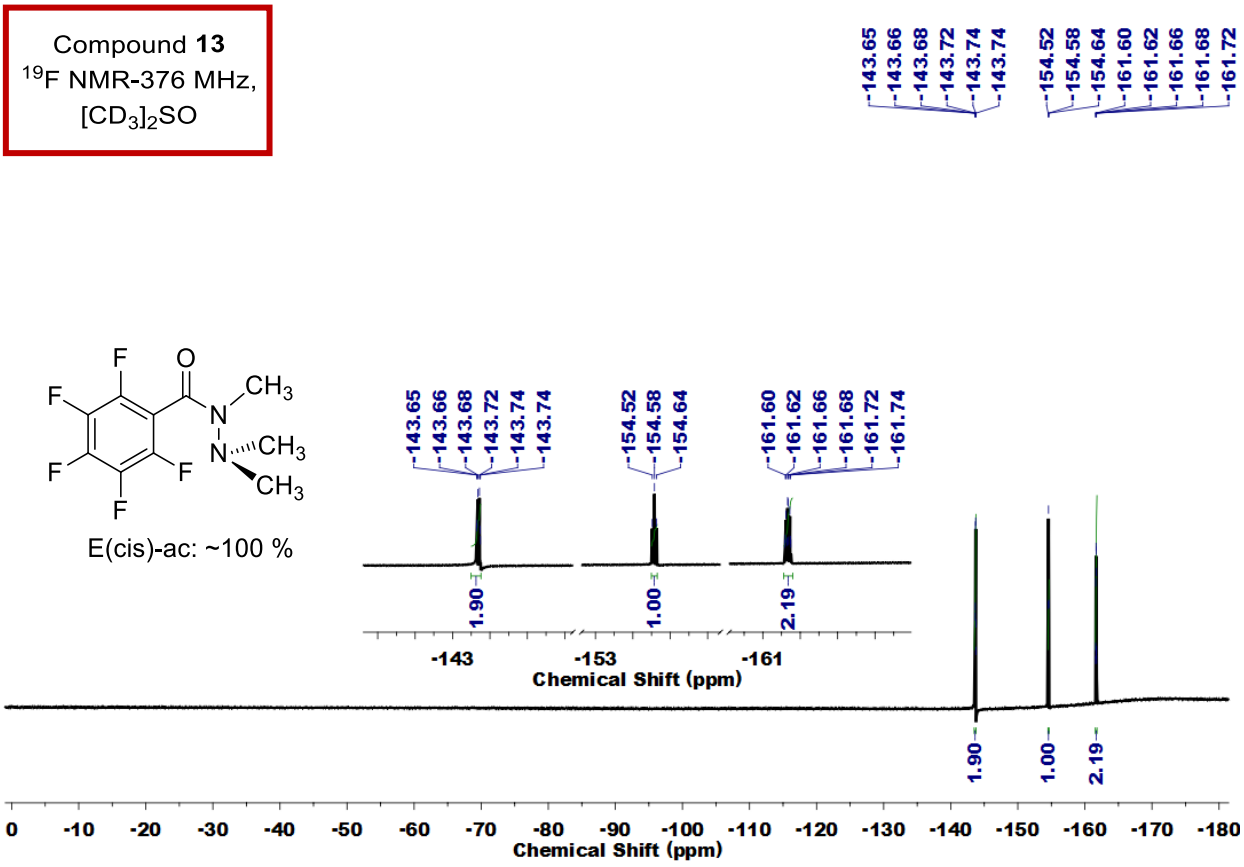
E(cis)-ac: ~100 %

Compound **13**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$

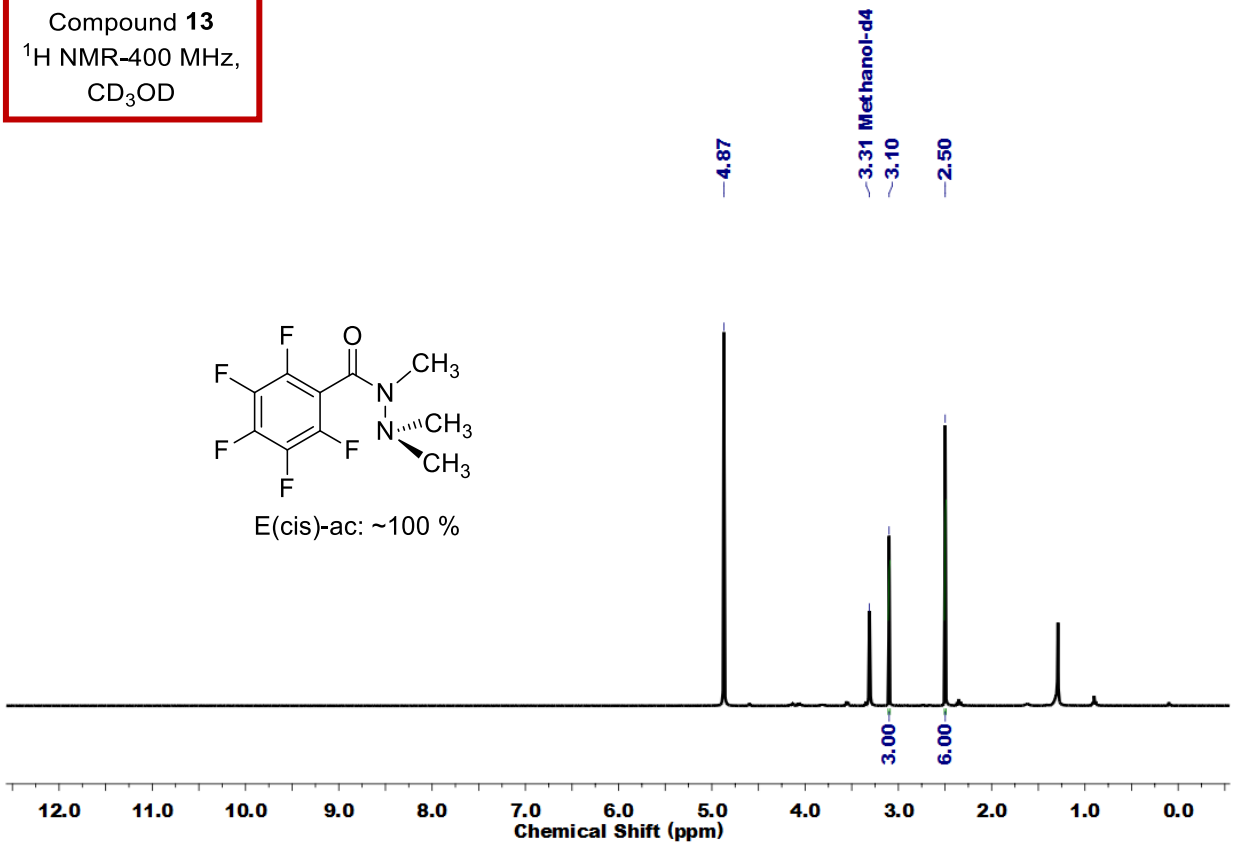


E(cis)-ac: ~100 %

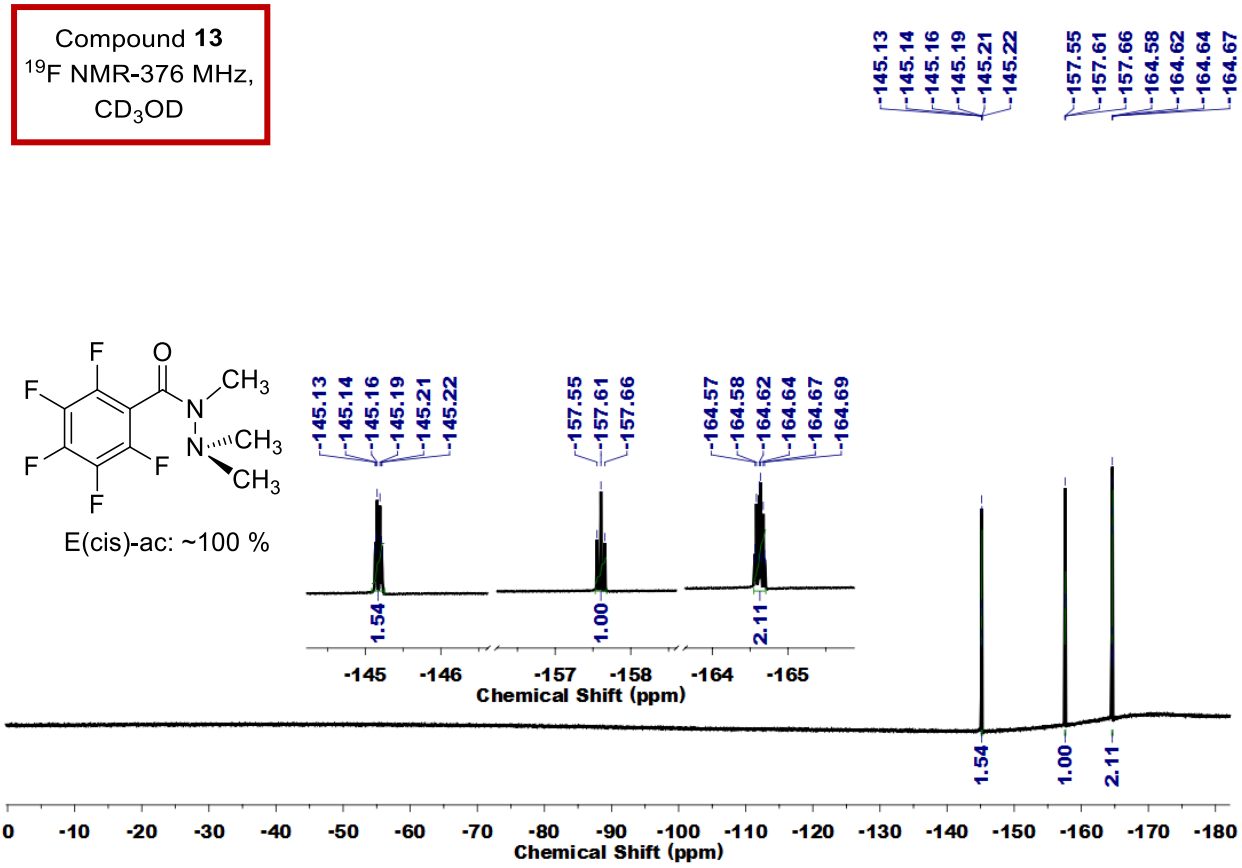
Compound **13**
^{19}F NMR-376 MHz,
$[CD_3]_2SO$



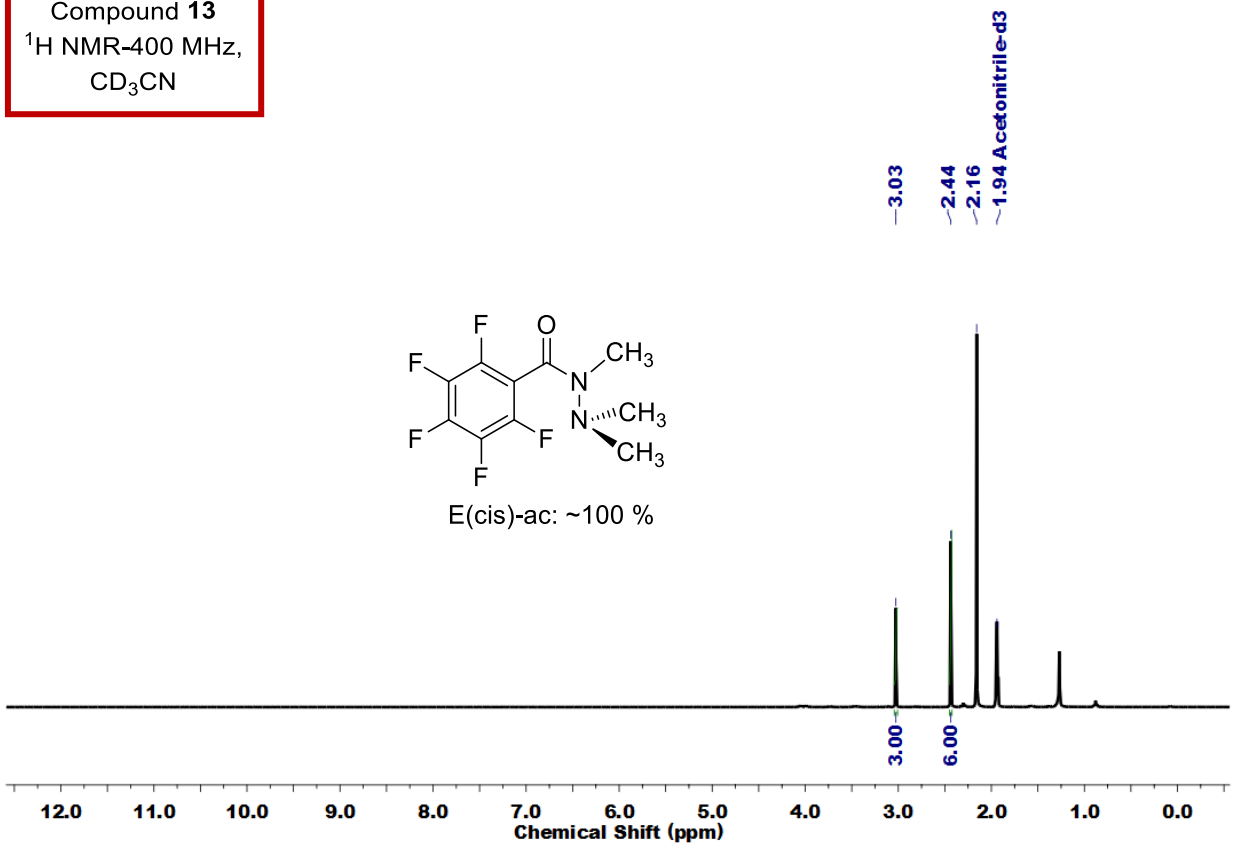
Compound **13**
^{1}H NMR-400 MHz,
CD_3OD



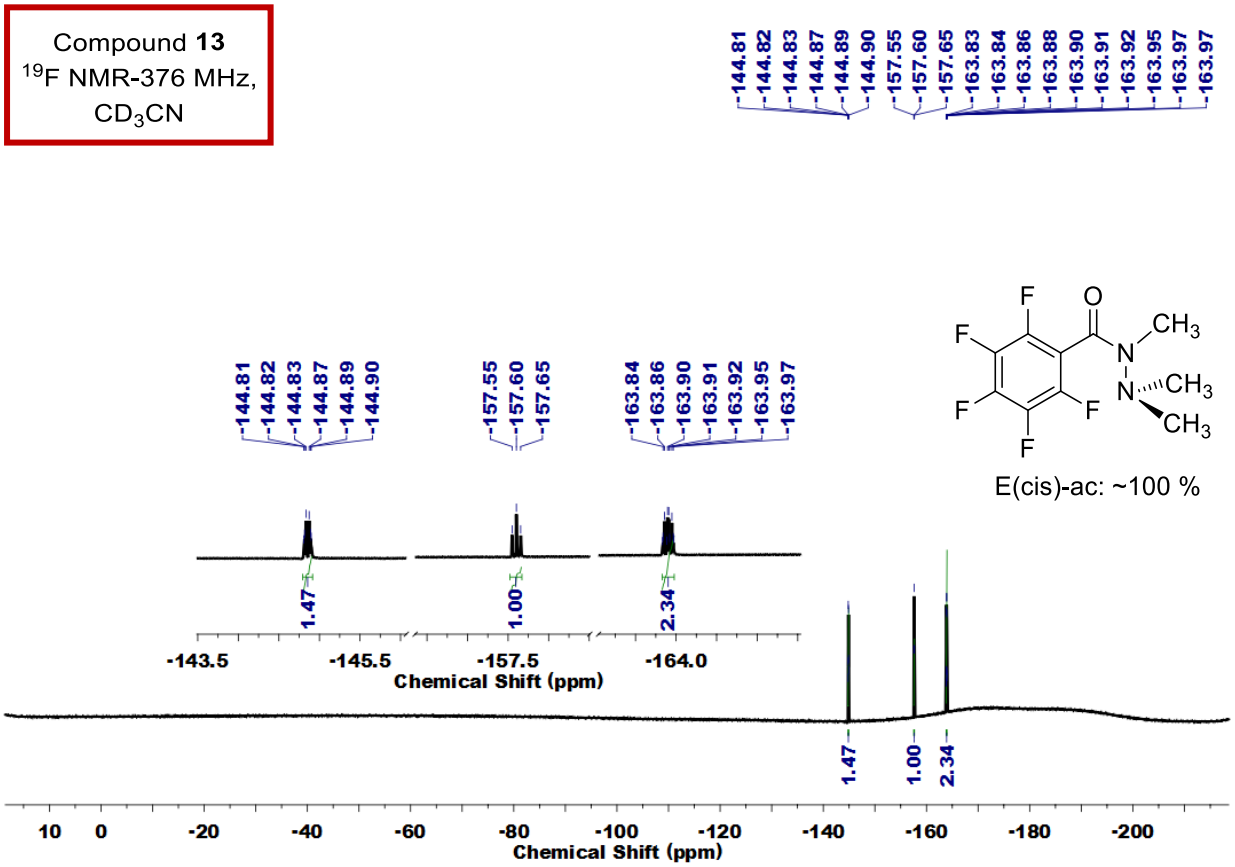
Compound **13**
^{19}F NMR-376 MHz,
CD_3OD



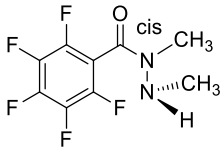
Compound **13**
^{1}H NMR-400 MHz,
CD_3CN



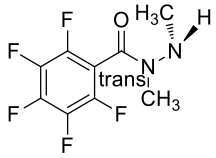
Compound **13**
^{19}F NMR-376 MHz,
CD_3CN



Compound **14**
^{1}H NMR-400 MHz,
$CDCl_3$

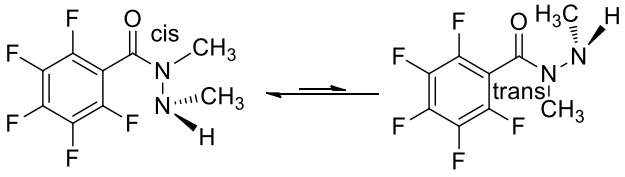


E(cis)-ac 82%



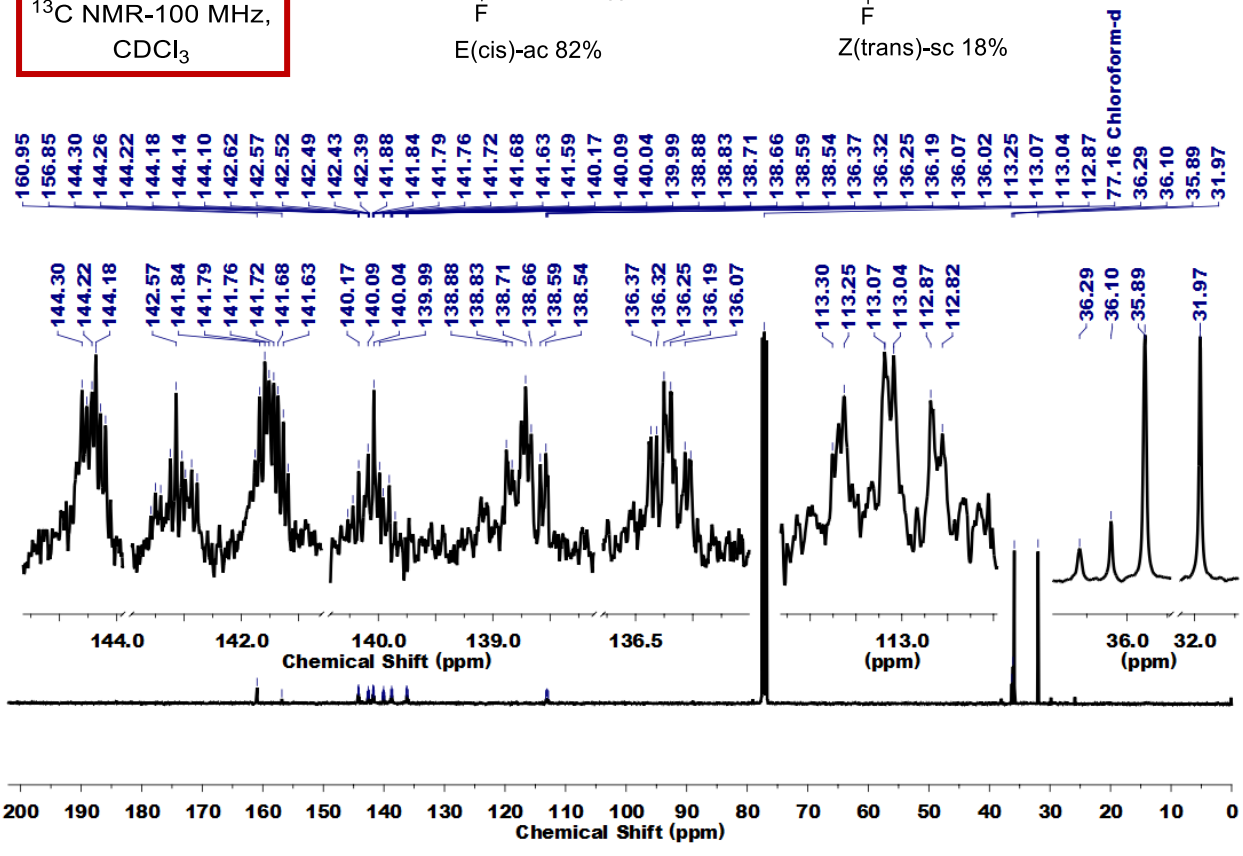
Z(trans)-sc 18%

Compound **14**
^{13}C NMR-100 MHz,
$CDCl_3$

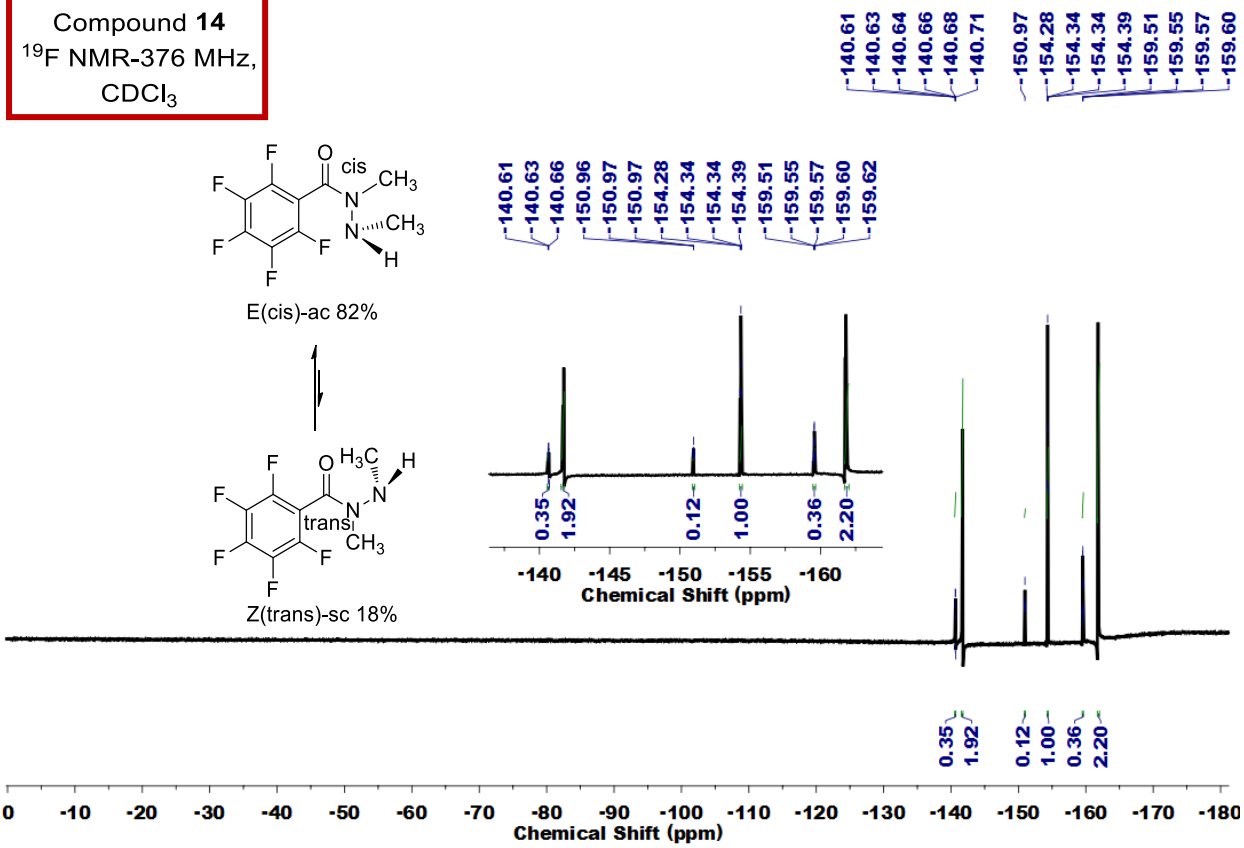


E(cis)-ac 82%

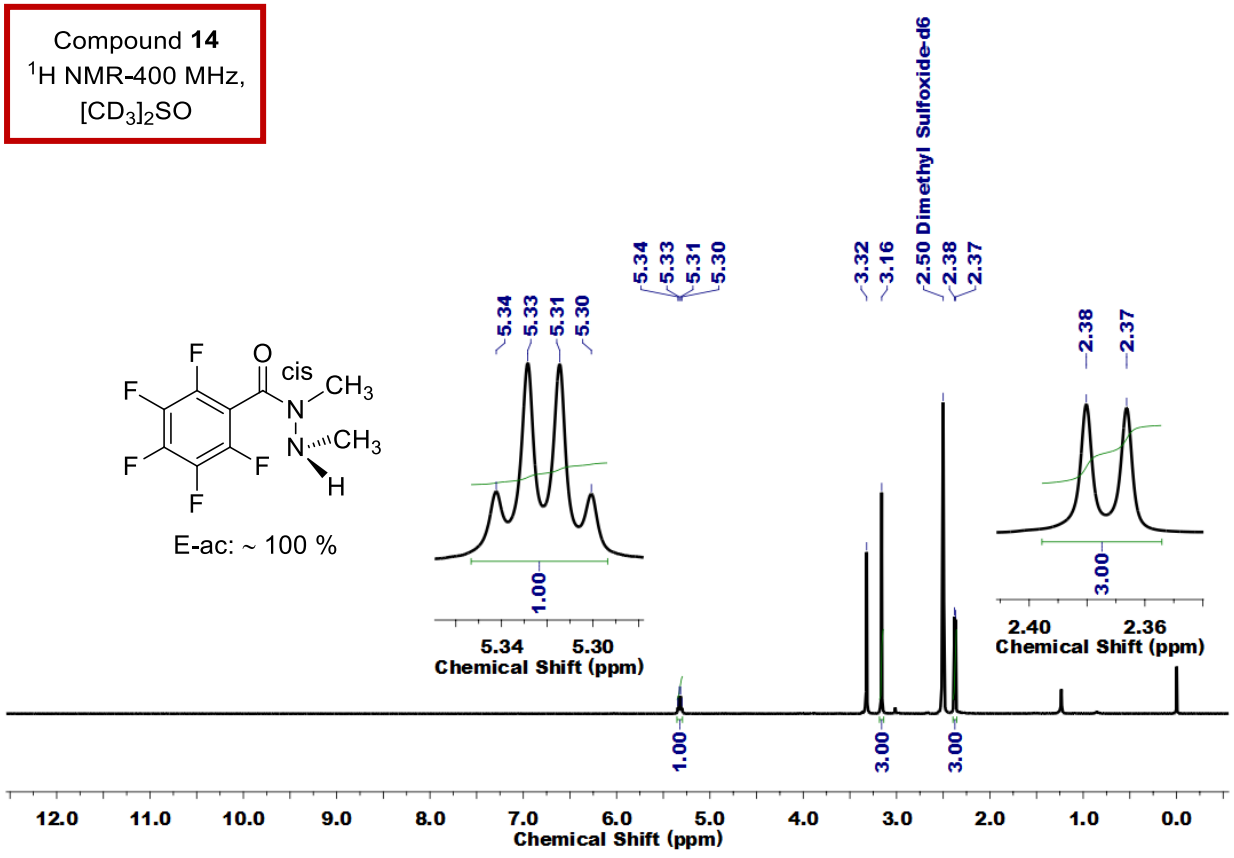
Z(trans)-sc 18%



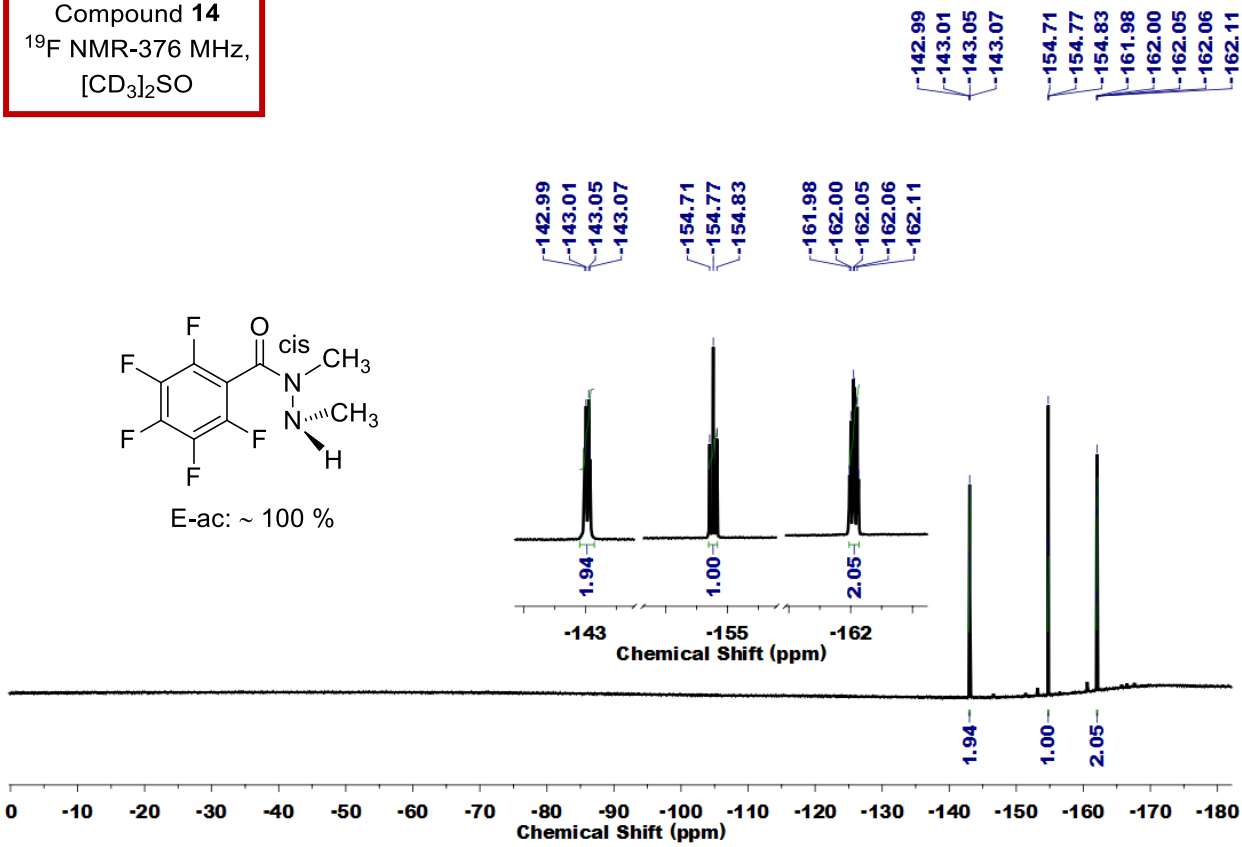
Compound **14**
^{19}F NMR-376 MHz,
$CDCl_3$



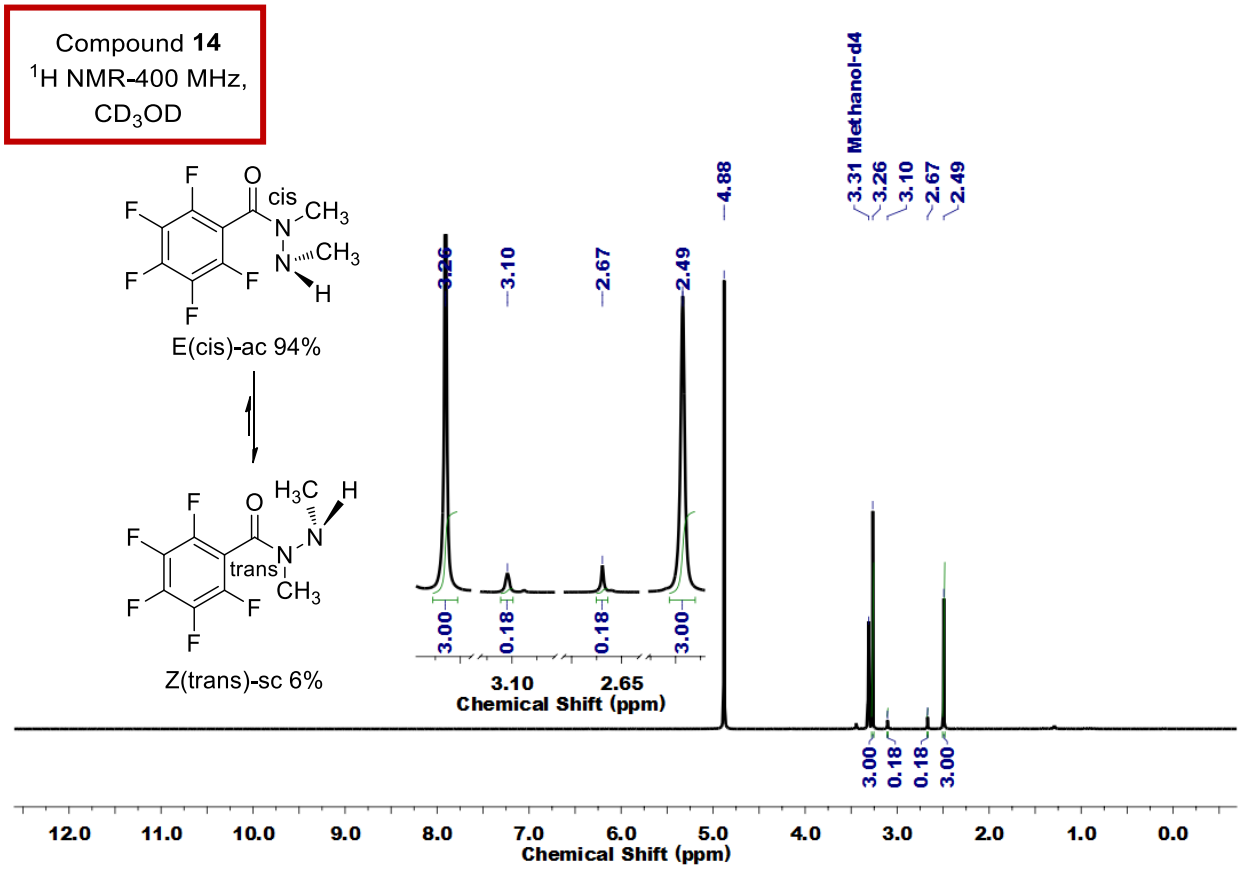
Compound **14**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



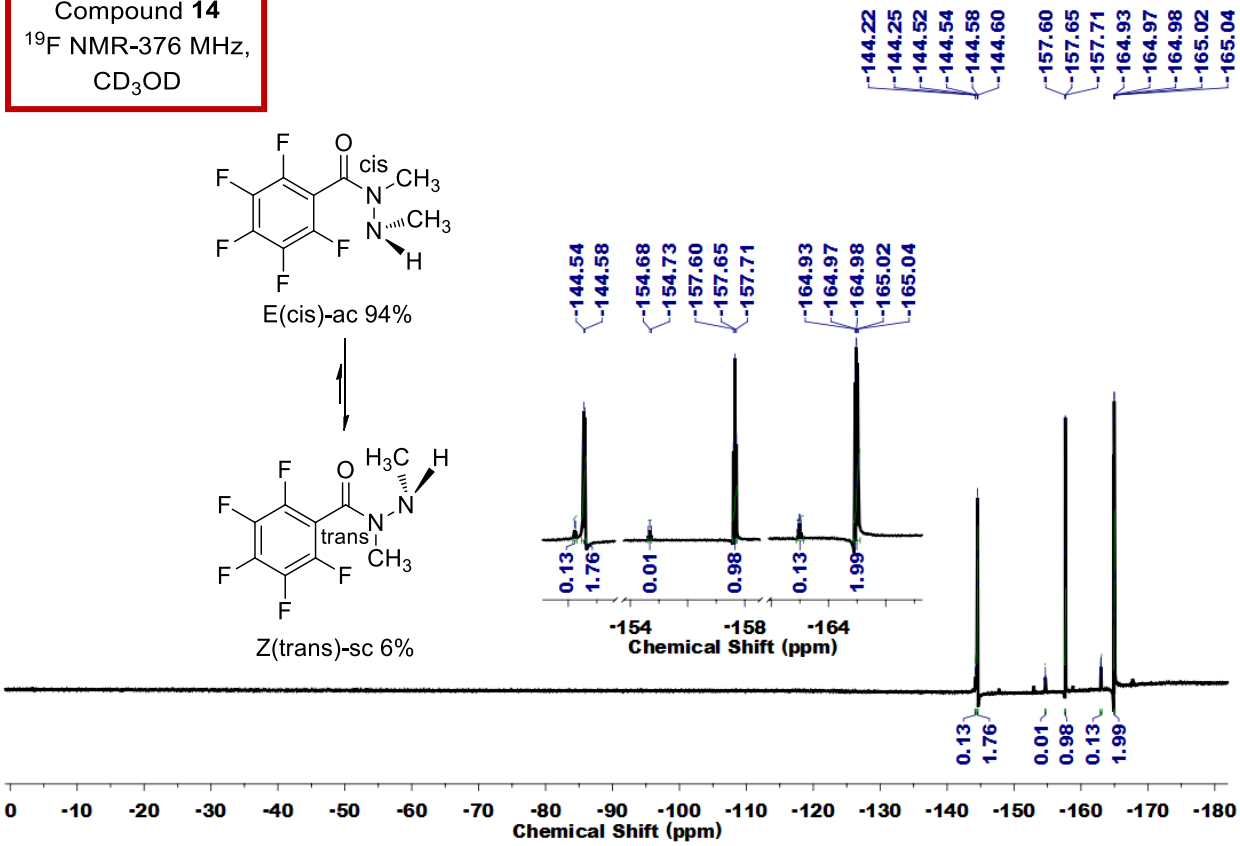
Compound **14**
^{19}F NMR-376 MHz,
$[CD_3]_2SO$



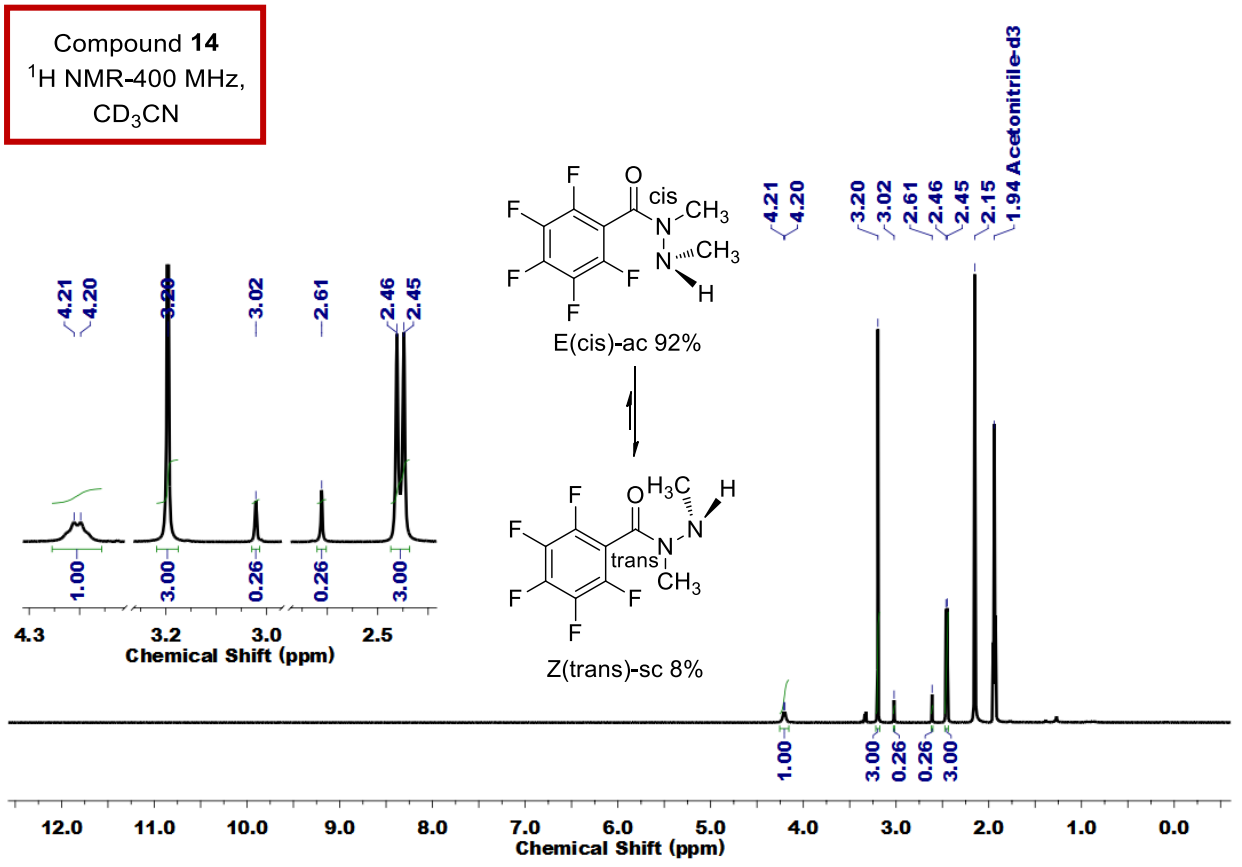
Compound **14**
^{1}H NMR-400 MHz,
CD_3OD



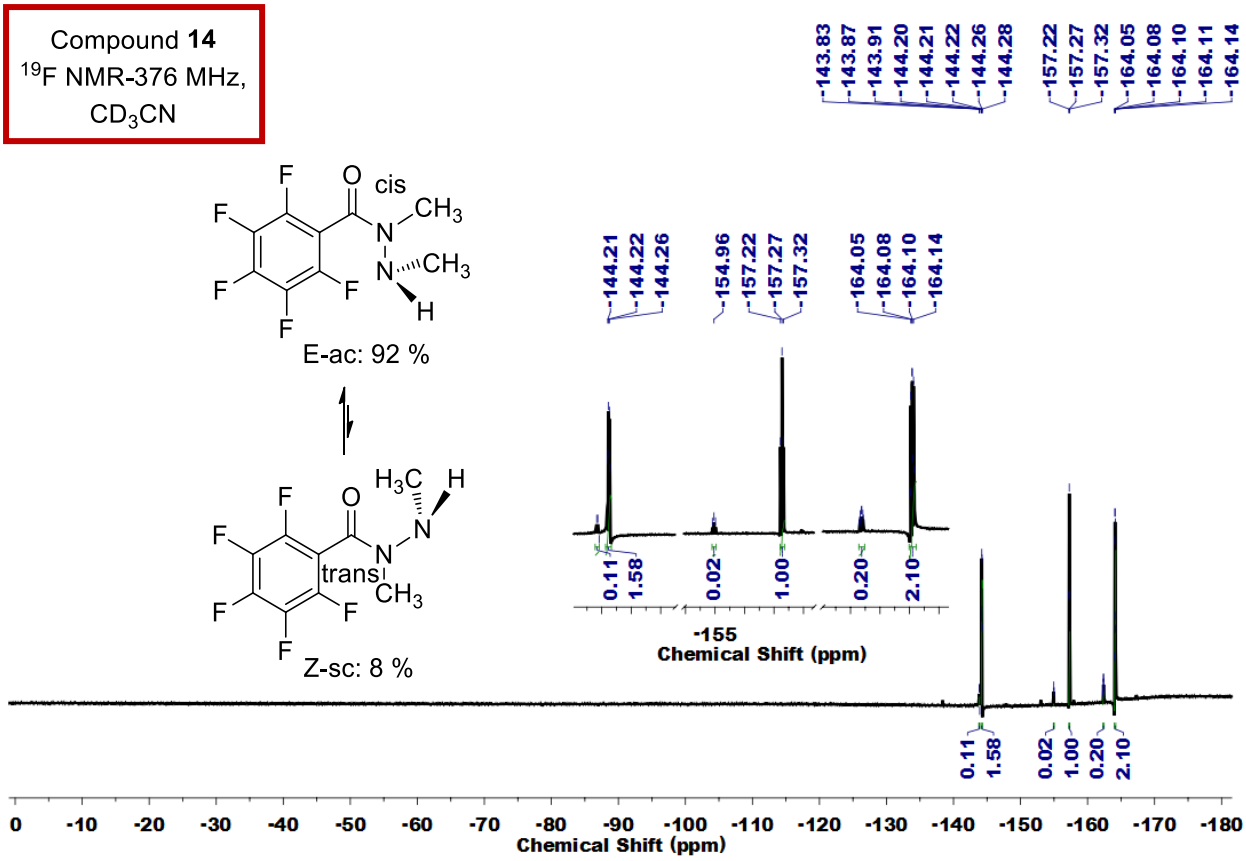
Compound **14**
^{19}F NMR-376 MHz,
CD_3OD



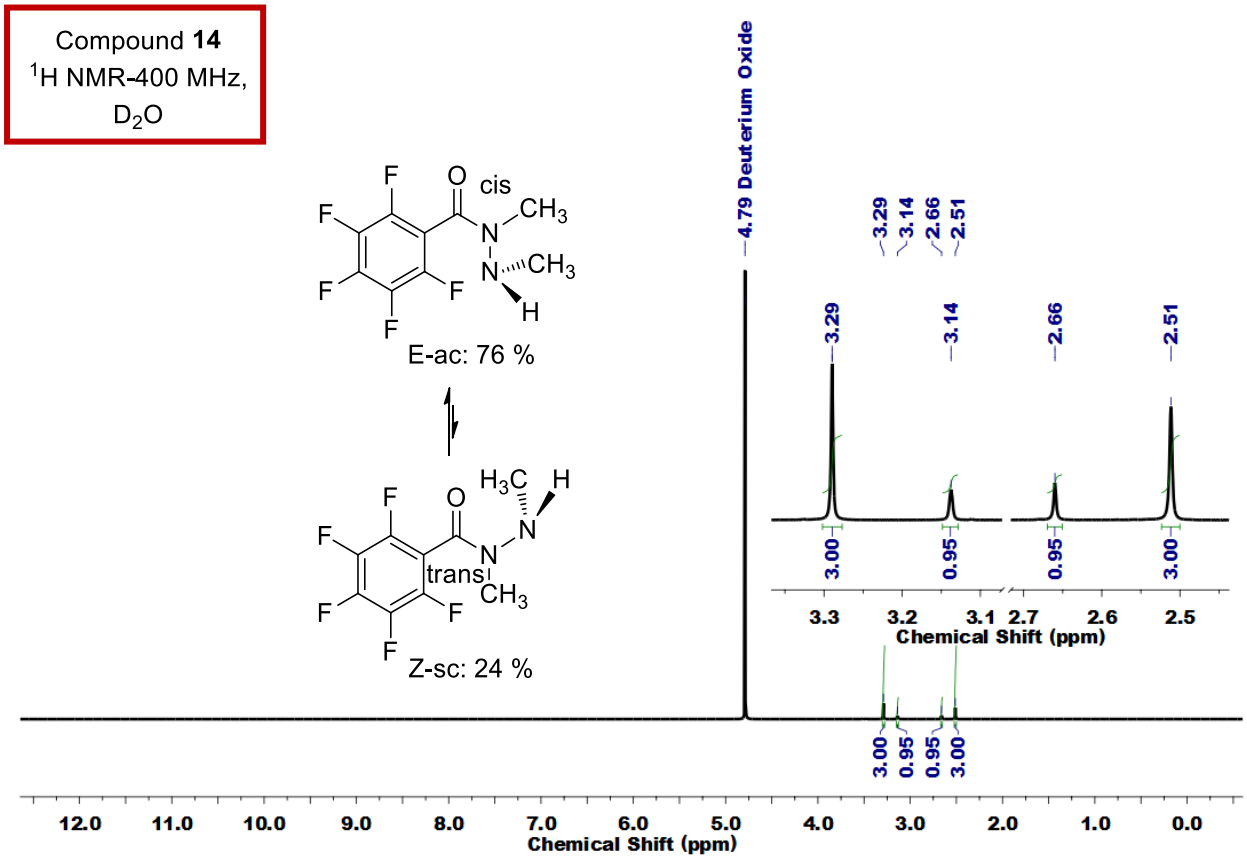
Compound **14**
^{1}H NMR-400 MHz,
CD_3CN



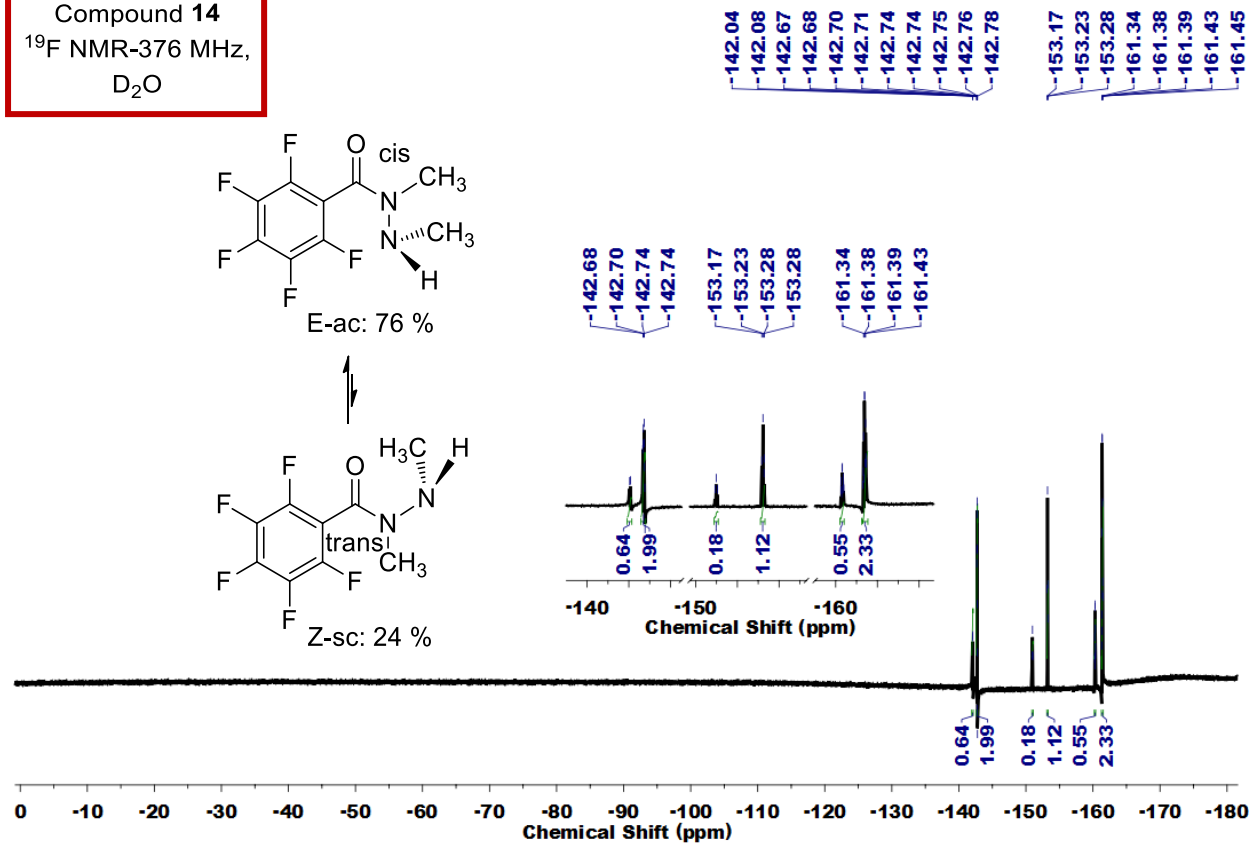
Compound **14**
^{19}F NMR-376 MHz,
CD_3CN



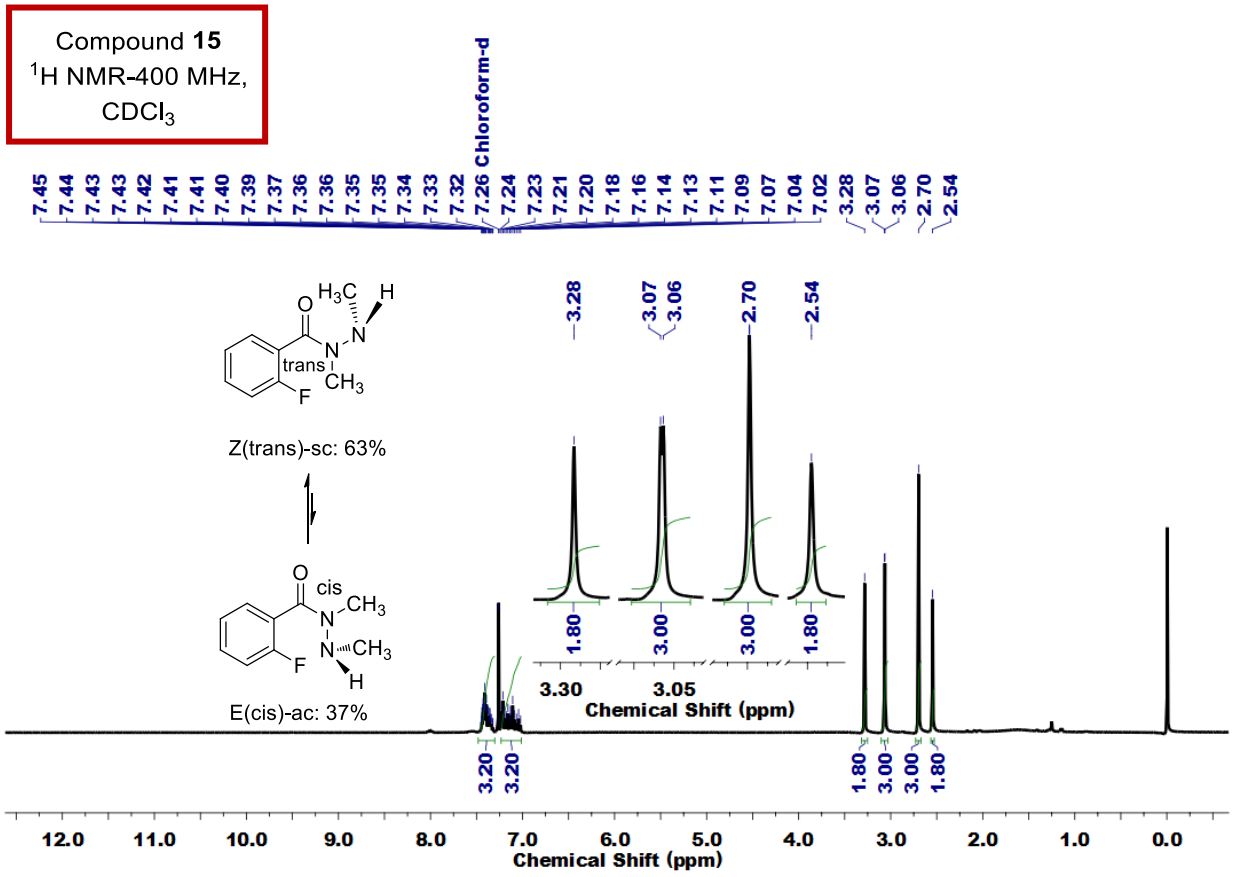
Compound **14**
^{1}H NMR-400 MHz,
D_2O

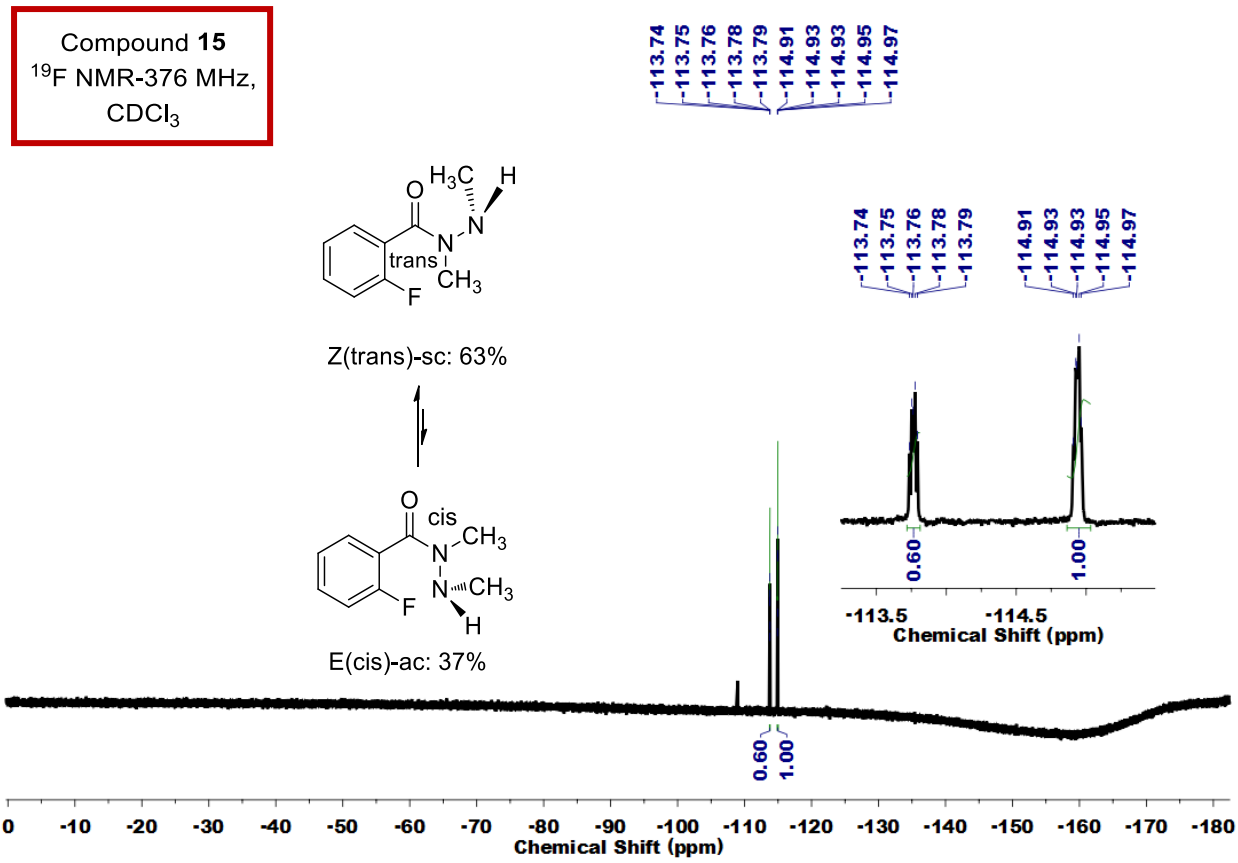


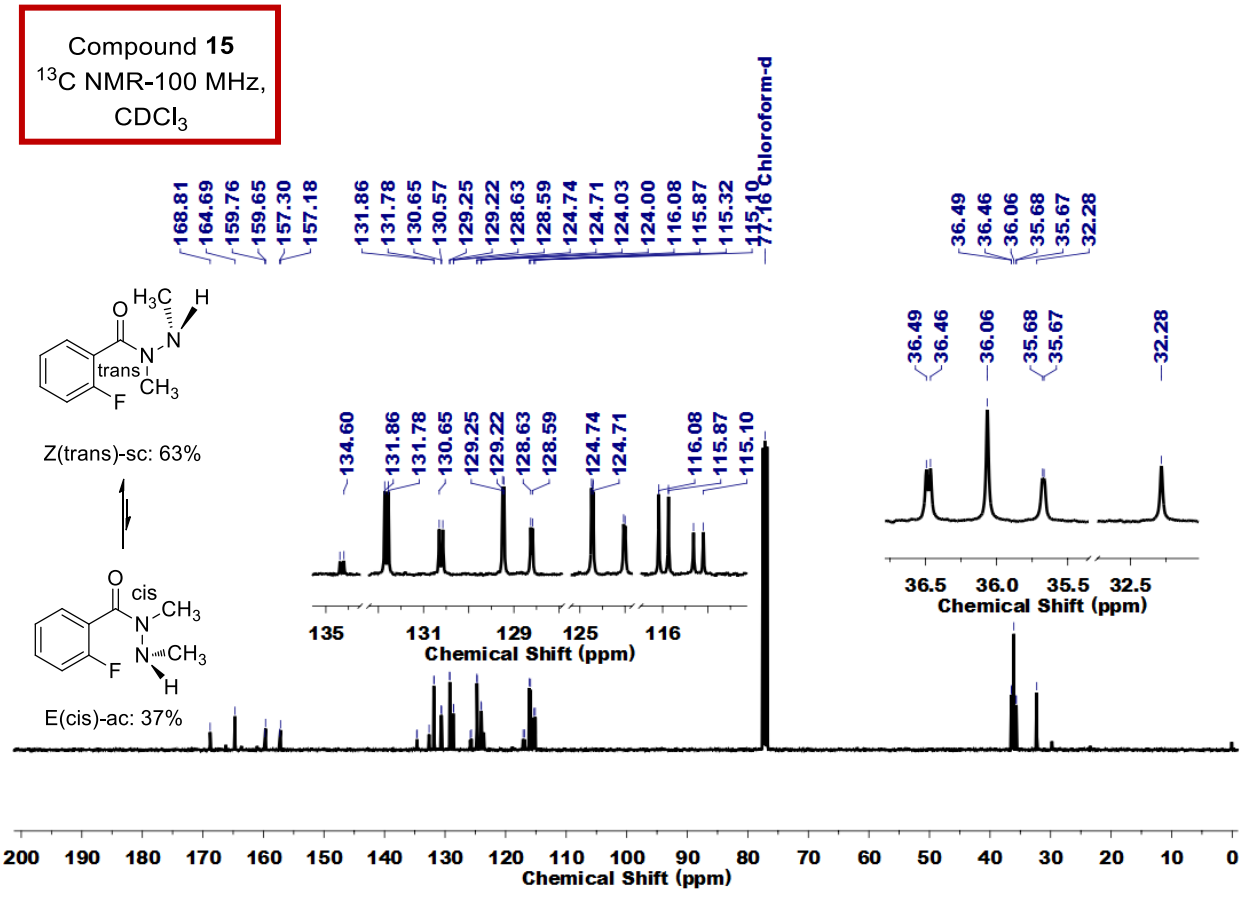
Compound **14**
^{19}F NMR-376 MHz,
D_2O



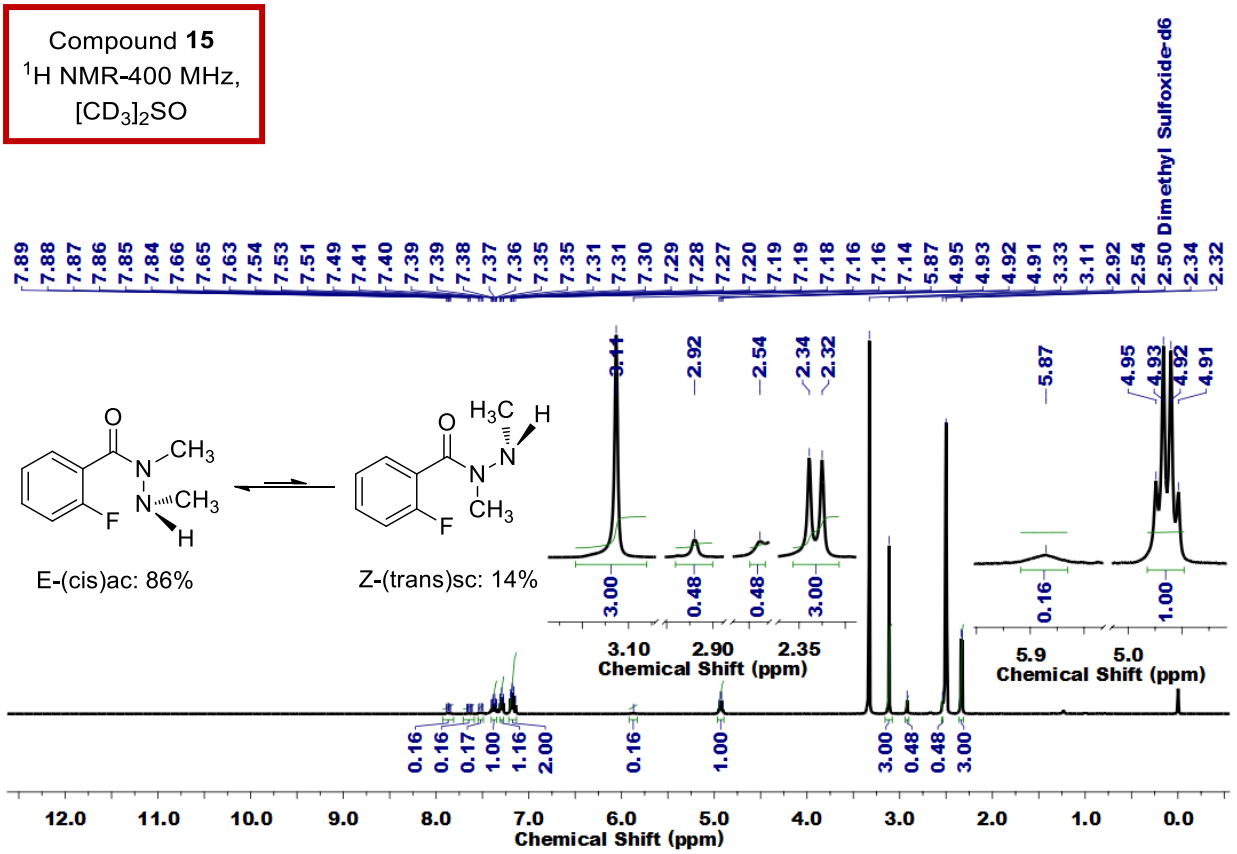
Compound **15**
^{1}H NMR-400 MHz,
$CDCl_3$



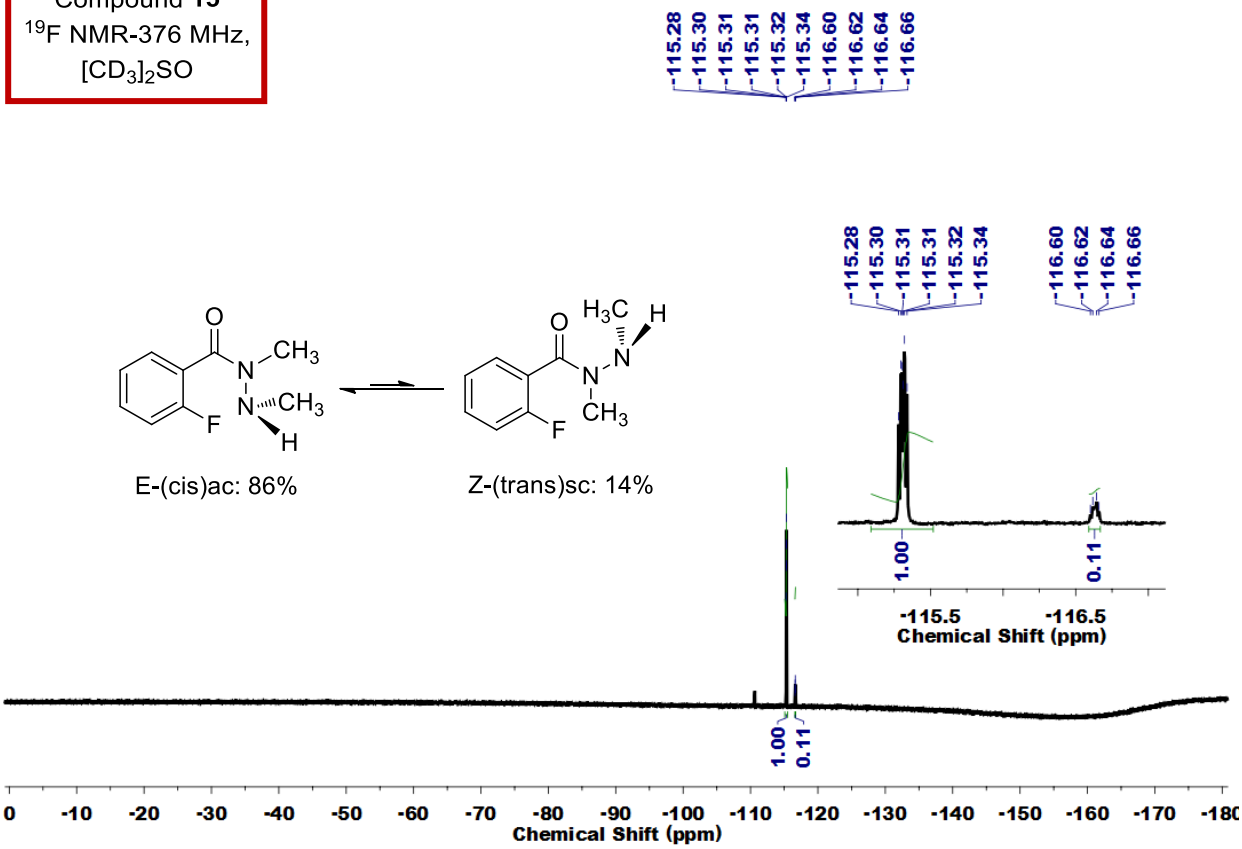

Compound 15
19F NMR-376 MHz,
CDCl3
-113.74
-113.75
-113.76
-113.78
-113.79
-114.91
-114.93
-114.93
-114.95
-114.97
Z(trans)-sc: 63%
E(cis)-ac: 37%
0.60
1.00
-113.5
-114.5
Chemical Shift (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
Chemical Shift (ppm)


Compound 15
13C NMR-100 MHz,
CDCl3
168.81
164.69
159.76
159.65
157.30
157.18
131.86
131.78
130.65
130.57
129.25
129.22
128.63
128.59
124.74
124.71
124.03
124.00
116.08
115.87
115.32
115.10
77.16 Chloroform-d
36.49
36.46
36.06
35.68
35.67
32.28
Z(trans)-sc: 63%
E(cis)-ac: 37%
135
131
129
125
116
36.5
36.0
35.5
32.5
Chemical Shift (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

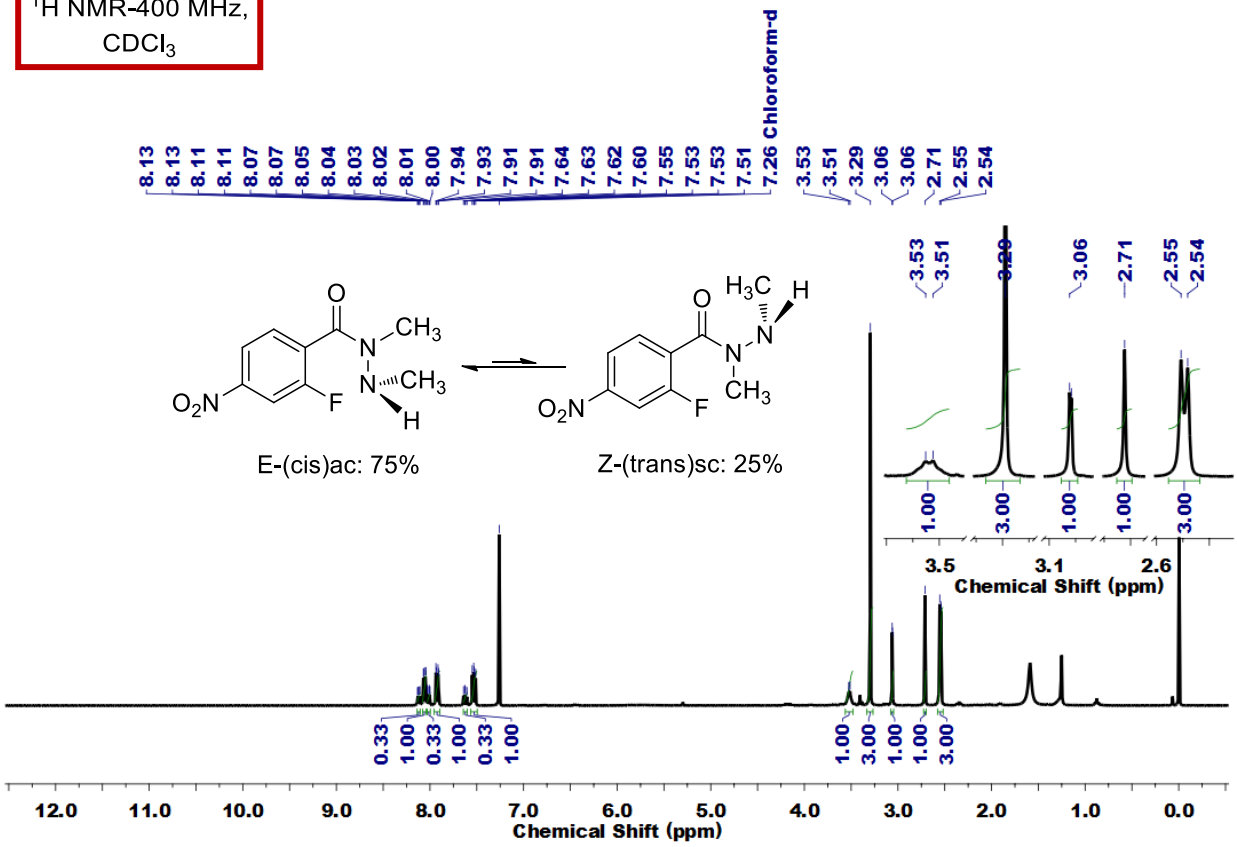
Compound **15**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



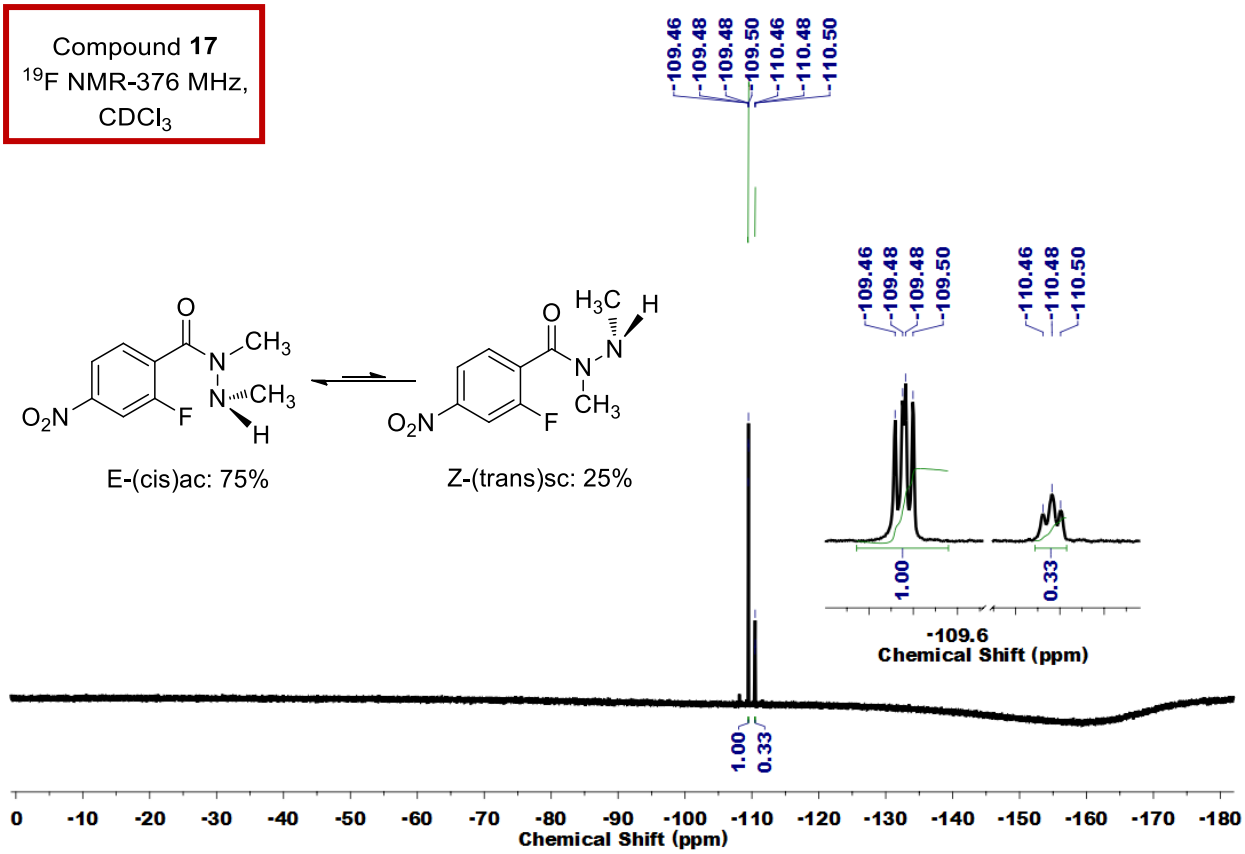
Compound **15**
^{19}F NMR-376 MHz,
$[CD_3]_2SO$



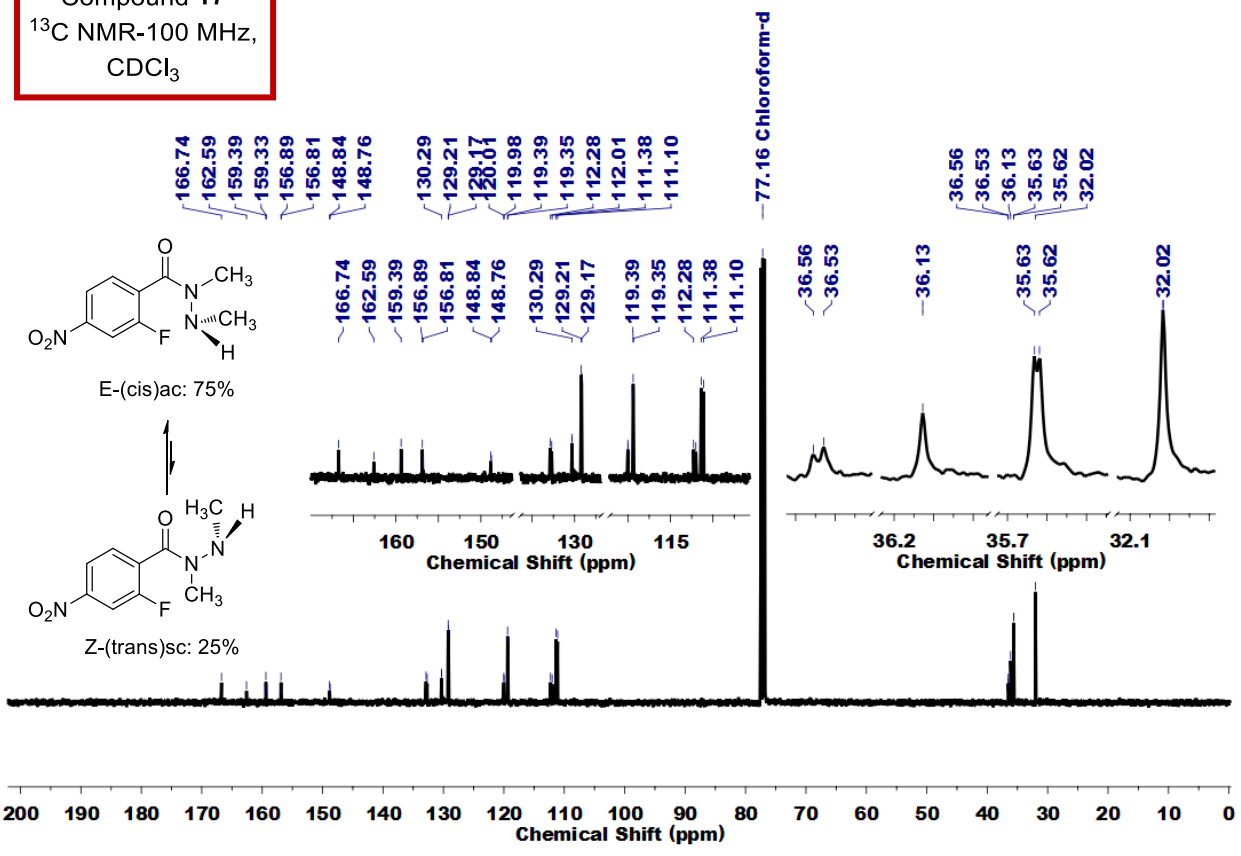
Compound **17**
^{1}H NMR-400 MHz,
$CDCl_3$



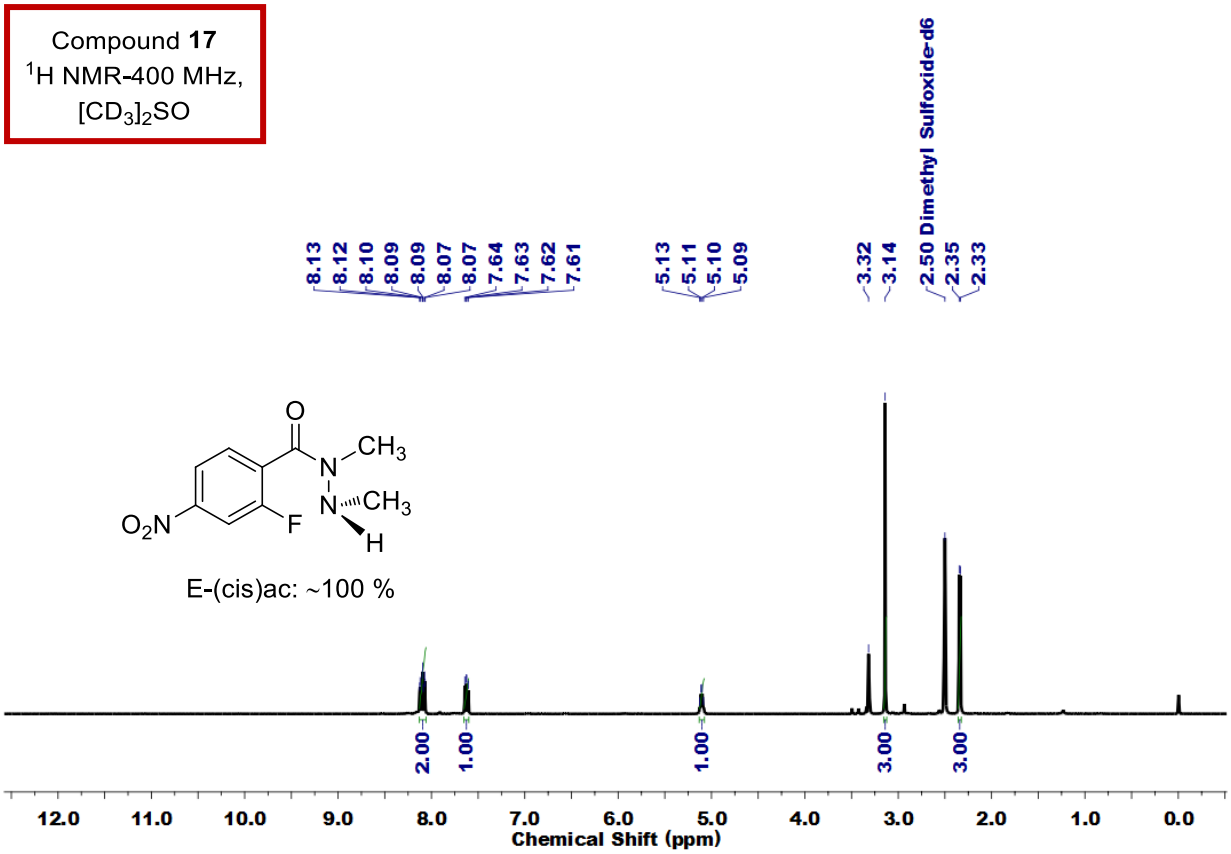
Compound **17**
^{19}F NMR-376 MHz,
$CDCl_3$



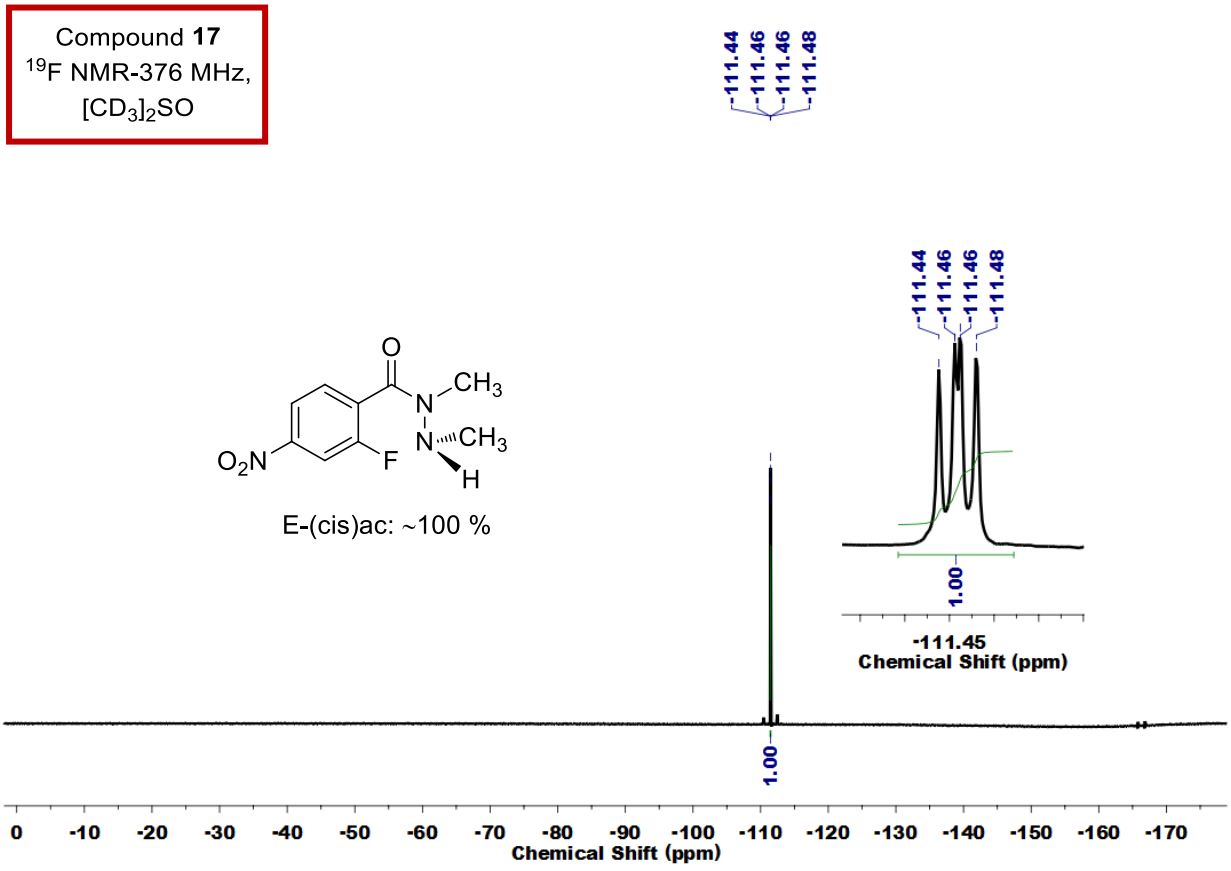
Compound **17**
^{13}C NMR-100 MHz,
$CDCl_3$



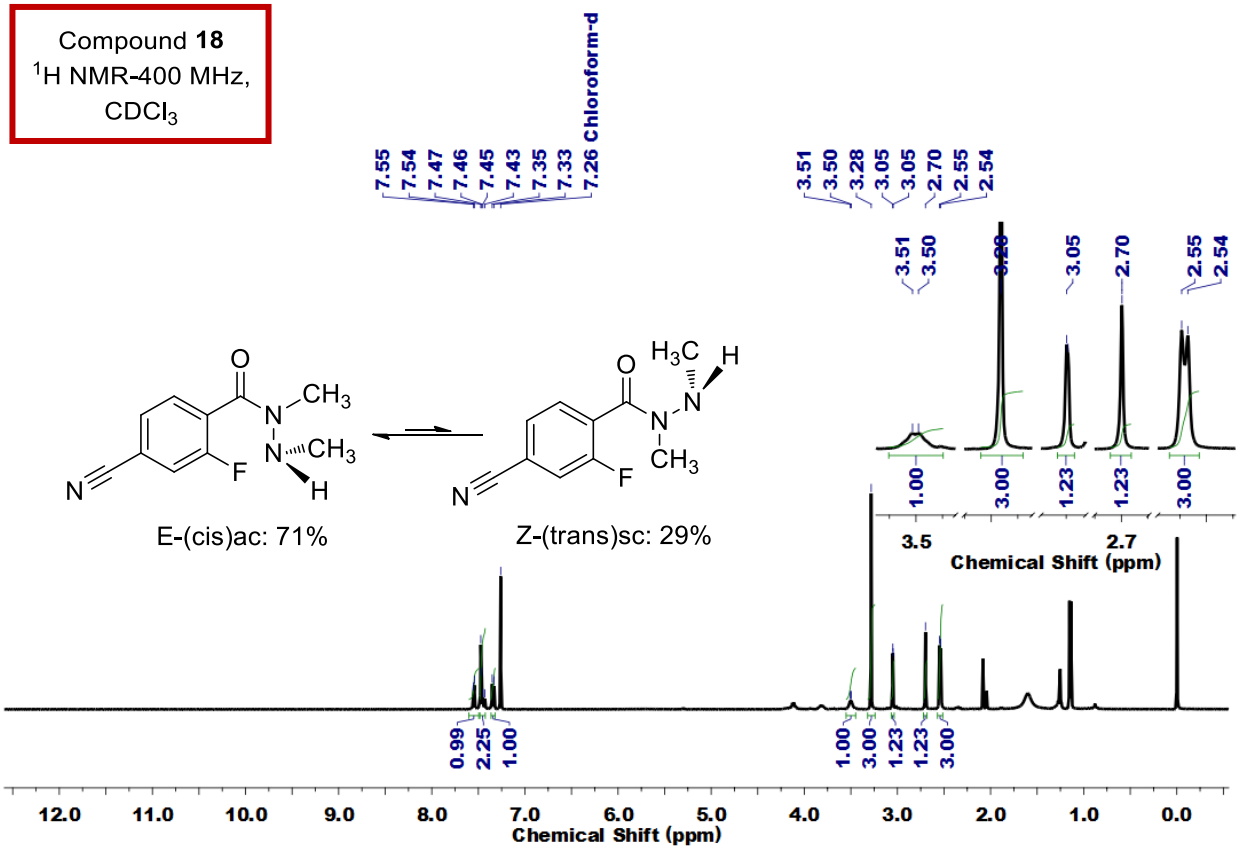
Compound **17**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



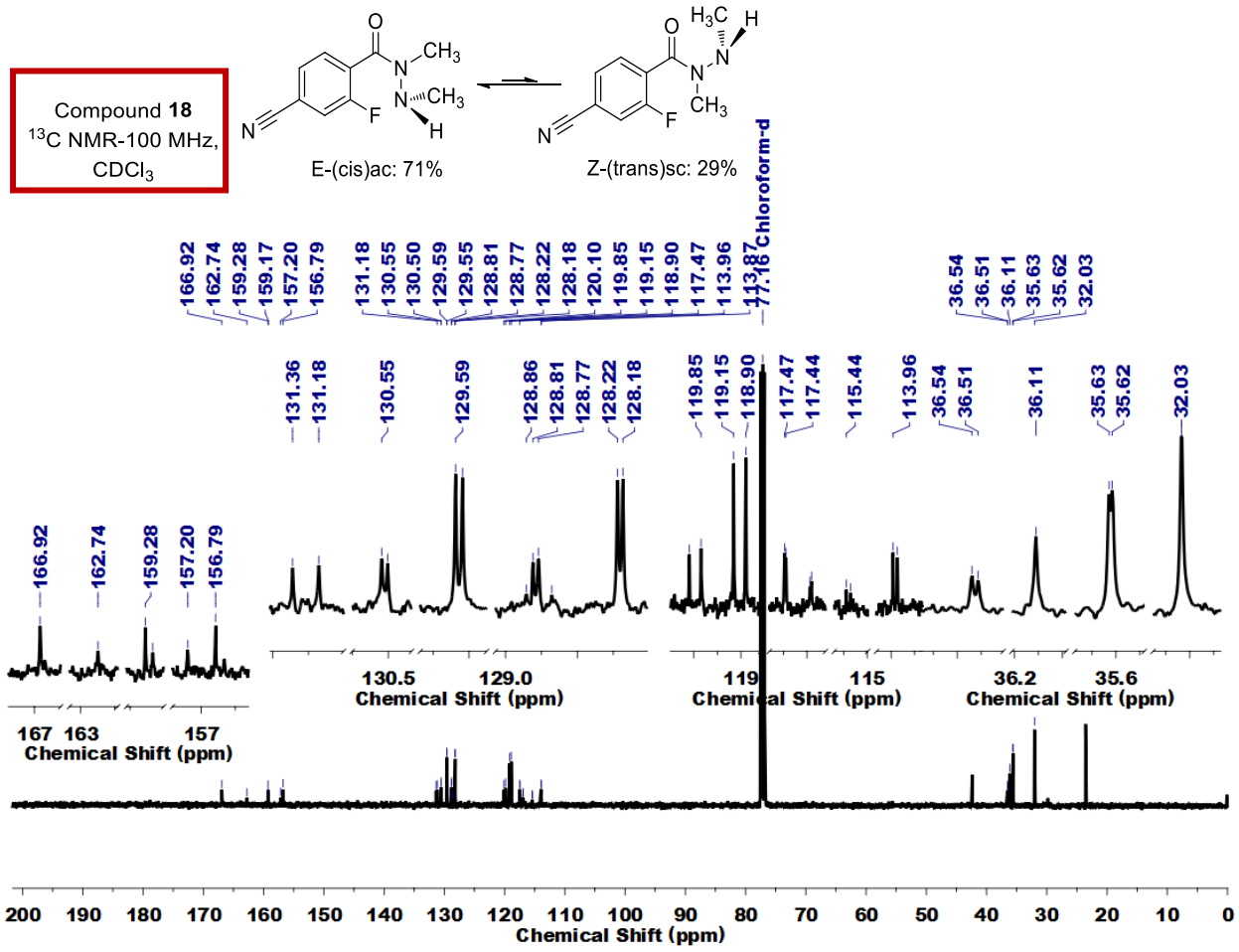
Compound **17**
^{19}F NMR-376 MHz,
$[CD_3]_2SO$



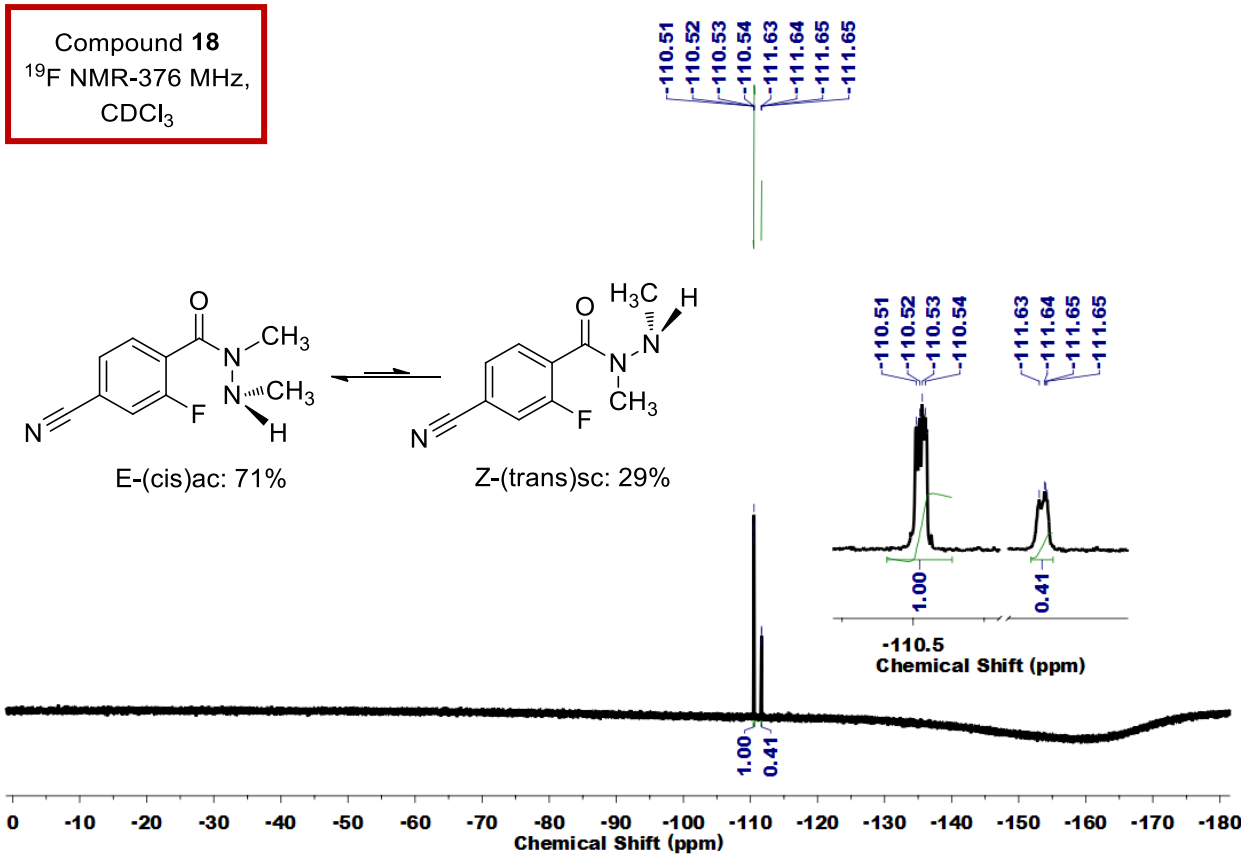
Compound **18**
^{1}H NMR-400 MHz,
$CDCl_3$



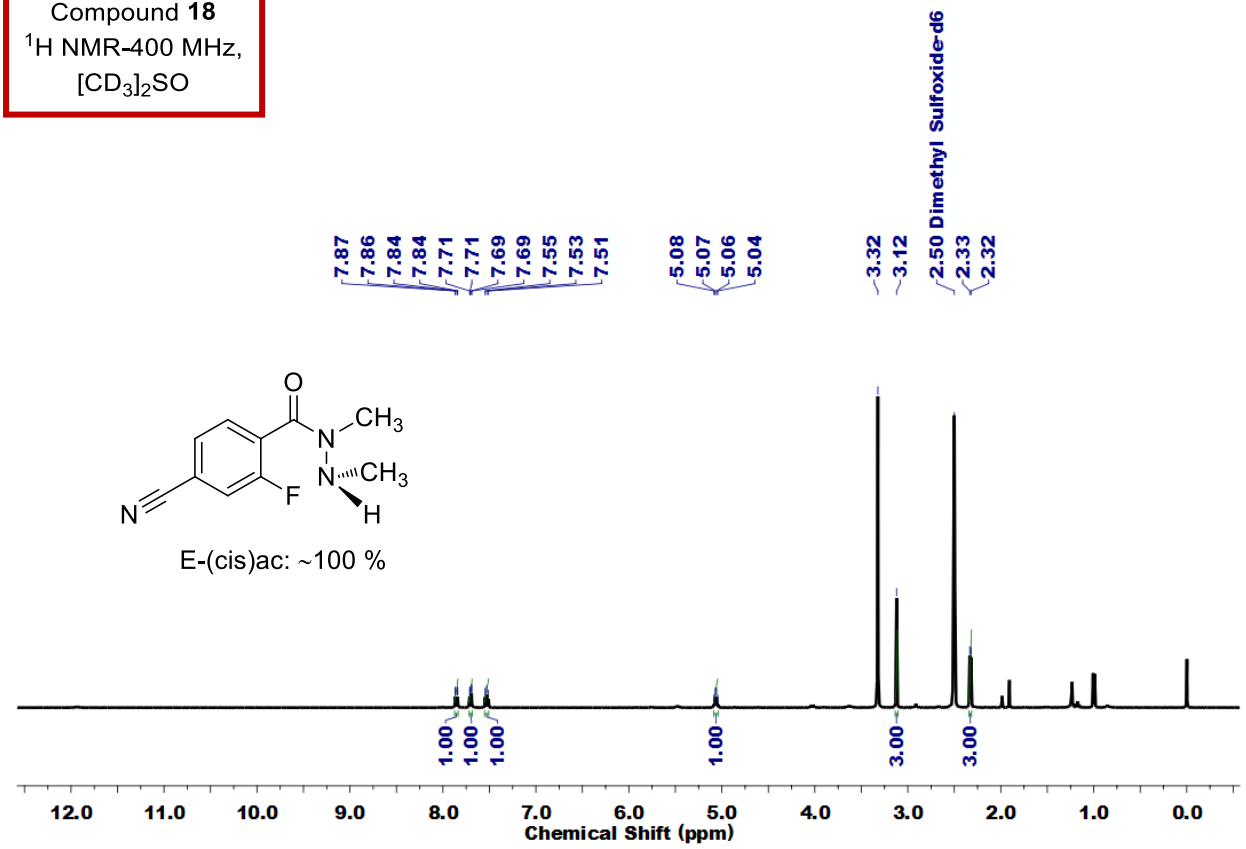
Compound **18**
^{13}C NMR-100 MHz,
$CDCl_3$



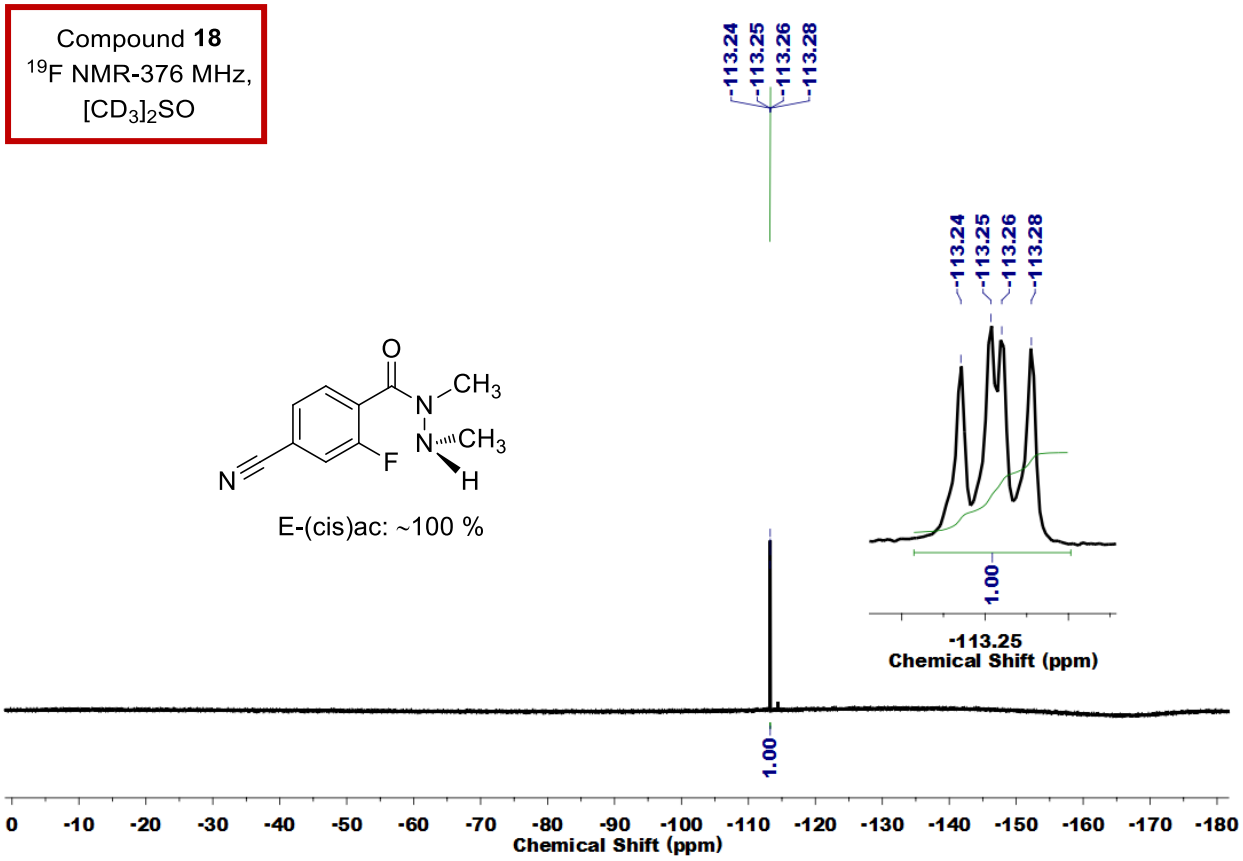
Compound **18**
^{19}F NMR-376 MHz,
$CDCl_3$



Compound **18**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$

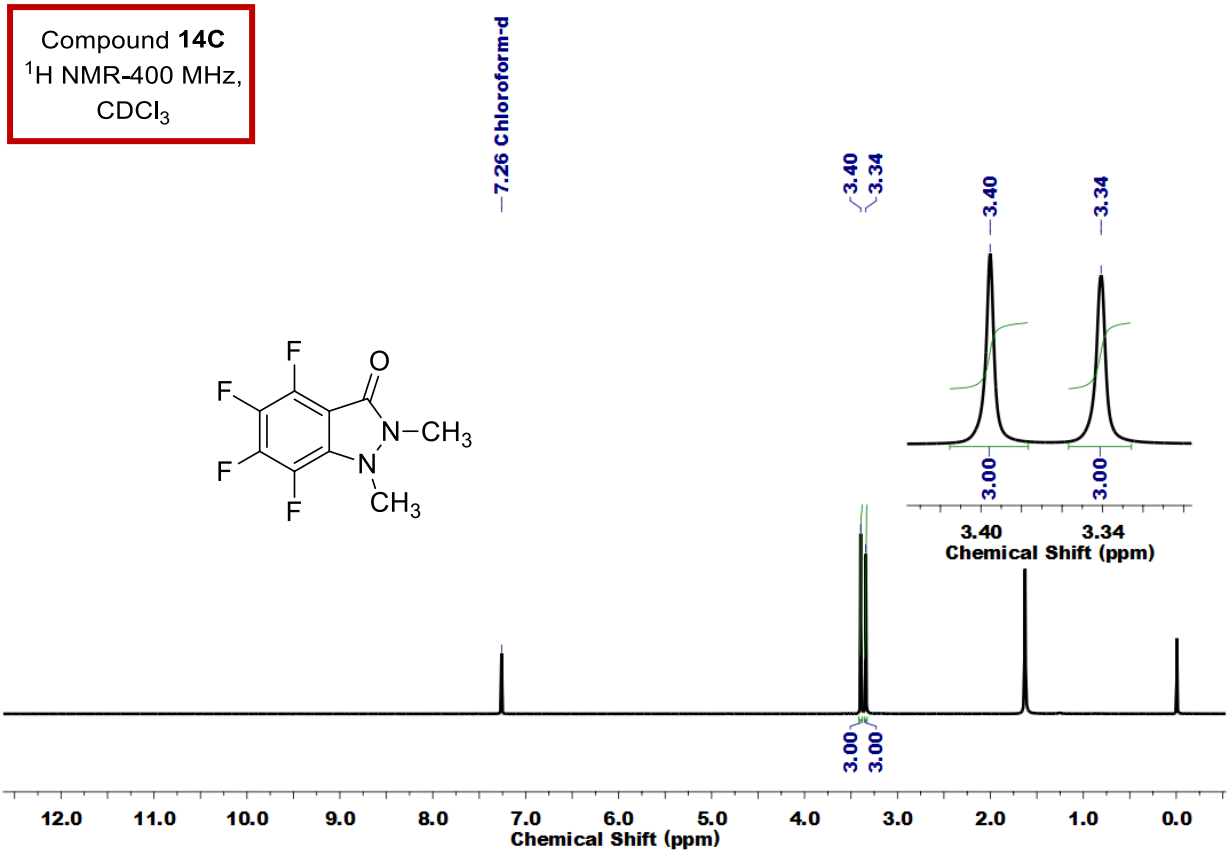


Compound **18**
^{19}F NMR-376 MHz,
$[CD_3]_2SO$

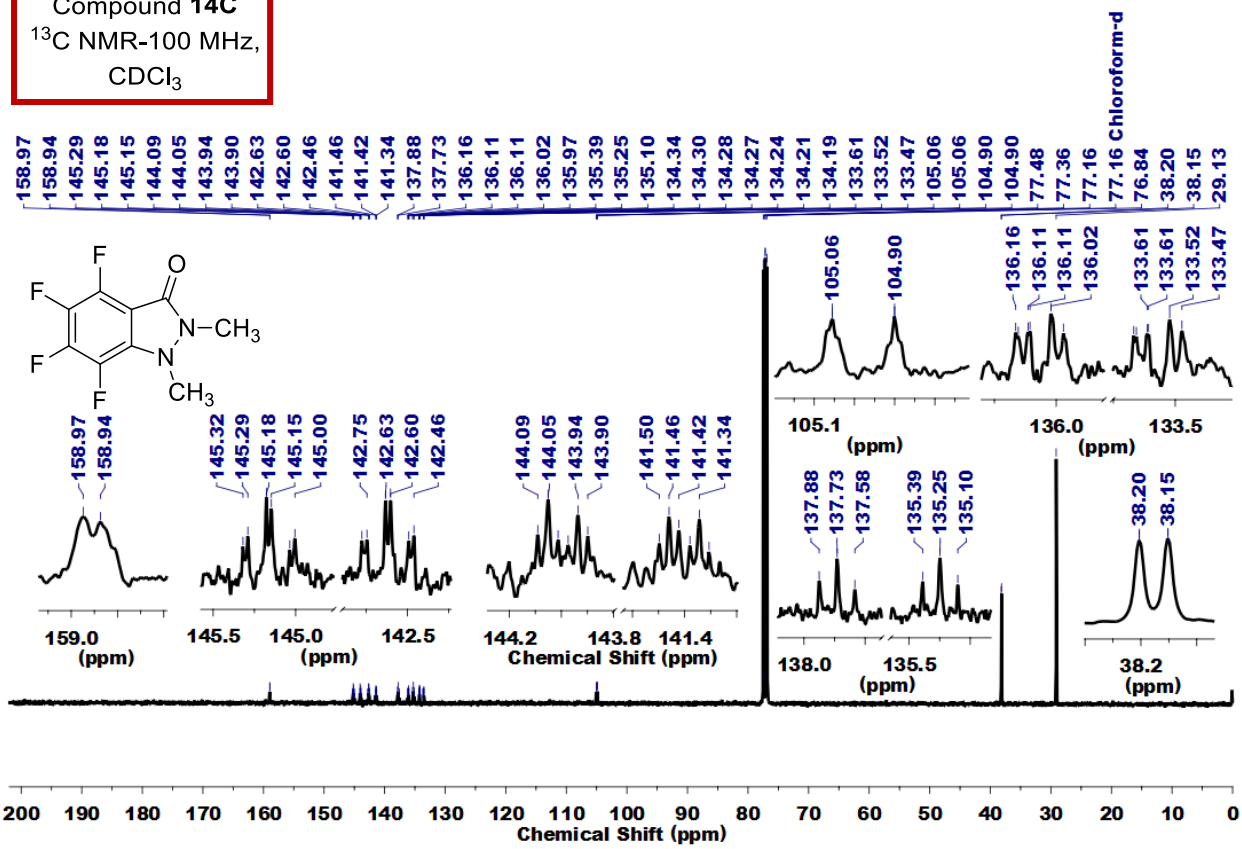


Cyclic Compounds

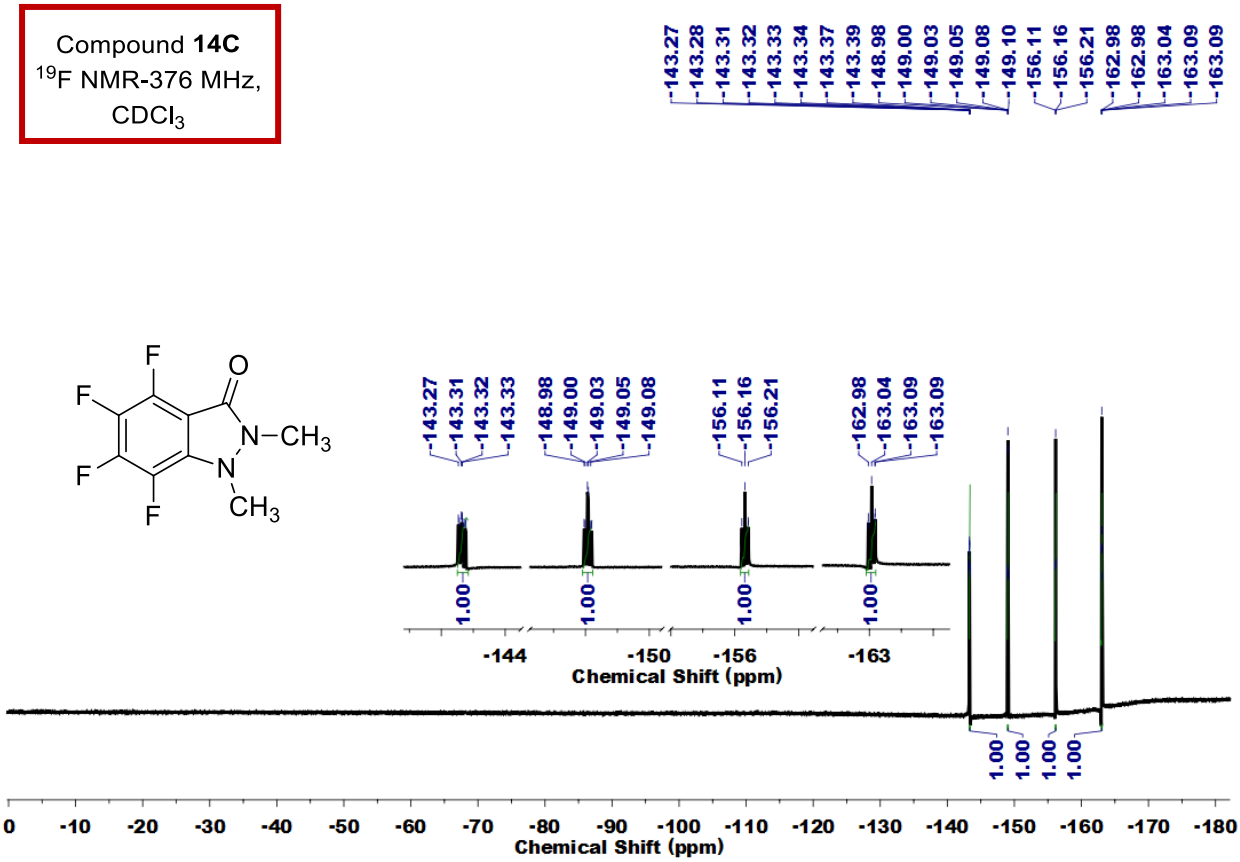
Compound **14C**
^{1}H NMR-400 MHz,
$CDCl_3$



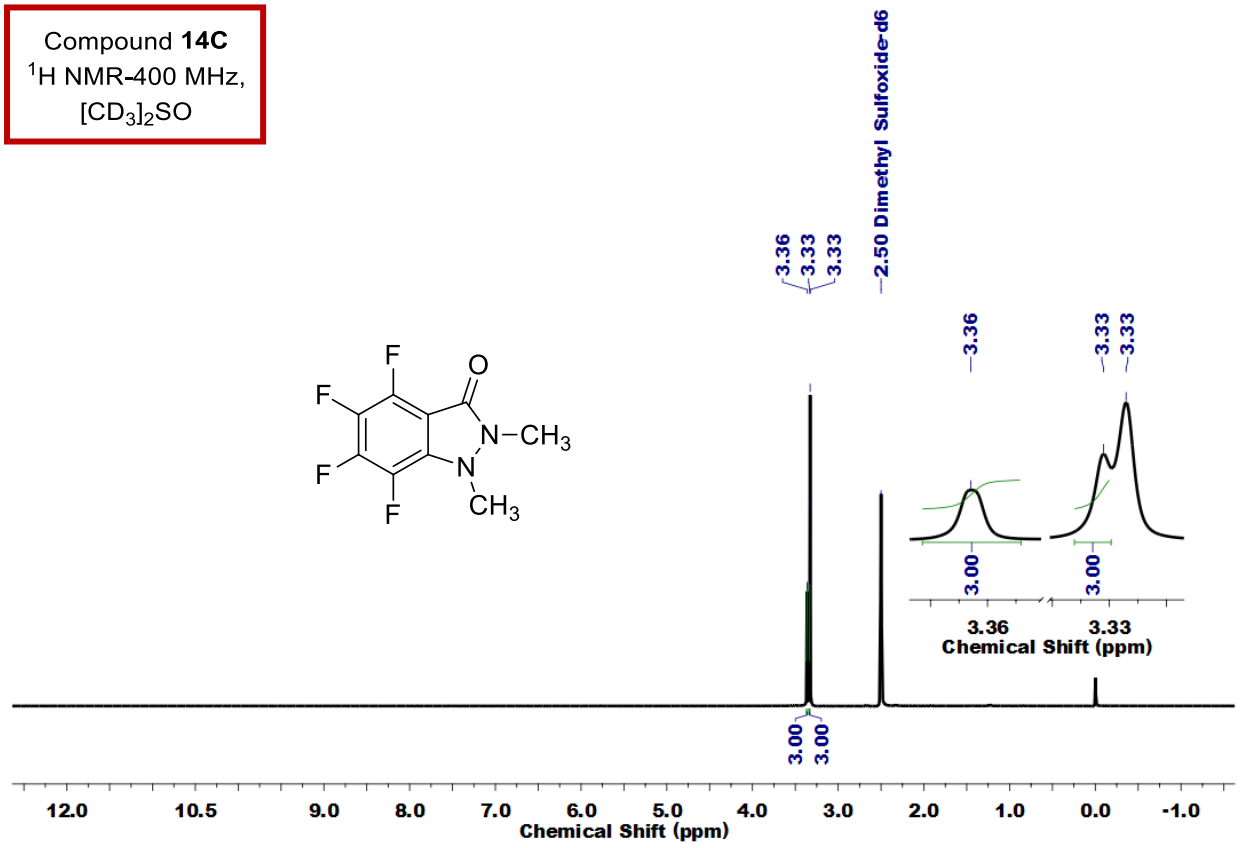
Compound **14C**
^{13}C NMR-100 MHz,
$CDCl_3$



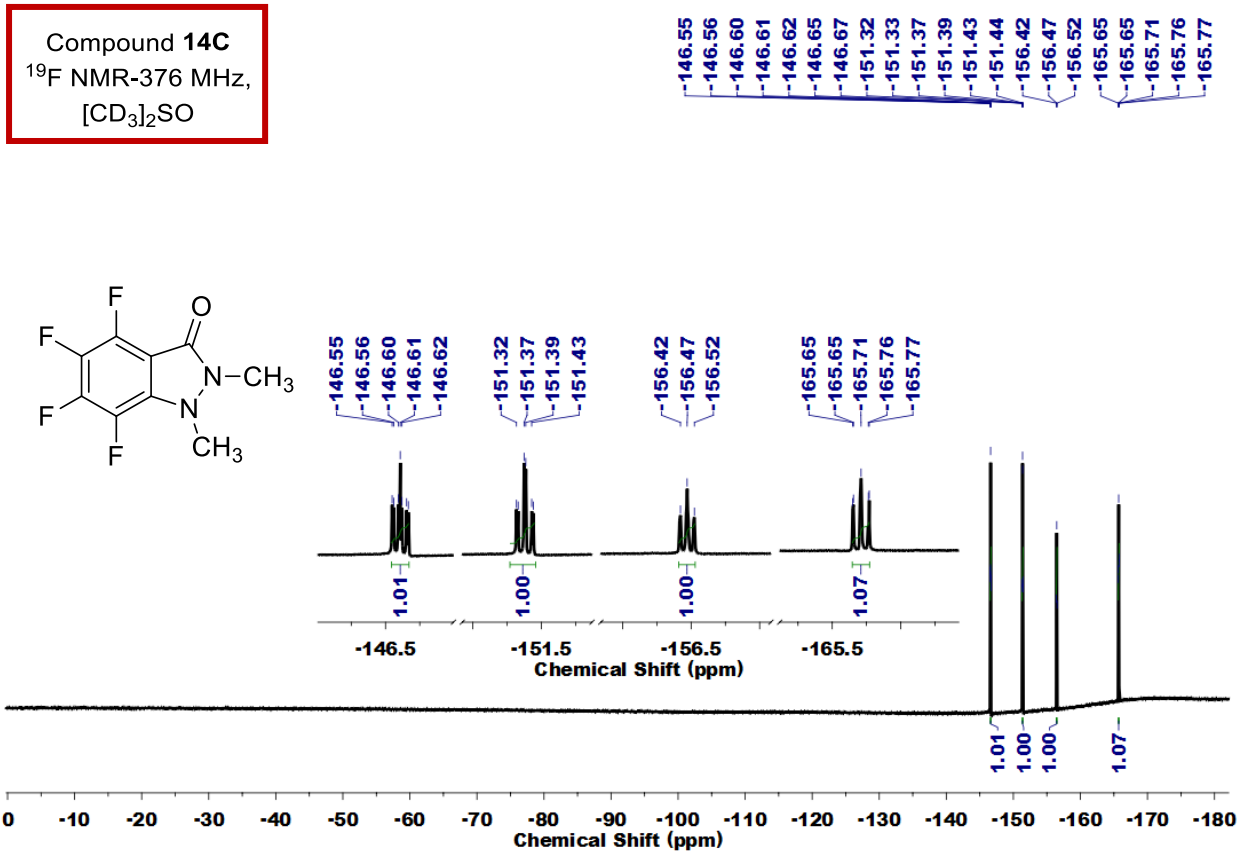
Compound **14C**
^{19}F NMR-376 MHz,
$CDCl_3$



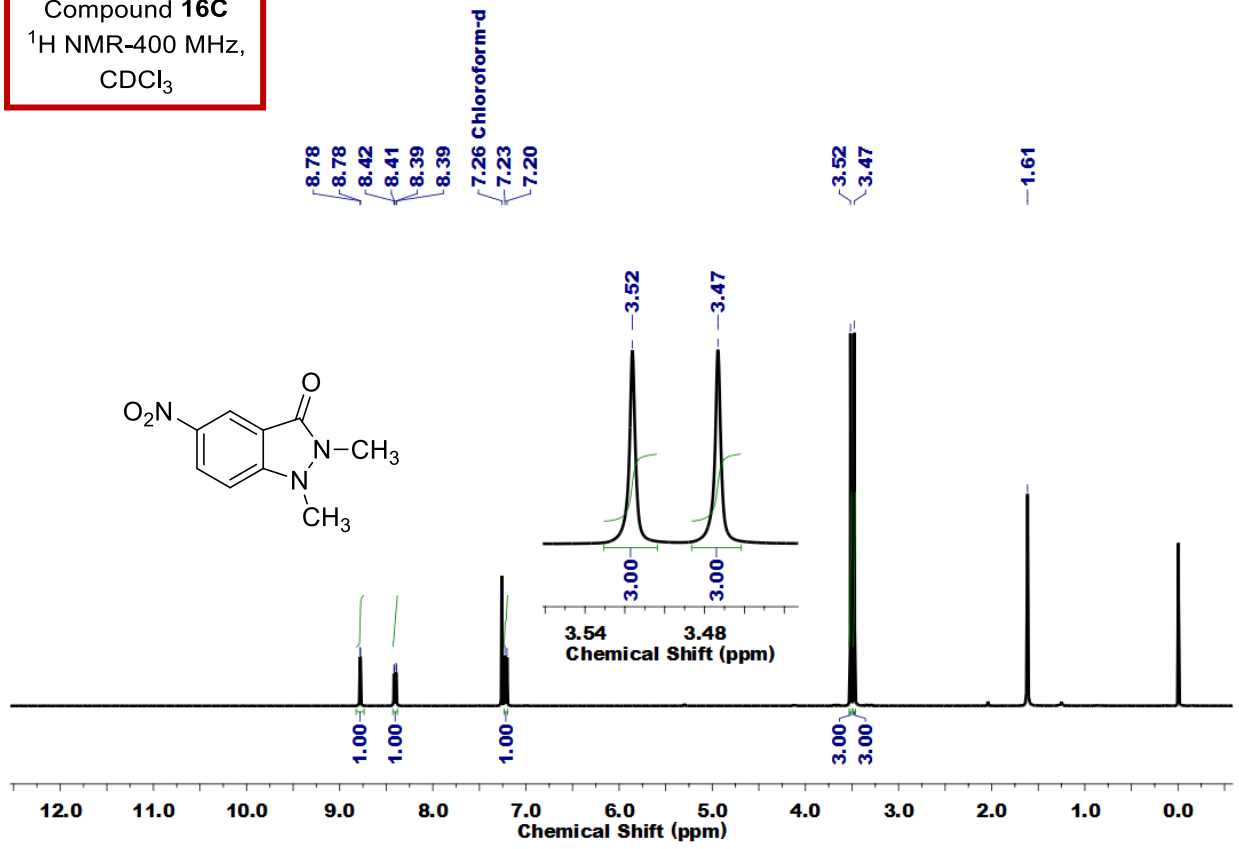
Compound **14C**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



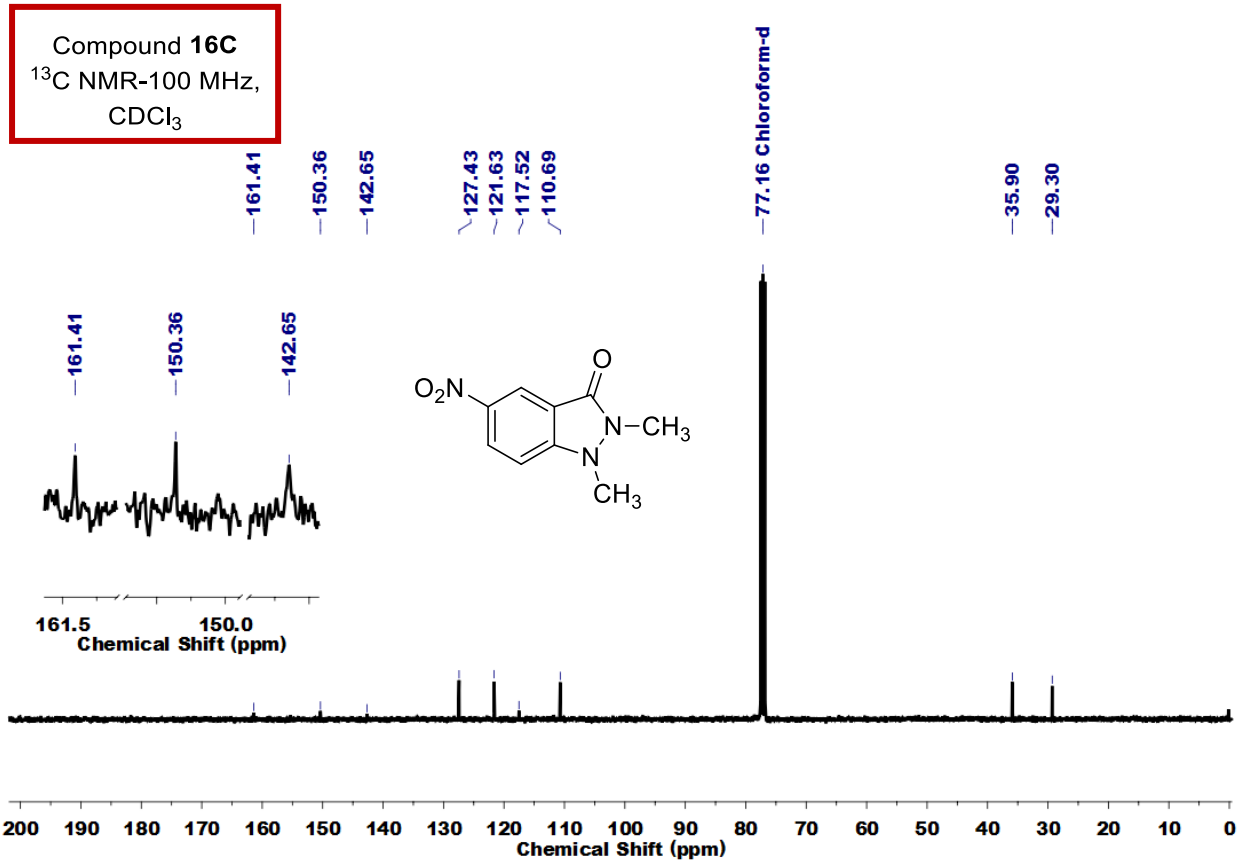
Compound **14C**
^{19}F NMR-376 MHz,
$[CD_3]_2SO$



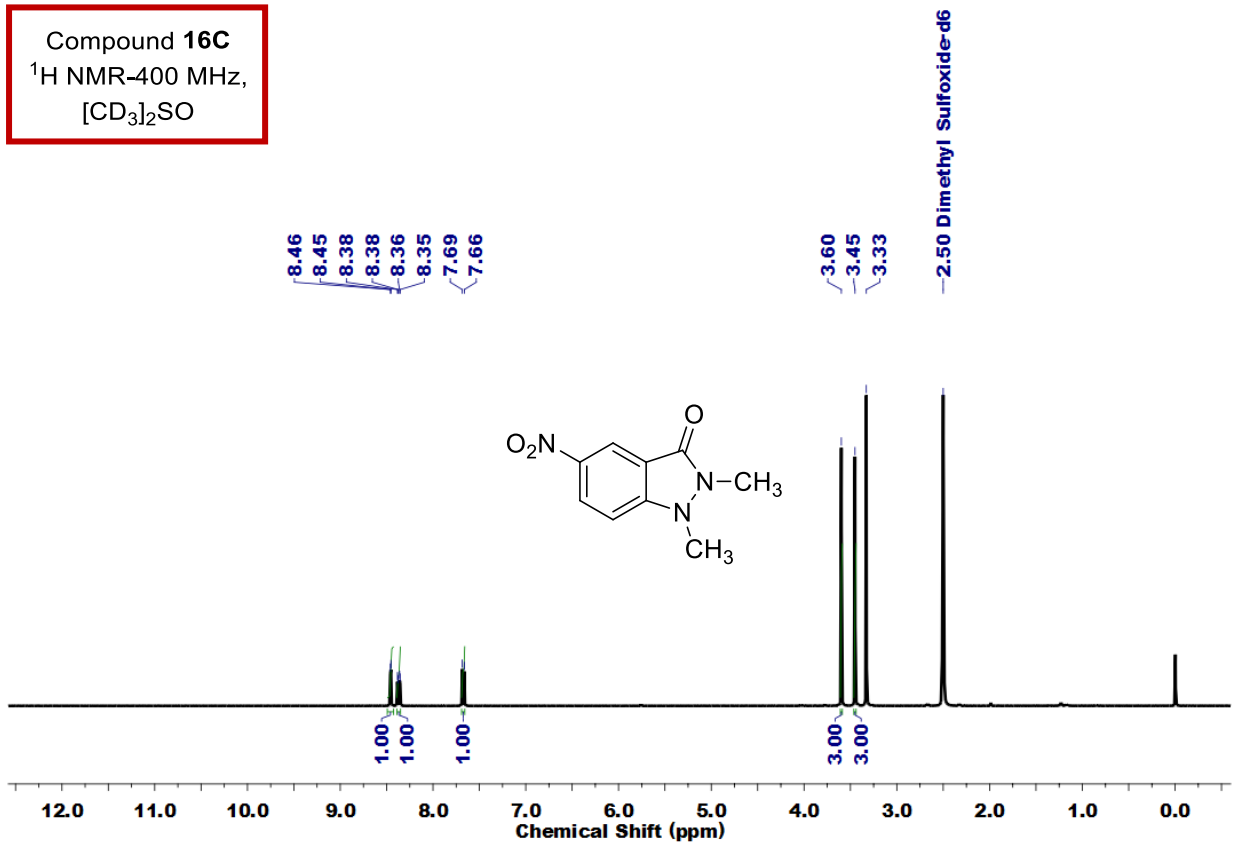
Compound **16C**
^{1}H NMR-400 MHz,
$CDCl_3$



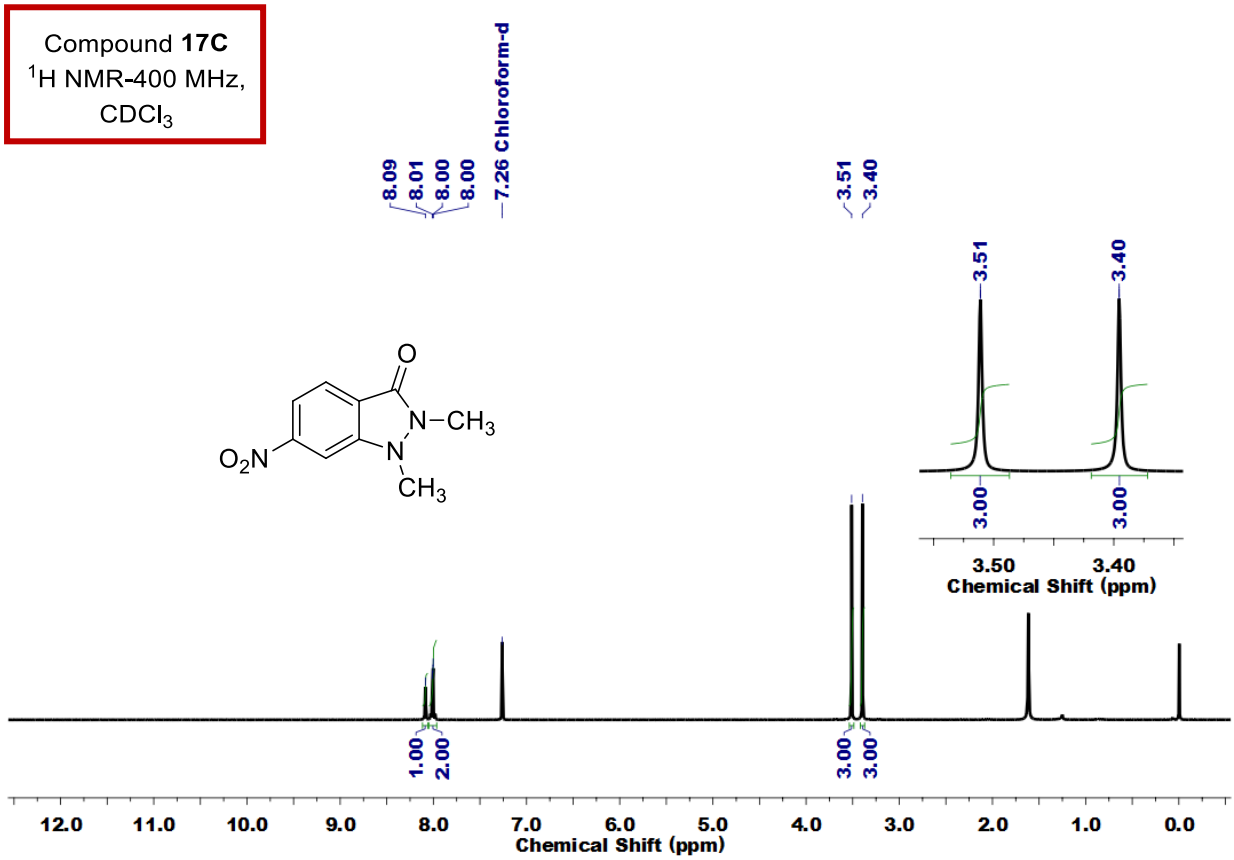
Compound **16C**
^{13}C NMR-100 MHz,
$CDCl_3$



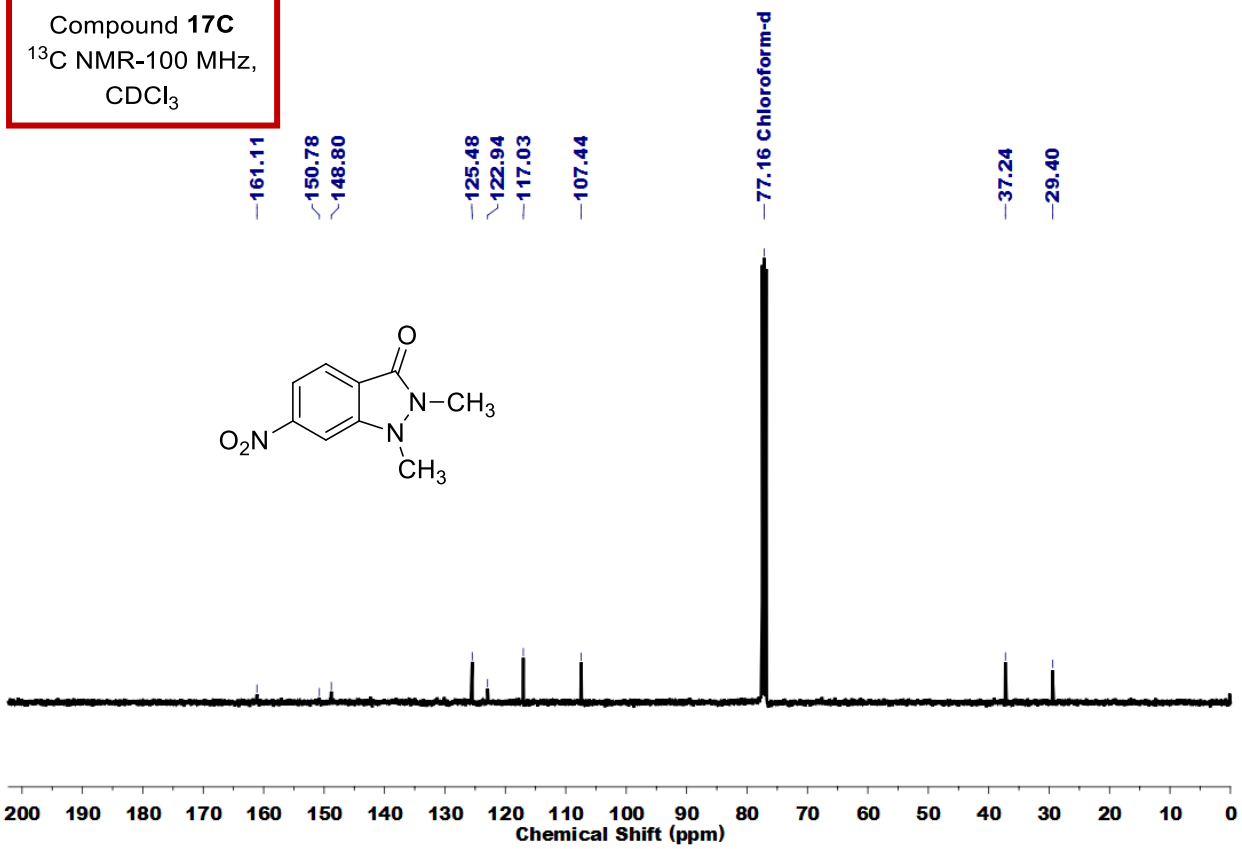
Compound **16C**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



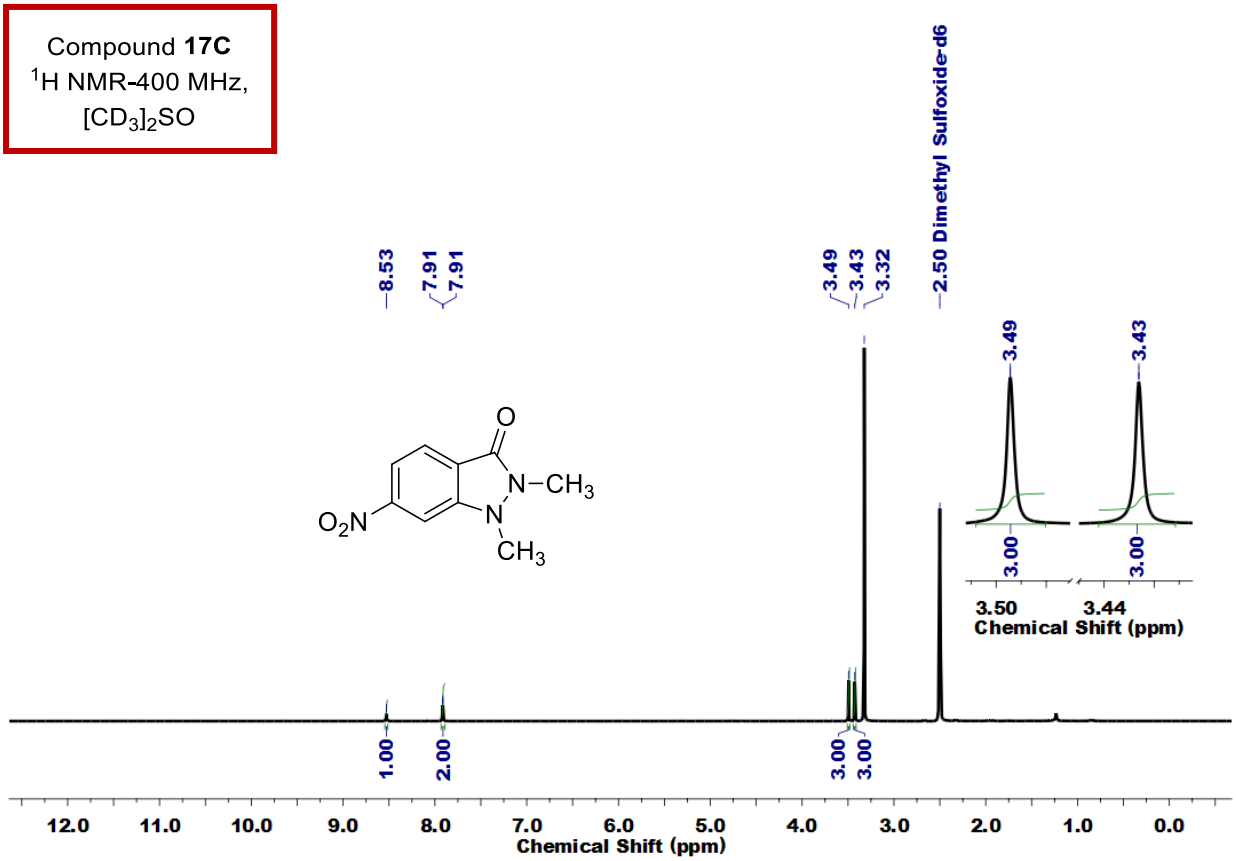
Compound **17C**
^{1}H NMR-400 MHz,
$CDCl_3$



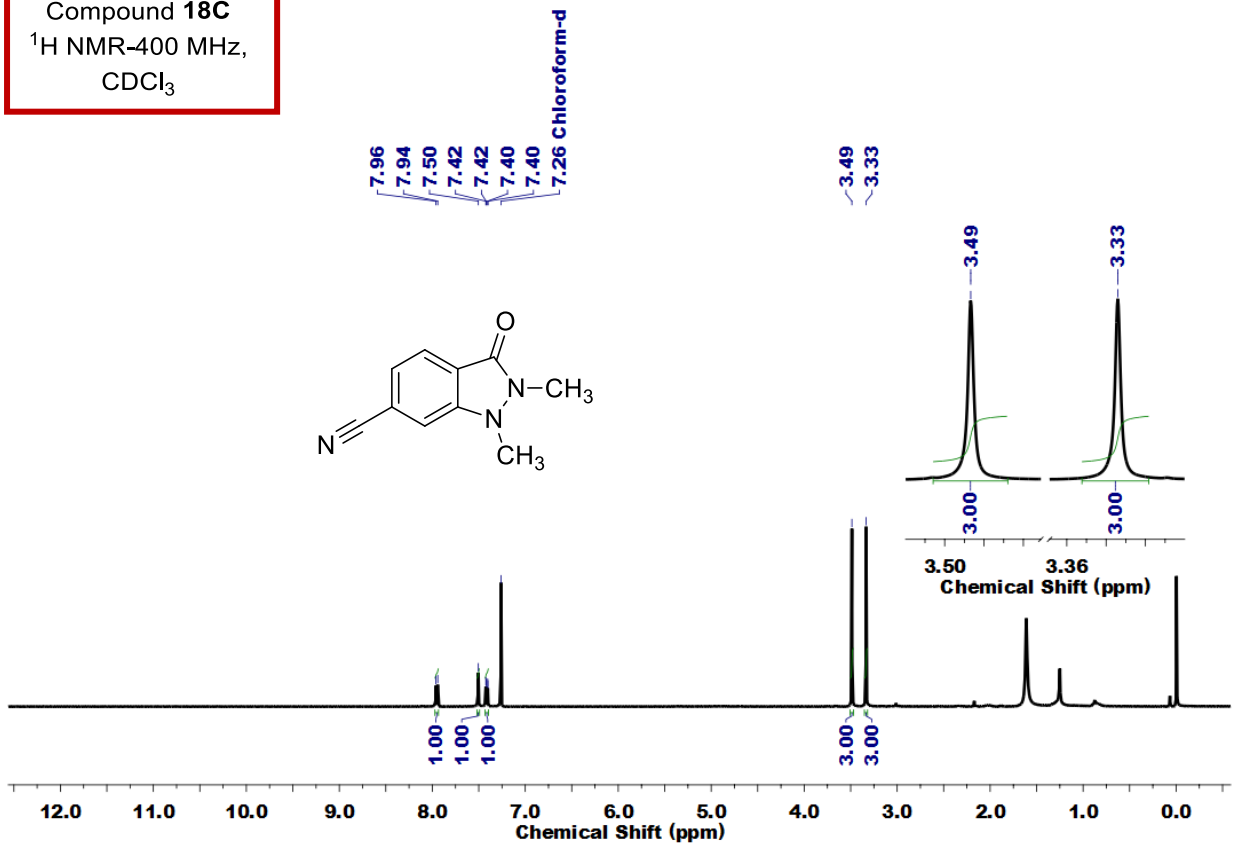
Compound **17C**
^{13}C NMR-100 MHz,
$CDCl_3$



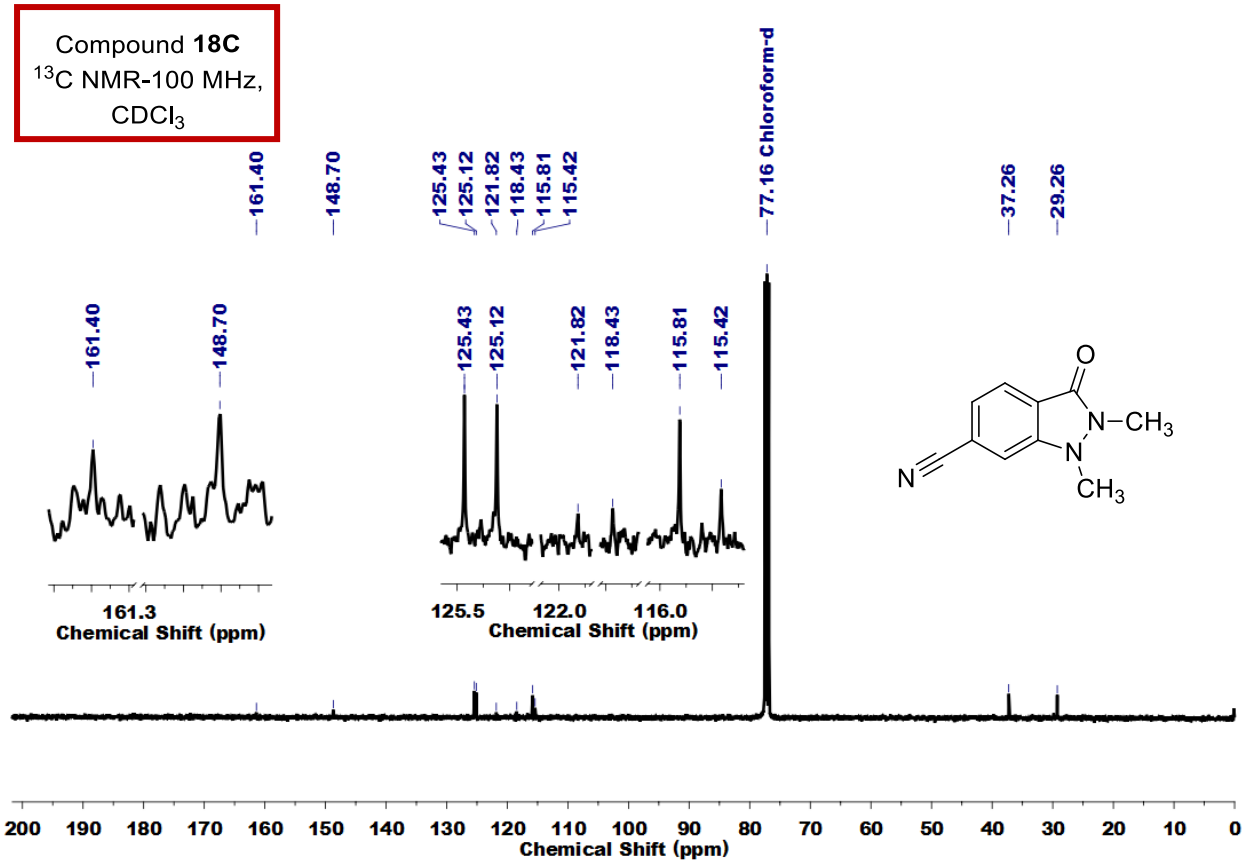
Compound **17C**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



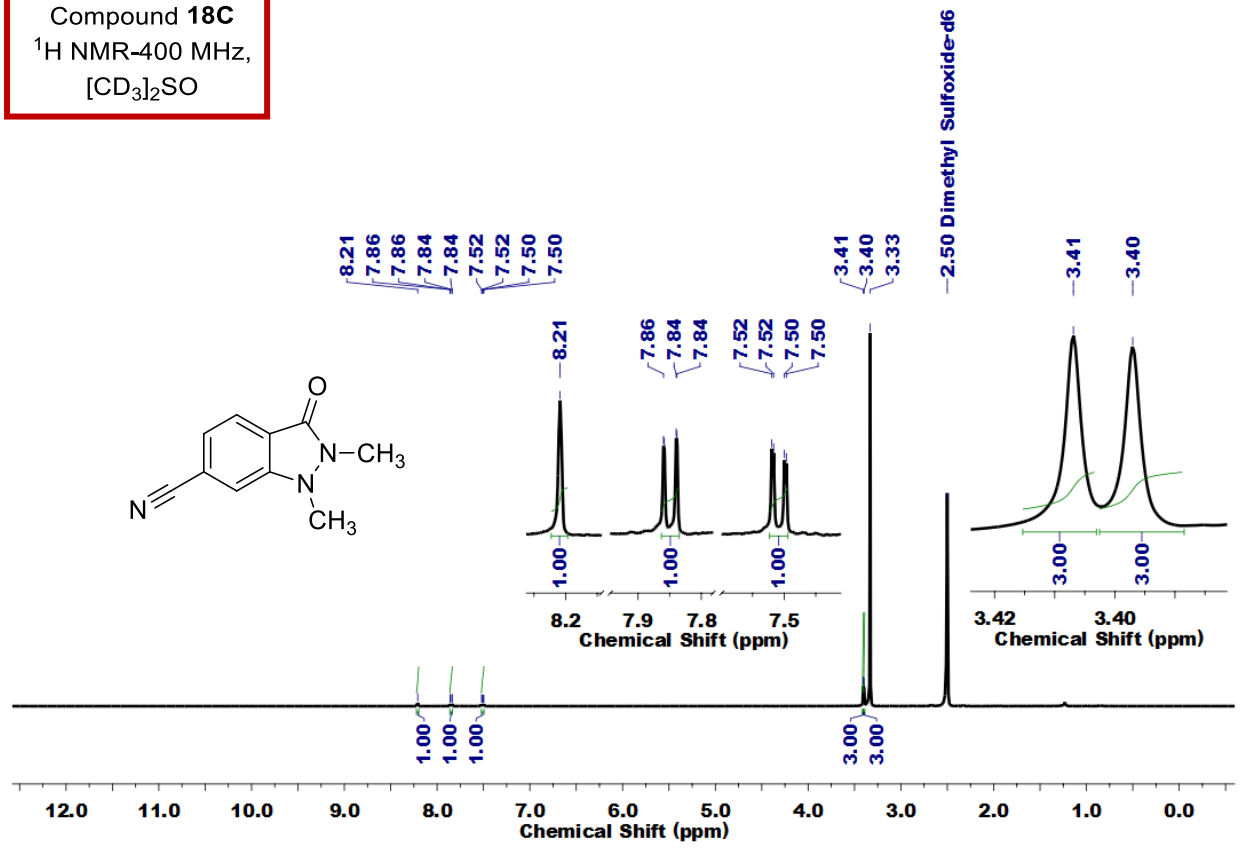
Compound **18C**
^{1}H NMR-400 MHz,
$CDCl_3$



Compound **18C**
^{13}C NMR-100 MHz,
$CDCl_3$



Compound **18C**
^{1}H NMR-400 MHz,
$[CD_3]_2SO$



K. References.

1. Bruker APEX 3, Version 2, User Manual S86 –EXS053 (Bruker AXS Inc., 2015).
2. Siemens, SMART system (Siemens Analytical X-ray Instruments Inc., 1995).
3. G. M. Sheldrick, SADABS (Bruker AXS Inc. 2007).
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