

NH stretching frequencies of intramolecularly hydrogen bonded systems.

An experimental and theoretical study.

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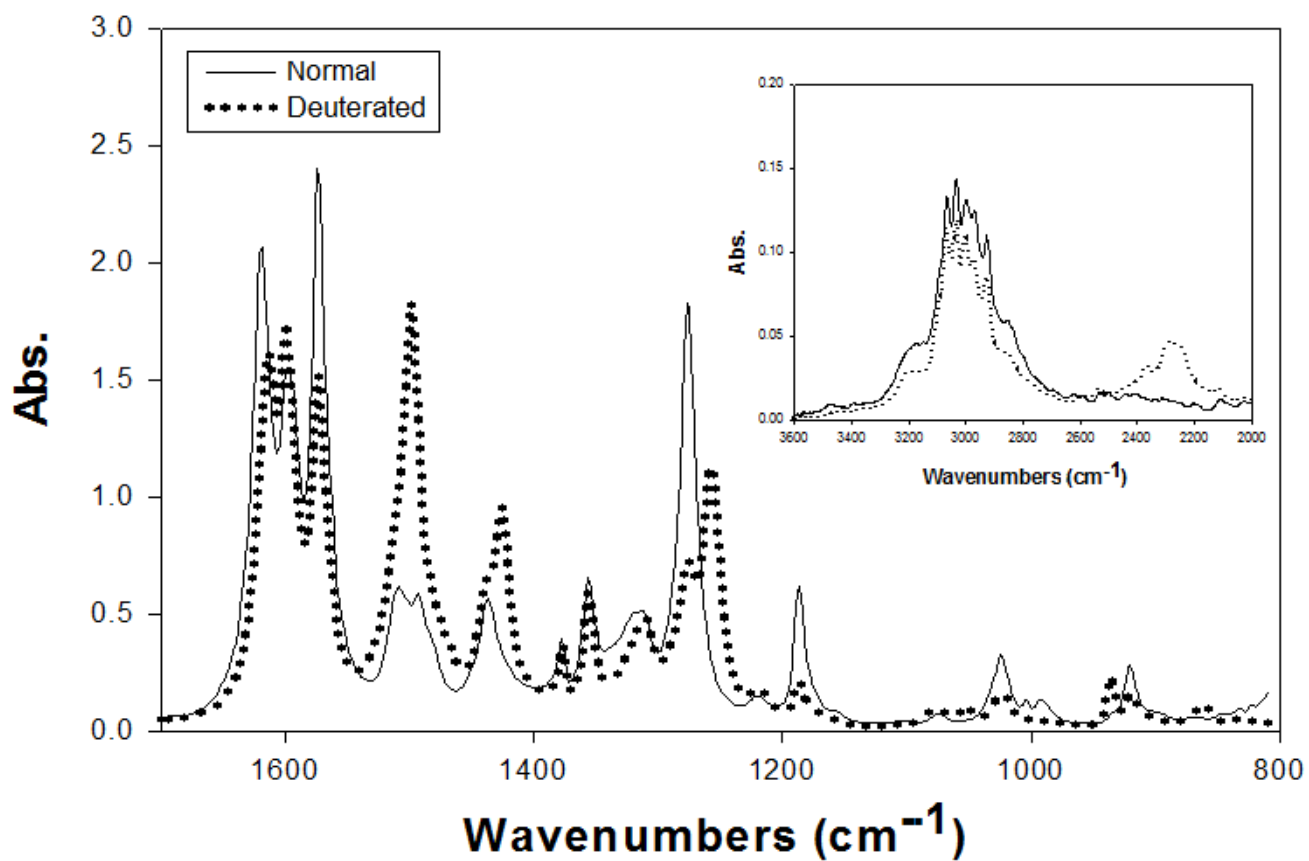
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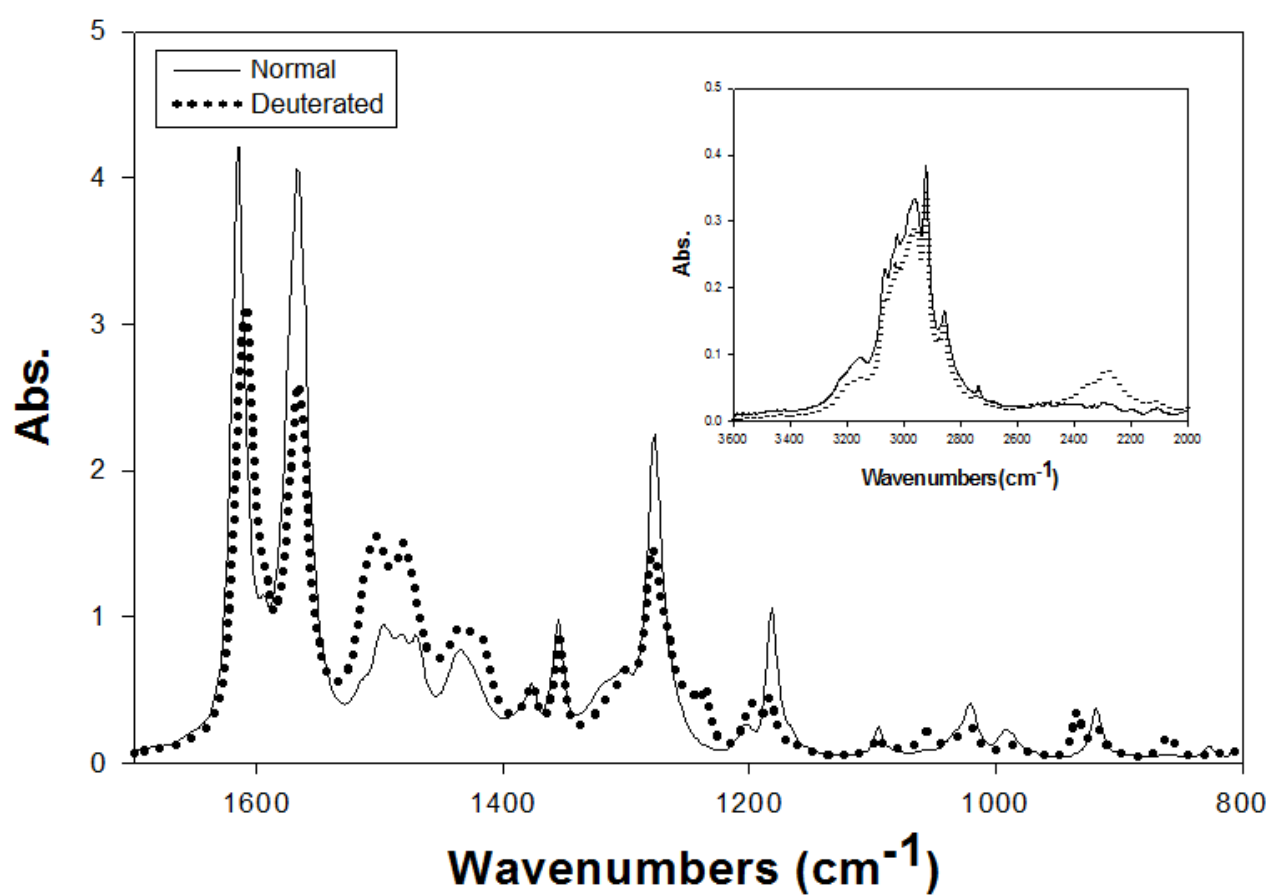
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Supplementary Material

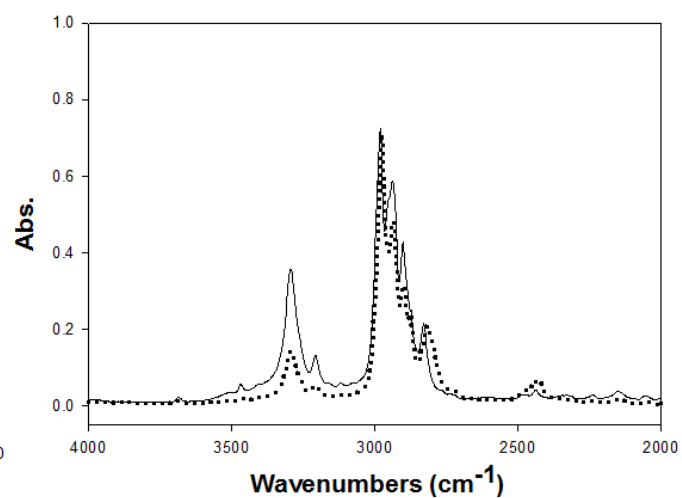
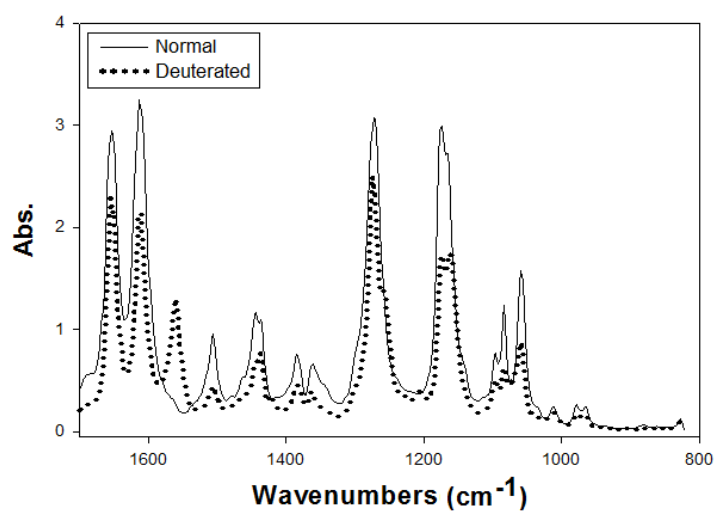
- S1.** IR spectrum of compound **6**.
- S2.** IR spectrum of compound **11**.
- S3.** IR spectrum of compound **17** (see also **S15**).
- S4.** IR spectrum of compound **19**.
- S5.** IR spectrum of compound **45**.
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- S20.** Fundamental band assignments for **17** (17-H) and deuterated **17** (17-D).
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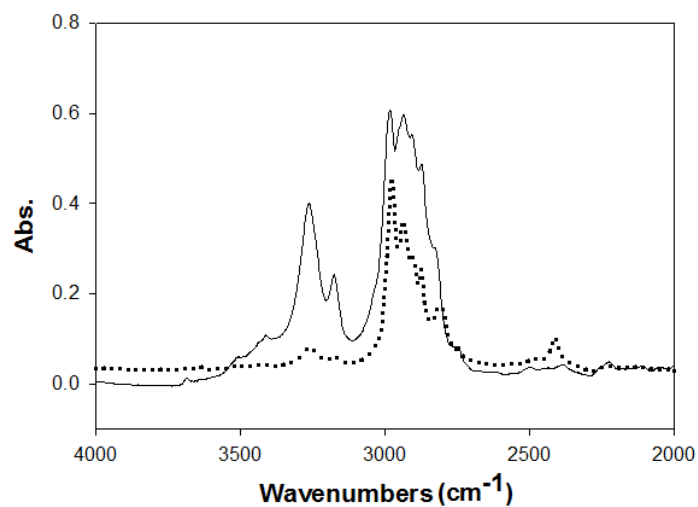
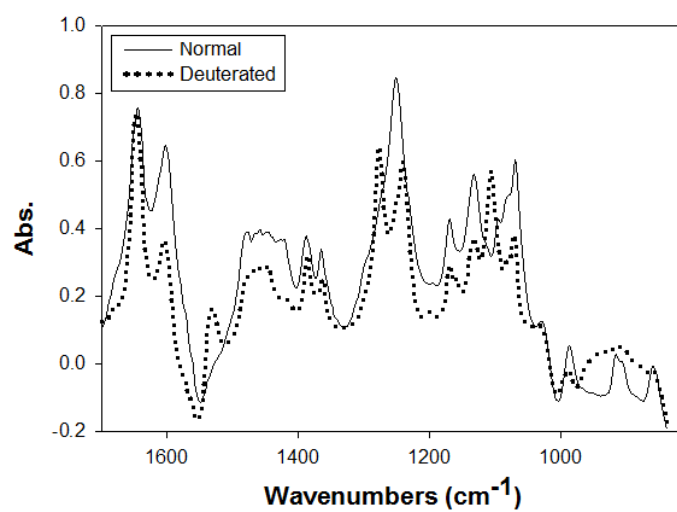
S1. IR spectrum of compound 6.



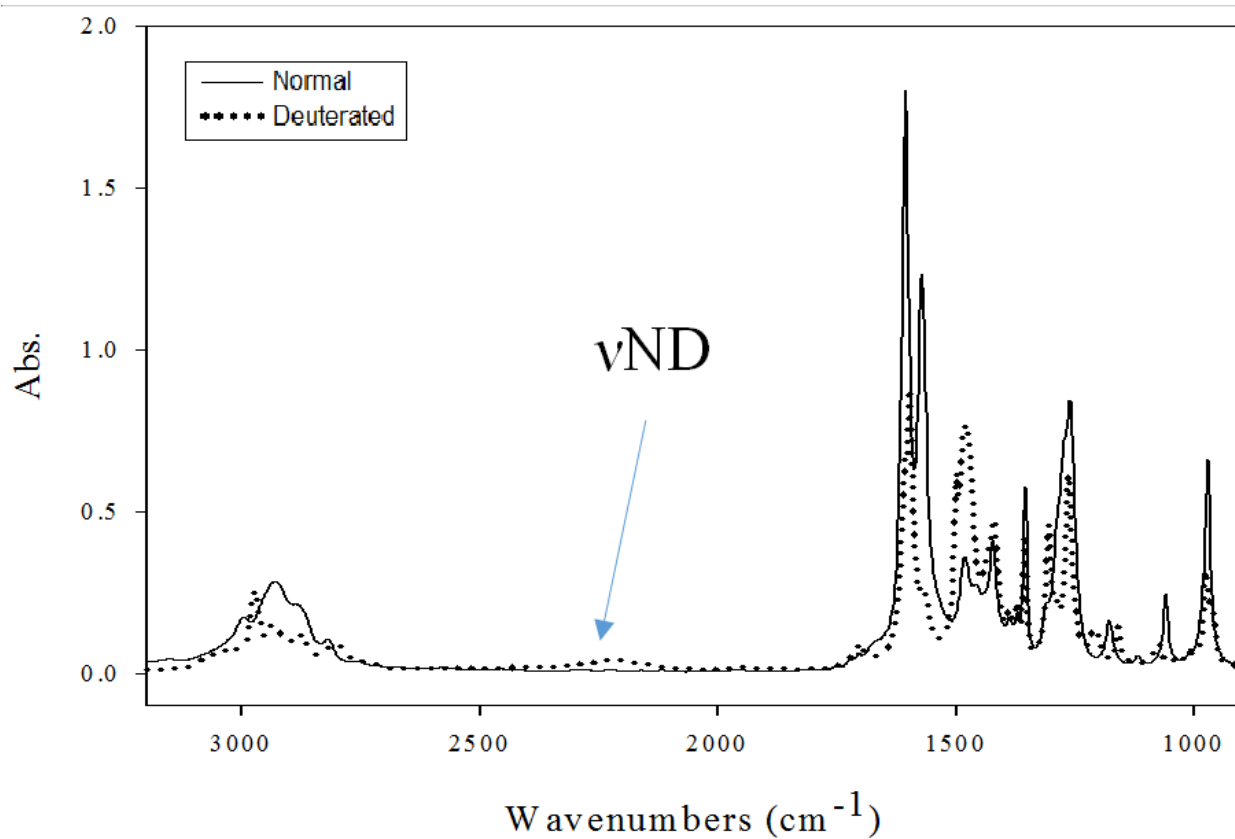
S2. IR spectrum of compound 11.



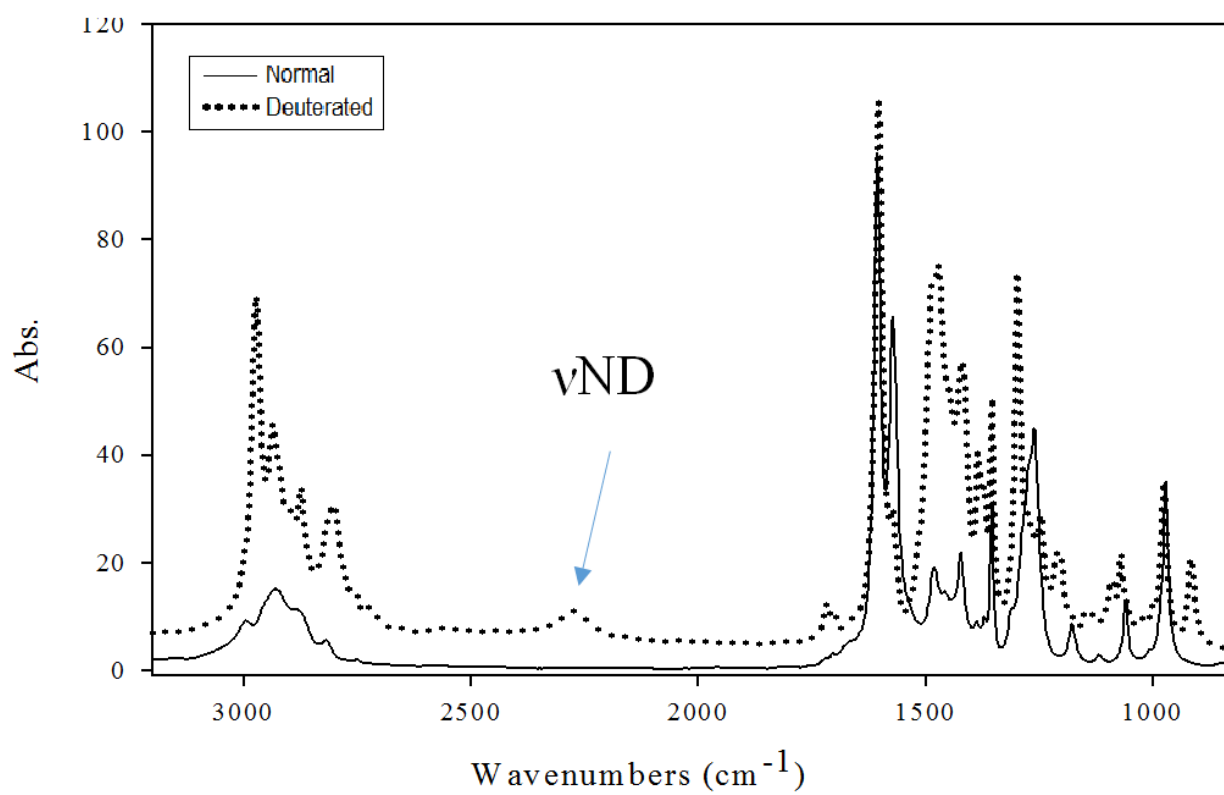
S3. IR spectrum of compound **17** (see also **S15**).



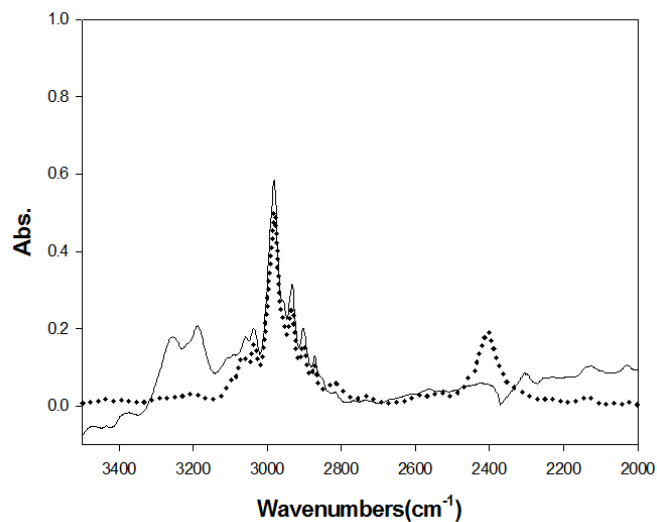
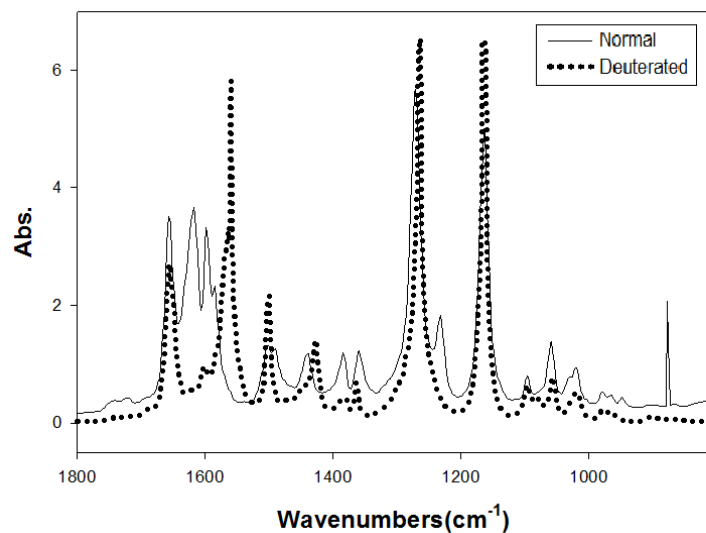
S4. IR spectrum of compound **19**.



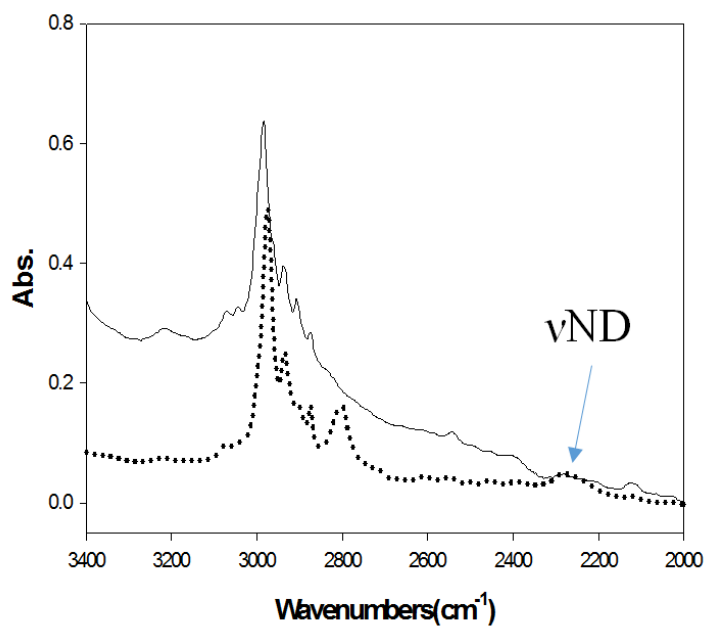
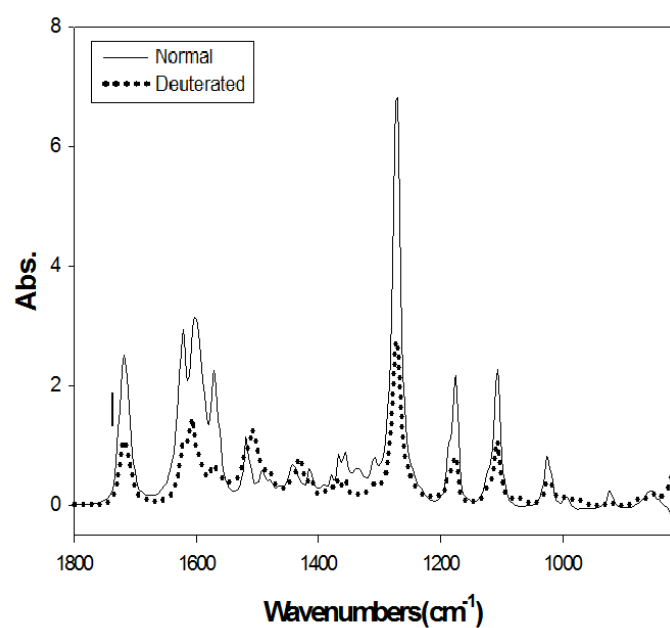
S5. IR spectrum of compound **45**.



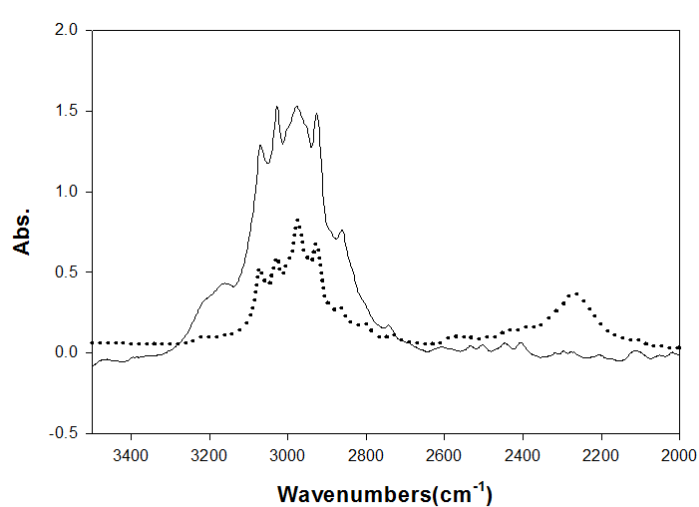
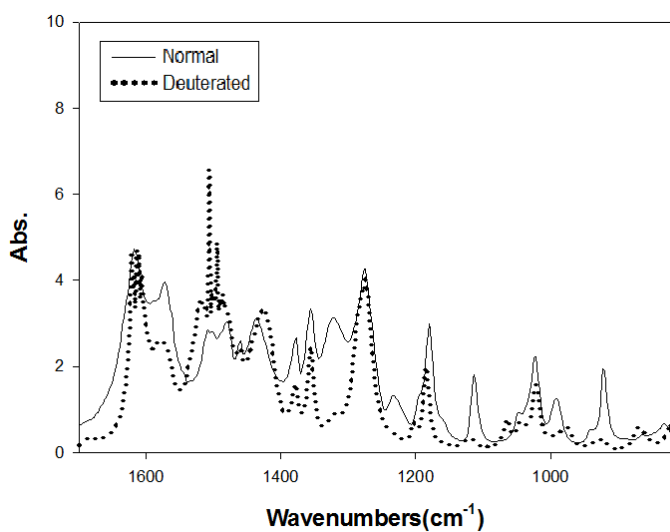
S6. IR spectrum of compound **14**.



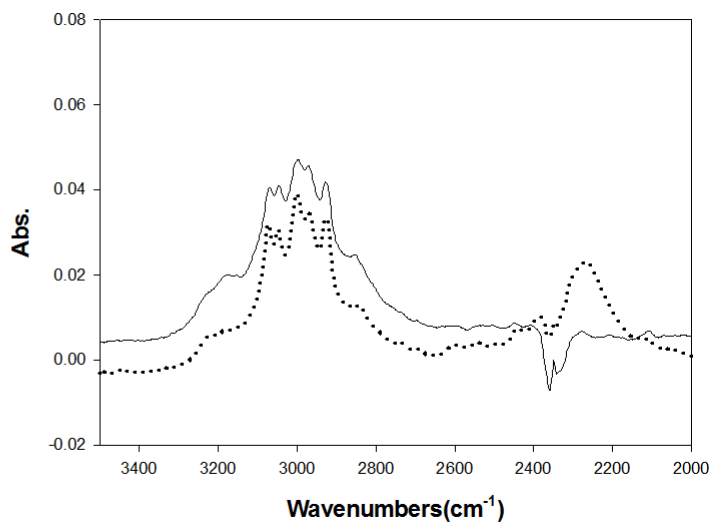
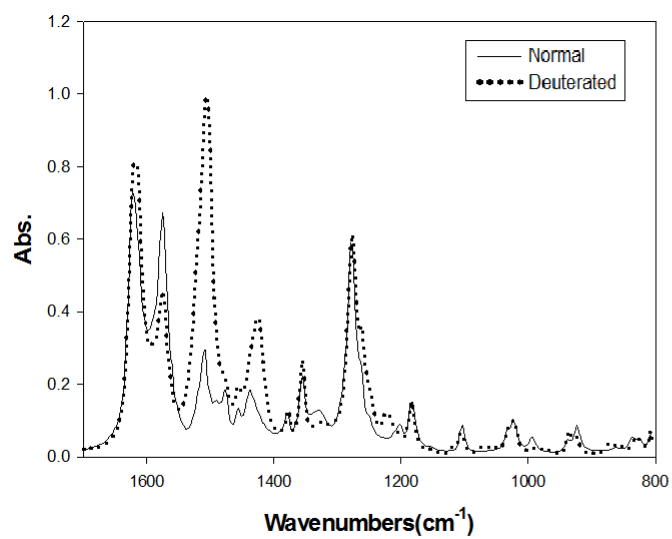
S7. IR spectrum of compound 16.



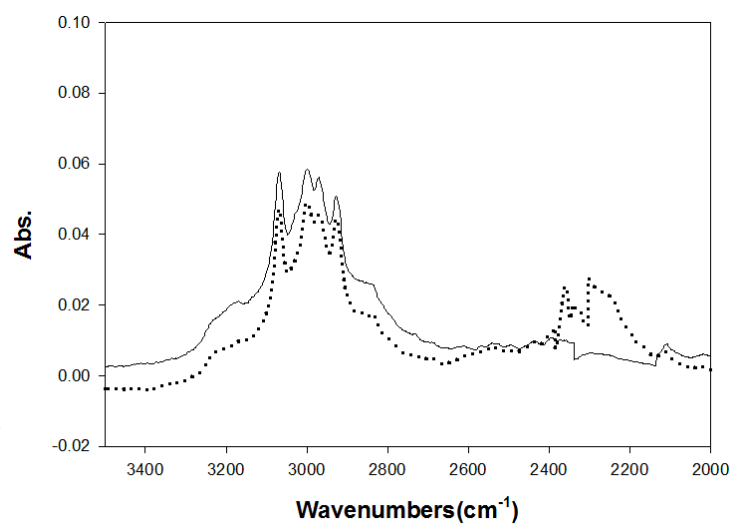
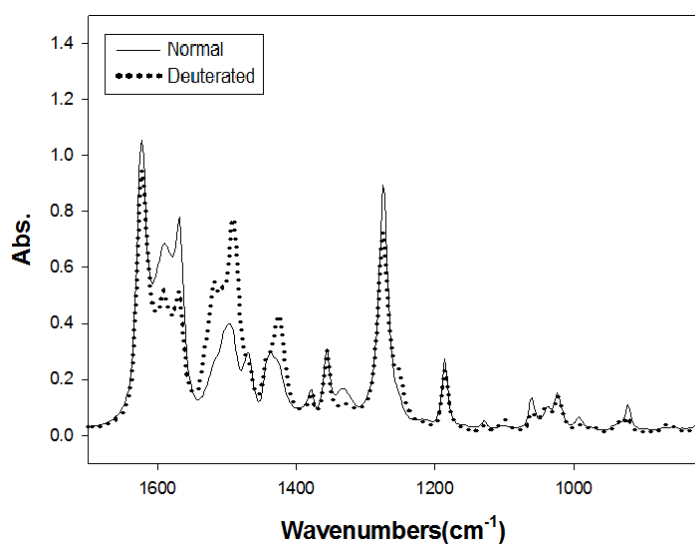
S8. IR spectrum of compound 44.



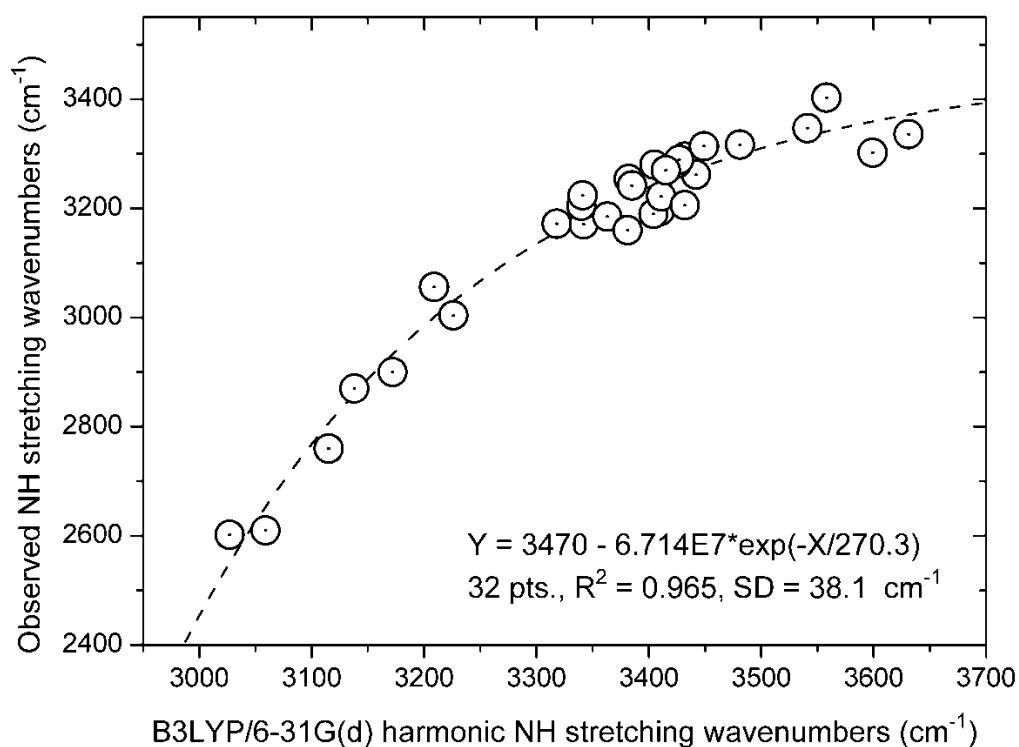
S9. IR spectrum of compound 8.



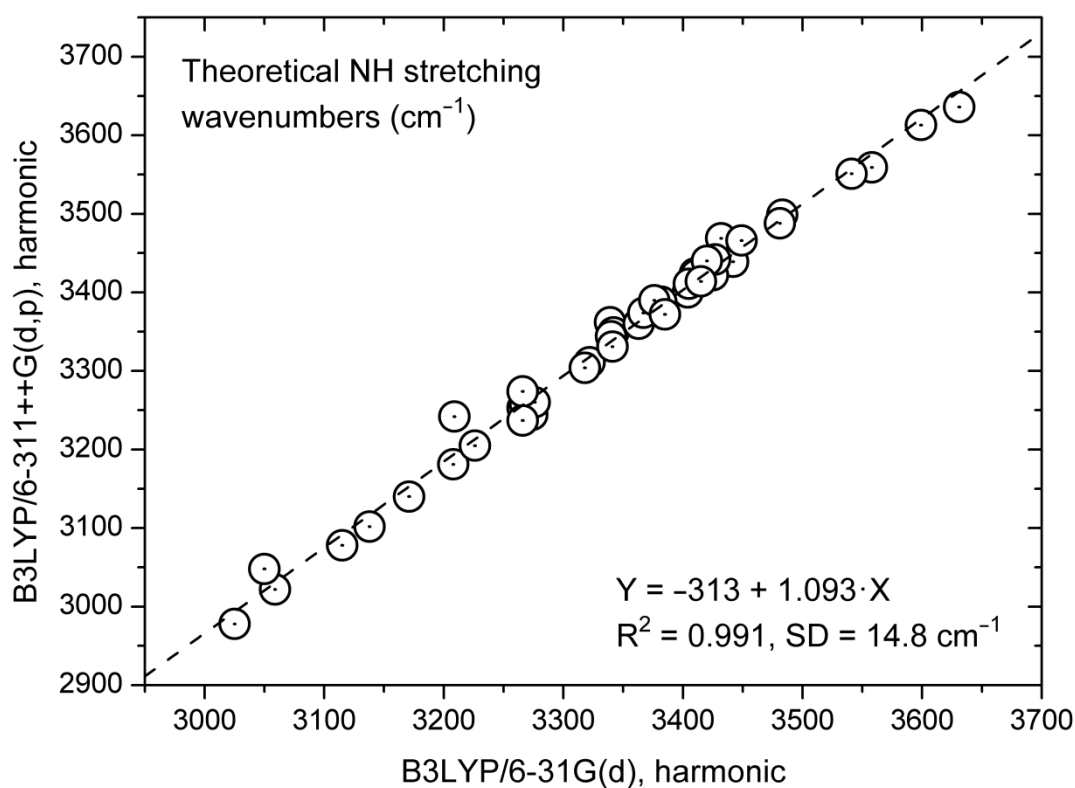
S10. IR spectrum of compound **9**.



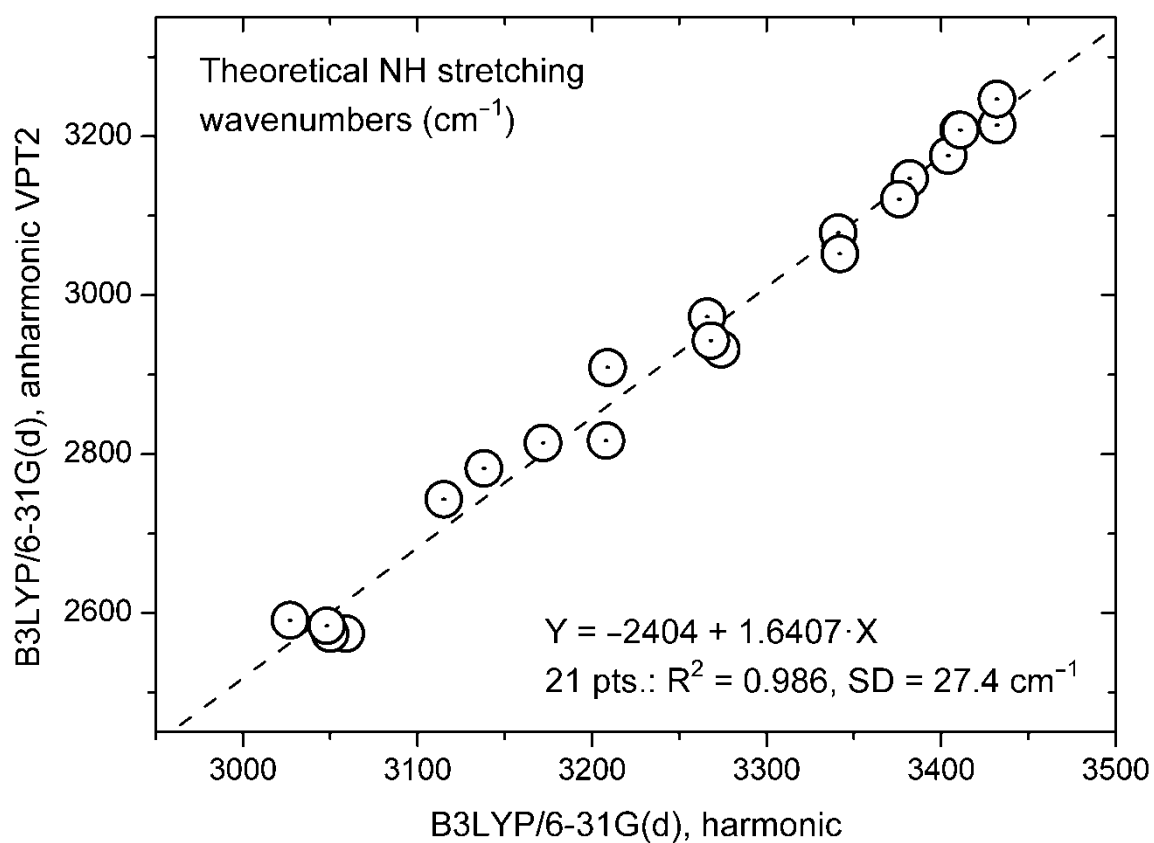
S11. IR spectrum of compound **10**.



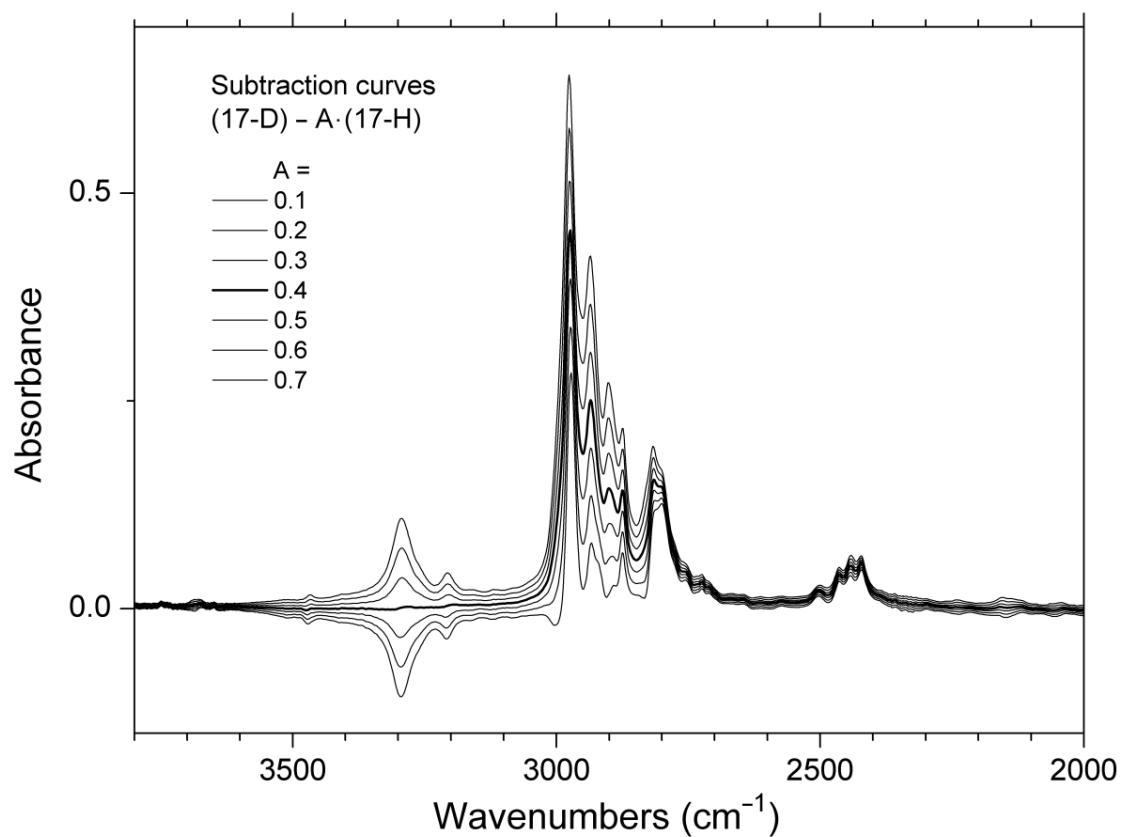
S12. Observed NH stretching wavenumbers (cm^{-1}) vs. harmonic values computed with B3LYP/6-31G(d). The points for compounds **25** and **26** are omitted and are not included in the correlation analysis.



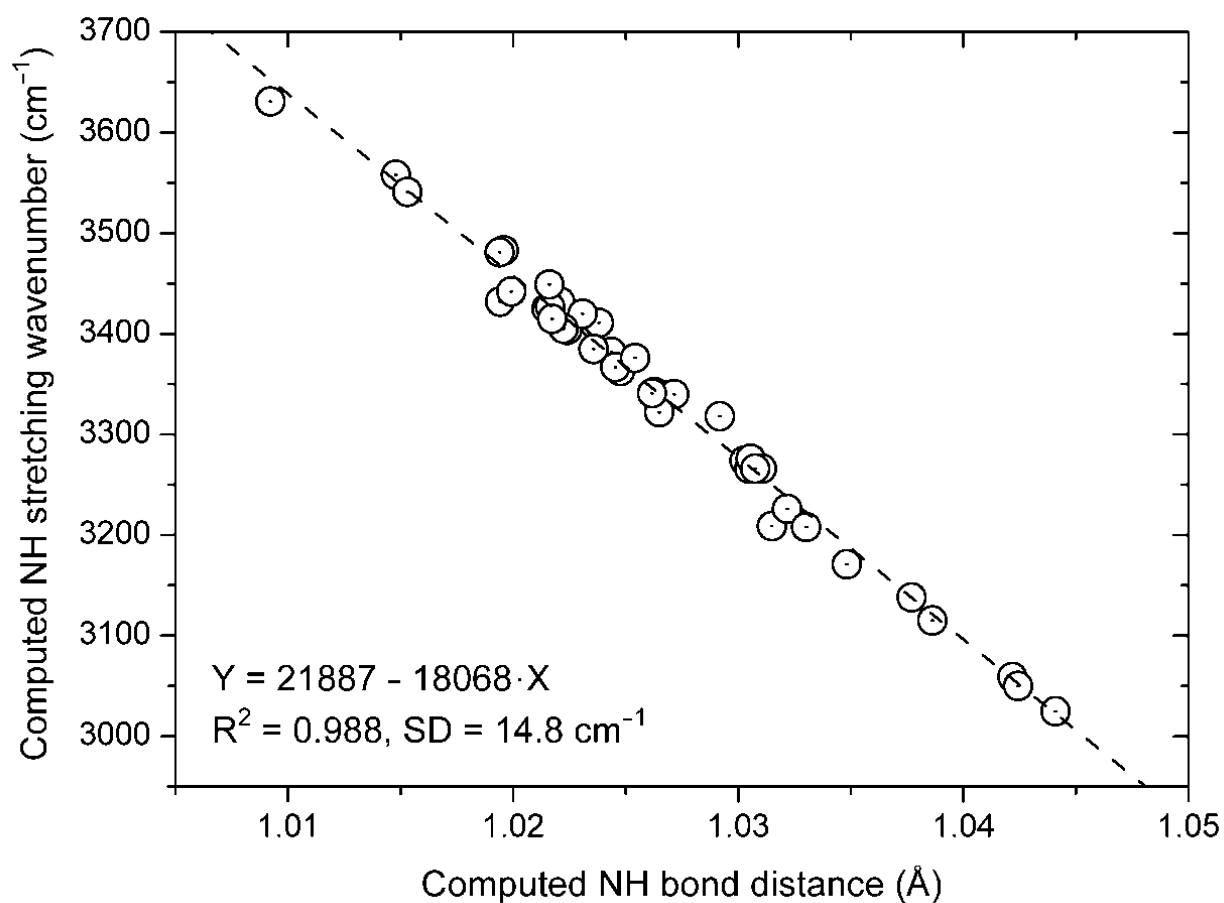
S13. Harmonic NH stretching wavenumbers (cm^{-1}) computed with B3LYP/6-311++G(d,p) against those obtained with B3LYP/6-31G(d).



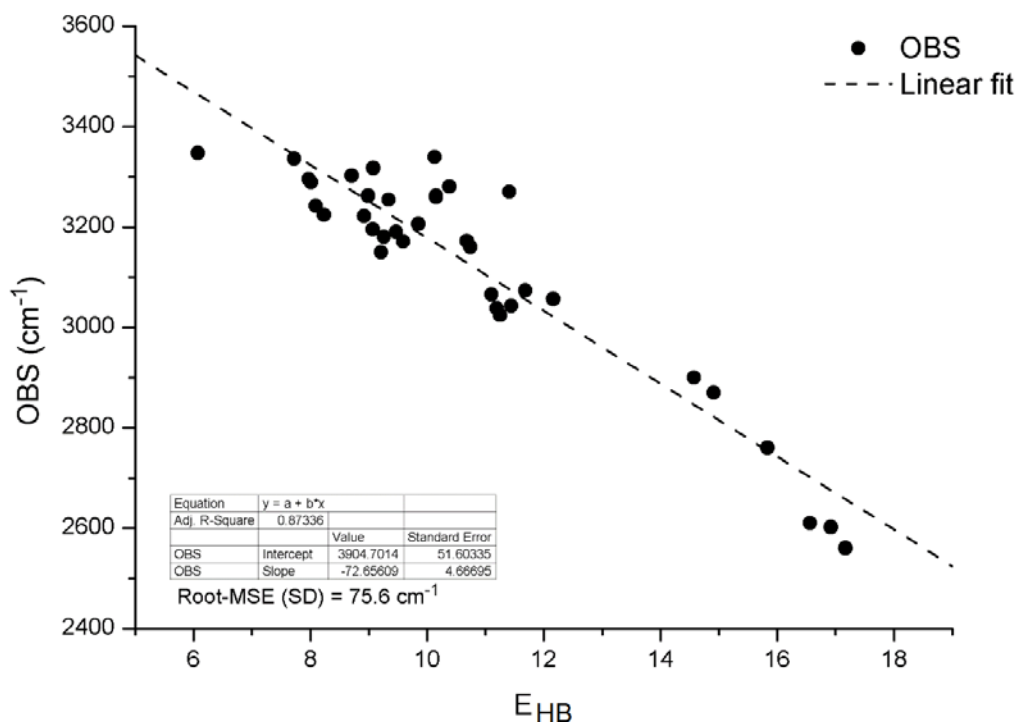
S14. B3LYP/6-31G(d) anharmonic VPT2 wavenumbers (cm^{-1}) vs. the corresponding harmonic ones.



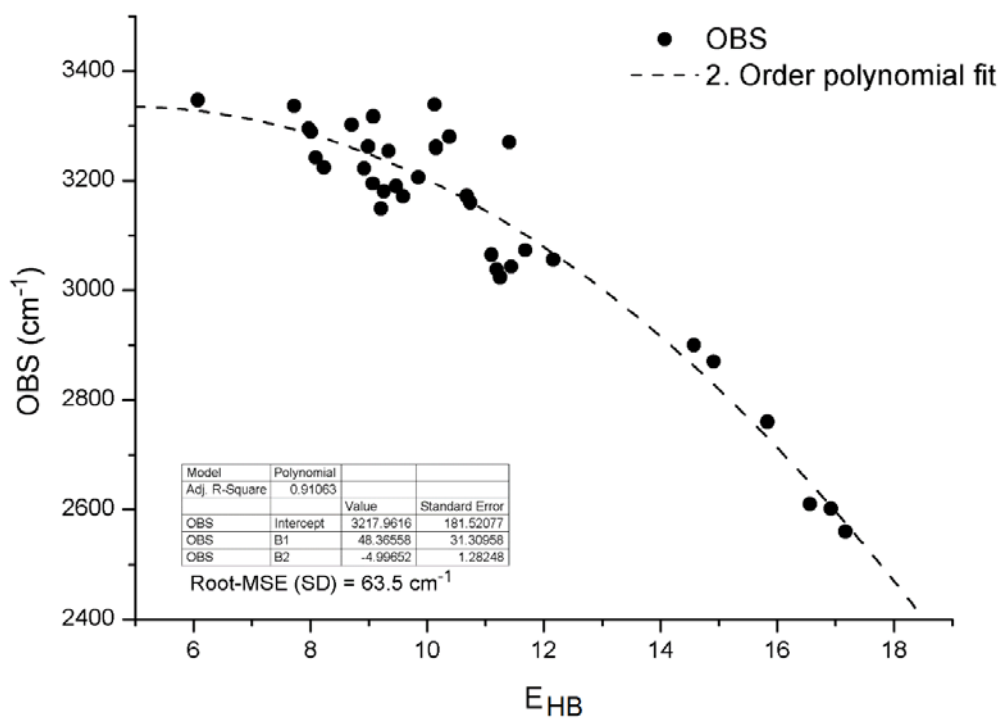
S15. Subtraction IR spectra of compound **17**.



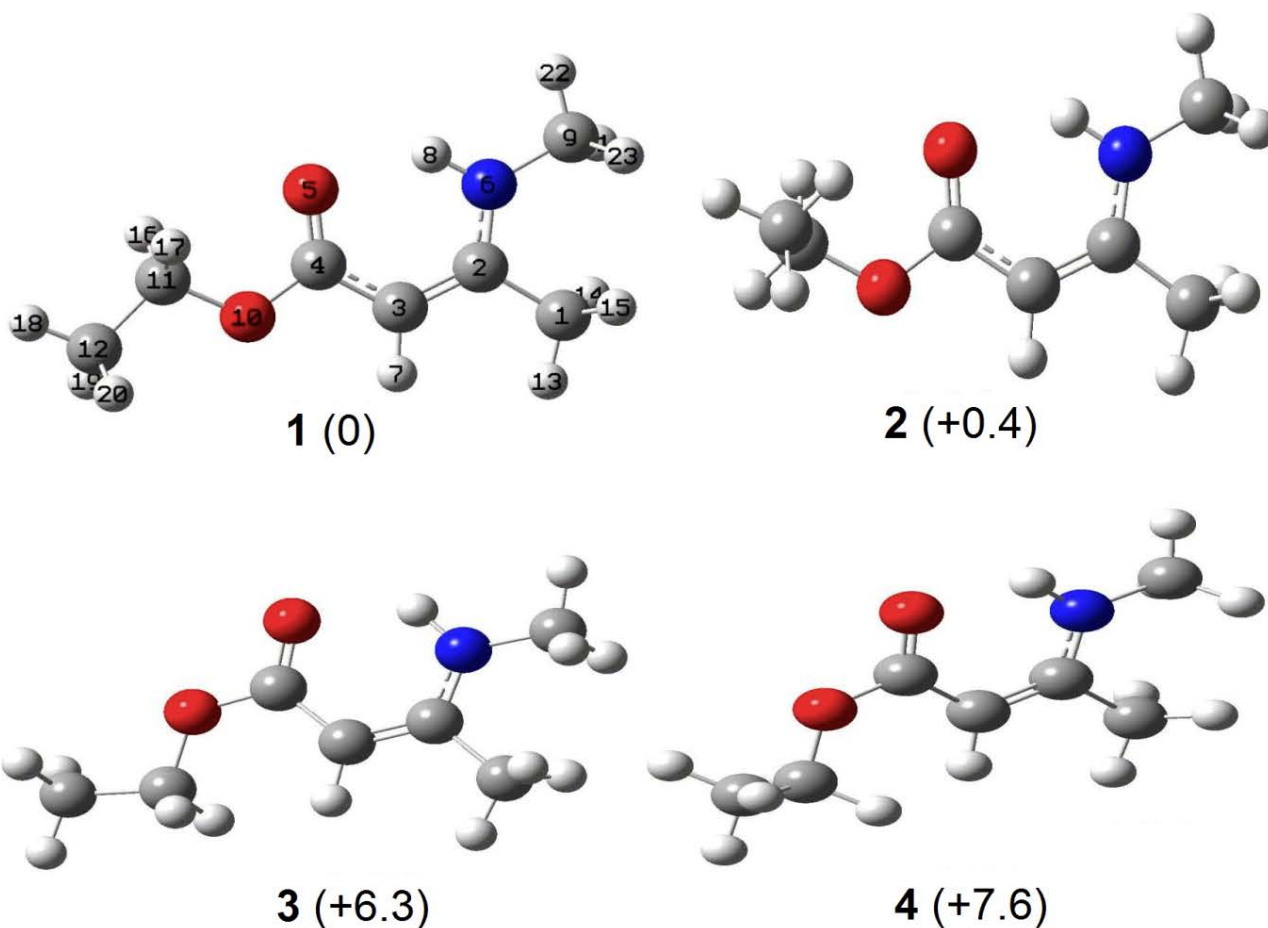
S16. Harmonic NH stretching wavenumbers vs. NH bond distances (B3LYP/6-31G(d)).



S17. Observed NH stretching wavenumbers vs. hydrogen bond energies, E_{HB} (kcal/mol), estimated according to E. Espinosa, E. Molins, C. Lecomte, Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities, Chem. Phys. Lett. 285 (1998) 170–173.



S18. Observed NH stretching wavenumbers vs. hydrogen bond energies, E_{HB} (kcal/mol), estimated according to E. Espinosa, E. Molins, C. Lecomte, Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities, Chem. Phys. Lett. 285 (1998) 170–173.



S19. Optimized molecular structures of (Z)-ethyl 3-(methylamino)but-2-enoate (**17**) computed with B3LYP/6-311++G(d,p) with relative energies in kcal/mol. The same harmonic NH stretching wavenumber is computed for all four structures, 3469 cm^{-1} . Two low-energy conformers, **1** and **2**, may coexist. This is consistent with previously reported results for β -keto esters by Tayyari et al. {1,2}.

{1} Tayyari, S.F.; Chahkandi, V.; Mehrani, S.; McClurg, R.W.; Keyes, C.A.; Sammelson, R.E. Conformational analysis, tautomerization, IR, Raman, and NMR studies of ethyl benzoylacetate. *J. Mol. Struct.* **2012**, *1015*, 74-85.

{2} Tayyari, S.F.; Naghavi, F.; Pojhan, S.; McClurg, R.W.; Sammelson, R.E. Conformational analysis, tautomerization, IR, Raman, and NMR studies of benzyl acetoacetate. *J. Mol. Struct.* **2011**, *987*, 241-254.

S20. Fundamental band assignments for **17** (17-H) and deuterated **17** (17-D).

17-H. Fundamental band assignments for **17**, conformations 1 and 2 (S19). **Freq.**, harmonic wavenumber in cm^{-1} (B3LYP/6-311++G(d,p)); **Int.**, corresponding IR intensity in km/mol ; **Expt.**, wavenumber in cm^{-1} measured in CCl_4 , relative intensity in parenthesis (s, strong; m, medium; w, weak; vw, very weak; sh, shoulder); **Assignment** (approximate): ν , stretching; δ , in-plane bending; ρ , in-plane rocking; π , out-of-plane bending; a, antisymmetric; s, symmetric; sci, scissor; Δ , in-plane chelated ring deformation; τ , torsion; for atom numbering, see S19, structure 1.

	Conformation 1		Conformation 2		Expt.	Assignment
	Freq.	Int.	Freq.	Int.		
					3465(w)	Summation band
1	3469	109	3469	110	3295(m)	νNH
2	3220	2	3222	2	3209(w)	νCH_7
3	3136	11	3136	10	2983(m)	νaC1H_3
4	3121	17	3120	17	do.	νaC9H_3
5	3110	43	3124	30	2956(sh)	νaC12H_3 , νaCH_2
6	3099	31	3104	12	do.	νaC12H_3 , νsCH_2
7	3078	14	3077	13	2938(m)	νaC1H_3
8	3077	6	3092	30	do.	νaCH_2 , νaC12H_3
9			3064	35	do.	νsCH_2
10	3048	32	3052	33	2899(m)	νaC9H_3
	3043	21			do.	νsCH_2
11	3033	23	3031	21	2870(sh)	νsC12H_3
12	3031	25	3030	26	do.	νsC1H_3
13	3006	80	3004	81	2826(w)	νsC9H_3
14	1685	331	1685	303	1650(s)	$\nu\text{aO}=\text{C}-\text{C}=\text{C}$, δCH_7 , $\nu\text{aN}-\text{C}-\text{C}-\text{C}$
15	1657	522	1657	530	1615(s)	δNH , $\nu\text{sO}=\text{C}-\text{C}=\text{C}$, $\nu\text{sN}-\text{C}-\text{C}-\text{C}$
16	1540	90	1539	102	1506(m)	$\nu\text{aN}-\text{C}=\text{C}-\text{C}$, δCH_7 , δNH , δaC9H_3 , sciCH_2
17	1521	3				sciCH_2 , δaC12H_3
			1509	21	1445(m)	δaC9H_3 , sciCH_2 , δaC12H_3
18	1508	17			do.	δaC9H_3 , δCH_7 , δNH , $\nu\text{aN}-\text{C}=\text{C}-\text{C}$, sciCH_2
			1505	3	do.	δaC12H_3 , δCH_7 , δNH , $\nu\text{aN}-\text{C}=\text{C}-\text{C}$, sciCH_2
19	1499	4	1490	16	1435(m)	δaC12H_3 , sciCH_2
20	1498	19	1496	18	do.	δaC1H_3 , δaC9H_3
21	1490	41	1487	17	do.	δaC1H_3 , δNH , δaC9H_3
22	1485	7	1485	19	do.	δaC12H_3
23	1479	1	1478	1		δaC1H_3 , δaC9H_3
24	1473	18	1470	20	do.	δsC9H_3 , δNH , δaC1H_3
25	1424	0	1422	46	1380(m)	δaC12H_3 , WCH_2 , δsC1H_3
26	1421	53	1417	10	do.	δsC1H_3 , δNH , δsC12H_3 , WCH_2
27	1396	3	1398	5	do.	δsC12H_3 , WCH_2 , δNH , $\nu\text{sC}=\text{C}$
29	1391	75	1391	89	1360(m)	ρNH , δsCH_3 , WCH_2 , δCH_7 , $\nu\text{aC}=\text{C}-\text{N}$
29			1333	29	1301(sh)	WCH_2
30	1298	569	1298	469	1270(s)	δCH_7 , $\nu\text{aO10C4C3}$, $\nu\text{sN}-\text{C}=\text{C}-\text{C}$, $\nu\text{C2}-\text{CH}_3$, wCH_2
	1293	1				τCH_2 , πC12H_3
31	1197	130	1196	159	1175(s)	δCH_7 , $\nu\text{N}-\text{CH}_3$, $\nu\text{aC}-\text{O}-\text{CH}_2$
32	1190	322	1194	21	do.	δCH_7 , $\nu\text{N}-\text{CH}_3$, ρC9H_3 , $\nu\text{aC}-\text{O}-\text{CH}_2$

33			1186	235	1165(m)	δCH_7 , $\nu\text{N-CH}_3$, $\rho\text{C}_9\text{H}_3$, $\nu\text{C-O-CH}_2$
	1176	3				ρCH_2 , $\rho\text{C}_{12}\text{H}_3$
34	1141	0	1139	5	1140(sh)	$\pi\text{C}_9\text{H}_3$
35	1134	4			do.	$\rho\text{C}_{12}\text{H}_3$, $\delta\text{O-CH}_2\text{-CH}_3$
			1115	51	1097(w)	$\rho\text{C}_{12}\text{H}_3$
36	1105	45	1105	54	1083(m)	ρNH , $\nu\text{N-CH}_3$, $\rho\text{C}_9\text{H}_3$
37	1076	140	1068	97	1058(m)	$\nu\text{aOCH}_2\text{-C}_{12}\text{H}_3$, $\nu\text{sC}_3\text{-C}_4\text{-O-CH}_2$, $\nu\text{C}_2\text{-CH}_3$, $\rho\text{C}_9\text{H}_3$
38	1057	2	1057	3	1033(w)	$\pi\text{C}_1\text{H}_3$
39	1029	6	1022	12	1011(w)	$\rho\text{C}_1\text{H}_3$, $\nu\text{aO-CH}_2\text{-C}_{12}\text{H}_3$
40	993	21			977(w)	$\rho\text{C}_1\text{H}_3$, $\nu\text{sC-O-CH}_2$, $\delta\text{C}_2\text{C}_3\text{C}_4$, $\nu\text{C-C}_{12}\text{H}_3$
			974	19	967(w)	$\rho\text{C}_1\text{H}_3$, $\nu\text{sC-O-CH}_2$, $\delta\text{C}_2\text{C}_3\text{C}_4$, $\nu\text{C-C}_{12}\text{H}_3$
41	898	1	889	1		$\rho\text{C}_{12}\text{H}_3$, $\nu\text{sC-O-CH}_2$, $\delta\text{C}_2\text{C}_3\text{C}_4$
42	838	6	836	5	825(w)	Δ , $\nu\text{N-C}_9\text{H}_3$, $\nu\text{C-C}_1\text{H}_3$, $\rho\text{C}_{12}\text{H}_3$

17-D. Fundamental band assignments for deuterated **17**. See heading to previous Table.

	Conformation 1		Conformation 2		Expt.	Assignment
	Freq.	Int.	Freq.	Int.		
1	3137	11	3136	11	2982(m)	$\nu\text{aC}_1\text{H}_3$
2	3121	16	3120	16	do.	$\nu\text{aC}_9\text{H}_3$
3	3109	43	3124	30	2955(sh)	$\nu\text{aC}_{12}\text{H}_3$, νaCH_2
4	3099	31	3104	12	do.	$\nu\text{aC}_{12}\text{H}_3$, νsCH_2
5	3078	14	3077	13	2938(m)	$\nu\text{aC}_1\text{H}_3$
6	3076	6	3092	30	do.	νaCH_2 , $\nu\text{aC}_{12}\text{H}_3$
7			3064	35	do.	νsCH_2
8	3048	32	3052	32	2900(sh)	$\nu\text{aC}_9\text{H}_3$
	3043	21			do.	νsCH_2
9	3033	23	3031	21	2870(sh)	$\nu\text{sC}_{12}\text{H}_3$
10	3031	26	3030	26	do.	$\nu\text{sC}_1\text{H}_3$
11	3007	77	3004	78	2815(w)	$\nu\text{sC}_9\text{H}_3$
12	2545	71	2545	72	2431(w)	νND
13	2379	1	2380	1	2240(w)	νCD_7
14	1679	316			1652(s)	$\nu\text{aO=C-C=C}$, $\nu\text{aN-C-C-C}$
			1679	291	do.	$\nu\text{aO=C-C=C}$, $\nu\text{sN-C-C-C}$
15	1597	601	1596	611	1560(s)	$\nu\text{sO=C-C=C}$, δND , $\nu\text{sN-C-C-C}$
16	1522	18	1519	28	1506 (vw)	$\delta\text{aC}_{12}\text{H}_3$, $\delta\text{aC}_9\text{H}_3$, sciCH_2
17	1518	11	1506	15	do.	sciCH_2 , $\delta\text{aC}_9\text{H}_3$, $\delta\text{aC}_{12}\text{H}_3$
18	1499	4	1494	28	1440(sh)	$\delta\text{aC}_{12}\text{H}_3$, sciC_2H_2
19	1498	19	1496	18	do.	$\delta\text{aC}_1\text{H}_3$, $\delta\text{aC}_9\text{H}_3$
20	1491	17	1487	6	do.	$\delta\text{sC}_9\text{H}_3$, νCN , sciCH_2
21	1485	7	1485	8	do.	$\delta\text{aC}_{12}\text{H}_3$, sciCH_2
22	1480	103	1479	50	1435(m)	$\delta\text{aC}_1\text{H}_3$
23	1478	1	1477	48	do.	$\delta\text{aC}_1\text{H}_3$, $\delta\text{aC}_9\text{H}_3$
24	1452	35	1450	32	1421(w)	$\delta\text{sC}_9\text{H}_3$, $\delta\text{SC}_1\text{H}_3$
25	1423	2	1418	9	1380(w)	$\delta\text{sC}_{12}\text{H}_3$, WCH_2 , $\delta\text{sC}_1\text{H}_3$
26	1412	2	1411	3	1370(w)	$\delta\text{sC}_1\text{H}_3$, $\delta\text{sC}_{12}\text{H}_3$

27	1394	5	1396	14	1360(w)	$\delta sC12H_3$, wCH_2
28			1333	26	1326(w)	wCH_2
	1293	1			1302(vw)	wCH_2
29	1279	768	1278	638	1270(s)	$\nu aO10C4C3$, $\nu sN-C=C-C$, $\nu C2-CH_3$, wCH_2 , ρND
30	1228	161	1228	138	1255(s)	ρND , $\nu N-C9H_3$, $\delta C2C3C4$, $\nu aC-O-CH_2$
31			1194	45	1175(sh)	ρCH_2
32	1179	54	1176	39	1165(m)	$\rho C9H_3$
	1176	3			do.	ρCH_2 , $\rho C12H_3$
33	1137	0	1136	5	do.	$\nu N-C9H_3$
34	1134	4			do.	$\rho C12H_3$, $\delta O-CH_2-CH_3$
			1115	83	1095(m)	$\rho C12H_3$, $\delta O-CH_2-CH_3$
35	1095	206			1066(m)	$\rho C1H_3$, $\nu aC-O-CH_2$, $\delta CD7$
			1086	130	do.	$\rho C1H_3$, $\nu aC-O-CH_2$
36	1055	2	1055	2	1054(w)	$\pi C1H_3$
37	1037	21			1033(vw)	$\rho C1H_3$, $\nu aO-CH_2-CH_3$, $\delta C2C3C4$, νCCH_3
			1028	27	1010(vw)	$\rho C1H_3$, $\nu aO-CH_2-CH_3$, $\delta C2C3C4$, νCCH_3
38	991	34			998(sh)	$\rho C1H_3$, $\nu sC-O-CH_2$, $\delta C2C3C4$, νCCH_3
			974	31	975(w)	$\rho C1H_3$, $\nu sC-O-CH_2$, $\delta C2C3C4$, νCCH_3
39	961	5	962	6	964(w)	δND , $\nu N-C9H_3$
40	920	3	918	1	930(vw)	$\delta CD7$, $\delta C-O-CH_2$, $\delta C2C3C4$, $\rho C12H_3$

Notes:

The observed IR bands in non-deuterated **17** at 967(w), 1097(w), 1165(m), and 1301(sh) cm^{-1} may be due to the presence of conformation 2. The NH stretching of **17** is observed at 3295 cm^{-1} , on deuteration the band is observed at 2431 cm^{-1} (**S3**, **S15**). The corresponding NH band in 4-methylamino-3-penten-2-one, APO-NMe, was observed at 3171 cm^{-1} by H. Raissi et al. {3}. This value indicates that the IHB strength of **17** is weaker than that of APO-NMe. Hence, replacement of the β -methyl group in APO-NMe with an OEt group (to yield **17**) decreases the IHB strength. - The spectrum of **17** in CCl_4 shows a weak band at 3465 cm^{-1} , this may be a summation band. In 4-amino-3-penten-2-one, APO, a corresponding band is seen at 3240 cm^{-1} {4}.

{3} Raissi, H.; Moshfeghi, E.; Farzad, F.; Vibrational assignment, structure and intramolecular hydrogen bond of 4-methylamino-3-penten-2-one. *Spectrochim. Acta A* **2005**, 62, 1004-1015.

{4} Tayyari, S.F.; Raissi, H.; Tayyari, F. Vibrational assignment of 4-amino-3-penten-2-one. *Spectrochim. Acta A* **2002**, 58, 1681-1695.

S21. Materials section: Synthesis, characterization, and NMR spectra.

All chemicals, unless stated otherwise, were purchased from Sigma-Aldrich, TCI, Chemicals and Alfa Aesar and were used without further purification. Solvents used were HPLC grade and dried on molecular sieves (4 Å) at least 2 days before use. Analytical thin-layer chromatography was done on Merck Alufolien SiO₂ 60 F254 0.2 mm thick precoated TLC plates. Column chromatography was performed using SiO₂ from VWR 40–63 µm. ¹H and ¹³C NMR spectra were recorded on a Bruker 500 MHz Ultrashield Plus 500 spectrometer. ¹H, ¹³C, and ¹⁹F NMR spectra were also recorded at 500, 125, and 470 MHz, respectively, on a Bruker Avance 3 spectrometer with a BBFO probe. All chemical shifts (δ) are quoted in ppm, and all coupling constants (J) are in Hertz (Hz). The following abbreviations are used for multiplicity for NMR resonances: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet and m = multiplet. HRMS LC/MS were recorded on a Dionex Acclaim RSLC 120 C18 2.2 µm 120 Å 2.150 mm column maintained at 40 °C carried out on a Bruker MicrOTOF-QII-system with ESI system.

Compounds **6**, **14**, **16**, **17**, **19**, and **45** were prepared by a modified procedure based on Martin, D.F.; Janusonis, G.A.; Martin, B.B. Stabilities of Bivalent Metal Complexes of some B-Ketoimines, *J. Am. Chem. Soc.* **1961**, *83*, 73-75.

Modified procedure: To a stirred solution of 1,3-dicarbonyl compound (5.0 mmol of 2,4-pentanedione, 3-methyl-2,4-pentanedione, ethyl 2-acetoacetate or ethyl 2-methylacetoacetate) and amine (5.0 mmol of methylamine or anilines) in absolute ethanol (15 mL) was added glacial acetic acid (0.01 mL) at room temperature. The reaction mixture was stirred at 80 °C and the progress of the reaction was monitored by TLC. After complete conversion of the starting material, the solvent was removed under reduced pressure and the crude product was purified by column chromatography using silica gel using a gradient of organic solvents as eluent. Evaporation of solvent under reduced pressure affords the pure compound.

The synthesis of **8**, **9**, **10**, and **11** has been described in Zheglova, D.Kh.; Genov, D.G.; Bolvig, S.; Hansen, P.E. Deuterium Isotope Effects on ¹³C Chemical Shifts of Enaminones. *Acta Chem. Scand.* **1997**, *51*, 1016-1023. Additional ¹³C NMR data and high resolution MS data are given below .

(Z)-4-(phenylamino)pent-3-en-2-one **6**:

The compound was isolated as a pale yellow solid after flash column chromatography on silica using dichloromethane/ethyl acetate (20:1) as eluent. In 94% yield. ¹H NMR (500 MHz, CDCl₃): δ 12.45 (brs, 1H, NH), 7.34-7.31 (m, 2H), 7.19-7.16 (m, 1H), 7.10-7.09 (m, 2H), 5.18 (s, 1H), 2.09 (s, 3H), 1.98 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 196.23, 160.36, 138.83, 129.18, 125.65, 124.84, 97.70, 29.26, 19.93. NMR results are similar to those of Ref. [i]. HRMS-ESI (m/z): [M + H]⁺ calcd. for C₁₁H₁₄NO: 176.0997, found: 176.0949.

(Z)-4-(o-tolylamino)pent-3-en-2-one **8**:

¹H NMR (500 MHz, CDCl₃): δ 12.33 (brs, 1H, NH), 7.23-7.21 (m, 1H), 7.17-7.13 (m, 2H), 7.08-7.06 (m, 1H), 5.19 (s, 1H), 2.28 (s, 3H), 2.10 (s, 3H), 1.86 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 196.12, 161.26, 137.58, 133.80, 130.87, 130.87, 126.48, 126.48, 97.12, 29.16, 19.70, 18.15. The NMR results are similar to those of Ref. [ii]. HRMS-ESI (m/z): [M + H]⁺ calcd. for C₁₁H₁₄NO: 176.0997, found: 176.0949.

(Z)-4-(2-fluorophenylamino)pent-3-en-2-one **9**:

¹H NMR (500 MHz, CDCl₃): δ 12.23 (brs, 1H, NH), 7.17 (m, 2H), 7.12 (m, 2H), 5.26 (s, 1H), 2.11 (s, 3H), 1.94 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 196.88, 160.61, 156.80 (J=247.5), 127.26 (J=7.61), 127.14, 127.04 (J=12.45), 124.44 (J=4.34), 116.39 (J=20.19), 98.26, 29.34, 19.60. NMR results are similar to those of Refs. [i] and [46]. ¹⁹F NMR (470 MHz, CDCl₃): δ 123.65 ppm (Reference hexafluorobenzene). HRMS-ESI (m/z): [M + H]⁺ calcd. for C₁₁H₁₃FNO: 194.0903, found: 194.0988.

(Z)-4-(2-chlorophenylamino)pent-3-en-2-one 10:

¹H NMR (500 MHz, CDCl₃): δ 12.42 (brs, 1H, NH), 7.46-7.44 (m, 1H), 7.25-7.20 (m, 2H), 7.17-7.14 (m, 1H), 5.27 (s, 1H), 2.13 (s, 3H), 1.95 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 196.87, 159.84, 136.46, 130.22, 129.98, 127.25, 126.92, 126.90, 98.52, 29.35, 19.88. HRMS-ESI (m/z): [M + H]⁺ calcd. for C₁₂H₁₆ClNO: 225.0920, found, 225.0952. The ¹³C data are different from those of Ref. [iii]. The spectrum contains a small degradation product, which is 2-chloroaniline. This proves that the compound is the correct one.

(Z)-4-(2,6-dimethylphenylamino)pent-3-en-2-one 11:

¹H NMR (500 MHz, CDCl₃): δ 11.92 (brs, 1H, NH), 7.08 (m, 3H), 5.20 (s, 1H), 2.19 (s, 3H), 2.10 (s, 3H), 1.62 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 195.62, 162.95, 136.64, 136.24, 135.65, 128.30, 127.51, 95.88, 29.14, 18.34. NMR results are similar to those of Ref. [i]. HRMS-ESI (m/z): [M + H]⁺ calcd. for C₁₃H₁₈NO: 204.1310, found: 204.1394.

(Z)-3-methyl-4-(methylamino)pent-3-en-2-one 14:

The compound was isolated as a light amber oil after flash column chromatography on silica using *n*-hexane/ethyl acetate (1:1) as eluent. In 74% yield. ¹H NMR (500 MHz, CDCl₃): δ 11.80 (brs, 1H, NH), 2.88 (d, J=5.2 Hz, 3H), 2.06 (s, 3H), 1.91 (s, 3H), 1.78 (s, 3H). The ¹H NMR results are similar to those of Ref. [iv]. ¹³C NMR (125 MHz, CDCl₃): δ 194.35, 163.15, 97.97, 29.84, 28.31, 14.93, 14.58. HRMS-ESI (m/z): [M + H]⁺ calcd. for C₁₃H₁₈NO: 204.1310, found: 204.1394.

(Z)-ethyl 3-(phenylamino)but-2-enoate 16:

The compound was isolated as creamy solid after flash column chromatography on silica using dichloromethane/ethyl acetate (20:1) as eluent. In 70% yield. ¹H NMR (500 MHz, CDCl₃): δ 10.39 (brs, 1H, NH), 7.31 (m, 2H), 7.14 (m, 1H), 7.08 (m, 2H), 4.69 (s, 1H), 4.15 (q, 2H), 1.99 (s, 3H), 1.28 (t, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 170.44, 158.96, 139.42, 129.58, 124.96, 124.45, 86.13, 58.80, 20.36, 14.66. The NMR results are similar to those of Ref. [v]. HRMS-ESI (m/z): [M + H]⁺ calcd. for C₁₂H₁₆NO₂: 206.1181, found: 206.1172.

(Z)-ethyl 3-(methylamino)but-2-enoate 17:

The compound was isolated as a light amber oil after flash column chromatography on silica using *n*-hexane/ethyl acetate (1:1) as eluent. In 61% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.46 (brs, 1H, NH), 4.45 (s, 1H), 4.07 (q, 2H), 2.89 (s, 3H), 1.90 (s, 3H), 1.23 (t, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 170.79, 162.91, 81.99, 58.38, 29.67, 19.28, 14.76. The NMR results are similar to those of Ref. [vi]. HRMS-ESI (m/z): [M + H]⁺ calcd. for C₇H₁₄NO₂: 144.2024.1310, found: 144.1037.

(Z)-ethyl 2-methyl-3-(methylamino)but-2-enoate 19:

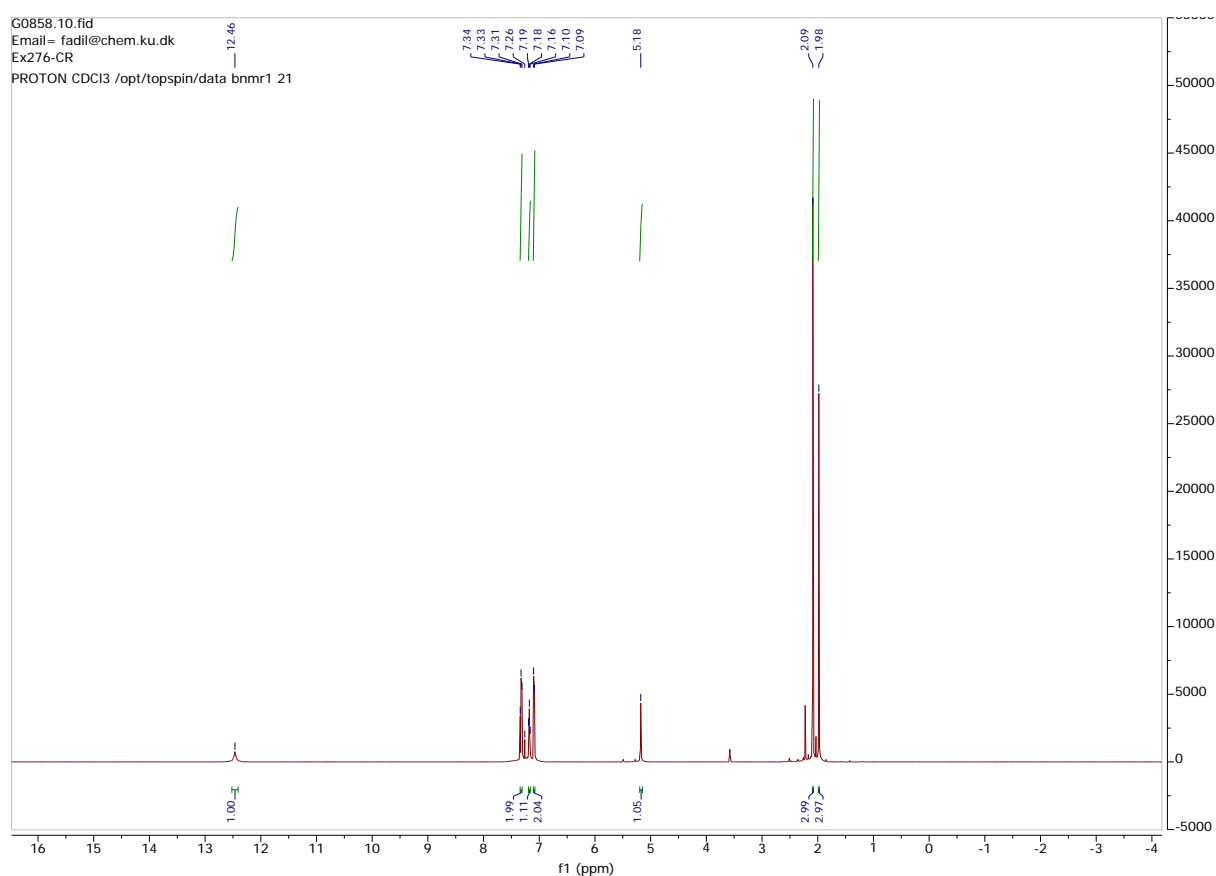
The compound was isolated as a colorless oil after flash column chromatography on silica using *n*-hexane/ethyl acetate (1:1) as eluent. In 68% yield. ¹H NMR (500 MHz, CDCl₃): δ 9.14 (brs, 1H, NH), 4.08 (q, J=7.1, 2H), 2.88 (d, J=5.2, 3H), 1.94 (s, 3H), 1.77 (s, 3H), 1.25 (t, J=7.1, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 170.96, 160.39, 86.18, 58.48, 29.85, 14.83, 14.55, 12.51. HRMS-ESI (m/z): [M + H]⁺ calcd. for C₈H₁₆NO₂: 158.1181, found: 158.1162.

(Z)-3-methyl-4-(phenylamino)pent-3-en-2-one 45:

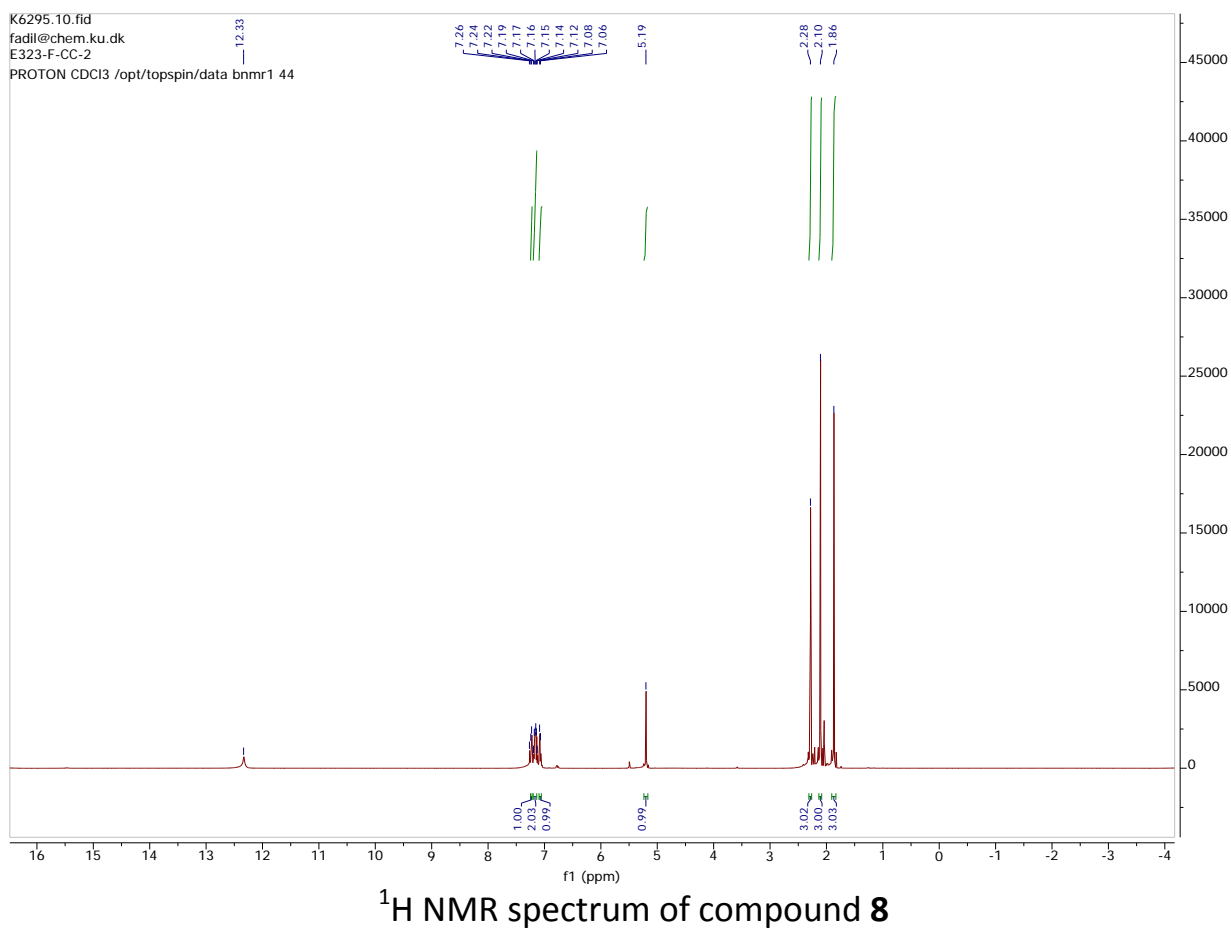
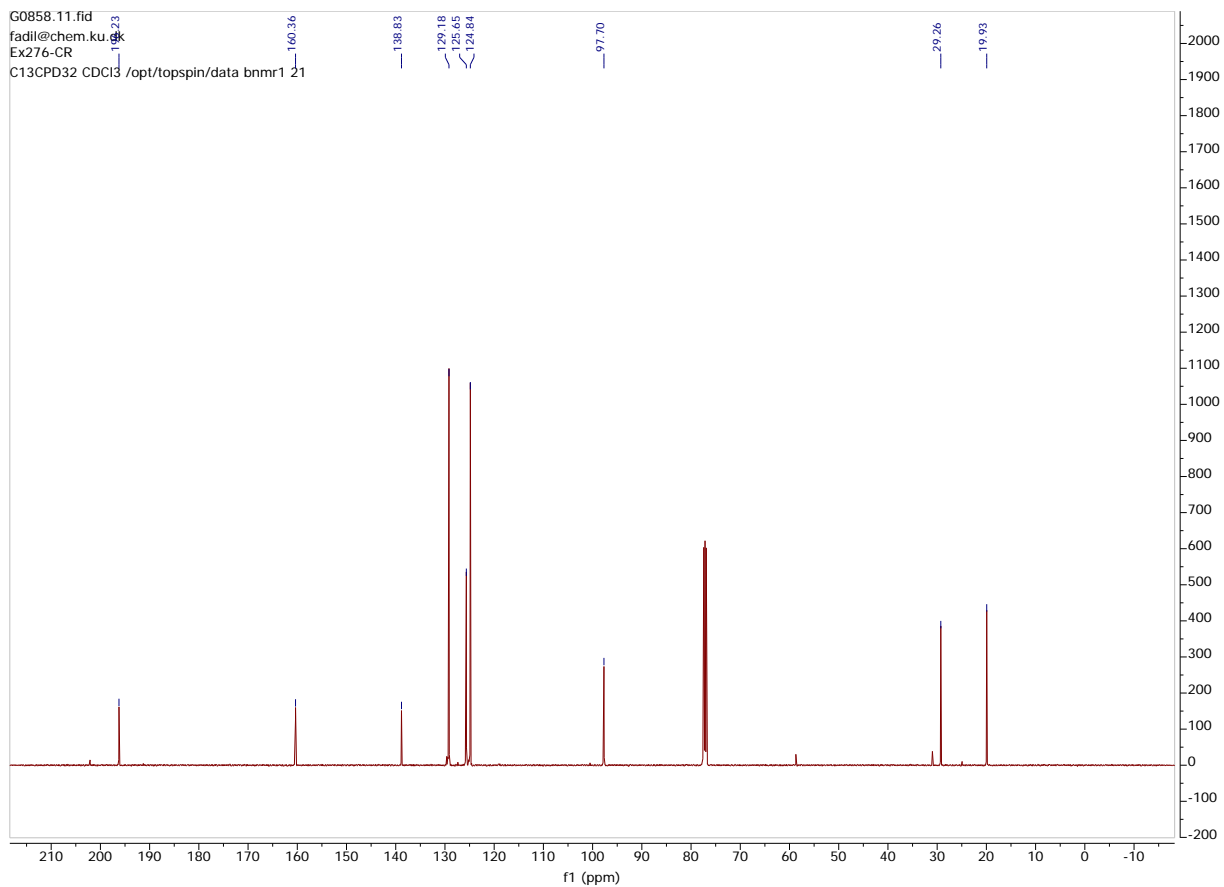
The compound was isolated as off white solid after flash column chromatography on silica using *n*-hexane/ethyl acetate (1:1) as eluent. In 78% yield. ¹H NMR (500 MHz, CDCl₃): δ 13.44 (brs, 1H, NH), 7.28 (t, 2H), 7.12 (t, 1H), 7.02 (d, J=7.4, 2H), 2.18 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 196.71, 158.50, 139.63, 129.66, 125.27, 101.15, 28.87, 17.21, 15.02. The NMR results are similar to those of Ref. [vii]. HRMS-ESI (m/z): [M + H]⁺ calcd. for C₁₃H₁₈NO₂: 220.1337, found: 220.1348.

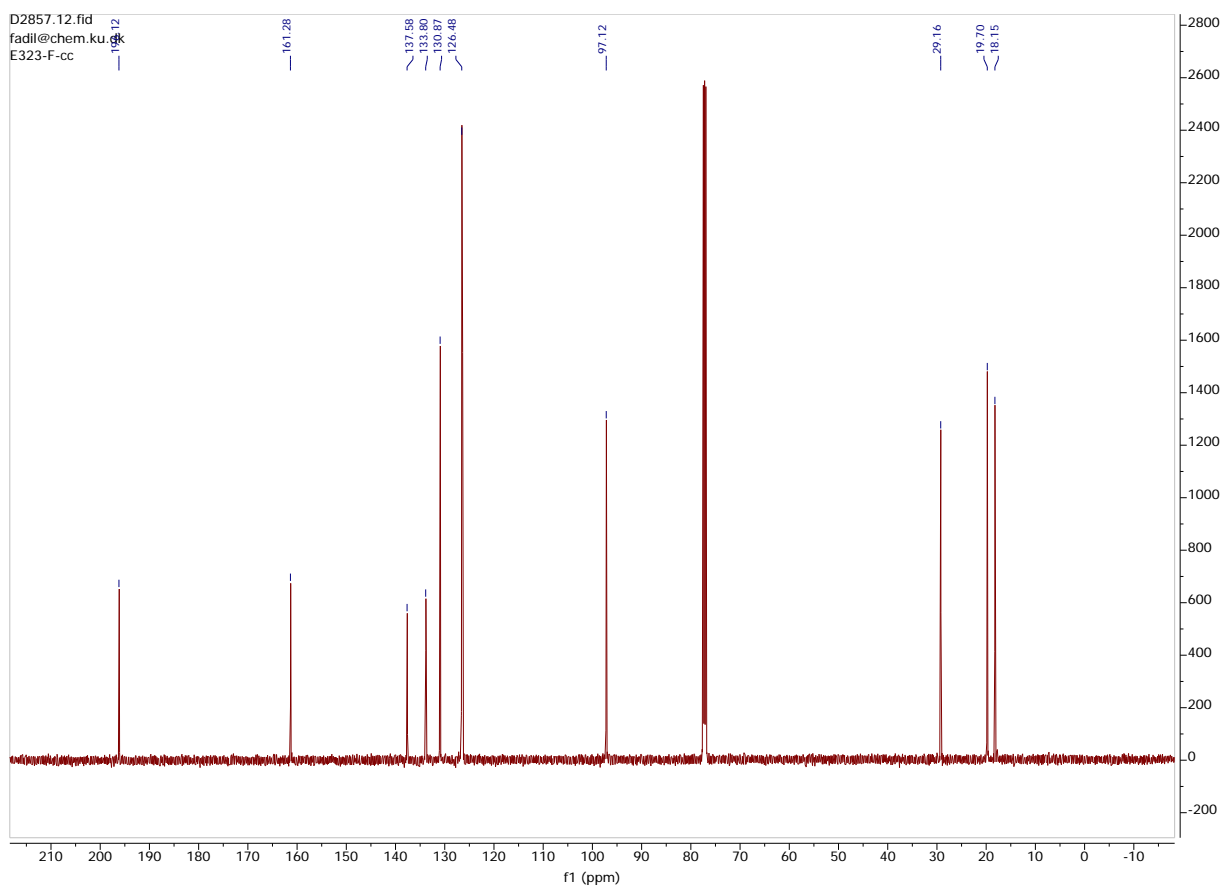
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- vi. Manzi, J.A.; Knapp, C.E; Carmalt, C.J. Aerosol-Assisted Chemical-Vapour Deposition of Zinc Oxide from Single-Source β -Iminoesterate Precursors. *Eur. J. Inorg. Chem.*, **2015**, *22*, 3658-3665.
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NMR:

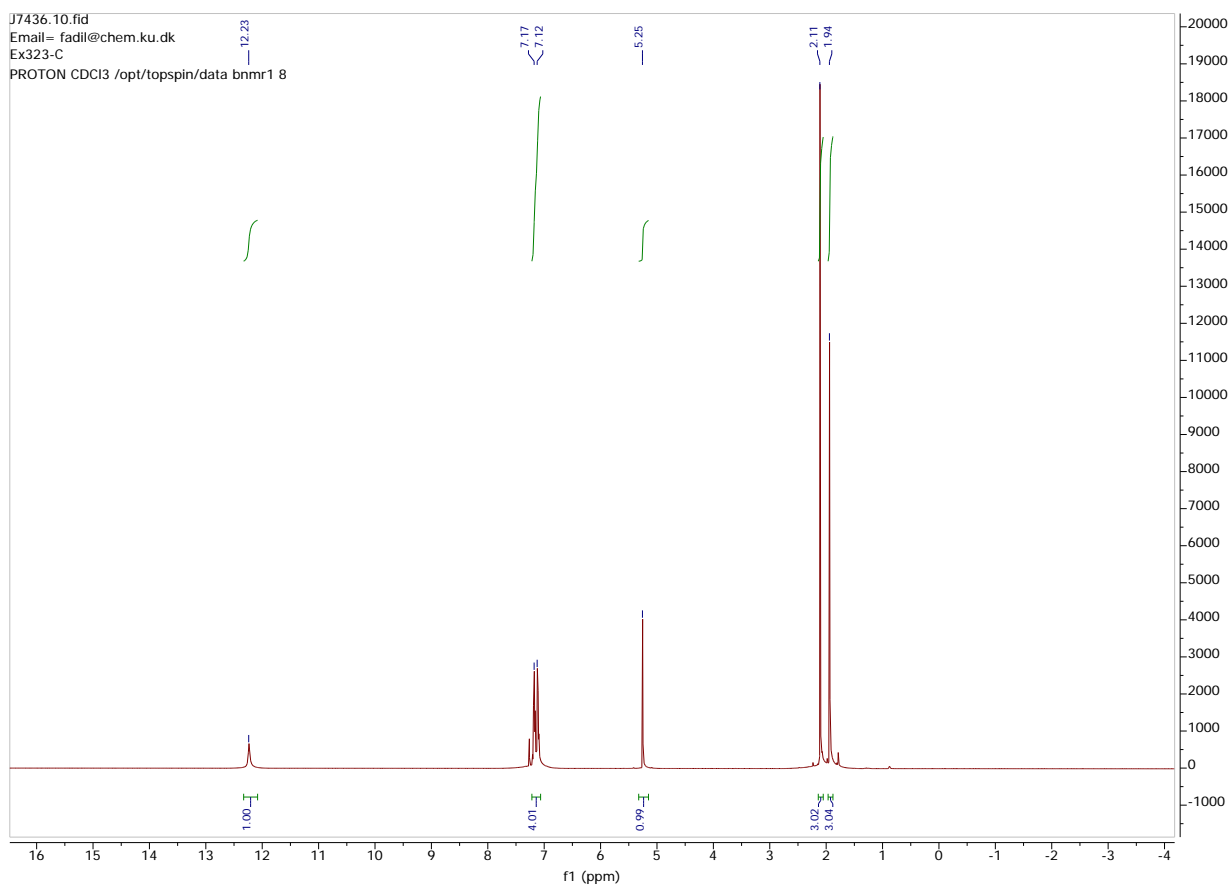


¹H NMR spectrum of compound 6

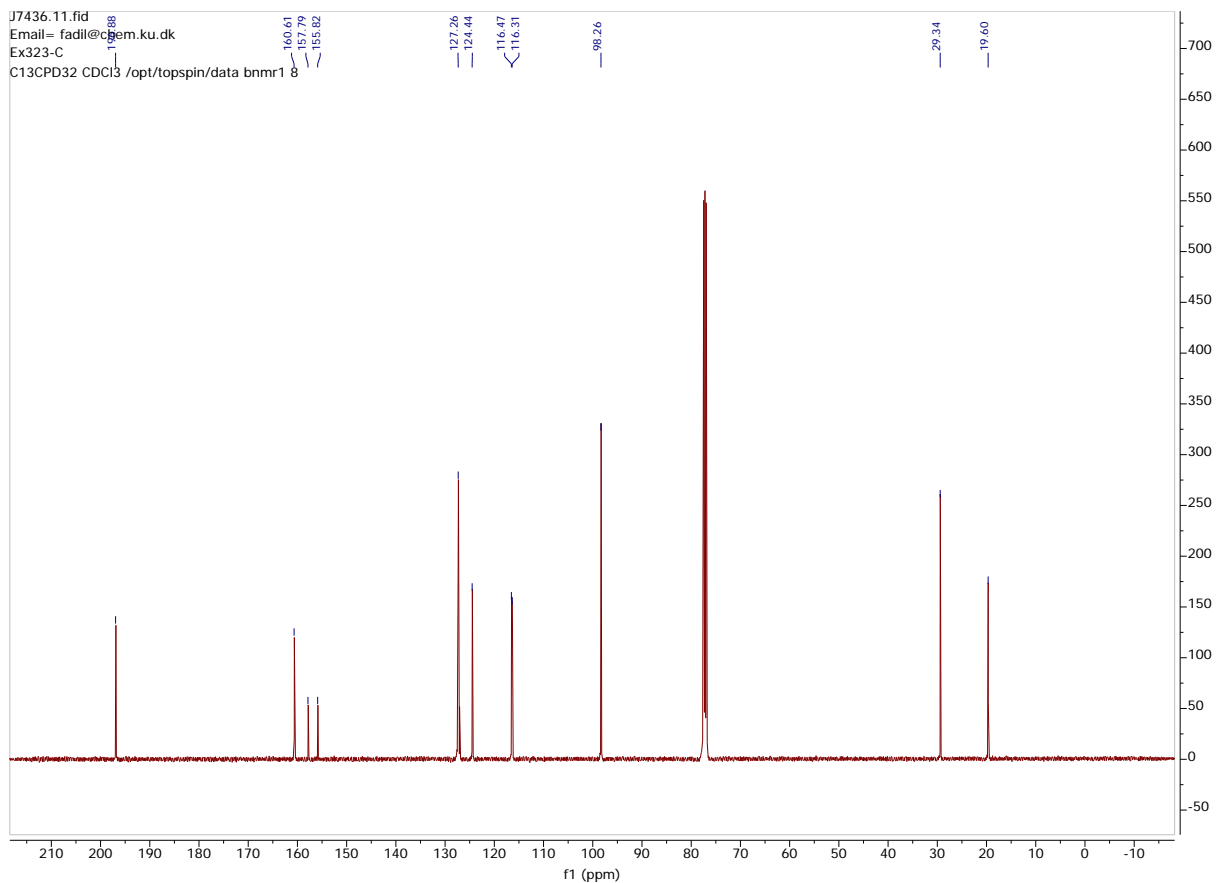




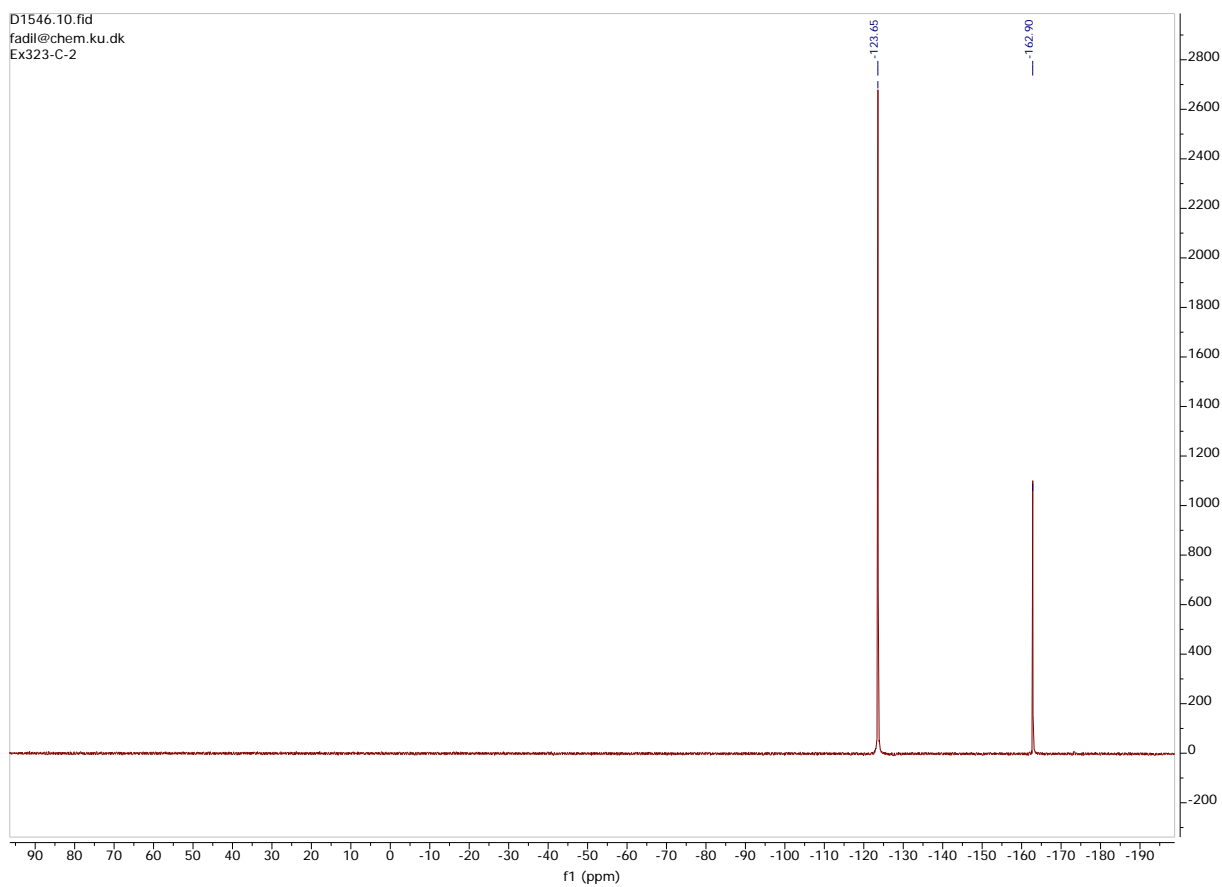
^{13}C NMR spectrum of compound **8**



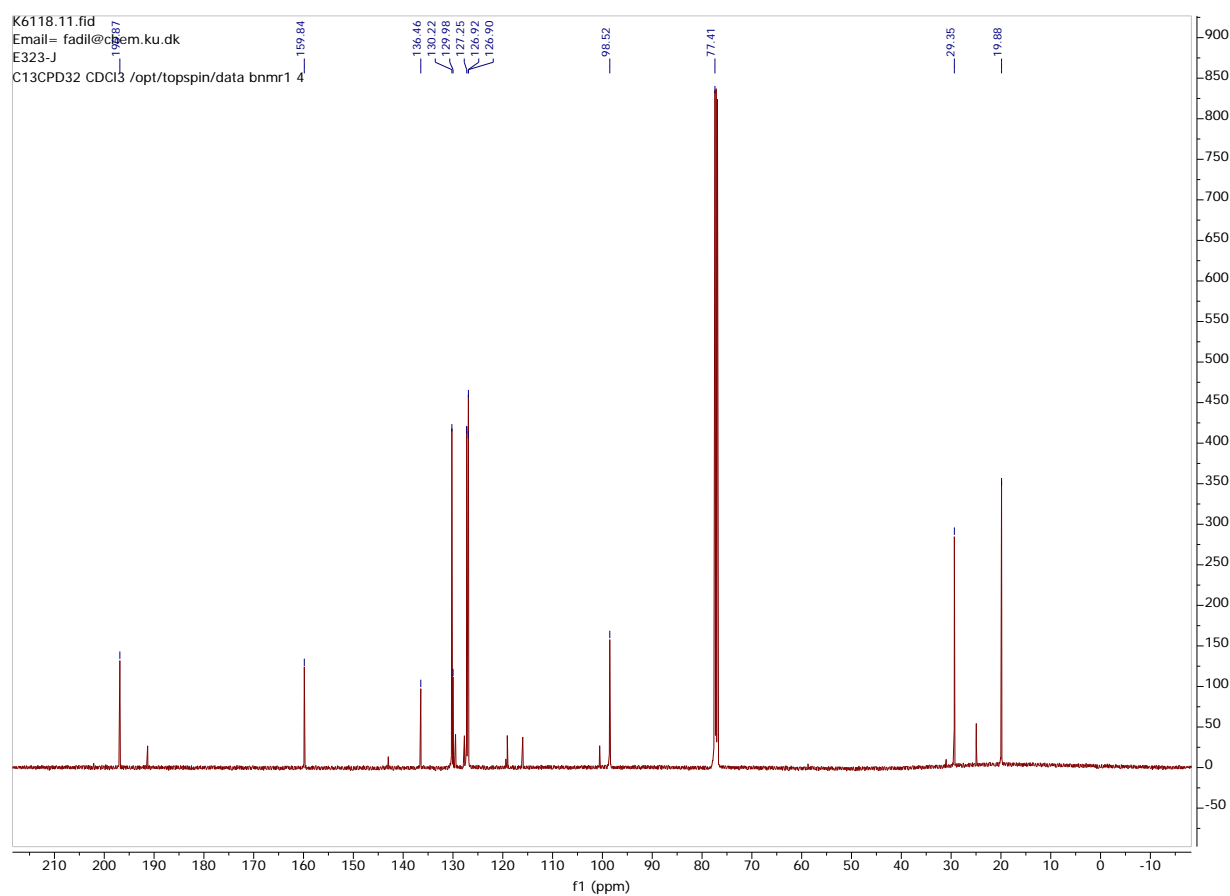
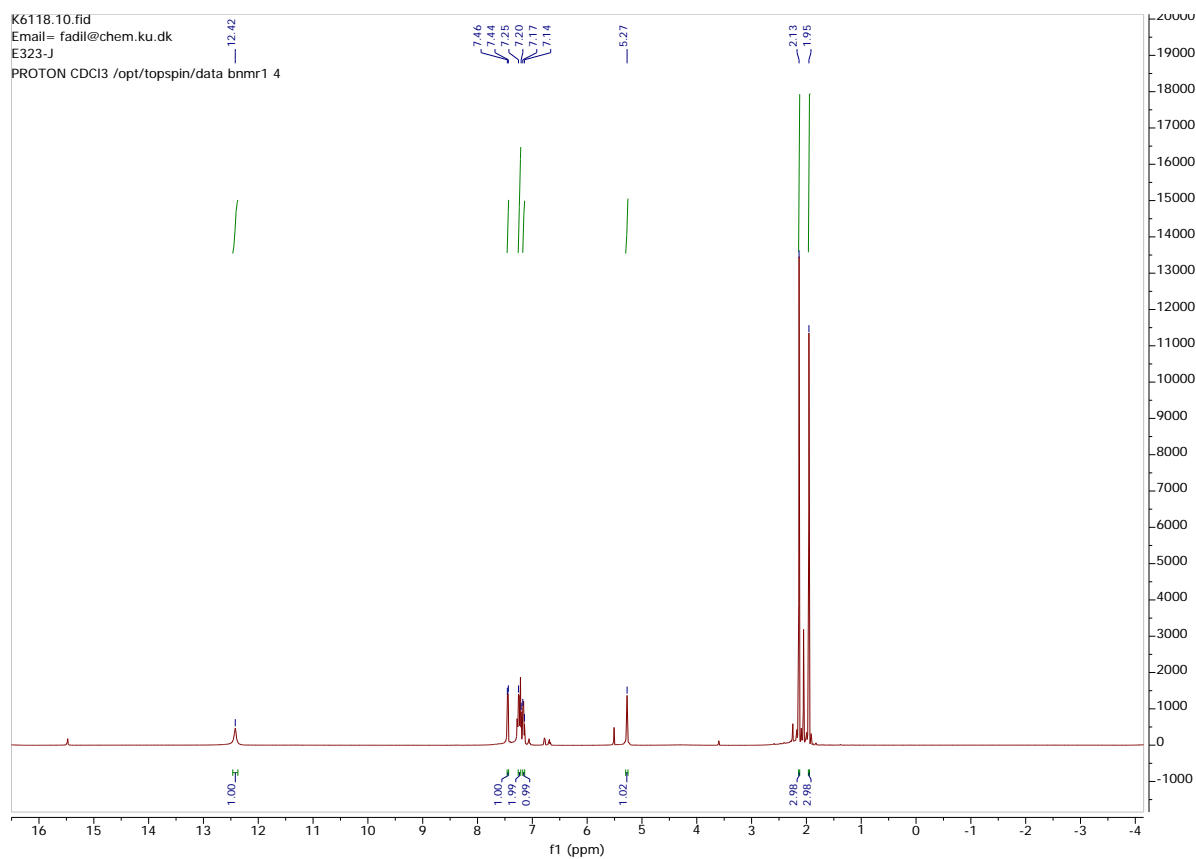
^1H NMR spectrum of compound **9**

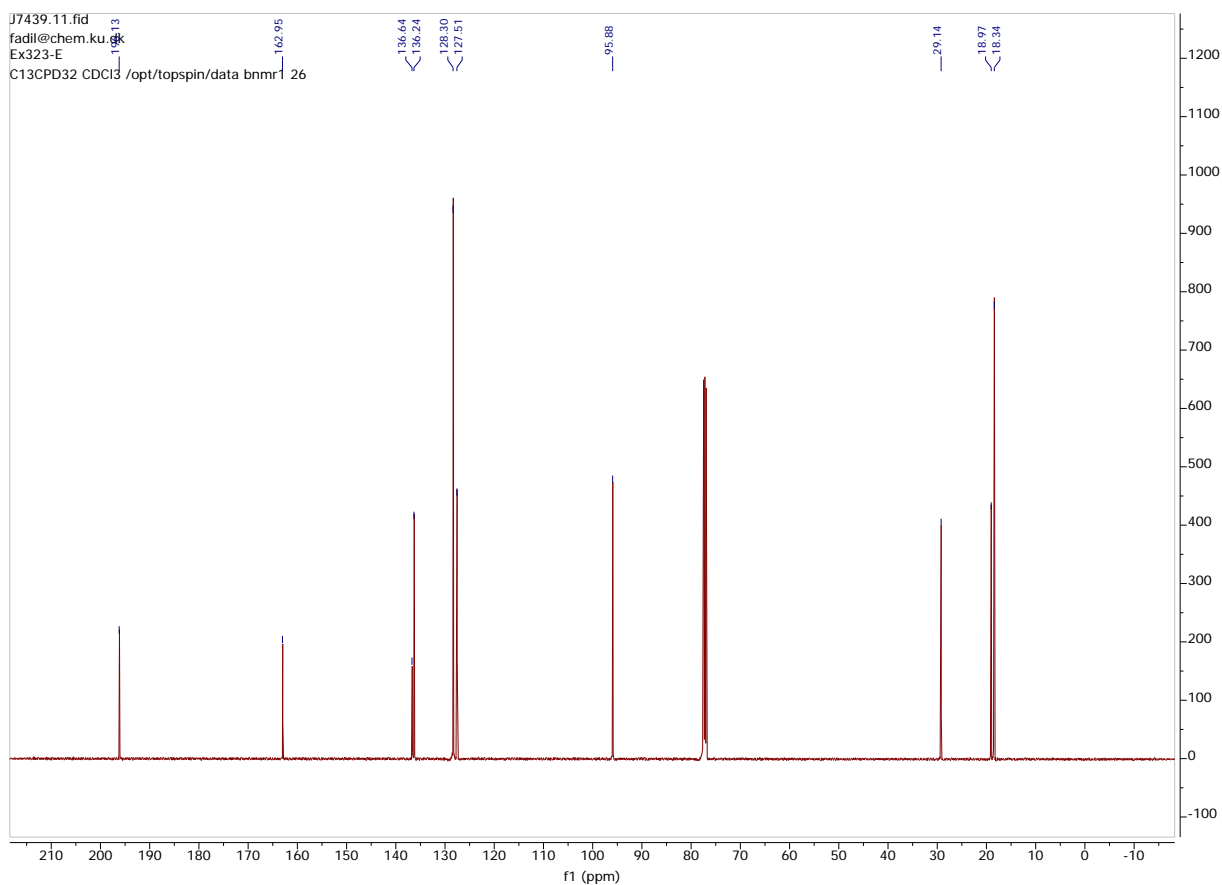
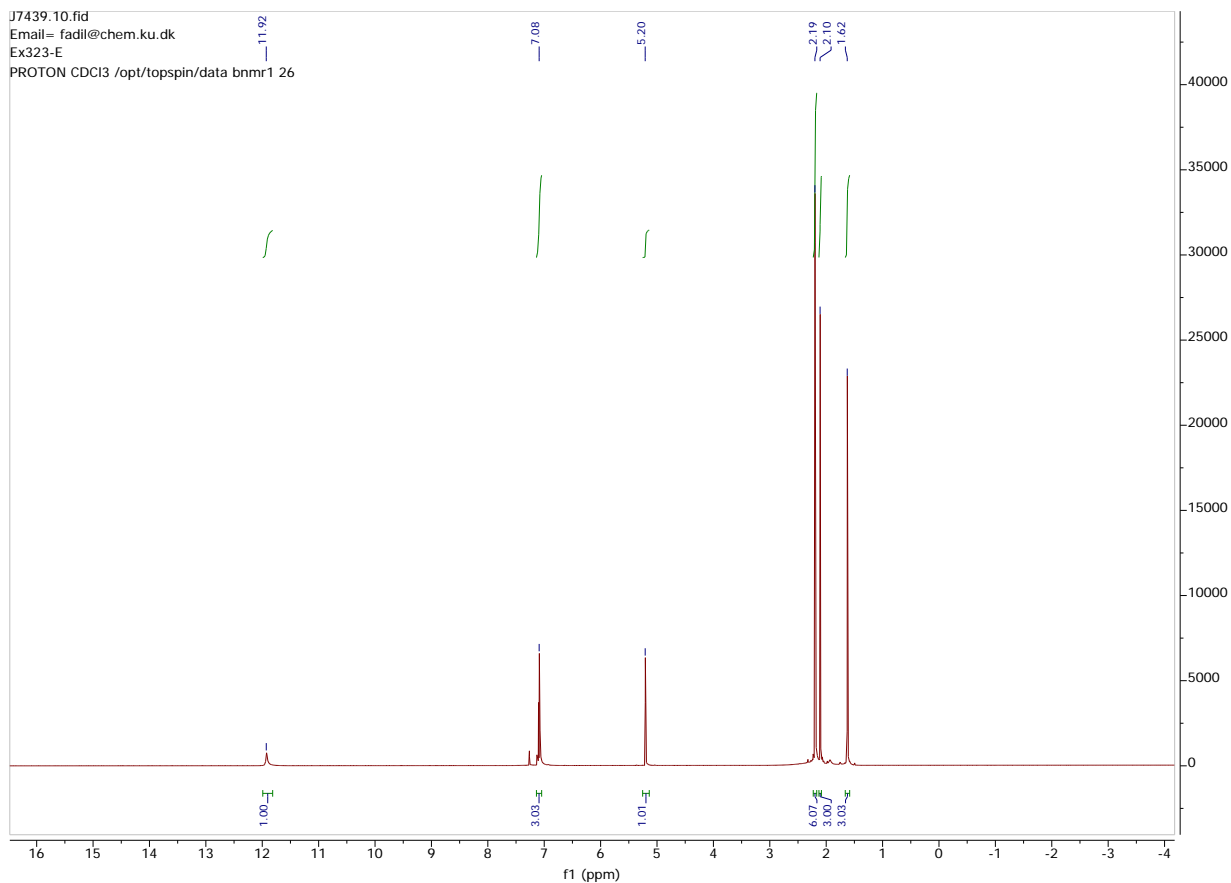


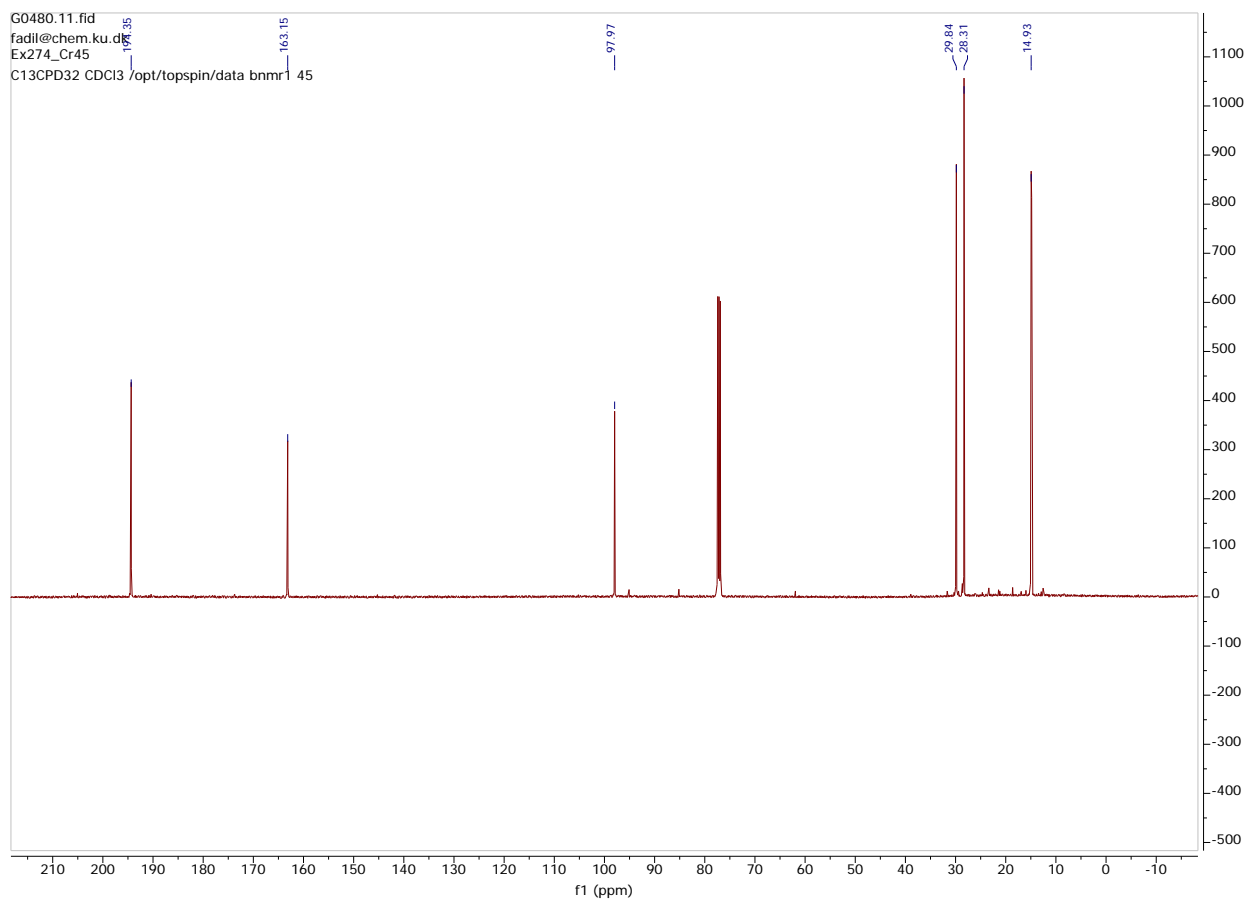
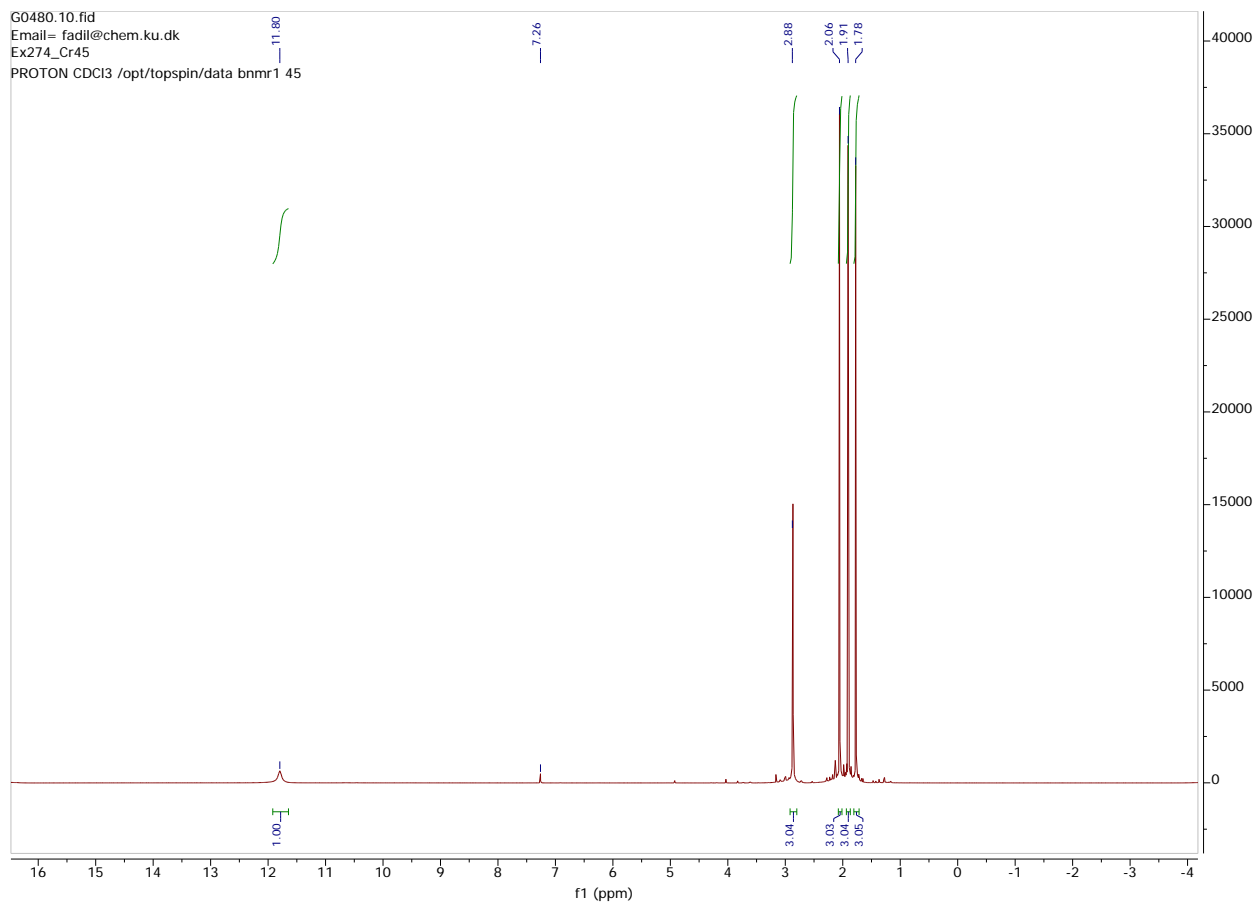
^{13}C NMR spectrum of compound 9

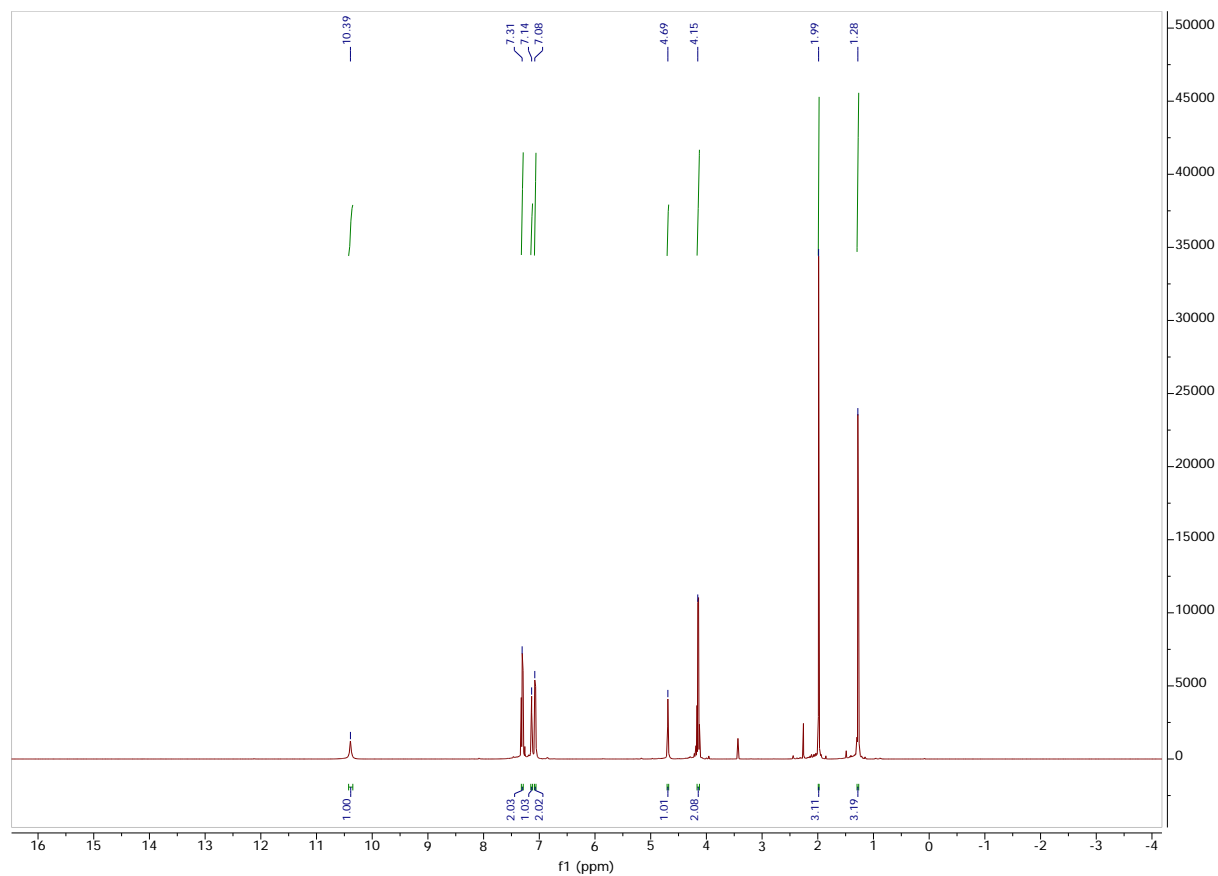


^{19}F NMR spectrum of compound 9

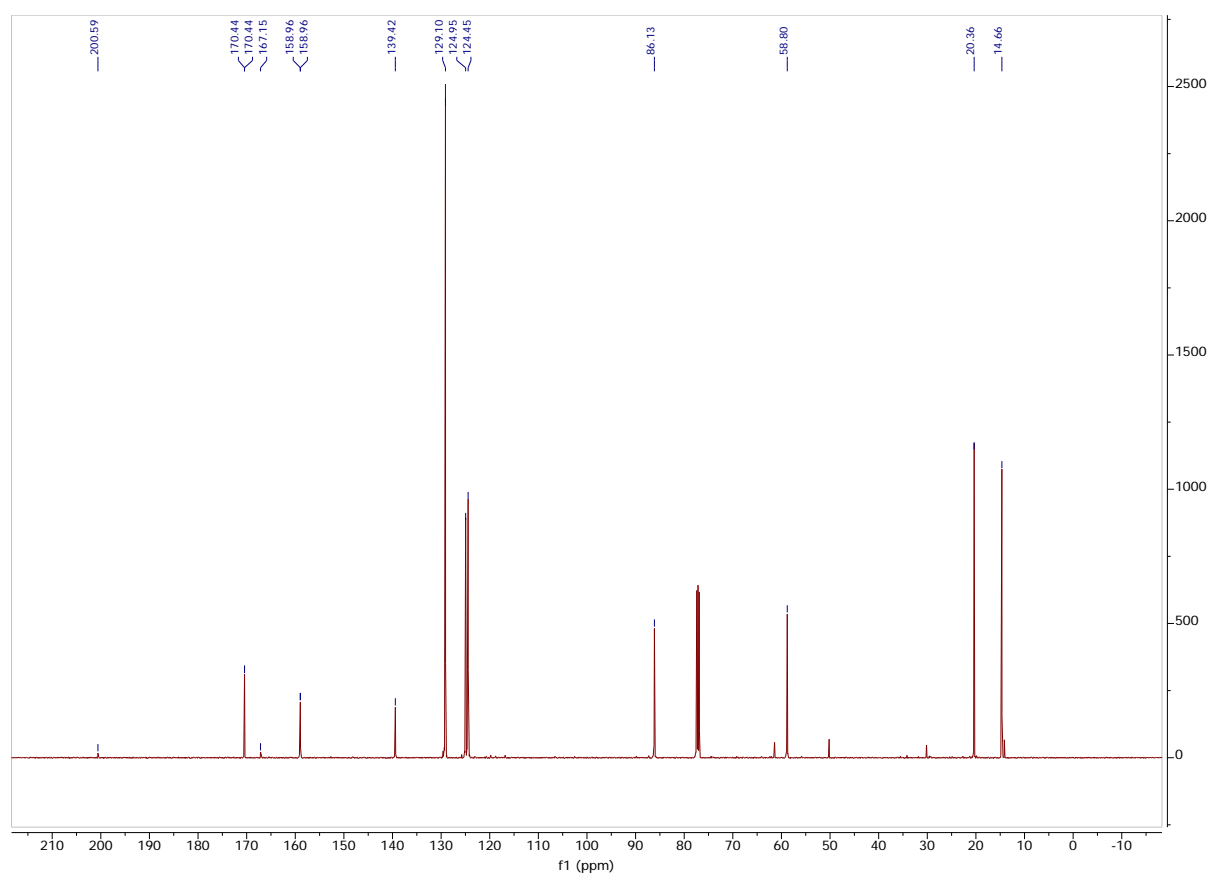




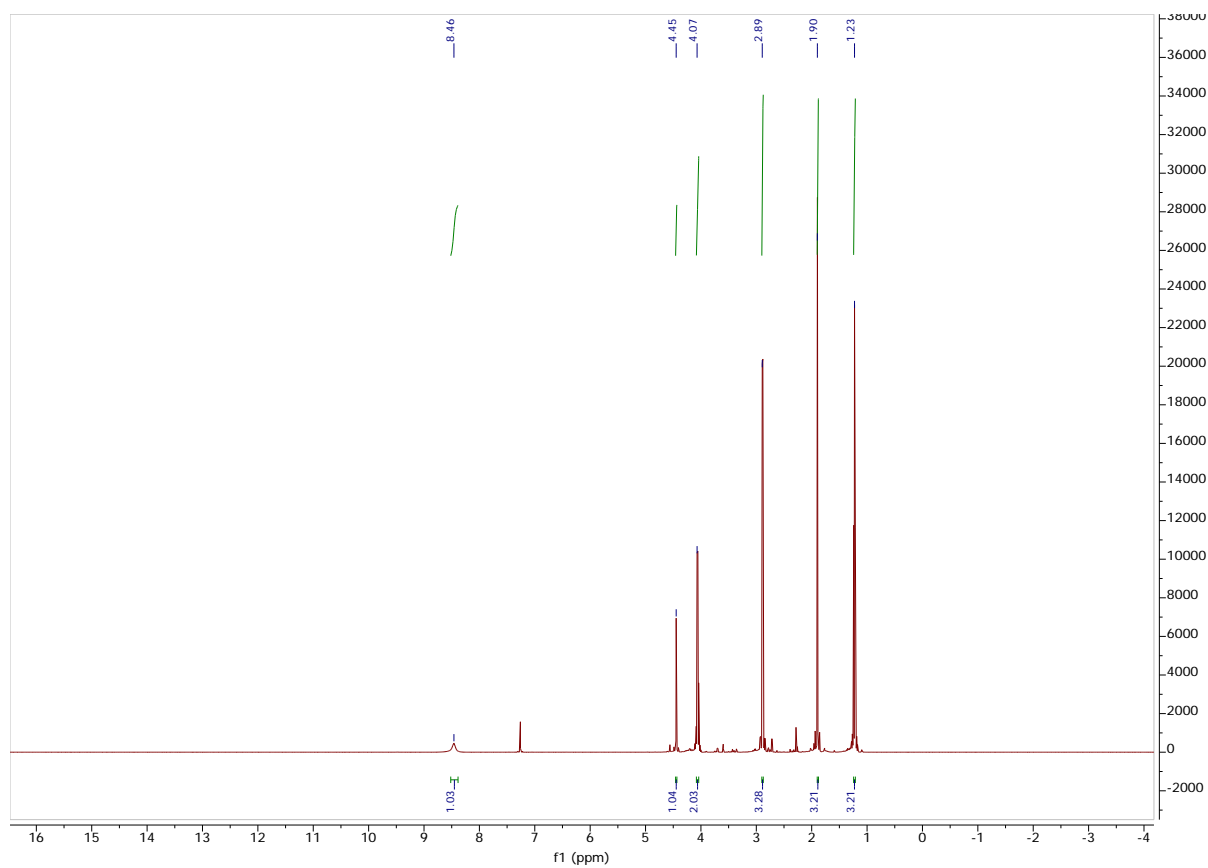




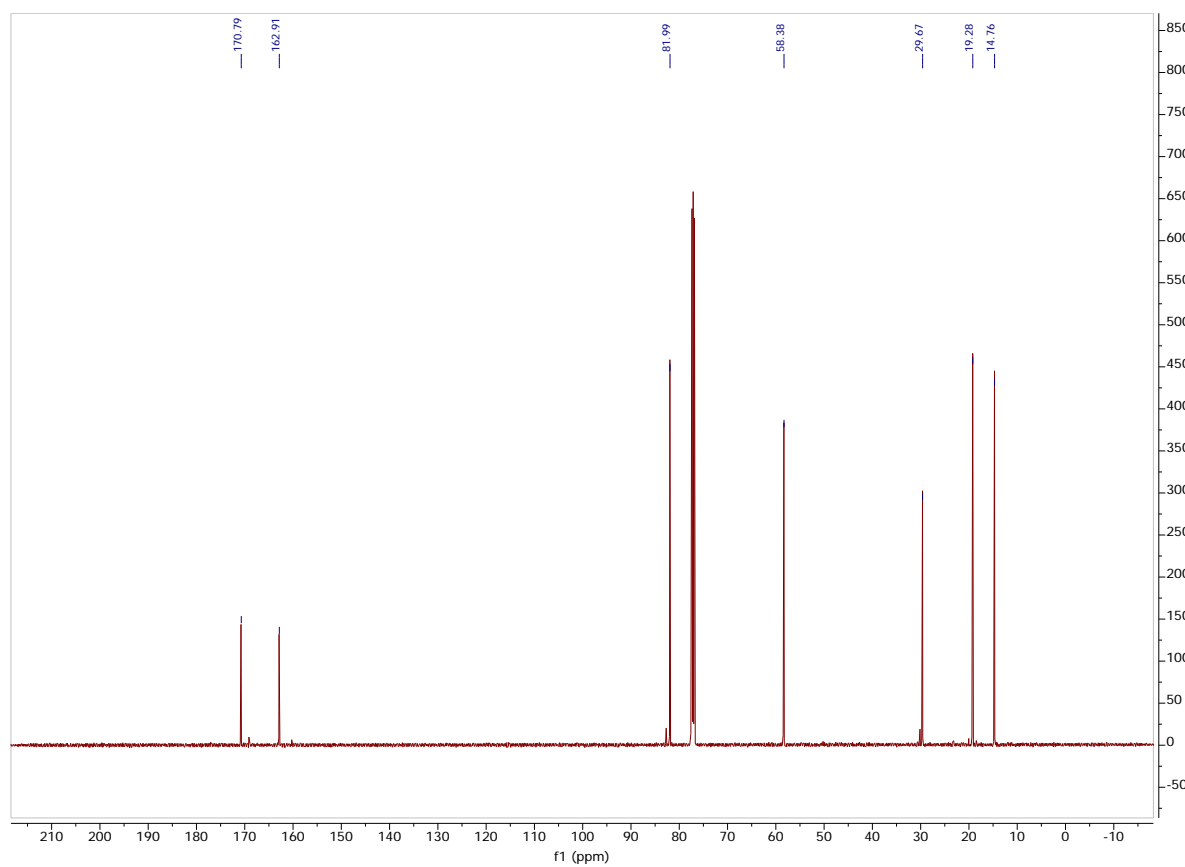
¹H NMR spectrum of compound **16**



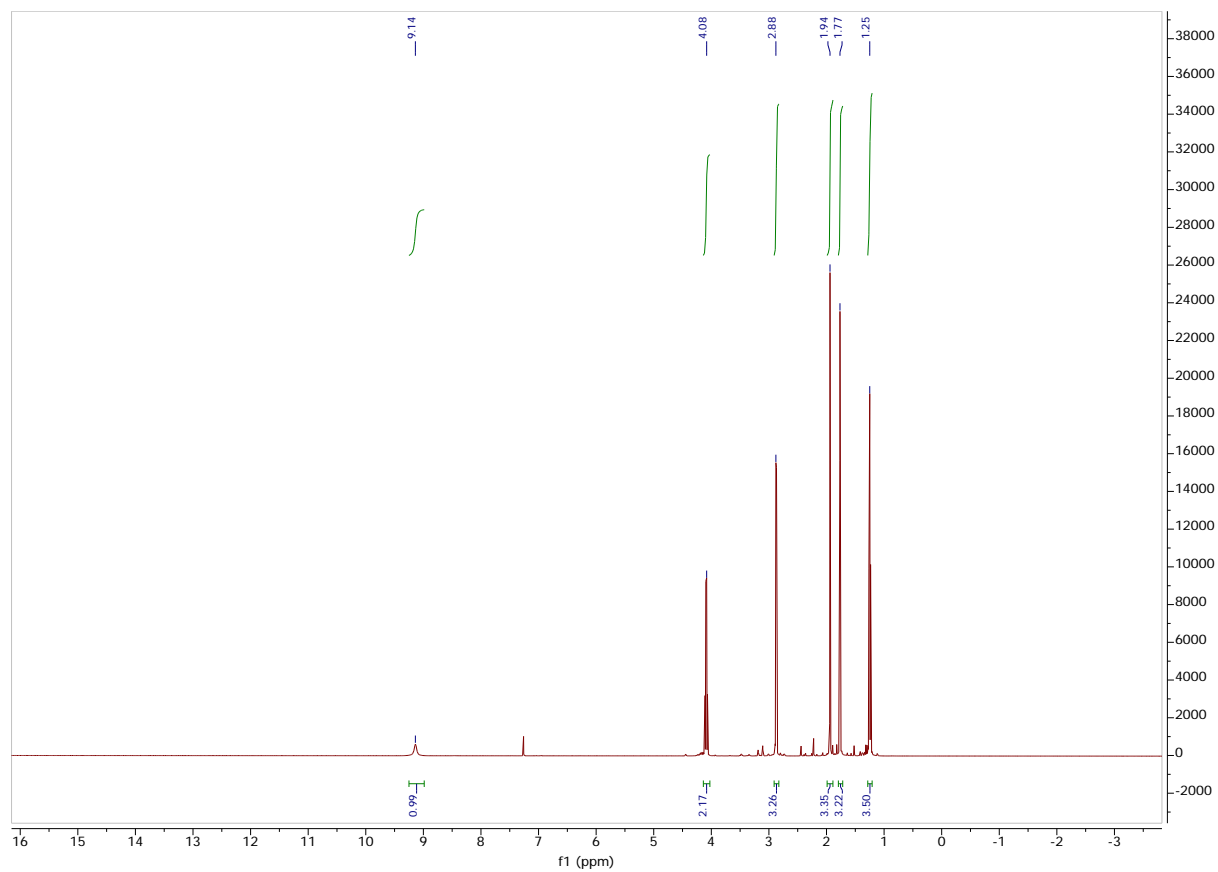
¹³C NMR spectrum of compound **16**



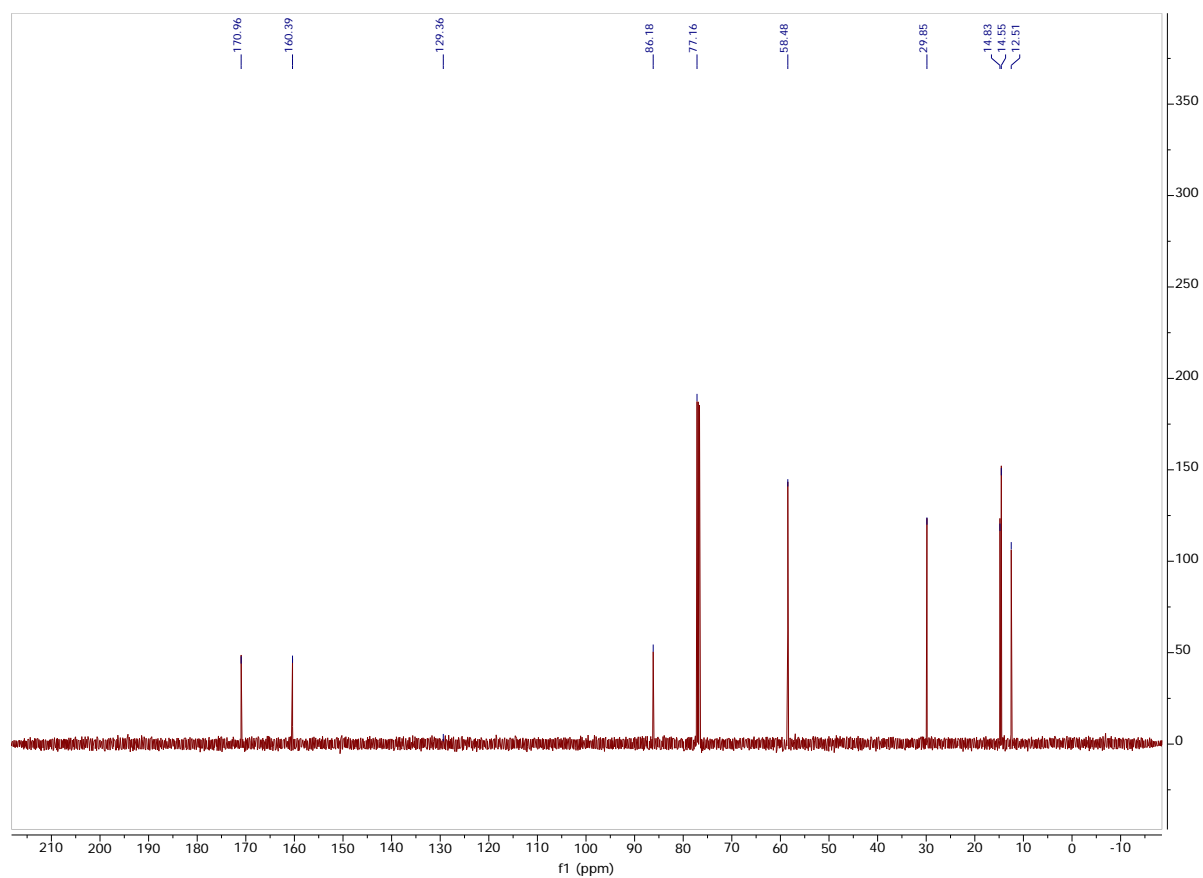
¹H NMR spectrum of compound **17**



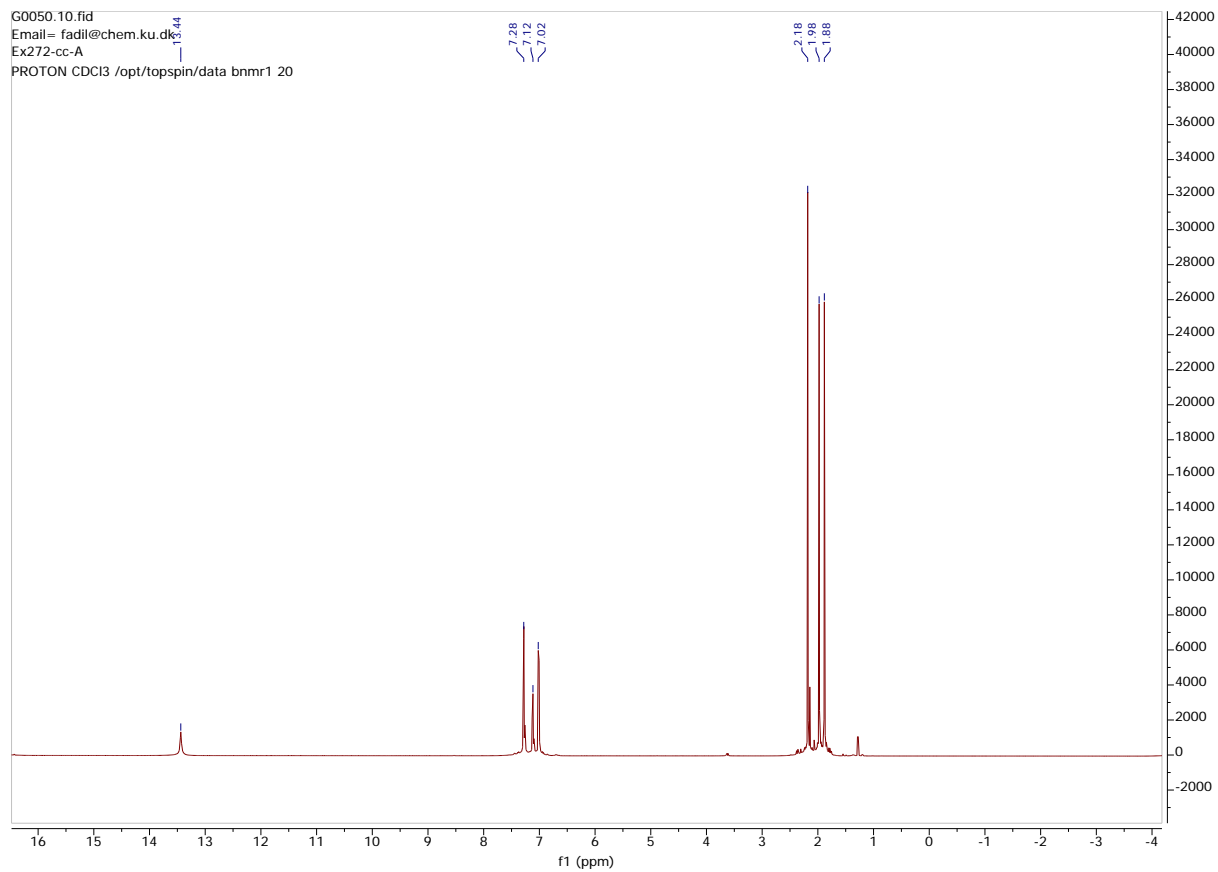
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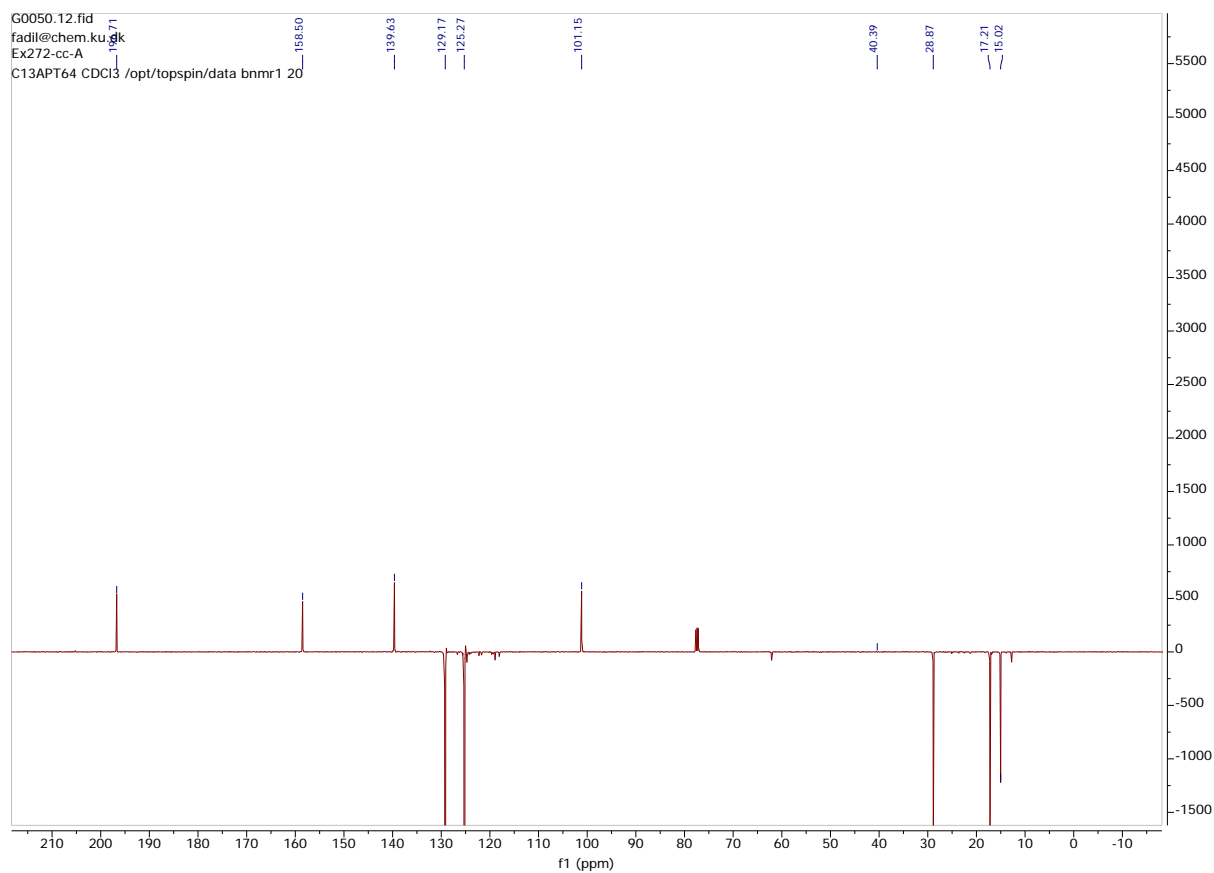
¹H NMR spectrum of compound **19**



¹³C NMR spectrum of compound **19**



¹H NMR spectrum of compound **45**



¹³C NMR spectrum of compound **45**